Electronic Supplementary Information

Environmentally friendly Miyaura borylations allowing for green, 1-pot borylation/Suzuki-Miyaura couplings

Chandler B. Nelson, Scott J. L'Heureux, Madison J. Wong, Simone L. Kuhn, Erika Ghiglietti, Bruce H. Lipshutz*

Department of Chemistry and Biochemistry, University of California, Santa Barbara, CA 93106

Phone: (805) 893–2521

Fax: (805) 893–8265

Email: lipshutz@chem.ucsb.edu

Website: https://lipshutz.chem.ucsb.edu/

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1. General Information

Reagents

Unless mentioned otherwise, all chemical reagents were utilized directly from vendors without any further purification. EtOAc, hexanes, Et_2O, methylene chloride, and methanol were obtained from Fischer Scientific and no special considerations were taken to ensure these solvents were anhydrous. When needed, EtOAc and water were degassed by sparging the solvent with a stream of argon gas. Deuterated chloroform was purchased from Cambridge Isotope Laboratories and kept over activated 4 Å molecular sieves in order to maintain dryness. AmPhos and $Pd(AmPhos)_2Cl_2$ were purchased from Combi Blocks Int. and Ambeed Inc. respectively. $Pd(OAc)_2$ was purchased from Johnson Matthey. *Tetrakis*(dimethylamino)diboron and 3,4-diethylhexane-3,4-diol were purchased from Ambeed Inc. Potassium 2-ethylhexanoate (2-KEH) was purchased from Ambeed Inc and was kept and handled in a glovebox under an atmosphere of argon. Potassium phosphate tribasic was purchased from Sigma Aldrich. TPGS-750-M^2 was obtained PHT International (TPGS-750-M is also available from Sigma-Aldrich catalog #733857). All other chemical reagents, including aryl/heteroaryl halides and organic and inorganic bases were purchased from Combi Blocks Int., Ambeed Inc., Fischer Scientific, Enamine, PHT International, Fluorochem, Alfa Aesar, Acros Organics, and Chem Scene. Thin Layer Chromatography (TLC) was performed using Silica Gel 60 F254 (Merck, 0.25mm thickness) and developed plates were visualized under a UV lamp (254 nm). Further analysis was performed via Cerium Molybdate Stain or Potassium Permanganate Stain, and subsequently developed using a heat gun. Manual flash chromatography was performed utilizing Silicycle Silicaflash P60 unbonded grade silica. Automatic flash chromatography was performed utilizing a Telydene Combi Flash and Silica Gel P60 (Teledyne). Gas Chromatography (GC) Spectrums were obtianed on an Agilent. High Resolution Mass Spectrums (HRMS) were obtained on a Waters GCT Premier GC TOF, Agilent 6230 TOF LC/MS System, or Xevo G2-XS UPLC-QTOF.

NMR

^1H, ^{13}C, ^{11}B, and ^{19}F NMR were recorded at 25 °C on either a Bruker Avance III HD 400 MHz, a Bruker Advance NEO 500 MHz, or on a Varian Unity Inova 500 MHz in $CDCl_3$ with residual $CHCl_3$ (^1H = 7.26 ppm, ^{13}C = 77.26 ppm). Chemical shifts are reported in parts per million (ppm) and coupling constants (J values) are reported in Hz. Peak splitting is reported in the following fashion: singlet (s), broad singlet (bs), doublet (d), triplet (t), quartet (q), pentet (p), and multiplet (m).

Note on obtaining ^{11}B NMR

Boron NMR suffers from significant background noise due to the borosilicate glass that comprises not only standard NMR tubes, but also the probe of the NMR instrument itself. For obtaining the ^{11}B NMR spectra in Section 6, the background noise was mitigated in two main ways. Firstly, Boron NMRs were taken in 5 mm Thin Wall Precision Quartz NMR Sample Tube 7" from Wilmad-LabGlass. Secondly, a ^{11}Bzgbsig pulse sequence was utilized and served to suppress background noise and, thus, significantly improve the quality of the obtained ^{11}B NMR spectra. This pulse sequence is available in Bruker's pulse program library. For information on the

development and implementation of this NMR technique, please see the associated reference.[3]

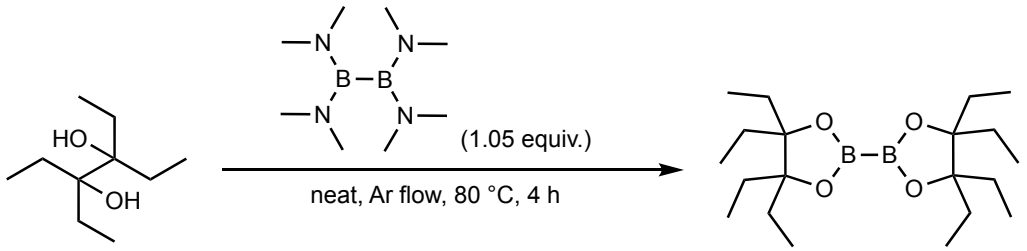
Generating a Solution of 2 wt % TPGS-750-M / H_2O

To a clean 100 mL round bottom flask charged with a PTFE coated stirbar was added 2 g of TPGS-750-M.[2] The flask was then fitted with a septum and attached to a vacuum/argon manifold via a needle through the septum. The flask was then subjected to three cycles of vacuum and then backfilling with argon. Under an atmosphere of argon, to the flask was then added 98 mL of degassed HPLC grade water. Still attached to the manifold and under an atmosphere of argon, the flask was fitted to a stir plate and vigorously stirred for 12 h. The flask was kept under a constant atmosphere of argon.

2. General Procedures

Unless stated otherwise, all reactions were carried out in a fume hood in order to ensure proper ventilation.

2.1. General Procedure: Preparation of *bis*(1,1,2,2-tetraethylethylene glycoato)diboron (B_2Epin_2):



To a flame dried 50 mL round bottom flask charged with PTFE coated stir bar, was added 3,4-diethylhexane-3,4-diol (70.6 mmol, 12.3 g) and *tetrakis*(dimethylamino)diboron (37.1 mmol, 0.525 equiv, 7.34 g). The flask was then sealed with a rubber septum and was set in an oil bath at 80 °C with stirring set to 500 rpm. A line of positive argon pressure was pierced through the septum. A drying tube filled with calcium chloride was also pierced through the septum to allow for the release of developing dimethylamine gas. The reaction was allowed to proceed until completion at 4 h (confirmed via TLC). The reaction was allowed to cool under the same argon flow. The crude reaction mixture was then purified directly via silica plug (R_f = 0.37; 5% ether/hexanes) to afford a crystalline white solid (11.25g, 87%). Purity was confirmed via ^{1}H NMR, ^{13}C NMR, ^{11}B NMR, HRMS (see Section 6), and Mp (58-62 °C). The white solid can be kept and weighed out on the bench top.

2.2. General Procedure: Preparation of Palladium Stock Solutions

2.2.1. General Procedure 2a: Preparation of Palladium Stock Solution from pre-ligated Palladium

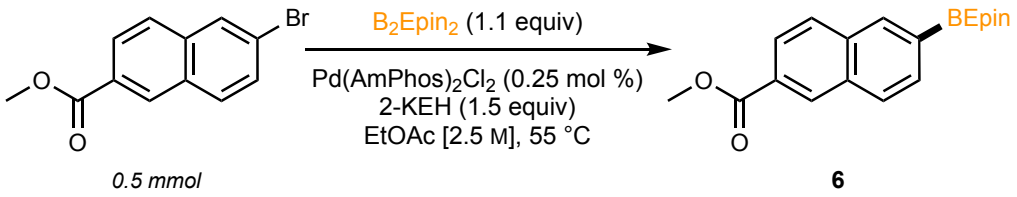
Preparation of catalyst solution to achieve 0.25 mol % on a 0.3 mmol scale: To a 1-dram microwave vial was added a PTFE coated magnetic stir bar. The vial was taken into the glove box and *bis*(di-(4-dimethylaminophenyl)phosphine)dichloropalladium(II) (0.0075 mmol, 5.3 mg) is added. If additional ligand was added, this was also added in the glovebox to the desired loading. The vial was then sealed with a septum, brought out of the glove box, and the septum was secured with Teflon® tape. The vial is attached to a vacuum/argon manifold and, under an atmosphere of argon, 0.5 mL of degassed DCM is syringed into the vial to achieve a concentration of [0.015 M]. The vial was allowed to stir and homogenize at rt on the stir plate for 5 min. From this stock solution, 50 µL could be taken up and added to the desired reaction vial to achieve a 0.25 mol % loading of the palladium catalyst. The catalyst stock solution was used within 1 h.

2.2.2. General Procedure 2b: Preparation of Pd Stock Solutions from Palladium Acetate and Ligand.

Preparation of catalyst solution to achieve 0.25 mol % on a 0.3 mmol scale: To two separate 1-dram microwave vials were added PTFE coated magnetic stir bars. The vials were taken into the glove box and, to one vial, palladium(II) acetate (0.075 mmol, 16.8 mg) is added. To the other vial is added the desired ligand (Pd:P 10:2). Both vials were then sealed with a septum, brought out of the glove box, and the septa were secured with Teflon tape. The vials were attached to a vacuum/argon manifold and, under an atmosphere of argon, 1 mL of degassed DCM is syringed into the vial containing palladium(II) acetate. Under an atmosphere of argon, 400 µL of degassed DCM is syringed into the vial containing the ligand of choice.* Both vials were stirred for 5 min. and allowed to homogenize at rt. From the vial containing palladium(II) acetate was taken up 100 µL, which was then added to the vial containing the Ligand in order to establish a catalyst stock solution (Pd:P 1:2) with a concentration of [0.015 M]. This vial, with combined palladium acetate and ligand, was stirred at rt for 15 min. to allow for ligation. From this stock solution, 50 µL could be taken up and added to the desired reaction vial to achieve a 0.25 mol % loading of the palladium catalyst. The catalyst stock solution was used within 1 h.

*When using [*t*-$Bu_3PH]BF_4$, 1 equiv of TEA (relative to the ligand) was added to deprotonate the phosphonium and, thus, promote ligation when stirred with palladium(II) acetate

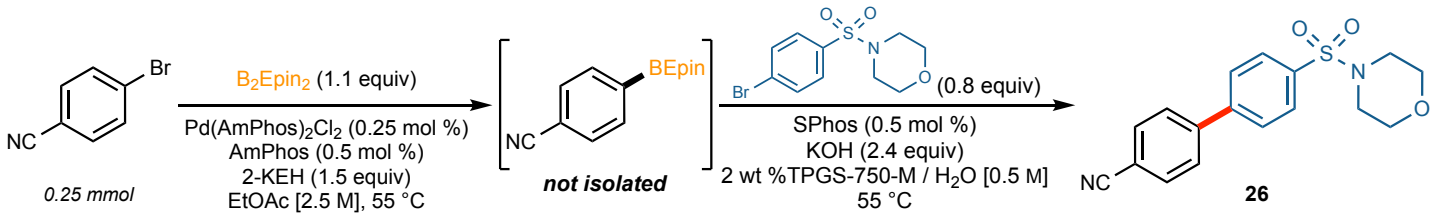
2.3. General Procedure: Preparation of Aryl and Heteroaryl BEpins.



0.5 mmol **6**

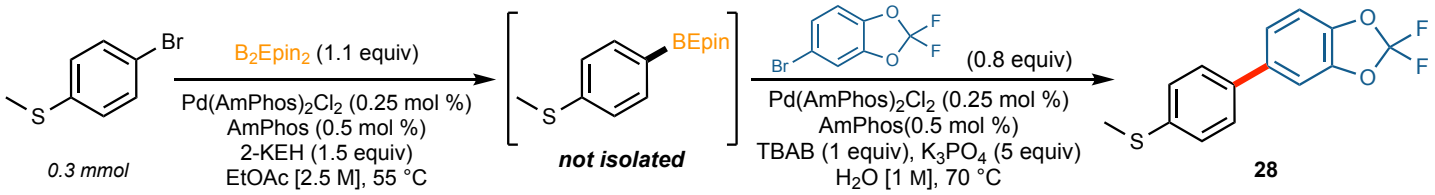
Representative case: *preparation of (6-(methoxycarbonyl)naphthalen-2-yl)boronic acid diethyl pinacol ester.* To 1-dram microwave vial is added a PTFE coated magnetic stir bar, methyl 6-bromo-2-naphthoate (1 equiv, 0.5 mmol, 184.1 mg), and B_2Epin_2 (1.1 equiv, 0.55 mmol, 201.38 mg). Subsequently, the vial was brought into a glove box under an atmosphere of argon. To the vial was added potassium 2-ethylhexanoate (2-KEH) (1.5 equiv, 0.75 mmol, 136.7 mg). The vial was resealed with the rubber septum and brought out of the glove box. An argon line was pierced through the septum, and 50 µL of [0.025 M] $Pd(AmPhos)_2Cl_2$ in DCM was added via micro syringe through the septum (see General Procedure 2.2 for generating the catalyst solution). The DCM was removed *in vacuo* and the vial was then backfilled with argon. To the vial was added via syringe 120 µL of degassed EtOAc (4 equiv). Moving rapidly, the septum was removed and capped as the cap served to limit the loss of EtOAc at higher temperatures. Alternatively, the vial can be capped in a glove box with an argon atmosphere in order to further limit oxygen exposure. The vial was further sealed by tightly wrapping the cap-vial partition with Teflon® tape. From here, the reaction was heated to achieve an internal temperature of 55 °C. Once the reaction mixture had reached temperature, stirring was set to 500 rpm. Upon completion of the reaction at 23 h (determined by TLC and GC), the vial was allowed to cool to rt. To the vial was then added 1 mL of saturated sodium bicarbonate solution and was extracted with 1 mL x 5 of EtOAc. The extracts were combined, passed through Celite, and then dried with anhydrous $MgSO_4$. The crude mixture was filtered, concentrated *in vacuo*, and purified via column chromatography (R_f = 0.47; 10% EtOAc/hexanes) to afford **6** (181.4 mg, 99 %) as a clear, viscous oil. Purity was confirmed via ^1H NMR, ^{13}C NMR, ^{11}B NMR, and HRMS (see Section 6).

2.4. General Procedure: Protocol for 1-Pot Borylation/Suzuki-Miyaura Reaction in TPGS



Representative case: *preparation of 4'-(morpholinosulfonyl)-[1,1'-biphenyl]-4-carbonitrile.* (4-Cyanophenyl)boronic acid ethyl pinacol ester was prepared on 0.25 mmol scale according to General Procedure 2.3. The reaction vial was allowed to cool to rt once the reaction was judged complete at 18 h (determined by TLC and GC). Moving rapidly in order to mitigate against oxygen exposure, the vial was decapped, fitted with a septum, and then fitted via needle to a vacuum/argon manifold. The vial was subjected to three cycles of exposure to vacuum and then backfilled with argon. The EtOAc from the first step was removed *in vacuo* with gentle heating (40 ^{o}C). The vial was then taken into a glovebox under an inert atmosphere of argon. To the reaction vial was added potassium hydroxide (2.4 equiv, 0.6 mmol, 33.7 mg) and 4-((4-bromophenyl)sulfonyl)morpholine (1 equiv, 0.25 mmol, 76.5 mg). The vial was fitted with a septum, brought out of the glove box, and attached via needle to a vacuum/argon manifold. To the reaction vial was then added 25 μL of degassed [0.025 M] stock solution of SPhos in DCM. The DCM was removed *in vacuo* and the vial was then backfilled with argon. To the vial via syringe was added 0.5 mL of 2 wt % TPGS-750-M to achieve a concentration of [0.5 M]. The vial was then disconnected from the manifold and set in a vial adapter on a heated stir plate. The reaction mixture allowed to reach an internal temperature of 55 ^{o}C and stirring was set to 1000 rpm. The reaction was monitored by TLC and judged complete at 20 h. The vial was allowed to cool to rt and 1 mL of saturated sodium bicarbonate solution was added. The reaction was extracted with 1 mL x 5 of EtOAc and the extracts were combined, passed through Celite, and then dried with anhydrous $MgSO_4$. The crude mixture was then filtered, concentrated *in vacuo*, and purified via column chromatography (R_f = 0.18; 30% EtOAc/hexanes) to afford **26** (76.4 mg, 93%) as a white solid. Purity was confirmed via ^{1}H NMR, ^{13}C NMR, and HRMS (see Section 6).

2.5. General Procedure: Protocol for 1-Pot Borylation/Suzuki-Miyaura Reaction using TBAB

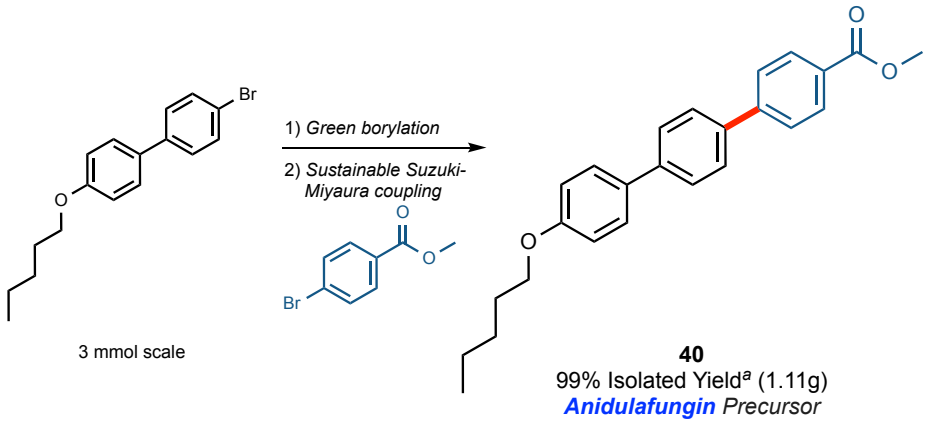


Representative case: *preparation of 2,2-difluoro-5-(4-(methylthio)phenyl)benzo[d][1,3]dioxole.*
4-Thioanisole boronic acid ethyl pinacol ester was prepared on 0.3 mmol scale according to General Procedure 2.3 with a 1:4 ratio of palladium to AmPhos ligand. The reaction vial was allowed to cool to rt once it was judged complete at 18 h (determined by TLC and GC). Moving rapidly in order to mitigate against oxygen exposure, the vial was decapped, fitted with a septum, and then fitted via needle to a vacuum/argon manifold. The vial was subjected to three cycles of exposure to vacuum and then backfilling with argon. The EtOAc from the first step was removed *in vacuo* with gentle heating (40 °C). The vial was then taken into a glovebox under an inert atmosphere of argon. To the reaction vial was added K_3PO_4 (5 equiv, 1.5 mmol, 318.4 mg) and tetrabutyl-ammonium bromide (1 equiv, 0.3 mmol, 96.7 mg).* The vial was fitted with a septum, brought out of the glove box, and attached via needle to a vacuum/argon manifold. To the reaction vial was then added 50 μL of [1.5 mM] catalyst stock solution (see General Procedure 2.2) in order to achieve 0.25 mol % of $Pd(AmPhos)_2Cl_2$ and 0.5 mol % AmPhos. The DCM was removed *in vacuo* and the vial was then backfilled with argon. Subsequently, via syringe through the septum, 5-bromo-2,2-difluorobenzo[d][1,3]dioxole (1.5 equiv,† 0.39 mmol, 92.43 mg (53 μL)) was added and 300 μL of sparged DI water also added. The vial was disconnected from the manifold and set in a vial adapter on a heated stir plate. The reaction mixture allowed to reach an internal temperature of 70 ^{o}C and stirring was set to 1000 rpm. The reaction was monitored by TLC and judged complete at 24 h. The vial was allowed to cool to rt and 1 mL of saturated sodium bicarbonate solution was added. The reaction was extracted with 1 mL x 5 of EtOAc and the extracts were combined, passed through Celite, and then dried with anhydrous $MgSO_4$. The crude mixture was then filtered, concentrated *in vacuo*, and purified via column chromatography (R_f = 0.19; hexanes) to afford **28** as a white solid (83.8 mg, quant.). Purity was confirmed via ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, and HRMS (see Section 6).

*If the second bromide added was a solid, it was added at this point in the glove box.

†Generally, 1.3 equivalents of the second bromide was sufficient for our method. However, 5-bromo-2,2-difluorobenzo[d][1,3]dioxole is vaporous and thus presented concerns of loss through the septum at temperature. Thus, 1.5 equivalents was utilized for this example.

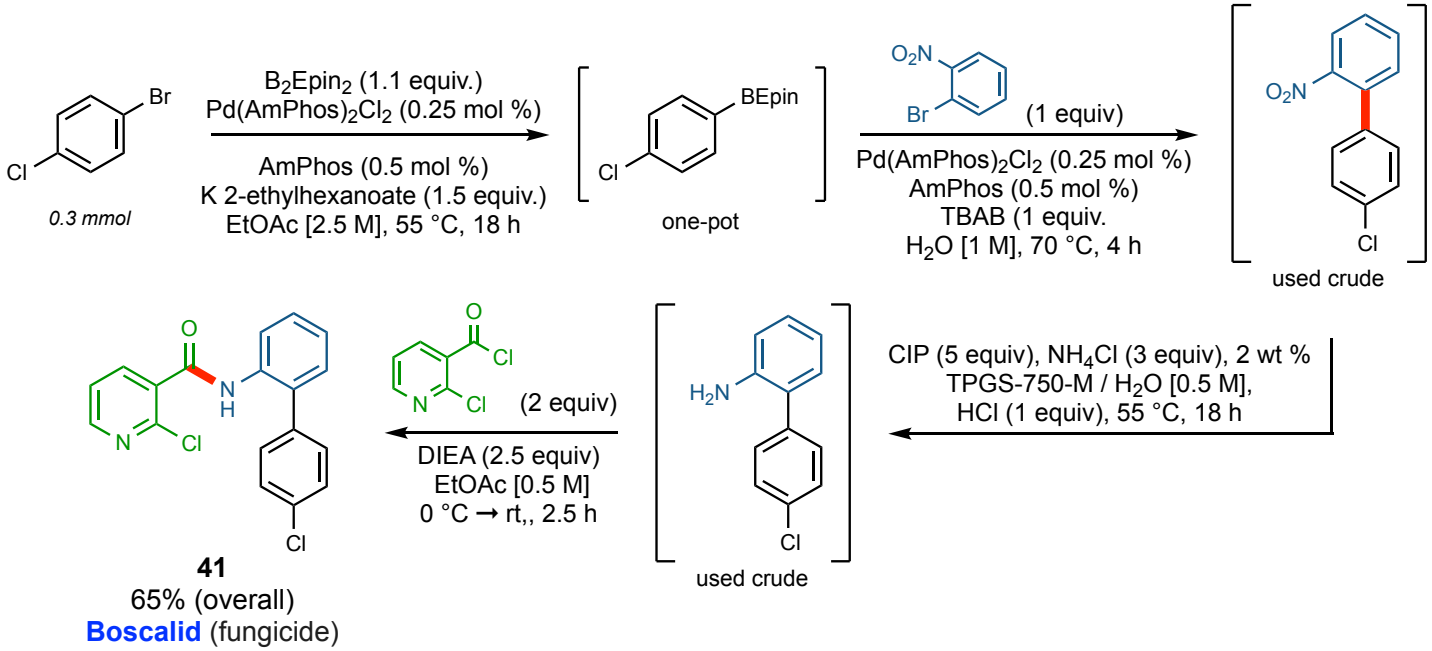
2.6. Gram Scale Synthesis of Anidulafungin Precursor (Compound 40)



To a 50 mL round bottom flask was added a PTFE coated magnetic stir bar, 4-bromo-4'-(pentyloxy)-1,1'-biphenyl (1 equiv, 3 mmol, 957.72 mg), and B_2Epin_2 (1.1 equiv, 3.3 mmol, 1.21 g). Subsequently, the flask was brought into a glove box under an atmosphere of argon. To the flask was added potassium 2-ethylhexanoate (2-KEH) (1.5 equiv, 4.5 mmol, 820.8 mg), $Pd(AmPhos)_2Cl_2$ (0.25 mol %, 0.0075 mmol, 5.30 mg) and AmPhos (0.50 mol %, 0.015 mmol, 4.0 mg). The flask was resealed with the rubber septum and brought out of the glove box. To the flask was added via syringe 1.5 mL of degassed EtOAc to achieve a concentration of [2.5 M]. Moving rapidly, the septum was removed and a reflux condenser connected to an argon line was fitted to the round bottom flask. From here, the round bottom was set in an oil bath and the reaction was heated to achieve an internal temperature of 55 °C. Once the reaction mixture had reached this temperature, stirring was set to 500 rpm. Upon completion of the reaction (determined by TLC and/or GC, 15.5 h), the flask was allowed to cool to rt and the residual EtOAc was removed *in vacuo* for at least 1 h with mild heating (40 °C). Subsequently, the reaction flask was allowed to cool to rt and then brought into the glove box under an inert atmosphere of argon. To the flask was added methyl 4-bromobenzoate (1.3 equiv, 3.9 mmol, 839 mg), K_3PO_4 (5 equiv, 15 mmol, 3.18 g), tetrabutyl-ammonium bromide (TBAB) (1 equiv, 3 mmol, 967 mg), $Pd(AmPhos)_2Cl_2$ (0.25 mol %, 0.0075 mmol, 5.30 mg) and AmPhos (0.50 mol %, 0.015 mmol, 4.0 mg). The flask was fitted with a rubber septum, brought out of the glove box, and the septum was secured to the flask with Teflon® tape. The flask was hooked up to a vacuum/argon manifold and, under an atmosphere of argon, was then added 4 mL of degassed DI H_2O in order to obtain a concentration of [0.75 M]. The reaction flask was added to an oil bath and heated to achieve an internal temperature of 70 °C. The stirring was set to 1000 rpm. After 1.5 h, 0.5 mL (12.5 % v/v) of degassed 2-MeTHF was added to the flask as a cosolvent. Upon completion of the reaction (as determined by TLC, 16.5 h), the reaction was allowed to cool to rt, then 10 mL of 1 M HCl was added. The reaction mixture was then cooled to 0 °C, and the solid precipitate was collected in a Buchner funnel. This solid was then rinsed with 20 mL aliquots of cold H_2O, cold EtOAc, and 200 mL of Et_2O. The filter cake was allowed to dry under vacuum, then was transferred to a flask and left under high-vac overnight to afford **40** as a white solid (99%, 1.12 g; R_f = 0.34, 10% EtOAc / hexanes).* Mp (decomp. 300°C). Purity was confirmed via ^1H NMR, ^{13}C NMR, and HRMS (see Section 6).

*For the E-Factor calculation associated with this procedure, please see Section 4.

2.7. Multistep sequence: boscalid



<1 ppm residual palladium

In a 1-dram vial, 4'-chloro-2-nitro-1,1'-biphenyl is prepared according to General Procedure 2.5 on a 0.3 mmol scale with borylation step running for 18 h, and the Suzuki-Miyaura coupling running for 4 h.* Once the reaction vial was allowed to cool to rt, 1 mL of cold saturated sodium bicarbonate solution was added to the reaction vial. The reaction vial was then extracted with 1 mL x 5 of EtOAc. The extracts were combined, passed through a pad of Celite, and the crude mixture concentrated *in vacuo* in a 2-dram vial. To the 2-dram vial was then added a PTFE coated stir bar, carbonyl iron powder (CIP) (1.5 mmol, 5 equiv, 83.8 mg), and ammonium chloride (0.9 mmol, 3 equiv, 48.1 mg).† The vial was fitted with a rubber septum that was secured with Teflon®. The vial was attached to a vacuum/argon manifold via a needle through the septum. The vial was then subjected to three cycles of exposure to vacuum and then backfilling with argon. To the vial was then added via syringe sparged 5M HCl (0.3 mmol, 1 equiv, 60 μL), and 0.6 mL of degassed 2 wt % TPGS-750-M / H_2O to establish a reaction concentration of [0.5 M]. The vial was removed from the manifold, set in a stirplate vial adapter, heated to an internal temperature of 55 °C, and set to stir at 300 rpm. The reaction was allowed to proceed for 18 h,* and then removed from the stirplate and allowed to cool to rt. To the 2-dram vial was added 1 mL of cold 1M NaOH, and the reaction vial extracted with 5 x 1 mL of EtOAc. The extracts were combined, passed through a pad of Celite, and the crude mixture concentrated *in vacuo* in a 2-dram vial. For the final step, the 2-dram vial containing crude 4'-chloro-[1,1'-biphenyl]-2-amine was charged with a PTFE coated stir bar and fitted with a rubber septum. The vial was attached to a vacuum/argon manifold via a needle through the septum. The vial was then subjected to three cycles of exposure to vacuum and then backfilling with argon. Next was added degassed, anhydrous DIEA (0.75 mmol, 2.5 equiv, 131 μL), and 0.6 mL of degassed, anhydrous EtOAc to establish of concentration of [0.5

*Each step was judged complete via TLC and GC.

†For more information on this nitro-reduction protocol, please see the associated reference.[4]

M]. The vial was set in an ice bath at 0 °C and stirred for 5 min. Moving rapidly to avoid exposure to moisture, the septum was removed, 2-chloronicotinoyl chloride (0.6 mmol, 2 equiv, 105.6 mg) was added, and the septum refitted. The vial was set back in the ice bath and stirred for 15 min at 600 rpm. Subsequently, the reaction was removed from the ice bath, set on a room temperature stir plate at 600 rpm, and allowed to proceed for 1 h and 45 min.* The reaction was then quenched with 1 mL of cold saturated sodium bicarbonate solution and removed from stirring. This was then extracted with 5 x 1 mL of EtOAc and the crude extracts combined. Due to difficulty in separating the product from residual 3,4-diethylhexane-3,4-diol, following work up, the crude reaction mixture was stirred at 80 °C with 2 equiv of 2-iodoxybenzoic acid (IBX) in wet EtOAc [0.5 M] under an inert atmosphere of argon for 4 h.[5] The reaction mixture was then cooled to rt, passed through a pad of Celite, concentrated *in vacuo*, and then further purified via column chromatography (R_f = 0.33, 40% EtOAc/hexanes) to afford boscalid (**41**) as a white solid (66.9 mg, 65 %). Purity was confirmed via ^{1}H NMR, ^{13}C NMR, HRMS (see Section 6), and Mp (139-142 °C).

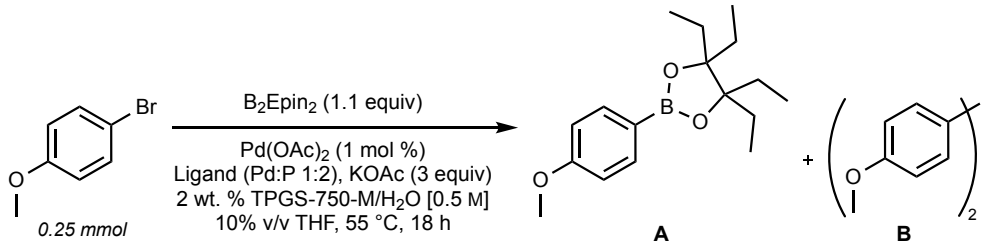
*Each step was judged complete via TLC and GC.

3. Optimization Data

3.1. Borylation Ligand Optimization

Reaction set up and conditions: a 1-dram glass vial was charged with a PTFE coated magnetic stir bar. To the vial was added 4-bromoanisole (0.25 mmol, 1 equiv, 46.8 mg) and B_2Epin_2 (0.275 mmol, 1.1 equiv, 100.7 mg). The vial was taken into the glove box and to the vial was added KOAc (0.75 mmol, 3 equiv, 73.6 mg). The vial was fitted with a septum secured with Teflon tape, and, subsequently, taken out of the glove box and attached to a vacuum/argon manifold. The catalyst (see General Procedure 2.2b) was generated utilizing the desired ligand and was added to the reaction vial under argon. Residual solvent from the catalyst stock solution was removed *in vacuo*, and the vial was then backfilled with argon. To the vial was then added 0.5 mL of 2 wt % TPGS-750-M / H_2O and 10 % v/v THF. The reaction vial was allowed to come to a temperature of 55 °C and set to a stirring rate of 1000 rpm. Upon completion (as determined by TLC), the reaction was allowed to cool and subsequently extracted with 5 x 1 mL of EtOAc. The extracts were combined, passed through Celite, and then dried with anhydrous $MgSO_4$. The crude mixture was filtered and then concentrated *in vacuo*. The crude reaction material was dissolved in 2 mL of $CDCl_3$, 1,3,5-trimethoxybenzene (0.5 or 1 equiv) was added, and the qNMR yield was subsequently determined via ^1H NMR.

Table 1: Ligand Optimization

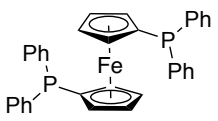


Entry[a]	Ligand	Yield (A%)[b]	Yield (B%)[b]
1	QPhos	46	9
2	**[*t*-Bu$_3$PH]BF$_4$**	**80**	**trace**
3	DPPF	38	trace
4	XPhos	25	trace
5	*t*-BuXPhos	13	trace
6	SPhos	26	trace
7	RuPhos	36	trace
8	*t*-BuXantPhos	trace	NR
9	DPPP	trace	trace
10	*t*-BuBrettPhos	11	trace
11	N_2Phos	trace	trace
12	EvanPhos	trace	trace
13	**AmPhos**	**82**	**trace**
14	DavePhos	42	trace
15	JohnPhos	8	NR
16	BINAP (racemic)	17	trace
17	2-(*t*-Bu$_2$P)-1-Ph-1H-pyrrole	14	10

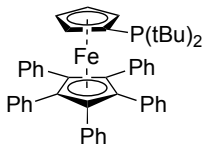
[a] Reactions run on a 0.25 mmol scale.
[b] Yield determined via qNMR using 1,3,5-trimethoxybenzene as an internal standard.

Ligand Structures

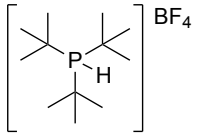
Figure 1: Structures for the ligands utilized during optimization.



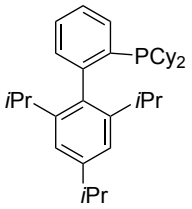
Dppf



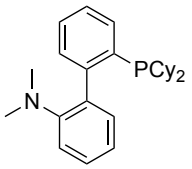
QPhos



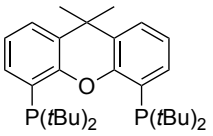
[(*t*-Bu)$_3$PH]BF$_4$



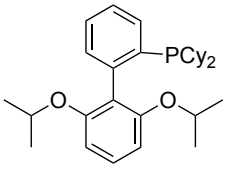
XPhos



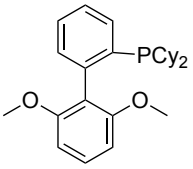
DavePhos



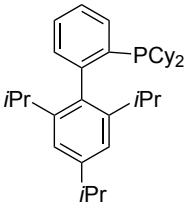
***t*BuXantPhos**



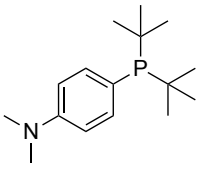
RuPhos



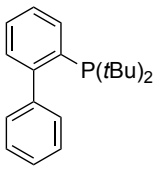
SPhos



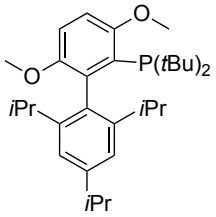
tBuXPhos



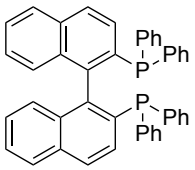
AmPhos



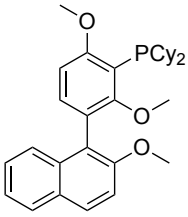
JohnPhos



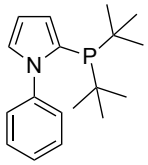
***t*BuBrettPhos**



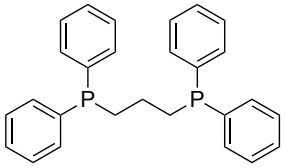
BINAP (±)



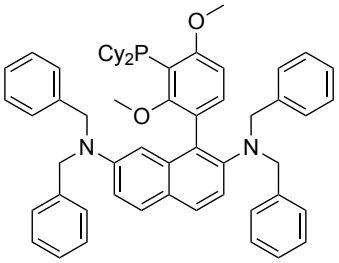
EvanPhos



2-(P(*t*Bu)$_2$)-1-Ph-1H-pyrrole



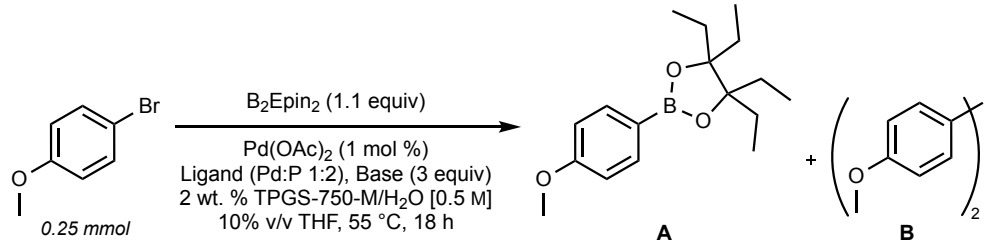
Dppp



N$_2$Phos

3.2. Base Optimization

Table 2: Base Optimization

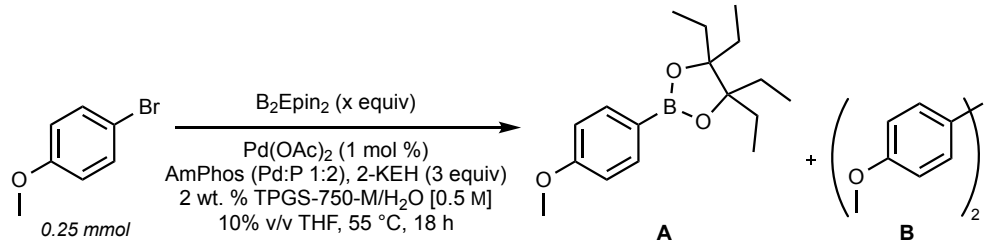


Entry[a]	Ligand	Base	Yield (A%)[b]	Yield (B%)[b]
1	[*t*-Bu_3PH]BF_4	KOAc	80	trace
2	[*t*-Bu_3PH]BF_4	NaOAc	77	trace
3	[*t*-Bu_3PH]BF_4	K_2CO_3	40	10
4	[*t*-Bu_3PH]BF_4	KF	34	trace
5	[*t*-Bu_3PH]BF_4	K_2HPO_4	78	trace
6	[*t*-Bu_3PH]BF_4	K_3PO_4	trace[c]	sig.[c]
7	[*t*-Bu_3PH]BF_4	NaOPh	trace[c]	sig.
8	[*t*-Bu_3PH]BF_4	2-KEH[d]	60	trace
9	[*t*-Bu_3PH]BF_4	KH_2PO_4	11	trace
10	[*t*-Bu_3PH]BF_4	tBuOK	19	33
11	[*t*-Bu_3PH]BF_4	TEA	27	25
12	[*t*-Bu_3PH]BF_4	DIPEA	25	10
13	[*t*-Bu_3PH]BF_4	Pyridine	trace	NR
14	[*t*-Bu_3PH]BF_4	KOTMS	trace[c]	sig.[c]
15	AmPhos	NaOAc	trace[c]	trace[c]
16	AmPhos	K_2HPO_4	73	8
17	**AmPhos**	**2-KEH[d]**	**87**	**trace**

[a] Reactions run on a 0.25 mmol scale. [b] Yield determined via qNMR using 1,3,5-trimethoxybenzene as an internal standard. [c] Qualitative assessment based off TLC of crude reaction mixture ("sig." = significant).
[d] Potassium 2-ethylhexanoate.

3.3. B_2Epin_2 Loading Screen

Table 3: B_2Epin_2 Loading Screen

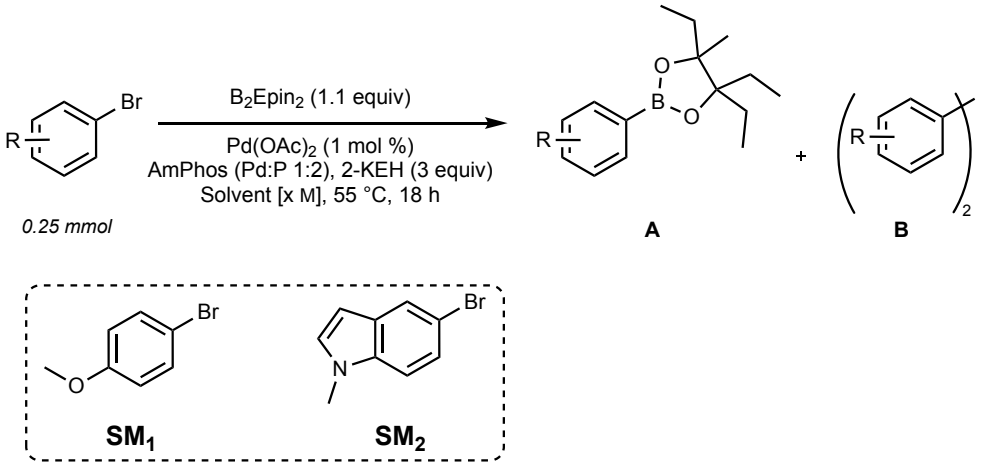


Entry[a]	B_2Epin_2 (x equiv)	Yield (A%)[b]	Yield (B%)[b]
1	**1.1**	**88**	**trace**
2	1.2	88	trace
3	1.3	38	trace
4	1.4	25	trace
5	1.5	13	trace

[a] Reactions run on a 0.25 mmol scale. [b] Yield determined via qNMR using 1,3,5-trimethoxybenzene as an internal standard.

3.4. Solvent/Surfactant Screen

Table 4: Solvent/Surfactant Screen

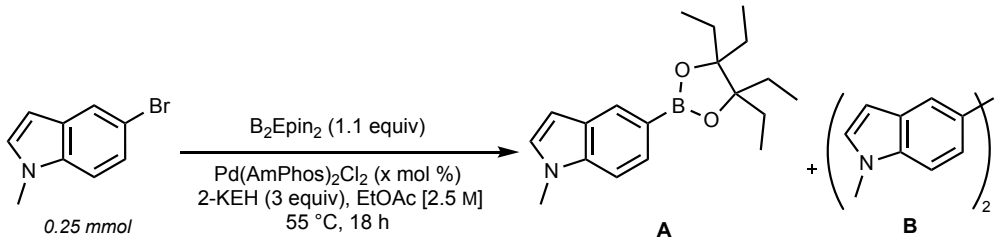


Entry[a]	Substrate	Solvent	[x M]	Yield (A%)[b]	Yield (B%)[b]
1	SM_1	H_2O	0.5	80	trace
2[e]	SM_1	2 wt % TPGS-750-M / H_2O	0.5	78	trace
3[e]	SM_1	2 wt % Savie / H_2O	0.5	76	trace
4[e]	SM_1	2 wt % MC-1 / H_2O	0.5	70	trace
5[e]	SM_1	2 wt % Coolade / H_2O	0.5	88	trace
6[e]	SM_1	2 wt % Brij / H_2O	0.5	69	trace
7	SM_2	H_2O	0.5	91	trace
8	**SM_2**	**EtOAc**	**0.5**	**95**	**trace**
9	SM_2	EtOH	0.5	trace[c]	trace[c]
10	SM_2	toluene	0.5	trace[d]	n.d.
11	SM_2	2-MeTHF	0.5	89	trace
12	SM_2	none	–	trace[c]	trace[c]

[a] Reactions performed on a 0.25 mmol scale.
[b] Yield determined via qNMR using 1,3,5-trimethoxybenzene as an internal standard. [c] Qualitative assesment based off TLC of crude reaction mixture. [d] Poor stirring of reaction mixture. [e] 10% v/v THF added as a cosolvent.

