Supporting Information

Selective C-5 Oxidative Radical Silylation of Imidazopyridines Promoted by Lewis Acid

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1 General Information

All reagents were obtained from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography. Column chromatography was performed using silica gel (300−400 mesh). The NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C) in $CDCl_3$ using tetramethylsilane as the internal standard. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet, hept = heptet. High-resolution mass spectra were obtained with an AB Triple 5600 mass spectrometer by ESI on a TOF mass analyzer. Melting points are uncorrected.

2 Experimental Procedures

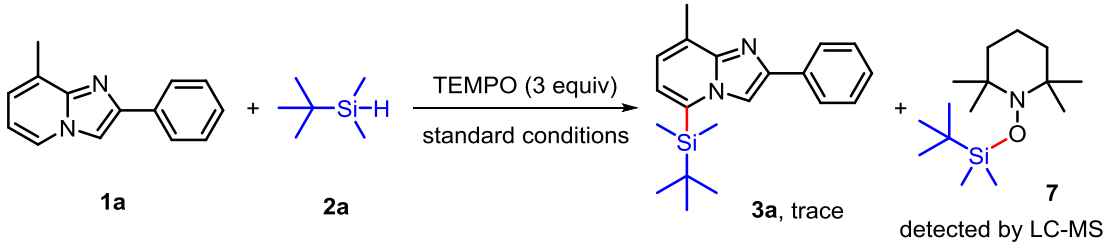
2.1 General Procedure for the Preparation of 3 and 4

To a sealed tube were added imidazo[1,2-*a*]pyridines **1** (0.2 mmol, 1.0 equiv), silanes (1.0 mmol, 5.0 equiv), DTBP (110 μL, 0.6 mmol, 3.0 equiv), $Zn(OTf)_2$ (29.1 mg, 0.08 mmol, 40 mol %) and $PhCF_3$ (2 mL). The reaction mixture was stirred at 120 ℃ for 36 h in oil bath under Ar. After being cooled to room temperature, the resulting solution was diluted with EtOAc (10 mL). The organic layer was washed with water (10 mL). The aqueous phase was re-extracted with EtOAc (5 mL). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography to afford the desired products **3** or **4**.

2.2 General Procedure for the Preparation of 6

To a sealed tube were added the product **3d** (0.5 mmol, 1.0 equiv), 1-iodo-4-methoxybenzene (1.0 mmol, 2 equiv), $Pd(PPh_3)_4$ (0.025 mmol, 5 mol %) and Ag_2O (0.5 mmol, 1.0 equiv). Then anhydrous DMF (5 mL) and TBAF (1.0 mol/L in THF, 0.25 mL, 0.5 equiv) were added under Ar. The reaction mixture was heated at 90 ℃ for 5 h. After being cooled to room temperature, the reaction mixture was diluted with H_2O, extracted with EtOAc (4 × 15 mL). The combined organic layers were washed with brine (20 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuum, and the resulting residue was purified by silica gel column chromatography to afford the desired product **6**.

3 The Control Experiment



To a sealed tube were added **1a** (41.6 mg, 0.2 mmol, 1.0 equiv), **2a** (165 μL, 1.0 mmol, 5.0 equiv), DTBP (110 μL, 0.6 mmol, 3.0 equiv), TEMPO (94.5 mg, 0.6 mmol, 3.0 equiv) and $PhCF_3$ (2 mL). The reaction mixture was stirred at 120 ℃ for 36 h under Ar. After the reaction was stopped, no desired product **3a** was detected by TLC and LC-MS, indicating that the reaction was completely inhibited. Meanwhile, a trapping product **7** was observed through the LC-MS analysis from the reaction solution (Figure S1).

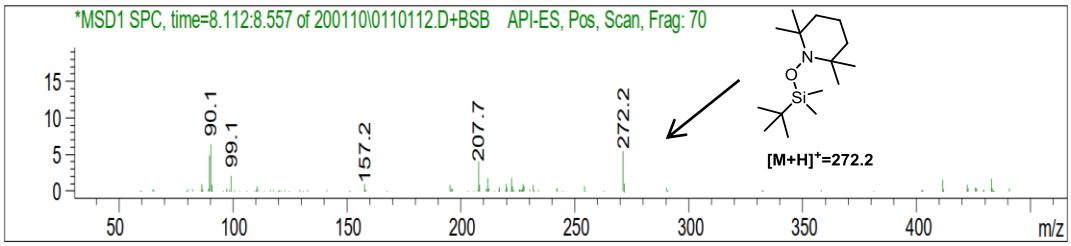
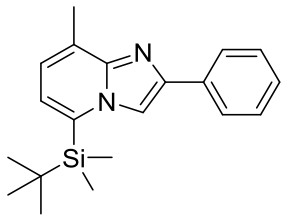


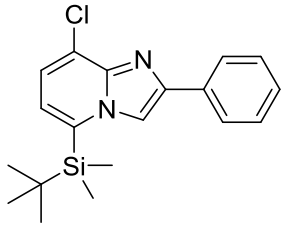
Figure S1. LC-MS analysis of the radical-trapping product **7**.

4 Experimental Data for the Products 3, 4 and 6

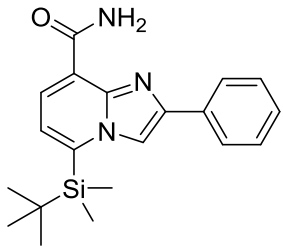


5-(*tert*-Butyldimethylsilyl)-8-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3a**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v) as eluent. Yellow oil (48.9 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02–7.99 (m, 3H), 7.48 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 6.95 (dd, J = 6.9, 1.1 Hz, 1H), 6.85 (d, J = 6.8 Hz, 1H), 2.71 (s, 3H), 1.02 (s, 9H), 0.52 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.6, 144.6, 135.8, 134.4, 128.7, 128.4, 127.7, 126.2, 122.6, 122.4, 110.8, 27.1, 18.4, 17.4, -4.8. IR (KBr) ν 2954, 2844,

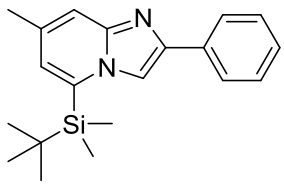
1608, 1472, 1255, 1184, 818, 770, 690 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2Si$ 323.1938; Found 323.1938.



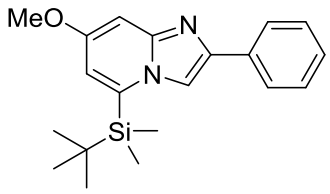
5-(*tert*-Butyldimethylsilyl)-8-chloro-2-phenylimidazo[1,2-*a*]pyridine (**3b**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v) as eluent. Yellow solid (39.0 mg, 57% yield). mp 78−80 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.06 (s, 1H), 8.00 (dd, J = 8.3, 1.3 Hz, 2H), 7.47 (t, J = 7.6 Hz, 2H), 7.39–7.35 (m, 1H), 7.23 (d, J = 7.4 Hz, 1H), 6.85 (d, J = 7.4 Hz, 1H), 1.02 (s, 9H), 0.54 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 145.8, 143.4, 137.6, 133.5, 128.7, 128.2, 126.4, 124.3, 122.7, 121.6, 111.8, 27.0, 18.4, -4.9. IR (KBr) ν 2933, 2857, 1611, 1465, 1252, 925, 808, 774, 692 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}ClN_2Si$ 343.1392; Found 343.1393.



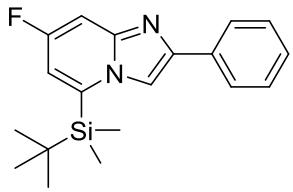
5-(*tert*-Butyldimethylsilyl)-2-phenylimidazo[1,2-*a*]pyridine-8-carboxamide (**3c**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v) as eluent. Yellow solid (42.1 mg, 60% yield). mp 259−261 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 10.39 (s, 1H), 8.15 (d, J = 7.2 Hz, 1H), 8.08 (s, 1H), 7.96 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.3 Hz, 1H), 7.09 (d, J = 7.1 Hz, 1H), 6.33 (s, 1H), 1.03 (s, 9H), 0.57 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 165.7, 144.5, 144.0, 143.4, 133.1, 128.8, 128.4, 126.8, 126.2, 121.8, 120.8, 110.5, 27.0, 18.4, -4.8. IR (KBr) ν 3308, 3169, 2929, 2852, 1677, 1619, 1489, 1256, 815, 776, 693 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{26}N_3OSi$ 352.1840; Found 352.1838.



5-(*tert*-Butyldimethylsilyl)-7-methyl-2-phenylimidazo[1,2-*a*]pyridine (**3d**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v) as eluent. Yellow solid (50.4 mg, 78% yield). mp 95−96 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.95 (d, J = 8.9 Hz, 3H), 7.47–7.41 (m, 3H), 7.32 (t, J = 7.4 Hz, 1H), 6.73 (s, 1H), 2.39 (s, 3H), 1.01 (s, 9H), 0.51 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.5, 144.8, 137.7, 134.2, 134.2, 128.7, 127.7, 126.0, 125.0, 116.8, 109.7, 27.0, 21.3, 18.3, -4.8. IR (KBr) ν 2930, 2860, 1627, 1474, 1254, 840, 776, 706 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{20}H_{27}N_2Si$ 323.1938; Found 323.1939.

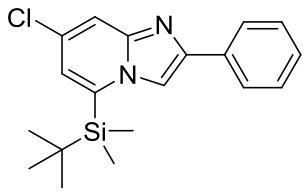


5-(*tert*-Butyldimethylsilyl)-7-methoxy-2-phenylimidazo[1,2-*a*]pyridine (**3e**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (6:1, v/v) as eluent. Yellow oil (52.1 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (d, J = 7.3 Hz, 2H), 7.83 (s, 1H), 7.45 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.3 Hz, 1H), 7.03 (s, 1H), 6.67 (d, J = 2.3 Hz, 1H), 3.89 (s, 3H), 1.02 (s, 9H), 0.52 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 157.1, 147.4, 144.0, 139.7, 133.5, 128.7, 127.8, 125.8, 117.3, 109.0, 95.2, 55.4, 27.0, 18.20, -4.9. IR (KBr) ν 2929, 2857, 1618, 1467, 1402, 1215, 873, 775, 707 cm^{-1}. HRMS (ESI) m/z: [M + Na]$^{+}$ Calcd for $C_{20}H_{26}N_2OSiNa$ 361.1707; Found 361.1701.

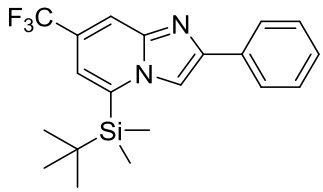


5-(*tert*-Butyldimethylsilyl)-7-fluoro-2-phenylimidazo[1,2-*a*]pyridine (**3f**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v) as eluent. Yellow solid (42.4 mg, 65% yield). mp 56−58 ^{o}C . ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (s, 1H), 7.93 (d, J = 7.3 Hz, 2H), 7.46 (t, J = 7.7 Hz, 2H), 7.36 (t, J = 7.3 Hz, 1H), 7.31–7.29 (m, 1H), 6.80 (dd, J = 7.7, 2.6 Hz, 1H), 1.03 (s, 9H), 0.55 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 159.4 (d, J = 253.1 Hz), 146.6 (d, J = 13.0 Hz), 146.1, 141.5 (d, J = 6.1 Hz), 133.6, 128.8, 128.1, 126.0, 113.8 (d, J = 26.2 Hz), 109.8, 101.6 (d, J = 22.9 Hz), 27.0, 18.3, -5.0. HRMS (ESI) m/z calcd for $C_{19}H_{24}FN_2Si^{+}$ [M+H]$^{+}$ 327.1687, found 327.1689. IR (KBr) ν 2927, 2856, 1624, 1470, 1253, 1182,

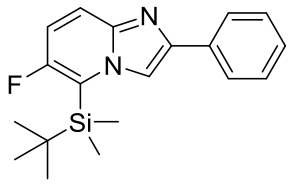
839, 775, 711 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}FN_2Si$ 327.1687; Found 327.1689.



5-(*tert*-butyldimethylsilyl)-7-chloro-2-phenylimidazo[1,2-*a*]pyridine (**3g**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (20:1, v/v) as eluent. Yellow solid (43.8 mg, 64% yield). mp 91−93 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97 (d, J = 0.7 Hz, 1H), 7.93 (dd, J = 8.3, 1.3 Hz, 2H), 7.67 (d, J = 1.8 Hz, 1H), 7.47 (t, J = 7.7 Hz, 2H), 7.39–7.35 (m, 1H), 6.87 (d, J = 2.1 Hz, 1H), 1.04 (s, 9H), 0.55 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 146.0, 145.9, 140.0, 133.5, 130.4, 128.8, 128.2, 126.1, 123.1, 116.9, 110.3, 27.0, 18.4, -4.9. IR (KBr) ν 2925, 2852, 1604, 1464, 1250, 1072, 850, 774, 715 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{24}ClN_2Si$ 343.1392; Found 343.1397.

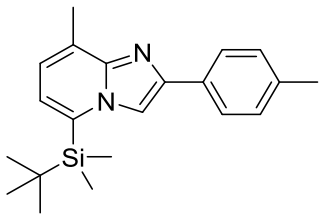


5-(*tert*-Butyldimethylsilyl)-2-phenyl-7-(trifluoromethyl)imidazo[1,2-*a*]pyridine (**3h**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v) as eluent. Yellow solid (45.9 mg, 61% yield). mp 75−77 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.12 (s, 1H), 7.97 (d, J = 7.5 Hz, 3H), 7.49 (t, J = 7.0 Hz, 2H), 7.39 (t, J = 6.9 Hz, 1H), 7.05 (s, 1H), 1.04 (s, 9H), 0.58 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 147.3, 144.0, 140.4, 133.2, 128.9, 128.5, 126.2, 125.4 (q, J = 33.5 Hz), 123.6 (q, J = 272.1 Hz), 117.3 (q, J = 2.9 Hz), 115.9 (q, J = 4.9 Hz), 111.5, 27.0, 18.4, -5.0. IR (KBr) ν 2956, 2861, 1630, 1416, 1340, 1244, 1125, 886, 767, 724, 681 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{24}F_3N_2Si$ 377.1655; Found 377.1657.

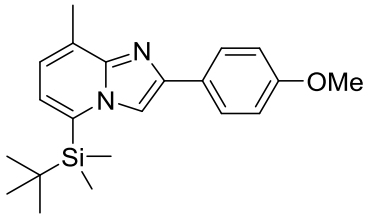


5-(*tert*-Butyldimethylsilyl)-6-fluoro-2-phenylimidazo[1,2-*a*]pyridine (**3i**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v) as eluent. Yellow solid

(37.8 mg, 58% yield). mp 85−87 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.05 (s, 1H), 7.93 (d, J = 7.3 Hz, 2H), 7.68 (dd, J = 9.7, 5.4 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 7.4 Hz, 1H), 7.05 (t, J = 9.2 Hz, 1H), 1.05 (s, 9H), 0.60 (d, J = 3.0 Hz, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 160.3 (d, J = 231.9 Hz), 146.0, 143.9, 133.6, 128.8, 128.1, 126.0, 123.7 (d, J = 49.3 Hz), 119.1 (d, J = 10.8 Hz), 116.3 (d, J = 32.0 Hz), 111.7, 26.6, 19.0, -3.3 (d, J = 6.5 Hz). IR (KBr) ν 2928, 2857, 1688, 1470, 1256, 1166, 840, 824, 771, 711 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{19}H_{24}FN_2Si$ 327.1687; Found 327.1689.

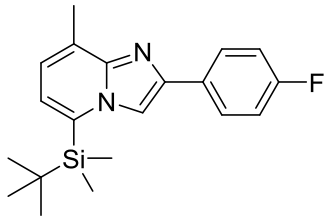


5-(*tert*-Butyldimethylsilyl)-8-methyl-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine (**3j**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v) as eluent. Yellow solid (52.6 mg, 78% yield). mp 93−95 ^{o}C.^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.99 (s, 1H), 7.89 (d, J = 8.2 Hz, 2H), 7.28 (d, J = 7.9 Hz, 2H), 6.94 (dd, J = 6.9, 1.1 Hz, 1H), 6.84 (d, J = 6.9 Hz, 1H), 2.71 (s, 3H), 2.42 (s, 3H), 1.02 (s, 9H), 0.52 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.5, 144.7, 137.4, 135.7, 131.6, 129.4, 128.3, 126.1, 122.5, 122.3, 110.5, 27.1, 21.4, 18.4, 17.4, -4.8. IR (KBr) ν 2925, 2851, 1649, 1472, 1247, 822, 775, 728, 687 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{21}H_{29}N_2Si$ 337.2095; Found 337.2094.

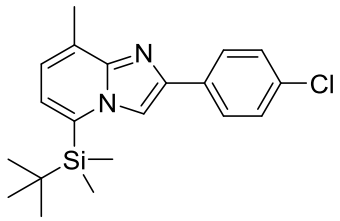


5-(*tert*-Butyldimethylsilyl)-2-(4-methoxyphenyl)-8-methylimidazo[1,2-*a*]pyridine (**3k**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. Red solid (56.3 mg, 80% yield). mp 123−125 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.92 (dd, J = 6.2, 2.6 Hz, 3H), 7.02–7.00 (m, 2H), 6.93 (dd, J = 6.9, 1.3 Hz, 1H), 6.83 (d, J = 6.9 Hz, 1H), 3.86 (s, 3H), 2.69 (s, 3H), 1.01 (s, 9H), 0.50 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 159.4, 146.4, 144.4, 135.7, 128.1, 127.5, 127.1, 122.5, 122.3, 114.1, 110.0, 55.3, 27.0, 18.4, 17.4, -4.8. IR (KBr) ν 2954, 2849, 1611, 1486, 1239, 1031, 838, 802, 766 cm^{-1}. HRMS (ESI) m/z:

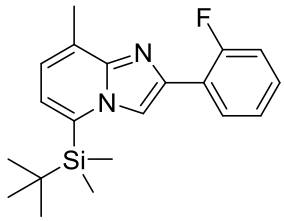
[M + H]$^+$ Calcd for $C_{21}H_{29}N_2OSi$ 353.2044; Found 353.2045.



5-(*tert*-Butyldimethylsilyl)-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (**3l**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v) as eluent. Light yellow solid (49.6 mg, 73% yield). mp 50−51 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96–7.93 (m, 3H), 7.15 (t, J = 8.7 Hz, 2H), 6.95 (dd, J = 6.8, 1.2 Hz, 1H), 6.85 (d, J = 6.9 Hz, 1H), 2.68 (s, 3H), 1.01 (s, 9H), 0.51 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 162.6 (d, J = 246.2 Hz), 146.5, 143.6, 135.9, 130.5 (d, J = 3.1 Hz), 128.3, 127.8 (d, J = 8.0 Hz), 122.8, 122.5, 115.6 (d, J = 21.6 Hz), 110.4, 27.0, 18.4, 17.3, -4.8. IR (KBr) ν 2954, 2853, 1609, 1483, 1227, 1146, 831, 806, 777 cm^{-1}. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{26}FN_2Si$ 341.1844; Found 341.1842.

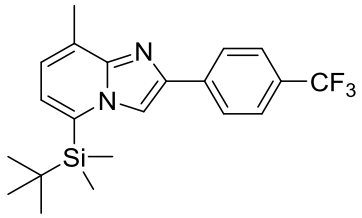


5-(*tert*-Butyldimethylsilyl)-2-(4-chlorophenyl)imidazo[1,2-*a*]pyridine (**3m**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v) as eluent. White solid (41.3 mg, 58% yield). mp 106−108 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98 (s, 1H), 7.93–7.91 (m, 2H), 7.43–7.41 (m, 2H), 6.95 (dd, J = 6.8, 1.3 Hz, 1H), 6.85 (d, J = 6.8 Hz, 1H), 2.68 (s, 3H), 1.01 (s, 9H), 0.51 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.6, 143.4, 136.0, 133.3, 132.9, 128.8, 128.4, 127.4, 122.8, 122.6, 110.8, 27.0, 18.4, 17.3, -4.8. IR (KBr) ν 2959, 2853, 1607, 1472, 1242, 1082, 835, 799, 734 cm^{-1}. HRMS (ESI) m/z: [M + H]$^+$ Calcd for $C_{20}H_{26}ClN_2Si$ 357.1548; Found 357.1549.

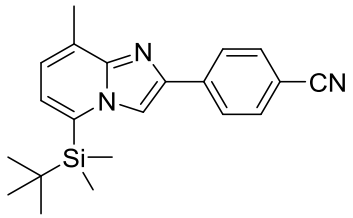


5-(*tert*-Butyldimethylsilyl)-2-(2-fluorophenyl)imidazo[1,2-*a*]pyridine (**3n**). Purified by silica

gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v) as eluent. Yellow solid (47.6 mg, 70% yield). mp 52−54 ^{o}C . ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.48–8.44 (m, 1H), 8.26 (d, J = 3.7 Hz, 1H), 7.31–7.28 (m, 2H), 7.18–7.13 (m, 1H), 6.97–6.95 (m, 1H), 6.85 (d, J = 6.8 Hz, 1H), 2.70 (s, 3H), 1.01 (s, 9H), 0.51 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 160.3 (d, J = 248.5 Hz), 145.6, 137.8 (d, J = 2.3 Hz), 136.2, 129.0 (d, J = 4.0 Hz), 128.5 (d, J = 8.6 Hz), 128.2, 124.5 (d, J = 3.3 Hz), 122.8, 122.4, 122.0 (d, J = 12.5 Hz), 115.5 (d, J = 22.2 Hz), 115.0 (d, J = 15.4 Hz), 27.0, 18.3, 17.3, -5.0. IR (KBr) ν 2966, 2853, 1613, 1489, 1253, 811, 779, 741, 680 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{20}H_{26}FN_2Si$ 341.1844; Found 341.1847.

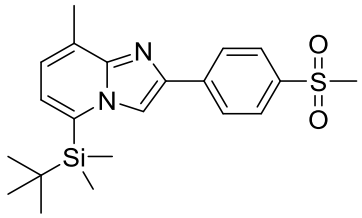


5-(*tert*-Butyldimethylsilyl)-8-methyl-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine (**3o**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v) as eluent. Yellow solid (48.4 mg, 62% yield). mp 86−88 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.09 (d, J = 7.8 Hz, 2H), 8.07 (s, 1H), 7.70 (d, J = 8.2 Hz, 2H), 6.97 (dd, J = 6.8, 1.2 Hz, 1H), 6.87 (d, J = 6.9 Hz, 1H), 2.69 (s, 3H), 1.02 (s, 9H), 0.52 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.8, 143.0, 137.9, 136.1, 129.4 (q, J = 32.4 Hz), 128.6, 126.2, 125.7, 125.6 (q, J = 3.8 Hz), 123.0, 122.8, 111.5, 27.0, 18.4, 17.3, -4.9. IR (KBr) ν 2959, 2859, 1620, 1330, 1250, 1168, 1122, 1066, 816, 775, 717 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{21}H_{26}F_3N_2Si$ 391.1812; Found 391.1810.

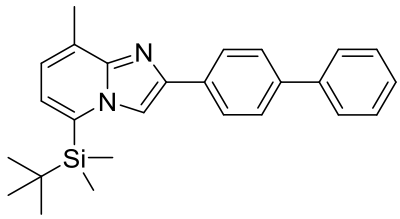


4-(5-(*tert*-Butyldimethylsilyl)-8-methylimidazo[1,2-*a*]pyridin-2-yl)benzonitrile (**3p**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v) as eluent. Yellow solid (37.5 mg, 54% yield). mp 119−121 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10 (s, 1H), 8.07 (d, J = 3.7 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 6.99 (dd, J = 6.8, 1.3 Hz, 1H), 6.89 (d, J = 6.9 Hz, 1H), 2.68 (s, 3H), 1.01 (s, 9H), 0.52 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm)

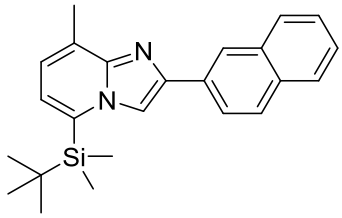
146.9, 142.3, 138.7, 136.3, 132.5, 128.6, 126.5, 123.5, 123.1, 119.2, 112.0, 110.7, 27.0, 18.4, 17.3, -4.8. IR (KBr) ν 2924, 2847, 2222, 1607, 1472, 1242, 940, 840, 805, 775, 745 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{26}N_3Si$ 348.1891; Found 348.1890.



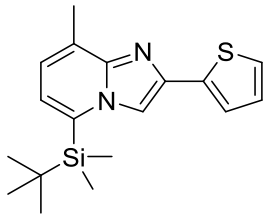
5-(*tert*-Butyldimethylsilyl)-8-methyl-2-(4-(methylsulfonyl)phenyl)imidazo[1,2-*a*]pyridine (**3q**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (3:1, v/v) as eluent. White solid (48.8 mg, 61% yield). mp 160−162 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.19 (d, J = 8.0 Hz, 2H), 8.09 (s, 1H), 8.01 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 6.9 Hz, 1H), 6.93 (d, J = 6.9 Hz, 1H), 3.10 (s, 3H), 2.72 (s, 3H), 1.01 (s, 9H), 0.53 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 146.5, 141.7, 139.2, 139.0, 136.6, 128.5, 127.9, 126.9, 124.2, 123.4, 112.1, 44.7, 27.0, 18.4, 17.4, -4.8. IR (KBr) ν 2930, 2859, 1602, 1468, 1309, 1256, 1151, 951, 840, 805, 775 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{29}N_2O_2SSi$ 401.1714; Found 401.1711.



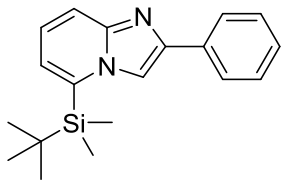
2-([1,1'-biphenyl]-4-yl)-5-(*tert*-Butyldimethylsilyl)-8-methylimidazo[1,2-*a*]pyridine (**3r**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v) as eluent. Orange oil (58.9 mg, 74% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.10–8.06 (m, 3H), 7.74–7.69 (m, 4H), 7.49 (t, J = 7.6 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 6.8 Hz, 1H), 6.88 (d, J = 6.9 Hz, 1H), 2.74 (s, 3H), 1.04 (s, 9H), 0.54 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 146.4, 144.0, 140.9, 140.5, 135.9, 133.1, 128.8, 128.3, 127.4, 127.3, 127.0, 126.7, 123.0, 122.6, 110.9, 27.1, 18.4, 17.4, -4.8. IR (KBr) ν 2924, 2847, 1649, 1602, 1478, 1247, 822, 805, 745, 693 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{26}H_{31}N_2Si$ 399.2251; Found 399.2255.



5-(*tert*-Butyldimethylsilyl)-8-methyl-2-(naphthalen-2-yl)imidazo[1,2-*a*]pyridine (**3s**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (30:1, v/v) as eluent. Brown oil (46.2 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.55 (s, 1H), 8.14 (s, 1H), 8.06 (dd, J = 8.5, 1.7 Hz, 1H), 7.99 (d, J = 7.8 Hz, 1H), 7.93 (d, J = 8.5 Hz, 1H), 7.88 (d, J = 7.6 Hz, 1H), 7.55–7.46 (m, 2H), 6.98 (dd, J = 6.8, 1.3 Hz, 1H), 6.88 (d, J = 6.8 Hz, 1H), 2.75 (s, 3H), 1.05 (s, 9H), 0.55 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.7, 144.5, 135.9, 133.8, 133.1, 131.6, 128.4, 128.4, 128.3, 127.7, 126.2, 125.8, 124.7, 124.5, 122.8, 122.5, 111.3, 27.1, 18.4, 17.4, -4.8. IR (KBr) ν 2959, 2853, 1607, 1472, 1242, 1082, 835, 799, 734, 684 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{24}H_{29}N_2Si$ 373.2095; Found 373.2096.

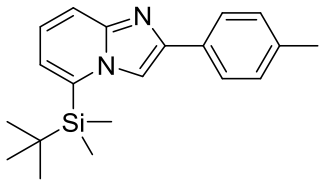


5-(*tert*-Butyldimethylsilyl)-7-methyl-2-(thiophen-2-yl)imidazo[1,2-*a*]pyridine (**3t**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (25:1, v/v) as eluent. Brown oil (38.7 mg, 59% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.89 (s, 1H), 7.53 (d, J = 3.1 Hz, 1H), 7.33–7.31 (m, 1H), 7.12 (dd, J = 5.0, 3.6 Hz, 1H), 6.96 (d, J = 6.8 Hz, 1H), 6.85 (d, J = 6.9 Hz, 1H), 2.68 (s, 3H), 1.00 (s, 9H), 0.50 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.2, 139.3, 135.8, 128.1, 127.8, 124.8, 123.9, 123.1, 122.7, 110.32, 27.0, 18.4, 17.4, -4.8. IR (KBr) ν 2930, 2847, 1643, 1465, 1296, 1260, 835, 820, 806, 778, 735, 689 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{18}H_{25}N_2SSi$ 329.1502; Found 329.1501.

