Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Ring-opening and cyclization of aziridines with aryl azides: metal-free synthesis of 6-(triflyloxy)quinolines

Ruxia Yi,[a,b] Xincheng Li[a] and Boshun Wan[a*]

[a]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China

[b] University of Chinese Academy of Sciences, Beijing 100049, China

*E-mail: bswan@dicp.ac.cn

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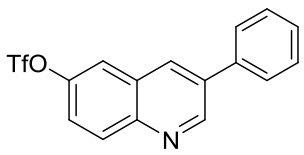
1. General Information

Commercially available reagents were used without further purification. Solvents were treated prior to use according to the standard methods. Column chromatography was carried out on basic alumina (200–300 mesh) using a forced flow of eluent at 0.3–0.5 bar pressure. For TLC, silica gel GF254 was used and visualized by fluorescence quenching under UV light. NMR Spectra were recorded on a Bruker 400 MHz NMR spectrometer in the solvents indicated. The chemical shifts for ^{1}H NMR were recorded in ppm downfield using the central peak of $CDCl_3$ (7.26 ppm) as the internal standard. The chemical shifts for ^{13}C NMR were recorded in ppm downfield using the central peak of $CDCl_3$ (77.16 ppm) as the internal standard. Coupling constants (*J*) are reported in Hz and refer to apparent peak multiplications. The following compounds have been previously prepared and characterized: **1**[1], **2**[2].

2. Synthesis of 6-(triflyloxy)quinolines from 2-azidobenzaldehydes and aziridines

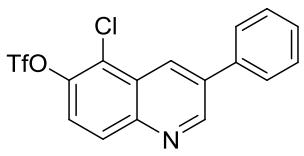
Typical procedure: Under an argon atmosphere, TfOH (4 equiv.) was added to a mixture of 2-azidobenzaldehyde **1** (0.3 mmol) and aziridine **2** (0.6 mmol) in DCE (3 mL). The mixture was stirred at 0 °C for 3 hours. The solvent was evaporated and the crude product was directly purified by flash column chromatography on basic alumina (eluent: petroleum ether/ethyl acetate/dichloromethane) to give the desired product.

3-phenylquinolin-6-yl trifluoromethanesulfonate (**3aa**):



yellow solid; 78.0 mg; 74% yield; mp 70–71°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (m, 1H), 8.29–8.20 (m, 2H), 7.79 (m, 1H), 7.69 (m, 2H), 7.60–7.44 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 147.5, 146.1, 137.0, 135.3, 133.1, 132.3, 129.4, 128. 8, 128.3, 127.6, 123.0, 119.5, 118.9 (q, *J* = 320.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{11}F_3NO_3S^+$ $[M + H]^+$ 354.0406, found 354.0407.

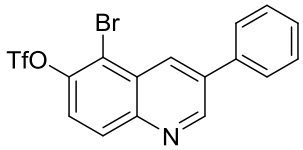
5-chloro-3-phenylquinolin-6-yl trifluoromethanesulfonate (**3ba**):



yellow solid; 69.5 mg; 60% yield; mp 89–90°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.26 (d, *J* = 2.2 Hz, 1H), 8.70 (dd, *J* = 2.2, 0.7 Hz, 1H), 8.15 (d, *J* = 9.3 Hz, 1H), 7.73 (m, 2H), 7.66 (d, *J* = 9.3 Hz, 1H), 7.57–7.46 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 146.2, 143.9, 136.8, 136.0, 130.4, 130.2, 129.5, 129.1, 127.7, 127.0, 124.4, 123.1, 118.8 (q, *J* = 320.6 Hz); ^{19}F NMR

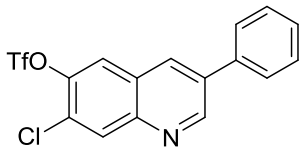
(376 MHz, $CDCl_3$) δ -73.3; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{10}ClF_3NO_3S^+$ [M + H]$^+$ 388.0017, found 388.0025.

5-bromo-3-phenylquinolin-6-yl trifluoromethanesulfonate (**3ca**):



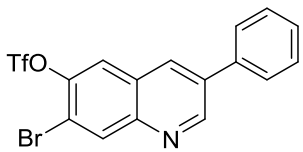
yellow solid; 75.1 mg; 58% yield; mp 146–147°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (m, 1H), 8.70 (m, 1H), 8.20 (m, 1H), 7.75–7.66 (m, 3H), 7.58–7.47 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.7, 146.3, 145.6, 136.8, 136.3, 133.0, 131.2, 129.5, 129.1, 128.4, 127.8, 123.2, 118.8 (q, *J* = 320.6 Hz), 115.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.2; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{10}BrF_3NO_3S^+$ [M + H]$^+$ 431.9511, found 431.9521.

7-chloro-3-phenylquinolin-6-yl trifluoromethanesulfonate (**3da**):



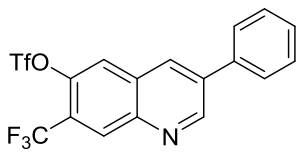
yellow solid; 89.2 mg; 77% yield; mp 84–85°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (m, 1H), 8.29 (m, 2H), 7.88 (s, 1H), 7.39 (m, 2H)，7.56–7.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 146.0, 143.8, 136.8, 135.5, 132.9, 131.8, 129.5, 129.0, 128.2, 127.6, 126.9, 121.0, 118.8 (q, *J* = 320.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.1; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{10}ClF_3NO_3S^+$ [M + H]$^+$ 388.0017, found 388.0031.

7-bromo-3-phenylquinolin-6-yl trifluoromethanesulfonate (**3ea**):



yellow solid; 96.8 mg; 75% yield; mp 97–98°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (m, 1H), 8.46 (m, 1H), 8.24 (m, 1H), 7.85 (m, 1H), 7.67 (m, 2H), 7.55–7.45 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 146.1, 144.8, 136.7, 135.5, 135.3, 132.8, 129.5, 128.9, 127.5, 127.3, 120.5, 118.8 (q, *J* = 320.8 Hz), 116.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.0; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{10}BrF_3NO_3S^+$ [M + H]$^+$ 431.9511, found 431.9524.

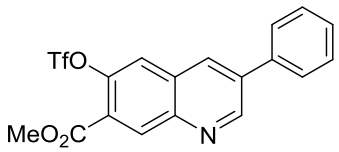
3-phenyl-7-(trifluoromethyl)quinolin-6-yl trifluoromethanesulfonate (**3fa**):



yellow solid; 97.1 mg; 77% yield; mp 90–92°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.32 (d, *J* = 2.1 Hz, 1H), 8.56 (s, 1H), 8.34 (d, *J* = 2.0 Hz, 1H), 8.01 (s, 1H), 7.73–7.71 (m, 2H), 7.58–7.49 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 144.6, 143.1, 137.2, 136.4, 132.6, 131.1 (q, *J* = 5.2 Hz), 130.0, 129.6, 129.4, 127.7, 123.9 (q, *J* = 33.1 Hz), 122.0 (q, *J* = 273.0 Hz), 120.7, 118.6 (q, *J* = 320.3 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.1 (q, *J* = 2.9 Hz), -73.7 (q, *J* = 2.8 Hz); HRMS (Q-TOF, ESI) calcd for $C_{17}H_{10}F_6NO_3S^+$ [M + H]$^+$ 422.0280, found 422.0284.

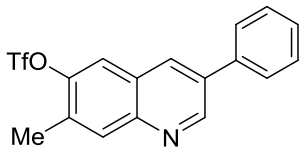
methyl 3-phenyl-6-(((trifluoromethyl)sulfonyl)oxy)quinoline-7-carboxylate (**3ga**):

yellow solid; 80.6 mg; 65% yield; mp 142–143°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ



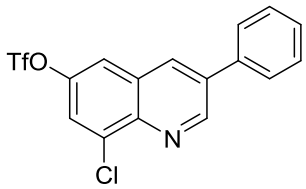
9.28 (d, *J* = 2.2 Hz, 1H), 8.84 (s, 1H), 8.28 (d, *J* = 2.0 Hz, 1H), 7.77 (s, 1H), 7.69 (m, 2H), 7.55–7.46 (m, 3H), 4.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.9, 152.4, 145.3, 145.1, 136.8, 136.5, 135.7, 132.3, 130.3, 129.5, 129.2, 127.6, 125.1, 121.2, 118.9 (q, *J* = 320.8 Hz), 53.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.2; HRMS (Q-TOF, ESI) calcd for $C_{18}H_{13}F_3NO_5S^+$ $[M + H]^+$ 412.0461, found 412.0465.

7-methyl-3-phenylquinolin-6-yl trifluoromethanesulfonate (**3ha**):



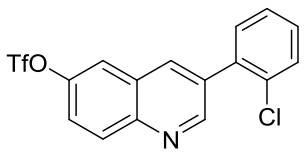
yellow solid; 92.2 mg; 84% yield; mp 92–93°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.15 (s, 1H), 8.18 (s, 1H), 8.01 (s, 1H), 7.74 (s, 1H), 7.65 (m, 2H), 7.52–7.42 (m, 3H), 2.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 147.3, 146.0, 137.1, 134.4, 132.7, 132.7, 132.3, 129.3, 128.5, 127.4, 126.7, 119.1, 118.8 (q, *J* = 320.2 Hz), 17.1; ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.6; HRMS (Q-TOF, ESI) calcd for $C_{17}H_{13}F_3NO_3S^+$ $[M + H]^+$ 368.0563, found 368.0561.

8-chloro-3-phenylquinolin-6-yl trifluoromethanesulfonate (**3ia**):



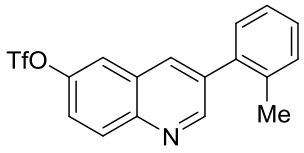
yellow solid; 50.3 mg; 43% yield; mp 78–79°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.34 (d, *J* = 2.2 Hz, 1H), 8.33 (d, *J* = 2.2 Hz, 1H), 7.75 (q, *J* = 2.6 Hz, 2H), 7.70 (m, 2H), 7.55 (m, 2H), 7.50 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 146.4, 142.6, 136.4, 136.3, 136.1, 133.6, 129.6, 129.2, 129.0, 127.6, 123.2, 118.9 (q, *J* = 321.0 Hz), 118.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.5; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{10}ClF_3NO_3S^+$ $[M + H]^+$ 388.0017, found 388.0019.

3-(2-chlorophenyl)quinolin-6-yl trifluoromethanesulfonate (**3ab**):



colorless oil; 75.3 mg; 65% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (d, *J* = 1.5 Hz, 1H), 8.25 (m, 2H), 7.81 (d, *J* = 2.6 Hz, 1H), 7.63 (dd, *J* = 9.3, 2.6 Hz, 1H), 7.55 (m, 1H), 7.48–7.33 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 147.5, 146.1, 136.3, 136.0, 134.0, 133.0, 132.4, 131.6, 130.5, 130.1, 127.8, 127.5, 123.4, 119.6, 118.9 (q, *J* = 321.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{10}ClF_3NO_3S^+$ $[M + H]^+$ 388.0017, found 388.0016.

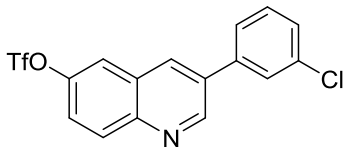
3-(*o*-tolyl)quinolin-6-yl trifluoromethanesulfonate (**3ac**):



yellow oil; 60.8 mg; 55% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.00 (d, *J* = 1.9 Hz, 1H), 8.25 (d, *J* = 9.2 Hz, 1H), 8.12 (d, *J* = 1.7 Hz, 1H), 7.79 (d, *J* = 2.6 Hz, 1H), 7.62 (dd, *J* = 9.2, 2.7 Hz, 1H), 7.36–7.26 (m, 4H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.0, 147.5, 145.8, 137.3, 136.5, 135.9,

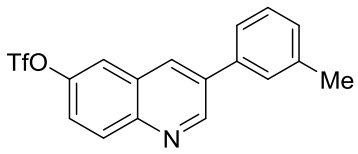
135.3, 132.3, 130.9, 130.2, 128.8, 128.1, 126.5, 123.1, 119.4, 118.9 (q, J = 320.7 Hz), 20.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7; HRMS (Q-TOF, ESI) calcd for $C_{17}H_{13}F_3NO_3S^+$ $[M + H]^+$ 368.0563, found 368.0561.

3-(3-chlorophenyl)quinolin-6-yl trifluoromethanesulfonate (**3ad**):



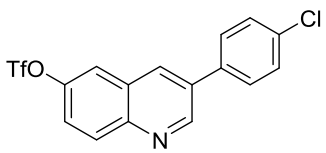
colorless oil; 91.3 mg; 78% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.07 (d, J = 2.0 Hz, 1H), 8.16 (d, J = 1.9 Hz, 1H), 8.11 (d, J = 9.2 Hz, 1H), 7.69 (d, J = 2.6 Hz, 1H), 7.55 (s, 1H), 7.51–7.44 (m, 2H), 7.37–7.30 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 147.6, 146.3, 138.8, 135.4, 133.9, 133.3, 132.3, 130.7, 128.8, 128.1, 127.6, 125.7, 123.76, 119.4, 118.9 (q, J = 320.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{10}ClF_3NO_3S^+$ $[M + H]^+$ 388.0017, found 388.0026.

3-(*m*-tolyl)quinolin-6-yl trifluoromethanesulfonate (**3ae**):



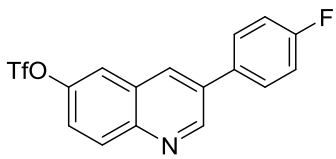
yellow solid; 75.0 mg; 68% yield; mp 73–74°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.22 (d, J = 1.8 Hz, 1H), 8.27 (d, J = 1.5 Hz, 1H), 8.20 (d, J = 9.2 Hz, 1H), 7.78 (d, J = 2.5 Hz, 1H), 7.57 (dd, J = 9.2, 2.6 Hz, 1H), 7.48 (m, 2H), 7.41 (t, J = 7.5 Hz, 1H), 7.27 (m, 1H), 2.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 147.5, 146.0, 139.2, 137.0, 135.4, 133.0, 132.2, 129.5, 129.3, 128.3, 128.3, 124.7, 122.9, 119.4, 118.9 (q, J = 320.8 Hz), 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7; HRMS (Q-TOF, ESI) calcd for $C_{17}H_{13}F_3NO_3S^+$ $[M + H]^+$ 368.0563, found 368.0562.

3-(4-chlorophenyl)quinolin-6-yl trifluoromethanesulfonate (**3af**):



white solid; 101.1 mg; 87% yield; mp 142–143°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.18 (d, J = 1.8 Hz, 1H), 8.27 (d, J = 1.7 Hz, 1H), 8.21 (d, J = 9.2 Hz, 1H), 7.79 (d, J = 2.5 Hz, 1H), 7.63–7.58 (m, 3H), 7.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 147.6, 146.2, 135.5, 135.2, 134.1, 133.1, 132.3, 129.7, 128.8, 128.2, 123.2, 119.5, 118.9 (q, J = 320.8 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{10}ClF_3NO_3S^+$ $[M + H]^+$ 388.0017, found 388.0021.

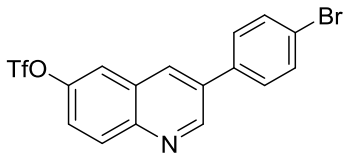
3-(4-fluorophenyl)quinolin-6-yl trifluoromethanesulfonate (**3ag**):



yellow solid; 75.2 mg; 68% yield; mp 70–71°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, J = 2.0 Hz, 1H), 8.24–8.19 (m, 2H), 7.78 (d, J = 2.6 Hz, 1H), 7.66–7.56 (m, 3H), 7.23–7.19 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3 (d, J = 249.1 Hz), 151.1, 147.6, 146.0, 134.3, 133.2 (d, J = 3.3 Hz), 132.9, 132.3, 129.3 (d, J = 8.3 Hz), 128.2, 123.0, 119.4, 118.9 (q, J = 320.9 Hz), 116.5 (d, J = 21.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7, -112.9; HRMS

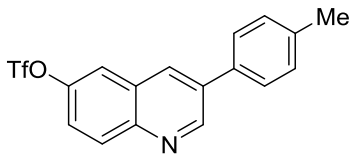
(Q-TOF, ESI) calcd for $C_{16}H_{10}F_4NO_3S^+$ $[M + H]^+$ 372.0312, found 372.0306.

3-(4-bromophenyl)quinolin-6-yl trifluoromethanesulfonate (**3ah**):



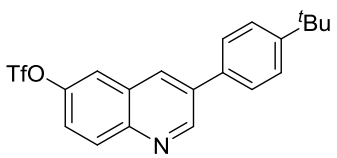
yellow solid; 102.3 mg; 79% yield; mp 141–142°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, *J* = 1.6 Hz, 1H), 8.26 (d, *J* = 1.5 Hz, 1H), 8.20 (d, *J* = 9.2 Hz, 1H), 7.79 (d, *J* = 2.5 Hz, 1H), 7.65–7.53 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.9, 147.6, 146.2, 135.9, 134.1, 133.0, 132.6, 132.3, 129.1, 128.2, 123.4, 123.2, 119.5, 118.9 (q, *J* = 320.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{10}BrF_3NO_3S^+$ $[M + H]^+$ 431.9511, found 431.9515.

3-(*p*-tolyl)quinolin-6-yl trifluoromethanesulfonate (**3ai**):



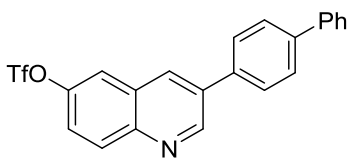
yellow solid; 82.2 mg; 75% yield; mp 87–88°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.23 (d, *J* = 1.7 Hz, 1H), 8.29 (m, 1H), 8.22 (m, 1H), 7.79 (d, *J* = 2.7 Hz, 1H), 7.62–7.56 (dd, *J* = 15.0, 5.4 Hz, 3H), 7.35 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.5, 147.5, 146.0, 138.9, 135.3, 134.1, 132.9, 132.3, 130.2, 128.4, 127.4, 122.8, 121.7 (d, *J* = 240.4 Hz), 119.4, 21.3; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7; HRMS (Q-TOF, ESI) calcd for $C_{17}H_{13}F_3NO_3S^+$ $[M + H]^+$ 368.0563, found 368.0566.

3-(4-(tert-butyl)phenyl)quinolin-6-yl trifluoromethanesulfonate (**3aj**):



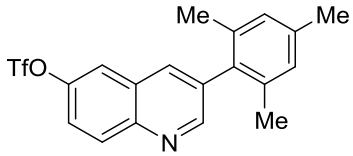
white solid; 90.0 mg; 73% yield; mp 88–89°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (d, *J* = 2.2 Hz, 1H), 8.29 (d, *J* = 2.1 Hz, 1H), 8.21 (d, *J* = 9.2 Hz, 1H), 7.79 (d, *J* = 2.7 Hz, 1H), 7.65 (m, 2H), 7.58 (m, 3H), 1.39 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 151.5, 147.5, 146.0, 135.2, 134.1, 132.7, 132.3, 128.4, 127.3, 126.5, 122.8, 119.4, 118.9 (q, *J* = 320.9 Hz), 34.8, 31.4; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7; HRMS (Q-TOF, ESI) calcd for $C_{20}H_{19}F_3NO_3S^+$ $[M + H]^+$ 410.1032, found 410.1030.

3-([1,1'-biphenyl]-4-yl)quinolin-6-yl trifluoromethanesulfonate (**3ak**):



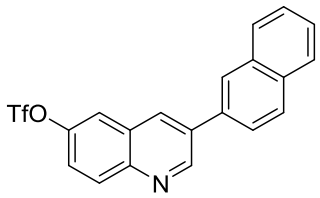
yellow solid; 20.5 mg; 16% yield; mp 126–127°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.31 (s, 1H), 8.38 (d, *J* = 1.2 Hz, 1H), 8.25 (d, *J* = 9.2 Hz, 1H), 7.84–7.77 (m, 5H), 7.67 (d, *J* = 7.4 Hz, 2H), 7.61 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 147.6, 146.2, 141.8, 140.3, 135.9, 133.0, 132.4, 129.10, 129.06, 128.2, 128.1, 128.0, 127.9, 127.3, 123.0, 119.5, 119.0 (d, *J* = 320.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.6; HRMS (Q-TOF, ESI) calcd for $C_{22}H_{15}F_3NO_3S^+$ $[M + H]^+$ 430.0719, found 430.0730.

3-mesitylquinolin-6-yl trifluoromethanesulfonate (**3al**):



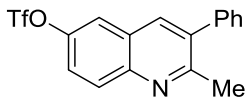
yellow oil; 30.0 mg; 25% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (s, 1H), 8.26 (d, *J* = 9.2 Hz, 1H), 7.99 (s, 1H), 7.77 (s, 1H), 7.63 (d, *J* = 9.1 Hz, 1H), 7.02 (s, 2H), 2.37 (s, 3H), 2.04 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 147.4, 145.9, 138.2, 136.4, 135.9, 134.2, 132.4, 128.7, 128.3, 123.0, 119.4, 118.9 (d, *J* = 321.0 Hz), 21.2, 21.0; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7; HRMS (Q-TOF, ESI) calcd for $C_{19}H_{17}F_3NO_3S^+$ $[M + H]^+$ 396.0876, found 396.0894.

3-(naphthalen-1-yl)quinolin-6-yl trifluoromethanesulfonate (**3am**):



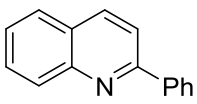
yellow solid; 26.0 mg; 21% yield; mp 98–99°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (d, *J* = 2.0 Hz, 1H), 8.43 (d, *J* = 1.8 Hz, 1H), 8.26 (d, *J* = 9.2 Hz, 1H), 8.18 (s, 1H), 8.02 (m, 1H), 7.96 (m, 1H), 7.92 (m, 1H), 7.87–7.81 (m, 2H), 7.62 (dd, *J* = 9.2, 2.5 Hz, 1H), 7.57 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 147.6, 146.2, 135.4, 134.3, 133.7, 133.4, 133.2, 132.4, 129.4, 128.5, 128.4, 127.9, 127.0, 127.0, 125.1, 123.1, 119.5, 119.0 (d, *J* = 321.0 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.6; HRMS (Q-TOF, ESI) calcd for $C_{20}H_{13}F_3NO_3S^+$ $[M + H]^+$ 404.0563, found 404.0553.

2-methyl-3-phenylquinolin-6-yl trifluoromethanesulfonate (**3aq**):



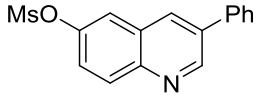
colorless oil; 30.0 mg; 27% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (d, *J* = 9.2 Hz, 1H), 7.99 (s, 1H), 7.72 (d, *J* = 1.8 Hz, 1H), 7.58 (dd, *J* = 9.2, 1.9 Hz, 1H), 7.52–7.43 (m, 3H), 7.40 (m, 2H), 2.68 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 146.9, 145.9, 139.2, 137.5, 136.0, 131.5, 129.2, 128.8, 128.2, 127.0, 123.0, 119.0, 118.9 (d, *J* = 320.8 Hz), 24.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.7; HRMS (Q-TOF, ESI) calcd for $C_{17}H_{13}F_3NO_3S^+$ $[M + H]^+$ 368.0563, found 368.0579.

2-phenylquinoline (**4aa**)[3]:



white solid; 29.6 mg; 48% yield; mp 86–87°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23–8.17 (m, 4H), 7.88 (d, *J* = 8.6 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.76–7.72 (m, 1H), 7.56–7.46 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.5, 148.4, 139.8, 136.9, 129.8, 129.8, 129.5, 129.0, 127.7, 127.6, 127.3, 126.4, 119.2.

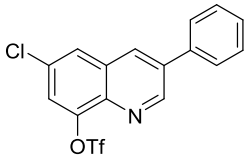
3-phenylquinolin-6-yl methanesulfonate (**5**):



yellow solid; 37.3 mg; 42% yield; mp 119–120°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (d, *J* = 2.2 Hz, 1H), 8.30 (d, *J* = 2.1 Hz, 1H), 8.20 (d, *J* = 9.1 Hz, 1H), 7.83 (d, *J* = 2.6 Hz, 1H), 7.71 (m, 2H), 7.62 (dd, *J* = 9.1, 2.6 Hz, 1H), 7.56–7.52 (m, 2H), 7.49–7.45 (m, 1H), 3.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.83, 147.28, 145.91, 137.36, 135.03, 133.15,

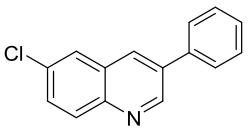
131.88, 129.45, 128.67, 128.51, 127.61, 124.23, 119.72, 37.88; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{14}NO_3S^+$ $[M + H]^+$ 300.0689, found 300.0692.

6-chloro-3-phenylquinolin-8-yl trifluoromethanesulfonate (**3ja**):



white solid; 36.0 mg; 31% yield; mp 89–90°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.30 (d, *J* = 2.1 Hz, 1H), 8.25 (d, *J* = 2.1 Hz, 1H), 7.90 (d, *J* = 2.1 Hz, 1H), 7.71–7.69 (m, 2H), 7.60–7.49 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.6, 146.2, 138.8, 136.7, 136.6, 131.92, 131.86, 129.9, 129.6, 129.1, 127.7, 127.2, 122.2, 119.02 (d, *J* = 320.5 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.52; HRMS (Q-TOF, ESI) calcd for $C_{16}H_{10}ClF_3NO_3S^+$ $[M + H]^+$ 388.0017, found 388.0018.

6-chloro-3-phenylquinoline (**6**)[4]:

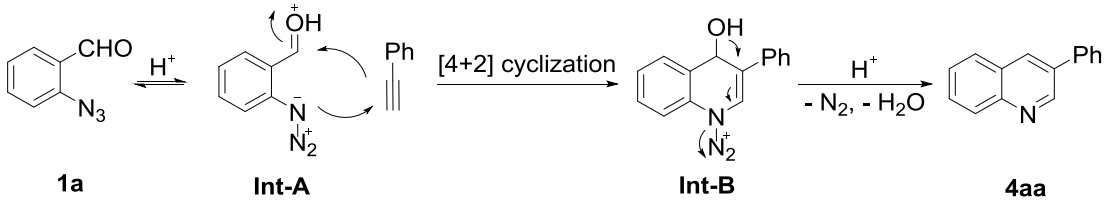


yellow solid; 39.8 mg; 55% yield; mp 92–93°C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.17 (d, J = 2.2 Hz, 1H), 8.21 (d, J = 2.0 Hz, 1H), 8.08 (d, J = 9.0 Hz, 1H), 7.86 (d, J = 2.3 Hz, 1H), 7.71–7.66 (m, 3H), 7.56–7.52 (m, 2H), 7.48–7.44 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 145.8, 137.5, 134.9, 132.9, 132.4, 131.0, 130.5, 129.4, 128.8, 128.6, 127.6, 126.7; HRMS (Q-TOF, ESI) calcd for $C_{15}H_{11}ClN^+$ $[M + H]^+$ 240.0575, found 240.0600.

3. Proposed Reaction Mechanism for the Synthesis of 4aa, 3ja, and 6

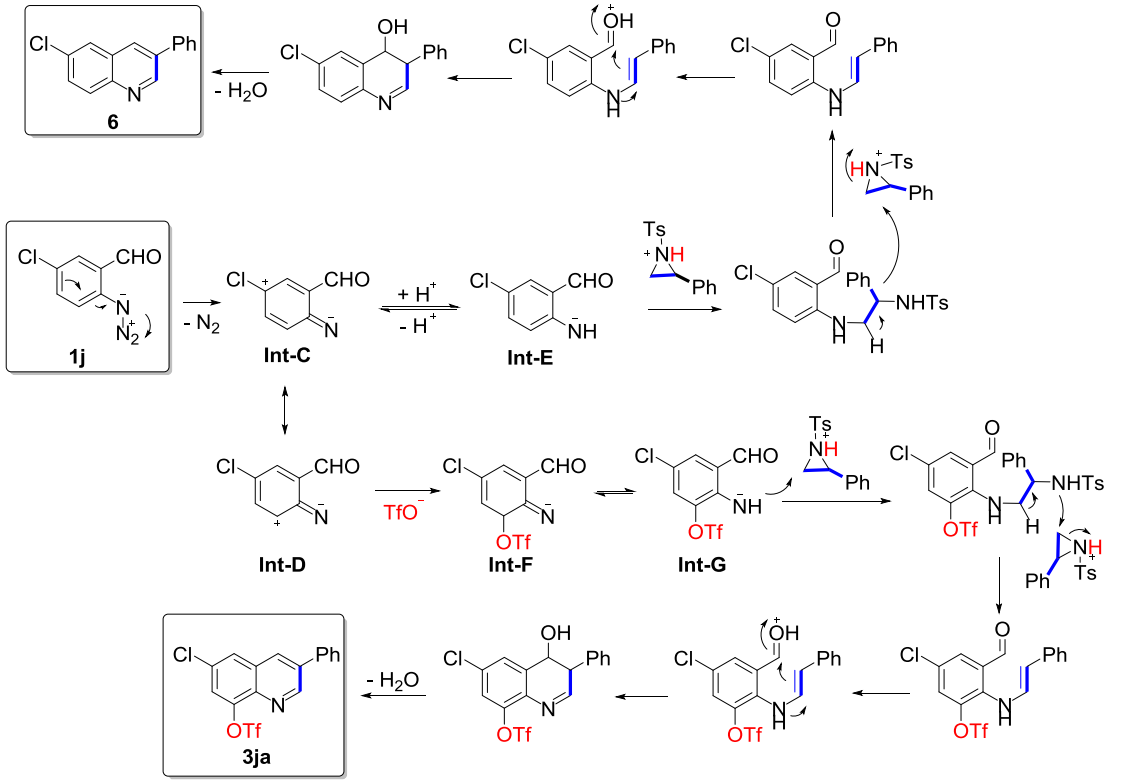
Synthesis of **4aa**:

The reaction was initiated by the TfOH-induced activation of the formyl group of **1a**, with the generation of **Int-A**, followed by a [4+2] cyclization with phenylacetylene. The final emission of N_2 gas and subsequent dehydration of **Int-B** lead to the formation of 3-phenylquinoline **4aa**.

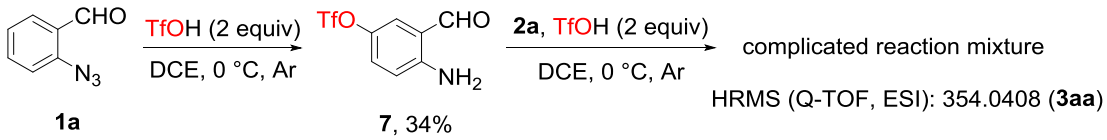


Synthesis of **3ja** and **6**:

Two resonant intermediates **Int-C** and **Int-D** were generated with a conjugate electron-donating atom (Cl) at 5-position of substrate **1j**. **Int-G** was then formed by the nucleophilic attack of oxygen anion of TfOH to the 3-position of **1j**. Meanwhile, unsubstutited intermediate **Int-E** was also generated because of the steric effect. Subsequently, a tandem nucleophilic addition/cyclization/dehydration reaction provides the formation of **3ja** and **6** from **Int-E** and **Int-G** respectively.

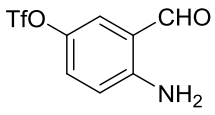


4. Control Experiments



Under an argon atmosphere, TfOH (2 equiv) was added to 2-azidobenzaldehyde **1a** (0.3 mmol) in DCE (3 mL). The mixture was stirred at 0 °C for 3 hours. The solvent was washed with K_2CO_3 (aq.) and the organic phase was collected. The solvent was evaporated and the crude product was directly purified by flash column chromatography (eluent: petroleum ether/ethyl acetate) to give the intermediate 4-amino-3-formylphenyl trifluoromethanesulfonate **7**.