3.5. Palladium Loading Screen

Table 5: Pd. Catalyst Loading Screen

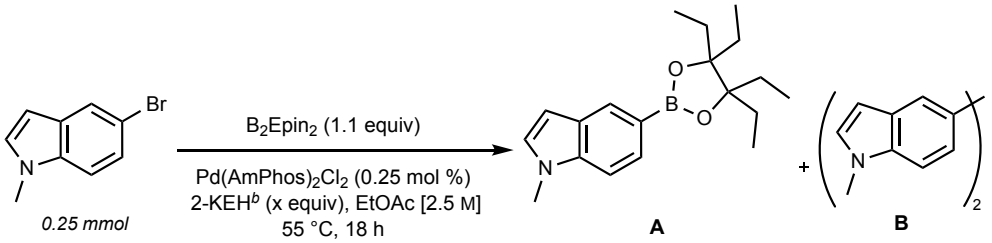


Entry[a]	Pd cat. (x mol %)	Yield (A%)[b]	Yield (B%)[b]
1	0.05	trace[c]	trace[c]
2	0.1	84	trace
3	0.15	90	trace
4	**0.25**	**96**	**trace**

[a] Reactions performed on a 0.25 mmol scale.
[b] Yield determined via qNMR using 1,3,5-trimethoxybenzene as an internal standard. [c] Qualitative assesment based off TLC of crude reaction mixture.

3.6. Base Loading Screen

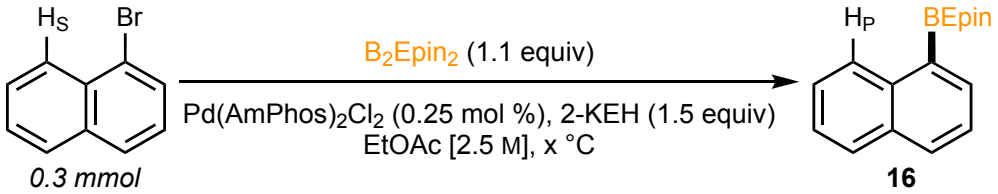
Table 6: Base Loading Screen



Entry[a]	2-KEH[b] (x equiv)	Yield (A%)[c]	Yield (B%)[c]
1	1.1	79	trace
2	**1.5**	**96**	**trace**
3	2	87	trace
4	2.5	87	trace
5	3	95	trace

[a] Reactions performed on a 0.25 mmol scale. [b] Potassium 2-ethylhexanoate. [c] Yield determined via qNMR using 1,3,5-trimethoxybenzene as an internal standard.

3.7. Temperature Study



Temperature Study Procedure: Six reaction vials containing 0.3 mmol 1-bromonaphthalene were prepared identically according to General Procedure 2.3 and each vial was set to individual hot plates with respective temperatures of 55 °C, 65 °C, 75 °C, 85 °C, and 95 °C. Each reaction was allowed to proceed for 16 h and then simultaneously removed from each respective hot plate. Upon cooling to rt, to each vial was added 1 mL of saturated sodium bicarbonate solution and each vial was extracted with 1 mL x 5 of EtOAc. For each respective reaction, the extracts were combined, passed through Celite, and then dried with anhydrous $MgSO_4$. The crude mixtures were filtered, and the solvent removed via roto evaporator. The crude reaction mixtures were dissolved in 2 mL of $CDCl_3$ and analyzed via ^{1}NMR. Specifically, the conversion was determined according to the following equation:

$$(\%)\ \text{Conversion} = \frac{\text{integration of H}_P}{\text{integration of H}_S} * 100\% \tag{1}$$

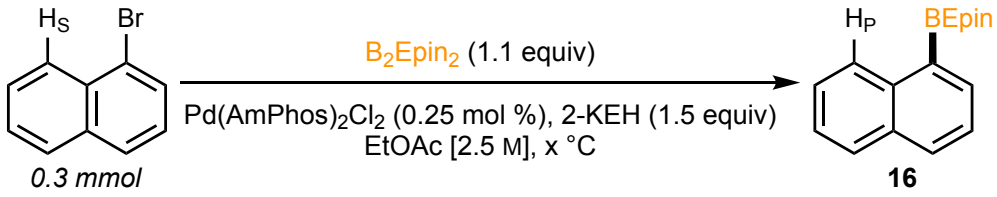
This analysis provided for the values depicted in Table 7 and Figure 2 (*vide infra*). Ultimately, it was shown that higher temperatures allowed for overcoming the high reaction barrier provided by the steric hindrace around the bromide center on 1-bromonahpthalene. However, it is noted that highly elevated temperatures (85 °C and more so 95 °C) gave increased side products (as determined by additional peaks seen via ^{1}NMR).

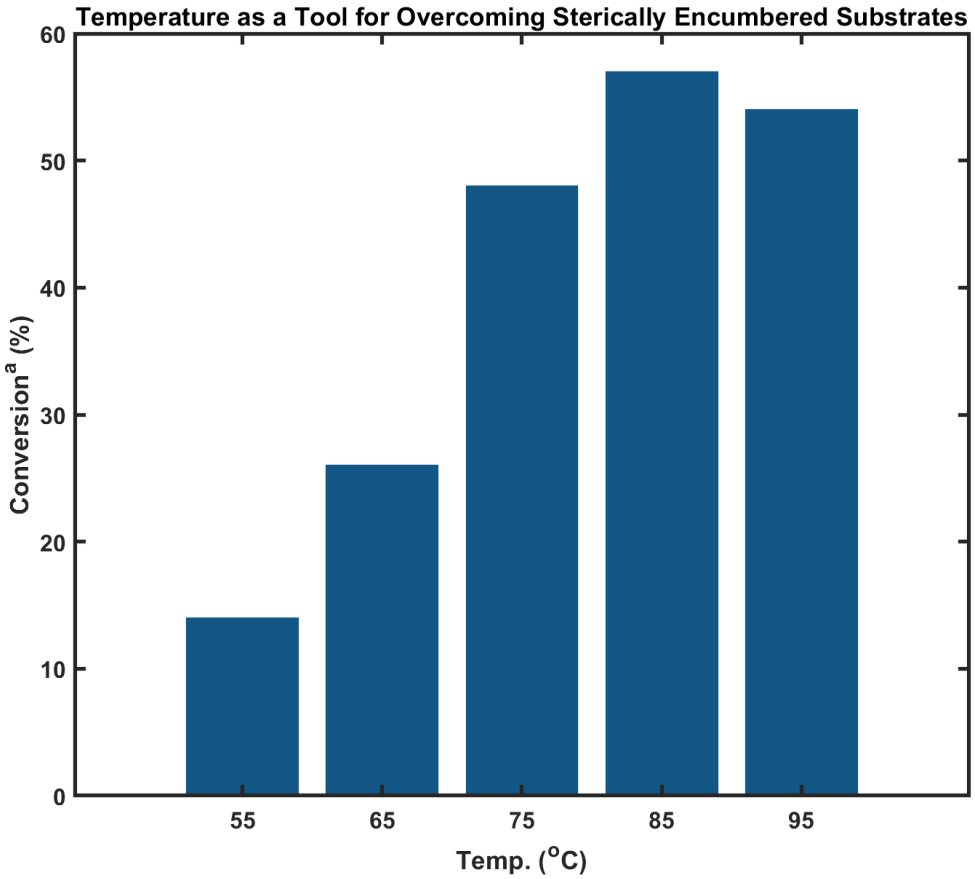
Table 7: Temperature Study

Entry[a]	**Temp. (x °C)**	**Conv. (%)**[b]
1	55	14
2	65	26
3	75	48
4	85	57
5	95	54

[a] See above for reaction conditions. [b] Calculated using Equation 1.

Figure 2: Temperature Study





[a]Conversion (%) determined via Equation 1.

4. E-Factor[1] Calculations* from Preparation of Anidulafungin Precursor

The procedure for the gram scale preparation of the Anidulafungin Precursor (**40**) *is provided in General Procedure 2.6.*

$$\text{E-Factor} = \frac{\text{mass of waste generated}^*}{\text{mass of product}} \tag{2}$$

Table 8: E-Factor Calculations

Source	**Mass of Waste***
B_2Epin_2	1.21 g
2-KEH	0.8208 g
$Pd(AmPhos)_2Cl_2$	0.0106 g
AmPhos	0.008 g
EtOAc	1.353 g
K_3PO_4	3.18 g
TBAB	0.967 g
Water	4 g
2-MeTHF	0.4285 g
Unreacted SM	0.0048 g
Excess 2nd Bromide	+ 0.194 g
TOTAL:	**12.175 g**

$$\text{E-Factor} = \frac{\text{mass of waste generated}^*}{\text{mass of product}} = \frac{12.175 \text{ g}}{1.12 \text{ g}} = \mathbf{10.9} \tag{3}$$

*For E-factor calculations, the work-up solvents of H_2O, Et_2O, and EtOAc are recyclable via distillation and other purification techniques, and are, thus, not considered for the E-factor calcualtion. Furthermore, it is noted that the relative volume of work up solvent is highly dependent on the scale utilized. For recent literature with representative E-factor calcultions, please see the associated references.[6,7]

5. References

[1] R. A. Sheldon, *Green Chem.*, 2007, **9**, 1273–1283.

[2] B. H. Lipshutz, S. Ghorai, A. R. Abela, R. Moser, T. Nishikata, C. Duplais, A. Krasovskiy, R. D. Gaston and R. C. Gadwood, *The J. Org. Chem.*, 2011, **76**, 4379–4391.

[3] J. M. Macho, R. M. Blue, H.-W. Lee and J. B. MacMillan, *Org. Lett.*, 2022, **24**, 3161–3166.

[4] N. R. Lee, A. A. Bikovtseva, M. Cortes-Clerget, F. Gallou and B. H. Lipshutz, *Org. Lett.*, 2017, **19**, 6518–6521.

[5] G. M. Gallego and R. Sarpong, *Chem. Sci.*, 2012, **3**, 1338–1342.

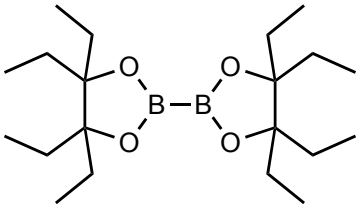
[6] M. J. Wong, E. Oftadeh, J. M. Saunders, A. B. Wood and B. H. Lipshutz, *ACS Catal.*, 2024, **14**, 1545–1552.

[7] K. M. Freiberg, E. Ghiglietti, M. Scurria and B. H. Lipshutz, *Green Chem.*, 2023, **25**, 9941–9947.

6. Analytical Data

6.1. Product Descriptions: Ar-BEpin Products

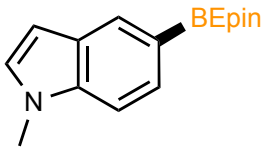
(1,1,2,2-Tetraethylethylene glycoato)diboron



Synthesized according to General Procedure 2.1.

^{1}H NMR (500 MHz, $CDCl_3$): δ 1.74 – 1.57 (m, 16H), 0.90 (t, J = 7.5 Hz, 24H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 88.42, 26.52, 9.08.
^{11}B NMR (128 MHz, $CDCl_3$): δ 29.96.
HRMS (ESI^+): Calcd for $C_{20}H_{40}B_2O_4Na$, $[M+Na]^+$ 389.3011; found 389.3025.

1-Methyl-5-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (1)

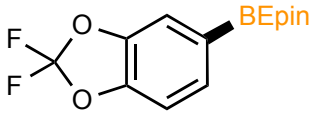


Product **1** was synthesized according to General Procedure 2.3 using 5-bromo-1-methyl-1H-indole on a 0.5 mmol scale for 18 h. Due to difficulty in separating the product from remaining B_2Epin_2 and residual 3,4-diethylhexane-3,4-diol, following work up, the crude reaction mixture was stirred at 80 °C with 2 equiv of 2-iodoxybenzoic acid (IBX) in wet EtOAc [0.5 M] under an inert atmosphere of argon.[5] The reaction mixture was then cooled to rt, passed through a pad of Celite, concentrated *in vacuo*, and then further purified via column chromatography using silica gel (R_f: 0.45; gradient of 0-5% EtOAc/hexanes). Yield: 84%, 131.1 mg; crystalline white solid. Mp* (60 - 63 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.18 (s, 1H), 7.70 (dd, J = 8.2, 1.1 Hz, 1H), 7.32 (d, J = 8.3 Hz, 1H), 7.04 (d, J = 3.1 Hz, 1H), 6.52 (d, J = 3.0 Hz, 1H), 3.79 (s, 3H), 1.80 (m, J = 33.3, 14.2, 7.2 Hz, 8H), 1.01 (t, J = 7.4 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 138.71, 128.96, 128.92, 128.34, 127.85, 108.65, 101.75, 88.46, 32.93, 26.65, 9.06. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 30.76.
HRMS (ESI^+): Calcd for $C_{19}H_{29}BNO_2$, $[M+H]^+$ 314.2291; found 314.2301.

*Melting point is stated for novel solids that haven't yet been reported prior to this publication.

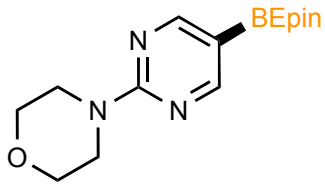
2-(2,2-Difluorobenzo[d][1,3]dioxol-5-yl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (2)



Product **2** was synthesized according to General Procedure 2.3 using 2-difluoro-5-bromo-benzodioxole on a 0.25 mmol scale for 18 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.50; hexanes). Yield: 84%, 72.0 mg; clear oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.58 (dd, J = 7.9, 1.1 Hz, 1H), 7.48 (s, 1H), 7.05 (d, J = 8.0 Hz, 1H), 1.84 – 1.66 (m, 8H), 0.96 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 146.06, 143.71, 131.58 (t, J = 254.6 Hz), 131.10, 115.16, 109.18, 89.33, 26.60, 8.95. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 29.66.
^{19}F NMR (371 MHz, $CDCl_3$): δ -50.21.
HRMS (GC-EI$^+$): Calcd for $C_{17}H_{23}BF_2O_4$, $[M]^+$ 340.1661; found 340.1668.

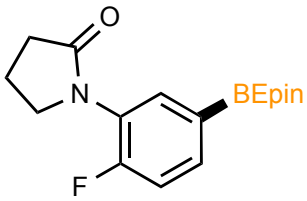
4-(5-(4,4,5,5-Tetraethyl-1,3,2-dioxaborolan-2-yl)pyrimidin-2-yl)morpholine (3)



Product **3** was synthesized according to General Procedure 2.3 using 5-bromo-2-morpholinopyrimidine on a 0.25 mmol scale for 4 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.20; 10% EtOAc/hexanes). Yield: 96%, 83.4 mg; light orange oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.61 (s, 2H), 3.86 (dd, J = 5.7, 4.1 Hz, 4H), 3.74 (dd, J = 5.7, 4.0 Hz, 4H), 1.72 (dtt, J = 21.8, 14.6, 7.5 Hz, 8H), 0.94 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 164.23, 162.56, 88.84, 66.99, 44.20, 26.54, 8.93. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 29.90.
HRMS (ESI$^+$): Calcd for $C_{18}H_{31}BN_3O_3$, $[M+H]^+$ 348.2458; found 348.2447.

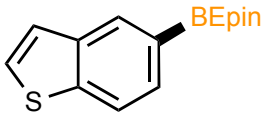
1-(2-Fluoro-5-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolidin-2-one (4)



Product **4** was synthesized according to General Procedure 2.3 using 1-(5-bromo-2-fluorophenyl)pyrrolidin-2-one on a 0.5 mmol scale for 18.5 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.31; 30% hexanes/Et_2O). The product streaks on silica. Yield: 49%, 88.3 mg; white solid. Mp (89-92 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (dd, J = 8.1, 1.6 Hz, 1H), 7.72 (ddd, J = 8.3, 5.4, 1.6 Hz, 1H), 7.13 (dd, J = 10.8, 8.2 Hz, 1H), 3.81 (t, J = 7.0 Hz, 2H), 2.57 (t, J = 8.1 Hz, 2H), 2.28 – 2.15 (m, 2H), 1.83 – 1.65 (m, 8H), 0.95 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 174.88, 159.63 (d, J = 254.7 Hz), 135.59 (d, J = 8.2 Hz), 134.77 (d, J = 2.3 Hz), 126.02 (d, J = 11.8 Hz), 116.29 (d, J = 19.3 Hz), 89.23, 50.23 (d, J = 2.9 Hz), 31.18, 26.53, 19.19, 8.97. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 29.63.
^{19}F NMR (376 MHz, $CDCl_3$): δ -116.11.
HRMS (ESI$^+$): Calcd for $C_{20}H_{29}BFNO_3Na$, $[M+Na]^+$ 384.2123; found 384.2142.

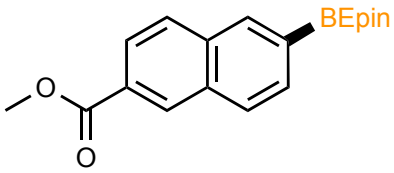
2-(Benzo[b]thiophen-5-yl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (5)



Product **5** was synthesized according to General Procedure 2.3 using 5-bromo-benzothiophene on a 0.5 mmol scale for 18 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.55; gradient of 0-5% Et_2O/hexanes). Yield: 87%, 136.8 mg; white solid. Mp (73-76 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (t, J = 0.9 Hz, 1H), 7.89 (dt, J = 8.1, 0.8 Hz, 1H), 7.78 (dd, J = 8.1, 1.1 Hz, 1H), 7.42 (d, J = 5.4 Hz, 1H), 7.37 (dd, J = 5.4, 0.8 Hz, 1H), 1.90 – 1.70 (m, 8H), 1.00 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 142.71, 139.32, 130.86, 129.99, 126.06, 124.27, 121.92, 88.95, 26.66, 9.04. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 30.46.
HRMS (ESI$^+$): Calcd for $C_{18}H_{25}BO_2S$, $[M]^+$ 316.1668; found 316.1667.

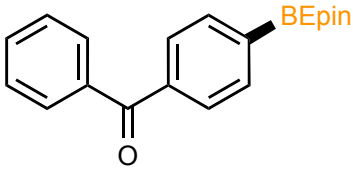
Methyl 6-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)-2-naphthoate (6)



Product **6** was synthesized according to General Procedure 2.3 using methyl 6-bromo-2-naphthoate on a 0.5 mmol scale for 23 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.47; 10% EtOAc/hexanes). Yield: 98%, 181.4 mg; clear, viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (dt, J = 1.7, 0.7 Hz, 1H), 8.40 (d, J = 1.1 Hz, 1H), 8.05 (dd, J = 8.6, 1.7 Hz, 1H), 7.96 – 7.91 (m, 3H), 3.98 (s, 3H), 1.81 (dtt, J = 21.7, 14.5, 7.5 Hz, 8H), 1.01 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 167.41, 135.91, 134.98, 134.13, 131.50, 130.98, 129.00, 128.45, 128.32, 125.27, 89.29, 52.40, 26.66, 9.03. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 30.14.
HRMS (GC-EI$^+$): Calcd for $C_{22}H_{29}BO_4$, $[M]^+$ 368.2159; found 368.2166.

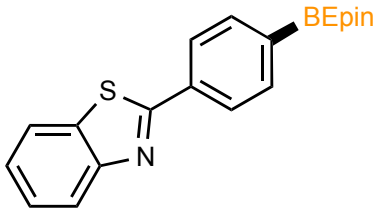
Phenyl(4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)phenyl)methanone (7)



Product **7** was synthesized according to General Procedure 2.3 using (4-bromophenyl)(phenyl)methanone on a 0.3 mmol scale for 21 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.22; gradient of 0-5% Et_2O/hexanes). Yield: 78%, 142.1 mg; clear, viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.97 – 7.91 (m, 2H), 7.83 – 7.74 (m, 4H), 7.62 – 7.56 (m, 1H), 7.51 – 7.45 (m, 2H), 1.79 (ddp, J = 21.7, 14.6, 7.5 Hz, 8H), 0.99 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 197.05, 139.77, 137.65, 134.71, 132.62, 130.25, 129.12, 128.39, 89.32, 26.60, 8.97. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 30.26.
HRMS (ESI$^+$): Calcd for $C_{23}H_{30}BO_3$, $[M+H]^+$ 365.2288; found 365.2306.

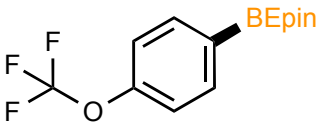
2-(4-(4,4,5,5-Tetraethyl-1,3,2-dioxaborolan-2-yl)phenyl)benzo[d]thiazole (8)



Product **8** was synthesized according to General Procedure 2.3 using (4-bromophenyl)benzo[d]thiazole on a 0.5 mmol scale for 21 h in a dilution of [1.67 M] EtOAc. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.30; 5% Et_2O/hexanes). Yield: quant., 200.3 mg; White solid. Mp (64-66 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.09 (dd, J = 8.1, 1.3 Hz, 3H), 8.00 – 7.86 (m, 3H), 7.50 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 7.39 (ddd, J = 8.3, 7.2, 1.2 Hz, 1H), 1.79 (qq, J = 14.5, 7.4 Hz, 8H), 0.99 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 168.23, 154.32, 135.85, 135.55, 135.29, 126.82, 126.50, 125.44, 123.48, 121.78, 89.25, 26.62, 9.01. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 30.17.
HRMS (ESI$^+$): Calcd for $C_{23}H_{29}BNO_2S$, $[M+H]^+$ 394.2012; found 394.2029.

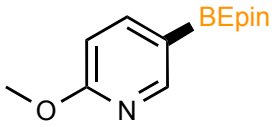
4,4,5,5-Tetraethyl-2-(4-(trifluoromethoxy)phenyl)-1,3,2-dioxaborolane (9)



Product **9** was synthesized according to General Procedure 2.3 using 4-bromo-trifluoromethoxybenzene on a 0.3 mmol scale for 24 h with 0.50 mol % Pd at a 1:4 ratio of Pd to AmPhos and at a concentration of 1.25M EtOAc. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.21; hexanes). Yield: 85%, 87.6 mg; clear, viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.85 (d, J = 8.6 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 1.76 (ddt, J = 24.3, 14.4, 7.2 Hz, 9H), 0.97 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 151.70 (d, J = 1.5 Hz), 136.67, 120.59 (q, J = 257.5 Hz), 120.03, 89.22, 26.59, 8.97. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (160 MHz, $CDCl_3$): δ 29.91.
^{19}F NMR (471 MHz, $CDCl_3$): δ -57.57.
HRMS (GC-EI$^+$): Calcd for $C_{17}H_{24}BF_3O_3$, $[M]^+$ 344.1771; found 344.1763.

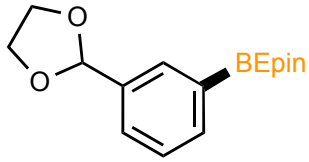
2-Methoxy-5-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pyridine (10)



Product **10** was synthesized according to General Procedure 2.3 using 5-bromo-2-methoxypyridine on a 0.5 mmol scale for 18.5 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.38; gradient of 0-10% Et_2O/hexanes). Yield: quant., 147.0 mg; clear, viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.56 (dd, J = 2.0, 0.9 Hz, 1H), 7.92 (dd, J = 8.3, 2.0 Hz, 1H), 6.71 (dd, J = 8.3, 0.9 Hz, 1H), 3.95 (s, 3H), 1.84 – 1.65 (m, 8H), 0.96 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 166.18, 154.33, 144.63, 110.37, 88.95, 53.55, 26.55, 8.95. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 30.09.
HRMS (ESI^+): Calcd for $C_{16}H_{27}BNO_3$, $[M+H]^+$ 292.2084; found 292.2093.

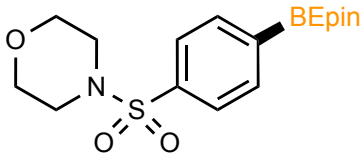
2-(3-(1,3-Dioxolan-2-yl)phenyl)-4,4,5,5-tetraethyl-1,3,2-dioxaborolane (11)



Product **11** was synthesized according to General Procedure 2.3 using 2-(3-bromophenyl)-1,3-dioxolane on a 0.5 mmol scale for 17.5 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.21; 10% Et_2O/hexanes). Yield: 69%, 114.8 mg; clear, viscous oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (ddt, J = 1.9, 1.2, 0.6 Hz, 1H), 7.83 (dt, J = 7.3, 1.3 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.43 – 7.34 (m, 1H), 5.83 (s, 1H), 4.19 – 3.99 (m, 4H), 1.75 (qq, J = 14.6, 7.0 Hz, 8H), 0.97 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 137.17, 135.90, 133.06, 129.19, 127.88, 104.03, 88.96, 65.46, 26.60, 9.01. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 30.18.
HRMS (ESI^+): Calcd for $C_{19}H_{30}BO_4$, $[M+H]^+$ 333.2237; found 333.2247.

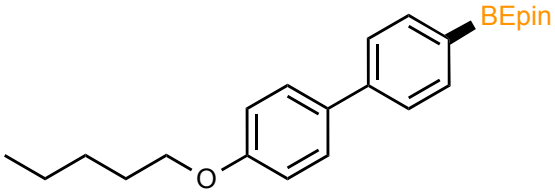
4-((4-(4,4,5,5-Tetraethyl-1,3,2-dioxaborolan-2-yl)phenyl)sulfonyl)morpholine (12)



Product **12** was synthesized according to General Procedure 2.3 using 4-((4-bromophenyl)sulfonyl)morpholine on a 0.3 mmol scale for 16 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.30; 40% Et_2O/hexanes). Yield: quant., 122.3 mg; clear, viscous oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.98 (d, J = 7.9 Hz, 2H), 7.72 (d, J = 8.0 Hz, 2H), 3.76 – 3.69 (m, 4H), 2.99 (dd, J = 5.9, 3.6 Hz, 4H), 1.77 (dhept, J = 21.8, 7.4 Hz, 8H), 0.97 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 137.21, 135.48, 126.92, 89.66, 66.24, 46.12, 26.58, 8.96.
^{11}B NMR (128 MHz, $CDCl_3$): δ 29.89.
HRMS (ESI^+): Calcd for $C_{20}H_{32}BNO_5SNa$, $[M+Na]^+$ 432.1992; found 432.2003.

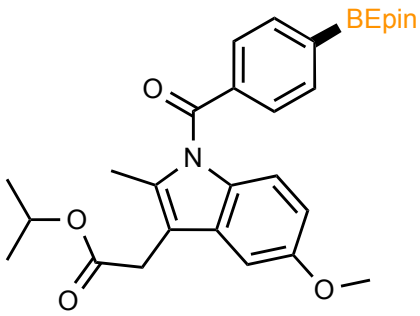
4,4,5,5-Tetraethyl-2-(4'-(pentyloxy)-[1,1'-biphenyl]-4-yl)-1,3,2-dioxaborolane (13)



Product **13** was synthesized according to General Procedure 2.3 using 4-bromo-4'-(pentyloxy)-1,1'-biphenyl on a 2.0 mmol scale for 18 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.45; 5% Et_2O/hexanes). Yield: 97%, 816.7 mg; clear, crystalline solid. Mp (38-40 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.84 (m, 2H), 7.60 – 7.51 (m, 4H), 7.00 – 6.94 (m, 2H), 4.00 (t, J = 6.6 Hz, 2H), 1.87 – 1.69 (m, 10H), 1.51 – 1.35 (m, 4H), 0.96 (m, 15H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 159.10, 143.55, 135.43, 133.52, 128.35, 126.09, 114.93, 88.87, 68.23, 29.14, 28.37, 26.62, 22.62, 14.18, 9.02. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 30.60.
HRMS (GC-EI^+): Calcd for $C_{27}H_{39}BO_3$, $[M]^+$ 422.2992; found 422.2992.

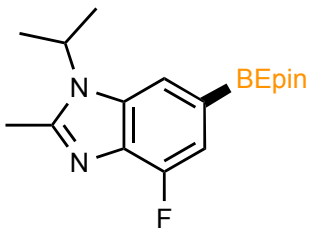
Isopropyl 2-(5-methoxy-2-methyl-1-(4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)benzoyl)-1H-indol-3-yl)acetate (17)



Product **17** was synthesized according to General Procedure 2.3 using isopropyl 2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate on a 0.25 mmol scale for 27 h with a catalyst loading of 0.5 mol % and a concentration of 0.5M EtOAc. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.43; 20% EtOAc/hexanes). Yield: 97%, 133.0 mg; yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 7.7 Hz, 2H), 7.68 (d, J = 7.7 Hz, 2H), 6.97 (d, J = 2.6 Hz, 1H), 6.94 (d, J = 9.0 Hz, 1H), 6.65 (dd, J = 9.0, 2.6 Hz, 1H), 5.02 (p, J = 6.2 Hz, 1H), 3.83 (s, 3H), 3.62 (s, 2H), 2.36 (s, 3H), 1.79 (th, J = 14.5, 7.4 Hz, 8H), 1.24 (d, J = 6.3 Hz, 6H), 0.99 (t, J = 7.4 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 170.57, 169.63, 156.02, 137.93, 135.98, 135.04, 131.05, 130.74, 128.69, 115.25, 112.80, 111.70, 101.26, 89.41, 68.51, 55.73, 30.87, 26.51, 21.92, 13.58, 8.93. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 29.75.
HRMS (ESI^+): Calcd for $C_{32}H_{42}BNO_6Na$, $[M+Na]^+$ 570.3003; found 570.3016.

4-Fluoro-1-isopropyl-2-methyl-6-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)-1H-benzo[d]imidazole (18)



Product **18** was synthesized according to General Procedure 2.3 using 6-bromo-4-fluoro-1-isopropyl-2-methyl-1H-benzo[d]imidazole on a 0.3 mmol scale for 44 h, at 70 ^{o}C, with a Pd:AmPhos ratio of 1:4, a Pd loading of 0.5 mol %, and at a concentration of 1.0M EtOAc. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.29; 40% hexanes/EtOAc). Yield: 84%, 94.5 mg; white solid. Mp (80-85 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.68 (s, 1H), 7.34 (d, J = 10.6 Hz, 1H), 4.69 (p, J = 7.0 Hz, 1H), 2.64 (s, 3H),

1.85 – 1.69 (m, 8H), 1.64 (d, *J* = 6.9 Hz, 6H), 0.98 (t, *J* = 7.5 Hz, 12H).

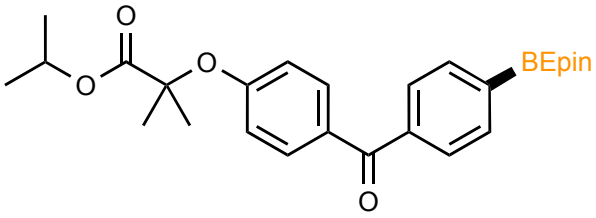
^{13}C NMR (126 MHz, $CDCl_3$): δ 153.42 (d, *J* = 252.2 Hz), 152.28, 136.83 (d, *J* = 8.2 Hz), 134.26 (d, *J* = 17.0 Hz), 113.58 (d, *J* = 3.5 Hz), 112.60 (d, *J* = 15.4 Hz), 89.07, 48.43, 26.57, 21.64, 15.33, 9.00. The boron-bound carbon was not detected likely due to quadropolar relaxation.

^{11}B NMR (160 MHz, $CDCl_3$): δ 30.26.

^{19}F NMR (471 MHz, $CDCl_3$): δ -130.57 (d, *J* = 10.6 Hz).

HRMS (ESI^+): Calcd for $C_{21}H_{33}BFN_2O_2$, $[M+H]^+$ 375.2619; found 375.2630.

Isopropyl 2-methyl-2-(4-(4-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)benzoyl)phenoxy)propanoate (19)



Product **19** synthesized according to General Procedure 2.3 using fenofibrate on a 0.3 mmol scale for 18.5 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.40; 10% EtOAc/hexanes). Yield: quant., 154 mg; clear, viscous oil.

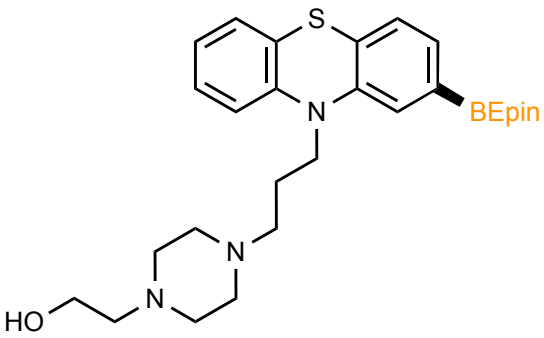
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.95 – 7.88 (m, 2H), 7.79 – 7.73 (m, 2H), 7.73 – 7.67 (m, 2H), 6.88 – 6.81 (m, 2H), 5.08 (hept, *J* = 6.3 Hz, 1H), 1.78 (ddp, *J* = 21.7, 14.5, 7.4 Hz, 8H), 1.66 (s, 6H), 1.20 (d, *J* = 6.2 Hz, 6H), 0.98 (t, *J* = 7.5 Hz, 12H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 195.85, 173.29, 159.74, 140.39, 134.65, 132.23, 130.69, 128.82, 117.25, 89.28, 79.49, 69.45, 26.60, 25.51, 21.64, 8.98. The boron-bound carbon was not detected likely due to quadropolar relaxation.

^{11}B NMR (128 MHz, $CDCl_3$): δ 30.35.

HRMS (ESI^+): Calcd for $C_{30}H_{41}BO_6Na$, $[M+Na]^+$ 531.2894; found 531.2919.

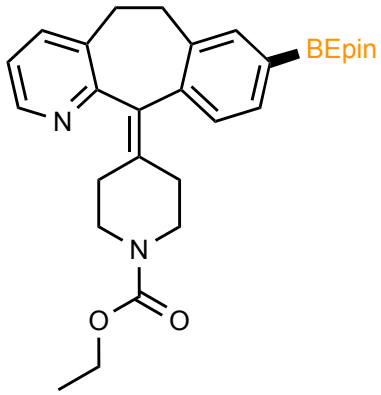
2-(4-(3-(2-(4,4,5,5-Tetraethyl-1,3,2-dioxaborolan-2-yl)-10H-phenothiazin-10-yl)propyl)piperazin-1-yl)ethan-1-ol (20)



Product **20** was synthesized according to General Procedure 2.3 using perphenazine on a 0.3 mmol scale for 4.5 h with a Pd:XPhos ratio of 1:4 and at a concentration of 2.0M H_2O. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.32; gradient of 0-5% MeOH/DCM). Yield: 74%, 123.0 mg; clear, yellow-green, waxy solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.36 (d, J = 7.5, 1.0 Hz, 1H), 7.27 (s, 1H), 7.16 – 7.08 (m, 3H), 6.92 – 6.85 (m, 2H), 3.97 (t, J = 6.8 Hz, 2H), 3.60 (t, 2H), 2.96 – 2.41 (m, 12H), 1.97 (p, J = 7.2 Hz, 2H), 1.82 – 1.67 (m, 8H), 0.96 (t, J = 7.4 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 145.26, 144.76, 129.17, 129.15, 127.52, 127.37, 126.98, 124.98, 122.45, 121.22, 115.73, 88.95, 59.33, 57.74, 55.76, 53.22, 52.91, 45.35, 26.60, 24.38, 9.02. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (160 MHz, $CDCl_3$): δ 30.43.
HRMS (ESI^+): Calcd for $C_{31}H_{47}BN_3O_3S$, $[M+H]^+$ 552.3431; found 552.3438.

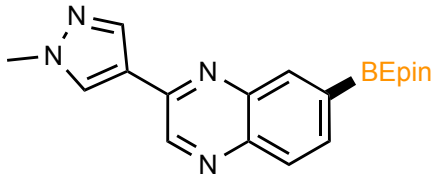
ethyl 4-(8-(4,4,5,5-Tetraethyl-1,3,2-dioxaborolan-2-yl)-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (21)



Product **21** was synthesized according to General Procedure 2.3 using Loratidine on a 0.3 mmol scale for 4 h using Pd:XPhos in a 1:4 ratio and at a concentration of 2.0M EtOAc. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.32; 50% EtOAc/hexanes). Yield: quant., 160.4 mg; white solid. Mp (68-78 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.38 (dd, J = 4.8, 1.7 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.41 (dd, J = 7.7, 1.7 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 7.06 (dd, J = 7.7, 4.8 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 3.80 (s, 2H), 3.49 – 3.28 (m, 2H), 3.18 – 3.07 (m, 2H), 2.91 – 2.79 (m, 2H), 2.49 (ddd, J = 14.1, 9.5, 4.6 Hz, 1H), 2.33 (dp, J = 18.2, 4.7 Hz, 3H), 1.84 – 1.63 (m, 8H), 1.24 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.4 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 157.21, 155.66, 146.65, 142.45, 137.71, 137.09, 136.97, 135.57, 135.46, 133.84, 132.76, 128.72, 122.24, 88.88, 61.42, 45.02, 44.99, 32.01, 31.71, 30.91, 30.66, 26.57 (d, J = 5.0 Hz), 14.83, 8.99 (d, J = 4.6 Hz). The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (128 MHz, $CDCl_3$): δ 31.02.
HRMS (ESI^+): Calcd for $C_{32}H_{44}BN_2O_4$, $[M+H]^+$ 531.3394; found 531.3411.

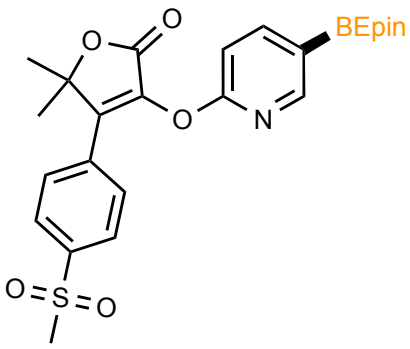
2-(1-Methyl-1H-pyrazol-4-yl)-7-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)quinoxaline (22)



Product **22** was synthesized according to General Procedure 2.3 using 7-bromo-2-(1-methyl-1H-pyrazol-4-yl)quinoxaline on a 0.125 mmol scale for 23 h with a Pd:AmPhos ratio of 1:4 and at a concentration of 1.25M EtOAc. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.24; 50% EtOAc/hexanes). Yield: 91%, 44.6 mg; clear, pale yellow waxy solid.

^{1}H NMR (600 MHz, $CDCl_3$): δ 9.04 (s, 1H), 8.53 (d, J = 1.2 Hz, 1H), 8.18 (s, 1H), 8.13 (s, 1H), 8.04 (d, J = 8.3, 1.3 Hz, 1H), 8.01 (d, J = 8.2 Hz, 1H), 4.01 (s, 3H), 1.87 – 1.73 (m, 8H), 1.00 (t, J = 7.5 Hz, 12H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 147.11, 143.76, 142.65, 141.97, 138.34, 136.82, 133.79, 129.89, 128.30, 121.29, 89.43, 39.49, 26.62, 8.98. The boron-bound carbon was not detected likely due to quadropolar relaxation.
^{11}B NMR (160 MHz, $CDCl_3$): δ 30.45.
HRMS (ESI^+): Calcd for $C_{22}H_{30}BN_4O_2$, $[M+H]^+$ 393.2462; found 393.2474.

5,5-Dimethyl-4-(4-(methylsulfonyl)phenyl)-3-((5-(4,4,5,5-tetraethyl-1,3,2-dioxaborolan-2-yl)pyridin-2-yl)oxy)furan-2(5H)-one (23)



Product **23** was synthesized according to General Procedure 2.3 using Merck Informer Compound X3 on a 0.2 mmol scale for 48 h using 0.5 mol % $PdAmPhos_2Cl_2$ and at a concentration of 0.5M EtOAc. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.33; 45% EtOAc/hexanes). Yield: 73%, 79.2 mg; white solid. Mp (72-82 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.51 (d, J = 1.7 Hz, 1H), 8.06 (dd, J = 8.3, 1.9 Hz, 1H), 7.97 (d, J = 8.2 Hz, 2H), 7.72 (d, J = 8.2 Hz, 2H), 6.96 (d, J = 8.1 Hz, 1H), 3.05 (s, 3H), 1.81 – 1.65 (m, 15H), 0.94 (t, J = 7.5 Hz, 12H).

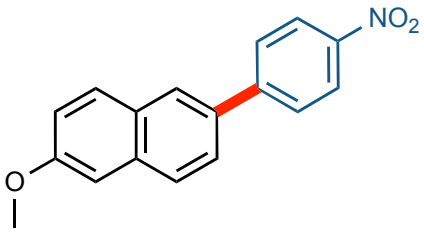
^{13}C NMR (126 MHz, $CDCl_3$): δ 165.90, 163.28, 154.39, 148.84, 146.11, 141.42, 137.85, 135.04, 129.02, 127.99, 110.36, 89.23, 84.47, 44.45, 26.49, 26.41, 8.88. The boron-bound carbon was not detected likely due to quadropolar relaxation.

^{11}B NMR (160 MHz, $CDCl_3$): δ 30.17.

HRMS (ESI^+): Calcd for $C_{28}H_{37}BNO_7S$, $[M+H]^+$ 542.2384; found 542.2396.

6.2. Product Descriptions: 1-Pot Borylation/Suzuki-Miyaura Couplings

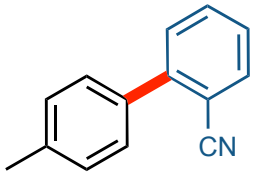
2-Methoxy-6-(4-nitrophenyl)naphthalene (24)



Product **24a** was synthesized according to General Procedure 2.4 using 2-bromo-6-methoxynaphthalene first to make the boronic ester on a 0.5 mmol scale and then adding 0.8 equiv of 4-bromo-nitrobenzene as the coupling partner, step 1 for 18 h and step 2 for 20 h. Yield: 97%, 108.9 mg; yellow solid. Mp (136-140 °C).
Product **24b** was synthesized according to General Procedure 2.5 using 2-bromo-6-methoxynaphthalene first to make the boronic ester on a 0.3 mmol scale and then adding 1.3 equiv of 4-bromo-nitrobenzene as the coupling partner, step 1 for 18 h and step 2 for 24 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.34; 15% EtOAc/hexanes). Yield: quant., 84.6; yellow solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.35 – 8.29 (m, 2H), 8.03 (d, J = 1.9 Hz, 1H), 7.84 (dt, J = 9.6, 7.6 Hz, 4H), 7.71 (dd, J = 8.5, 1.9 Hz, 1H), 7.22 (dd, J = 8.9, 2.6 Hz, 1H), 7.18 (d, J = 2.5 Hz, 1H), 3.96 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 158.66, 147.80, 146.98, 134.77, 133.87, 130.13, 129.10, 127.93, 127.82, 126.75, 125.50, 124.32, 119.90, 105.75, 55.54.
HRMS (GC-EI$^+$): Calcd for $C_{17}H_{13}NO_3$, $[M]^+$ 279.0895; found 279.0900.

2-Cyano-4'-methylbiphenyl (25)

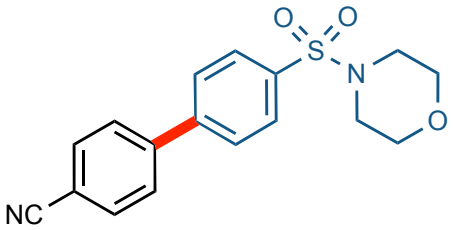


Product **25** was synthesized according to General Procedure 2.4 using 4-bromotoluene first to make the boronic ester on a 0.3 mmol scale, and then adding 1 equiv of 2-bromobenzonitrile as the coupling partner, step 1 for 5 h and step 2 for 15 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.43; gradient of 5-13% Et_2O/hexanes). Yield: 66%, 38.3 mg; white solid. Mp (48-56 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.75 (dd, J = 7.8, 1.4 Hz, 1H), 7.63 (td, J = 7.7, 1.4 Hz, 1H), 7.53 – 7.49 (m, 1H), 7.47 (d, J = 8.0 Hz, 2H), 7.42 (td, J = 7.6, 1.2 Hz, 1H), 7.31 (d, J = 7.8 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 145.61, 138.78, 135.36, 133.80, 132.86, 130.07, 129.54, 128.70, 127.37, 118.97, 111.27, 21.34.
HRMS (GC-EI$^+$): Calcd for $C_{14}H_{11}N$, $[M]^+$ 193.0891; found 193.0894.

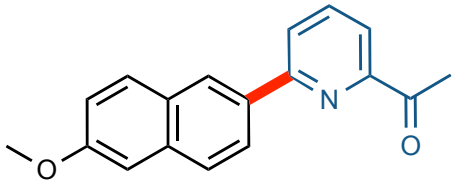
4'-(Morpholinosulfonyl)-[1,1'-biphenyl]-4-carbonitrile (26)



Product **26** was synthesized according to General Procedure 2.4 using 4-bromobenzonitrile first to make the boronic ester on a 0.25 mmol scale and then adding 1 equiv of 4-bromophenylsulfonylmorpholine as the coupling partner, step 1 for 6 h and step 2 for 18 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.18; 30% EtOAc/hexanes). Yield: 93%, 76.4 mg; white solid. Mp (190-192 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.90 – 7.83 (m, 2H), 7.82 – 7.73 (m, 4H), 7.73 – 7.68 (m, 2H), 3.80 – 3.73 (m, 4H), 3.05 (dd, J = 5.7, 3.8 Hz, 4H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 143.96, 143.67, 135.34, 133.01, 128.77, 128.18, 128.11, 118.58, 112.50, 66.22, 46.11.
HRMS (GC-EI$^+$): Calcd for $C_{17}H_{16}N_2O_3S$, $[M]^+$ 328.0882; found 328.0887.