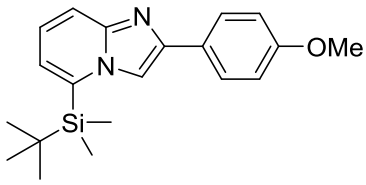


5-(*tert*-butyldimethylsilyl)-2-phenylimidazo[1,2-*a*]pyridine (**3u**). Purified by silica gel column

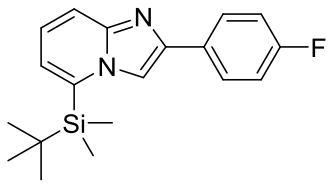
chromatography with petroleum ether/ethyl acetate (8:1, v/v) as eluent. Yellow oil (38.2 mg, 62% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.03 (s, 1H), 7.97 (d, J = 7.3 Hz, 2H), 7.68 (d, J = 9.0 Hz, 1H), 7.46 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 7.4 Hz, 1H), 7.14 (dd, J = 9.0, 6.8 Hz, 1H), 6.93 (d, J = 6.7 Hz, 1H), 1.02 (s, 9H), 0.53 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 145.9, 145.1, 138.7, 134.0, 128.7, 127.9, 126.1, 123.7, 122.3, 118.3, 110.3, 27.0, 18.4, -4.8. IR (KBr) ν 2924, 2853, 1613, 1472, 1247, 1182, 835, 769, 717, 692 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{19}H_{25}N_2Si$ 309.1782; Found 309.1782.



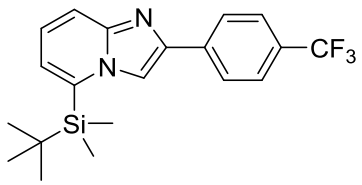
5-(*tert*-Butyldimethylsilyl)-2-(*p*-tolyl)imidazo[1,2-*a*]pyridine (**3v**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v) as eluent. Yellow oil (41.9 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.99 (s, 1H), 7.86 (d, J = 8.1 Hz, 2H), 7.66 (d, J = 8.9 Hz, 1H), 7.27 (d, J = 8.0 Hz, 2H), 7.12 (dd, J = 9.0, 6.7 Hz, 1H), 6.91 (dd, J = 6.7, 1.3 Hz, 1H), 2.41 (s, 3H), 1.01 (s, 9H), 0.52 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 145.84, 145.2, 138.6, 137.7, 131.2, 129.4, 126.0, 123.5, 122.2, 118.2, 110.0, 27.0, 21.3, 18.4, -4.8. IR (KBr) ν 2930, 2853, 1615, 1490, 1325, 1250, 829, 780, 740, 693 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2Si$ 323.1938; Found 323.1939.



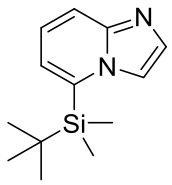
5-(*tert*-Butyldimethylsilyl)-2-(4-methoxyphenyl)imidazo[1,2-*a*]pyridine (**3w**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (4:1, v/v) as eluent. Yellow solid (47.3 mg, 70% yield). mp 89−91 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.93 (s, 1H), 7.89 (d, J = 8.8 Hz, 2H), 7.65 (d, J = 8.9 Hz, 1H), 7.12 (dd, J = 9.0, 6.8 Hz, 1H), 7.00 (d, J = 8.8 Hz, 2H), 6.92–6.90 (m, 1H), 3.87 (s, 3H), 1.01 (s, 9H), 0.52 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 159.5, 145.8, 145.0, 138.5, 127.3, 126.7, 123.5, 122.2, 118.0, 114.1, 109.5, 55.3, 27.0, 18.4, -4.8. IR (KBr) ν 2929, 2851, 1614, 1485, 1250, 1162, 1030, 836, 778, 740 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2OSi$ 339.1887; Found 339.1889.



5-(*tert*-Butyldimethylsilyl)-2-(4-fluorophenyl)imidazo[1,2-*a*]pyridine (**3x**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v) as eluent. Light yellow solid (39.8 mg, 61% yield). mp 66−68 ^{o}C . ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96 (s, 1H), 7.93 (dd, J = 8.5, 5.5 Hz, 2H), 7.66 (d, J = 9.0 Hz, 1H), 7.17–7.13 (m, 3H), 6.94 (d, J = 6.7 Hz, 1H), 1.02 (s, 9H), 0.53 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 162.7 (d, J = 246.6 Hz), 145.9, 144.2, 138.8, 130.2 (d, J = 3.2 Hz), 127.7 (d, J = 8.1 Hz), 123.8, 122.4, 118.2, 115.7 (d, J = 21.6 Hz), 109.9, 27.0, 18.4, -4.8. IR (KBr) ν 2924, 2853, 1607, 1484, 1218, 1148, 840,787, 741, 687 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{19}H_{24}FN_2Si$ 327.1687; Found 327.1686.

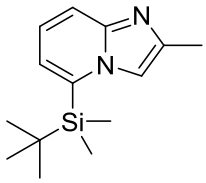


5-(*tert*-Butyldimethylsilyl)-2-(4-(trifluoromethyl)phenyl)imidazo[1,2-*a*]pyridine (**3y**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (10:1, v/v) as eluent. Yellow solid (41.4 mg, 55% yield). mp 95−97 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.07 (d, J = 7.4 Hz, 3H), 7.71–7.66 (m, 3H), 7.17 (dd, J = 9.0, 6.7 Hz, 1H), 6.96 (dd, J = 6.8, 1.2 Hz, 1H), 1.02 (s, 9H), 0.54 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.1, 143.5, 139.1, 137.5, 129.6 (q, J = 32.4 Hz), 126.1, 125.7 (q, J = 3.8 Hz), 124.2, 123.0, 122.7, 118.4, 111.1, 27.0, 18.4, -4.9. IR (KBr) ν 2925, 2860, 1617, 1468, 1334, 1249, 1164, 1105, 836, 772, 732 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{20}H_{24}F_3N_2Si$ 377.1655; Found 377.1657.

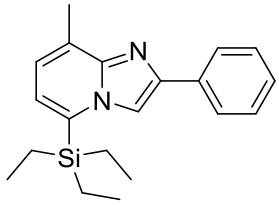


5-(*tert*-Butyldimethylsilyl)imidazo[1,2-*a*]pyridine (**3z**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. Yellow oil (27.7 mg, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.74 (s, 1H), 7.64 (d, J = 6.7 Hz, 2H), 7.12 (dd, J = 9.0, 6.7 Hz, 1H), 6.92 (d, J = 6.6 Hz, 1H), 0.97 (s, 9H), 0.48 (s, 6H). ^{13}C{^{1}H} NMR (100 MHz,

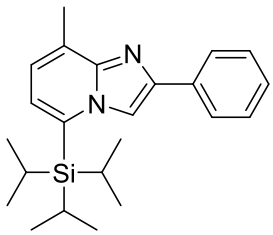
$CDCl_3$) δ (ppm) 145.5, 138.8, 132.9, 123.3, 122.3, 118.6, 114.5, 27.0, 18.3, -4.9. IR (KBr) ν 2930, 2859, 1613, 1472, 1283, 1148, 829, 775 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{21}N_2Si$ 233.1469; Found 233.1470.



5-(*tert*-Butyldimethylsilyl)-2-methylimidazo[1,2-*a*]pyridine (3aa). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (5:1, v/v) as eluent. Brown oil (26.1 mg, 53% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.52 (d, J = 8.9 Hz, 1H), 7.46 (s, 1H), 7.06 (dd, J = 8.9, 6.8 Hz, 1H), 6.86 (dd, J = 6.7, 1.0 Hz, 1H), 2.46 (s, 3H), 0.96 (s, 9H), 0.46 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 145.2, 142.5, 138.1, 122.9, 121.7, 117.5, 111.6, 27.0, 18.3, 14.5, -4.9. IR (KBr) ν 2928, 2852, 1611, 1482, 1263, 840, 776, 691 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{13}H_{21}N_2Si$ 247.1625; Found 247.1623.

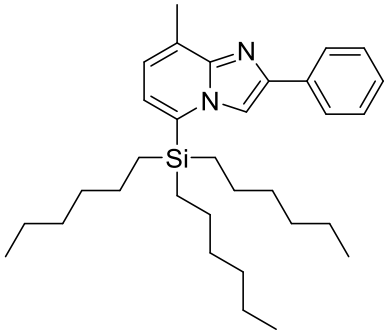


8-Methyl-2-phenyl-5-(triethylsilyl)imidazo[1,2-*a*]pyridine (**4a**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v) as eluent. Yellow oil (45.1 mg, 70% yield). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02 (dd, J = 8.2, 1.3 Hz, 2H), 7.96 (s, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 6.95 (dd, J = 6.8, 1.2 Hz, 1H), 6.84 (d, J = 6.8 Hz, 1H), 2.71 (s, 3H), 1.03 (s, 15H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 146.4, 144.9, 134.9, 134.3, 128.7, 128.3, 127.7, 126.3, 122.8, 121.88, 109.4, 17.4, 7.3, 2.6. IR (KBr) ν 2948, 2871, 1602, 1448, 1182, 1017, 714 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{20}H_{27}N_2Si$ 323.1938; Found 323.1942.

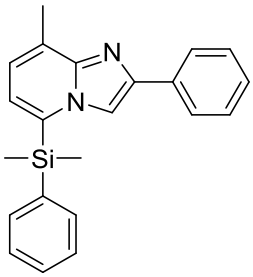


8-Methyl-2-phenyl-5-(triisopropylsilyl)imidazo[1,2-*a*]pyridine (**4b**). Purified by silica gel

column chromatography with petroleum ether/ethyl acetate (40:1, v/v) as eluent. Yellow solid (43.7 mg, 60% yield). mp 141−142 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.01–7.99 (m, 2H), 7.97 (s, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 6.96 (t, J = 5.9 Hz, 2H), 2.72 (s, 3H), 1.63 (hept, J = 7.5 Hz, 3H), 1.20 (d, J = 7.5 Hz, 18H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.6, 144.4, 134.6, 134.0, 128.7, 128.0, 127.8, 126.3, 123.0, 122.9, 110.5, 18.8, 17.4, 12.0. IR (KBr) ν 2953, 2865, 1620, 1461, 1395, 1189, 887, 717, 679, 651 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{23}H_{33}N_2Si$ 365.2408; Found 365.2408.

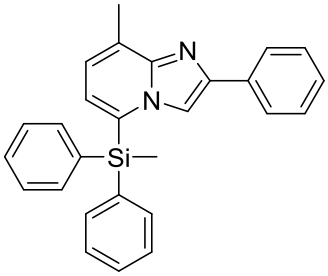


8-Methyl-2-phenyl-5-(trihexylsilyl)imidazo[1,2-*a*]pyridine (**4c**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v) as eluent. Yellow solid (61.8 mg, 63% yield). mp 48−50 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.02–8.00 (m, 2H), 7.94 (s, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.37 (d, J = 7.4 Hz, 1H), 6.95 (d, J = 7.4 Hz, 1H), 6.82 (d, J = 6.8 Hz, 1H), 2.70 (s, 3H), 1.36–1.26 (m, 26H), 1.02–0.98 (m, 5H), 0.89–0.86 (m, 8H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ (ppm) 146.3, 144.8, 135.7, 134.3, 128.7, 128.1, 127.7, 126.3, 122.9, 121.6, 109.4, 33.2, 31.4, 23.6, 22.6, 17.4, 14.1, 11.4. IR (KBr) ν 2924, 2847, 1602, 1461, 1377, 1247, 1182, 740, 698 cm^{-1}. HRMS (ESI) m/z: [M + H]$^{+}$ Calcd for $C_{32}H_{51}N_2Si$ 491.3816; Found 491.3817.

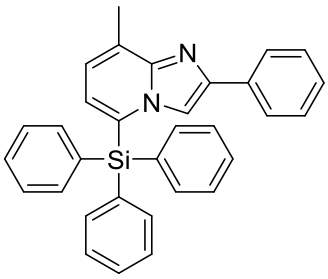


5-(Dimethyl(phenyl)silyl)-8-methyl-2-phenylimidazo[1,2-*a*]pyridine (**4d**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v) as eluent. Yellow oil (46.5 mg, 68% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.88–7.86 (m, 2H), 7.71 (s, 1H), 7.60 (dd, J = 7.7, 1.6 Hz, 2H), 7.47–7.40 (m, 5H), 7.32 (t, J = 7.4 Hz, 1H), 6.99 (dd, J = 6.8, 1.2 Hz, 1H),

6.92 (d, J = 6.8 Hz, 1H), 2.73 (s, 3H), 0.75 (s, 6H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 146.1, 144.7, 135.3, 134.7, 134.1, 134.1, 130.2, 128.8, 128.6, 128.5, 127.7, 126.2, 122.8, 122.0, 109.9, 17.5, -3.3. IR (KBr) ν 3065, 2953, 2841, 1602, 1484, 1247, 1106, 816, 717, 690, 504, 475 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{22}H_{23}N_2Si$ 343.1625; Found 343.1623.

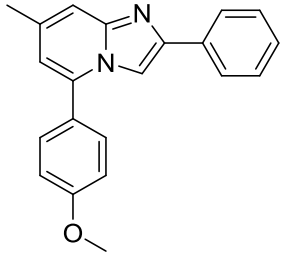


8-Methyl-5-(methyldiphenylsilyl)-2-phenylimidazo[1,2-*a*]pyridine (**4e**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v) as eluent. White solid (44.5 mg, 55% yield). mp 158−159 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.80 (d, J = 7.3 Hz, 2H), 7.64 (s, 1H), 7.60 (d, J = 7.7 Hz, 4H), 7.51 (t, J = 7.3 Hz, 2H), 7.46–7.37 (m, 6H), 7.32–7.29 (m, 1H), 6.95 (d, J = 6.8 Hz, 1H), 6.78 (d, J = 6.8 Hz, 1H), 2.74 (s, 3H), 1.02 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 146.1, 144.5, 135.1, 134.0, 133.9, 132.7, 130.4, 129.1, 128.6, 128.5, 127.7, 126.2, 124.1, 122.9, 110.5, 17.5, -4.4. IR (KBr) ν 3054, 2966, 2918, 1478, 1431, 1100, 793, 740, 721, 698, 563, 468 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{27}H_{25}N_2Si$ 405.1782; Found 405.1781.



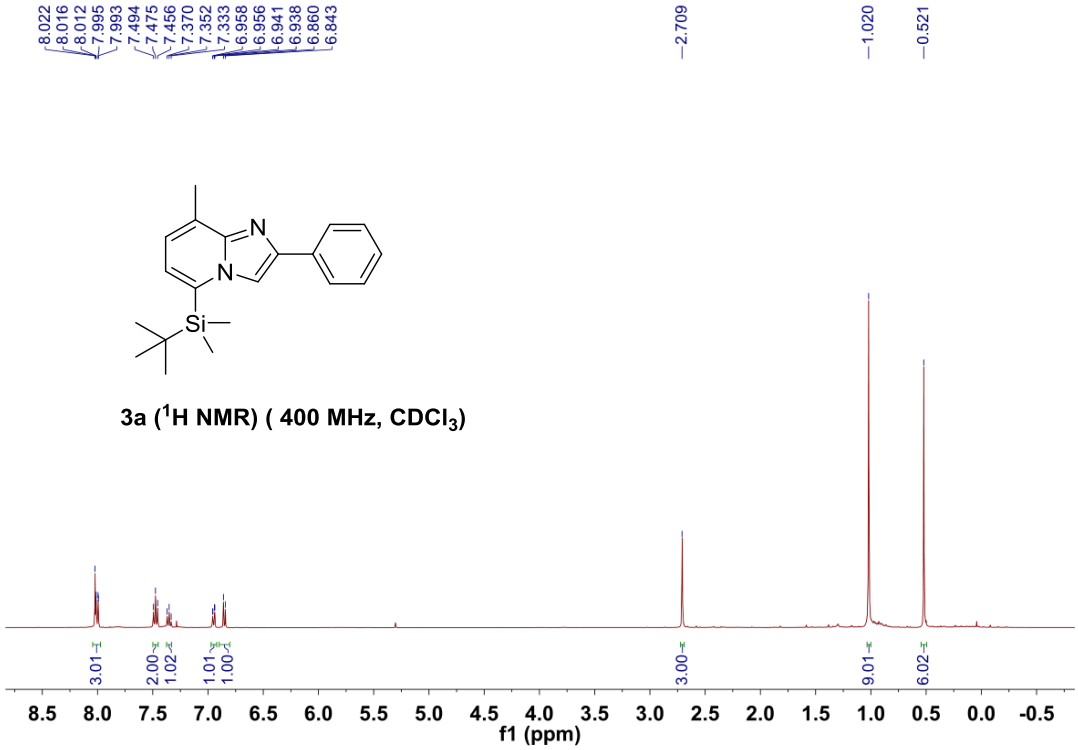
8-Methyl-2-phenyl-5-(triphenylsilyl)imidazo[1,2-*a*]pyridine (**4f**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (40:1, v/v) as eluent. White solid (60.6 mg, 65% yield). mp 240−242 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.71 (d, J = 7.4 Hz, 2H), 7.63 (d, J = 6.8 Hz, 6H), 7.53–7.50 (m, 4H), 7.44 (t, J = 7.3 Hz, 6H), 7.34 (t, J = 7.5 Hz, 2H), 7.25 (d, J = 7.3 Hz, 1H), 6.96 (d, J = 6.8 Hz, 1H), 6.77 (d, J = 6.8 Hz, 1H), 2.77 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 146.0, 144.1, 136.1, 132.8, 131.3, 130.6, 129.3, 128.6, 128.5, 127.9, 127.7, 126.2, 125.8, 123.1, 111.5, 17.6. IR (KBr) ν 3072, 2946, 2917, 1652, 1478, 1106, 747, 709, 699, 511,

493 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{32}H_{27}N_2Si$ 467.1938; Found 467.1938.

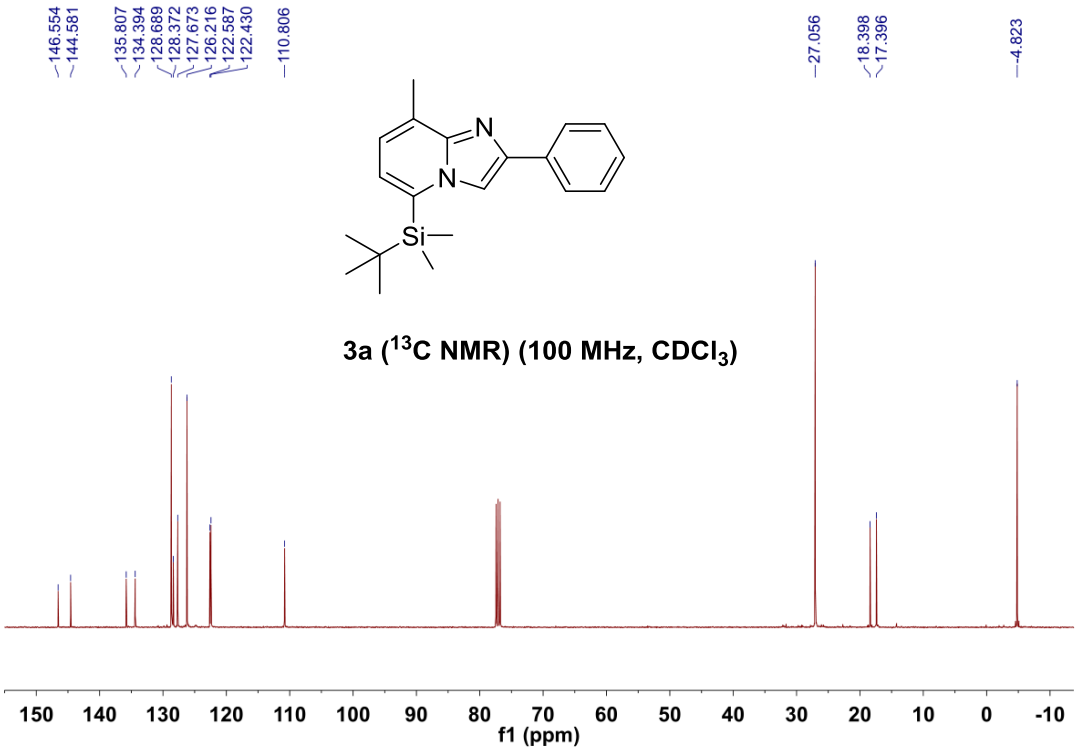


5-(4-Methoxyphenyl)-7-methyl-2-phenylimidazo[1,2-*a*]pyridine (**6**). Purified by silica gel column chromatography with petroleum ether/ethyl acetate (2:1, v/v) as eluent. Yellow solid (106.8 mg, 68% yield). mp 159−161 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.82 (d, J = 7.0 Hz, 1H), 7.70 (dd, J = 8.2, 1.3 Hz, 2H), 7.46 (s, 1H), 7.38–7.36 (m, 2H), 7.32–7.23 (m, 3H), 7.08–7.06 (m, 2H), 6.59 (dd, J = 7.0, 1.5 Hz, 1H), 3.91 (s, 3H), 2.43 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ (ppm) 159.9, 145.0, 141.5, 135.7, 134.2, 132.1, 128.3, 127.9, 127.3, 122.6, 121.9, 120.3, 115.7, 115.0, 114.9, 55.4, 21.4. IR (KBr) ν 2966, 2846, 1649, 1513, 1253, 1176, 1023, 775, 698 cm^{-1}. HRMS (ESI) m/z: $[M + H]^+$ Calcd for $C_{21}H_{19}N_2O$ 315.1492; Found 315.1496.

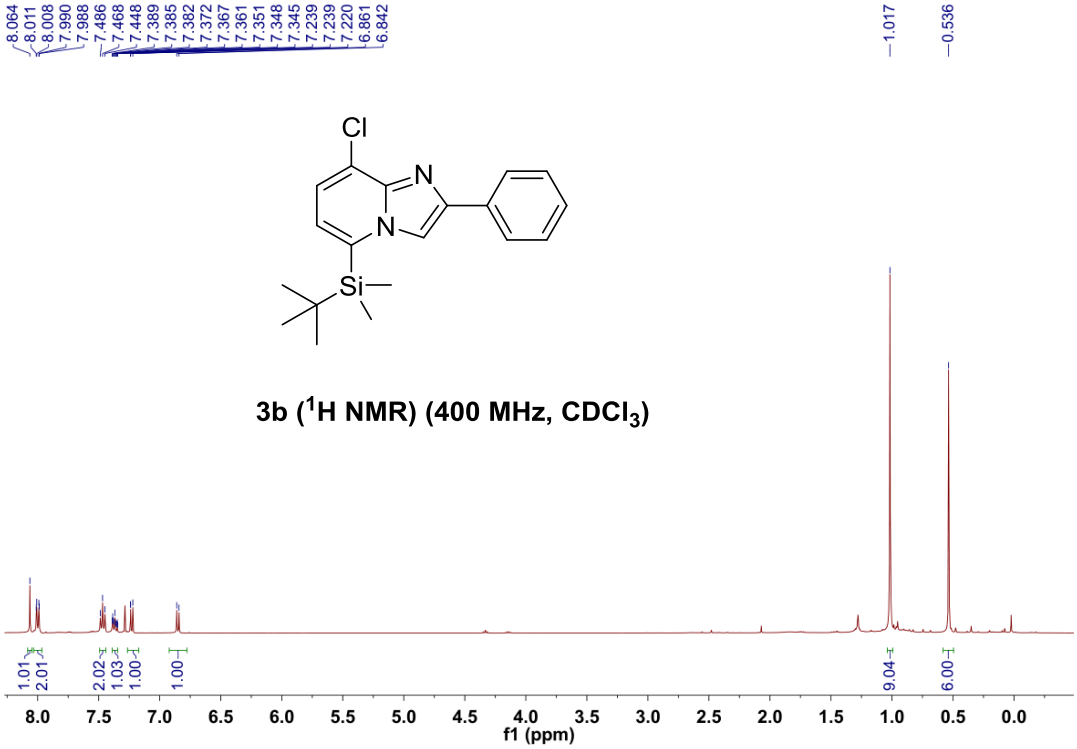
6 ^{1}H and ^{13}C NMR Spectra of the Products



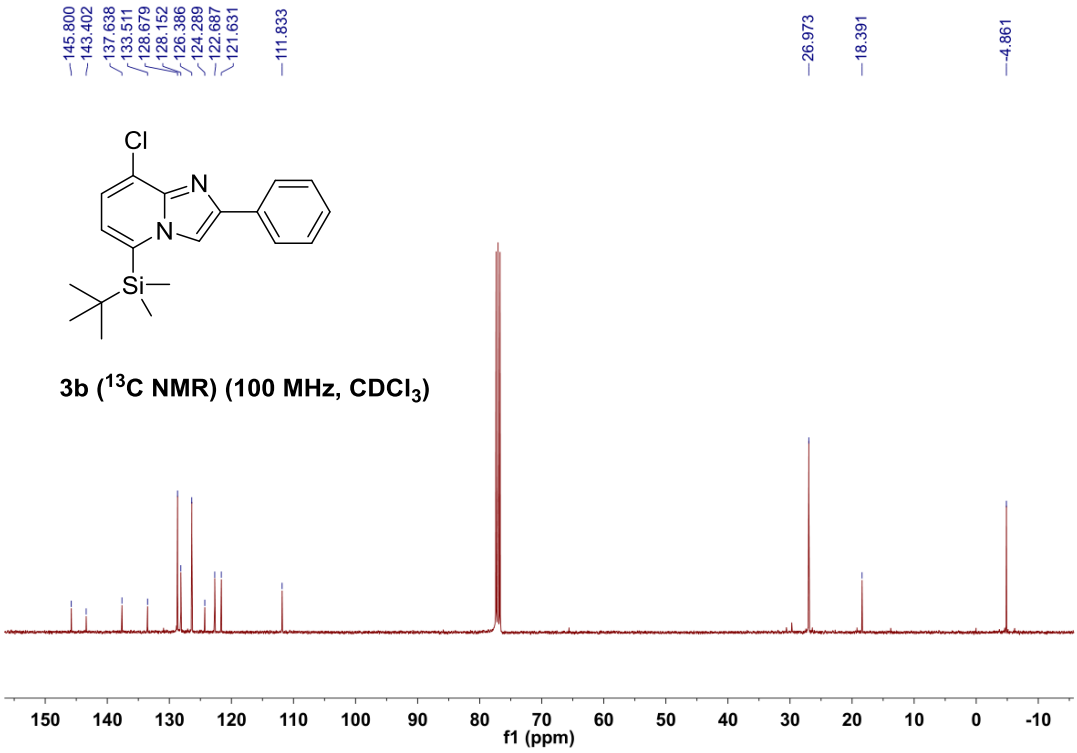
3a (^{1}H NMR) (400 MHz, $CDCl_3$)