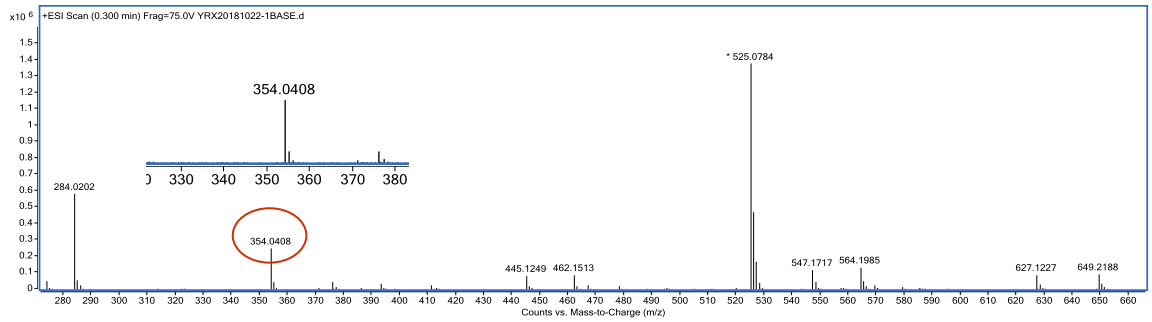
4-amino-3-formylphenyl trifluoromethanesulfonate (**7**):



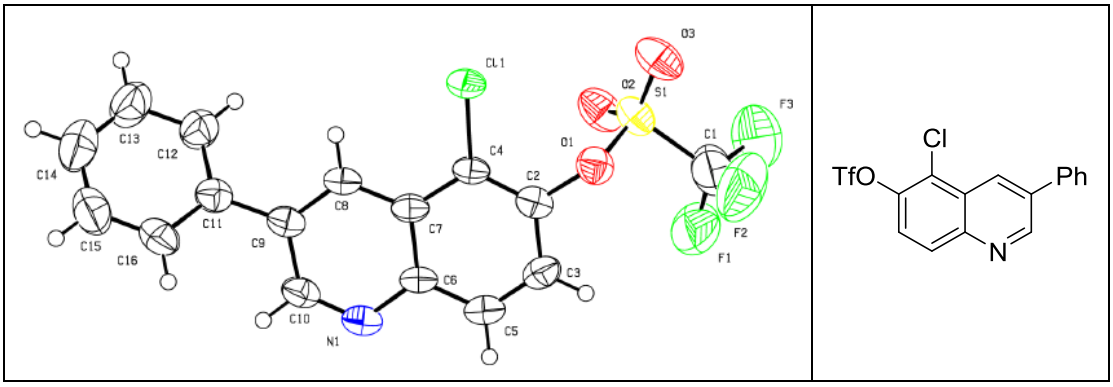
yellow oil; 27.5 mg; 34% yield; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.83 (d, *J* = 1.6 Hz, 1H), 7.39 (d, *J* = 2.8 Hz, 1H), 7.22 (ddd, *J* = 9.1, 2.7, 1.0 Hz, 1H), 6.69 (d, *J* = 9.1 Hz, 1H), 6.32 (br, 2H).; ^{13}C NMR (100 MHz, $CDCl_3$) δ 192.5, 149.5, 139.4, 128.6, 127.3, 118.9 (d, *J* = 321.0 Hz), 118.1, 117.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.68; HRMS (Q-TOF, ESI) calcd for $C_8H_7ClF_3NO_4S^+$ $[M + H]^+$ 270.0042, found 270.0044.

Next, the reaction of the intermediate **7** with **2a** was conducted under standard

reaction conditions, giving a complicated reaction mixture. By micromass HPLC-Q-TOF mass spectrometer analysis, the mass of the product **3aa** was detected in the reaction mixture, HRMS (Q-TOF, ESI) calcd for $C_{16}H_{11}F_3NO_3S^+$ $[M + H]^+$ 354.0406, found 354.0408.



5. Crystal structure of 3ba



ORTEP drawing of **3ba** (CCDC 1830626) with thermal ellipsoids at the 50% probability

Table S1 Crystal data and structure refinement.

Identification code	YRX-74C
Empirical formula	$C_{16}H_9ClF_3NO_3S$
Formula weight	387.75
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	Iba2
a/Å	15.569(2)
b/Å	29.973(4)
c/Å	7.0564(10)
α/°	90
β/°	90
γ/°	90

Volume/$Å^3$	3292.9(8)
Z	8
$\rho_{calc}g/cm^3$	1.564
μ/mm^{-1}	0.406
F(000)	1568.0
Crystal size/mm^3	0.4 × 0.2 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	5.898 to 50.976
Index ranges	$-16 \leq h \leq 16$, $-32 \leq k \leq 32$, $-7 \leq l \leq 7$
Reflections collected	4604
Independent reflections	2015 [R_{int} = 0.0474, R_{sigma} = 0.0450]
Data/restraints/parameters	2015/1/226
Goodness-of-fit on F^2	1.115
Final R indexes [I>=2σ (I)]	R_1 = 0.0494, wR_2 = 0.1180
Final R indexes [all data]	R_1 = 0.0547, wR_2 = 0.1234
Largest diff. peak/hole / e $Å^{-3}$	0.44/-0.52
Flack parameter	-0.01(10)

6. References

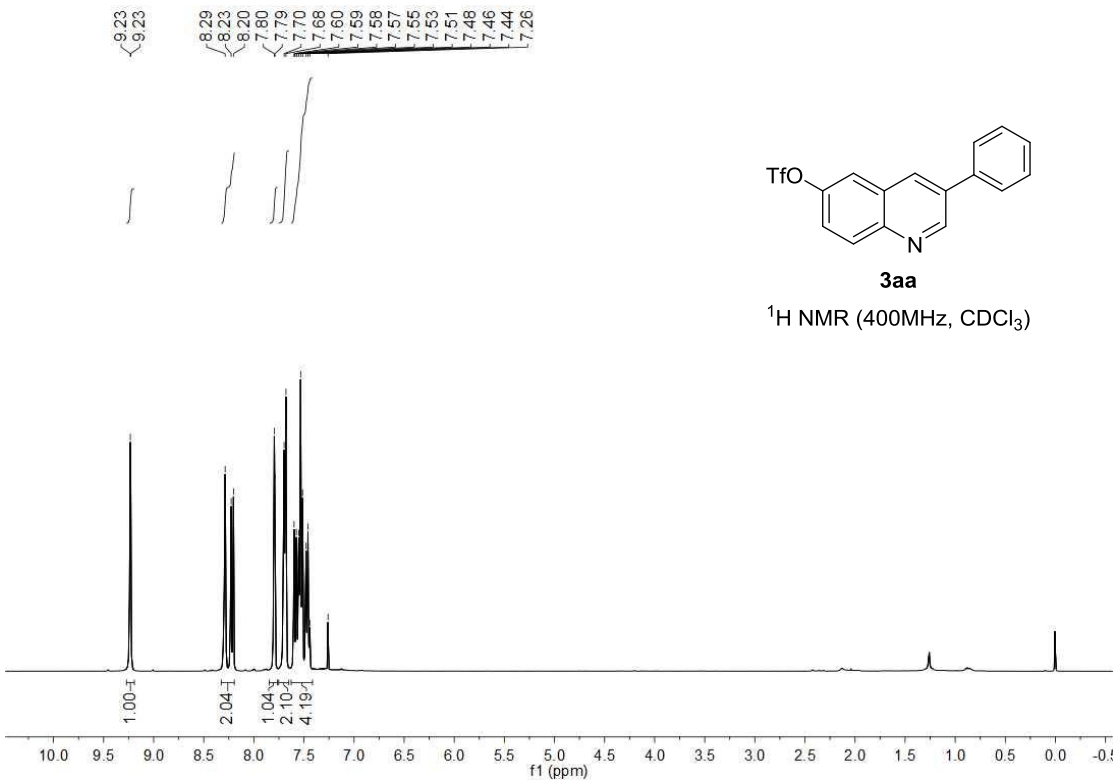
[1] a) J. Hu, Y. Cheng, Y. Yang, and Y. Rao, *Chem. Commun*., 2011, **47**, 10133; b) B. J. Stokes, S. Liu, and T. G. Driver, *J. Am. Chem. Soc*., 2011, **133**, 4702; c) K. Sun, S. Liu, P. M. Bec, and T. G. Driver, *Angew. Chem. Int. Ed*., 2011, **50**, 1702.

[2] P. Dauban, L. Sanière, A. Tarrade, and R. H. Dodd, *J. Am. Chem. Soc*., 2001, **123**, 7707.

[3] A. I. R. N. A. Barros, A. F. R. Dias, and A. M. S. Silva, *Monatshefte für Chemie*, 2007, **138**, 585.

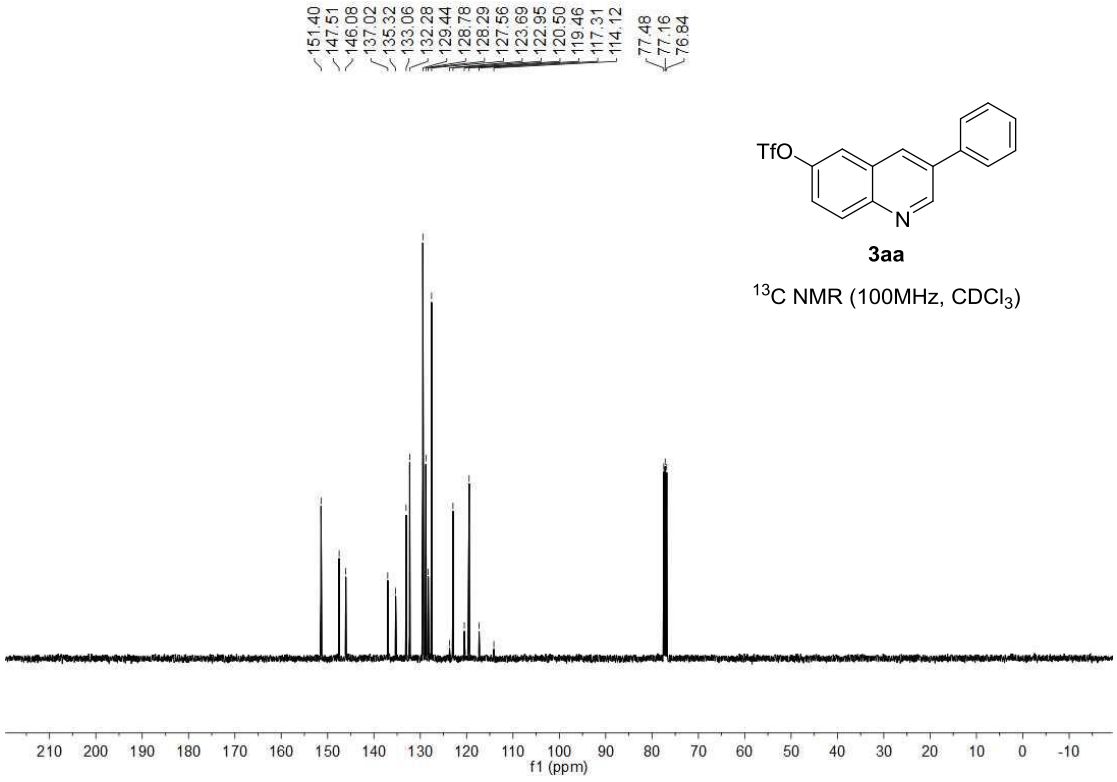
[4] R. K. Saunthwal, M. Patel, and A. K. Verma, *J. Org. Chem*., 2016, **81**, 6563.

7. Copies of NMR Spectra



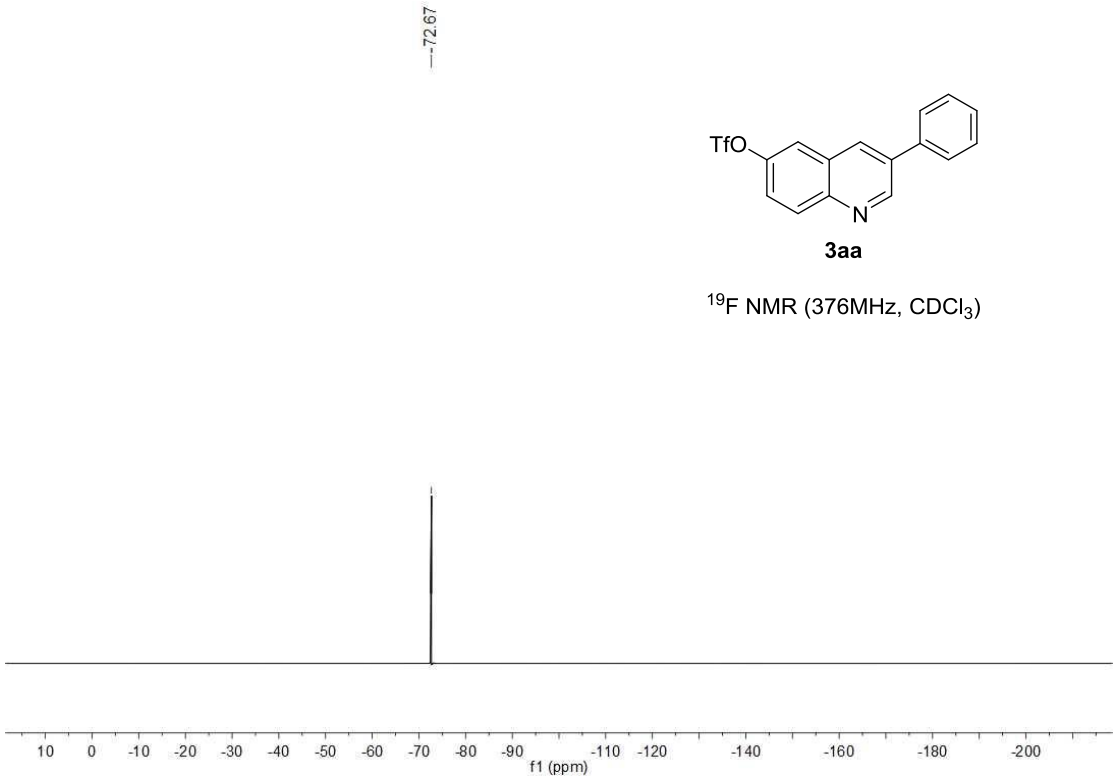
3aa

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



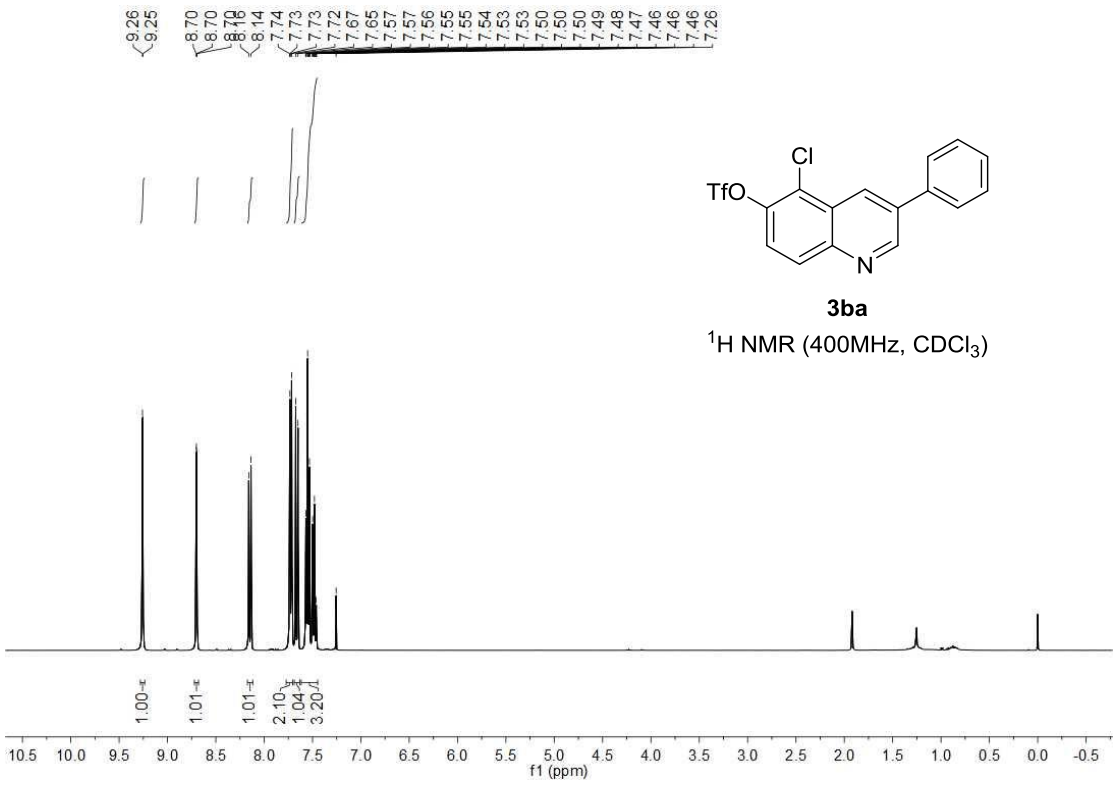
3aa

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



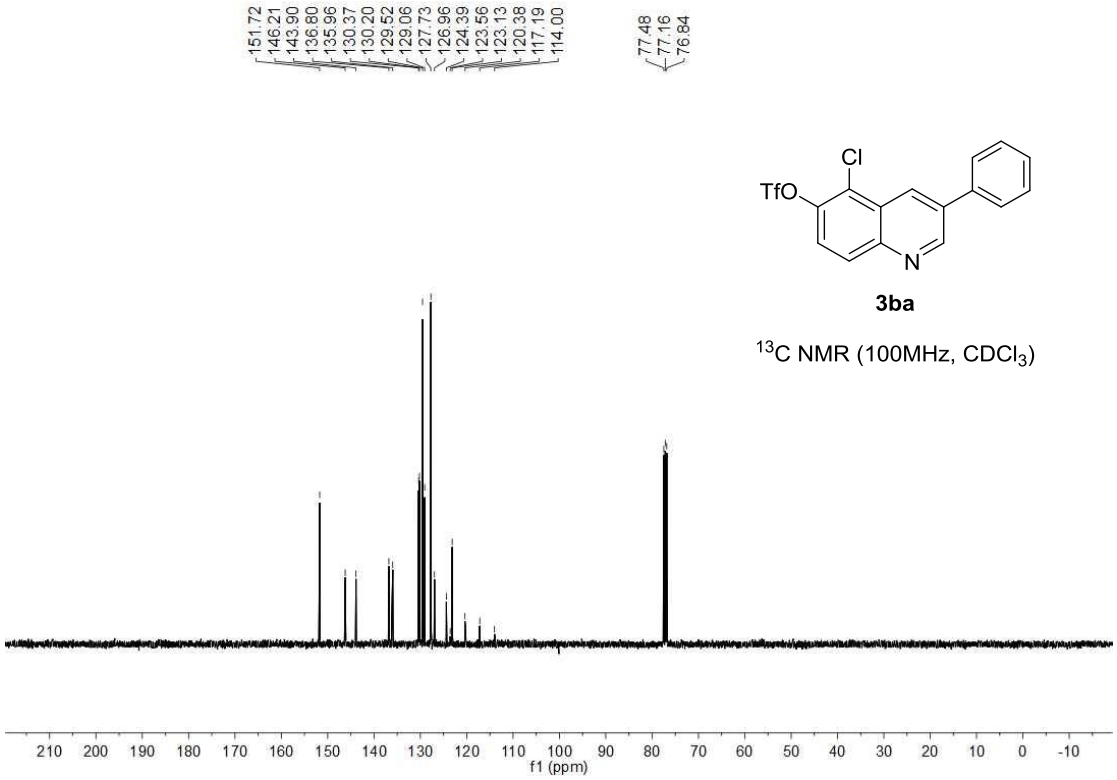
3aa

^{19}F NMR (376MHz, $CDCl_3$)



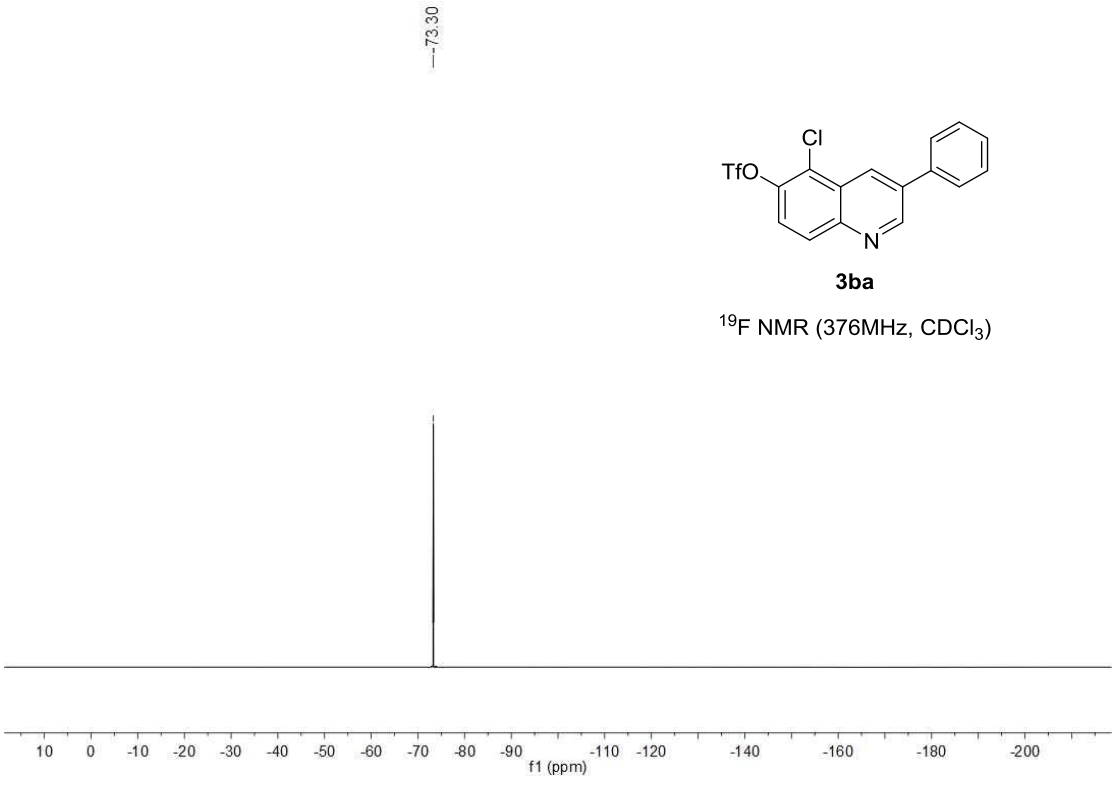
3ba

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



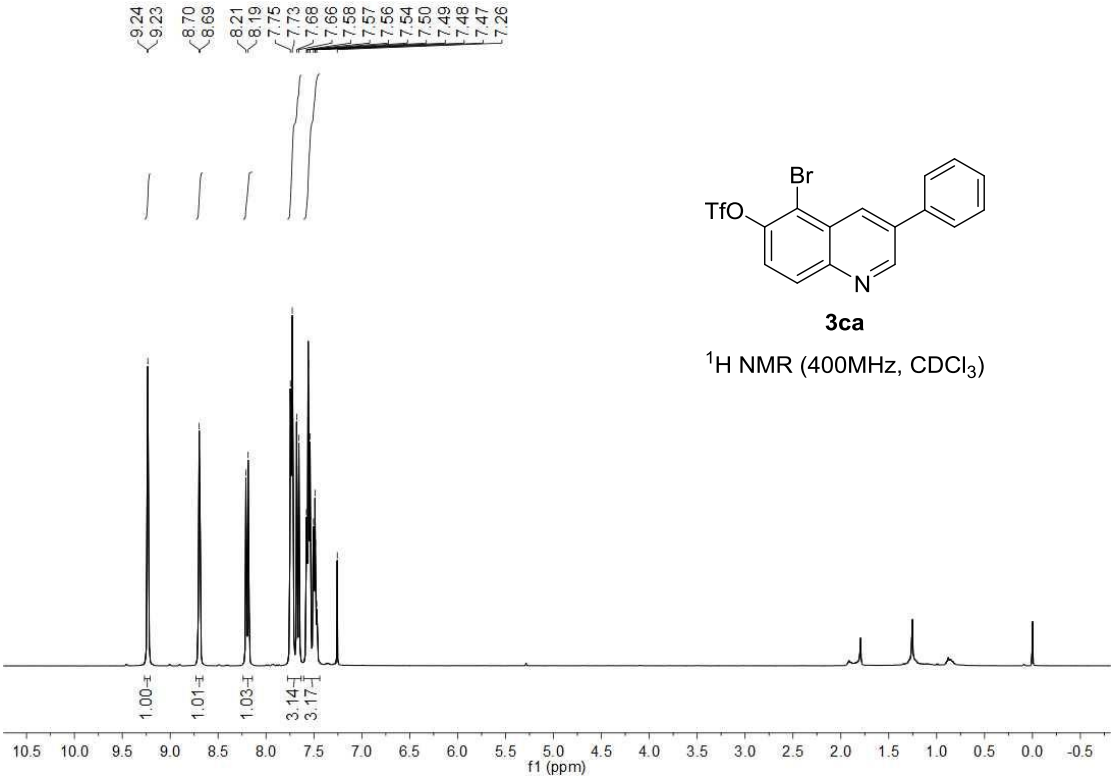
3ba

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



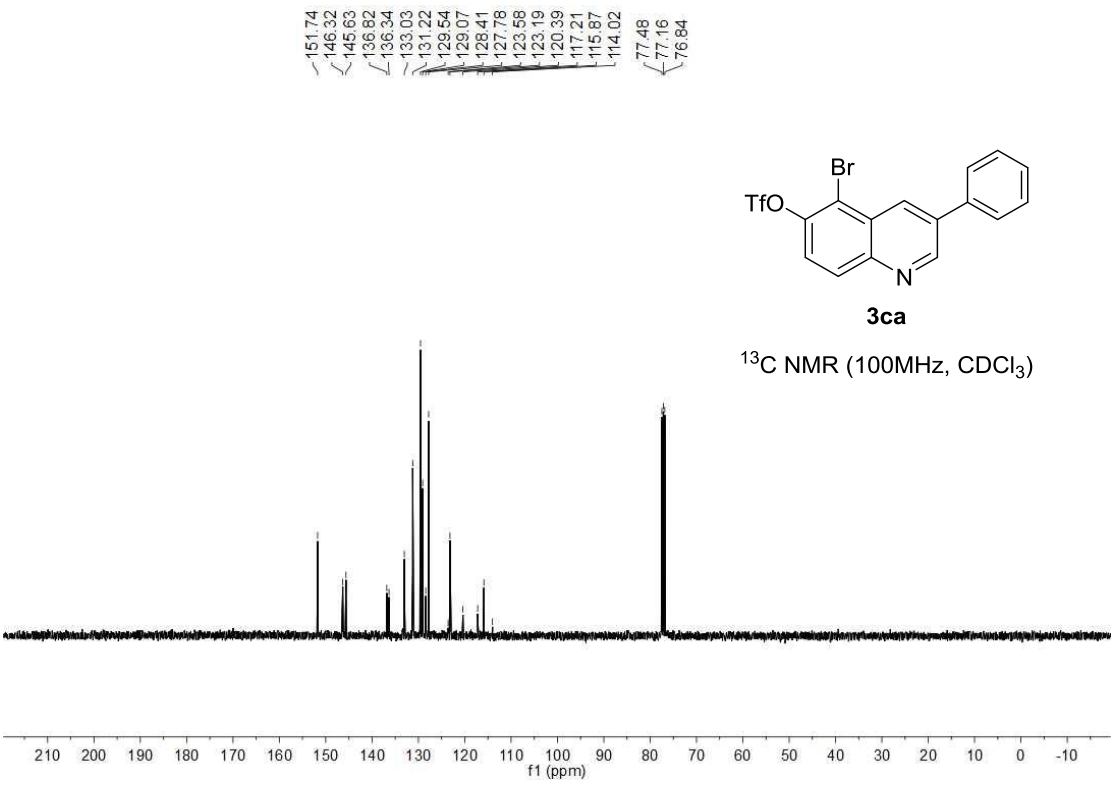
3ba

^{19}F NMR (376MHz, $CDCl_3$)



