Electronic Supplementary Material (ESI) for Dalton Transactions.

On the mechanism of sp2 C-H borylation using ortho-N-substituted pyridinium cation

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Supplementary Information

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General considerations

Unless otherwise noted, all reactions and manipulations were performed under an argon atmosphere in a glovebox (Mbraun Unilab) or using standard Schlenk techniques with dried and degassed solvents. All Schlenk flasks and materials were dried prior to their use. All solvents were purified by common distillation techniques: Dichloromethane (CH_2Cl_2), dimethylformamide (DMF), ethyl acetate (EtOAc) and dichloroethane (DCE) were distilled over CaH_2. n-Hexane (C_6H_{14}), toluene (C_7H_8) and diethyl ether (Et_2O) were distilled under argon over sodium/benzophenone. d6-Benzene (C_6D_6), d8-Toluene (C_7D_8), $CDCl_3$ and CD_2Cl_2 were dried over molecular sieves (4Å). Deuterated solvents were purchased from Eurisotop. $[Li(Et_2O)_{2,5}][B(C_6F_5)_4]$ (lithium tetrakis(pentafluorophenyl)borate diethylether complex (1:2.5), 97%) was purchased from ABCR and used as received. Catecholborane (CatBH), pentafluoropiridine, morpholine, 2-bromopyridine, N,N-dimethylpyridin-2-amine, benzo[b]thiophene n-butyllithium (n-BuLi, 2M, cyclohexane solution), thiophene, 2-methylthiophene, 3-methylthiophene, lithium dimethylamide ($LiNMe_2$), 2-fluoropiridine, piperidine, aniline, 1-phenylpyrrolidine, 1-phenylpiperidine, hexamethylbenzene (HMB), 3,4-ethylenedioxythiophene, HCl (1M, diethylether solution), bromobenzene, N-phenylpyrrole, $B(C_6F_5)_3$, 4-phenylmorpholine and 2,2,6,6-tetramethylpiperidine (TMP) were purchased from Sigma-Aldrich, TCI, Alfa Aesar, Fluorochem and were used as received

All new compounds have been characterized by ^1H, ^{13}C, ^{19}F, ^{11}B NMR spectroscopy and ESI-HRMS. The structures of compound **3a** have been authenticated by Xray diffraction studies and their corresponding CIF files deposited in the Cambridge Crystallographic Data Centre with nos. CCDC-2288120.

Borylations were performed in J. Young valve NMR tubes purchased from Fisher Scientific. Schlenk vessels were equipped with gas-tight Teflon valves and Glindemann PTFE sealing rings.

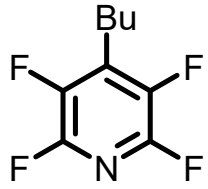
NMR spectra were recorded at Bruker Avance NEO 400 MHz or 500 MHz spectrometers. If not otherwise stated: NMR spectra were recorded at 25 °C; ^{13}C spectra were ^1H decoupled; ^{11}B spectra were not ^1H decoupled. Chemical shifts for the ^1H and ^{13}C spectra were referenced to the residual $^1H/^{13}C$ resonances of the deuterated solvent: C_6D_6: $\delta = 7.16$; $\delta = 128.06$; CD_2Cl_2: $\delta = 5.32$; $\delta = 53.84$; $CDCl_3$: $\delta = 7.26$; $\delta = 77.16$; and are reported as ppm relative to Me_4Si. Chemical shifts for the ^{11}B and ^{19}F spectra were referenced to external standard ($BF_3{\cdot}Et_2O$, $CFCl_3$, respectively).

Gas chromatographic analyses were carried out an Agilent 6890N GC equipped with 5973 MSD using a HP-5MS UI (30m, 0.25 mm, 0.25 µm) column.

High-resolution mass spectra (ESI-HRMS) were recorded on Bruker microTOF mass spectrometer by electrospray ionization time of flight reflectron experiments. The mass detector was calibrated with HCOONa solution in 1:1 H_2O:iPrOH. All HRMS experiments were recorded with positive and negative ion detector and the recorded masses were under 5 ppm error unless otherwise noted.

Preparation

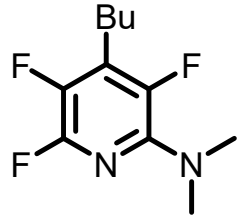
4-butyl-2,3,5,6-tetrafluoropyridine (1)



Compound **1** was synthesized by modifying the published procedure.[1] To a solution of pentafluoropyridine (3 g, 17.75 mmol) dissolved in diethyl ether 40 mL at -93 °C (frozen acetone bath) in a 100 mL Schlenk tube, n-BuLi (9.76 mL, 19.52 mmol, 2M solution in cyclohexane) was added dropwise over 30 min via syringe. The reaction was then allowed to warm up to room temperature while stirring overnight immersed in the cooling bath. After 16 hours, the red-orange solution was extracted with CH_2Cl_2 (3x50 mL). Combined organic layers were washed with Brine and dried over $MgSO_4$. After drying, $MgSO_4$ filtered on a short silica pad and the volatiles were removed in the rotary evaporator. The residue yellowish oil was purified by flash column chromatography on silica gel (0→5% CH_2Cl_2 in Hexane, v/v) to afford colorless liquid **1** (3.12 g, 85%). R_f 0.5 (CH_2Cl_2/Hexane – 1:19, v/v). Spectroscopic data are in agreement with literature[2].

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 2.81 (tt, *J* = 7.7, 1.5 Hz, 2H, C**H_2**$CH_2CH_2CH_3$), 1.63 (p, *J* = 7.5 Hz, 2H, CH_2C**H_2**CH_2CH_3), 1.40 (dq, *J* = 14.6, 7.3 Hz, CH_2CH_2C**H_2**CH_3), 0.96 (t, *J* = 7.3 Hz, 3H, $CH_2CH_2CH_2C$**H_3**).
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C) δ -92.09 (m), -145.74 (m).
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C) 14.25, 22.81, 23.62, 31.74, 135.62, 139.55, 139.20, 142.03, 144.62.

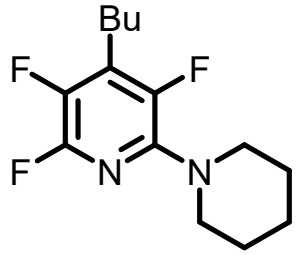
4-Butyl-3,5,6-trifluoro-*N*,*N*-dimethylpyridin-2-amine (2a)



Compound **2a** was synthesized by modifying the published procedure.[1] To a suspension of lithium dimethylamide (285 mg, 5.31 mmol) in diethyl ether 20 mL at -93 °C (frozen acetone bath) in a 100 mL Schlenk tube, **1** (0.8 mL, 4.83 mmol) was added dropwise via syringe. The reaction was allowed to warm up to room temperature while stirring overnight immersed in the cooling bath. After 48 hours, formed red-orange solution was extracted with CH_2Cl_2 (3x50 mL). Combined organic layers were washed with Brine and dried over $MgSO_4$. After drying, $MgSO_4$ filtered on a short silica pad and the volatiles were removed in the rotary evaporator. The residue oil was purified by flash column chromatography on silica gel (5→25% CH_2Cl_2 in Hexane, v/v) to afford colorless liquid **2a** (868 mg, 77%). R_f 0.33 (CH_2Cl_2/Hexane – 1:9, v/v). Spectroscopic data are in agreement with literature[1].

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 3.00 (s, 3H, NC**H_3**), 3.00 (s, 3H, NC**H_3**), 2.68 (tt, *J* = 7.7, 1.7 Hz, 2H, C**H_2**$CH_2CH_2CH_3$), 1.58 (p, *J* = 7.4 Hz, 2H, C**H_2**CH_2CH_3), 1.38 (h, *J* = 7.3 Hz, 2H, C**H_2**CH_3), 0.94 (t, *J* = 7.3 Hz, 3H, C**H_3**).
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C) δ -94.18 (dd, *J* = 31.2, 25.7 Hz), -137.57 (d, *J* = 31.2 Hz), -158.77 (d, *J* = 25.7 Hz).
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C) δ 145.58 (d, J = 17.1 Hz), 143.64 – 142.68 (m), 144.60 – 141.43 (m), 136.93 – 133.11 (m), 131.75 (ddd, J = 20.0, 16.5, 3.3 Hz), 40.15, 40.09, 31.05, 23.24, 22.52, 13.85.

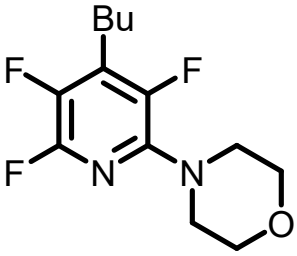
4-butyl-2,3,5-trifluoro-6-(piperidin-1-yl)pyridine (2b)



To a solution of piperidine (324 mg, 3.8 mmol) in diethyl ether 10 mL at 0 °C in a 50 mL Schlenk tube, n-BuLi (2 mL, 4 mmol, 2M in cyclohexane solution) was added dropwise via syringe. After 10 minutes stirring, mixture was frozen to -93°C (frozen acetone bath). Upon -93°C, **1** (750 mg, 3.62 mmol) was added via syringe. After 48 hours, formed red-orange solution was extracted CH_2Cl_2 (3x50 mL). Combined organic layers were washed with Brine and dried over $MgSO_4$. After drying, $MgSO_4$ filtered on a short silica pad and the volatiles were removed in the rotary evaporator. The residue oil was purified by flash column chromatography on silica gel (5→25% CH_2Cl_2 in Hexane, v/v) to afford colorless liquid **2b** (596 mg, 60%). R_f 0.15 (CH_2Cl_2/Hexane – 1:19, v/v).

^{1}H NMR (400 MHz, C_6D_6, 25 °C) δ 3.24 (m, 4H, C**H_2**NC**H_2**), 2.43 (tt, J = 7.7, 1.7 Hz, 2H, C**H_2**$CH_2CH_2CH_3$), 1.41 (m, 6H, C**H_2CH_2CH_2**), 1.29 (m, 2H, C**H_2**CH_2CH_3), 1.14 (h, J = 7.3 Hz, 2H, C**H_2**CH_3), 0.76 (t, J = 7.3 Hz, 3H, C**H_3**).
^{19}F {^{1}H} NMR (376 MHz, C_6D_6, 25 °C) δ -93.20 (dd, J = 31.6, 26.0 Hz), -135.70 (d, J = 31.9 Hz), -156.69 (d, J = 26.4 Hz).
^{13}C {^{1}H} NMR (101 MHz, C_6D_6, 25 °C) δ 146.37, 144.11 (d, J = 251.4 Hz), 143.74 (d, J = 65.0 Hz), 136.35 (dd, J = 250.1, 31.1 Hz), 131.77 (m), 49.11 (d, J = 5.4 Hz), 31.11, 25.94, 24.78, 23.22, 22.57, 13.81.
ESI-HRMS m/z: exp. for 273.1566 $[M+H]^+$ (calcd. for $C_{14}N_2F_3H_{20}$ 273.157

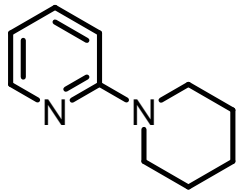
4-(4-butyl-3,5,6-trifluoropyridin-2-yl)morpholine (2c)



To morpholine (205 mg, 5.8 mmol) in diethyl ether 10 mL at 0 °C in a 50 ml Schlenk tube, n-BuLi (2.9 mL, 5.8 mmol, 2M solution in cyclohexane) was added dropwise via syringe. After 10 minutes stirring, mixture was frozen to -93°C (frozen acetone bath). Upon -93°C, **1** (1 g, 4.83 mmol) was added via syringe. After 18 hours, formed red-orange solution was extracted with CH_2Cl_2 (3x50 mL). Combined organic layers were washed with Brine and dried over $MgSO_4$. After drying, $MgSO_4$ filtered on a short silica pad and the volatiles were removed in the rotary evaporator. The residue oil was purified by flash column chromatography on silica gel (0→2% EtOAc in CH_2Cl_2, v/v) to afford colorless liquid **2c** (650 mg, 49%). R_f 0.4 (CH_2Cl_2).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 3.86 – 3.76 (m, 4H, morpholine), 3.42 – 3.32 (m, 4H, morpholine), 2.70 (t, J = 7.6 Hz, 2H, C**H_2**$CH_2CH_2CH_3$), 1.58 (p, J = 7.5 Hz, 2H, C**H_2**CH_2CH_3), 1.38 (h, J = 7.3 Hz, 2H, C**H_2**CH_3), 0.94 (t, J = 7.3 Hz, 3H, C**H_3**).
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C) δ -93.41 (dd, J = 31.2, 25.0 Hz), -135.81 (d, J = 31.2 Hz), -154.98 (d, J = 25.7 Hz).
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C) δ 145.83, 144.28 (d, J = 252.1 Hz), 142.98 (d, J = 132.2 Hz), 138.98 – 134.44 (m), 132.86 – 131.09 (m), 66.84, 48.27, 30.99, 23.24, 22.50, 13.83.
ESI-HRMS m/z: exp. for 297.1190 $[M+Na]^+$ (calcd. for $C_{13}H_{17}F_3N_2ONa$ 297.1185)

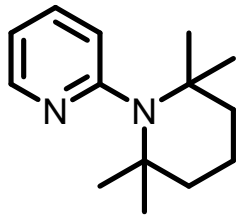
4-butyl-2,3,5-trifluoro-6-(piperidin-1-yl)pyridine (2d)



Compound **2d** was synthesized by modifying the published procedure.[3] A 50 mL round-bottom flask was charged with 2-bromopyridine (1.5 g, 9.49 mmol), CuI (180.8 mg, 0.95 mmol), 2-picolinic acid (233.7 mg, 1.90 mmol), anhydrous K_2CO_3 (1.97 g, 14.24 mmol), piperidine (808.4 mg, 9.49 mmol) and DMF (8 mL). Then, the flask was equipped with bulb condenser and the reaction mixture was degassed and purged with argon gas 3 times. The reaction was heated in the oil bath at 130°C and stirred for 48 h. Then, the reaction mixture was cooled to room temperature, diluted with water (20 mL) and extracted with ethyl acetate (3x20 mL). The combined organic layer was washed with water (3x20 mL), brine (50 mL) and dried over anhydrous $MgSO_4$. After drying, $MgSO_4$ filtered on a short silica pad and the volatiles were removed in the rotary evaporator. The residue oil was purified by flash column chromatography on silica gel (0→10% EtOAc in Hexane, v/v) to afford colorless liquid **2d** (1,003 g, 65%). R_f 0.5 (EtOAc/Hexane – 1:9, v/v). Spectral data are in agreement with literature[3].

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.17 (ddd, J = 4.9, 2.1, 1.0 Hz, 1H), 7.43 (ddd, J = 8.8, 7.1, 2.0 Hz, 1H), 6.66 – 6.61 (m, 1H), 6.54 (ddd, J = 7.2, 4.9, 1.0 Hz, 1H), 3.56 – 3.48 (m, 4H, C**H$_2$**NC**H$_2$**), 1.69 – 1.60 (m, 6H, C**H$_2$**C**H$_2$**C**H$_2$**).
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C) δ 159.89, 148.07, 137.41, 112.51, 107.22, 46.44, 25.64, 24.87.

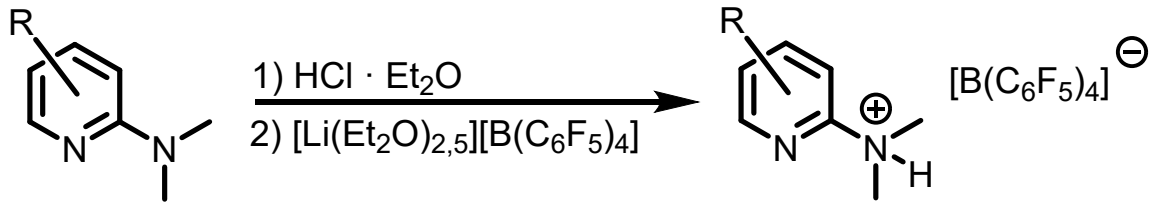
2-(2,2,6,6-tetramethylpiperidin-1-yl)pyridine (2e)



To 2,2,6,6-tetramethylpiperidine (8.08 mg, 61.8 mmol) in diethyl ether 20 mL at 0 °C in a 100 mL Schlenk tube, n-BuLi (8.24 mL, 20.6 mmol, 2.5M solution in hexane) was added dropwise via syringe. After 10 minutes stirring, 2-fluoropyridine (1 g, 10.3 mmol) was added via syringe. After 2 hours, reaction was extracted with EtOAc (3x50 mL). Combined organic layers were washed with Brine and dried over $MgSO_4$. After drying, $MgSO_4$ filtered on a short silica pad and the volatiles were removed in the rotary evaporator. The residue oil was purified by flash column chromatography on silica gel (0→10% EtOAc in Hexane, v/v) to afford colorless liquid **2e** (802 mg, 36%). R_f 0.5 (EtOAc/Hexane – 1:9, v/v).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 8.49 (ddd, J = 4.8, 2.2, 0.8 Hz, 1H), 7.59 – 7.52 (m, 1H), 7.07 (ddd, J = 7.4, 4.8, 1.2 Hz, 2H), 7.03 (dt, J = 7.9, 1.1 Hz, 1H), 1.79 – 1.72 (m, 1H), 1.58 – 1.53 (m, 3H), 1.09 (s, 12H).
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C) δ 18.32, 29.35, 41.75, 54.40, 120.68, 128.81, 136.23, 147.96, 161.04.
ESI-HRMS m/z: exp. for 219.1861 $[M+H]^+$ (calcd. for $C_{14}H_{23}N_2$ 219.1816)

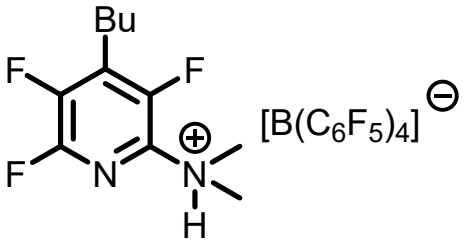
Gereral procedure for ortho-aminopyridinium salts 3a-f



Compounds **3a-f** were synthesized according to the published procedure.[1] $[Li(Et_2O)_{2,5}][B(C_6F_5)_4]$ was used instead of $[Li(Et_2O)_4][B(C_6F_5)_4]$.

To a solution of corresponding aminopyridine (1 eq) in CH_2Cl_2 5 mL in a 50 mL flask, HCl (1 eq, ether solution) was added. After 5 minutes, a solution of $[Li(Et_2O)_{2,5}][B(C_6F_5)_4]$ (1 eq) in CH_2Cl_2 10 ml was added. The solution was stirred for 30 min, the precipitate formed was filtered and washed with CH_2Cl_2 5 mL. Mother liquor was removed in the rotary evaporator and dried in vacuum (1 mbar) at room temperature for 1h. The solid was redissolved in CH_2Cl_2 10 mL, and the filtration and evaporation procedure was repeated. Dried in vacuum (1 mbar) at room temperature for 1 h gave 77-96% of powder **3a-f**.

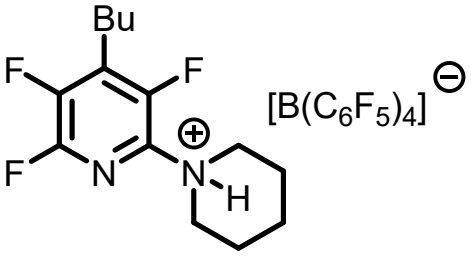
4-Butyl-2-(dimethylamino)-3,5,6-trifluoropyridinium tetrakis(pentafluorophenyl)borate(1-) (3a)



Compound **3a** was synthesized according to the general procedure using aminopyridine **2a** (342 mg, 1.47 mmol).[1] The yield is 96% (1,29 g).

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 4.38 (br. s, 1H, N**H**), 3.38 (s, 6H, NH(C**H$_3$**)$_2$), 2.87 (tt, *J* = 7.7, 1.5 Hz, 2H, C**H$_2$**CH$_2$CH$_2$CH$_3$), 1.63 (p, *J* = 7.5 Hz, 2H, C**H$_2$**CH$_2$CH$_3$), 1.41 (h, *J* = 7.3 Hz, 2H, C**H$_2$**CH$_3$), 0.95 (t, *J* = 7.3 Hz, 3H, C**H$_3$**).
^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2, 25 °C) δ -85.28 (dd, J = 28.4, 21.5 Hz, 1F, cation), -132.30 (d, J = 18.0 Hz, 1F, cation), -133.18 – -133.44 (m, 8F, anion), -134.22 (dd, J = 28.4, 8.3 Hz, 1F, cation), -163.41 (t, J = 20.5 Hz, 4F, anion), -167.45 (t, J = 20.1 Hz, 8F, anion).
^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C) δ -16.68.
^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ 13.59, 22.79, 24.03, 30.79, 46.10, 135.66, 138.12, 147.38, 149.67.
ESI-HRMS m/z: exp. for 233.1249 $[M+H]^+$ (calcd. for $C_{11}H_{16}N_2F_3$ 233.1260)
ESI-HRMS m/z: exp. for 678.9779 $[M]^-$ (calcd. for $C_{24}F_{20}B$ 678.9772)

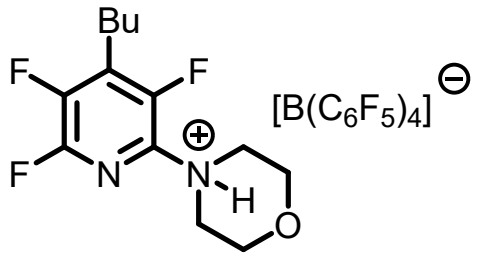
1-(4-butyl-3,5,6-trifluoropyridin-2-yl)piperidin-1-ium tetrakis(pentafluorophenyl)borate(1-) (3b)



Compound **3b** was synthesized according to the general procedure using aminopyridine **2b** (228 mg, 0.837 mmol).[1] The yield is 96% (764 mg).