1-(6-(6-Methoxynaphthalen-2-yl)pyridin-2-yl)ethan-1-one (27)

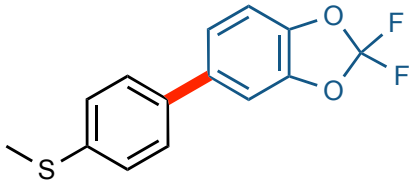


Product **27** was synthesized according to General Procedure 2.5 using 2-bromo-6-methoxynaphthalene first to make the boronic ester on a 0.3 mmol scale and then adding 1.3 equiv of 1-(6-bromopyridin-2-yl)ethan-1-one as the coupling partner, step 1 for 18 h and step 2 for 5.5 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.29; 15% EtOAc/hexanes). Yield: 93%, 77.0 mg; white solid. Mp (114-115 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.48 (d, J = 1.4 Hz, 1H), 8.24 (dd, J = 8.6, 1.8 Hz, 1H), 8.04 (dd, J = 7.8, 1.1 Hz, 1H), 7.98 (dd, J = 7.7, 1.1 Hz, 1H), 7.94 – 7.84 (m, 3H), 7.23 – 7.17 (m, 2H), 3.96 (s, 3H), 2.88 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 200.81, 158.57, 156.60, 153.52, 137.70, 135.33, 133.73, 130.38, 128.99, 127.52, 126.33, 125.01, 123.47, 119.62, 119.48, 105.79, 55.47, 25.98.
HRMS (ESI$^+$): Calcd for $C_{18}H_{16}NO_2$, $[M+H]^+$ 278.1181; found 278.1181.

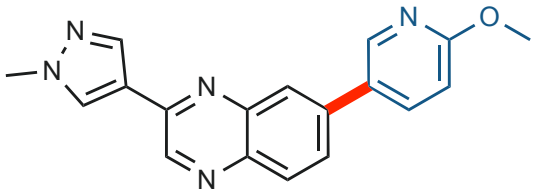
2,2-Difluoro-5-(4-(methylthio)phenyl)benzo[d][1,3]dioxole (28)



Product **28** was synthesized according to General Procedure 2.5 using 4-bromothioanisole first to make the boronic ester on a 0.3 mmol scale and then adding 1.5 equivalents of 2,2-difluorobenzodioxole as the coupling partner, step 1 for 17 h and step 2 for 23.5 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.19; hexanes). Yield: quant., 83.8 mg; white solid. Mp (82-85 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.43 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.5 Hz, 2H), 7.24 (d, J = 1.9 Hz, 2H), 7.10 (d, J = 8.8 Hz, 1H), 2.52 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 144.45, 143.22, 138.45, 137.31, 136.83, 131.84 (t, J = 255.3 Hz), 127.53, 127.05, 122.29, 109.73, 108.32, 15.90.
^{19}F NMR (471 MHz, $CDCl_3$): δ -49.99.
HRMS (GC-EI$^+$): Calcd for $C_{14}H_{10}F_2O_2S$, $[M]^+$ 280.0370; found 280.0369.

7-(6-Methoxypyridin-3-yl)-2-(1-methyl-1H-pyrazol-4-yl)quinoxaline (29)



Product **29** was synthesized according to General Procedure 2.5 using 7-bromo-2-(1-methyl-1H-pyrazol-4-yl)quinoxaline first to make the boronic ester on a 0.3 mmol scale and then adding 1.3 equiv of 5-bromo-2-methoxypyridine as the coupling partner, step 1 for 24 h and step 2 for 16 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.24; gradient of 1-2% MeOH/DCM). Yield: 88%, 83.6 mg; pale yellow solid. Mp (200 °C).

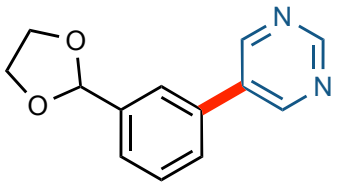
^{1}H NMR (500 MHz, $CDCl_3$): δ 9.03 (s, 1H), 8.57 (d, J = 2.5 Hz, 1H), 8.18 (d, J = 21.3 Hz, 2H), 8.15 (d, J = 2.1 Hz, 1H), 8.11 (d, J = 8.6 Hz, 1H), 7.96 (dd, J = 8.7, 2.6 Hz, 1H), 7.87 (dd, J = 8.7, 2.1 Hz, 1H), 6.89 (d, J =

8.6 Hz, 1H), 4.03 (s, 3H), 4.02 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 164.32, 147.68, 145.70, 143.12, 142.90, 140.54, 139.92, 138.45, 137.74, 130.03, 129.96, 128.92, 127.87, 125.84, 121.21, 111.36, 53.85, 39.56.

HRMS (ESI$^+$): Calcd for $C_{18}H_{16}N_5O$, $[M+H]^+$ 318.1355; found 318.1354.

5-(3-(1,3-Dioxolan-2-yl)phenyl)pyrimidine (30)



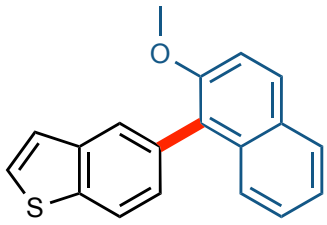
Product **30** was synthesized according to General Procedure 2.5 using 2-(3-bromophenyl)-1,3-dioxolane first to make the boronic ester on a 0.3 mmol scale and then adding 1.3 equiv of 5-bromo-pyrimidine as the coupling partner, step 1 for 15.5 h and step 2 for 9 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.39; 25% hexanes/EtOAc). Yield: 88%, 60.6 mg; yellow oil.

^{1}H NMR (500 MHz, $CDCl_3$): δ 9.21 (s, 1H), 8.96 (s, 2H), 7.71 (t, J = 1.8 Hz, 1H), 7.59 (dd, J = 6.5, 1.9 Hz, 2H), 7.57 – 7.52 (m, 1H), 5.89 (s, 1H), 4.20 – 4.05 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 157.77, 155.12, 139.54, 134.65, 134.26, 129.68, 127.92, 127.37, 125.18, 103.37, 65.59.

HRMS (ESI$^+$): Calcd for $C_{13}H_{13}N_2O_2$, $[M+H]^+$ 229.0977; found 229.0980.

5-(2-Methoxynaphthalen-1-yl)benzo[b]thiophene (31)

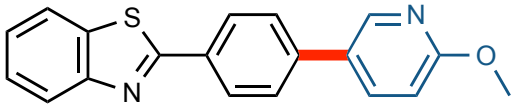


Product **31** was synthesized according to General Procedure 2.5 using 5-bromo-benzothiophene first to make the boronic ester on a 0.3 mmol scale and then adding 1 equiv of 1-bromo-2-methoxy-naphthalene as the coupling partner, step 1 for 23 h and step 2 for 18 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.40; gradient of 0-3% Et_2O/hexanes). Yield: 73%, 63.8 mg; white solid. Mp (79-82 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.02 (d, J = 8.2 Hz, 1H), 7.92 (d, J = 9.0 Hz, 1H), 7.89 – 7.82 (m, 2H), 7.56 –

7.46 (m, 2H), 7.45 – 7.29 (m, 5H), 3.86 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 154.08, 139.93, 138.76, 134.01, 132.59, 129.28, 129.17, 127.99, 127.62, 126.66, 126.47, 125.99, 125.48, 125.36, 124.21, 123.67, 122.32, 113.91, 56.91.
HRMS (GC-EI$^+$): Calcd for $C_{19}H_{14}OS$, $[M]^+$ 290.0765; found 290.0774.

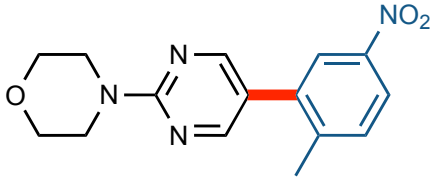
2-(4-(6-Methoxypyridin-3-yl)phenyl)benzo[d]thiazole (32)



Product **32** was synthesized according to General Procedure 2.5 using 2-(4-bromophenyl)benzo[d]thiazole first to make the boronic ester on a 0.3 mmol scale and then adding 1.3 equiv of 5-bromo-2-methoxypyridine as the coupling partner, step 1 for 21 h and step 2 for 17 h. The reaction mixture was then cooled to rt, and 1 mL of 1.0M HCl was added to the vial, and was set to stir for 10 min. Then the reaction mixture was cooled to 0 °C and collected on a buchner funnel and washed with 5 mL of cold water, 5 mL of cold EtOAc and 5 mL of cold Et_2O. The resulting solid was concentrated in vacuo. (R_f: 0.11; 10% Et_2O/hexanes). The product streaks on silica. Yield: 81%, 77.6 mg; white solid. Mp (196-198 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (dd, J = 2.6, 0.7 Hz, 1H), 8.24 – 8.13 (m, 2H), 8.09 (dt, J = 8.2, 1.0 Hz, 1H), 7.92 (ddd, J = 8.0, 1.3, 0.6 Hz, 1H), 7.89 – 7.76 (m, 1H), 7.70 – 7.62 (m, 2H), 7.51 (ddd, J = 8.3, 7.2, 1.3 Hz, 1H), 7.40 (ddd, J = 8.2, 7.2, 1.2 Hz, 1H), 6.86 (dd, J = 8.6, 0.7 Hz, 1H), 4.00 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 167.63, 164.18, 154.37, 145.30, 140.59, 137.45, 135.22, 132.72, 129.16, 128.34, 127.22, 126.55, 125.41, 123.39, 121.79, 111.20, 53.80.
HRMS (ESI$^+$): Calcd for $C_{19}H_{15}N_2OS$, $[M+H]^+$ 319.0905; found 319.0918.

4-(5-(2-Methyl-5-nitrophenyl)pyrimidin-2-yl)morpholine (33)

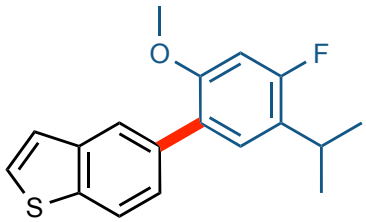


Product **33** was synthesized according to General Procedure 2.5 using 4-(5-bromo-pyrimidin-2-yl)morpholine first to make the boronic ester on a 0.5 mmol scale and then adding 1.3 equiv of 1-bromo-2-methyl-4-nitrobenzene as the coupling partner, step 1 for 20.5 h and step 2 for 19 h. The reaction mixture was then cooled to rt, and 1 mL of 1.0M HCl was added to the vial, and was set to stir for 10 min. Then the reaction mixture was cooled to 0 ^{o}C and collected on a buchner funnel and washed with 5 mL of cold water, 5 mL of cold EtOAc and 5 mL of cold

Et_2O. The resulting solid was concentrated in vacuo. (R_f: 0.31; 33% EtOAc/hexanes). The product streaks on silica. Yield: 65%, 97.0 mg; yellow, powder solid. Mp (188-192 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.34 (s, 2H), 8.12 (dd, J = 8.4, 2.5 Hz, 1H), 8.06 (d, J = 2.4 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 3.92 – 3.85 (m, 4H), 3.83 – 3.78 (m, 4H), 2.41 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.09, 157.56, 146.69, 144.05, 137.15, 131.66, 124.68, 122.70, 121.87, 66.94, 44.42, 20.97.
HRMS (ESI^+): Calcd for $C_{15}H_{17}N_4O_3$, $[M+H]^+$ 301.1300; found 301.1311.

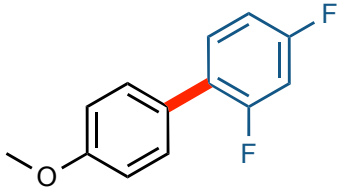
5-(4-Fluoro-5-isopropyl-2-methoxyphenyl)benzo[b]thiophene (34)



Product **34** was synthesized according to General Procedure 2.5 using 5-bromobenzothiophene first to make the boronic ester on a 0.3 mmol scale and then adding 1.5 equivalents of 1-bromo-4-fluoro-5-isopropyl-2-methoxybenzene as the coupling partner, step 1 for 23 h and step 2 for 24 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.39; gradient of 45% EtOAc/hexanes). Yield: 48%, 43.4 mg; white solid. Mp (146-149 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.96 – 7.89 (m, 2H), 7.51 (dd, J = 8.3, 1.8 Hz, 1H), 7.47 (d, J = 5.5 Hz, 1H), 7.38 (d, J = 5.4 Hz, 1H), 7.24 (d, J = 8.7 Hz, 1H), 6.72 (d, J = 12.2 Hz, 1H), 3.80 (s, 3H), 3.24 (h, J = 6.9 Hz, 1H), 1.31 (d, J = 7.0 Hz, 6H).
^{13}C NMR (101 MHz, $CDCl_3$): δ 160.43 (d, J = 245.1 Hz), 155.49 (d, J = 9.9 Hz), 139.86, 138.57, 134.51, 129.55 (d, J = 7.1 Hz), 127.05 (d, J = 15.0 Hz), 126.75, 126.54 (d, J = 3.6 Hz), 126.34, 124.42, 124.15, 122.01, 99.61 (d, J = 27.4 Hz), 56.02, 26.90 (d, J = 1.7 Hz), 23.03.
^{19}F NMR (376 MHz, $CDCl_3$): δ -117.97 (dd, J = 12.2, 8.8 Hz).
HRMS (GC-EI^+): Calcd for $C_{18}H_{17}FOS$, $[M]^+$ 300.0984; found 300.0998.

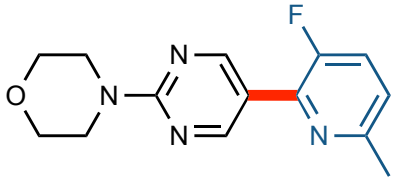
2,4-Difluoro-4'-methoxy-1,1'-biphenyl (35)



Product **35** was synthesized according to General Procedure 2.5 using 4-bromoanisole first to make the boronic ester on a 0.3 mmol scale and then adding 1.5 equivalents of 2,2-difluorobenzodioxole as the coupling partner, step 1 for 15 h and step 2 for 24 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.14; hexanes). Yield: 81%, 53.4 mg; white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 7.46 – 7.41 (m, 2H), 7.37 (td, J = 8.7, 6.5 Hz, 1H), 7.00 – 6.96 (m, 2H), 6.96 – 6.87 (m, 2H), 3.86 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 162.16 (dd, J = 226.6, 11.8 Hz), 159.69 (dd, J = 228.1, 11.8 Hz), 159.41, 131.27 (dd, J = 9.3, 5.0 Hz), 130.16 (d, J = 3.0 Hz), 127.49 (d, J = 1.4 Hz), 125.14 (dd, J = 13.7, 3.9 Hz), 114.14, 111.58 (dd, J = 21.0, 3.8 Hz), 104.43 (dd, J = 26.9, 25.2 Hz), 55.46.
^{19}F NMR (376 MHz, $CDCl_3$): δ -112.37 (d, J = 7.3 Hz), -113.81 (d, J = 7.4 Hz).
HRMS (GC-EI$^+$): Calcd for $C_{13}H_{10}F_2O$, $[M]^+$ 220.0700; found 220.0701.

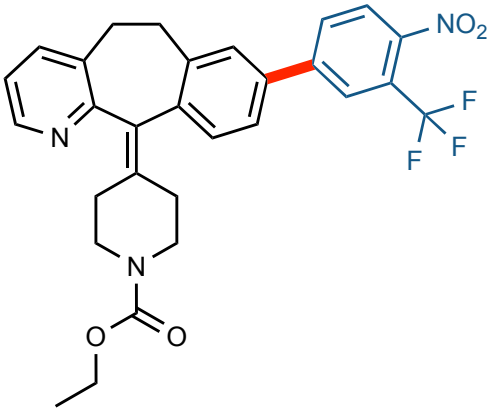
4-(5-(3-Fluoro-6-methylpyridin-2-yl)pyrimidin-2-yl)morpholine (36)



Product **36** was synthesized according to General Procedure 2.5 using 4-(5-bromo-pyrimidin-2-yl)morpholine first to make the boronic ester on a 0.5 mmol scale and then adding 1.3 equiv of 2-bromo-3-fluoro-5-methylpyridine as the coupling partner, step 1 for 20.5 h and step 2 for 19 h. The reaction mixture was then cooled to rt, and 1 mL of 1.0M HCl was added to the vial, and was set to stir for 10 min. Then the reaction mixture was cooled to 0 °C and collected on a buchner funnel and washed with 5 mL of cold water, 5 mL of cold EtOAc and 5 mL of cold Et_2O. The resulting solid was concentrated in vacuo. (R_f: 0.33; 33% EtOAc/hexanes). The product streaks on silica. Yield: 69%, 95.1 mg; white, powder solid. Mp (149 °C).

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.97 (d, J = 1.2 Hz, 2H), 7.33 (dd, J = 10.9, 8.4 Hz, 1H), 7.04 (dd, J = 8.4, 3.4 Hz, 1H), 3.94 – 3.87 (m, 4H), 3.81 – 3.75 (m, 4H), 2.56 (d, J = 1.0 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 161.29, 157.91 (d, J = 7.8 Hz), 155.71 (d, J = 256.2 Hz), 154.41 (d, J = 4.7 Hz), 140.81 (d, J = 11.5 Hz), 124.25 (d, J = 20.2 Hz), 122.60 (d, J = 3.7 Hz), 118.65 (d, J = 6.3 Hz), 66.99, 44.48, 24.01 (d, J = 1.8 Hz).
^{19}F NMR (376 MHz, $CDCl_3$): δ -129.30.
HRMS (ESI$^+$): Calcd for $C_{14}H_{16}FN_4O$, $[M+H]^+$ 275.1308; found 275.1318.

Ethyl 4-(8-(4-Nitro-3-(trifluoromethyl)phenyl)-5,6-dihydro-11H-benzo[5,6]cyclohepta[1,2-b]pyridin-11-ylidene)piperidine-1-carboxylate (37)



Product **37** was synthesized according to General Procedure 2.5 using loratadine first to make the boronic ester on a 0.3 mmol scale using 0.25 mol % Pd:XPhos (1:4 ratio) and then adding 1.3 equivalents of 4-bromo-1-nitro-2-(trifluoromethyl)benzene as the coupling partner, step 1 for 4 h and step 2 for 22 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.31; 30% hexanes/EtOAc). Yield: quant., 165.7 mg; yellow solid. Mp (84-92 °C).

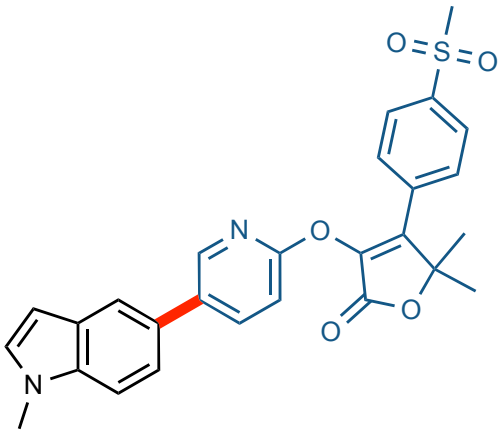
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.42 (dd, J = 4.9, 1.6 Hz, 1H), 8.00 – 7.95 (m, 2H), 7.86 (dd, J = 8.4, 1.9 Hz, 1H), 7.48 (dd, J = 7.8, 1.6 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.35 (d, J = 8.4 Hz, 1H), 7.12 (dd, J = 7.7, 4.7 Hz, 1H), 4.14 (q, J = 7.0 Hz, 2H), 3.84 (s, 2H), 3.52 (ddd, J = 15.8, 9.9, 4.6 Hz, 1H), 3.42 (ddd, J = 15.7, 8.4, 4.6 Hz, 1H), 3.22 – 3.12 (m, 2H), 2.93 (dddd, J = 20.3, 15.8, 8.6, 4.7 Hz, 2H), 2.51 (ddd, J = 14.1, 9.4, 4.6 Hz, 1H), 2.47 – 2.30 (m, 3H), 1.25 (t, J = 7.1 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$): δ 157.13, 155.64, 146.93, 146.79, 145.88, 140.78, 139.12, 137.92, 137.69, 136.65, 134.52, 133.56, 130.93, 130.53, 128.21, 126.45 (q, J = 5.4 Hz), 126.03, 125.16, 124.50 (q, J = 33.9 Hz), 122.52, 122.12 (q, J = 273.7 Hz), 61.49, 44.97, 44.92, 32.12, 31.71, 30.98, 30.71, 14.81.

^{19}F NMR (471 MHz, $CDCl_3$): δ -59.90.

HRMS (ESI^+): Calcd for $C_{29}H_{27}F_3N_3O_4$, $[M+H]^+$ 538.1953; found 538.1958.

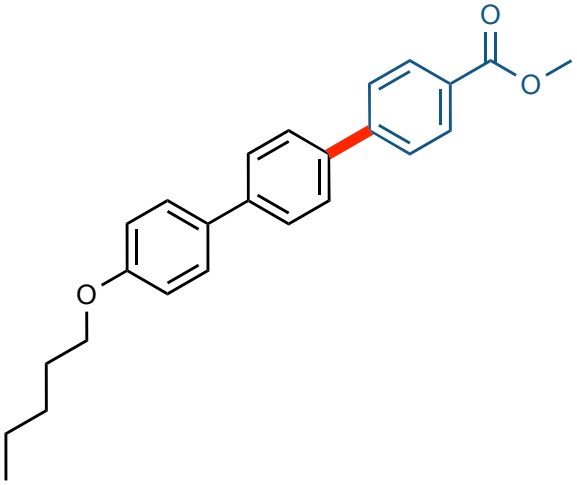
5,5-Dimethyl-3-((5-(1-methyl-1H-indol-5-yl)pyridin-2-yl)oxy)-4-(4-(methylsulfonyl)phenyl)furan-2(5H)-one (38)



Product **38** was synthesized according to General Procedure 2.5 using 5-bromo-1-methyl-1H-indole first to make the boronic ester on a 0.125 mmol scale and then adding 1.3 equivalents of Merck Informer Compound X3 as the coupling partner, step 1 for 18 h and step 2 for 36 h. The reaction mixture was then cooled to rt, passed through a pad of Celite, and then further purified via column chromatography using silica gel (R_f: 0.21; 50% EtOAc/hexanes). Yield: quant., 62.9 mg; off-white solid.

^{1}H NMR (500 MHz, $CDCl_3$): δ 8.38 (d, J = 2.6 Hz, 1H), 8.00 (d, J = 8.1 Hz, 2H), 7.95 (dd, J = 8.6, 2.5 Hz, 1H), 7.80 (d, J = 8.1 Hz, 2H), 7.74 (s, 1H), 7.38 (q, J = 8.5 Hz, 2H), 7.10 (d, J = 3.2 Hz, 1H), 7.07 (d, J = 8.5 Hz, 1H), 6.53 (d, J = 3.2 Hz, 1H), 3.82 (s, 3H), 3.05 (s, 3H), 1.78 (s, 6H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 166.08, 160.10, 148.37, 145.68, 141.40, 138.93, 138.13, 136.51, 135.14, 134.85, 129.95, 129.11, 128.66, 128.01, 121.01, 119.42, 110.87, 109.94, 101.46, 84.47, 77.41, 77.16, 76.91, 44.47, 33.07, 29.81, 26.54.
HRMS (ESI$^+$): Calcd for $C_{27}H_{24}N_2O_5SNa$, $[M+Na]^+$ 511.1304; found 511.1305.

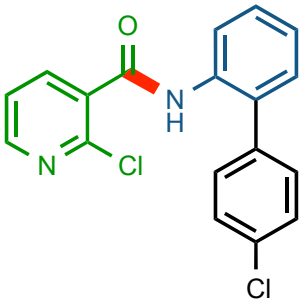
1-Carbomethoxy-4”-(pentyloxy)terphenyl (40)



Product **40** was synthesized according to Procedure 2.6.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.14 – 8.09 (m, 2H), 7.73 – 7.63 (m, 6H), 7.60 – 7.54 (m, 2H), 7.02 – 6.96 (m, 2H), 4.01 (t, J = 6.6 Hz, 2H), 3.95 (s, 3H), 1.87 – 1.78 (m, 2H), 1.52 – 1.35 (m, 4H), 0.95 (t, J = 7.1 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 167.17, 159.14, 145.35, 140.88, 138.25, 132.81, 130.29, 128.95, 128.19, 127.74, 127.29, 126.97, 115.03, 68.27, 52.28, 29.14, 28.37, 22.63, 14.19.
HRMS (GC-EI$^+$): Calcd for $C_{25}H_{26}O_3$, $[M]^+$ 374.1882; found 374.1880.

2-Chloro-N-(4’-chlorobiphenyl-2-yl)nicotinamide (boscalid) (41)



Product **41** was synthesized according to Procedure 2.7.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (dd, J = 4.8, 2.0 Hz, 1H), 8.34 (d, J = 8.2 Hz, 1H), 8.11 – 8.03 (m, 2H), 7.41 – 7.34 (m, 2H), 7.27 (m, 3H), 7.22 – 7.16 (m, 2H).
^{13}C NMR (126 MHz, $CDCl_3$): δ 162.61, 151.47, 146.83, 140.31, 136.39, 134.59, 134.47, 132.37, 131.20, 130.93, 130.37, 129.45, 129.03, 125.46, 123.05, 122.23.
HRMS (ESI$^+$): Calcd for $C_{18}H_{12}Cl_2N_2ONa$, $[M+Na]^+$ 365.0225; found 365.0229.

6.3. ICPMS Data

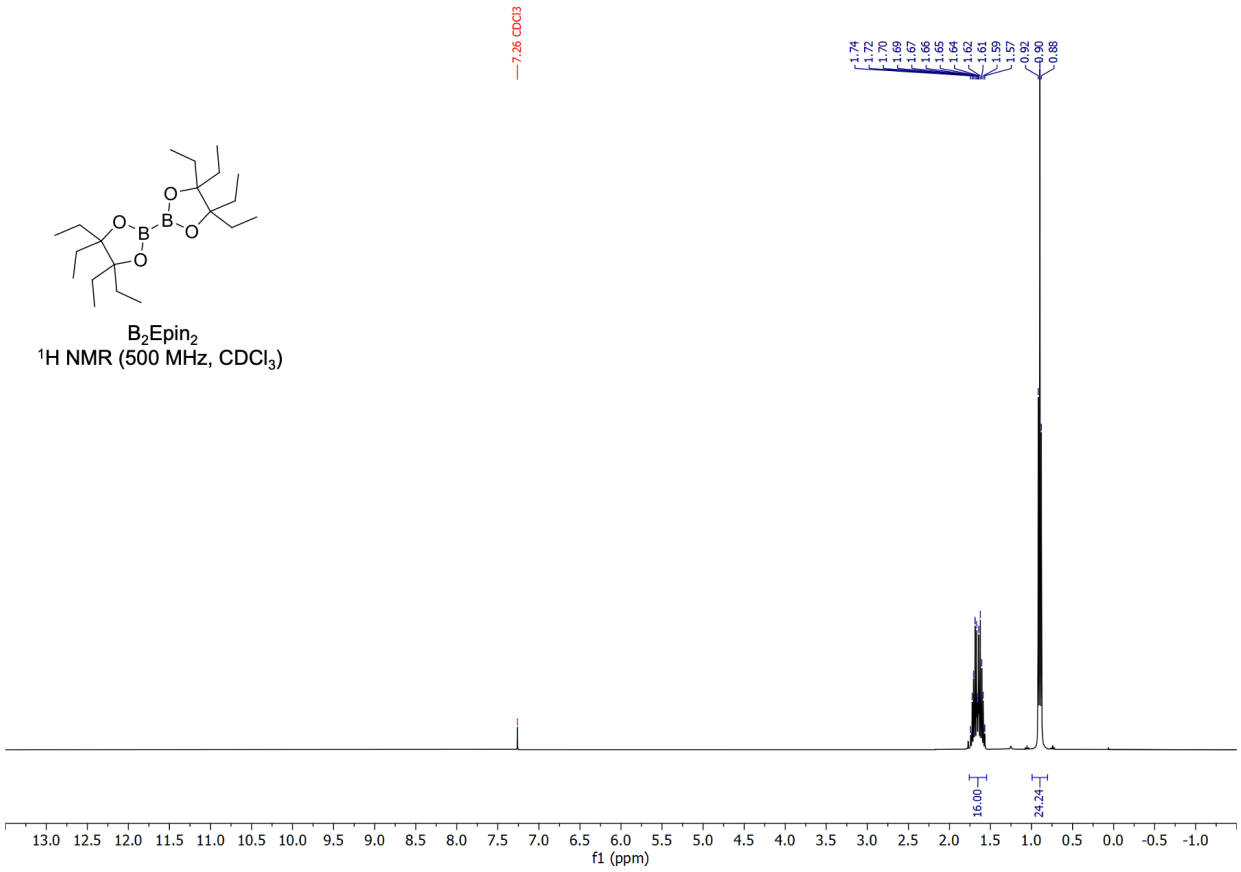
Compounds listed in Table 9 were analyzed via Inductively Coupled Plasma Mass Spectrometry (ICPMS) by the Nano and Pico Characterization Lab at the California NanoSystems Institute at UCLA, Dr. Chong Hyun "Paul" Chang, P.h.D.

Table 9: ICPMS Data

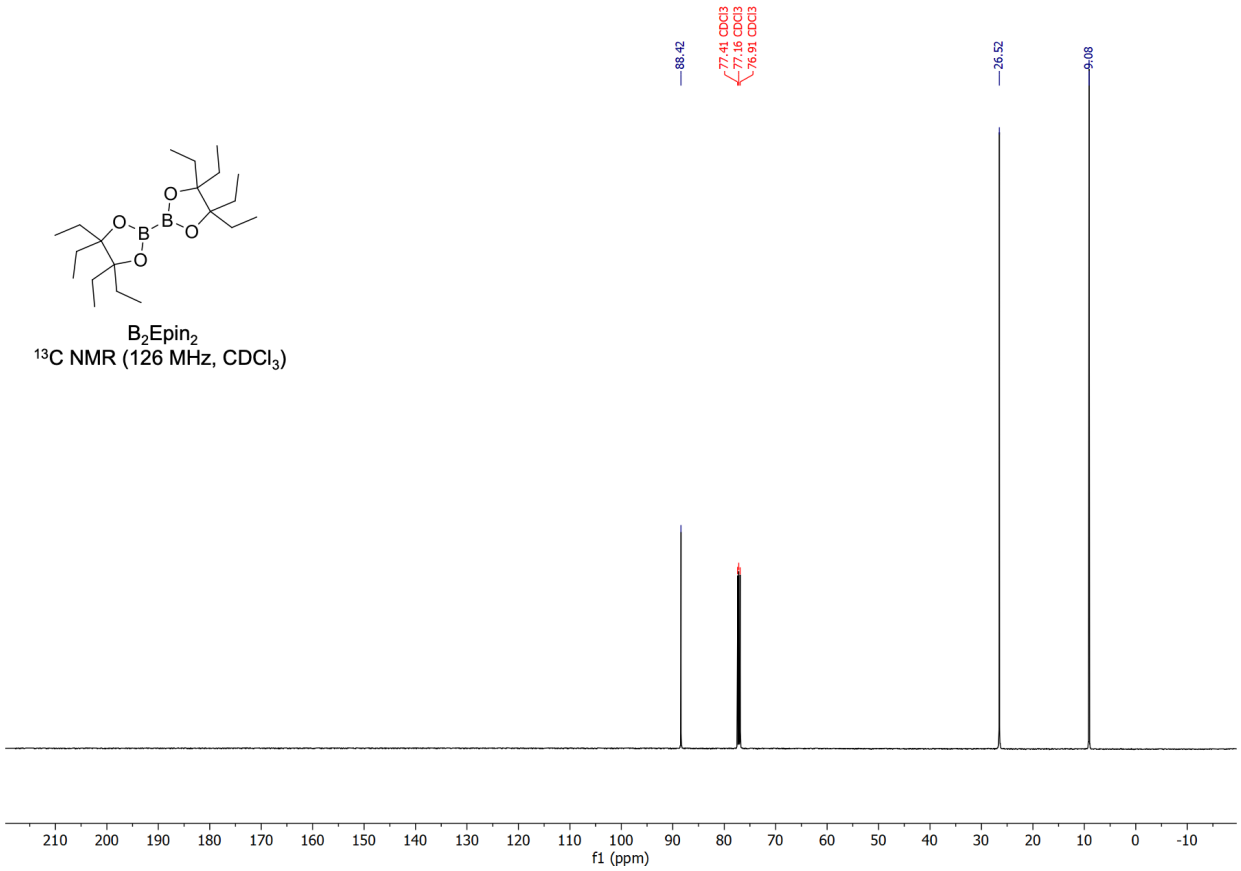
		Palladium [μg/g]	
Sample:	**Sample weight in analysis [mg]:**	**Average***	**stdev**
Product **41**	4.70	0.696	0.013
Product **37**	6.60	7.857	0.039

* Each sample was done in triplicated measurements with background correction.

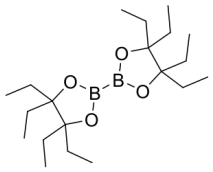
6.4. NMR Spectra



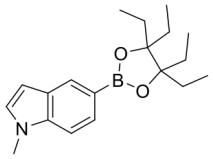
B_2Epin_2
^1H NMR (500 MHz, $CDCl_3$)



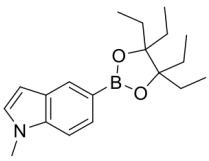
B_2Epin_2
^{13}C NMR (126 MHz, $CDCl_3$)



B_2Epin_2
^{11}B NMR (128 MHz, $CDCl_3$)

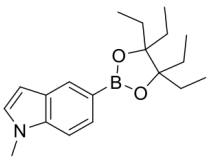


1
^{1}H NMR (500 MHz, $CDCl_3$)



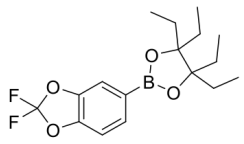
1

^{13}C NMR (126 MHz, $CDCl_3$)



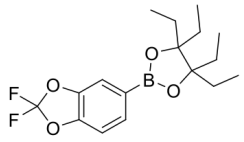
1

^{11}B NMR (128 MHz, $CDCl_3$)



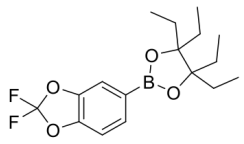
2

^{1}H NMR (500 MHz, $CDCl_3$)



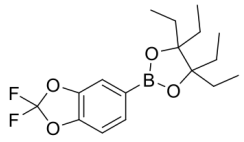
2

^{13}C NMR (126 MHz, $CDCl_3$)



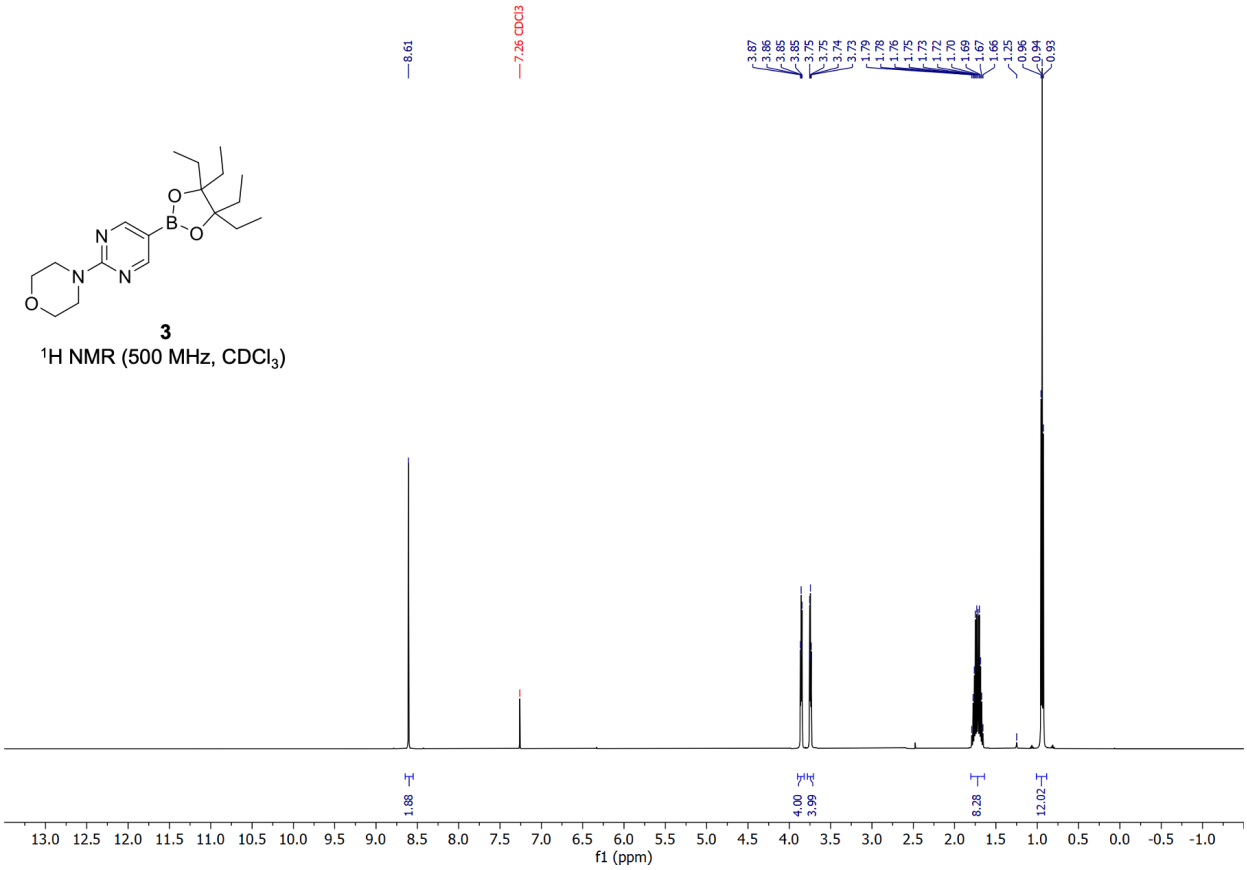
2

^{11}B NMR (128 MHz, $CDCl_3$)



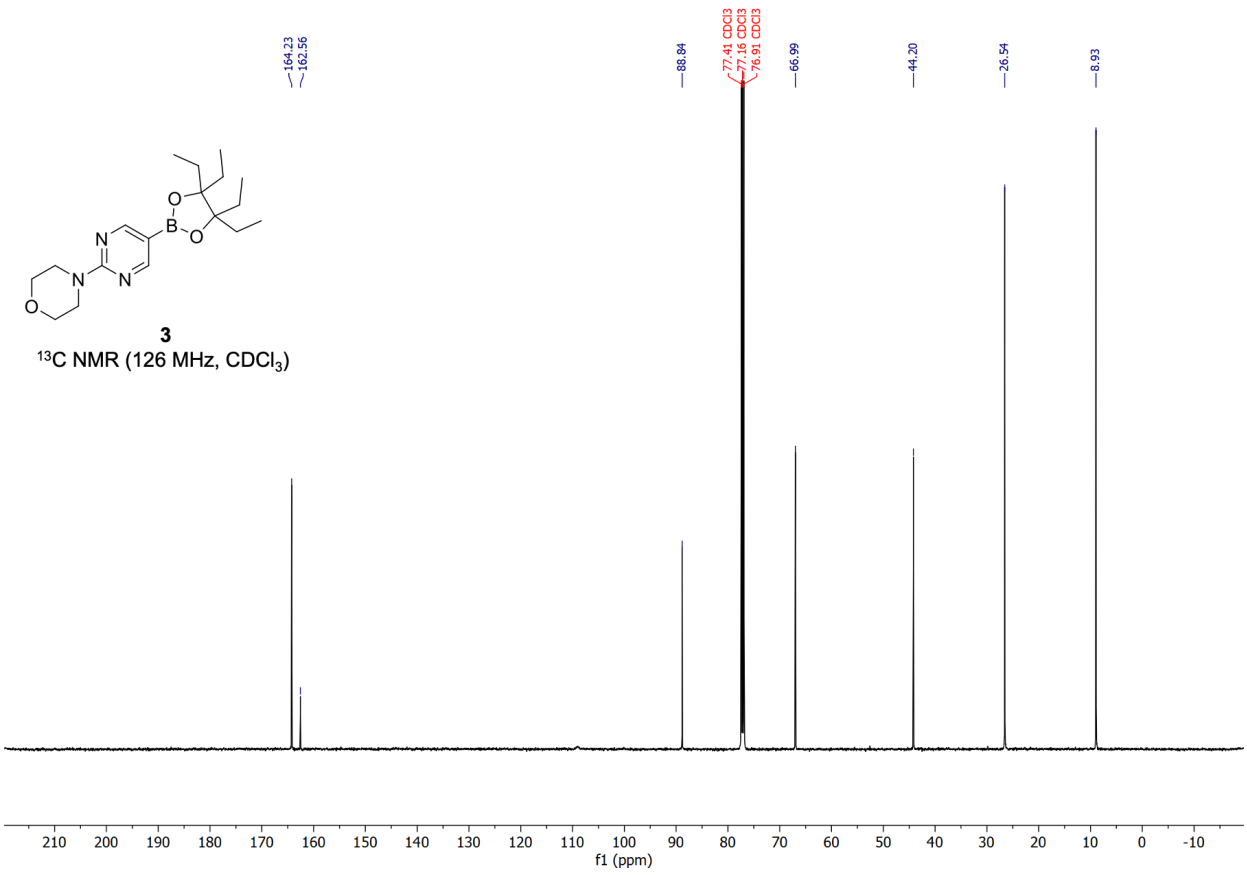
2

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



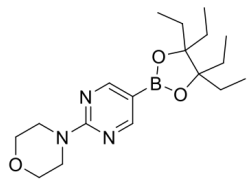
3

^{1}H NMR (500 MHz, $CDCl_3$)



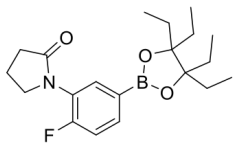
3

^{13}C NMR (126 MHz, $CDCl_3$)



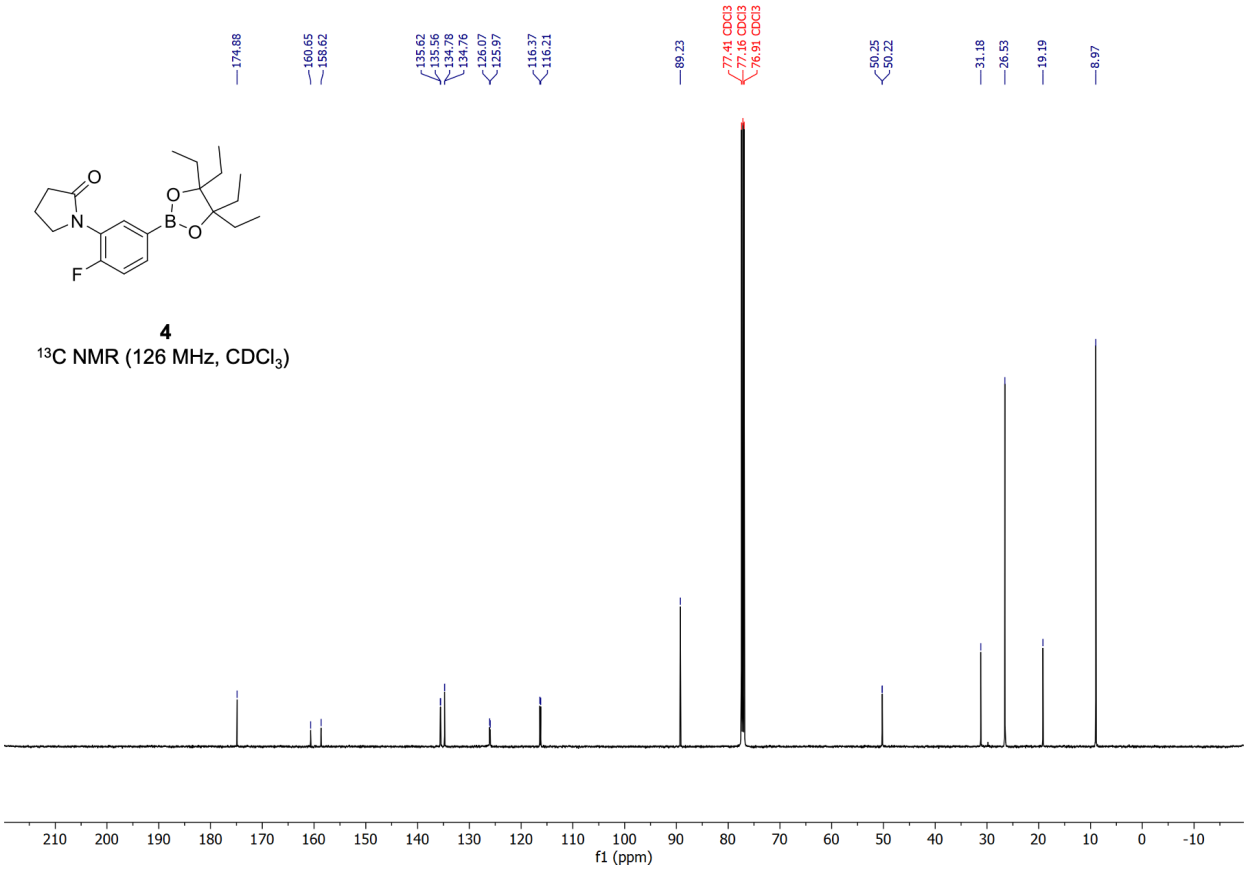
3

^{11}B NMR (128 MHz, $CDCl_3$)