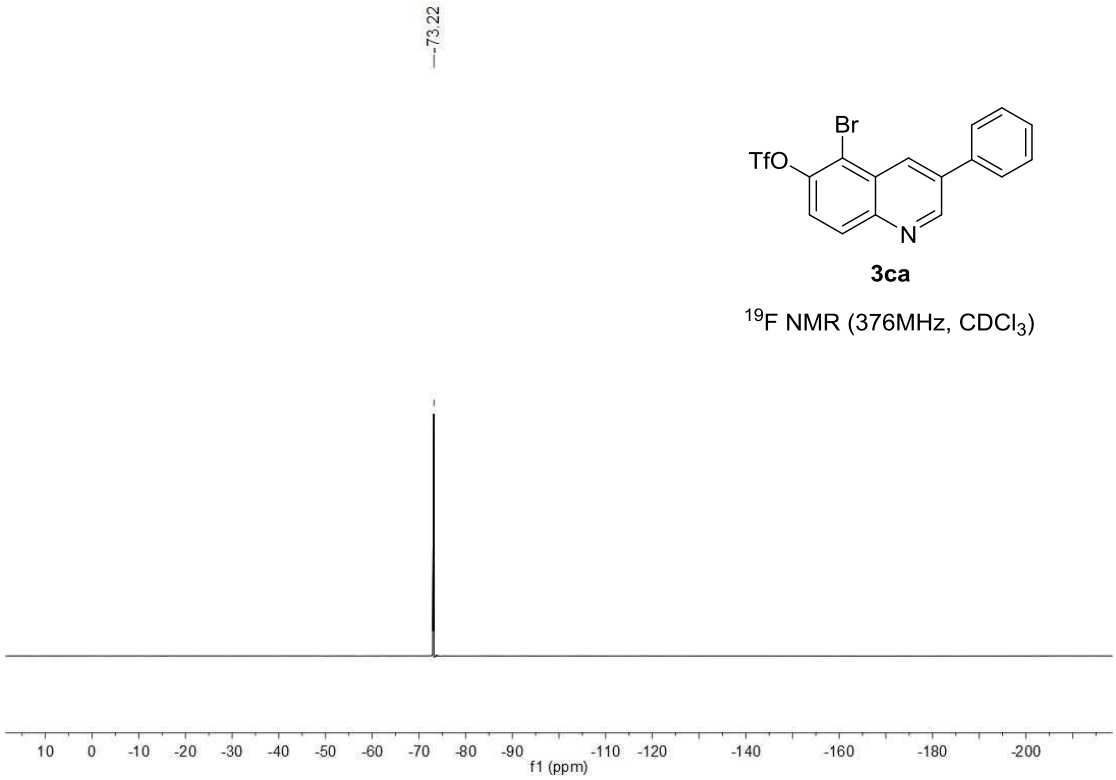
3ca

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



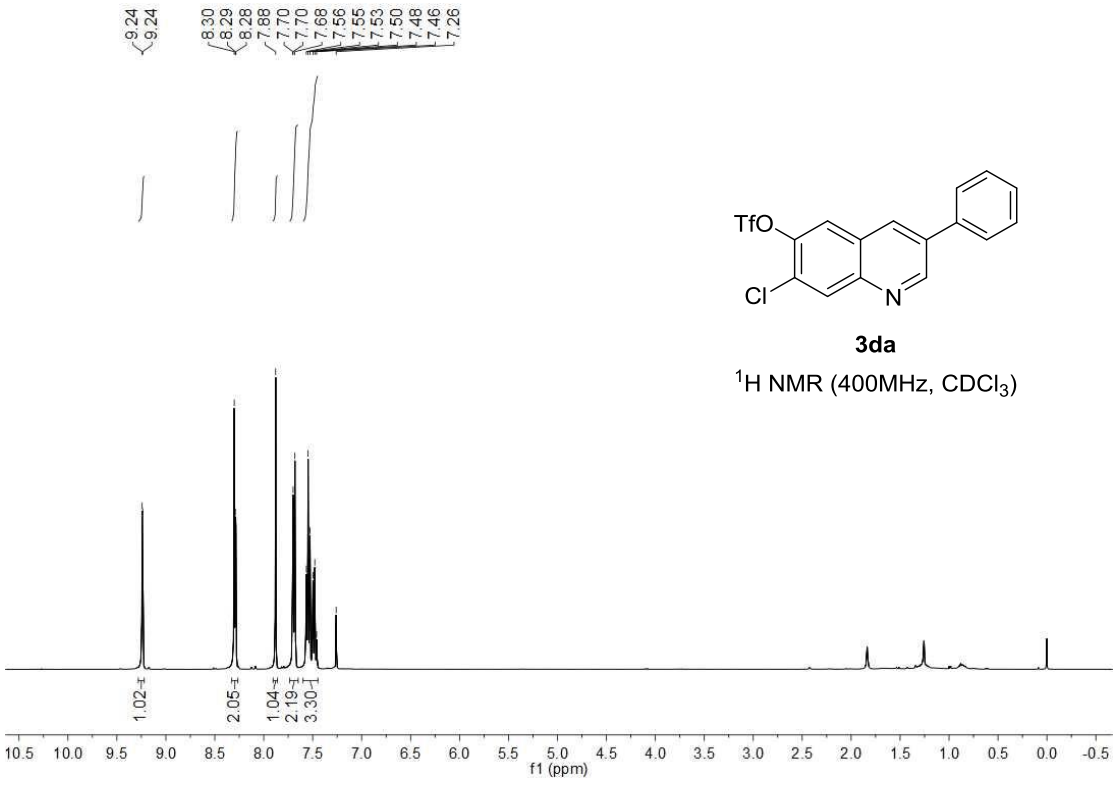
3ca

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



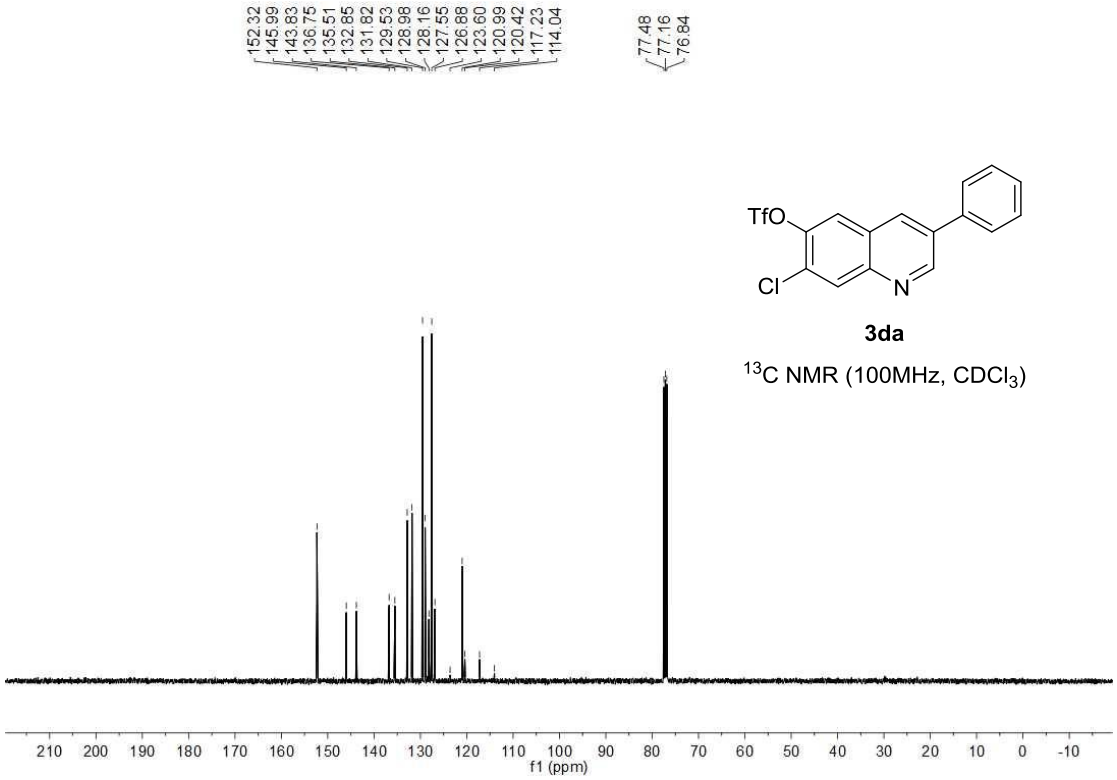
3ca

^{19}F NMR (376MHz, $CDCl_3$)



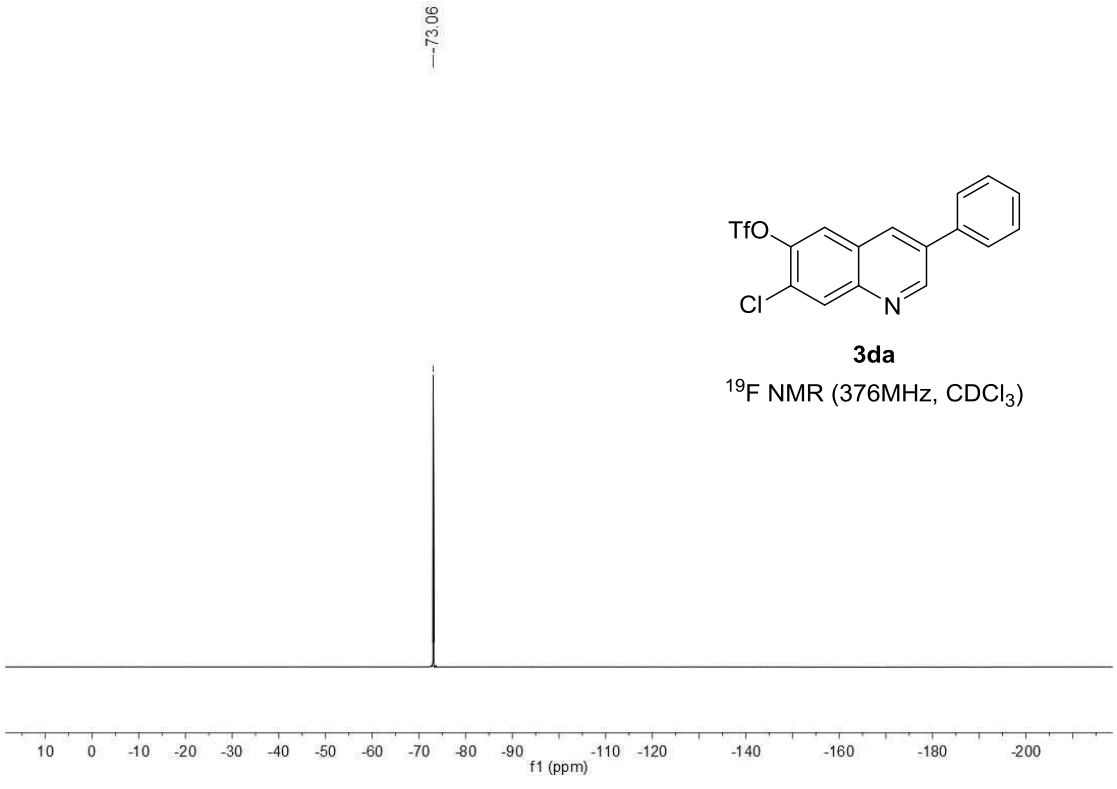
3da

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



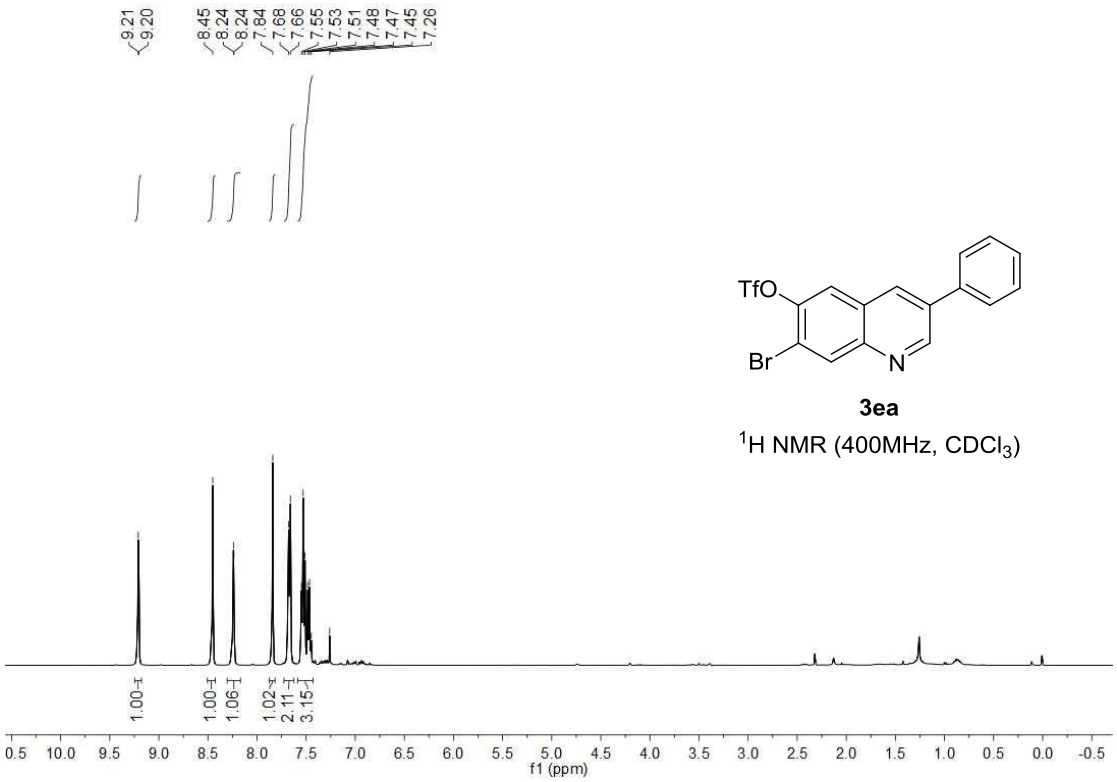
3da

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



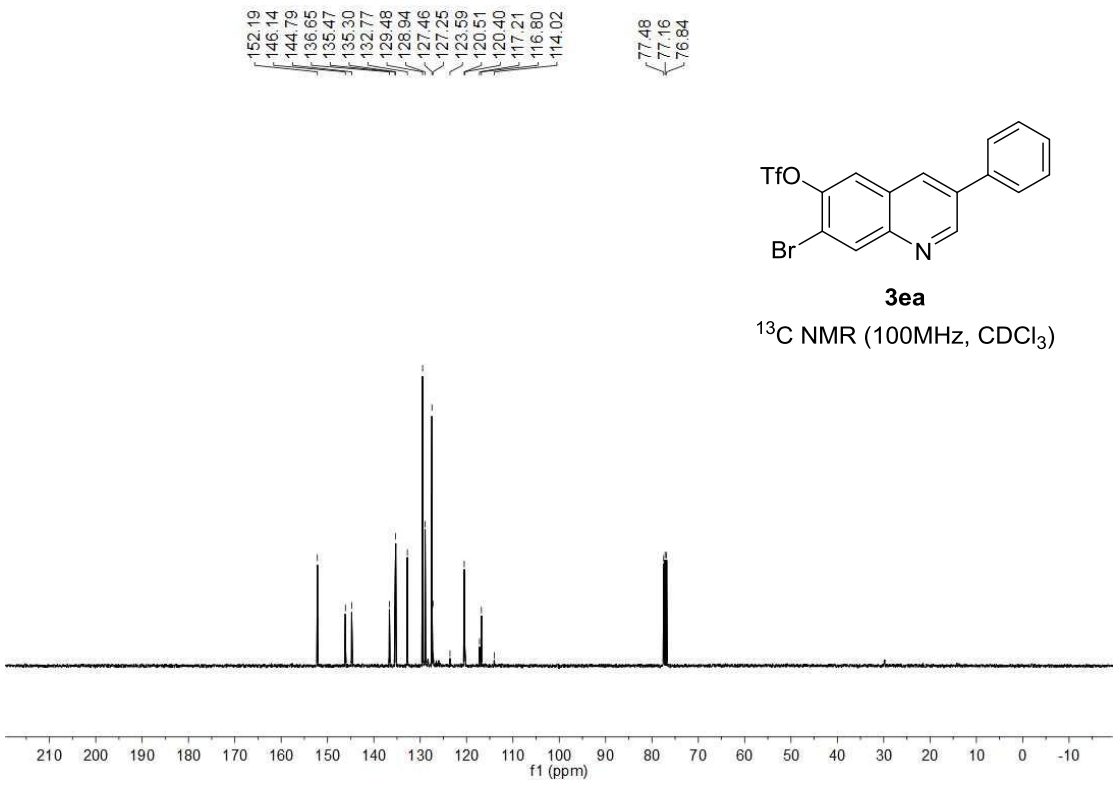
3da

^{19}F NMR (376MHz, $CDCl_3$)



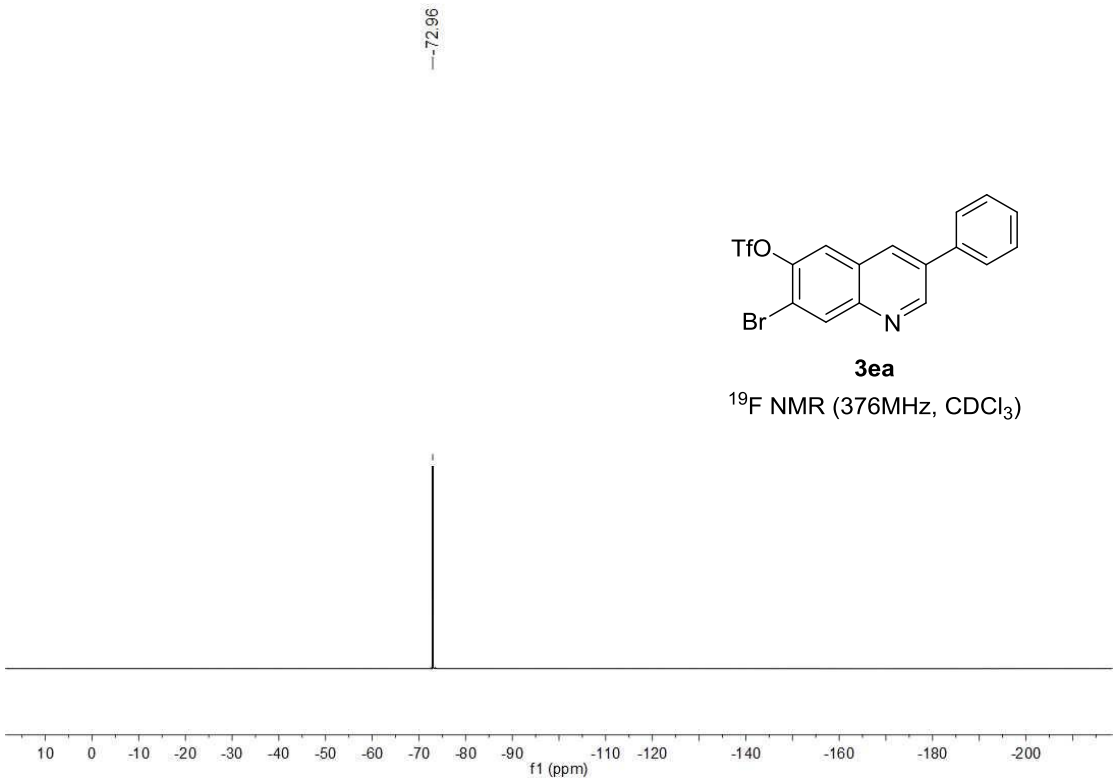
3ea

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



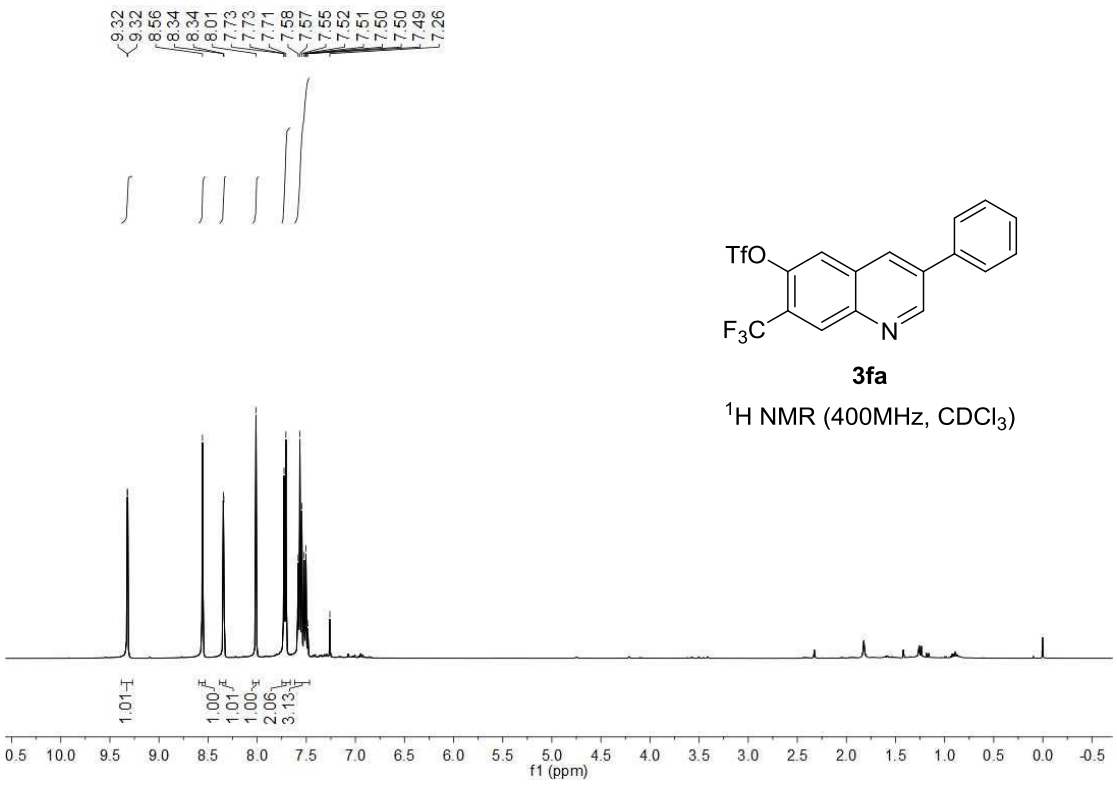
3ea

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



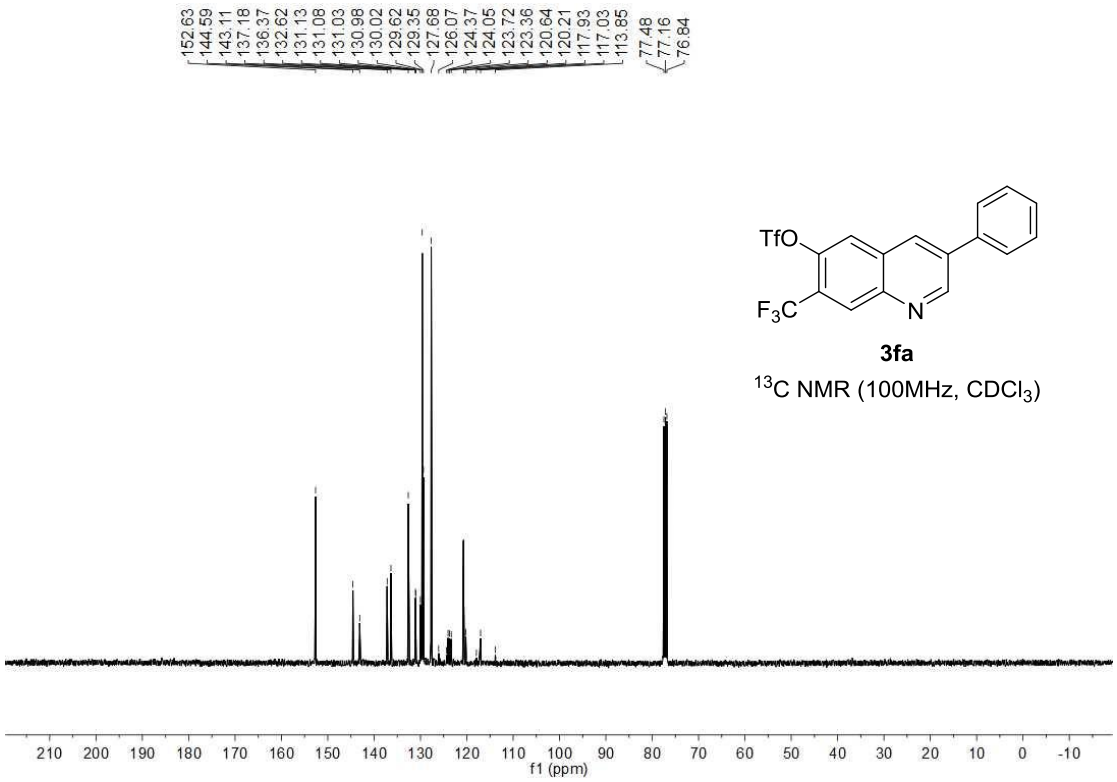
3ea

^{19}F NMR (376MHz, $CDCl_3$)



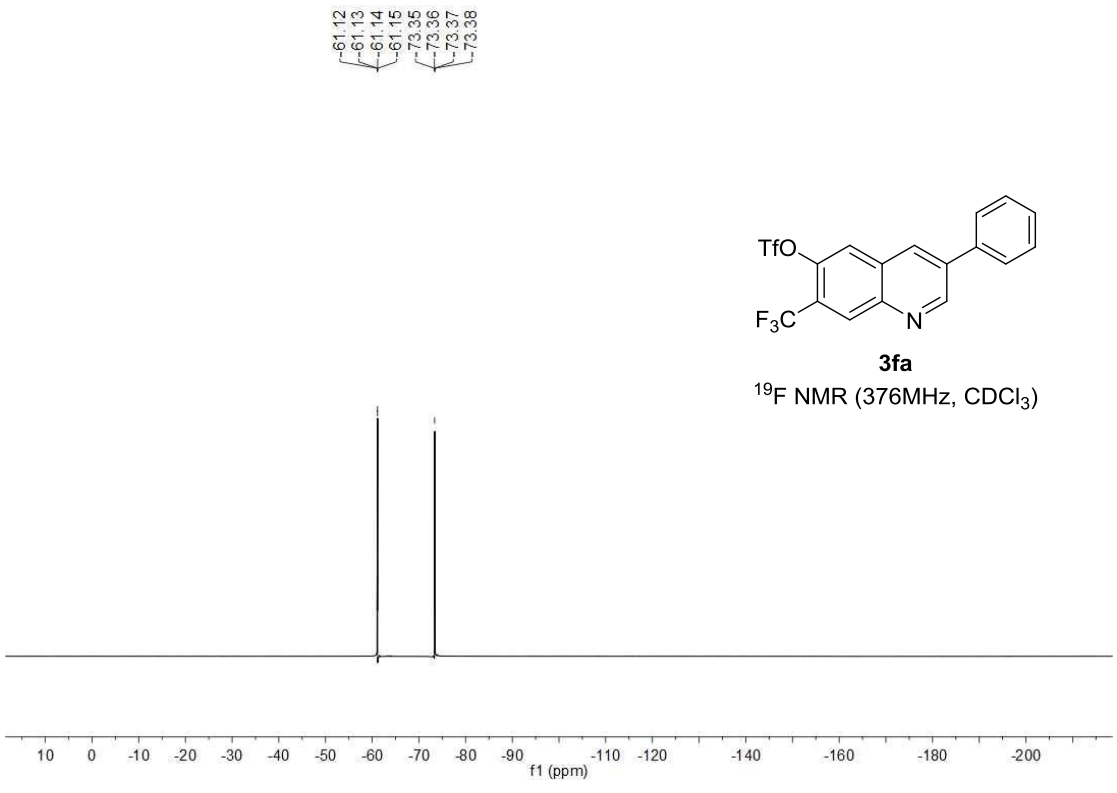
3fa

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



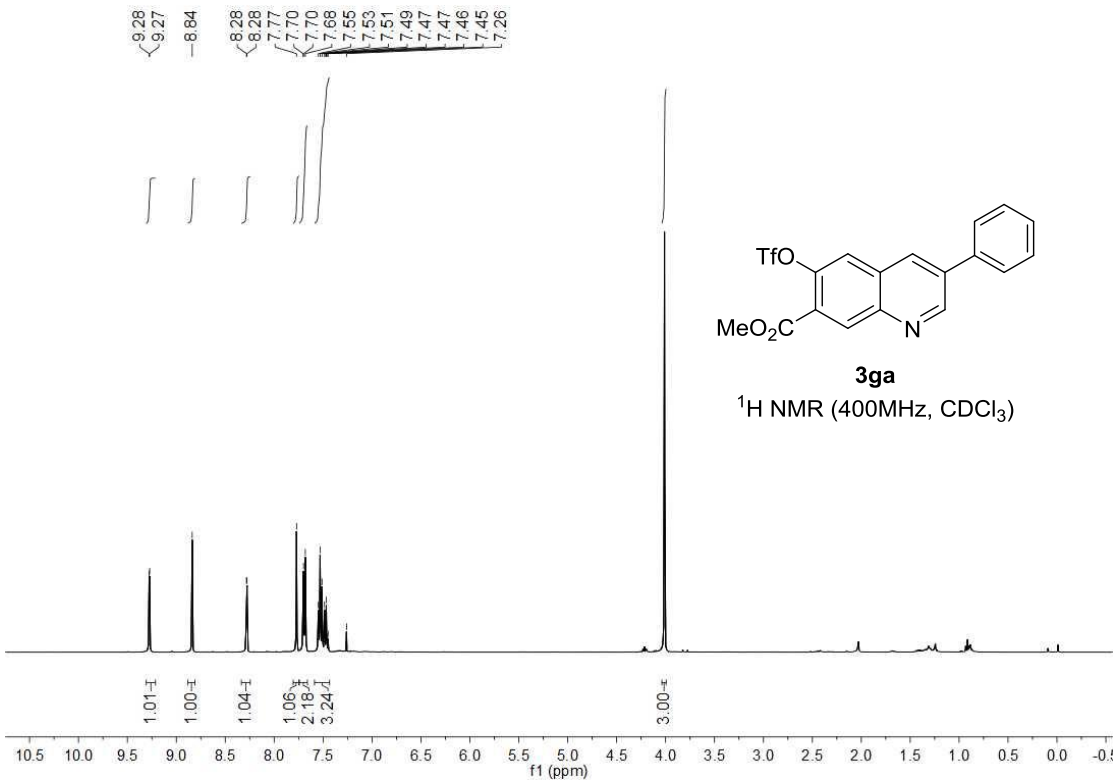
3fa

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



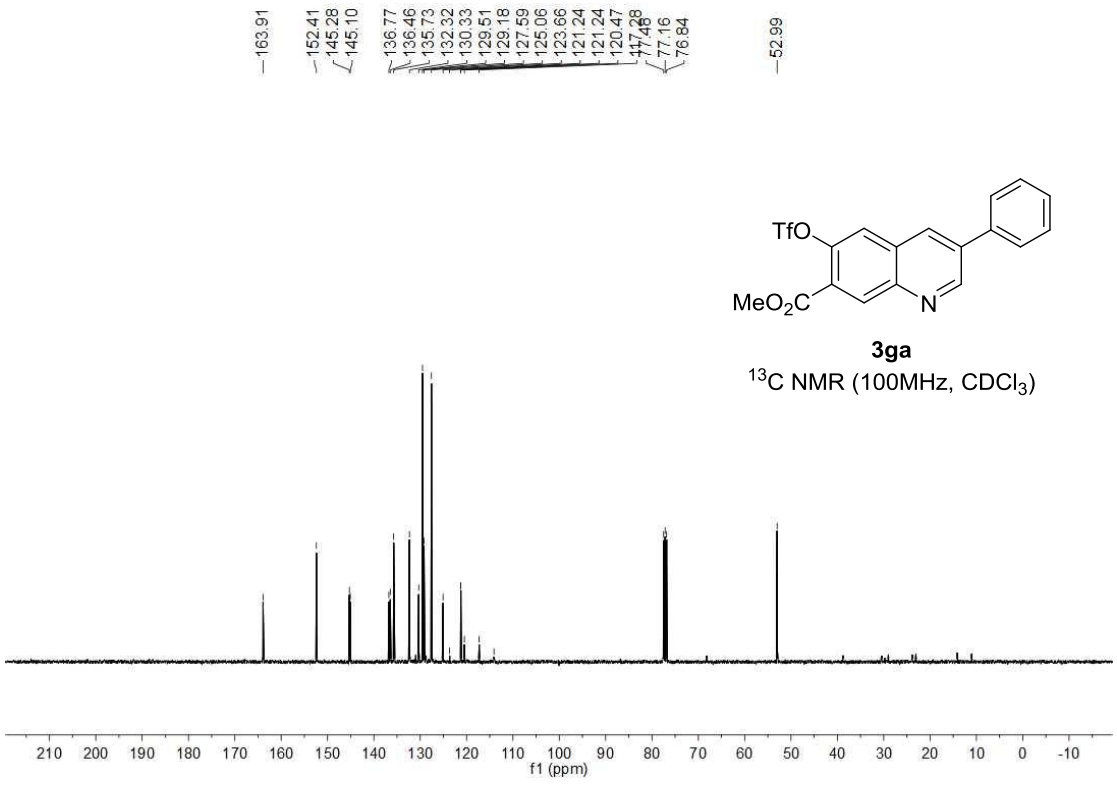
3fa

^{19}F NMR (376MHz, $CDCl_3$)



