Supplemental Information

Phosphine-catalyzed Hydroboration of Propiolonitriles: Access to (E)-1,2-vinylcyanotrifluoroborate derivatives

Johnathan Bowen, Carla Slebodnick, and Webster L. Santos*

Department of Chemistry, Virginia Tech, Blacksburg, VA 24061 (USA)
*E-mail: santosw@vt.edu

Table of Contents

1. Materials and Methods

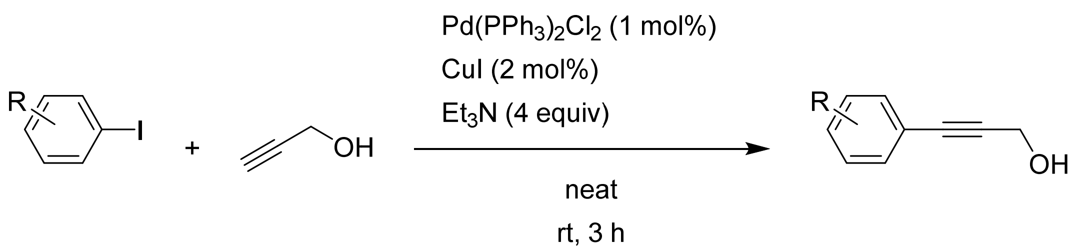
Reactions were performed using Schlenk technique under Argon or Nitrogen atmosphere. All glassware used was flame-dried or oven-dried overnight. Chemicals were obtained from commercial sources unless otherwise noted. THF, $PhCH_3$, CH_2Cl_2 and CH_3CN were dried using the Innovative Technology Pure SolvMD solvent purification system. Column chromatography was performed using SiliaFlash P60 40-63 μm, 60 Å. TLC analyses were performed using Silicycle aluminum backed silica gel F-254 plates.

2. Instrumentation

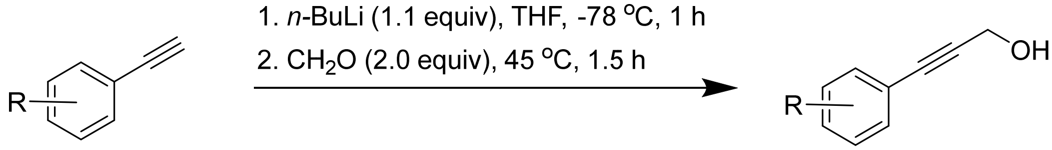
NMR spectroscopic experiments were performed using an Agilent 400-MR 400 MHz, an Agilent U4-DD2 400 Hz, or a Bruker Avance II 500 MHz spectrometer. Chemical shifts are reported in δ ppm and ^1H and ^{13}C NMR are referenced to an internal standard ($CDCl_3$, CD_3OD, DMSO, TMS, or acetone-d_6). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets, ddt = doublet of doublet of triplets, m = multiplet), coupling constants (Hz), and integration. When present, the Z-isomer of 1,2-vinylcyanoboranes is reported as minor (Z/cis-isomer). ESI mass spectra were acquired using an Agilent 6220 TOF LC-MS.

3. General Procedures for Preparing Propiolonitriles

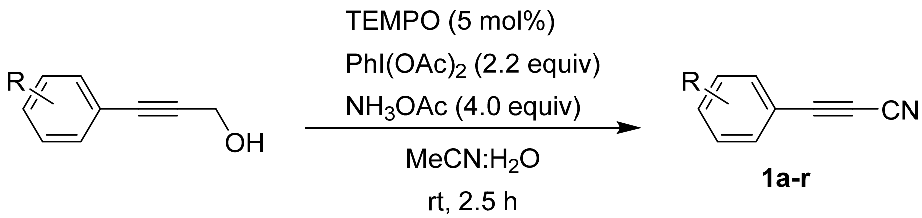
Propiolonitriles **1a** and **1d-r** were prepared in accordance with **Procedure 3.1** and propiolonitriles **1b-c** were prepared via **Procedure 3.2**. References for the spectra of previously known propiolonitriles are provided in Table S1. Propiolonitriles **1n** and **1p** were prepared according to the following general procedures unless noted otherwise.



Procedure 3.1.[1] To an oven-dried flask equipped with a stir bar was added $Pd(PPh_3)_2Cl_2$ (0.01 equiv, 0.05 mmol) and copper(I) iodide (0.02 equiv, 0.10 mmol). After purging with N_2, aryl iodide (1 equiv, 5.0 mmol), propargyl alcohol (1.1 equiv, 5.5 mmol), and triethylamine (4 equiv, 20 mmol) were added. The suspension was stirred at room temperature for 4 hours and filtered. Concentration of the filtrate *in vacuo* yielded the crude product which was subjected to silica column chromatography (eluted with 1:4 ethyl acetate:hexanes) to afford the crude propargyl alcohol as a yellow oil, which was concentrated *in vacuo*. The crude alcohol was used without further purification.



Procedure 3.2[2]. An oven-dried round bottom flask was charged with aryl alkyne (1 equiv, 5.0 mmol) and placed under N_2 via Schlenk technique. The reaction was diluted with THF (15 mL) and stirred at –78 °C (dry ice/acetone bath). n-Butyllithium (1.1 equiv, 5.5 mmol) was then added dropwise to the mixture and stirred for 1 hour. Paraformaldehyde (2.0 equiv, 10 mmol) was then added in one portion and the reaction allowed to warm to room temperature before stirring at 45 °C for 1.5 hours. Upon completion, the reaction was quenched with water (15 mL) and diluted with diethyl ether (10 mL). The organic layer was washed with brine (10 mL) and dried over anhydrous sodium sulfate. Concentration *in vacuo* yielded a yellow oil which upon purification by silica gel column chromatography (1:4 ethyl acetate:hexanes) yielded the propargyl alcohol as a yellow oil. The crude alcohol was used without further purification.



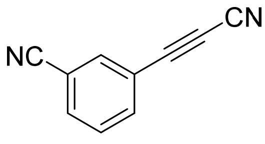
Procedure 3.3.[3] To an oven-dried flask equipped with a stir bar was added the crude alcohol, ammonium acetate (4 equiv, 19.2 mmol), TEMPO (0.05 equiv, 241 µmol), and $PhI(OAc)_2$ (2.2 equiv, 11 mmol). After purging with N_2, the reaction was diluted with a MeCN (18 mL) and water (2 mL) and stirred at room temperature for 2.5 hours. Upon completion, the reaction was quenched with water (15 mL) and diluted with diethyl ether (10 mL). The organic layer was washed with brine (10 mL) and dried over anhydrous sodium sulfate. Concentration *in vacuo* yielded a yellow oil which upon purification by silica gel column chromatography (0-5% ethyl acetate:hexanes) yielded the propiolonitrile as a yellow solid.

4. Characterization of Propiolonitriles:

Table S1. References for Propiolonitrile Substrates

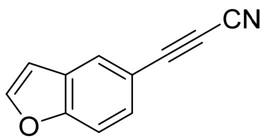
Substrate	**R[1]**	**Reference**
1a	H	*Synlett* **2014,** *25*, 1275-1278.
1b	*o*-Me	*Can. J. Chem.* **2017,** *95*, 144-148.
1c	*p*-Et	*Org. Lett.* **2019,** *21*, 8308-8311.
1d	*p-t*Bu	*Tetrahedron Lett.* **2018,** *59*, 4622-4625.
1e	*o*-OMe	*Adv. Synth. Catal.* **2013,** *355*, 1207-1210.
1f	*m*-OMe	*Adv. Synth. Catal.* **2013,** *355*, 1207-1210.
1g	*p*-OMe	*Tetrahedron Lett.* **2018,** *59*, 4622-4625.
1h	*o*-F	*Org. Lett.* **2017,** *19*, 5613-5616.
1i	*p*-F	*Org. Lett.* **2019,** *21*, 8308-8311.
1j	*o*-Cl	*Can. J. Chem.* **2017,** *95*, 144-148.
1k	*m*-Cl	*Tetrahedron Lett.* **2018,** *59*, 4622-4625.
1l	*p*-Cl	*Can. J. Chem.* **2017,** *95*, 144-148.
1m	*p*-CN	*Org. Lett.* **2019,** *21*, 8308-8311.
1o	3-(naphthalen-2-yl)	*Can. J. Chem.* **2017,** *95*, 144-148.
1q	3-(benzo[d][1,3]dioxol-5-yl)	*Chem. Eur. J.* **2018,** *24*, 12767-12772.
1r	3-([1,1'-biphenyl]-4-yl)	*Can. J. Chem.* **2017,** *95*, 144-148.

3-(cyanoethynyl)benzonitrile (1n)



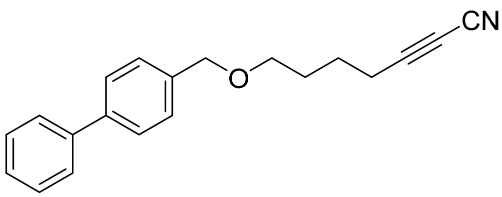
Prepared according to **Procedures 3.1 and 3.2.** Yellow solid (563 mg, 85%) Purified using a 0-5% gradient ethyl acetate in hexanes solvent system. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 1.8 Hz, 1H), 7.83 (d, *J* = 10.5 Hz, 2H), 7.58 (t, *J* = 7.9 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.3, 136.7, 135.0, 130.1, 119.5, 117.0, 114.0, 104.9, 79.9, 65.0.

3-(benzofuran-6-yl)propiolonitrile (1p)



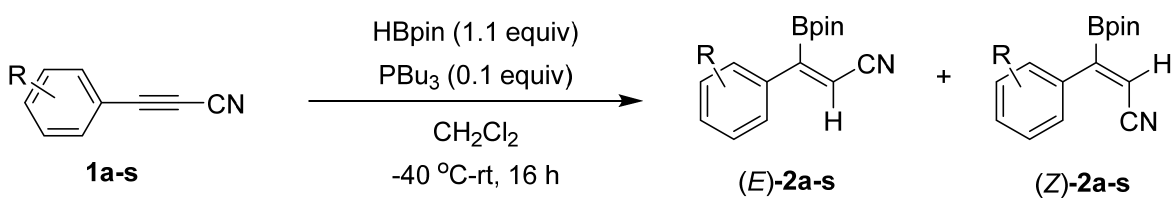
Prepared according to **Procedures 3.1 and 3.2.** Yellow solid (432 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.71 (d, *J* = 2.3 Hz, 1H), 7.51 (s, 2H), 6.80 (d, *J* = 2.3 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.3, 147.0, 129.5, 127.7, 112.5, 105.8, 83.9, 62.2. HRMS: (ESI) $[M]^+$ calc. for $C_{11}H_5NO$, 167.0371, observed, 167.0348.

7-([1,1'-biphenyl]-4-ylmethoxy)hept-2-ynenitrile (1s)



Prepared according to **Procedures 3.1 and 3.3.** Yellow solid (103 mg, 51%) Purified using a 0-5% gradient ethyl acetate in hexanes solvent system. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 – 7.59 (m, 4H), 7.52 – 7.36 (m, 5H), 4.57 (s, 2H), 3.56 (t, *J* = 5.1 Hz, 2H), 2.41 (t, *J* = 6.6 Hz, 2H), 1.81 – 1.70 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.9, 140.6, 137.4, 128.8, 128.1, 127.4, 127.2, 127.1, 105.3, 87.3, 72.8, 69.3, 55.5, 28.8, 24.2, 18.7.

5. General Procedures for Hydroboration of Propiolonitriles:



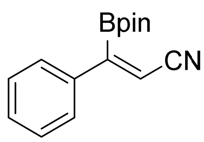
Procedure 5.1. An oven-dried round bottom flask was charged with propiolonitrile (1 equiv, 0.30 mmol) and placed under N_2 via Schlenk technique. The solid was dissolved in dichloromethane (0.40 mL), and pinacolborane (1.1 equiv, 0.33 mmol) was added. The reaction was cooled to –40 °C (dry ice/acetonitrile bath) for 15 minutes. Tributylphosphine (0.1 equiv, 30 µmol) was added, and the reaction was allowed to slowly warm to room temperature overnight. The crude mixture was concentrated *in vacuo* and filtered through a plug of silica (1:1 ethyl acetate:hexanes). The crude mixture was concentrated *in vacuo*, and dissolved in $CDCl_3$ (0.750 mL, 0.05% TMS) for yield determination *via* ^{1}H NMR. The sample was concentrated *in vacuo* and the crude 1,2-vinylcyanoborane was used without further purification.

Note 1: When this reaction was performed with 3-(2,6-dimethylphenyl)propiolonitrile using optimized conditions. Surprisingly, the expected vinylcyanopinacolborane was not observed.
Note 2: ^{1}H NMR doublets at 6 and 7.4 ppm for the crude mixture of the aforementioned reaction are the result of protodeboronation of the pinacolboronate ester to the cyano alkene. Substrates containing electron withdrawing substituents have increased susceptibility to this type of degradation. The subsequent conversion to the BF_3 salt removes this impurity.

6. General Procedure For ^{31}P NMR Studies

Procedure 6.1. An oven-dried 2-dram vial was charged with **1a** (1 equiv, 80 µmol) and placed under N_2 via Schlenk technique. The solid was dissolved in $CDCl_3$ (0.75 mL), and BF_3•OEt_2 (1 equiv, 80 µmol) was added. Triphenylphosphine (1 equiv, 80 µmol) was added in one portion and ^{31}P NMR data was immediately obtained.

6. Characterization of (*E*)-1,2-vinylcyanoborane (2a):

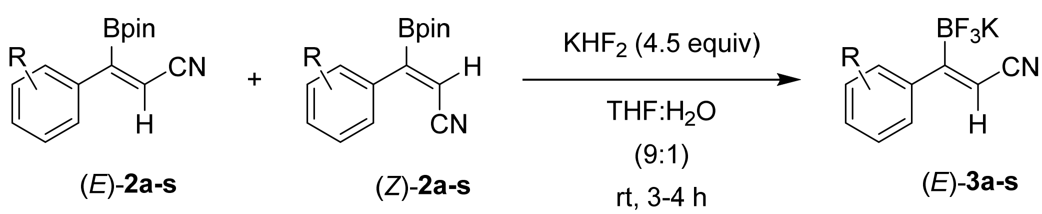


Prepared according to **Procedure 5.1.** Yellow solid (29 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.33 (m, 5H), 6.03 (s, 1H), 1.41 (s, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.0, 129.9, 128.9, 127.0, 117.6, 106.5, 85.4, 24.8. HRMS: (ESI) $[M+H]^+$ calc. for $C_{15}H_{19}BNO_2$, 256.1503, observed, 256.1511

Procedure for 4.6 mmol scale:

An oven-dried round bottom flask was charged with propiolonitrile (1 equiv, 4.6 mmol) and placed under N_2 via Schlenk technique. The solid was dissolved in dichloromethane (5.00 mL), and pinacolborane (1.1 equiv, 5.1 mmol) was added. The reaction was cooled to –78 °C (dry ice/acetone bath) for 15 minutes. Tributylphosphine (0.1 equiv, 0.46 mmol) was added, and the reaction was allowed to slowly warm to room temperature overnight. MeI (0.3 equiv, 1.39 mmol) was added and the reaction was stirred at room temperature for one hour. The crude mixture was concentrated *in vacuo* and filtered over a plug of silica (1:1 ethyl acetate:hexanes solvent system). The sample was concentrated *in vacuo* to yield a yellow oil which upon purification by silica gel column chromatography (15% ethyl acetate:hexanes solvent system) yielded the 1,2-vinylcyanoborane as a yellow solid (767 mg, 65%).

7. General Procedure for Preparing Potassium Trifluoroborate Salts

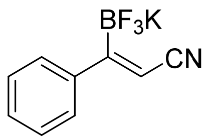


Procedure 6.1. The crude 1,2-vinylcyanoborane (1 equiv, 0.2 mmol) was dissolved in THF (2 mL) and KHF_2 (4.5 equiv, 0.9 mmol) was added. The minimum amount of water necessary to dissolve KHF_2 was added, and the reaction was stirred for 4 hours at room temperature. Solvent was removed *in vacuo.* Water was removed by addition of toluene (5 mL) and concentration *in vacuo* three times. The resulting solid was dissolved in acetonitrile (5 mL) and filtered. The filtrate was concentrated and the corresponding trifluoroborate salt was precipitated as a single isomer from acetonitrile and diethyl ether.

Note: Compound **3s** was isolated as a 90:10 mixture of *E/Z* isomers.

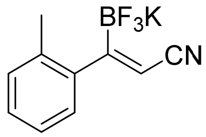
8. Characterization of Potassium Trifluoroborate Salts

(*E*)-3-phenyl-3-(trifluoro-λ[4]-boraneyl)acrylonitrile, potassium salt (3a)



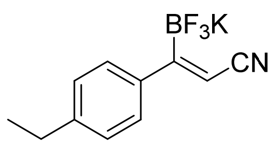
Prepared according to **Procedure 6.1.** White Solid (30 mg, 64%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.48 – 7.33 (m, 2H), 7.33 – 7.16 (m, 3H), 5.54 (s, 1H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 144.2, 128.1, 127.7, 127.4, 120.4, 99.4. ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -136.05 –136.88 (m). ^{11}B NMR (128 MHz, DMSO-*d*$_6$) δ 1.65 (q, *J* = 50.4 Hz). HRMS: (ESI) [M]$^-$ calc. for $C_9H_6BF_3N^-$, 196.0545, observed, 196.0548.

(E)-3-(o-tolyl)-3-(trifluoro- λ[4]-boraneyl)acrylonitrile, potassium salt (3b)



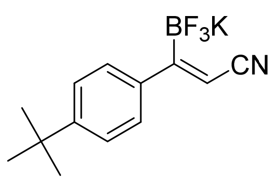
Prepared according to **Procedure 6.1.** White solid (41 mg, 76%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.18 – 7.02 (m, 3H), 6.90 (d, *J* = 5.4 Hz, 1H), 5.24 (s, 1H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 145.8, 133.9, 129.4, 126.3, 125.9, 124.7, 119.7, 100.4, 19.3. ^{19}F NMR (376 MHz, CD_3CN) δ -140.88 (d, *J* = 47.0 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.34 (q, *J* = 48.9 Hz). HRMS: (ESI) [M]$^-$ calc. for $C_{10}H_8BF_3N^-$, 210.0702, observed, 210.0703.

(*E*)-3-(4-ethylphenyl)-3-(trifluoro- λ[4]-boraneyl)acrylonitrile, potassium salt (3c)



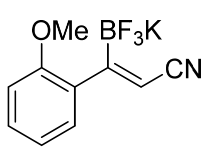
Prepared according to **Procedure 6.1.** White solid (44 mg, 75%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.36 (d, *J* = 8.2 Hz, 2H), 7.14 (d, *J* = 8.4 Hz, 2H), 5.54 (s, 1H), 2.62 (q, *J* = 7.6 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 143.8, 141.5, 127.3, 127.1, 120.4, 98.4, 28.2, 15.1. ^{19}F NMR (376 MHz, CD_3CN) δ -139.00 (q, *J* = 46.7 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.79 (q, *J* = 49.9 Hz). HRMS: (ESI) [M]$^-$ calc. for $C_{11}H_{10}BF_3N^-$, 224.0858, observed, 224.0856.

(*E*)-3-(4-(tert-butyl)phenyl)-3-(trifluoro- λ[4]-boraneyl)acrylonitrile, potassium salt (3d)



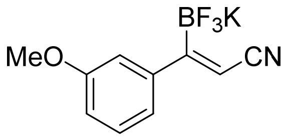
Prepared according to **Procedure 6.1.** White solid (46 mg, 74%). ^{1}H NMR (400 MHz, DMSO-*d*$_6$) δ 7.32 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 5.49 (s, 1H), 1.23 (s, 9H). ^{13}C NMR (101 MHz, DMSO-*d*$_6$) δ 150.1, 141.2, 127.2, 124.8, 120.6, 98.8 – 98.4 (m), 34.6, 31.5. ^{19}F NMR (376 MHz, DMSO-*d*$_6$) δ -136.28. ^{11}B NMR (128 MHz, DMSO-*d*$_6$) δ 1.36 (t, *J* = 51.2 Hz). HRMS: (ESI) [M]$^-$ calc. for $C_{13}H_{14}BF_3N^-$, 252.1177, observed, 252.1172.

(*E*)-3-(2-methoxyphenyl)-3-(trifluoro- λ[4]-boraneyl)acrylonitrile, potassium salt (3e)



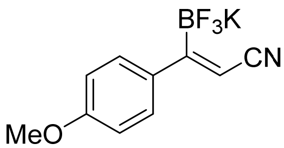
Prepared according to **Procedure 6.1.** White solid (67 mg, 45%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.18 – 7.02 (m, 3H), 6.90 (d, *J* = 5.4 Hz, 1H), 5.24 (s, 1H), 2.20 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 145.8, 133.9, 129.4, 126.3, 125.9, 124.7, 119.7, 100.4, 19.3. ^{19}F NMR (376 MHz, CD_3CN) δ -140.88 (d, J = 47.0 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.34 (q, J = 48.9 Hz). HRMS: (ESI) $[M]^-$calc. for $C_{13}H_{14}BF_3N^-$, 226.0657, observed, 226.0653.

(*E*)-3-(3-methoxyphenyl)-3-(trifluoro- λ^4-boraneyl)acrylonitrile, potassium salt (3f)



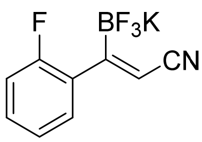
Prepared according to **Procedure 6.1.** White solid (33 mg, 46%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.23 (t, J = 7.9 Hz, 1H), 7.09 – 6.99 (m, 2H), 6.84 (d, J = 8.2 Hz, 1H), 5.59 (s, 1H), 3.80 (s, 3H). ^{13}C NMR (126 MHz, CD_3CN) δ 159.3, 145.9, 128.7, 120.0, 119.5, 112.7, 112.4, 99.3 (d, J = 1.7 Hz), 54.7. ^{19}F NMR (376 MHz, CD_3CN) δ -139.17 (d, J = 46.0 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.67 (q, J = 49.0 Hz). HRMS: (ESI) $[M]^-$ calc. for $C_{10}H_8BF_3NO^-$, 226.0657, observed, 226.0651.

(*E*)-3-(4-methoxyphenyl)-3-(trifluoro- λ^4-boraneyl)acrylonitrile, potassium salt (3g)



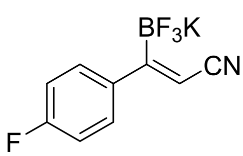
Prepared according to **Procedure 6.1.** White solid (44 mg, 66%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.45 (d, J = 8.7 Hz, 1H), 6.88 (d, J = 8.7 Hz, 1H), 3.78 (s, 2H). ^{13}C NMR (101 MHz, CD_3CN) δ 159.6, 136.1, 128.5, 120.7, 113.2, 97.3, 54.8. ^{19}F NMR (376 MHz, CD_3CN) δ -138.71 (d, J = 44.4 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.86 (q, J = 50.8 Hz). HRMS: (ESI) $[M]^-$ calc. for $C_{10}H_8BF_3NO^-$, 226.0657, observed, 226.0646.

(*E*)-3-(2-fluorophenyl)-3-(trifluoro- λ^4-boraneyl)acrylonitrile, potassium salt (3h)



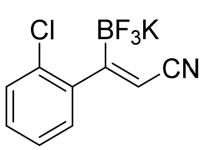
Prepared according to **Procedure 6.1.** White solid (42 mg, 63%). ^{1}H NMR (600 MHz, CD_3CN) δ 7.34 – 7.23 (m, 2H), 7.16 – 7.04 (m, 2H), 5.59 (s, 1H). ^{13}C NMR (151 MHz, CD_3CN) δ 158.8 (d, J = 244.7 Hz), 132.1 (d, J = 15.1 Hz), 129.9 (d, J = 4.0 Hz), 128.5 (d, J = 8.2 Hz), 123.6 (d, J = 3.6 Hz), 119.6, 115.2 (d, J = 23.0 Hz), 102.4 (d, J = 4.0 Hz). ^{19}F NMR (376 MHz, CD_3CN) δ -117.30, -140.94 (d, J = 45.5 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.37 (q, J = 48.1 Hz). HRMS: (ESI) $[M]^-$ calc. for $C_9H_5BF_4N^-$, 214.0457, observed, 214.0452.

(*E*)-3-(4-fluorophenyl)-3-(trifluoro- λ^4-boraneyl)acrylonitrile, potassium salt (3i)



Prepared according to **Procedure 6.1.** White solid (62 mg, 66%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.50 (t, J = 8.5 Hz, 2H), 7.06 (t, J = 8.8 Hz, 2H), 5.58 (s, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 162.4 (d, J = 243.9 Hz), 140.2 (d, J = 3.1 Hz), 129.0 (d, J = 8.2 Hz), 120.2, 114.5 (d, J = 21.3 Hz), 99.2. ^{19}F NMR (376 MHz, CD_3CN) δ -117.08 – -117.22 (m), -139.26 (q, J = 47.5 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.74 (q, J = 49.6 Hz). HRMS: (ESI) $[M]^-$ calc. for $C_9H_5BF_4N^-$, 214.0457, observed, 214.0453.

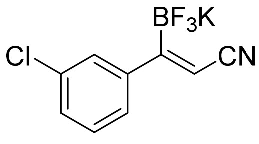
(*E*)-3-(2-chlorophenyl)-3-(trifluoro- λ^4-boraneyl)acrylonitrile, potassium salt (3j)



Prepared according to **Procedure 6.1.** White solid (57 mg, 64%). ^{1}H NMR (600 MHz, CD_3CN) δ 7.35 (d, J = 7.9 Hz, 1H), 7.22 (d, J = 7.5 Hz, 1H), 7.17 (d, J = 7.6 Hz, 1H), 7.13 (d, J = 7.5 Hz, 1H), 5.39 (d, J = 8.1 Hz, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ

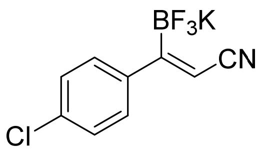
146.3, 132.7, 131.8, 131.5, 129.9, 120.5, 119.9, 112.6, 102.1 (d, J = 1.7 Hz). ^{19}F NMR (376 MHz, CD_3CN) δ -141.16 (q, J = 45.6 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.21 (q, J = 47.8 Hz). HRMS: (ESI) $[M]^-$ calc. for $C_9H_5BClF_3N^-$, 230.0161, observed, 230.0154.

(*E*)-3-(3-chlorophenyl)-3-(trifluoro- λ^4-boraneyl)acrylonitrile, potassium salt (3k)



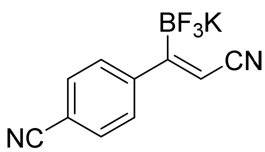
Prepared according to **Procedure 6.1.** White solid (46 mg, 72%). ^{1}H NMR (600 MHz, CD_3CN) δ 7.48 (s, 1H), 7.38 (d, J = 7.3 Hz, 1H), 7.34 – 7.25 (m, 2H), 5.61 (s, 1H). ^{13}C NMR (151 MHz, CD_3CN) δ 146.3, 133.2, 129.5, 127.1, 126.9, 125.4, 119.8, 100.4. ^{19}F NMR (376 MHz, CD_3CN) δ -139.45 (q, J = 46.3 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.61 (q, J = 49.3 Hz). HRMS: (ESI) $[M]^-$ calc. for $C_9H_5BClF_3N^-$, 230.0161, observed, 230.0156.

(*E*)-3-(4-chlorophenyl)-3-(trifluoro- λ^4-boraneyl)acrylonitrile, potassium salt (3l)



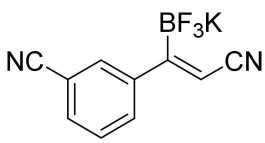
Prepared according to **Procedure 6.1.** White solid (40 mg, 61%). ^{1}H NMR (600 MHz, CD_3CN) δ 7.45 (d, J = 8.5 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 5.61 – 5.57 (m, 1H). ^{13}C NMR (151 MHz, CD_3CN) δ 142.8, 132.8, 128.7, 127.8, 120.0, 99.7. ^{19}F NMR (376 MHz, CD_3CN) δ -139.33 (q, J = 46.5 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.66 (q, J = 49.4 Hz). HRMS: (ESI) $[M]^-$ calc. for $C_9H_5BClF_3N^-$, 230.0161, observed, 230.0152.

(*E*)-4-(2-cyano-1-(trifluoro- λ^4-boraneyl)vinyl)benzonitrile, potassium salt (3m)



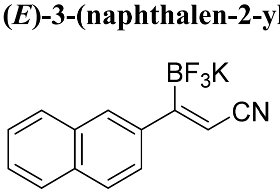
Prepared according to **Procedure 6.1.** White solid (43 mg, 85%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.70 – 7.64 (m, 2H), 7.61 – 7.55 (m, 2H), 5.65 – 5.62 (m, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 149.2, 131.7, 127.7, 119.5, 119.0, 110.4, 101.5 (d, J = 1.7 Hz), 29.9. ^{19}F NMR (376 MHz, CD_3CN) δ -139.58 (q, J = 46.5 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.55 (q, J = 48.8 Hz). HRMS: (ESI) $[M]^-$ calc. for $C_{10}H_5BF_3N_2^-$, 221.0498, observed, 221.0496.

(*E*)-3-(2-cyano-1-(trifluoro- λ^4-boraneyl)vinyl)benzonitrile, potassium salt (3n)



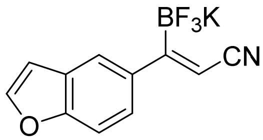
Prepared according to **Procedure 6.1.** White solid (67 mg, 73%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.75 (s, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 7.7 Hz, 1H), 7.45 (d, J = 7.8 Hz, 1H), 5.61 (s, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 145.3, 131.7, 130.8, 130.5, 128.9, 119.5, 118.9, 111.7, 101.1 (d, J = 1.8 Hz). ^{19}F NMR (376 MHz, CD_3CN) δ -139.76 (q, J = 47.5 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.58 (q, J = 48.6 Hz). HRMS: (ESI) $[M]^-$ calc. for $C_{10}H_5BF_3N_2^-$, 221.0498, observed, 221.0496.

(*E*)-3-(naphthalen-2-yl)-3-(trifluoro- λ^4-boraneyl)acrylonitrile, potassium salt (3o)



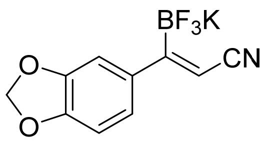
Prepared according to **Procedure 6.1.** White solid (63 mg, 89%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.13 – 7.71 (m, 4H), 7.71 – 7.33 (m, 3H), 5.72 (s, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 141.7, 133.2, 132.8, 128.6, 127.7, 127.3, 126.3, 126.2, 126.1, 120.4, 99.9. ^{19}F NMR (376 MHz, DMSO-d_6) δ -136.05. ^{11}B NMR (128 MHz, DMSO-d_6) δ 1.72 (q, J = 51.0 Hz). HRMS: (ESI) [M]$^-$ calc. for $C_{13}H_8BF_3N^-$, 246.0707, observed, 246.0703.

(*E*)-3-(benzofuran-6-yl)-3-(trifluoro- λ^4-boraneyl)acrylonitrile, potassium salt (3p)



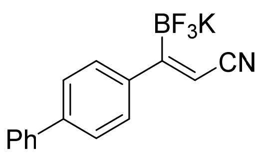
Prepared according to **Procedure 6.1.** White solid (90 mg, 46%). ^{1}H NMR (600 MHz, CD_3CN) δ 7.73 (s, 1H), 7.71 (d, J = 2.2 Hz, 1H), 7.43 (s, 2H), 6.84 (d, J = 2.2 Hz, 1H), 5.59 (d, J = 6.7 Hz, 1H). ^{13}C NMR (151 MHz, CD_3CN) δ 154.6, 145.7, 139.1, 127.2, 123.9, 120.4, 119.9, 110.4, 106.9, 98.8. ^{19}F NMR (376 MHz, CD_3CN) δ -138.89 (d, J = 45.7 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.86 (q, J = 50.3 Hz). HRMS: (ESI) [M]$^-$ calc. for $C_{11}H_6BF_3NO^-$, 236.0500, observed, 236.0490.

(*E*)-3-(benzo[d][1,3]dioxol-5-yl)-3-(trifluoro- λ^4-boraneyl)acrylonitrile, potassium salt (3q)



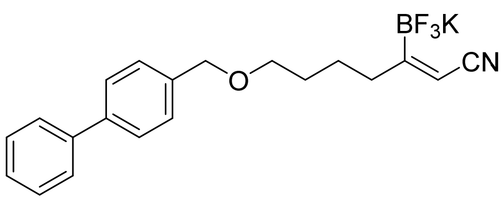
Prepared according to **Procedure 6.1.** White solid (35 mg, 62%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.08 – 7.00 (m, 2H), 6.81 (d, J = 8.5 Hz, 1H), 5.97 (s, 2H), 5.56 (s, 1H). ^{13}C NMR (101 MHz, CD_3CN) δ 147.3, 147.3, 138.1, 121.0, 120.4, 107.5, 107.4, 101.2, 98.0. ^{19}F NMR (376 MHz, CD_3CN) δ -138.83 (q, J = 46.4 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.72 (q, J = 49.5 Hz). HRMS: (ESI) [M]$^-$ calc. for $C_{10}H_6BF_3NO_2^-$, 240.0449, observed, 240.0442.

(*E*)-3-([1,1'-biphenyl]-4-yl)-3-(trifluoro- λ^4-boraneyl)acrylonitrile, potassium salt (3r)



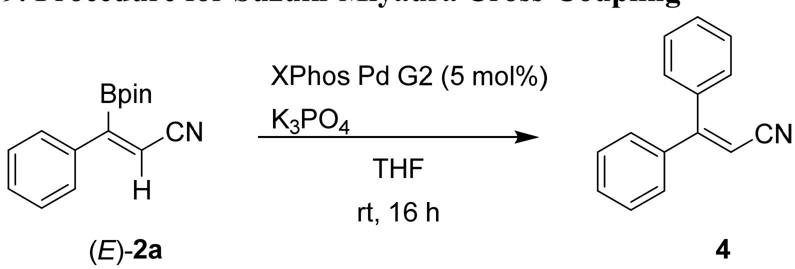
Prepared according to **Procedure 6.1.** White solid (42 mg, 88%). ^{1}H NMR (400 MHz, CD_3CN) δ 7.69 – 7.62 (m, 2H), 7.58 (d, J = 8.7 Hz, 2H), 7.54 (d, J = 8.5 Hz, 2H), 7.46 (t, J = 7.4 Hz, 2H), 7.36 (t, J = 7.9 Hz, 1H), 5.63 (s, 1H). ^{13}C NMR (126 MHz, CD_3CN) δ 144.9, 142.2, 141.4, 130.5, 129.2, 128.9, 128.4, 128.0, 121.8, 100.7. ^{19}F NMR (376 MHz, CD_3CN) δ -139.01 (q, J = 44.9 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.79 (q, J = 50.5 Hz). HRMS: (ESI) [M]$^-$ calc. for $C_{15}H_{10}BF_3N^-$, 272.0858 observed, 272.0868.

(*E*)-7-([1,1'-biphenyl]-4-ylmethoxy)-3-(trifluoro-λ^4-boraneyl)hept-2-enenitrile, potassium salt (3s)



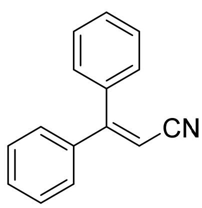
Prepared according to **Procedure 6.1.** White solid (46 mg, 81%). ^{1}H NMR (500 MHz, CD_3CN) δ 7.68 – 7.59 (m, 4H), 7.48 – 7.40 (m, 4H), 7.36 (t, J = 7.3 Hz, 1H), 5.37 (s, 1H), 4.52 (s, 2H), 3.54 – 3.45 (m, 2H), 2.37 (t, J = 7.4 Hz, 2H), 1.67 – 1.52 (m, 4H). ^{13}C NMR (126 MHz, CD_3CN) δ 141.57, 140.80, 139.39, 129.77, 129.06, 128.25, 127.77, 127.73, 97.87 – 96.98 (m), 72.83, 71.08, 35.41, 30.74, 26.19. ^{19}F NMR (376 MHz, CD_3CN) δ -145.71 (q, J = 52.9 Hz). ^{11}B NMR (128 MHz, CD_3CN) δ 1.84 (q, J = 52.8 Hz). HRMS: (ESI) [M]$^-$ calc. for $C_{20}H_{20}BF_3NO^-$, 358.1596 observed, 358.1595.

9. Procedure for Suzuki-Miyaura Cross-Coupling



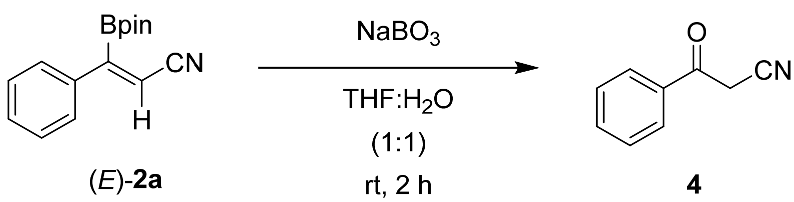
Procedure 8.1. An oven-dried round bottom flask was charged with (*E*)-**2a** (1 equiv, 0.10 mmol) and XPhos Pd G2 (6 µmol, 0.05 equiv) and placed under N_2 via Schlenk technique. The reaction was diluted with THF (1 mL). Aqueous K_3PO_4 (0.6 M, 0.2 mmol, 1.6 equiv) and bromobenzene (0.18 mmol, 1.5 equiv) were added, and the reaction was stirred at room temperature overnight. Upon completion, the reaction was quenched with water (15 mL) and diluted with diethyl ether (10 mL). The organic layer was washed with brine (10 mL) and dried over anhydrous sodium sulfate. Concentration *in vacuo* yielded a brown oil which upon purification by silica gel column chromatography (1% ethyl acetate:hexanes solvent system) yielded the product as a white solid.

10. Characterization for 3,3-diphenylacrylonitrile (4)



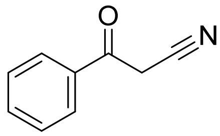
White Solid. 50% (12 mg). The spectra for compound **4** are in accordance with *J. Org. Chem.* **2020,** *85*, 2654-2665.

11. Procedure for Oxidation of (*E*)-1,2-vinylcyanoborane



Procedure 10.1. An oven-dried round bottom flask was charged with (*E*)-**2a** (1 equiv, 0.40 mmol) and placed under N_2 via Schlenk technique. The reaction was diluted with THF (0.25 mL), and a solution of Sodium perborate monohydrate (0.59 mmol, 1.5 equiv) in water (0.25 mL) was added. The reaction was stirred at room temperature for 2 hours. Upon completion, the reaction was quenched with water (15 mL) and diluted with diethyl ether (10 mL). The organic layer was washed with brine (10 mL) and dried over anhydrous sodium sulfate. Concentration *in vacuo* yielded a brown oil which upon purification by silica gel column chromatography (10% ethyl acetate:hexanes solvent system) yielded the products as a white solid.

12. Characterization for 3-oxo-3-phenylpropanenitrile (5)



White solid. 69% (39 mg). The spectra for compound **5** are in accordance with *Org. Lett.* **2006,** *8*, 1161-1163.

Compounds **1n**, **1p**, **1s**, **2a** and **3a-s** are new and first time characterized.

13. General Procedure For NMR Studies

Procedure 13.1. An oven-dried 2-dram vial was charged with **1a** (1 equiv, 80 μmol) and placed under N_2 via Schlenk technique. The solid was dissolved in $CDCl_3$ (0.75 mL), and BF_3•OEt_2 (1 equiv, 80 μmol) was added. Triphenylphosphine (1 equiv, 80 μmol) was added in one portion, and the solution was transferred to an NMR tube. ^{31}P NMR data was immediately obtained.

Procedure 13.2. An oven-dried 2-dram vial was charged with **1a** (1 equiv, 80 μmol) and placed under N_2 via Schlenk technique. The solid was dissolved in $CDCl_3$ (0.75 mL), and pinacolborane (1 equiv, 80 μmol) was added. Triphenylphosphine (1 equiv, 80 μmol) was added in one portion, and the solution was transferred to an NMR tube. ^{13}C NMR data was obtained every 30 minutes.

Procedure 13.3. An oven-dried 2-dram vial was charged with **1a** (1 equiv, 80 μmol) and placed under N_2 via Schlenk technique. The solid was dissolved in $CDCl_3$ (0.75 mL), and pinacolborane (1 equiv, 80 μmol) was added. The mixture was cooled to -40 °C and Tributylphosphine (1 equiv, 80 μmol) was added, and the solution was transferred to an NMR tube. ^{13}C NMR data was obtained at -20 °C after 30 minutes.

14. X-Ray Crystallography Experimental

Colorless crystals were grown by slow diffusion using a acetonitrile/diethyl ether solvent system. The diffusion chamber (2 dram vial containing one isomer of **3a** dissolved in about 0.5 mL of acetonitrile inserted into a 6 dram vial containing about 10 mL of diethyl ether) was stored at room temperature for 7 days.

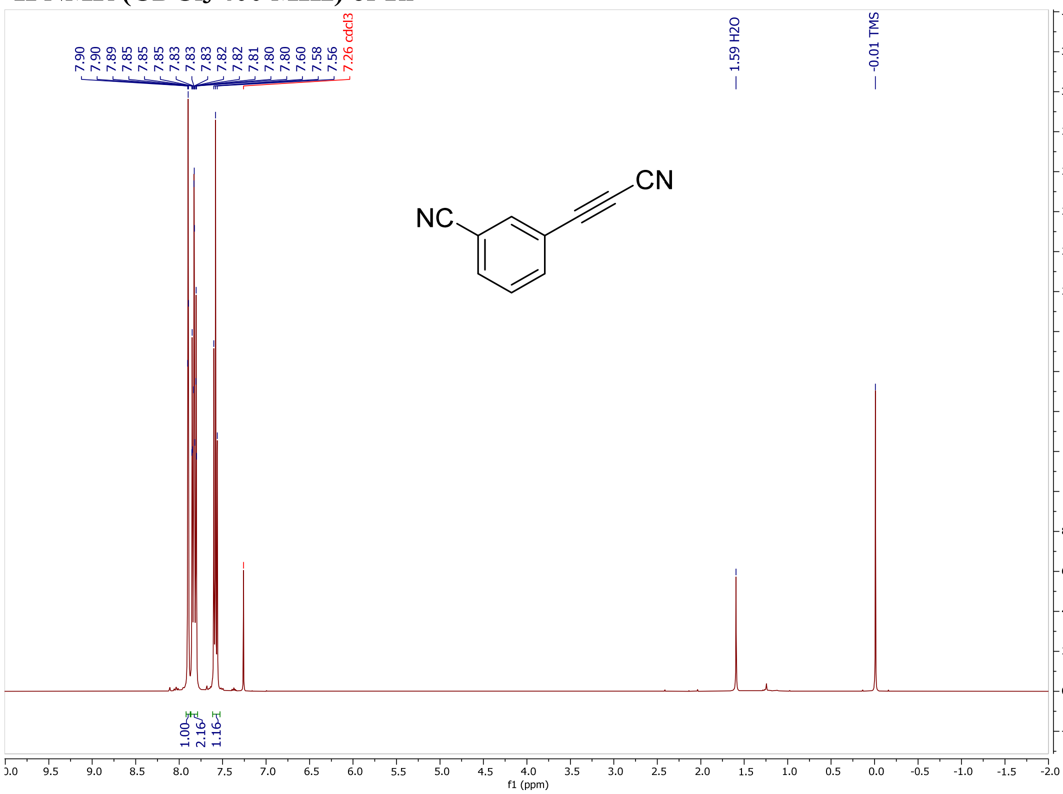
A colorless prism (0.07 x 0.19 x 0.21 mm3) was centered on the goniometer of a Rigaku Oxford Diffraction Synergy-S diffractometer equipped with a HyPix6000HE detector and operating with CuKα radiation. The data collection routine, unit cell refinement, and data processing were carried out with the program CrysAlisPro. The Laue symmetry and systematic absences were consistent with the monoclinic space group P21/c. The structure was solved using SHELXT and refined using SHELXL via Olex2. The final refinement model involved anisotropic displacement parameters for non-hydrogen atoms and a riding model for all hydrogen atoms: Olex2 and Mercury were used for molecular graphics generation.

15. References

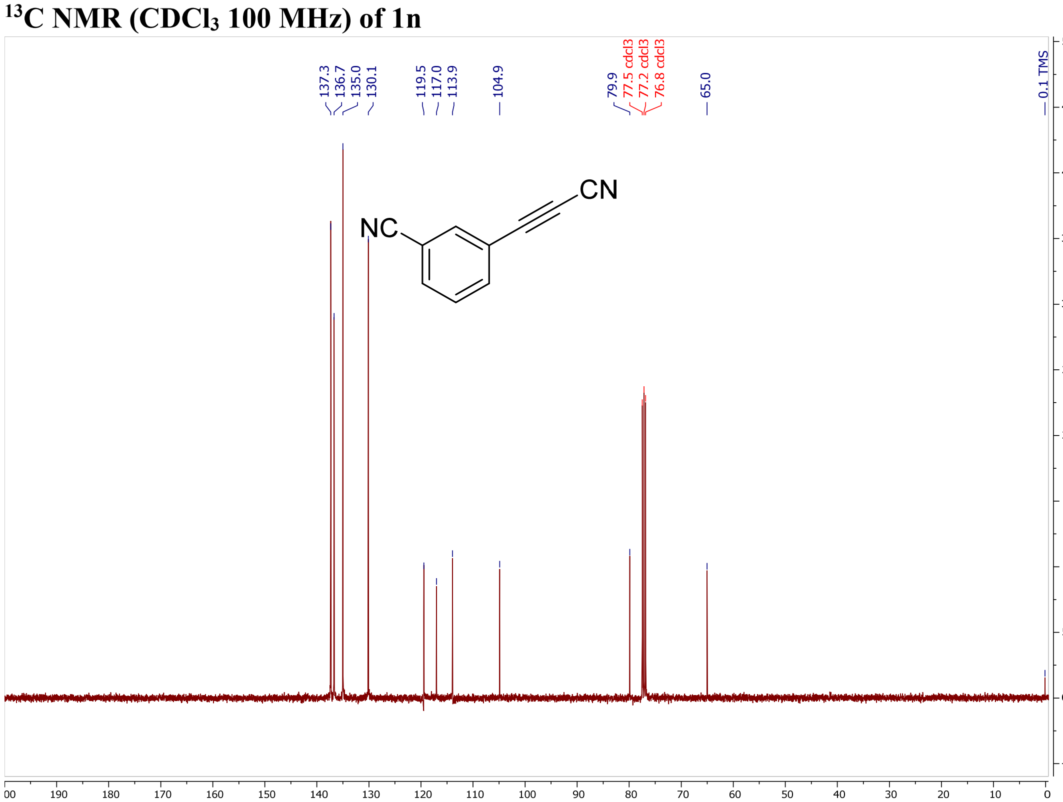
1. J. Panteleev, R. Y. Huang, E. K. J. Lui and M. Lautens, *Org. Lett.*, 2011, **13**, 5314-5317.
2. A. S. K. Hashmi, P. Haufe and A. Rivas Nass, *Adv. Synth. Catal.*, 2003, **345**, 1237-1241.
3. J.-M. Vatèle, *Synlett*, 2014, **25**, 1275-1278.

