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Supplementary Information

Pyrimidine-directed metal-free C-H borylation of 2-pyrimidylanilines: A useful process for tetra-coordinated triarylborane synthesis

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1. General information

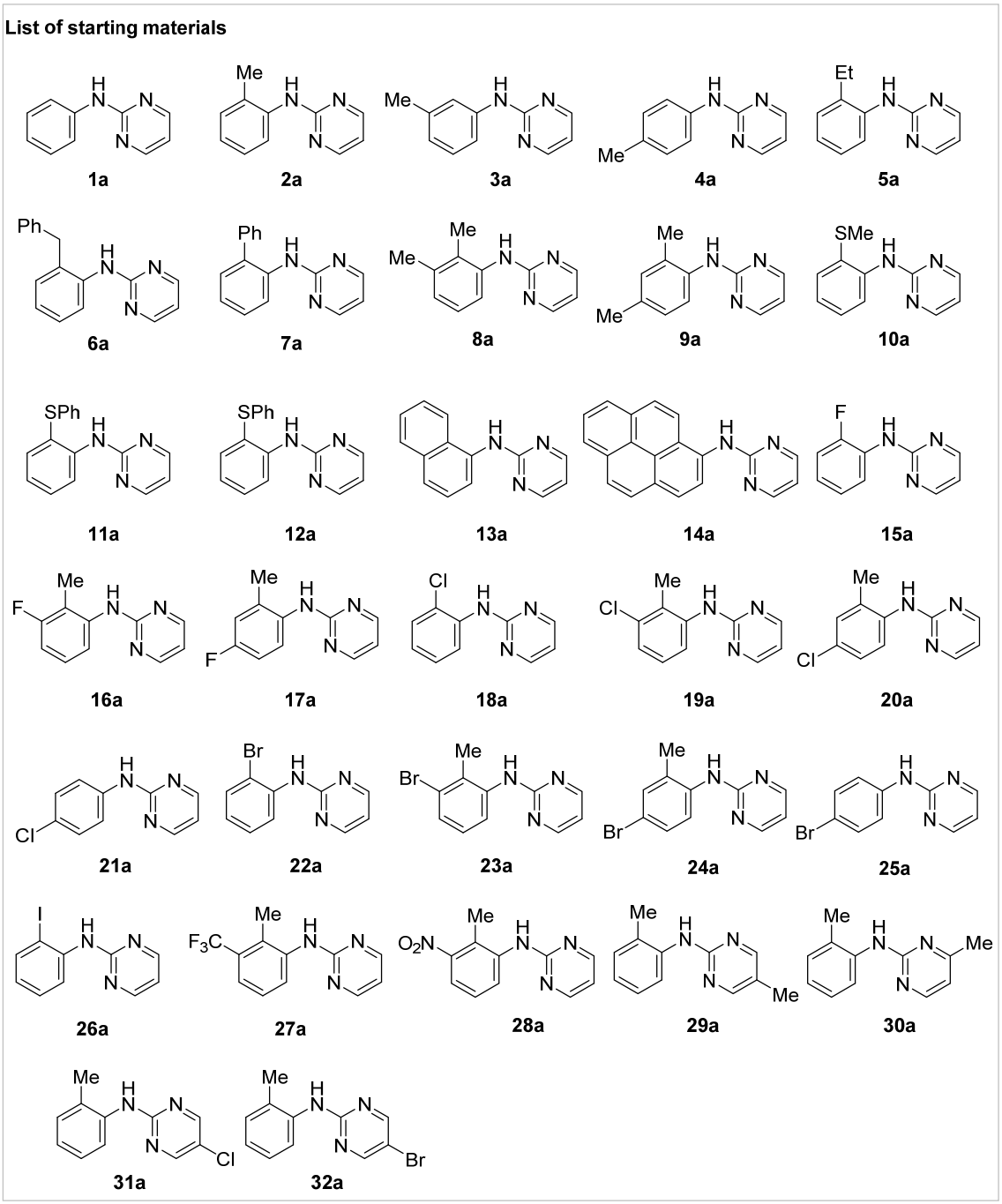
All reactions were performed inside a nitrogen filled glove box. ^{1}H NMR (400 MHz), and $^{13}C\{^{1}H\}$ NMR (100 MHz) spectra recorded on a JEOL ECS-400 spectrometer in $CDCl_3$ with tetramethylsilane. All ^{1}H NMR chemical shifts were recorded in ppm (δ) and referenced to the tetramethylsilane. All $^{13}C\{^{1}H\}$ NMR chemical shifts were recorded in ppm (δ) relative to carbon resonances in $CDCl_3$ at δ 77.16. Data are reported as follows: chemical shifts in ppm (δ), multiplicity (s = singlet, brs = broad singlet, d = doublet, t = triplet, dd = doublet of doublet, q = quartet, m = multiplet and dm = doublet of multiplet), coupling constant (Hz), and integration. Infrared spectra (IR) were obtained using a JASCO FT/IR-4200 spectrometer; absorptions are reported in reciprocal centimetres. High resolution mass spectra (HRMS) were obtained using a JEOL JMS-700 spectrometer. Melting points were determined using a Stanford research systems apparatus. Flash column chromatography was performed using SiO_2 F60 (0.040–0.0663 nm, 230-400 mesh). Some compounds were purified by LC-908 HPLC (GPC).

2. Materials

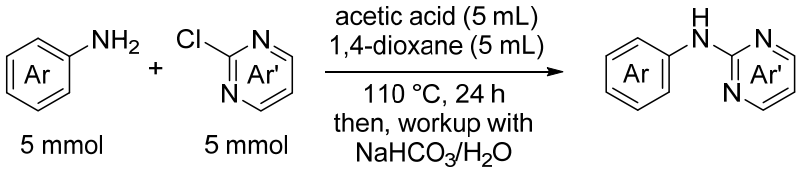
BBr_3 (17% in dichloromethane, *ca*. 1mol/L; CAS No.- 10294-33-4) was purchased from Tokyo Chemical Industry Co., Ltd. Neat boron tribromide, 99.85% (CAS No.- 10294-33-4) was purchased from Fujifilm Wako Pure Chemical Industries, Ltd. All the chemicals were used as it is received without further purification. Procedure for preparation and characterization of synthesized starting materials are given below. Dry solvents (DCM, DCE and $CHCl_3$) were purchased from Kanto Chemicals Co. Inc. Solvents ($CHCl_3$, EtOAc, Hexane, and $CDCl_3$) were used without further purification.

3. Preparation and characterization of starting materials

Table S1. List of starting materials which have been used for substrate scope.



General Procedure for the synthesis of starting materials:

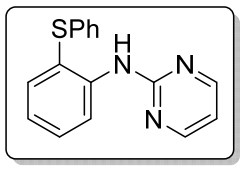


Starting materials were synthesized by following a literature mentioned report.[1–4] A general synthetic procedure is dictated below.

To a dry three-necked round bottom flask, 2-chloropyrimidine (573 mg, 5.0 mmol, 1.0 equiv), aniline derivative (5.0 mmol, 1.0 equiv), 1,4-dioxane (5 mL), and acetic acid (5 mL) were added in that order. The reaction mixture was refluxed at 110 °C under a N_2 atmosphere for 24 h. The reaction mixture was allowed to cool to room temperature and extracted with EtOAc, which was then washed with a saturated aq. $NaHCO_3$ solution. The organic phase was collected and the solvent was removed under reduced pressure. The resulting crude product was purified by column chromatography (eluent: hexane/EtOAc = 5/1) to afford the desired 2-pyrimidylanilines:

Note: Compound **1a**–**10a**, **13a**, **15a**–**20a**, **22a**–**24a**, **27a**, and **28a** were previously reported in literature.[1,3,5]

***N*-(2-(phenylthio)phenyl)pyrimidin-2-amine (11a)**



Yield – 1006 mg, 72%. Yellow oil.

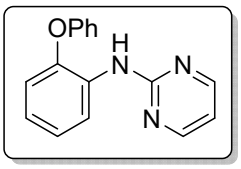
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.41 (d, *J* = 4.8 Hz, 2H), 8.24 (s, 1H), 7.60 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.51 – 7.39 (m, 1H), 7.23 – 7.15 (m, 2H), 7.15 – 7.08 (m, 3H), 7.04 (td, *J* = 7.5, 1.4 Hz, 1H), 6.73 (t, *J* = 4.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.90, 158.03, 141.64, 137.07, 136.49, 130.86, 129.26, 127.36, 126.05, 122.75, 119.71, 119.59, 113.24.

IR (neat, ν/cm^{-1}) 3352, 3055, 2994, 1768, 1576, 1513, 1477, 1434, 1396, 1305, 1246, 1060, 988, 795, 739, 689.

HRMS Calcd for $C_{16}H_{13}N_3S$: 279.0830, found 279.0830.

***N*-(2-phenoxyphenyl)pyrimidin-2-amine (12a)**



Yield – 671 mg, 51%. White solid, **MP** – 79-81 °C.

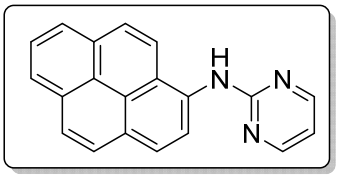
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (dd, *J* = 8.2, 1.5 Hz, 1H), 8.43 (d, *J* = 4.8 Hz, 2H), 7.74 (s, 1H), 7.37 – 7.27 (m, 2H), 7.20 – 7.13 (m, 1H), 7.12 – 7.06 (m, 1H), 7.06 – 6.99 (m, 2H), 6.98 – 6.88 (m, 2H), 6.72 (t, *J* = 4.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.03, 158.05, 157.05, 145.25, 131.64, 129.94, 124.18, 123.52, 122.22, 119.69, 118.51, 118.34, 112.88.

IR (neat, ν/cm^{-1}) 3419, 3041, 1773, 1577, 1528, 1442, 1403, 1244, 1212, 1106, 989, 865, 795, 748, 690.

HRMS Calcd for $C_{16}H_{13}N_3O$: 263.1059, found 263.1057.

***N*-(pyren-1-yl)pyrimidin-2-amine (14a)**



Yield – 945 mg, 64%. Yellow solid, **MP** – 212-214 °C.

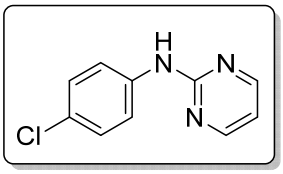
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 8.3 Hz, 1H), 8.47 – 8.37 (m, 2H), 8.31 – 8.24 (m, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 8.17 (t, *J* = 6.7 Hz, 2H), 8.13 – 7.94 (m, 5H), 6.74 (t, *J* = 4.6 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.59, 158.50, 132.36, 131.59, 131.19, 128.79, 127.78, 127.53, 126.60, 126.22, 125.65, 125.42, 125.31, 125.10, 124.94, 124.26, 122.22, 121.19, 112.83.

IR (neat, ν/cm^{-1}) 3237, 3045, 2993, 1769, 1579, 1520, 1445, 1412, 1244, 1049, 843, 798, 712, 682.

HRMS Calcd for $C_{20}H_{13}N_3$: 295.1109, found 295.1105.

***N*-(4-chlorophenyl)pyrimidin-2-amine (21a)**



Yield – 631 mg, 61%. Yellow solid, **MP** – 175-177 °C.

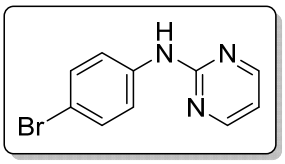
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.8 Hz, 2H), 7.61 – 7.54 (m, 2H), 7.52 (s, 1H), 7.32 – 7.27 (m, 2H), 6.74 (t, *J* = 4.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.10, 158.15, 138.15, 129.03, 127.63, 120.82, 112.97.

IR (neat, ν/cm^{-1}) 3257, 3099, 1574, 1538, 1490, 1452, 1420, 1283, 1249, 1173, 1087, 1012, 913, 809, 788, 744, 695, 658.

HRMS Calcd for $C_{10}H_8ClN_3$: 205.0407, found 205.0404.

***N*-(4-bromophenyl)pyrimidin-2-amine (25a)**



Yield – 992 mg, 79%. Yellow solid, **MP** – 172-174 °C.

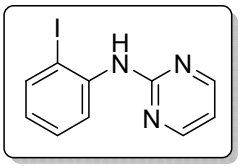
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, *J* = 4.8 Hz, 2H), 7.62 – 7.37 (m, 5H), 6.75 (t, *J* = 4.8 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.04, 158.15, 138.67, 131.96, 121.13, 115.09, 113.02.

IR (neat, ν/cm^{-1}) 3256, 3096, 1610, 1572, 1535, 1489, 1452, 1421, 1285, 1245, 1174, 1072, 1007, 913, 811, 793, 744, 705.

HRMS Calcd for $C_{10}H_8BrN_3$: 248.9902, found 248.9901.

***N*-(2-iodophenyl)pyrimidin-2-amine (26a)**



Yield – 564 mg, 38%. Off-white solid, **MP** – 148-150 °C.

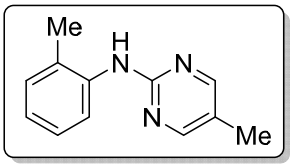
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, *J* = 4.8 Hz, 2H), 7.83 (brs, 1H), 7.62 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 6.75 (td, *J* = 4.8, 2.0 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.00, 158.13, 139.38, 137.88, 121.55, 113.01, 85.35.

IR (neat, ν/cm^{-1}) 3254, 3172, 3092, 2987, 1741, 1613, 1580, 1530, 1452, 1419, 1373, 1245, 1048, 792, 700.

HRMS Calcd for $C_{10}H_8IN_3$: 296.9763, found 296.9762.

5-methyl-*N*-(*o*-tolyl)pyrimidin-2-amine (29a)



Yield – 578 mg, 58%. White solid, **MP** – 110-112 °C.

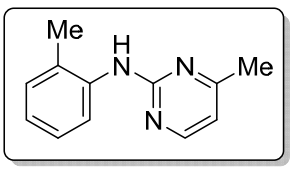
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (s, 2H), 7.93 (d, *J* = 8.0 Hz, 1H), 7.28 – 7.15 (m, 2H), 7.02 (td, *J* = 7.5, 1.0 Hz, 2H), 2.30 (s, 3H), 2.16 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.20, 158.11, 137.71, 130.60, 128.95, 126.70, 123.67, 121.84, 120.87, 18.20, 14.87.

IR (neat, ν/cm^{-1}) 3433, 3241, 3000, 1757, 1591, 1518, 1453, 1427, 1247, 1112, 1046, 990, 919, 792, 747, 711, 664.

HRMS Calcd for $C_{12}H_{13}N_3$: 199.1109, found 199.1110.

4-methyl-*N*-(o-tolyl)pyrimidin-2-amine (30a)



Yield – 558 mg, 56%. White solid, **MP** – 78-80 °C.

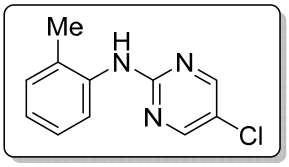
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (d, *J* = 5.0 Hz, 1H), 8.03 (d, *J* = 8.2 Hz, 1H), 7.27 – 7.18 (m, 2H), 7.02 (td, *J* = 7.5, 1.2 Hz, 1H), 6.83 (s, 1H), 6.58 (d, *J* = 5.0 Hz, 1H), 2.40 (s, 3H), 2.32 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.32, 160.53, 157.73, 137.63, 130.61, 128.70, 126.73, 123.66, 121.81, 112.17, 24.30, 18.29.

IR (neat, ν/cm^{-1}) 3440, 3238, 2995, 1769, 1566, 1526, 1446, 1409, 1247, 1050, 796, 747, 715, 667.

HRMS Calcd for $C_{12}H_{13}N_3$: 199.1109, found 199.1107.

5-chloro-*N*-(*o*-tolyl)pyrimidin-2-amine (31a)



Yield – 593 mg, 54%. White solid, **MP** – 70-72 °C.

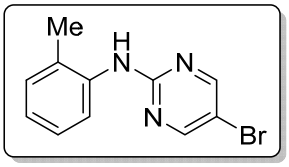
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (s, 2H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.29 – 7.19 (m, 3H), 7.08 (t, *J* = 7.4 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.00, 156.41, 136.86, 130.76, 130.09, 126.76, 124.78, 122.84, 120.55, 18.15.

IR (neat, ν/cm^{-1}) 3246, 2993, 1740, 1577, 1517, 1458, 1419, 1373, 1235, 1136, 1050, 935, 787, 751, 727.

HRMS Calcd for $C_{11}H_{10}ClN_3$: 219.0563, found 219.0565.

5-bromo-*N*-(*o*-tolyl)pyrimidin-2-amine (32a)



Yield – 647 mg, 49%. White solid, **MP** – 101-103 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (s, 2H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.20 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 2.31 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 159.14, 158.44, 136.77, 130.74, 126.74, 124.85, 122.97, 108.10, 18.14.

IR (neat, ν/cm^{-1}) 3424, 3246, 2994, 1769, 1571, 1514, 1457, 1416, 1245, 1112, 1051, 934,

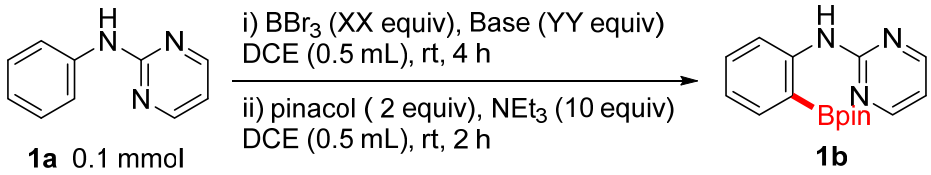
786, 749, 720.

HRMS Calcd for $C_{11}H_{10}BrN_3$: 263.0058, found 263.0053.

4. Optimization study

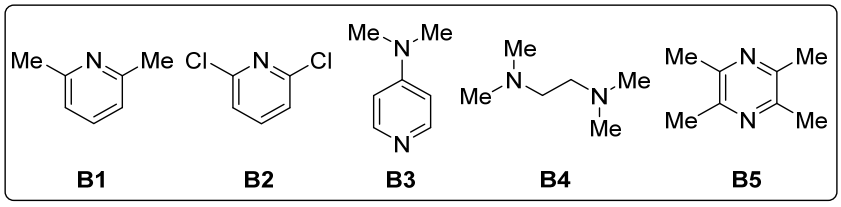
To a dry sample vial in a glovebox, 2-pyrimidylaniline derivative (0.1 mmol, 1 equiv), base (no base; 0.12 mmol, 1.2 equiv; 0.2 mmol, 2 equiv; or 0.3 mmol, 3 equiv), and DCE (0.5 mL) were added. BBr_3 (0.1 mmol, 1 equiv; 0.2 mmol, 2 equiv; or 0.3 mmol, 3 equiv; in the form of a 1 mol/L solution in DCM) was then added dropwise into the reaction mixture with stirring, and the reaction mixture was continuously stirred for 4 h at room temperature. The reaction was quenched with pinacol (0.1 mmol, 1 equiv; 0.2 mmol, 2 equiv; or 0.3 mmol, 3 equiv) and triethylamine (1.0 mmol, 10 equiv; 2.0 mmol, 10 equiv; or 3.0 mmol, 10 equiv), and stirred for another 2 h at room temperature. The volatiles were then removed under reduced pressure and the crude mixture was dissolved in a mixture of $CDCl_3$ (1 mL) and H_2O (1 mL). Mesitylene (7.0 μL, 0.05 mmol, 0.5 equiv) was then added to the mixture as an internal standard and an ^1H NMR spectrum was obtained for the contents of the $CDCl_3$ layer. The yield of the desired product was determined by ^1H NMR analysis and the data are given below.

Table S2. Optimization of metal-free borylation of 2-pyrimidylaniline **1a**



1a 0.1 mmol **1b**

Entry	Base (YY equiv)	BBr_3 (XX equiv)	Solvent	Yield of **1b** (%)
1[a]	-	1 equiv	DCE	21
2	-	2 equiv	DCE	50
3	**B1** (2 equiv)	2 equiv	DCE	71
4	**B2** (2 equiv)	2 equiv	DCE	66
5	pyridine (2 equiv)	2 equiv	DCE	5
6	NE*t*iPr$_2$ (2 equiv)	2 equiv	DCE	65
7	**B3** (2 equiv)	2 equiv	DCE	3
8	**B4** (2 equiv)	2 equiv	DCE	17
9	NEt_3 (2 equiv)	2 equiv	DCE	61
10	**B5** (2 equiv)	2 equiv	DCE	84
11[b]	**B5** (3 equiv)	3 equiv	DCE	93
12[b]	**B5** (1.2 equiv)	3 equiv	DCE	92 (77)
13[b]	**B5** (1.2 equiv)	3 equiv	$CHCl_3$	90 (76)

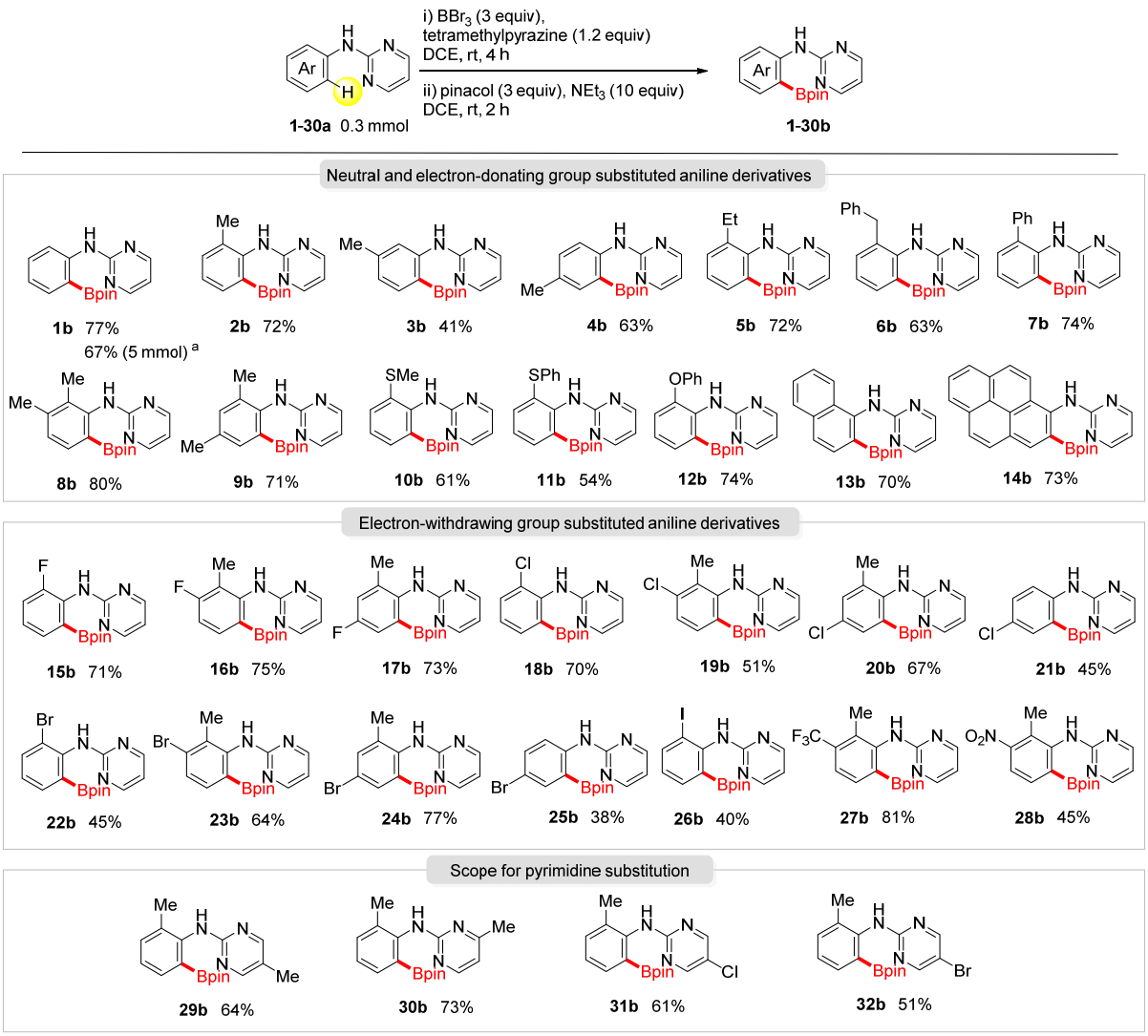


Reaction condition: 2-pyrimidylaniline (0.1 mmol, 1 equiv), BBr_3 and base in DCE (0.5 mL) at rt for 4 h, then pinacol (0.2 mmol) and NEt_3 (1.0 mmol) in DCE (0.5 mL) for 2 h at rt. Yields of the product were determined by ^{1}H NMR of the crude mixture using 1,1,2,2-tetrachloroethane as an internal standard. Isolated yields are given in parentheses. [a] 1 equiv of pinacol was used in final step. [b] 3 equiv of pinacol was used in final step.

5. General procedure A: metal-free directed C-H borylation to access boronic esters

To a dry sample vial in a glovebox, the 2-pyrimidylaniline derivative (0.3 mmol, 1 equiv), tetramethylpyrazine (49 mg, 0.36 mmol, 1.2 equiv), and DCE (0.5 mL) were added. BBr_3 (0.9 mmol, 3 equiv; in the form of a 1 mol/L solution in DCM) was then added dropwise into the reaction mixture while stirring, and the reaction mixture was stirred for an additional 4 h at room temperature. The reaction was quenched with pinacol (106 mg, 0.9 mmol, 3 equiv) and triethylamine (0.42 mL, 3.0 mmol, 10 equiv), and stirred for another 2 h at room temperature. After the reaction reached completion, the volatiles were removed under reduced pressure and the crude mixture was dissolved in EtOAc (5 mL) and H_2O (5 mL). The aqueous layer was washed with EtOAc (3 x 10 mL) and the organic layers were collected, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the product was isolated by column chromatography (eluent: hexane/$CHCl_3$ = 10/1 to 2/1)

Table S3. Substrate scope for metal-free borylation of 2-pyrimidylanilines

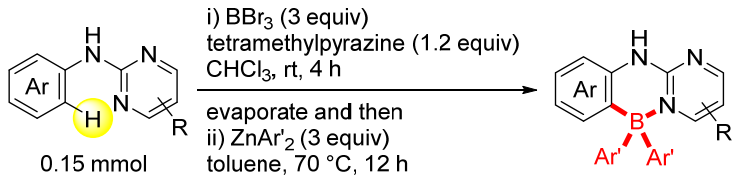


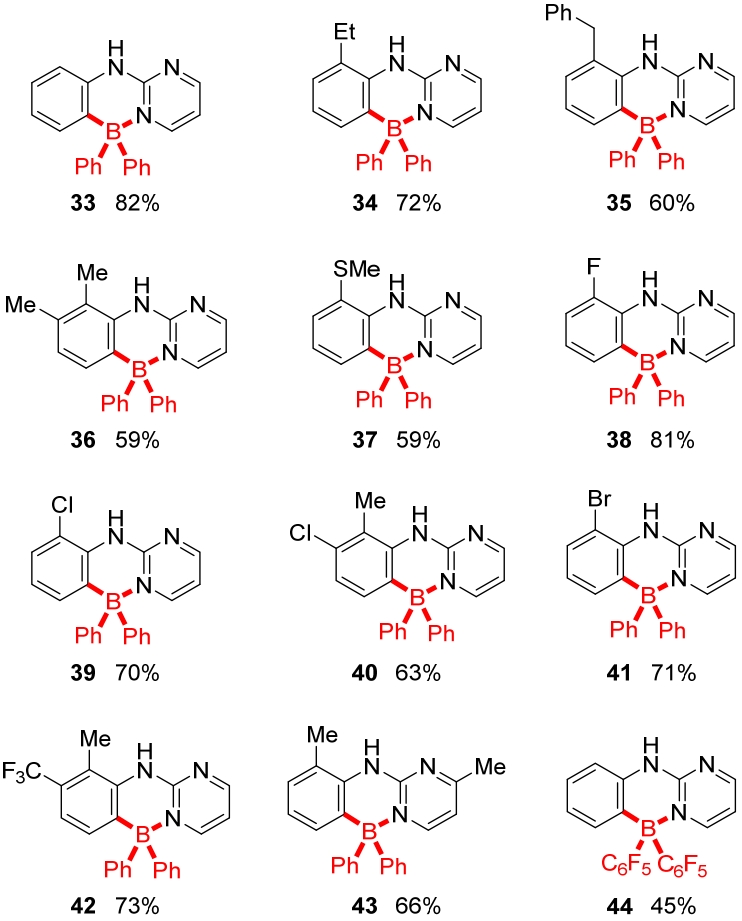
Substrate scope. Reaction conditions: 2-pyrimidylaniline derivative (0.3 mmol, 1 equiv), BBr_3 (0.9 mmol, 3 equiv) and tetramethylpyrazine (0.36 mmol, 1.2 equiv) in DCE (1.0 mL) at rt for 4 h, then pinacol (0.9 mmol, 3 equiv) and NEt_3 (3.0 mmol, 10 equiv) in DCE (1.0 mL) for 2 h at rt. Isolated yields of the product are given. [a] Reaction was performed on a 5 mmol scale.

6. General procedure B: metal-free directed C-H borylation to access triarylboranes

To a dry sample vial in a glovebox, 2-pyrimidylaniline derivatives (0.15 mmol, 1 equiv), tetramethylpyrazine (25 mg, 0.18 mmol, 1.2 equiv), and $CHCl_3$ (0.5 mL) were added. BBr_3 (42.7 μL, 0.45 mmol, 3 equiv) was then added dropwise into the reaction mixture with stirring, and the reaction stirred for an additional 4 h at room temperature. The volatiles were removed by evaporation under reduced pressure and 1 mL of toluene was added. $ZnAr'_2$ (0.45 mmol, 3 equiv) was then added into the mixture which was then heated at 70°C for 12 h. After the reaction reached completion, the volatiles were removed under reduced pressure and the crude mixture was partitioned between EtOAc (5 mL) and H_2O (5 mL). The aqueous layer was washed with EtOAc (3 x 10 mL) and the organic layers were collected, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the product was isolated by column chromatography (eluent: hexane/EtOAc = 20/1 to 2/1).

Table S4. Synthesis of tetra-coordinated triarylborane via a metal-free C-H borylation

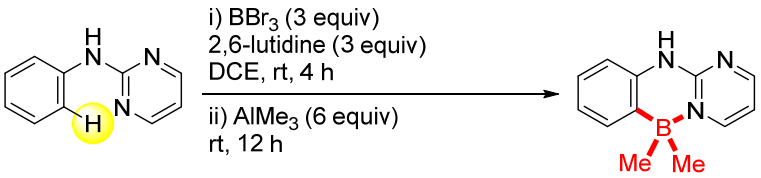




Reaction conditions: 2-pyrimidylaniline derivative (0.15 mmol, 1 equiv), BBr_3 (0.45 mmol, 3 equiv), and tetramethylpyrazine (0.18 mmol, 1.2 equiv) in $CHCl_3$ (1.0 mL) at rt for 4 h, evaporated under reduced pressure, then toluene (1.5 mL) and $ZnAr'_2$ (0.45 mmol, 3 equiv) was added and heated at 70°C for 12 h.

7. General procedure C: metal-free directed C-H borylation to access dimethyl substituted arylborane

To a dry sample vial in a glovebox, 2-pyrimidylaniline **1a** (25.7 mg, 0.15 mmol, 1 equiv) and 2,6-lutidine (52 μL, 0.45 mmol, 3 equiv), and DCE (0.5 mL) were added. BBr_3 (0.45 mmol, 3 equiv; in the form of a 1 mol/L solution in DCM) was then added dropwise into the reaction mixture with stirring, and the reaction stirred for 4 h at room temperature. $AlMe_3$ (0.9 mmol, 6 equiv; in the form of 1.8 mol/L solution in toluene) was then added dropwise into the reaction mixture which was then stirred at room temperature for another 12 h. After the reaction reached completion, the volatiles were removed under reduced pressure and the crude mixture was partitioned between EtOAc (5 mL) and H_2O (5 mL). The aqueous layer was washed with EtOAc (3 x 10 mL) and the organic layers were collected, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the product was isolated by column chromatography (eluent: hexane/EtOAc = 20/1 to 2/1).

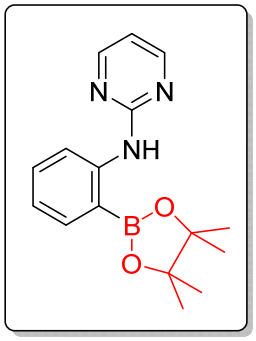


0.15 mmol

45 74%

8. Spectral data of products

N-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (1b)



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 69 mg, 77%. Pale-yellow solid, **MP** – 205-207 °C.

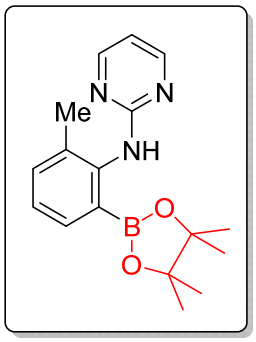
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.05 (brs, 1H), 8.65 (d, *J* = 5.1 Hz, 2H), 7.72 (d, *J* = 7.1 Hz, 1H), 7.22 – 7.02 (m, 3H), 6.88 (t, *J* = 5.1 Hz, 1H), 1.32 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.44, 140.21, 132.24, 128.25, 123.67, 115.75, 111.59, 81.26, 26.45.

IR (neat, ν/cm^{-1}) 3055, 2976, 1770, 1626, 1565, 1538, 1461, 1366, 1245, 1150, 1041, 989, 913, 758, 730.

HRMS Calcd for $C_{16}H_{20}BN_3O_2$: 297.1649, found 297.1645.

N-(2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (2b)



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 67 mg, 72%. Pale-yellow solid, **MP** – 211-213 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (brs, 1H), 8.58 (brs, 1H), 8.38 (brs, 1H), 7.58 (d, *J* = 7.0 Hz, 1H), 7.09 (t, *J* = 7.4 Hz, 1H), 7.03 (d, *J* = 7.4 Hz, 1H), 6.98 – 6.91 (m, 1H), 2.25 (s, 3H), 1.27 (s, 12H).

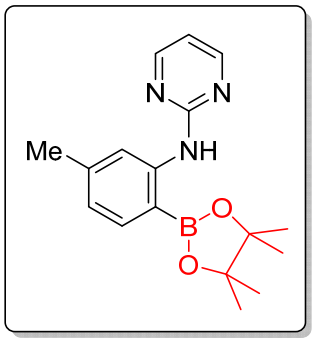
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.90, 154.54, 148.81, 137.26, 129.23, 129.07, 124.23, 122.46, 111.69, 80.54, 26.58, 17.20.

^{11}B NMR (128 MHz, $CDCl_3$) δ 6.05.

IR (neat, ν/cm^{-1}) 2984, 1738, 1624, 1538, 1373, 1237, 1045, 916, 732.

HRMS Calcd for $C_{17}H_{22}BN_3O_2$: 311.1805, found 311.1800.

***N*-(5-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (3b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Note: >5% of pinacol present as an impurity, which could not be removed by column chromatography.

Yield – 38 mg, 41%. Yellow solid, **MP** – 197-199 °C.

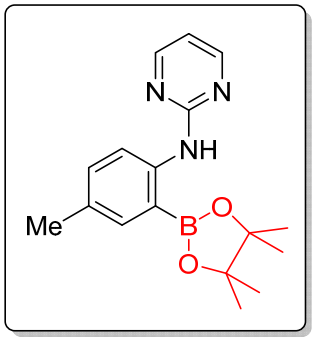
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 5.1 Hz, 2H), 8.59 (s, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.21 (s, 1H), 6.94 (dd, *J* = 7.5, 0.7 Hz, 1H), 6.86 (t, *J* = 5.1 Hz, 1H), 2.33 (s, 3H), 1.31 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.46, 155.94, 141.27, 139.11, 133.09, 124.43, 116.68, 111.84, 81.70, 26.20, 21.71.

IR (neat, ν/cm^{-1}) 2971, 2925, 1628, 1568, 1540, 1490, 1457, 1365, 1215, 1154, 1133, 1114, 1016, 989, 813, 753, 674.

HRMS Calcd for $C_{17}H_{22}BN_3O_2$: 311.1805, found 311.1809.

***N*-(4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (4b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 59 mg, 63%. Yellow solid, **MP** – 189-191 °C.

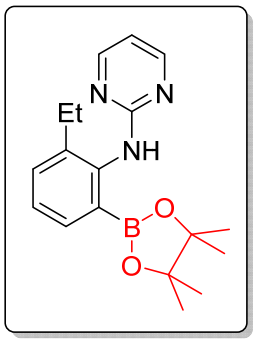
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 5.1 Hz, 2H), 8.42 (s, 1H), 7.53 (d, *J* = 1.6 Hz, 1H), 7.25 – 7.19 (m, 1H), 7.09 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.87 (t, *J* = 5.1 Hz, 1H), 2.34 (s, 3H), 1.31 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.20, 155.83, 138.50, 133.26, 132.86, 129.54, 116.00, 111.71, 81.58, 26.32, 21.18.

IR (neat, ν/cm^{-1}) 2965, 1622, 1565, 1538, 1482, 1453, 1364, 1221, 1180, 1147, 1116, 1034, 987, 911, 816, 772, 747.

HRMS Calcd for $C_{17}H_{22}BN_3O_2$: 311.1805, found 311.1802.

***N*-(2-ethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (5b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 70 mg, 72%. Pale-yellow solid, **MP** – 169-171 °C.

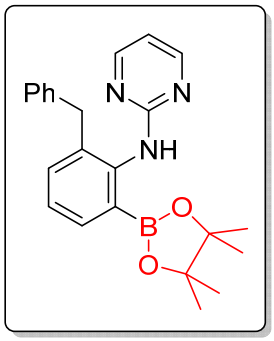
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.87 (brs, 1H), 8.59 (brs, 1H), 8.25 (brs, 1H), 7.59 (d, *J* = 7.0 Hz, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 7.09 (d, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 5.2 Hz, 1H), 2.65 (q, *J* = 7.5 Hz, 2H), 1.33 – 1.21 (m, 15H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.99, 154.63, 148.85, 136.61, 129.29, 127.93, 126.86, 124.42, 111.78, 80.53, 26.66, 23.54, 13.79.

IR (neat, ν/cm^{-1}) 3056, 2968, 1623, 1565, 1537, 1430, 1244, 1156, 1080, 1043, 984, 890, 786, 758, 731.

HRMS Calcd for $C_{18}H_{24}BN_3O_2$: 325.1962, found 325.1965.

_N_-(2-benzyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (6b)



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 73 mg, 63%. Pale-yellow solid, **MP** – 176-178 °C.

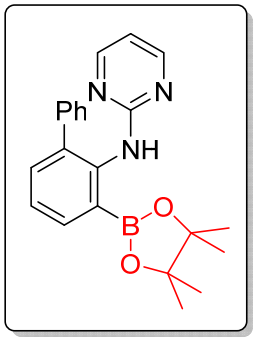
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (brs, 1H), 8.53 (brs, 1H), 8.17 (s, 1H), 7.66 (dd, *J* = 7.4, 1.1 Hz, 1H), 7.35 – 7.27 (m, 2H), 7.25 – 7.18 (m, 3H), 7.16 (t, *J* = 7.4 Hz, 1H), 7.02 (dd, *J* = 7.4, 1.4 Hz, 1H), 6.93 (t, *J* = 5.2 Hz, 1H), 4.02 (s, 2H), 1.26 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.09, 154.47, 148.87, 138.84, 137.20, 130.26, 129.30, 129.01, 128.95, 126.77, 125.10, 124.40, 111.88, 80.59, 37.73, 26.75.

IR (neat, ν/cm^{-1}) 3057, 2978, 1738, 1622, 1536, 1462, 1429, 1369, 1243, 1155, 1064, 999, 969, 894, 783, 733.

HRMS Calcd for $C_{23}H_{26}BN_3O_2$: 387.2118, found 387.2117.

***N*-(3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-2-yl)pyrimidin-2-amine (7b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 83 mg, 74%. White solid, **MP** – 200-202 °C.

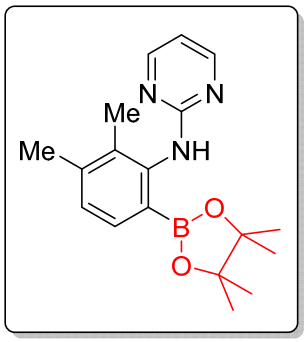
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (brs, 1H), 8.56 (brs, 1H), 8.18 (s, 1H), 7.76 (dd, *J* = 7.2, 1.5 Hz, 1H), 7.55 – 7.38 (m, 5H), 7.28 – 7.18 (m, 2H), 6.98 (t, *J* = 5.2 Hz, 1H), 1.29 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.24, 154.50, 149.03, 138.25, 135.54, 131.13, 129.58, 129.44, 128.93, 128.45, 128.00, 124.40, 111.95, 80.64, 26.85.

IR (neat, ν/cm^{-1}) 3403, 2978, 1736, 1619, 1566, 1524, 1459, 1243, 1155, 1097, 1040, 1012, 789, 761, 731.

HRMS Calcd for $C_{22}H_{24}BN_3O_2$: 373.1962, found 373.1963.

***N*-(2,3-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (8b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 78 mg, 80%. Yellow solid, **MP** – 184-186 °C.

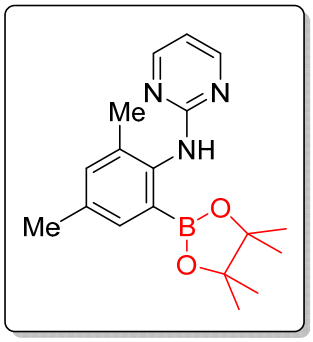
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (brs, 1H), 8.61 (brs, 1H), 8.19 (s, 1H), 7.47 (d, *J* = 7.4 Hz, 1H), 7.02 (d, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 5.2 Hz, 1H), 2.30 (s, 3H), 2.22 (s, 3H), 1.25 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.83, 154.76, 148.79, 137.38, 135.54, 128.51, 126.29, 120.92, 111.64, 80.50, 26.60, 20.64, 12.70.

IR (neat, ν/cm^{-1}) 2983, 1738, 1623, 1541, 1450, 1373, 1239, 1157, 1045, 917, 848, 790, 732.

HRMS Calcd for $C_{18}H_{24}BN_3O_2$: 325.1962, found 325.1964.

***N*-(2,4-dimethyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (9b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 69 mg, 71%. Yellow solid, **MP** – 202-204 °C.

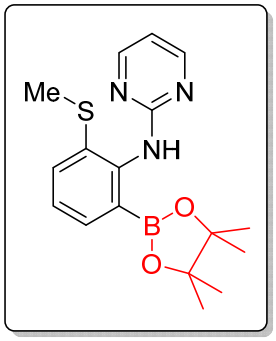
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (brs, 1H), 8.60 (brs, 1H), 7.99 (s, 1H), 7.37 (s, 1H), 6.95 (td, *J* = 5.2, 0.6 Hz, 1H), 6.90 (d, *J* = 0.6 Hz, 1H), 2.32 (s, 3H), 2.30 (s, 3H), 1.26 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.88, 154.61, 149.04, 134.97, 133.60, 130.00, 129.79, 122.00, 111.62, 80.52, 26.69, 21.23, 17.13.

IR (neat, ν/cm^{-1}) 3206, 2979, 1769, 1624, 1566, 1539, 1461, 1363, 1244, 1183, 1150, 1089, 988, 899, 819, 784, 732.

HRMS Calcd for $C_{18}H_{24}BN_3O_2$: 325.1962, found 325.1959.

***N*-(2-(methylthio)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (10b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 63 mg, 61%. Pale-yellow solid, **MP** – 116-118 °C.

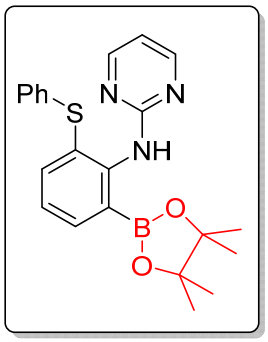
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.21 (s, 1H), 8.90 (brs, 1H), 8.67 (brs, 1H), 7.69 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.48 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.06 – 6.99 (m, 1H), 2.41 (s, 3H), 1.27 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.52, 154.57, 149.01, 139.47, 133.18, 131.95, 124.90, 121.31, 112.20, 80.67, 26.81, 20.06.

IR (neat, ν/cm^{-1}) 3349, 2986, 2359, 1740, 1614, 1522, 1450, 1376, 1244, 1156, 1048, 915, 788, 735.

HRMS Calcd for $C_{17}H_{22}BN_3O_2S$: 343.1526, found 343.1521.

***N*-(2-(phenylthio)-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (11b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 66 mg, 54%. Off-white solid, **MP** – 144-146 °C.

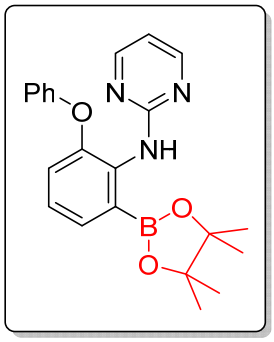
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.09 (s, 1H), 8.89 (brs, 1H), 8.61 (brs, 1H), 7.84 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.55 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.26 – 7.15 (m, 3H), 7.14 – 7.07 (m, 3H), 7.01 (t, *J* = 5.2 Hz, 1H), 1.28 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.62, 154.36, 149.02, 140.57, 136.58, 136.03, 133.82, 129.26, 127.33, 126.06, 125.12, 116.52, 112.36, 80.77, 26.92.

IR (neat, ν/cm^{-1}) 3357, 2979, 1770, 1614, 1578, 1520, 1450, 1384, 1245, 1141, 1050, 1019, 788, 740, 692.

HRMS Calcd for $C_{22}H_{24}BN_3O_2S$: 405.1682, found 405.1678.

_N_-(2-phenoxy-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (12b)



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 86 mg, 74%. White solid, **MP** – 120-122 °C.

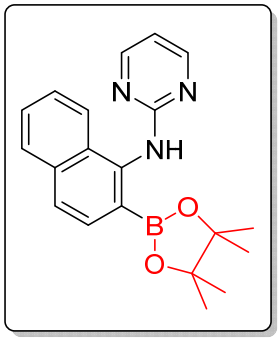
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.78 (brs, 2H), 8.62 (s, 1H), 7.46 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.34 (t, *J* = 7.9 Hz, 2H), 7.19 – 7.03 (m, 4H), 7.00 (t, *J* = 5.2 Hz, 1H), 6.77 (dd, *J* = 8.0, 1.2 Hz, 1H), 1.29 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 156.39, 154.51, 143.86, 129.98, 129.81, 125.96, 124.59, 123.94, 119.17, 115.56, 111.99, 80.68, 26.84.

IR (neat, ν/cm^{-1}) 3419, 3066, 2980, 1770, 1621, 1564, 1532, 1490, 1460, 1246, 1155, 1080, 972, 931, 904, 784, 748, 694.

HRMS Calcd for $C_{22}H_{24}BN_3O_3$: 389.1911, found 389.1910.

***N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-yl)pyrimidin-2-amine (13b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Note: 8% of pinacol present as an impurity, which could not be removed by column chromatography.

Yield – 73 mg, 70%. Yellow solid, **MP** – 210-212 °C.

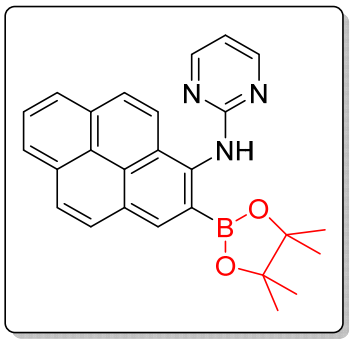
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 8.86 (brs, 2H), 7.89 (d, *J* = 8.4 Hz, 1H), 7.86 – 7.78 (m, 2H), 7.64 (d, *J* = 8.2 Hz, 1H), 7.53 – 7.39 (m, 2H), 7.04 (t, *J* = 5.2 Hz, 1H), 1.32 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.52, 133.53, 128.94, 125.84, 125.29, 124.27, 122.43, 118.68, 112.22, 80.72, 26.80.

IR (neat, ν/cm^{-1}) 3051, 2978, 1769, 1633, 1615, 1573, 1533, 1452, 1359, 1242, 1154, 1095, 1049, 988, 809, 741.

HRMS Calcd for $C_{20}H_{22}BN_3O_2$: 347.1805, found 347.1804.

***N*-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyren-1-yl)pyrimidin-2-amine (14b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 92 mg, 73%. Orange solid, **MP** – 258-260 °C.

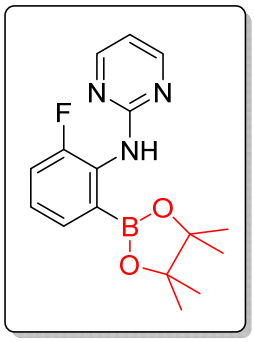
^{1}H NMR (400 MHz, $CDCl_3$) δ 10.75 (s, 1H), 8.91 (brs, 1H), 8.58 (brs, 1H), 8.28 (s, 1H), 7.89 (d, *J* = 9.2 Hz, 1H), 7.83 (d, *J* = 6.9 Hz, 1H), 7.77 – 7.67 (m, 2H), 7.66 – 7.56 (m, 2H), 7.36 (d, *J* = 8.8 Hz, 1H), 6.92 (t, *J* = 5.1 Hz, 1H), 1.52 (d, *J* = 15.0 Hz, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 154.71, 132.50, 130.93, 130.36, 128.29, 127.85, 127.51, 126.27, 125.09, 124.75, 124.33, 124.11, 123.82, 119.24, 117.37, 111.33, 81.12, 26.55.

IR (neat, ν/cm^{-1}) 3038, 2978, 1619, 1561, 1530, 1452, 1429, 1358, 1246, 1194, 1135, 1089, 1055, 1001, 970, 823, 729.

HRMS Calcd for $C_{26}H_{24}BN_3O_2$: 421.1962, found 421.1967.

_N_-(2-fluoro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (15b)



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 67 mg, 71%. White solid, **MP** – 183-185 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 – 8.69 (m, 3H), 7.48 (d, *J* = 7.2 Hz, 1H), 7.12 (td, *J* = 7.8, 5.0 Hz, 1H), 7.08 – 6.95 (m, 2H), 1.27 (s, 12H).

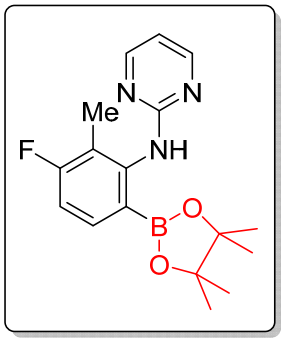
^{13}C NMR (101 MHz, $CDCl_3$) δ 154.58, 150.69 (d, *J* = 245.3 Hz), 126.79 (d, *J* = 8.6 Hz), 126.60 (d, *J* = 3.3 Hz), 124.77 (d, *J* = 5.9 Hz), 113.25 (d, *J* = 17.6 Hz), 112.35, 80.78, 26.68.

^{19}F NMR (376 MHz, $CDCl_3$) δ -136.27.

IR (neat, ν/cm^{-1}) 2976, 1630, 1568, 1534, 1445, 1363, 1251, 1154, 1082, 970, 901, 845, 777.

HRMS Calcd for $C_{16}H_{19}BFN_3O_2$: 315.1554, found 315.1551.

***N*-(3-fluoro-2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (16b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 74 mg, 75%. White solid, **MP** – 204-206 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 9.01 – 8.45 (m, 3H), 7.50 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 5.2 Hz, 1H), 6.88 (dd, *J* = 8.4, 1.2 Hz, 1H), 2.10 (d, *J* = 1.5 Hz, 3H), 1.28 (s, 12H).

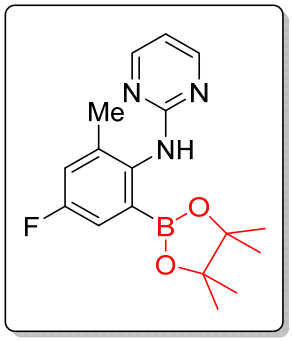
^{13}C NMR (101 MHz, $CDCl_3$) δ 160.56 (d, *J* = 240.9 Hz), 154.74, 138.41 (d, *J* = 6.5 Hz), 129.60 (d, *J* = 9.3 Hz), 111.95, 111.07 (d, *J* = 21.9 Hz), 110.37 (d, *J* = 19.3 Hz), 80.69, 26.51, 8.43 (d, *J* = 5.9 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -119.26.

IR (neat, ν/cm^{-1}) 3205, 2978, 1738, 1628, 1600, 1566, 1544, 1474, 1362, 1249, 1149, 1075, 972, 795, 762, 730.

HRMS Calcd for $C_{17}H_{21}BFN_3O_2$: 329.1711, found 329.1713.

***N*-(4-fluoro-2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (17b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 72 mg, 73%. White solid, **MP** – 245-247 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (brs, 1H), 8.66 (s, 1H), 8.55 (brs, 1H), 7.23 (dd, *J* = 8.5, 2.9 Hz, 1H), 6.94 (t, *J* = 5.2 Hz, 1H), 6.71 (ddd, *J* = 9.2, 2.9, 0.6 Hz, 1H), 2.18 (s, 3H), 1.28 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.98, 160.03 (d, *J* = 242.7 Hz), 154.36, 148.57, 133.20, 125.28 (d, *J* = 7.3 Hz), 115.72 (d, *J* = 23.6 Hz), 114.56 (d, *J* = 19.6 Hz), 111.59, 80.76, 26.51, 17.28.

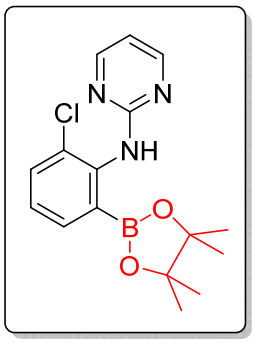
^{19}F NMR (376 MHz, $CDCl_3$) δ -120.04.

^{11}B NMR (128 MHz, $CDCl_3$) δ 5.52.

IR (neat, ν/cm^{-1}) 3218, 2994, 1740, 1630, 1550, 1461, 1367, 1240, 1178, 1137, 1082, 1002, 966, 899, 782, 722, 667.

HRMS Calcd for $C_{17}H_{21}BFN_3O_2$: 329.1711, found 329.1712.

***N*-(2-chloro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (18b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 70 mg, 70%. White solid, **MP** – 114-116 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (brs, 1H), 8.70 (brs, 1H), 8.51 (s, 1H), 7.63 (dd, *J* = 7.3, 1.0 Hz, 1H), 7.31 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.13 (t, *J* = 7.8 Hz, 1H), 7.07 (t, *J* = 5.2 Hz, 1H), 1.26 (s, 12H).

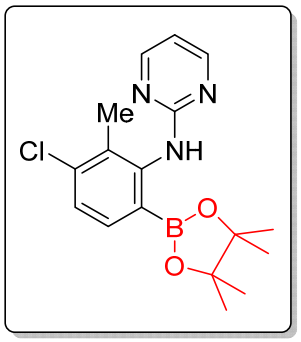
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.63, 154.49, 148.97, 135.04, 130.00, 127.65, 125.18, 119.94, 112.67, 80.80, 26.71.

^{11}B NMR (128 MHz, $CDCl_3$) δ 5.85.

IR (neat, ν/cm^{-1}) 3407, 2972, 1739, 1618, 1575, 1528, 1433, 1364, 1234, 1139, 1049, 1014, 886, 786, 743.

HRMS Calcd for $C_{16}H_{19}BClN_3O_2$: 331.1259, found 331.1255.

***N*-(3-chloro-2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (19b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 53 mg, 51%. White solid, **MP** – 198-200 °C.

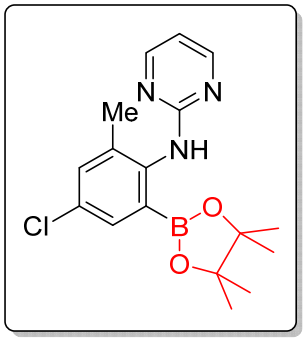
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.86 (brs, 1H), 8.62 (brs, 1H), 8.52 (s, 1H), 7.48 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.00 (t, *J* = 5.2 Hz, 1H), 2.31 (s, 3H), 1.27 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.16, 154.65, 148.76, 138.37, 133.46, 129.69, 125.19, 120.78, 112.16, 80.75, 26.57, 13.67.

IR (neat, ν/cm^{-1}) 2978, 1621, 1564, 1535, 1452, 1246, 1155, 1082, 1002, 969, 915, 788, 761, 732.

HRMS Calcd for $C_{17}H_{21}BClN_3O_2$: 345.1415, found 345.1415.

***N*-(4-chloro-2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (20b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 69 mg, 67%. White solid, **MP** – 238-240 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (brs, 1H), 8.65 (s, 1H), 8.57 (brs, 1H), 7.49 (d, *J* = 2.3 Hz, 1H), 7.01 – 6.94 (m, 2H), 2.17 (s, 3H), 1.28 (s, 12H).

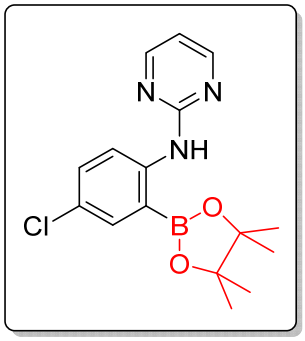
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.17, 154.41, 148.82, 135.74, 129.49, 128.81, 128.74, 124.72, 111.98, 80.82, 26.60, 17.07.

^{11}B NMR (128 MHz, $CDCl_3$) δ 5.66.

IR (neat, ν/cm^{-1}) 2978, 1738, 1623, 1565, 1536, 1458, 1363, 1243, 1156, 1087, 1002, 968, 897, 802, 735.

HRMS Calcd for $C_{17}H_{21}BClN_3O_2$: 345.1415, found 345.1415.

***N*-(4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (21b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 45 mg, 45%. Off-white solid, **MP** – 224-226 °C.

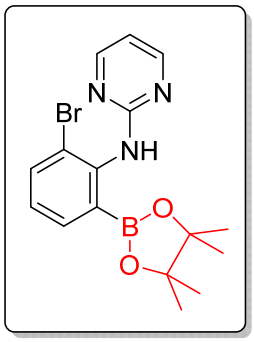
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H), 8.66 (d, *J* = 5.1 Hz, 2H), 7.64 (d, *J* = 2.4 Hz, 1H), 7.11 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.97 – 6.87 (m, 2H), 1.31 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) NMR (101 MHz,) δ 155.10, 138.41, 131.71, 129.26, 127.98, 117.12, 111.87, 81.41, 26.55.

IR (neat, ν/cm^{-1}) 2871, 1625, 1570, 1537, 1459, 1365, 1250, 1192, 1168, 1149, 1137, 1116, 1088, 1017, 894, 849, 784, 746, 712, 661.

HRMS Calcd for $C_{16}H_{19}BClN_3O_2$: 331.1259, found 331.1256.

***N*-(2-bromo-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (22b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 51 mg, 45%. Yellow solid, **MP** – 167-169 °C.

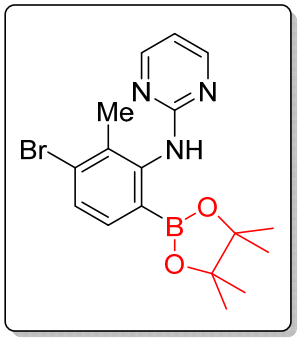
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.91 (d, *J* = 4.3 Hz, 1H), 8.70 (s, 1H), 8.52 (s, 1H), 7.67 (dd, *J* = 7.3, 0.9 Hz, 1H), 7.47 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.14 – 7.00 (m, 2H), 1.25 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.65, 154.53, 148.95, 136.12, 130.87, 130.71, 125.67, 112.71, 110.39, 80.81, 26.71.

IR (neat, ν/cm^{-1}) 3394, 2980, 1771, 1616, 1574, 1522, 1449, 1431, 1246, 1156, 1136, 1046, 1014, 885, 785, 742.

HRMS Calcd for $C_{16}H_{19}BBrN_3O_2$: 375.0754, found 375.0753.

***N*-(3-bromo-2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (23b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 75 mg, 64%. White solid, **MP** – 206-208 °C.

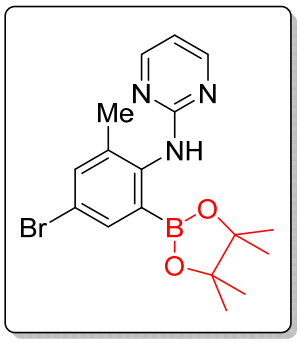
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (brs, 1H), 8.73 – 8. 45 (m, 2H, overlapped with brs), 7.46 – 7.34 (m, 2H), 6.99 (t, *J* = 5.2 Hz, 1H), 2.34 (s, 3H), 1.27 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.17, 154.61, 148.74, 138.24, 130.11, 128.47, 124.30, 122.53, 112.12, 80.77, 26.53, 16.86.

IR (neat, ν/cm^{-1}) 2984, 1738, 1446, 1373, 1236, 1097, 1044, 918, 848, 787, 733.

HRMS Calcd for $C_{17}H_{21}BBrN_3O_2$: 389.0910, found 389.0908.

***N*-(4-bromo-2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (24b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 90 mg, 77%. White solid, **MP** – 232-234 °C.

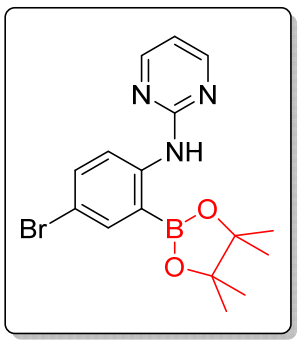
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.85 (brs, 1H), 8.60 (brs, 1H), 8.46 (s, 1H), 7.64 (d, J = 2.1 Hz, 1H), 7.19 – 7.13 (m, 1H), 6.98 (t, J = 5.2 Hz, 1H), 2.21 (s, 3H), 1.27 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.17, 154.42, 148.84, 136.22, 131.84, 131.55, 125.12, 117.74, 112.02, 80.84, 26.60, 17.00.

IR (neat, ν/cm^{-1}) 2973, 1739, 1622, 1536, 1458, 1364, 1232, 1155, 1088, 1002, 897, 791, 735.

HRMS Calcd for $C_{17}H_{21}BBrN_3O_2$: 389.0910, found 389.0905.

***N*-(4-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (25b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Note: >5% of pinacol present as an impurity, which could not be removed by column chromatography.

Yield – 43 mg, 38%. Off-white solid, **MP** – 221-223 °C.

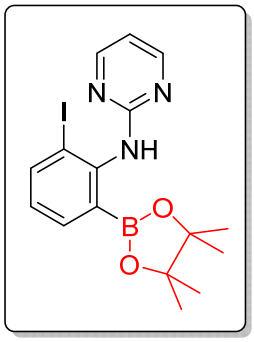
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 5.1 Hz, 2H), 8.54 (s, 1H), 7.80 (d, *J* = 2.3 Hz, 1H), 7.33 (dd, *J* = 8.5, 2.3 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.95 (t, *J* = 5.1 Hz, 1H), 1.30 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.46, 139.13, 135.07, 131.18, 117.58, 117.25, 112.21, 81.59, 26.48.

IR (neat, ν/cm^{-1}) 2973, 1624, 1567, 1533, 1453, 1365, 1247, 1197, 1150, 1116, 1012, 949, 891, 848, 813, 757, 705.

HRMS Calcd for $C_{16}H_{19}BBrN_3O_2$: 375.0754, found 375.0756.

***N*-(2-iodo-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (26b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Note: >5% of pinacol present as an impurity, which could not be removed by column chromatography.

Yield – 51 mg, 40%. Off-white solid, **MP** – decomposed over >280 °C.

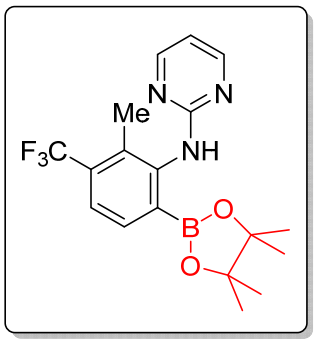
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.74 (brs, 1H), 8.68 (d, *J* = 5.1 Hz, 2H), 7.99 (d, *J* = 2.0 Hz, 1H), 7.49 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.94 (t, *J* = 5.1 Hz, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 1.30 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 155.57, 155.31, 141.00, 139.66, 136.90, 117.94, 112.11, 88.41, 81.50, 26.48.

IR (neat, ν/cm^{-1}) 2979, 2962, 2925, 1771, 1625, 1573, 1528, 1453, 1246, 1151, 1043, 913, 785, 744.

HRMS Calcd for $C_{16}H_{19}BIN_3O_2$: 423.0615, found 423.0613.

***N*-(2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(trifluoromethyl)phenyl)pyrimidin-2-amine (27b)**



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 92 mg, 81%. White solid, **MP** – 244-246 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (brs, 1H), 8.72 (brs, 1H), 8.63 (brs, 1H), 7.65 (d, *J* = 7.8 Hz, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.02 (t, *J* = 5.2 Hz, 1H), 2.32 (s, 3H), 1.28 (s, 12H).

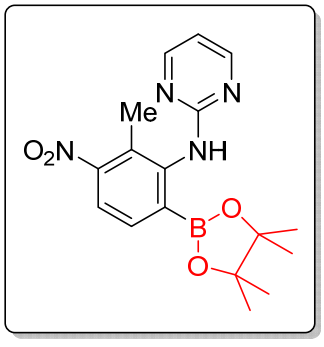
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.39, 154.71, 148.73, 138.43, 128.84, 128.21 (q, *J* = 29.1 Hz), 124.79 (q, *J* = 273.4 Hz), 121.43 (q, *J* = 5.5 Hz), 121.18, 112.33, 80.92, 26.54, 12.99.

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.58.

IR (neat, ν/cm^{-1}) 2975, 1739, 1623, 1543, 1453, 1364, 1318, 1245, 1172, 1104, 1085, 1005, 969, 830, 791, 768, 733.

HRMS Calcd for $C_{18}H_{21}BF_3N_3O_2$: 379.1679, found 379.1676.