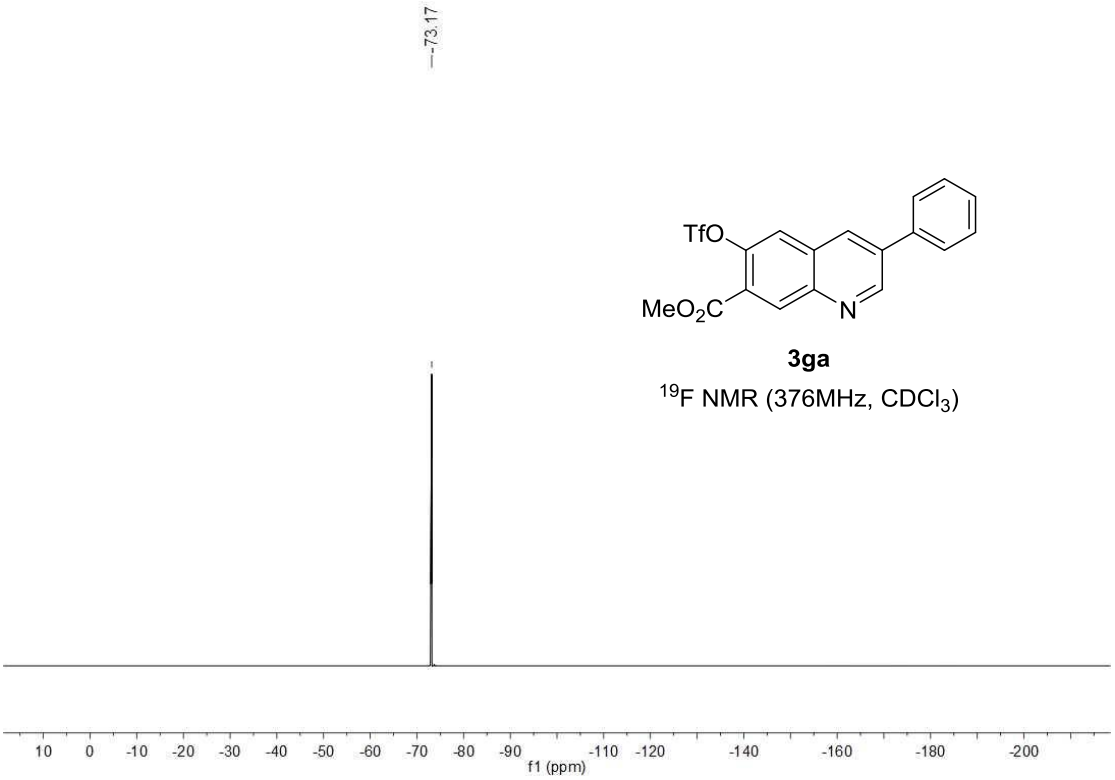
3ga

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



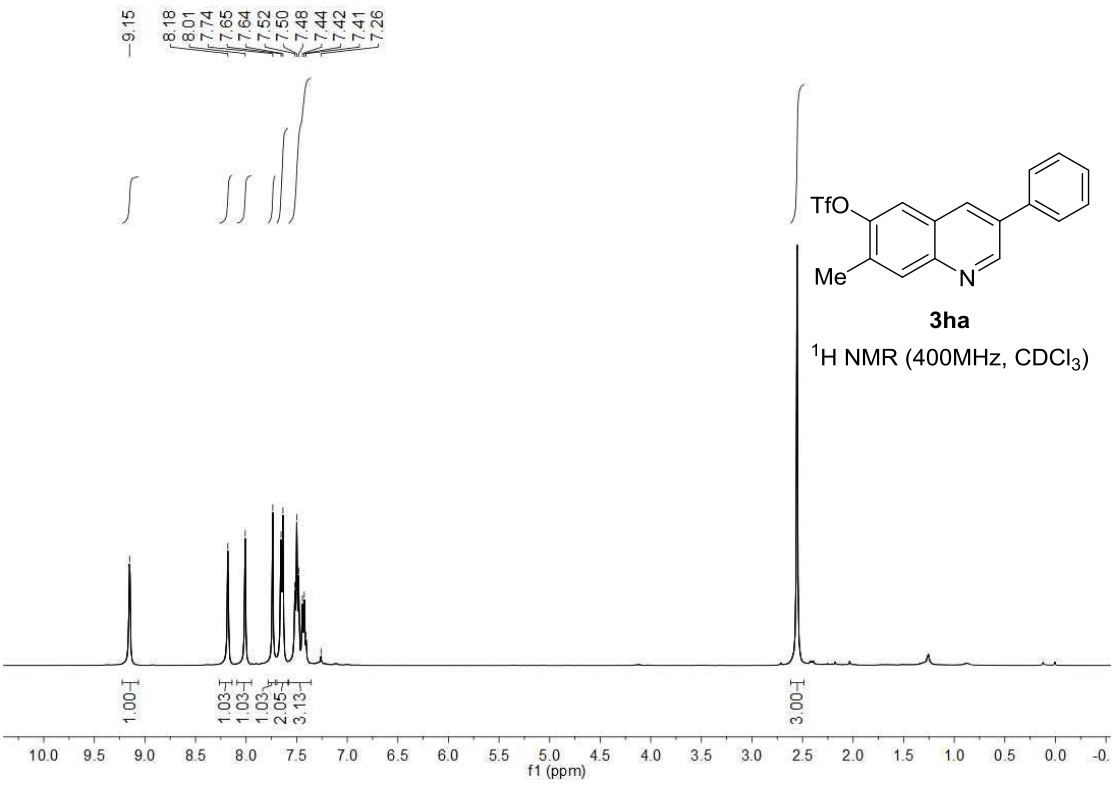
3ga

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



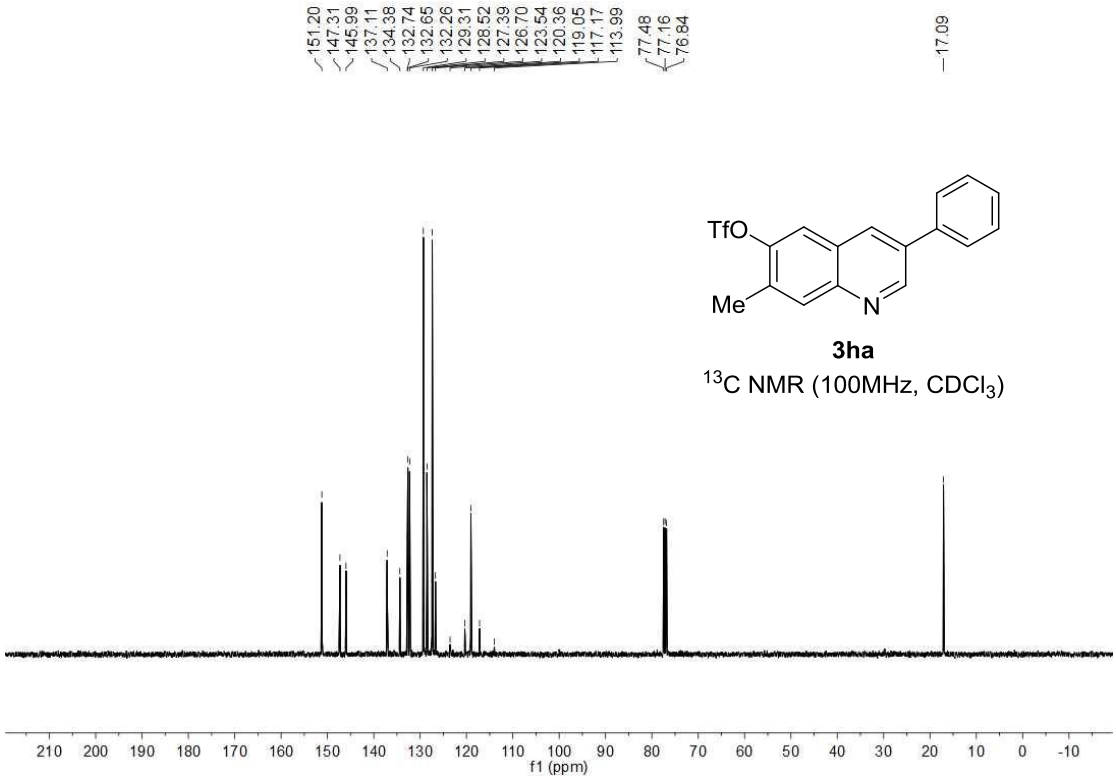
3ga

^{19}F NMR (376MHz, $CDCl_3$)



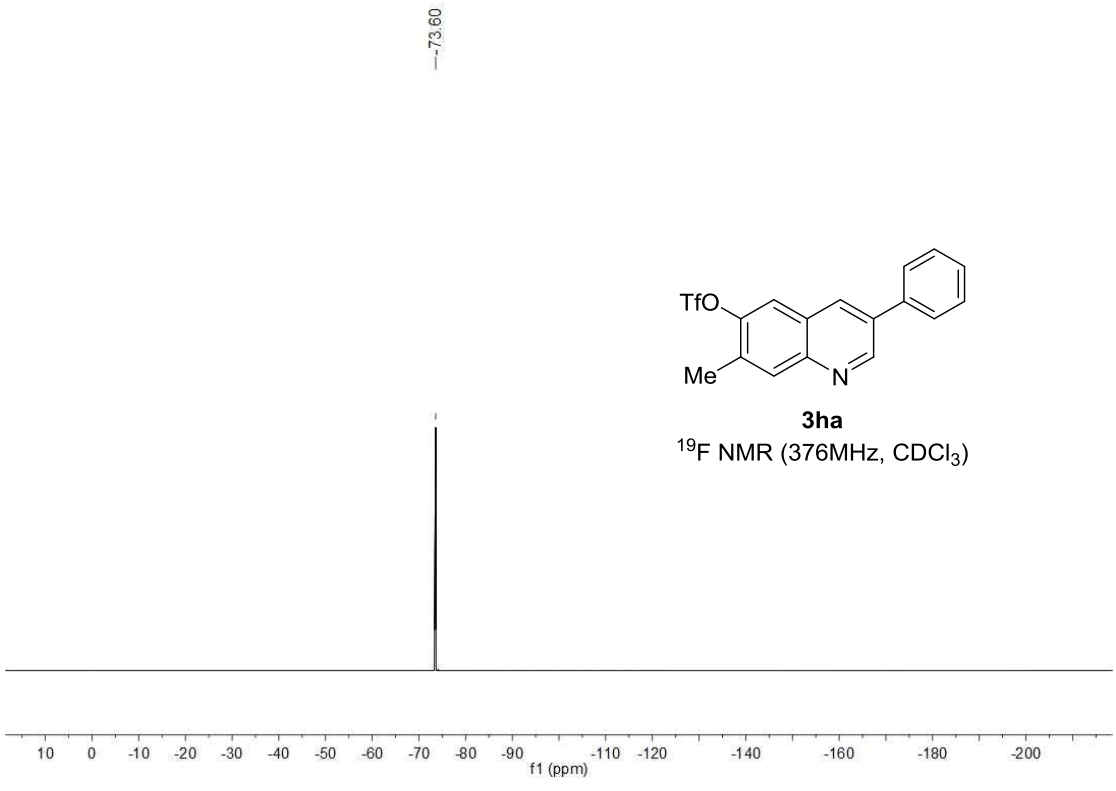
3ha

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



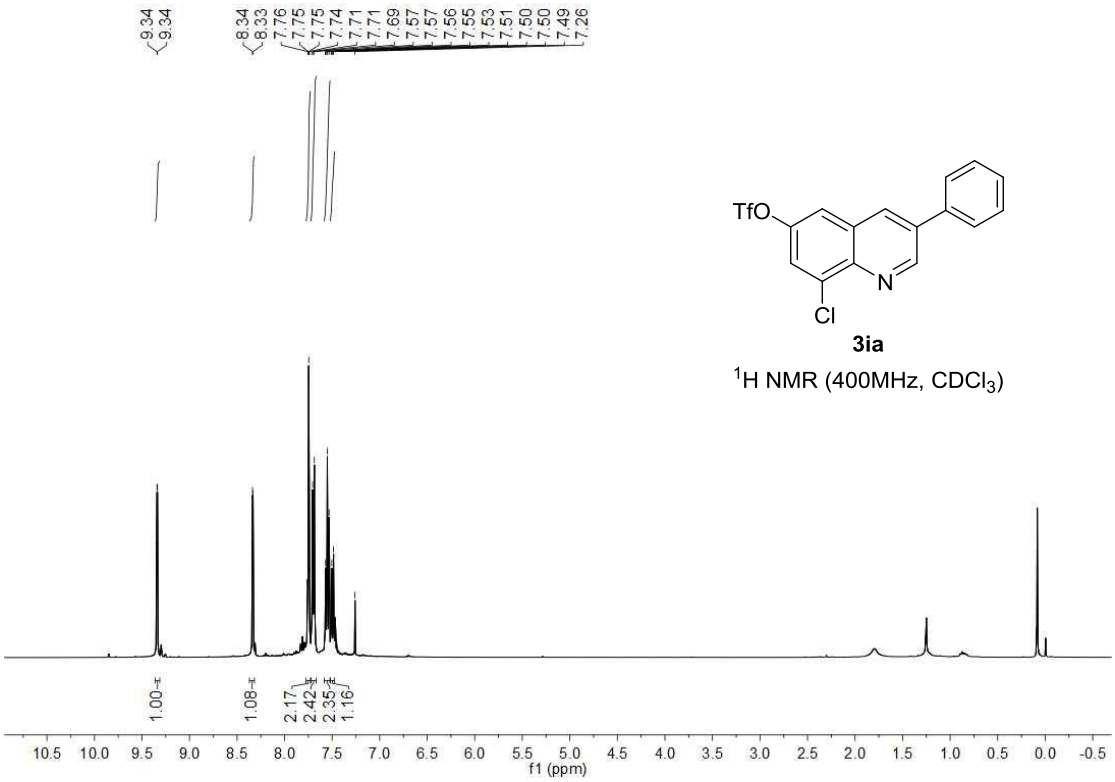
3ha

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



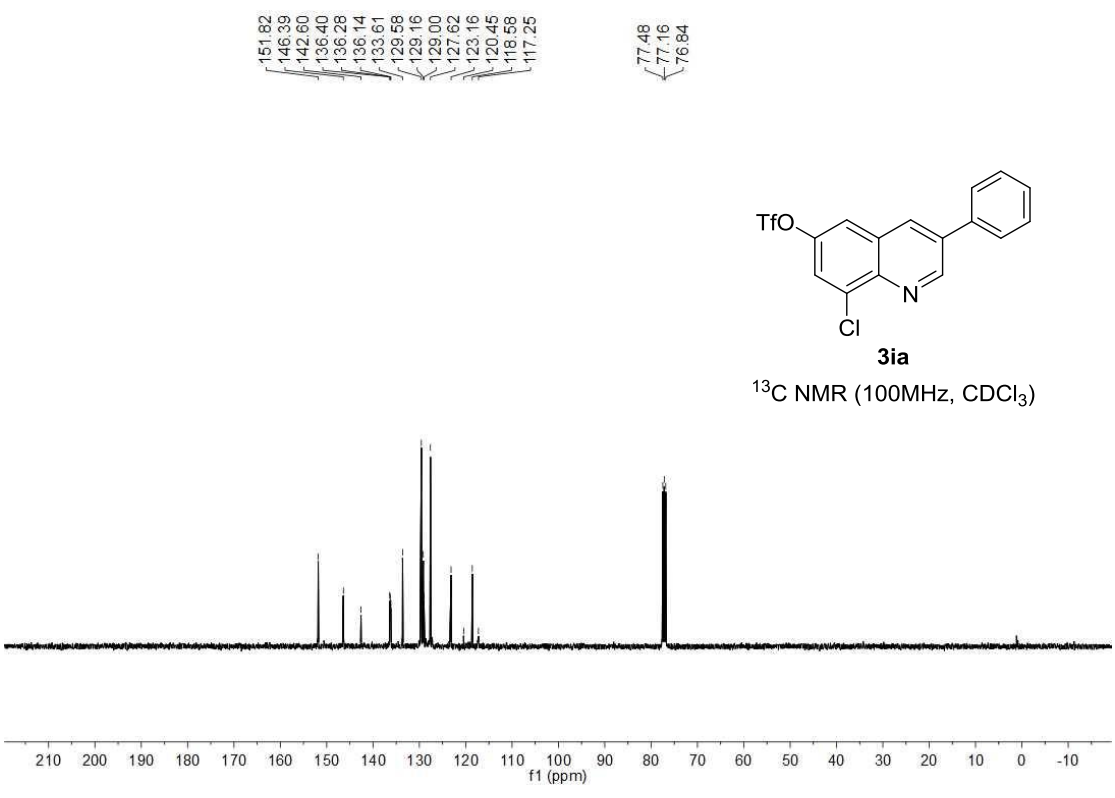
3ha

^{19}F NMR (376MHz, $CDCl_3$)



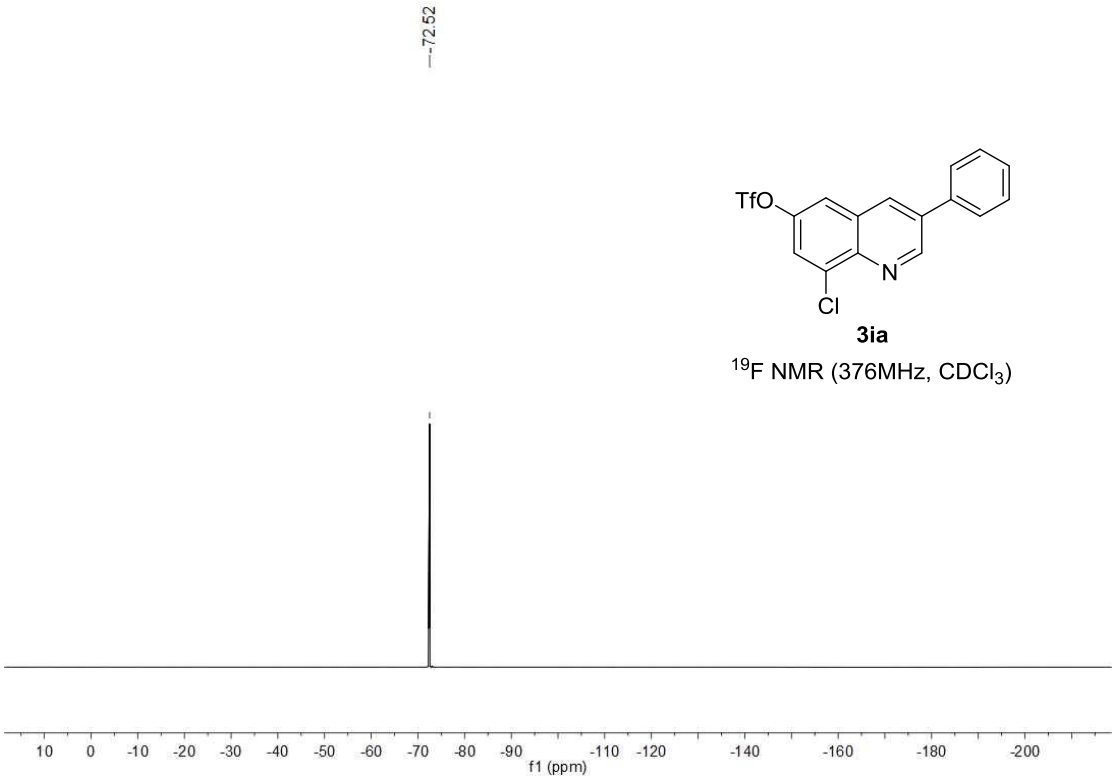
3ia

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



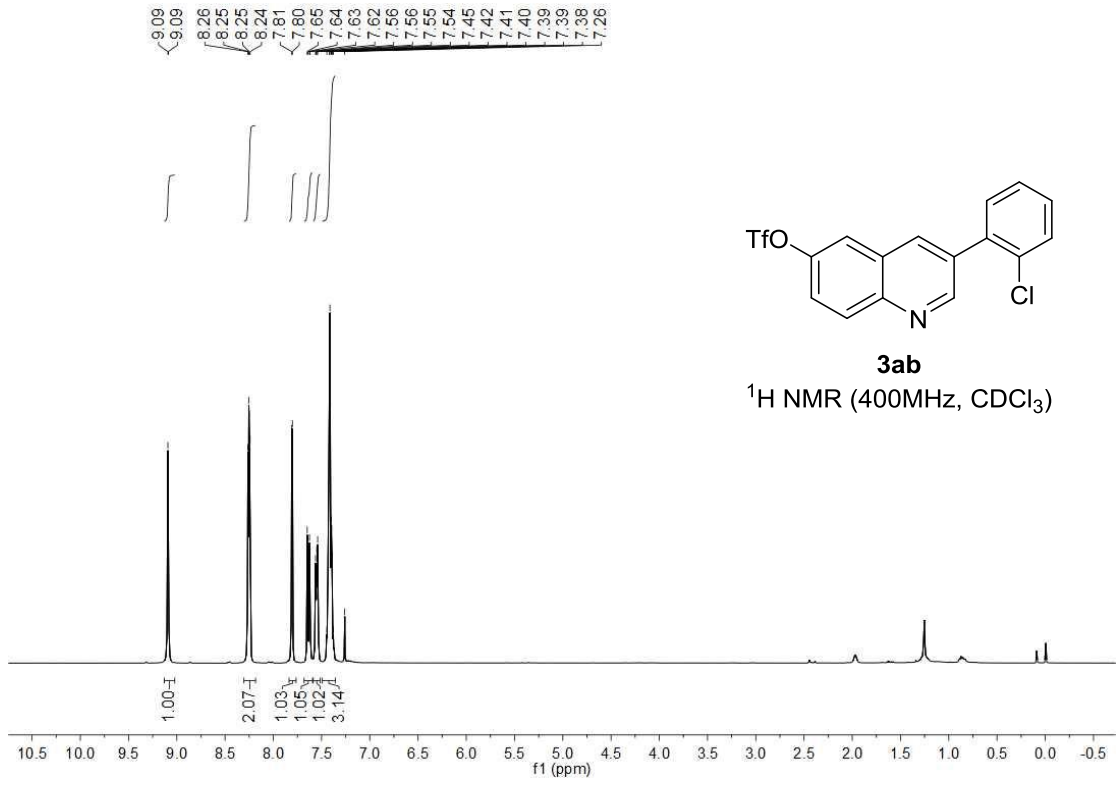
3ia

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



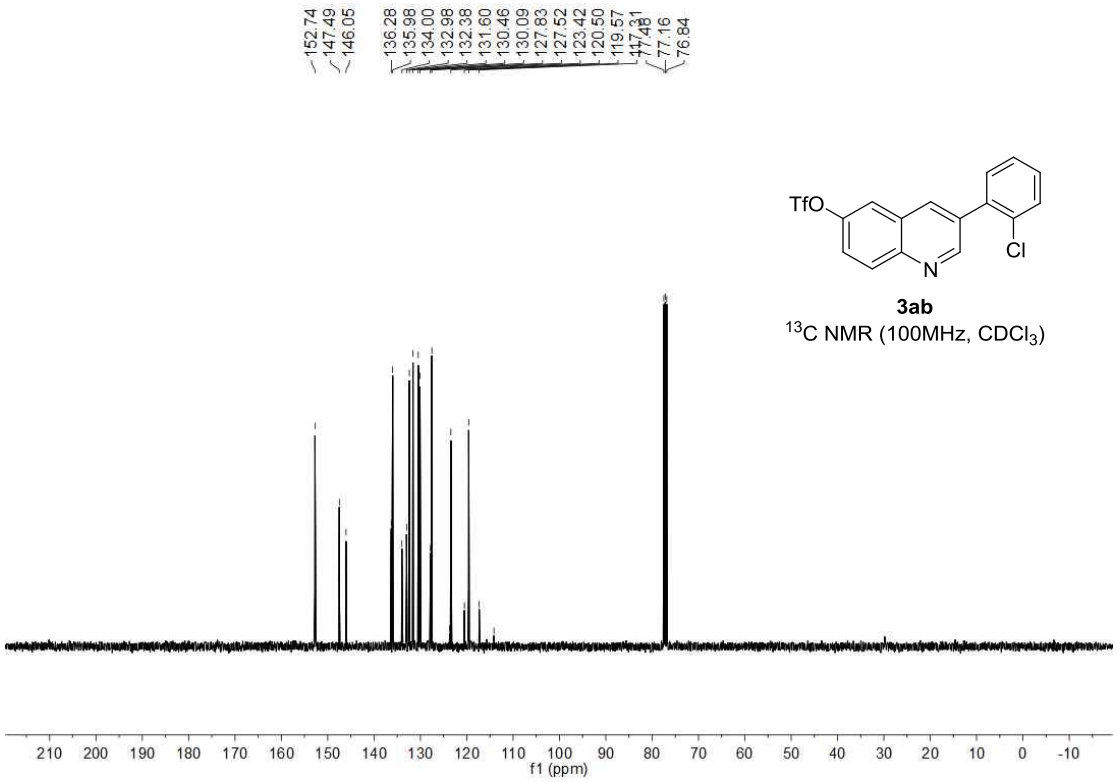
3ia

^{19}F NMR (376MHz, $CDCl_3$)



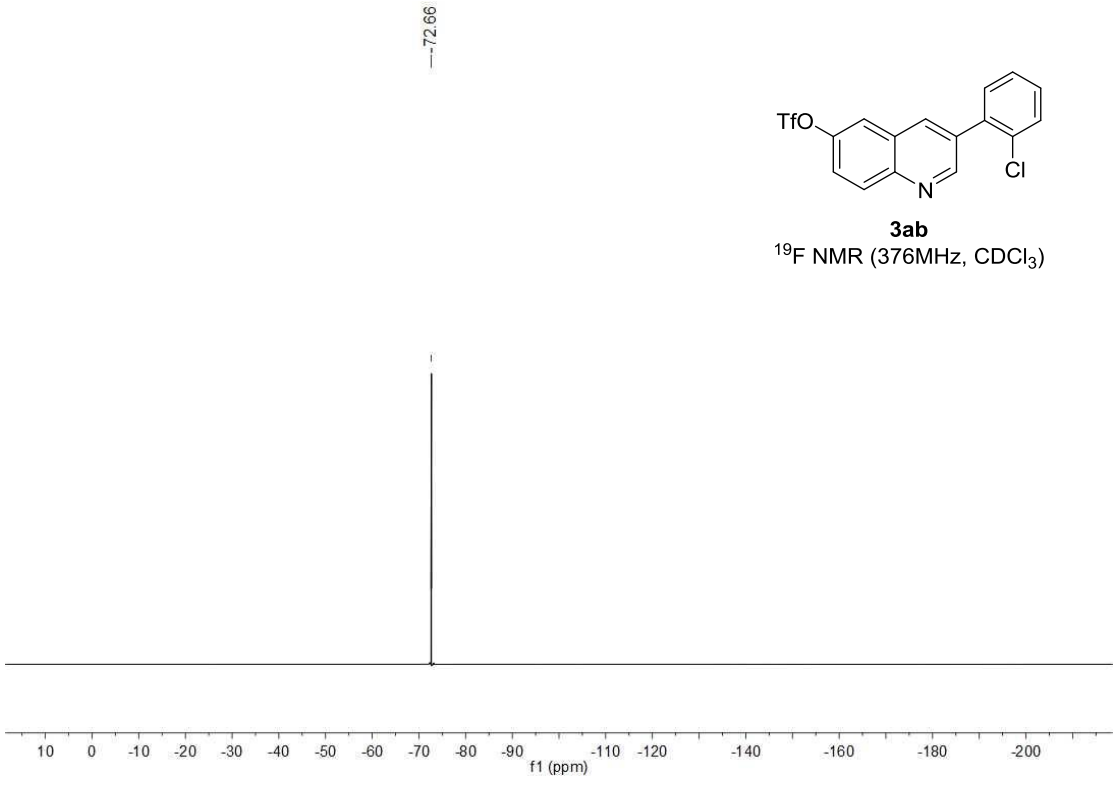
3ab

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



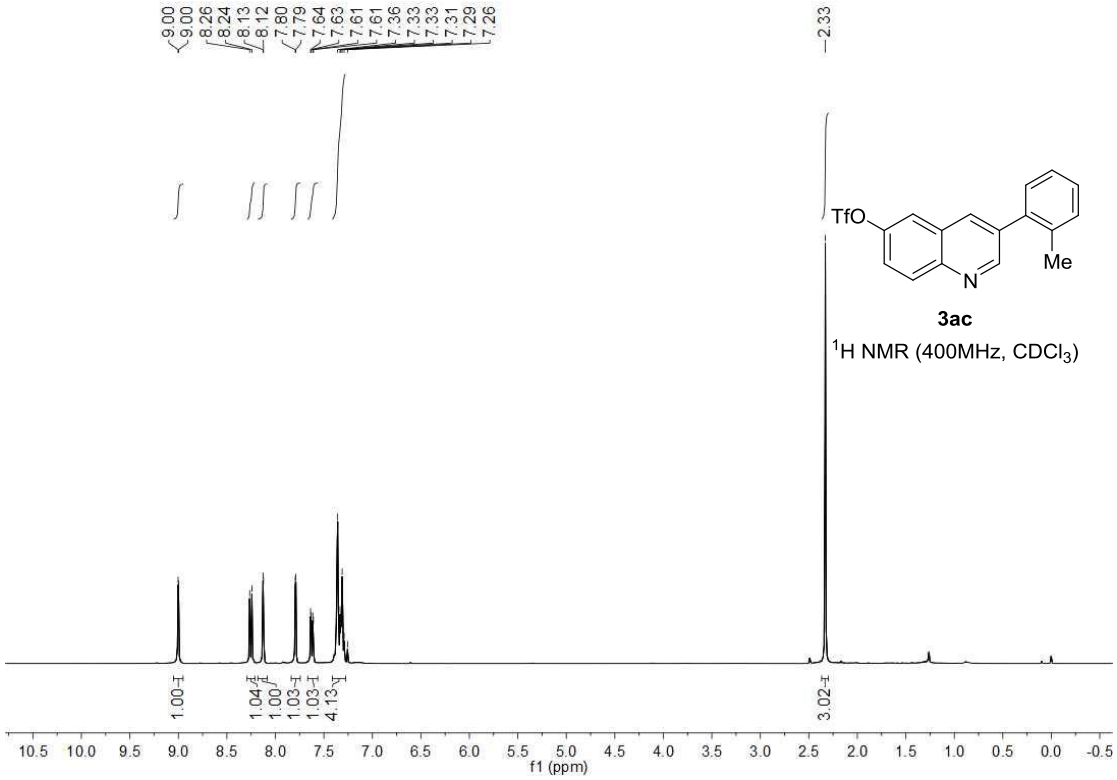
3ab

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



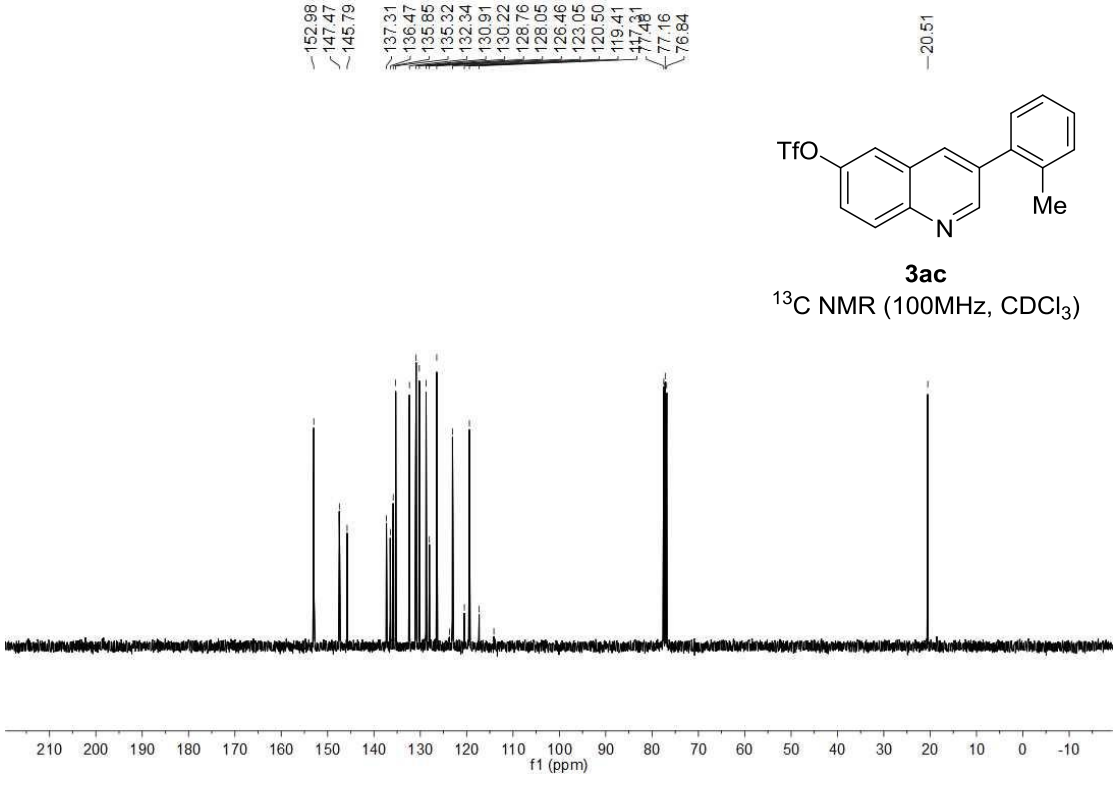
3ab

^{19}F NMR (376MHz, $CDCl_3$)



