

Supporting Information

Visible-Light-Promoted Direct Trifluoromethylation and Perfluoroalkylation of Imidazopyridines

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1. General Information

Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Imidazo[1,2-a]pyridines and liquid trifluoromethylation reagents TMG CF₃I were prepared according to the literature procedures.^{1,2} Products were purified by column chromatography on 200-300 mesh silica gel, SiO₂. ¹H NMR, ¹⁹F NMR and ¹³C NMR spectra were measured on a 400 MHz NMR spectrometer using CDCl₃ as the solvent. The chemical shifts are given in δ relative to TMS, and the coupling constants are given in Hertz. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; qui, quintet; sxt, sextet. The HRMS analyses were conducted using a TOF MS instrument with an EI source. Melting points were measured by a melting point instrument and were uncorrected.

2. Experimental section

2.1 General experimental procedure for trifluoromethylation reaction.

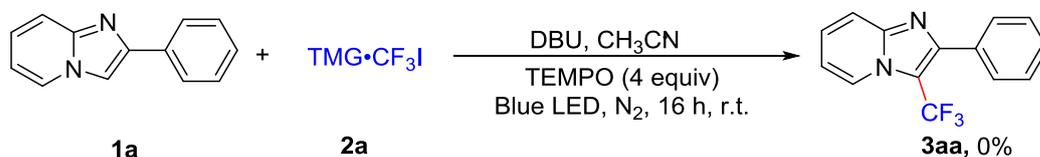
Imidazo[1,2-a]pyridine **1** (0.3 mmol, 1.0 eq) was added to a 10 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. The flask was evacuated and backfilled with nitrogen for 3 times, and then TMG CF₃I **2** (0.6 mmol, 2.0 eq), DBU (0.9mmol, 3.0 eq) and CH₃CN (0.75 mL) were added. The mixture was stirred under Blue LED strip irradiation for 16 h. When the reaction was completed, the solvent was removed in vacuum, and the product was purified by silica gel chromatography using petroleum ether/ethyl acetate (20:1 to 8:1, v/v) as eluent to afford the pure product **3**.

Larger-scale synthesis of 3aa. 2-phenylimidazo[1,2-a]pyridine **1a** (388.5 mg, 2.0mmol) was added to a 25 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. The flask was evacuated and backfilled with nitrogen for 3 times, and then TMG CF₃I **2a** (0.8 mL, 4.0

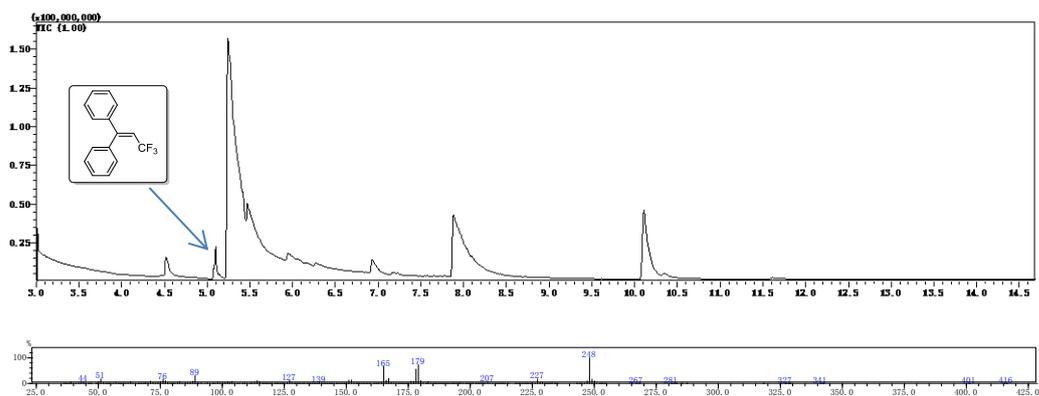
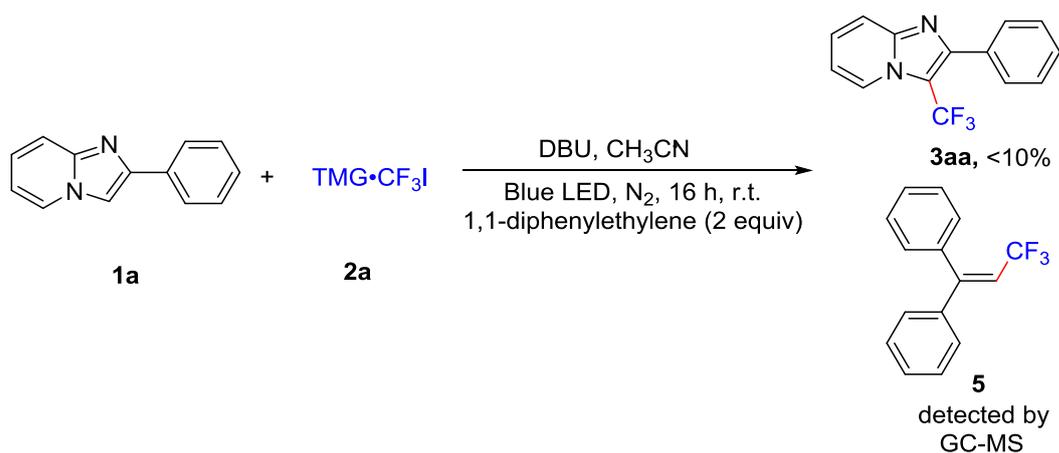
mmol)), DBU (913.4 mg, 6.0 mmol) and CH₃CN (5.0 mL) were added. The mixture was stirred under blue LED strip irradiation for 16 h. When the reaction was completed, the solvent was removed in vacuum. The residue was purified by silica gel chromatography using petroleum ether/ethyl acetate (10:1, v/v) as eluent to afford the pure product **3aa** (411.1 mg, 78% yield).

2.2 Mechanism experiments.

2-phenylimidazo[1,2-a]pyridine **1a** (58.3 mg, 0.3 mmol) and TEMPO (187.5 mg, 1.2 mmol) were added to a 10 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. The flask was evacuated and backfilled with nitrogen for 3 times, and then TMG CF₃I **2a** (0.12 mL, 0.6 mmol), DBU (137.0 mg, 0.9 mmol) and CH₃CN (0.75 mL) were added. The mixture was stirred under Blue LED strip irradiation for 16 h. When the reaction was completed, products **3aa** and TEMPO-bound adduct could not be detected.



2-phenylimidazo[1,2-a]pyridine **1a** (58.3 mg, 0.3 mmol) were added to a 10 mL Schlenk flask equipped with a high-vacuum PTFE valve-to-glass seal. The flask was evacuated and backfilled with nitrogen for 3 times, and then TMG CF₃I **2a** (0.12 mL, 0.6 mmol), DBU (137.0 mg, 0.9 mmol) 1,1-diphenylethylene (108.2 mg, 0.6 mmol) and CH₃CN (0.75 mL) were added. The mixture was stirred under Blue LED strip irradiation for 16 h. When the reaction was completed, species **5** was detected in the reaction mixture by GC-MS analysis.



2.3 UV/Vis absorption spectra.

The UV/Vis absorption spectra of CH_3CN solutions of DBU (0.1 M), TMG CF_3I (0.1 M), and a mixture of TMG CF_3I and DBU are shown in Figure S1. A bathochromic shift can be observed, indicating the formation of an EDA complex.

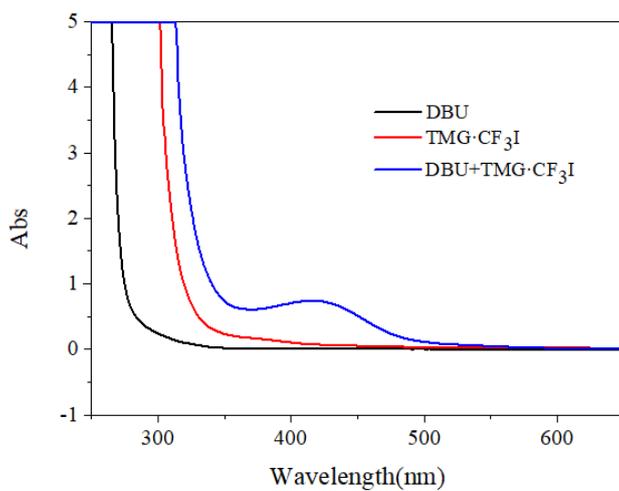


Fig S1, UV-Vis spectroscopy

2.4 Determination of Binding Stoichiometry and Association Constant by ^{19}F NMR

The ^{19}F NMR spectra of mixtures of TMG CF_3I (**2a**) and DBU in CDCl_3 were recorded at 298 K by using benzotrifluoride ($\delta = -63.2$ ppm) as internal standard (Fig S2). The total volume of the solution was 0.7 mL. The total amount of **2a** and DBU was kept constant at 0.35 mmol (0.5 M). The amount of **2a** was varied from 0 to 0.35 mmol, corresponding to 0.0, 0.2, 0.4, 0.5, 0.6, 0.8, 1.0 molar ratio. The chemical shift difference ($\Delta\delta$) between CF_3I in the different mixtures was calculated and the binding stoichiometry was then determined using Job's plot analysis,³ plotting $[2\text{a}]/[2\text{a} + \text{DBU}]$ vs $[2\text{a}] \times \Delta\delta$.

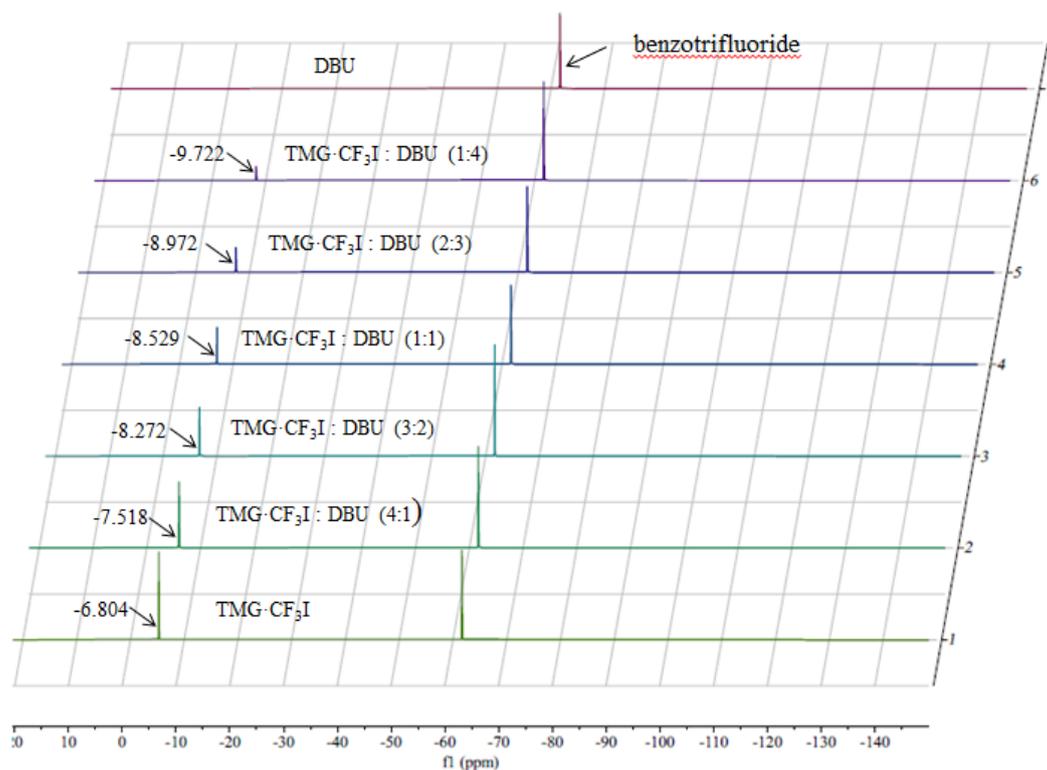


Fig S2, ^{19}F NMR shift of **2a** with DBU

Table S1. Experimental data for Job plot analysis

Molar Ratio	[2a]	[DBU]	$\Delta\delta$	$[2\text{a}]/[2\text{a}+\text{DBU}]$	$[2\text{a}]\times\Delta\delta$
0.0	0	0.5	0	0	0
0.2	0.1	0.4	2.918	0.2	0.292

0.4	0.2	0.3	2.168	0.4	0.434
0.5	0.25	0.25	1.725	0.5	0.431
0.6	0.3	0.2	1.468	0.6	0.440
0.8	0.4	0.1	0.714	0.8	0.286
1.0	0.5	0	0	1	0

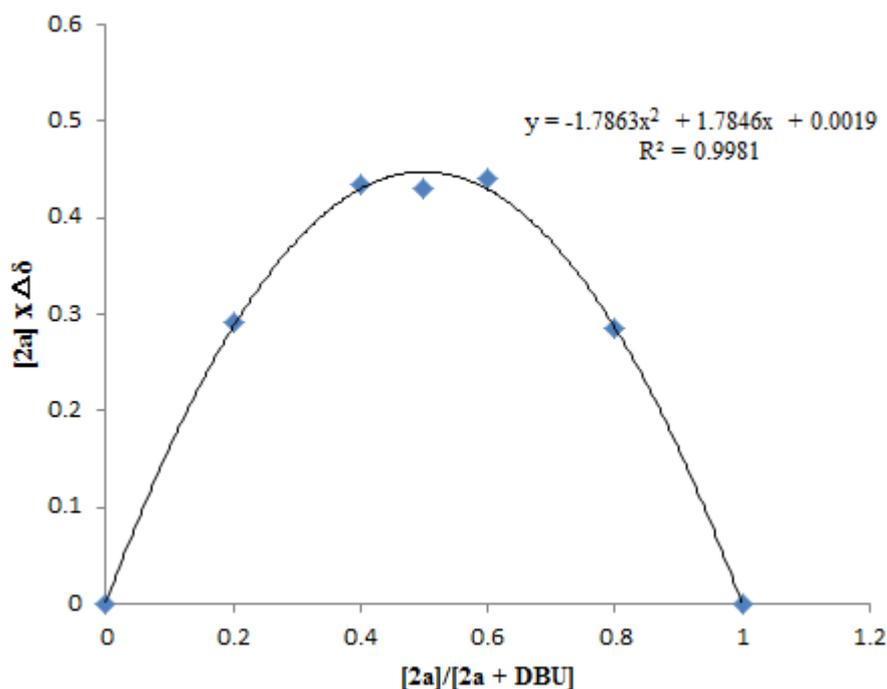


Fig S3, Job's plot analysis

$$x_{max} = \frac{1.7846}{-2 \times (-1.7863)} = 0.50$$

The Job plot analysis has demonstrated that **2a** and DBU are associated in 1:1 ratio complex ratio through halogen bonding.

Then, the association constant (K_a) of the complex has been calculated using Hanna and Ashbaugh's method.⁴ ^{19}F NMR spectra of nine mixtures of TMG CF_3I (**2a**) and DBU were recorded in the CDCl_3 . Benzotrifluoride was used as the internal standard (25 μL , $\delta = -63.2$ ppm). The total volume of the solution was 0.7 mL. The amount of **2a** was kept constant at 0.1 mmol (0.143 M). The amount of DBU was varied from 0 to 3 mmol, corresponding to 0, 1, 1.5, 3, 6, 10, 12, 20, 30 equivalents with respect to **2a**. The chemical shift difference

($\Delta\delta$) between CF₃I in the different mixtures was calculated and the association constant was then determined plotting 1/[DBU] vs 1/ $\Delta\delta$.

Table S2. Experimental data for association constant determination.

Entry	[2a]	[DBU]	1/[DBU]	$\Delta\delta$	1/ $\Delta\delta$
1	0.143	0	0	0	0
2	0.143	0.14	7	1.63	0.61
3	0.143	0.21	4.67	2.33	0.43
4	0.143	0.43	2.33	4.23	0.24
5	0.143	0.86	1.17	6.72	0.15
6	0.143	1.43	0.70	9.39	0.106
7	0.143	1.71	0.58	10.13	0.099
8	0.143	2.86	0.35	12.14	0.082
9	0.143	4.29	0.23	13.43	0.074

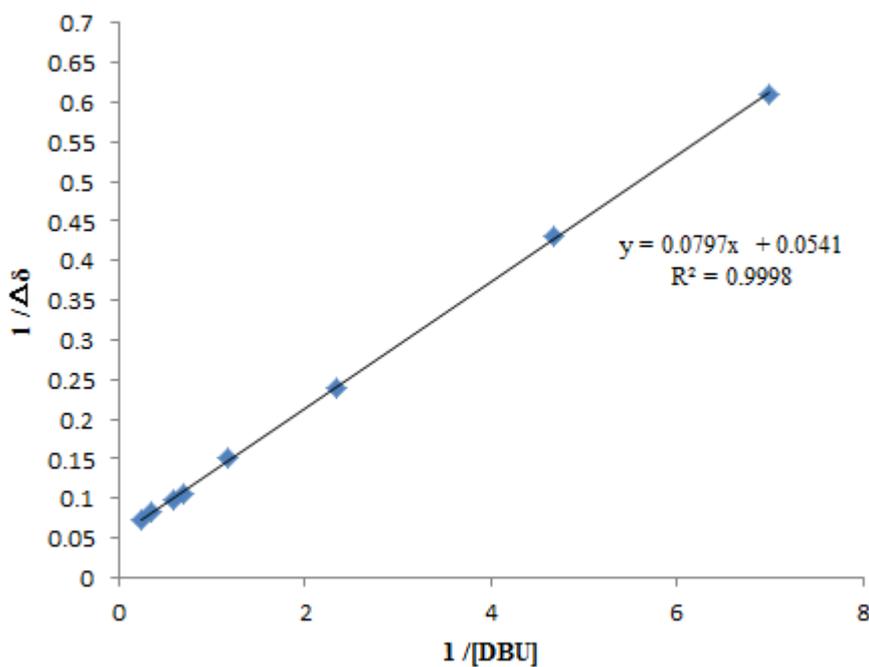


Fig S4, Association constant determination

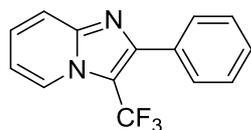
$$K_a = \frac{\text{intercept}}{\text{gradient}} = \frac{0.0541}{0.0797} = 0.68 \text{ M}^{-1}$$

The association constant between **2a** and DBU was calculated to be 0.68 M⁻¹ in CDCl₃.

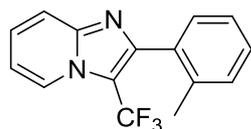
2.5 Light on/off experiments.

Under an N₂ atmosphere, a mixture of 2-phenylimidazo[1,2-a]pyridine **1a** (116.6 mg, 0.6 mmol),

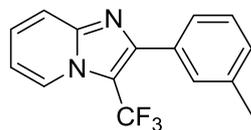
3. Characterization data of products



2-phenyl-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3aa). White solid, 69 mg, Yield: 88%; ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 6.9$ Hz, 1H), 7.75 – 7.67 (m, 3H), 7.50 – 7.41 (m, 3H), 7.32 (t, $J = 8.0$ Hz, 1H), 6.91 (t, $J = 7.0$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 147.9 (d, $J = 2.1$ Hz), 146.0, 132.8, 129.5 (d, $J = 1.7$ Hz), 128.8, 128.0, 126.8, 125.3 (q, $J = 3.8$ Hz), 121.8 (q, $J = 265.9$ Hz), 117.9, 113.8 109.4 (q, $J = 39.6$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -57.6. The spectral data were in accordance with the literature.⁵

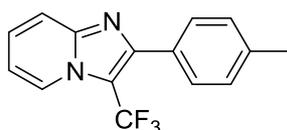


2-(o-tolyl)-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3ba). Yellow liquid, 59 mg, Yield: 71%; ^1H NMR (400 MHz, CDCl_3) δ 8.32 (d, $J = 7.0$ Hz, 1H), 7.74 (d, $J = 9.1$ Hz, 1H), 7.44 – 7.24 (m, 5H), 7.02 (t, $J = 7.0$ Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.5 (d, $J = 2.0$ Hz), 146.0, 136.9, 132.5, 130.1, 129.9, 128.8, 126.8, 125.2, 121.6 (q, $J = 265.7$ Hz), 118.0, 113.8, 110.6 (q, $J = 38.8$ Hz), 19.7. ^{19}F NMR (376 MHz, CDCl_3) δ -59.4. The spectral data were in accordance with the literature.⁶

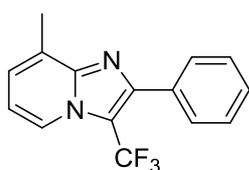


2-(m-tolyl)-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3ca) White solid, 63 mg, Yield: 76%; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 6.9$ Hz, 1H), 7.72 (d, $J = 9.2$ Hz, 1H), 7.54 (s, 1H), 7.47 (d, $J = 7.7$ Hz, 1H), 7.40 – 7.30 (m, 2H), 7.25 (d, $J = 8.0$ Hz, 1H), 6.96 (t, $J = 6.9$ Hz, 1H),

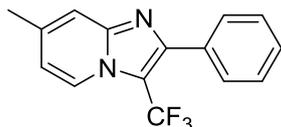
2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.2 (d, $J = 2.1$ Hz), 146.0, 137.8, 132.7, 130.1 (d, $J = 1.0$ Hz), 129.7, 128.0, 126.8, 126.7 (q, $J = 1.9$ Hz), 125.4 (q, $J = 3.7$ Hz), 122.0 (q, $J = 267.5$ Hz), 118.0, 113.8, 109.4 (q, $J = 39.5$ Hz), 21.3. ^{19}F NMR (376 MHz, CDCl_3) δ -57.6. The spectral data were in accordance with the literature.⁶



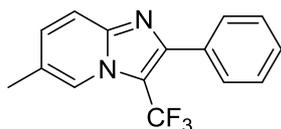
2-(p-tolyl)-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3da) White solid, 69 mg, Yield: 83%; ^1H NMR (400 MHz, CDCl_3) δ 8.29 (d, $J = 6.9$ Hz, 1H), 7.71 (d, $J = 9.1$ Hz, 1H), 7.60 (d, $J = 7.7$ Hz, 2H), 7.36 (t, $J = 8.0$ Hz, 1H), 7.27 (d, $J = 7.7$ Hz, 2H), 6.96 (t, $J = 6.9$ Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 148.1 (d, $J = 2.6$ Hz), 146.0, 138.8, 129.9, 129.4 (q, $J = 2.0$ Hz), 128.8, 126.8, 125.4 (q, $J = 4.2$ Hz), 121.9 (q, $J = 267.4$ Hz), 117.9, 113.7, 109.2 (q, $J = 39.5$ Hz), 21.2. ^{19}F NMR (376 MHz, CDCl_3) δ -57.6. The spectral data were in accordance with the literature.⁶



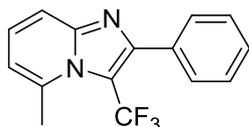
8-methyl-2-phenyl-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3ea) Yellow liquid, 67 mg, Yield: 81%; ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 6.9$ Hz, 1H), 7.69 (d, $J = 6.9$ Hz, 2H), 7.50 – 7.40 (m, 3H), 7.17 (d, $J = 6.9$ Hz, 1H), 6.90 (t, $J = 7.0$ Hz, 1H), 2.68 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.5 (d, $J = 2.4$ Hz), 146.5, 133.2, 129.7 (d, $J = 1.7$ Hz), 128.8, 128.2, 128.1, 125.6, 123.2 (q, $J = 4.1$ Hz), 121.0 (q, $J = 266.7$ Hz), 113.9, 109.8, 17.1. ^{19}F NMR (376 MHz, CDCl_3) δ -57.8. The spectral data were in accordance with the literature.⁷



7-methyl-2-phenyl-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3fa) Yellow solid, 62 mg, Yield: 74%; ^1H NMR (400 MHz, CDCl_3) δ 8.15 (d, $J = 7.1$ Hz, 1H), 7.68 (d, $J = 7.2$ Hz, 2H), 7.50 – 7.37 (m, 4H), 6.82 – 6.73 (m, 1H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.9 (d, $J = 2.3$ Hz), 146.5, 138.2, 133.0, 129.5 (q, $J = 1.7$ Hz), 128.8, 128.1, 124.5 (q, $J = 3.6$ Hz), 122.0 (q, $J = 265.6$ Hz), 116.4, 116.3, 108.9 (q, $J = 39.1$ Hz), 21.2. ^{19}F NMR (376 MHz, CDCl_3) δ -57.5. The spectral data were in accordance with the literature.⁷

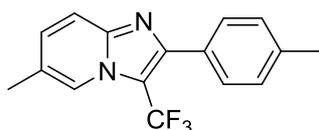


6-methyl-2-phenyl-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3ga) Yellow solid, 58 mg, Yield: 70%; ^1H NMR (400 MHz, CDCl_3) δ 8.07 (s, 1H), 7.68 (d, $J = 7.0$ Hz, 2H), 7.62 (d, $J = 9.2$ Hz, 1H), 7.49 – 7.39 (m, 3H), 7.22 (d, $J = 9.3$ Hz, 1H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.7 (d, $J = 1.9$ Hz), 145.1, 133.1, 130.0, 129.5 (q, $J = 1.6$ Hz), 128.7, 128.1, 123.8, 123.1 (q, $J = 3.6$ Hz), 121.9 (q, $J = 265.7$ Hz), 117.2, 109.1 (q, $J = 39.4$ Hz), 18.3. ^{19}F NMR (376 MHz, CDCl_3) δ -57.7. The spectral data were in accordance with the literature.⁶

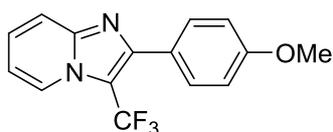


5-methyl-2-phenyl-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3ha) White solid; m.p. 69.2-69.9 °C, 47 mg, Yield: 56%; ^1H NMR (400 MHz, CDCl_3) δ 7.69 – 7.58 (m, 3H), 7.49 – 7.38 (m,

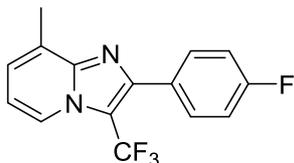
3H), 7.32 (t, $J = 8.0$ Hz, 1H), 6.78 (d, $J = 6.4$ Hz, 1H), 2.80 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.8 (d, $J = 2.5$ Hz), 148.2, 137.4, 134.3, 129.7 (q, $J = 1.6$ Hz), 128.7, 127.9, 127.5, 121.9 (q, $J = 265.5$ Hz), 115.7, 109.7 (q, $J = 39.8$ Hz), 20.5 (q, $J = 6.9$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -46.6; HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{11}\text{F}_3\text{N}_2$ 276.0869, found 276.0876.



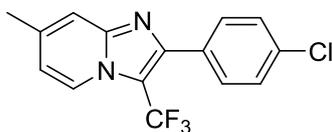
6-methyl-2-(p-tolyl)-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3ia) Pale yellow solid, 66 mg, Yield: 76%; ^1H NMR (400 MHz, CDCl_3) δ 8.06 (s, 1H), 7.65 – 7.52 (m, 3H), 7.29 – 7.17 (m, 3H), 2.41 (s, 3H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.9, 145.1, 138.7, 130.2, 129.9, 129.4 (q, $J = 1.7$ Hz), 128.8, 123.6, 123.1 (q, $J = 4.3$ Hz), 122.0 (q, $J = 265.7$ Hz), 117.2, 109.0 (q, $J = 39.5$ Hz), 21.3, 18.3. ^{19}F NMR (376 MHz, CDCl_3) δ -57.7. The spectral data were in accordance with the literature.⁸



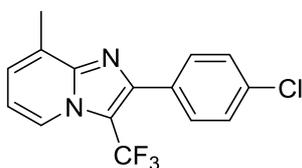
2-(4-methoxyphenyl)-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3ja) White solid, 74 mg, Yield: 84%; ^1H NMR (400 MHz, CDCl_3) δ 8.26 (d, $J = 6.9$ Hz, 1H), 7.68 (d, $J = 9.1$ Hz, 1H), 7.64 (d, $J = 8.3$ Hz, 2H), 7.32 (t, $J = 8.0$ Hz, 1H), 7.02 – 6.88 (m, 3H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.2, 147.8 (d, $J = 2.3$ Hz), 146.0, 130.8 (q, $J = 1.9$ Hz), 126.7, 125.4 (q, $J = 3.8$ Hz), 125.2, 122.0 (q, $J = 265.7$ Hz), 117.8, 113.6, 113.6, 108.9 (q, $J = 39.5$ Hz), 55.2. ^{19}F NMR (376 MHz, CDCl_3) δ -57.6. The spectral data were in accordance with the literature.⁷



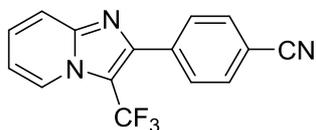
2-(4-fluorophenyl)-8-methyl-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3ka) White solid, m.p. 90.8- 91.7, 45 mg, Yield: 76%; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 6.9$ Hz, 1H), 7.72 – 7.62 (m, 2H), 7.21 – 7.08 (m, 3H), 6.89 (t, $J = 7.0$ Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.2 (d, $J = 246.7$ Hz), 146.5, 146.4 (d, $J = 2.0$ Hz), 131.5 (dq, $J = 8.5, 1.7$ Hz), 129.3 (d, $J = 3.2$ Hz), 128.2, 125.7, 123.1 (q, $J = 3.5$ Hz), 121.9 (q, $J = 265.7$ Hz), 115.2 (d, $J = 21.8$ Hz), 114.0, 109.9 (q, $J = 39.6$ Hz), 17.1. ^{19}F NMR (376 MHz, CDCl_3) δ -57.8, -112.9. HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{10}\text{F}_4\text{N}_2$ 294.0775, found 294.0780.



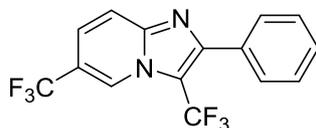
2-(4-chlorophenyl)-7-methyl-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3la) White solid, m.p. 110.3- 110.8, 74 mg, Yield: 80%; ^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 7.1$ Hz, 1H), 7.64 (d, $J = 8.1$ Hz, 2H), 7.50 – 7.39 (m, 3H), 6.82 (d, $J = 6.5$ Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.5, 138.5, 134.9, 131.5, 130.8 (q, $J = 1.8$ Hz), 128.5, 128.3, 124.5 (q, $J = 3.7$ Hz), 121.8 (q, $J = 265.6$ Hz), 116.6, 116.3, 109.0 (q, $J = 39.5$ Hz), 21.2. ^{19}F NMR (376 MHz, CDCl_3) δ -57.5. HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_{10}\text{ClF}_3\text{N}_2$ 310.0479, found 310.0484.



2-(4-chlorophenyl)-8-methyl-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3ma) White solid, 74 mg, Yield: 80%; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 6.3$ Hz, 1H), 7.64 (d, $J = 7.5$ Hz, 2H), 7.48 – 7.36 (m, 2H), 7.16 (d, $J = 7.0$ Hz, 1H), 6.89 (t, $J = 6.8$ Hz, 1H), 2.66 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.5, 146.1 (d, $J = 2.0$ Hz), 134.9, 131.6, 130.9 (q, $J = 1.7$ Hz), 128.3, 128.2, 125.7, 123.1 (q, $J = 3.6$ Hz), 121.8 (q, $J = 265.7$ Hz), 114.0, 109.9 (q, $J = 39.5$ Hz), 17.0. ^{19}F NMR (376 MHz, CDCl_3) δ -57.8. The spectral data were in accordance with the literature.⁵

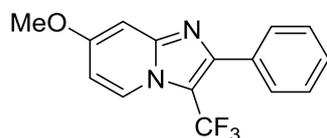


4-(3-(trifluoromethyl)imidazo[1,2-a]pyridin-2-yl)benzonitrile (3na) White solid, 64 mg, Yield: 74%; ^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, $J = 7.0$ Hz, 1H), 7.84 – 7.68 (m, 5H), 7.48 – 7.37 (m, 1H), 7.10 – 6.99 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.2, 145.7 (d, $J = 1.9$ Hz), 137.4, 131.9, 130.2 (q, $J = 1.8$ Hz), 127.5, 125.5 (q, $J = 3.8$ Hz), 121.5 (q, $J = 265.9$ Hz), 118.5, 118.2, 114.5, 112.6, 110.1 (q, $J = 39.7$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -57.6. The spectral data were in accordance with the literature.⁵

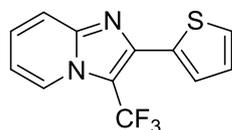


2-phenyl-3,6-bis(trifluoromethyl)imidazo[1,2-a]pyridine (3oa) White solid, 80 mg, Yield: 81%; ^1H NMR (400 MHz, CDCl_3) δ 8.65 (s, 1H), 7.83 (d, $J = 9.3$ Hz, 1H), 7.74 – 7.66 (m, 2H), 7.57 – 7.42 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.8 (d, $J = 2.2$ Hz), 145.8, 132.0, 129.5 (q, $J = 1.7$ Hz), 129.4, 128.3, 124.4 (q, $J = 2.1$ Hz), 123.0 (q, $J = 269.8$ Hz), 122.9 (q, $J = 2.6$ Hz), 121.4 (q, $J = 266.3$

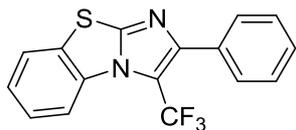
Hz), 118.9 (d, $J = 34.1$ Hz), 118.3 (q, $J = 34.6$ Hz), 110.9 (q, $J = 40.0$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -57.5, -62.4. The spectral data were in accordance with the literature.⁶



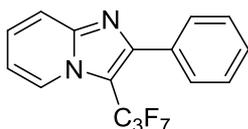
7-methoxy-2-phenyl-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3pa) White solid, 69 mg, Yield: 78%; ^1H NMR (400 MHz, CDCl_3) δ 8.07 (d, $J = 7.5$ Hz, 1H), 7.68 (d, $J = 7.0$ Hz, 2H), 7.48 – 7.37 (m, 3H), 6.94 (d, $J = 2.6$ Hz, 1H), 6.65 (dd, $J = 7.7, 2.5$ Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.1, 147.9 (d, $J = 1.5$ Hz), 132.9, 129.4 (q, $J = 1.7$ Hz), 128.7, 128.0, 125.7 (q, $J = 3.6$ Hz), 121.9 (d, $J = 265.3$ Hz), 108.7, 108.3 (q, $J = 39.6$ Hz), 95.0, 55.5. ^{19}F NMR (376 MHz, CDCl_3) δ -57.2. The spectral data were in accordance with the literature.⁶



2-(thiophen-2-yl)-3-(trifluoromethyl)imidazo[1,2-a]pyridine (3qa) White solid, 48 mg, Yield: 60%; ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 7.0$ Hz, 1H), 7.69 (d, $J = 9.1$ Hz, 1H), 7.53 – 7.42 (m, 2H), 7.35 (t, $J = 7.9$ Hz, 1H), 7.16 – 7.09 (m, 1H), 6.95 (t, $J = 6.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.9, 141.5 (d, $J = 2.0$ Hz), 134.8, 128.0 (q, $J = 4.2$ Hz), 127.8, 127.7, 127.1, 125.4 (q, $J = 4.2$ Hz), 121.9 (q, $J = 265.7$ Hz), 117.8, 114.0, 108.3 (q, $J = 40.2$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -57.6. The spectral data were in accordance with the literature.⁷



2-phenyl-3-(trifluoromethyl)benzo[d]imidazo[2,1-b]thiazole (3ra) White solid, 69 mg, Yield: 72%; ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 8.4$ Hz, 1H), 7.79 – 7.61 (m, 3H), 7.56 – 7.36 (m, 5H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.8, 150.0 (q, $J = 2.6, 0.6$ Hz), 132.8, 132.1, 130.1, 129.5 (q, $J = 1.8$ Hz), 128.9, 128.1, 126.8, 125.5, 124.3, 121.4 (q, $J = 267.1$ Hz), 114.7 (q, $J = 4.6$ Hz), 112.5 (q, $J = 40.7$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -55.0. The spectral data were in accordance with the literature.⁹

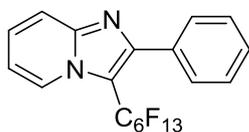


3-(perfluoropropyl)-2-phenylimidazo[1,2-a]pyridine (3ab) White solid, 94 mg, Yield: 86%; ^1H NMR (400 MHz, CDCl_3) δ 8.29 (d, $J = 7.0$ Hz, 1H), 7.72 (d, $J = 9.0$ Hz, 1H), 7.65 – 7.57 (m, 2H), 7.47 – 7.31 (m, 4H), 6.93 (t, $J = 6.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.7, 146.9, 133.3, 129.5, 128.7, 127.8, 127.1, 126.1 – 125.8 (m), 119.7 – 118.7 (m), 118.1, 117.1 – 115.8 (m), 113.8, 110.6 – 109.0 (m), 107.6 (t, $J = 31.8$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -80.2 (t, $J = 10.6$ Hz, 3F), -106.5 – -107.2 (m, 2F), -125.0 – -125.4 (m, 2F). The spectral data were in accordance with the literature.¹⁰

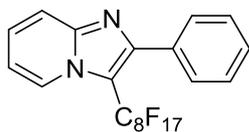


3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3ac) White solid, 108 mg, Yield: 87%;

^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, $J = 7.0$ Hz, 1H), 7.73 (d, $J = 9.1$ Hz, 1H), 7.66 – 7.57 (m, 2H), 7.49 – 7.34 (m, 4H), 6.97 (t, $J = 7.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.9, 146.9, 133.3, 129.5, 128.8, 127.9, 127.1, 126.0, 119.2 – 118.4 (m), 118.2, 116.8 – 115.5 (m), 115.4 – 114.4 (m), 113.9, 108.3 – 107.3 (m). ^{19}F NMR (376 MHz, CDCl_3) δ -80.8 – -81.1 (m, 3F), -105.9 – -106.2 (m, 2F), -121.5 – -121.9 (m, 2F), -125.7 – -126.1 (m, 2F). The spectral data were in accordance with the literature.¹¹

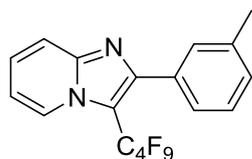


3-(perfluorohexyl)-2-phenylimidazo[1,2-a]pyridine (3ad) Pale yellow solid, 117 mg, Yield: 76%; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 7.1$ Hz, 1H), 7.73 (d, $J = 9.1$ Hz, 1H), 7.65 – 7.57 (m, 2H), 7.47 – 7.32 (m, 4H), 6.94 (t, $J = 7.0$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.8 (d, $J = 1.9$ Hz), 146.9, 133.3, 129.5, 128.8, 127.9, 127.1, 126.1 – 125.8 (m), 119.0 – 117.0 (m), 118.1, 116.1 – 115.2 (m), 115.3 – 114.3 (m), 113.9, 108.4 – 107.1 (m). ^{19}F NMR (376 MHz, CDCl_3) δ -80.7 – -81.3 (m, 3F), -105.5 – -106.5 (m, 2F), -120.4 – -121.1 (m, 2F), -121.5 – -122.2 (m, 2F), -122.5 – -123.3 (m, 2F), -126.0 – -126.5 (m, 2F). The spectral data were in accordance with the literature.¹¹



3-(perfluorooctyl)-2-phenylimidazo[1,2-a]pyridine (3ae) White solid, 132 mg, Yield: 72%; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 7.0$ Hz, 1H), 7.73 (d, $J = 7.8$ Hz, 1H), 7.65 – 7.57 (m, 2H), 7.48 – 7.31 (m, 4H), 6.92 (t, $J = 6.9$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.9, 146.9, 133.3,

129.5, 128.8, 127.9, 127.1, 126.2 – 125.7 (m), 118.2, 119.2 – 116.7 (m), 116.0 – 114.4 (m), 113.9, 113.0 – 112.0 (m), 111.7 – 109.8 (m), 108.4 – 107.3 (m). ^{19}F NMR (376 MHz, CDCl_3) δ -80.4 – -81.7 (m, 3F), -105.6 – -106.3 (m, 2F), -120.4 – -121.1 (m, 2F), -121.3 – -122.4 (m, 4F), -122.6 – -123.4 (m, 2F), -125.9 – -126.6 (m, 2F). The spectral data were in accordance with the literature.¹¹



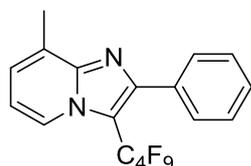
3-(perfluorobutyl)-2-(m-tolyl)imidazo[1,2-a]pyridine (3bc) Yellow liquid, 105 mg, Yield: 82%;

^1H NMR (400 MHz, CDCl_3) δ 8.31 (d, $J = 7.0$ Hz, 1H), 7.73 (d, $J = 8.9$ Hz, 1H), 7.53 – 7.18 (m, 5H), 6.99 – 6.90 (m, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 146.8, 137.5, 133.2, 130.2, 129.5, 127.7, 127.1, 126.5, 126.1 – 125.7 (m), 119.5 – 118.3 (m), 118.1, 117.8 – 116.9 (m), 116.4 – 115.4 (m), 115.3 – 114.0 (m), 113.8, 108.2 – 107.0 (m), 21.2. ^{19}F NMR (376 MHz, CDCl_3) δ -80.3 – -82.0 (m, 3F), -105.5 – -106.9 (m, 2F), -120.9 – -122.3 (m, 2F), -125.3 – -126.8 (m, 2F). HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{18}\text{H}_{11}\text{F}_9\text{N}_2$ 426.0773, found 426.0776.

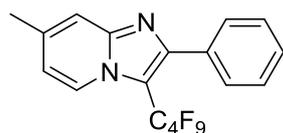


3-(perfluorobutyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (3cc) White solid, 101 mg, Yield: 79%; ^1H NMR (400 MHz, CDCl_3) δ 8.30 (d, $J = 7.0$ Hz, 1H), 7.72 (d, $J = 9.0$ Hz, 1H), 7.50 (d, $J = 7.7$ Hz, 2H), 7.42 – 7.33 (m, 1H), 7.29 – 7.20 (m, 2H), 6.95 (t, $J = 7.2$ Hz, 1H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 151.0, 146.9, 138.6, 130.4, 129.4, 128.6, 127.0, 126.1 – 125.7 (m), 119.2 – 118.3 (m), 118.1, 116.5 – 115.5 (m), 115.3 – 114.2 (m), 113.7, 108.2 – 107.0 (m), 21.2. ^{19}F NMR (376 MHz, CDCl_3) δ

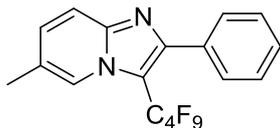
-79.4 – -83.0 (m, 3F), -104.6 – -107.6 (m, 2F), -120.4 – -122.8 (m, 2F), -124.4 – -127.5 (m, 2F). The spectral data were in accordance with the literature.¹¹



8-methyl-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3dc) White solid, 100 mg, Yield: 78%; ¹H NMR (400 MHz, CDCl₃) δ 8.18 (d, *J* = 7.1 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.48 – 7.36 (m, 3H), 7.17 (d, *J* = 6.9 Hz, 1H), 6.87 (t, *J* = 7.0 Hz, 1H), 2.67 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.3, 147.3, 133.6, 129.7, 128.6, 128.2, 127.9, 125.8, 123.9 – 123.5 (m), 119.3 – 118.1 (m), 116.5 – 115.5 (m), 115.3 – 114.4 (m), 113.9, 113.2 – 111.1 (m), 108.7 – 107.7 (m), 17.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.0 – -82.1 (m, 3F), -105.1 – -106.9 (m, 2F), -120.8 – -122.7 (m, 2F), -125.3 – -127.3 (m, 2F)). The spectral data were in accordance with the literature.¹¹



7-methyl-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3ec) White solid, m.p. 65.6–66.8 °C, 112 mg, Yield: 88%; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 7.2 Hz, 1H), 7.64 – 7.57 (m, 2H), 7.49 – 7.36 (m, 4H), 6.76 (d, *J* = 7.2 Hz, 1H), 2.42 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.7, 147.3, 138.5, 133.4, 129.5, 128.6, 127.8, 125.3 – 124.8 (m), 119.3 – 118.2 (m), 118.0 – 116.7 (m), 116.4 (d, *J* = 3.4 Hz), 116.0 – 114.0 (m), 107.8 – 106.6 (m), 21.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.6 – -81.6 (m, 3F), -105.6 – -106.6 (m, 2F), -121.3 – -122.4 (m, 2F), -125.7 – -126.7 (m, 2F). HRMS (EI) *m/z*: [M]⁺ calcd for C₁₈H₁₁F₉N₂ 426.0773, found 426.0778.



6-methyl-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3fc) White solid, 94 mg, Yield: 73%; ^1H NMR (400 MHz, CDCl_3) δ 8.07 (s, 1H), 7.66 – 7.55 (m, 3H), 7.46 – 7.38 (m, 3H), 7.24 (d, J = 9.3 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.6, 145.9, 133.5, 130.2, 129.5, 128.6, 127.8, 126.1, 123.8, 123.7 – 123.4 (m), 119.6 – 118.3 (m), 117.3, 116.4 – 115.5 (m), 115.3 – 114.4 (m), 107.9 – 106.9 (m), 18.4. ^{19}F NMR (376 MHz, CDCl_3) δ -80.4 – -81.4 (m, 3F), -105.4 – -106.4 (m, 2F), -121.3 – -122.1 (m, 2F), -125.5 – -126.4 (m, 2F). The spectral data were in accordance with the literature.¹¹



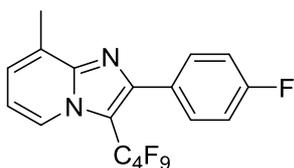
5-methyl-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3gc) Yellow solid, m.p. 131.5-132.4 °C, 70 mg, Yield: 55%; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (d, J = 8.9 Hz, 1H), 7.55 – 7.47 (m, 2H), 7.44 – 7.37 (m, 3H), 7.32 (t, J = 8.0 Hz, 1H), 6.80 (d, J = 6.9 Hz, 1H), 2.75 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.0 (d, J = 3.1 Hz), 149.6, 138.4, 135.2, 129.9, 128.5, 127.8, 127.6, 119.5 – 118.3 (m), 116.9, 116.4, 116.1 – 115.2 (m), 115.0 – 113.9 (m), 112.4 – 110.8 (m), 109.2 – 107.8 (m), 22.7 – 22.2 (m). ^{19}F NMR (376 MHz, CDCl_3) δ -80.5 – -81.7 (m, 3F), -93.6 – -94.7 (m, 2F), -118.4 – -119.8 (m, 2F), -125.7 – -126.9 (m, 2F). HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{18}\text{H}_{11}\text{F}_9\text{N}_2$ 426.0773, found 426.0778.