***N*-(2-methyl-3-nitro-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (28b)**



This compound was synthesized by following general procedure A. The reaction was

performed on a 0.3 mmol scale.

Yield – 48 mg, 45%. White solid, **MP** – 248-250 °C.

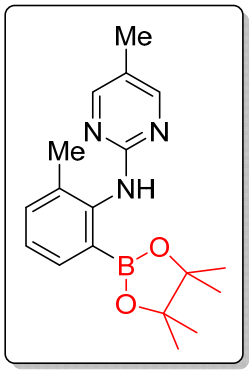
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.98 (brs, 1H), 8.88 (brs, 1H), 8.65 (brs, 1H), 7.72 7.60 (m, 2H), 7.07 (t, *J* = 5.2 Hz, 1H), 2.30 (s, 3H), 1.29 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.58, 154.78, 150.05, 148.69, 138.42, 129.33, 119.89, 117.72, 112.70, 81.14, 26.48, 12.96.

IR (neat, ν/cm^{-1}) 2985, 1738, 1623, 1519, 1448, 1373, 1240, 1046, 917, 734.

HRMS Calcd for $C_{17}H_{21}BN_4O_4$: 356.1656, found 356.1661.

5-methyl-*N*-(2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (29b)



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 62 mg, 64%. White solid, **MP** – 184-186 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (brs, 2H), 7.86 (s, 1H), 7.61 – 7.56 (m, 1H), 7.11 – 7.06 (m, 2H), 2.34 (s, 3H), 2.32 (s, 3H), 1.26 (s, 12H).

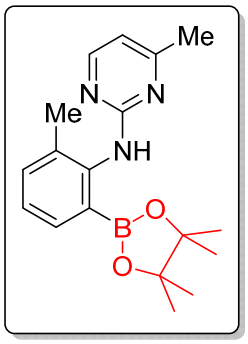
^{13}C NMR (101 MHz, $CDCl_3$) δ 162.06, 153.37, 147.72, 137.59, 129.45, 129.04, 123.95, 121.71, 121.38, 80.49, 26.73, 17.20, 15.03.

IR (neat, ν/cm^{-1}) 3220, 3055, 2973, 1739, 1631, 1569, 1537, 1468, 1410, 1372, 1245, 1217, 1157, 1089, 992, 896, 854, 759, 726.

HRMS Calcd for $C_{18}H_{24}BN_3O_2$: 325.1962, found 325.1958.

4-methyl-*N*-(2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-

yl)phenyl)pyrimidin-2-amine (30b)



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 71 mg, 73%. White solid, **MP** – 231-233 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 6.2 Hz, 1H), 7.96 (s, 1H), 7.58 (dd, *J* = 6.7, 1.9 Hz, 1H), 7.12 – 7.02 (m, 2H), 6.83 (d, *J* = 6.2 Hz, 1H), 2.52 (s, 3H), 2.32 (s, 3H), 1.26 (s, 12H).

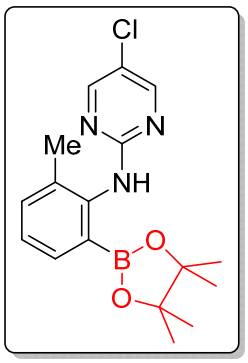
^{13}C NMR (101 MHz, $CDCl_3$) δ 172.19, 154.10, 147.92, 137.39, 129.39, 128.97, 124.02, 121.84, 112.16, 80.38, 26.76, 24.67, 17.23.

δ 194.8, 141.4, 135.6, 133.1, 130.9, 128.0, 84.5, 25.0.

IR (neat, ν/cm^{-1}) 3184, 3055, 2995, 1771, 1631, 1545, 1456, 1246, 1154, 1078, 986, 901, 777, 758.

HRMS Calcd for $C_{18}H_{24}BN_3O_2$: 325.1962, found 325.1964.

5-chloro-*N*-(2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (31b)



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 63 mg, 61%. Yellow solid, **MP** – 151-153 °C.

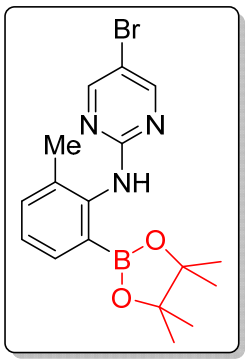
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (s, 2H), 8.29 (s, 1H), 7.57 (dd, *J* = 6.7, 2.0 Hz, 1H), 7.16 – 7.05 (m, 2H), 2.25 (s, 3H), 1.27 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.92, 137.79, 130.02, 124.82, 124.44, 120.01, 81.28, 26.36, 17.47.

IR (neat, ν/cm^{-1}) 3206, 3058, 2980, 1770, 1625, 1537, 1466, 1410, 1368, 1246, 1155, 1088, 994, 776, 749, 710, 665.

HRMS Calcd for $C_{17}H_{21}BClN_3O_2$: 345.1415, found 345.1410.

5-bromo-*N*-(2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrimidin-2-amine (32b)



This compound was synthesized by following general procedure A. The reaction was performed on a 0.3 mmol scale.

Yield – 60 mg, 51%. Yellow solid, **MP** – 156-158 °C.

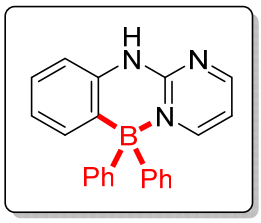
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (brs, 2H), 8.29 (brs, 1H), 7.57 (d, *J* = 6.1 Hz, 1H), 7.17 – 7.05 (m, 2H), 2.25 (s, 3H), 1.27 (s, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.94, 137.69, 129.99, 124.82, 124.29, 106.62, 81.26, 26.38, 17.46.

IR (neat, ν/cm^{-1}) 3198, 3063, 2978, 1770, 1622, 1535, 1466, 1408, 1370, 1246, 1155, 1086, 994, 777, 754, 704.

HRMS Calcd for $C_{17}H_{21}BBrN_3O_2$: 389.0910, found 389.0914.

***N*-(2-(diphenylboraneyl)phenyl)pyrimidin-2-amine (33)**



This compound was synthesized by following general procedure B. The reaction was performed on a 0.15 mmol scale.

Yield – 41 mg, 82%. Yellow solid, **MP** – 232-234 °C.

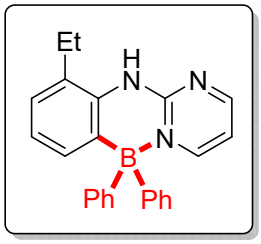
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 4.4, 2.3 Hz, 1H), 8.10 (dd, *J* = 6.2, 2.3 Hz, 1H), 7.87 (s, 1H), 7.24 – 7.02 (m, 13H), 6.83 – 6.72 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.60, 154.12, 153.07, 136.70, 134.43, 134.05, 127.44, 126.36, 125.75, 124.78, 113.67, 112.17.

IR (neat, ν/cm^{-1}) 3351, 3064, 3000, 1621, 1585, 1533, 1475, 1456, 1371, 1244, 1180, 1045, 784, 734.

HRMS Calcd for [M+H] = $C_{22}H_{19}BN_3$: 336.1672, found 336.1673.

***N*-(2-(diphenylboraneyl)-6-ethylphenyl)pyrimidin-2-amine (34)**



This compound was synthesized by following general procedure B. The reaction was performed on a 0.15 mmol scale.

Yield – 39 mg, 72%. Yellow solid, **MP** – 182-184 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (dd, *J* = 4.4, 2.3 Hz, 1H), 8.09 (dd, *J* = 6.1, 2.3 Hz, 1H), 7.82 (s, 1H), 7.27 – 7.08 (m, 10H), 7.04 – 6.94 (m, 3H), 6.79 (dd, *J* = 6.1, 4.4 Hz, 1H), 2.67 (q, *J* = 7.6 Hz, 2H), 1.32 (t, *J* = 7.6 Hz, 3H).

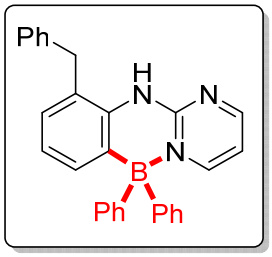
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.52, 154.19, 152.94, 134.52, 134.06, 132.40, 127.39, 126.21, 125.86, 125.68, 124.59, 112.21, 23.68, 13.93.

^{11}B NMR (128 MHz, $CDCl_3$) δ -1.19.

IR (neat, ν/cm^{-1}) 3433, 3063, 3004, 1620, 1565, 1528, 1461, 1433, 1394, 1187, 913, 869, 772, 704.

HRMS Calcd for $C_{24}H_{22}BN_3$: 363.1907, found 363.1905.

***N*-(2-benzyl-6-(diphenylboraneyl)phenyl)pyrimidin-2-amine (35)**



This compound was synthesized by following general procedure B. The reaction was performed on a 0.15 mmol scale.

Yield – 38 mg, 60%. Pale-yellow solid, **MP** – 249-251 °C.

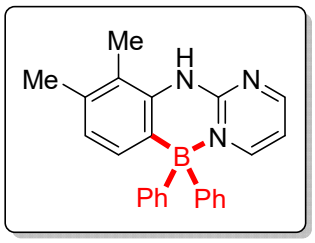
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (dd, *J* = 4.4, 2.3 Hz, 1H), 8.08 (dd, *J* = 6.1, 2.3 Hz, 1H), 7.72 (s, 1H), 7.36 – 7.28 (m, 2H), 7.25 – 7.08 (m, 13H), 7.05 – 6.95 (m, 3H), 6.74 (dd, *J* = 6.1, 4.4 Hz, 1H), 4.06 (s, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.52, 153.93, 152.77, 138.84, 135.20, 134.11, 133.22, 129.13, 128.68, 128.39, 127.39, 126.91, 125.69, 124.52, 123.14, 112.25, 37.78.

IR (neat, ν/cm^{-1}) 3408, 3062, 3002, 1619, 1566, 1527, 1460, 1433, 1220, 1169, 1124, 1075, 1029, 913, 868, 772, 702.

HRMS Calcd for [M+H] = $C_{29}H_{25}BN_3$: 426.2142, found 426.2137.

***N*-(6-(diphenylboraneyl)-2,3-dimethylphenyl)pyrimidin-2-amine (36)**



This compound was synthesized by following general procedure B. The reaction was performed on a 0.15 mmol scale.

Yield – 32 mg, 59%. Yellow solid, **MP** – 234-236 °C.

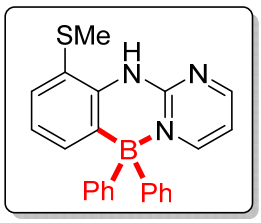
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (dd, *J* = 4.4, 2.3 Hz, 1H), 8.08 (dd, *J* = 6.1, 2.2 Hz, 1H), 7.84 (s, 1H), 7.23 – 7.07 (m, 10H), 6.94 – 6.84 (m, 2H), 6.80 (dd, *J* = 6.1, 4.4 Hz, 1H), 2.28 (s, 3H), 2.24 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.46, 154.34, 152.90, 135.27, 134.36, 134.02, 131.65, 127.39, 126.48, 125.65, 119.02, 112.14, 20.55, 12.63.

IR (neat, ν/cm^{-1}) 3436, 3044, 3002, 2924, 1619, 1576, 1532, 1474, 1362, 1220, 1167, 1030, 912, 871, 771, 704.

HRMS Calcd for $C_{24}H_{22}BN_3$: 363.1907, found 363.1909.

***N*-(2-(diphenylboraneyl)-6-(methylthio)phenyl)pyrimidin-2-amine (37)**



This compound was synthesized by following general procedure B. The reaction was performed on a 0.15 mmol scale.

Yield – 34 mg, 59%. Yellow solid, **MP** – 218-220 °C.

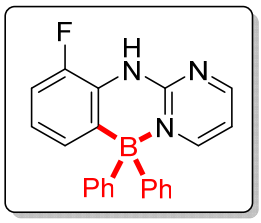
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.06 (s, 1H), 8.58 (dd, *J* = 4.4, 2.3 Hz, 1H), 8.10 (dd, *J* = 6.1, 2.3 Hz, 1H), 7.36 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.24 – 6.98 (m, 12H), 6.82 (dd, *J* = 6.1, 4.4 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.81, 154.10, 152.96, 137.33, 134.61, 134.00, 131.82, 127.46, 125.80, 125.02, 120.01, 112.42, 20.11.

IR (neat, ν/cm^{-1}) 3342, 3044, 3006, 2921, 1615, 1577, 1523, 1449, 1430, 1380, 1179, 1124, 1029, 867, 773, 704.

HRMS Calcd for $C_{23}H_{20}BN_3S$: 381.1471, found 381.1466.

***N*-(2-(diphenylboraneyl)-6-fluorophenyl)pyrimidin-2-amine (38)**



This compound was synthesized by following general procedure B. The reaction was performed on a 0.15 mmol scale.

Yield – 43 mg, 81%. Pale-yellow solid, **MP** – 222-224 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (dd, *J* = 4.5, 2.3 Hz, 1H), 8.27 (s, 1H), 8.11 (dd, *J* = 6.1, 2.3 Hz, 1H), 7.27 – 7.07 (m, 10H), 7.03 – 6.80 (m, 4H).

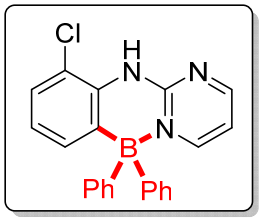
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.94, 153.89, 153.22, 149.90 (d, *J* = 245.6 Hz), 133.96, 129.26 (d, *J* = 3.1 Hz), 127.53, 125.94, 124.84 (d, *J* = 6.0 Hz), 124.58 (d, *J* = 8.0 Hz), 112.72, 112.05 (d, *J* = 17.5 Hz).

^{19}F NMR (376 MHz, $CDCl_3$) δ -138.04.

IR (neat, ν/cm^{-1}) 3419, 3276, 3065, 3004, 1626, 1568, 1532, 1461, 1255, 1223, 1190, 1031, 913, 846, 773, 743, 704.

HRMS Calcd for $C_{22}H_{17}BFN_3$: 353.1500, found 353.1501.

***N*-(2-chloro-6-(diphenylboraneyl)phenyl)pyrimidin-2-amine (39)**



This compound was synthesized by following general procedure B. The reaction was performed on a 0.15 mmol scale.

Yield – 39 mg, 70%. Off-white solid, **MP** – 213-215 °C.

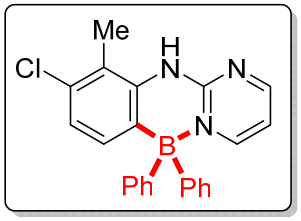
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.5, 2.3 Hz, 1H), 8.35 (s, 1H), 8.14 – 8.05 (m, 1H), 7.27 – 7.13 (m, 7H), 7.12 – 7.05 (m, 4H), 7.05 – 6.94 (m, 2H), 6.84 (dd, *J* = 6.1, 4.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.92, 154.00, 152.98, 133.95, 132.98, 132.73, 127.54, 126.39, 125.96, 125.28, 118.84, 112.91.

IR (neat, ν/cm^{-1}) 3402, 3293, 3063, 1615, 1576, 1523, 1448, 1388, 1219, 1176, 1119, 915, 866, 818, 773, 739, 704.

HRMS Calcd for $C_{22}H_{17}BClN_3$: 369.1204, found 369.1200.

***N*-(3-chloro-6-(diphenylboraneyl)-2-methylphenyl)pyrimidin-2-amine (40)**



This compound was synthesized by following general procedure B. The reaction was performed on a 0.15 mmol scale.

Yield – 36 mg, 63%. Pale-yellow solid, **MP** – 242-244 °C.

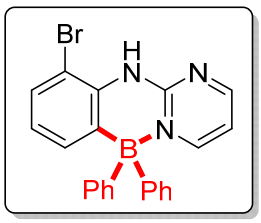
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.5, 2.3 Hz, 1H), 8.09 (dd, *J* = 6.1, 2.3 Hz, 1H), 7.81 (s, 1H), 7.24 – 7.13 (m, 6H), 7.11 – 7.04 (m, 5H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.85 (dd, *J* = 6.1, 4.5 Hz, 1H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.73, 154.20, 152.92, 136.29, 133.95, 132.73, 132.29, 127.51, 125.90, 125.27, 118.60, 112.76, 13.49.

IR (neat, ν/cm^{-1}) 3429, 3064, 3004, 1618, 1524, 1452, 1366, 1218, 1168, 1025, 974, 912, 871, 771, 704.

HRMS Calcd for $C_{23}H_{19}BClN_3$: 383.1361, found 383.1357.

***N*-(2-bromo-6-(diphenylboraneyl)phenyl)pyrimidin-2-amine (41)**



This compound was synthesized by following general procedure B. The reaction was

performed on a 0.15 mmol scale.

Yield – 44 mg, 71%. Off-white solid, **MP** – 236-238 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (dd, *J* = 4.4, 2.3 Hz, 1H), 8.37 (s, 1H), 8.09 (dd, *J* = 6.1, 2.3 Hz, 1H), 7.33 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.25 – 7.13 (m, 6H), 7.12 – 7.01 (m, 5H), 6.94 – 6.87 (m, 1H), 6.84 (dd, *J* = 6.1, 4.5 Hz, 1H).

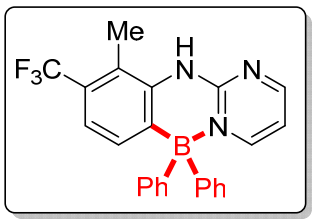
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.92, 154.12, 152.91, 134.07, 133.95, 133.48, 129.60, 127.54, 125.96, 125.77, 112.94, 109.33.

^{11}B NMR (128 MHz, $CDCl_3$) δ -0.60.

IR (neat, ν/cm^{-1}) 3386, 3004, 1739, 1614, 1573, 1521, 1434, 1366, 1217, 1107, 1031, 913, 866, 771, 704.

HRMS Calcd for $C_{22}H_{17}BBrN_3$: 413.0699, found 413.0691.

N-(6-(diphenylboraneyl)-2-methyl-3-(trifluoromethyl)phenyl)pyrimidin-2-amine (42)



This compound was synthesized by following general procedure B. The reaction was performed on a 0.15 mmol scale.

Yield – 46 mg, 73%. Off-white solid, **MP** – 235-237 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (dd, *J* = 4.5, 2.3 Hz, 1H), 8.09 (dd, *J* = 6.1, 2.3 Hz, 1H), 7.91 (s, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.25 – 7.14 (m, 6H), 7.12 – 7.04 (m, 5H), 6.89 (dd, *J* = 6.1, 4.5 Hz, 1H), 2.42 (s, 3H).

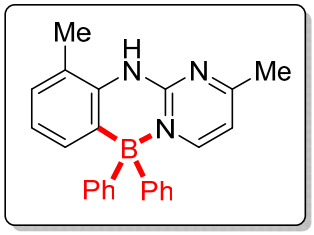
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.87, 154.20, 152.92, 136.39, 133.87, 131.82, 127.53, 127.10 (d, *J* = 29.2 Hz), 125.98, 121.52 (d, *J* = 5.5 Hz), 120.00 (d, *J* = 270.3 Hz), 112.90, 12.79.

^{19}F NMR (376 MHz, $CDCl_3$) δ -59.39.

IR (neat, ν/cm^{-1}) 3441, 3067, 1618, 1580, 1533, 1478, 1317, 1168, 1113, 1028, 980, 771, 737, 704.

HRMS Calcd for $C_{24}H_{19}BF_3N_3$: 417.1624, found 417.1623.

***N*-(2-(diphenylboraneyl)-6-methylphenyl)-4-methylpyrimidin-2-amine (43)**



This compound was synthesized by following general procedure B. The reaction was performed on a 0.15 mmol scale.

Yield – 36 mg, 66%. Off-white solid, **MP** – 203-205 °C.

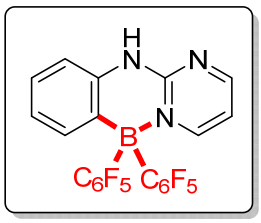
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 6.3 Hz, 1H), 7.64 (s, 1H), 7.23 – 7.09 (m, 10H), 7.01 – 6.91 (m, 3H), 6.65 (d, *J* = 6.3 Hz, 1H), 2.50 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.67, 153.61, 151.93, 135.38, 134.05, 132.43, 127.93, 127.34, 125.57, 124.19, 120.28, 112.55, 24.71, 17.16.

IR (neat, ν/cm^{-1}) 3410, 3063, 1626, 1539, 1462, 1252, 1167, 1032, 913, 772, 746, 705.

HRMS Calcd for $C_{24}H_{22}BN_3$: 363.1907, found 363.1908.

***N*-(2-(bis(perfluorophenyl)boraneyl)phenyl)pyrimidin-2-amine (44)**



This compound was synthesized by following general procedure B. The reaction was performed on a 0.15 mmol scale.

Yield – 35 mg, 45%. Yellow solid, **MP** – 186-188 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (dd, *J* = 4.3, 2.1 Hz, 1H), 8.09 (dd, *J* = 6.3, 2.1 Hz, 1H), 8.03 (s, 1H), 7.25 (d, *J* = 6.1 Hz, 1H, overlapped with $CDCl_3$ residual peak), 7.20 (td, *J* = 7.5, 1.5 Hz, 1H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 6.92 (dd, *J* = 6.3, 4.3 Hz, 1H), 6.83 (dd, *J* = 7.8, 0.5 Hz, 1H).

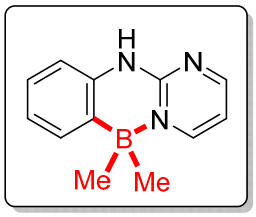
^{13}C NMR (101 MHz, $CDCl_3$) δ 163.23, 153.29, 151.68, 148.06 (dm, *J* = 245.0 Hz), 139.95 (dm, *J* = 243.9 Hz), 137.37 (dm, *J* = 247.1 Hz), 134.89, 132.42, 127.55, 125.65, 114.52, 113.13.

^{19}F NMR (376 MHz, $CDCl_3$) δ -132.54 (d, *J* = 23.5 Hz, 2F), -156.78 (d, *J* = 23.5 Hz, 1F), -162.87 (t, *J* = 19.5 Hz, 2F).

IR (neat, ν/cm^{-1}) 3422, 3044, 1635, 1546, 1517, 1458, 1282, 1092, 977, 913, 840, 772, 669.

HRMS Calcd for $C_{22}H_8BF_{10}N_3$: 515.0652, found 515.0645.

***N*-(2-(dimethylboraneyl)phenyl)pyrimidin-2-amine (45)**



This compound was synthesized by following general procedure C. The reaction was performed on a 0.15 mmol scale.

Yield – 23 mg, 74%. Yellow solid, **MP** – 168-170 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 4.5, 2.3 Hz, 1H), 8.34 (dd, *J* = 6.1, 2.3 Hz, 1H), 7.59 (s, 1H), 7.33 (dd, *J* = 5.5, 3.3 Hz, 1H), 7.11 – 7.02 (m, 2H), 6.85 (dd, *J* = 6.1, 4.5 Hz, 1H), 6.71 – 6.64 (m, 1H), 0.12 (s, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 160.91, 153.88, 151.60, 135.98, 131.96, 125.61, 124.57, 113.50, 112.39.

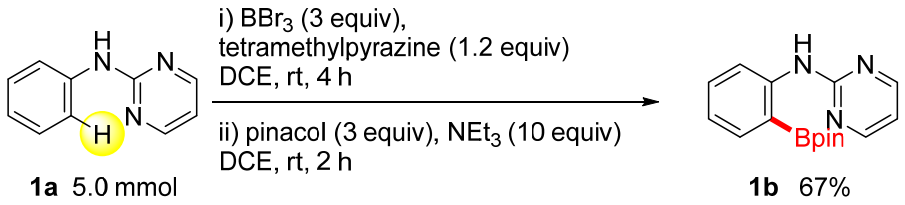
IR (neat, ν/cm^{-1}) 3276, 2993, 2909, 1769, 1628, 1538, 1461, 1411, 1369, 1272, 1245, 1056, 1024, 950, 914, 784, 735.

HRMS Calcd for [M+H] = $C_{12}H_{15}BN_3$: 212.1359, found 212.1357.

9. Gram-scale synthesis of metal-free directed C-H borylation

In a dry flux in a glovebox, the 2-pyrimidylaniline (856 mg, 5.0 mmol, 1 equiv) and tetramethylpyrazine (817mg, 6.0 mmol, 1.2 equiv), and DCE (10 mL) were added. BBr_3 (15.0 mmol, 3 equiv; in the form of a 1 mol/L solution in DCM) was then added dropwise

into the reaction mixture with stirring, and the reaction mixture was stirred for 4 h at room temperature. The reaction was quenched with pinacol (1773 mg, 15.0 mmol, 3 equiv) and triethylamine (7 mL, 50 mmol, 10 equiv), and stirred for another 2 h at room temperature. After the reaction reached completion, the volatiles were removed under reduced pressure and the crude mixture was dissolved in EtOAc (50 mL) and H_2O (25 mL). The aqueous layer was washed with EtOAc (3 x 50 mL) and the organic layers were collected, dried over $MgSO_4$ and filtered. The solvent was removed under reduced pressure and the product was isolated by column chromatography (eluent: hexane/$CHCl_3$ = 10/1 to 2/1).



1a 5.0 mmol **1b** 67%

10. Effects of external additives

Procedure for evaluating the effect of external impurities:

To a dry sample vial inside a glovebox, **1a** (17 mg, 0.1 mmol, 1 equiv), tetramethylpyrazine (16 mg, 0.12 mmol, 1.2 equiv), **external additive** (0.1 mmol, 1 equiv), and 0.5 mL of DCE were added. BBr_3 (0.3 mmol, 3 equiv; in the form of a 1 mol/L solution in DCM) was added dropwise into the reaction mixture with stirring and the reaction was stirred for an additional 4 h at room temperature. The reaction was quenched with pinacol (35 mg, 0.3 mmol, 3 equiv) and triethylamine (0.14 mL, 1.0 mmol, 10 equiv) and stirred for another 2 h at room temperature after which, the volatiles were removed under reduced pressure. The crude mixture was dissolved in $CDCl_3$ (1 mL) and H_2O (1 mL). Mesitylene (7.0 μL, 0.05 mmol, 0.5 equiv) was added into the mixture and an ^1H NMR spectrum was obtained on the $CDCl_3$ layer. The yield of the desired product was determined by quantitative ^1H NMR analysis and data are given below. A graphical presentation is presented to emphasize the effect of external impurities on this process.

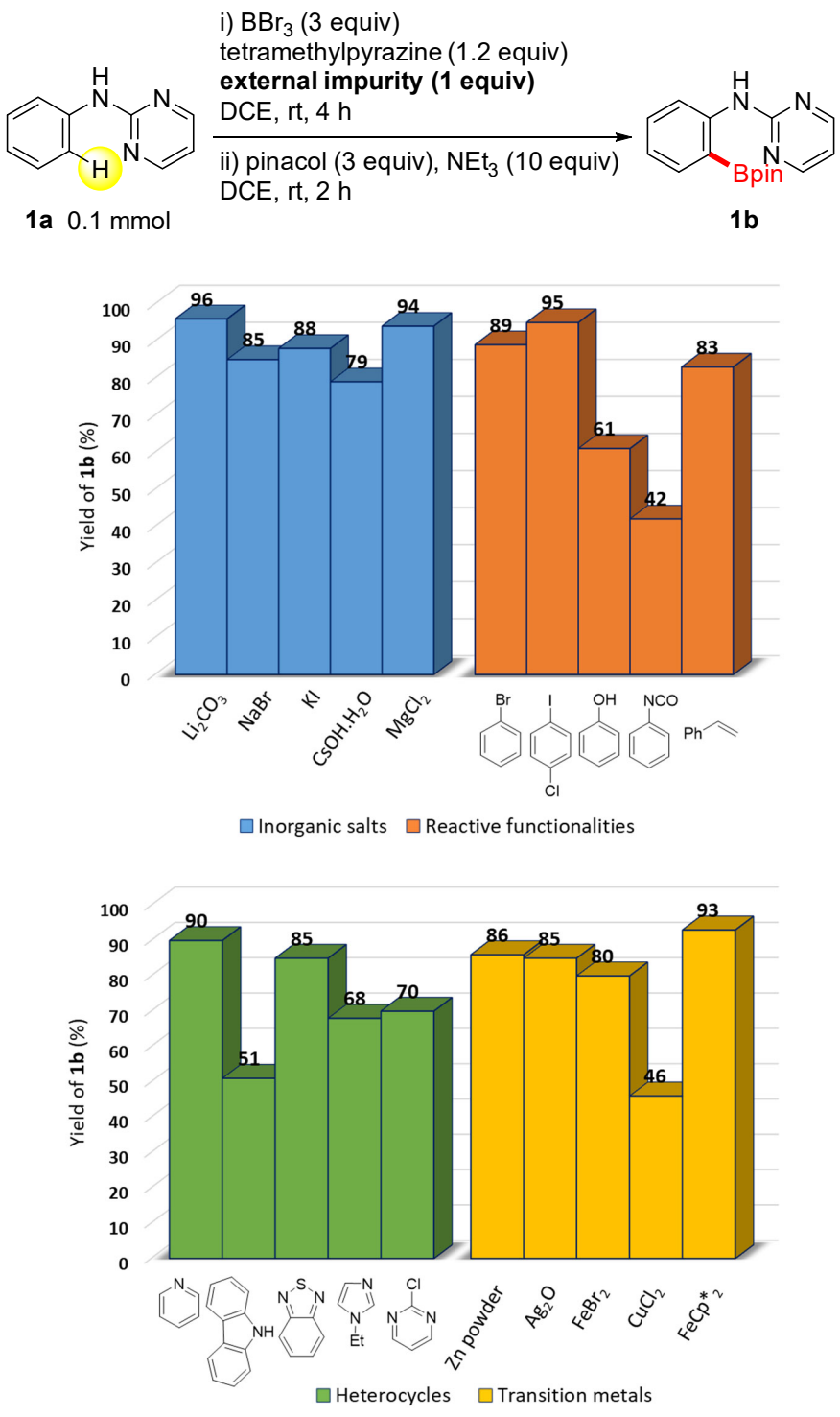
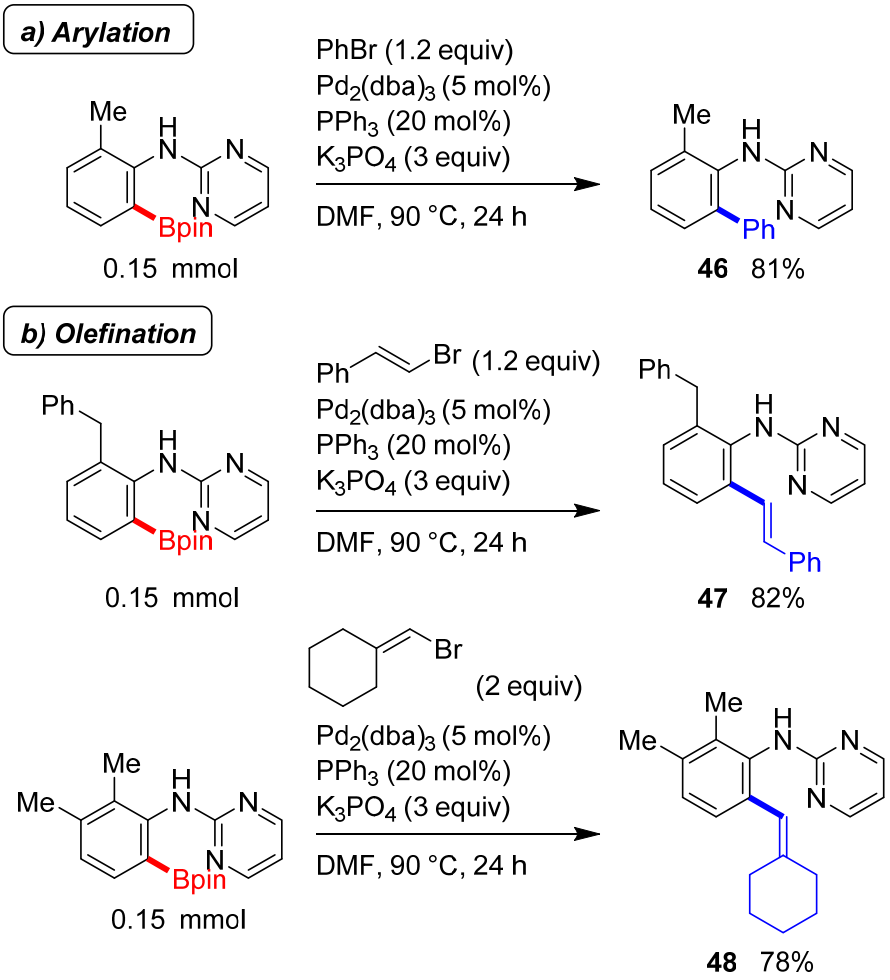


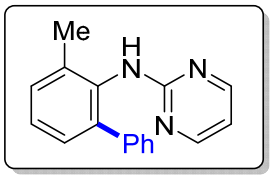
Figure S1. Metal-free directed borylation of 2-pyrimidylaniline in the presence of (a) inorganic salts and reactive functionalities (b) heterocycles and transition metals as external impurities.

11. Derivatization of borylated product



***N*-(3-methyl-[1,1'-biphenyl]-2-yl)pyrimidin-2-amine (46)**

The boronic ester (47 mg, 0.15 mmol, 1 equiv), PPh_3 (8 mg, 0.03 mmol, 20 mol%), K_3PO_4 (95 mg, 0.45 mmol, 3 equiv), and $Pd_2(dba)_3$ (7 mg, 0.0075mmol, 5 mol%) were added to a dry sealed tube. The sealed tube was degassed, flushed with nitrogen and DMF (2 mL) and phenyl bromide (19 μL, 0.18 mmol, 1.2 equiv) were then added. The tube was sealed and the reaction mixture was heated at 90 °C for 24 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: hexane/EtOAc = 4/1) to give the corresponding product in 81% yield.



Yield – 32 mg, 81%. White solid, **MP** – 87-89 °C.

^{1}H NMR (400 MHz, $CDCl_3$) NMR δ 8.28 (d, *J* = 4.8 Hz, 2H), 7.37 – 7.19 (m, 8H), 6.58 (t, *J* = 4.8 Hz, 1H), 6.46 (s, 1H), 2.29 (s, 3H).

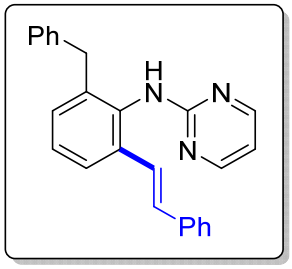
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.70, 158.42, 140.00, 139.81, 137.05, 134.22, 130.33, 129.03, 128.36, 128.32, 127.29, 127.08, 111.67, 19.03.

IR (neat, ν/cm^{-1}) 3220, 3026, 2969, 1579, 1519, 1445, 1406, 1256, 1221, 1032, 993, 911, 795, 754, 700, 665.

HRMS Calcd for $C_{17}H_{15}N_3$: 261.1266, found 261.1264.

(*E*)-*N*-(2-benzyl-6-styrylphenyl)pyrimidin-2-amine (47)

The boronic ester (58 mg, 0.15 mmol, 1 equiv), PPh_3 (8 mg, 0.03 mmol, 20 mol%), K_3PO_4 (95 mg, 0.45 mmol, 3 equiv), and $Pd_2(dba)_3$ (7 mg, 0.0075mmol, 5 mol%) were added to a dry sealed tube. The sealed tube was degassed, flushed with nitrogen and DMF (2 mL) and (*E*)-(2-bromovinyl)benzene (23 μL, 0.18 mmol, 1.2 equiv) were then added. The tube was sealed and the reaction mixture was heated at 90 °C for 24 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: hexane/EtOAc = 4/1) to give the corresponding product in 82% yield.



Yield – 45 mg, 82%. White solid, **MP** – 204-206 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, *J* = 4.8 Hz, 2H), 7.68 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.40 – 7.02 (m, 14H, overlapped with $CDCl_3$ residual peak), 6.60 (t, *J* = 4.8 Hz, 1H), 6.47 (s, 1H), 3.96 (s, 2H).

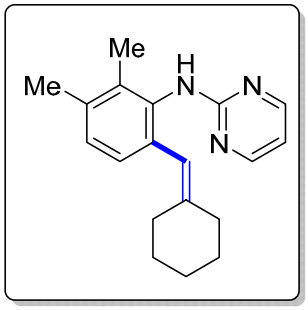
^{13}C NMR (101 MHz, $CDCl_3$) δ 161.86, 158.55, 140.14, 139.84, 137.59, 136.53, 134.63, 130.60, 130.23, 128.97, 128.71, 128.65, 127.77, 127.75, 126.75, 126.25, 125.09, 124.63, 111.94, 38.69.

IR (neat, ν/cm^{-1}) 3219, 3025, 2924, 1580, 1519, 1494, 1446, 1409, 1267, 1178, 1074, 964, 772, 694.

HRMS Calcd for $C_{25}H_{21}N_3$: 363.1735, found 363.1729.

***N*-(6-(cyclohexylidenemethyl)-2,3-dimethylphenyl)pyrimidin-2-amine (48)**

The boronic ester (49 mg, 0.15 mmol, 1 equiv), PPh_3 (8 mg, 0.03 mmol, 20 mol%), K_3PO_4 (95 mg, 0.45 mmol, 3 equiv), and $Pd_2(dba)_3$ (7 mg, 0.0075mmol, 5 mol%) were added to a dry sealed tube. The sealed tube was degassed, flushed with nitrogen and DMF (2 mL) and (bromomethylene)cyclohexane (40 μL, 0.3 mmol, 2 equiv) were then added. The tube was sealed and the reaction mixture was heated at 90 °C for 24 h. The solvent was removed under reduced pressure and the crude product was purified by column chromatography (eluent: hexane/EtOAc = 4/1) to give the corresponding product in 78% yield.



Yield – 34 mg, 78%. Off white, **MP** – 146-148 °C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 4.8 Hz, 2H), 7.06 (d, *J* = 7.8 Hz, 1H), 6.99 (d, *J* = 7.7 Hz, 1H), 6.59 (t, *J* = 4.8 Hz, 1H), 6.55 (s, 1H), 6.04 (s, 1H), 2.31 (s, 3H), 2.23 – 2.09 (m, 7H), 1.58 – 1.37 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 161.78, 158.41, 144.18, 136.01, 135.00, 134.85, 133.49, 128.10, 127.48, 119.17, 111.49, 37.36, 29.87, 28.74, 27.97, 26.76, 20.67, 15.13.

IR (neat, ν/cm^{-1}) 3225, 2924, 2853, 1584, 1522, 1446, 1404, 1264, 1217, 1178, 1088, 990, 909, 799, 753, 700.

HRMS Calcd for $C_{19}H_{23}N_3$: 293.1892, found 293.1894.

12. Reaction profile for the borylation reaction

A stock solution of pinacol (354 mg, 3 mmol, 3 equiv) and triethylamine (1.4 mL, 10 mmol, 10 equiv) in 3 mL $CDCl_3$ were prepared beforehand in a glovebox. The stock solution was distributed in 15 sample vials (0.3 mL in each vial). A magnetic stir bar was added to each

vial and the resulting solution was continuously stirred.

To a dry sample vial in a glovebox, **1a** (171 mg, 1.0 mmol, 1 equiv), tetramethylpyrazine (163 mg, 1.2 mmol, 1.2 equiv), mesitylene (70 μL, 0.5 mmol, 0.5 equiv) and $CDCl_3$ (2.5 mL) were added. Neat BBr_3 (285 μL, 3.0 mmol, 3 equiv) was then quickly added to the reaction mixture in one portion while the stirring continued. From the reaction mixture, 15 fractions (each 0.2 mL) were obtained at regular intervals (1 min, 2.5 min, 5 min, 7.5 min, 10 min, 12.5 min, 15 min, 17.5 min, 20 min, 22.5 min, 25 min, 27.5 min, 30 min, 32.5 min, 35 min) and each fraction was immediately injected into a vial that contained pinacol and NEt_3 that had been prepared beforehand. All of these reactions were stirred for another 30 min at room temperature. $CDCl_3$ (0.5 mL) and H_2O (0.5 mL) was then added to the reaction mixtures. ^1H NMR spectra were obtained for the $CDCl_3$ layer. The yield of the desired product was determined by quantitative ^1H NMR analysis and the data are given below. Yield (%) vs time (min) plots are given in Figure S2.

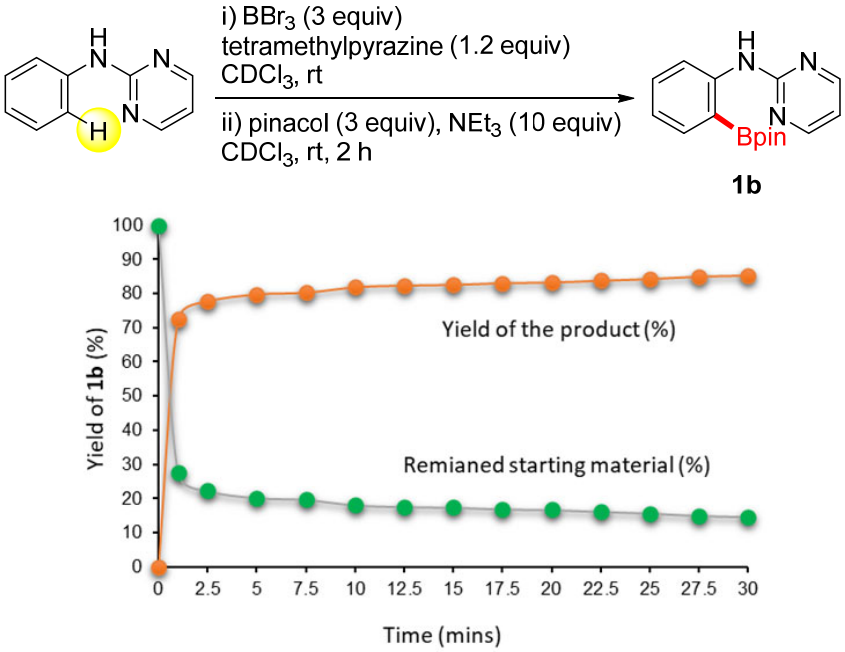
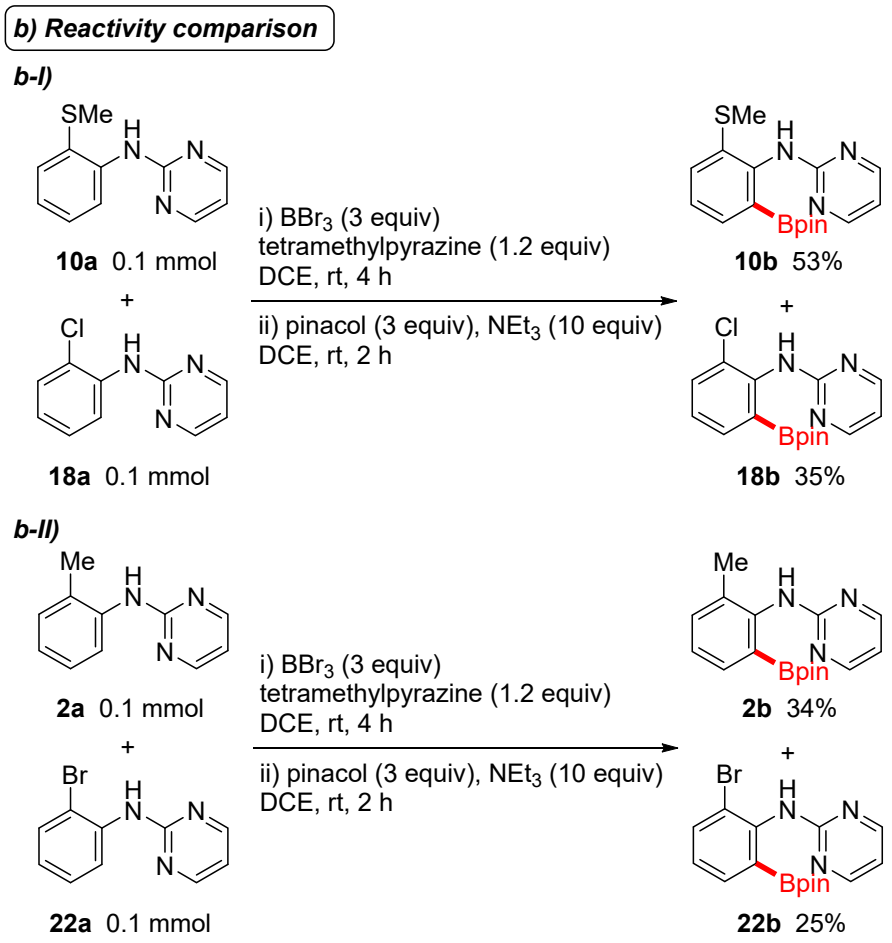


Figure S2. Yield (%) vs. time (min) reaction profile for directed metal-free *ortho*-C-H borylation of 2-pyrimidylanilines

13. Competition reaction

To a dry sample vial in a glovebox, **10a** (22 mg, 0.1 mmol, 1 equiv), **18a** (21 mg, 0.1 mmol, 1 equiv), tetramethylpyrazine (16 mg, 0.12 mmol, 1.2 equiv), and DCE (0.5 mL) were added. BBr_3 (0.3 mmol, 3 equiv; in the form of a 1 mol/L solution in DCM) was added dropwise into the reaction mixture with stirring and the reaction mixture was stirred for 4 h at room temperature. The reaction was quenched with pinacol (35 mg, 0.3 mmol, 3 equiv) and triethylamine (0.14 mL, 1.0 mmol, 10 equiv), and stirred for another 2 h at room temperature. After the reaction reached completion, the volatiles were removed unde reduced pressure and the crude mixture was dissolved in $CDCl_3$ (1 mL) and H_2O (1 mL). Mesitylene (7.0 μL, 0.05 mmol, 0.5 equiv) was added into the mixture and an ^1H NMR spectrum was obtained on the $CDCl_3$ layer. The yields of **10b** and **18b** were determined by quantitative ^1H NMR analysis.

Another competition reaction similar to that described above, was performed between **2a** and **22a**. The results are presented in below Scheme.



14. NMR studies

The reaction of tetramethylpyrazine and BBr_3 resulted in only one NMR signal which appeared in the negative region, and corresponds to the formation of the adduct complex (**49**). The signal for a similar adduct complex Br_3B•pyridine was reported to appear at $\delta = -7.8$.[6]

A similar signal was also observed in the case of the reaction of 2-pyrimidylaniline **1a** with BBr_3, which could be attributed to the formation of the adduct complex **50**. Unfortunately, we were not able to detect the exact species that is responsible for the reaction, due to the speed of the reaction.

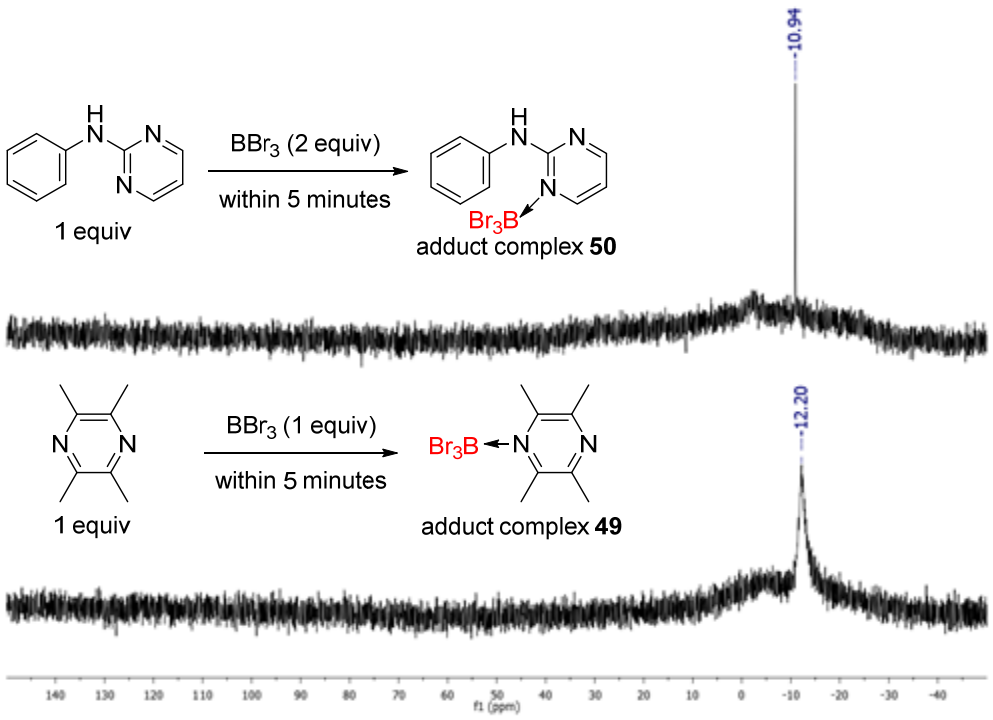
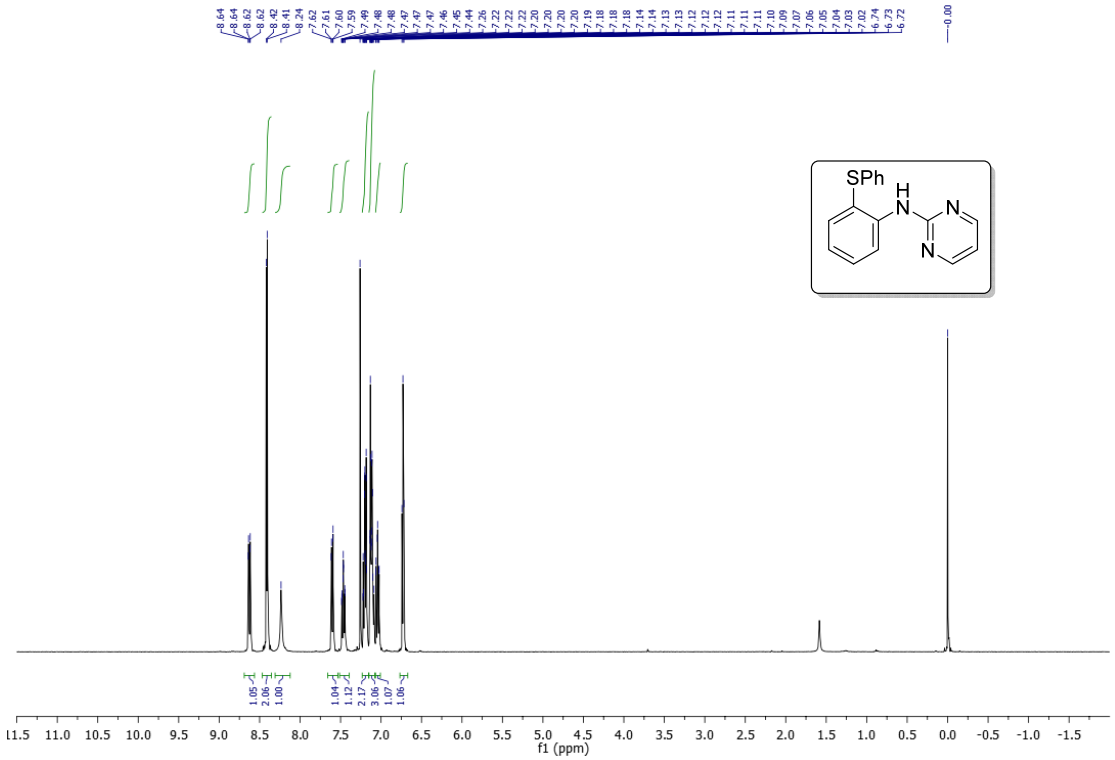


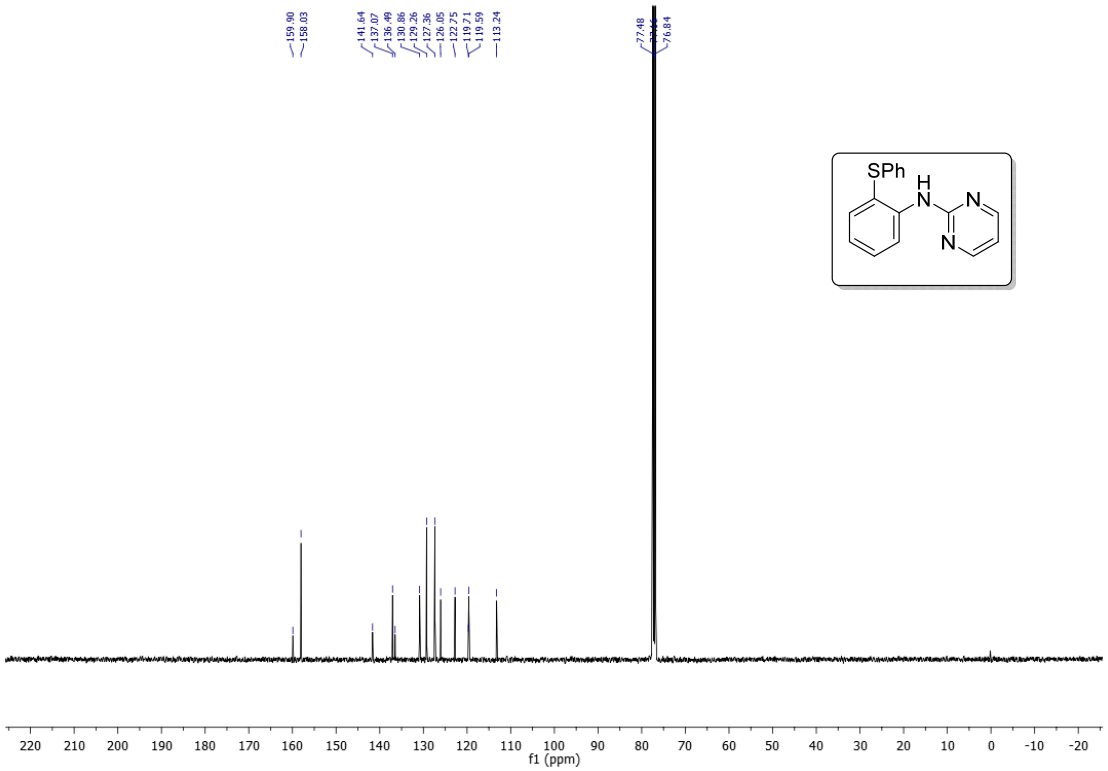
Figure S3. Reaction of 2-pyrimidylaniline and BBr_3 (top) and reaction of tetramethylpyrazine and BBr_3 (bottom).

15. NMR spectra of starting materials

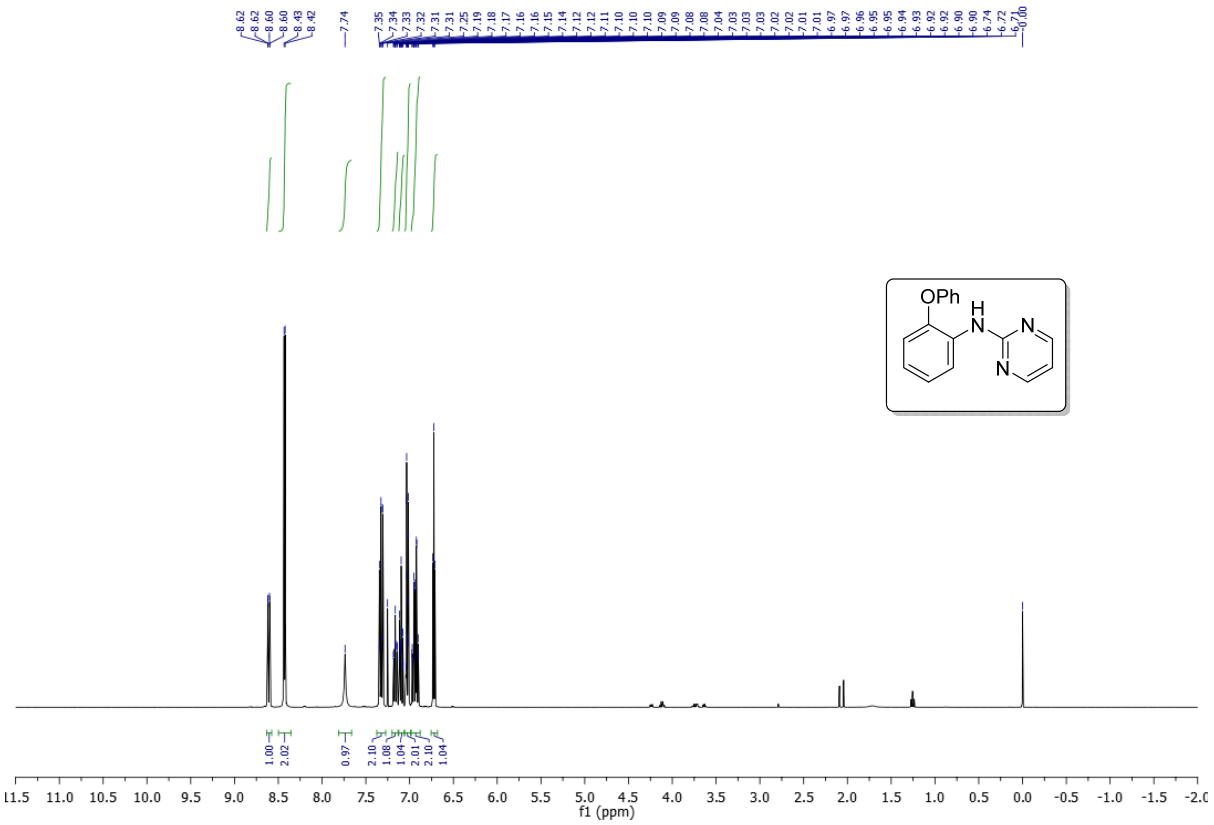
^{1}H NMR spectrum of **11a** (400 MHz, $CDCl_3$):



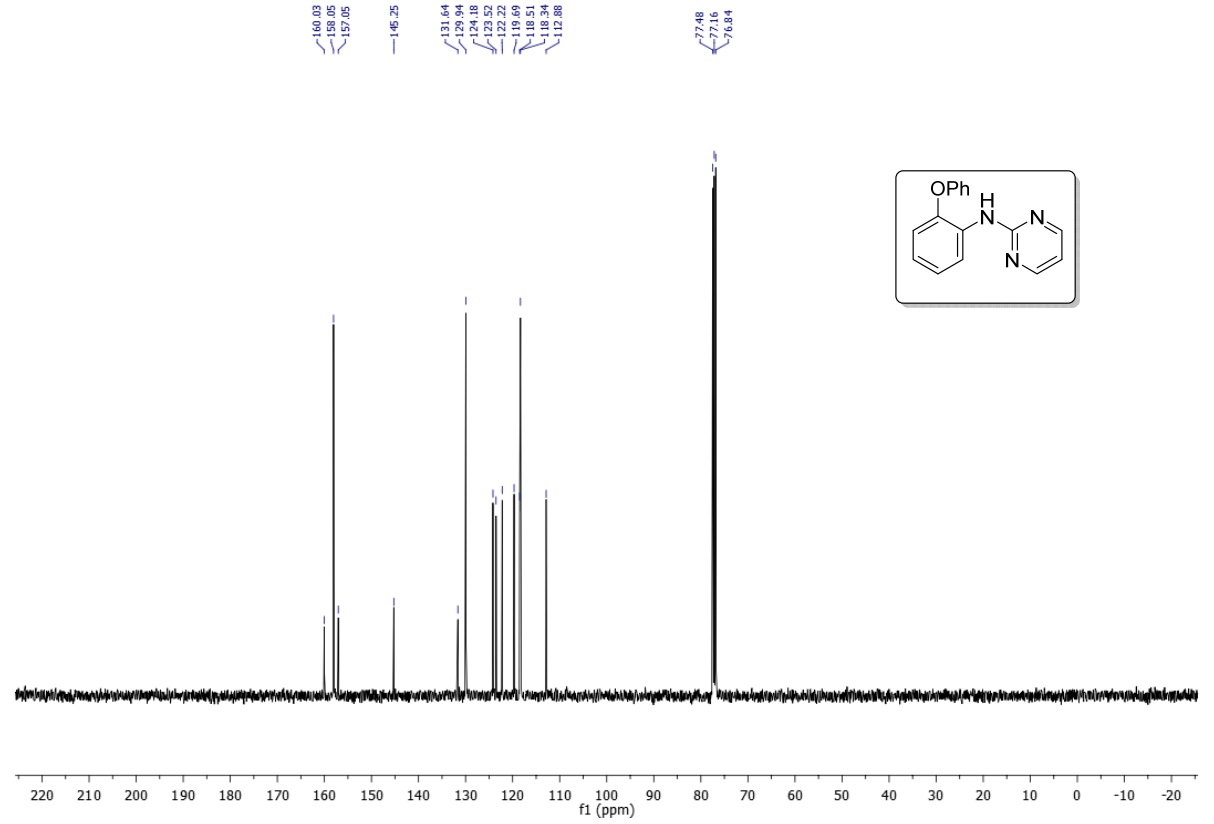
^{13}C NMR spectrum of **11a** (101 MHz, $CDCl_3$):



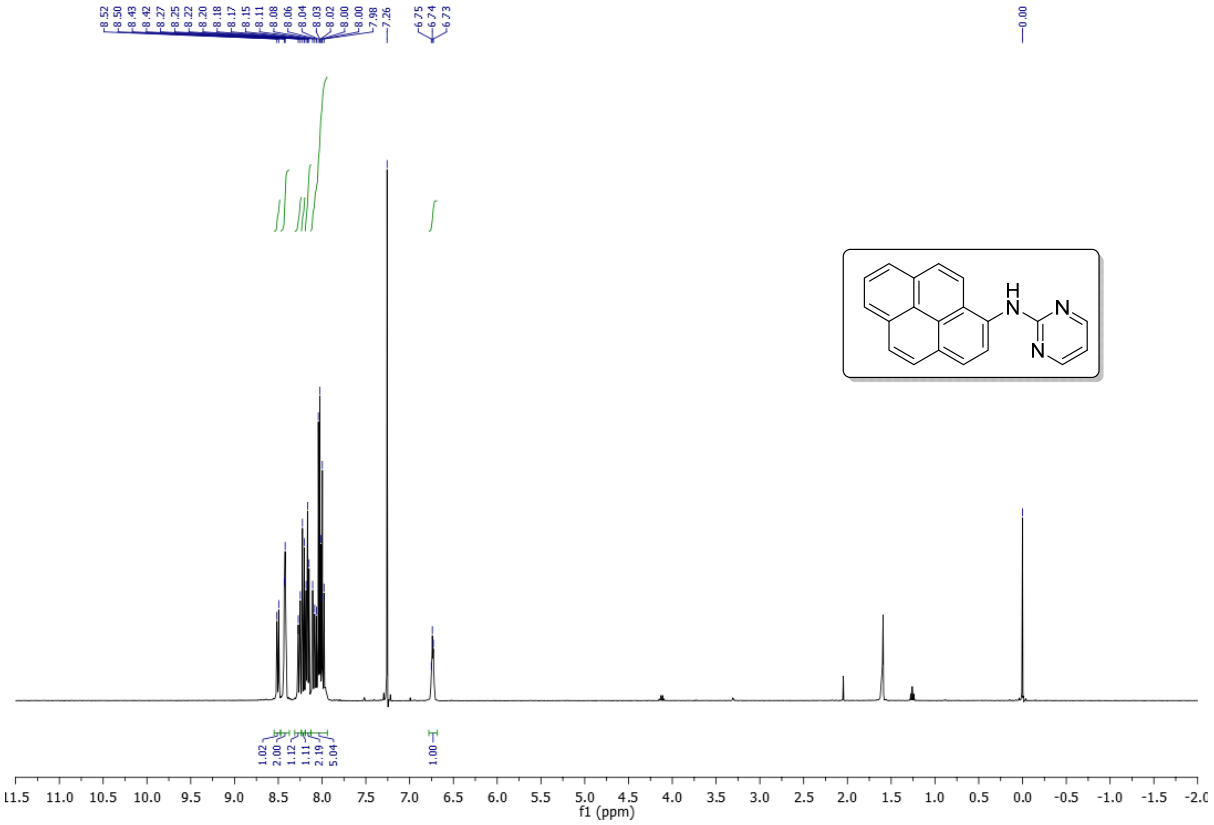
^{1}H NMR spectrum of **12a** (400 MHz, $CDCl_3$):



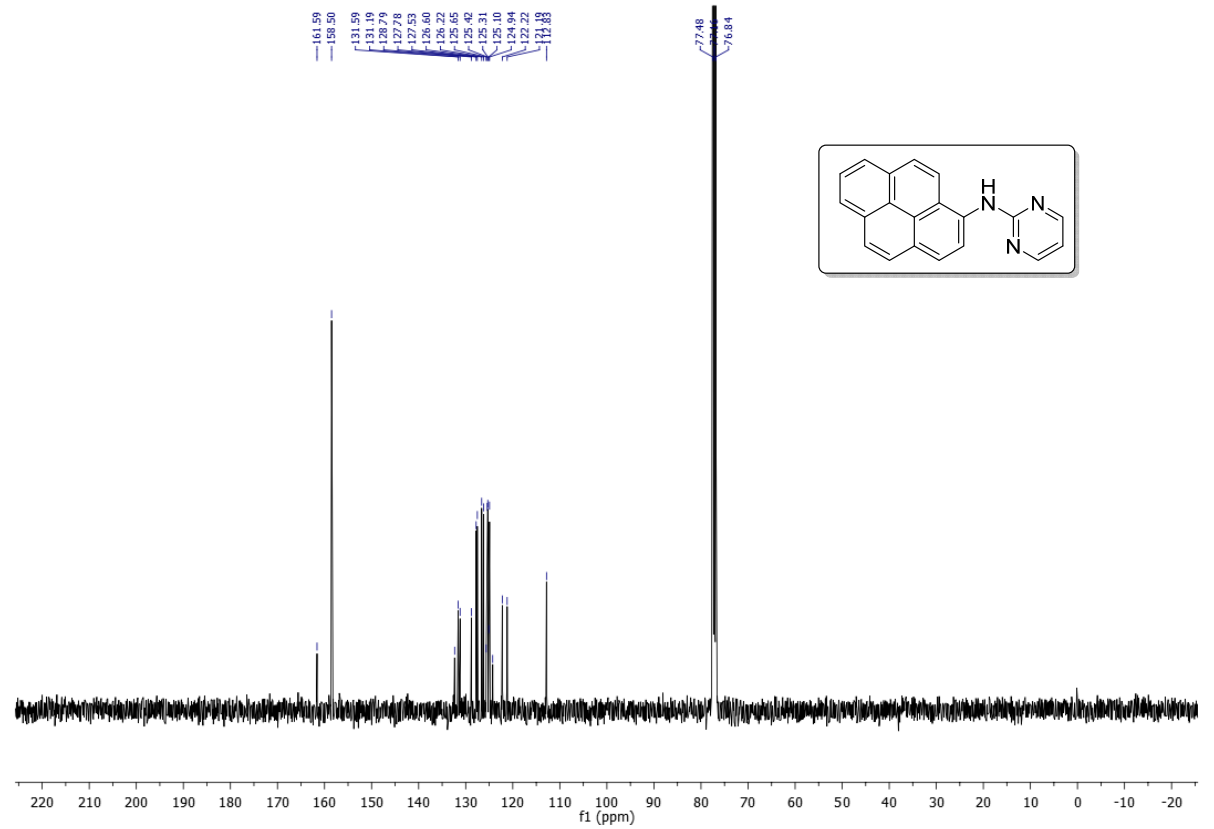
^{13}C NMR spectrum of **12a** (101 MHz, $CDCl_3$):



