Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Visible-light-induced Synthesis of a Variety of Trifluoromethylated Alkenes from Potassium Vinyltrifluoroborates by Photoredox Catalysis

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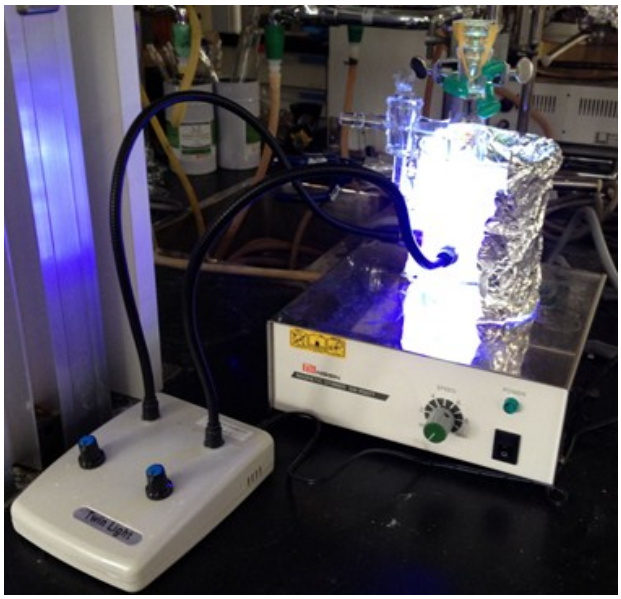
Contents

Materials and methods

$[Ru(bpy)_3](PF_6)_2$[1a] and [*fac*-$Ir(ppy)_3$][1b] were prepared according to the literature procedures. Togni's reagent (**1a**) was purchased from TCI. Potassium (*E*)-vinyltrifluoroborate, **2b**,[2a] **2c**,[2b] **2d**,[2c] **2f**[2b] and **2v**[2b] were prepared according to the literature procedures. Trifluoromethylated alkene **3v** was assigned by ^{1}H NMR spectroscopy based on the previous report.[2d] Catalytic reactions were performed under an atmosphere of nitrogen using standard Schlenk techniques unless otherwise noted. Methanol (dehydrated solvent, KANTO CHEMICAL CO., INC.) was degassed with ultrasonic bath, and stored under N_2 atmosphere. NMR solvents (CD_3OD) was dried over molecular sieves 3Å, degassed and stored under N_2. Thin-layer chromatography was performed on Merck TLC plate with 60 F_{254}. Visible light irradiations were performed with a Relyon LED lamp (3 W x 2; λ_{max} = 425 nm). The ^{1}H NMR was acquired on Bruker AVANCE-400 (400 MHz). NMR chemical shifts were referenced to residual protio impurities in the deuterated solvent. HRMS (ESI-TOF Mass spectra) were obtained with a Bruker micrOTOF II. HRMS (EI Mass spectra) were recorded on a JEOL JMS-700 mass spectrometers at Center for Advanced Materials Analysis, Technical Department, Tokyo Institute of Technology. Single-crystal X-ray measurement was made on a Bruker SMART APEX II ULTRA. The crystallographic data for **3q** are summarized in Table S1-S5. The crystallographic data were deposited at the Cambridge Crystallographic Data Centre: CCDC 900630 (**3q**).

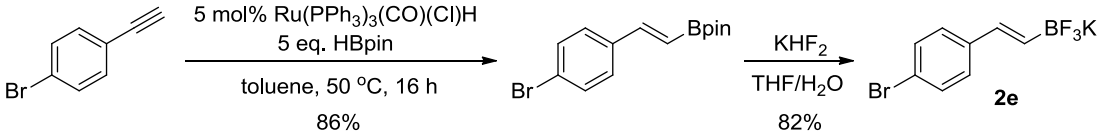
Reaction apparatus

Irradiation of visible light was performed with a Relyon LED lamp (3 W x 2; λ_{max} = 425 nm).



Synthesis of potassium (*E*)-vinyltrifluoroborate

Potassium (*E*)-2-(4-bromophenyl)ethenyltrifluoroborate (2e)



A 2-neck 100 mL round-bottom flask was charged with alkyne (1.15 g, 6.35 mmol), carbonylchlorohydridotris(triphenylphosphine)ruthenium (303 mg, 0.32 mmol) and dry toluene (26 mL), then 4,4,5,5-tetramethyl-1,3,2-dioxaborane (4.62 mL, 31.8 mmol, 5 eq.) was added to the mixture under N_2. The reaction mixture was stirred at 50 °C for 16 h. After cooling to room temperature, the solvent was removed under vaccum. Resulting reaction mixture was diluted with Et_2O, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 10/1) to afford the (*E*)-2-(4-bromostyryl)ethenylboronic acid pinacol ester as a white solid (1.69 g, 86% yield). The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.46 (dd, J = 6.8, 1.6 Hz, 2 H), 7.35-7.29 (m, 3 H), 6.14 (d, J = 18.4 Hz, 1 H), 1.30 (s, 12 H). **^{11}B NMR** (125.7 MHz, $CDCl_3$, rt) δ 29.6.

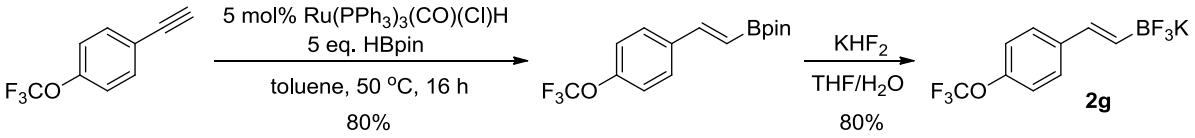
Ref.: H. Jang, A. R. Zhugralin, Y. Lee, A. H. Hoveyda, *J. Am. Chem. Soc.* **2011**, *133*, 7859–7871.

To a solution of (*E*)-2-(4-bromophenyl)ethenylboronic acid pinacol ester (1.69 g, 5.47 mmol) in dry THF (30 mL) was added a solution of KHF_2 (2.56 g, 32.8 mmol) in water (10 mL). The raction mixture was stirred at room temperature for overnight. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether and pentane for several times to afford the title compound as a white solid (1.3 g, 82% yield). The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, DMSO, rt) δ 7.41 (d, J = 8.4 Hz, 2 H), 7.26 (d, J = 8.4 Hz, 2 H), 6.42 (d, J = 18.4 Hz, 1 H), 6.20 (dq, J = 18.0, 3.2 Hz, 1 H). **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.36. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -138.0.

Ref.: A. T. Parsons, T. D. Senecal, S. L. Buchwald, *Angew. Chem. Int. Ed.* **2012**, *51*, 2947–2950.

Potassium (*E*)-2-(4-trifluoromethoxyphenyl)ethenyltrifluoroborate (2g)



A 2-neck 100 mL round-bottom flask was charged with alkyne (1.0 g, 5.37 mmol), carbonylchlorohydridotris(triphenylphosphine)ruthenium (256 mg, 0.27 mmol) and dry toluene (21 mL), then 4,4,5,5-tetramethyl-1,3,2-dioxaborane (3.91 mL, 26.9 mmol, 5 eq.) was added to the mixture under N_2. The reaction mixture was stirred at 50 °C for 16 h. After cooling to room

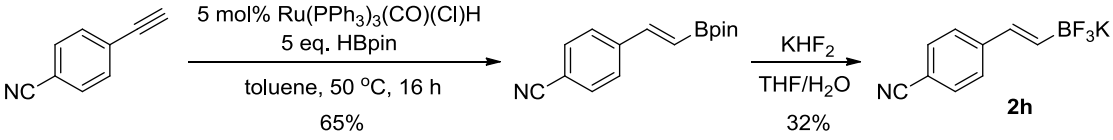
temperature, the solvent was removed under vaccum. Resulting reaction mixture was diluted with Et_2O, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 10/1→4/1) to afford the (*E*)-2-(4-trifluoromethoxyphenyl)ethenylboronic acid pinacol ester as a pale yellow oil (1.35 g, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.49 (dd, J = 6.8, 2.0 Hz, 2 H), 7.35 (d, J = 18.4 Hz, 1 H), 7.17 (d, J = 8.8 Hz, 2 H), 6.13 (d, J = 18.4 Hz, 1 H), 1.31 (s, 12 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 149.6, 147.8, 136.4, 128.4, 121.0, 120.6 (q, J = 256 Hz), 83.6, 24.9. **^{11}B NMR** (125.7 MHz, $CDCl_3$, rt) δ 30.0. **HRMS** (ESI-TOF): calculated for $[C_{15}H_{18}BF_3O_3\text{-}H]^-$ requires 313.1231, found 313.1230.

To a solution of (*E*)-2-(4-trifluoromethoxyphenyl)ethenylboronic acid pinacol ester (1.1 g, 3.5 mmol) in dry THF (20 mL) was added a solution of KHF_2 (1.64 g, 21 mmol) in water (10 mL). The raction mixture was stirred at room temperature for overnight. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was diluted acetone, and excess amount of ether was added. The precipitate was filtered, washed with pentane for several times, and dried *in vacuo*. Resulting solid was wash with CH_2Cl_2 to afford the title compound as a white solid (0.82 g, 80% yield).

^{1}H NMR (400 MHz, acetone, rt) δ 7.41 (d, J = 8.0 Hz, 2 H), 7.17 (d, J = 8.0 Hz, 2 H), 6.68 (d, J = 18.4 Hz, 1 H), 6.20 (dq, J = 18.4, 3.6 Hz, 1 H). **^{13}C NMR** (100 MHz, acetone, rt) δ 148.1, 141.1, 133.5, 127.8, 121.6, 121.5 (q, J = 253 Hz). **^{11}B NMR** (128.4 MHz, acetone, rt) δ 3.06. **^{19}F NMR** (376.5 MHz, acetone, rt) δ -58.6, -141.8. **HRMS** (ESI-TOF): calculated for $[C_9H_6BF_6O]^-$ requires 255.0423, found 255.0442.

Potassium (*E*)-2-(4-cyanophenyl)ethenyltrifluoroborate (2h)



A 2-neck 100 mL round-bottom flask was charged with alkyne (1.0 g, 7.87 mmol), carbonylchlorohydridotris(triphenylphosphine)ruthenium (373 mg, 0.39 mmol) and dry toluene (31 mL), then 4,4,5,5-tetramethyl-1,3,2-dioxaborane (5.72 mL, 39.3 mmol, 5 eq.) was added to the mixture under N_2. The reaction mixture was stirred at 50 °C for 16 h. After cooling to room temperature, the solvent was removed under vaccum. Resulting reaction mixture was diluted with Et_2O, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 4/1) to afford the (*E*)-2-(4-cyanophenyl)ethenylboronic acid pinacol ester as a yellow solid (1.3 g, 65% yield).

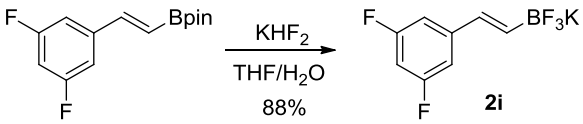
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.62 (d, J = 8.4 Hz, 2 H), 7.54 (d, J = 8.4 Hz, 2 H), 7.36 (d, J = 18.4 Hz, 1 H), 6.27 (d, J = 18.4 Hz, 1 H), 1.31 (s, 12 H). **^{11}B NMR** (125.7 MHz, $CDCl_3$, rt) δ 29.3.

To a solution of (*E*)-2-(4-cyanophenyl)ethenylboronic acid pinacol ester (1.3 g, 5.1 mmol) in

dry THF (20 mL) was added a solution of KHF_2 (2.39 g, 31 mmol) in water (10 mL). The raction mixture was stirred at room temperature for overnight. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether, pentane and CH_2Cl_2 for several times to afford the title compound as a yellow solid (0.38 g, 32 % yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 7.67 (d, J = 8.4 Hz, 2 H), 7.49 (d, J = 8.4 Hz, 2 H), 6.53 (d, J = 18.4 Hz, 1 H), 6.42 (dq, J = 18.4, 3.2 Hz, 1 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 144.9, 132.1, 131.8, 126.0, 119.2, 107.8. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.42. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -138.4. **HRMS** (ESI-TOF): calculated for $[C_9H_6BF_3N]^-$requires 196.0553, found 196.0560.

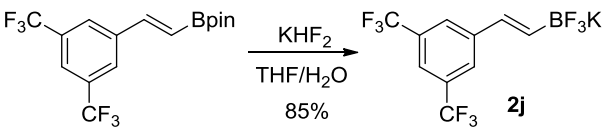
Potassium (*E*)-2-(3,5-difluorophenyl)ethenyltrifluoroborate (2i)



To a solution of (*E*)-2-(3,5-difluorophenyl)ethenylboronic acid pinacol ester (1.0 g, 3.75 mmol) in dry THF (20 mL) was added a solution of KHF_2 (1.76 g, 23 mmol) in water (10 mL). The raction mixture was stirred at room temperature for 5 h. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether and pentane for several times to afford the title compound as a white solid (0.81 g, 88% yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 7.00 (d, J = 7.6 Hz, 2 H), 6.90 (dd, J = 9.2, 2.0 Hz, 1 H), 6.46 (d, J = 18.4 Hz, 1 H), 6.32 (dq, J = 18.4, 3.6 Hz, 1 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 162.6 (d, J = 293 Hz), 162.5 (d, J = 293 Hz), 144.5, 131.1, 107.9 (d, J = 18.2 Hz), 107.8 (d, J = 18.2 Hz), 100.8 (d, J = 26.0 Hz), 100.5 (d, J = 26.0 Hz). **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.46. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -111.0 (d, J = 8.66 Hz), -138.2. **HRMS** (ESI-TOF): calculated for $[C_8H_5BF_5]^-$ requires 207.0411, found 207.0453.

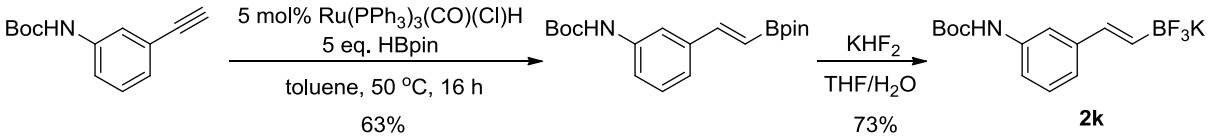
Potassium (*E*)-2-[3,5-bis(trifluoromethyl)phenyl]ethenyltrifluoroborate (2j)



To a solution of (*E*)-2-[3,5-bis(trifluoromethyl)phenyl)ethenylboronic acid pinacol ester (1.0 g, 2.73 mmol) in dry THF (20 mL) was added a solution of KHF_2 (1.3 g, 16 mmol) in water (10 mL). The raction mixture was stirred at room temperature for 5 h. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a pale yellow oil. The crude oil was diluted ether, and excess amount of pentane was added. The precipitate was filtered and washed with pentane for several times. The resulting solid was dried *in vacuo* to afford the title compound as a white solid (0.80 g, 85% yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 7.94 (s, 2 H), 7.76 (s, 1 H), 6.66 (d, J = 18.4 Hz, 1 H), 6.50 (dq, J = 18.4, 3.6 Hz, 1 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 142.9, 130.4, 130.3 (q, J = 32.2 Hz), 125.5, 123.5 (q, J = 271 Hz), 118.8. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.16. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -61.4, -138.5. **HRMS** (ESI-TOF): calculated for $[C_{10}H_5BF_9]^-$ requires 307.0348, found 307.0358.

Potassium (*E*)-2-(3-*tert*-butoxycarbonylaminophenyl)ethenyltrifluoroborate (2k)



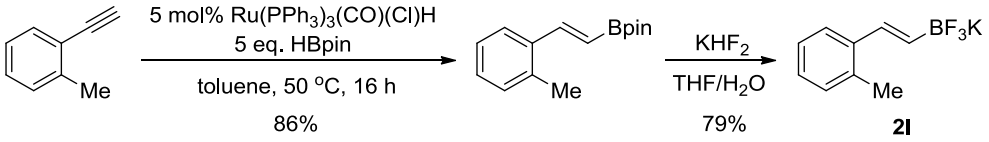
A 2-neck 100 mL round-bottom flask was charged with Boc-protected alkyne[3] (2.0 g, 9.2 mmol), carbonylchlorohydridotris(triphenylphosphine)ruthenium (447 mg, 0.47 mmol) and dry toluene (37 mL), then 4,4,5,5-tetramethyl-1,3,2-dioxaborane (6.8 mL, 46.8 mmol, 5 eq.) was added to the mixture under N_2. The reaction mixture was stirred at 50 °C for 16 h. After cooling to room temperature, the solvent was removed under vaccum. Resulting reaction mixture was diluted with Et_2O, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (pentane/Et_2O = 10/1→9/1→4/1) to afford the (*E*)-2-(3-*tert*-butoxycarbonylaminophenyl)ethenylboronic acid pinacol ester as a white solid (2.0 g, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.45 (s, 1 H), 7.38-7.22 (m, 3 H), 7.16 (d, J = 7.6 Hz, 1 H), 6.46 (bs, 1 H), 6.15 (d, J = 18.4 Hz, 1 H), 1.51 (s, 9 H), 1.30 (s, 12 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 152.8, 149.3, 138.8, 138.6, 129.2, 121.9, 119.2, 117.2, 83.4, 80.7, 28.4, 24.9. **^{11}B NMR** (125.7 MHz, $CDCl_3$, rt) δ 30.5. **HRMS** (ESI-TOF): calculated for $[C_{19}H_{28}BNO_4+H]^-$ requires 344.2195, found 344.2196.

To a solution of (*E*)-2-(3-*tert*-butoxycarbonylaminophenyl)ethylenylboronic acid pinacol ester (1.2 g, 3.5 mmol) in dry THF (20 mL) was added a solution of KHF_2 (1.64 g, 21 mmol) in water (10 mL). The raction mixture was stirred at room temperature for overnight. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether, pentane and CH_2Cl_2 for several times to afford the title compound as a white solid (0.82 g, 73 % yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 7.37 (s, 1 H), 7.25 (d, J = 8.0 Hz, 1 H), 7.10 (dd, J = 8.0, 7.6 Hz, 1 H), 6.88 (d, J = 7.6 Hz, 1 H), 6.37 (d, J = 18.0 Hz, 1 H), 6.10 (dq, J = 18.0, 3.2 Hz, 1 H), 1.47 (s, 9 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 152.7, 140.7, 139.4, 133.1, 133.0, 128.2, 119.4, 115.8, 115.1, 78.7, 39.5, 28.1. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.70. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -138.0. **HRMS** (ESI-TOF): calculated for $[C_{13}H_{16}BF_3NO_2]^-$ requires 286.1234, found 286.1233.

Potassium (*E*)-2-(2-tolyl)ethenyltrifluoroborate (2l)



A 2-neck 100 mL round-bottom flask was charged with alkyne (1.0 g, 8.61 mmol), carbonylchlorohydridotris(triphenylphosphine)ruthenium (407 mg, 0.43 mmol) and dry toluene (35 mL), then 4,4,5,5-tetramethyl-1,3,2-dioxaborane (6.25 mL, 43 mmol, 5 eq.) was added to the mixture under N_2. The reaction mixture was stirred at 50 °C for 16 h. After cooling to room temperature, the solvent was removed under vaccum. Resulting reaction mixture was diluted with Et_2O, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 9/1→4/1) to afford the (*E*)-2-(2-tolyl)ethenylboronic acid pinacol ester as a pale yellow solid (1.8 g, 86% yield). The spectral data of the product were identical with those reported in the literature.

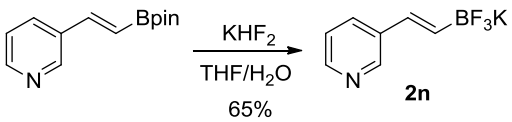
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.64 (d, J = 18.0 Hz, 1 H), 7.55 (d, J = 5.6 Hz, 1 H), 7.20-7.12 (m, 3 H), 6.08 (d, J = 18.0Hz, 1 H), 1.31 (s, 12 H). **^{11}B NMR** (125.7 MHz, $CDCl_3$, rt) δ 29.8.

Ref.: H. Jang, A. R. Zhugralin, Y. Lee, A. H. Hoveyda, *J. Am. Chem. Soc.* **2011**, *133*, 7859–7871.

To a solution of (*E*)-2-(2-tolyl)ethenylboronic acid pinacol ester (1.80 g, 7.37 mmol) in dry THF (30 mL) was added a solution of KHF_2 (3.46 g, 44.2 mmol) in water (10 mL). The raction mixture was stirred at room temperature for overnight. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether, pentane and CH_2Cl_2 for several times to afford the title compound as a white solid (1.3 g, 79% yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 7.38 (d, J = 7.6 Hz, 1 H), 7.11-6.99 (m, 3 H), 6.68 (d, J = 18.0 Hz, 1 H), 6.06 (dq, J = 18.0, 3.2 Hz, 1 H), 2.25 (s, 3 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 139.2, 133.5, 130.2 (d, J = 4.0 Hz), 129.7, 125.6, 125.4, 124.4, 19.3. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.55. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -137.7. **HRMS** (ESI-TOF): calculated for $[C_9H_9BF_3]^-$ requires 185.0757, found 185.0759.

Potassium (*E*)-2-(3-pyridine)ethenyltrifluoroborate (2n)



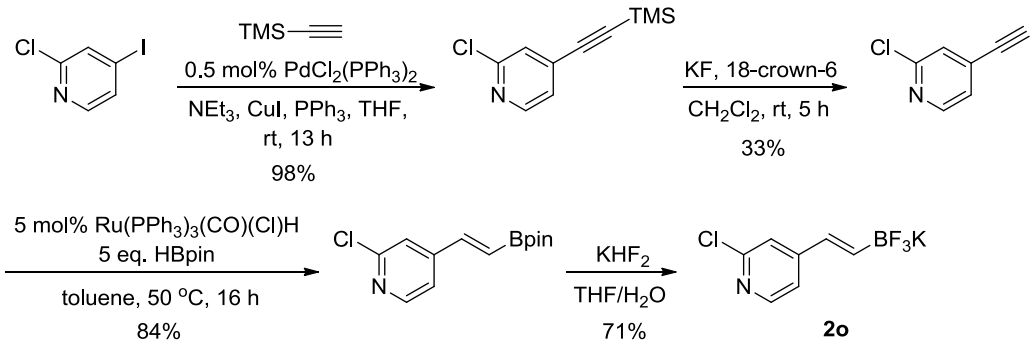
To a solution of (*E*)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]pyridine[4] (2.2 g, 9.5 mmol) in dry THF (35 mL) was added a solution of KHF_2 (4.5 g, 57 mmol) in water (10 mL). The raction mixture was stirred at room temperature for 5 h. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether, pentane

and CH_2Cl_2 for several times to afford the title compound as a pale yellow solid (1.3 g, 65 % yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 8.47 (s, 1 H), 8.31 (dd, J = 4.8, 1.6 Hz, 1 H), 7.73 (dd, J = 8.0, 1.6 Hz, 1 H), 7.26 (dd, J = 8.0, 4.8 Hz, 1 H), 6.48 (d, J = 18.4 Hz, 1 H), 6.33 (dq, J = 18.0, 3.2 Hz, 1 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 147.4, 146.9, 135.4, 131.7, 129.7, 129.6, 123.5. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.38. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -138.2.

HRMS (ESI-TOF): calculated for $[C_7H_6BF_3N]^-$ requires 172.0552, found 172.0560.

Potassium (*E*)-2-[4-(2-chloropyridine)]ethenyltrifluoroborate (2o)



A 2-neck 300 mL round-bottom flask was charged with 4-iodo-2-chloropyridine (5.0 g, 20.9 mmol), $PdCl_2(PPh_3)_2$ (77 mg, 0.11 mmol), PPh_3 (55 mg, 0.22 mmol), dry THF (16 mL) and NEt_3 (25 mL) under N_2. After bubbling N_2 into the solution for 15 min, CuI (40 mg, 0.33 mmol) and trimethylsilylacetylene (3.3 mL, 23.0 mmol) were added sequentially. The reaction mixture was stirred at room temperature. After 13 h, the precipitate (NEt_3•HI) was filtered off and washed with EtOAc. The filtrate solution was concentrated and residue was diluted with ether/hexane. The crude product was purified by flash column chromatography on silica gel (hexane→ hexane/AcOEt = 9/1) to afford the 4-TMS-ethynyl-2-chloropyridine as a pale yellow oil (4.30 g, 98% yield). The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.32 (dd, J = 5.2, 0.8 Hz, 1 H), 7.35 (dd, J = 1.2, 0.8 Hz, 1 H), 7.21 (dd, J = 5.2, 1.2 Hz, 1 H), 0.25 (s, 9 H).

Ref.: Y. Takayama, T. Hanazawa, T. Andou, K. Muraoka, H. Ohtani, M. Takahashi, F. Sato, *Org. Lett.* **2004**, *6*, 4253–4256.

A 2-neck 100 mL round-bottom flask was charged with TMS-alkyne (4.3 g, 20.5 mmol), 18-crown-6-ether (5.42 g, 20.5 mmol) and dry CH_2Cl_2 (28 mL), then KF (2.38 g, 41 mmol) was added to the mixture under N_2. The reaction mixture was stirred at room temperature for 5 h. Resulting reaction mixture was extracted with CH_2Cl_2, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (pentane/Et_2O = 4/1) to afford the 4-ethynyl-2-chloropyridine as a colorless crystal (0.94 g, 33% yield). The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.37 (dd, J = 4.8, 0.4 Hz, 1 H), 7.39 (br s, 1 H), 7.27 (dd, J = 5.2, 1.6 Hz, 1 H), 3.35 (s, 1 H).

Ref.: A. Conte, H. Kuehne, T. Luebbers, P. Mattei, C. Maugeais, W. Mueller, P. Pflieger, Patent:

US2007/185058 A1, 2007, 12.

A 2-neck 100 mL round-bottom flask was charged with 4-ethynyl-2-chloropyridine (0.82 g, 8.96 mmol), carbonylchlorohydridotris(triphenylphosphine)ruthenium (281 mg, 0.30 mmol) and dry toluene (23 mL), then 4,4,5,5-tetramethyl-1,3,2-dioxaborane (4.3 mL, 29.8 mmol, 5 eq.) was added to the mixture under N_2. The reaction mixture was stirred at 50 °C for 16 h. After cooling to room temperature, the solvent was removed under vaccum. Resulting reaction mixture was diluted with Et_2O, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 9/1→4/1) to afford the (*E*)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]-2-chloropyridine as a colorless oil (1.34 g, 84% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.39 (d, J = 4.8 Hz, 1 H), 7.38 (d, J = 0.8 Hz, 1 H), 7.29 (dd, J = 5.6, 1.6 Hz, 1 H), 7.28 (d, J = 18.4 Hz, 1 H), 6.41 (d, J = 18.4, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 152.2, 150.0, 147.8, 144.9, 121.8, 119.8, 83.9, 24.8. **^{11}B NMR** (128.4 MHz, $CDCl_3$, rt) δ 29.5.

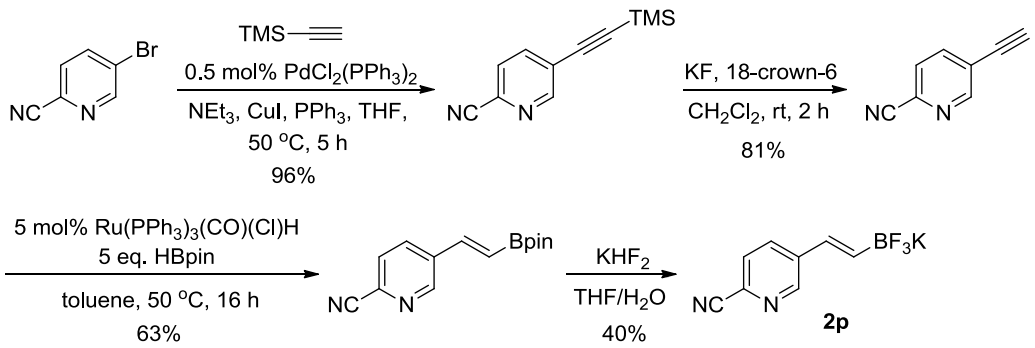
HRMS (ESI-TOF): calculated for $[C_{13}H_{17}ClBNO_2]^-$ requires 266.1127, found 266.1198.

To a solution of (*E*)-4-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]-2-chloropyridi--ne (1.2 g, 4.52 mmol) in dry THF (20 mL) was added a solution of KHF_2 (2.30 g, 29.4 mmol) in water (10 mL). The raction mixture was stirred at room temperature for overnight. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether, pentane and CH_2Cl_2 for several times to afford the title compound as a white solid (0.79 g, 71% yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 8.21 (d, J = 5.2 Hz, 1 H), 7.35-7.33 (m, 2 H), 6.61 (dq, J = 18.0, 3.2 Hz, 1 H), 6.45 (q, J = 18.0 Hz, 2 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 151.1, 150.9, 149.6, 130.0, 120.3, 119.4. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 1.90. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -138.7.

HRMS (ESI-TOF): calculated for $[C_7H_5ClBF_3N]^-$ requires 206.0162, found 206.0166.

Potassium (*E*)-2-[3-(2-cyanopyridine)]ethenyltrifluoroborate (2p)



A 2-neck 300 mL round-bottom flask was charged with 5-bromo-2-cyanopyridine (5.0 g, 27.3 mmol), $PdCl_2(PPh_3)_2$ (111 mg, 0.158 mmol), PPh_3 (86 mg, 0.328 mmol), dry THF (25 mL) and NEt_3 (37 mL) under N_2. After bubbling N_2 into the solution for 15 min, CuI (64 mg, 0.33 mmol) and trimethylsilylacetylene (4.8 mL, 34 mmol) were added sequentially. The reaction mixture was stirred

at 50 °C for 5 h. After cooling to room temperature, the precipitate (NEt_3•HBr) was filtered off and washed with EtOAc. The filtrate solution was concentrated and residue was diluted with ether/hexane. The crude product was purified by flash column chromatography on silica gel (hexane→ hexane/AcOEt = 4/1) to afford the 5-TMS-ethynyl-2-cyanopyridine as a pale yellow solid (5.27 g, 96% yield). The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.73 (dd, J = 2.0, 0.8 Hz, 1 H), 7.84 (dd, J = 8.4, 2.0 Hz, 1 H), 7.62 (dd, J = 8.4, 0.8 Hz, 1 H), 0.27 (s, 9 H).

Ref.: A. A. Farahat, A. Kumar, M. Say, A. E.-D. M. Barghash, F. E. Goda, H. M. Eisa, T. Wenzler, R. Brun, Y. Liu, L. Mickelson, W. D. Wilson, D. W. Boykin, *Bioorganic & Medicinal Chemistry*, **2010**, *18*, 557–566.

A 2-neck 100 mL round-bottom flask was charged with TMS-alkyne (4.0 g, 20.0 mmol), 18-crown-6-ether (5.28 g, 20.0 mmol) and dry CH_2Cl_2 (30 mL), then KF (2.32 g, 40 mmol) was added to the mixture under N_2. The reaction mixture was stirred at room temperature for 2 h. Resulting reaction mixture was extracted with CH_2Cl_2, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (pentane/Et_2O = 4/1→2/1) to afford the 5-ethynyl-2-cyanopyridine as an orange solid (2.08 g, 81% yield). The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.77 (dd, J = 2.0, 1.0 Hz, 1 H), 7.90 (dd, J = 8.0, 2.0 Hz, 1 H), 7.66 (dd, J = 8.0, 1.0 Hz, 1 H), 3.45 (s, 1 H).

Ref.: A. A. Farahat, A. Kumar, M. Say, A. E.-D. M. Barghash, F. E. Goda, H. M. Eisa, T. Wenzler, R. Brun, Y. Liu, L. Mickelson, W. D. Wilson, D. W. Boykin, *Bioorganic & Medicinal Chemistry*, **2010**, *18*, 557–566.

A 2-neck 100 mL round-bottom flask was charged with 5-ethynyl-2-cyanopyridine (1.2 g, 9.36 mmol), carbonylchlorohydridotris(triphenylphosphine)ruthenium (447 mg, 0.47 mmol) and dry toluene (37 mL), then 4,4,5,5-tetramethyl-1,3,2-dioxaborane (6.8 mL, 46.8 mmol, 5 eq.) was added to the mixture under N_2. The reaction mixture was stirred at 50 °C for 16 h. After cooling to room temperature, the solvent was removed under vaccum. Resulting reaction mixture was diluted with Et_2O, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 10/1→4/1) to afford the (*E*)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]-2-cyanopyridine as a white solid (1.50 g, 63% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.76 (d, J = 2.0 Hz, 1 H), 7.87 (dd, J = 8.4, 2.0 Hz, 1 H), 7.66 (d, J = 8.4 Hz, 1 H), 7.36 (d, J = 18.4 Hz, 1 H), 6.38 (d, J = 18.4, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 150.1, 143.5, 136.2, 134.0, 133.2, 128.4, 117.3, 84.1, 24.9. **^{11}B NMR** (128.4 MHz, $CDCl_3$, rt) δ 29.3.

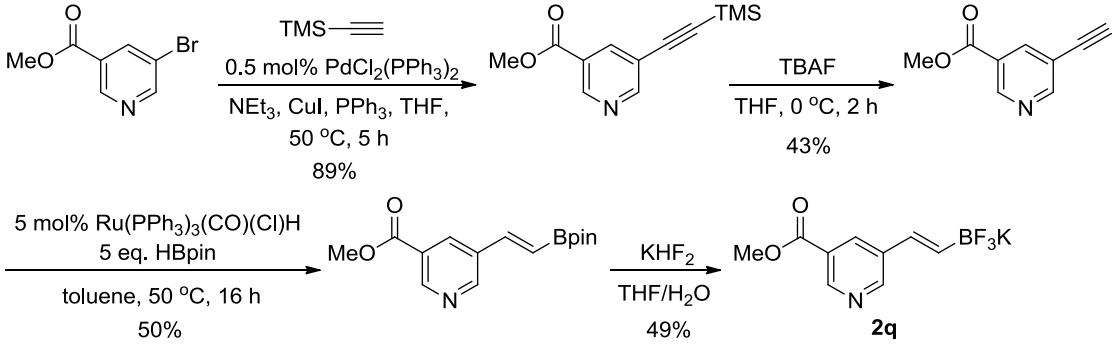
HRMS (ESI-TOF): calculated for $[C_{14}H_{17}BN_2O_2\text{-}H]^-$ requires 255.1313, found 255.1310.

To a solution of (*E*)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]-2-cyanopyridi--ne (1.3 g, 5.47 mmol) in dry THF (20 mL) was added a solution of KHF_2 (2.38 g, 30.5 mmol) in water (10 mL). The raction mixture was stirred at room temperature for 5 h. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced

under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether, pentane and CH_2Cl_2 for several times to afford the title compound as a white solid (0.48 g, 40% yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 8.67 (d, J = 2.0 Hz, 1 H), 7.95 (dd, J = 8.4, 2.0 Hz, 1 H), 7.86 (d, J = 8.4 Hz, 1 H), 6.61-6.58 (m, 2 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 148.8, 139.0, 132.7, 129.1, 128.7, 128.5, 117.8. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.35. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -138.8. **HRMS** (ESI-TOF): calculated for $[C_8H_5BF_3N]^-$ requires 197.0505, found 197.0508.

Potassium (*E*)-2-[3-(3-pyridinecarboxylic acid methyl ester)]ethenyltrifluoroborate (2q)



A 2-neck 300 mL round-bottom flask was charged with 5-bromo-3-pyridinecarboxylic acid methyl ester (2.5 g, 11.6 mmol), $PdCl_2(PPh_3)_2$ (39 mg, 0.056 mmol), PPh_3 (30 mg, 0.11 mmol), dry THF (25 mL) and NEt_3 (13 mL) under N_2. After bubbling N_2 into the solution for 15 min, CuI (22 mg, 0.11 mmol) and trimethylsilylacetylene (1.8 mL, 12.7 mmol) were added sequentially. The reaction mixture was stirred at 50 °C for 5 h. After cooling to room temperature, the precipitate (NEt_3•HBr) was filtered off and washed with EtOAc. The filtrate solution was concentrated and residue was diluted with ether/hexane. The crude product was purified by flash column chromatography on silica gel (hexane→ hexane/AcOEt = 10/1→4/1) to afford the 5-TMS-ethynyl-3-pyridinecarboxylic acid methyl ester as a pale yellow solid (2.42 g, 89% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.10 (d, J = 2.0 Hz, 1 H), 8.81 (d, J = 2.0 Hz, 1 H), 8.33 (dd, J = 2.0, 2.0 Hz, 1 H), 3.95 (s, 3 H), 0.27 (s, 9 H).

A 2-neck 100 mL round-bottom flask was charged with TMS-alkyne (1.86 g, 7.9 mmol), and dry THF (15 mL), then TBAF(1.0 M THF soln.) (13 mL, 13 mmol) was added to the solution at 0 °C under N_2. The reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was extracted with CH_2Cl_2, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 4/1→3/1) to afford the 5-ethynyl-3-pyridinecarboxylic acid methyl ester as a white solid (0.72 g, 43% yield). The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.15 (d, J = 2.4 Hz, 1 H), 8.85 (d, J = 2.0 Hz, 1 H), 8.36 (dd, J = 2.4, 2.0 Hz, 1 H), 3.96 (s, 3 H), 3.27 (s, 1 H).

Ref.: S. L. Bender, D. Bhumralkar, M. R. Collins, S. J. Cripps, J. G. Deal, L. Jia, M. D. Nambu, C. L. Palmer, Z. Peng, M. D. Varney, Patent: US2002/103203 A1, **2002**.

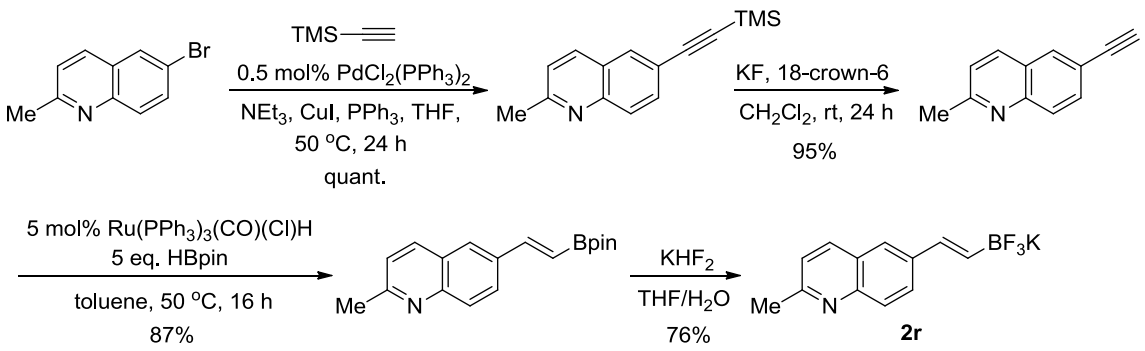
A 2-neck 100 mL round-bottom flask was charged with 5-ethynyl-3-pyridinecarboxylic acid methyl ester (1.22 g, 7.57 mmol), carbonylchlorohydridotris(triphenylphosphine)ruthenium (358 mg, 0.38 mmol) and dry toluene (31 mL), then 4,4,5,5-tetramethyl-1,3,2-dioxaborane (5.5 mL, 37.9 mmol, 5 eq.) was added to the mixture under N_2. The reaction mixture was stirred at 50 ^oC for 16 h. After cooling to room temperature, the solvent was removed under vaccum. Resulting reaction mixture was diluted with Et_2O, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (hexane→hexane/AcOEt = 9/1→4/1) to afford the (*E*)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan--2-yl)vinyl]-3-pyridinecarboxylic acid methyl ester as a white solid (1.10 g, 50% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.11 (d, J = 2.0 Hz, 1 H), 8.82 (d, J = 2.4 Hz, 1 H), 8.39 (dd, J = 2.4, 2.0 Hz, 1 H), 7.40 (d, J = 18.8 Hz, 1 H), 6.34 (d, J = 18.8 Hz, 1 H), 3.96 (s, 3 H), 1.32 (s, 9 H).
^{13}C NMR (100 MHz, $CDCl_3$, rt) δ 165.7, 152.4, 150.6, 144.5, 134.3, 133.0, 126.2, 83.8, 52.6, 24.9.
^{11}B NMR (128.4 MHz, $CDCl_3$, rt) δ 28.5. **HRMS** (ESI-TOF): calculated for $[C_{15}H_{20}BNO_4\text{-}H]^-$ requires 288.1415, found 288.1463.