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 3.69 (d, J = 5.6 Hz, 4H, C**H$_2$**NHC**H$_2$**), 3.51 (br. s., 1H, N**H**), 2.84 (tt, J = 7.7, 1.6 Hz, 2H, C**H$_2$**CH$_2$CH$_2$CH$_3$), 2.04 (p, J = 6.0 Hz, 4H, C**H$_2$**CH$_2$NHCH$_2$C**H$_2$**), 1.82 (p, J = 6.0 Hz, 2H, NHCH$_2$CH$_2$C**H$_2$**), 1.61 (p, J = 7.5 Hz, 2H, C**H$_2$**CH$_2$CH$_3$), 1.39 (h, J = 7.3 Hz, 2H, C**H$_2$**CH$_3$), 0.94 (t, J = 7.4 Hz, 3H, C**H$_3$**).
^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2, 25 °C) δ -86.43 (br.s., 1F, cation), -133.24 (m, 9F, anion + cation) -134.27 (dd, J = 28.4, 7.6 Hz, 1F, cation), -163.46 (t, J = 20.5 Hz, 4F, anion), -167.46 (t, J = 19.8 Hz, 8F, anion).
^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C) δ -16.67.
^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ 13.60, 21.57, 22.76, 23.93, 24.33, 30.84, 56.52, 135.85, 137.94, 147.38, 149.75.
ESI-HRMS m/z: exp. for 273.1561 $[M+H]^+$ (calcd. for $C_{14}H_{20}N_2F_3$ 273.1573)
ESI-HRMS m/z: exp. for 678.9761 $[M]^-$ (calcd. for $C_{24}F_{20}B$ 678.9772)

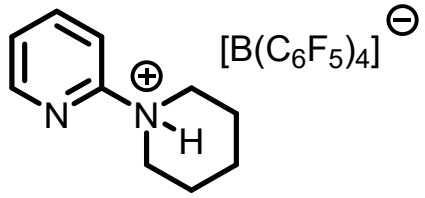
4-(4-butyl-3,5,6-trifluoropyridin-2-yl)morpholin-4-ium tetrakis(pentafluorophenyl)borate(1-) (3c)



Compound **3c** was synthesized according to the general procedure using aminopyridine **2c** (300 mg, 1.09 mmol).[1] The yield is 94% (980 mg).

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C) δ 4.03 (t, J = 4.8 Hz, 4H, morpholine), 3.66 (t, J = 4.9 Hz, 4H, morpholine), 2.78 (t, J = 7.7 Hz, 2H, C**H$_2$**$CH_2CH_2CH_3$), 2.23 (s, 1H, N**H**), 1.60 – 1.50 (m, 2H, C**H$_2$**CH_2CH_3), 1.34 (h, J = 7.3 Hz, 2H, C**H$_2$**CH_3), 0.88 (t, J = 7.3 Hz, 3H, C**H$_3$**).
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C) δ -84.42 (br.s., 4F, cation), -131.21 (d, J = 22.2 Hz, 9F, cation + anion), -132.12 (br.s., 1F, cation), -161.16 (dq, J = 40.2, 20.5 Hz, 4F anion), -165.24 (br.s., 8F, anion).
^{11}B NMR (128 MHz, $CDCl_3$, 25 °C) δ -14.76.
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C) δ 13.16, 22.27, 23.42, 30.37, 31.52, 64.07, 134.97, 137.42, 146.82, 149.14.
ESI-HRMS m/z: exp. for 275.1360 $[M+H]^+$ (calcd. for $C_{13}H_{18}F_3N_2O$ 275.1366)
ESI-HRMS m/z: exp. for 678.9785 $[M]^-$ (calcd. for $C_{24}F_{20}B$ 678.9772)

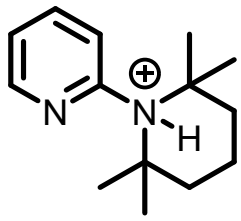
1-(pyridin-2-yl)piperidin-1-ium tetrakis(pentafluorophenyl)borate(1-) (3d)



Compound **3d** was synthesized according to the general procedure using aminopyridine **2d** (100 mg, 0.616 mmol).[1] The yield is 77% (400 mg).

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 9.98 (br.s, 1H, N**H**), 7.98 – 7.91 (m, 1H), 7.69 (td, J = 6.5, 2.4 Hz, 1H), 7.14 (dd, J = 9.5, 2.6 Hz, 1H), 6.90 (t, J = 6.8 Hz, 1H), 3.64 – 3.55 (m, 4H C**H$_2$**NHC**H$_2$**), 1.83 – 1.76 (m, 6H, C**H$_2$**C**H$_2$**C**H$_2$**).
^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2, 25 °C) δ -133.01 – -133.34 (m, 8F), -163.53 (t, J = 20.5 Hz, 4F), -167.47 (t, J = 20.1 Hz, 8F).
^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C) δ -16.67.
^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ 23.26, 25.22, 47.87, 113.35, 113.50, 135.07, 135.50, 145.32, 147.30, 149.75, 151.57.
ESI-HRMS m/z: exp. for 163.1232 $[M+H]^+$ (calcd. for $C_{10}H_{15}N_2$ 163.1230)
ESI-HRMS m/z: exp. for 678.9737 $[M]^-$ (calcd. for $C_{24}F_{20}B$ 678.9772)

1-(pyridin-2-yl)-2,2,6,6-tetramethylpiperidin-1-ium tetrakis(pentafluorophenyl)borate(1-) (3e)

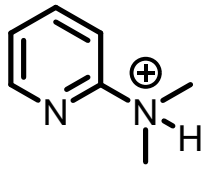


$[B(C_6F_5)_4]^{\ominus}$

Compound **3e** was synthesized according to the general procedure using aminopyridine **2e** (100 mg, 0.458 mmol).[1] The yield is 95% (392 mg) of the crude product. Differents attempt to purify it was not successful.

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 8.56 (d, J = 3.7 Hz, 1H), 8.18 – 8.07 (m, 1H), 7.70 (dd, J = 7.6, 4.8 Hz, 1H), 7.57 (d, J = 8.3 Hz, 1H), 6.75 (s, 1H, N**H**), 2.00 (m, 6H, C**H$_2$**C**H$_2$**C**H$_2$**), 1.41 (br.s, 12H, C(C**H$_3$**)$_2$)$_2$).
^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2, 25 °C) δ -133.02 – -133.14 (m), -163.61 (t, J = 20.5 Hz), -167.37 – -167.60 (m).
^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C) δ -16.66.
^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ 150.30, 148.59 (d, J = 244.1 Hz), 140.30, 136.74 (d, J = 245.2 Hz), 127.19 (d, J = 32.0 Hz), 40.05, 31.45, 22.29, 16.41.
ESI-HRMS m/z: exp. for 219.1851 $[M+H]^+$ (calcd. for $C_{14}H_{23}N_2$ 219.1856)
ESI-HRMS m/z: exp. for 678.9735 $[M]^-$ (calcd. for $C_{24}F_{20}B$ 678.9772)

N,N-dimethylpyridin-2-aminium tetrakis(pentafluorophenyl)borate(1-) (3f)



$[B(C_6F_5)_4]^{\ominus}$

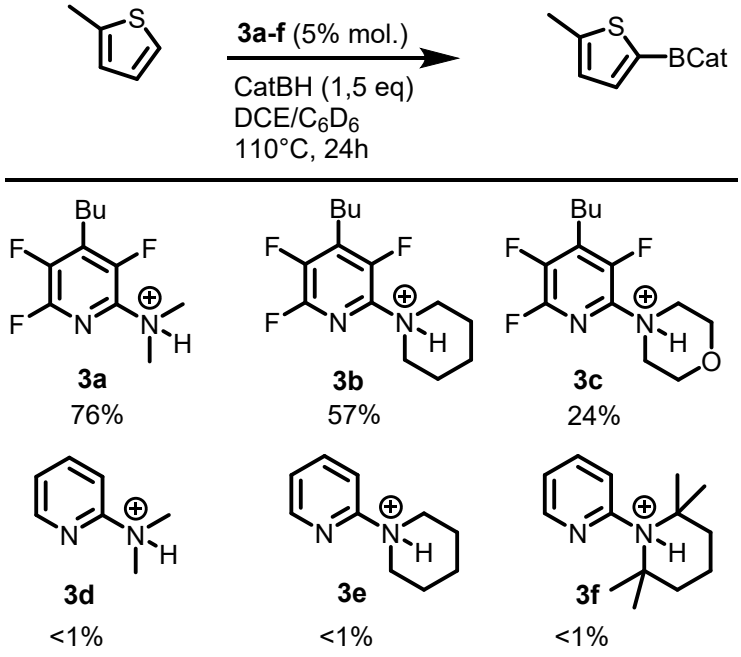
Compound **3f** was synthesized according to the general procedure using *N*,*N*-dimethylpyridin-2-amine (100 mg, 0.819 mmol).[1] The yield is 87% (573 mg).

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C) δ 9.75 (s, 1H, N**H**), 7.97 (ddd, J = 8.9, 7.1, 1.7 Hz, 1H), 7.74 (ddd, J = 6.6, 1.8, 0.9 Hz, 1H), 7.06 (dt, J = 9.4, 0.9 Hz, 1H), 6.96 (td, J = 6.8, 1.1 Hz, 1H), 3.28 (s, 6H, C**H$_3$**NHC**H$_3$**).
^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2, 25 °C) δ -133.06 – -133.28 (m, 8F), -163.43 (t, J = 20.5 Hz, 4F), -167.21 – -167.67 (m, 8F).
^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C) δ -16.67.
^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C) δ 152.26, 148.54 (d, J = 236.5 Hz), 145.06, 138.63 (d, J = 244.1 Hz), 136.70 (d, J = 240.5 Hz), 135.01, 113.39, 112.81, 39.48.
ESI-HRMS m/z: exp. for 145.0731 $[M+Na]^+$ (calcd. for $C_7H_{10}N_2Na$ 145.0736)
ESI-HRMS m/z: exp. for 678.9768 $[M]^-$ (calcd. for $C_{24}F_{20}B$ 678.9772)

Borylations

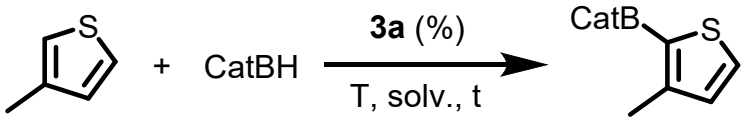
Comparison of different ortho-N-substituted pyridinium catalysts in sp² C-H borylation of 3-methylthiophene

In a glovebox, J. Young-NMR tube was charged with the appropriate catalyst (**3a-f**) (5% mol.), 50 mg of 2-methylthiophene (0,5 mmol), 500 µl DCE and 100 µl C_6D_6. HMB was measured individually for each reaction (3-5 mg) and added. Then, ^{1}H NMR was recorded from samples as a reference point. J. Young-NMR tubes were heated in the oil bath at 110°C for 24 h. After heating, ^{1}H and ^{11}B NMR were recorded from samples. Yields were calculated based on hexamethylbenzene signal and the most characteristic signal of the product on the ^{1}H NMR.



Optimization of sp² C-H borylation of 3-methylthiophene with catalyst 3a

All reactions were carried out in the J. Young-NMR tubes and were charged in the glovebox according to the presented table based on 50 mg of 3-methylthiophene. Before the reaction, ^{1}H NMR was acquired from samples as a reference point. After reaction, ^{1}H and ^{11}B NMR were recorded from samples. Convertions were calculated based on reference spectra and the spectra of reaction on the ^{1}H NMR.

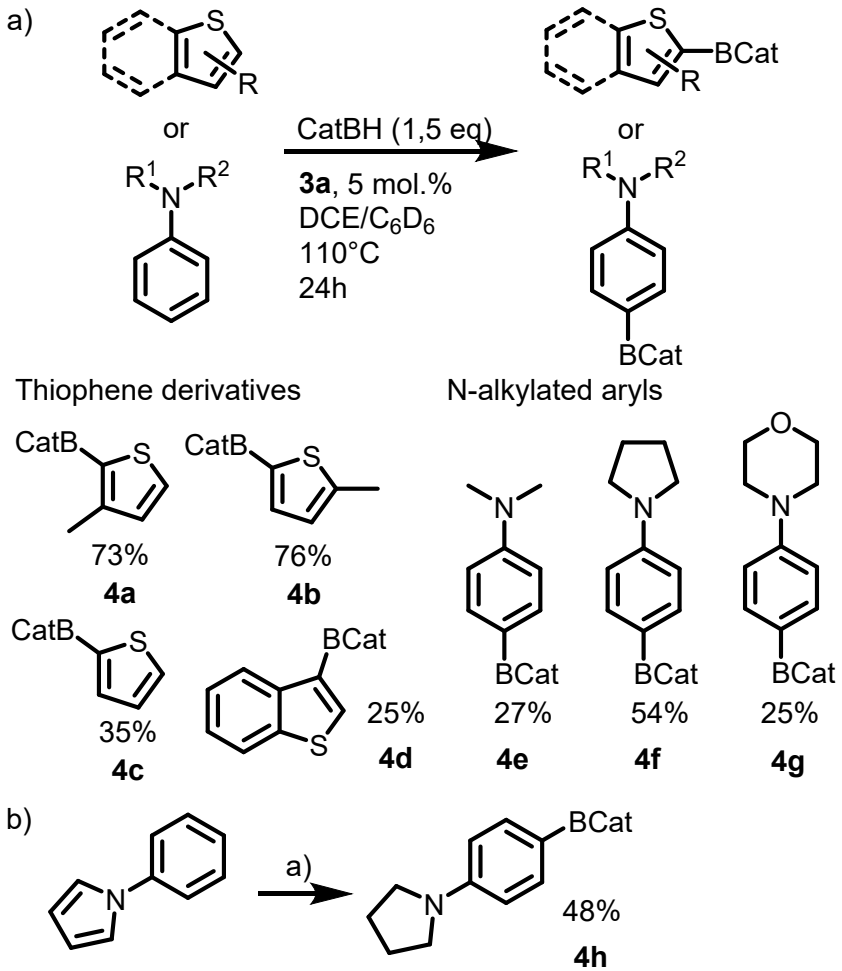


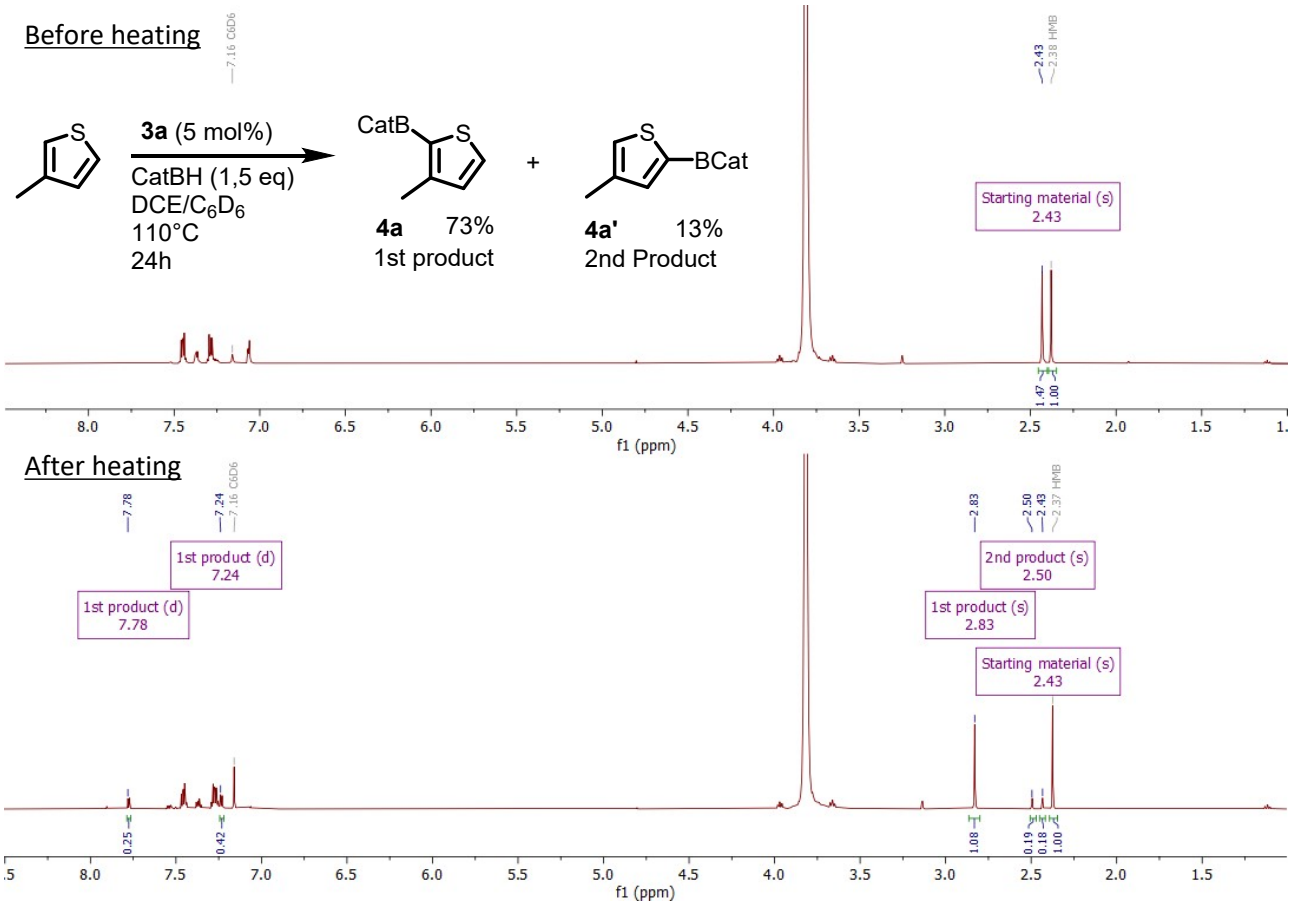
Entry	Temp, °C	Solvent	eq. CatBH	mol % **3a**	time, h	conversion
Solvent screening						
1	80	PhMe	1	4	24	54
2	80	PhBr	1	4	24	87,5
3	80	neat	1	4	24	69
4	80	C_6D_6	1	4	24	74
5	80	DCE	1	4	24	63
6	80	neat	2	4	120	65
7	80	C_6D_6	2	4	48	95
Time-temperature screening						
8	RT	DCE	1	4	24	0
9	80	DCE	1	4	2	12
10	80	DCE	1	4	4	18
11	80	DCE	1	4	8	29
12	80	DCE	1	4	16	51
13	80	DCE	1	4	24	63
14	80	DCE	1	4	36	70
15	80	DCE	1	4	48	73
16	110	PhMe-d8	1	4	2	20
17	110	PhMe-d8	1	4	4	26
18	110	PhMe-d8	1	4	16	49,5
19	110	PhMe-d8	1	4	24	58
20	110	PhMe-d8	1	4	36	67
21	110	PhMe-d8	1	4	48	68
Catalyst loading screening						
22	110	C_6D_6	1	0,1	24	9
23	110	C_6D_6	1	1	24	37
24	110	C_6D_6	1	5	24	82
25	110	C_6D_6	1	10	24	89
26	110	C_6D_6[a]	1	0,1	120	21
27	110	C_6D_6[a]	1	1	120	81
CatBH loading screening						
28	110	DCE	1	5	24	78
29	110	DCE	1,5	5	24	88
30	110	DCE	2	5	24	87
31	110	DCE	5	5	24	91

Conversion higher than 75% is coloured green. DCE – 1,2-dichloroethane. a) Entries 26 and 27 are entries 22 and 24 respectively with prolonged heating.

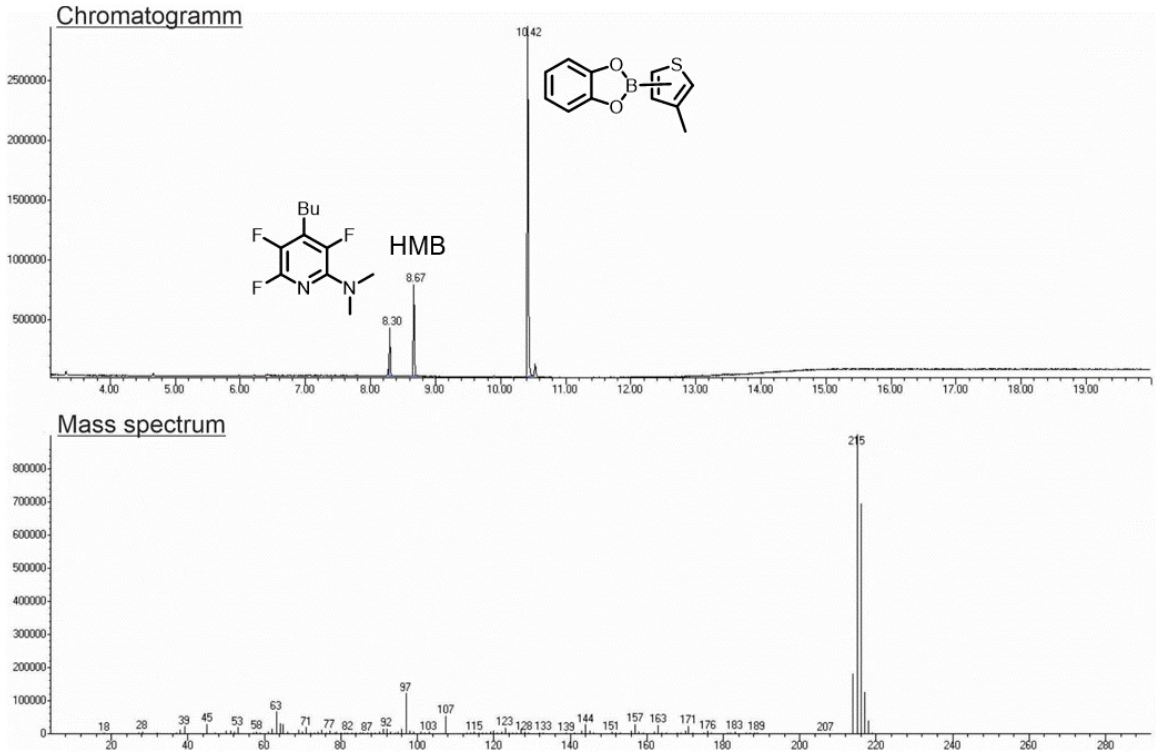
Substrate scope of sp^2 C-H borylation with catalyst 3a

In a glovebox, J. Young-NMR tube was charged with catalyst **3a** (5% mol.), corresponding substrate (exact mass is in the description of each spectrum for the substrate scope), 500 µl DCE and 100 µl C_6D_6. Hexamethylbenzene was measured individually for each reaction (3-6 mg) and added. Then, ^{1}H NMR was recorded from samples as a reference point (d_1 = 10 sec). J. Young-NMR tubes were heated in the oil bath at 110°C for 24 h. After heating, ^{1}H and ^{11}B NMR were recorded from samples (d_1 = 10 sec). After that, 10 µl aliquots were drawn and diluted in 1 mL EtOAc. Prepared samples were screened on GC-MS. Yields were calculated based on hexamethylbenzene (HMB) signal and the most characteristic signal of the product on the ^{1}H NMR.