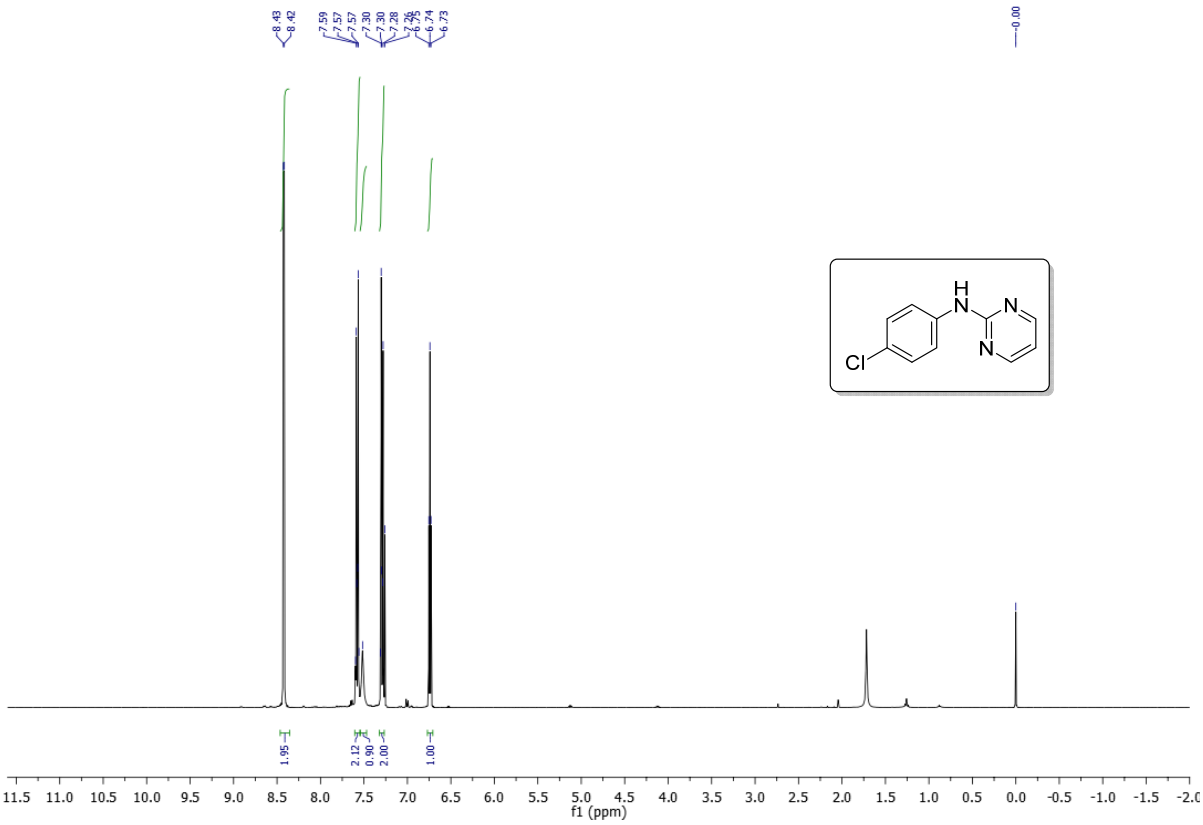
^{1}H NMR spectrum of **14a** (400 MHz, $CDCl_3$):



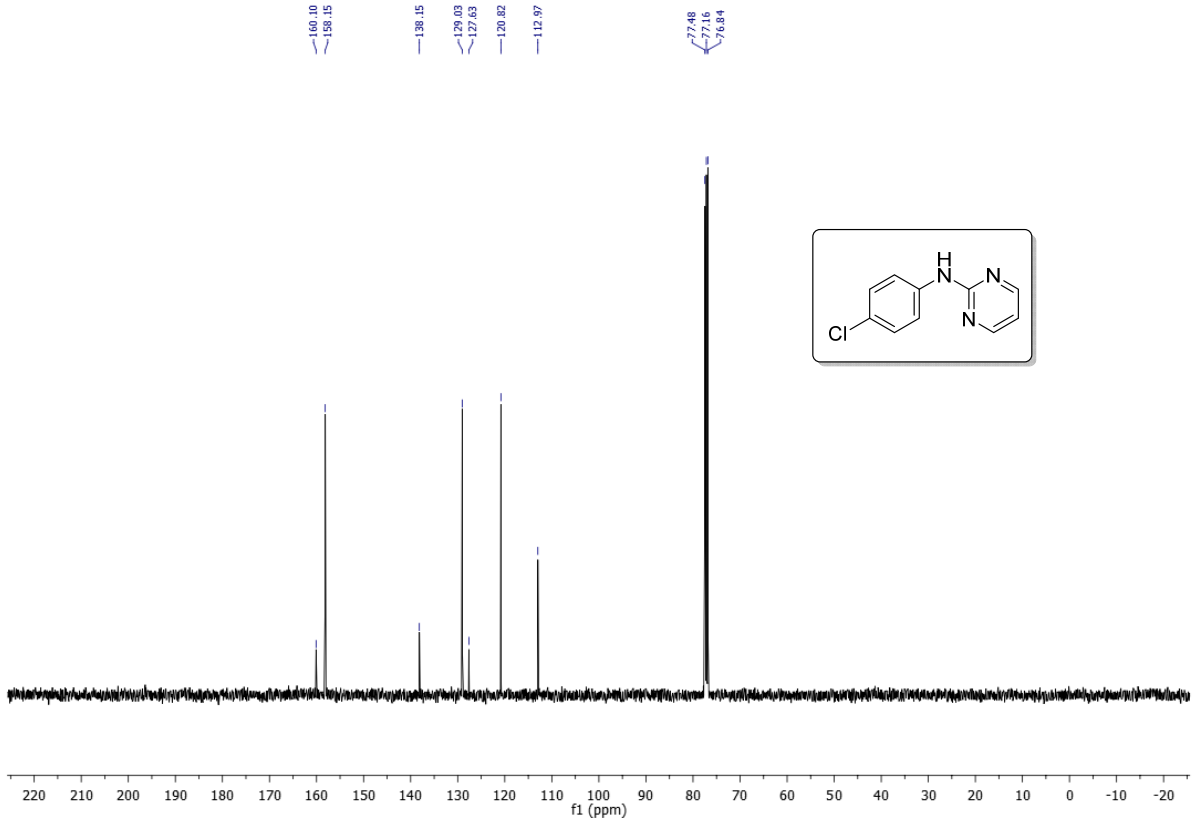
^{13}C NMR spectrum of **14a** (101 MHz, $CDCl_3$):



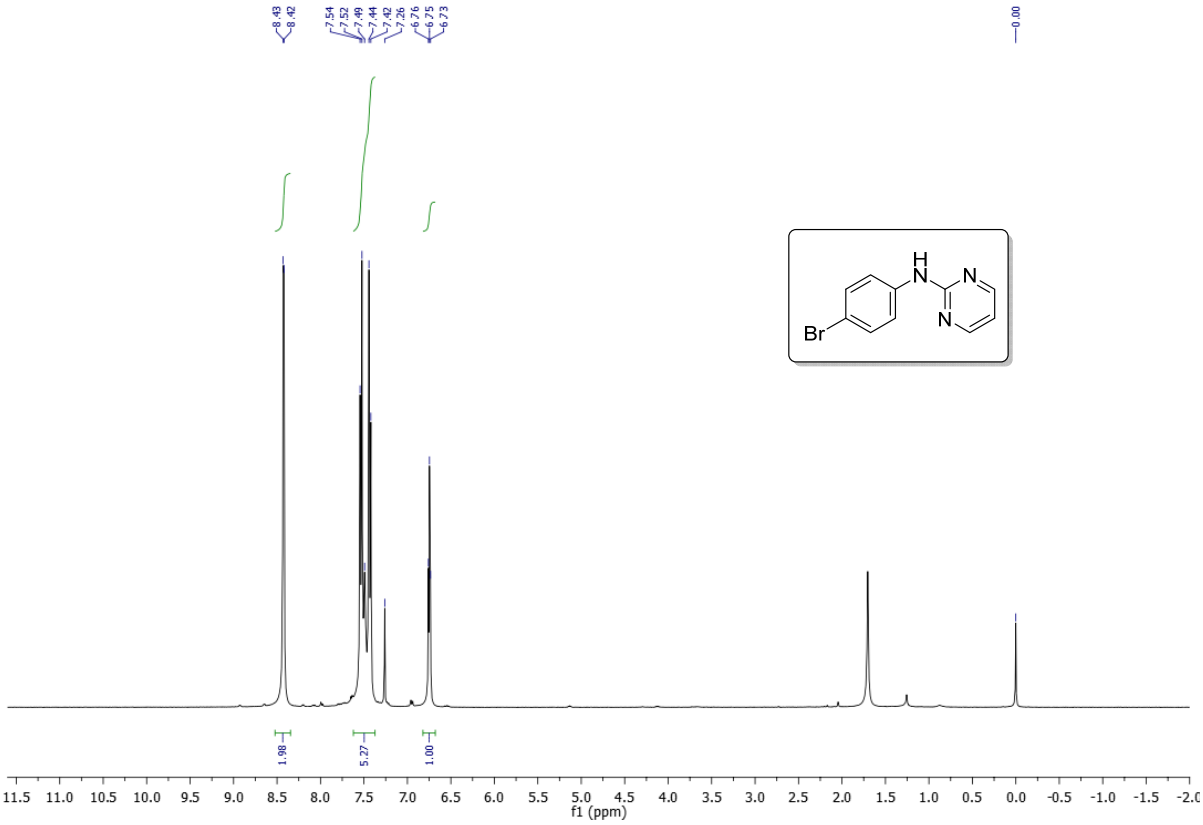
^{1}H NMR spectrum of **21a** (400 MHz, $CDCl_3$):



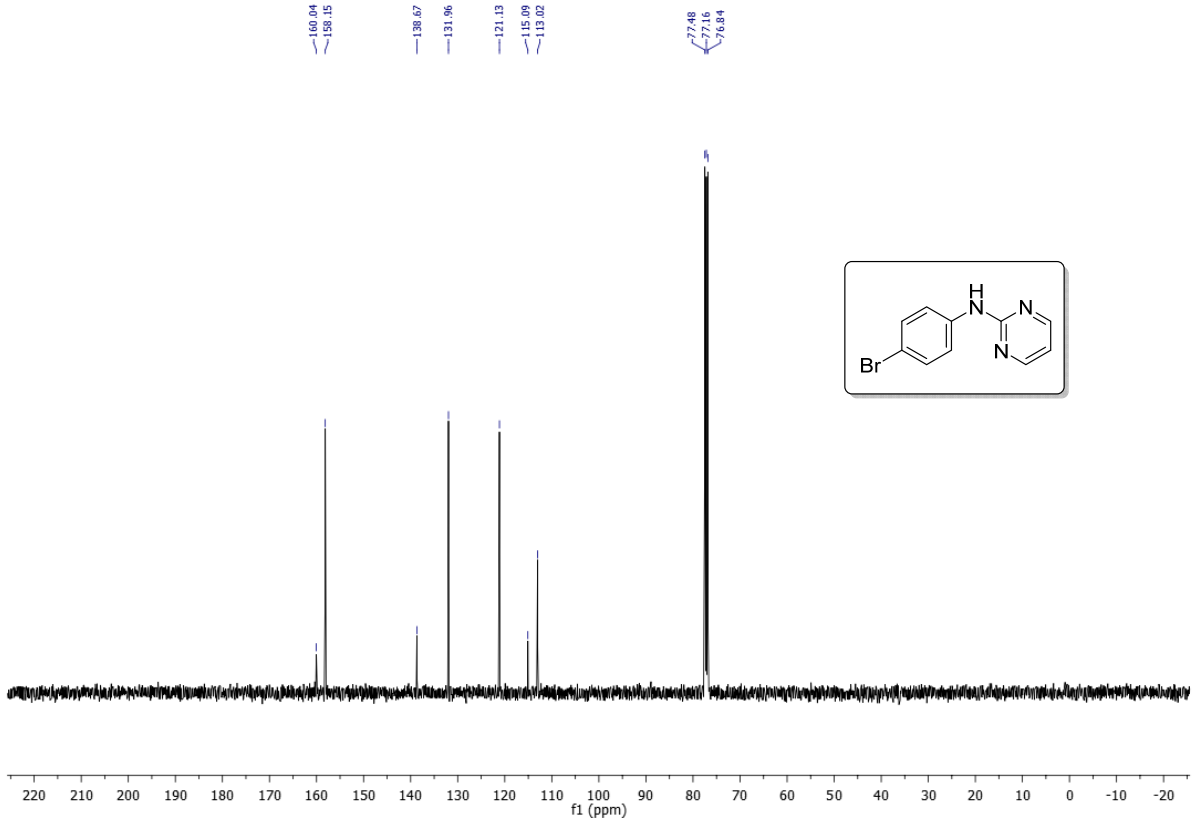
^{13}C NMR spectrum of **21a** (101 MHz, $CDCl_3$):



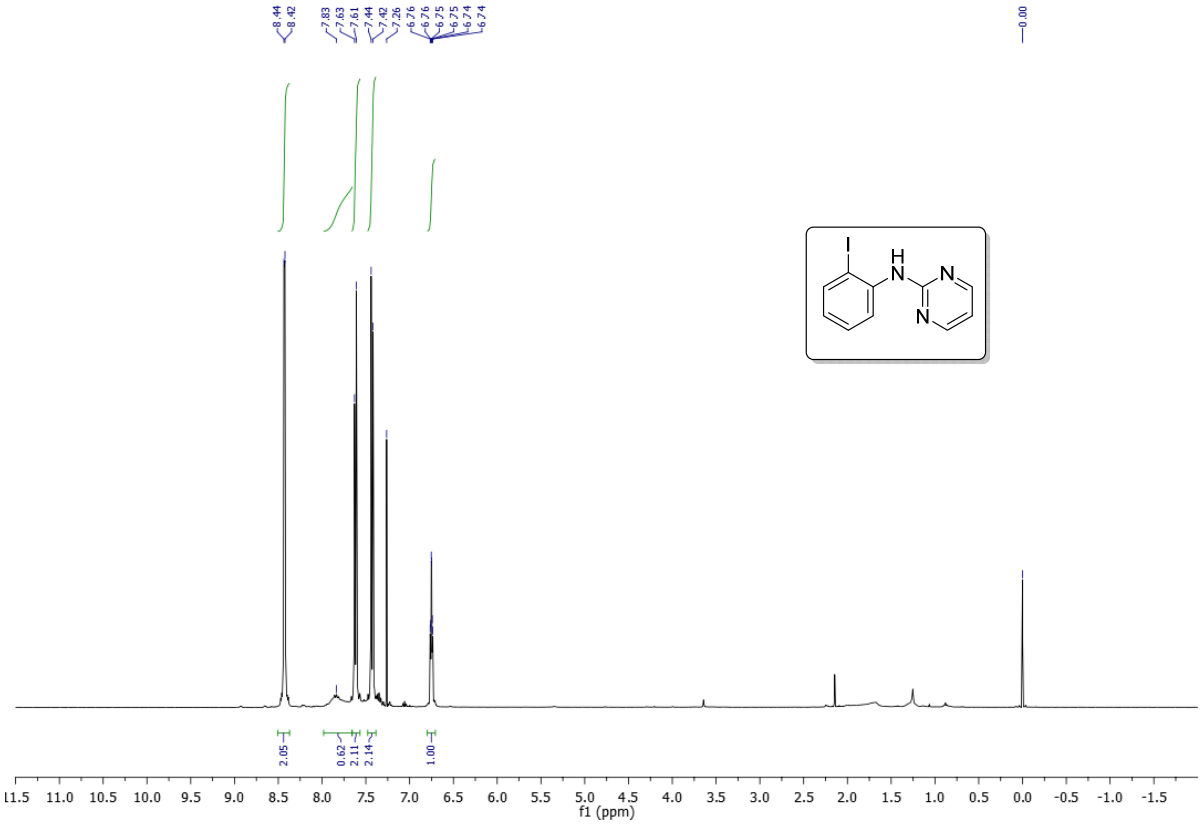
^{1}H NMR spectrum of **25a** (400 MHz, $CDCl_3$):



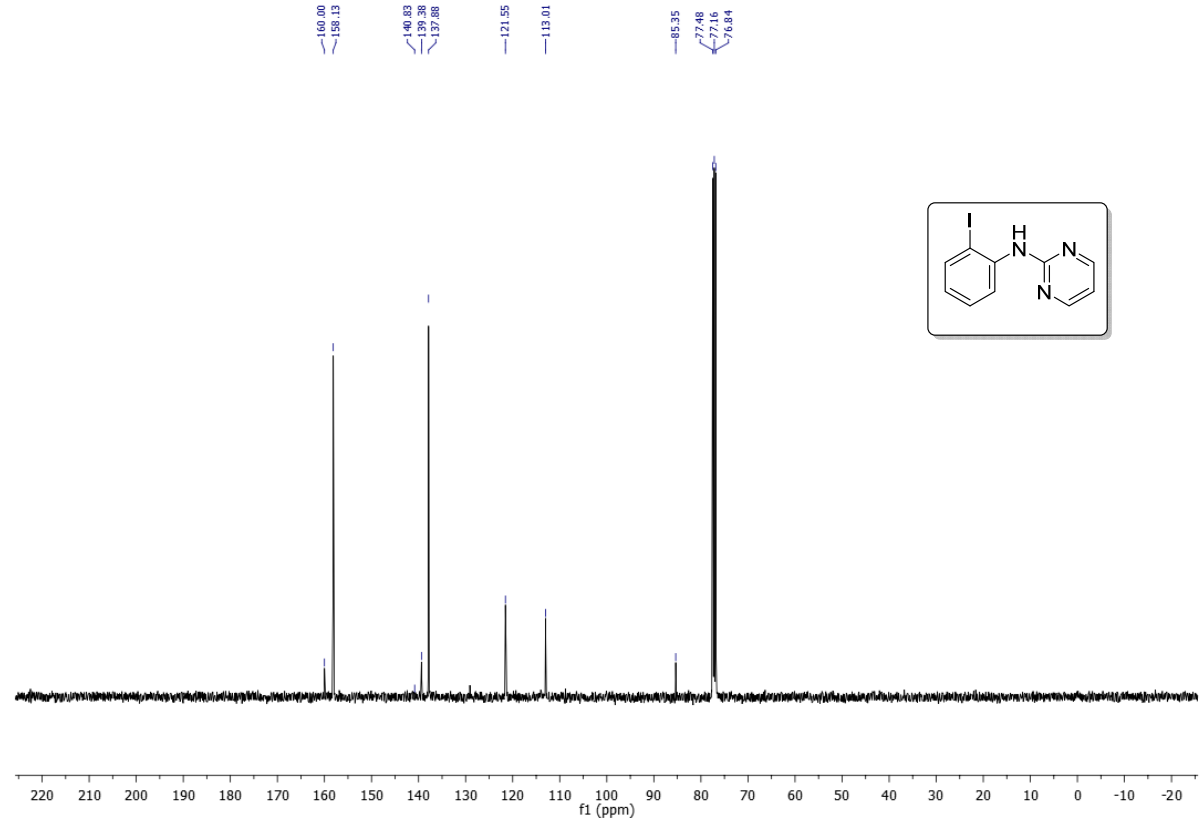
^{13}C NMR spectrum of **25a** (101 MHz, $CDCl_3$):



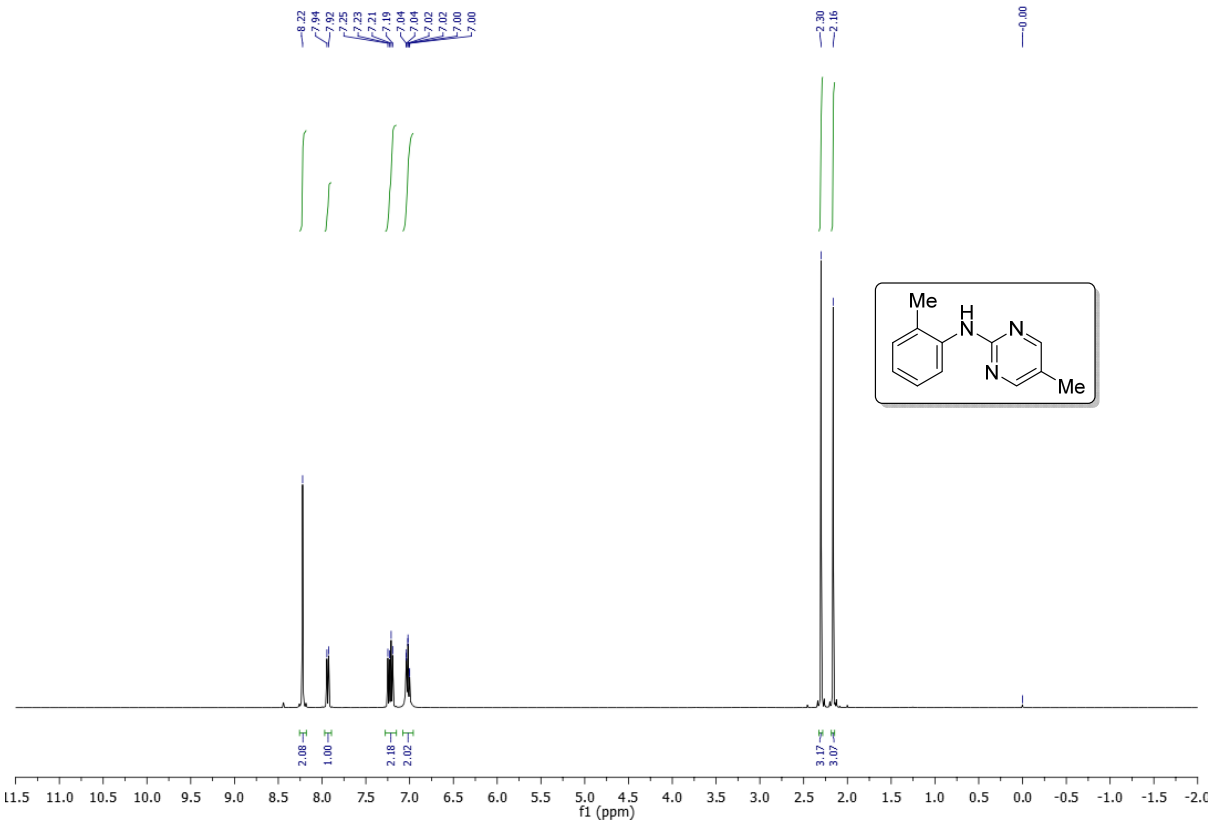
^{1}H NMR spectrum of **26a** (400 MHz, $CDCl_3$):



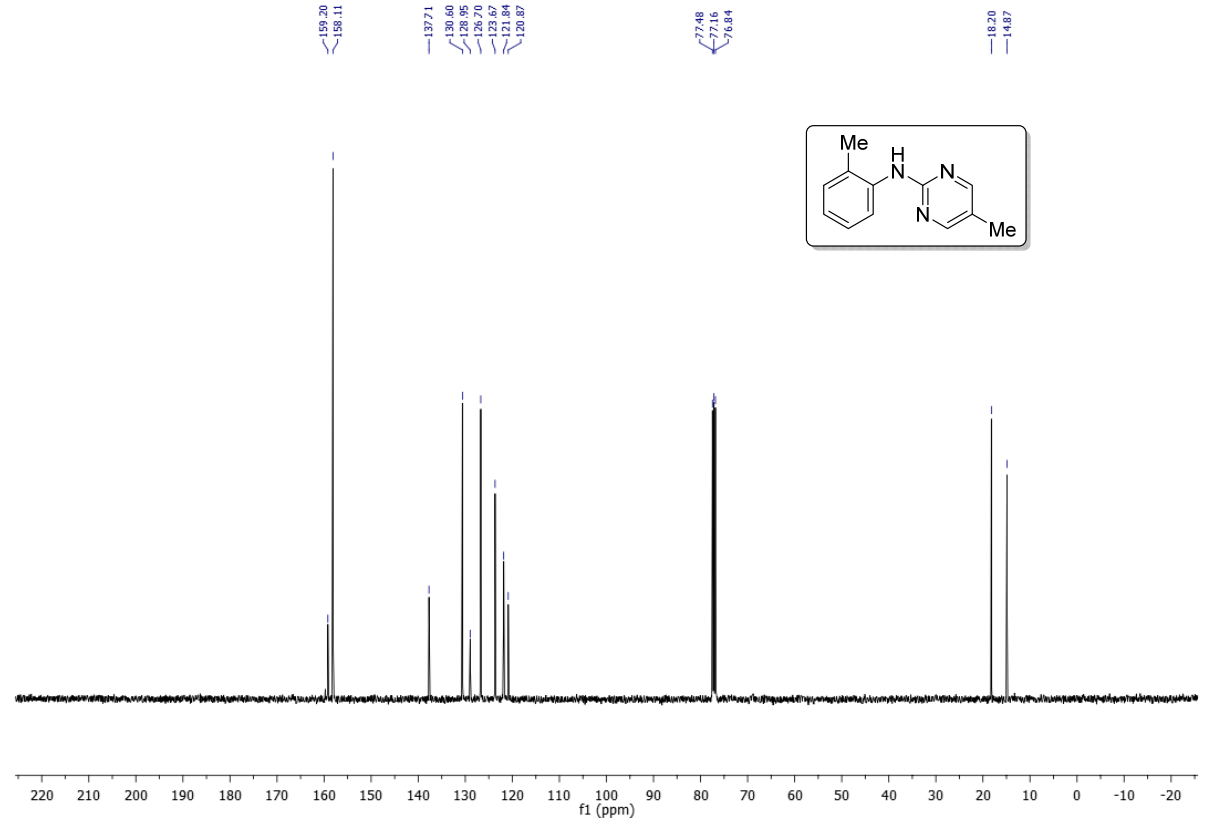
^{13}C NMR spectrum of **26a** (101 MHz, $CDCl_3$):



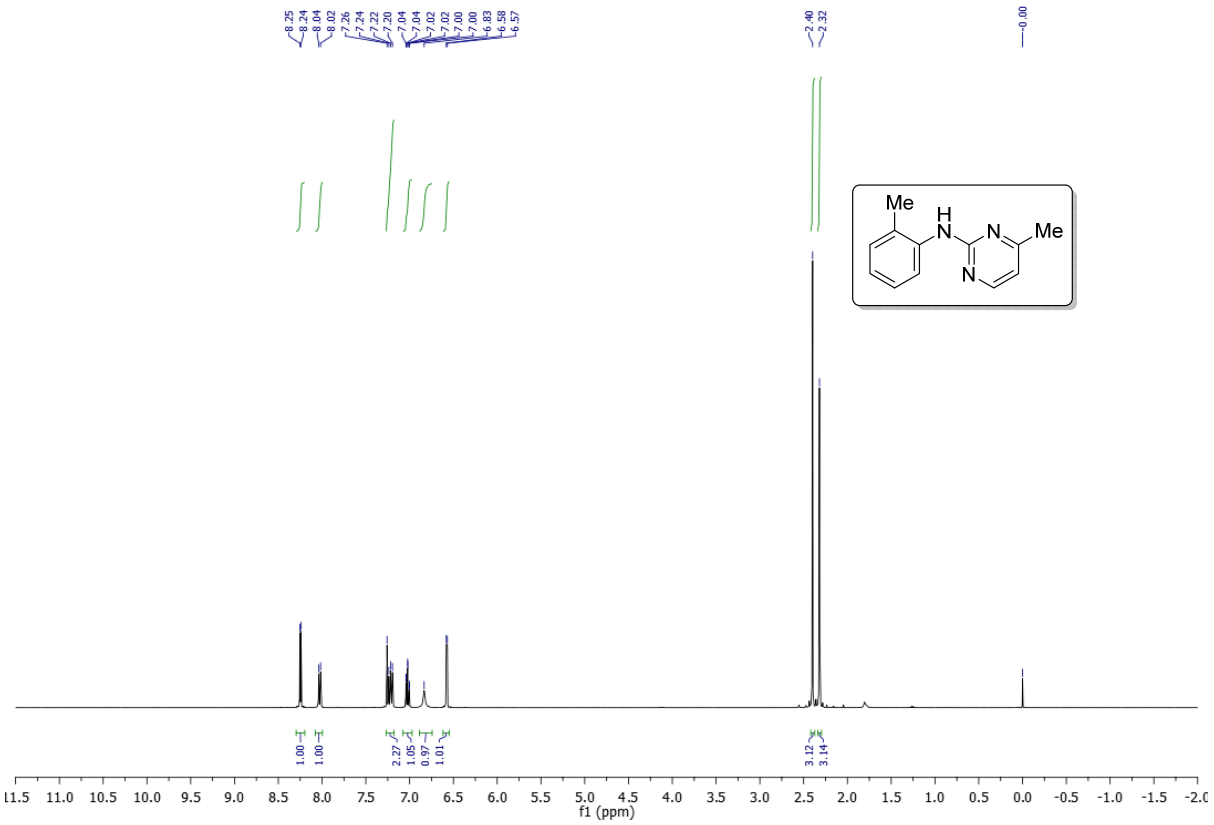
^{1}H NMR spectrum of **29a** (400 MHz, $CDCl_3$):



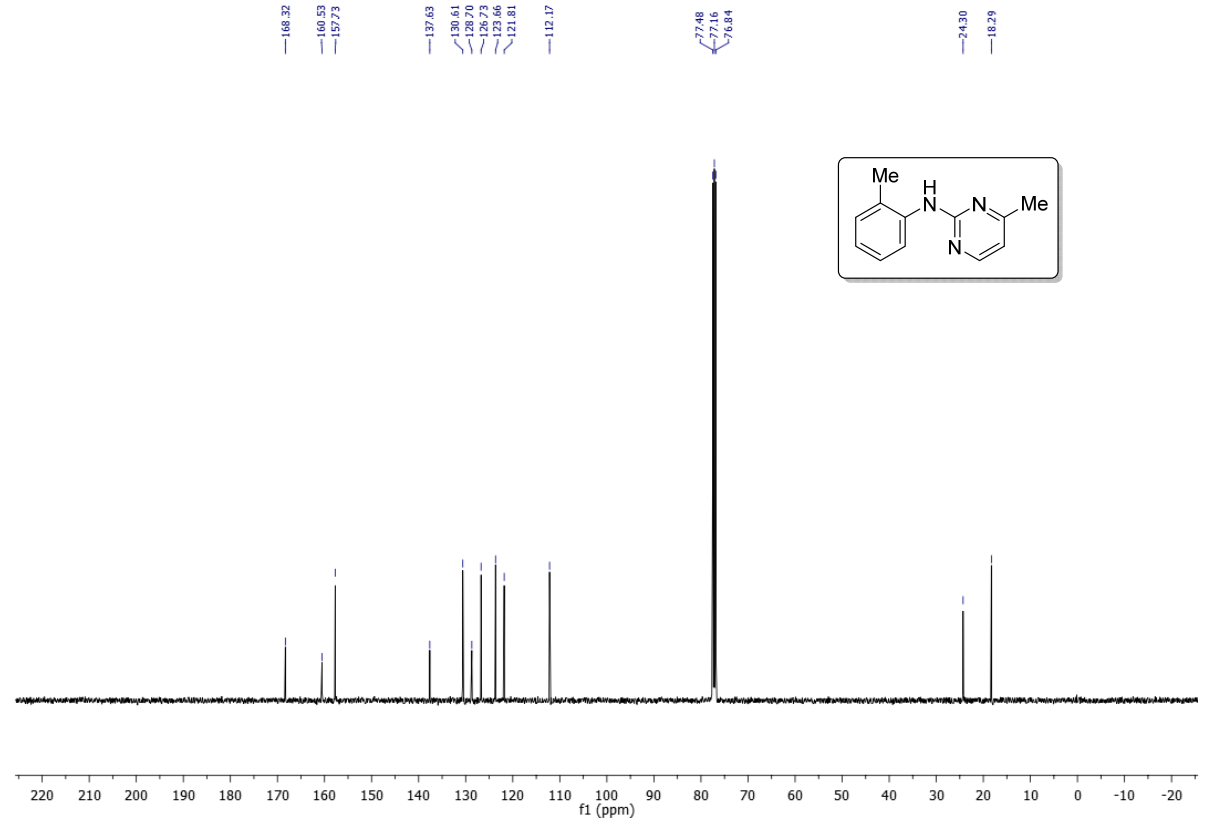
^{13}C NMR spectrum of **29a** (101 MHz, $CDCl_3$):



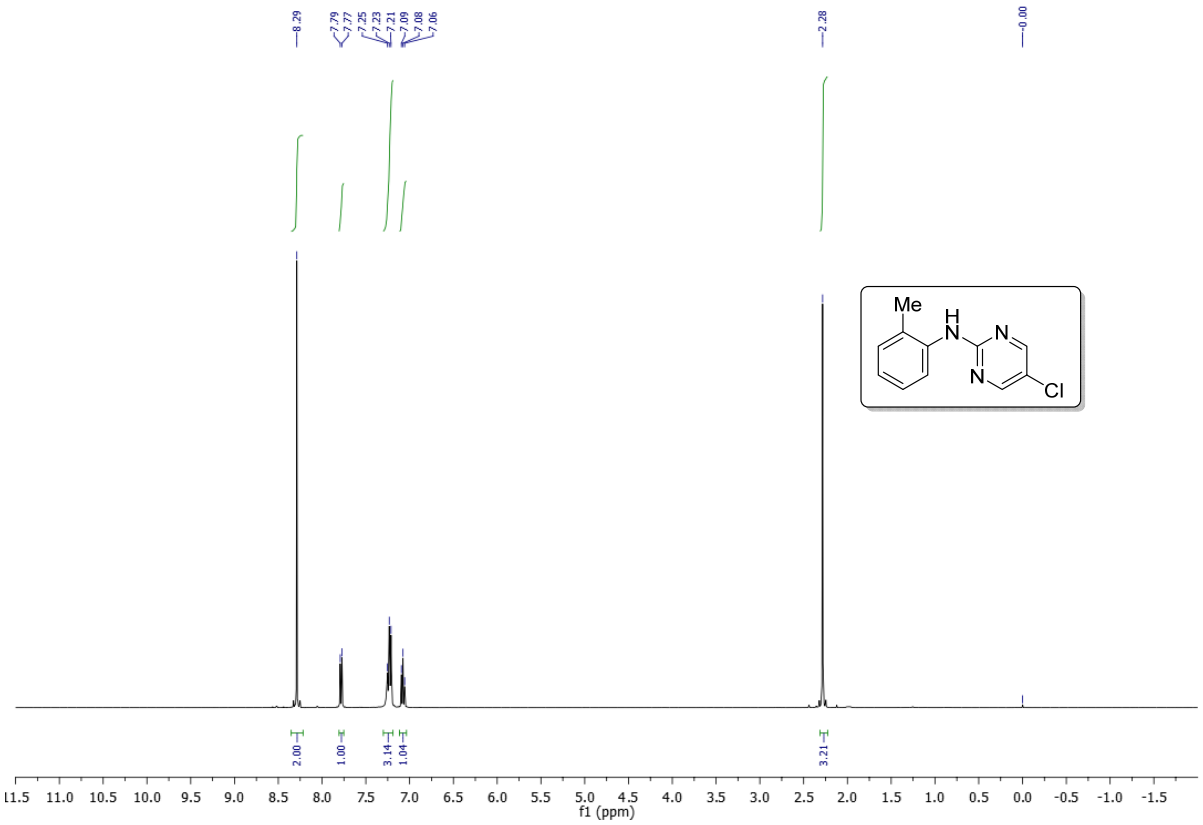
^{1}H NMR spectrum of **30a** (400 MHz, $CDCl_3$):



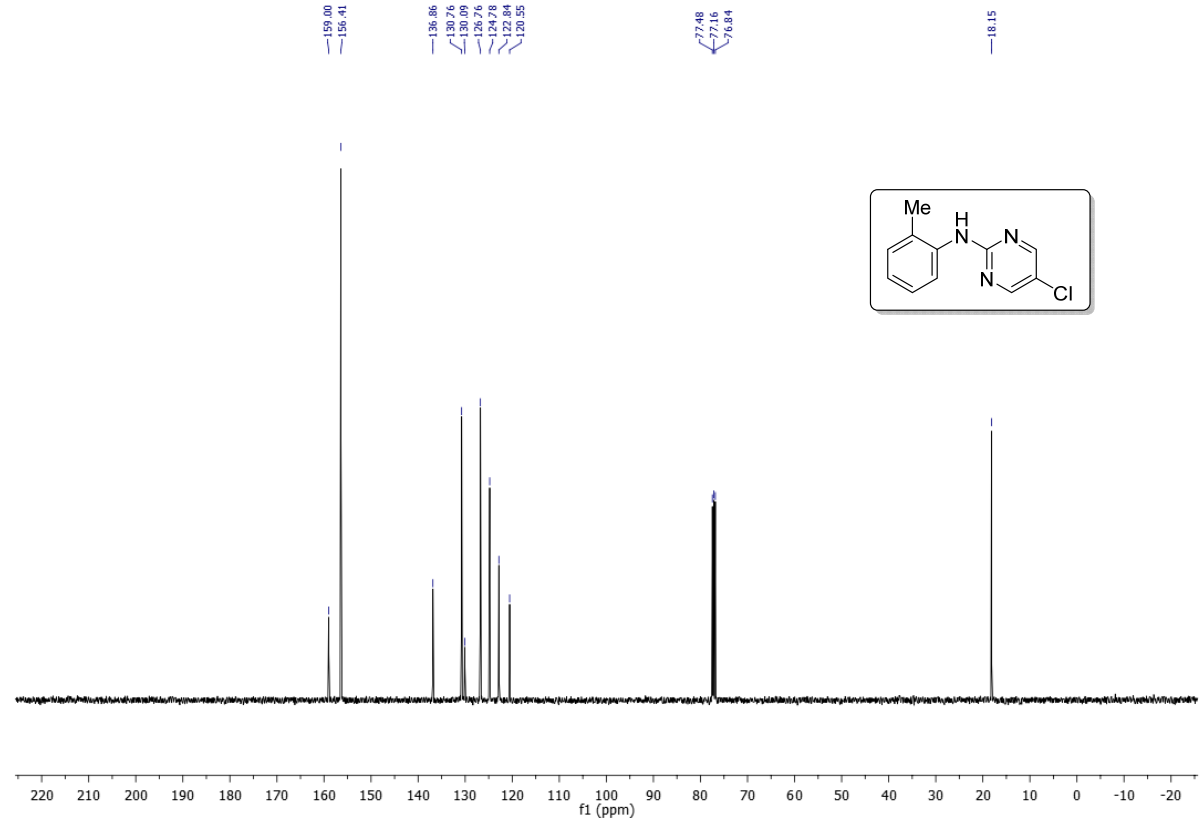
^{13}C NMR spectrum of **30a** (101 MHz, $CDCl_3$):



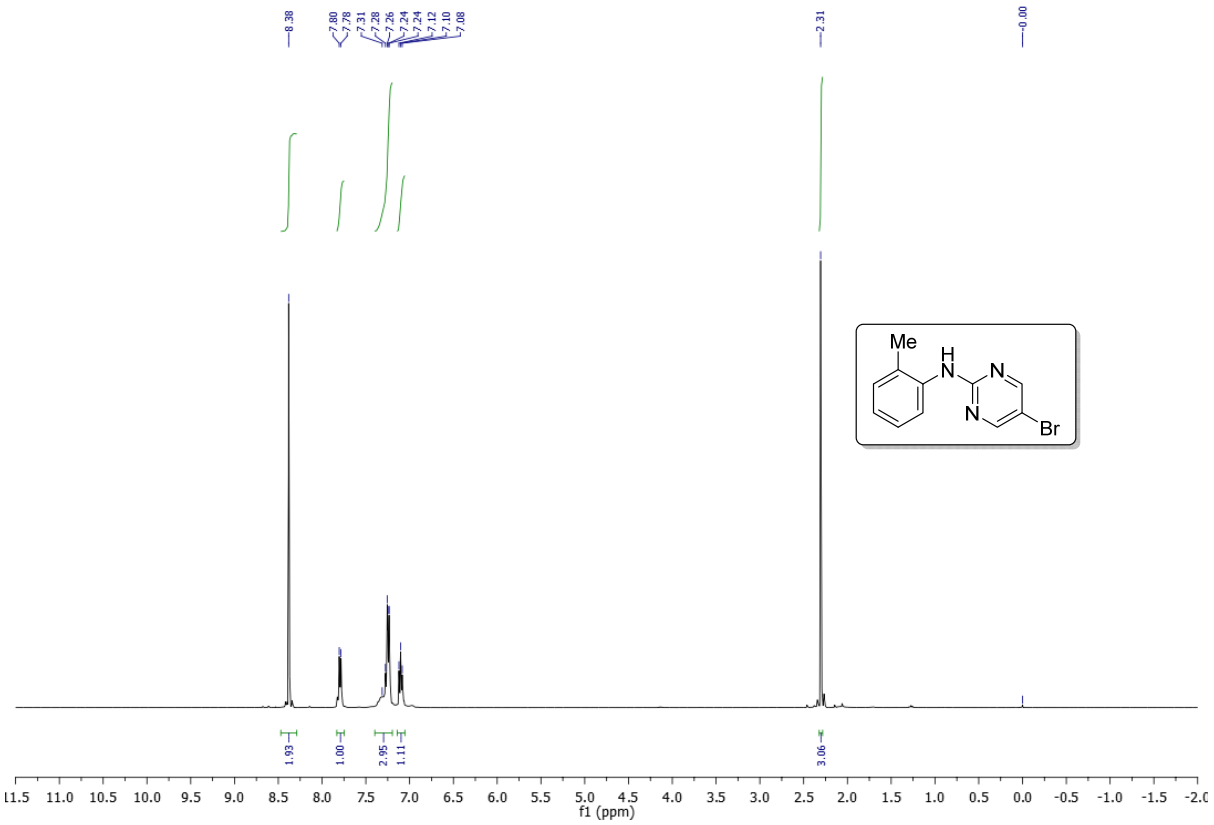
^{1}H NMR spectrum of **31a** (400 MHz, $CDCl_3$):



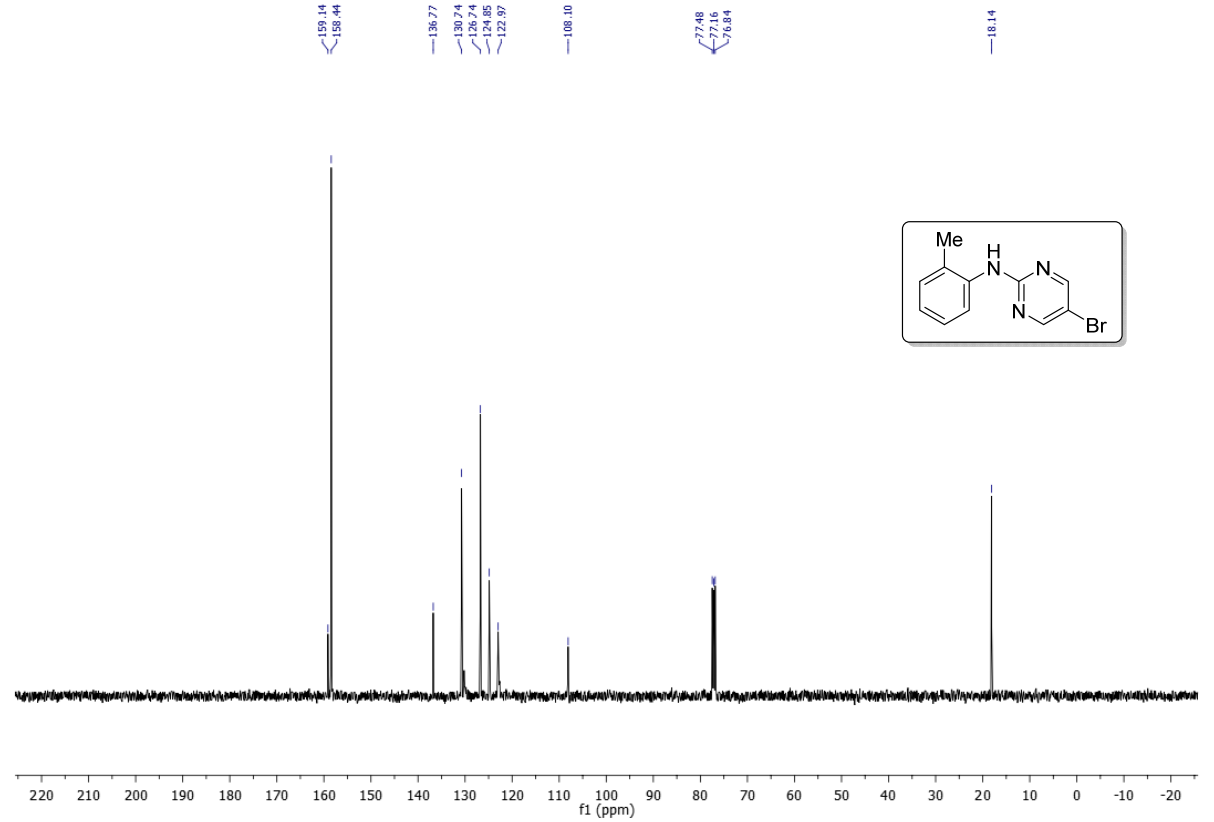
^{13}C NMR spectrum of **31a** (101 MHz, $CDCl_3$):



^{1}H NMR spectrum of **32a** (400 MHz, $CDCl_3$):

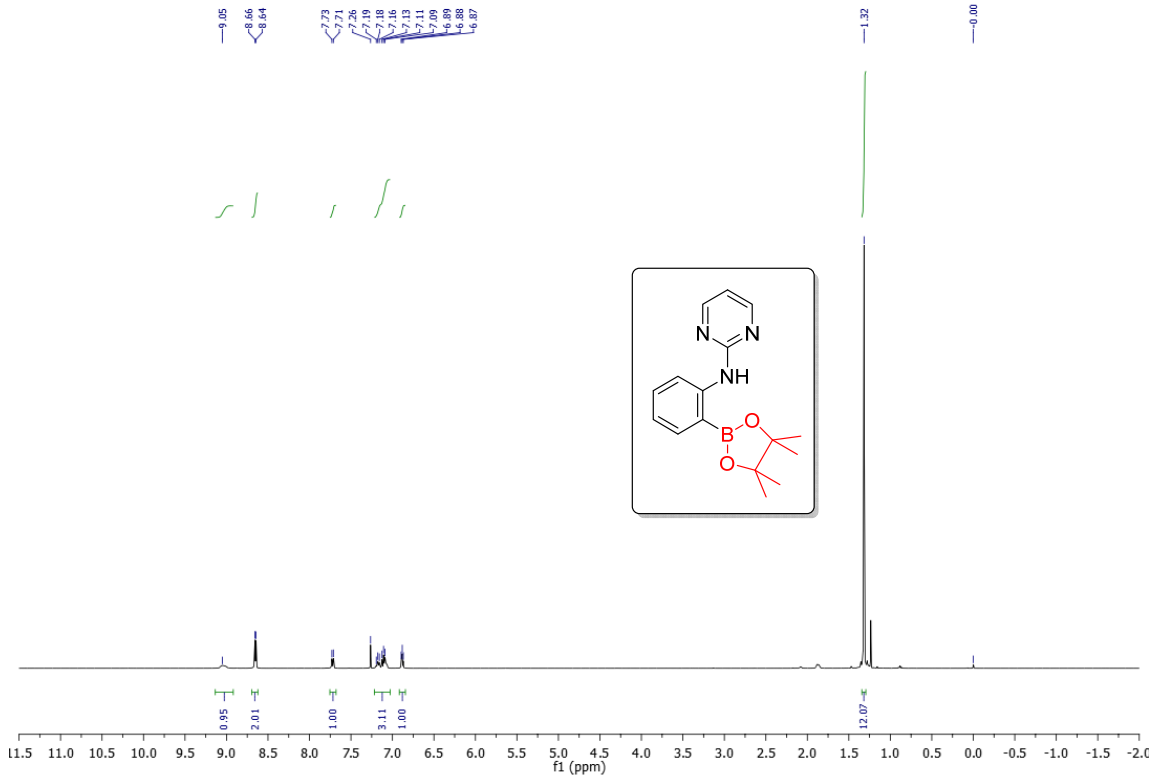


^{13}C NMR spectrum of **32a** (101 MHz, $CDCl_3$):

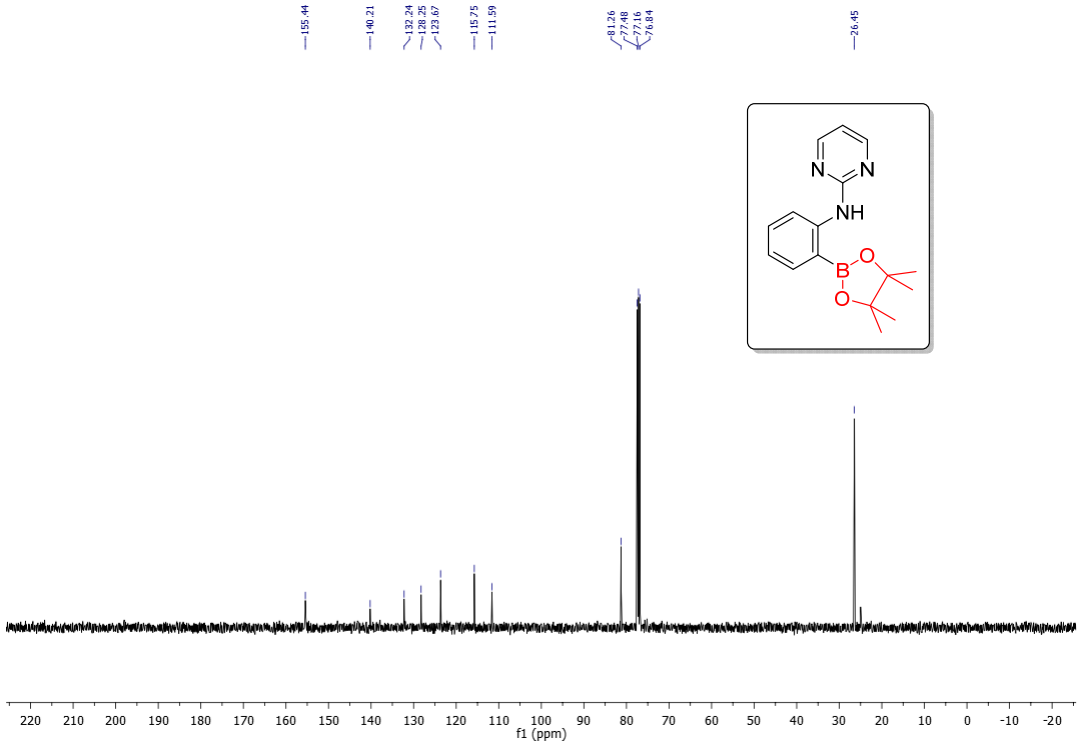


16. NMR spectra of products

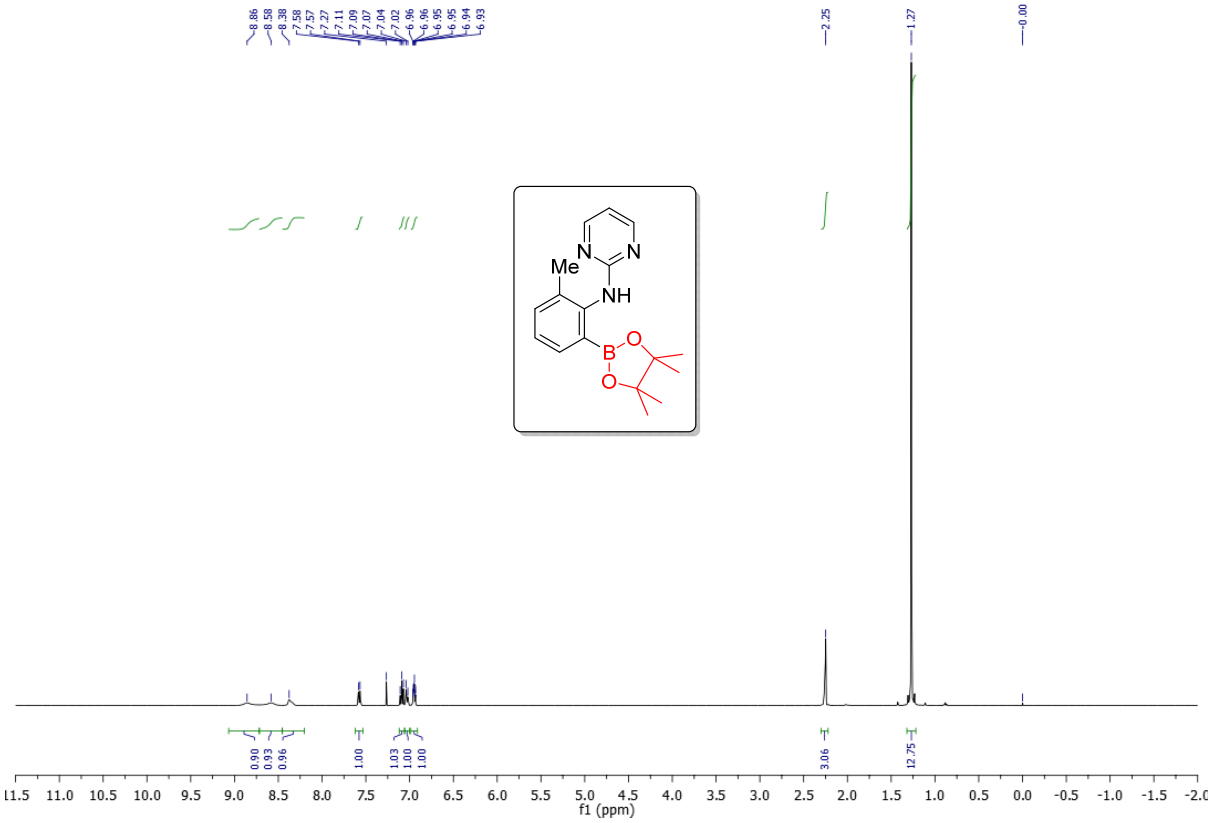
^{1}H NMR spectrum of **1b** (400 MHz, $CDCl_3$):



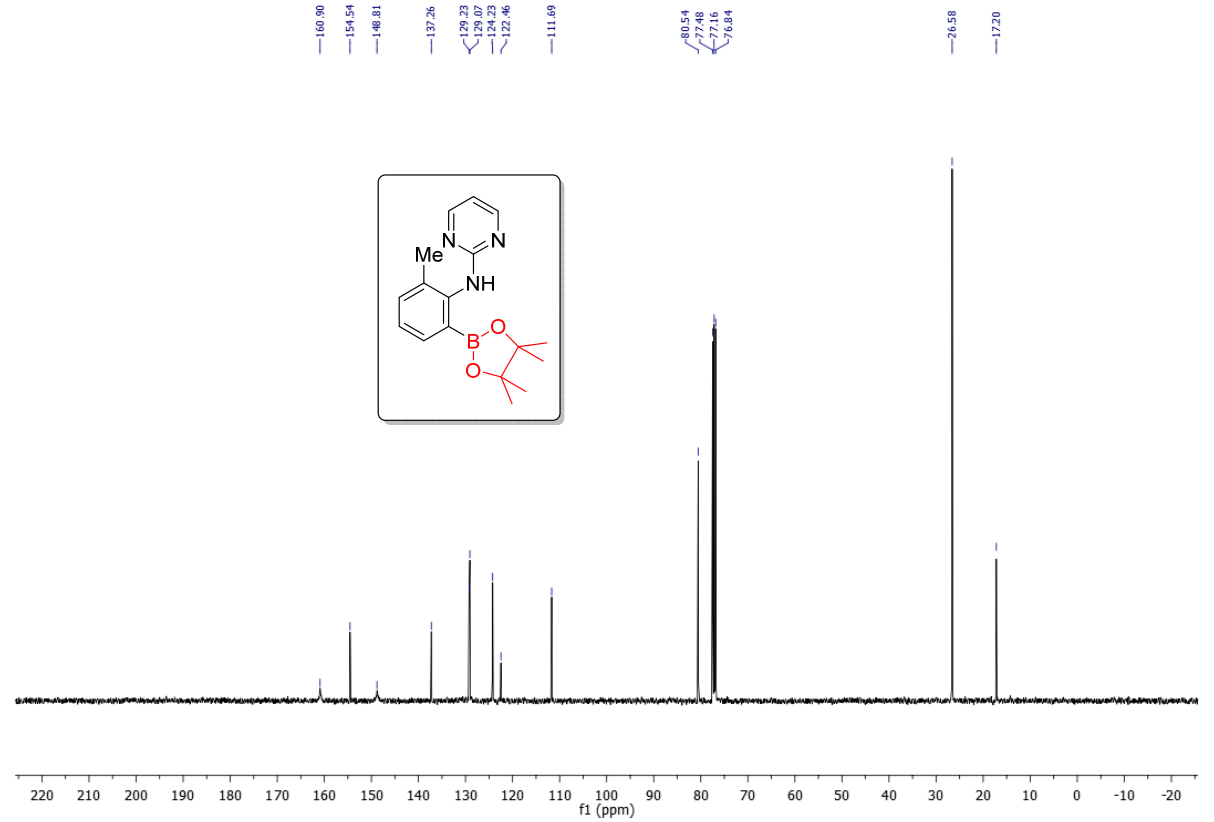
^{13}C NMR spectrum of **1b** (101 MHz, $CDCl_3$):



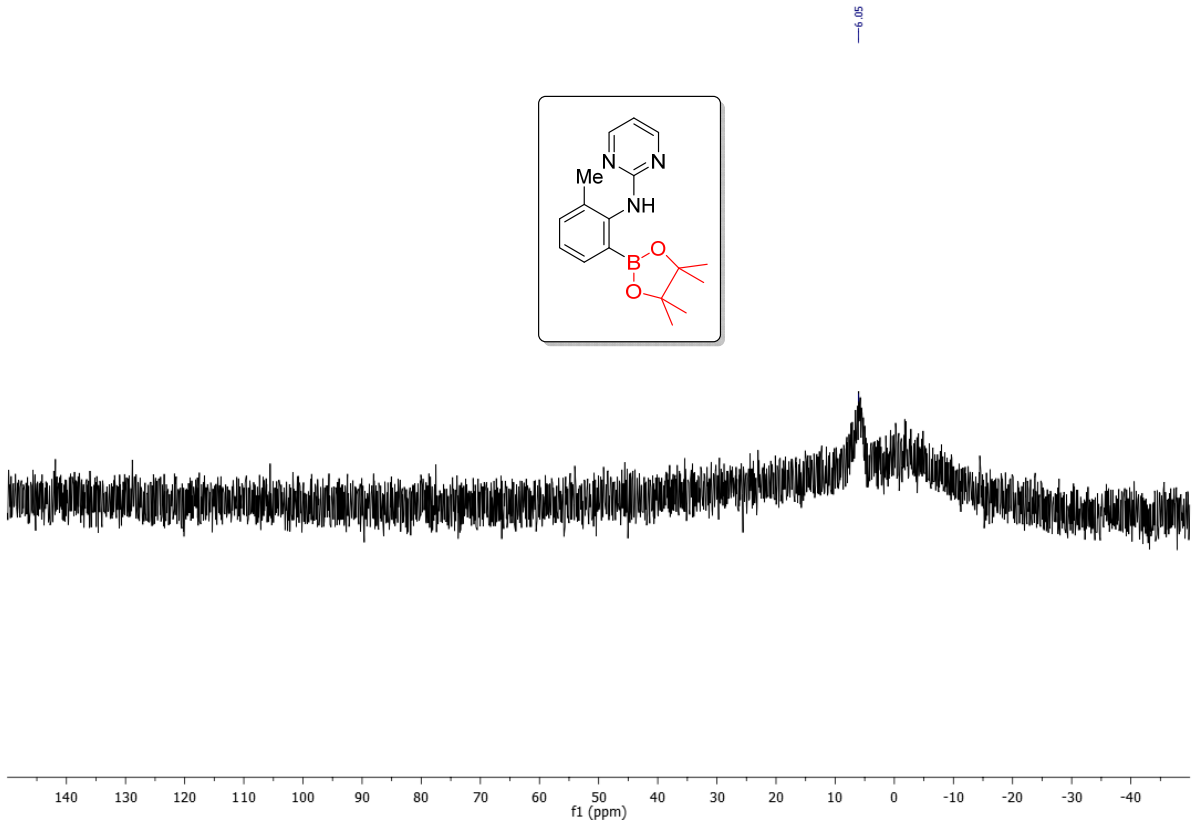
^{1}H NMR spectrum of **2b** (400 MHz, $CDCl_3$):



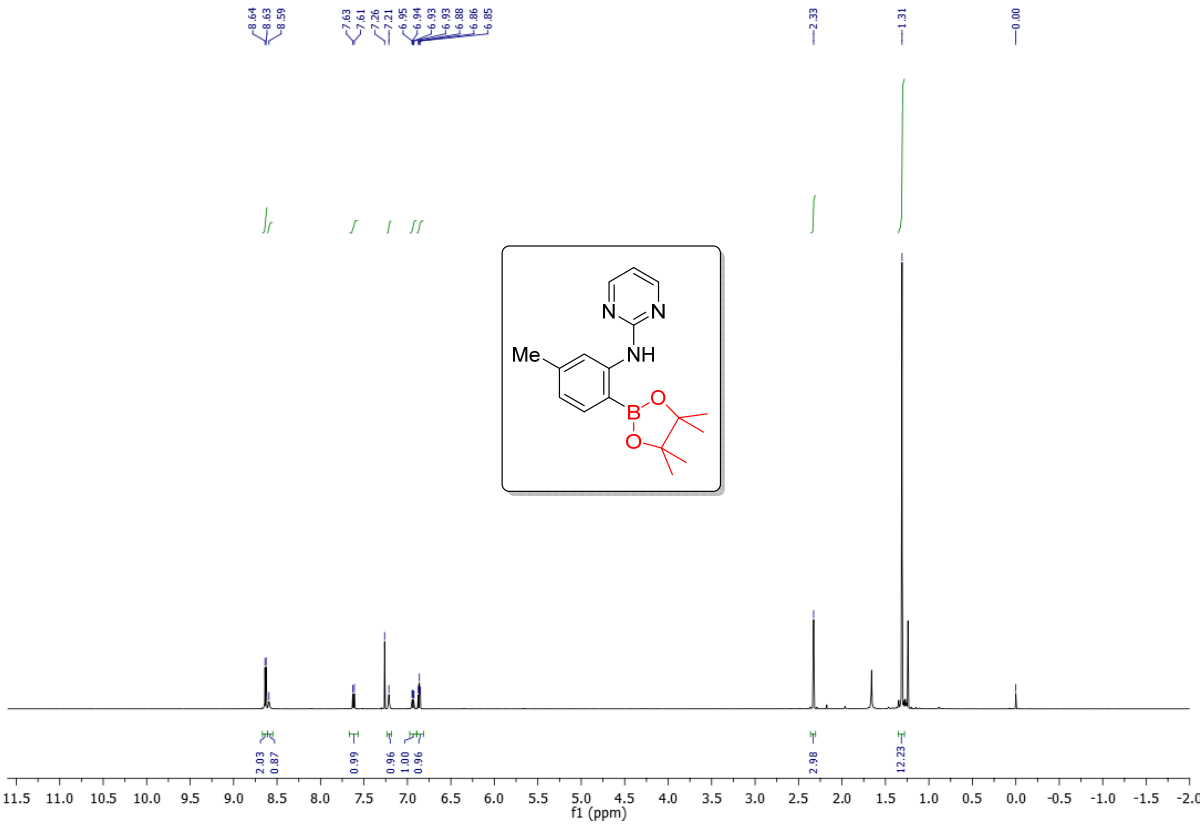
^{13}C NMR spectrum of **2b** (101 MHz, $CDCl_3$):