16. NMR Spectra of Propiolonitriles

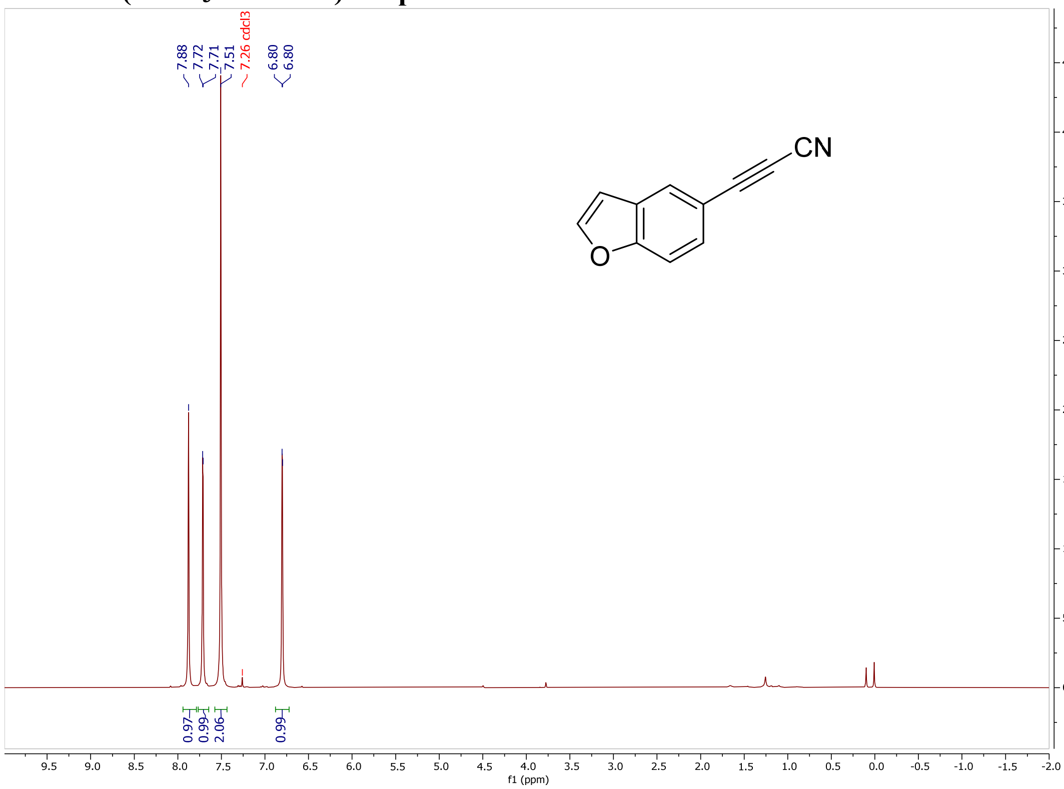
^{1}H NMR ($CDCl_3$ 400 MHz) of 1n



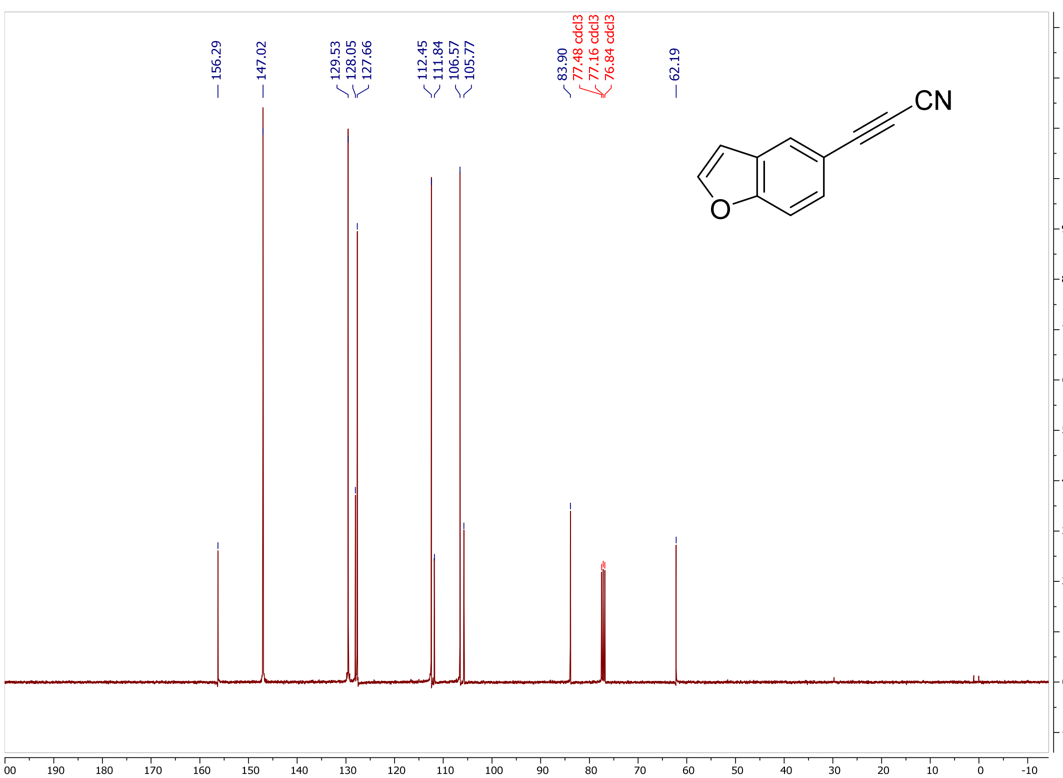
^{13}C NMR ($CDCl_3$ 100 MHz) of 1n



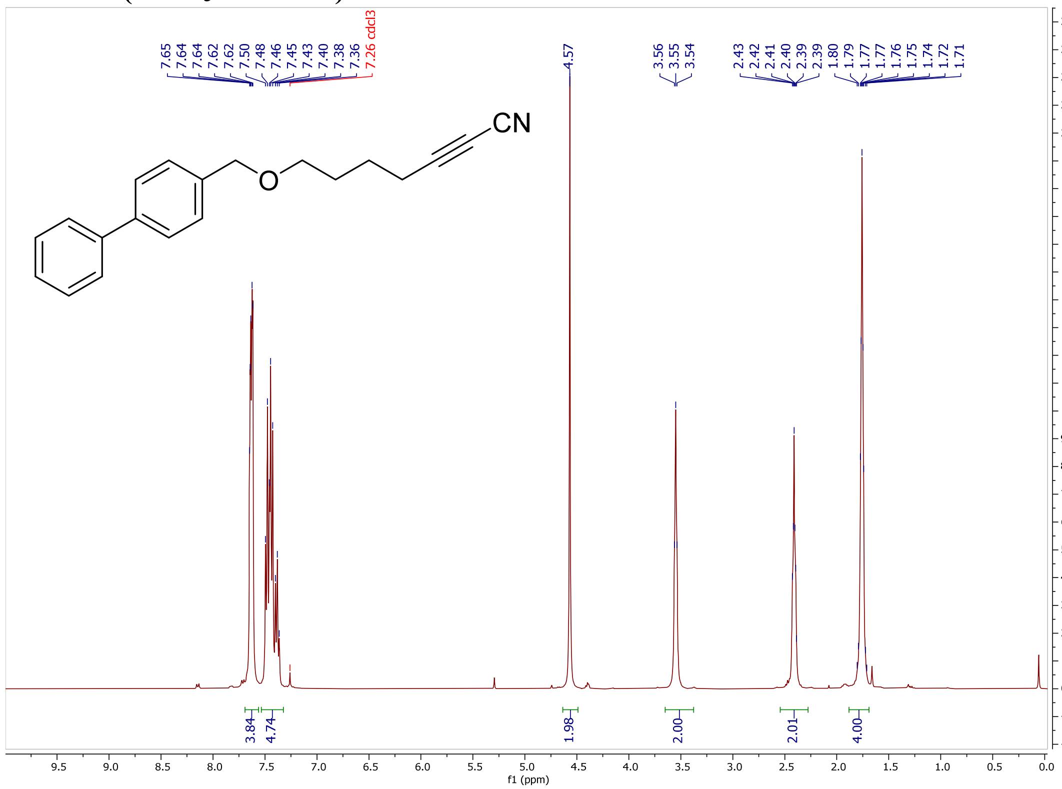
^{1}H NMR ($CDCl_3$ 400 MHz) of 1p



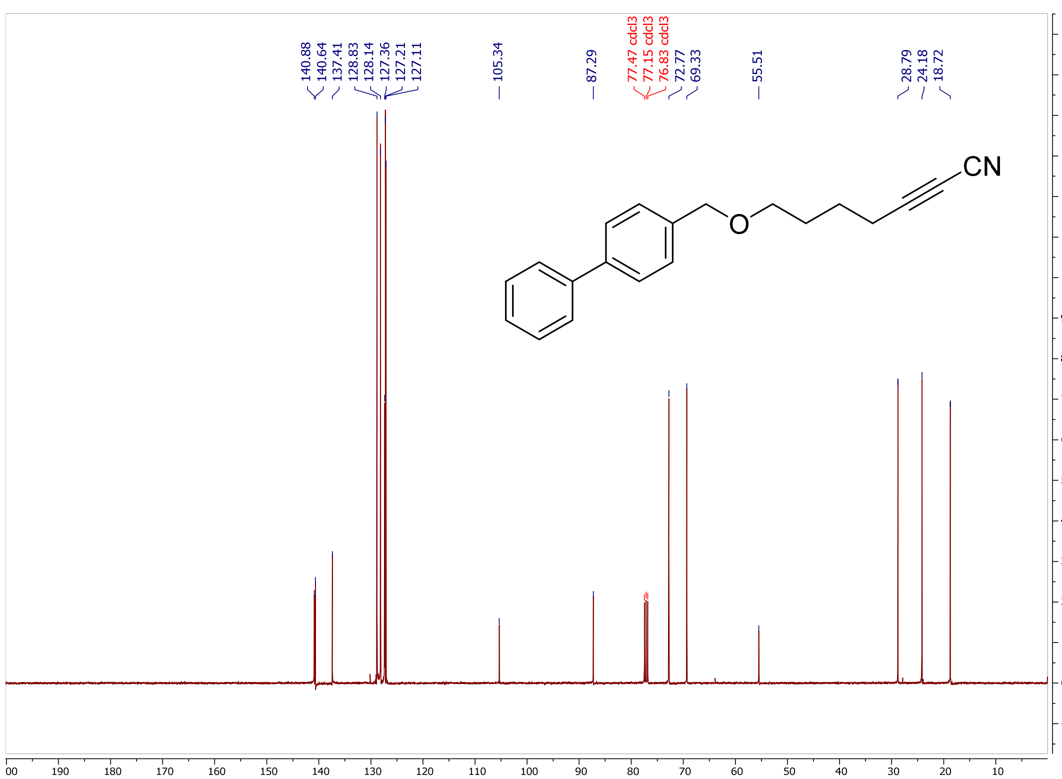
^{13}C NMR ($CDCl_3$ 100 MHz) of 1p



[1]H NMR ($CDCl_3$ 400 MHz) of 1s

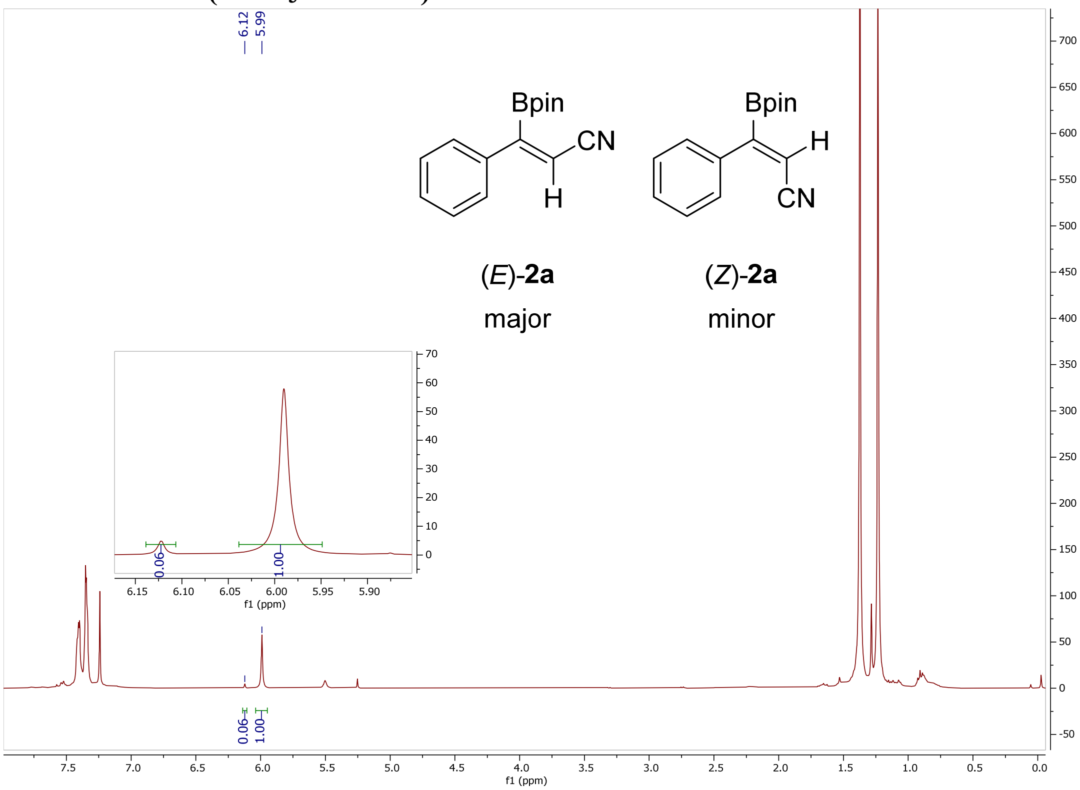


[13]C NMR ($CDCl_3$ 100 MHz) of 1s

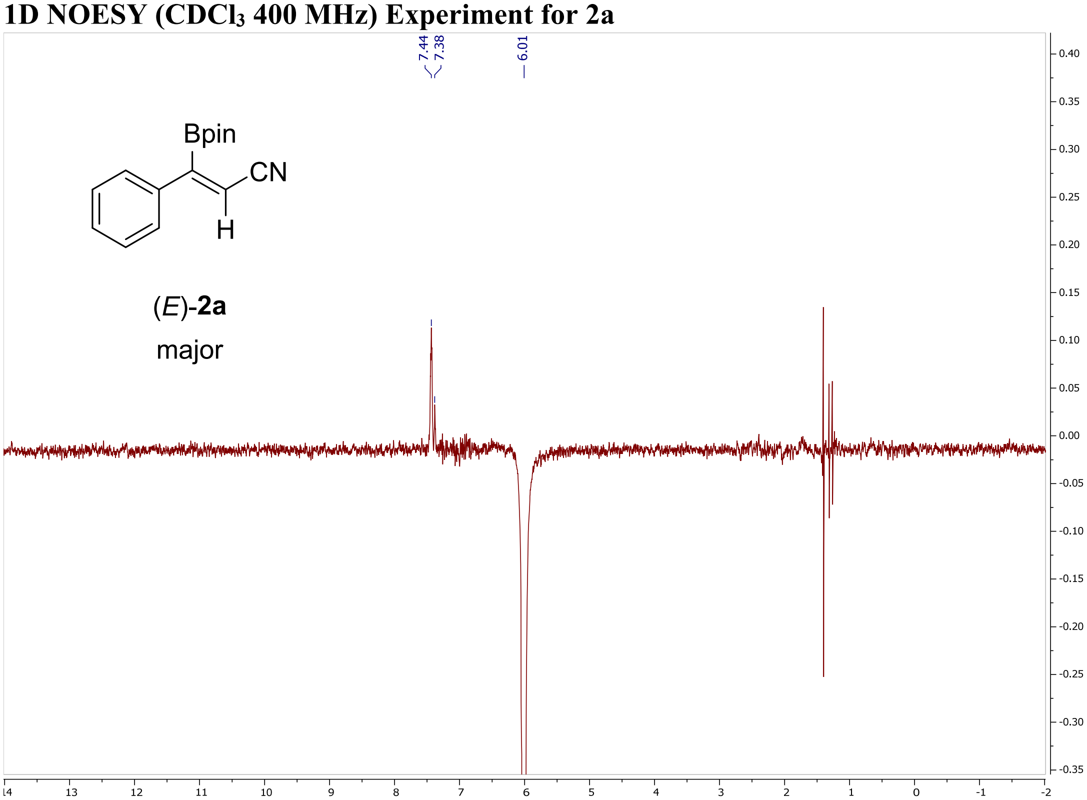


17. NMR Spectra of Crude 1,2-vinylcyanoboranes

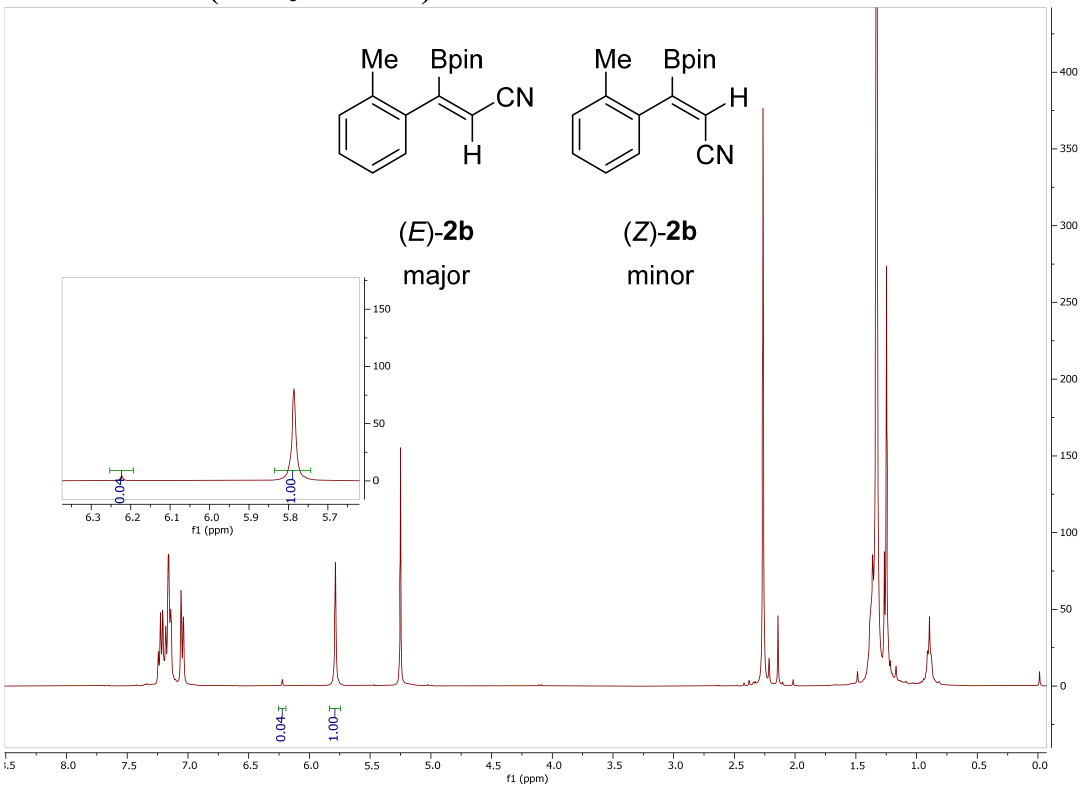
Crude ^{1}H NMR ($CDCl_3$ 400 MHz) of 2a



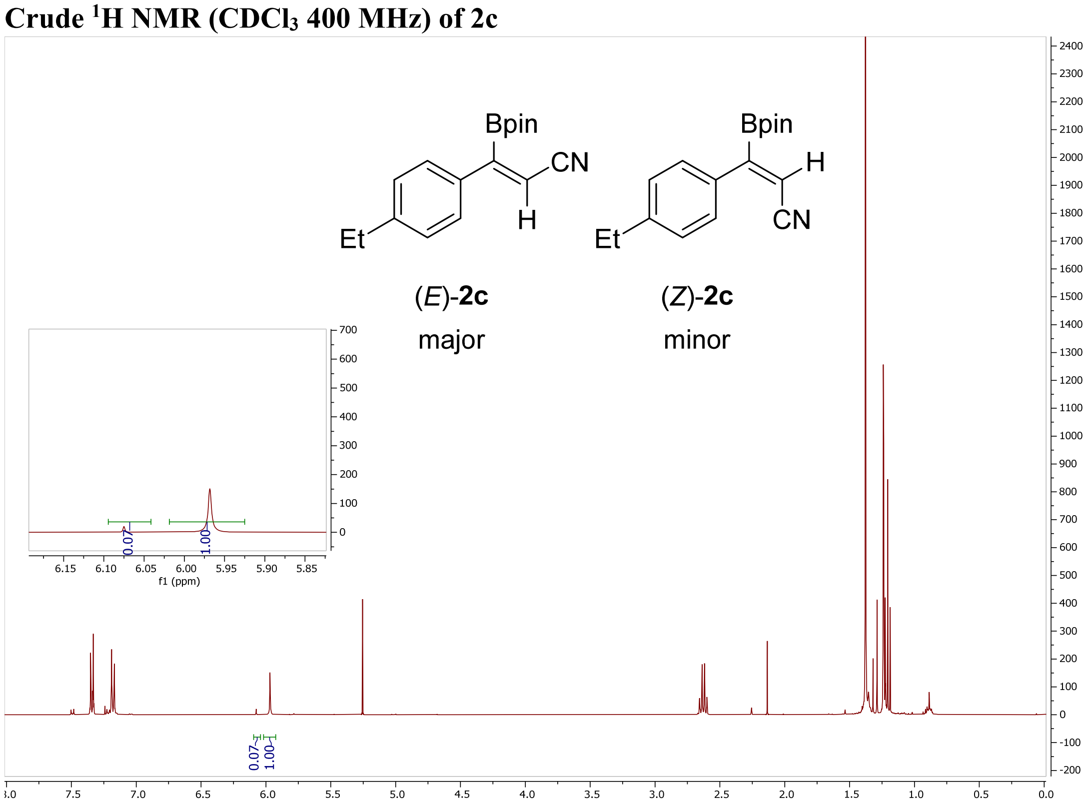
1D NOESY ($CDCl_3$ 400 MHz) Experiment for 2a



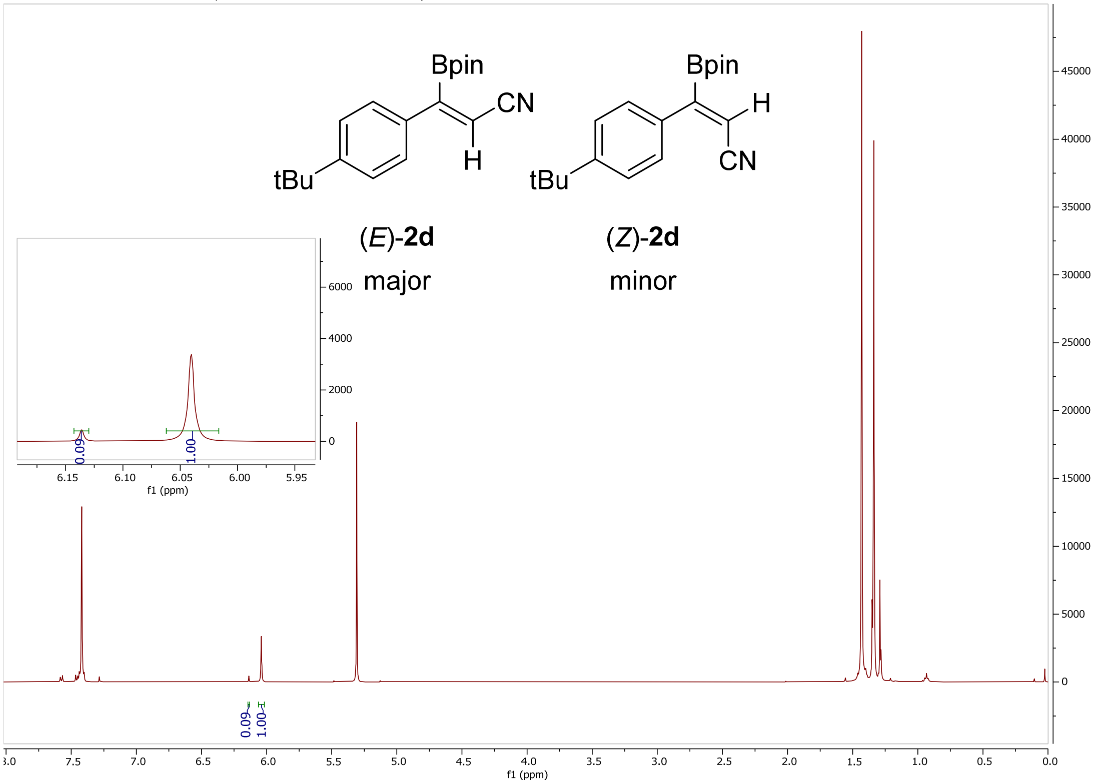
Crude ¹H NMR (CDCl₃ 400 MHz) of 2b



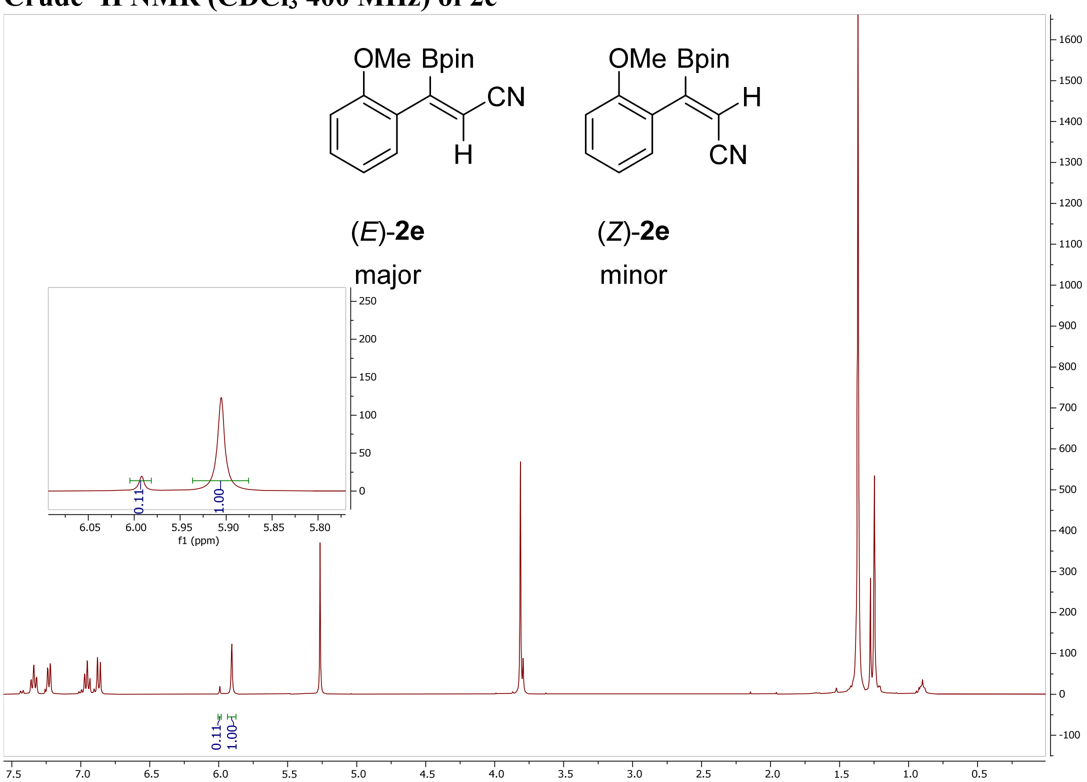
Crude ¹H NMR (CDCl₃ 400 MHz) of 2c



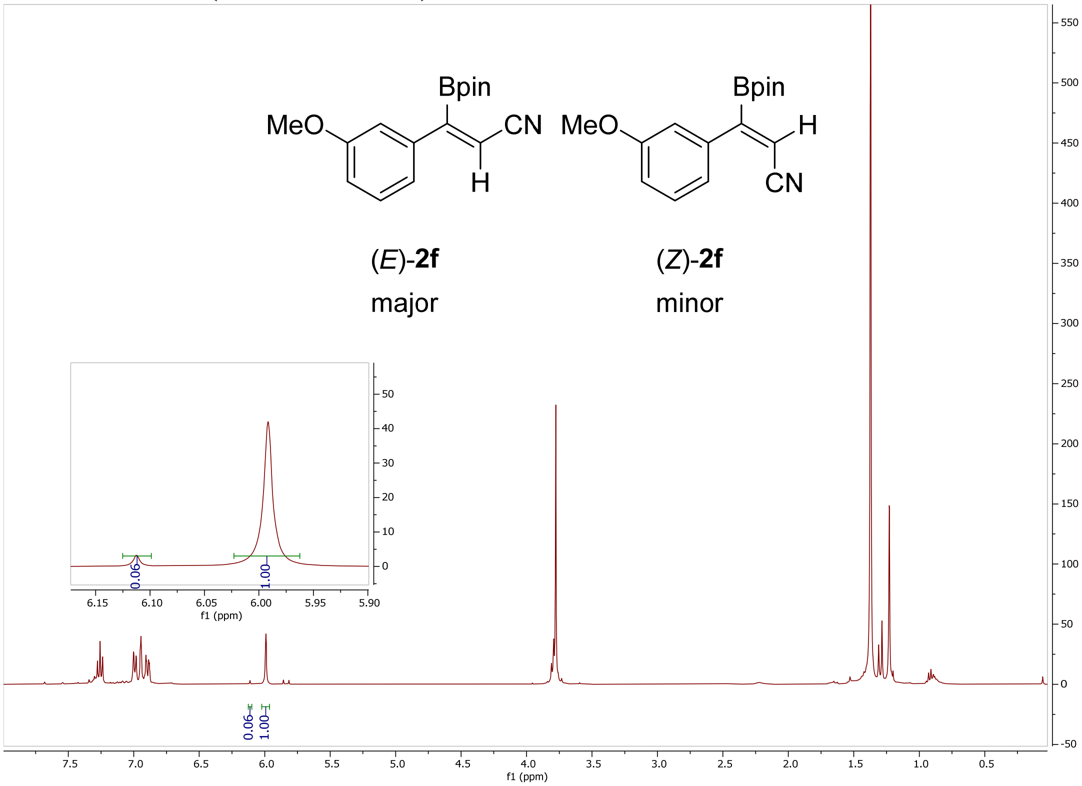
Crude ^{1}H NMR ($CDCl_3$ 400 MHz) of 2d



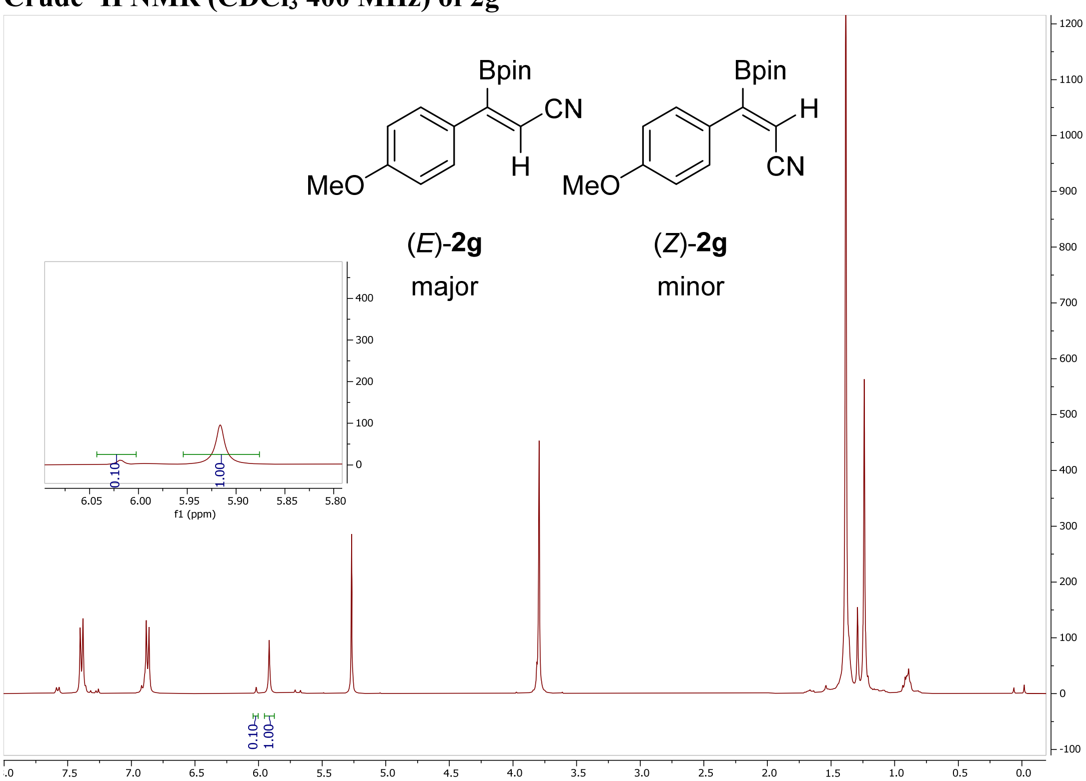
Crude ^{1}H NMR ($CDCl_3$ 400 MHz) of 2e



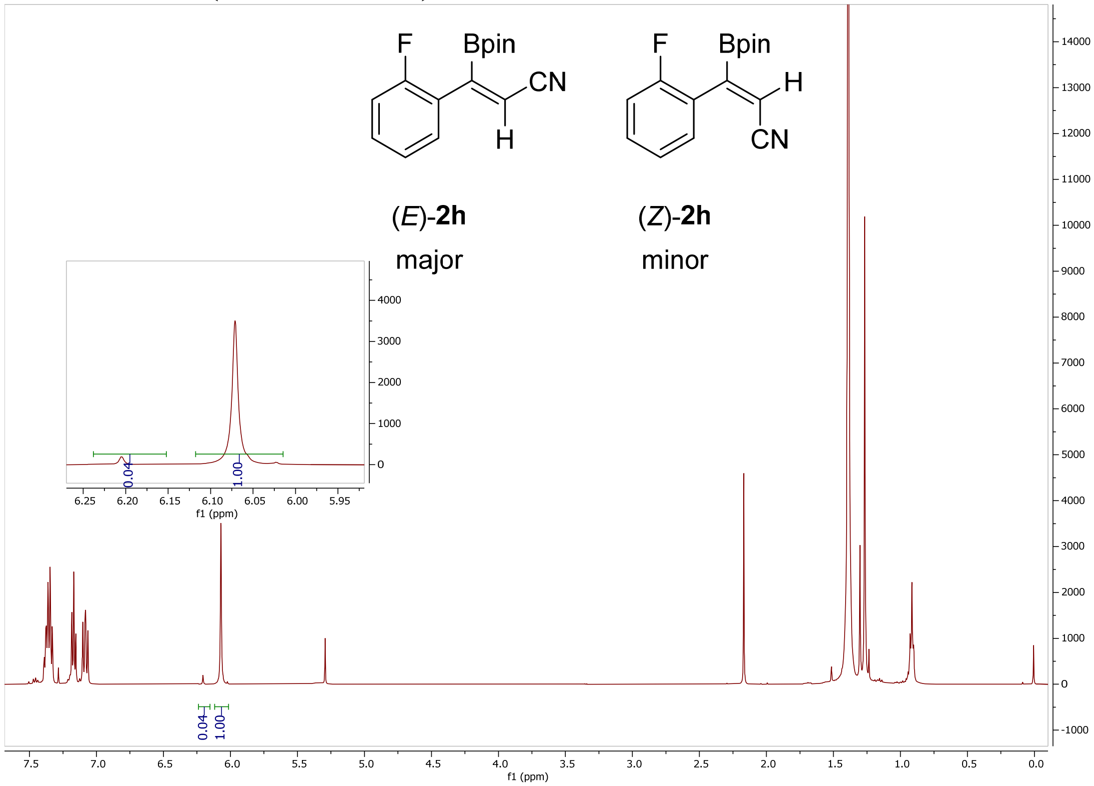
Crude ^{1}H NMR ($CDCl_3$ 400 MHz) of 2f



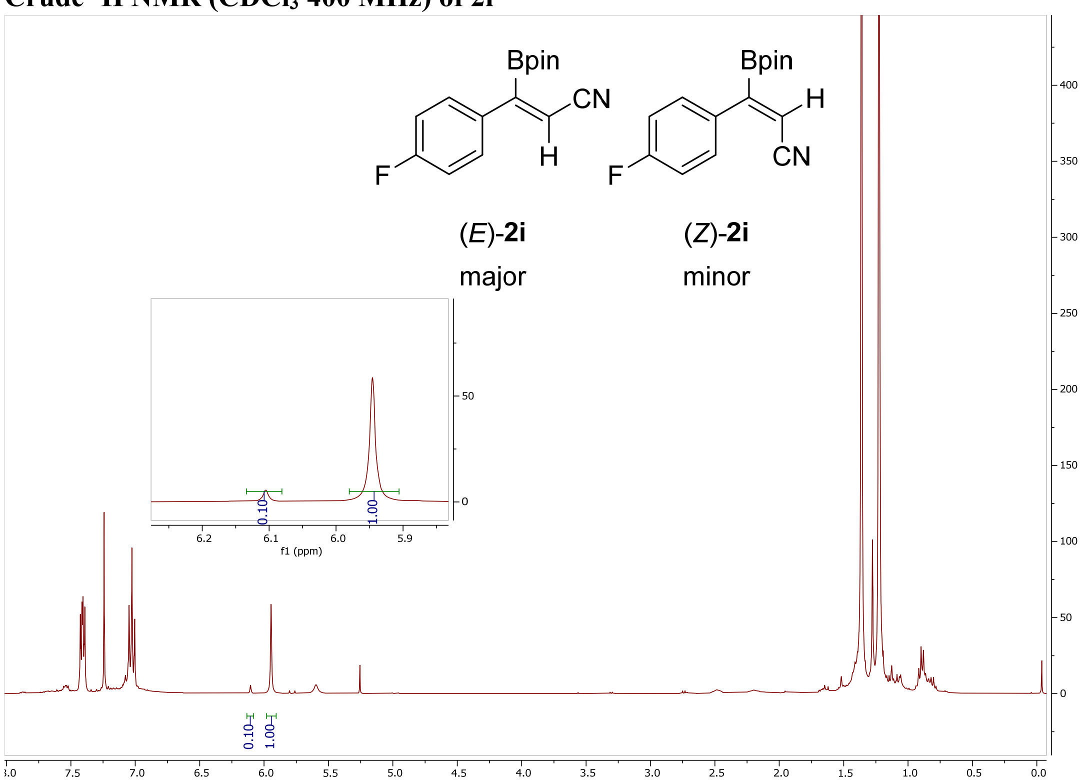
Crude ^{1}H NMR ($CDCl_3$ 400 MHz) of 2g



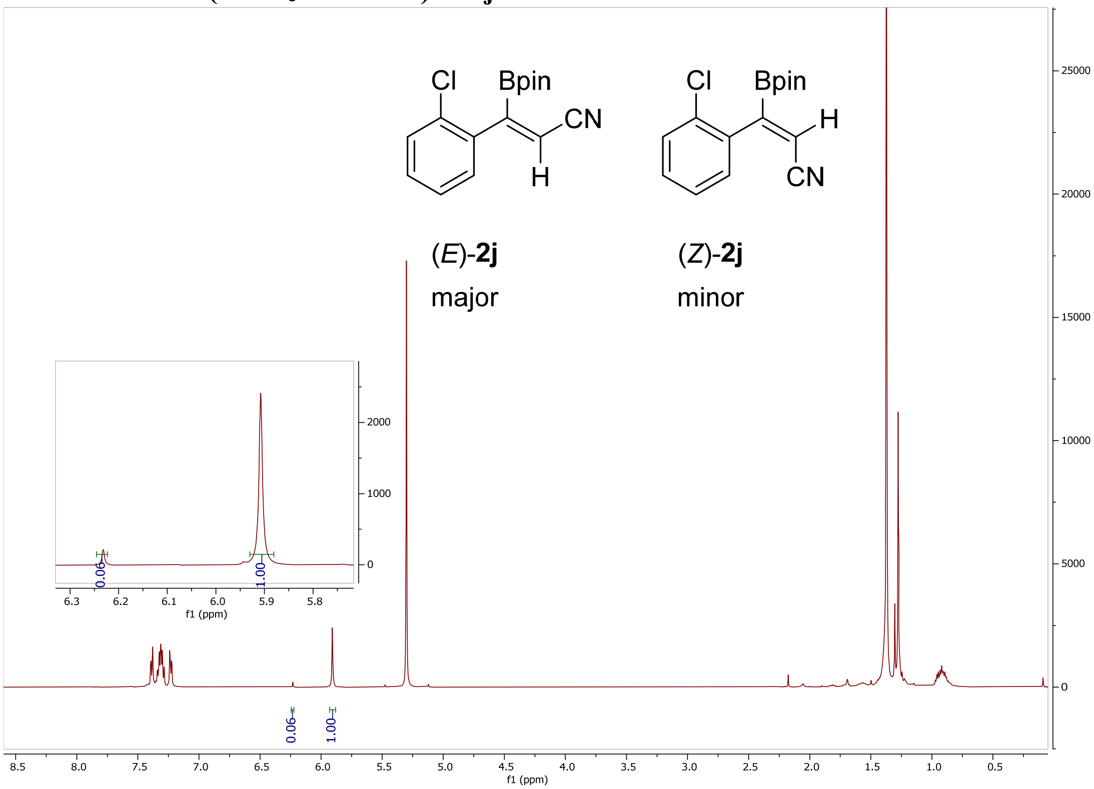
Crude ^{1}H NMR (CDCl$_3$ 400 MHz) of 2h



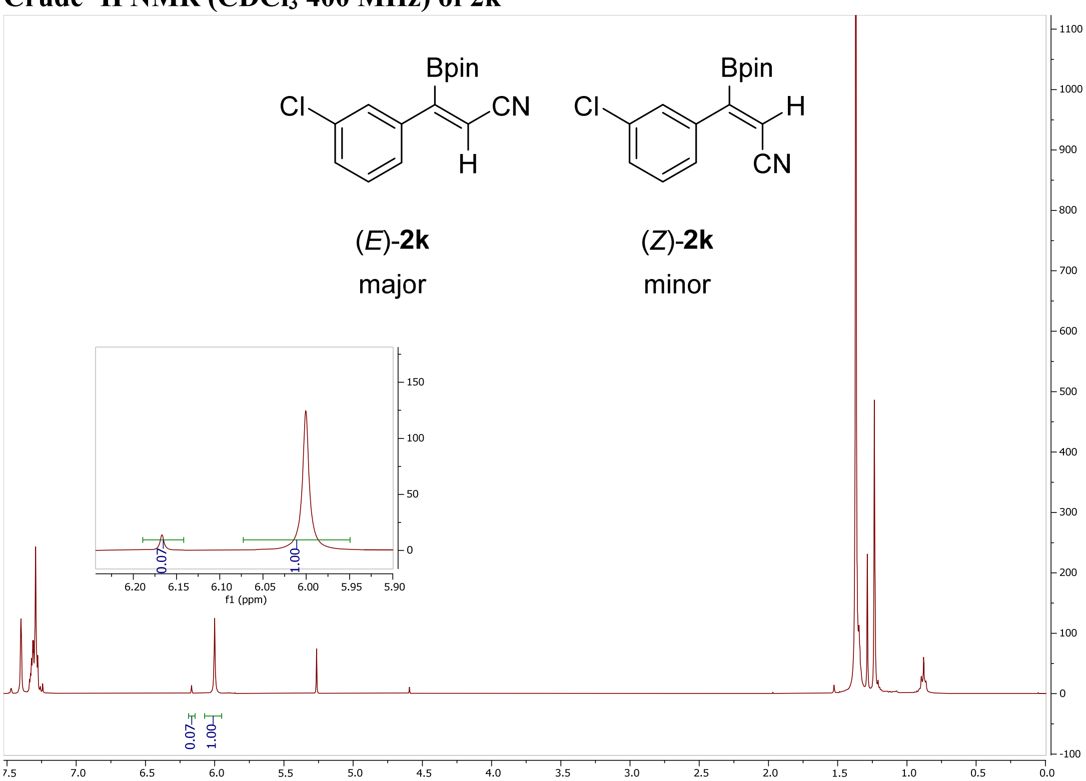
Crude ^{1}H NMR (CDCl$_3$ 400 MHz) of 2i