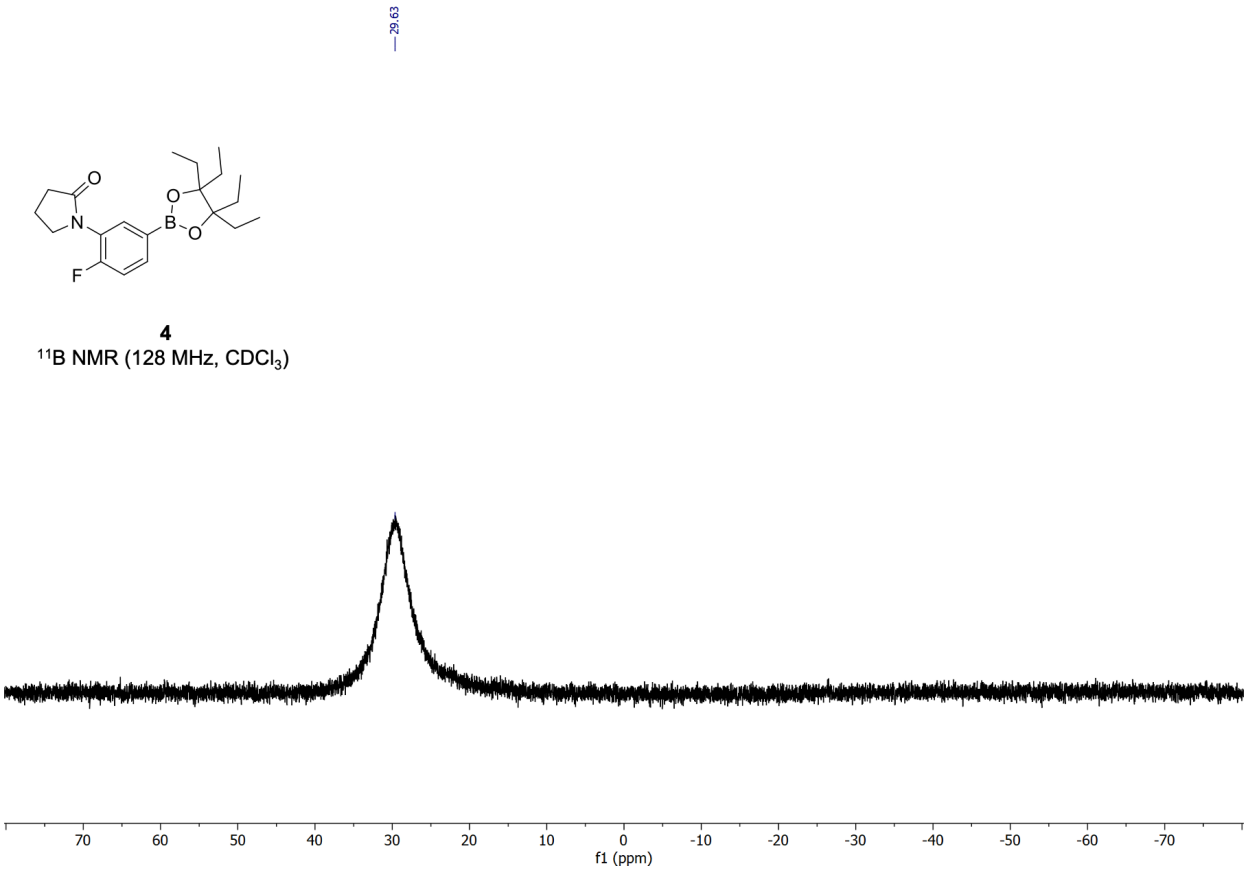
4

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



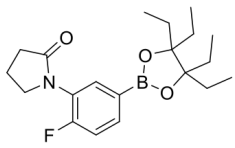
4

^{13}C NMR (126 MHz, $CDCl_3$)



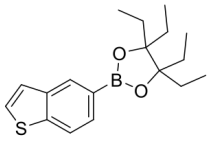
4

^{11}B NMR (128 MHz, $CDCl_3$)



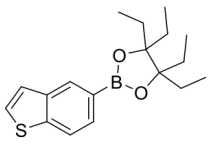
4

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



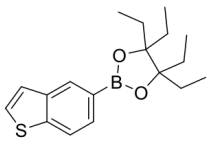
5

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



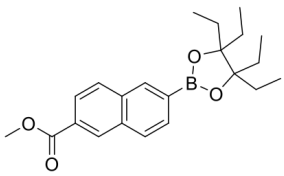
5

^{13}C NMR (126 MHz, $CDCl_3$)



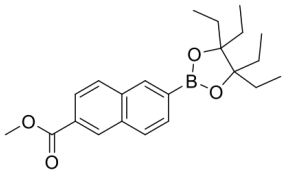
5

^{11}B NMR (128 MHz, $CDCl_3$)



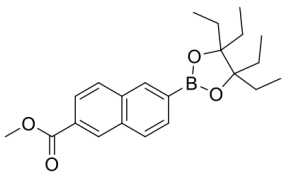
6

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



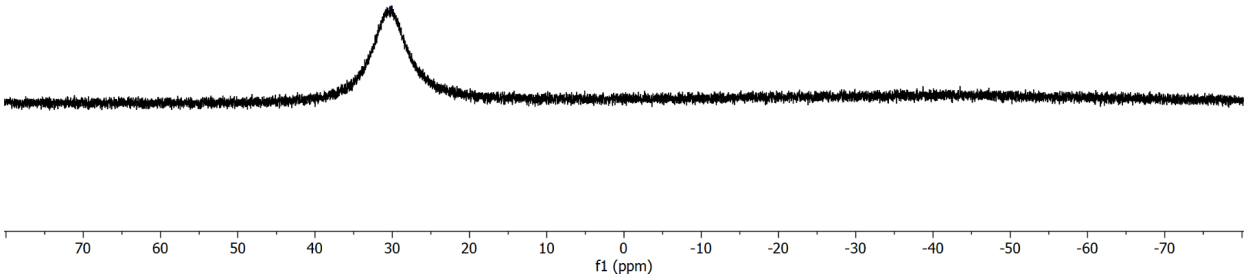
6

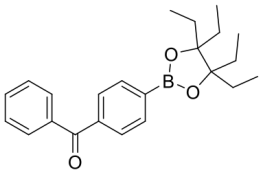
^{13}C NMR (126 MHz, $CDCl_3$)



6

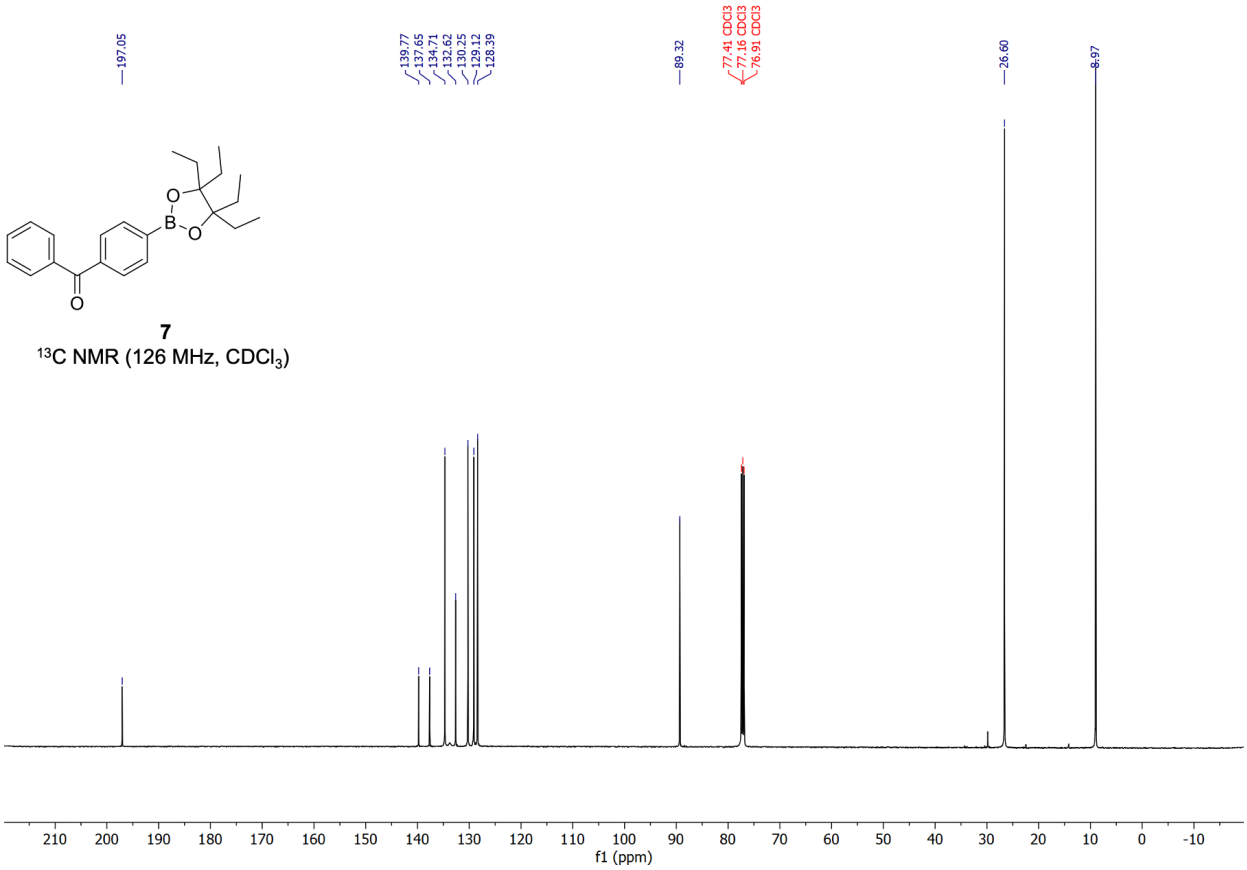
^{11}B NMR (128 MHz, $CDCl_3$)





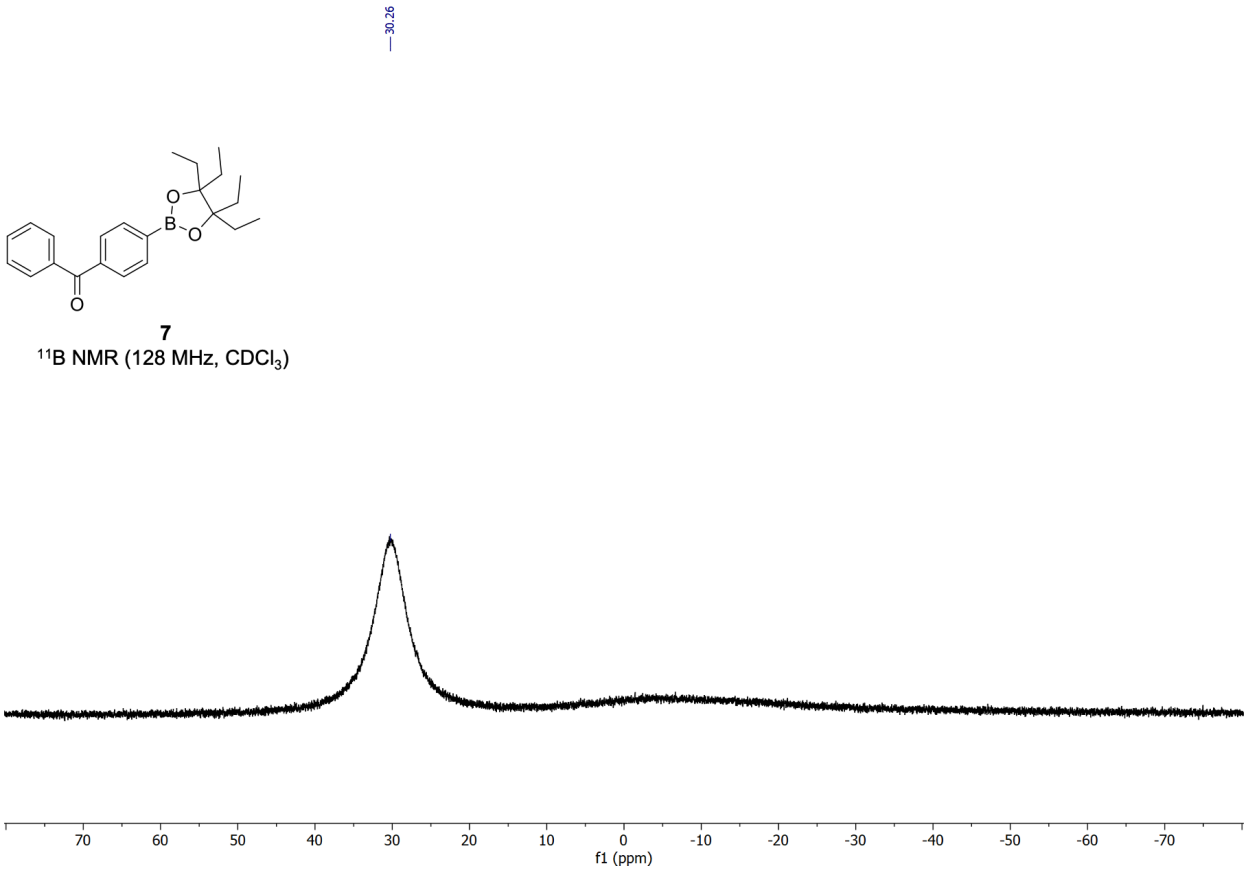
7

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



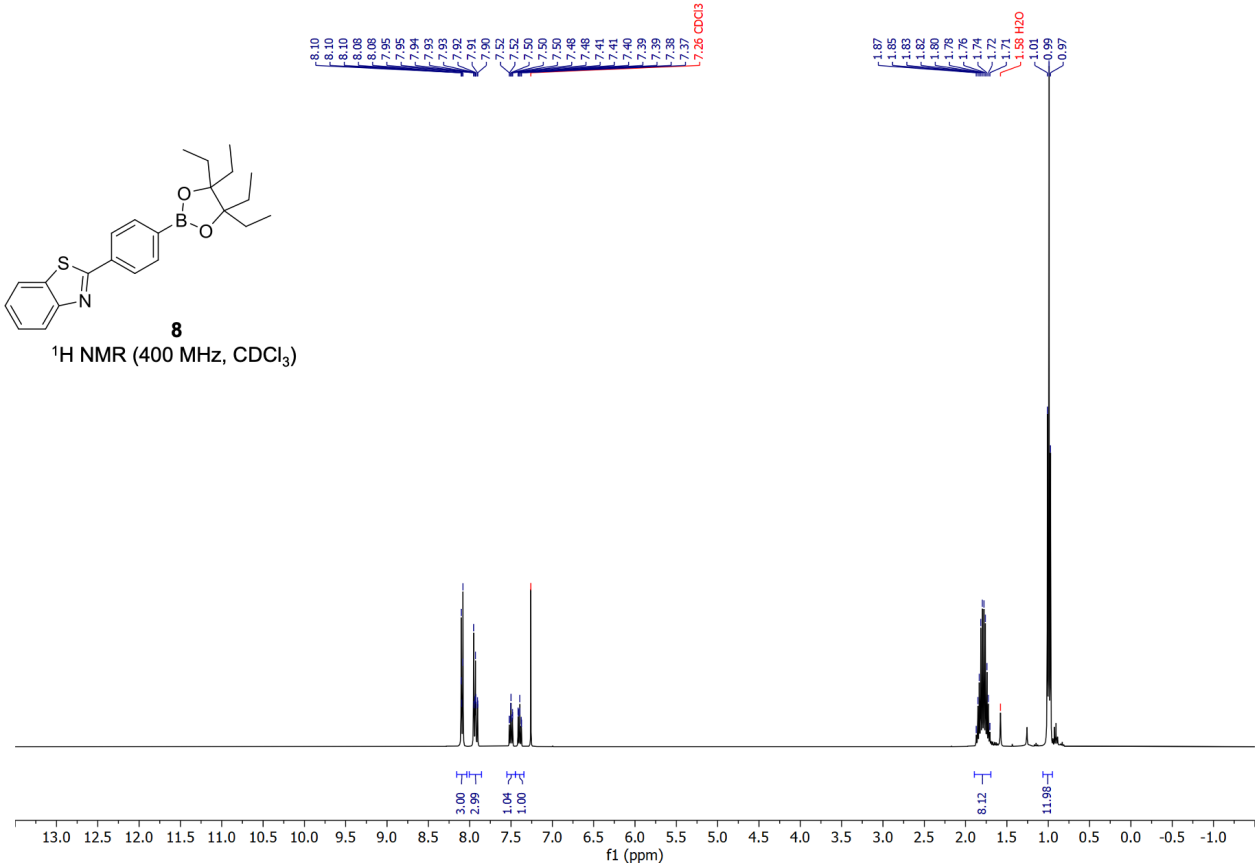
7

^{13}C NMR (126 MHz, $CDCl_3$)



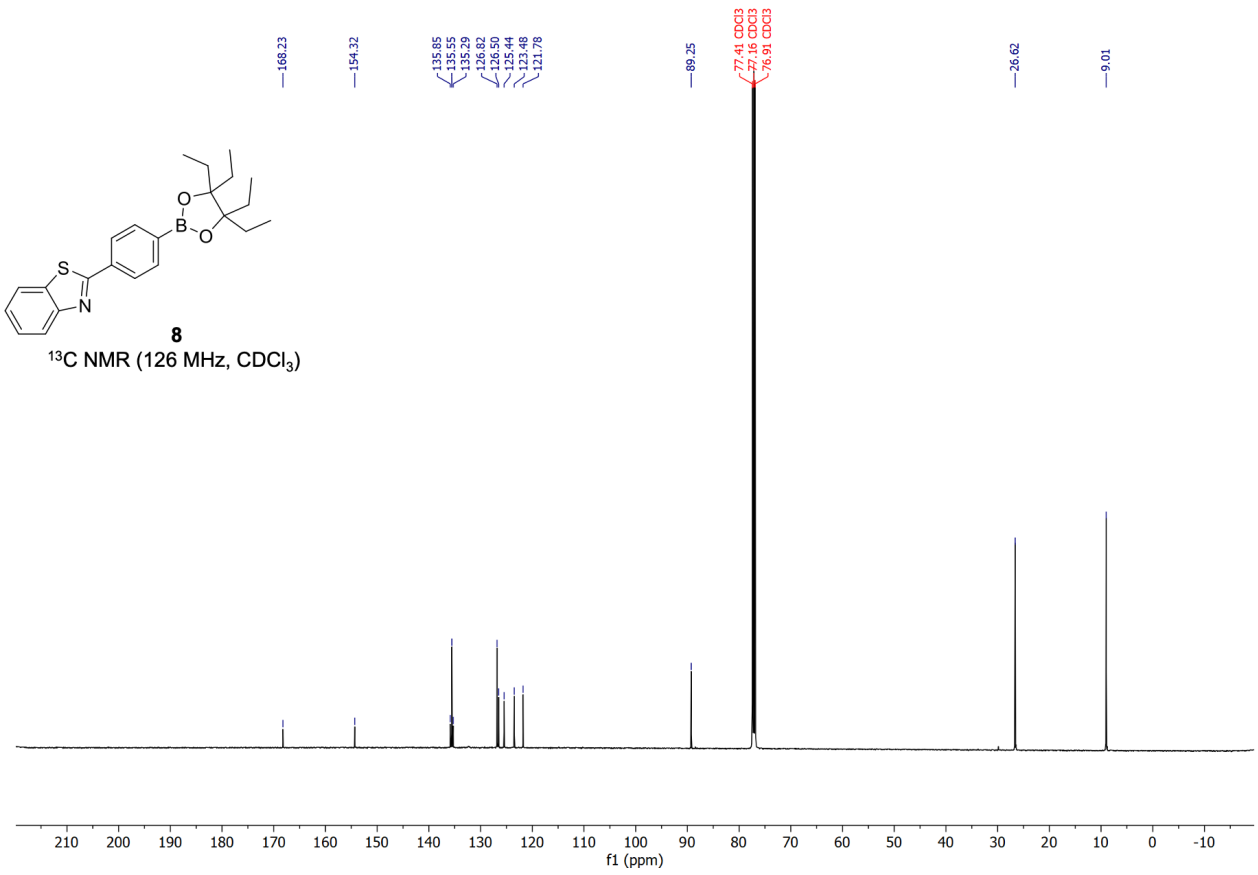
7

^{11}B NMR (128 MHz, $CDCl_3$)



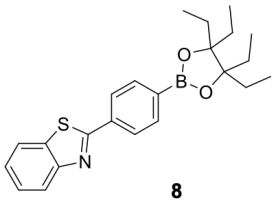
8

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



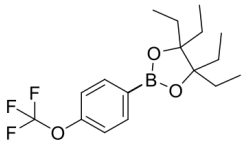
8

^{13}C NMR (126 MHz, $CDCl_3$)



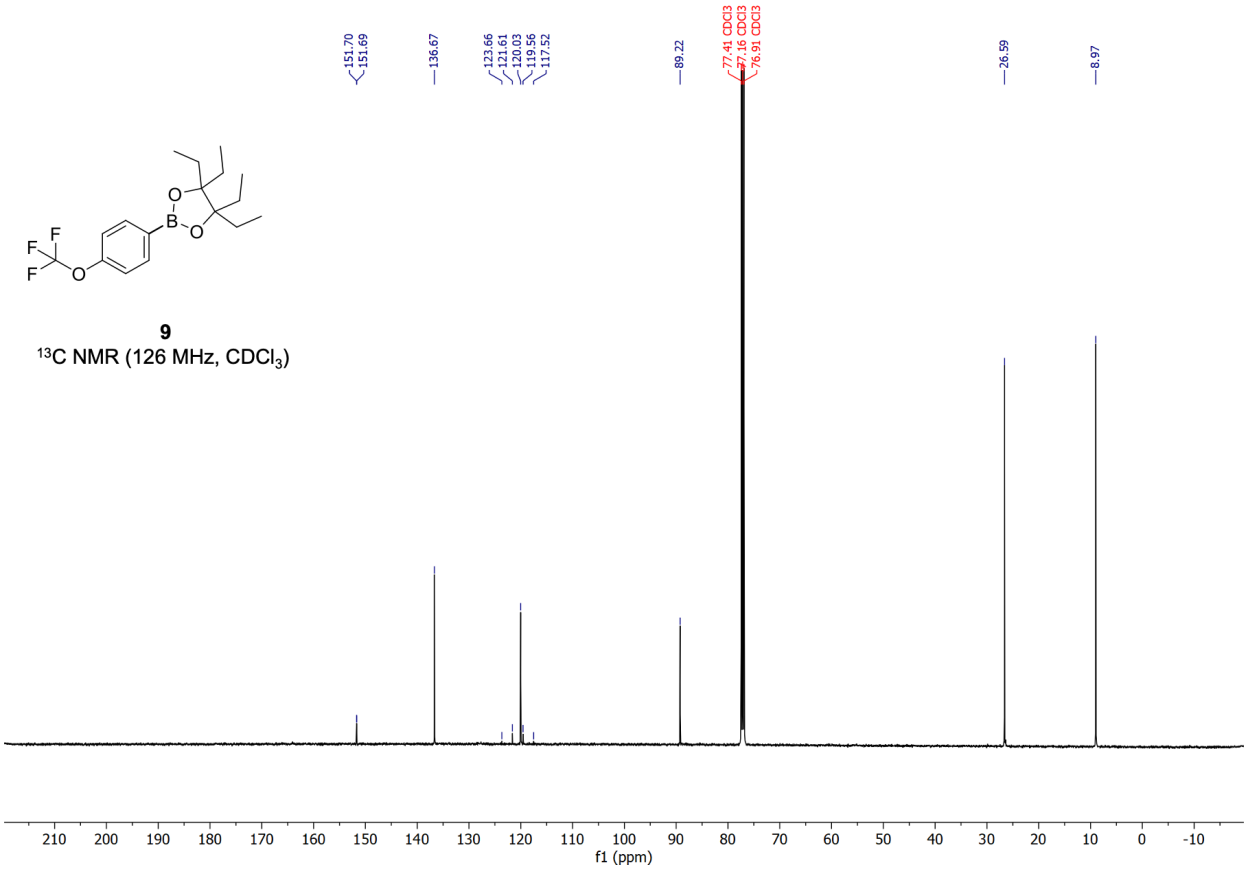
8

^{11}B NMR (128 MHz, $CDCl_3$)



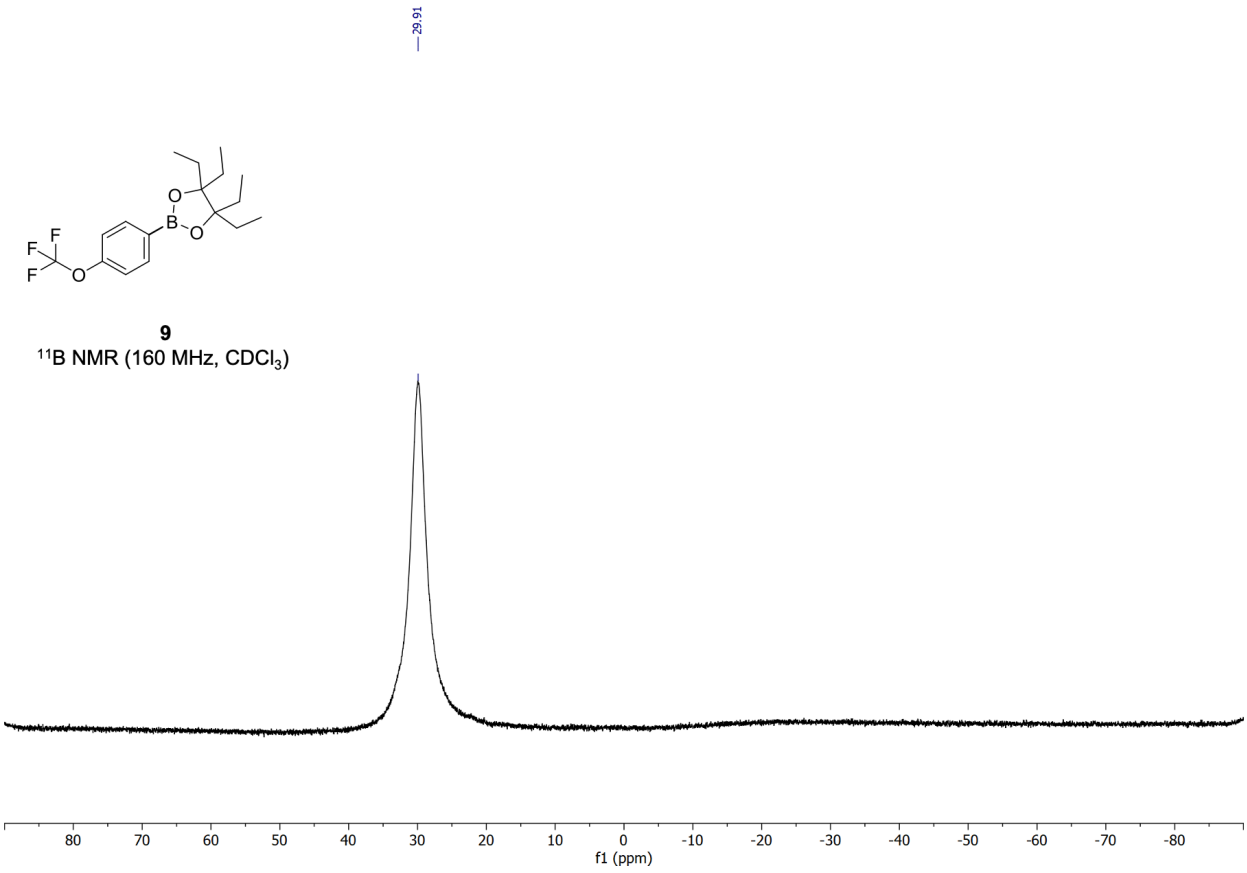
9

^{1}H NMR (500 MHz, $CDCl_3$)



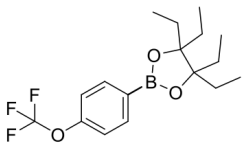
9

^{13}C NMR (126 MHz, $CDCl_3$)



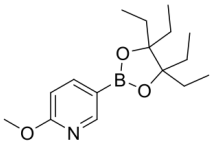
9

^{11}B NMR (160 MHz, $CDCl_3$)



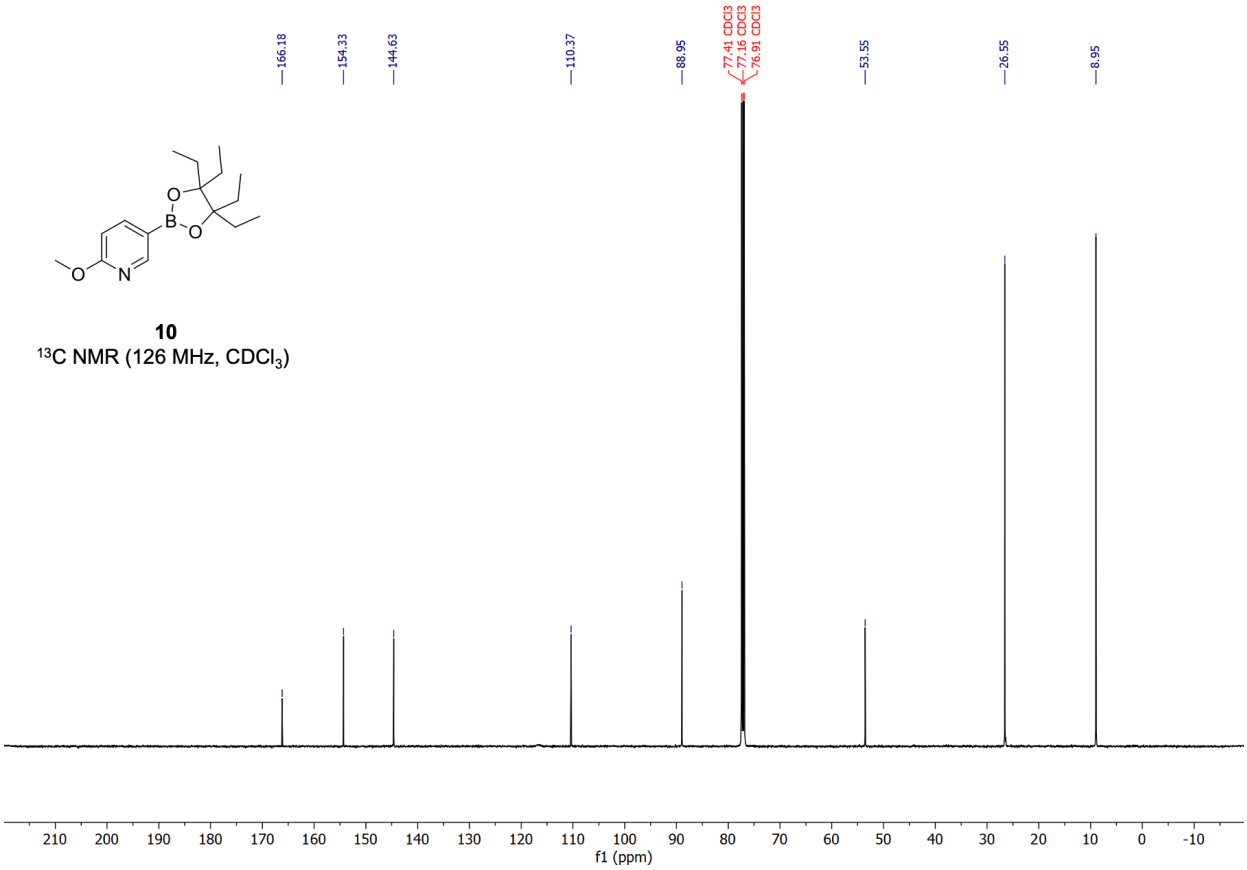
9

^{19}F NMR (471 MHz, $CDCl_3$)



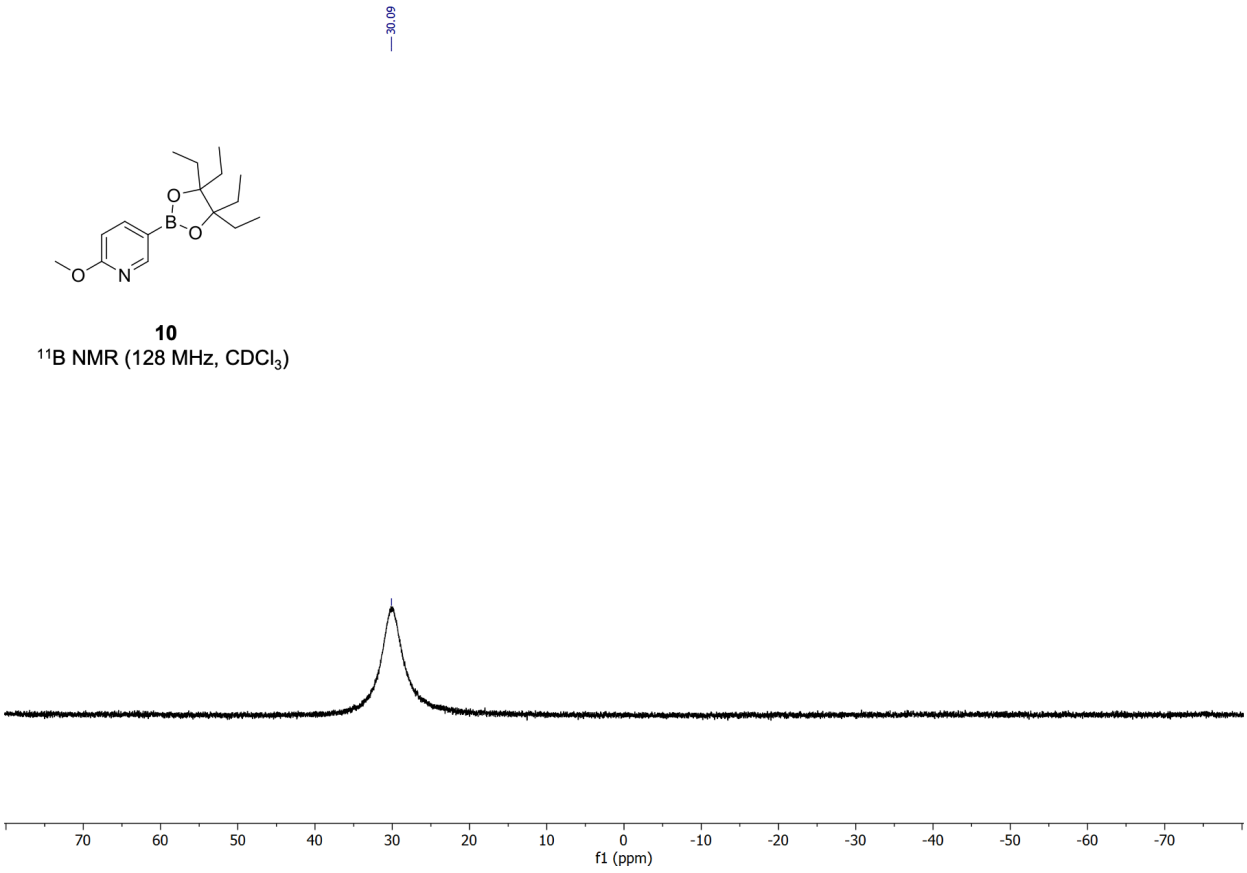
10

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



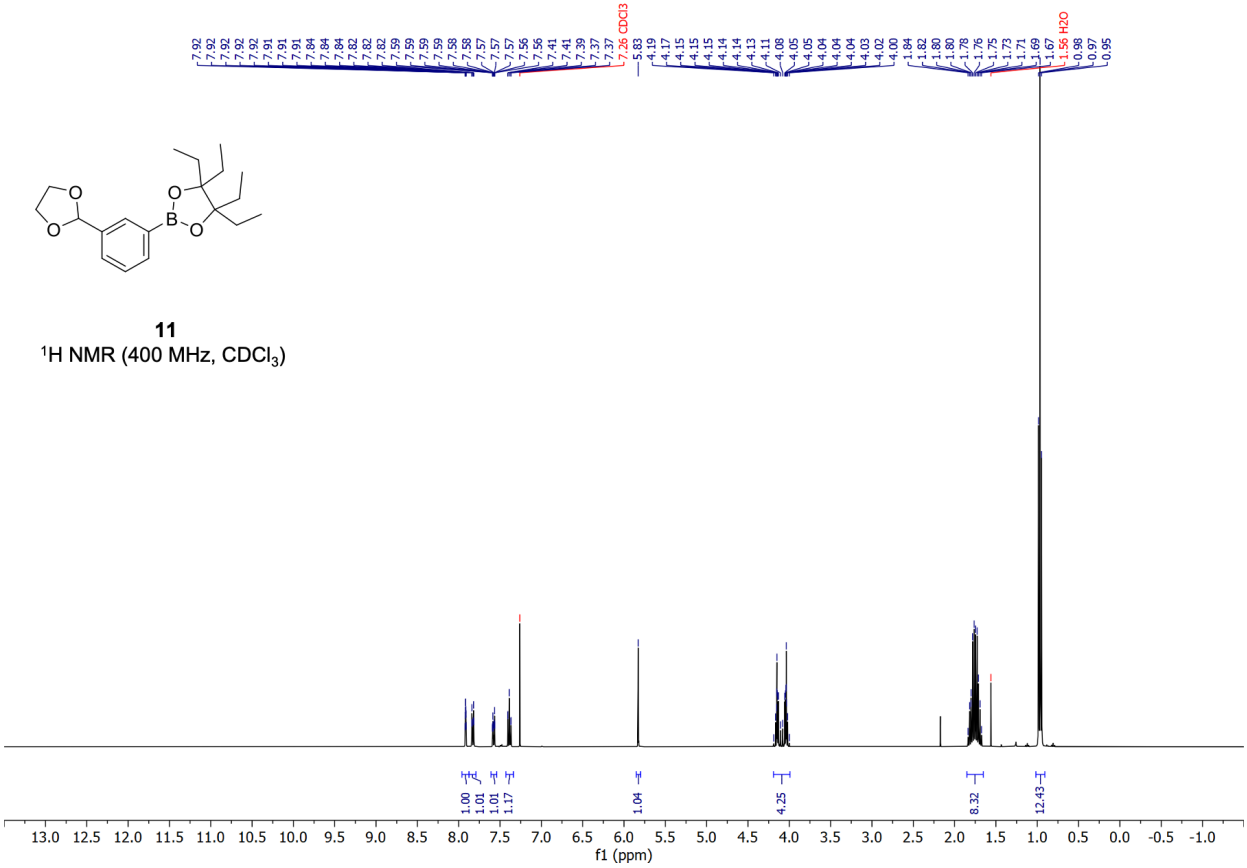
10

^{13}C NMR (126 MHz, $CDCl_3$)

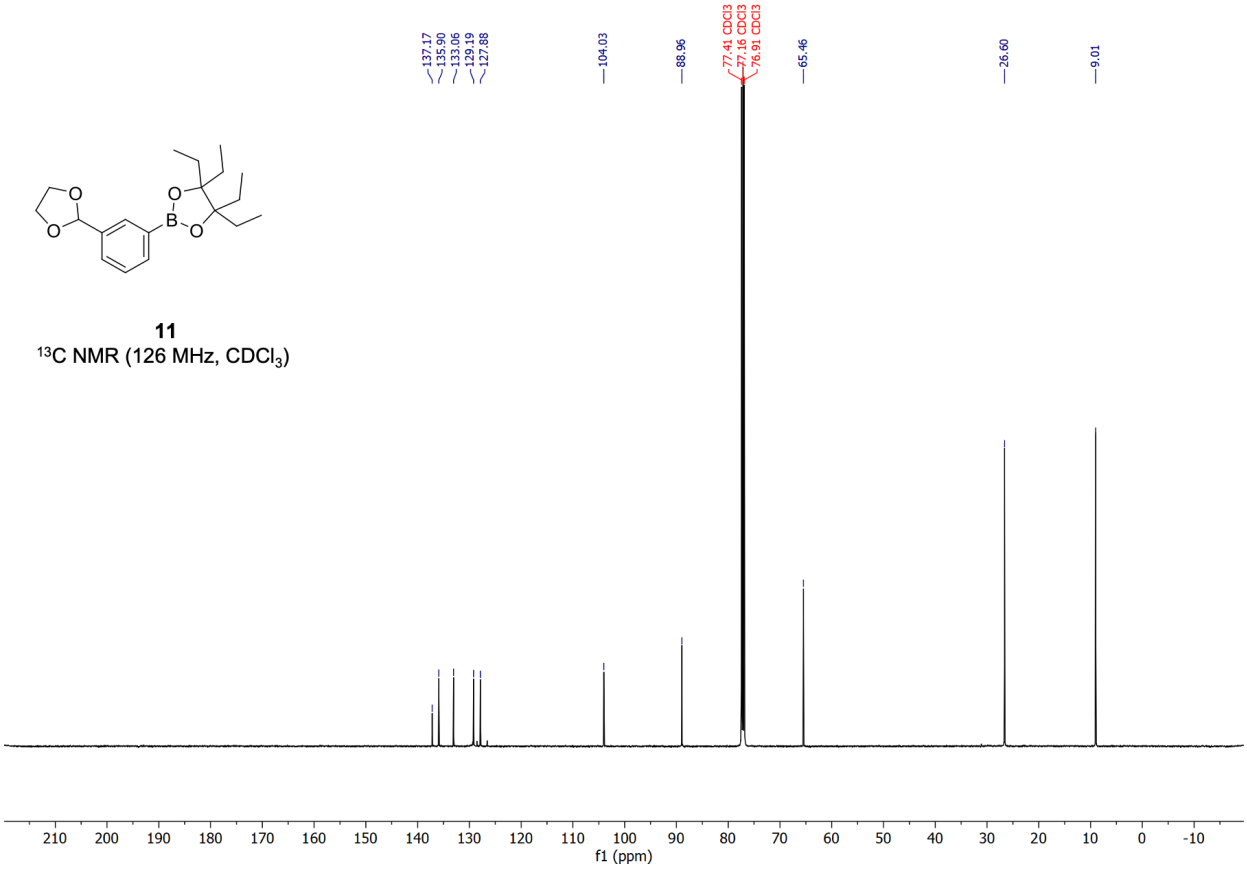


10

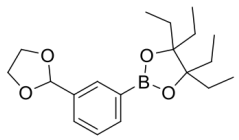
^{11}B NMR (128 MHz, $CDCl_3$)



11
^{1}H NMR (400 MHz, $CDCl_3$)

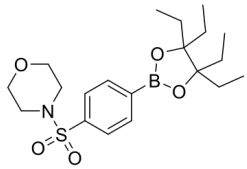


11
^{13}C NMR (126 MHz, $CDCl_3$)