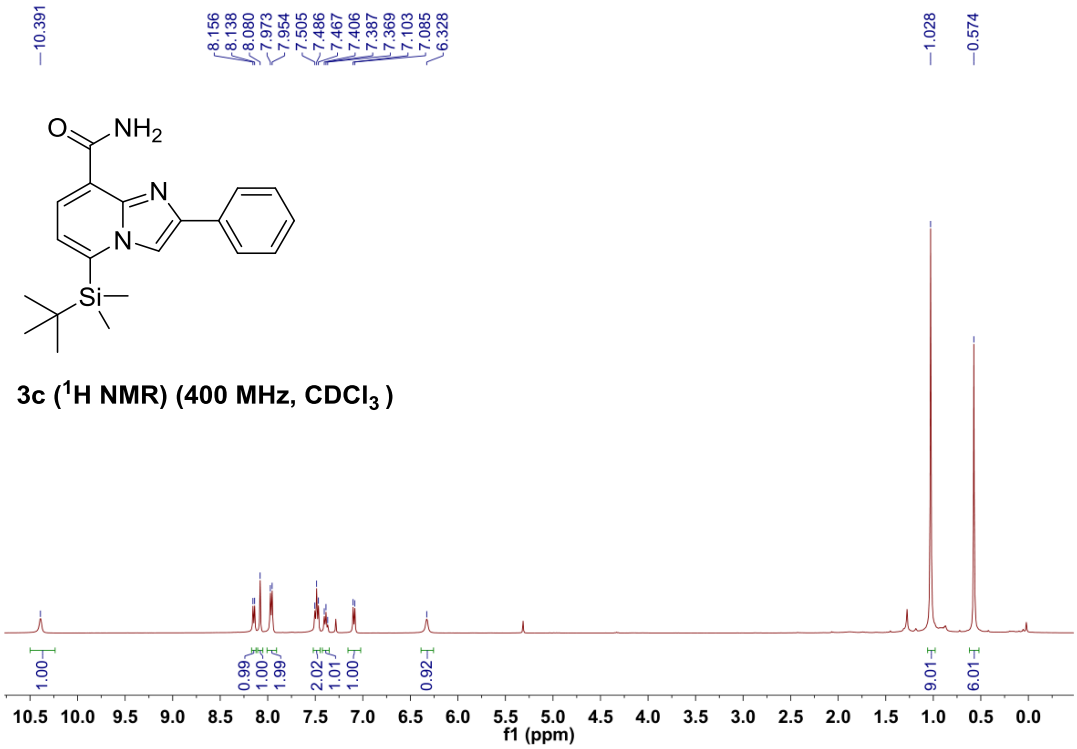
3a (^{13}C NMR) (100 MHz, $CDCl_3$)



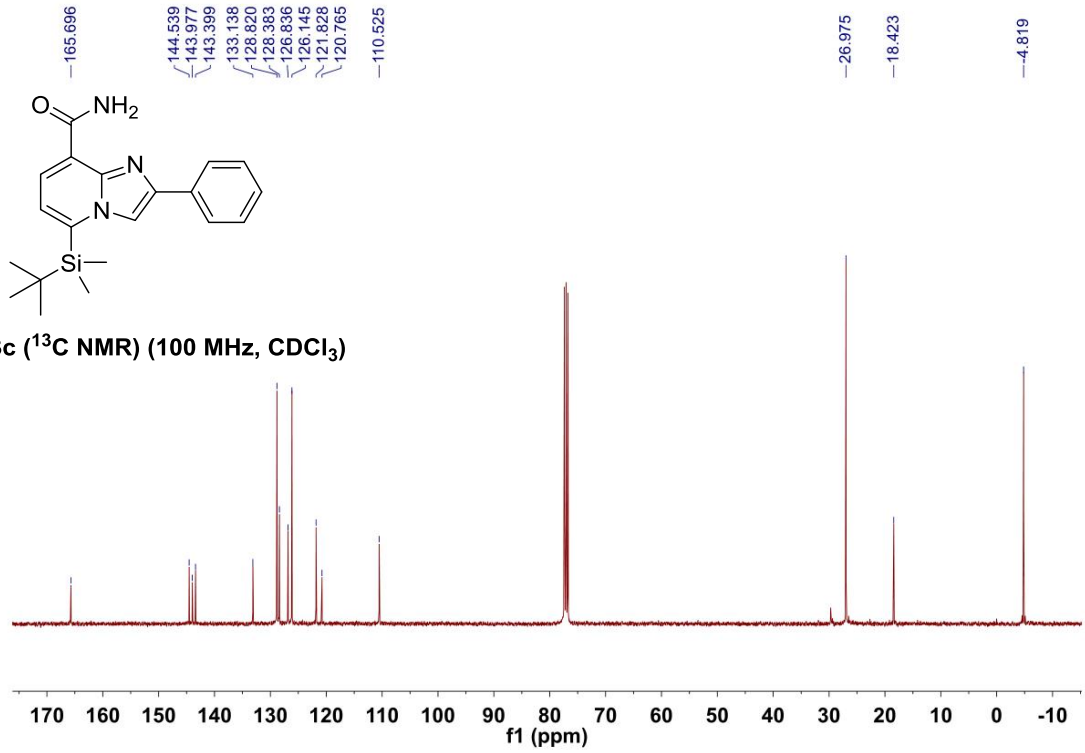
3b (^{1}H NMR) (400 MHz, $CDCl_3$)



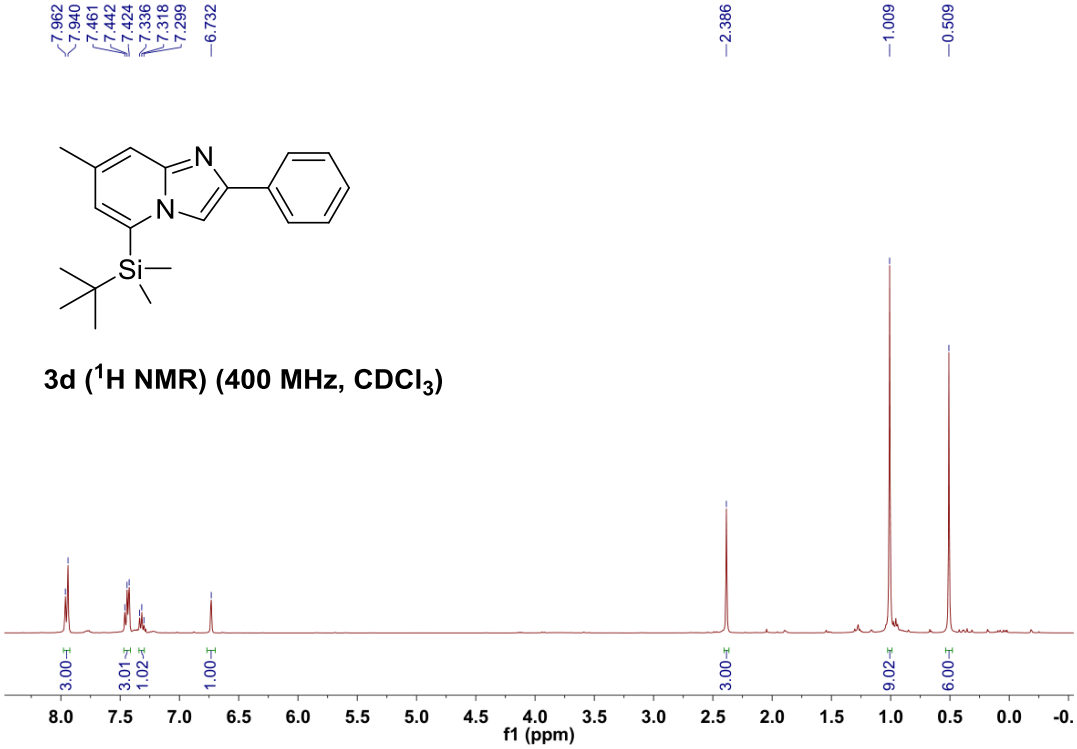
3b (^{13}C NMR) (100 MHz, $CDCl_3$)



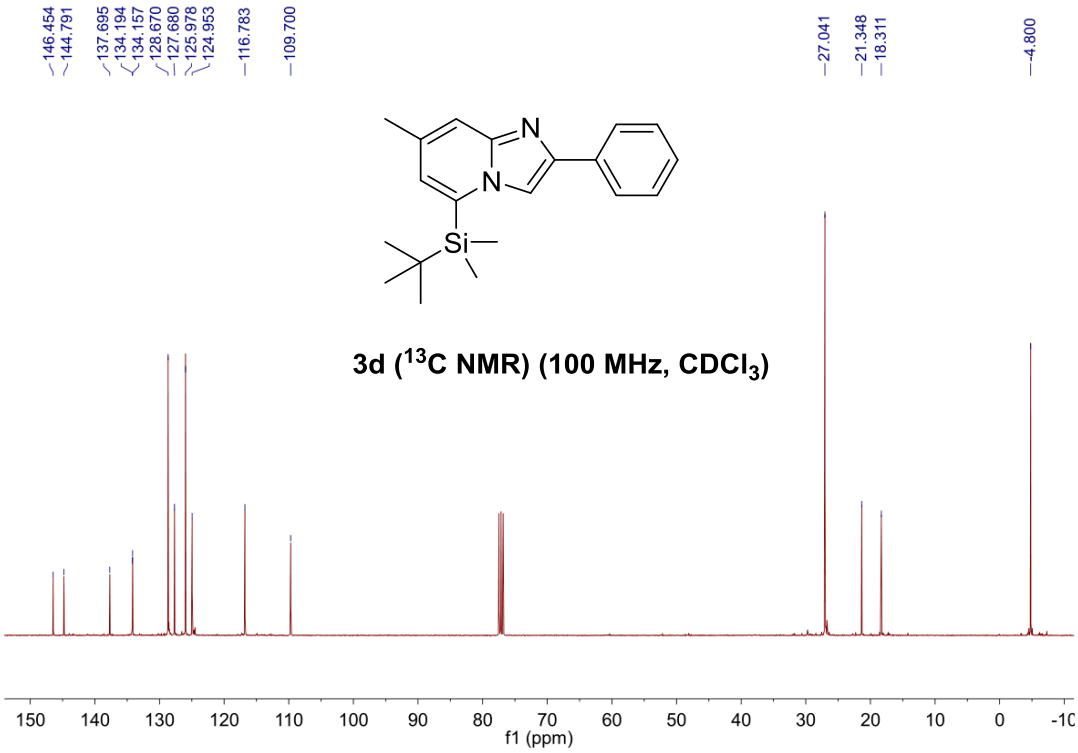
3c (^{1}H NMR) (400 MHz, $CDCl_3$)



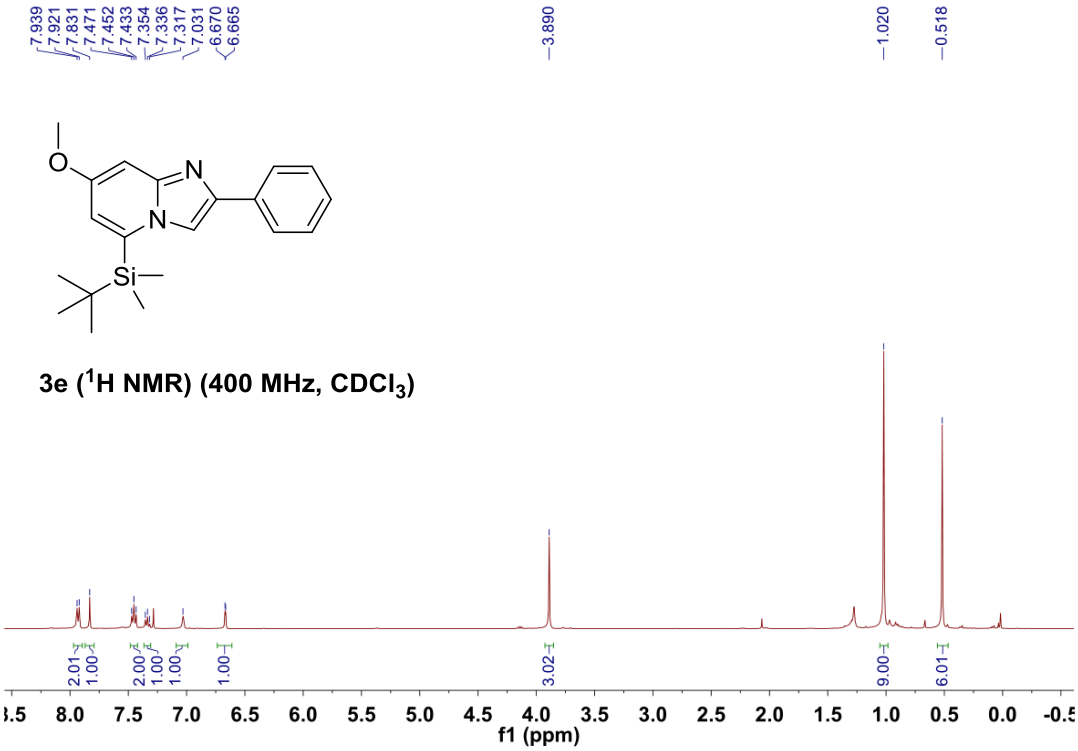
3c (^{13}C NMR) (100 MHz, $CDCl_3$)

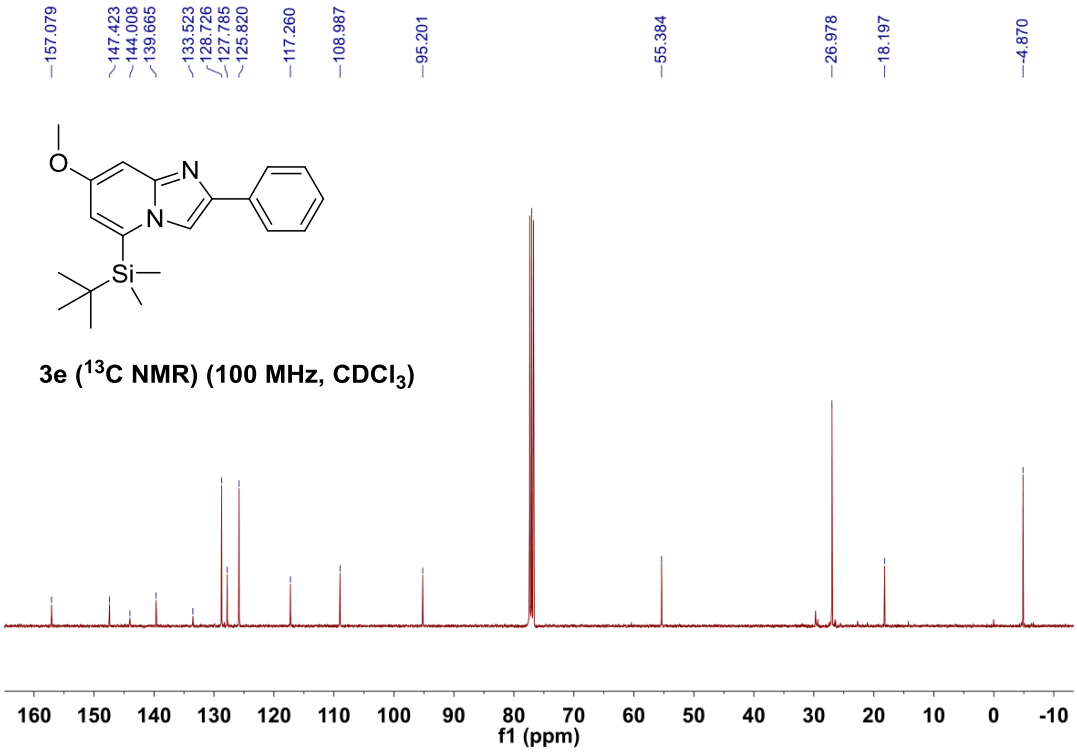


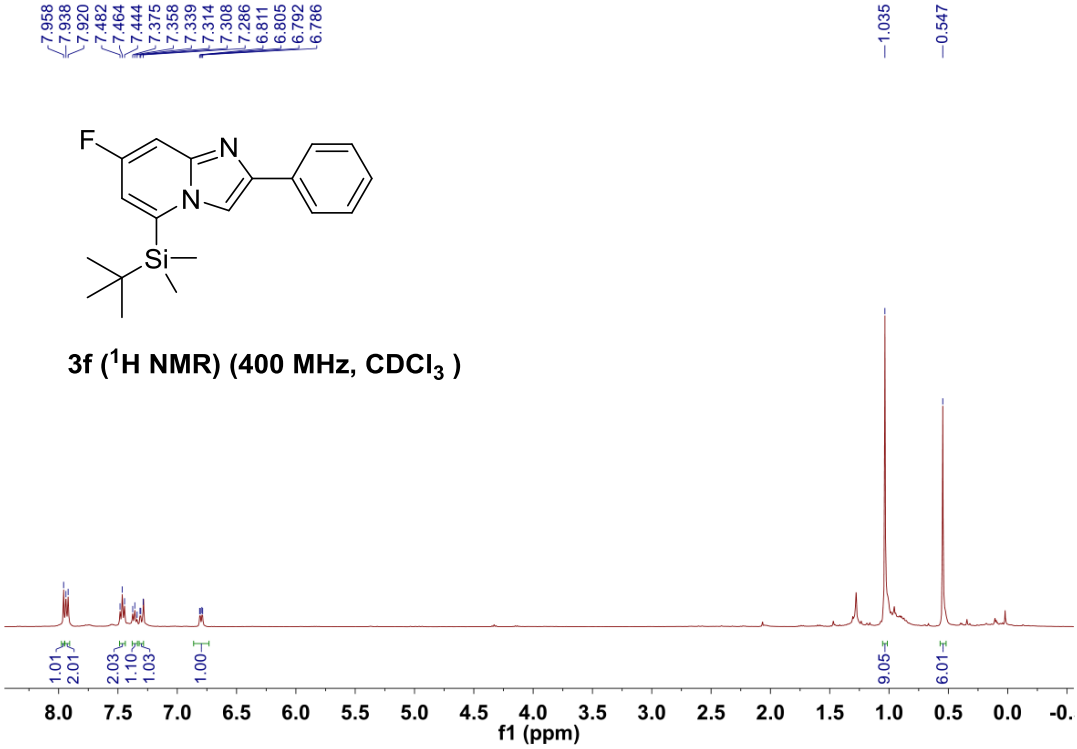
3d (^{1}H NMR) (400 MHz, $CDCl_3$)



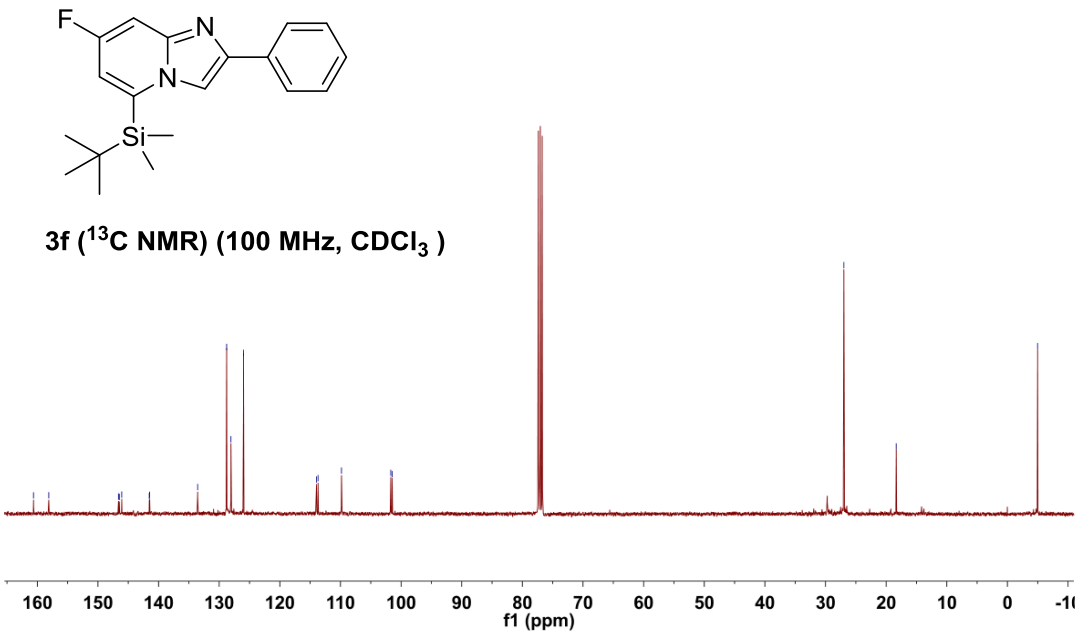
3d (^{13}C NMR) (100 MHz, $CDCl_3$)


7.939
7.921
7.831
7.471
7.452
7.433
7.354
7.336
7.317
7.031
6.670
6.665
3.890
1.020
0.518
O
N
N
Si
3e (1H NMR) (400 MHz, CDCl3)
2.01
1.00
2.00
1.00
1.00
1.00
3.02
9.00
6.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


157.079
147.423
144.008
139.665
133.523
128.726
127.785
125.820
117.260
108.987
95.201
55.384
26.978
18.197
-4.870
O
N
N
Si
3e (13C NMR) (100 MHz, CDCl3)
160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

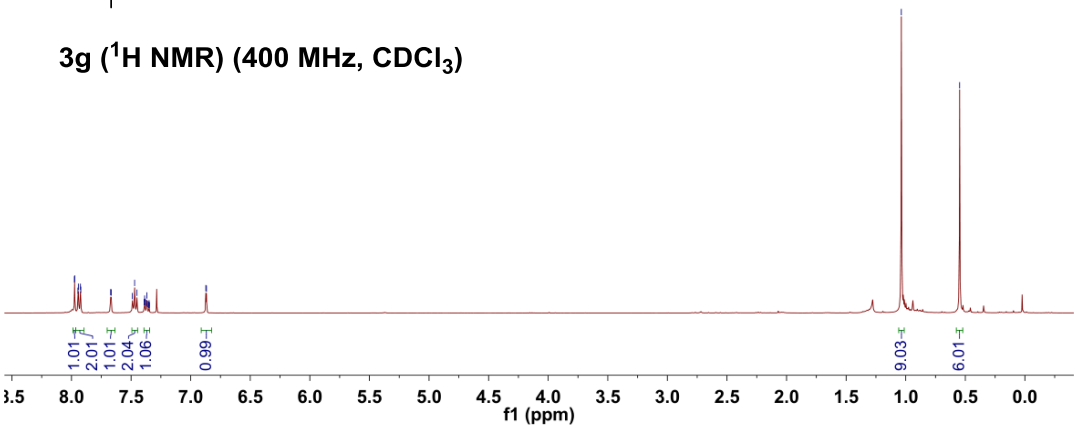


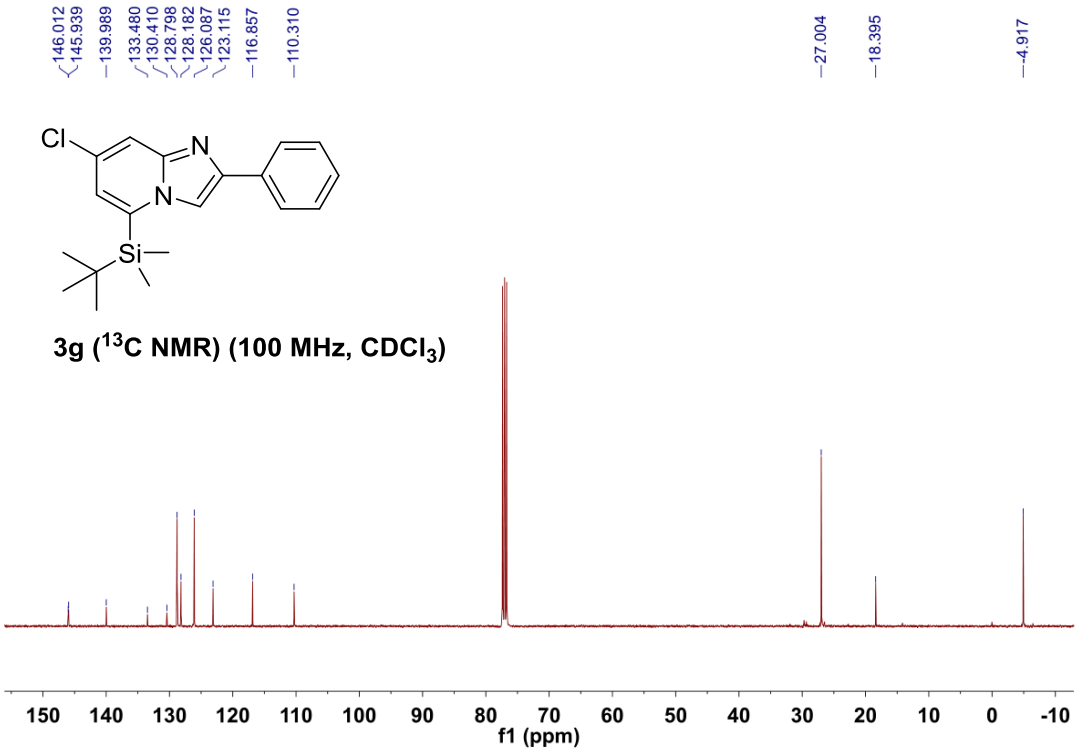
3f (^{1}H NMR) (400 MHz, $CDCl_3$)



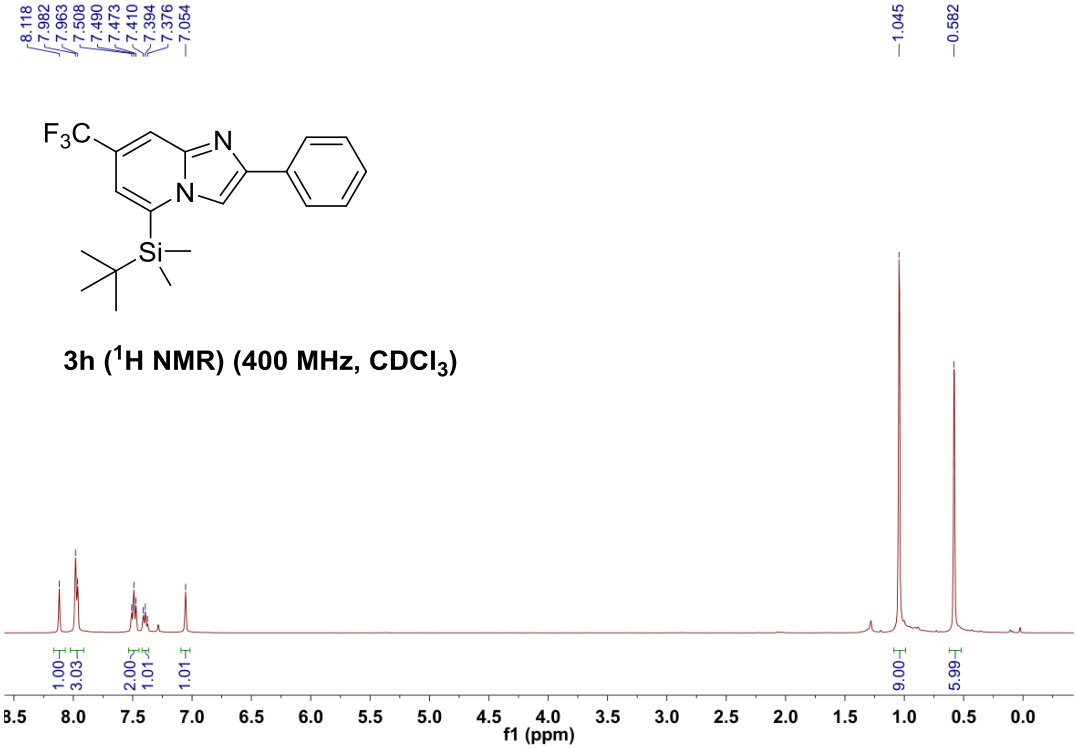
3f (^{13}C NMR) (100 MHz, $CDCl_3$)

3g (^{1}H NMR) (400 MHz, $CDCl_3$)