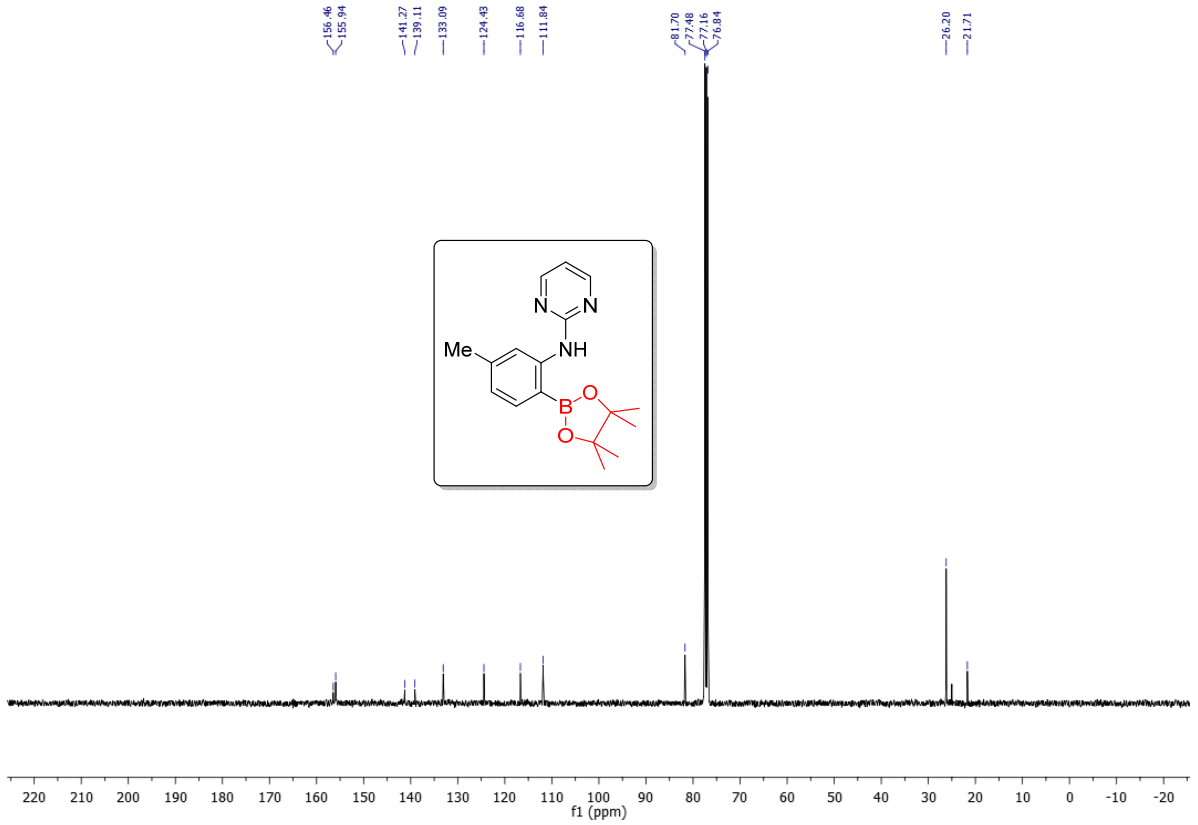
^{11}B NMR spectrum of **2b** (128 MHz, $CDCl_3$):



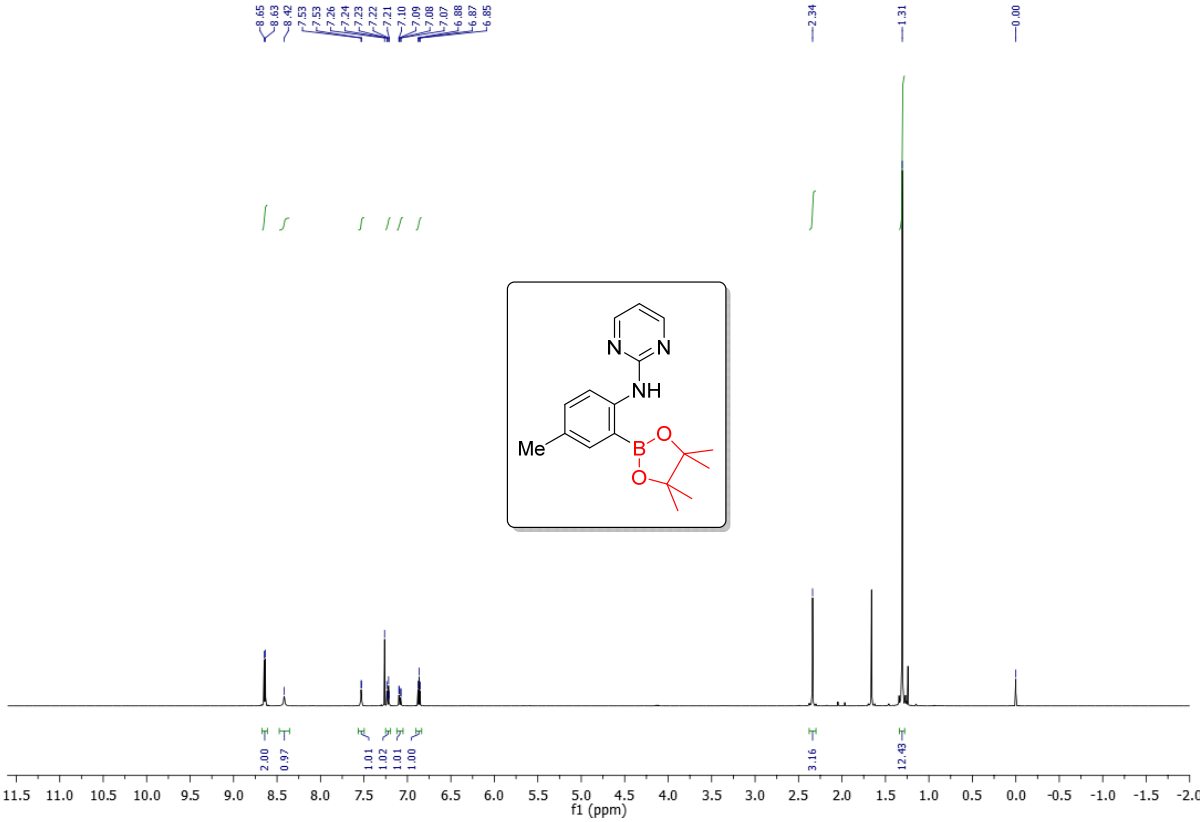
^{1}H NMR spectrum of **3b** (400 MHz, $CDCl_3$):



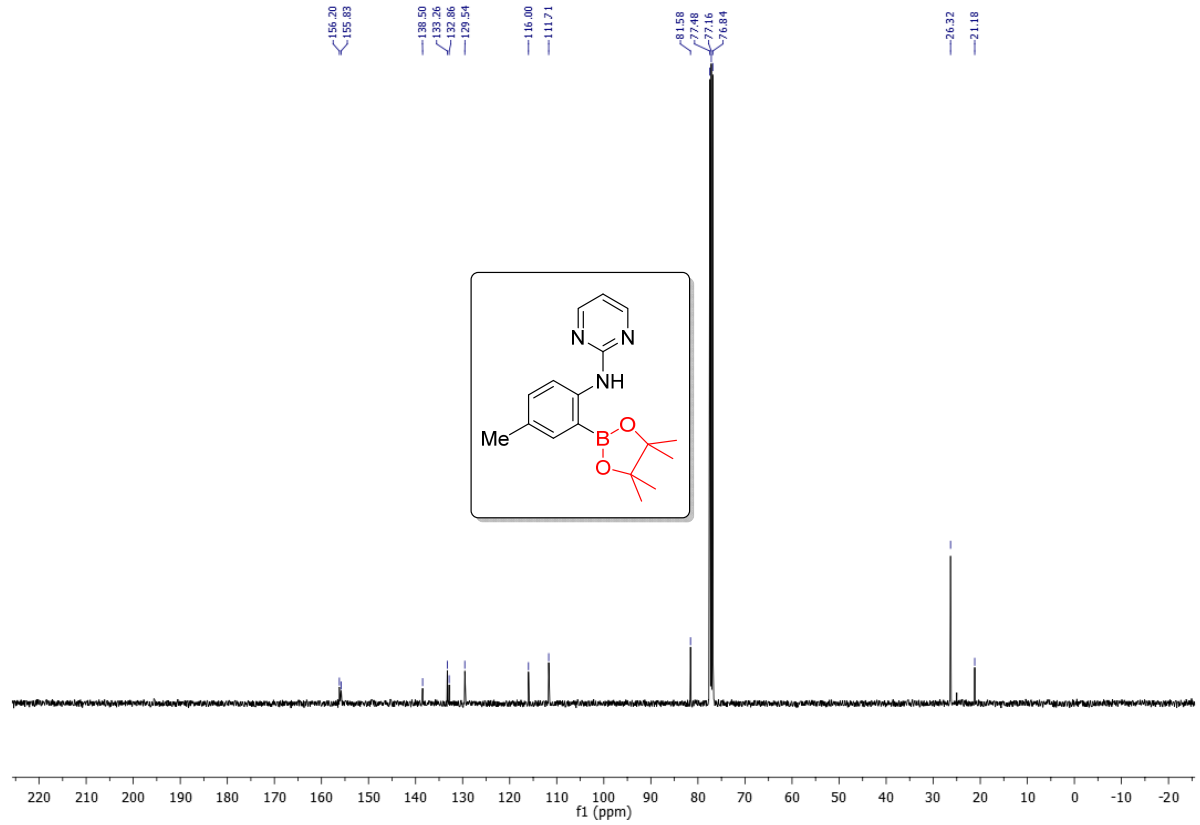
^{13}C NMR spectrum of **3b** (101 MHz, $CDCl_3$):



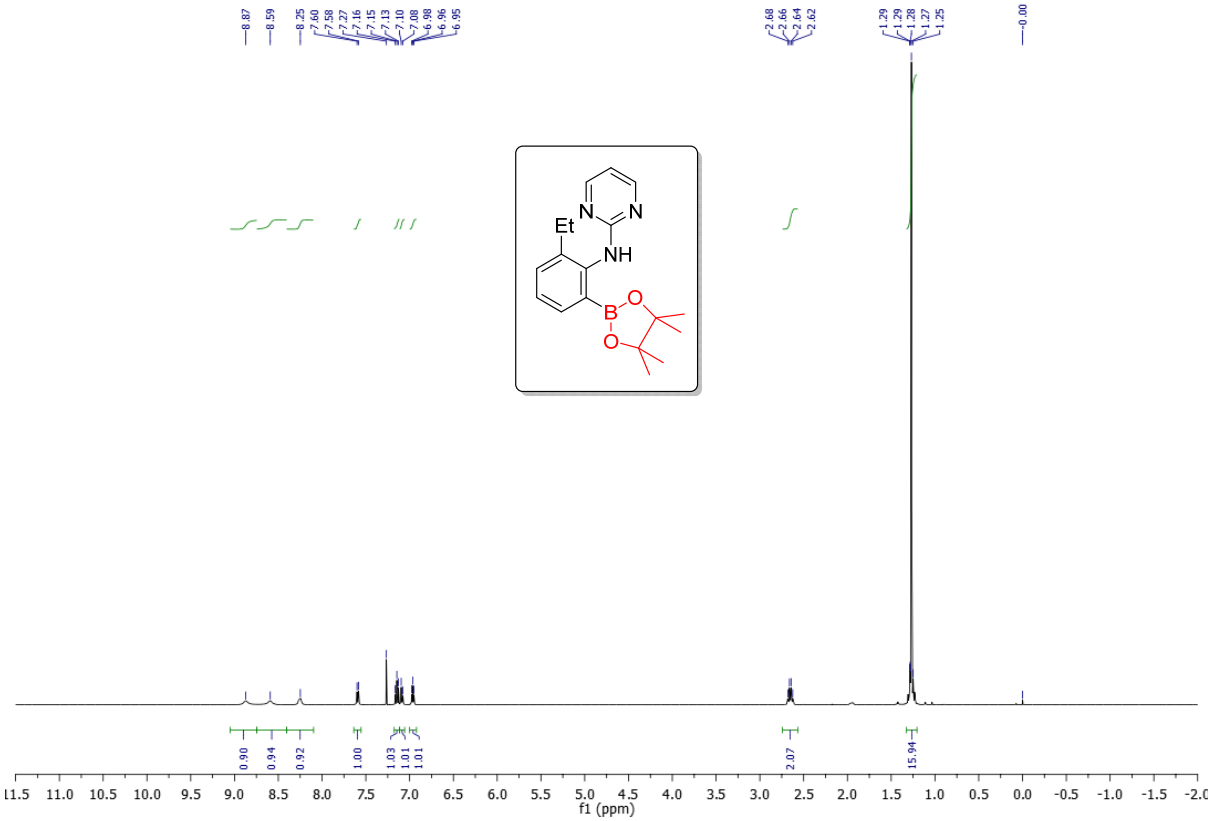
^{1}H NMR spectrum of **4b** (400 MHz, $CDCl_3$):



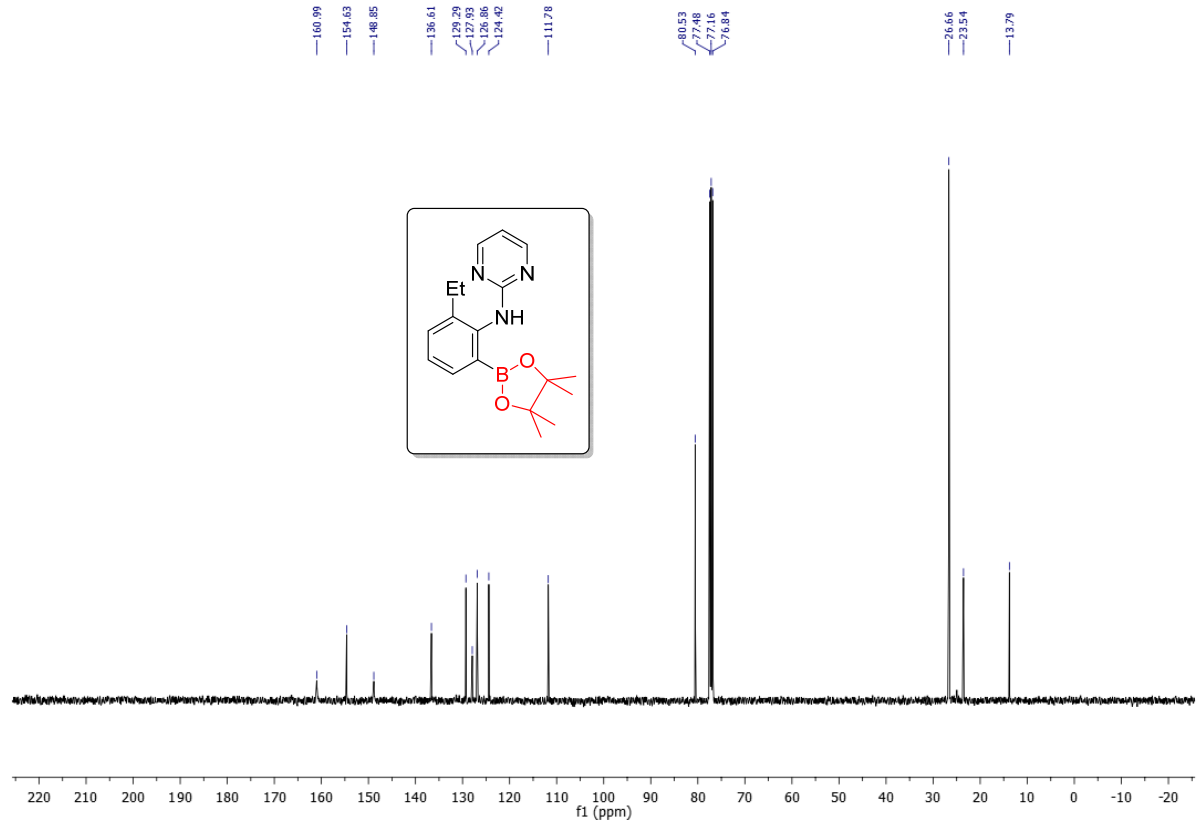
^{13}C NMR spectrum of **4b** (101 MHz, $CDCl_3$):



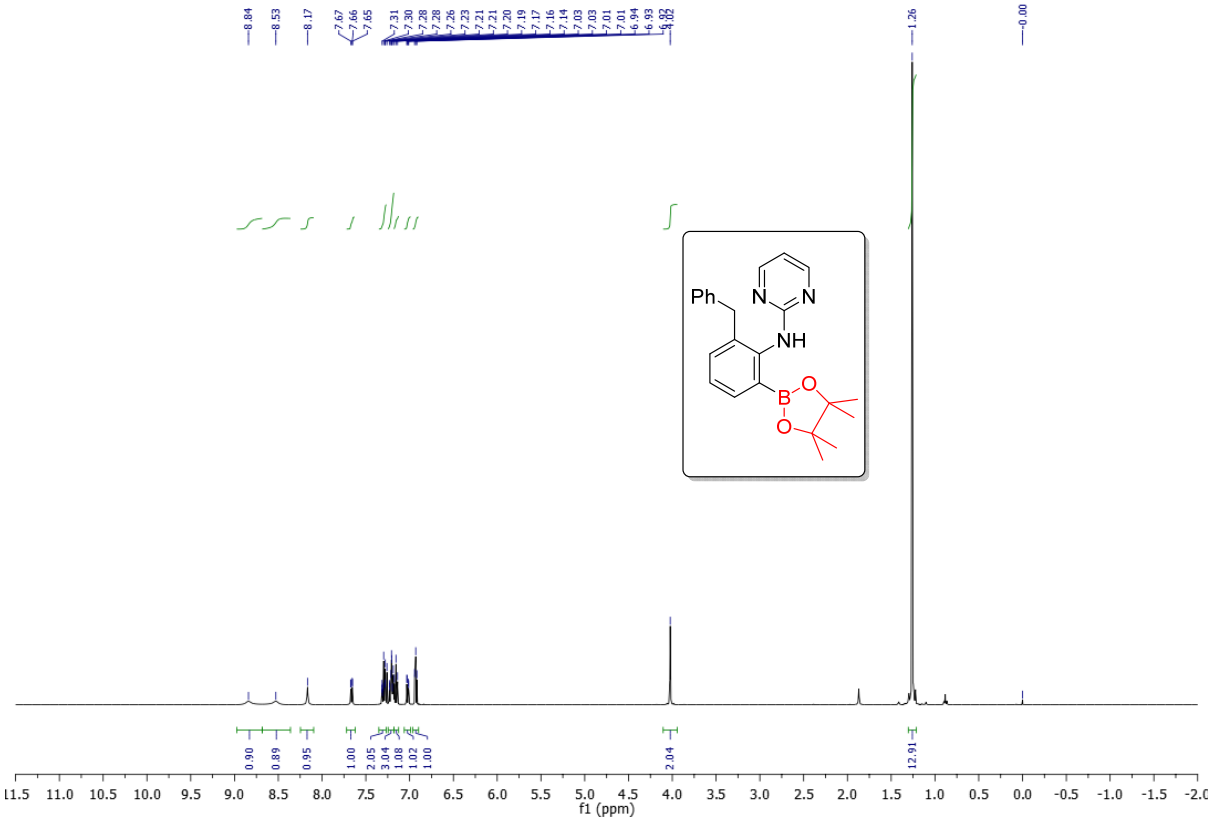
^{1}H NMR spectrum of **5b** (400 MHz, $CDCl_3$):



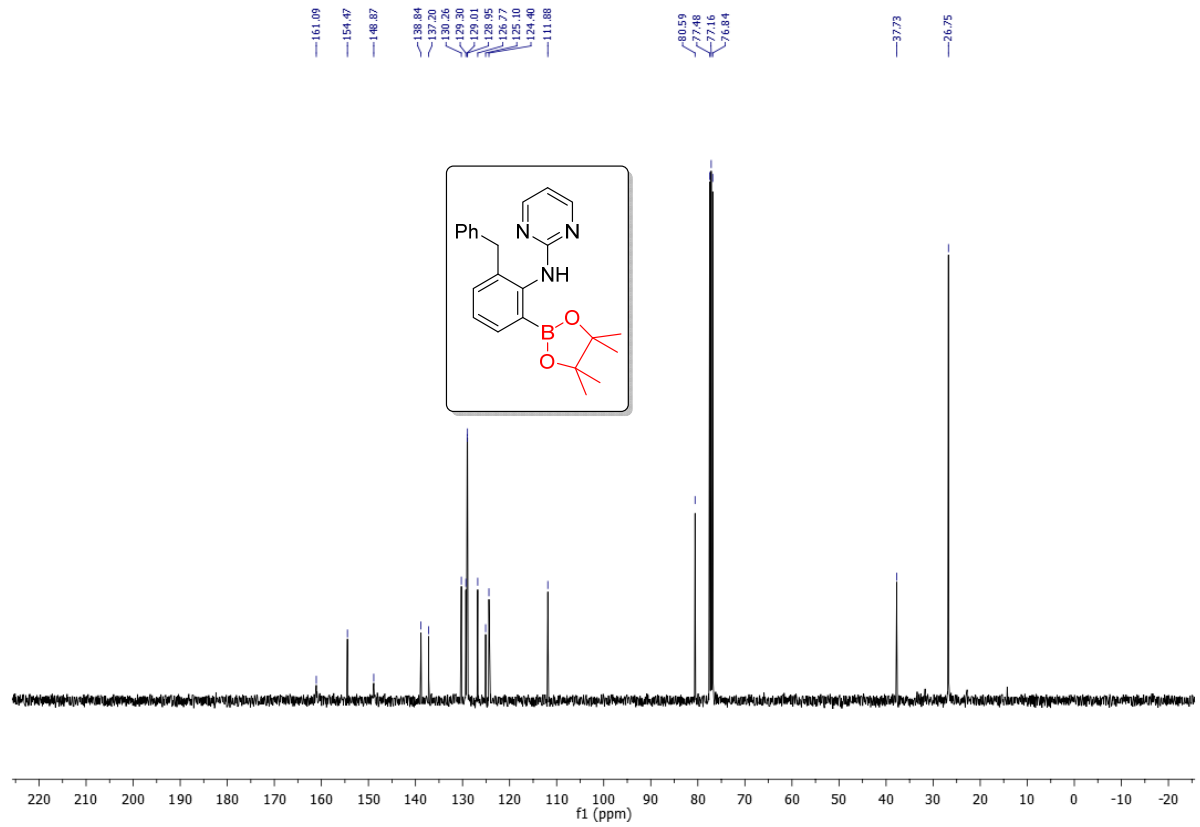
^{13}C NMR spectrum of **5b** (101 MHz, $CDCl_3$):



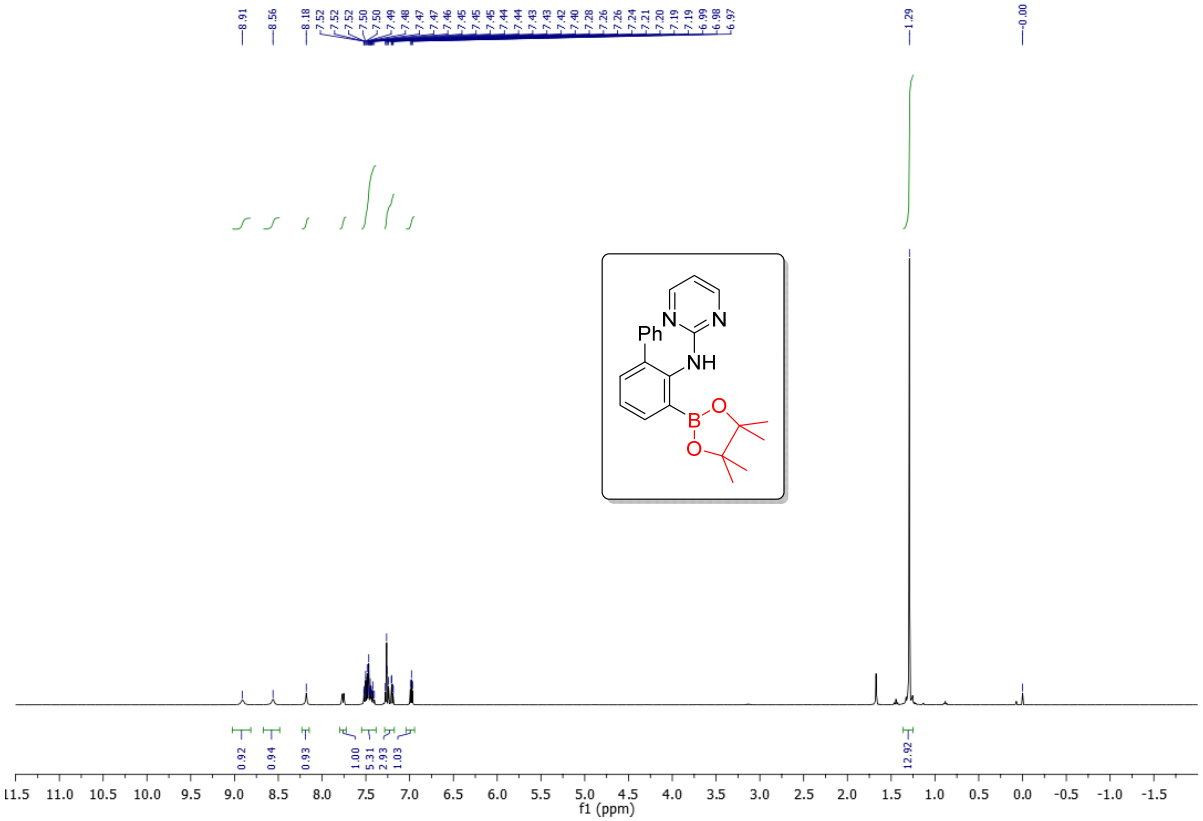
^{1}H NMR spectrum of **6b** (400 MHz, $CDCl_3$):



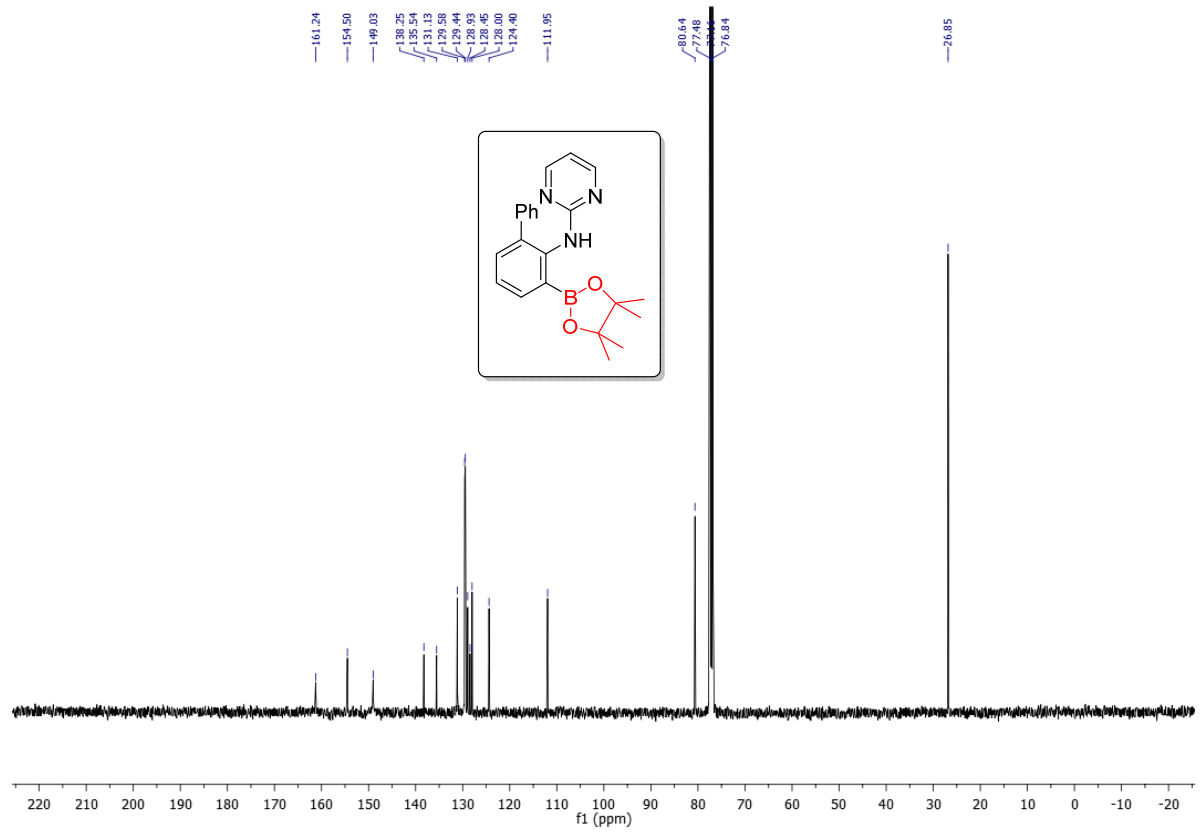
^{13}C NMR spectrum of **6b** (101 MHz, $CDCl_3$):



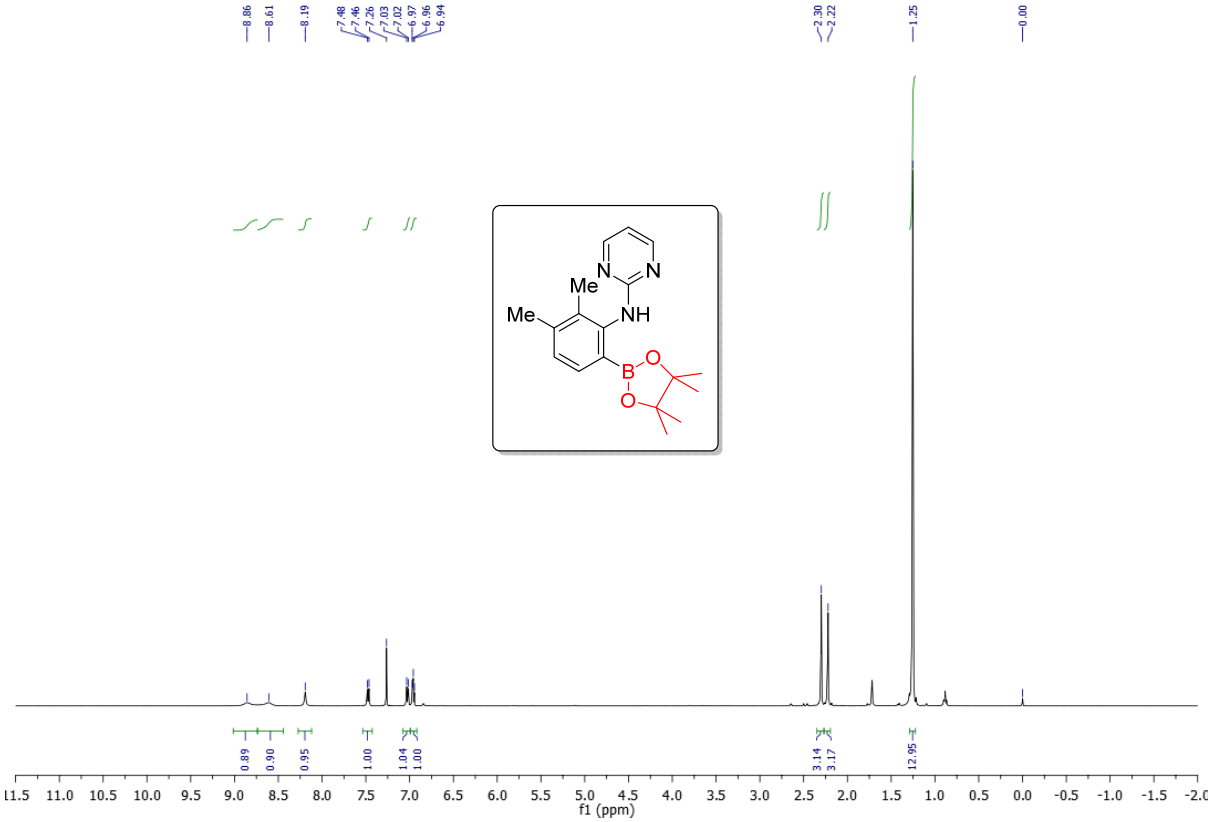
^{1}H NMR spectrum of **7b** (400 MHz, $CDCl_3$):



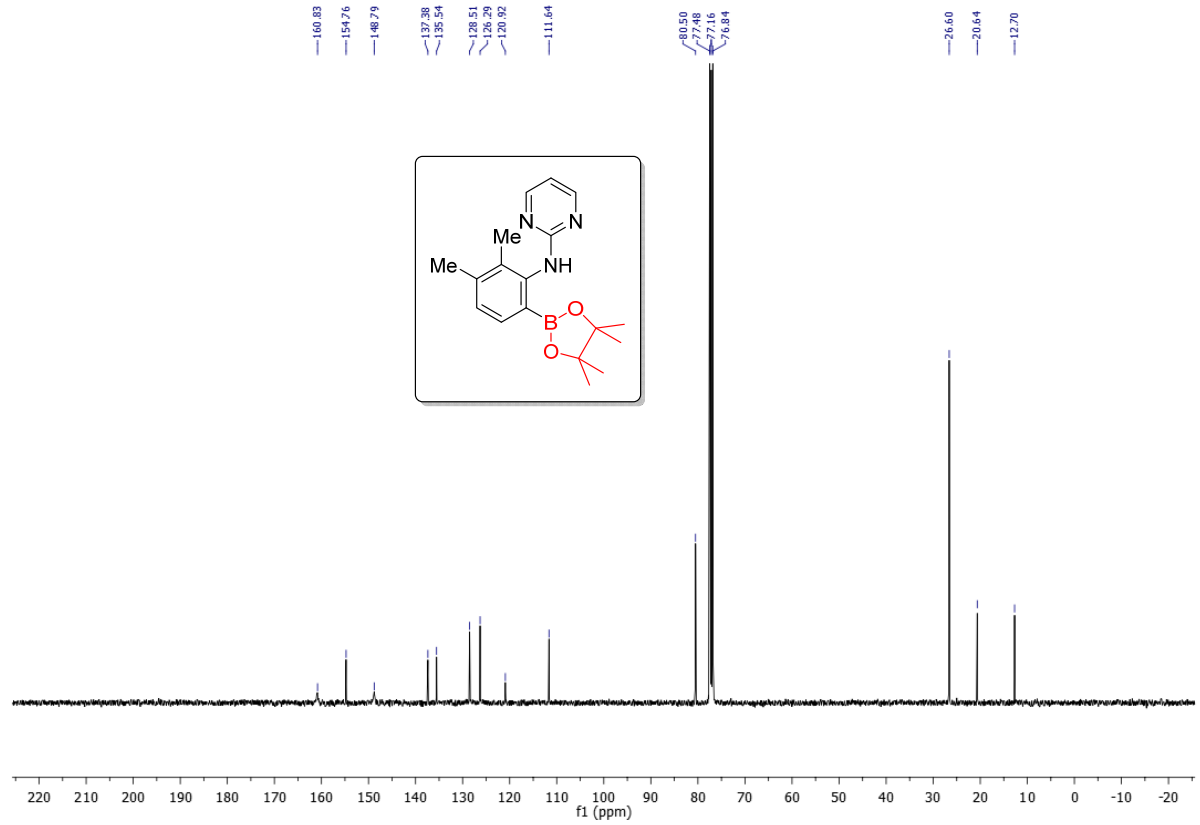
^{13}C NMR spectrum of **7b** (101 MHz, $CDCl_3$):



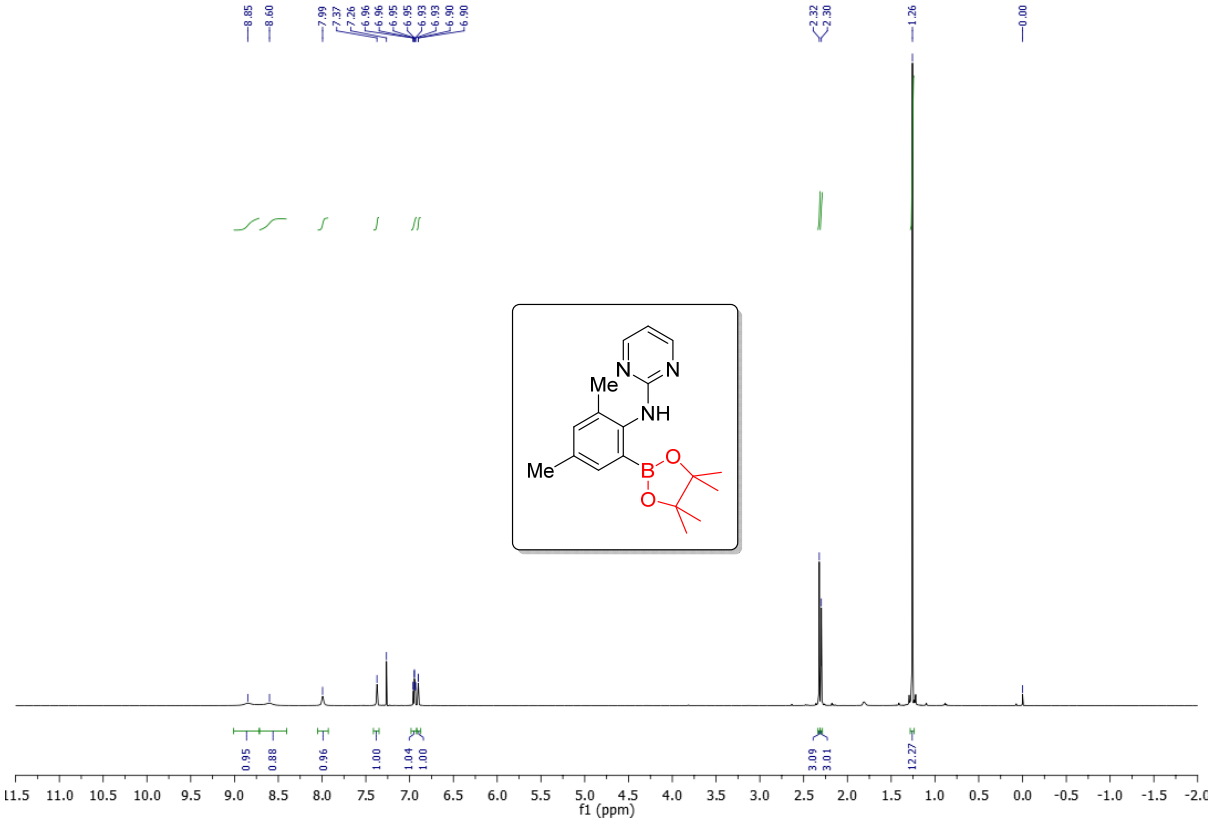
^{1}H NMR spectrum of **8b** (400 MHz, $CDCl_3$):



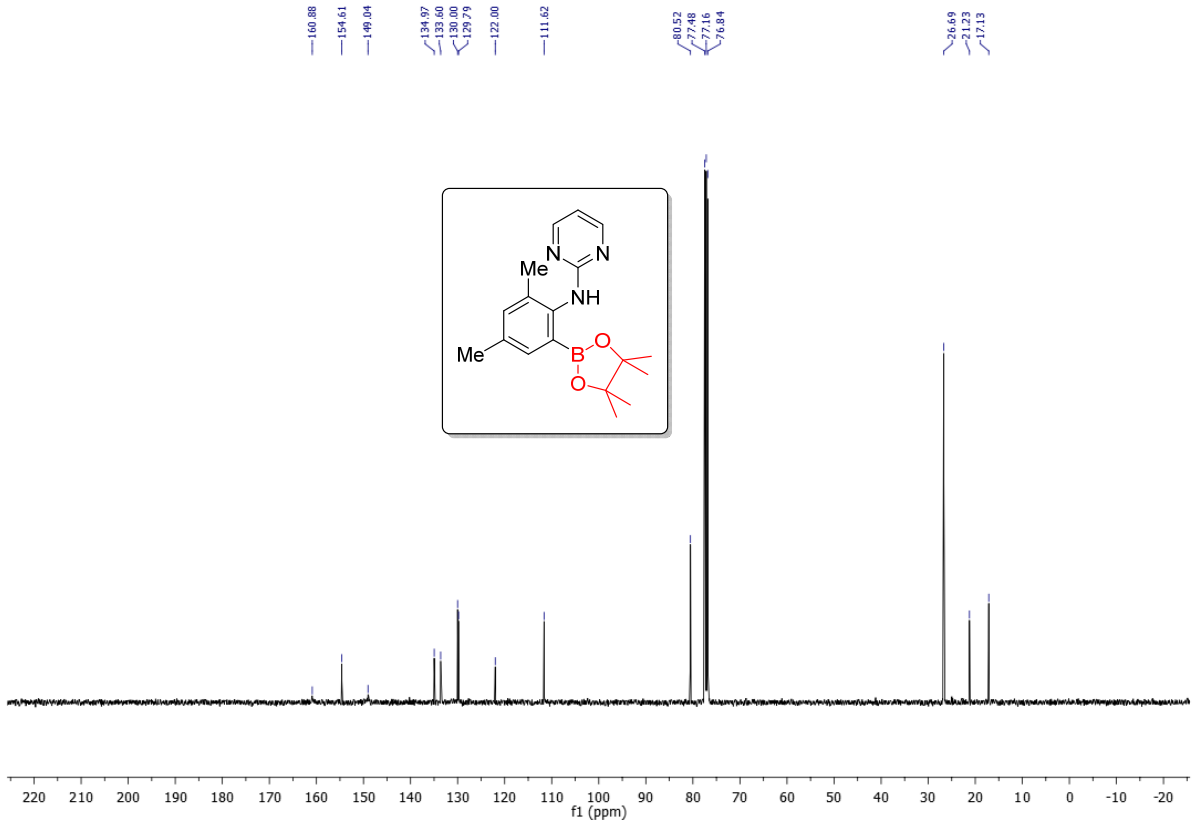
^{13}C NMR spectrum of **8b** (101 MHz, $CDCl_3$):



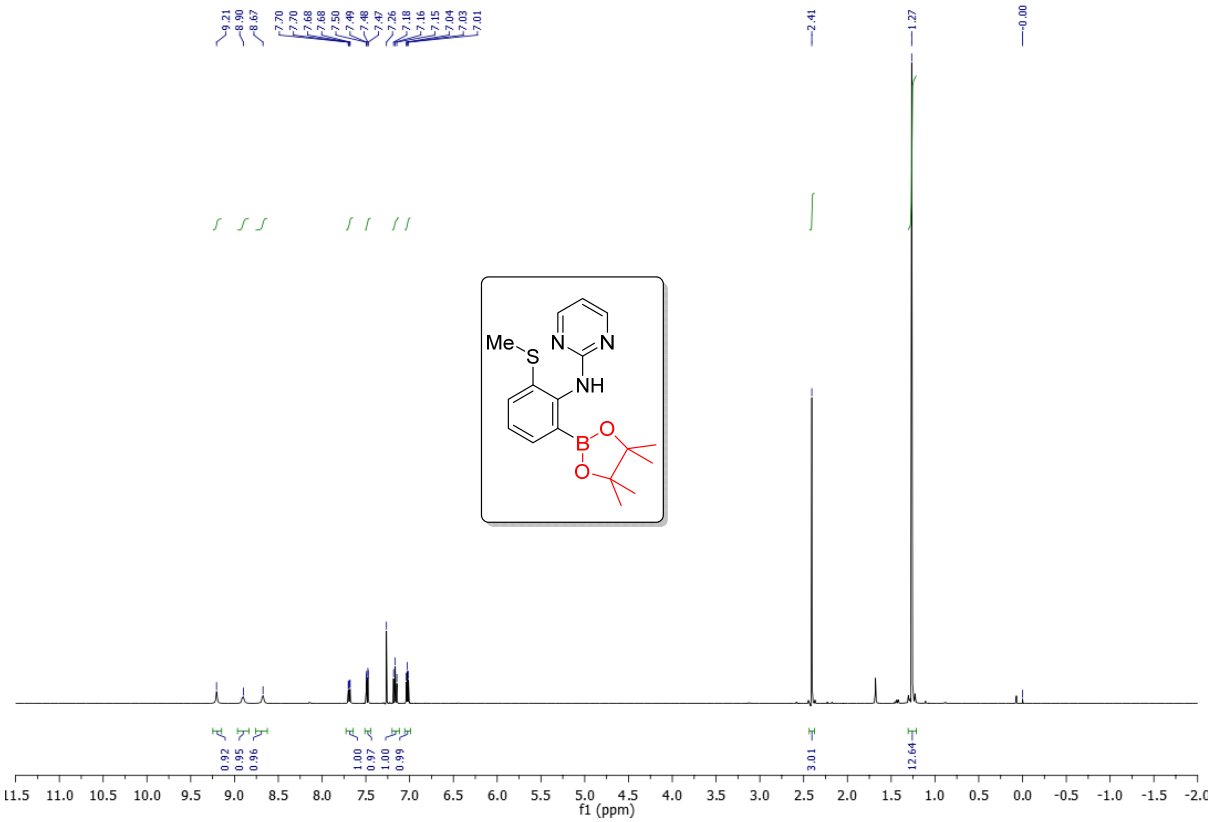
^{1}H NMR spectrum of **9b** (400 MHz, $CDCl_3$):



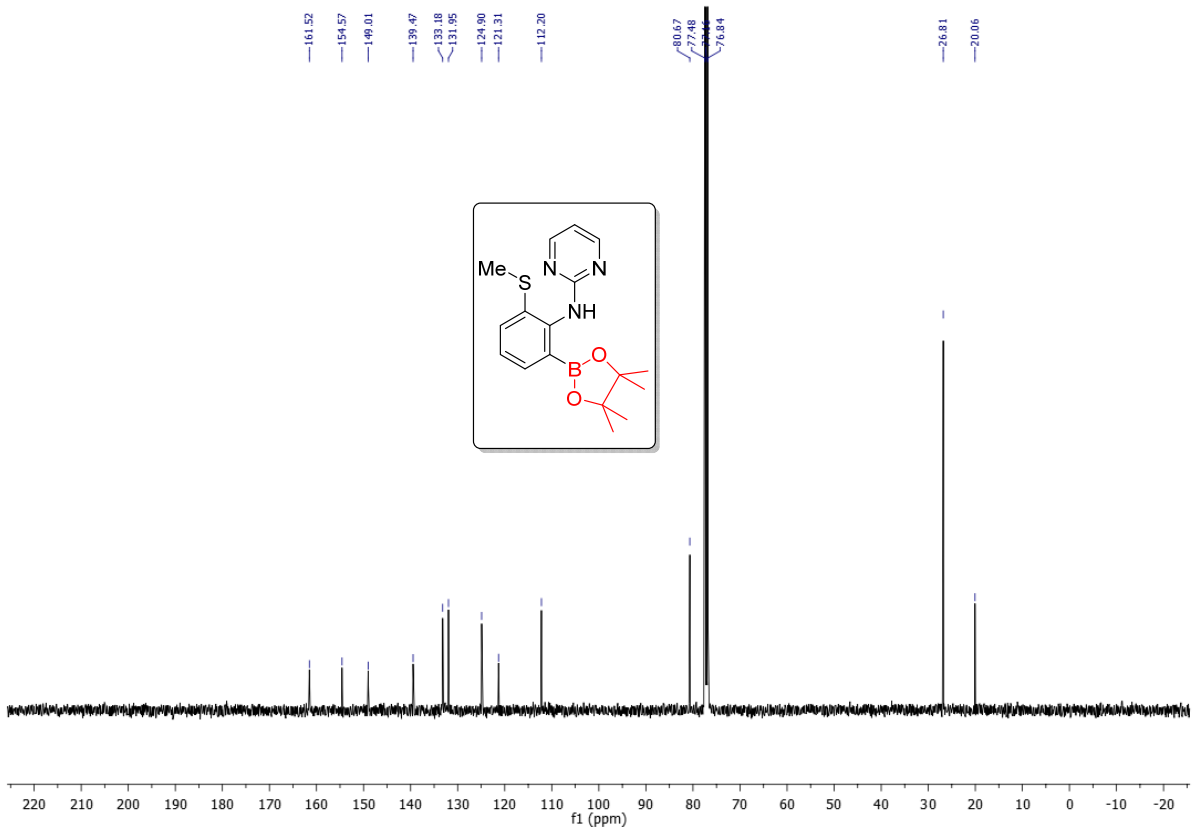
^{13}C NMR spectrum of **9b** (101 MHz, $CDCl_3$):



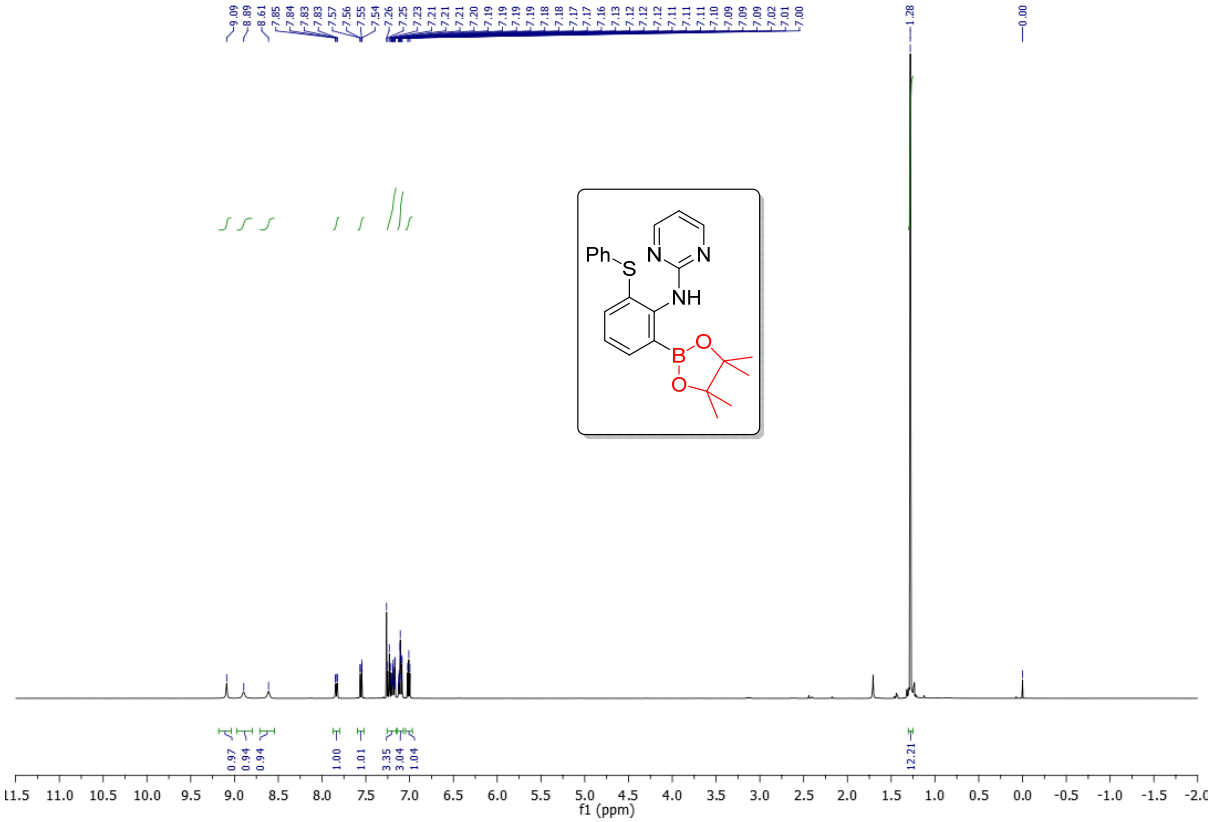
^{1}H NMR spectrum of **10b** (400 MHz, $CDCl_3$):



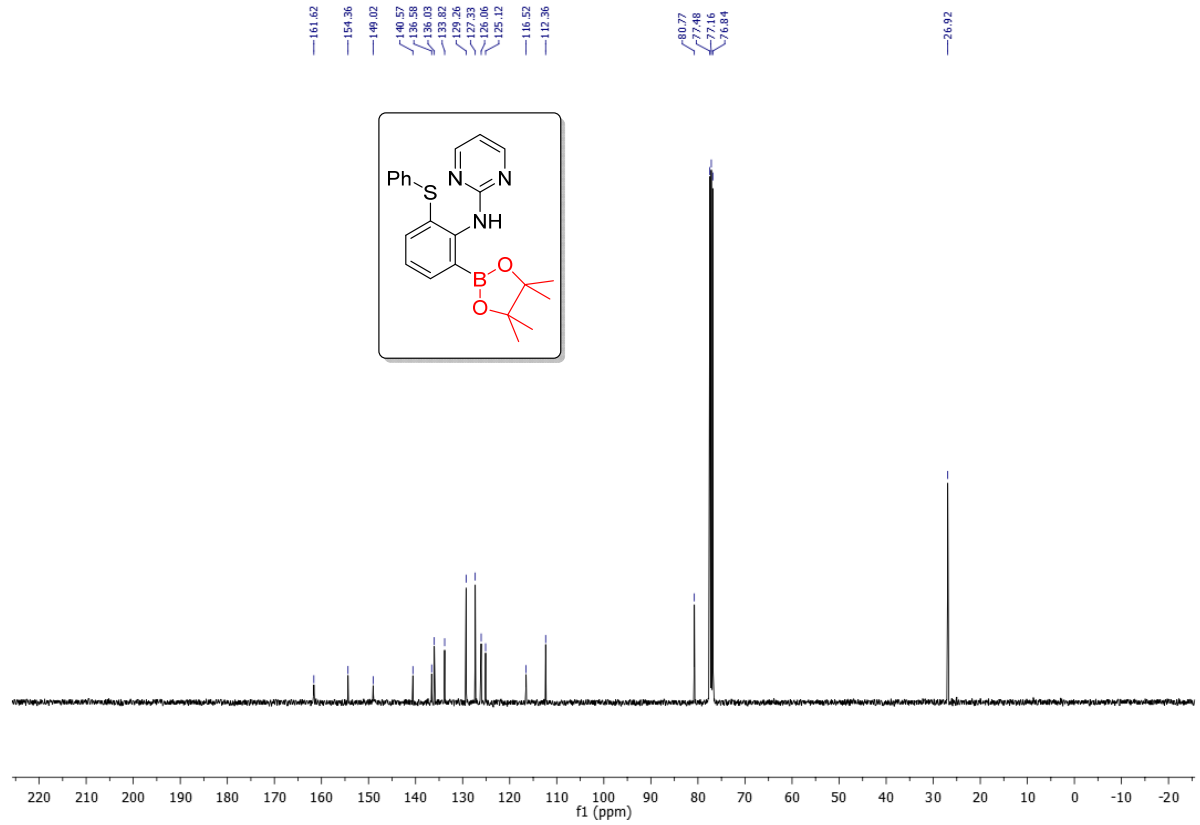
^{13}C NMR spectrum of **10b** (101 MHz, $CDCl_3$):



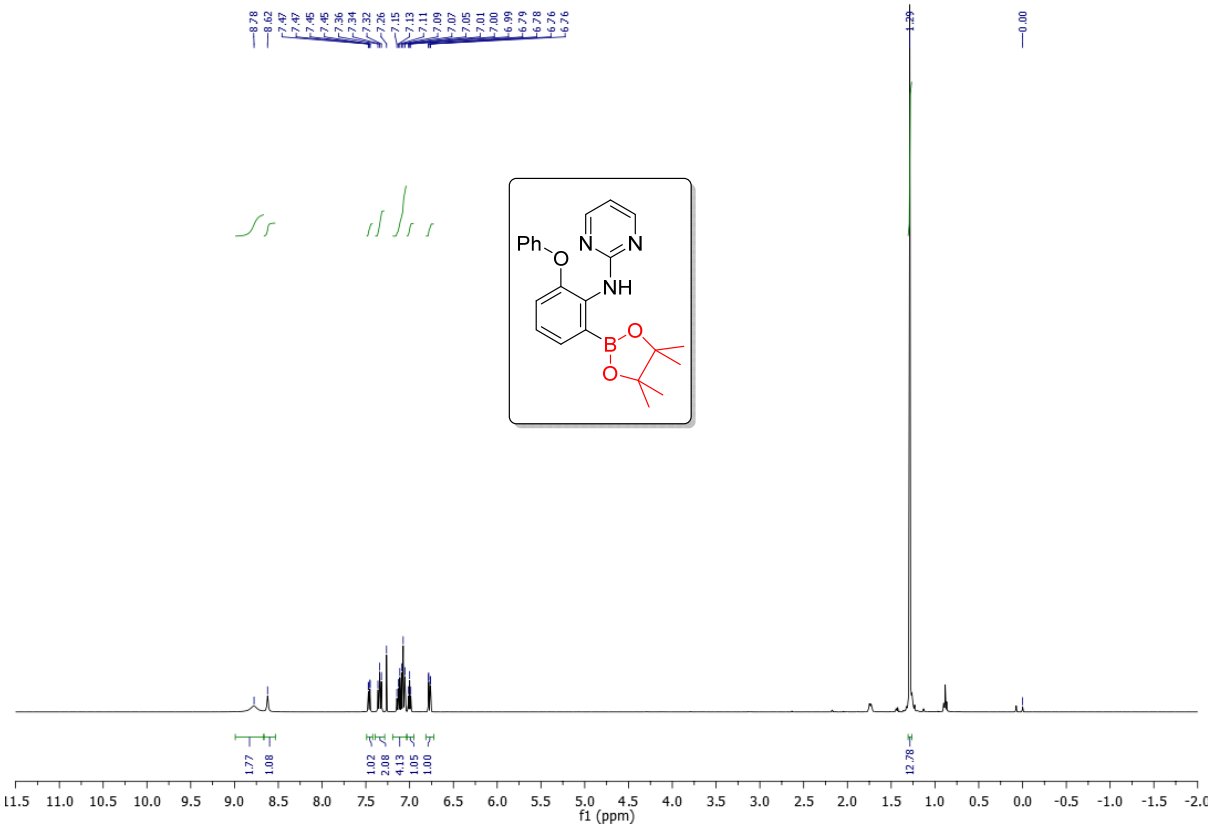
^{1}H NMR spectrum of **11b** (400 MHz, $CDCl_3$):



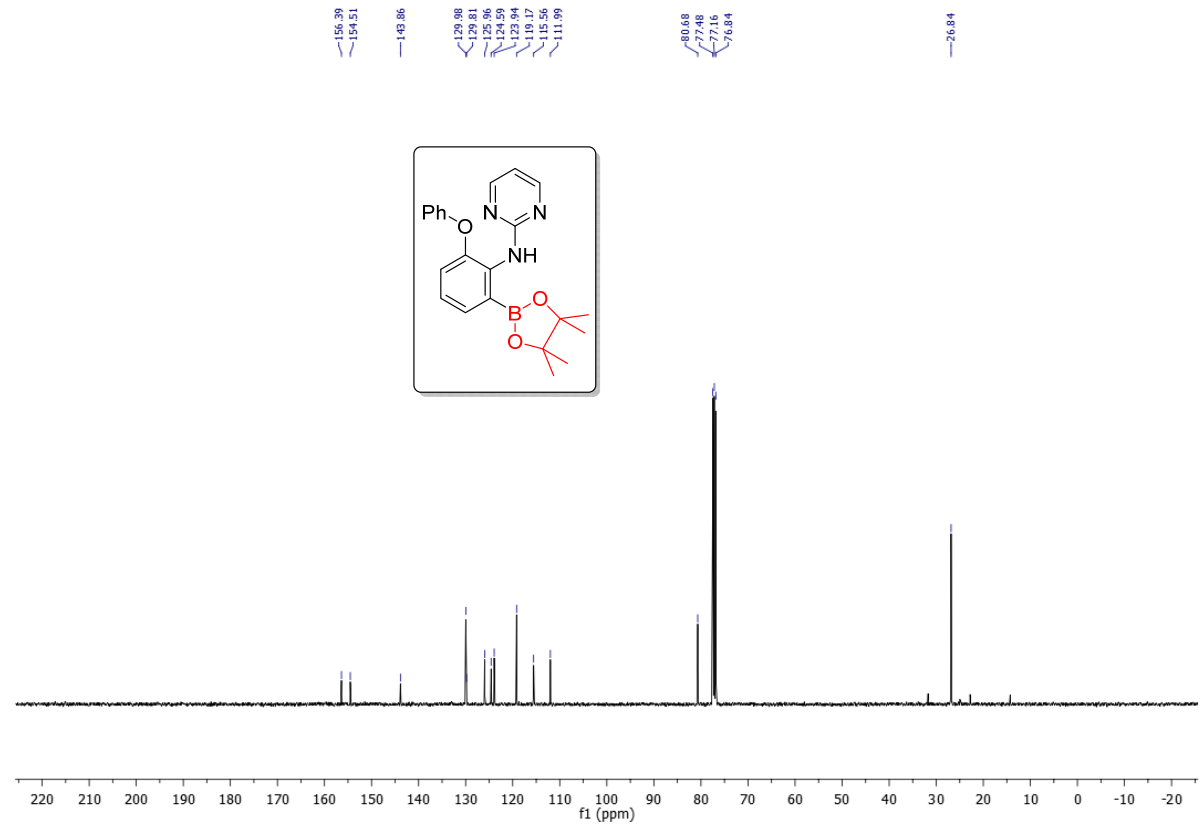
^{13}C NMR spectrum of **11b** (101 MHz, $CDCl_3$):



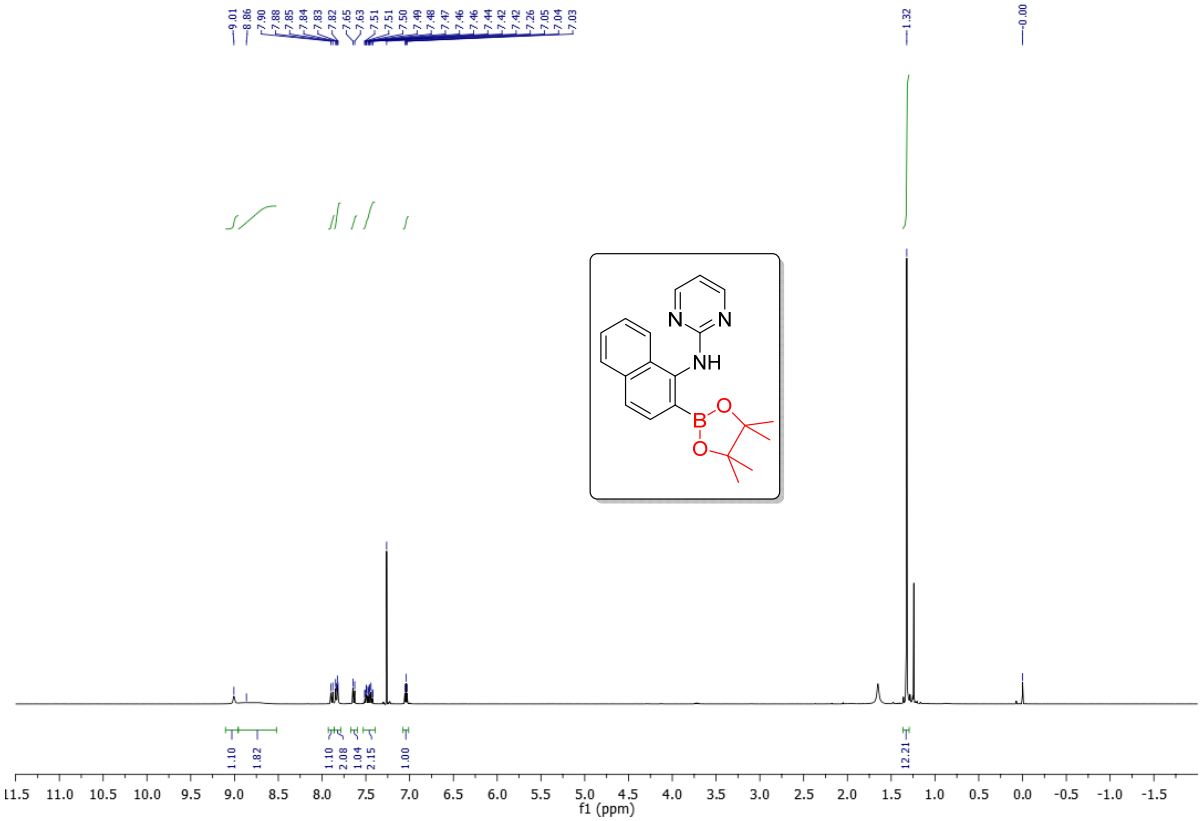
^{1}H NMR spectrum of **12b** (400 MHz, $CDCl_3$):



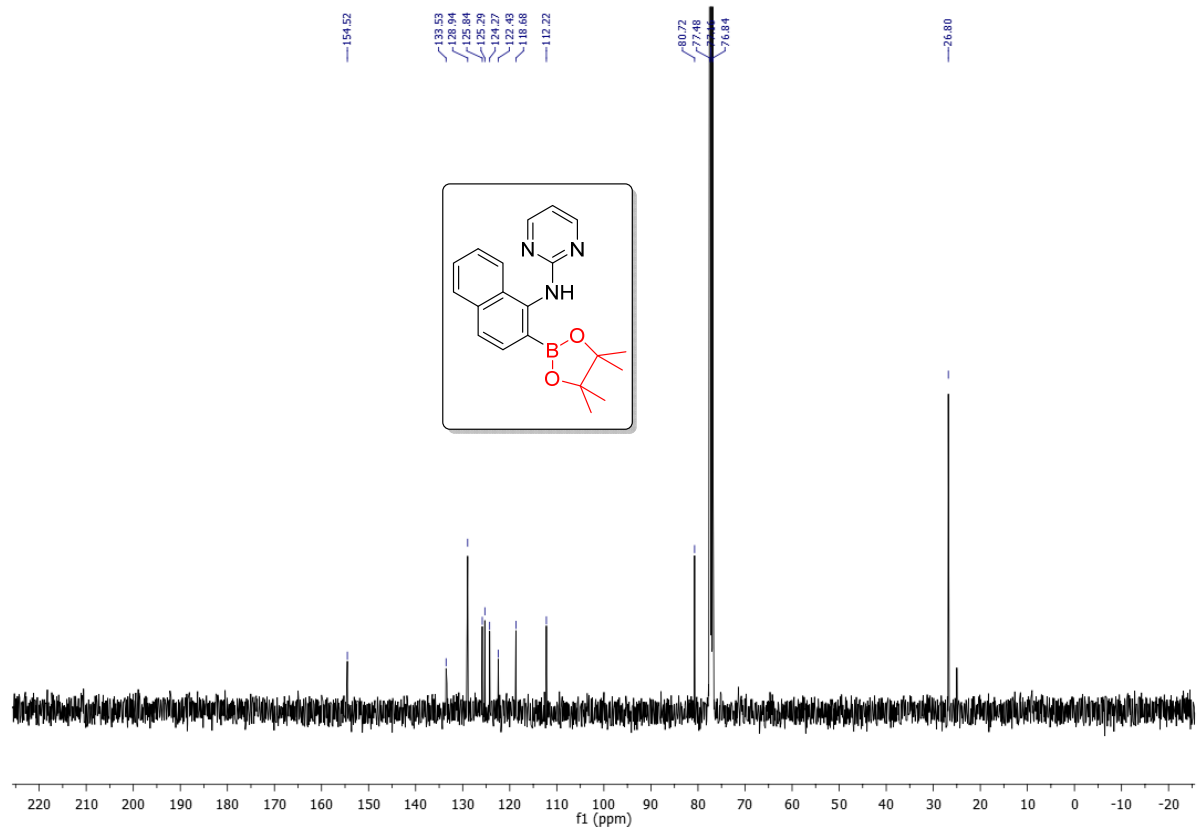
^{13}C NMR spectrum of **12b** (101 MHz, $CDCl_3$):