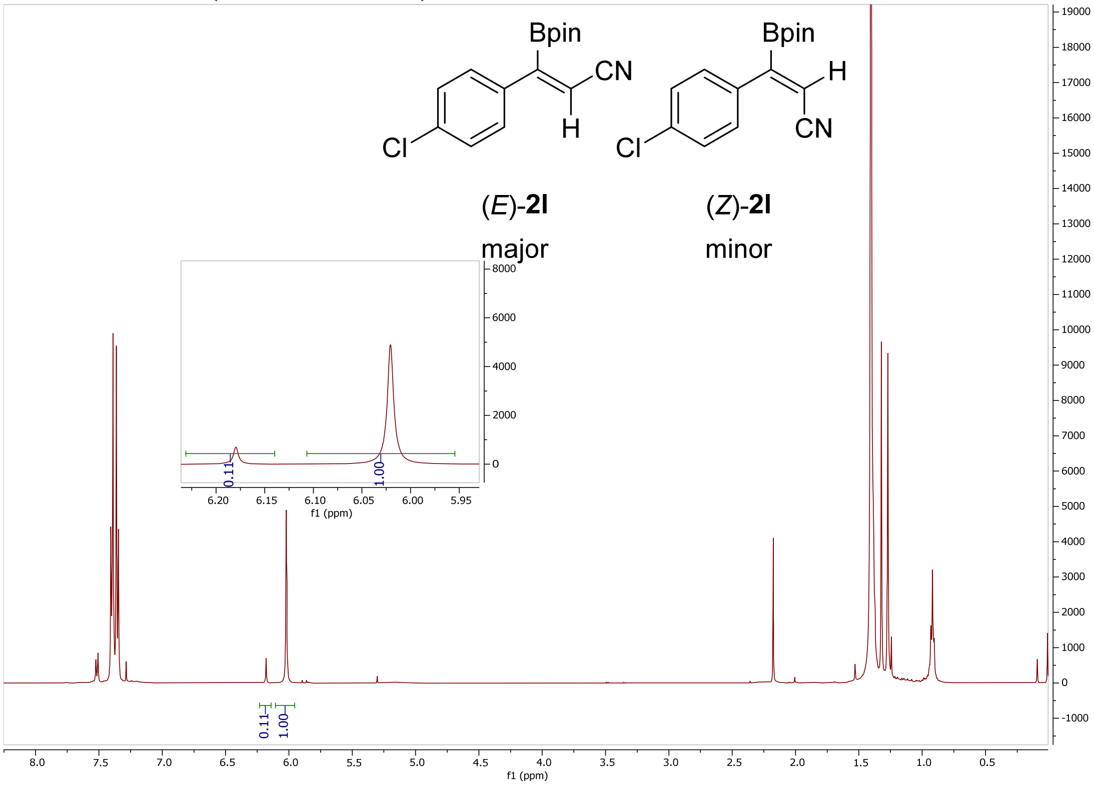
Crude ^{1}H NMR ($CDCl_3$ 400 MHz) of 2j



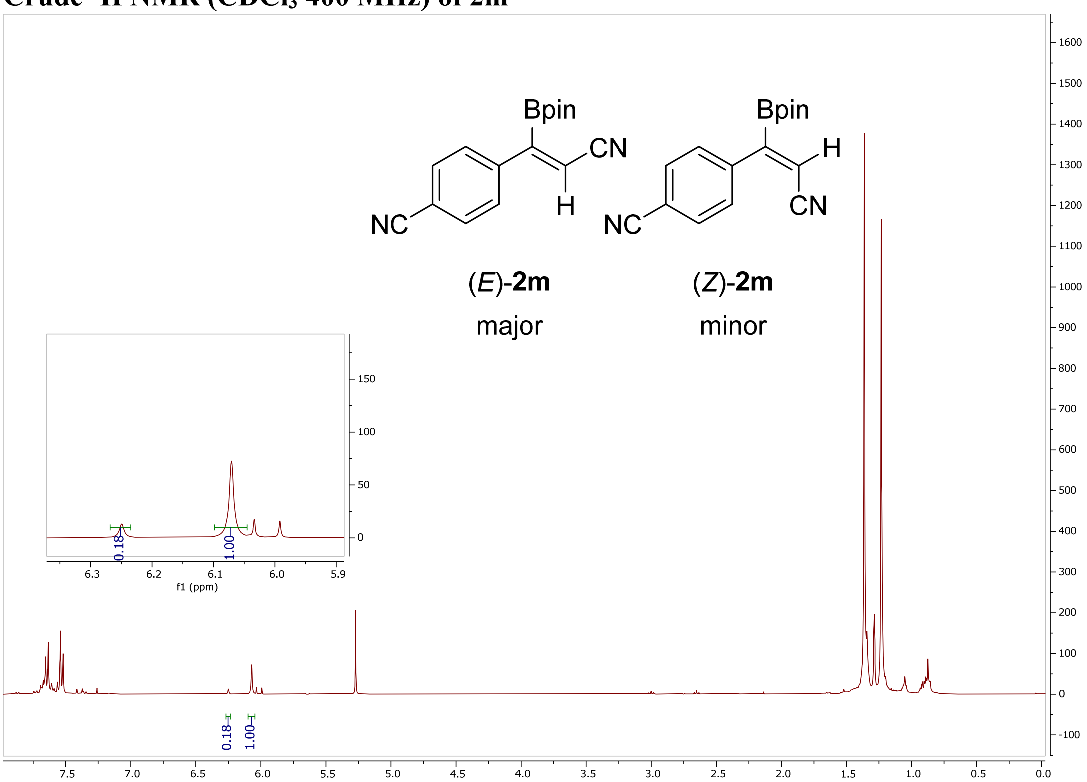
Crude ^{1}H NMR ($CDCl_3$ 400 MHz) of 2k



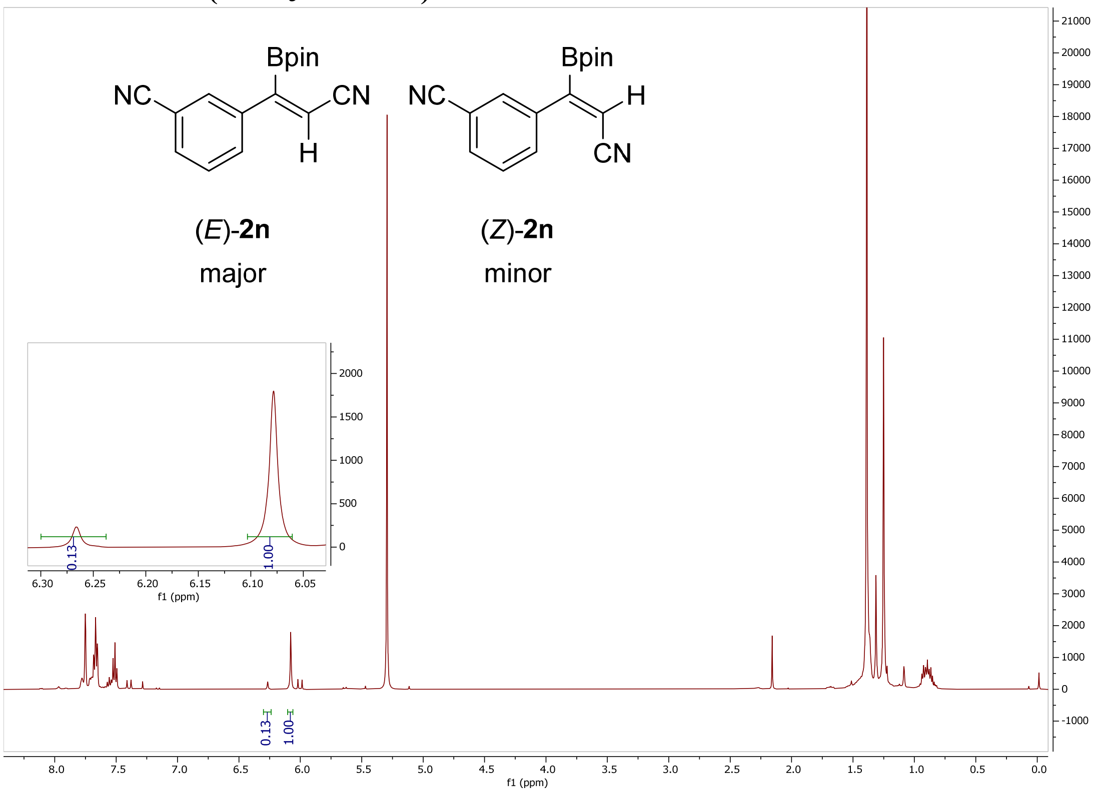
Crude ^{1}H NMR (CDCl$_3$ 400 MHz) of 2l



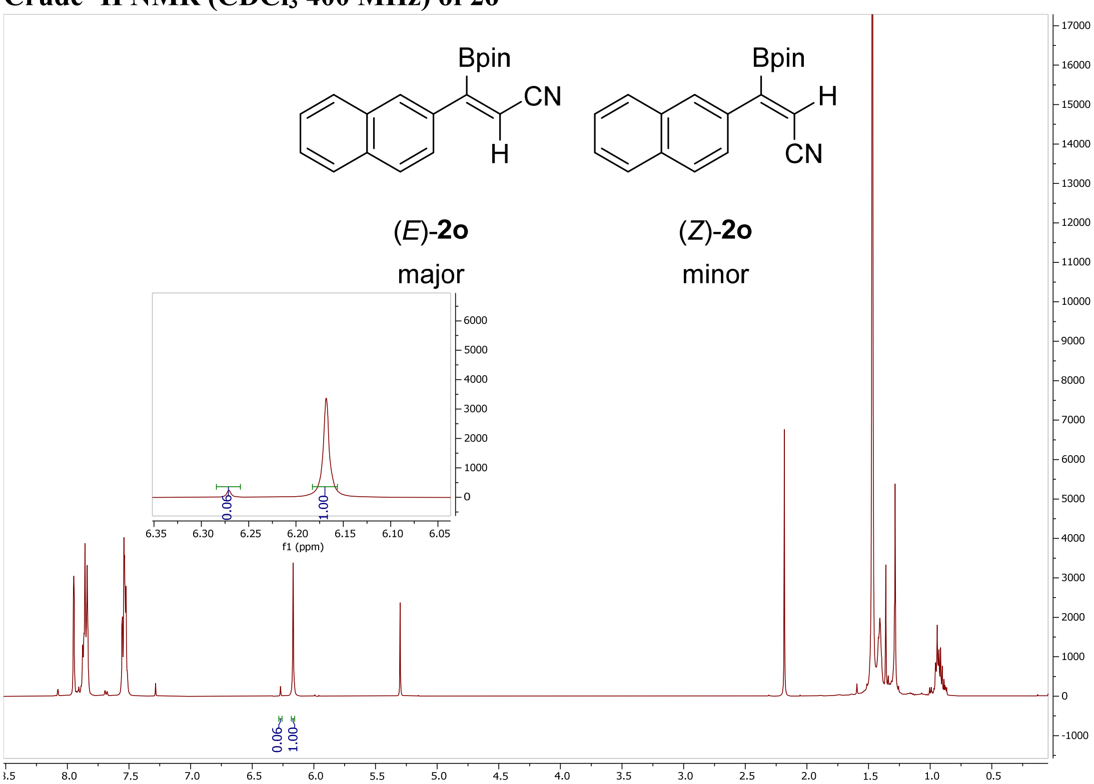
Crude ^{1}H NMR (CDCl$_3$ 400 MHz) of 2m



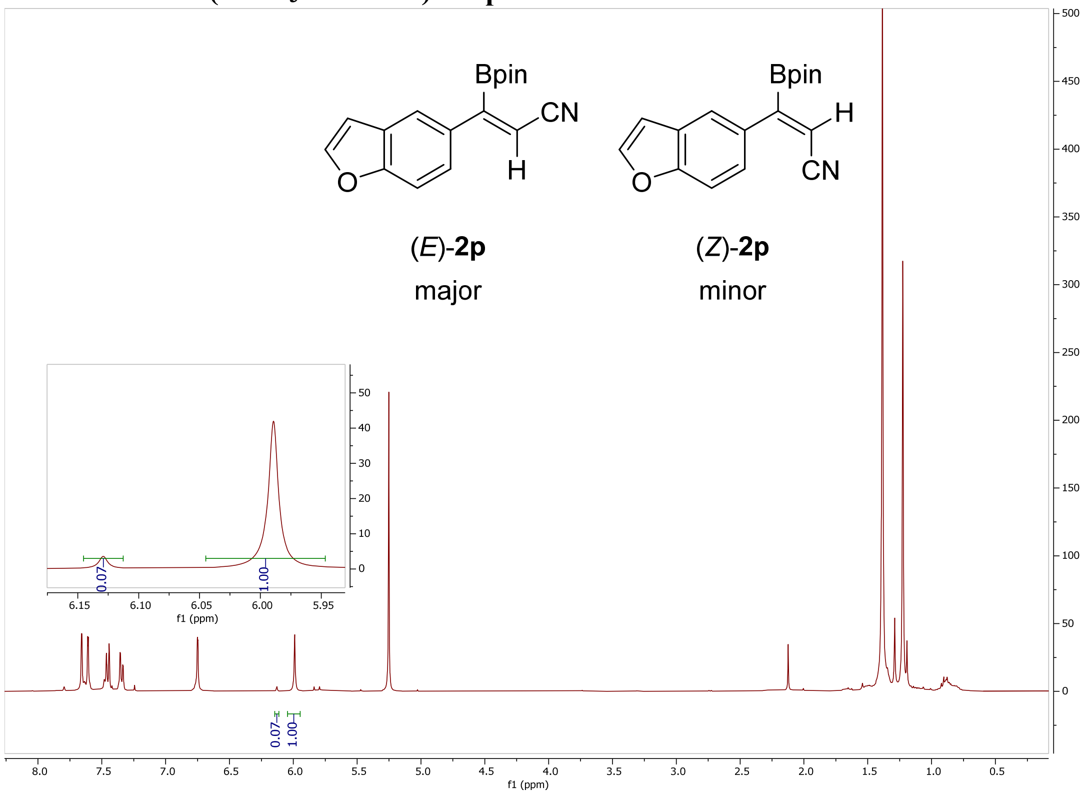
Crude ^{1}H NMR ($CDCl_3$ 400 MHz) of 2n



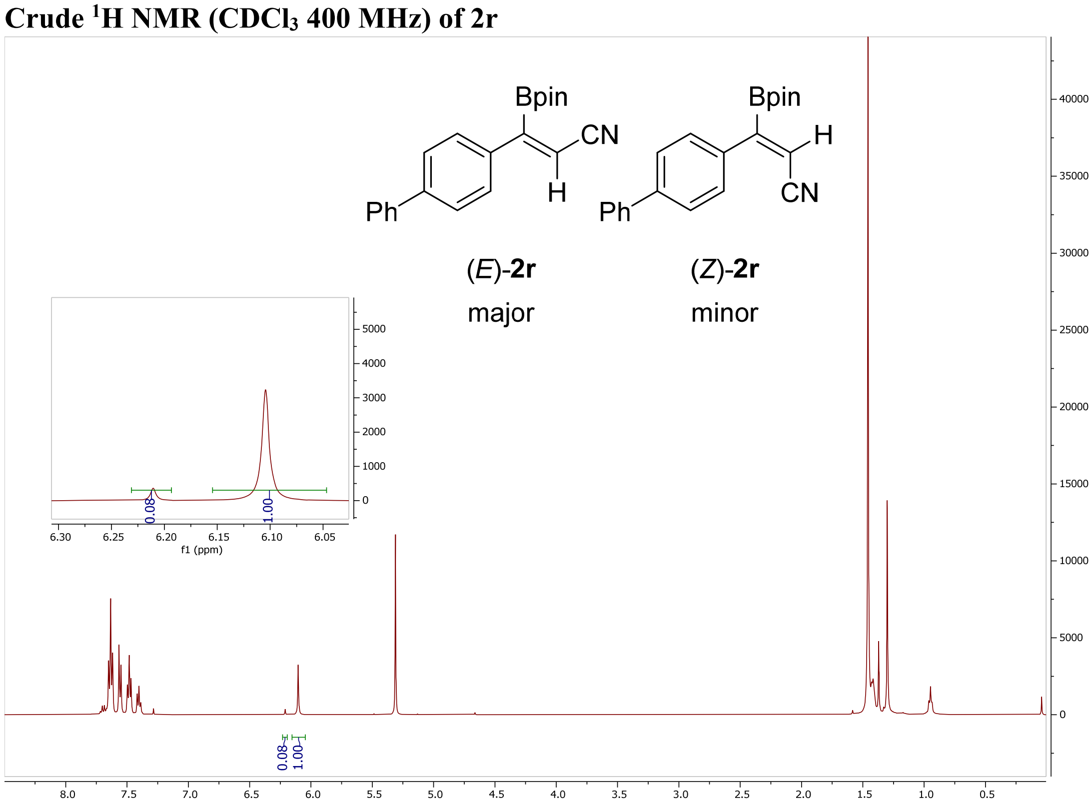
Crude ^{1}H NMR ($CDCl_3$ 400 MHz) of 2o



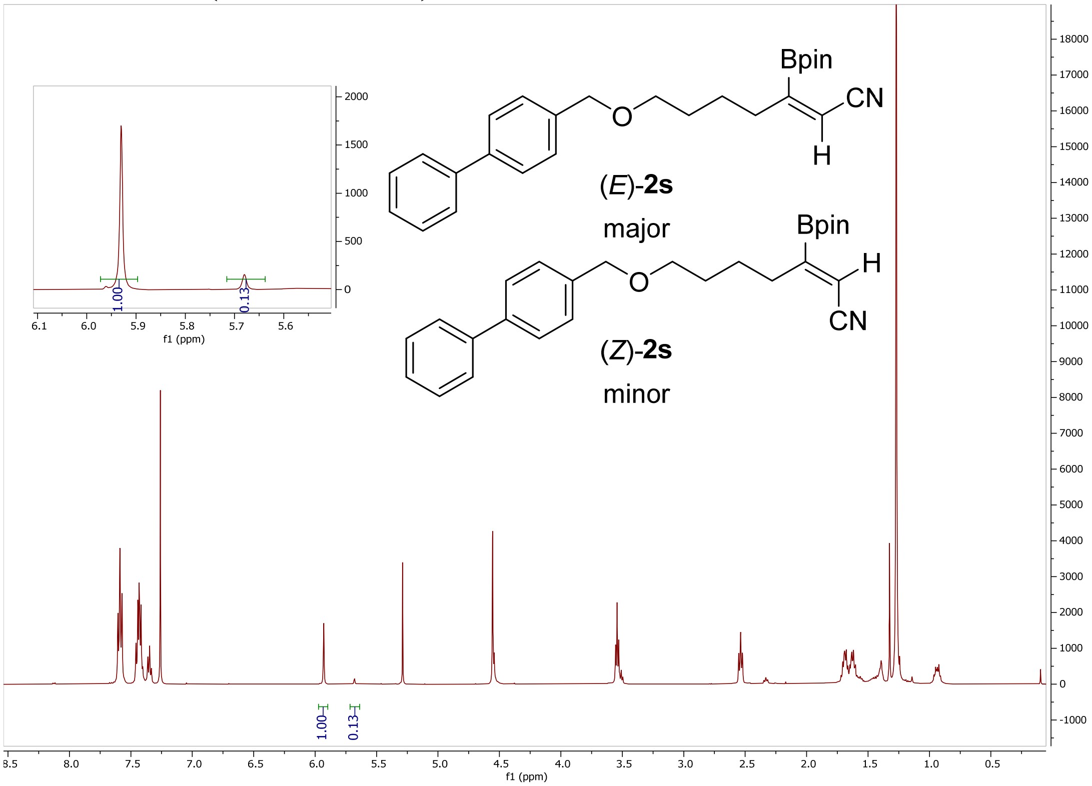
Crude ^{1}H NMR ($CDCl_3$ 400 MHz) of 2p