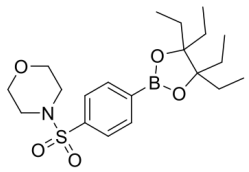
11

^{11}B NMR (128 MHz, $CDCl_3$)



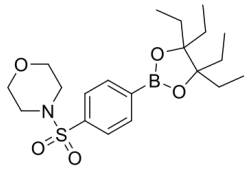
12

^{1}H NMR (500 MHz, $CDCl_3$)



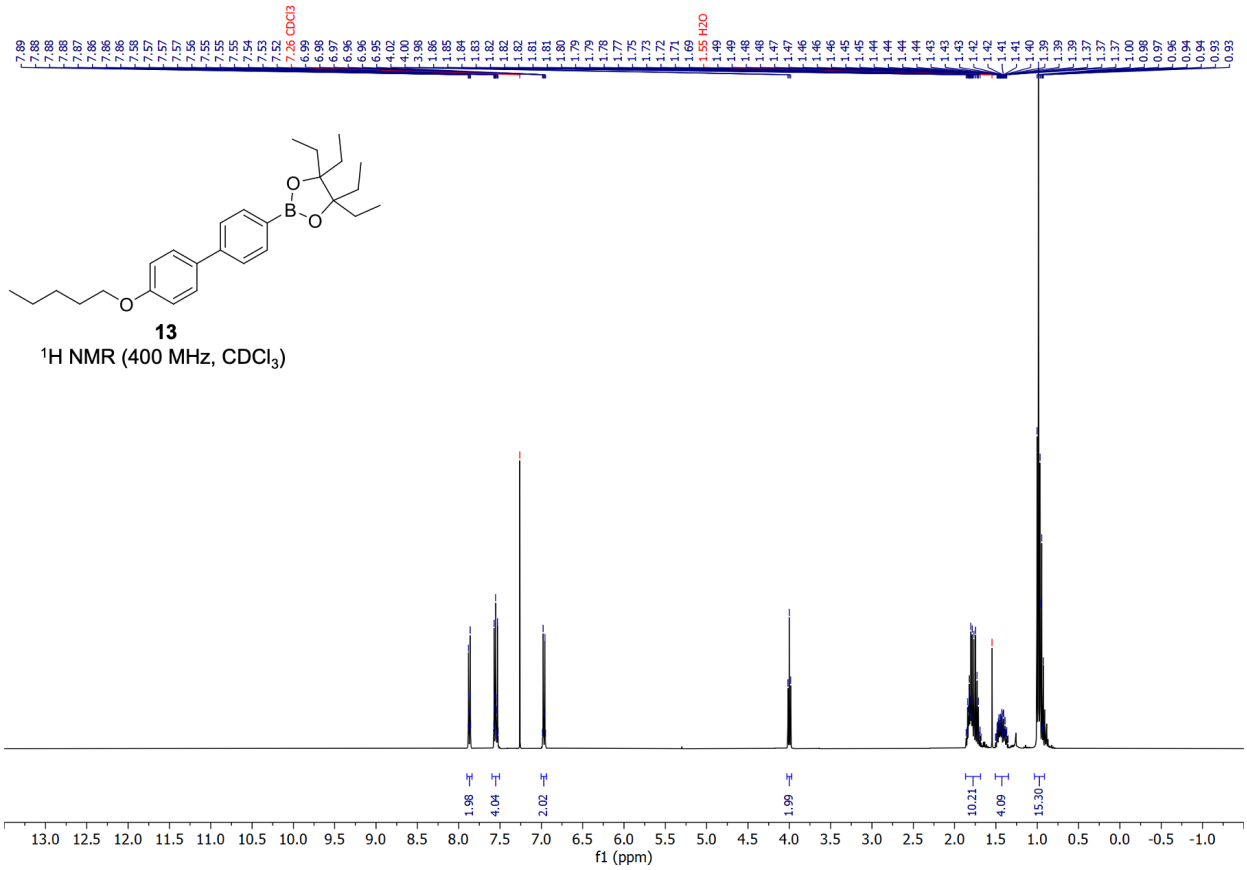
12

^{13}C NMR (126 MHz, $CDCl_3$)



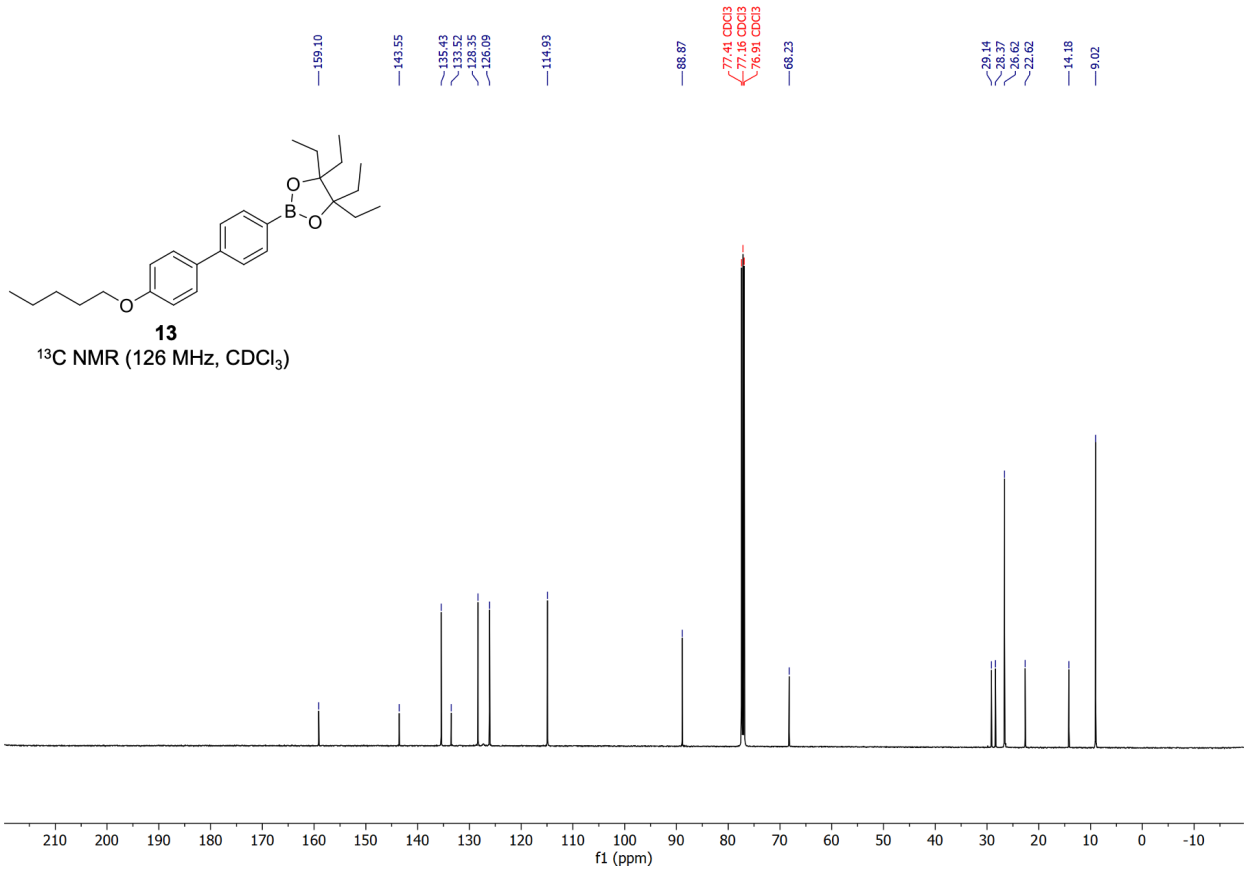
12

^{11}B NMR (128 MHz, $CDCl_3$)



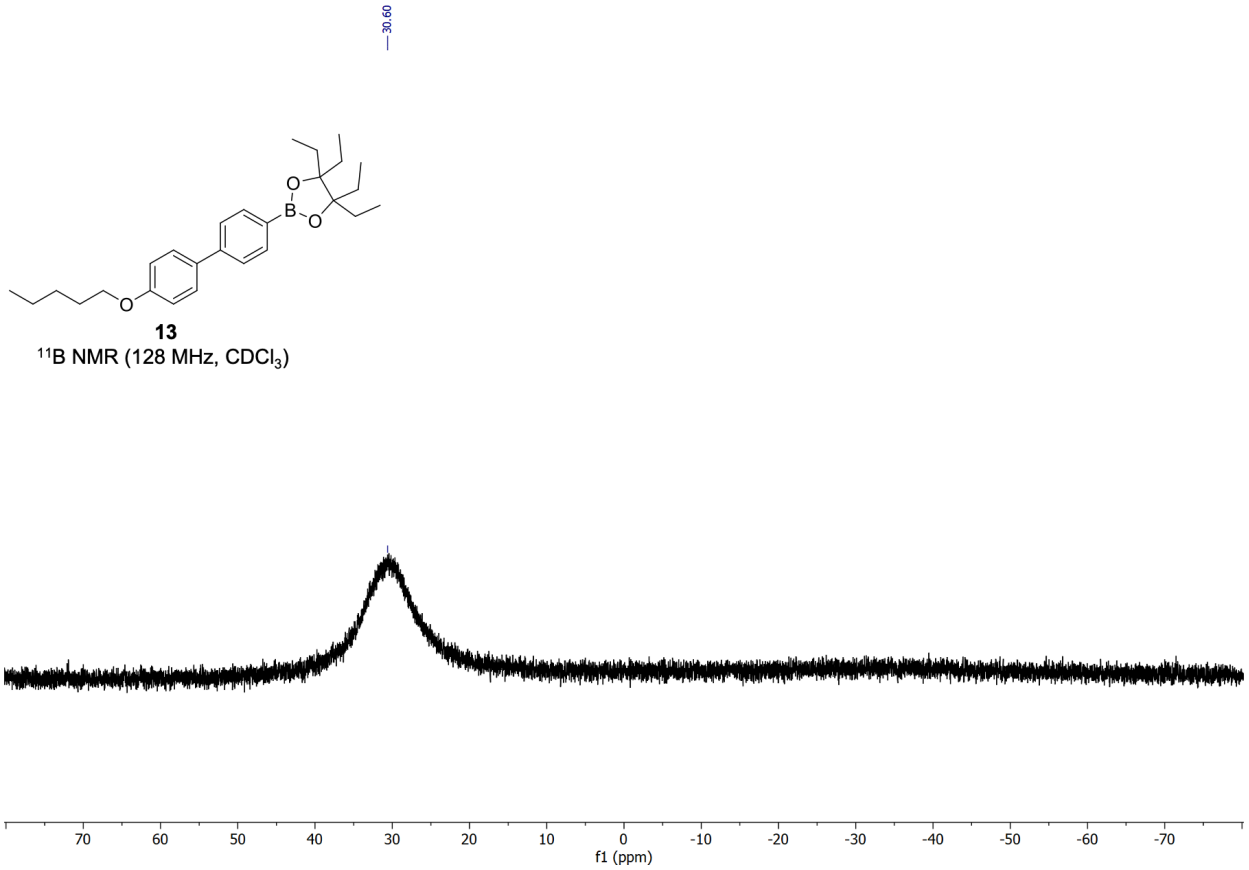
13

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



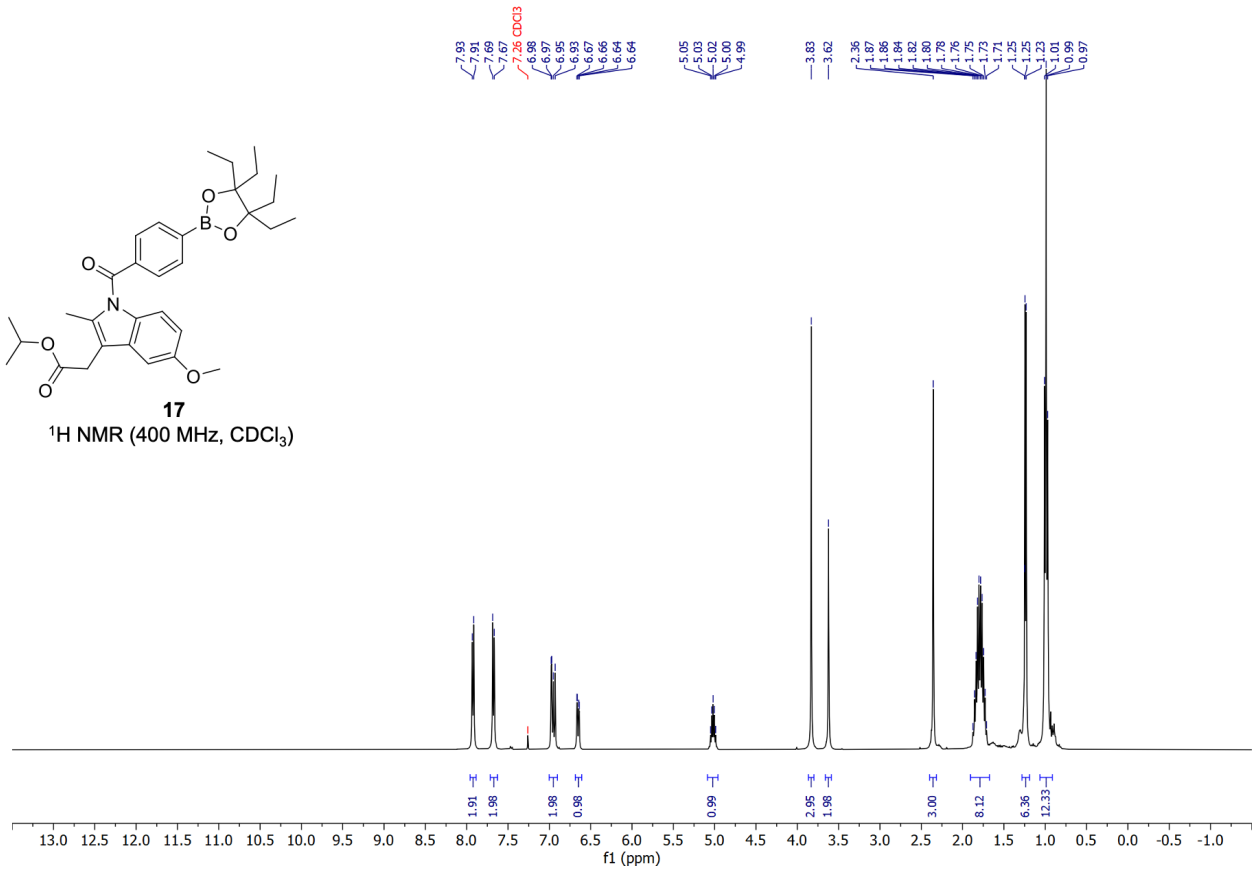
13

^{13}C NMR (126 MHz, $CDCl_3$)



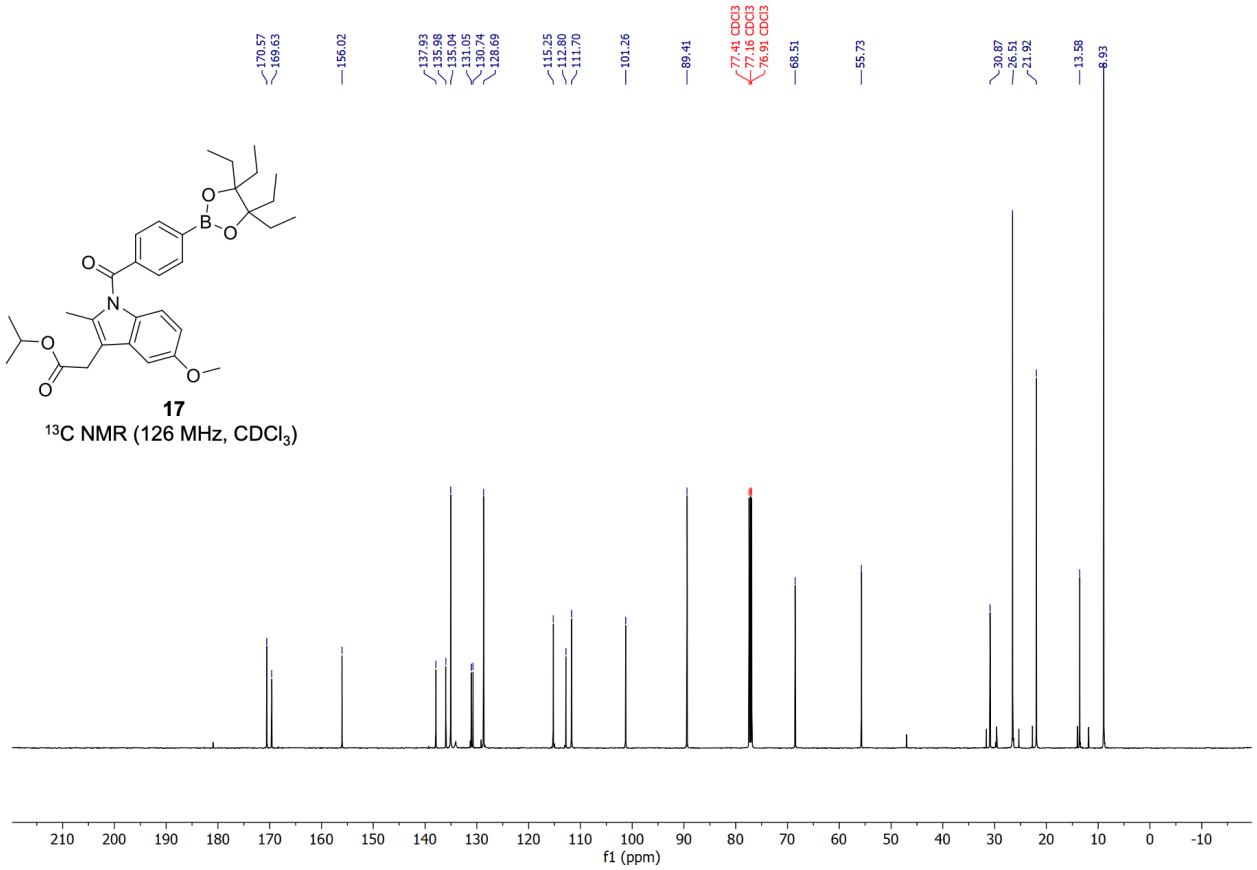
13

^{11}B NMR (128 MHz, $CDCl_3$)



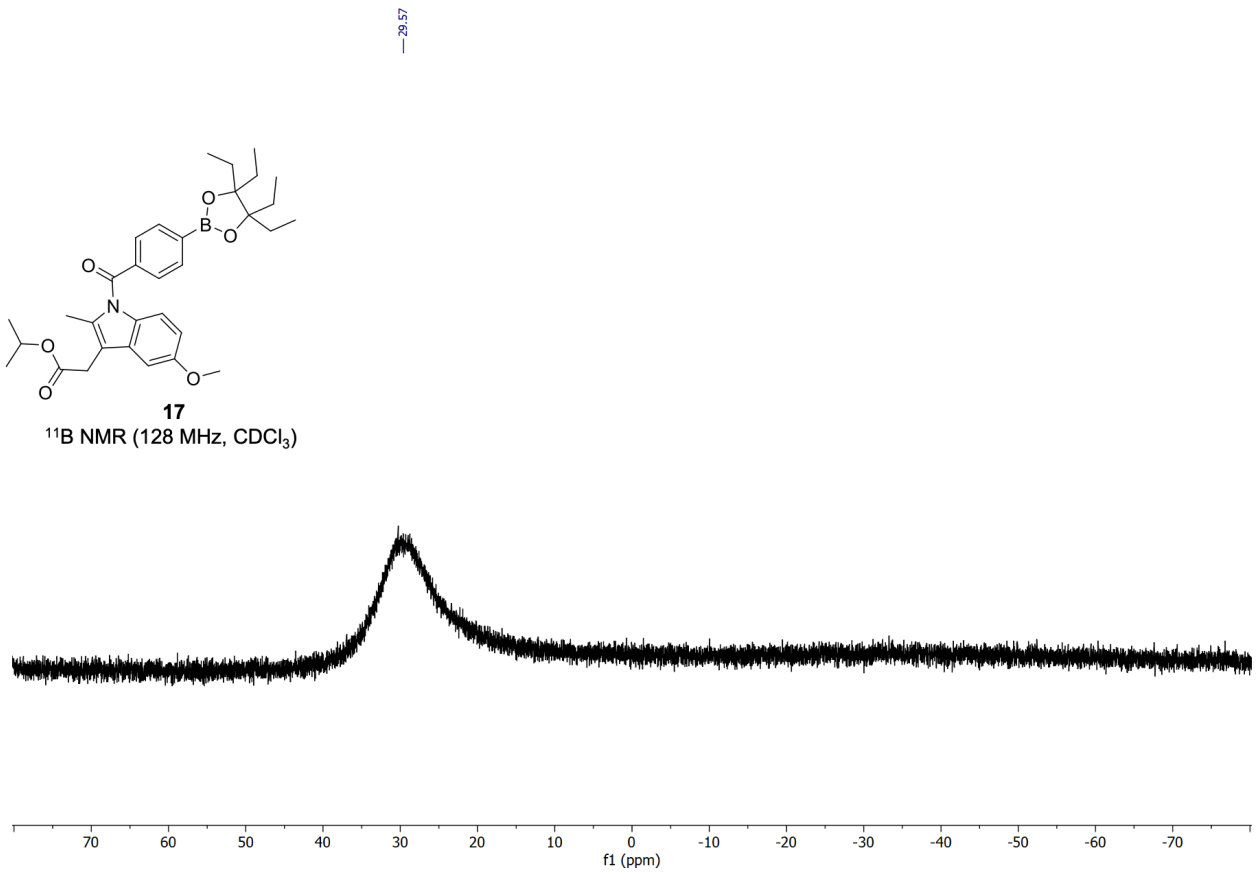
17

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



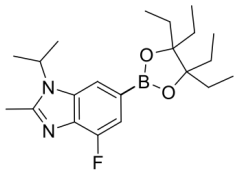
17

^{13}C NMR (126 MHz, $CDCl_3$)



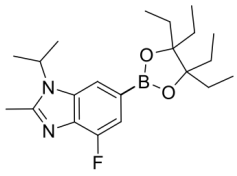
17

^{11}B NMR (128 MHz, $CDCl_3$)



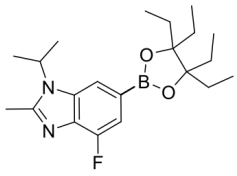
18

^{1}H NMR (500 MHz, $CDCl_3$)



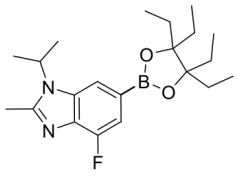
18

^{13}C NMR (126 MHz, $CDCl_3$)



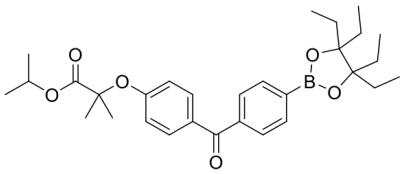
18

^{11}B NMR (160 MHz, $CDCl_3$)



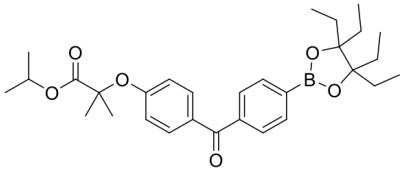
18

^{19}F NMR (471 MHz, $CDCl_3$)



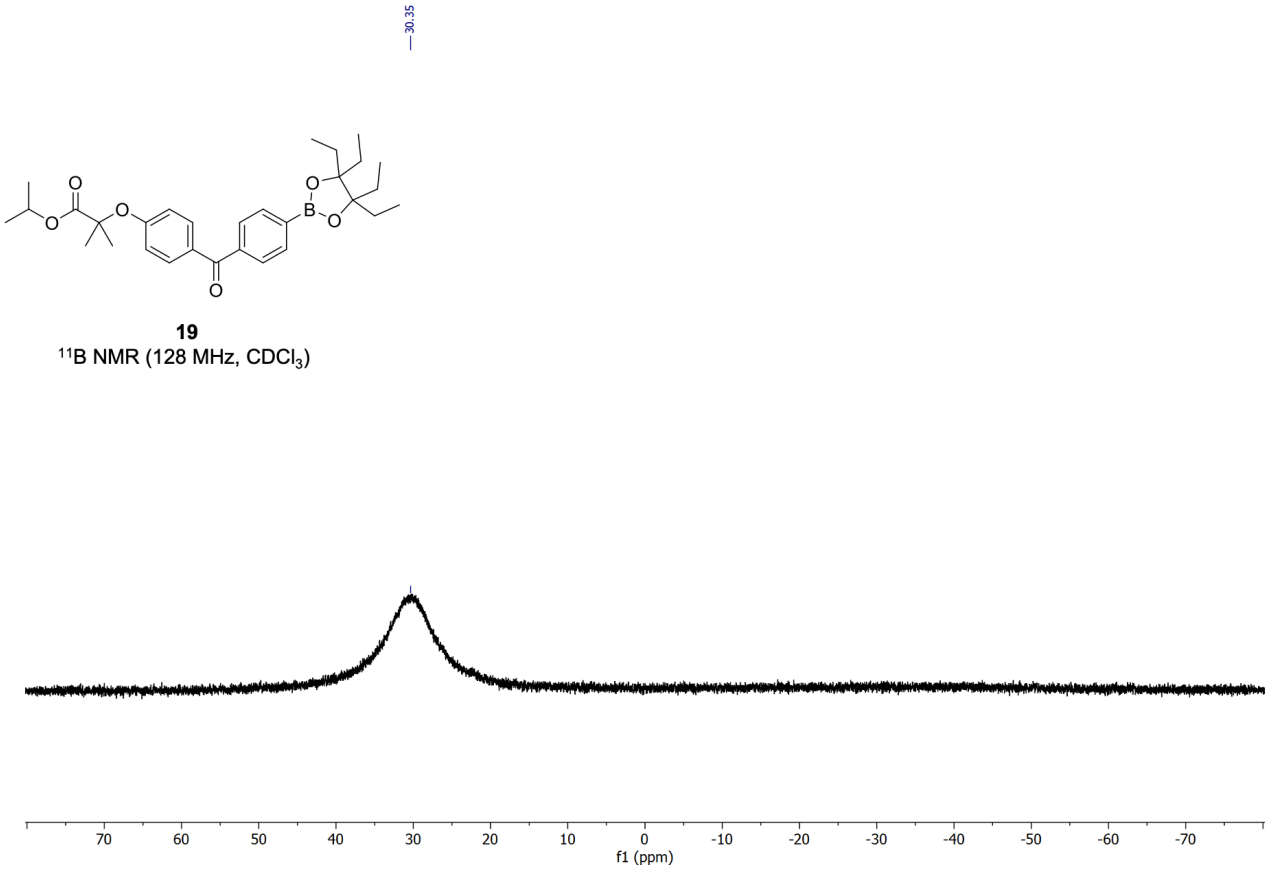
19

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



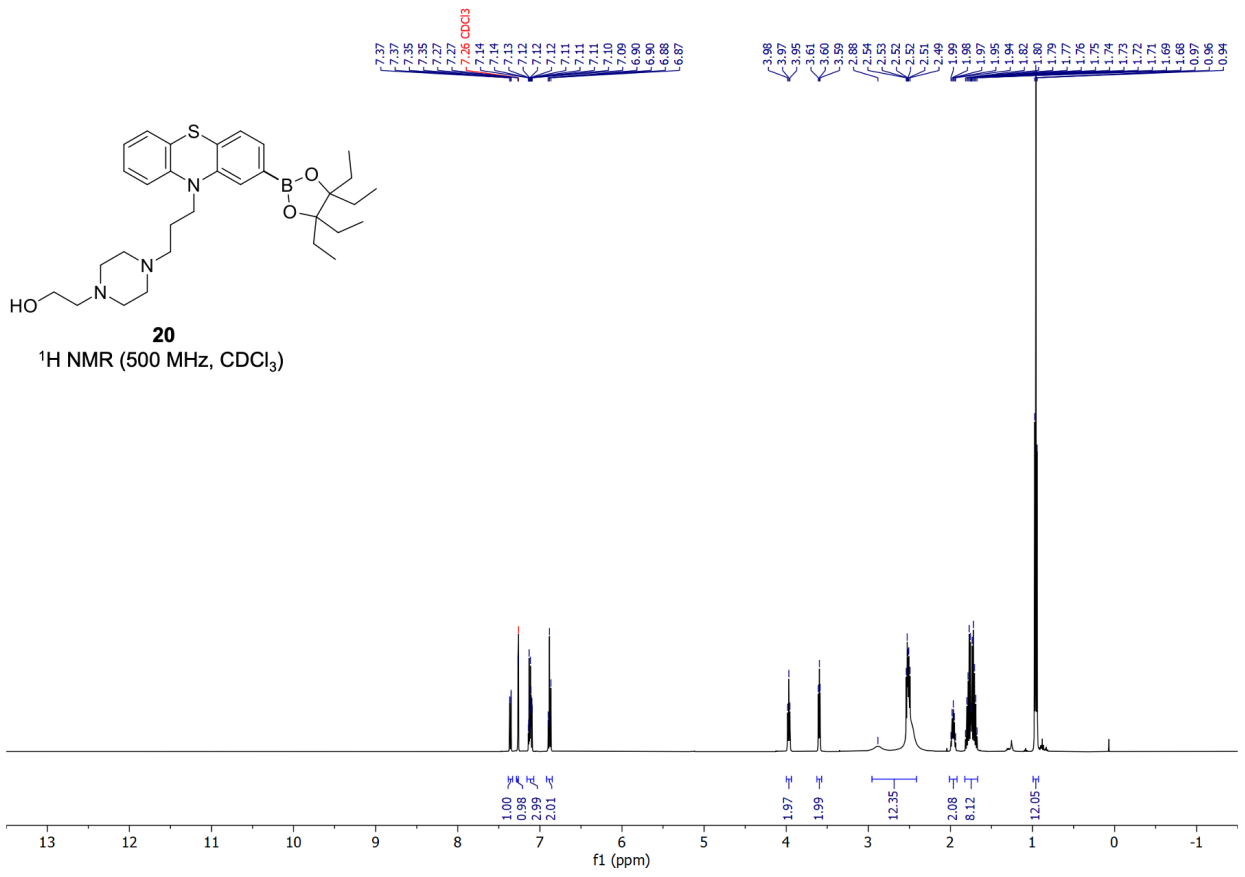
19

^{13}C NMR (126 MHz, $CDCl_3$)



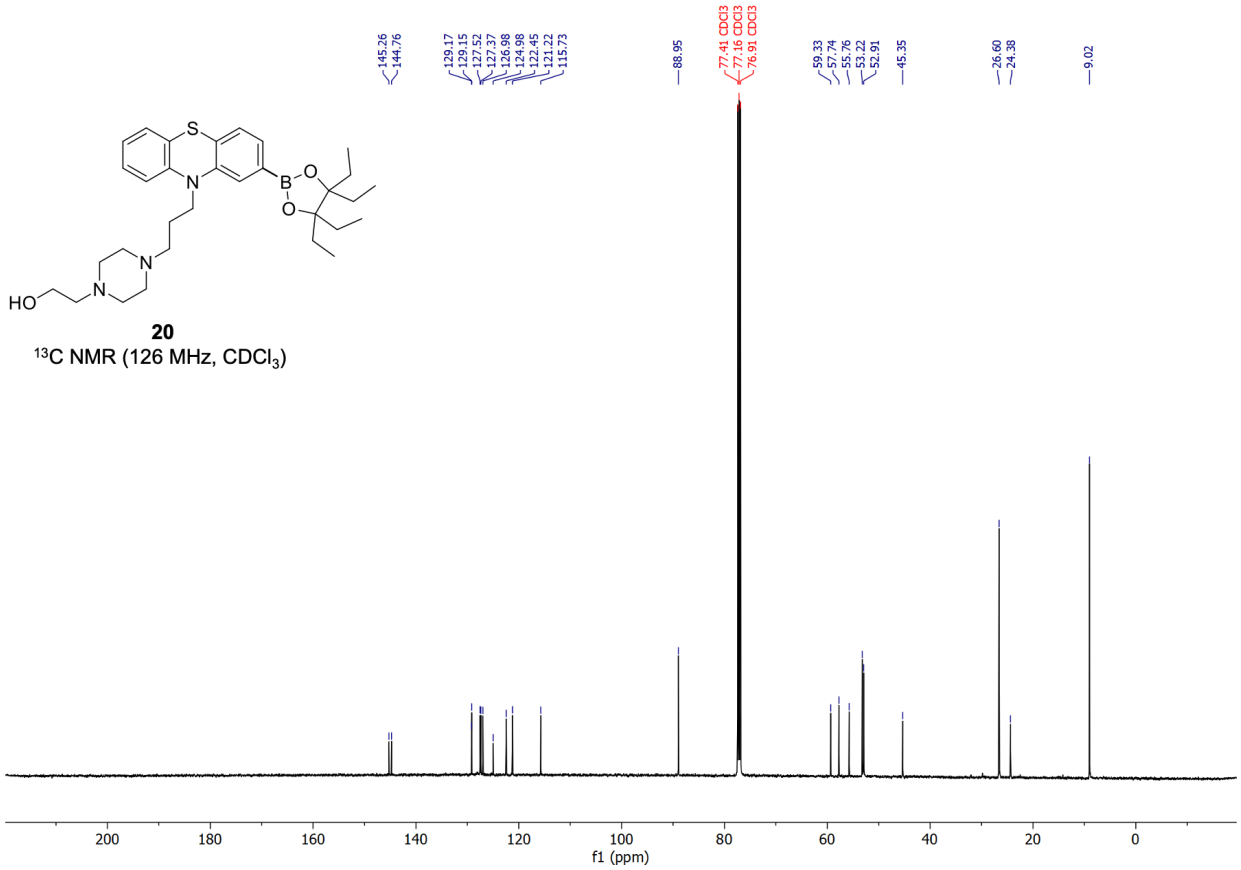
19

^{11}B NMR (128 MHz, $CDCl_3$)



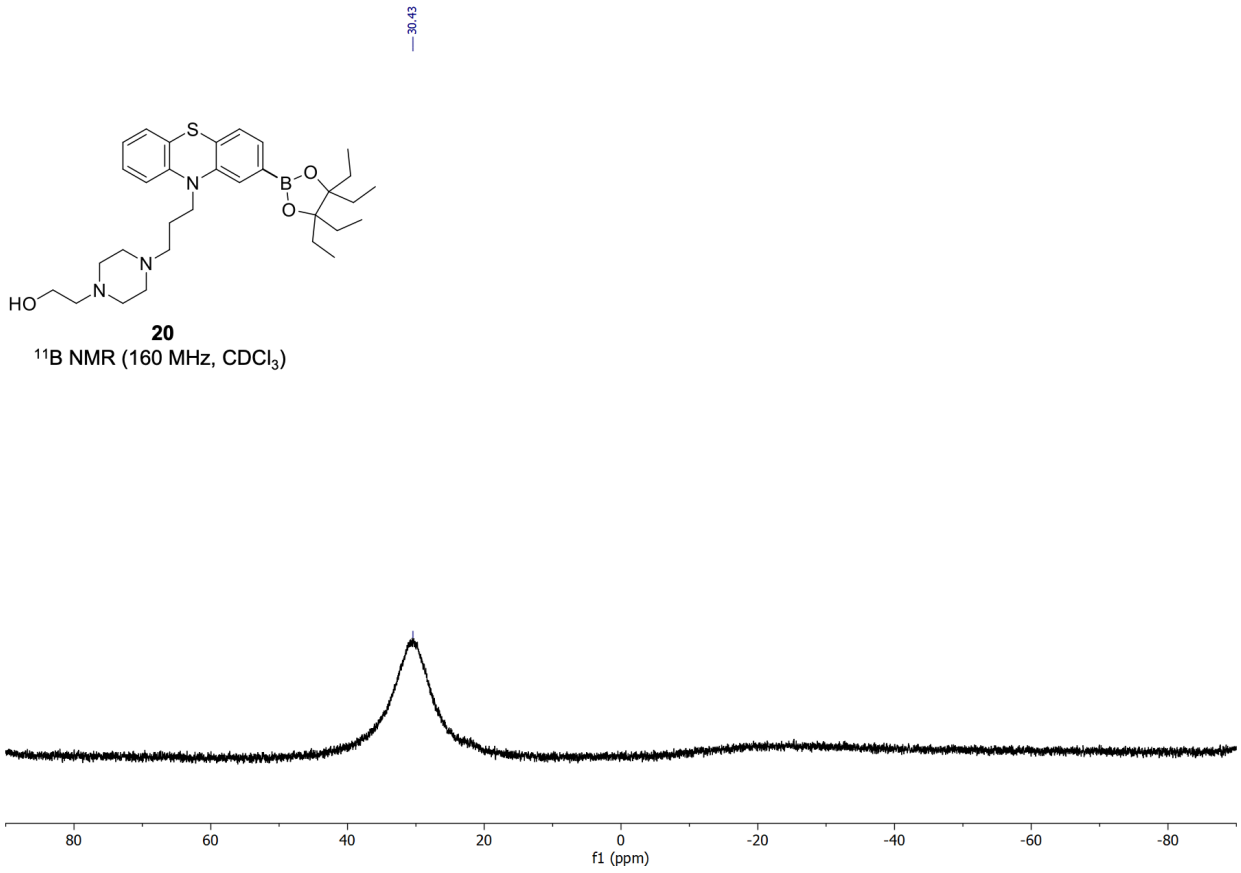
20

^{1}H NMR (500 MHz, $CDCl_3$)



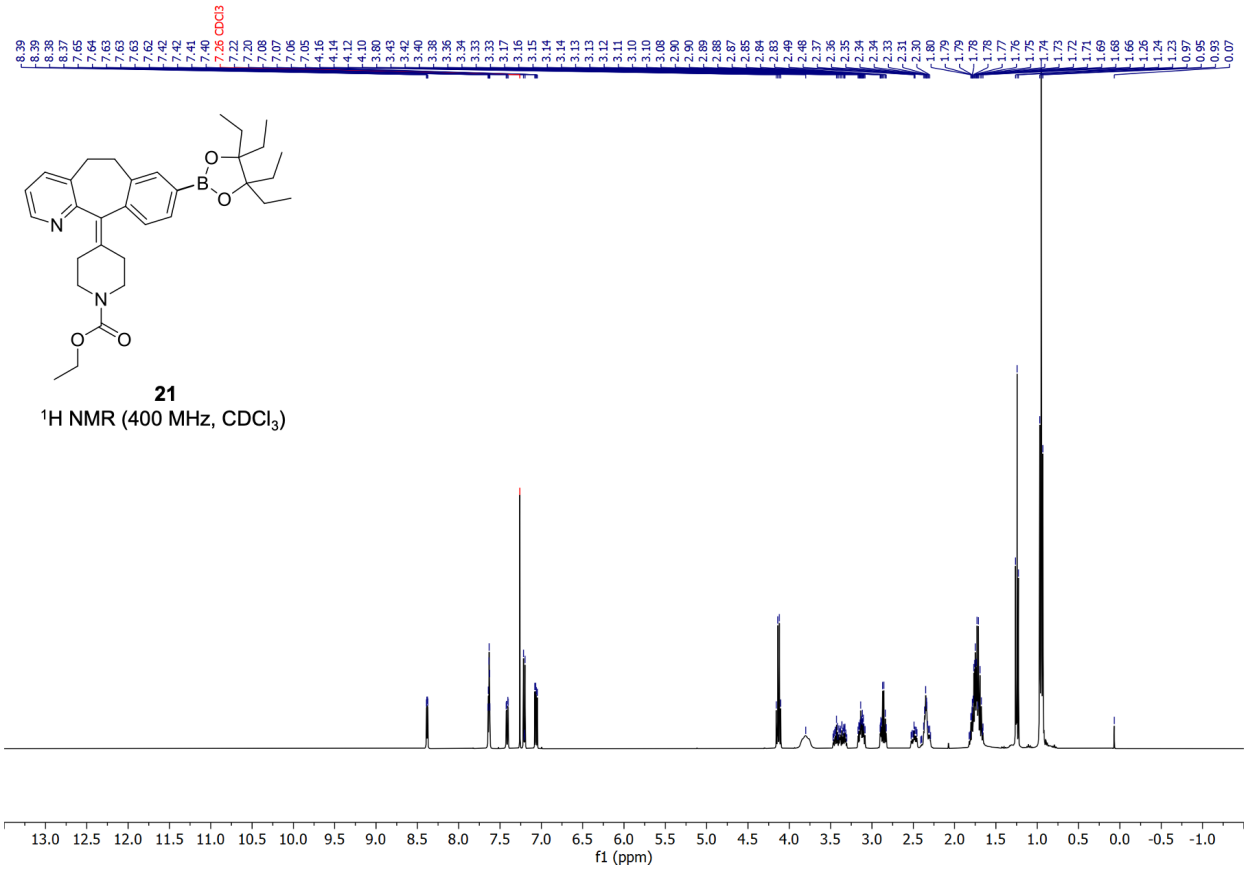
20

^{13}C NMR (126 MHz, $CDCl_3$)



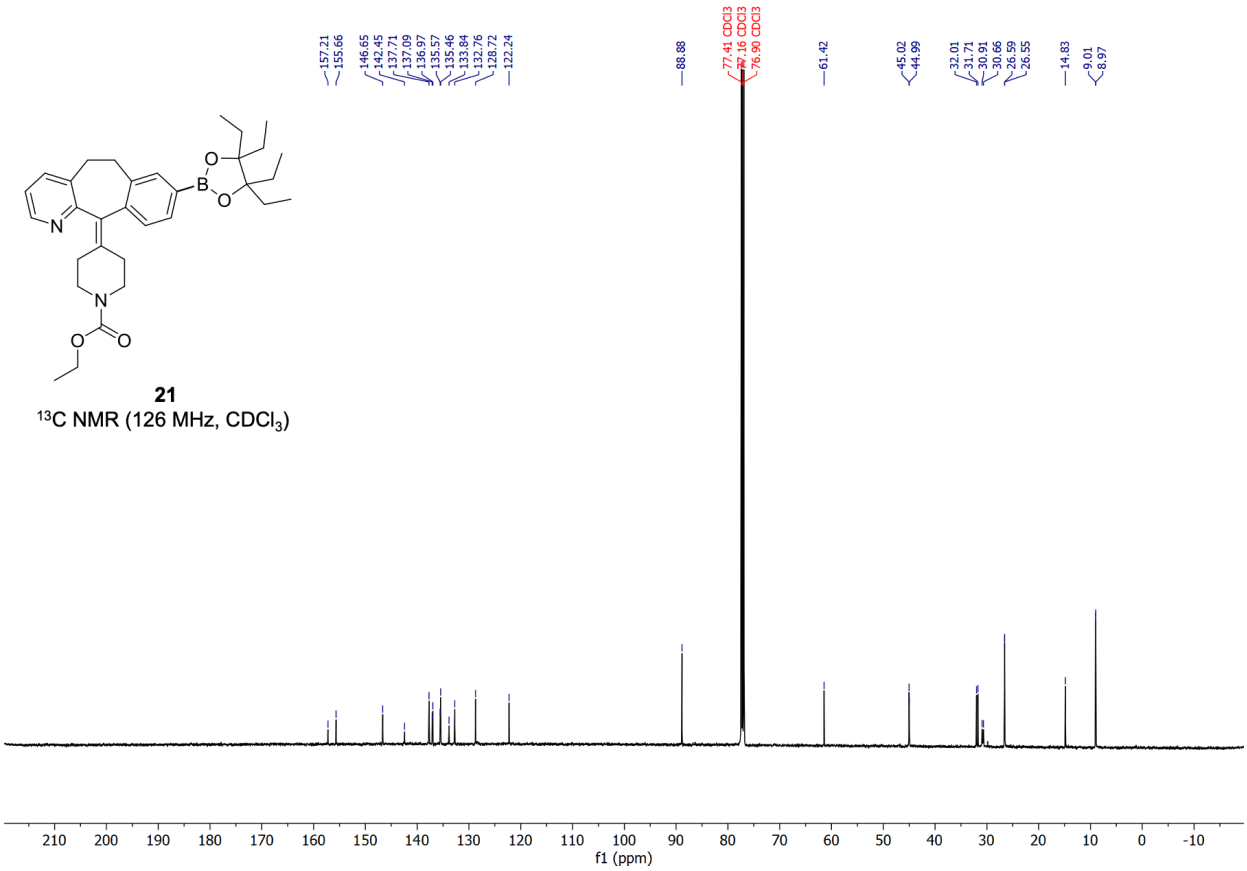
20

^{11}B NMR (160 MHz, $CDCl_3$)