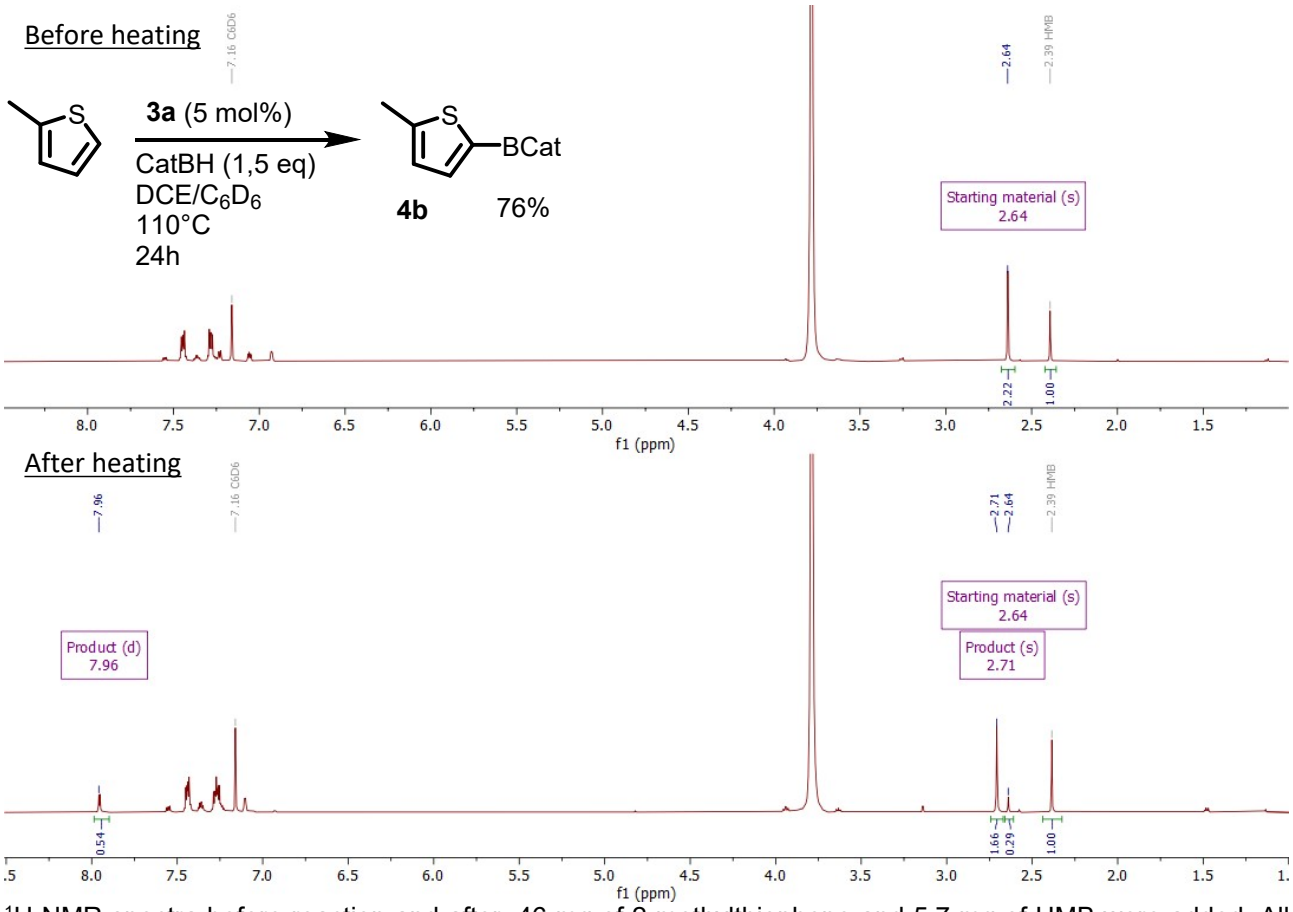




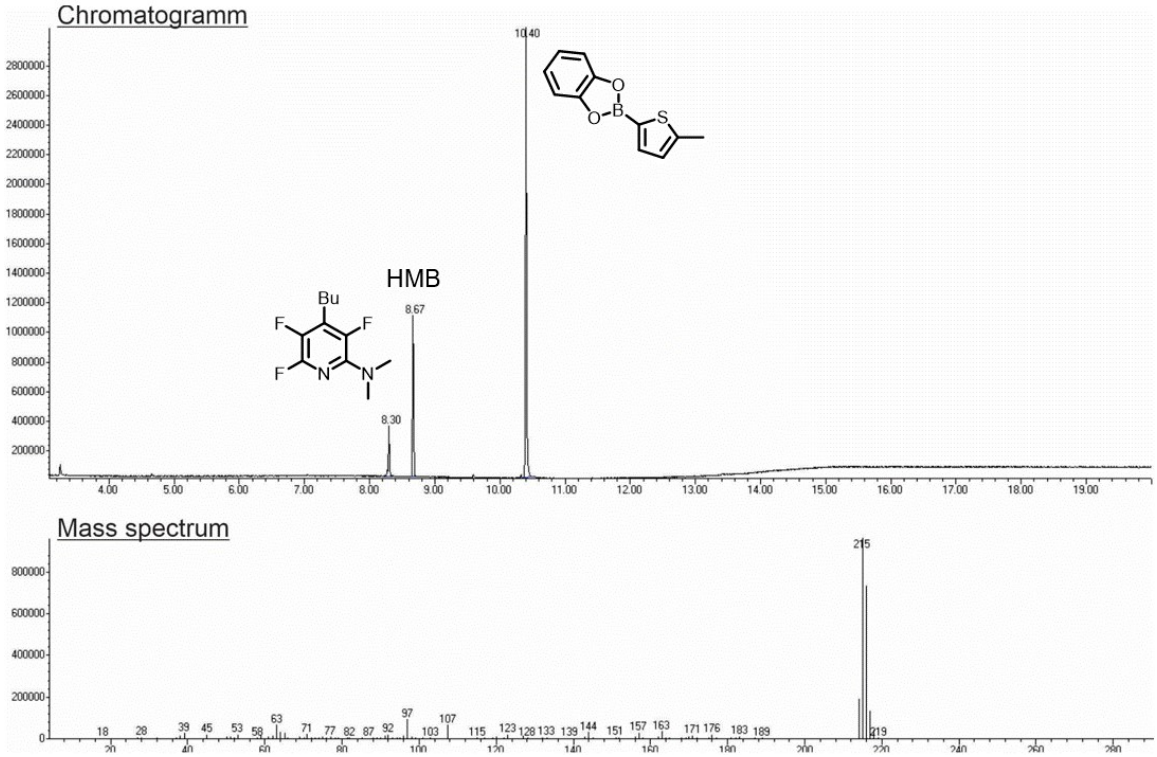
^{1}H NMR spectra before reaction and after. 21 mg of 3-methylthiophene and 4.1 mg of HMB were added. All signals are aligned to C_6D_6. All signals are shifted from original place in C_6D_6 because of high amount DCE. Conversion is determined by integration of the signals of starting material from δ 2.43 and the products from δ 2.83 (1st product) and δ 2.50 (2nd product).



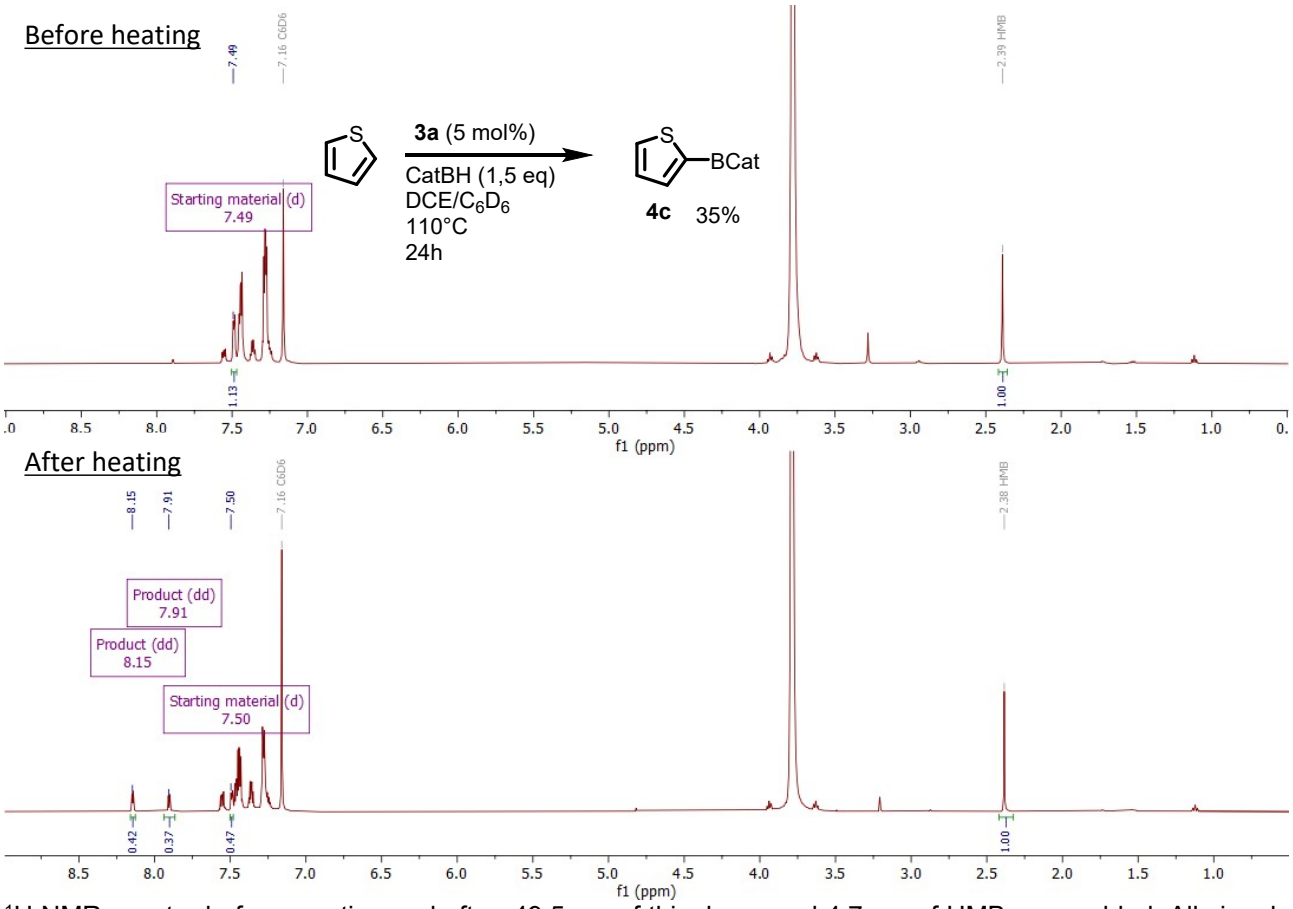
GC-MS data after reaction. Mass spectrum depicts peak of the product at 10.42 seconds.



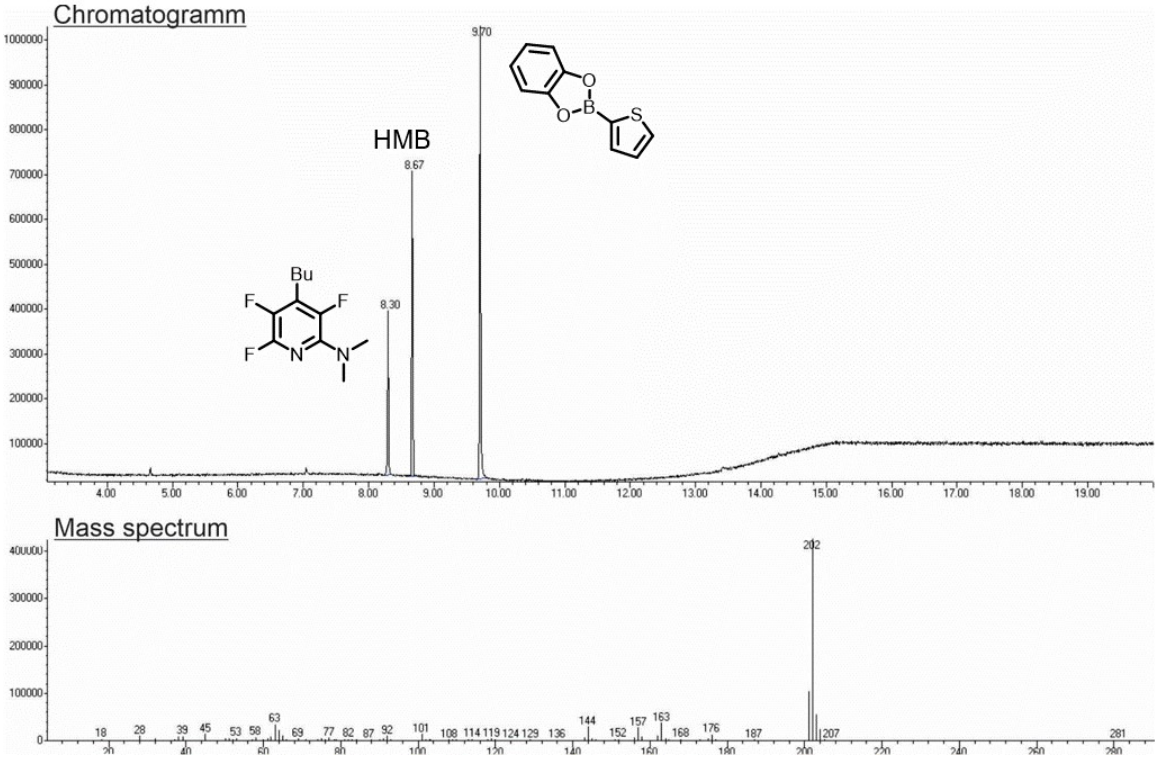
^{1}H NMR spectra before reaction and after. 46 mg of 2-methylthiophene and 5.7 mg of HMB were added. All signals are aligned to C_6D_6. All signals are shifted from original place in C_6D_6 because of high amount DCE. Conversion is determined by integration of the signals of starting material from δ 2.64 and the product from δ 2.71.



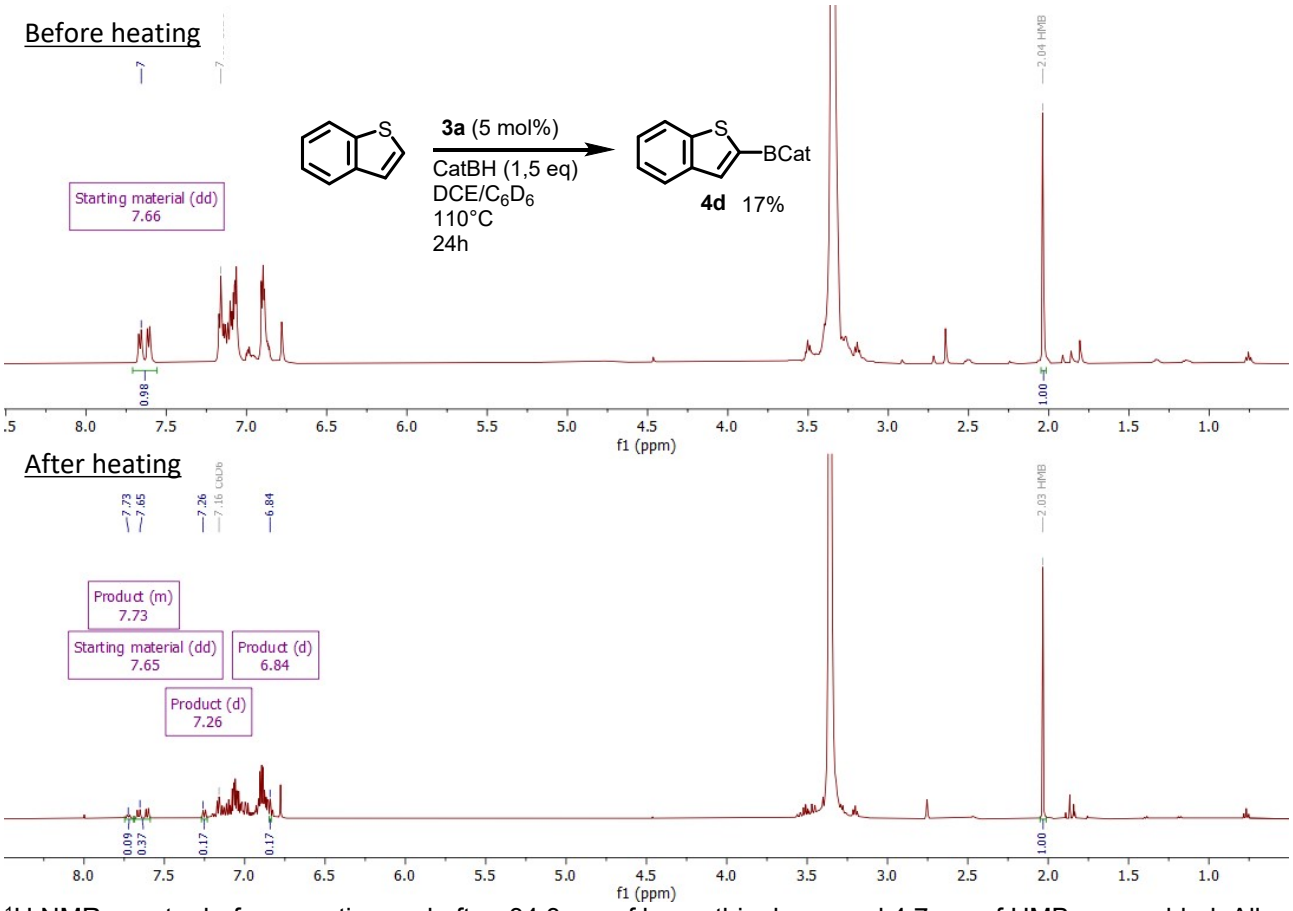
GC-MS data after reaction. Mass spectrum depicts peak of the product at 10.40 seconds.



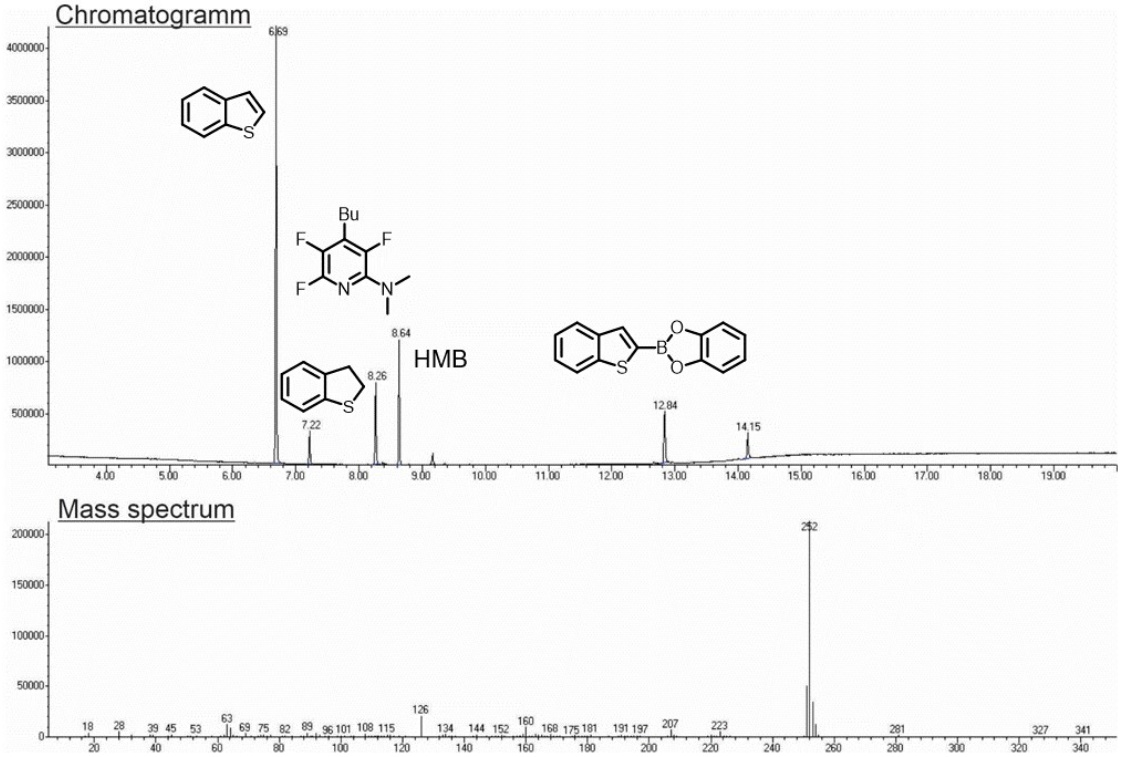
^{1}H NMR spectra before reaction and after. 49.5 mg of thiophene and 4.7 mg of HMB were added. All signals are aligned to C_6D_6. All signals are shifted from original place in C_6D_6 because of high amount DCE. Conversion is determined by integration of the signals of starting material from δ 7.49 and the product from δ 7.90 and δ 8.14.