Crude ^{1}H NMR ($CDCl_3$ 400 MHz) of 2r

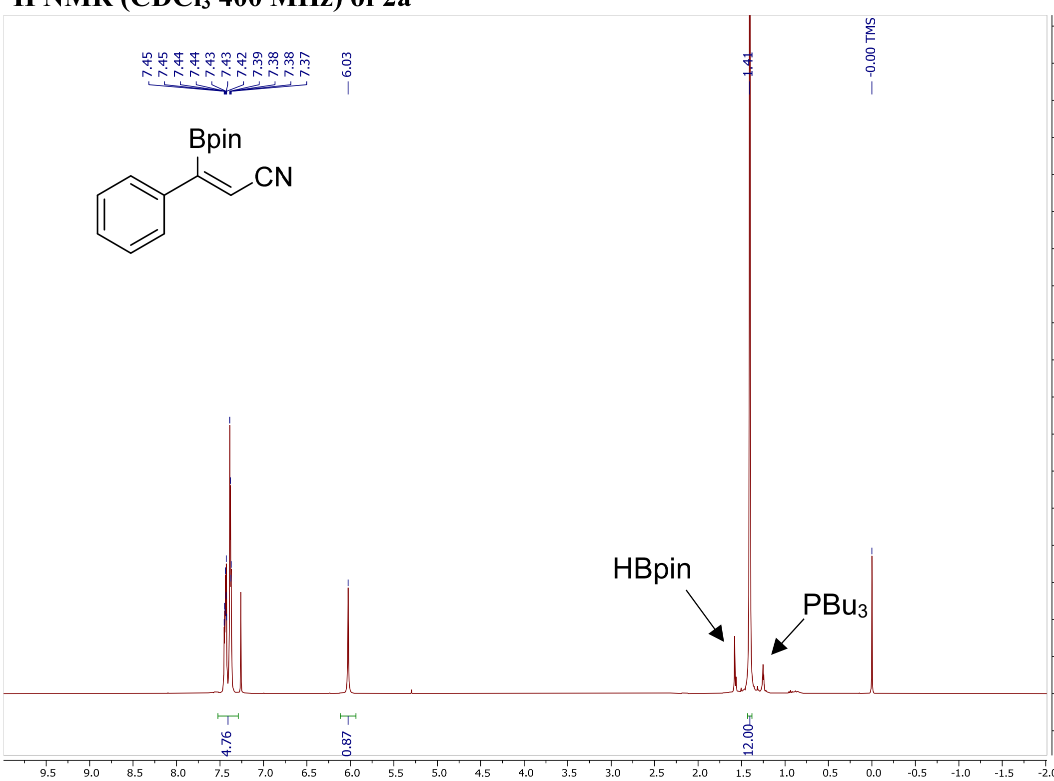


Crude ^{1}H NMR (CDCl$_3$ 400 MHz) of 2s

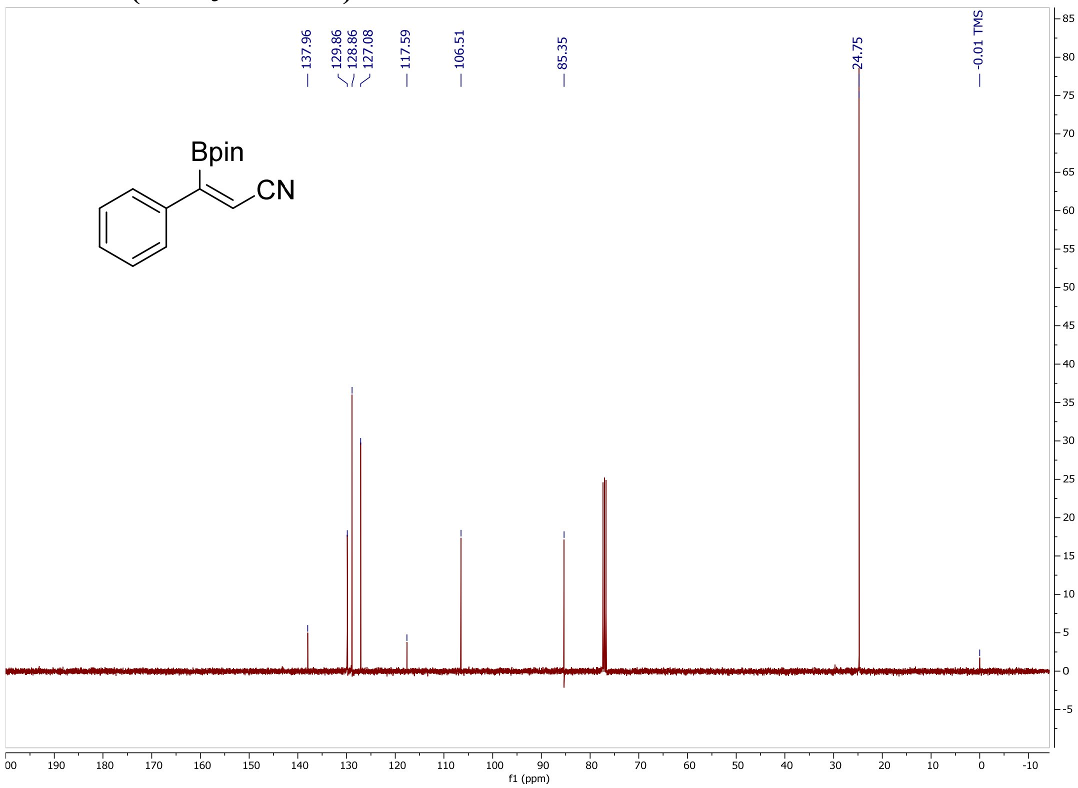


18. NMR Spectra of 1,2-vinylcyanoboronate esters

^{1}H NMR (CDCl$_3$ 400 MHz) of 2a

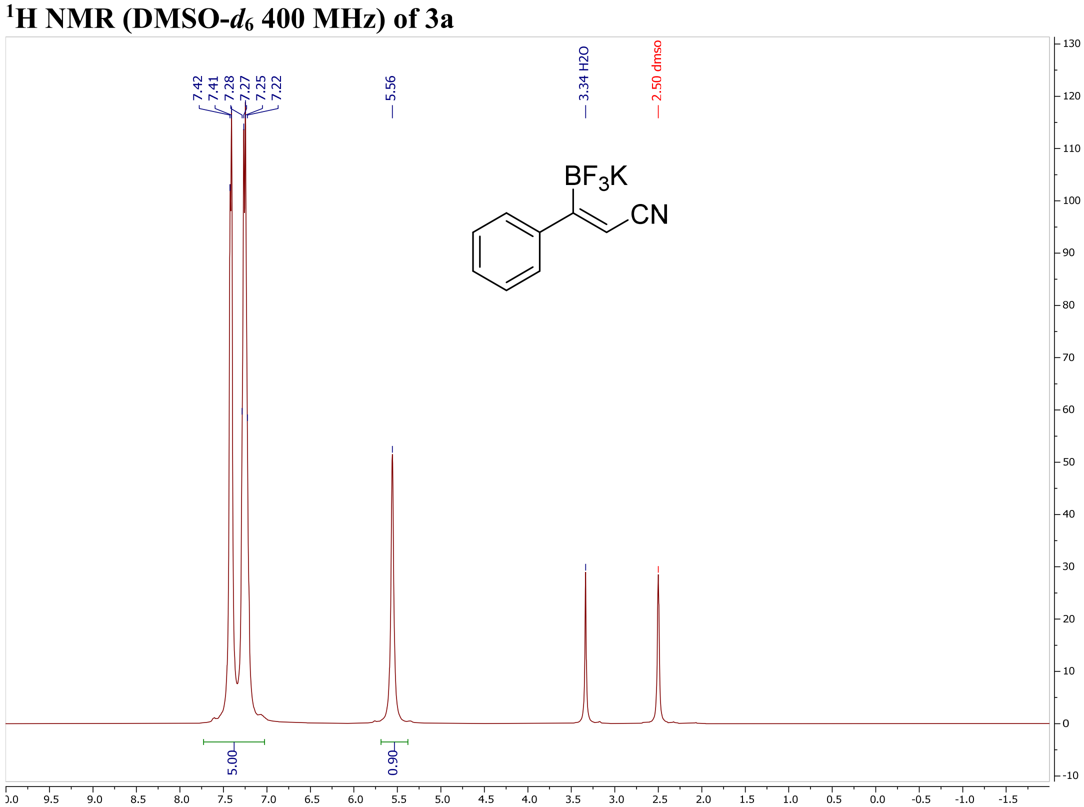


^{13}C NMR ($CDCl_3$ 100 MHz) of 2a

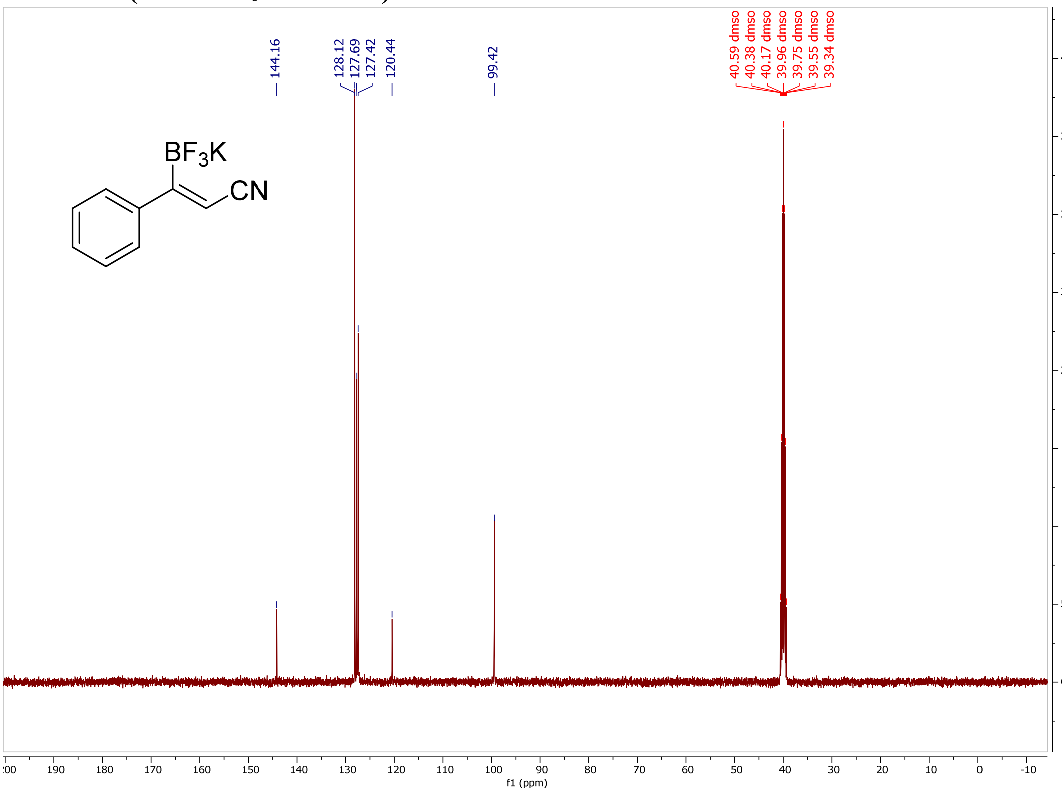


19. NMR Spectra of 1,2-vinylcyanoborane Potassium Trifluoroborate Salts

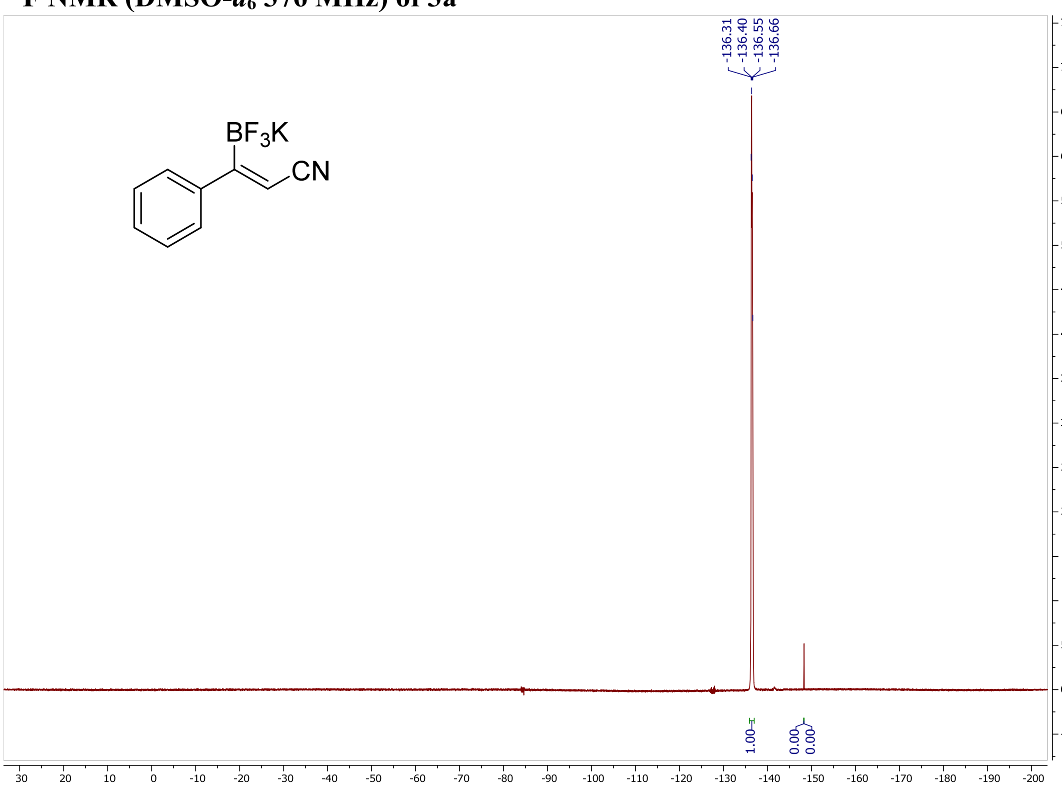
^1H NMR (DMSO-d_6 400 MHz) of 3a



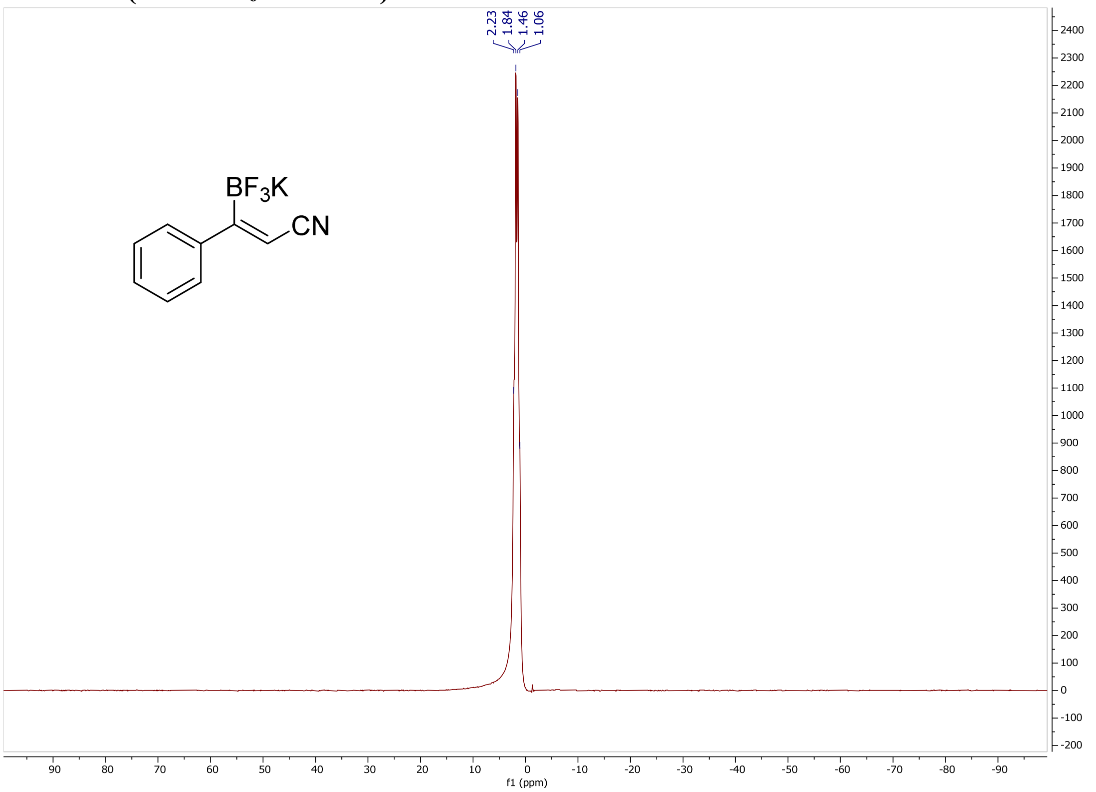
^{13}C NMR (DMSO-d_6 100 MHz) of 3a



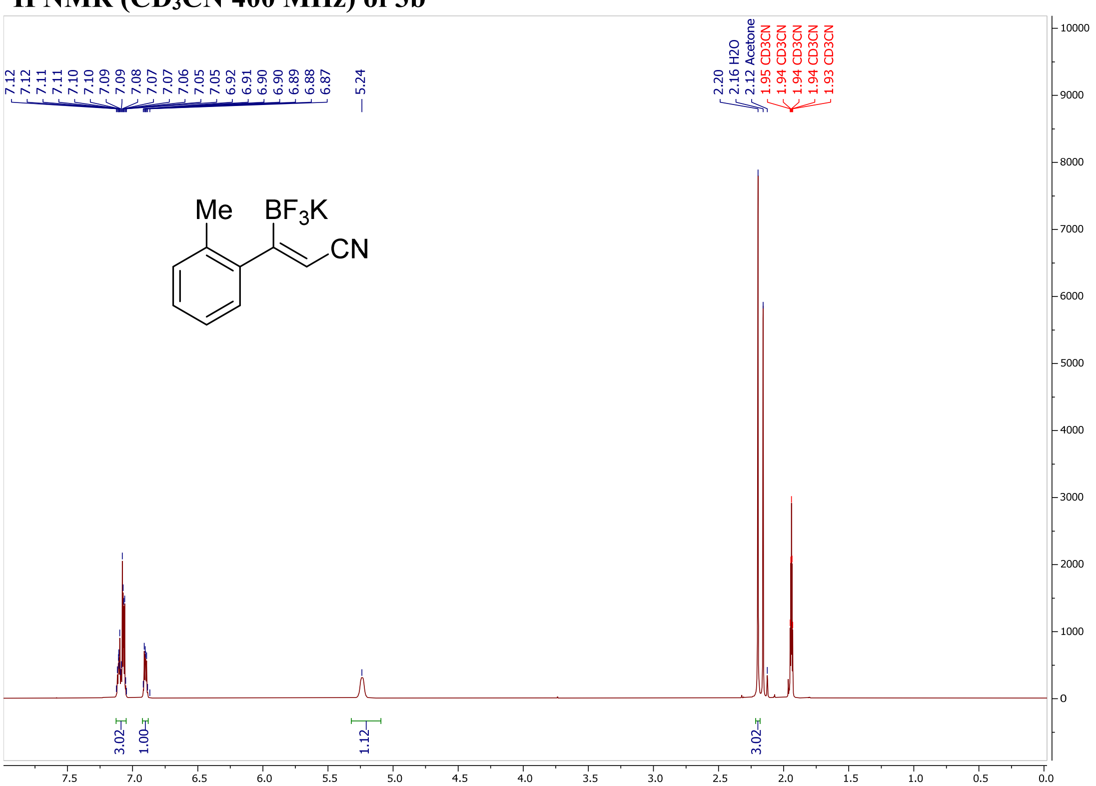
^{19}F NMR (DMSO-d_6 376 MHz) of 3a



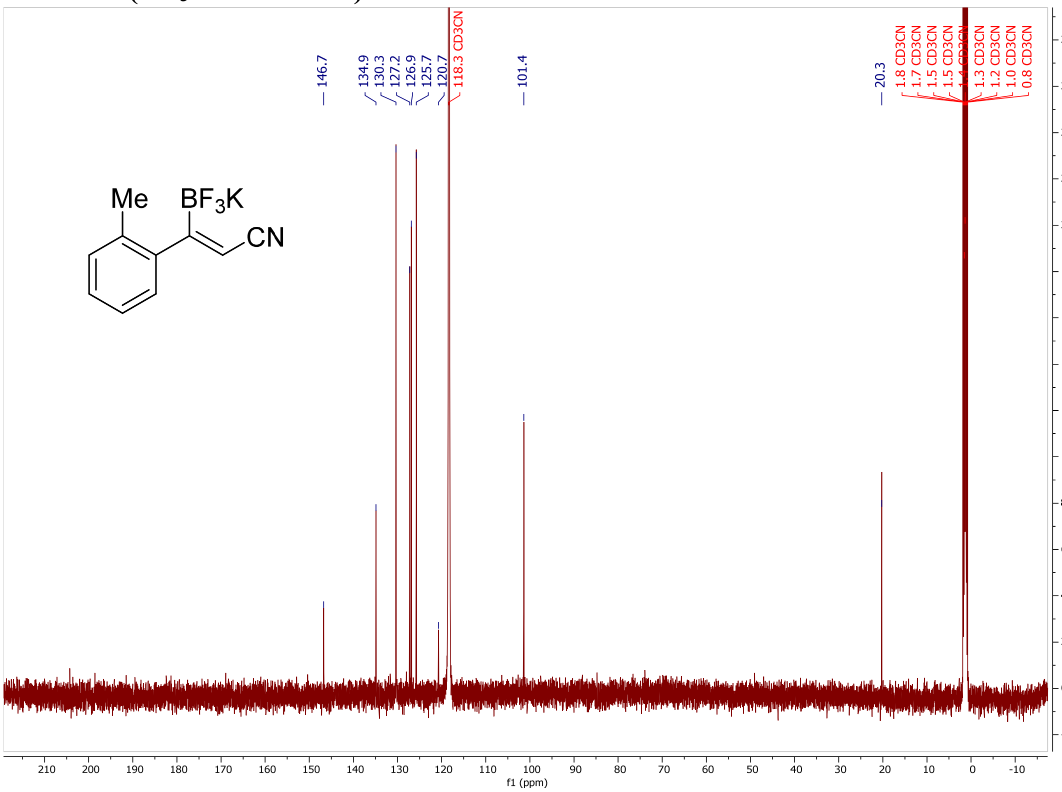
^{11}B NMR (DMSO-d_6 128 MHz) of 3a



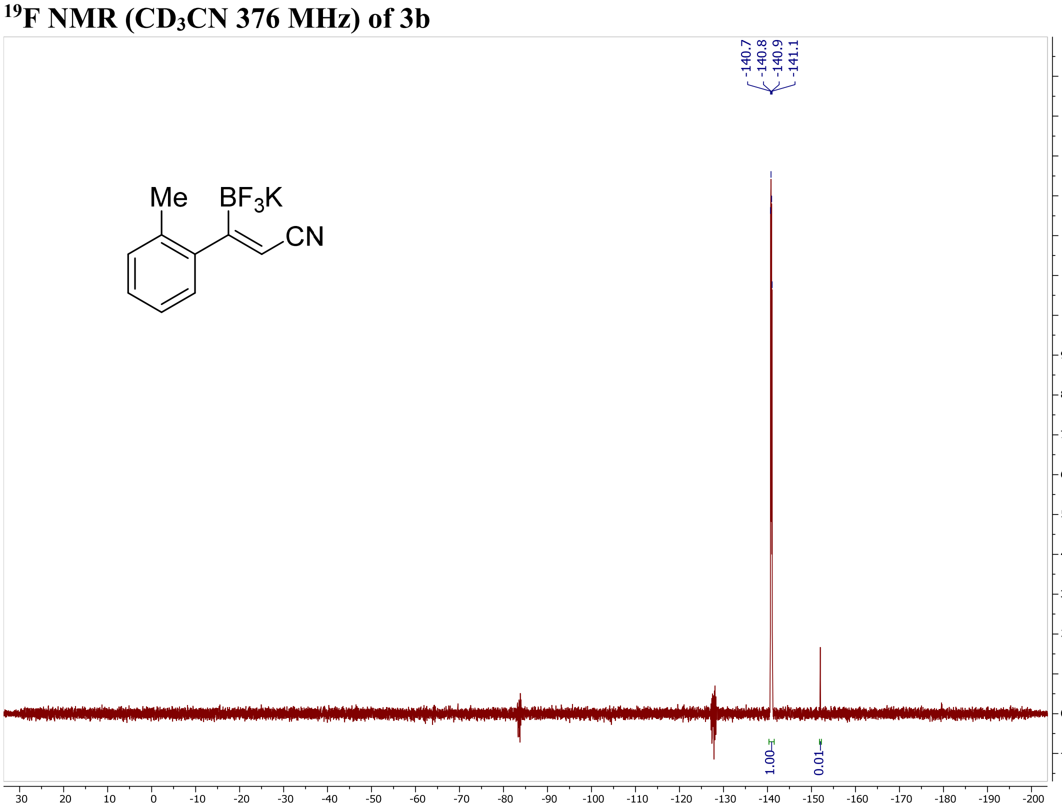
^{1}H NMR (CD_3CN 400 MHz) of 3b



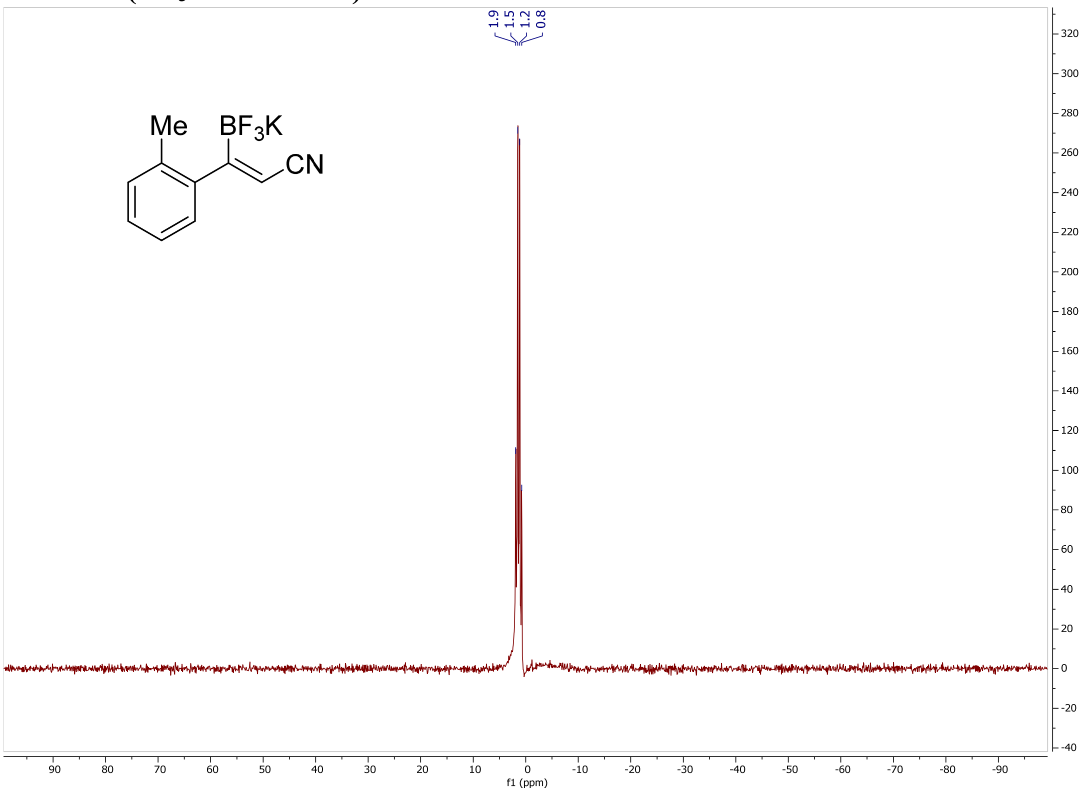
^{13}C NMR (CD_3CN 100 MHz) of 3b



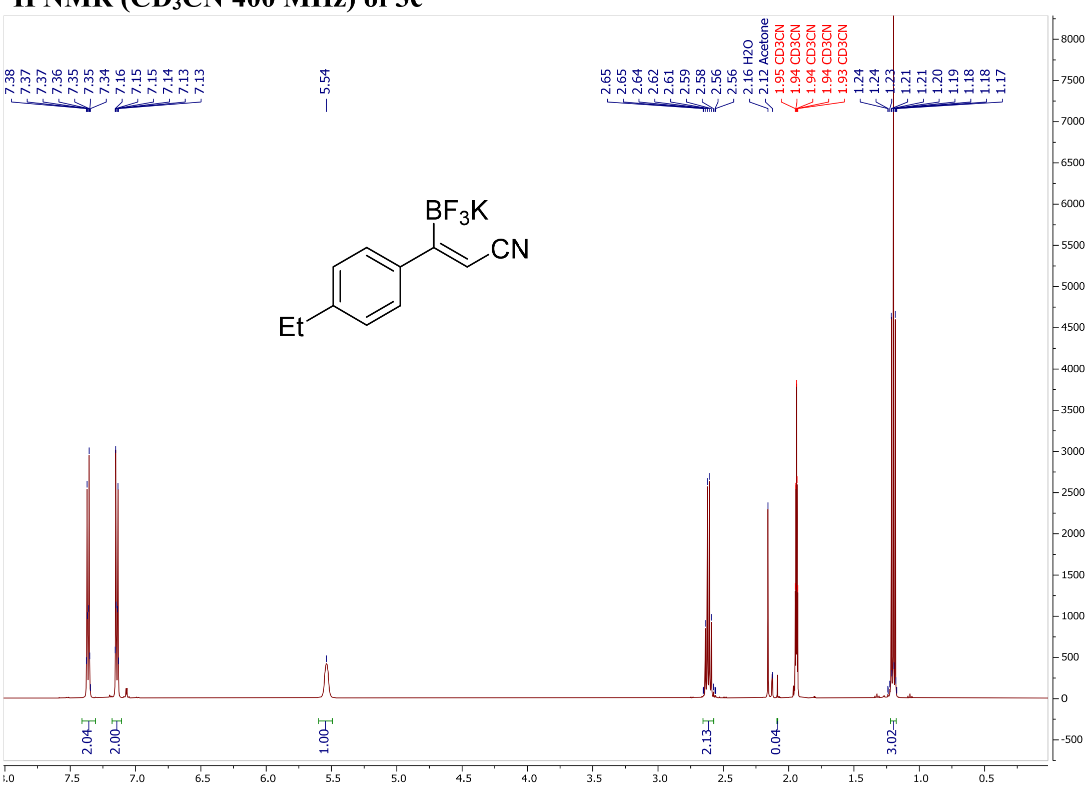
^{19}F NMR (CD_3CN 376 MHz) of 3b



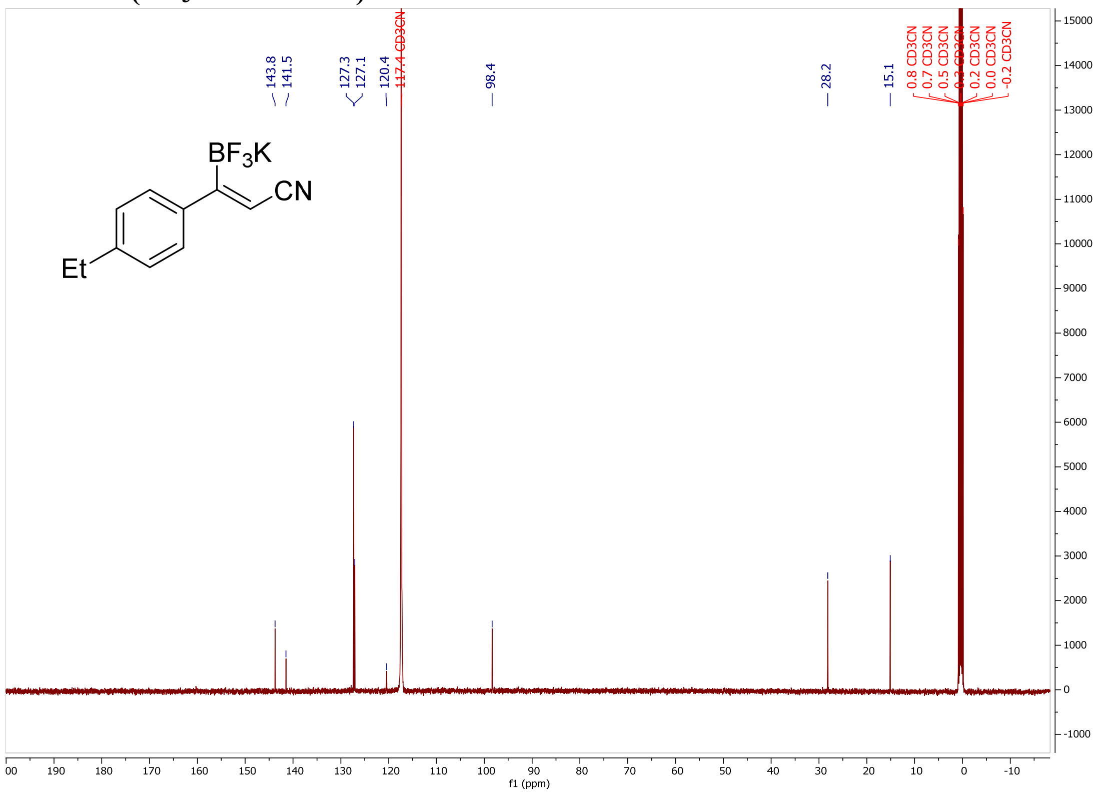
^{11}B NMR (CD_3CN 128 MHz) of 3b



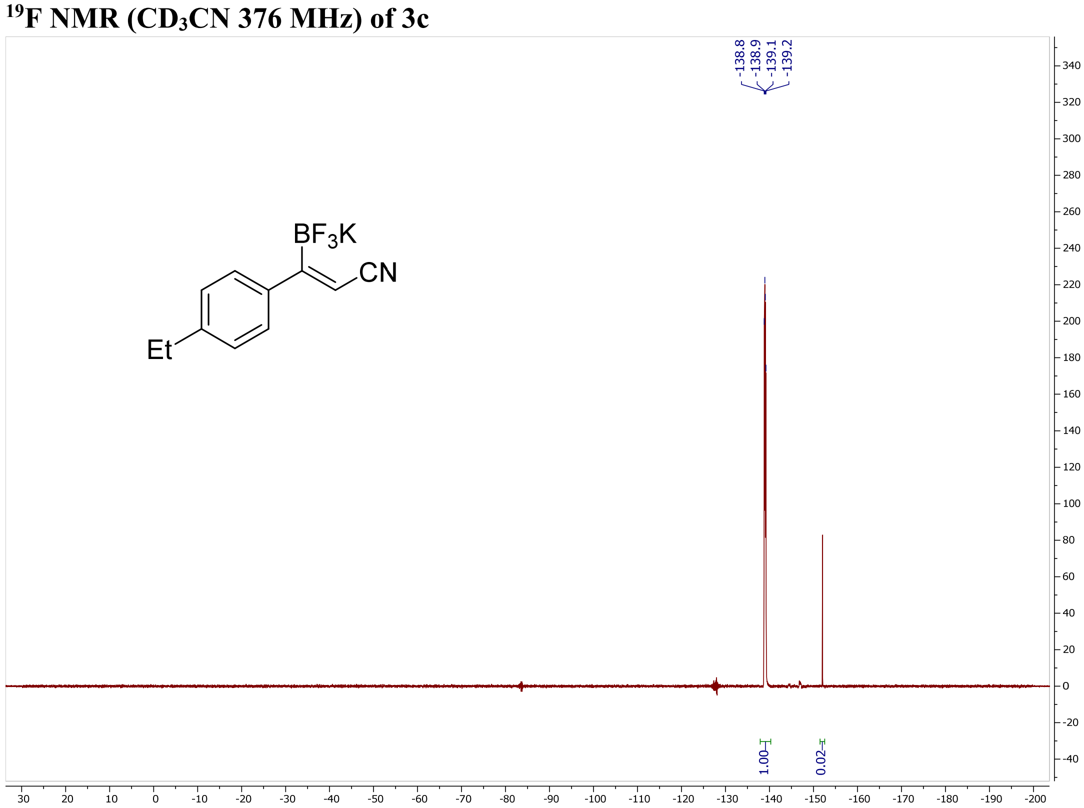
^{1}H NMR (CD_3CN 400 MHz) of 3c



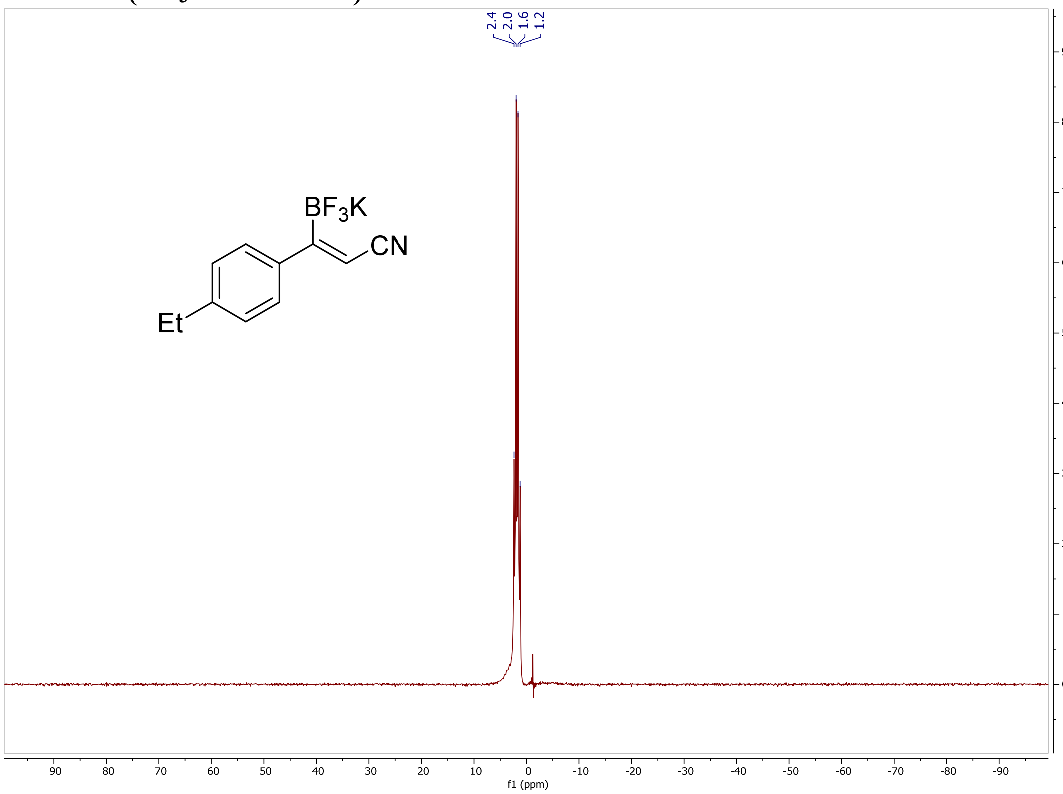
^{13}C NMR (CD_3CN 100 MHz) of 3c



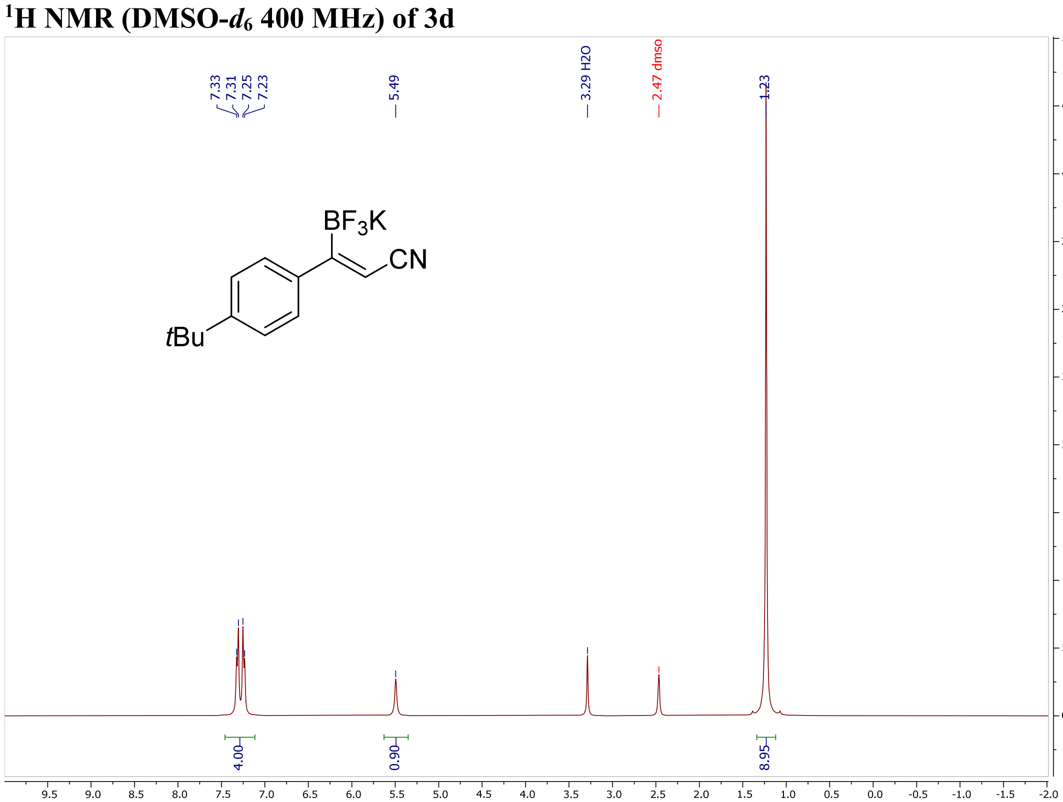
^{19}F NMR (CD_3CN 376 MHz) of 3c



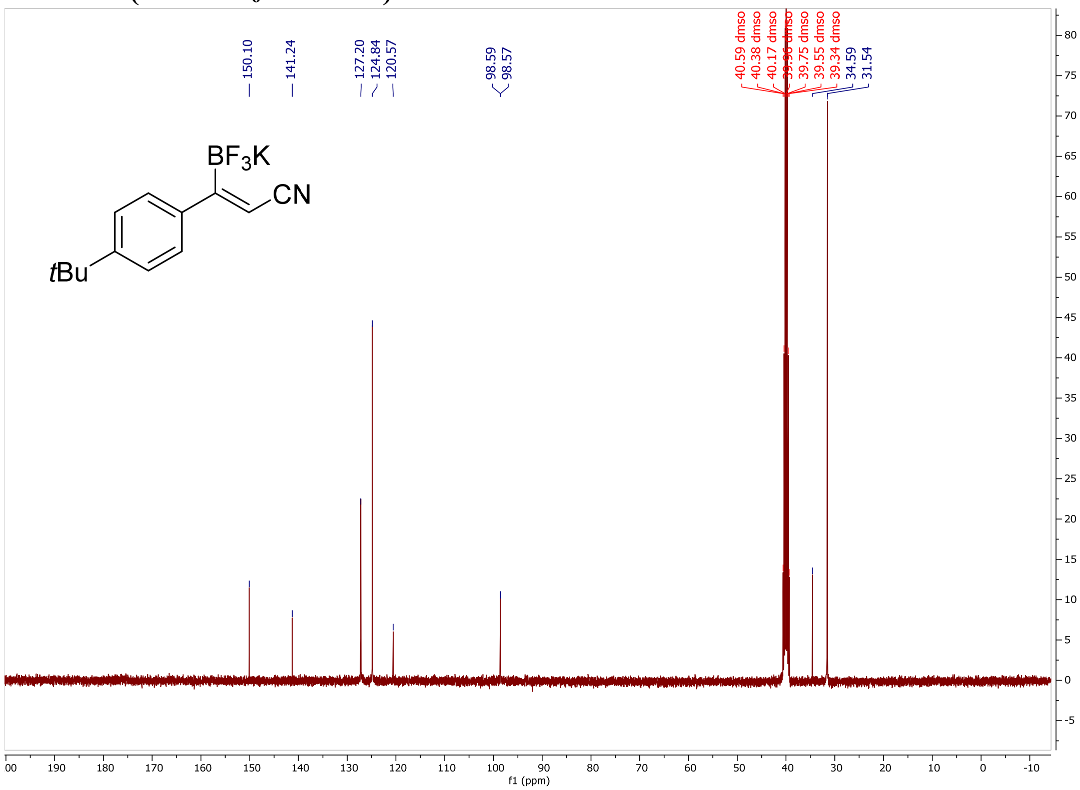
^{11}B NMR (CD_3CN 128 MHz) of 3c



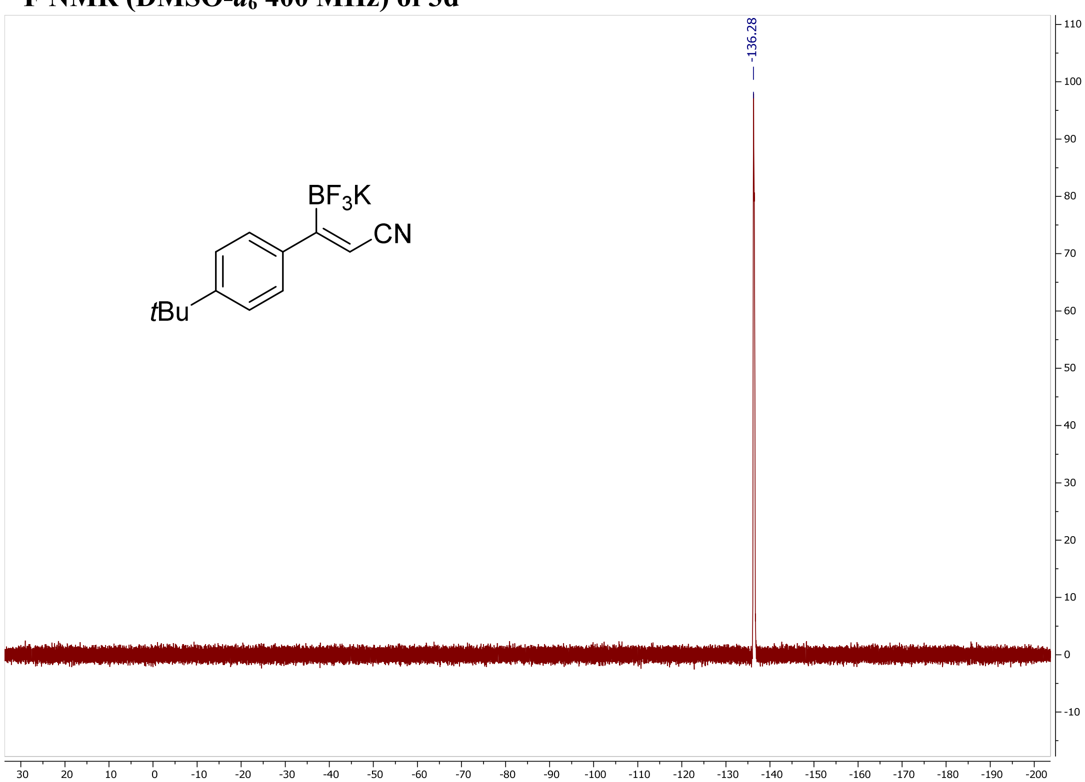
^{1}H NMR (DMSO-d_6 400 MHz) of 3d



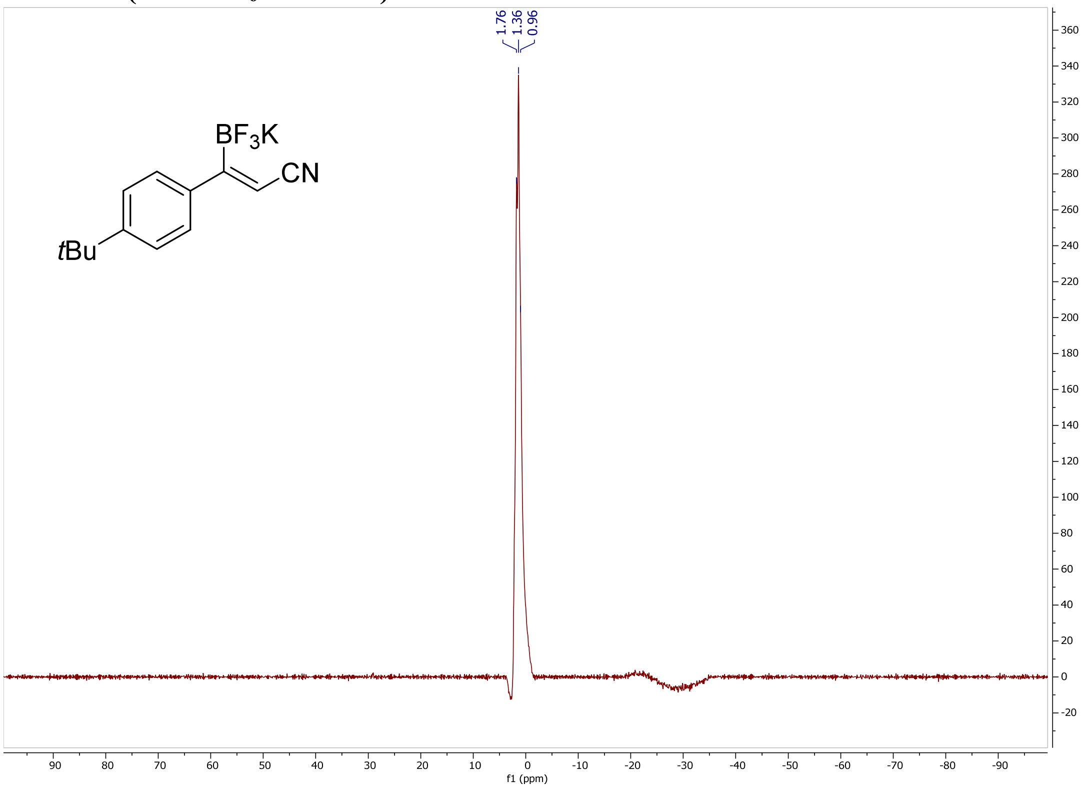
^{13}C NMR (DMSO-d_6 400 MHz) of 3d



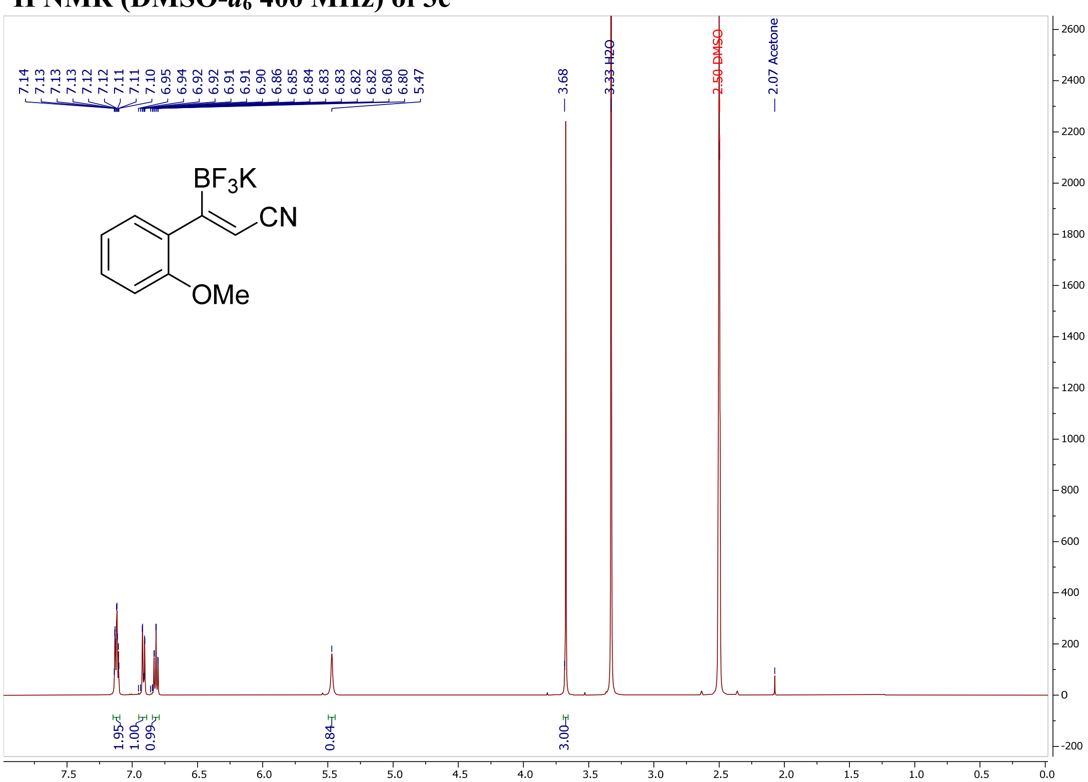
^{19}F NMR (DMSO-d_6 400 MHz) of 3d



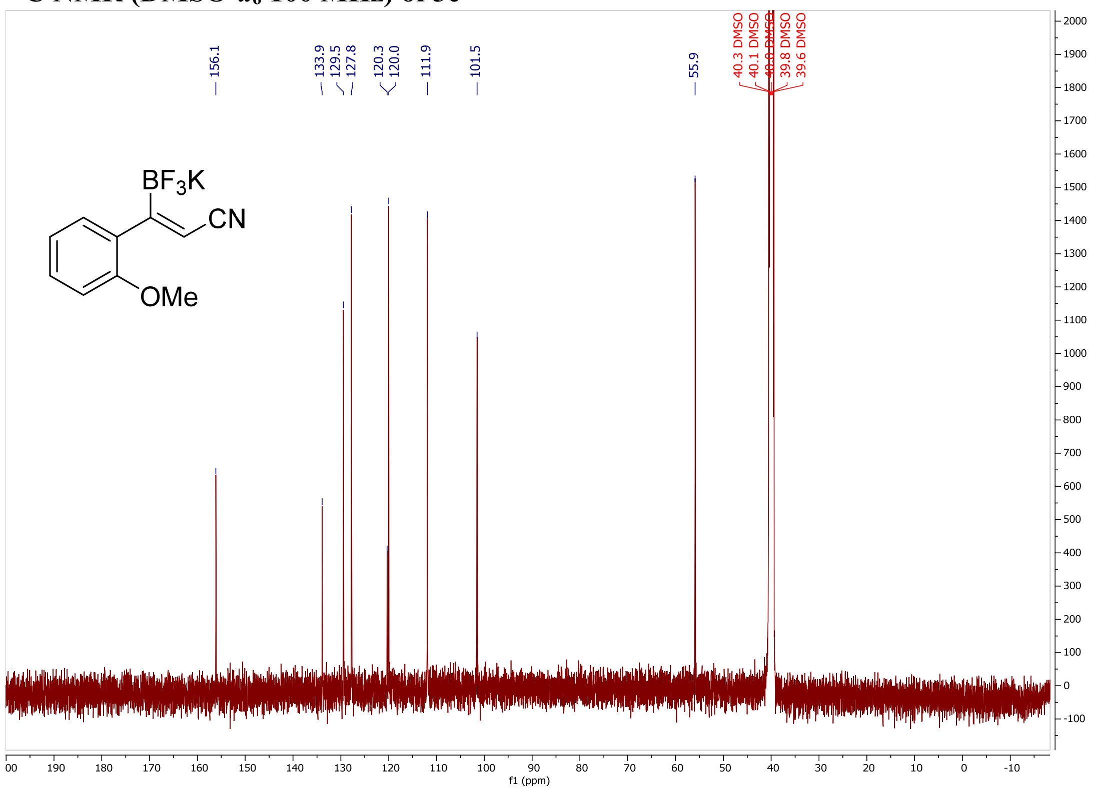
^{11}B NMR (DMSO-d_6 400 MHz) of 3d



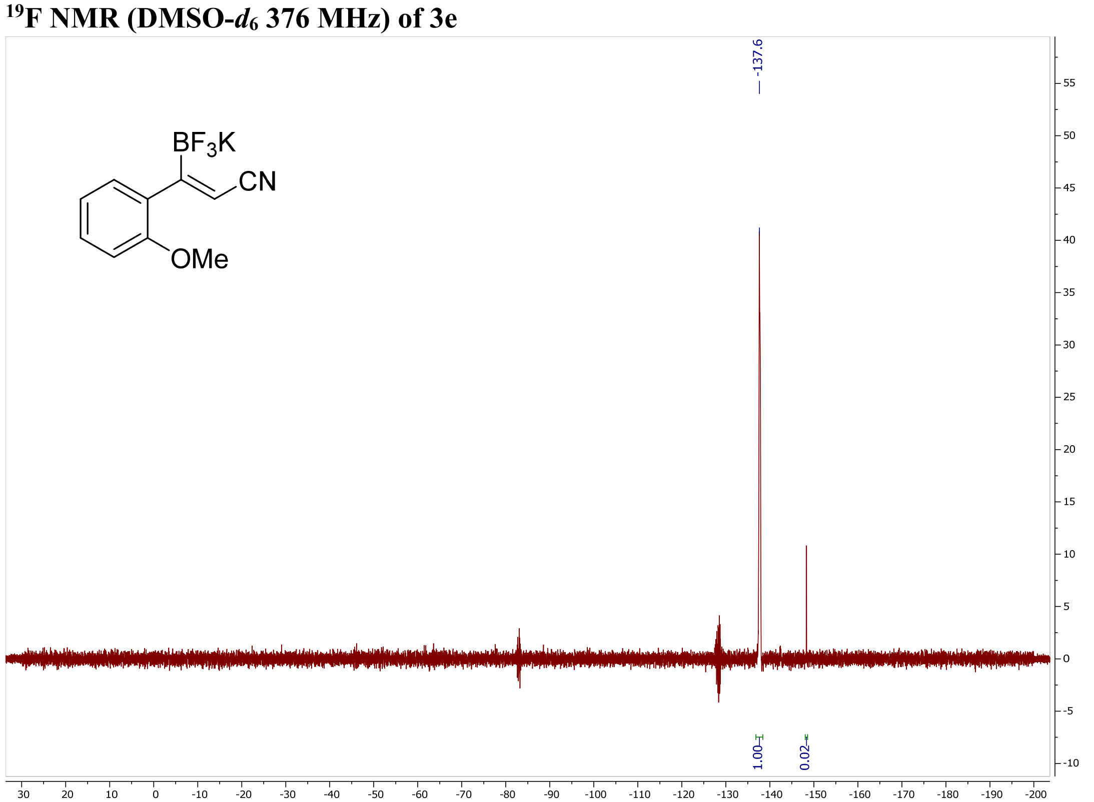
^{1}H NMR (DMSO-d_6 400 MHz) of 3e



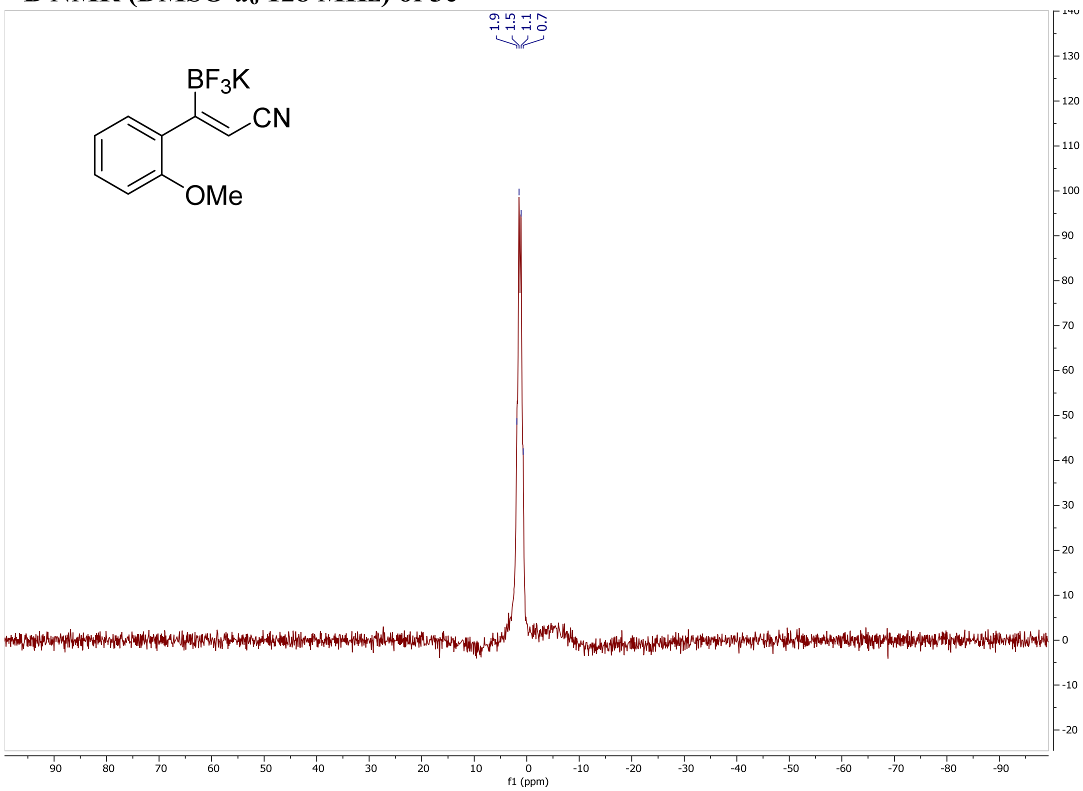
^{13}C NMR (DMSO-d_6 100 MHz) of 3e



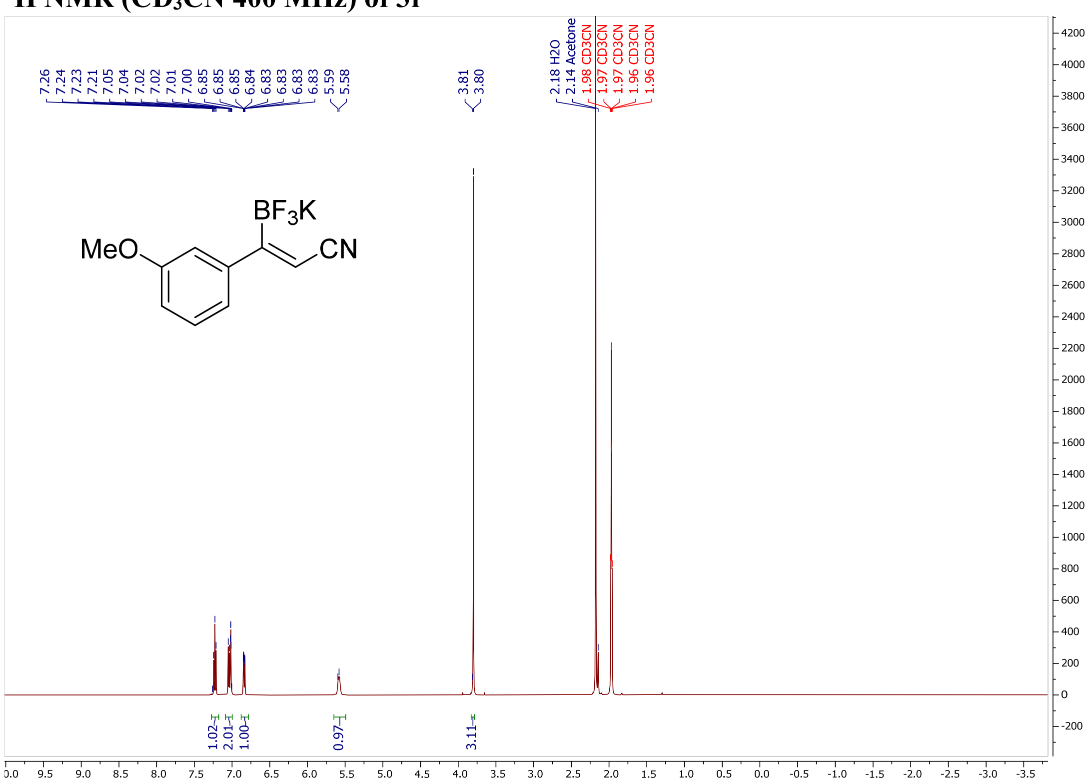
^{19}F NMR (DMSO-d_6 376 MHz) of 3e



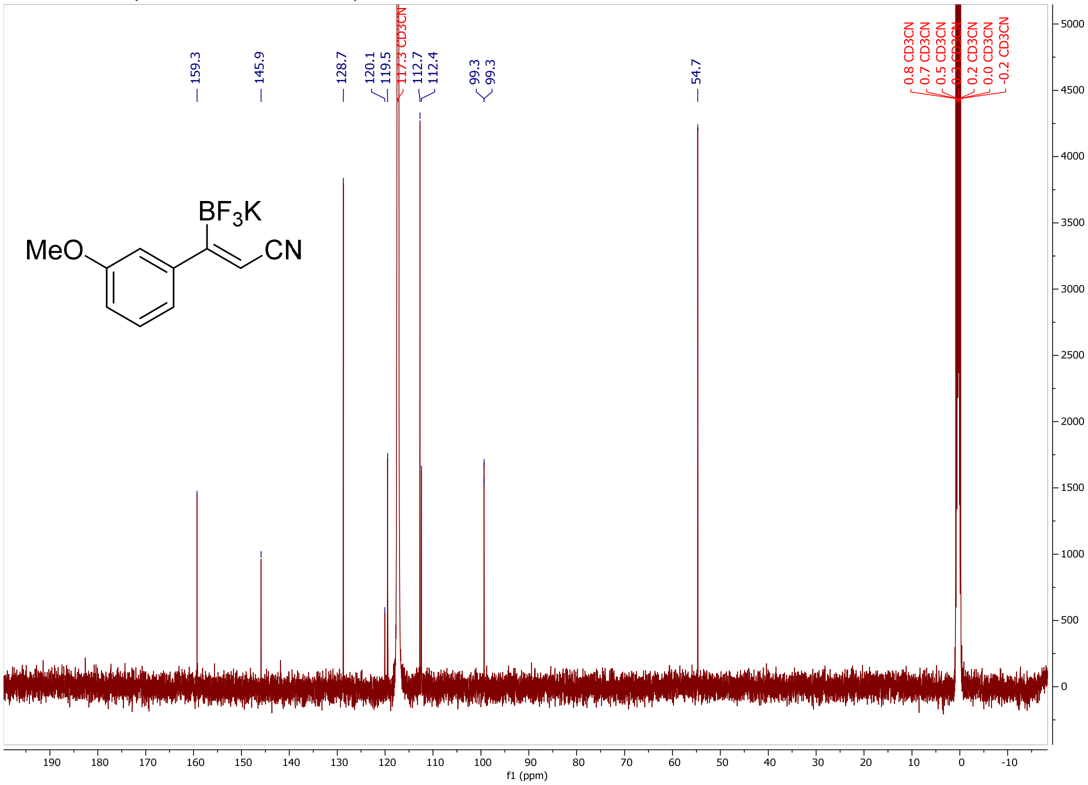
^{11}B NMR (DMSO-d_6 128 MHz) of 3e



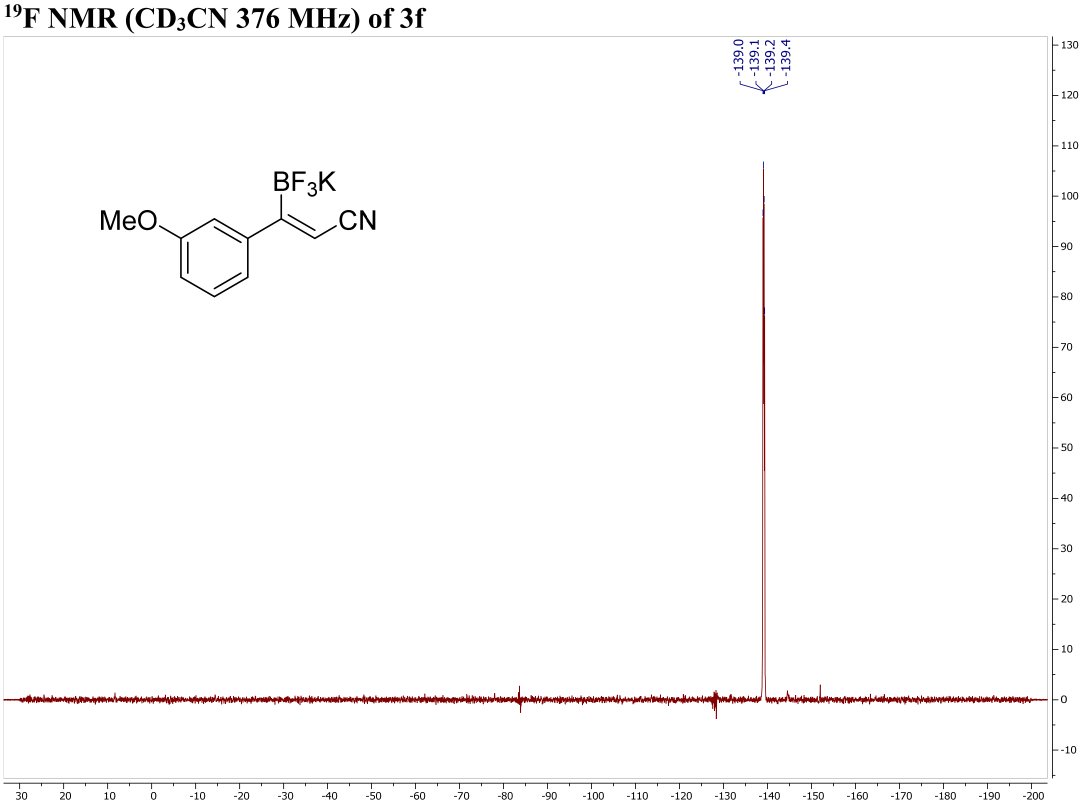
^{1}H NMR (CD_3CN 400 MHz) of 3f



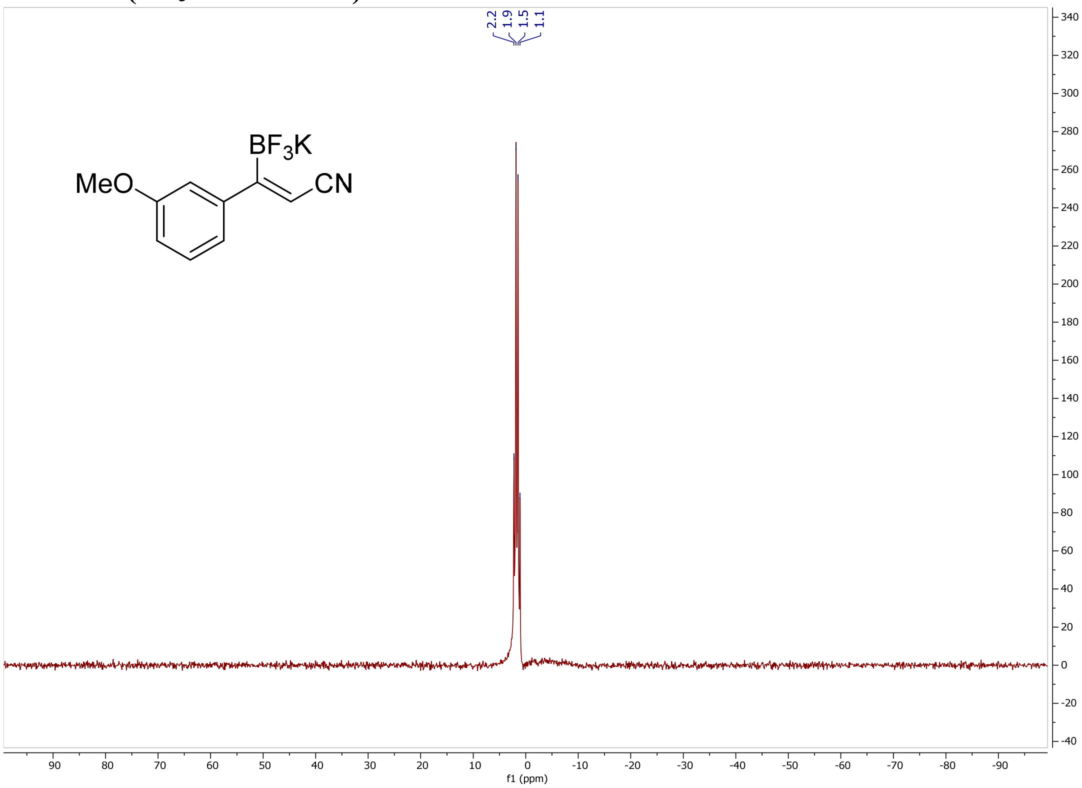
^{13}C NMR (CD_3CN 100 MHz) of 3f



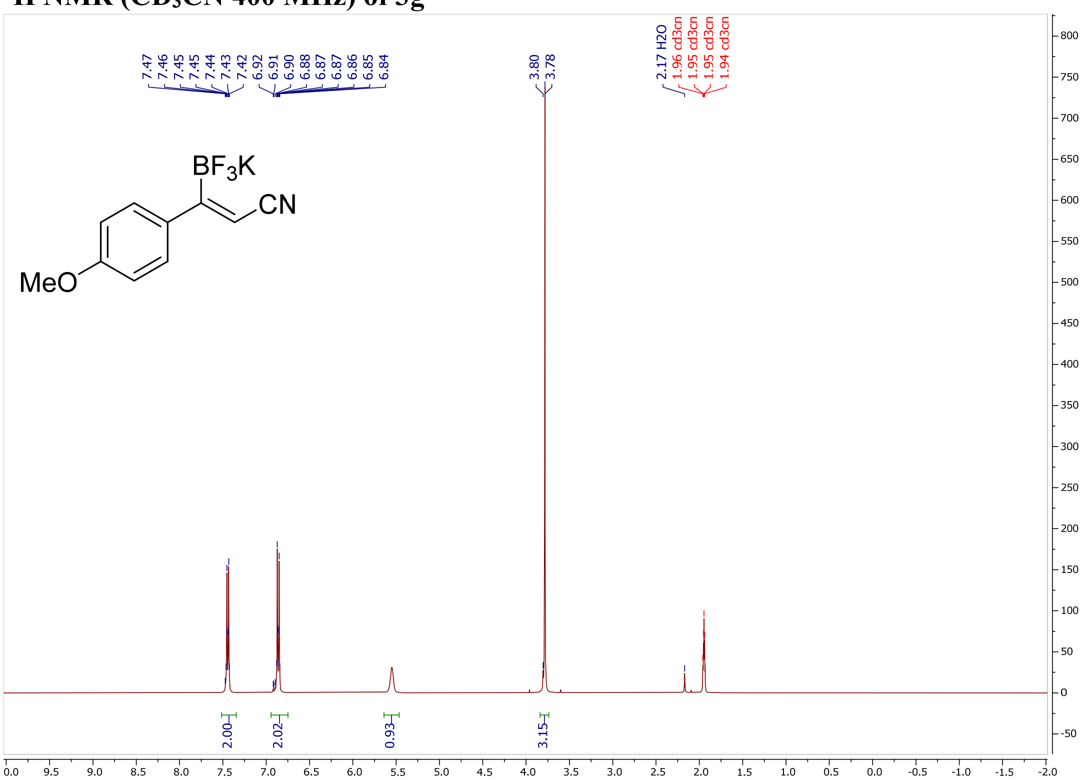
^{19}F NMR (CD_3CN 376 MHz) of 3f



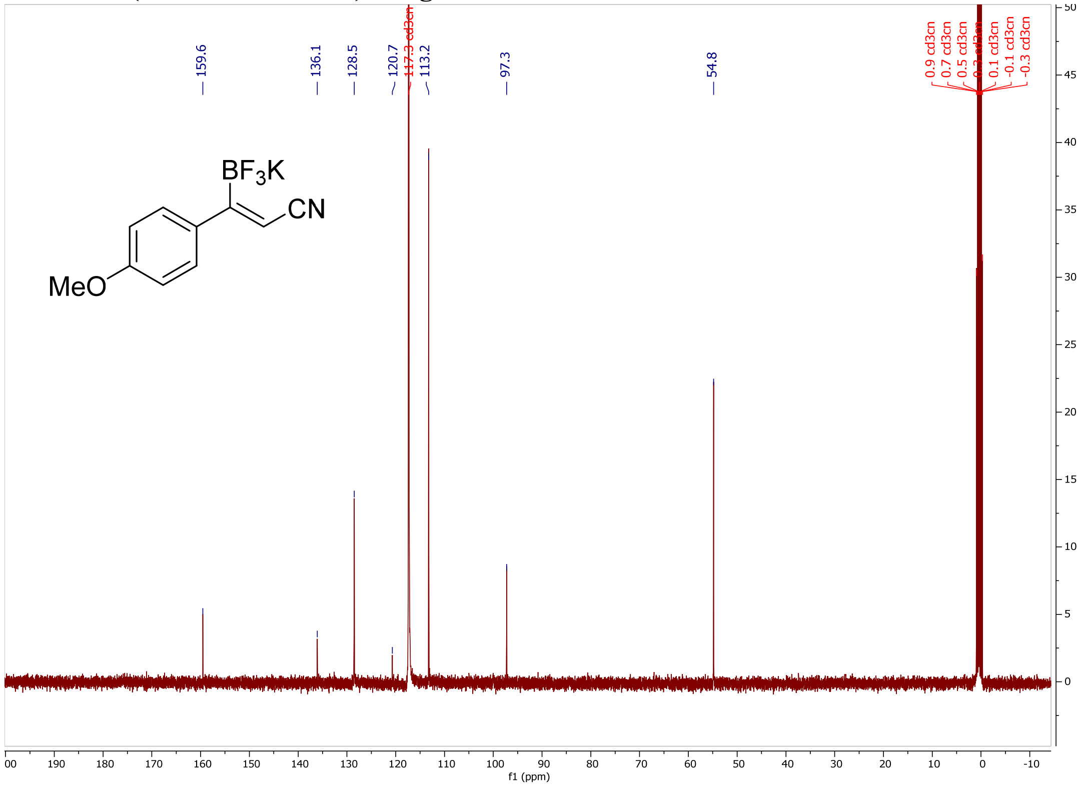
[11]B NMR (CD_3CN 128 MHz) of 3f



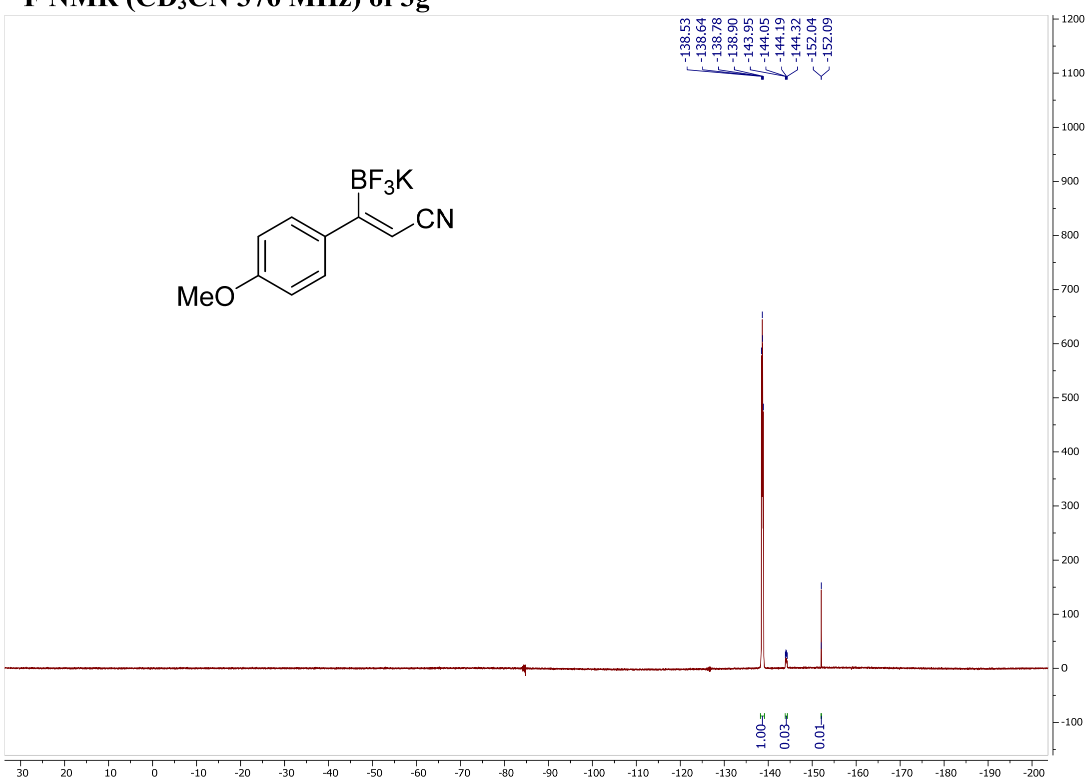
[1]H NMR (CD_3CN 400 MHz) of 3g



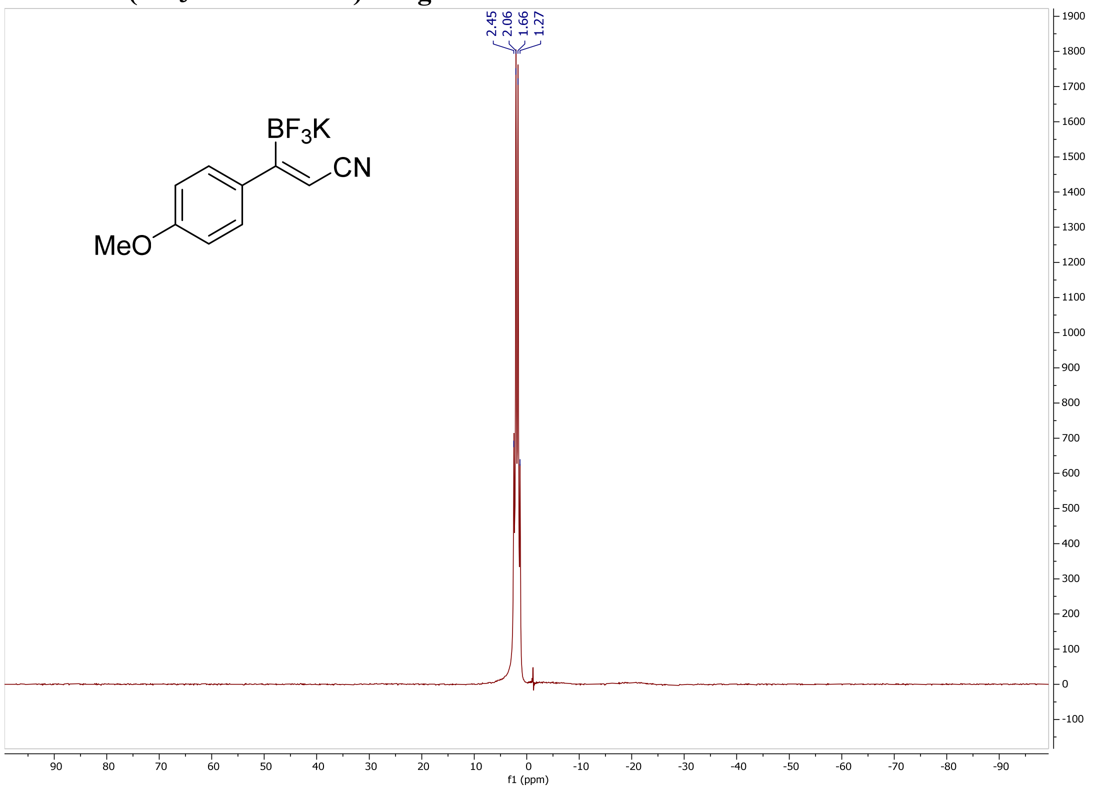
^{13}C NMR (CD_3CN 100 MHz) of 3g



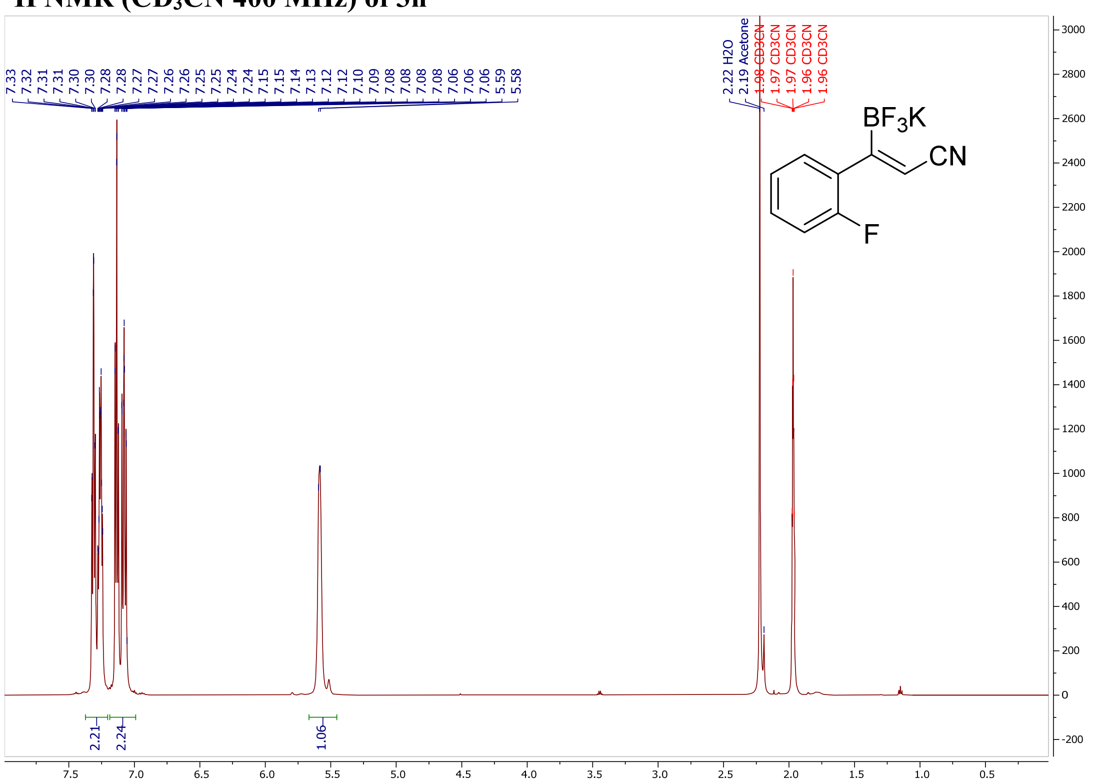
^{19}F NMR (CD_3CN 376 MHz) of 3g



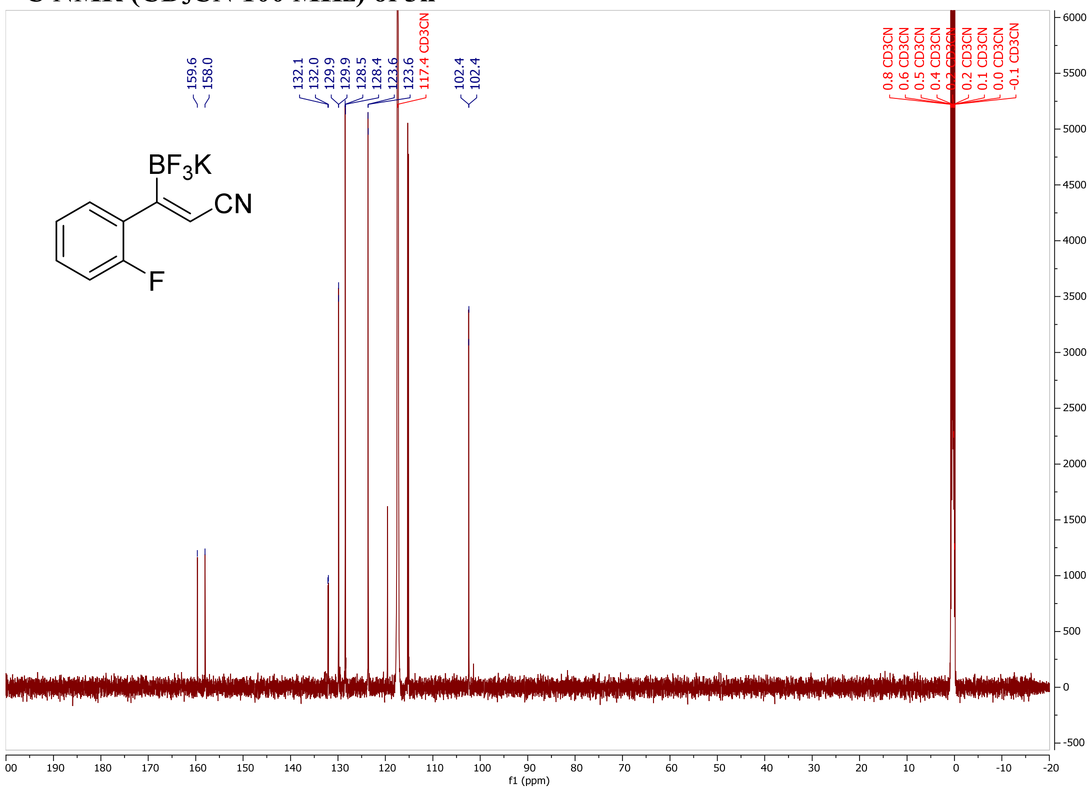
^{11}B NMR (CD_3CN 128 MHz) of 3g



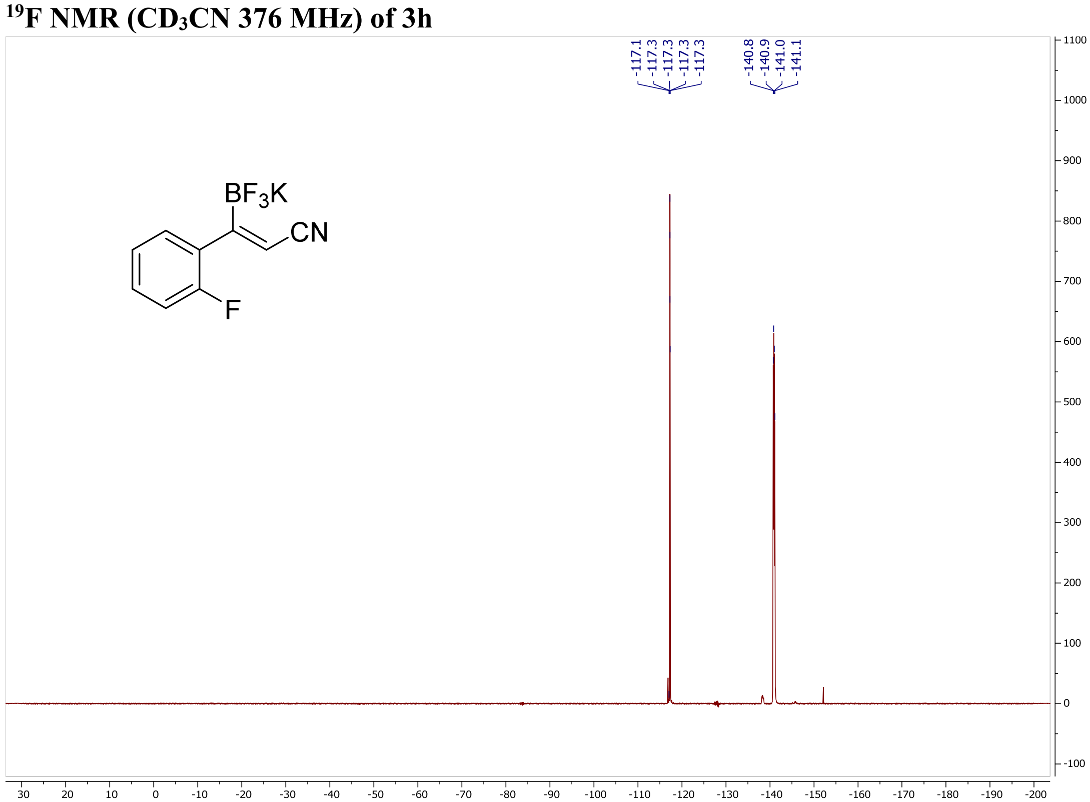
^{1}H NMR (CD_3CN 400 MHz) of 3h



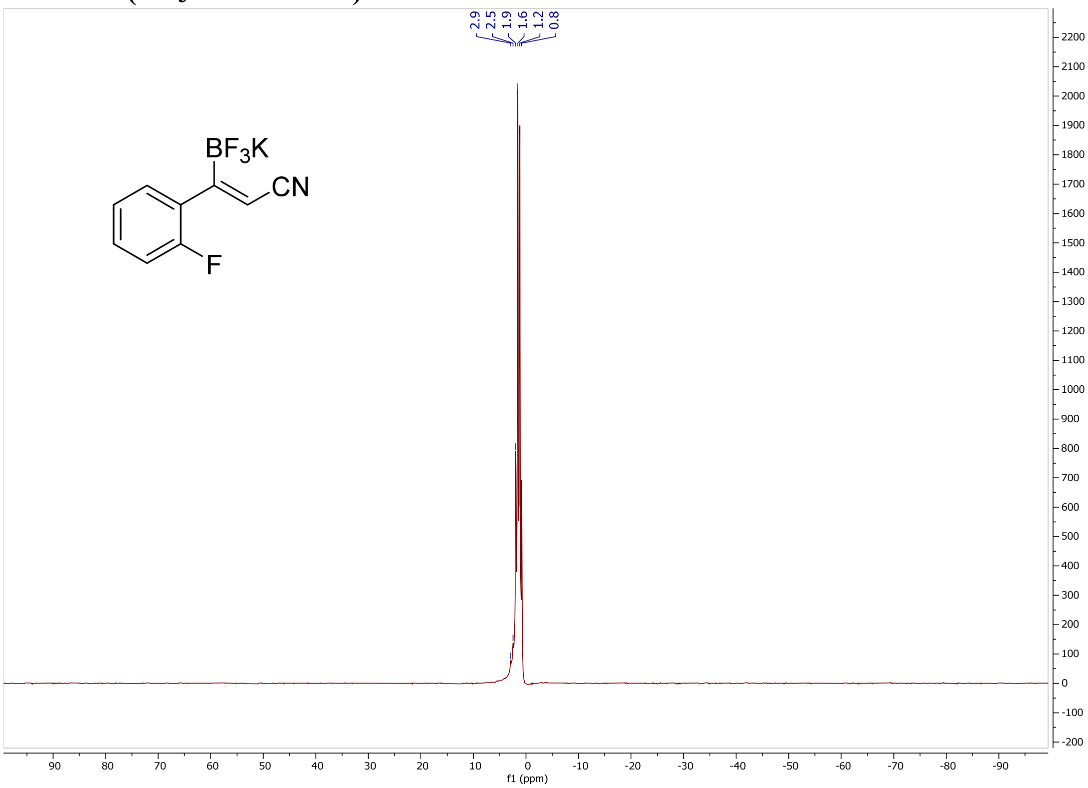