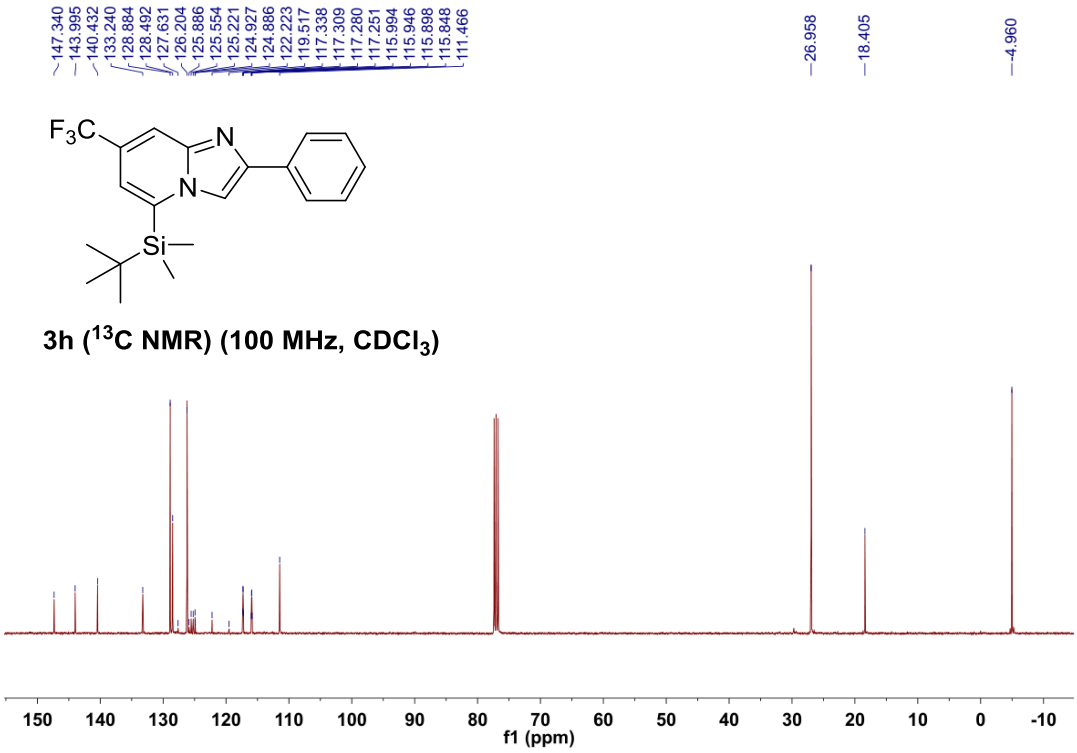




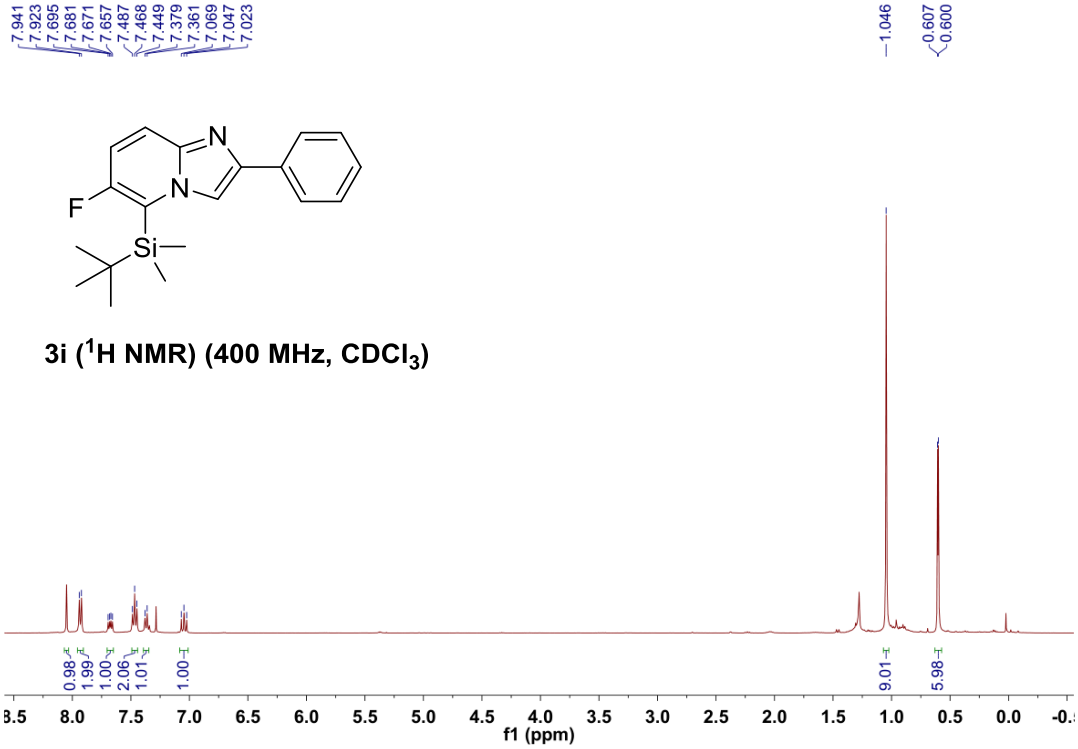
3g (^{13}C NMR) (100 MHz, $CDCl_3$)



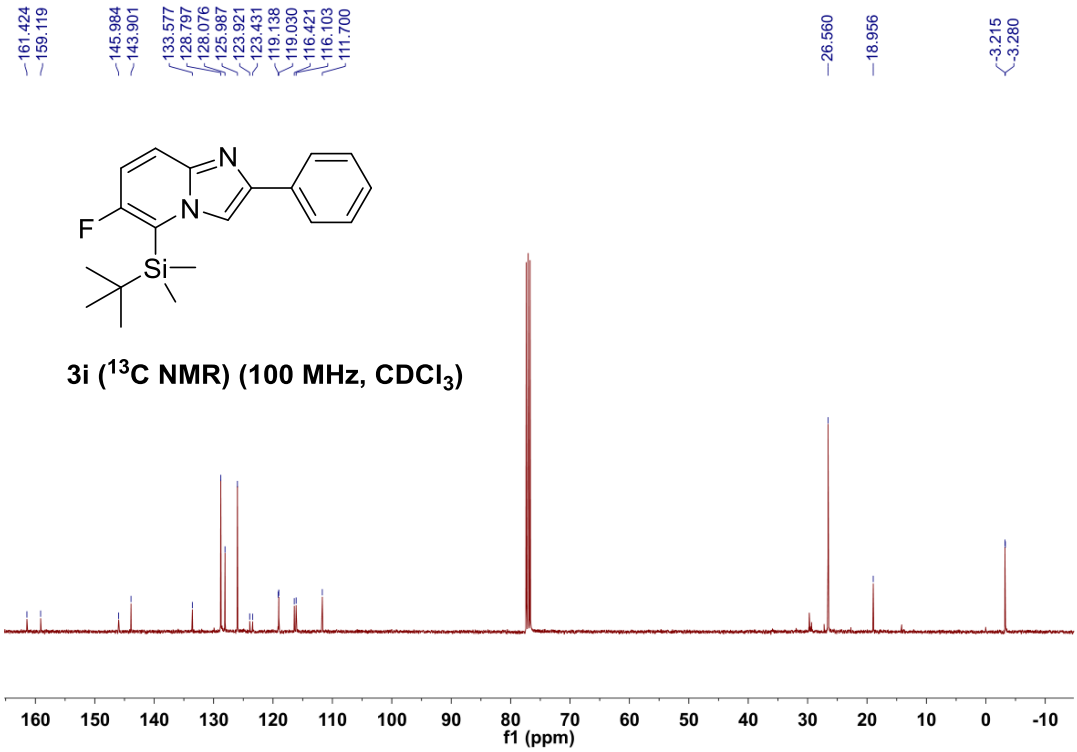
3h (^{1}H NMR) (400 MHz, $CDCl_3$)



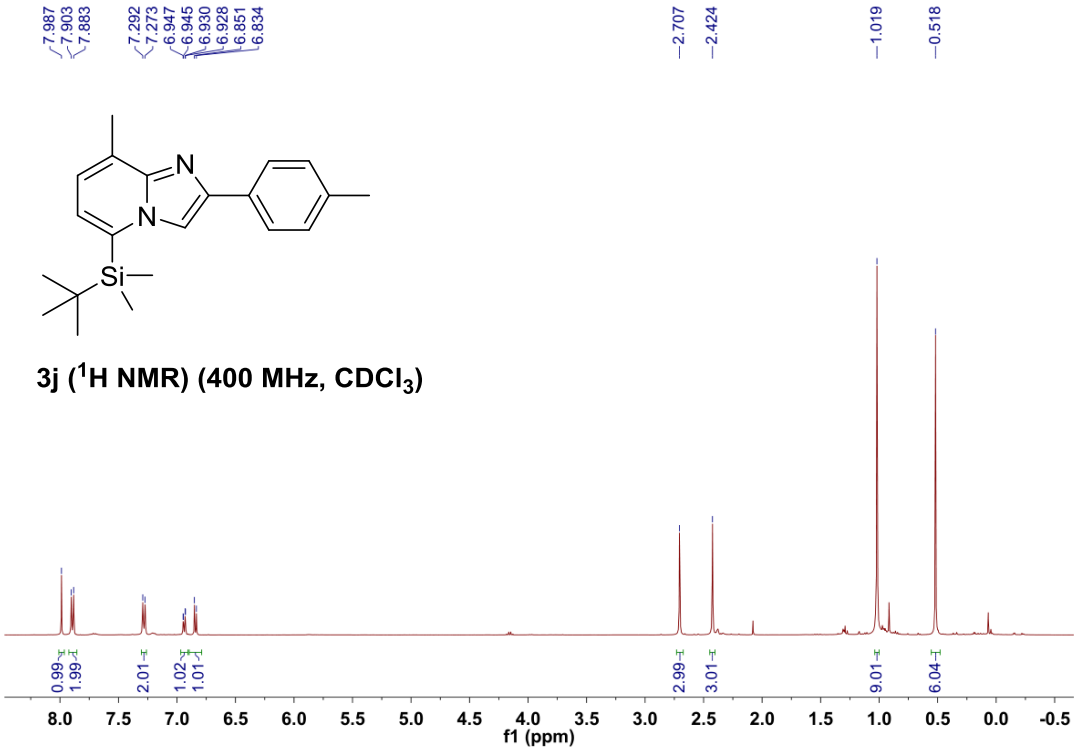
3h (^{13}C NMR) (100 MHz, $CDCl_3$)



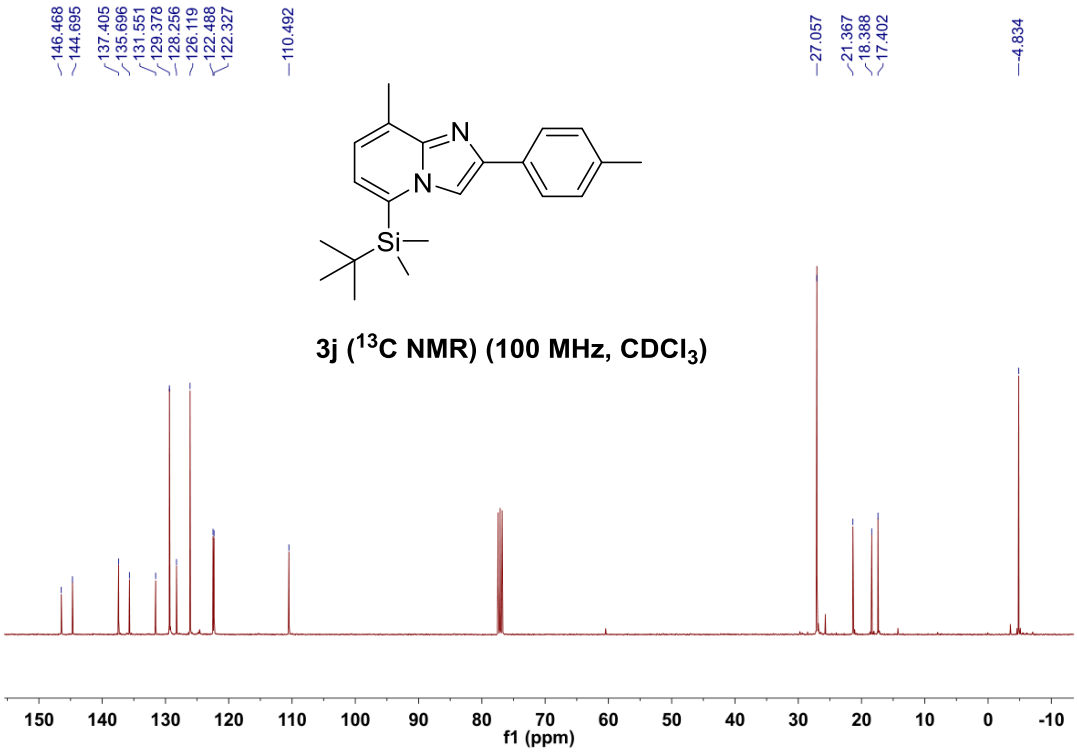
3i (^{1}H NMR) (400 MHz, $CDCl_3$)



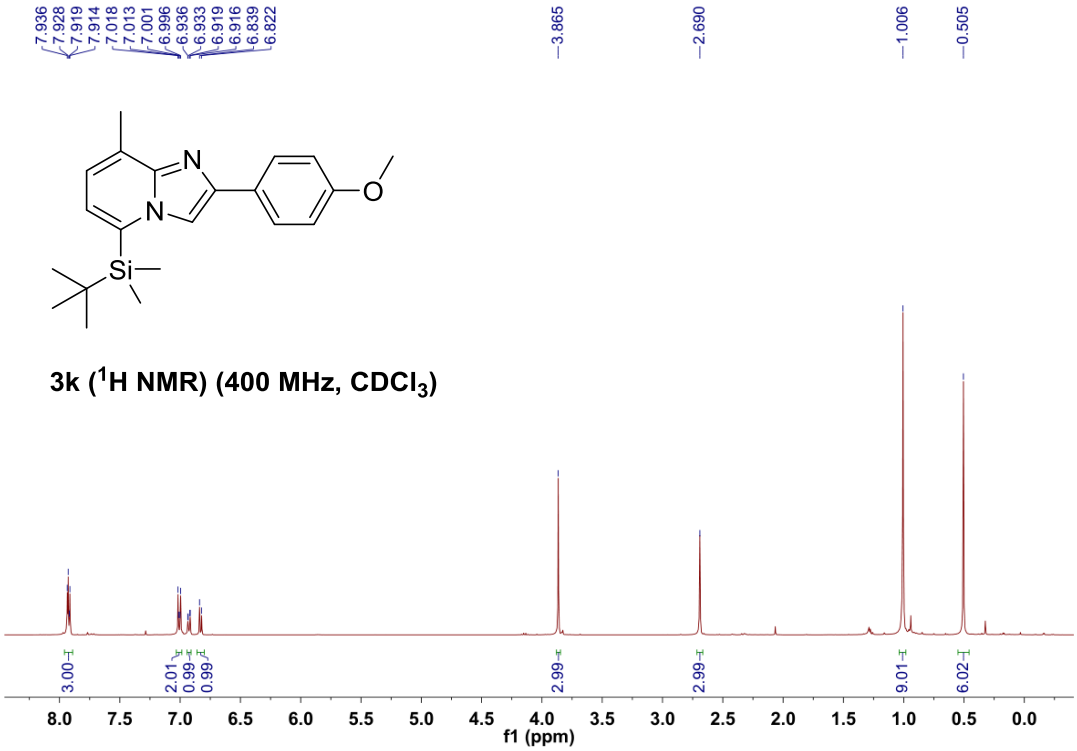
3i (^{13}C NMR) (100 MHz, $CDCl_3$)



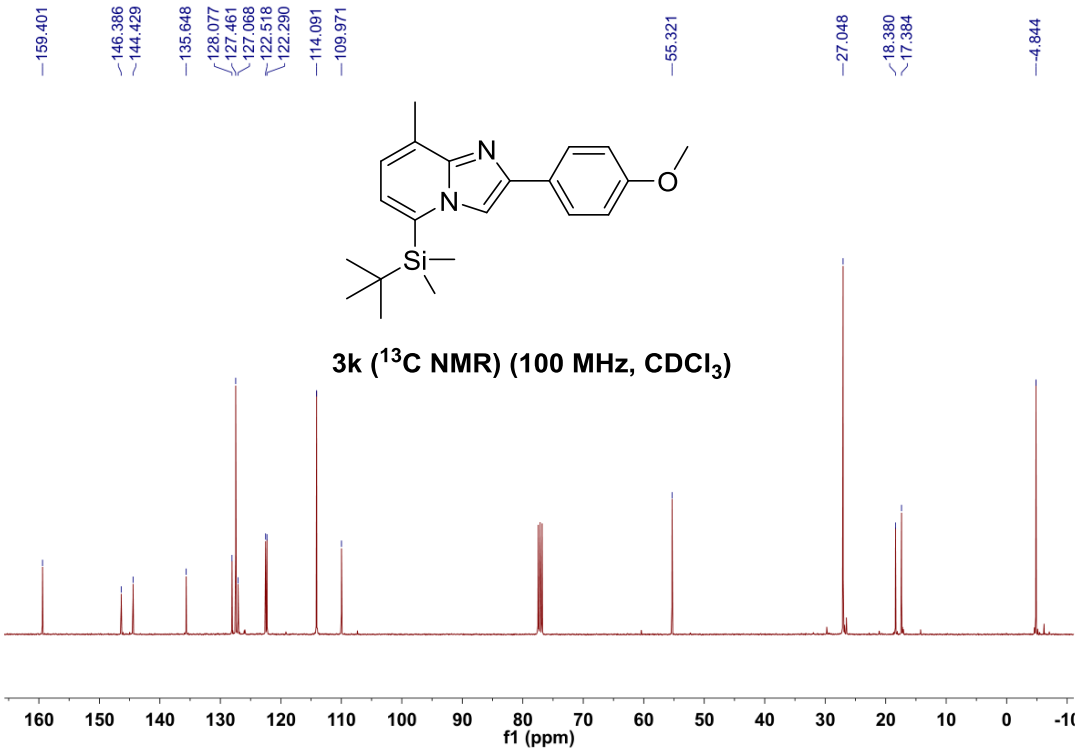
3j (^{1}H NMR) (400 MHz, $CDCl_3$)



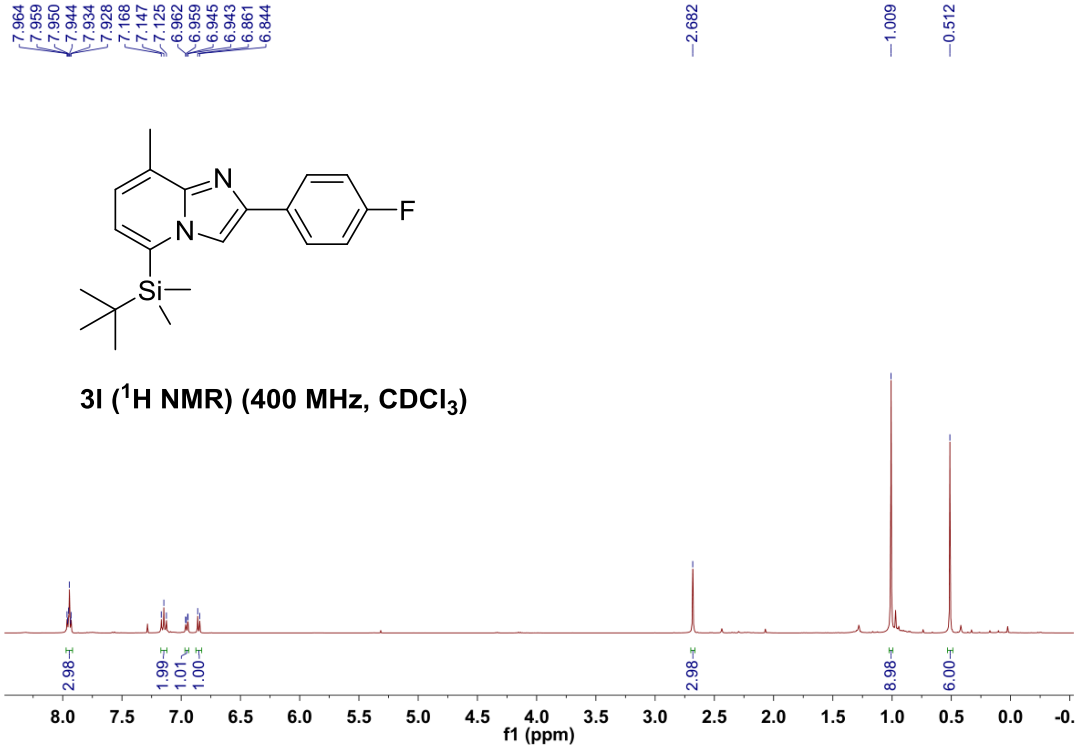
3j (^{13}C NMR) (100 MHz, $CDCl_3$)

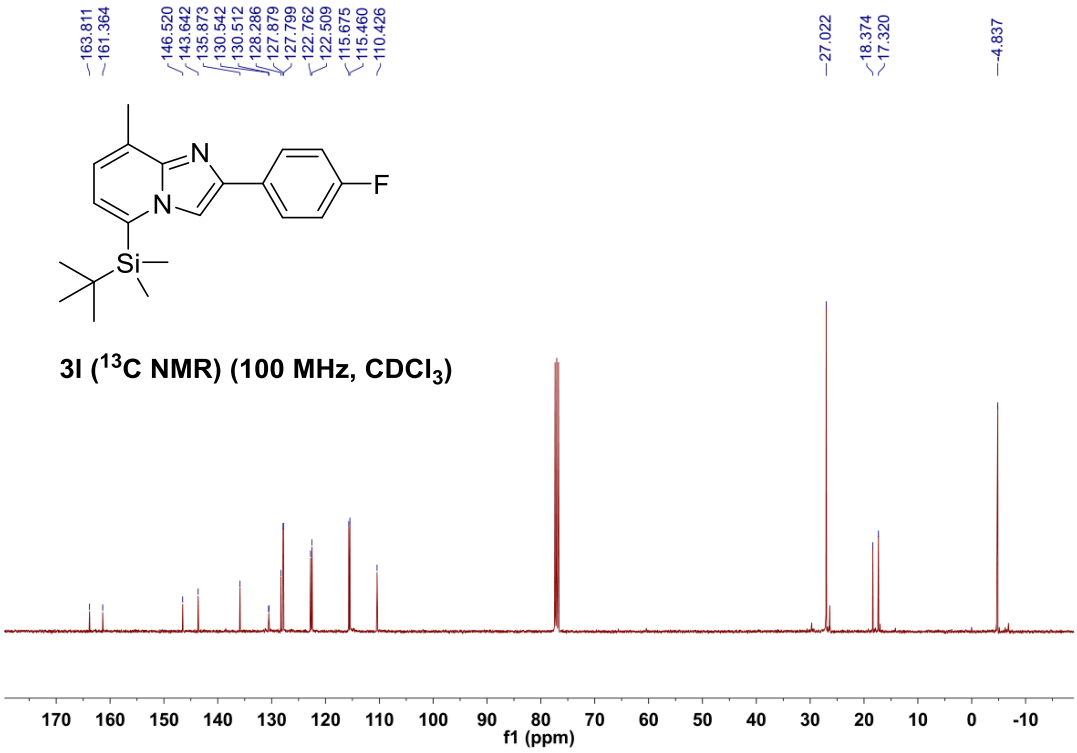


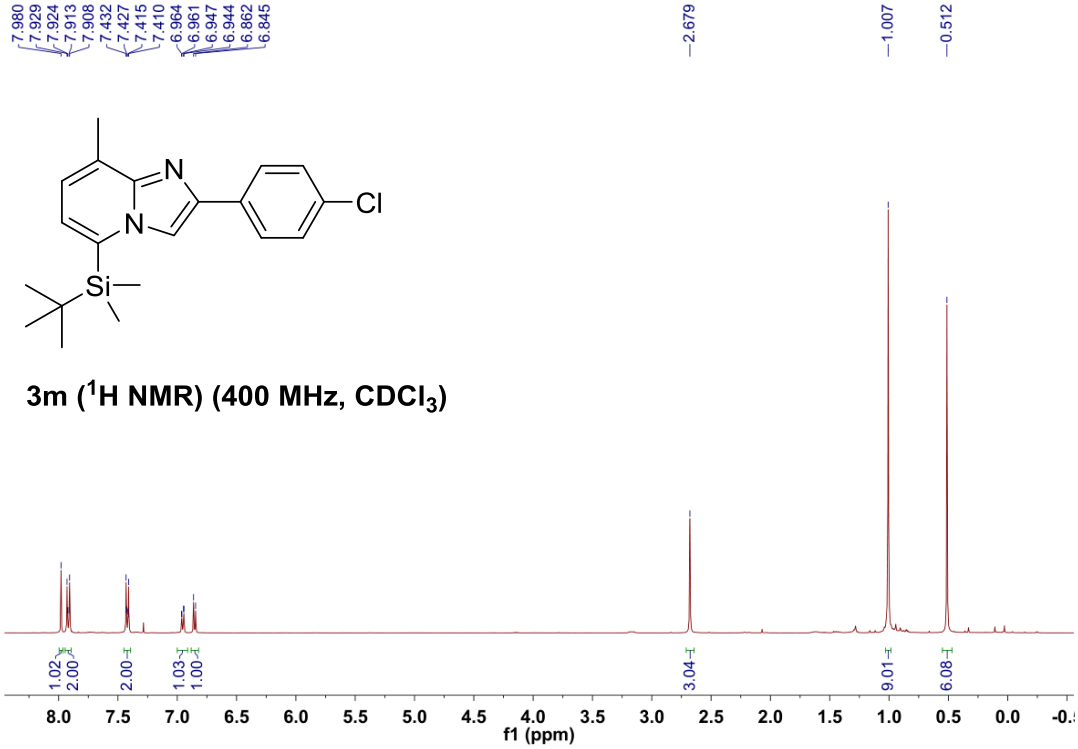
3k (^{1}H NMR) (400 MHz, $CDCl_3$)



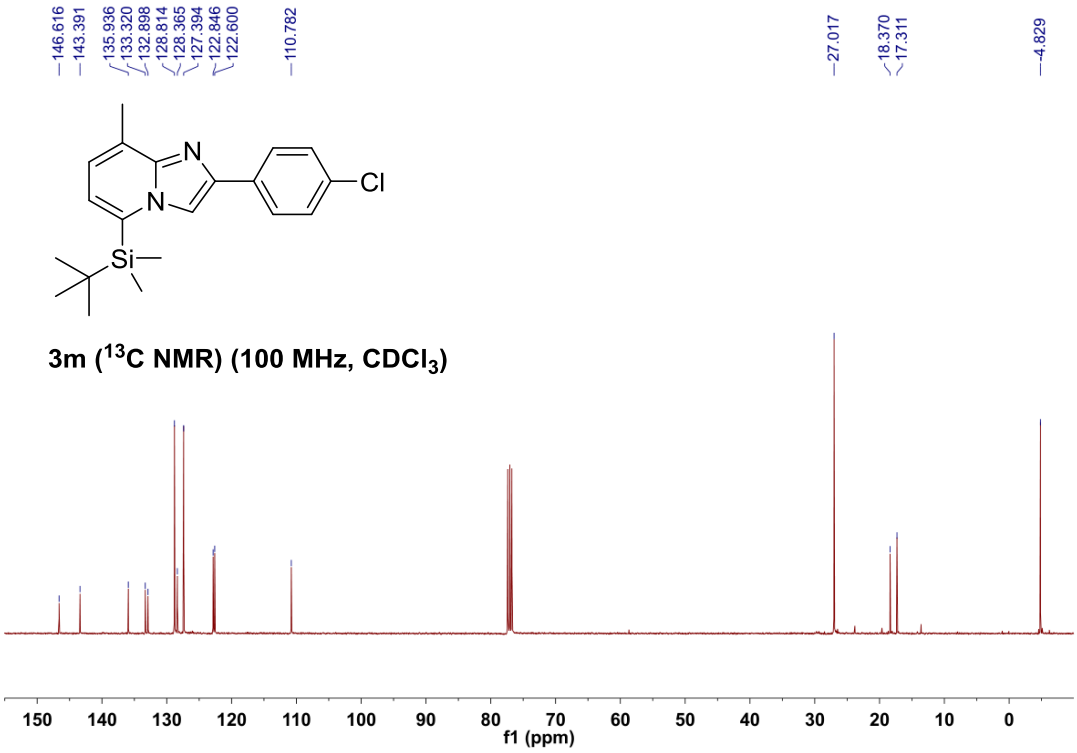
3k (^{13}C NMR) (100 MHz, $CDCl_3$)


7.964
7.959
7.950
7.944
7.934
7.928
7.168
7.147
7.125
6.962
6.959
6.945
6.943
6.861
6.844
2.682
1.009
0.512
N
N
F
Si
3l (1H NMR) (400 MHz, CDCl3)
2.98
1.99
1.01
1.00
2.98
8.98
6.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)

