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Supporting Information

Hydrogen Bond Directed *ortho*-Selective C–H Borylation of Secondary Aromatic Amides

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SUPPORTING INFORMATION

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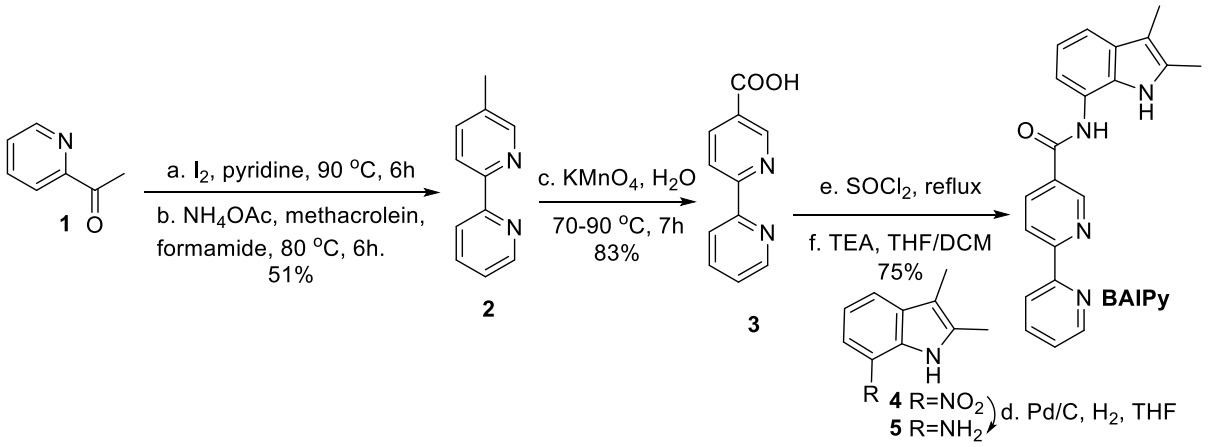
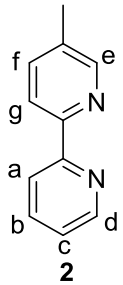
General Information

All reactions involving air- or moisture sensitive materials were carried out under nitrogen atmosphere using standard Schlenk techniques or in Glove-Box. THF, pentane, hexane and toluene were distilled from sodium-benzophenone under nitrogen atmosphere; dichloromethane, methanol were distilled from CaH_2 under nitrogen atmosphere; triethylamine was distilled from KOH pellets under nitrogen atmosphere. Toluene-d8 and CD_2Cl_2 were dried over molecular sieves (3Å) and degassed by three freeze-pump-thaw cycles. ^{1}H NMR, 1D ^{1}H NOESY NMR, 2D ^{1}H NOESY NMR, ^{1}H-^{1}H COSY and ^{13}C NMR experiments were performed on Bruker AMX 300 MHz, Bruker AMX 400 MHz or Bruker AMX 500 MHz. ^{1}H NMR chemical shifts are given in ppm, and were calibrated by using the residual solvent as internal reference ($CHCl_3$ 7.26 ppm, CH_2Cl_2 5.32 ppm, THF 3.58 ppm, DMSO 2.50 ppm, Acetone 2.05 ppm). ^{13}C NMR chemical shifts were reported in ppm with the solvent peaks used as internal reference ($CHCl_3$ 77.16 ppm, CH_2Cl_2 53.84 ppm, THF 67.21 ppm, DMSO 39.52 ppm, Acetone 29.84 ppm). Mass spectra were collected on an AccuTOF GC v 4g, JMS-T100GCV Mass spectrometer (JEOL, Japan), GCMS (EI) or FD/FI probe (FD/FI) equipped with FD Emitter, Carbotec (Germany), FD 13 µm, current rate 51.2 mA/min over 1.2 min, or FI Emitter, Carbotec (Germany), FI 10 µm, flashing current 40 mA on every spectra of 30 ms. All reagents were purchased from commercial suppliers and used without further purification, unless otherwise noted.

Synthesis of supramolecular ligand (BAIPy)

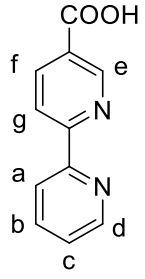


Scheme S1. Synthesis of supramolecular ligand **BAIPy**



2

5-Methyl-2,2'-bipyridine (**2**)
2-Acetylpyridine (5.6 mL, 50.0 mmol) and I_2 (14.2 g, 56.0 mmol) were dissolved in pyridine (60 mL) and refluxed for 6 hours. The reaction mixture was then cooled to room temperature and the resulting suspension was filtered, and washed with ethyl ether. The pure 1-(2-pyridylacetyl)pyridinium iodide was obtained after re-crystallization from a saturated EtOH solution and used subsequently. Methacrolein (4.0 mL, 48.3 mmol) and NH_4OAc (18.6 g, 241.3 mmol) were subsequently added to a solution of 1-(2-pyridylacetyl)pyridinium iodide in formamide. The resulting reaction mixture was heated at 80 °C under nitrogen atmosphere for 6 hours. Then the crude mixture was cooled, water was added and the mixture was carefully extracted with Et_2O (3x300 mL). The combined organic phases were dried and filtered and the solvent was removed. The residue was purified by column chromatography (eluent of DCM/MeOH 20/1) to give orange product **2**. Identical to literature.[1,2]
Yield of 51%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 – 8.66 (m, 1H, Ha), 8.51 (brs, 1H, He), 8.35 (dt, *J* = 7.9, 1.1 Hz, 1H, Hg), 8.28 (d, *J* = 8.1 Hz, 1H, Hd), 7.80 (td, *J* = 7.8, 1.7 Hz, 1H, Hb), 7.64 – 7.61 (m, 1H, Hf), 7.28 (ddd, *J* = 7.2, 4.8, 1.1 Hz, 1H, Hc), 2.40 (s, 3H, Me).



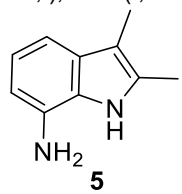
3

2,2'-Bipyridinyl-5-carboxylic acid (**3**)

Potassium permanganate (15.0 g, 94.9 mmol) was added in 7 portions with 1 hour intervals to a solution of 5-methyl-2,2'-bipyridine 2 (3.9 g, 22.9 mmol) in water. The mixture was heated at 70 °C for 3 hours and then at 90 °C for 4 hours. The resulting brown mixture was then filtered while hot through celite and washed with hot water (2x25 mL). The filtrate was concentrated to approximately 10 mL under reduced pressure, and then 1M HCl was added slowly until a pH of 4 was obtained. The residue was then filtered and dried to obtain pure 3 as white powder. Identical to literature.[2]

Yield of 83%.

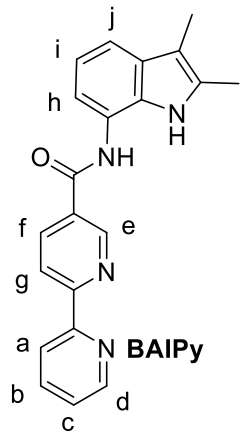
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.16 (s, 1H, He), 8.73 (d, *J* = 4.7 Hz, 1H, Ha), 8.51 (d, *J* = 8.3 Hz, 1H, Hg), 8.46 – 8.40 (m, 2H, Hd,f), 8.00 (t, *J* = 7.7 Hz, 1H, Hb), 7.54 – 7.50 (m, 1H, Hc).



5

2,3-Dimethyl-1*H*-indol-7-amine (**5**)

2,3-Dimethyl-7-nitro-1*H*-indol 4 (1.74 g, 0.2 mmol) was dissolved in a suspension of Pd/C (0.4 g) in THF/Methanol. The suspension was stirred vigorously under 1 bar of H_2 atmosphere for 2 hours. After completion (monitored by TLC, ethyl acetate/petroleum ether 1/1), the suspension was filtered over celite and the filtrate was concentrated to dry for subsequent condensation reaction without further purification.



N-(2,3-dimethyl-1*H*-indol-7-yl)-[2,2'-bipyridine]-5-carboxamide (**BAIPy**)

2,2'-Bipyridinyl-5-carboxylic acid **3** (2.0 g, 10.0 mmol) was suspended in $SOCl_2$ (10 mL). The suspension was heated to reflux for 2 hours until the suspension became homogeneous solution. The volatiles were then removed under vacuum and the resulting acyl chloride was dried for following condensation reaction without further purification.

The acyl chloride was re-dissolved in dry THF and DCM mixtures. Then the acyl chloride solution was added slowly into a solution of the crude amine **5** in THF, followed by adding TEA (4.5 mL, 30.0 mmol) into the reaction mixtures under ice-water bath. The resulting mixture was stirred overnight under room temperature. Then the volatiles were removed and supramolecular ligand **BAIPy** was obtained after column chromatography as dark brownish powder (ethyl acetate/petroleum ether 2/1 to 1/1).

Yield of 75%.

^{1}H NMR (500 MHz, DMSO-d_6) δ 10.48 (s, 1H, indole-NH), 10.27 (s, 1H, amide-NH), 9.30 (s, 1H, He), 8.76 (d, *J* = 4.4 Hz, 1H, Hd), 8.57 – 8.49 (m, 3H, Ha,f,g), 8.01 (td, *J* = 7.7, 1.8 Hz, 1H, Hc), 7.53 (dd, *J* = 7.5, 5.0 Hz, 1H, Hb), 7.27 – 7.25 (m, 2H, Hh,j), 6.96 (t, *J* = 7.6 Hz, 1H, Hi), 2.34 (s, 3H, Me), 2.18 (s, 3H, Me).

^{13}C NMR (126 MHz, DMSO-d_6) δ 163.65, 157.25, 154.43, 149.54, 148.88, 137.55, 136.90, 131.40, 130.47, 130.40, 129.11, 124.82, 121.51, 121.08, 119.85, 117.89, 115.47, 115.05, 105.54, 11.22, 8.44.

HRMS (PD+(eiFi)) calcd. for $C_{21}H_{18}N_4O$ $[M]^+$ 342.1481, found 342.1455.

SUPPORTING INFORMATION

Hydrogen bonding interaction studies between ligand BAIPy and substrate 1s

Table S1. ^{1}H NMR titration experiments of aromatic amide **1s** and **BAIPy** in toluene-d_8

BAIPy/conc(M)	**1s**/conc(M)	Indole-NH	Amide-NH
0.0050	0.00000	9.8185	9.0494
0.0050	0.00250	9.8294	9.0665
0.0050	0.00500	9.8378	9.0837
0.0050	0.01000	9.8568	9.1224
0.0050	0.01500	9.8772	9.1433
0.0050	0.02000	9.8957	9.1744
0.0050	0.02500	9.9051	9.1885
0.0050	0.03000	9.9224	9.2178
0.0050	0.03500	9.9355	9.2373
0.0050	0.04000	9.9469	9.2562
0.0050	0.04500	9.9572	9.2701
0.0050	0.05000	9.9676	9.2854
0.0050	0.05500	9.9782	9.302
0.0050	0.06000	9.9865	9.3144
0.0050	0.06500	9.996	9.3265
0.0050	0.07000	10.0042	9.3383
0.0050	0.07500	10.0119	9.3483
0.0050	0.08000	10.0188	9.3575
0.0050	0.08500	10.025	9.3659
0.0050	0.09000	10.0317	9.3745
0.0050	0.10000	10.0451	9.3904

Conditions: titration experiments were performed at room temperature.

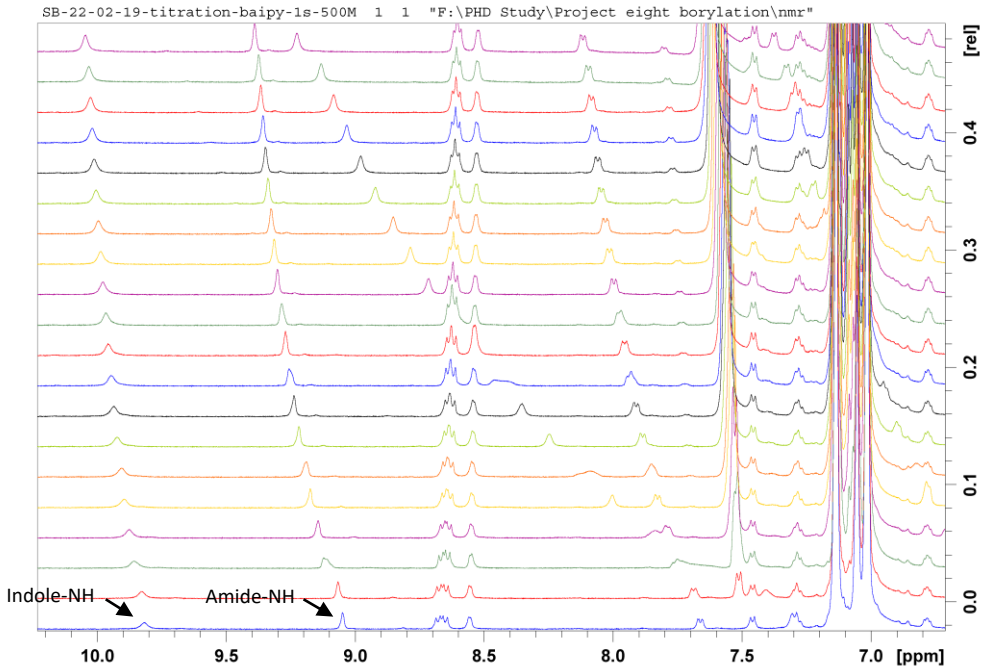


Figure S1. ^{1}H NMR experiments of aromatic amide **1s** and **BAIPy** in Toluene-d8 (indole-NH and amide-NH of the ligand indicated by arrows)

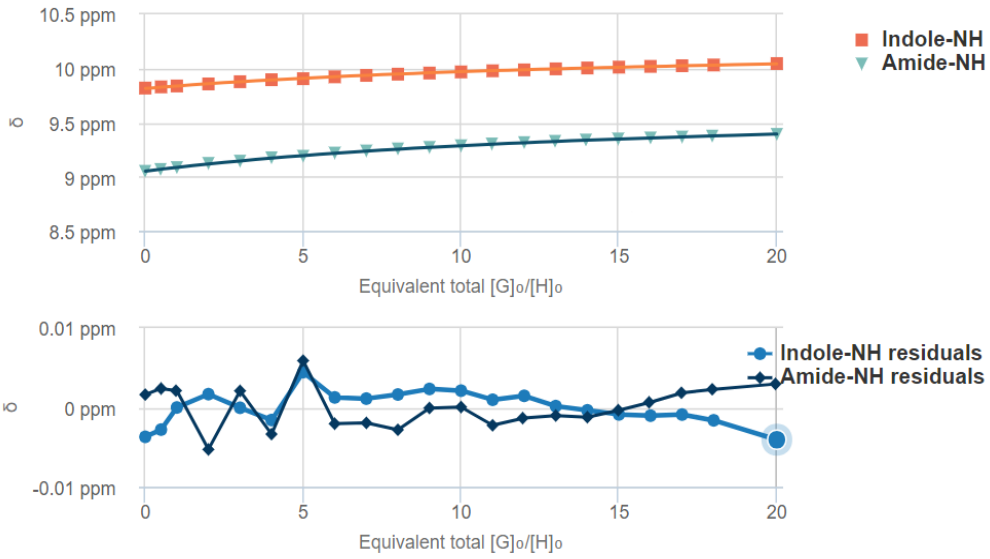


Figure S2. Fitting curve of the titration experiments (http://app.supramolecular.org/bindif), using the assumption of 1:1 binding, and using a Nelder-Mead alogorithm (the binding energy calculated according to equation of $\Delta G=RTLn(K_{bind})$).

Details

Time to fit	0.2527 s
SSR	2.2160e-4
Fitted datapoints	42
Fitted params	5

Parameters

Parameter (bounds)	Optimised	Error	Initial
K (0 → 1000)	12.52 M^{-1}	± 0.7373 %	26.00 M^{-1}

Figure S3. Fitting results of the titration experiments (http://app.supramolecular.org/bindif), using the assumption of 1:1 binding, and using a Nelder-Mead alogorithm (the binding energy of 6.3 kJ/mol in toluene calculated according to equation of $\Delta G=RTLn(K_{bind})$).

Table S2. ^{1}H NMR titration experiments of aromatic amide **1s** and **BAIPy** in THF-d_8

BAIPy/conc(M)	**1s**/conc(M)	Indole-NH	Amide-NH
0.0050	0.00000	9.6836	9.6590
0.0050	0.00250	9.6834	9.6594
0.0050	0.00500	9.6848	9.6607
0.0050	0.01000	9.6877	9.6631
0.0050	0.01500	9.6906	9.6656
0.0050	0.02000	9.6928	9.6676
0.0050	0.02500	9.6958	9.6702
0.0050	0.03000	9.6991	9.6731
0.0050	0.03500	9.7038	9.6754
0.0050	0.04000	9.7066	9.6798
0.0050	0.04500	9.7086	9.6823
0.0050	0.05000	9.7110	9.6840
0.0050	0.05500	9.7184	9.6904
0.0050	0.06000	9.7227	9.6945
0.0050	0.06500	9.7235	9.6950
0.0050	0.07000	9.7254	9.6968
0.0050	0.07500	9.7277	9.6989
0.0050	0.08000	9.7306	9.7015
0.0050	0.08500	9.7316	9.7027
0.0050	0.09000	9.7354	9.7058
0.0050	0.10000	9.7398	9.7115

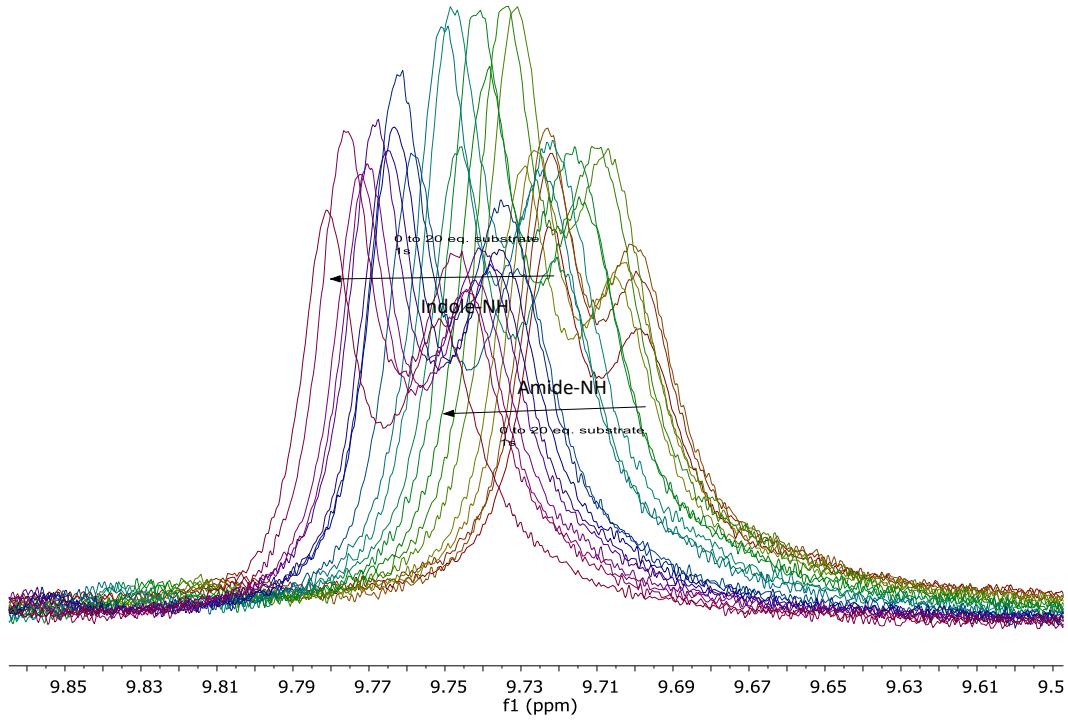


Figure S4. ^{1}H NMR experiments of aromatic amide **1s** and **BAIPy** in THF-d_8 (indole-NH and amide-NH of the ligand indicated)

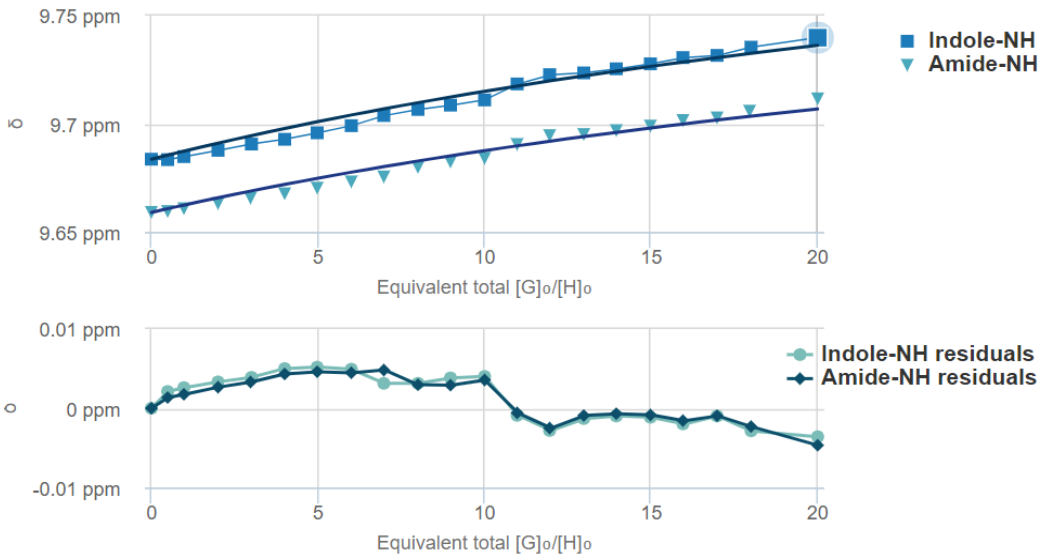


Figure S5. Fitting curve of the titration experiments in THF-d_8 (http://app.supramolecular.org/bindif), using the assumption of 1:1 binding, and using a L-BFGS-B alogorithm (the binding energy calculated according to equation of $\Delta G=RTLn(K_{bind})$).

Details

Time to fit	3.7100e-3 s
SSR	3.7834e-4
Fitted datapoints	42
Fitted params	3

Parameters

Parameter (bounds)	Optimised	Error	Initial
K (5 → 35)	5.00 M^{-1}	± 4.4155 %	5.00 M^{-1}

Figure S6. Fitting results of the titration experiments in THF-d_8 (http://app.supramolecular.org/bindif), using the assumption of 1:1 binding, and using a L-BFGS-B alogorithm (the binding energy of 4.0 kJ/mol in THF calculated according to equation of $\Delta G=RTLn(K_{bind})$).

Computational methods, results and coordinates

Turbomole program[3] coupled to the PQS Baker optimizer[4] via the BOpt package[5] was used for all DFT geometry optimizations. Geometries were fully optimized as minima using the BP86 functional[6,7] and the resolution-of-identity (ri) method[8] using the Turbomole def2-TZVP basis[9] for all atoms. Grimme's dispersion corrections (D3 version, implemented with the keyword disp3 in Turbomole)[9] were applied in all calculations. All minima (no imaginary frequencies) were characterized by calculating the Hessian matrix. ZPE and gas-phase thermal corrections (entropy and enthalpy, 298 K, 1 bar) from these analyses were calculated. The relative enthalpy (free) energies obtained from these calculations are reported in the main text of this paper.

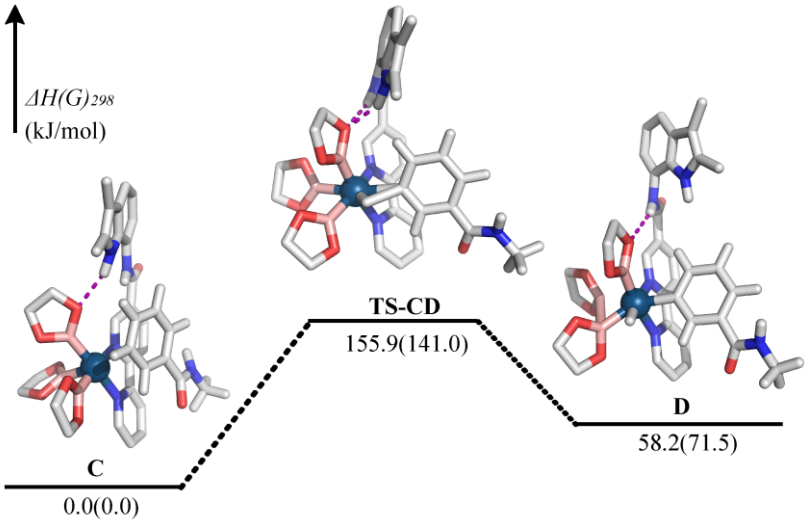


Figure S7. DFT calculated pathway for the C-H bond activation step in **BAIPy**-Ir catalyzed *meta*-selective C-H borylation of **1s** without substrate pre-binding to the catalyst via hydrogen bonds (BP86-D3/def2-TZVP and hydrogen bonds shown in purple dots; Enthalpy and Gibbs Free energies were reported)

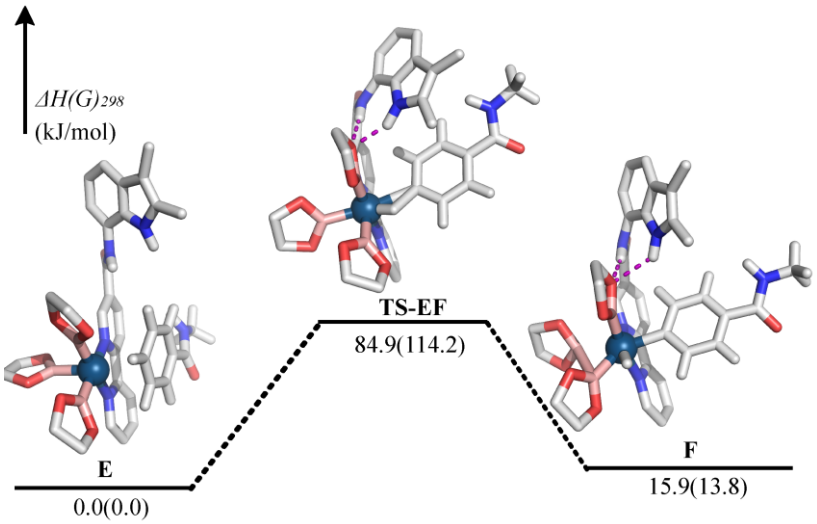


Figure S8. DFT calculated pathway for the C-H bond activation step in **BAIPy**-Ir catalyzed *para*-selective C-H borylation of **1s** without substrate pre-binding to the catalyst via hydrogen bonds (BP86-D3/def2-TZVP and hydrogen bonds shown in purple dots; Enthalpy and Gibbs Free energies were reported)

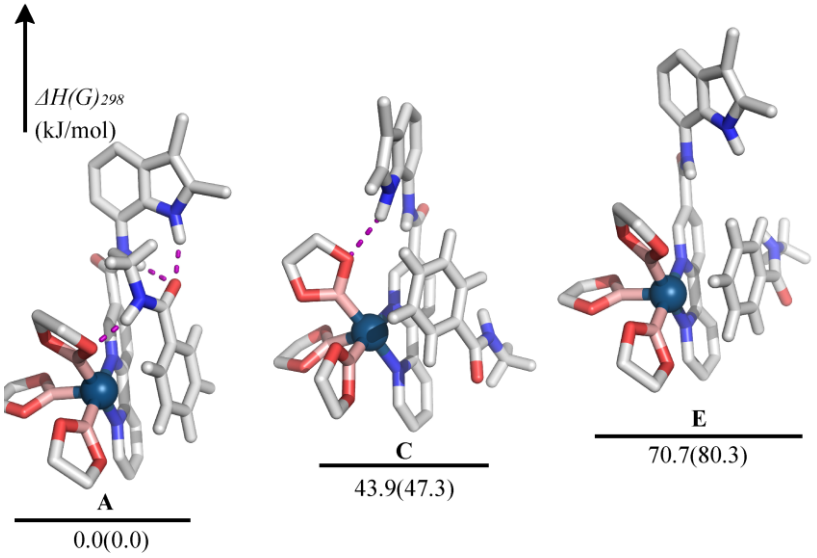


Figure S9. DFT calculated energies of the starting complexes for **BAIPy**-Ir catalyzed *ortho*-, *meta*-, and *para*-selective C-H borylation of **1s** (BP86-D3/def2-TZVP; hydrogen bonds shown in purple dots; Enthalpy and Gibbs Free energies were reported)

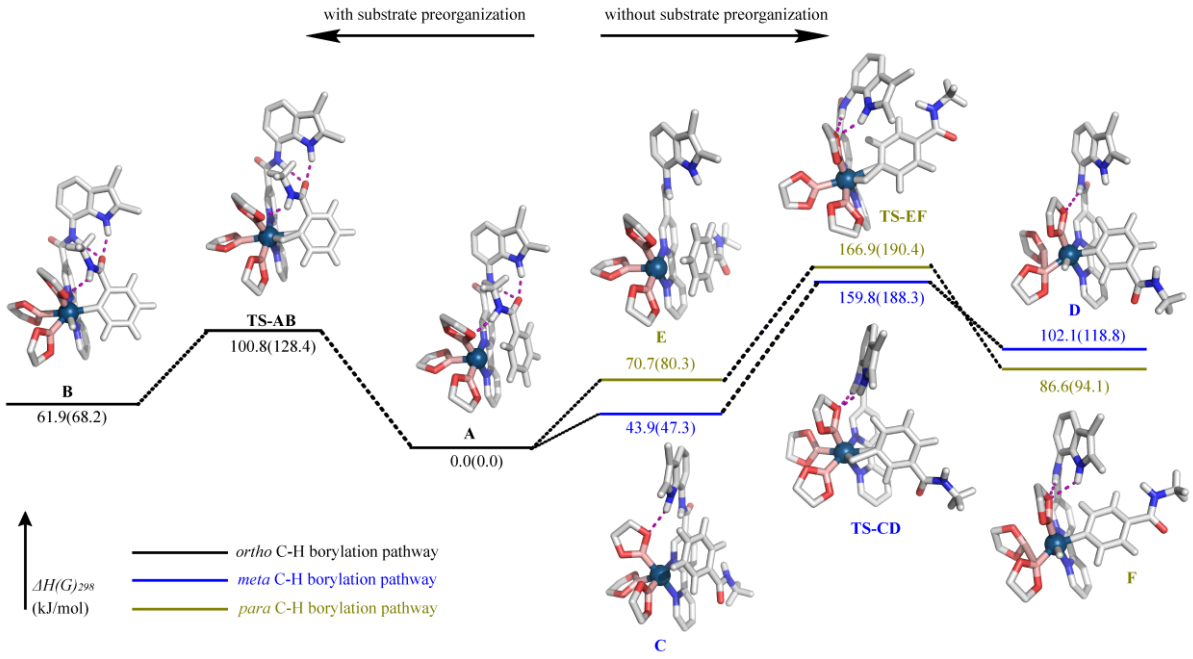


Figure S10. DFT calculated energies of the C-H activation step for **BAIPy**-Ir catalyzed *ortho*-, *meta*-, and *para*-selective C-H borylation of **1s** (BP86-D3/def2-TZVP and hydrogen bonds shown in purple dots; Enthalpy and Gibbs Free energies were reported)

Table S3. Gas phase thermochemical data (BP86-D3/def2-TZVP)[a]

species	SCF	ZPE	Enthalpy correction	Free energy correction	SCF+ZPE	Enthalpy	Free Energy
A	-2413.3984	0.7002	0.7515	0.6121	-2412.0861	-2412.0348	-2412.7863
B	-2413.3713	0.6979	0.7490	0.6110	-2412.0624	-2412.0113	-2412.7603
TS-AB	-2413.3498	0.6919	0.7408	0.6125	-2412.0454	-2411.9965	-2412.7373
C	-2413.3782	0.6989	0.7503	0.6098	-2412.0695	-2412.0180	-2412.7684
D	-2413.3480	0.6949	0.7452	0.6070	-2412.0461	-2411.9959	-2412.7411
TS-CD	-2413.3255	0.6915	0.7408	0.6108	-2412.0232	-2411.9739	-2412.7147
E	-2413.3659	0.6977	0.7478	0.6101	-2412.0581	-2412.0079	-2412.7557
F	-2413.3568	0.6965	0.7485	0.6063	-2412.0539	-2412.0019	-2412.7504
TS-EF	-2413.3243	0.6919	0.7410	0.6120	-2412.0203	-2411.9713	-2412.7123

[a] SCF = self-consistent field energy of the stationary point geometry (atomic units)

ZPE = Zero-point energy (atomic units)

H_{corr} and G_{corr} = correction to enthalpy and Gibb's free energy respectively at 298 K (atomic units)

H and ***G*** = enthalpy and Gibb's free energy (atomic units)

SUPPORTING INFORMATION

XYZ Coordinates

A

C	2.314000	2.348000	-1.758000
C	3.082000	1.262000	-1.321000
C	2.655000	-0.048000	-1.547000
C	1.427000	-0.274000	-2.217000
C	0.651000	0.819000	-2.638000
C	1.108000	2.130000	-2.415000
Ir	-0.482000	-0.184000	-0.264000
N	-0.856000	1.990000	-0.093000
C	-0.034000	2.679000	0.745000
C	-0.195000	4.060000	0.935000
C	-1.209000	4.737000	0.267000
C	-2.050000	4.016000	-0.583000
C	-1.841000	2.650000	-0.735000
C	1.013000	1.892000	1.420000
N	1.065000	0.574000	1.100000
C	2.006000	-0.200000	1.673000
C	2.936000	0.285000	2.593000
C	2.852000	1.633000	2.964000
C	1.899000	2.439000	2.362000
B	-1.711000	-0.547000	1.300000
O	-1.332000	-0.174000	2.598000
C	-2.452000	-0.415000	3.474000
C	-3.398000	-1.307000	2.649000
O	-2.995000	-1.092000	1.282000
B	-2.022000	-0.754000	-1.493000
O	-2.605000	-2.024000	-1.626000
C	-3.793000	-1.915000	-2.425000
C	-3.624000	-0.585000	-3.176000
O	-2.663000	0.147000	-2.386000
B	-0.198000	-2.197000	-0.189000
O	-0.387000	-3.014000	0.937000
C	-0.039000	-4.374000	0.615000
C	-0.003000	-4.396000	-0.917000
O	0.256000	-3.020000	-1.275000
H	1.117000	-1.275000	-2.509000
H	-2.452000	2.035000	-1.397000
H	0.472000	4.603000	1.601000
H	-2.859000	4.501000	-1.128000
H	-1.339000	5.810000	0.408000
H	1.834000	3.491000	2.634000
H	3.531000	2.021000	3.723000
H	1.975000	-1.254000	1.400000
H	-4.557000	-0.006000	-3.248000
H	-3.216000	-0.729000	-4.191000
H	-4.672000	-1.903000	-1.758000
H	-3.868000	-2.782000	-3.097000
H	4.017000	1.413000	-0.782000
H	2.663000	3.365000	-1.575000
H	-0.272000	0.650000	-3.190000
H	0.500000	2.974000	-2.743000
H	-2.097000	-0.899000	4.395000
H	-2.916000	0.552000	3.736000
H	-3.269000	-2.375000	2.889000
H	-4.458000	-1.039000	2.765000
H	0.945000	-4.609000	1.058000
H	-0.790000	-5.056000	1.037000
H	0.784000	-5.042000	-1.333000
H	-0.975000	-4.686000	-1.347000
C	7.467000	-4.476000	3.445000
C	6.534000	-4.041000	4.383000
C	5.589000	-3.042000	4.085000
C	5.557000	-2.438000	2.821000
C	6.505000	-2.871000	1.873000
C	7.454000	-3.891000	2.167000
N	4.608000	-1.457000	2.449000

N	6.730000	-2.458000	0.578000
C	7.766000	-3.204000	0.030000
C	8.246000	-4.088000	0.980000
C	3.931000	-0.606000	3.287000
O	4.071000	-0.531000	4.508000
C	9.373000	-5.062000	0.850000
H	8.193000	-5.251000	3.694000
H	6.526000	-4.480000	5.382000
H	4.881000	-2.718000	4.842000
H	6.107000	-1.837000	0.051000
H	10.184000	-4.836000	1.561000
H	9.041000	-6.091000	1.061000
H	9.807000	-5.055000	-0.159000
H	4.534000	-1.251000	1.445000
C	8.192000	-2.956000	-1.378000
H	8.981000	-3.657000	-1.675000
H	8.582000	-1.934000	-1.508000
H	7.353000	-3.075000	-2.083000
C	3.493000	-1.150000	-0.983000
O	4.603000	-0.894000	-0.450000
N	2.999000	-2.401000	-1.025000
C	3.702000	-3.526000	-0.427000
H	3.138000	-4.439000	-0.646000
H	4.714000	-3.622000	-0.838000
H	3.794000	-3.421000	0.665000
H	2.014000	-2.561000	-1.289000

B

C	3.363000	1.931000	-3.248000
C	3.752000	0.986000	-2.306000
C	2.798000	0.202000	-1.628000
C	1.404000	0.398000	-1.806000
C	1.060000	1.346000	-2.796000
C	2.000000	2.088000	-3.513000
Ir	-0.259000	-0.252000	-0.534000
N	-0.655000	1.932000	-0.301000
C	0.075000	2.532000	0.672000
C	-0.016000	3.913000	0.894000
C	-0.879000	4.679000	0.117000
C	-1.641000	4.046000	-0.866000
C	-1.497000	2.673000	-1.041000
C	0.944000	1.646000	1.460000
N	0.975000	0.332000	1.094000
C	1.774000	-0.518000	1.766000
C	2.574000	-0.119000	2.836000
C	2.495000	1.209000	3.263000
C	1.690000	2.092000	2.559000
B	-1.659000	-0.634000	1.071000
O	-1.773000	0.356000	2.053000
C	-2.725000	-0.087000	3.045000
C	-2.902000	-1.588000	2.756000
O	-2.405000	-1.759000	1.411000
B	-2.198000	-0.777000	-1.138000
O	-2.657000	-2.058000	-1.466000
C	-4.092000	-1.996000	-1.504000
C	-4.390000	-0.517000	-1.791000
O	-3.229000	0.175000	-1.280000
B	0.093000	-2.266000	-0.555000
O	0.245000	-3.059000	0.591000
C	0.256000	-4.449000	0.215000
C	0.141000	-4.448000	-1.329000
O	0.188000	-3.060000	-1.712000
H	-0.897000	-0.557000	-1.996000
H	-2.081000	2.123000	-1.776000
H	0.588000	4.390000	1.663000
H	-2.338000	4.601000	-1.492000
H	-0.955000	5.754000	0.278000

H	1.636000	3.134000	2.865000
H	3.073000	1.531000	4.129000
H	1.732000	-1.557000	1.445000
H	-5.288000	-0.145000	-1.278000
H	-4.481000	-0.315000	-2.872000
H	-4.485000	-2.308000	-0.522000
H	-4.469000	-2.675000	-2.282000
H	4.809000	0.821000	-2.089000
H	4.109000	2.524000	-3.779000
H	0.005000	1.530000	-3.010000
H	1.664000	2.801000	-4.269000
H	-2.326000	0.116000	4.048000
H	-3.662000	0.479000	2.911000
H	-2.301000	-2.217000	3.432000
H	-3.950000	-1.917000	2.801000
H	1.186000	-4.915000	0.576000
H	-0.596000	-4.949000	0.697000
H	0.963000	-4.989000	-1.822000
H	-0.814000	-4.873000	-1.674000
C	7.385000	-4.608000	3.428000
C	6.373000	-4.396000	4.362000
C	5.346000	-3.457000	4.147000
C	5.311000	-2.694000	2.974000
C	6.340000	-2.899000	2.034000
C	7.375000	-3.854000	2.242000
N	4.302000	-1.758000	2.668000
N	6.579000	-2.287000	0.823000
C	7.718000	-2.834000	0.245000
C	8.239000	-3.798000	1.091000
C	3.488000	-1.084000	3.541000
O	3.474000	-1.190000	4.767000
C	9.464000	-4.633000	0.894000
H	8.172000	-5.341000	3.614000
H	6.366000	-4.969000	5.290000
H	4.574000	-3.305000	4.897000
H	5.954000	-1.605000	0.380000
H	10.201000	-4.461000	1.695000
H	9.224000	-5.709000	0.908000
H	9.959000	-4.418000	-0.062000
H	4.280000	-1.413000	1.695000
C	8.184000	-2.344000	-1.084000
H	9.080000	-2.886000	-1.406000
H	8.431000	-1.271000	-1.054000
H	7.412000	-2.479000	-1.859000
C	3.402000	-0.883000	-0.795000
O	4.347000	-0.666000	0.007000
N	2.942000	-2.126000	-1.032000
C	3.432000	-3.305000	-0.338000
H	3.079000	-4.194000	-0.872000
H	4.528000	-3.315000	-0.317000
H	3.068000	-3.349000	0.700000
H	2.145000	-2.229000	-1.662000

TS-AB

C	3.180000	1.993000	-3.113000
C	3.608000	1.002000	-2.236000
C	2.689000	0.140000	-1.608000
C	1.297000	0.322000	-1.785000
C	0.898000	1.302000	-2.714000
C	1.812000	2.125000	-3.372000
Ir	-0.295000	-0.326000	-0.324000
N	-0.668000	1.903000	-0.079000
C	0.041000	2.508000	0.908000
C	-0.094000	3.882000	1.156000
C	-0.971000	4.640000	0.388000
C	-1.704000	4.005000	-0.614000
C	-1.522000	2.639000	-0.814000

C	0.957000	1.648000	1.677000
N	1.014000	0.342000	1.307000
C	1.879000	-0.477000	1.931000
C	2.739000	-0.049000	2.943000
C	2.627000	1.273000	3.384000
C	1.741000	2.123000	2.739000
B	-1.774000	-0.638000	1.160000
O	-1.672000	-0.004000	2.403000
C	-2.867000	-0.288000	3.163000
C	-3.547000	-1.435000	2.392000
O	-2.939000	-1.404000	1.084000
B	-1.942000	-0.781000	-1.498000
O	-2.422000	-2.049000	-1.822000
C	-3.739000	-1.902000	-2.377000
C	-3.789000	-0.440000	-2.849000
O	-2.763000	0.211000	-2.067000
B	-0.086000	-2.340000	-0.072000
O	-0.093000	-2.986000	1.175000
C	0.087000	-4.403000	0.977000
C	-0.053000	-4.602000	-0.544000
O	0.130000	-3.285000	-1.098000
H	0.040000	-0.805000	-1.831000
H	-2.082000	2.085000	-1.567000
H	0.489000	4.360000	1.941000
H	-2.410000	4.552000	-1.240000
H	-1.081000	5.710000	0.573000
H	1.663000	3.161000	3.058000
H	3.244000	1.615000	4.215000
H	1.846000	-1.519000	1.621000
H	-4.756000	0.046000	-2.659000
H	-3.539000	-0.338000	-3.919000
H	-4.479000	-2.101000	-1.583000
H	-3.880000	-2.625000	-3.193000
H	4.670000	0.868000	-2.021000
H	3.905000	2.646000	-3.600000
H	-0.168000	1.435000	-2.911000
H	1.456000	2.878000	-4.078000
H	-2.587000	-0.566000	4.189000
H	-3.492000	0.620000	3.198000
H	-3.346000	-2.418000	2.850000
H	-4.634000	-1.304000	2.293000
H	1.081000	-4.696000	1.353000
H	-0.678000	-4.948000	1.550000
H	0.697000	-5.289000	-0.963000
H	-1.057000	-4.959000	-0.825000
C	7.663000	-4.457000	3.298000
C	6.758000	-4.175000	4.318000
C	5.705000	-3.255000	4.148000
C	5.534000	-2.580000	2.931000
C	6.457000	-2.856000	1.902000
C	7.515000	-3.794000	2.067000
N	4.488000	-1.668000	2.675000
N	6.556000	-2.342000	0.627000
C	7.630000	-2.932000	-0.028000
C	8.248000	-3.829000	0.827000
C	3.742000	-0.967000	3.589000
O	3.849000	-1.019000	4.814000
C	9.448000	-4.681000	0.560000
H	8.472000	-5.174000	3.449000
H	6.857000	-4.675000	5.283000
H	5.020000	-3.047000	4.965000
H	5.896000	-1.676000	0.212000
H	10.272000	-4.443000	1.253000
H	9.219000	-5.751000	0.692000
H	9.828000	-4.547000	-0.462000
H	4.378000	-1.366000	1.695000
C	7.941000	-2.549000	-1.436000

H	8.806000	-3.110000	-1.809000
H	8.174000	-1.475000	-1.520000
H	7.092000	-2.752000	-2.108000
C	3.314000	-0.942000	-0.783000
O	4.321000	-0.711000	-0.066000
N	2.803000	-2.179000	-0.911000
C	3.297000	-3.327000	-0.169000
H	2.859000	-4.231000	-0.603000
H	4.391000	-3.390000	-0.230000
H	3.021000	-3.278000	0.897000
H	1.932000	-2.306000	-1.428000

C

C	3.3358592	1.6264111	-1.0409786
C	3.7777583	0.2938755	-1.0661452
C	2.9877177	-0.6893559	-1.6492179
C	1.7411909	-0.3609826	-2.2145682
C	1.3144982	0.9765523	-2.2158096
C	2.1145368	1.9798379	-1.6197632
Ir	-0.2673339	-0.2027680	-0.3213489
N	-1.0400714	1.8900352	-0.3931152
C	-0.5571579	2.7463679	0.5520365
C	-1.0930577	4.0302984	0.7090064
C	-2.1180490	4.4554828	-0.1295313
C	-2.5908106	3.5791460	-1.1061067
C	-2.0337024	2.3071512	-1.2003102
C	0.5632550	2.2365830	1.3561923
N	0.8525844	0.9216666	1.1716500
C	1.9217831	0.3997371	1.7848761
C	2.8071250	1.1477499	2.5616498
C	2.4803773	2.4865238	2.8152904
C	1.3478493	3.0254799	2.2144332
B	-1.7742928	-0.7014466	0.9287401
O	-1.6722260	-0.4579592	2.3095464
C	-2.9417500	-0.7940419	2.9071795
C	-3.6583487	-1.6279882	1.8308346
O	-3.0120382	-1.2521239	0.6001719
B	-1.3454133	-1.0837977	-1.8289671
O	-1.0035977	-2.2658025	-2.5143551
C	-2.0451158	-2.5792842	-3.4584111
C	-2.8579527	-1.2776098	-3.5847647
O	-2.4840240	-0.5064146	-2.4273728
B	0.3298754	-2.0882177	0.1953331
O	-0.5225178	-3.1193121	0.6257571
C	0.2395656	-4.1354470	1.2912200
C	1.6700696	-3.9119936	0.7969332
O	1.6905145	-2.5226705	0.3817107
H	1.1676132	-1.1227897	-2.7402718
H	-2.3810510	1.5695440	-1.9248786
H	-0.7096295	4.6921191	1.4837260
H	-3.3854021	3.8689149	-1.7924577
H	-2.5400493	5.4546831	-0.0211320
H	1.0933955	4.0719547	2.3776947
H	3.1290660	3.0796258	3.4605784
H	2.0500747	-0.6708080	1.6247346
H	-3.9444565	-1.4472024	-3.5750859
H	-2.5968470	-0.7102043	-4.4942198
H	-2.6516956	-3.4069743	-3.0555249
H	-1.5965655	-2.8994045	-4.4100878
H	4.7580899	0.0378669	-0.6597057
H	3.9890625	2.3867200	-0.6095142
H	0.4240263	1.2865988	-2.7616080
H	2.6792146	3.9058437	-0.0096851
H	-2.7720988	-1.3481857	3.8415367
H	-3.4855731	0.1375996	3.1402325
H	-3.5140267	-2.7102506	1.9878074
H	-4.7347785	-1.4151341	1.7613314

H	0.1556915	-3.9964331	2.3830795
H	-0.1546088	-5.1274892	1.0281939
H	2.4378518	-4.0775796	1.5659221
H	1.8979405	-4.5455657	-0.0762898
C	7.8092514	-3.1644526	2.3831958
C	7.6972346	-2.1609959	3.3430596
C	6.6084128	-1.2685103	3.3701815
C	5.5885795	-1.3777879	2.4181793
C	5.6829051	-2.4103092	1.4656892
C	6.7874426	-3.2995056	1.4257993
N	4.4821093	-0.5220898	2.3131140
N	4.8418230	-2.7346729	0.4153753
C	5.3772502	-3.8247896	-0.2729372
C	6.5748150	-4.1895336	0.3119149
C	4.0795477	0.5445857	3.0849133
O	4.6758225	0.9865913	4.0653955
C	7.5135460	-5.2719793	-0.1161494
H	8.6716411	-3.8322595	2.3722841
H	8.4783954	-2.0461985	4.0955405
H	6.5492628	-0.4794137	4.1152939
H	3.8633171	-2.4556155	0.3219404
H	8.4915794	-4.8618685	-0.4150726
H	7.7019173	-5.9824734	0.7042378
H	7.1203705	-5.8427150	-0.9676886
H	3.9362222	-0.6486162	1.4651489
C	4.6878336	-4.3503064	-1.4867697
H	5.0417874	-5.3586651	-1.7315289
H	4.8728531	-3.7095649	-2.3646063
H	3.5984544	-4.4005001	-1.3455160
C	1.6036087	3.3907604	-1.6859564
O	0.7461268	3.7411293	-2.5017818
N	2.1368885	4.2721706	-0.7835109
C	1.6654465	5.6437921	-0.7167053
H	1.9517812	6.0749411	0.2500030
H	2.0989387	6.2558553	-1.5215695
H	0.5720212	5.6707426	-0.8261846
H	3.3328868	-1.7200079	-1.6937980

D

C	3.4961092	1.6046358	-3.1124394
C	3.7367782	0.7561126	-2.0310814
C	2.6702094	0.2245183	-1.2978982
C	1.3295753	0.5229628	-1.6085100
C	1.1180714	1.3826901	-2.6986242
C	2.1711808	1.9232734	-3.4508115
Ir	-0.3477535	-0.1594163	-0.4558475
N	-0.8736066	2.0040880	-0.2857612
C	-0.1269795	2.7043835	0.6112947
C	-0.1851165	4.1029831	0.6719910
C	-1.0119528	4.7934946	-0.2075403
C	-1.7699574	4.0672224	-1.1262215
C	-1.6762179	2.6785503	-1.1274334
C	0.7470212	1.8981296	1.4721856
N	0.7495274	0.5593497	1.2208427
C	1.5325801	-0.2518280	1.9497408
C	2.4292141	0.2187831	2.9024116
C	2.4112976	1.5869261	3.2034333
C	1.5557511	2.4195657	2.4946820
B	-1.5299068	-0.8913882	1.1794831
O	-2.3807194	-0.1017536	1.9516810
C	-2.6624841	-0.7870681	3.1905246
C	-1.8652272	-2.1126801	3.1111055
O	-1.2056649	-2.0799967	1.8288265
B	-2.3129452	-0.7970693	-0.8432825
O	-2.8115057	-2.0986919	-0.9688414
C	-4.2225673	-2.0188420	-1.2328805
C	-4.4589512	-0.5558881	-1.6529553

O	-3.3085133	0.1491084	-1.1517881
B	0.4590039	-2.0394586	-0.6614659
O	1.5746058	-2.5114864	0.0868457
C	1.7591800	-3.9126623	-0.2161862
C	0.9874080	-4.1127359	-1.5306584
O	0.0714996	-3.0049381	-1.5842840
H	-0.9695356	-0.5700090	-1.8874755
H	-2.2611058	2.0608295	-1.8052367
H	0.4262056	4.6489979	1.3883256
H	-2.4214800	4.5631055	-1.8441312
H	-1.0555150	5.8824481	-0.1822210
H	1.5301205	3.4846492	2.7166782
H	3.0790802	1.9688923	3.9759386
H	1.4220502	-1.3095676	1.7185311
H	-5.3699334	-0.1222526	-1.2158350
H	-4.5012694	-0.4422244	-2.7495234
H	-4.7730432	-2.2778681	-0.3126214
H	-4.4873771	-2.7410977	-2.0182571
H	4.7662199	0.5177970	-1.7508326
H	4.3332170	2.0500683	-3.6536561
H	0.1077606	1.6707081	-2.9945691
H	3.3841732	2.1501961	-5.6902082
H	-2.3416927	-0.1500615	4.0285452
H	-3.7481465	-0.9479211	3.2686169
H	-1.1021711	-2.1942385	3.8999940
H	-2.5125953	-3.0009790	3.1560028
H	2.8341705	-4.1280153	-0.3008221
H	1.3358724	-4.5096469	0.6078944
H	1.6499110	-4.0714094	-2.4113696
H	0.4221109	-5.0554097	-1.5552116
C	7.0337337	-4.4446599	3.3805372
C	6.1848225	-4.1126662	4.4347509
C	5.0978282	-3.2366312	4.2592127
C	4.8322399	-2.6757127	3.0084521
C	5.6911593	-3.0021566	1.9481868
C	6.7974541	-3.8787043	2.1159757
N	3.7610193	-1.7830640	2.7661654
N	5.7006365	-2.5730383	0.6369046
C	6.8032939	-3.1182001	-0.0228200
C	7.4894706	-3.9383440	0.8526604
C	3.4473606	-0.6819309	3.5387022
O	3.9827356	-0.4072624	4.6087767
C	8.7283111	-4.7346890	0.5918114
H	7.8760601	-5.1202974	3.5359752
H	6.3614169	-4.5352893	5.4244709
H	4.4580845	-2.9735118	5.0987361
H	5.1118924	-1.8437077	0.2514452
H	9.5362723	-4.4479846	1.2836486
H	8.5515479	-5.8125978	0.7348138
H	9.1025876	-4.5929196	-0.4305613
H	3.2782397	-1.8866661	1.8732175
C	7.0749780	-2.7557841	-1.4430797
H	7.9661263	-3.2780906	-1.8100636
H	7.2529236	-1.6736728	-1.5557335
H	6.2325625	-3.0207620	-2.1011056
C	1.8134025	2.8559294	-4.5718477
O	0.7963009	3.5563492	-4.5545534
N	2.6954067	2.8913058	-5.6239418
C	2.4279961	3.6997810	-6.8011008
H	3.3596604	3.8478937	-7.3615628
H	1.6778667	3.2359387	-7.4629223
H	2.0350689	4.6728440	-6.4827140
H	2.8883420	-0.4469472	-0.4628404

TS-CD

C	3.8198333	1.6349854	-2.7964066
C	3.9792379	0.4782229	-2.0149197

C	2.8557569	-0.1486854	-1.4443175
C	1.5630324	0.3731536	-1.6408750
C	1.4127170	1.5143165	-2.4399570
C	2.5274601	2.1593749	-3.0175453
Ir	-0.2174313	-0.3578239	-0.1415559
N	-0.8124258	1.8406803	-0.2971815
C	0.0557972	2.6848228	0.3350159
C	0.1527515	4.0430479	-0.0253867
C	-0.6708177	4.5476639	-1.0362838
C	-1.6047389	3.6885984	-1.6318550
C	-1.6406017	2.3444581	-1.2366672
C	0.9094814	2.0627143	1.3654483
N	0.8114134	0.7050819	1.4610619
C	1.5647618	0.0376229	2.3490207
C	2.5922266	0.6506842	3.0793976
C	2.6716037	2.0569947	3.0407064
C	1.8022181	2.7650110	2.2049079
B	-1.5259523	-1.1196218	1.3149965
O	-2.8715501	-0.8007728	1.5025350
C	-3.4060576	-1.6811387	2.5021457
C	-2.1631000	-2.2521608	3.2201917
O	-1.0829891	-2.0152255	2.3011398
B	-1.8490391	-1.1694630	-1.1368525
O	-2.4135107	-2.4346622	-0.9752264
C	-3.7214242	-2.4204675	-1.5513656
C	-3.7159630	-1.1981438	-2.4950107
O	-2.6231730	-0.3982429	-2.0205455
B	0.6103243	-2.2183652	0.0585717
O	1.7298677	-2.5191920	0.9275257
C	1.6882145	-3.9474843	1.1581760
C	1.0287240	-4.4821490	-0.1188566
O	0.2270968	-3.3907427	-0.5776632
H	0.0337200	-0.6899291	-1.7086160
H	-2.3096361	1.6084274	-1.7082176
H	0.9003641	4.6907276	0.4512243
H	-2.2749117	4.0380889	-2.4294512
H	-0.5693049	5.5900440	-1.3682049
H	1.8470518	3.8615260	2.1661758
H	3.4417721	2.5613421	3.6434866
H	1.3533795	-1.0381524	2.4095979
H	-4.6579045	-0.6122638	-2.4551306
H	-3.5275531	-1.4834998	-3.5547271
H	-4.4746228	-2.3044138	-0.7385847
H	-3.9177382	-3.3778873	-2.0777317
H	4.9871459	0.0778468	-1.8195957
H	4.7088280	2.1511657	-3.1931009
H	0.4242970	1.9587811	-2.6269362
H	3.8385575	2.9904810	-5.0424549
H	-4.0821464	-1.1196867	3.1799432
H	-3.9973589	-2.4815392	2.0023672
H	-1.9506528	-1.7260049	4.1779471
H	-2.2445224	-3.3383226	3.4320451
H	2.7126491	-4.3320992	1.3362831
H	1.0624005	-4.1387789	2.0569234
H	1.7827571	-4.7470379	-0.8961224
H	0.3912508	-5.3720949	0.0611507
C	7.4525918	-3.6684185	2.6517160
C	7.1590137	-3.0297171	3.8637237
C	5.9752215	-2.2740638	4.0467467
C	5.0444480	-2.1482596	3.0001908
C	5.3404943	-2.7935809	1.7745830
C	6.5348178	-3.5515642	1.5815163
N	3.8679841	-1.3717480	3.0598069
N	4.6502748	-2.7866586	0.5768605
C	5.3510318	-3.5347576	-0.3683739
C	6.5234594	-4.0168925	0.2103746
C	3.7052819	-0.1536556	3.7038766

O	4.4477440	0.2918669	4.5754518
C	7.5988683	-4.8414578	-0.4304766
H	8.3836027	-4.2421688	2.5282010
H	7.8664249	-3.1071593	4.7034167
H	5.7764646	-1.7571794	4.9930987
H	3.6888525	-2.4445165	0.4474560
H	8.5853595	-4.3314767	-0.3826061
H	7.7220848	-5.8202284	0.0817627
H	7.3850784	-5.0509723	-1.4970772
H	3.1770300	-1.5841242	2.3303570
C	4.7995239	-3.6859891	-1.7503324
H	5.5055746	-4.2349873	-2.4004653
H	4.5967657	-2.6992297	-2.2195989
H	3.8376551	-4.2441178	-1.7521739
C	2.2623522	3.4289317	-3.7868246
O	1.3017540	4.1636003	-3.5258747
N	3.1558375	3.7080210	-4.7971398
C	3.0318909	4.8737453	-5.6493970
H	3.9644793	5.4773455	-5.6564222
H	2.7851291	4.5969284	-6.6975991
H	2.2057964	5.4901358	-5.2469117
H	2.9983190	-1.0348468	-0.8098152