^{13}C NMR (CD_3CN 100 MHz) of 3h



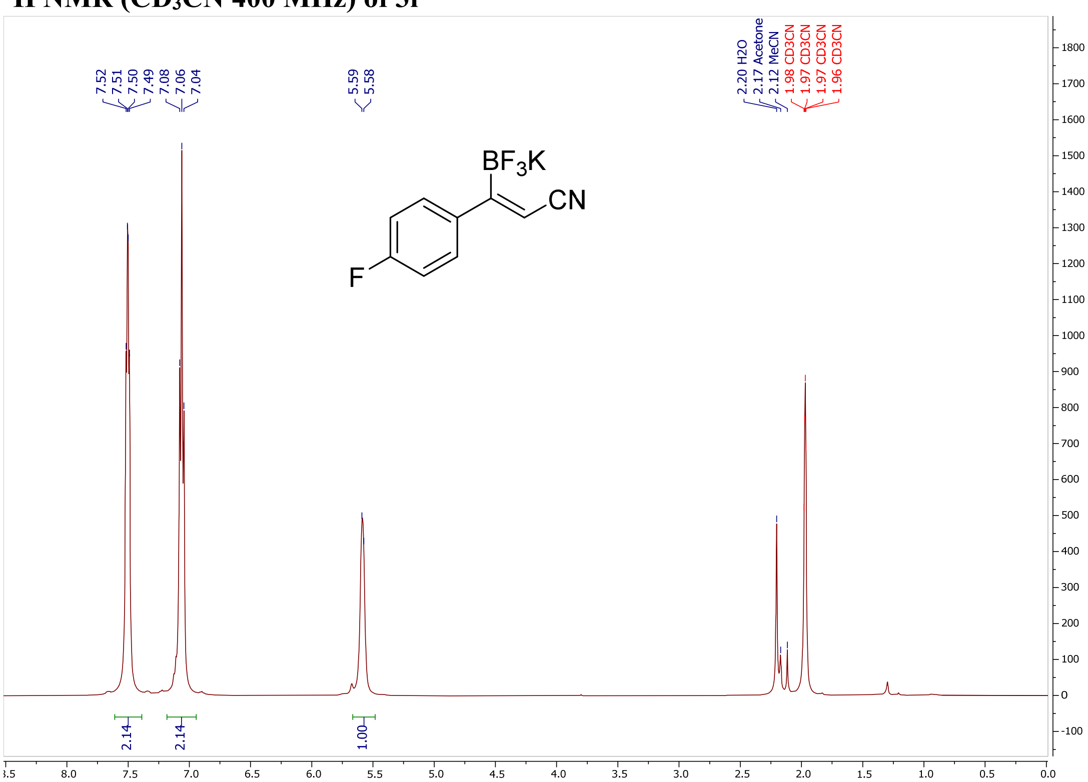
^{19}F NMR (CD_3CN 376 MHz) of 3h



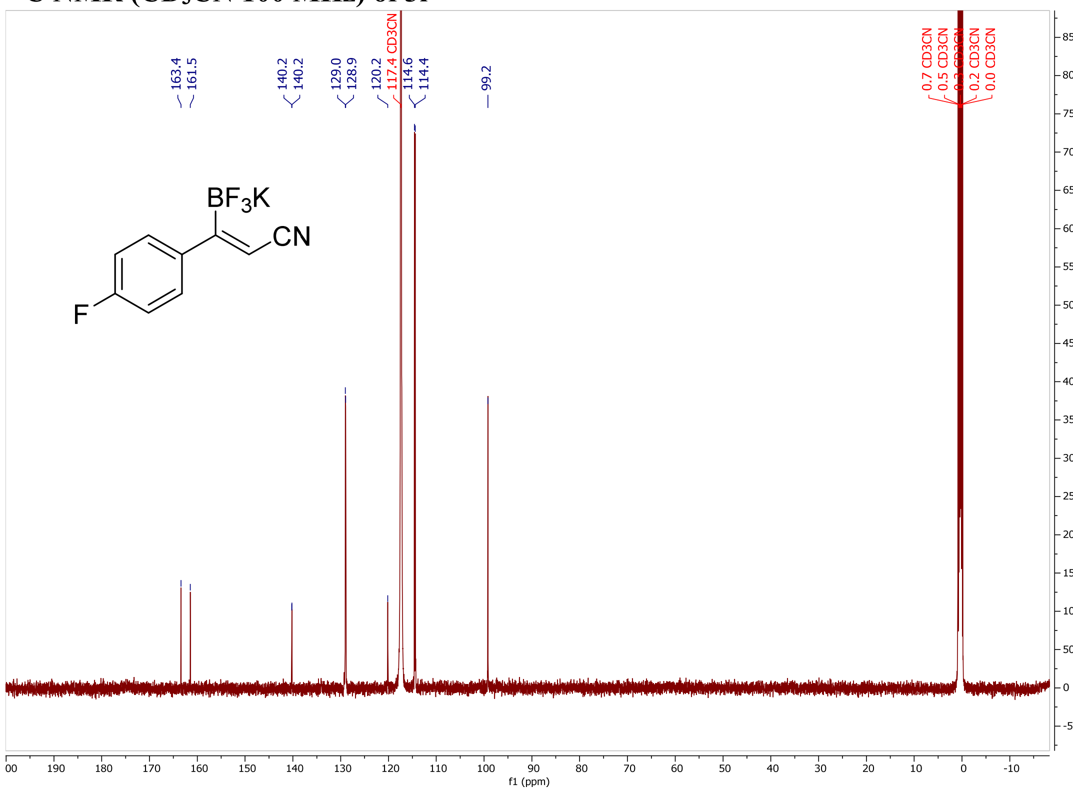
^{11}B NMR (CD_3CN 128 MHz) of 3h



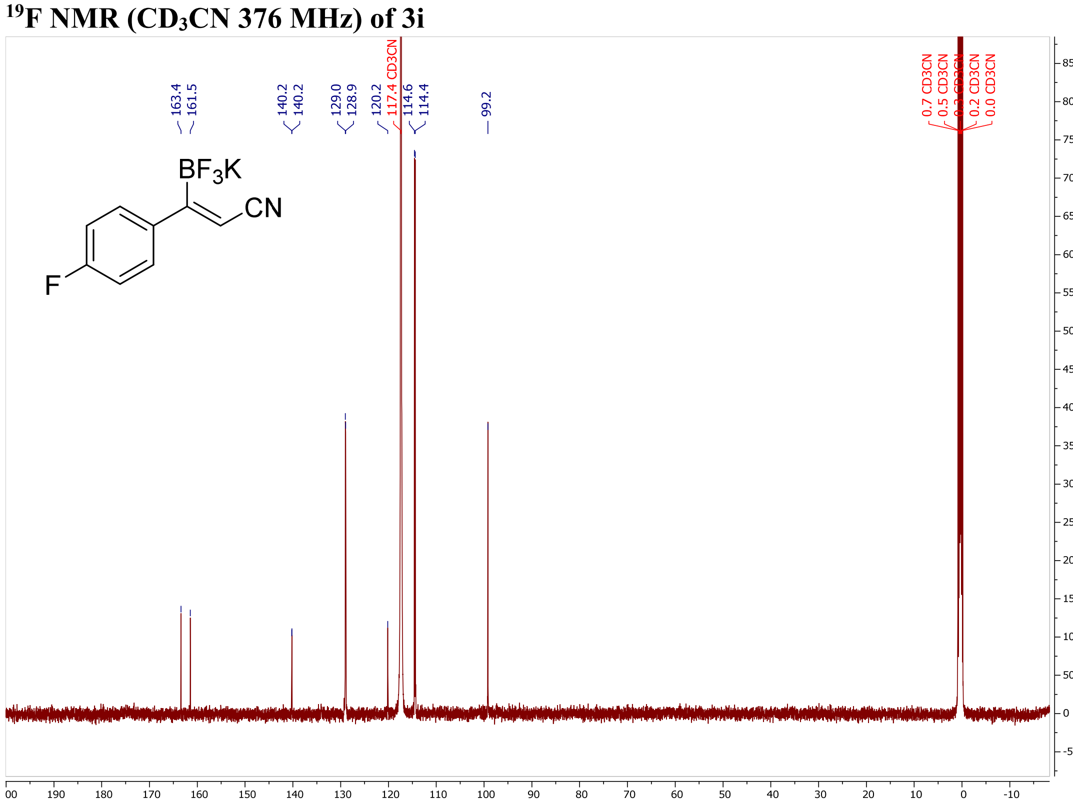
^{1}H NMR (CD_3CN 400 MHz) of 3i



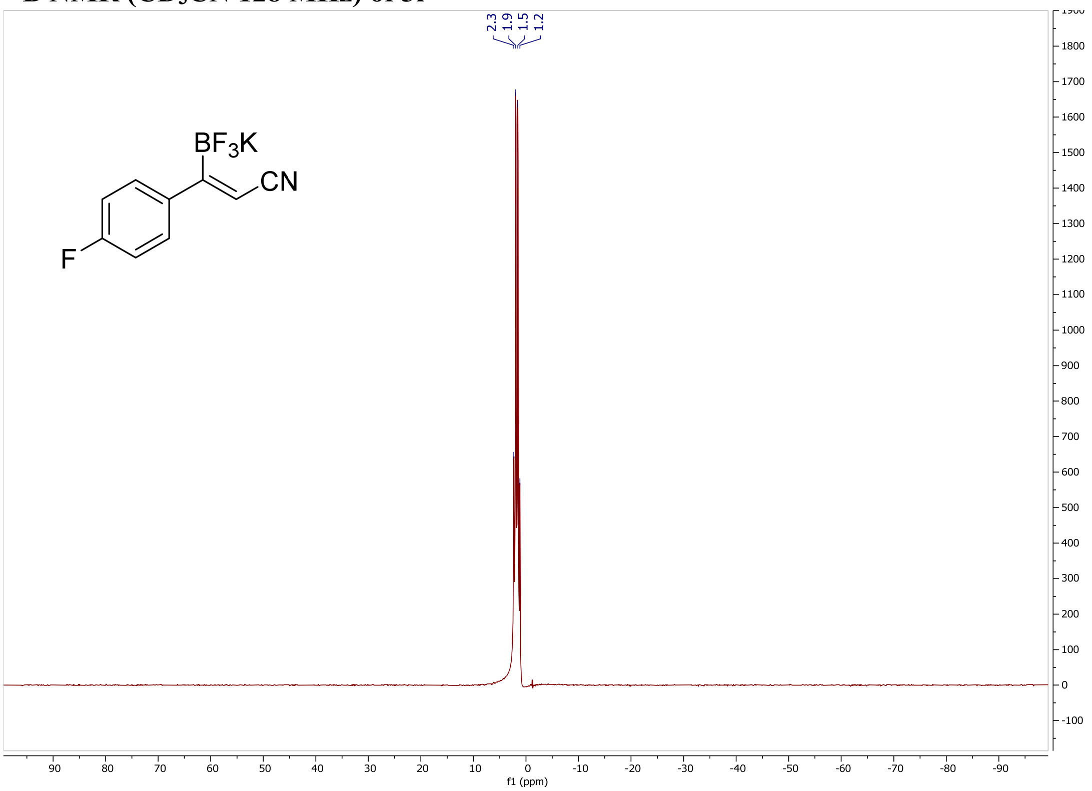
^{13}C NMR (CD_3CN 100 MHz) of 3i



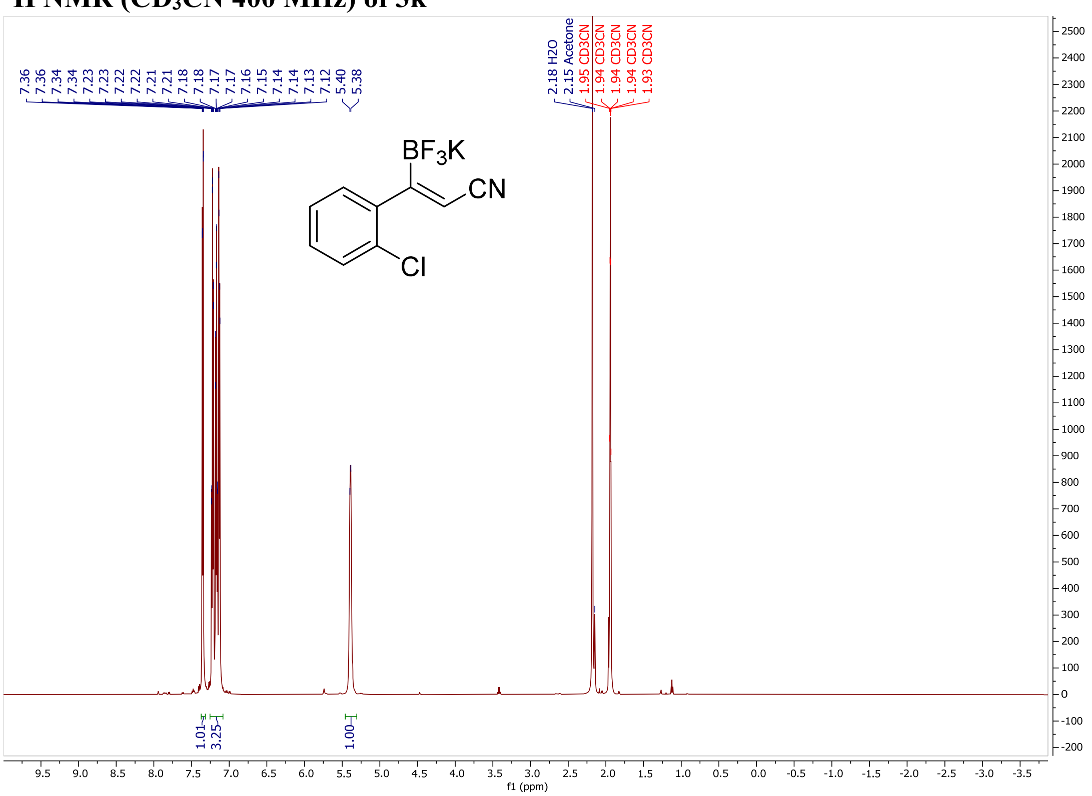
^{19}F NMR (CD_3CN 376 MHz) of 3i



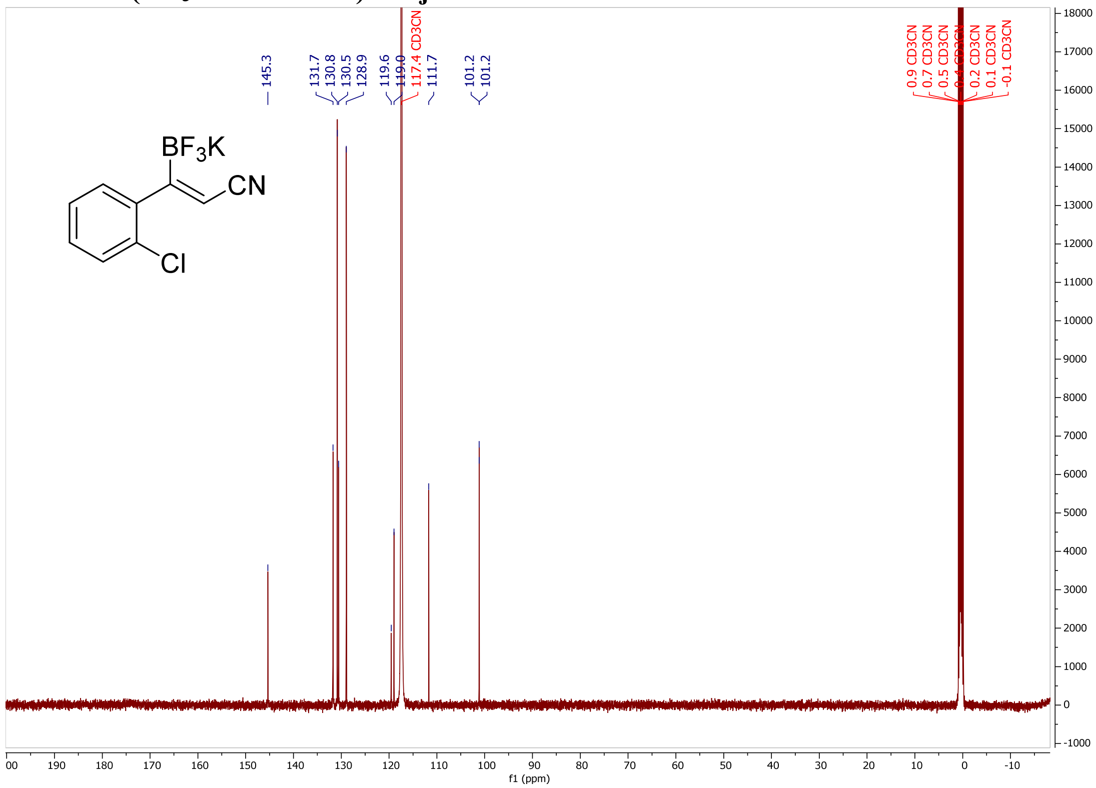
^{11}B NMR (CD_3CN 128 MHz) of 3i



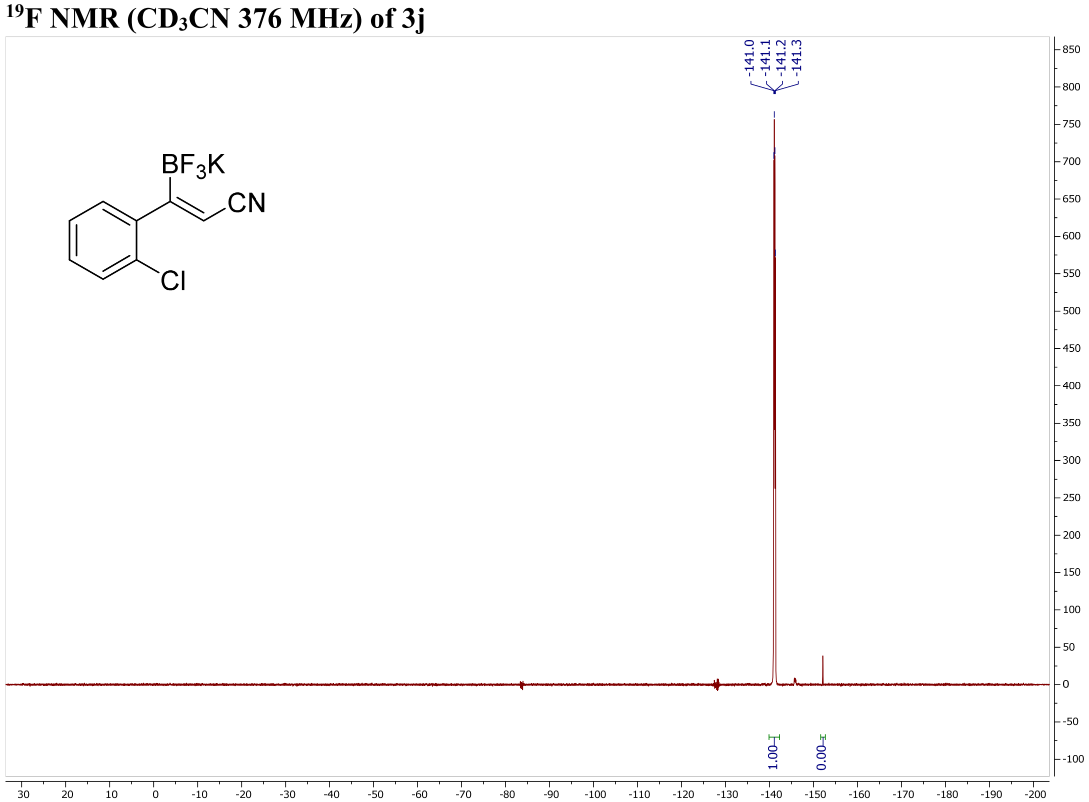
^{1}H NMR (CD_3CN 400 MHz) of 3k



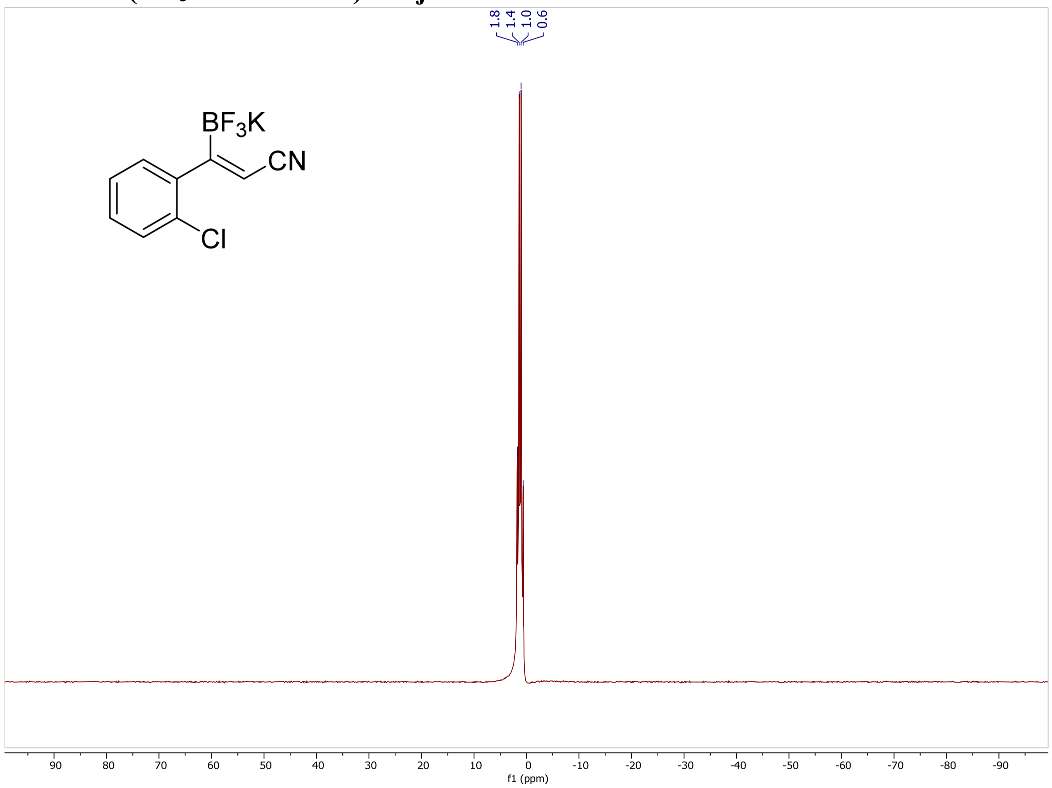
^{13}C NMR (CD_3CN 100 MHz) of 3j



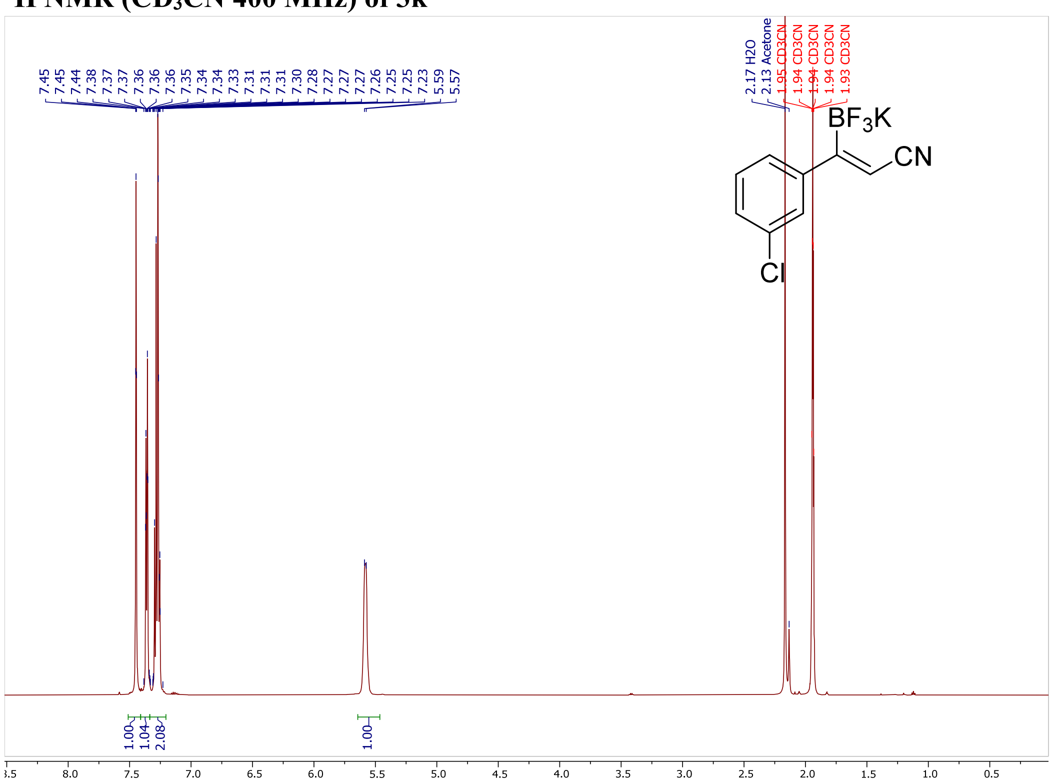
^{19}F NMR (CD_3CN 376 MHz) of 3j



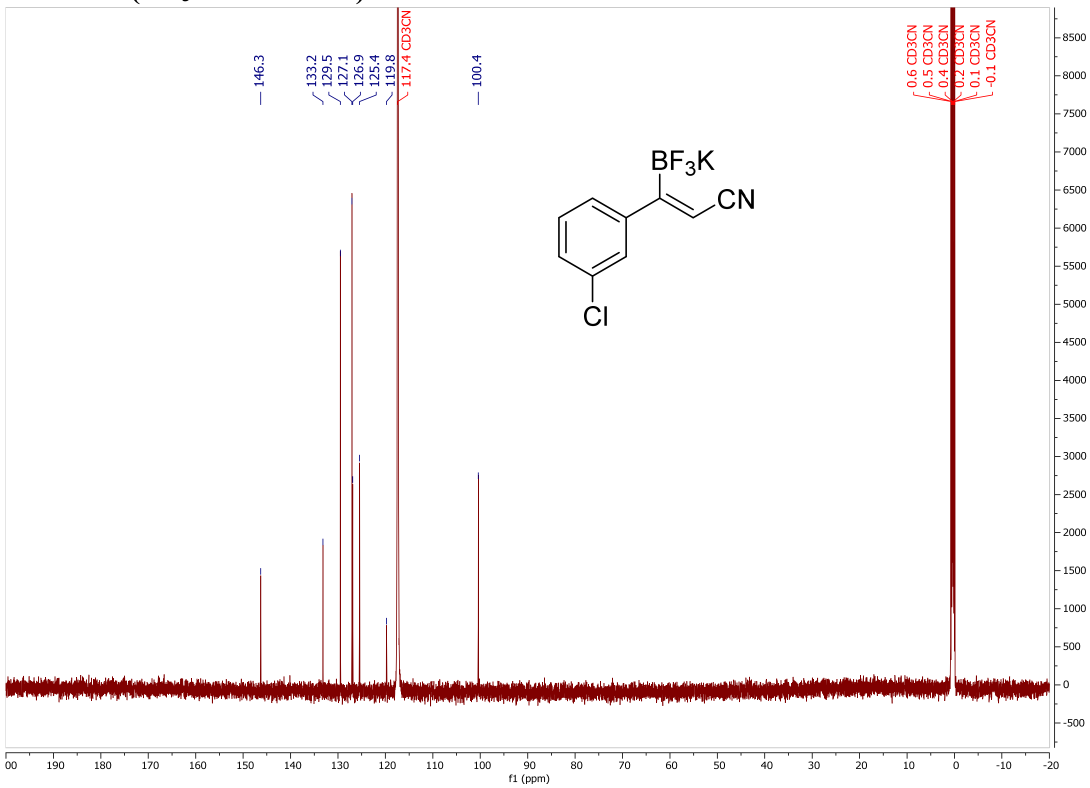
^{11}B NMR (CD_3CN 128 MHz) of 3j



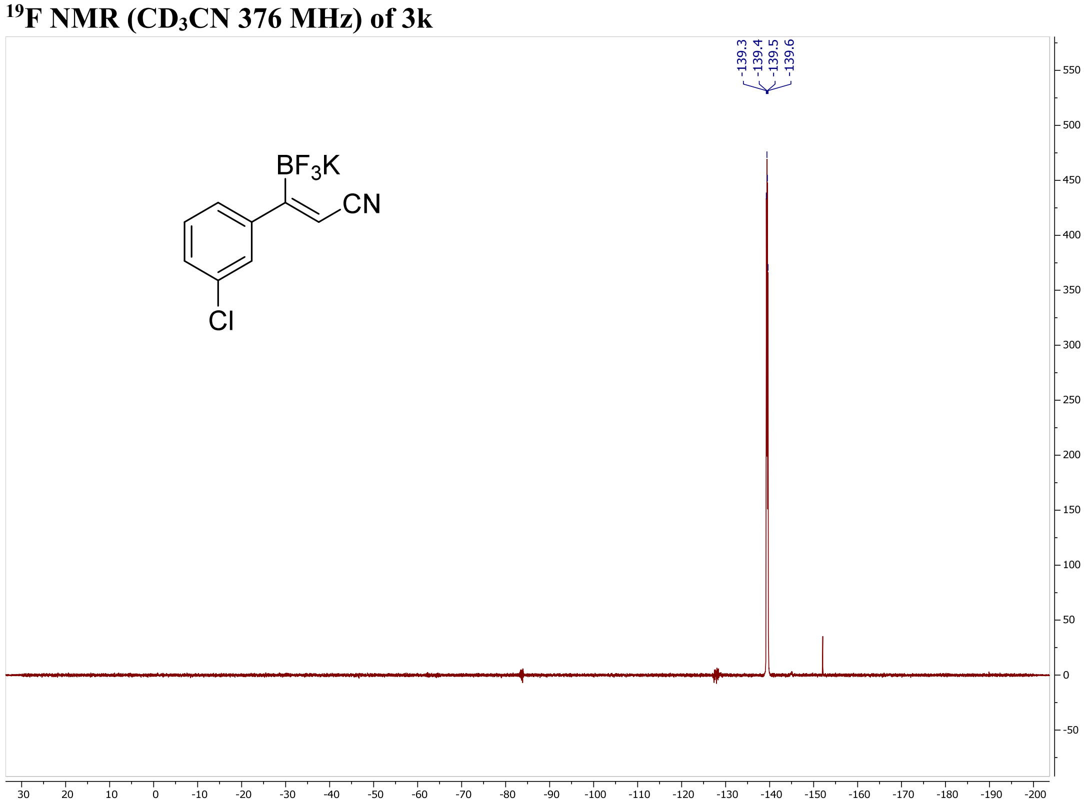
^{1}H NMR (CD_3CN 400 MHz) of 3k



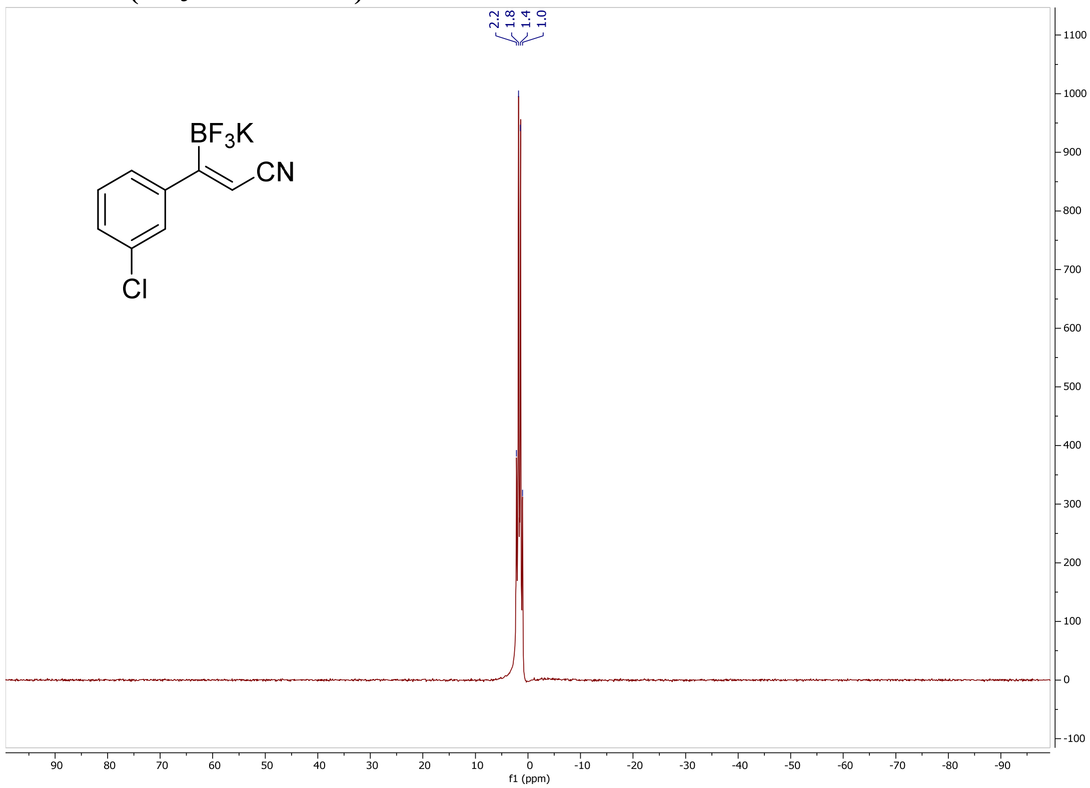
[13]C NMR (CD_3CN 100 MHz) of 3k



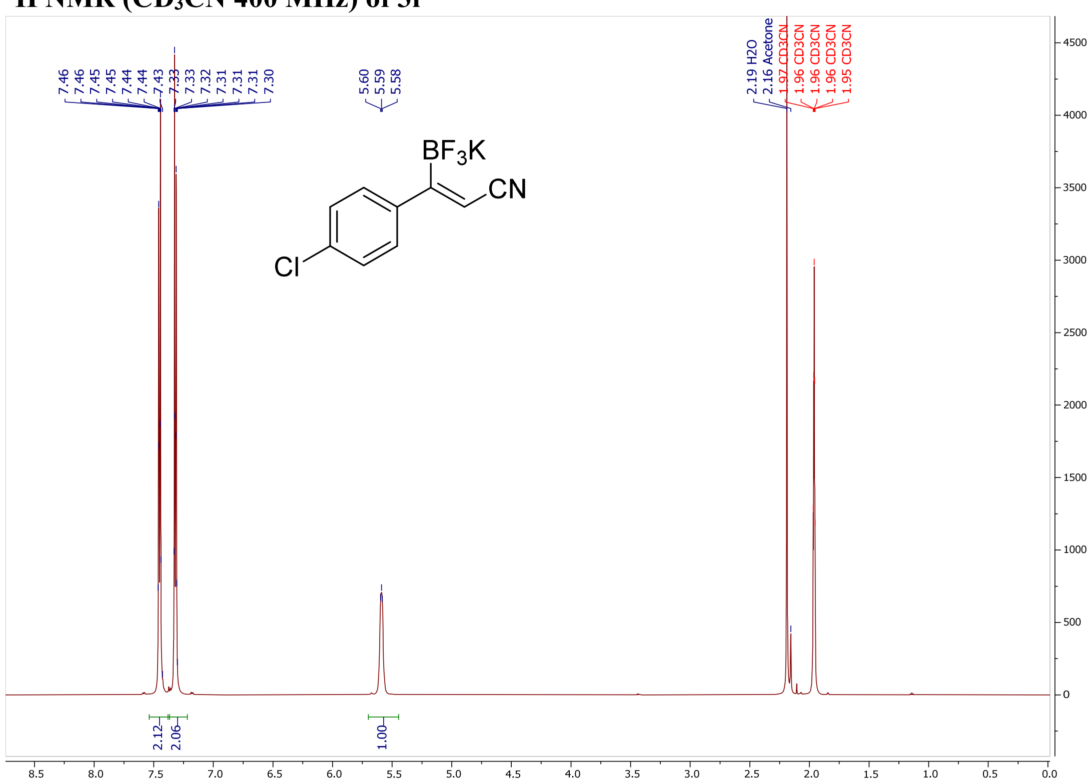
[19]F NMR (CD_3CN 376 MHz) of 3k



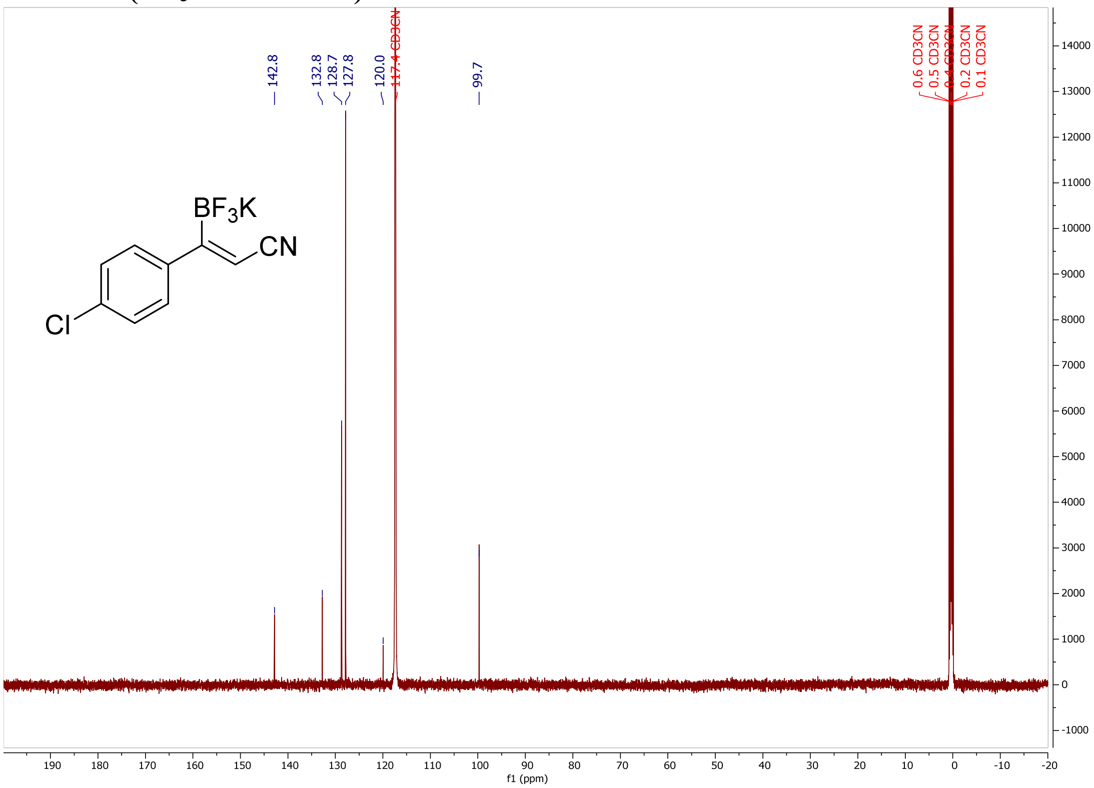
^{11}B NMR (CD_3CN 128 MHz) of 3k



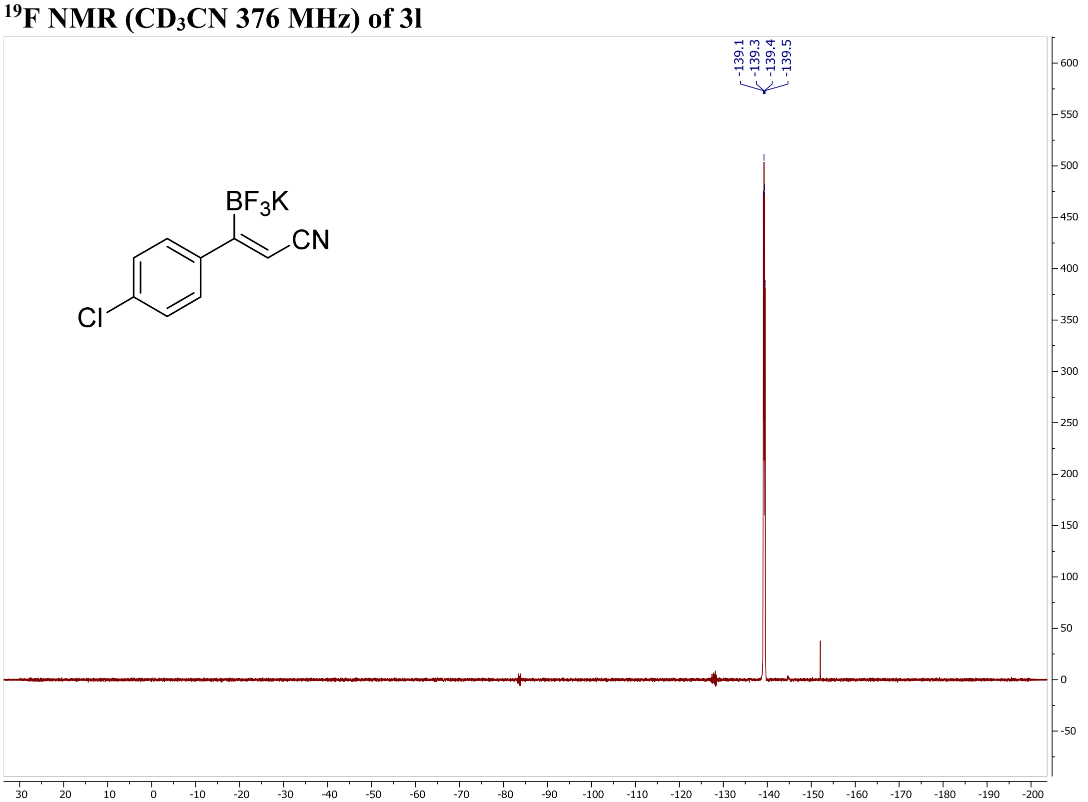
^{1}H NMR (CD_3CN 400 MHz) of 3l



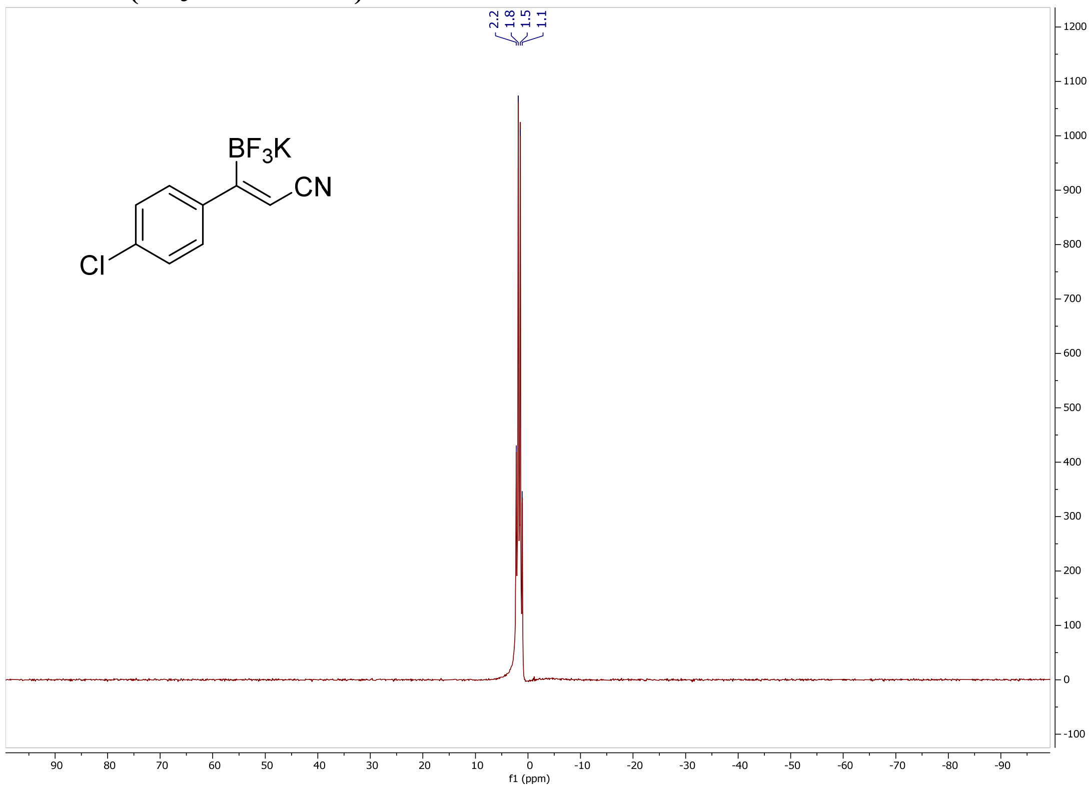
^{13}C NMR (CD_3CN 100 MHz) of 3l



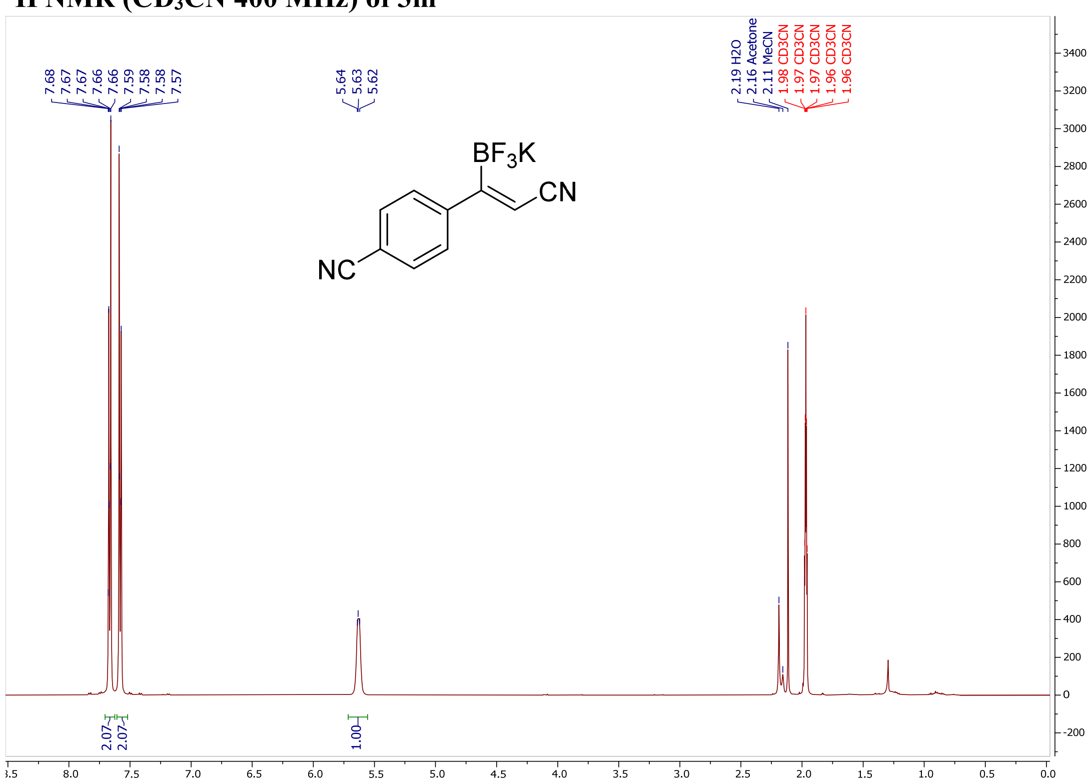
^{19}F NMR (CD_3CN 376 MHz) of 3l



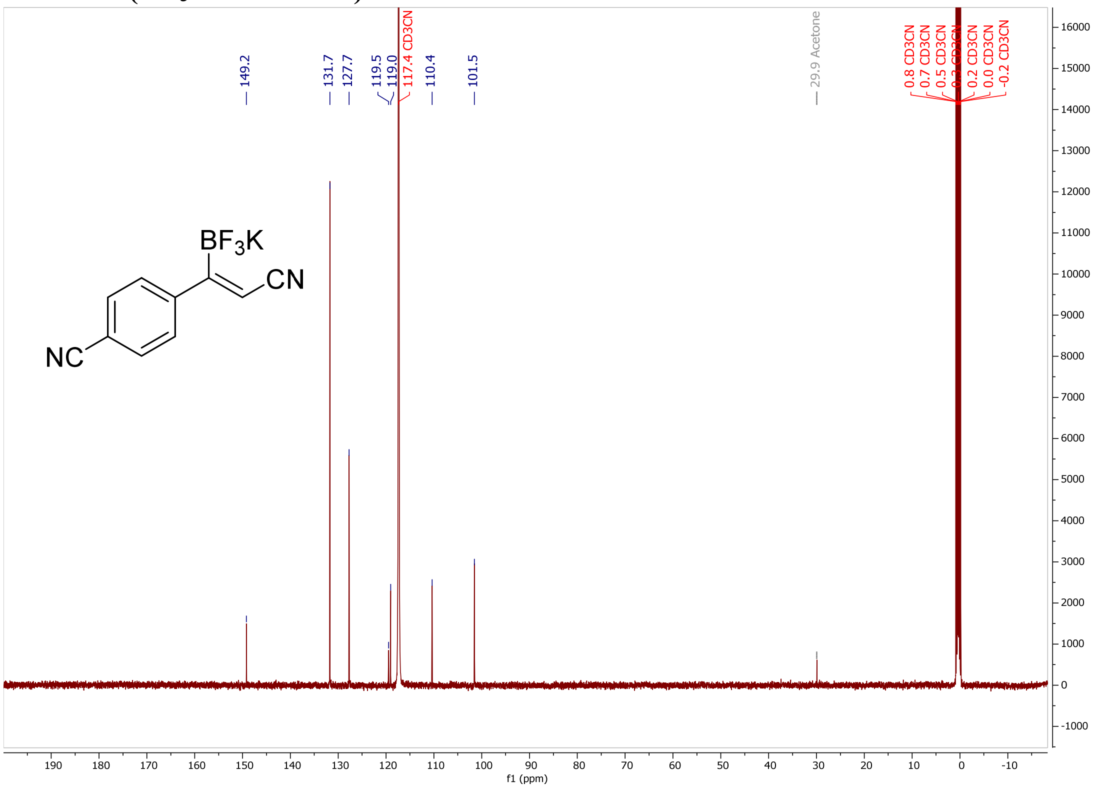
^{11}B NMR (CD_3CN 128 MHz) of 3l



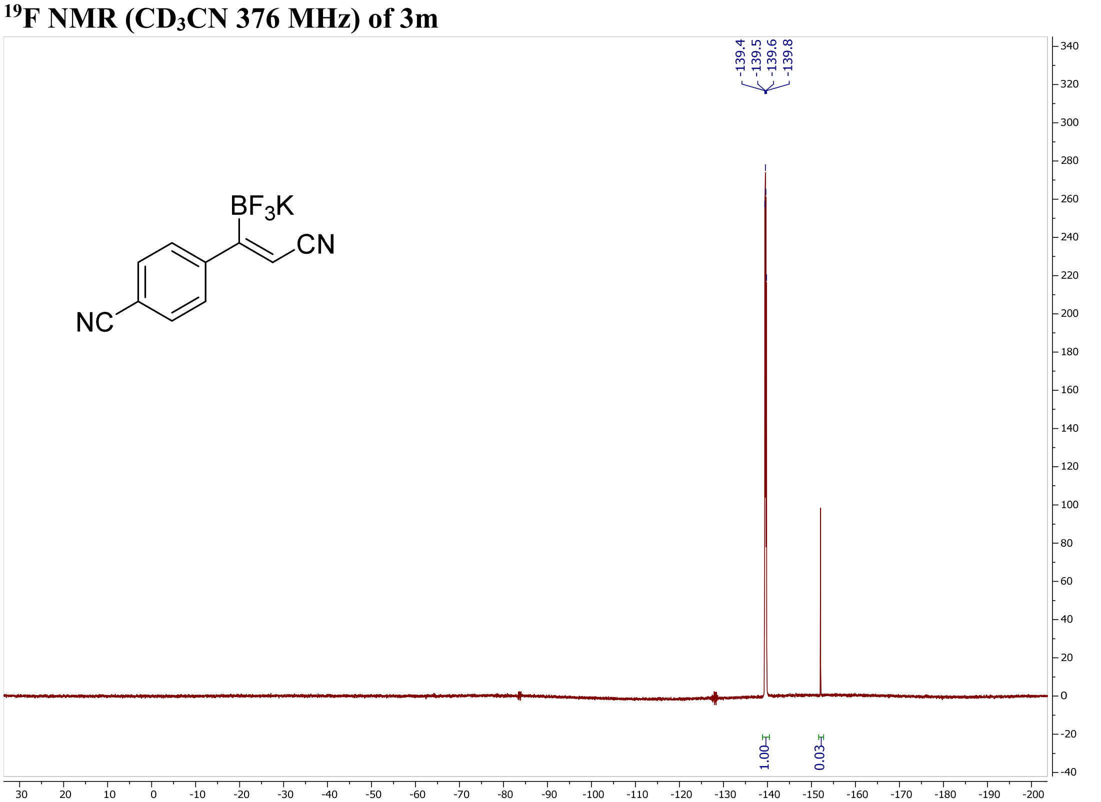
^{1}H NMR (CD_3CN 400 MHz) of 3m



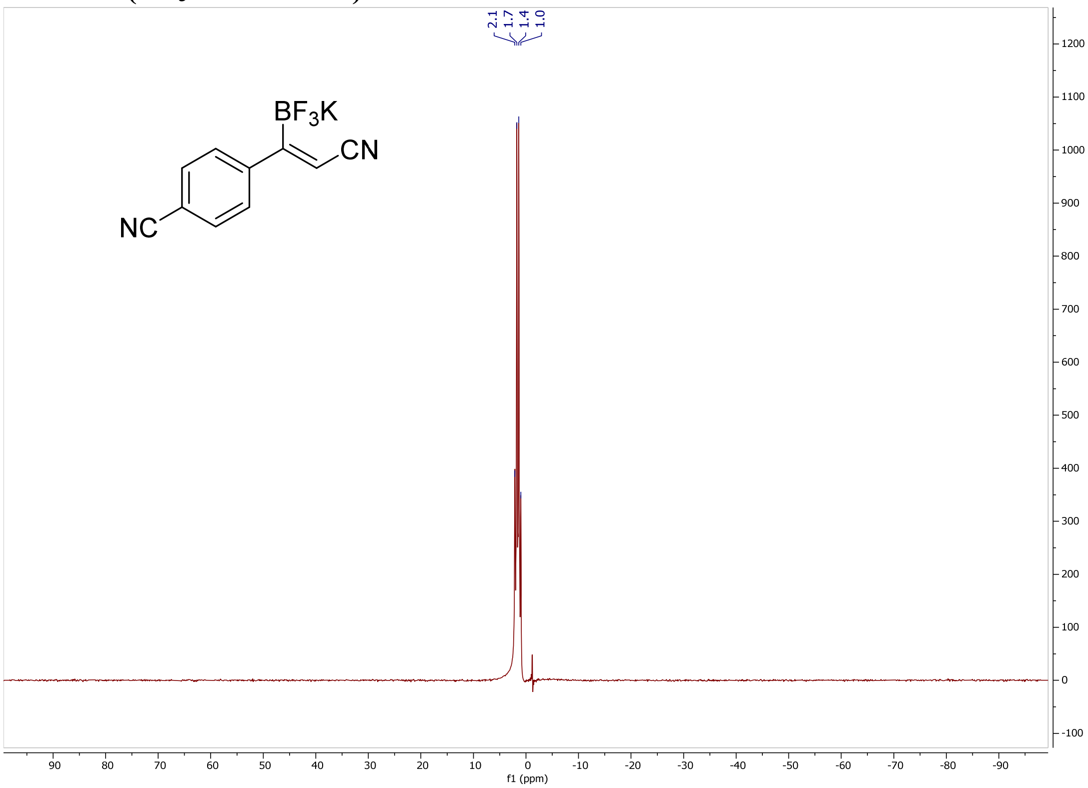
^{13}C NMR (CD_3CN 100 MHz) of 3m



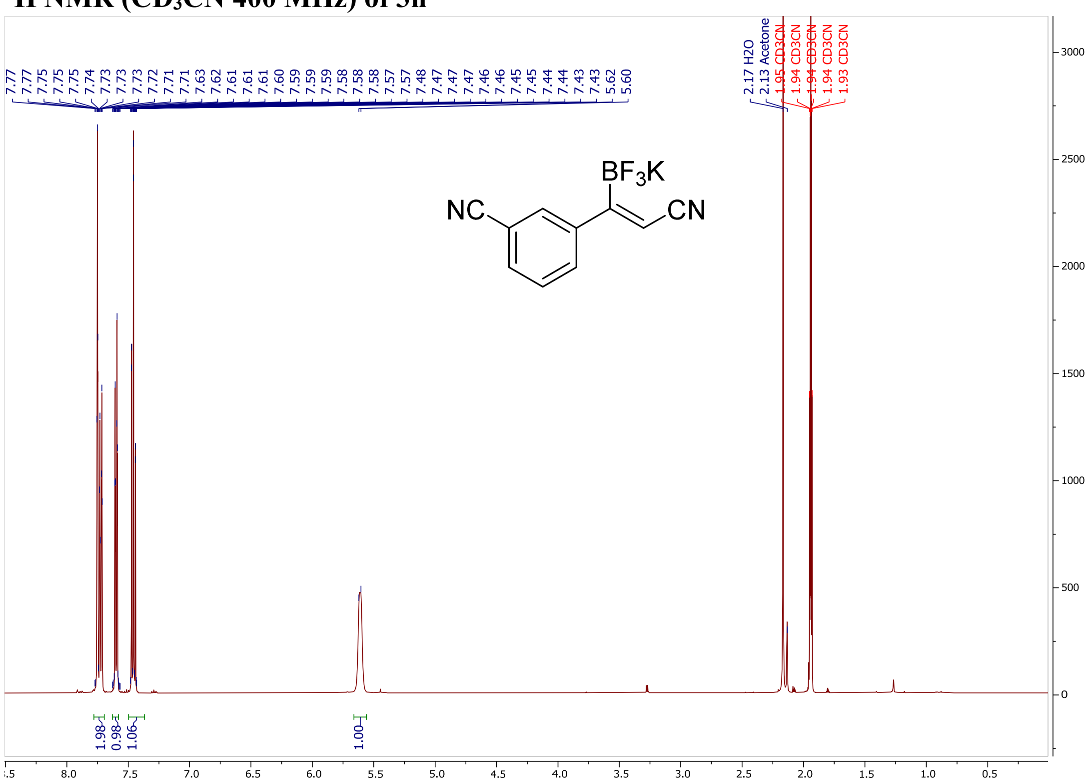
^{19}F NMR (CD_3CN 376 MHz) of 3m



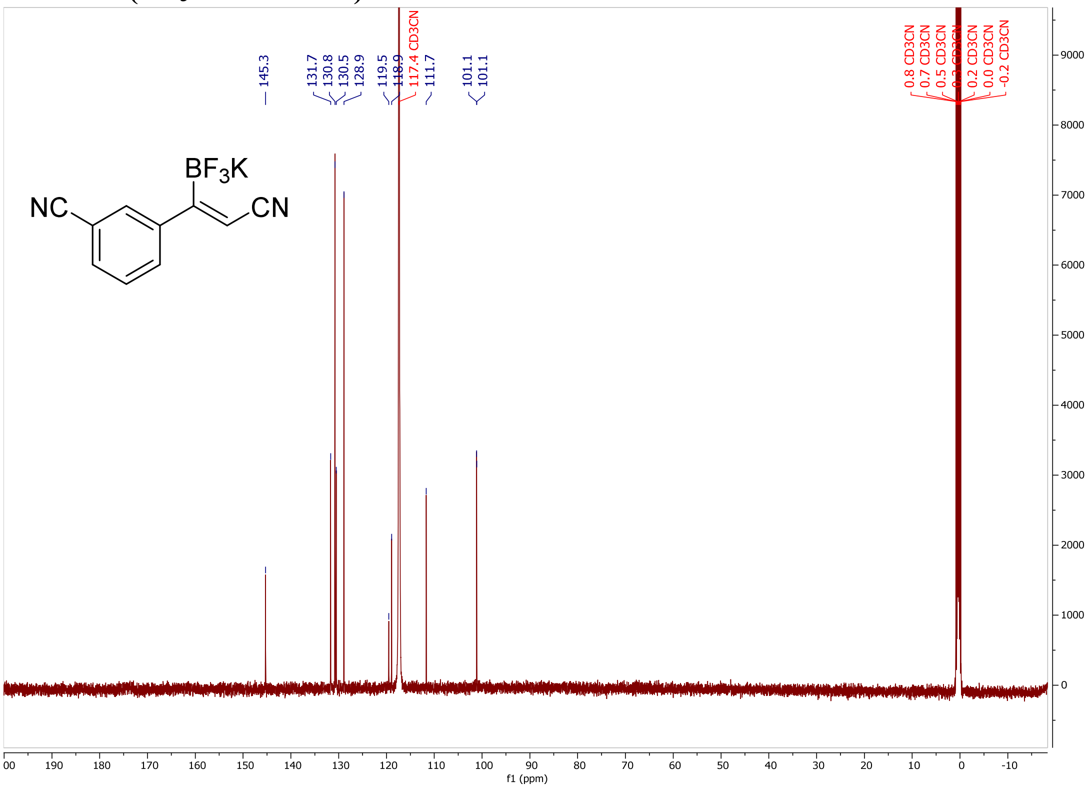
^{11}B NMR (CD_3CN 128 MHz) of 3m



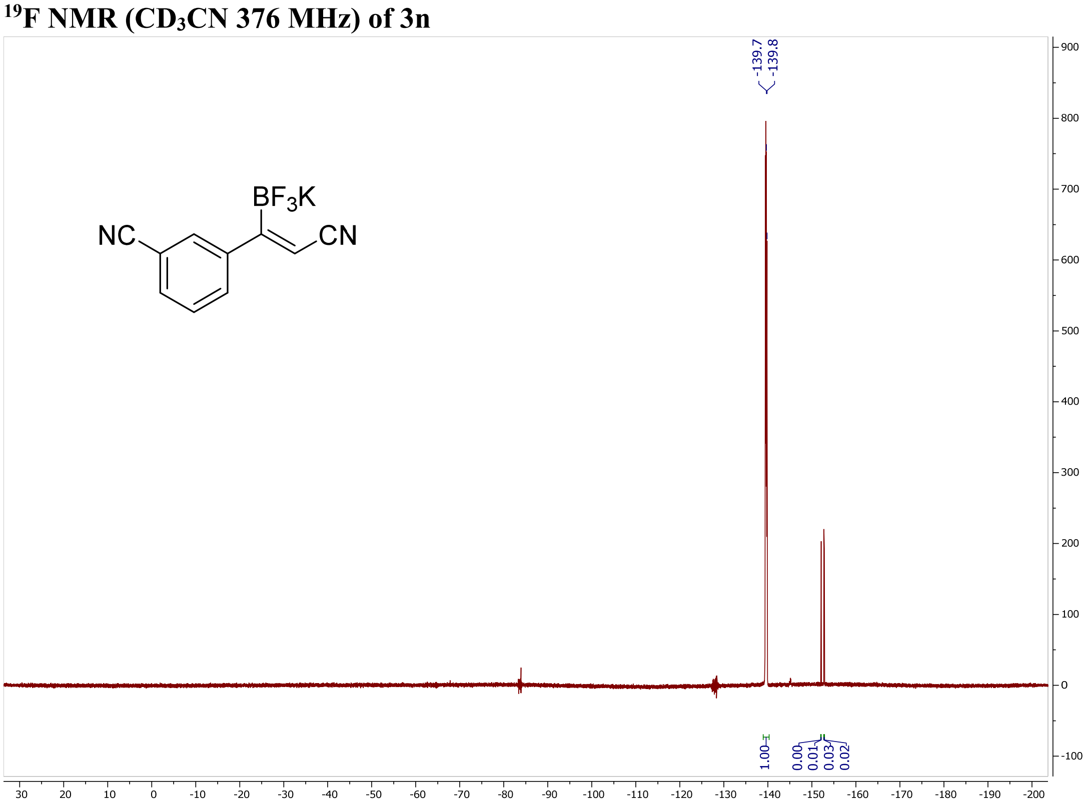
^{1}H NMR (CD_3CN 400 MHz) of 3n



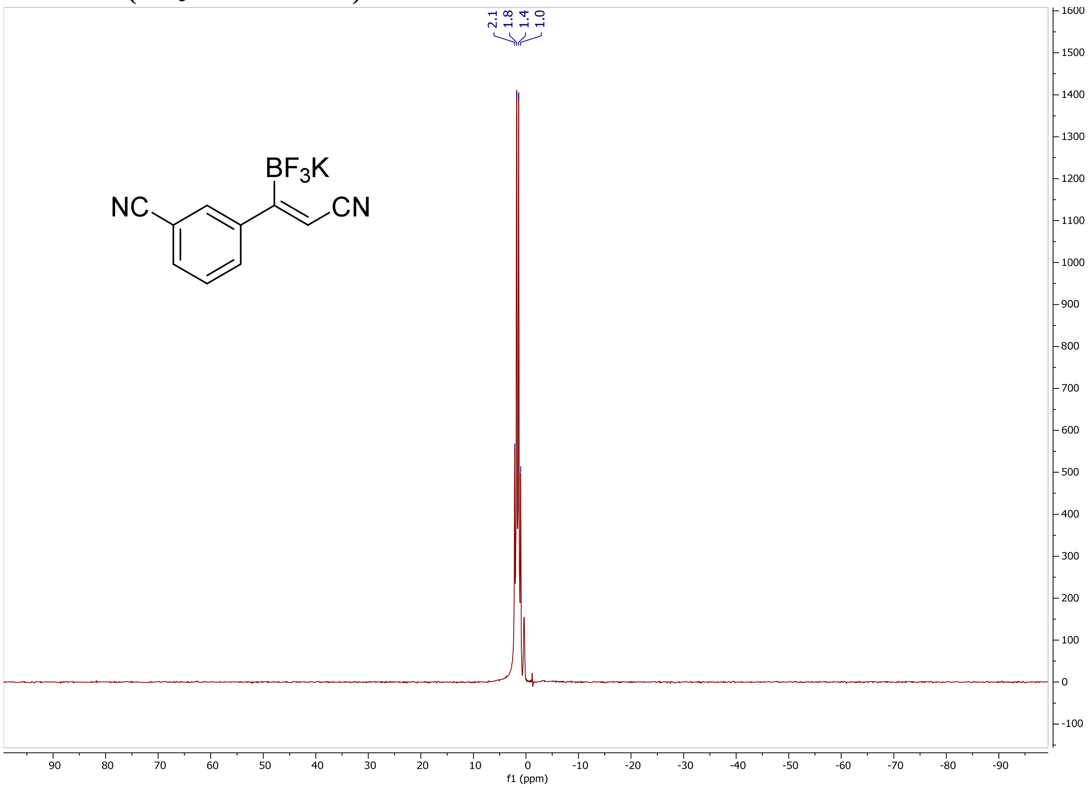
^{13}C NMR (CD_3CN 100 MHz) of 3n



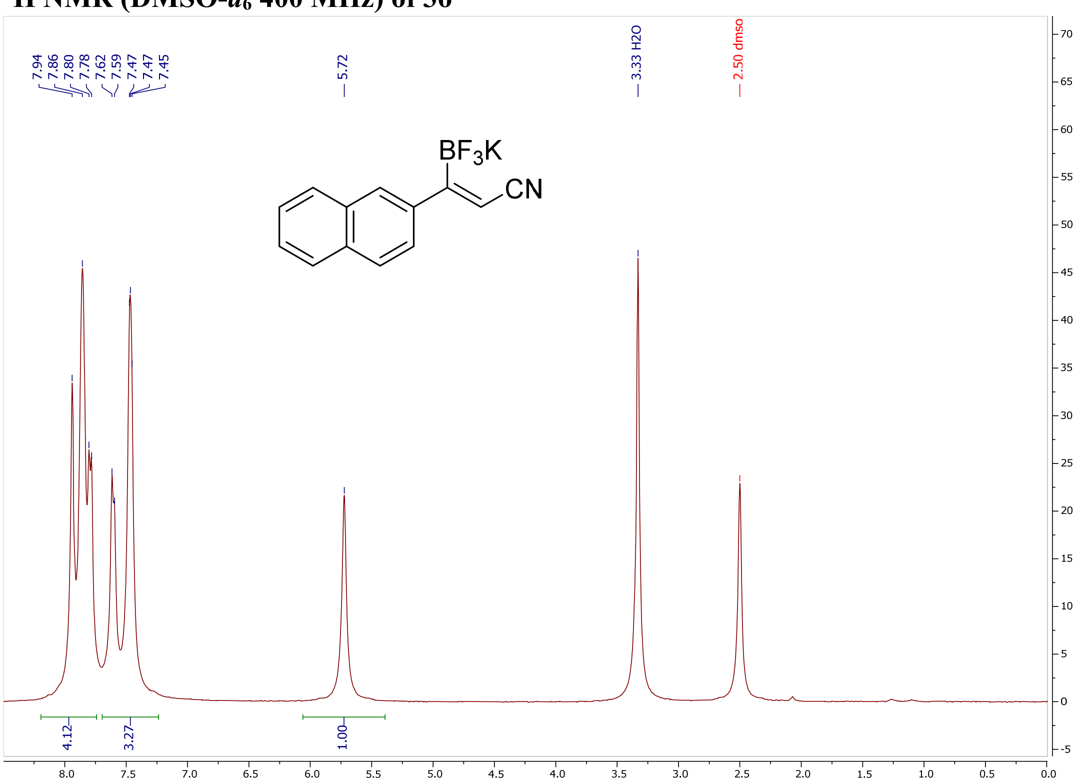
^{19}F NMR (CD_3CN 376 MHz) of 3n



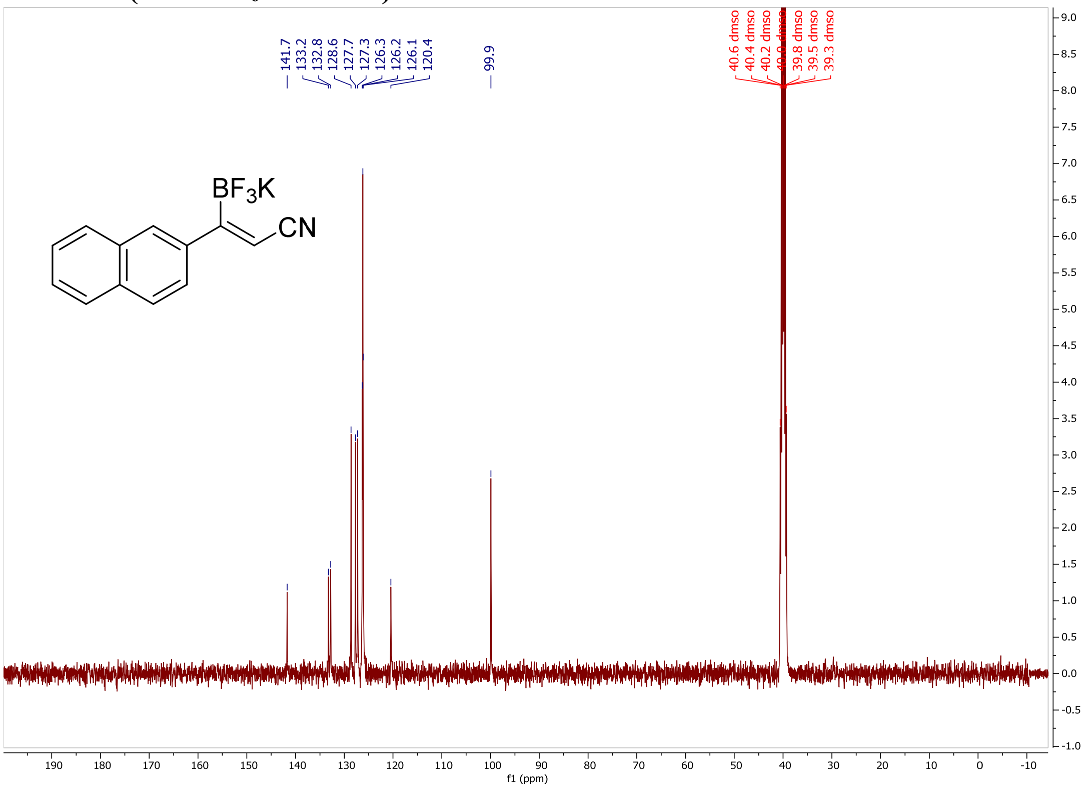
^{11}B NMR (CD_3CN 128 MHz) of 3n



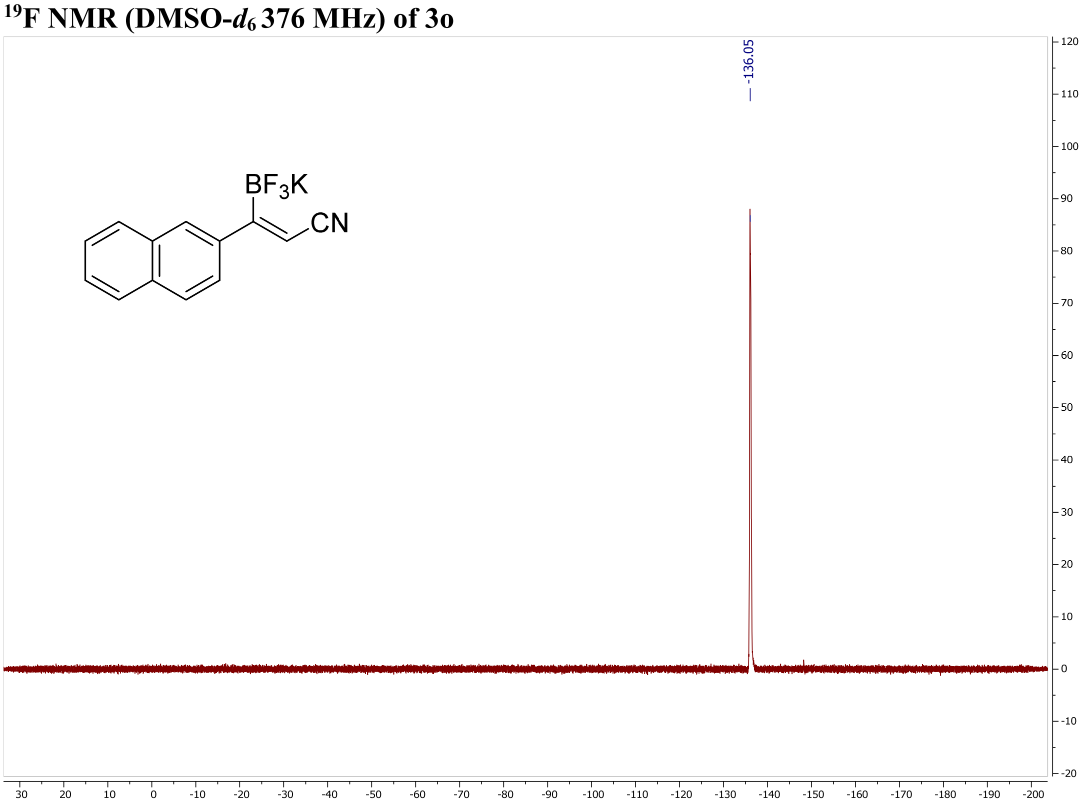
^{1}H NMR (DMSO-d_6 400 MHz) of 3o



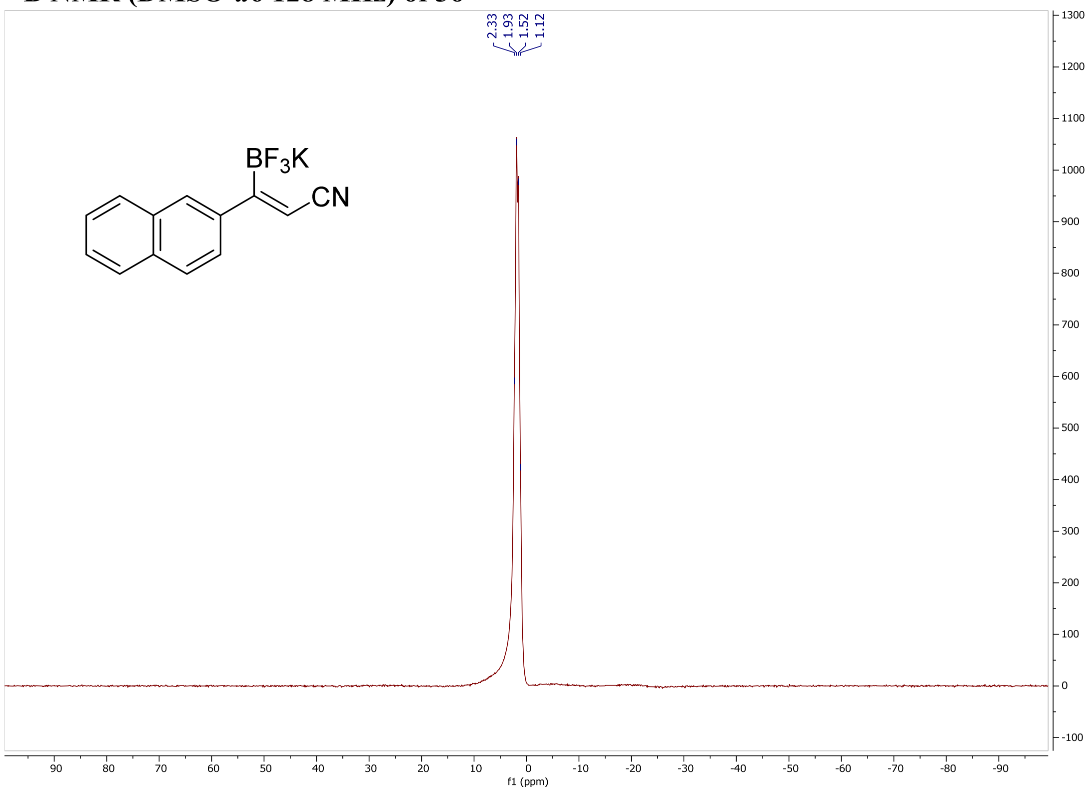
^{13}C NMR (DMSO-d_6 100 MHz) of 3o



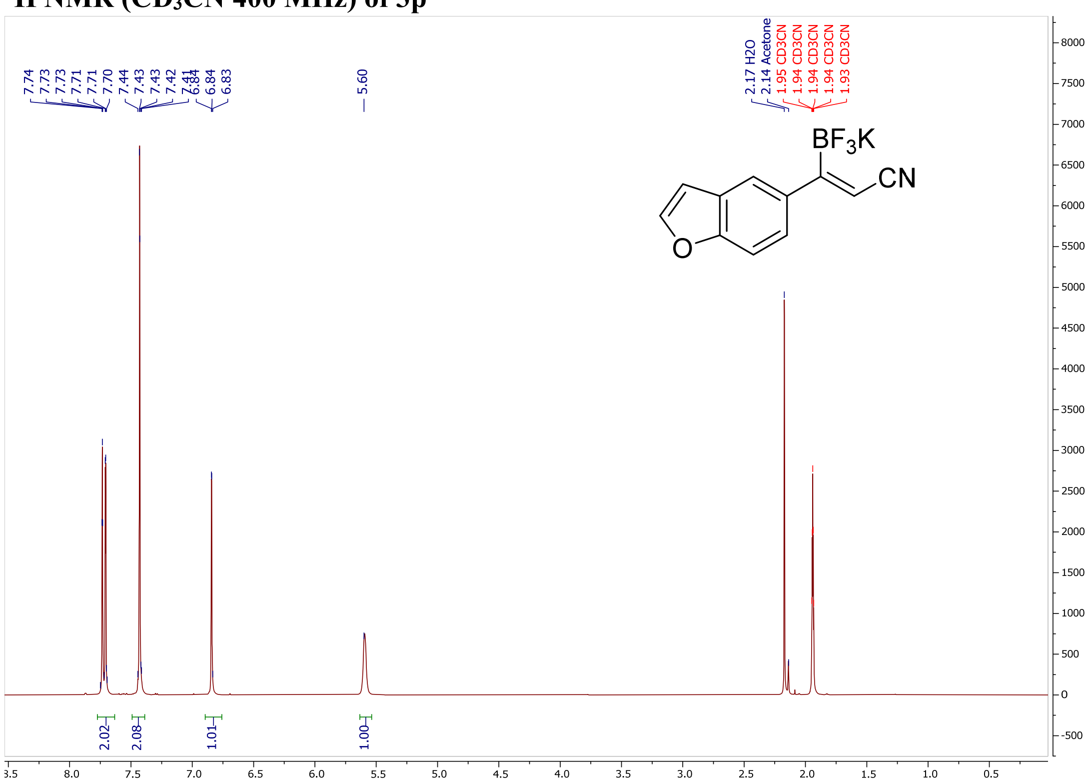
^{19}F NMR (DMSO-d_6 376 MHz) of 3o



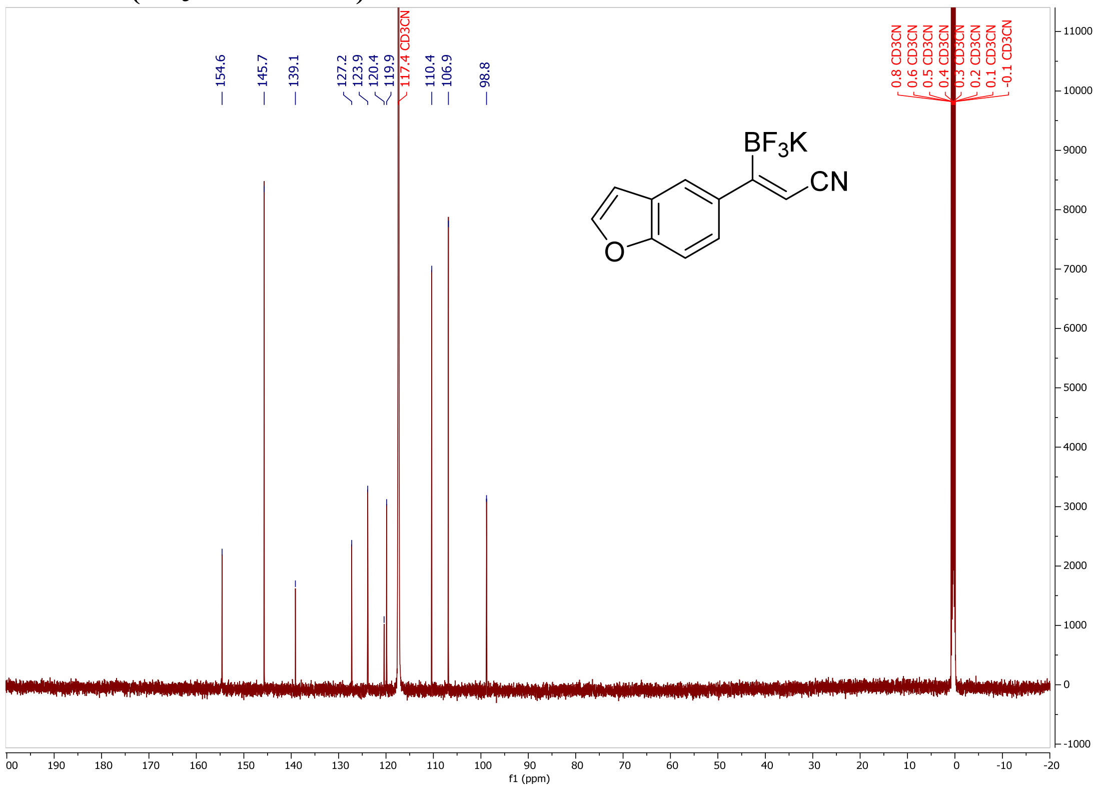
^{11}B NMR (DMSO-*d6* 128 MHz) of 3o



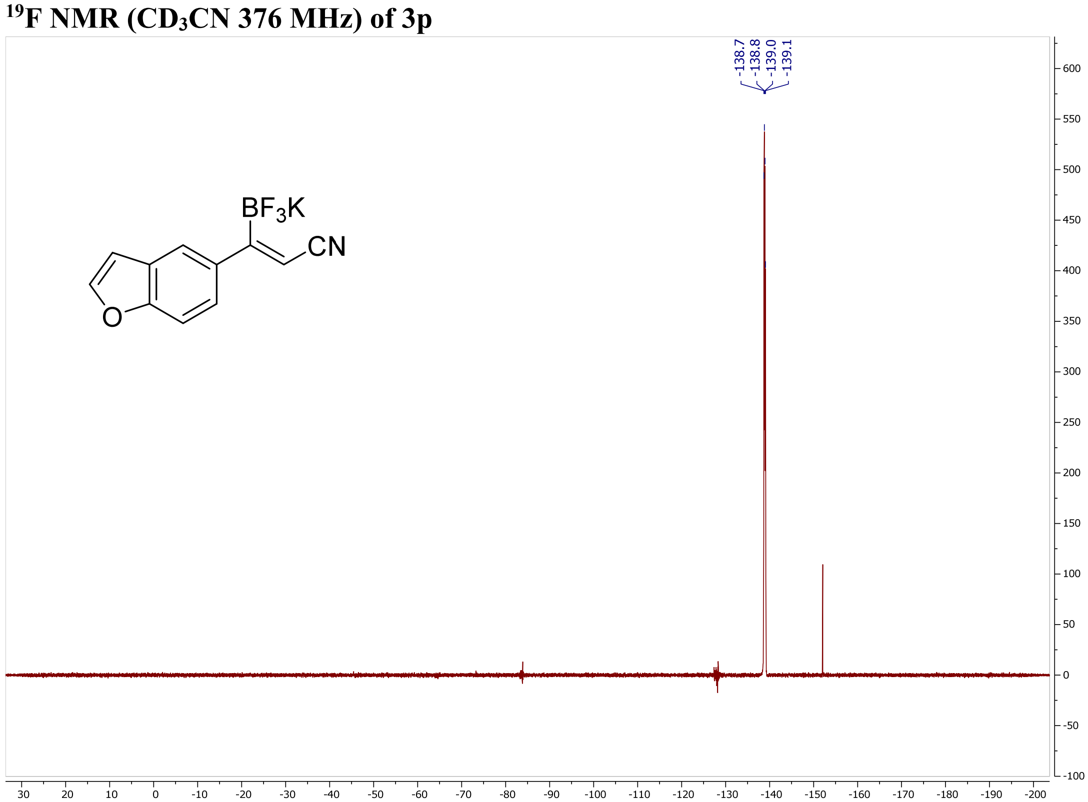
^{1}H NMR (CD_3CN 400 MHz) of 3p



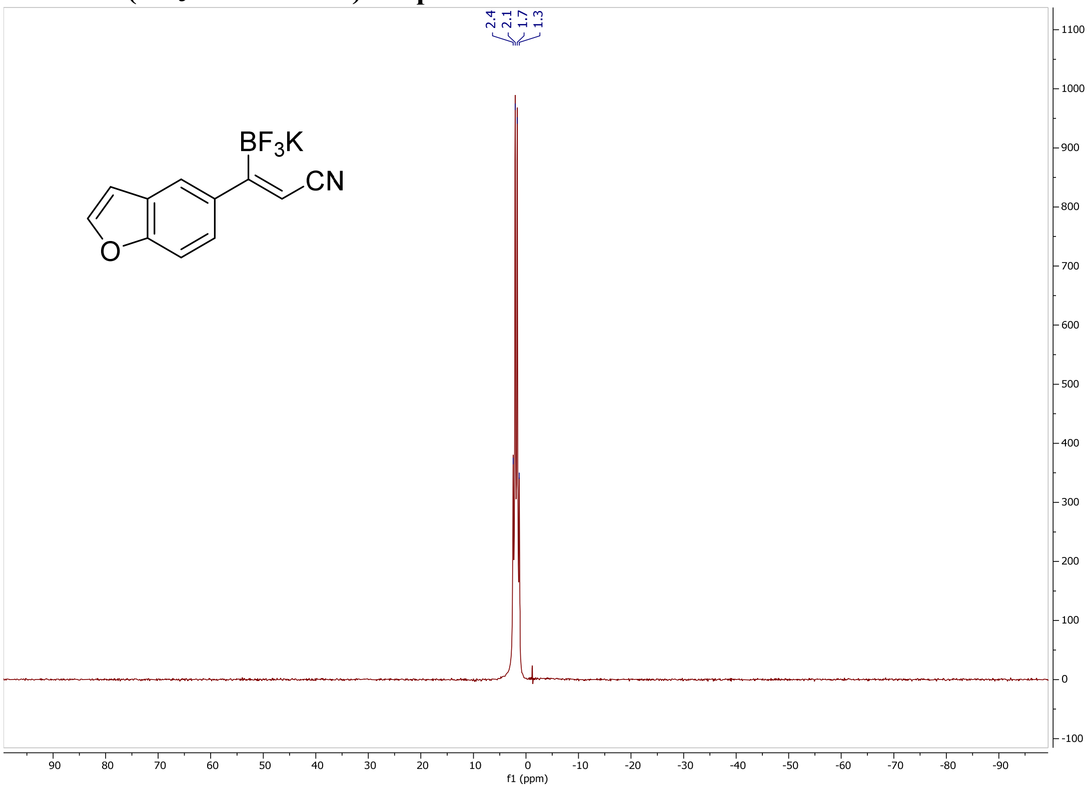
^{13}C NMR (CD_3CN 100 MHz) of 3o



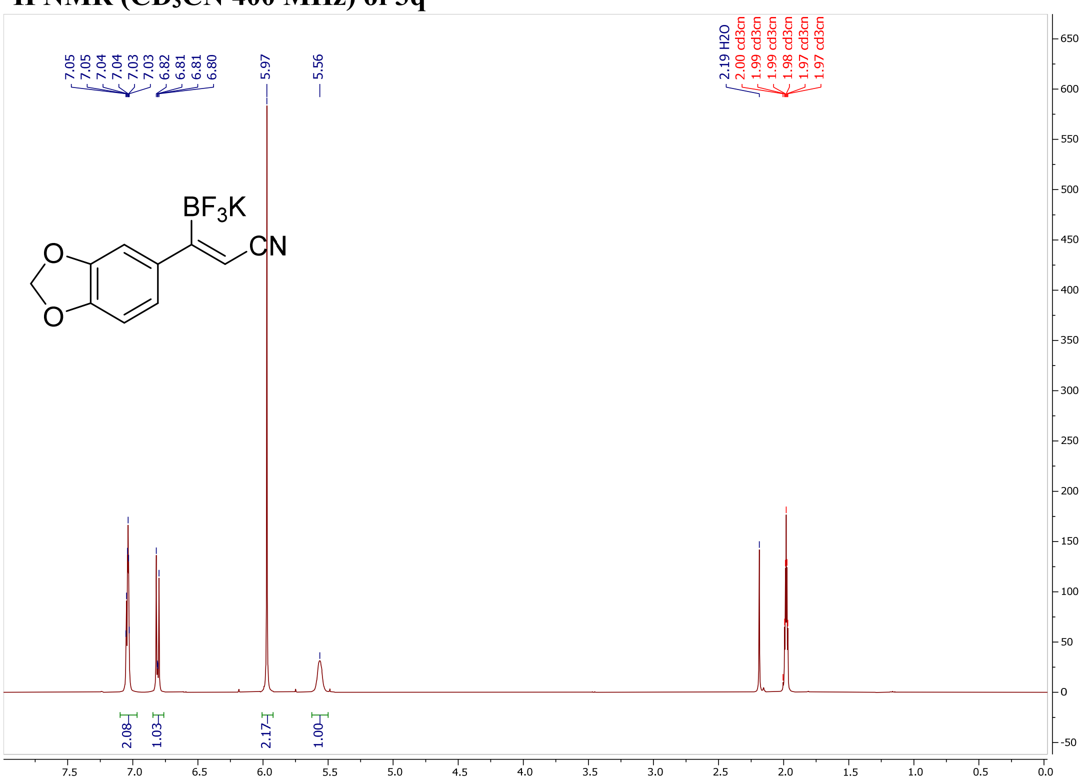
^{19}F NMR (CD_3CN 376 MHz) of 3p



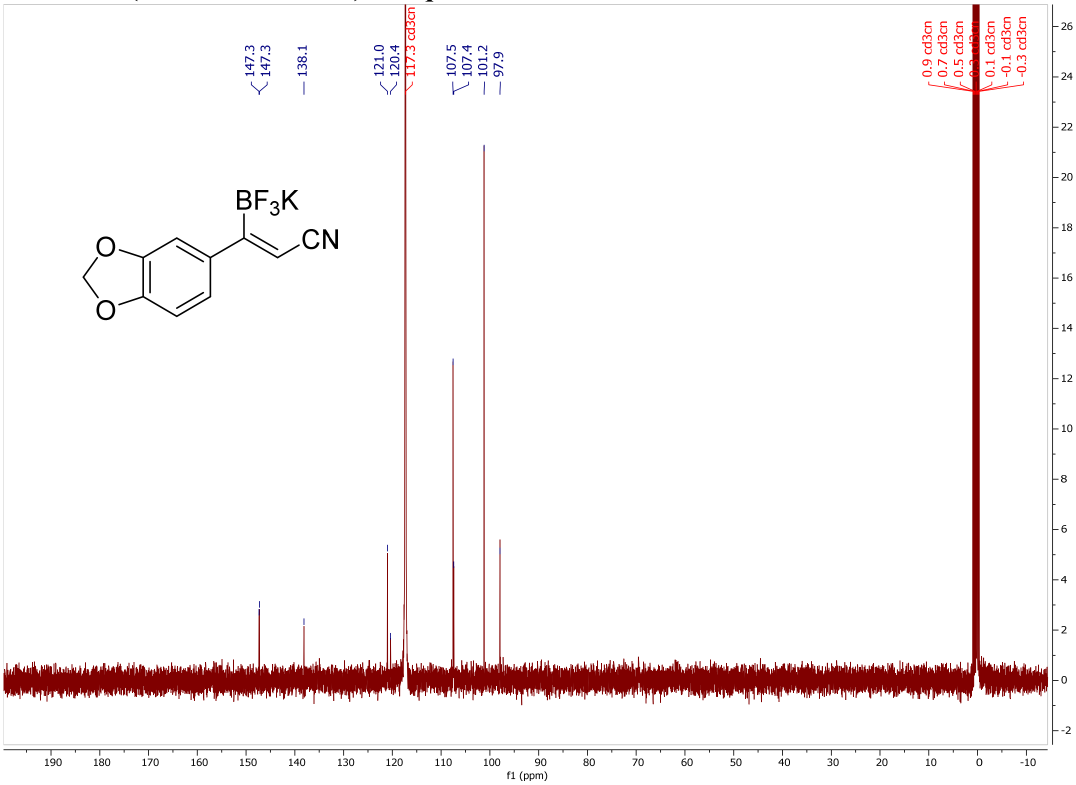
^{11}B NMR (CD_3CN 128 MHz) of 3p



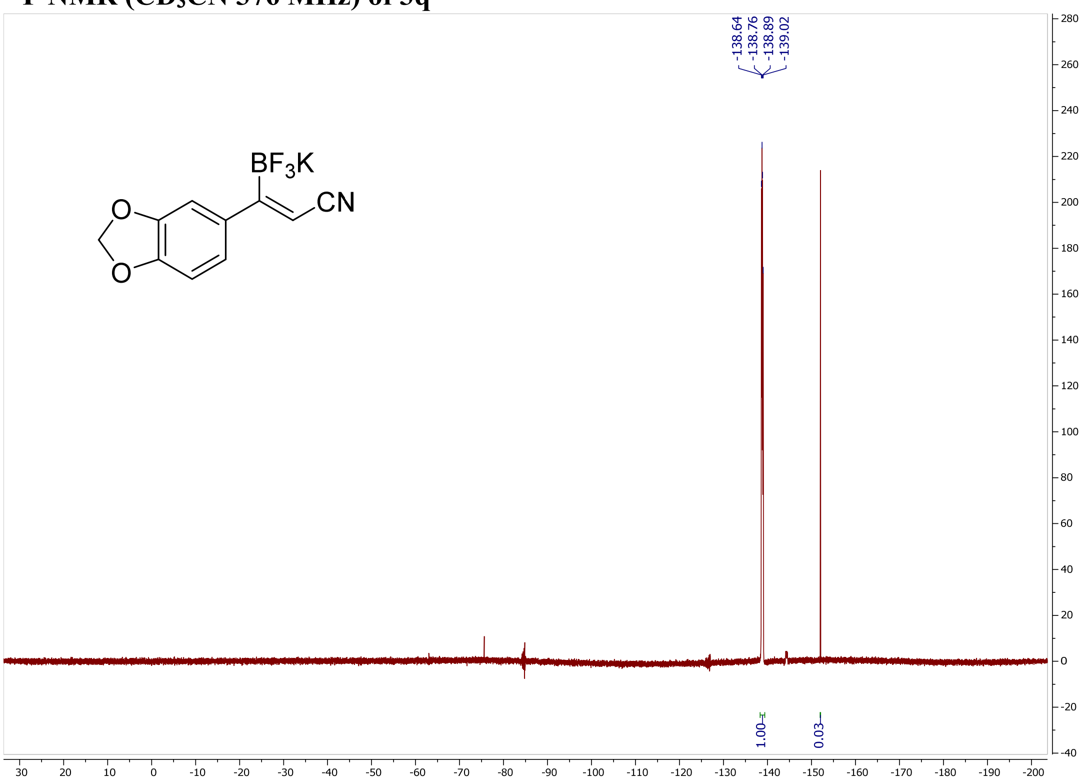