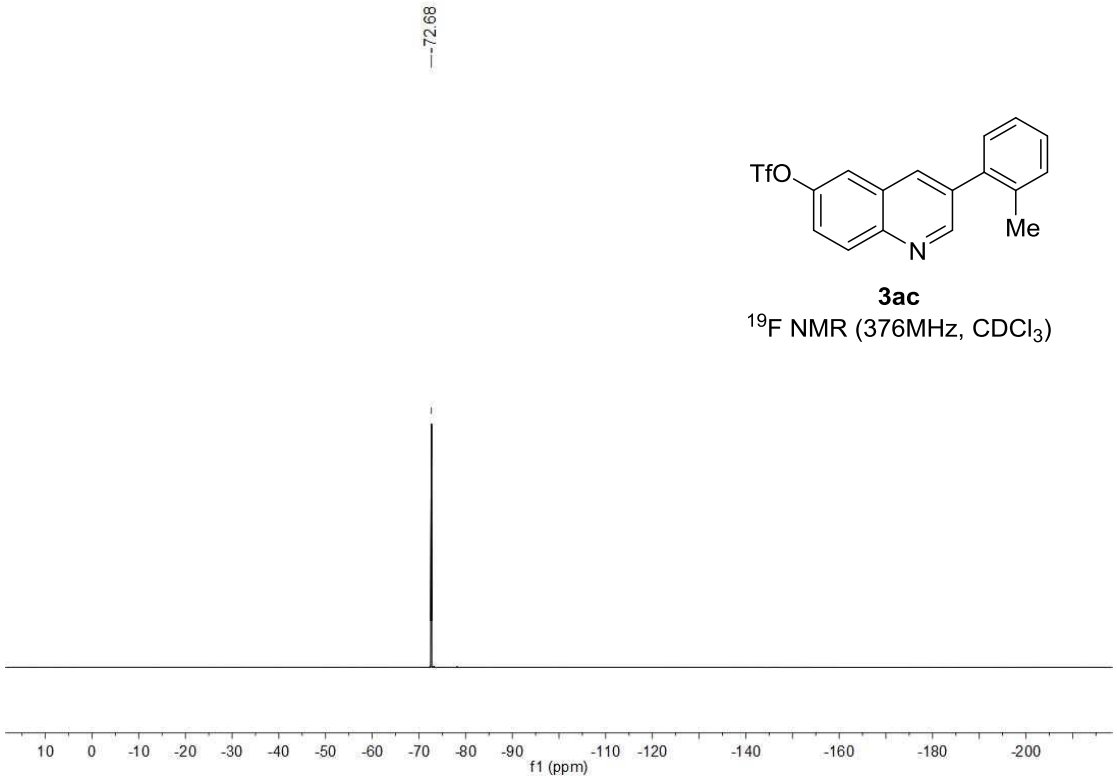
3ac

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



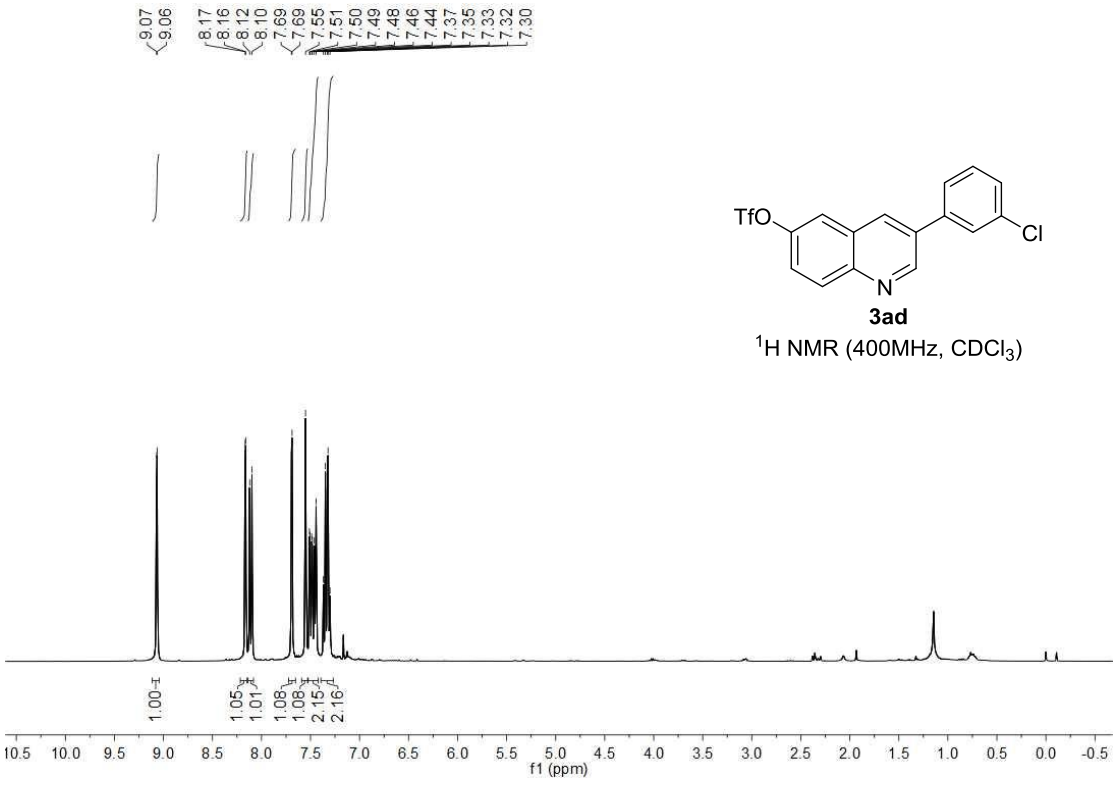
3ac

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



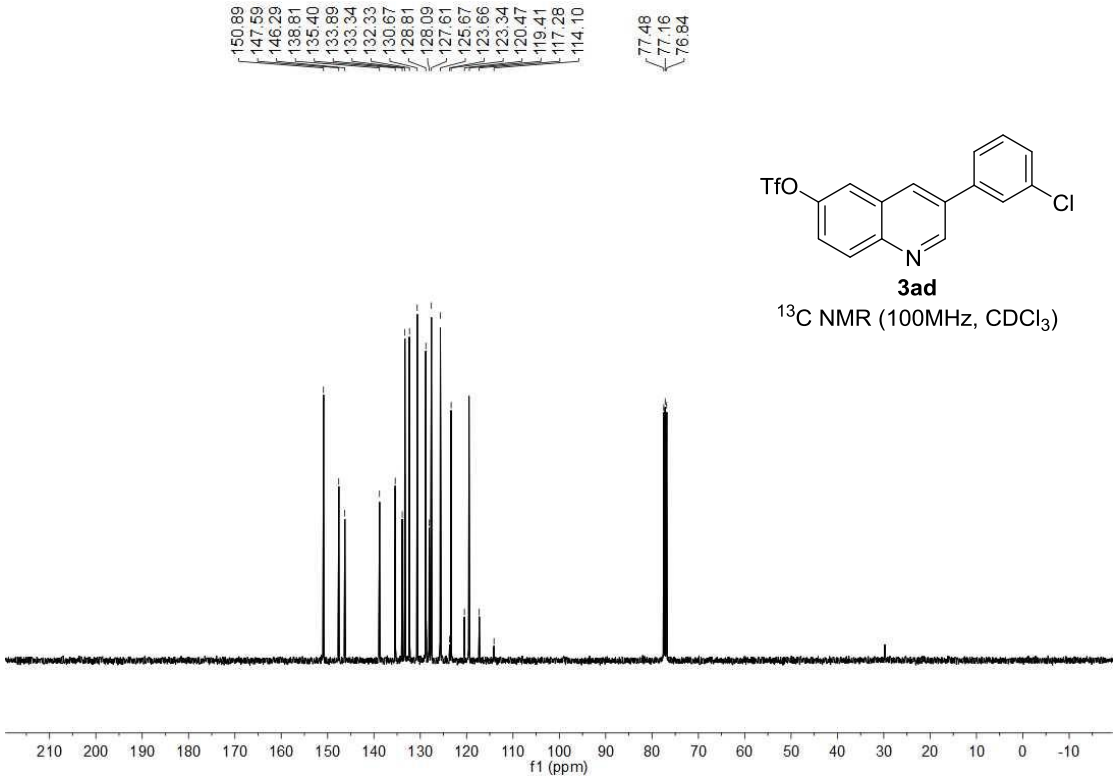
3ac

^{19}F NMR (376MHz, $CDCl_3$)



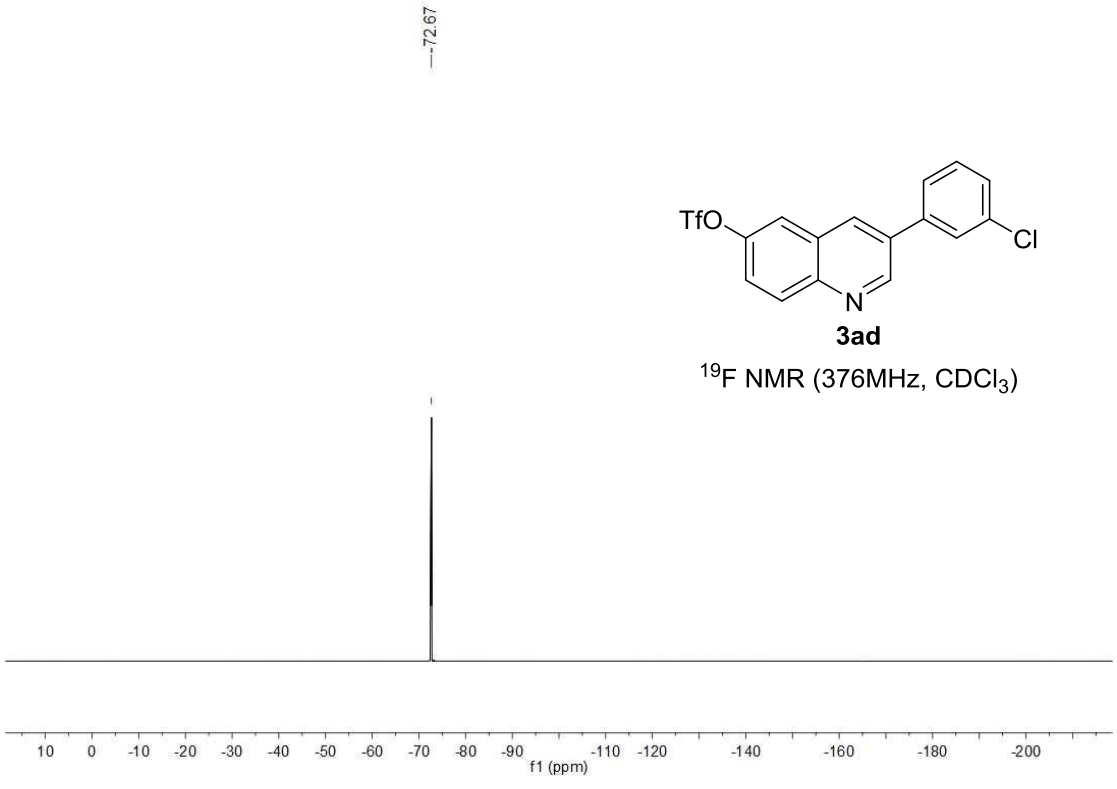
3ad

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



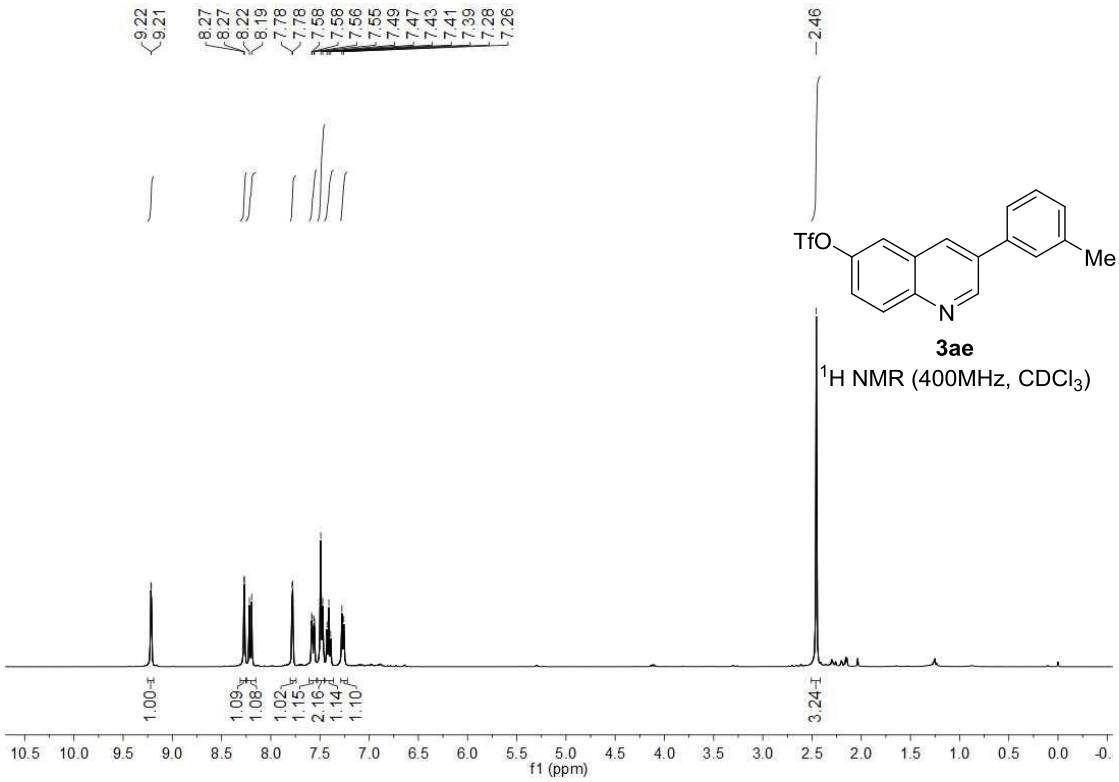
3ad

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



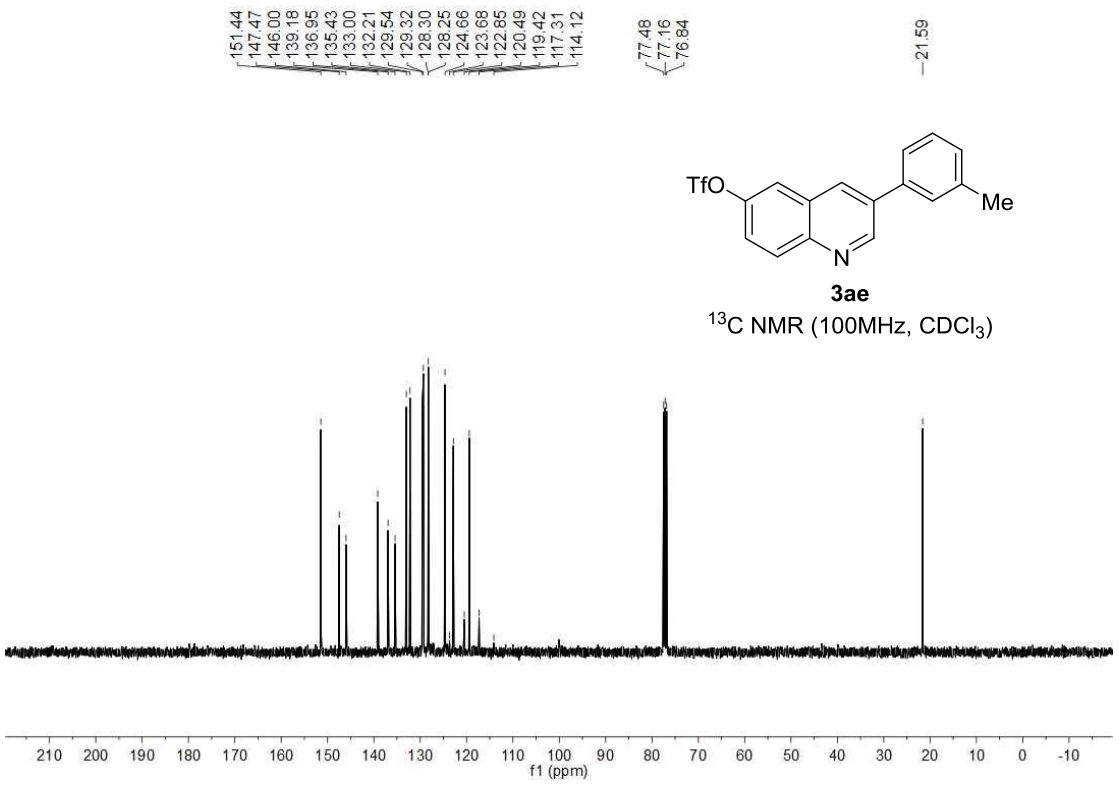
3ad

^{19}F NMR (376MHz, $CDCl_3$)



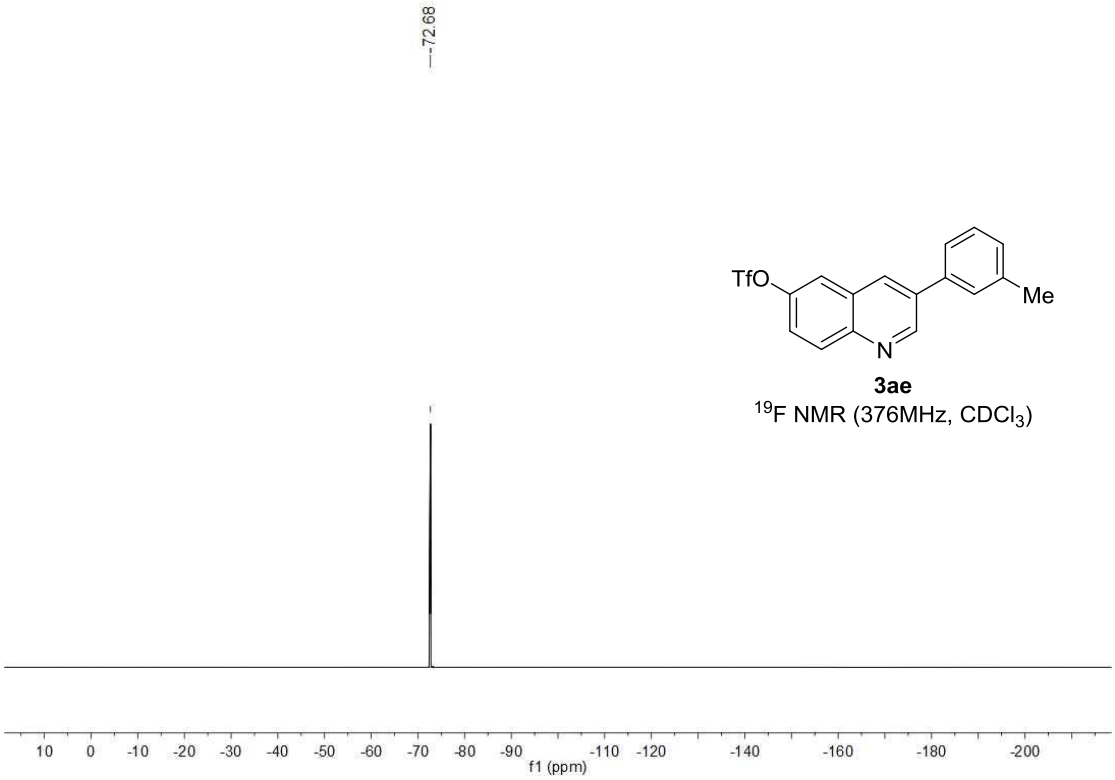
3ae

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



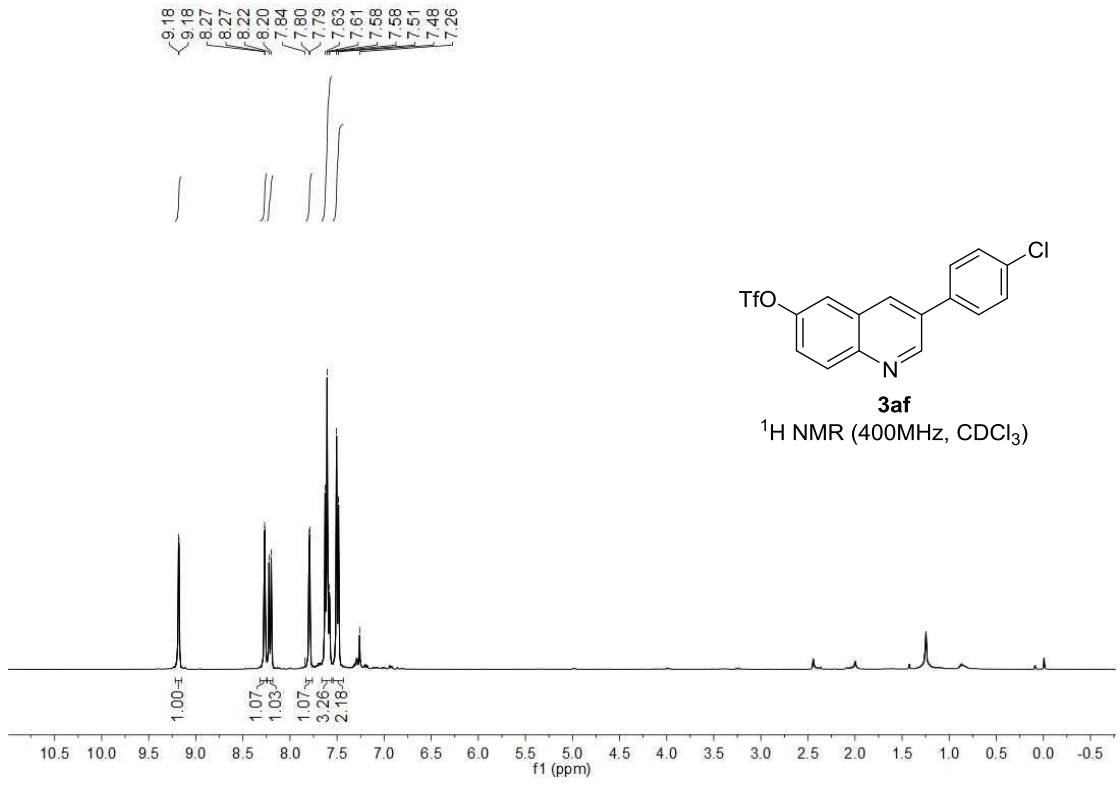
3ae

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



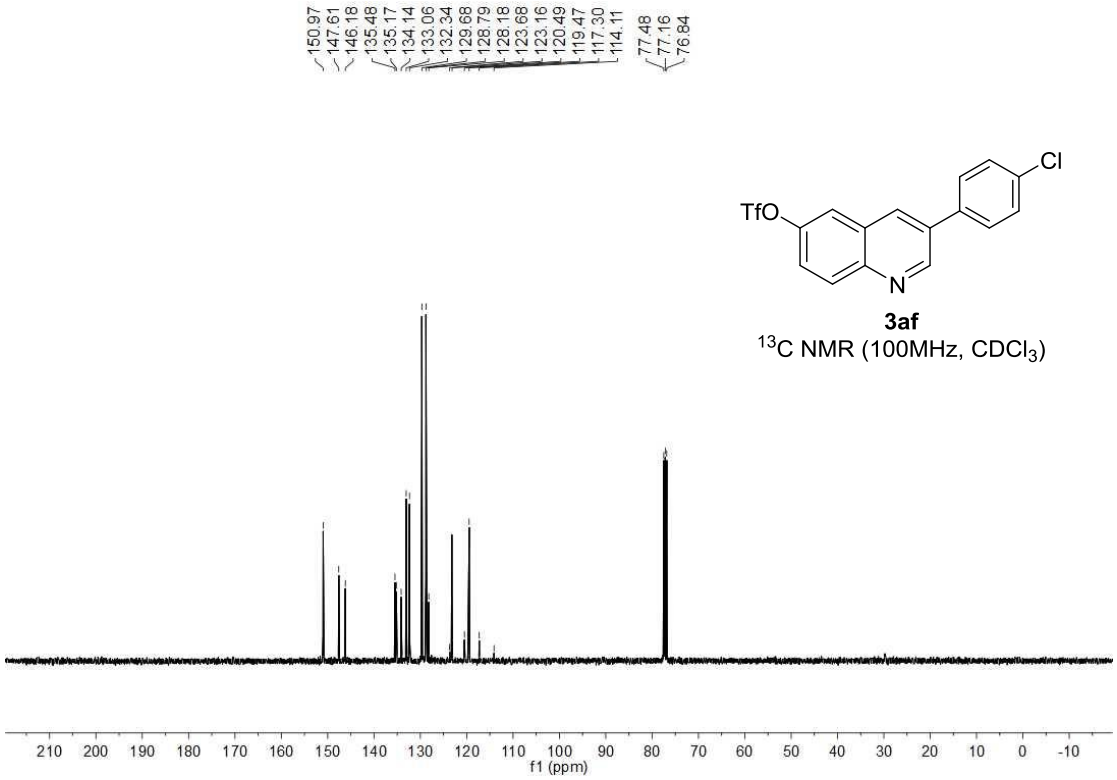
3ae

^{19}F NMR (376MHz, $CDCl_3$)



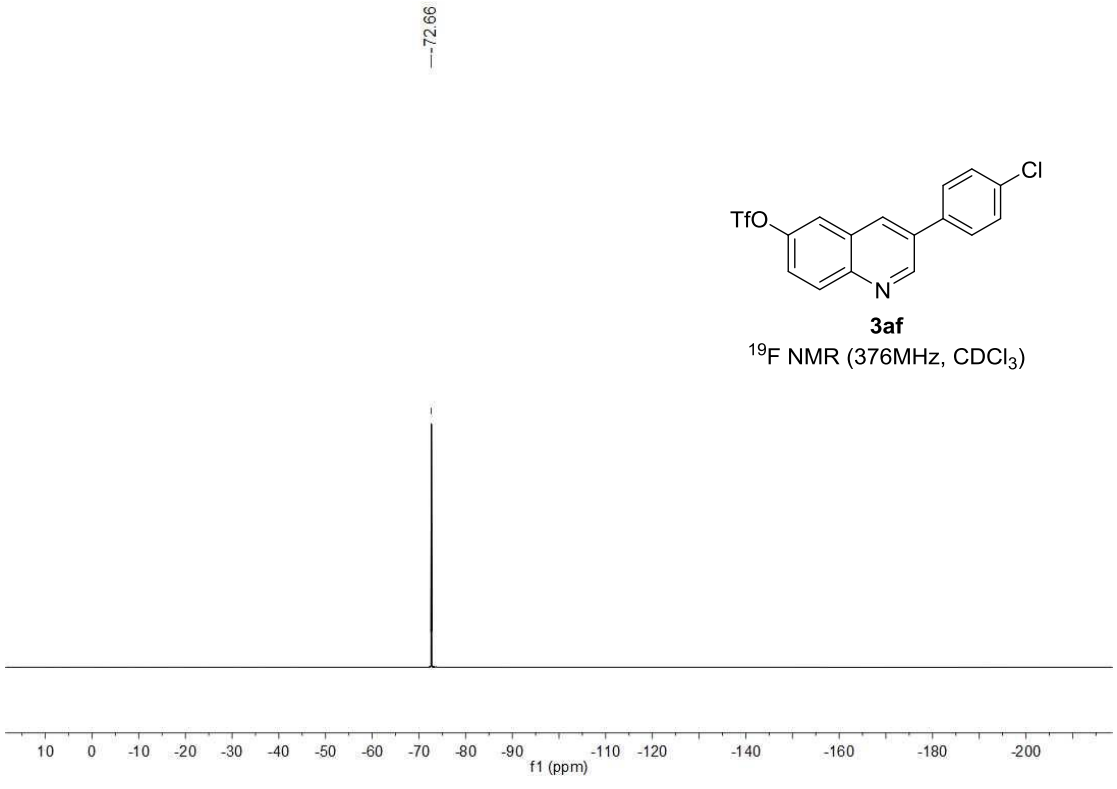
3af

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



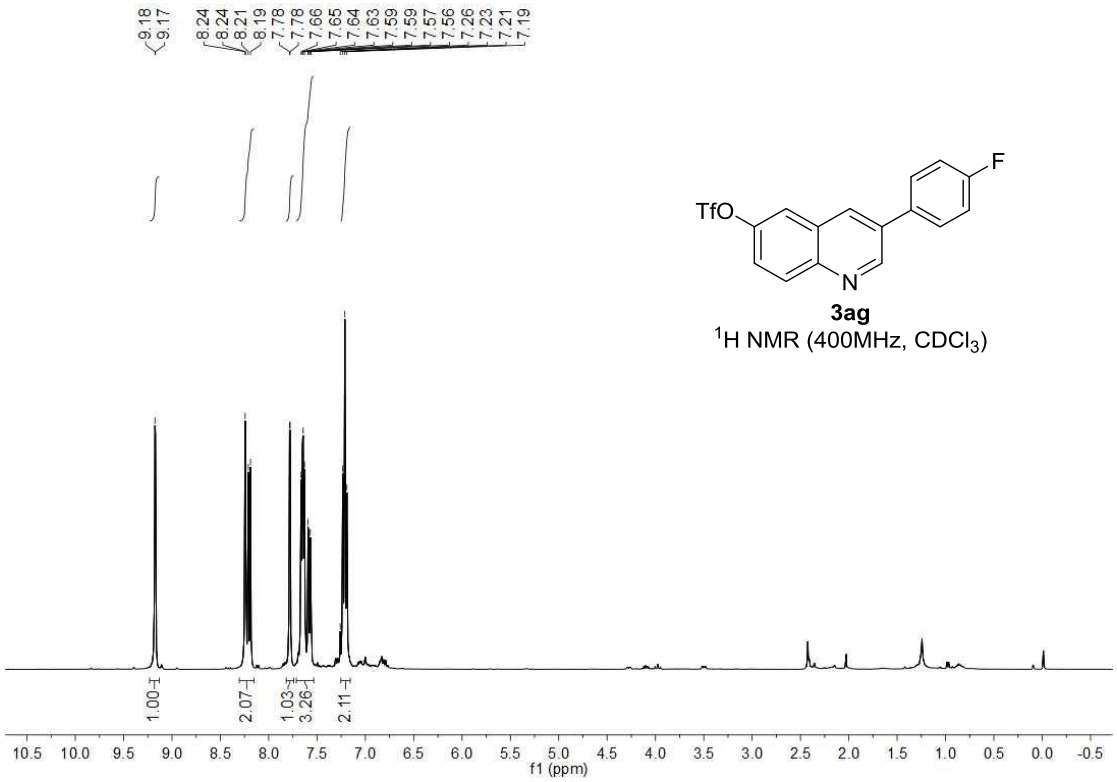
3af

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



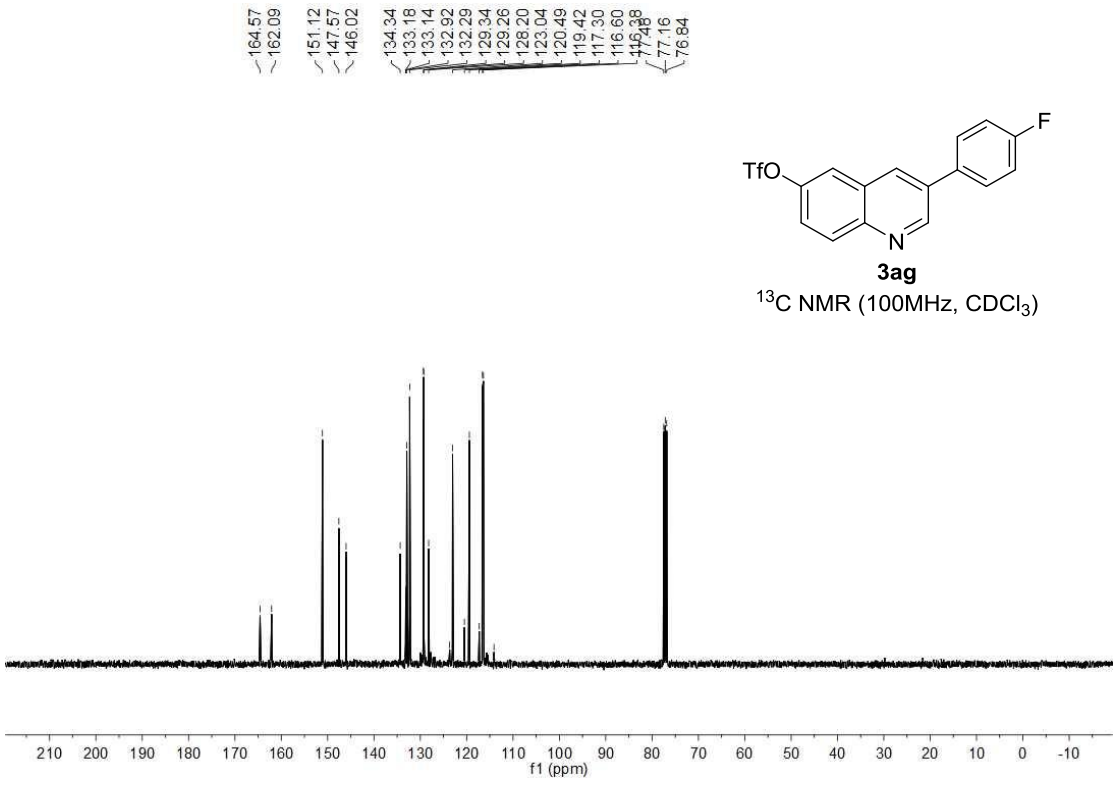
3af

^{19}F NMR (376MHz, $CDCl_3$)