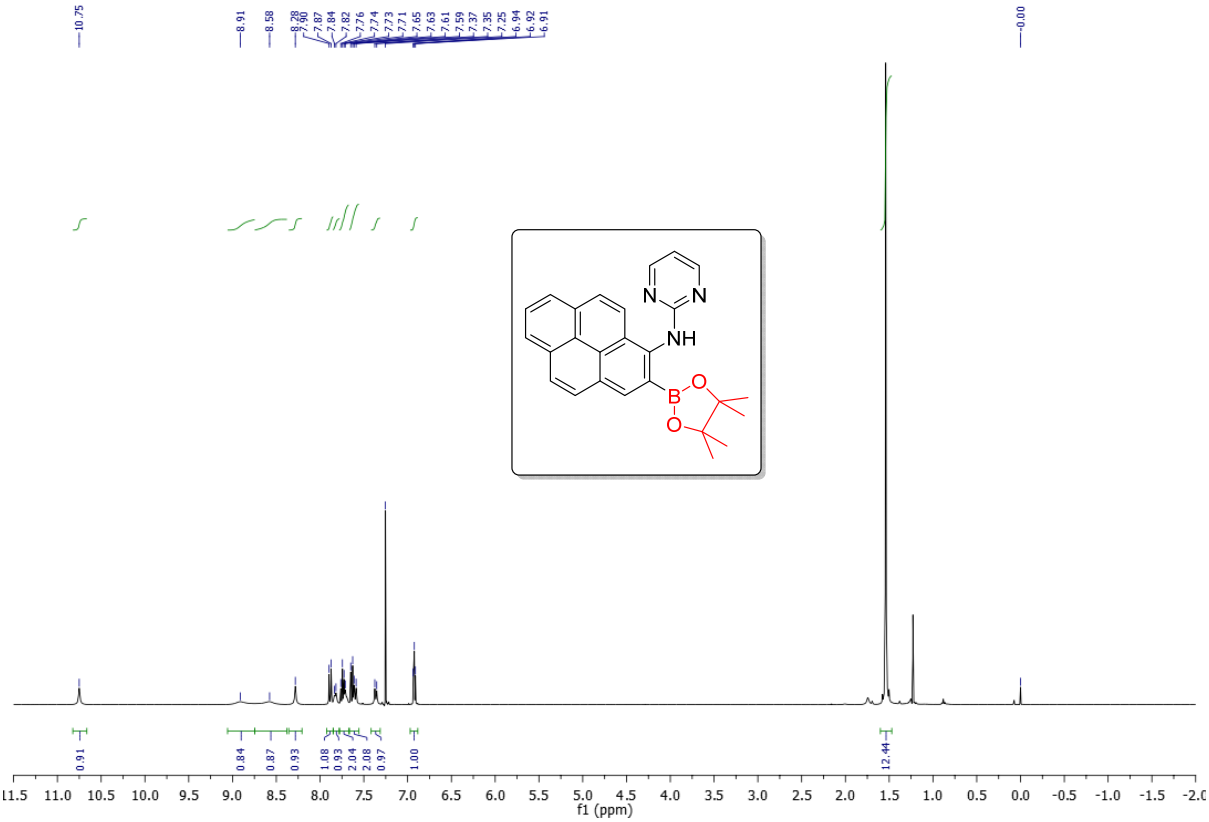
^{1}H NMR spectrum of **13b** (400 MHz, $CDCl_3$):



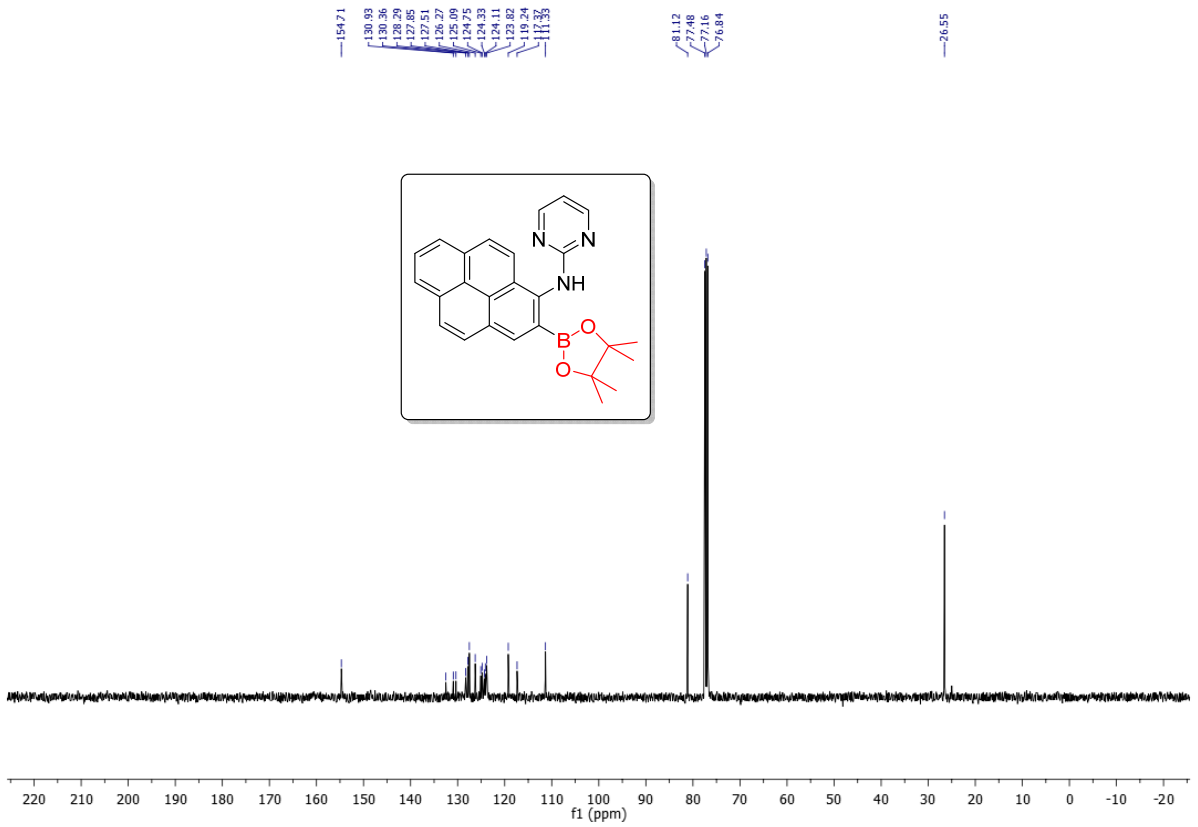
^{13}C NMR spectrum of **13b** (101 MHz, $CDCl_3$):



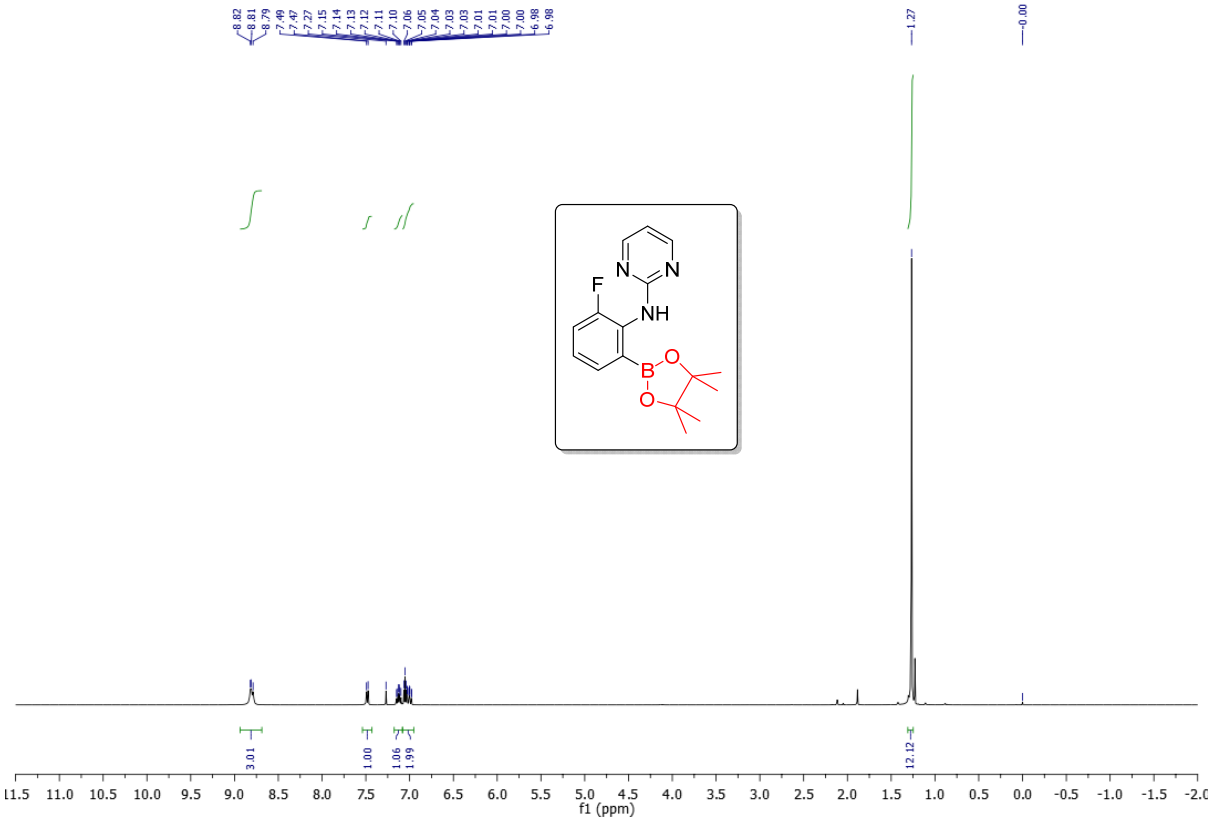
^{1}H NMR spectrum of **14b** (400 MHz, $CDCl_3$):



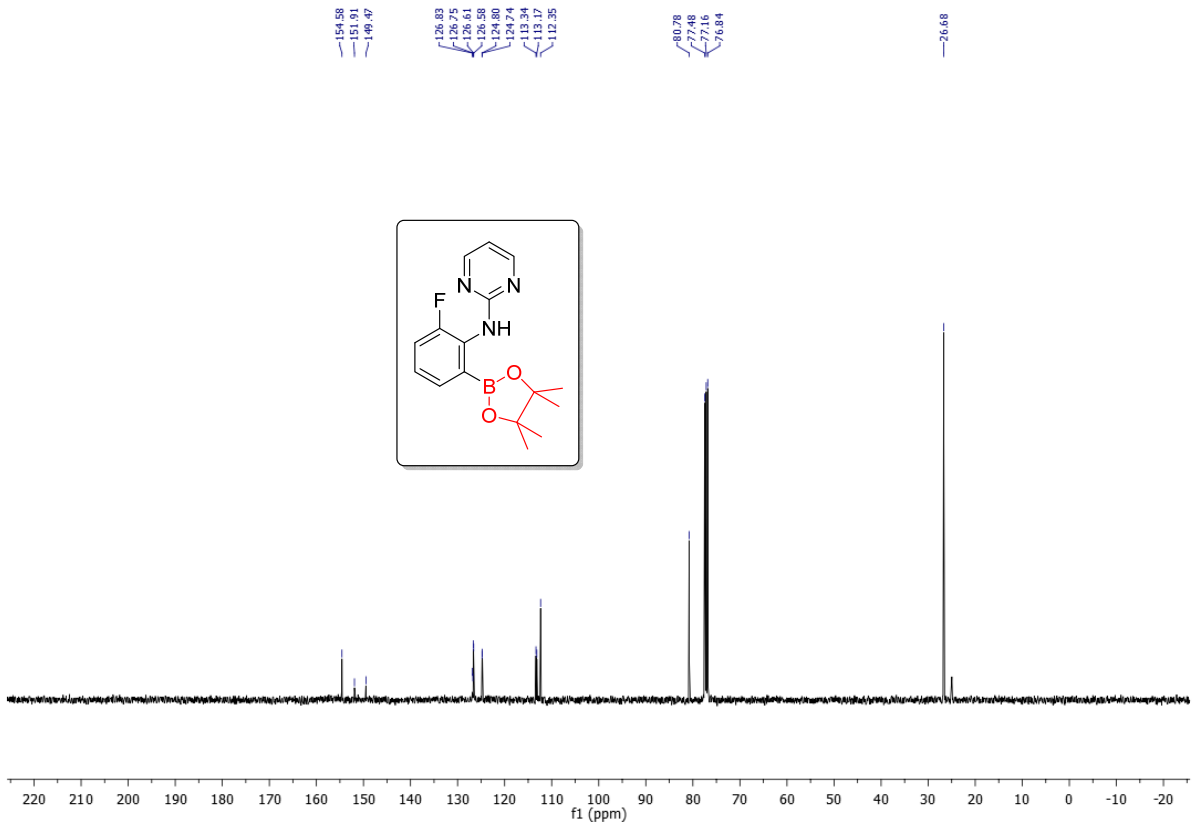
^{13}C NMR spectrum of **14b** (101 MHz, $CDCl_3$):



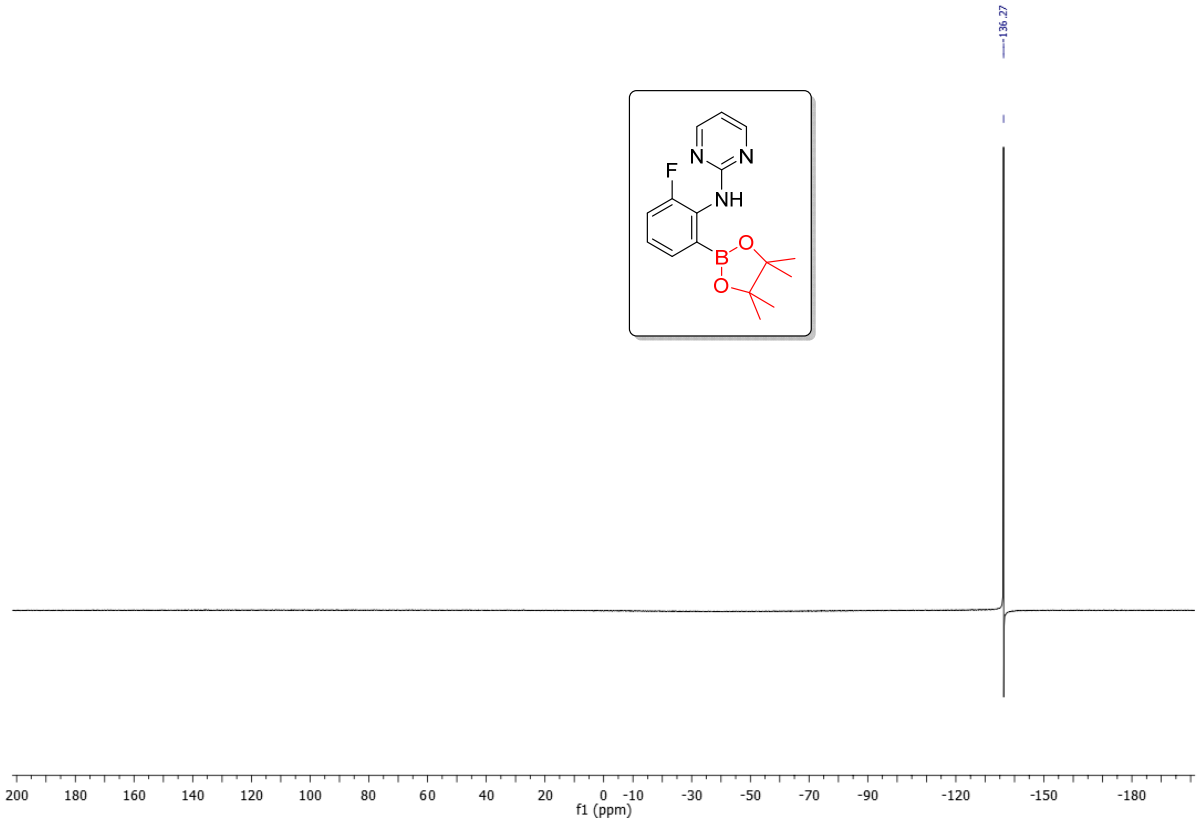
^{1}H NMR spectrum of **15b** (400 MHz, $CDCl_3$):



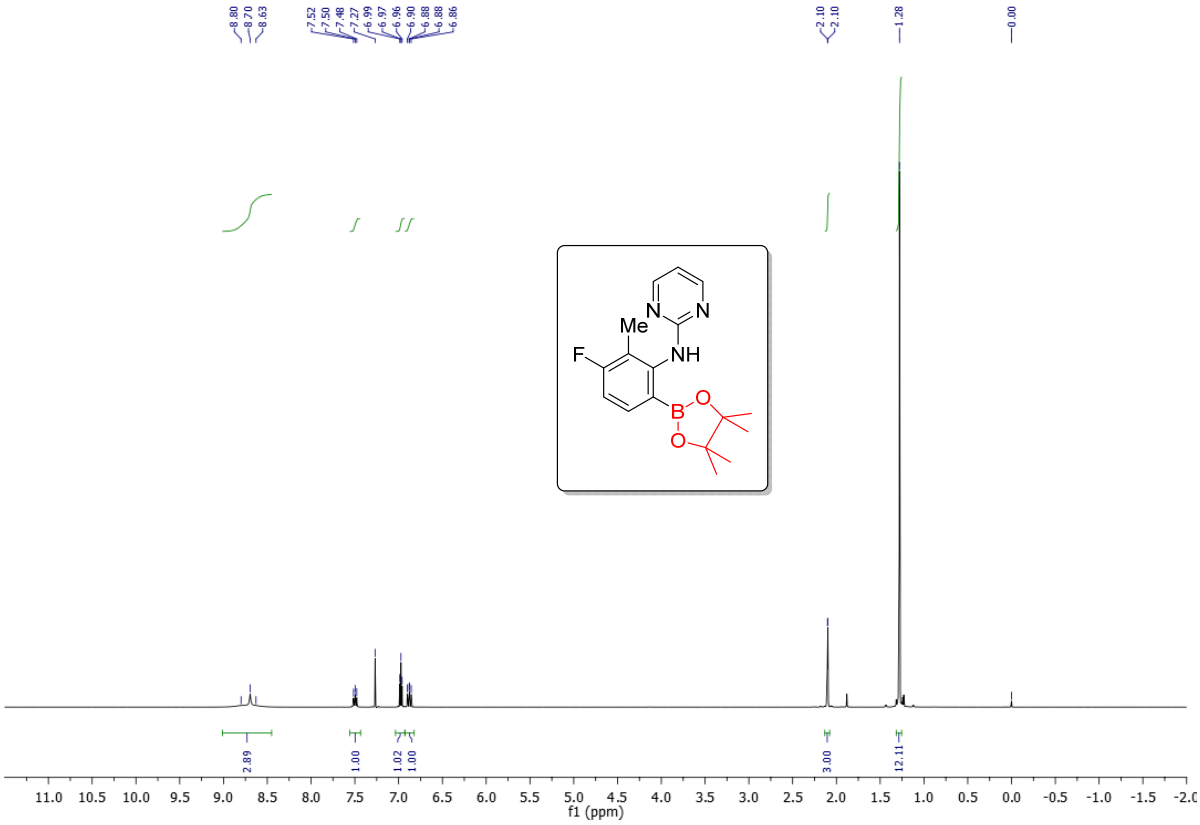
^{13}C NMR spectrum of **15b** (101 MHz, $CDCl_3$):



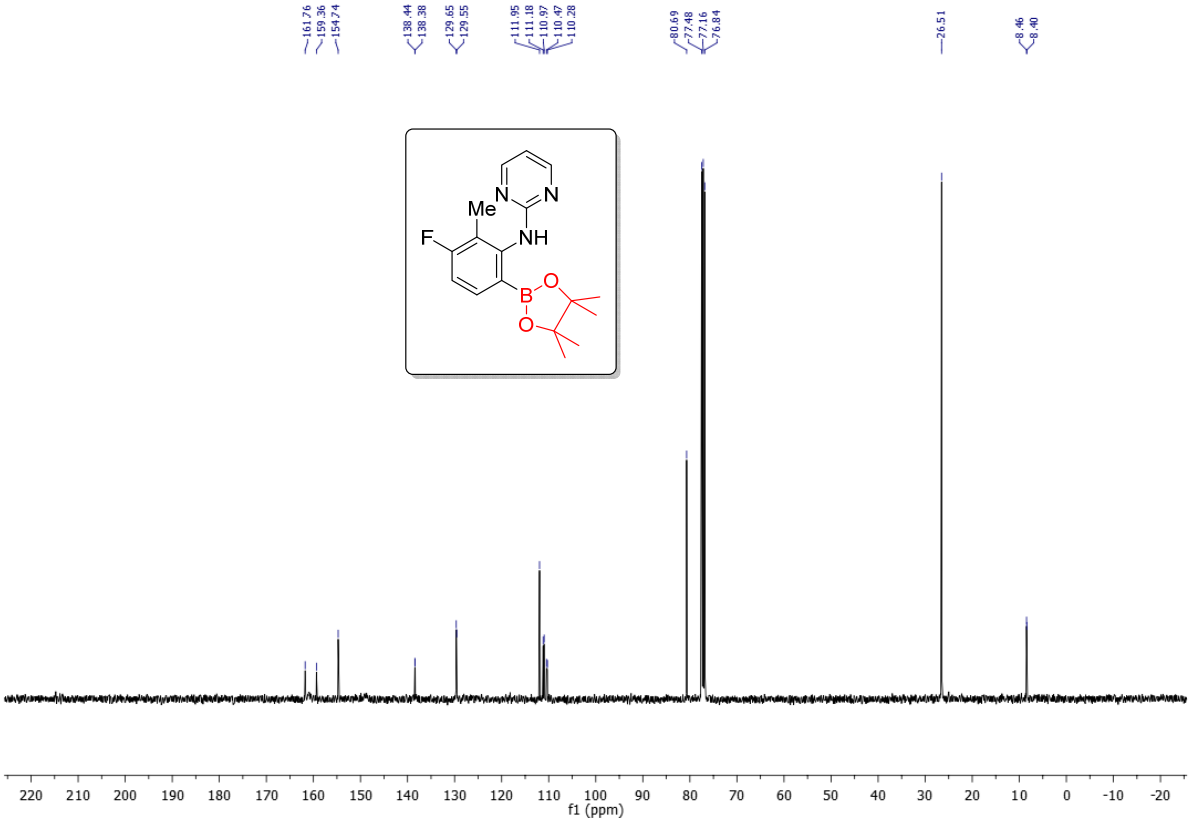
^{19}F NMR spectrum of **15b** (376 MHz, $CDCl_3$):



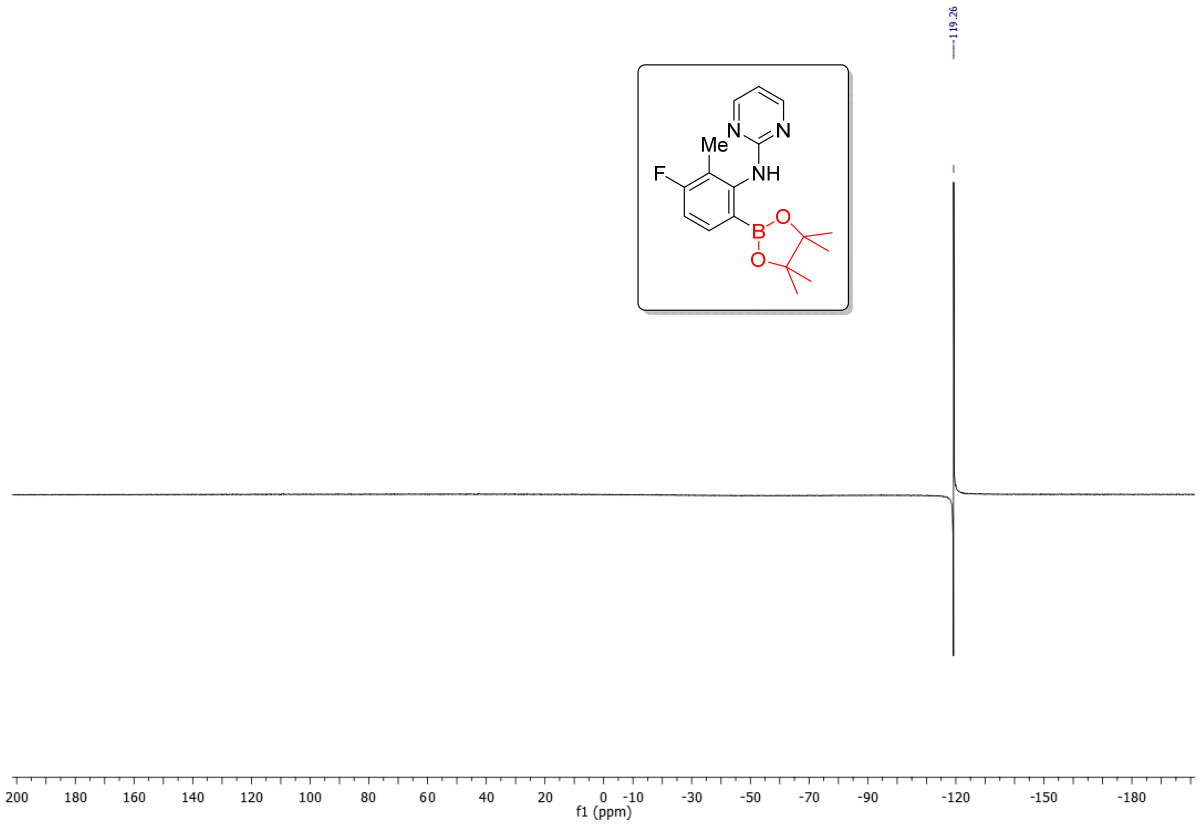
^{1}H NMR spectrum of **16b** (400 MHz, $CDCl_3$):



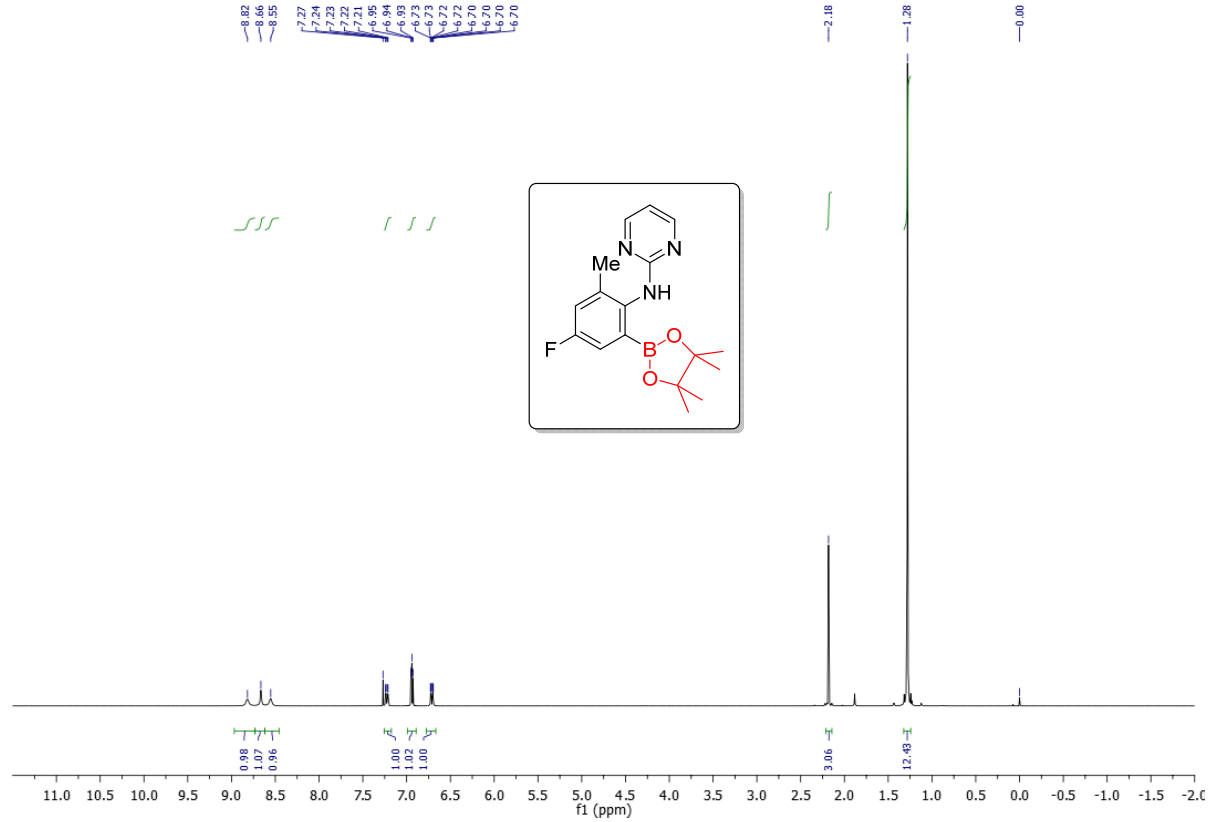
^{13}C NMR spectrum of **16b** (101 MHz, $CDCl_3$):



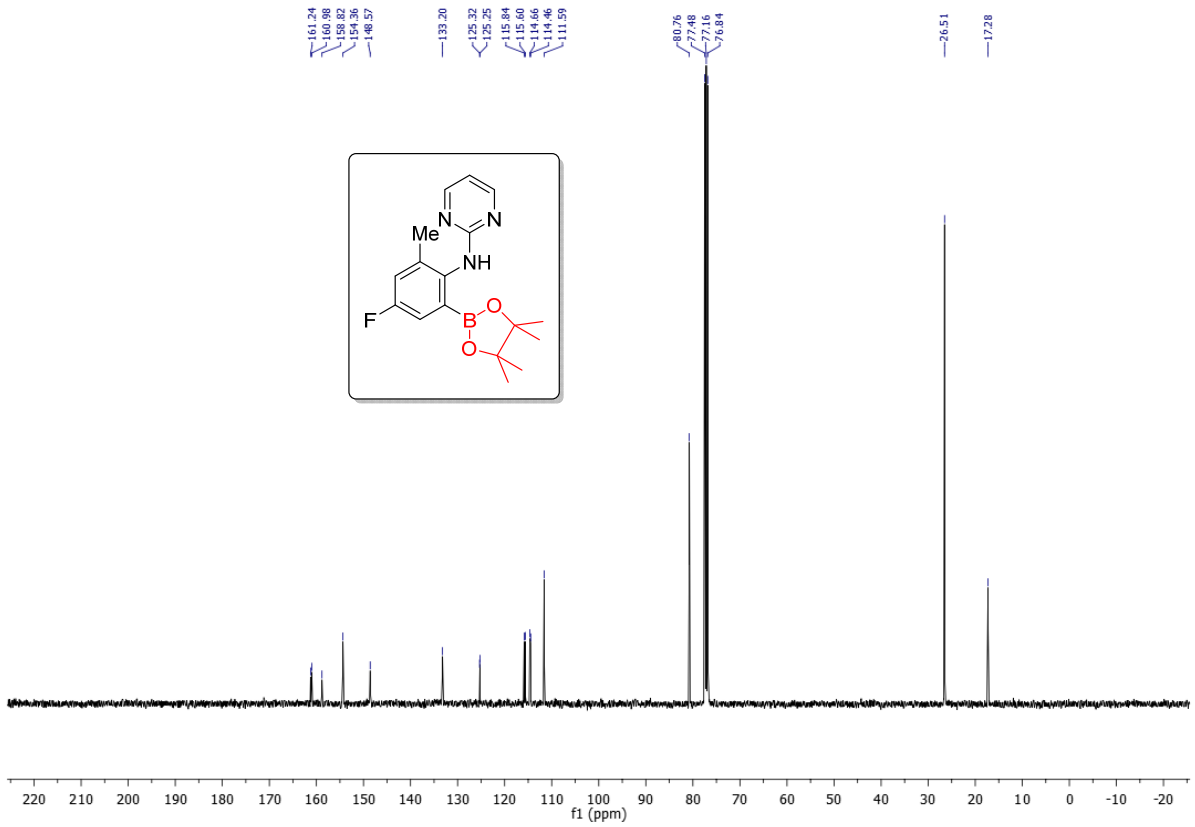
^{19}F NMR spectrum of **16b** (376 MHz, $CDCl_3$):



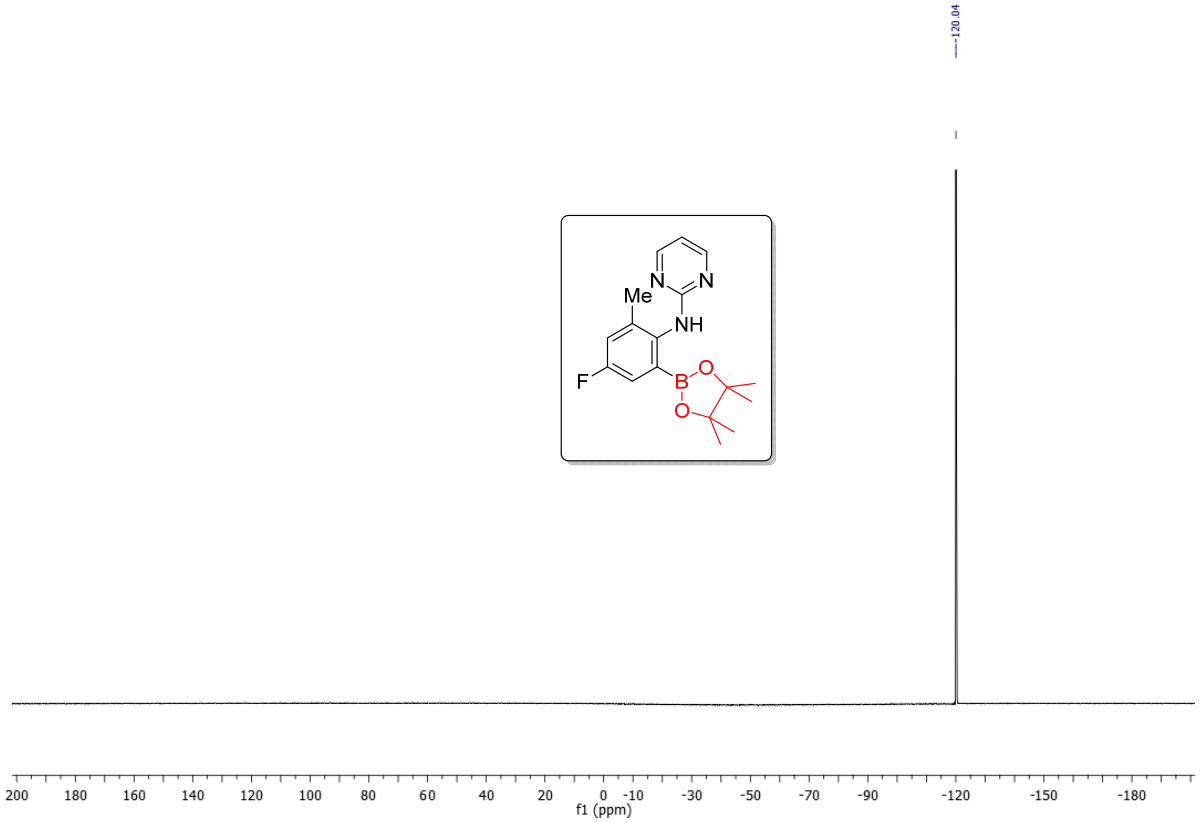
^{1}H NMR spectrum of **17b** (400 MHz, $CDCl_3$):



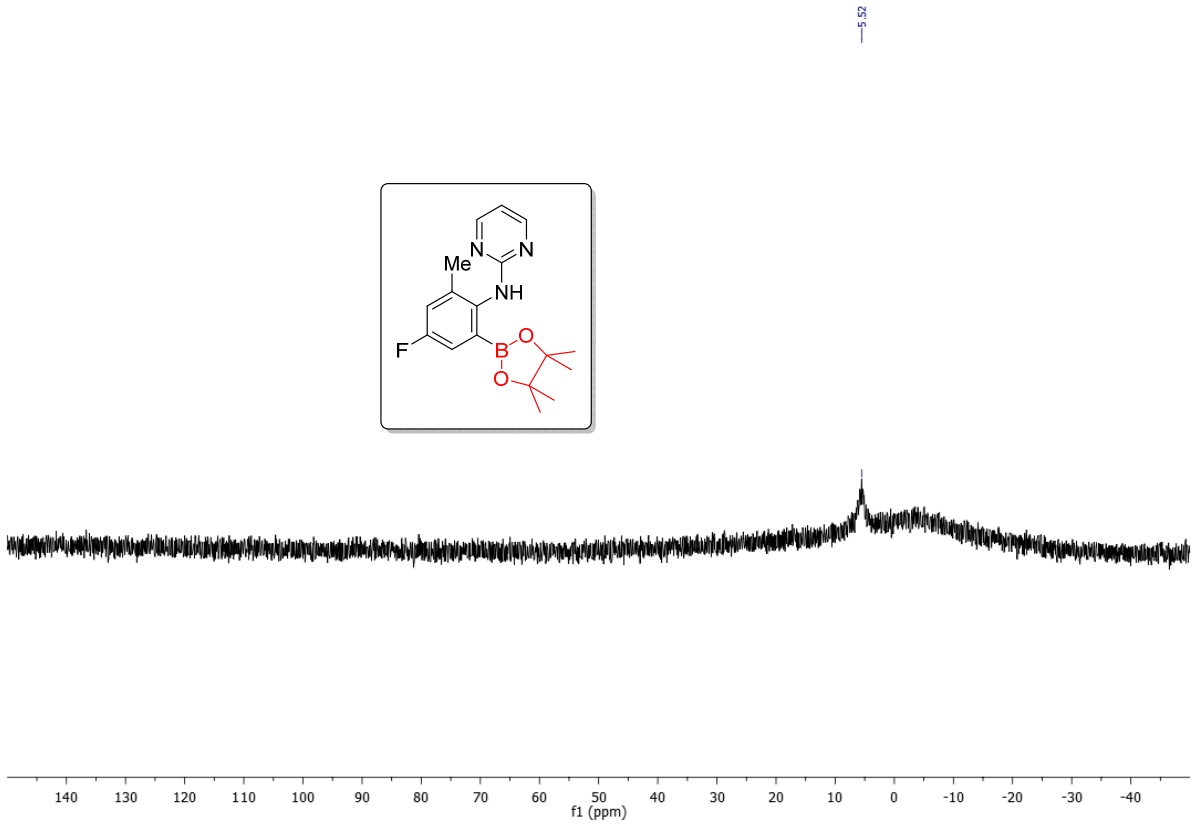
^{13}C NMR spectrum of **17b** (101 MHz, $CDCl_3$):



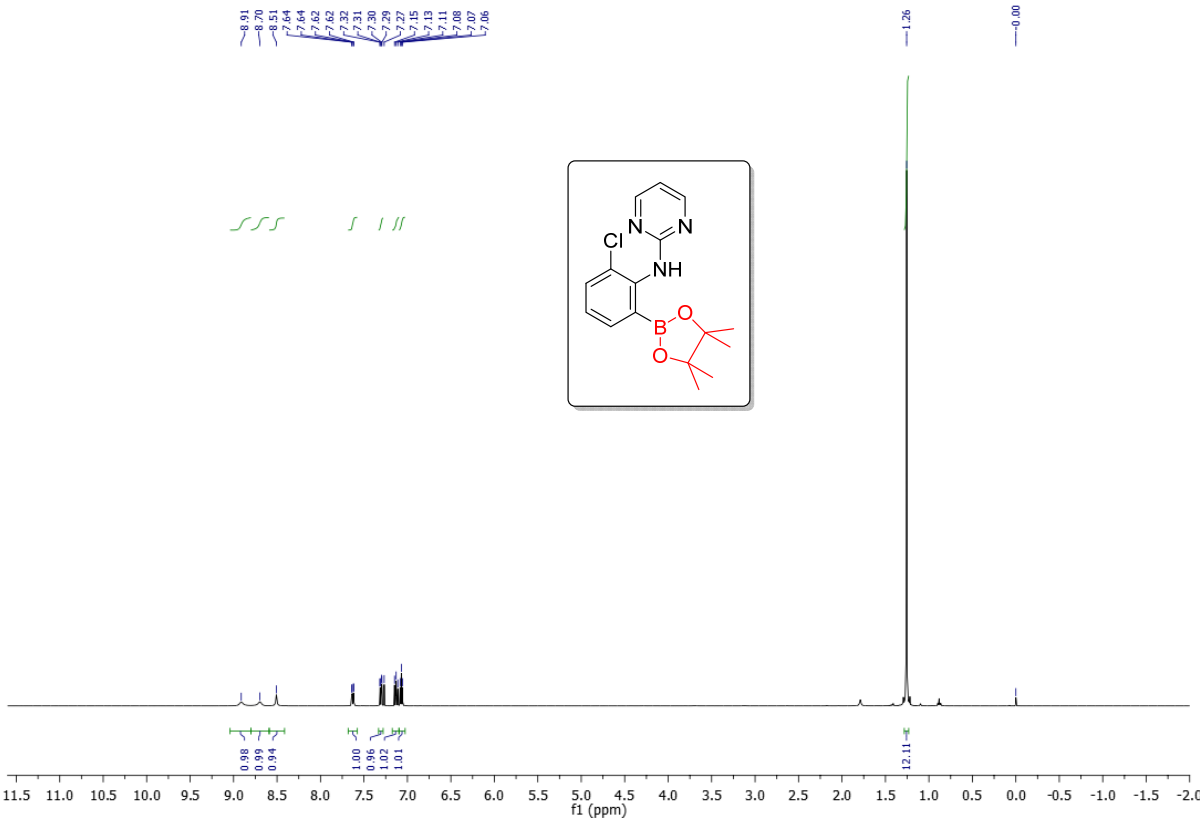
^{19}F NMR spectrum of **17b** (376 MHz, $CDCl_3$):



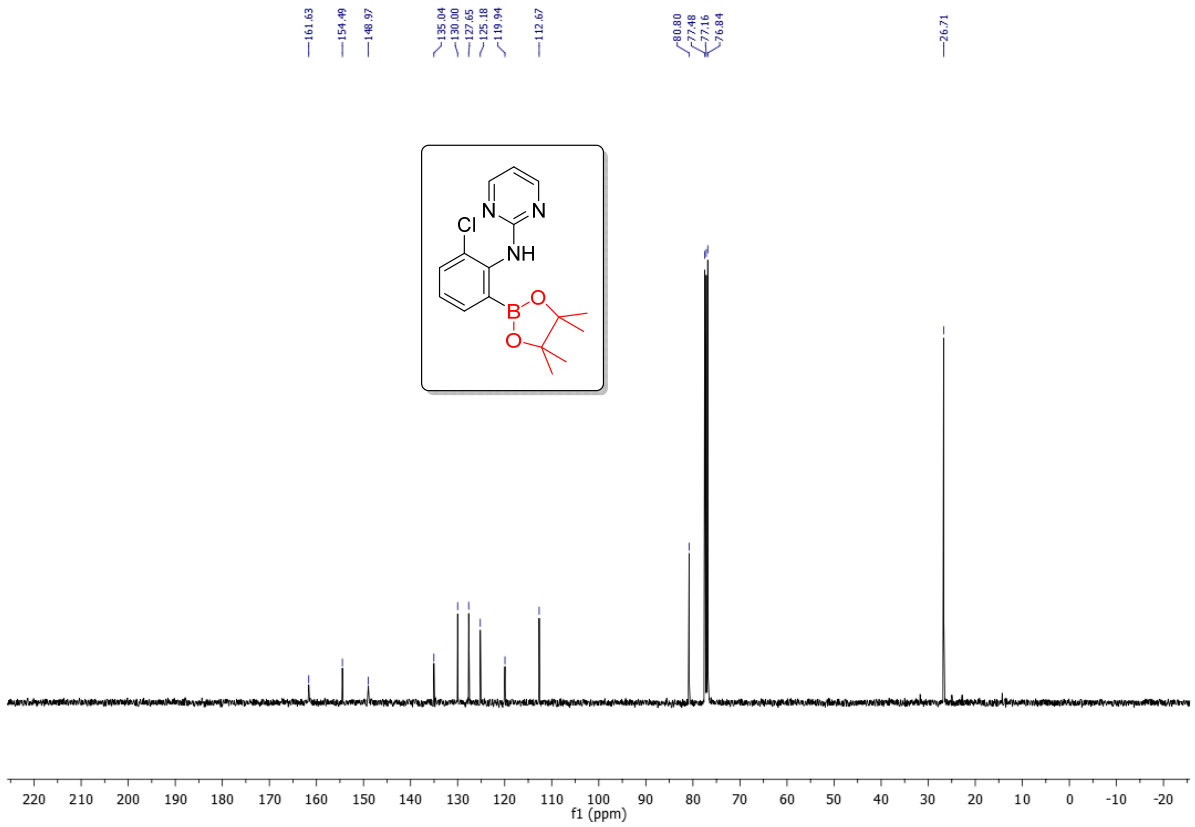
^{11}B NMR spectrum of **17b** (128 MHz, $CDCl_3$):



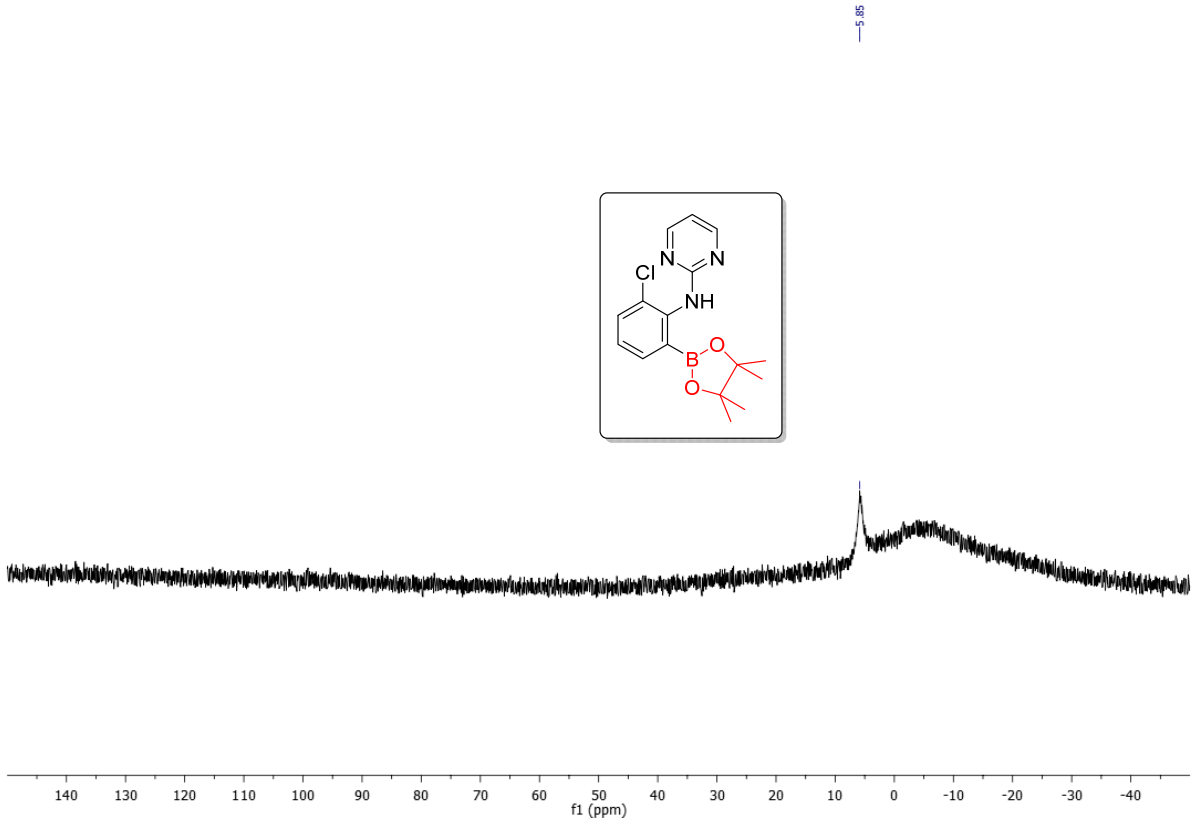
^{1}H NMR spectrum of **18b** (400 MHz, $CDCl_3$):



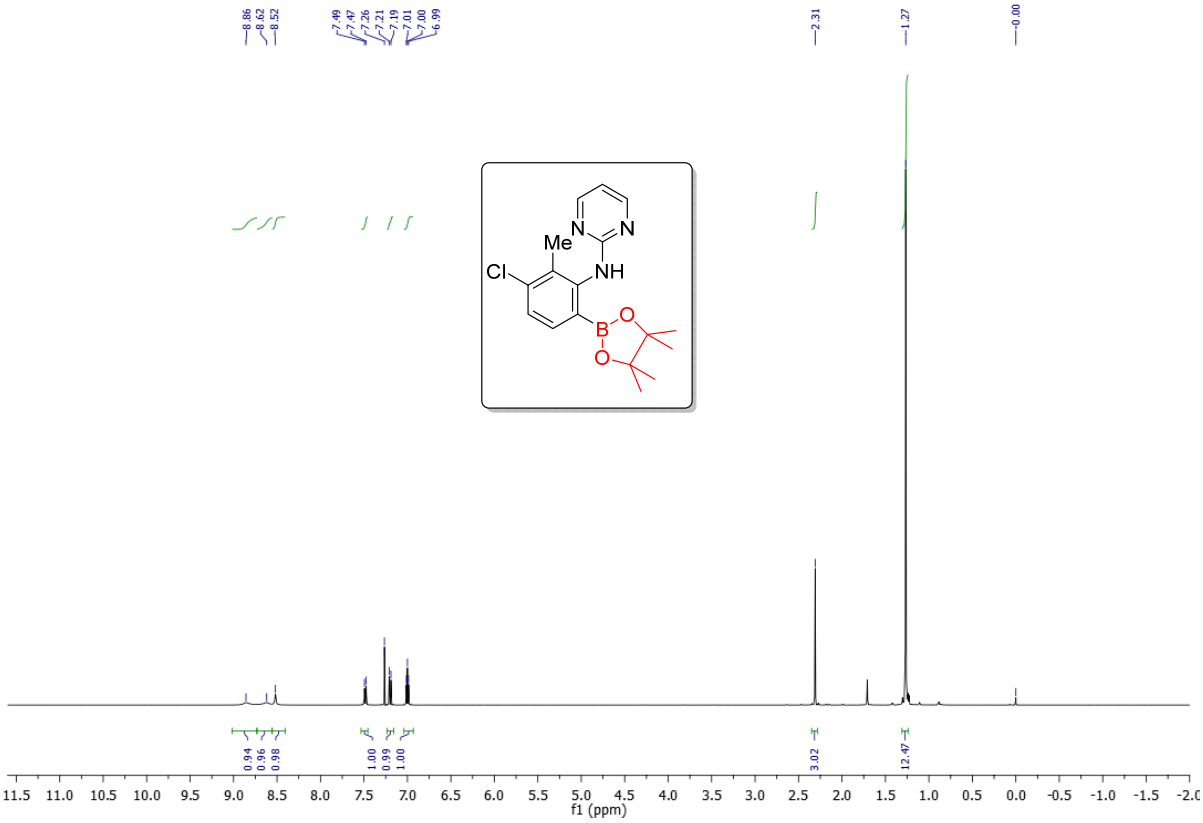
^{13}C NMR spectrum of **18b** (101 MHz, $CDCl_3$):



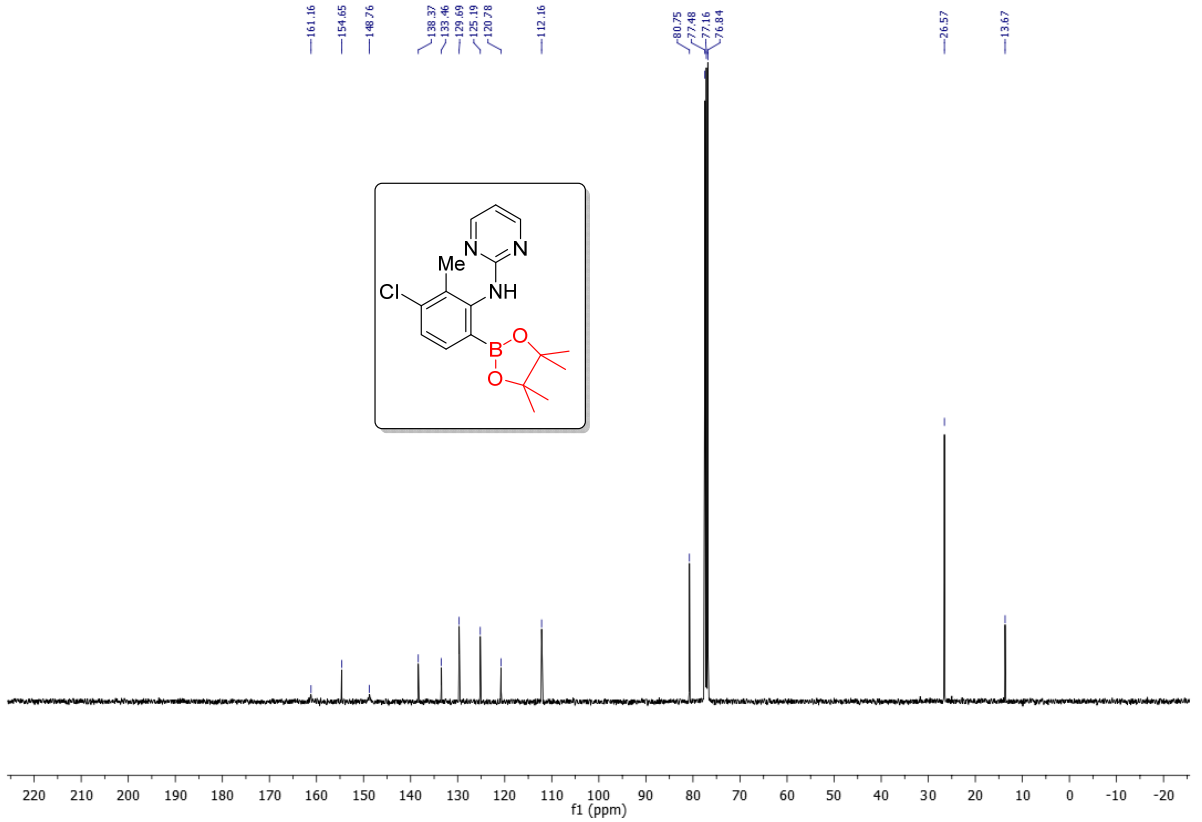
^{11}B NMR spectrum of **18b** (128 MHz, $CDCl_3$):



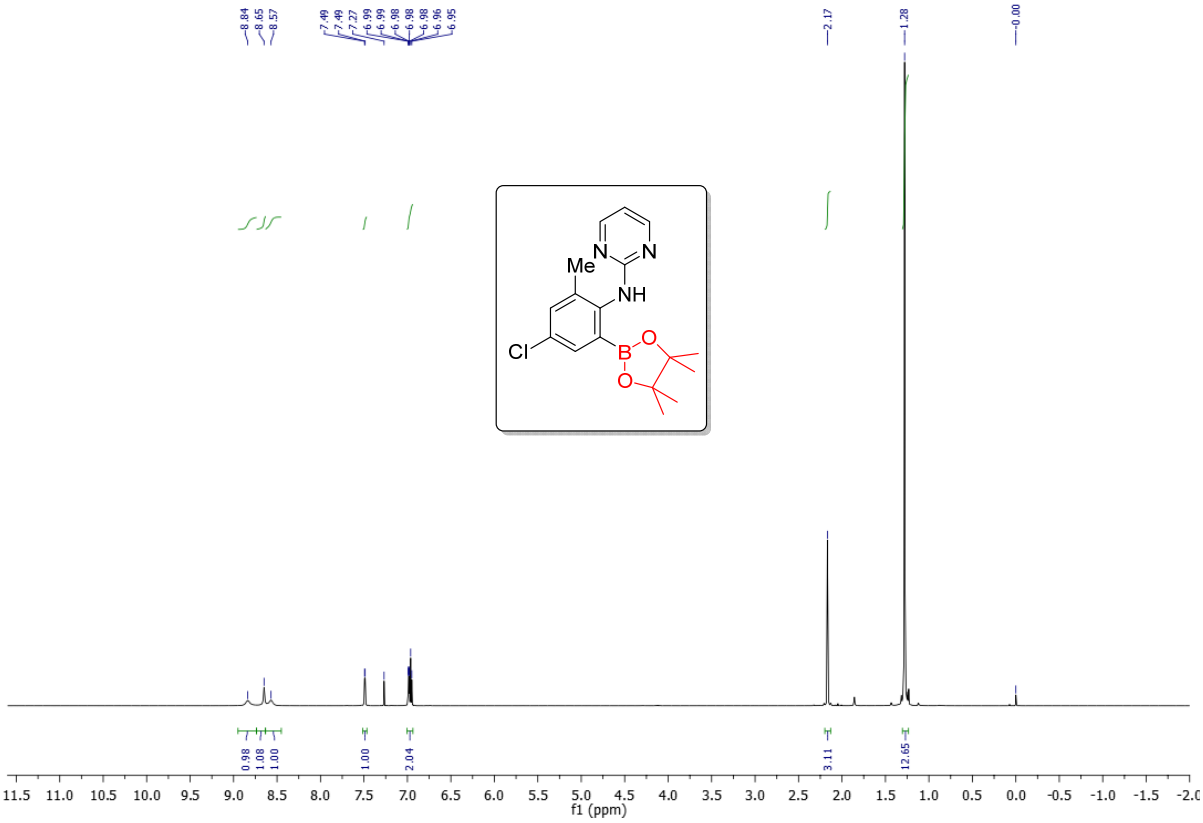
^{1}H NMR spectrum of **19b** (400 MHz, $CDCl_3$):



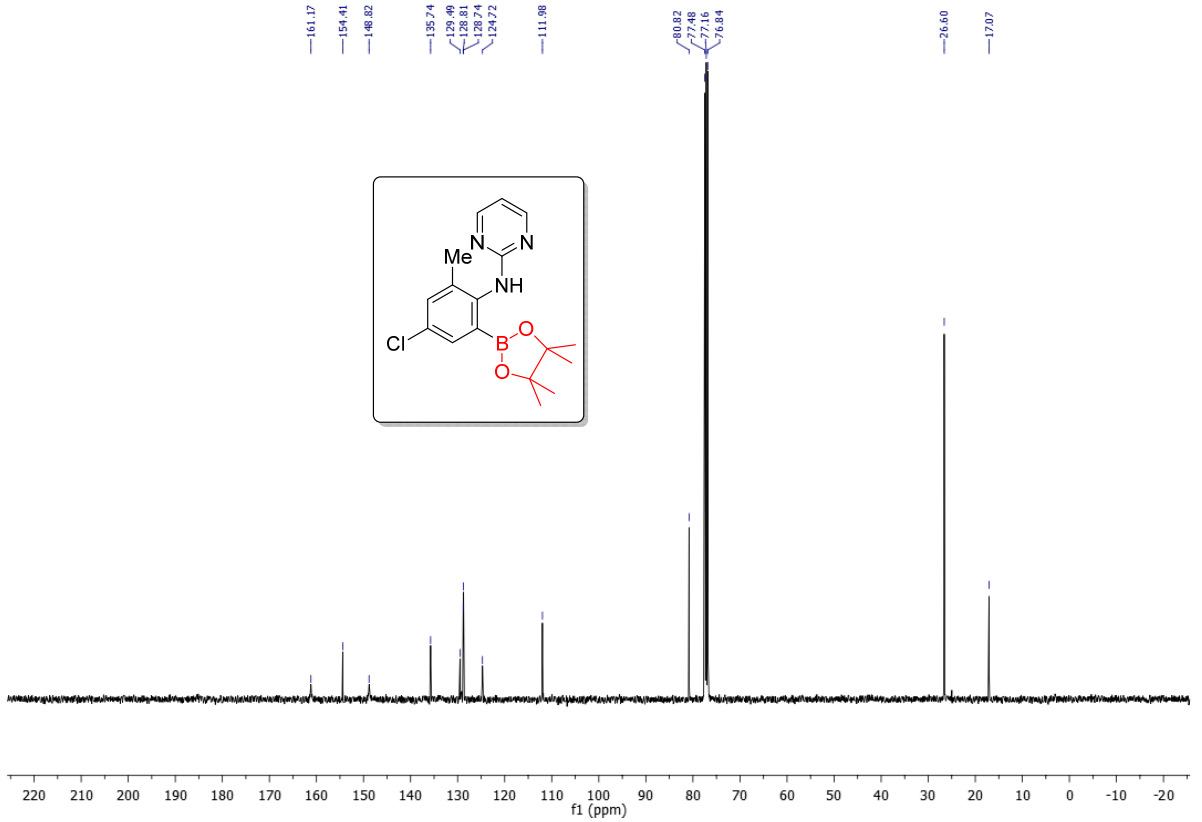
^{13}C NMR spectrum of **19b** (101 MHz, $CDCl_3$):



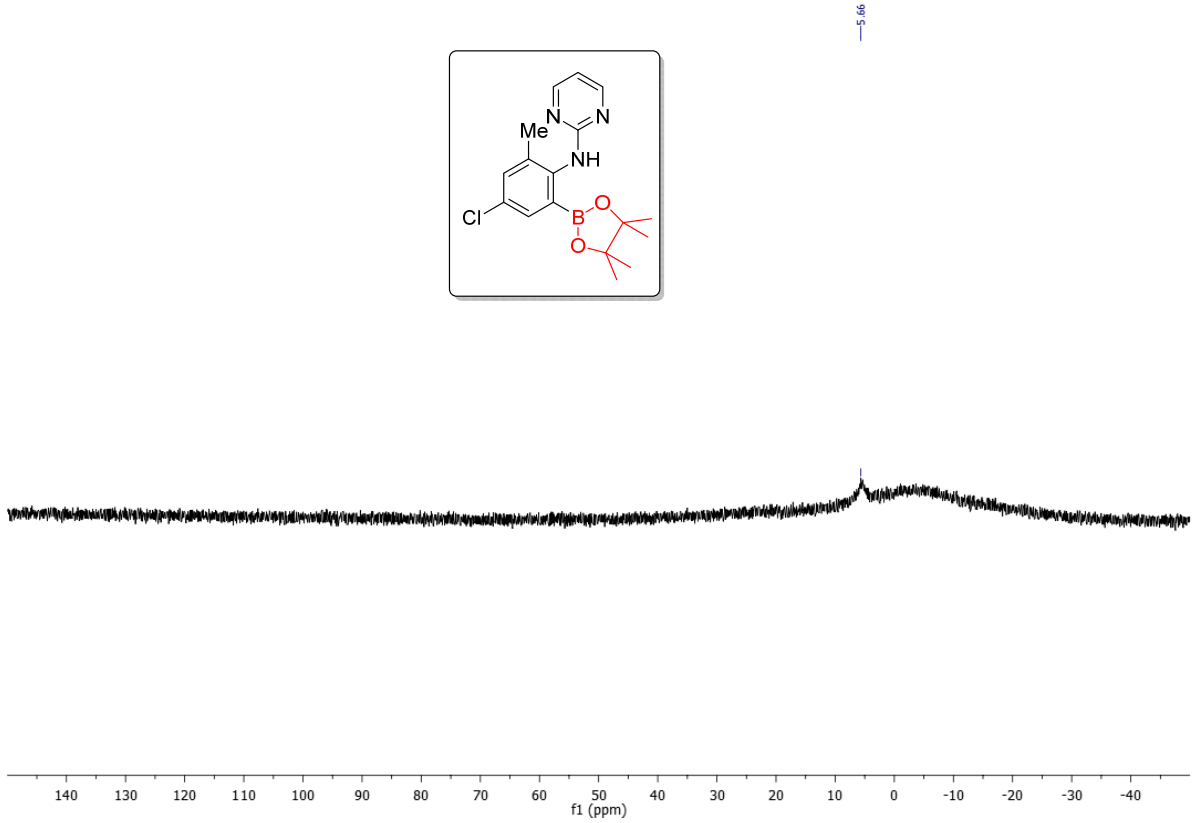
^{1}H NMR spectrum of **20b** (400 MHz, $CDCl_3$):