To a solution of (*E*)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]-3-pyridinecarb--oxylic acid methyl ester (1.0 g, 3.45 mmol) in dry THF (20 mL) was added a solution of KHF_2 (1.62 g, 20.8 mmol) in water (10 mL). The raction mixture was stirred at room temperature for 5 h. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether, pentane and CH_2Cl_2 for several times to afford the title compound as a white solid (0.45 g, 49% yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 8.82 (d, J = 1.6 Hz, 1 H), 8.72 (d, J = 2.0 Hz, 1 H), 8.15 (dd, J = 2.0, 1.6 Hz, 1 H), 6.56 (d, J = 18.4 Hz, 1 H), 6.42 (dq, J = 18.4, 3.6 Hz, 1 H), 3.88 (s, 3 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 165.4, 151.0, 146.9, 135.4, 131.8, 128.3, 125.3, 52.1. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.27. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -138.5. **HRMS** (ESI-TOF): calculated for $[C_9H_8BF_3NO_2]^-$ requires 230.0607, found 230.0610.

Potassium (*E*)-2-[6-(2-methylquinoline)]ethenyltrifluoroborate (2r)



A 2-neck 300 mL round-bottom flask was charged with 6-bromo-2-methylquinoline (5.0 g, 22.5 mmol), $PdCl_2(PPh_3)_2$ (79 mg, 0.112 mmol), PPh_3 (59 mg, 0.225 mmol), dry THF (21 mL) and NEt_3 (30 mL) under N_2. After bubbling N_2 into the solution for 15 min, CuI (43 mg, 0.225 mmol) and

trimethylsilylacetylene (3.5 mL, 24.8 mmol) were added sequentially. The reaction mixture was stirred at 50 °C for 24 h. After cooling to room temperature, the precipitate (NEt_3•HBr) was filtered off and washed with EtOAc. The filtrate solution was concentrated and residue was diluted with ether/hexane. The crude product was purified by flash column chromatography on silica gel (hexane → hexane/AcOEt = 4/1) to afford the 6-TMS-ethynyl-2-methylquinoline as a pale yellow solid (5.5 g, quant.). The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 7.96 (d, J = 8.4 Hz, 1 H), 7.92-7.90 (m, 2 H), 7.70 (d, J = 8.8 Hz, 1 H), 7.28 (d, J = 8.4 Hz, 1 H), 2.73 (s, 3 H), 0.27 (s, 9 H).

Ref.: CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE, P. Dalko, M. Petit, D. Ogden, F. Acher, WO2011/86469 A1, 40.

A 2-neck 100 mL round-bottom flask was charged with TMS-alkyne (3.0 g, 12.5 mmol), 18-crown-6-ether (3.3 g, 12.5 mmol) and dry CH_2Cl_2 (20 mL), then KF (1.45 g, 25 mmol) was added to the mixture under N_2. The reaction mixture was stirred at room temperature for 24 h. Resulting reaction mixture was extracted with CH_2Cl_2, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (pentane/Et_2O = 4/1→3/1) to afford the 6-ethynyl-2-methylquinoline as a white solid (1.99 g, 95% yield). The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.00-7.93 (m, 3 H), 7.71 (dd, J = 8.4, 2.0 Hz, 1 H), 7.29 (d, J = 8.8, Hz, 1 H), 3.15 (s, 1 H), 2.74 (s, 3 H).

Ref.: CENTRE NATIONAL DE LA RECHERCHE SCIENTIFIQUE, P. Dalko, M. Petit, D. Ogden, F. Acher, WO2011/86469 A1, 40.

A 2-neck 100 mL round-bottom flask was charged with 6-ethynyl-2-methylquinoline (1.5 g, 8.97 mmol), carbonylchlorohydridotris(triphenylphosphine)ruthenium (427 mg, 0.45 mmol) and dry toluene (36 mL), then 4,4,5,5-tetramethyl-1,3,2-dioxaborane (6.5 mL, 45 mmol, 5 eq.) was added to the mixture under N_2. The reaction mixture was stirred at 50 °C for 16 h. After cooling to room temperature, the solvent was removed under vaccum. Resulting reaction mixture was diluted with Et_2O, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 10/1 → 4/1 → 2/1 → 1/1) to afford the (*E*)-6-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]-2-methylquinoline as a white solid (2.3 g, 87% yield).

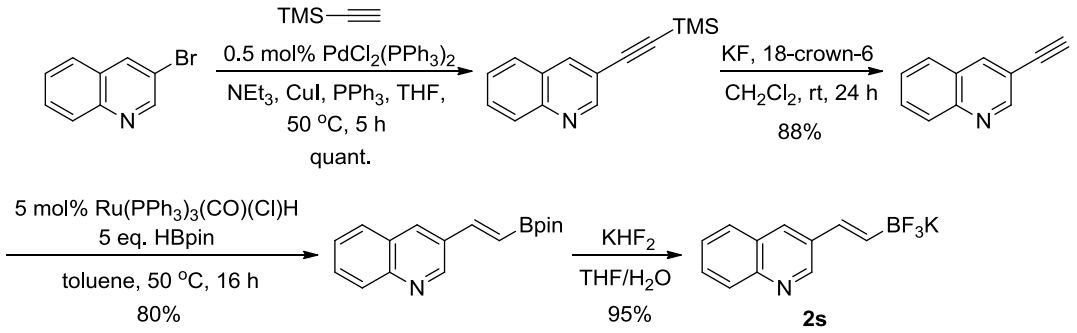
^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.01 (dd, J = 8.4, 3.6 Hz, 1 H), 7.96 (d, J = 8.8 Hz, 1 H), 7.87 (dd, J = 8.8, 1.6 Hz, 1 H), 7.76 (s, 1 H), 7.54 (d, J = 18.4 Hz, 1 H), 7.29-7.25 (m, 1 H), 6.28 (d, J = 18.4, 1 H), 2.72 (s, 3 H), 1.32 (s, 12 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 159.4, 148.7, 148.3, 136.5, 135.0, 129.0, 127.3, 127.1, 126.5, 122.4, 83.5, 25.0, 24.9. **^{11}B NMR** (128.4 MHz, $CDCl_3$, rt) δ 29.8. **HRMS (ESI-TOF)**: calculated for $[C_{18}H_{22}BNO_2\text{-}H]^-$ requires 294.1674, found 294.1643.

To a solution of (*E*)-6-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]-2-methylquino--line (1.3 g, 4.4 mmol) in dry THF (10 mL) was added a solution of KHF_2 (2.06 g, 26.4 mmol) in water (10 mL). The raction mixture was stirred at room temperature for 5 h. The mixture was

concentrated in vacuo. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether, pentane and CH_2Cl_2 for several times to afford the title compound as a white solid (0.92 g, 76% yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 8.14 (d, J = 8.4 Hz, 1 H), 7.82-7.76 (m, 2 H), 7.67 (s, 1 H), 7.33 (d, J = 8.4 Hz, 1 H), 6.64 (d, J = 18.0 Hz, 1 H), 6.35 (dq, J = 18.0, 3.6 Hz, 1 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 157.2, 146.5, 137.5, 135.7, 132.4, 127.9, 126.9, 126.4, 123.5, 121.9, 24.6. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.40. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -137.9. **HRMS (ESI-TOF)**: calculated for $[C_{12}H_{10}BF_3N]^-$ requires 236.0866, found 236.0873.

Potassium (*E*)-2-[6-(2-methylquinoline)]ethenyltrifluoroborate (2s)



A 2-neck 300 mL round-bottom flask was charged with 3-bromoquinoline (6.0 g, 28.8 mmol), $PdCl_2(PPh_3)_2$ (82 mg, 0.117 mmol), PPh_3 (61 mg, 0.233 mmol), dry THF (18 mL) and NEt_3 (27 mL) under N_2. After bubbling N_2 into the solution for 15 min, CuI (44 mg, 0.233 mmol) and trimethylsilylacetylene (4.5 mL, 31.7 mmol) were added sequentially. The reaction mixture was stirred at 50 °C for 24 h. After cooling to room temperature, the precipitate (NEt_3•HBr) was filtered off and washed with EtOAc. The filtrate solution was concentrated and residue was diluted with ether/hexane. The crude product was purified by flash column chromatography on silica gel (hexane → hexane/AcOEt = 9/1) to afford the 3-TMS-ethynylquinoline as a brown oil (6.7 g, quant.). The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.91 (d, J = 2.0 Hz, 1 H), 8.24 (br s, 1 H), 8.07 (d, J = 8.4 Hz, 1 H), 7.75 (d, J = 8.0 Hz, 1 H), 7.70 (dd, J = 8.0, 8.4 Hz, 1 H), 7.54 (dd, J = 8.4, 8.0 Hz, 1 H), 0.29 (s, 9 H).

Ref.: T. Li, L. Guo, Y. Zhang, J. Wang, Z. Li, L. Lin, Z. Zhang, L. Li, J. Lin, W. Zhao, J. Li, P. G. Wang, Carbohydrate Research, **2011**, *346*, 1083–1092.

A 2-neck 100 mL round-bottom flask was charged with TMS-alkyne (6.7 g, 29.7 mmol), 18-crown-6-ether (7.86 g, 29.7 mmol) and dry CH_2Cl_2 (40 mL), then KF (3.45 g, 59.4 mmol) was added to the mixture under N_2. The reaction mixture was stirred at room temperature for 24 h. Resulting reaction mixture was extracted with CH_2Cl_2, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (pentane/Et_2O = 4/1→3/2) to afford the 3-ethynyl-quinoline as a pale yellow solid (4.0 g, 88% yield). The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.94 (d, J = 2.0 Hz, 1 H), 8.28 (br s, 1 H), 8.09 (d, J = 8.4 Hz, 1 H),

7.78 (d, J = 8.0 Hz, 1 H), 7.73 (dd, J = 7.6, 7.2 Hz, 1 H), 7.57 (dd, J = 7.6, 7.2 Hz, 1 H), 3.27 (s, 1 H). Ref.: N. S. Gulykina, T.M. Dolgina, G. N. Bondarenko, and I. P. Beletskaya, *Russian Journal of Organic Chemistry*, **2003**, *39*, 797–807.

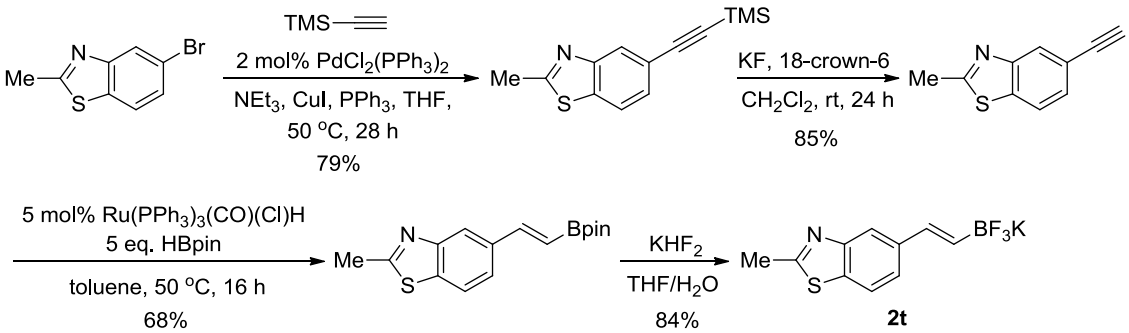
A 2-neck 100 mL round-bottom flask was charged with 6-ethynyl-2-methylquinoline (1.5 g, 9.79 mmol), carbonylchlorohydridotris(triphenylphosphine)ruthenium (464 mg, 0.49 mmol) and dry toluene (39 mL), then 4,4,5,5-tetramethyl-1,3,2-dioxaborane (7.1 mL, 49 mmol, 5 eq.) was added to the mixture under N_2. The reaction mixture was stirred at 50 °C for 16 h. After cooling to room temperature, the solvent was removed under vaccum. Resulting reaction mixture was diluted with Et_2O, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4), and filtered. The filtrate was concentrated in vacuo and the residue was purified by flash column chromatography on silica gel (hexane/AcOEt = 9/1→4/1) to afford the (*E*)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]quinoline as a yellow solid (2.2 g, 80% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 9.08 (dd, J = 1.6 Hz, 1 H), 8.15 (br s, 1 H), 8.07 (d, J = 8.4 Hz, 1 H), 7.82 (d, J = 8.4 Hz, 1 H), 7.69 (dd, J = 7.6, 7.6 Hz, 1 H), 7.60-7.52 (m, 2 H), 6.41 (d, J = 18.8, 1 H), 1.33 (s, 12 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 149.6, 148.2, 146.0, 133.7, 130.4, 129.8, 129.4, 128.3, 128.0, 127.1, 83.7, 24.9. **^{11}B NMR** (128.4 MHz, $CDCl_3$, rt) δ 29.4. **HRMS (ESI-TOF)**: calculated for $[C_{17}H_{20}BNO_2\text{-}H]^-$ requires 280.1517, found 281.1541.

To a solution of (*E*)-3-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]quinoline (2.0 g, 7.1 mmol) in dry THF (28 mL) was added a solution of KHF_2 (3.33 g, 42.7 mmol) in water (10 mL). The raction mixture was stirred at room temperature for overnight. The mixture was concentrated in vacuo. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether, pentane and CH_2Cl_2 for several times to afford the title compound as a white solid (1.77 g, 95% yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 8.97 (s, 1 H), 8.14 (s, 1 H), 7.94 (d, J = 8.4 Hz, 1 H), 7.91 (d, J = 8.0 Hz, 1 H), 7.64 (m, 1 H), 7.53 (dd, J = 8.0, 8.0 Hz, 1 H), 6.68 (d, J = 18.4 Hz, 1 H), 6.53 (dq, J = 18.4, 3.2 Hz, 1 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 149.4, 146.3, 132.9, 130.1, 129.8, 128.5, 128.1, 128.0, 127.8, 126.4. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.51. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -138.2. **HRMS (ESI-TOF)**: calculated for $[C_{11}H_8BF_3N]^-$ requires 222.0709, found 222.0746.

Potassium (*E*)-2-[5-(2-methylbenzothiazole)]ethenyltrifluoroborate (2t)



A 2-neck 300 mL round-bottom flask was charged with 5-bromo-2-methylbenzothiazole (5.0 g, 21.9 mmol), $PdCl_2(PPh_3)_2$ (294 mg, 0.42 mmol), PPh_3 (220 mg, 0.84 mmol), dry THF (17 mL) and NEt_3

(25 mL) under N_2. After bubbling N_2 into the solution for 15 min, CuI (160 mg, 0.84 mmol) and trimethylsilylacetylene (3.4 mL, 24.1 mmol) were added sequentially. The reaction mixture was stirred at 50 °C for 28 h. After cooling to room temperature, the precipitate (NEt_3•HBr) was filtered off and washed with EtOAc. The filtrate solution was concentrated and residue was precipitated with ether/pentane. The crude product was washed with ether/penrane (1/1) for several times to afford the 5-TMS-ethynyl-2-methylbenzothiazole as a pale pink solid (4.2 g, 79% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.02 (d, J = 1.4 Hz, 1 H), 7.72 (dd, J = 8.0, 0.4 Hz, 1 H), 7.43 (dd, J = 8.0, 1.4 Hz, 1 H), 2.83 (s, 3 H), 0.27 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 168.0, 153.3, 136.1, 128.4, 125.9, 121.3, 121.0, 104.8, 94.5, 20.3, 0.11. **HRMS (ESI-TOF)**: calculated for $[C_{13}H_{15}NSSi+H]^+$ requires 246.0767, found 246.0768.

A 2-neck 100 mL round-bottom flask was charged with TMS-alkyne (2.5 g, 10.2 mmol), 18-crown-6-ether (2.7 g, 10.2 mmol) and dry CH_2Cl_2 (15 mL), then KF (1.2 g, 20.4 mmol) was added to the mixture under N_2. The reaction mixture was stirred at room temperature for 24 h. Resulting reaction mixture was extracted with CH_2Cl_2, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (pentane/Et_2O = 4/1→3/2) to afford the 5-ethynyl-2-methylbenzothiazole as a yellow solid (1.50 g, 85% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.05 (d, J = 1.2 Hz, 1 H), 7.74 (d, J = 8.4 Hz, 1 H), 7.44 (dd, J = 8.4, 1.2 Hz, 1 H), 3.11 (s, 1 H), 2.82 (s, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 168.3, 153.3, 136.5, 128.4, 126.2, 121.4, 119.9, 83.5, 77.4, 20.3. **HRMS (ESI-TOF)**: calculated for $[C_{10}H_7NS+H]^+$ requires 174.0372, found 174.0356.

A 2-neck 100 mL round-bottom flask was charged with 5-ethynyl-2-methylbenzothiazole (1.30 g, 7.5 mmol), carbonylchlorohydridotris(triphenylphosphine)ruthenium (356 mg, 0.375 mmol) and dry toluene (30 mL), then 4,4,5,5-tetramethyl-1,3,2-dioxaborane (5.4 mL, 37.5 mmol, 5 eq.) was added to the mixture under N_2. The reaction mixture was stirred at 50 °C for 16 h. After cooling to room temperature, the solvent was removed under vaccum. Resulting reaction mixture was diluted with Et_2O, washed with sat. aq. $NaHCO_3$, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by flash column chromatography on silica gel (pentane→pentane/Et_2O = 4/1→3/2) to afford the (*E*)-5-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]-2-methylbenzothiazole as a yellow solid (1.54 g, 68% yield).

^{1}H NMR (400 MHz, $CDCl_3$, rt) δ 8.01 (d, J = 1.2 Hz, 1 H), 7.75 (d, J = 8.4 Hz, 1 H), 7.53-7.47 (m, 2 H), 6.2 (d, J = 18.0 Hz, 1 H), 2.82 (s, 3 H), 1.32 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt) δ 167.7, 154.0, 149.1, 136.3, 136.1, 123.5, 121.4, 121.2, 83.5, 24.9, 20.2. **^{11}B NMR** (128.4 MHz, $CDCl_3$, rt) δ 29.5. **HRMS** (ESI-TOF): calculated for $[C_{16}H_{20}BNO_2S-H]^-$ requires 300.1238, found 300.1220.

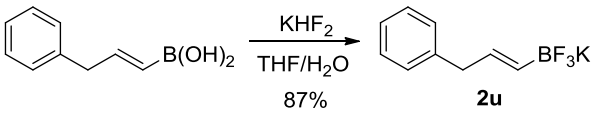
To a solution of (*E*)-5-[2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)vinyl]-2-methylbenzo--thiazole (1.2 g, 3.98 mmol) in dry THF (20 mL) was added a solution of KHF_2 (1.87 g, 23.9 mmol) in water (10 mL). The raction mixture was stirred at room temperature for overnight. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced

under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether, pentane and CH_2Cl_2 for several times to afford the title compound as a pale pink solid (0.94 g, 84% yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 7.85 (d, J = 8.0 Hz, 1 H), 7.75 (d, J = 1.2 Hz, 1 H), 7.40 (dd, J = 8.4, 1.6 Hz, 1 H), 6.56 (d, J = 18.4 Hz, 1 H), 6.26 (dq, J = 18.4, 3.2 Hz, 1 H), 2.76 (s, 3 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 166.6, 153.6, 138.8, 132.6, 132.4, 122.4, 121.2, 118.3, 19.6. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.80. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -137.8.

HRMS (ESI-TOF): calculated for $[C_{10}H_8BF_3NS]^-$ requires 242.0430, found 242.0436.

Potassium (*E*)-3-phenyl-1-propen-1-yltrifluoroborate (2u)



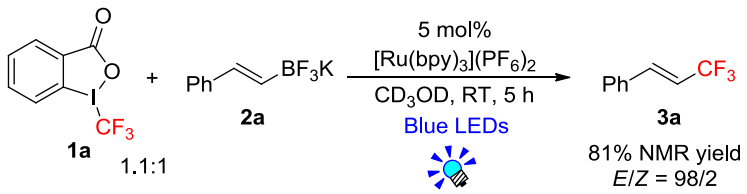
2u

To a solution of (*E*)-3-phenyl-1-propen-1-ylboronic acid (1.0 g, 6.17 mmol) in dry THF (30 mL) was added a solution of KHF_2 (2.9 g, 37 mmol) in water (15 mL). The raction mixture was stirred at room temperature for 4 h. The mixture was concentrated *in vacuo*. The residue was dissolved in hot acetone, and filtered. The filtrate was reduced under vacuum to yield a mixture of potassium trifluoroborate and pinacol. The crude product was washed with ether, pentane and CH_2Cl_2 for several times to afford the title compound as a white solid (1.2 g, 87% yield).

^{1}H NMR (400 MHz, DMSO, rt) δ 7.28-7.23 (m, 2 H), 7.16-7.12 (m, 3 H), 5.66-5.58 (m, 1 H), 5.35-5.28 (m, 1 H), 3.21 (d, J = 6.4 Hz, 2 H). **^{13}C NMR** (100 MHz, DMSO, rt) δ 141.8, 132.4, 128.3, 127.9, 125.4, 41.9. **^{11}B NMR** (128.4 MHz, DMSO, rt) δ 2.41. **^{19}F NMR** (376.5 MHz, DMSO, rt) δ -137.4. **HRMS** (ESI-TOF): calculated for $[C_9H_9BF_3]^-$ requires 185.0757, found 185.0765.

Typical NMR experimental procedure (reaction conditions in Table 1) and NMR spectra

*photocatalytic trifluoromethylation of (E)-styryltrifluoroborate (**2a**)*



Under N_2, $[Ru(bpy)_3](PF_6)_2$ (1.0 mg, 1.25 μmol), Togi's reagent (**1a**) (8.7 mg, 27.5 μmol), (*E*)-styryltrifluoroborate (**2a**) (5.4 mg, 25 μmol), $SiEt_4$ (~1 μL) as an internal standard, CD_3OD (0.5 mL) were added to the NMR tube. The reaction was carried out at room temperarure (water bath) under irradiation of visible light (placed at a distance of ~3 cm from Blue LED lamp: hν = 425 ± 15 nm).

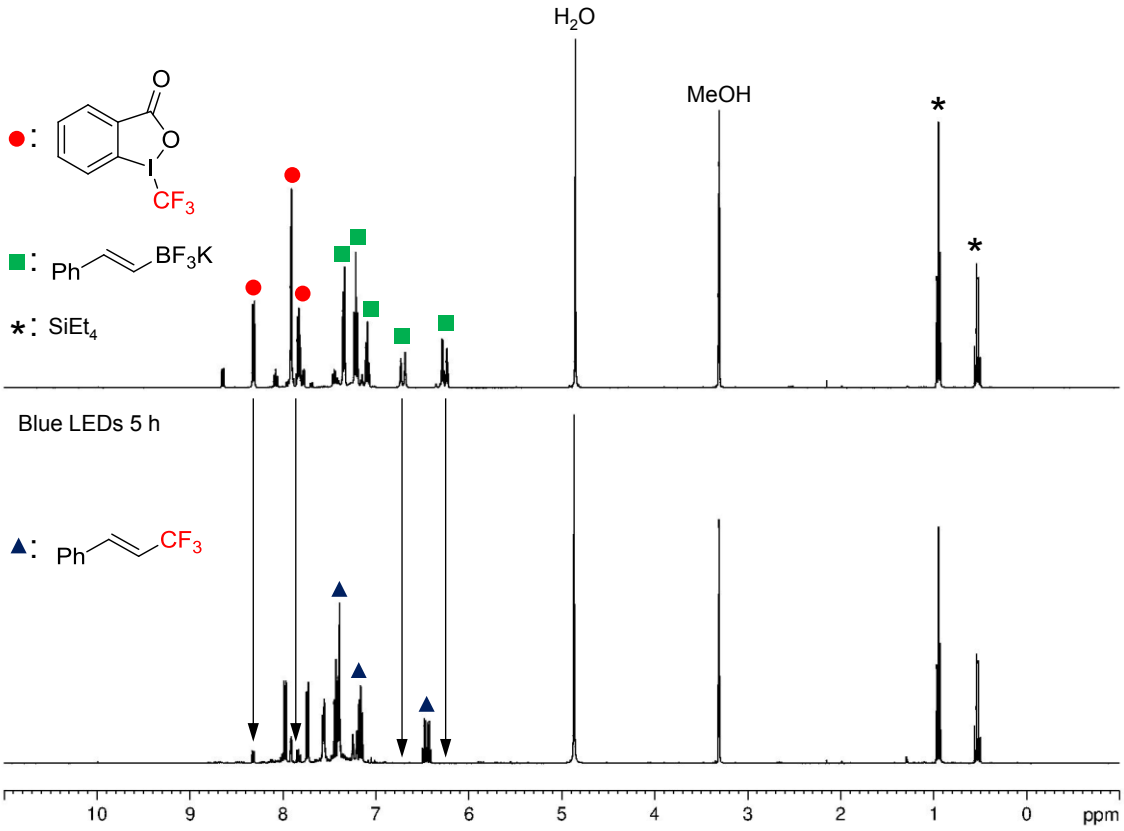
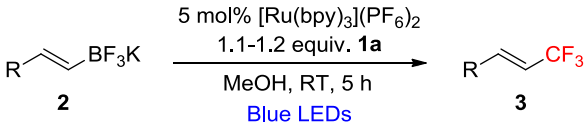


Figure S1. ^1H NMR spectra (400 MHz, CD_3OD, rt)

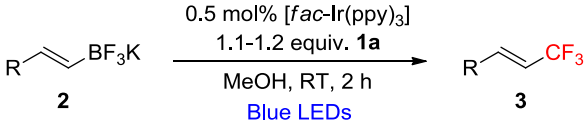
General procedure for the photocatalytic synthesis of trifluoromethylated alkenes (reaction conditions in Table 2)

General procedure A



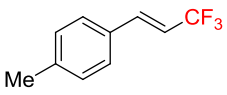
20 mL-Schlenk tube was charged with Togni's reagent (**1a**) (0.275–0.30 mmol, 1.1 eq–1.2 eq), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 12.5 µmol, 5 mol%), vinylborate (**2**) (0.25 mmol, 1.0 eq) and MeOH (5.0–10.0 mL) under N_2. The vinylborate (**2**) was dissolved with ultrasonic bath. The tube was placed at a distance of 2–3 cm from 3W Blue LED lamp (hν = 425 ± 15 nm). The red solution was stirred at room temperature (water bath) under visible light irradiation. After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with ether or pentane, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel to afford trifluoromethylated alkene.

General procedure B



20 mL-Schlenk tube was charged with Togni's reagent (**1a**) (0.275–0.30 mmol, 1.1 eq–1.2 eq), [*fac*-Ir(ppy)$_3$] (0.8 mg, 1.25 µmol, 0.5 mol%), vinylborate (**2**) (0.25 mmol, 1.0 eq) and MeOH (5.0 mL) under N_2. The vinylborate (**2**) was dissolved with ultrasonic bath. The tube was placed at a distance of 2–3 cm from 3W Blue LED lamp (hν = 425 ± 15 nm). The yellow solution was irradiated with visible light at room temperature (the stirring cause a lowering of *E*/*Z* selectivity). After 2 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with ether or pentane, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel to afford trifluoromethylated alkene.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)-4-methylbenzene (3b)



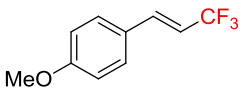
According to general procedure A, Togni's reagent (**1a**) (348 mg, 1.1 mmol), $[Ru(bpy)_3](PF_6)_2$ (40 mg, 46.5 µmol), (*E*)-vinylborate (**2b**) (224 mg, 1.0 mmol) and MeOH (20 mL) were stirred at room temperature under visible light irradiation (3 W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane) afford the title compound (151.2 mg, 81% yield) as a white solid containing approximately 1% of (*Z*)-product. The

spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.34 (d, J = 8.0 Hz, 2 H), 7.19 (d, J = 8.0 Hz, 2 H), 7.10 (dq, J = 16.4, 2.0 Hz, 1 H), 6.15 (dq, J = 16.4, 6.4 Hz, 1 H), 2.37 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 140.4, 137.7 (q, J = 6.6 Hz), 130.8, 129.7, 127.6, 123.9 (q, J = 267 Hz), 115.0 (q, J = 33.6 Hz), 21.4. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.11 (dd, J = 6.6, 2.2 Hz, 3 F).

Ref.: T. Liu, Q. Shen, *Org. Lett.* **2011**, *13*, 2342–2345.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)-4-methoxylbenzene (3c)

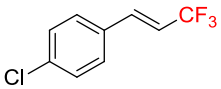


According to general procedure A, Togni's reagent (**1a**) (84 mg, 0.266 mmol), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 12.5 μmol), (*E*)-vinylborate (**2c**) (56 mg, 0.233 mmol) and MeOH (10 mL) were stirred at room temperature under visible light irradiation (3 W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 20/1) afford the title compound (42 mg, 88% yield) as a white solid containing approximately 1% of (*Z*)-product. The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.39 (dd, J = 7.0, 2.0 Hz, 2 H), 7.07 (dq, J = 16.0, 2.0 Hz, 1 H), 7.91 (dd, J = 7.0, 2.0 Hz, 2 H), 6.06 (dq, J = 16.0, 6.8 Hz, 1 H), 3.83 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 161.2, 137.3 (q, J = 6.7 Hz), 129.1, 126.3, 124.1 (q, J = 262 Hz), 114.5, 113.6 (q, J = 33.7 Hz), 21.4. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -62.85 (d, J = 6.7 Hz, 3 F).

Ref.: T. Liu, Q. Shen, *Org. Lett.* **2011**, *13*, 2342–2345.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)-4-chlorobenzene (3d)

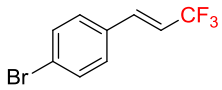


According to general procedure A, Togni's reagent (**1a**) (87 mg, 0.275 mmol), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 12.5 μmol), (*E*)-vinylborate (**2d**) (87 mg, 0.25 mmol) and MeOH (5.0 mL) were stirred at room temperature under visible light irradiation (3 W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane) afford the title compound (37 mg, 72% yield) as a colorless oil containing approximately 3% of (*Z*)-product. The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.41-7.35 (m, 4 H), 7.10 (dq, J = 16.4, 2.0 Hz, 1 H), 6.18 (dq, J = 16.4, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 136.6 (q, J = 6.7 Hz), 136.1, 132.1, 129.3, 128.8, 123.5 (q, J = 267 Hz), 116.7 (q, J = 33.7 Hz). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.44 (d, J = 7.3 Hz, 3 F).

Ref.: T. Hanamoto, N. Morita, K. Shindo, *Eur. J. Org. Chem.* **2003**, *21*, 4279–4285.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)-4-bromobenzene (3e)

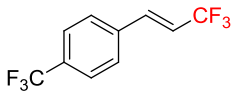


According to general procedure A, Togni's reagent (**1a**) (90 mg, 0.284 mmol), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 12.5 µmol), (*E*)-vinylborate (**2e**) (72 mg, 0.25 mmol) and MeOH (5.0 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane) afford the title compound (47 mg, 81% yield) as a colorless oil containing approximately 4% of (*Z*)-product. The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.53 (d, J = 8.4 Hz, 2 H), 7.31 (d, J = 8.4 Hz, 2 H), 7.09 (dq, J = 16.4, 2.0 Hz, 1 H), 6.20 (dq, J = 16.4, 6.8 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 136.6 (q, J = 6.6 Hz), 132.5, 132.3, 129.1, 124.4, 123.5 (q, J = 267 Hz), 116.9 (q, J = 33.8 Hz). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.49 (d, J = 6.9 Hz, 3 F).

Ref.: A. T. Parsons, T. D. Senecal, S. L. Buchwald, *Angew. Chem. Int. Ed*. **2012**, *51*, 2947–2950.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)-4-trifluoromethylbenzene (3f)

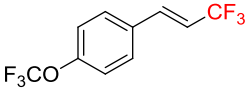


According to general procedure B, Togni's reagent (**1a**) (87 mg, 0.275 mmol), [*fac*-Ir(ppy)$_3$] (0.8 mg, 1.25 µmol), (*E*)-vinylborate (**2f**) (70 mg, 0.25 mmol) and MeOH (5.0 mL) were irrradiated with visible light (3 W Blue LEDs : hν = 425 ± 15 nm) at room temperature. After 2 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane) afford the title compound (47 mg, 79% yield) as a colorless oil containing approximately 4% of (*Z*)-product. The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.66 (d, J = 8.4 Hz, 2 H), 7.56 (d, J = 8.4 Hz, 2 H), 7.19 (dq, J = 16.0, 2.0 Hz, 1 H), 6.30 (dq, J = 16.0, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 137.0, 136.4 (q, J = 6.5 Hz), 131.2 (q, J = 32.7 Hz), 127.9, 126.1, 123.9 (q, J = 271 Hz), 123.3 (q, J = 268 Hz), 118.7 (q, J = 34.0 Hz). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -62.92 (s, 3 F), -63.80 (d, J = 5.1 Hz, 3 F).

Ref.: T. Hanamoto, N. Morita, K. Shindo, *Eur. J. Org. Chem.* **2003**, *21*, 4279–4285.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)-4-trifluoromethoxybenzene (3g)

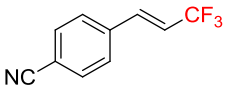


According to general procedure A, Togni's reagent (**1a**) (90 mg, 0.284 mmol), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 12.5 µmol), (*E*)-vinylborate (**2g**) (70 mg, 0.238 mmol) and MeOH (5.0 mL) were stirred at room

temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 10/1) afford the title compound (42 mg, 69% yield) as a colorless oil containing approximately 6% of (*Z*)-product.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.49 (d, J = 8.8 Hz, 2 H), 7.24 (d, J = 8.8 Hz, 2 H), 7.13 (dq, J = 16.0, 2.0 Hz, 1 H), 6.19 (dq, J = 16.0, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 150.4, 136.3 (q, J = 6.8 Hz), 132.2, 129.1, 123.4 (q, J = 267 Hz), 121.4, 120.6 (q, J = 262 Hz), 117.0 (q, J = 34.0 Hz). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -57.84 (s, 3 F), -63.56 (d, J = 6.6 Hz, 3 F). **HRMS** (ESI-TOF): calculated for $[C_{10}H_6F_6O+Na]^+$ requires 279.0215, found 279.0210.

(*E*)-4-(3,3,3-Trifluoroprop-1-enyl)benzenecarbonitrile (3h)

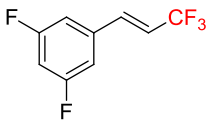


According to general procedure A, Togni's reagent (**1a**) (90 mg, 0.284 mmol), $[Ru(bpy)_3](PF_6)_2$ (8.9 mg, 10.3 μmol), (*E*)-vinylborate (**2h**) (52 mg, 0.221 mmol) and MeOH (10 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 20/1) afford the title compound (34 mg, 78% yield) as a white solid containing approximately 3% of (*Z*)-product. The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.69 (d, J = 8.4 Hz, 2 H), 7.55 (d, J = 8.4 Hz, 2 H), 7.17 (dq, J = 16.0, 2.4 Hz, 1 H), 6.31 (dq, J = 16.4, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 137.8, 136.0 (q, J = 6.7Hz), 132.8, 128.1, 123.1 (q, J = 268 Hz), 119.6 (q, J = 34.2 Hz), 118.3, 113.6. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.90 (d, J = 4.5 Hz, 3 F).

Ref.: T. Kobayashi, T. Eba, O. Tamura, H. Ishibashi, *J. Org. Chem.* **2002**, *67*, 3156–3159.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)-3,5-difluorobenzene (3i)

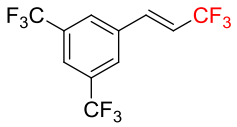


According to general procedure A, Togni's reagent (**1a**) (87 mg, 0.275 mmol), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 12.5 μmol), (*E*)-vinylborate (**2i**) (61 mg, 0.25 mmol) and MeOH (5.0 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane) afford the title compound (35 mg, 68% yield) as a colorless oil containing approximately 5% of (*Z*)-product.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.07 (dq, J = 16.0, 2.0 Hz, 1 H), 7.01-6.94 (m, 2 H), 6.88-6.81 (m, 1

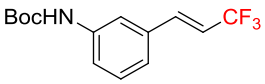
H), 6.22 (dq, J = 16.0, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 163.4 (d, J = 248 Hz), 136.9 (q, J = 9.4 Hz), 135.8, 123.1 (q, J = 267 Hz), 118.9 (q, J = 34.3 Hz), 110.5 (d, J = 26.0 Hz), 105.4 (t, J = 25.3 Hz). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.84 (d, J = 7.5 Hz, 3 F), -108.75 (m, 2 F). **HRMS** (ESI-TOF): calculated for $[C_9H_5F_5+Na]^+$ requires 231.0204, found 231.0208.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)-3,5-ditrifluoromethylbenzene (3j)



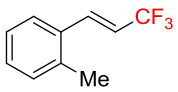
According to general procedure B, Togni's reagent (**1a**) (94 mg, 0.30 mmol), [*fac*-Ir(ppy)$_3$] (0.8 mg, 1.25 µmol), (*E*)-vinylborate (**2j**) (86.5 mg, 0.25 mmol) and MeOH (5.0 mL) were irrradiated with visible light (3 W Blue LEDs : hν = 425 ± 15 nm) at room temperature. After 2 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane) afford the title compound (63 mg, 81% yield) as a colorless oil containing approximately 2% of (*Z*)-product.
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.89 (br s, 3 H), 7.24 (dq, J = 16.4, 2.0 Hz, 1 H), 6.39 (dq, J = 16.4, 6.0 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 135.7, 135.3 (q, J = 6.6 Hz), 132.8 (J = 33.6 Hz), 127.5, 123.5, 123.1 (q, J = 271 Hz), 122.9 (q, J = 268 Hz), 120.2 (q, J = 34.5 Hz). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.13 (s, 3 F), -63.14 (s, 3 F), -64.06 (d, J = 6.4 Hz, 3 F). **HRMS** (ESI-TOF): calculated for $[C_{11}H_5F_9+Na]^+$ requires 331.0140, found 331.0145.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)-3-*tert*-butoxycarbonylaminobenzene (3k)



According to general procedure A, Togni's reagent (**1a**) (90 mg, 0.284 mmol), $[Ru(bpy)_3](PF_6)_2$ (9.0 mg, 10.5 µmol), (*E*)-vinylborate (**2k**) (78 mg, 0.240 mmol) and MeOH (5.0 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with ether, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 10/1) afford the title compound (64 mg, 93% yield) as a white solid containing approximately 5% of (*Z*)-product.
^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.64 (s, 1 H), 7.32-7.22 (m, 2 H), 7.13-7.09 (m, 2 H), 6.56 (br s, 1 H), 6.21 (dq, J = 16.0, 6.4 Hz, 1 H), 1.53 (s, 9 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 152.8, 139.2, 137.6 (q, J = 6.6 Hz), 134.5, 129.6, 124.0 (q, J = 267 Hz), 122.4, 120.1, 117.3, 116.5 (q, J = 33.8 Hz), 81.0, 28.4. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.37 (d, J = 3.8 Hz, 3 F). **HRMS** (ESI-TOF): calculated for $[C_{14}H_{16}F_3NO_2+Na]^+$ requires 310.1025, found 310.1025.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)-2-methylbenzene (3l)

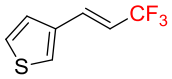


According to general procedure A, Togni's reagent (**1a**) (90 mg, 0.284 mmol), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 12.5 µmol), (*E*)-vinylborate (**2k**) (56 mg, 0.25 mmol) and MeOH (5.0 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane) afford the title compound (33 mg, 70% yield) as a colorless oil containing approximately 3% of (*Z*)-product.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.48-7.40 (m, 2 H), 7.31-7.20 (m, 3 H), 6.12 (dq, J = 19.6, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 137.0, 135.7 (q, J = 6.7 Hz), 132.8, 130.0, 129.9, 126.5, 126.3, 123.7 (q, J = 267 Hz), 117.3 (q, J = 33.4 Hz),19.7. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.32 (dd, J = 6.7, 2.2 Hz, 3 F).

Ref.: G. K. S. Prakash, H. S. Krishnan, P. V. Jog, A. P. Lyer, G. A. Olah, *Org. Lett*. **2012**, *14*, 1146–1149.

(*E*)-1-(3,3,3-Trifluoroprop-1-enyl)-3-thiophene (3m)

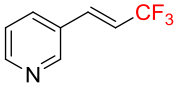


According to general procedure A, Togni's reagent (**1a**) (79 mg, 0.25 mmol), $[Ru(bpy)_3](PF_6)_2$ (8.9 mg, 10.3 µmol), (*E*)-vinylborate (**2m**) (60 mg, 0.275 mmol) and MeOH (10 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 20/1) afford the title compound (28 mg, 63% yield) as a pale yellow solid containing approximately 2% of (*Z*)-product and 2% of protodeboronated by-product. The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.42 (d, J = 2.4 Hz, 1 H), 7.35 (dd, J = 5.2, 0.4 Hz, 1 H), 7.24 (dd, J = 5.2, 1.2 Hz, 1H), 7.14 (dq, J = 16.0, 2.0 Hz, 1 H), 6.05 (dq, J = 16.0, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 136.4, 131.6 (q, J = 6.8 Hz), 127.2, 127.0, 126.5 (q, J = 267 Hz), 125.0, 115.5 (q, J = 34.1 Hz). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.29 (dd, J = 6.7, 2.2 Hz, 3 F).