3ag

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



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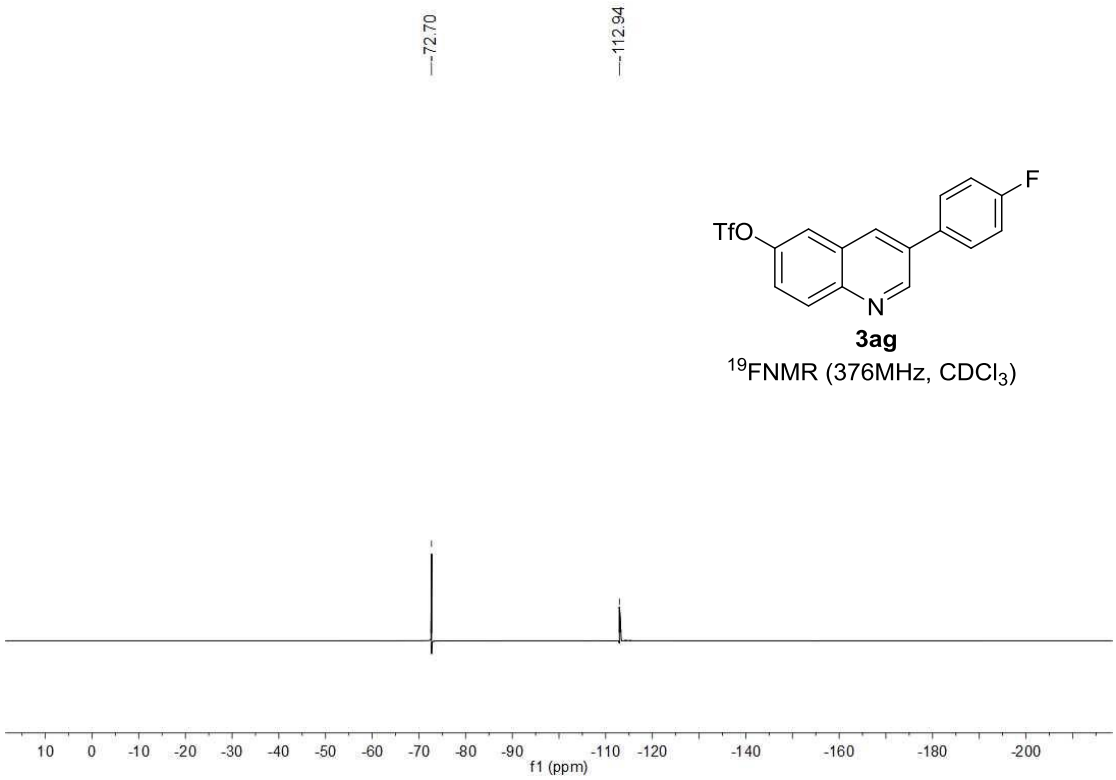
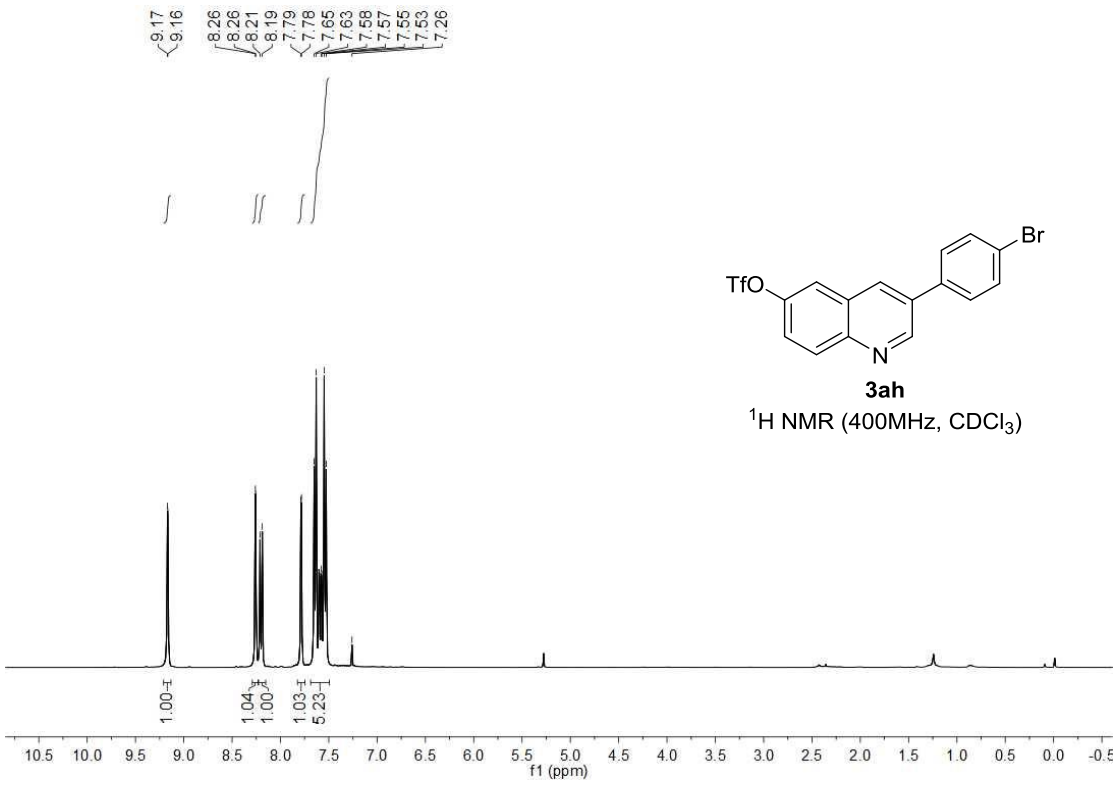
^{13}C NMR (100MHz, $CDCl_3$)



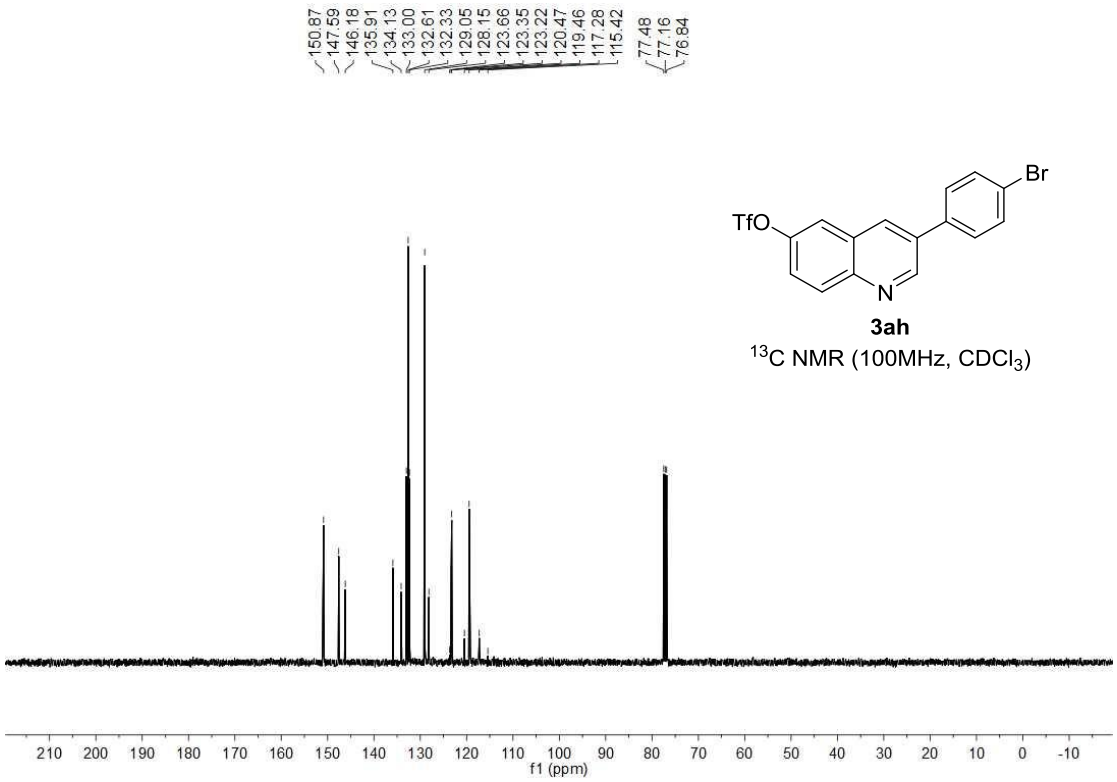
3ag

^{19}FNMR (376MHz, $CDCl_3$)



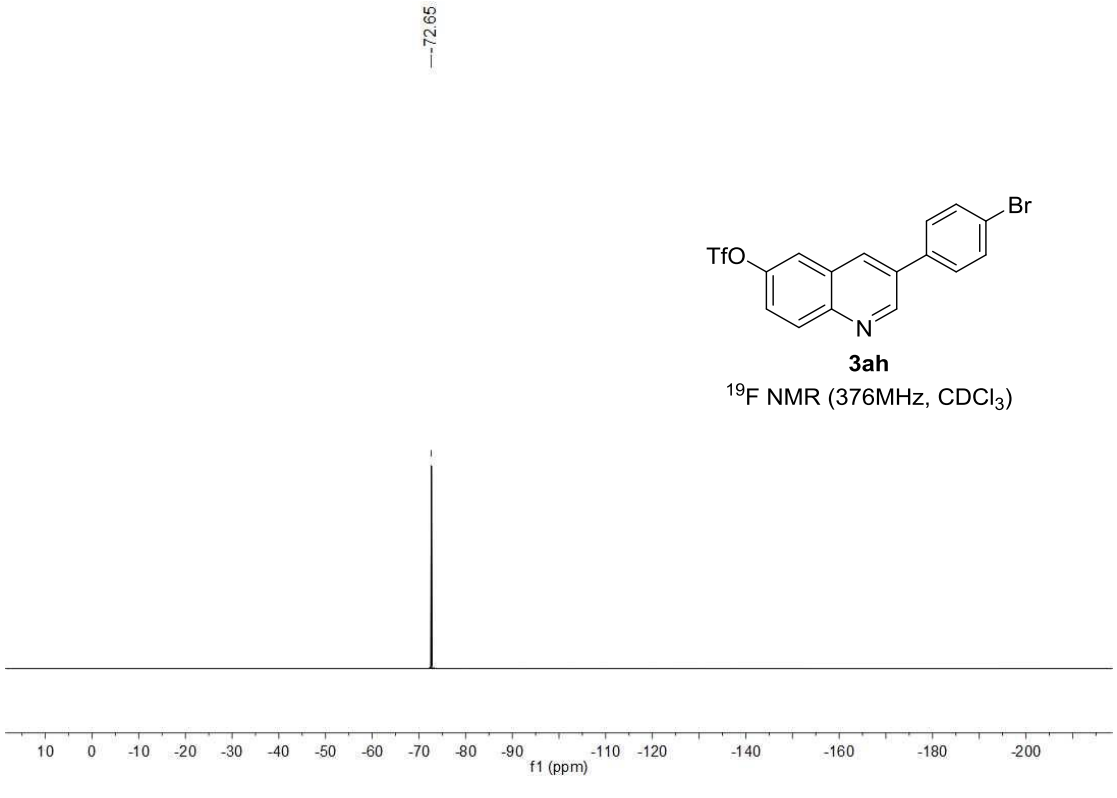
3ah

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



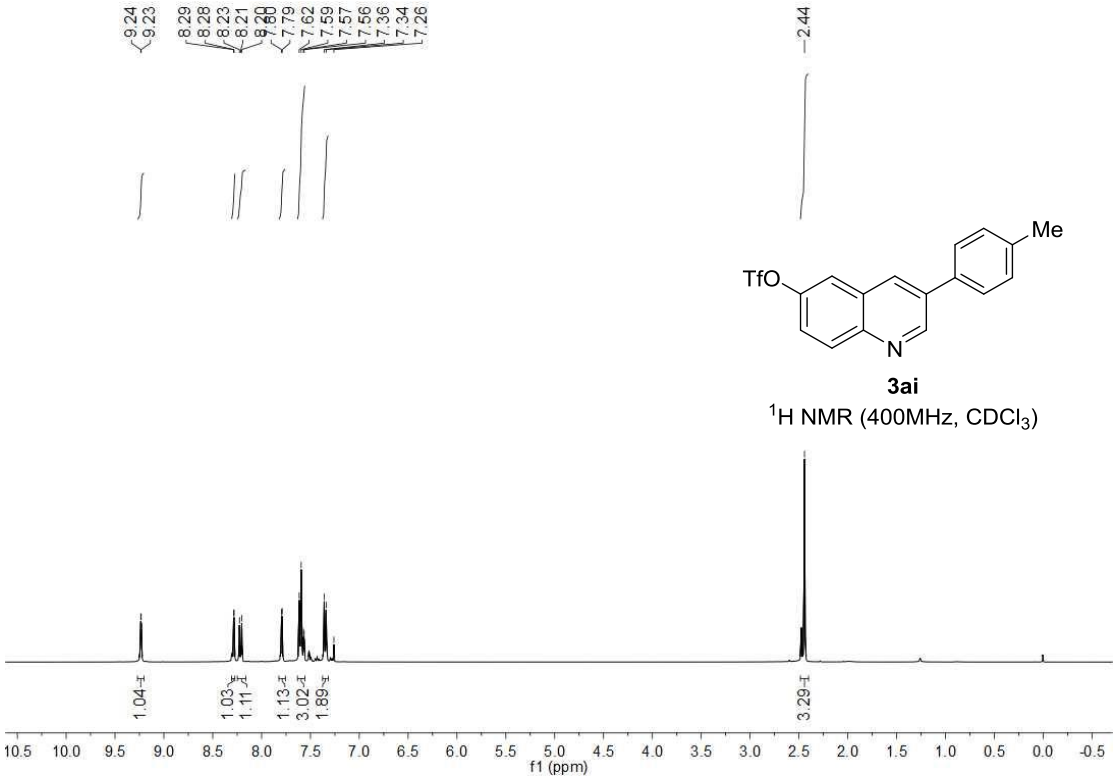
3ah

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



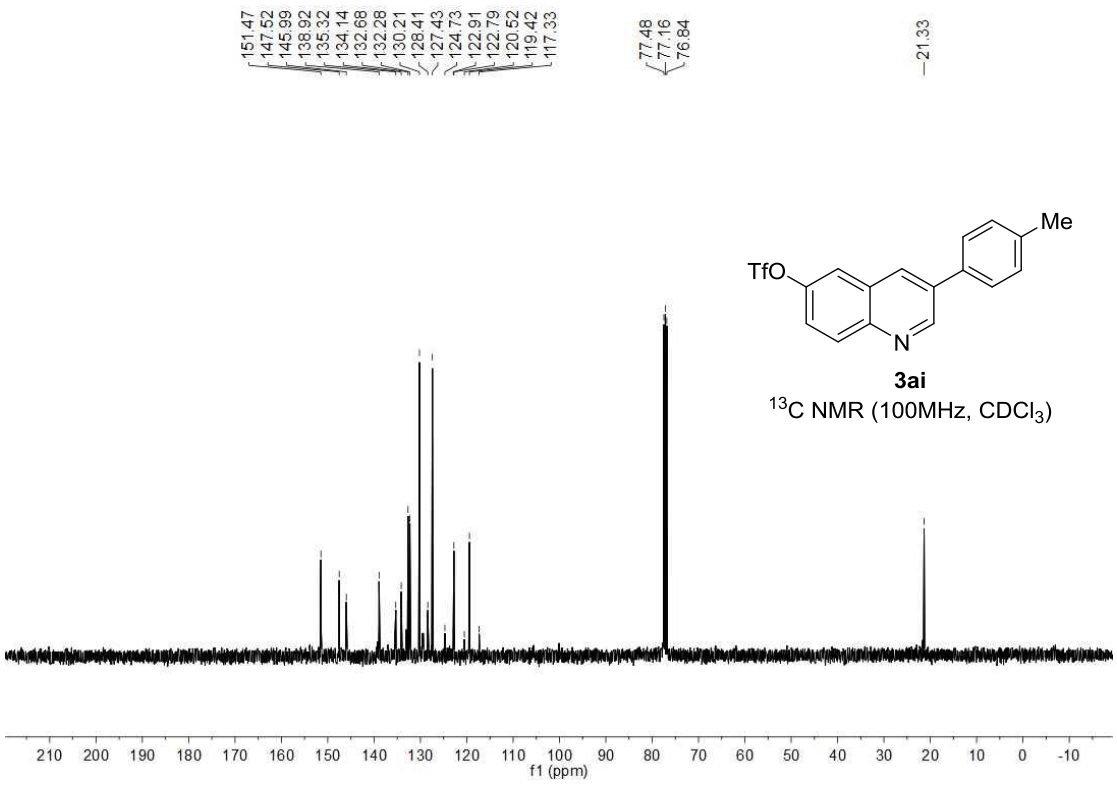
3ah

^{19}F NMR (376MHz, $CDCl_3$)



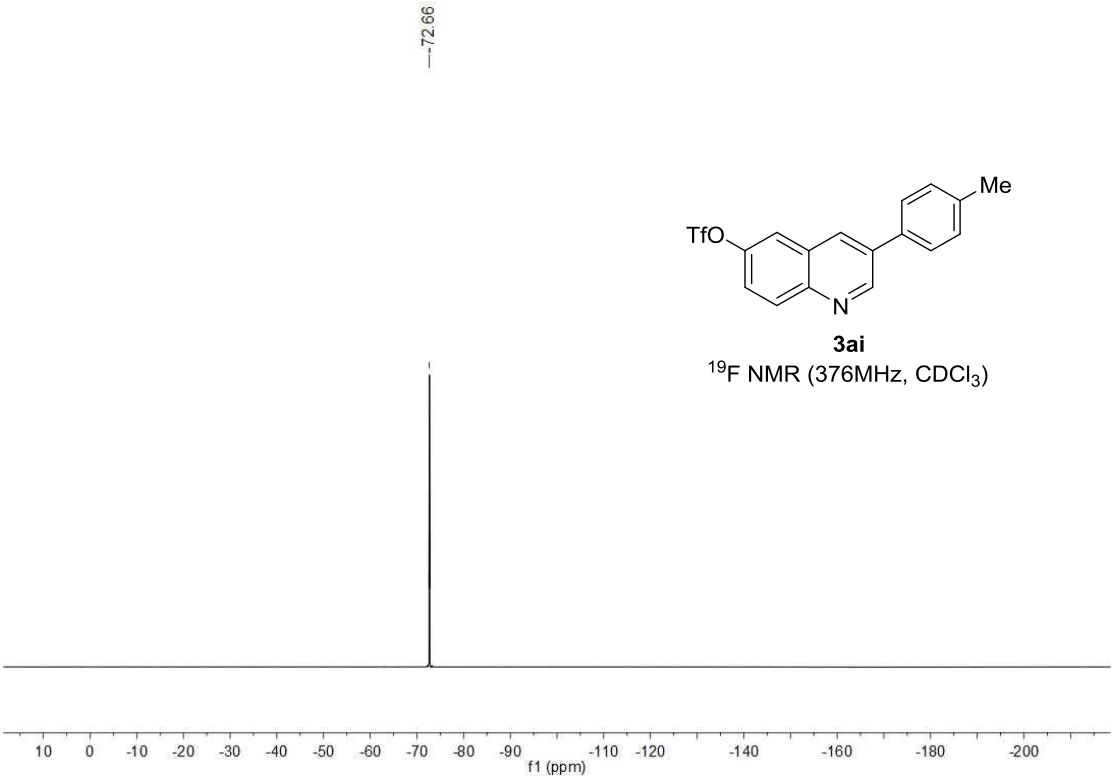
3ai

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



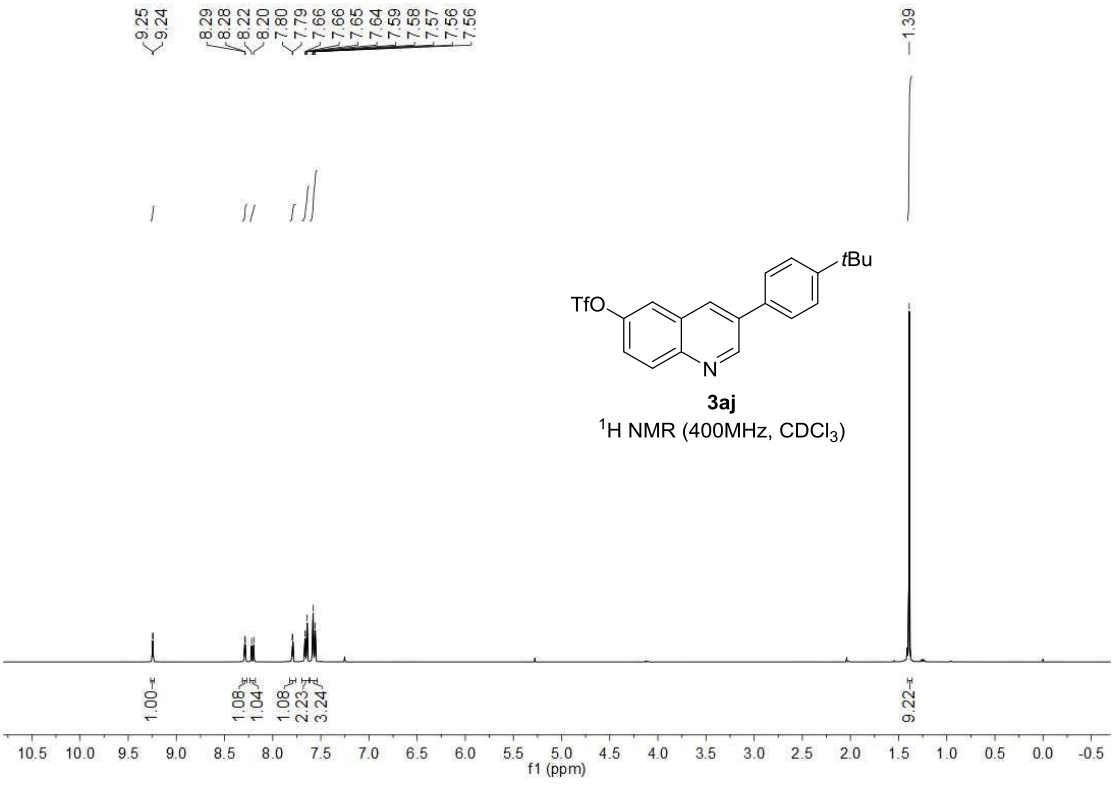
3ai

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



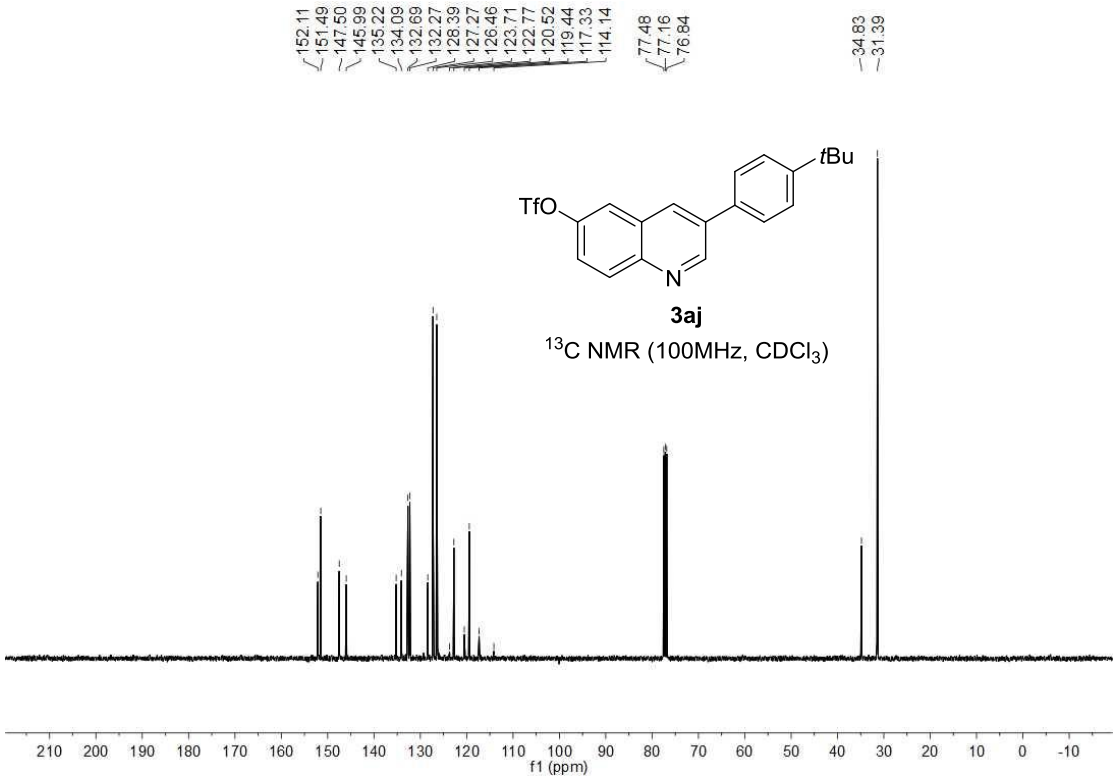
3ai

^{19}F NMR (376MHz, $CDCl_3$)



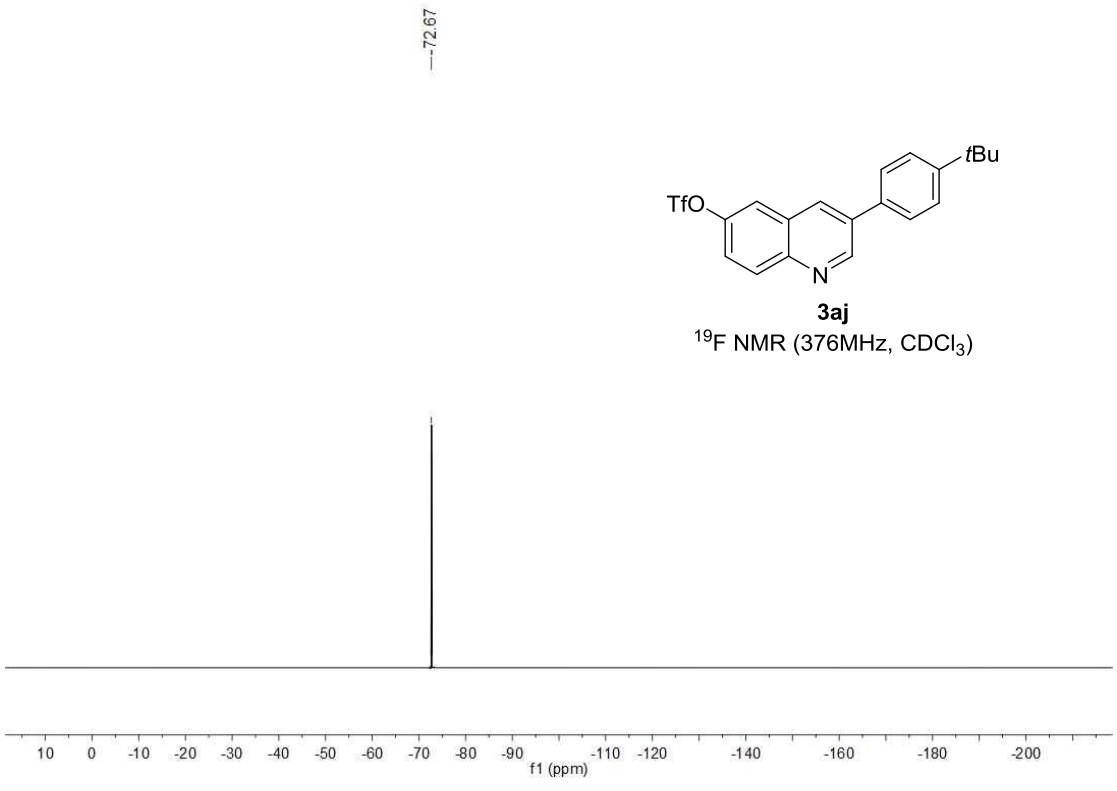
3aj

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



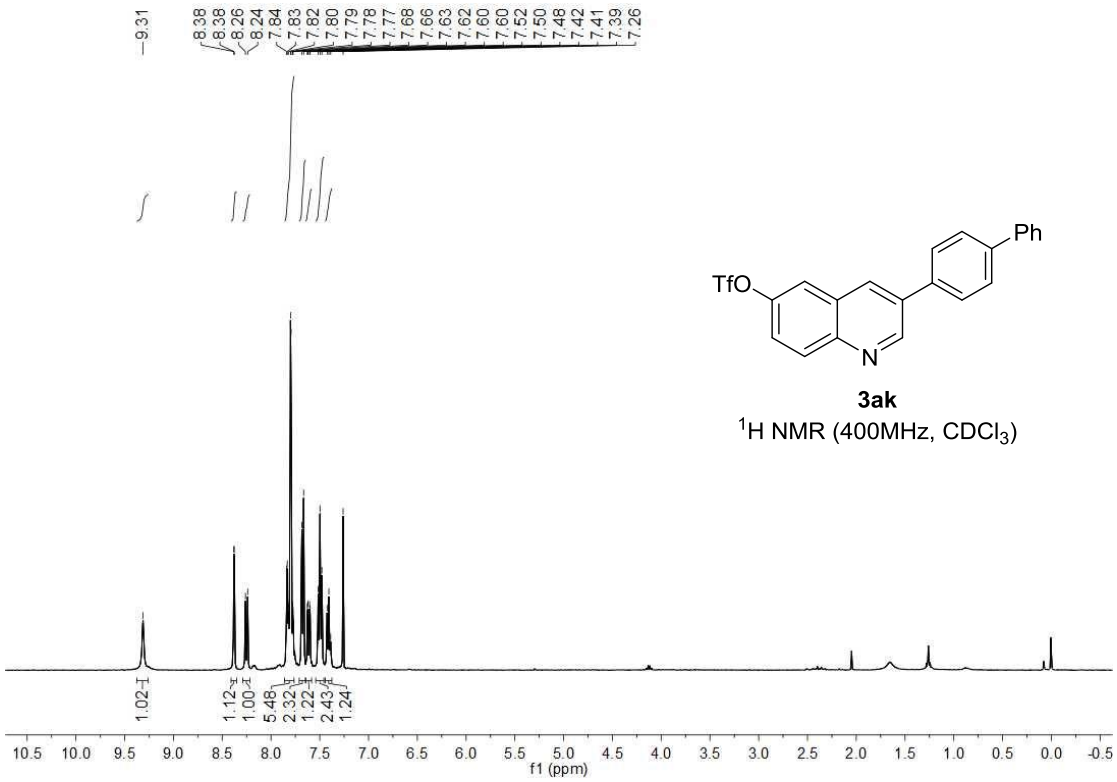
3aj

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



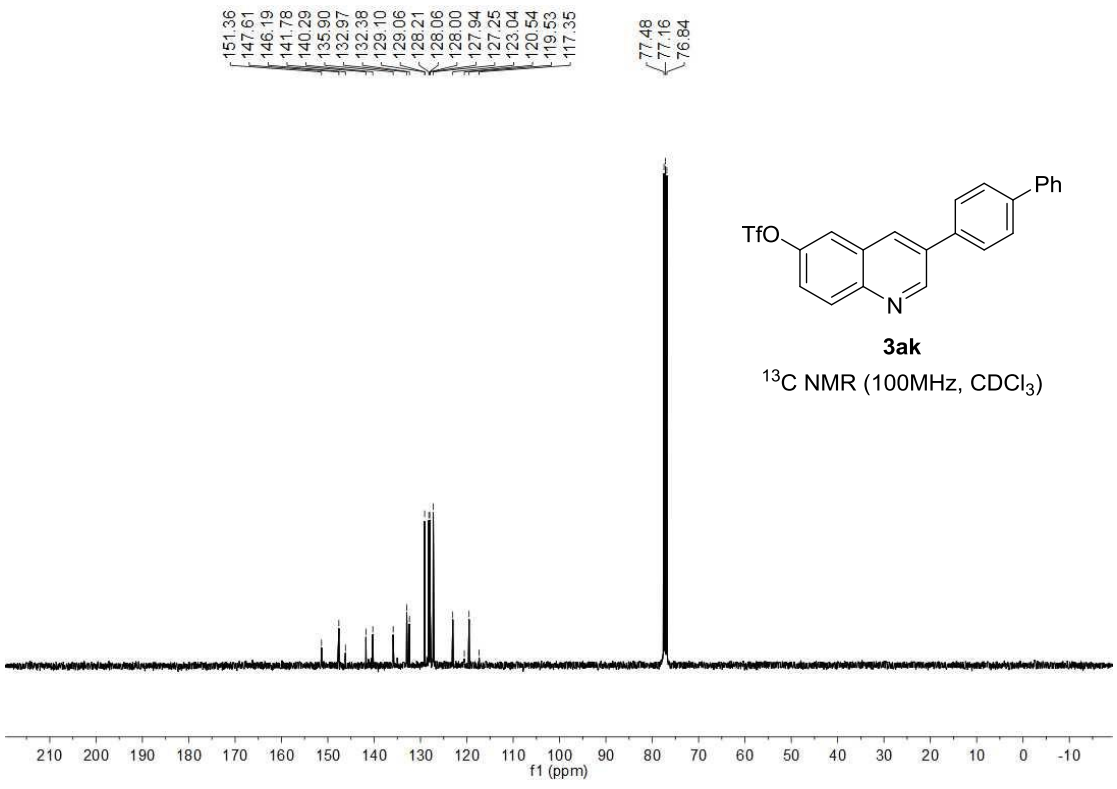
3aj

^{19}F NMR (376MHz, $CDCl_3$)