GC-MS data after reaction. Mass spectrum depicts peak of the product at 9.7 seconds.

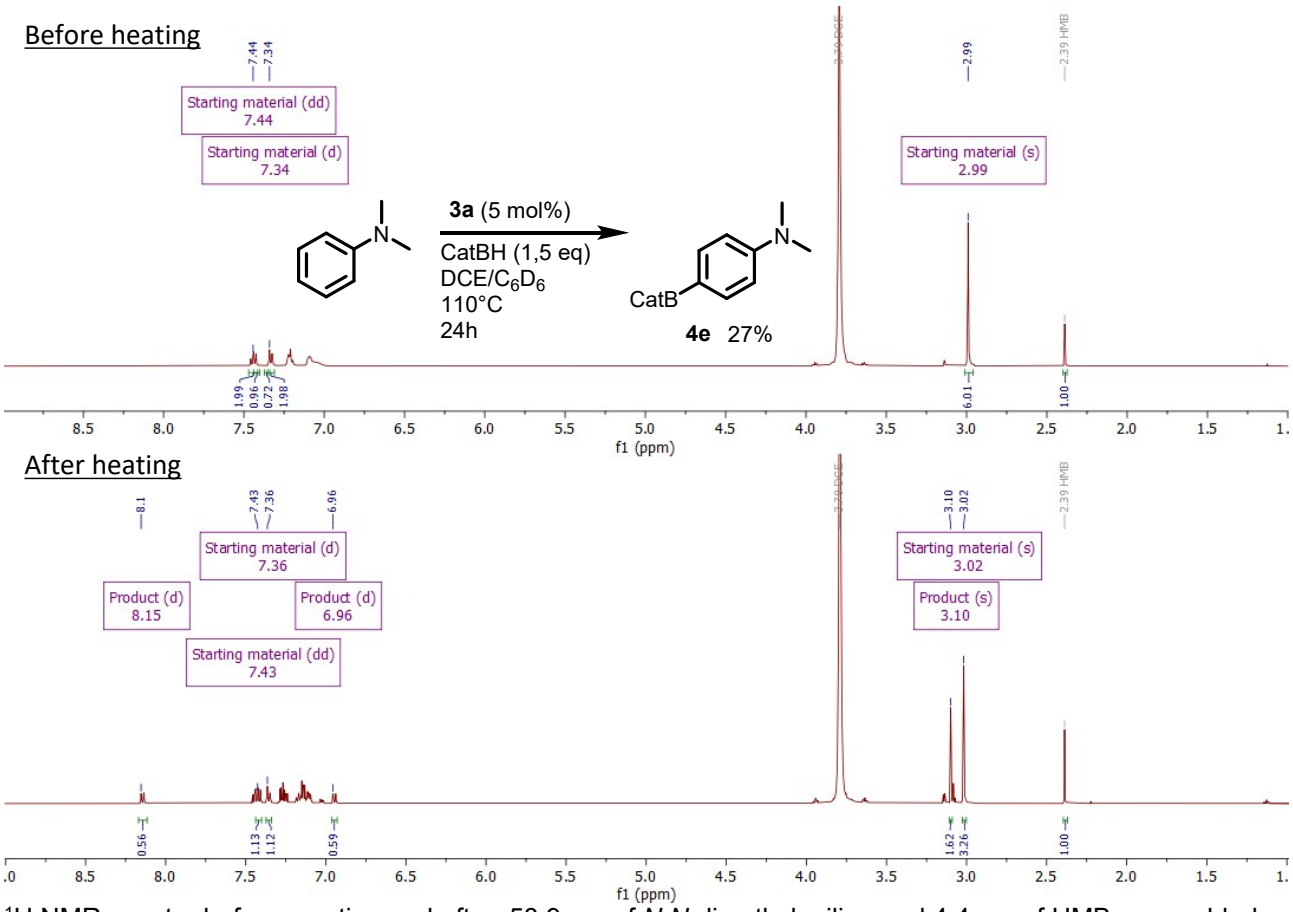


^{1}H NMR spectra before reaction and after. 34.3 mg of benzothiophene and 4.7 mg of HMB were added. All signals are aligned to C_6D_6. All signals are shifted from original place in C_6D_6 because of high amount DCE.

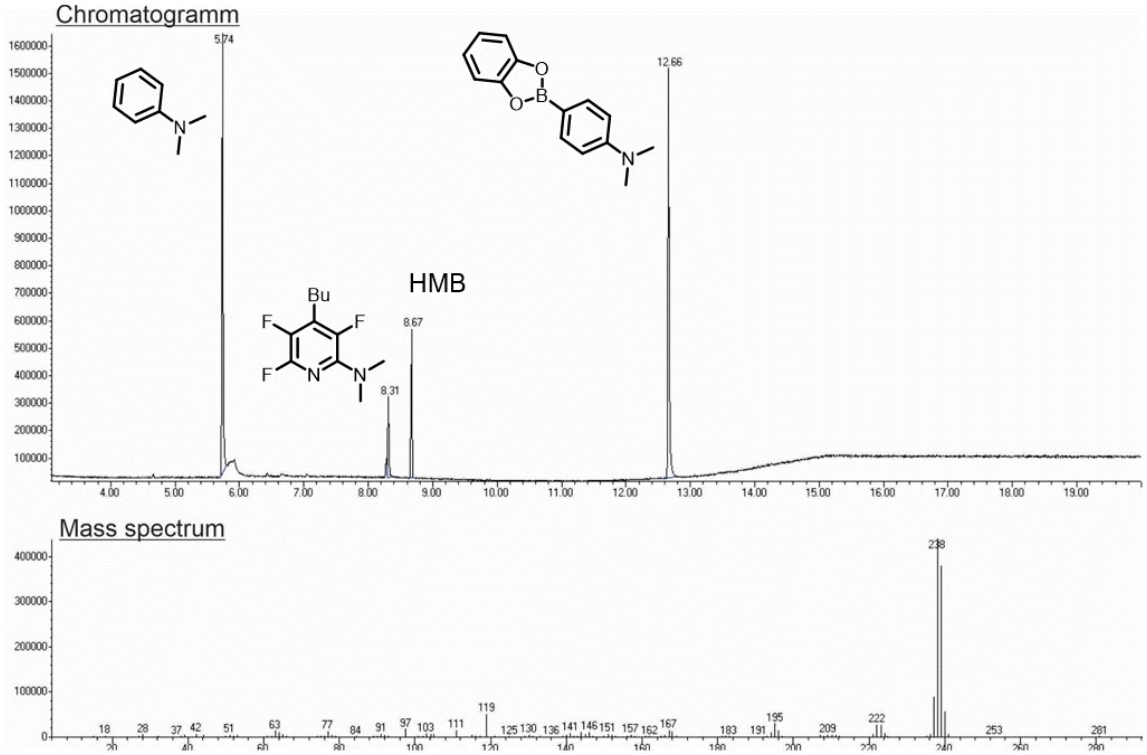


Conversion is determined by integration of the signals of starting material from δ 7.67-7.60 and the product from δ 7.26.

GC-MS data after reaction. Mass spectrum depicts peak of the product at 12.84 seconds.

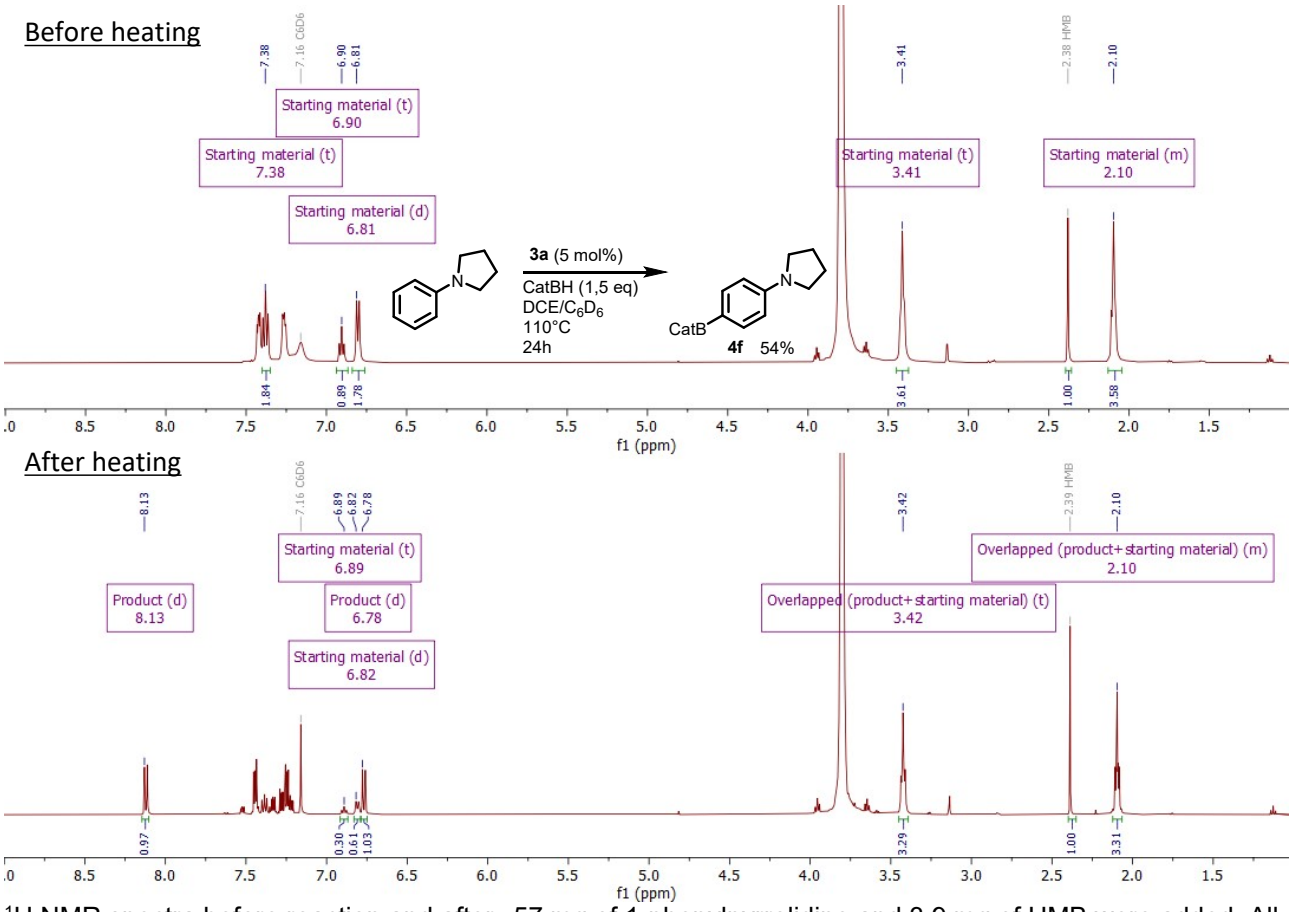


^{1}H NMR spectra before reaction and after. 58.9 mg of *N*,*N*-dimethylaniline and 4.4 mg of HMB were added. All signals are aligned to DCE at 3.79. All signals are shifted from original place in C_6D_6 because of high

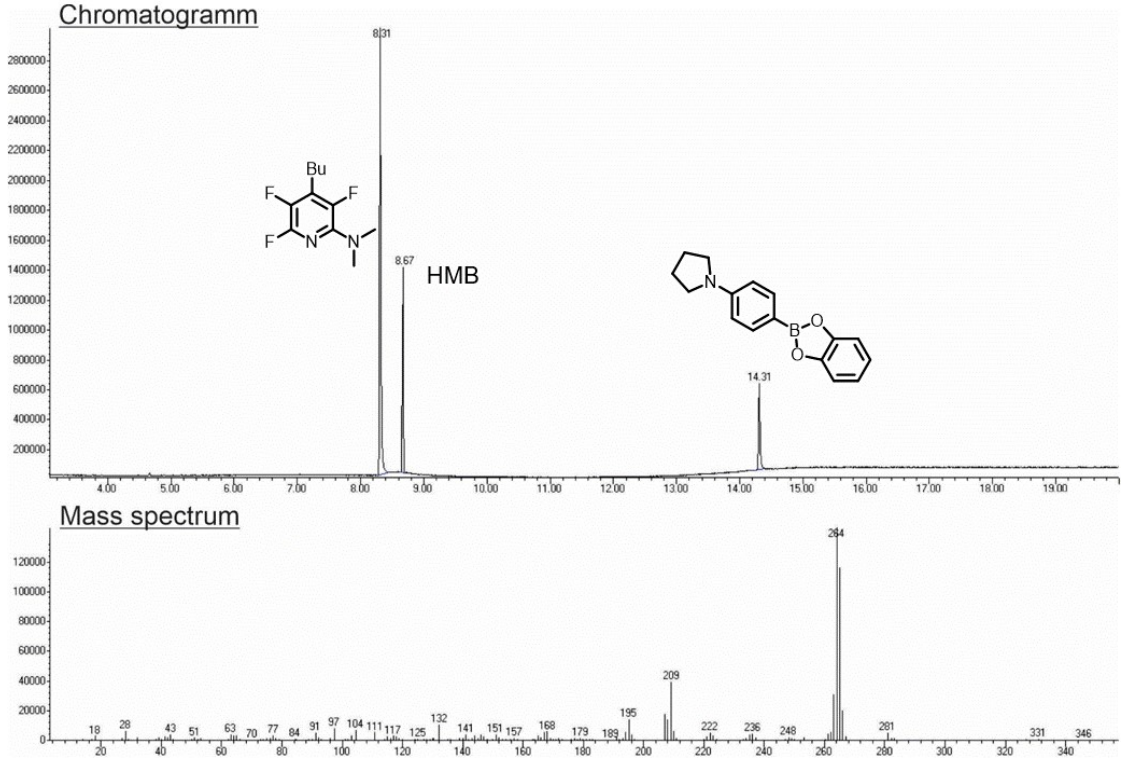


amount DCE. Conversion is determined by integration of the signals of starting material from δ 2.99 and the product from δ 3.10.

GC-MS data after reaction. Mass spectrum depicts peak of the product at 12.66 seconds.



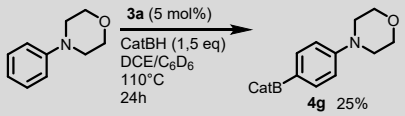
^{1}H NMR spectra before reaction and after. 57 mg of 1-phenylpyrrolidine and 3.9 mg of HMB were added. All signals are aligned to C_6D_6. All signals are shifted from original place in C_6D_6 because of high amount DCE. Conversion is determined by integration of the signals of starting material from δ 3.41 and the product from δ



8.12.

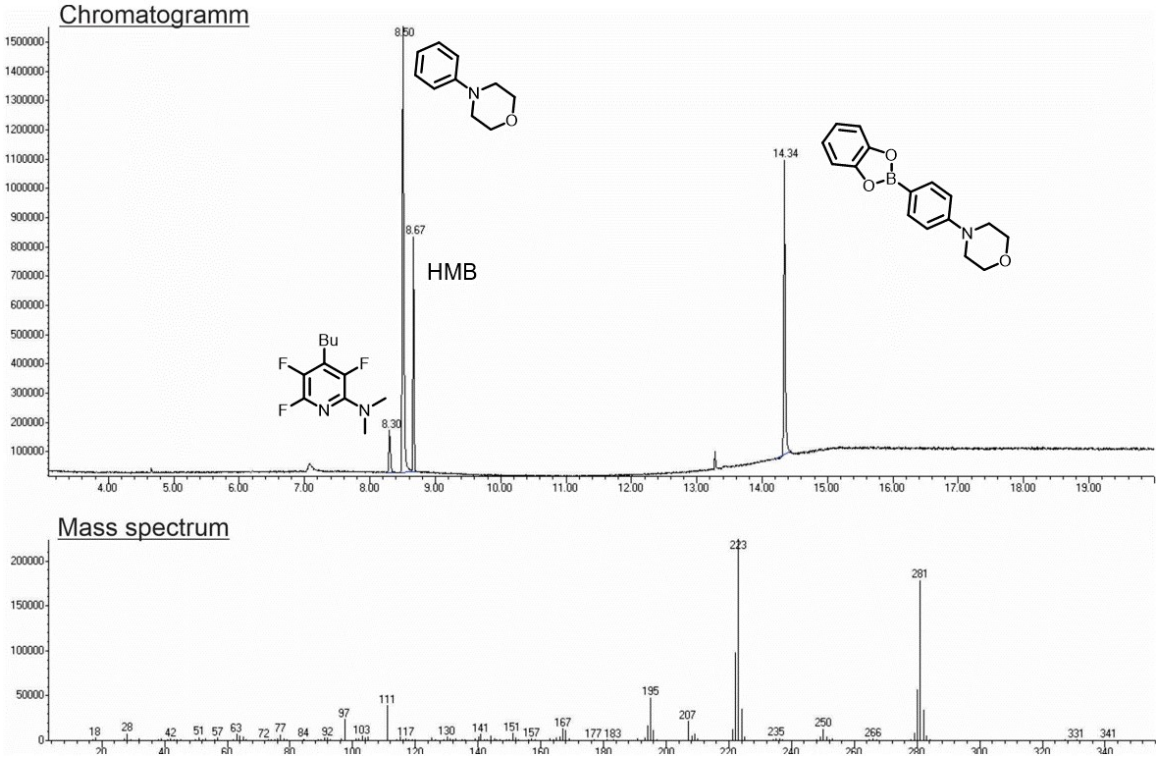
GC-MS data after reaction. Mass spectrum depicts peak of the product at 14.31 seconds.

Before heating



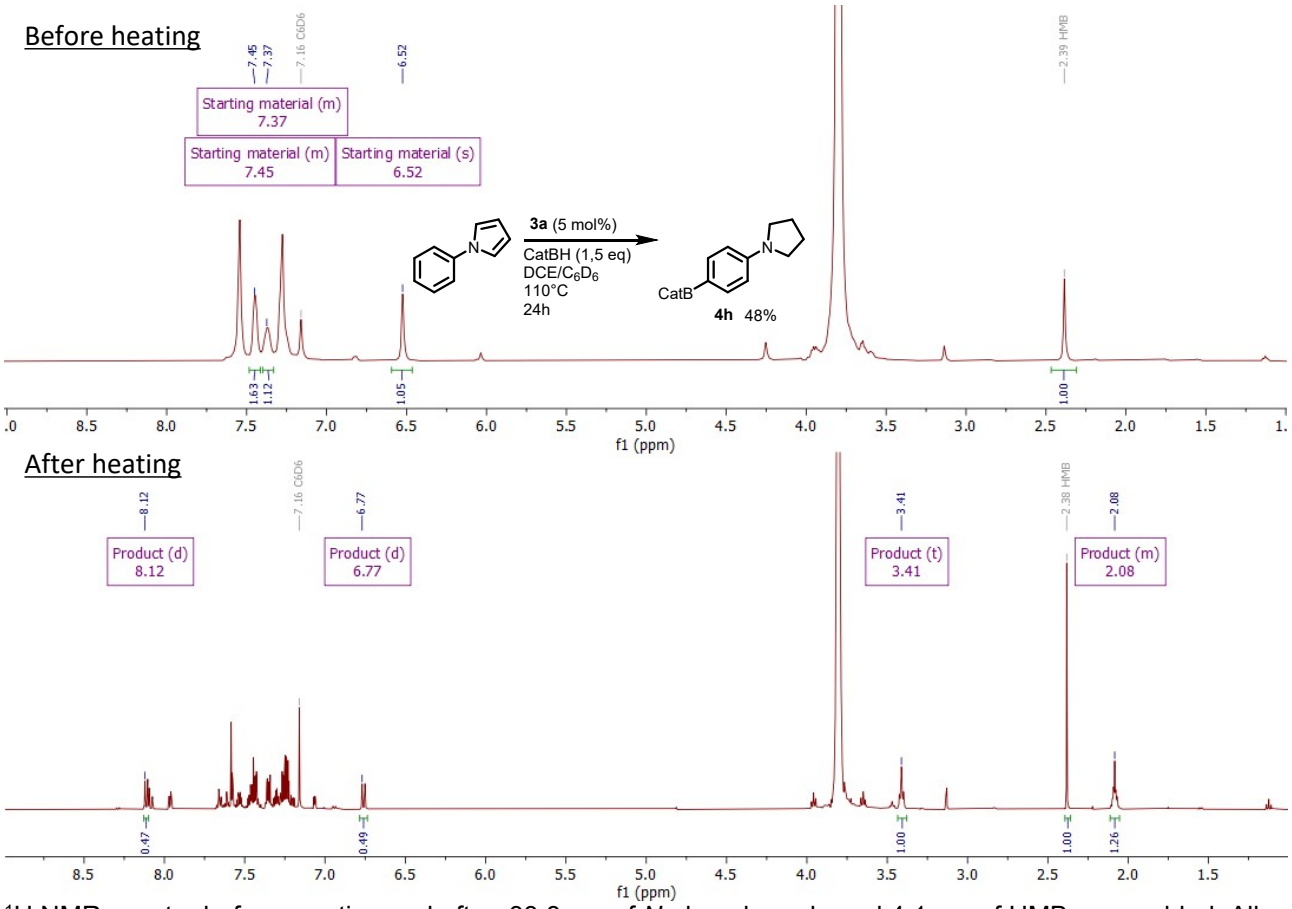
After heating

^{1}H NMR spectra before reaction and after. 54.4 mg of 1-phenylmorpholine and 6.2 mg of HMB were added. All signals are aligned to DCE at 3.80. All signals are shifted from original place in C_6D_6 because of high amount DCE. Conversion is determined by integration of the signals of starting material from δ 3.26 and the