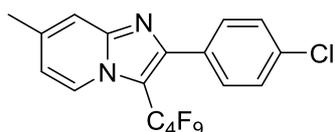
6-methyl-3-(perfluorobutyl)-2-(p-tolyl)imidazo[1,2-a]pyridine (3hc) Yellow solid, m.p. 103.2-104.3 °C, 99 mg, Yield: 75%; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (s, 1H), 7.61 (d, *J* = 9.2 Hz, 1H), 7.50 (d, *J* = 7.7 Hz, 2H), 7.28 – 7.15 (m, 3H), 2.39 (s, 3H), 2.36 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 150.7, 145.9, 138.5, 130.6, 130.1, 129.4, 128.6, 123.6, 123.7 – 123.4 (m), 119.4 – 118.2 (m), 117.3, 116.5 – 115.4 (m), 115.3 – 113.9 (m), 112.5 – 110.5 (m), 107.8 – 106.8 (m), 21.2, 18.4. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.5 – -81.4 (m, 3F), -105.6 – -106.3 (m, 2F), -121.3 – -122.0 (m, 2F), -125.7 – -126.3 (m, 2F). HRMS (EI) *m/z*: [M]⁺ calcd for C₁₉H₁₃F₉N₂ 440.0930, found 440.0934.



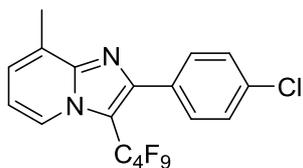
2-(4-methoxyphenyl)-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3ic) White solid, 115 mg, Yield: 87%; ¹H NMR (400 MHz, CDCl₃) δ 8.28 (d, *J* = 7.0 Hz, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.56 (d, *J* = 8.2 Hz, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.02 – 6.85 (m, 3H), 3.83 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 160.1, 150.6, 146.8, 130.8, 127.0, 126.1 – 125.8 (m), 125.6, 119.3 – 118.4 (m), 118.0, 116.5 – 115.4 (m), 115.3 – 114.1 (m), 113.7, 113.4, 112.6 – 111.1 (m), 107.8 – 106.8 (m), 55.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.2 – -81.6 (m, 3F), -105.5 – -106.8 (m, 2F), -121.0 – -122.4 (m, 2F), -125.2 – -126.8 (m, 2F). The spectral data were in accordance with the literature.¹¹



2-(4-fluorophenyl)-8-methyl-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3jc) White solid, m.p. 80.7- 81.8 °C, 115 mg, Yield: 87%; ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 7.0 Hz, 1H), 7.63 – 7.52 (m, 2H), 7.18 (d, *J* = 7.0 Hz, 1H), 7.15 – 7.07 (m, 2H), 6.87 (t, *J* = 7.0 Hz, 1H), 2.66 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.2 (d, *J* = 246.4 Hz), 149.3, 147.3, 131.6 (d, *J* = 8.4 Hz), 129.7 (d, *J* = 3.5 Hz), 128.3, 126.0, 123.9 – 123.5 (m), 119.3 – 118.4 (m), 117.8 – 117.0 (m), 116.5 – 115.4 (m), 114.9 (d, *J* = 21.8 Hz), 114.0, 112.4 – 110.9 (m), 108.9 – 107.7 (m), 17.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.8 – -81.2 (m, 3F), -105.8 – -106.2 (m, 2F), -113.2(s, 1F), -121.5 – -122.1 (m, 2F), -125.7 – -126.3 (m, 2F). HRMS (EI) *m/z*: [M]⁺ calcd for C₁₈H₁₀F₁₀N₂ 444.0679, found 444.0680.

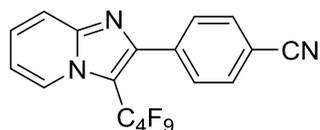


2-(4-chlorophenyl)-7-methyl-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3ke) White solid, m.p. 76.5- 77.7 °C, 113 mg, Yield: 82%; ¹H NMR (400 MHz, CDCl₃) δ 8.16 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.46 (s, 1H), 7.39 (d, *J* = 8.2 Hz, 2H), 6.79 (d, *J* = 7.2 Hz, 1H), 2.44 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.5, 147.4, 138.7, 134.9, 132.0, 130.9, 128.2, 125.3 – 124.9 (m), 119.3 – 118.2 (m), 116.7, 116.5, 115.3 – 114.3 (m), 112.6 – 111.0 (m), 107.9 – 106.8 (m), 21.2. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.5 – -81.3 (m, 3F), -105.5 – -106.2 (m, 2F), -121.4 – -122.2 (m, 2F), -125.5 – -126.4 (m, 2F). HRMS (EI) *m/z*: [M]⁺ calcd for C₁₈H₁₀ClF₉N₂ 460.0383, found 460.0385.

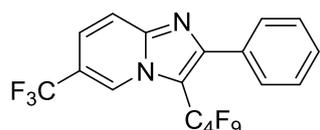


2-(4-chlorophenyl)-8-methyl-3-(perfluorobutyl)imidazo[1,2-a]pyridine (3lc) Pale yellow solid,

m.p. 82.8- 83.7 °C, 93 mg, Yield: 82%; ¹H NMR (400 MHz, CDCl₃) δ 8.17 (d, *J* = 7.0 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 6.9 Hz, 1H), 6.88 (t, *J* = 7.0 Hz, 1H), 2.66 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 149.0, 147.4, 134.9, 132.2, 131.0, 128.3, 128.2, 126.0, 124.0 – 123.5 (m), 119.3 – 118.2 (m), 116.8 – 115.5 (m), 115.3 – 114.3 (m), 114.1, 112.0 – 110.8 (m), 109.0 – 107.7 (m), 17.1. ¹⁹F NMR (376 MHz, CDCl₃) δ -80.5 – -81.5 (m, 3F), -105.5 – -106.6 (m, 2F), -121.3 – -122.2 (m, 2F), -125.4 – -126.6 (m, 2F). HRMS (EI) *m/z*: [M]⁺ calcd for C₁₈H₁₀ClF₉N₂ 460.0383, found 460.0390.



4-(3-(perfluorobutyl)imidazo[1,2-a]pyridin-2-yl)benzonitrile (3mc) White solid, m.p. 122.3-122.9 °C, 106 mg, Yield: 81%; ¹H NMR (400 MHz, CDCl₃) δ 8.32 (d, *J* = 7.1 Hz, 1H), 7.78 – 7.70 (m, 5H), 7.49 – 7.40 (m, 1H), 7.03 (t, *J* = 7.0 Hz, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 148.6, 147.1, 138.0, 131.8, 130.3, 127.8, 126.3 – 125.8 (m), 118.6, 118.4, 114.5, 112.7, 108.9 – 107.9 (m). ¹⁹F NMR (376 MHz, CDCl₃) δ -80.7 – -81.1 (m, 3F), -105.9 – -106.2 (m, 2F), -121.6 – -121.9 (m, 2F), -125.8 – -126.0 (m, 2F). HRMS (EI) *m/z*: [M]⁺ calcd for C₁₈H₈F₉N₃ 437.0569, found 437.0573.

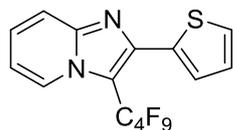


3-(perfluorobutyl)-2-phenyl-6-(trifluoromethyl)imidazo[1,2-a]pyridine (3nc) White solid, m.p. 99.8-101.1 °C, 117 mg, Yield: 81%; ¹H NMR (400 MHz, CDCl₃) δ 8.64 (s, 1H), 7.84 (d, *J* = 9.5 Hz,

1H), 7.67 – 7.58 (m, 2H), 7.54 (d, $J = 9.5$ Hz, 1H), 7.49 – 7.40 (m, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 146.7, 132.5, 129.5, 129.3, 128.1, 125.1 – 124.7 (m), 124.4 (q, $J = 269.8$ Hz), 123.2 (q, $J = 2.7$ Hz), 119.0, 118.6 (q, $J = 34.4$ Hz), 117.7 – 116.6 (m), 116.4 – 115.4 (m), 115.1 – 113.9 (m), 112.5 – 110.7 (m), 109.9 – 108.7 (m). ^{19}F NMR (376 MHz, CDCl_3) δ -62.6 (s, 3F), -80.9 – -81.2 (m, 3F), -106.1 – -106.4 (m, 2F), -121.5 – -121.9 (m, 2F), -125.8 – -126.2 (m, 2F). HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{18}\text{H}_8\text{F}_{12}\text{N}_2$ 480.0490, found 480.0497.

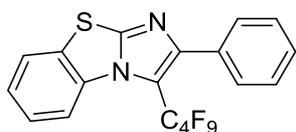


7-methoxy-3-(perfluorobutyl)-2-phenylimidazo[1,2-a]pyridine (3oc) White solid, m.p. 142.8-143.3 °C, 114 mg, Yield: 86%; ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 7.7$ Hz, 1H), 7.64 – 7.56 (m, 2H), 7.45 – 7.36 (m, 3H), 6.95 (s, 1H), 6.63 (d, $J = 7.7$ Hz, 1H), 3.85 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.3, 150.9, 148.8, 133.4, 129.4, 128.6, 127.8, 127.0 – 125.6 (m), 119.2 – 118.4 (m), 117.9 – 116.8 (m), 116.4 – 114.3 (m), 112.4 – 110.8 (m), 108.8, 107.2 – 106.1 (m), 95.2, 55.5. ^{19}F NMR (376 MHz, CDCl_3) δ -80.6 – -81.4 (m, 3F), -105.3 – -105.9 (m, 2F), -121.5 – -122.1 (m, 2F), -125.7 – -126.3 (m, 2F). HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{18}\text{H}_{11}\text{F}_9\text{N}_2\text{O}$ 442.0722, found 442.0729.

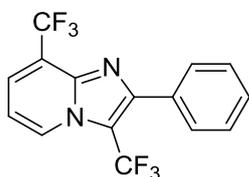


3-(perfluorobutyl)-2-(thiophen-2-yl)imidazo[1,2-a]pyridine (3pc) White solid, m.p. 80.9-81.4 °C, 98 mg, Yield: 78% ^1H NMR (400 MHz, CDCl_3) δ 8.27 (d, $J = 7.1$ Hz, 1H), 7.70 (d, $J = 9.1$ Hz, 1H), 7.49 – 7.40 (m, 2H), 7.35 (t, $J = 8.0$ Hz, 1H), 7.14 – 7.06 (m, 1H), 6.91 (t, $J = 7.0$ Hz, 1H).

^{13}C NMR (100 MHz, CDCl_3) δ 146.7, 144.0, 135.0, 127.9, 127.8 – 127.6 (m), 127.6, 127.3, 126.1 – 125.7 (m), 119.3 – 118.4 (m), 117.9, 116.4 – 114.5 (m), 114.0, 112.6 – 111.4 (m), 109.5 – 108.1 (m), 106.9 – 105.9 (m). ^{19}F NMR (376 MHz, CDCl_3) δ -80.8 – -81.1 (m, 3F), -106.7 – -107.0 (m, 2F), -122.1 – -122.4 (m, 2F), -125.8 – -126.1 (m, 2F). HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{15}\text{H}_7\text{F}_9\text{N}_2\text{S}$ 418.0181, found 418.0186.



3-(perfluorobutyl)-2-phenylbenzo[d]imidazo[2,1-b]thiazole (3qc) White solid, m.p. 113.1–113.8 °C, 82 mg, Yield: 58% ^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 8.5 Hz, 1H), 7.79 – 7.72 (m, 1H), 7.63 – 7.56 (m, 2H), 7.54 – 7.47 (m, 1H), 7.46 – 7.39 (m, 4H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.8, 152.0, 133.3, 132.8, 130.1, 129.6, 128.8, 127.8, 126.7, 125.5, 124.3, 119.3 – 118.1 (m), 117.2 – 116.2 (m), 115.7 – 115.3 (m), 114.9 – 113.9 (m), 113.4 – 113.0 (m), 111.8 – 110.6 (m). ^{19}F NMR (376 MHz, CDCl_3) δ -80.4 – -81.3 (m, 3F), -101.4 – -102.0 (m, 2F), -120.1 – -120.5 (m, 2F), -125.4 – -126.2 (m, 2F). HRMS (EI) m/z : $[\text{M}]^+$ calcd for $\text{C}_{19}\text{H}_9\text{F}_9\text{N}_2\text{S}$ 468.0337, found 468.0342.



2-phenyl-3,8-bis(trifluoromethyl)imidazo[1,2-a]pyridine (4) Colorless oil, 4 mg, Yield: 4% ^1H NMR (400 MHz, CDCl_3) δ 8.47 (d, J = 7.0 Hz, 1H), 7.77 – 7.67 (m, 3H), 7.51 – 7.41 (m, 3H), 7.08 (t, J = 7.1 Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 141.7, 132.2, 129.8, 129.3, 128.7 (q, J = 4.1 Hz), 128.2, 125.2 (q, J = 5.2 Hz), 122.3 (q, J = 270.8 Hz), 121.6 (q, J = 266.3 Hz), 120.0 (q, J = 34.3

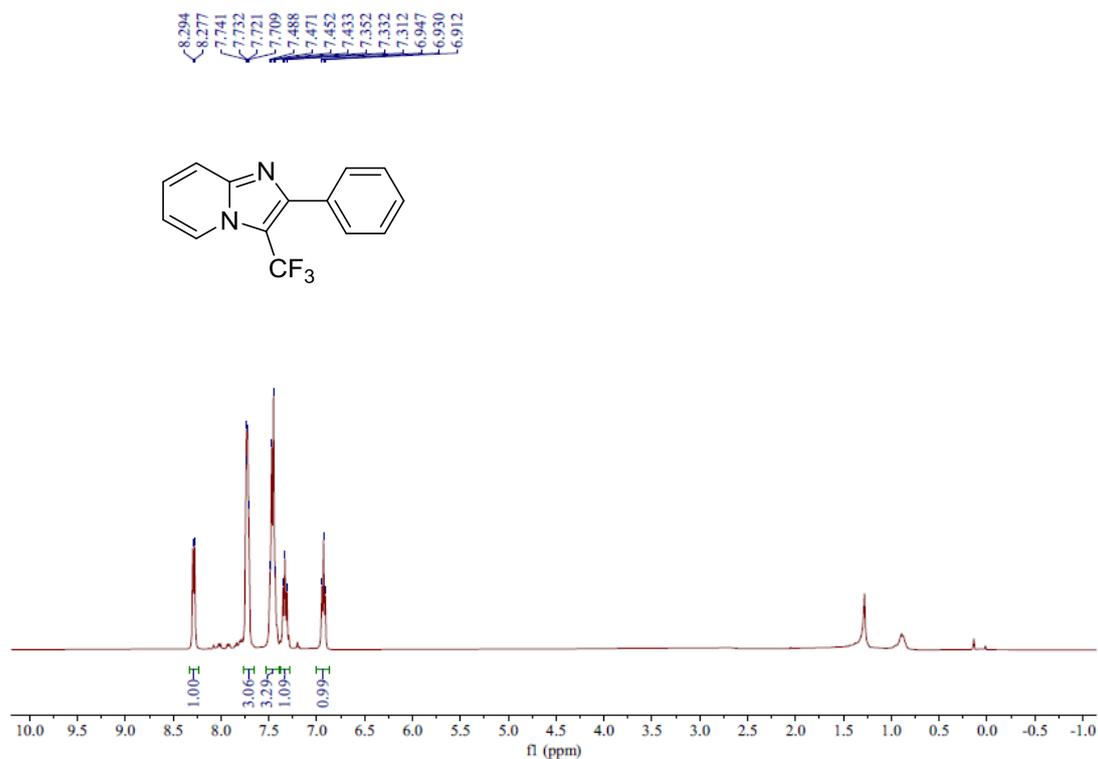
Hz), 112.3, 110.7 (q, $J = 39.7$ Hz). ^{19}F NMR (376 MHz, CDCl_3) δ -57.6, -63.4. HRMS (ESI) m/z : $[\text{M} + \text{H}]^+$ calcd for $\text{C}_{15}\text{H}_8\text{F}_6\text{N}_2$ 331.0665, found 331.0667.

References

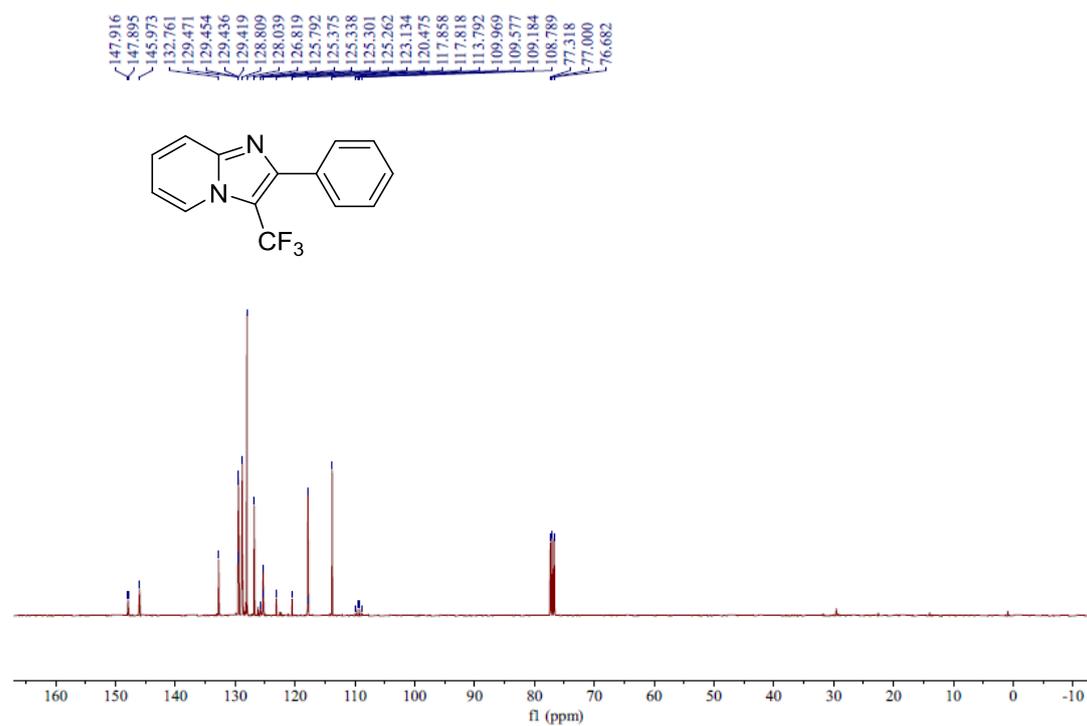
- [1] (a) S.-Y. Takizawa, J.-I. Nishida, T. Tsuzuki, S. Tokito and Y. Ymashita, *Inorg. Chem.*, 2007, **46**, 4308; (b) G. S. Kumar, S. P. Ragini, A. S. Kumar and H. M. Meshram, *RSC Adv.*, 2015, **5**, 51576.
- [2] F. Sladojevich, E. McNeill, J. BÖrgel, S.-L. Zheng and T. Ritter, *Angew. Chem. Int. Ed.*, 2015, **54**, 3712.
- [3] P. Job, *Justus Liebigs Ann. Chem.*, 1928, **9**, 113.
- [4] M. W. Hanna and A. L. Ashbaugh, *J. Phys. Chem.*, 1964, **68**, 811.
- [5] K. Monir, A. K. Bagdi, M. Ghosh and A. Hajra, *J. Org. Chem.*, 2015, **80**, 1332.
- [6] X. Mi, Y. Kong, H. Yang, J. Zhang, C. Pi and X. Cui, *Eur. J. Org. Chem.*, 2020, **8**, 1019.
- [7] Y. Wu, H.-R. Zhang, R.-X. Jin, Q. Lan and X.-S. Wang, *Adv. Synth. Catal.*, 2016, **358**, 3528.
- [8] Q. Zhou, S. Xu and R. Zhang, *Tetrahedron Lett.*, 2019, **60**, 734.
- [9] C.-P. Zhang, Z.-L. Wang, Q.-Y. Chen, C.-T. Zhang, Y.-C. Gu, J.-C. Xiao, *Angew. Chem. Int. Ed.*, 2011, **50**, 1896.
- [10] S. Han, X. Gao, Q. Wu, J. Li, D. Zou, Y. Wu and Y. Wu, *Adv. Synth. Catal.*, 2019, **361**, 1559.
- [11] J. Huang, D. Wu, X. Bai, P. Cai and W.-G. Zhu, *New J. Chem.*, 2021, **45**, 4925.

4. NMR spectrum

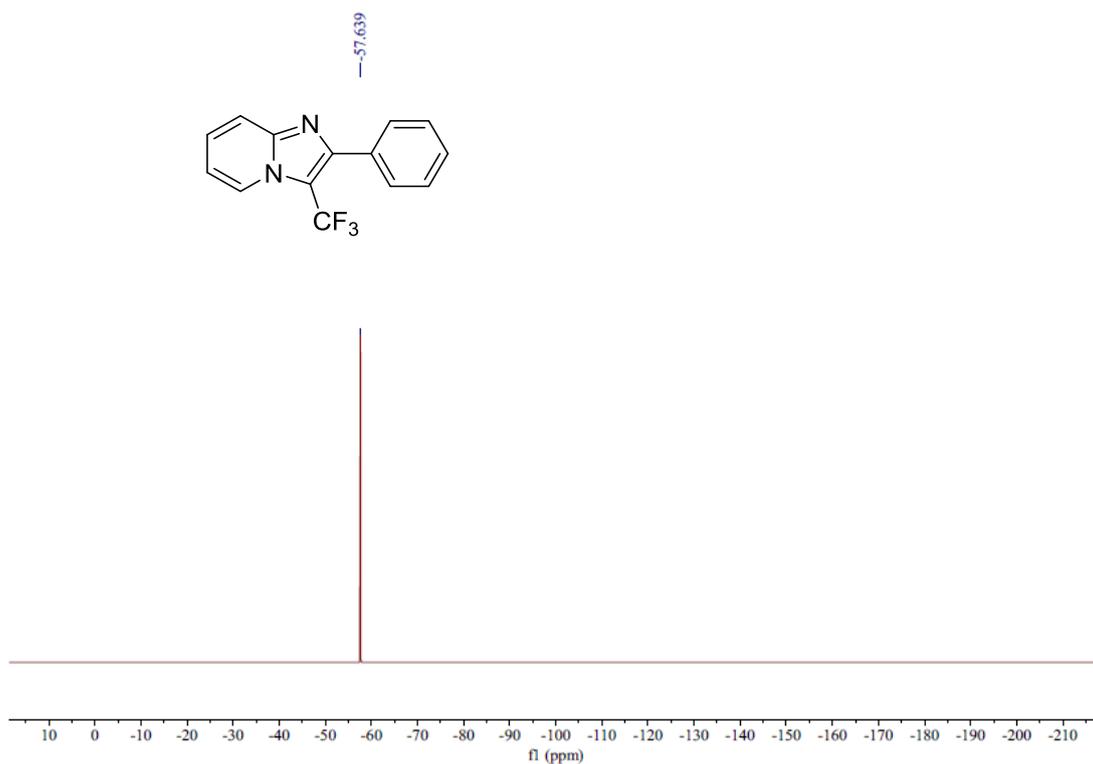
^1H NMR (400 MHz, CDCl_3) Spectrum of **3aa**



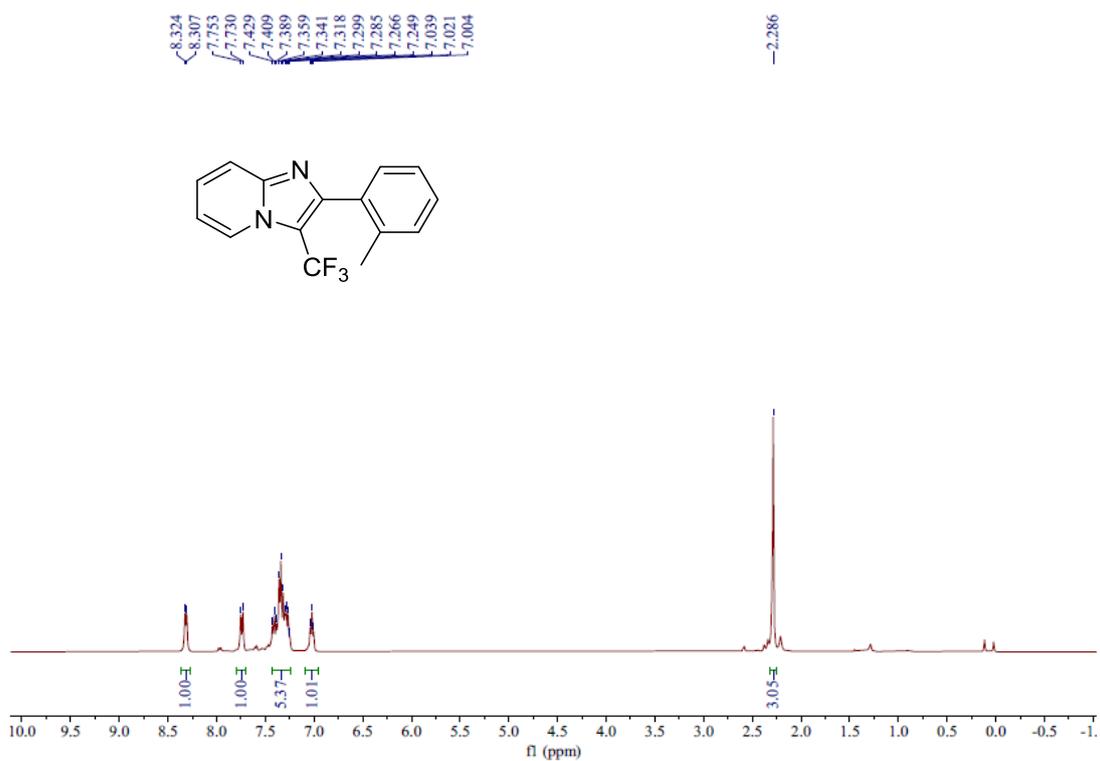
^{13}C NMR (100 MHz, CDCl_3) Spectrum of **3aa**



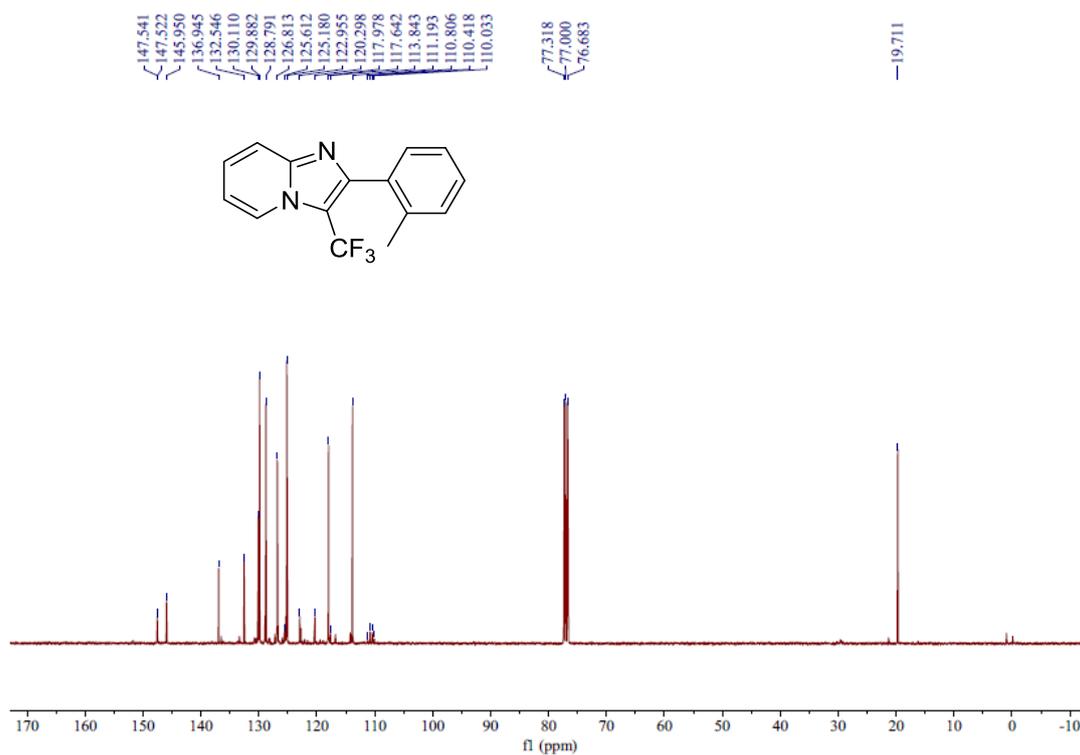
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3aa**



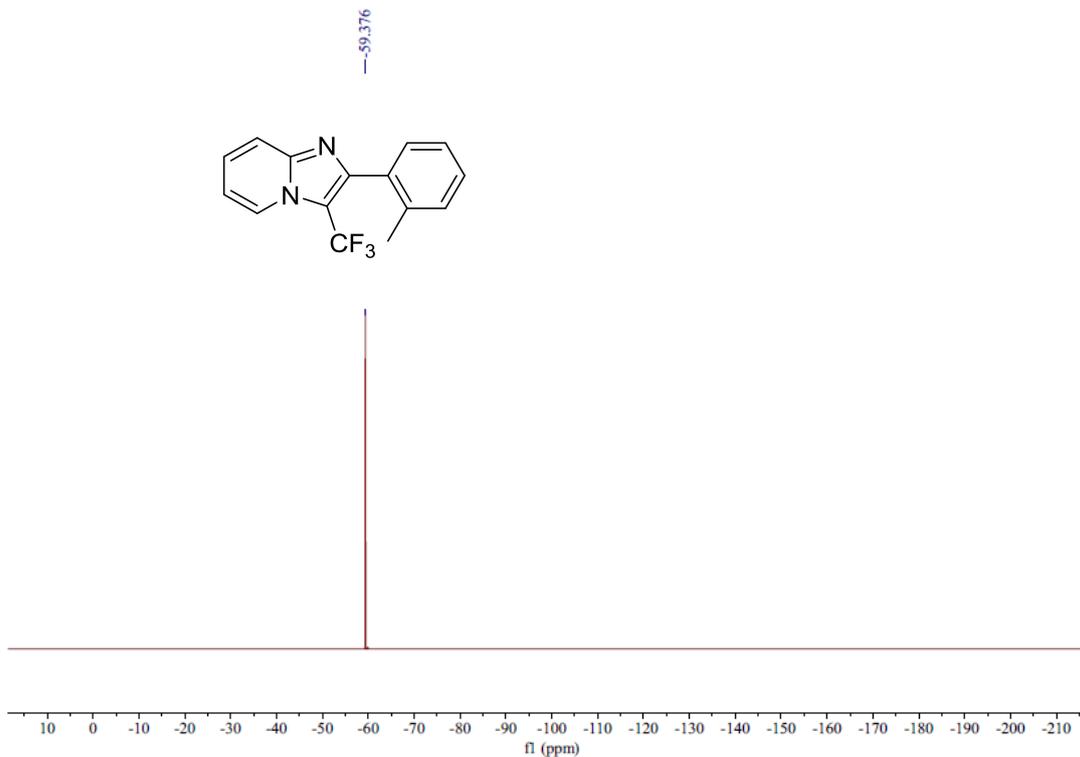
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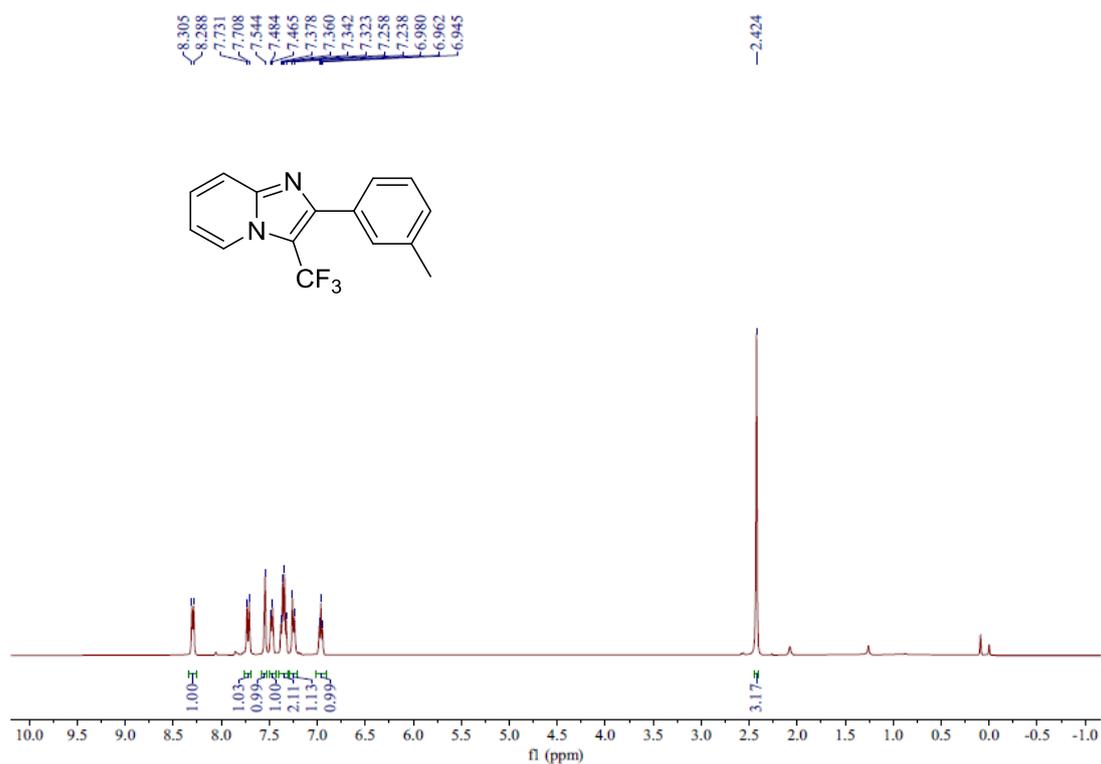
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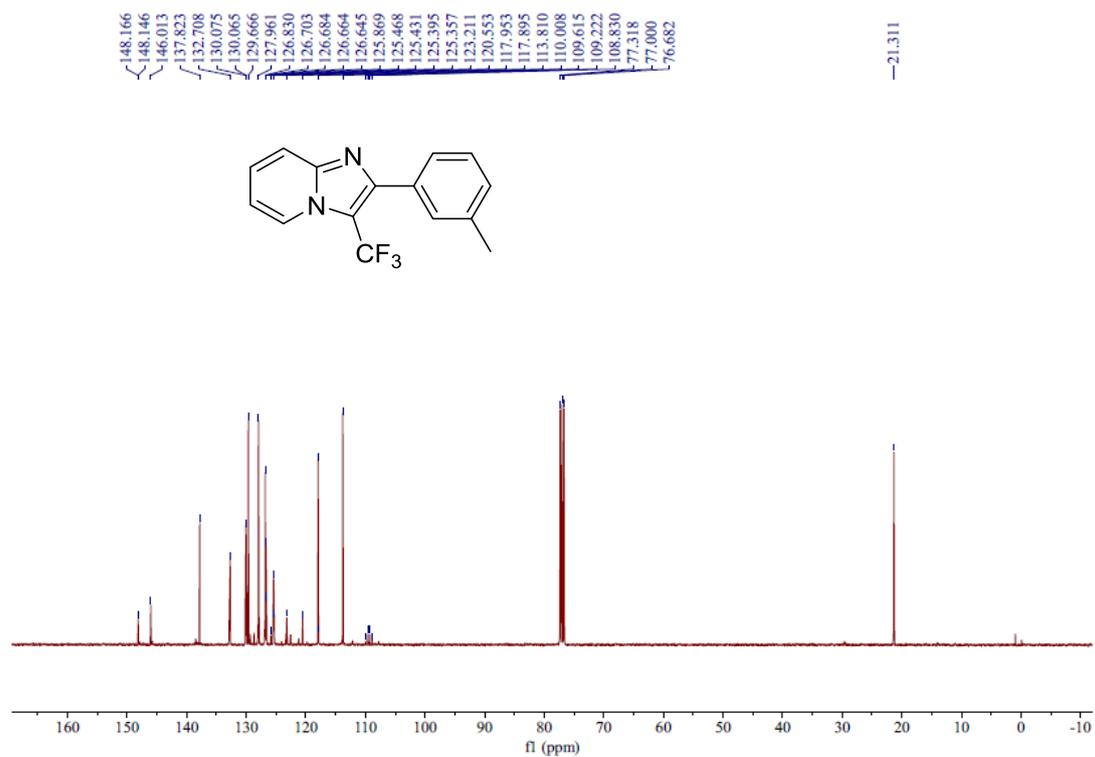
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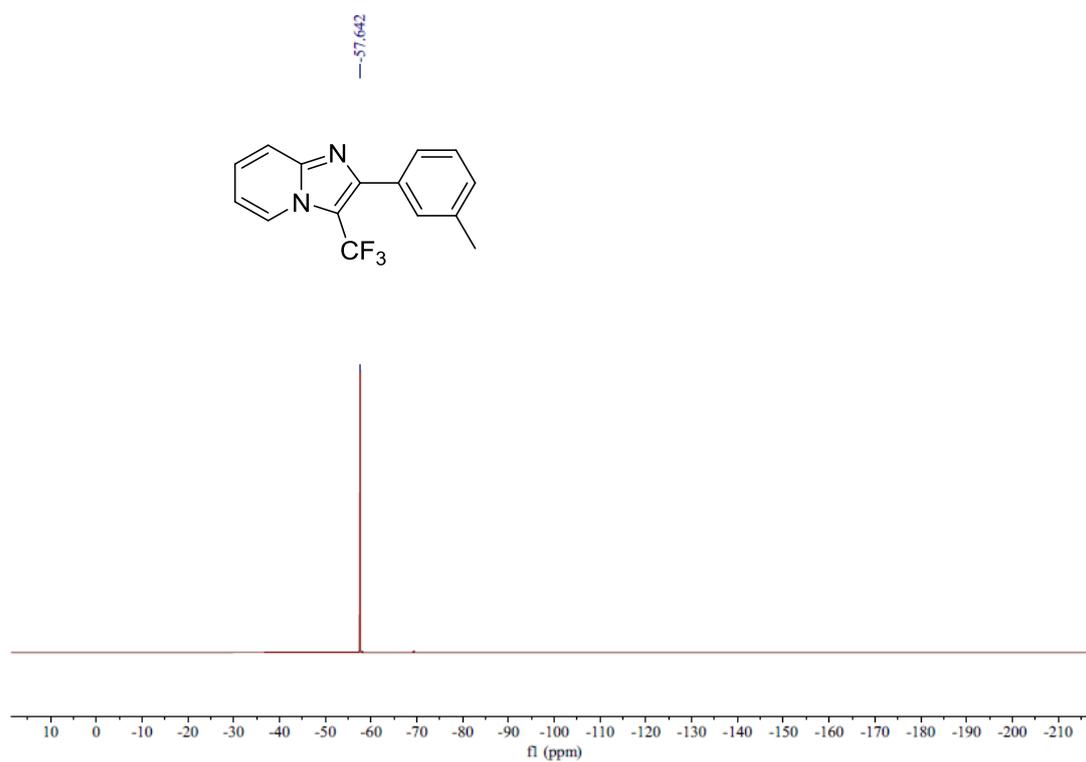
¹H NMR (400 MHz, CDCl₃) Spectrum of **3ca**



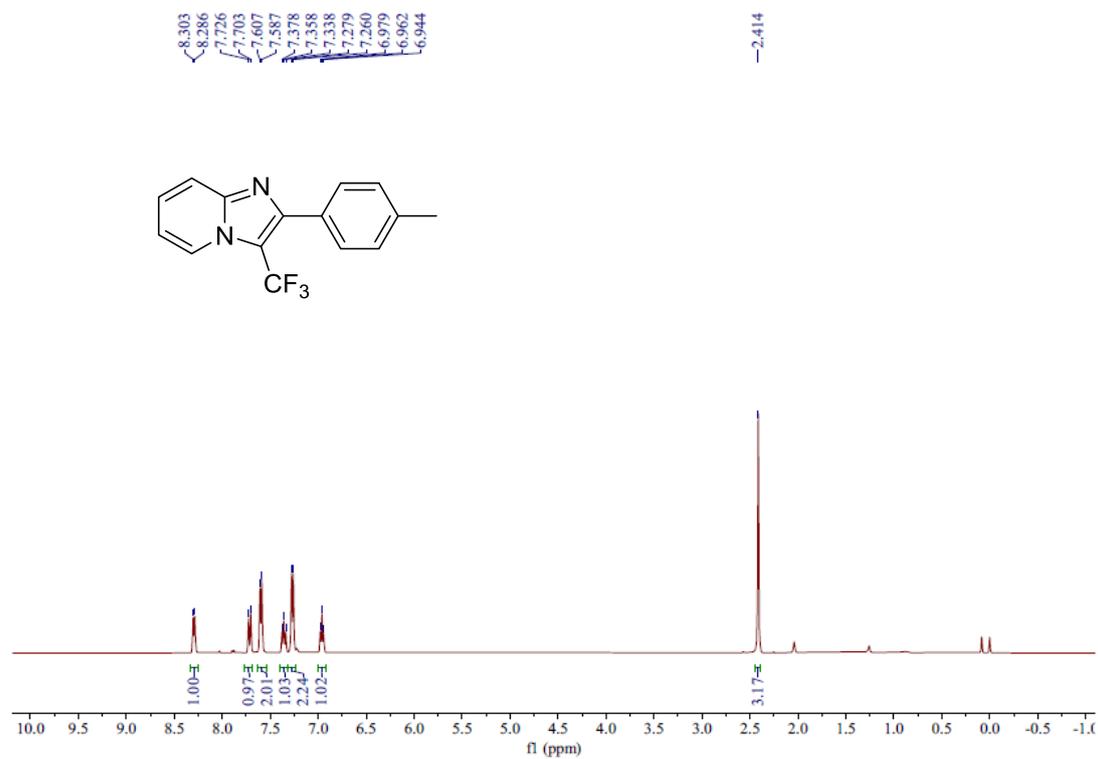
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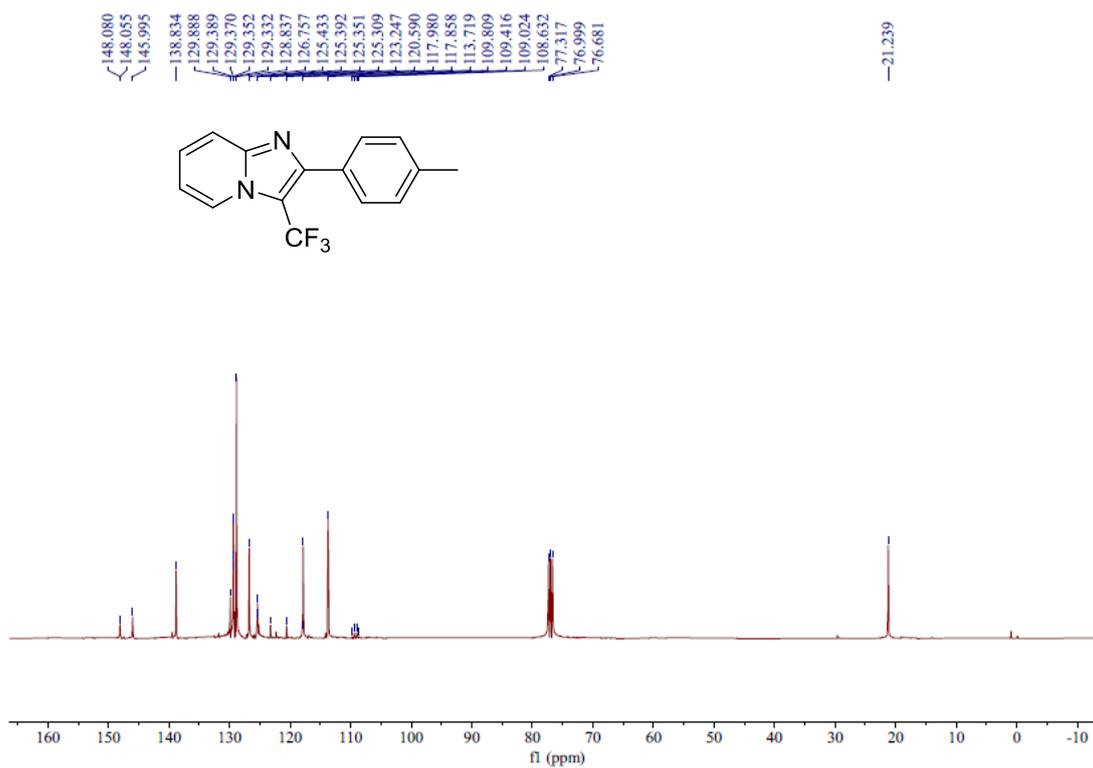
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3ca**