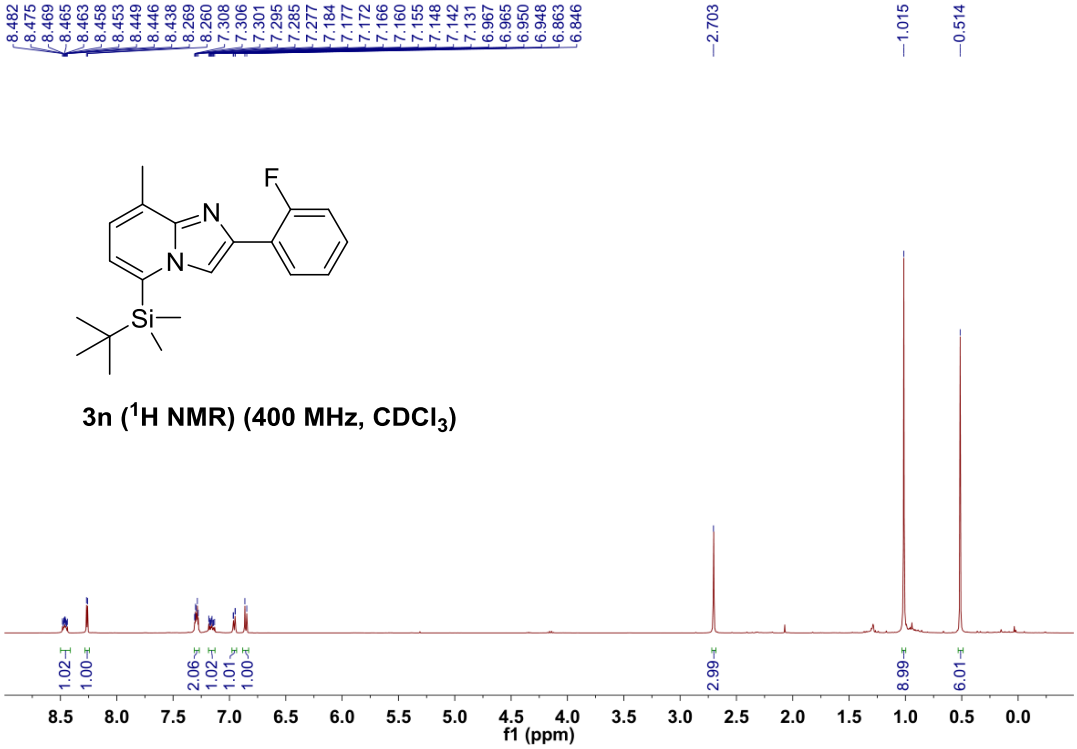

163.811
161.364
146.520
143.642
135.873
130.542
130.512
128.286
127.879
127.799
122.762
122.509
115.675
115.460
110.426
27.022
18.374
17.320
-4.837
N
N
F
Si
3l (13C NMR) (100 MHz, CDCl3)
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



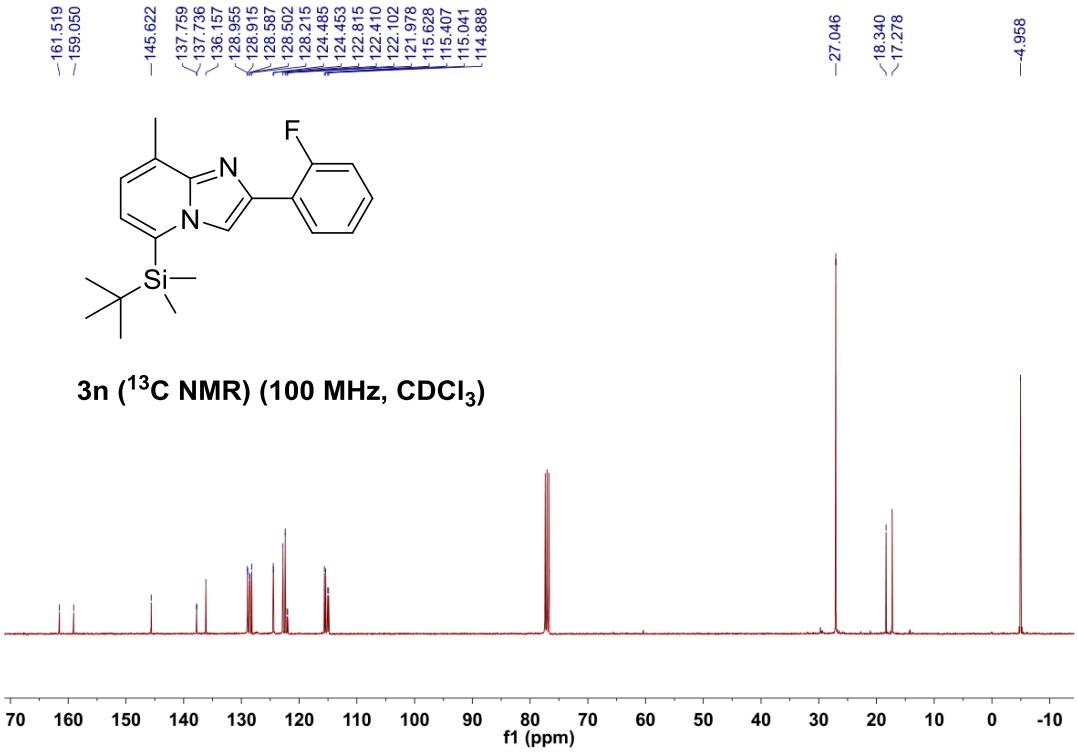
3m (^{1}H NMR) (400 MHz, $CDCl_3$)



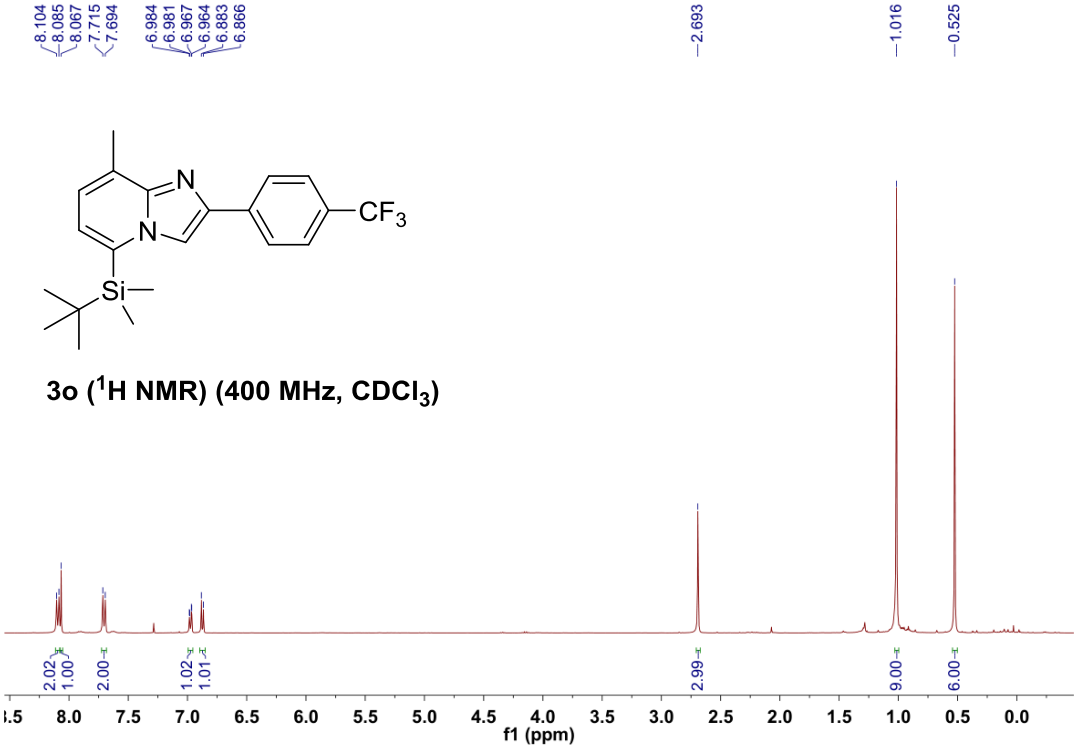
3m (^{13}C NMR) (100 MHz, $CDCl_3$)



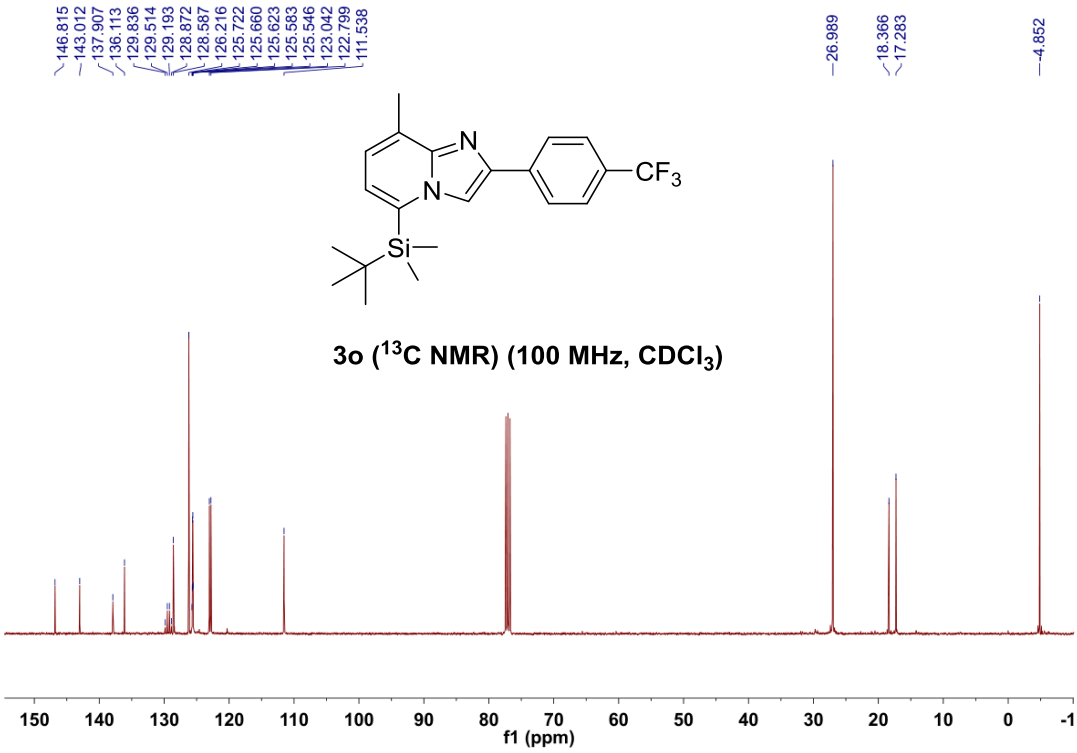
3n (^{1}H NMR) (400 MHz, $CDCl_3$)



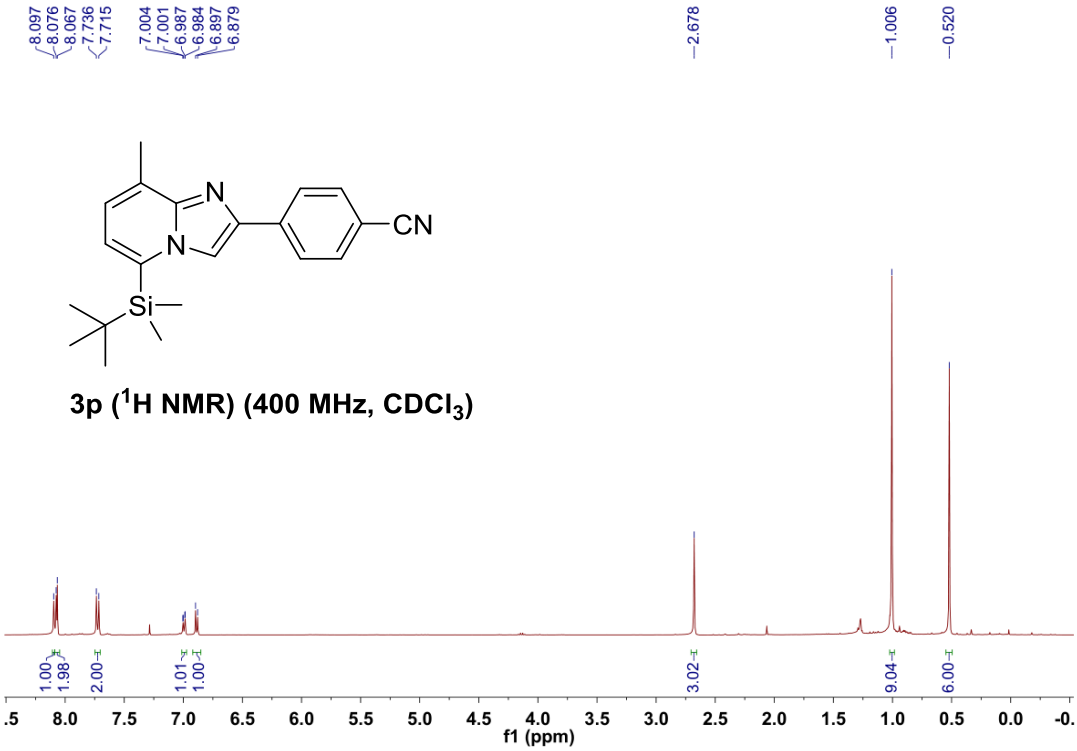
3n (^{13}C NMR) (100 MHz, $CDCl_3$)



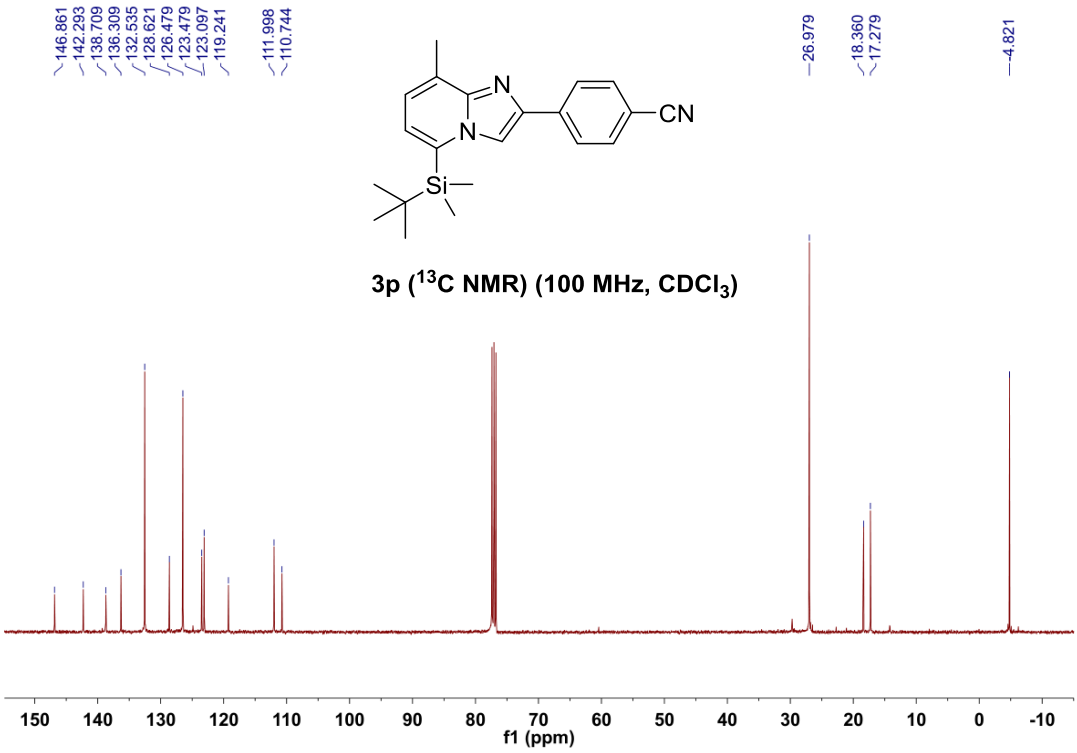
3o (^{1}H NMR) (400 MHz, $CDCl_3$)



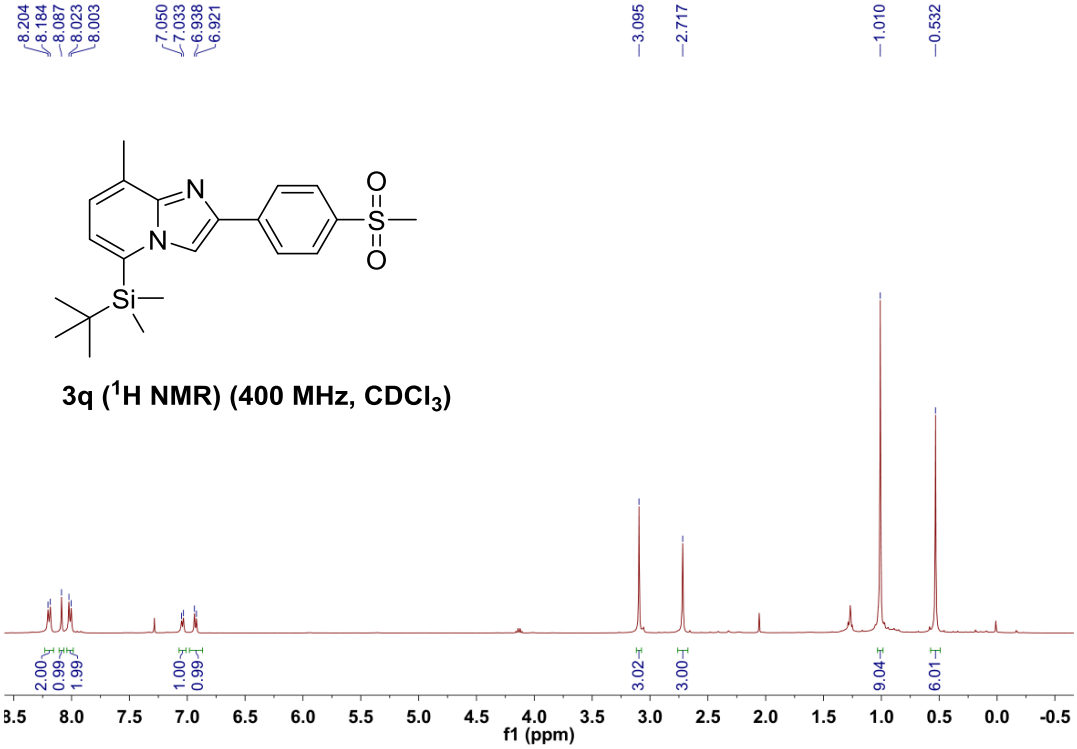
3o (^{13}C NMR) (100 MHz, $CDCl_3$)



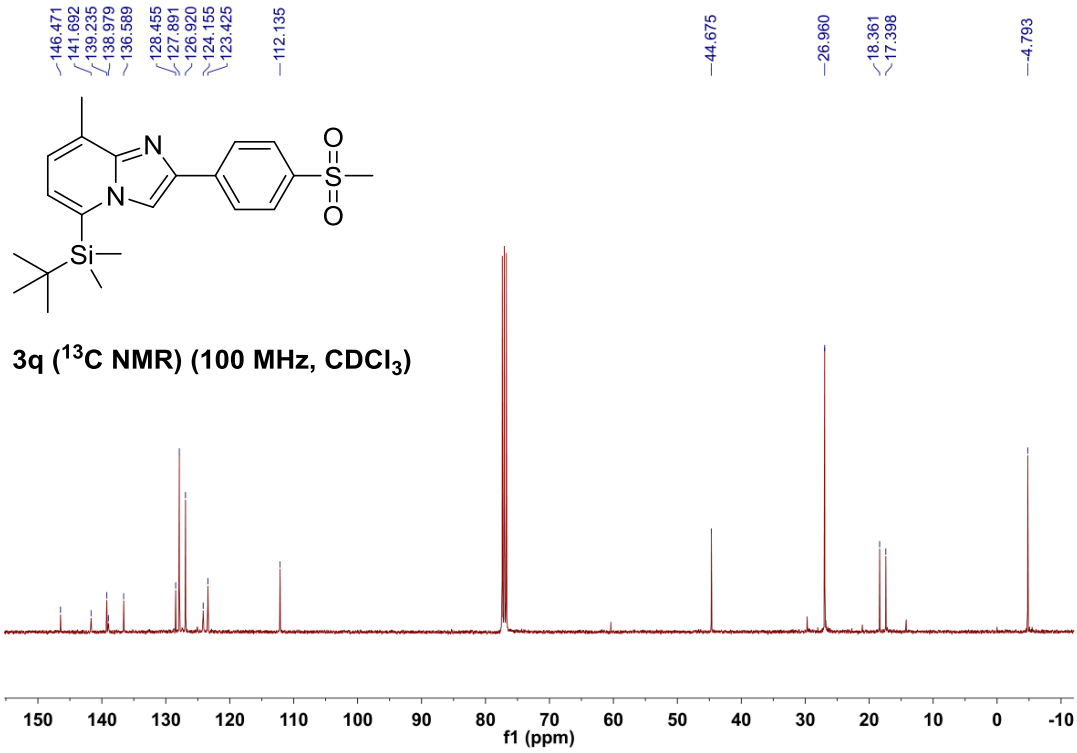
3p (^{1}H NMR) (400 MHz, $CDCl_3$)



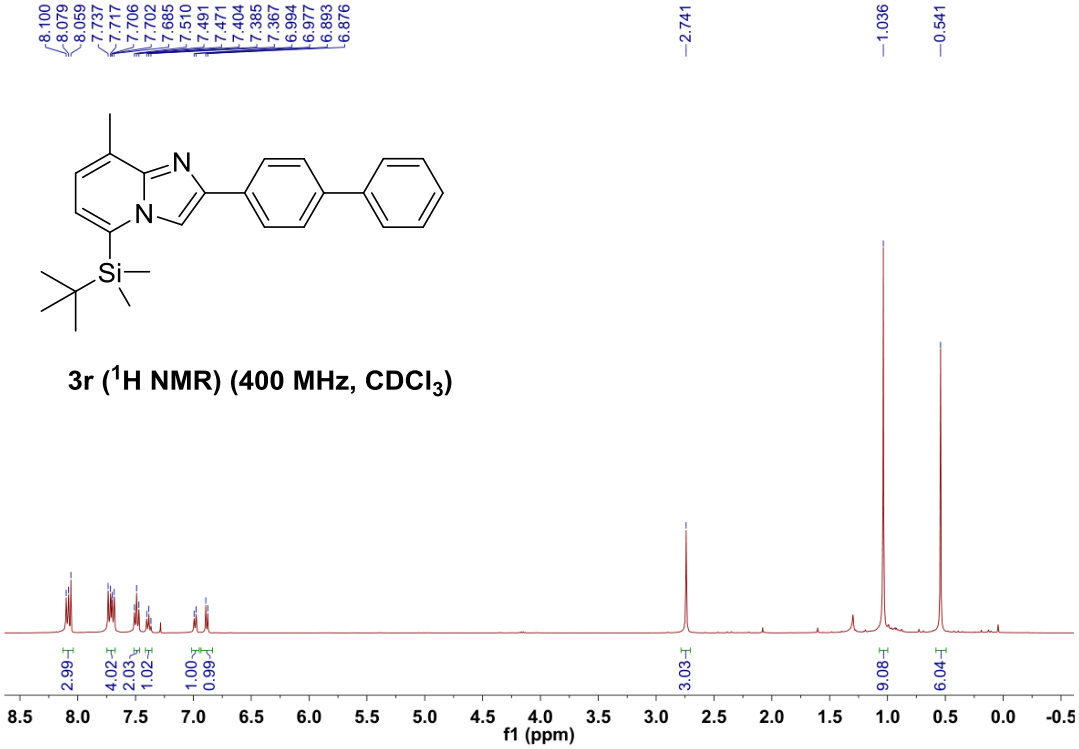
3p (^{13}C NMR) (100 MHz, $CDCl_3$)



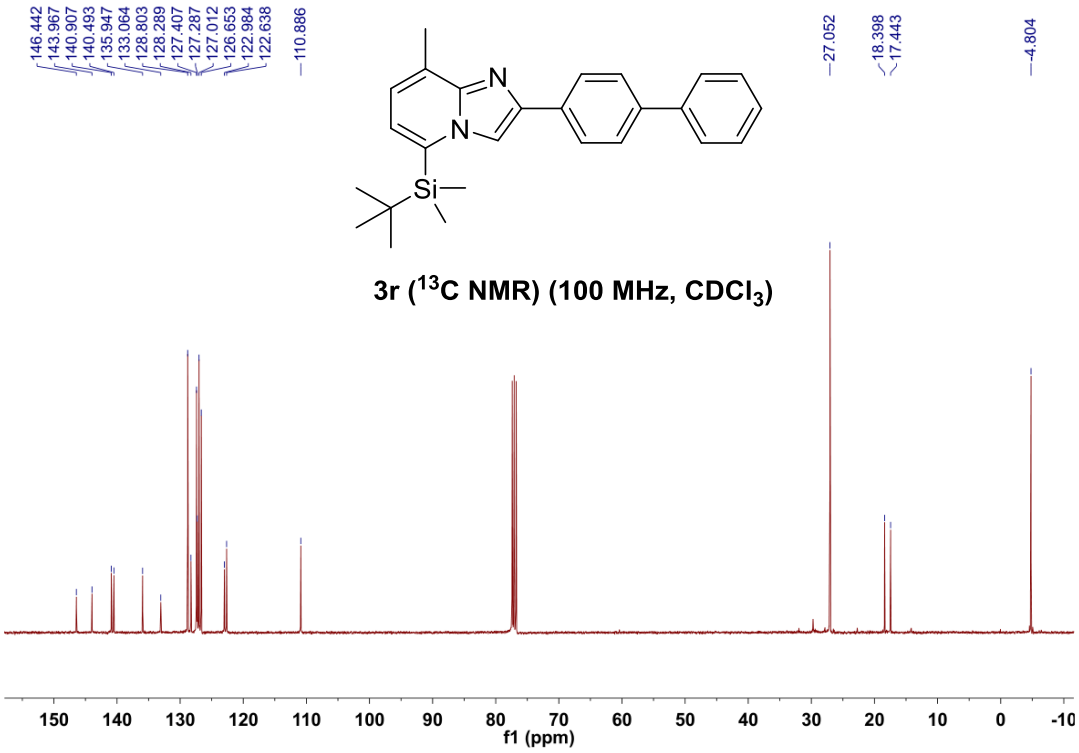
3q (^{1}H NMR) (400 MHz, $CDCl_3$)



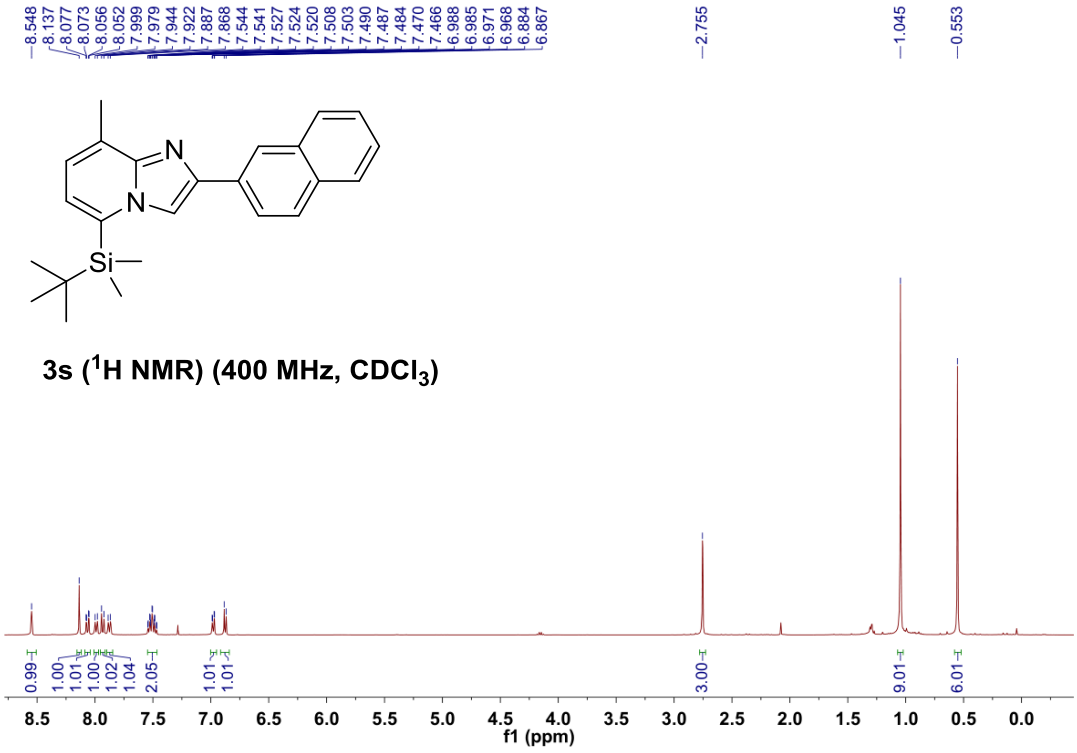
3q (^{13}C NMR) (100 MHz, $CDCl_3$)