Ref.: A. T. Parsons, T. D. Senecal, S. L. Buchwald, *Angew. Chem. Int. Ed*. **2012**, *51*, 2947–2950.

(*E*)-3-(3,3,3-Trifluoroprop-1-enyl)pyridine (3n)



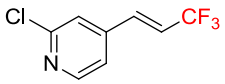
According to general procedure A, Togni's reagent (**1a**) (90 mg, 0.284 mmol), $[Ru(bpy)_3](PF_6)_2$ (9.5

mg, 11.0 μmol), (*E*)-vinylborate (**2n**) (52 mg, 0.246 mmol) and MeOH (5.0 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 10/1→0/1) afford the title compound (29 mg, 68% yield) as a pale yellow oil approximately 2% of (*Z*)-product. The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.69 (d, J = 2.0 Hz, 1 H), 8.62 (dd, J = 4.8, 2.0 Hz, 1 H), 7.78 (dt, J = 8.0, 2.0 Hz, 1 H), 7.34 (dd, J = 8.0, 4.8 Hz, 1 H), 7.16 (dq, J = 16.4, 2.0 Hz, 1 H), 6.29 (dq, J = 16.4, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 151.1, 149.3, 134.6 (q, J = 6.8 Hz), 129.3, 123.8, 123.2 (q, J = 267 Hz), 118.4 (q, J = 34.3 Hz). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.82 (d, J = 7.2 Hz, 3 F).

Ref.: T. Kobayashi, T. Eba, O. Tamura, H. Ishibashi, *J. Org. Chem.* **2002**, *67*, 3156–3159.

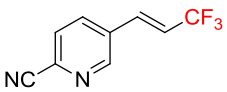
(*E*)-4-(3,3,3-Trifluoroprop-1-enyl)-2-chloropyridine (3o)



According to general procedure A, Togni's reagent (**1a**) (87 mg, 0.275 mmol), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 12.5 μmol), (*E*)-vinylborate (**2o**) (61 mg, 0.25 mmol) and MeOH (8.0 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 9/1→3/2) afford the title compound (29 mg, 56% yield) as a colorless crystal.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.44 (d, J = 4.8 Hz, 1 H), 7.37 (s, 1 H), 7.25 (dd, J = 4.8, 1.6 Hz, 1 H), 7.07 (dq, J = 16.0, 2.0 Hz, 1 H), 6.41 (dq, J = 16.0, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 152.8, 150.5, 143.9, 134.3 (q, J = 6.5 Hz), 122.6 (q, J = 268 Hz), 122.4, 121.9 (q, J = 34.6 Hz), 120.3. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -64.36 (d, J = 5.6 Hz, 3 F). **HRMS** (ESI-TOF): calculated for $[C_8H_5F_3NCl+Na]^+$ requires 229.9955, found 229.9956.

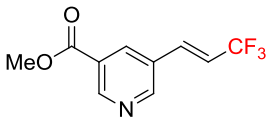
(*E*)-3-(3,3,3-Trifluoroprop-1-enyl)-2-cyanopyridine (3p)



According to general procedure A, Togni's reagent (**1a**) (90 mg, 0.284 mmol), $[Ru(bpy)_3](PF_6)_2$ (8.6 mg, 10.0 μmol), (*E*)-vinylborate (**2p**) (58 mg, 0.246 mmol) and MeOH (5.0 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 10/1→0/1) afford the title compound (32 mg, 66% yield) as a pale yellow solid containing approximately 1% of (*Z*)-product.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.79 (d, J = 2.0 Hz, 1 H), 7.91 (dd, J = 8.0, 2.4 Hz, 1 H), 7.74 (d, J = 8.0 Hz, 1 H), 7.19 (dq, J = 16.4, 2.0 Hz, 1 H), 6.41 (dq, J = 16.4, 6.0 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 150.2, 135.0, 134.6, 132.9 (q, J = 6.7 Hz), 132.4, 128.5, 122.6 (q, J = 268 Hz), 121.6 (q, J = 34.7 Hz), 116.8. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -64.26 (d, J = 7.1 Hz, 3 F). **HRMS** (ESI-TOF): calculated for $[C_9H_5F_3N_2+Na]^+$ requires 221.0297, found 221.0301.

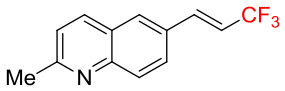
(*E*)-3-(3,3,3-Trifluoroprop-1-enyl)-3-pyridinecarboxylic acid methy ester (3q)



According to general procedure A, Togni's reagent (**1a**) (90 mg, 0.284 mmol), $[Ru(bpy)_3](PF_6)_2$ (9.2 mg, 10.6 μmol), (*E*)-vinylborate (**2q**) (63 mg, 0.234 mmol) and MeOH (10 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with ether, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 10/1→0/1) afford the title compound (38 mg, 70% yield) as a colorless solid containing approximately 1% of (*Z*)-product.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 9.20 (d, J = 2.0 Hz, 1 H), 8.83 (d, J = 2.0 Hz, 1 H), 8.39 (dd, J = 2.0, 2.0 Hz, 1 H), 7.20 (dq, J = 16.0, 2.0 Hz, 1 H), 6.41 (dq, J = 16.0, 6.4 Hz, 1 H), 3.98 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 165.2, 152.6, 151.8, 134.9, 133.5 (q, J = 6.7 Hz), 129.3, 126.4, 123.0 (q, J = 268 Hz), 119.7 (q, J = 34.4 Hz), 52.7. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -64.01 (d, J = 4.1 Hz, 3 F). **HRMS** (ESI-TOF): calculated for $[C_{10}H_8F_3NO_2+Na]^+$ requires 254.0399, found 254.0399.

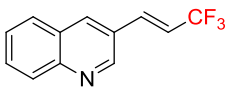
(*E*)-6-(3,3,3-Trifluoroprop-1-enyl)-2-methylquinoline (3r)



According to general procedure A, Togni's reagent (**1a**) (95 mg, 0.30 mmol), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 12.5 μmol), (*E*)-vinylborate (**2r**) (66 mg, 0.24 mmol) and MeOH (5.0 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with ether, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 10/1) afford the title compound (39 mg, 69% yield) as a colorless solid containing approximately 2% of (*Z*)-product.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 8.07-8.01 (m, 2 H), 7.82-7.79 (m, 2 H), 7.35-7.27 (m, 2 H), 6.32 (dq, J = 16.4, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 160.4, 148.7, 137.2 (q, J = 6.7 Hz), 136.4, 130.9, 129.7, 128.3, 127.0, 126.5, 123.7 (q, J = 267 Hz), 122.9, 116.8 (q, J = 33.9 Hz), 25.5. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.28 (d, J = 6.7 Hz, 3 F). **HRMS** (ESI-TOF): calculated for $[C_{13}H_{10}F_3N+H]^+$ requires 238.0838, found 238.0839.

(*E*)-3-(3,3,3-Trifluoroprop-1-enyl)-quinoline (3s)

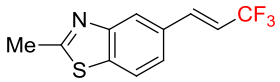


According to general procedure A, Togni's reagent (**1a**) (87 mg, 0.275 mmol), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 12.5 μmol), (*E*)-vinylborate (**2s**) (63 mg, 0.241 mmol) and MeOH (5.0 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 10/1 → 3/2) afford the title compound (38 mg, 71% yield) as a pale yellow crystal.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 9.03 (s, 1 H), 8.20 (d, J = 2.0 Hz, 1 H), 8.12 (d, J = 8.0 Hz, 1 H), 7.85 (d, J = 8.0 Hz, 1 H), 7.77 (dt, J = 7.2, 1.6 Hz, 1 H), 7.60 (dt, J = 7.2, 1.6 Hz, 1 H), 7.33 (dq, J = 16.0, 2.0 Hz, 1 H), 6.45 (dq, J = 16.0, 6.4 Hz, 1 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 148.9, 148.7, 135.0, 134.8 (q, J = 6.6 Hz), 130.7, 129.6, 128.3, 127.6, 127.3, 126.5, 123.3 (q, J = 267 Hz), 118.0 (q, J = 34.1 Hz). **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.63 (dd, J = 5.2, 2.2 Hz, 3 F).

HRMS (ESI-TOF): calculated for $[C_{12}H_8F_3N+H]^+$ requires 224.0682, found 224.0682.

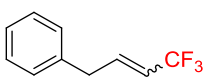
(*E*)-5-(3,3,3-Trifluoroprop-1-enyl)-2-methyl-1,3-benzothiazole (3t)



According to general procedure A, Togni's reagent (**1a**) (87 mg, 0.275 mmol), $[Ru(bpy)_3](PF_6)_2$ (9.5 mg, 10.4 μmol), (*E*)-vinylborate (**2t**) (70 mg, 0.25 mmol) and MeOH (5.0 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with ether, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane/ether = 10/1) afford the title compound (50 mg, 82% yield) as a white solid containing ca. 3% of (*Z*)-product.

^{1}H NMR (400 MHz, $CDCl_3$, rt): δ 7.99 (s, 1 H), 7.83 (dd, J = 8.0, 4.4 Hz, 1 H), 7.45 (d, J = 8.4 Hz, 1 H), 7.26 (d, J = 16.0 Hz, 1 H), 6.28 (dq, J = 16.0, 6.4 Hz, 1 H), 2.85 (s, 3 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 168.5, 154.0, 137.5 (q, J = 6.7 Hz), 131.2, 123.7 (q, J = 267 Hz), 123.5, 121.8, 116.2 (q, J = 32.9 Hz), 20.2. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -63.21 (d, J = 6.4 Hz, 3 F). **HRMS** (ESI-TOF): calculated for $[C_{11}H_8F_3NS+H]^+$ requires 244.0402, found 244.0402.

(4,4,4-Trifluorobut-2-enyl)benzene (3u)



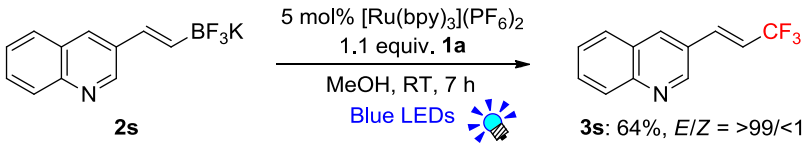
According to general procedure A, Togni's reagent (**1a**) (87 mg, 0.275 mmol), $[Ru(bpy)_3](PF_6)_2$ (10.7 mg, 12.5 μmol), (*E*)-vinylborate (**2u**) (56 mg, 0.25 mmol) and MeOH (5.0 mL) were stirred at room temperature under visible light irradiation (3W Blue LEDs : hν = 425 ± 15 nm). After 5 h, aqueous

saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. Purification by column chromatography on silica gel (pentane) afford the title compound (28 mg, 60% yield, *E*/*Z* = 65/35) as a colorless oil. The spectral data of the product were identical with those reported in the literature.

^{1}H NMR (400 MHz, $CDCl_3$, rt) of (*E*)-product: δ 7.36-7.18 (m, 5 H), 6.58-6.52 (m, 1 H), 5.68-5.57 (m, 1 H), 3.50-3.47 (m, 2 H). **^{1}H NMR** (400 MHz, $CDCl_3$, rt) of (*Z*)-product: δ 7.36-7.18 (m, 5 H), 6.17-6.10 (m, 1 H), 5.75-5.62 (m, 1 H), 3.64 (d, J = 8.0 Hz, 2 H). **^{13}C NMR** (100 MHz, $CDCl_3$, rt): δ 141.2 (q, J = 5.2 Hz, (*Z*)-product), 139.5 (q, J = 6.4 Hz, (*E*)-product), 138.3, 137.4, 128.9, 128.8, 128.6, 127.0, 126.8, 123.1 (q, J = 267 Hz), 119.7 (q, J = 33.3 Hz, (*E*)-product), 118.9 (q, J = 33.3 Hz, (*Z*)-product), 37.8, 34.7, 31.7, 29.8, 22.8, 14.2. **^{19}F NMR** (376.5 MHz, $CDCl_3$, rt): δ -57.66 (dd, J = 7.9, 3.0 Hz, 3 F, (*Z*)-product), -63.97 (dd, J = 6.0, 2.6Hz, 3 F, (*E*)-product).

Ref.: T. Chu, F.–L. Qing, *Org. Lett.* **2010**, *12*, 5060–5063.

Gram-scale synthesis of 3s (Scheme 2)



300 mL-Schlenk tube was charged with Togni's reagent (**1a**) (2.6 g, 8.25 mmol), $[Ru(bpy)_3](PF_6)_2$ (320 mg, 0.372 mmol), vinylborate (**2s**) (1.96 g, 7.5 mmol) and MeOH (145 mL) under N_2. The vinylborate (**2s**) was dissolved with ultrasonic bath. The tube was placed at a distance of 2–3 cm from 3W Blue LED lamp (hν = 425 ± 15 nm). The red solution was stirred at room temperature (water bath) under visible light irradiation. After 7 h, aqueous saturated $NaHCO_3$ solution was added. The resulting mixture was extracted with pentane, dried (Na_2SO_4), and filtered. The filtrate was concentrated *in vacuo* and the residue was purified by chromatography on silica gel (pentane/ether = 10/1 → 3/2) to afford the title compound (1.06 g, 64% yield) as a pale yellow solid.

Crystallographic data for (*E*)-3-(3,3,3-Trifluoroprop-1-enyl)-3-pyridinecarboxylic acid methy ester (3q)

Diffraction measurements were made on a Bruker SMART APEX II ULTRA/CCD. Intensity measurements were performed using monochromated (doubly curved silicon crystal) Mo-Kα-radiation (0.71073 Å) from a sealed microfocus tube. Data were acquired using three sets of Omega scans at different Phi settings. The frame width was 0.5 °. The crystallographic data are summarized in Table S1. The structural analysis was performed on an APEX2 software for preliminary determination of the unit cell. Determination of integrated intensities and unit cell refinement were performed using SAINT. Unless otherwise stated, all non-hydrogen atoms were refined anisotropically by full-matrix least-square techniques based on F^2. All hydrogen atoms were fixed at the calculated positions.

Table 1. Crystal data and structure refinement for VitaminB3_CF3_alkene.

Identification code	VitaminB3_CF3_alkene	
Empirical formula	C10 H8 F3 N O2	
Formula weight	231.17	
Temperature	93(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 13.040(2) Å	α = 90°
	b = 12.456(2) Å	β = 104.452(2)°
	c = 19.177(4) Å	γ = 90°
Volume	3016.3(10) $Å^3$	
Z	12	
Density (calculated)	1.527 g/cm^3	
Absorption coefficient	0.143 mm^{-1}	
F(000)	1416	
Crystal size	0.25 x 0.30 x 0.40 mm^3	
Theta range for data collection	1.61 to 28.76°	
Index ranges	-12<=h<=17, -16<=k<=12, -24<=l<=20	
Reflections collected	17047	
Independent reflections	7077 [R(int) = 0.0332]	
Completeness to theta = 28.76°	90.1%	
Absorption correction	Multiscan	

Max. and min. transmission	0.9652 and 0.9451
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7077 / 0 / 436
Goodness-of-fit on F^2	1.084
Final R indices [I>2sigma(I)]	R1 = 0.0534, wR2 = 0.1382
R indices (all data)	R1 = 0.0982, wR2 = 0.1546
Largest diff. peak and hole	0.668 and -0.296

$R_{int} = \Sigma|F_o^2 - F_o^2(mean)| / \Sigma[F_o^2]$

$R_1 = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$

$GOOF = S = \{\Sigma[w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$

$wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$

$w = 1 / [\sigma(F_o^2) + (aP)^2 + bP]$ where P is $[2F_c^2 + Max(F_o^2, 0)] / 3$

Table 2. Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for VitaminB3_CF3_alkene.

U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
N1	10591(2)	9312(1)	4390(1)	27(1)
C2	9343(2)	7862(2)	4015(1)	21(1)
C3	10178(2)	7132(2)	4100(1)	19(1)
C1	9600(2)	8942(2)	4168(1)	24(1)
C4	11206(2)	7504(2)	4331(1)	21(1)
C5	11376(2)	8597(2)	4468(1)	25(1)
O2	13032(1)	7195(1)	4713(1)	31(1)
C6	12098(2)	6729(2)	4430(1)	22(1)
O1	11993(1)	5790(1)	4278(1)	31(1)
C7	13933(2)	6481(2)	4852(1)	46(1)
C8	8222(2)	7565(2)	3788(1)	23(1)
C9	7858(2)	6565(2)	3739(1)	26(1)
C10	6695(2)	6293(2)	3538(1)	32(1)
F1	6087(1)	7160(1)	3397(1)	47(1)
F2	6425(1)	5782(1)	4075(1)	52(1)
F3	6444(1)	5670(1)	2967(1)	57(1)

	x	y	z	U(eq)
N2	-574(1)	5956(1)	2382(1)	23(1)
C14	-1360(2)	4195(2)	2242(1)	19(1)
C12	527(2)	4370(2)	2602(1)	19(1)
C11	374(2)	5485(2)	2565(1)	21(1)
C13	-368(2)	3723(2)	2437(1)	20(1)
C15	-1425(2)	5312(2)	2224(1)	23(1)
O4	-3203(1)	4080(1)	1866(1)	31(1)
C16	-2314(2)	3499(2)	2062(1)	21(1)
O3	-2297(1)	2529(1)	2086(1)	28(1)
C17	-4180(2)	3482(2)	1693(1)	38(1)
C18	1581(2)	3873(2)	2804(1)	24(1)
C19	2491(2)	4393(2)	2969(1)	28(1)
C20	3520(2)	3833(2)	3176(1)	38(1)
F4	3445(1)	2764(1)	3169(1)	52(1)
F6	4140(1)	4072(1)	2734(1)	65(1)
F5	4071(1)	4096(1)	3838(1)	68(1)
O5	7884(1)	799(1)	3533(1)	32(1)
O6	6826(1)	2210(1)	3559(1)	31(1)
N3	9269(2)	4317(1)	4167(1)	27(1)
C22	10524(2)	2861(2)	4255(1)	21(1)
C23	9695(2)	2135(2)	4029(1)	21(1)
C25	8487(2)	3602(2)	3950(1)	25(1)
C24	8660(2)	2511(2)	3875(1)	21(1)
C21	10259(2)	3941(2)	4315(1)	25(1)
C26	7773(2)	1738(2)	3639(1)	24(1)
C27	5925(2)	1501(2)	3353(2)	45(1)
C28	11646(2)	2562(2)	4452(1)	23(1)
C29	12016(2)	1568(2)	4520(1)	24(1)
C30	13184(2)	1300(2)	4763(1)	32(1)
F9	13773(1)	2173(1)	4925(1)	50(1)
F7	13512(1)	772(1)	4271(1)	59(1)
F8	13366(1)	701(1)	5355(1)	54(1)

Table 3. Bond lengths (Å) and angles (°) for VitaminB3_CF3_alkene.

N1-C5	1.337(3)
N1-C1	1.339(3)
C2-C3	1.397(3)
C2-C1	1.399(3)
C2-C8	1.465(3)
C3-C4	1.382(3)
C4-C5	1.393(3)
C4-C6	1.487(3)
O2-C6	1.337(2)
O2-C7	1.445(3)
C6-O1	1.205(2)
C8-C9	1.327(3)
C9-C10	1.507(3)
C10-F3	1.315(3)
C10-F1	1.328(3)
C10-F2	1.331(3)
N2-C11	1.333(3)
N2-C15	1.341(3)
C14-C13	1.385(3)
C14-C15	1.394(3)
C14-C16	1.485(3)
C12-C13	1.388(3)
C12-C11	1.402(3)
C12-C18	1.469(3)
O4-C16	1.338(3)
O4-C17	1.441(3)
C16-O3	1.209(2)
C18-C19	1.319(3)
C19-C20	1.476(3)
C20-F5	1.335(3)
C20-F4	1.336(3)
C20-F6	1.342(3)

O5-C26	1.202(3)
O6-C26	1.342(3)
O6-C27	1.444(3)
N3-C21	1.336(3)
N3-C25	1.339(3)
C22-C23	1.394(3)
C22-C21	1.400(3)
C22-C28	1.465(3)
C23-C24	1.388(3)
C25-C24	1.391(3)
C24-C26	1.487(3)
C28-C29	1.323(3)
C29-C30	1.514(3)
C30-F7	1.306(3)
C30-F9	1.323(3)
C30-F8	1.329(3)
C5-N1-C1	117.23(19)
C3-C2-C1	117.5(2)
C3-C2-C8	124.16(19)
C1-C2-C8	118.3(2)
C4-C3-C2	119.01(19)
N1-C1-C2	124.0(2)
C3-C4-C5	118.9(2)
C3-C4-C6	119.22(18)
C5-C4-C6	121.8(2)
N1-C5-C4	123.3(2)
C6-O2-C7	115.07(19)
O1-C6-O2	123.8(2)
O1-C6-C4	124.22(19)
O2-C6-C4	111.98(18)
C9-C8-C2	124.8(2)
C8-C9-C10	123.2(2)
F3-C10-F1	107.4(2)
F3-C10-F2	107.6(2)

F1-C10-F2	106.64(19)
F3-C10-C9	111.84(19)
F1-C10-C9	112.4(2)
F2-C10-C9	110.68(18)
C11-N2-C15	117.11(18)
C13-C14-C15	118.54(19)
C13-C14-C16	119.13(19)
C15-C14-C16	122.33(19)
C13-C12-C11	117.55(19)
C13-C12-C18	119.56(19)
C11-C12-C18	122.88(19)
N2-C11-C12	124.1(2)
C14-C13-C12	119.34(19)
N2-C15-C14	123.4(2)
C16-O4-C17	116.07(18)
O3-C16-O4	123.9(2)
O3-C16-C14	124.6(2)
O4-C16-C14	111.48(18)
C19-C18-C12	125.7(2)
C18-C19-C20	122.4(2)
F5-C20-F4	105.9(2)
F5-C20-F6	106.3(2)
F4-C20-F6	105.6(2)
F5-C20-C19	112.2(2)
F4-C20-C19	114.1(2)
F6-C20-C19	112.1(2)
C26-O6-C27	115.23(19)
C21-N3-C25	116.93(19)
C23-C22-C21	117.4(2)
C23-C22-C28	124.21(19)
C21-C22-C28	118.32(19)
C24-C23-C22	118.97(19)
N3-C25-C24	123.4(2)
C23-C24-C25	118.8(2)

C23-C24-C26	119.15(19)
C25-C24-C26	122.0(2)
N3-C21-C22	124.4(2)
O5-C26-O6	123.6(2)
O5-C26-C24	124.4(2)
O6-C26-C24	112.03(19)
C29-C28-C22	125.4(2)
C28-C29-C30	123.4(2)
F7-C30-F9	107.9(2)
F7-C30-F8	108.2(2)
F9-C30-F8	106.93(18)
F7-C30-C29	112.01(18)
F9-C30-C29	111.8(2)
F8-C30-C29	109.7(2)

Table 4. Anisotropic displacement parameters ($Å^2x10^3$) for VitaminB3_CF3_alkene.

The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
N1	38(1)	17(1)	29(1)	-2(1)	-2(1)	-3(1)
C2	30(1)	17(1)	19(1)	2(1)	2(1)	2(1)
C3	26(1)	14(1)	19(1)	-0(1)	-0(1)	2(1)
C1	36(1)	15(1)	25(1)	2(1)	2(1)	3(1)
C4	27(1)	18(1)	17(1)	0(1)	0(1)	-0(1)
C5	33(1)	21(1)	23(1)	-0(1)	-0(1)	-6(1)
O2	24(1)	28(1)	39(1)	5(1)	5(1)	-6(1)
C6	23(1)	22(1)	22(1)	3(1)	3(1)	-4(1)
O1	27(1)	19(1)	47(1)	1(1)	1(1)	0(1)
C7	20(1)	42(2)	71(2)	21(1)	21(1)	-1(1)
C8	28(1)	20(1)	24(1)	2(1)	2(1)	8(1)
C9	24(1)	22(1)	30(1)	1(1)	1(1)	6(1)
C10	36(1)	29(1)	32(1)	1(1)	1(1)	13(1)
F1	28(1)	40(1)	74(1)	4(1)	4(1)	12(1)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F2	39(1)	55(1)	65(1)	13(1)	13(1)	-11(1)
F3	33(1)	66(1)	70(1)	-36(1)	-36(1)	-10(1)
N2	25(1)	17(1)	27(1)	0(1)	0(1)	1(1)
C14	25(1)	17(1)	17(1)	-1(1)	-1(1)	-2(1)
C12	24(1)	19(1)	15(1)	0(1)	0(1)	-0(1)
C11	25(1)	18(1)	22(1)	-1(1)	-1(1)	-2(1)
C13	27(1)	17(1)	17(1)	-1(1)	-1(1)	-2(1)
C15	26(1)	19(1)	24(1)	1(1)	1(1)	2(1)
O4	21(1)	24(1)	45(1)	-1(1)	-1(1)	-1(1)
C16	25(1)	21(1)	19(1)	-2(1)	-2(1)	-2(1)
O3	30(1)	20(1)	35(1)	-0(1)	-0(1)	-4(1)
C17	23(1)	32(1)	58(2)	-2(1)	-2(1)	-4(1)
C18	28(1)	21(1)	23(1)	1(1)	1(1)	2(1)
C19	25(1)	28(1)	32(1)	2(1)	2(1)	3(1)
C20	31(1)	40(2)	46(1)	8(1)	8(1)	5(1)
F4	38(1)	34(1)	82(1)	11(1)	11(1)	14(1)
F6	40(1)	66(1)	99(1)	22(1)	22(1)	11(1)
F5	43(1)	77(1)	67(1)	-12(1)	-12(1)	17(1)
O5	27(1)	20(1)	46(1)	-2(1)	-2(1)	1(1)
O6	25(1)	25(1)	43(1)	-1(1)	-1(1)	3(1)
N3	40(1)	16(1)	25(1)	0(1)	0(1)	3(1)
C22	29(1)	16(1)	18(1)	1(1)	1(1)	-1(1)
C23	30(1)	14(1)	19(1)	1(1)	1(1)	1(1)
C25	32(1)	19(1)	24(1)	3(1)	3(1)	4(1)
C24	28(1)	18(1)	18(1)	0(1)	0(1)	0(1)
C21	37(1)	15(1)	22(1)	0(1)	0(1)	-3(1)
C26	25(1)	22(1)	24(1)	2(1)	2(1)	3(1)
C27	23(1)	38(2)	71(2)	2(1)	2(1)	-3(1)
C28	27(1)	21(1)	22(1)	-0(1)	-0(1)	-6(1)
C29	24(1)	21(1)	26(1)	-2(1)	-2(1)	-4(1)
C30	47(2)	25(1)	24(1)	-5(1)	-5(1)	-15(1)
F9	31(1)	40(1)	75(1)	-4(1)	-4(1)	-12(1)
F7	38(1)	76(1)	58(1)	-24(1)	-24(1)	20(1)

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
F8	39(1)	55(1)	59(1)	23(1)	23(1)	6(1)

Table 5. Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2x10^3$) for VitaminB3_CF3_alkene.

	x	y	z	U(eq)
H3	10042	6392	4000	23
H1	9035	9443	4111	29
H5	12085	8845	4625	30
H7A	13818	5892	5163	70
H7B	14573	6878	5091	70
H7C	14018	6187	4395	70
H8	7718	8129	3668	28
H9	8356	5993	3835	31
H11	983	5932	2677	25
H13	-300	2964	2459	24
H15	-2107	5633	2092	27
H17A	-4183	2991	1293	56
H17B	-4778	3980	1553	56
H17C	-4243	3069	2115	56
H18	1610	3111	2819	28
H19	2484	5155	2953	34
H23	9835	1393	3982	25
H25	7777	3853	3842	30
H21	10821	4439	4470	29
H27A	5922	1157	2893	67
H27B	5271	1916	3302	67
H27C	5969	950	3724	67
H28	12150	3128	4537	28
H29	11524	992	4411	29

X-ray data of 3q

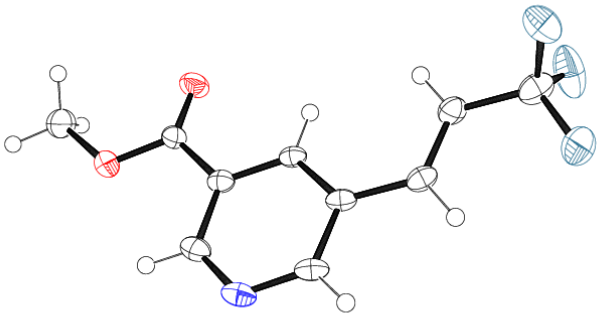
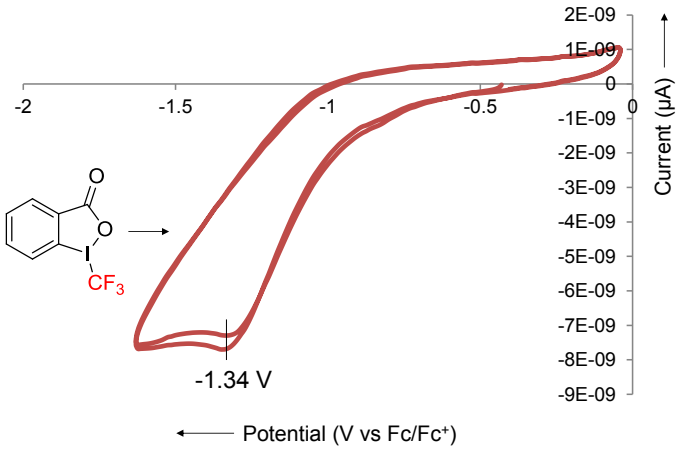
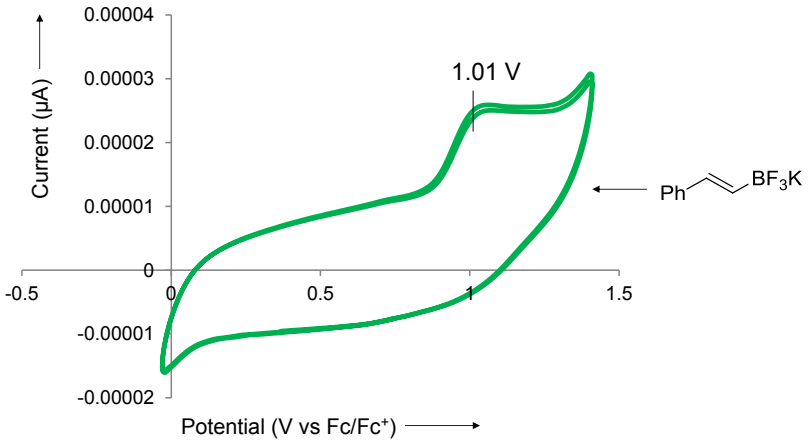


Figure S2. ORTEP plot of the molecular structure.

Cyclic voltammograms

Cyclic voltammetry experiments were performed using Hokutodenkou HZ-5000 analyzer under N_2 at room temperature (observed in 0.002 M CH_3CN; $[(NBu_4)PF_6]$= 0.1 M; Ag/AgCl = electrode; reported with respect to the $[FeCp_2]/[FeCp_2]$+couple).





References

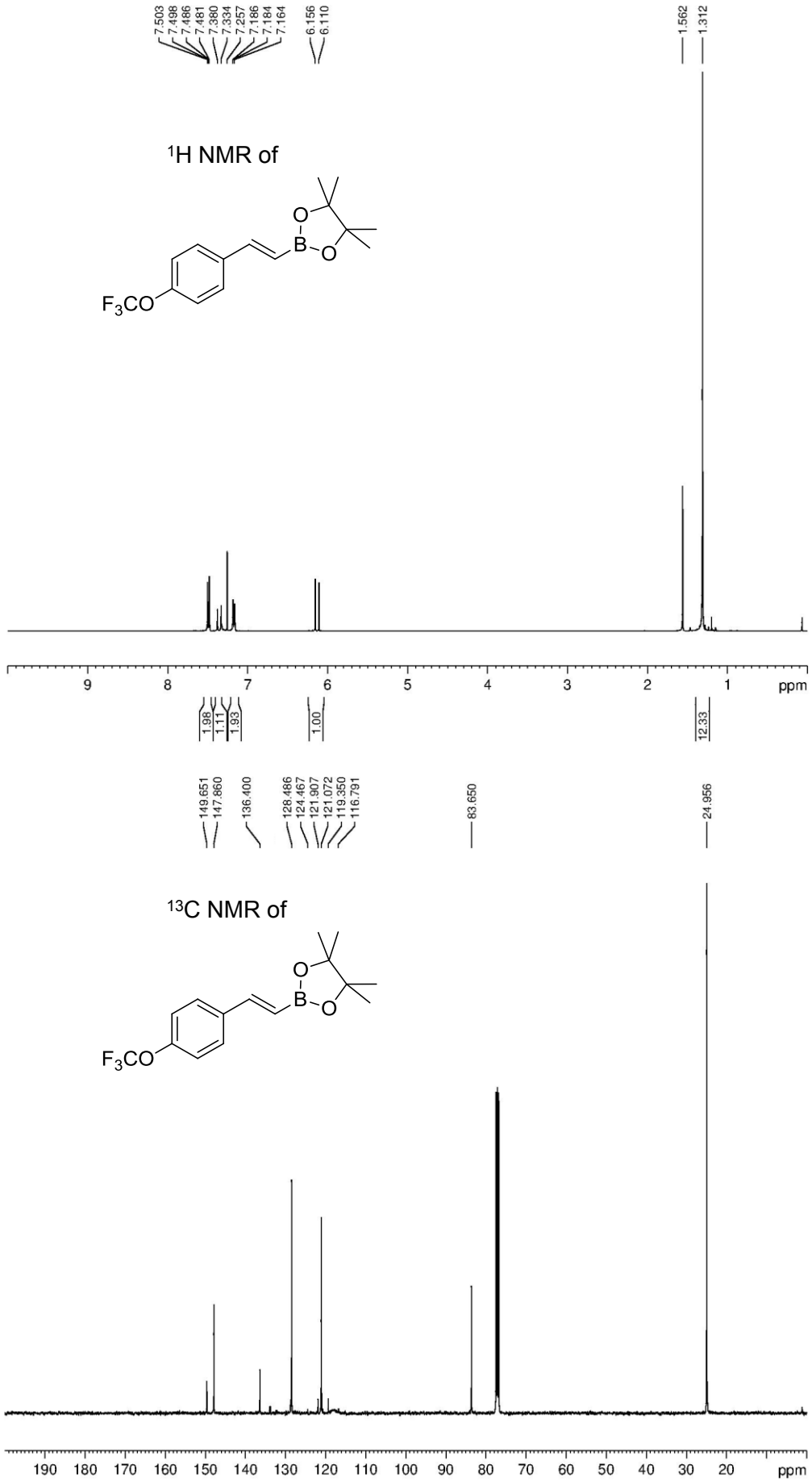
[1] a) H. B. Ross, M. Boldaji, D. P. Rillema, C. B. Blanton and R. P. White, *Inorg. Chem*. **1989**, *28*, 1013; b) A. B. Tamayo, B. D. Alleyne, P. I. Djurovich, S. Lamansky, I. Tsyba, N. N. Ho, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* **2003**, *125*, 7377.

[2] a) M. Weber, F. V. Singh, A. S. Vieira, H. A. Stefani, M. W. Paixão, *Tetrahedron Lett.* **2009**, *50*, 4324; b) K. Brak, J. A. Ellman, *J. Am. Chem. Soc.* **2009**, *131*, 3850; c) G. W. Kabalka, A. R. Mereddy, J. F. Green, *J. Label. Compd. Radiopharm.* **2006**, *49*, 11; d) S. Elsheimer, C. J. Foti, M. D. Bartberger, *J. Org. Chem*. **1996**, *61*, 6252.

[3] ASTRAZENECA AB; ASTRAZENECA UK LIMITED, WO2005/60970 A1, **2005**, 148.

[4] Y. Yu, R. Lin, P. J. Connolly, US2008/103172 A1, **2008**, 13.