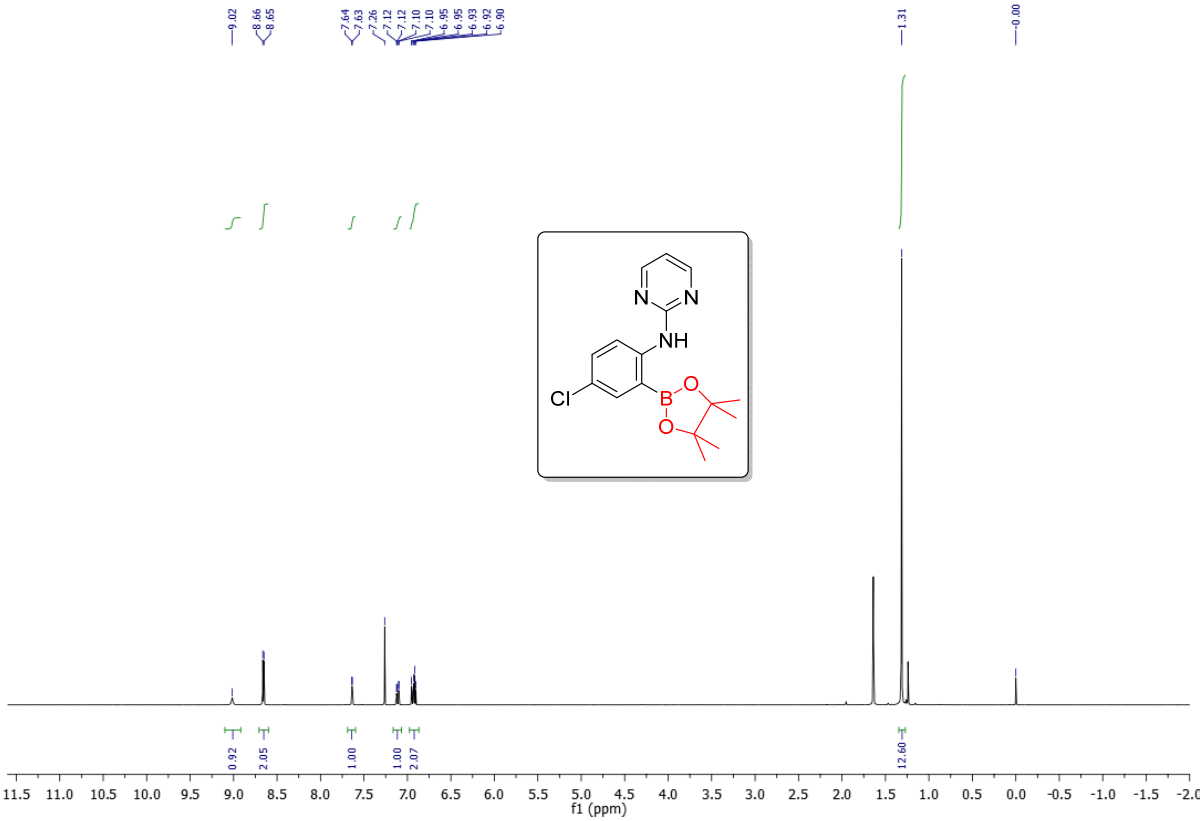
^{13}C NMR spectrum of **20b** (101 MHz, $CDCl_3$):



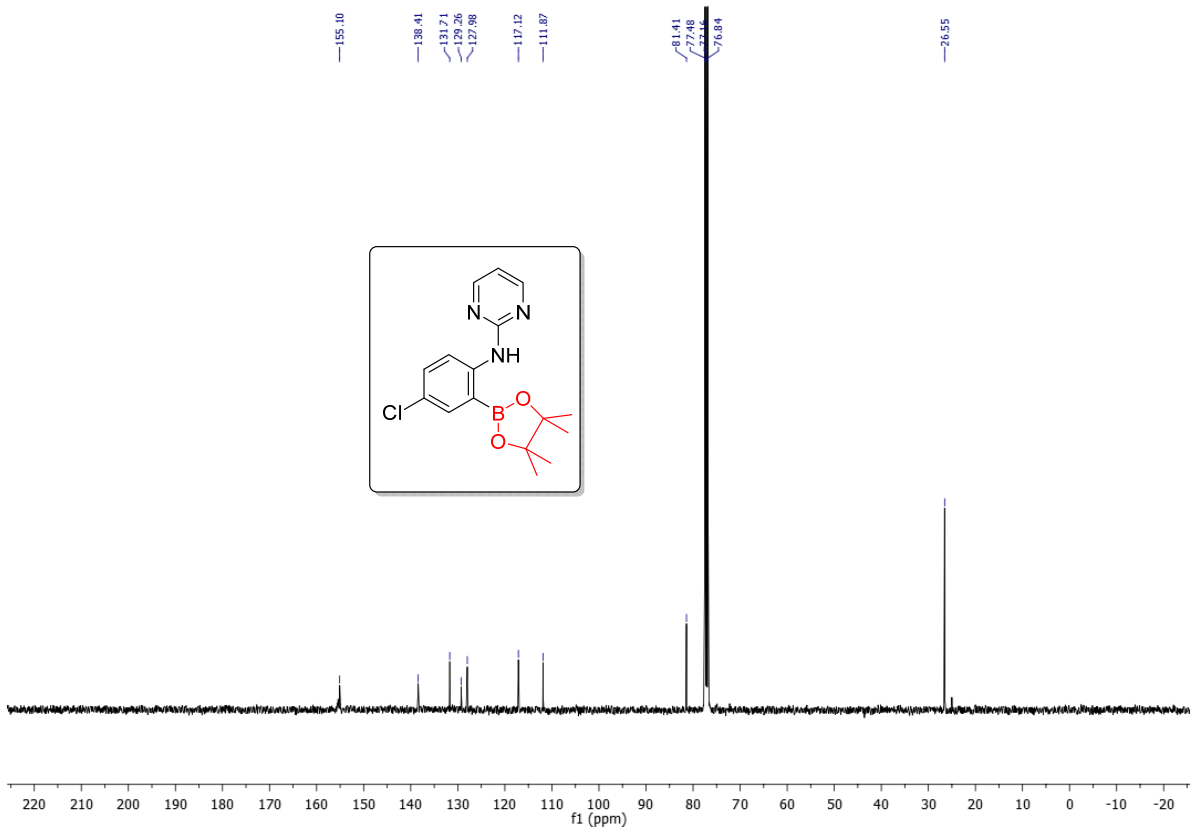
^{11}B NMR spectrum of **20b** (128 MHz, $CDCl_3$):



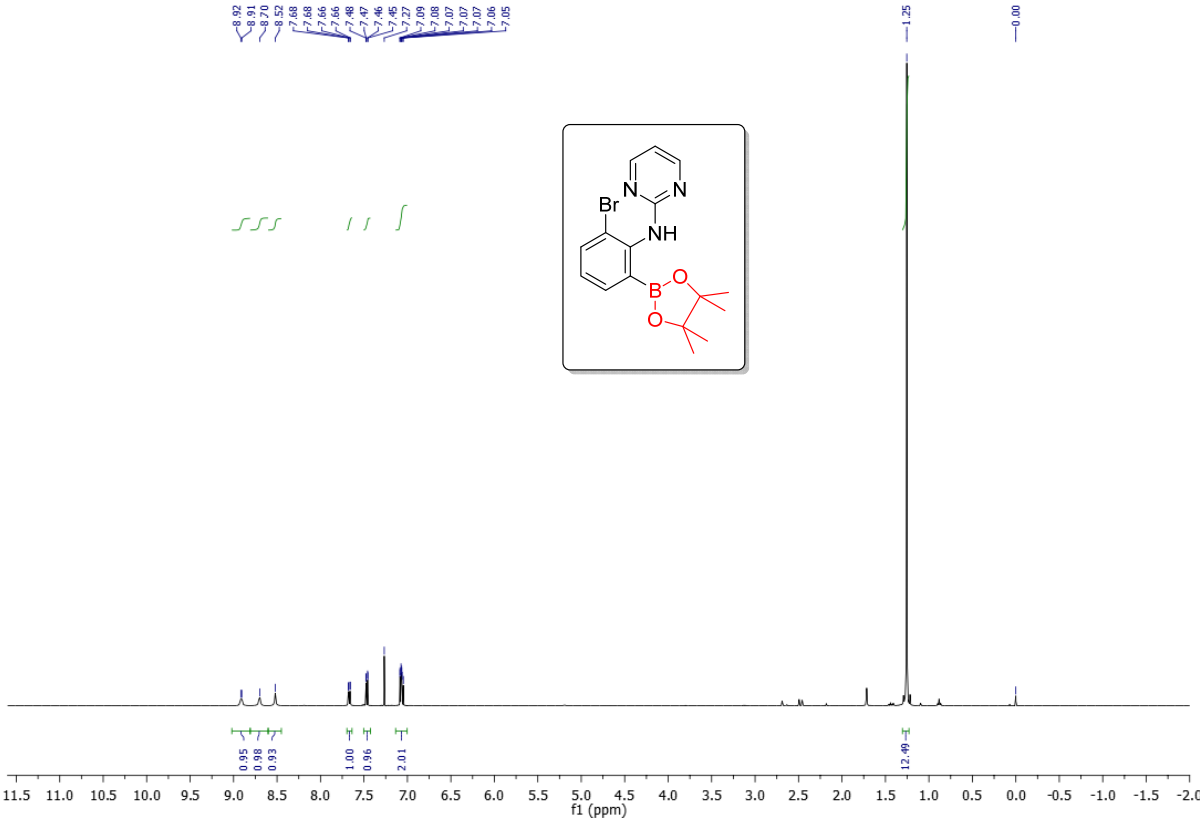
^{1}H NMR spectrum of **21b** (400 MHz, $CDCl_3$):



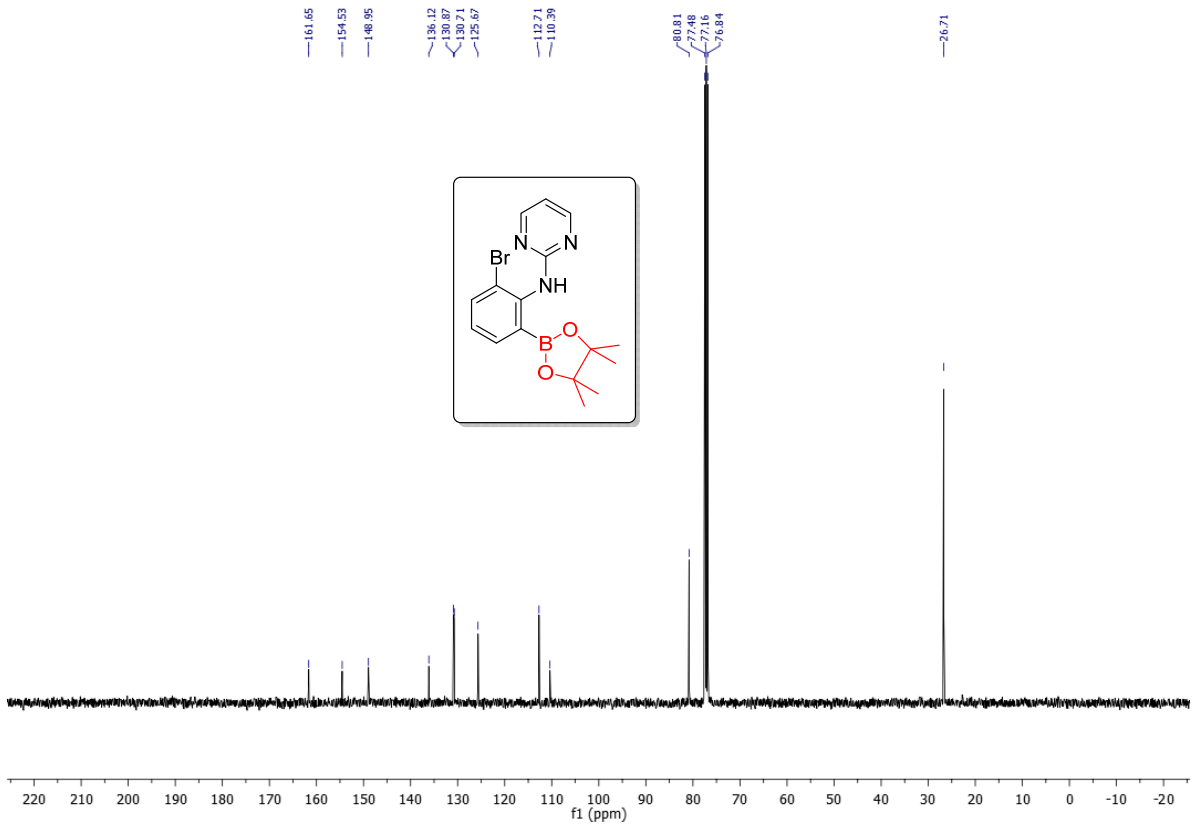
^{13}C NMR spectrum of **21b** (101 MHz, $CDCl_3$):



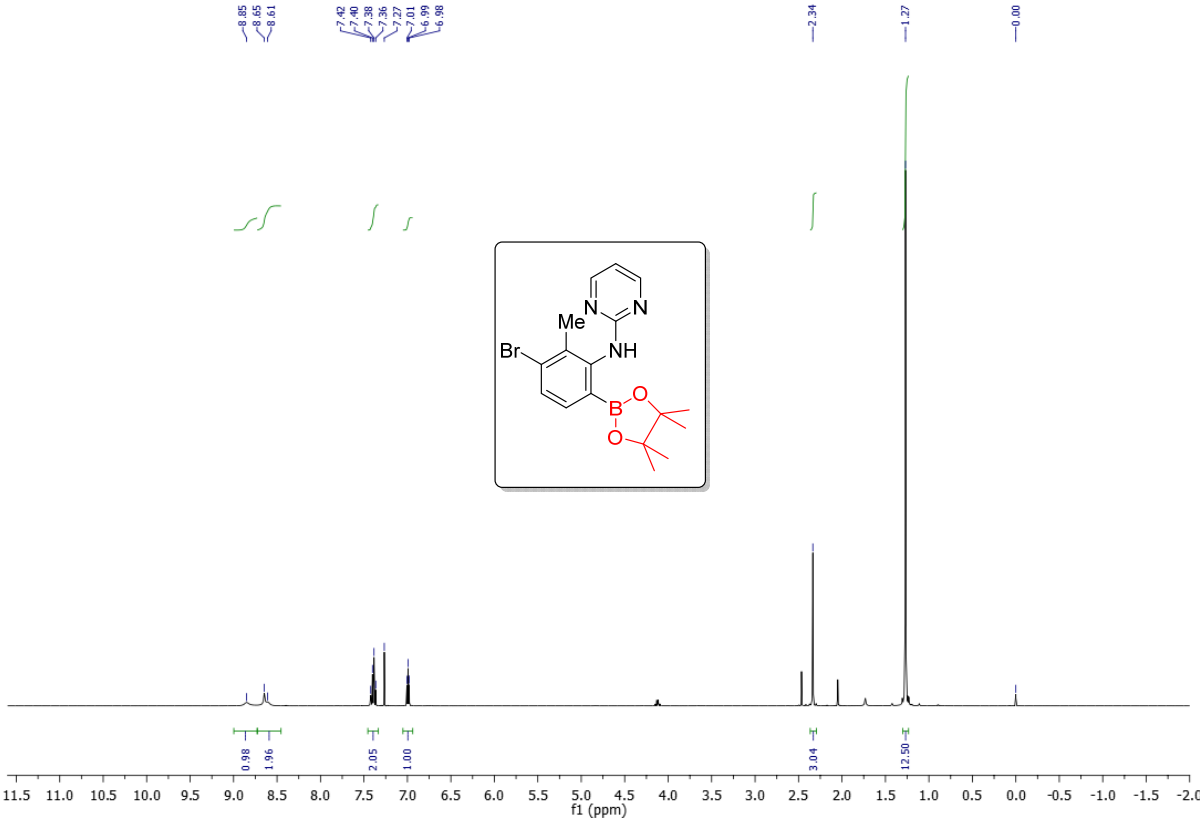
^{1}H NMR spectrum of **22b** (400 MHz, $CDCl_3$):



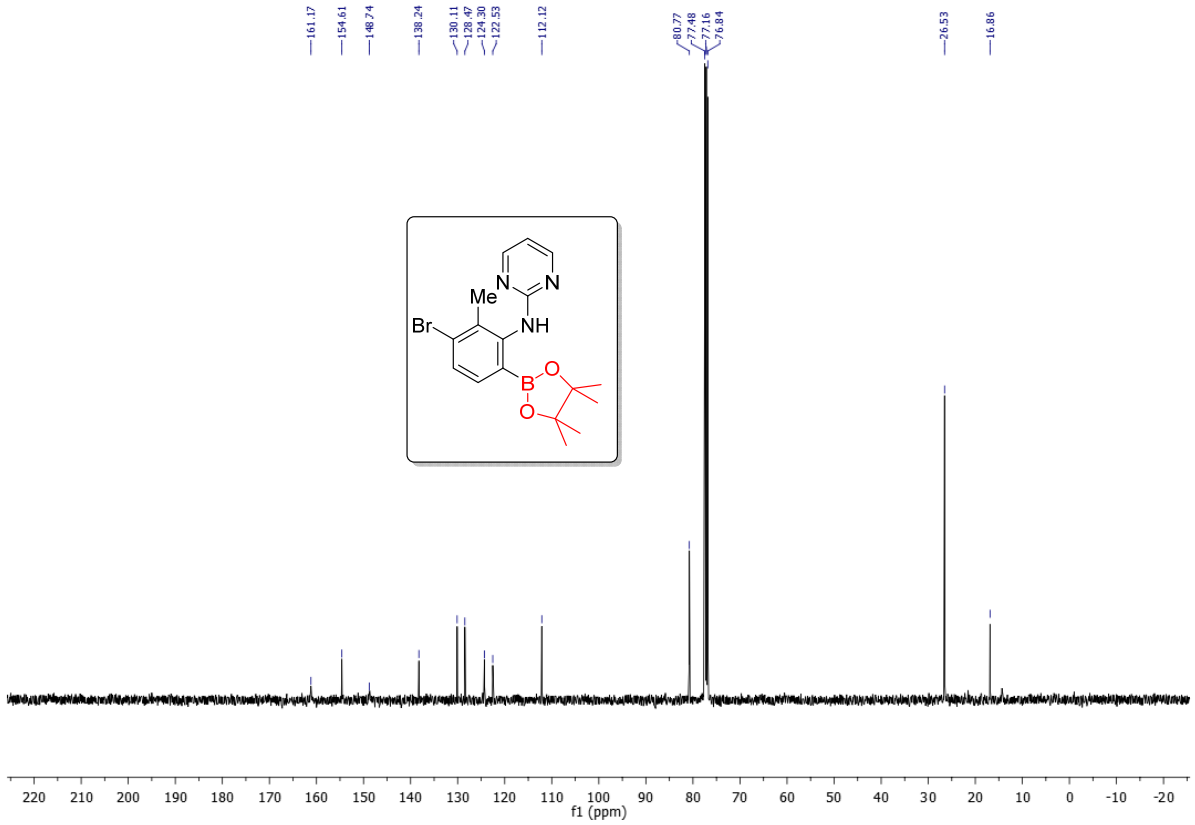
^{13}C NMR spectrum of **22b** (101 MHz, $CDCl_3$):



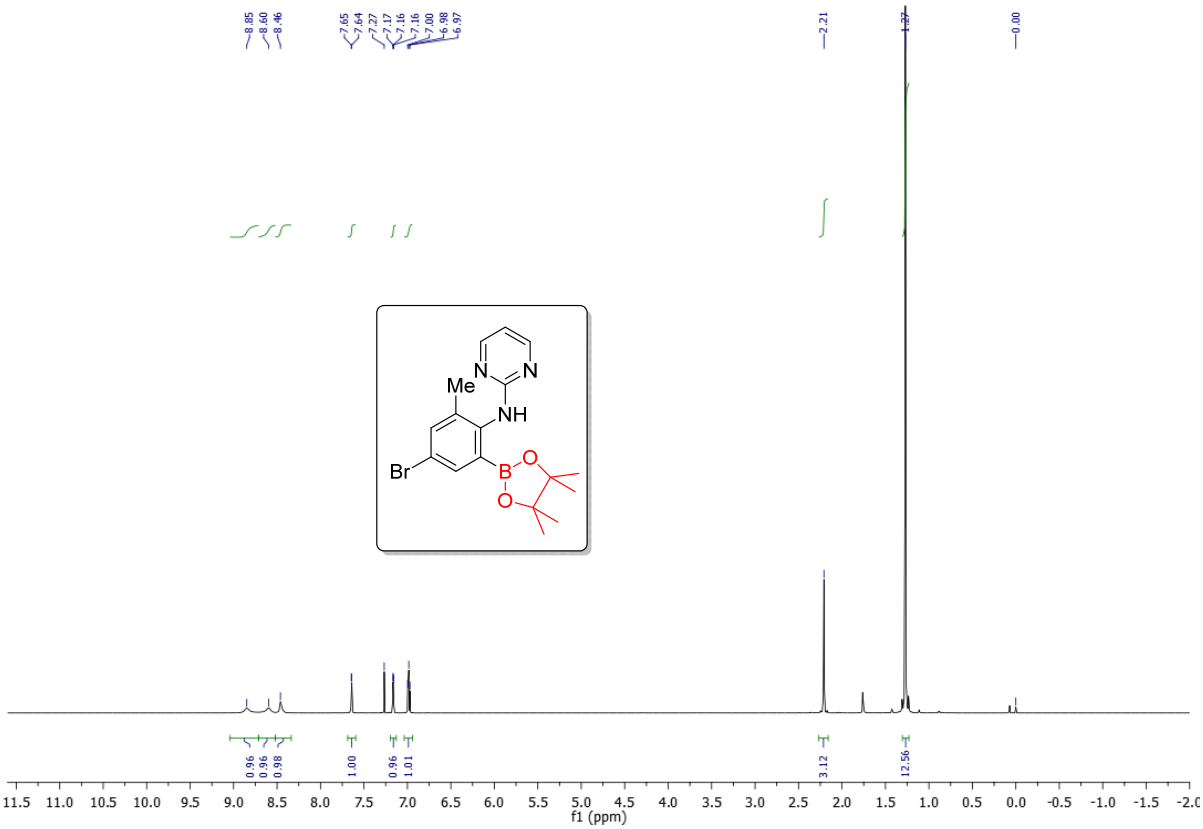
^{1}H NMR spectrum of **23b** (400 MHz, $CDCl_3$):



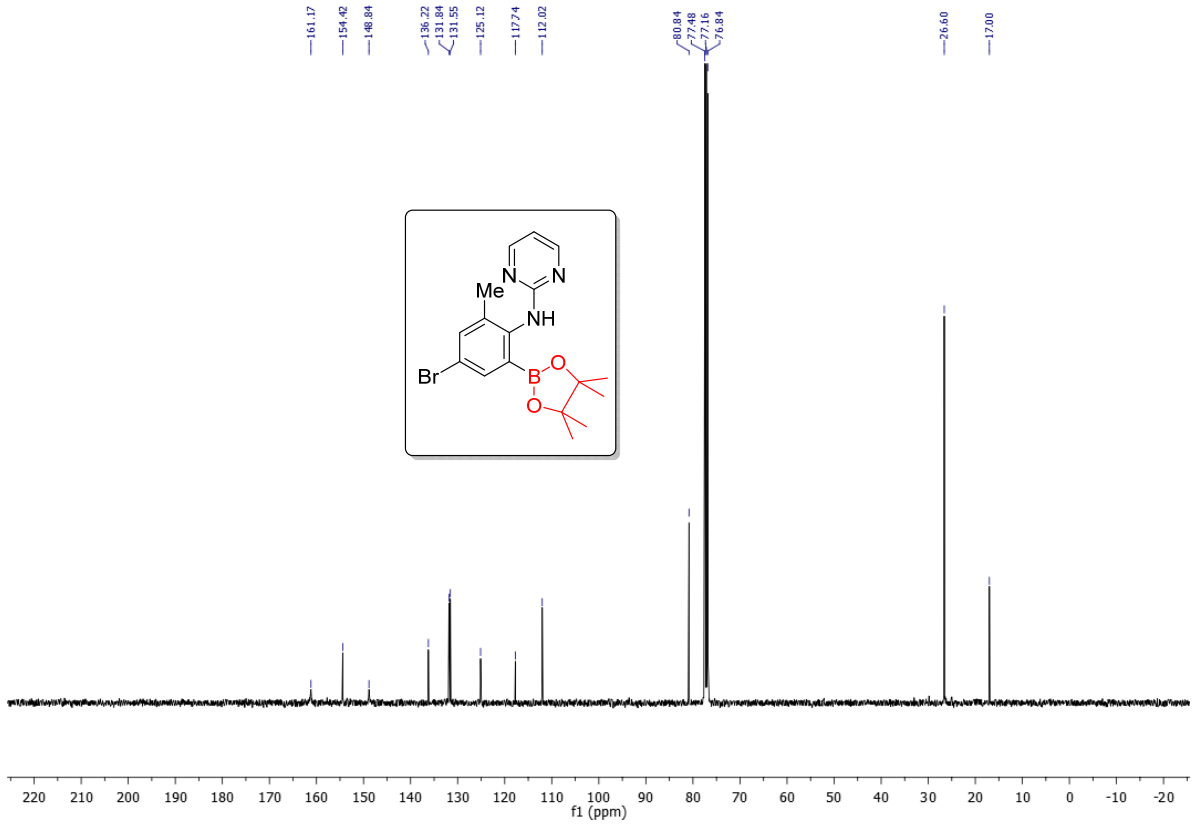
^{13}C NMR spectrum of **23b** (101 MHz, $CDCl_3$):



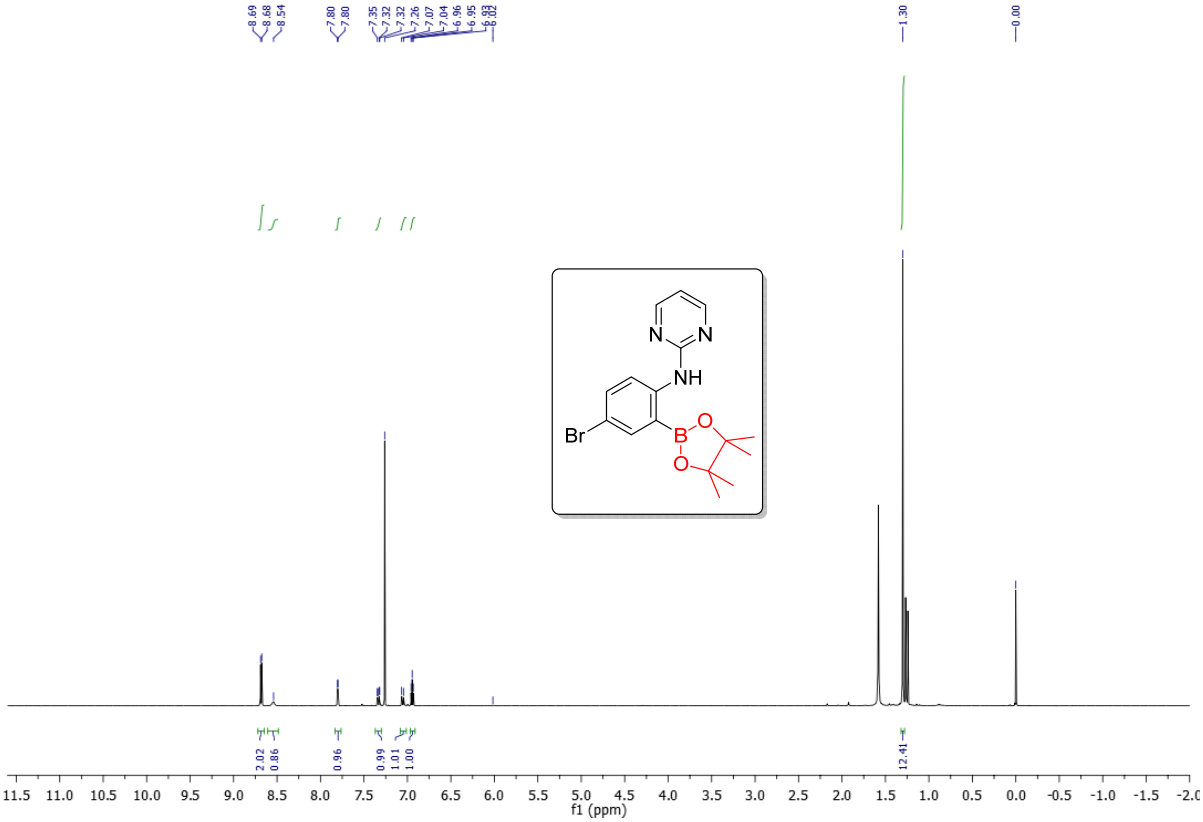
^{1}H NMR spectrum of **24b** (400 MHz, $CDCl_3$):



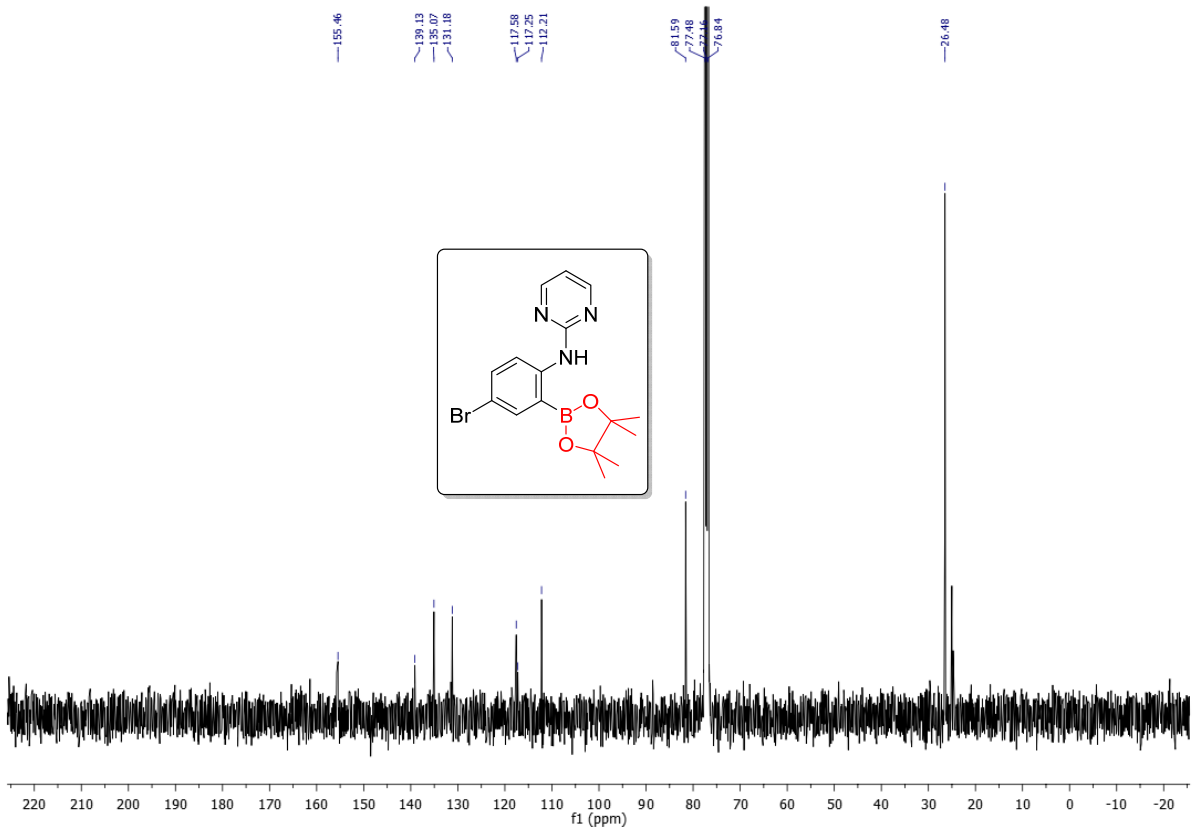
^{13}C NMR spectrum of **24b** (101 MHz, $CDCl_3$):



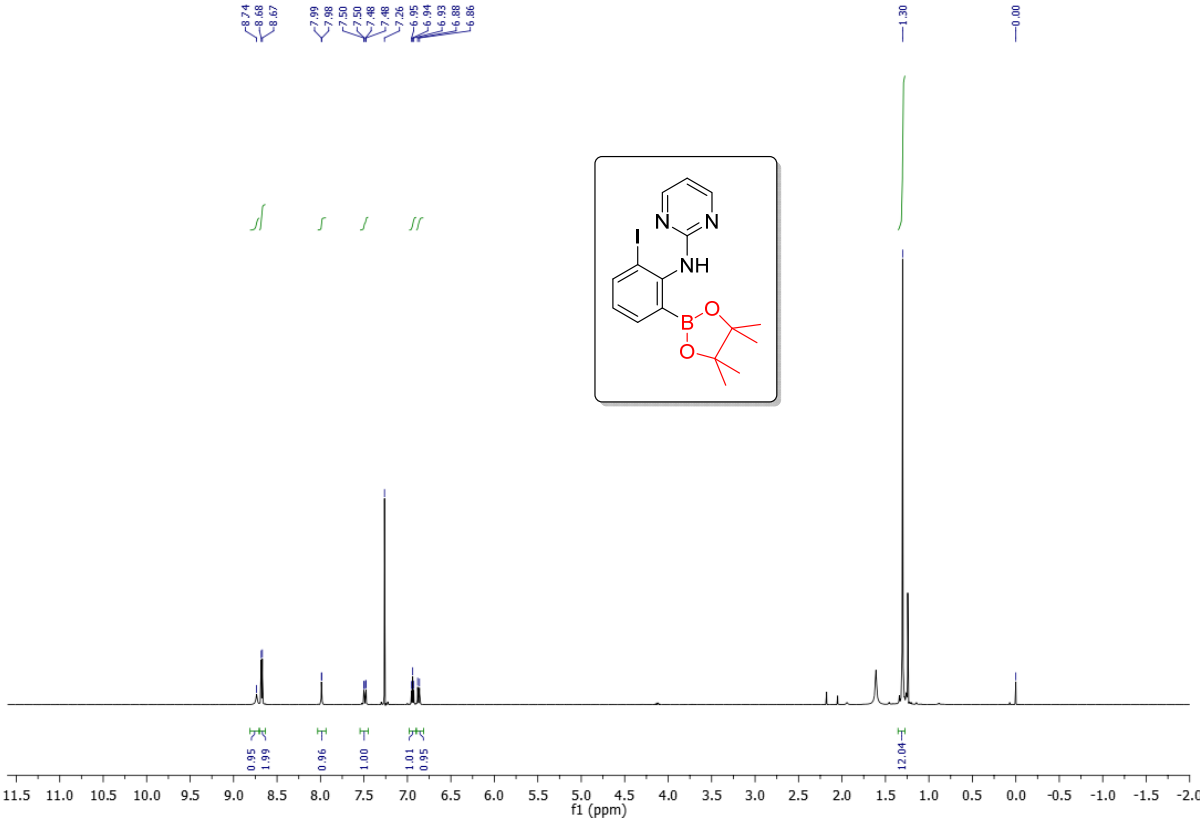
^{1}H NMR spectrum of **25b** (400 MHz, $CDCl_3$):



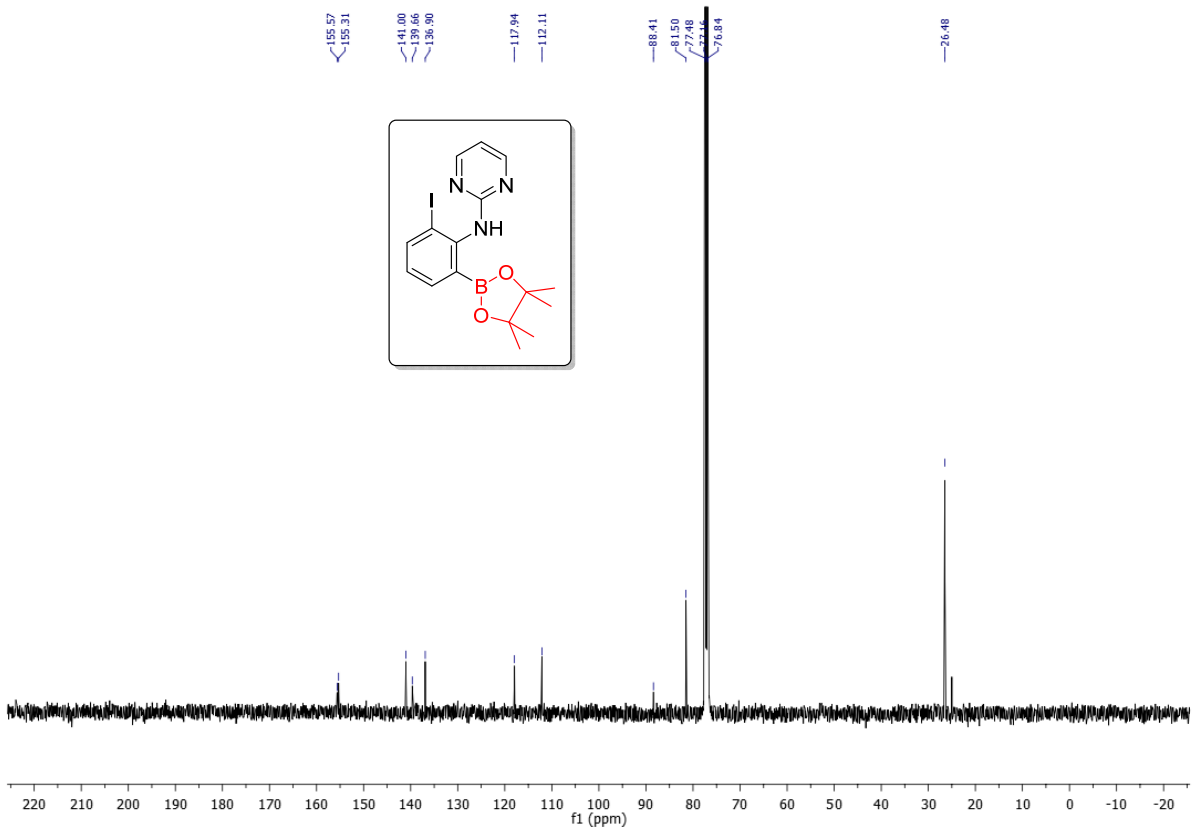
^{13}C NMR spectrum of **25b** (101 MHz, $CDCl_3$):



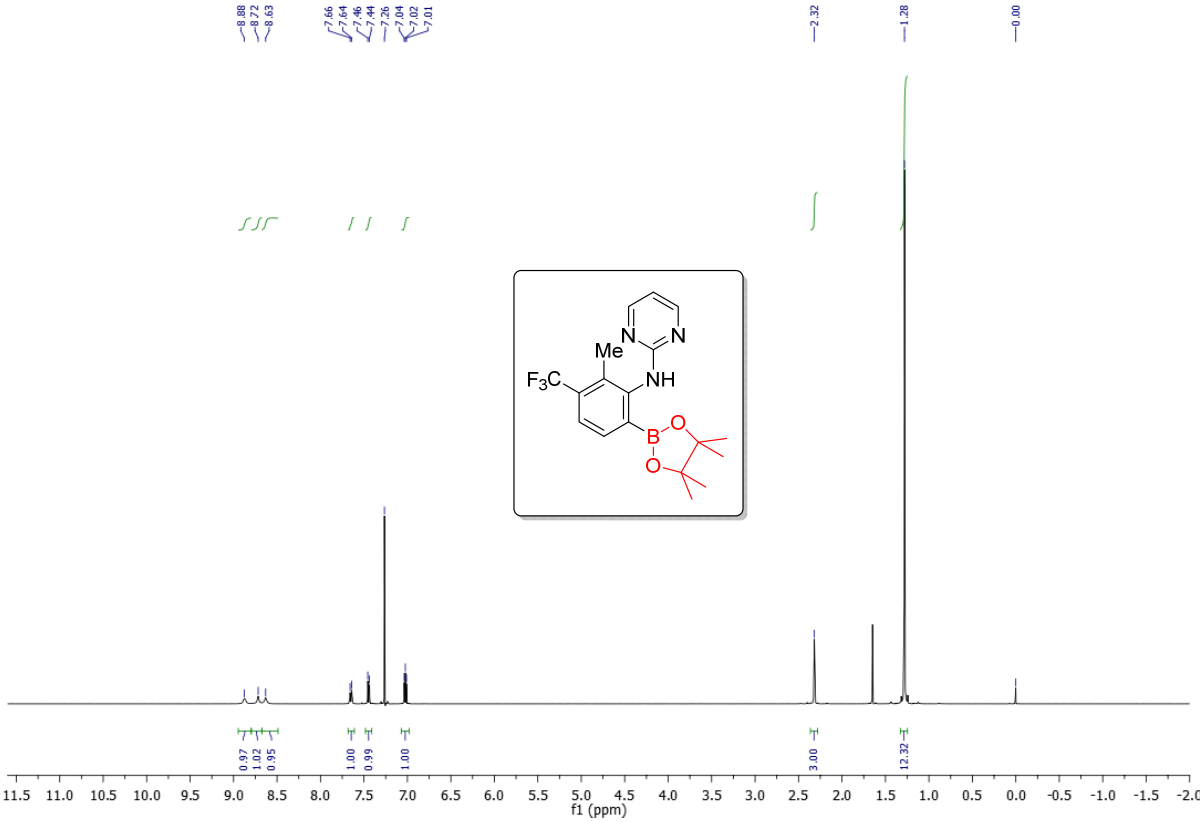
^{1}H NMR spectrum of **26b** (400 MHz, $CDCl_3$):



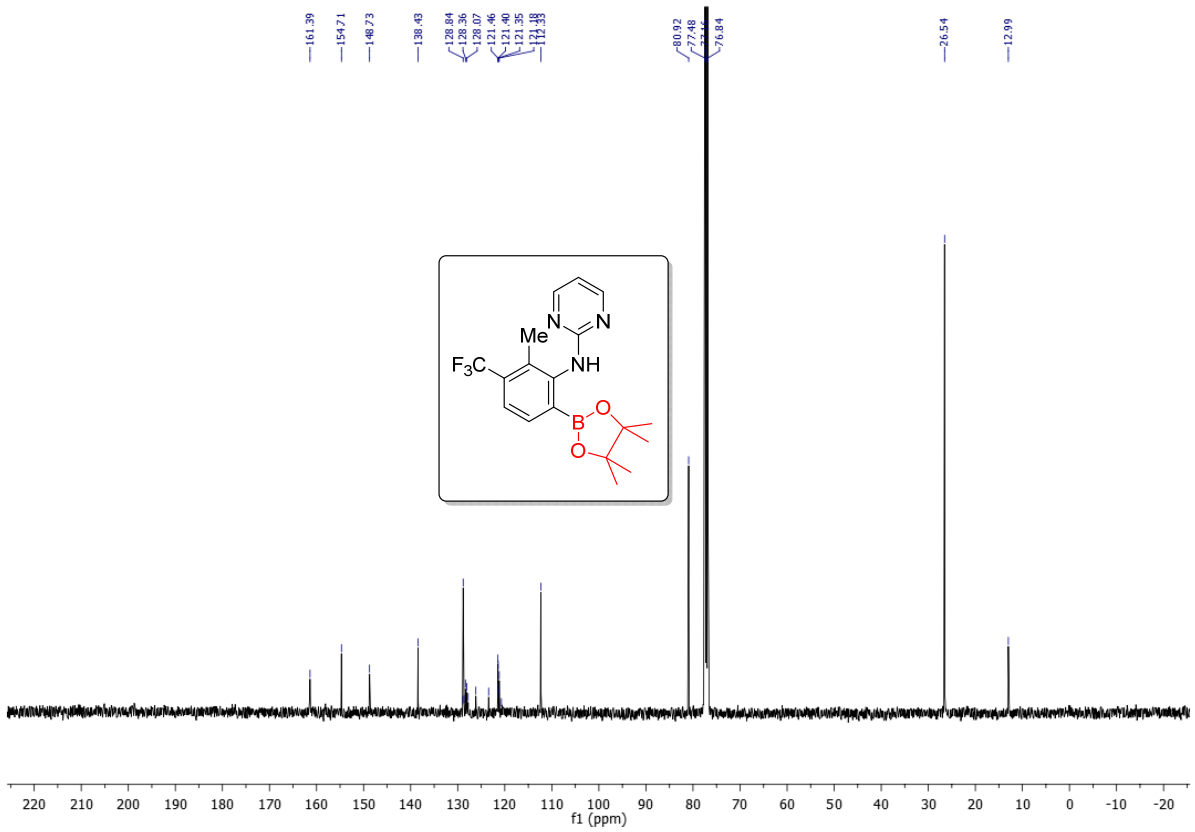
^{13}C NMR spectrum of **26b** (101 MHz, $CDCl_3$):



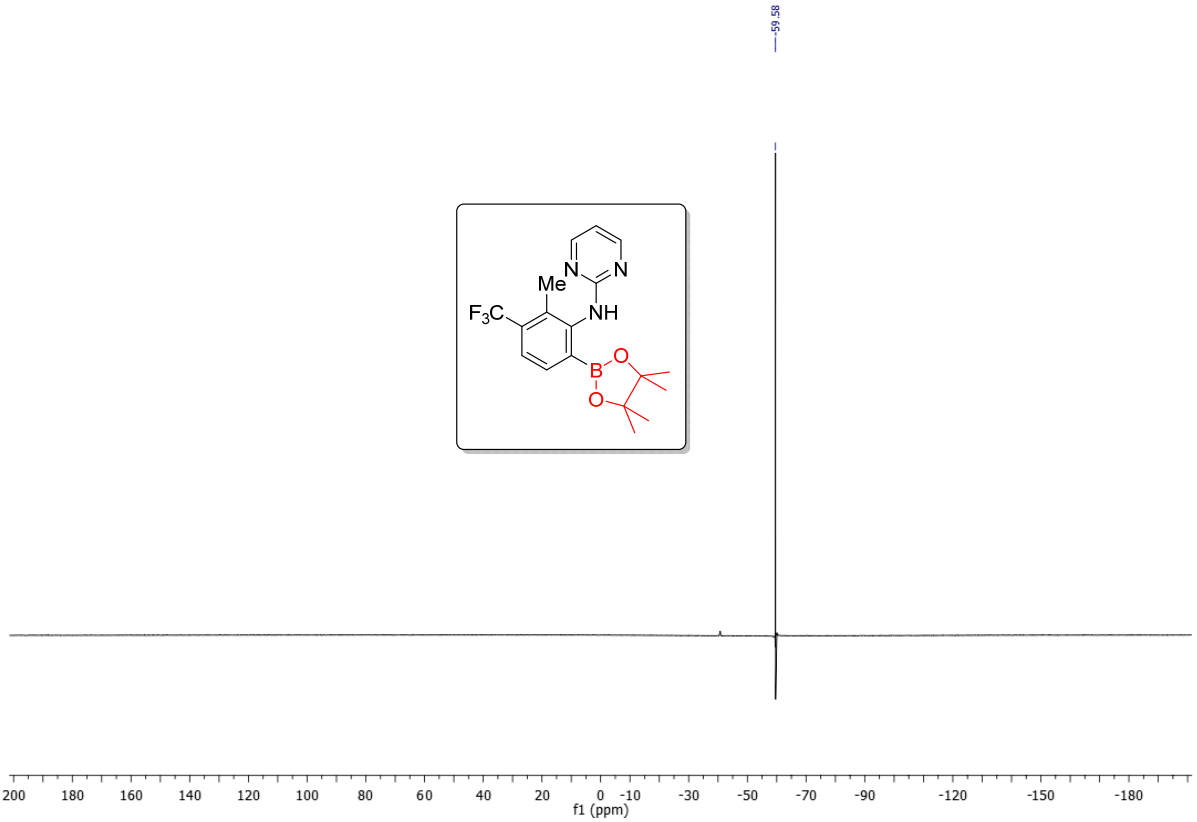
^{1}H NMR spectrum of **27b** (400 MHz, $CDCl_3$):



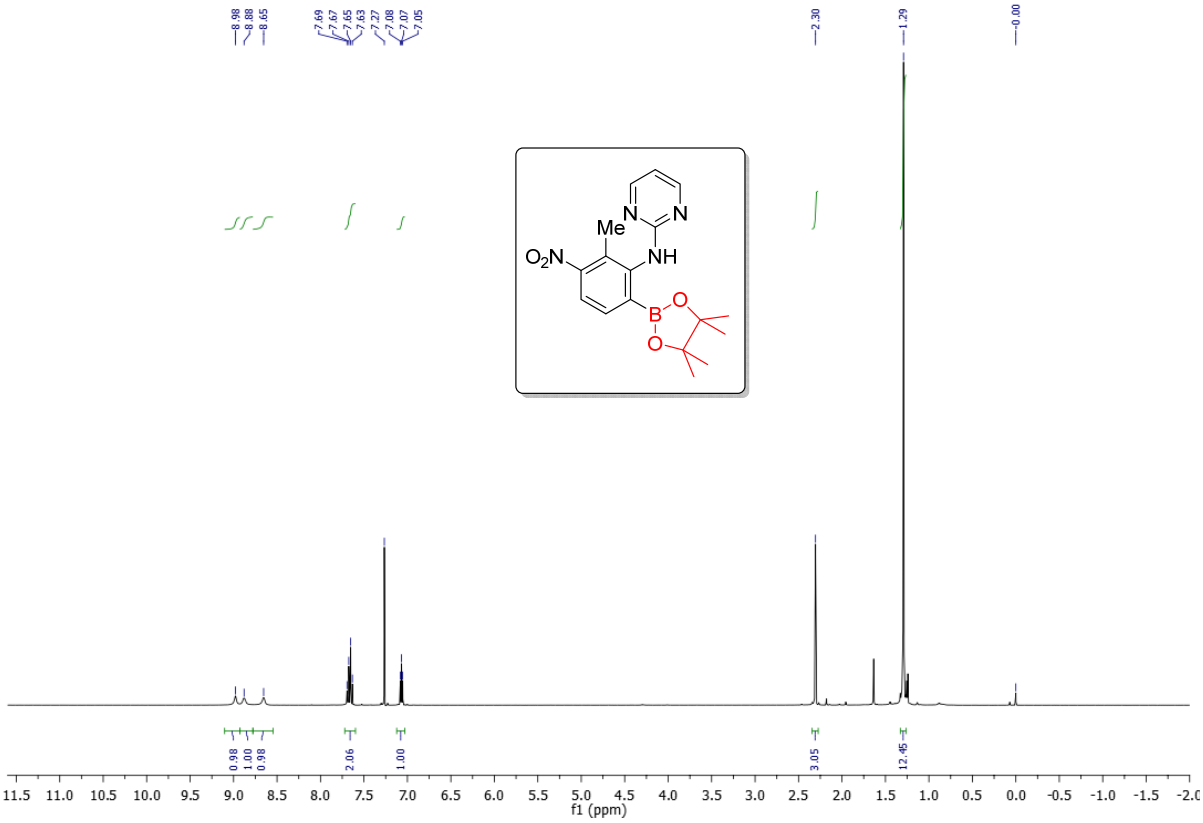
^{13}C NMR spectrum of **27b** (101 MHz, $CDCl_3$):



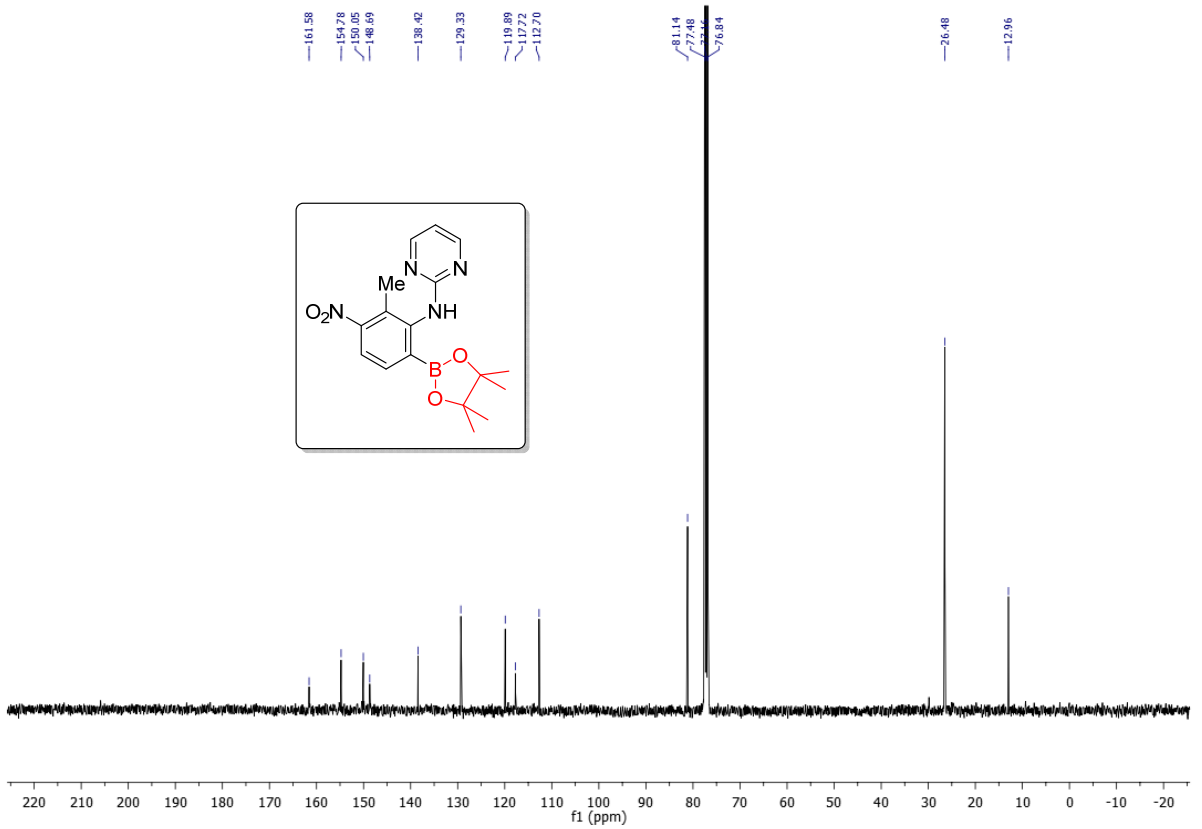
^{19}F NMR spectrum of **27b** (376 MHz, $CDCl_3$):



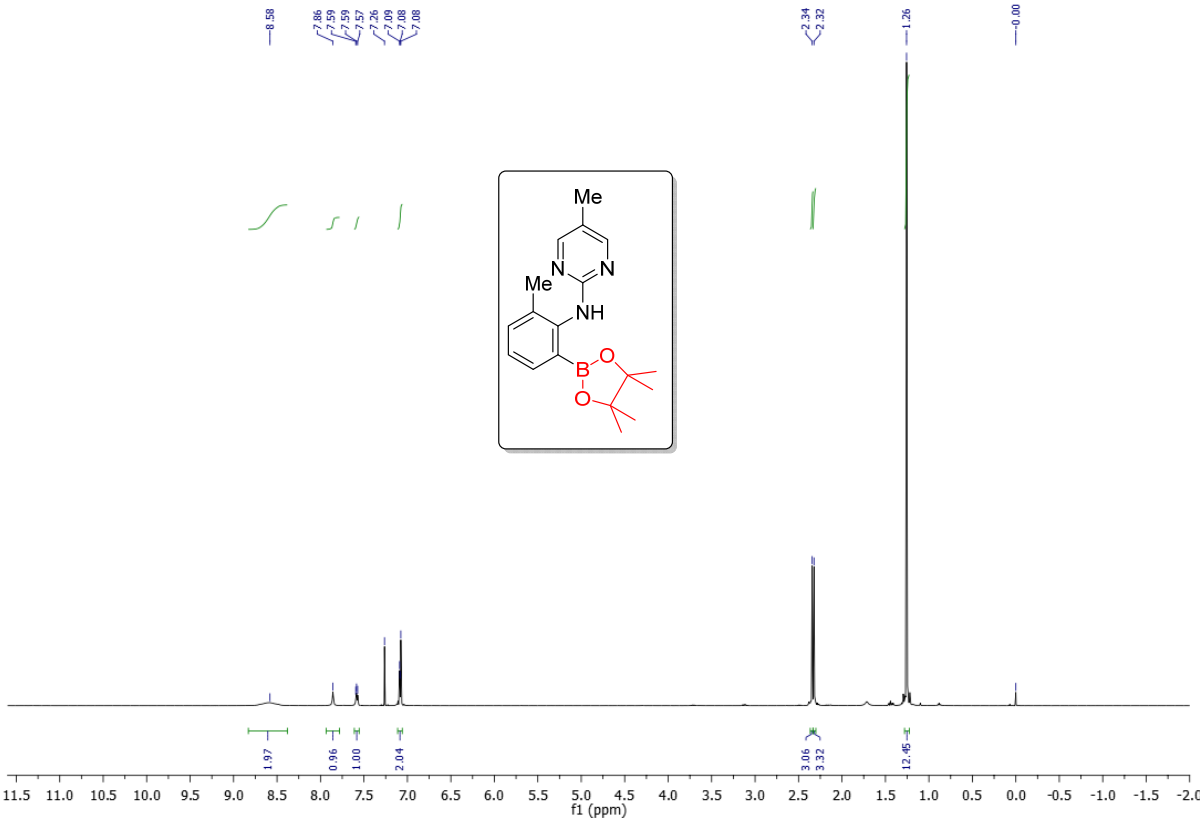
^{1}H NMR spectrum of **28b** (400 MHz, $CDCl_3$):



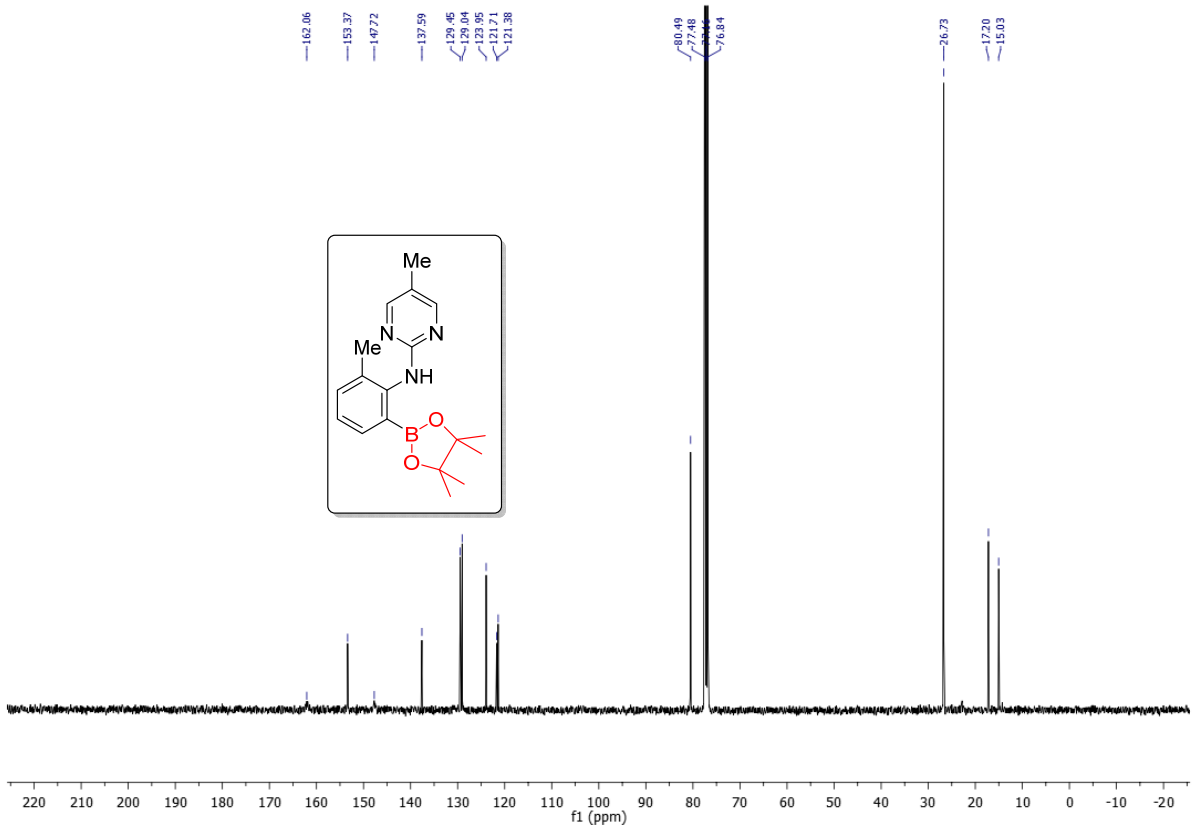
^{13}C NMR spectrum of **28b** (101 MHz, $CDCl_3$):



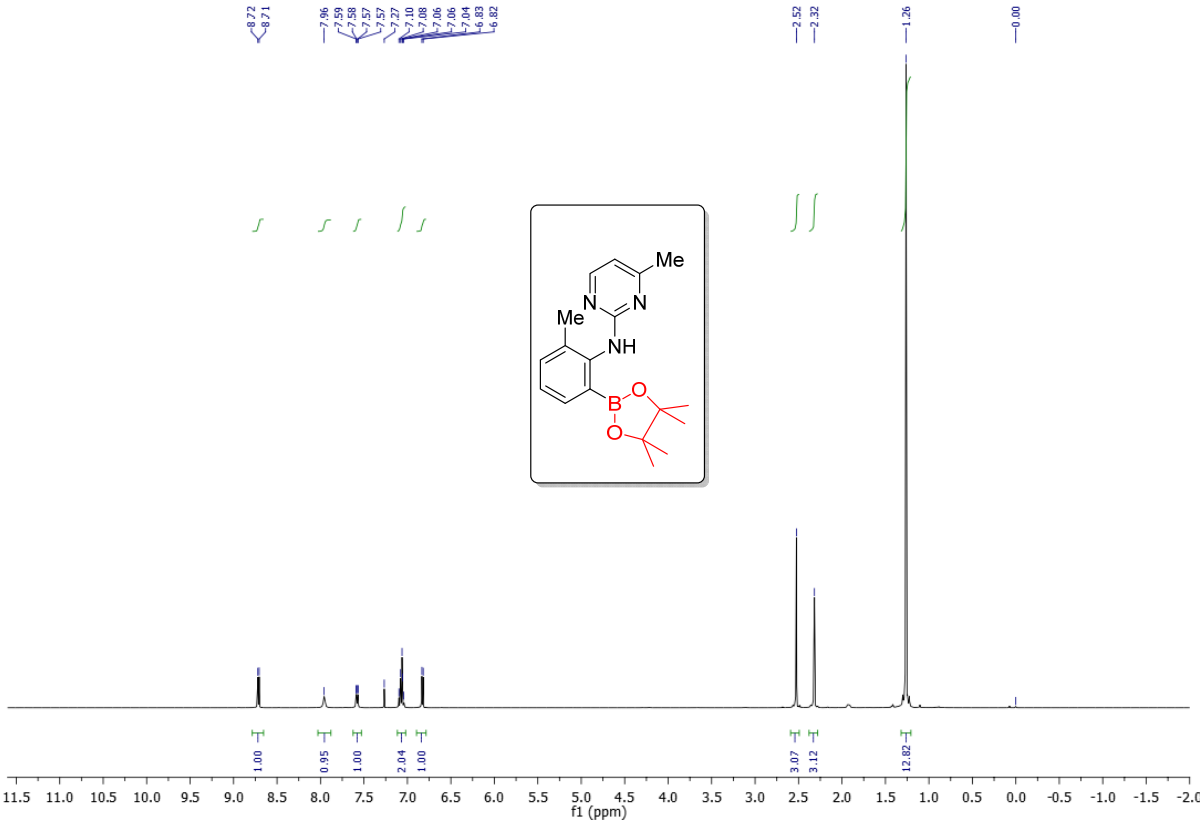
^{1}H NMR spectrum of **29b** (400 MHz, $CDCl_3$):



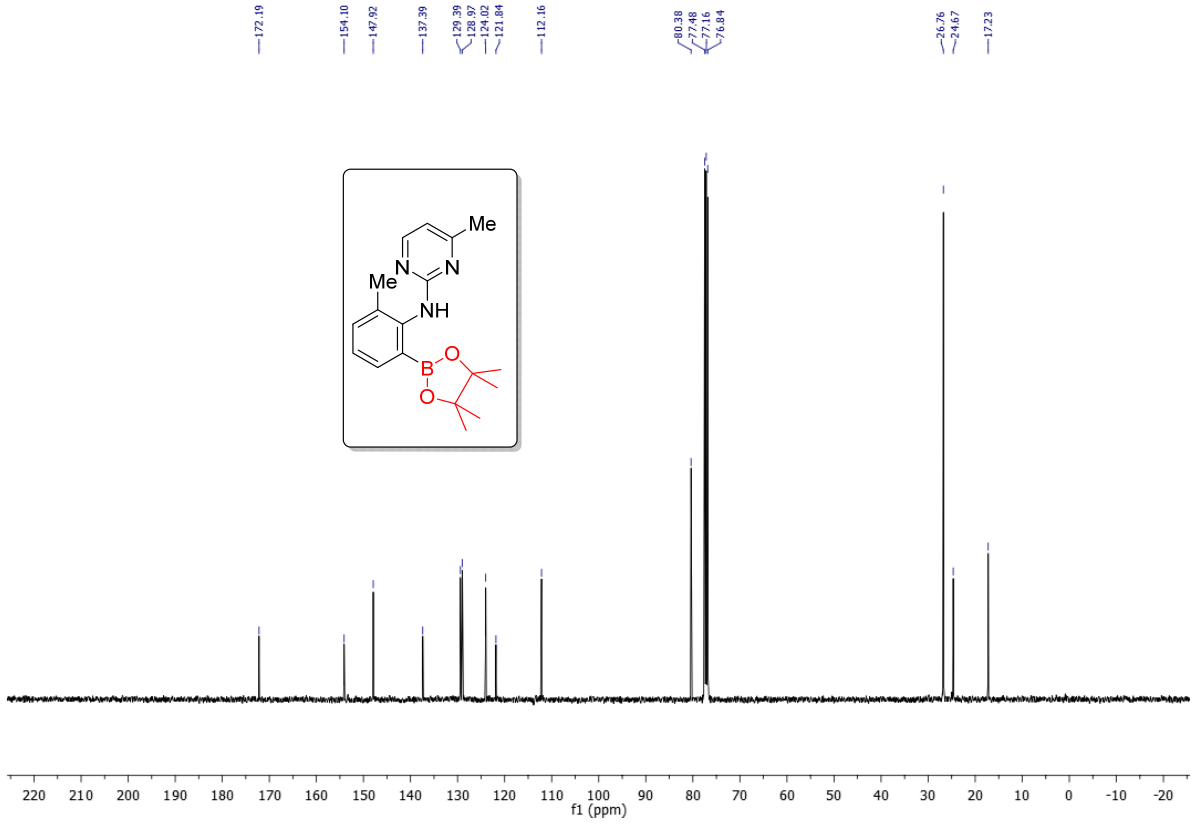
^{13}C NMR spectrum of **29b** (101 MHz, $CDCl_3$):