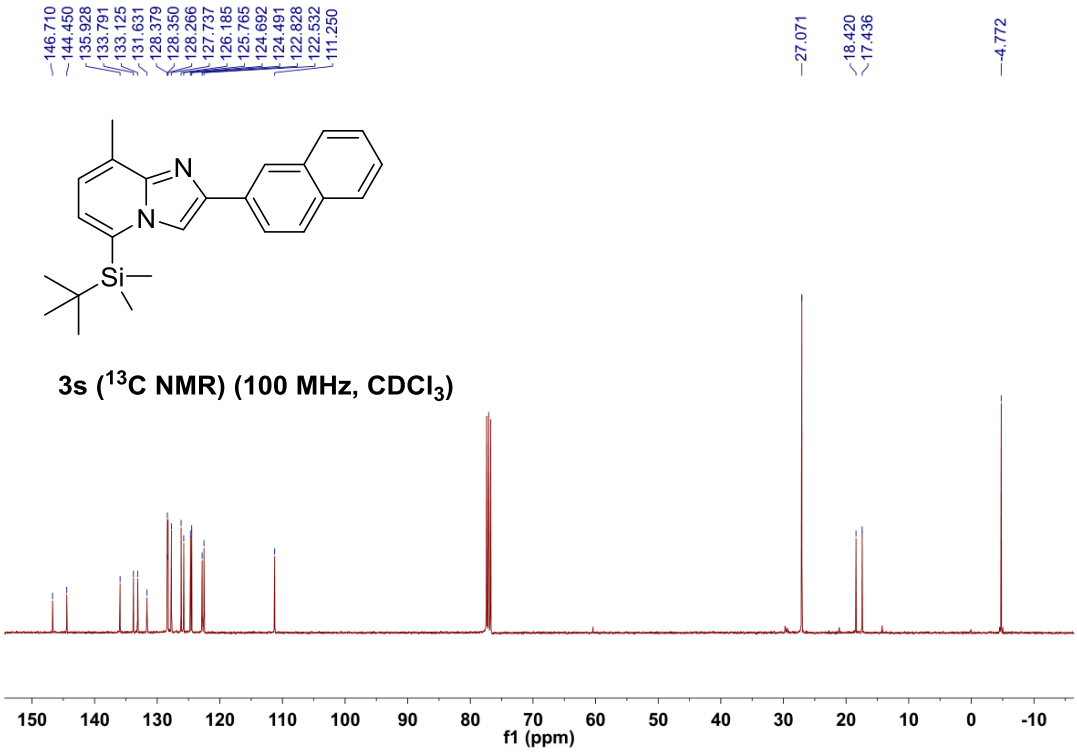
3r (^{1}H NMR) (400 MHz, $CDCl_3$)



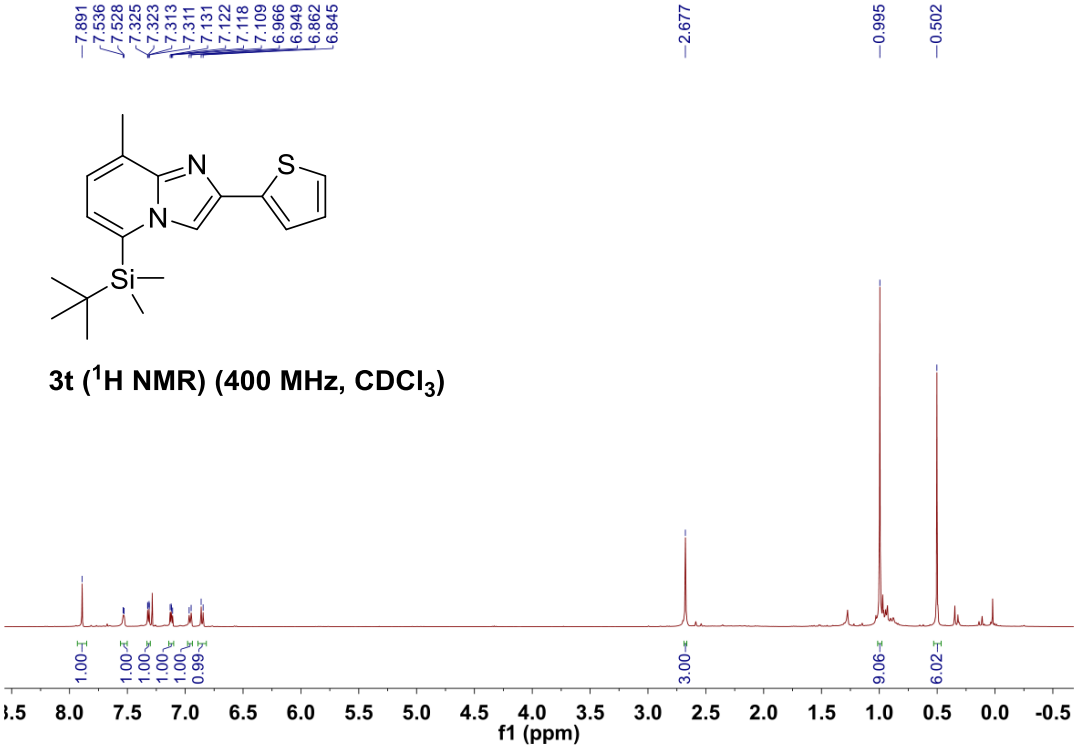
3r (^{13}C NMR) (100 MHz, $CDCl_3$)



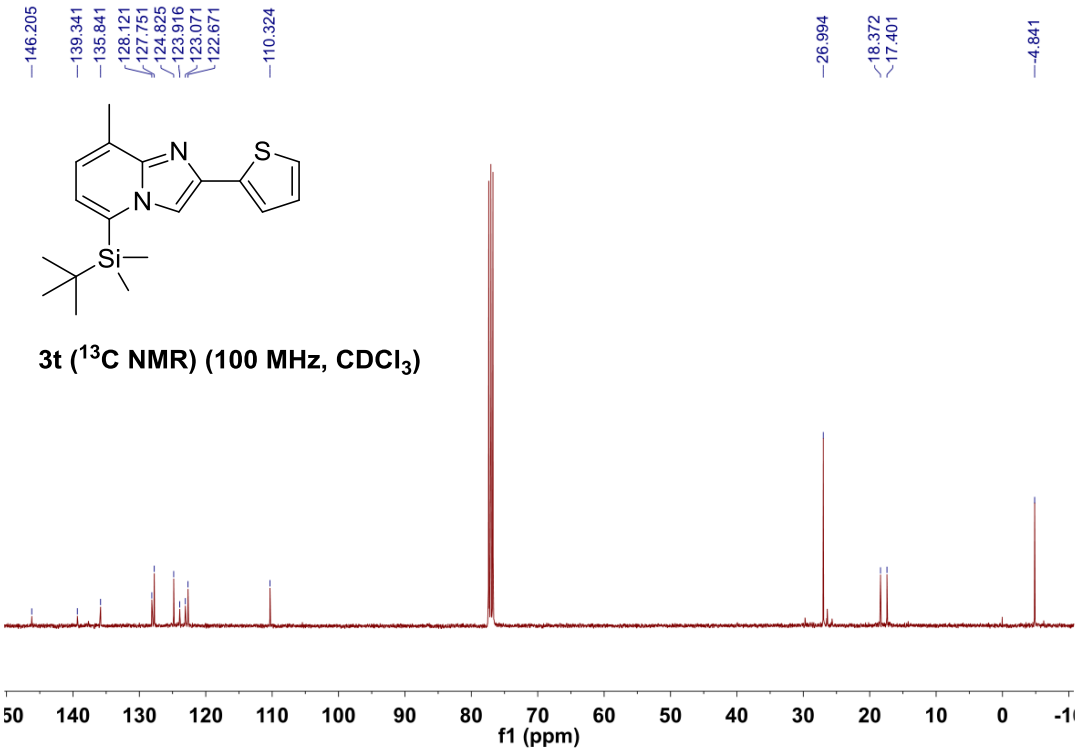
3s (^{1}H NMR) (400 MHz, $CDCl_3$)



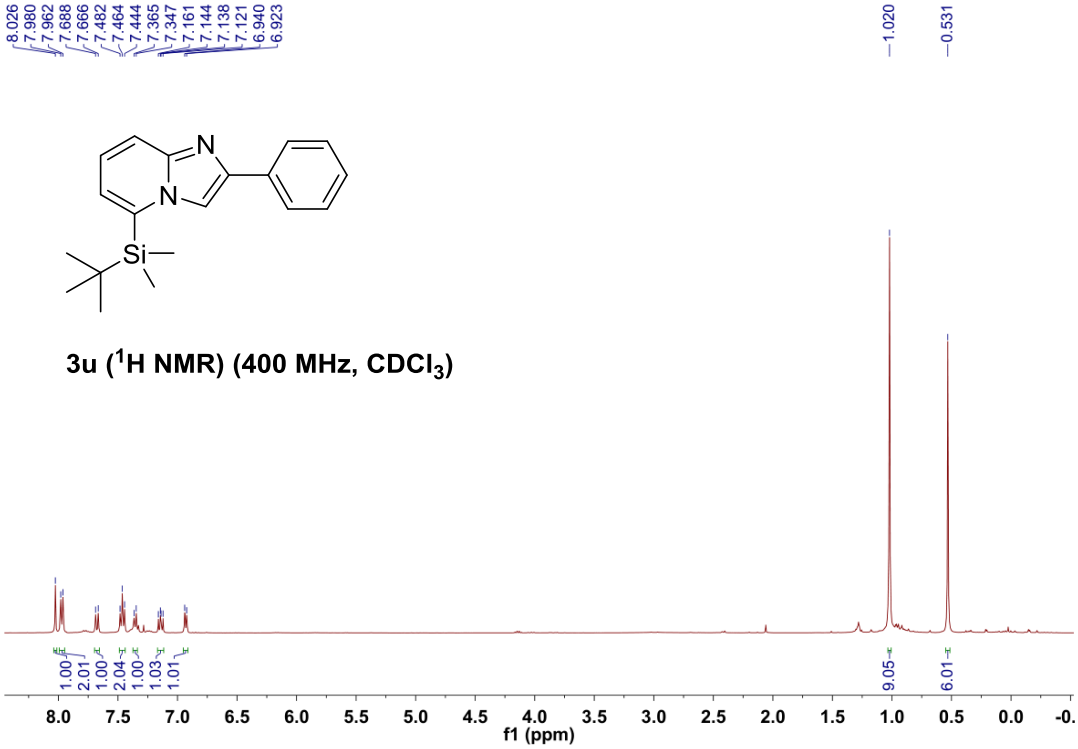
3s (^{13}C NMR) (100 MHz, $CDCl_3$)



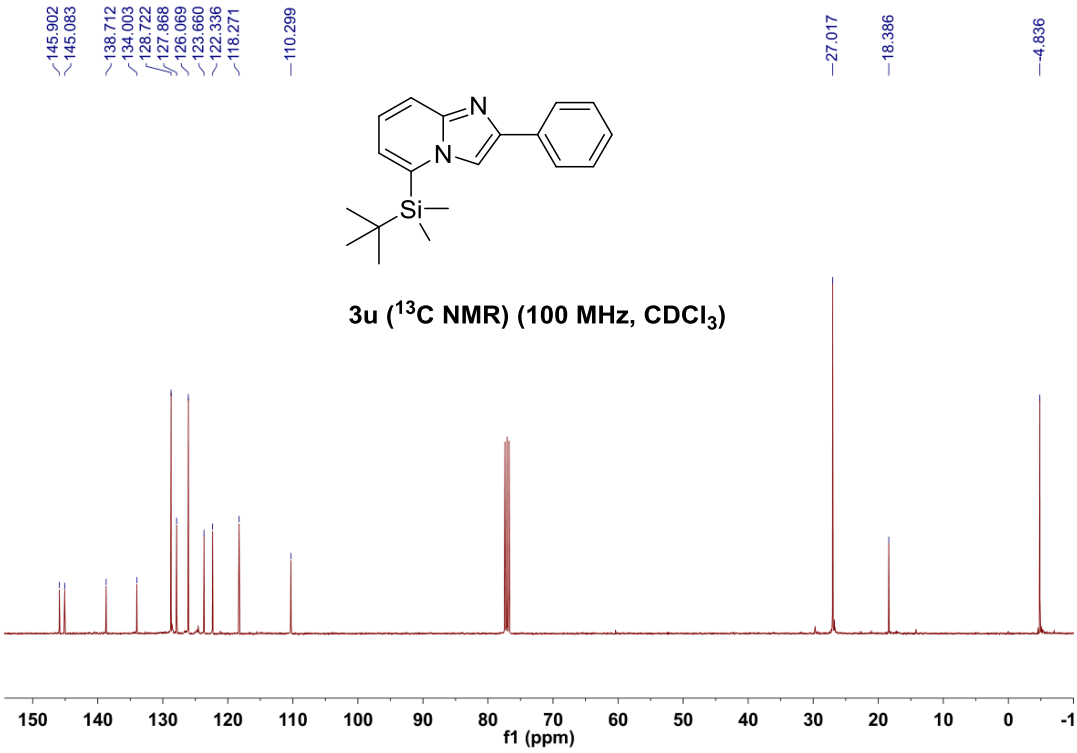
3t (^{1}H NMR) (400 MHz, $CDCl_3$)



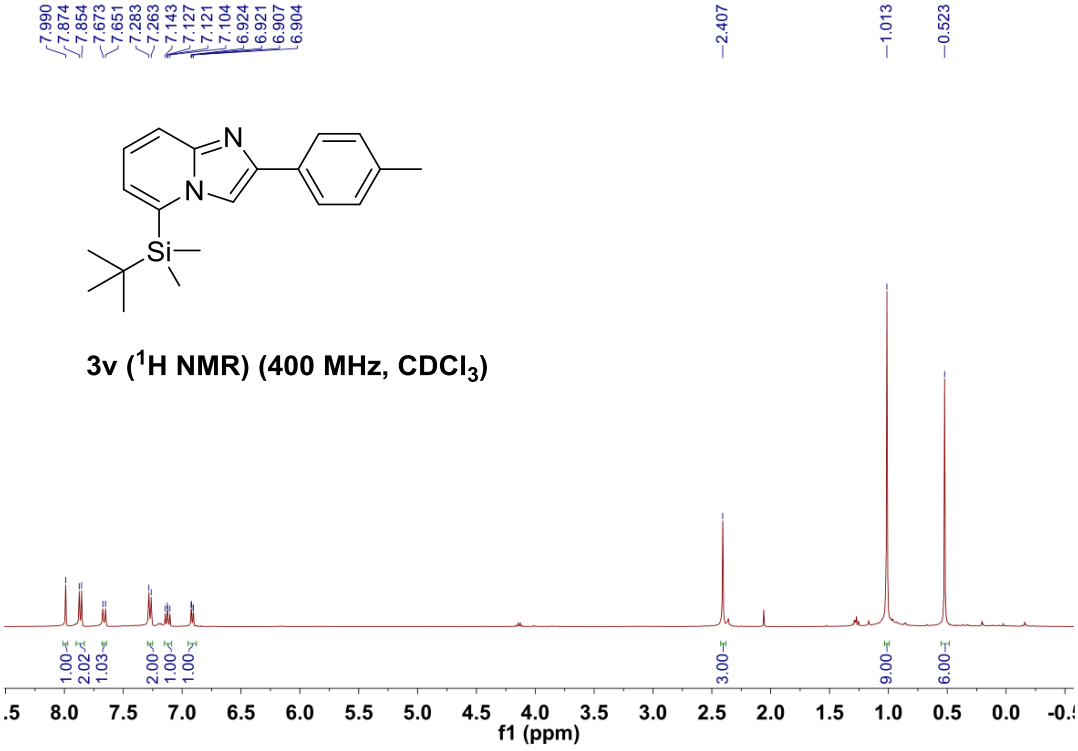
3t (^{13}C NMR) (100 MHz, $CDCl_3$)



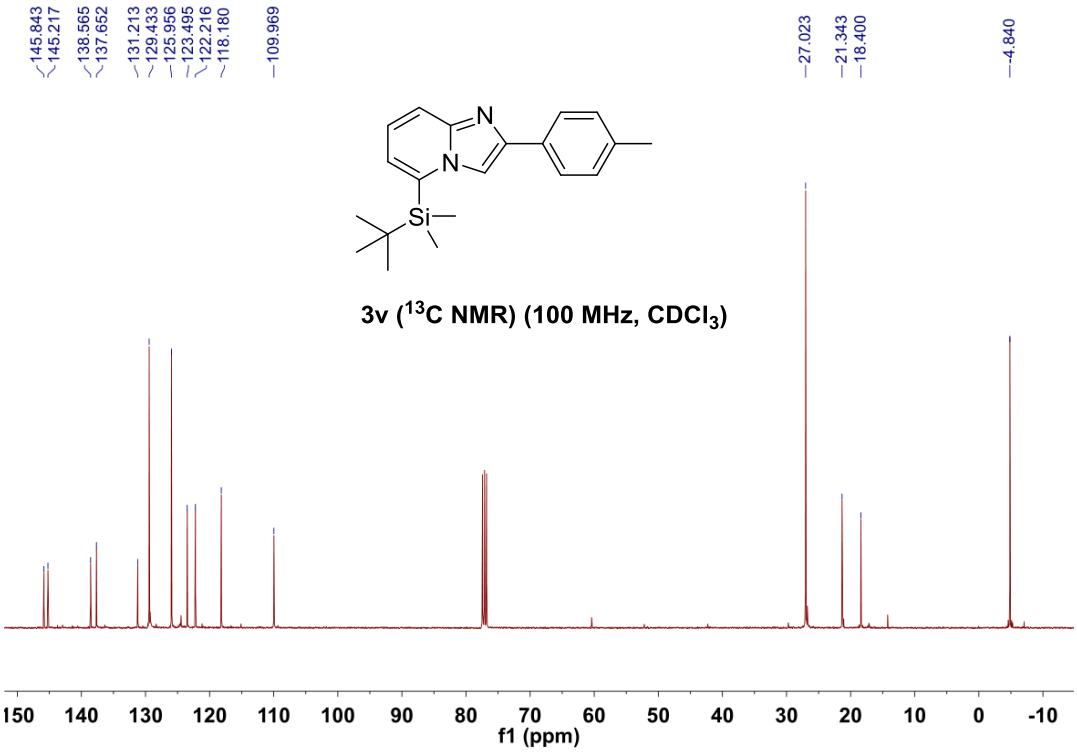
3u (^{1}H NMR) (400 MHz, $CDCl_3$)



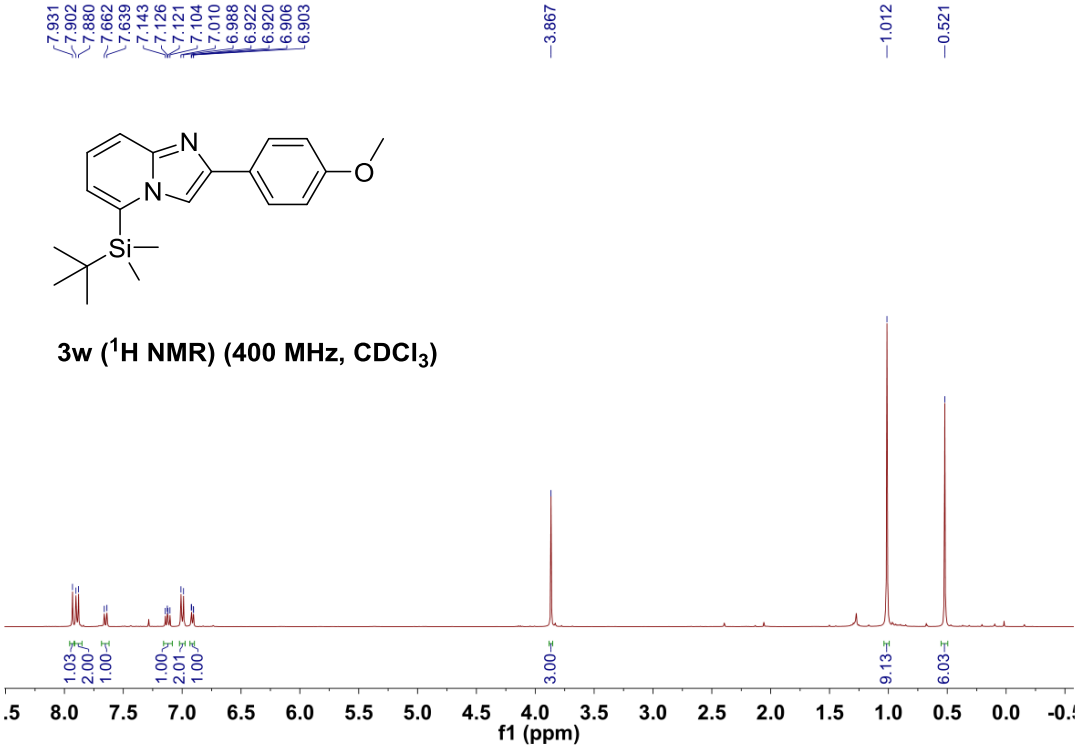
3u (^{13}C NMR) (100 MHz, $CDCl_3$)



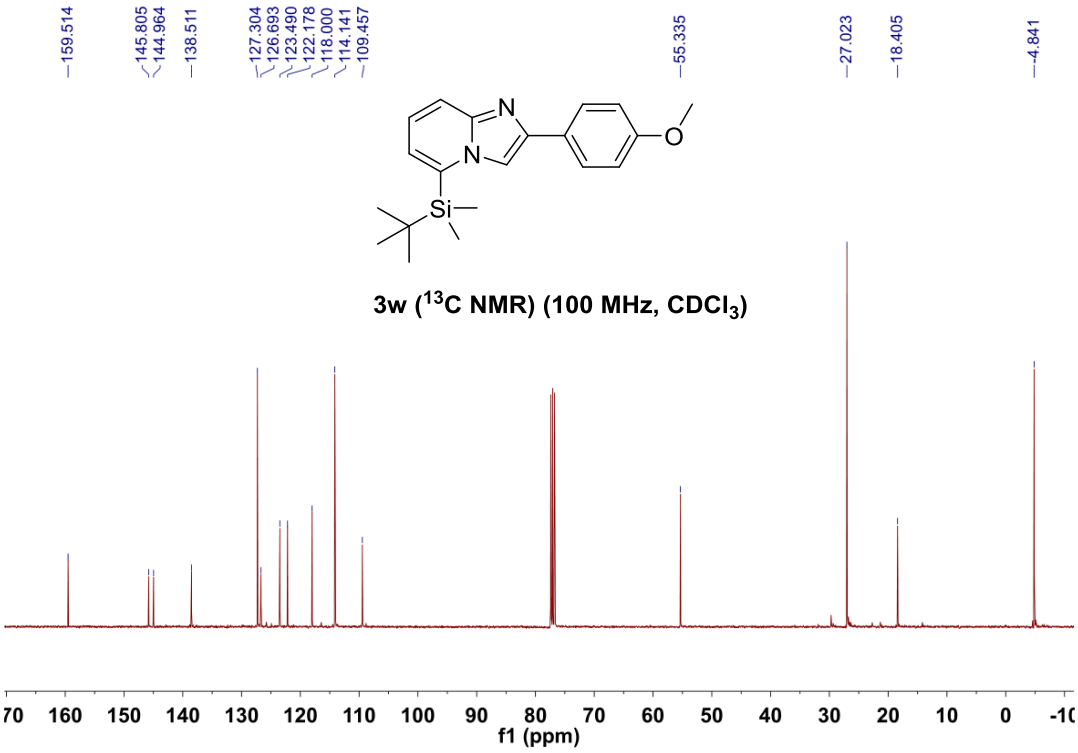
3v (^{1}H NMR) (400 MHz, $CDCl_3$)



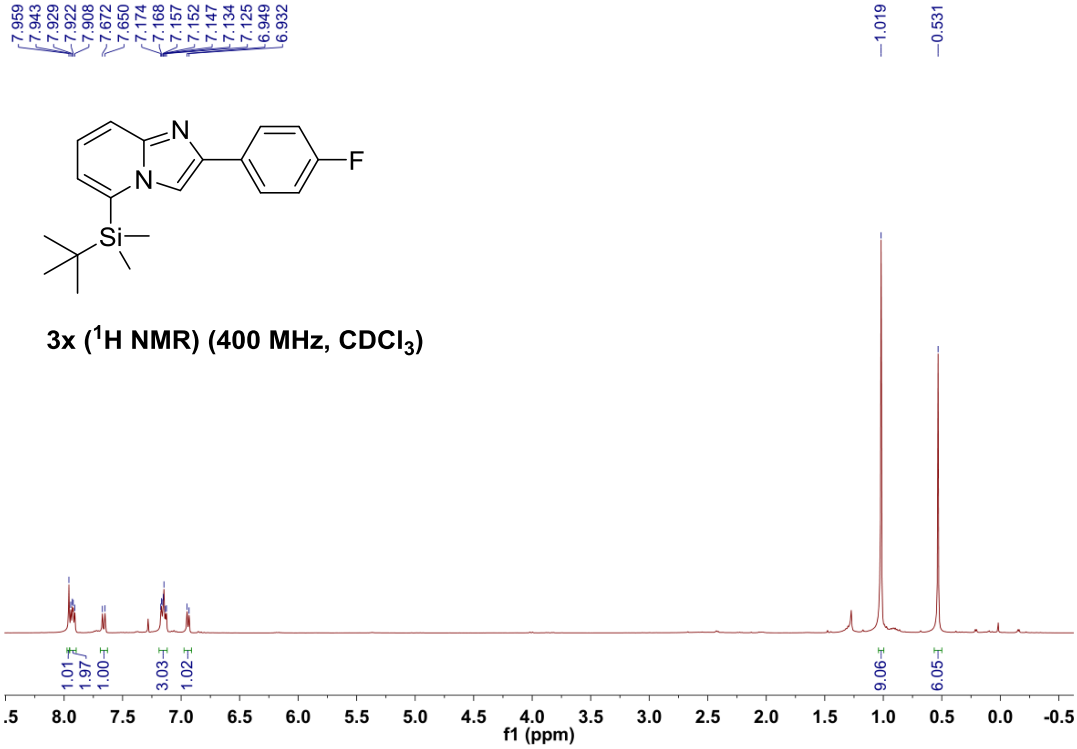
3v (^{13}C NMR) (100 MHz, $CDCl_3$)



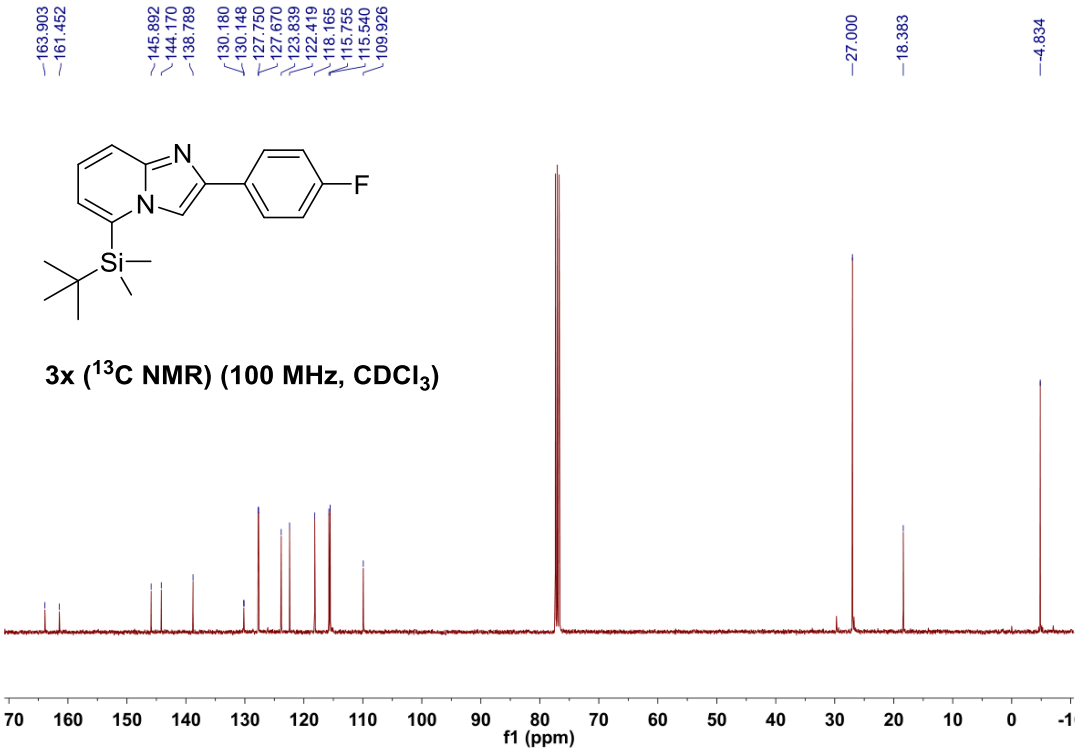
3w (^{1}H NMR) (400 MHz, $CDCl_3$)