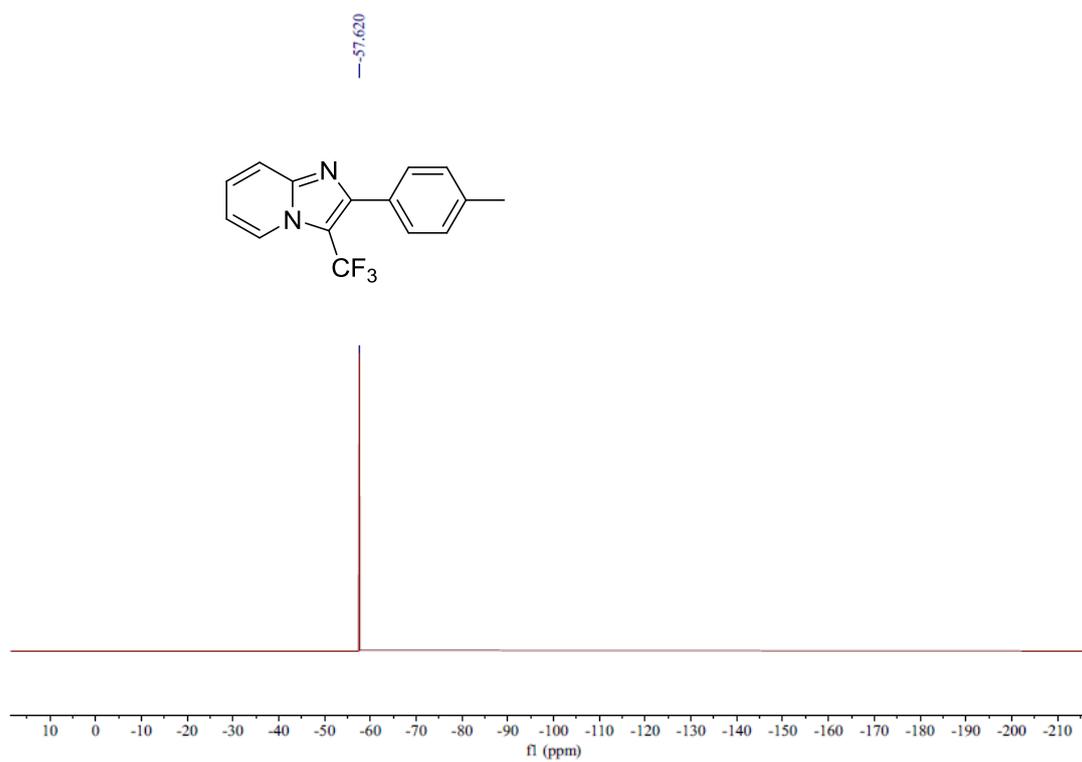
¹H NMR (400 MHz, CDCl₃) Spectrum of **3da**



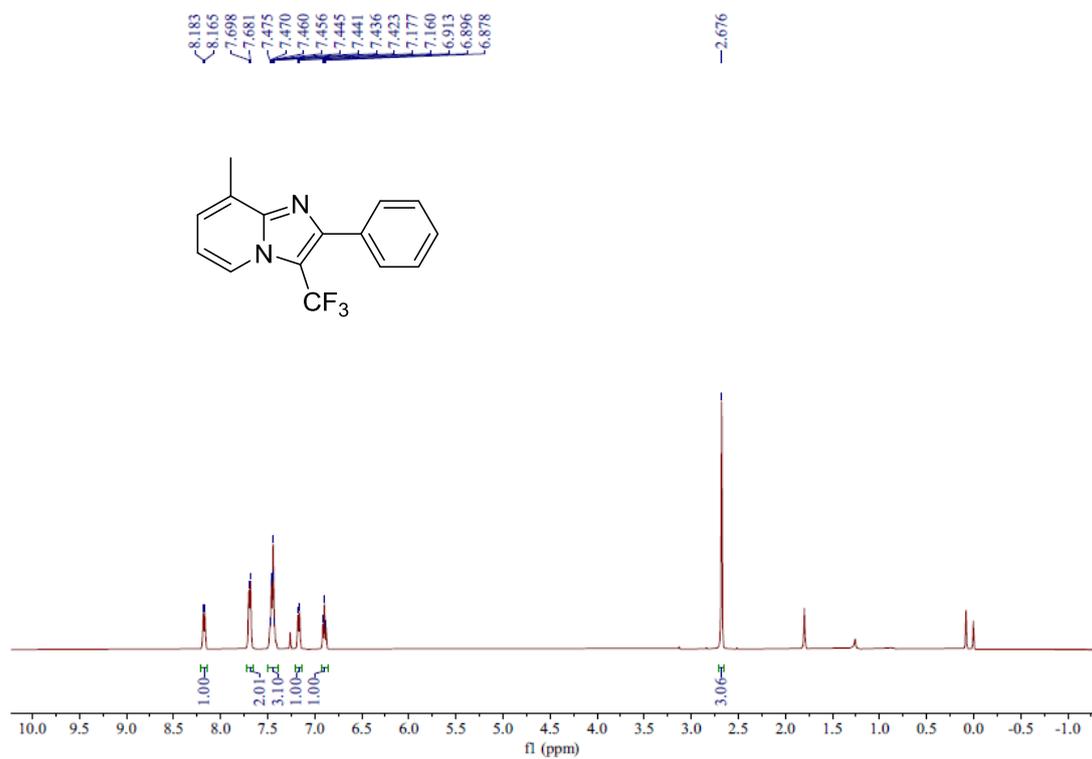
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3da**



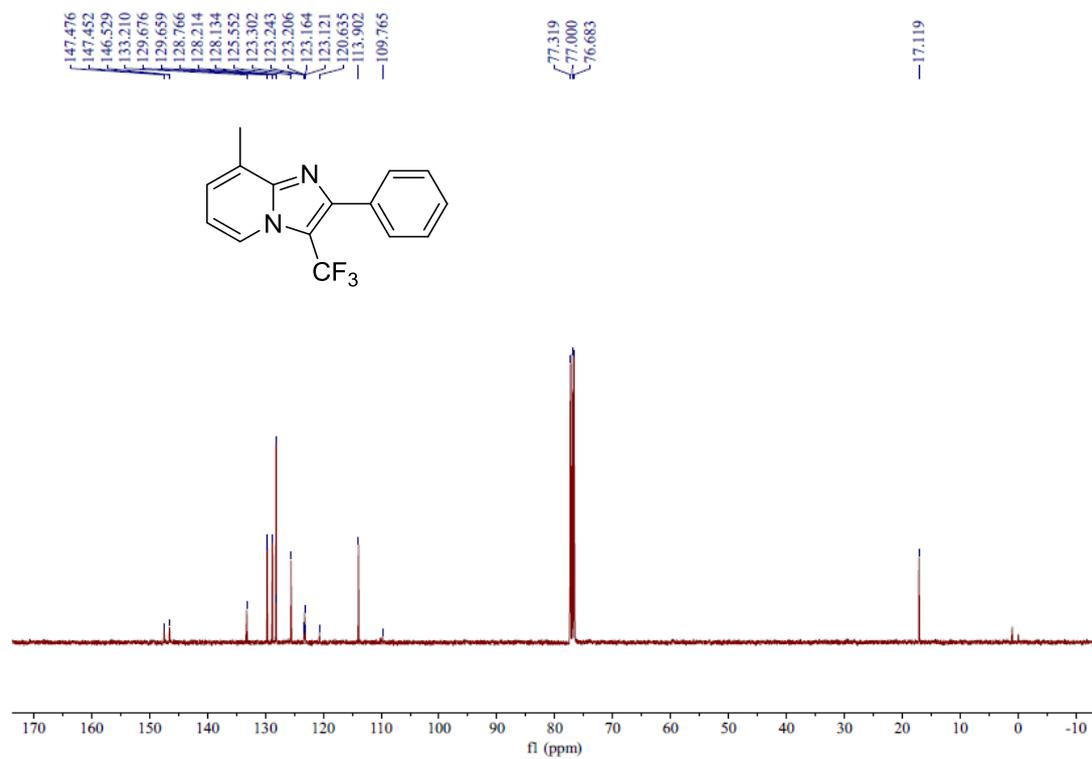
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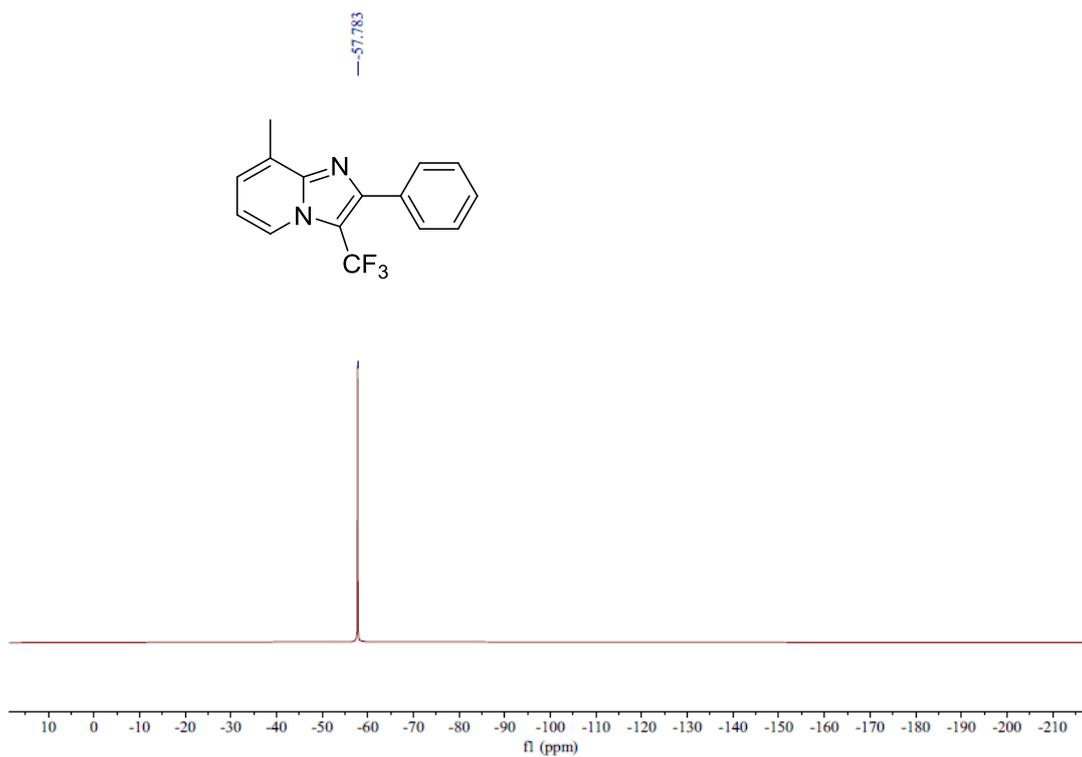
¹H NMR (400 MHz, CDCl₃) Spectrum of **3ea**



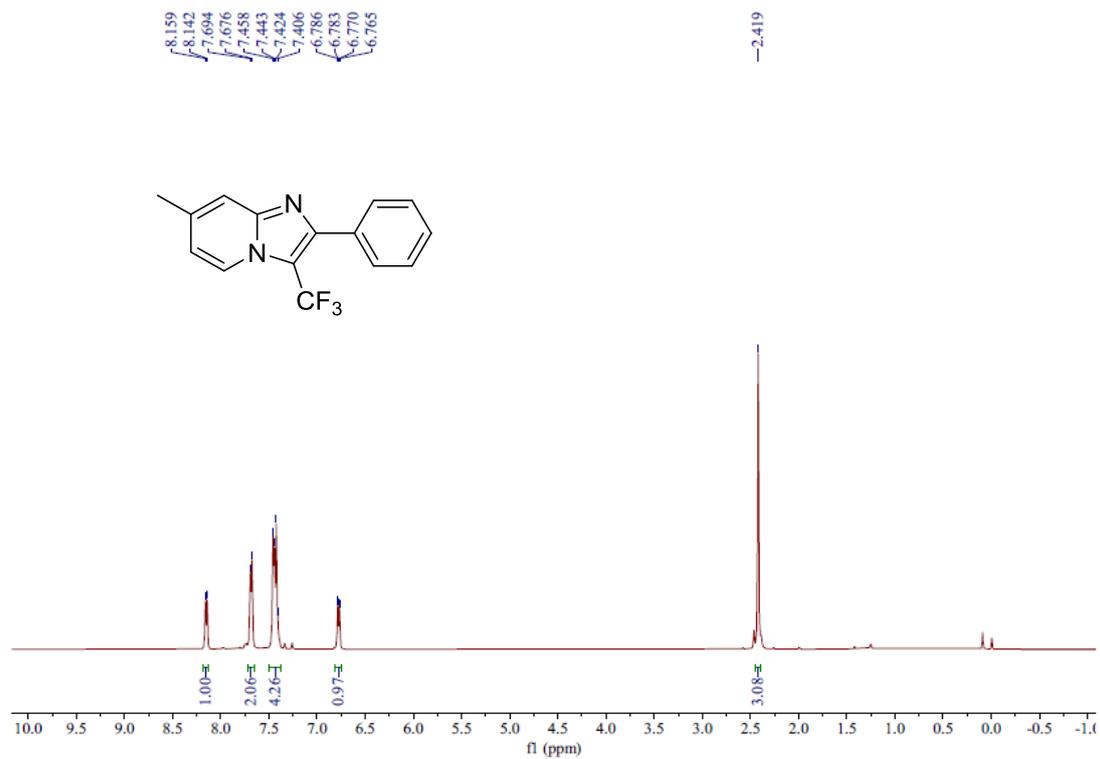
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ea**



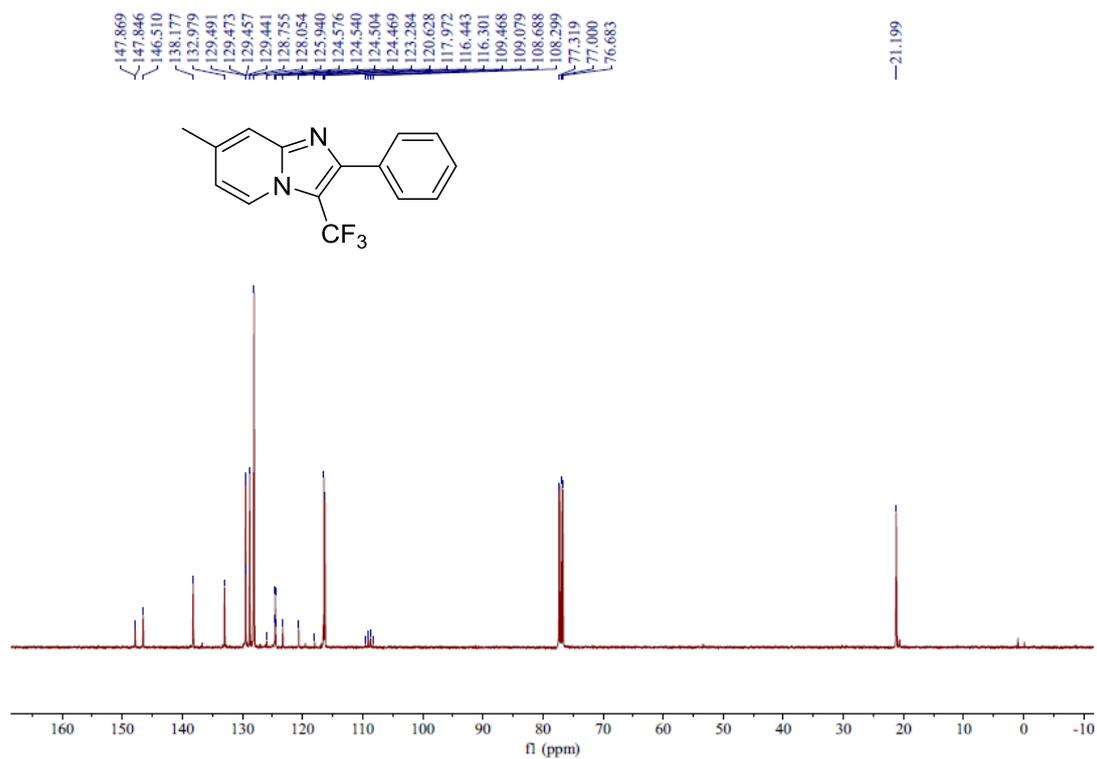
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3ea**



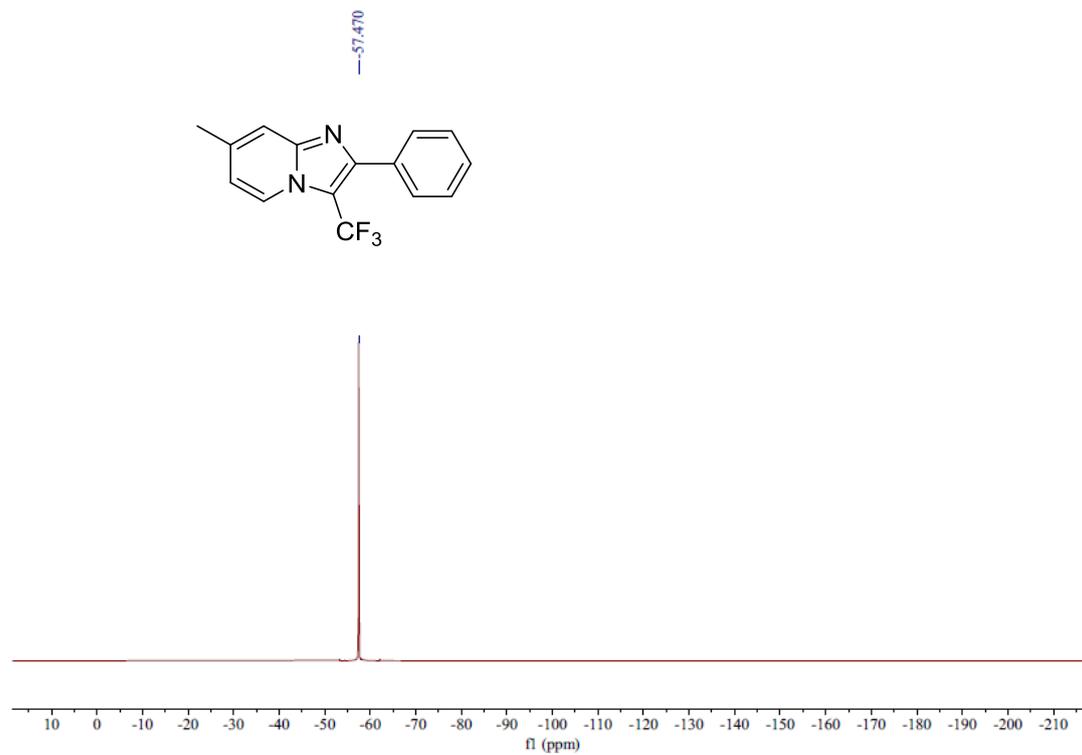
¹H NMR (400 MHz, CDCl₃) Spectrum of **3fa**



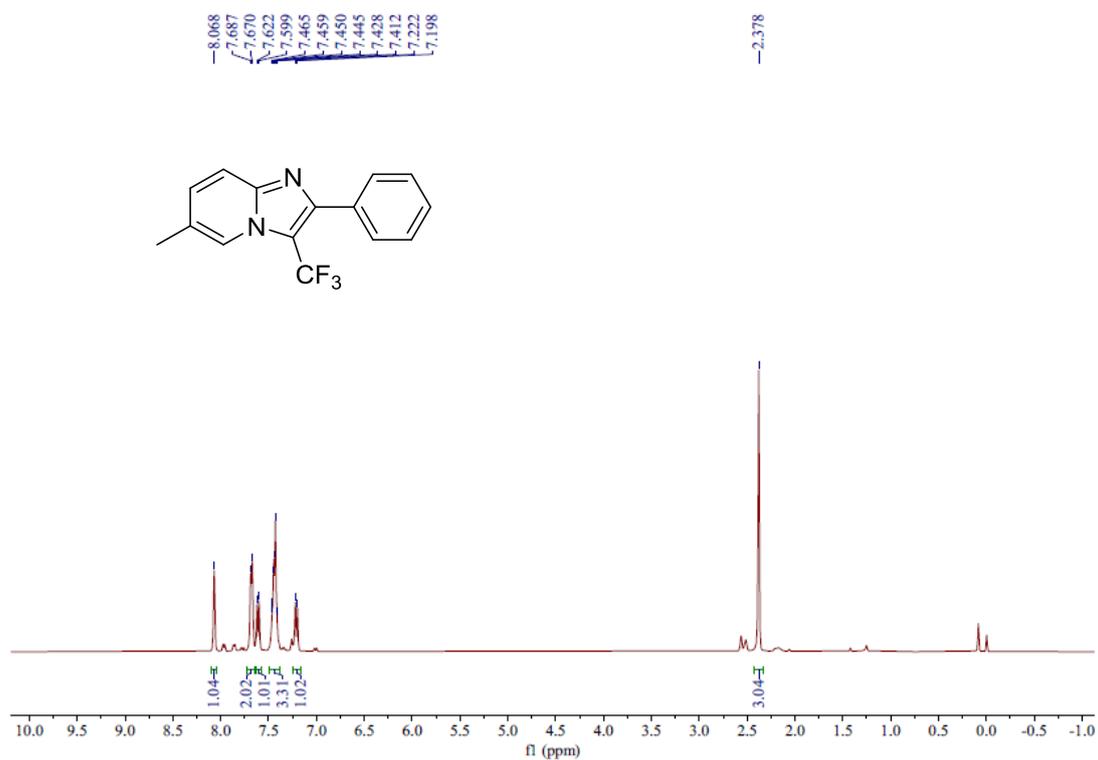
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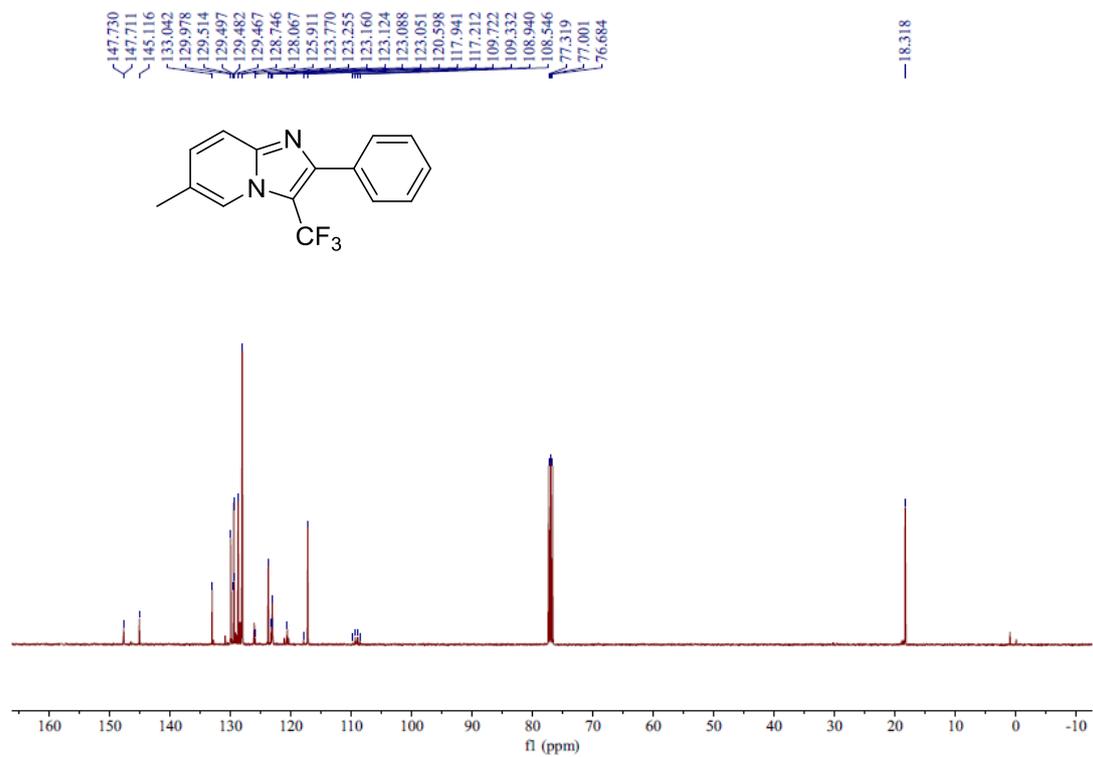
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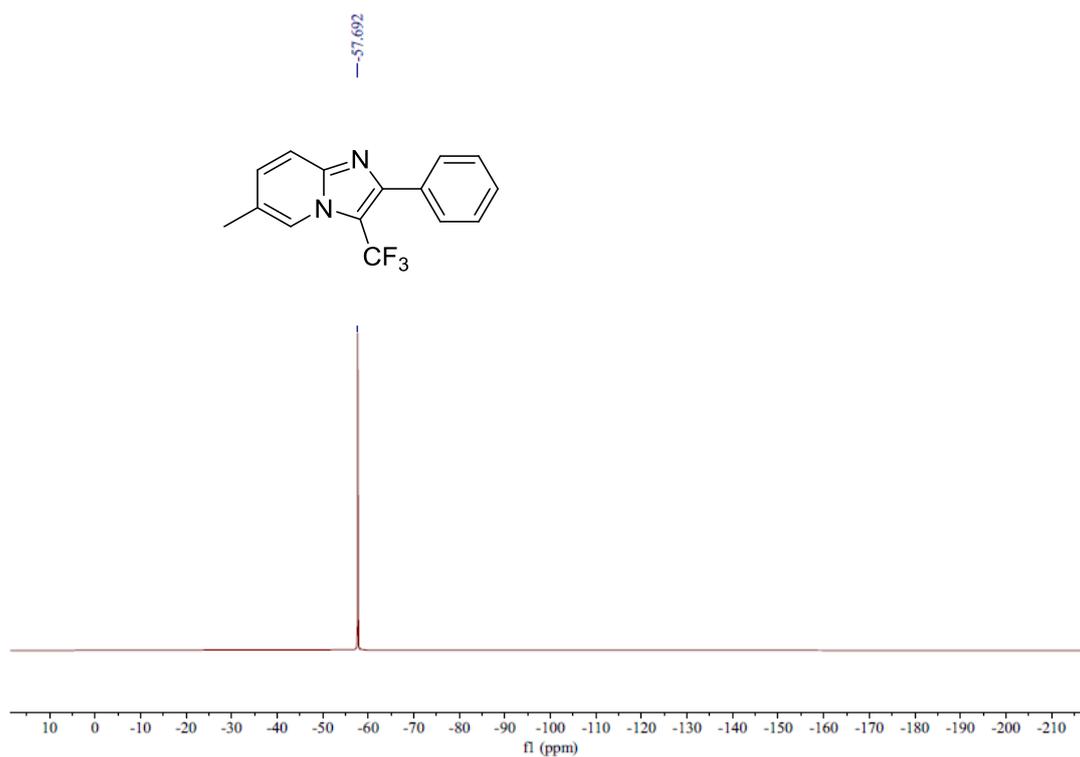
¹H NMR (400 MHz, CDCl₃) Spectrum of **3ga**



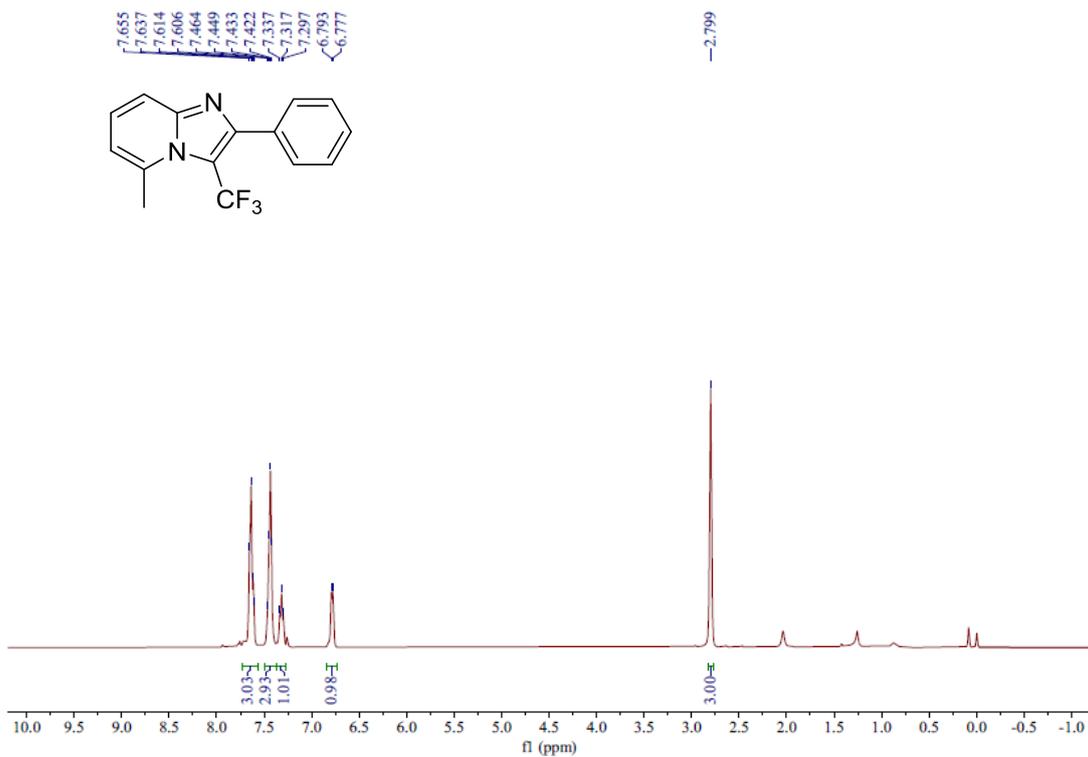
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ga**



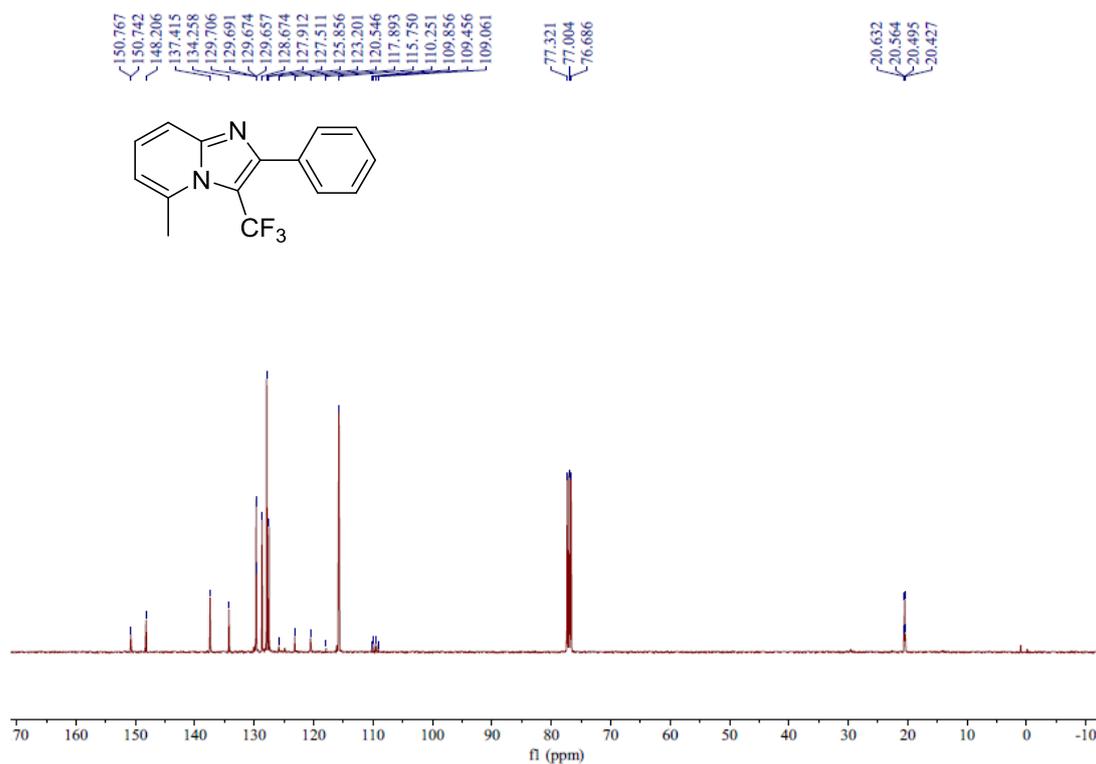
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3ga**



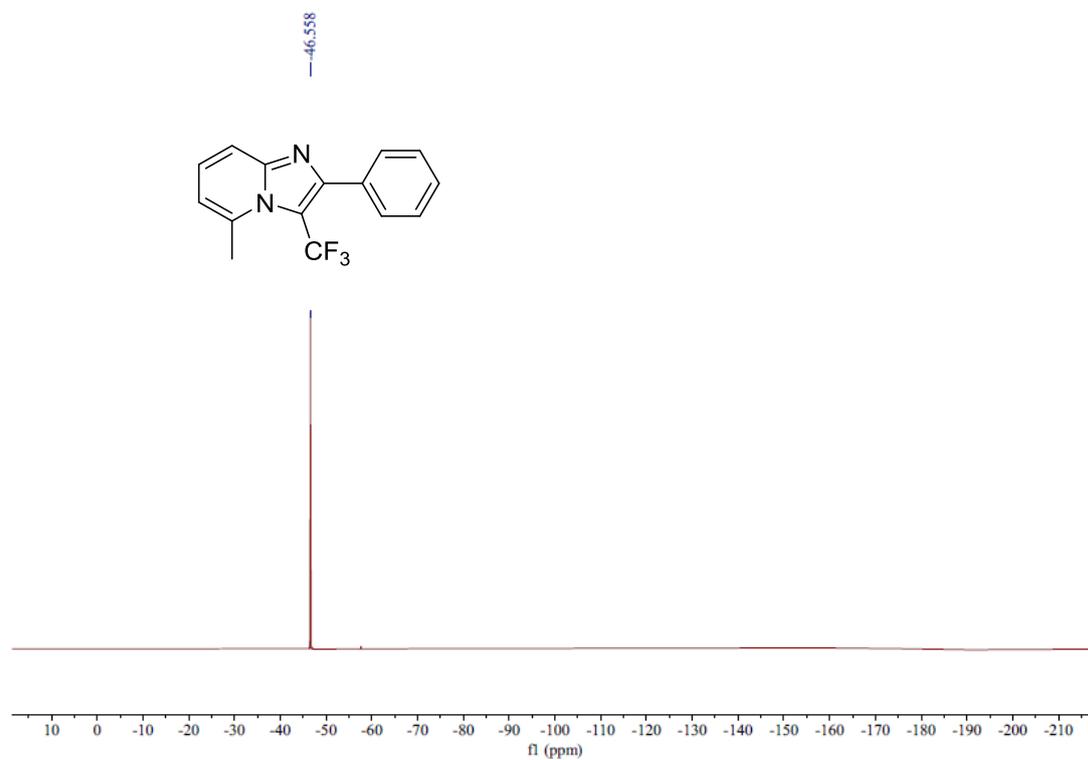
^1H NMR (400 MHz, CDCl_3) Spectrum of **3ha**



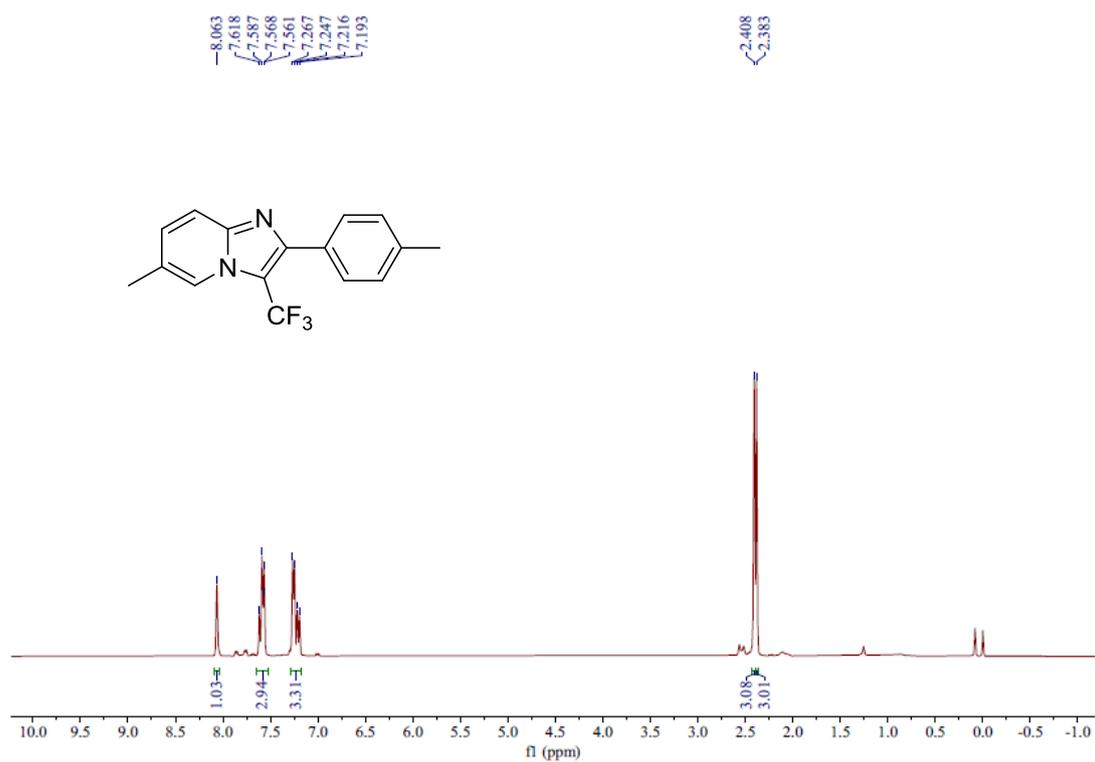
^{13}C NMR (100 MHz, CDCl_3) Spectrum of **3ha**



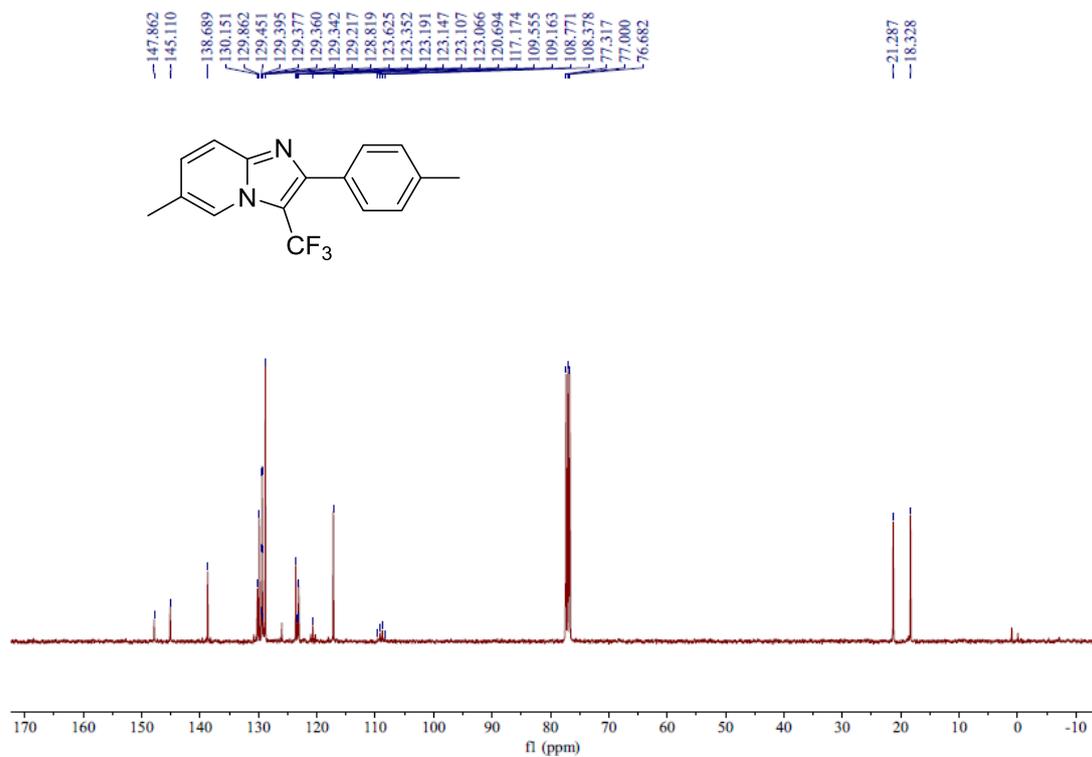
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3ha**



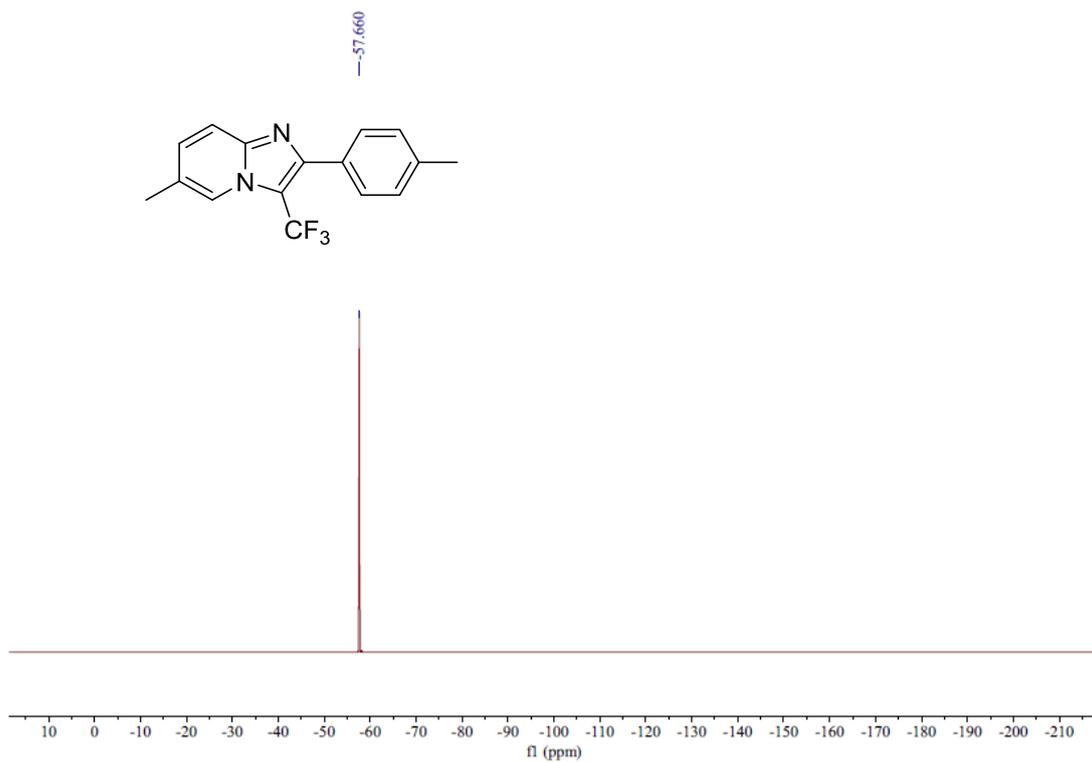
¹H NMR (400 MHz, CDCl₃) Spectrum of **3ia**



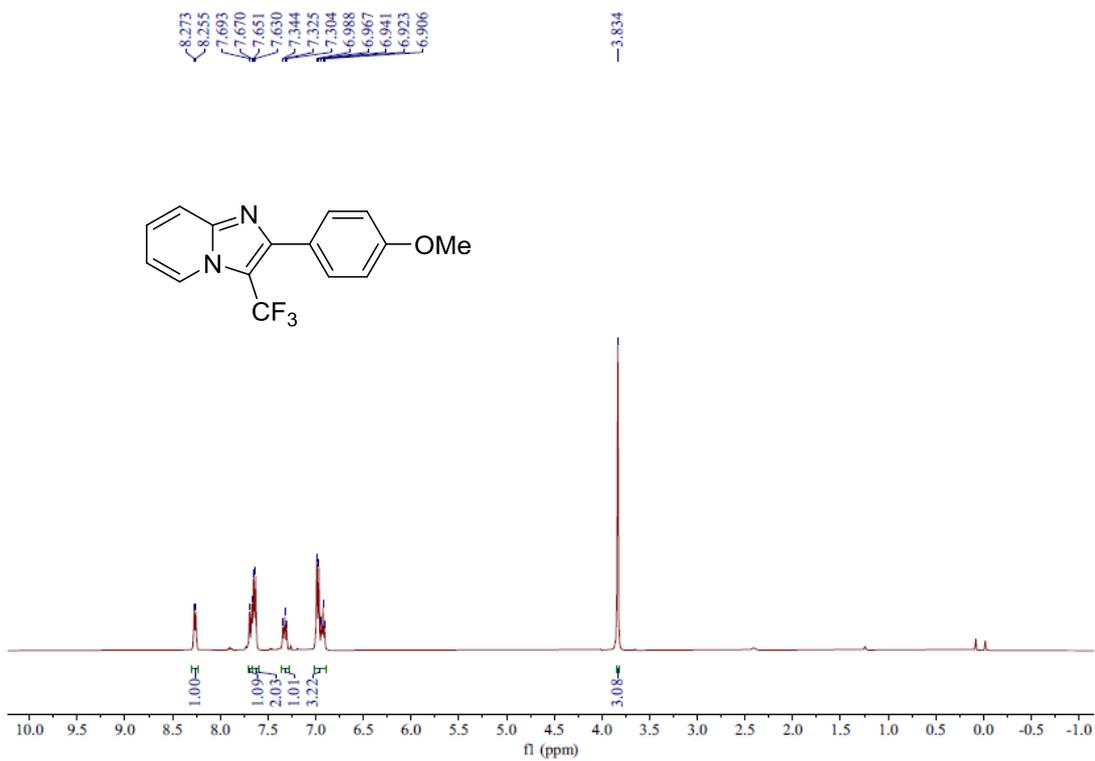
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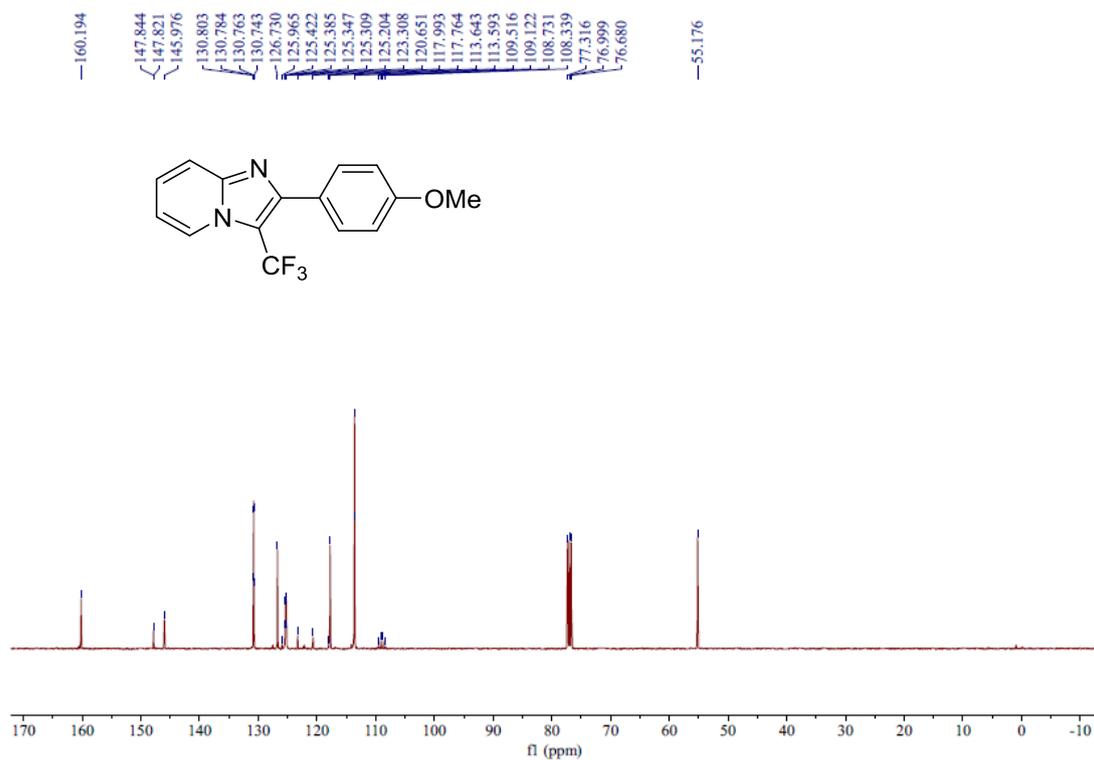
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3ia**