E

C	2.4554303	2.2861134	-1.5989489
C	3.1625081	1.0829529	-1.3740214
C	2.6181582	-0.1328159	-1.7627755
C	1.3494573	-0.1881537	-2.3760935
C	0.6566667	1.0093990	-2.6311395
C	1.2274254	2.2364245	-2.2594857
Ir	-0.4407021	-0.0948782	-0.3315772
N	-0.9889245	2.0604901	-0.2317267
C	-0.1572519	2.8516284	0.5035118
C	-0.2785196	4.2470544	0.4854409
C	-1.2824988	4.8399661	-0.2710349
C	-2.1573003	4.0187245	-0.9851902
C	-1.9767997	2.6388045	-0.9411047
C	0.8970930	2.1537128	1.2556100
N	1.0014754	0.8192275	1.0200099
C	1.9651022	0.1198826	1.6407852
C	2.9030340	0.7013368	2.4942077
C	2.7621579	2.0665322	2.7885629
C	1.7521810	2.7883301	2.1704908
B	-1.6285285	-0.5912873	1.2283710
O	-1.3505886	-0.0792213	2.5082020
C	-2.4204356	-0.4752687	3.3888487
C	-3.1721479	-1.5714497	2.6101508
O	-2.7813013	-1.3758960	1.2380541
B	-1.9016880	-0.8365464	-1.5655085
O	-2.3529686	-2.1547726	-1.6966115
C	-3.5320374	-2.1683869	-2.5165446
C	-3.4913335	-0.8272174	-3.2679561
O	-2.6181051	-0.0018782	-2.4678702
B	0.1841695	-2.0379342	-0.1773626
O	0.2968076	-2.7162978	1.0593717
C	0.9087889	-4.0020609	0.8371821
C	0.8312768	-4.1996811	-0.6847602
O	0.6709329	-2.8689689	-1.2072373
H	0.9636362	-1.1426529	-2.7275619
H	-2.5985029	1.9494904	-1.5140306
H	0.4343743	4.8674685	1.0243986
H	-2.9600702	4.4367804	-1.5917234
H	-1.3703410	5.9254417	-0.3132257
H	1.6319547	3.8477953	2.3885283
H	3.4487131	2.5268705	3.4993198
H	1.9251427	-0.9559315	1.4626543
H	-4.4771979	-0.3466690	-3.3516035

H	-3.0594585	-0.9290288	-4.2782422
H	-4.4192754	-2.2485971	-1.8650626
H	-3.5055262	-3.0385415	-3.1887416
H	4.1502196	1.1047389	-0.9091704
H	3.1548777	-1.0665584	-1.5883590
H	-0.2971197	0.9850456	-3.1581436
H	4.0320043	2.7677061	0.3718099
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H	-3.0584508	0.4014453	3.5938134
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H	-0.0447275	-4.8028676	-0.9755812
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C	5.6730187	-2.5052527	4.1056950
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C	8.7218707	-5.2059598	0.5991852
H	8.0798807	-4.9043073	3.6042410
H	6.8161040	-3.7646366	5.4239835
H	5.1332557	-2.0180715	4.9138414
H	5.6954176	-1.7723358	-0.0690731
H	9.6187220	-4.9639616	1.1906924
H	8.3696180	-6.1925844	0.9396077
H	9.0330769	-5.3084060	-0.4485101
H	3.9156423	-1.3727075	1.5549011
C	7.2385235	-3.3692885	-1.6822808
H	8.0416442	-4.0510907	-1.9848548
H	7.5120339	-2.3593447	-2.0290278
H	6.3240028	-3.6664778	-2.2195559
C	2.9188236	3.6316101	-1.1196274
O	2.4422291	4.6870027	-1.5476637
N	3.8908497	3.6266600	-0.1500976
C	4.2794885	4.8695106	0.4941252
H	5.1782946	4.6982688	1.0977697
H	4.4899244	5.6253482	-0.2714121
H	3.4786768	5.2661904	1.1419510
H	0.7038874	3.1753775	-2.4412135

F

C	3.8103749	1.5613137	-2.6868651
C	3.9327314	0.9968116	-1.4086817
C	2.8089194	0.4966760	-0.7465013
C	1.5217413	0.5157212	-1.3161852
C	1.4252380	1.0881268	-2.6026230
C	2.5335144	1.6108424	-3.2668812
Ir	-0.2341730	-0.1970140	-0.3130975
N	-0.8966085	1.9445729	-0.3420801
C	-0.2382897	2.7551614	0.5331891
C	-0.3878436	4.1477327	0.4893612
C	-1.2180227	4.7187218	-0.4687834
C	-1.8856408	3.8804699	-1.3633673
C	-1.6998680	2.5045001	-1.2641643
C	0.6323295	2.0686681	1.4949856
N	0.6187791	0.7092131	1.4228733
C	1.3990501	-0.0083520	2.2432673
C	2.3797709	0.5698147	3.0446754

C	2.3811071	1.9659171	3.1652958
C	1.4755625	2.7093231	2.4172428
B	-1.5077138	-1.0053542	1.2145742
O	-2.5566022	-0.3481526	1.8573425
C	-2.7817315	-0.9978847	3.1300314
C	-2.0284750	-2.3352384	3.0180977
O	-1.0936470	-2.1281151	1.9364281
B	-2.1000829	-1.0010192	-0.8596883
O	-2.4963253	-2.3416302	-0.9279499
C	-3.8743165	-2.3825521	-1.3393985
C	-4.1469709	-0.9840797	-1.9206776
O	-3.1081362	-0.1578462	-1.3595054
B	0.7173547	-2.0169751	-0.3227435
O	1.8211969	-2.3527779	0.5252196
C	1.9855773	-3.7939490	0.4542809
C	1.3795312	-4.1488628	-0.9045773
O	0.4355071	-3.0909388	-1.1565322
H	-0.6437381	-0.7371354	-1.7734434
H	-2.2140243	1.8015366	-1.9167147
H	0.1459115	4.7802536	1.1964934
H	-2.5462595	4.2807005	-2.1315696
H	-1.3389980	5.8008627	-0.5184325
H	1.4719321	3.7948314	2.4953587
H	3.1200694	2.4414363	3.8109206
H	1.2580876	-1.0842788	2.1747751
H	-5.1277499	-0.5794031	-1.6333171
H	-4.0622865	-0.9697049	-3.0203121
H	-4.5026684	-2.5915121	-0.4574271
H	-4.0107372	-3.1901646	-2.0722779
H	4.8971185	0.9766954	-0.8947376
H	2.9513489	0.1010707	0.2614510
H	0.4527551	1.1369890	-3.0975760
H	6.3041428	0.9155006	-2.5010913
H	-2.3738709	-0.3553619	3.9275224
H	-3.8618414	-1.1199529	3.2901338
H	-1.4769472	-2.5997761	3.9309289
H	-2.6962316	-3.1695167	2.7483136
H	3.0502322	-4.0454638	0.5480105
H	1.4239192	-4.2461604	1.2869456
H	2.1383645	-4.1530265	-1.7060300
H	0.8558712	-5.1146755	-0.9041609
C	7.3375303	-3.6305298	2.3219639
C	6.9307905	-3.2076430	3.5863833
C	5.7581746	-2.4514387	3.7762758
C	4.9625866	-2.0978379	2.6836450
C	5.3819575	-2.5052180	1.4039484
C	6.5586413	-3.2778075	1.2048785
N	3.7715359	-1.3483199	2.7711091
N	4.8441566	-2.2445859	0.1613074
C	5.6213367	-2.8526686	-0.8187934
C	6.6889141	-3.4941559	-0.2149421
C	3.5358730	-0.2417272	3.5634419
O	4.2416008	0.1238025	4.4985113
C	7.7886644	-4.2674385	-0.8702710
H	8.2485824	-4.2177977	2.1989070
H	7.5288543	-3.4686886	4.4602496
H	5.4613578	-2.1244201	4.7701447
H	3.9488280	-1.7970815	-0.0263073
H	8.7756571	-3.8290478	-0.6524231
H	7.8149558	-5.3079186	-0.5089745
H	7.6720681	-4.3008762	-1.9614959
H	3.1100649	-1.5182955	2.0095985
C	5.2154733	-2.7354466	-2.2492188
H	6.0125923	-3.0899046	-2.9130958
H	4.9797122	-1.6923230	-2.5134293
H	4.3117555	-3.3290638	-2.4638491
C	4.9545281	2.1521013	-3.4543640

O	4.7896384	2.9862271	-4.3503590
N	6.2102429	1.7242712	-3.1043033
C	7.3818224	2.2100981	-3.8134064
H	8.2843500	1.8846870	-3.2820949
H	7.4158959	1.8406652	-4.8511552
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TS-EF

C	4.2090061	0.8280511	-2.5318092
C	4.1314888	0.6233507	-1.1402058
C	2.8859360	0.4333034	-0.5207460
C	1.6937025	0.4503102	-1.2678162
C	1.7674165	0.7328118	-2.6482550
C	3.0116341	0.9306635	-3.2708783
Ir	-0.2724613	-0.1741232	0.1628300
N	-0.9805838	1.9812254	0.2166080
C	-0.4302489	2.7735094	1.1843589
C	-0.7669752	4.1383637	1.2964470
C	-1.6784441	4.6985493	0.3958503
C	-2.2256419	3.8784995	-0.6042825
C	-1.8513062	2.5298204	-0.6578562
C	0.5397679	2.1075115	2.0734527
N	0.6200457	0.7528617	1.9291361
C	1.5278797	0.0605505	2.6381884
C	2.5404836	0.6793023	3.3856208
C	2.4326596	2.0685019	3.5994458
C	1.4010266	2.7752357	2.9719395
B	-1.7613866	-1.0312185	1.3495918
O	-3.0601228	-0.5411941	1.4893391
C	-3.7504494	-1.3456950	2.4573861
C	-2.8187033	-2.5584165	2.6998333
O	-1.5535227	-2.1550355	2.1547000
B	-1.6852055	-0.8608997	-1.1876699
O	-2.3992671	-2.0559137	-1.1291710
C	-3.4924779	-1.9865656	-2.0479081
C	-3.1421165	-0.8048115	-2.9811949
O	-2.1370321	-0.0716951	-2.2627533
B	0.5463188	-2.0510743	0.2387883
O	1.6627460	-2.4041088	1.0843659
C	1.7698569	-3.8459551	1.0773848
C	1.1193075	-4.2346900	-0.2582617
O	0.2314138	-3.1500636	-0.5479206
H	0.2479265	-0.4439998	-1.3454914
H	-2.2374176	1.8425356	-1.4264165
H	-0.3211720	4.7547248	2.0887216
H	-2.9393124	4.2727257	-1.3416308
H	-1.9544754	5.7607019	0.4718291
H	1.3192736	3.8615582	3.1110640
H	3.1977781	2.5718069	4.2092384
H	1.4660255	-1.0292387	2.5145093
H	-4.0097652	-0.1460664	-3.1942210
H	-2.7183592	-1.1450854	-3.9522586
H	-4.4332131	-1.8015039	-1.4813207
H	-3.5954937	-2.9503620	-2.5886770
H	5.0467314	0.5895968	-0.5273665
H	2.8711336	0.2538351	0.5643449
H	0.8446666	0.7708549	-3.2501880
H	6.3627269	-0.4235512	-1.9456734
H	-3.9124822	-0.7482770	3.3829631
H	-4.7450228	-1.6412056	2.0619480
H	-2.7045260	-2.8108928	3.7750144
H	-3.1704348	-3.4676024	2.1632529
H	2.8360564	-4.1397597	1.1608550
H	1.2091578	-4.2475849	1.9490877
H	1.8738749	-4.3229173	-1.0727885
H	0.5521787	-5.1864467	-0.2033058

C	7.8485263	-2.2649189	1.2603333
C	7.7503705	-1.8481725	2.5934793
C	6.5109349	-1.4971788	3.1825493
C	5.3192223	-1.5820459	2.4404364
C	5.4103838	-2.0539309	1.1051457
C	6.6654524	-2.3557869	0.4898800
N	4.0600010	-1.1276977	2.8950652
N	4.4300918	-2.2133802	0.1471095
C	5.0081365	-2.5436213	-1.0707500
C	6.3902373	-2.6586926	-0.8995745
C	3.8373359	-0.0232310	3.7112710
O	4.6609610	0.4478702	4.4911848
C	7.4036295	-3.0608112	-1.9297811
H	8.8256182	-2.5058075	0.8151867
H	8.6607706	-1.7702402	3.2069045
H	6.4644172	-1.1207626	4.2108342
H	3.4316435	-1.9945429	0.2643053
H	8.3147978	-2.4296150	-1.8700514
H	7.7360898	-4.1133995	-1.7948918
H	7.0026061	-2.9721245	-2.9591764
H	3.2690858	-1.4154881	2.3079337
C	4.1584958	-2.6994527	-2.2924758
H	4.7023243	-2.3455376	-3.1900390
H	3.2326272	-2.0940914	-2.2101531
H	3.8666467	-3.7570010	-2.4732499
C	5.5193080	0.9408604	-3.2689063
O	5.6338410	1.6013812	-4.3058653
N	6.5612564	0.2367719	-2.7058943
C	7.8916843	0.2489701	-3.2788655
H	8.6599144	0.3935086	-2.4911454
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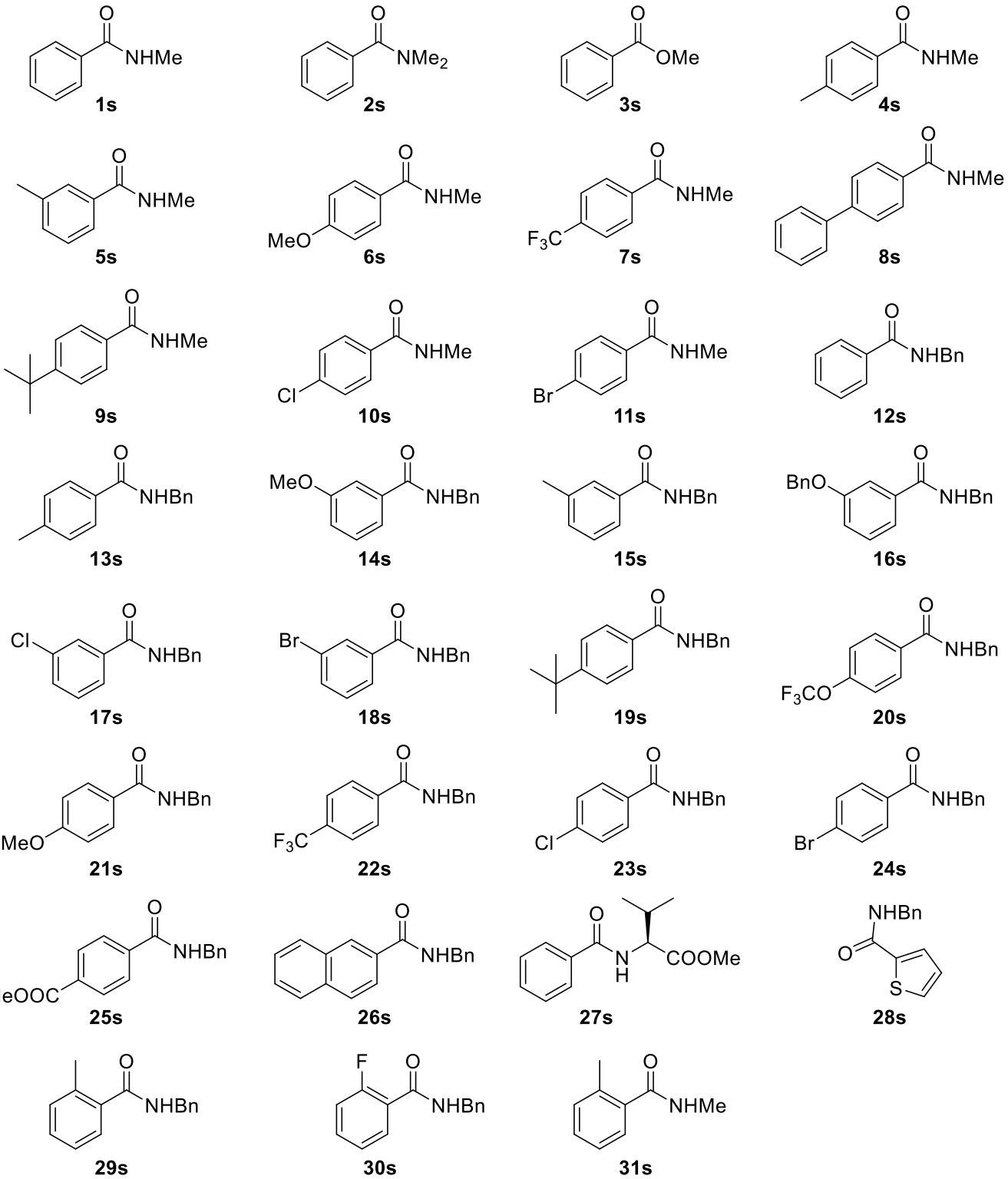
H	7.9436511	1.0852256	-4.0019139
H	3.0851539	1.1376274	-4.3497624

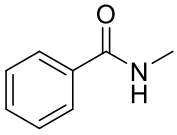
SUPPORTING INFORMATION

Aromatic compounds 1s-31s



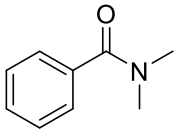
General procedures **A** for the synthesis of substrates: To a dichloromethane solution of benzoic acid derivative (1 eq.), 1 drop of DMF and oxalyl chloride (1.5 eq.) were added slowly. The reaction mixture was stirred vigorously for 1-2 hours. After the suspension becoming homogeneous solution, the volatiles were removed under vacuum. The resulting crude acyl chloride was re-dissolved in dichloromethane. $MeNH_2$ (1.5 eq.) in water and TEA (3 eq.) was added sequentially dropwise into the reaction mixture under ice-water bath and then stirred at room temperature overnight. Water was added into the suspension and the resulting mixture was extracted with ethyl acetate (3x100 mL). The combined organic phase was dried over $MgSO_4$, filtrated and evaporated. The pure product was obtained after crystallization using ethyl acetate and hexane or pentane mixture.

General procedures **B** for the synthesis of substrates: Benzoic acid derivative (1 eq.), benzylamine (1.0 eq.) and EDC (1.5 eq.) were dissolved in DMF followed by vigorously stirring overnight. Then 1M HCl solution was added into the suspension and the resulting mixture was extracted with ethyl acetate (300 mL), followed by washing with 1M HCl solution two times and then Na_2CO_3 saturated solution three times (3x200mL). The organic phase was dried over $MgSO_4$, filtered and evaporated. The pure product was obtained after crystallization using ethyl acetate and hexane or pentane mixture.



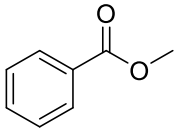
1s

N-Methylbenzamide (**1s**)[10]
Obtained from commercial source.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 – 7.74 (m, 2H), 7.51 – 7.47 (m, 1H), 7.47 – 7.40 (m, 2H), 6.18 (brs, 1H), 3.02 (d, *J* = 4.8 Hz, 3H).



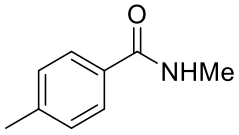
2s

N-Dimethylbenzamide (**2s**)[11]
Obtained from commercial source.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.38 (m, 5H), 3.11 (s, 3H), 2.98 (s, 3H).



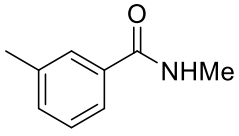
3s

Methyl benzoate (**3s**)[12]
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.58 – 7.54 (m, 1H), 7.46 – 7.42 (m, 2H), 3.92 (s, 3H).



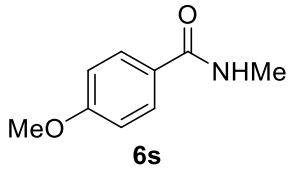
4s

N,4-dimethylbenzamide (**4s**)
General procedures **A**; Yield of 85%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 7.5 Hz, 2H), 7.16 (d, *J* = 7.7 Hz, 2H), 6.55 (brs, 1H), 2.94 (d, *J* = 4.6 Hz, 3H), 2.35 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.36, 141.65, 131.94, 129.19, 126.98, 26.79, 21.43.
HRMS (EI+(eiFi)) calcd. for $C_9H_{11}NO$ $[M]^+$ 149.0841, found 149.0851.



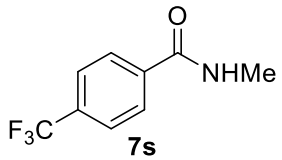
5s

N,3-dimethylbenzamide (**5s**)
General procedures **A**; Yield of 98%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.54 – 7.52 (m, 1H), 7.34 – 7.25 (m, 1H, amide-NH), 7.18 – 7.14 (m, 2H), 2.87 (d, *J* = 4.8 Hz, 3H), 2.24 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.69, 137.99, 134.47, 131.79, 128.11, 127.64, 123.94, 26.61, 21.10.
HRMS (EI+(eiFi)) calcd. for $C_9H_{11}NO$ $[M]^+$ 149.0841, found 149.0841



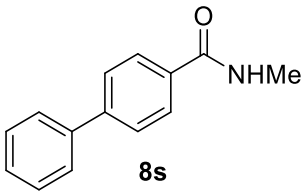
6s

4-Methoxy-*N*-methylbenzamide (**6s**)
General procedures **A**; Yield of 97%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 - 7.72 (m, 2H), 6.91 – 6.87 (m, 2H), 6.37 (brs, 1H), 3.82 (d, *J* = 4.7 Hz, 3H), 2.96 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.95, 162.14, 128.75, 127.04, 113.79, 55.47, 26.88.
HRMS (FD+(eiFi)) calcd. for $C_9H_{11}NO_2$ $[M]^+$ 165.0790, found 165.0843



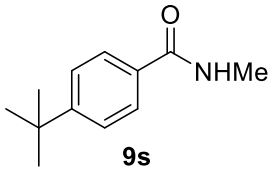
7s

N-Methyl-4-(trifluoromethyl)benzamide (**7s**)
General procedures **A**; Yield of 87%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 6.49 (brs, 1H), 3.01 (d, *J* = 4.7 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.14, 138.02, 133.24 (m, two bond F-C coupling), 127.48, 125.70 (m, three bonds F-C coupling), 123.79 (m, one bond C-F coupling), 27.08.
HRMS (EI+(eiFi)) calcd. for $C_9H_8F_3NO$ $[M]^+$ 203.0558, found 203.0507.



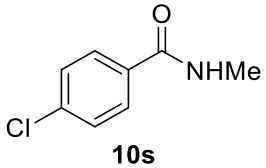
8s

N-Methyl-[1,1'-biphenyl]-4-carboxamide (**8s**)
General procedures **A**; Yield of 83%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.83 (m, 2H), 7.65 – 7.58 (m, 4H), 7.47 – 7.43 (m, 2H), 7.39 – 7.36 (m, 1H), 6.39 (brs, 1H), 3.03 (d, *J* = 4.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.09, 144.27, 140.19, 133.49, 129.01, 128.06, 127.51, 127.30, 26.97.
HRMS (EI+(eiFi)) calcd. for $C_{14}H_{13}NO$ $[M]^+$ 211.0997, found 211.0985



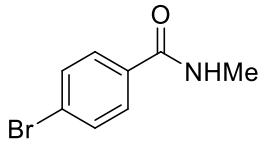
9s

4-(Tert-butyl)-*N*-methylbenzamide (**9s**)
General procedures **A**; Yield of 87%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.7 Hz, 2H), 7.42 (d, *J* = 8.8 Hz, 2H), 6.29 (brs, 1H), 2.99 (d, *J* = 5.1 Hz, 3H), 1.32 (s, 9H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 168.36, 154.91, 131.87, 126.79, 125.58, 35.01, 31.29, 26.90.
HRMS (EI+(eiFi)) calcd. for $C_{12}H_{17}NO$ $[M]^+$ 191.1310, found 191.1306



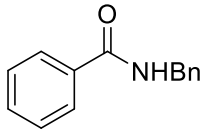
10s

4-Chloro-*N*-methylbenzamide (**10s**)
General procedures **A**; Yield of 89%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.3 Hz, 2H), 6.33 (brs, 1H), 2.98 (d, *J* = 4.8 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.34, 137.73, 133.20, 128.92, 128.44, 26.99.
HRMS (EI+(eiFi)) calcd. for C_8H_8ClNO $[M]^+$ 169.0294, found 169.0293



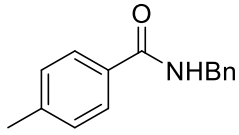
11s

4-Bromo-*N*-methylbenzamide (**11s**)
General procedures **A**; Yield of 97%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 6.18 (brs, 1H), 3.00 (d, *J* = 4.9 Hz, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 167.39, 133.69, 131.95, 128.61, 126.17, 27.02.
HRMS (EI+(eiFi)) calcd. for C_8H_7BrNO $[M-H]^+$ 211.9711, found 211.9712.



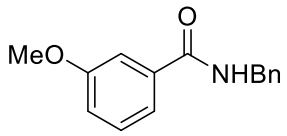
12s

N-Benzylbenzamide (**12s**)[13]
General procedures **B**; Yield of 90%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 – 7.78 (m, 2H), 7.53 – 7.48 (m, 1H), 7.45 – 7.41 (m, 2H), 7.37 – 7.27 (m, 5H), 6.40 (brs, 1H), 4.66 (d, *J* = 5.6 Hz, 2H).



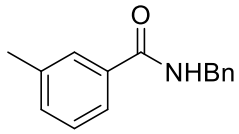
13s

N-Benzyl-4-methylbenzamide (**13s**) [14]
General procedures **B**; Yield of 90%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.27 (m, 5H), 7.23 (d, *J* = 8.0 Hz, 2H), 6.36 (brs, 1H), 4.65 (d, *J* = 5.6 Hz, 2H), 2.39 (s, 3H).



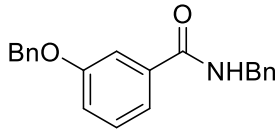
14s

N-Benzyl-3-methoxybenzamide (**14s**) [14]
General procedures **B**; Yield of 90%.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.36 – 7.27 (m, 8H), 7.06 – 7.03 (m, 1H), 6.59 (brs, 1H), 4.60 (d, *J* = 5.8 Hz, 2H), 3.83 (s, 3H).



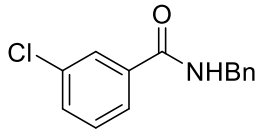
15s

N-Benzyl-3-methylbenzamide (**15s**) [15]
General procedures **B**; Yield of 91%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.58 – 7.55 (m, 1H), 7.37 – 7.29 (m, 7H), 6.38 (brs, 1H), 4.65 (d, *J* = 5.4 Hz, 2H), 2.39 (s, 3H).



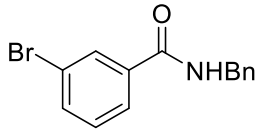
16s

N-Benzyl-3-benzyloxybenzamide (**16s**) [15]
General procedures **B**; Yield of 95%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 – 7.29 (m, 13H), 7.12 – 7.09 (m, 1H), 6.37 (brs, 1H), 5.10 (s, 2H), 4.64 (d, *J* = 5.2 Hz, 2H).



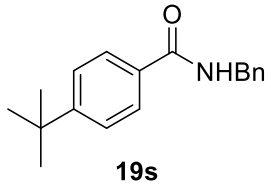
17s

N-Benzyl-3-chlorobenzamide (**17s**) [16]
General procedures **B**; Yield of 95%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.69 (m, 1H), 7.45 – 7.28 (m, 8H), 6.48 (brs, 1H), 4.94 – 4.59 (m, 2H).



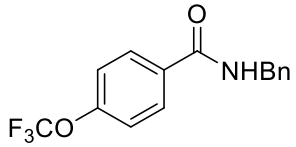
18s

N-Benzyl-3-benzyloxybenzamide (**18s**) [17]
General procedures **B**; Yield of 89%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 1.8 Hz, 1H), 7.70 (d, *J* = 7.8 Hz, 1H), 7.62 (d, *J* = 8.0 Hz, 1H), 7.40 – 7.27 (m, 6H), 6.46 (brs, 1H), 4.72 – 4.57 (m, 2H).



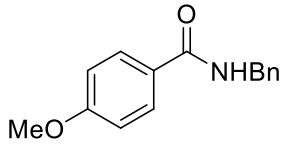
19s

N-Benzyl-4-(tert-butyl)benzamide (**19s**) [15]
General procedures **B**; Yield of 89%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 2H), 7.46 – 7.44 (m, 2H), 7.36 – 7.27 (m, 5H), 6.35 (brs, 1H), 4.66 (d, *J* = 5.7 Hz, 2H), 1.33 (s, 9H).



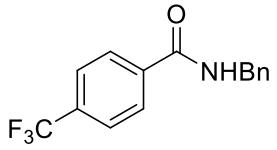
20s

N-Benzyl-4-(trifluoromethoxy)benzamide (**20s**) [18]
General procedures **B**; Yield of 95%.
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 2H), 7.38 – 7.27 (m, 5H), 7.27 – 7.24 (m, 2H), 6.39 (brs, 1H), 4.64 (d, *J* = 5.6 Hz, 2H).



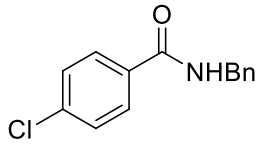
21s

N-Benzyl-4-methoxybenzamide (**21s**) [16]
General procedures **B**; Yield of 95%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 – 7.74 (m, 2H), 7.36 – 7.27 (m, 5H), 6.93 – 6.90 (m, 2H), 6.32 (brs, 1H), 4.64 (d, *J* = 5.6 Hz, 2H), 3.84 (s, 3H).



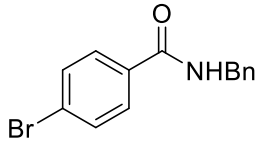
22s

N-Benzyl-4-(trifluoromethyl)benzamide (**22s**) [16]
General procedures **B**; Yield of 87%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.38 – 7.27 (m, 5H), 6.56 (brs, 1H), 4.64 (d, *J* = 5.6 Hz, 2H).



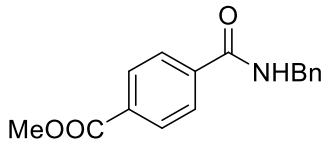
23s

N-Benzyl-4-chlorobenzamide (**23s**)[14]
General procedures **B**; Yield of 89%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 – 7.72 (m, 2H), 7.40 – 7.38 (m, 2H), 7.35 – 7.27 (m, 5H), 6.46 (brs, 1H), 4.63 (d, *J* = 5.5 Hz, 2H).



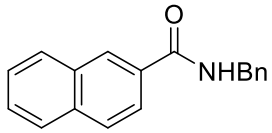
24s

N-benzyl-4-bromobenzamide (**24s**)[18]
General procedures **B**; Yield of 89%.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.68 – 7.65 (m, 2H), 7.60 – 7.57 (m, 2H), 7.36 – 7.27 (m, 5H), 6.49 (brs, 1H), 4.60 (d, *J* = 5.9 Hz, 2H).



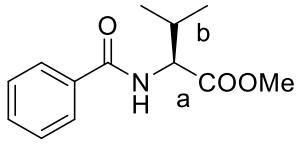
25s

Methyl 4-(benzylcarbamoyl)benzoate (**25s**)[16]
General procedures **B**; Yield of 87%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.86 – 7.83 (m, 2H), 7.38 – 7.27 (m, 5H), 6.42 (brs, 1H), 4.66 (s, 2H), 3.94 (s, 3H).



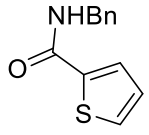
26s

N-Benzyl-2-naphthamide (**26s**)[15]
General procedures **B**; Yield of 89%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 1.6 Hz, 1H), 7.97 – 7.81 (m, 4H), 7.59 – 7.51 (m, 2H), 7.45 – 7.29 (m, 5H), 6.57 (brs, 1H), 4.72 (d, *J* = 5.6 Hz, 2H).



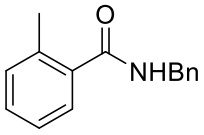
27s

Methyl benzoyl-L-valinate (**27s**)[19]
General procedures **B**; Yield of 95%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 – 7.80 (m, 2H), 7.54 7.43 (m, 3H), 6.64 (d, *J* = 8.6 Hz, 1H, amide-NH), 4.79 (dd, *J* = 8.6, 4.9 Hz, 1H, Ha), 3.77 (s, 3H, OMe), 2.33 – 2.23 (m, 1H, Hb), 1.21 – 0.94 (m, 6H, isopropyl-Me).



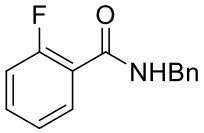
28s

N-Benzylthiophene-2-carboxamide (**28s**)[14]
General procedures **B**; Yield of 88%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 3.8 Hz, 1H), 7.49 (d, *J* = 5.0 Hz, 1H), 7.37 – 7.29 (m, 5H), 7.08 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.21 (brs, 1H), 4.64 – 4.62 (m, 2H).



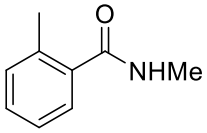
29s

N-Benzyl-2-methylbenzamide (**29s**) [16]
General procedures **B**; Yield of 89%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.29 (m, 7H), 7.23 – 7.17 (m, 2H), 6.01 (brs, 1H, amide-NH), 4.65 – 4.63 (m, 2H, Bn-CH_2), 2.48 (s, 3H, aryl-Me).



30s

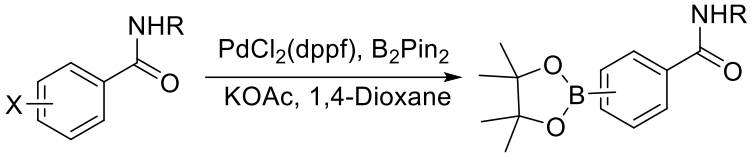
N-Benzyl-2-fluorobenzamide (**30s**) [20]
General procedures **B**; Yield of 85%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.15 (td, *J* = 7.9, 1.9 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.38 – 7.27 (m, 6H), 7.16 – 7.08 (m, 1H), 7.04 (brs, 1H, amide-NH), 4.69 (dd, *J* = 5.6, 1.5 Hz, 2H, Bn-CH_2).



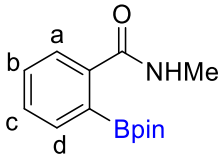
31s

N-Methyl-2-methylbenzamide (**31s**)[21]
General procedures **B**; Yield of 89%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.13 (m, 2H), 7.13 – 7.00 (m, 2H), 5.85 (s, 1H), 2.84 (d, *J* = 4.9 Hz, 3H), 2.30 (s, 3H).
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.94, 136.62, 136.08, 131.03, 129.84, 126.76, 125.75, 77.42, 77.16, 76.91, 26.67, 19.83.
HRMS (EI+(eiFi)) calcd. for $C_9H_{11}NO$ $[M]^+$ 149.0841, found 149.0905

Preparation of the reference borylated compounds

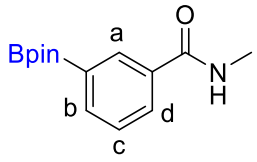


General procedures: A mixture of halogenate aromatic amides (1 eq.), $PdCl_2$(dppf) (0.03 eq.), KOAc (3 eq.) and bis(pinacolato)diboron (1.5 eq.) in 1,4-dioxane was heated at 80 °C overnight. After cooling to room temperature, the reaction mixture was diluted with water and extracted with ethyl acetate. The combined organic layers were washed with water and brine, dried over Na_2SO_4, filtered off and concentrated under reduced pressure. The product was purified by chromatography using deactivated silica gel and ethyl acetate and petroleum ether or hexane as the eluent.[22-26]



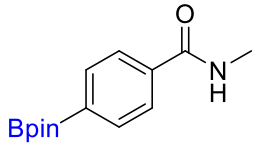
1so

N-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**1so**)
Gray solid; Isolated Yield of 30%.
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (s, 1H, amide-NH), 7.80 (d, *J* = 7.6 Hz, 1H, Ha), 7.60 (d, *J* = 7.1 Hz, 1H, Hd), 7.40 (t, *J* = 7.3 Hz, 1H, Hc), 7.14 (t, *J* = 7.6 Hz, 1H, Hb), 2.46 (d, *J* = 4.5 Hz, 3H, Me), 1.35 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.41, 133.29, 132.76, 130.36, 127.52, 123.61, 81.19, 27.26, 25.33.
HRMS (FD+(eiFi)) calcd. for $C_{14}H_{20}BNO_3$ $[M]^+$ 261.1539, found 261.1511.



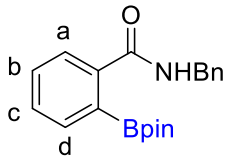
1sm

N-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**1sm**)
Gray solid; Isolated Yield of 70%.
^{1}H NMR (500 MHz, THF-d_8) δ 8.15 (s, 1H, Ha), 7.95 (dt, *J* = 7.7, 1.6 Hz, 1H, Hd), 7.82 – 7.81 (m, 1H, Hb), 7.65 – 7.62 (m, 1H, amide-NH), 7.37 (t, *J* = 7.5 Hz, 1H, Hc), 2.87 (d, *J* = 4.5 Hz, 3H, Me), 1.33 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, THF-d_8) δ 167.19, 137.55, 135.47, 133.40, 131.04, 128.02, 84.42, 26.41, 25.62.
HRMS (FD+(eiFi)) calcd. for $C_{14}H_{20}BNO_3$ [M]$^+$ 261.1536, found 261.1511.



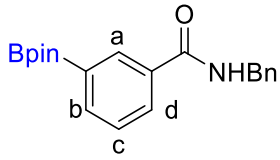
1sp

N-methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**1sp**)
Gray solid; Isolated Yield of 80%.
^{1}H NMR (500 MHz, THF-d_8) δ 7.80 – 7.76 (m, 4H), 7.58 (brs, 1H, amide-NH), 2.87 (d, *J* = 4.7 Hz, 3H, Me), 1.32 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, THF-d_8) δ 167.01, 138.34, 135.07, 126.72, 84.43, 25.62.
HRMS (FD+(eiFi)) calcd. for $C_{14}H_{20}BNO_3$ [M]$^+$ 261.1536, found 261.1525.



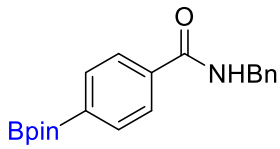
12so

N-benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**12so**)
Gray solid; Isolated Yield of 25%.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.72 (brs, 1H, amide-NH), 8.05 (d, *J* = 7.9 Hz, 1H, Ha), 7.65 (d, *J* = 7.3 Hz, 1H, Hb), 7.54 (t, *J* = 7.3 Hz, 1H, Hc), 7.39 – 7.26 (m, 6H, Hd and Bn-aryl-H), 4.03 (d, *J* = 6.0 Hz, 2H, Bn-CH_2), 1.27 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.93, 137.53, 134.59, 132.93, 131.11, 128.89, 128.42, 128.17, 127.99, 124.77, 81.96, 44.86, 25.13.
HRMS (FD+(eiFi)) calcd. for $C_{20}H_{24}BNO_3$ [M]$^+$ 337.1853, found 337.1850.



12sm

N-benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**12sm**)
Gray solid; Isolated Yield of 65%.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.08 (t, *J* = 1.4 Hz, 1H, Ha), 8.02 (dt, *J* = 7.7, 1.6 Hz, 1H, Hd), 7.93 (dt, *J* = 7.3, 1.2 Hz, 1H, Hb), 7.47 (t, *J* = 7.6 Hz, 1H, Hc), 7.40 – 7.28 (m, 5H, Bn-aryl-H), 6.49 (brs, 1H, amide-NH), 4.66 (d, *J* = 5.7 Hz, 2H, Bn-CH_2), 1.34 (s, 12H, pin-Me).
^{13}C NMR (75 MHz, $CDCl_3$) δ 167.35, 138.36, 138.07, 133.80, 132.22, 130.83, 128.92, 128.38, 128.19, 127.76, 84.30, 44.30, 25.02.
HRMS (FD+(eiFi)) calcd. for $C_{20}H_{24}BNO_3$ [M]$^+$ 337.1853, found 337.1851.

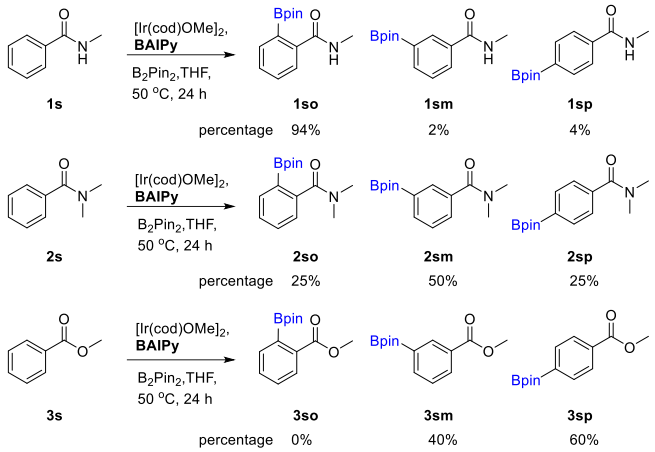


12sp

N-benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**12sp**)
Gray solid; Isolated Yield of 85%.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88 – 7.85 (m, 2H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.37 – 7.26 (m, 5H, Bn-aryl-H), 6.40 (brs, 1H, amide-NH), 4.66 (d, *J* = 5.7 Hz, 2H, Bn-CH_2), 1.35 (s, 12H, pin-Me).
^{13}C NMR (75 MHz, $CDCl_3$) δ 167.39, 138.24, 136.69, 135.11, 128.94, 128.11, 127.79, 126.21, 84.28, 44.32, 25.02.
HRMS (FD+(eiFi)) calcd. for $C_{20}H_{24}BNO_3$ $[M]^+$ 337.1853, found 337.1847.

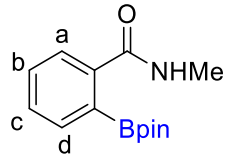
Control experiments with substrates that can form 2 or 3 hydrogen bonds



Scheme S2. Control experiments with substrates that can form 2 (**2s**, **3s**) or 3 (**1s**) hydrogen bonds.

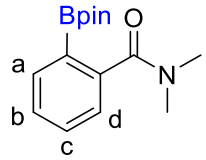
Iridium catalyzed *ortho*-selective C-H borylation

General procedures: A mixture of $[Ir(OMe)(cod)]_2$ (5.967 mg, 9.0 μmol, 1.5 mol%), ligand **BAIPy** (6.174 mg, 19.8 μmol, 3.3 mol%) or **BPy** (2.808 mg, 19.8 μmol, 3.3 mol%) in THF (3.0 ml) was added into pre-dried vial with bis(pinacolato)diboron (228.0 mg, 0.898 mmol, 1.50 equiv.) and aromatic amides (0.598 mmol, 1.0 equiv.) in Glove-box. The mixture was then stirred at 50-60 °C for 24-96 hours under nitrogen atmosphere. The conversion and selectivity was analysed by GC (Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min) using 1,3,5-trimethoxybenzene as the internal standard and NMR technique of the purified reaction mixture. The product was isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether or hexane (10:0.5 to 2:1) as the eluent (for details see below). Isolated yield is lower than the calculated yield due to decomposition of the borylated compound during purification using silica (the off up to 25%). The decomposed boronic acid were observed by NMR. Attempt to convert the borylated products to BF_3K salts without success for easy separation of the product via crystallization.



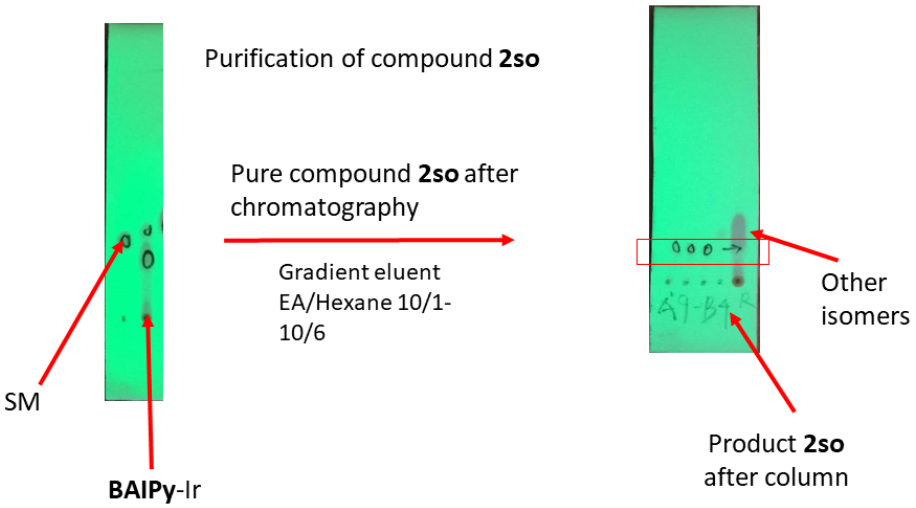
1so

N-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**1so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 2:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 63%.
BPy-Ir catalyst; Isolated yield of 0%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 12.683 min, t (*ortho*)= 19.275 min, t (*meta*)= 20.535 min and t (*para*)= 20.272 min.
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.78 (s, 1H, amide-NH), 7.80 (d, *J* = 7.6 Hz, 1H, Ha), 7.60 (d, *J* = 7.1 Hz, 1H, Hd), 7.40 (t, *J* = 7.3 Hz, 1H, Hc), 7.14 (t, *J* = 7.6 Hz, 1H, Hb), 2.46 (d, *J* = 4.5 Hz, 3H, Me), 1.35 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.41, 133.29, 132.76, 130.36, 127.52, 123.61, 81.19, 27.26, 25.33.
HRMS (FD+(eiFi)) calcd. for $C_{14}H_{20}BNO_3$ $[M]^+$ 261.1539, found 261.1511.

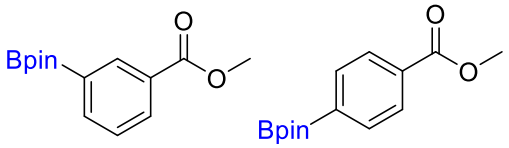


2so

N,N-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**2so**)

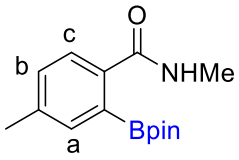


Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (5:1 to 1:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 25%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 12.642 min, t (*ortho*)= 18.723 min, t (*meta*)= 24.397 min and t (*para*)= 24.815 min.
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.76 – 7.74 (m, 1H, Hd), 7.46 (td, *J* = 7.5, 1.4 Hz, 1H, Hb), 7.37 (td, *J* = 7.5, 1.2 Hz, 1H, Hc), 7.24 (d, *J* = 7.6 Hz, 1H, Ha), 2.99 – 2.84 (m, 6H, amide-Me), 1.30 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 172.28, 143.68, 135.28, 131.26, 128.18, 125.88, 84.10, 25.09.
HRMS (FD+(eiFi)) calcd. for $C_{15}H_{22}BNO_3$ $[M]^+$ 275.1696, found 275.1693.



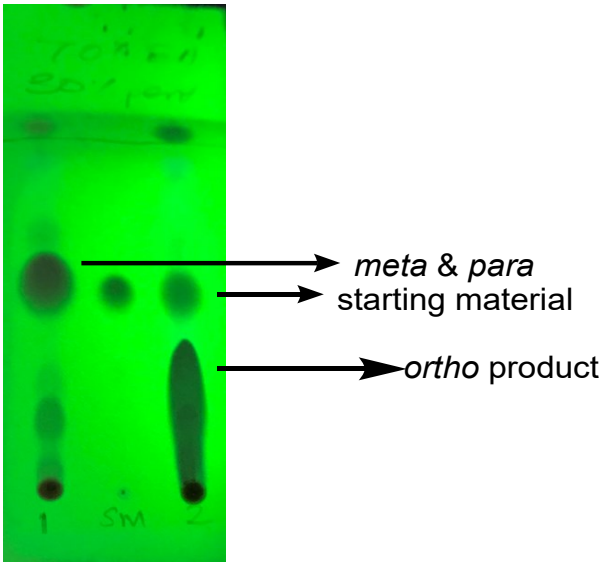
3sm **3sp**

Methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**3sm**) and Methyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**3sp**)
^{1}H NMR in line with literature.[15,16]



4so

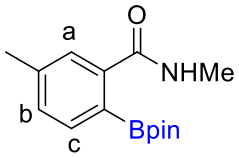
N,4-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**4so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 2:1) as the eluent**.**



EtOAc:Pentane (70:30)

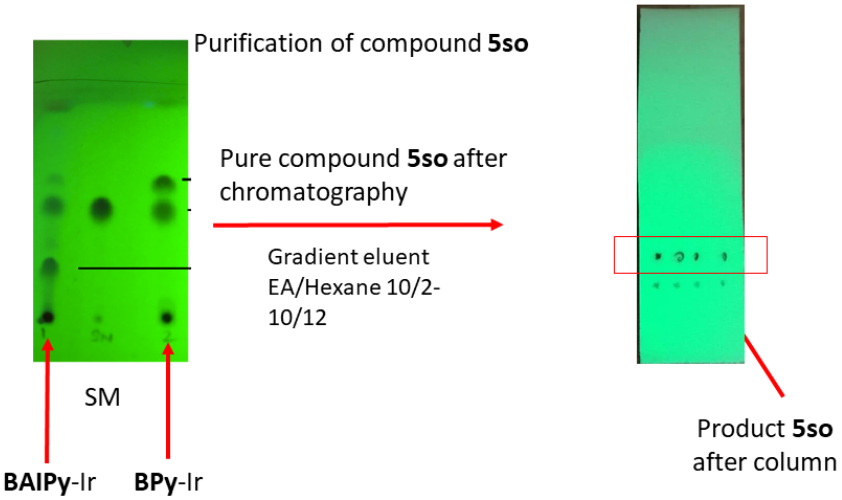
purification of ortho product by
Column chromatography
Start 10%, 20%, 30%, 40%, 50%, 60% in 100 mL
At 30% EA - get starting material
At 60% EA - get product

BAIPy-Ir catalyst; Isolated yield of 61%.
BPy-Ir catalyst; Isolated yield of -%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 14.857 min, t (*ortho*)= 20.905 min, t (*meta*)= 20.308 min.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.77 (s, 1H, amide-NH), 7.59 (d, *J* = 7.9 Hz, 1H, Hc), 7.39 (s, 1H, Ha), 7.00 (d, *J* = 7.8 Hz, 1H, Hb), 2.65 – 2.62 (m, 3H, Me), 1.36 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.24, 143.06, 131.11, 128.39, 123.58, 81.23, 27.27, 25.35, 21.90.
HRMS (FD+(eiFi)) calcd. for $C_{15}H_{22}BNO_3$ $[M]^+$ 275.1696, found 275.1693.



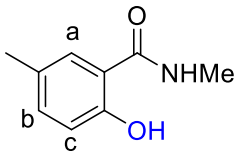
5so

N,5-dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**5so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent.



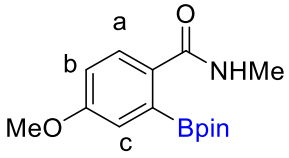
BAIPy-Ir catalyst; Isolated yield of 45%.
BPy-Ir catalyst; Isolated yield of 0%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 14.745 min, t (*ortho*)= 20.965 min, t (*meta*)= 21.780 min.
^{1}H NMR (500 MHz, CD_2Cl_2) δ 7.73 (brs, 1H, amide-NH), 7.50 (s, 1H, Ha), 7.46 (d, *J* = 7.4 Hz, 1H, Hb), 7.27 (d, *J* = 7.5 Hz, 1H, Hc), 2.74 (d, *J* = 4.8 Hz, 3H, amide-Me), 2.36 (s, 3H, aryl-Me), 1.33 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.21, 138.98, 132.55, 132.12, 125.33, 82.73, 27.11, 25.21, 21.43.

The borylated product was also transformed into hydroxyl group functionalized product for confirmation as shown below.
HRMS (FD+(eiFi)) calcd. for $C_{15}H_{23}BNO_3$ $[M+H]^+$ 276.1771, found 276.1495.



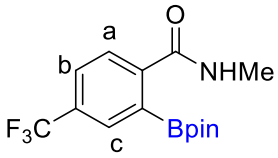
5so'

2-Hydroxy-*N*,5-dimethyl-benzamide (**5so'**)
^{1}H NMR in line with commercial compound.
^{1}H NMR (500 MHz, $CDCl_3$) δ 12.09 (s, 1H, OH), 7.20 (d, *J* = 8.4 Hz, 1H, Hb), 7.12 (s, 1H, Ha), 6.89 (d, *J* = 8.6 Hz, 1H, Hc), 6.31 (brs, 1H, amide-NH), 3.01 (d, *J* = 4.8 Hz, 3H, Me), 2.28 (s, 3H, aryl-Me).



6so

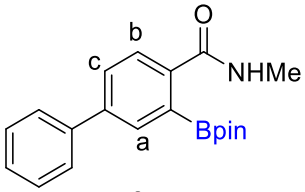
4-Methoxy-*N*-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**6so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent.
BAIPy-Ir catalyst; Isolated yield of 59%.
BPy-Ir catalyst; Isolated yield of 64%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 16.605 min, t (*ortho*)= 22.218 min, t (*meta*)= 21.535 min.
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.80 (brs, 1H, amide-NH), 7.70 (d, *J* = 8.5 Hz, 1H, Ha), 7.05 (d, *J* = 2.4 Hz, 1H, Hc), 6.58 (dd, *J* = 8.5, 2.3 Hz, 1H, Hb), 3.83 (s, 3H, OMe), 2.50 – 2.49 (m, 3H, Me), 1.33 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.20, 163.83, 125.44, 125.31, 114.09, 114.02, 80.97, 55.47, 27.42, 25.36.
HRMS (FD+(eiFi)) calcd. for $C_{15}H_{22}BNO_4$ $[M]^+$ 291.1645, found 291.1637.



7so

N-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethyl)benzamide (**7so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent.

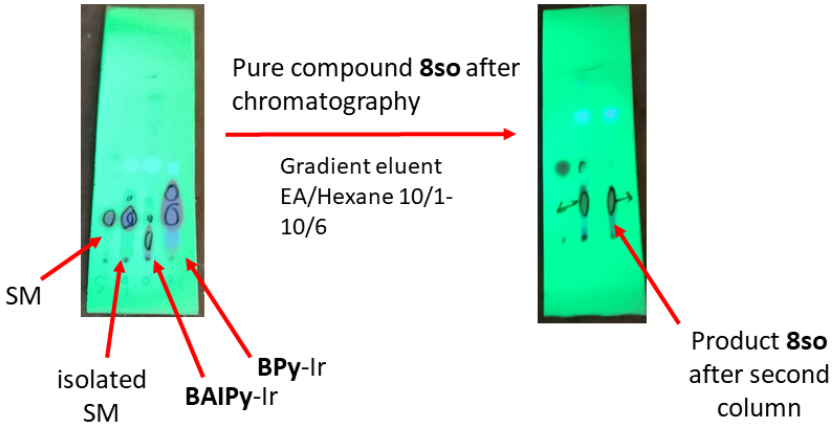
BAIPy-Ir catalyst; Isolated yield of 77%.
BPy-Ir catalyst; Isolated yield of -%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 13.195 min, t (*ortho*)= 19.230 min, t (*meta*)= 17.618 min.
^{1}H NMR (500 MHz, THF-d_8) δ 9.19 – 9.18 (m, 1H, amide-NH), 7.80 (d, *J* = 8.1 Hz, 1H, Ha), 7.73 (d, *J* = 1.7 Hz, 1H, Hc), 7.52 (dd, *J* = 8.1, 1.9 Hz, 1H, Hb), 2.86 (d, *J* = 4.6 Hz, 3H, Me), 1.32 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, THF-d_8) δ 170.15, 139.22, 133.34 (m, two bonds C-F coupling), 127.92 (m, three bonds C-F coupling), 125.20 (m, three bonds C-F coupling), 125.13 (m, one C-F coupling),), 82.18, 27.32, 25.43.
HRMS (FD+(eiFi)) calcd. for $C_{15}H_{20}BF_3NO_3$ [M-H]$^+$ 330.1413, found 330.1460.



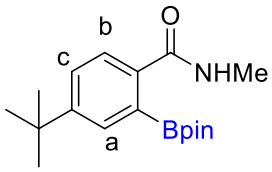
8so

N-methyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-[1,1'-biphenyl]-4-carboxamide (**8so**)

Purification of compound **8so**

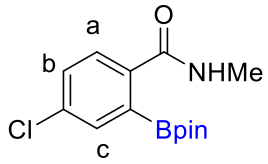


Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 2:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 56%.
BPy-Ir catalyst; Isolated yield of 0%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 21.670 min, t (*ortho*)= 26.152 min, t (*meta*)= 27.382 min.
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (s, 1H, amide-NH), 7.81 (s, 1H, Ha), 7.77 (d, *J* = 7.9 Hz, 1H, Hb), 7.47 (d, *J* = 6.5 Hz, 2H), 7.37 (d, *J* = 6.1 Hz, 3H), 7.26 (d, *J* = 2.5 Hz, 1H), 2.69 (s, 3H, Me), 1.38 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.91, 145.14, 140.66, 132.60, 129.10, 128.80, 127.80, 127.36, 126.77, 123.89, 81.44, 27.33, 25.25.
HRMS (FD+(eiFi)) calcd. for $C_{20}H_{24}BNO_3$ [M]$^+$ 337.1853, found 337.1846.



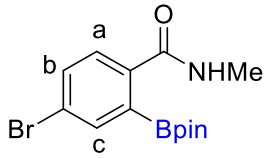
9so

4-(Tert-butyl)-*N*-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**9so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 41%.
BPy-Ir catalyst; Isolated yield of -%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 17.562 min, t (*ortho*)= 22.218 min, t (*meta*)= 21.535 min.
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.59 (s, 1H, amide-NH), 7.80 – 7.78 (m, 1H, Hb), 7.59 – 7.56 (m, 1H, Ha), 7.20 (dd, *J* = 8.2, 1.8 Hz, 1H, Hc), 2.43 – 2.42 (m, 3H, Me), 1.36 (s, 12H, pin-Me), 1.28 (s, 9H, tert-butyl).
^{13}C NMR (126 MHz, $CDCl_3$) δ 172.27, 155.94, 130.95, 126.86, 124.95, 123.42, 81.18, 35.25, 27.07, 25.38.
HRMS (FD+(eiFi)) calcd. for $C_{18}H_{28}BNO_3$ [M]$^+$ 317.2166, found 317.2157.



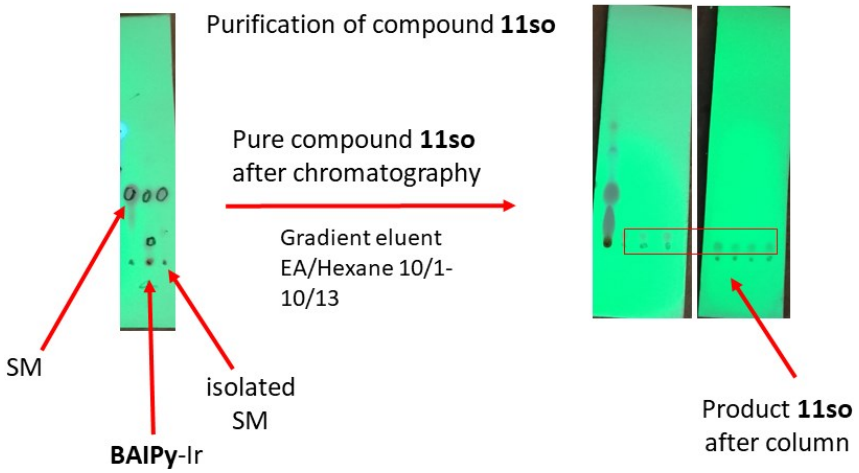
10so

4-Chloro-*N*-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**10so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 65%.
BPy-Ir catalyst; Isolated yield of 0%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 15.508 min, t (*ortho*)= 21.555 min, t (*meta*)= 24.407 min.
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.66 (s, 1H, amide-NH), 7.69 (d, *J* = 8.2 Hz, 1H, Ha), 7.54 (d, *J* = 2.0 Hz, 1H, Hc), 7.15 (dd, *J* = 8.3, 2.0 Hz, 1H, Hb), 2.62 (d, *J* = 4.5 Hz, 3H, Me), 1.34 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, $CDCl_3$) δ 171.56, 140.05, 131.38, 130.66, 127.99, 124.76, 81.52, 27.59, 25.31.
HRMS (FD+(eiFi)) calcd. for $C_{14}H_{19}BClNO_3$ $[M]^+$ 295.1147, found 295.1140.