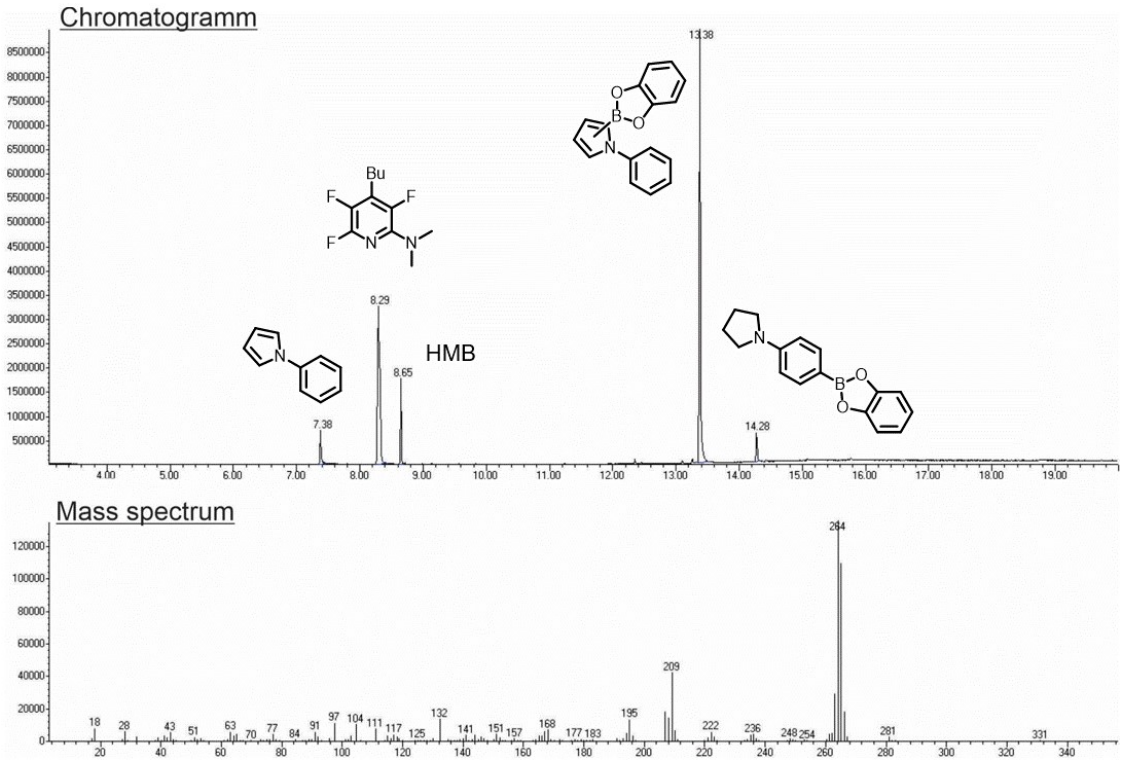


product from δ 3.33.

GC-MS data after reaction. Mass spectrum depicts peak of the product at 14.34 seconds.



^{1}H NMR spectra before reaction and after. 33.8 mg of *N*-phenylpyrrole and 4.1 mg of HMB were added. All signals are aligned to C_6D_6. All signals are shifted from original place in C_6D_6 because of high amount DCE.

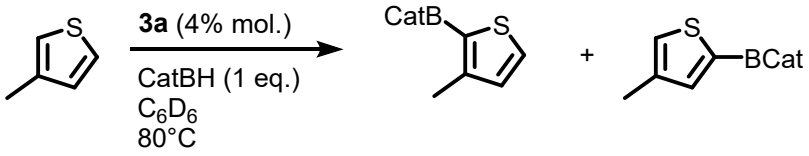


Conversion is determined by integration of the signals of starting material from δ 6.52 and the product from δ 3.41.

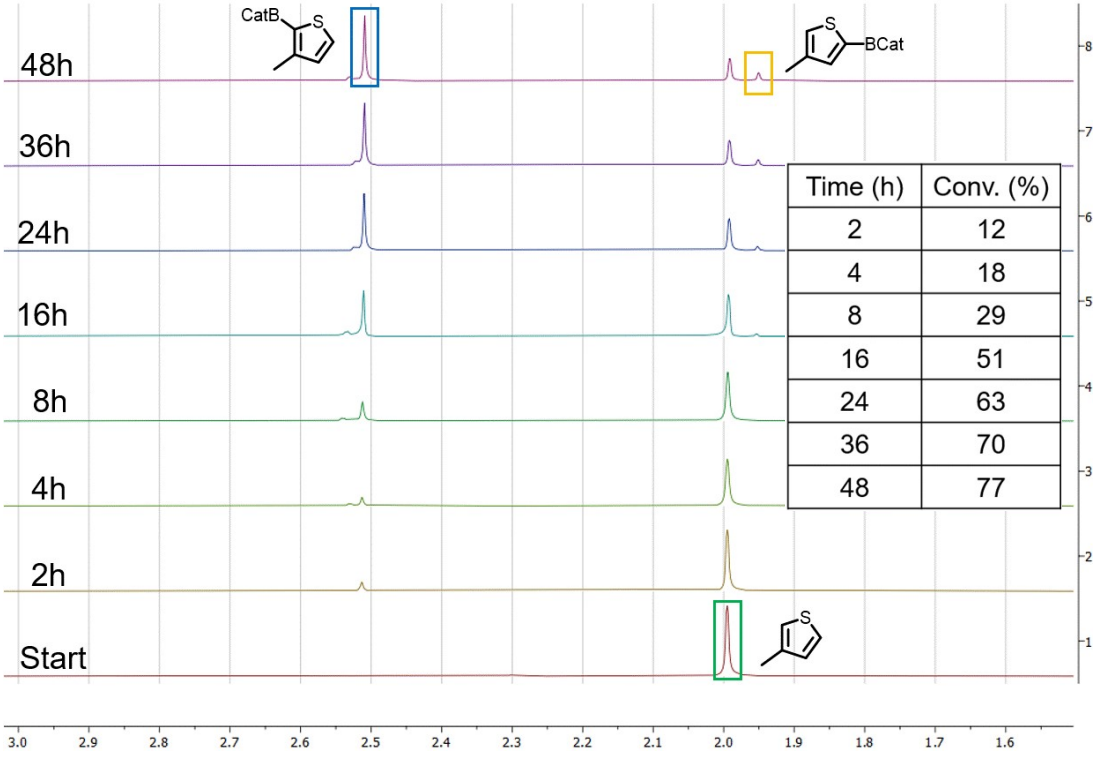
GC-MS data after reaction. Mass spectrum depicts peak of the product at 14.28 seconds.

Mechanistic studies

Time-depemdent ^{1}H and ^{11}B NMR of C-H borylation of 3-methylthiophene with catalyst 3a

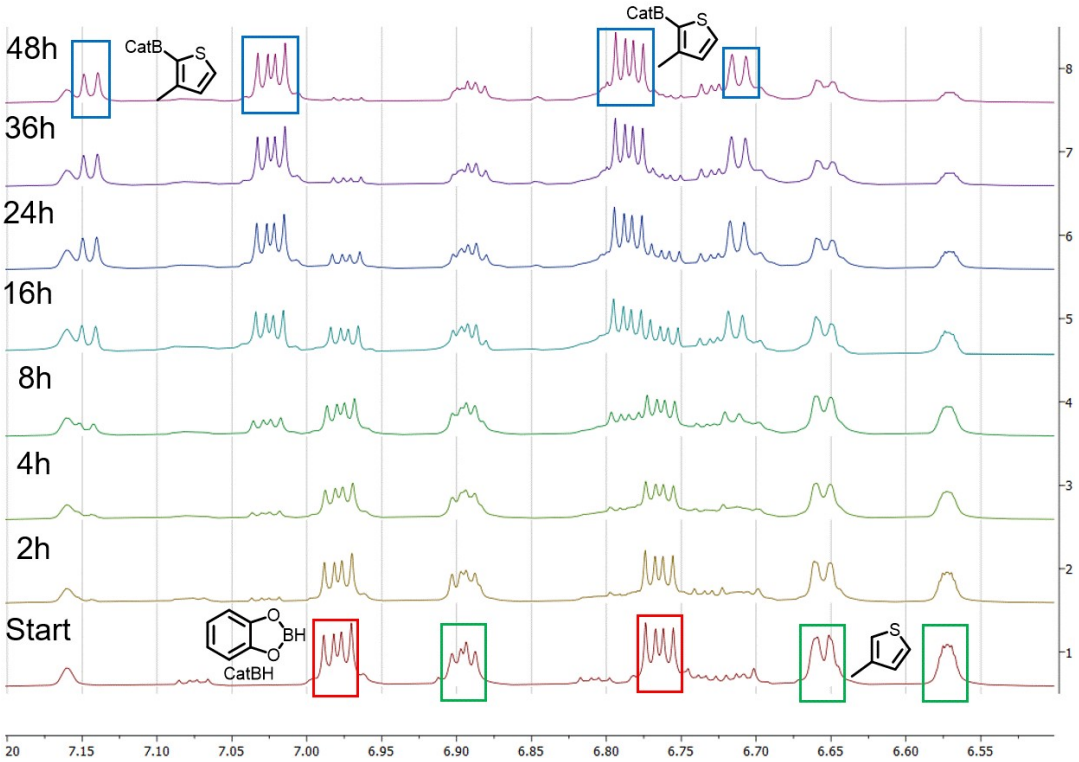


In a J. Young-NMR tube, 3-methylthiophene (50mg, 0.509 mmol), **3a** (18,59 mg, 0.020 mmol) and CatBH (61.08mg, 0.509 mmol) were mixed in 650 µL C_6D_6 and shaked for 1 minute. Before heating, ^{1}H and ^{11}B NMR of sample were recorded as a reference. Further, J. Young-NMR tube were placed in oil bath at 80°C. After 2, 4, 8, 16, 24, 36 and 48 hours, ^{1}H and ^{11}B NMR of sample were recorded. Conversion was calculated based on integration of ^{1}H spectrum between 1.5 and 3.0 ppm. Hydrogen (H_2) peak increased over time.

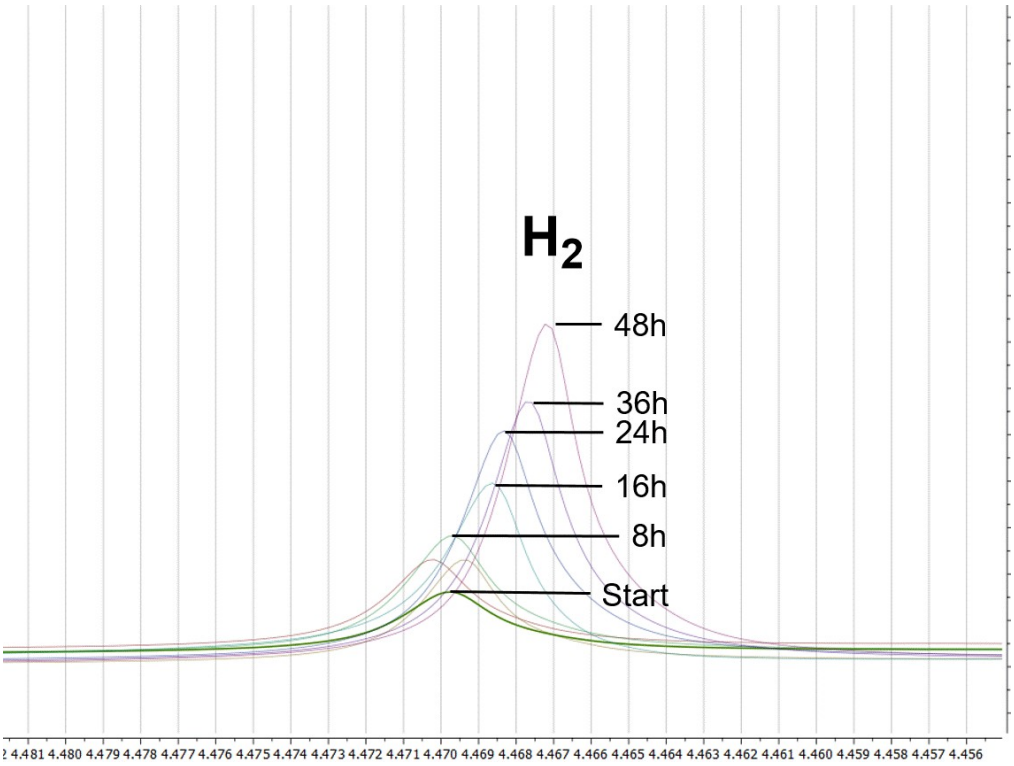


Time (h)	Conv. (%)
2	12
4	18
8	29
16	51
24	63
36	70
48	77

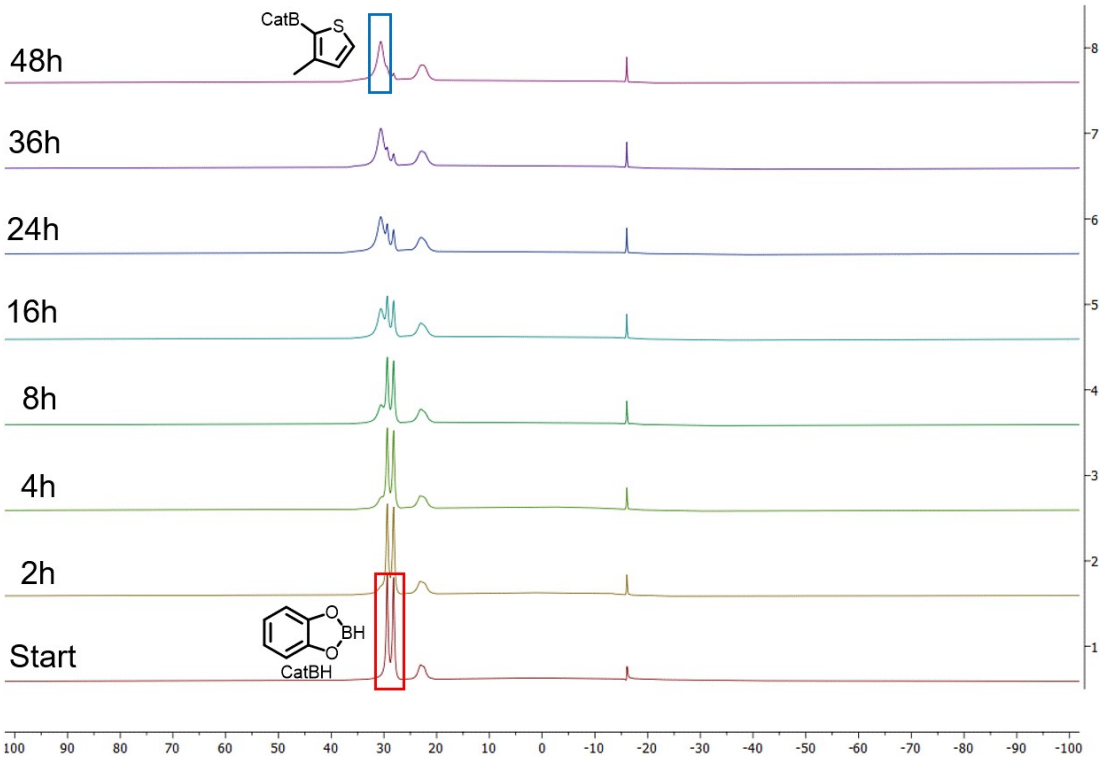
Stacked aliphatic part of ^{1}H NMR.



Stacked aromatic part of ^{1}H NMR.

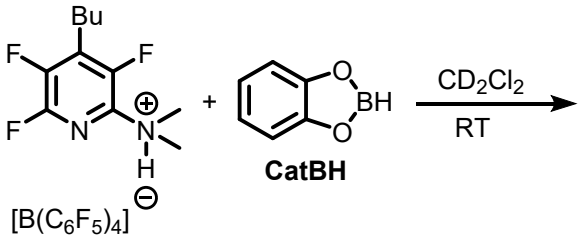


Stacked ^{1}H NMR of hydrogen molecule (H_2) area.



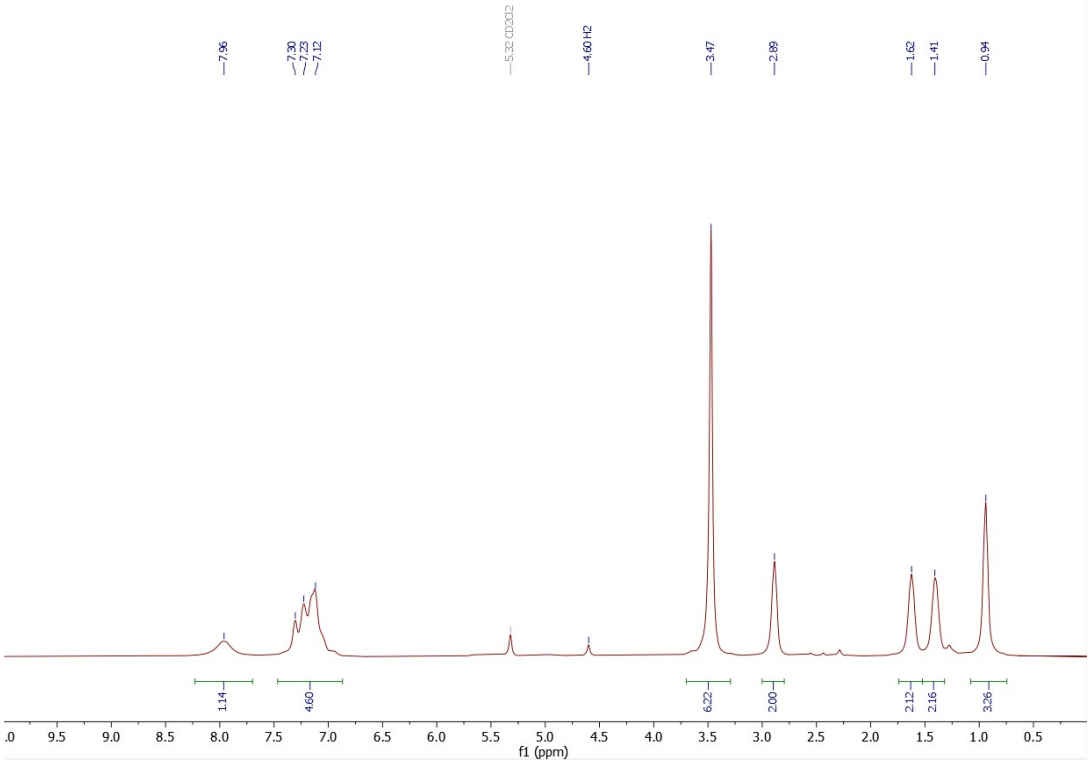
Stacked ^{11}B NMR.

Stochiometric reaction between CatBH and 3a at RT

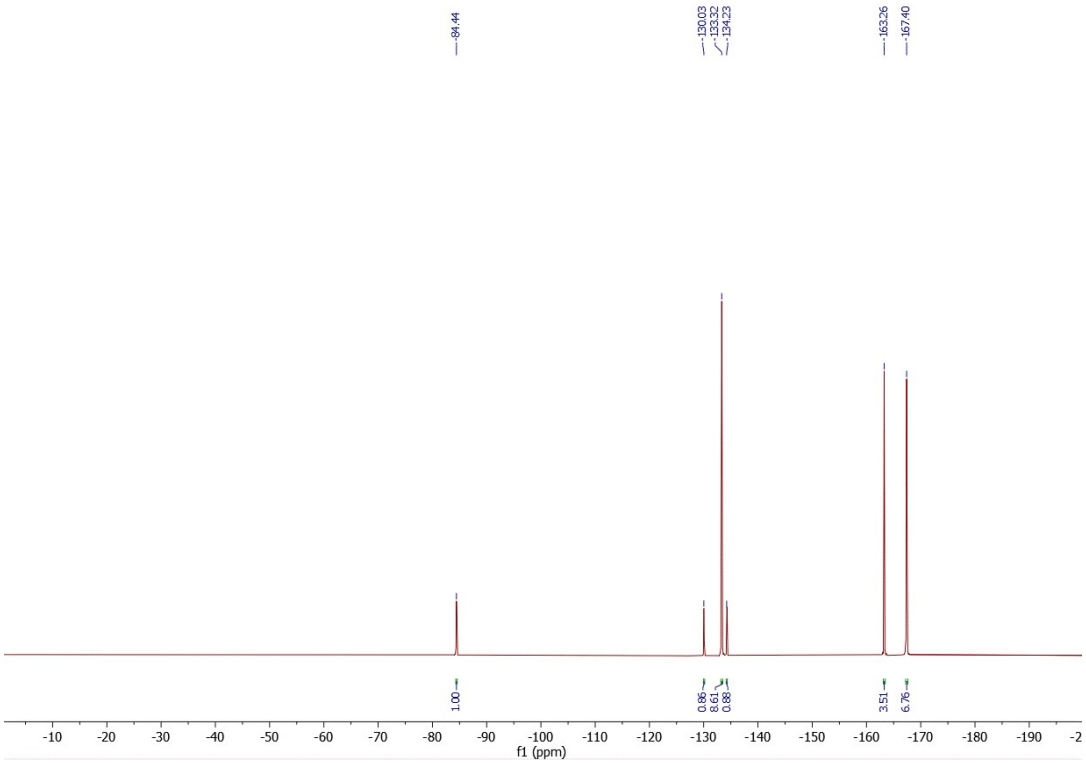


3a

In a J. Young-NMR tube, **3a** (70.5 mg, 0.077 mmol) and CatBH (9.3 mg, 0.077 mmol) were mixed in 700 µL CD_2Cl_2 and shaked for 1 minute upon RT. After 45 minutes, NMR spectra were recorded. New broad singlet at 7.96 was observed. Hydrogen (H_2) at 4.60 ppm was observed. Formation of Cat_3B_2 was observed at 22.38 ppm in ^{11}B NMR.