NMR data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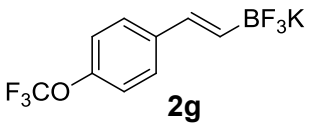
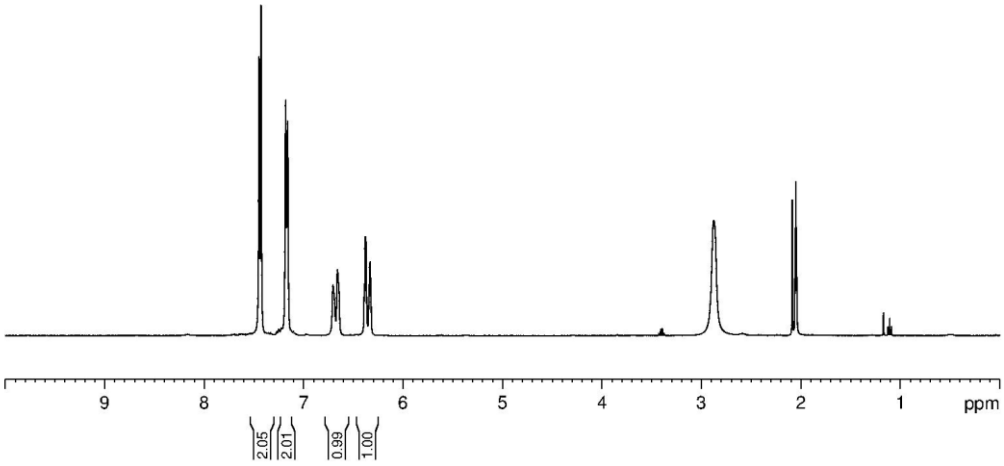
7.481
7.380
7.334
7.257
7.186
7.184
7.164
6.156
6.110
1.562
1.312
^{1}H NMR of
O
B
O
F_3CO
9
8
7
6
5
4
3
2
1
ppm
1.98
1.11
1.93
1.00
12.33
149.651
147.860
136.400
128.486
124.467
121.907
121.072
119.350
116.791
83.650
24.956
^{13}C NMR of
O
B
O
F_3CO
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

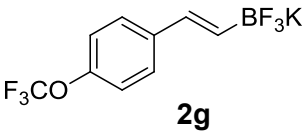
^{1}H NMR of



2g



^{13}C NMR of



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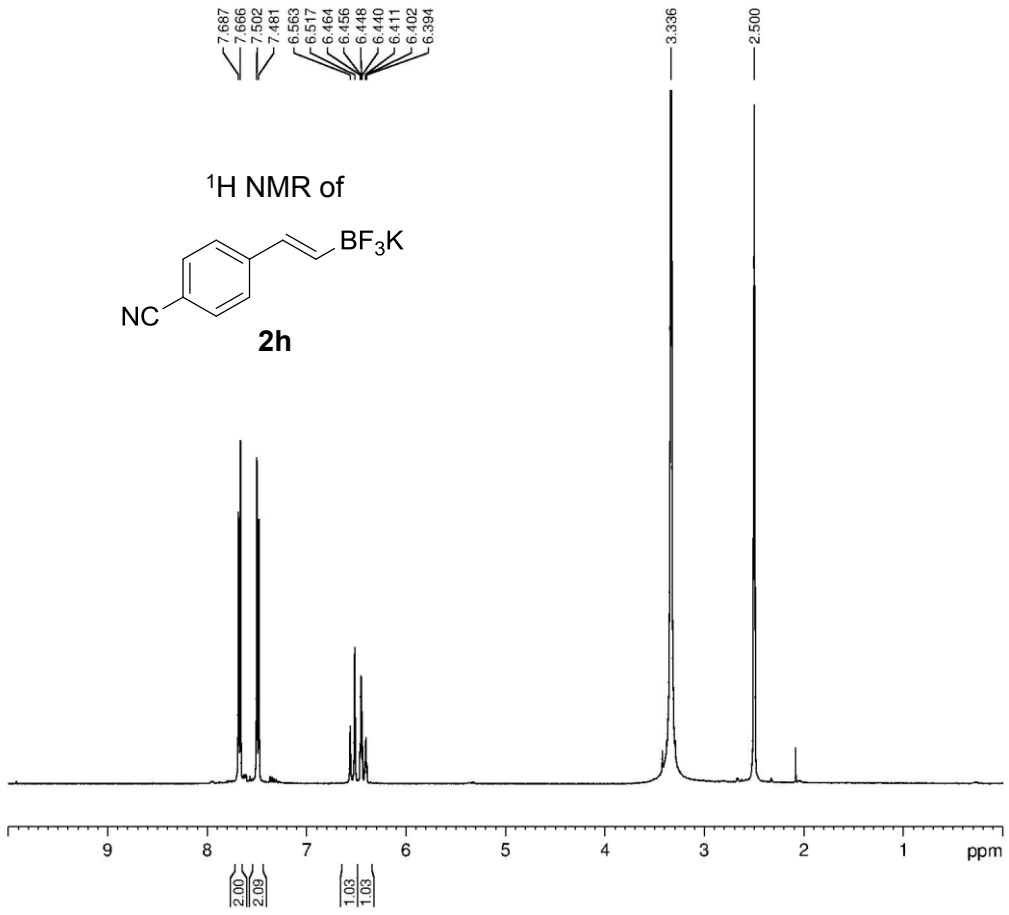
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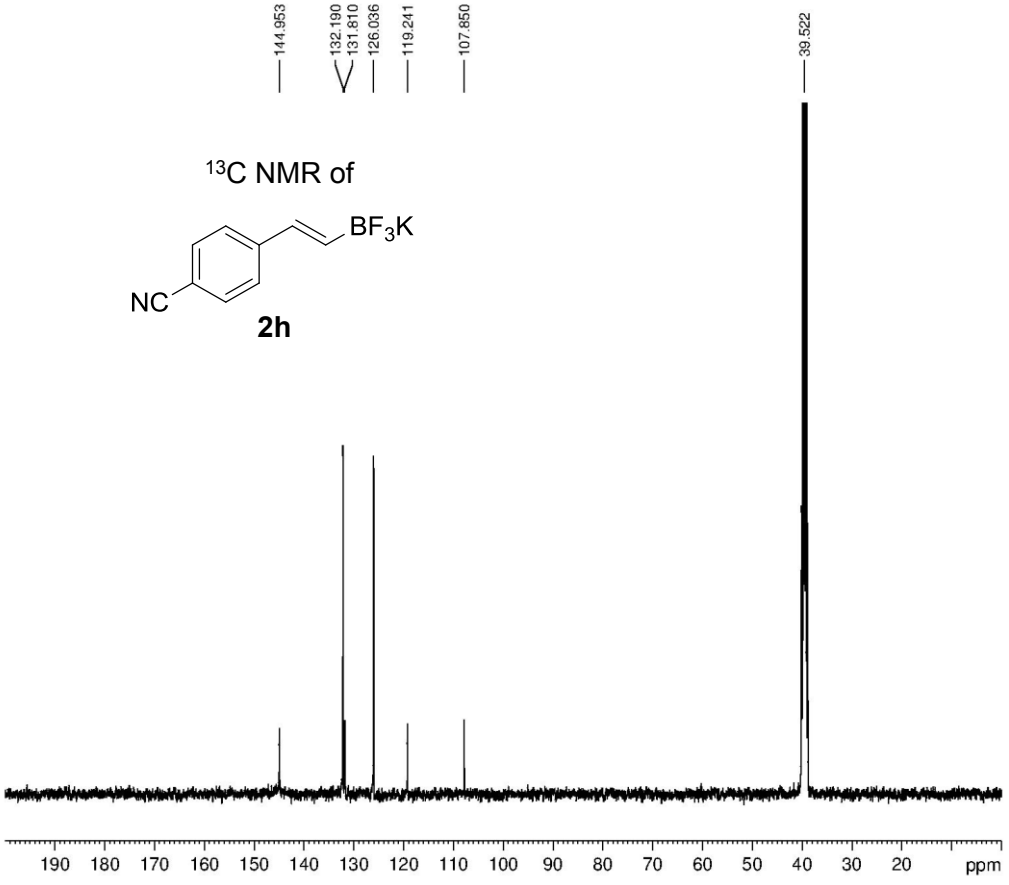
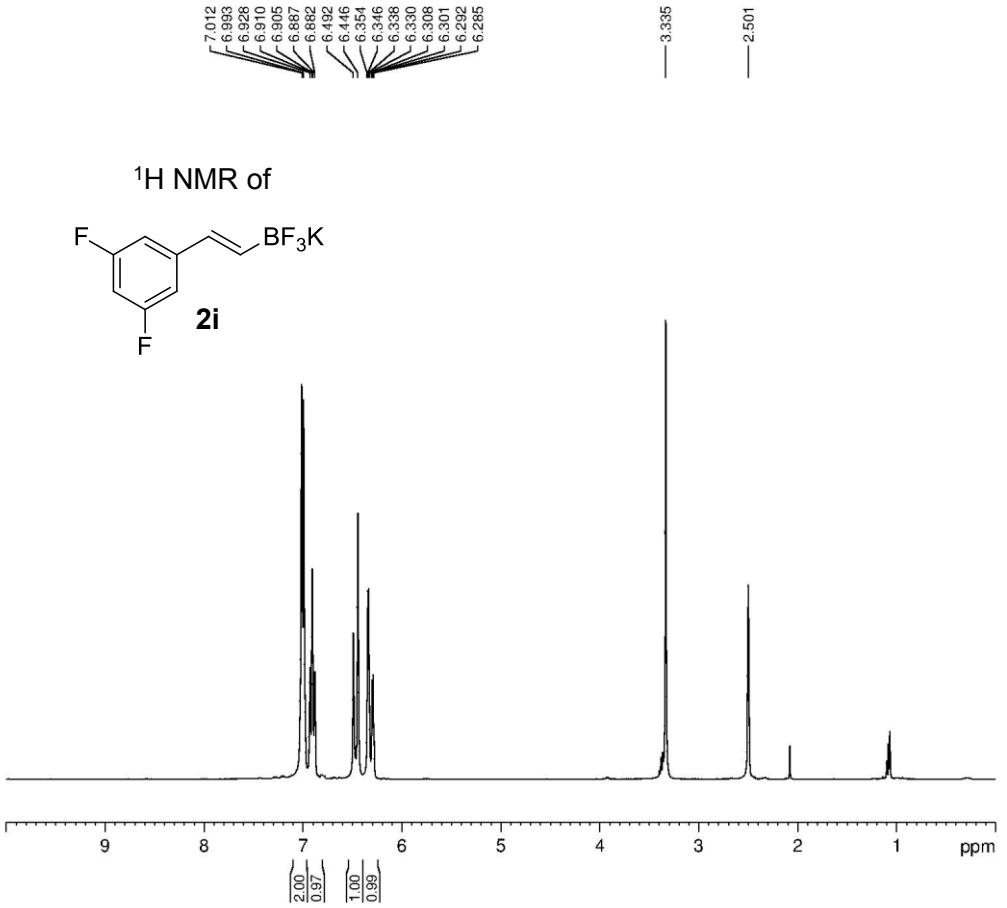
7.666
7.502
7.481
6.563
6.517
6.464
6.456
6.448
6.440
6.411
6.402
6.394
3.336
2.500
1H NMR of
BF3K
NC
2h
9
8
7
6
5
4
3
2
1
ppm
2.00
2.09
1.03
1.03


144.953
132.190
131.810
126.036
119.241
107.850
39.522
13C NMR of
BF3K
NC
2h
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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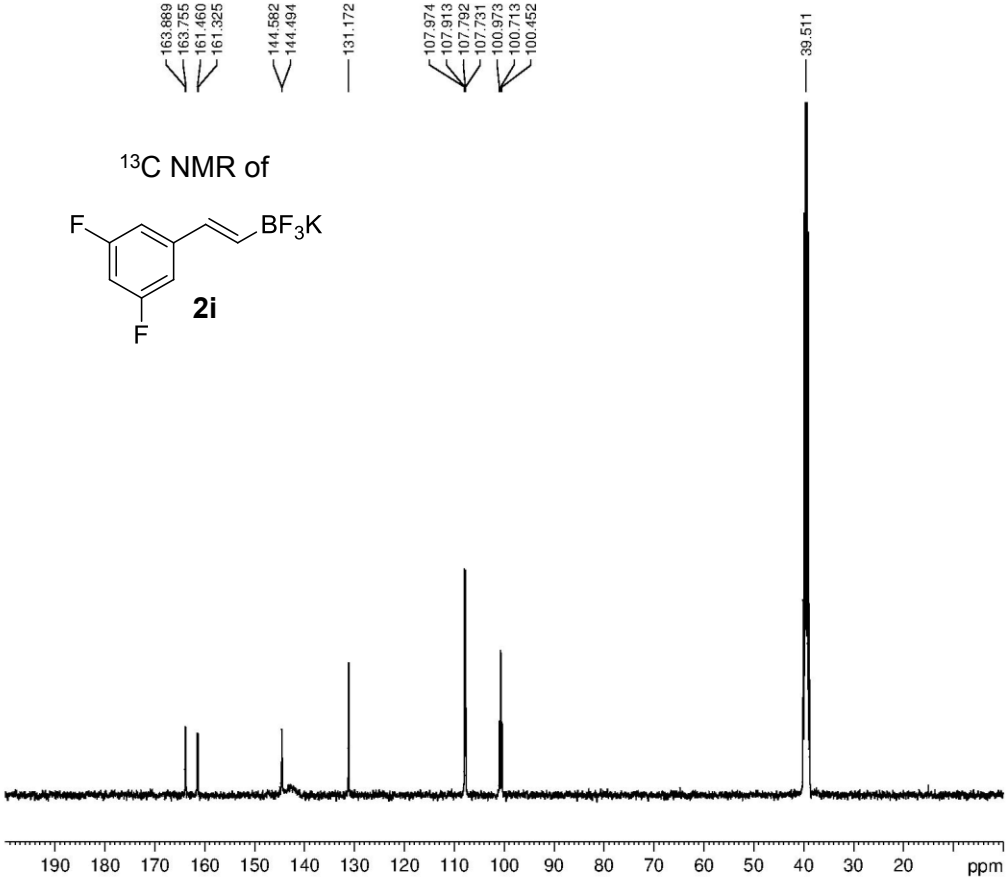
6.993
6.928
6.910
6.905
6.887
6.882
6.492
6.446
6.354
6.346
6.338
6.330
6.308
6.301
6.292
6.285
3.335
2.501
^{1}H NMR of
F
BF_3K
F
2i
9
8
7
6
5
4
3
2
1
ppm
2.00
0.97
1.00
0.99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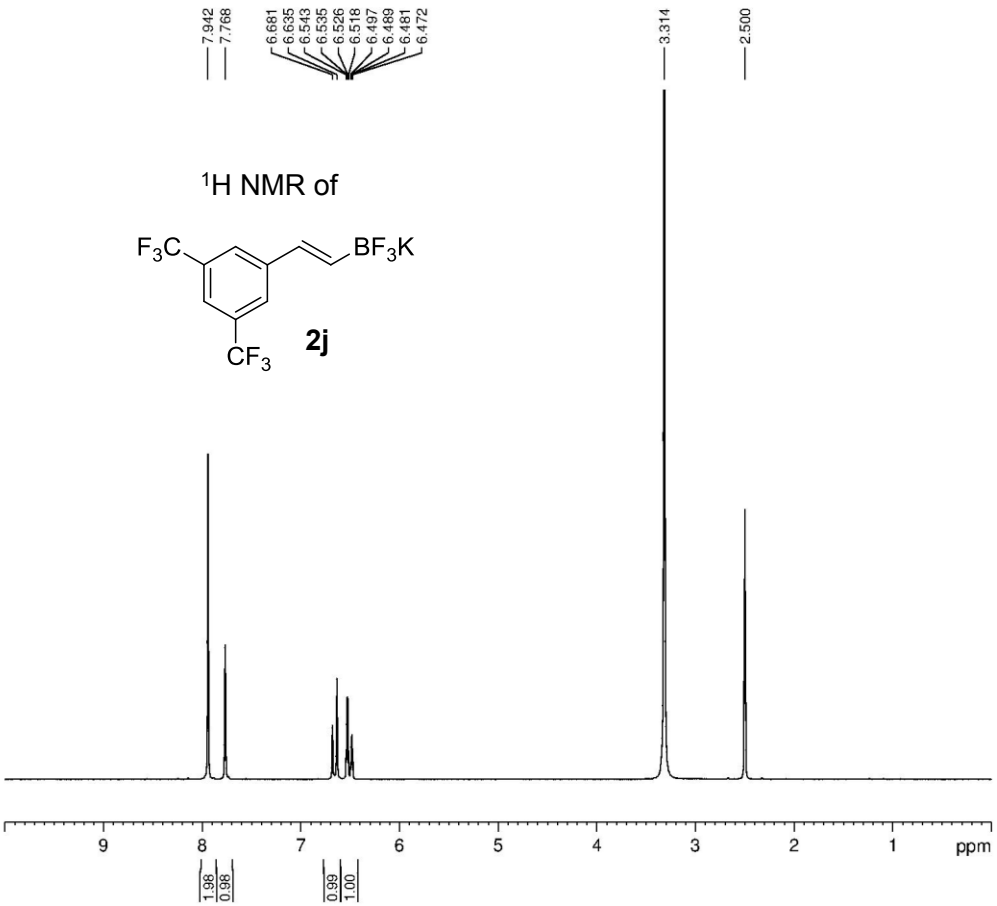
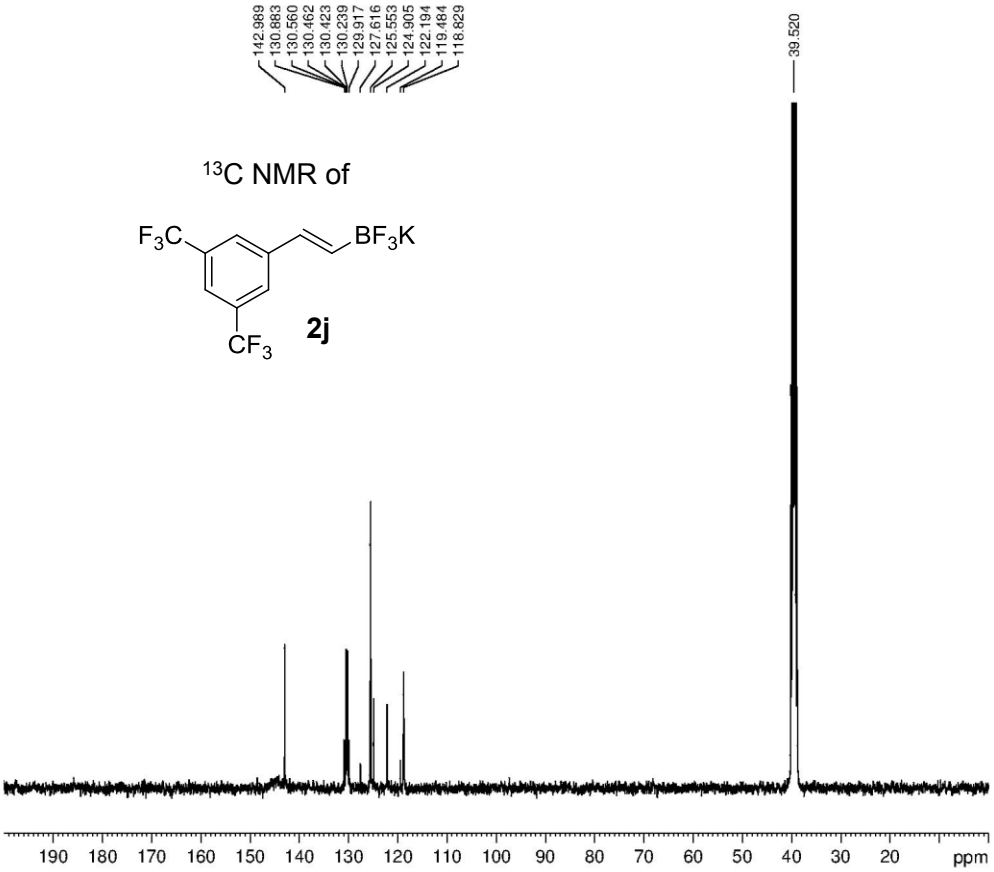
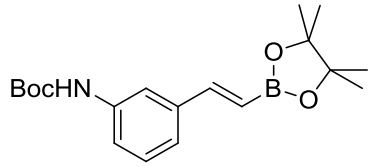
163.755
161.460
161.325
144.582
144.494
131.172
107.974
107.913
107.792
107.731
100.973
100.713
100.452
39.511
^{13}C NMR of
F
BF_3K
F
2i
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

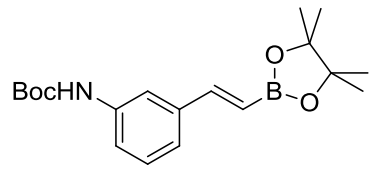


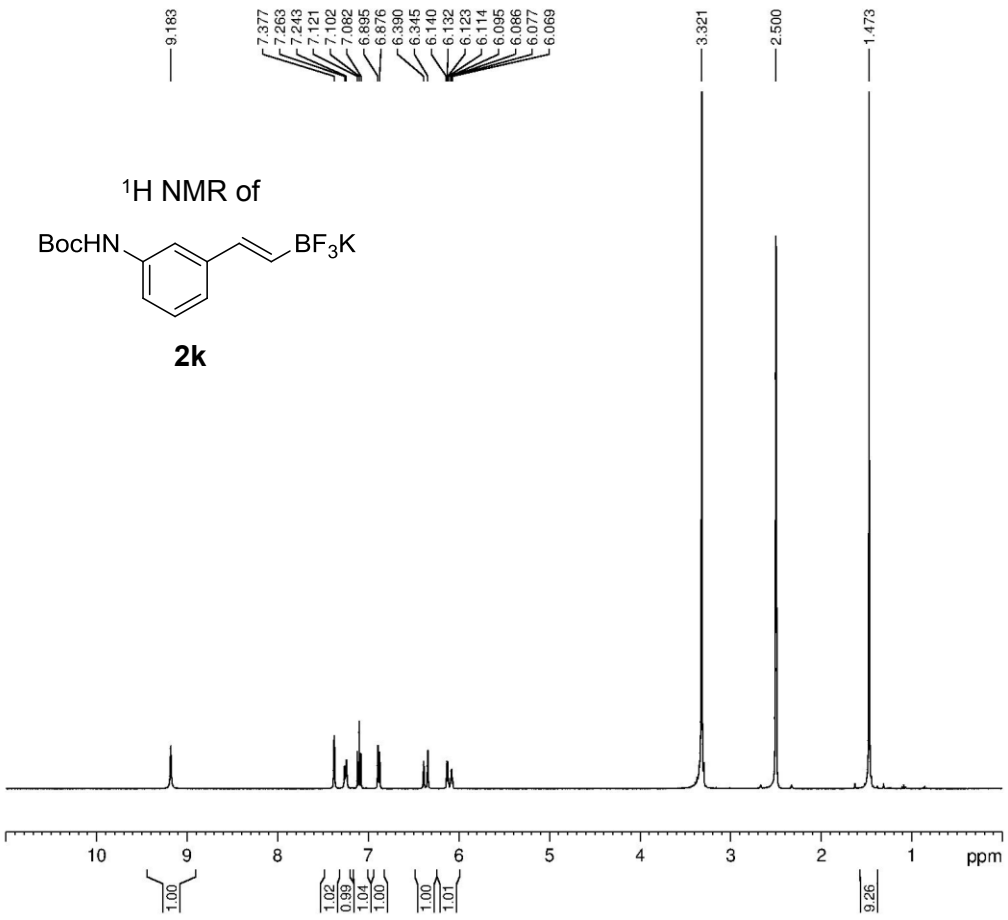


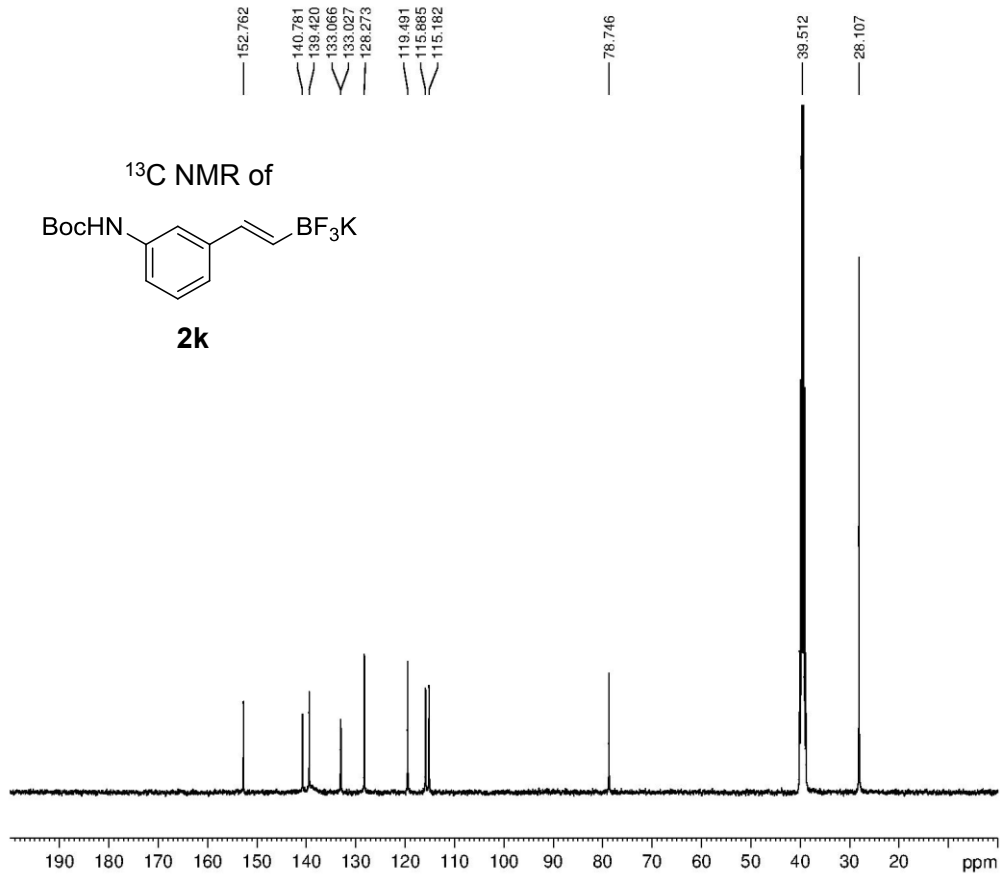
^{1}H NMR of

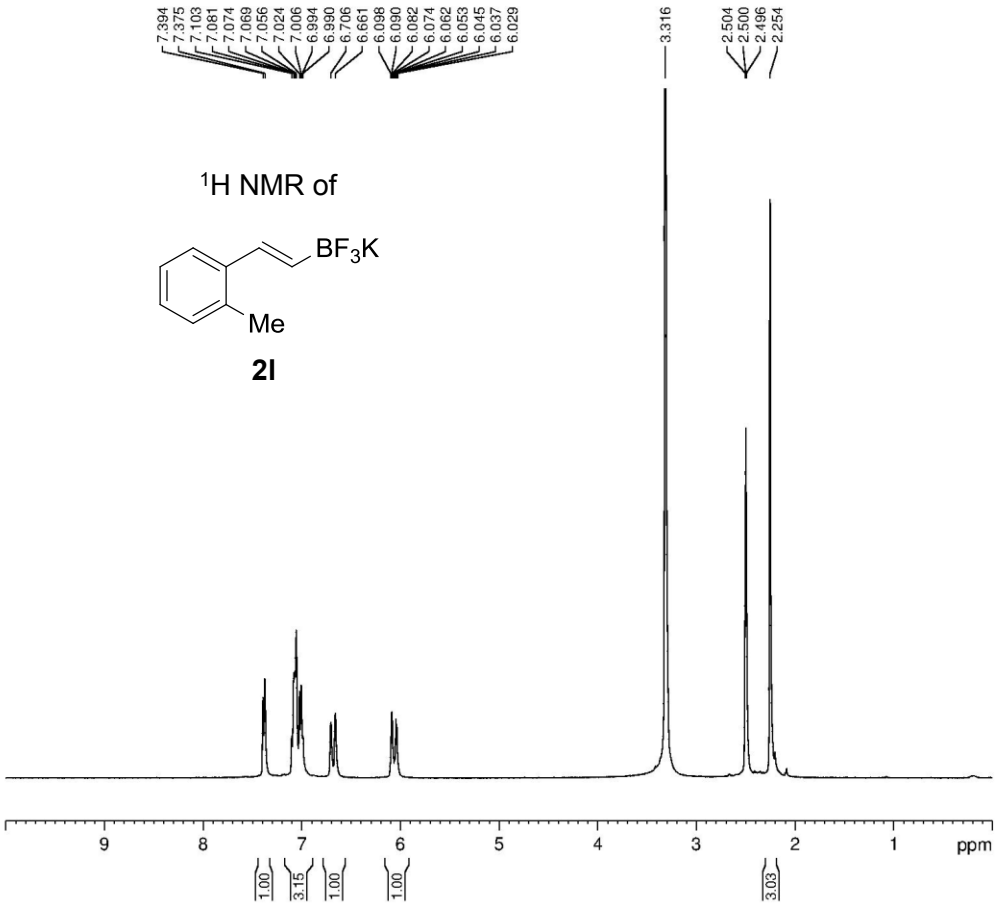


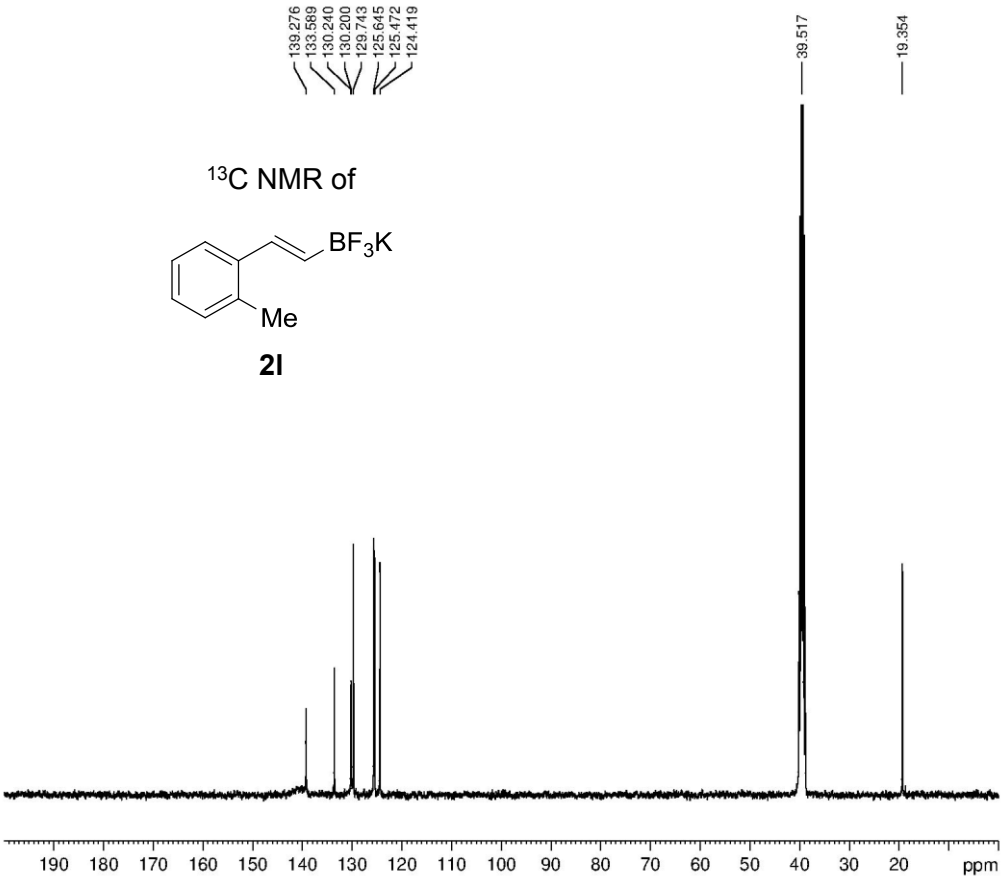
^{13}C NMR of

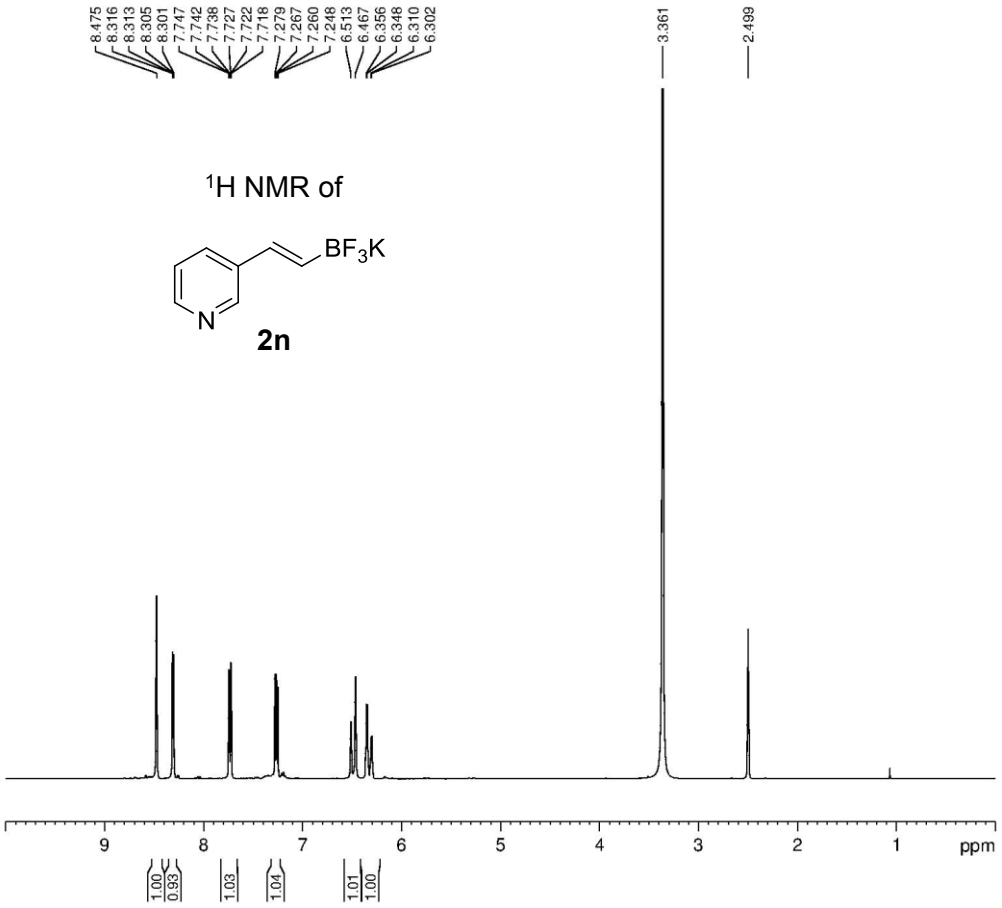






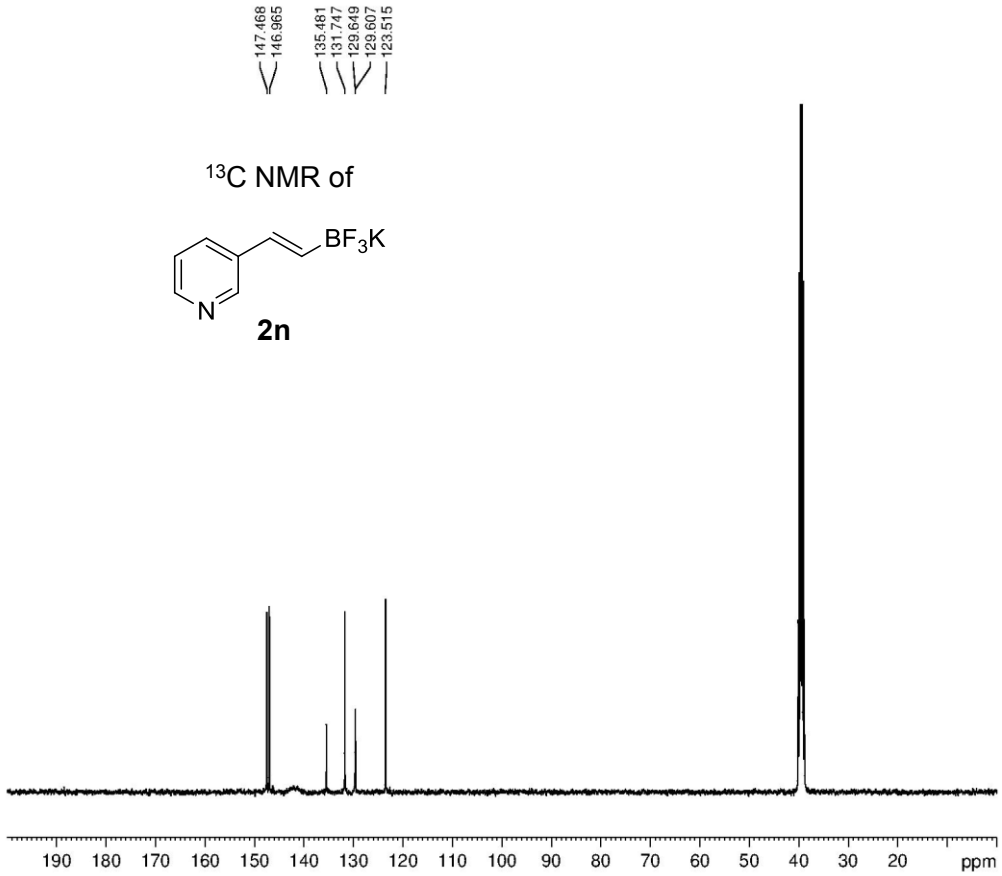






^{1}H NMR of

2n



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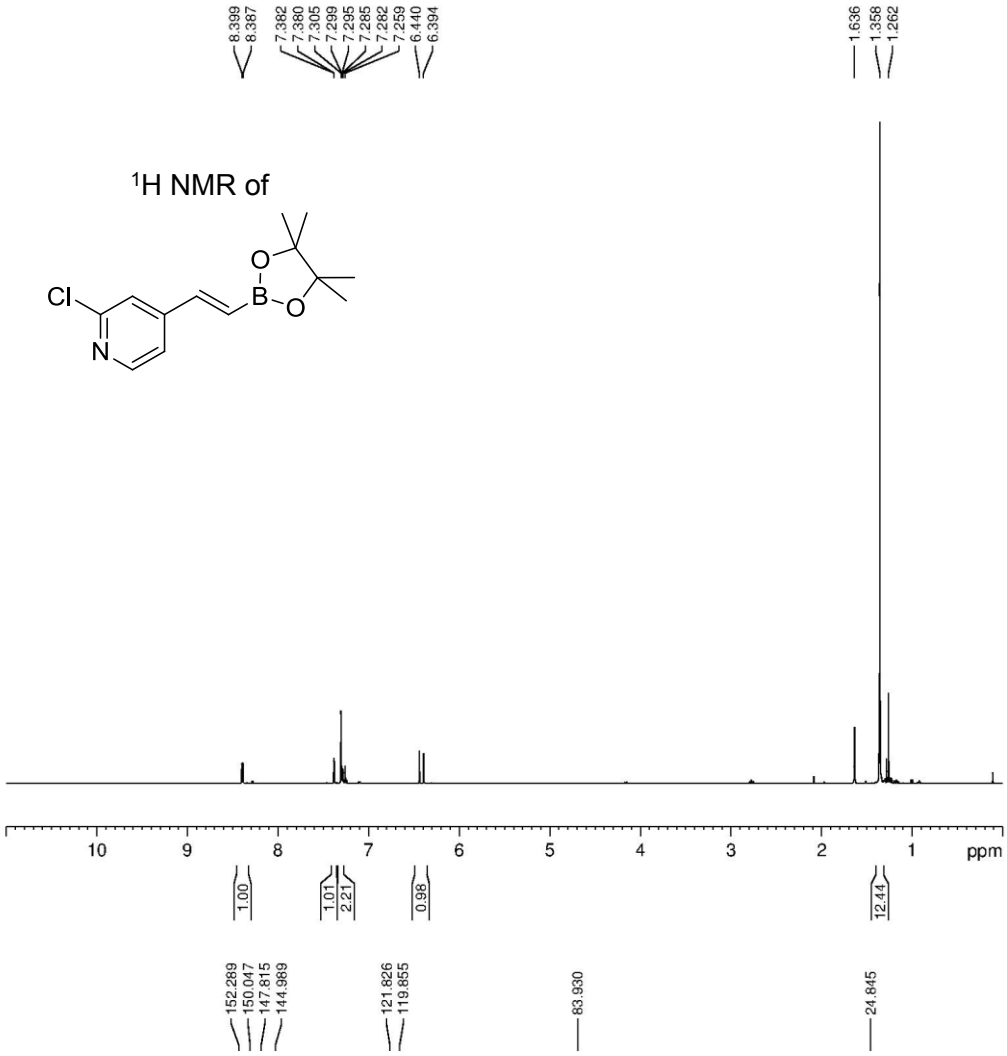