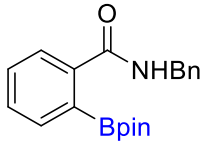


11so

4-Bromo-*N*-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**11so**)



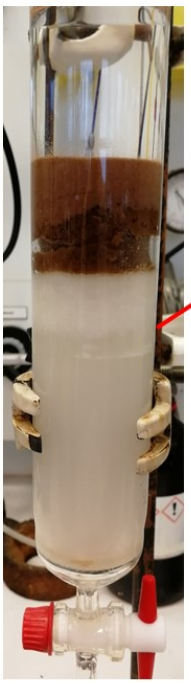
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 70%.
BPy-Ir catalyst; Isolated yield of 0%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 16.623 min.
^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.96 (s, 1H, amide-NH), 7.70 (d, *J* = 1.9 Hz, 1H, Hc), 7.65 (d, *J* = 8.2 Hz, 1H, Ha), 7.34 (dd, *J* = 8.2, 1.9 Hz, 1H, Hb), 2.59 (d, *J* = 4.7 Hz, 3H, Me), 1.32 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.82, 133.61, 132.14, 131.11, 129.21, 125.52, 81.66, 27.66, 25.35.
HRMS (FD+(eiFi)) calcd. for $C_{14}H_{19}BBrNO_3$ $[M]^+$ 339.0644, found 339.1269.



12so

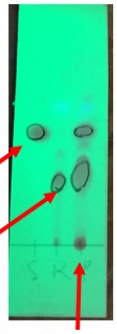
N-Benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**12so**)

General Catalysis setup
4 reactions in one oil bath



Purification of compound **12so**
@2.3 gram scale

Product shown
by UV-lamp



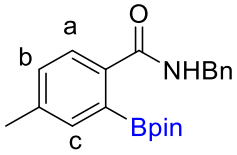
SM
12so

Chromatography
using deactivated
silica

Gradient eluent
EA/Hexane 10/1-
10/7

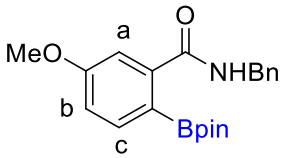
Catalysis mixture

Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent.
BAIPy-Ir catalyst; Isolated yield of 65%.
BPy-Ir catalyst; Isolated yield of 0%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 19.867 min, t (*ortho*)= 25.213 min, t (*meta*)= 26.078 min and t (*para*)= 26.815 min.
^{1}H NMR (400 MHz, CD_2Cl_2) δ 9.72 (brs, 1H, amide-NH), 8.05 (d, *J* = 7.9 Hz, 1H, Ha), 7.65 (d, *J* = 7.3 Hz, 1H, Hb), 7.54 (t, *J* = 7.3 Hz, 1H, Hc), 7.39 – 7.26 (m, 6H, Hd and Bn-aryl-H), 4.03 (d, *J* = 6.0 Hz, 2H, Bn-CH_2), 1.27 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.93, 137.53, 134.59, 132.93, 131.11, 128.89, 128.42, 128.17, 127.99, 124.77, 81.96, 44.86, 25.13.
HRMS (FD+(eiFi)) calcd. for $C_{20}H_{24}BNO_3$ $[M]^+$ 337.1853, found 337.1850.



13so

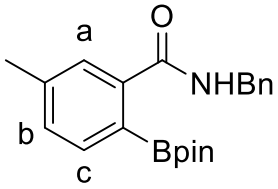
N-Benzyl-4-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**13so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (6:1 to 1:1) as the eluent.
BAIPy-Ir catalyst; Isolated yield of 71%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 21.605 min, t (*ortho*)= 26.025 min, t (*meta*)= 31.597 min.
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.72 (m, 1H, amide-NH), 7.61 – 7.57 (m, 1H, Ha), 7.42 (s, 1H, Hc), 7.36 – 7.27 (m, 5H, Bn-aryl-H), 7.11 (d, *J* = 7.9 Hz, 1H, Hb), 4.43 – 4.39 (m, 2H, Bn-CH_2), 2.37 (s, 3H, aryl-Me), 1.31 (s, 12H, pin-Me).
^{13}C NMR (101 MHz, $CDCl_3$) δ 170.37, 142.27, 137.51, 133.23, 132.78, 129.24, 128.82, 128.26, 127.83, 124.19, 82.54, 44.80, 25.09.
HRMS (FD+(eiFi)) calcd. for $C_{21}H_{26}BNO_3$ $[M]^+$ 351.2010, found 351.2004.



14so

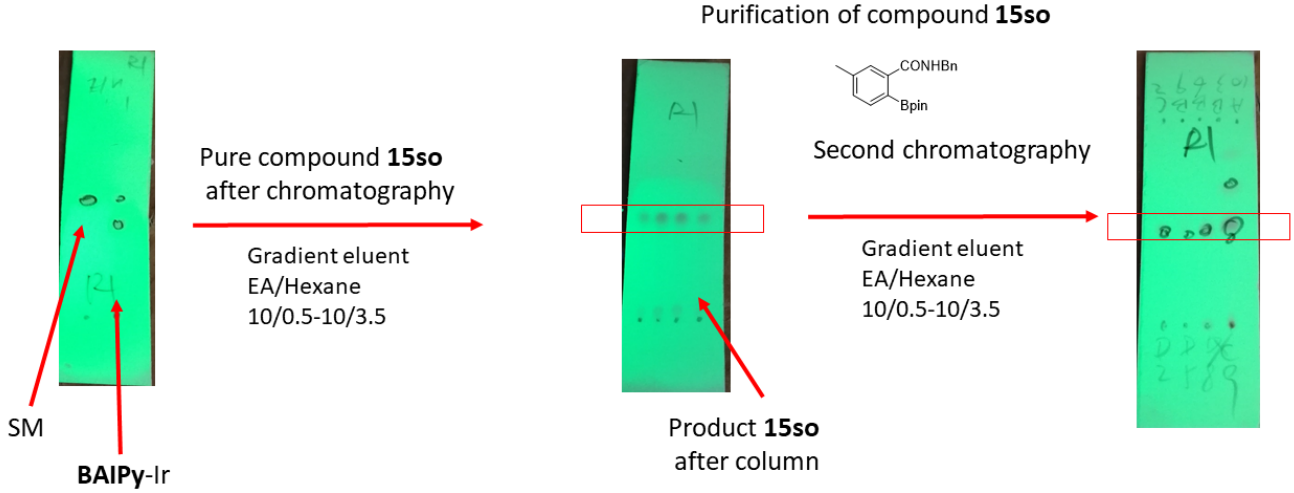
N-Benzyl-5-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**14so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent.
BAIPy-Ir catalyst; Isolated yield of 81%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 22.013 min, t (*ortho*)= 26.440 min, t (*meta*)= 26.890 min.

^{1}H NMR (500 MHz, THF-d_8) δ 8.07 (s, 1H, amide-NH), 7.42 (d, *J* = 8.1 Hz, 1H, Hc), 7.40 – 7.38 (m, 2H), 7.29 – 7.26 (m, 2H), 7.21 – 7.18 (m, 2H), 6.95 (dd, *J* = 8.2, 2.4 Hz, 1H, Hb), 4.56 (d, *J* = 5.9 Hz, 2H, Bn-CH_2), 3.78 (s, 3H, OMe), 1.29 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, THF-d_8) δ 169.13, 161.12, 142.22, 140.45, 134.63, 128.82, 128.51, 127.45, 115.71, 111.58, 83.20, 55.29, 44.34, 24.82.
HRMS (FD+(eiFi)) calcd. for $C_{21}H_{26}BNO_4$ $[M]^+$ 367.1959, found 367.1963.

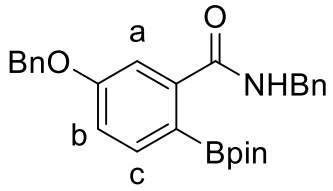


15so

N-Benzyl-5-methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**15so**)



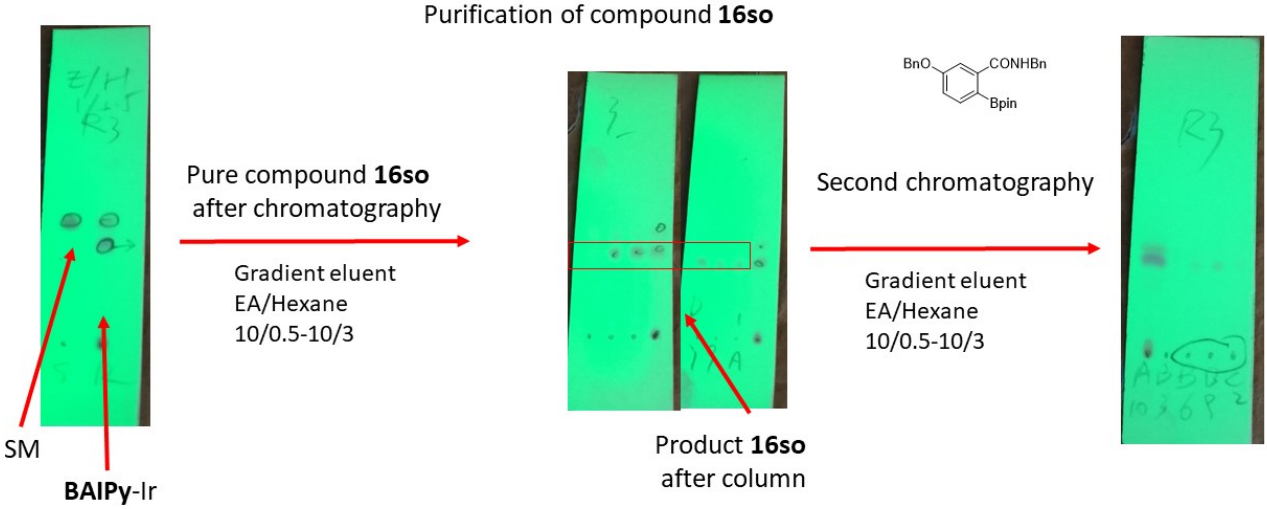
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:0.5 to 10:3.5) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 62%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 20.753 min, t (*ortho*)= 25.383 min, t (*meta*)= 23.213 min.
^{1}H NMR (500 MHz CD_2Cl_2) δ 8.66 – 8.59 (m, 1H, amide-NH), 7.71 – 7.67 (m, 1H, Ha), 7.55 – 7.51 (m, 1H, Hc), 7.35 – 7.26 (m, 6H, Hb & Bn-aryl-H), 4.25 (d, *J* = 5.7 Hz, 2H, Bn-CH_2), 2.37 (s, 2H, aryl-Me), 1.27 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 171.05, 138.14, 136.80, 132.94, 132.15, 128.91, 128.37, 128.34, 127.88, 125.53, 82.71, 44.67, 25.12, 21.47.
HRMS (FD+(eiFi)) calcd. for $C_{21}H_{26}BNO_3$ $[M]^+$ 351.2010, found 351.2011.



16so

N-Benzyl-5-(benzyloxy)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**16so**)

Purification of compound **16so**



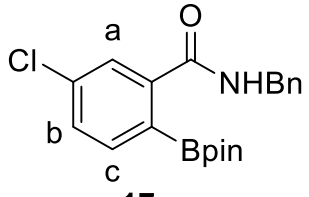
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:0.5 to 10:4.0) as the eluent.

BAIPy-Ir catalyst; Isolated yield of 69%.

^{1}H NMR (500 MHz CD_2Cl_2) δ 7.61 (d, *J* = 8.1 Hz, 1H, Hc), 7.50 – 7.25 (m, 11H, 2xBn-aryl & Ha), 7.05 (dd, *J* = 8.2, 2.6 Hz, 1H, Hb), 6.95 (s, 1H, amide-NH), 5.11 (s, 2H, OBn-CH_2), 4.59 (d, *J* = 5.7 Hz, 2H, NHBn-CH_2), 1.29 (s, 12H, pin-Me).

^{13}C NMR (126 MHz, CD_2Cl_2) δ 169.13, 160.52, 142.35, 138.86, 137.09, 136.30, 128.98, 128.94, 128.44, 128.33, 127.96, 127.78, 116.69, 113.71, 84.20, 70.44, 44.61, 25.05.

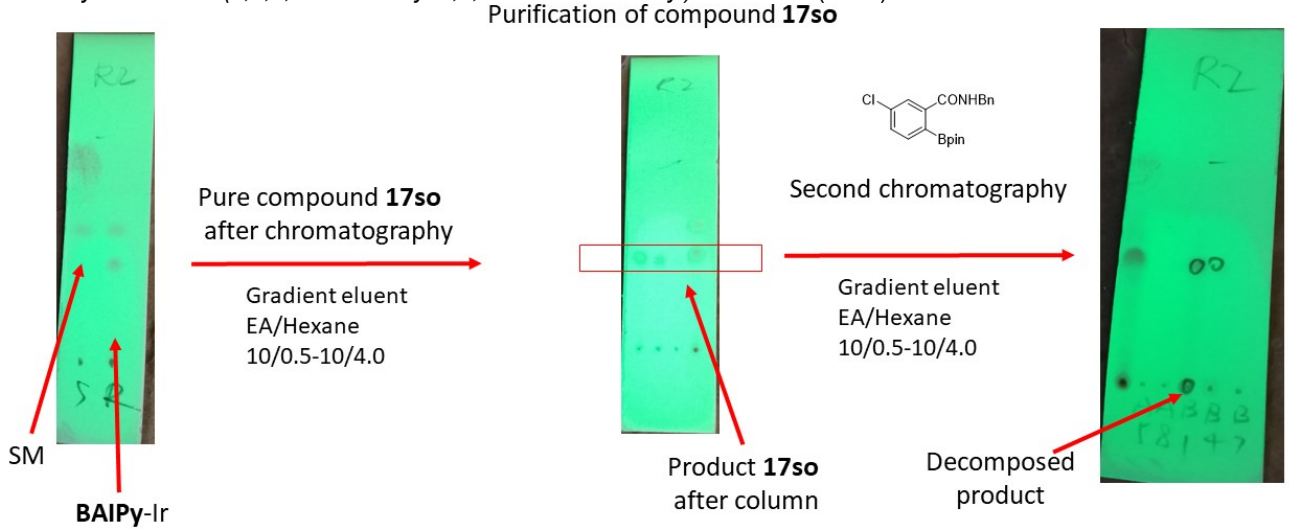
HRMS (FD+(eiFi)) calcd. for $C_{27}H_{30}BNO_4$ $[M]^+$ 443.2273, found 443.2272.



17so

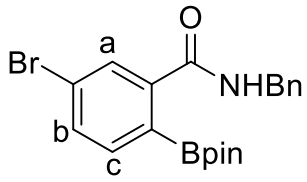
N-Benzyl-5-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**17so**)

Purification of compound **17so**



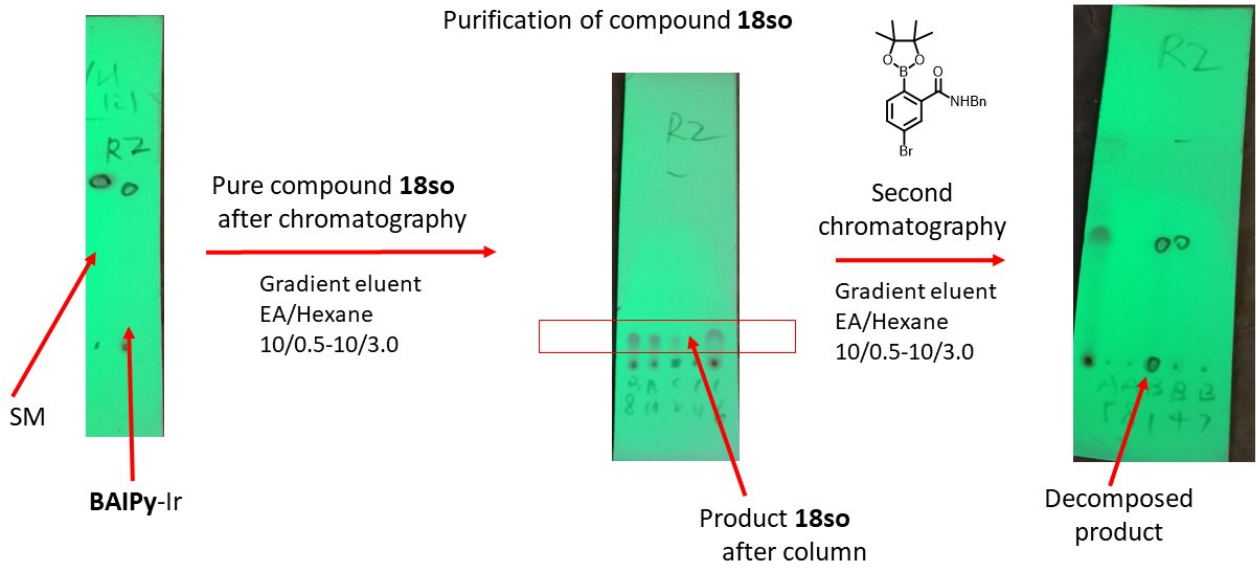
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:0.5 to 10:4.0) as the eluent.

BAIPy-Ir catalyst; Isolated yield of 39%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 20.888 min, t (*ortho*)= 25.492 min, t (*meta*)= 26.518 min.
^{1}H NMR (500 MHz CD_2Cl_2) δ 7.56 (d, *J* = 7.3 Hz, 2H, Hb&c), 7.45 – 7.33 (m, 7H, Ha & Bn-aryl-H & amide-NH), 4.74 (d, *J* = 5.7 Hz, 2H, Bn-CH_2), 1.31 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 169.46, 137.19, 133.27, 131.12, 131.10, 130.57, 130.19, 129.23, 128.37, 128.32, 82.49, 45.74, 25.29.
HRMS (FD+(eiFi)) calcd. for $C_{20}H_{23}BClNO_3$ $[M]^+$ 371.1463, found 371.1478.

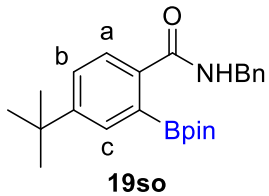


18so

N-Benzyl-5-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**18so**)



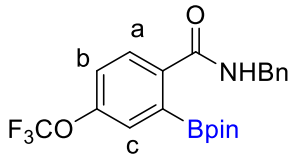
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:0.5 to 10:3.0) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 64%.
^{1}H NMR (500 MHz CD_2Cl_2) δ 9.54 (s, 1H, amide-NH), 8.19 (s, 1H, Ha), 7.67 (dd, *J* = 7.7, 1.8 Hz, 1H, Hb), 7.57 (d, *J* = 7.9 Hz, 1H, Hc), 7.43 – 7.23 (m, 5H, Bn-aryl-H), 4.11 (d, *J* = 5.9 Hz, 2H, Bn-CH_2), 1.27 (s, 12H, pin-Me).
7.62 (d, J = 7.7 Hz, 1H, Ha), 7.58 (d, J = 7.4 Hz, 1H, Hd), 7.49 (t, J = 7.3 Hz, 1H, Hb), 7.44 (t, J = 7.5 Hz, 1H, Hc), 6.85 (d, J = 8.6 Hz, 1H, amide-NH), 4.71 (dd, J = 8.6, 5.2 Hz, 1H, He), 3.76 (s, 3H, OMe), 2.26 (h, J = 6.7 Hz, 1H, Hg), 1.35 (d, J = 5.9 Hz, 12H, pin-Me), 1.03 – 0.98 (m, 6H).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.28, 137.30, 137.23, 135.68, 133.24, 128.97, 128.45, 128.15, 127.58, 122.79, 82.61, 44.98, 25.23.
HRMS (FD+(eiFi)) calcd. for $C_{20}H_{23}BBrNO_3$ $[M]^+$ 415.0954, found 415.0950.



19so

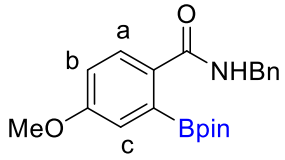
N-Benzyl-4-(tert-butyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**19so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 55%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 23.132 min.
^{1}H NMR (500 MHz, THF-d_8) δ 8.43 (s, 1H, amide-NH), 7.63 (d, *J* = 8.2 Hz, 1H, Ha), 7.52 (d, *J* = 2.3 Hz, 1H, Hc), 7.37 – 7.34 (m, 3H), 7.28 – 7.25 (m, 2H), 7.21 – 7.18 (m, 1H, Hb), 4.52 (d, *J* = 5.8 Hz, 2H, Bn-CH_2), 1.32 (s, 9H, tert-butyl), 1.31 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, THF-d_8) δ 169.65, 153.94, 140.08, 135.79, 135.76, 128.88, 128.85, 128.42, 127.54, 125.49, 124.51, 82.67, 44.42, 35.28, 31.42, 24.97.

HRMS (FD+(eiFi)) calcd. for $C_{24}H_{32}BF_3NO_3$ $[M]^+$ 393.2480, found 393.2494.



20so

N-Benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethoxy)benzamide (**20so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (8:1 to 1:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 63%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 20.075 min, t (*ortho*)= 24.377 min, t (*meta*)= 25.197 min.
^{1}H NMR (500 MHz, $CDCl_3$) δ 9.37 (s, 1H, amide-NH), 8.00 (d, *J* = 8.2 Hz, 1H, Ha), 7.41 (s, 1H, Hc), 7.32 – 7.27 (m, 3H), 7.20 – 7.19 (m, 2H), 7.11 (d, *J* = 8.1 Hz, 1H, Hb), 4.16 (m, 2H, Bn-CH_2), 1.23 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.37, 152.94, 136.33, 132.38, 128.91, 128.14, 127.93, 126.08, 122.86, 120.27, 82.17, 44.99, 24.99.
HRMS (FD+(eiFi)) calcd. for $C_{21}H_{23}BF_3NO_4$ $[M]^+$ 421.1676, found 421.1672.



21so

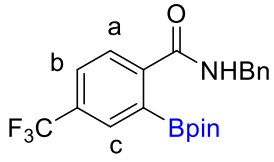
N-Benzyl-4-methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**21so**)

Purification of compound **21so**

Pure compound **21so** after chromatography

Gradient eluent EA/Hexane 10/1-10/7

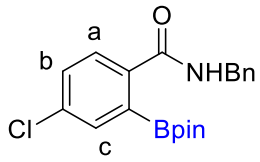
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 43%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 22.408 min, t (*ortho*)= 26.468 min, t (*meta*)= 27.472 min.
^{1}H NMR (500 MHz, $CDCl_3$) δ 8.35 (brs, 1H, amide-NH), 7.75 – 7.72 (m, 1H, Ha), 7.36 – 7.26 (m, 5H), 7.11 (s, 1H, Hc), 6.81 – 6.77 (m, 1H, Hb), 4.36 – 4.34 (m, 2H, Bn-CH_2), 3.87 (s, 3H, OMe), 1.33 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, $CDCl_3$) δ 170.86, 163.51, 137.07, 128.83, 128.27, 127.92, 126.75, 125.49, 115.33, 114.70, 82.03, 55.54, 45.06, 25.12.
HRMS (FD+(eiFi)) calcd. for $C_{21}H_{26}BNO_4$ $[M]^+$ 367.1959, found 367.1956.



22so

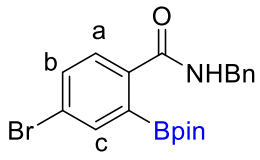
N-Benzyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-4-(trifluoromethxy)benzamide (**22so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 40%.

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.67 (s, 1H, amide-NH), 7.94 (d, *J* = 8.3 Hz, 1H, Ha), 7.87 (s, 1H, Hc), 7.57 – 7.56 (m, 2H), 7.36 – 7.22 (m, 4H), 4.29 (d, *J* = 5.5 Hz, 2H, Bn-CH_2), 1.28 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, $CDCl_3$) δ 169.66, 138.63, 136.50, 133.83 (m, two bonds C-F coupling), 128.95 (m, three bond C-F coupling), 128.77, 128.15, 128.01, 126.19 (m, one bond C-F coupling), 125.59 (m, three bond C-F coupling), 124.79, 82.89, 45.01, 24.99.
HRMS (FD+(eiFi)) calcd. for $C_{21}H_{23}BF_3NO_3$ $[M]^+$ 405.1727, found 405.1743.



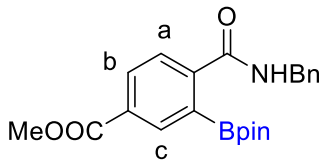
23so

N-Benzyl-4-chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**23so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 75%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 21.518 min, t (*ortho*)= 25.950 min, t (*meta*)= 26.437 min.
^{1}H NMR (500 MHz, THF-d_8) δ 8.52 (s, 1H, amide-NH), 7.65 (d, *J* = 8.3 Hz, 1H, Ha), 7.43 – 7.42 (m, 1H, Hc), 7.38 – 7.34 (m, 2H), 7.38 – 7.36 (m, 2H), 7.34 – 7.28 (m, 1H, Hb), 7.24 – 7.21 (m, 1H), 4.61 (d, *J* = 5.8 Hz, 2H, Bn-CH_2), 1.31 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, THF-d_8) δ 168.90, 139.49, 137.86, 136.29, 135.24, 132.01, 129.00, 128.60, 128.36, 127.82, 125.89, 82.79, 44.84, 24.82.
HRMS (FD+(eiFi)) calcd. for $C_{20}H_{23}BClNO_3$ $[M]^+$ 371.1463, found 371.1456.



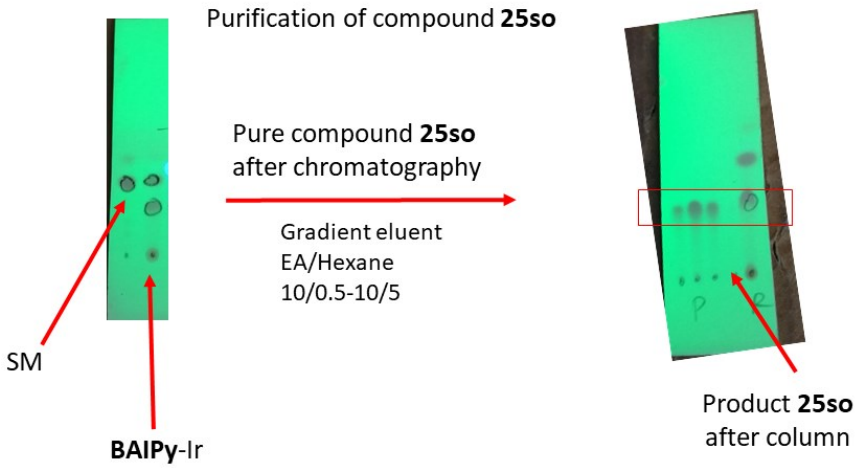
24so

N-Benzyl-4-bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**24so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 67%.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 22.460 min, t (*ortho*)= 26.720 min, t (*meta*)= 39.940 min.
^{1}H NMR (500 MHz, THF-d_8) δ 8.49 (s, 1H, amide-NH), 7.59 – 7.57 (m, 2H), 7.50 – 7.47 (m, 1H), 7.38 – 7.36 (m, 2H), 7.31 – 7.27 (m, 2H), 7.24 – 7.20 (m, 1H), 4.60 (d, *J* = 5.8 Hz, 2H, Bn-CH_2), 1.31 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, THF-d_8) δ 169.96, 139.51, 135.07, 131.37, 128.99, 128.60, 127.81, 126.13, 82.86, 44.83, 24.82.
HRMS (FD+(eiFi)) calcd. for $C_{20}H_{23}BBrNO_3$ $[M]^+$ 415.0940, found 415.0959.



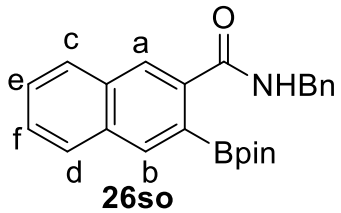
25so

Methyl 4-(benzylcarbamoyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**25so**)



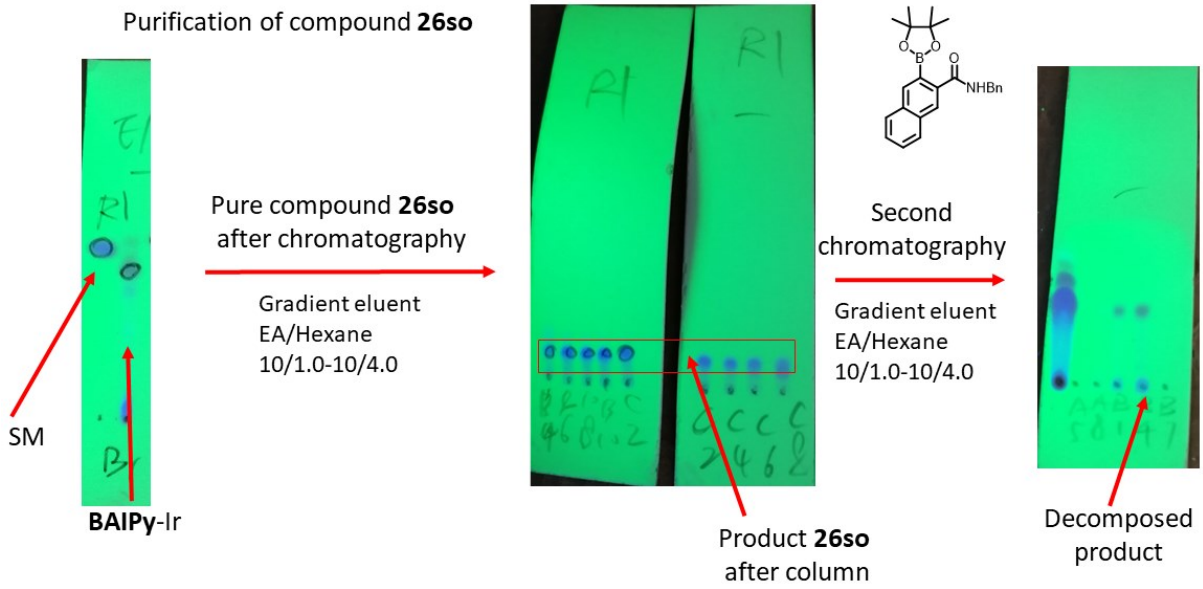
BAIPy-Ir catalyst; Isolated yield of 32%.

Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (5:1 to 2:1) as the eluent.
Rtx-1 column, method: Initial temperature = 50 ºC for 2 min, then 10ºC/min to 300ºC for 15 min. Retention time: t (Sub) = 24.250 min, t (*ortho*)= 28.308 min, t (*meta*)= 29.335 min.
^{1}H NMR (500 MHz, CD_2Cl_2) δ 9.08 (s, 1H, amide-NH), 8.22 (s, 1H, Hc), 8.09 – 7.91 (m, 2H, Ha &, Hb), 7.34 – 7.25 (m, 5H, Bn-aryl-H), 4.20 (d, *J* = 5.8 Hz, 2H, Bn-CH_2), 3.94 (s, 3H, COOMe), 1.28 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.39, 166.86, 139.50, 137.34, 133.47, 132.74, 129.92, 128.99, 128.35, 128.11, 124.93, 82.82, 52.64, 45.03, 25.11.
HRMS (FD+(eiFi)) calcd. for $C_{22}H_{26}BF_3NO_5$ $[M]^+$ 395.1904, found 395.1959.

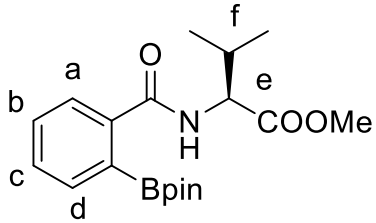


26so

N-Benzyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-2-naphthamide (**26so**)

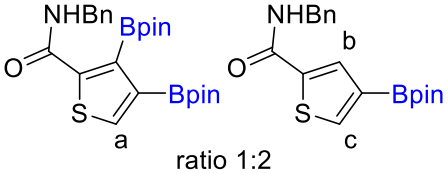


Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:0.5 to 10:3.0) as the eluent.
BAIPy-Ir catalyst; Isolated yield of 64%.
^{1}H NMR (500 MHz CD_2Cl_2) δ 8.30 (s, 1H, amide-H), 8.15 (brs, 1H, Ha), 8.06 (s, 1H, Hb), 7.90 (d, *J* = 7.6 Hz, 1H, Hd), 7.87 – 7.82 (m, 1H, Hc), 7.56 – 7.50 (m, 2H, He&f), 7.33 – 7.25 (m, 5H, Bn-aryl-H), 4.33 (d, *J* = 5.8 Hz, 2H, Bn-CH_2), 1.37 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 170.44, 138.35, 135.09, 134.66, 133.21, 132.95, 129.08, 128.92, 128.49, 128.23, 128.09, 127.84, 127.19, 125.47, 83.34, 44.67, 25.19.
HRMS (FD+(eiFi)) calcd. for $C_{24}H_{26}BNO_3$ $[M]^+$ 387.2010, found 387.1994.



27so

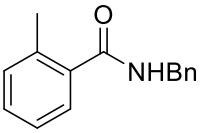
Methyl (2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoyl)valinate (**27so**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (5:1 to 2:1) as the eluent.
BAIPy-Ir catalyst; Isolated yield of 63%.
^{1}H NMR (500 MHz CD_2Cl_2) δ 7.62 (d, J = 7.7 Hz, 1H, Ha), 7.58 (d, J = 7.4 Hz, 1H, Hd), 7.49 (t, J = 7.3 Hz, 1H, Hb), 7.44 (t, J = 7.5 Hz, 1H, Hc), 6.85 (d, J = 8.6 Hz, 1H, amide-NH), 4.71 (dd, J = 8.6, 5.2 Hz, 1H, He), 3.76 (s, 3H, OMe), 2.26 (h, J = 6.7 Hz, 1H, Hf), 1.35 (d, J = 5.9 Hz, 12H, pin-Me), 1.03 – 0.98 (m, 6H, isopropyl-Me).
^{13}C NMR (126 MHz, CD_2Cl_2) δ 172.61, 168.99, 138.57, 133.24, 130.97, 129.36, 125.24, 83.85, 58.33, 52.48, 32.01, 25.02, 24.95, 19.23, 18.25.
HRMS (FD+(eiFi)) calcd. for $C_{19}H_{28}BNO_5$ $[M]^+$ 361.2064, found 361.2059.



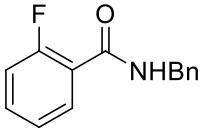
ratio 1:2

28so+28sm

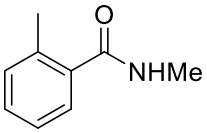
N-benzyl-3,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carboxamide (**28so**) and *N*-Benzyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)thiophene-2-carboxamide (**28sm**)
Isolated by chromatography using deactivated silica gel and ethyl acetate and petroleum ether (10:1 to 1:1) as the eluent**.**
BAIPy-Ir catalyst; Isolated yield of 85%.
^{1}H NMR (500 MHz, $CDCl_3$) **28so** δ 9.11 (t, *J* = 4.9 Hz, 1H, amide-NH), 7.92 (s, 1H, Ha), 7.31 – 7.27 (m, 5H, Bn-aryl-H), 4.51 (d, *J* = 4.8 Hz, 2H, Bn-CH_2), 1.29 (s, 12H, pin-Me), 1.18 (s, 12H, pin-Me).
^{1}H NMR (500 MHz, $CDCl_3$) **28sm** δ 7.57 (d, *J* = 3.7 Hz, 1H, Hb), 7.48 (d, *J* = 3.6 Hz, 1H, Hc), 7.27 – 7.18 (m, 5H, Bn-aryl-H), 6.68 (t, *J* = 5.8 Hz, 1H, amide-NH), 4.53 (d, *J* = 5.8 Hz, 2H, Bn-CH_2), 1.29 (s, 12H, pin-Me).
^{13}C NMR (126 MHz, $CDCl_3$) **28so** and **28sm** 1:2 mixtures δ 161.80, 161.77, 156.14, 146.13, 144.50, 138.04, 137.76, 137.18, 129.63, 128.76, 128.70, 128.68, 127.88, 127.63, 127.60, 84.89, 84.55, 84.42, 44.73, 44.04, 24.88, 24.80, 24.51.
28sm HRMS (FD+(eiFi)) calcd. for $C_{18}H_{22}BNO_3S$ $[M]^+$ 343.1413, found 343.1378.
28so HRMS (FD+(eiFi)) calcd. for $C_{24}H_{33}B_2NO_5S$ $[M]^+$ 469.2274, found 469.2272.



29s

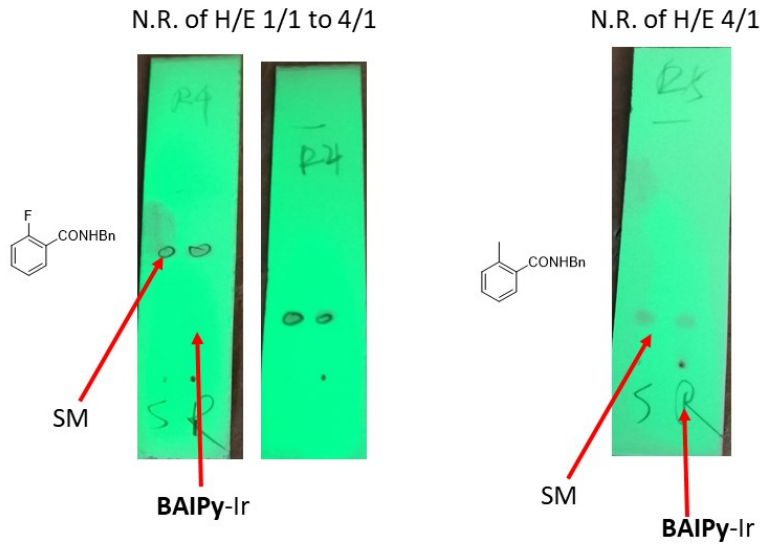


30s

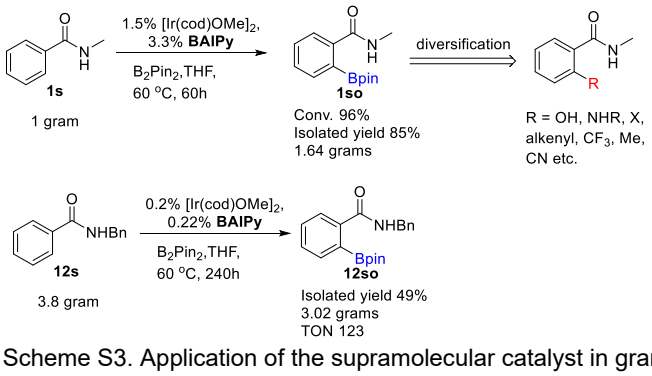


31s

BAIPy-Ir catalyst showed no reactivity for *Ortho*-functionalized benzamides under optimized reaction conditions.



Application of the supramolecular catalyst in gram scale *ortho*-CH borylation



Scheme S3. Application of the supramolecular catalyst in gram scale *ortho*-CH borylation.

Spectra

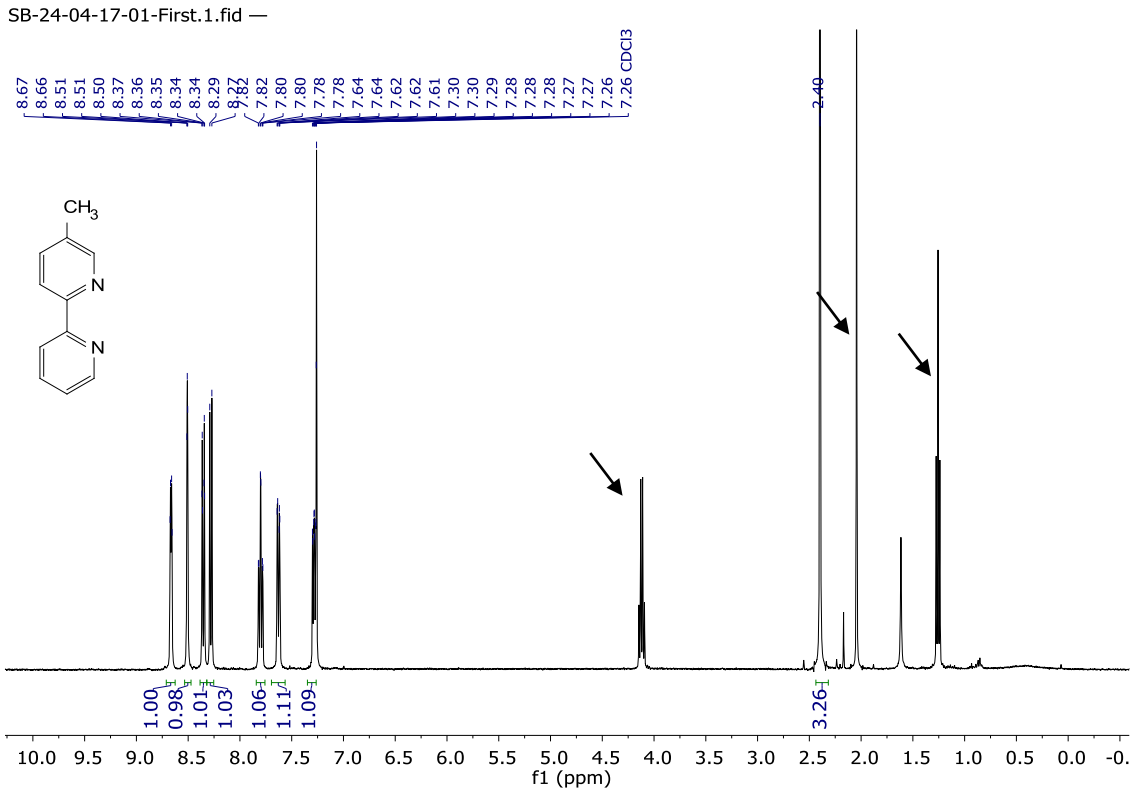


Figure S11. ^{1}H NMR spectra of 5-methyl-2,2'-bipyridine **2** (ethyl acetate indicated by arrows)

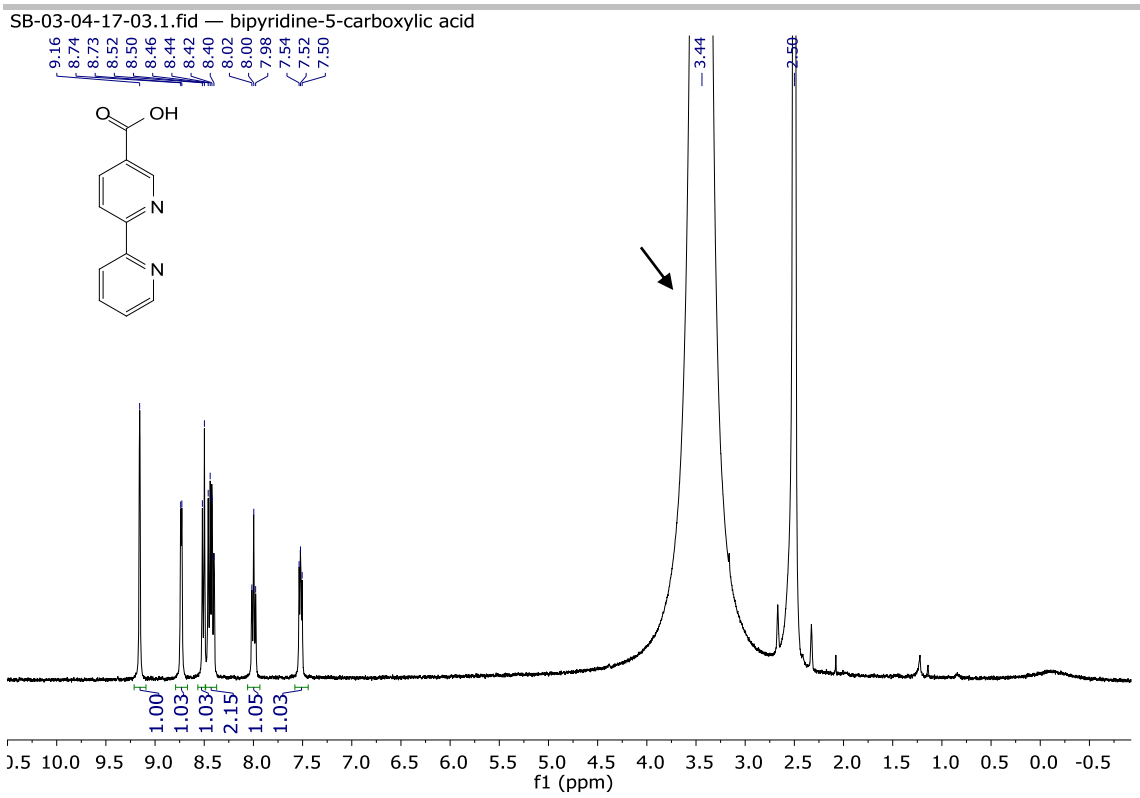


Figure S12. ^{1}H NMR spectra of 2,2'-Bipyridinyl-5-carboxylic acid **3** (water indicated by arrows)

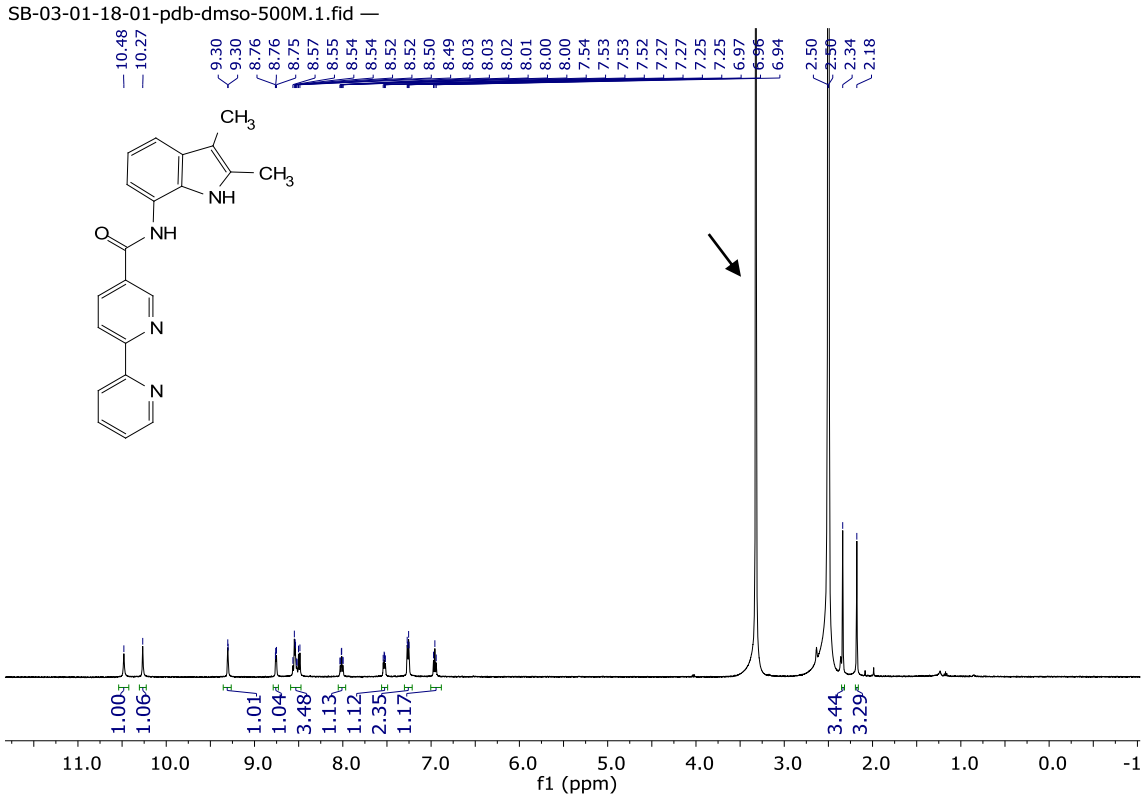


Figure S13. ^{1}H NMR spectra of supramolecular ligand **BAIPy** (water indicated by arrows)