^{1}H NMR (CD_3CN 400 MHz) of 3q



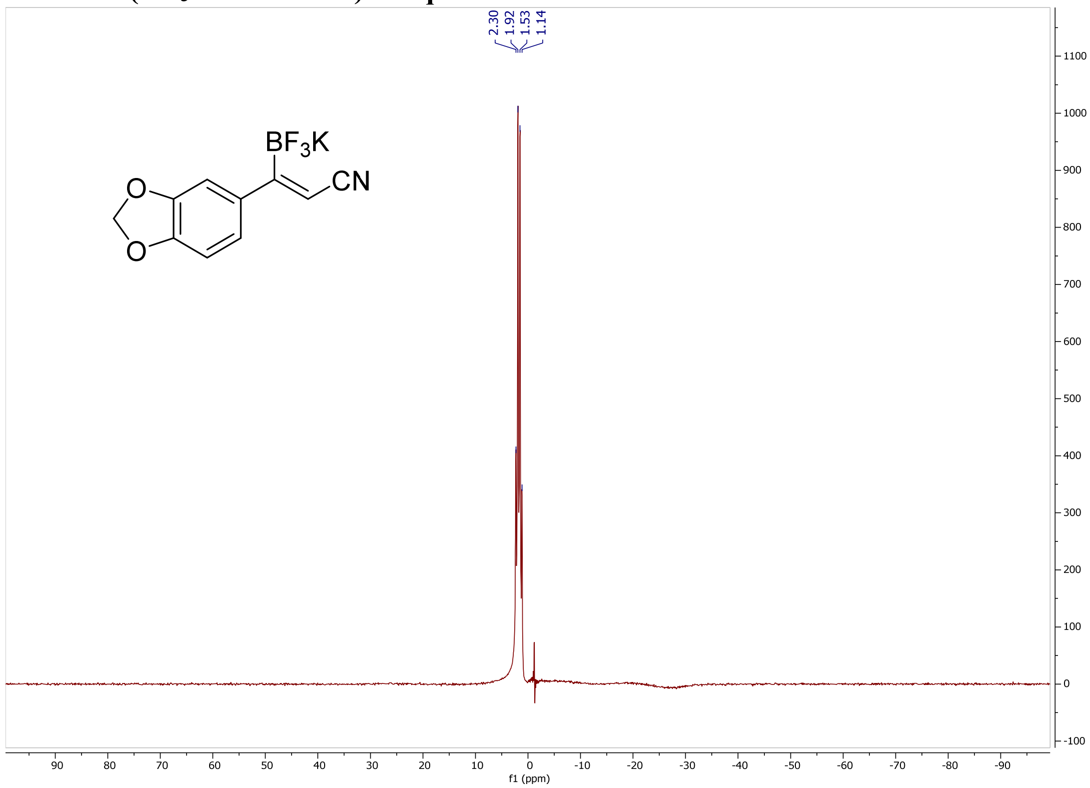
^{13}C NMR (CD_3CN 100 MHz) of 3q



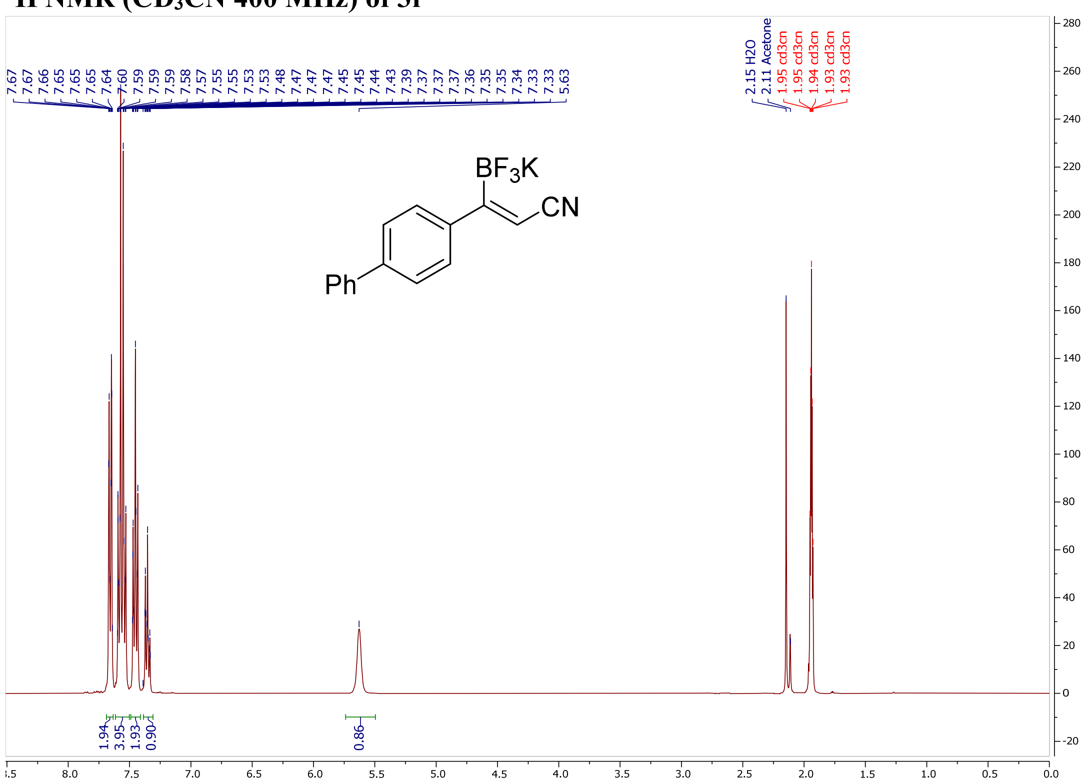
^{19}F NMR (CD_3CN 376 MHz) of 3q



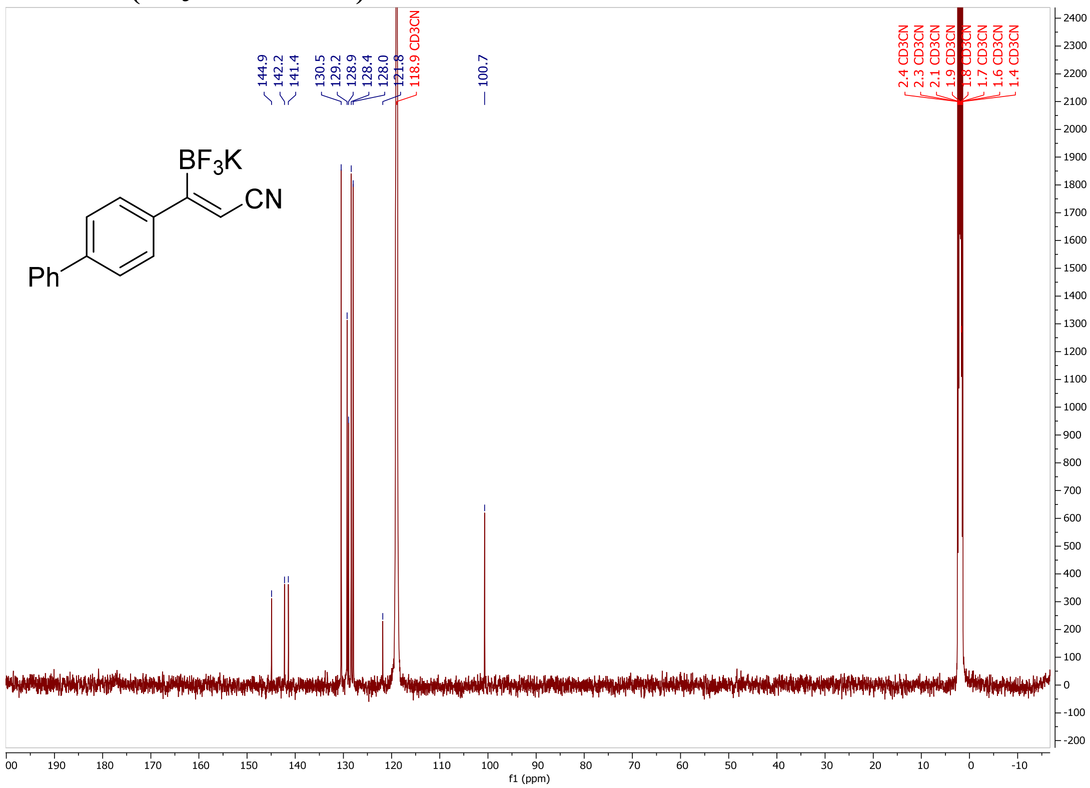
11B NMR (CD_3CN 128 MHz) of 3q



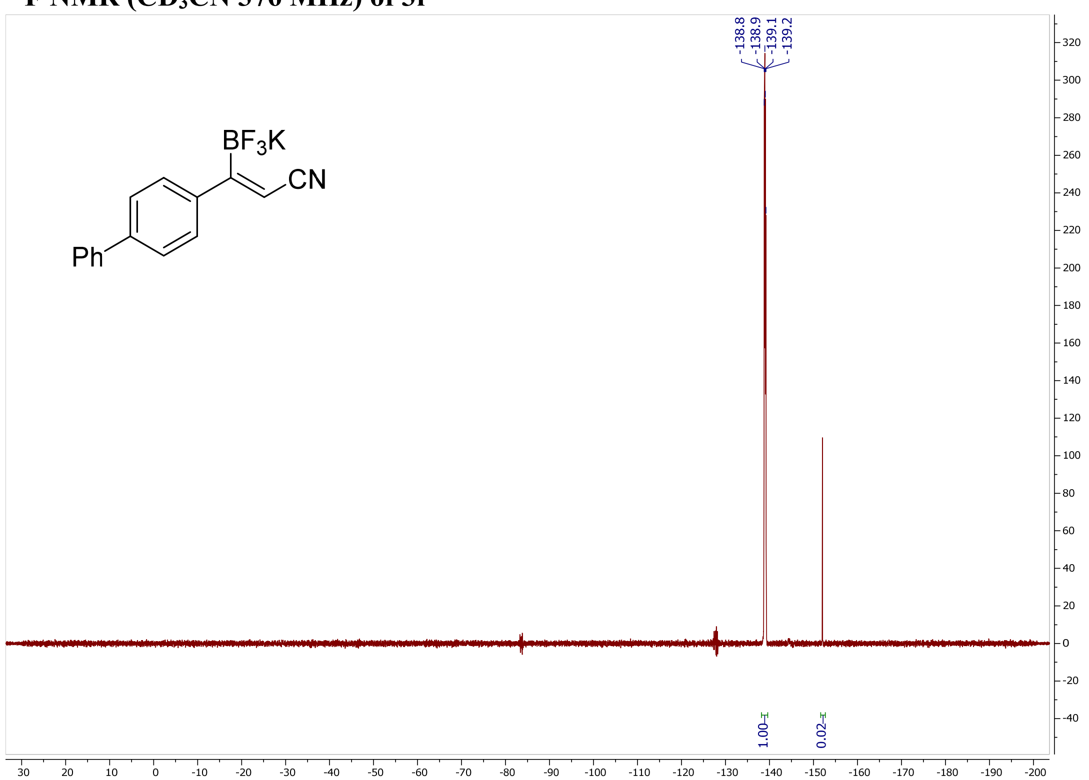
1H NMR (CD_3CN 400 MHz) of 3r



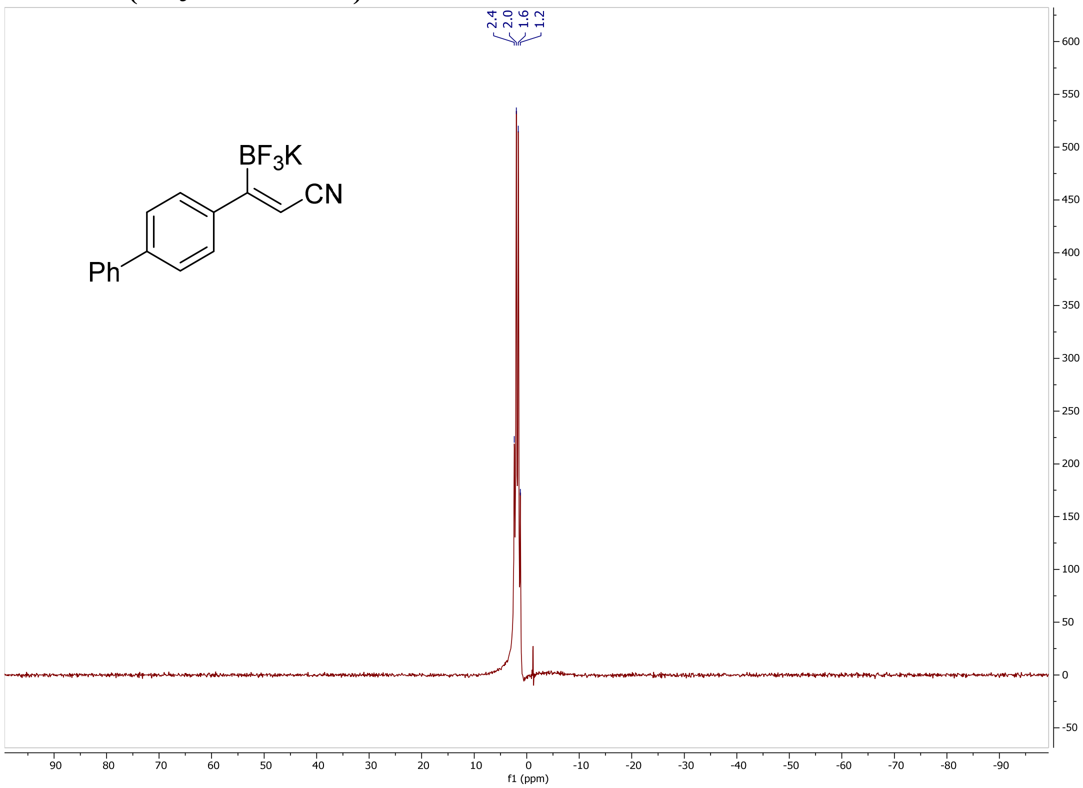
^{13}C NMR (CD_3CN 100 MHz) of 3r



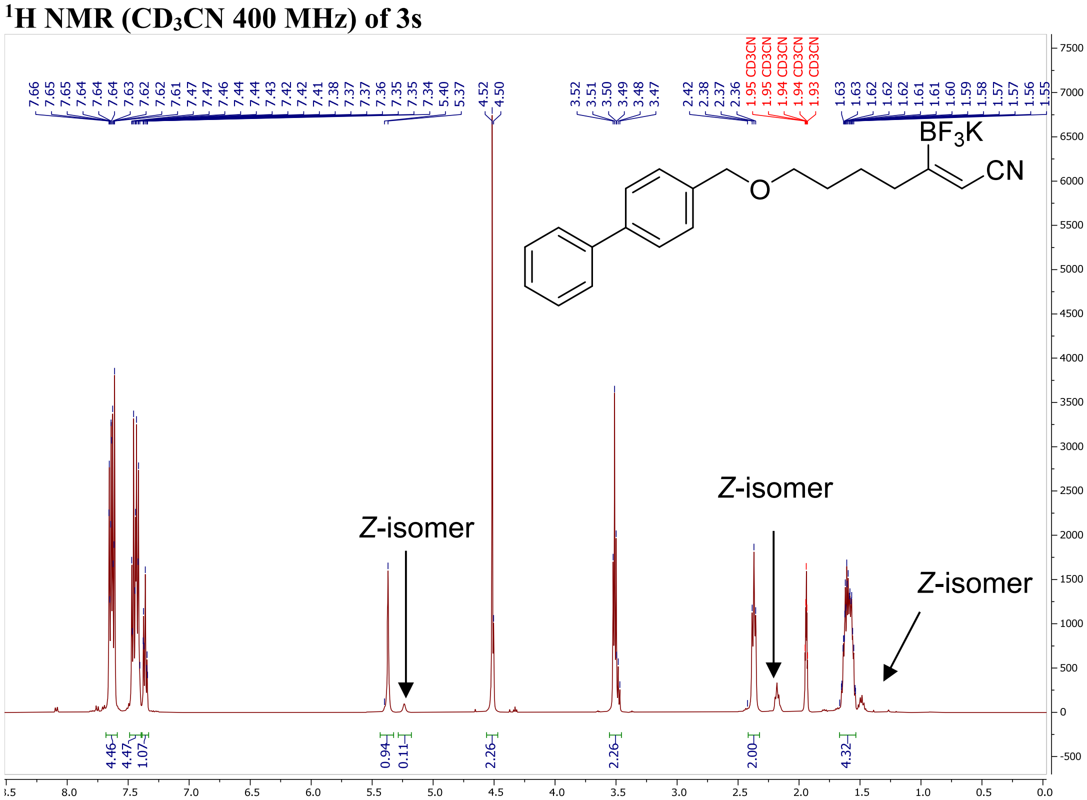
^{19}F NMR (CD_3CN 376 MHz) of 3r



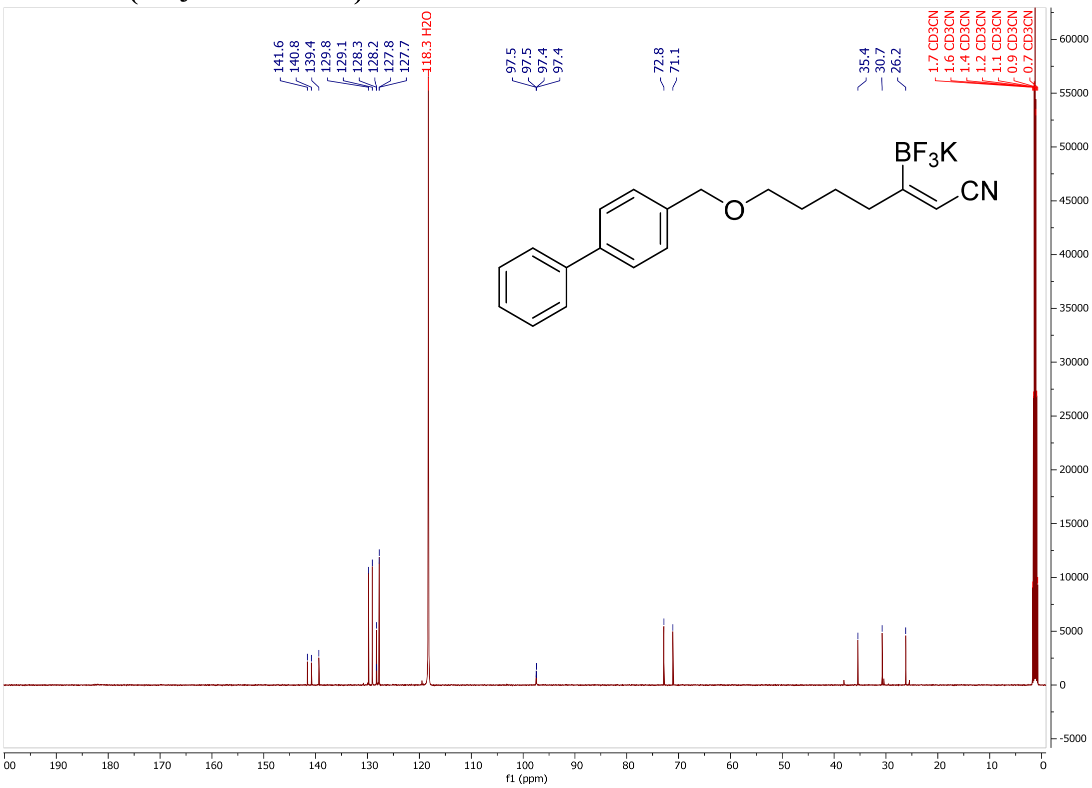
^{11}B NMR (CD_3CN 128 MHz) of 3r



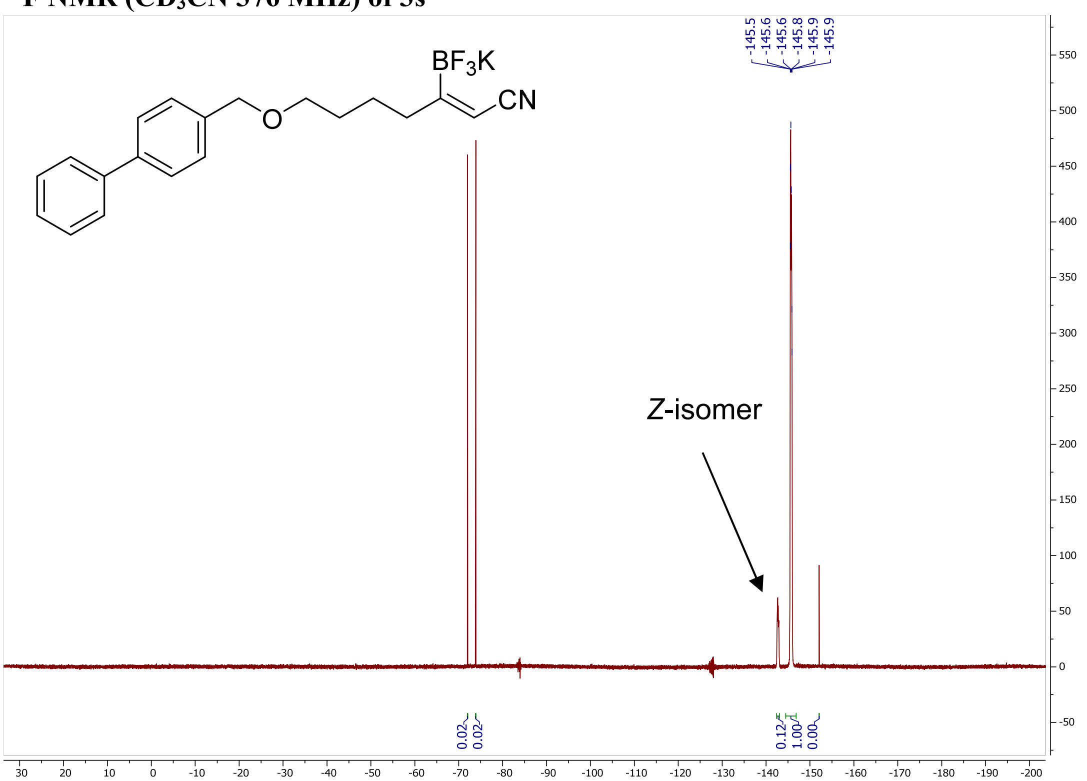
^{1}H NMR (CD_3CN 400 MHz) of 3s



^{13}C NMR (CD_3CN 100 MHz) of 3s



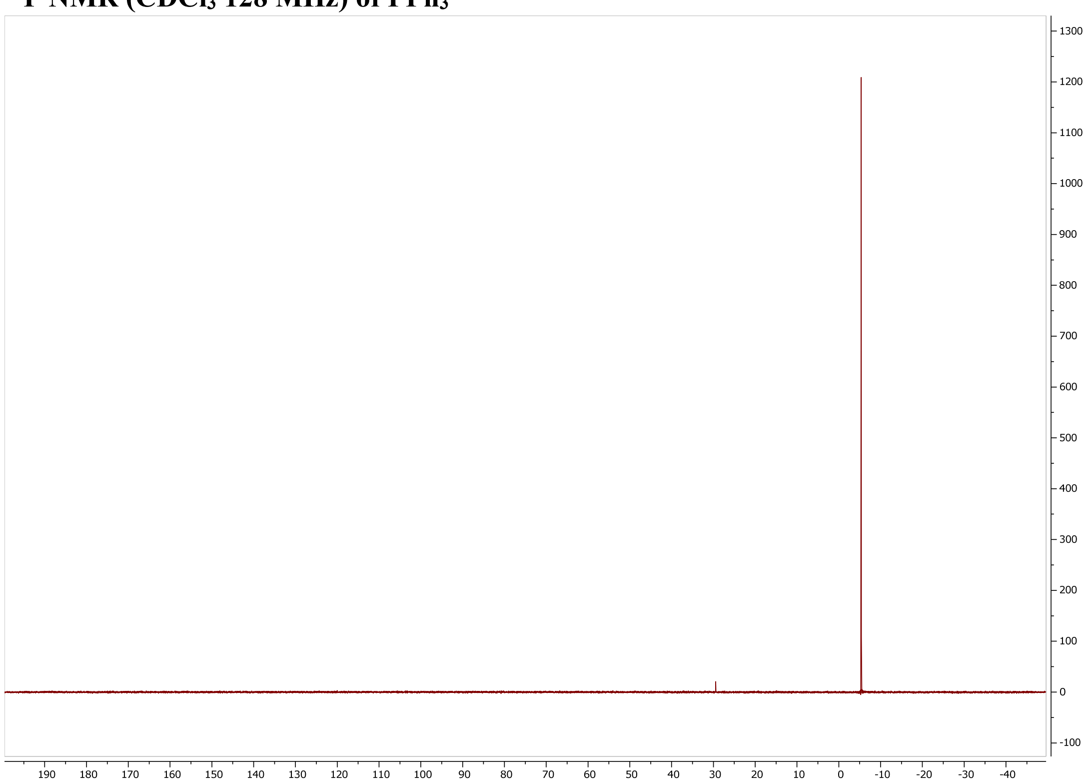
^{19}F NMR (CD_3CN 376 MHz) of 3s



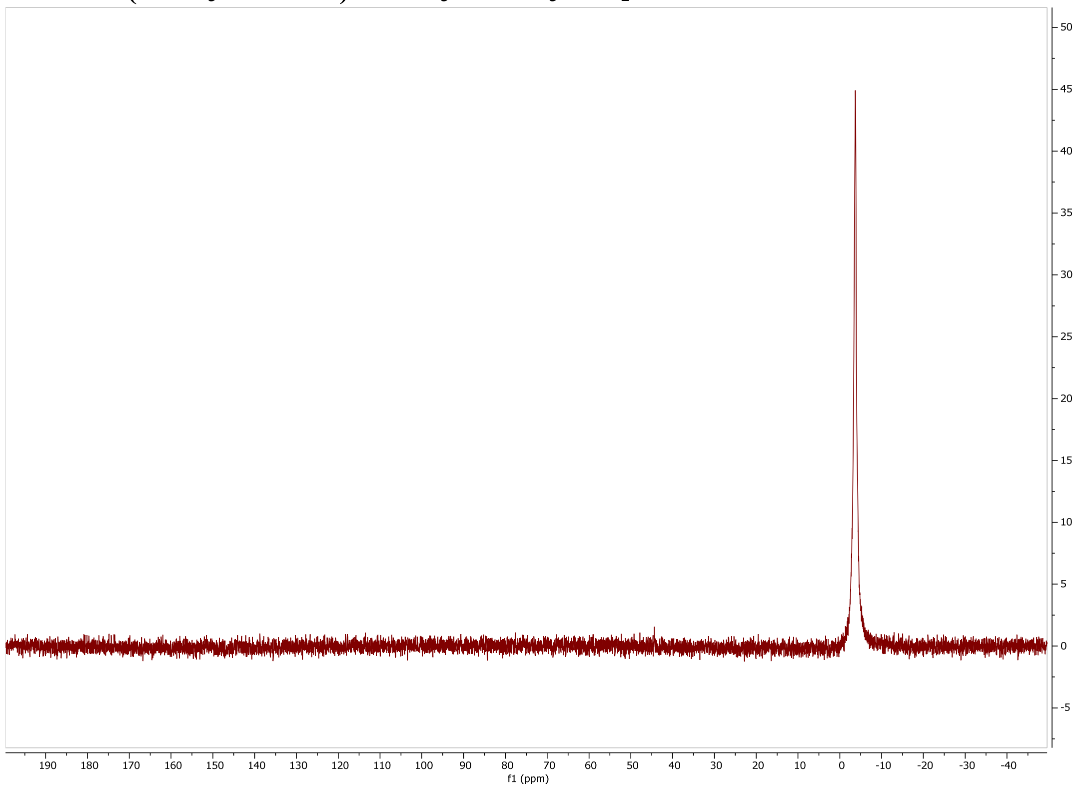
^{11}B NMR (CD_3CN 128 MHz) of 3s

20. Spectra for NMR studies

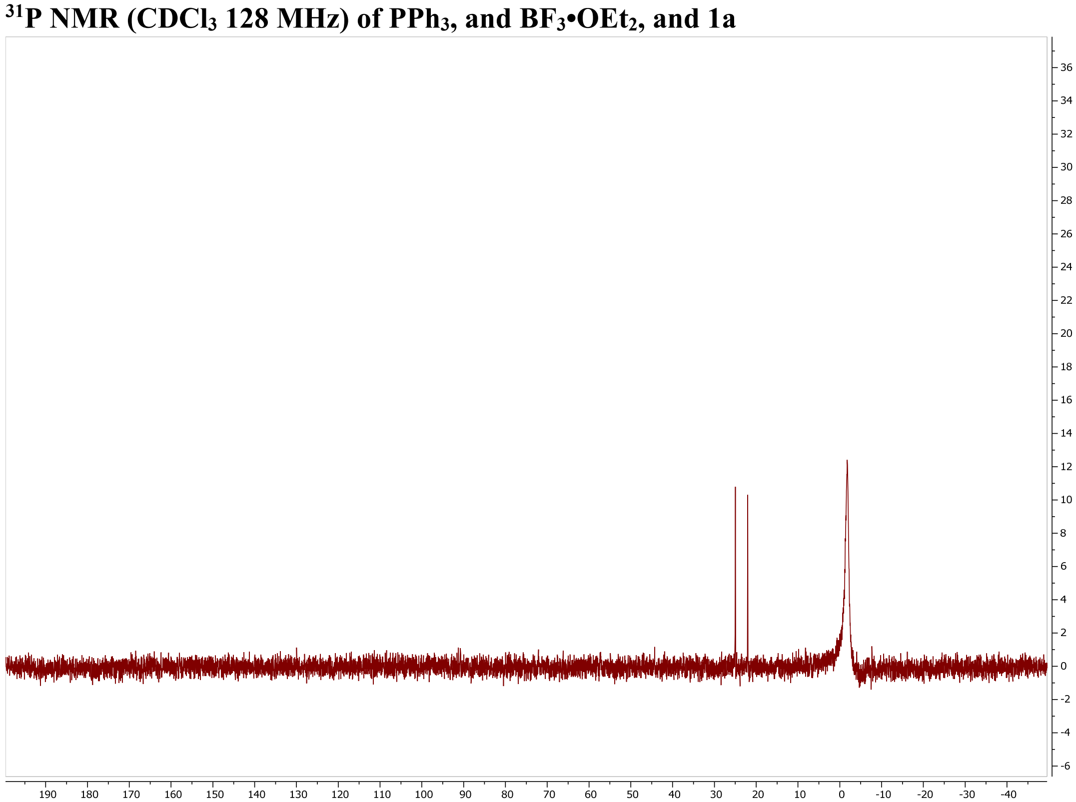
^{31}P NMR ($CDCl_3$ 128 MHz) of PPh_3



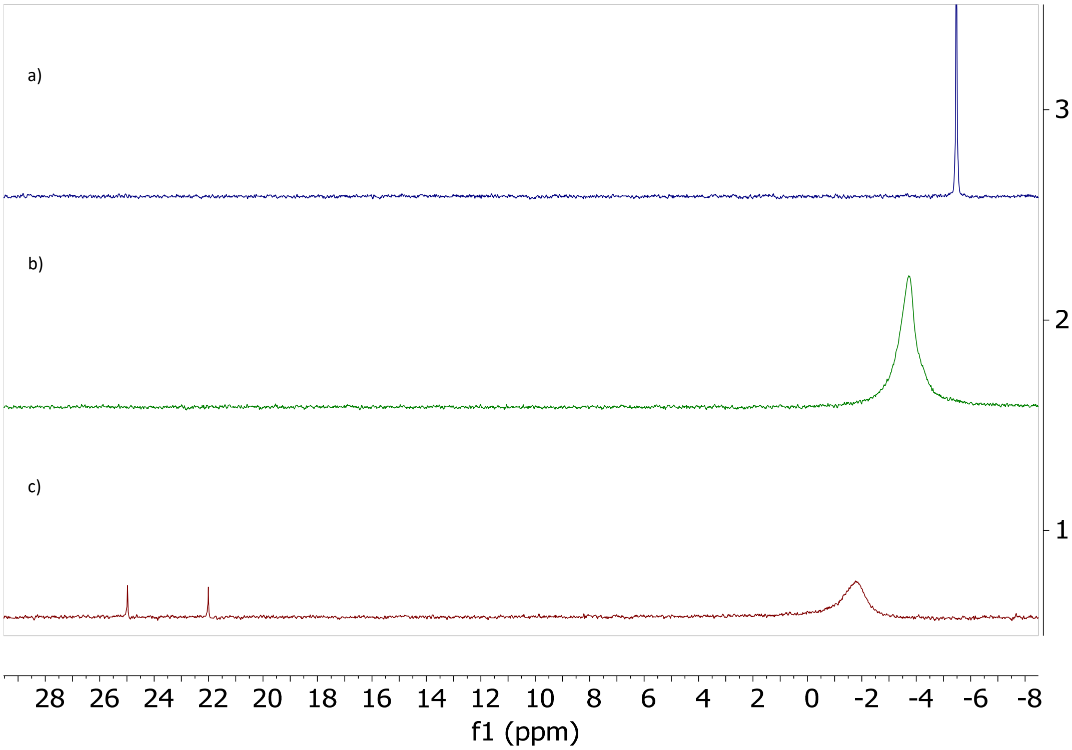
^{31}P NMR ($CDCl_3$ 128 MHz) of PPh_3 and BF_3•OEt_2



^{31}P NMR ($CDCl_3$ 128 MHz) of PPh_3, and BF_3•OEt_2, and 1a

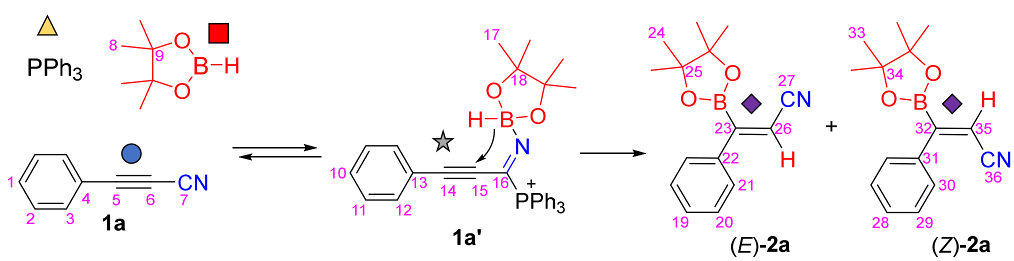


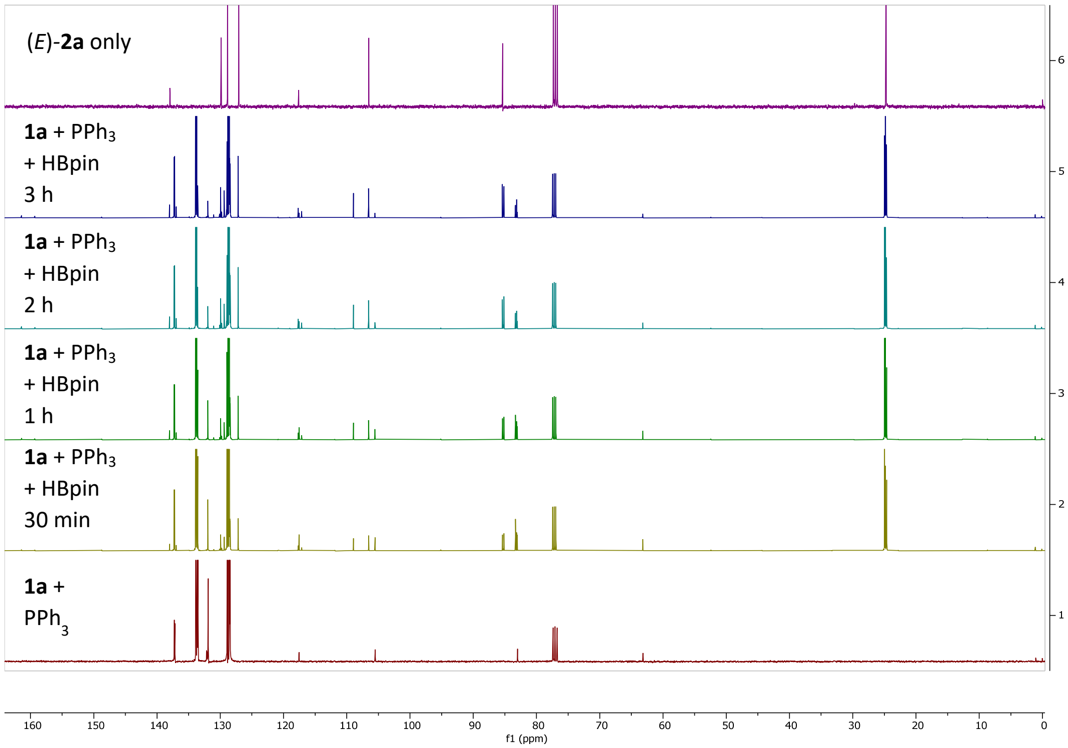
Combined ^{31}P NMR spectra ($CDCl_3$ 128 MHz)



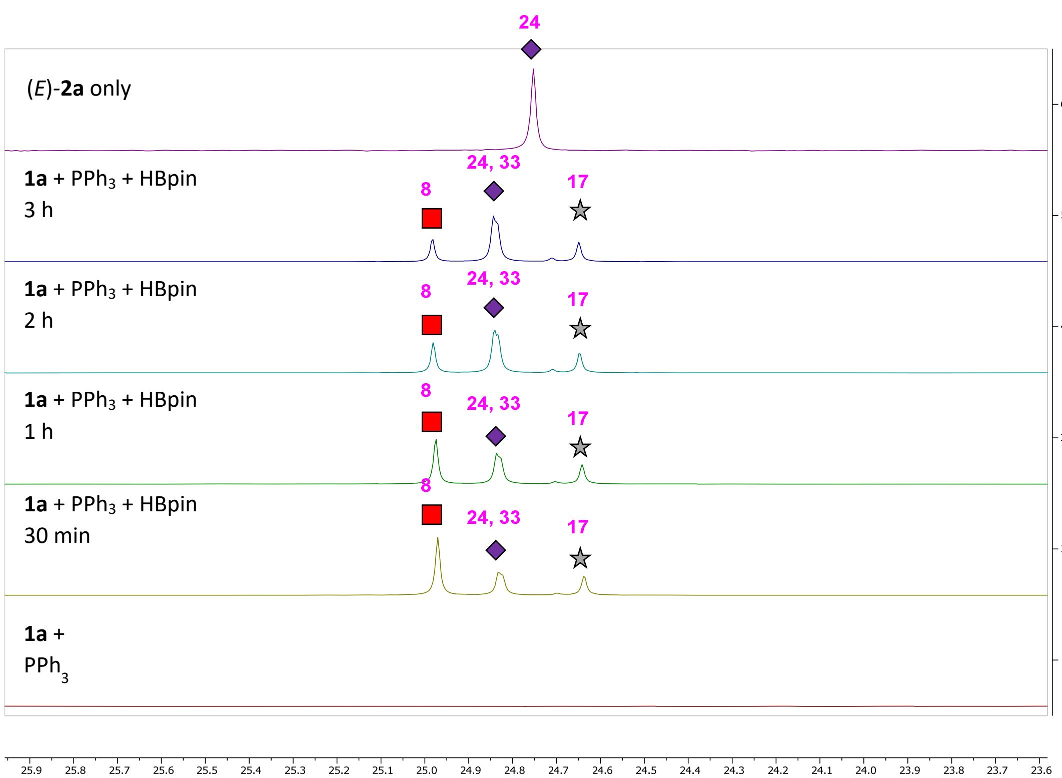
^{31}P NMR studies in chloroform: a) PPh_3 (80 µmol), b) PPh_3 (80 µmol) and $BF_3 \cdot OEt_2$ (80 µmol) and c) PPh_3 (80 µmol), $BF_3 \cdot OEt_2$ (80 µmol), and **1a** (80 µmol).

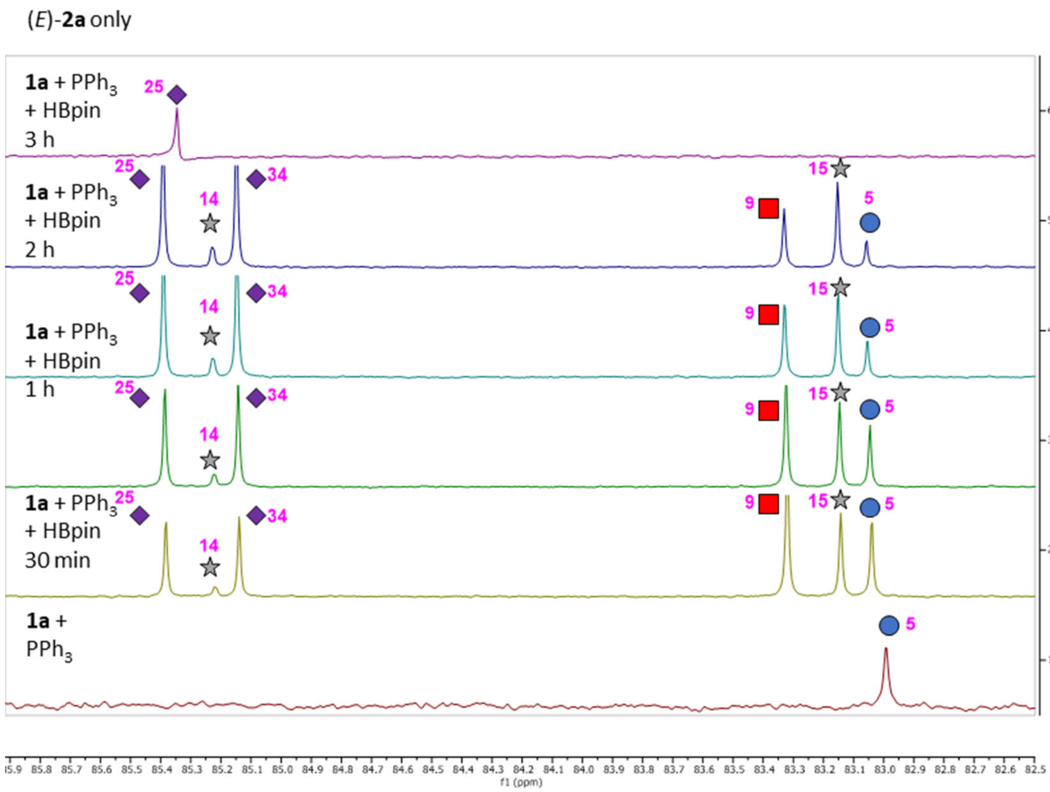
Combined Time Course ^{13}C NMR studies in chloroform at rt. PPh_3 (0.39 mmol), pinacolborane (0.43 mmol), and 1a (0.39 mmol).

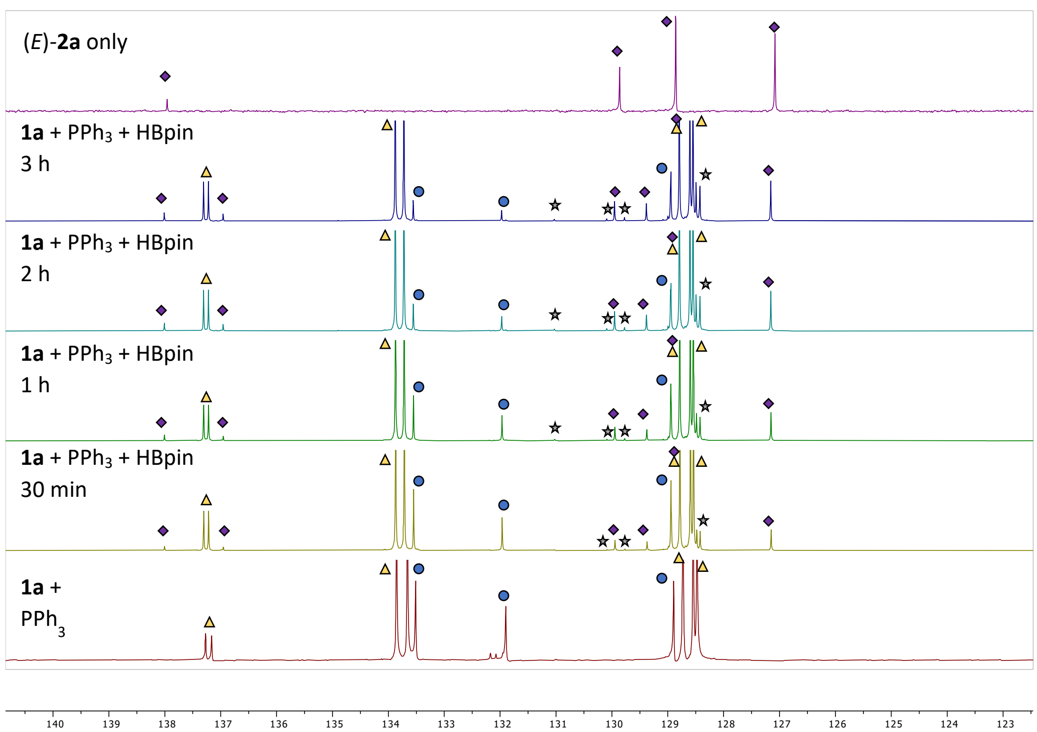




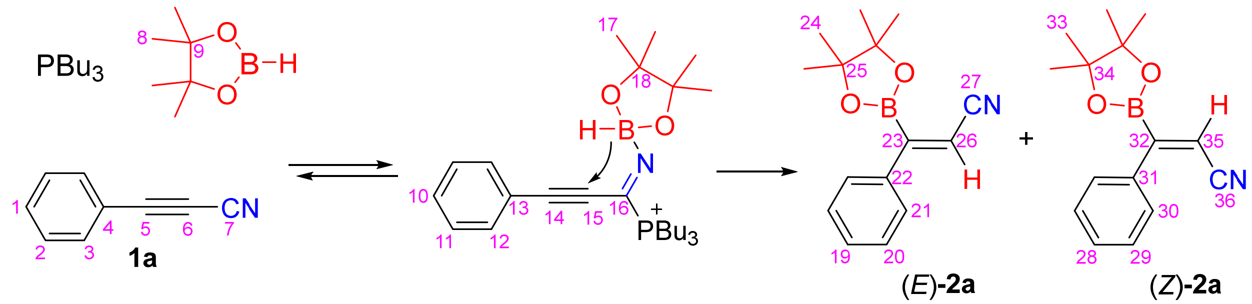
Peaks marked with ☆ correspond to intermediate **1a'**

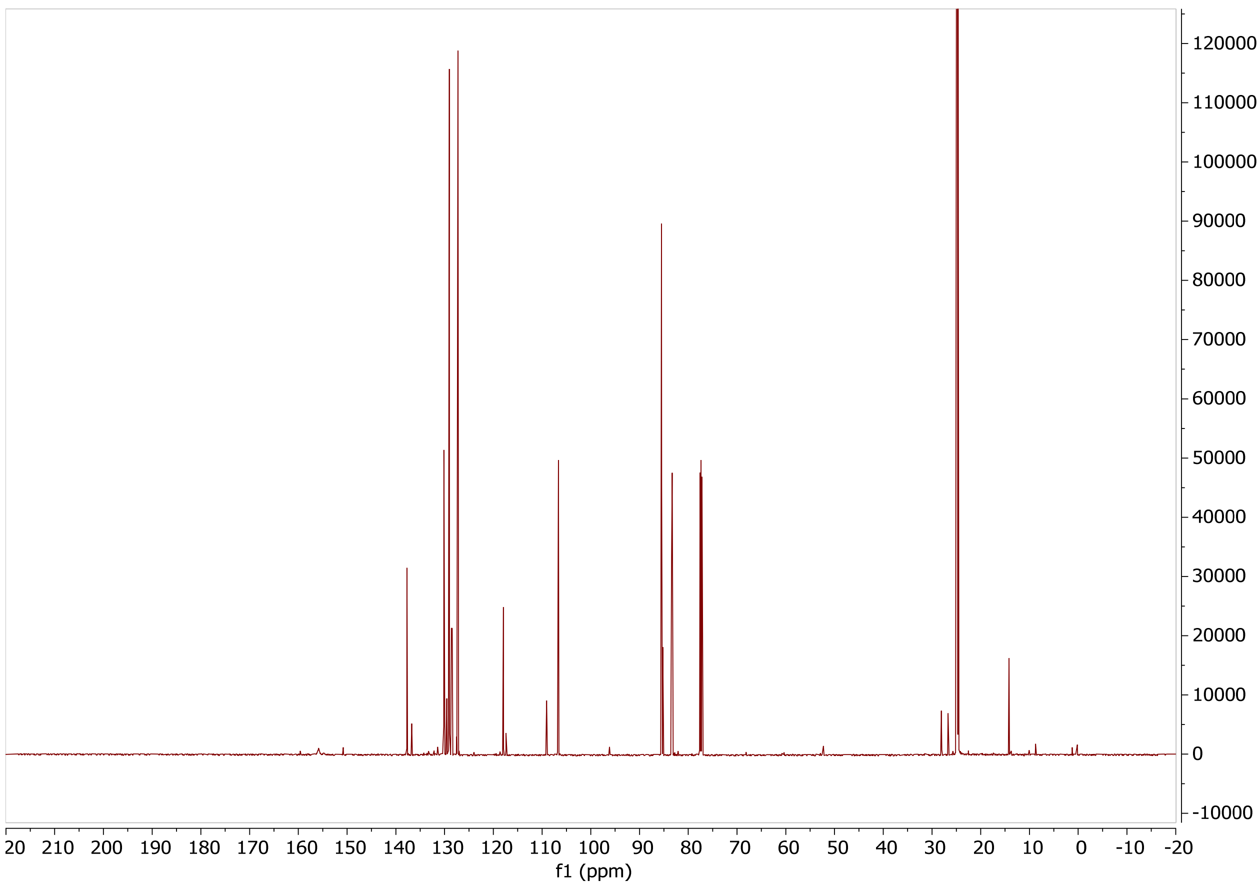



(E)-2a only
1a + PPh3 + HBpin 3 h
1a + PPh3 + HBpin 2 h
1a + PPh3 + HBpin 1 h
1a + PPh3 + HBpin 30 min
1a + PPh3
25
34
14
9
15
5
f1 (ppm)

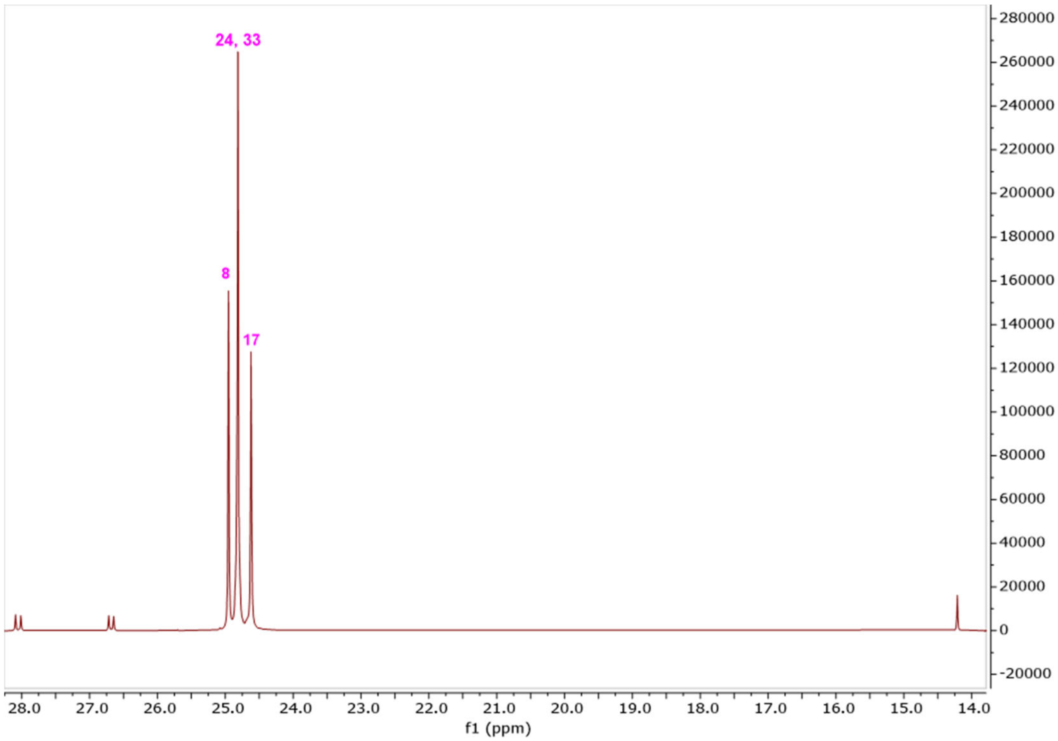

(E)-2a only
1a + PPh3 + HBpin 3 h
1a + PPh3 + HBpin 2 h
1a + PPh3 + HBpin 1 h
1a + PPh3 + HBpin 30 min
1a + PPh3
f1 (ppm)

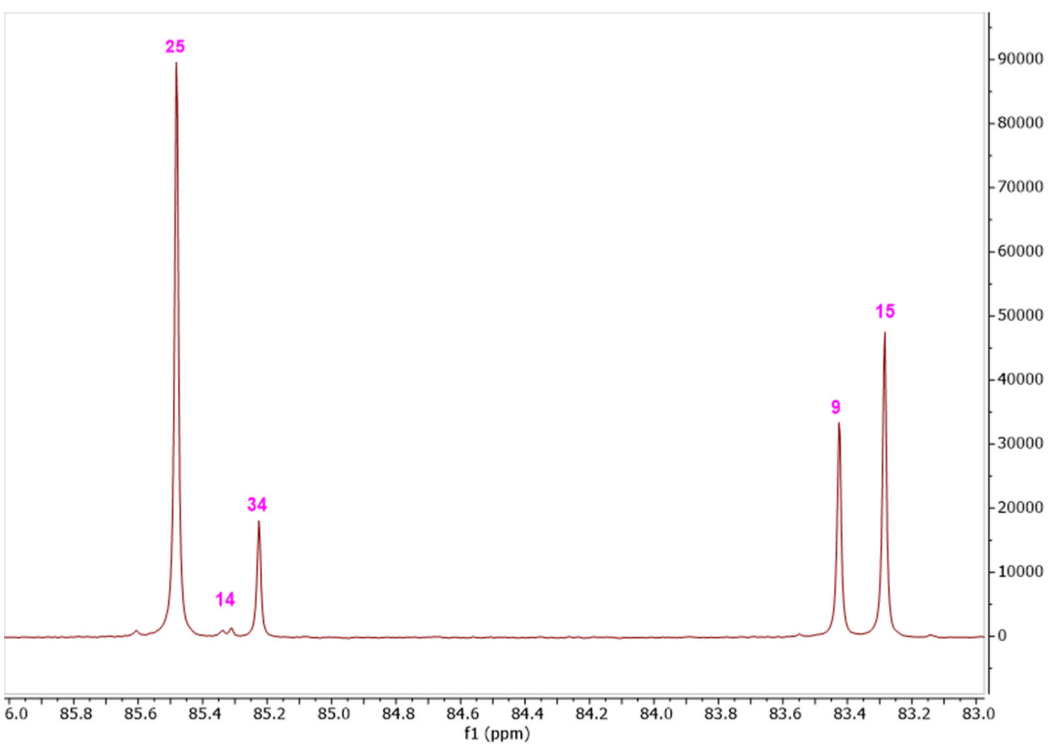
Annotated ^{13}C NMR spectra for reaction with PBu_3 at -20 °C after 30 minutes ($CDCl_3$ 128 MHz)
^{13}C NMR studies in chloroform at -20 °C. PBu_3 (0.039 mmol), pinacolborane (0.43 mmol), and 1a (0.39 mmol).

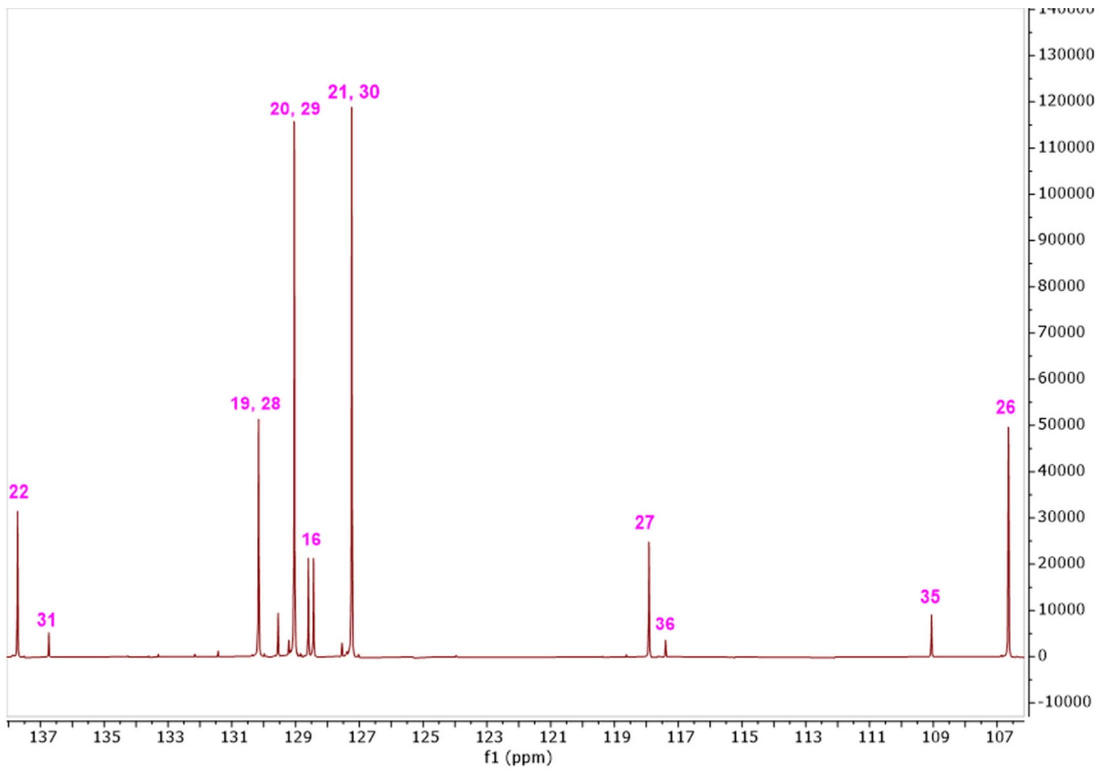




This spectra has been expanded in the following figures.


24, 33
8
17
280000
260000
240000
220000
200000
180000
160000
140000
120000
100000
80000
60000
40000
20000
0
-20000
28.0 27.0 26.0 25.0 24.0 23.0 22.0 21.0 20.0 19.0 18.0 17.0 16.0 15.0 14.0
f1 (ppm)


25
34
14
9
15
90000
80000
70000
60000
50000
40000
30000
20000
10000
0