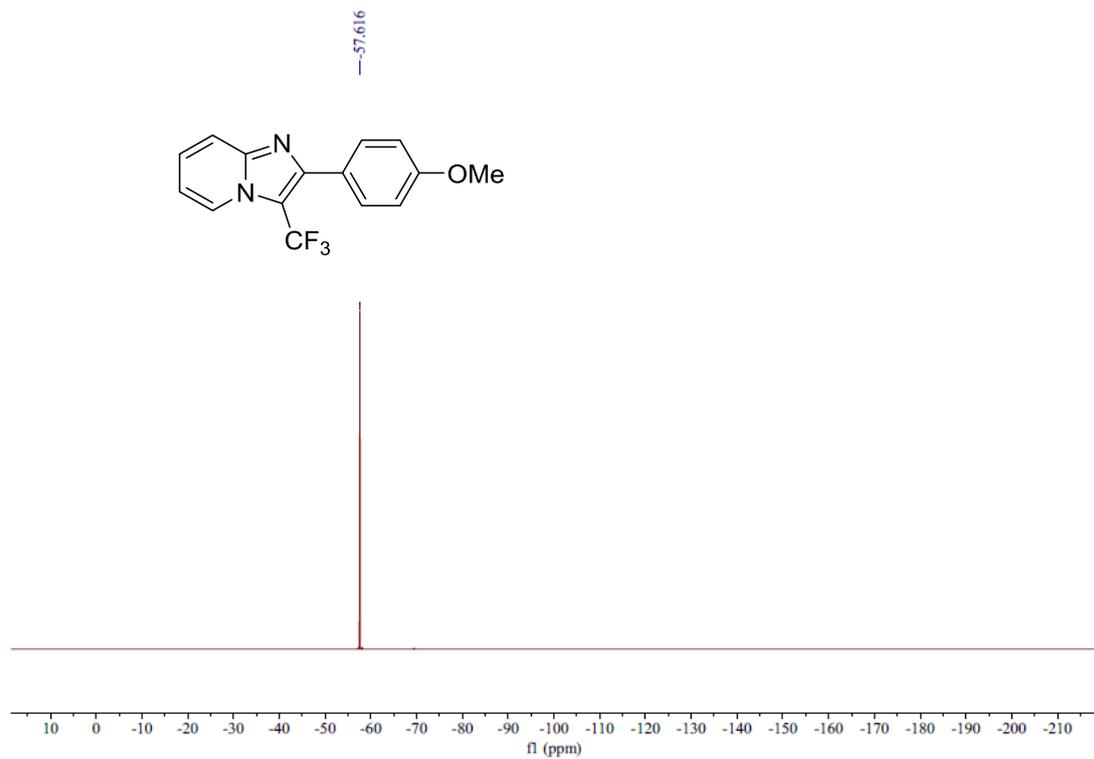
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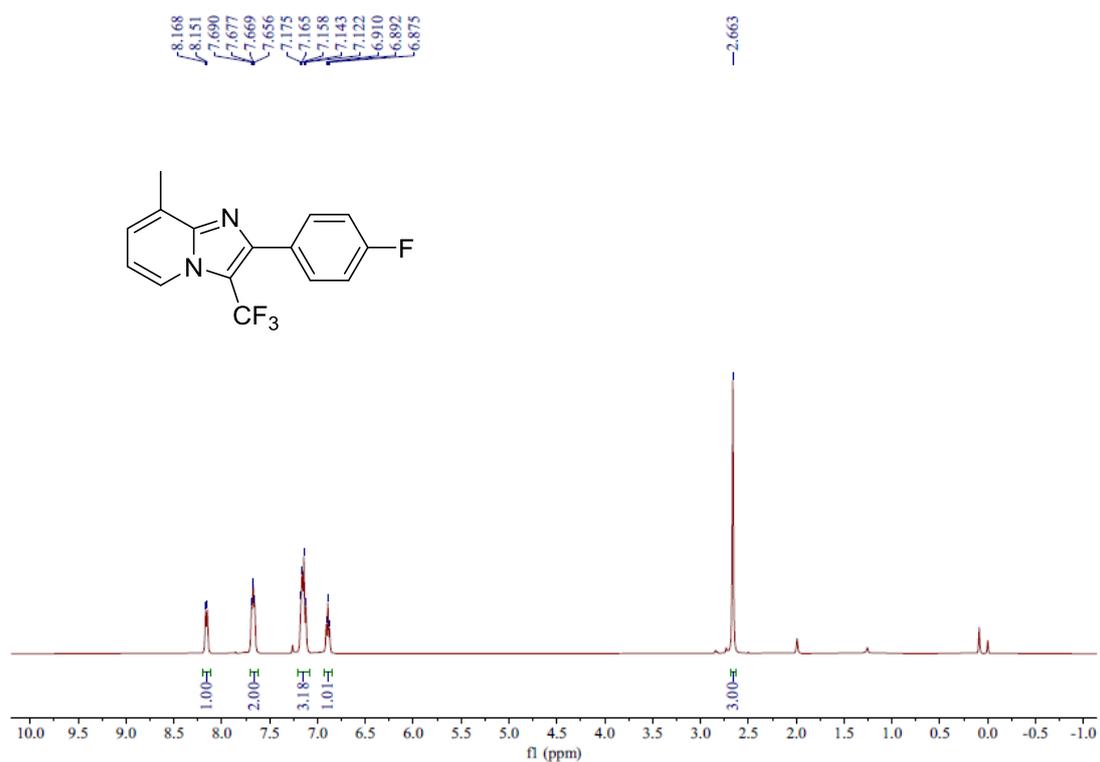
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ja**



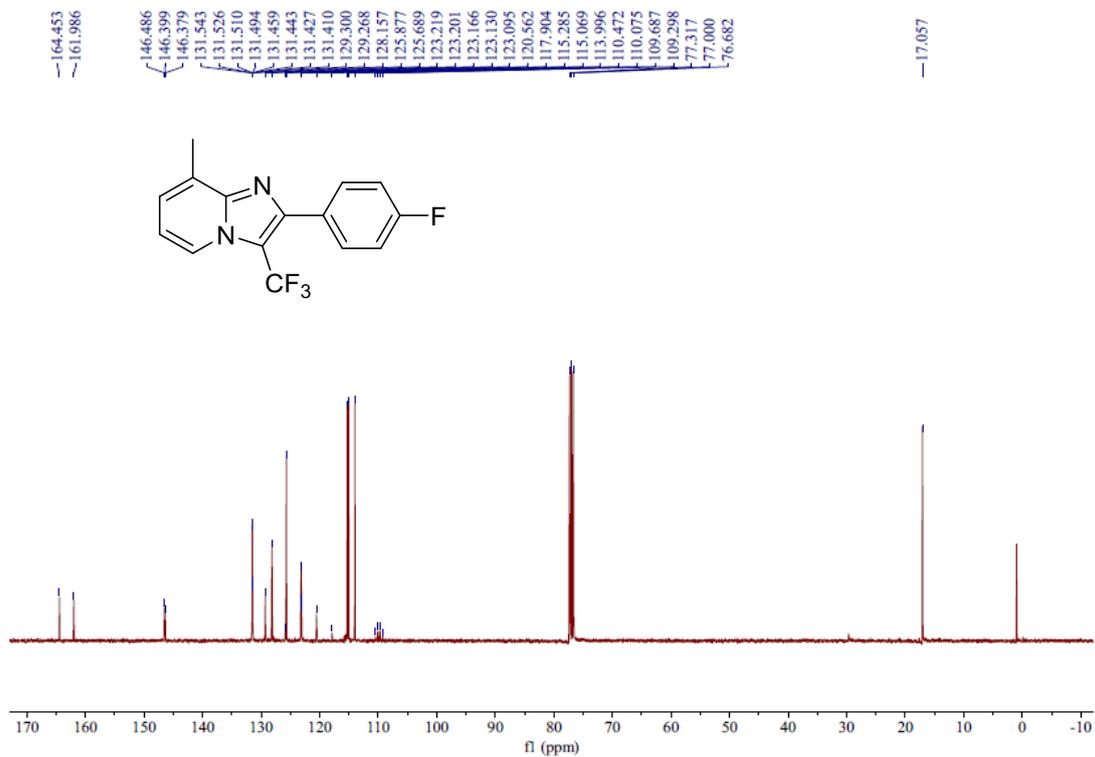
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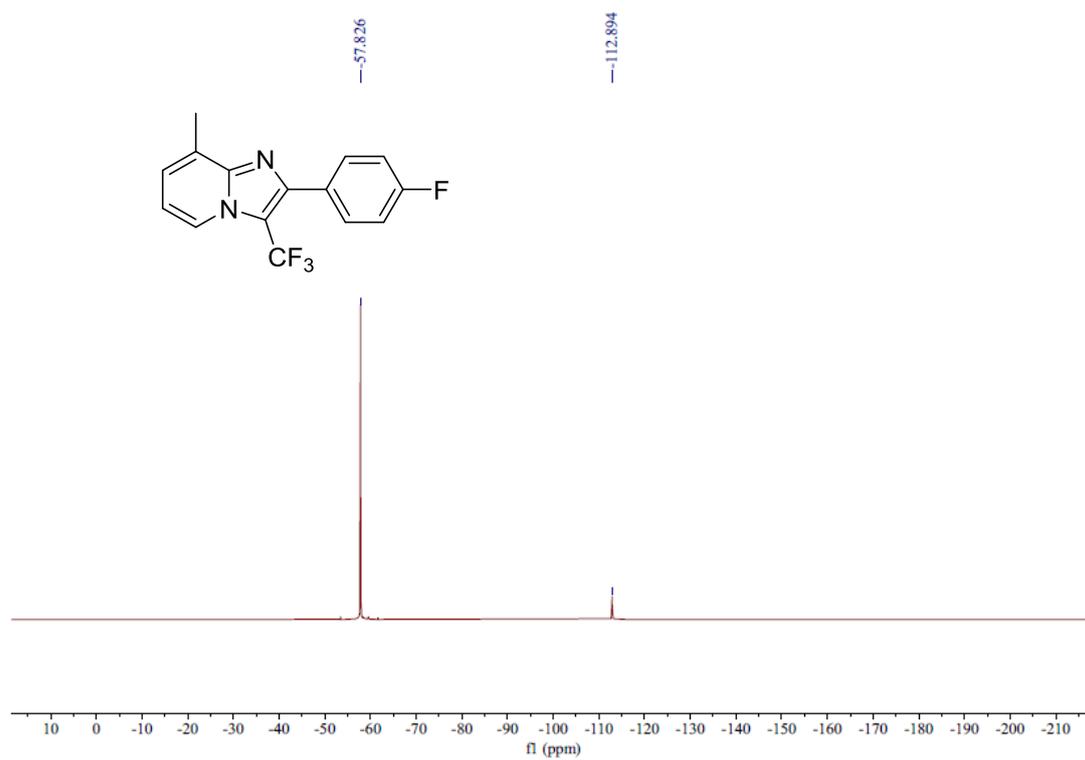
¹H NMR (400 MHz, CDCl₃) Spectrum of **3ka**



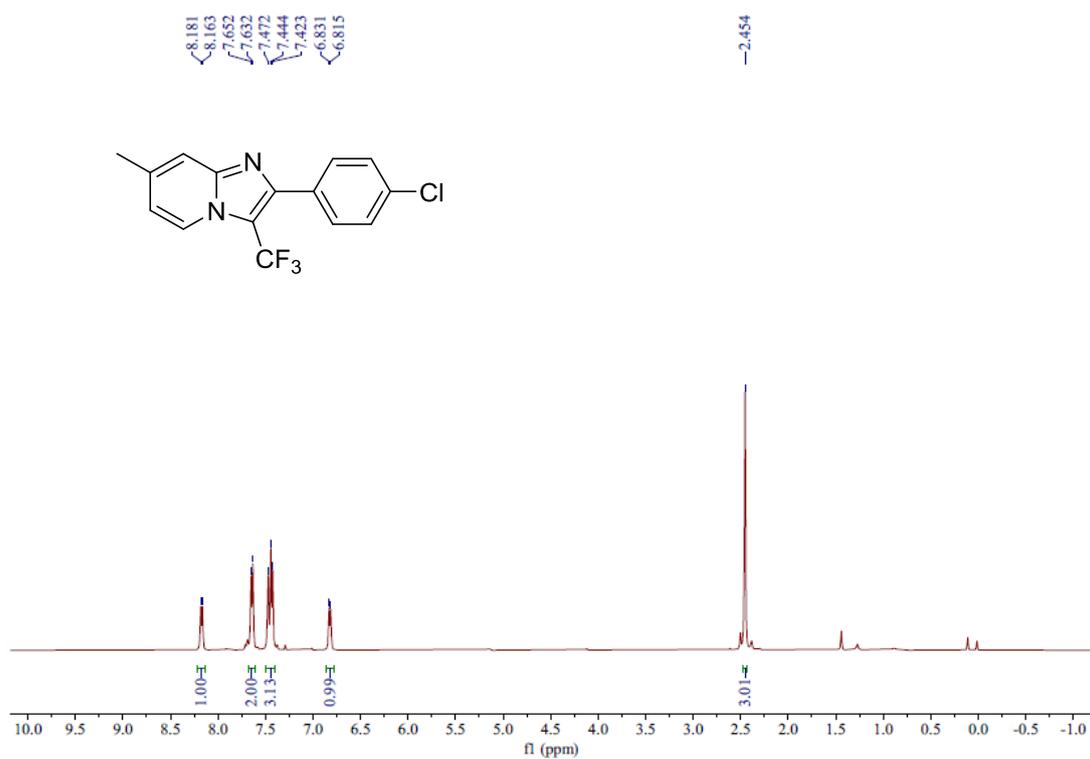
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ka**



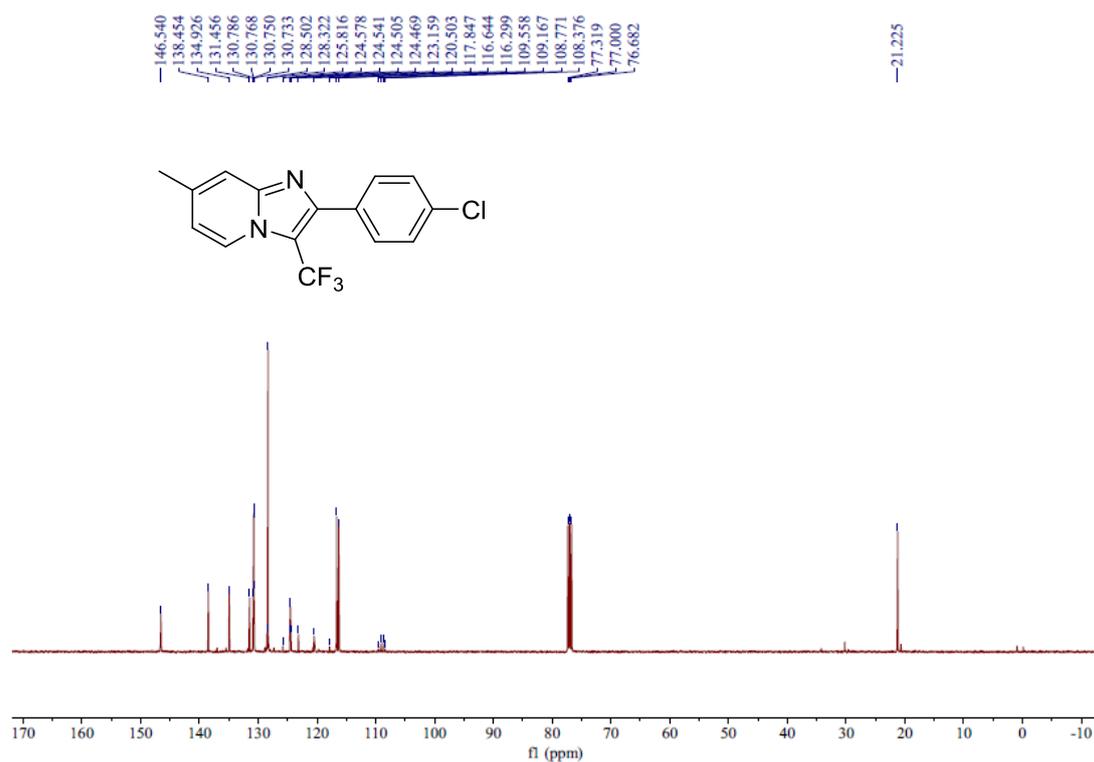
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3ka**



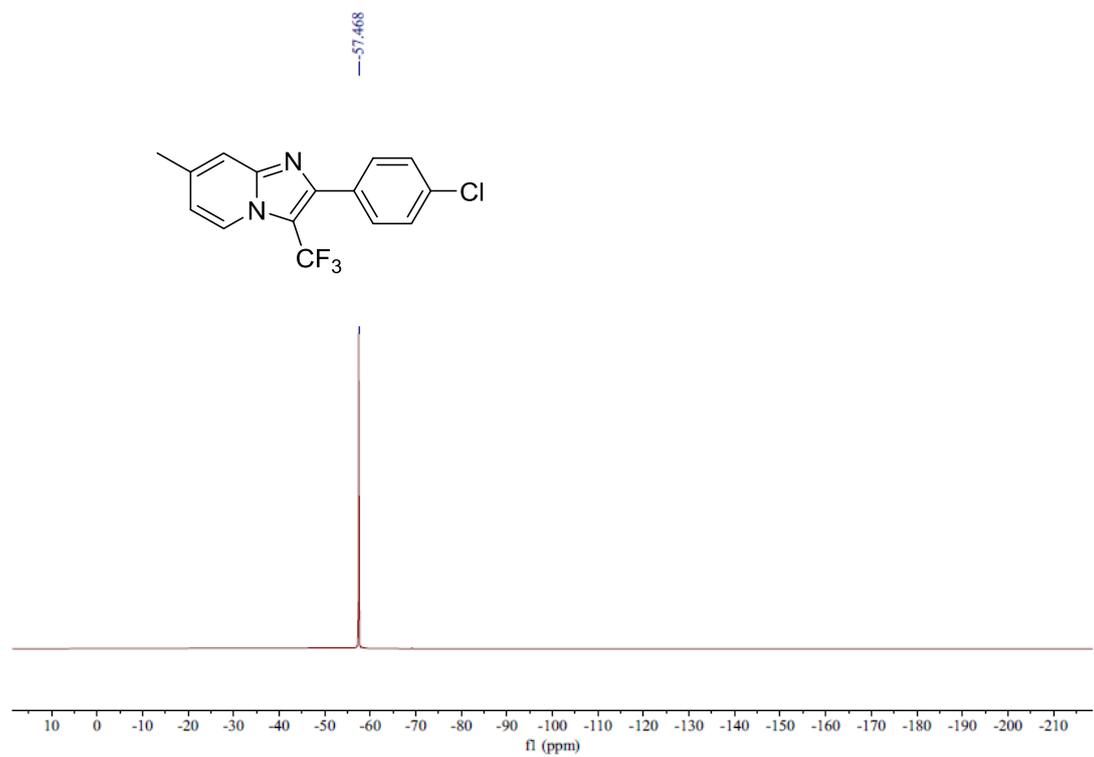
^1H NMR (400 MHz, CDCl_3) Spectrum of **3la**



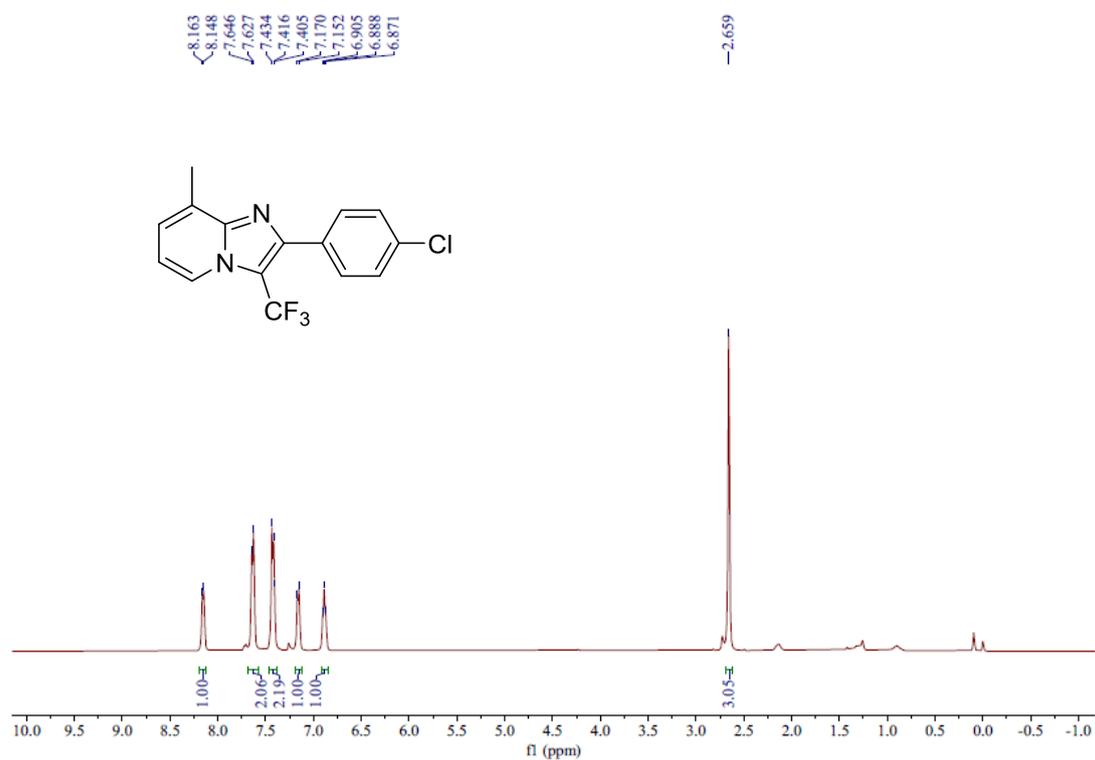
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3la**



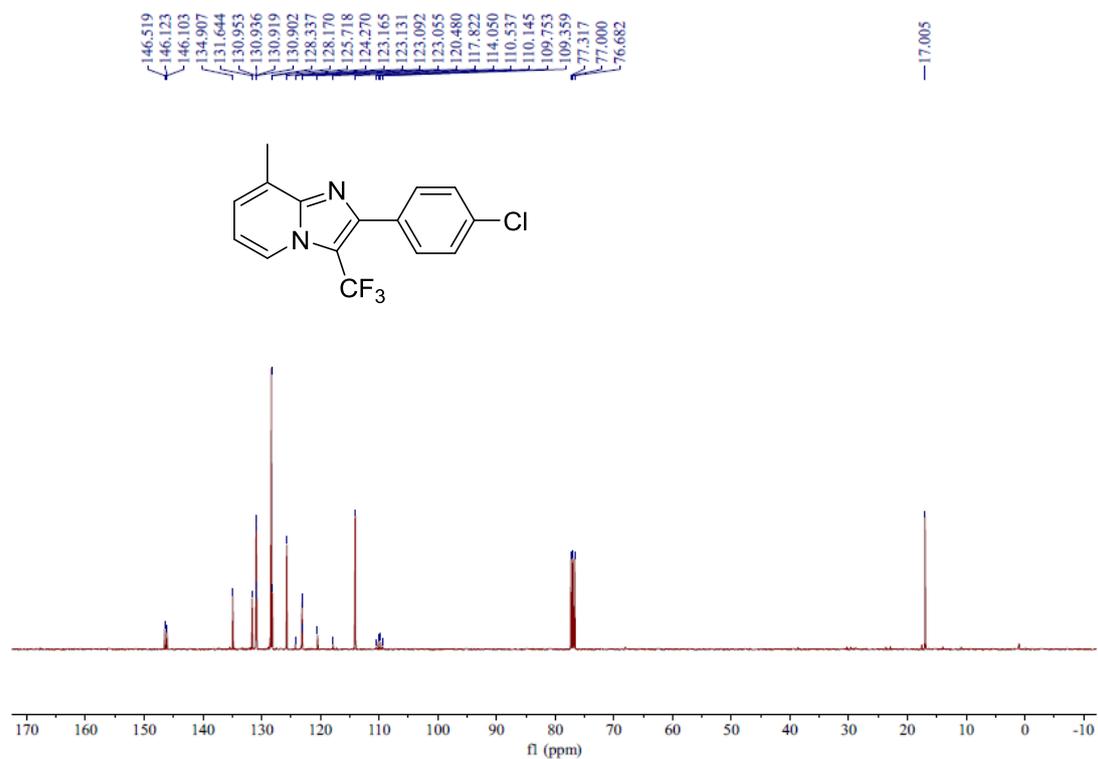
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3la**



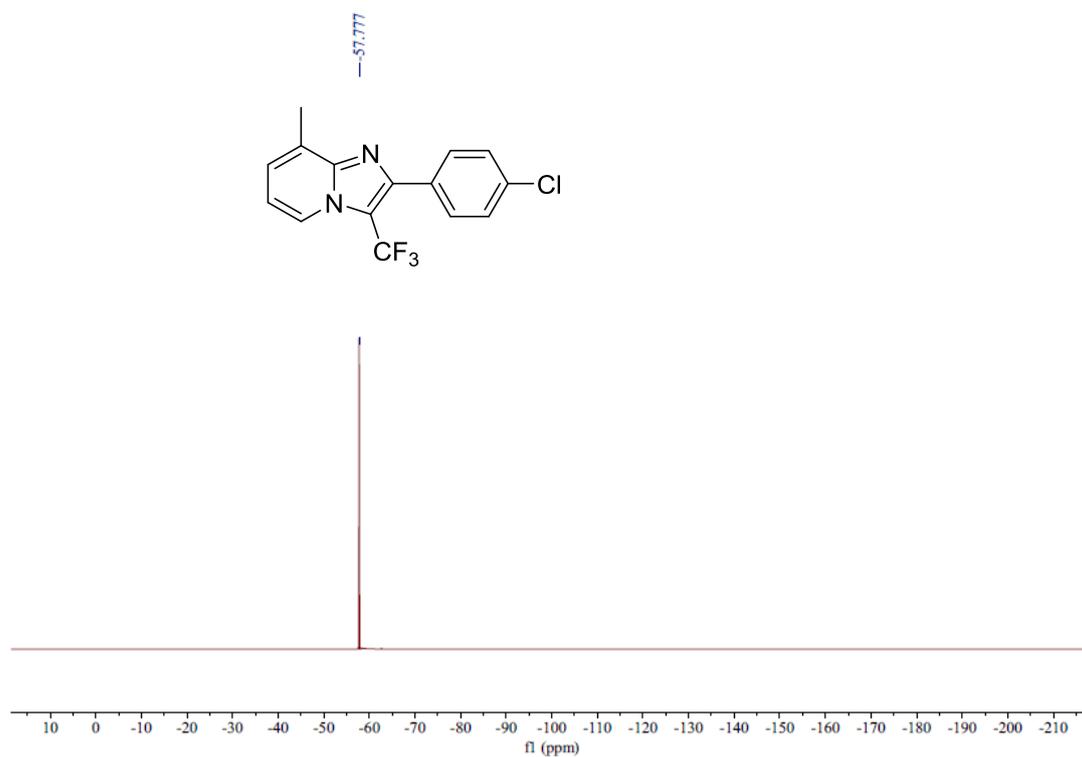
¹H NMR (400 MHz, CDCl₃) Spectrum of **3ma**



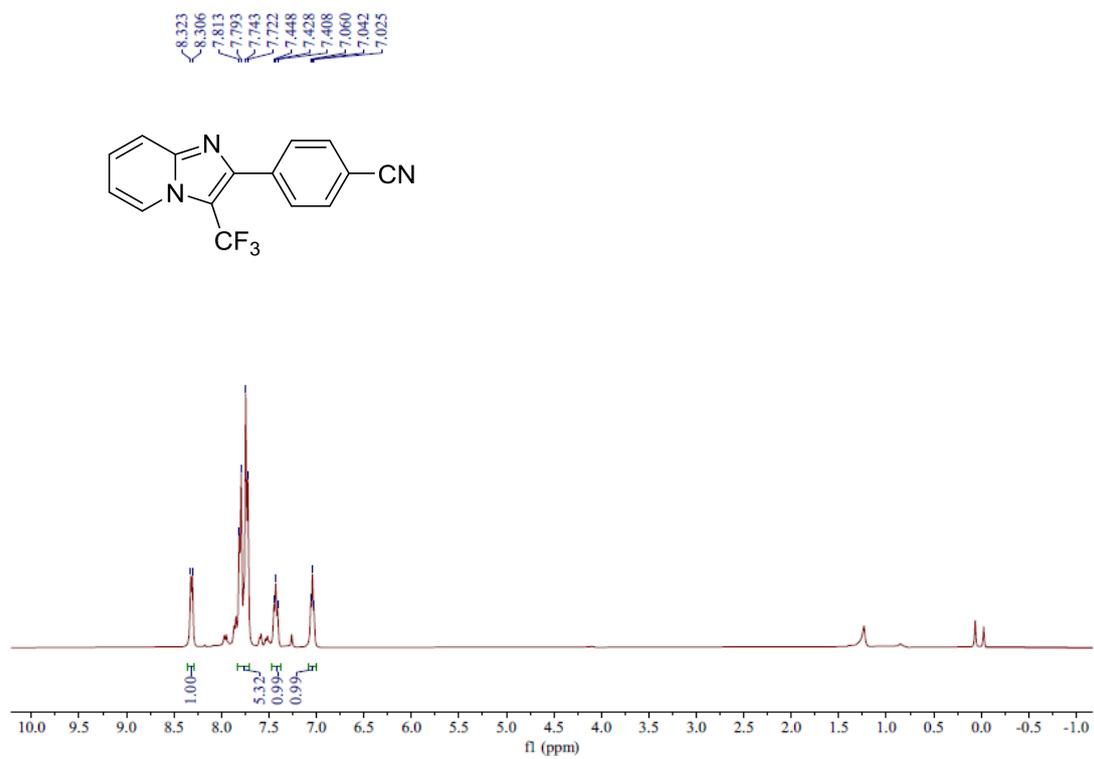
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ma**



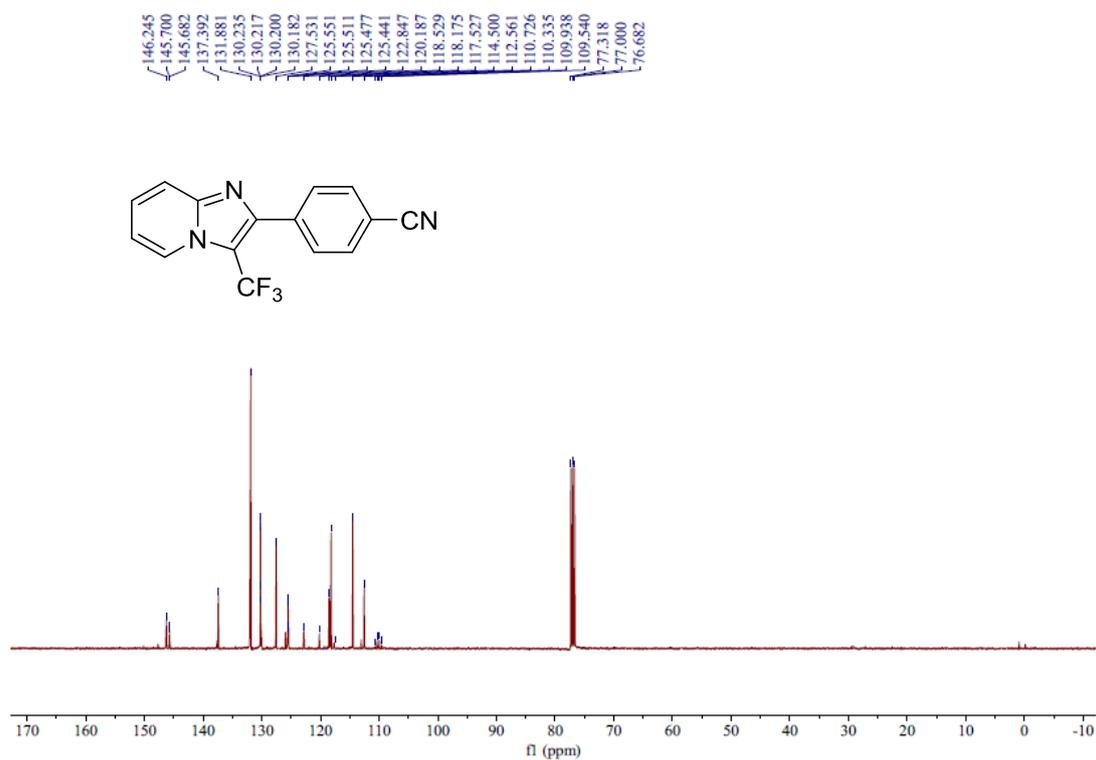
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3ma**



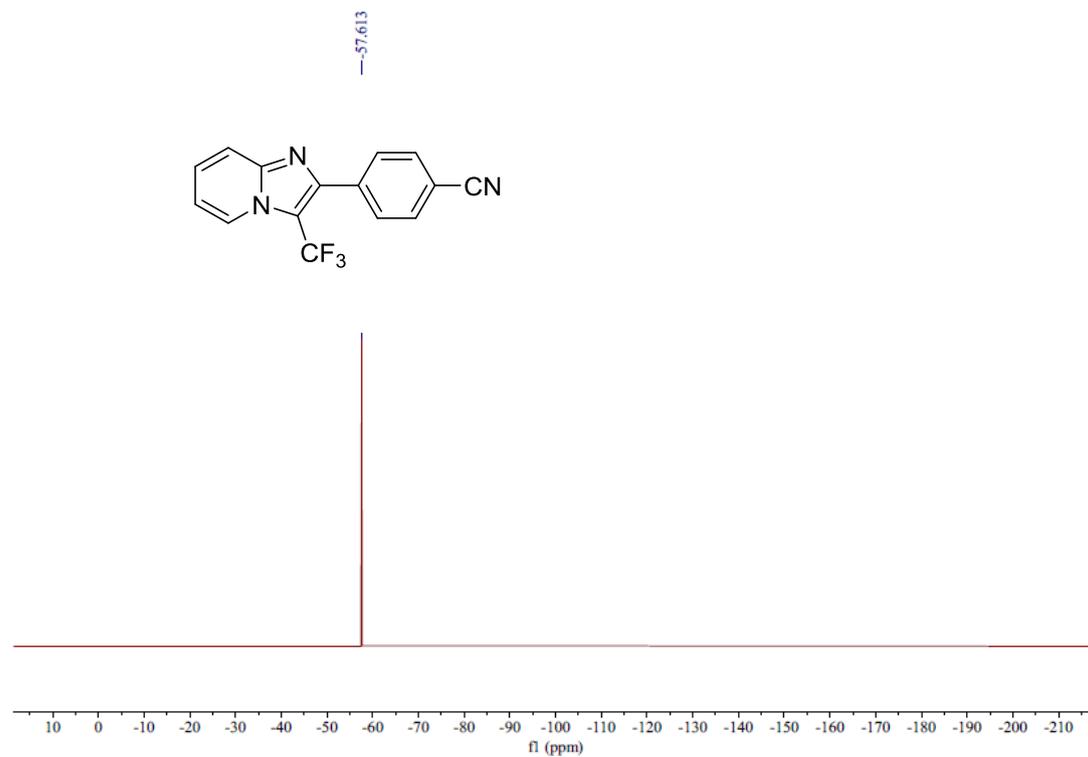
^1H NMR (400 MHz, CDCl_3) Spectrum of **3na**



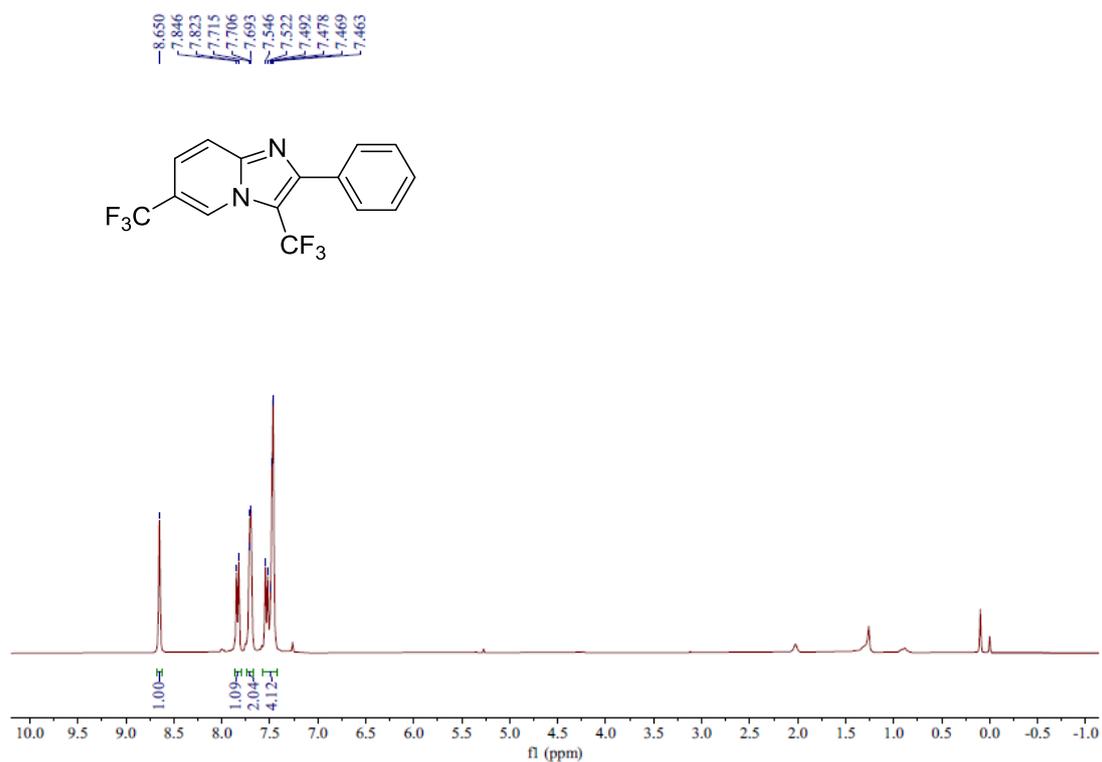
^{13}C NMR (100 MHz, CDCl_3) Spectrum of **3na**



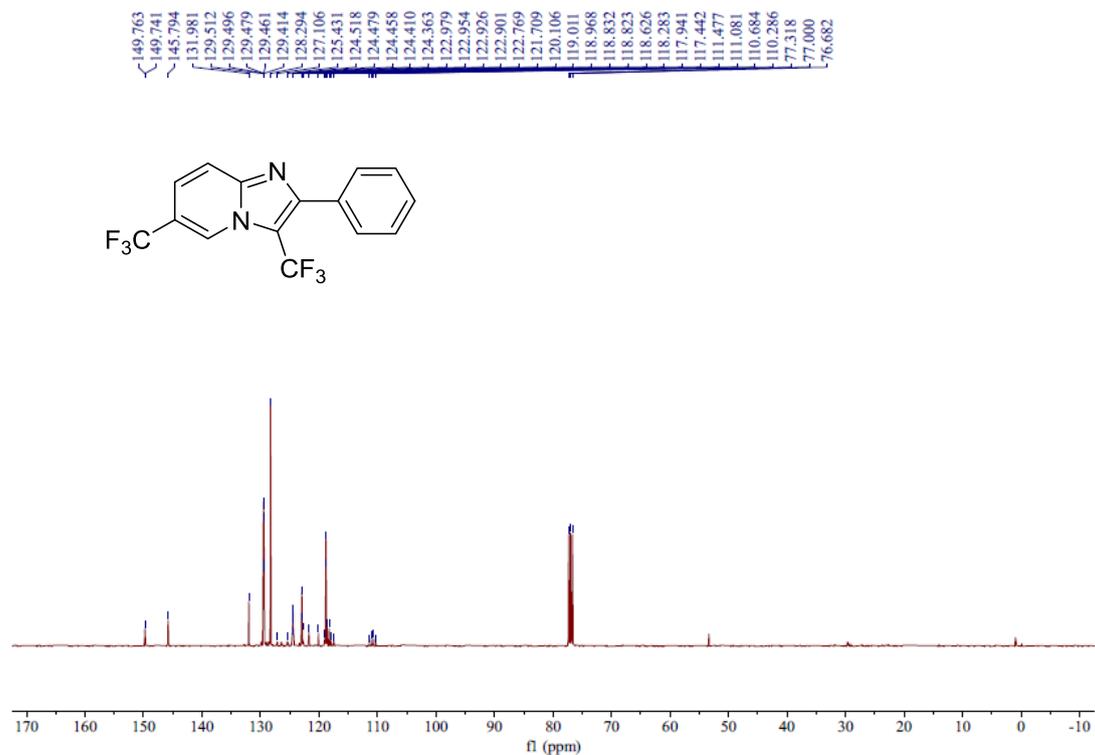
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3na**



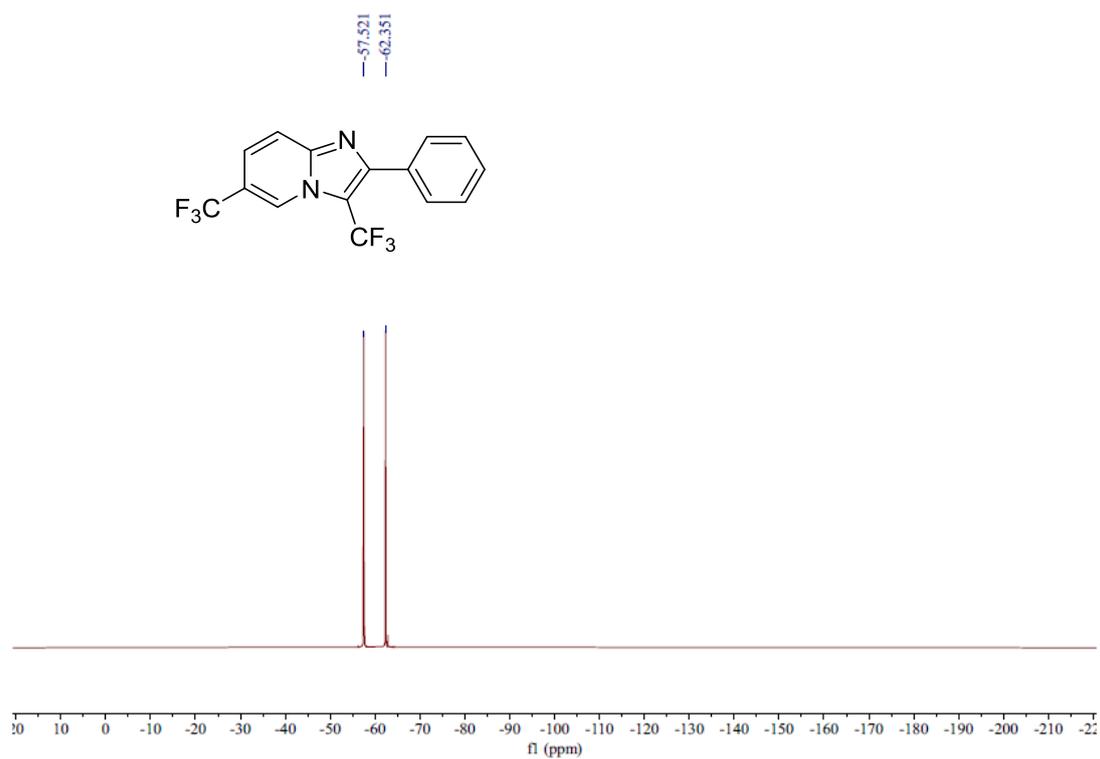
¹H NMR (400 MHz, CDCl₃) Spectrum of **30a**