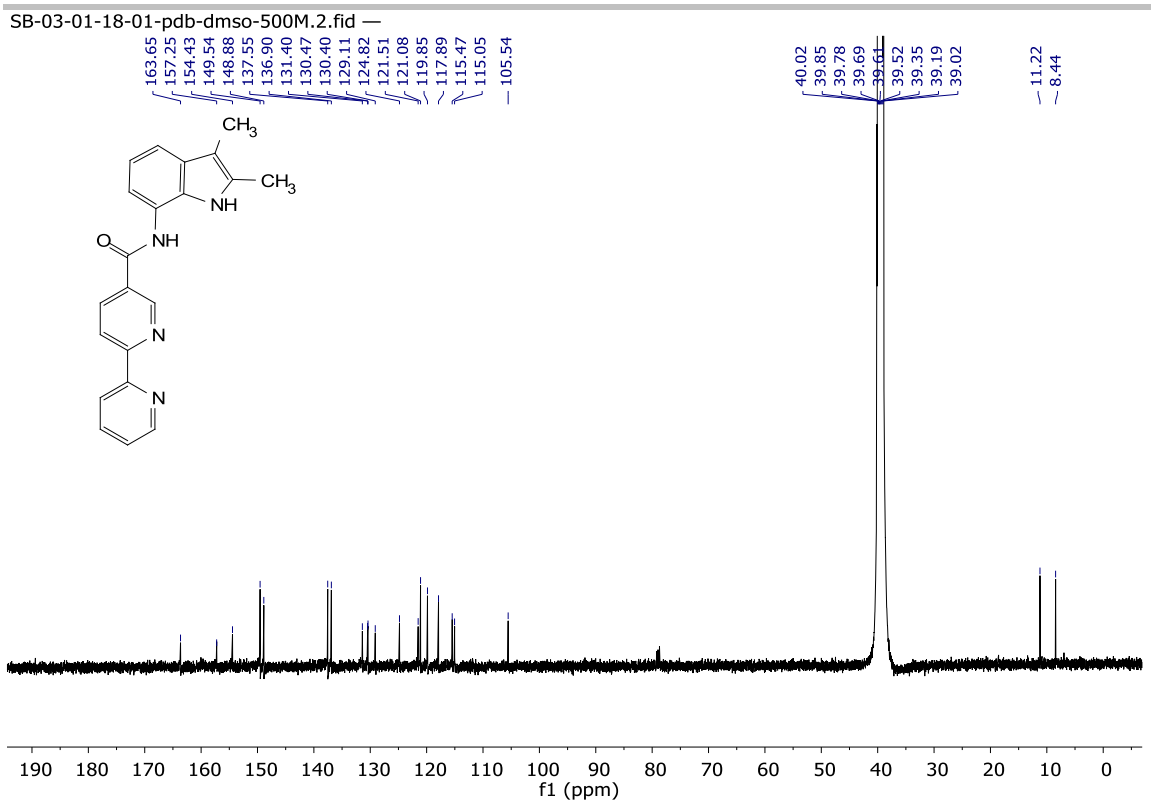


Figure S14. ^{13}C NMR spectra of supramolecular ligand **BAIPy**

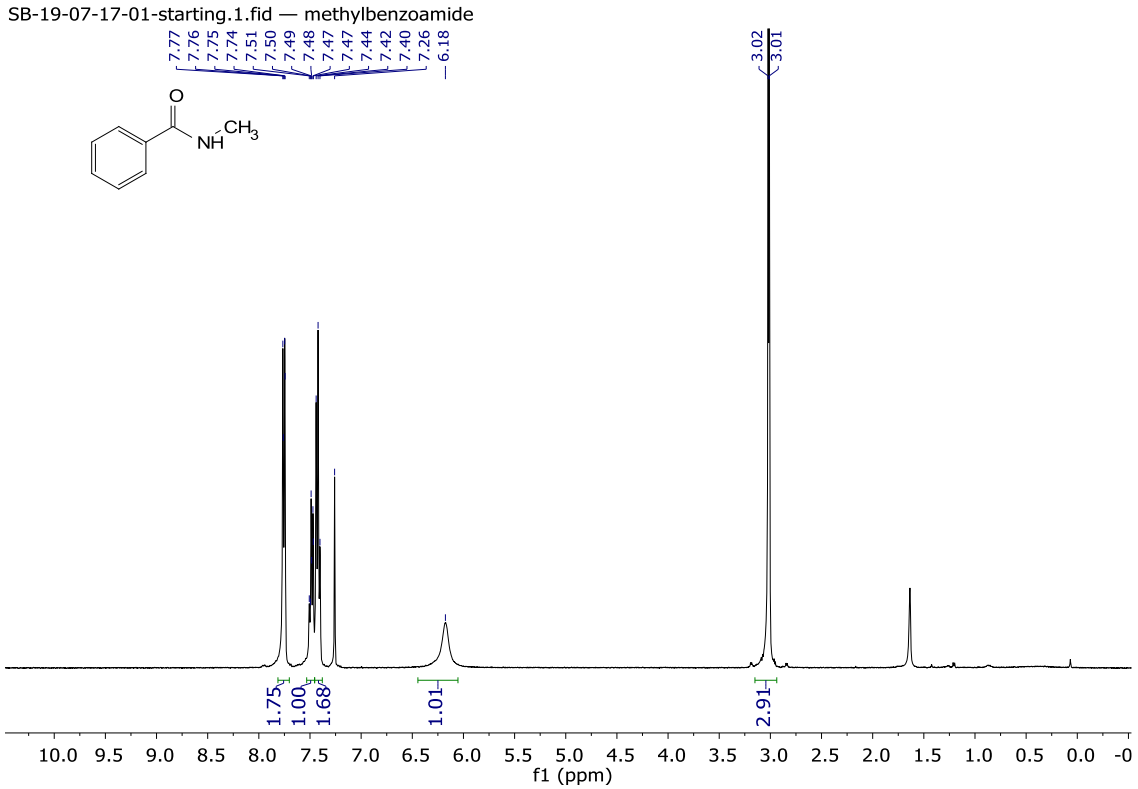


Figure S15. ^{1}H NMR spectra of aromatic amide **1s**

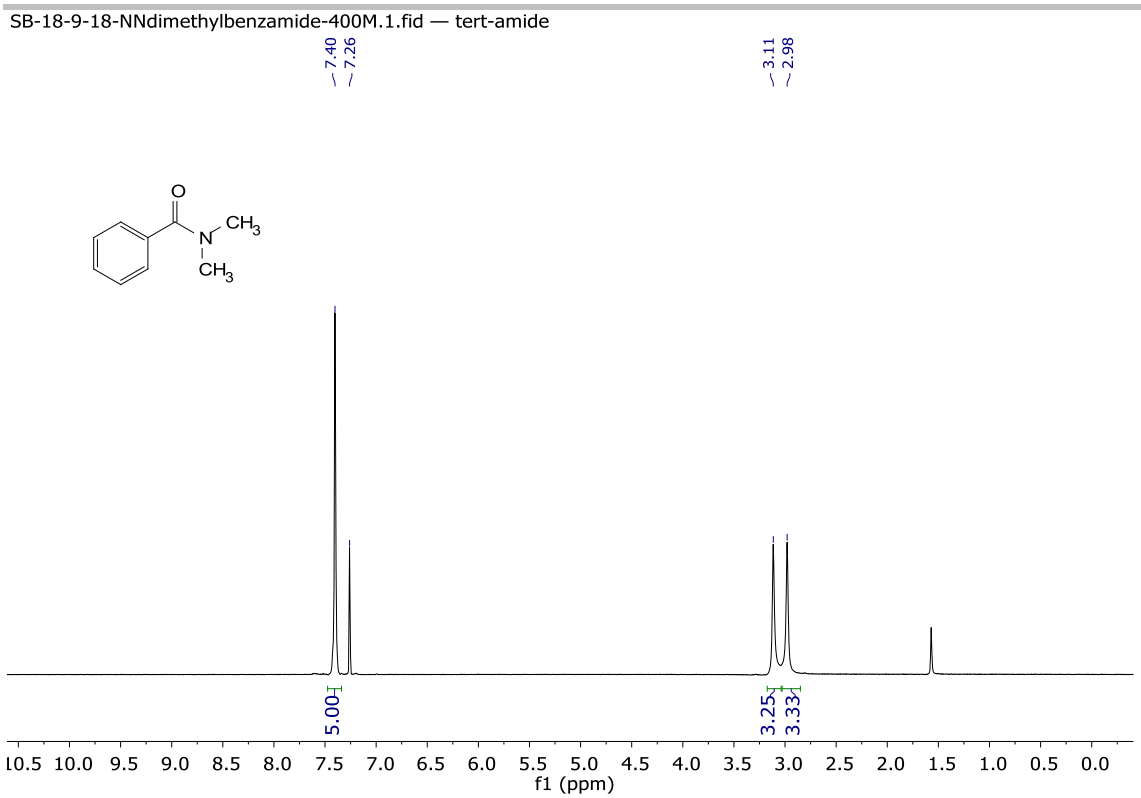


Figure S16. ^{1}H NMR spectra of aromatic amide **2s**

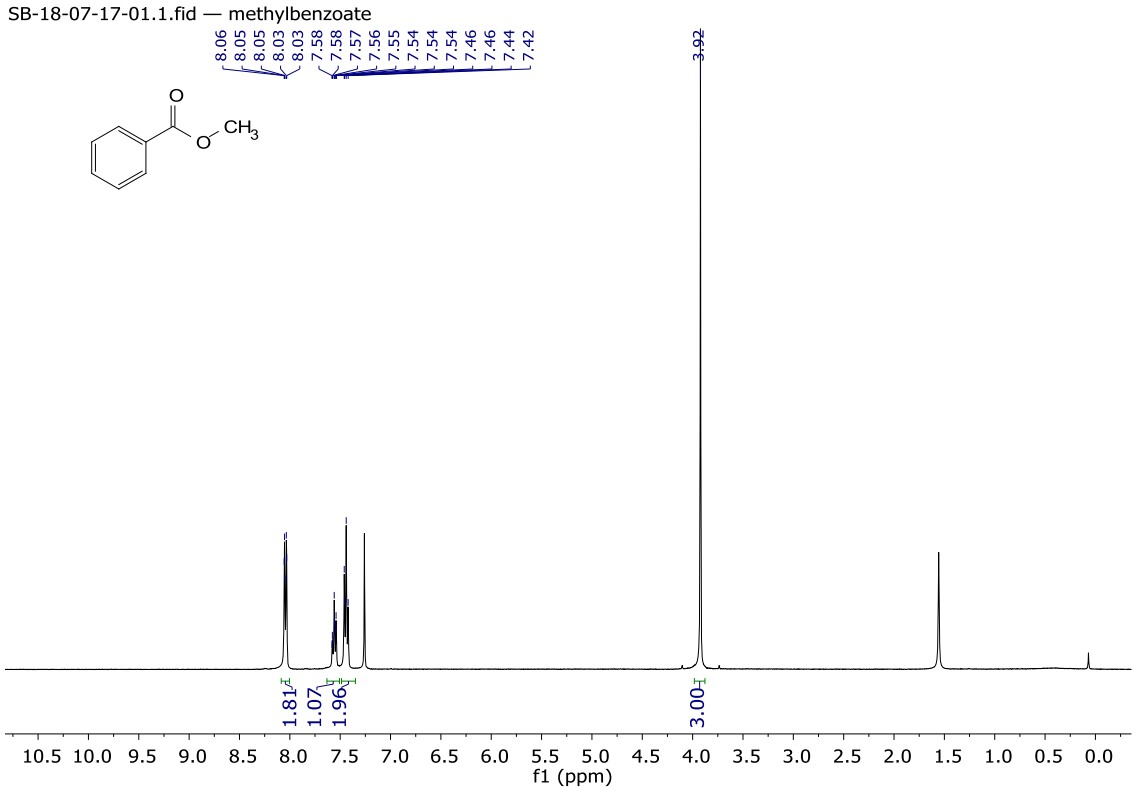


Figure S17. ^{1}H NMR spectra of aromatic amide **3s**

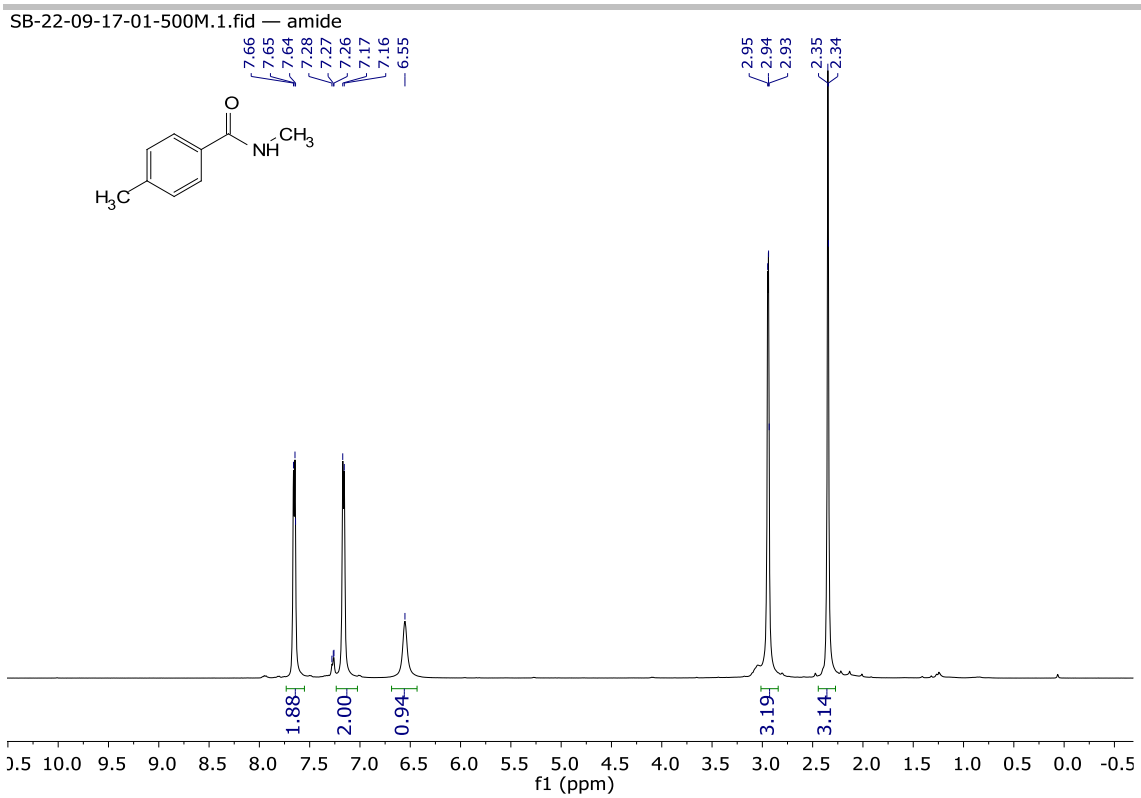


Figure S18. ^{1}H NMR spectra of aromatic amide **4s**

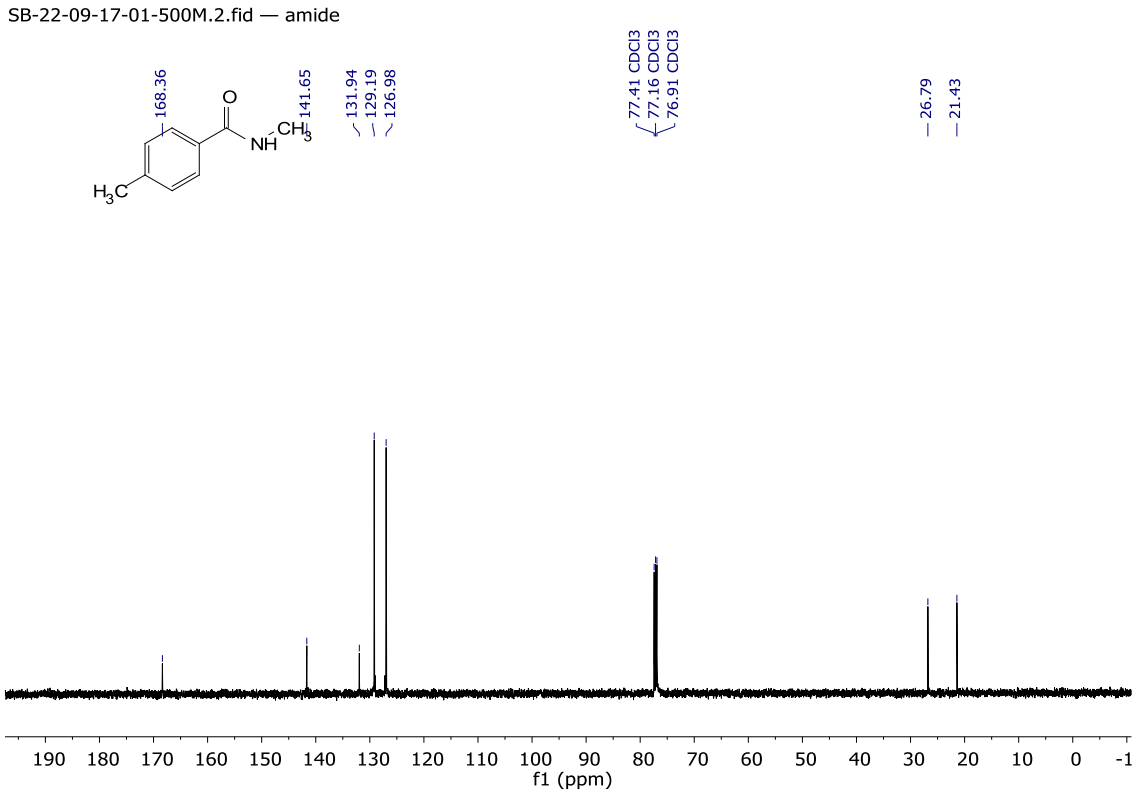


Figure S19. ^{13}C NMR spectra of aromatic amide **4s**

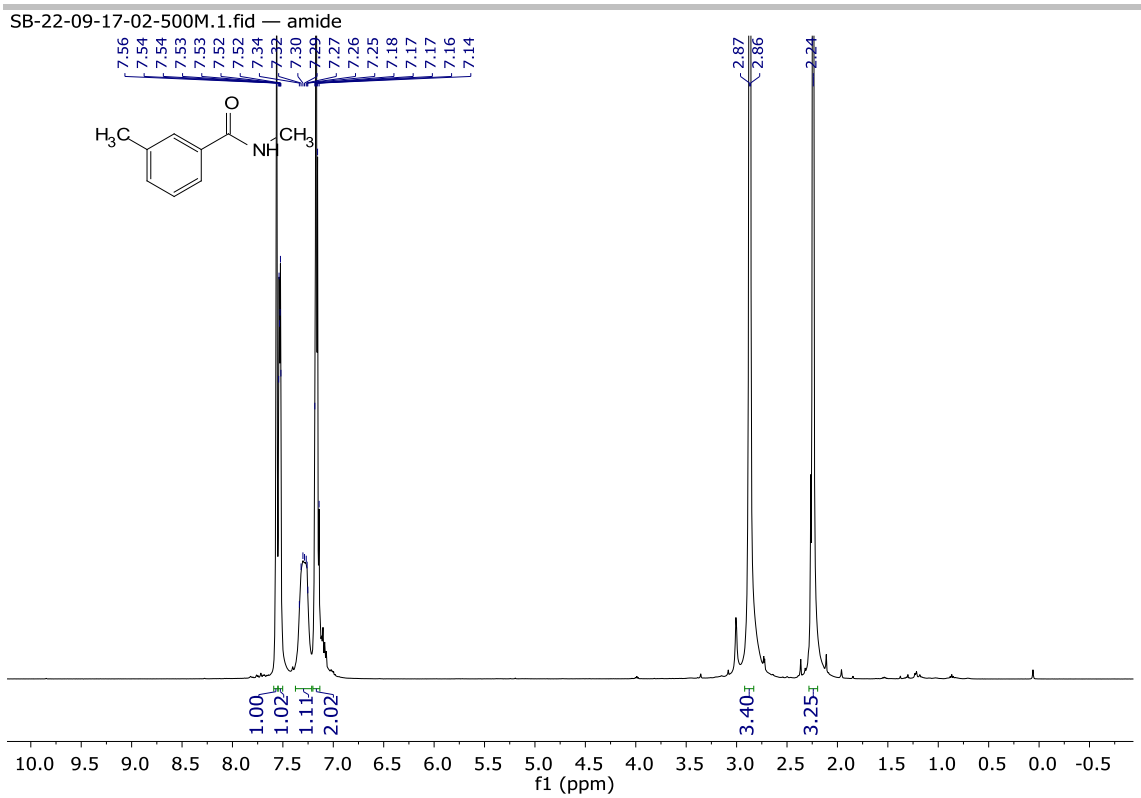


Figure S20. ^{1}H NMR spectra of aromatic amide **5s**

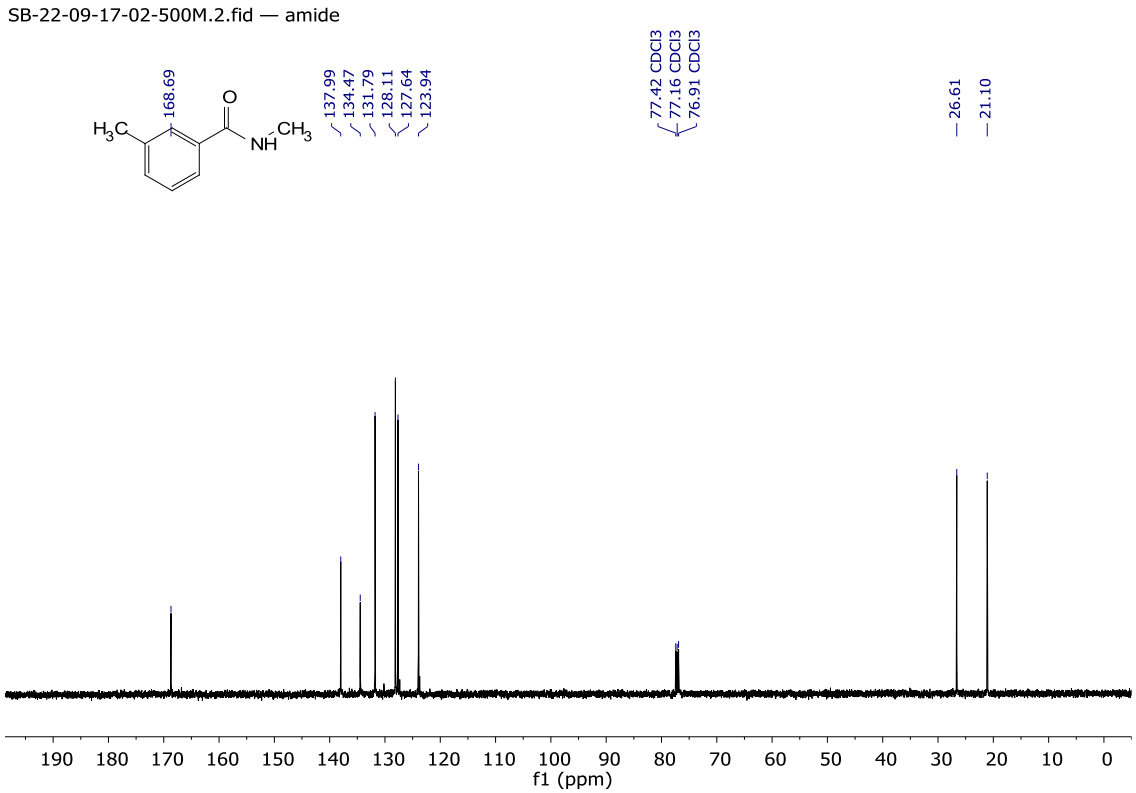


Figure S21. ^{13}C NMR spectra of aromatic amide **5s**

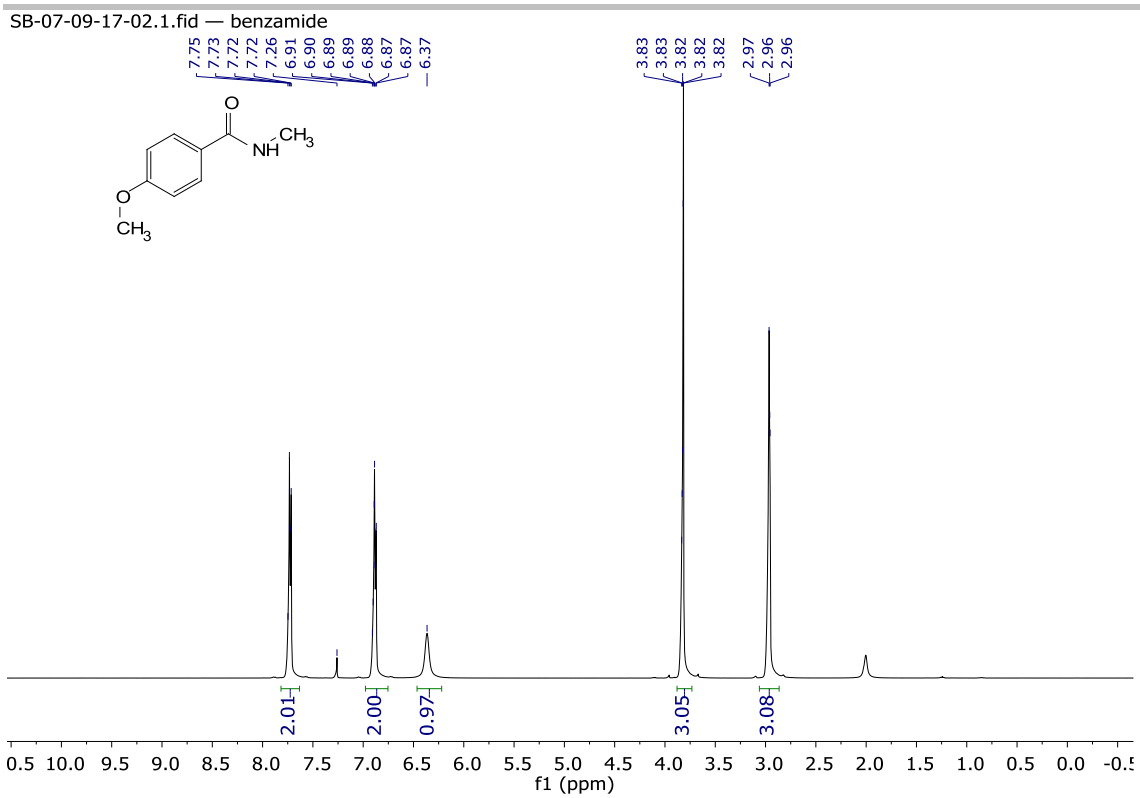


Figure S22. ^{1}H NMR spectra of aromatic amide **6s**

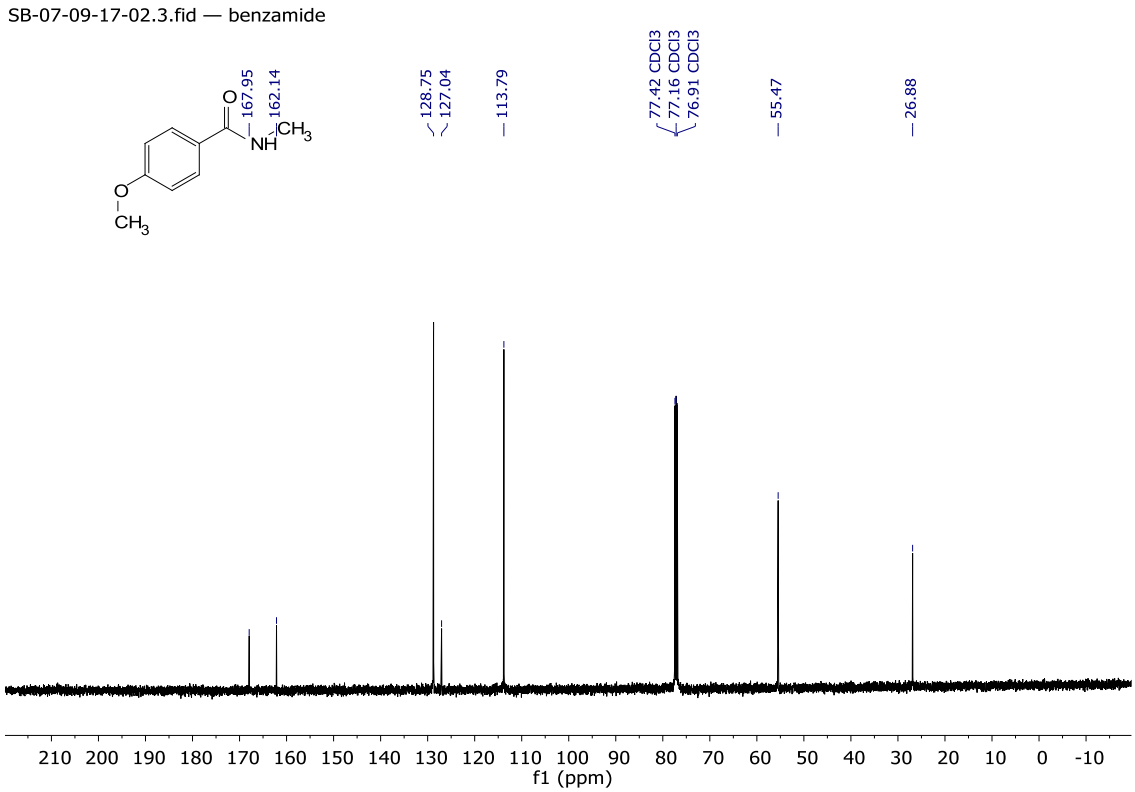


Figure S23. ^{13}C NMR spectra of aromatic amide **6s**

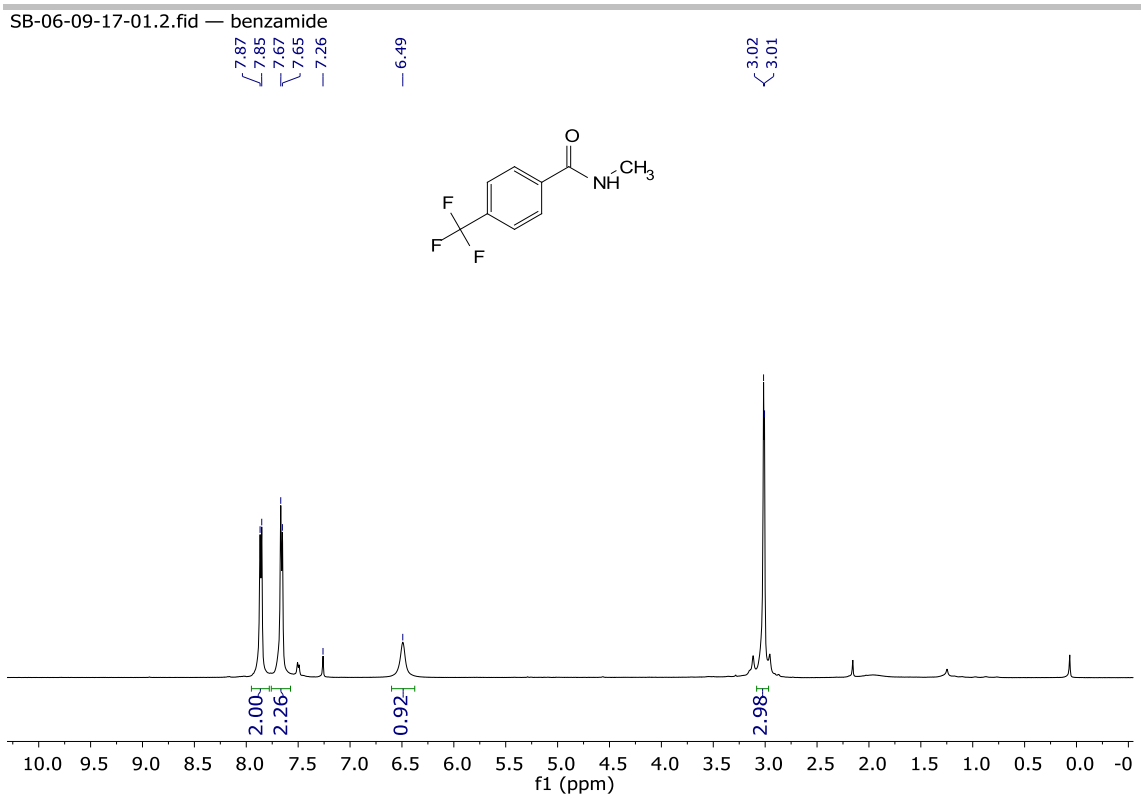


Figure S24. ^{1}H NMR spectra of aromatic amide **7s**

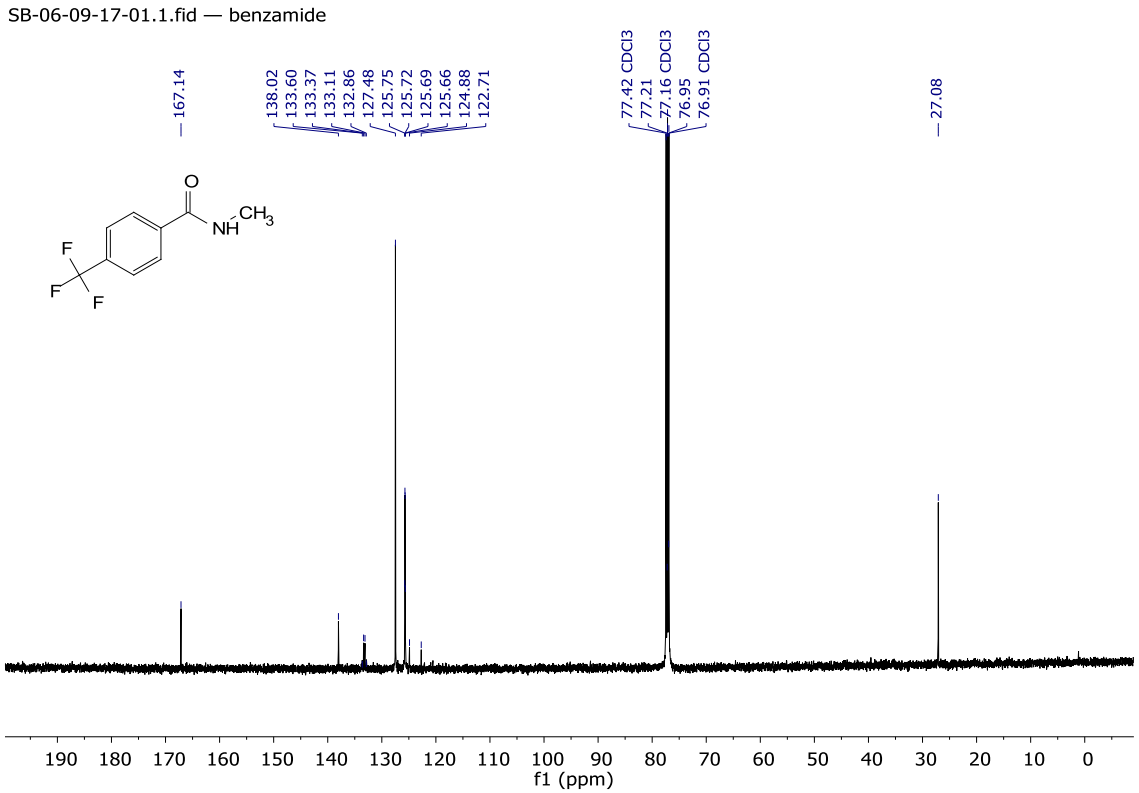


Figure S25. ^{13}C NMR spectra of aromatic amide **7s**

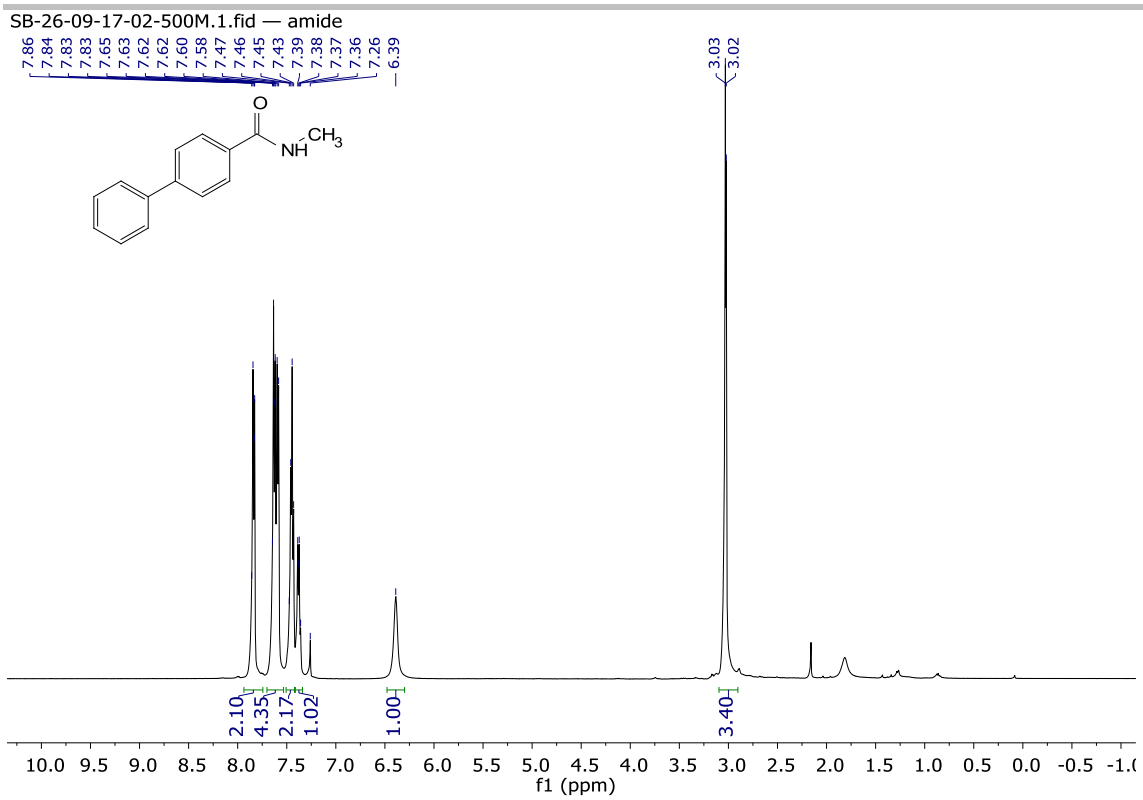


Figure S26. ^{1}H NMR spectra of aromatic amide **8s**

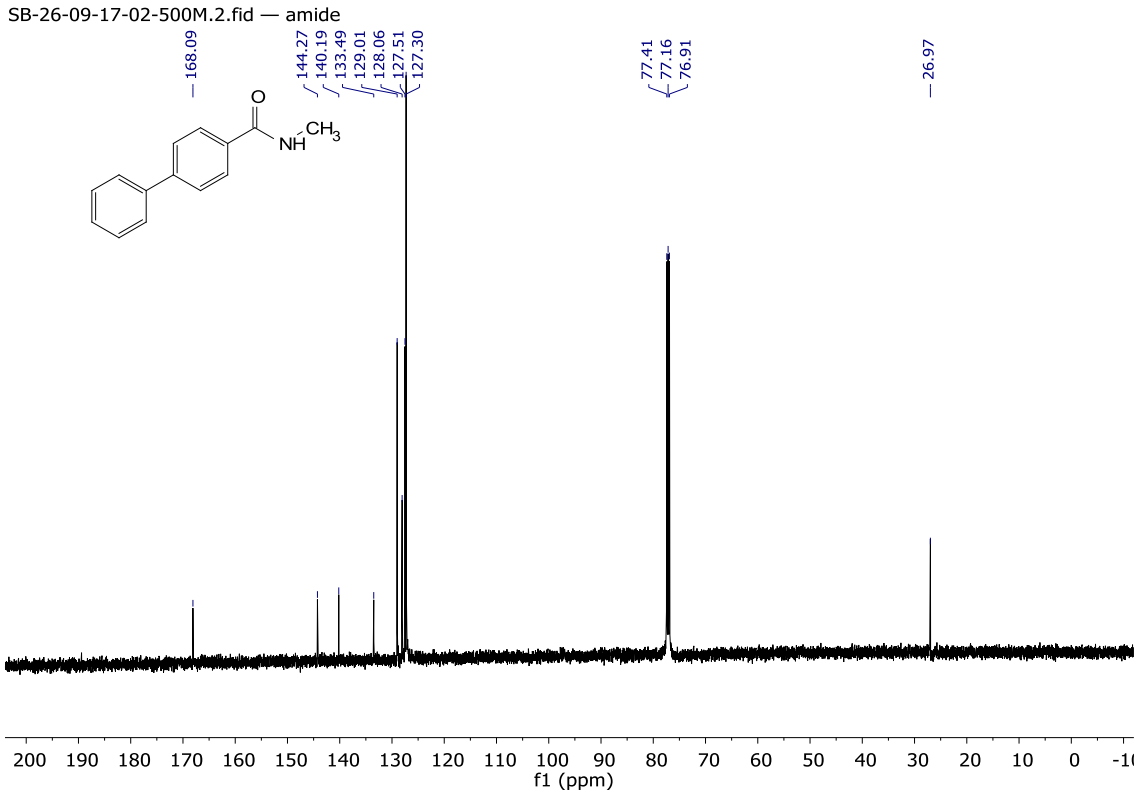


Figure S27. ^{13}C NMR spectra of aromatic amide **8s**

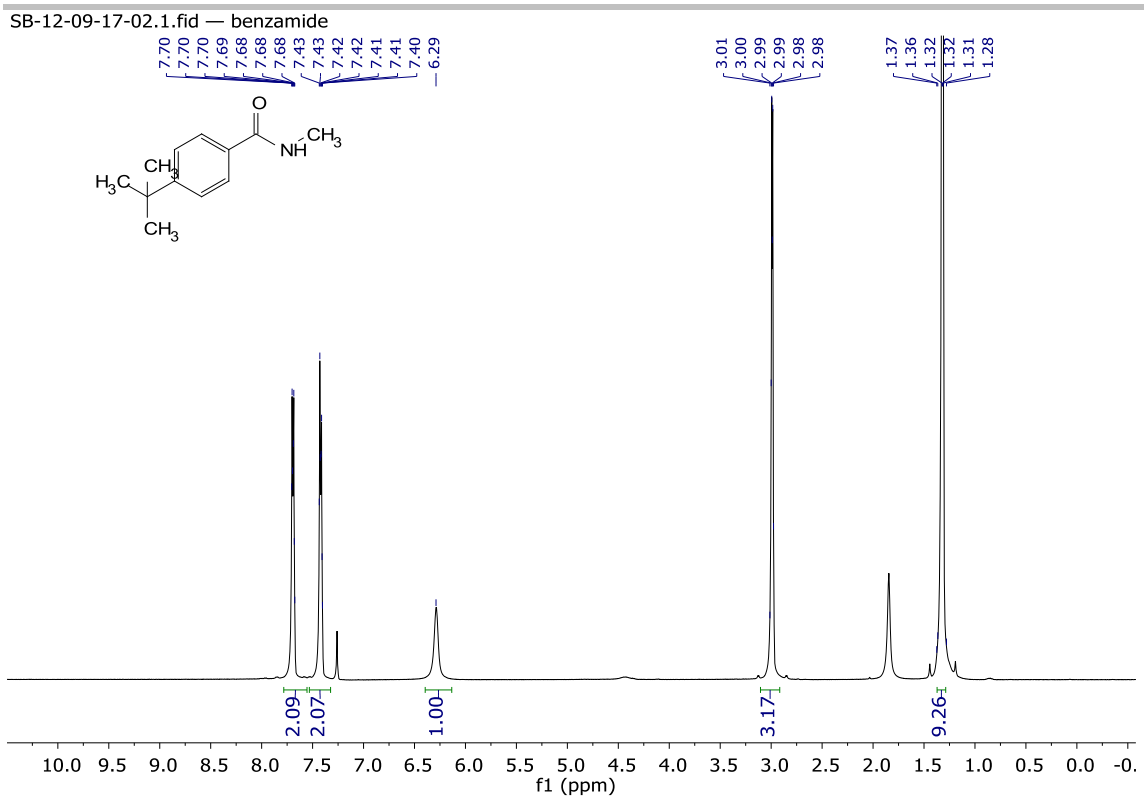


Figure S28. ^{1}H NMR spectra of aromatic amide **9s**

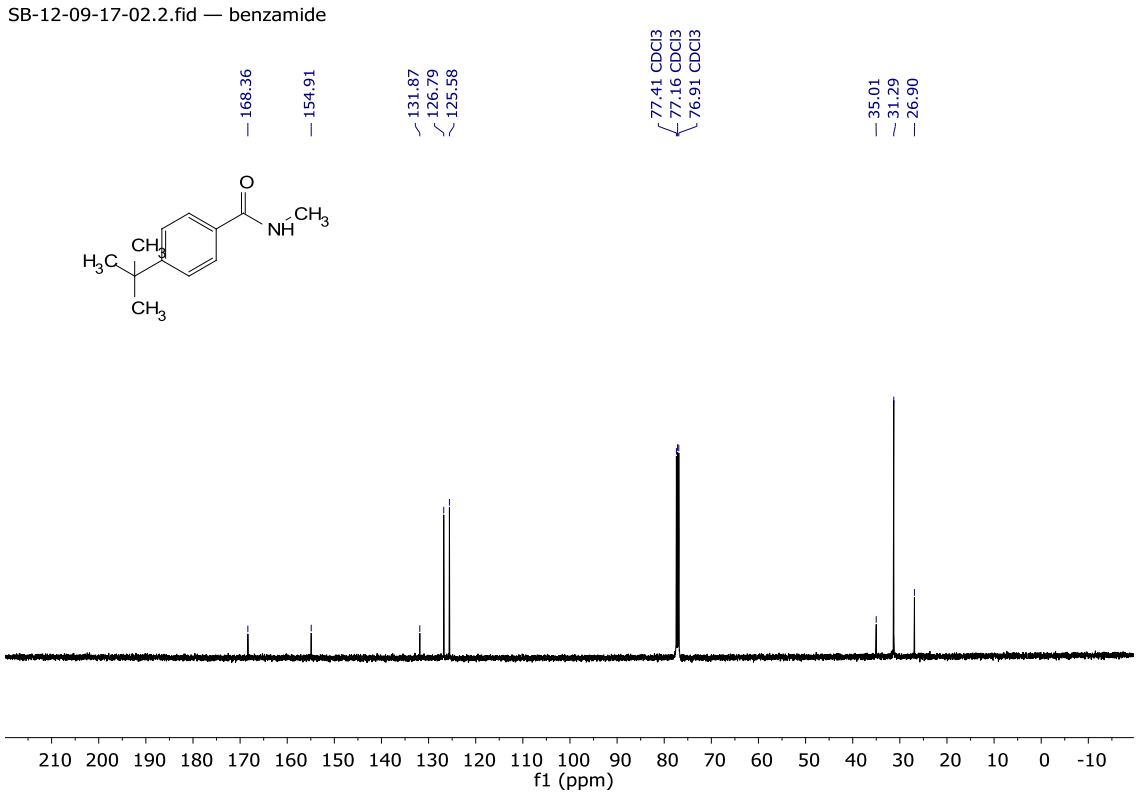


Figure S29. ^{13}C NMR spectra of aromatic amide **9s**

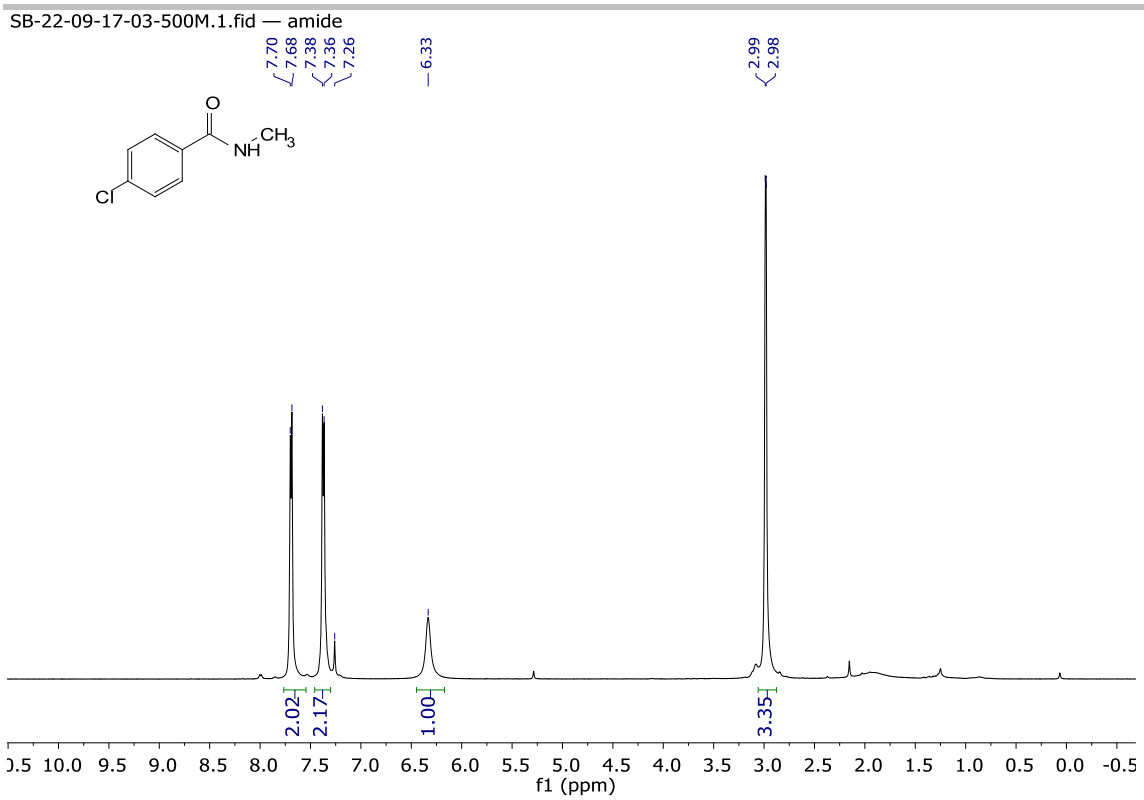


Figure S30. ^{1}H NMR spectra of aromatic amide **10s**

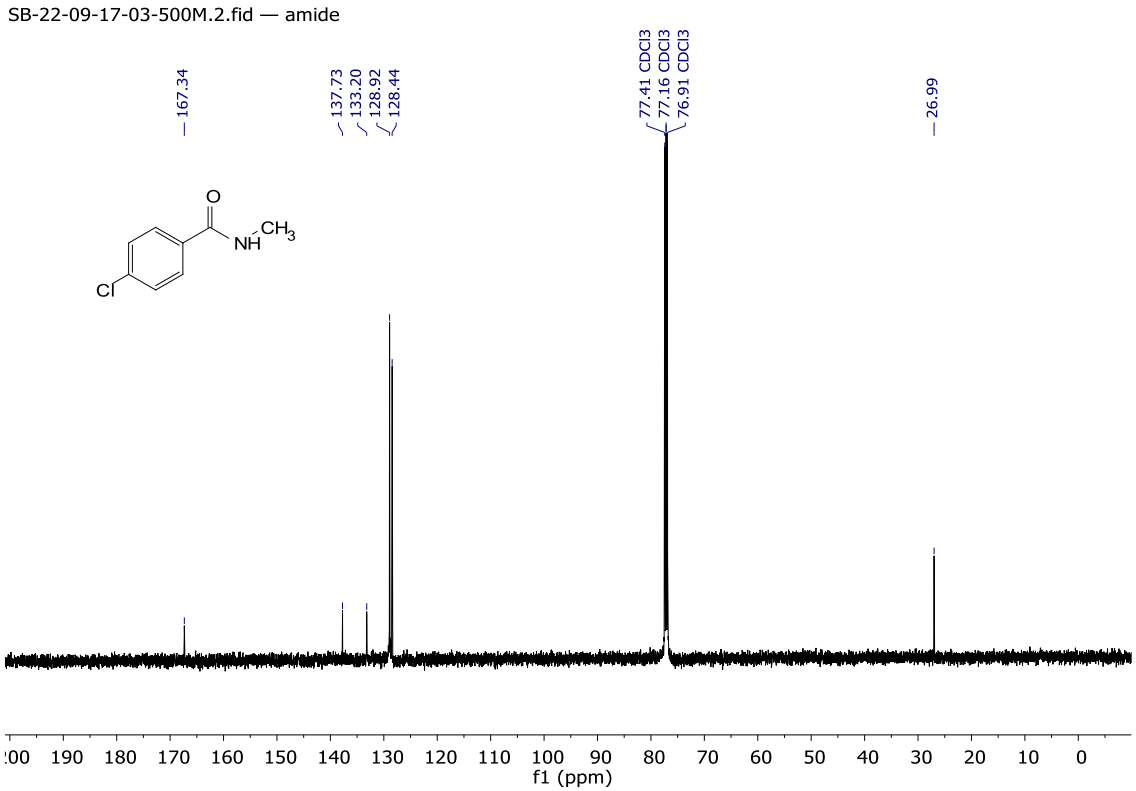


Figure S31. ^{13}C NMR spectra of aromatic amide **10s**

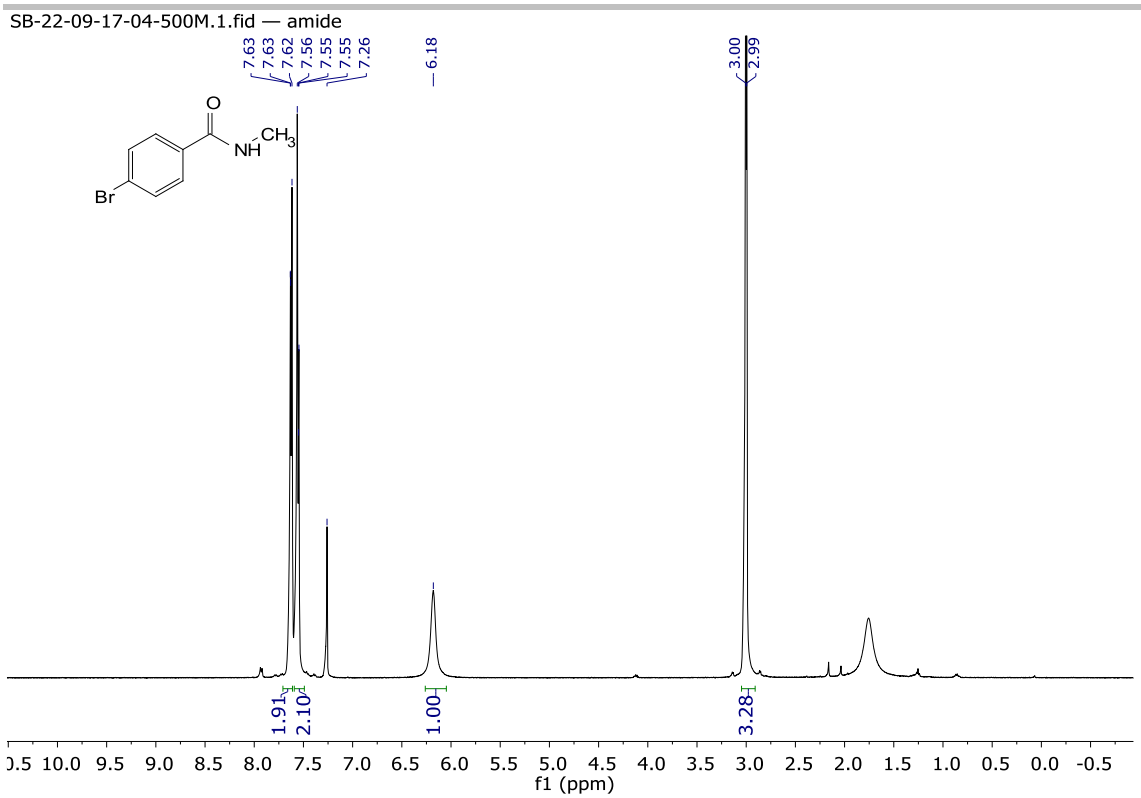


Figure S32. ^{1}H NMR spectra of aromatic amide **11s**

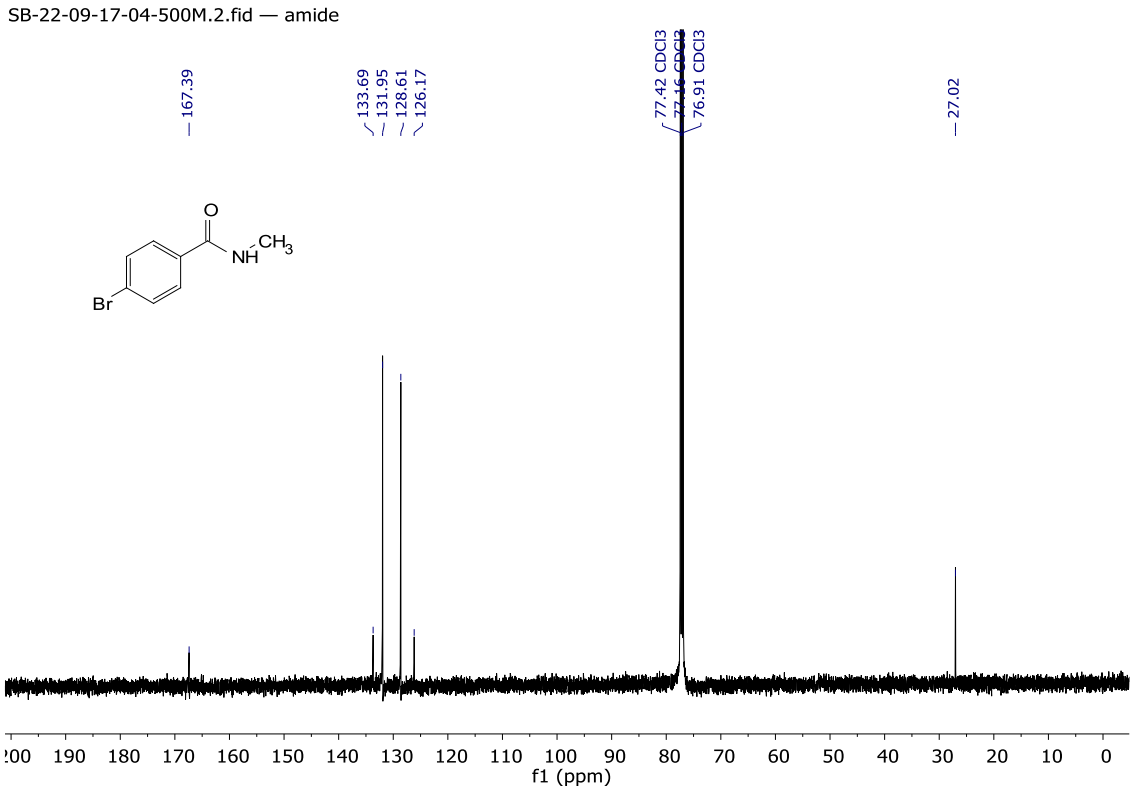


Figure S33. ^{13}C NMR spectra of aromatic amide **11s**

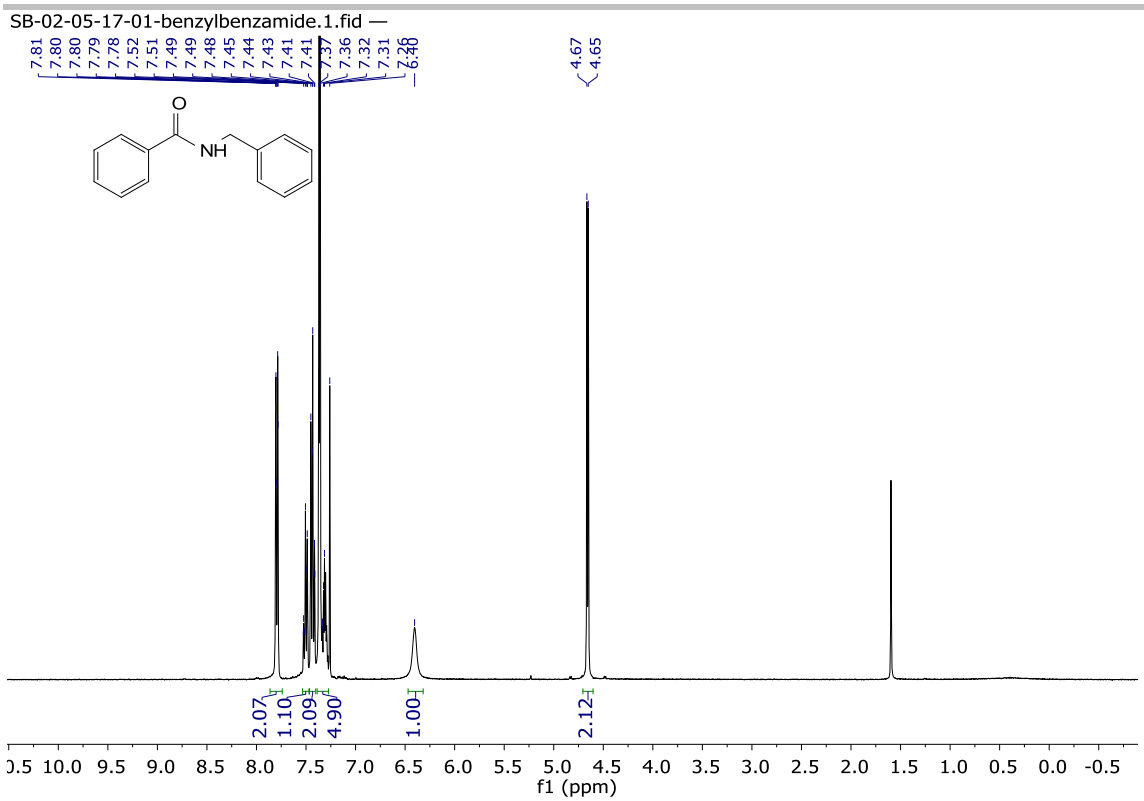


Figure S34. ^{1}H NMR spectra of aromatic amide **12s**

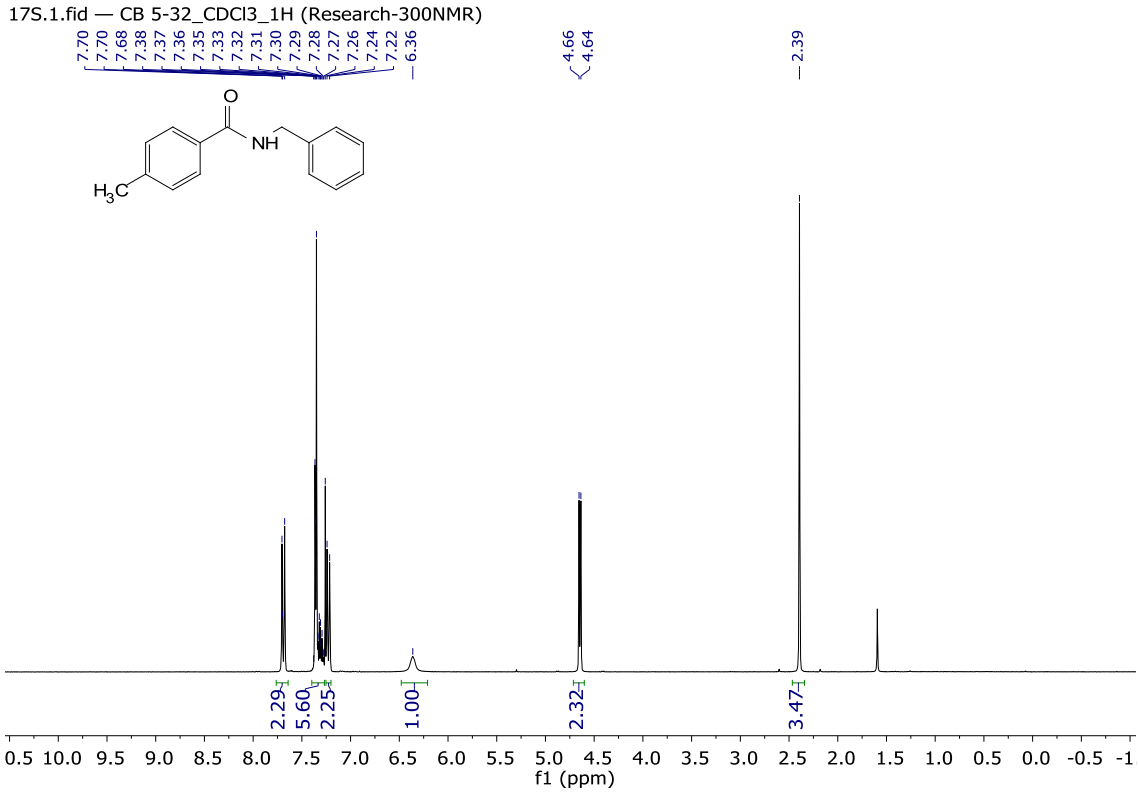


Figure S35. ^{1}H NMR spectra of aromatic amide **13s**

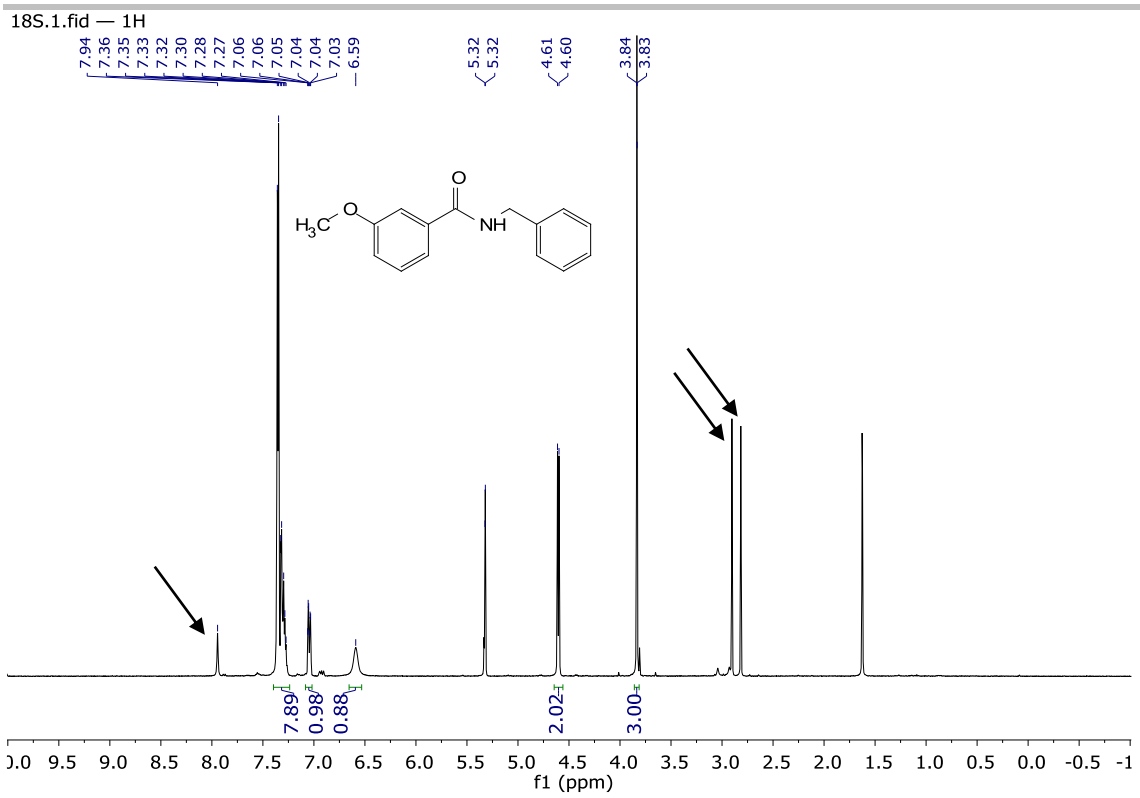


Figure S36. ^{1}H NMR spectra of aromatic amide **14s** (DMF indicated by arrows)