6.0 85.8 85.6 85.4 85.2 85.0 84.8 84.6 84.4 84.2 84.0 83.8 83.6 83.4 83.2 83.0
f1 (ppm)



Additional rate determination studies were attempted using low temperature ^{1}H NMR. Due to the fast rate of reaction and temperature fluctuation during sample transfer, the rate of reaction could not be obtained from these experiments.

Attempts to observe the imine phosphonium intermediate by ^{1}H NMR at room temperature with triphenylphosphine as the catalyst were unsuccessful, with spectra only showing the starting material and product peaks.

Table 1 Crystal data and structure refinement for cs2643.

Identification code	JMB-05-071
Empirical formula	$C_{10}H_8BF_3KNO$
Formula weight	265.08
Temperature/K	99.98(11)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.55436(11)
b/Å	7.90140(4)
c/Å	8.22574(5)
α/°	90
β/°	102.6760(6)
γ/°	90
Volume/Å^3	1176.545(12)
Z	4
ρ_{calc}g/cm^3	1.497
μ/mm^{-1}	4.187
F(000)	536.0
Crystal size/mm^3	0.21 × 0.19 × 0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	4.882 to 156.154
Index ranges	$-23 \leq h \leq 23$, $-10 \leq k \leq 10$, $-9 \leq l \leq 10$
Reflections collected	32096
Independent reflections	2515 [R_{int} = 0.0425, R_{sigma} = 0.0157]
Data/restraints/parameters	2515/0/155

Goodness-of-fit on F^2	1.058
Final R indexes [I>=2σ (I)]	R_1 = 0.0240, wR_2 = 0.0631
Final R indexes [all data]	R_1 = 0.0241, wR_2 = 0.0632
Largest diff. peak/hole / e Å^{-3}	0.34/-0.32

Table 2 Bond Lengths for cs2643.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
F1	B1	1.4141(13)	N1	K1^{2}	3.0032(10)
F1	K1^{1}	2.6426(7)	N1	K1^{5}	2.8559(10)
F1	K1^{2}	2.7853(7)	C1	C2	1.4334(16)
F2	B1	1.4180(13)	C1	K1^{2}	3.4518(11)
F2	K1^{3}	2.6823(7)	C2	C3	1.3513(16)
F2	K1^{2}	2.8028(7)	C3	C4	1.4811(15)
F3	B1	1.4020(14)	C3	B1	1.6302(16)
F3	K1	2.6327(7)	C4	C5	1.4063(16)
F3	K1^{3}	3.1597(8)	C4	C9	1.3954(16)
O1	C7	1.3720(14)	C5	C6	1.3840(16)
O1	C10	1.4284(17)	C6	C7	1.3946(18)
N1	C1	1.1510(16)	C7	C8	1.3909(17)
N1	K1^{4}	2.9935(10)	C8	C9	1.3930(16)

^{1}1-X,1/2+Y,1/2-Z; ^{2}1-X,1-Y,1-Z; ^{3}+X,1/2-Y,1/2+Z; ^{4}+X,1+Y,+Z; ^{5}+X,3/2-Y,1/2+Z

Table 3 Bond Angles for cs2643.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
B1	F1	K1^{1}	156.35(6)	F3	B1	C3	112.71(9)
B1	F1	K1^{2}	103.03(6)	F1^{6}	K1	F1^{2}	108.62(2)

Table 3 Bond Angles for cs2643.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
K1[1]	F1	K1[2]	99.56(2)	F1[6]	K1	F2[7]	81.57(2)
B1	F2	K1[3]	113.22(6)	F1[2]	K1	F2[2]	47.782(18)
B1	F2	K1[2]	102.10(6)	F1[6]	K1	F2[2]	69.06(2)
K1[3]	F2	K1[2]	99.11(2)	F1[6]	K1	F3[7]	66.495(19)
B1	F3	K1	132.31(6)	F1[2]	K1	F3[7]	172.34(2)
B1	F3	K1[3]	91.65(6)	F1[2]	K1	N1[8]	78.42(2)
K1	F3	K1[3]	90.94(2)	F1[6]	K1	N1[8]	136.34(3)
C7	O1	C10	117.08(10)	F1[2]	K1	N1[9]	112.55(2)
C1	N1	K1[4]	147.51(9)	F1[2]	K1	N1[2]	68.02(2)