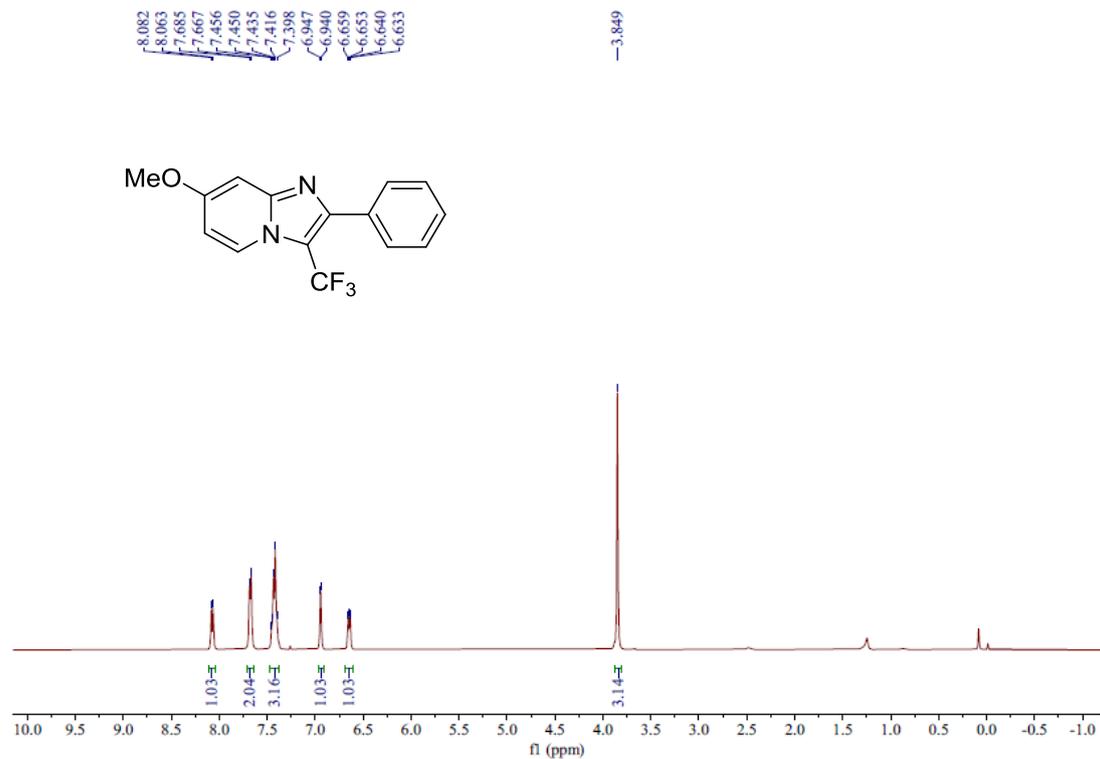
¹³C NMR (100 MHz, CDCl₃) Spectrum of **30a**



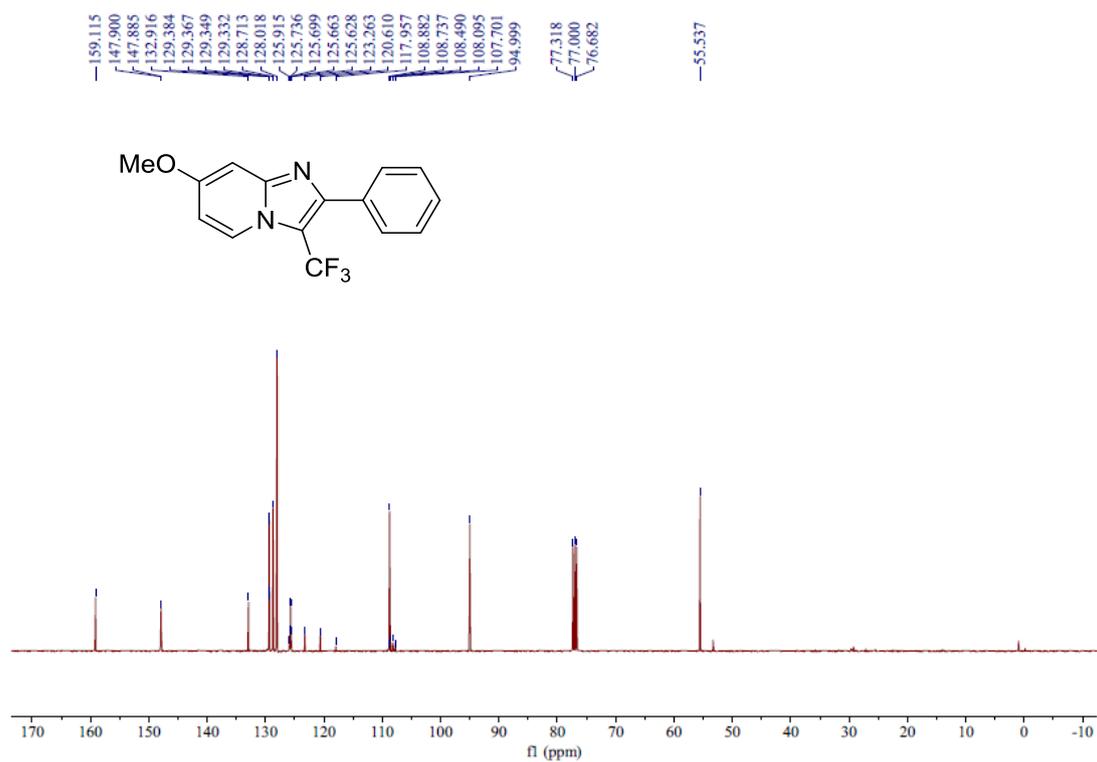
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3oa**



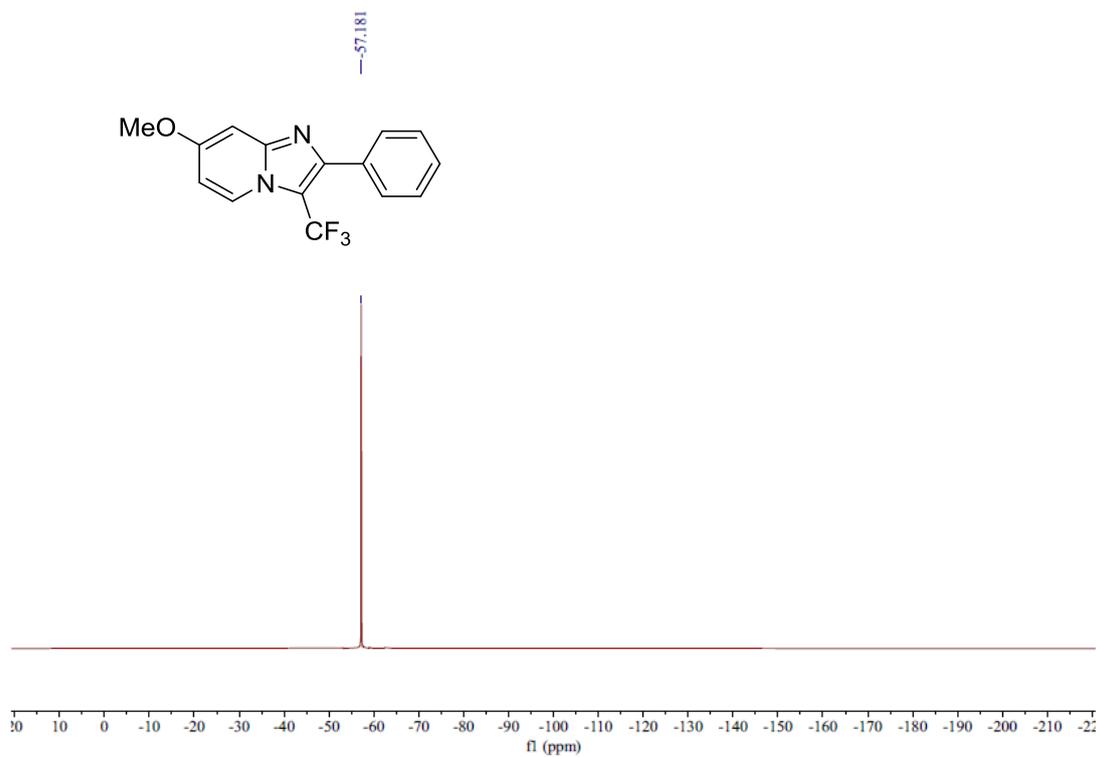
^1H NMR (400 MHz, CDCl_3) Spectrum of **3pa**



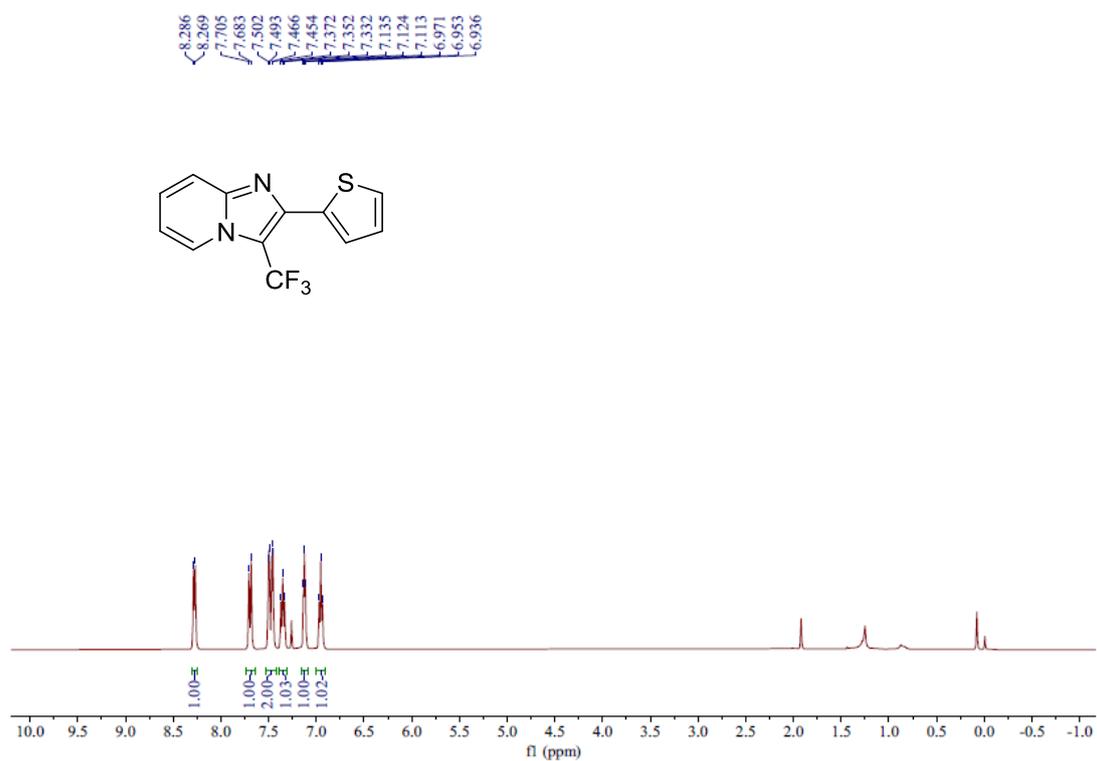
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3pa**



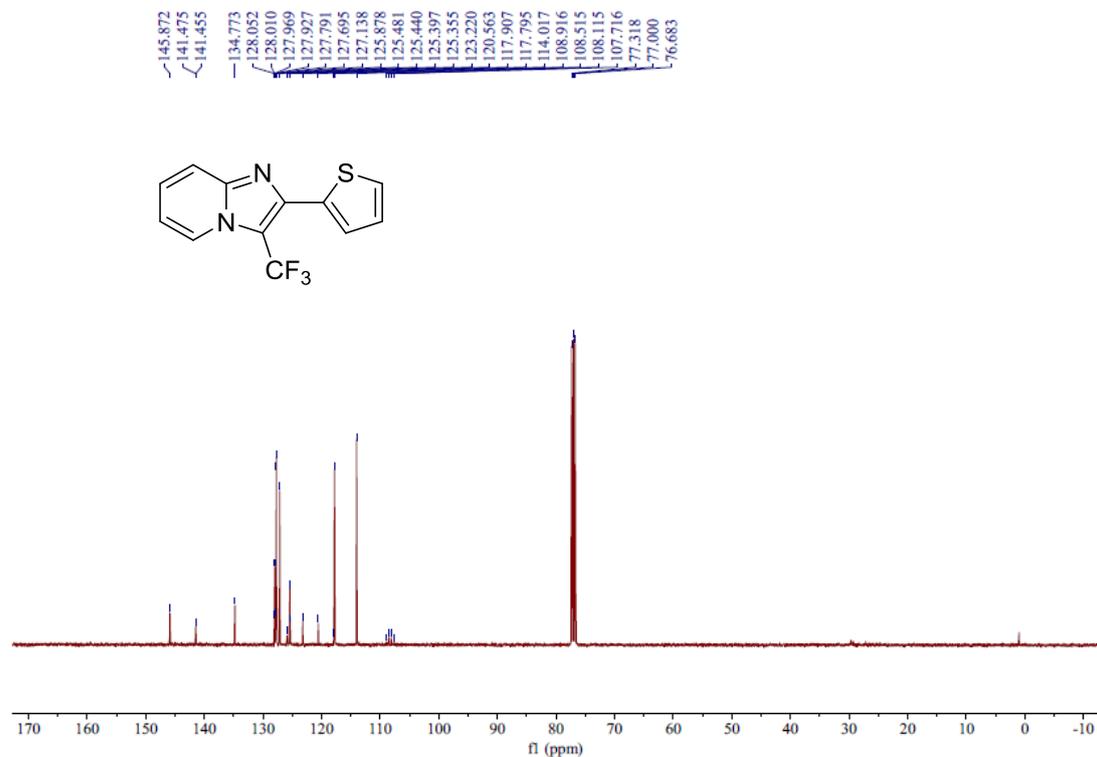
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3pa**



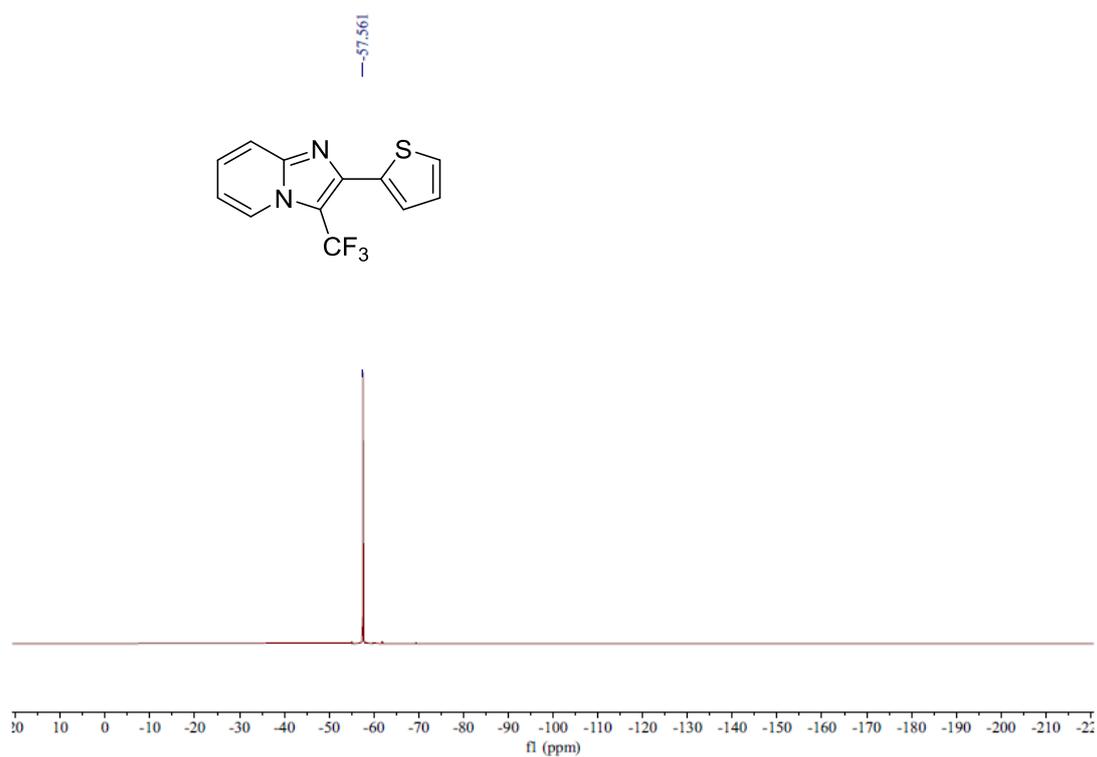
¹H NMR (400 MHz, CDCl₃) Spectrum of **3qa**



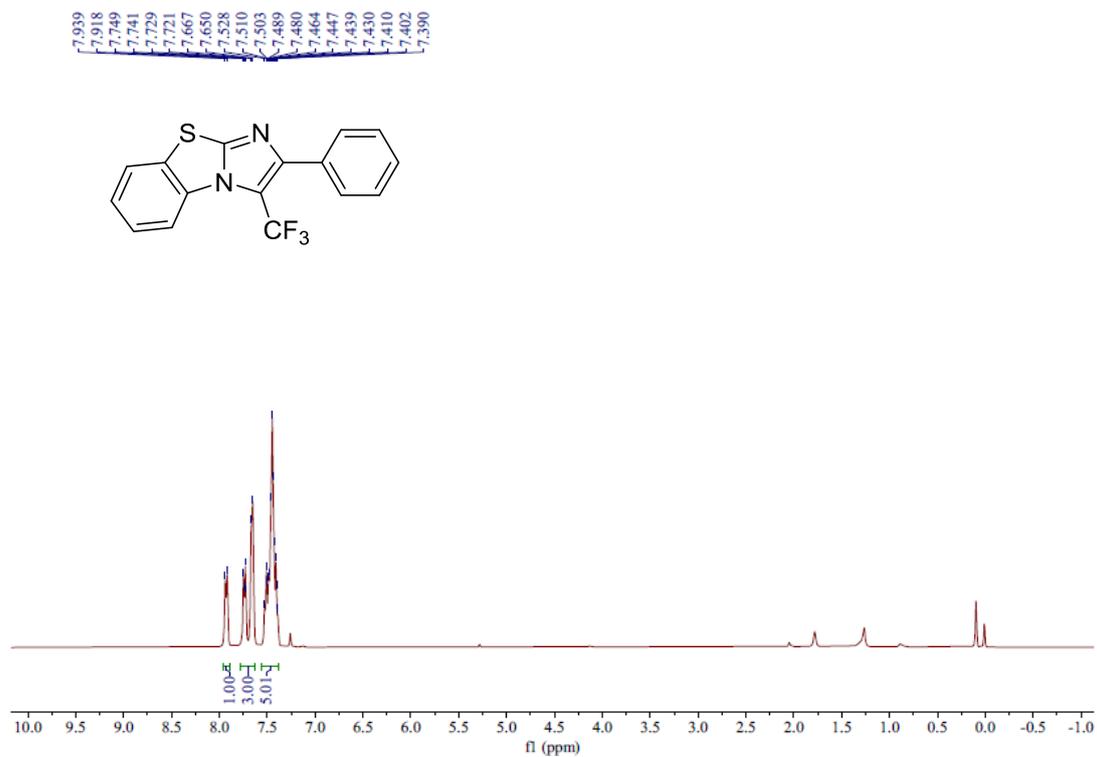
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3qa**



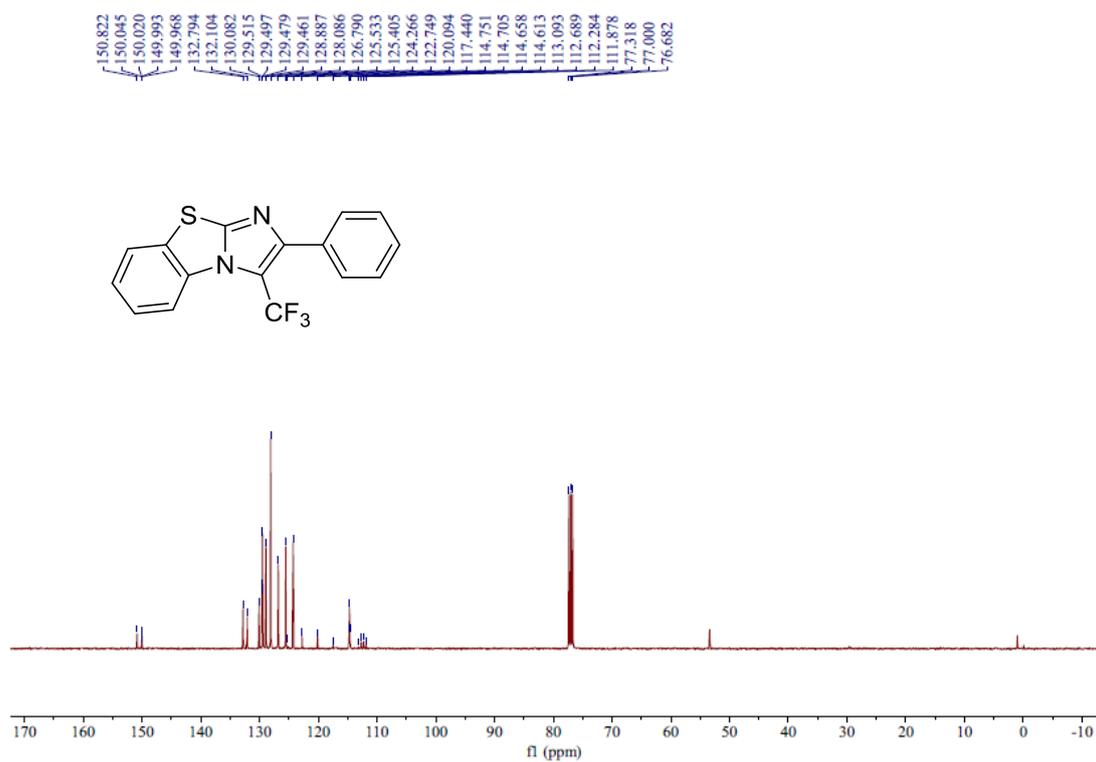
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3qa**



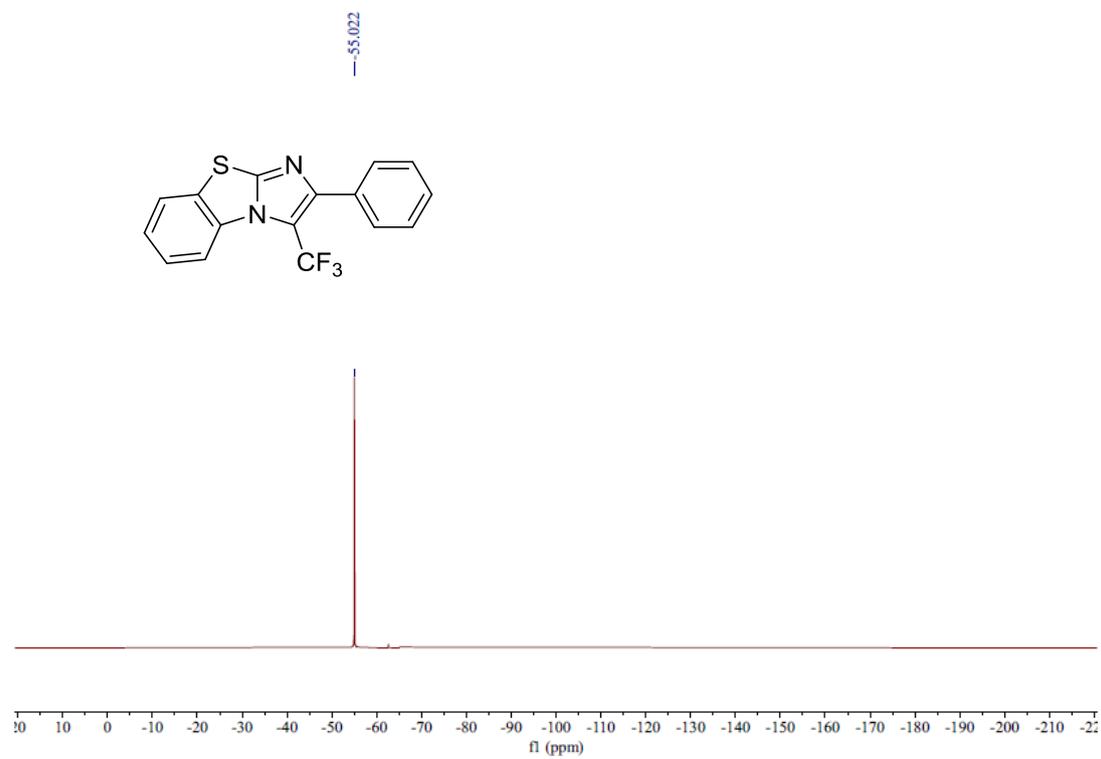
¹H NMR (400 MHz, CDCl₃) Spectrum of **3ra**



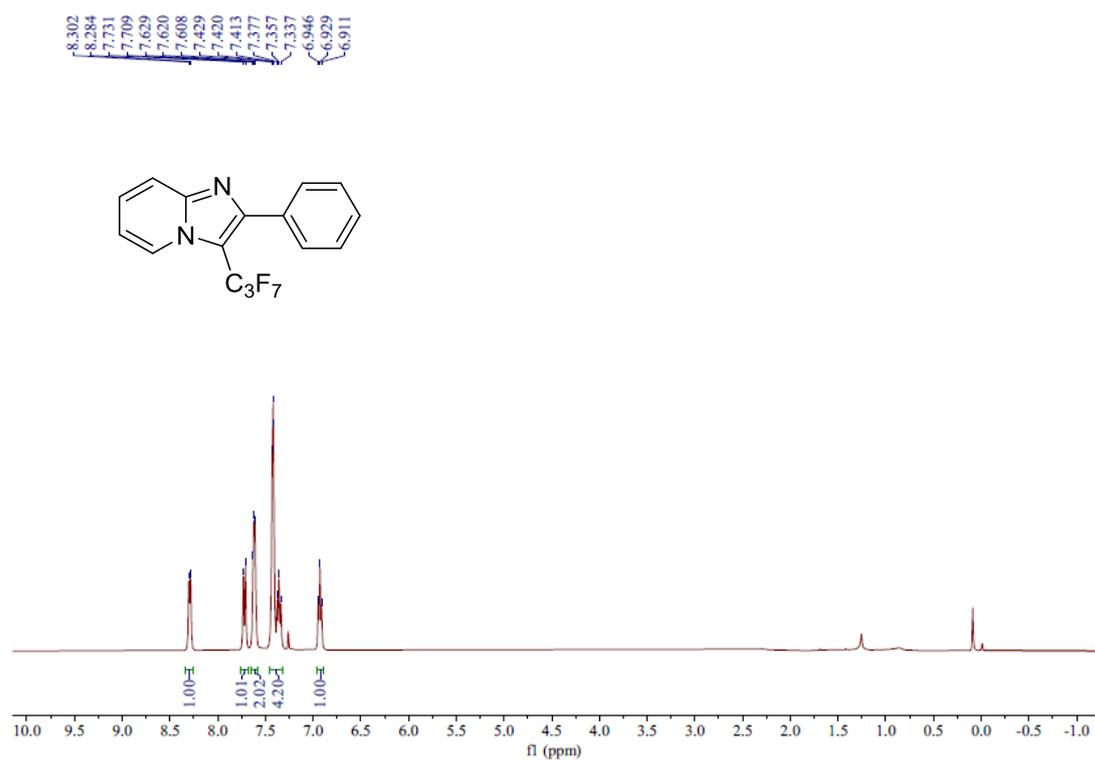
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ra**



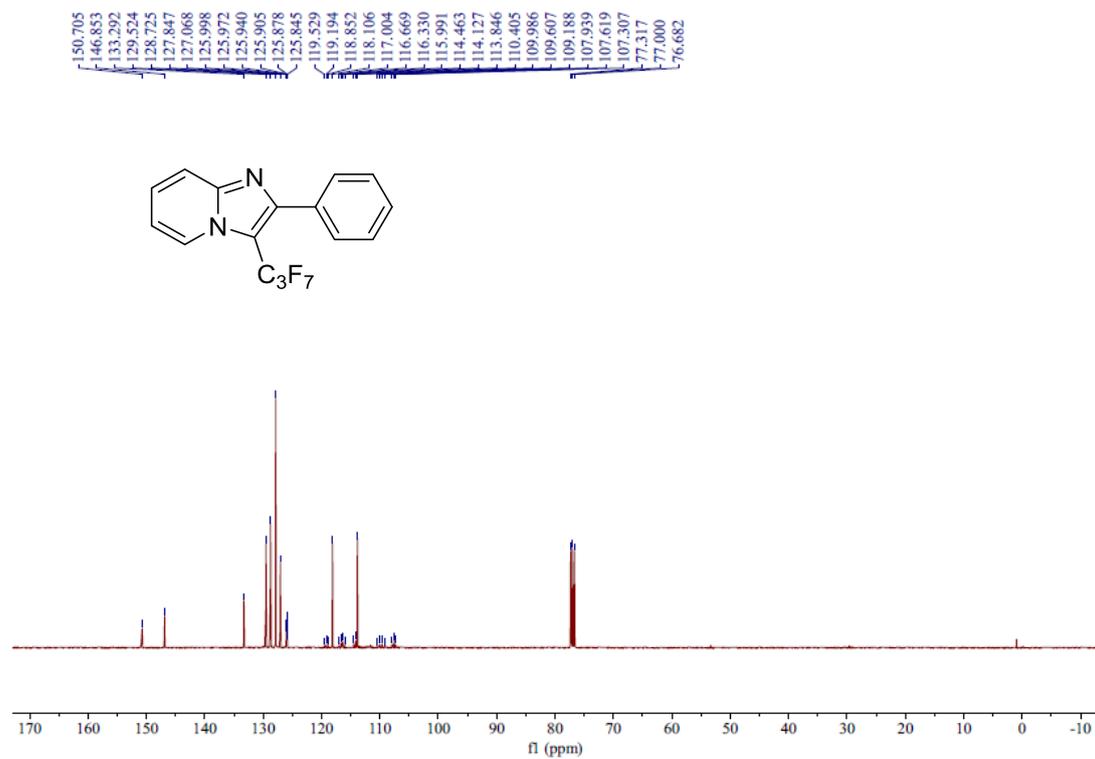
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3ra**



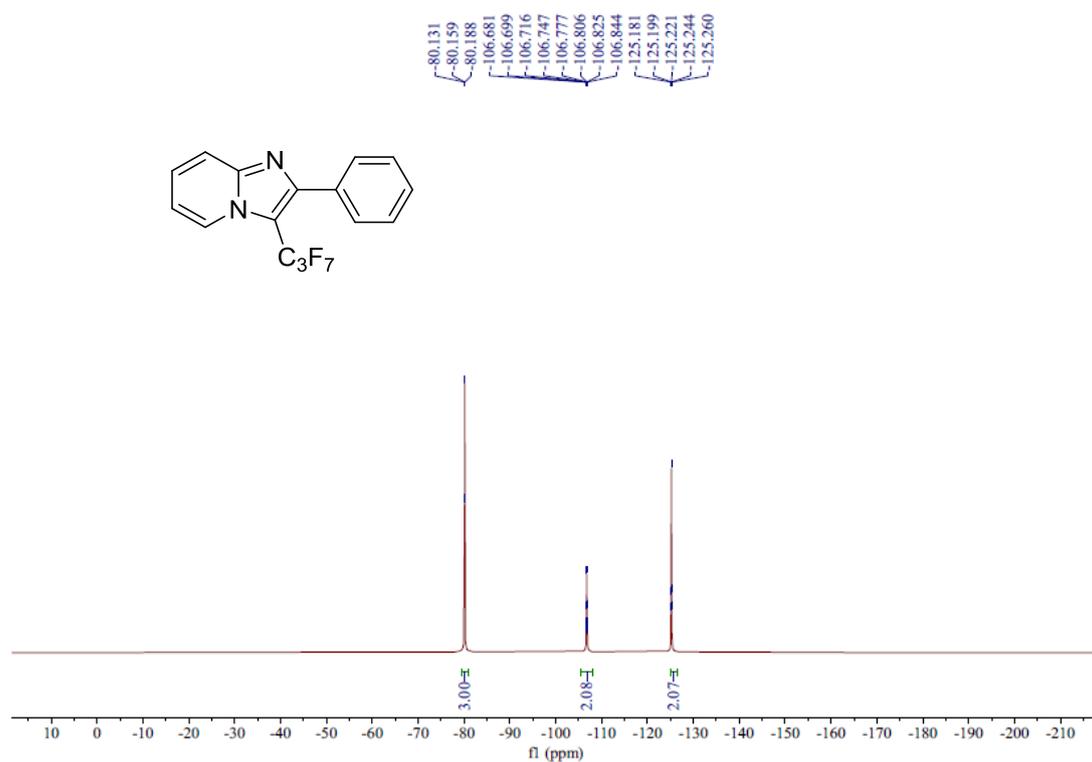
¹H NMR (400 MHz, CDCl₃) Spectrum of **3ab**



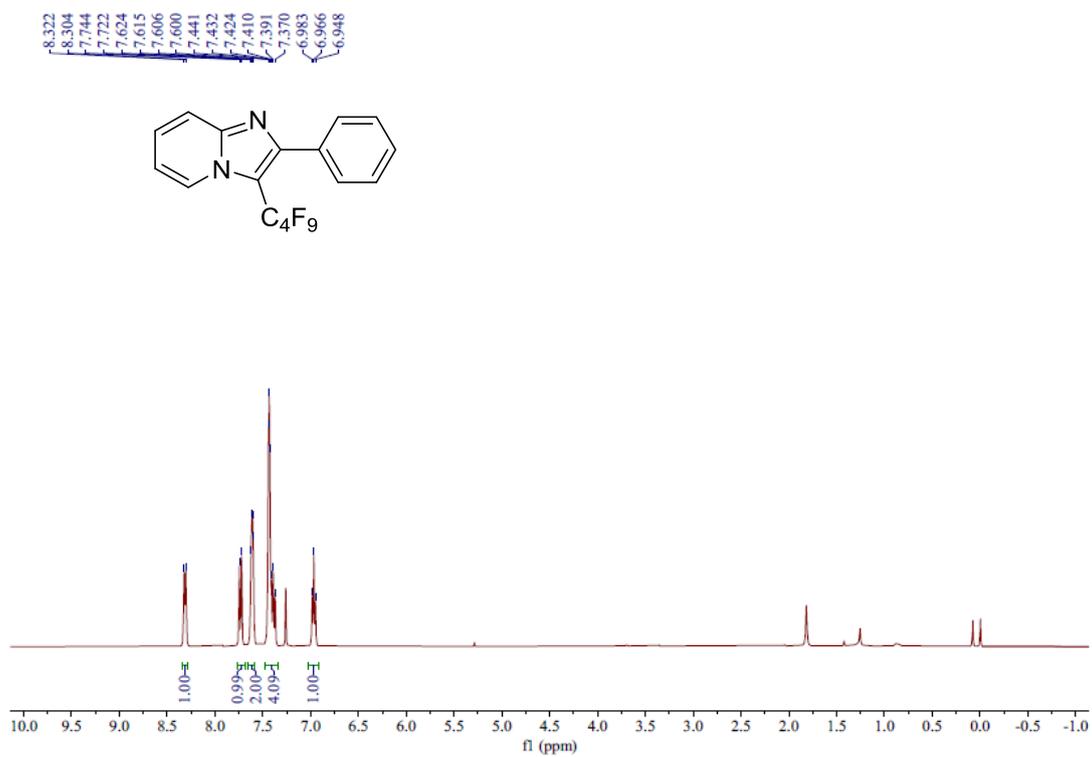
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ab**



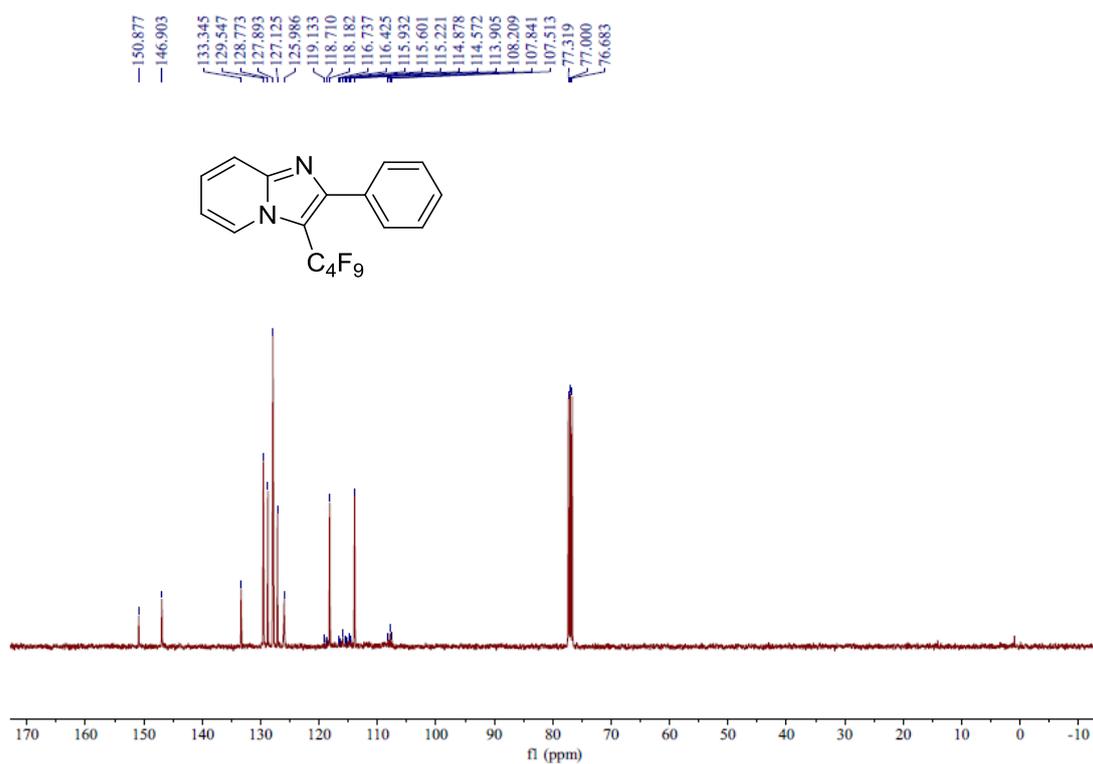
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3ab**



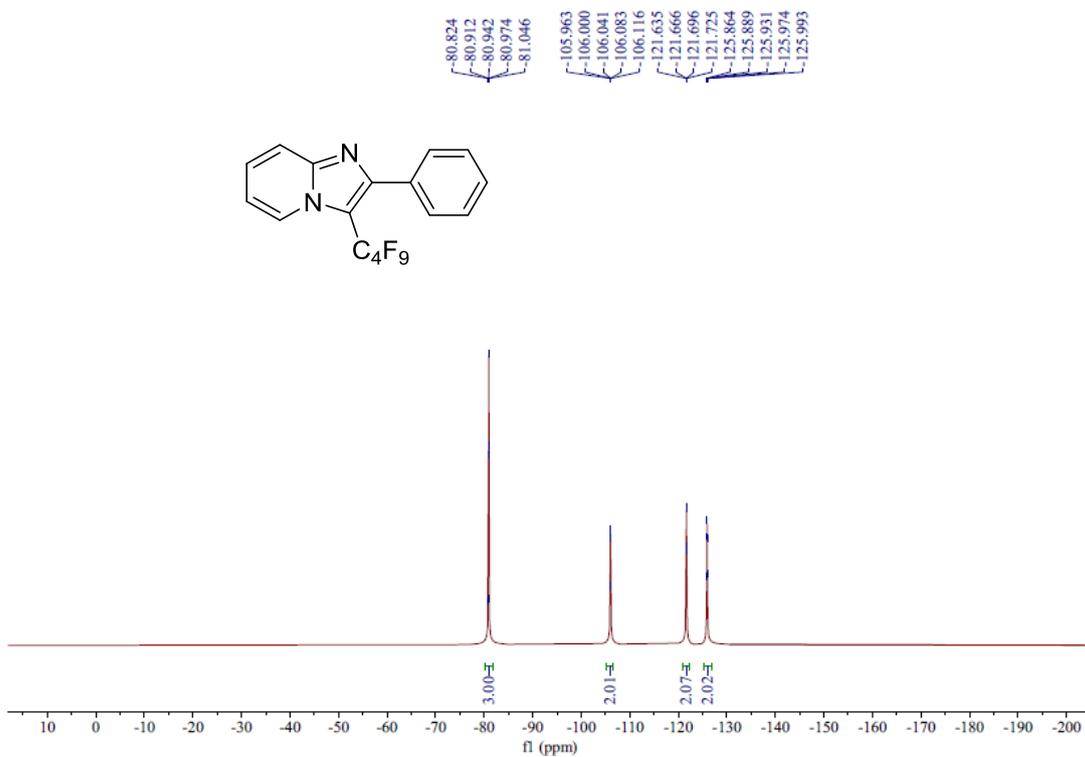
¹H NMR (400 MHz, CDCl₃) Spectrum of **3ac**



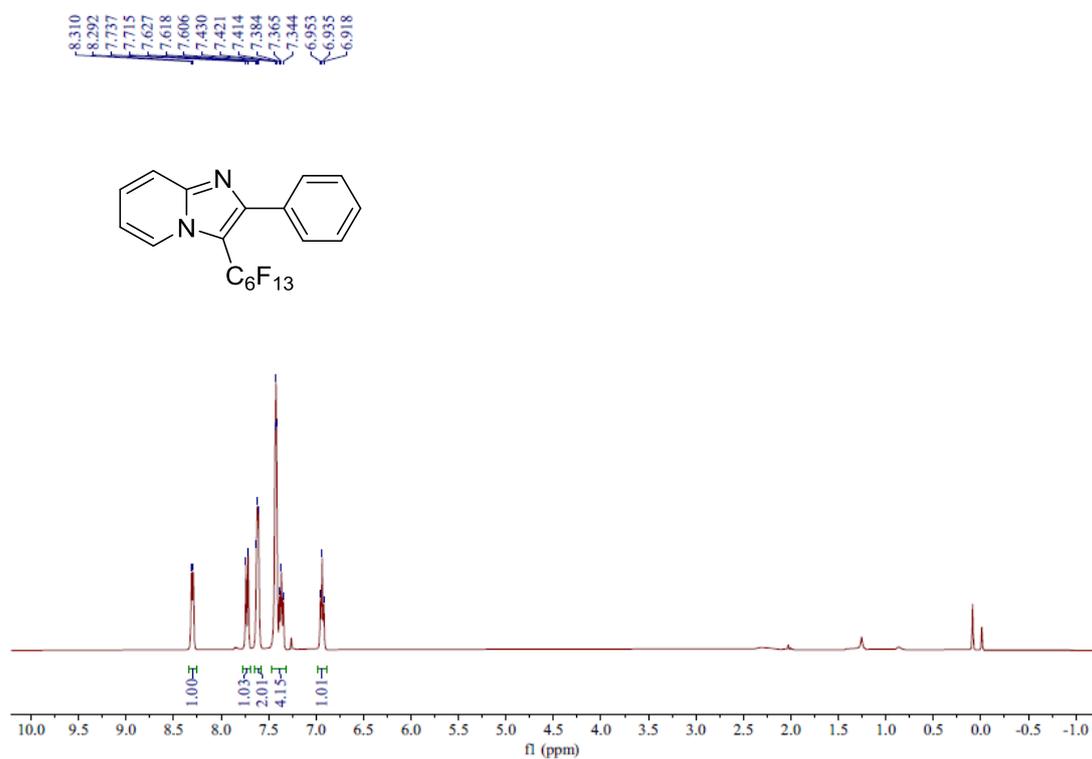
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ac**



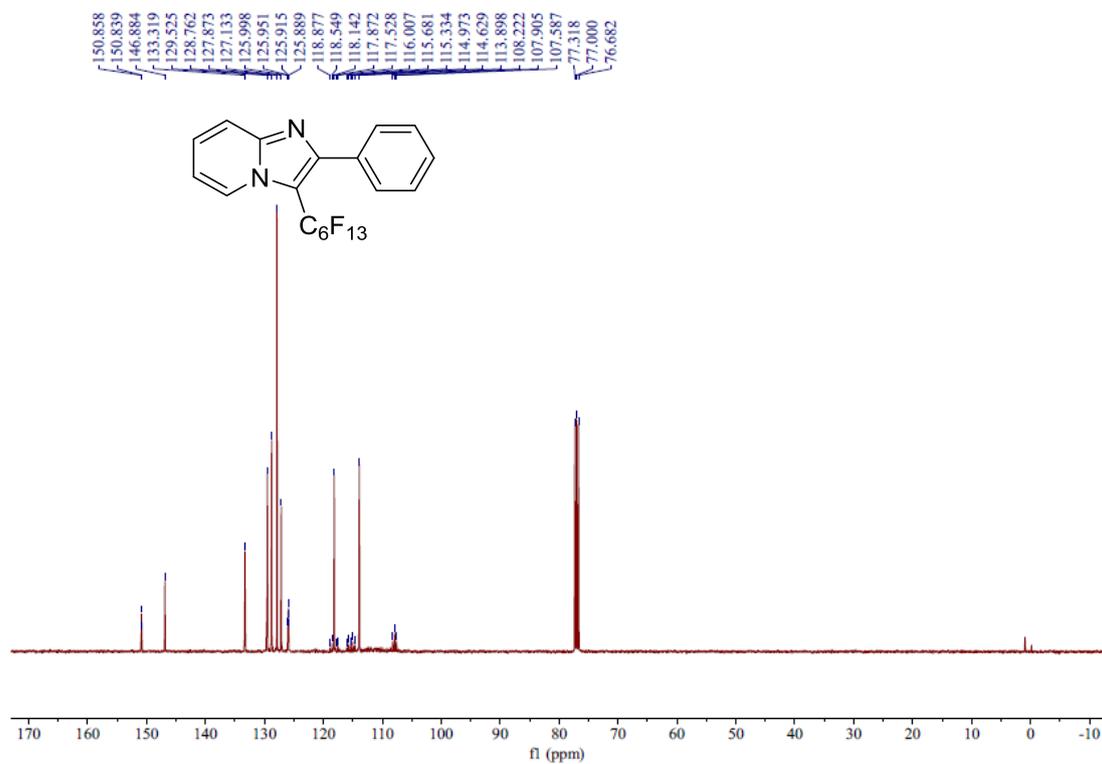
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3ac**