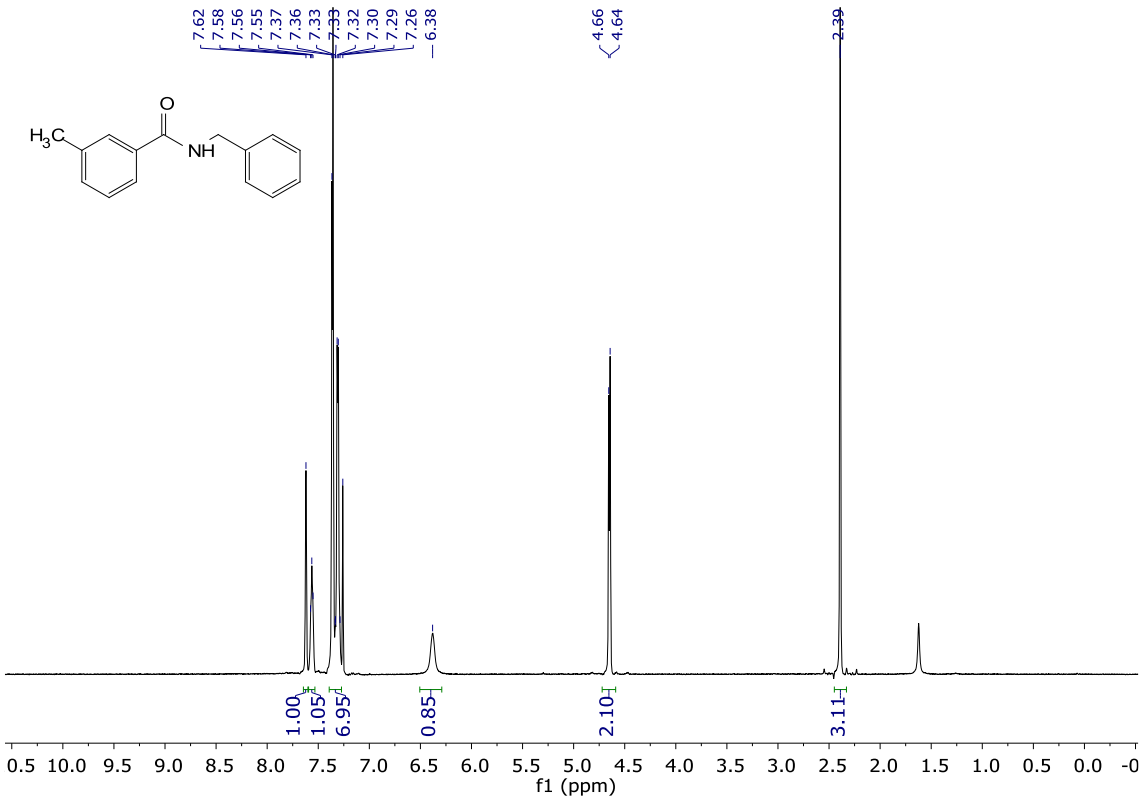


Figure S37. ^{1}H NMR spectra of aromatic amides **15s**

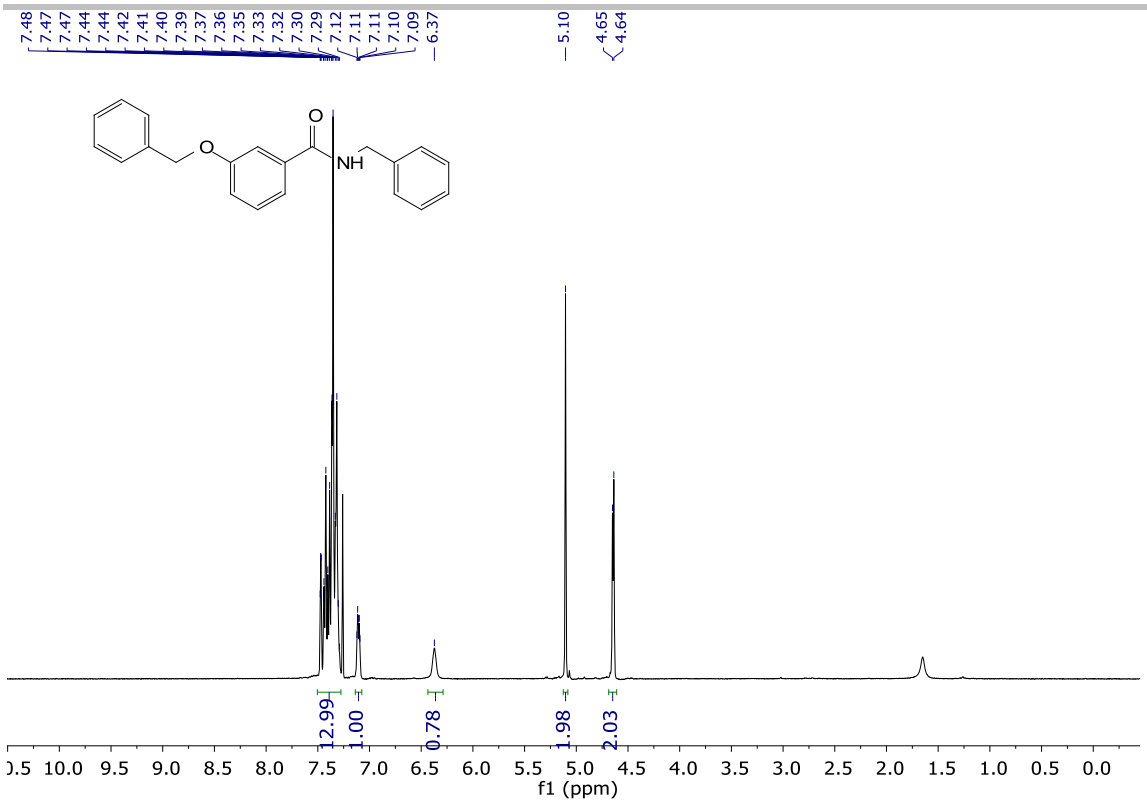


Figure S38. ^{1}H NMR spectra of aromatic amides **16s**

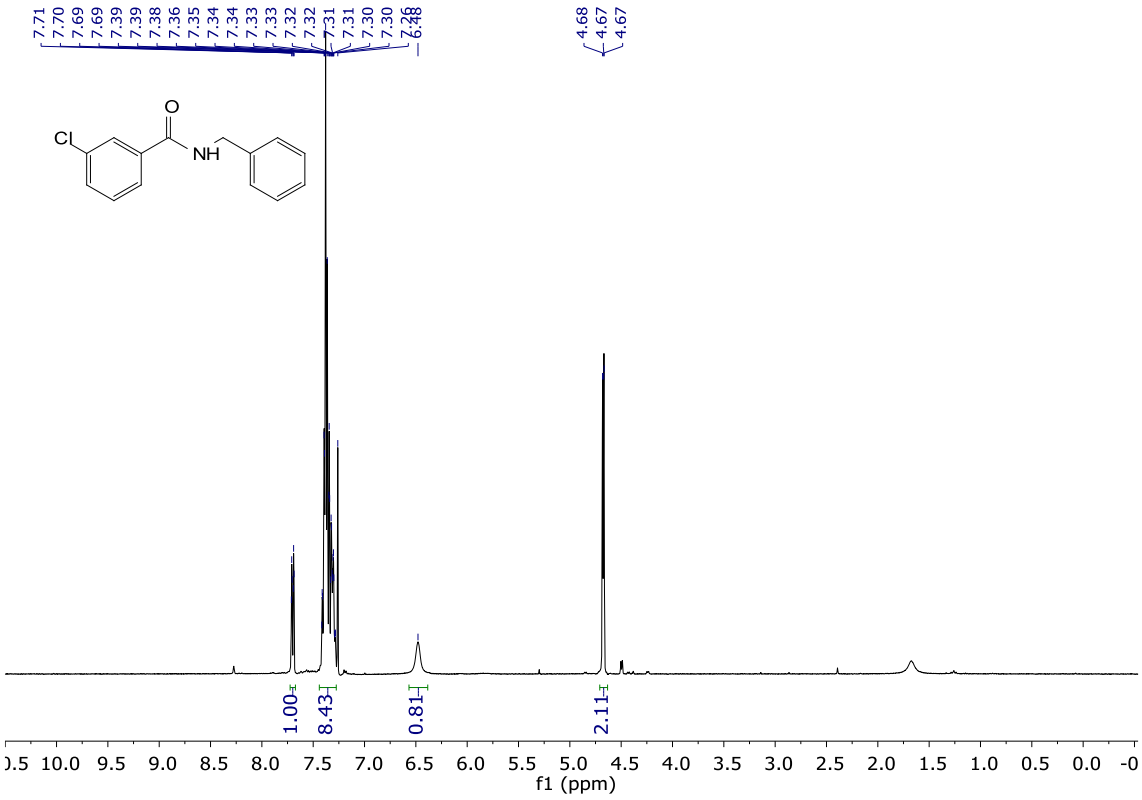


Figure S39. ^{1}H NMR spectra of aromatic amides **17s**

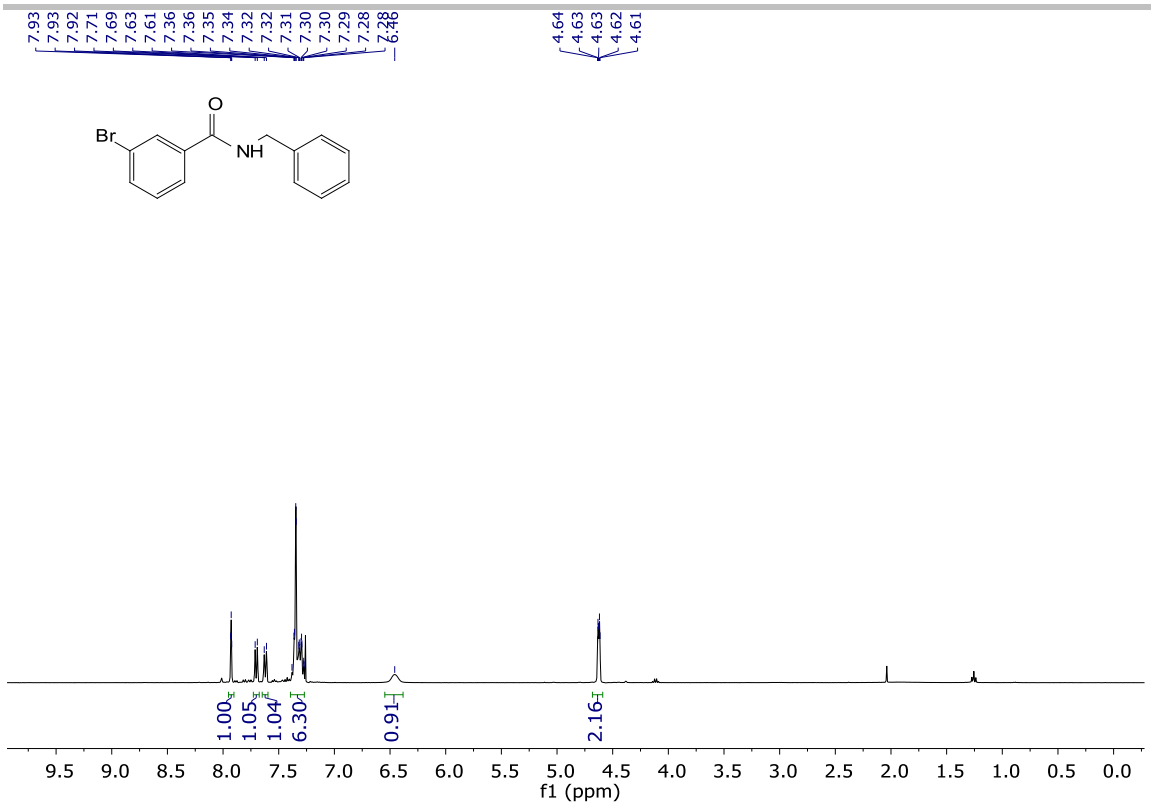


Figure S40. ^{1}H NMR spectra of aromatic amides **18s**

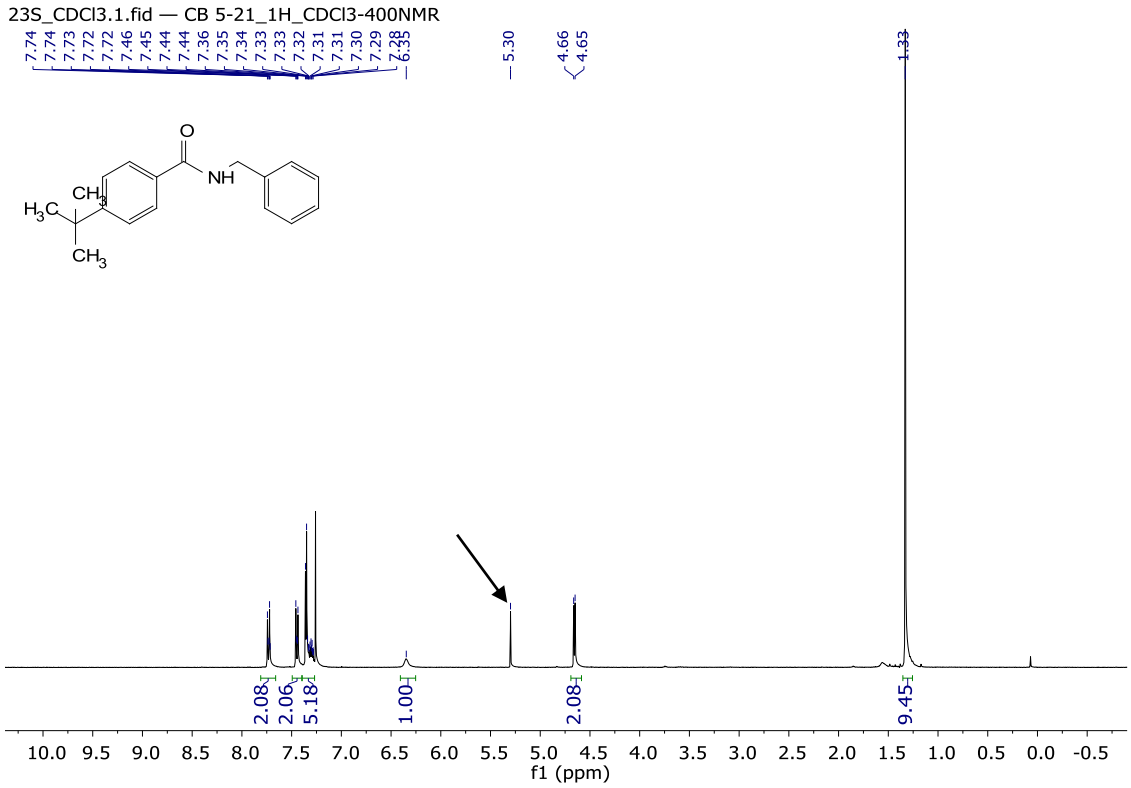


Figure S41. ^{1}H NMR spectra of aromatic amide **19s** (DCM indicated by arrow)

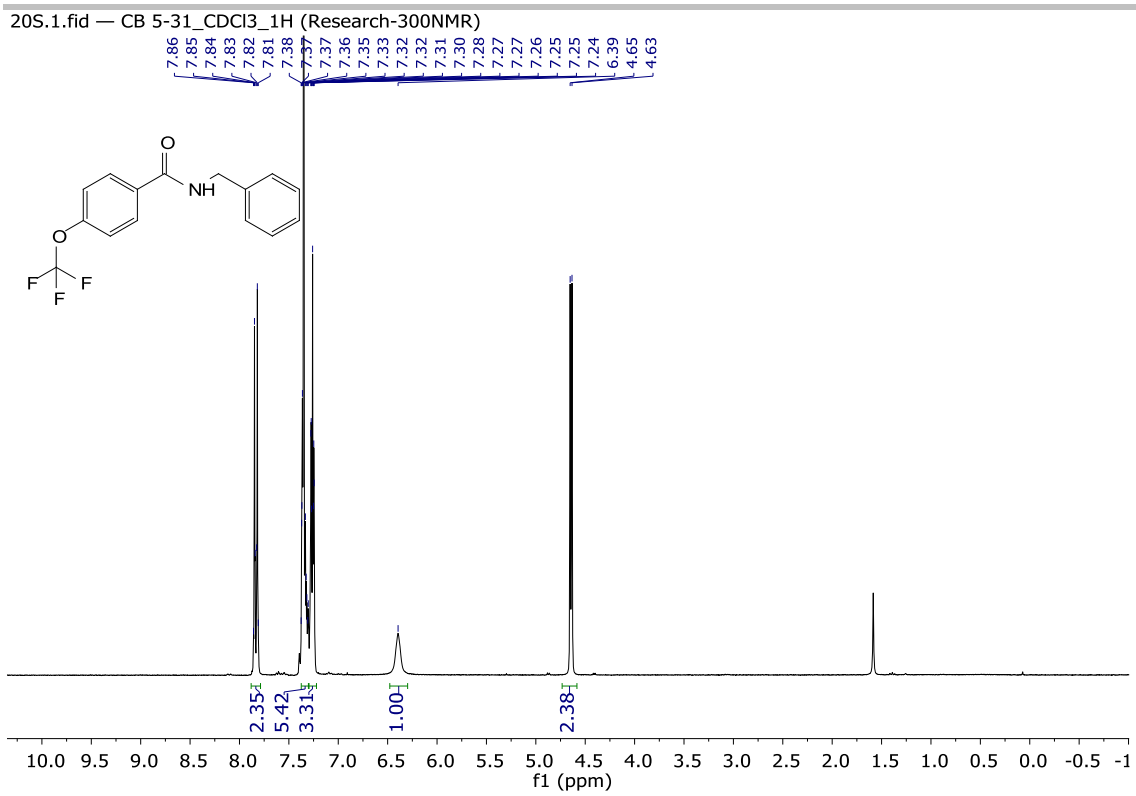


Figure S42. ^{1}H NMR spectra of aromatic amide **20s**

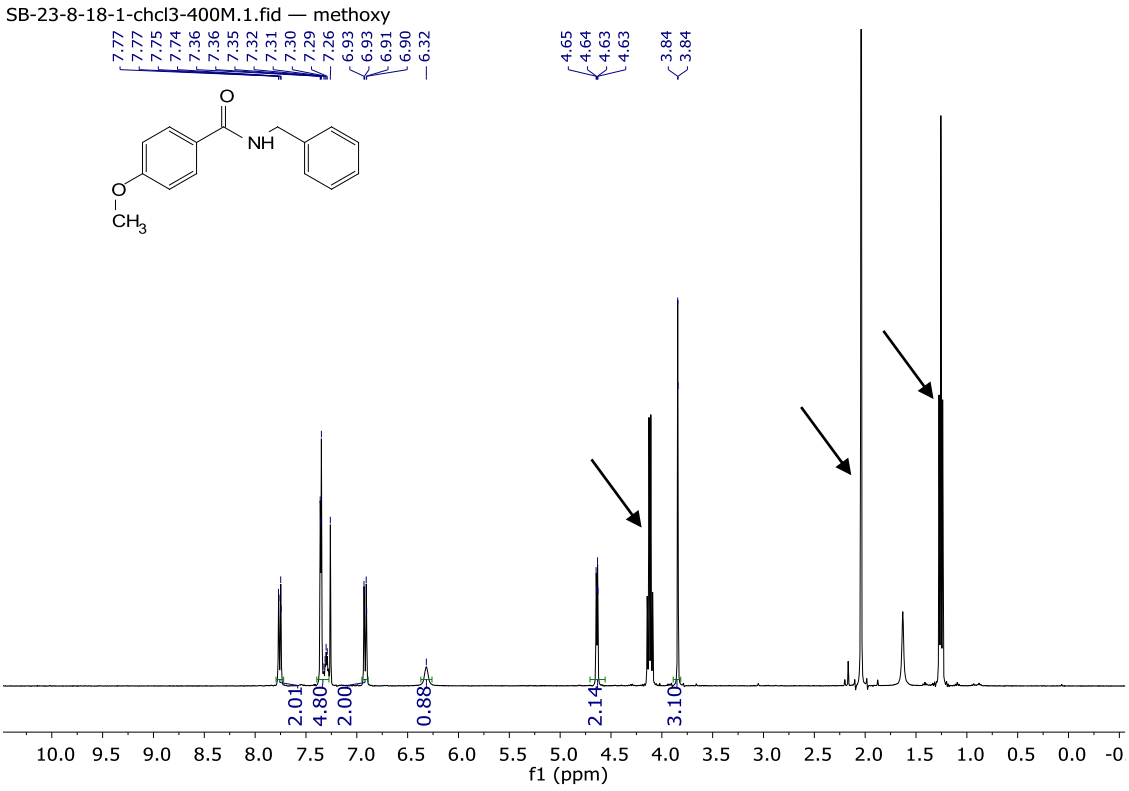


Figure S43. ^{1}H NMR spectra of aromatic amide **21s** (ethyl acetate indicated by arrows)

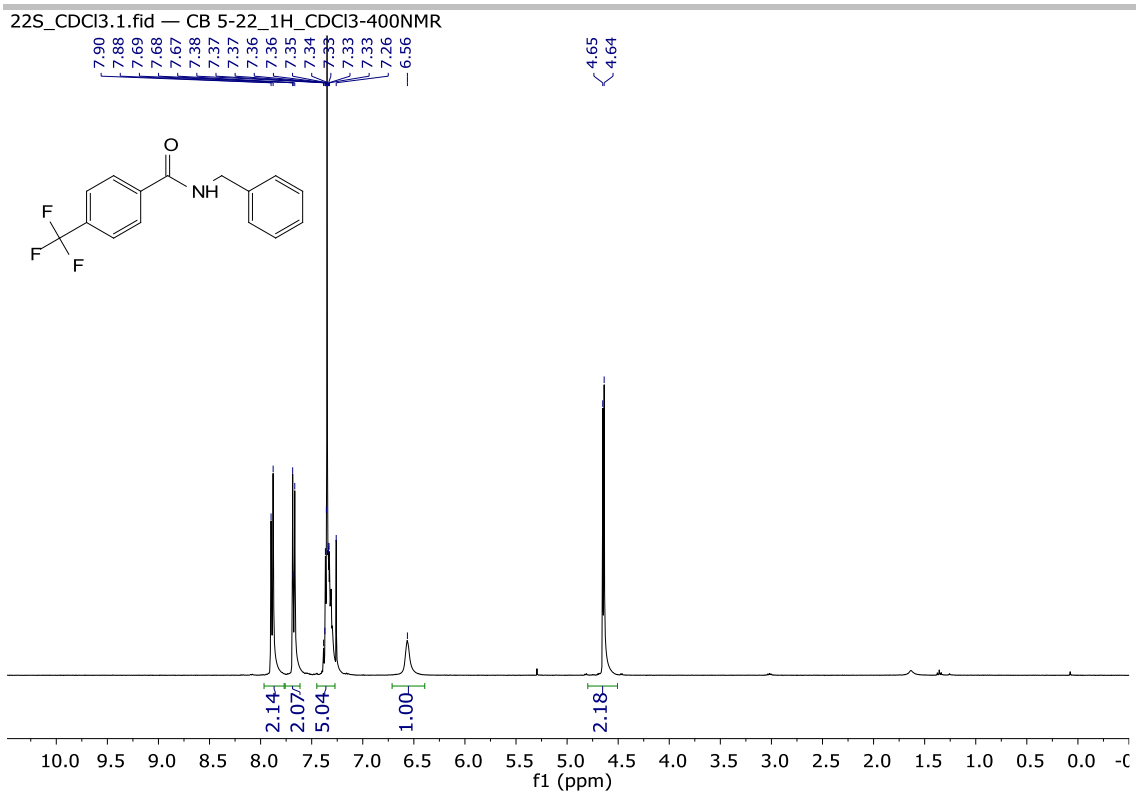


Figure S44. ^{1}H NMR spectra of aromatic amide **22s**

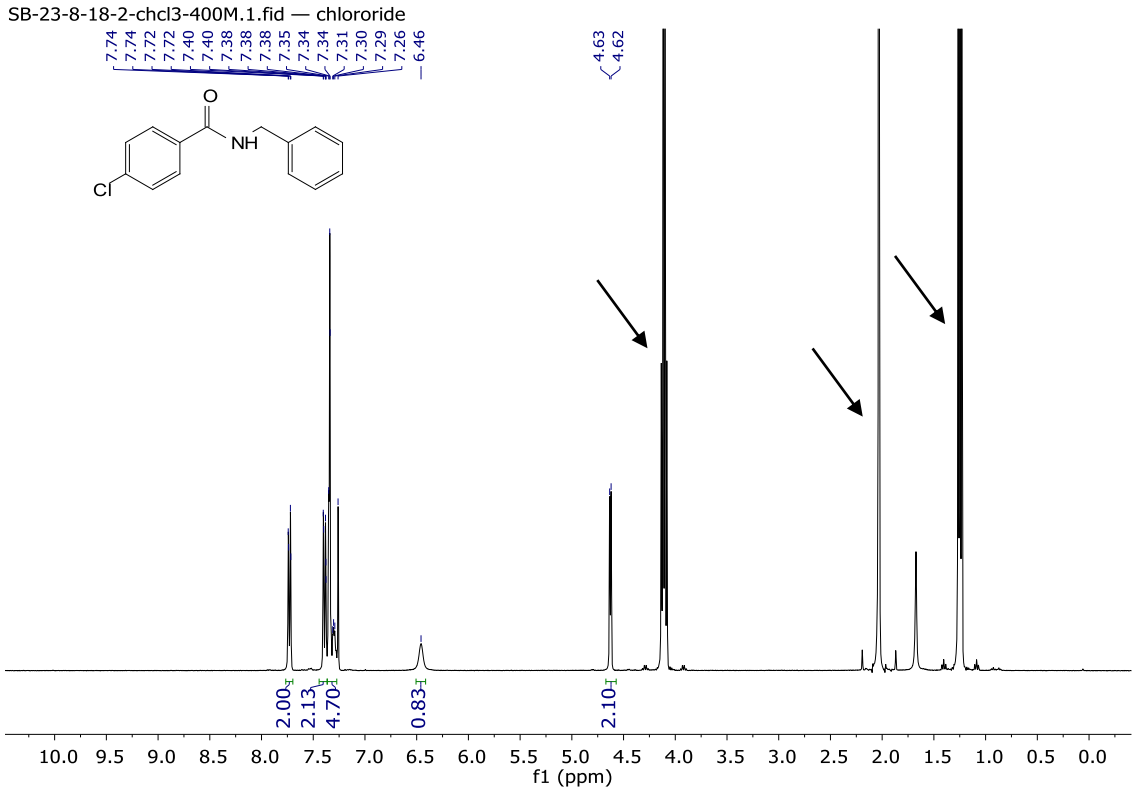


Figure S45. ^{1}H NMR spectra of aromatic amide **23s** (ethyl acetate indicated by arrows)