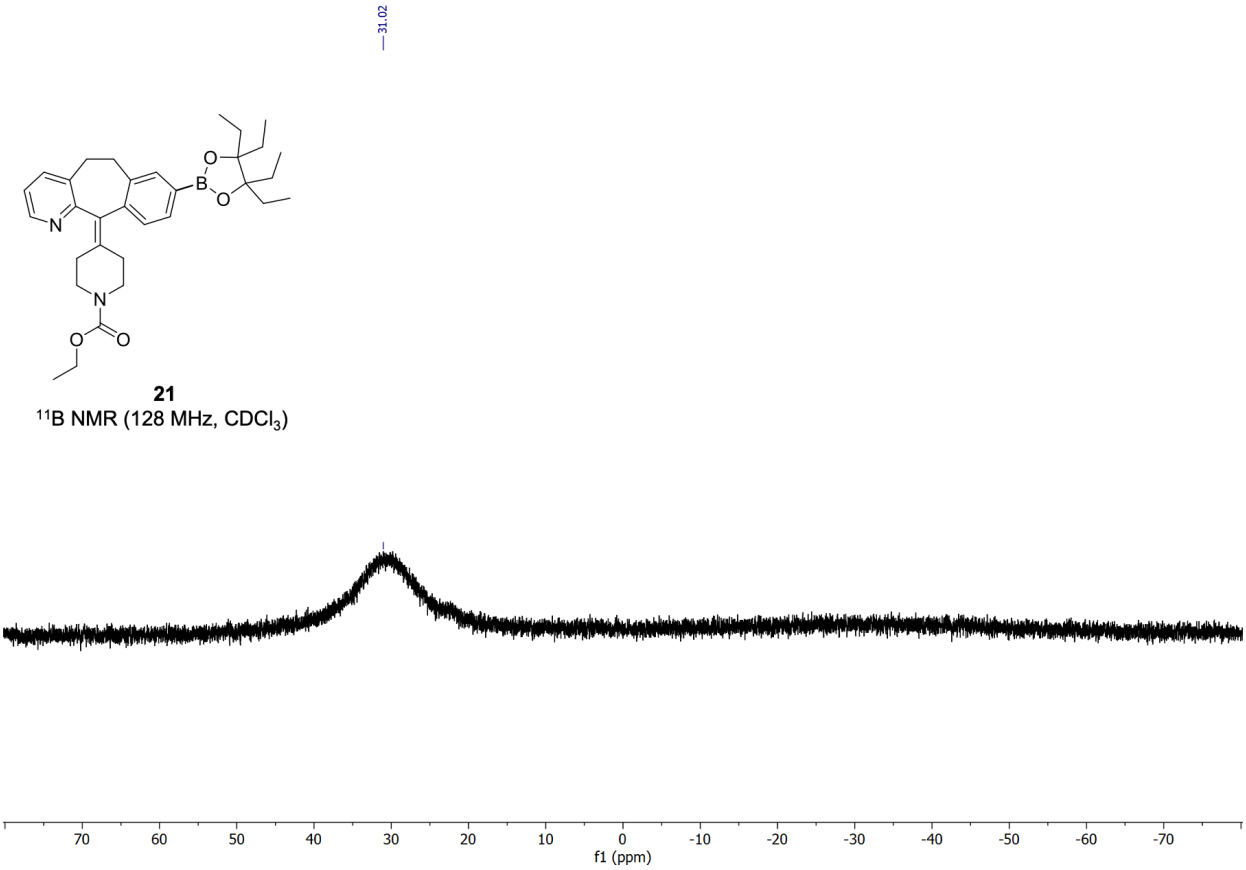
21

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



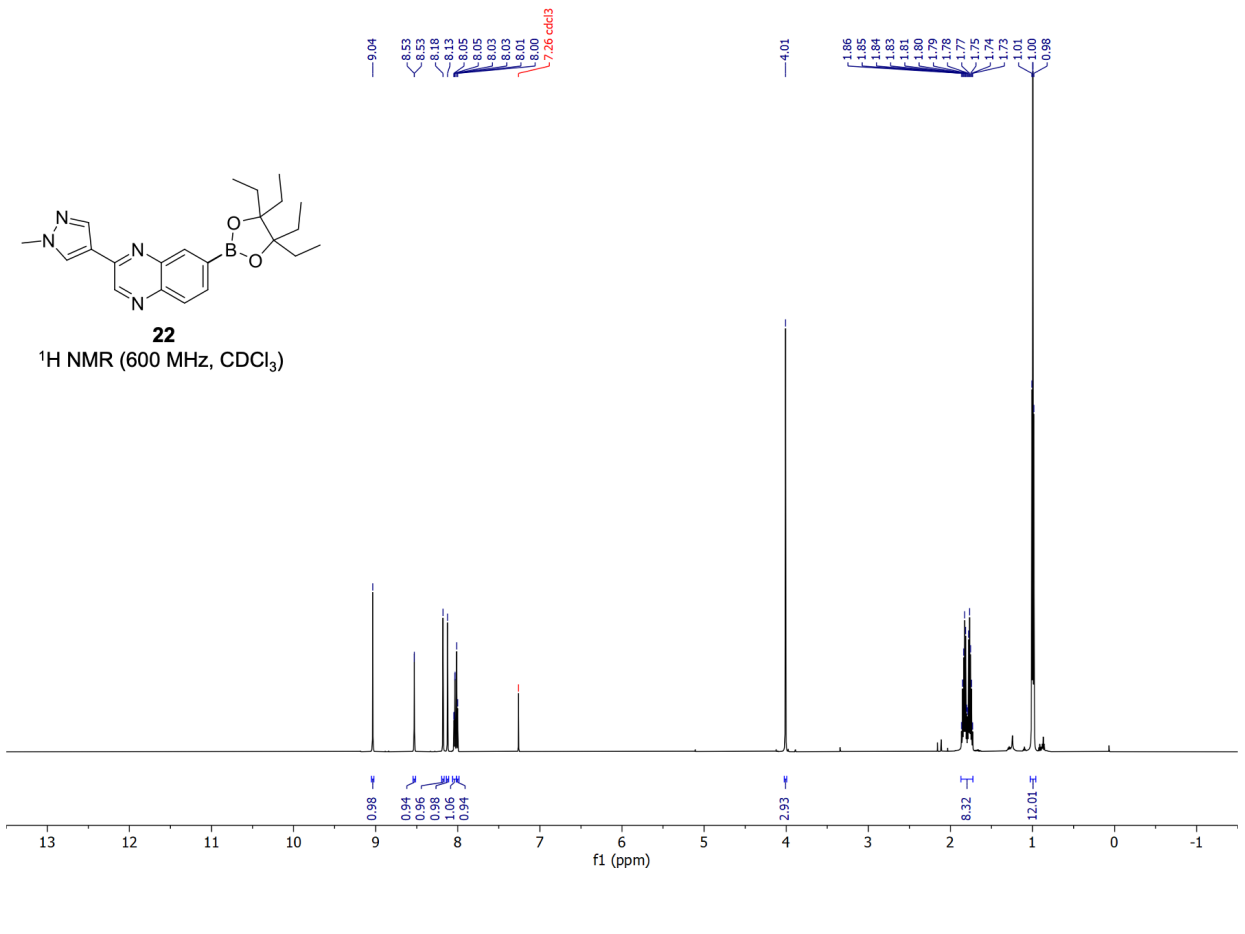
21

^{13}C NMR (126 MHz, $CDCl_3$)



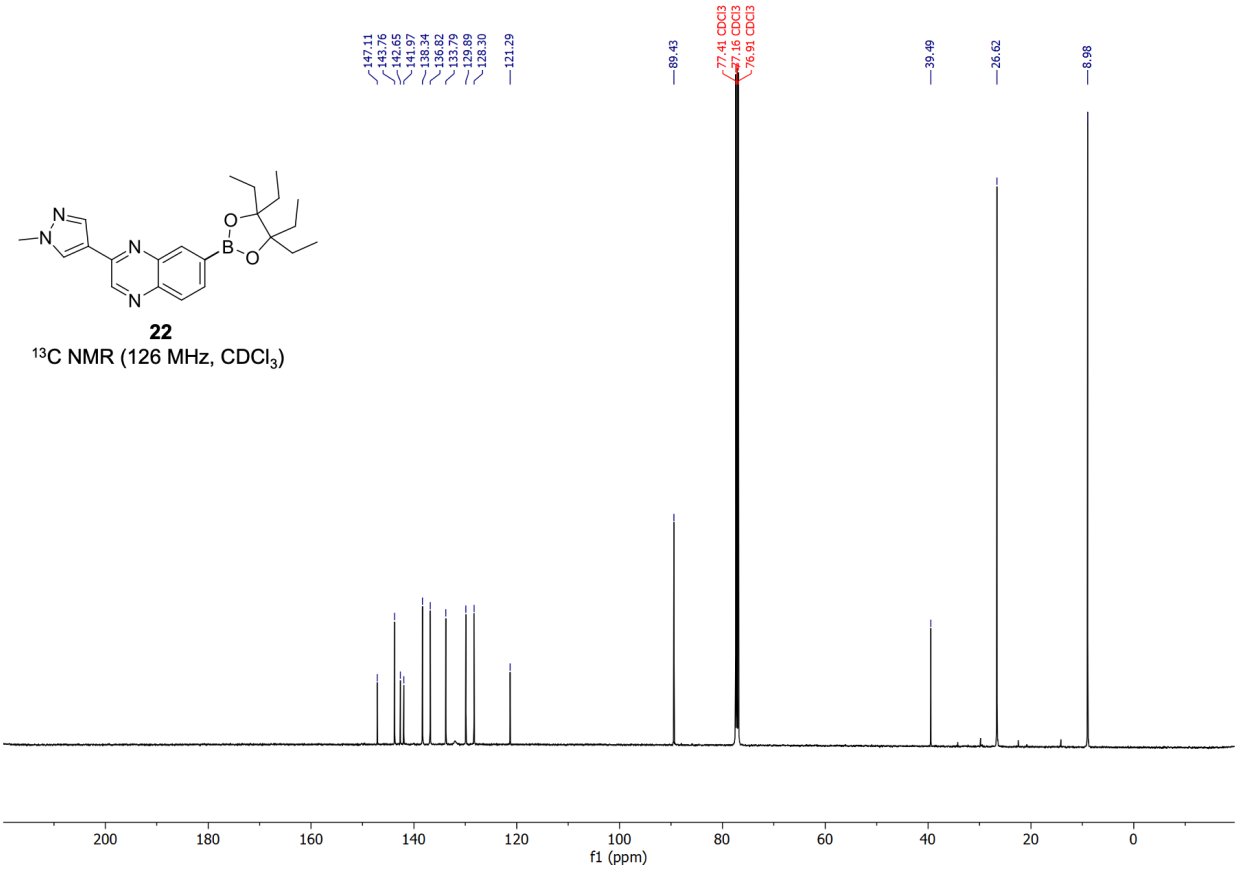
21

^{11}B NMR (128 MHz, $CDCl_3$)



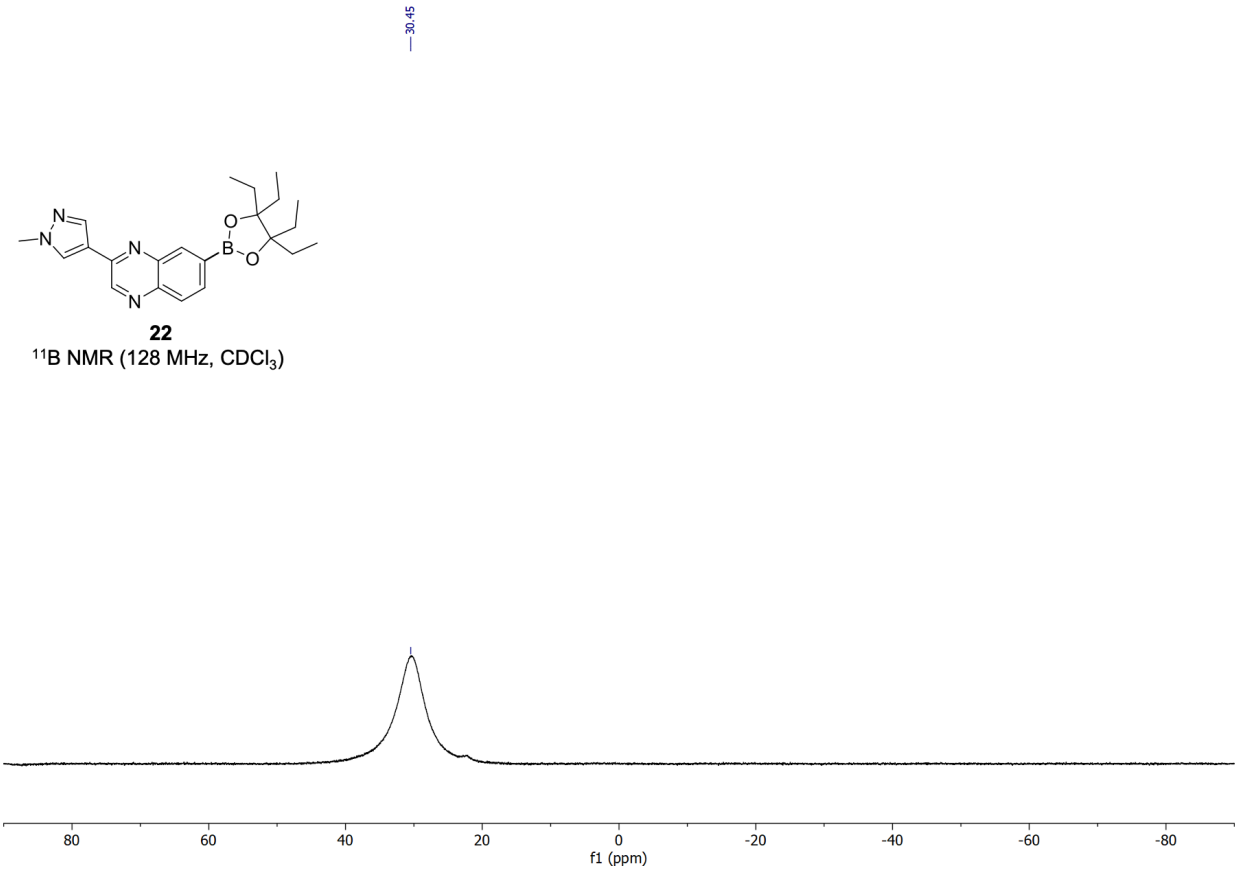
22

^{1}H NMR (600 MHz, $CDCl_3$)



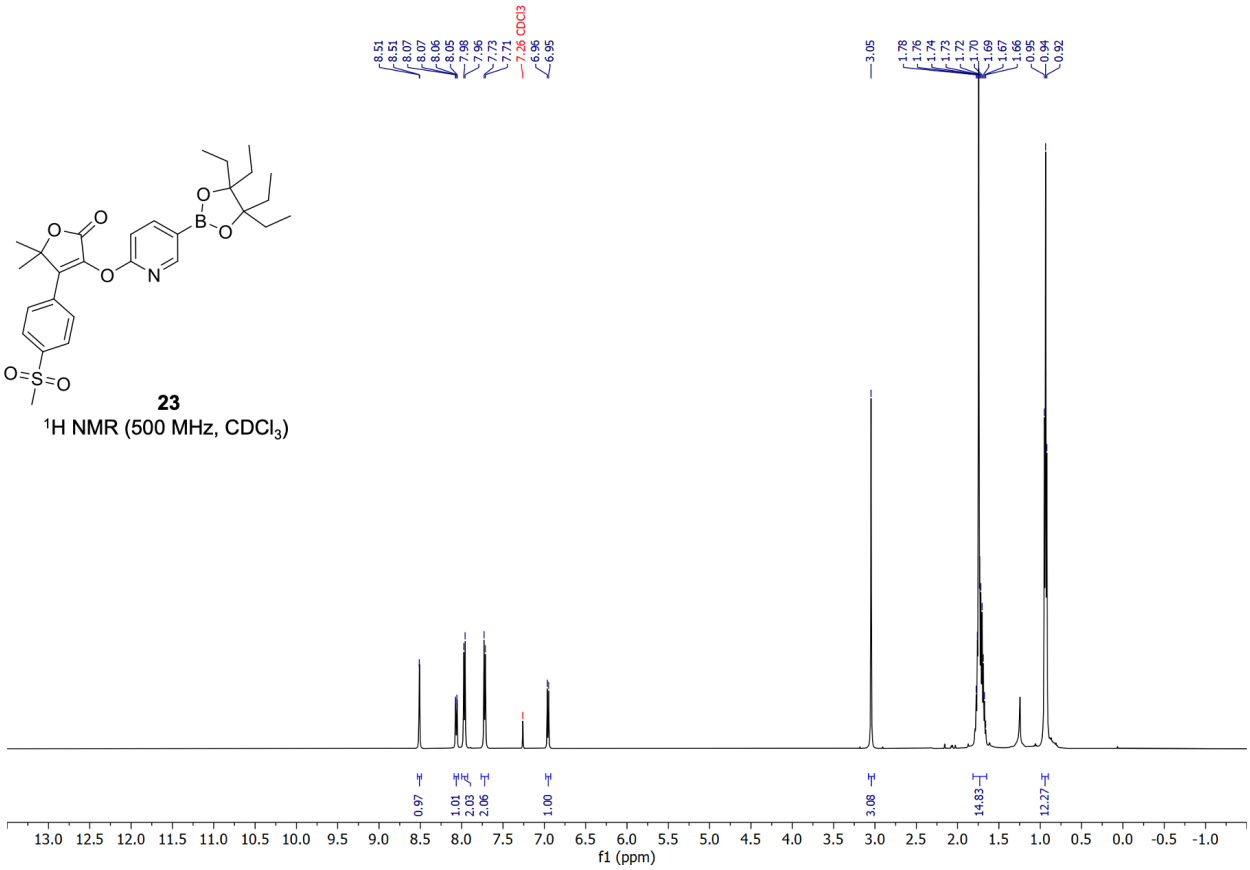
22

^{13}C NMR (126 MHz, $CDCl_3$)



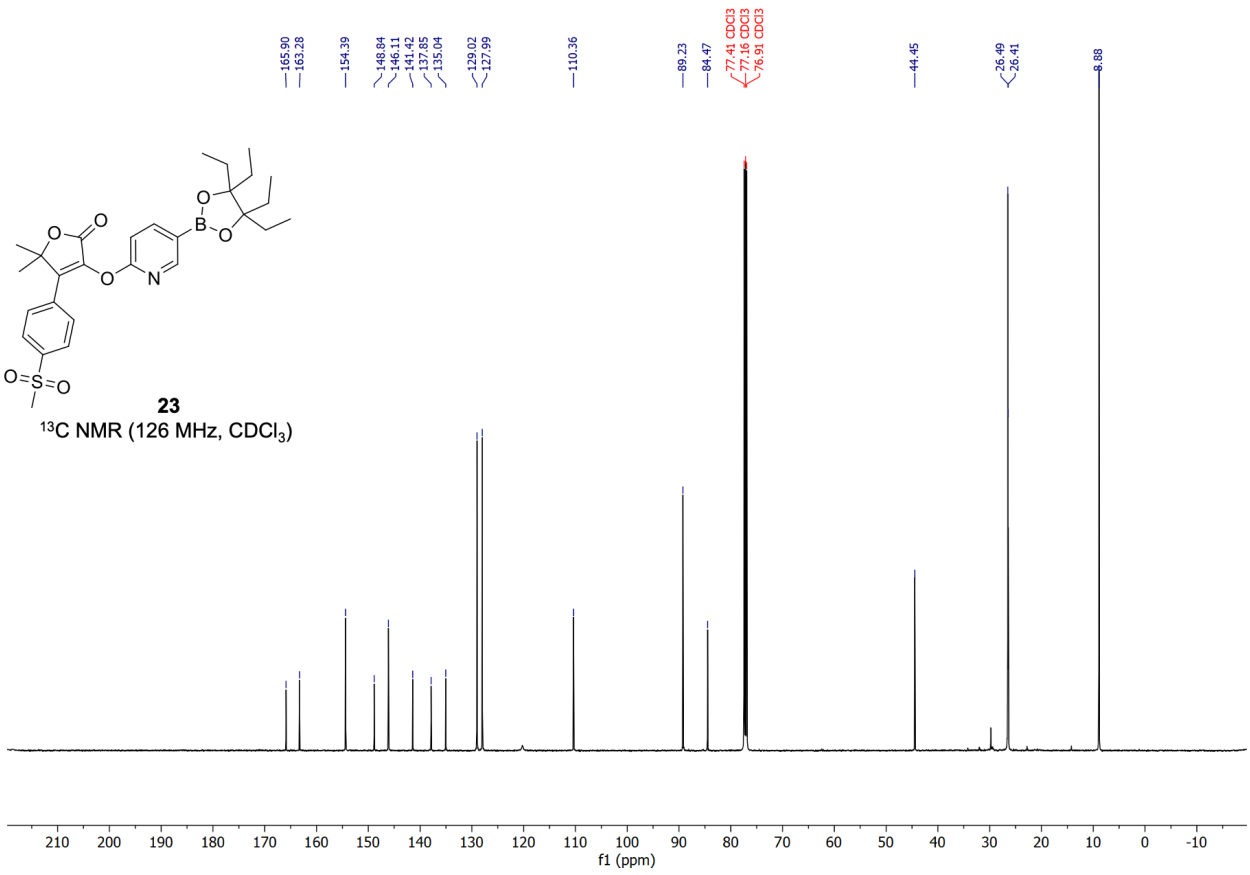
22

^{11}B NMR (128 MHz, $CDCl_3$)



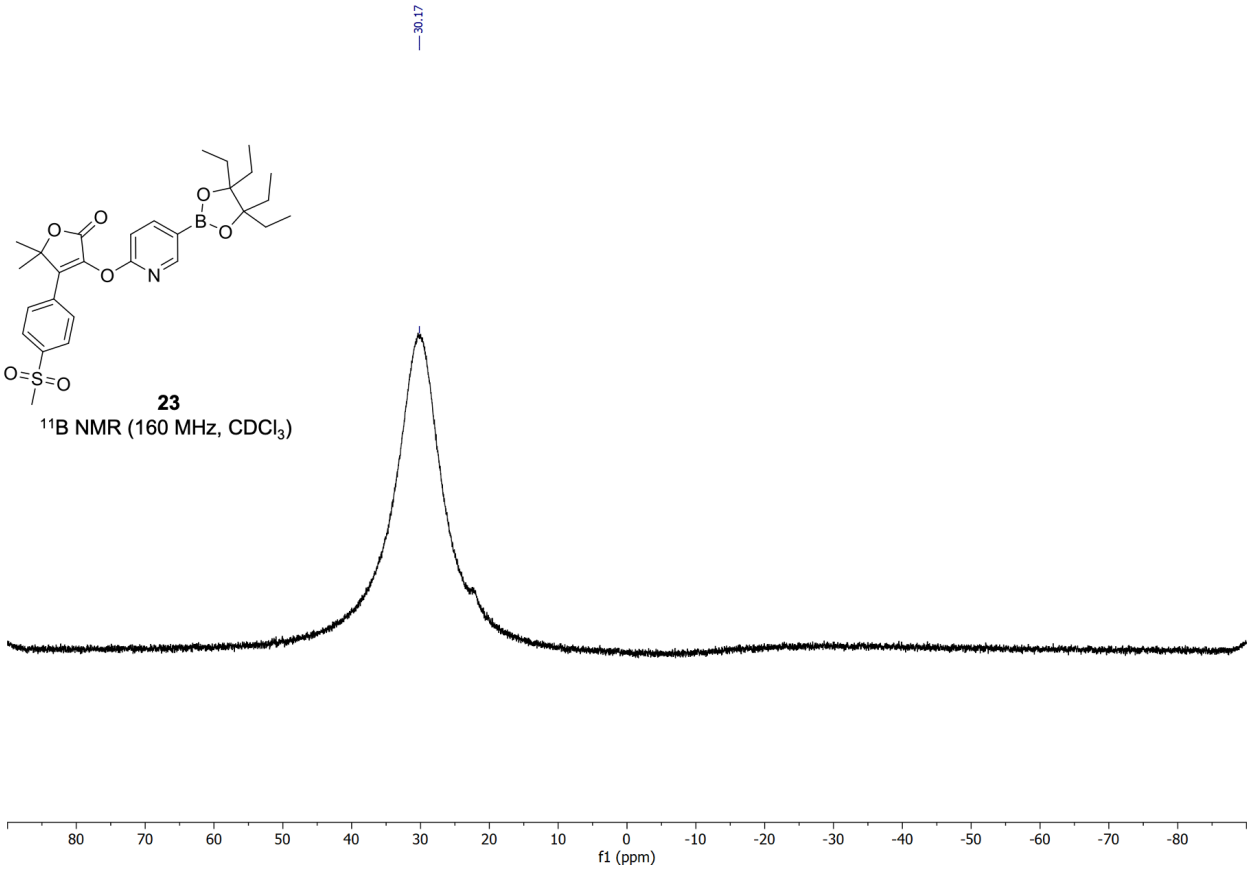
23

^{1}H NMR (500 MHz, $CDCl_3$)



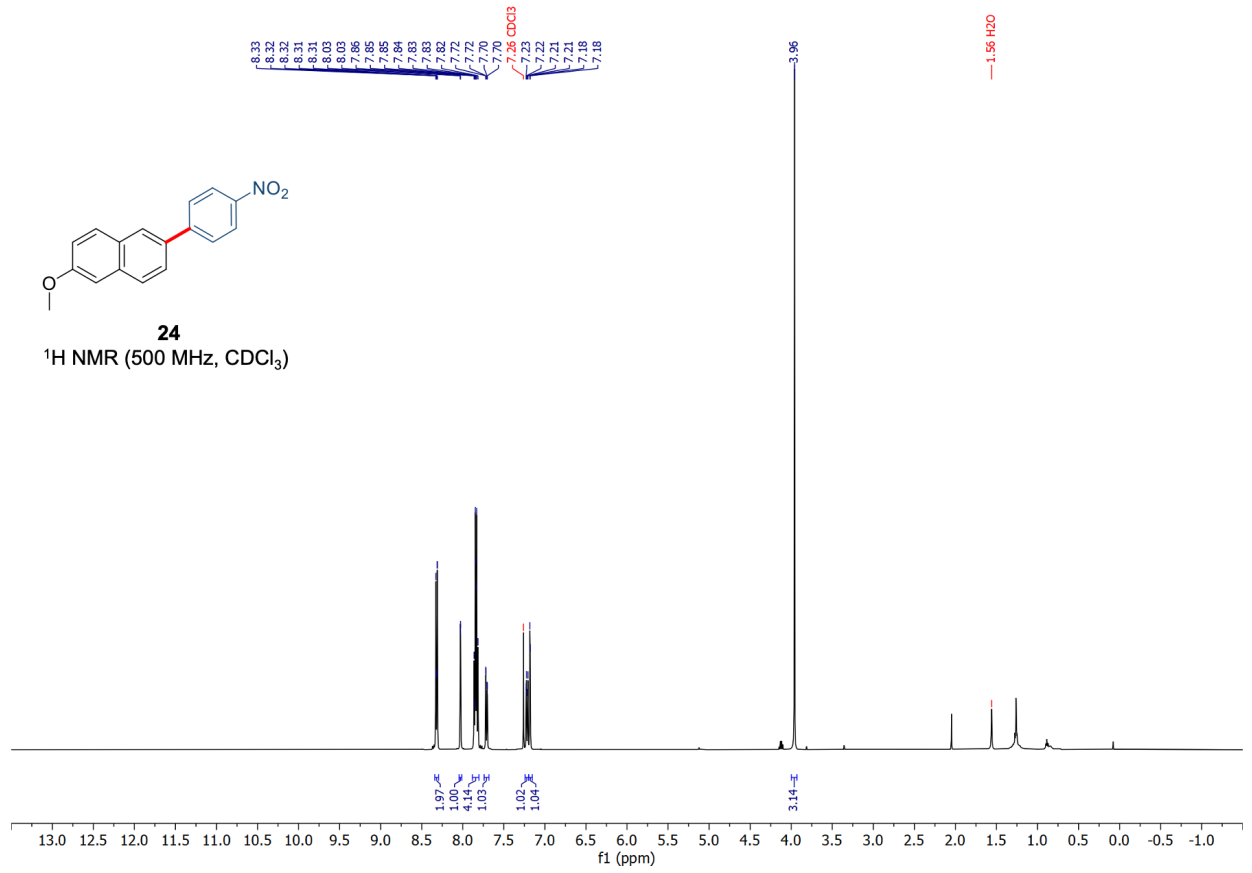
23

^{13}C NMR (126 MHz, $CDCl_3$)



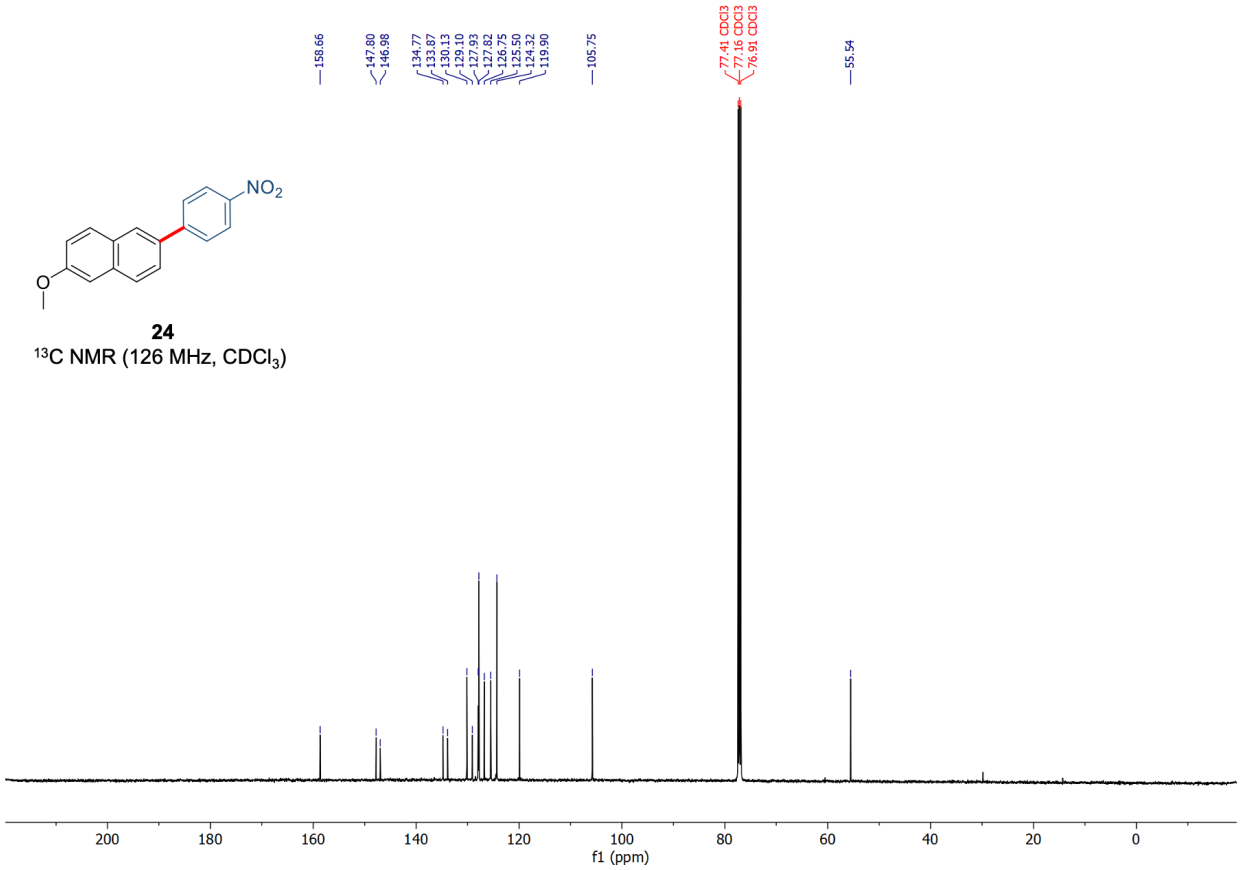
23

^{11}B NMR (160 MHz, $CDCl_3$)



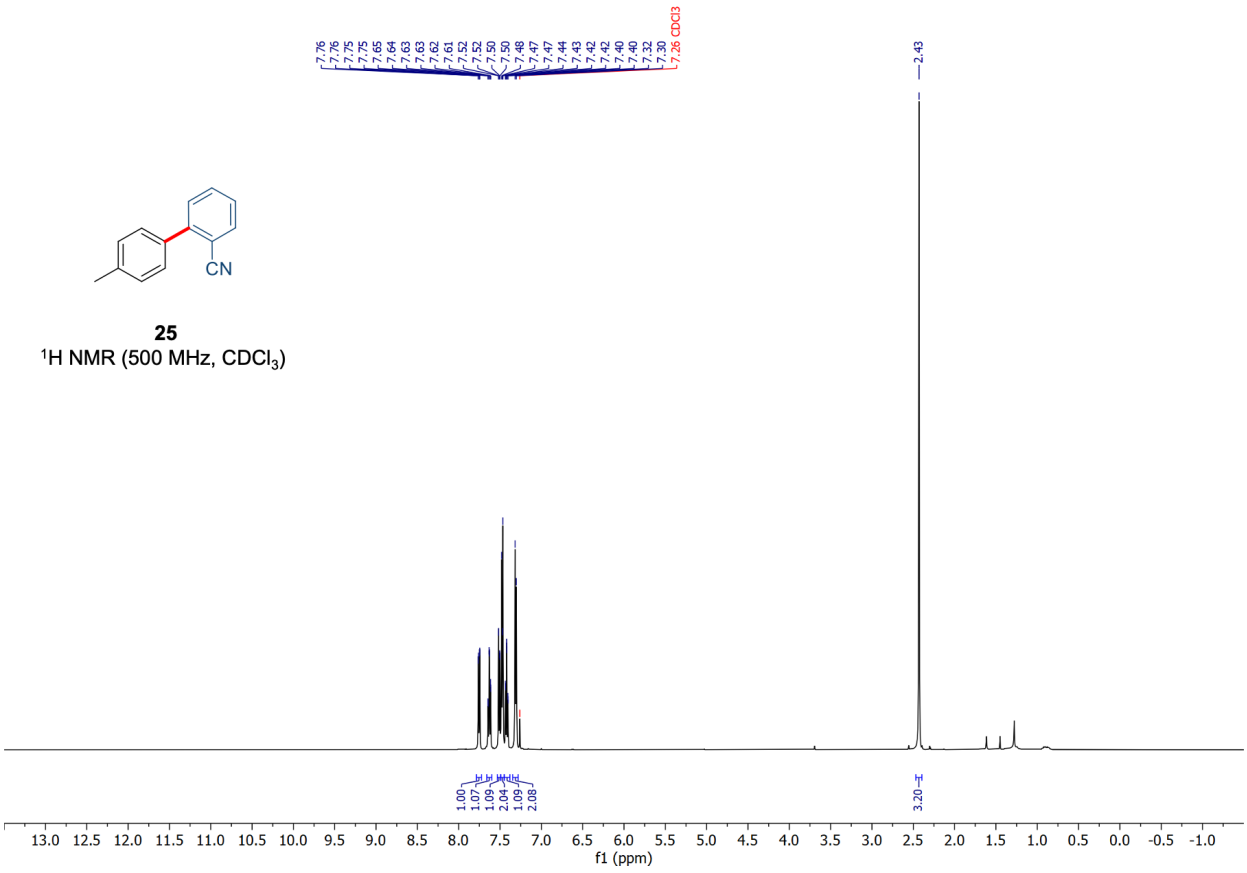
24

^{1}H NMR (500 MHz, $CDCl_3$)



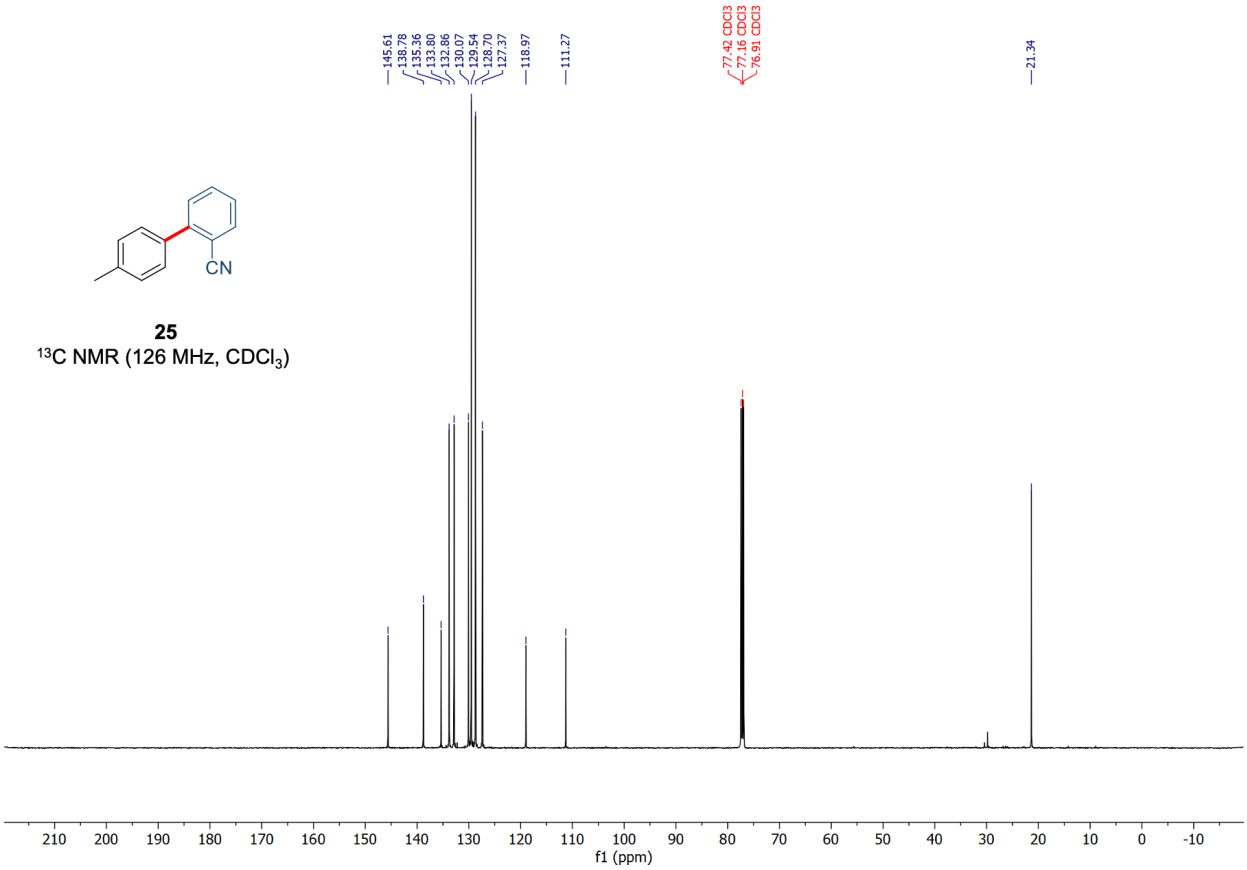
24

^{13}C NMR (126 MHz, $CDCl_3$)



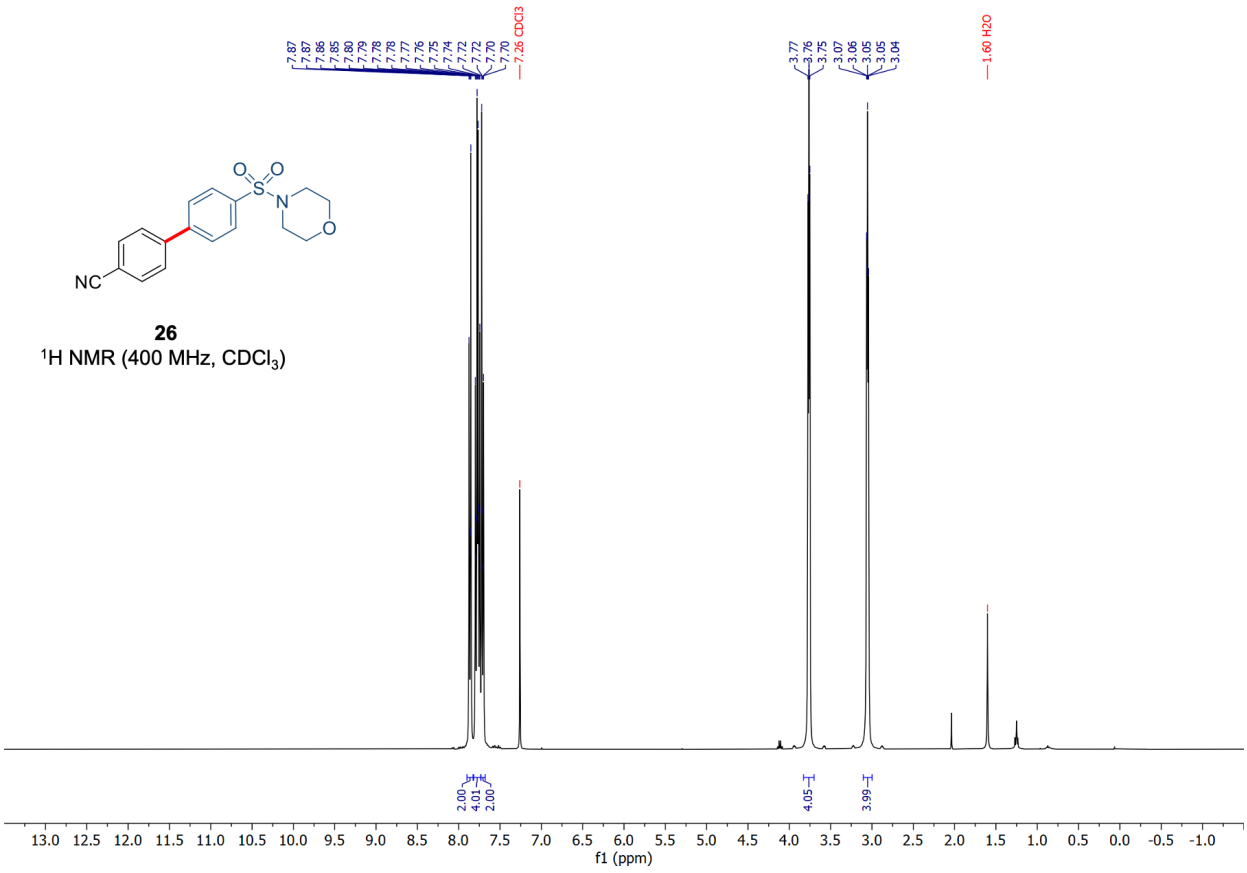
25

^{1}H NMR (500 MHz, $CDCl_3$)