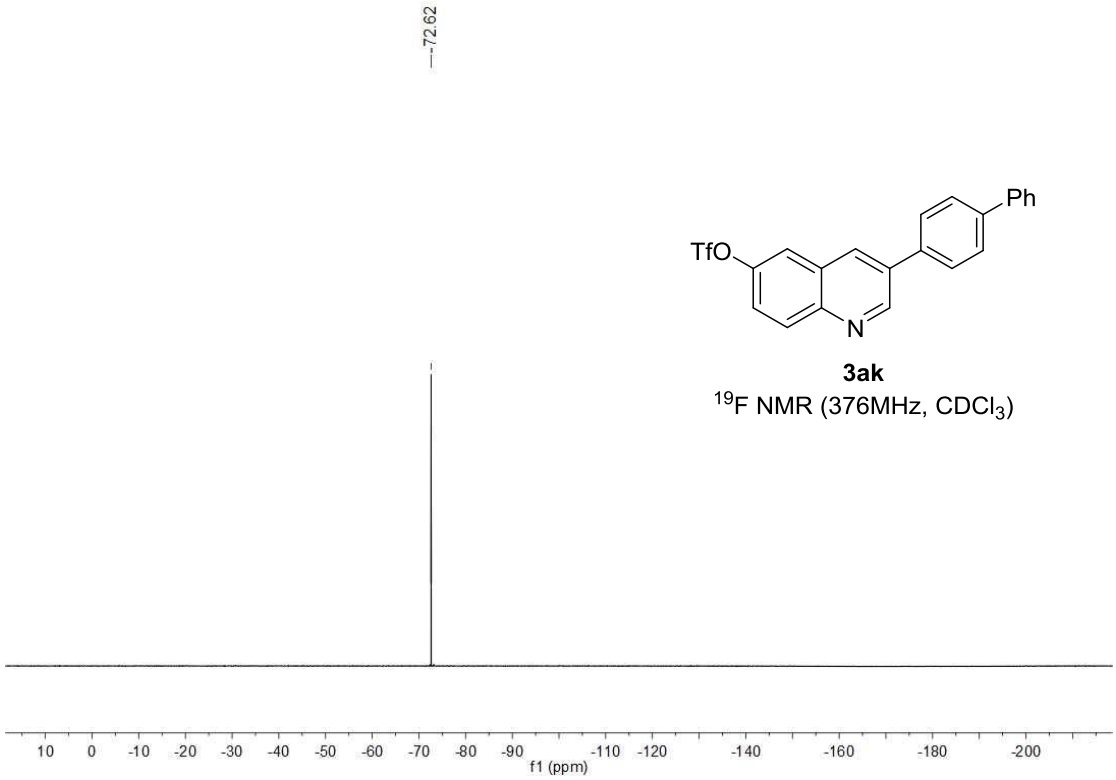
3ak

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



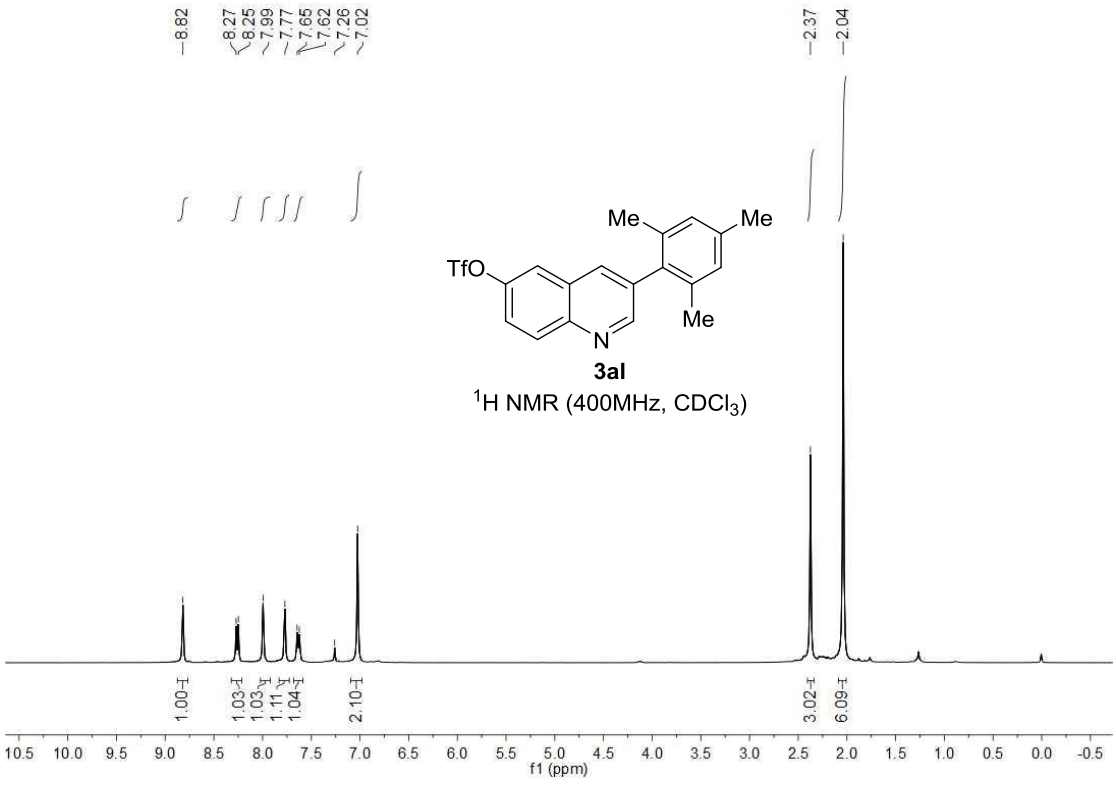
3ak

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



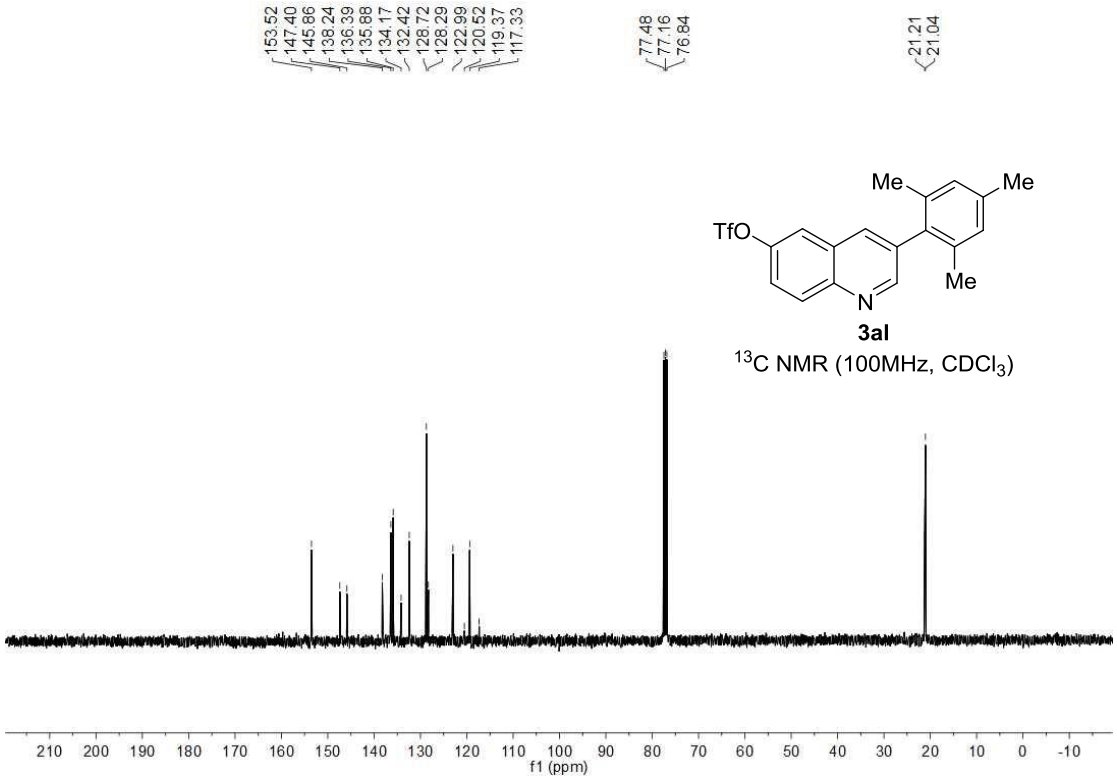
3ak

^{19}F NMR (376MHz, $CDCl_3$)



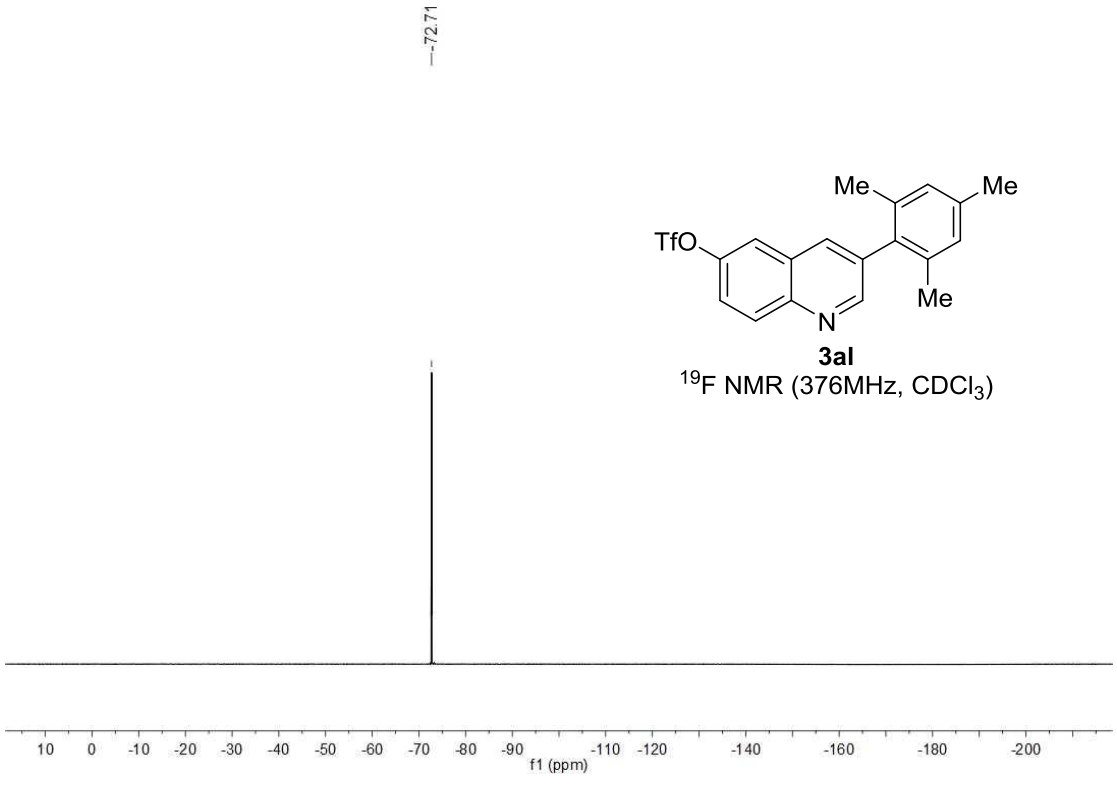
3al

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



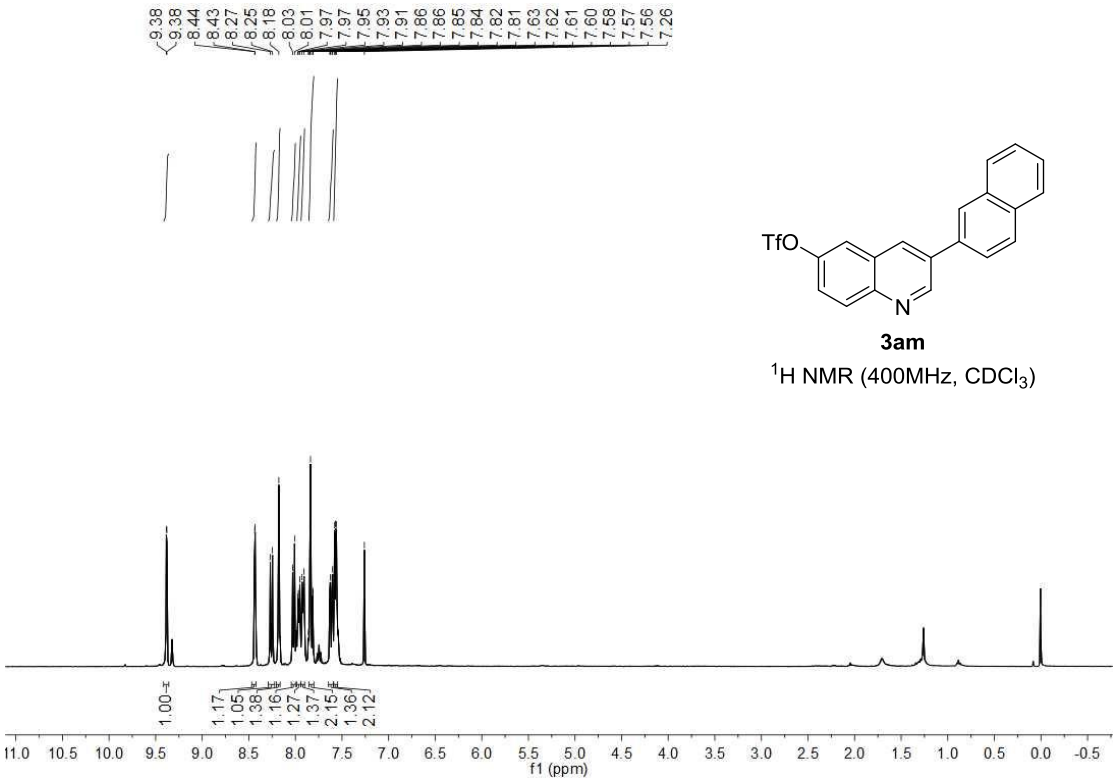
3al

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



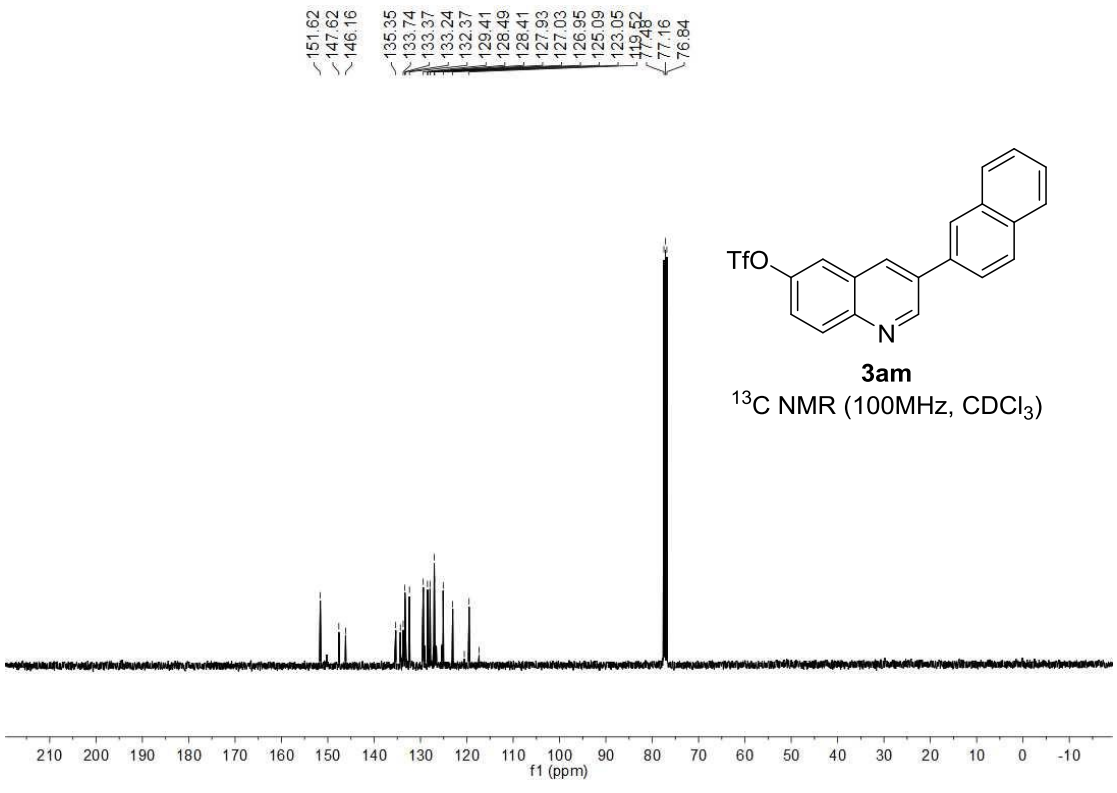
3al

^{19}F NMR (376MHz, $CDCl_3$)



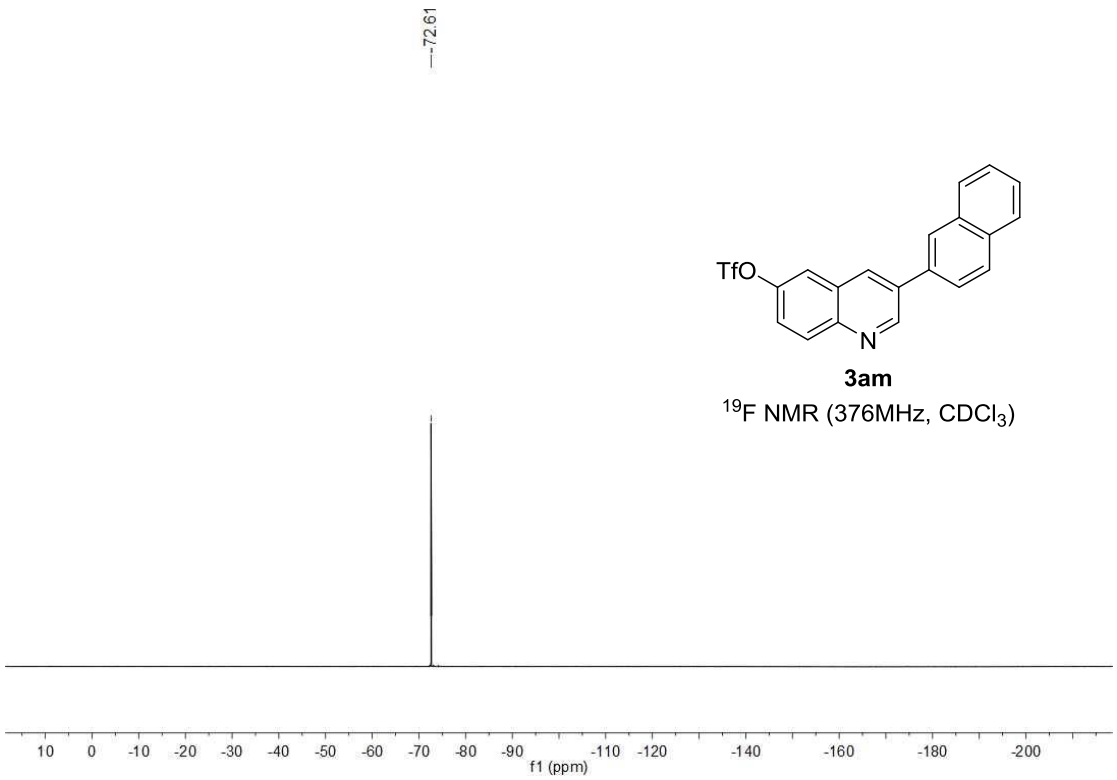
3am

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



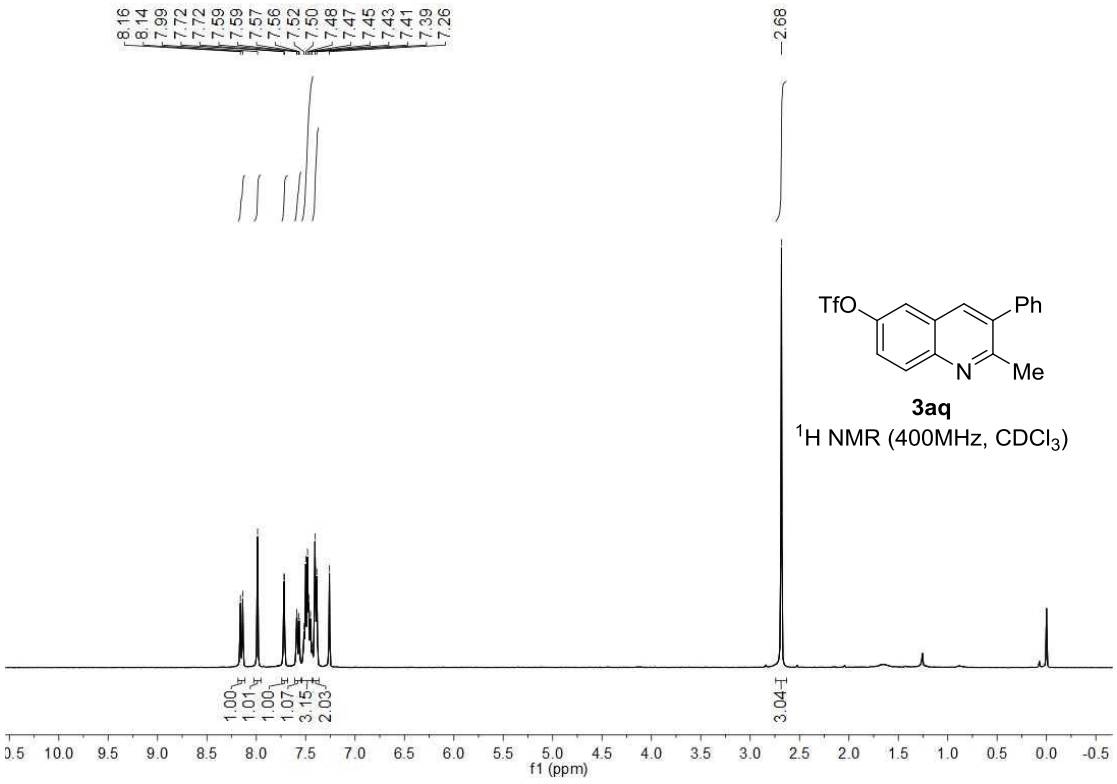
3am

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



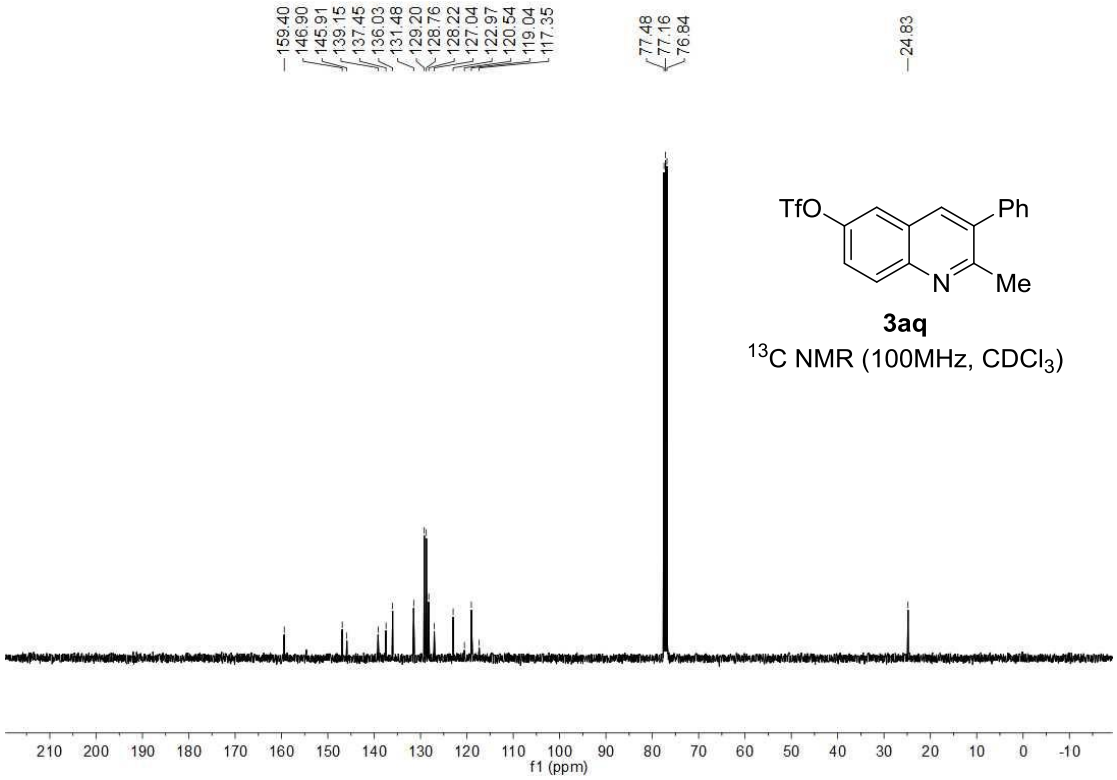
3am

^{19}F NMR (376MHz, $CDCl_3$)



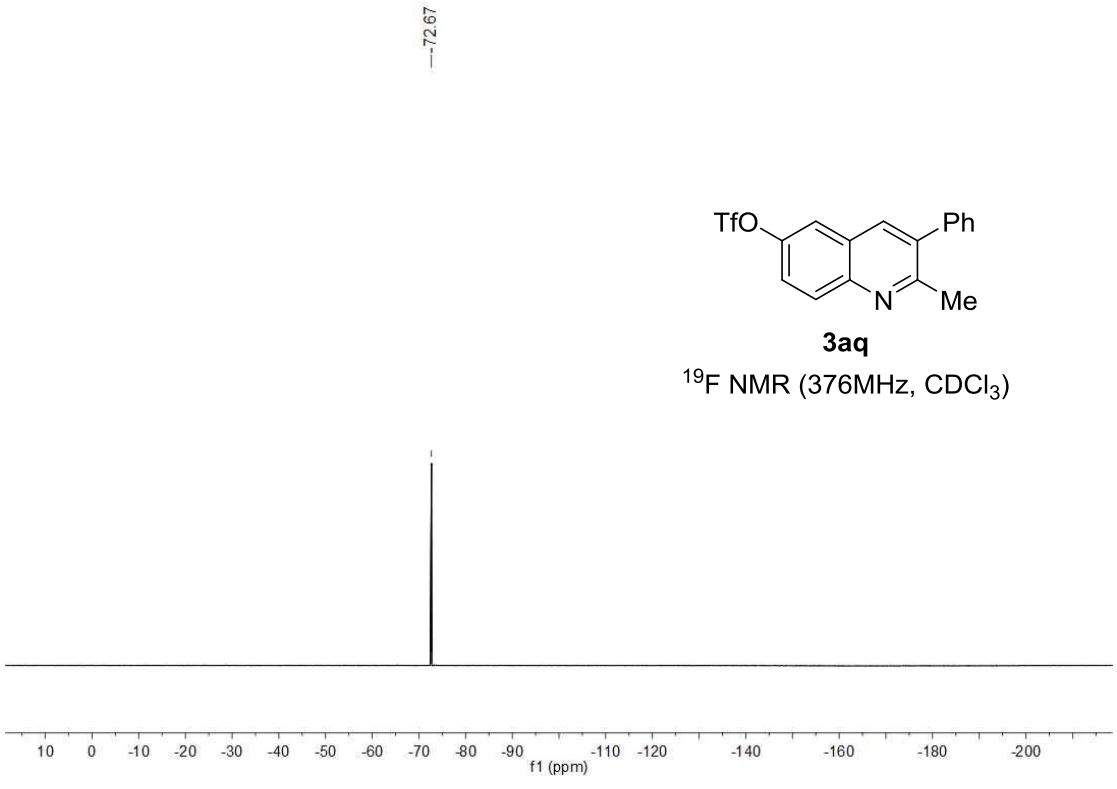
3aq

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



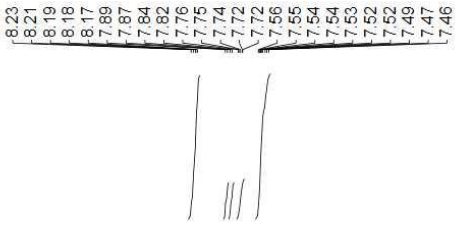
3aq

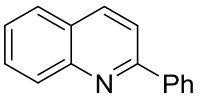
^{13}C NMR (100MHz, $CDCl_3$)