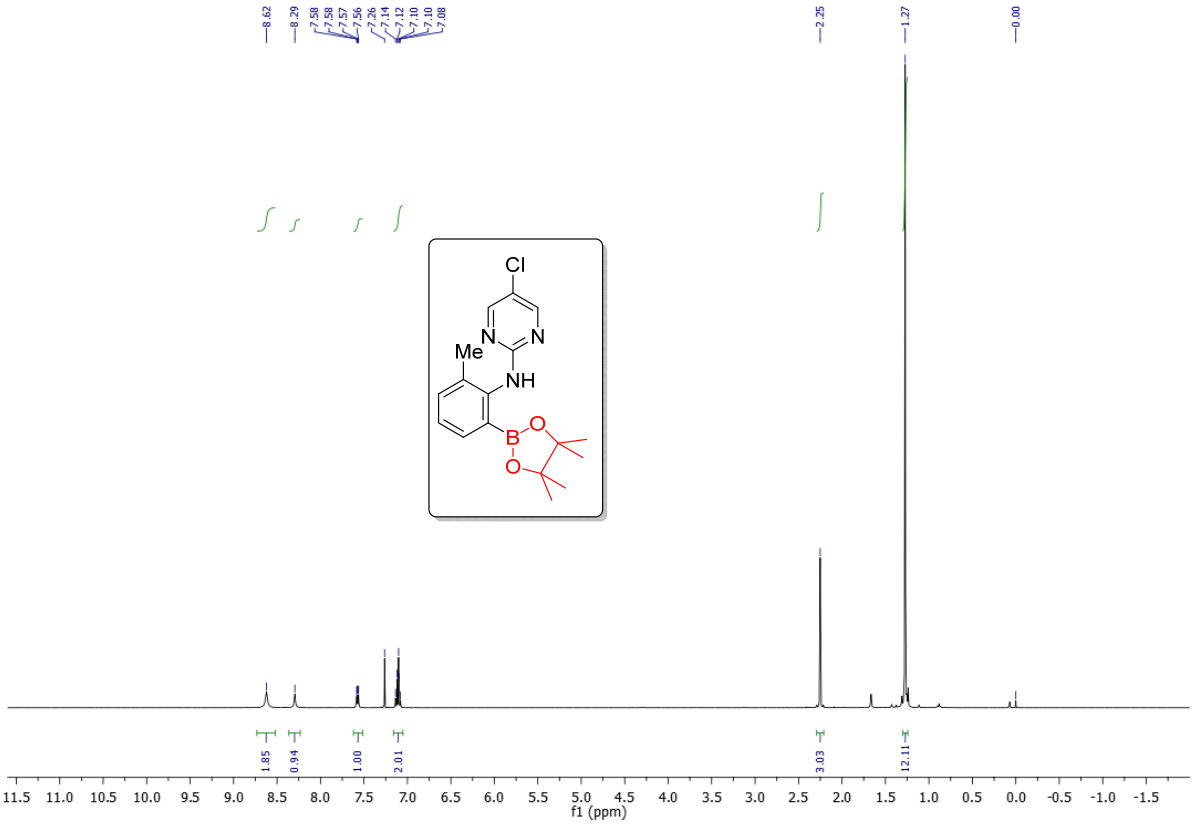
^{1}H NMR spectrum of **30b** (400 MHz, $CDCl_3$):



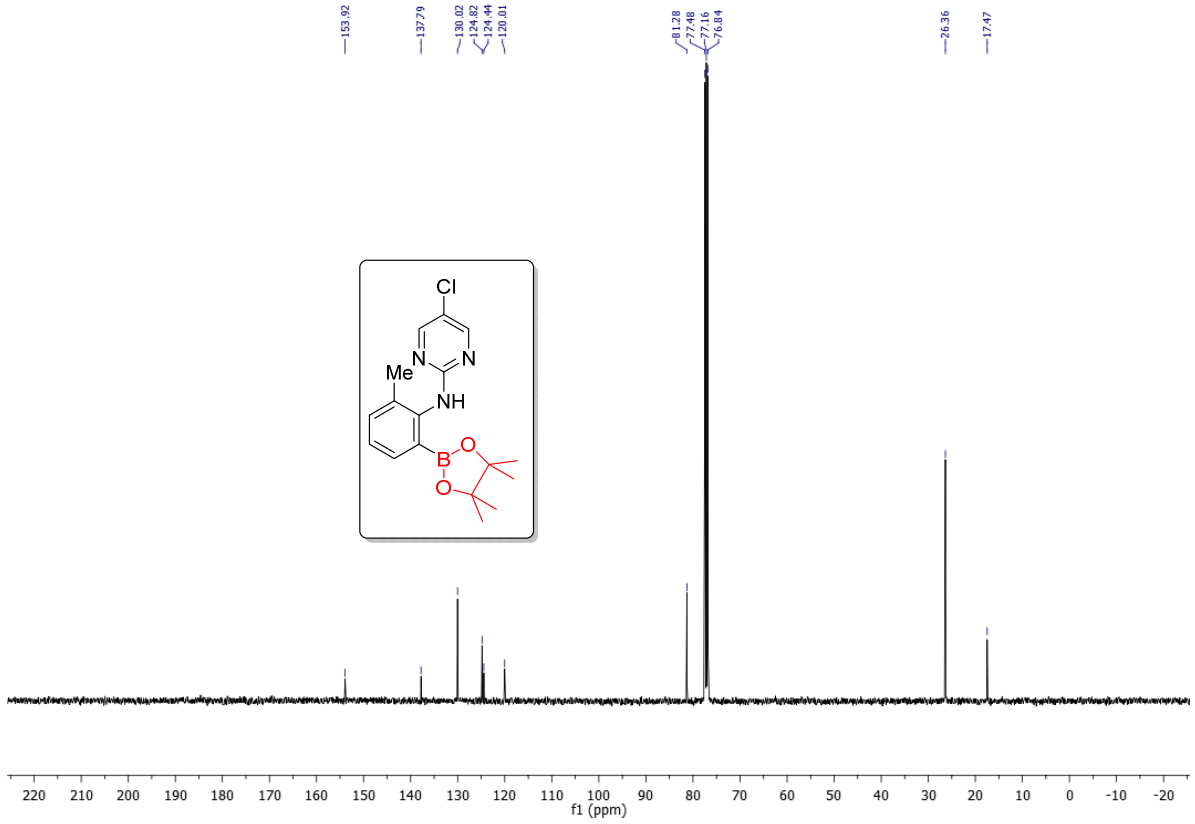
^{13}C NMR spectrum of **30b** (101 MHz, $CDCl_3$):



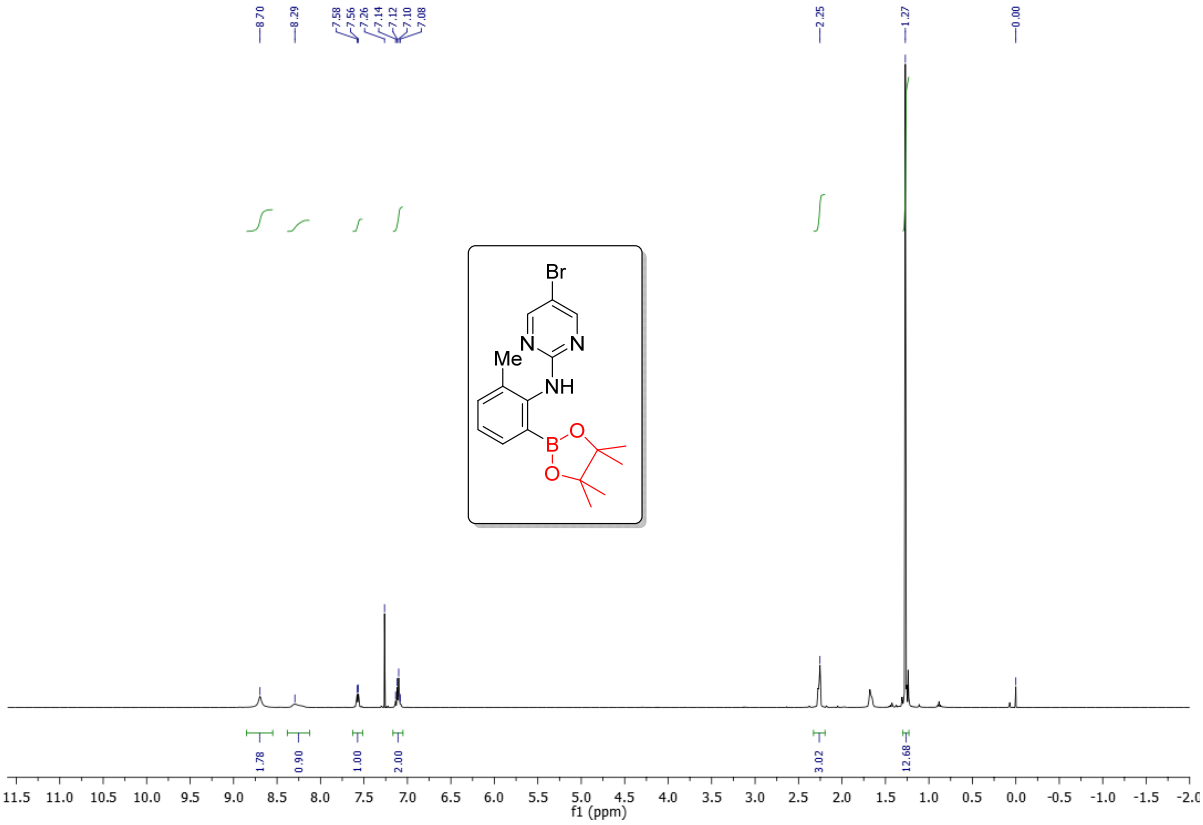
^{1}H NMR spectrum of **31b** (400 MHz, $CDCl_3$):



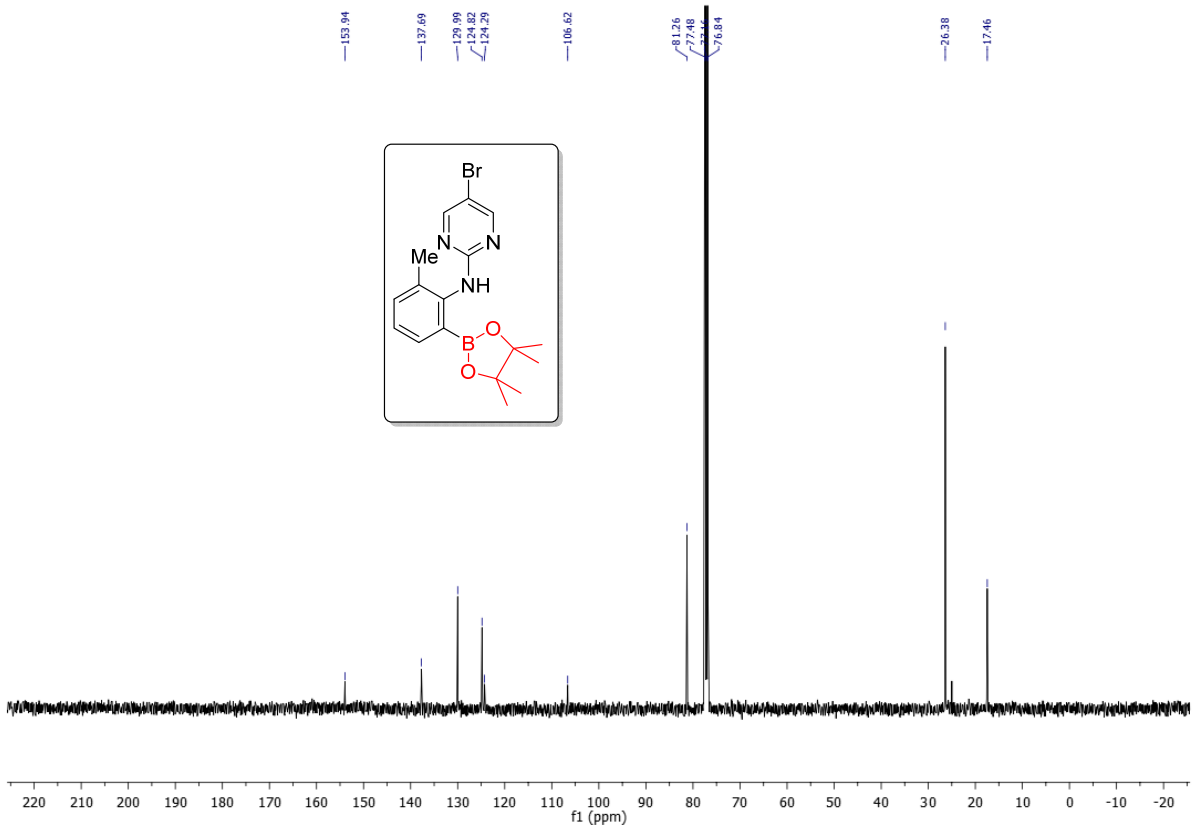
^{13}C NMR spectrum of **31b** (101 MHz, $CDCl_3$):



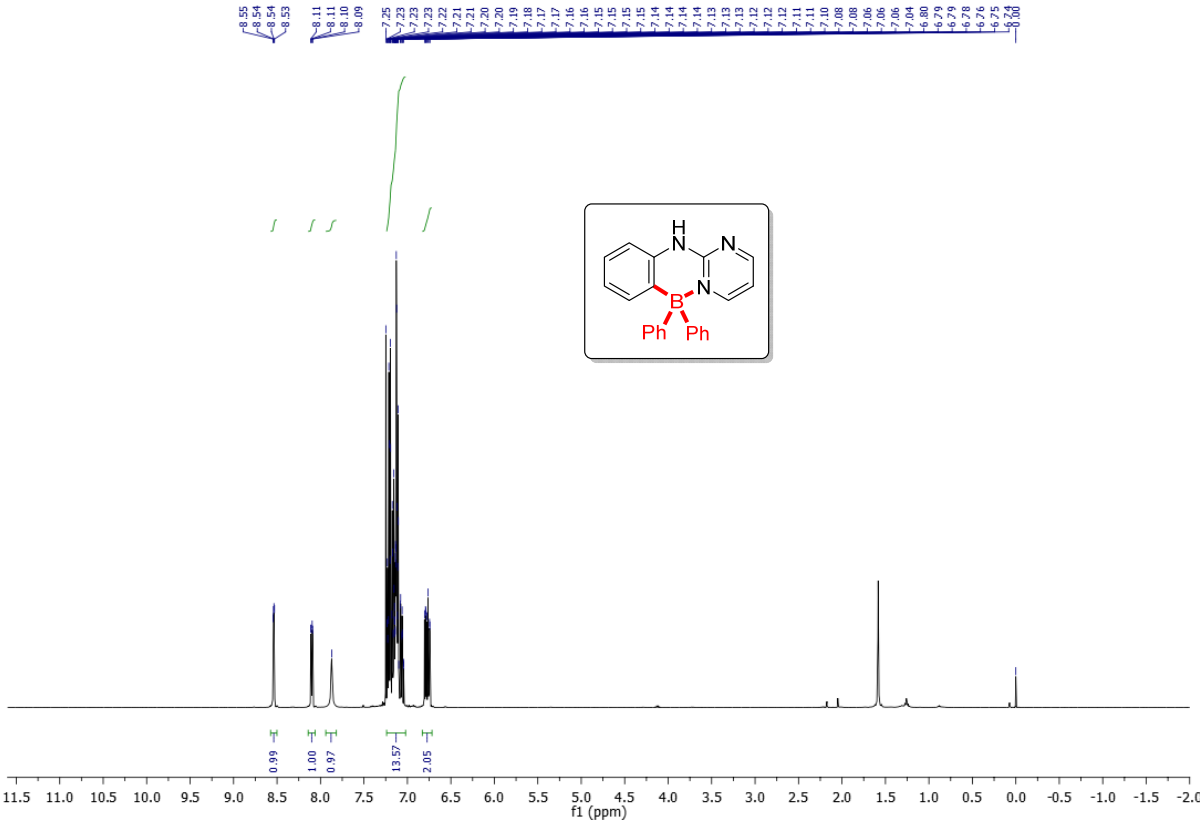
^{1}H NMR spectrum of **32b** (400 MHz, $CDCl_3$):



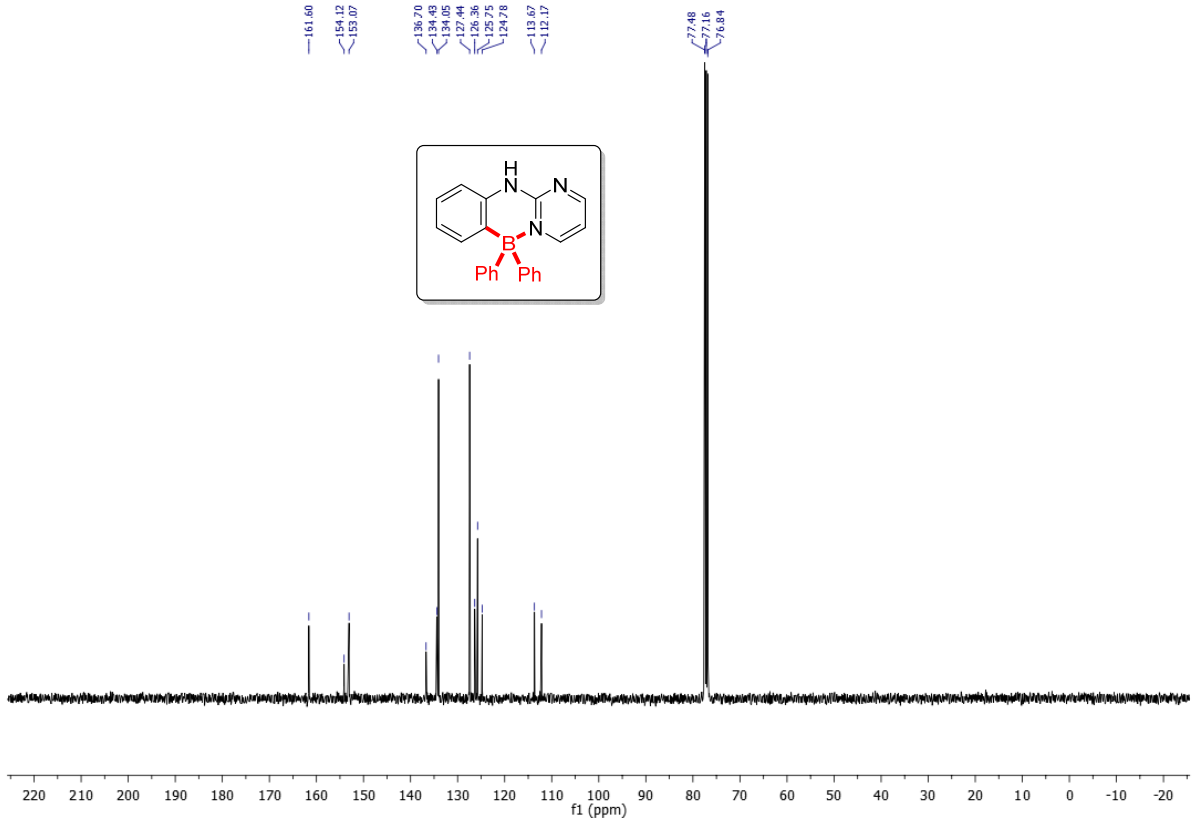
^{13}C NMR spectrum of **32b** (101 MHz, $CDCl_3$):



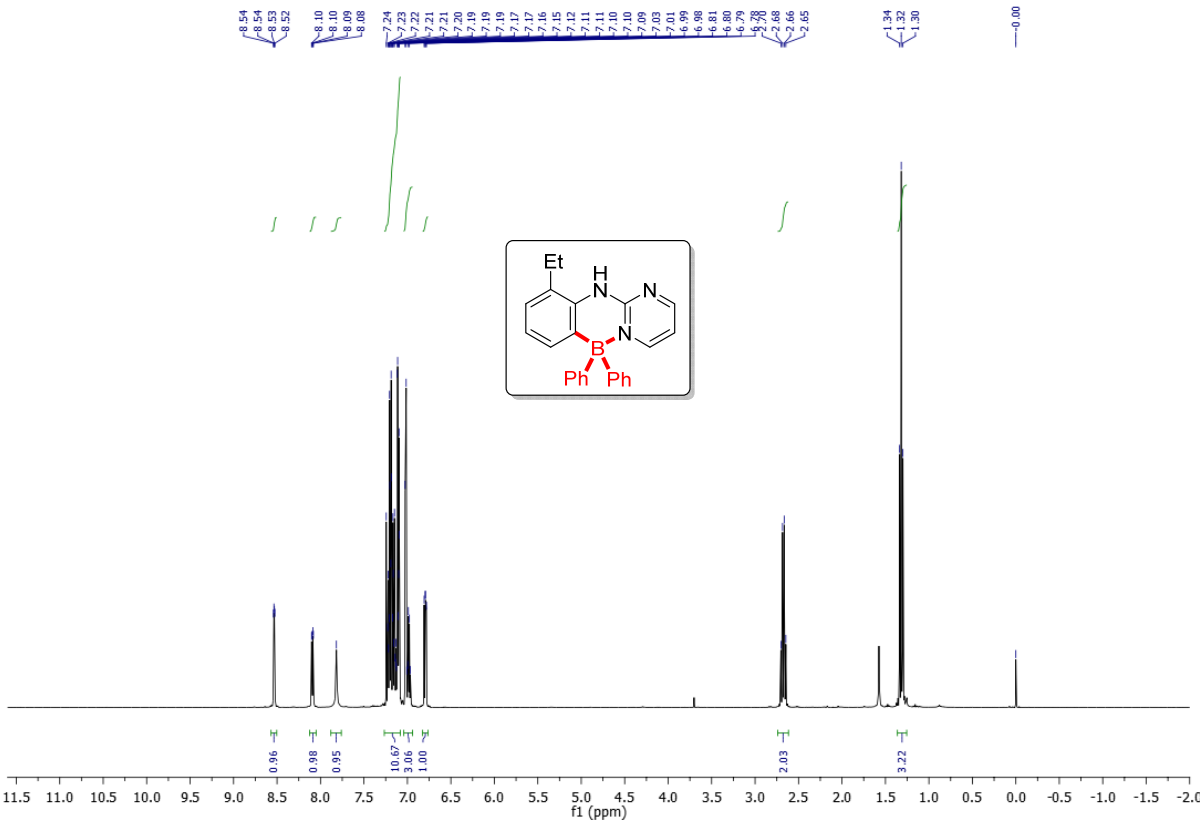
^{1}H NMR spectrum of **33** (400 MHz, $CDCl_3$):



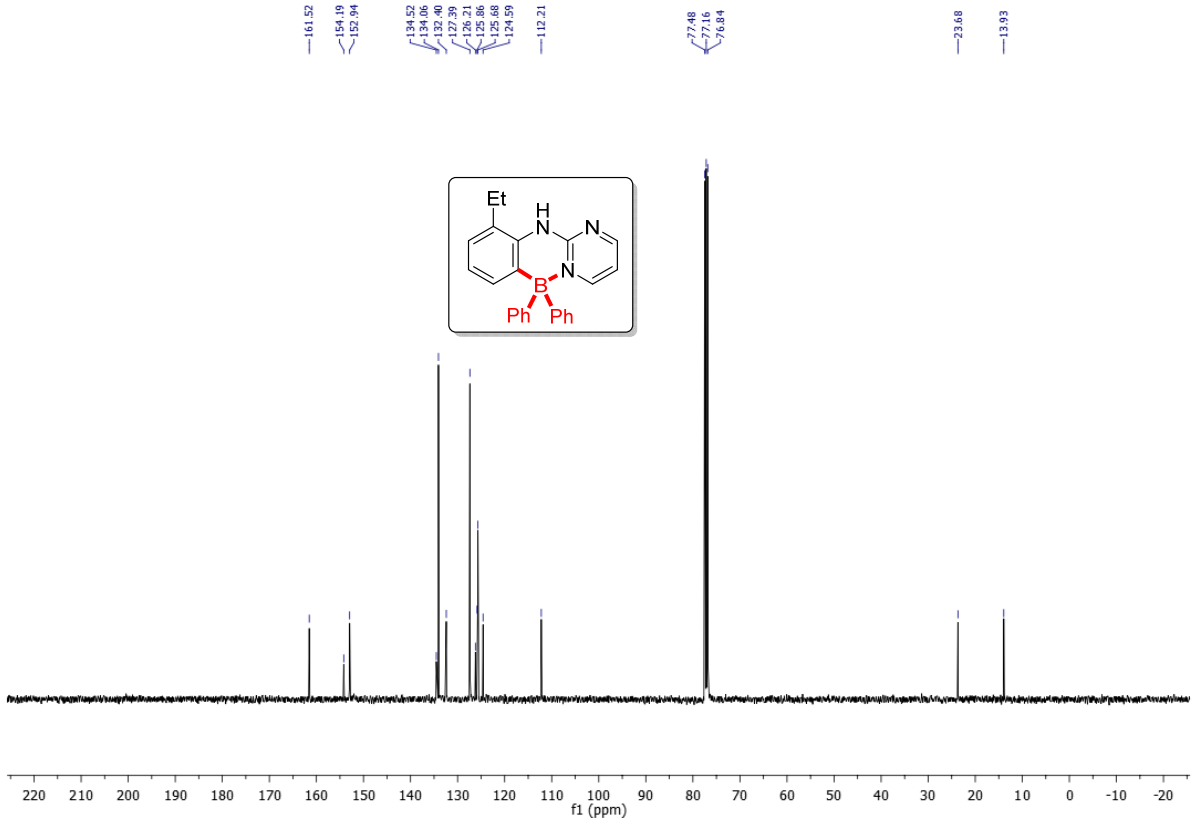
^{13}C NMR spectrum of **33** (101 MHz, $CDCl_3$):



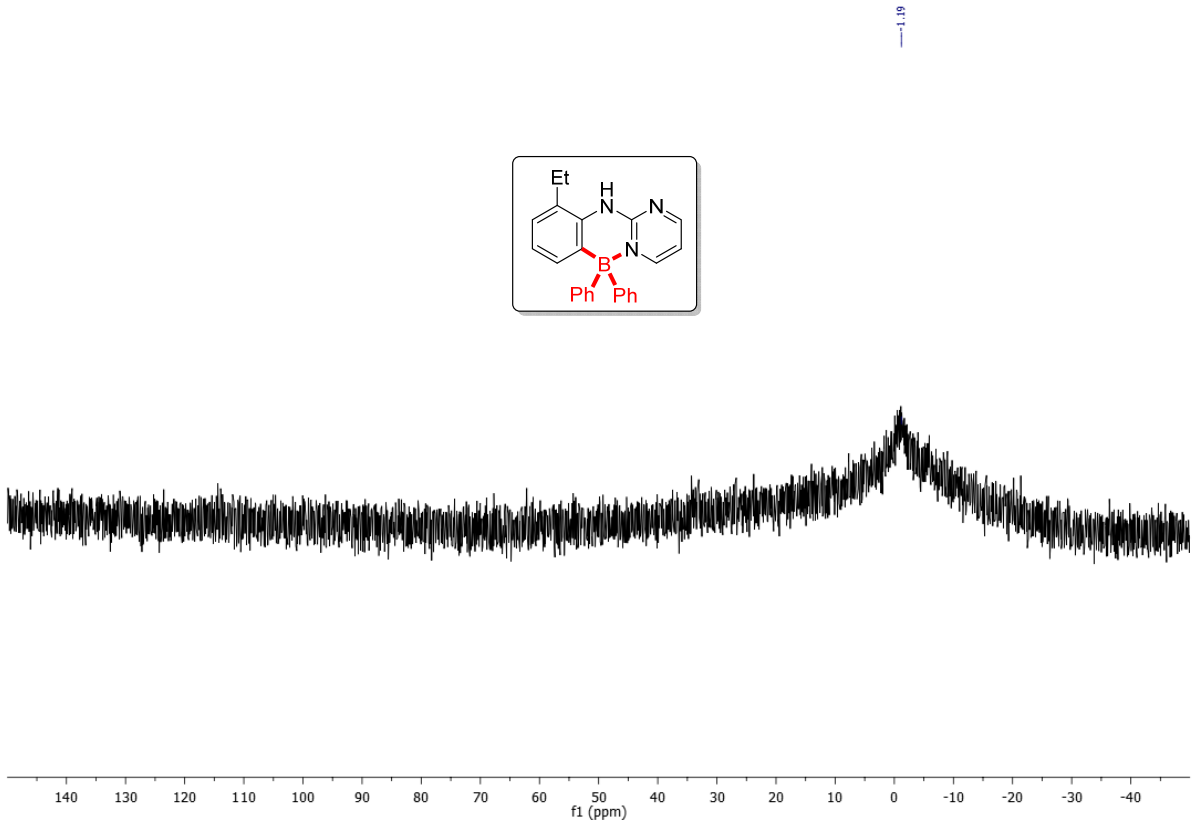
^{1}H NMR spectrum of **34** (400 MHz, $CDCl_3$):



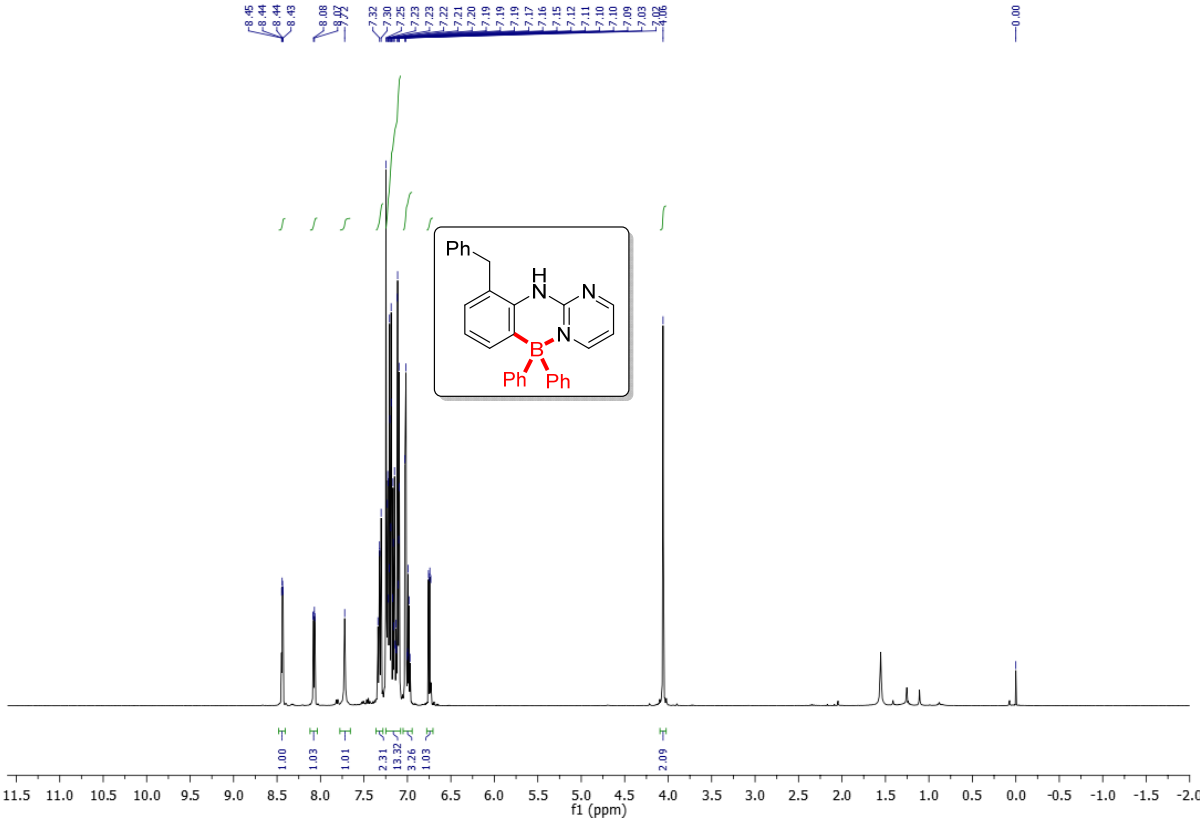
^{13}C NMR spectrum of **34** (101 MHz, $CDCl_3$):



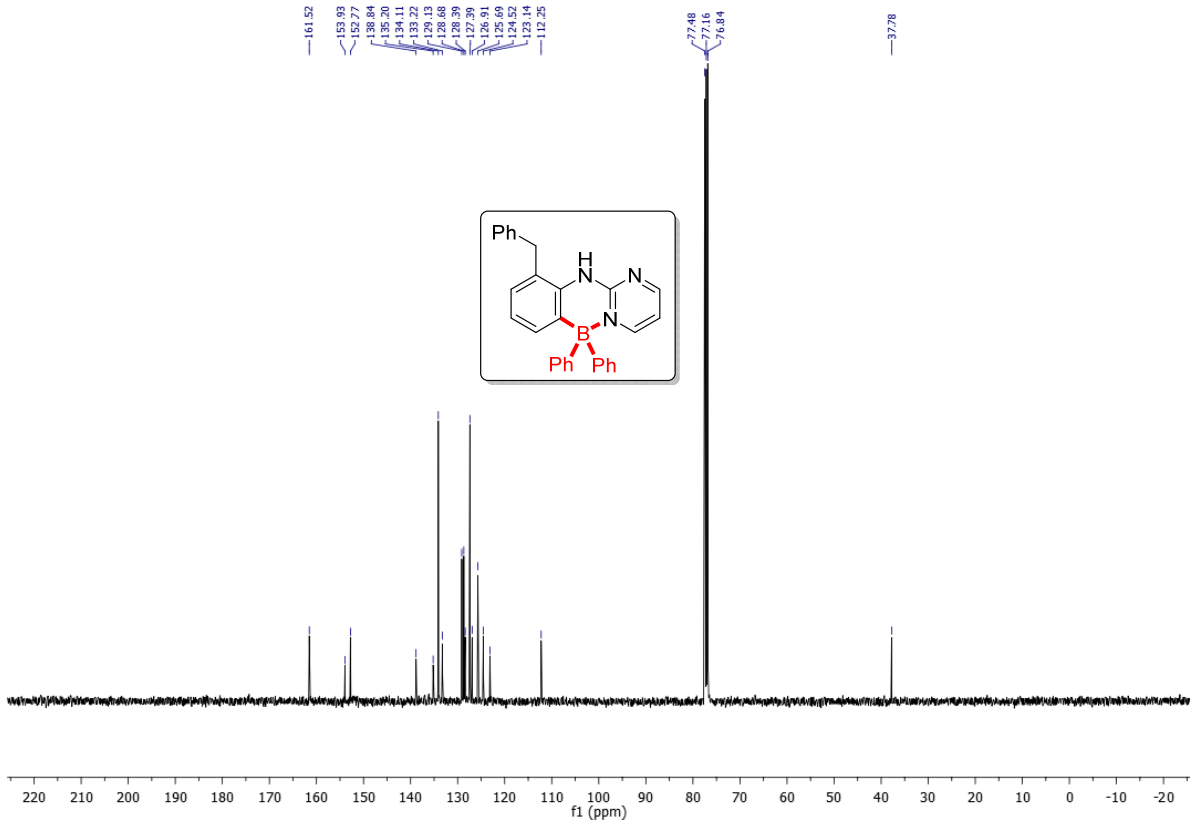
^{11}B NMR spectrum of **34** (128 MHz, $CDCl_3$):



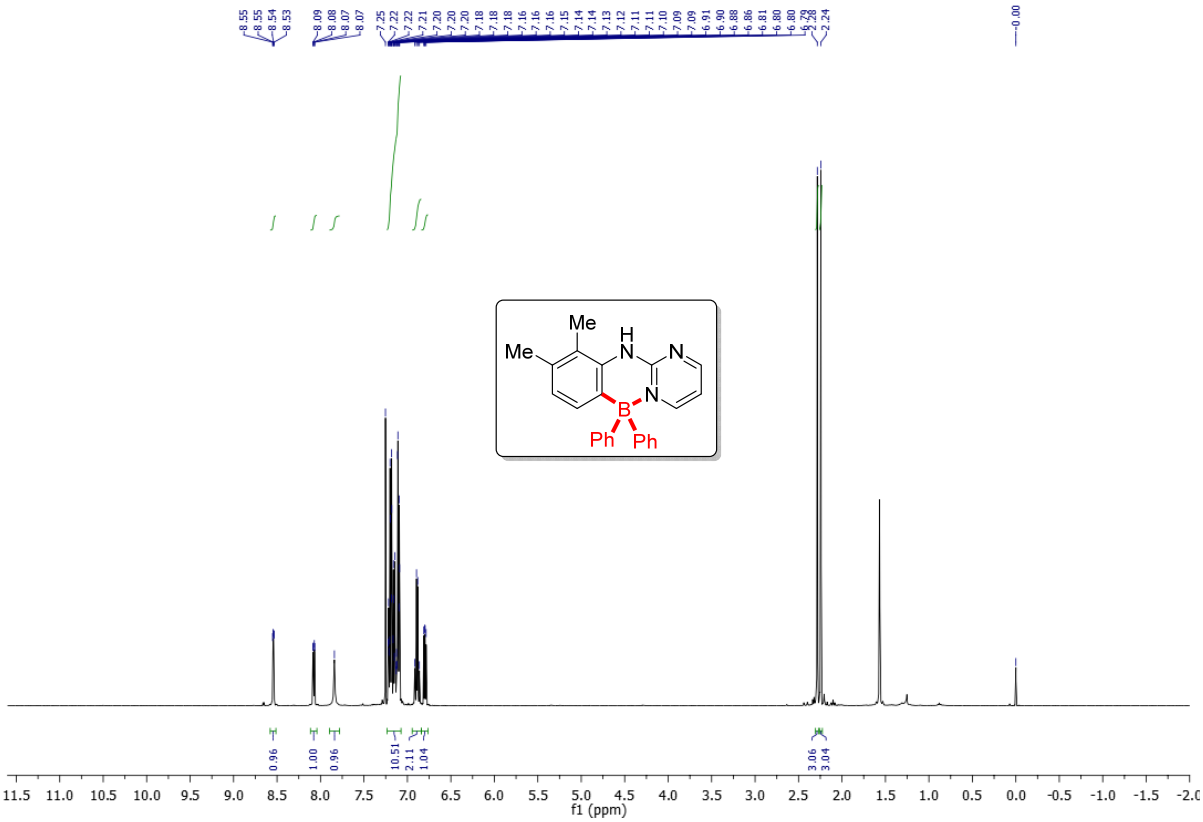
^{1}H NMR spectrum of **35** (400 MHz, $CDCl_3$):



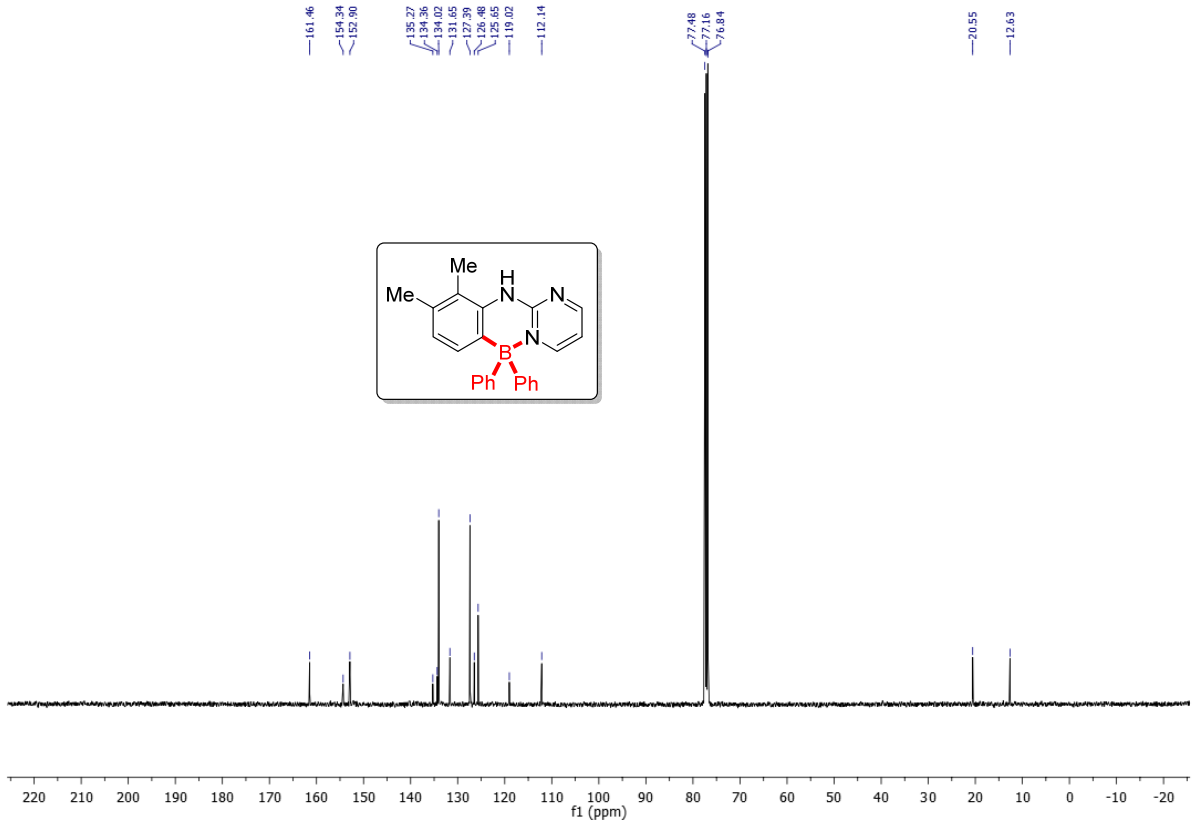
^{13}C NMR spectrum of **35** (101 MHz, $CDCl_3$):



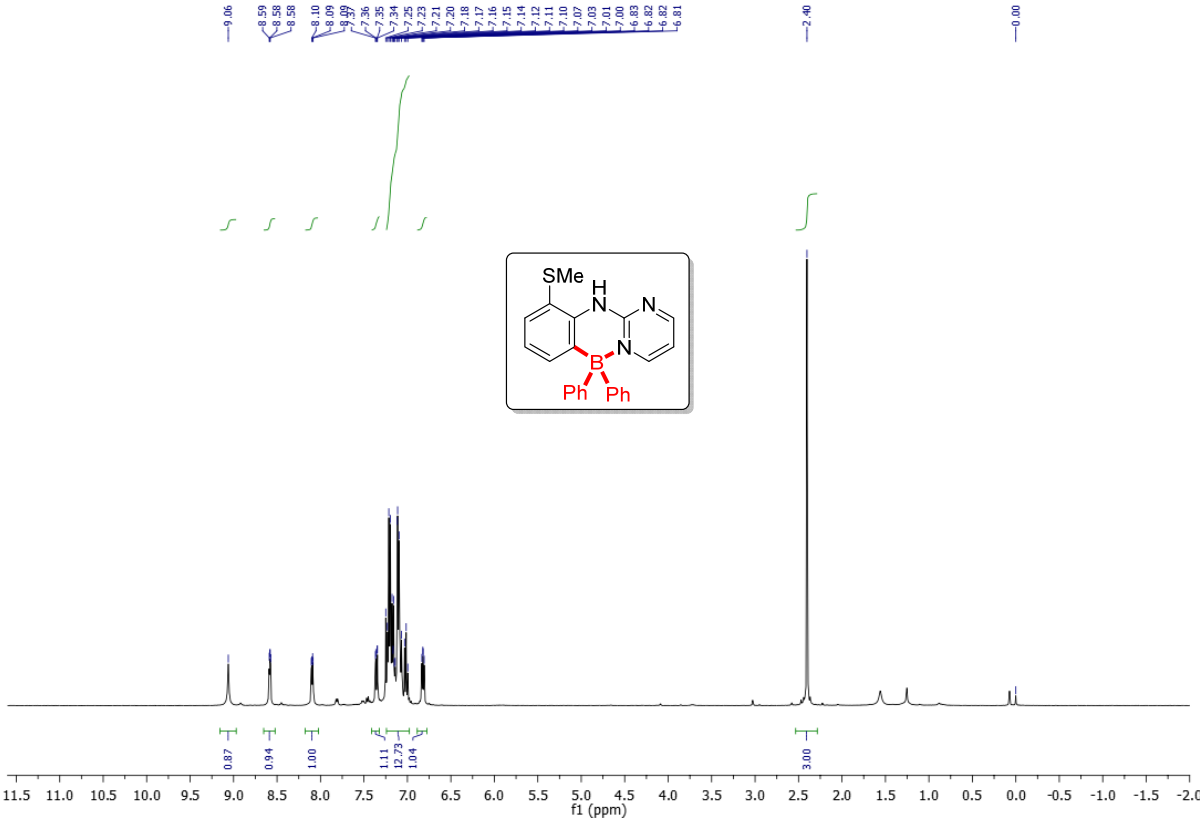
^{1}H NMR spectrum of **36** (400 MHz, $CDCl_3$):



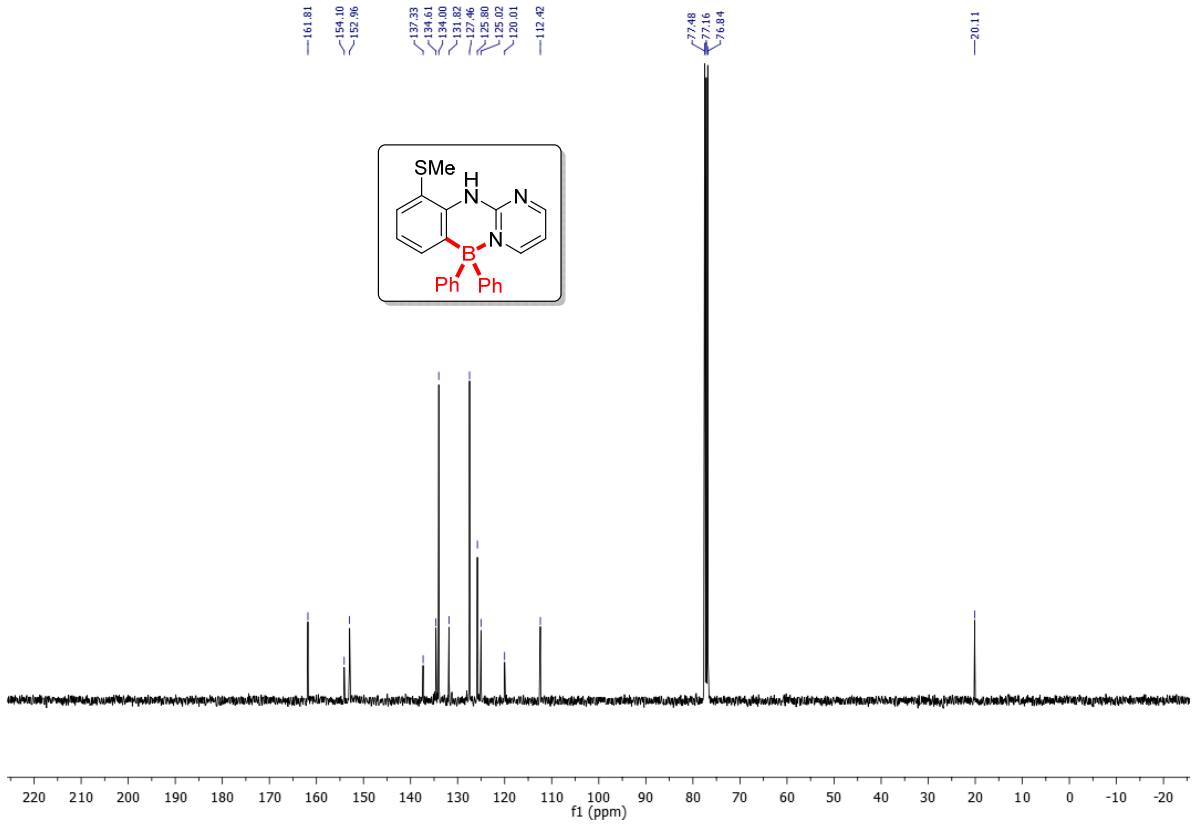
^{13}C NMR spectrum of **36** (101 MHz, $CDCl_3$):



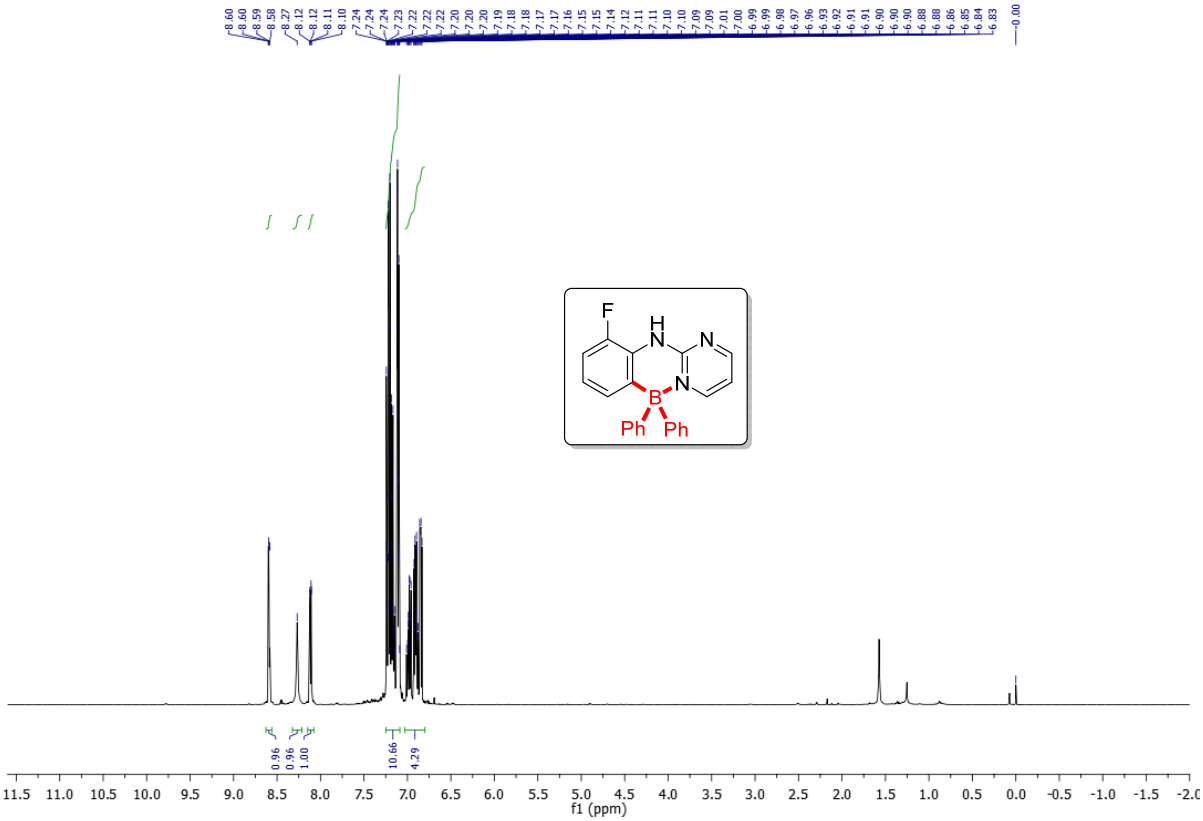
^{1}H NMR spectrum of **37** (400 MHz, $CDCl_3$):



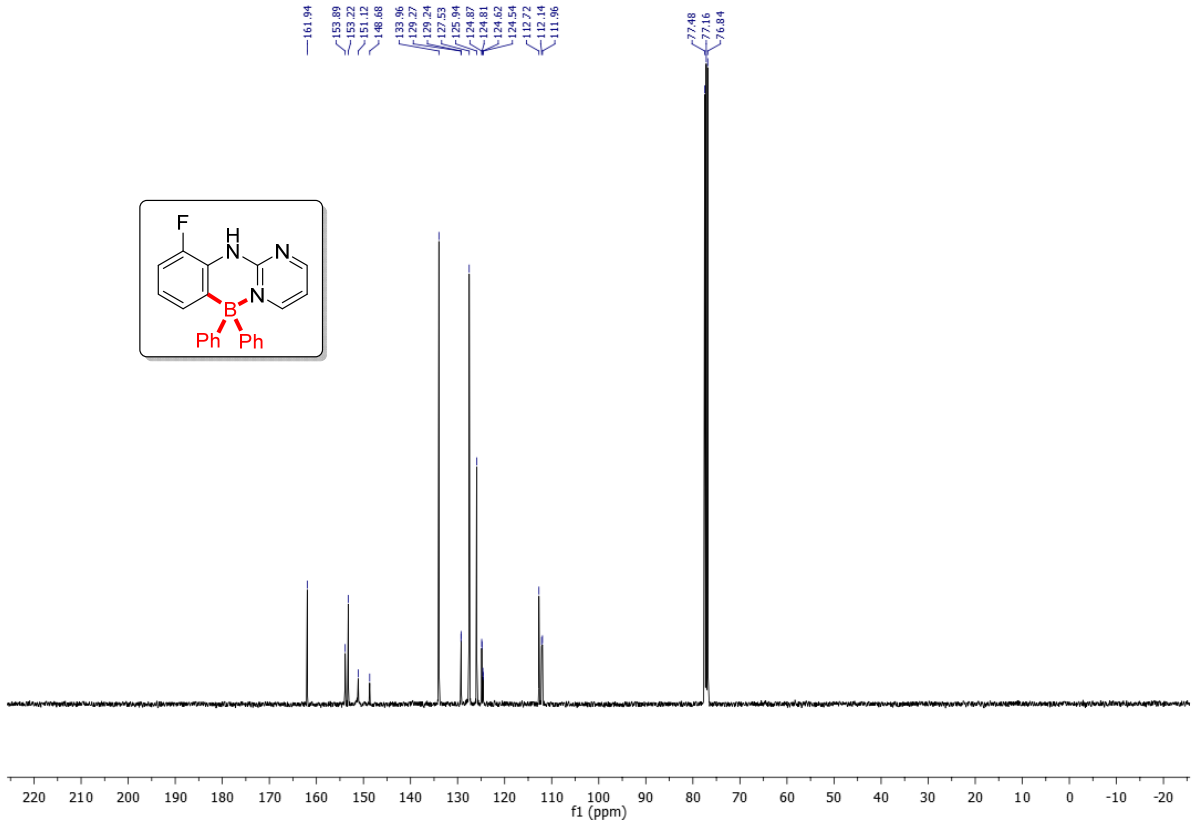
^{13}C NMR spectrum of **37** (101 MHz, $CDCl_3$):



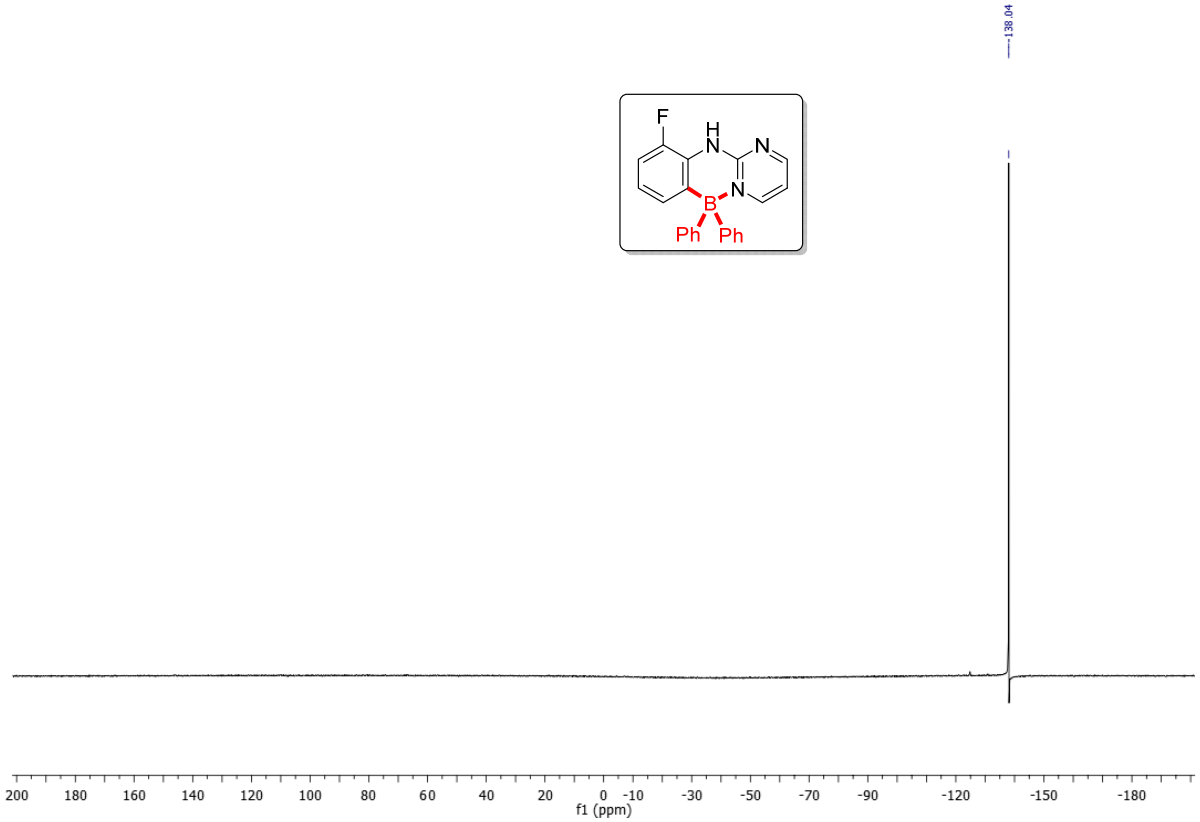
^{1}H NMR spectrum of **38** (400 MHz, $CDCl_3$):



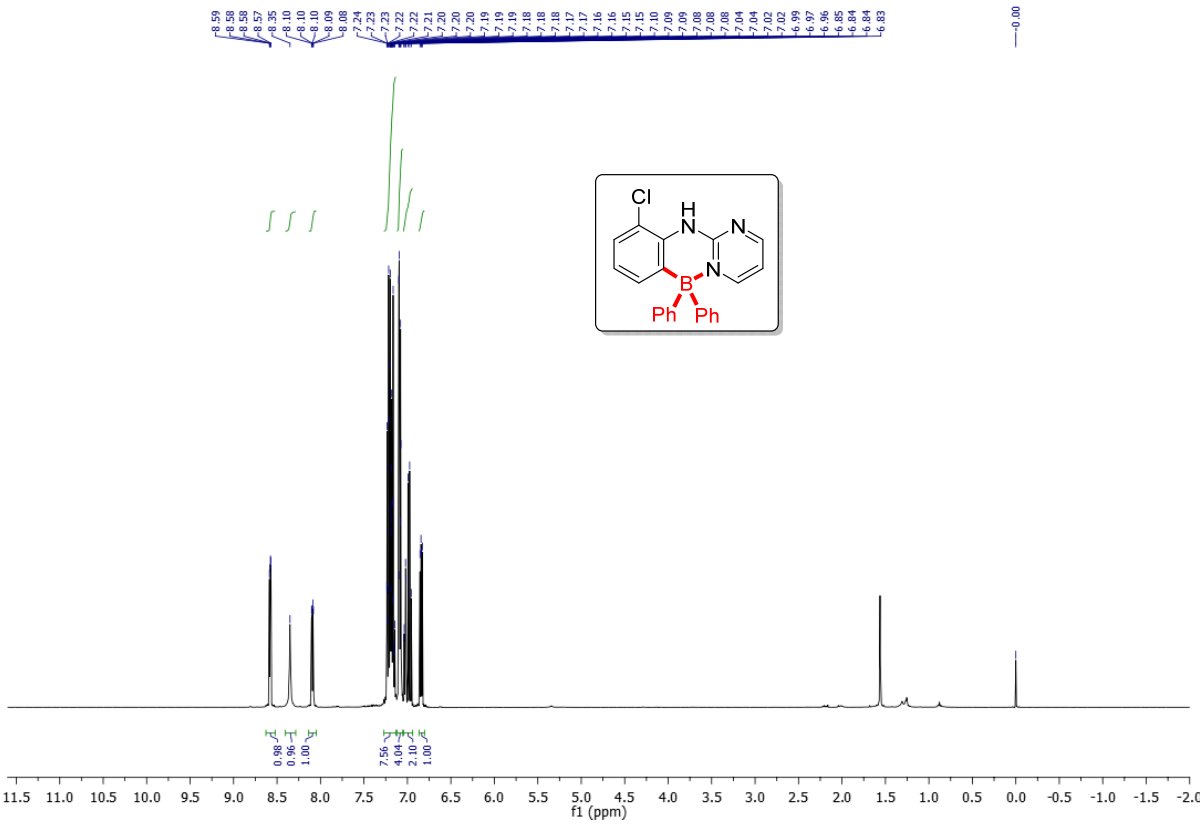
^{13}C NMR spectrum of **38** (101 MHz, $CDCl_3$):



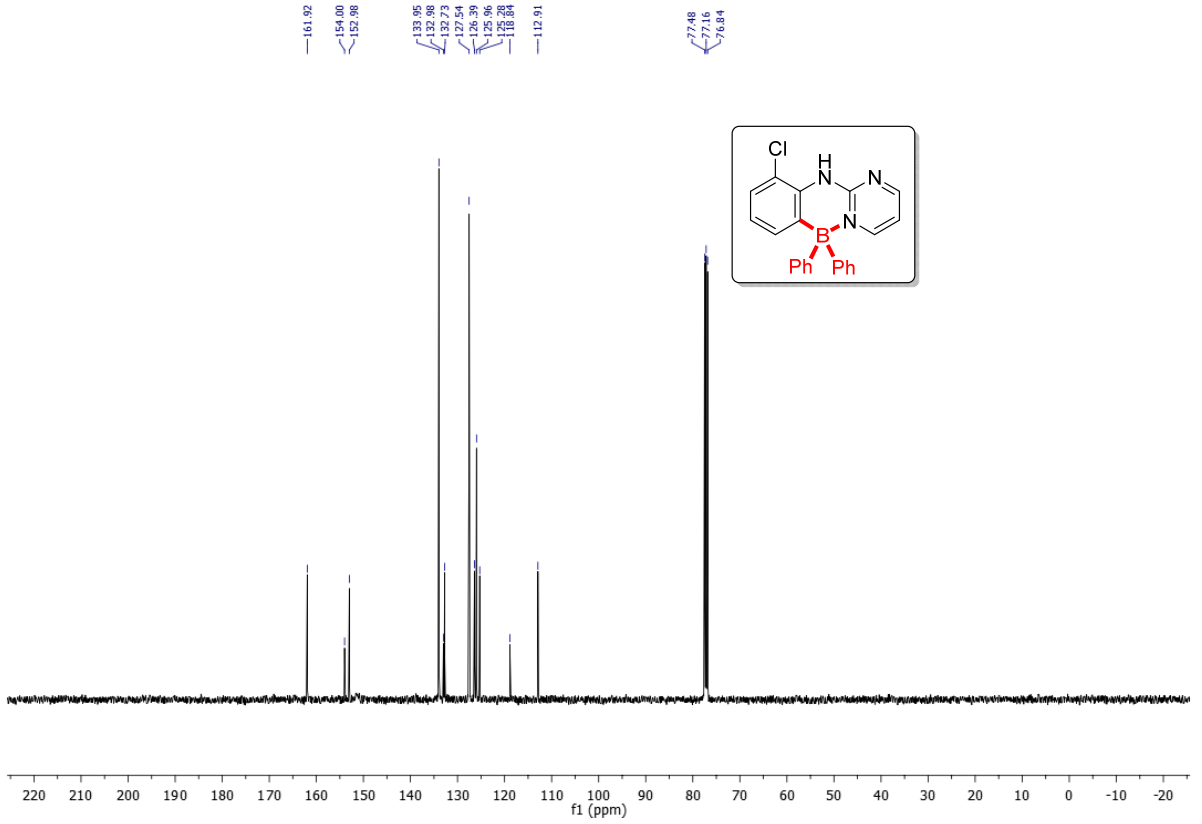
^{19}F NMR spectrum of **38** (376 MHz, $CDCl_3$):