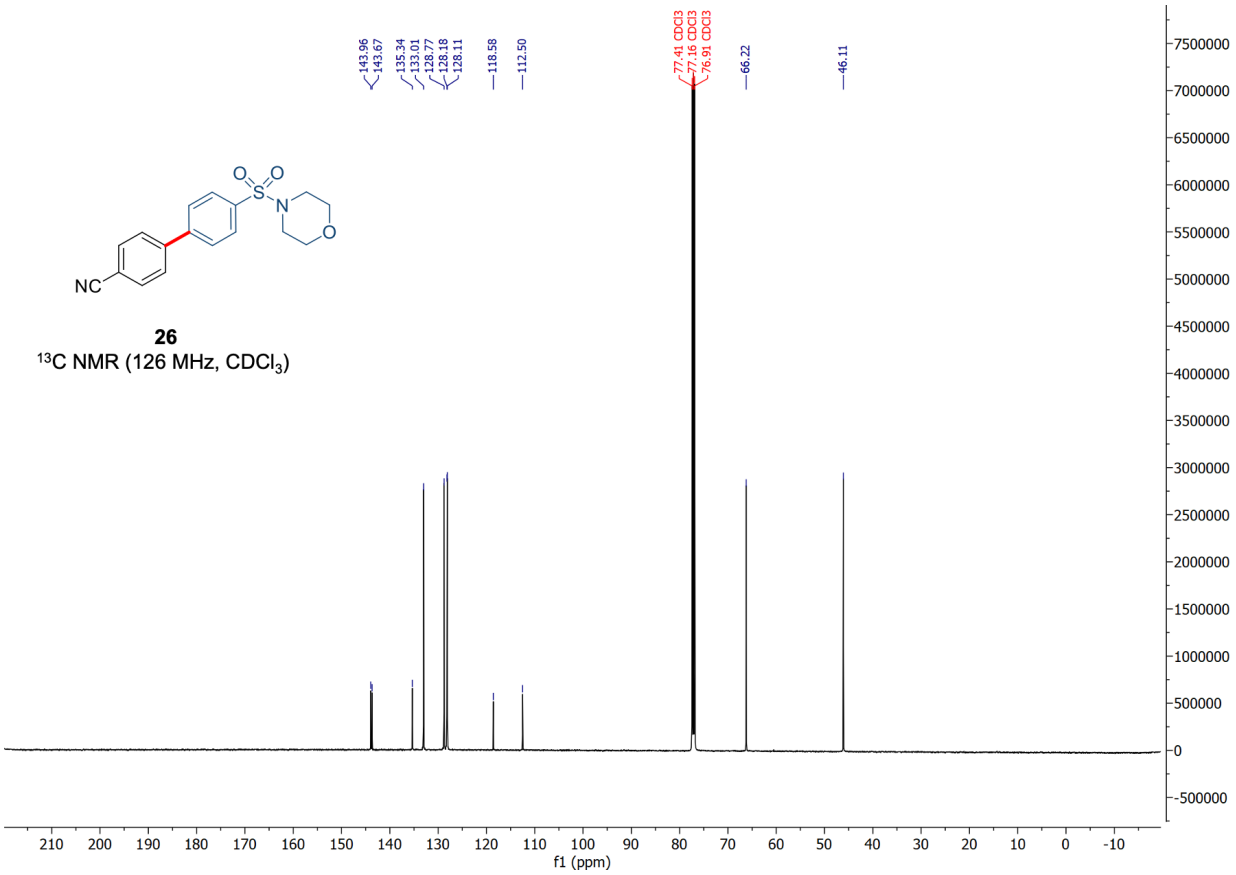
25

^{13}C NMR (126 MHz, $CDCl_3$)



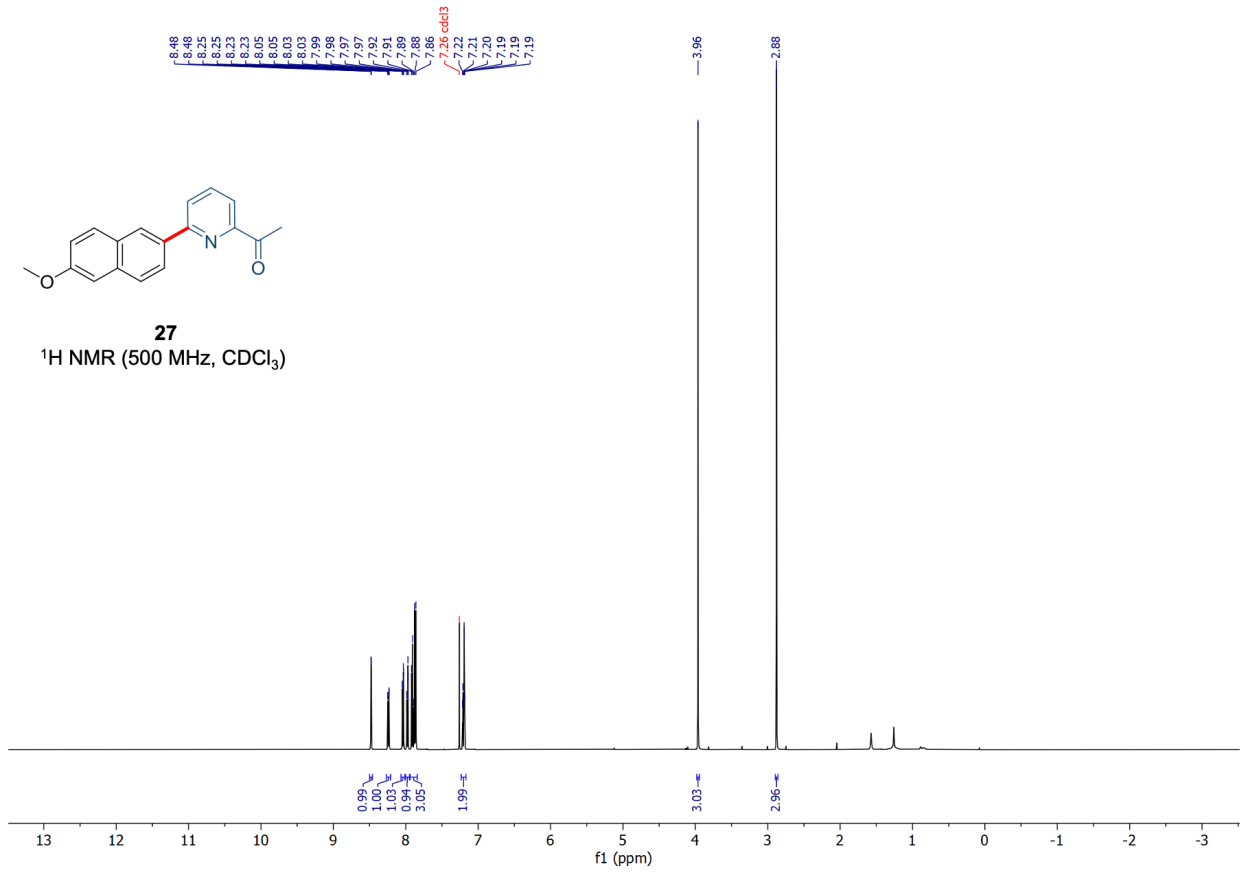
26

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



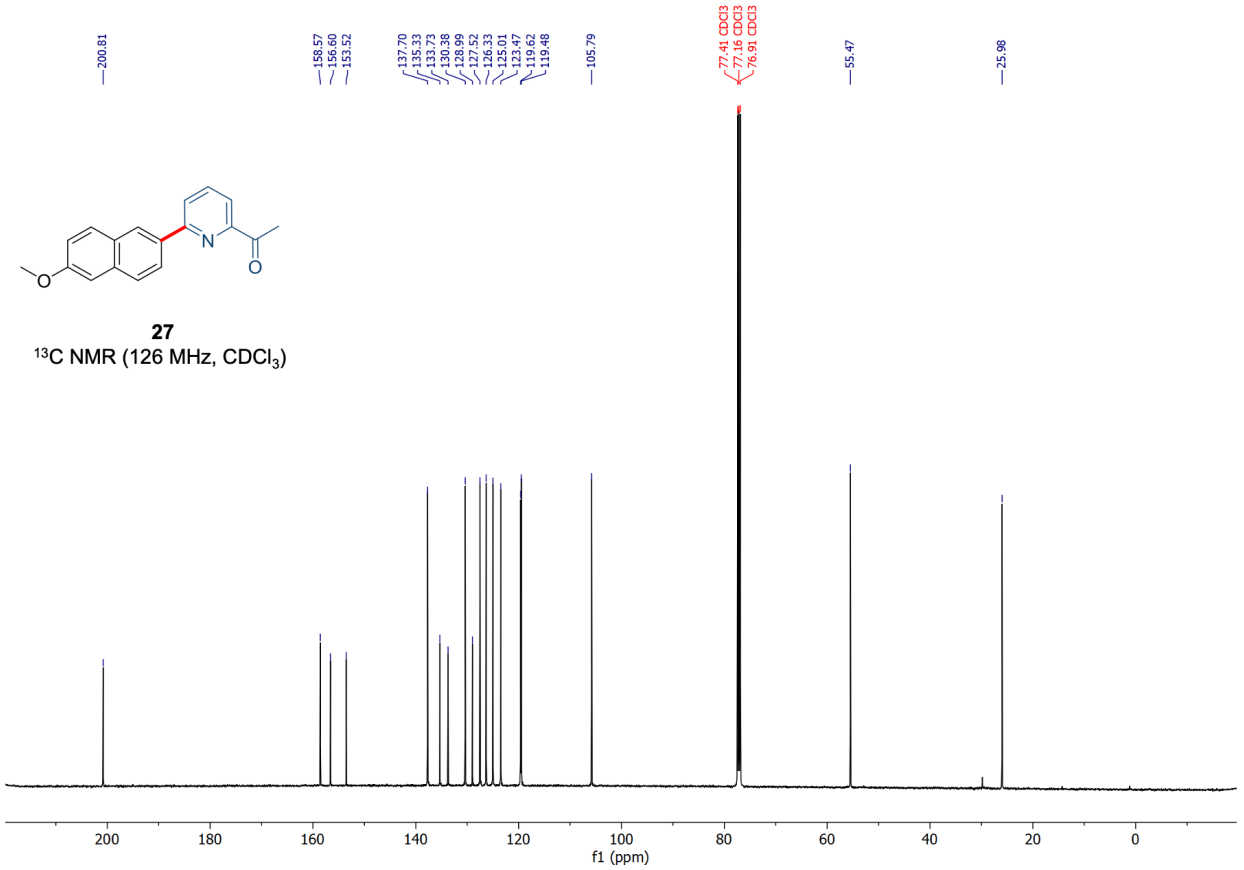
26

^{13}C NMR (126 MHz, $CDCl_3$)



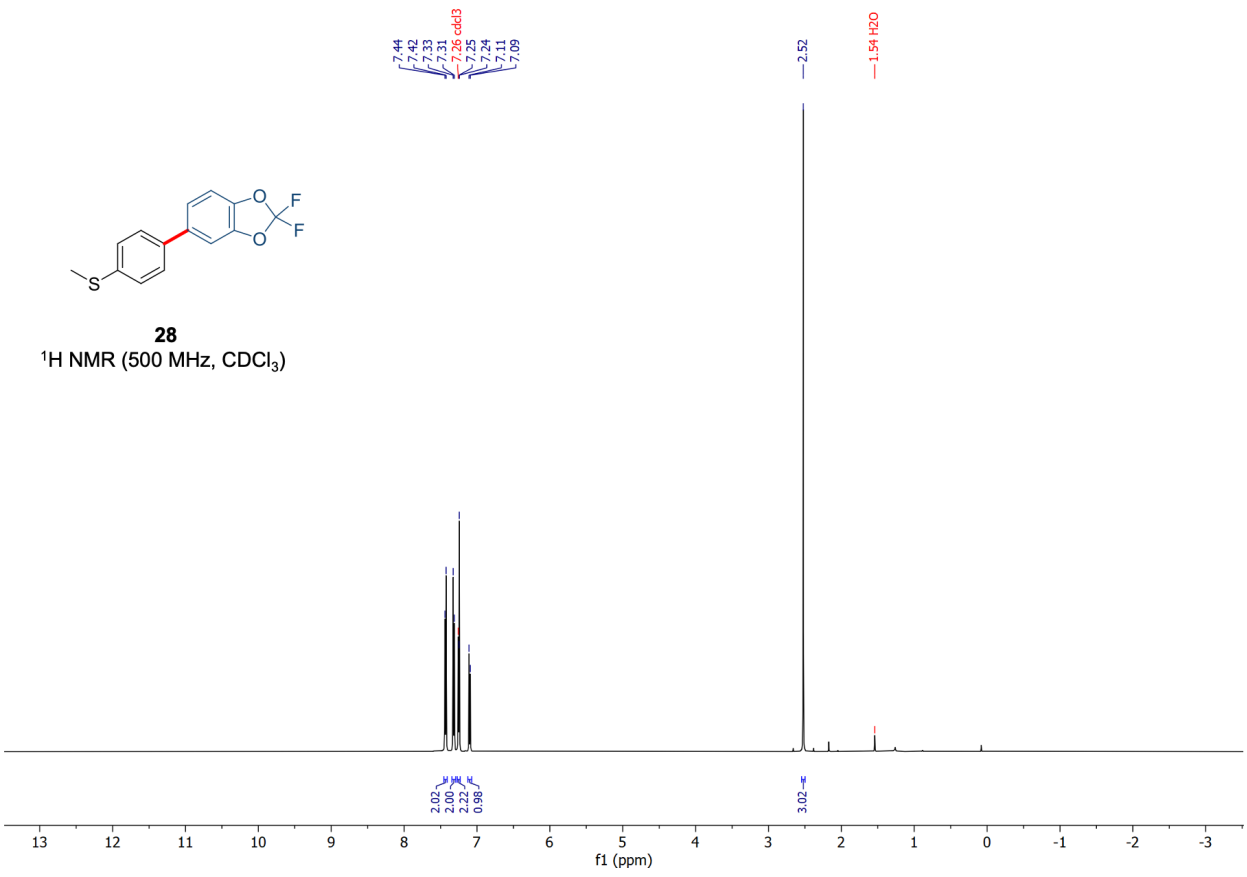
27

^{1}H NMR (500 MHz, $CDCl_3$)



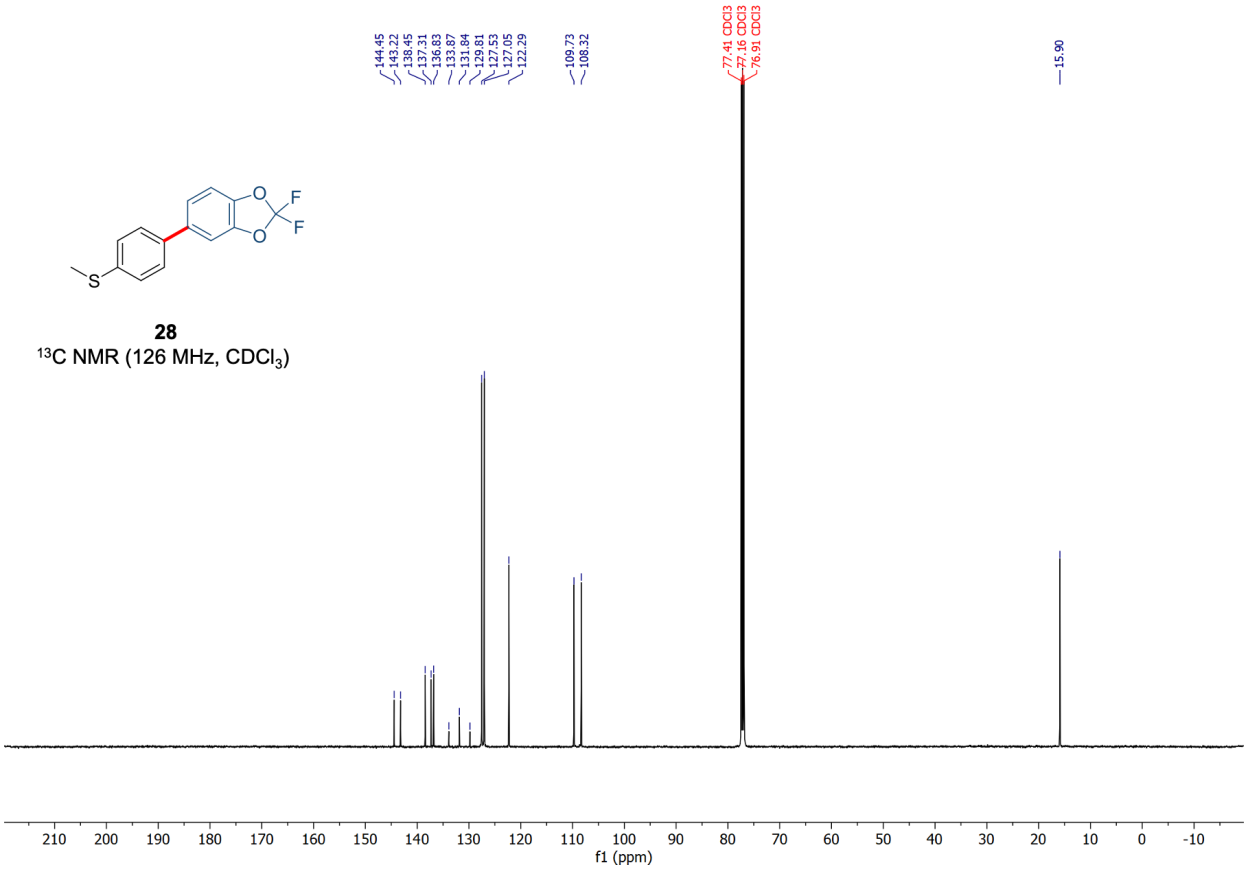
27

^{13}C NMR (126 MHz, $CDCl_3$)



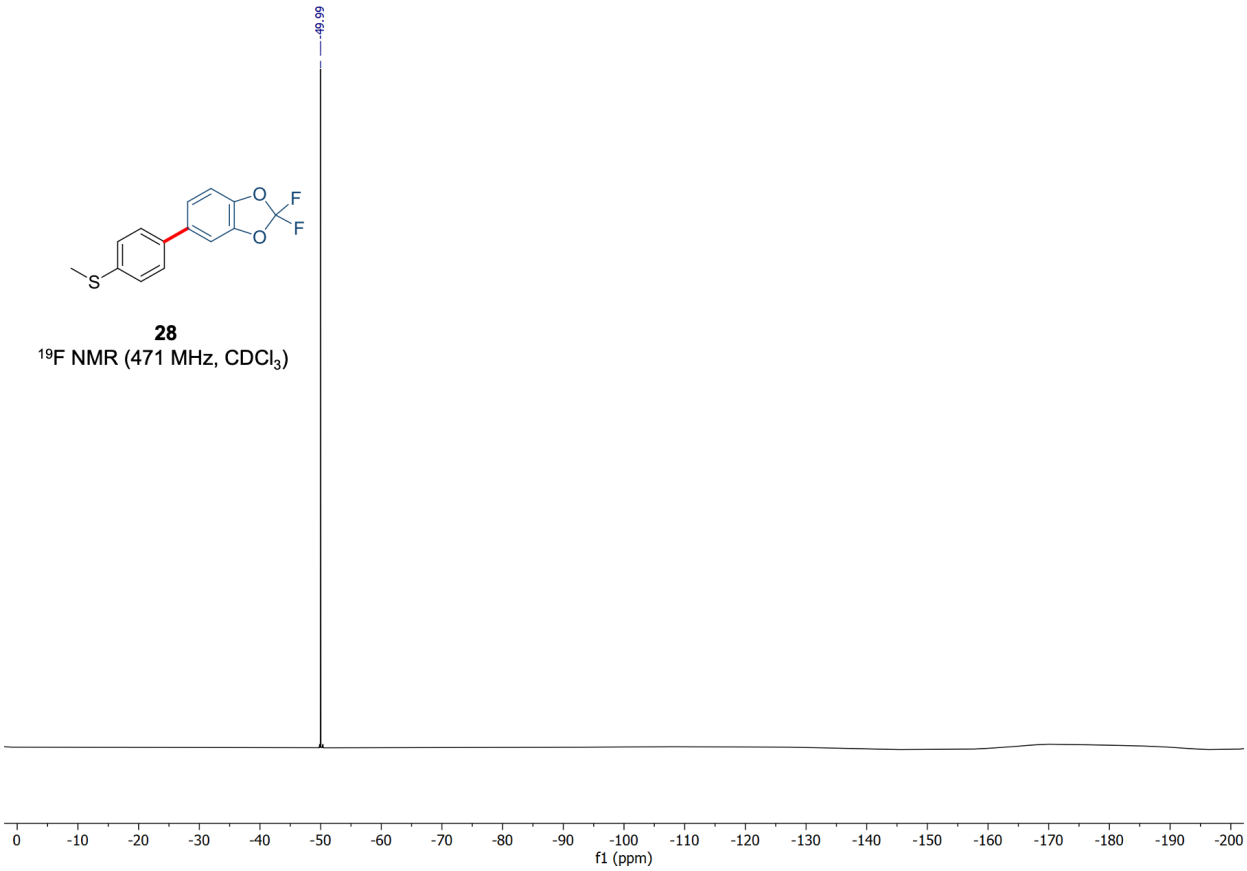
28

^{1}H NMR (500 MHz, $CDCl_3$)



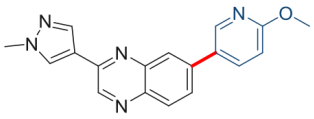
28

^{13}C NMR (126 MHz, $CDCl_3$)



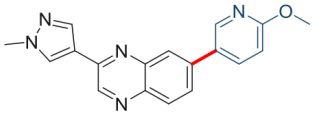
28

^{19}F NMR (471 MHz, $CDCl_3$)



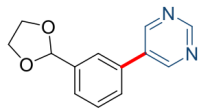
29

^{1}H NMR (500 MHz, $CDCl_3$)



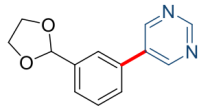
29

^{13}C NMR (126 MHz, $CDCl_3$)



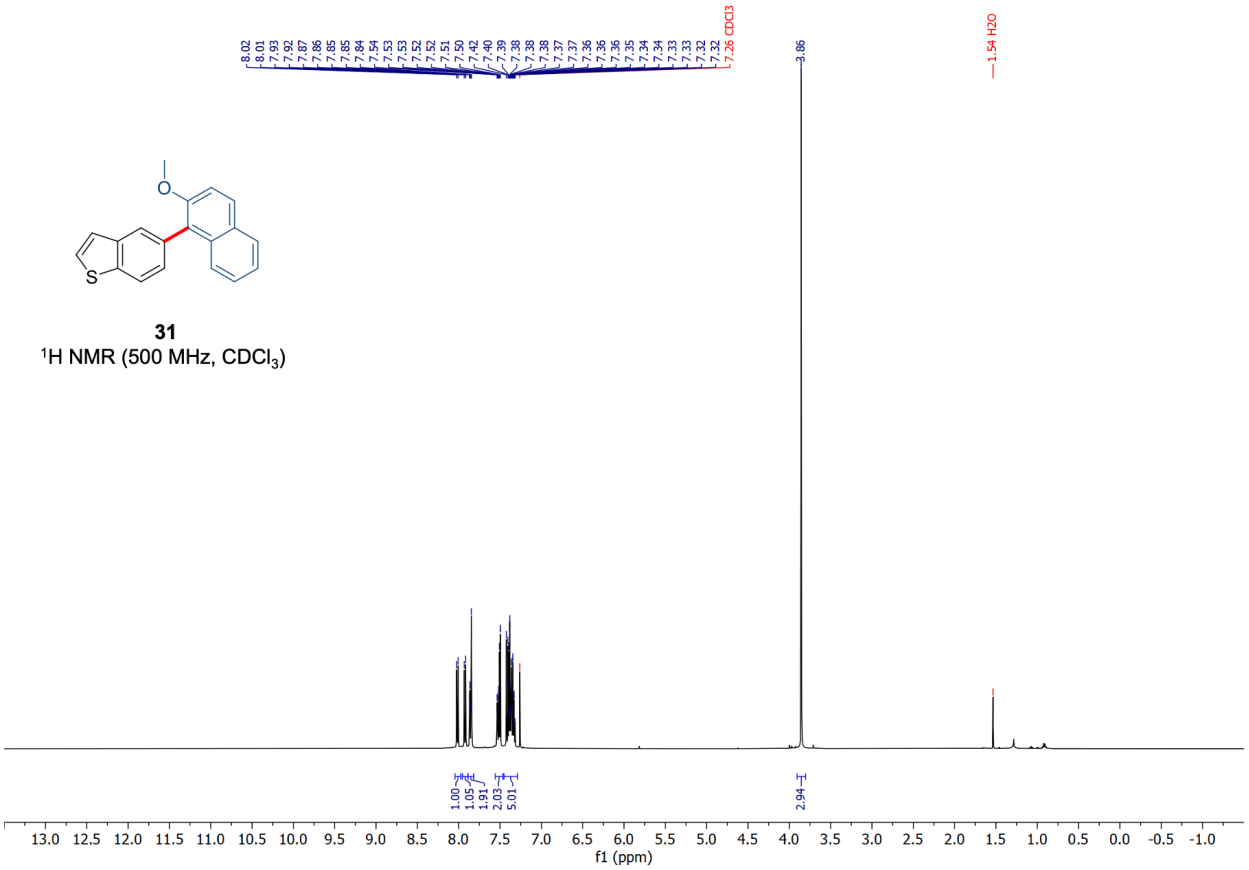
30

^{1}H NMR (500 MHz, $CDCl_3$)



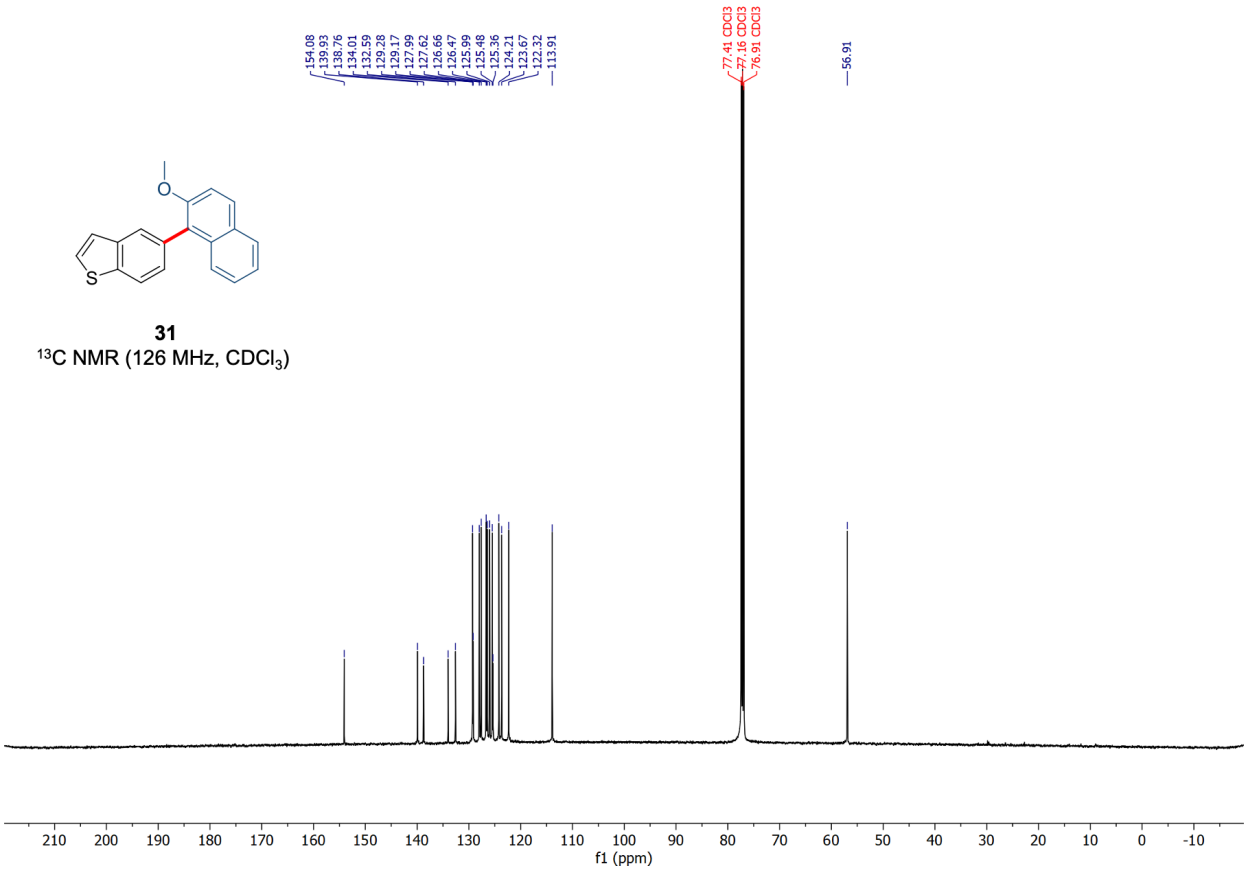
30

^{13}C NMR (126 MHz, $CDCl_3$)



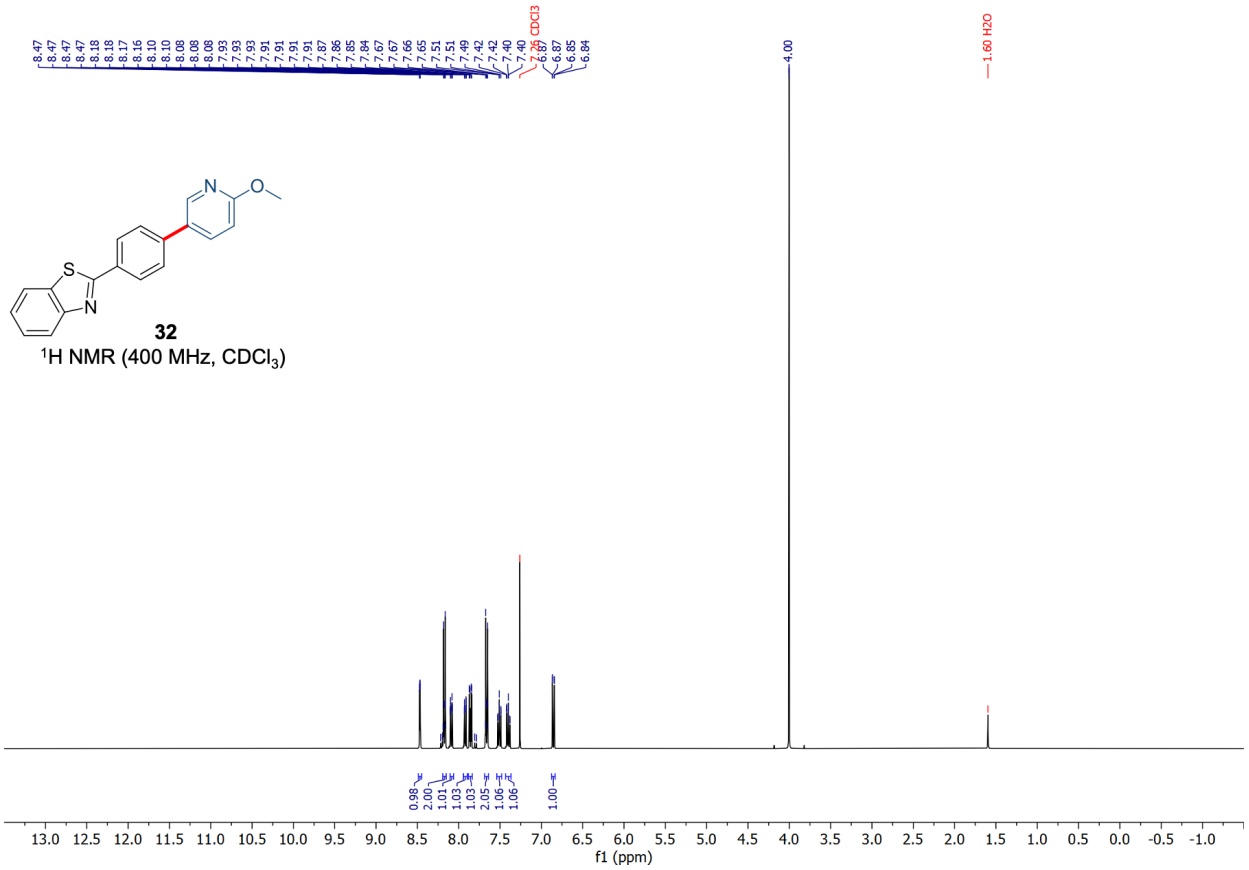
31

^{1}H NMR (500 MHz, $CDCl_3$)



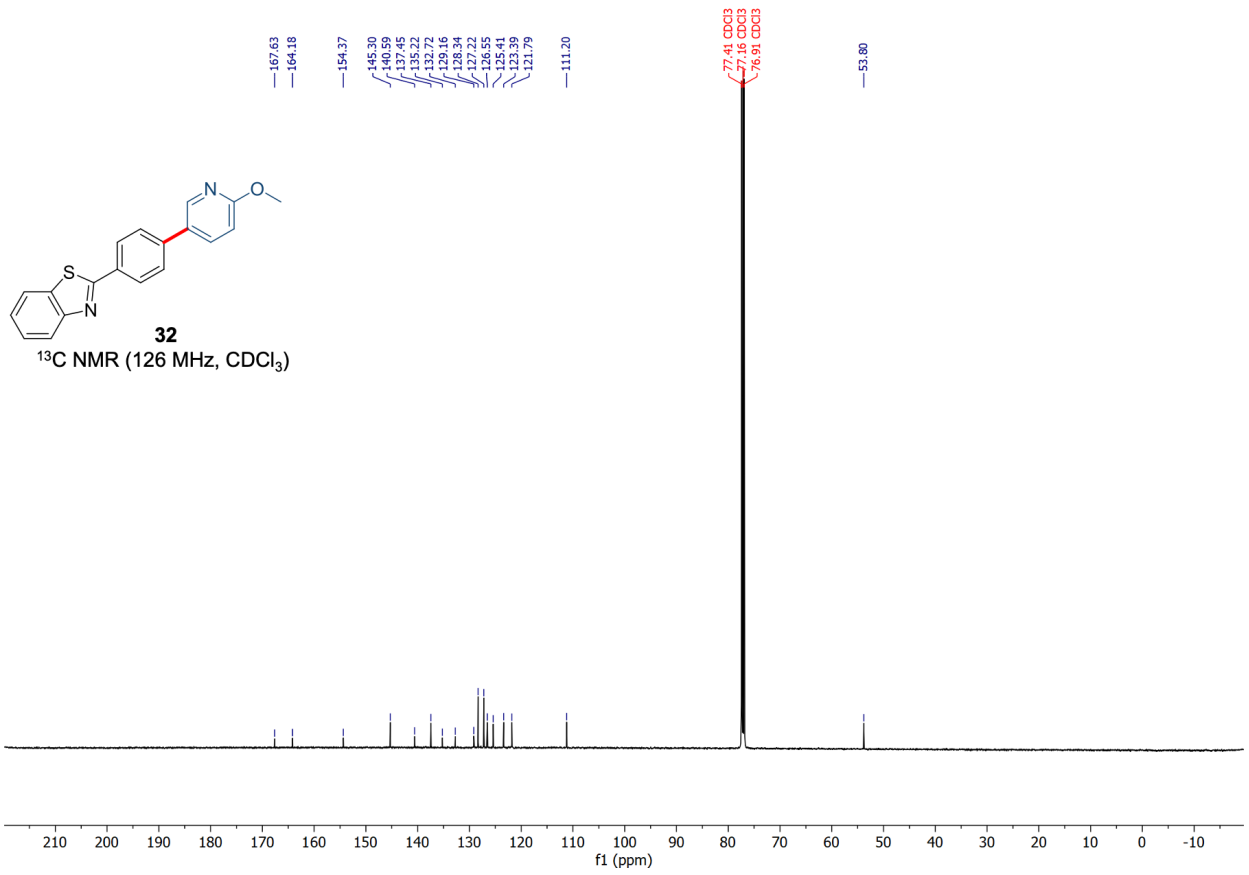
31

^{13}C NMR (126 MHz, $CDCl_3$)



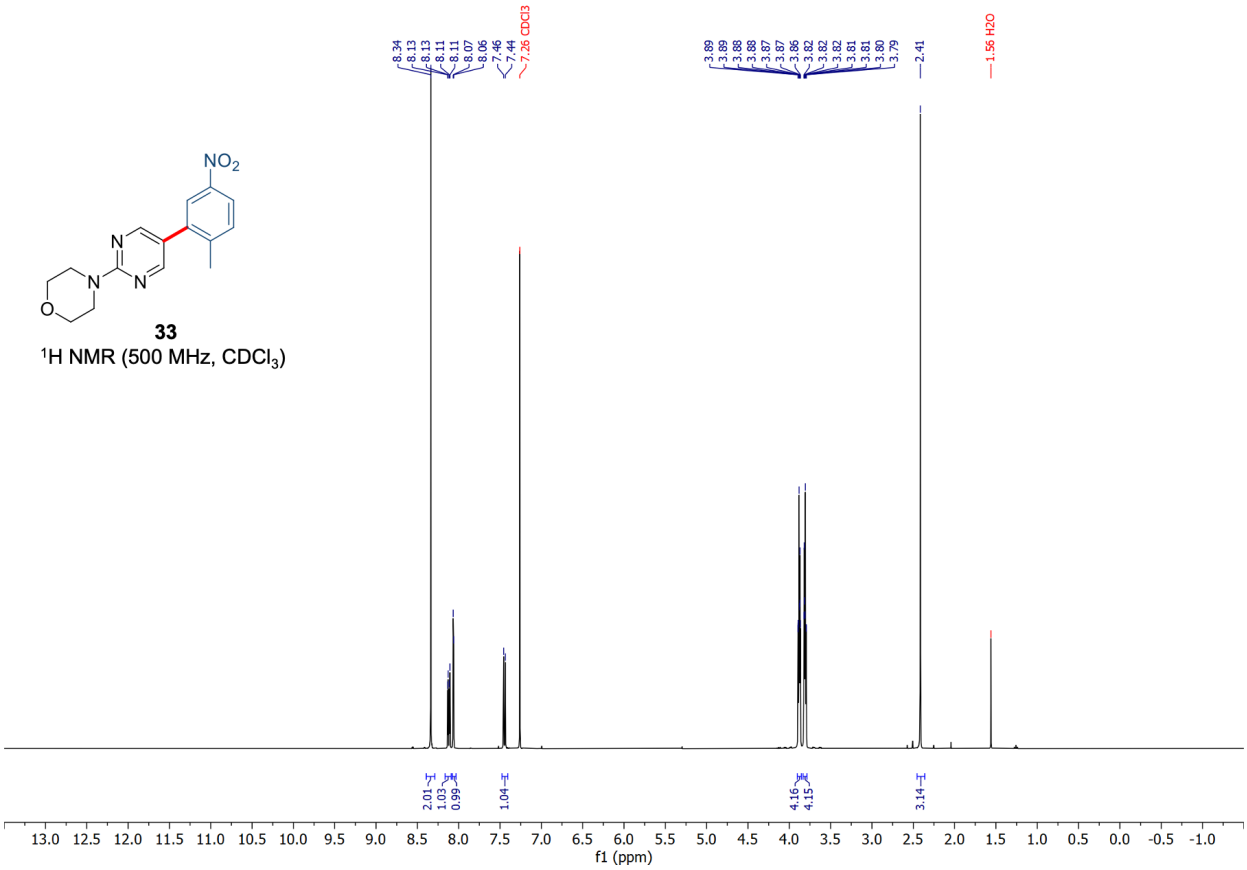
32

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



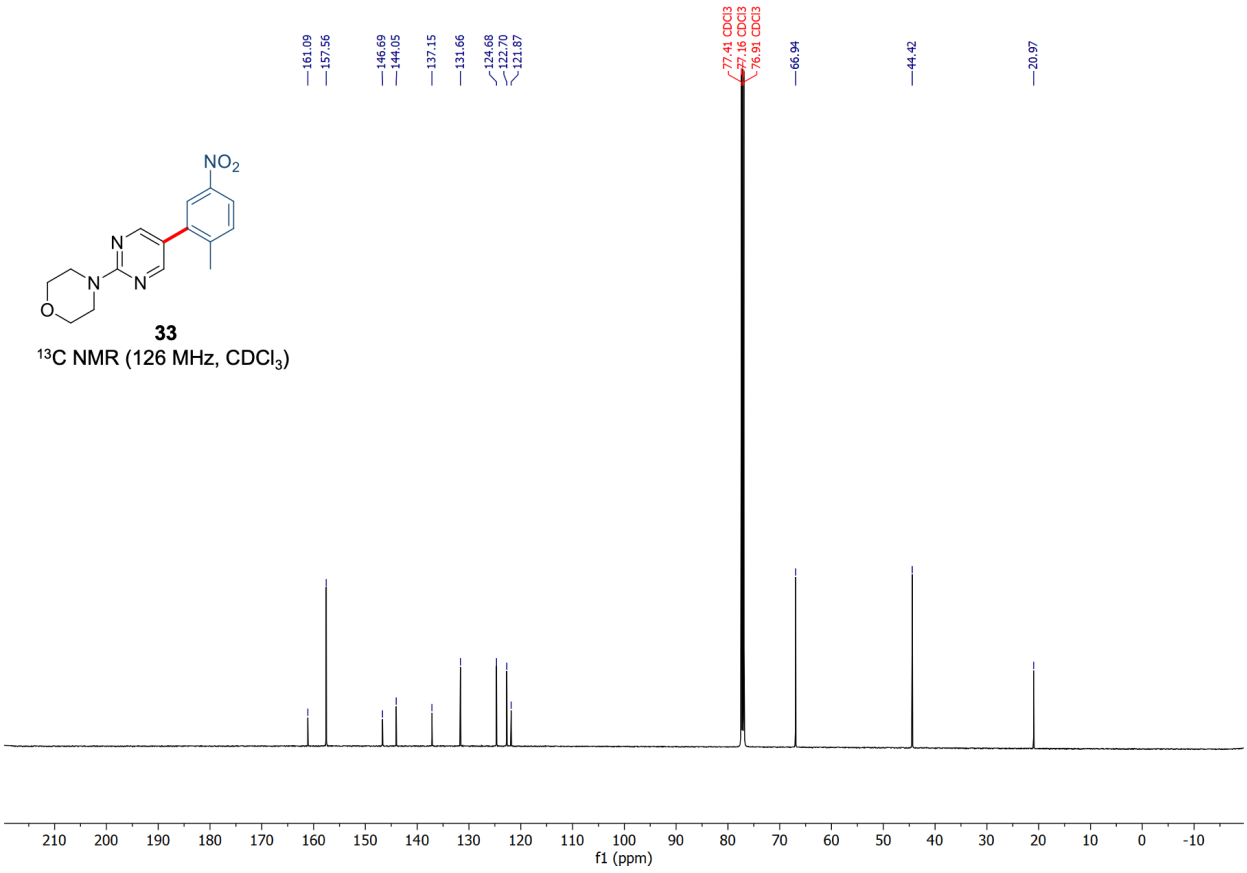
32

^{13}C NMR (126 MHz, $CDCl_3$)



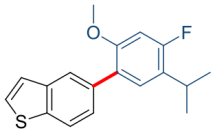
33

^{1}H NMR (500 MHz, $CDCl_3$)



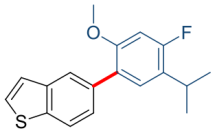
33

^{13}C NMR (126 MHz, $CDCl_3$)



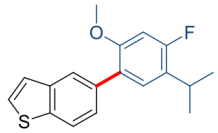
34

^{1}H NMR (500 MHz, $CDCl_3$)



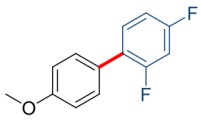
34

^{13}C NMR (101 MHz, $CDCl_3$)