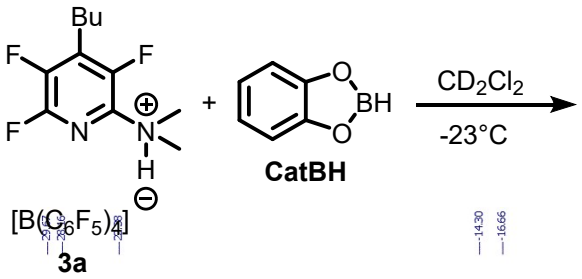


^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.96 (s, 1H), 7.47 – 6.87 (m, 5H), 3.47 (s, 6H), 2.89 (s, 2H), 1.62 (s, 2H), 1.41 (s, 2H), 0.94 (s, 3H).

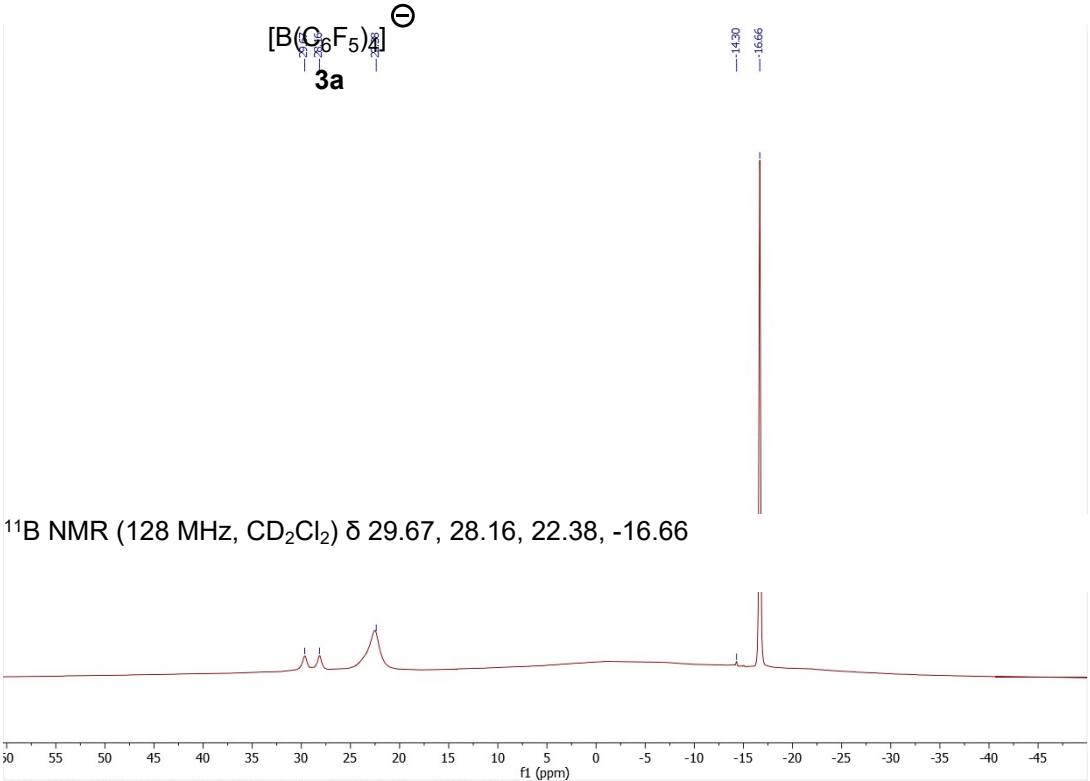


^{19}F NMR (376 MHz, CD_2Cl_2) δ -84.44 (dd, J = 28.1, 21.2 Hz), -130.05 (dd, J = 21.5, 9.0 Hz), -133.32, -134.26 (dd, J = 27.7, 9.0 Hz), -163.26 (t, J = 20.5 Hz), -167.40 (t, J = 19.1 Hz).

Stochiometric reaction between CatBH and 3a at -23°C

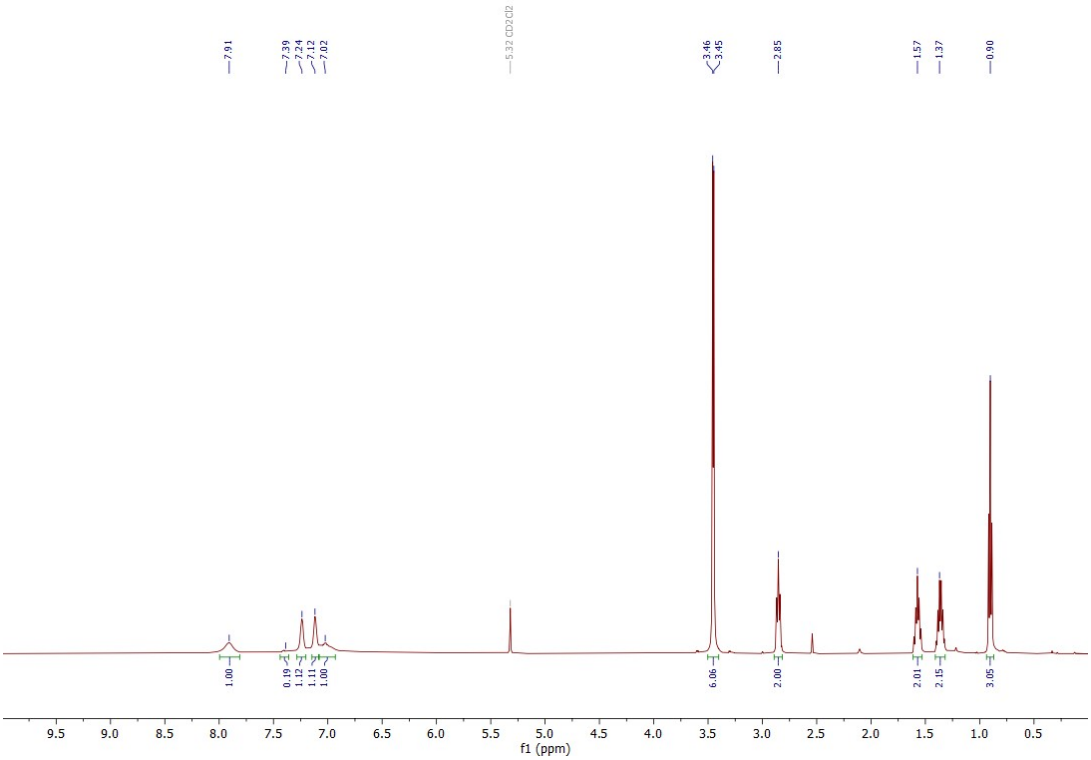


3a

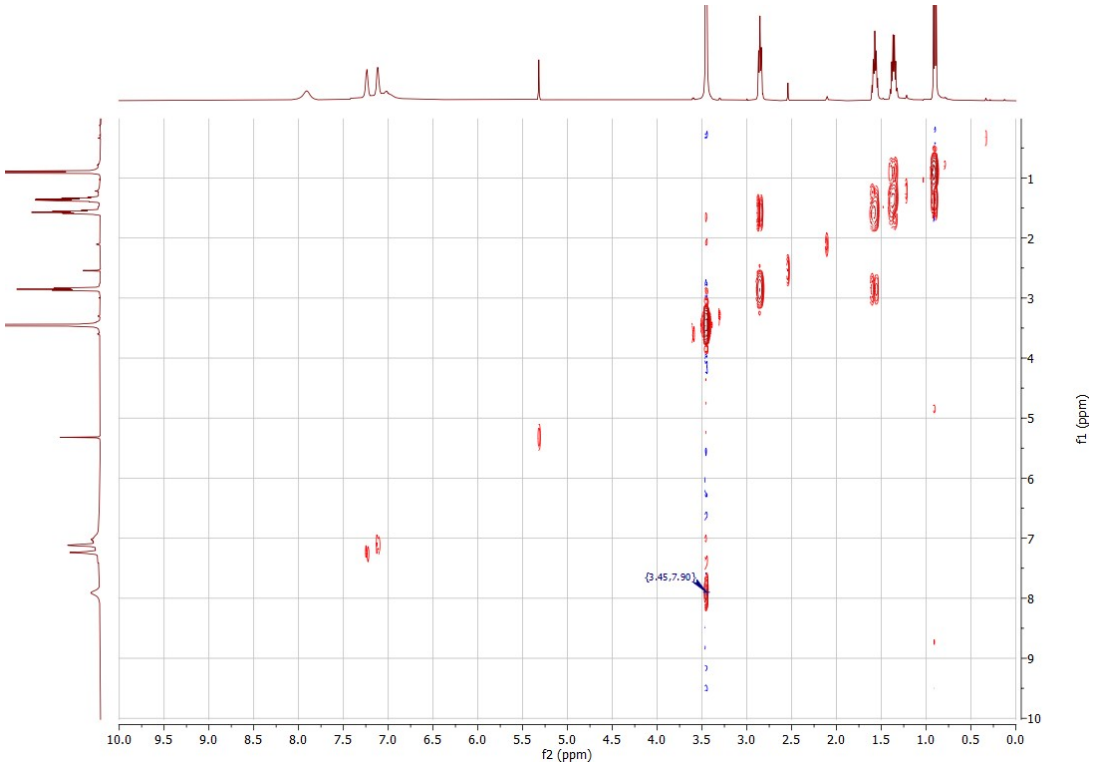


^{11}B NMR (128 MHz, CD_2Cl_2) δ 29.67, 28.16, 22.38, -16.66

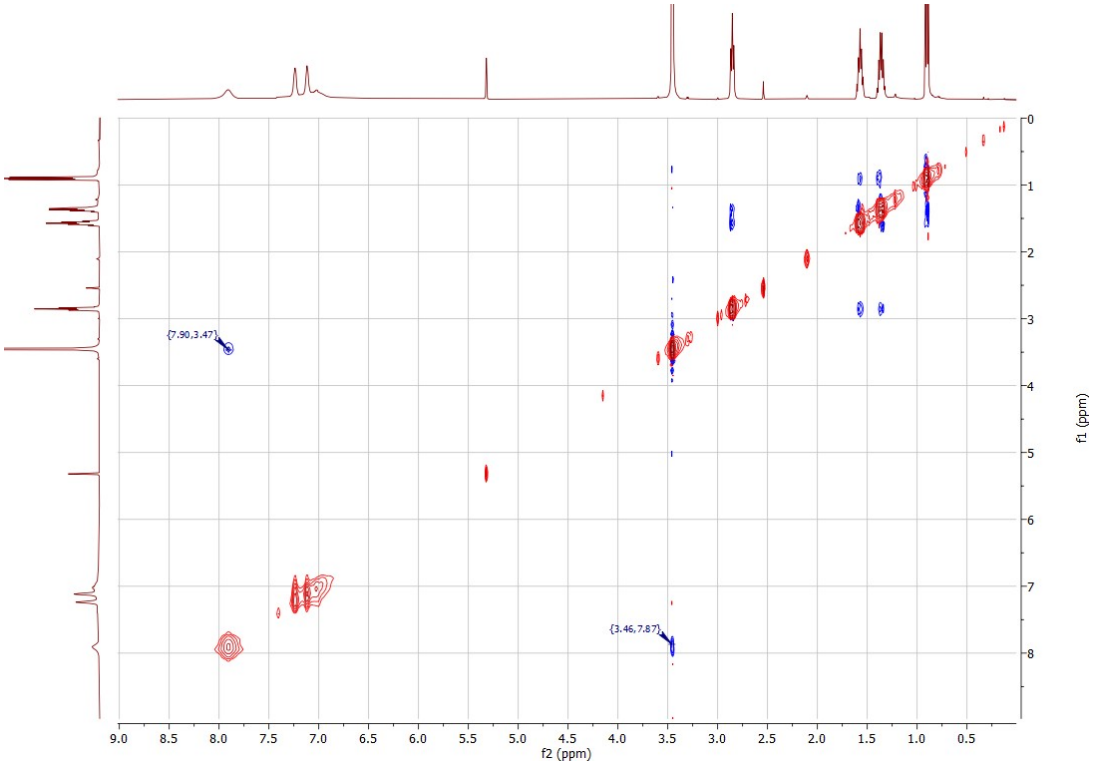
In a J. Young-NMR tube, **3a** (70.5 mg, 0.077 mmol) was dissolved in 700 µL CD_2Cl_2. The sample was frozen at -80°C. The frozen sample was transferred in glovebox and CatBH (9.3 mg, 0.077mmol) was added. The J. Young-NMR tube was delivered in precooled NMR spectrometer at -23°C. After 30 minutes, NMR spectra were recorded.



^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.91 (s, 1H), 7.28 – 7.20 (m, 1H), 7.15 – 7.08 (m, 1H), 7.08 – 6.93 (m, 1H), 3.45 (d, J = 5.2 Hz, 6H), 2.85 (t, J = 7.8 Hz, 2H), 1.57 (p, J = 7.7 Hz, 2H), 1.36 (h, J = 7.3 Hz, 2H), 0.90 (t, J = 7.4 Hz, 3H).

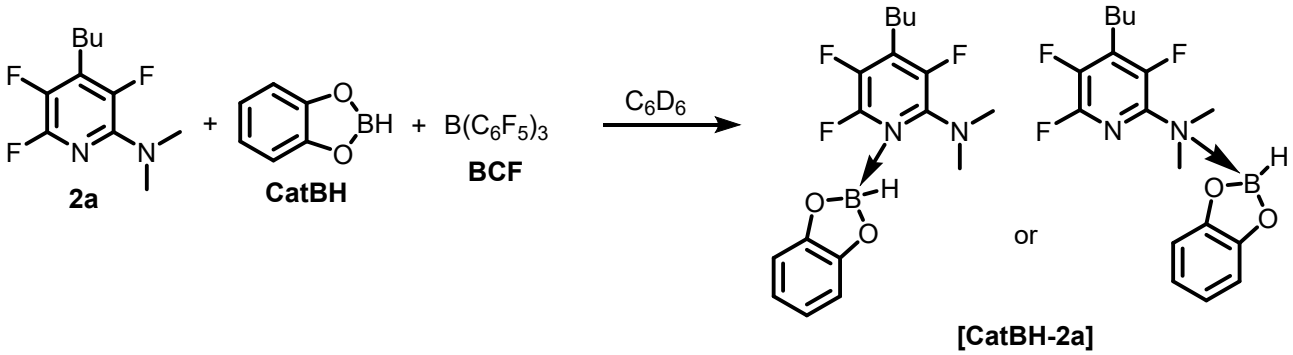


^{1}H-^{1}H COSY NMR (500 MHz, CD_2Cl_2). Cross-peak at {3.45, 7.90} shows correlation between NH and dimethylamino group. This cross-peak demonstrates artifact, where it does not have visible symmetric counterpart at {7.90, 3.45}. Such artifacts can occur when there are big differences in T_2-values of the coupling partners and the acquisition times in indirectly detected dimension f_1, t_{1max}, and in directly detected f_2-dimension ,t_2, are very different (as is commonly the case). The severity then is dependent on the utilized window functions[5]. Here, the observed COSY cross peak between NH and dimethyl group indicate existing $^{2}J_{HH}$ and thus acidic proton is still bonded to dimethylamino group.



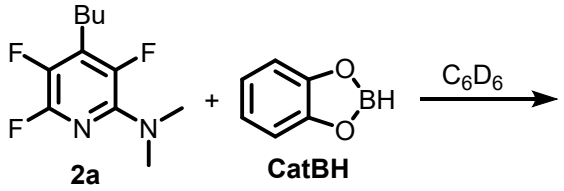
NOESY NMR (500 MHz, CD_2Cl_2). NOESY cross-peaks at {7.90, 3.47} and {3.46, 7.87} show correlation between NH and dimethylamino group, indicating proximity of dimethylamino group and acidic proton.

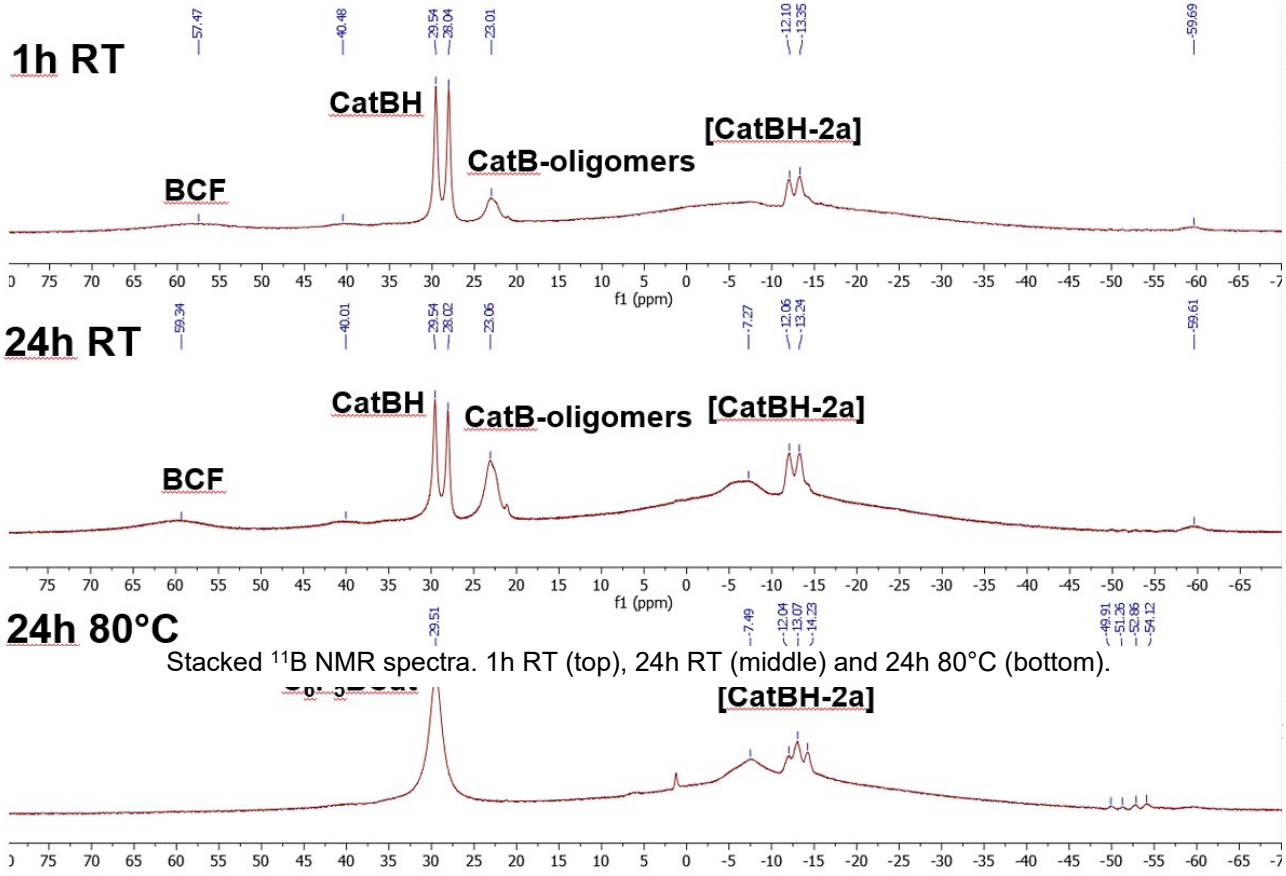
Stochiometric reaction between CatBH, 2a and BCF



[CatBH-2a]

In a J. Young-NMR tube, **2a** (15 mg, 0.065 mmol), CatBH (7.7 mg, 0.065 mmol) and BCF (33.1 mg, 0.065 mmol) were dissolved in 700 µL C_6D_6. ^{11}B NMR spectra were recorded after 1h and 24h. Then, the sample was heated 24h additionally at 80°C and ^{11}B NMR was recorded again. [CatBH-**2a**] was observed at -12 ppm (doublet). After heating the sample all CatBH, BCF and CatB-oligomers are decomposed forming C_6F_5BCat signal at 29.5 ppm.[3]





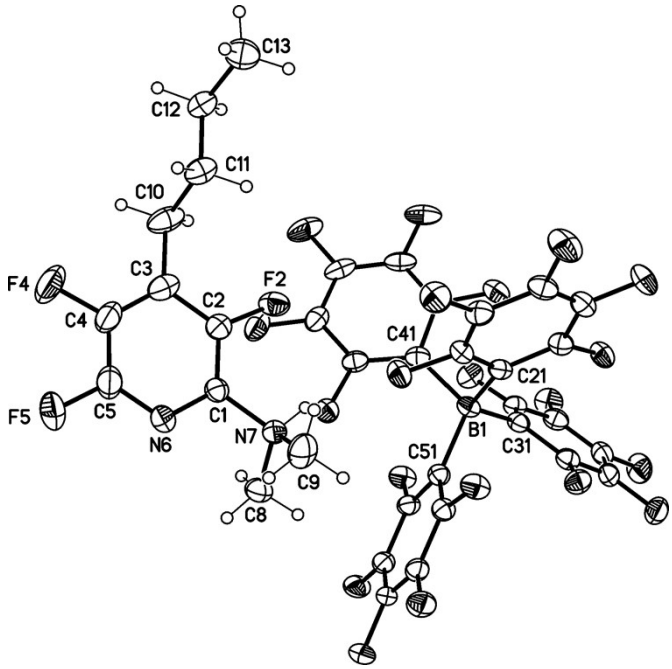
Stacked ^{11}B NMR spectra. 1h RT (top), 24h RT (middle) and 24h 80°C (bottom).