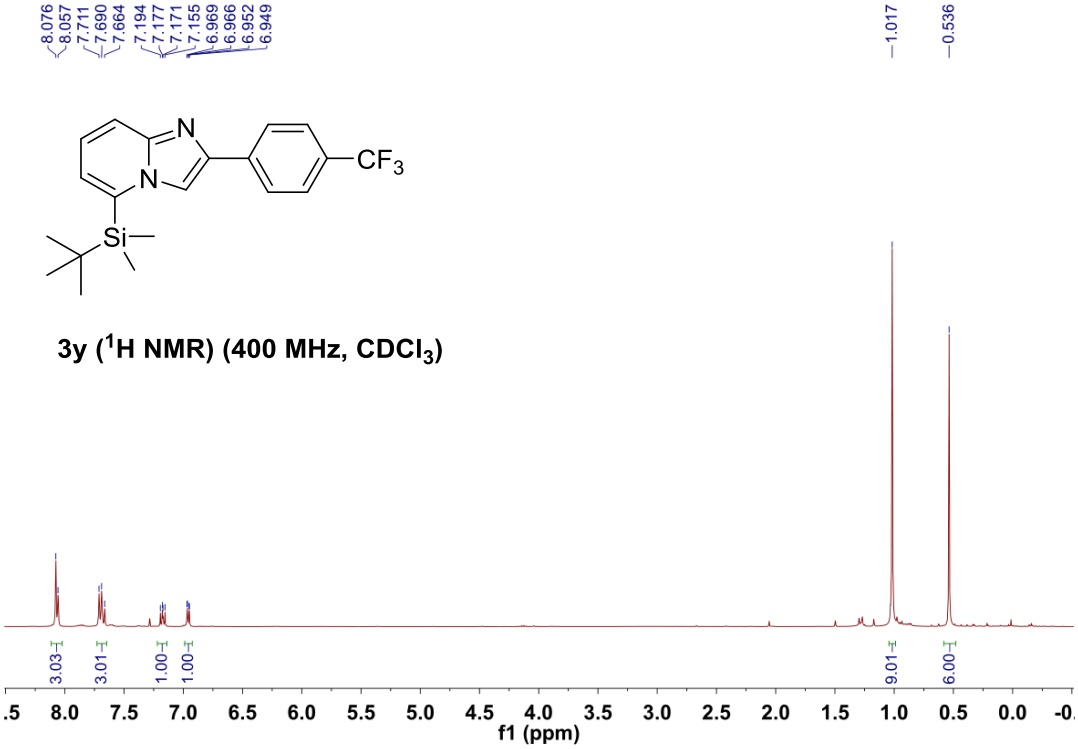
3w (^{13}C NMR) (100 MHz, $CDCl_3$)

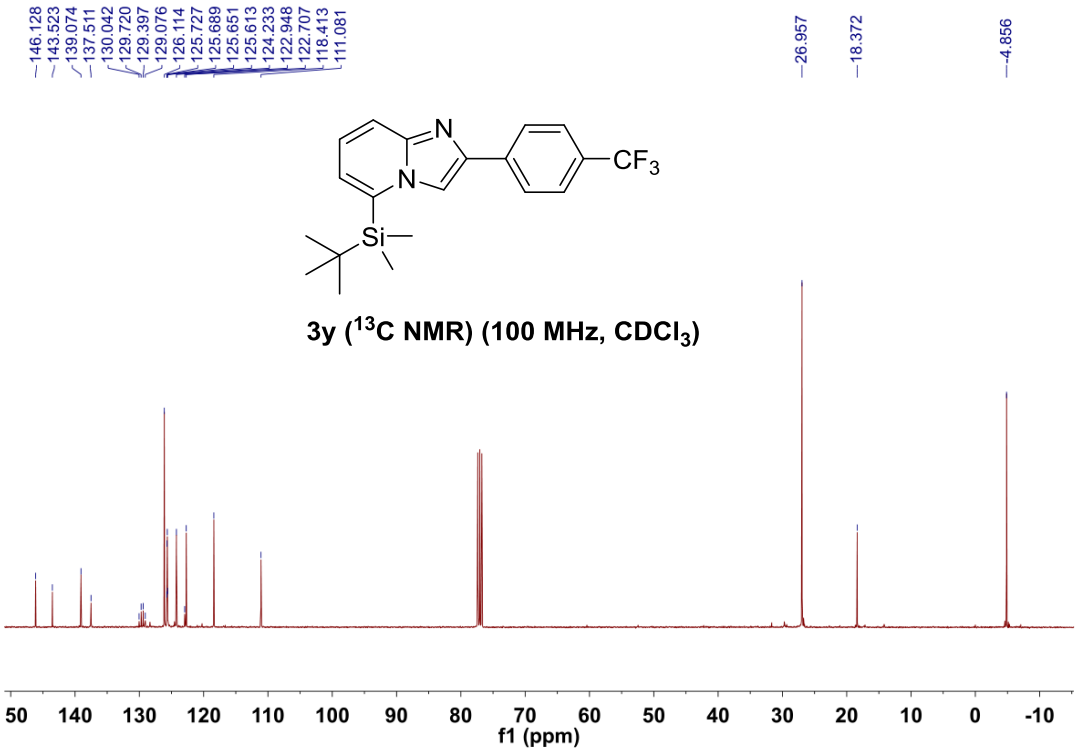


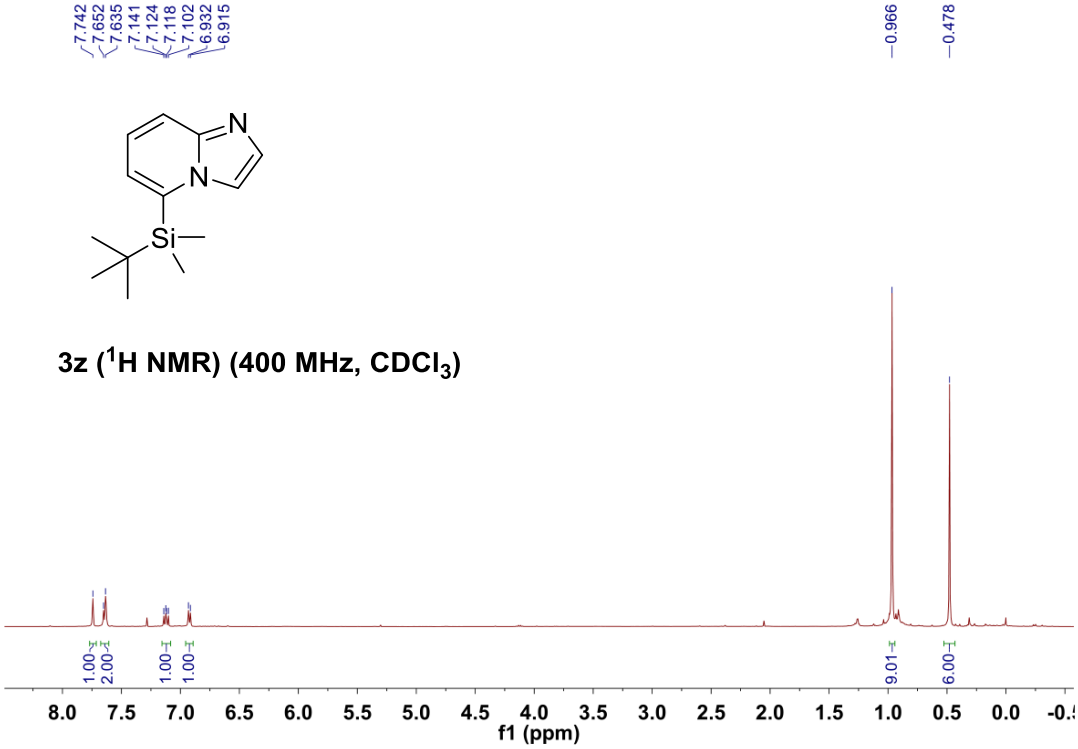
3x (^{1}H NMR) (400 MHz, $CDCl_3$)



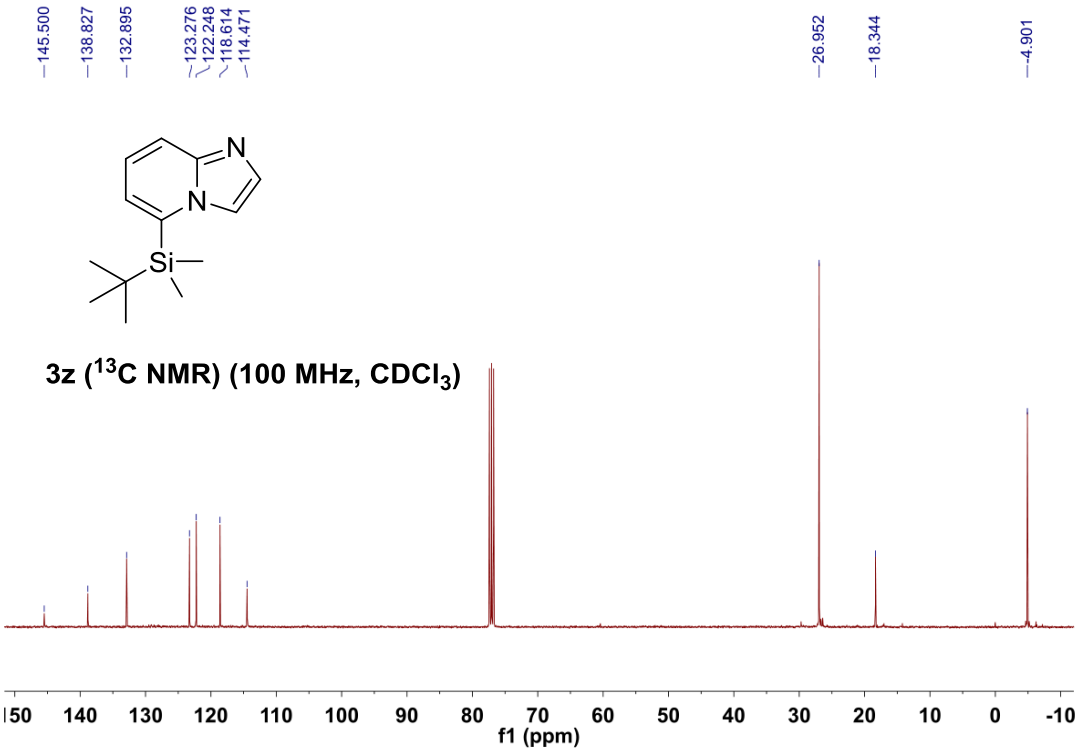
3x (^{13}C NMR) (100 MHz, $CDCl_3$)


8.076
8.057
7.711
7.690
7.664
7.194
7.177
7.171
7.155
6.969
6.966
6.952
6.949
1.017
0.536
N
N
CF3
Si
3y (1H NMR) (400 MHz, CDCl3)
3.03
3.01
1.00
1.00
9.01
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

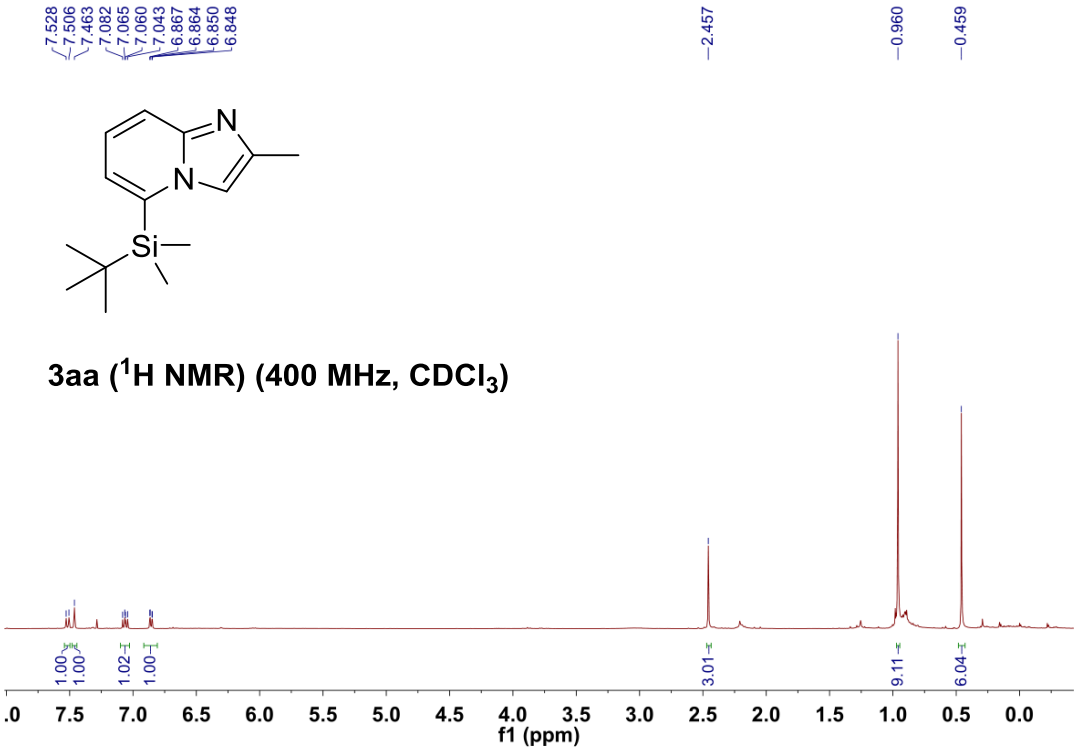

146.128
143.523
139.074
137.511
130.042
129.720
129.397
129.076
126.114
125.727
125.689
125.651
125.613
124.233
122.948
122.707
118.413
111.081
26.957
18.372
-4.856
N
N
CF3
Si
3y (13C NMR) (100 MHz, CDCl3)
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)



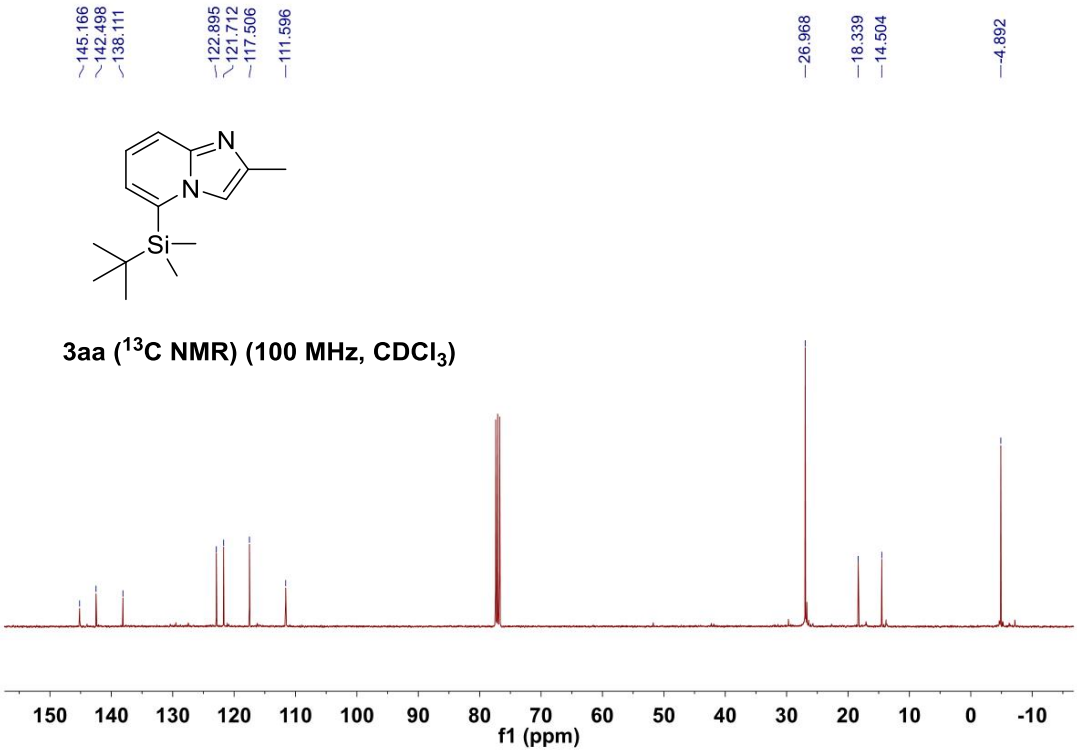
3z (^{1}H NMR) (400 MHz, $CDCl_3$)



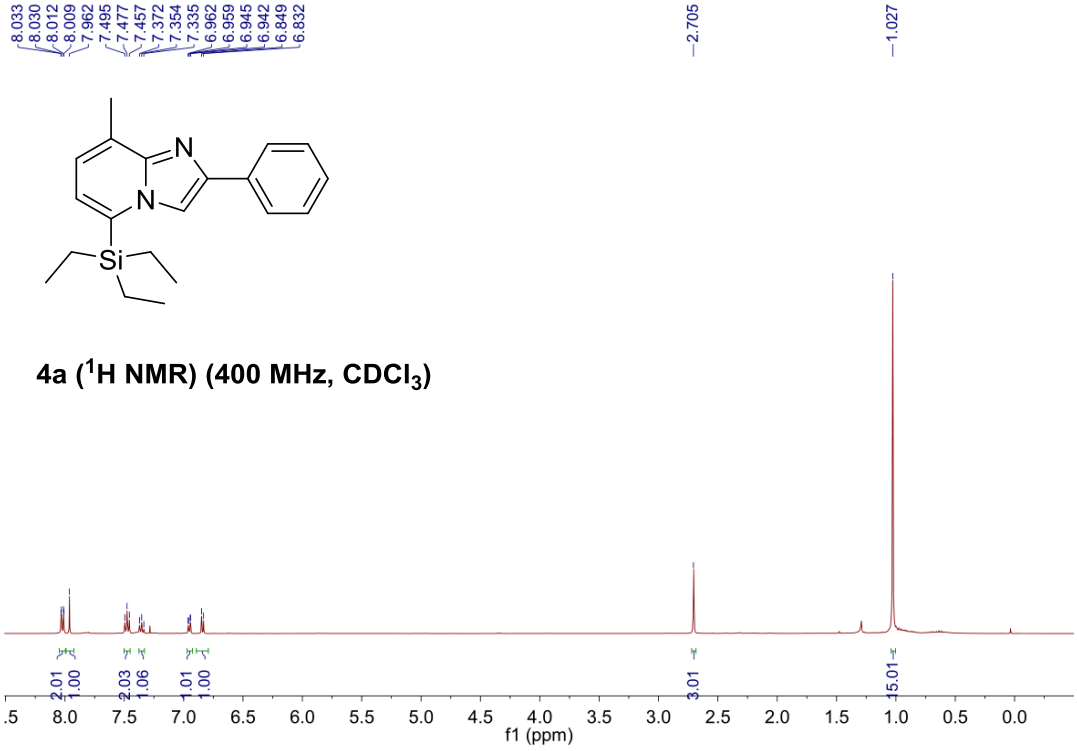
3z (^{13}C NMR) (100 MHz, $CDCl_3$)



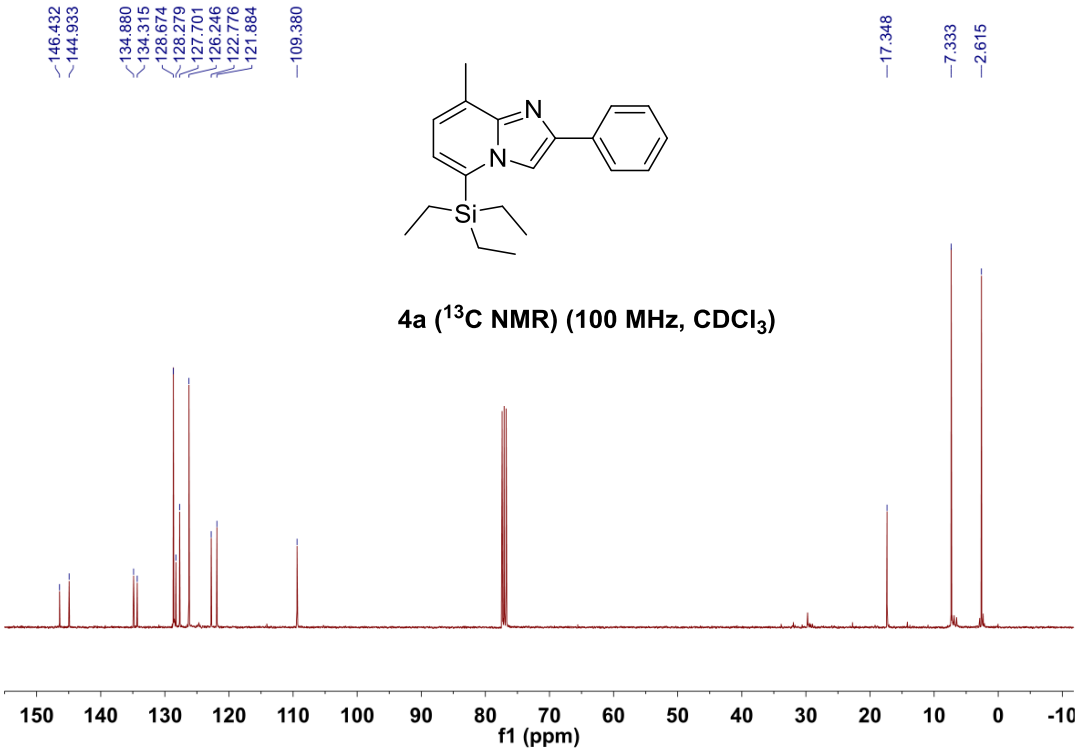
3aa (^{1}H NMR) (400 MHz, $CDCl_3$)



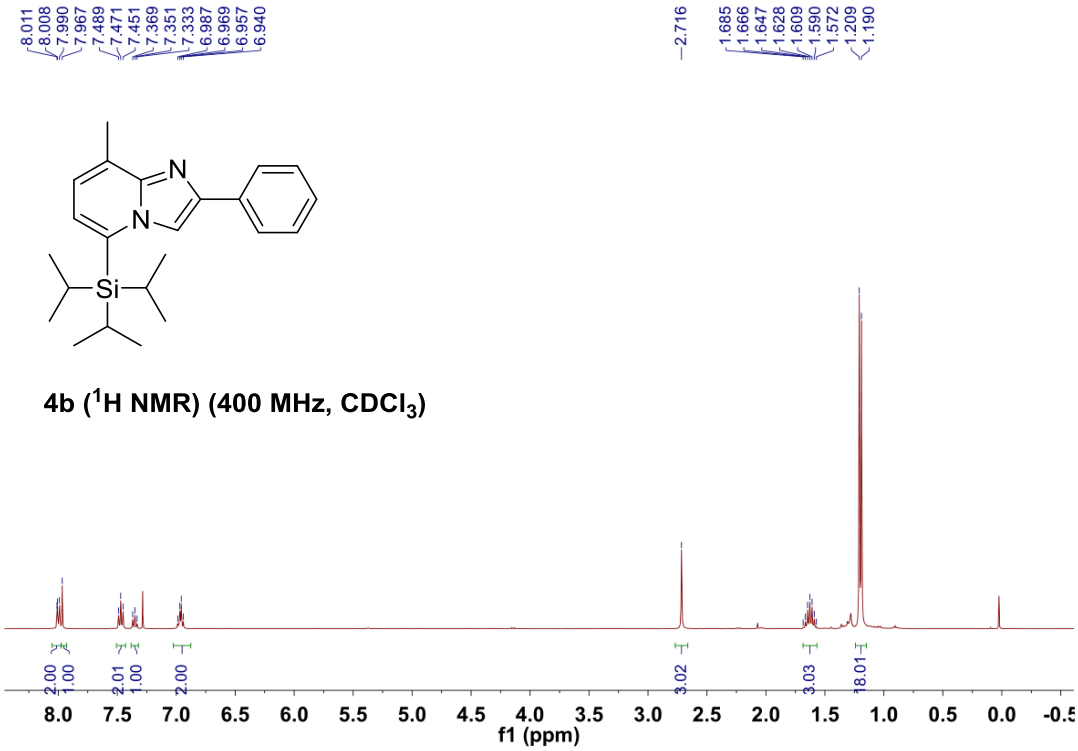
3aa (^{13}C NMR) (100 MHz, $CDCl_3$)



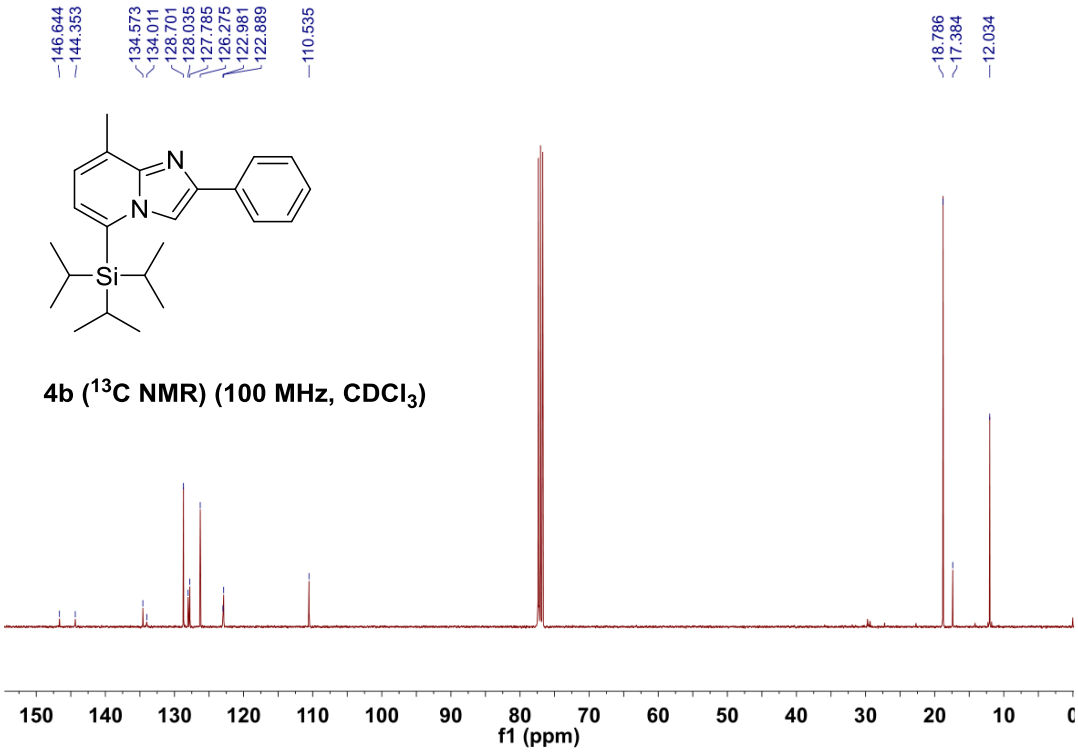
4a (^{1}H NMR) (400 MHz, $CDCl_3$)



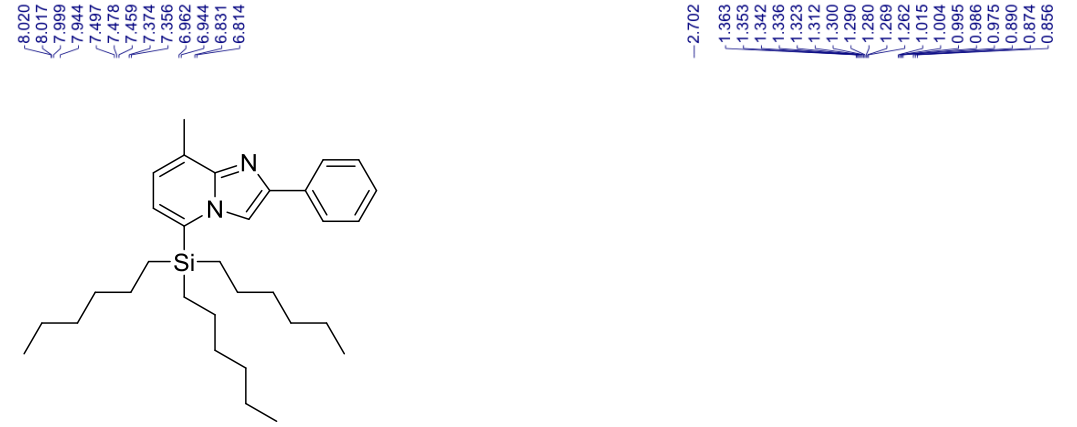
4a (^{13}C NMR) (100 MHz, $CDCl_3$)