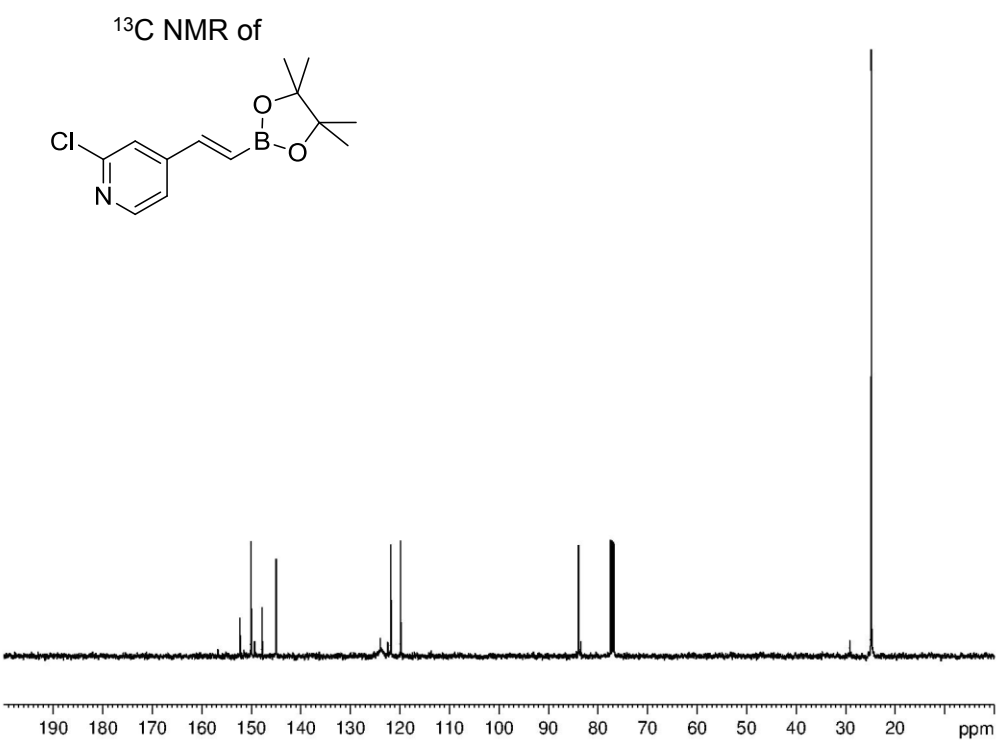

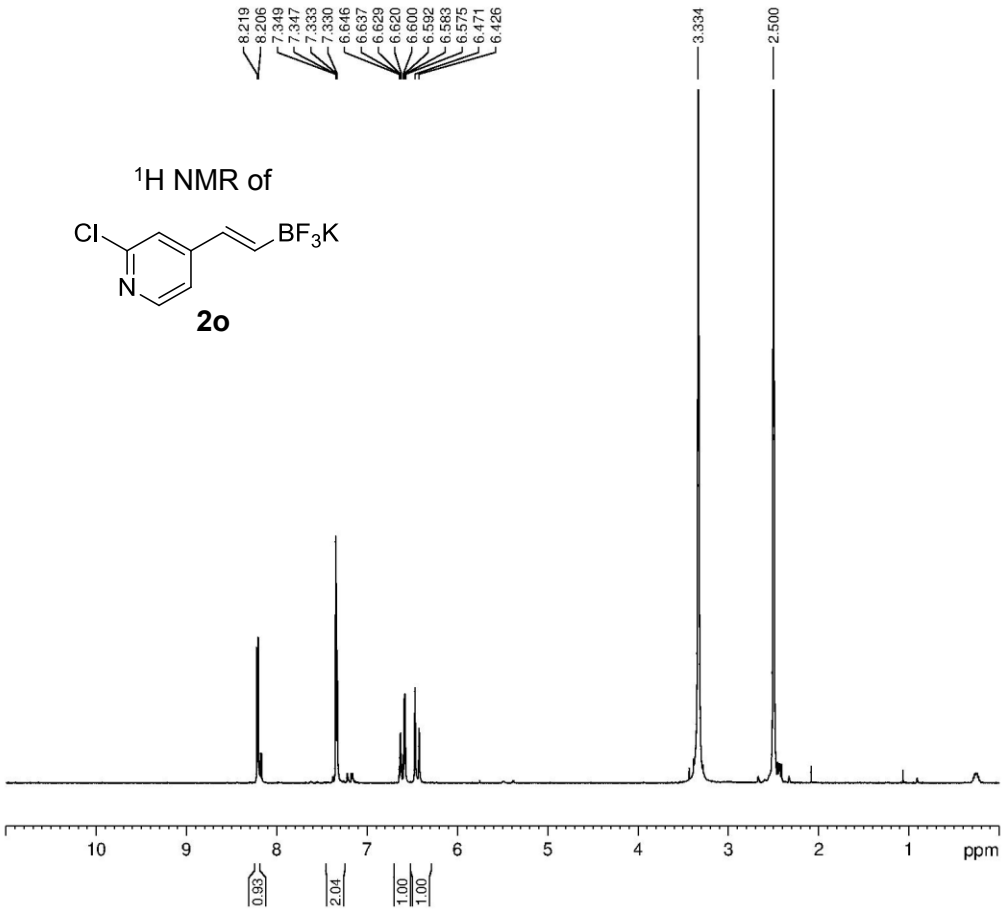
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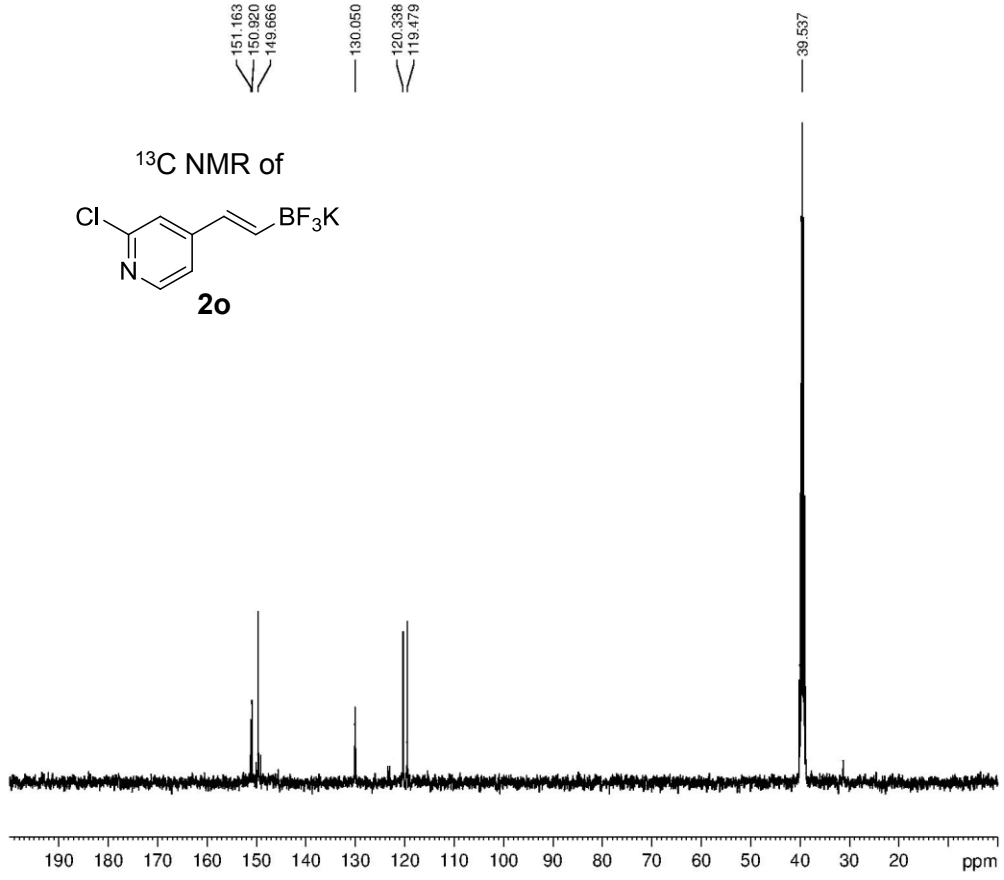
7.330
6.646
6.637
6.629
6.620
6.600
6.592
6.583
6.575
6.471
6.426
3.334
2.500
1H NMR of
Cl
BF3K
N
2o
10
9
8
7
6
5
4
3
2
1
ppm
0.93
2.04
1.00
1.00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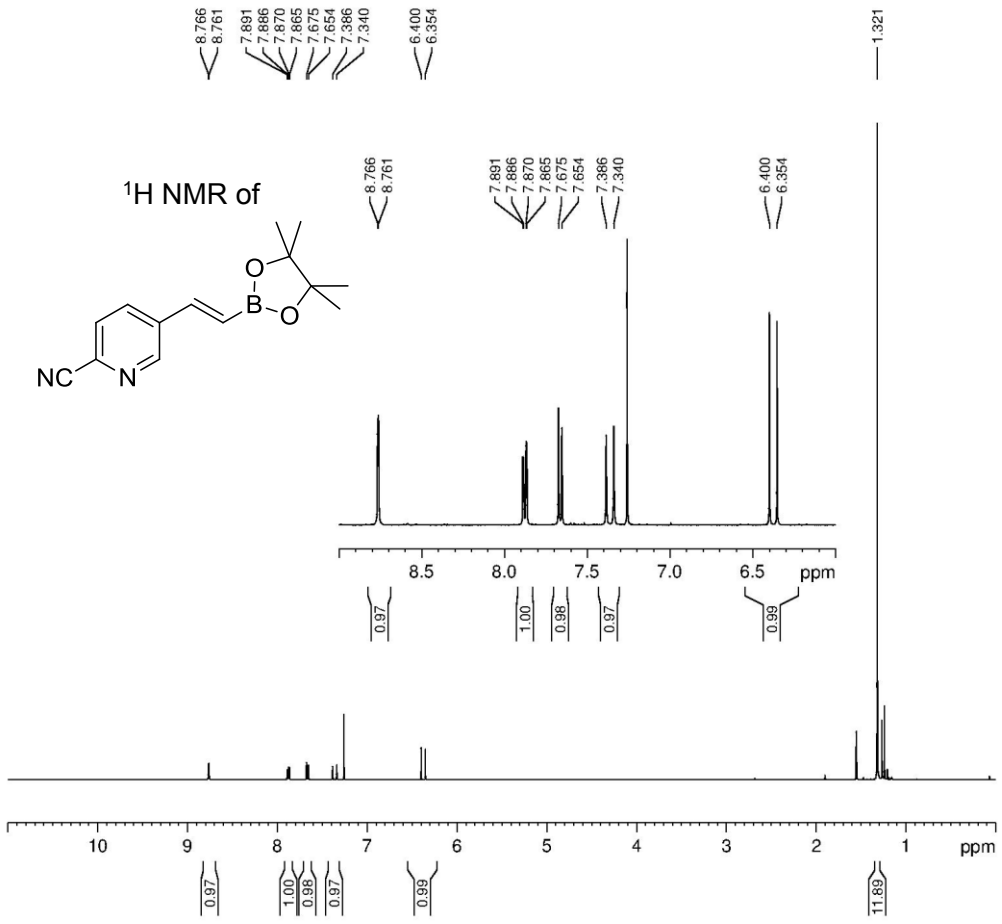
150.920
149.666
130.050
120.338
119.479
39.537
13C NMR of
Cl
BF3K
N
2o
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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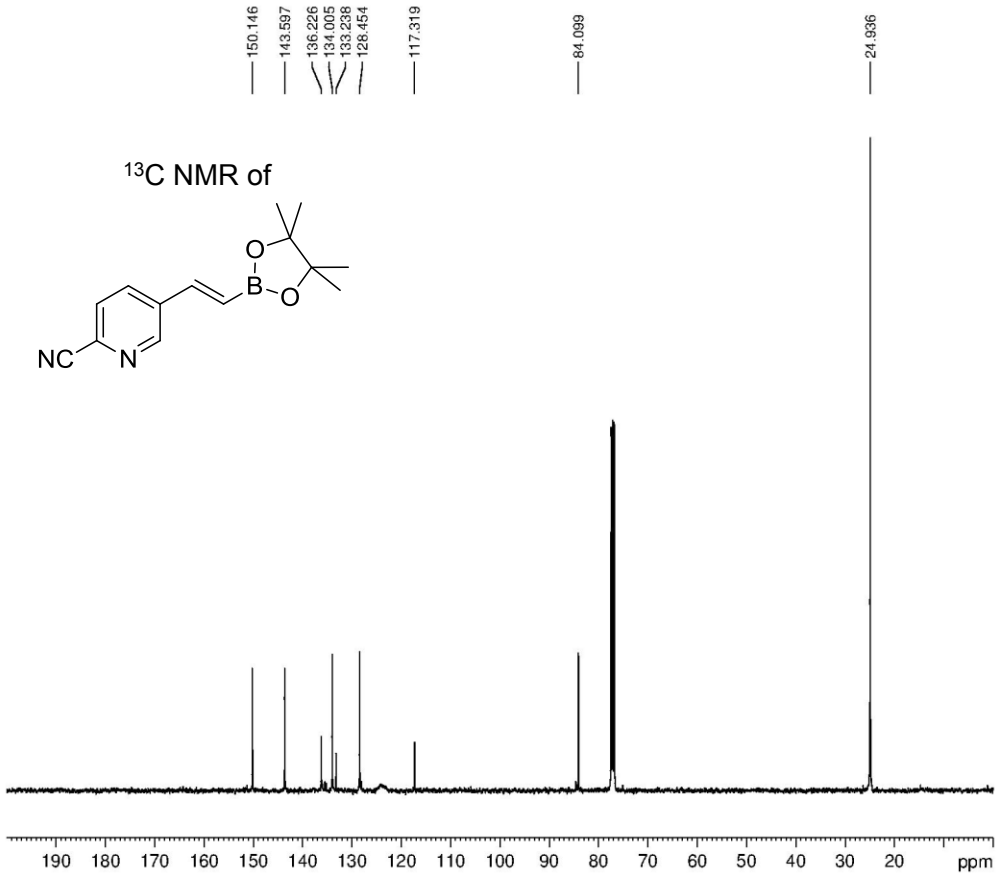
8.761
7.891
7.886
7.870
7.865
7.675
7.654
7.386
7.340
6.400
6.354
1.321
^{1}H NMR of
O
B
O
NC
N
8.5
8.0
7.5
7.0
6.5
ppm
0.97
1.00
0.98
0.97
0.99
10
9
8
7
6
5
4
3
2
1
ppm
0.97
1.00
0.98
0.97
0.99
11.89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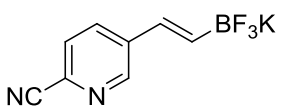
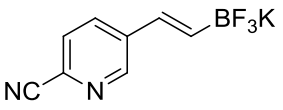
143.597
136.226
134.005
133.238
128.454
117.319
84.099
24.936
^{13}C NMR of
O
B
O
NC
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

^{1}H NMR of



2p

^{13}C NMR of



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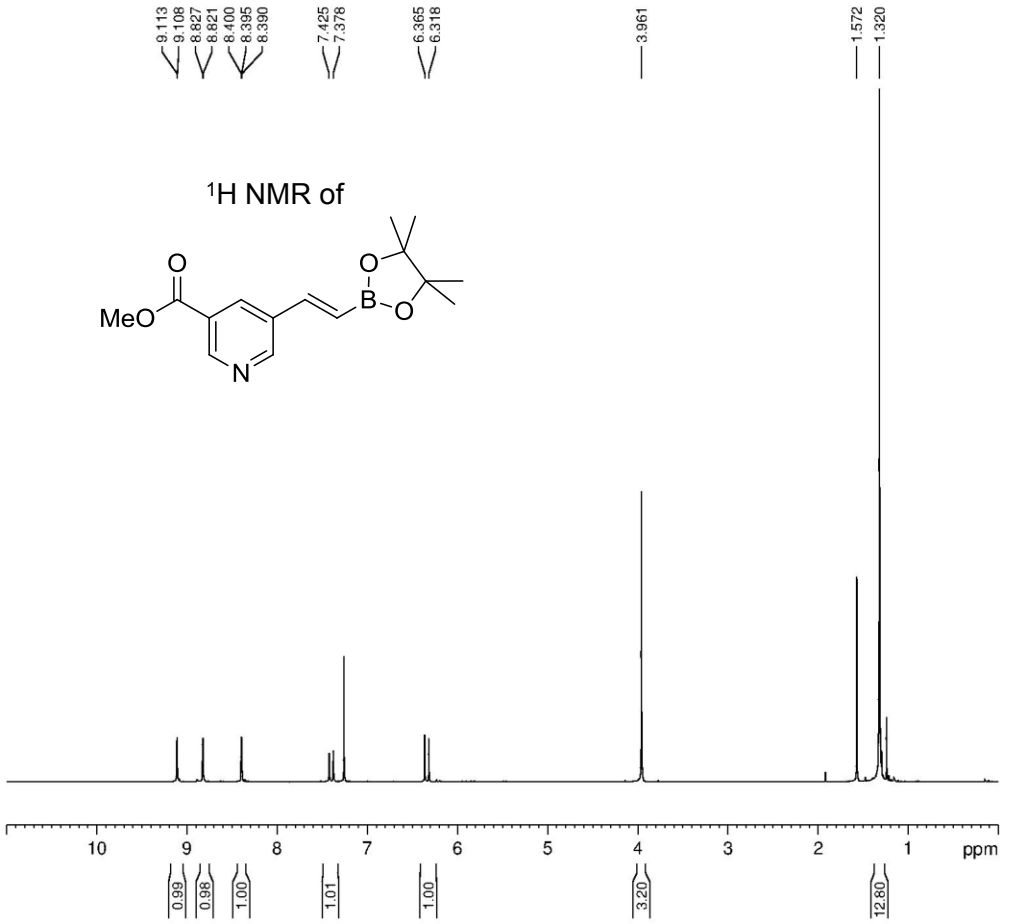

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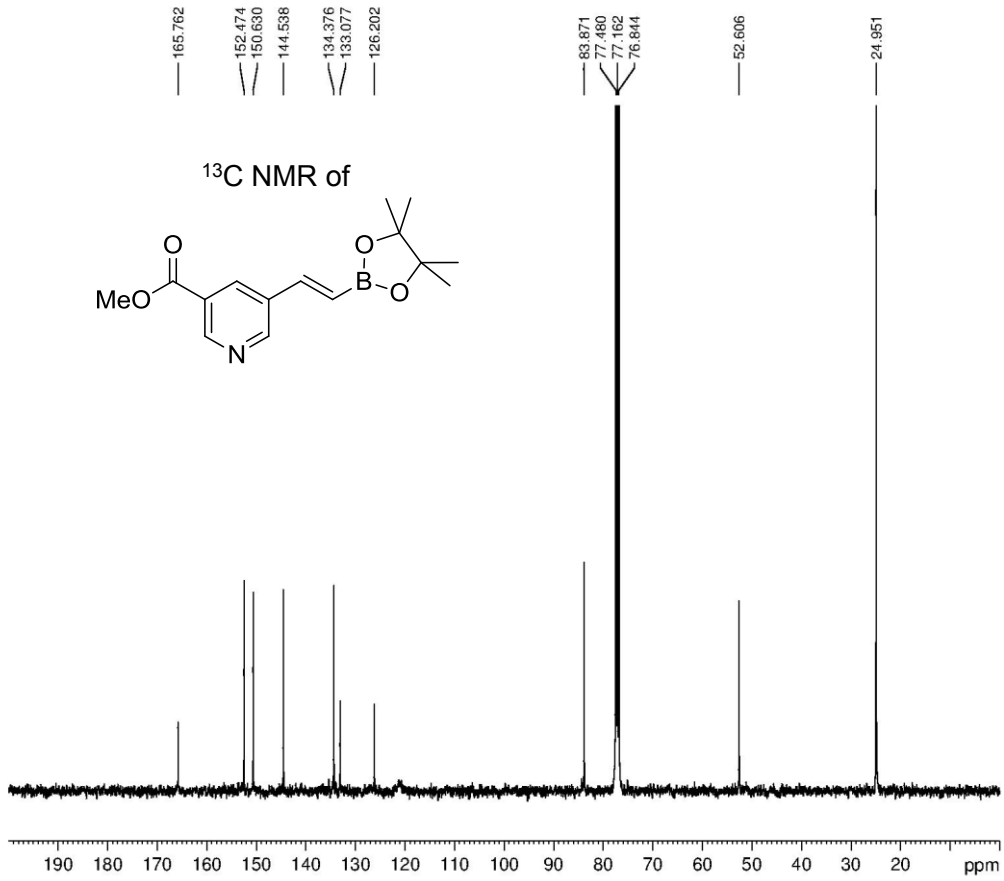

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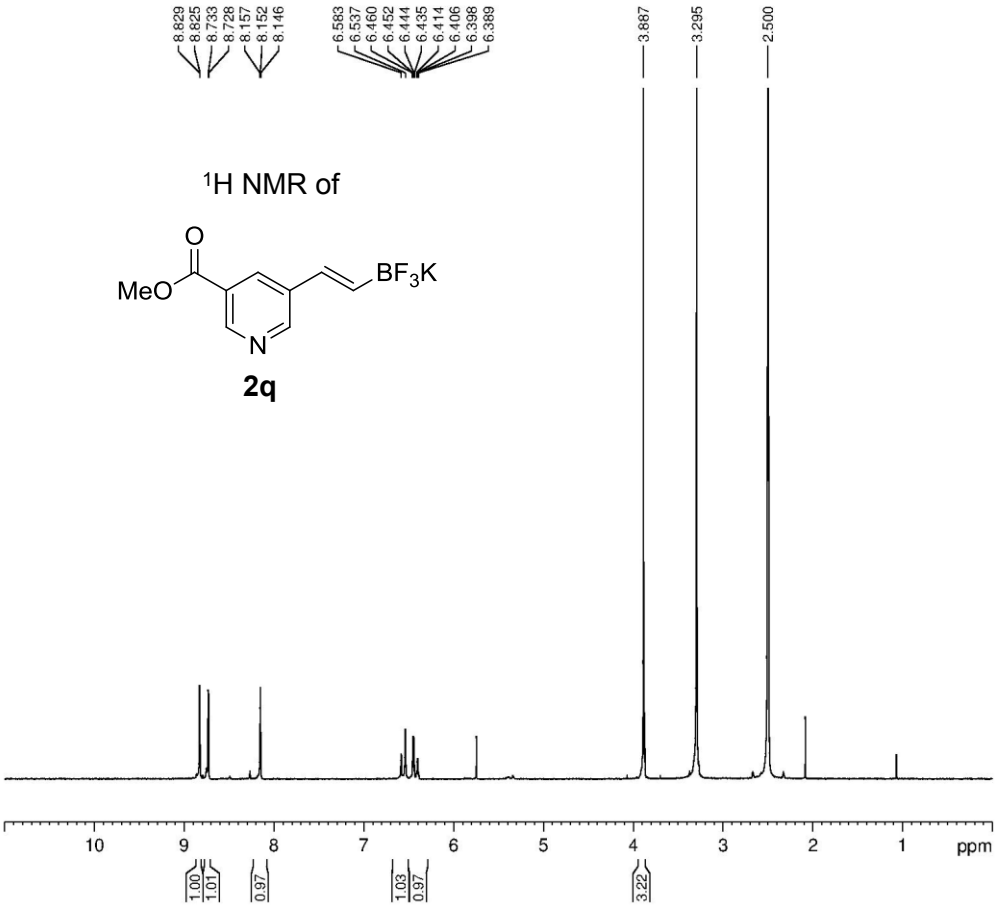
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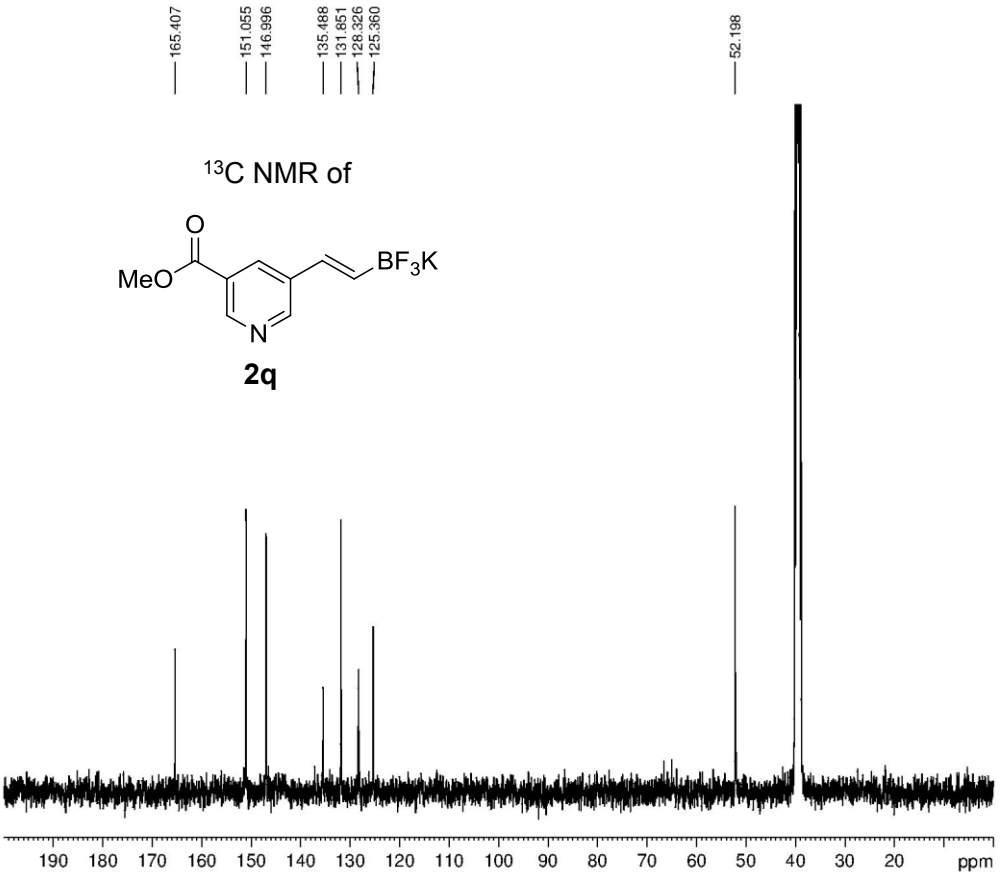
6.583
6.537
6.460
6.452
6.444
6.435
6.414
6.406
6.398
6.389
3.887
3.295
2.500
1H NMR of
O
MeO
BF3K
N
2q
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
0.97
1.03
0.97
3.22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131.851
128.326
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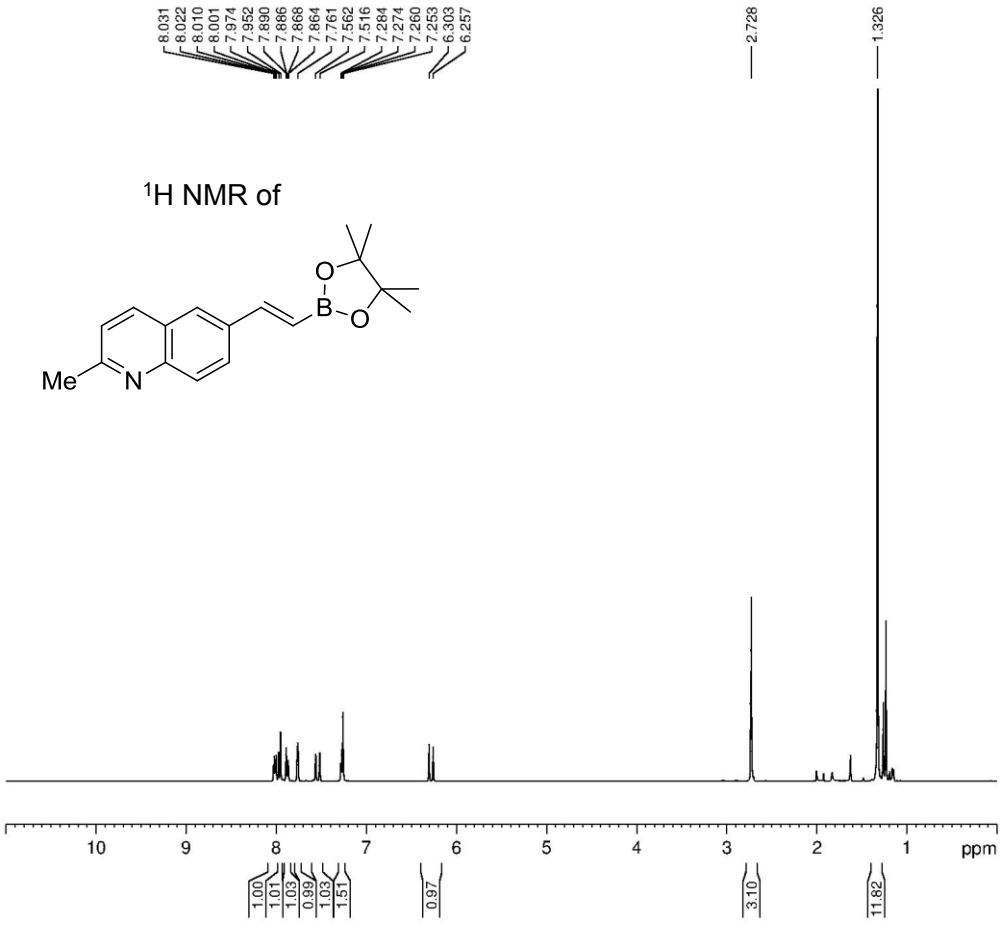
52.198
13C NMR of
O
MeO
BF3K
N
2q
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm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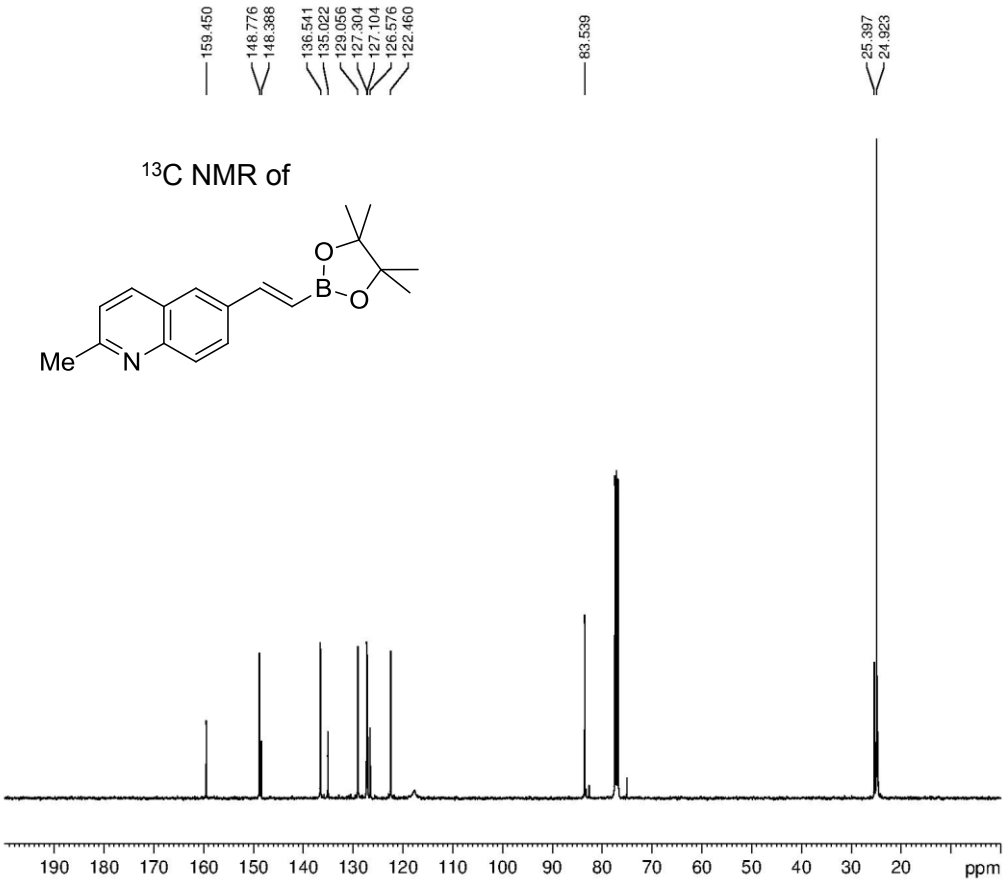
7.952
7.890
7.886
7.868
7.864
7.761
7.562
7.516
7.284
7.274
7.260
7.253
6.303
6.257
2.728
1.326
1H NMR of
O
B
O
Me
N
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.01
1.03
0.99
1.03
1.51
0.97
3.10
11.82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148.388
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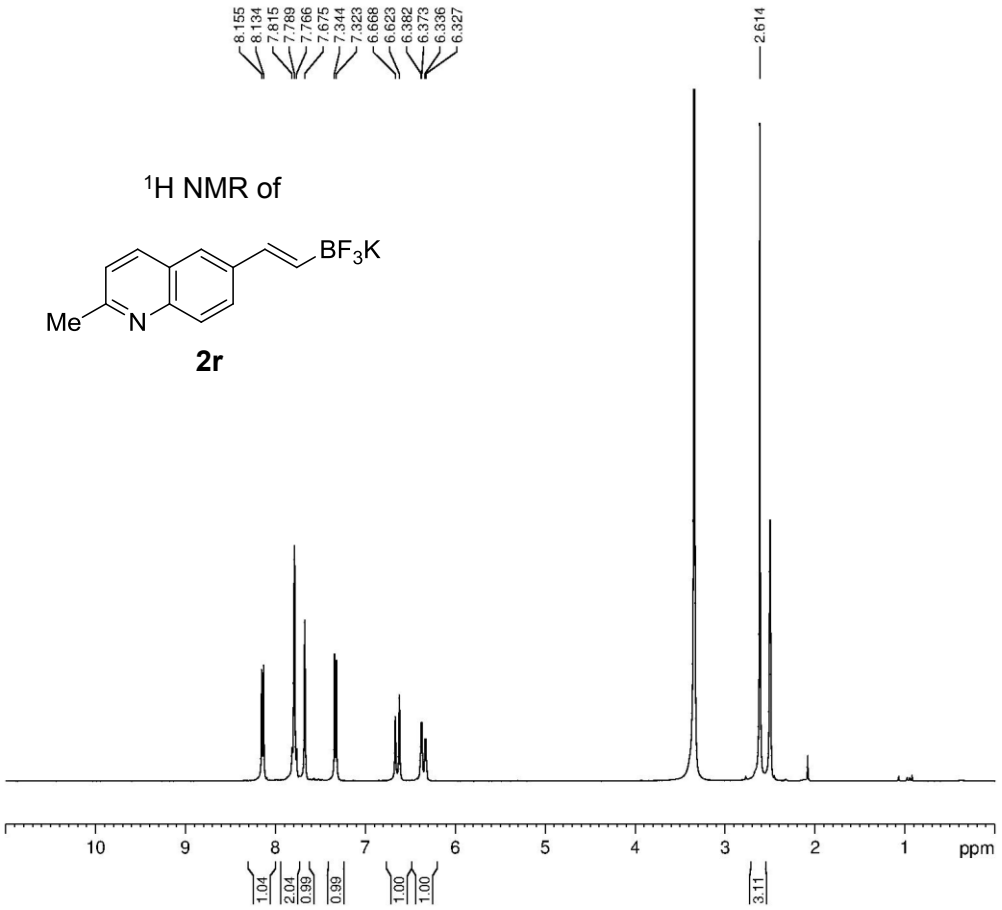
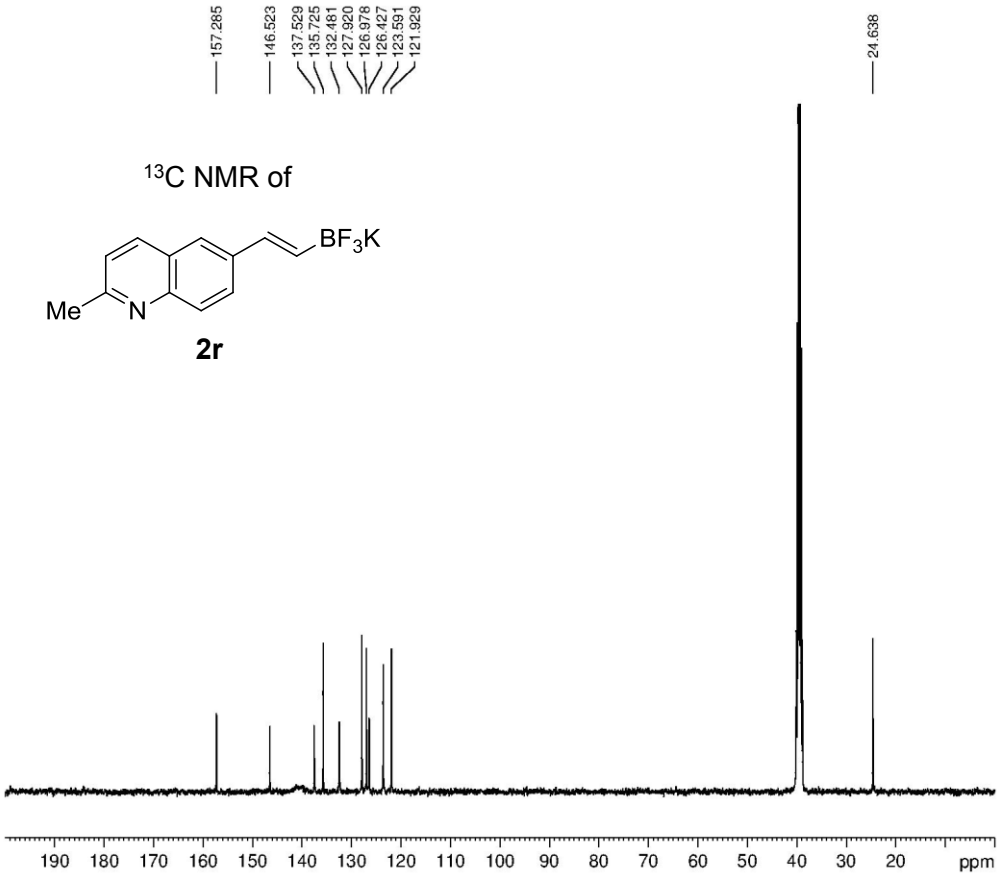
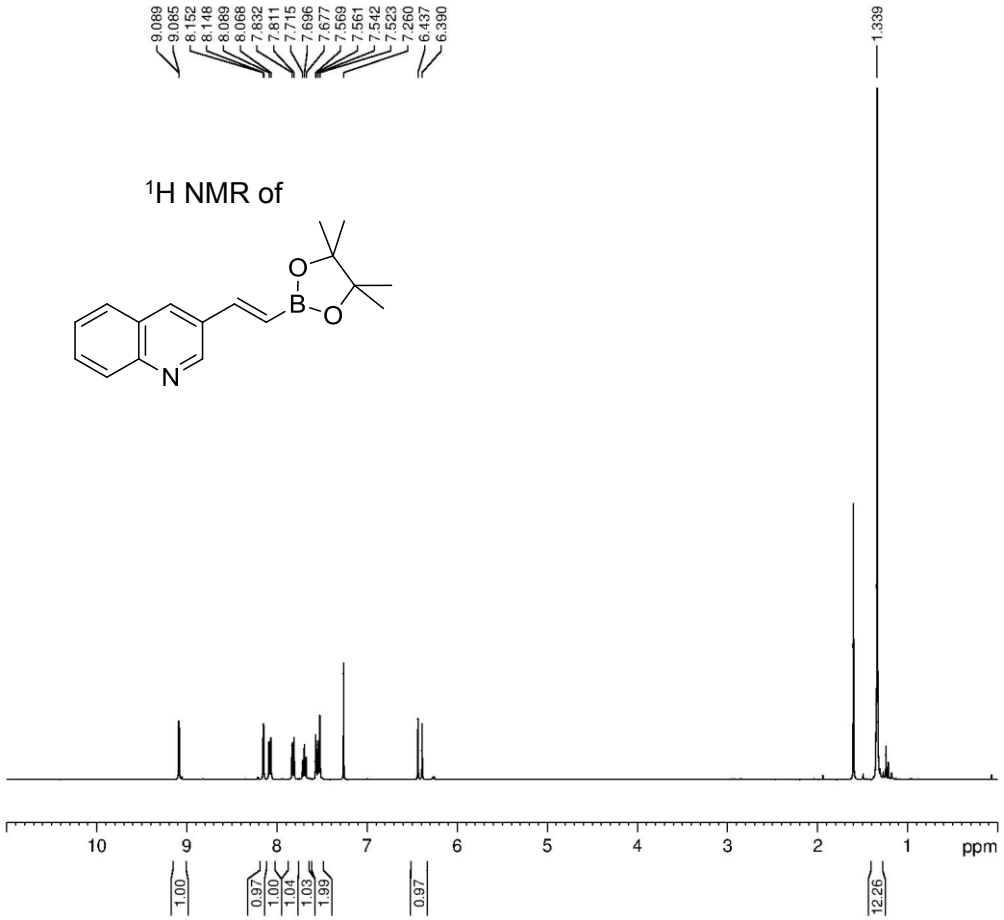
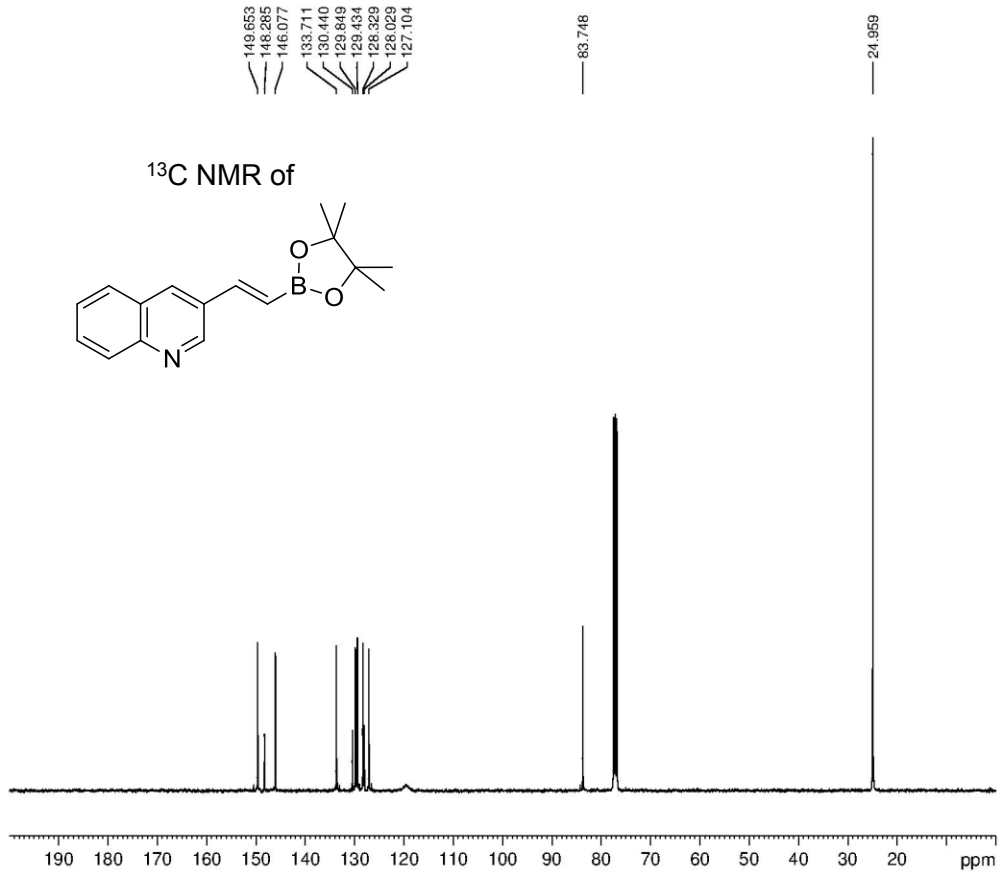
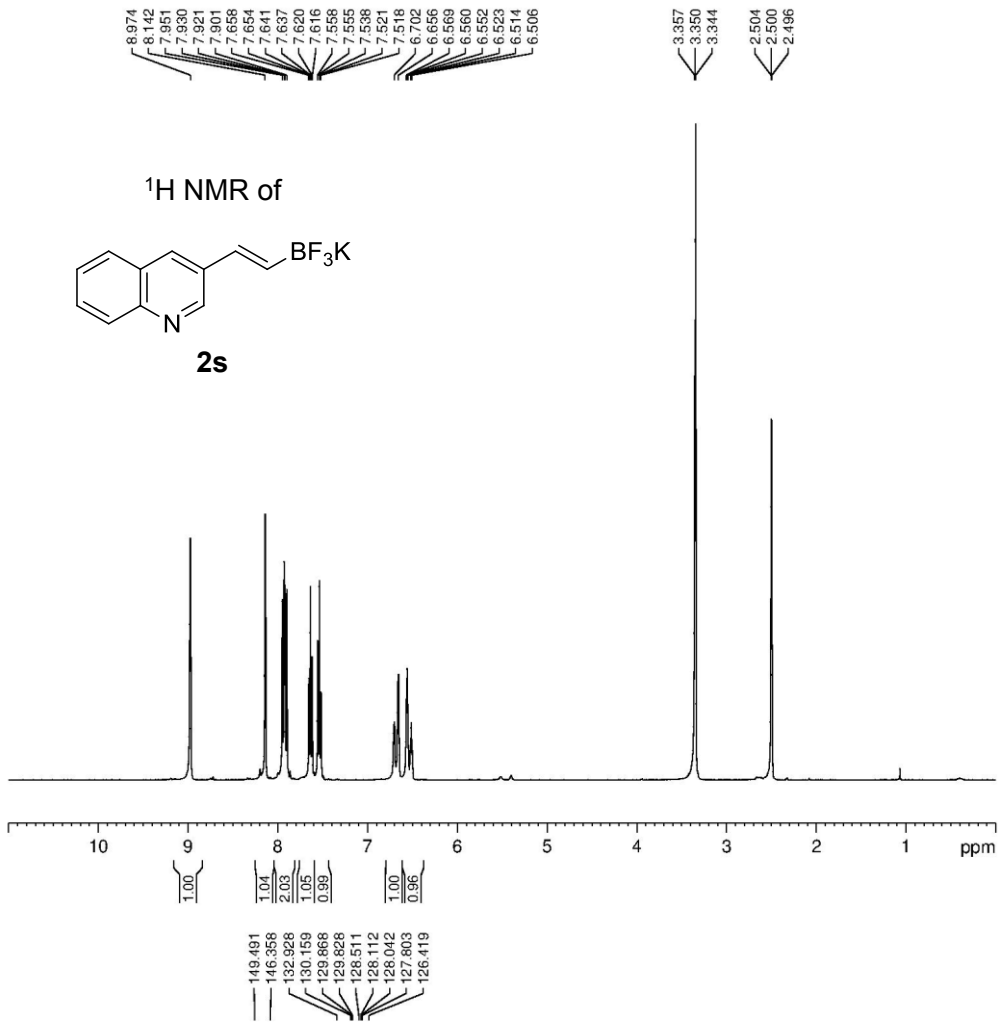
129.056
127.304
127.104
126.576
122.460
83.539
25.397
24.923
13C NMR of
O
B
O
Me
N
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm







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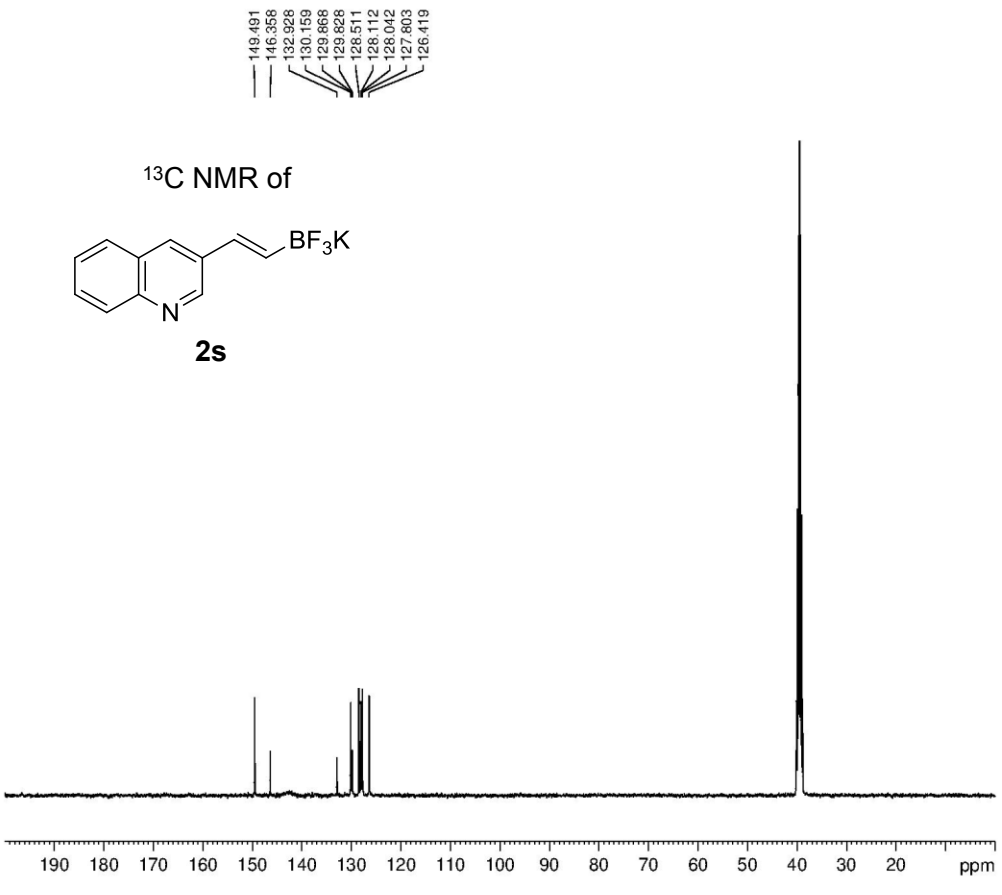
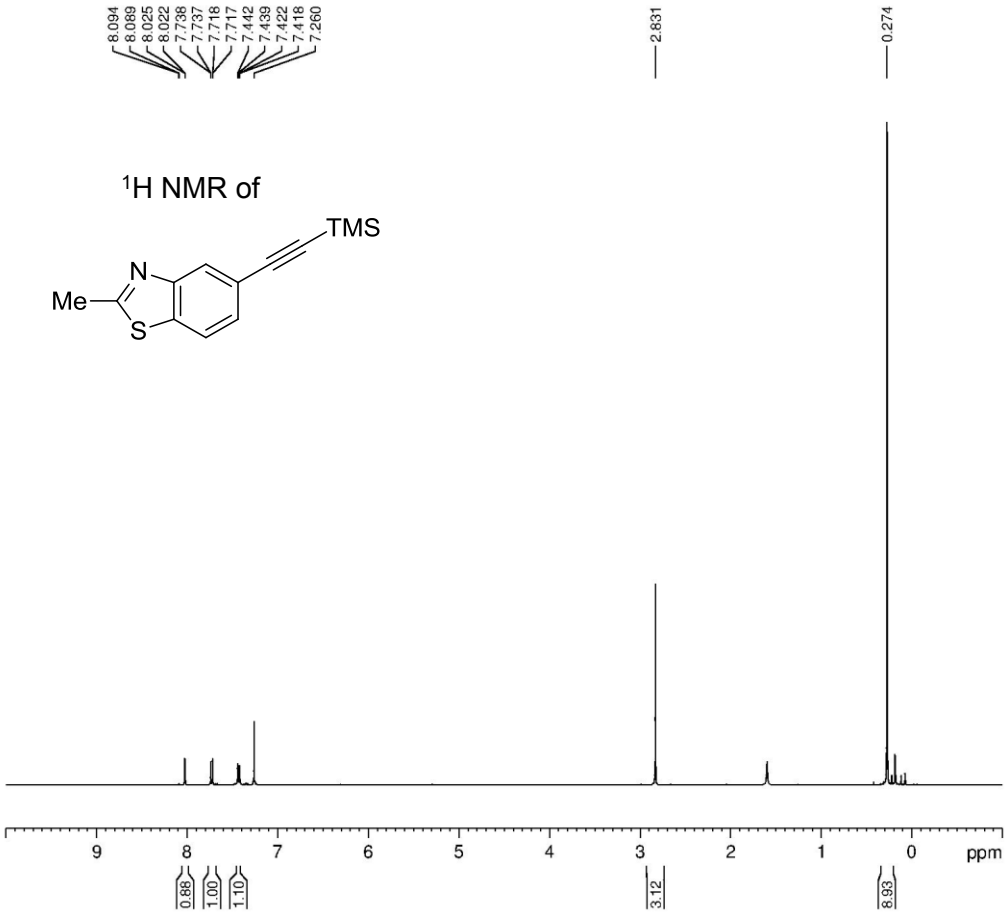
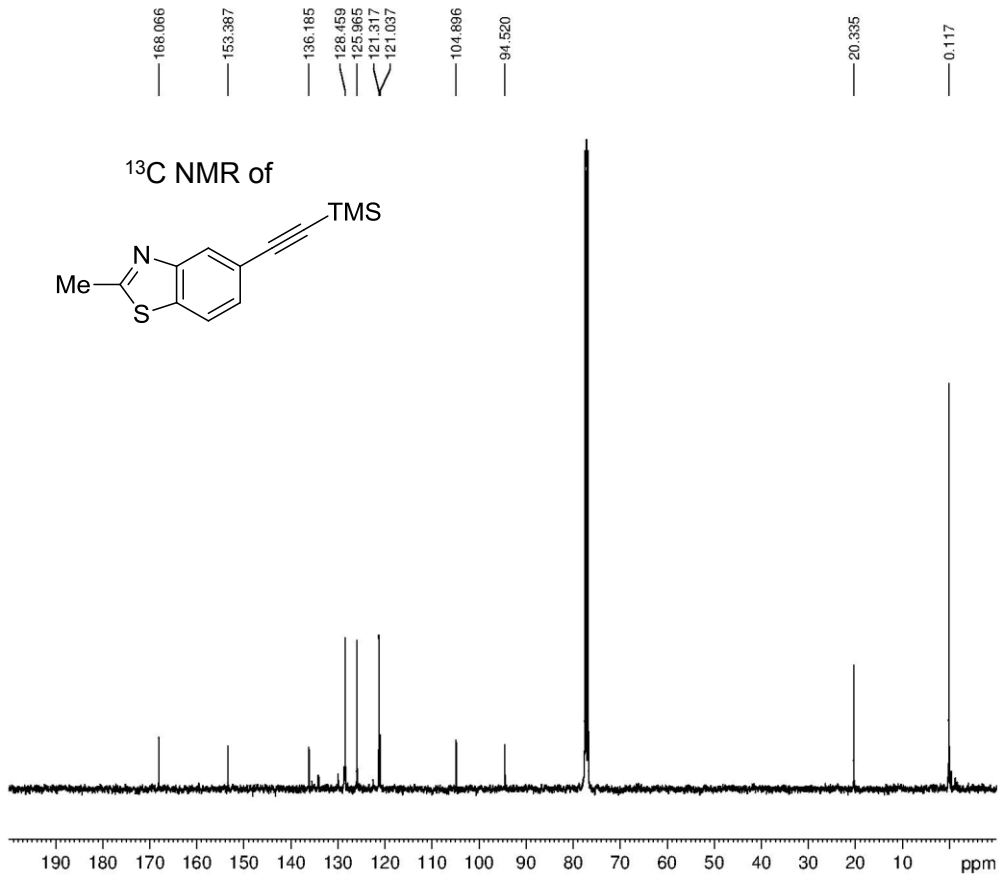
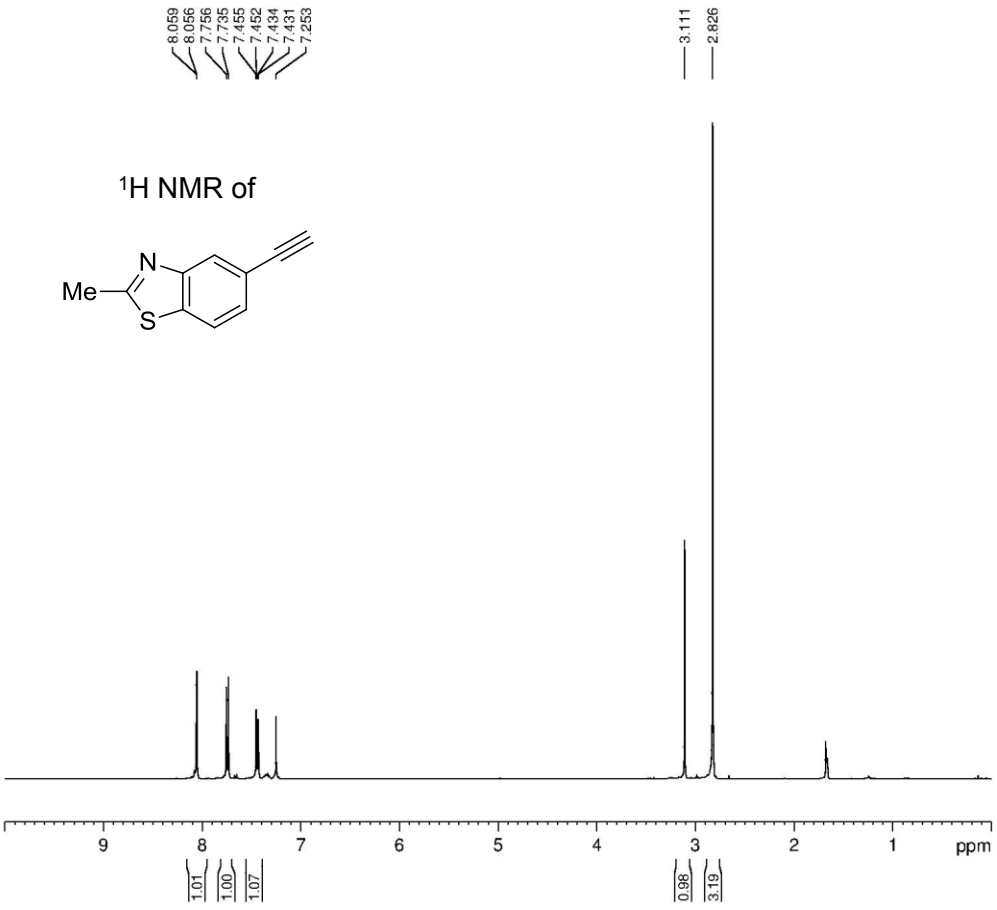
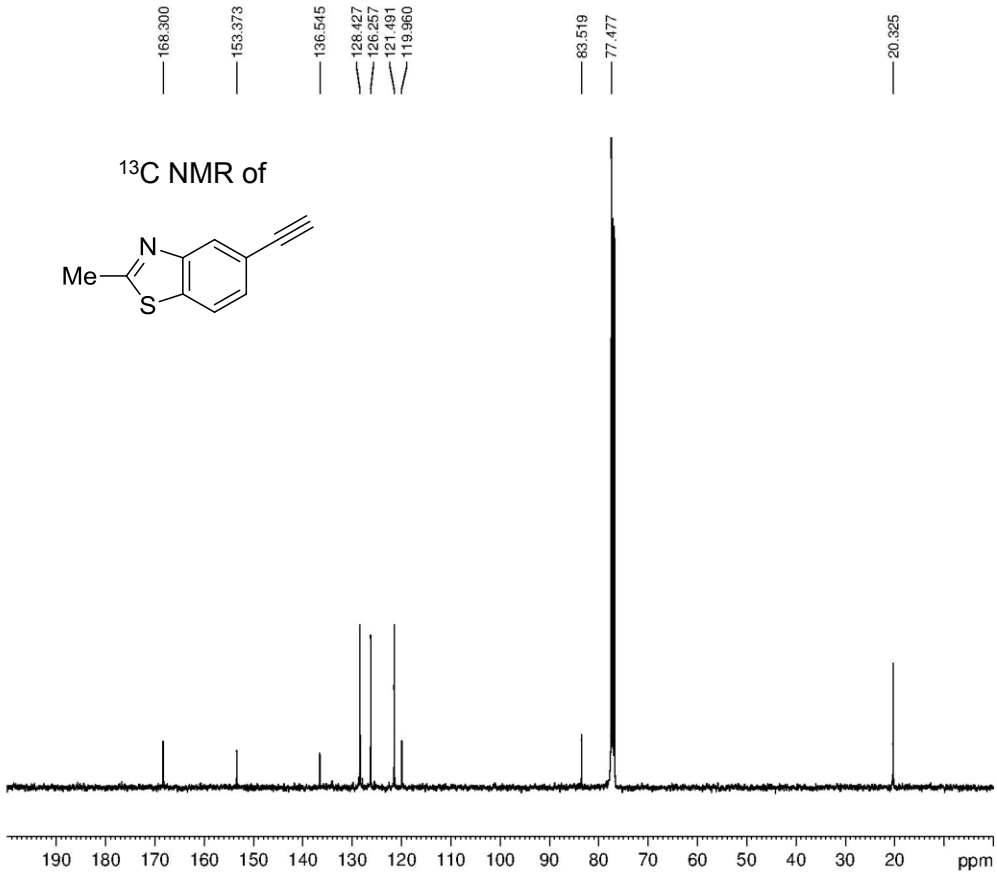
8.142
7.951
7.930
7.921
7.901
7.658
7.654
7.641
7.637
7.620
7.616
7.558
7.555
7.538
7.521
7.518
6.702
6.656
6.569
6.560
6.552
6.523
6.514
6.506
3.357
3.350
3.344
2.504
2.500
2.496
1H NMR of
BF3K
N
2s
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.04
2.03
1.05
0.99
1.00
0.96

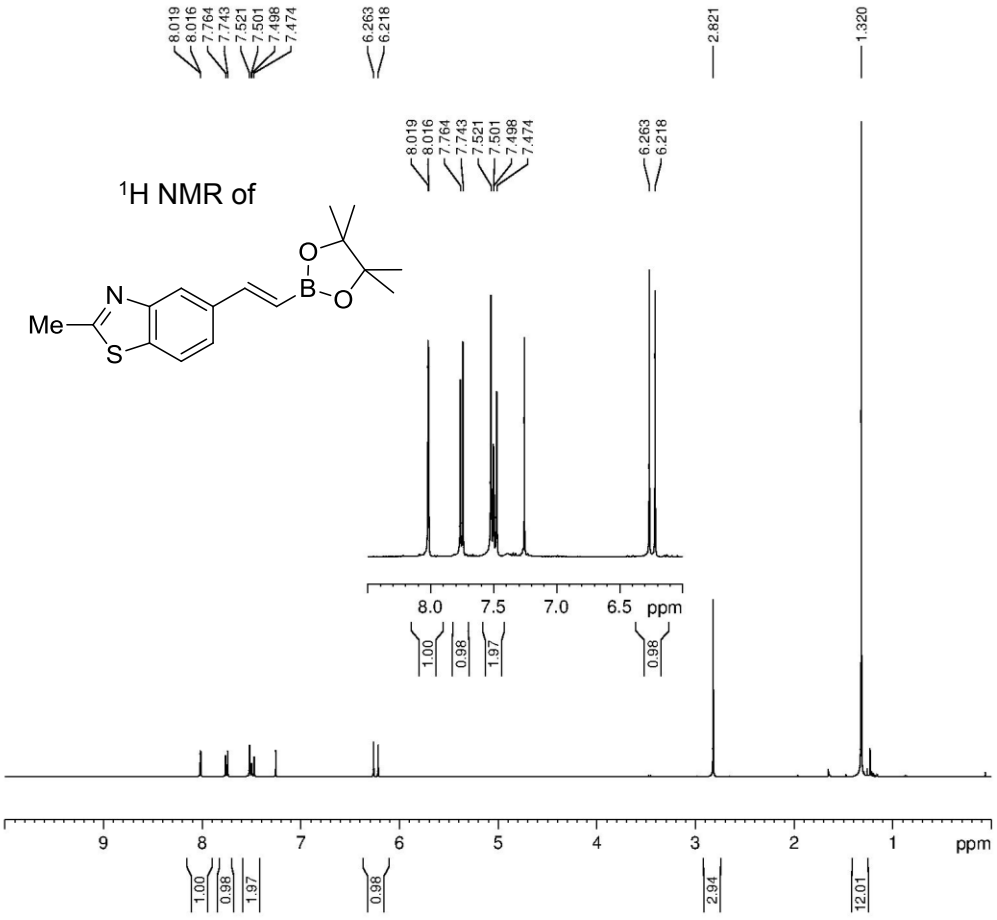

149.491
146.358
132.928
130.159
129.868
129.828
128.511
128.112
128.042
127.803
126.419
13C NMR of
BF3K
N
2s
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

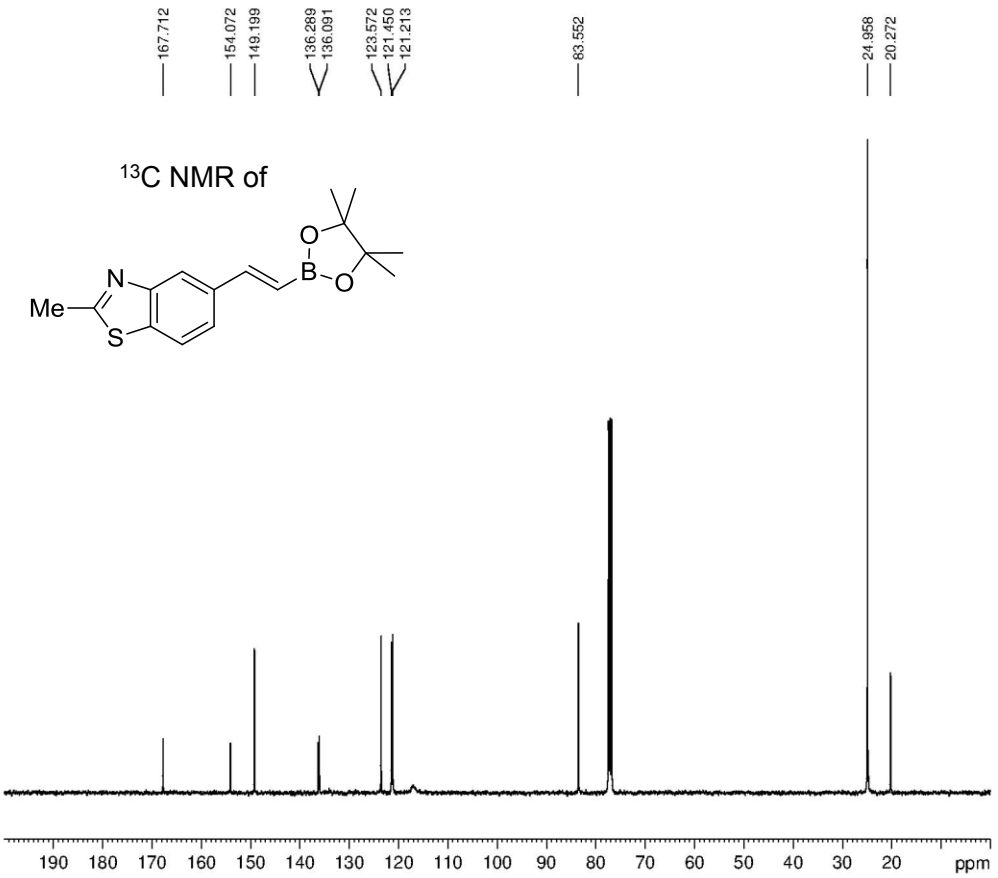




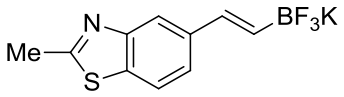

8.059
8.056
7.756
7.735
7.455
7.452
7.434
7.431
7.253
3.111
2.826
1H NMR of
N
Me
S
9
8
7
6
5
4
3
2
1
ppm
1.01
1.00
1.07
0.98
3.19


168.300
153.373
136.545
128.427
126.257
121.491
119.960
83.519
77.477
20.325
13C NMR of
N
Me
S
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm


8.019
8.016
7.764
7.743
7.521
7.501
7.498
7.474
6.263
6.218
2.821
1.320
^{1}H NMR of
Me
N
S
O
B
O
8.0
7.5
7.0
6.5
ppm
1.00
0.98
1.97
0.98
9
8
7
6
5
4
3
2
1
ppm
1.00
0.98
1.97
0.98
2.94
12.01

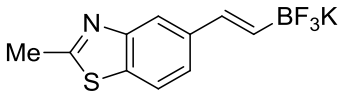

167.712
154.072
149.199
136.289
136.091
123.572
121.450
121.213
83.552
24.958
20.272
^{13}C NMR of
Me
N
S
O
B
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

^{1}H NMR of

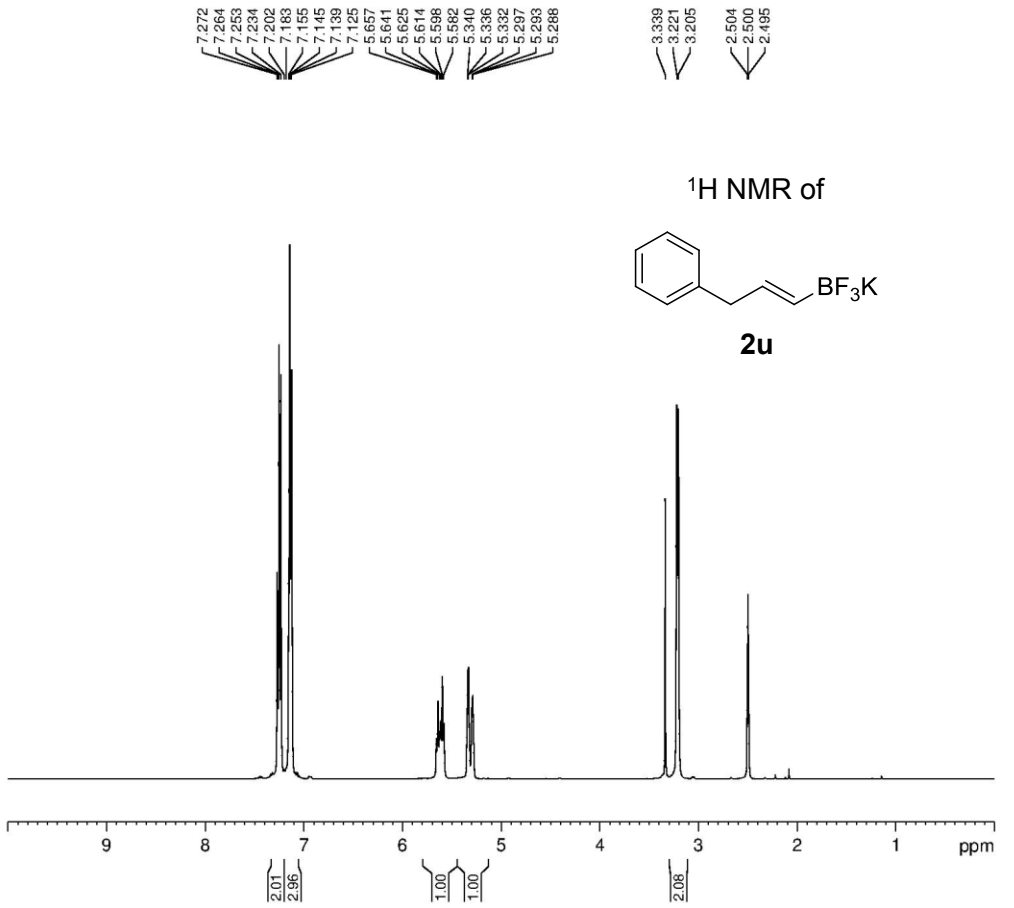


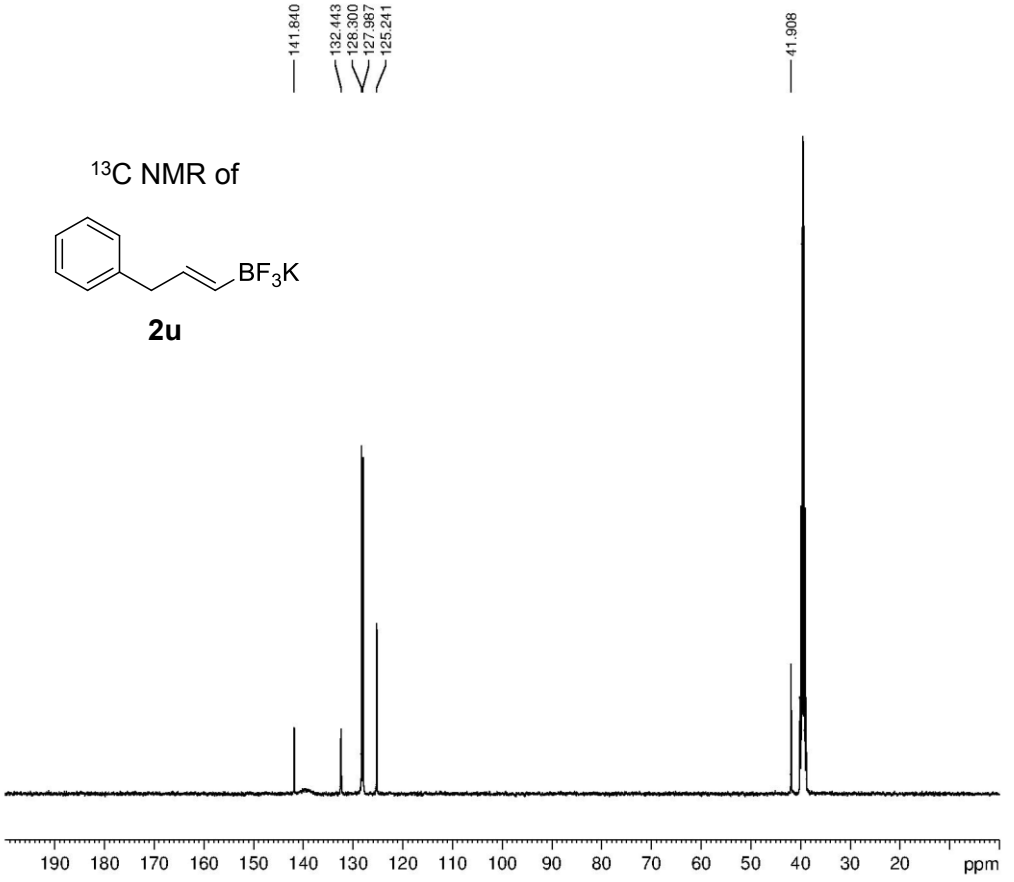
2t

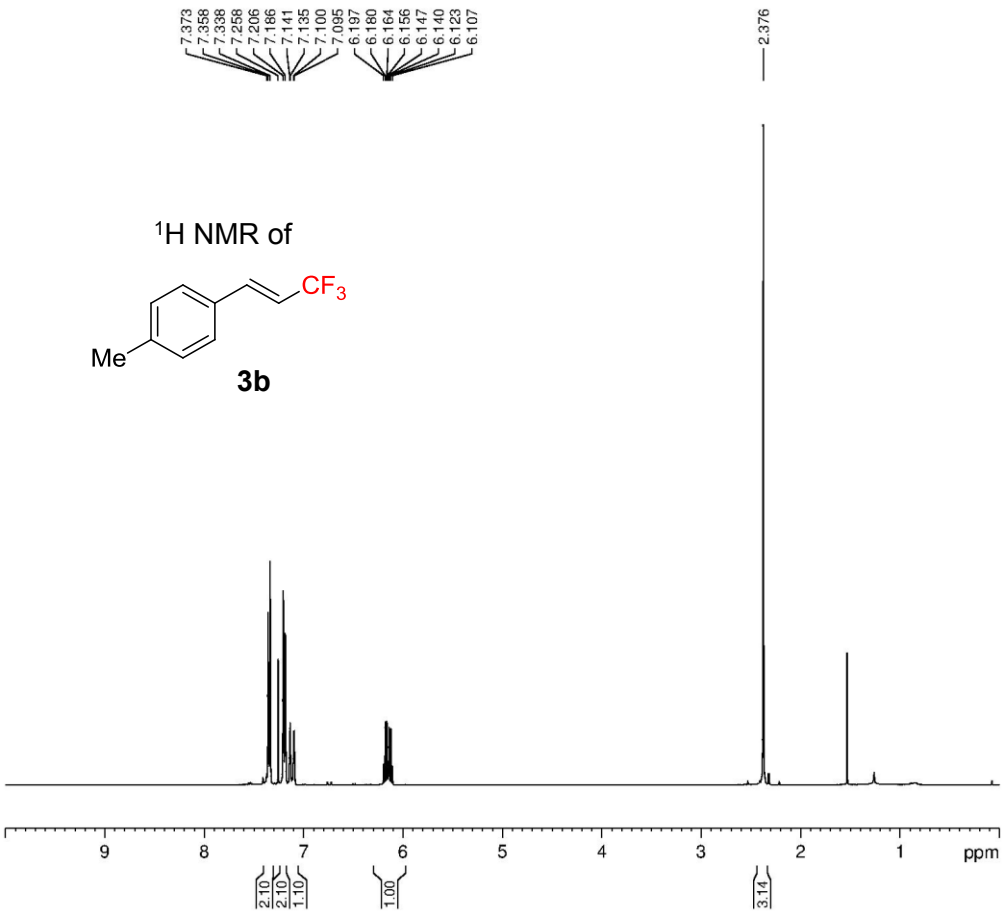
^{13}C NMR of

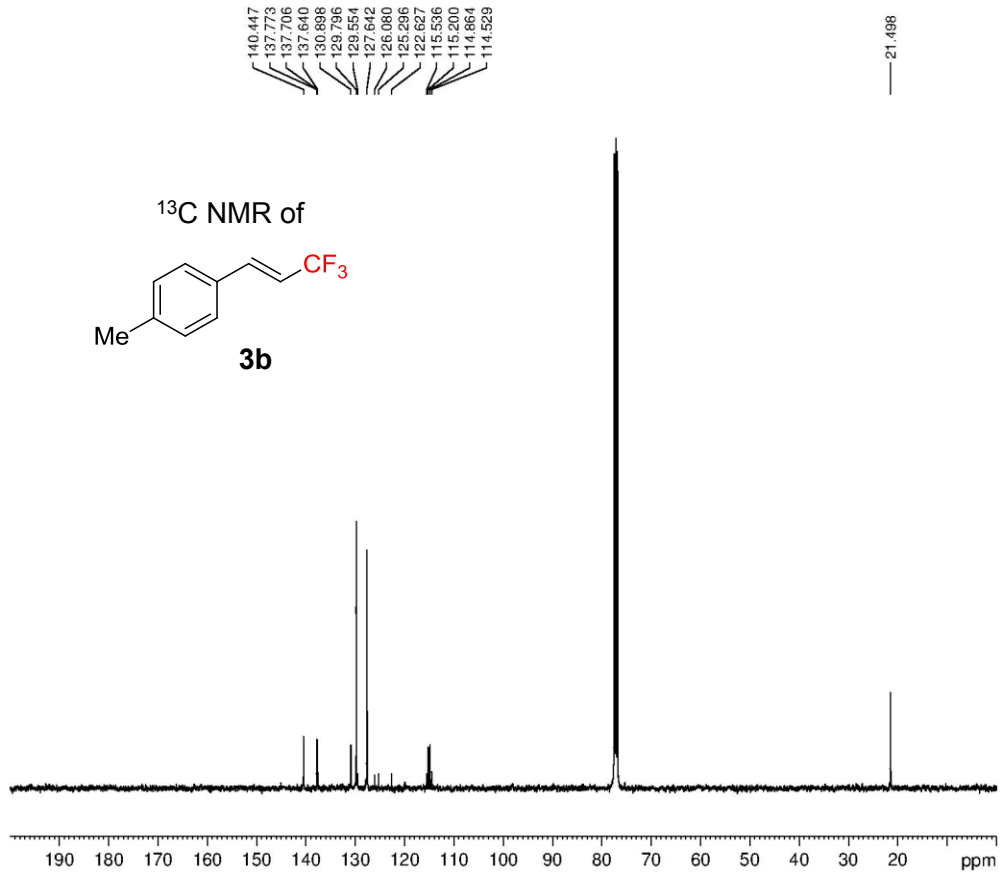


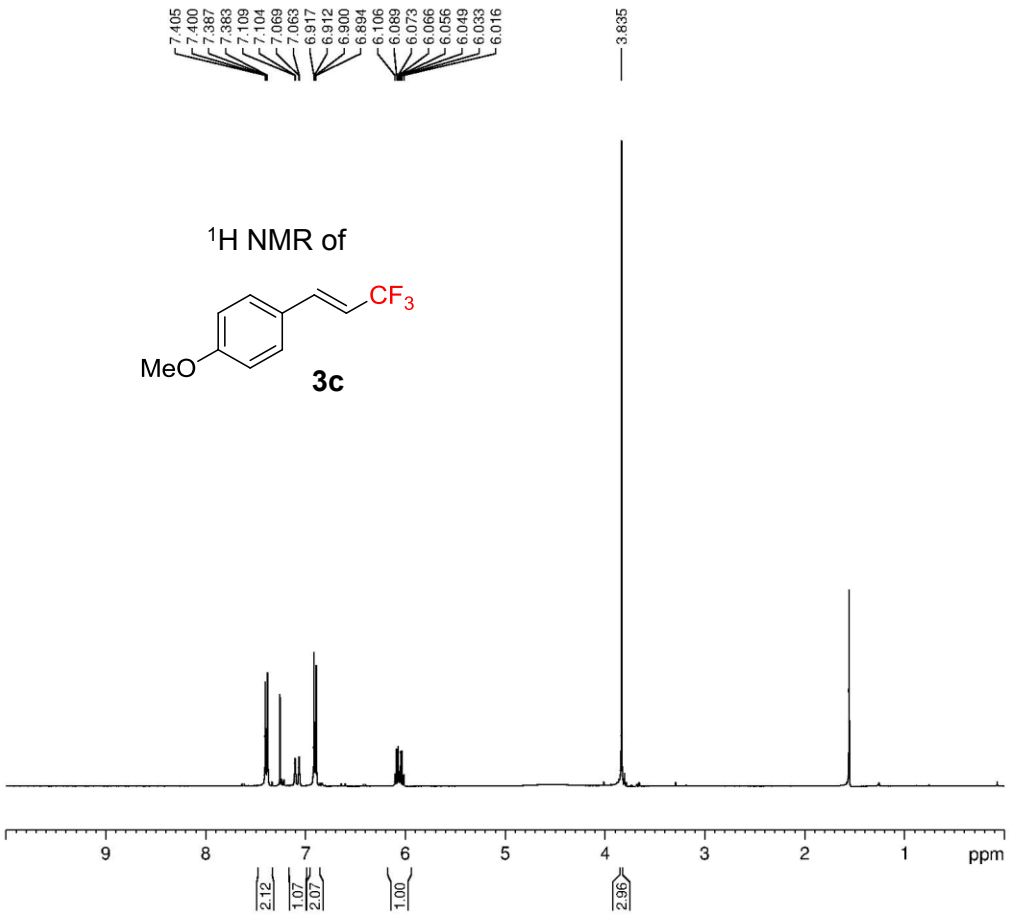
2t

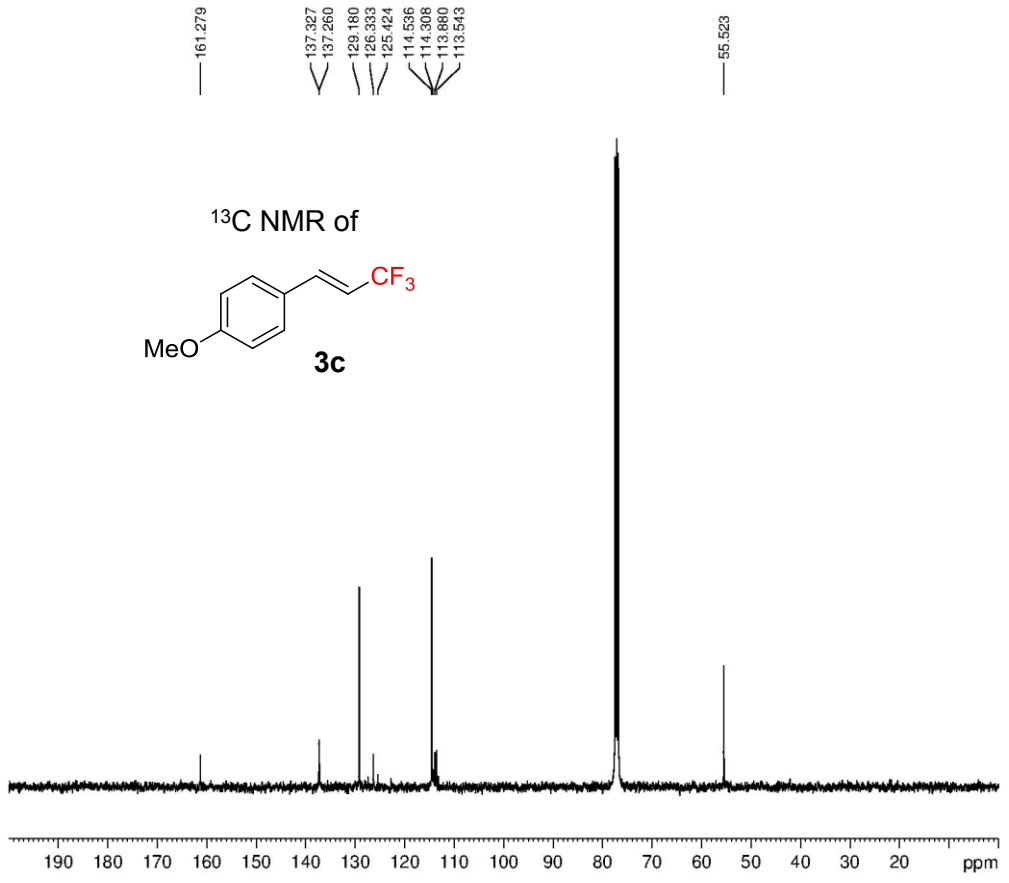

7.272
7.264
7.253
7.234
7.202
7.183
7.155
7.145
7.139
7.125
5.657
5.641
5.625
5.614
5.598
5.582
5.340
5.336
5.332
5.297
5.293
5.288
3.339
3.221
3.205
2.504
2.500
2.495
1H NMR of
BF3K
2u
9
8
7
6
5
4
3
2
1
ppm
2.01
2.96
1.00
1.00
2.08