Crystal Structure Determination of 3a

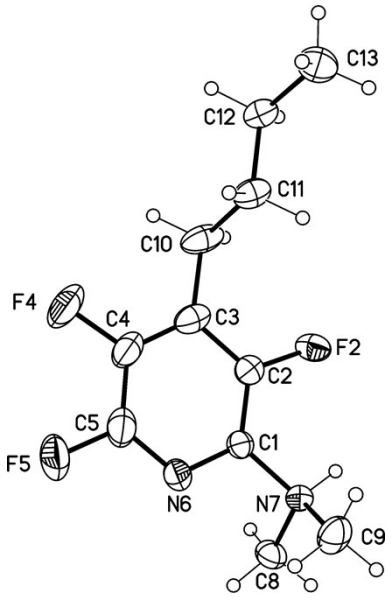
The single-crystal X-ray diffraction study was carried out on a STOE IPDS 2T diffractometer with STOE image plates detector at 120(2) K using Mo-Kα radiation (λ = 0.71073 Å). Dual space methods (SHELXT)[5] were used for structure solution and refinement was carried out using SHELXL-2014 (full-matrix least-squares on F^2).[6] Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(N) free). An absorption correction by Gaussian integration (see cif-file for details) was applied. The absolute structure could not be determined reliably.[7]

3a colourless crystals, $C_{11}H_{16}F_3N_2 \cdot C_{24}BF_{20}$, M_r = 912.31, crystal size 0.25 × 0.13 × 0.08 mm, orthorhombic, space group *Pca*2$_1$ (No. 29), a = 20.8363(9) Å, b = 11.7036(4) Å, c = 14.1501) Å, V = 3450.6(2) Å^3, Z = 4, ρ = 1.756 Mg/m^{-3}, μ(Mo-K$_\alpha$) = 0.19 mm^{-1}, F(000) = 1808, $2\theta_{max}$ = 55.8°, T = 120 K, 24592 reflections, of which 8188 were independent (R_{int} = 0.061), 556 parameters, 2 restraints, R_1 = 0.039 (for 6724 I > 2σ(I)), wR_2 = 0.089 (all data), S = 1.06, largest diff. peak / hole = 0.21 / -0.21 e Å^{-3}. x = 0.4(4).

CCDC 2288120 (**3a**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



Molecular structure of **3a** (displacement parameters are drawn at 50 % probability level). Selected bond lengths (Å): C1—N7 = 1.470(5); C1—N6 = 1.322(5); N7—C9 = 1.499(5); N7—C8 = 1.513(5); Selected bond angles (°): N6—C1—N7 = 115.1(3); C9—N7—C8 = 111.6(3).



Molecular structure of the cation of **3a** (displacement parameters are drawn at 50 % probability level).

Computing details

Data collection: *X-AREA* WinXpose 2.0.22.0[8]; cell refinement: *X-AREA* Recipe 1.37.0.0[9]; data reduction: *X-AREA* Integrate 2.5.1.0[9], *X-AREA X-RED* 2.3.0.0[9]; program(s) used to solve structure: SHELXT[7]; program(s) used to refine structure: *SHELXL2014*/7[7].

3-butyl-2,4,5-trifluoro-N,N-dimethylpyridinium tetrakis(perfluorophenyl)borate (3a)

*Crystal data for **3a***

$C_{11}H_{16}F_3N_2 \cdot C_{24}BF_{20}$	D_x = 1.756 Mg m^{-3}
M_r = 912.31	Mo $K\alpha$ radiation, λ = 0.71073 Å
Orthorhombic, $Pca2_1$ (no.29)	Cell parameters from 19082 reflections
a = 20.8363 (9) Å	θ = 2.4–28.5°
b = 11.7036 (4) Å	μ = 0.19 mm^{-1}
c = 14.1501 (4) Å	T = 120 K
V = 3450.6 (2) Å^3	Blocks, colourless
Z = 4	0.25 × 0.13 × 0.08 mm
F(000) = 1808	

*Data collection for **3a***

STOE IPDS 2T diffractometer with STOE inamge plate detector	8188 independent reflections
Radiation source: sealed X-ray tube, 12 x 0.4 mm long-fine focus	6724 reflections with $I > 2\sigma(I)$
Plane graphite monochromator	R_{int} = 0.061
Detector resolution: 6.67 pixels mm^{-1}	θ_{max} = 27.9°, θ_{min} = 2.4°
rotation method, ω scans 1°	h = -23→27
Absorption correction: integration STOE *X-RED32*, absorption correction by Gaussian integration, analogous to Coppens P.[10]	k = -13→15
T_{min} = 0.953, T_{max} = 0.986	l = -18→18
24592 measured reflections	

*Refinement for **3a***

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)]$ = 0.039	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.089	$w = 1/[\sigma^2(F_o^2) + (0.0296P)^2 + 1.4933P]$ where $P = (F_o^2 + 2F_c^2)/3$
S = 1.06	$(\Delta/\sigma)_{max} < 0.001$

8188 reflections	$\Delta\rangle_{max}$ = 0.21 e Å^{-3}
556 parameters	$\Delta\rangle_{min}$ = -0.21 e Å^{-3}
2 restraints	Absolute structure: Flack x determined using 2690 quotients [(I+)-(I-)]/[(I+)+(I-)][7]. Absolute structure cannot be determined reliably.
Primary atom site location: dual	Absolute structure parameter: 0.4 (4)

Computational details

All computational work reported here was carried out at the density functional theory (DFT) level, using Gaussian16 (Revision C.02).[11] The exchange correlation functional PBE1PBE[12-14] was employed in conjunction with the Def2-TZVP[15,16] basis set, Grimme's empirical dispersion correction (GD3BJ)[17] and an ultrafine integration grid for the optimization and frequency calculations. Single-point calculations were performed for the Def2-TZVP optimized geometries at the PBE1PBE-GD3BJ/Def2-TZVP (PCM, solvent = dichloroethane)[14,16,18] level. The nature of the stationary points and transition states was confirmed by analytical frequency calculations at the Def2-TZVP level and are characterized by zero (minima) or one (transition state) imaginary frequency. Intrinsic reaction coordinate (IRC) calculations were done to the optimized TS structures to ensure the transition states are connected to the respective minima on the potential energy surface.

Optimised xyz-coordinates

3a + HBcat

46
SCF done: -1243.838719

B	1.866977	0.959535	-1.840347
O	2.994624	0.405045	-2.440674
C	3.834768	0.088258	-1.395290
C	3.229635	0.461119	-0.206173
O	2.010596	1.025022	-0.475604
C	5.074242	-0.504219	-1.439223
C	5.696562	-0.719395	-0.210201
C	5.089165	-0.350047	0.986032
C	3.833548	0.254877	1.012608
H	3.355622	0.546773	1.939597
H	5.604375	-0.533627	1.921505
H	6.676008	-1.182345	-0.189136
H	5.542523	-0.781676	-2.375444
N	1.172130	-1.959560	-1.648816
C	1.431529	-2.747020	-2.673955
N	2.285733	-2.155988	-3.699708
C	0.933396	-4.027797	-2.765857
F	1.215003	-4.785825	-3.822811
C	0.133178	-4.549947	-1.752728
C	-0.446272	-5.922060	-1.833867
C	-0.116122	-3.696233	-0.694672
F	-0.869055	-4.085650	0.322795
C	0.423943	-2.417073	-0.688963
F	0.175709	-1.614347	0.330143
H	0.924612	1.339997	-2.443122
C	1.579548	-1.949832	-4.996759
H	2.509817	-1.216222	-3.333350
C	3.584626	-2.869456	-3.868718
H	4.204991	-2.264772	-4.527036
H	4.050140	-2.971240	-2.891203
H	3.402577	-3.843000	-4.314994
H	2.248236	-1.392463	-5.649376
H	1.344402	-2.916778	-5.432765
H	0.672943	-1.379718	-4.805293
H	-0.586894	-6.309521	-0.822979
C	-1.781342	-5.928228	-2.580710
H	0.263104	-6.577170	-2.344263
C	-2.368105	-7.324967	-2.685148
H	-2.485683	-5.267844	-2.063451
H	-1.637257	-5.511948	-3.583737
C	-3.696719	-7.342465	-3.418233
H	-1.652580	-7.977362	-3.198271
H	-2.495065	-7.737321	-1.677916
H	-4.101231	-8.355604	-3.484267
H	-4.437689	-6.721292	-2.906275
H	-3.590220	-6.959593	-4.437647

3-Methyl-thiophene

12
SCF Done: -592.0493486

C	2.068899	0.000043	0.444658
C	1.284786	-0.000589	-0.743319
C	-0.055183	-0.000785	-0.500019
S	-0.384248	-0.000203	1.173095
C	1.278541	0.000308	1.558659
C	3.562002	0.000372	0.460793
H	-0.863050	-0.001240	-1.215617
H	1.708019	-0.000887	-1.740133
H	1.597234	0.000780	2.590450
H	3.946478	0.000856	1.481310
H	3.962074	-0.880150	-0.049397
H	3.961694	0.880667	-0.050088

TS1

46
SCF Done: -1243.792262

B	2.544709	-1.237352	-1.532899
O	3.940751	-1.292848	-1.588386
C	4.341409	-0.497684	-0.529246
C	3.228820	-0.076518	0.184501
O	2.080626	-0.577425	-0.397790
C	5.617644	-0.148548	-0.164629
C	5.741193	0.657285	0.967519
C	4.628447	1.078463	1.682085
C	3.336726	0.715418	1.300503
H	2.463133	1.039476	1.851075
H	4.762460	1.704191	2.555553
H	6.728761	0.959226	1.293050
H	6.480228	-0.483304	-0.726219
N	1.828880	-2.616091	-1.886534
C	1.505203	-2.953942	-3.165311
N	1.939639	-2.052297	-4.155131
C	0.805161	-4.116641	-3.398352
F	0.522946	-4.446640	-4.648433
C	0.418515	-4.983617	-2.375743
C	-0.362601	-6.221842	-2.637061
C	0.804200	-4.609490	-1.101461
F	0.527834	-5.364352	-0.062894
C	1.522102	-3.444285	-0.888744
F	1.929543	-3.147751	0.304851
H	2.069549	-0.339665	-2.565761
C	0.973454	-1.701703	-5.204305
H	2.057364	-0.923246	-3.247878
C	3.293711	-2.333321	-4.669921
H	3.615373	-1.475551	-5.260135
H	3.983220	-2.462551	-3.836737
H	3.289299	-3.226521	-5.299110
H	1.298404	-0.761950	-5.651505
H	0.917649	-2.465506	-5.979791
H	-0.011136	-1.556257	-4.761308
H	-0.125667	-6.964441	-1.873227
C	-1.871122	-5.932058	-2.624947
H	-0.075968	-6.631371	-3.607557
C	-2.685806	-7.188103	-2.887183
H	-2.149803	-5.504339	-1.656167

H	-2.102303	-5.175281	-3.382352
C	-4.179213	-6.916149	-2.875811
H	-2.391452	-7.613302	-3.852711
H	-2.438734	-7.940848	-2.131088
H	-4.744480	-7.829824	-3.065222
H	-4.502568	-6.520634	-1.909731
H	-4.456073	-6.189789	-3.644158

Int1

44

SCF Done: -1242.650389

C	1.682717	0.225995	1.179602
C	1.664421	0.014969	-0.189556
C	2.397533	0.780918	-1.063000
C	3.164449	1.790369	-0.487218
C	3.183094	2.002168	0.888189
C	2.436096	1.216257	1.761503
O	0.821060	-1.051310	-0.469098
B	0.360179	-1.426431	0.753772
O	0.847545	-0.697871	1.789061
N	-2.233950	-1.509888	-0.378031
C	-2.996540	-1.533321	-1.617522
C	-1.761037	-2.624331	0.195360
C	-2.412013	-3.870566	0.148198
C	-1.961191	-4.990063	0.808322
C	-0.783163	-4.853851	1.557235
C	-0.145559	-3.655116	1.604658
N	-0.589464	-2.574544	0.911567
F	-0.300076	-5.874937	2.237464
C	-2.685807	-6.289203	0.757880
C	-2.131707	-7.185150	-0.359094
C	-2.849576	-8.523597	-0.414099
C	-2.313545	-9.418798	-1.516696
F	-3.577105	-3.931124	-0.485172
F	0.960308	-3.481302	2.275804
C	-2.061080	-0.192405	0.206190
H	-4.066353	-1.414895	-1.432999
H	-2.649398	-0.702615	-2.234998
H	-2.821848	-2.455493	-2.163418
H	-3.027729	0.316344	0.190238
H	-1.748354	-0.263976	1.248424
H	-1.345171	0.413151	-0.355634
H	-2.576144	-6.796597	1.718560
H	-3.748236	-6.107033	0.590637
H	-2.233070	-6.669170	-1.319855
H	-1.060450	-7.346205	-0.199268
H	-2.748961	-9.025222	0.554268
H	-3.921260	-8.351822	-0.561594
H	-2.841326	-10.373478	-1.537937
H	-2.431633	-8.952710	-2.498276
H	-1.250957	-9.630452	-1.373287
H	2.382788	0.604912	-2.130592
H	3.763952	2.424454	-1.128188
H	3.796046	2.797984	1.292253
H	2.447357	1.371424	2.832295

H_2

2

SCF Done: -1.168412961

H	0.000000	0.000000	-0.053207
H	0.000000	0.000000	0.693207

TS2

56

SCF Done: -1834.692733

C	2.983299	-1.144031	-1.113201
C	2.865531	-1.737175	0.135645
C	3.740008	-2.706631	0.569227
C	4.751932	-3.070401	-0.316401
C	4.867742	-2.477920	-1.569203
C	3.978575	-1.493420	-1.995391
O	1.791144	-1.203973	0.794429
B	1.336695	-0.161113	-0.034468
O	1.995539	-0.213618	-1.272509
C	1.911624	1.532832	0.866679
C	1.551268	2.585868	0.001030
C	2.637945	3.030592	-0.756002
C	3.821130	2.435066	-0.384109
S	3.640626	1.329930	0.870795
C	0.183117	3.162351	-0.105614
N	-0.239881	0.015958	-0.085434
C	-0.992487	-0.057974	1.064404
C	-2.358876	0.143741	0.966416
C	-3.027019	0.443181	-0.215903
C	-2.218646	0.503184	-1.333053
C	-0.856359	0.286140	-1.243557
N	-0.350550	-0.300886	2.263927
C	-0.661512	0.595690	3.369442
F	-3.081005	0.017460	2.070739
C	-4.503860	0.607102	-0.287226
C	-5.200983	-0.741549	-0.513893
C	-6.711192	-0.590567	-0.588768
C	-7.411681	-1.918164	-0.815175
F	-2.721467	0.775046	-2.520918
F	-0.154991	0.387510	-2.332708
C	-0.266378	-1.701472	2.674717
H	1.390113	1.308817	1.790120
H	4.795328	2.601288	-0.822511
H	2.569295	3.771844	-1.541233
H	0.211003	4.224546	0.151632
H	-0.196783	3.101427	-1.129387
H	-0.525415	2.681959	0.568541
H	3.643779	-3.161798	1.546668
H	5.463010	-3.831777	-0.021120
H	5.667111	-2.788175	-2.230629
H	4.062160	-1.026678	-2.968411
H	-4.861487	1.051864	0.643338
H	-4.750260	1.287457	-1.104666
H	-4.826803	-1.190540	-1.439999
H	-4.936477	-1.427102	0.298033

H	-7.073502	-0.131760	0.337562
H	-6.963601	0.105553	-1.395896
H	-8.493724	-1.787470	-0.865685
H	-7.089442	-2.381114	-1.751301
H	-7.199827	-2.620843	-0.005251
H	0.185569	0.587491	4.059100
H	-0.790714	1.615823	3.004647
H	-1.558362	0.305136	3.924678
H	0.559008	-1.811612	3.378503
H	-1.196110	-2.026329	3.156990
H	-0.059716	-2.334901	1.816671

Int2

56

SCF Done: -1834.687312

C	1.574184	2.477394	0.196944
C	1.103233	2.143077	-1.075349
C	0.553582	3.086725	-1.922581
C	0.487429	4.401306	-1.441019
C	0.954713	4.734574	-0.168399
C	1.511353	3.769753	0.682054
O	1.290424	0.801907	-1.291082
B	1.749254	0.303382	-0.052042
O	2.071312	1.356230	0.806658
C	2.743164	-0.983219	-0.113462
C	3.344341	-1.405427	1.134338
C	4.733454	-1.454787	1.073204
C	5.225193	-1.099231	-0.181417
S	4.040554	-0.694900	-1.297926
C	2.549960	-1.683572	2.356862
N	0.112450	-0.487333	0.596958
C	-0.505899	-1.382739	-0.210944
C	-1.883744	-1.539920	-0.130268
C	-2.675327	-0.830107	0.781231
C	-1.984865	0.038898	1.613503
C	-0.598450	0.167343	1.499420
N	0.291144	-2.162957	-1.081311
C	0.272285	-3.591636	-0.772375
F	-2.473780	-2.409586	-0.937948
C	-4.160471	-0.969469	0.823366
C	-4.843506	-0.057151	-0.203438
C	-6.360083	-0.183232	-0.174211
C	-7.046309	0.717235	-1.187804
F	-2.612907	0.744617	2.528187
F	0.020879	0.949119	2.344776
C	0.121938	-1.870662	-2.504952
H	1.957638	-1.684593	-0.557558
H	6.280235	-1.064051	-0.465654
H	5.377159	-1.732638	1.908806
H	3.162100	-2.155074	3.135452
H	2.156551	-0.731945	2.753555
H	1.682924	-2.323426	2.140332
H	0.194725	2.817366	-2.917091
H	0.061703	5.179790	-2.077170
H	0.886523	5.769073	0.173837
H	1.880469	4.018061	1.677985
H	-4.426991	-2.017803	0.620715
H	-4.515788	-0.723516	1.834584
H	-4.551081	0.988830	-0.008296
H	-4.468307	-0.301137	-1.212268
H	-6.638722	-1.235482	-0.358037
H	-6.722284	0.051850	0.841633
H	-8.139298	0.605358	-1.144529
H	-6.813783	1.778053	-1.004331
H	-6.728781	0.479934	-2.215493
H	1.083058	-4.083805	-1.329531
H	0.452240	-3.746269	0.301107
H	-0.680034	-4.077029	-1.045660
H	0.926500	-2.371138	-3.063763
H	-0.846501	-2.230514	-2.892990
H	0.210787	-0.789725	-2.666093

TS3

56

SCF Done: -1834.689761

C	1.551962	2.435835	0.216865
C	1.106641	2.118353	-1.059611
C	0.569405	3.064699	-1.899112
C	0.489851	4.366145	-1.403377
C	0.932703	4.682695	-0.126105
C	1.477595	3.713711	0.716387
O	1.305226	0.779617	-1.296971
B	1.751304	0.267286	-0.059625
O	2.051441	1.309015	0.822408
C	2.780769	-0.998568	-0.131074
C	3.356165	-1.419251	1.129847
C	4.732895	-1.326403	1.149591
C	5.253708	-0.885051	-0.060646
S	4.109037	-0.573711	-1.228441
C	2.535791	-1.840633	2.287416
N	0.109848	-0.564772	0.560597
C	-0.530269	-1.391866	-0.298454
C	-1.903267	-1.524073	-0.213060
C	-2.678590	-0.864085	0.738097
C	-1.967412	-0.073118	1.616967
C	-0.588922	0.034714	1.505134
N	0.253397	-2.123106	-1.216361
C	0.242979	-3.562645	-0.962716
F	-2.517707	-2.339695	-1.064920
C	-4.162446	-0.987154	0.788850
C	-4.837512	0.028303	-0.139986
C	-6.352178	-0.084357	-0.100436
C	-7.030568	0.918720	-1.015925
F	-2.576909	0.581147	2.587515
F	0.050765	0.744850	2.403434
C	0.024085	-1.797988	-2.623574
H	2.083602	-1.716681	-0.621982
H	6.304385	-0.732401	-0.276462
H	5.349007	-1.566021	2.005858
H	3.142837	-2.342892	3.039092

H	2.088301	-0.953209	2.748687
H	1.716993	-2.494566	1.986329
H	0.230876	2.811713	-2.895902
H	0.074429	5.144746	-2.030986
H	0.855540	5.703882	0.225859
H	1.827154	3.951845	1.712763
H	-4.448983	-1.998813	0.494022
H	-4.501691	-0.828641	1.814178
H	-4.533229	1.039928	0.149036
H	-4.481383	-0.124893	-1.164394
H	-6.645067	-1.101828	-0.381667
H	-6.696859	0.060279	0.929210
H	-8.116498	0.821078	-0.971920
H	-6.777943	1.944308	-0.734766
H	-6.726244	0.774065	-2.055808
H	1.030074	-4.025414	-1.561150
H	0.454685	-3.756772	0.090114
H	-0.709674	-4.036425	-1.222638
H	0.821359	-2.252467	-3.214734
H	-0.935525	-2.176928	-2.990822
H	0.071041	-0.719463	-2.756615