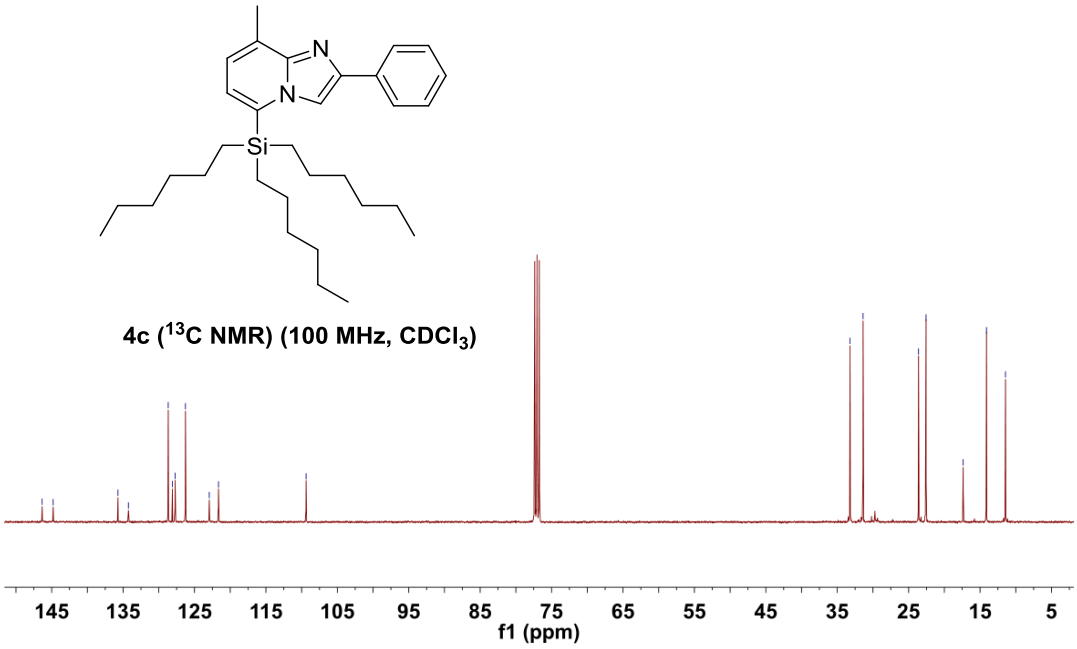
4b (^{1}H NMR) (400 MHz, $CDCl_3$)



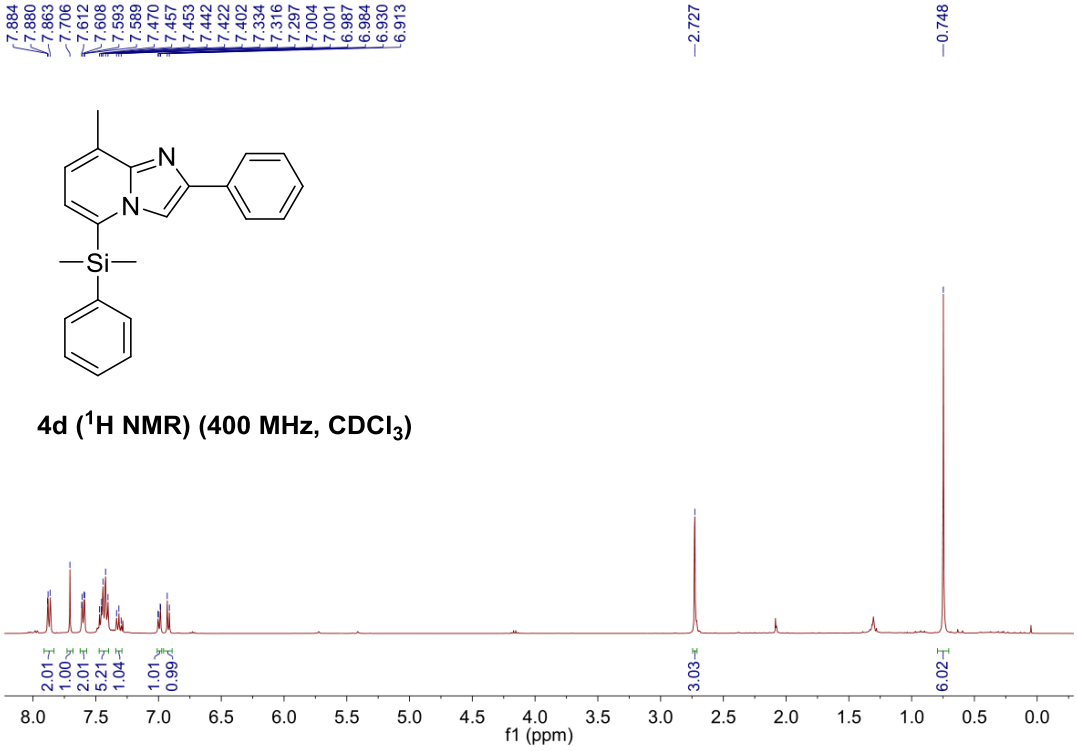
4b (^{13}C NMR) (100 MHz, $CDCl_3$)



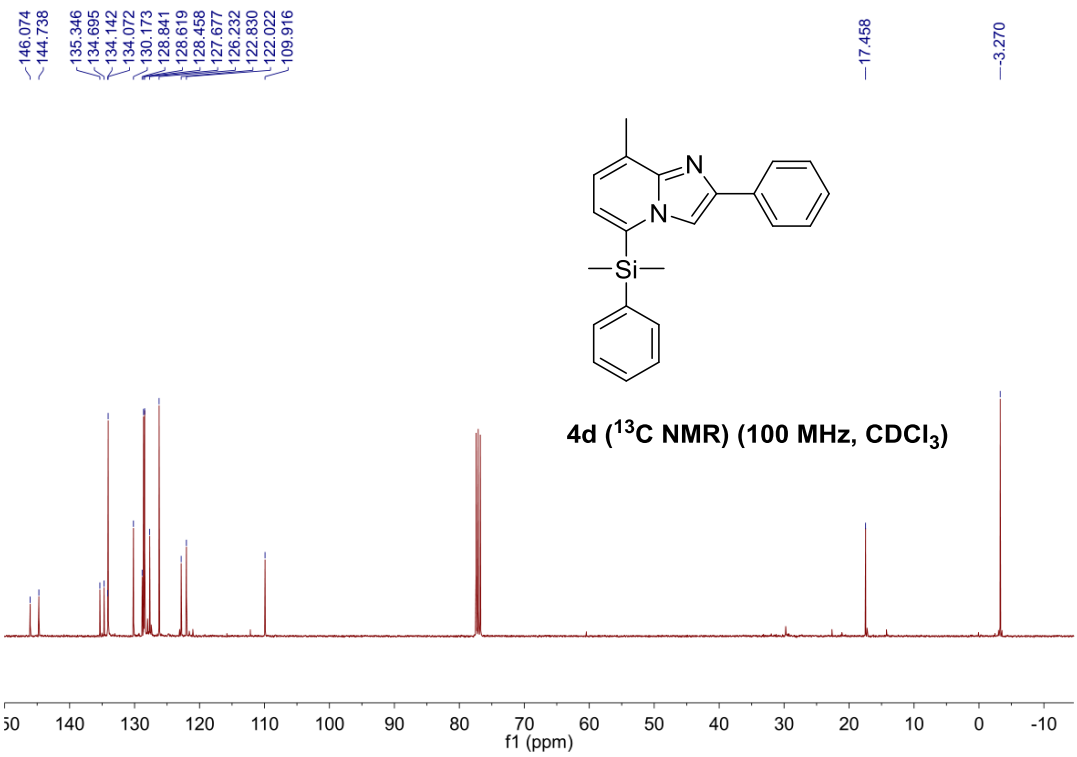
4c (^{1}H NMR) (400 MHz, $CDCl_3$)



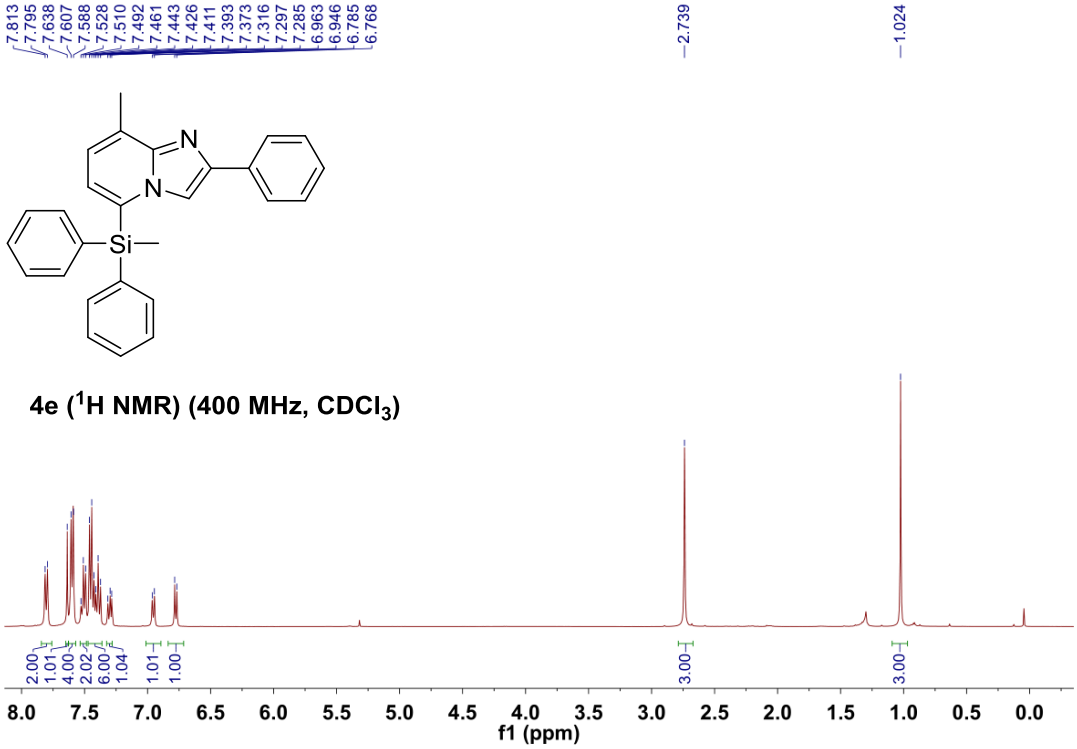
4c (^{13}C NMR) (100 MHz, $CDCl_3$)



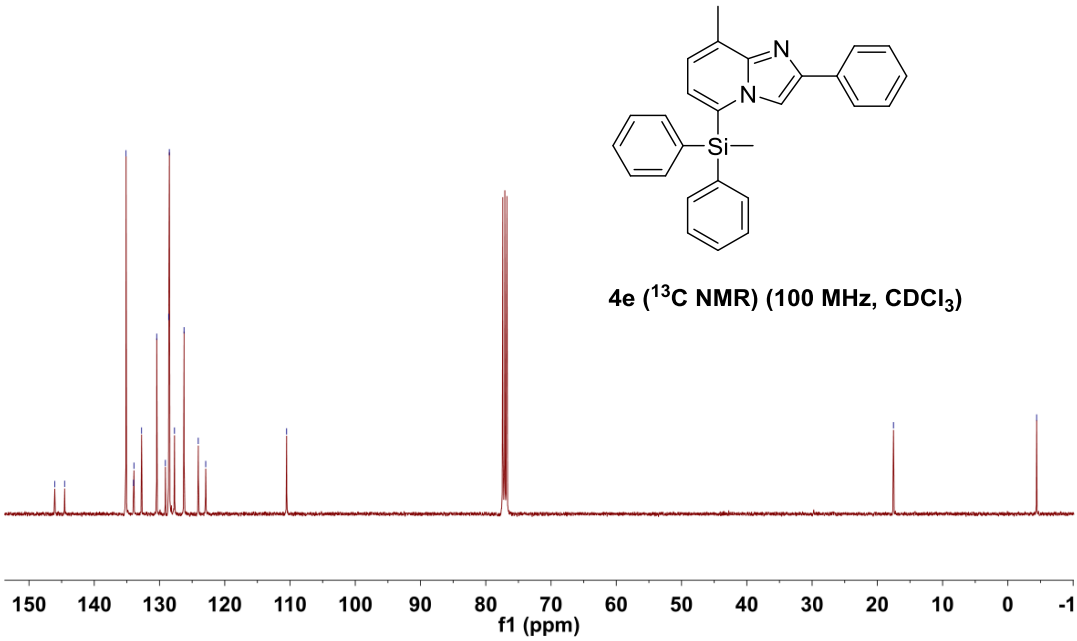
4d (^{1}H NMR) (400 MHz, $CDCl_3$)



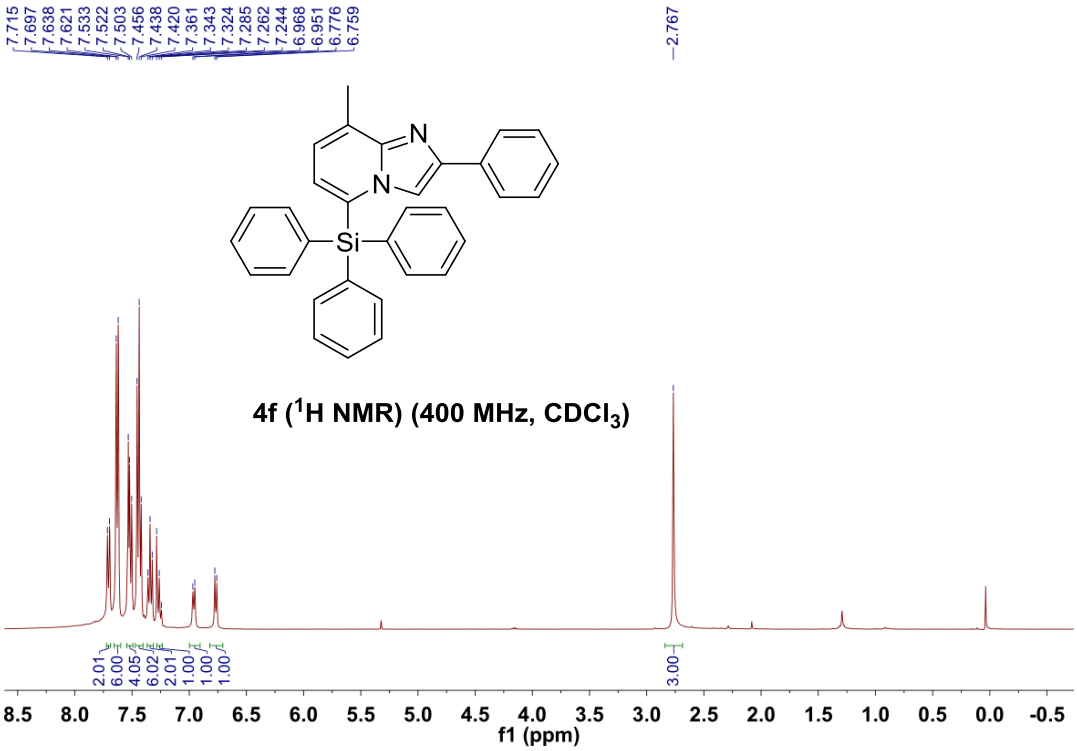
4d (^{13}C NMR) (100 MHz, $CDCl_3$)



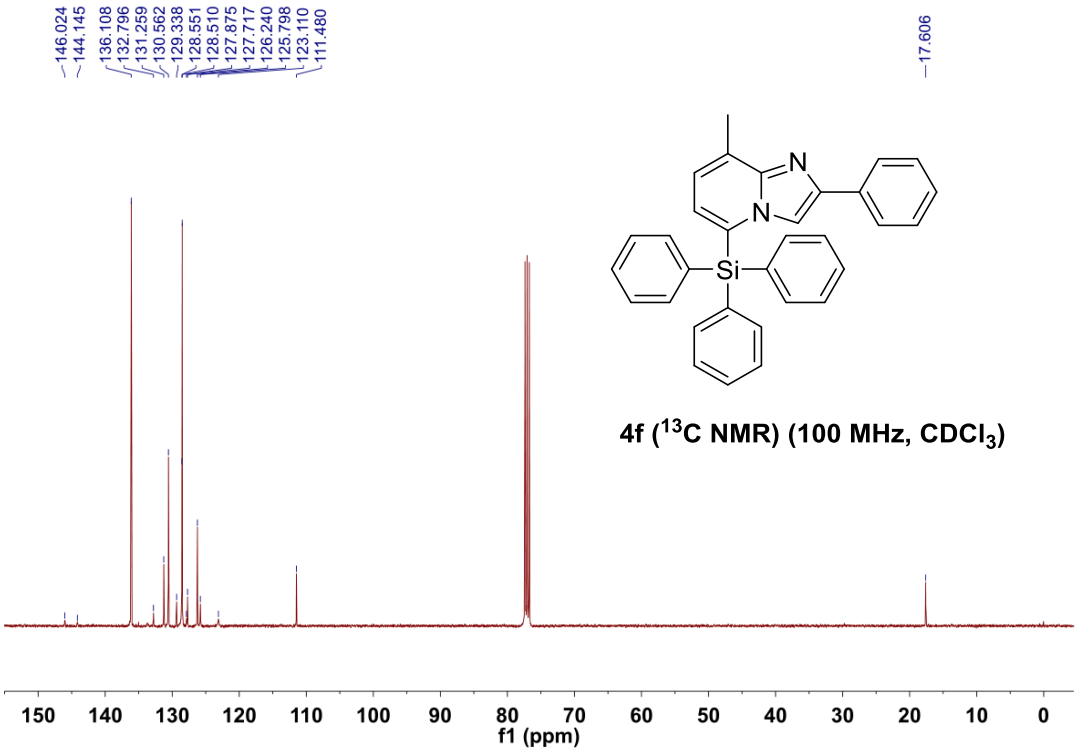
4e (^{1}H NMR) (400 MHz, $CDCl_3$)



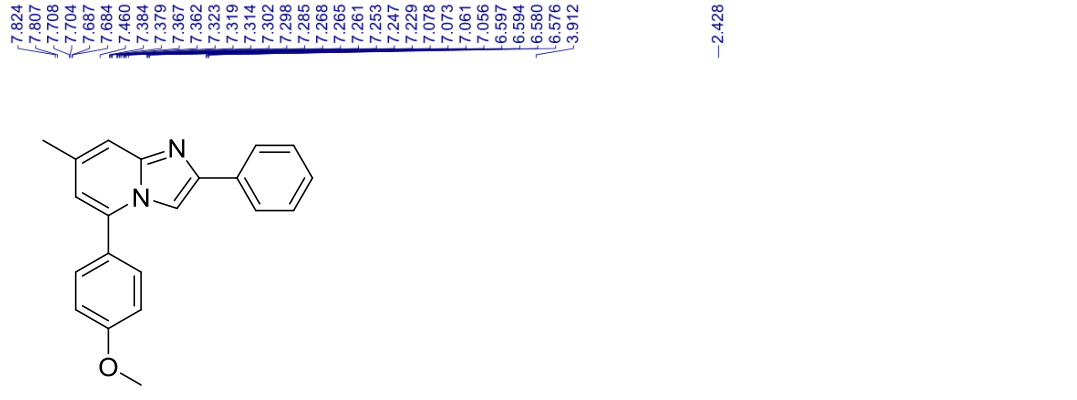
4e (^{13}C NMR) (100 MHz, $CDCl_3$)



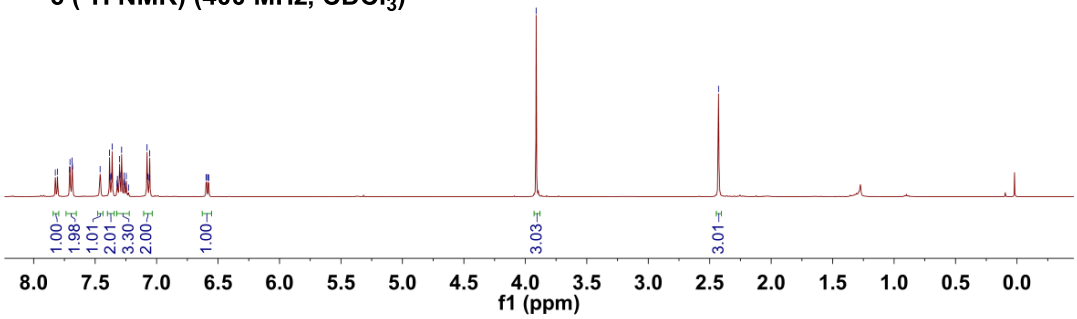
4f (^{1}H NMR) (400 MHz, $CDCl_3$)

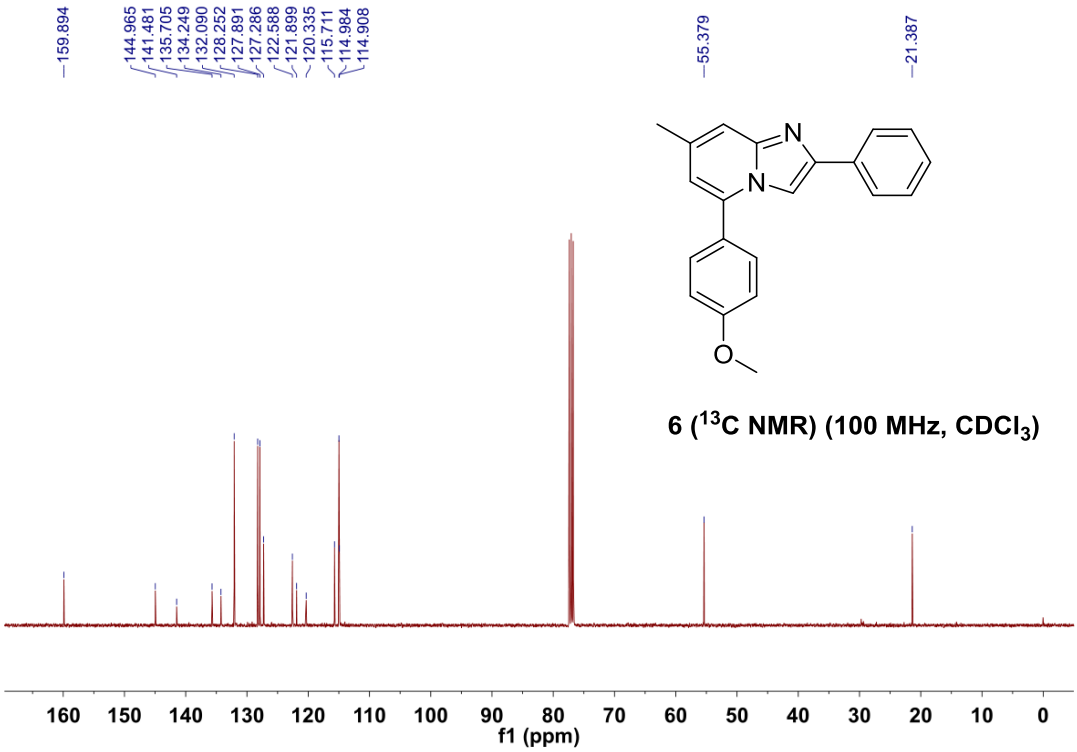


4f (^{13}C NMR) (100 MHz, $CDCl_3$)



6 (^{1}H NMR) (400 MHz, $CDCl_3$)





6 (^{13}C NMR) (100 MHz, $CDCl_3$)

6. The X-ray Single-crystal Diffraction Analysis of 3k

Single crystal suitable for X-ray diffraction was obtained by slow evaporation of dichloromethane and *n*-hexane (1:1) solution of **3k** at ambient temperature.

The ellipsoid contour percent probability levels of the thermal ellipsoid plot is 50%.

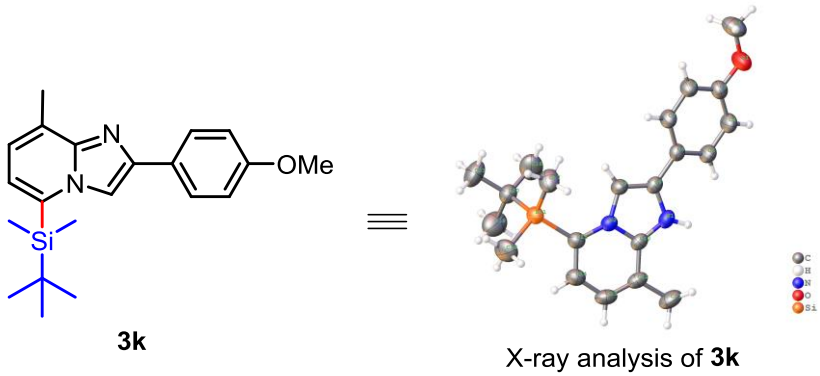


Figure S2. Crystal structures of **3k** (CCDC: 2011379).

Table S1. Crystal data and structure refinement for **3k**.

Identification code	**3k**
Empirical formula	$C_{21}H_{29}N_2OSi$
Formula weight	353.55
Temperature/K	296.15
Crystal system	orthorhombic
Space group	Pbca
a/Å	10.7466(15)
b/Å	15.132(2)
c/Å	25.050(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	4073.7(10)
Z	8
ρ_{calc}g/cm^3	1.153
μ/mm^{-1}	0.126
F(000)	1528
Crystal size/mm^3	0.03 × 0.02 × 0.01
Radiation	MoKα (λ = 0.71073)

2Θ range for data collection/°	3.252 to 55.104
Index ranges	$-13 \leq h \leq 13$, $-19 \leq k \leq 18$, $-32 \leq l \leq 32$
Reflections collected	43785
Independent reflections	4689 [R_{int} = 0.0516, R_{sigma} = 0.0283]
Data/restraints/parameters	4689/0/233
Goodness-of-fit on F^2	1.021
Final R indexes [I>=2σ (I)]	R_1 = 0.0478, wR_2 = 0.1246
Final R indexes [all data]	R_1 = 0.0816, wR_2 = 0.1452
Largest diff. peak/hole / e $Å^{-3}$	0.23/-0.52

Table S2. Bond lengths (Å) and angles (˚) for compound **3k**.

Si1—C15	1.896 (2)	C4—C5	1.379 (3)
Si1—C17	1.865 (2)	C5—C6	1.390 (2)
Si1—C18	1.871 (2)	C6—C7	1.389 (3)
Si1—C20	1.894 (2)	C6—C8	1.466 (3)
N1—C8	1.364 (2)	C8—C9	1.374 (3)
N1—C10	1.320 (2)	C10—C12	1.418 (3)
N2—C9	1.381 (2)	C11—C12	1.504 (3)
N2—C10	1.397 (2)	C12—C13	1.350 (3)
N2—C15	1.396 (2)	C13—C14	1.419 (3)
O1—C1	1.410 (3)	C14—C15	1.365 (3)
O1—C3	1.367 (2)	C16—C20	1.517 (3)
C2—C3	1.385 (3)	C19—C20	1.537 (3)
C2—C7	1.383 (3)	C20—C21	1.535 (3)
C3—C4	1.386 (3)		
C20—Si1—C15	109.58 (9)	N1—C8—C6	121.72 (16)
C17—Si1—C15	111.42 (10)	N1—C8—C9	110.22 (17)
C17—Si1—C20	112.17 (11)	C9—C8—C6	128.01 (17)
C17—Si1—C18	107.84 (12)	C8—C9—N2	106.78 (16)
C18—Si1—C15	106.27 (11)	N2—C10—C12	119.50 (17)
C18—Si1—C20	109.37 (12)	N1—C10—N2	111.34 (16)
C10—N1—C8	106.28 (15)	N1—C10—C12	129.16 (17)
C9—N2—C10	105.37 (15)	C10—C12—C11	118.3 (2)
C9—N2—C15	130.86 (16)	C13—C12—C10	117.18 (18)
C15—N2—C10	123.76 (16)	C13—C12—C11	124.5 (2)
C3—O1—C1	117.80 (17)	C12—C13—C14	121.83 (19)
C7—C2—C3	119.73 (19)	C15—C14—C13	122.9 (2)
O1—C3—C2	125.19 (19)	N2—C15—Si1	123.89 (14)
O1—C3—C4	115.58 (17)	C14—C15—Si1	121.24 (15)

C2—C3—C4	119.24 (19)	C14—C15—N2	114.87 (17)
C5—C4—C3	120.39 (18)	C19—C20—Si1	109.62 (17)
C4—C5—C6	121.33 (19)	C16—C20—Si1	111.76 (16)
C7—C6—C8	121.99 (16)	C16—C20—C19	108.3 (2)
C7—C6—C5	117.48 (18)	C16—C20—C21	109.2 (2)
C5—C6—C8	120.50 (17)	C21—C20—Si1	109.81 (17)
C2—C7—C6	121.84 (17)	C21—C20—C19	108.0 (2)