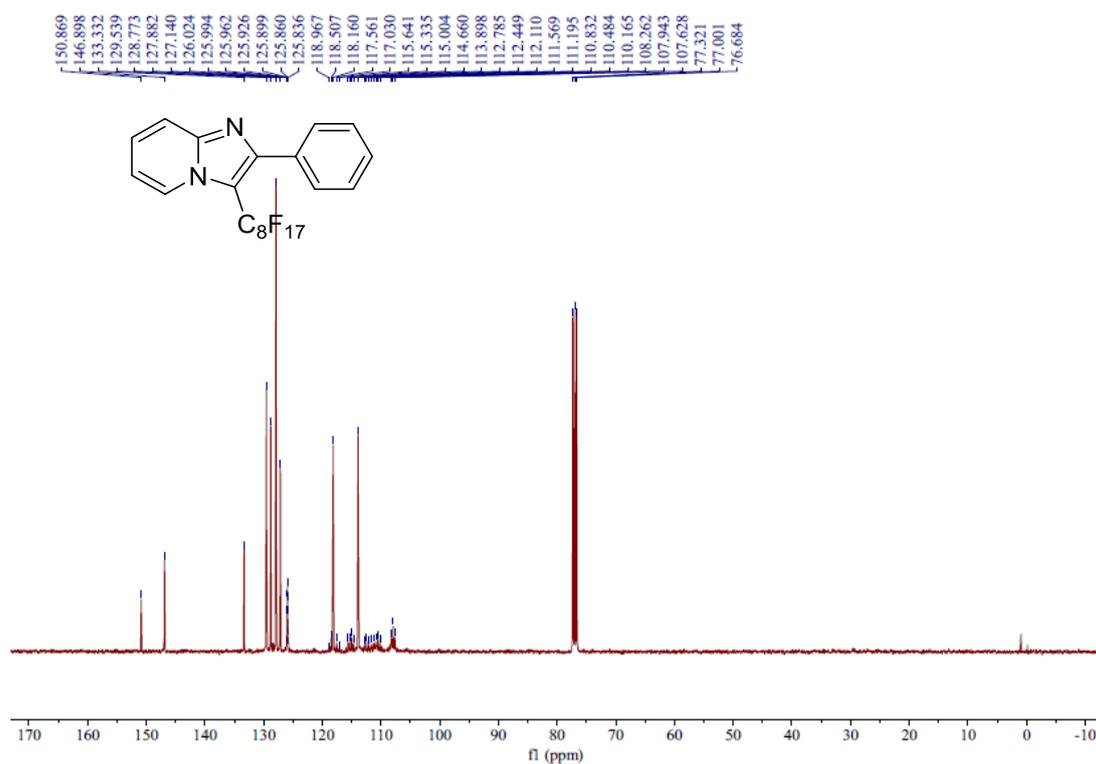
¹H NMR (400 MHz, CDCl₃) Spectrum of **3ad**



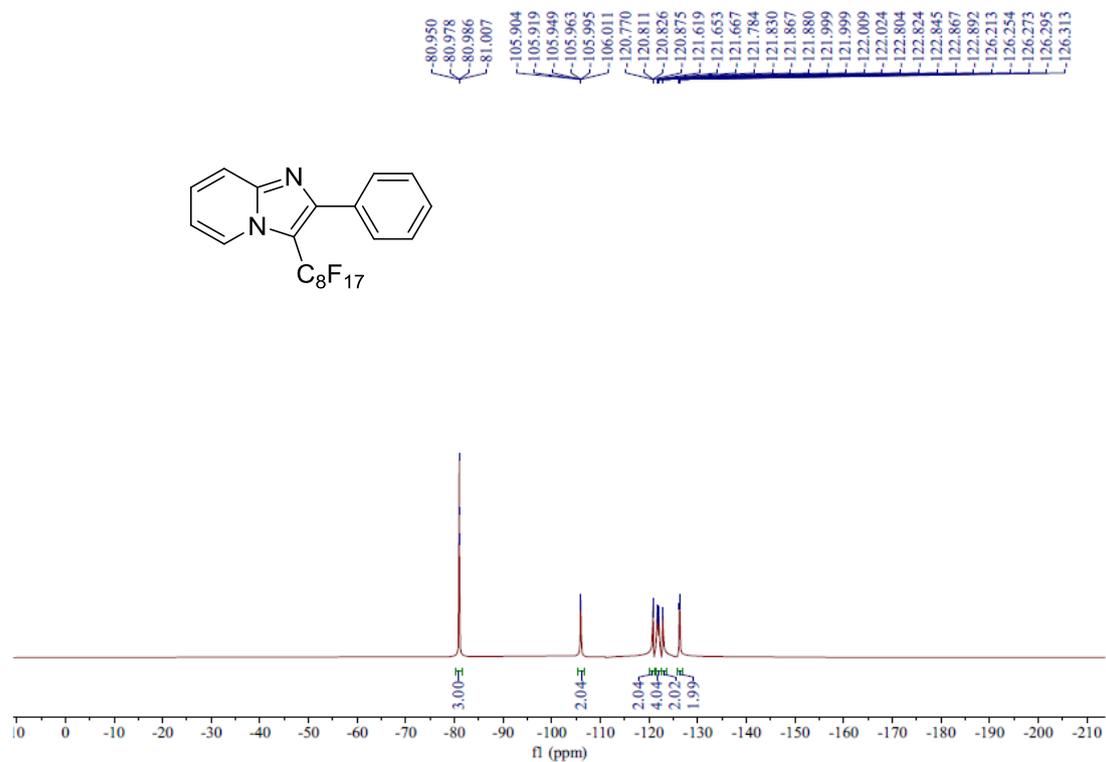
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ad**



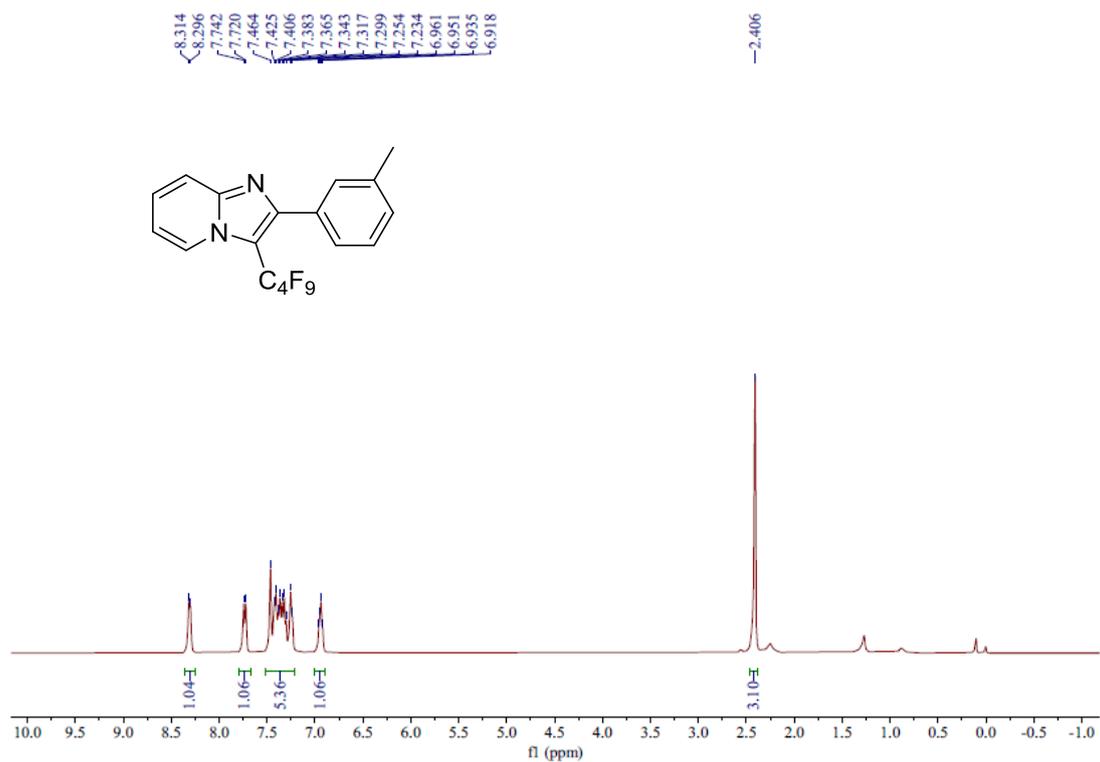
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ae**



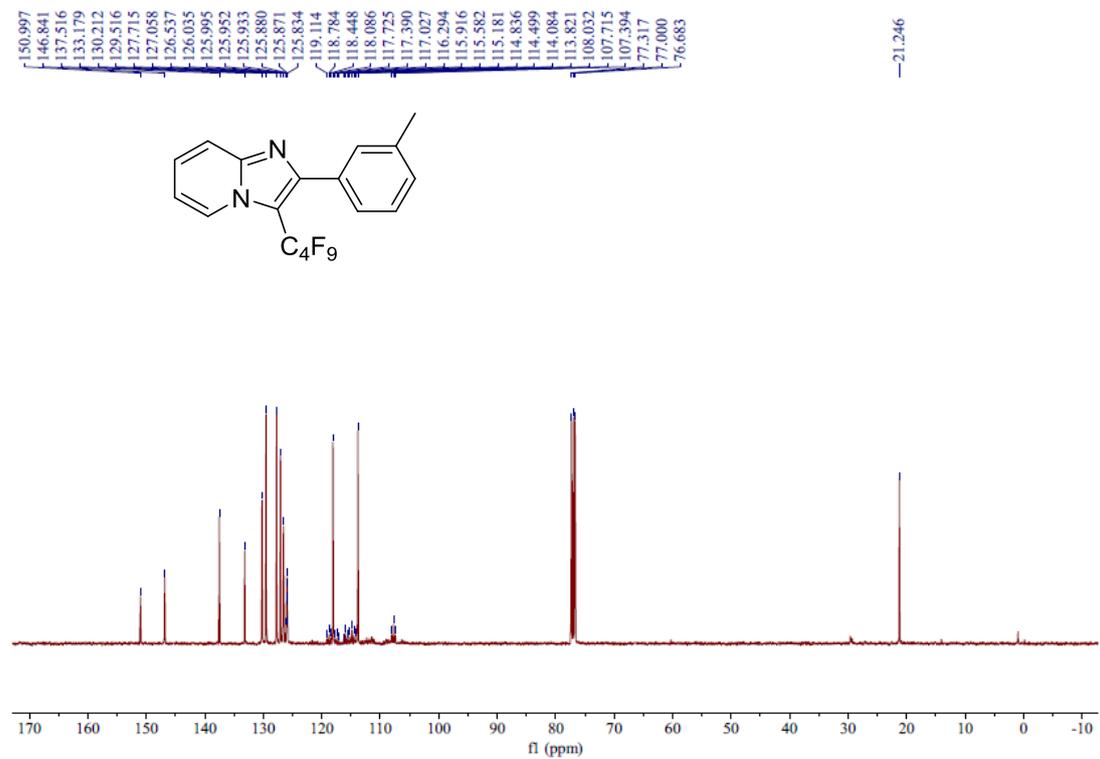
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3ae**



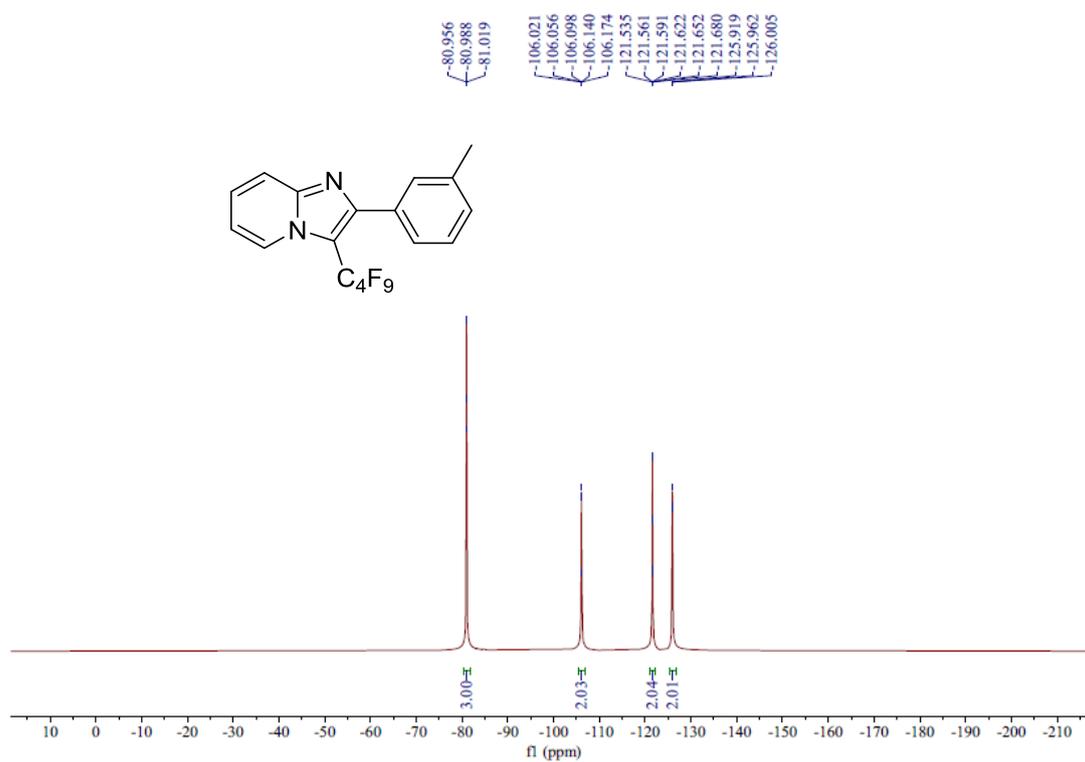
¹H NMR (400 MHz, CDCl₃) Spectrum of **3bc**



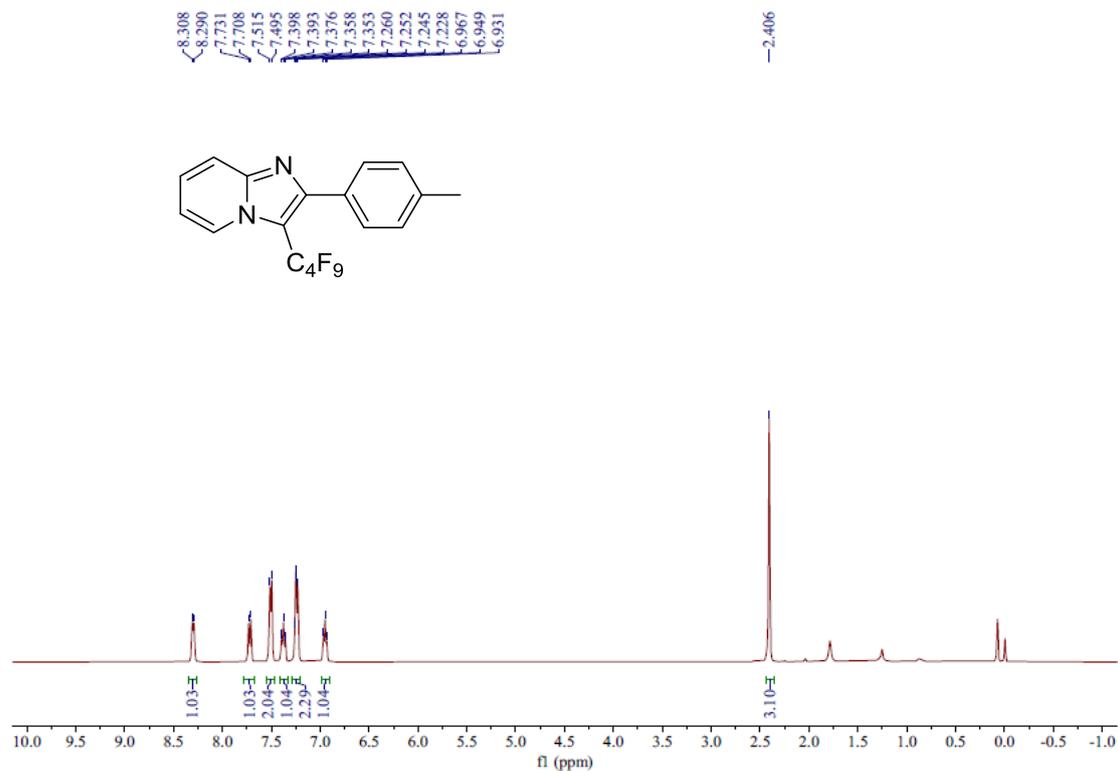
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3bc**



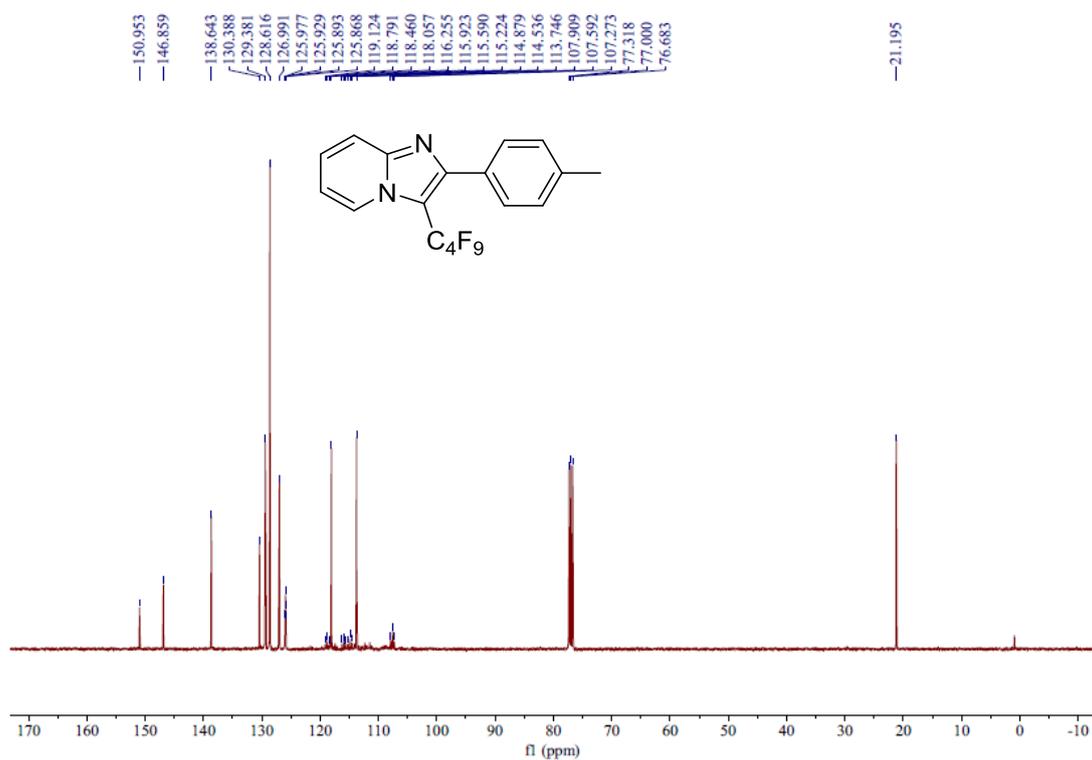
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3bc**



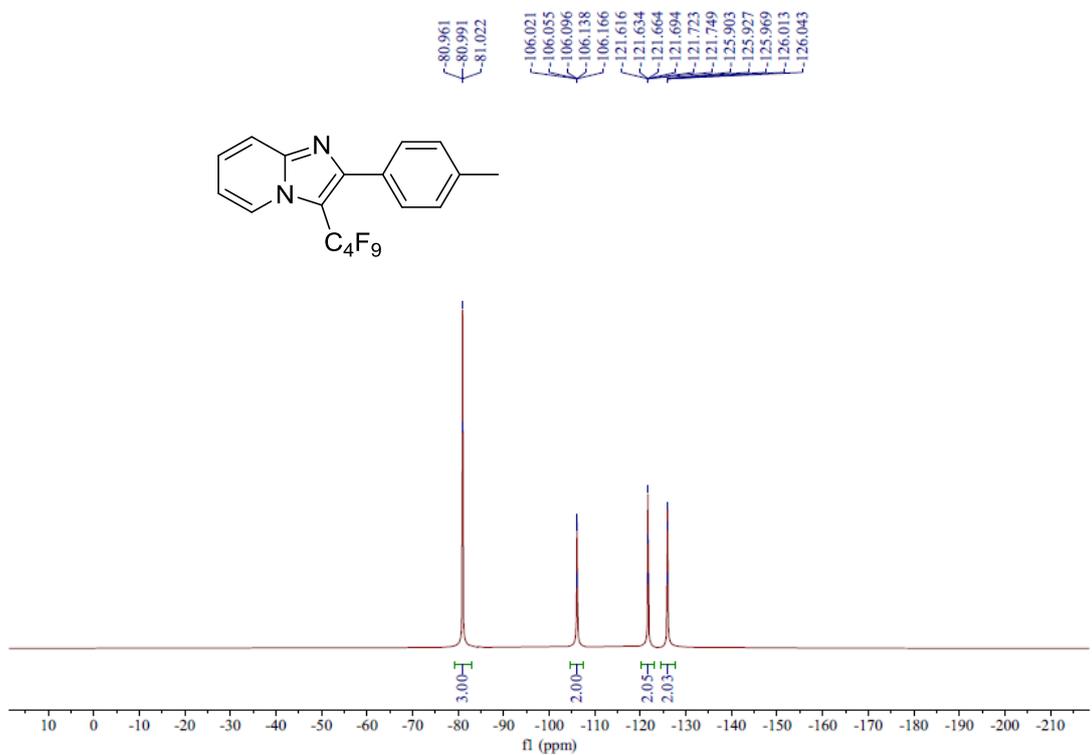
^1H NMR (400 MHz, CDCl_3) Spectrum of **3cc**



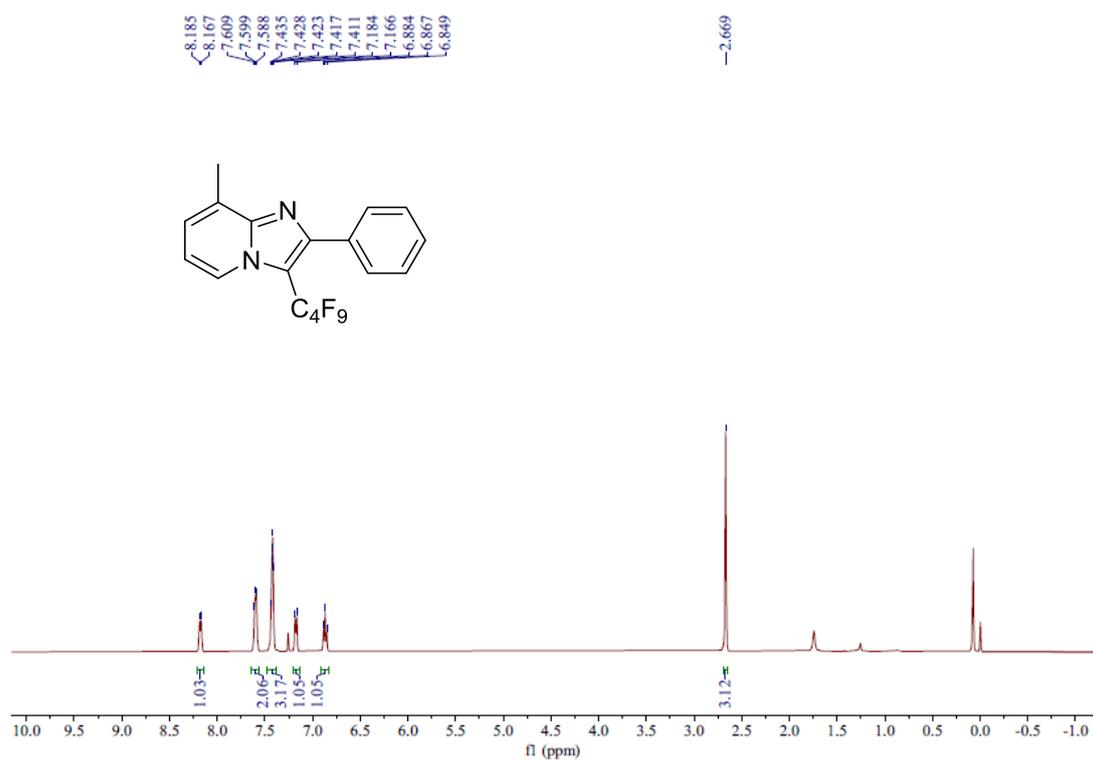
^{13}C NMR (100 MHz, CDCl_3) Spectrum of **3cc**



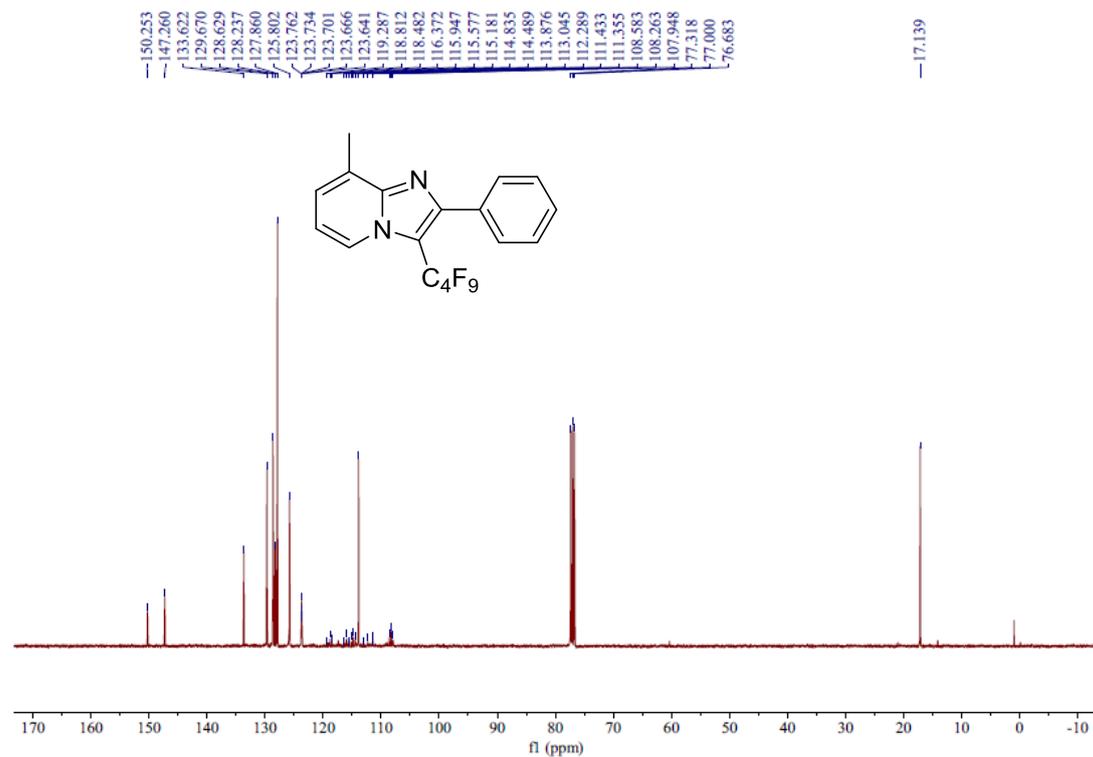
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3cc**



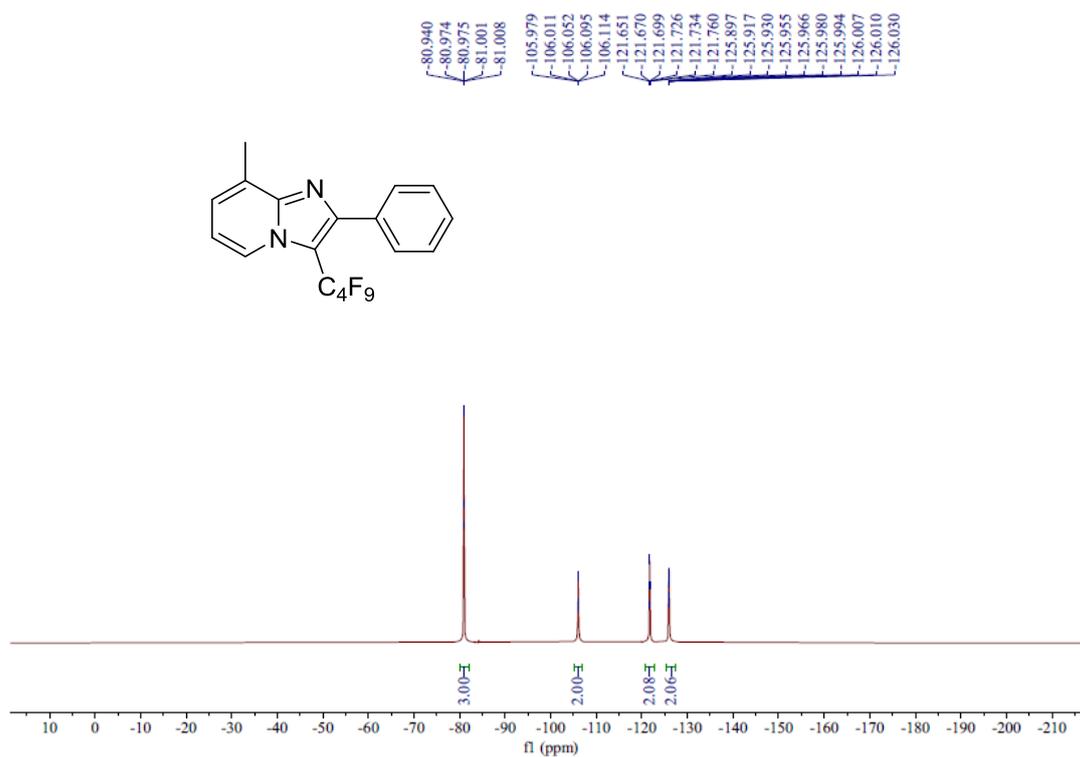
^1H NMR (400 MHz, CDCl_3) Spectrum of **3dc**



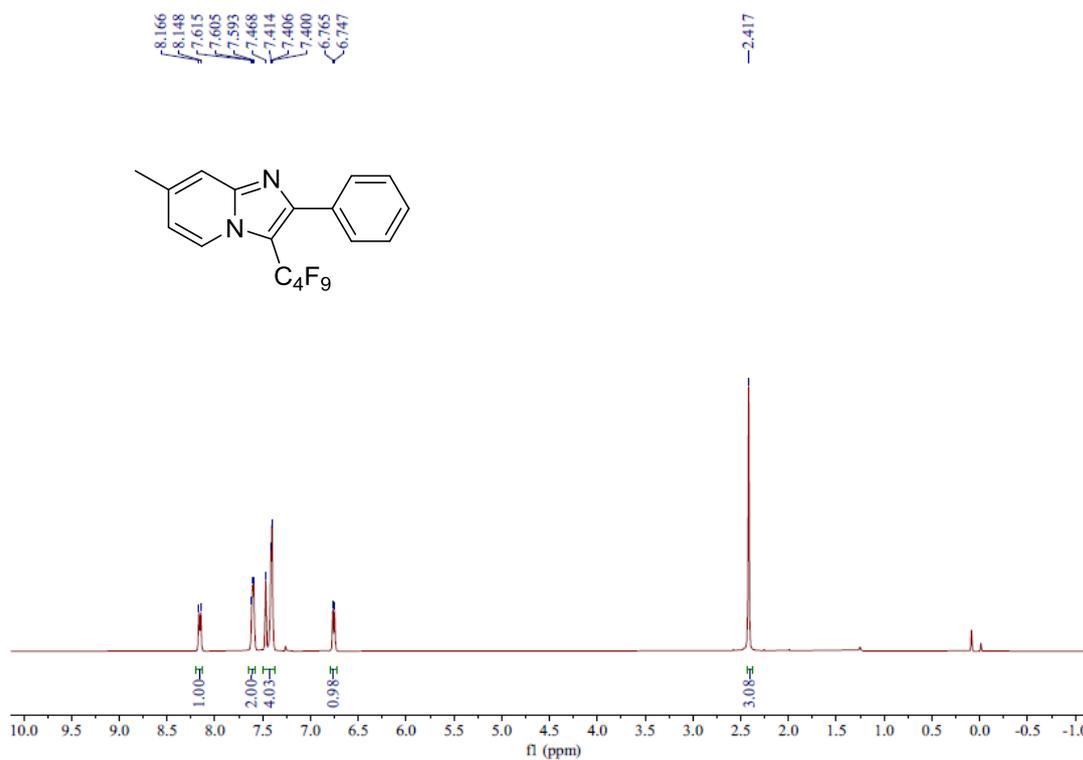
^{13}C NMR (100 MHz, CDCl_3) Spectrum of **3dc**



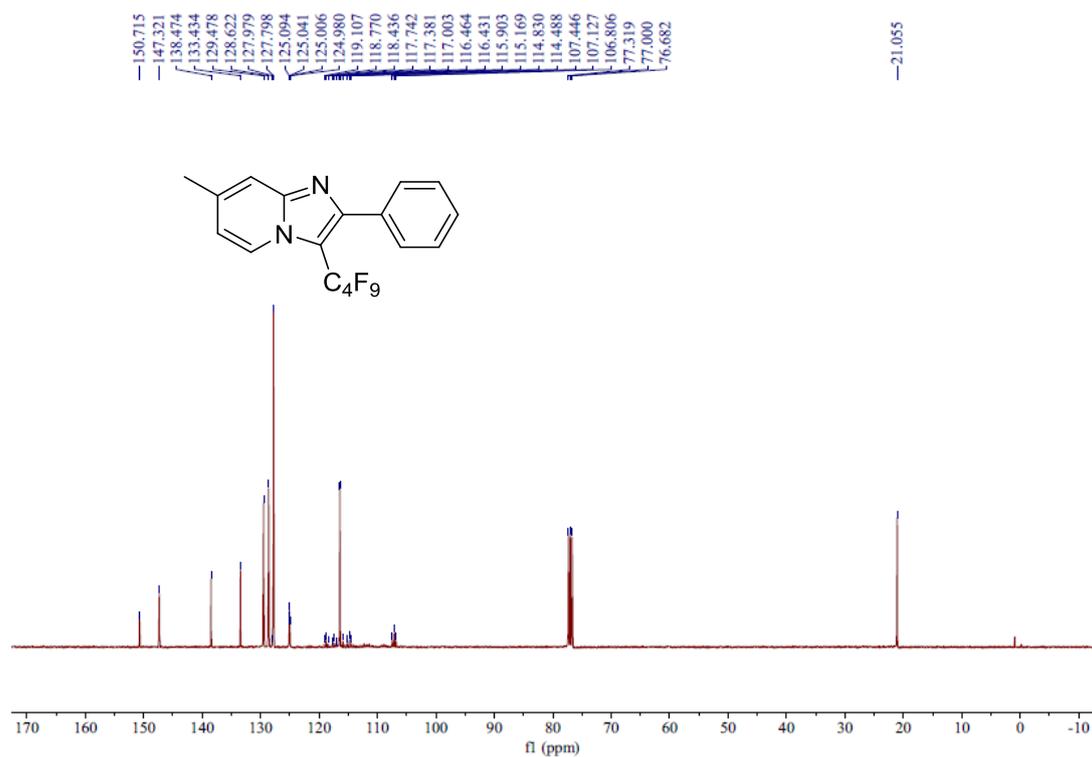
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3dc**



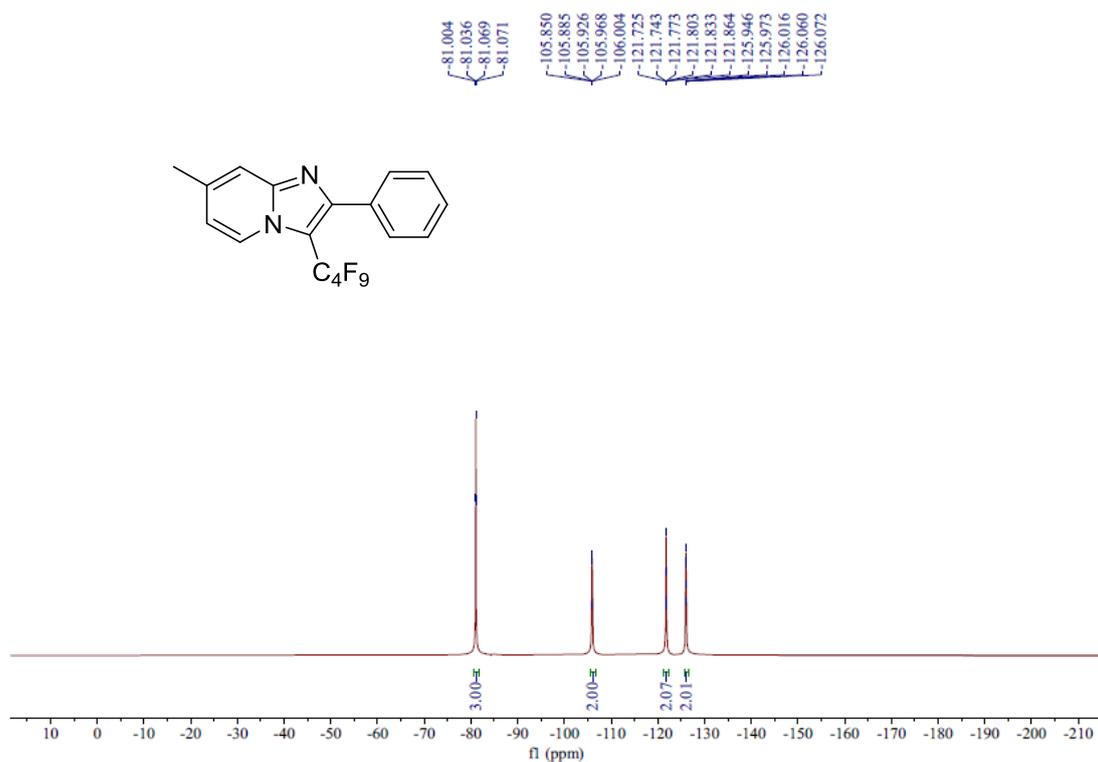
^1H NMR (400 MHz, CDCl_3) Spectrum of **3ec**



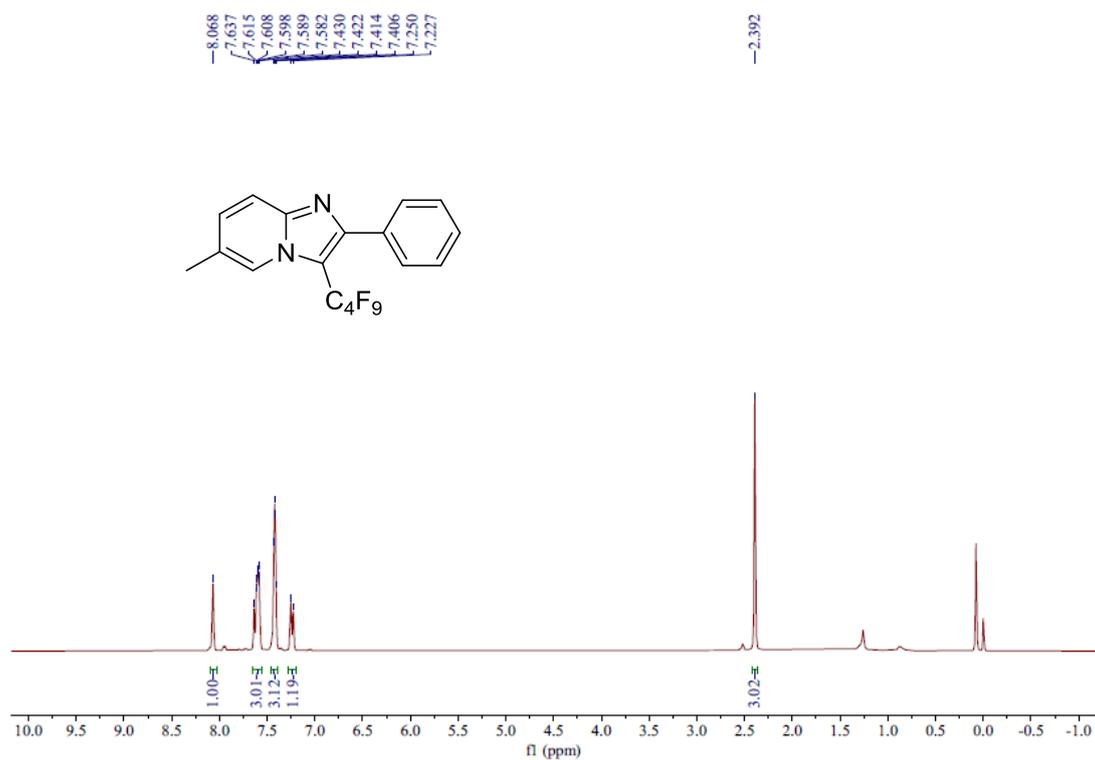
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ec**



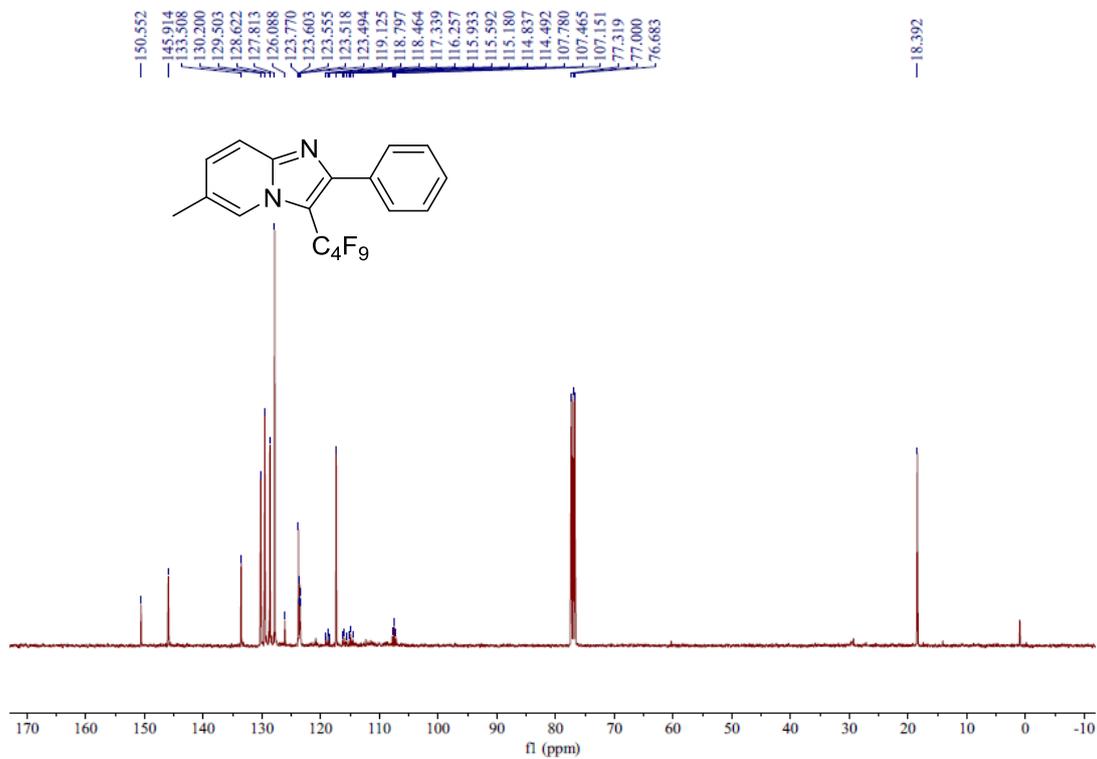
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3ec**



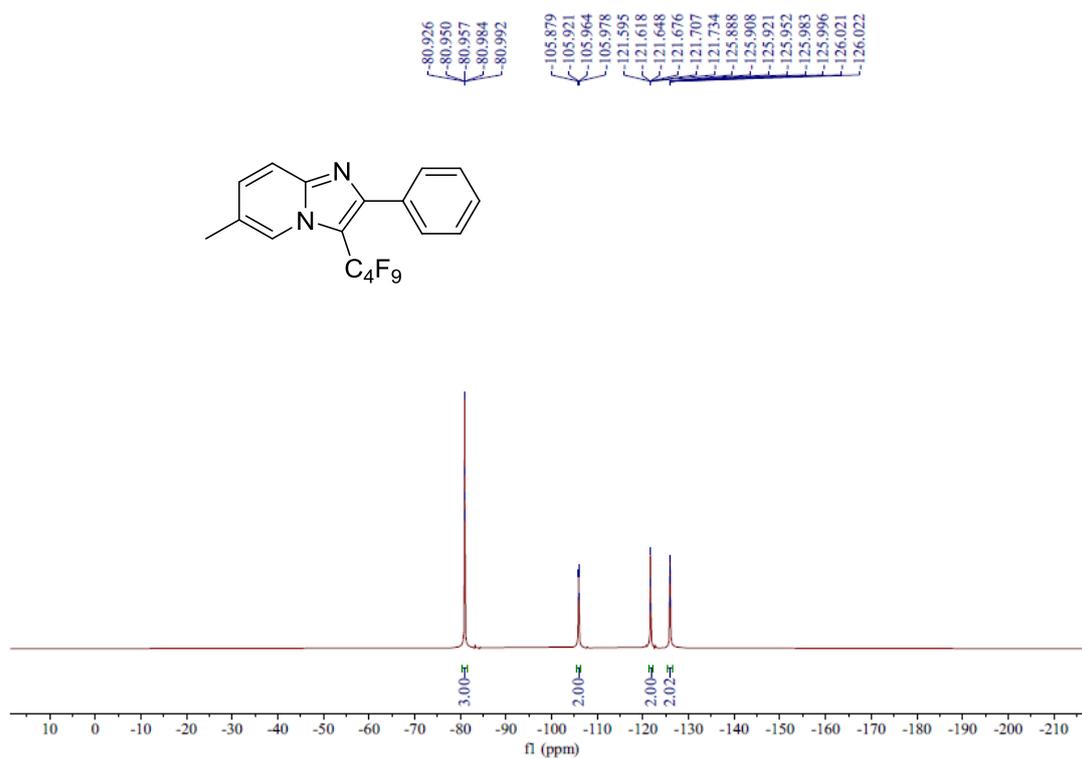
¹H NMR (400 MHz, CDCl₃) Spectrum of **3fc**