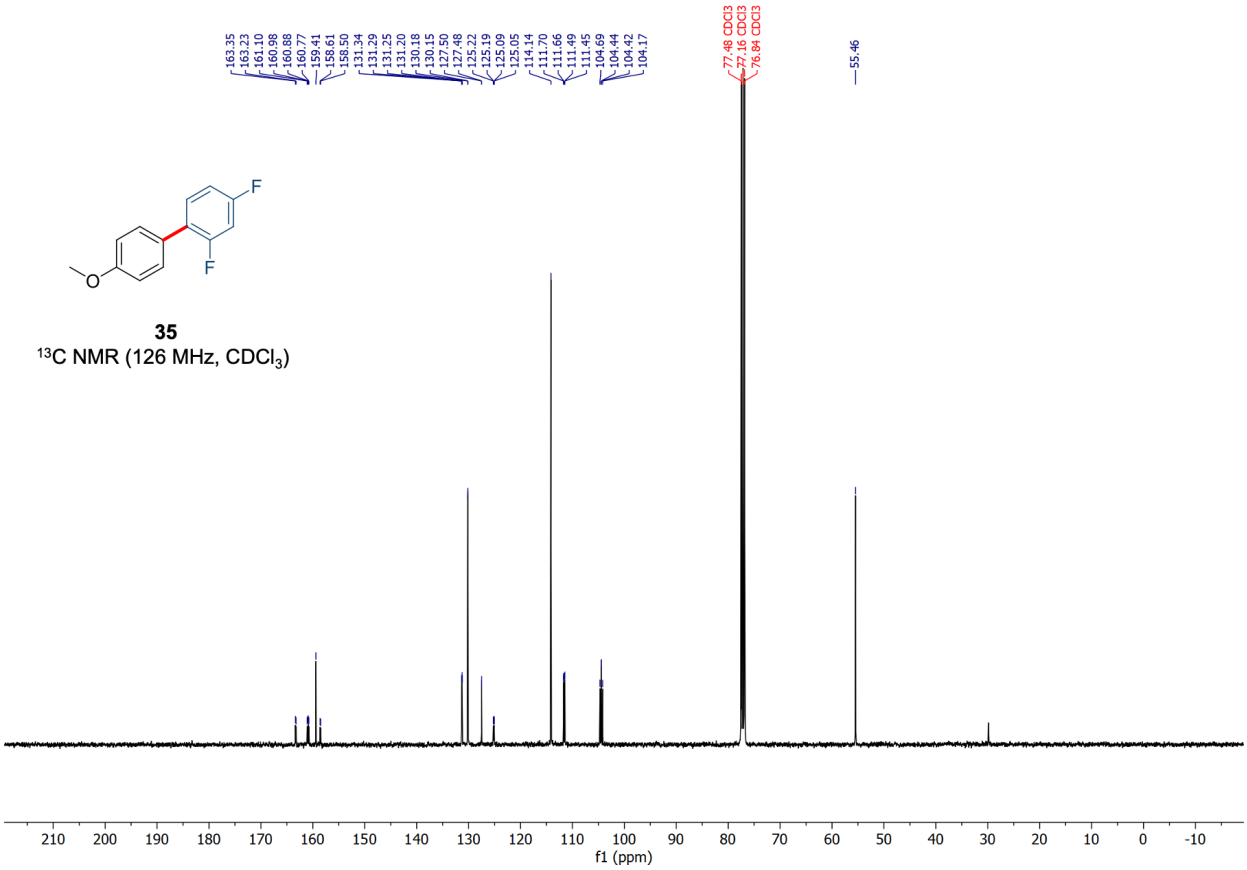
34

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



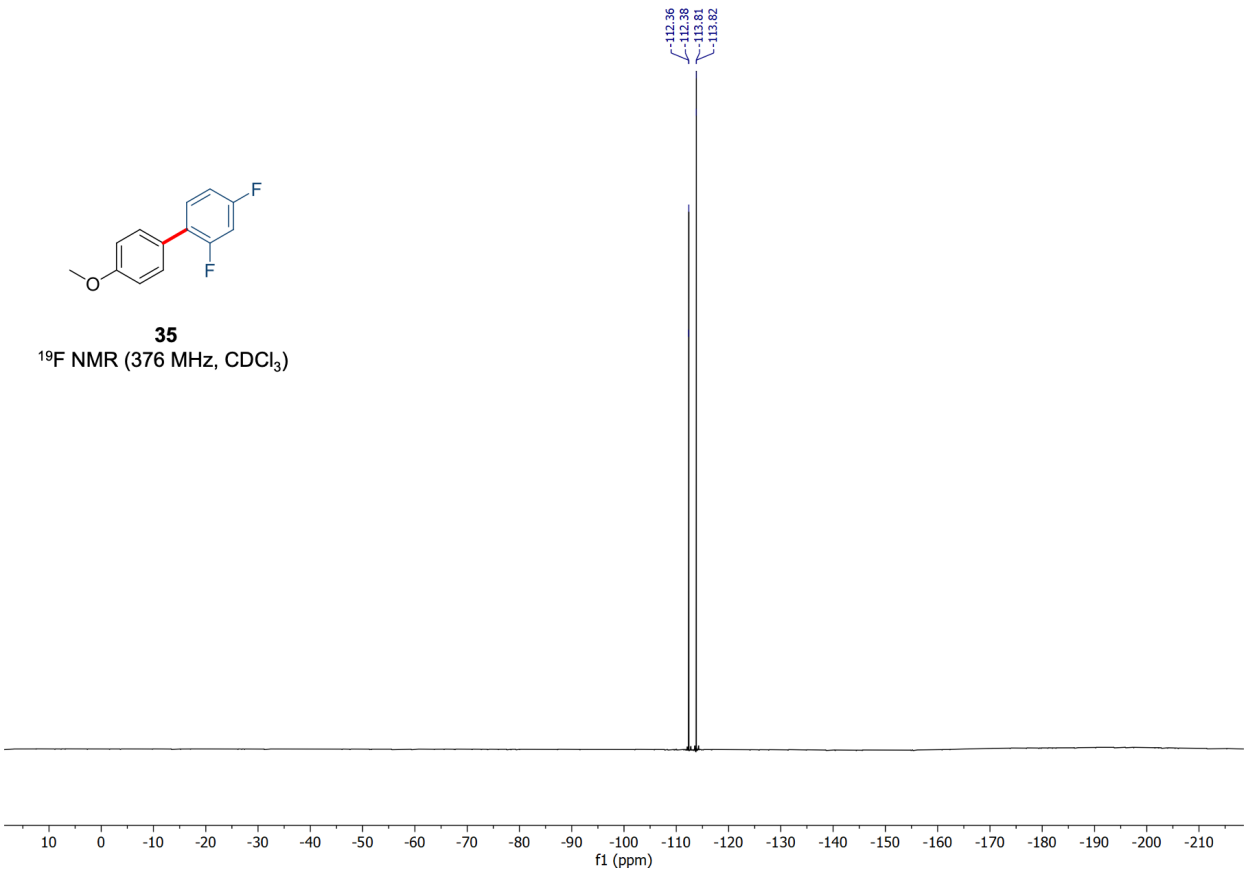
35

^{1}H NMR (500 MHz, $CDCl_3$)



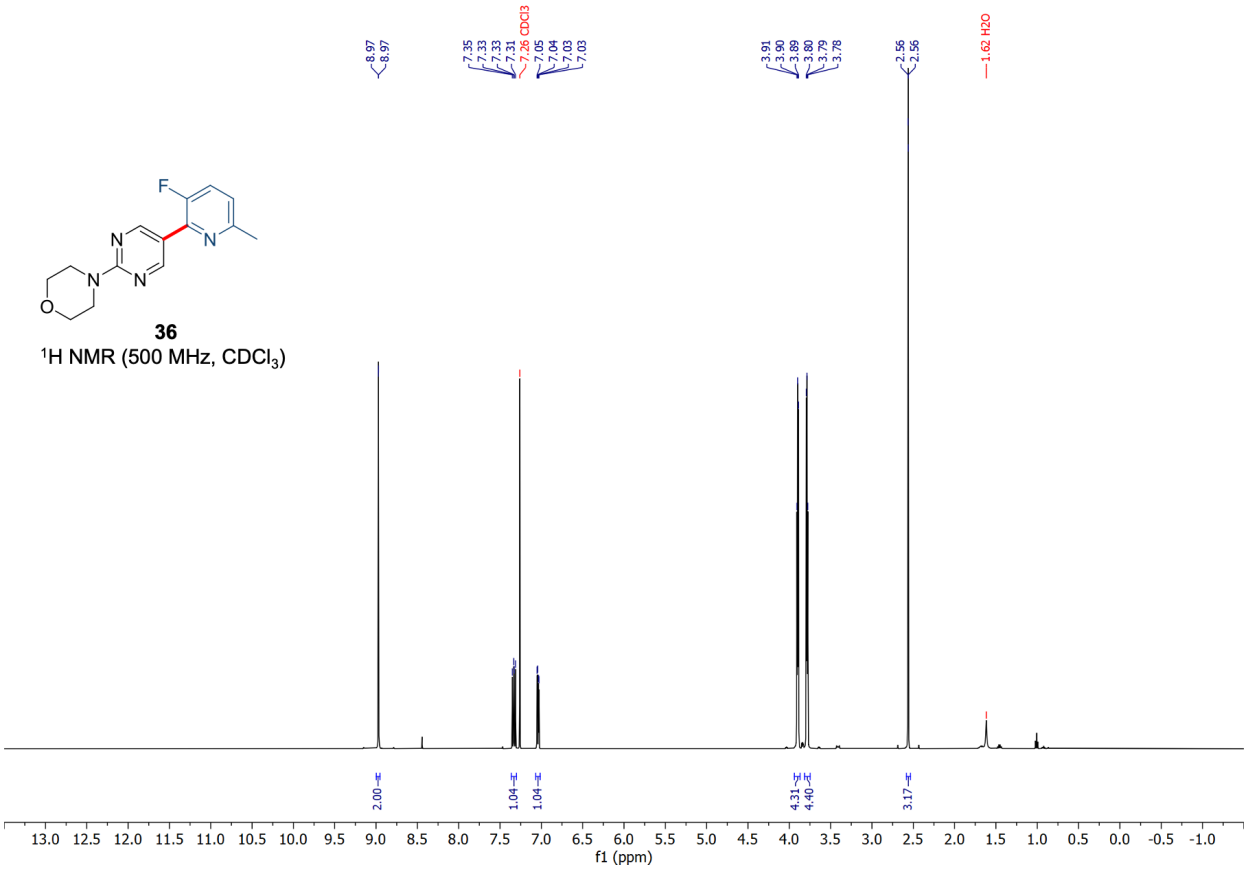
35

^{13}C NMR (126 MHz, $CDCl_3$)



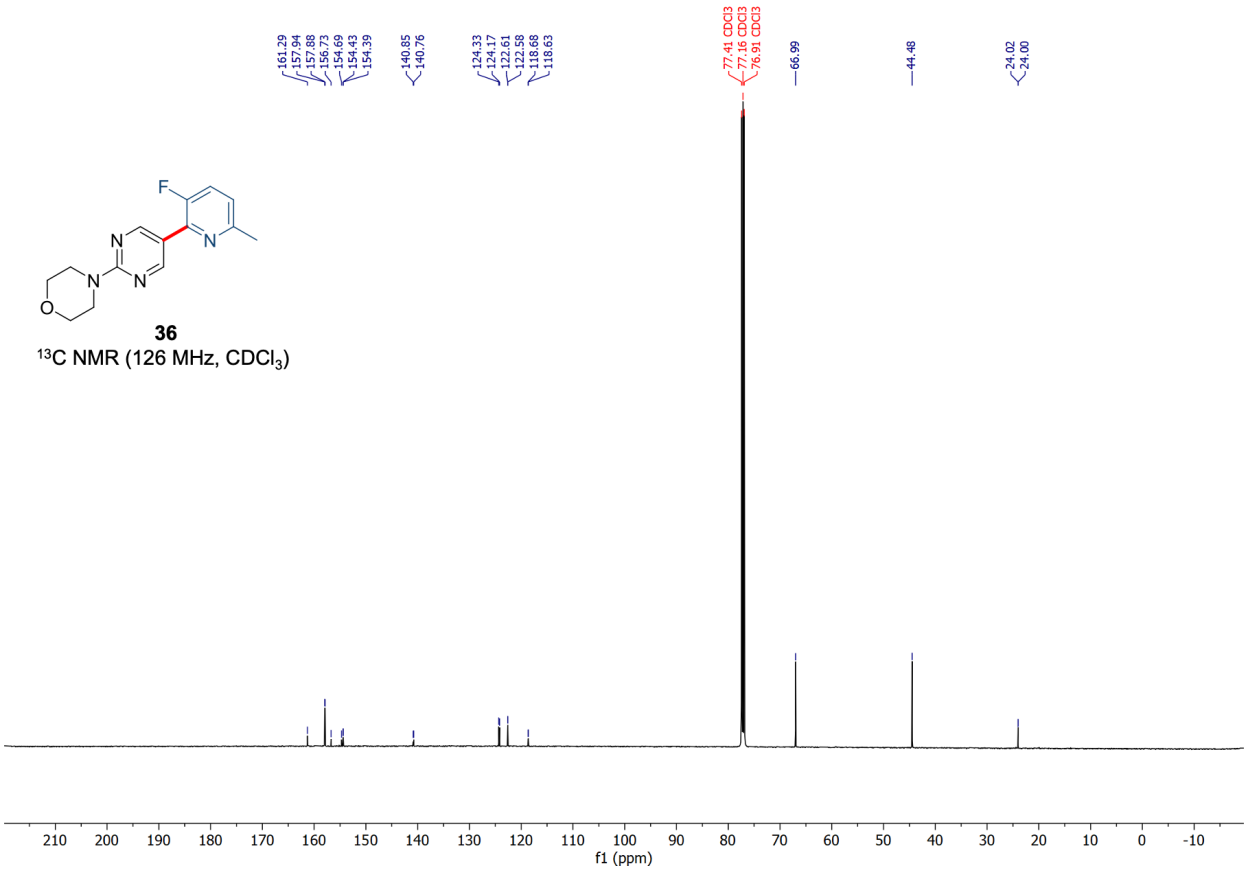
35

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



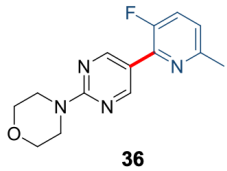
36

^{1}H NMR (500 MHz, $CDCl_3$)



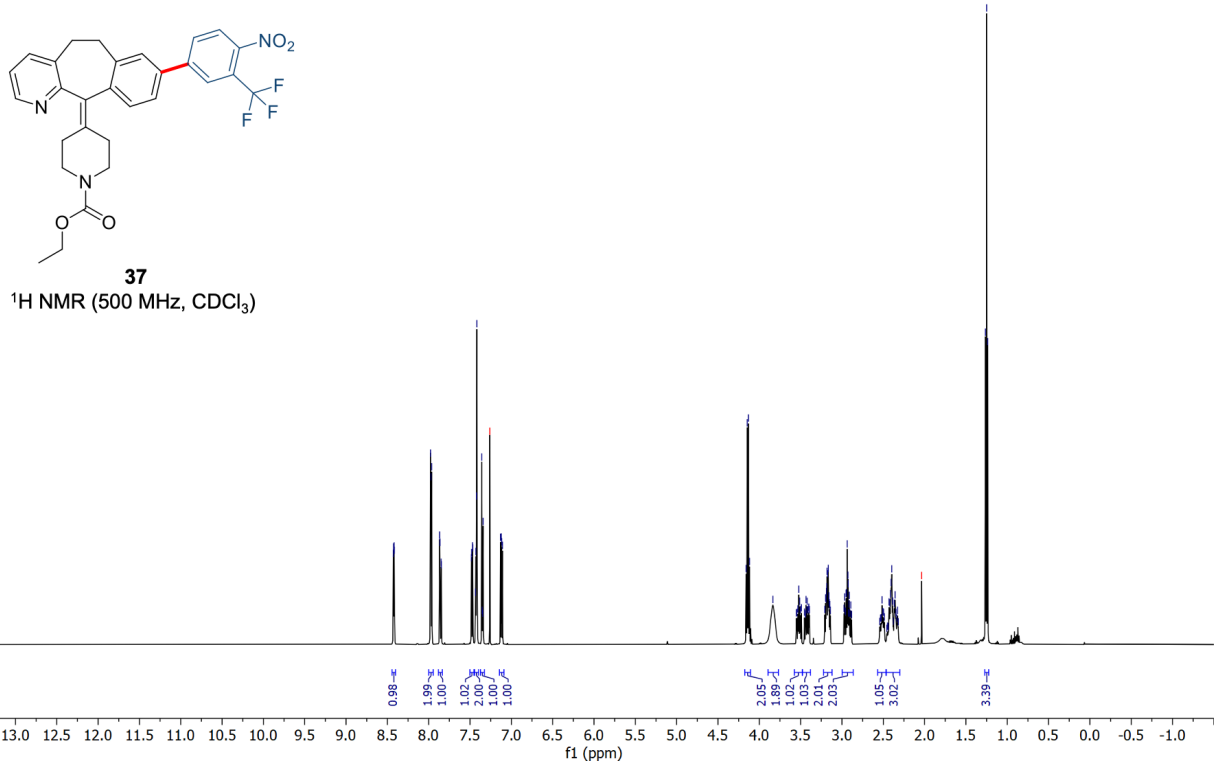
36

^{13}C NMR (126 MHz, $CDCl_3$)



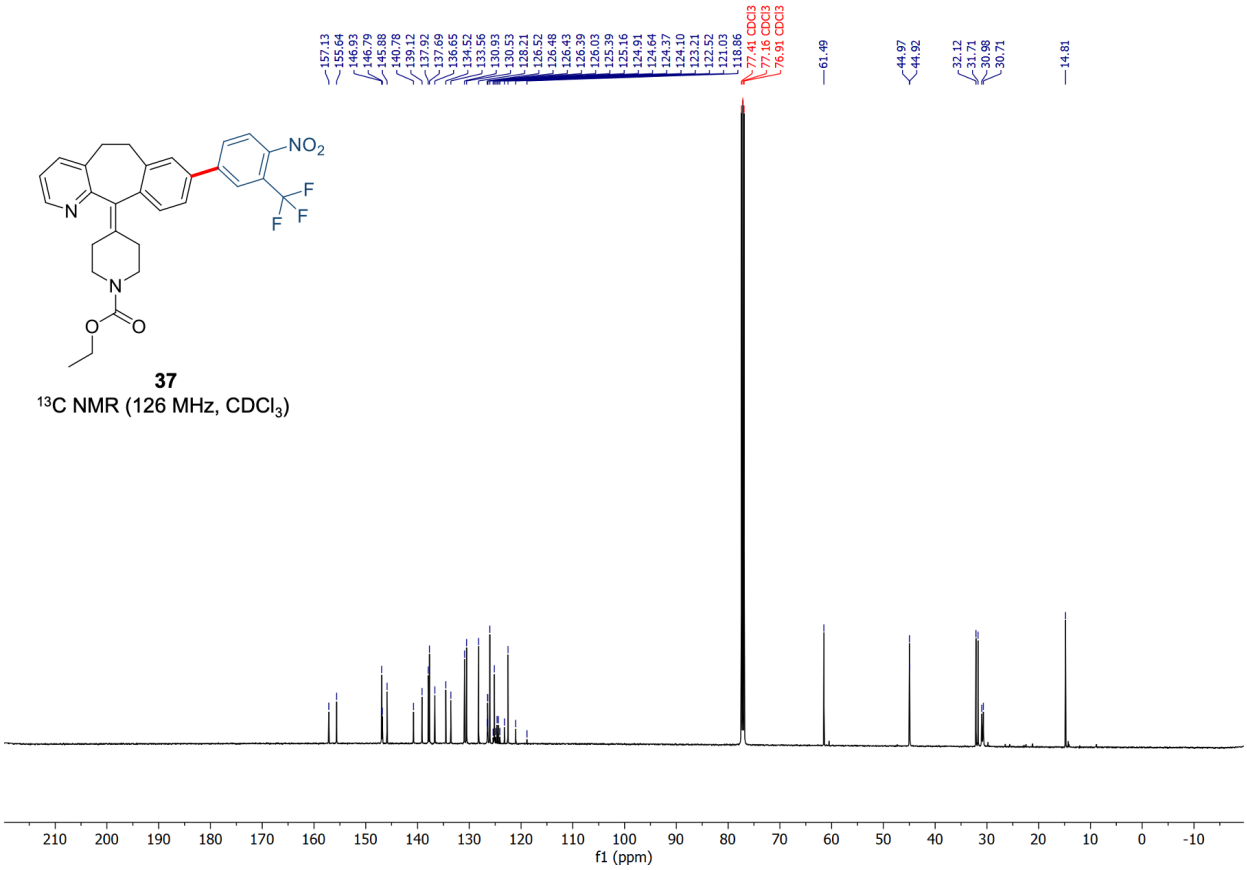
36

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



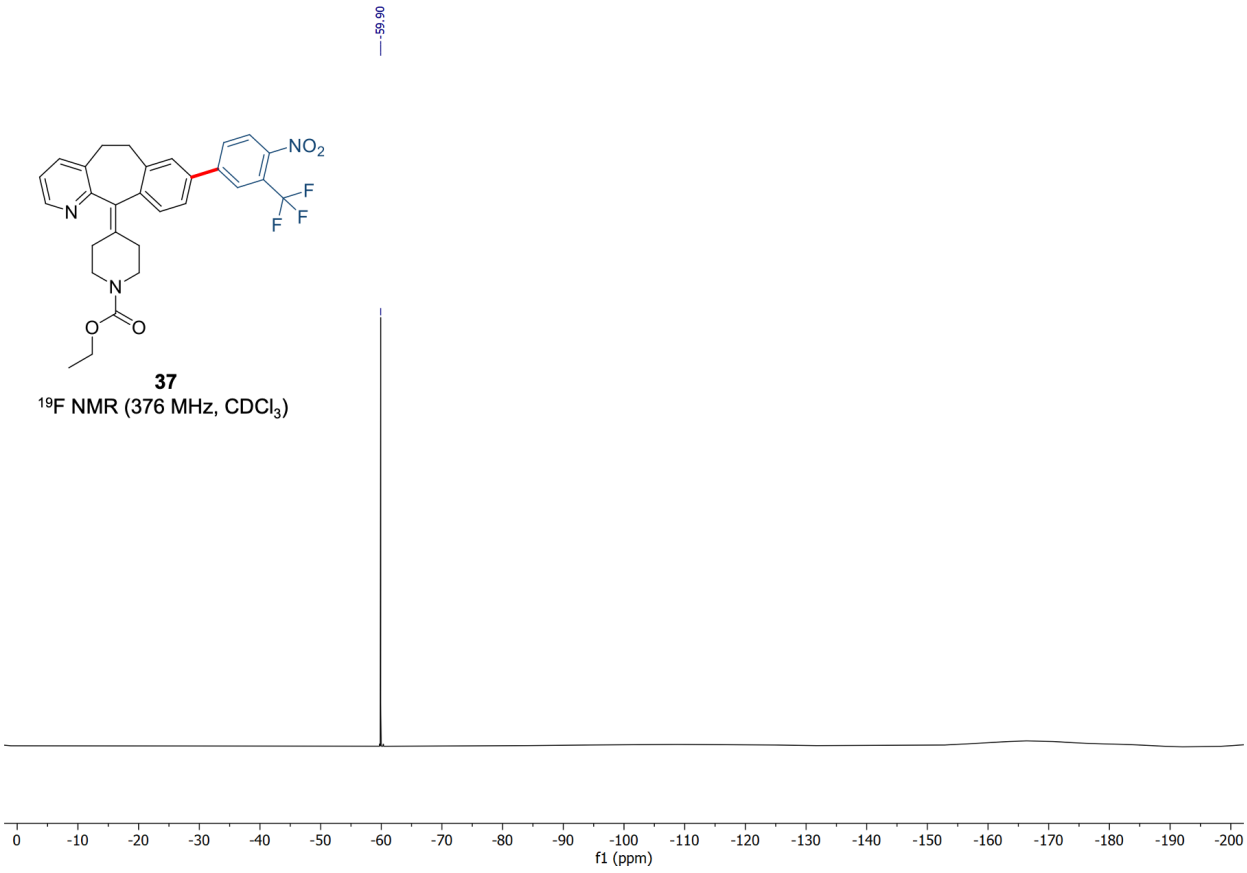
37

^{1}H NMR (500 MHz, $CDCl_3$)



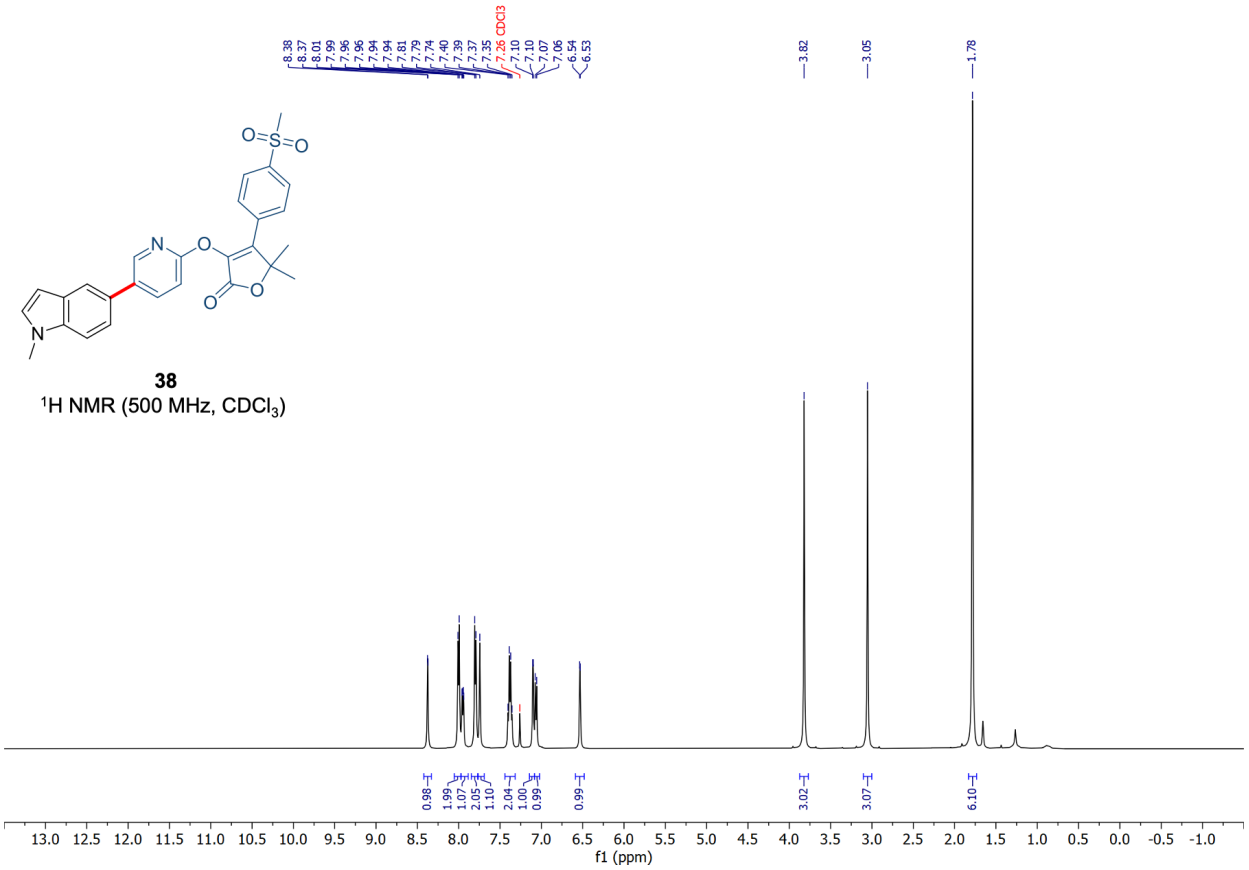
37

^{13}C NMR (126 MHz, $CDCl_3$)



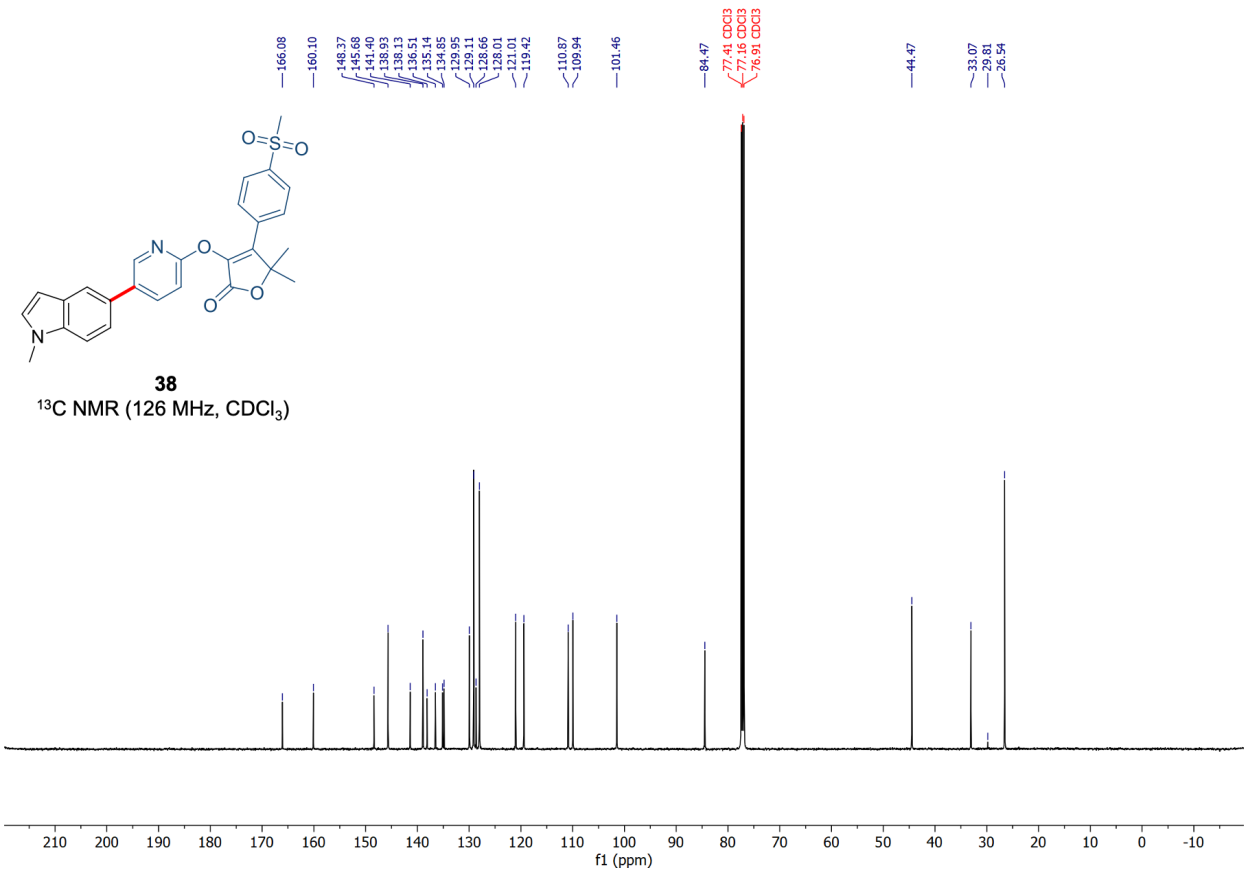
37

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



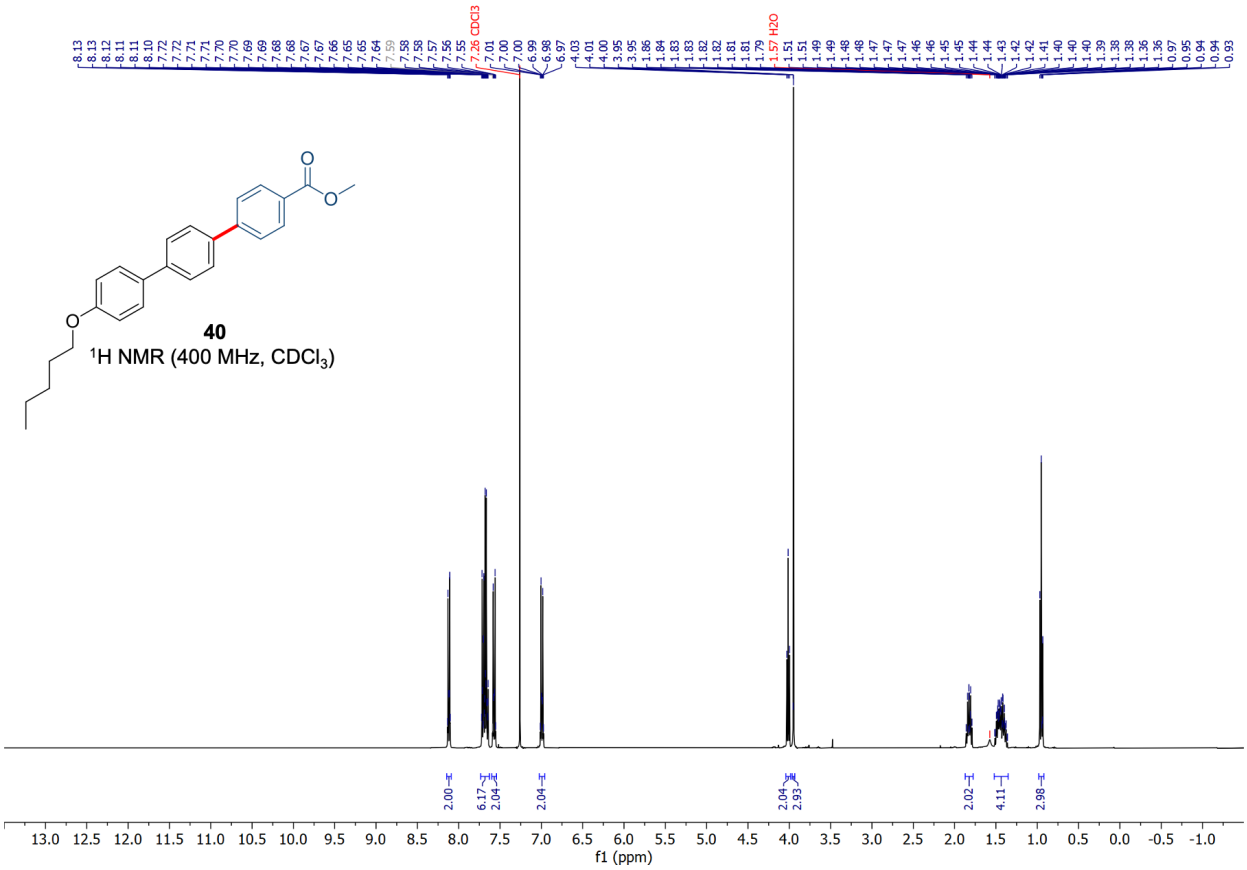
38

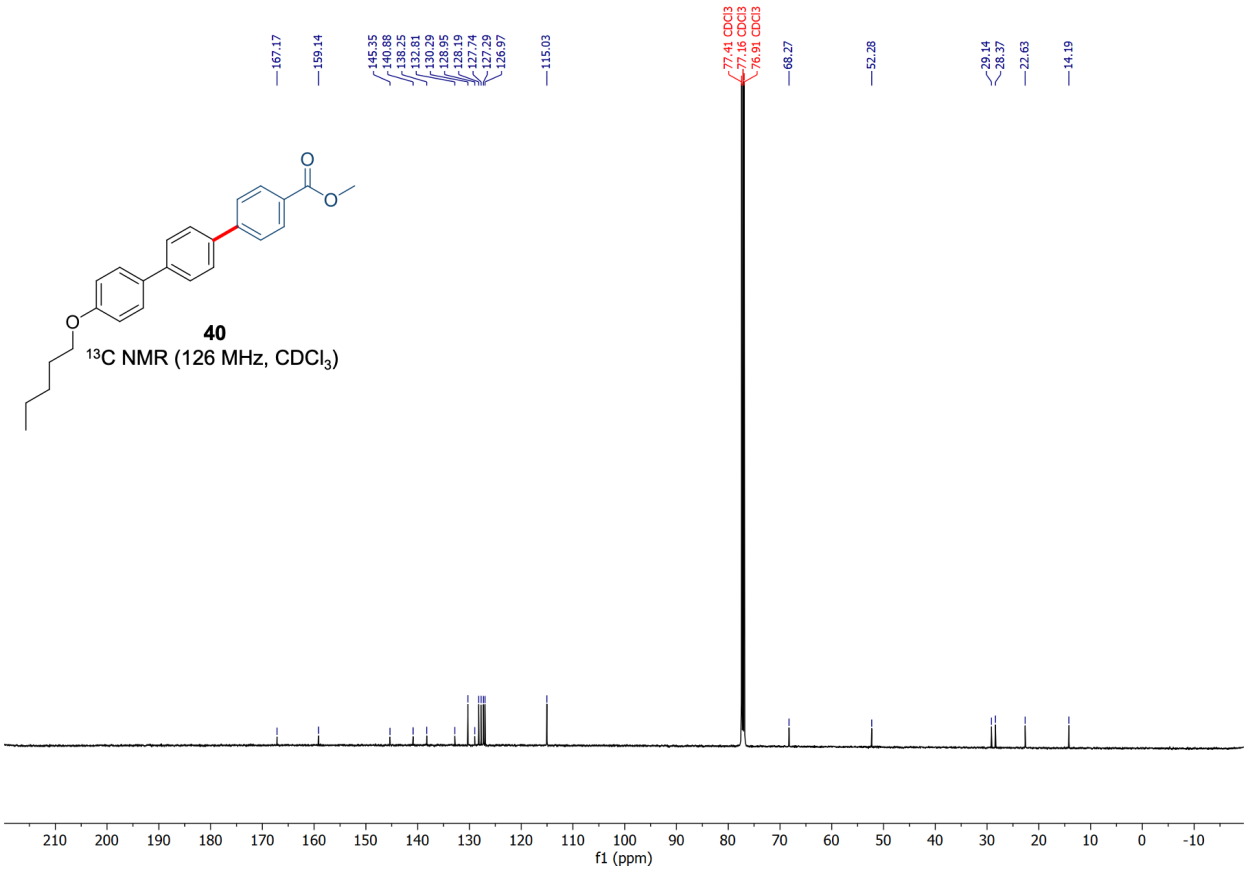
^{1}H NMR (500 MHz, $CDCl_3$)

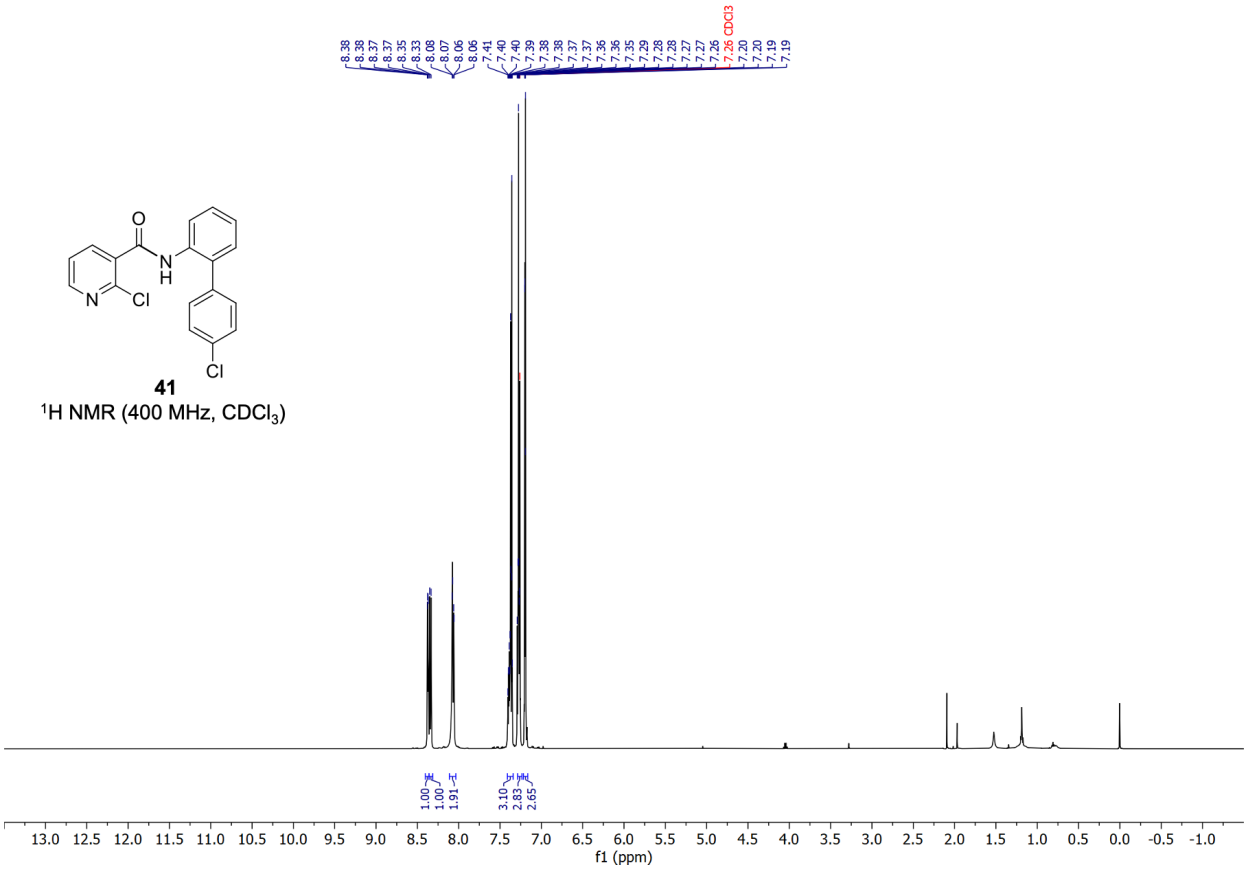


38

^{13}C NMR (126 MHz, $CDCl_3$)

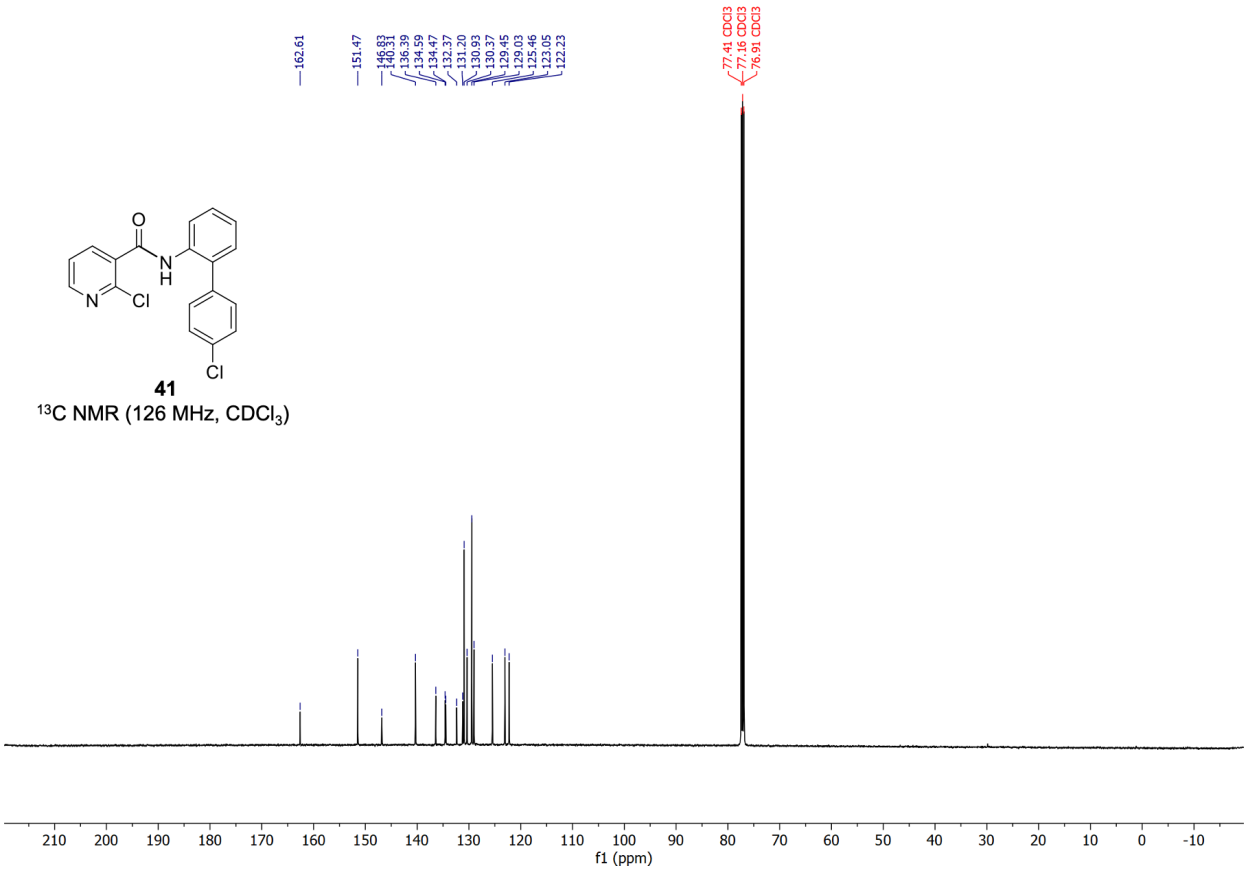

40
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)


40
^{13}C NMR (126 MHz, $CDCl_3$)
f1 (ppm)



41

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



41

^{13}C NMR (126 MHz, $CDCl_3$)