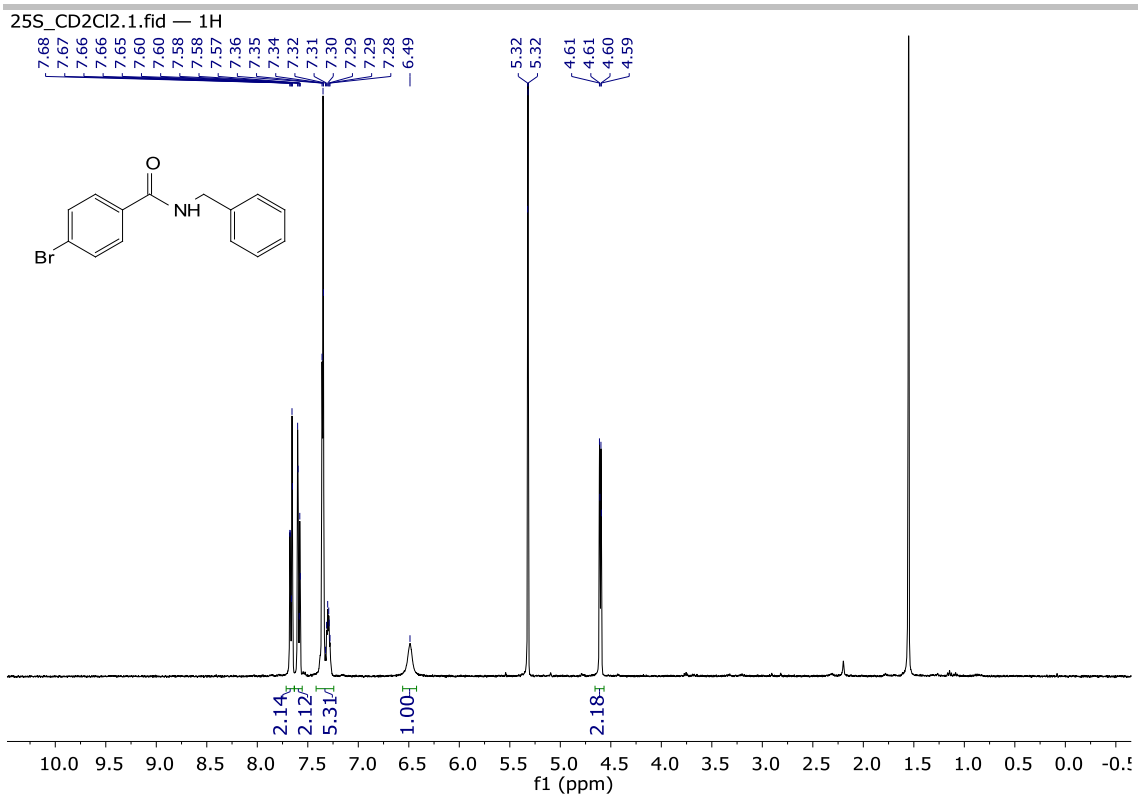


Figure S46. ^{1}H NMR spectra of aromatic amide **24s**

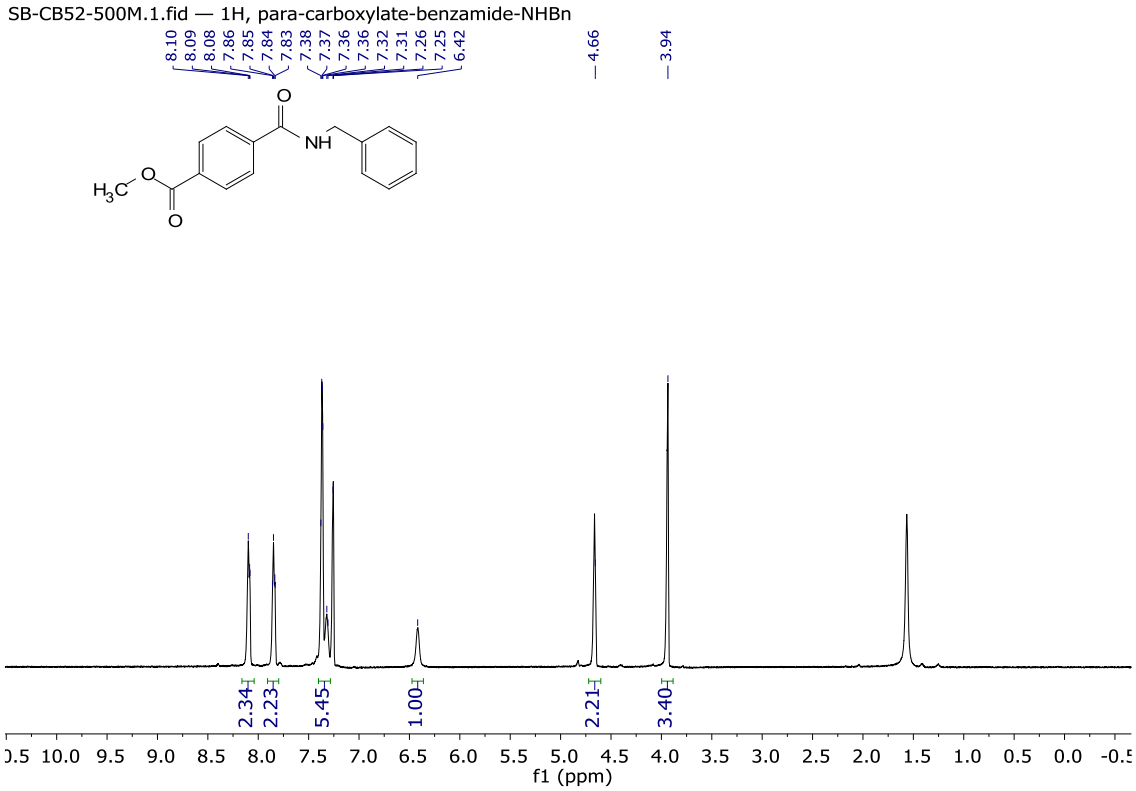


Figure S47. ^{1}H NMR spectra of aromatic amide **25s**

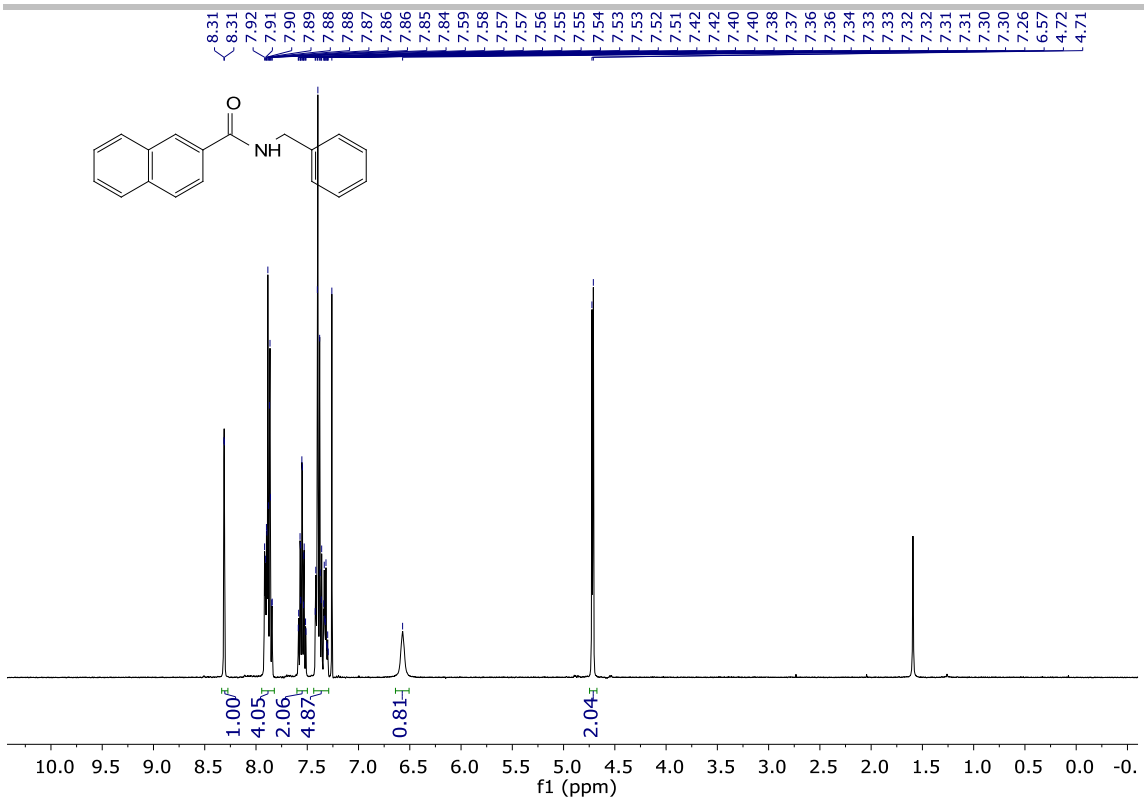


Figure S48. ^{1}H NMR spectra of aromatic amides **26s**

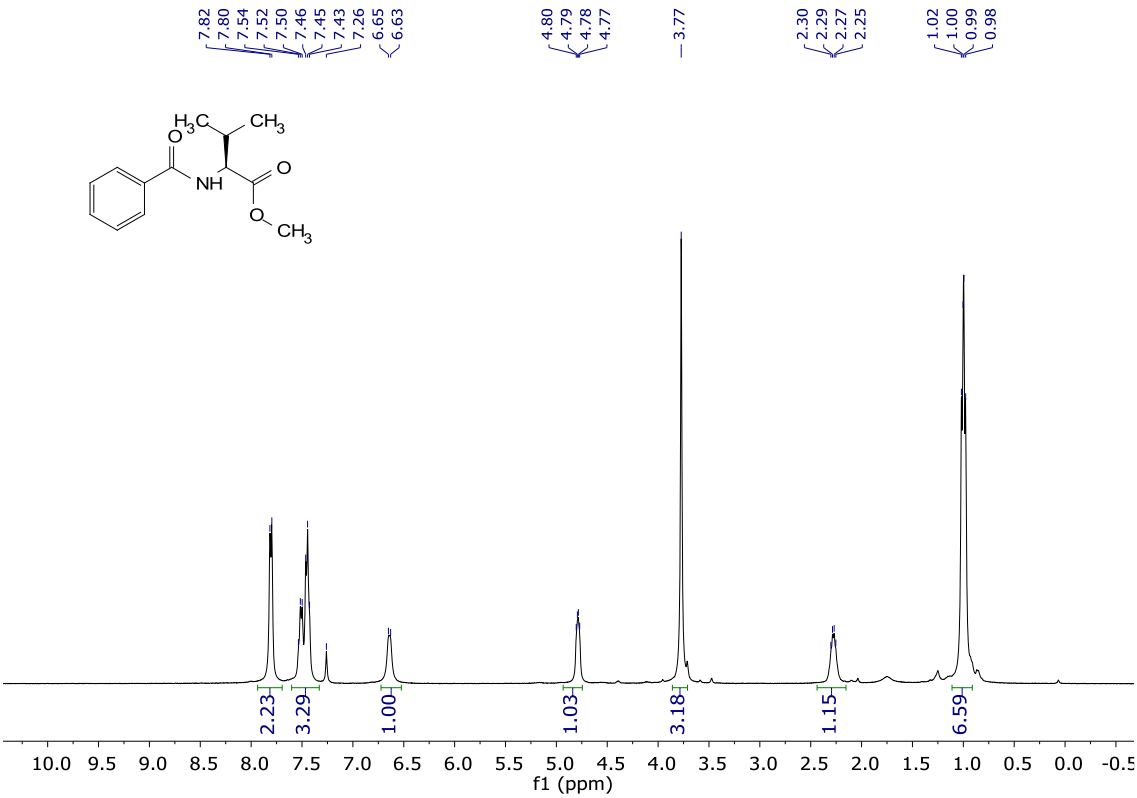


Figure S49. ^{1}H NMR spectra of aromatic amides **27s**

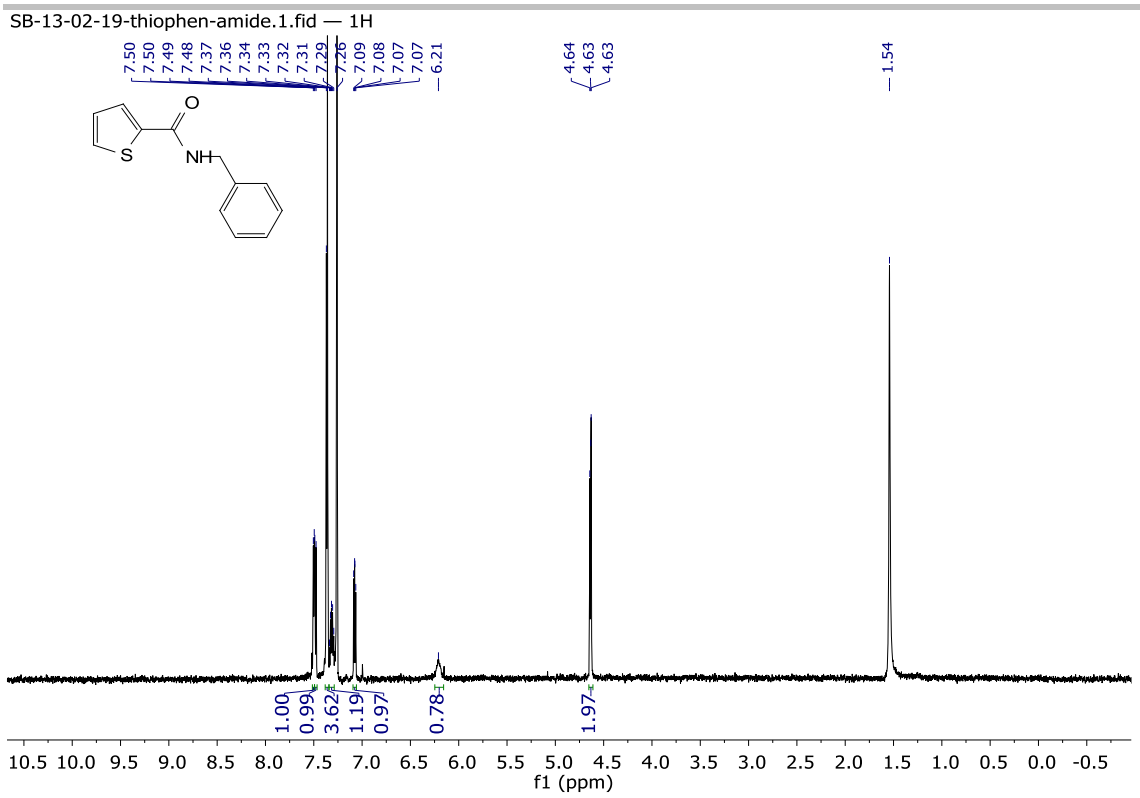


Figure S50. ^{1}H NMR spectra of aromatic amide **28s**

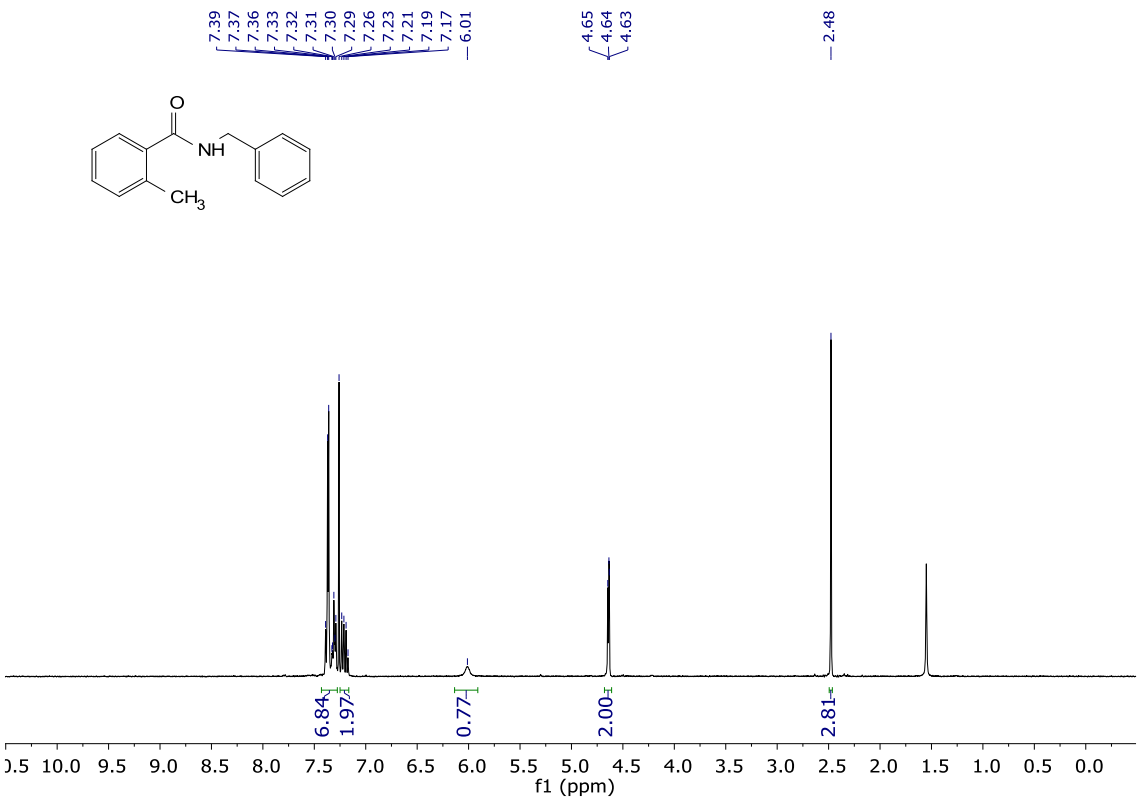


Figure S51. ^{1}H NMR spectra of aromatic amides **29s**

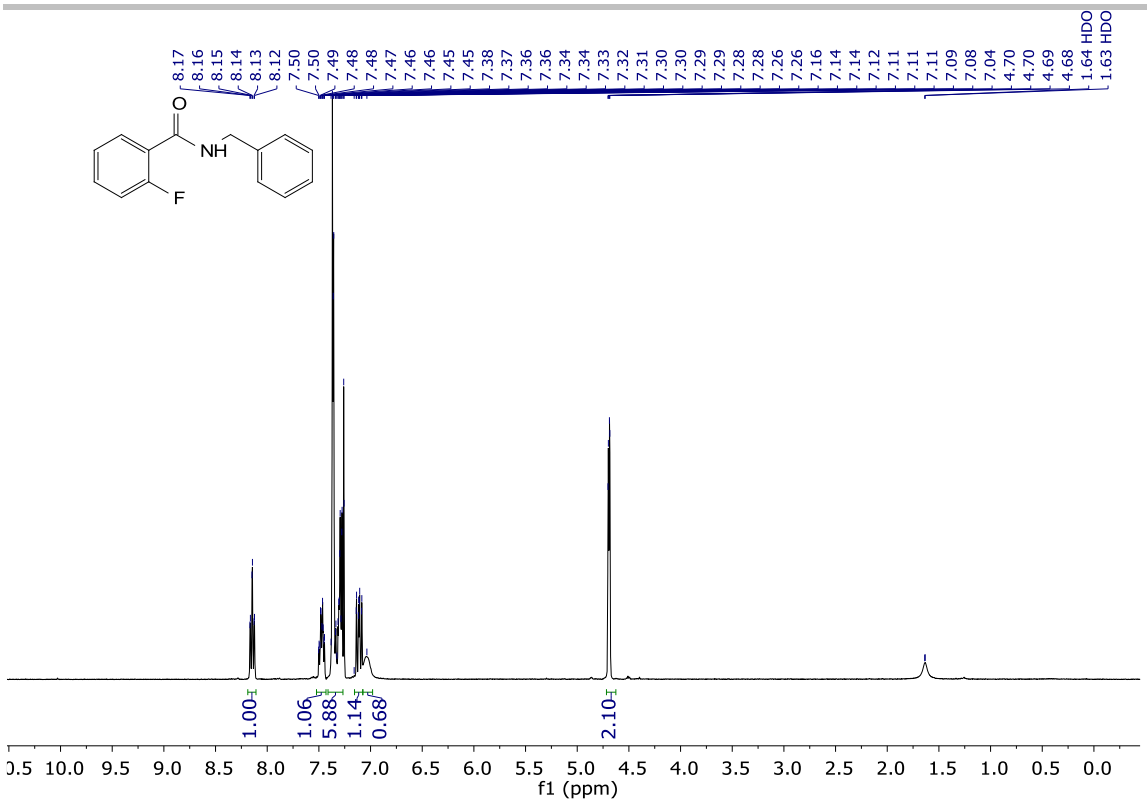


Figure S52. ^{1}H NMR spectra of aromatic amides **30s**

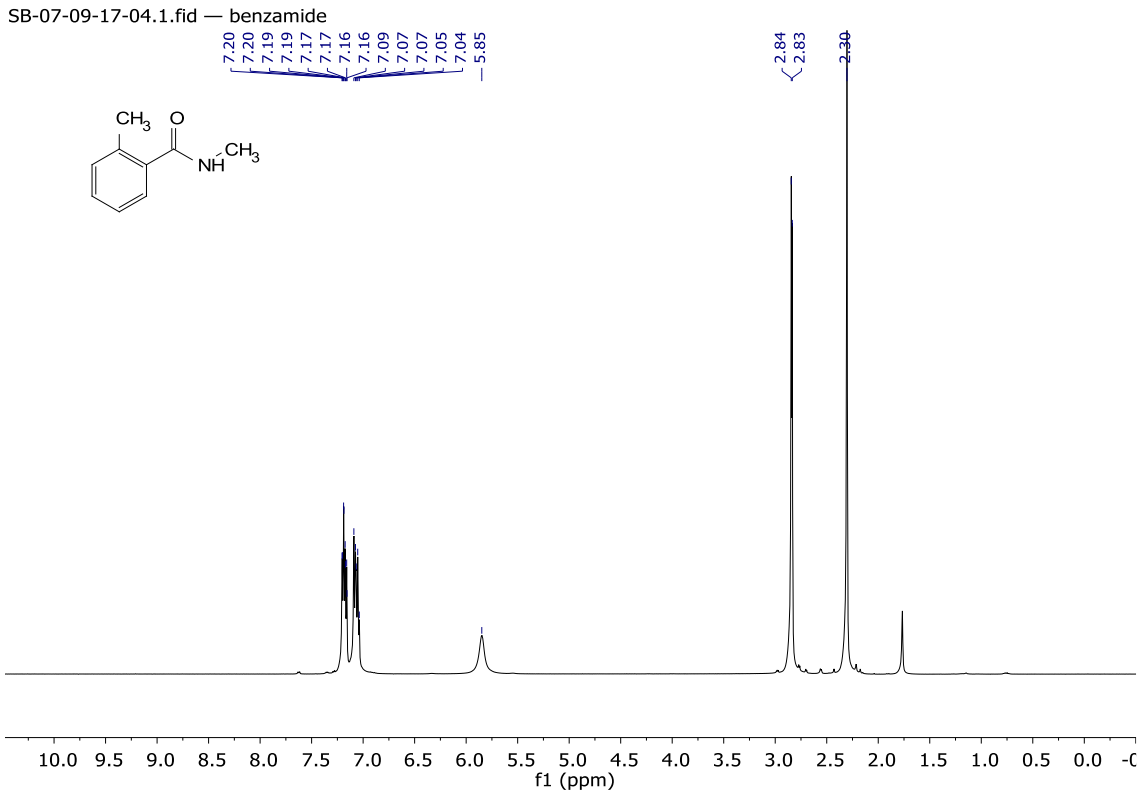


Figure S53. ^{1}H NMR spectra of aromatic amides **31s**

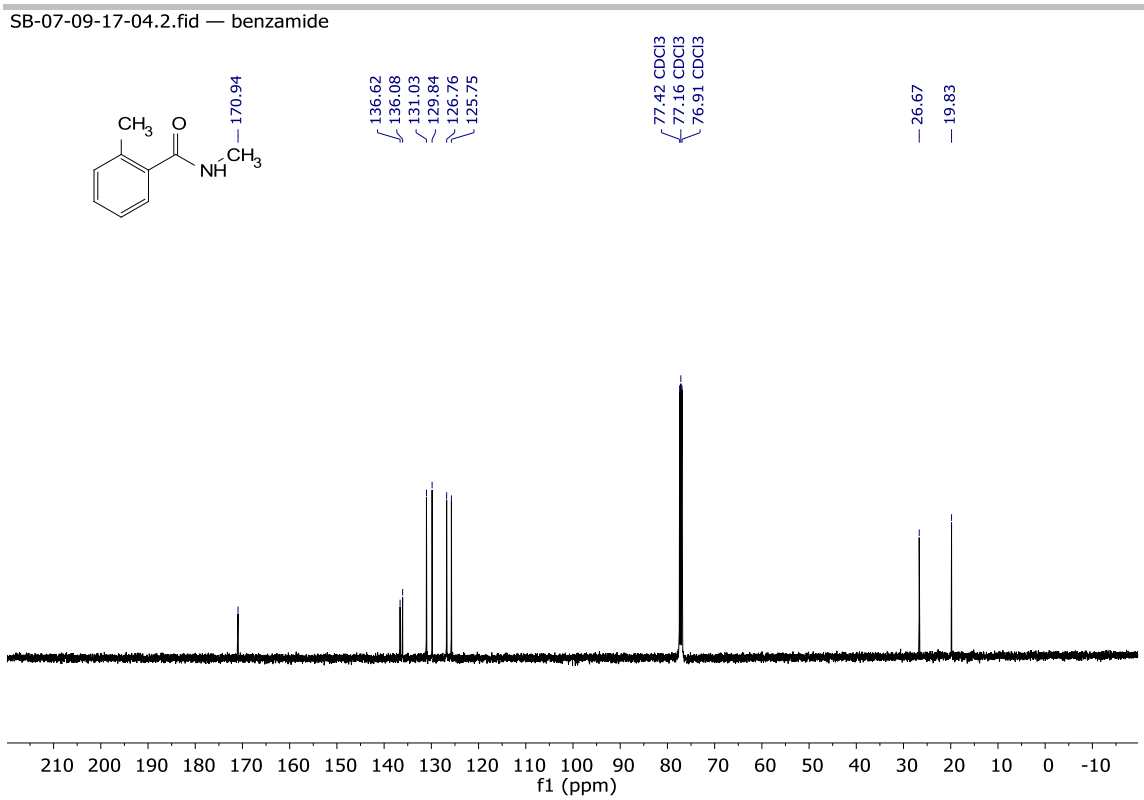


Figure S54. ^{13}C NMR spectra of aromatic amides **31s**

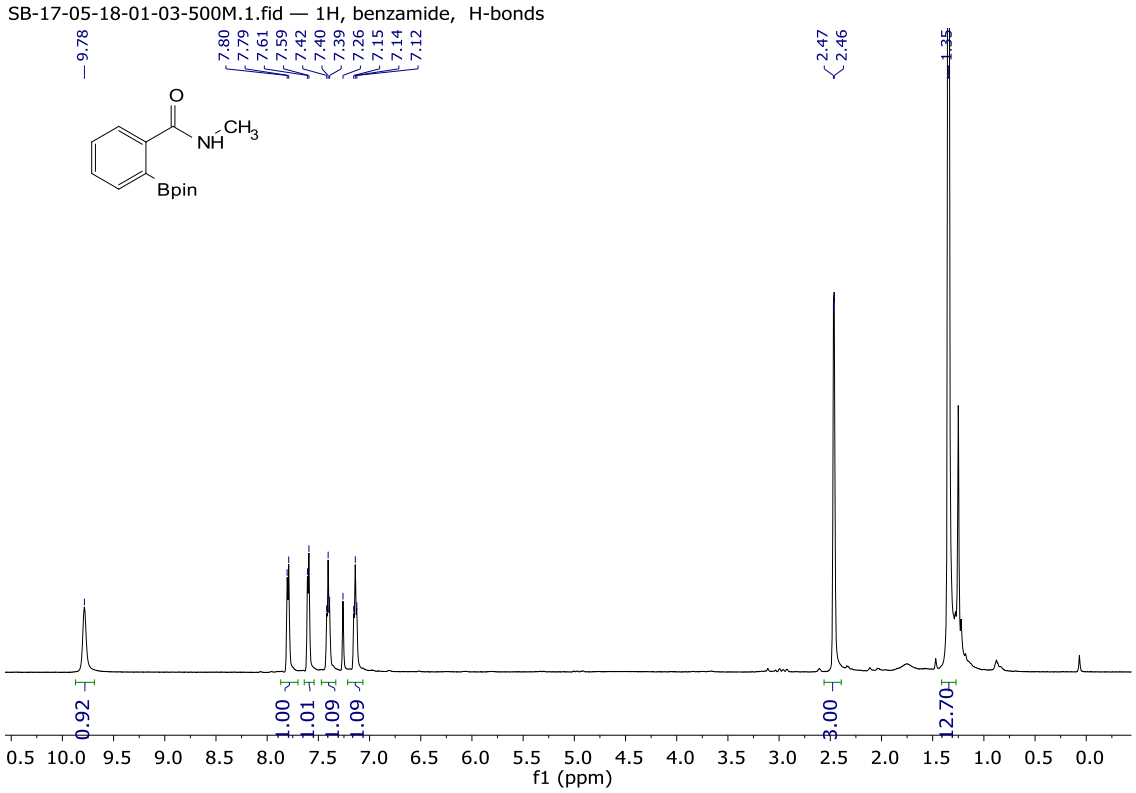


Figure S55. ^{1}H NMR spectra of borylated aromatic amide **1so**

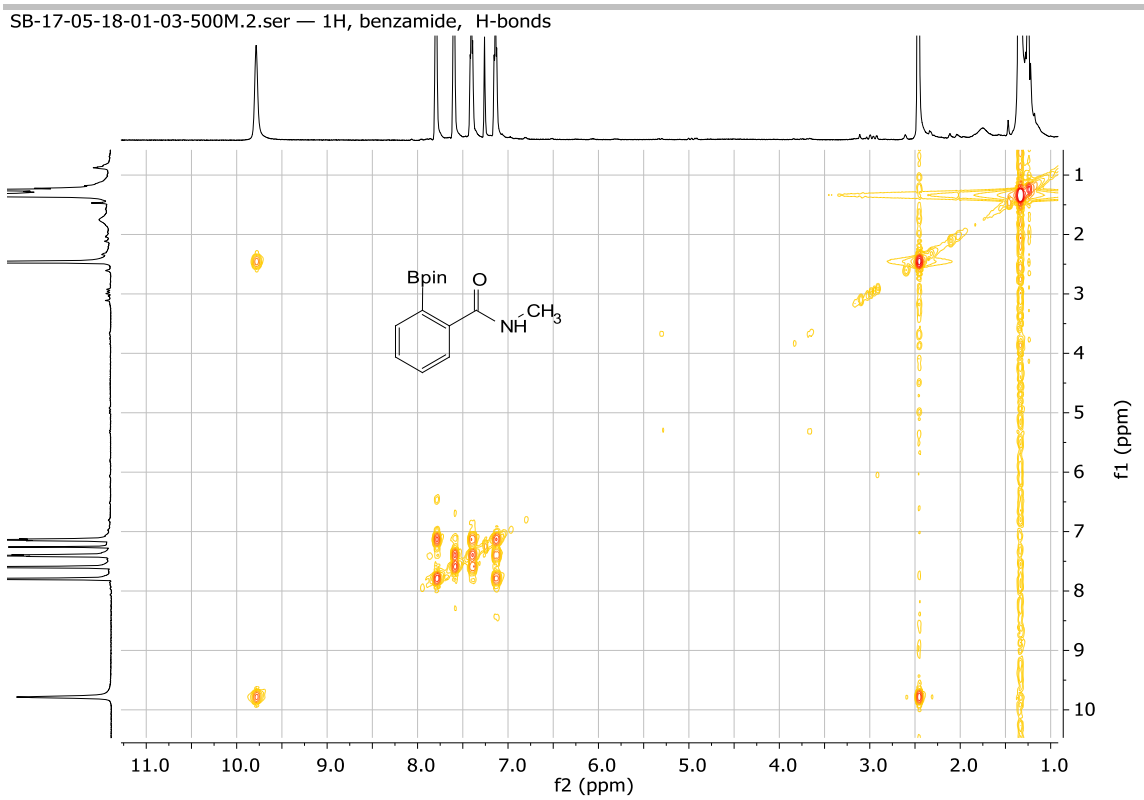


Figure S56. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **1so**

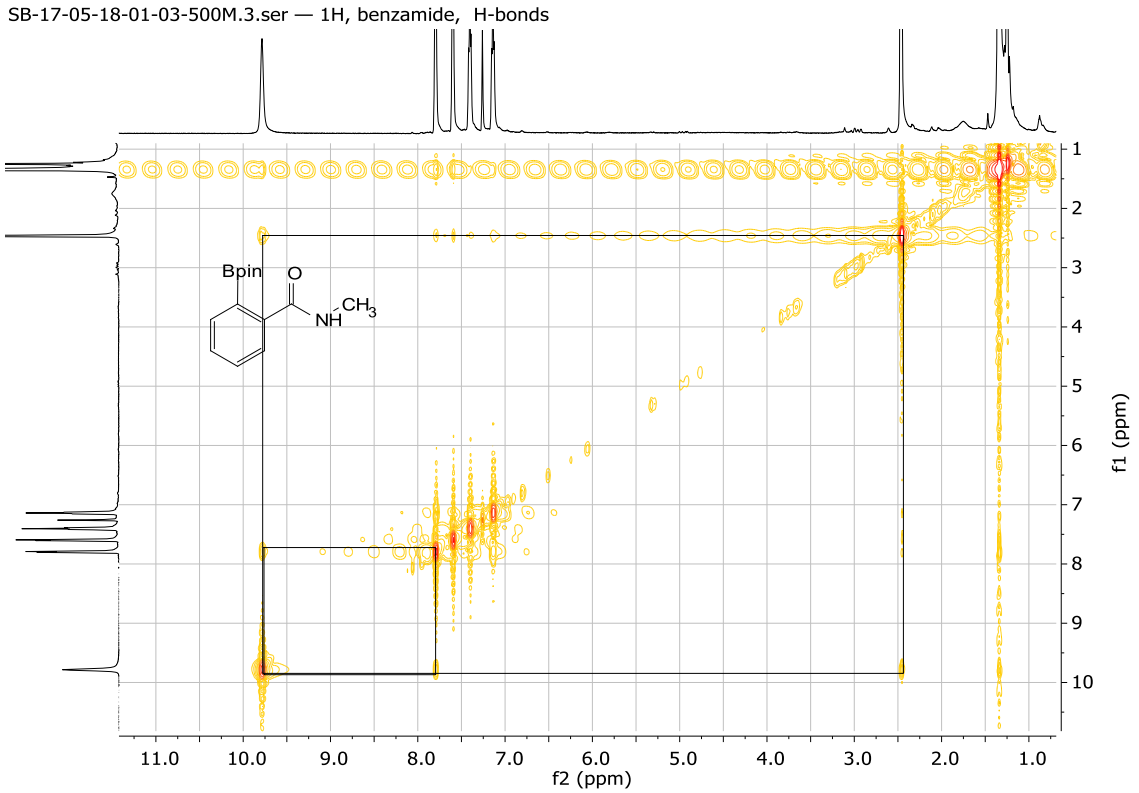


Figure S57. ^{1}H-^{1}H NOESY NMR spectra of borylated aromatic amide **1so**

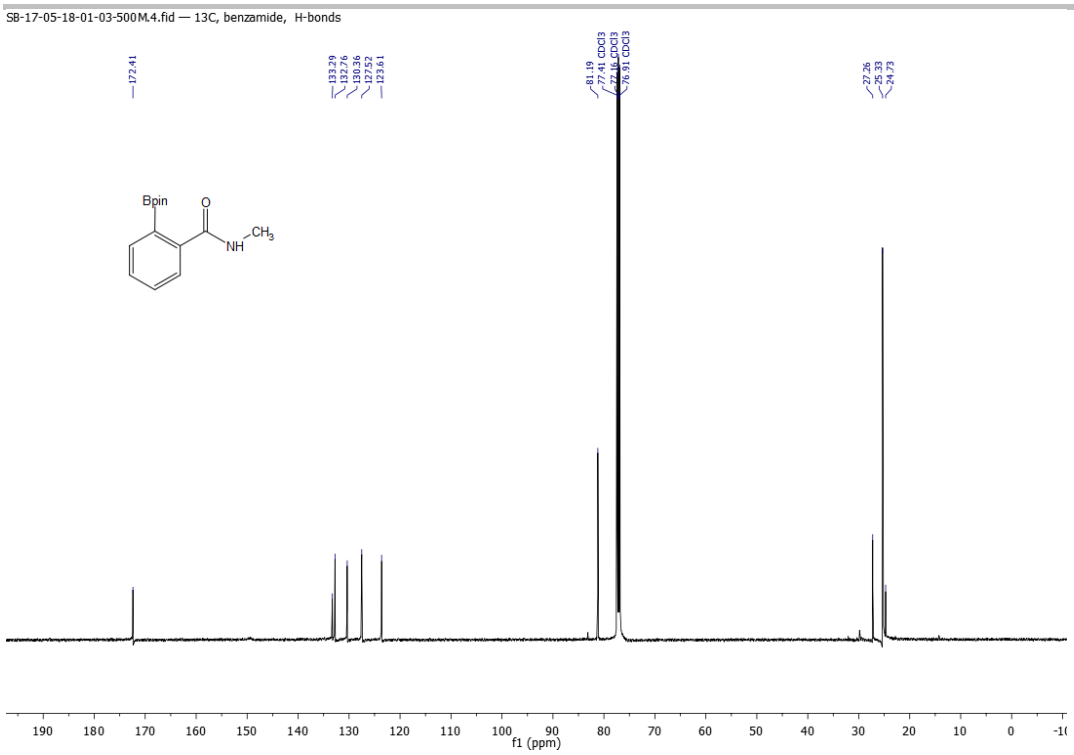


Figure S58. ^{13}C NMR spectra of borylated aromatic amide **1so**

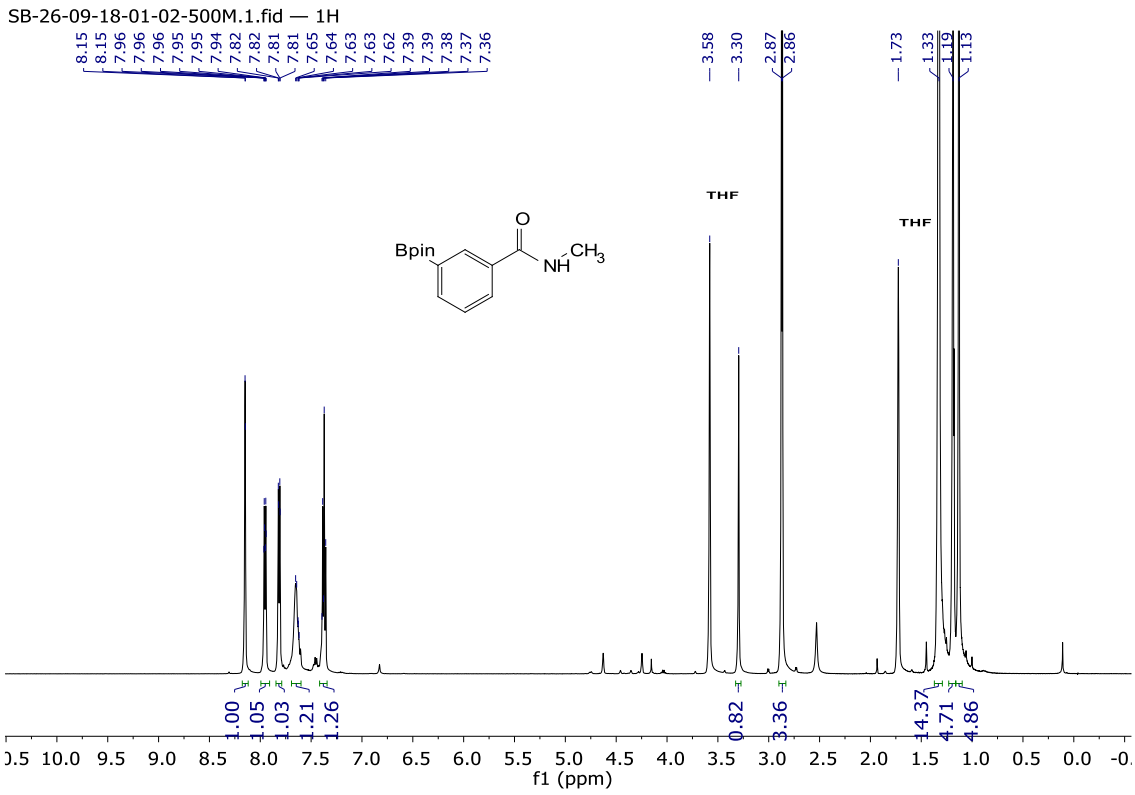


Figure S59. ^{1}H NMR spectra of borylated aromatic amide **1sm**

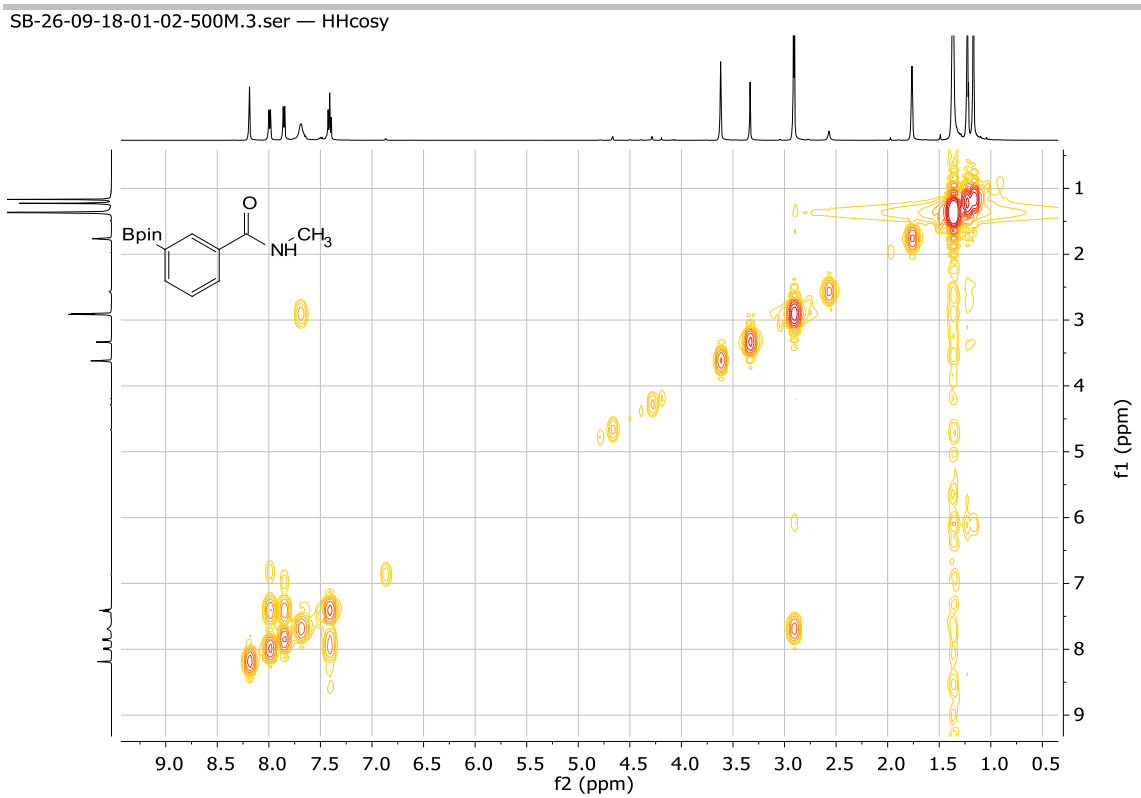


Figure S60. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **1sm**

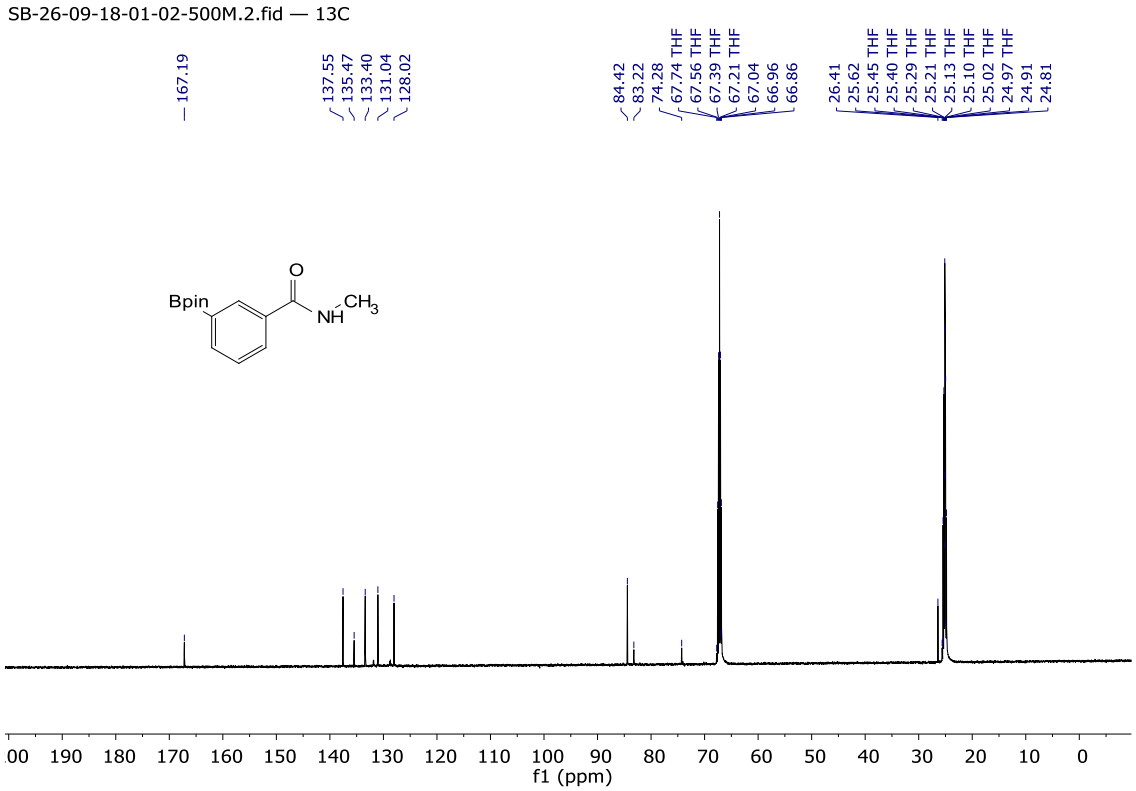


Figure S61. ^{13}C NMR spectra of borylated aromatic amide **1sm**

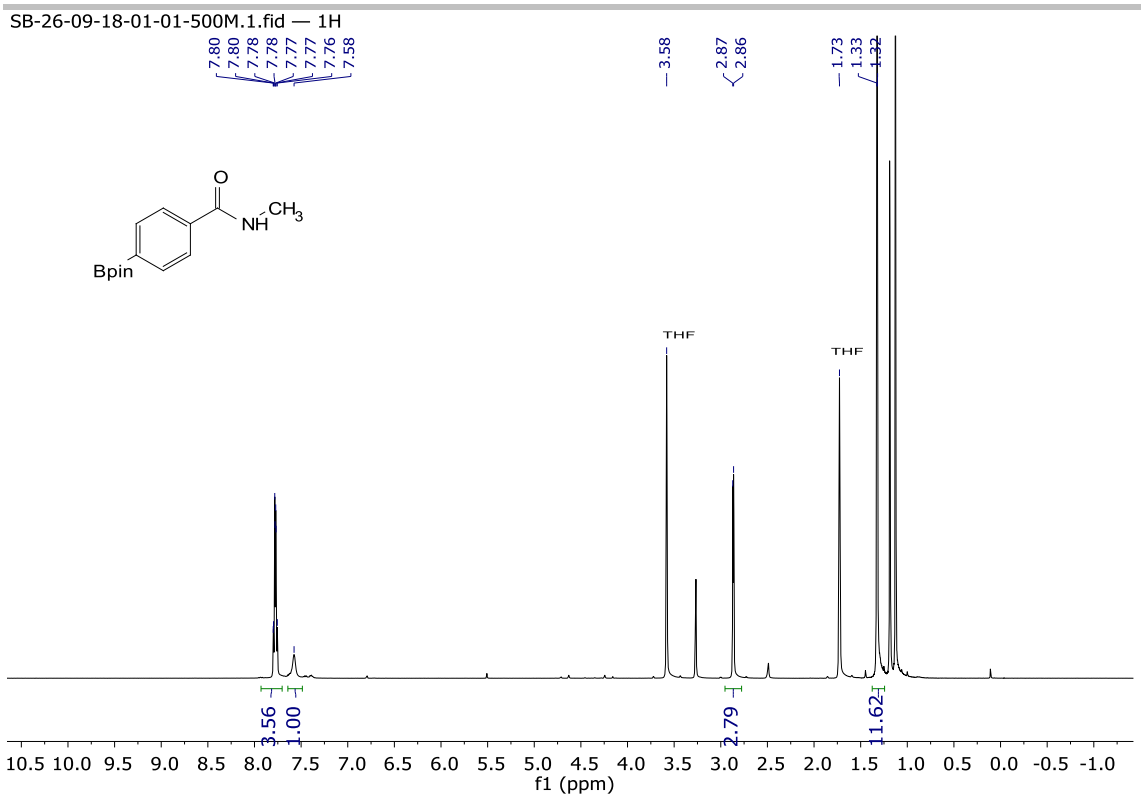


Figure S62. ^{1}H NMR spectra of borylated aromatic amide **1sp**

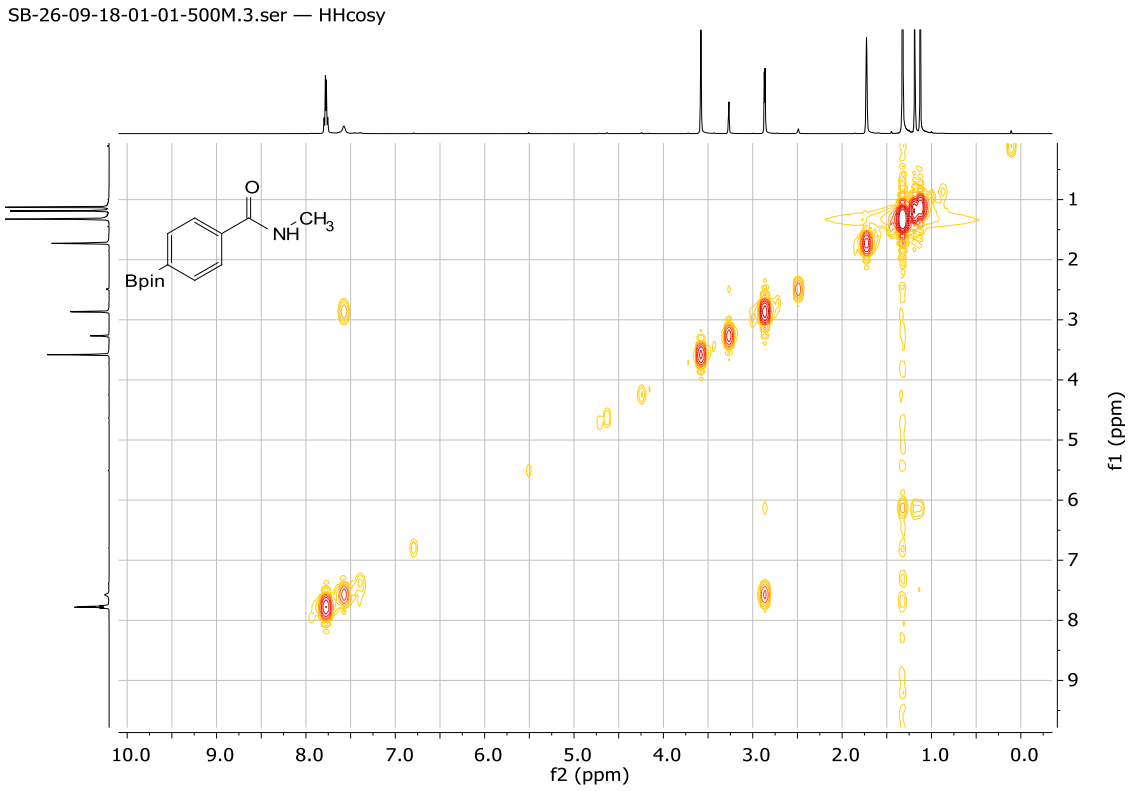


Figure S63. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **1sp**

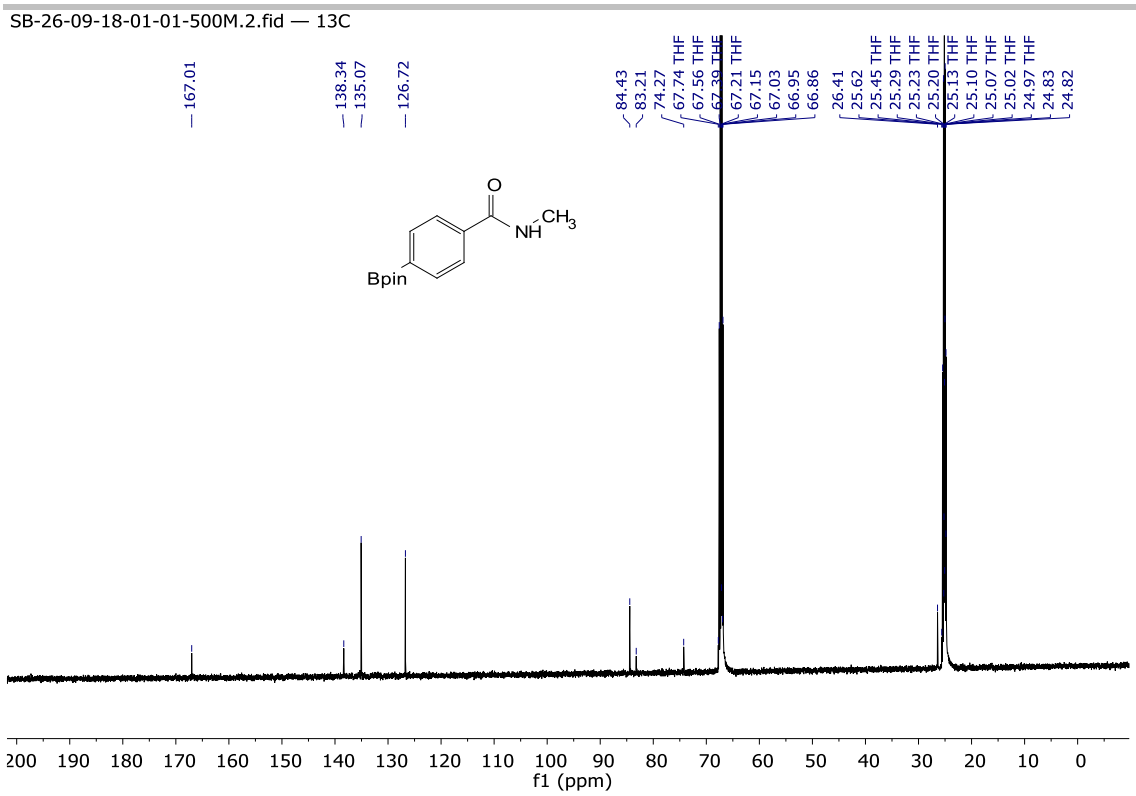


Figure S64. ^{13}C NMR spectra of borylated aromatic amide **1sp**

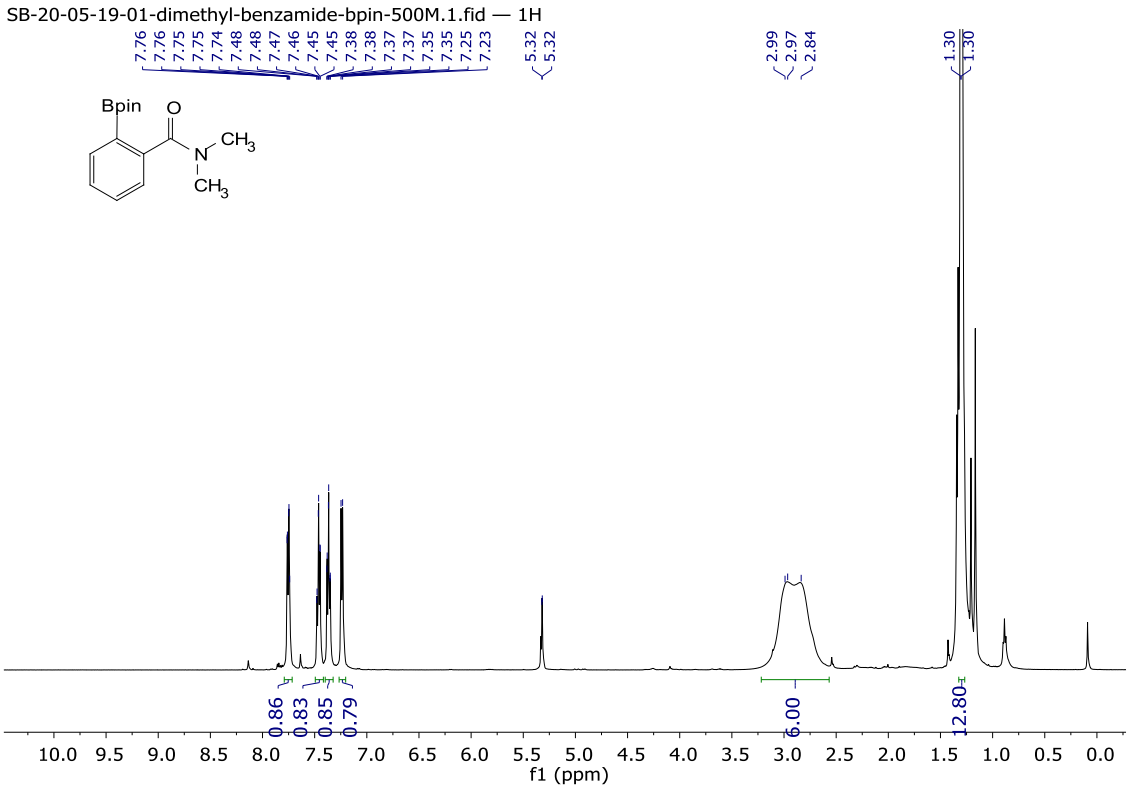


Figure S65. ^{1}H NMR spectra of borylated aromatic amide **2so**

SB-18-09-18-01-01B-500M.3.ser — HHcosy

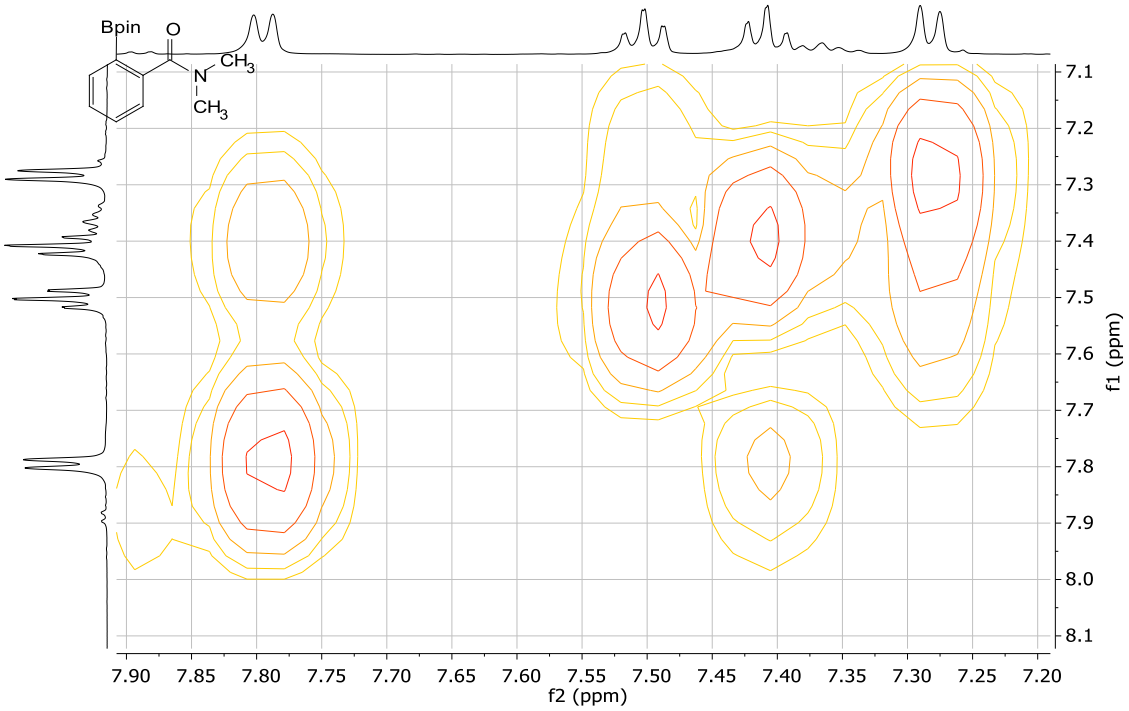


Figure S66. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **2so**

SB-20-05-19-01-dimethyl-benzamide-bpin-500M.2.fid — 13C

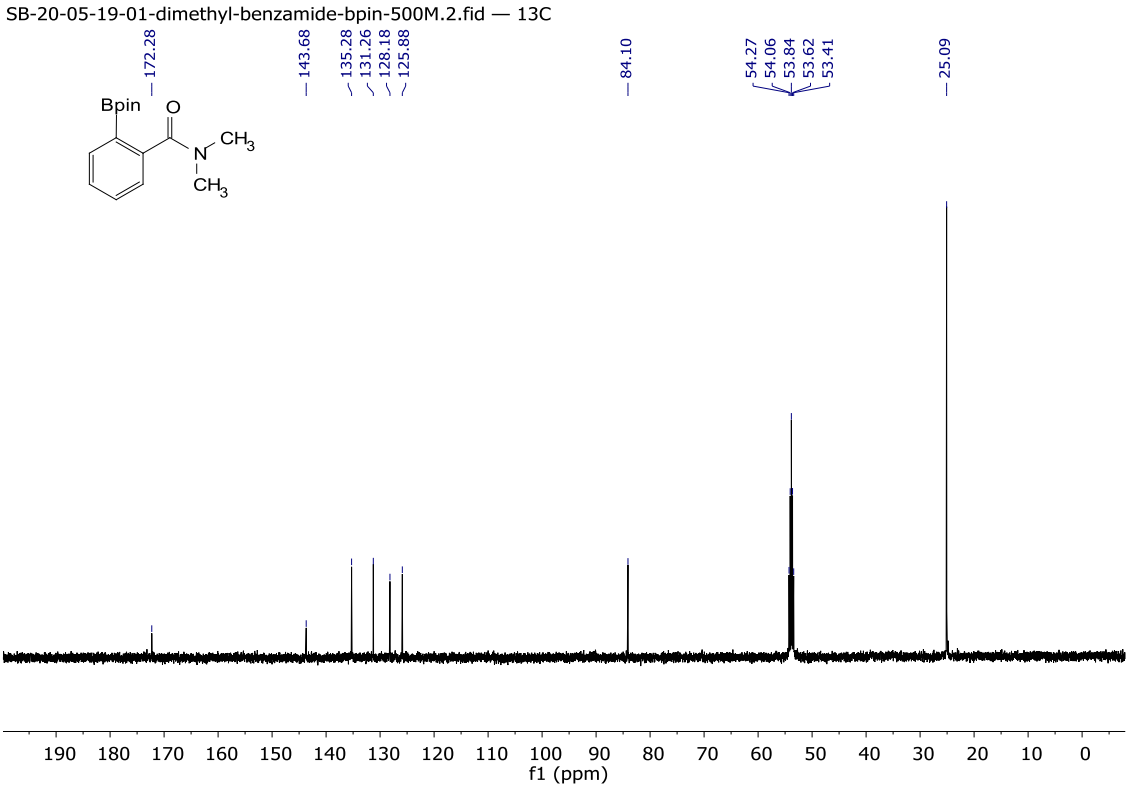


Figure S67. ^{13}C NMR spectra of borylated aromatic amide **2so**

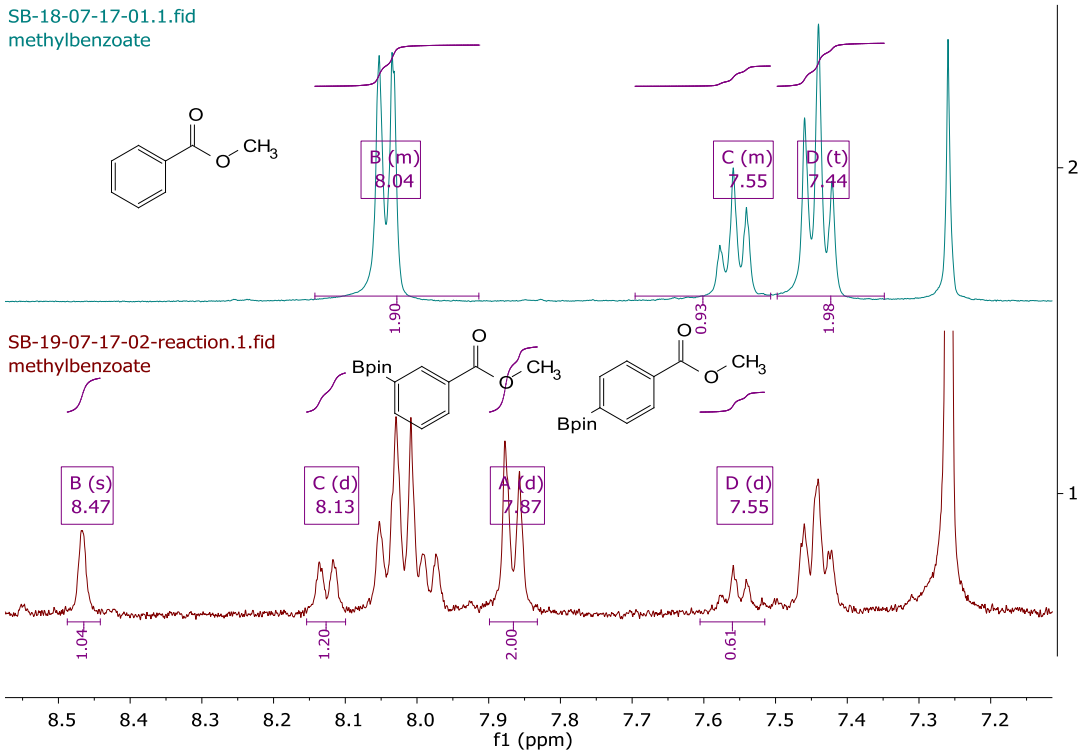


Figure S68. ^{1}H NMR spectra of borylated aromatic amides **3sm** and **3sp** mixture (top spectra of substrate vs. bottom spectra of reaction mixture)

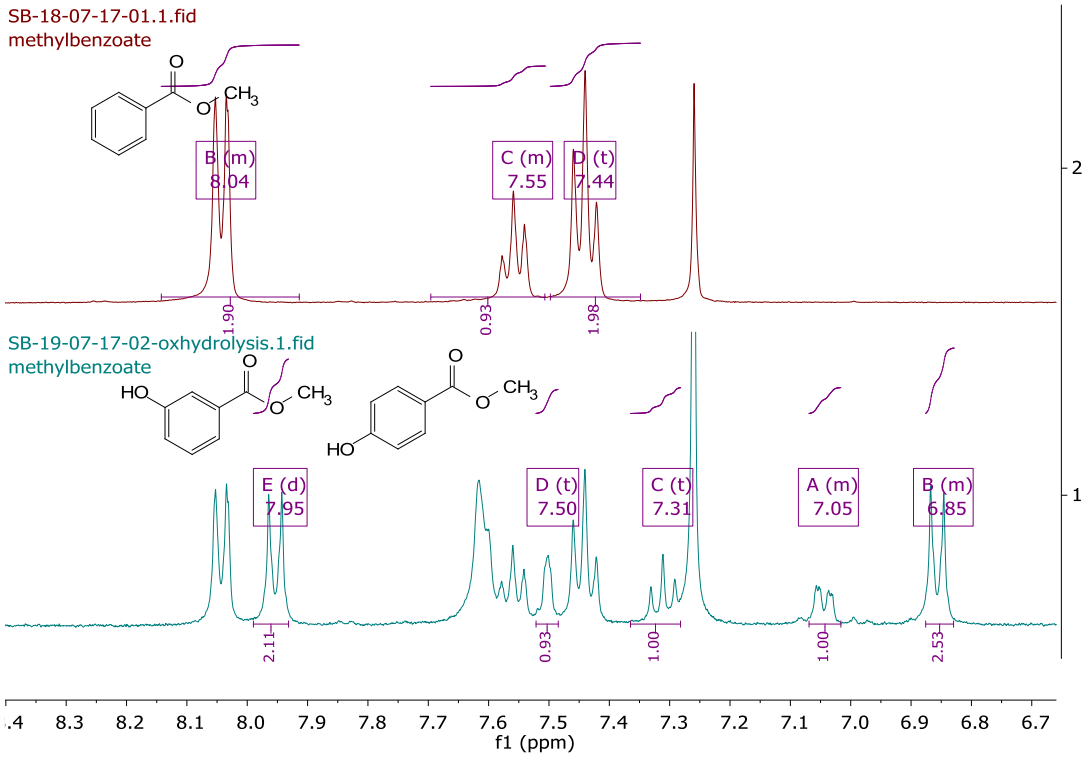


Figure S69. ^{1}H NMR spectra of oxidation hydrolysis of borylated aromatic amide **3sm** and **3sp** mixture (top spectra of substrate vs. bottom spectra of converted products)