3aq

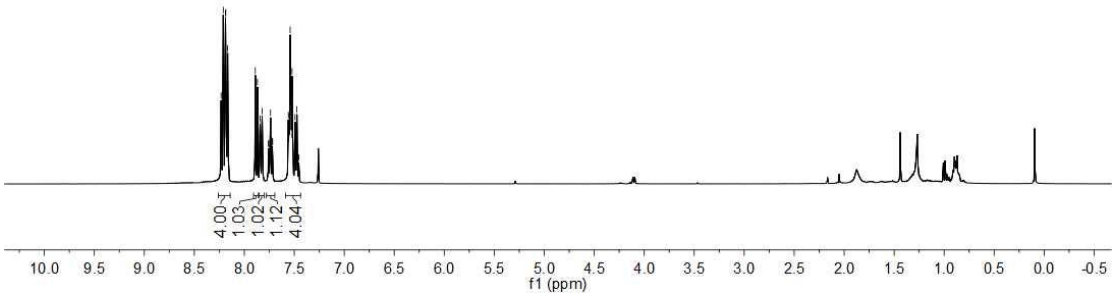
^{19}F NMR (376MHz, $CDCl_3$)

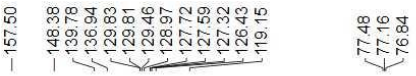


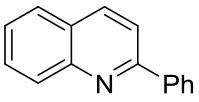


4aa

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

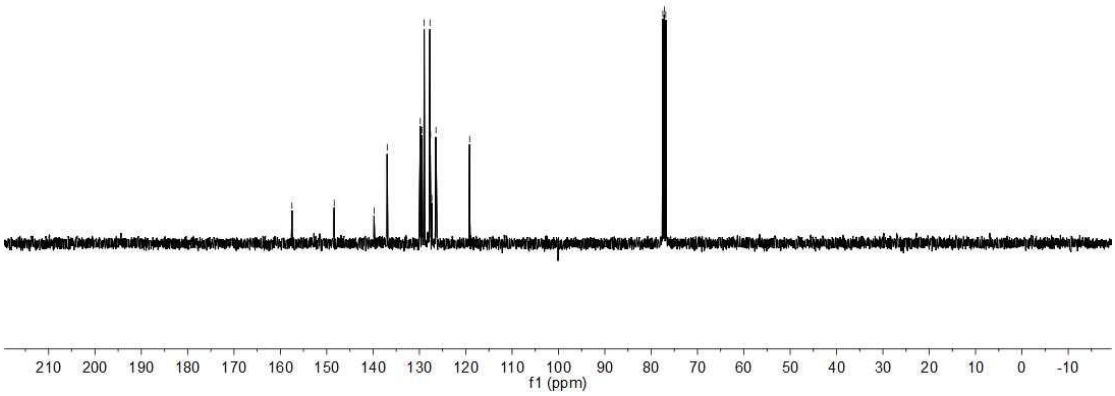


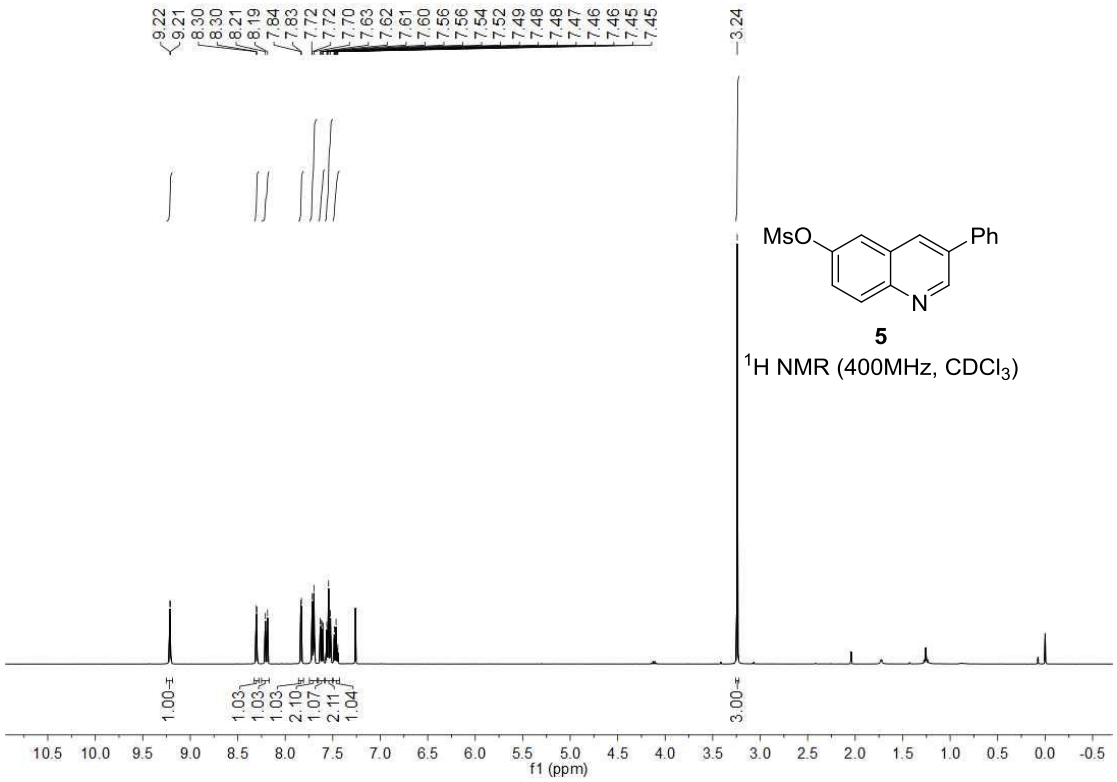




4aa

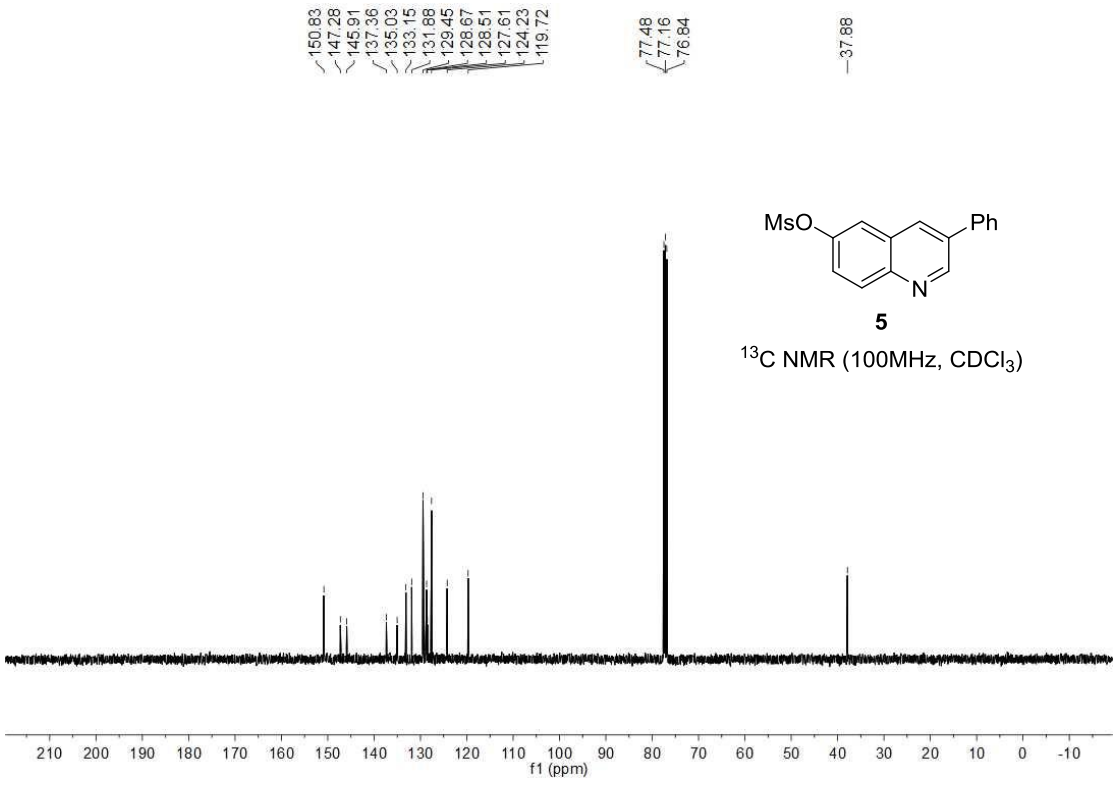
^{13}C NMR (100MHz, $CDCl_3$)





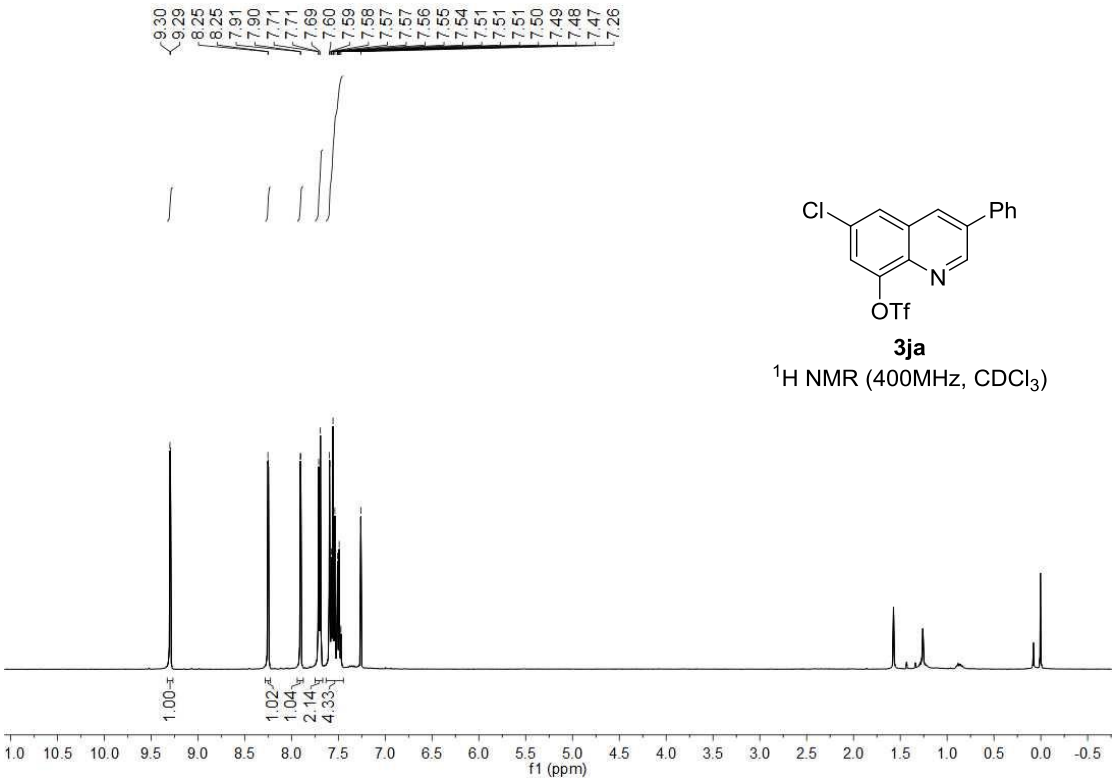
5

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



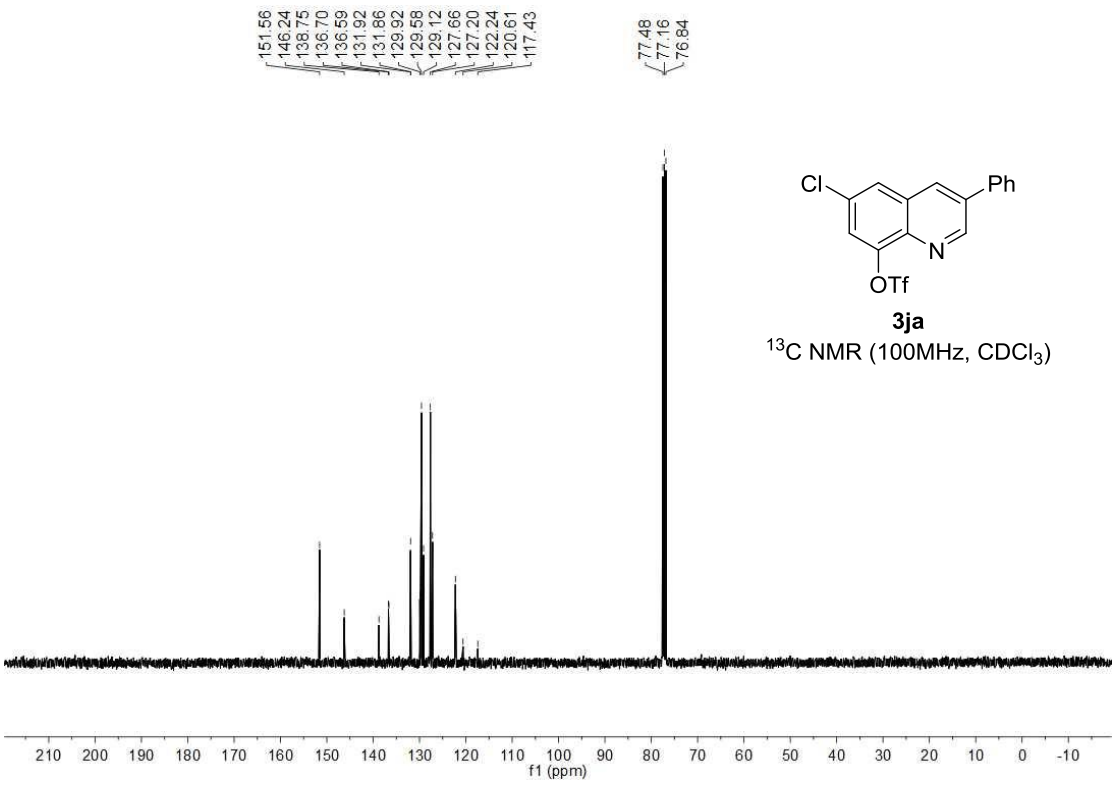
5

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



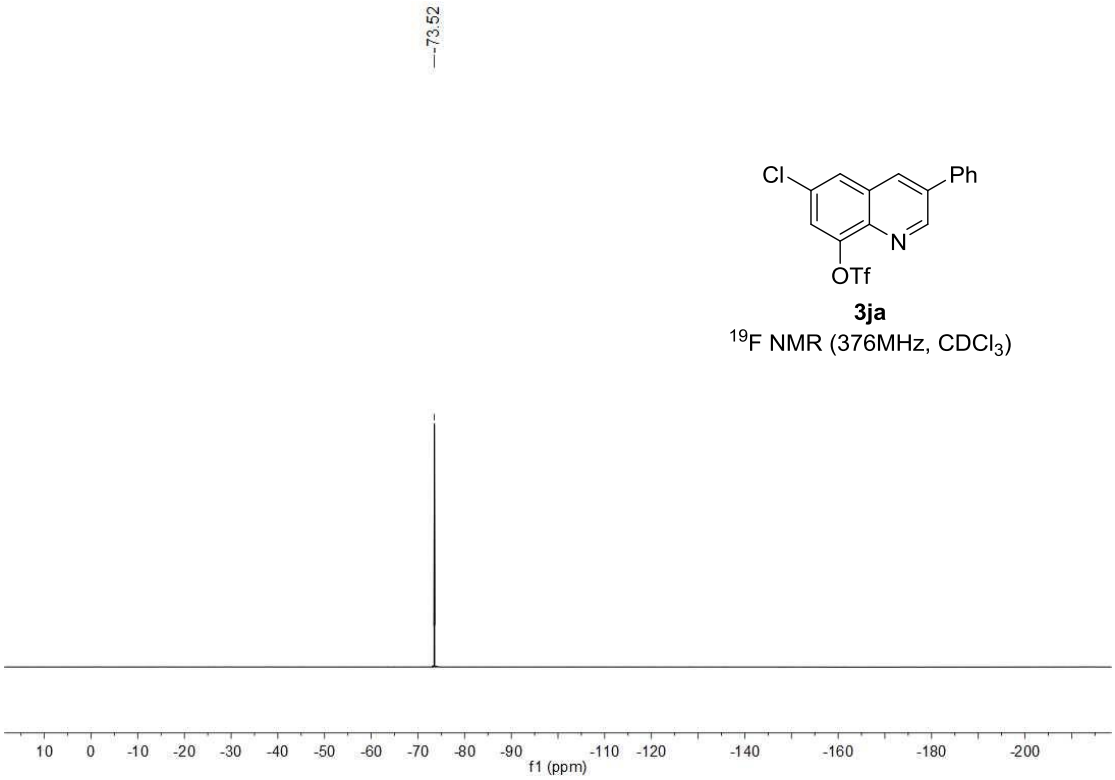
3ja

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



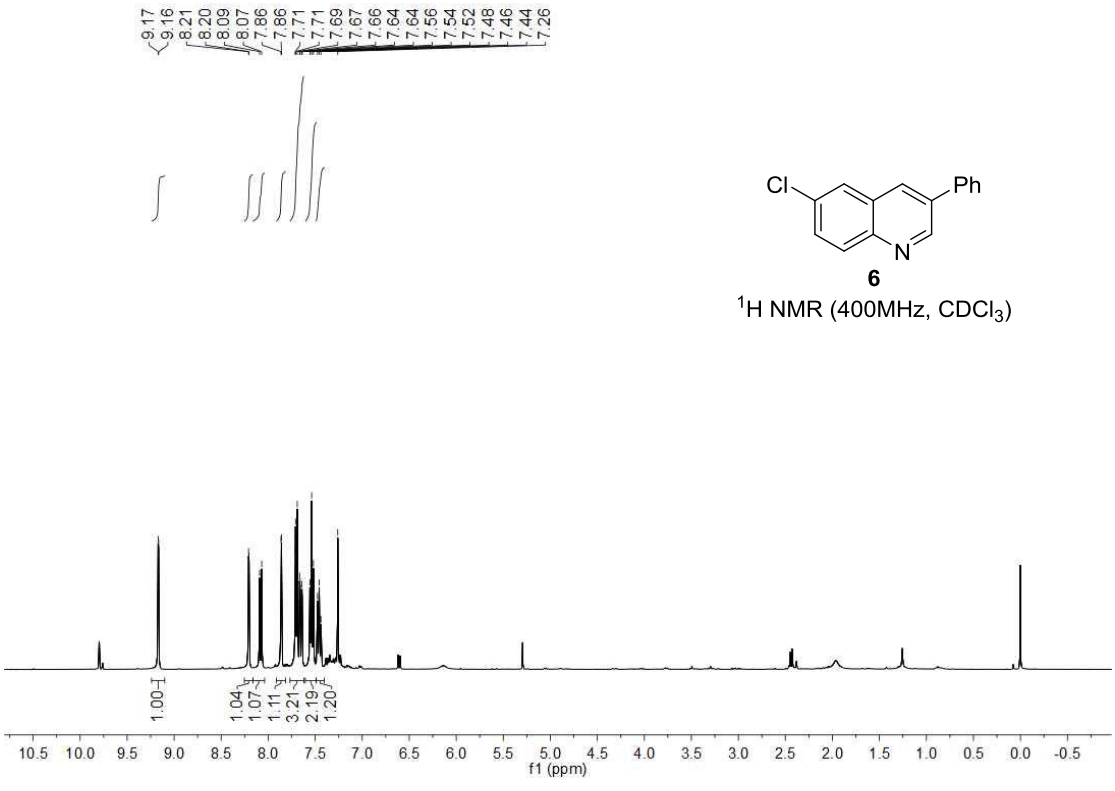
3ja

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



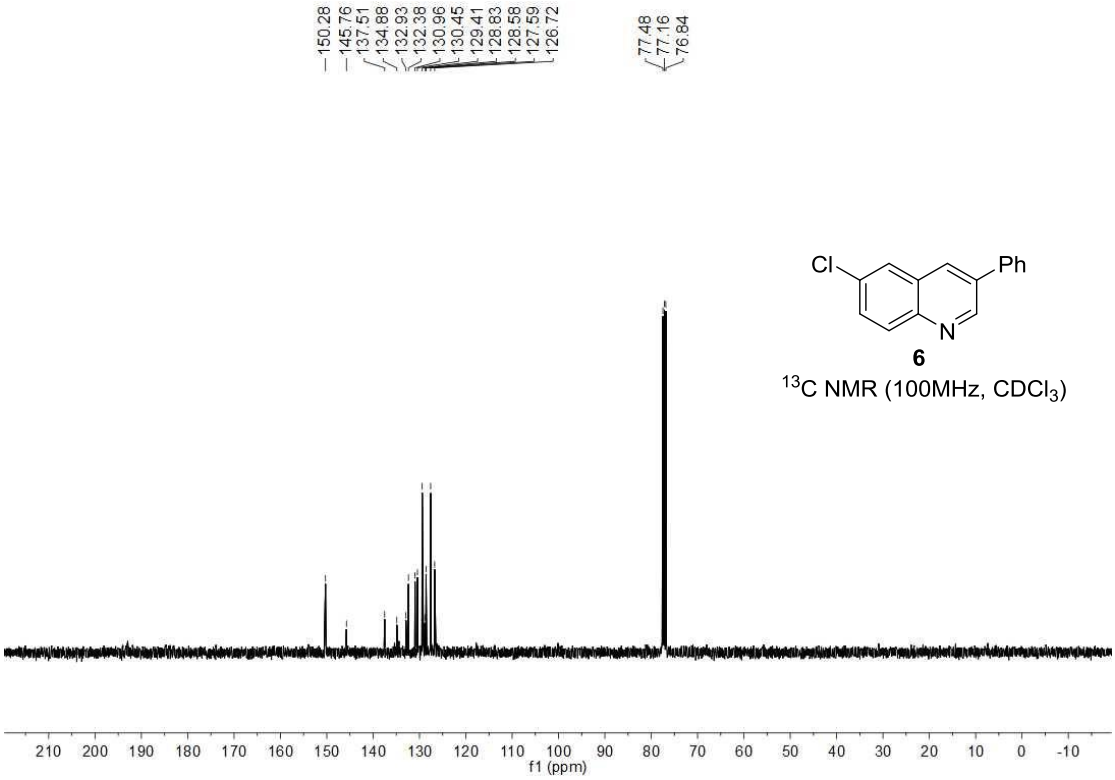
3ja

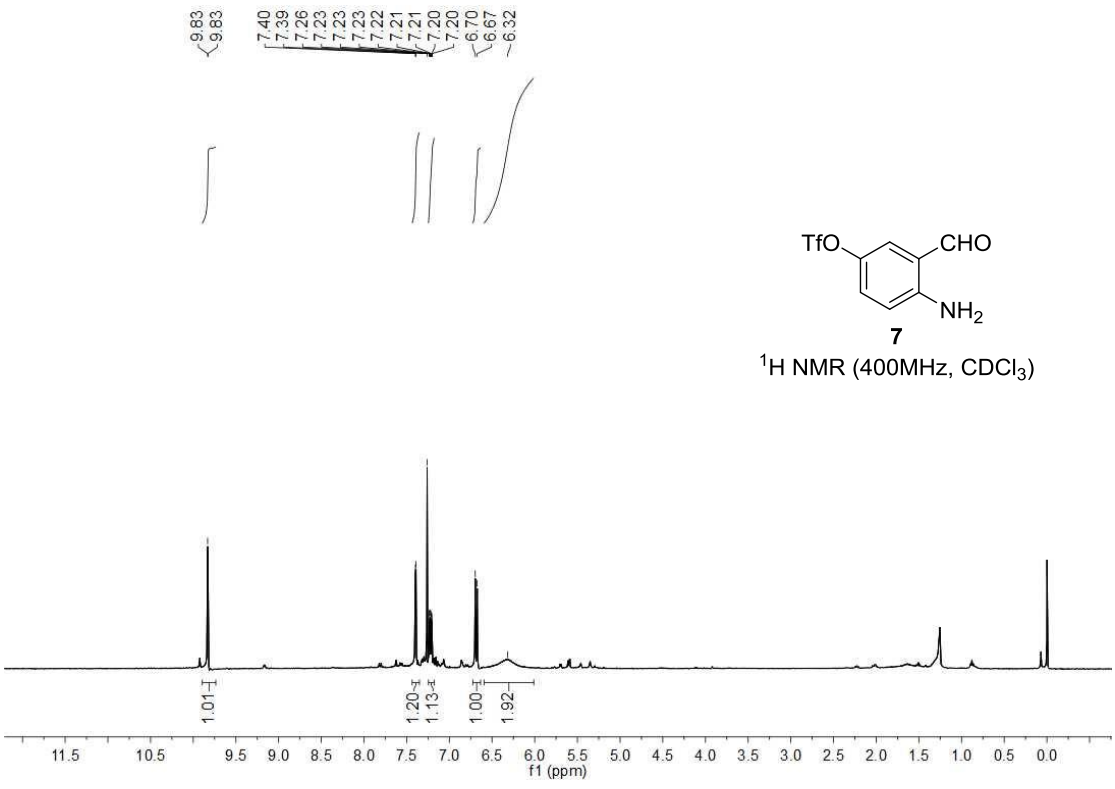
^{19}F NMR (376MHz, $CDCl_3$)

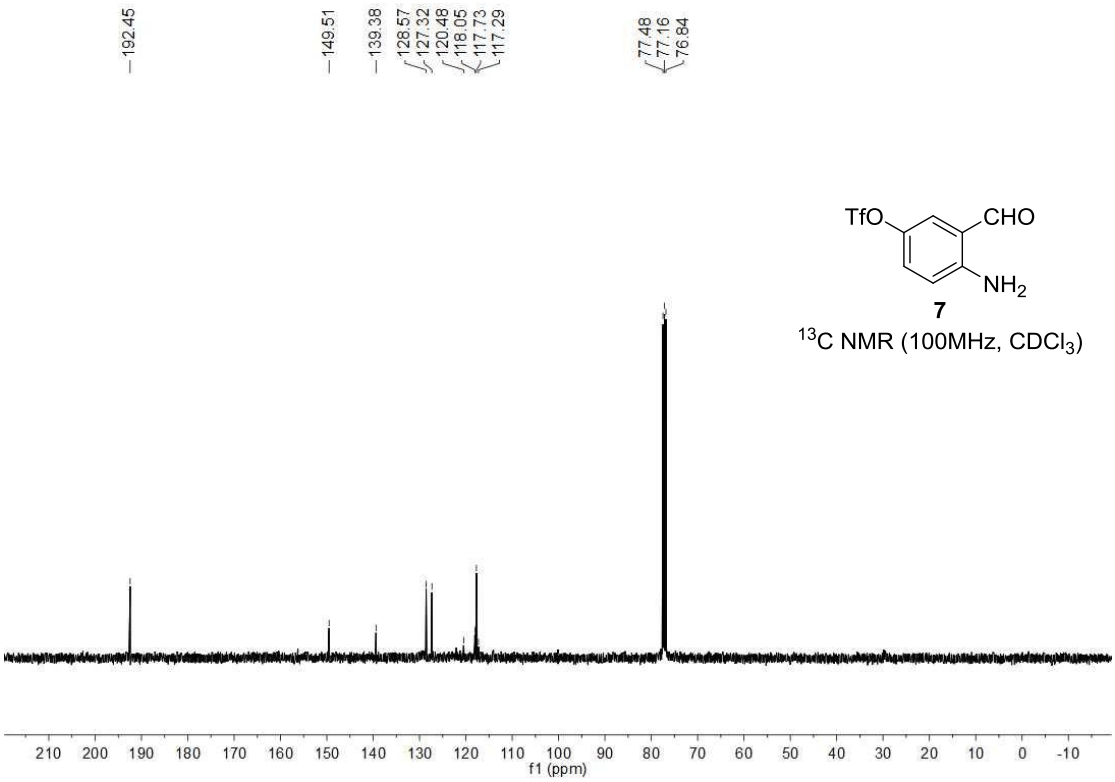


6

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

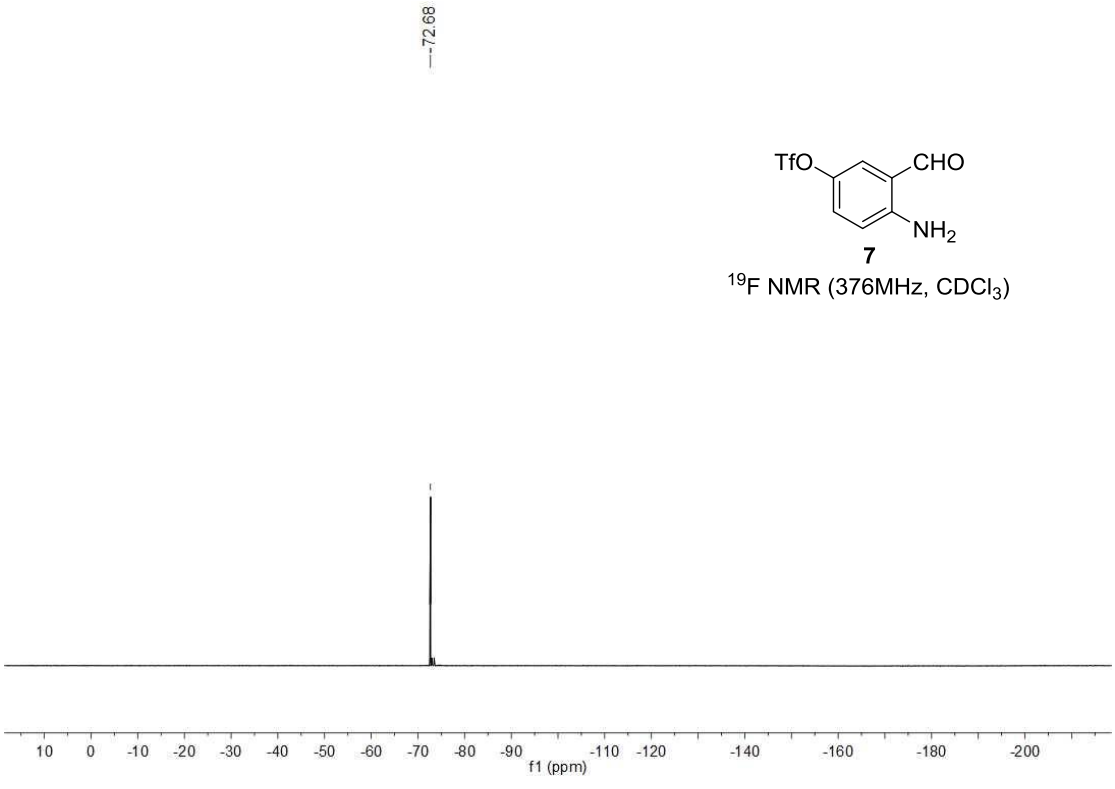

150.28
145.76
137.51
134.88
132.93
132.38
130.96
130.45
129.41
128.83
128.58
127.59
126.72
77.48
77.16
76.84
Cl
Ph
N
6
13C NMR (100MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


9.83
9.83
7.40
7.39
7.26
7.23
7.23
7.23
7.22
7.21
7.21
7.20
7.20
6.70
6.67
6.32
TfO
CHO
NH2
7
1H NMR (400MHz, CDCl3)
1.01
1.20
1.13
1.00
1.92
11.5 10.5 9.5 9.0 8.5 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)



7

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



7

^{19}F NMR (376MHz, $CDCl_3$)