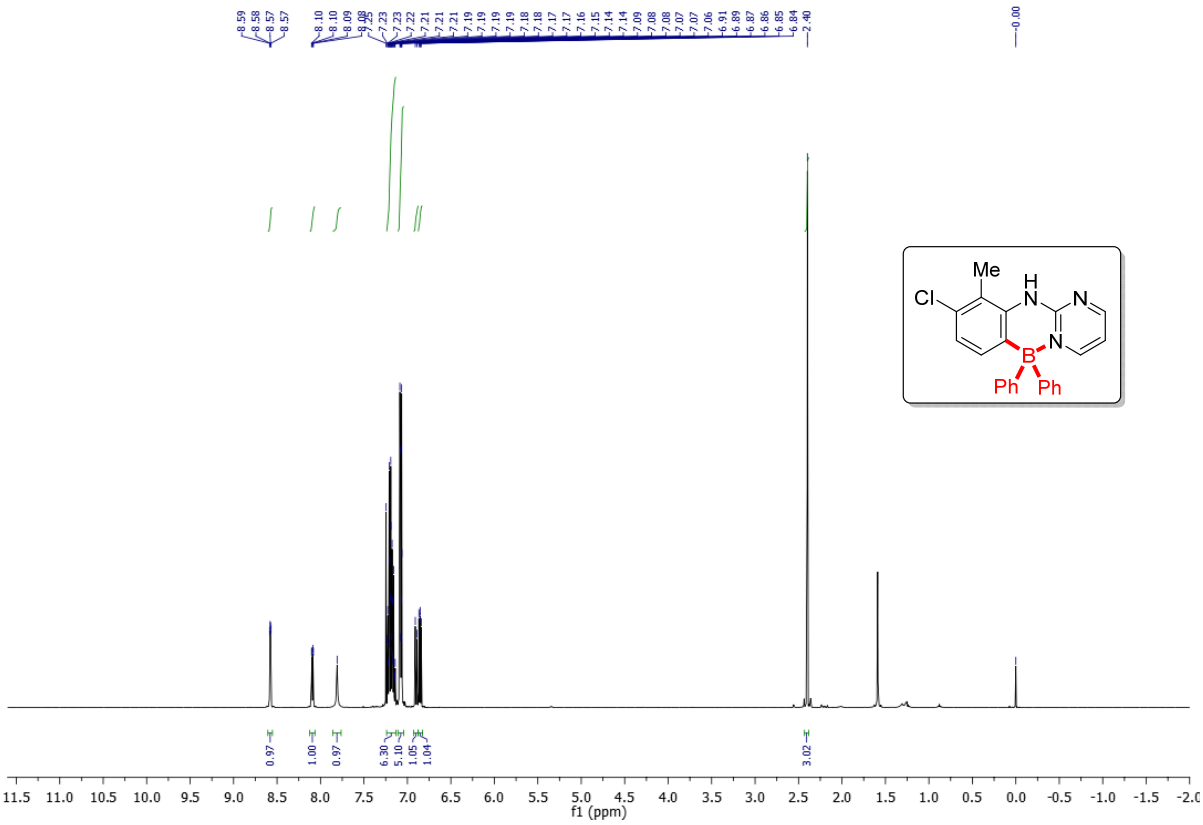
^{1}H NMR spectrum of **39** (400 MHz, $CDCl_3$):



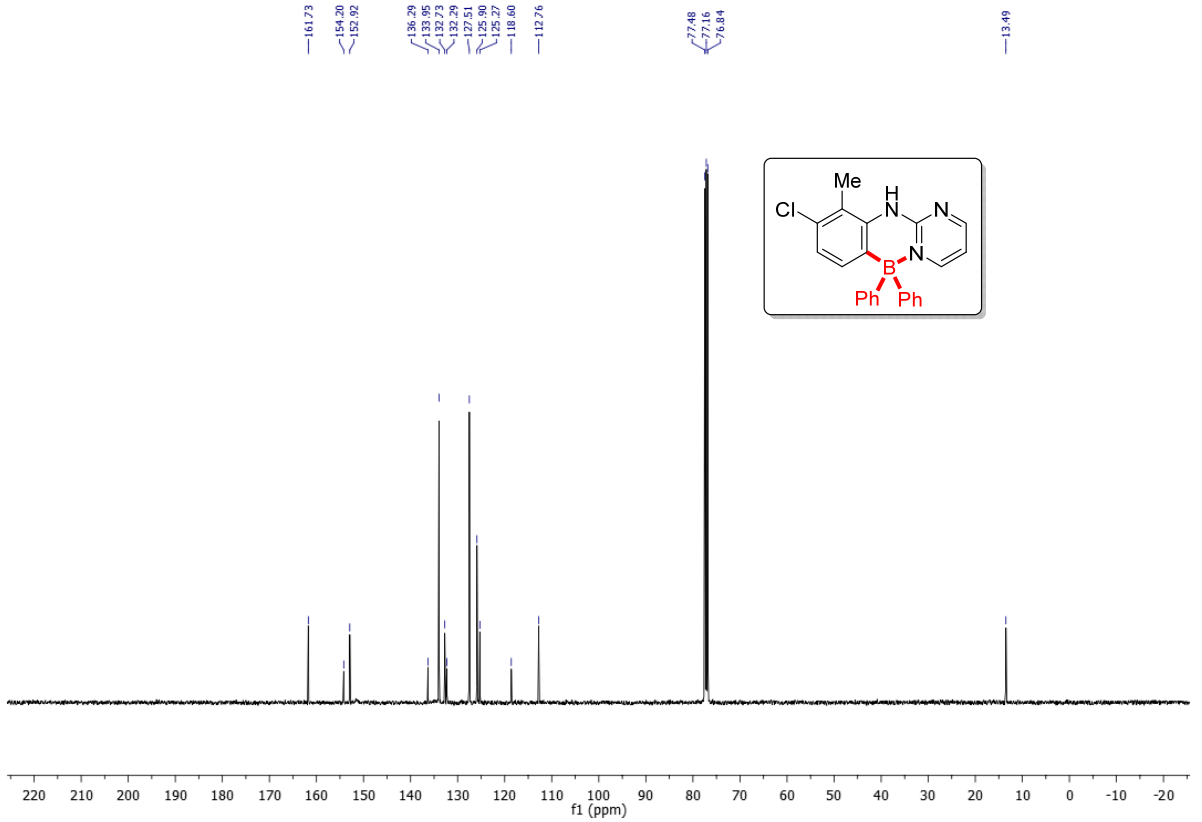
^{13}C NMR spectrum of **39** (101 MHz, $CDCl_3$):



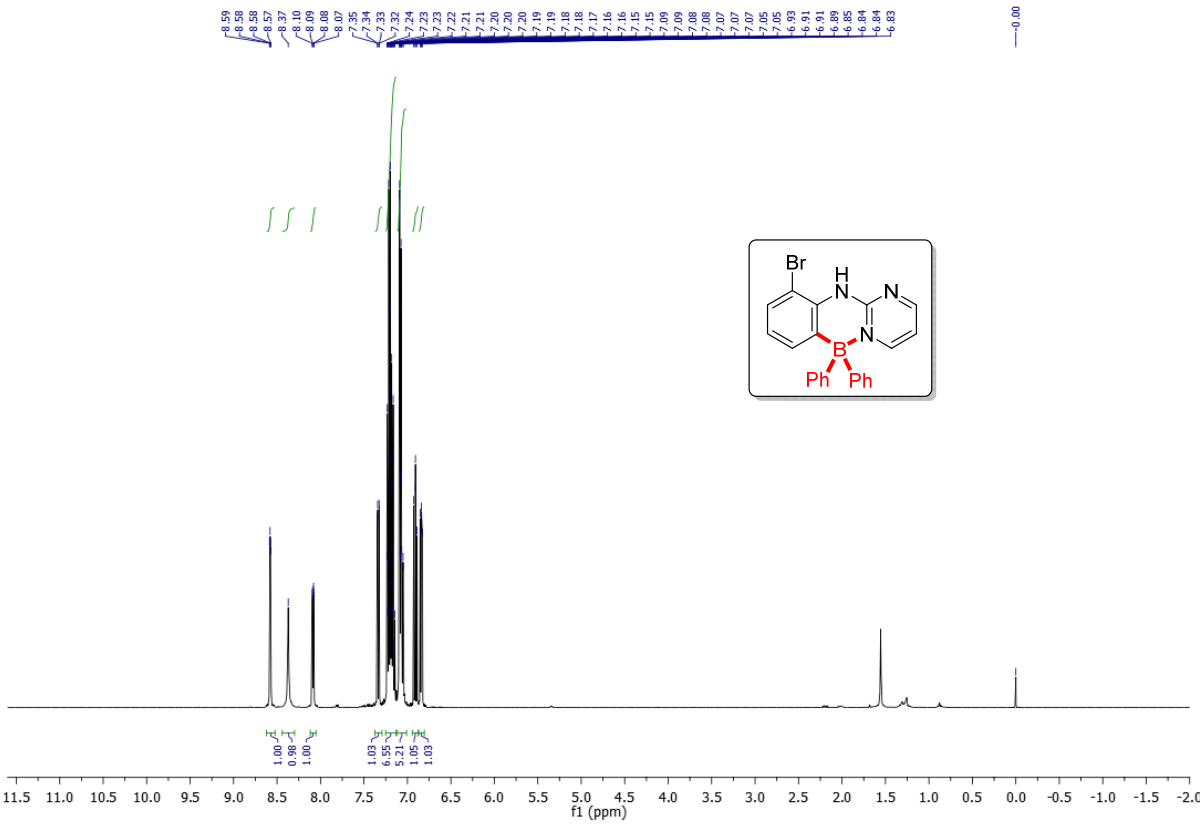
^{1}H NMR spectrum of **40** (400 MHz, $CDCl_3$):



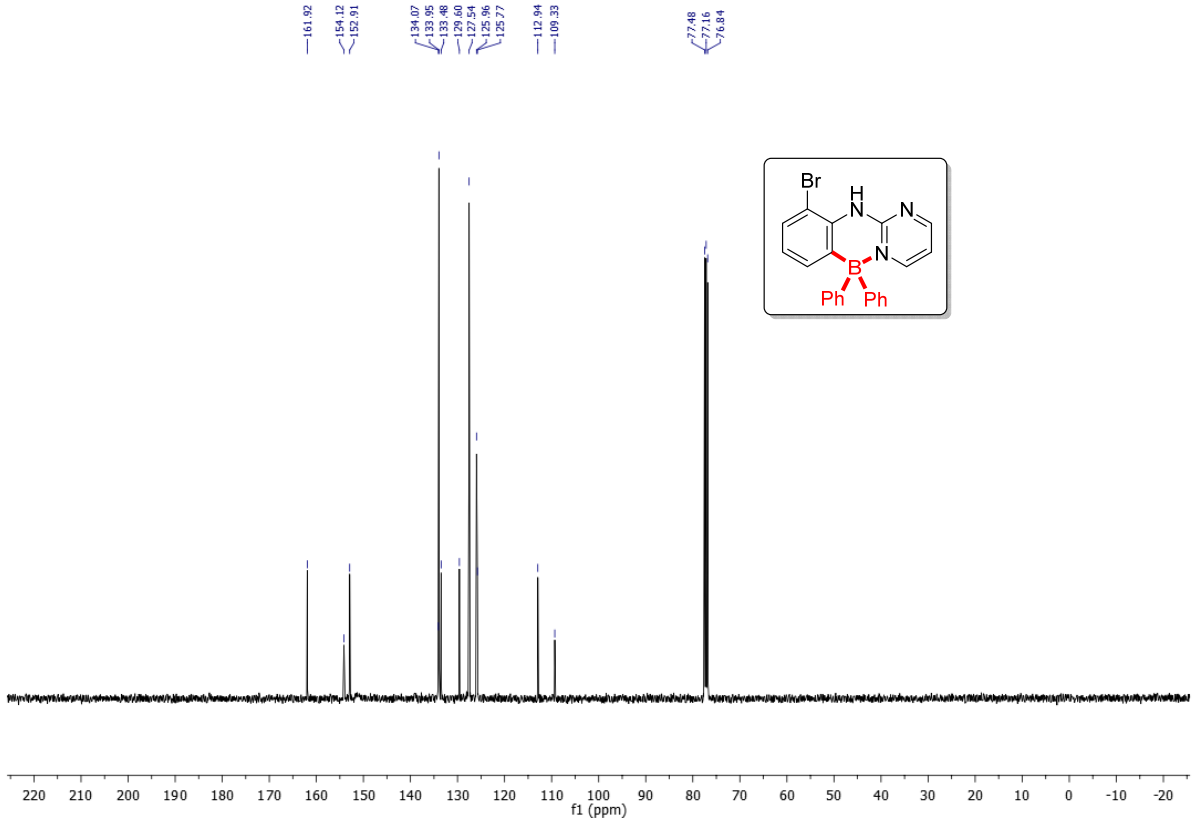
^{13}C NMR spectrum of **40** (101 MHz, $CDCl_3$):



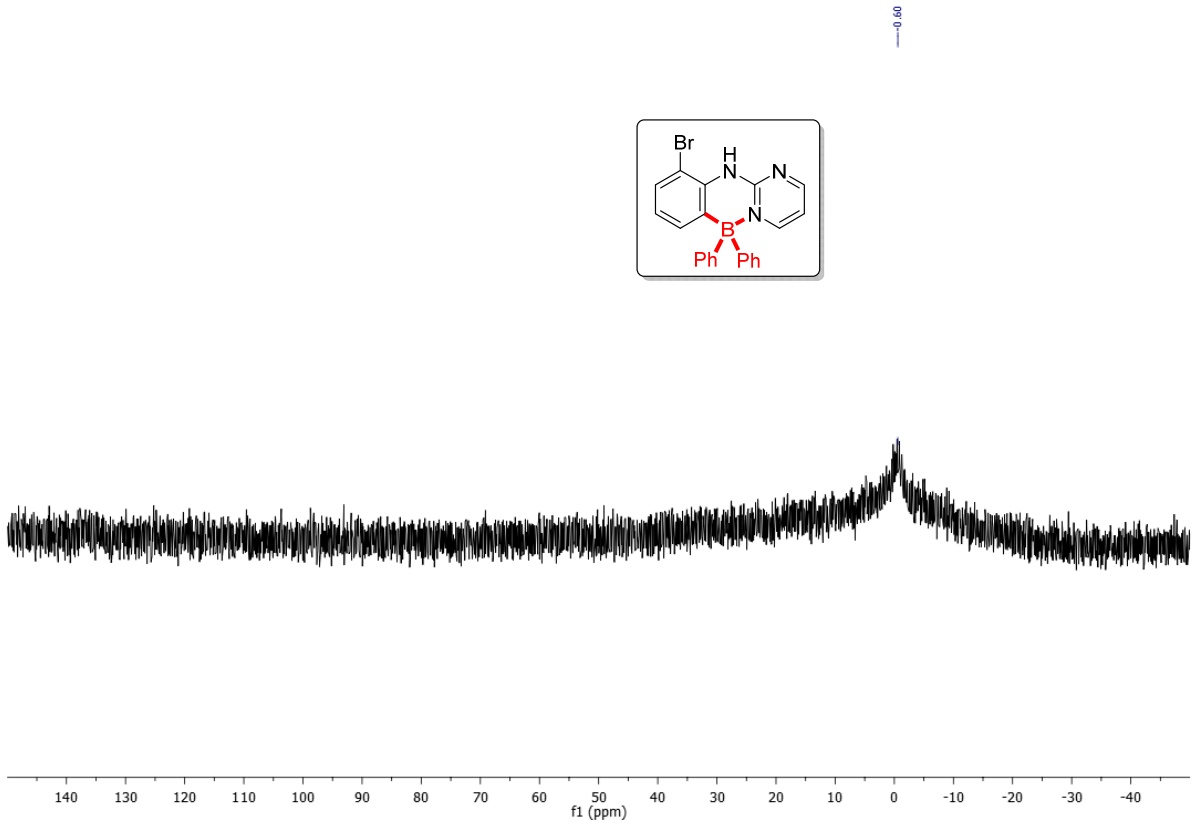
^{1}H NMR spectrum of **41** (400 MHz, $CDCl_3$):



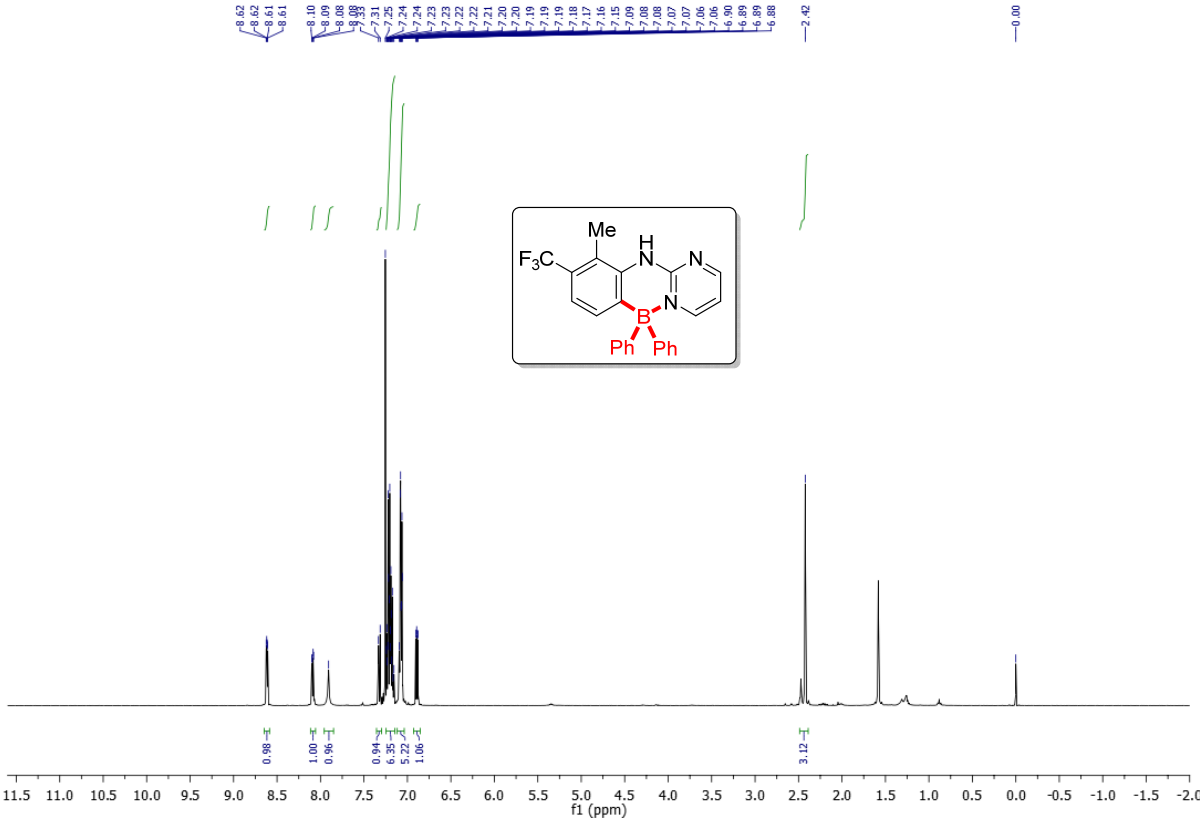
^{13}C NMR spectrum of **41** (101 MHz, $CDCl_3$):



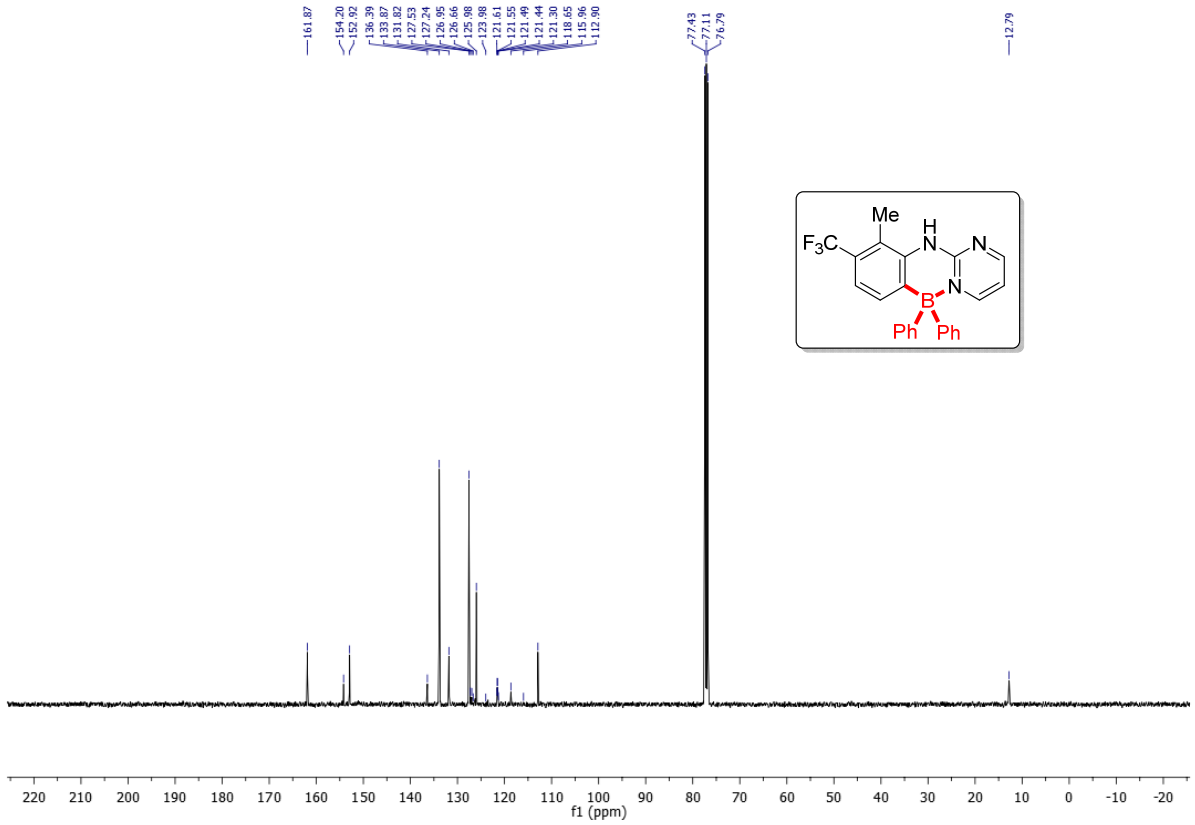
^{11}B NMR spectrum of **41** (128 MHz, $CDCl_3$):



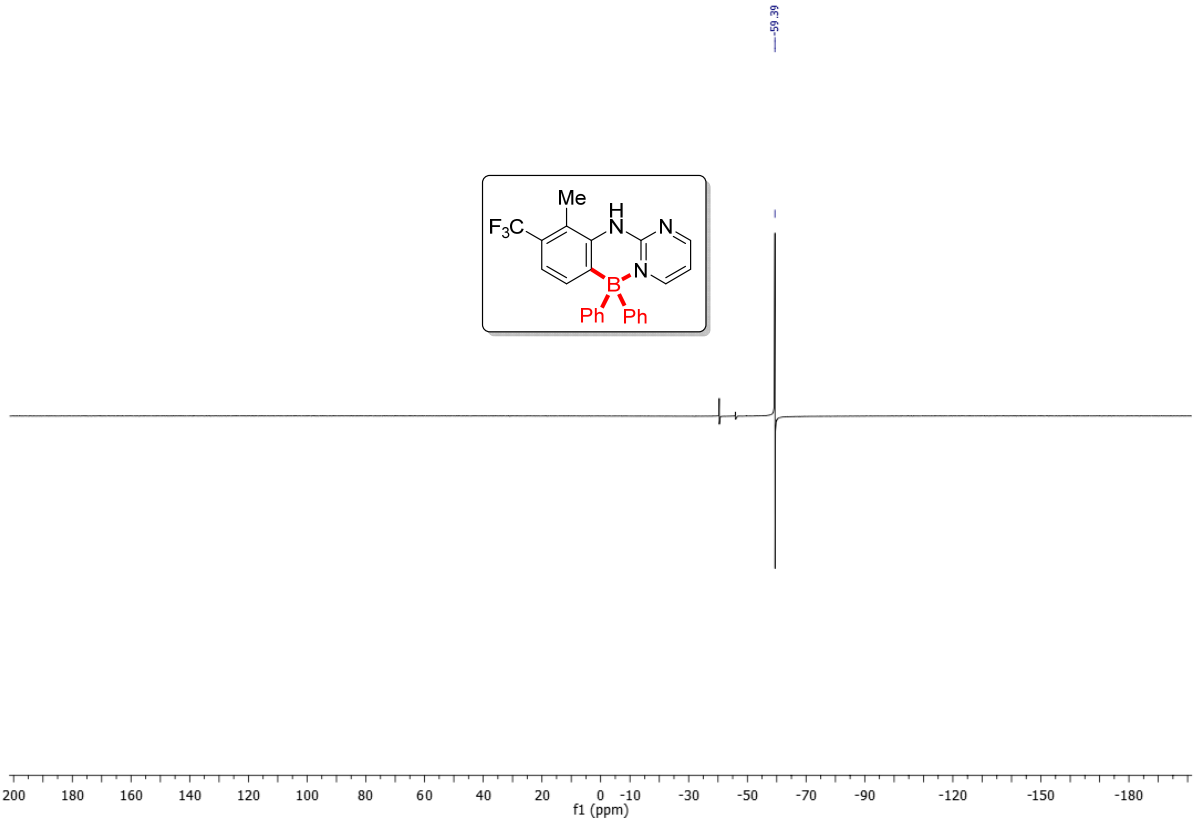
^{1}H NMR spectrum of **42** (400 MHz, $CDCl_3$):



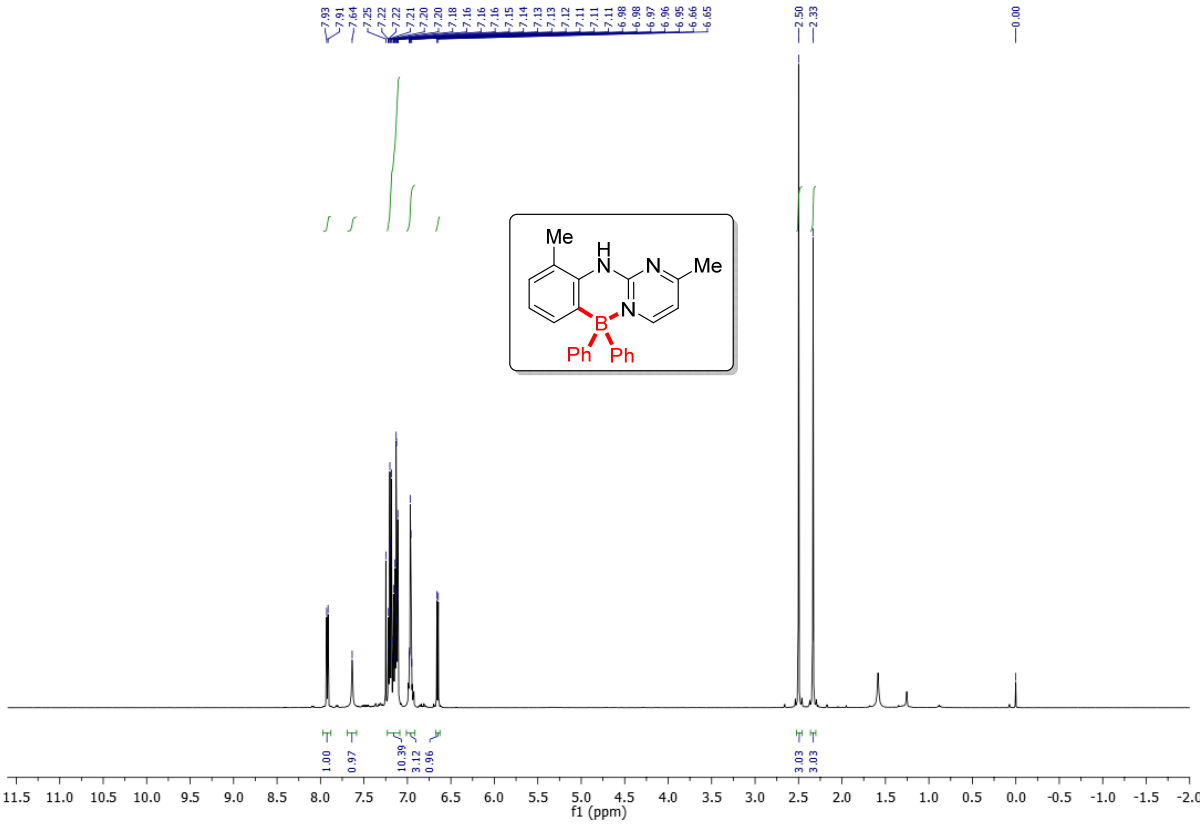
^{13}C NMR spectrum of **42** (101 MHz, $CDCl_3$):



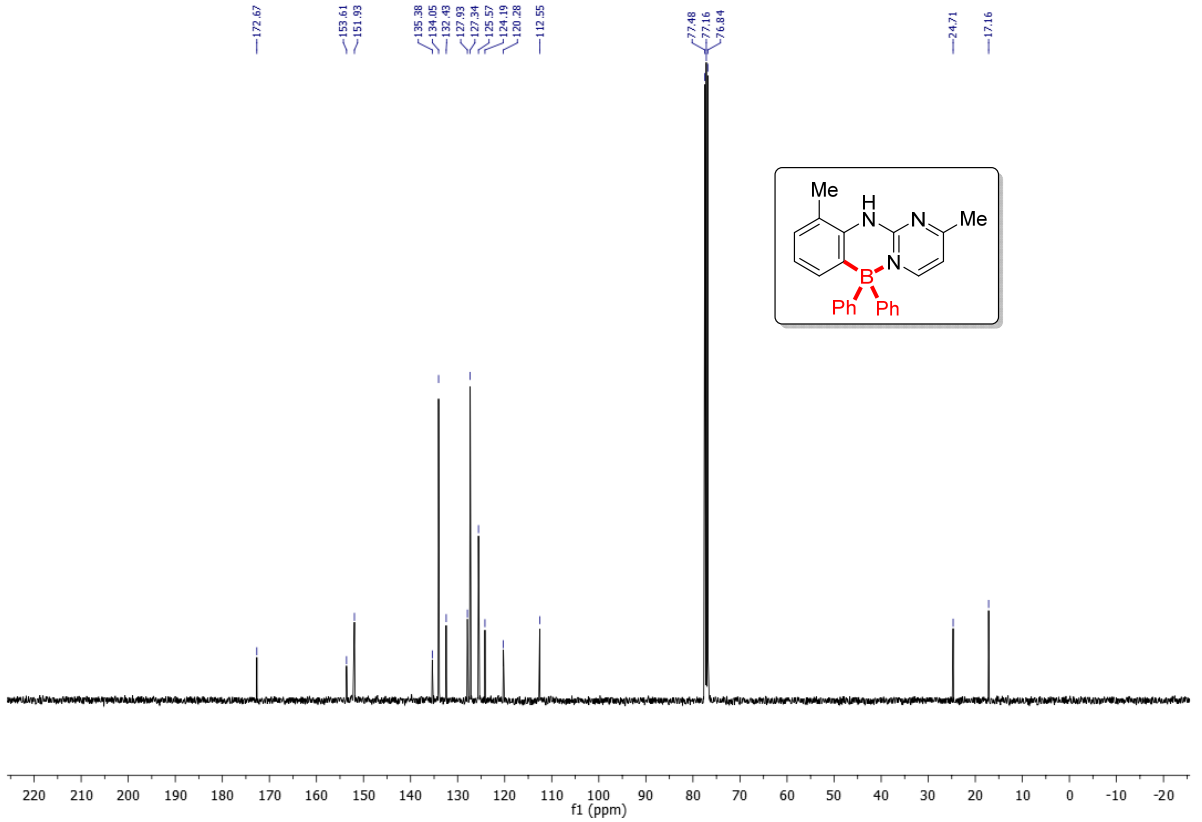
^{19}F NMR spectrum of **42** (376 MHz, $CDCl_3$):



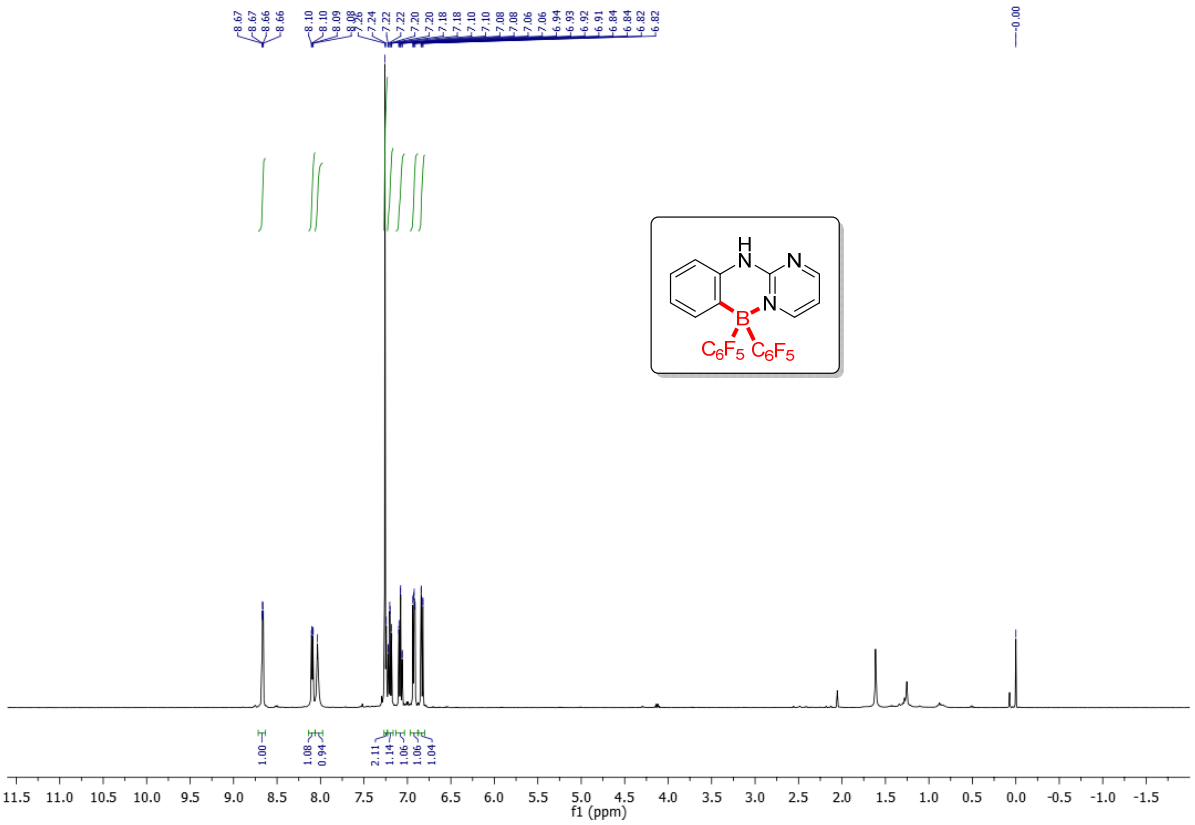
^{1}H NMR spectrum of **43** (400 MHz, $CDCl_3$):



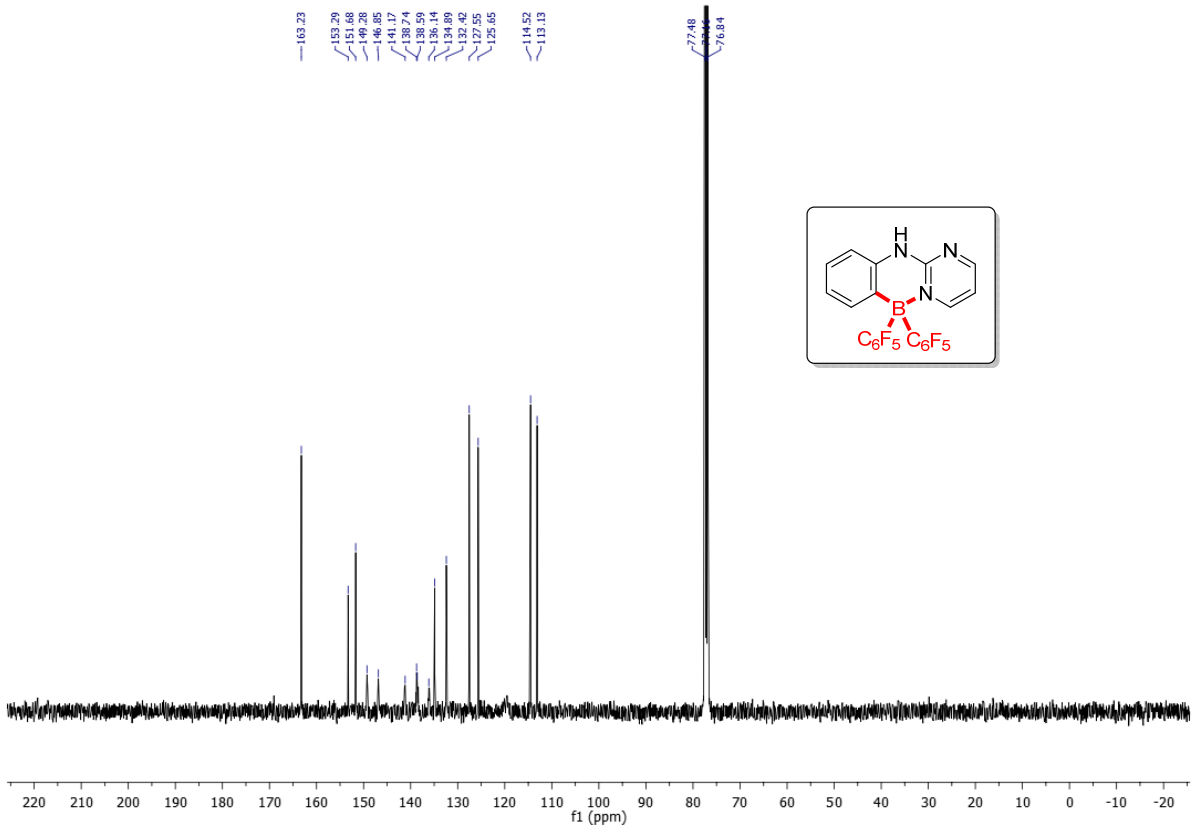
^{13}C NMR spectrum of **43** (101 MHz, $CDCl_3$):



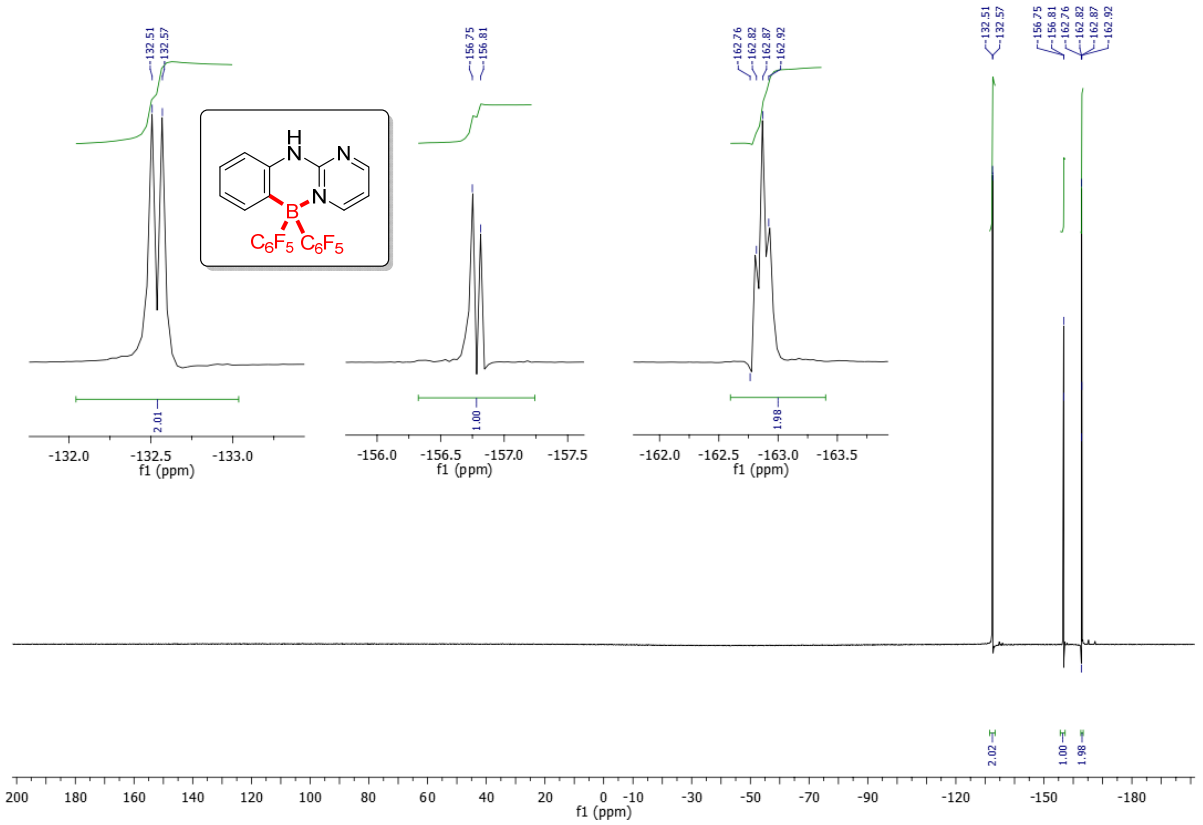
^{1}H NMR spectrum of **44** (400 MHz, $CDCl_3$):



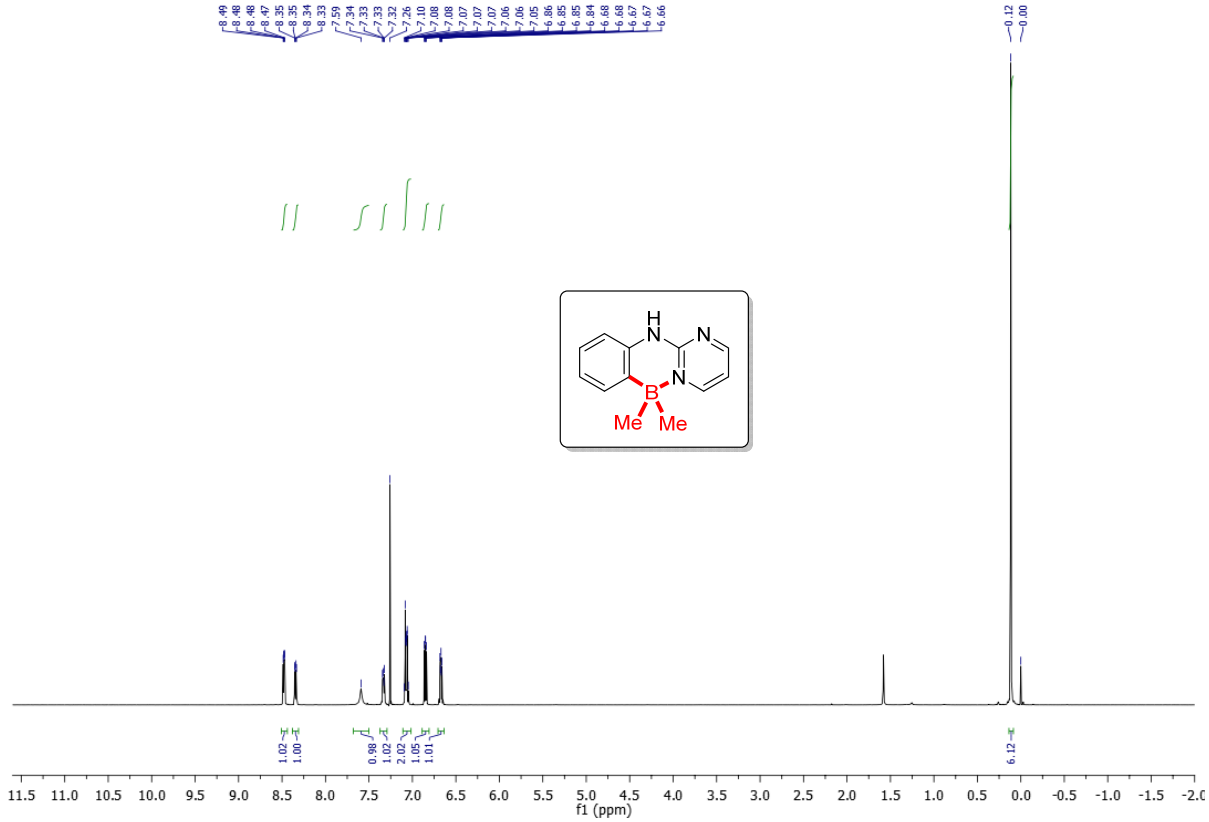
^{13}C NMR spectrum of **44** (101 MHz, $CDCl_3$):



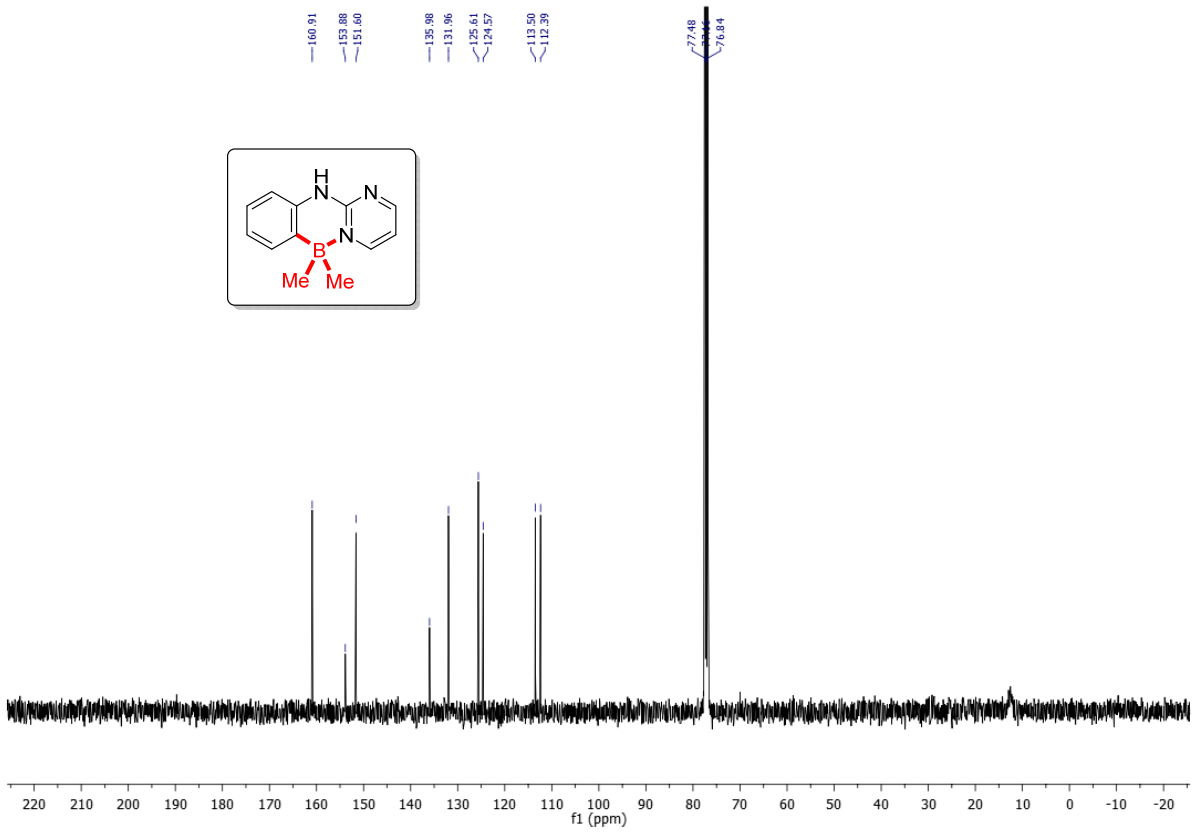
^{19}F NMR spectrum of **44** (376 MHz, $CDCl_3$):



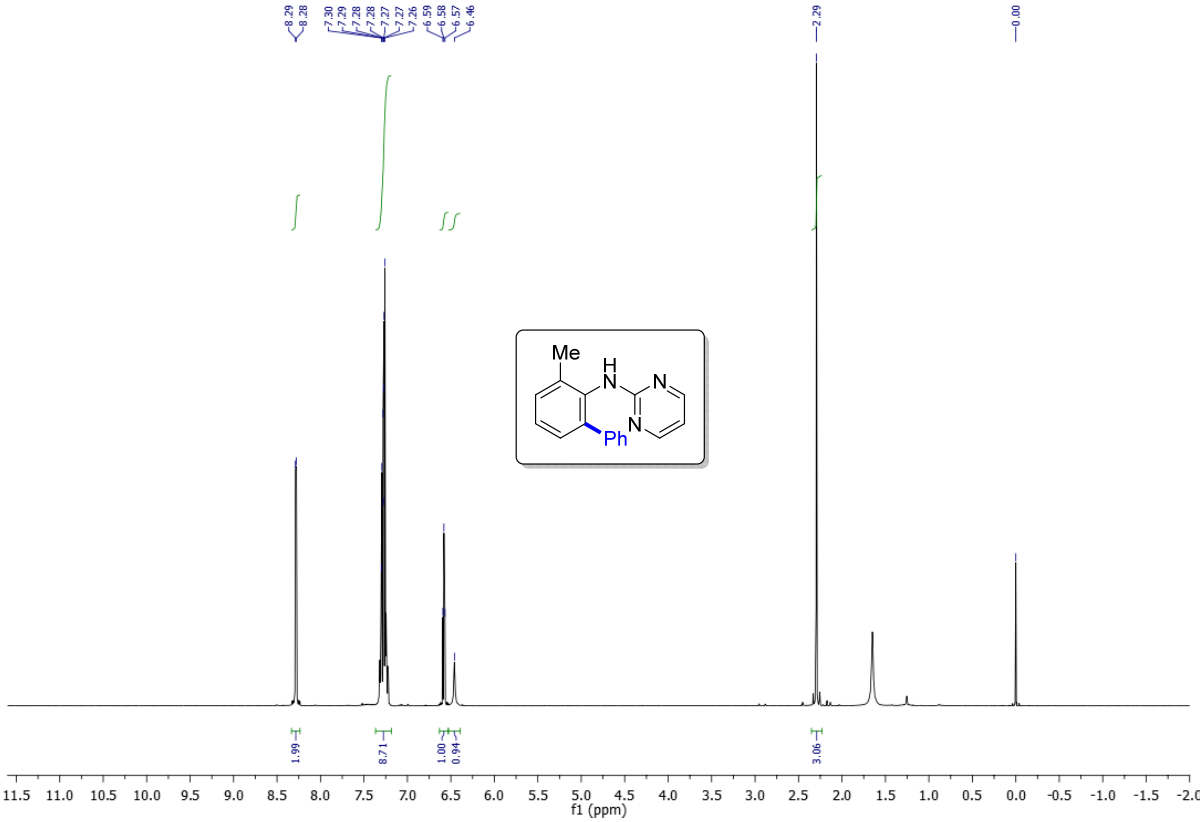
^{1}H NMR spectrum of **45** (400 MHz, $CDCl_3$):



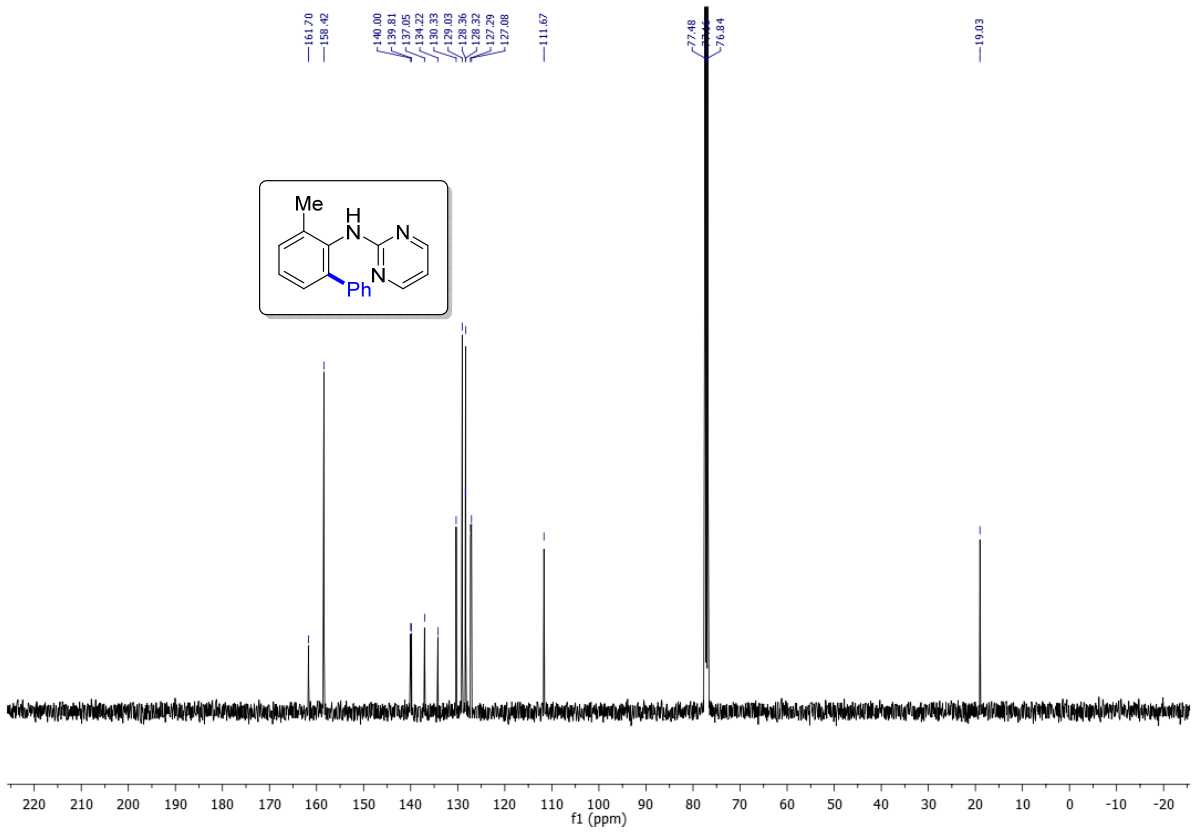
^{13}C NMR spectrum of **45** (101 MHz, $CDCl_3$):



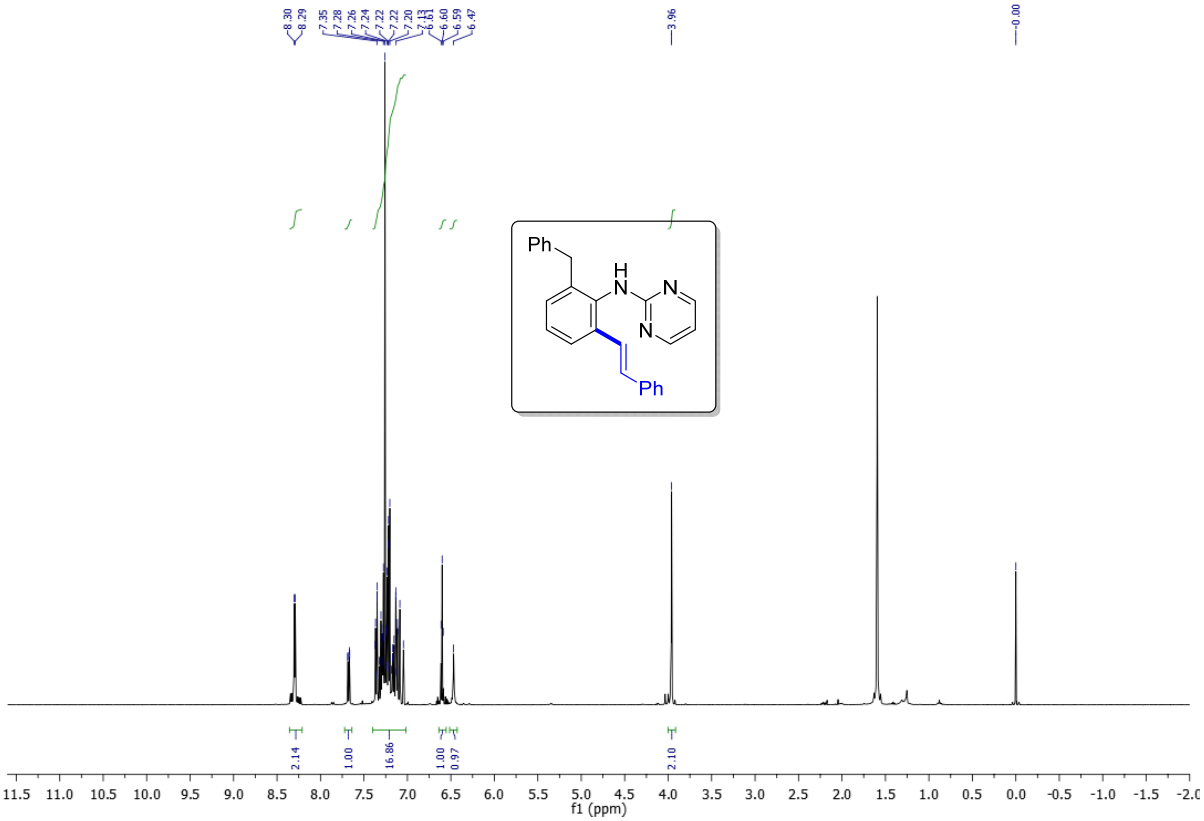
^{1}H NMR spectrum of **46** (400 MHz, $CDCl_3$):



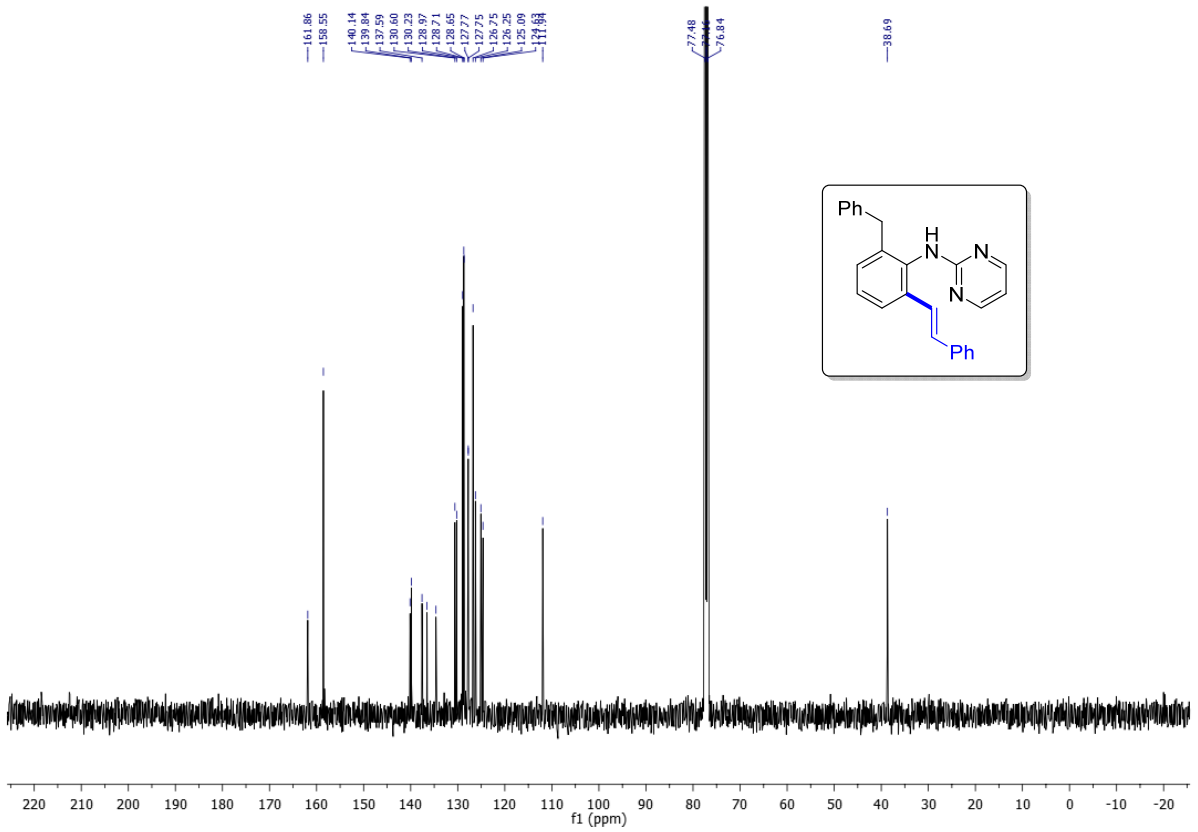
^{13}C NMR spectrum of **46** (101 MHz, $CDCl_3$):



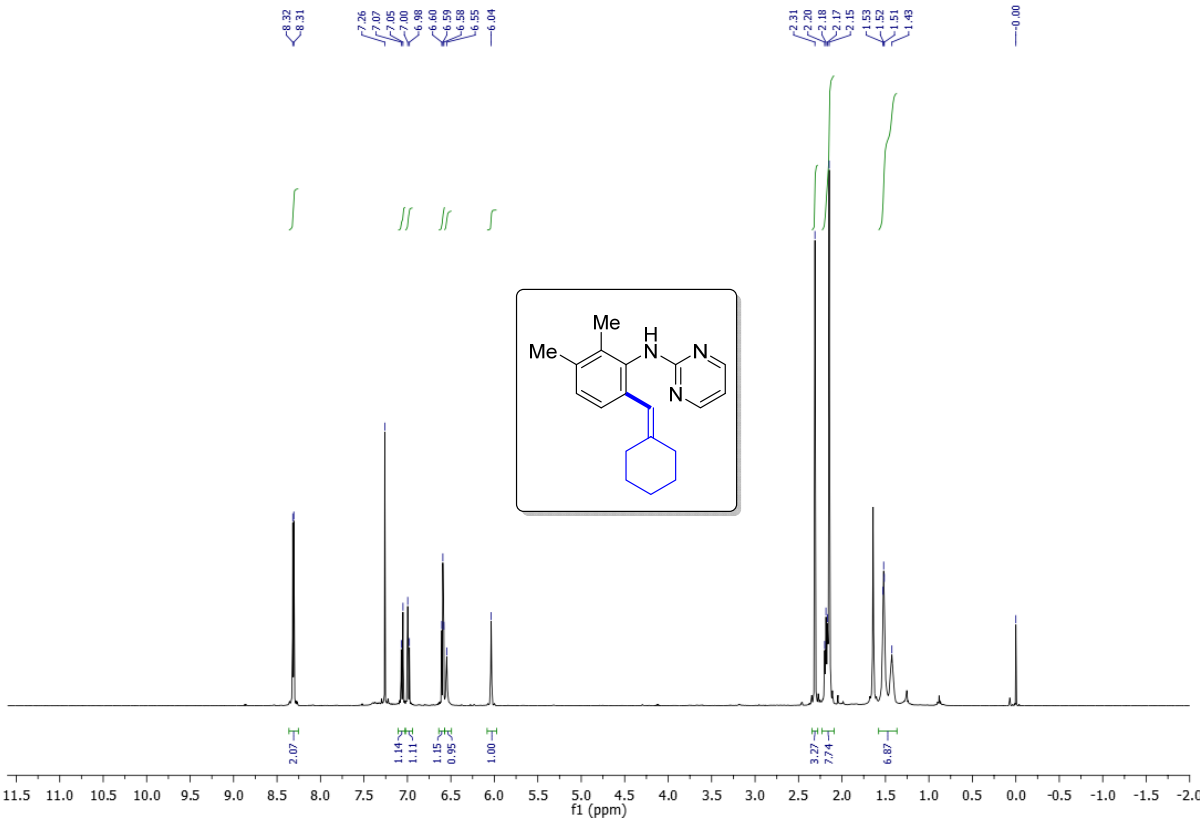
^{1}H NMR spectrum of **47** (400 MHz, $CDCl_3$):



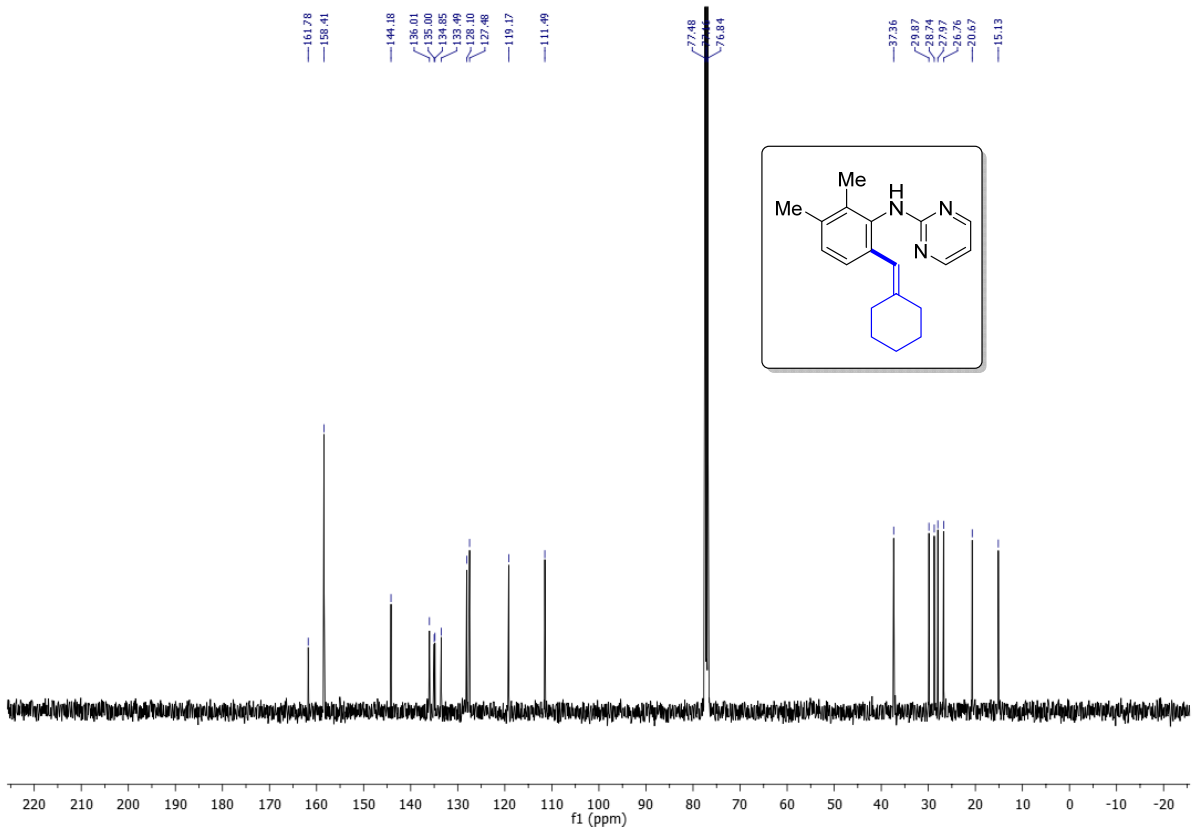
^{13}C NMR spectrum of **47** (101 MHz, $CDCl_3$):



^{1}H NMR spectrum of **48** (400 MHz, $CDCl_3$):



^{13}C NMR spectrum of **48** (101 MHz, $CDCl_3$):



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