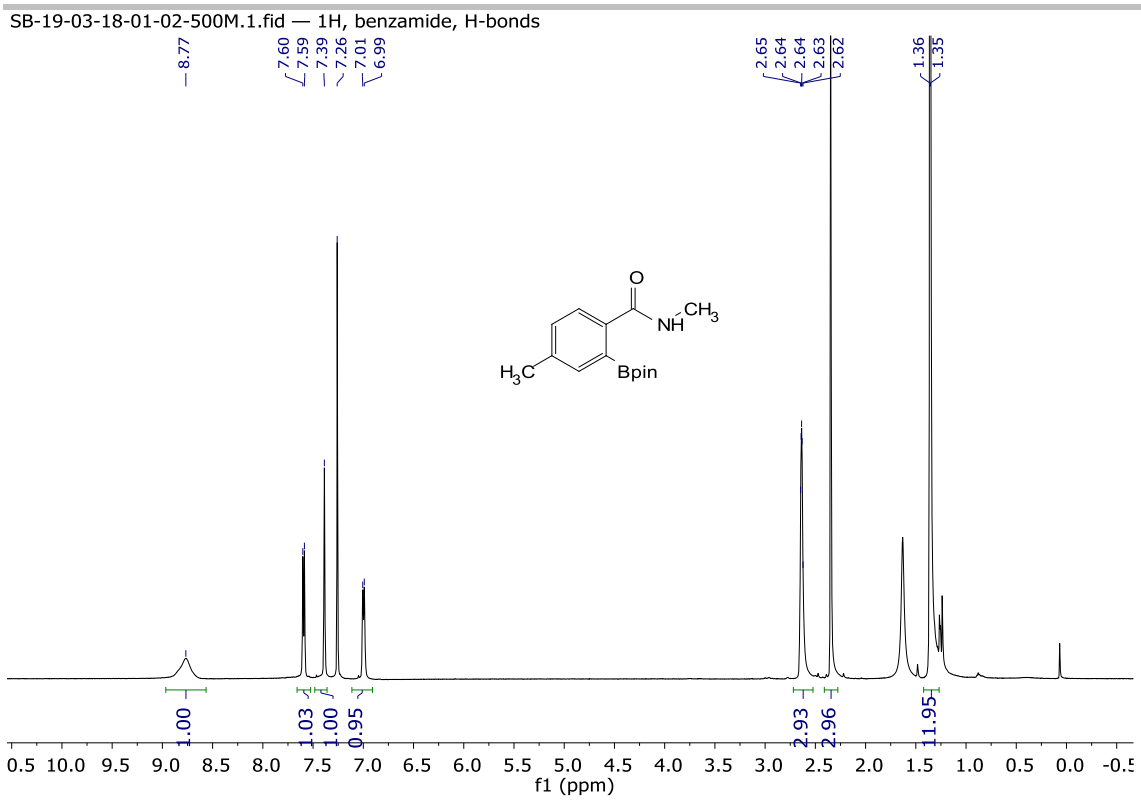


Figure S70. ^{1}H NMR spectra of borylated aromatic amide **4so**

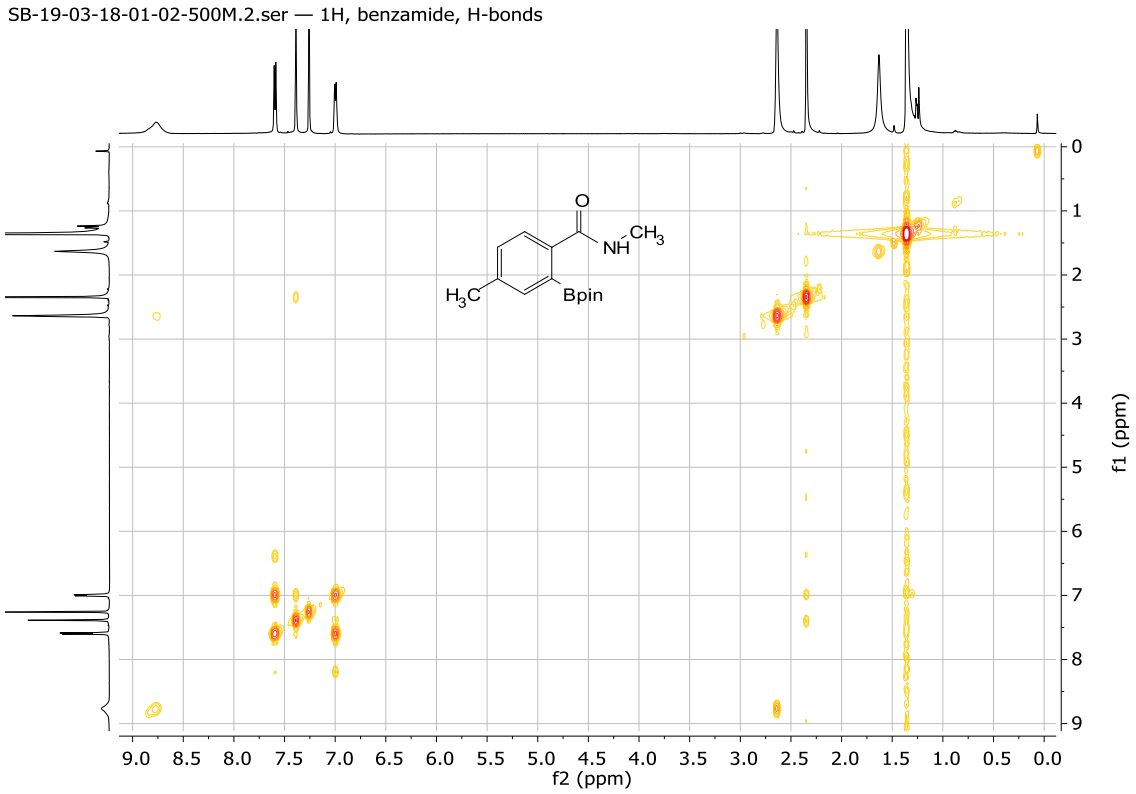


Figure S71. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **4so**

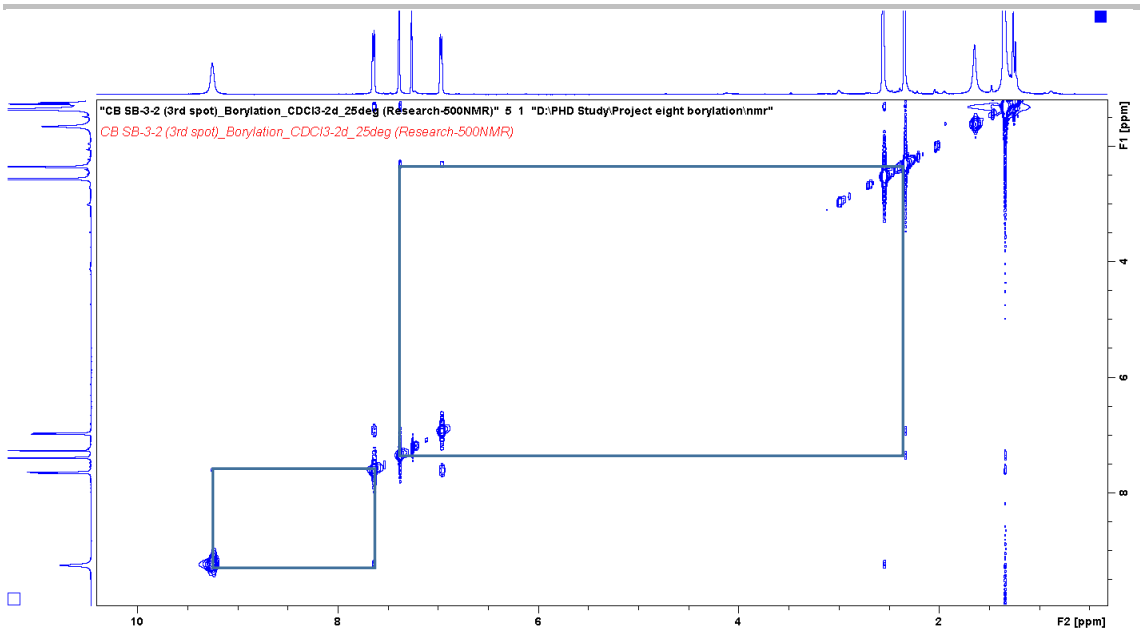


Figure S72. ^{1}H-^{1}H NOESY NMR spectra of borylated aromatic amide **4so**

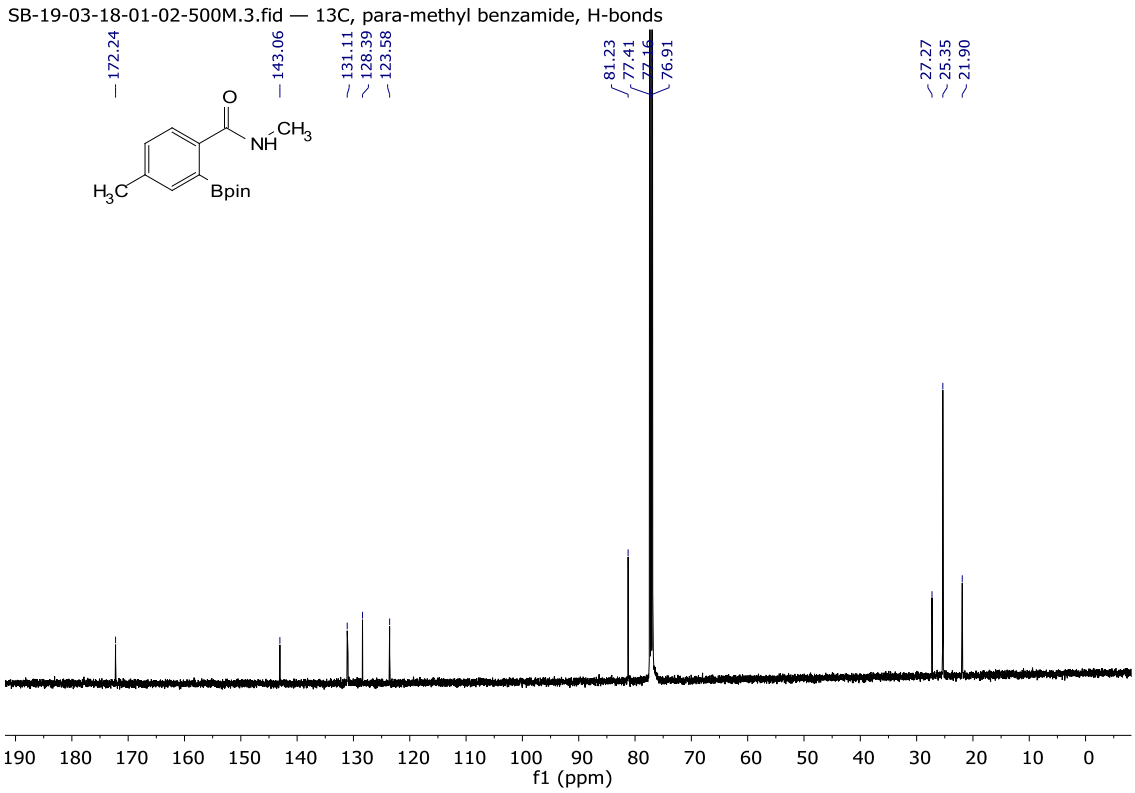


Figure S73. ^{13}C NMR spectra of borylated aromatic amide **4so**

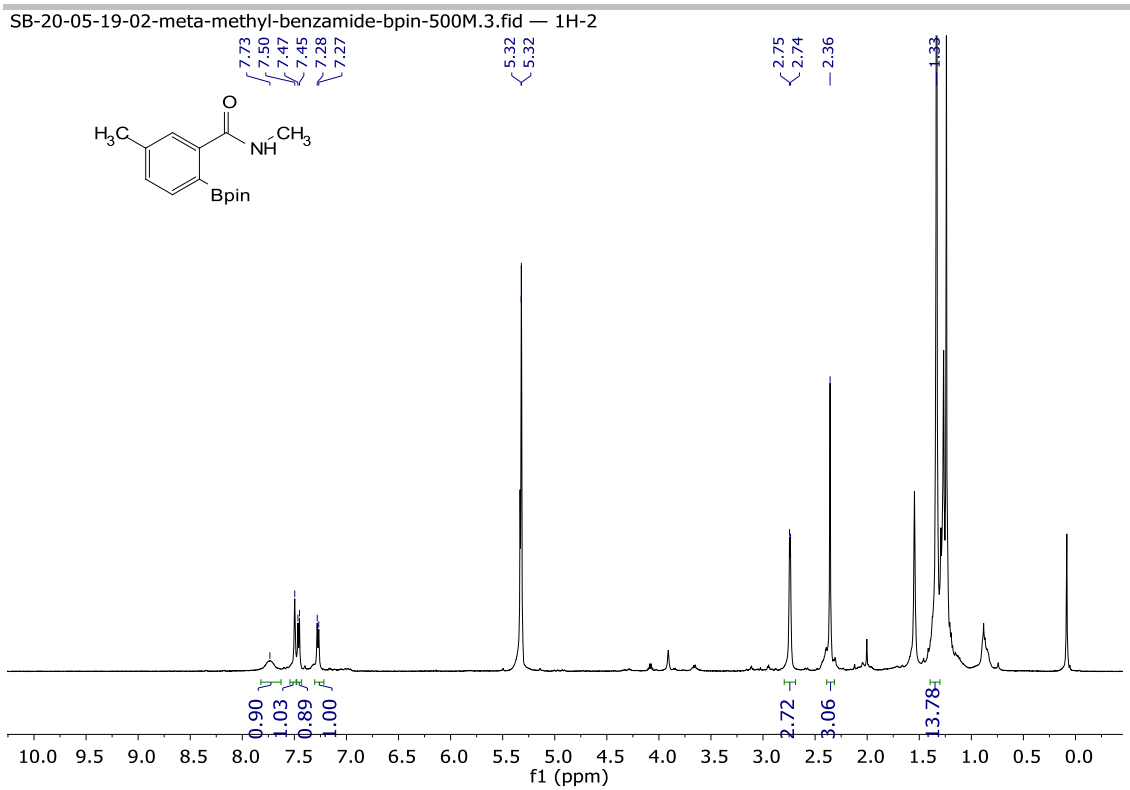


Figure S74. ^{1}H NMR spectra of borylated aromatic amide **5so**

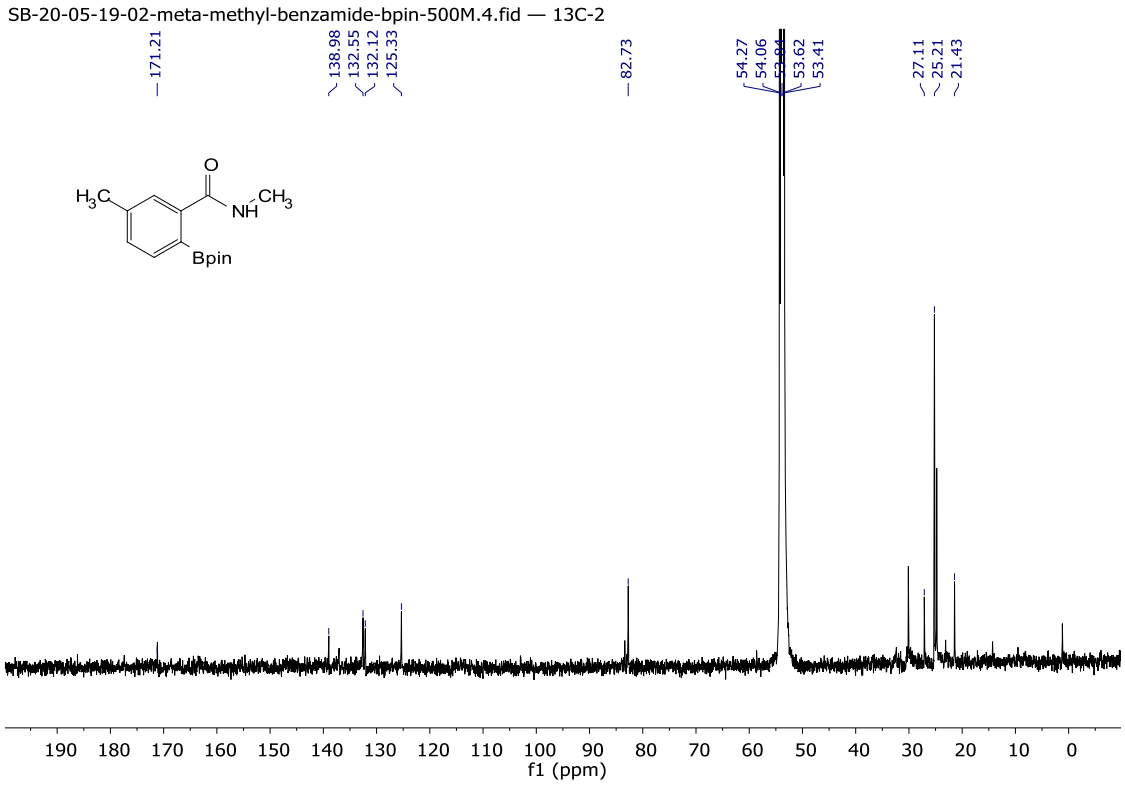


Figure S75. ^{13}C NMR spectra of borylated aromatic amide **5so**

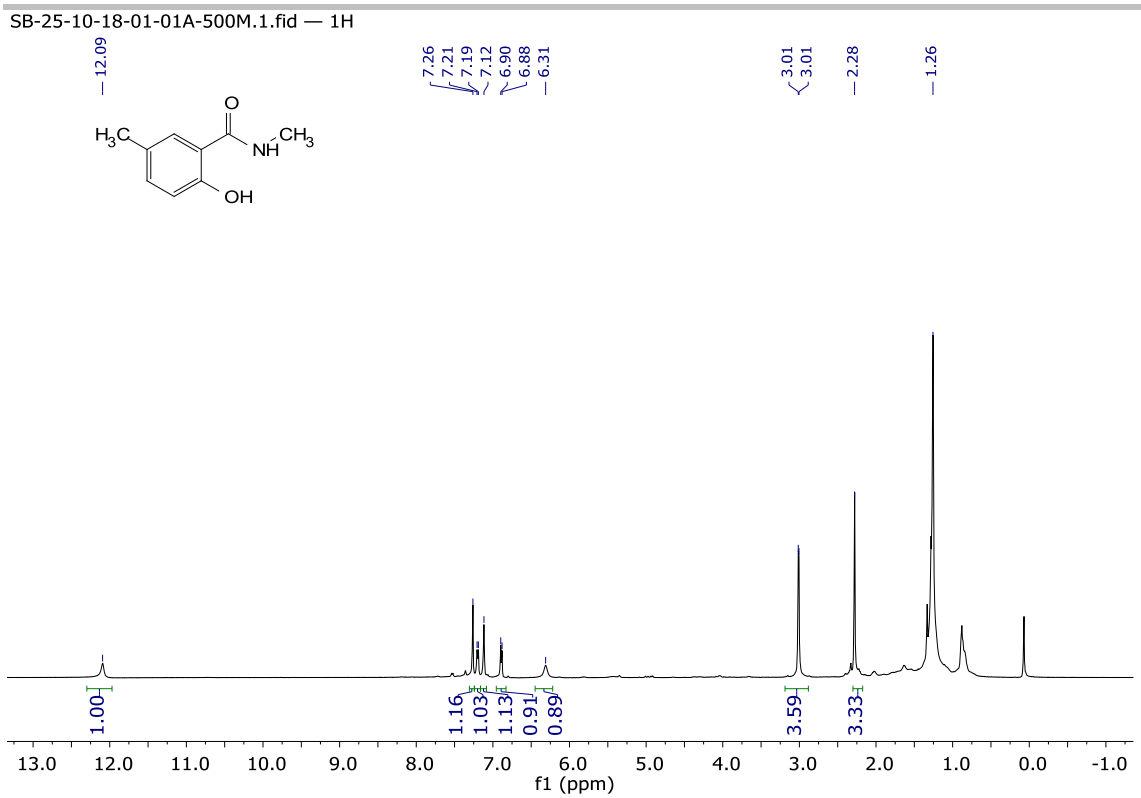


Figure S76. ^{1}H NMR spectra of borylated aromatic amide **5so'**

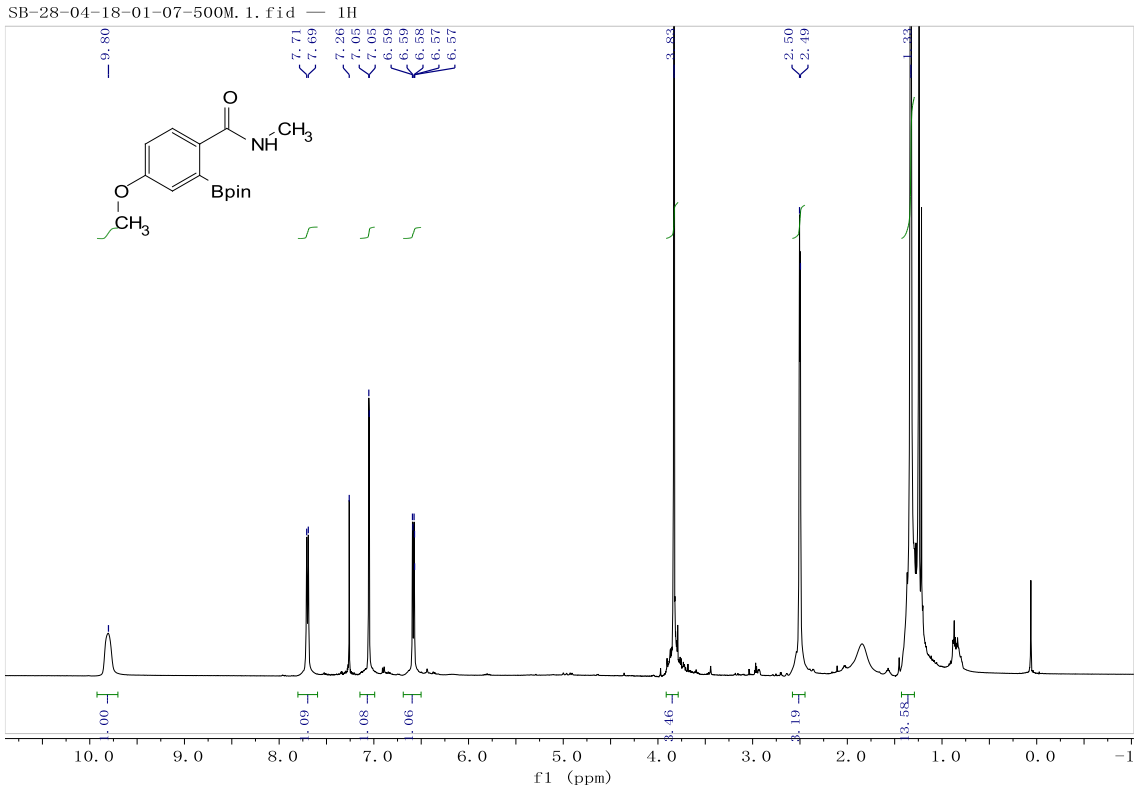


Figure S77. ^{1}H NMR spectra of borylated aromatic amide **6so**

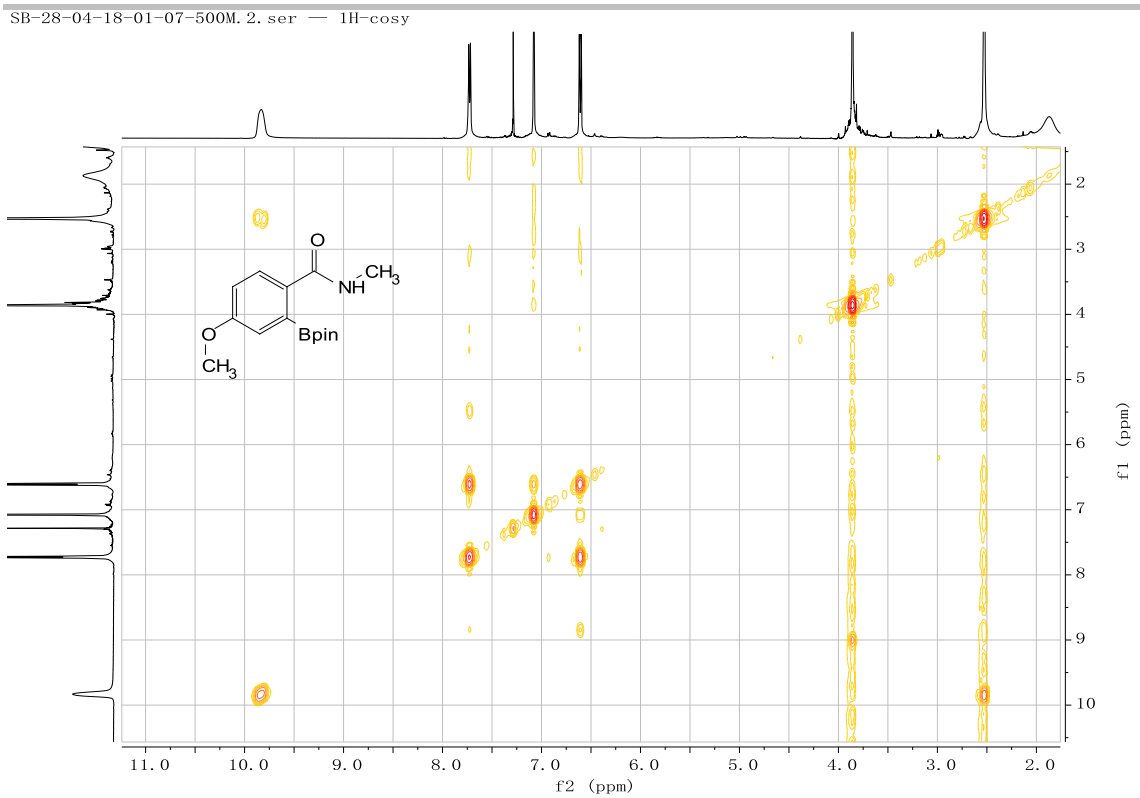


Figure S78. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **6so**

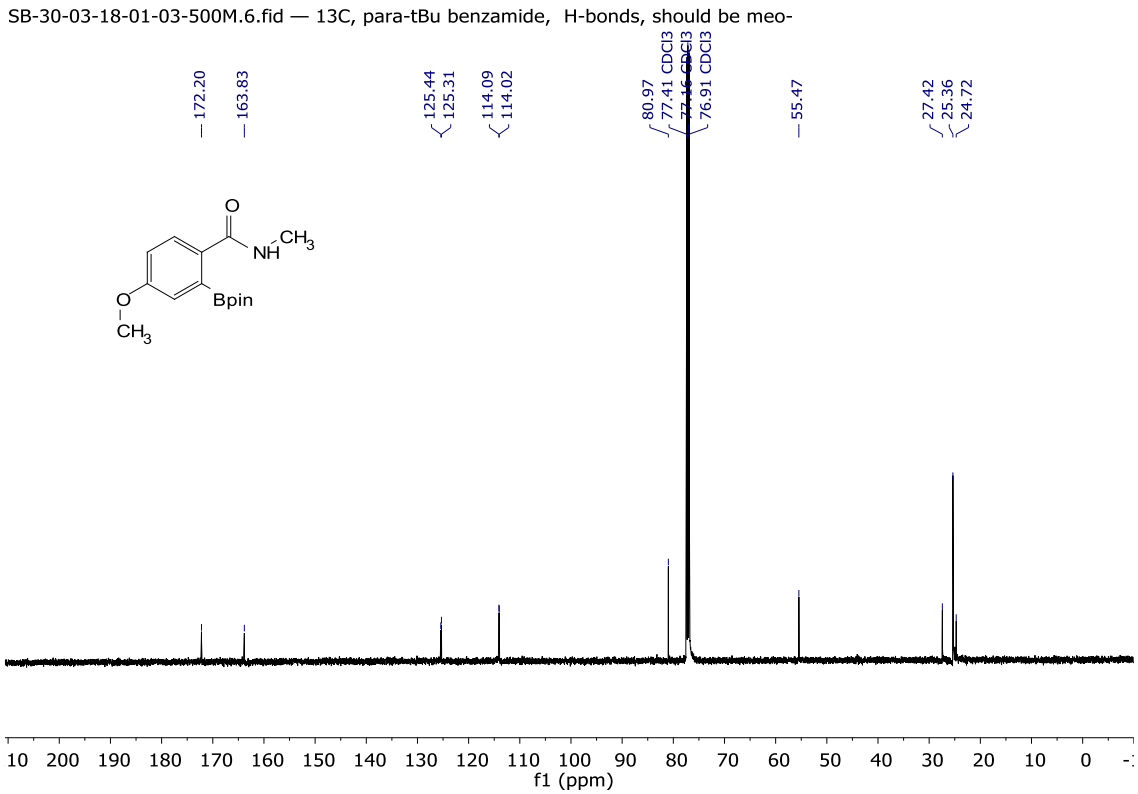


Figure S79. ^{13}C NMR spectra of borylated aromatic amide **6so**

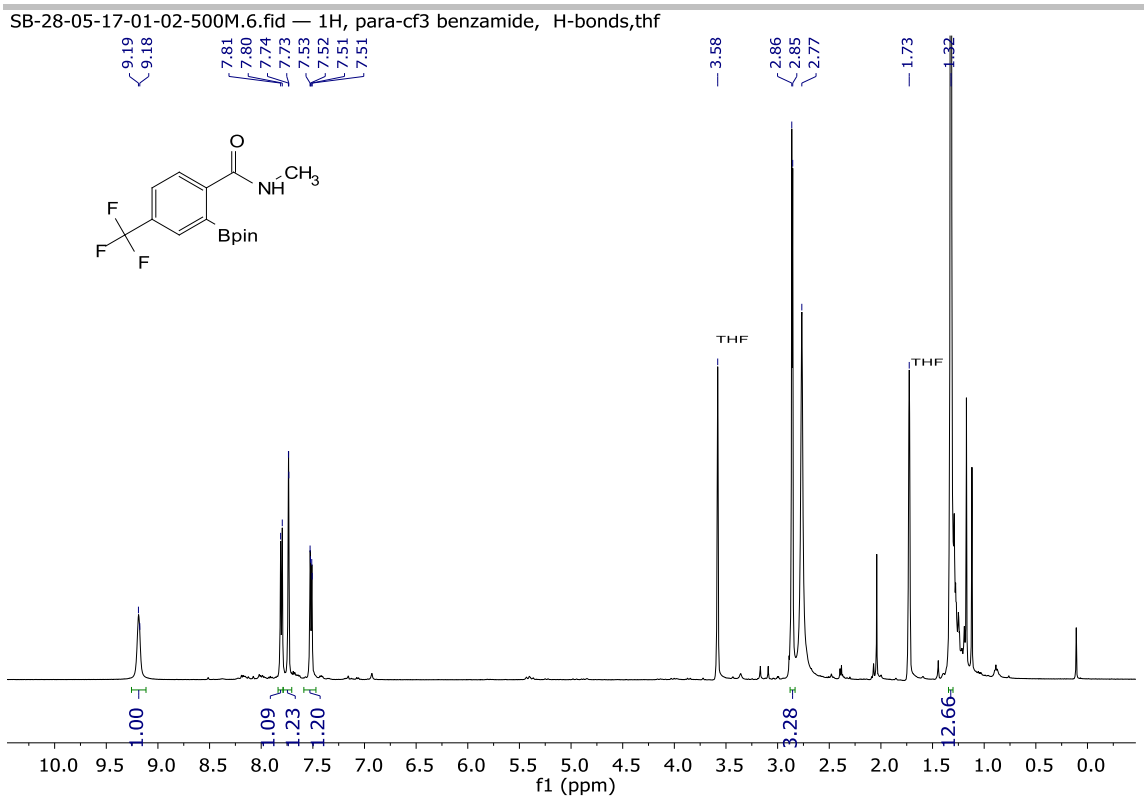


Figure S80. ^{1}H NMR spectra of borylated aromatic amide **7so**

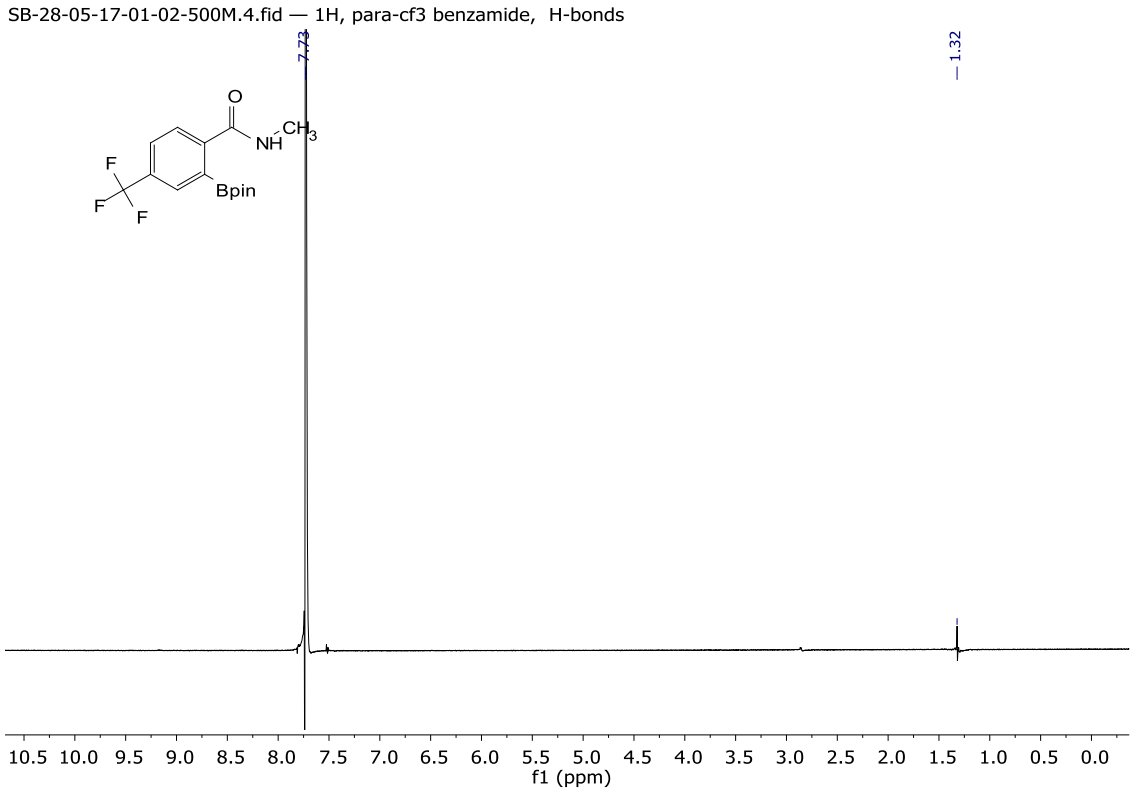


Figure S81. ^{1}H-^{1}H 1D NOESY NMR spectra of borylated aromatic amide **7so**

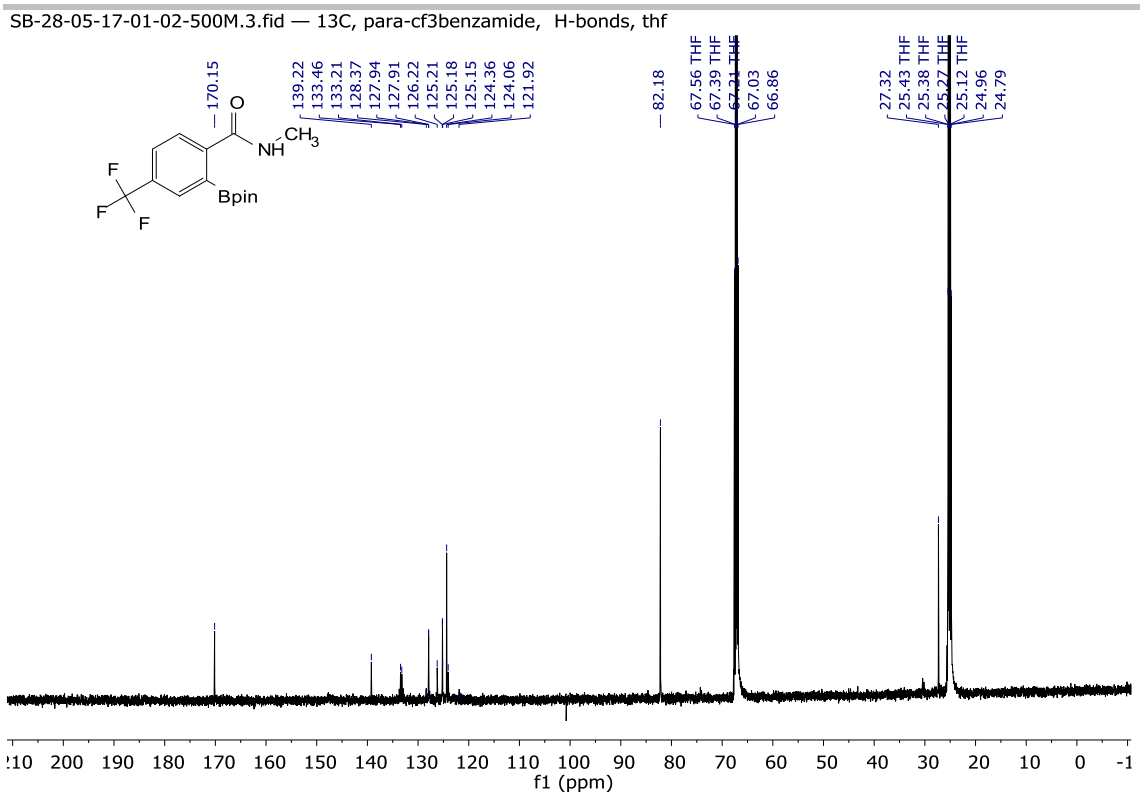


Figure S82. ^{13}C NMR spectra of borylated aromatic amide **7so**

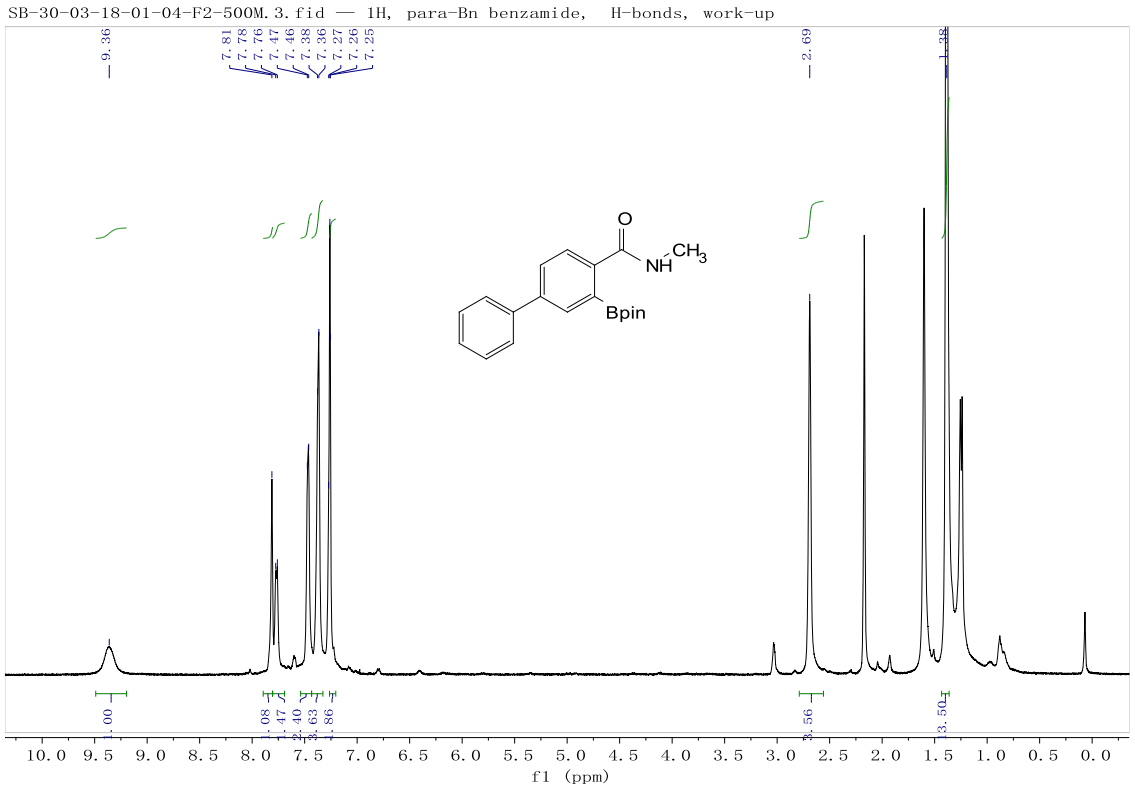


Figure S83. ^{1}H NMR spectra of borylated aromatic amide **8so**

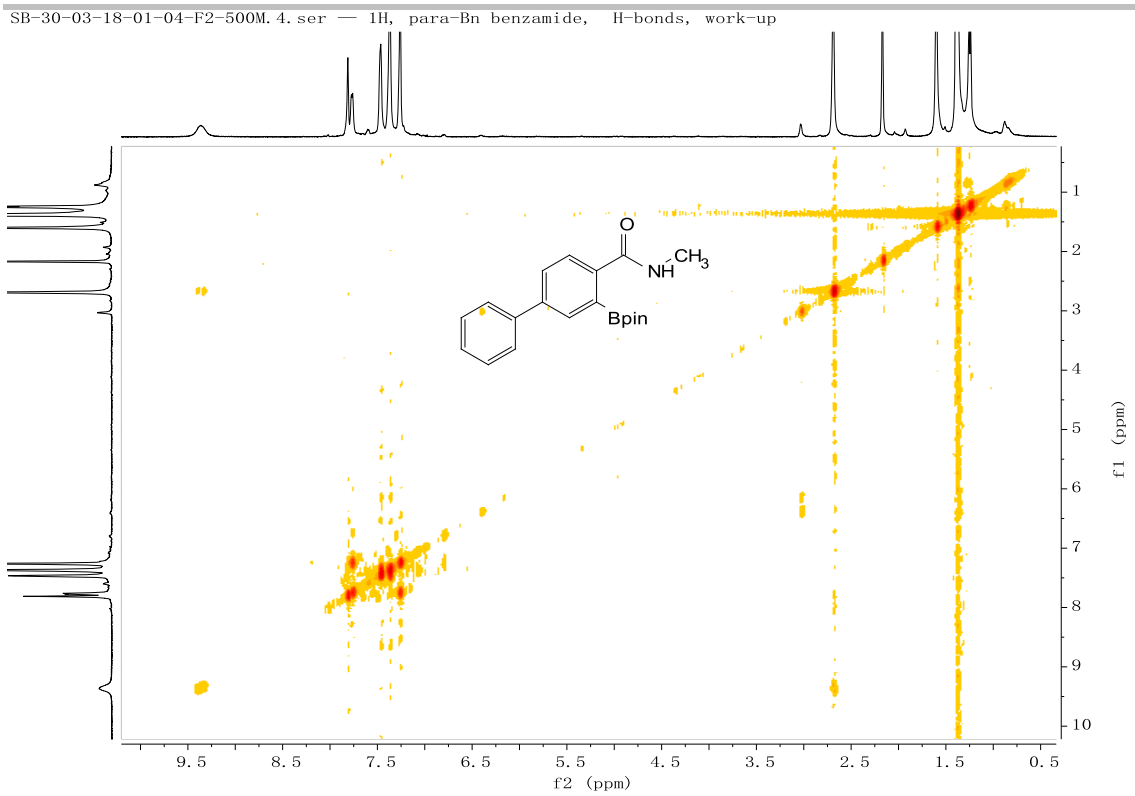


Figure S84. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **8so**

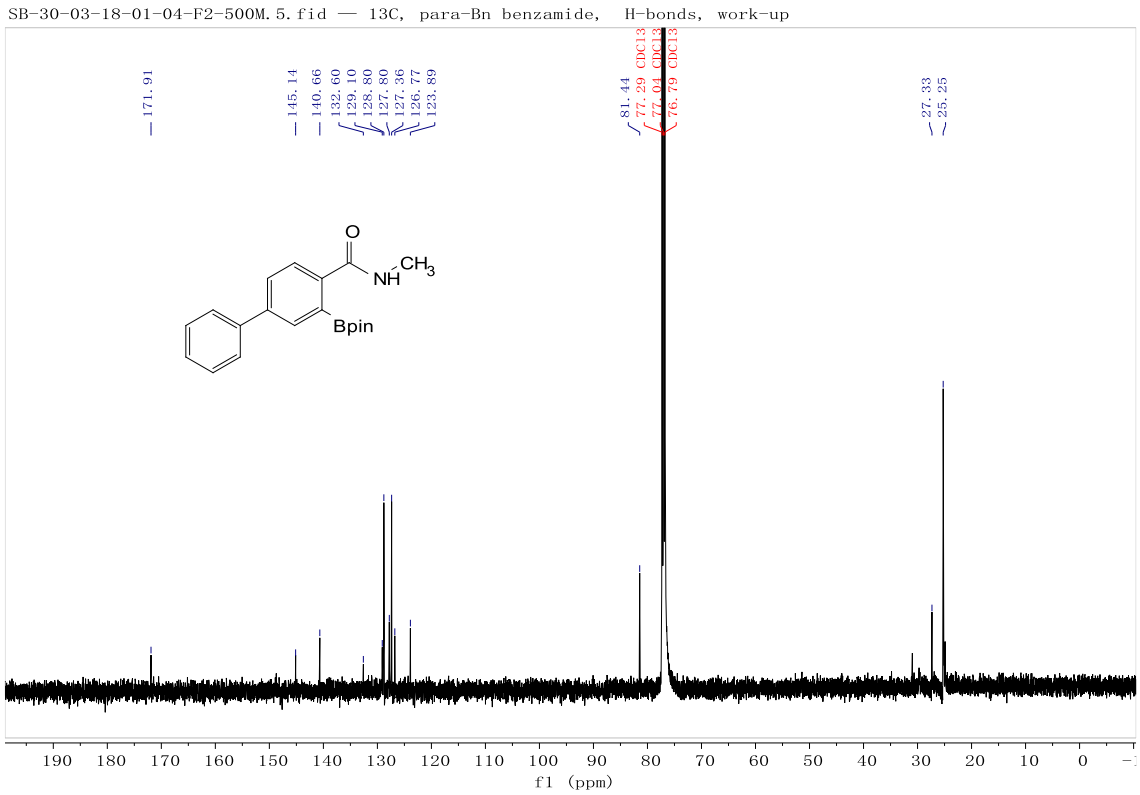


Figure S85. ^{13}C NMR spectra of borylated aromatic amide **8so**

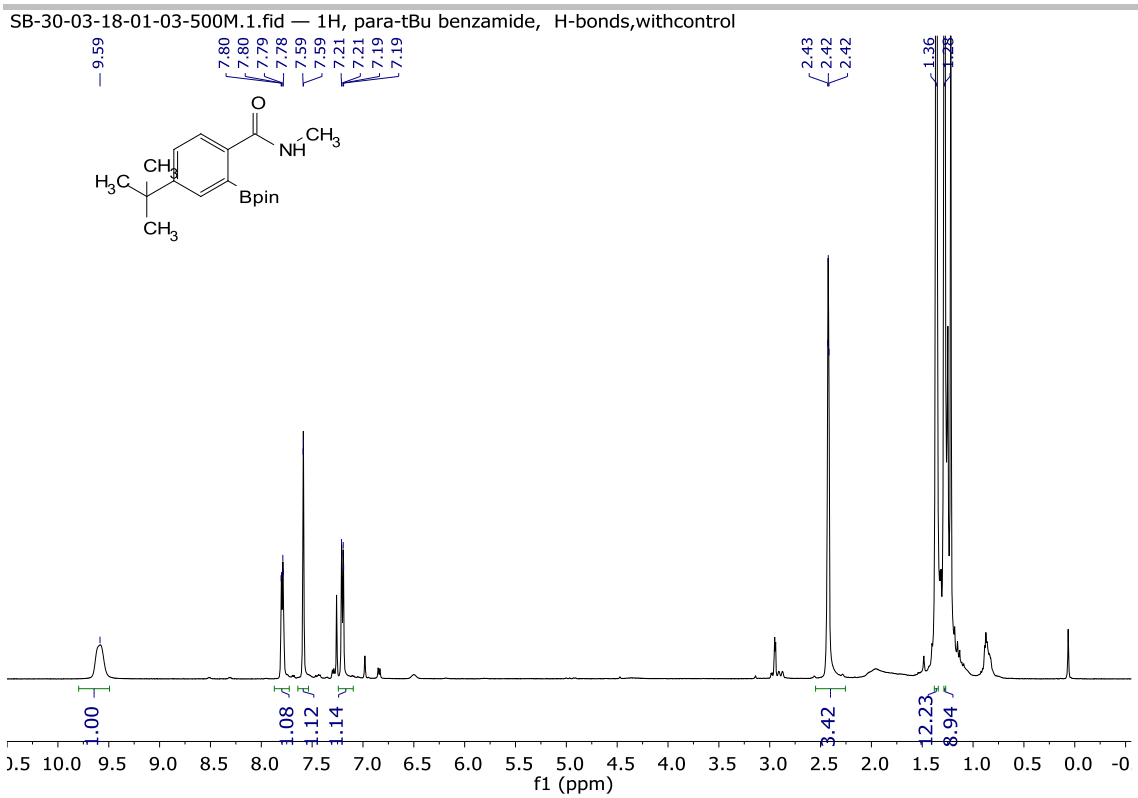


Figure S86. ^{1}H NMR spectra of borylated aromatic amide **9so**

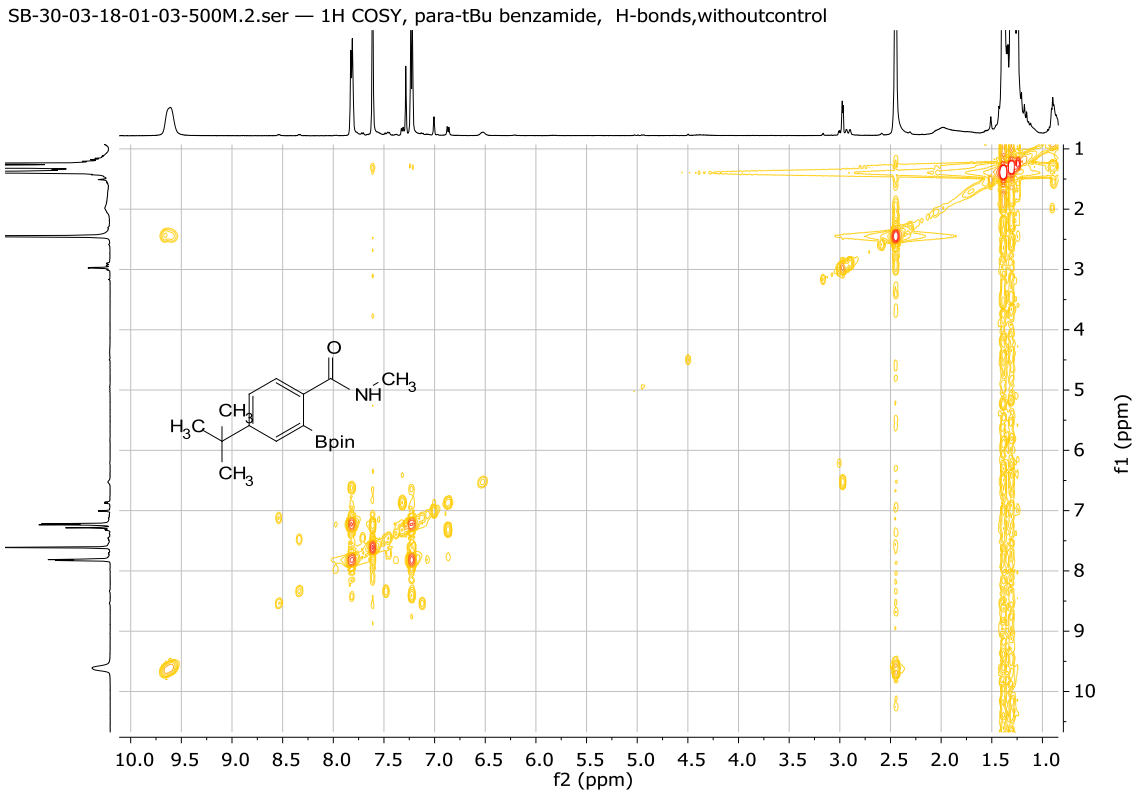


Figure S87. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **9so**

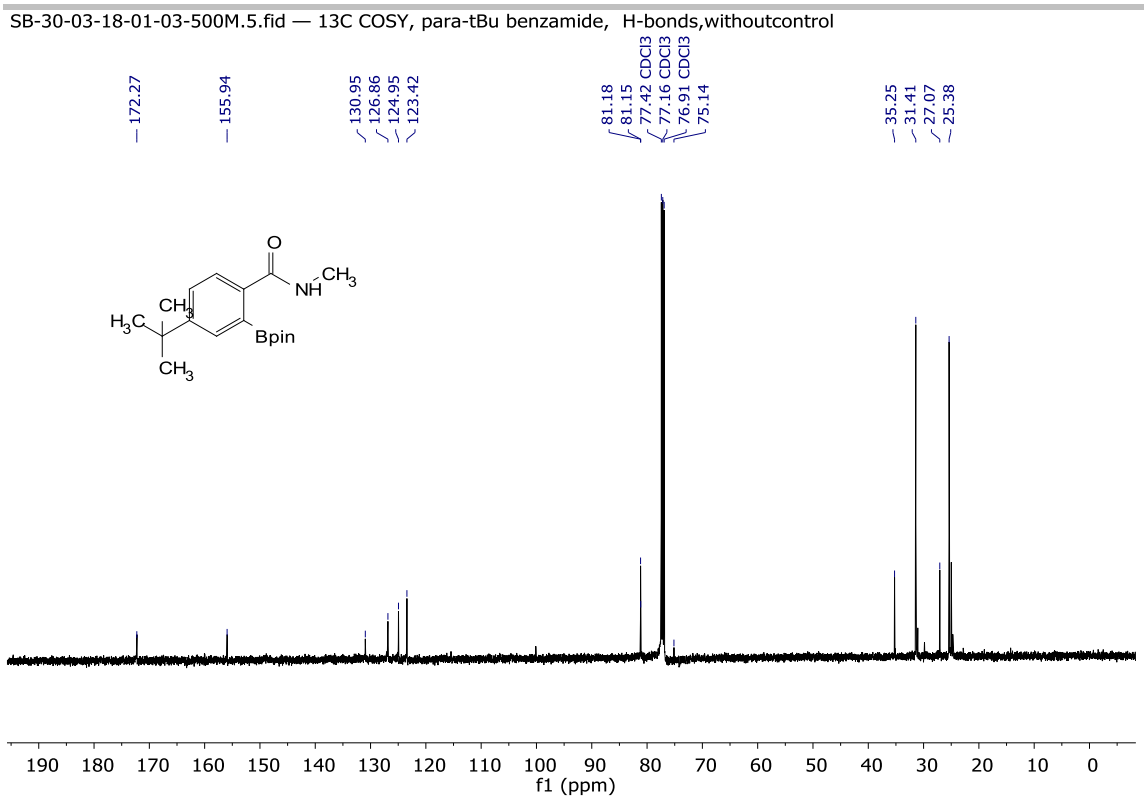


Figure S88. ^{13}C NMR spectra of borylated aromatic amide **9so**

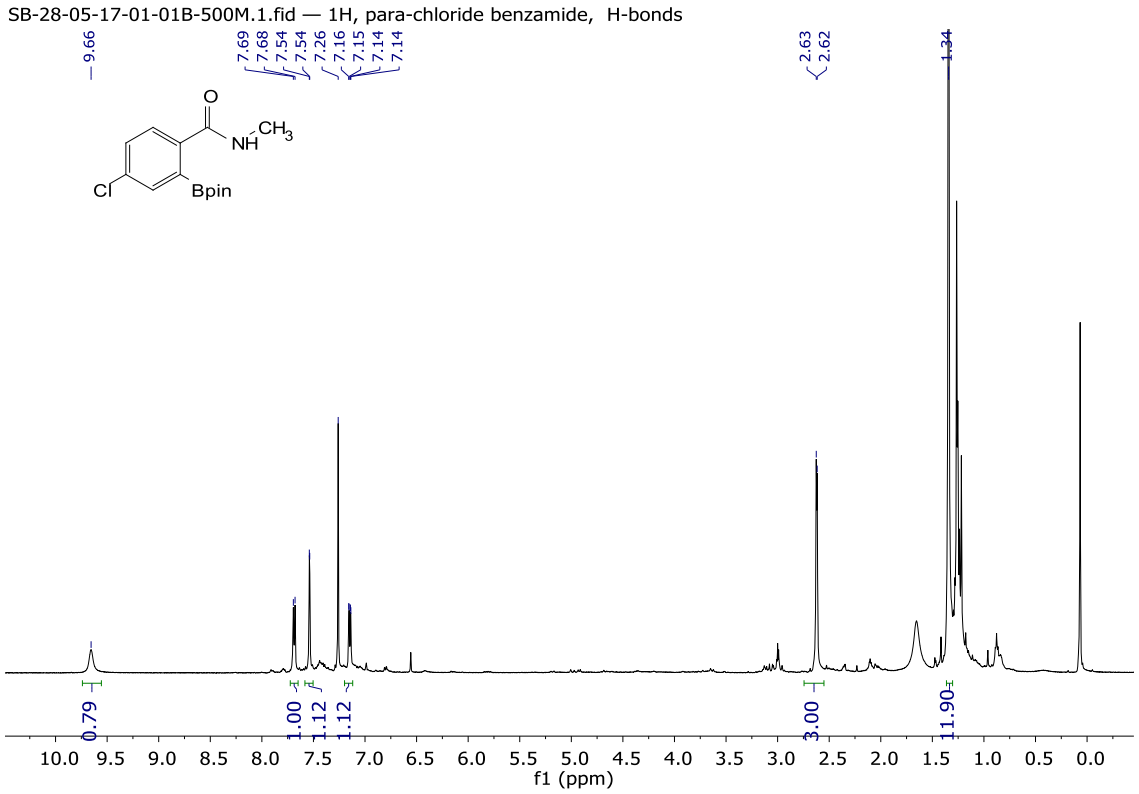


Figure S89. ^{1}H NMR spectra of borylated aromatic amide **10so**

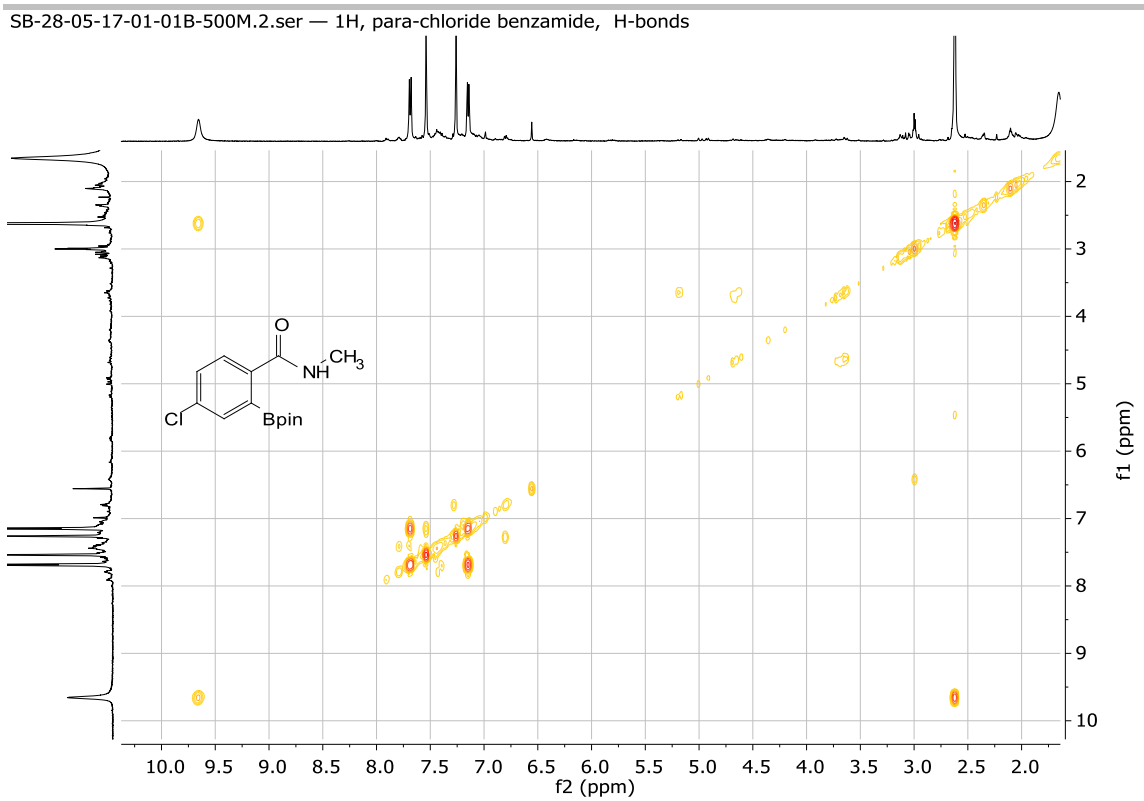


Figure S90. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **10so**

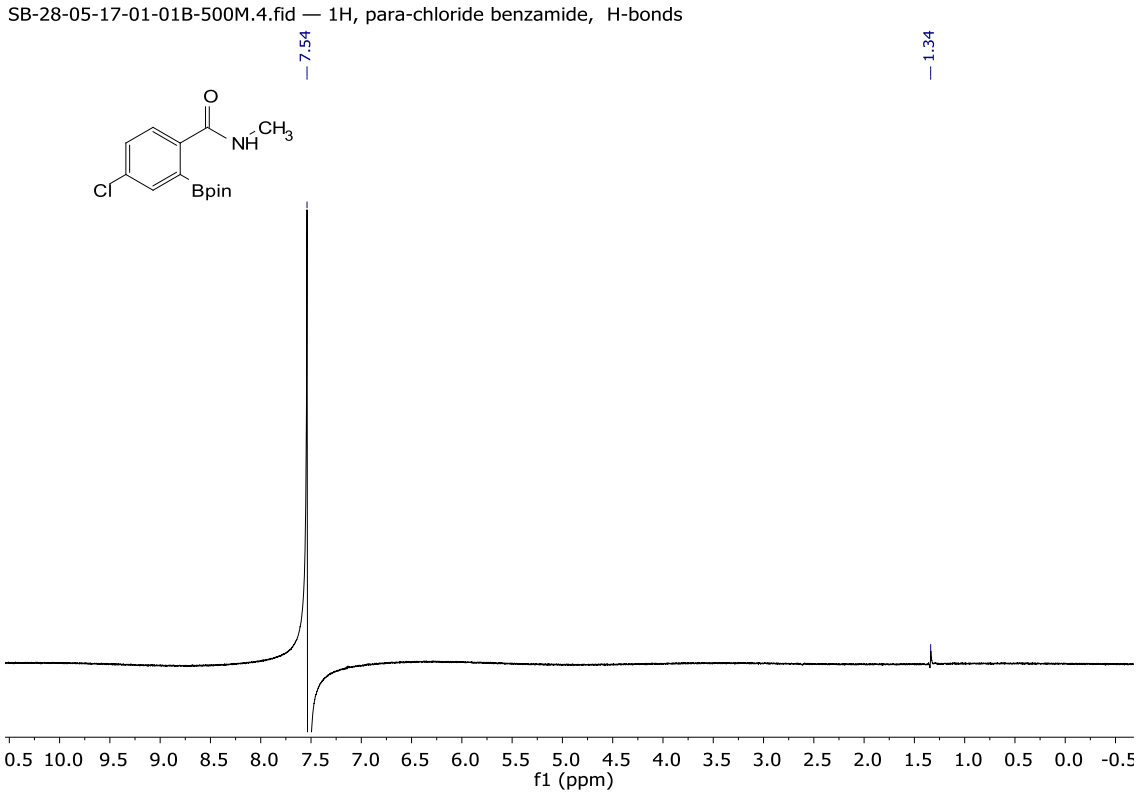


Figure S91. ^{1}H-^{1}H 1D NOESY NMR spectra of aromatic amide **10so**

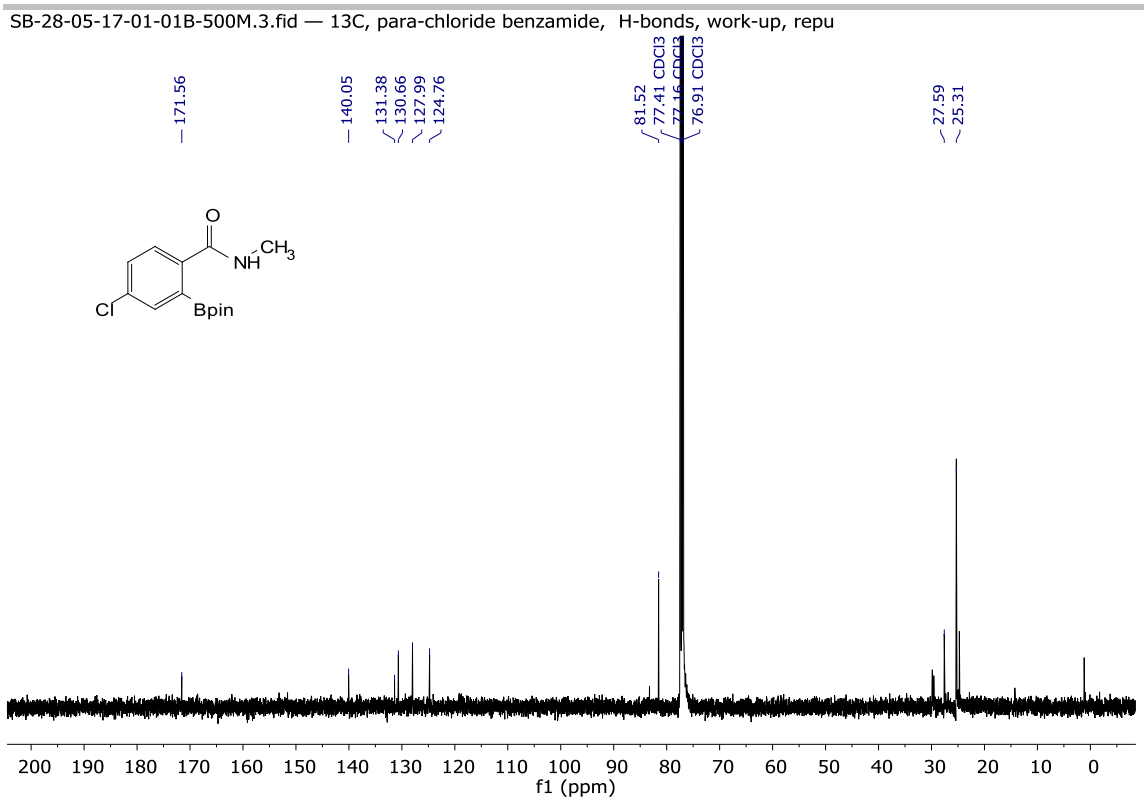


Figure S92. ^{13}C NMR spectra of borylated aromatic amide **10so**

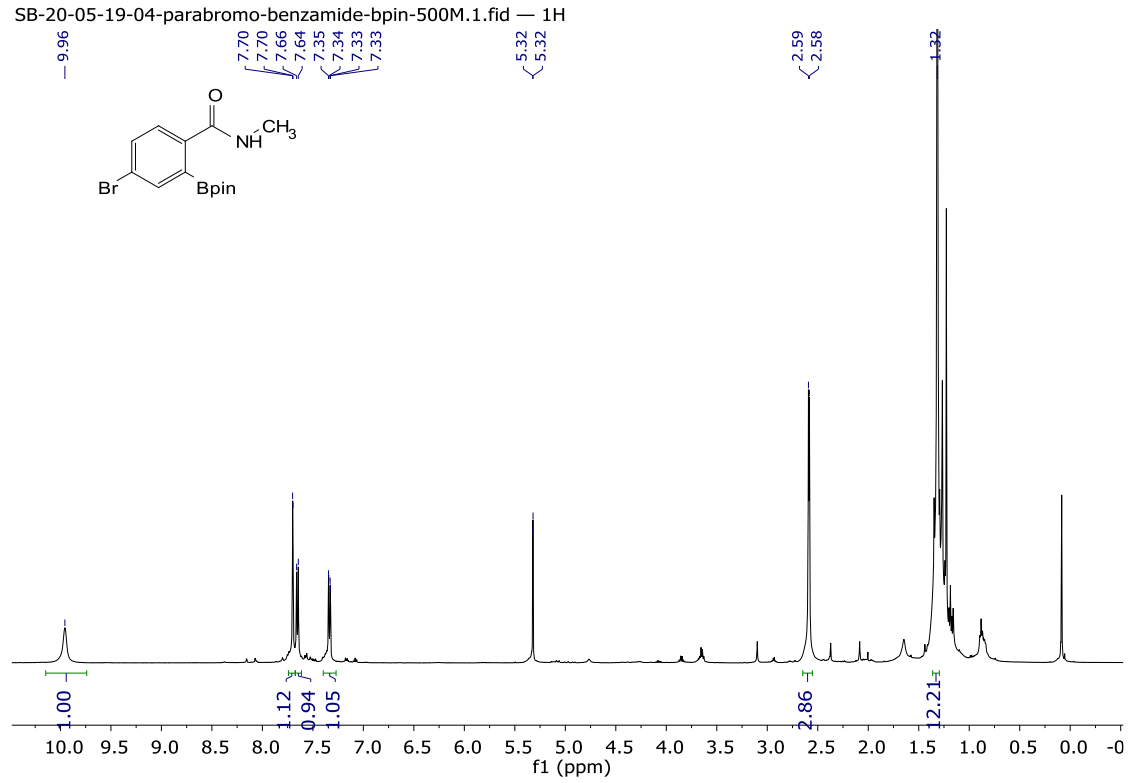


Figure S93. ^{1}H NMR spectra of borylated aromatic amide **11so**

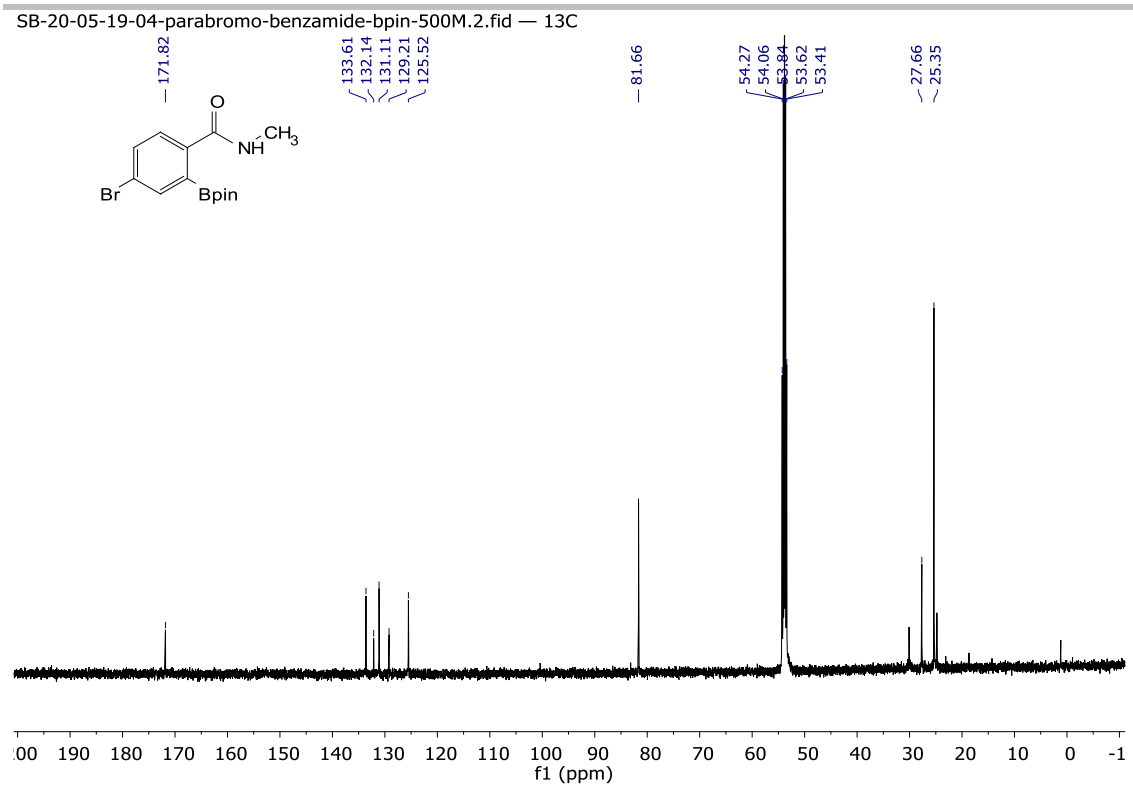


Figure S94. ^{13}C NMR spectra of borylated aromatic amide **11so**

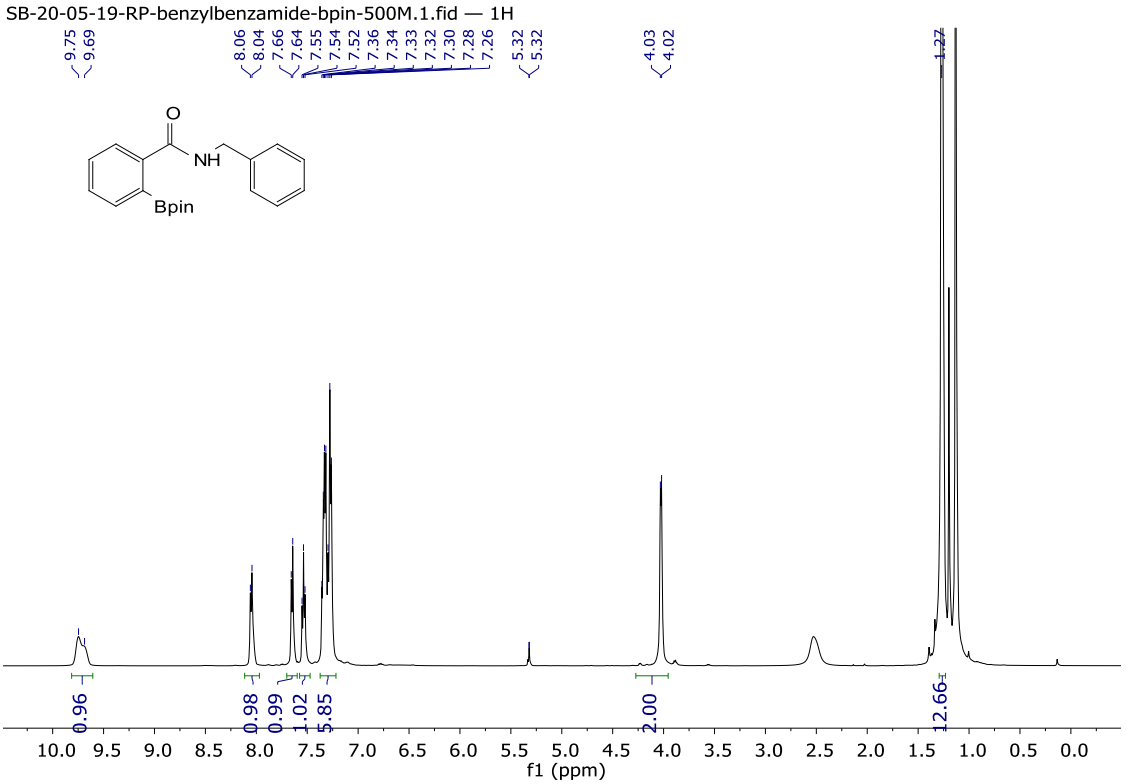


Figure S95. ^{1}H NMR spectra of the borylated aromatic amide **12so**

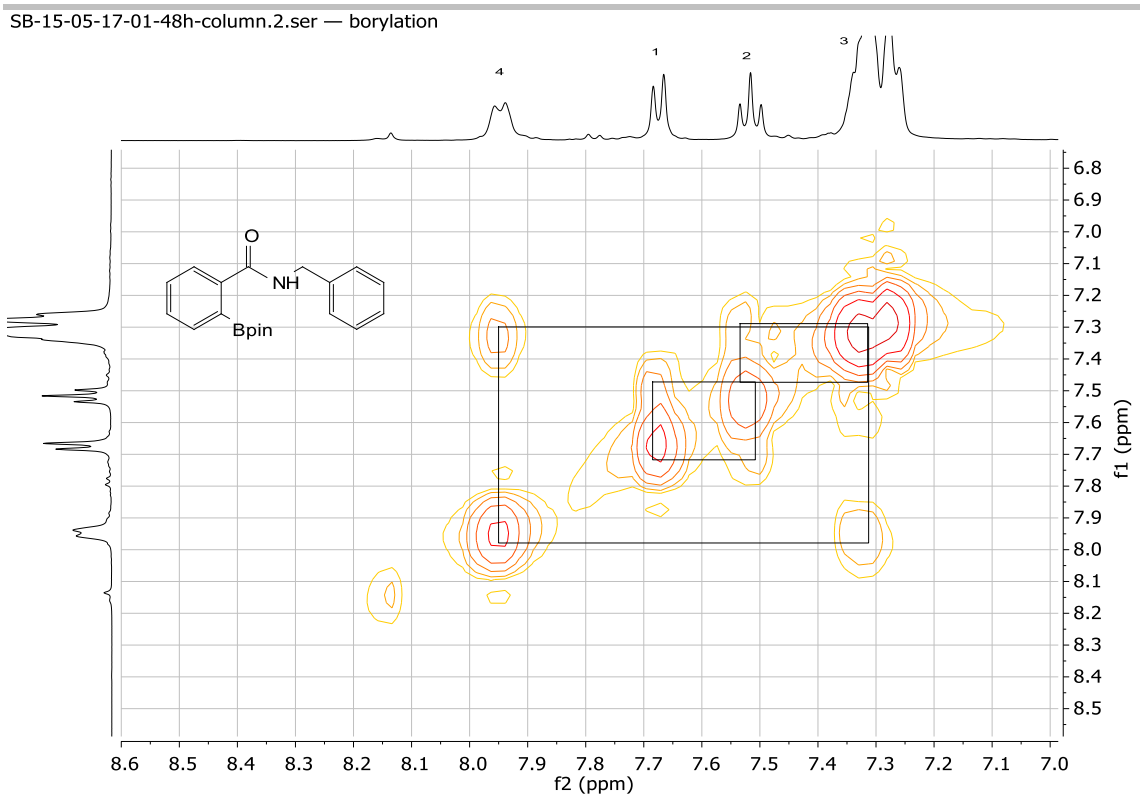


Figure S96. ^{1}H-^{1}H COSY NMR spectra of the borylated aromatic amide **12so**