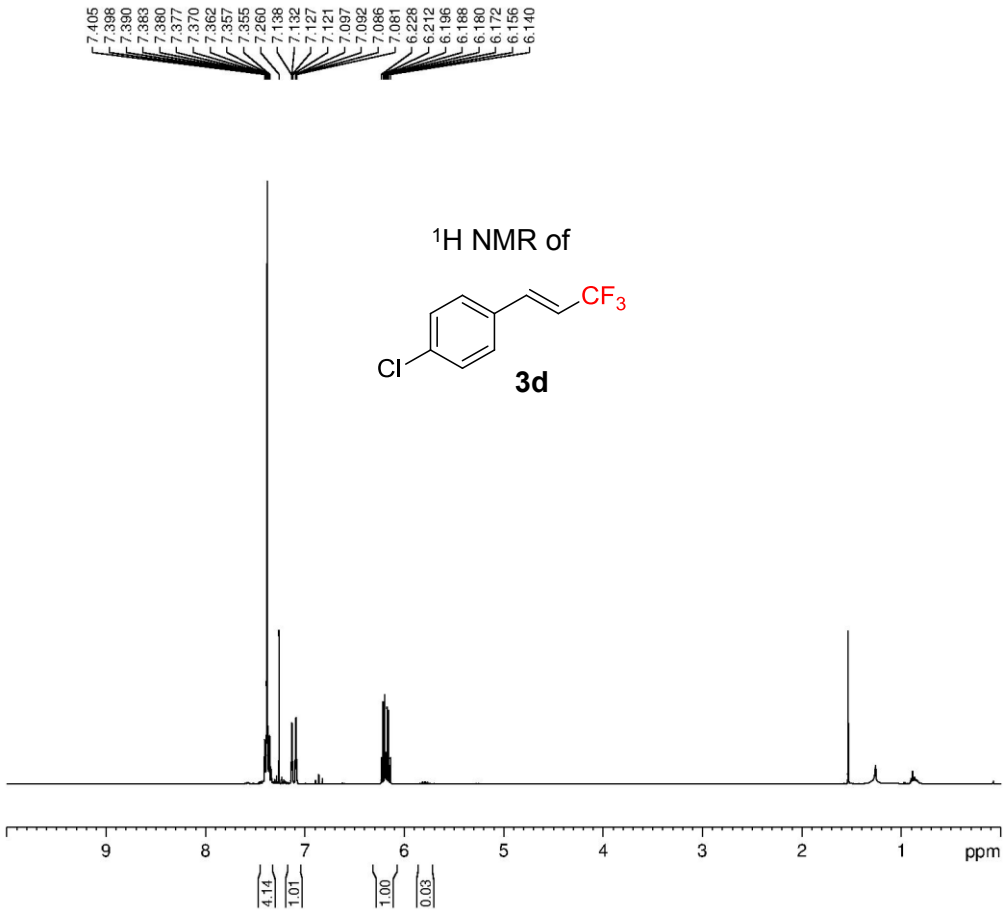

141.840
132.443
128.300
127.987
125.241
41.908
13C NMR of
BF3K
2u
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

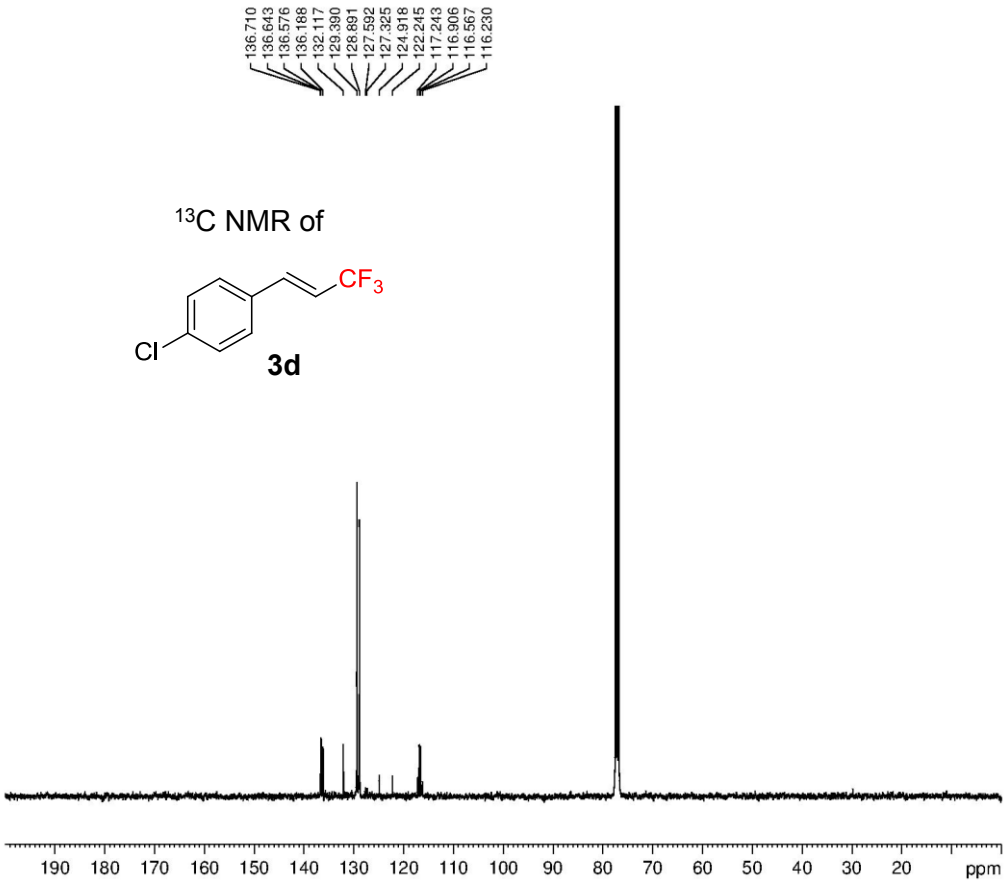

7.373
7.358
7.338
7.258
7.206
7.186
7.141
7.135
7.100
7.095
6.197
6.180
6.164
6.156
6.147
6.140
6.123
6.107
2.376
^{1}H NMR of
CF$_3$
Me
3b
9
8
7
6
5
4
3
2
1
ppm
2.10
2.10
1.10
1.00
3.14

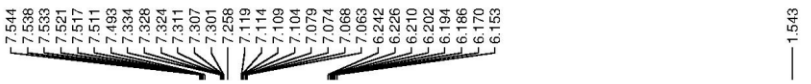

140.447
137.773
137.706
137.640
130.898
129.796
129.554
127.642
126.080
125.296
122.627
115.536
115.200
114.864
114.529
21.498
^{13}C NMR of
CF$_3$
Me
3b
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



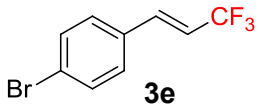



7.405
7.398
7.390
7.383
7.380
7.377
7.370
7.362
7.357
7.355
7.260
7.138
7.132
7.127
7.121
7.097
7.092
7.086
7.081
6.228
6.212
6.196
6.188
6.180
6.172
6.156
6.140
1H NMR of
CF3
Cl
3d
9
8
7
6
5
4
3
2
1
ppm
4.14
1.01
1.00
0.03

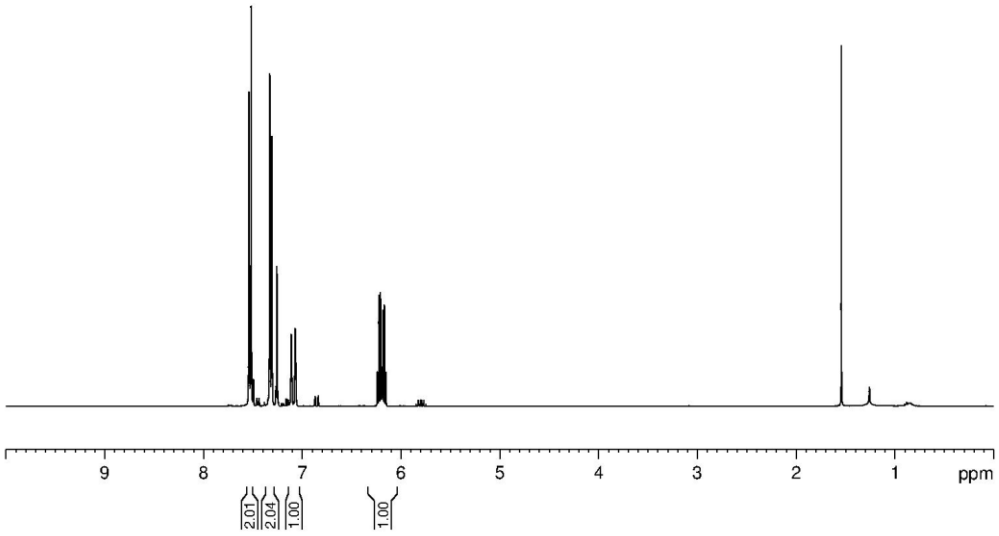

136.710
136.643
136.576
136.188
132.117
129.390
128.891
127.592
127.325
124.918
122.245
117.243
116.906
116.567
116.230
13C NMR of
CF3
Cl
3d
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

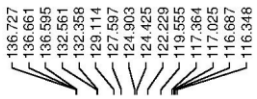


^{1}H NMR of

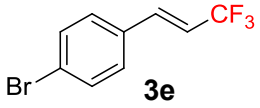


3e

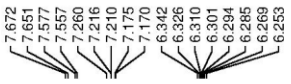




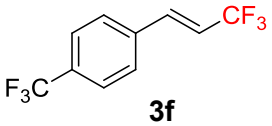
^{13}C NMR of



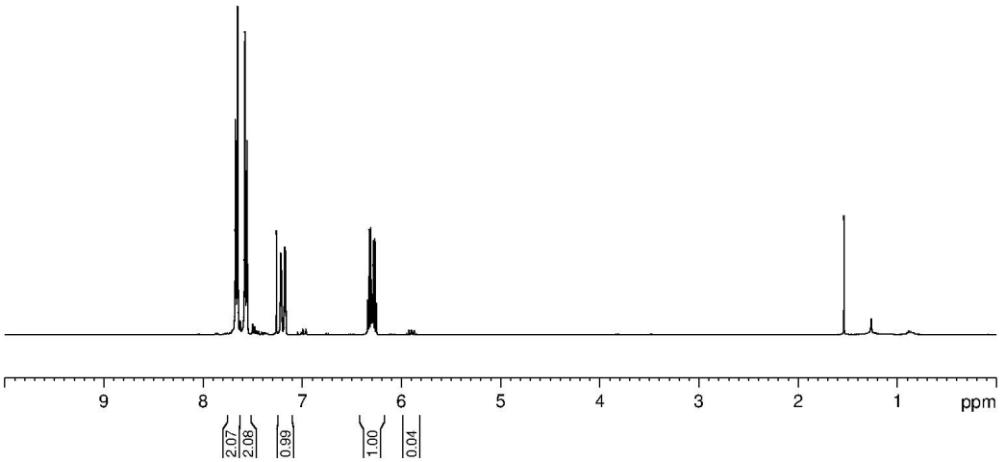
3e

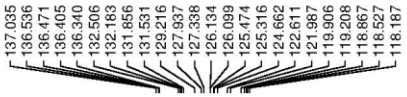


^{1}H NMR of

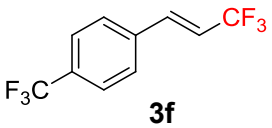


3f

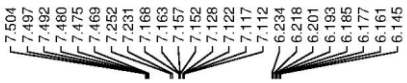




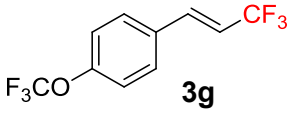
^{13}C NMR of



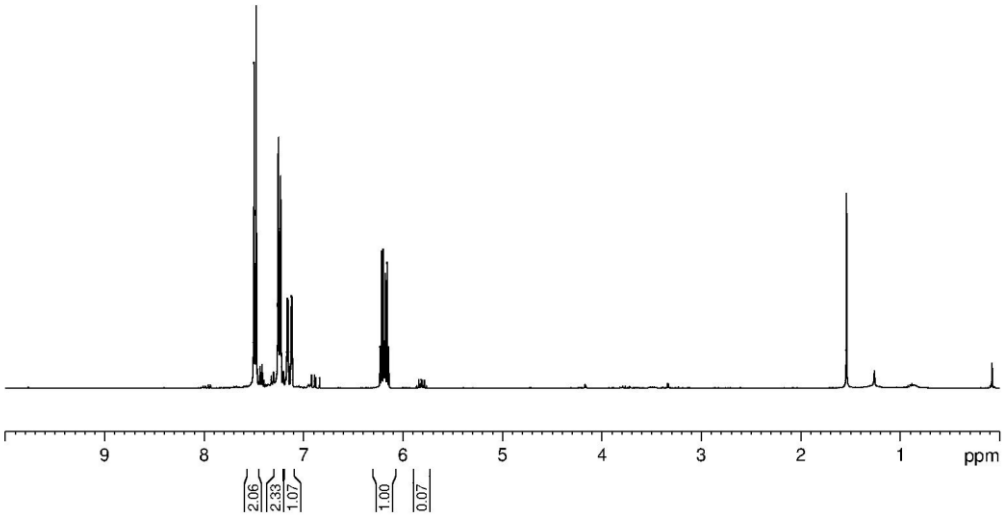
3f

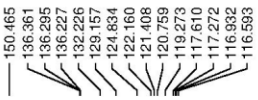


^{1}H NMR of

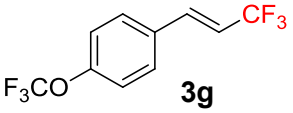


3g



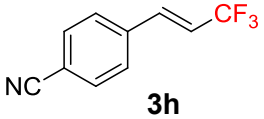


^{13}C NMR of

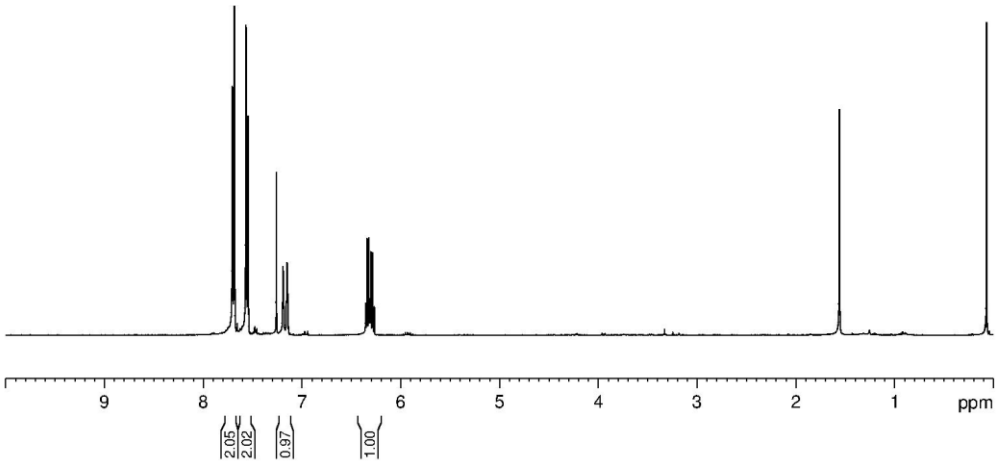


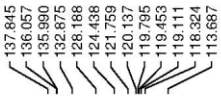
3g

^{1}H NMR of

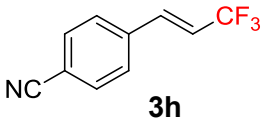


3h

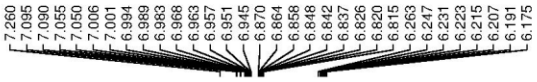




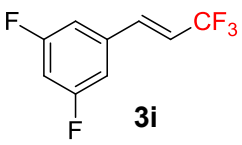
^{13}C NMR of



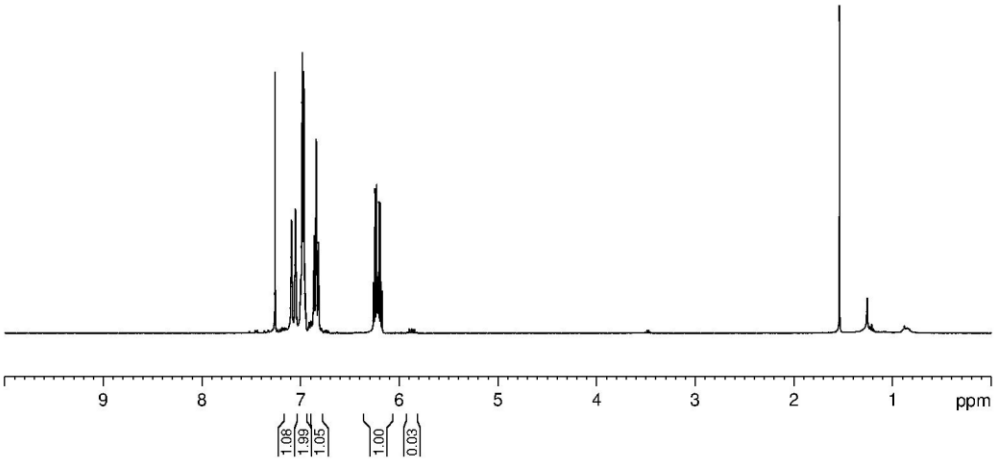
3h

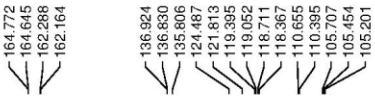


^{1}H NMR of

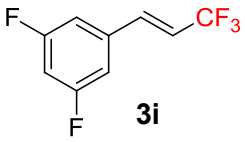


3i

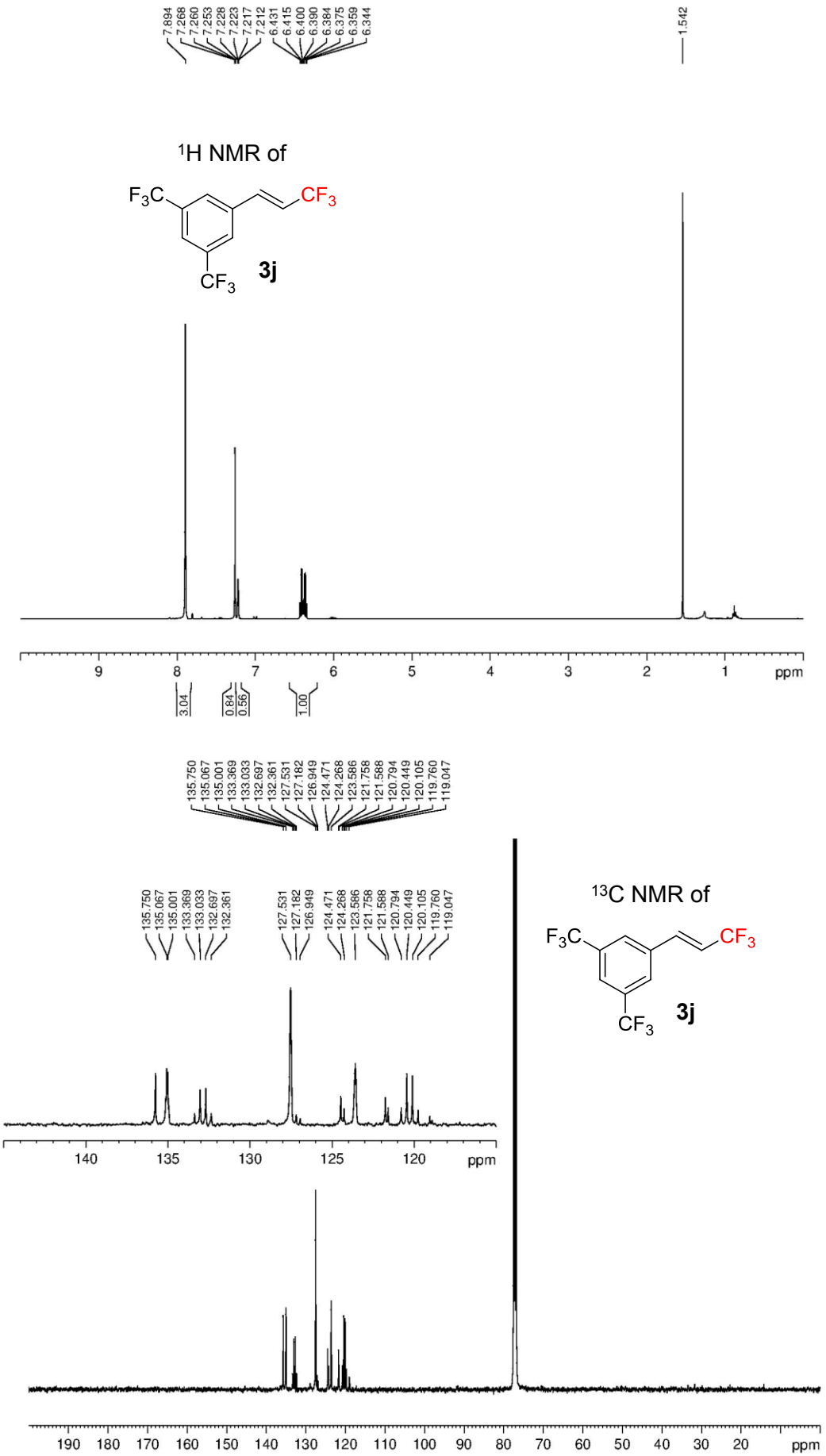


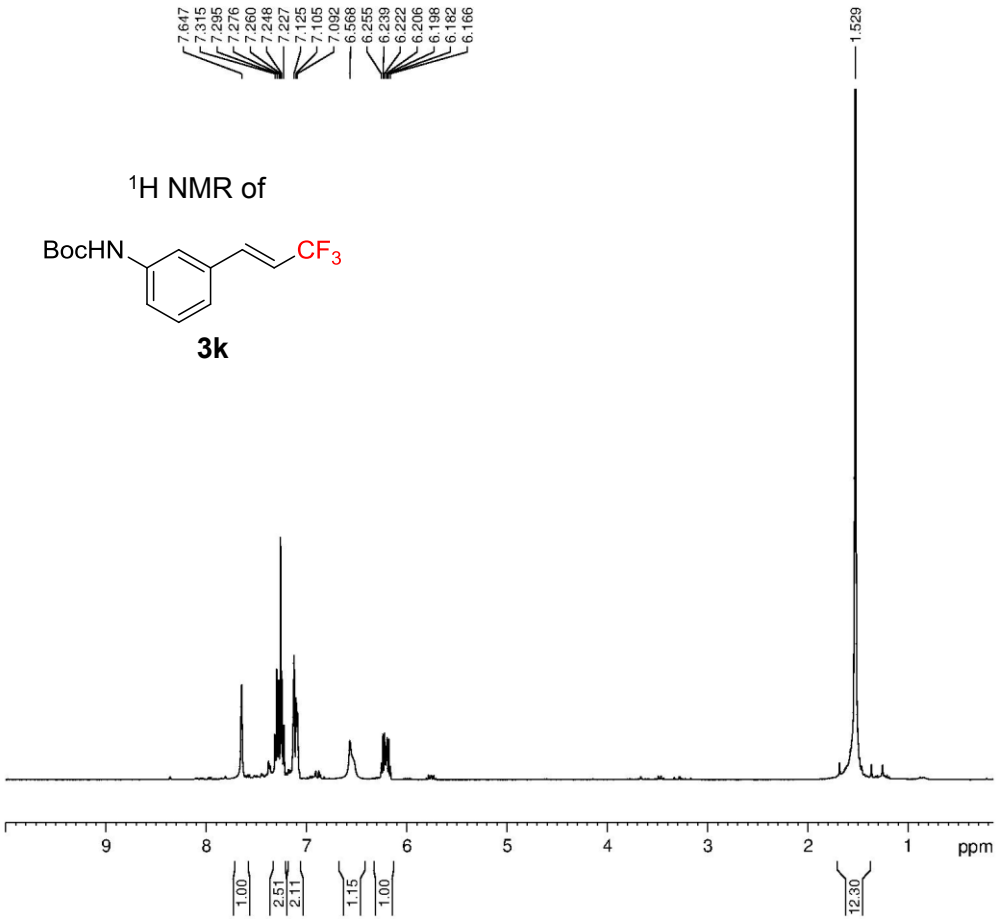


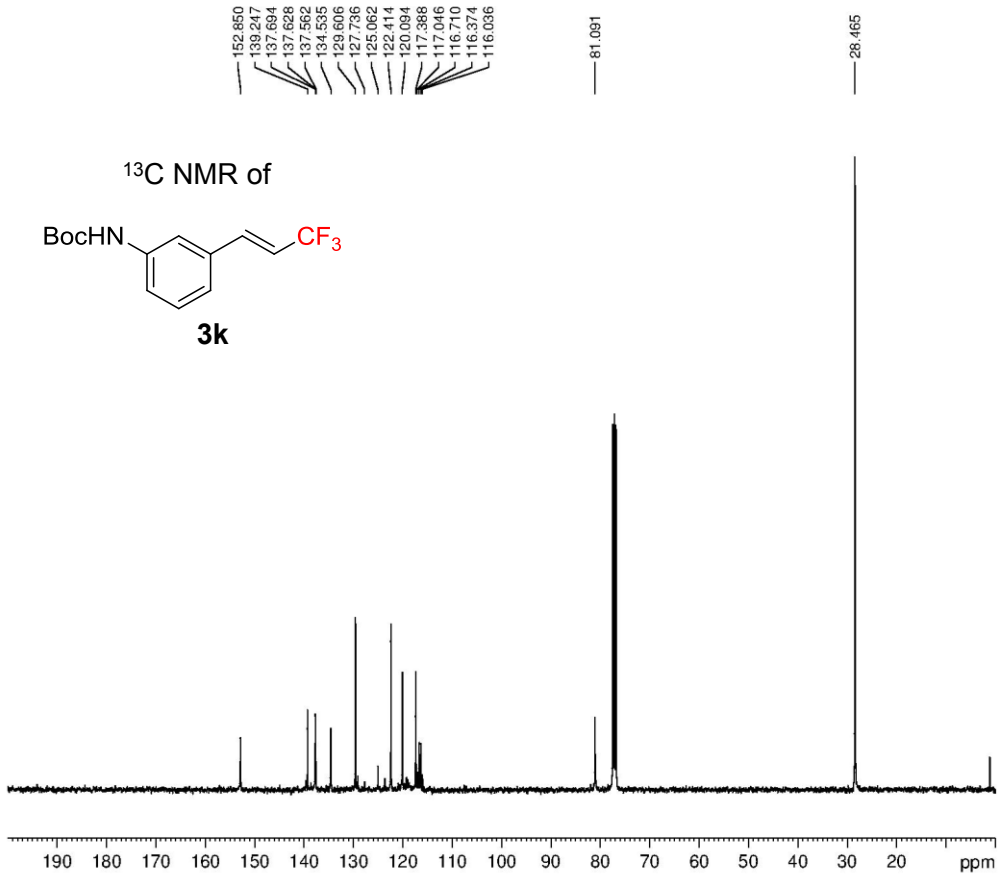
^{13}C NMR of

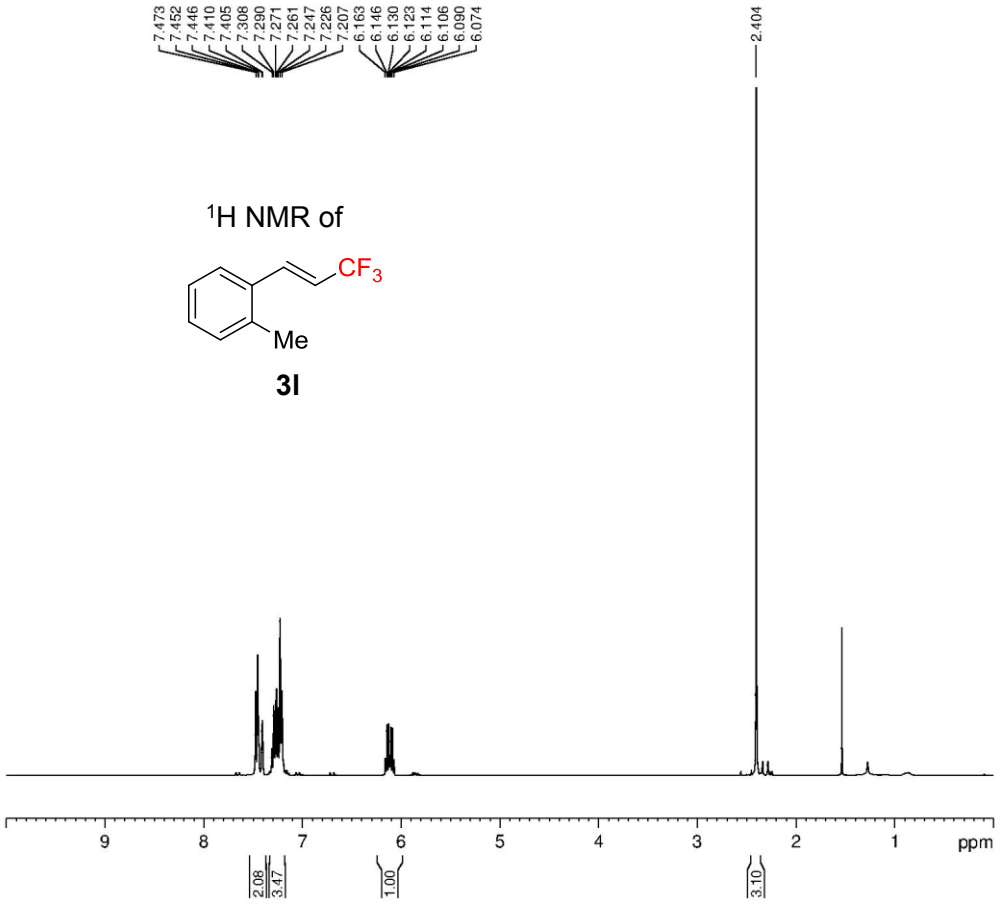


3i



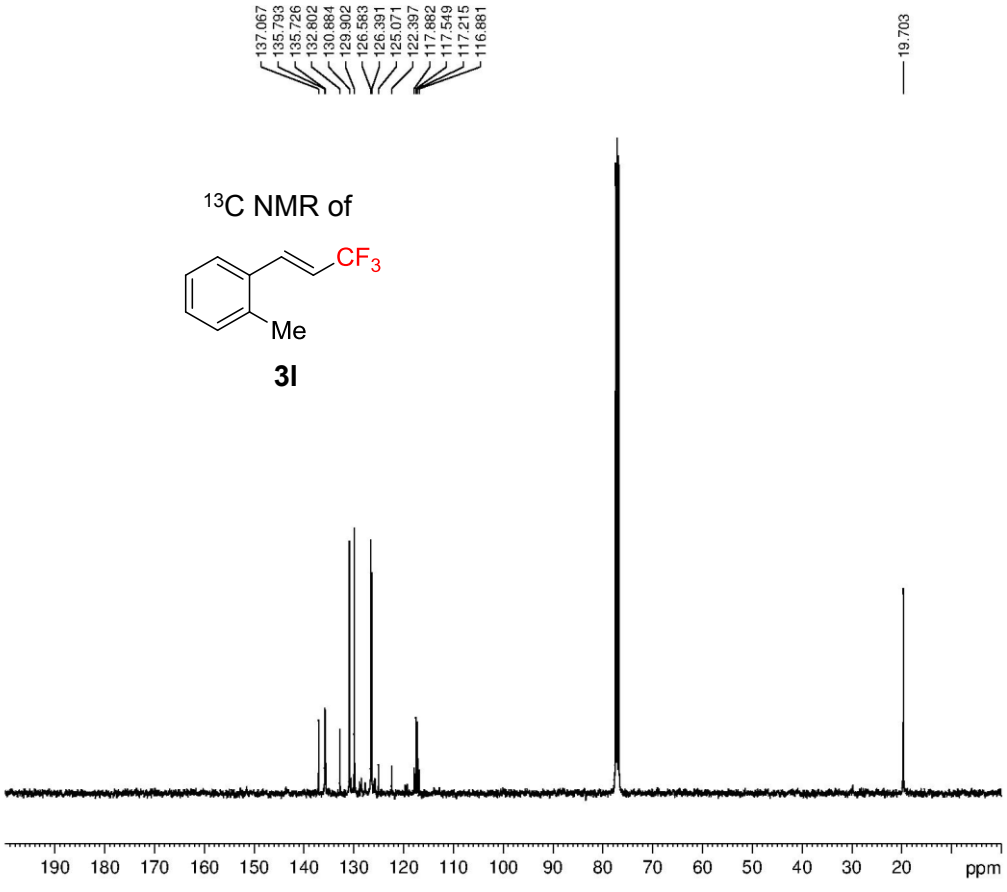






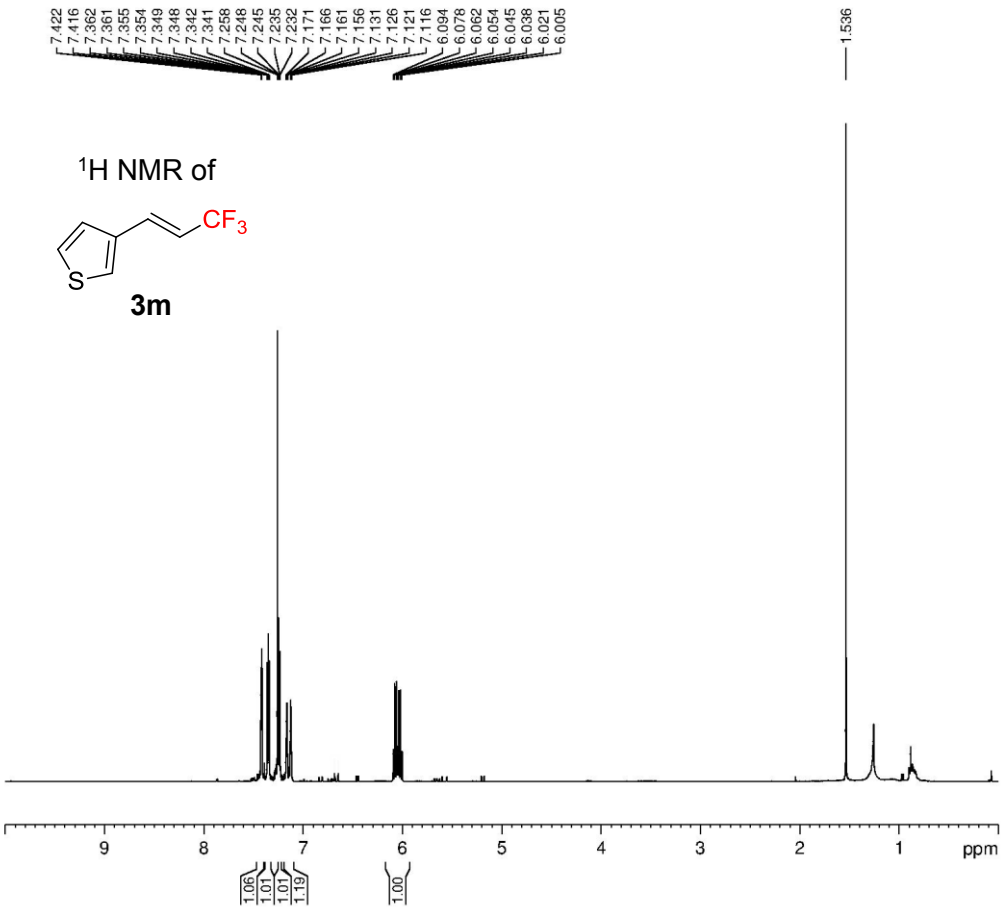
^{1}H NMR of

3l



^{13}C NMR of

3l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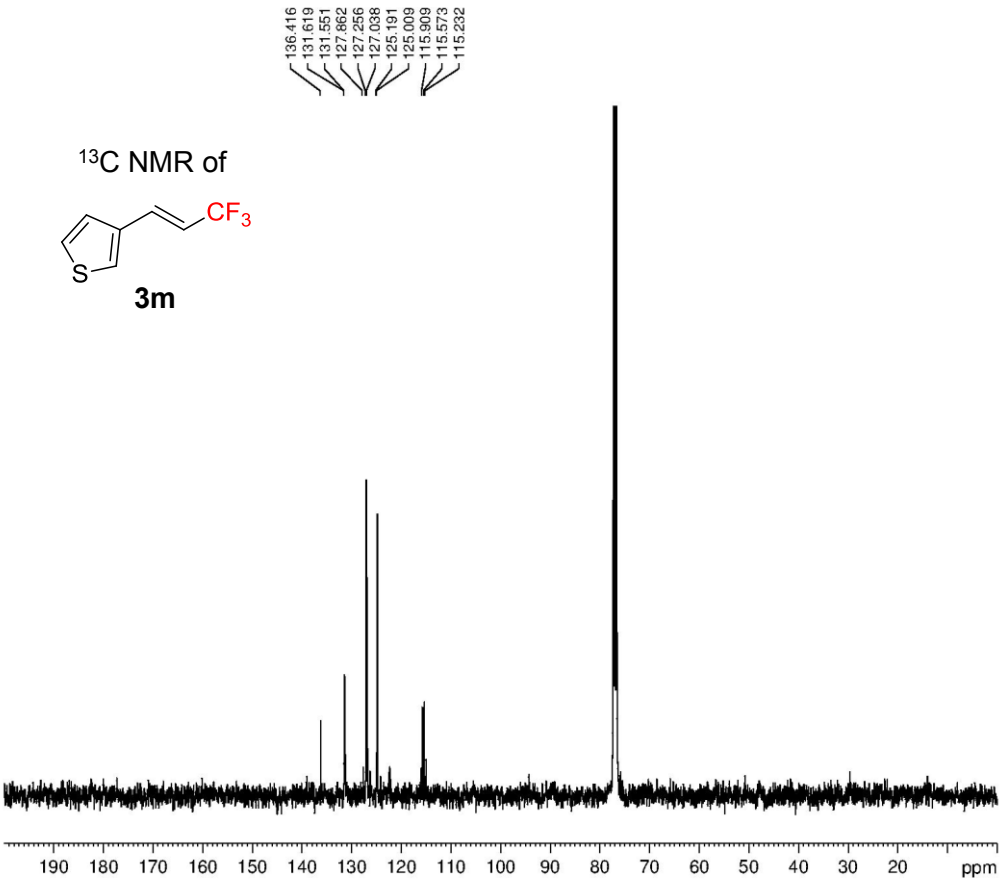
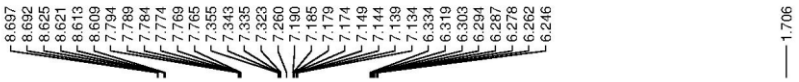
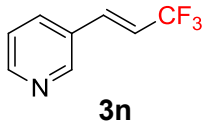
7.416
7.362
7.361
7.355
7.354
7.349
7.348
7.342
7.341
7.258
7.248
7.245
7.235
7.232
7.171
7.166
7.161
7.156
7.131
7.126
7.121
7.116
6.094
6.078
6.062
6.054
6.045
6.038
6.021
6.005
1.536
1H NMR of
CF3
S
3m
9
8
7
6
5
4
3
2
1
ppm
1.06
1.01
1.01
1.19
1.00