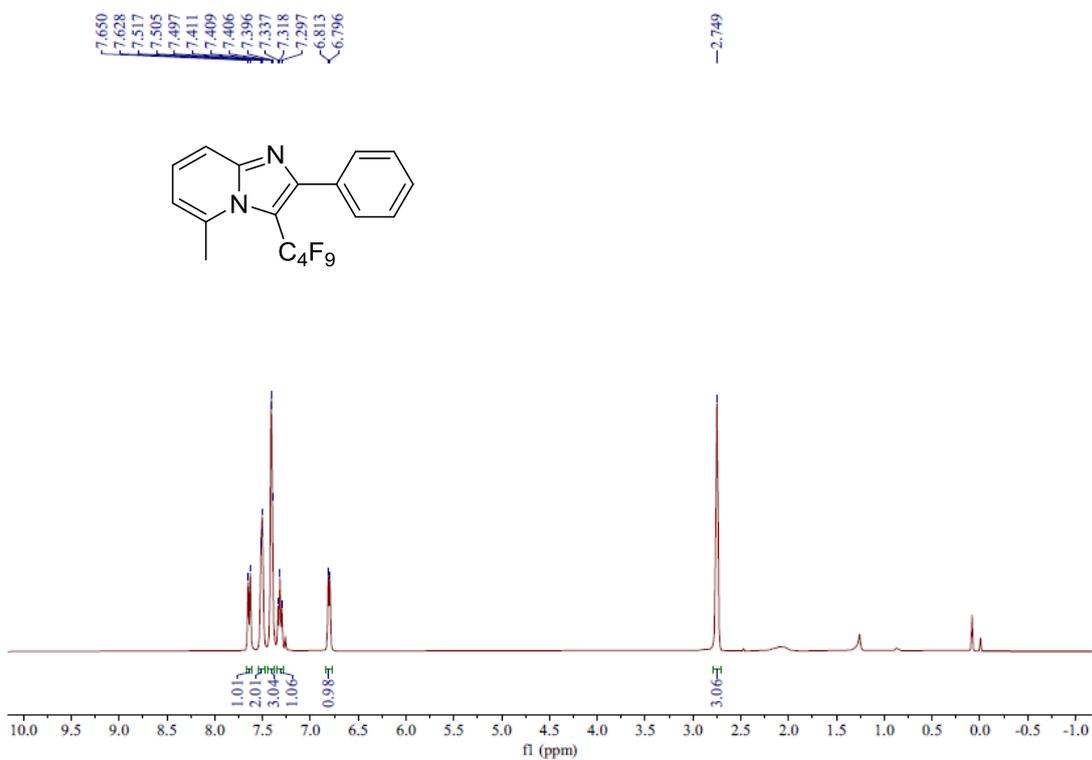
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3fc**



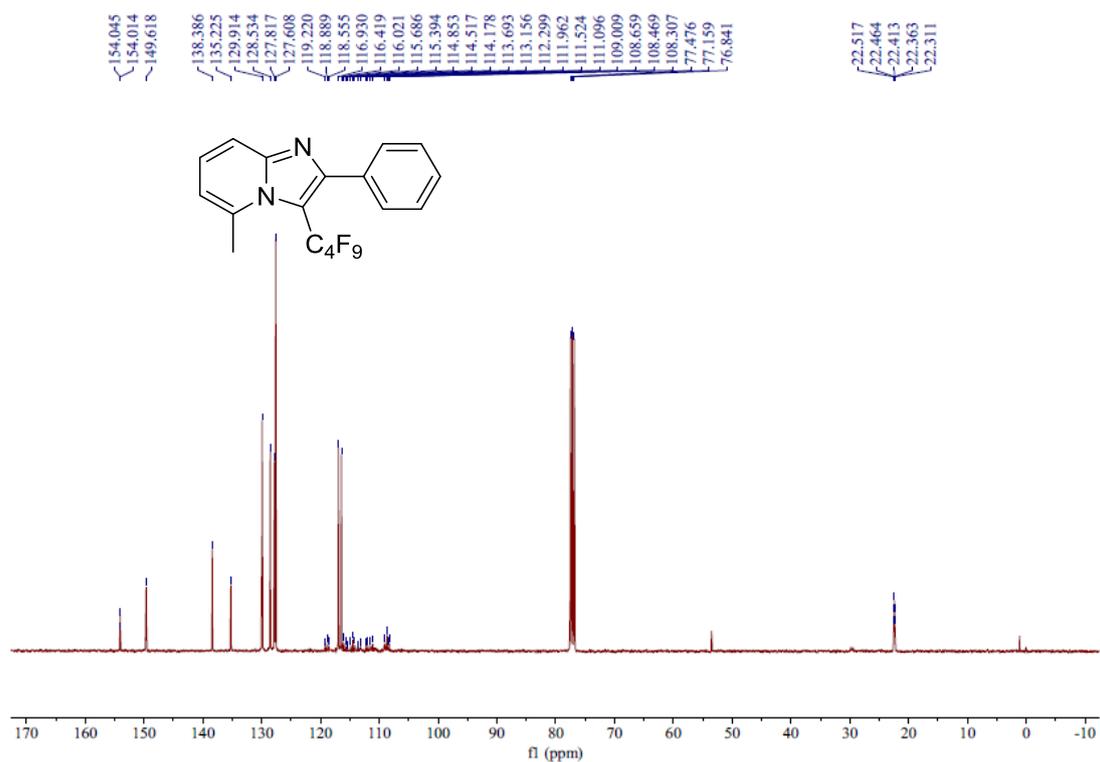
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3fc**



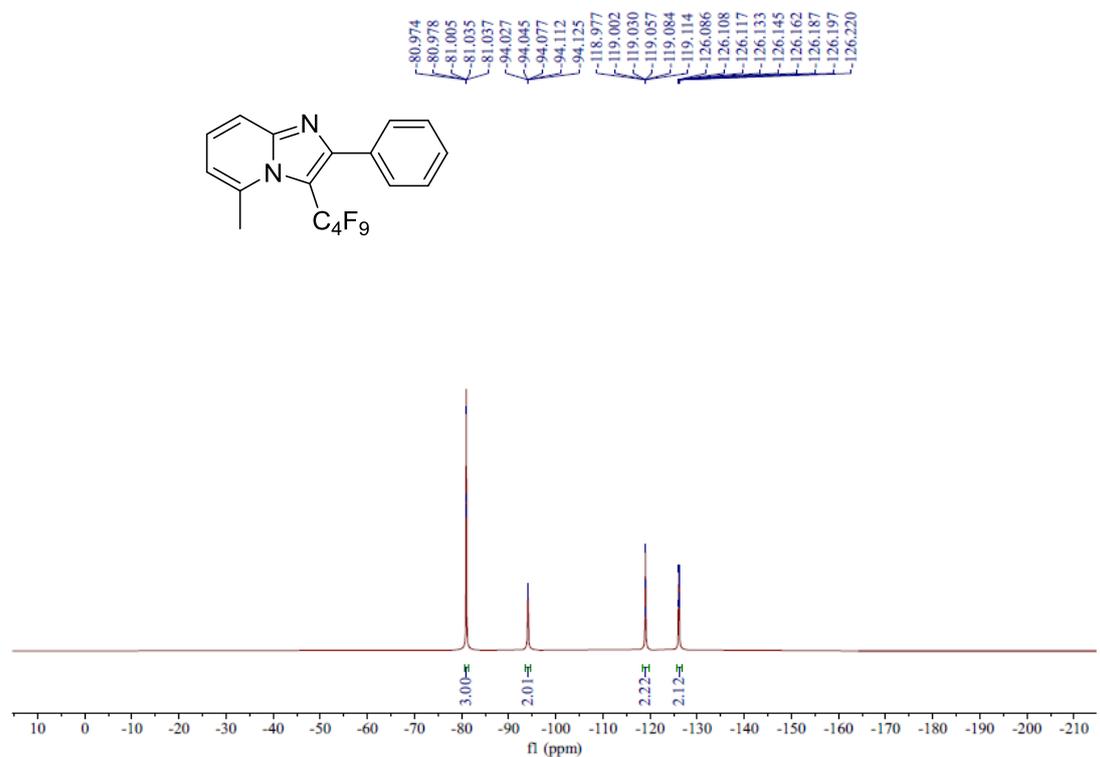
¹H NMR (400 MHz, CDCl₃) Spectrum of **3gc**



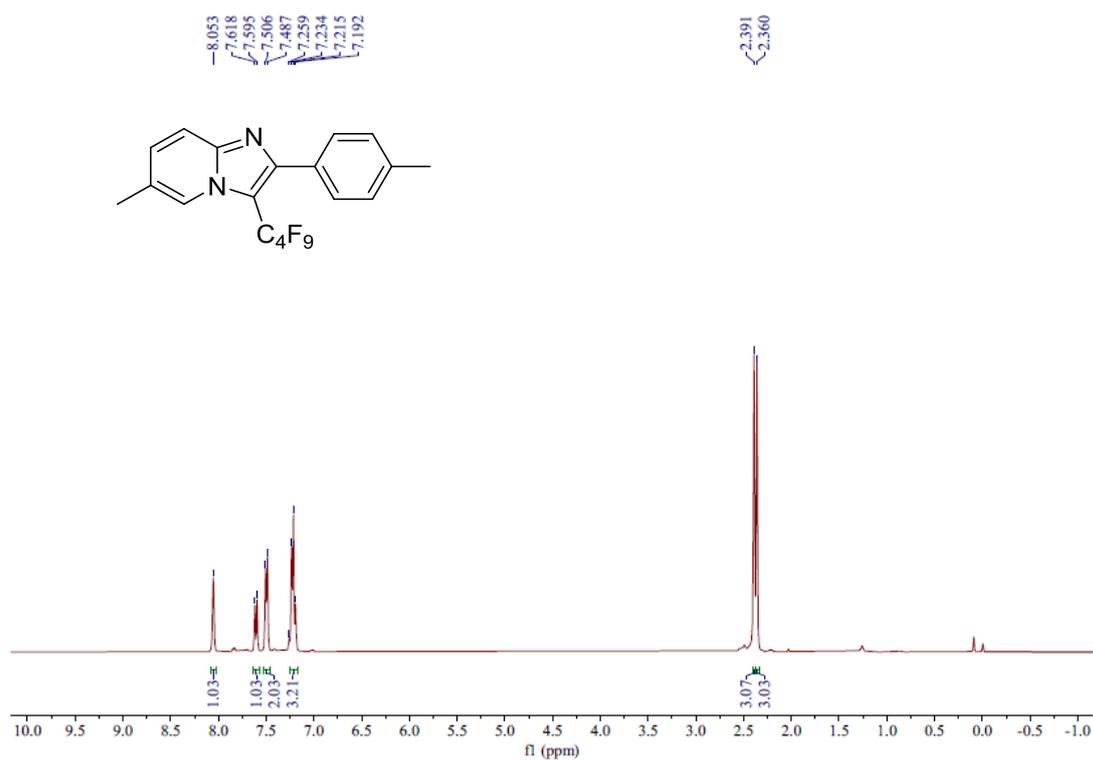
^{13}C NMR (100 MHz, CDCl_3) Spectrum of **3gc**



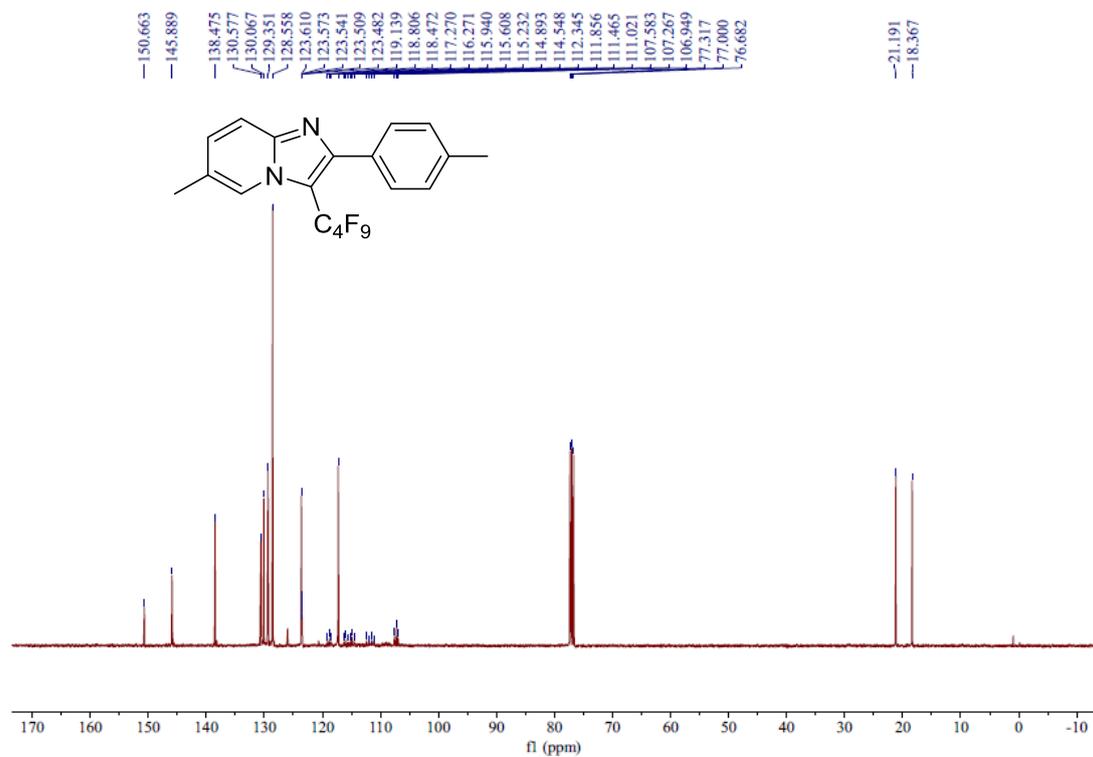
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3gc**



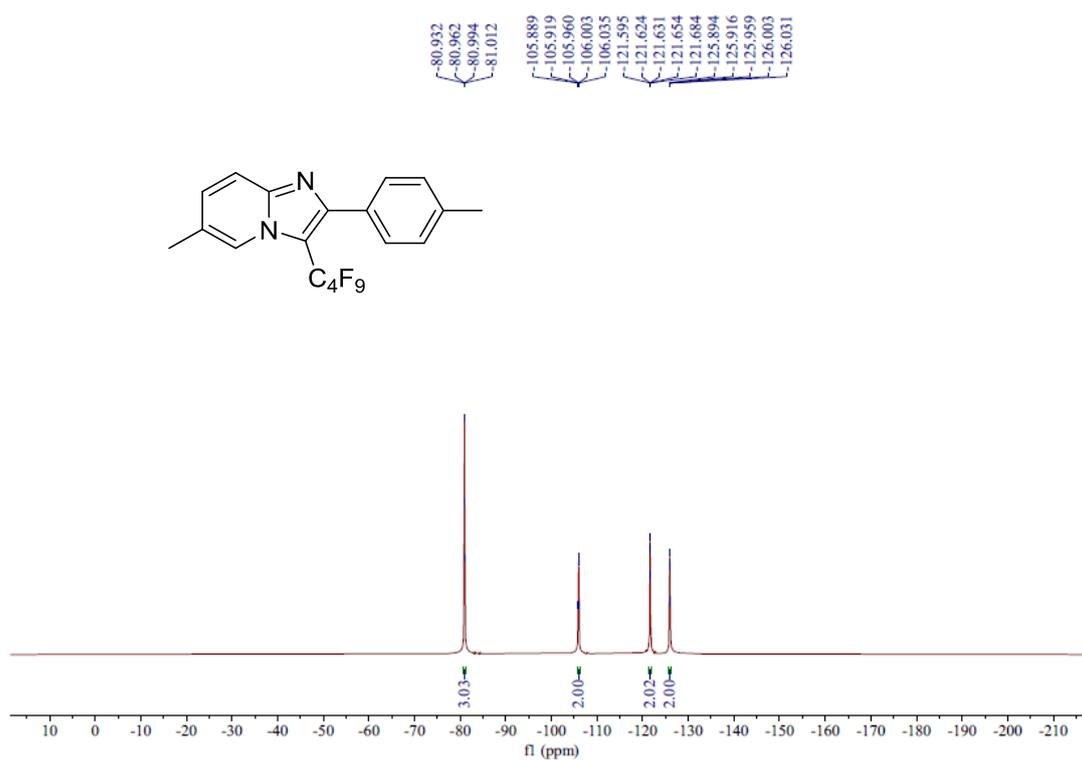
^1H NMR (400 MHz, CDCl_3) Spectrum of **3hc**



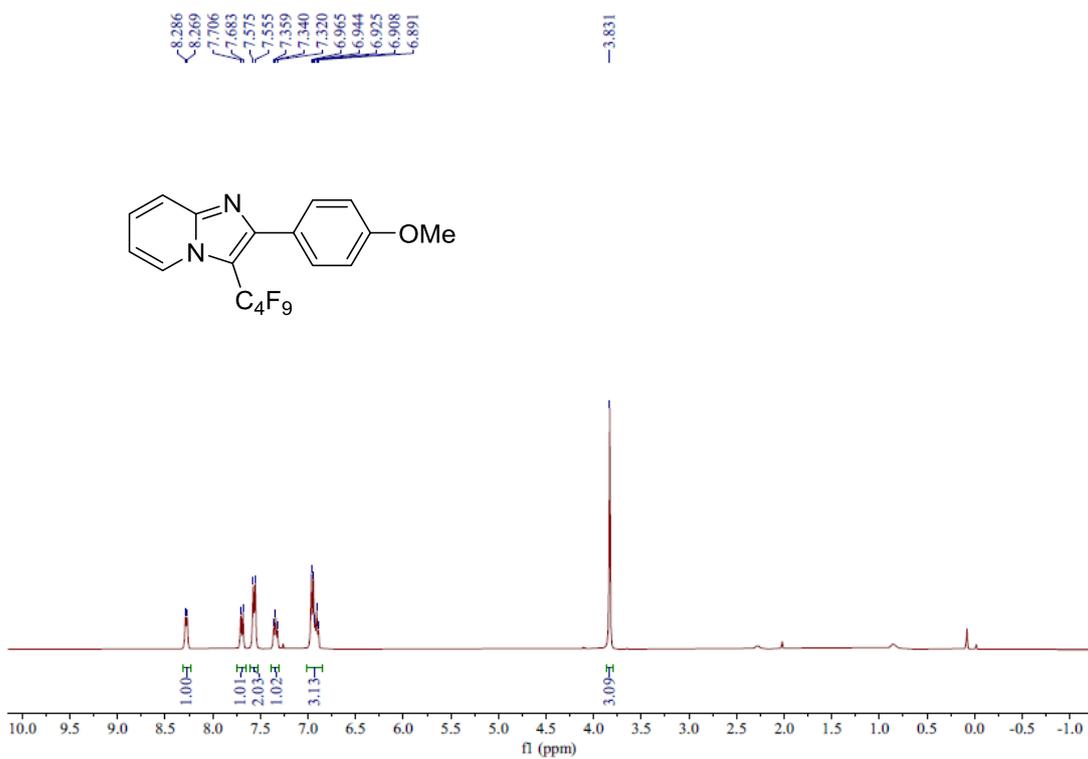
^{13}C NMR (100 MHz, CDCl_3) Spectrum of **3hc**



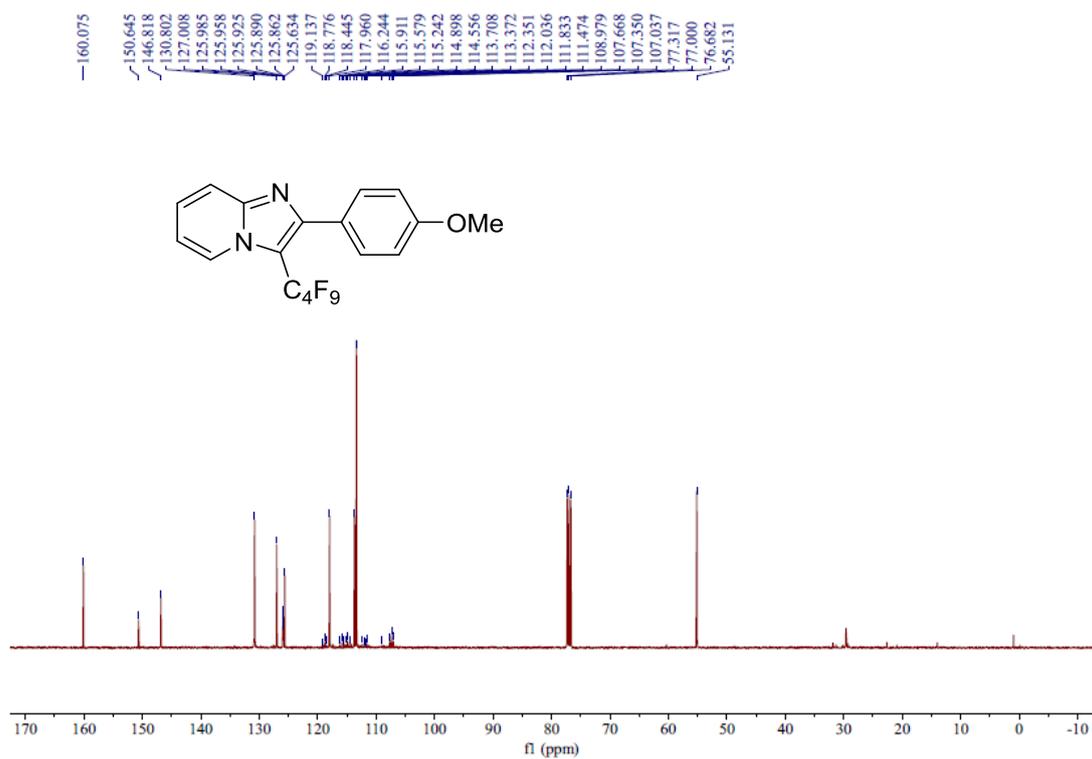
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3hc**



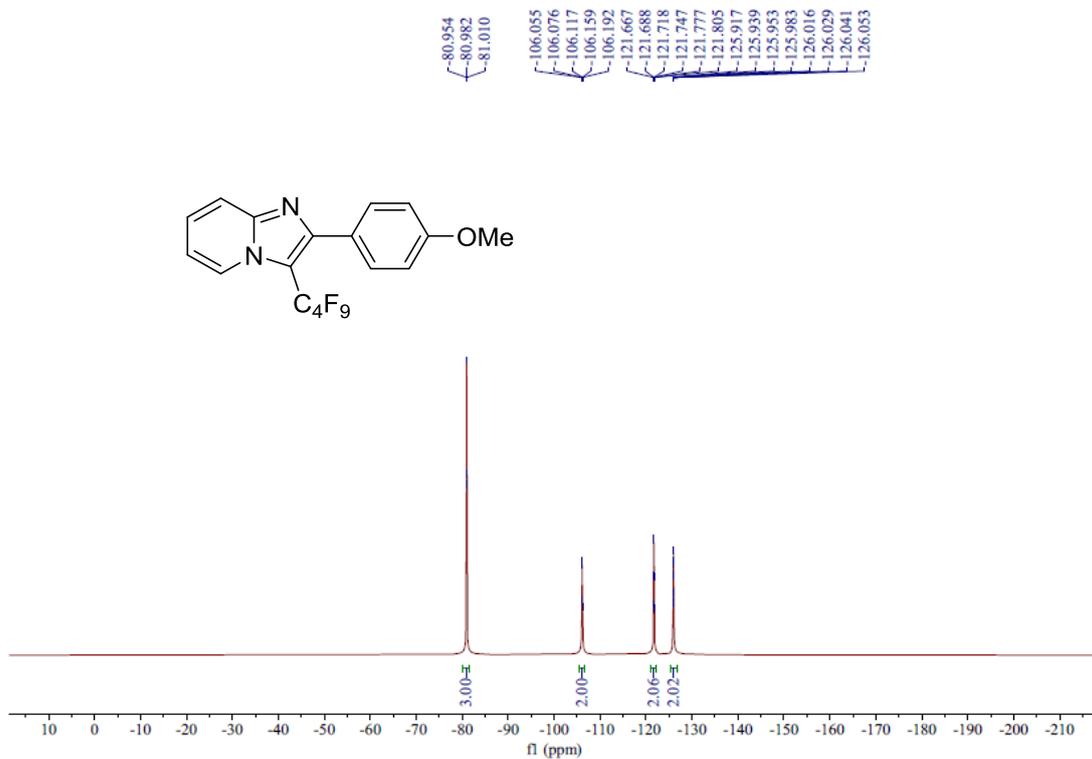
¹H NMR (400 MHz, CDCl₃) Spectrum of **3ic**



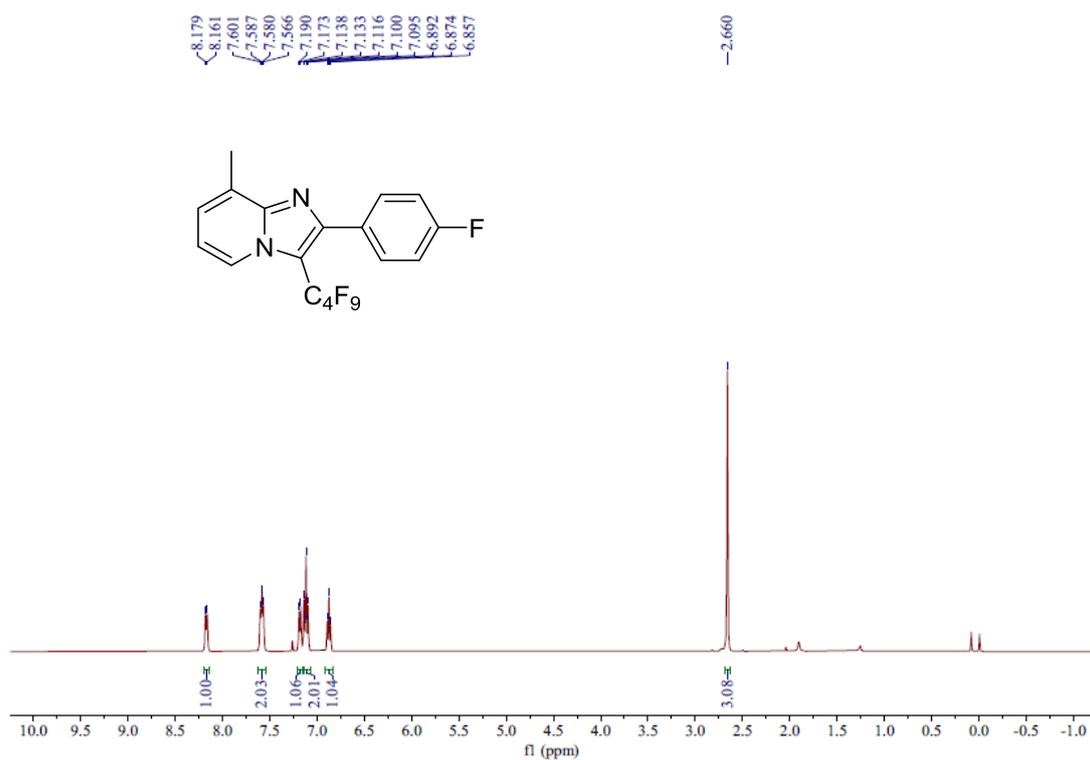
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3ic**



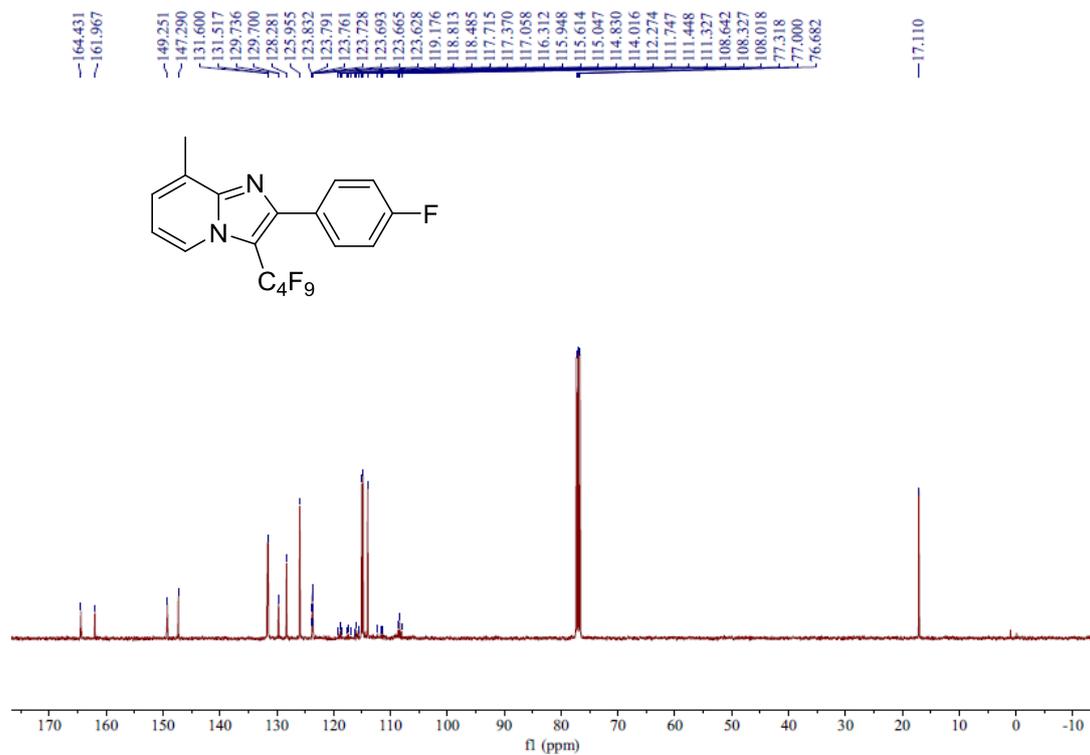
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3ic**



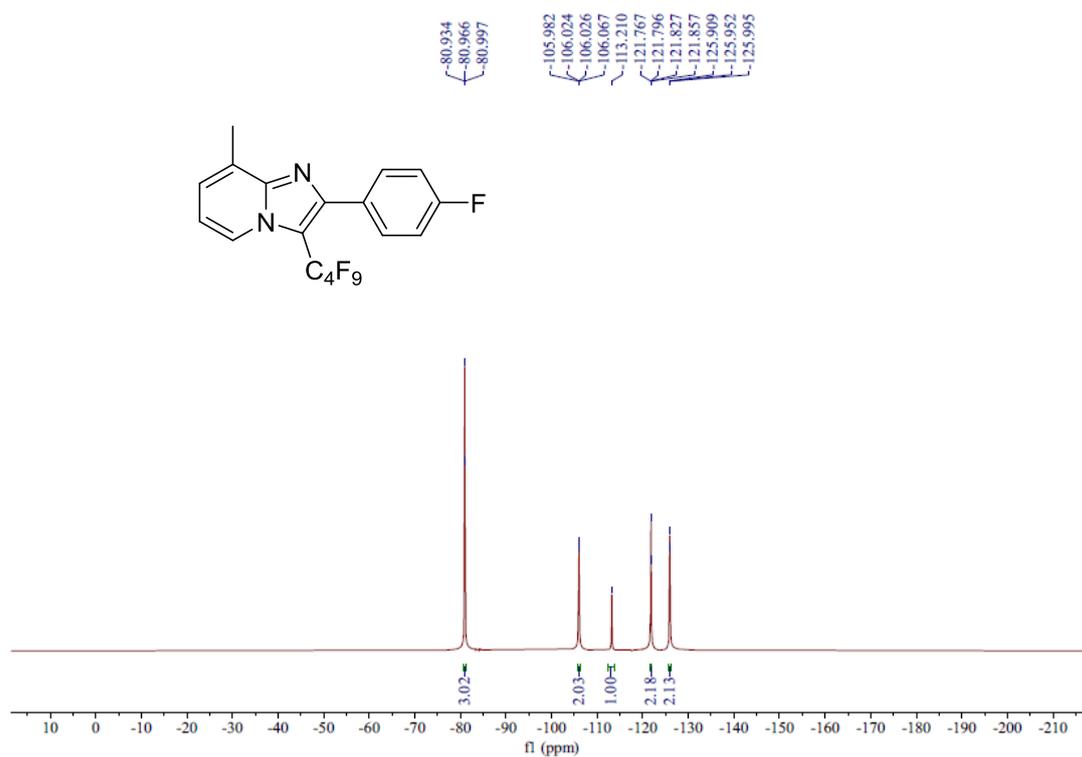
¹H NMR (400 MHz, CDCl₃) Spectrum of **3jc**



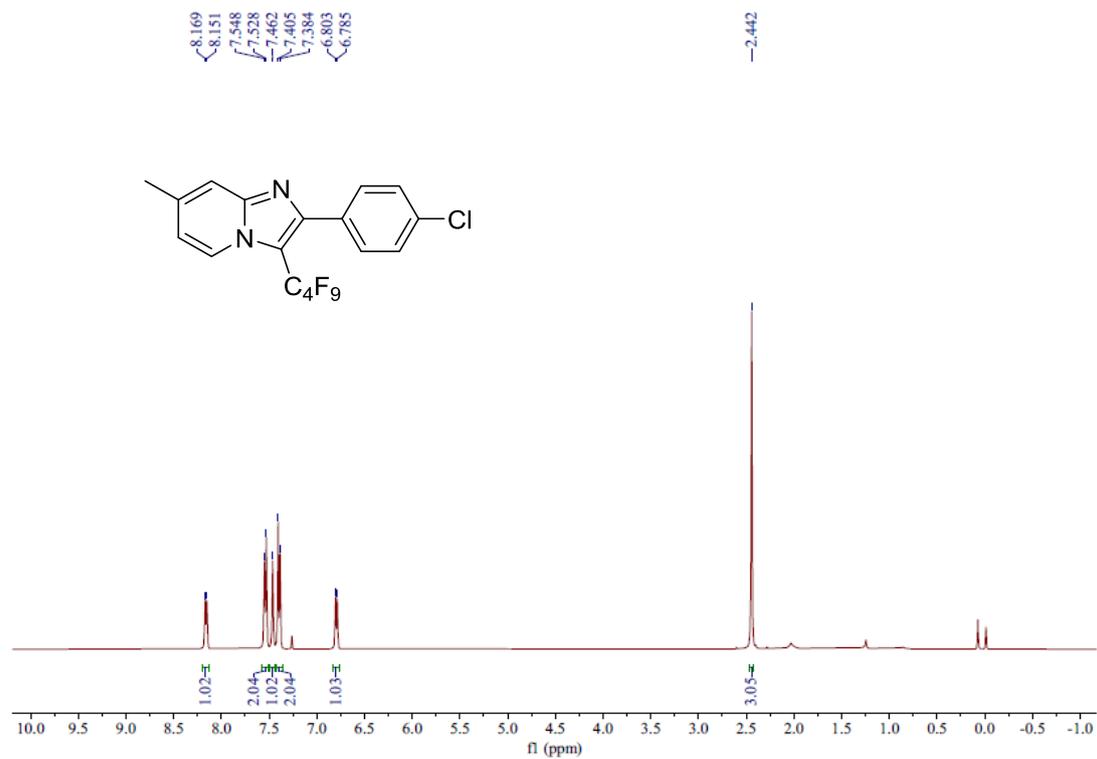
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3jc**



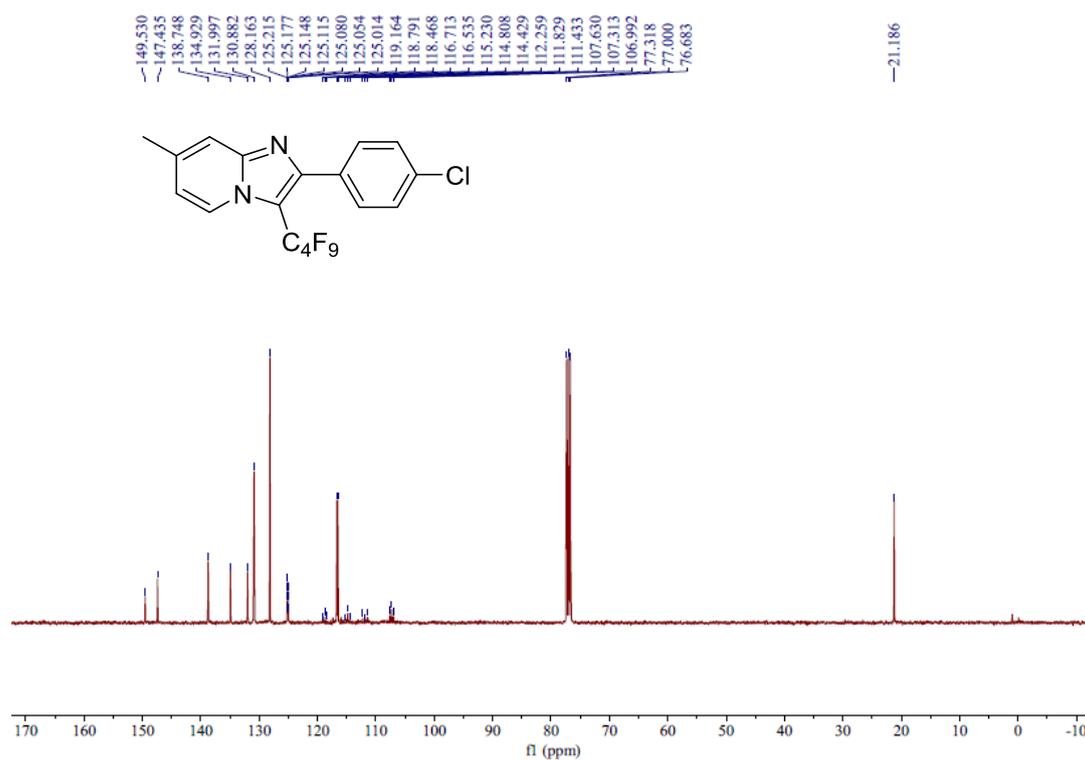
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3jc**



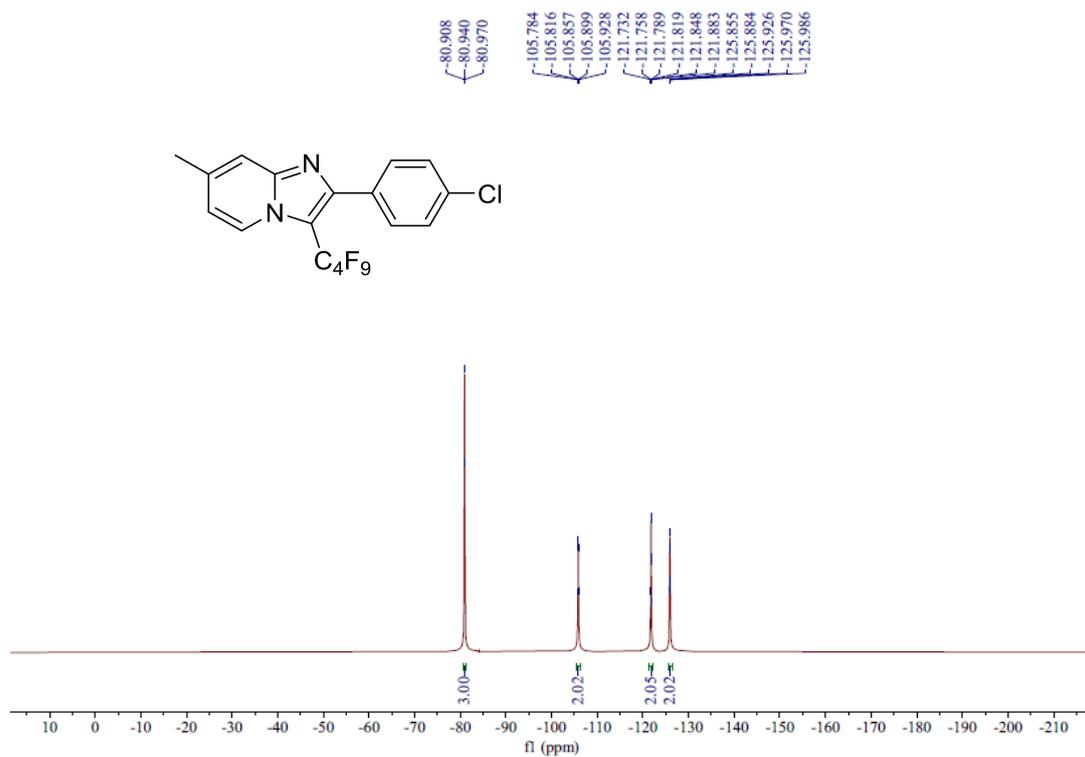
¹H NMR (400 MHz, CDCl₃) Spectrum of **3kc**



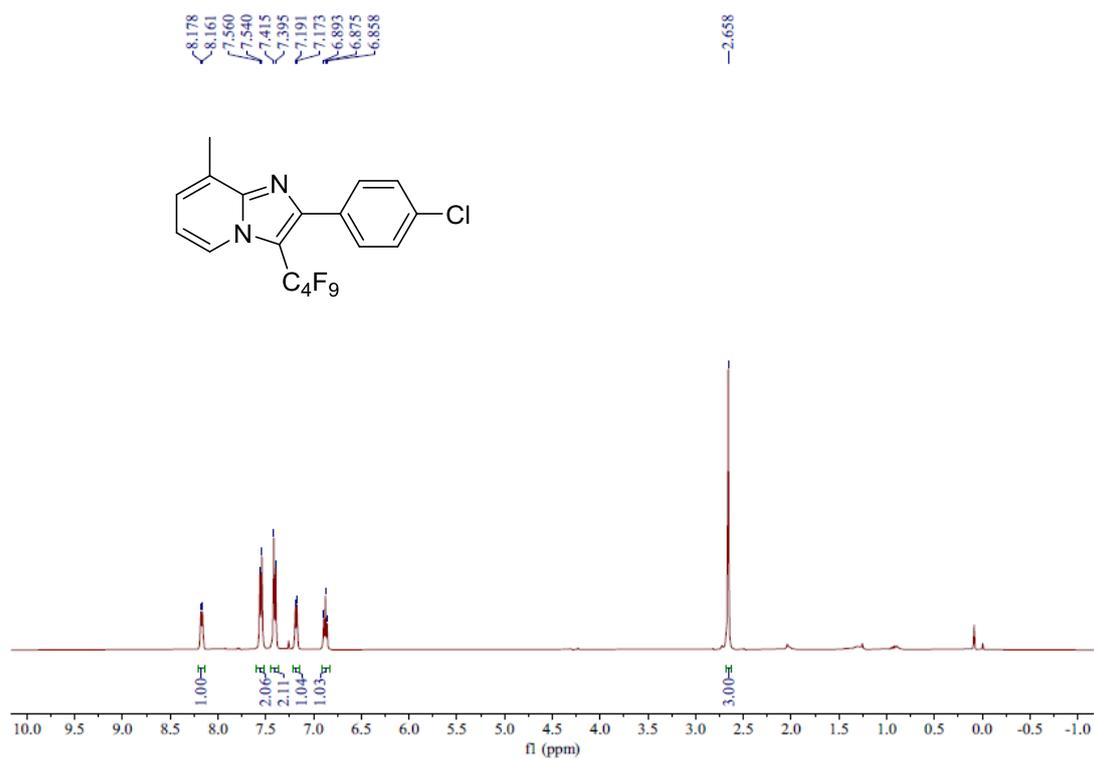
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3kc**



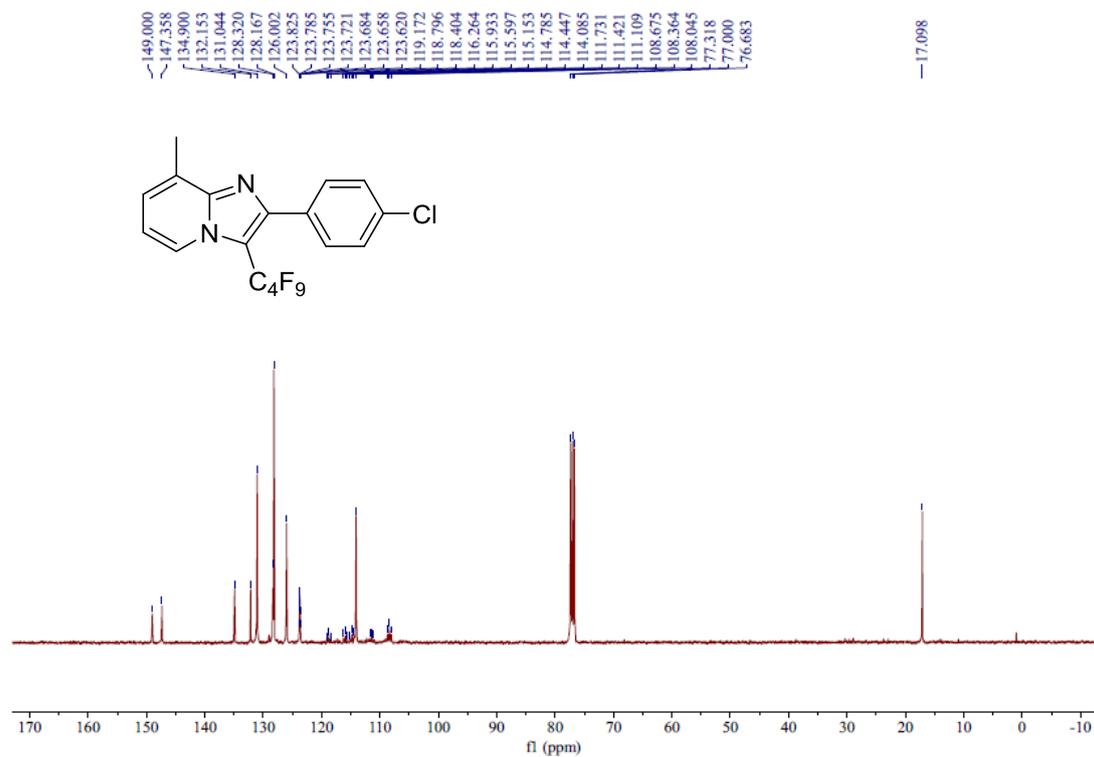
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3kc**