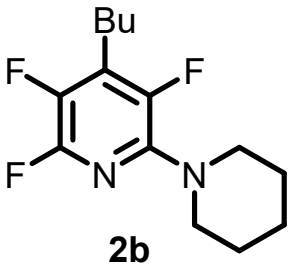
Product

56

SCF Done: -1834.729762

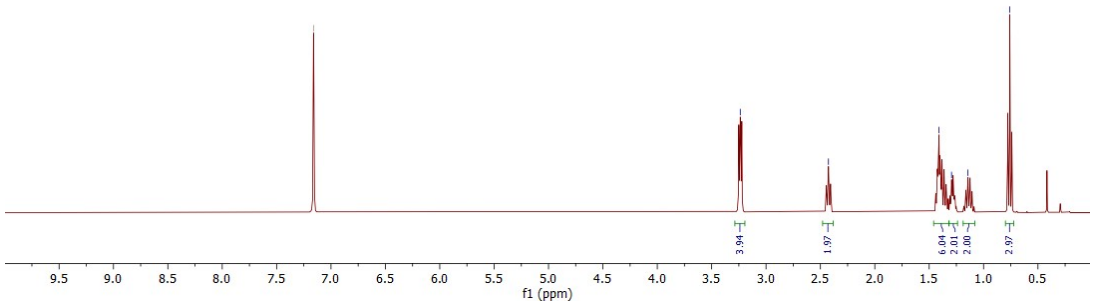
N	1.028592	-2.647516	0.360407
C	1.185921	-2.128274	1.755631
H	1.916834	-2.749426	2.269919
C	0.025317	-1.872250	-0.392537
N	0.470443	-1.011952	-1.275832
C	-0.405241	-0.320419	-1.950659
C	-1.780429	-0.451250	-1.757029
C	-2.277680	-1.358971	-0.836968
C	-1.310563	-2.080226	-0.143101
B	1.890688	1.373580	0.395271
C	3.286436	0.770559	0.284817
F	0.038218	0.513775	-2.857405
F	-2.604249	0.281612	-2.475741
C	-3.739530	-1.523916	-0.589336
C	-4.254447	-0.504743	0.430346
C	-5.743497	-0.651035	0.689498
C	-6.255313	0.374401	1.685313
F	-1.666215	-2.997045	0.761413
O	1.020610	1.166878	1.466221
C	-0.152748	1.779492	1.105370
C	-1.332978	1.861796	1.805953
C	-2.374806	2.548845	1.184404
C	-2.222065	3.113829	-0.076682
C	-1.018828	3.026345	-0.775165
C	0.003967	2.350509	-0.150344
O	1.273424	2.113228	-0.598197
H	-4.273360	-1.396542	-1.533672
H	-3.934318	-2.537918	-0.234483
H	-3.700706	-0.618693	1.369021
H	-4.035513	0.504083	0.068445
H	-6.285546	-0.550656	-0.257014
H	-5.952163	-1.662058	1.056104
H	-7.324950	0.254102	1.863695
H	-5.746255	0.279441	2.648291
H	-6.093448	1.392309	1.320738
H	-0.887464	3.471627	-1.752858
H	-3.052746	3.645022	-0.524772
H	-3.321099	2.650279	1.701540
H	-1.439666	1.432799	2.794381
C	4.113920	0.238603	1.260347
C	5.311116	-0.285304	0.713270
C	5.383657	-0.143495	-0.643424
S	4.011569	0.631585	-1.271806
H	6.189064	-0.445187	-1.296988
H	6.097847	-0.731702	1.308373
C	3.839436	0.251088	2.729222
H	3.942592	-0.749207	3.159649
H	4.567321	0.885534	3.241932
H	2.847087	0.633680	2.961301
C	2.343462	-2.726252	-0.340926
H	2.183970	-3.105306	-1.347109
H	2.774167	-1.728598	-0.382905
H	2.978829	-3.397369	0.233046
H	0.222472	-2.180491	2.256842
H	1.525634	-1.098265	1.694247
H	0.656922	-3.596355	0.436192

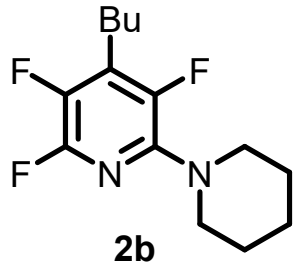
NMR data



2b

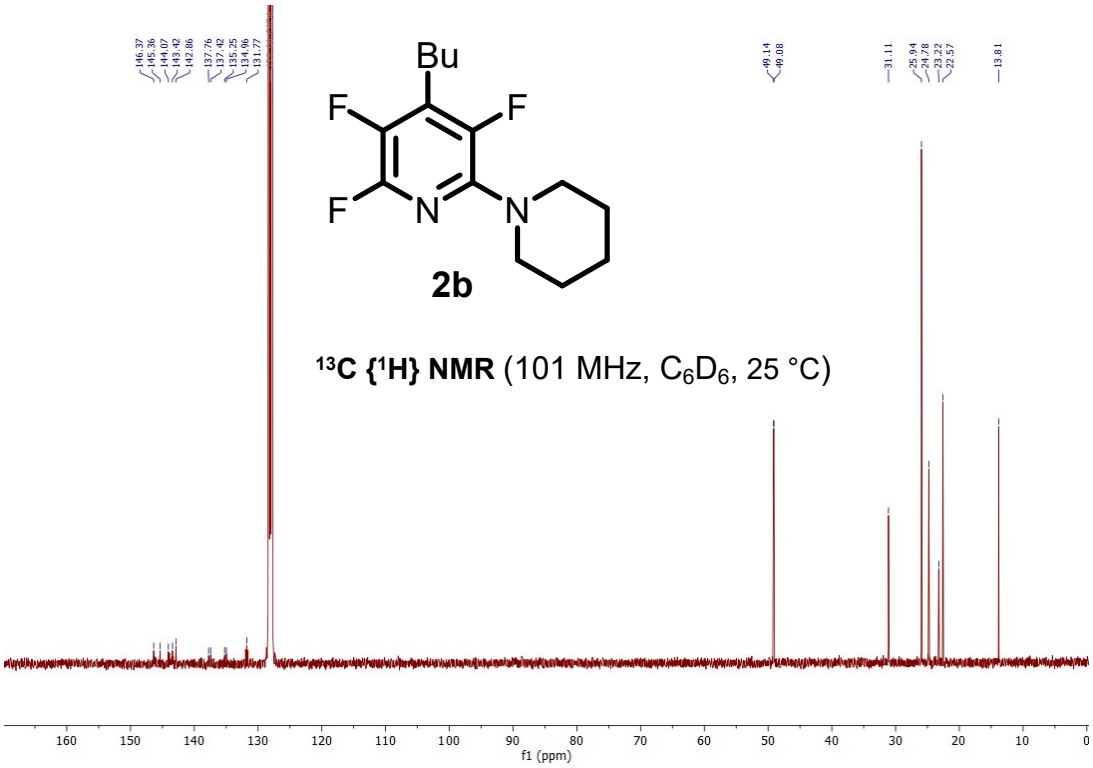
^{1}H NMR (400 MHz, C_6D_6, 25 °C)



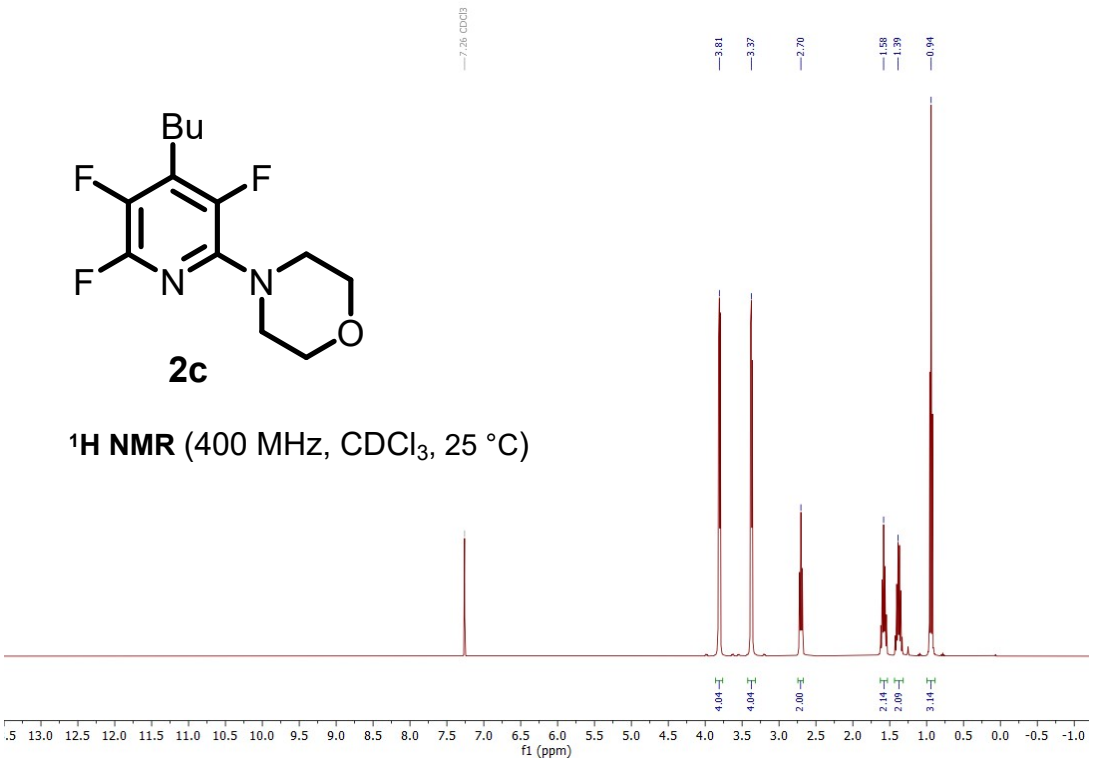


2b

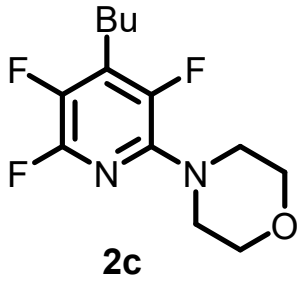
^{19}F {^{1}H} NMR (376 MHz, C_6D_6, 25 °C)



^{13}C {^{1}H} NMR (101 MHz, C_6D_6, 25 °C)

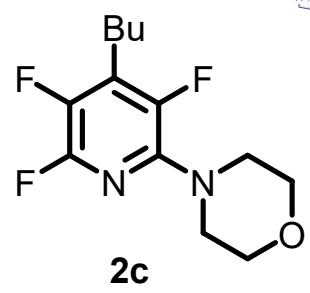


^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)



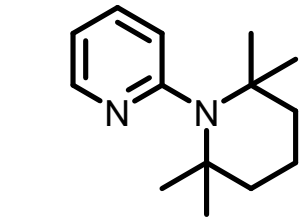
2c

^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$, 25°C)



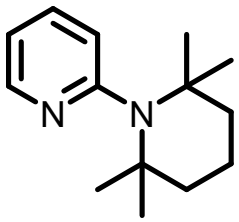
2c

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C)



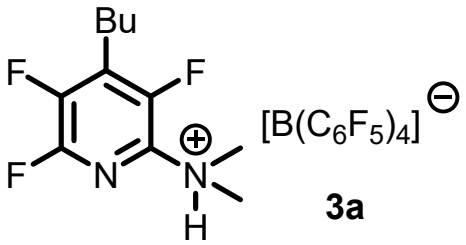
2e

^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)



2e

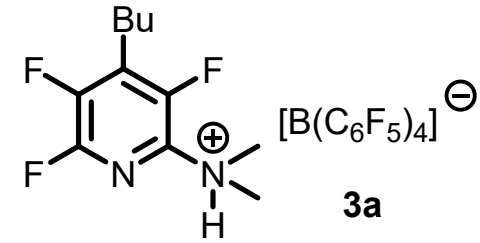
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C)



$[B(C_6F_5)_4]^{\ominus}$

3a

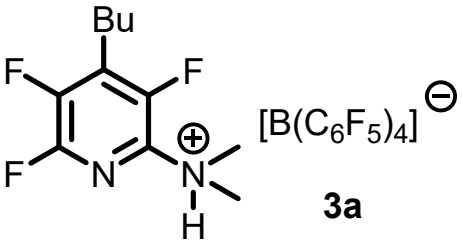
^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C)



$[B(C_6F_5)_4]^{\ominus}$

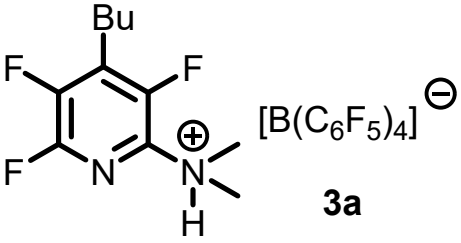
3a

^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2, 25 °C)



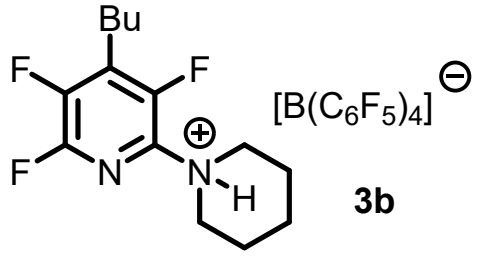
3a

^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C)



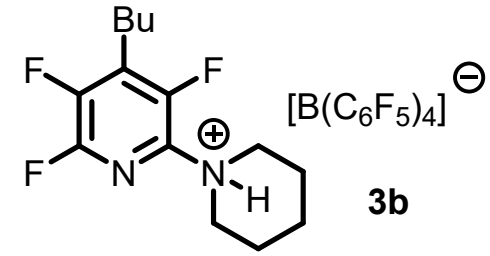
3a

^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C)



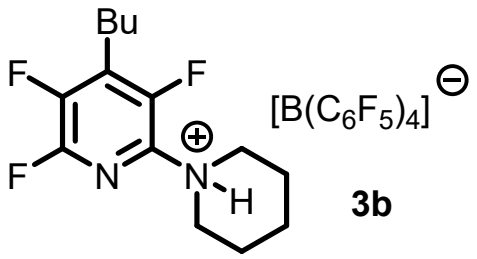
3b

^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C)



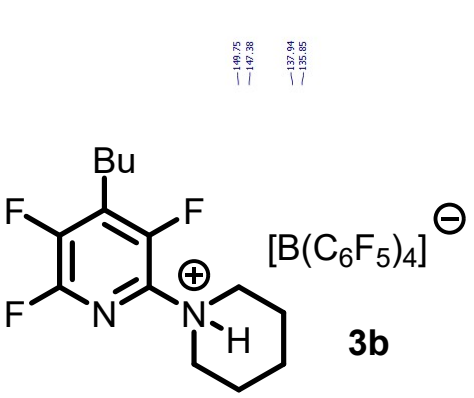
3b

^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2, 25 °C)



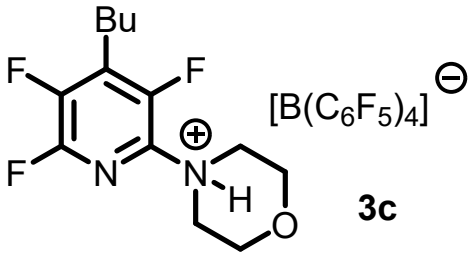
3b

^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C)



3b

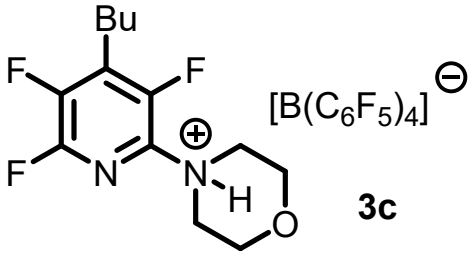
^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C)



$[B(C_6F_5)_4]^{\ominus}$

3c

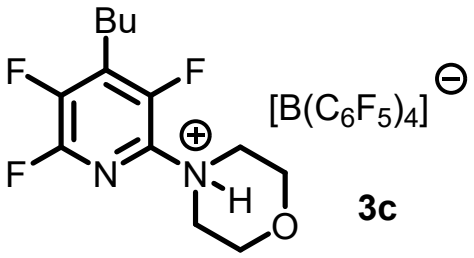
^{1}H NMR (400 MHz, $CDCl_3$, 25 °C)



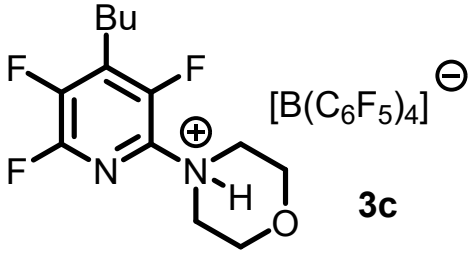
$[B(C_6F_5)_4]^{\ominus}$

3c

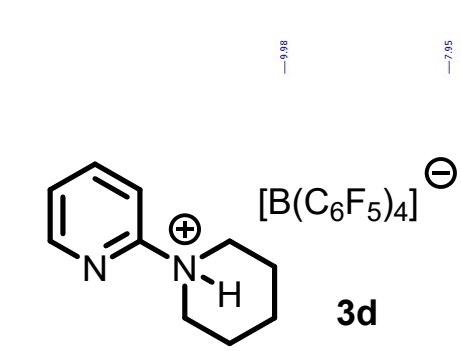
^{19}F {^{1}H} NMR (376 MHz, $CDCl_3$, 25 °C)



^{11}B NMR (128 MHz, $CDCl_3$, 25 °C)



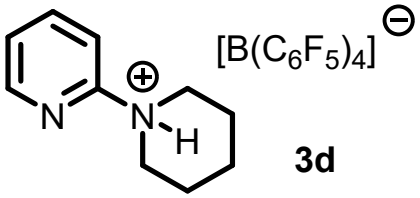
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$, 25 °C)



$[B(C_6F_5)_4]^{\ominus}$

3d

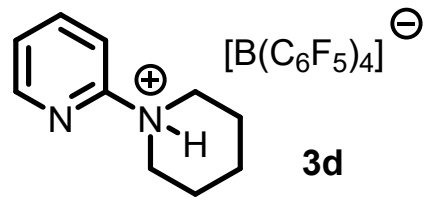
^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C)



$[B(C_6F_5)_4]^{\ominus}$

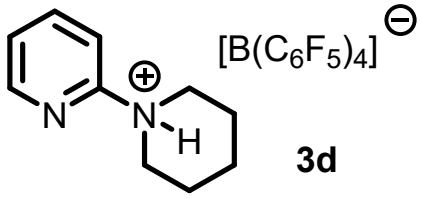
3d

^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2, 25 °C)



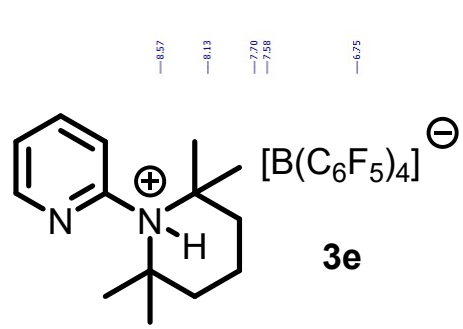
3d

^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C)

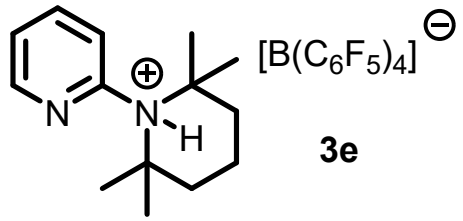


3d

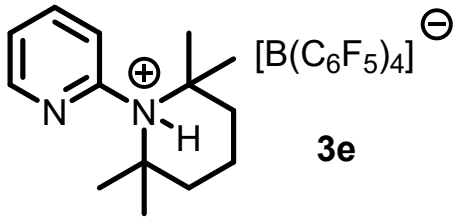
^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C)



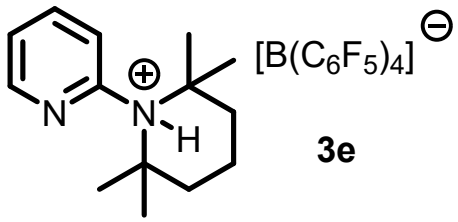
^{1}H NMR (400 MHz, CD_2Cl_2, 25 °C)



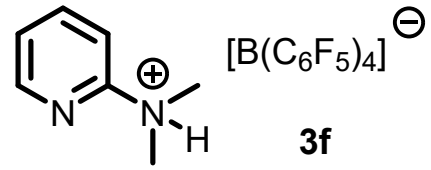
^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2, 25 °C)



^{11}B NMR (128 MHz, CD_2Cl_2, 25 °C)



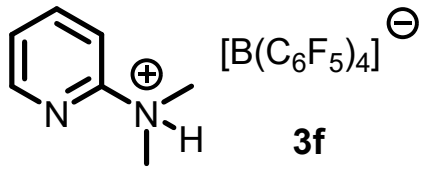
^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2, 25 °C)



$[B(C_6F_5)_4]^{\ominus}$

3f

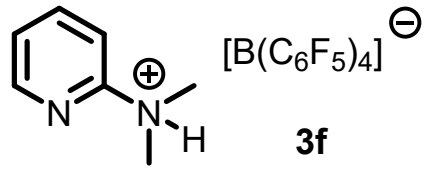
^{1}H NMR (400 MHz, CD_2Cl_2)



$[B(C_6F_5)_4]^{\ominus}$

3f

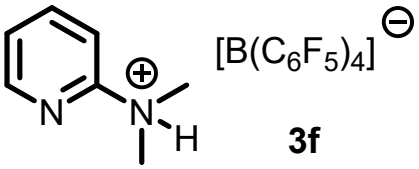
^{19}F {^{1}H} NMR (376 MHz, CD_2Cl_2)



$[B(C_6F_5)_4]^{\ominus}$

3f

^{11}B NMR (128 MHz, CD_2Cl_2)



$[B(C_6F_5)_4]^{\ominus}$

3f

^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2)

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