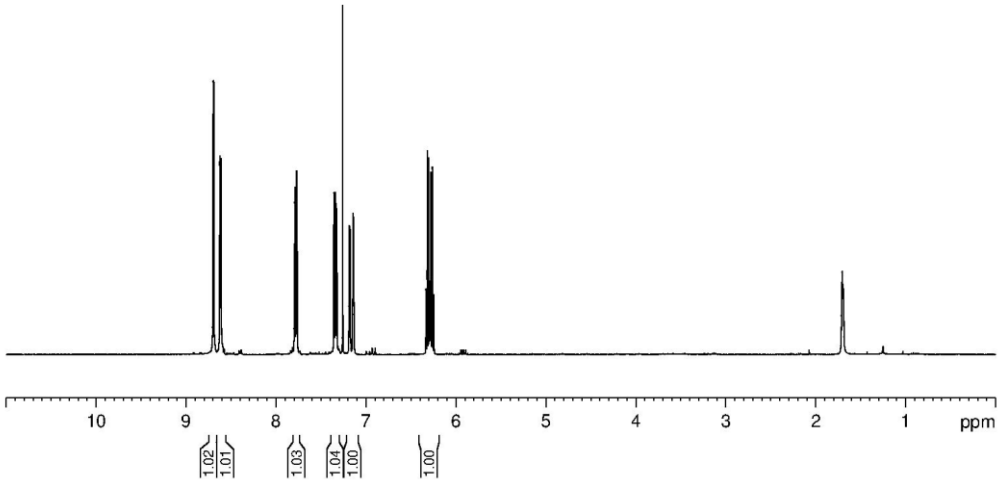

136.416
131.619
131.551
127.862
127.256
127.038
125.191
125.009
115.909
115.573
115.232
13C NMR of
CF3
S
3m
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

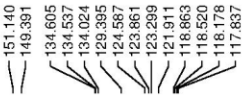


^{1}H NMR of

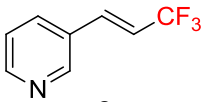


3n

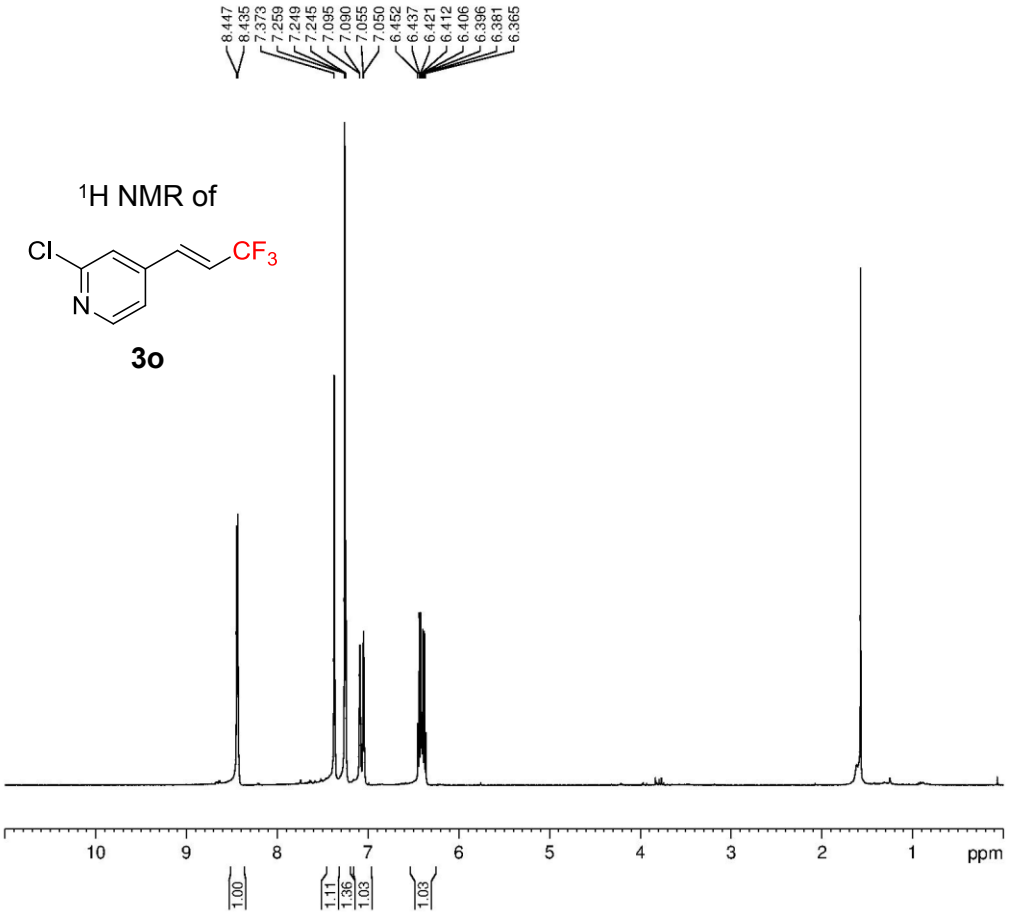




^{13}C NMR of



3n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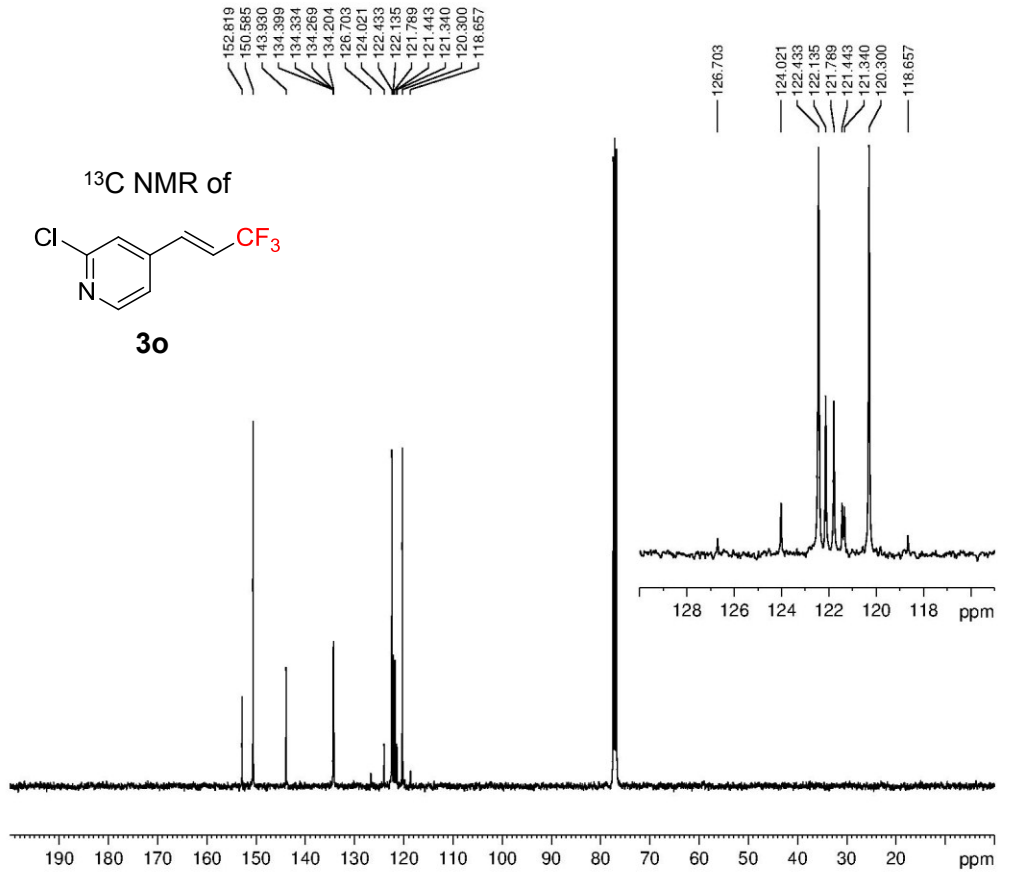
8.435
7.373
7.259
7.249
7.245
7.095
7.090
7.055
7.050
6.452
6.437
6.421
6.412
6.406
6.396
6.381
6.365
1H NMR of
Cl
CF3
N
3o
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.11
1.36
1.03
1.03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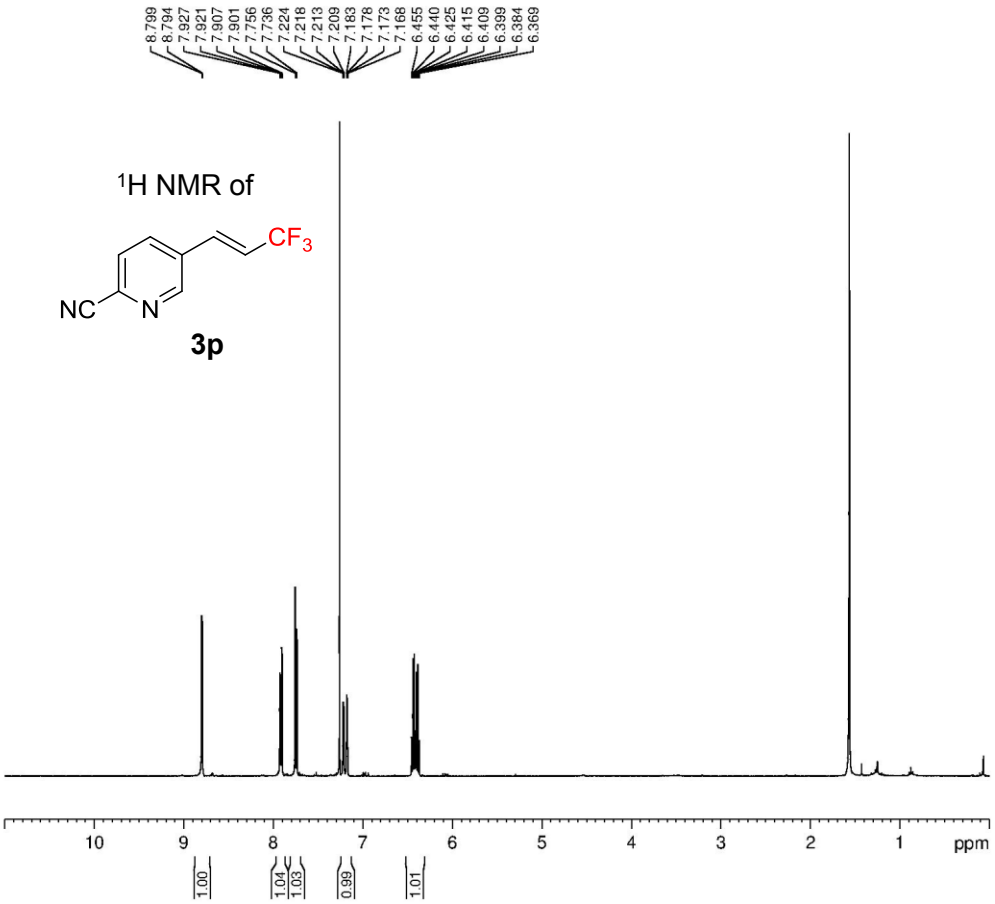
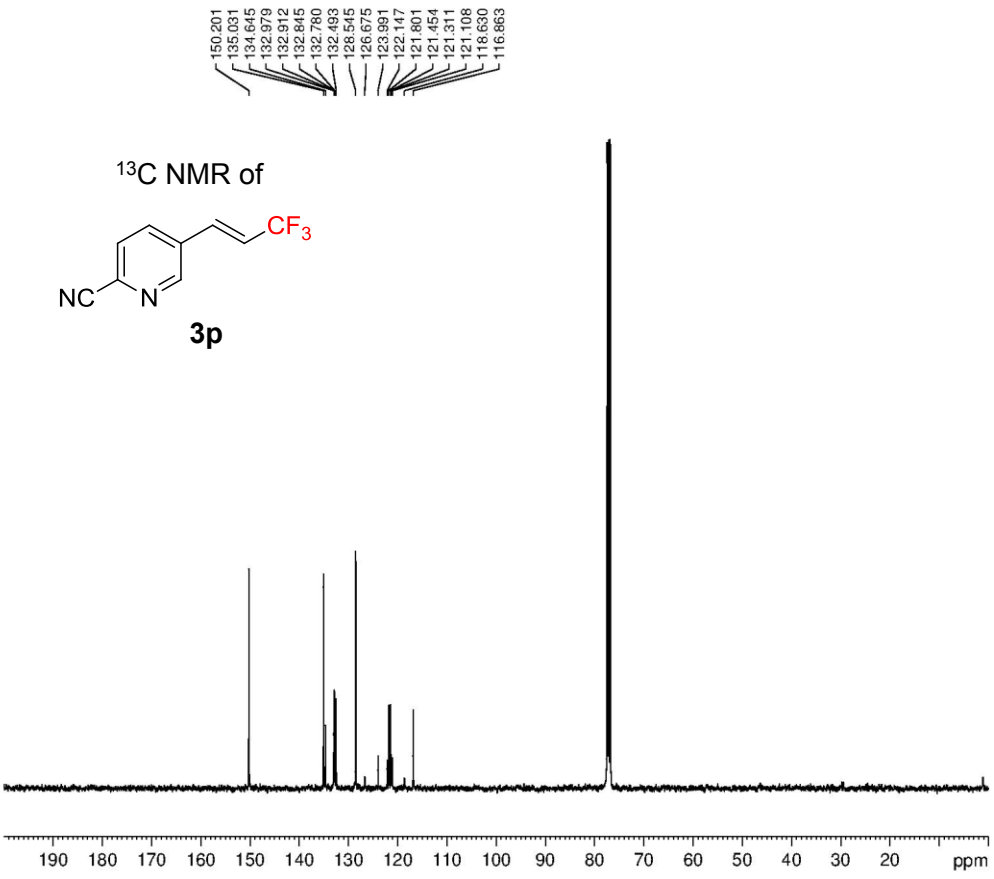
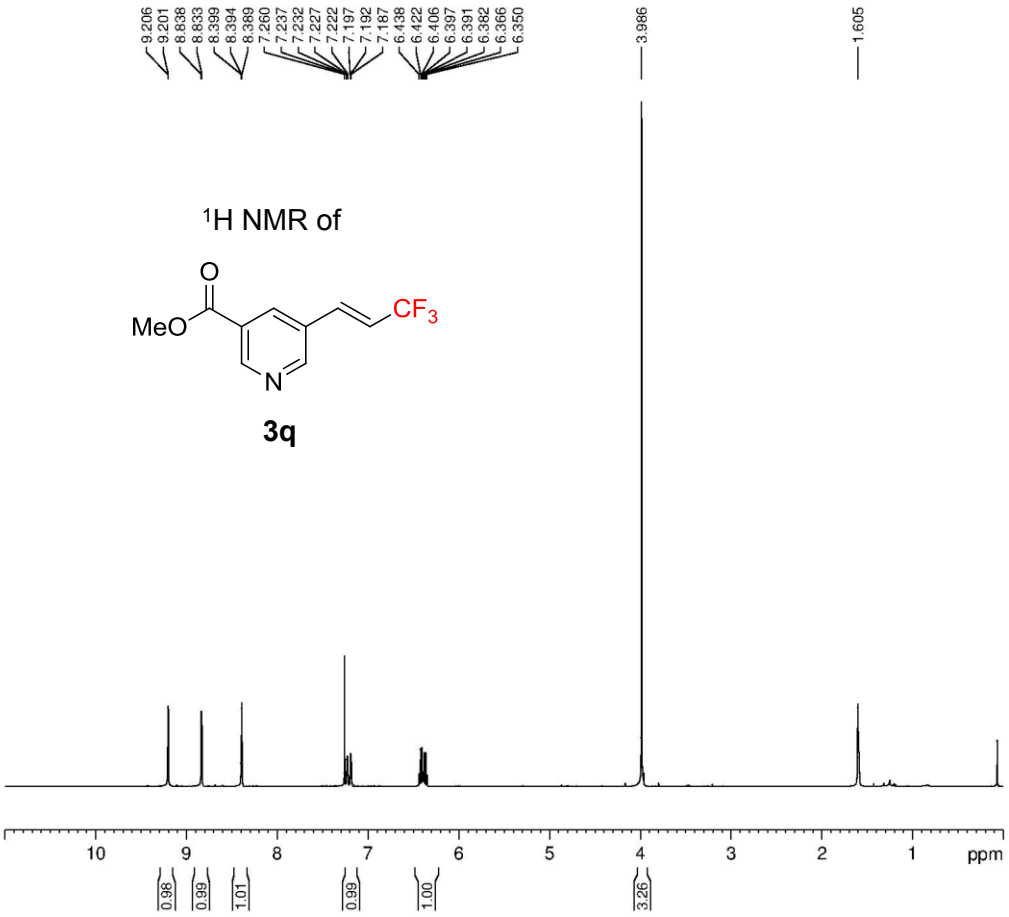
150.585
143.930
134.399
134.334
134.269
134.204
126.703
124.021
122.433
122.135
121.789
121.443
121.340
120.300
118.657
13C NMR of
Cl
CF3
N
3o
126.703
124.021
122.433
122.135
121.789
121.443
121.340
120.300
118.657
128
126
124
122
120
118
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

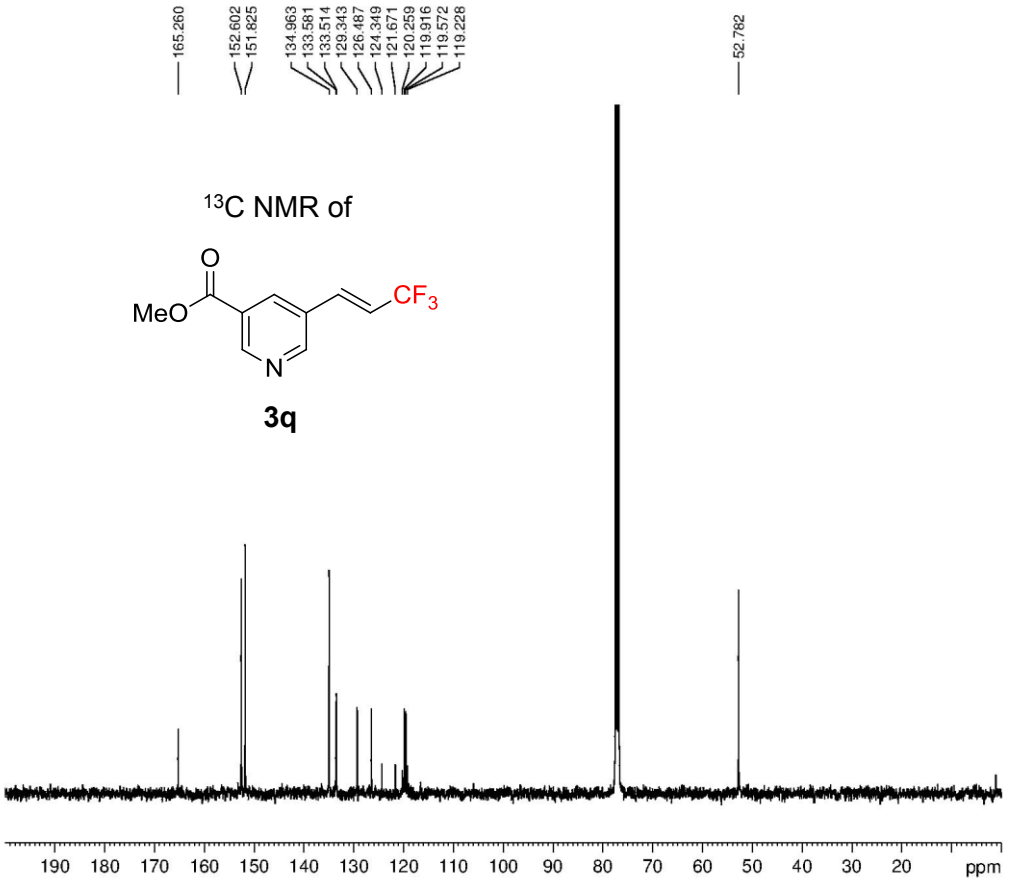

8.799
8.794
7.927
7.921
7.907
7.901
7.756
7.736
7.224
7.218
7.213
7.209
7.183
7.178
7.173
7.168
6.455
6.440
6.425
6.415
6.409
6.399
6.384
6.369
1H NMR of
CF3
NC
N
3p
10
9
8
7
6
5
4
3
2
1
ppm
1.00
1.04
1.03
0.99
1.01


150.201
135.031
134.645
132.979
132.912
132.845
132.780
132.493
128.545
126.675
123.991
122.147
121.801
121.454
121.311
121.108
118.630
116.863
13C NMR of
CF3
NC
N
3p
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm



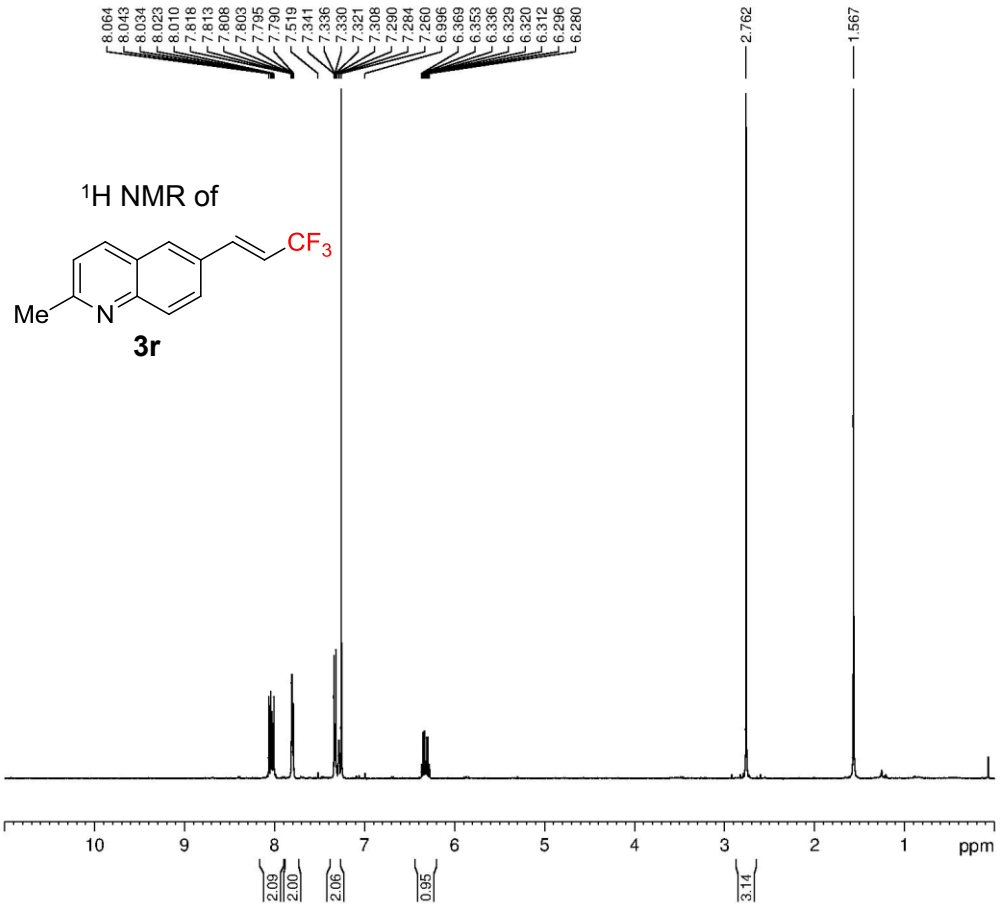
^{1}H NMR of

3q



^{13}C NMR of

3q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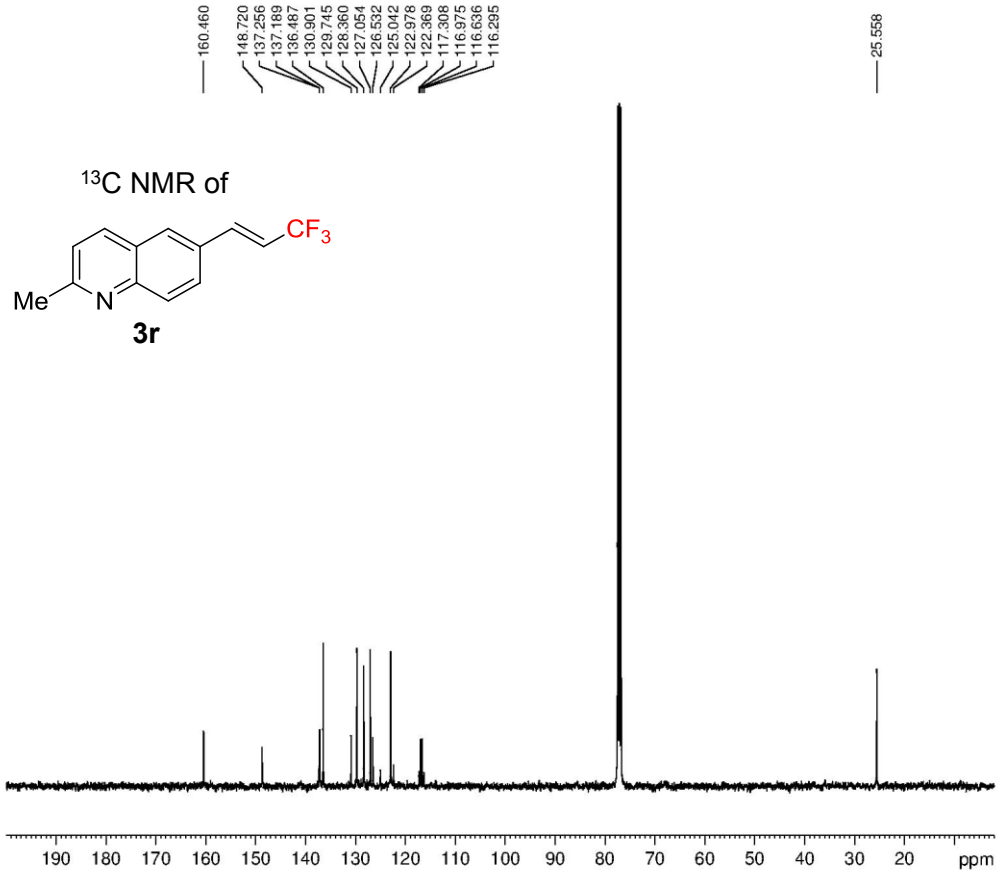
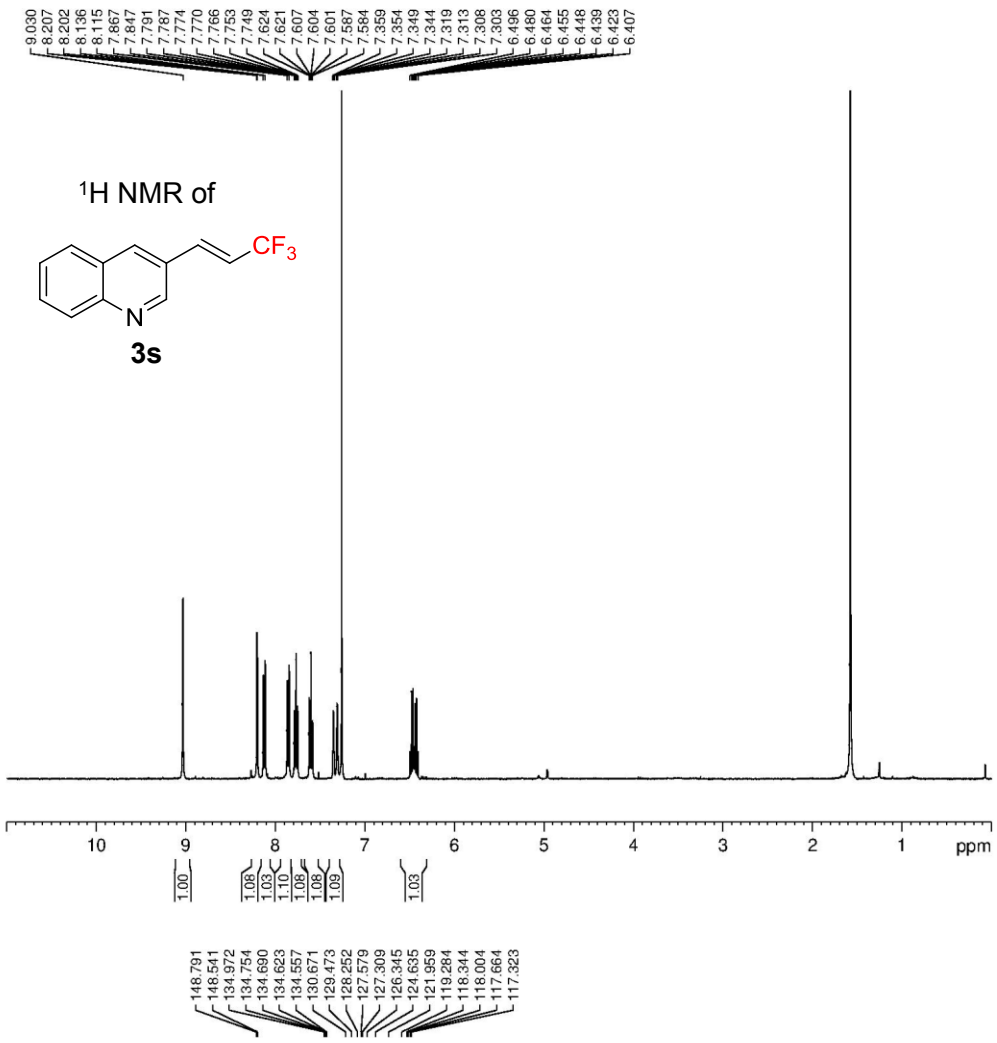
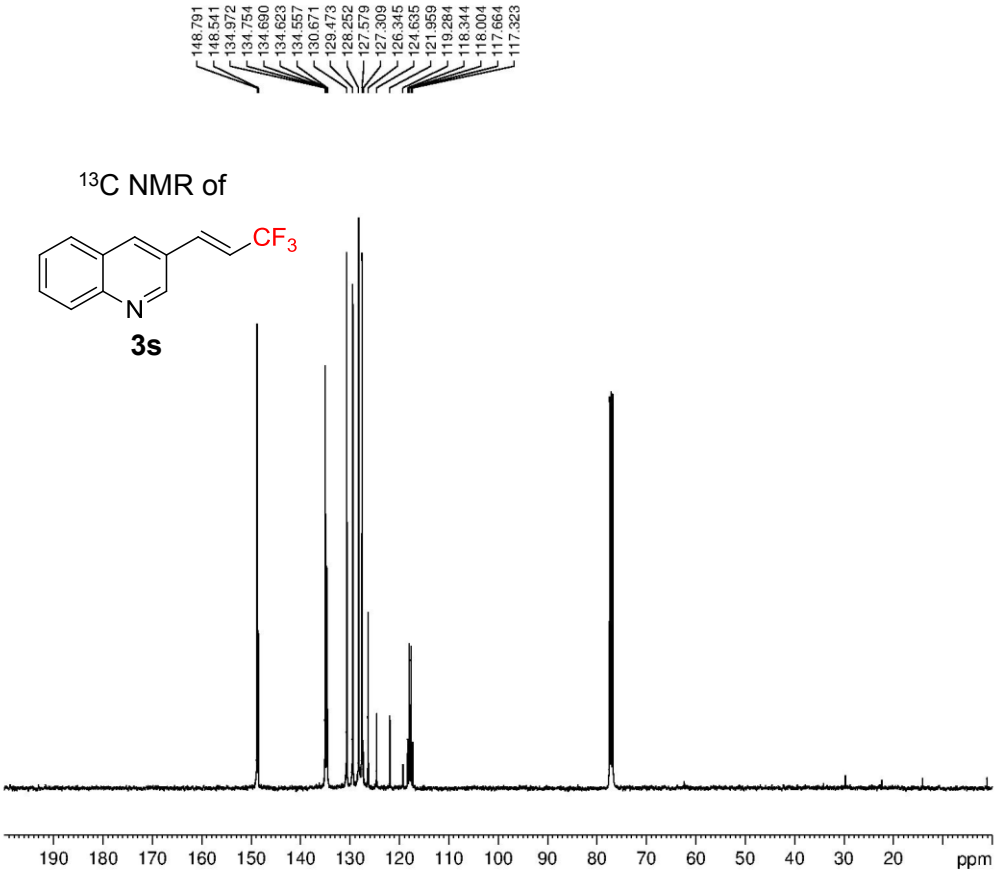
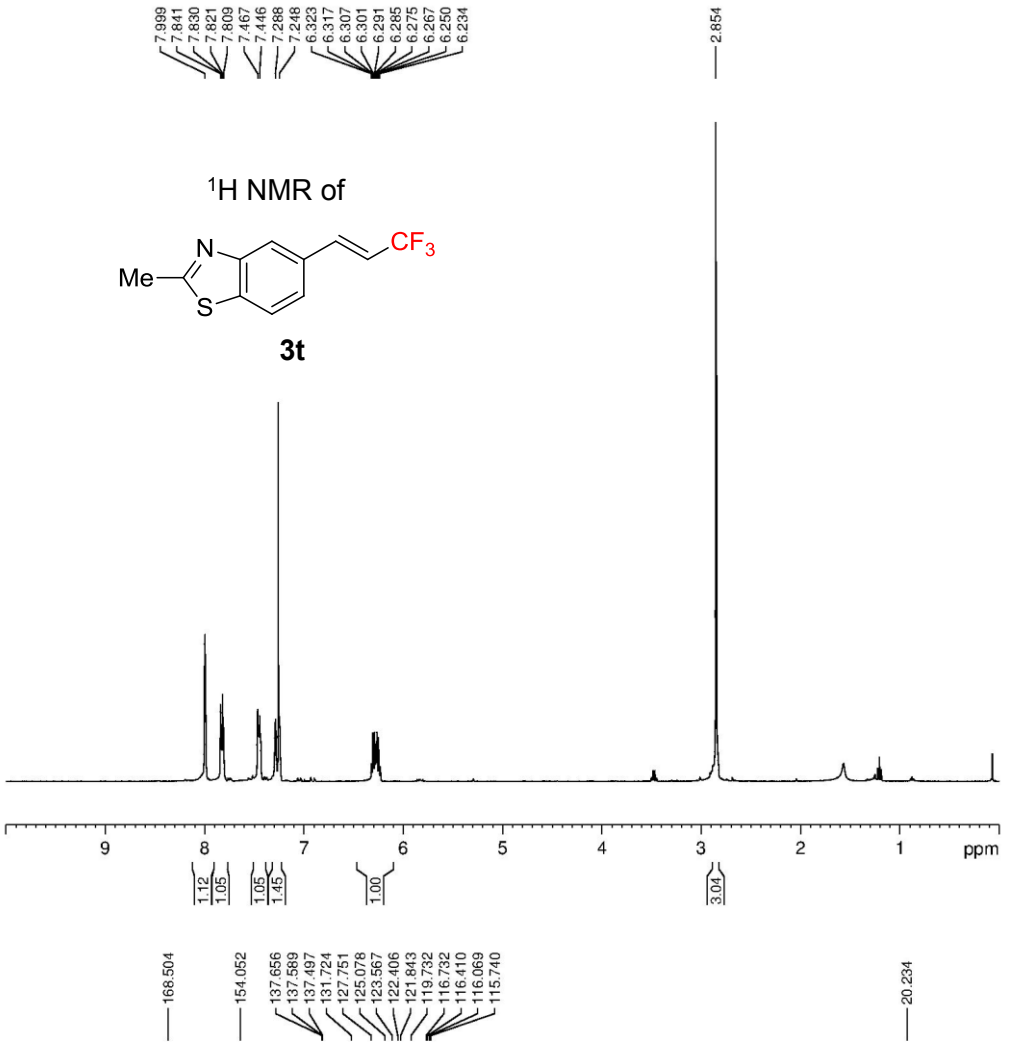
8.034
8.023
8.010
7.818
7.813
7.808
7.803
7.795
7.790
7.519
7.341
7.336
7.330
7.321
7.308
7.290
7.284
7.260
6.996
6.369
6.353
6.336
6.329
6.320
6.312
6.296
6.280
2.762
1.567
1H NMR of
CF3
Me
N
3r
10
9
8
7
6
5
4
3
2
1
ppm
2.09
2.00
2.06
0.95
3.14


160.460
148.720
137.256
137.189
136.487
130.901
129.745
128.360
127.054
126.532
125.042
122.978
122.369
117.308
116.975
116.636
116.295
25.558
13C NMR of
CF3
Me
N
3r
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
ppm

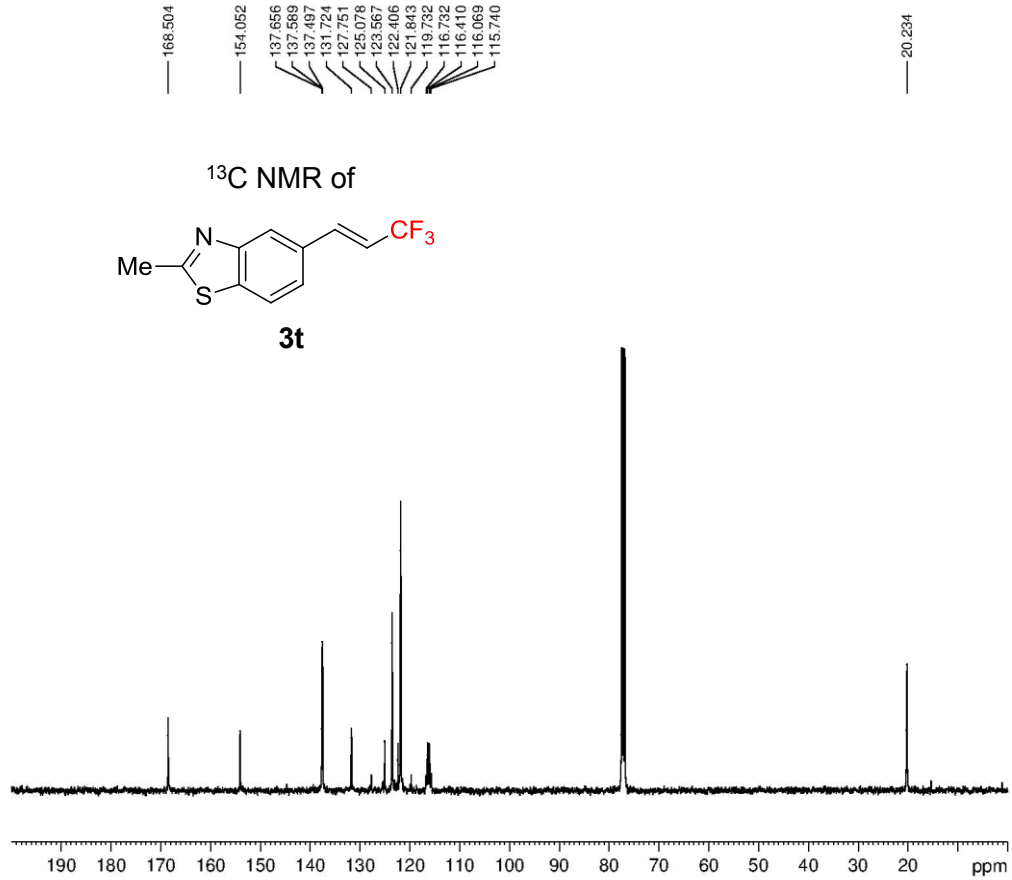






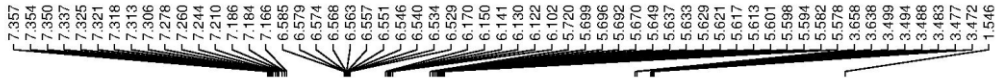
^{1}H NMR of

3t

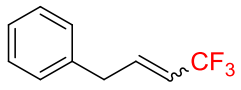


^{13}C NMR of

3t

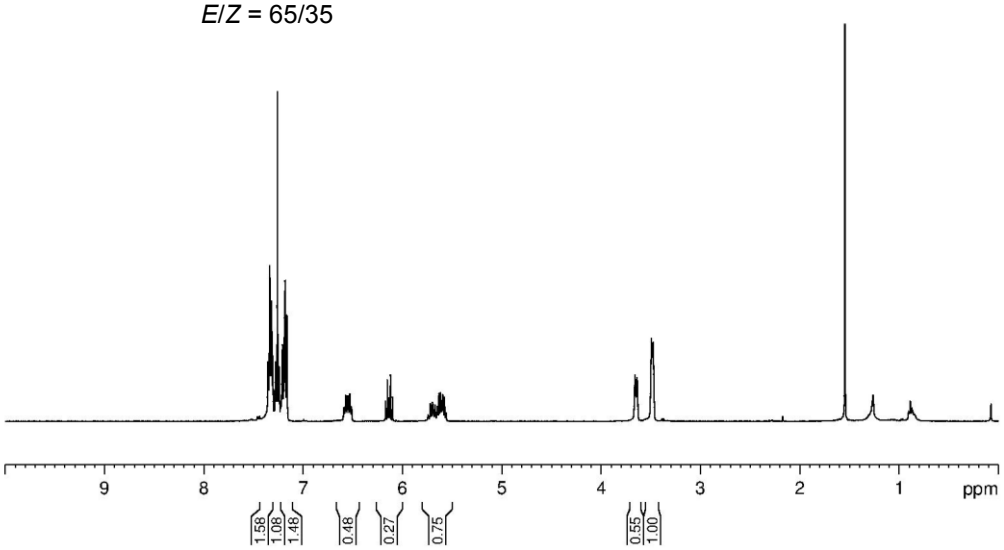


^{1}H NMR of

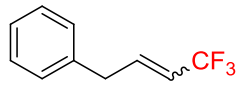


3u

E/*Z* = 65/35



^{13}C NMR of



3u

E/*Z* = 65/35