¹H NMR (400 MHz, CDCl₃) Spectrum of **3lc**



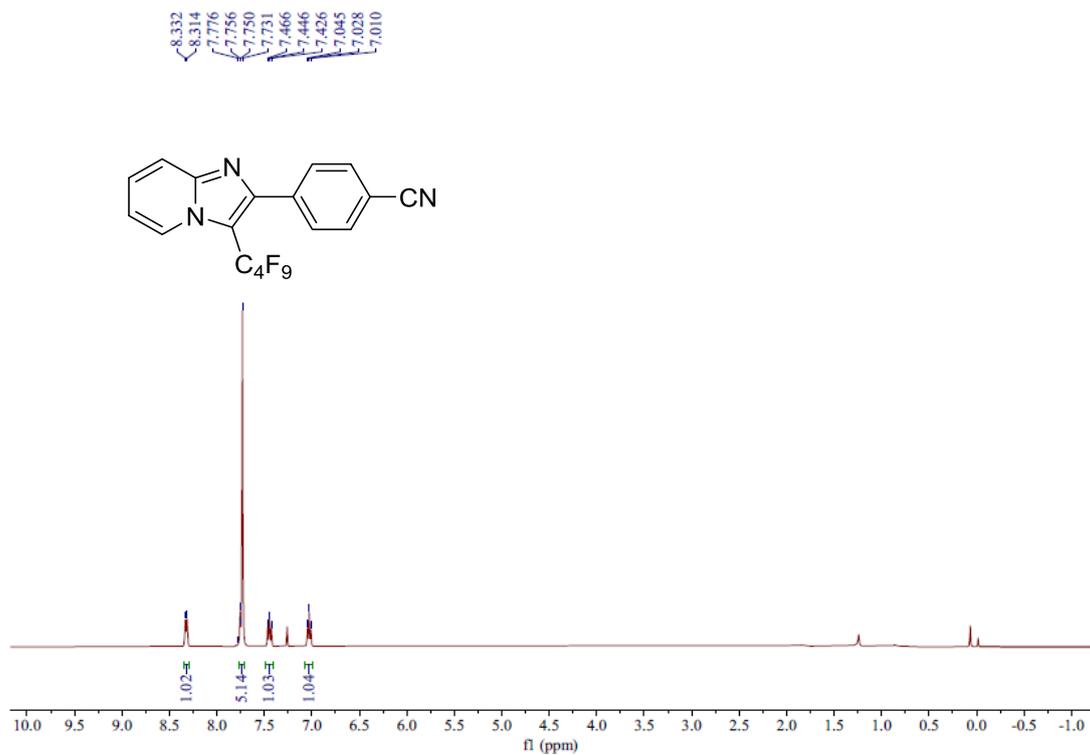
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3lc**



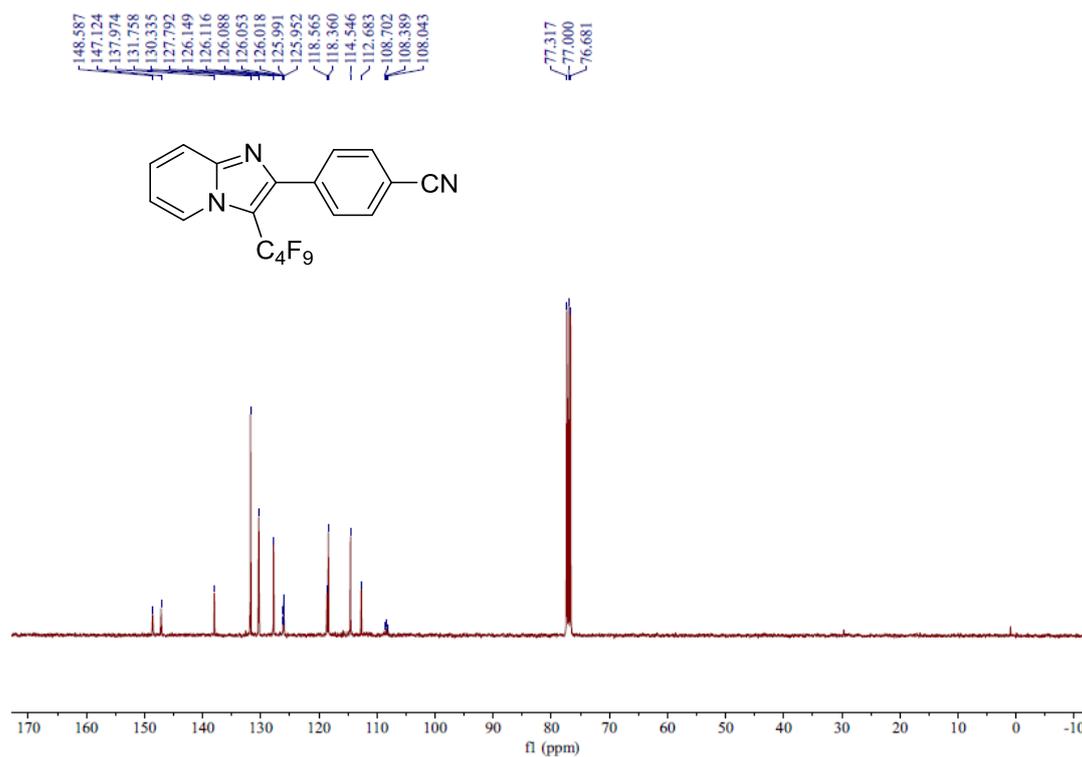
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3lc**



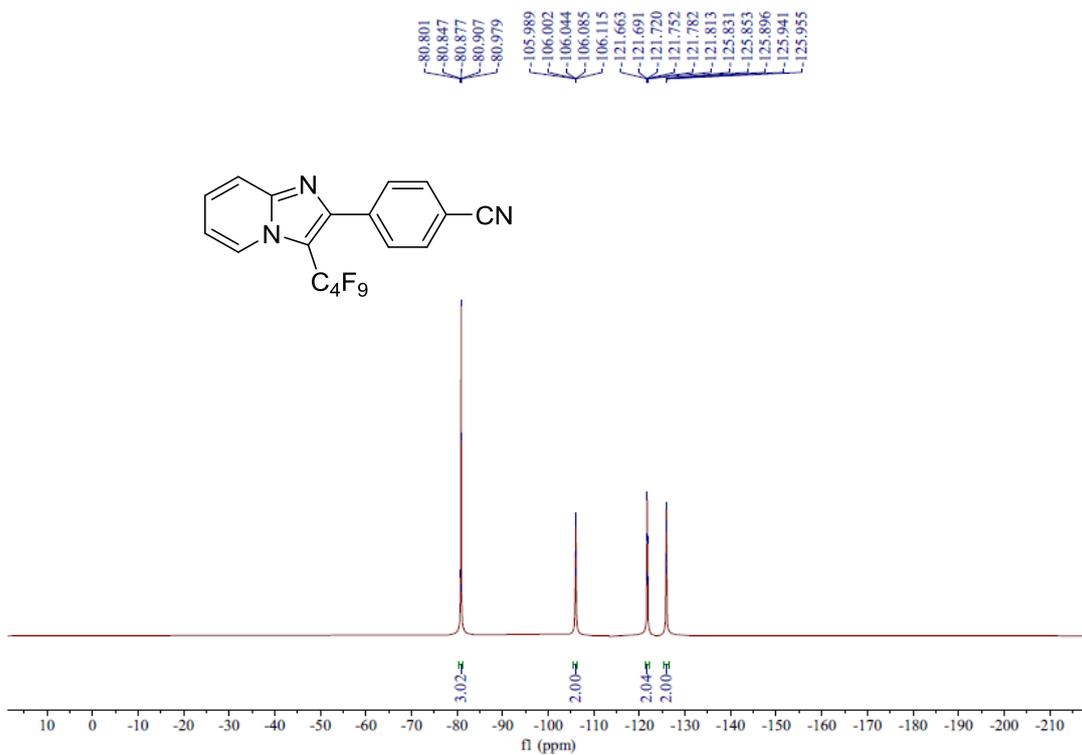
^1H NMR (400 MHz, CDCl_3) Spectrum of **3mc**



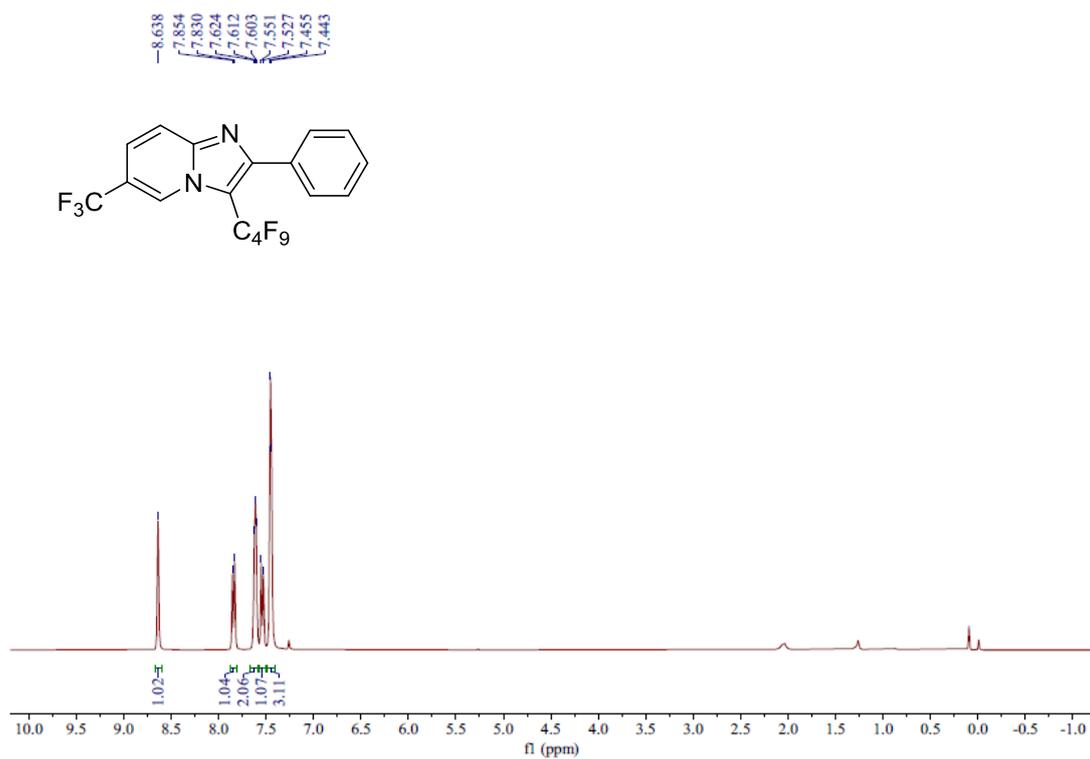
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3mc**



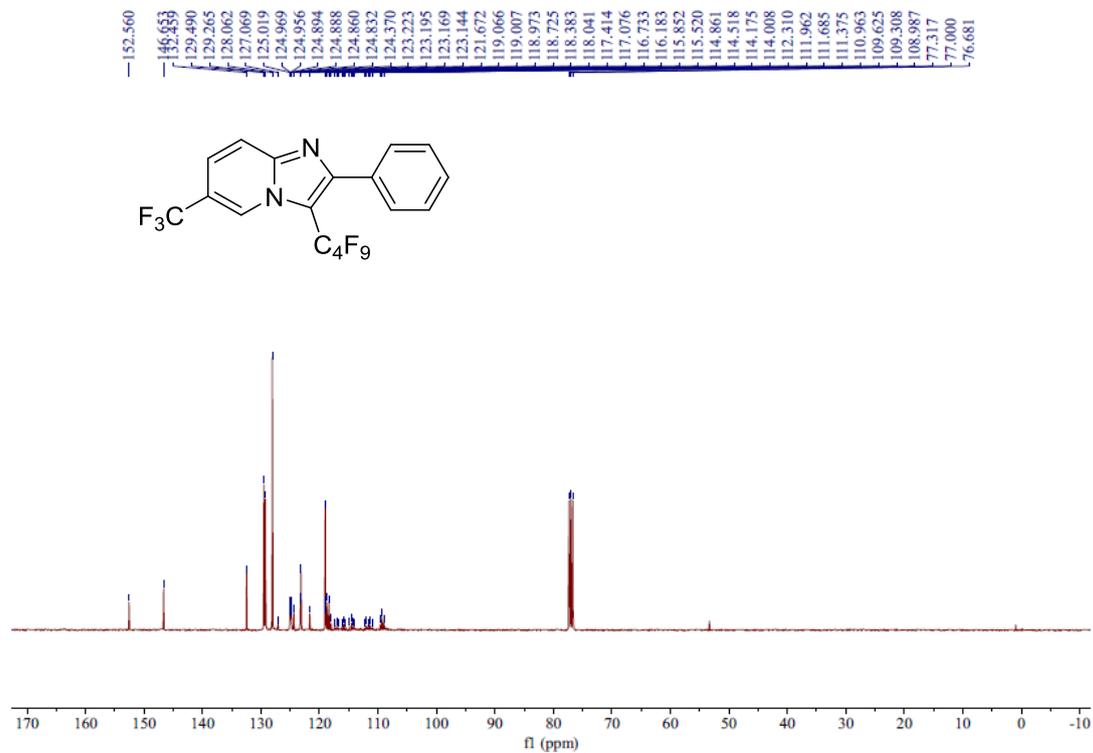
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3mc**



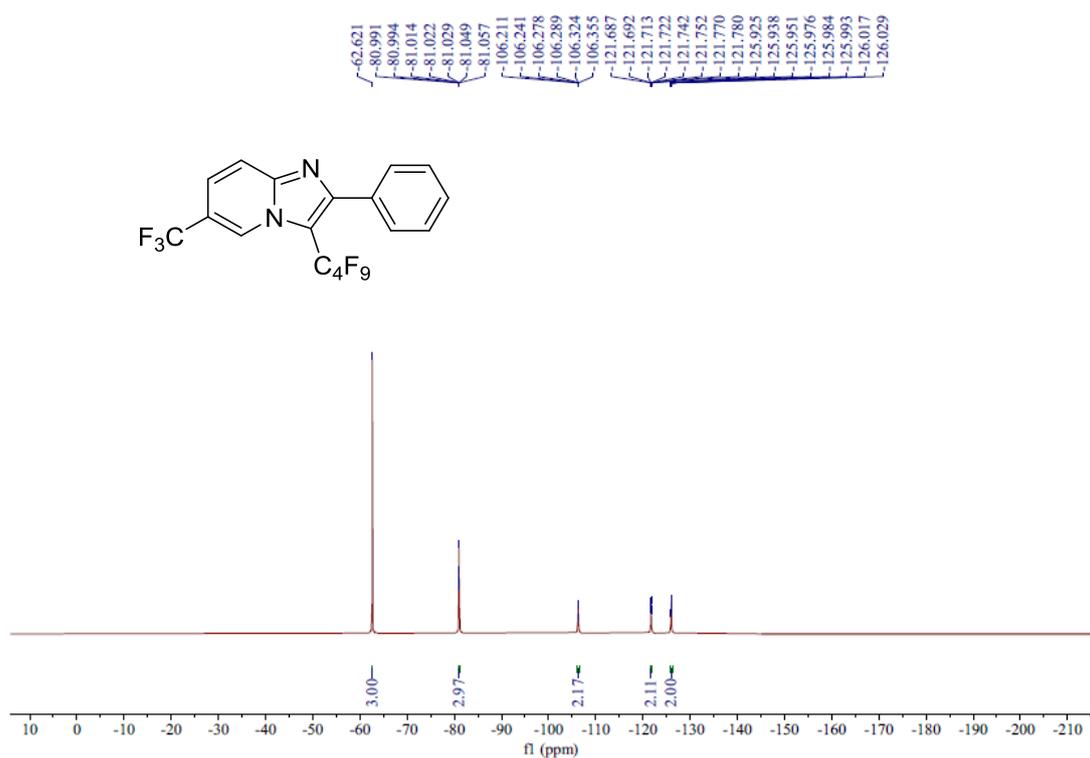
¹H NMR (400 MHz, CDCl₃) Spectrum of **3nc**



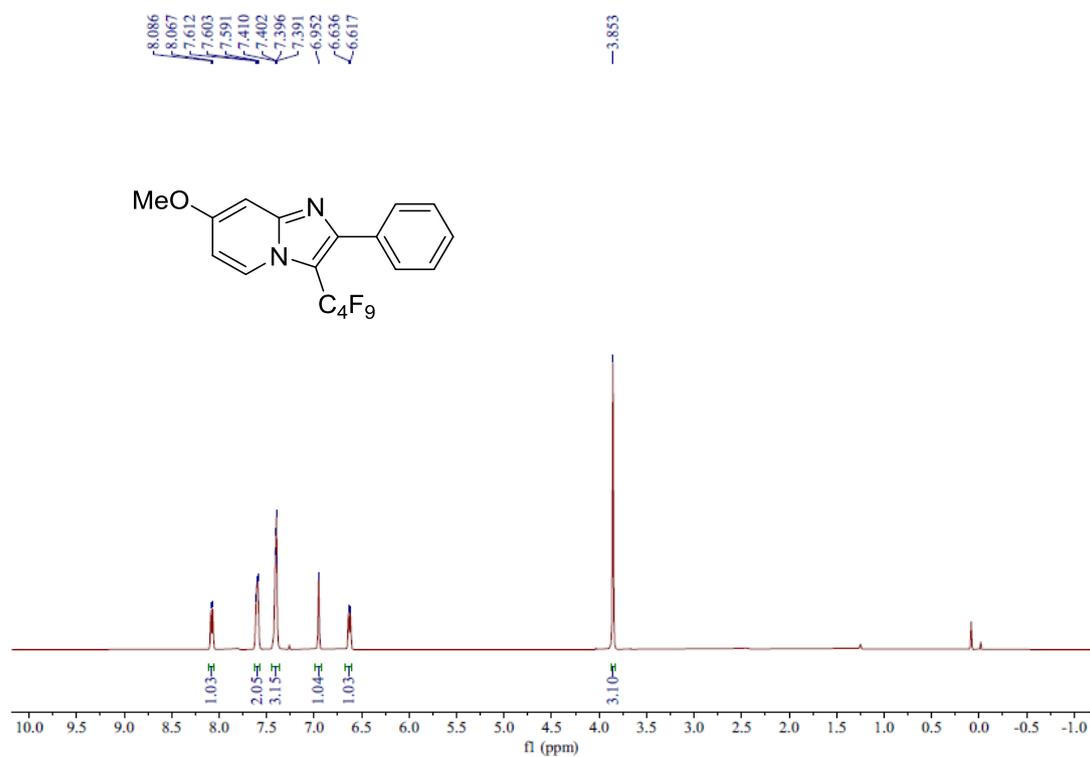
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3nc**



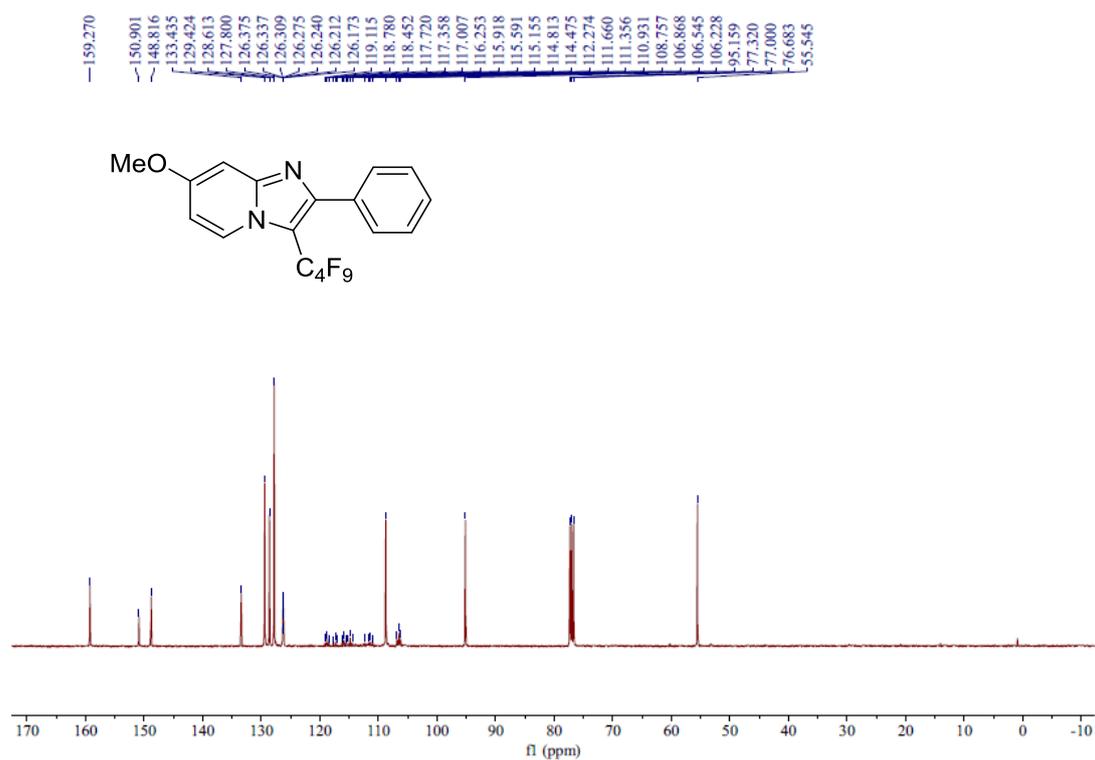
^{19}F NMR (376 MHz, CDCl_3) Spectrum of **3nc**



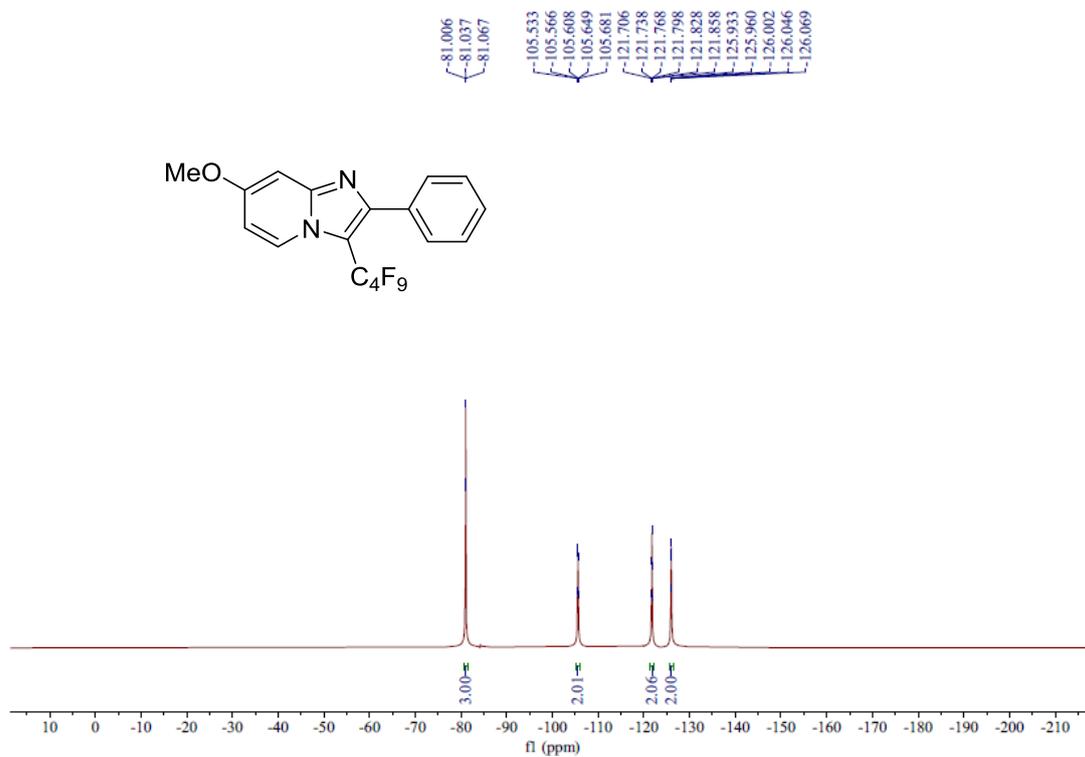
^1H NMR (400 MHz, CDCl_3) Spectrum of **3oc**



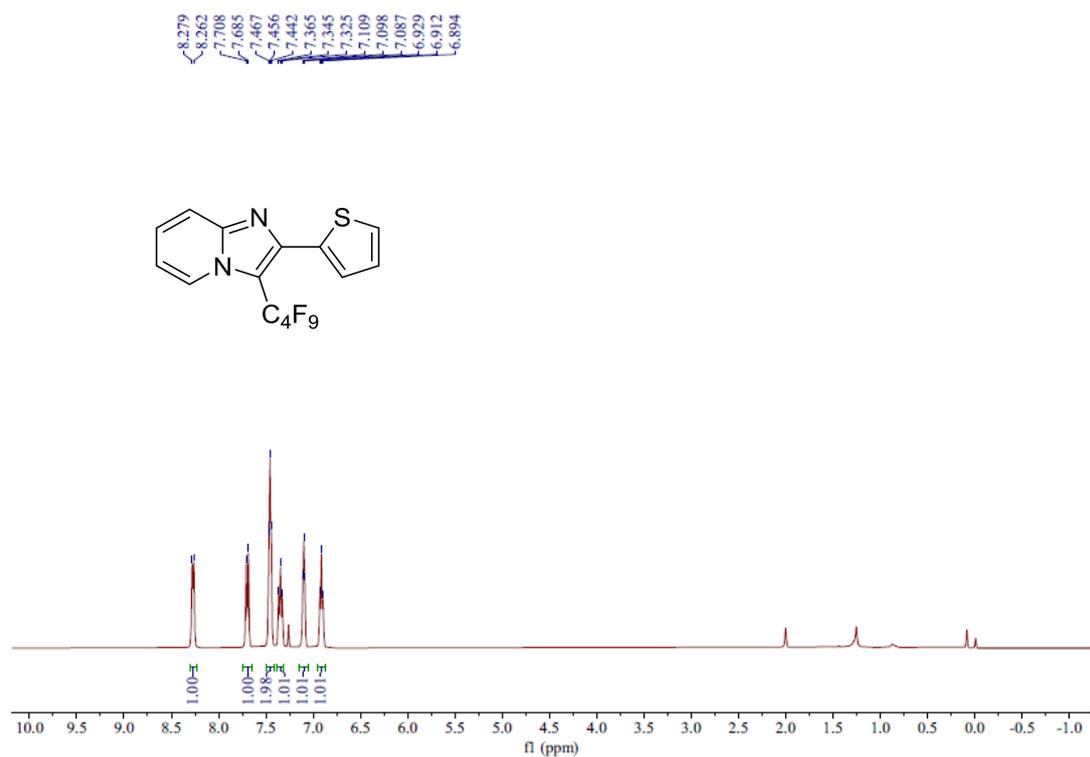
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3oc**



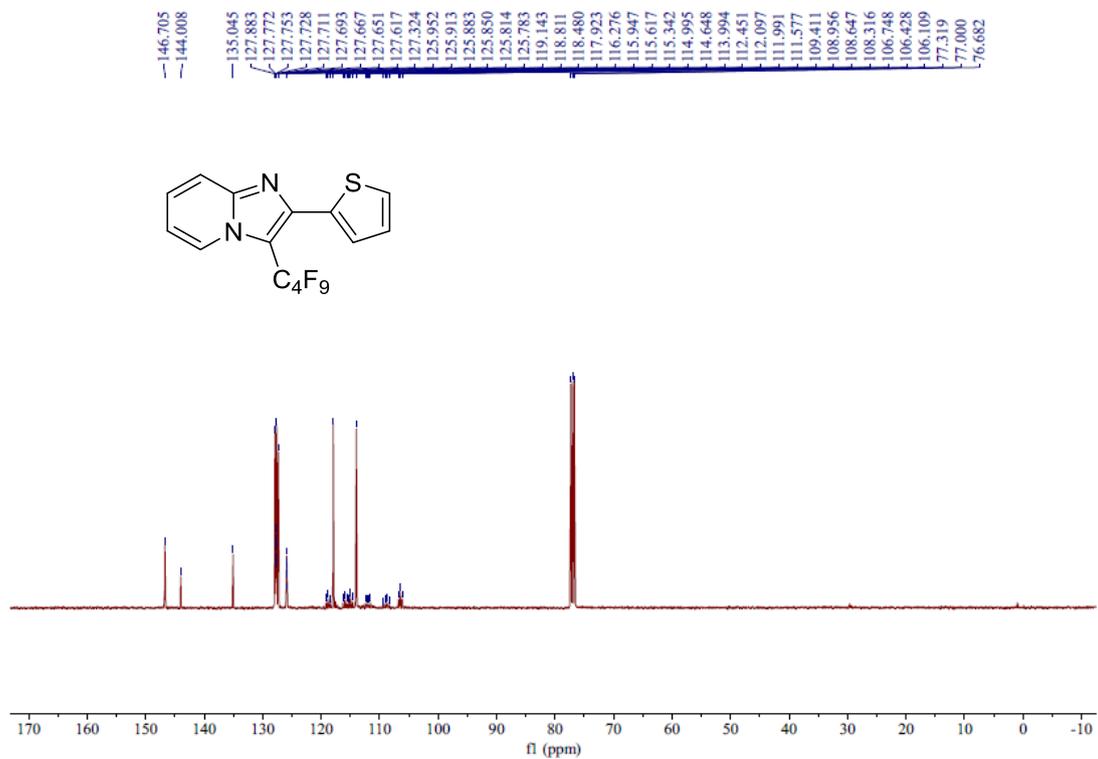
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3oc**



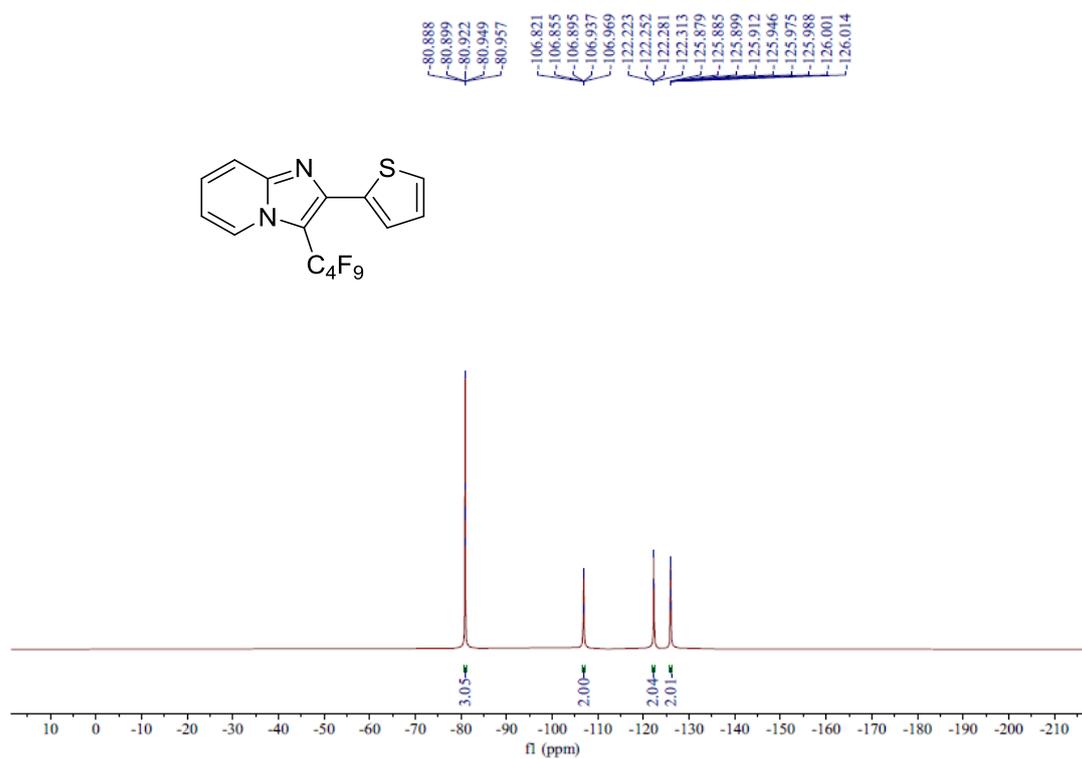
¹H NMR (400 MHz, CDCl₃) Spectrum of **3pc**



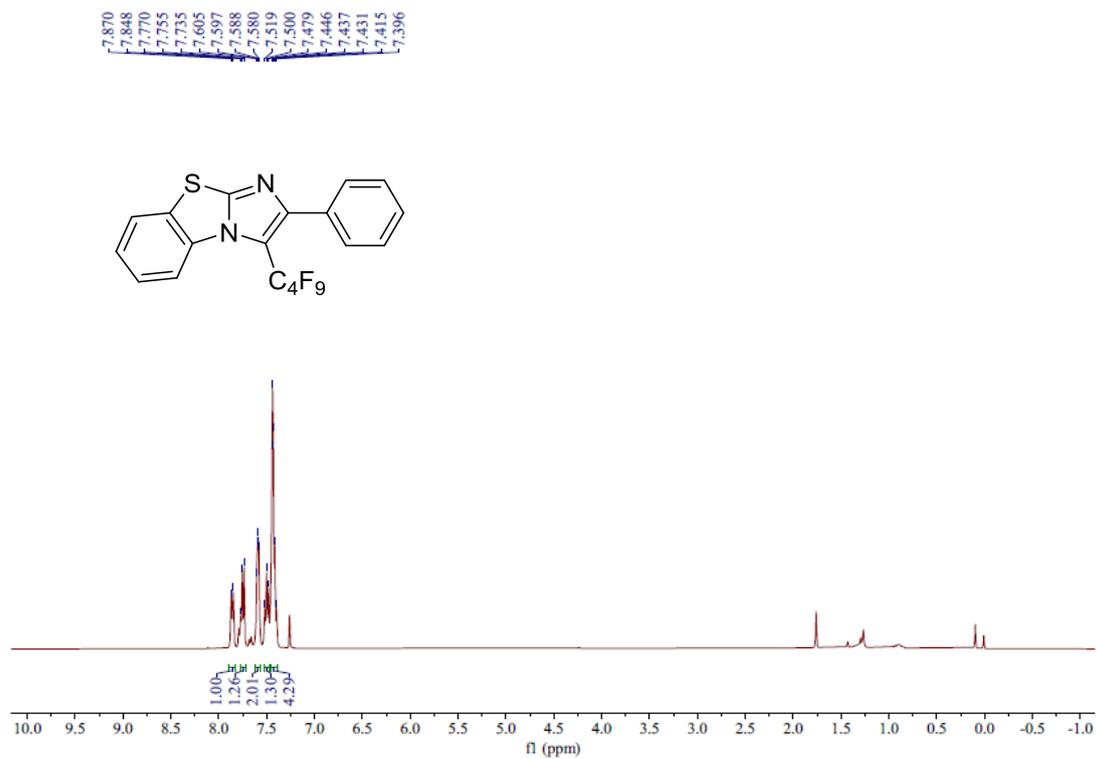
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3pc**



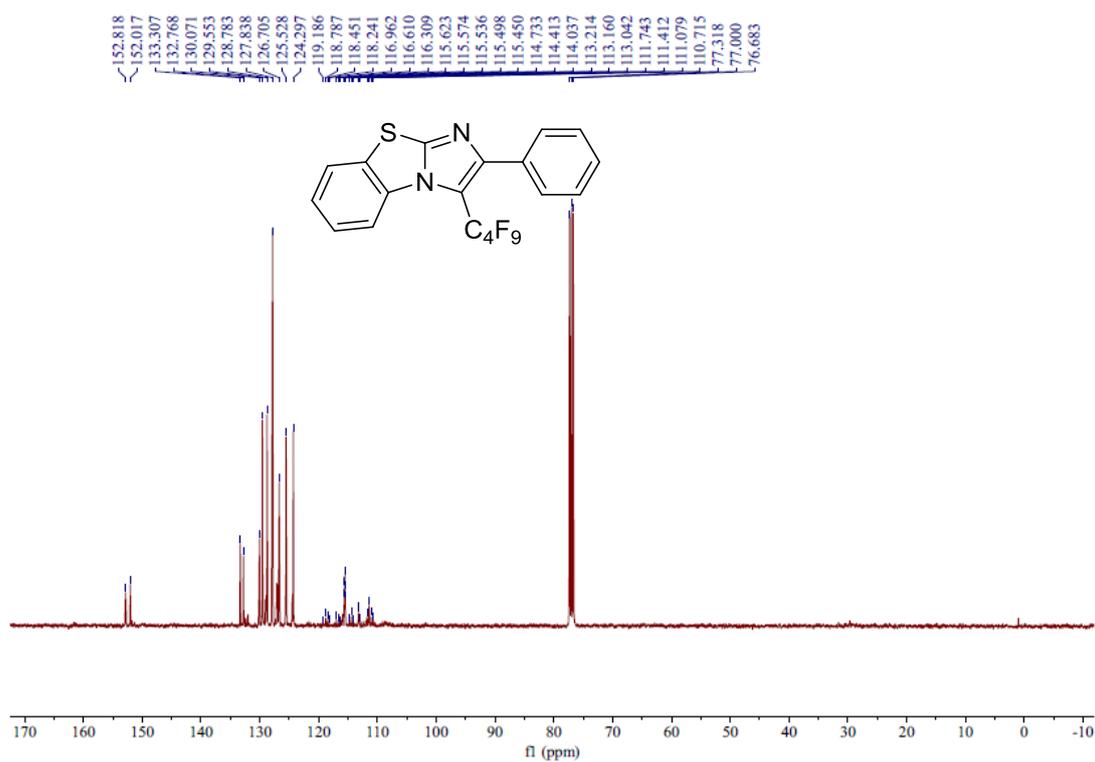
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3pc**



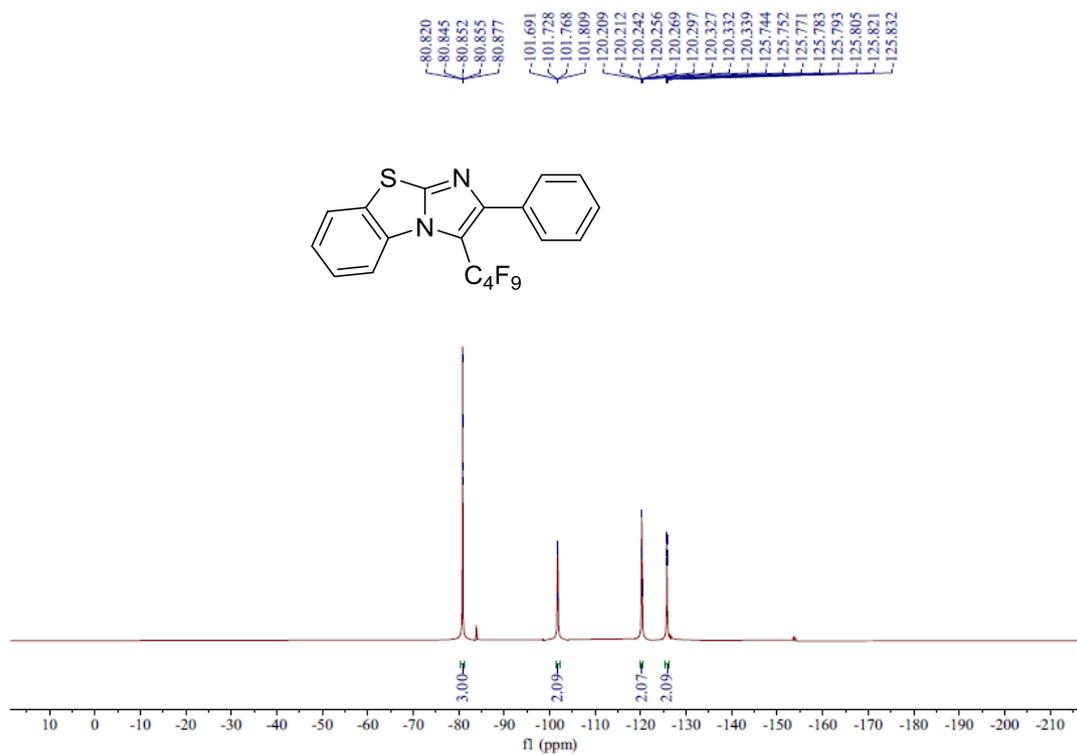
¹H NMR (400 MHz, CDCl₃) Spectrum of **3qc**



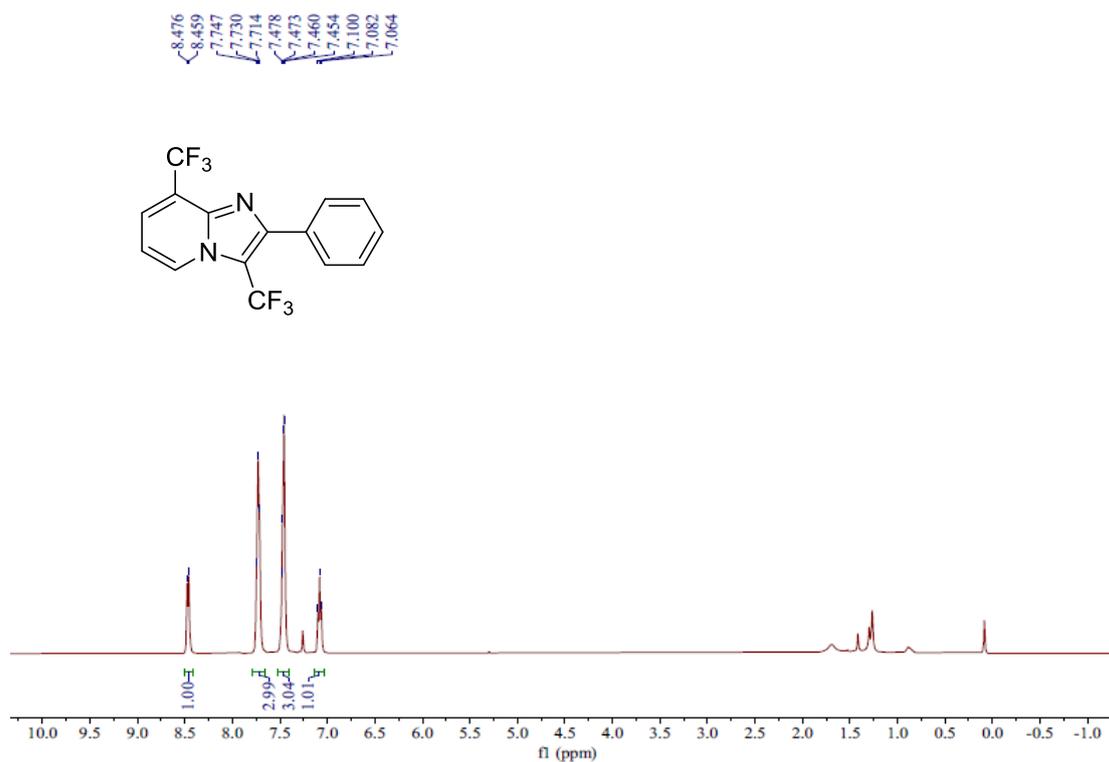
¹³C NMR (100 MHz, CDCl₃) Spectrum of **3qc**



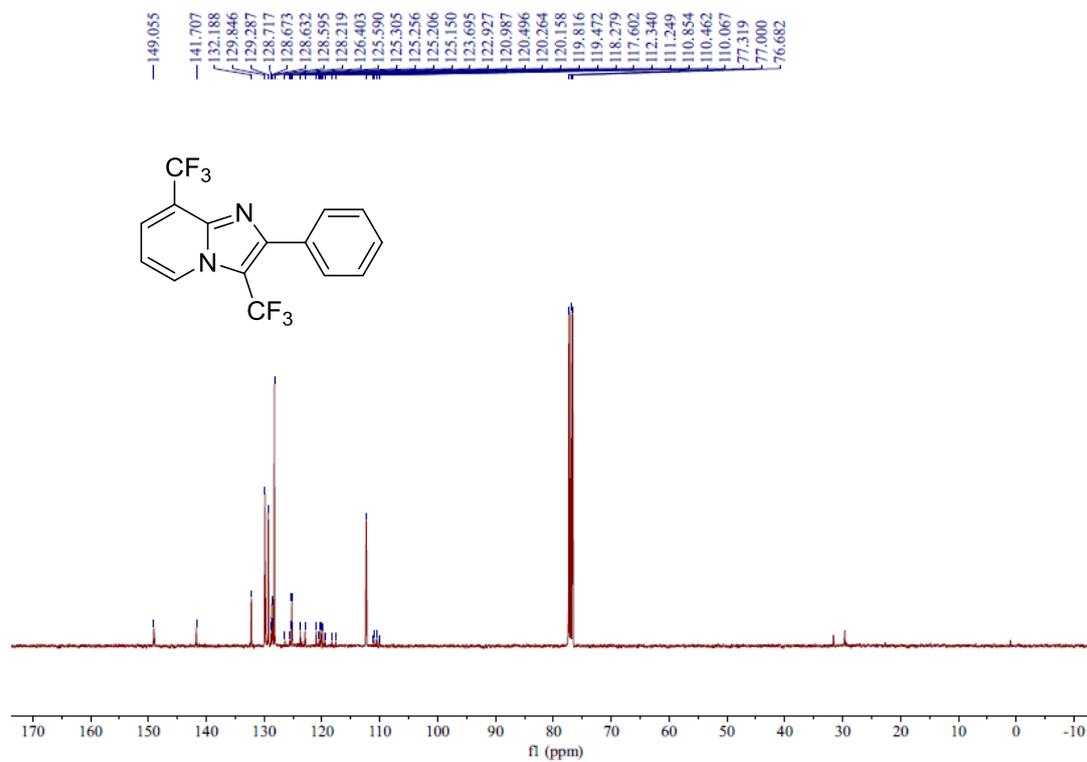
¹⁹F NMR (376 MHz, CDCl₃) Spectrum of **3qc**



¹H NMR (400 MHz, CDCl₃) Spectrum of **4**



¹³C NMR (100 MHz, CDCl₃) Spectrum of **4**



^{19}F NMR (376 MHz, CDCl_3) Spectrum of **4**