C1	N1	K1[5]	112.01(8)	F1[6]	K1	N1[2]	72.11(2)
C1	N1	K1[2]	103.13(8)	F1[6]	K1	N1[9]	83.27(3)
K1[4]	N1	K1[2]	90.85(3)	F2[7]	K1	F1[2]	141.94(2)
K1[5]	N1	K1[2]	108.72(3)	F2[7]	K1	F2[2]	148.885(17)
K1[4]	N1	K1[5]	90.23(3)	F2[7]	K1	F3[7]	44.801(19)
N1	C1	C2	178.01(12)	F2[2]	K1	F3[7]	124.759(19)
N1	C1	K1[2]	57.92(7)	F2[2]	K1	N1[2]	79.91(2)
C2	C1	K1[2]	123.43(7)	F2[7]	K1	N1[9]	104.92(3)
C3	C2	C1	122.30(10)	F2[7]	K1	N1[2]	81.54(2)
C2	C3	C4	117.72(10)	F2[2]	K1	N1[8]	125.52(2)
C2	C3	B1	121.26(10)	F2[2]	K1	N1[9]	82.21(2)
C4	C3	B1	121.02(10)	F2[7]	K1	N1[8]	70.31(2)
C5	C4	C3	121.58(10)	F3	K1	F1[6]	157.14(2)
C9	C4	C3	120.78(10)	F3	K1	F1[2]	72.62(2)
C9	C4	C5	117.64(11)	F3	K1	F2[7]	111.99(2)

Table 3 Bond Angles for cs2643.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C6	C5	C4	121.26(11)	F3	K1	F2^{2}	99.13(2)
C5	C6	C7	119.91(11)	F3	K1	F3^{7}	109.43(2)
O1	C7	C6	115.52(11)	F3	K1	N1^{2}	126.55(3)
O1	C7	C8	124.40(11)	F3	K1	N1^{8}	66.50(3)
C8	C7	C6	120.08(11)	F3	K1	N1^{9}	75.59(3)
C7	C8	C9	119.34(11)	N1^{2}	K1	F3^{7}	114.43(2)
C8	C9	C4	121.75(11)	N1^{8}	K1	F3^{7}	109.22(2)
F1	B1	F2	106.10(9)	N1^{9}	K1	F3^{7}	61.79(2)
F1	B1	C3	111.17(9)	N1^{9}	K1	N1^{2}	153.462(11)
F2	B1	C3	111.23(9)	N1^{9}	K1	N1^{8}	135.24(4)
F3	B1	F1	108.13(9)	N1^{8}	K1	N1^{2}	71.28(3)
F3	B1	F2	107.18(9)				

^{1}1-X,1/2+Y,1/2-Z; ^{2}1-X,1-Y,1-Z; ^{3}+X,1/2-Y,1/2+Z; ^{4}+X,3/2-Y,1/2+Z; ^{5}+X,1+Y,+Z; ^{6}1-X,-1/2+Y,1/2-Z; ^{7}+X,1/2-Y,-1/2+Z; ^{8}+X,-1+Y,+Z; ^{9}+X,3/2-Y,-1/2+Z

Table 4 Torsion Angles for cs2643.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
O1	C7	C8	C9	-179.29(11)	B1	C3	C4	C9	-37.54(15)
C1	C2	C3	C4	-178.92(10)	K1^{1}	F1	B1	F2	-153.02(11)
C1	C2	C3	B1	0.54(16)	K1^{2}	F1	B1	F2	9.46(9)
C2	C3	C4	C5	-37.77(16)	K1^{1}	F1	B1	F3	-38.3(2)
C2	C3	C4	C9	141.92(11)	K1^{2}	F1	B1	F3	124.17(7)
C2	C3	B1	F1	45.82(14)	K1^{2}	F1	B1	C3	-111.60(8)
C2	C3	B1	F2	-72.18(13)	K1^{1}	F1	B1	C3	85.92(17)
C2	C3	B1	F3	167.41(10)	K1^{3}	F2	B1	F1	96.19(8)

Table 4 Torsion Angles for cs2643.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C3	C4	C5	C6	179.69(10)	$K1^{2}$	F2	B1	F1	-9.37(9)
C3	C4	C9	C8	-178.74(11)	$K1^{3}$	F2	B1	F3	-19.17(10)
C4	C3	B1	F1	-134.74(10)	$K1^{2}$	F2	B1	F3	-124.72(7)
C4	C3	B1	F2	107.26(11)	$K1^{3}$	F2	B1	C3	-142.79(7)
C4	C3	B1	F3	-13.15(14)	$K1^{2}$	F2	B1	C3	111.66(8)
C4	C5	C6	C7	-0.59(18)	$K1^{3}$	F3	B1	F1	-99.14(8)
C5	C4	C9	C8	0.95(17)	K1	F3	B1	F1	-6.37(13)
C5	C6	C7	O1	-179.79(11)	$K1^{3}$	F3	B1	F2	14.85(8)
C5	C6	C7	C8	0.26(18)	K1	F3	B1	F2	107.62(9)
C6	C7	C8	C9	0.66(19)	K1	F3	B1	C3	-129.67(8)
C7	C8	C9	C4	-1.29(19)	$K1^{3}$	F3	B1	C3	137.55(8)
C9	C4	C5	C6	0.00(17)	$K1^{4}$	N1	C1	$K1^{2}$	-116.73(7)
C10	O1	C7	C6	-175.19(11)	$K1^{5}$	N1	C1	$K1^{2}$	113.25(16)
C10	O1	C7	C8	4.76(18)	$K1^{2}$	C1	C2	C3	12.25(15)
B1	C3	C4	C5	142.77(11)					