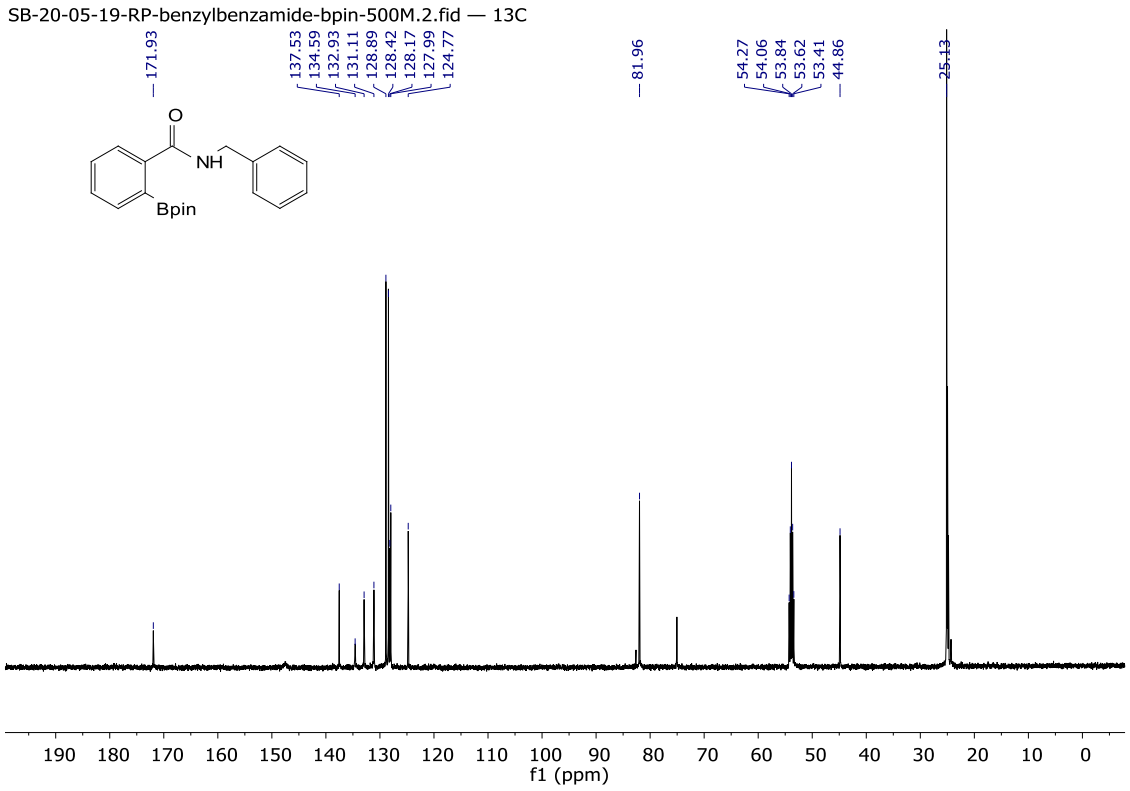


Figure S97. ^{13}C NMR spectra of borylated aromatic amide **12so**

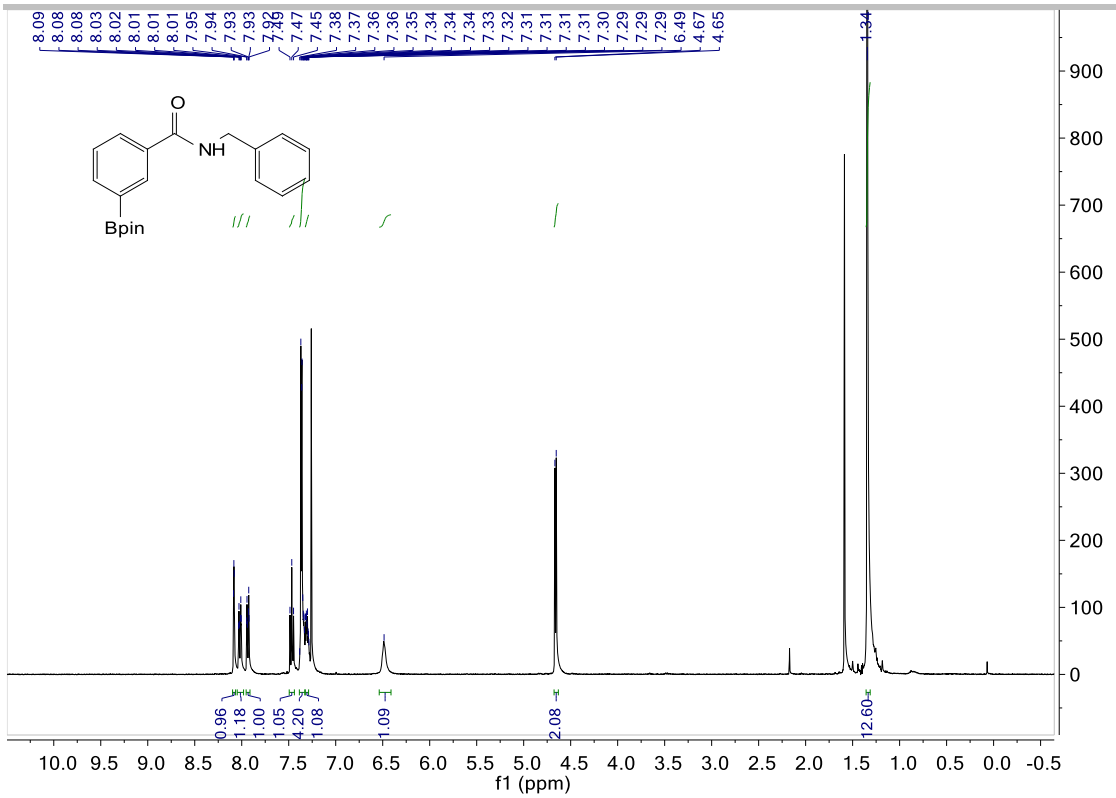


Figure S98. ^{1}H NMR spectra of borylated aromatic amide **12sm**

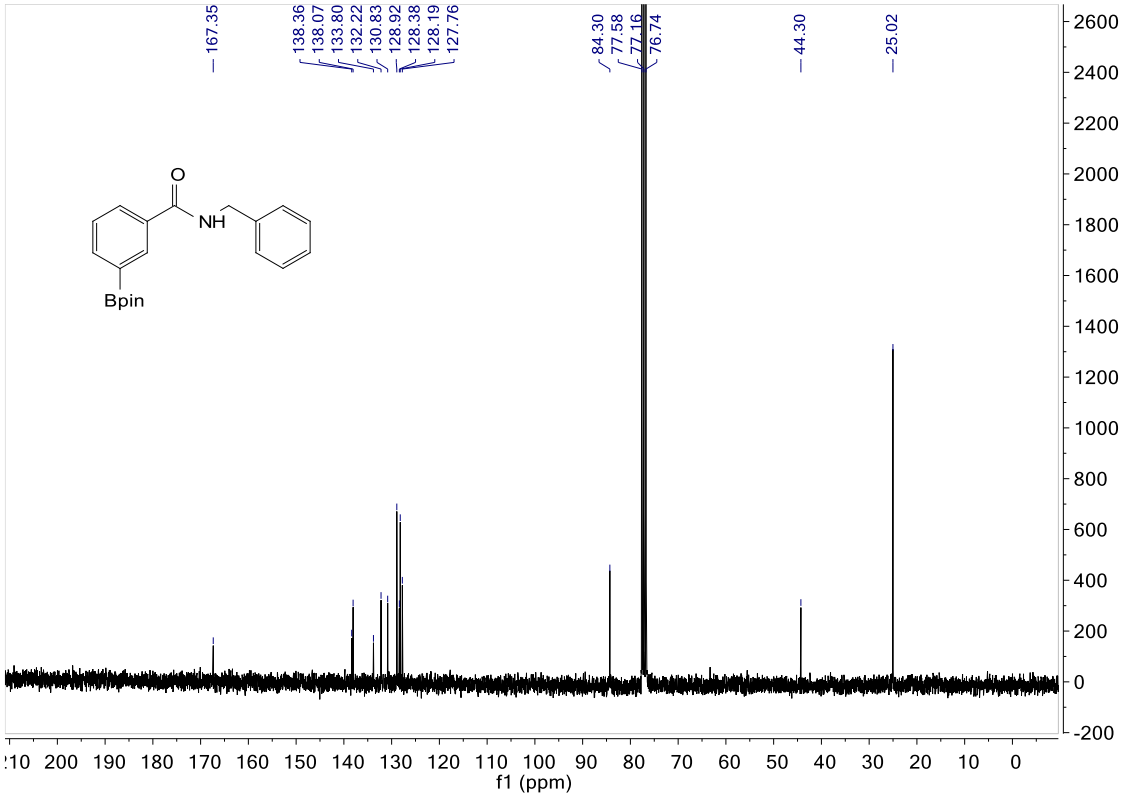


Figure S99. ^{13}C NMR spectra of borylated aromatic amide **12sm**

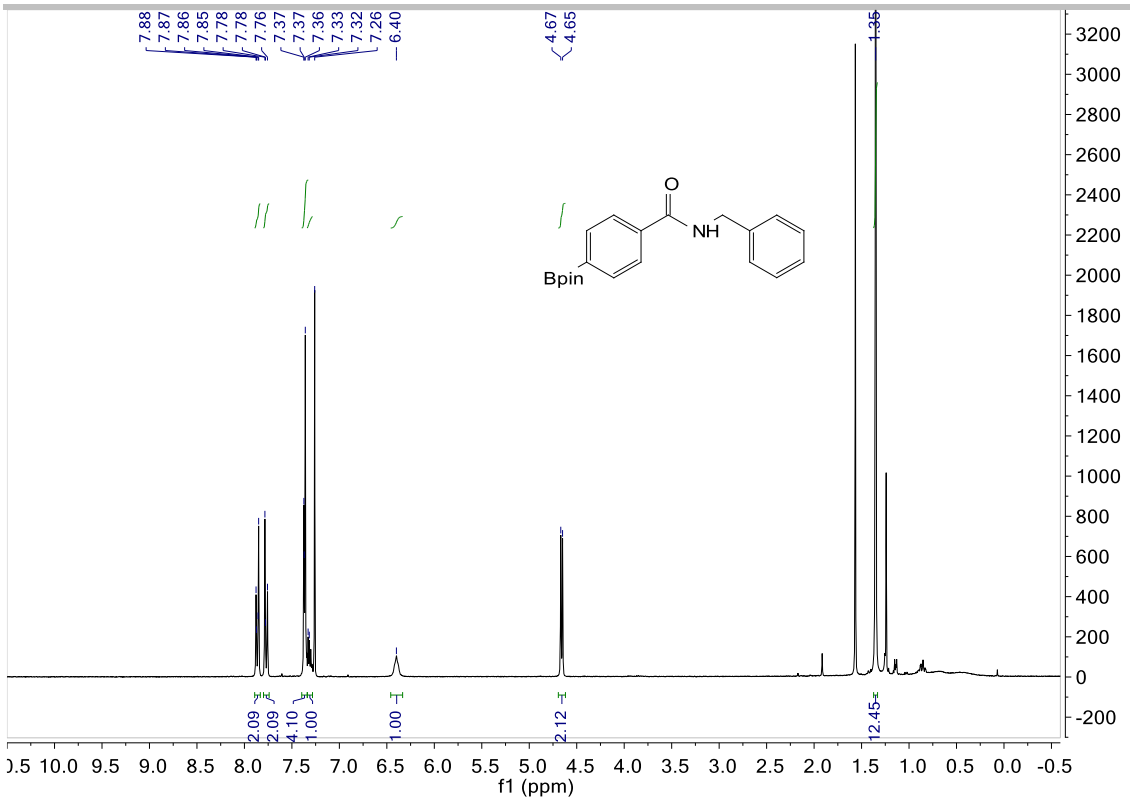


Figure S100. ^{1}H NMR spectra of borylated aromatic amide **12sp**

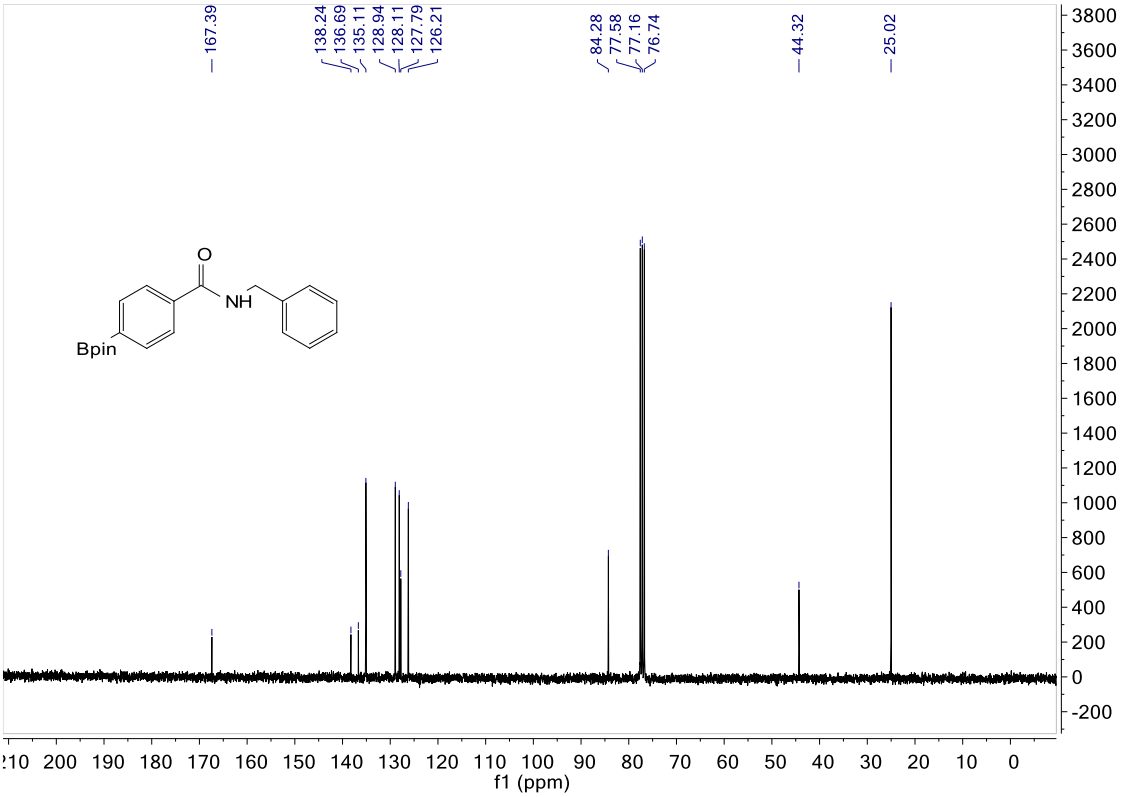


Figure S101. ^{13}C NMR spectra of borylated aromatic amide **12sp**

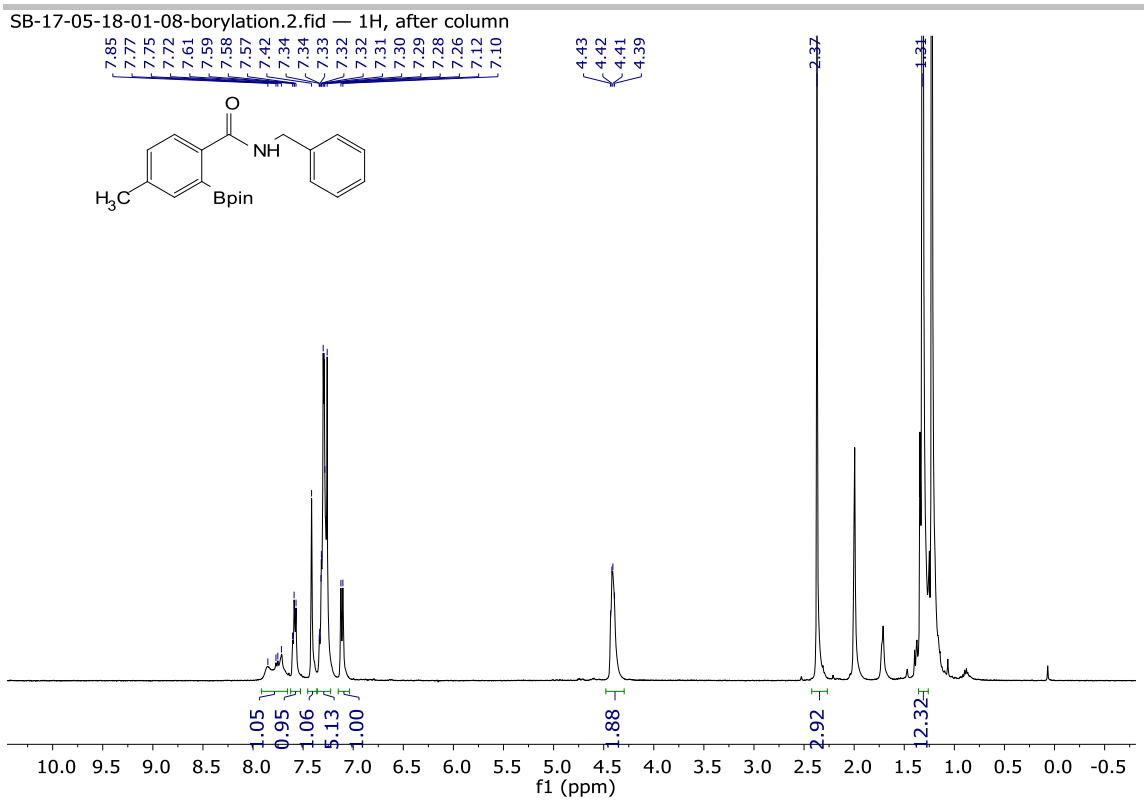


Figure S102. ^{1}H NMR spectra of borylated aromatic amide **13so**

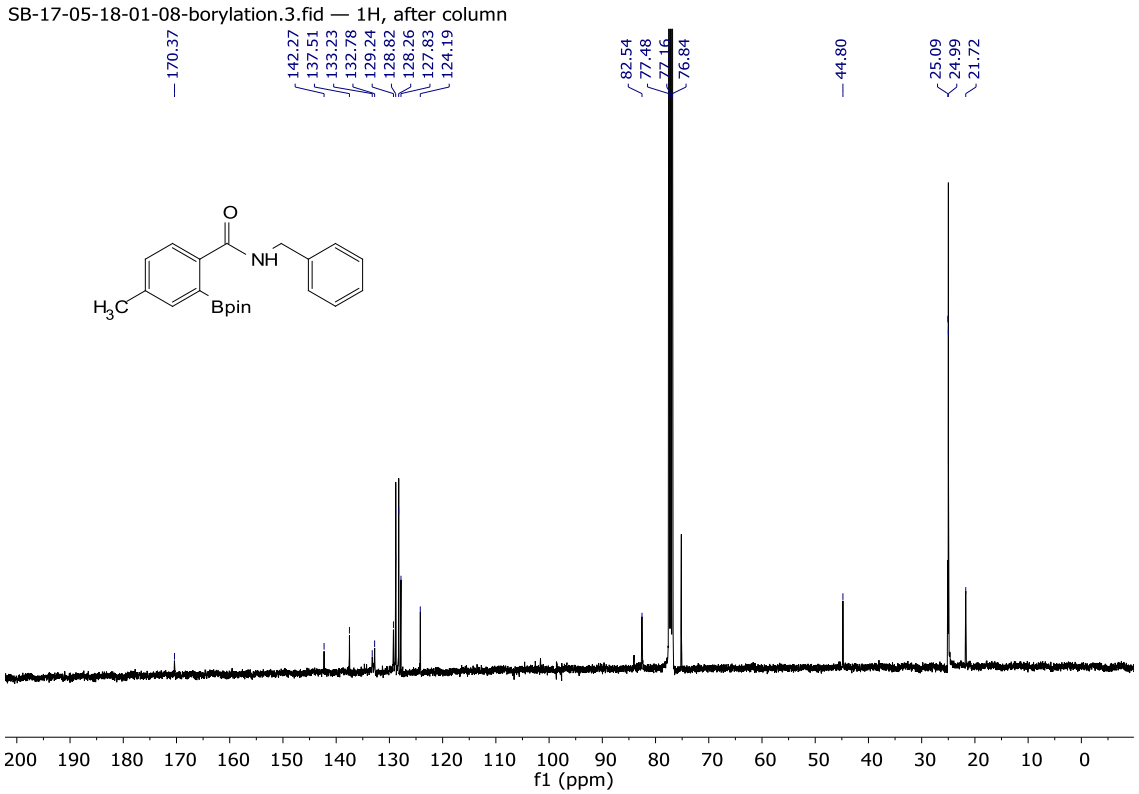


Figure S103. ^{13}C NMR spectra of borylated aromatic amide **13so**

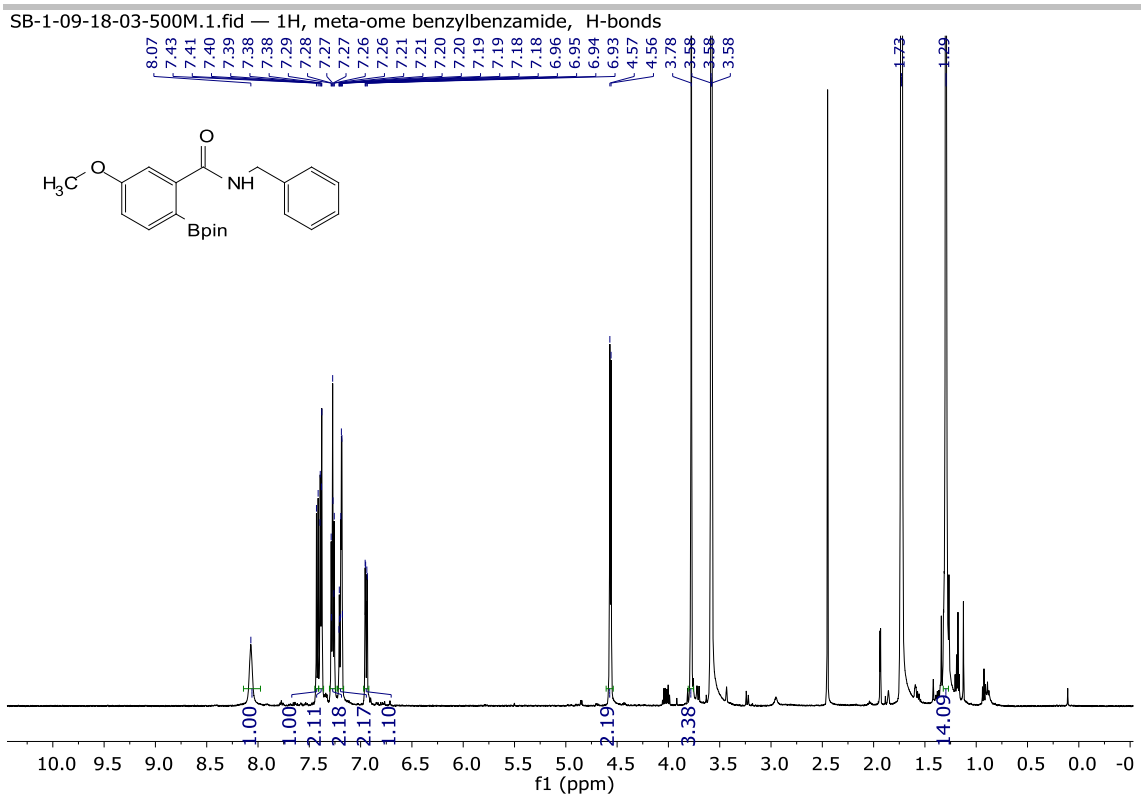


Figure S104. ^{1}H NMR spectra of borylated aromatic amide **14so**

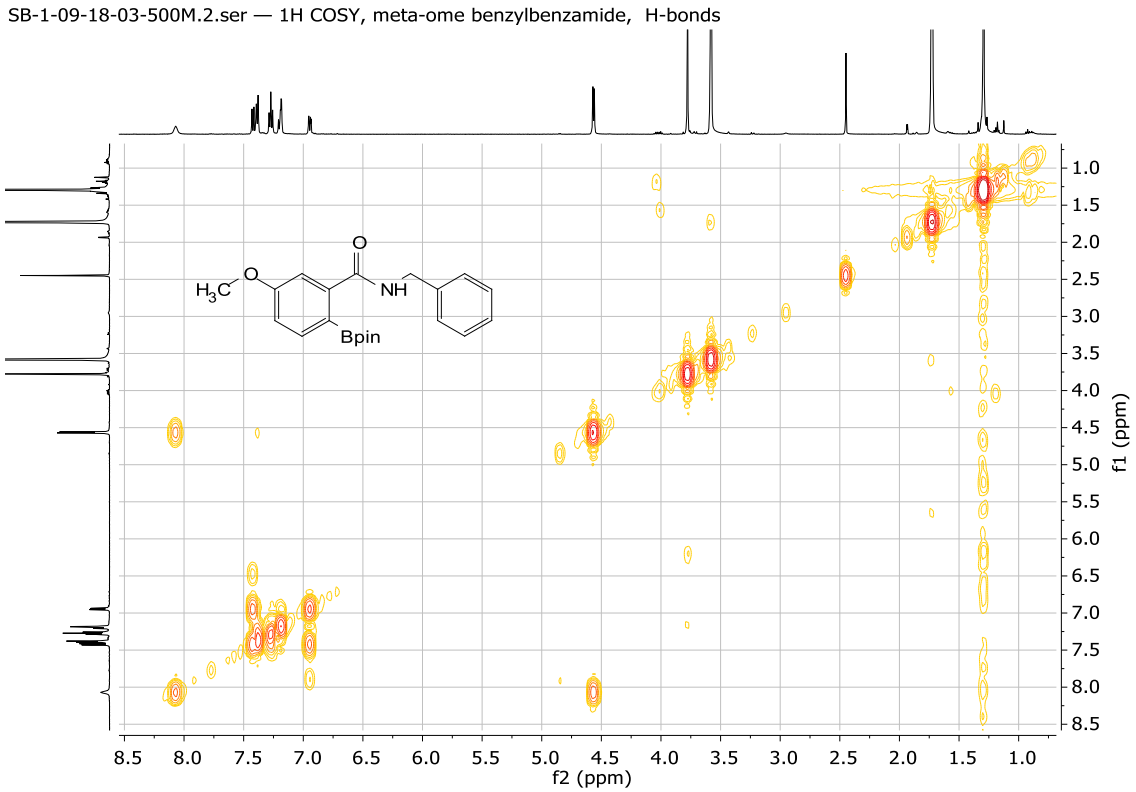


Figure S105. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **14so**

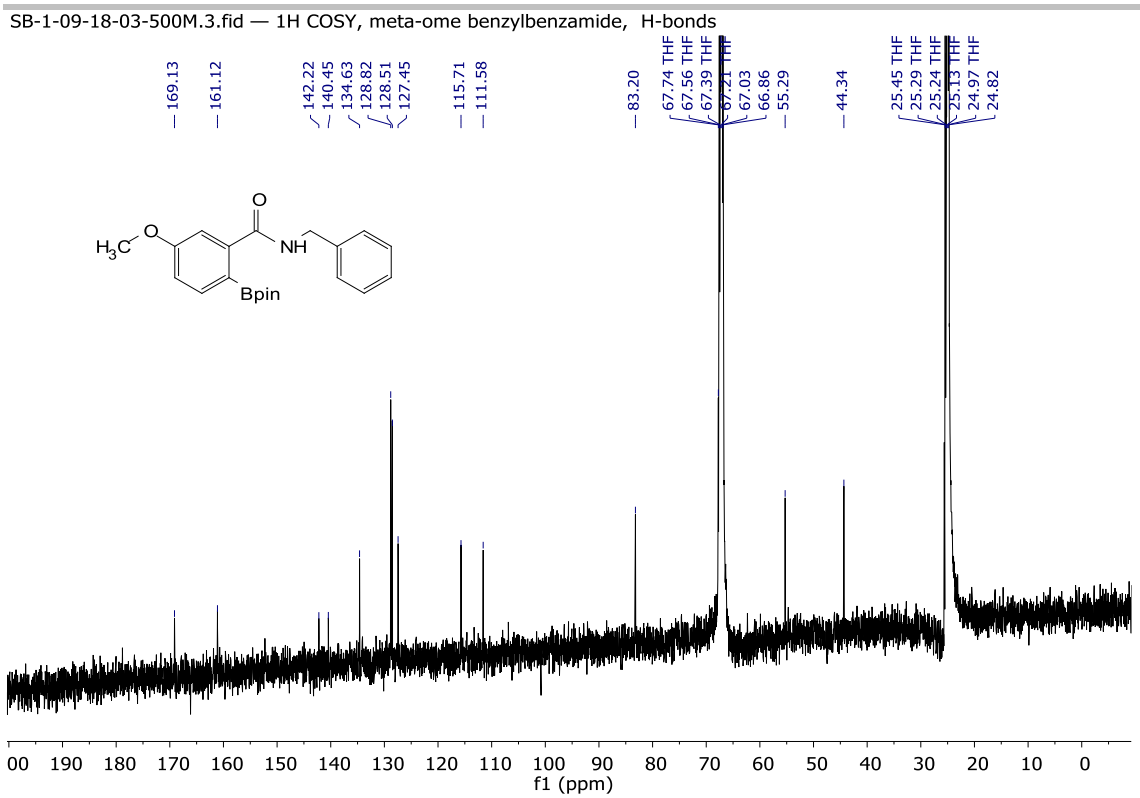


Figure S106. ^{13}C NMR spectra of borylated aromatic amide **14so**

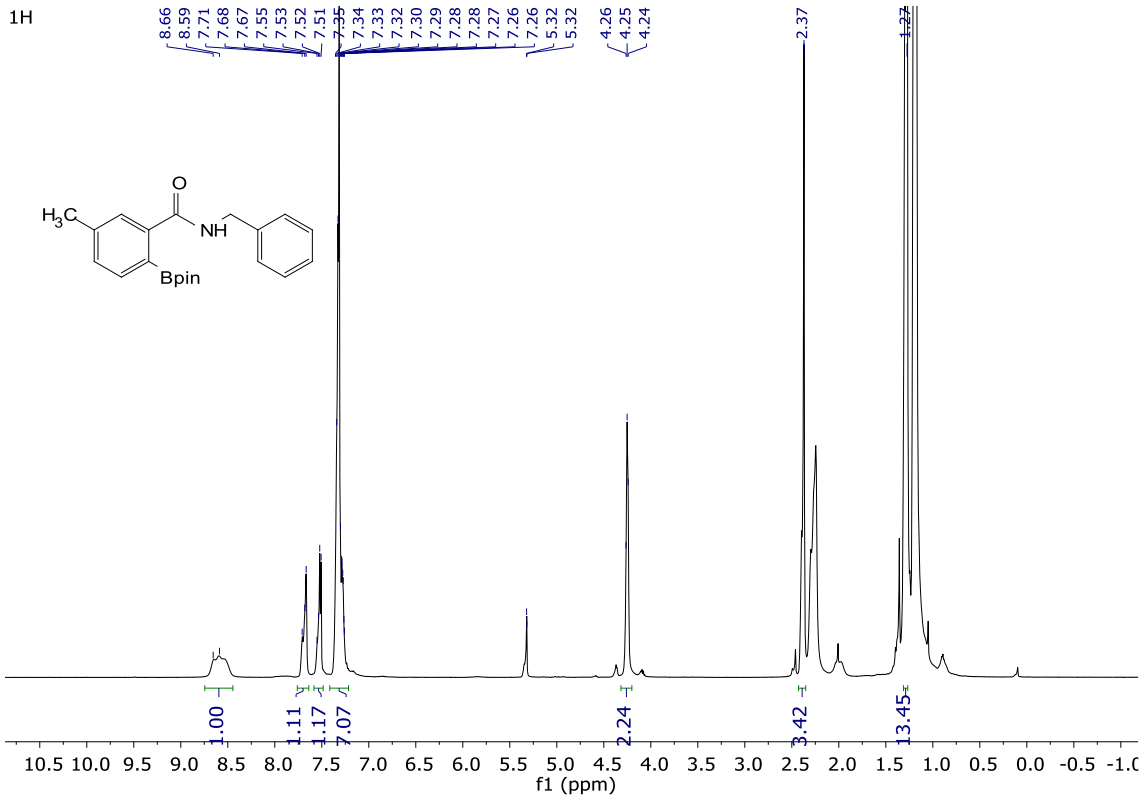


Figure S107. ^{1}H NMR spectra of borylated aromatic amides **15so**

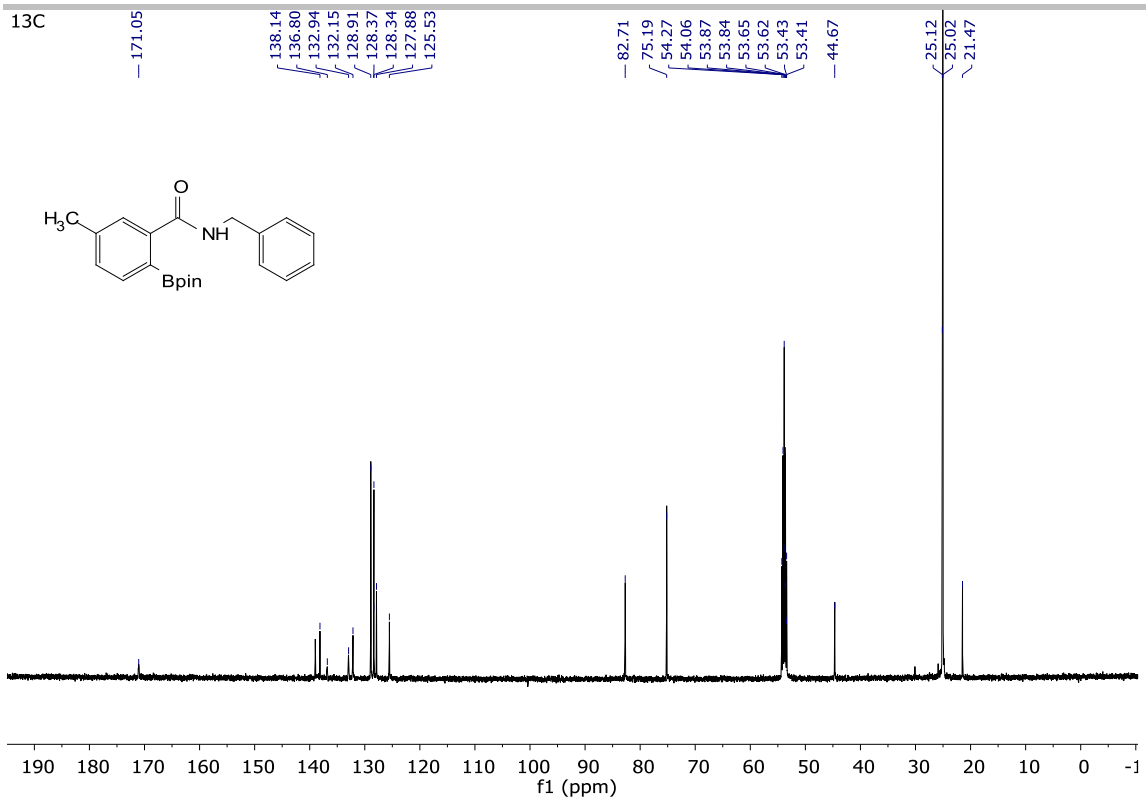


Figure S108. ^{13}C NMR spectra of borylated aromatic amides **15so**

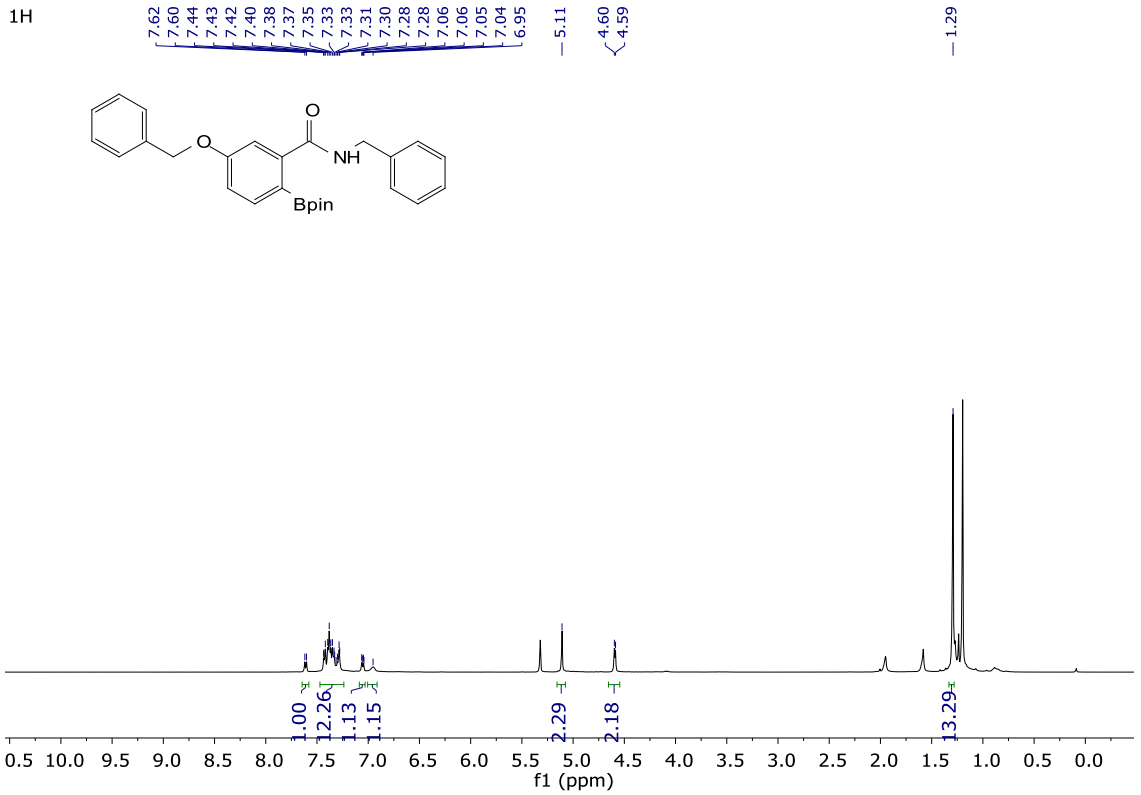


Figure S109. ^{1}H NMR spectra of borylated aromatic amides **16so**

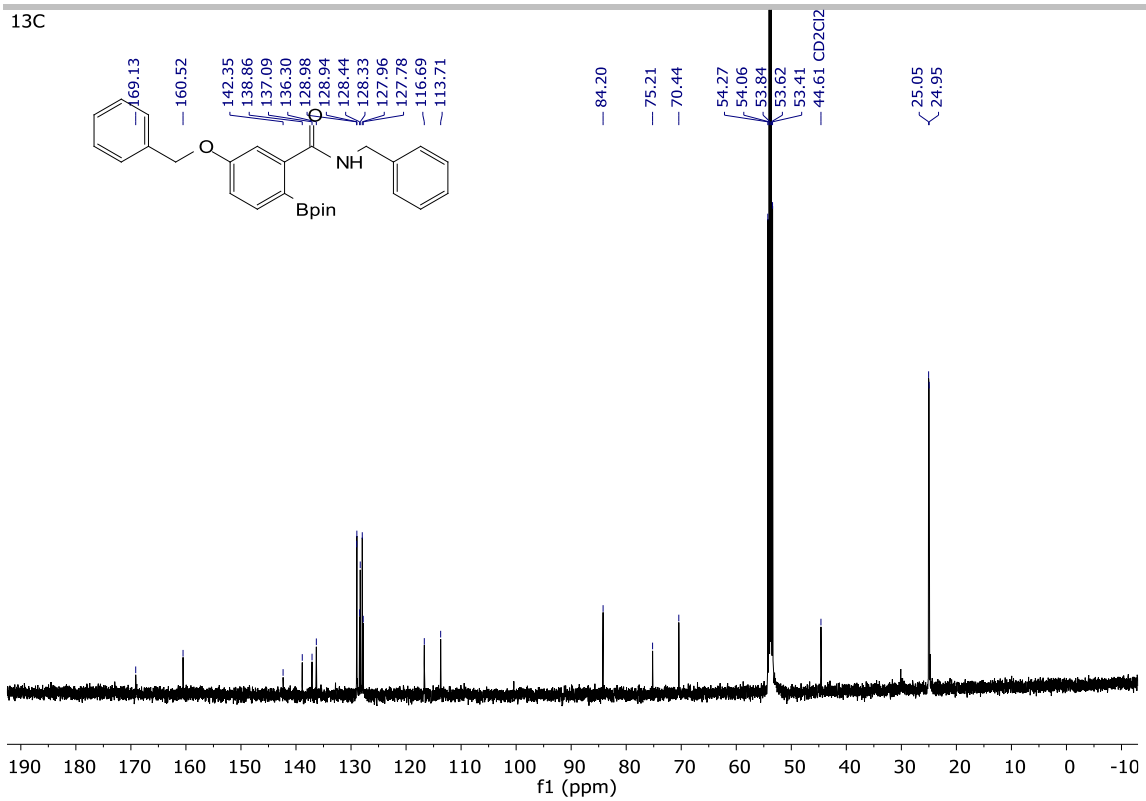


Figure S110. ^{13}C NMR spectra of borylated aromatic amides **16so**

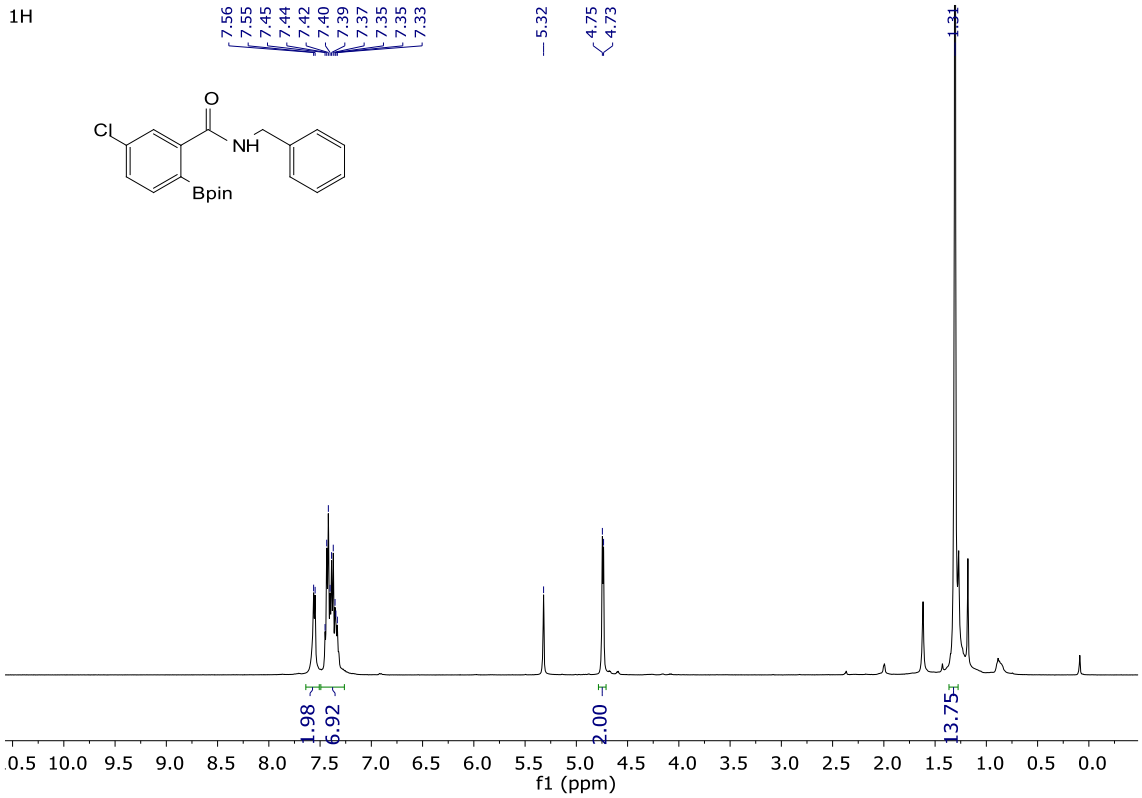


Figure S111. ^{1}H NMR spectra of borylated aromatic amides **17so**

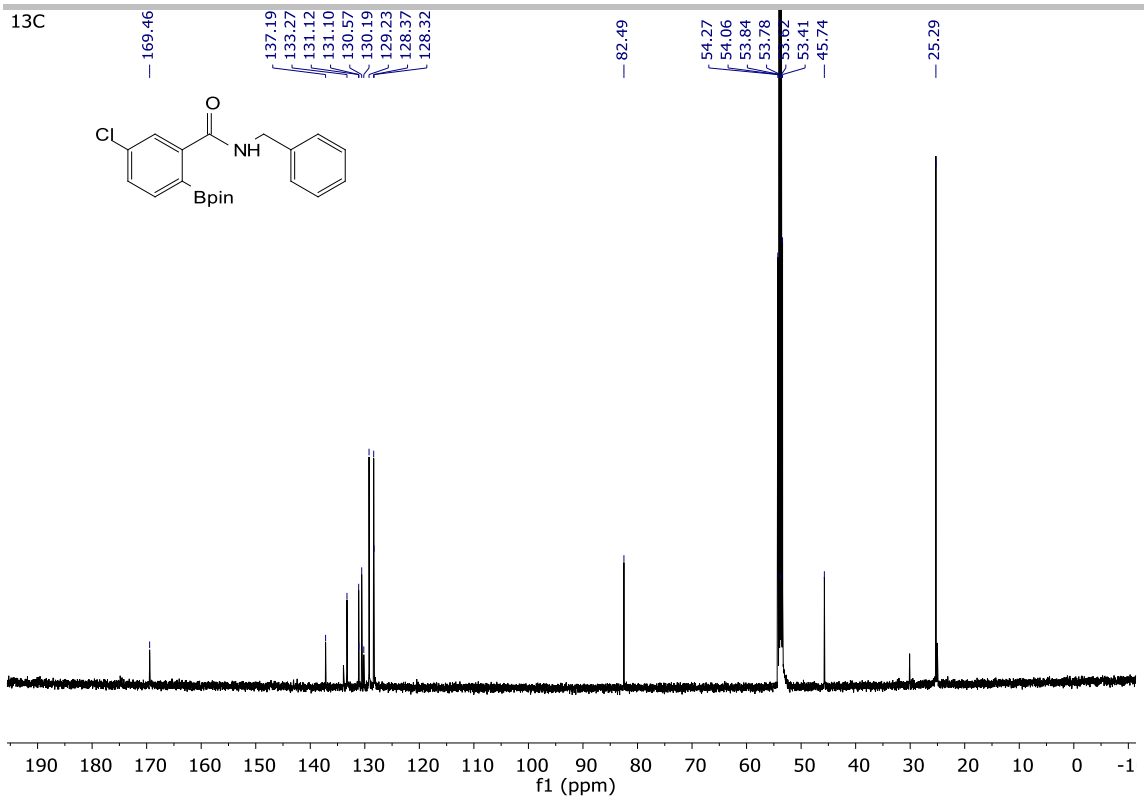


Figure S112. ^{13}C NMR spectra of borylated aromatic amides **17so**

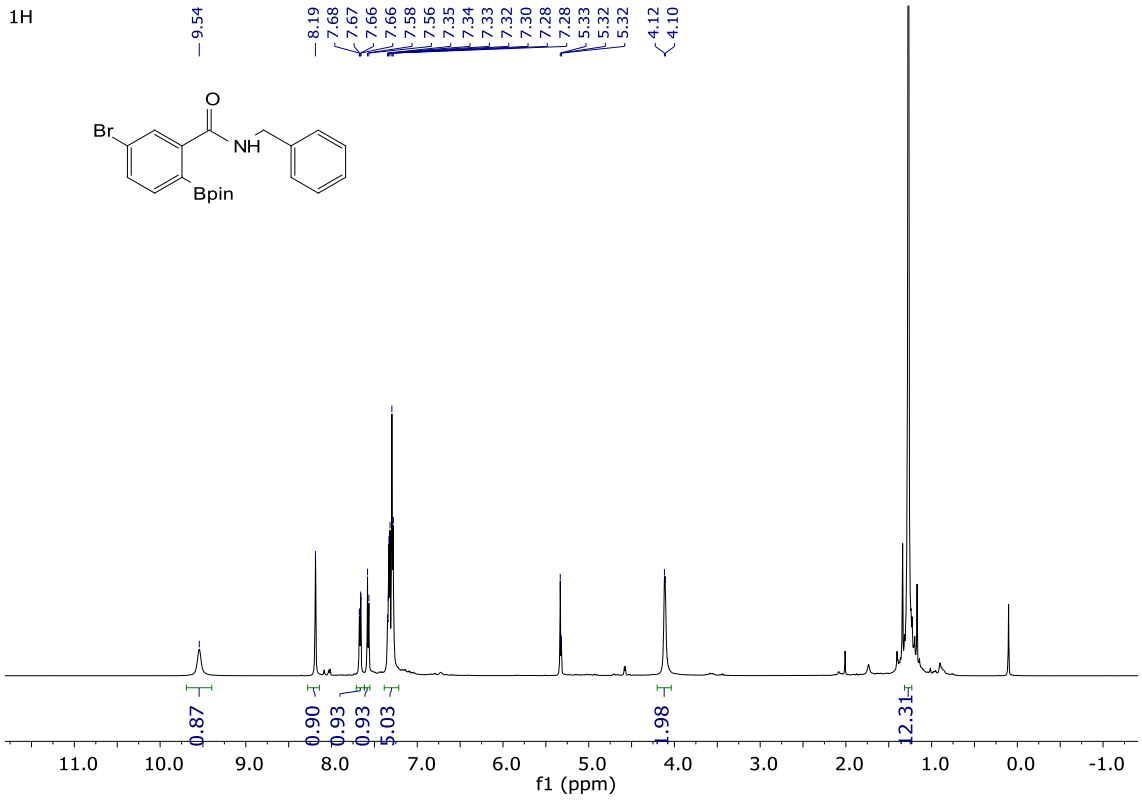


Figure S113. ^{1}H NMR spectra of borylated aromatic amides **18so**

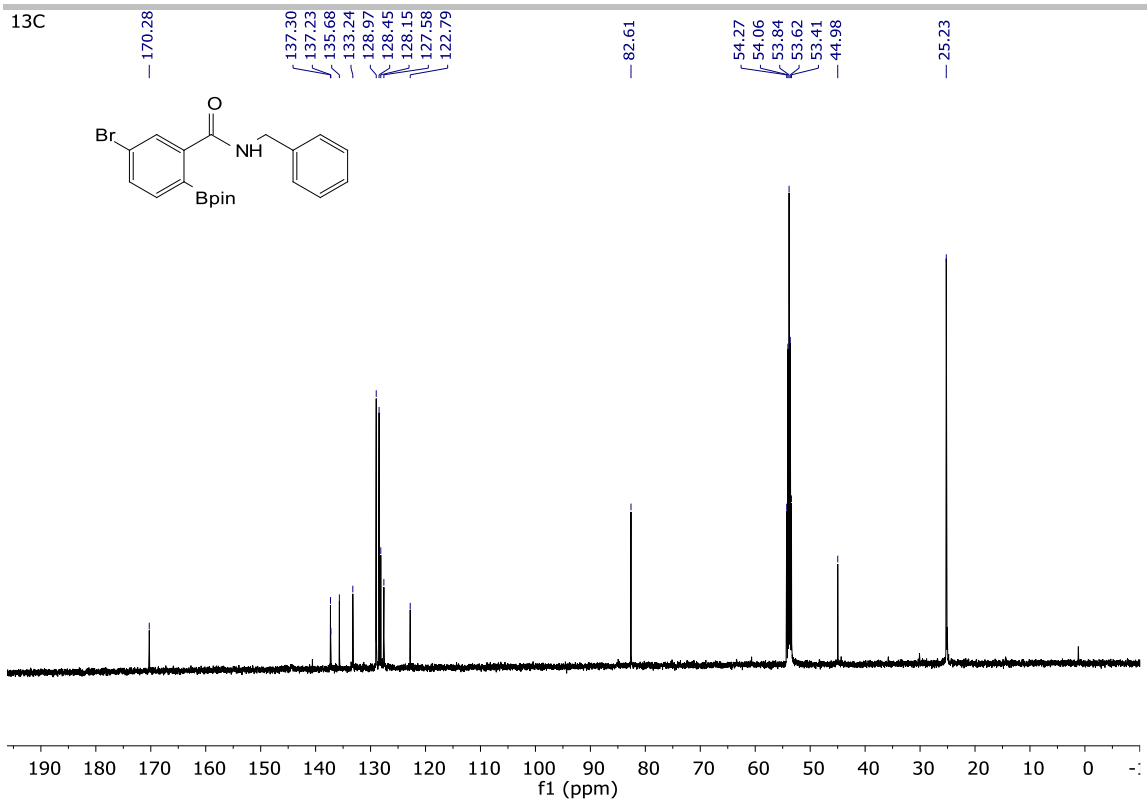


Figure S114. ^{13}C NMR spectra of borylated aromatic amides **18so**

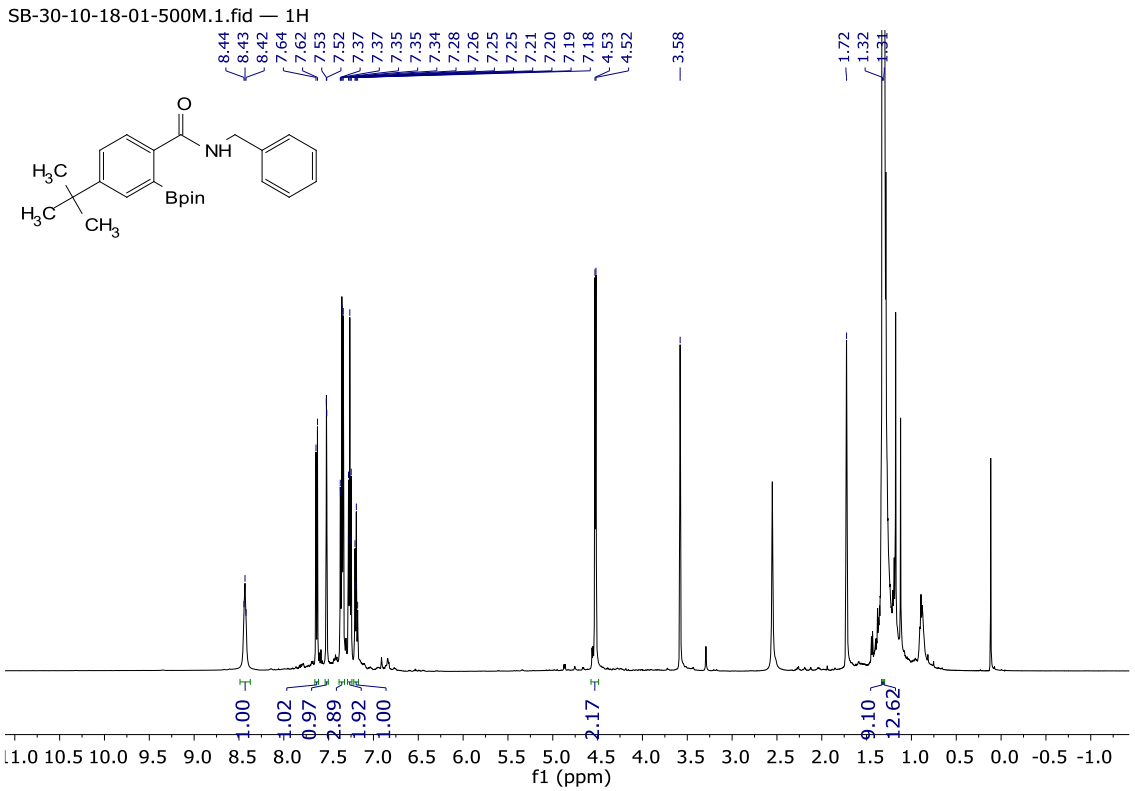


Figure S115. ^{1}H NMR spectra of borylated aromatic amide **19so**

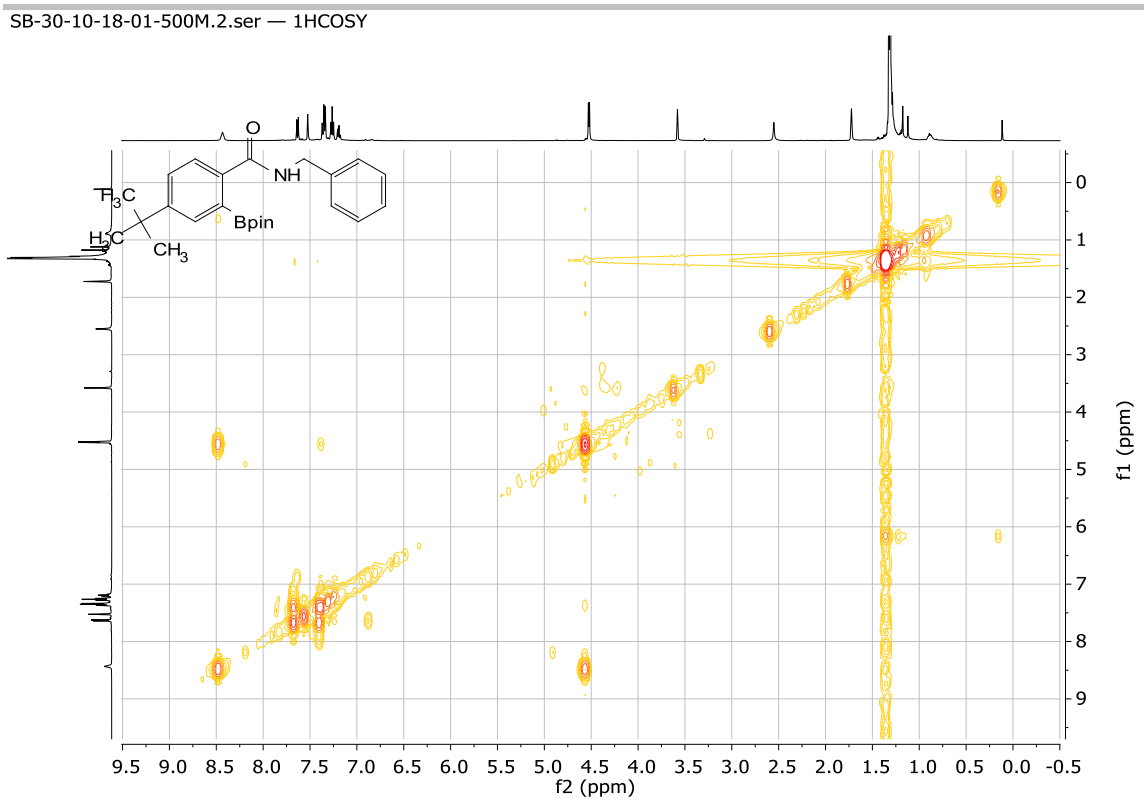


Figure S116. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **19so**

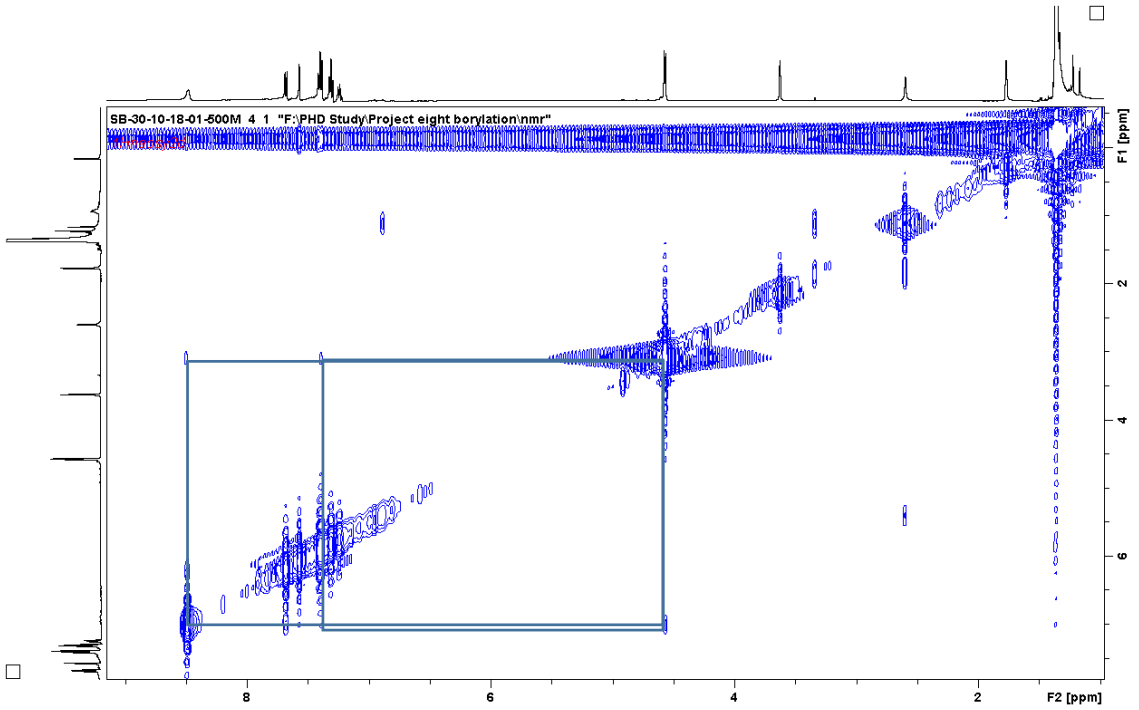


Figure S117. ^{1}H-^{1}H NOESY NMR spectra of borylated aromatic amide **19so**

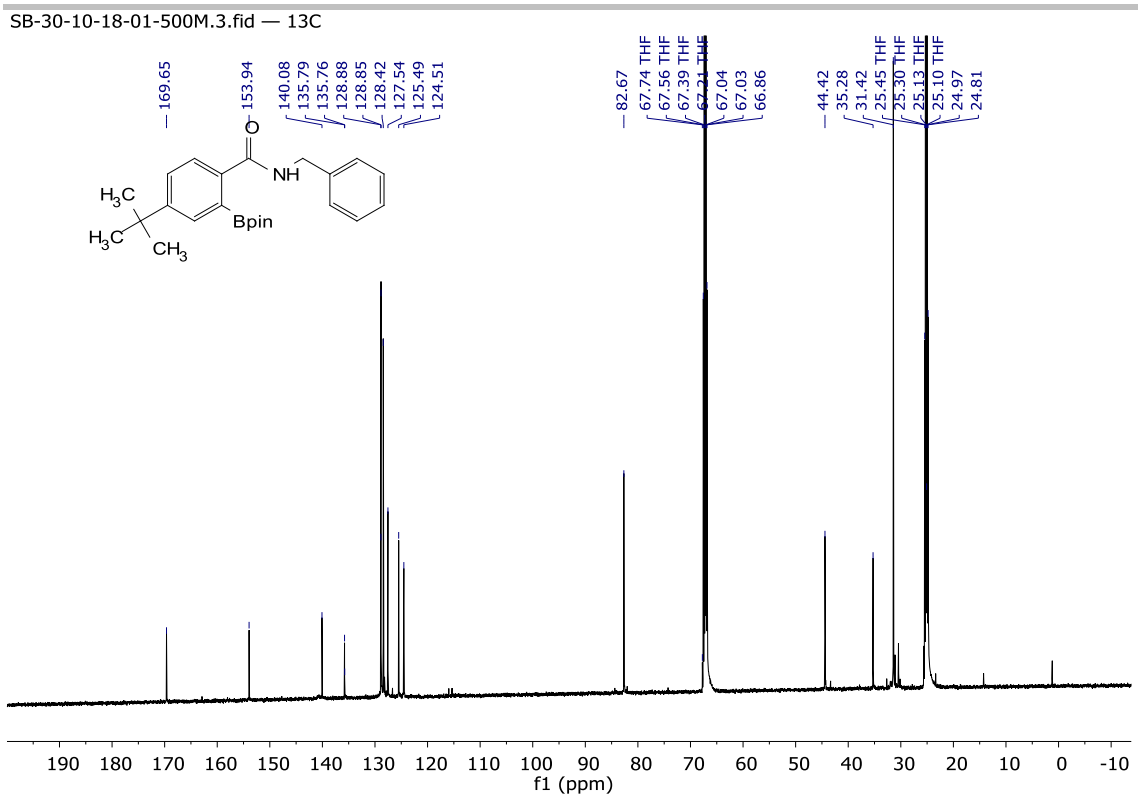


Figure S118. ^{13}C NMR spectra of borylated aromatic amide **19so**

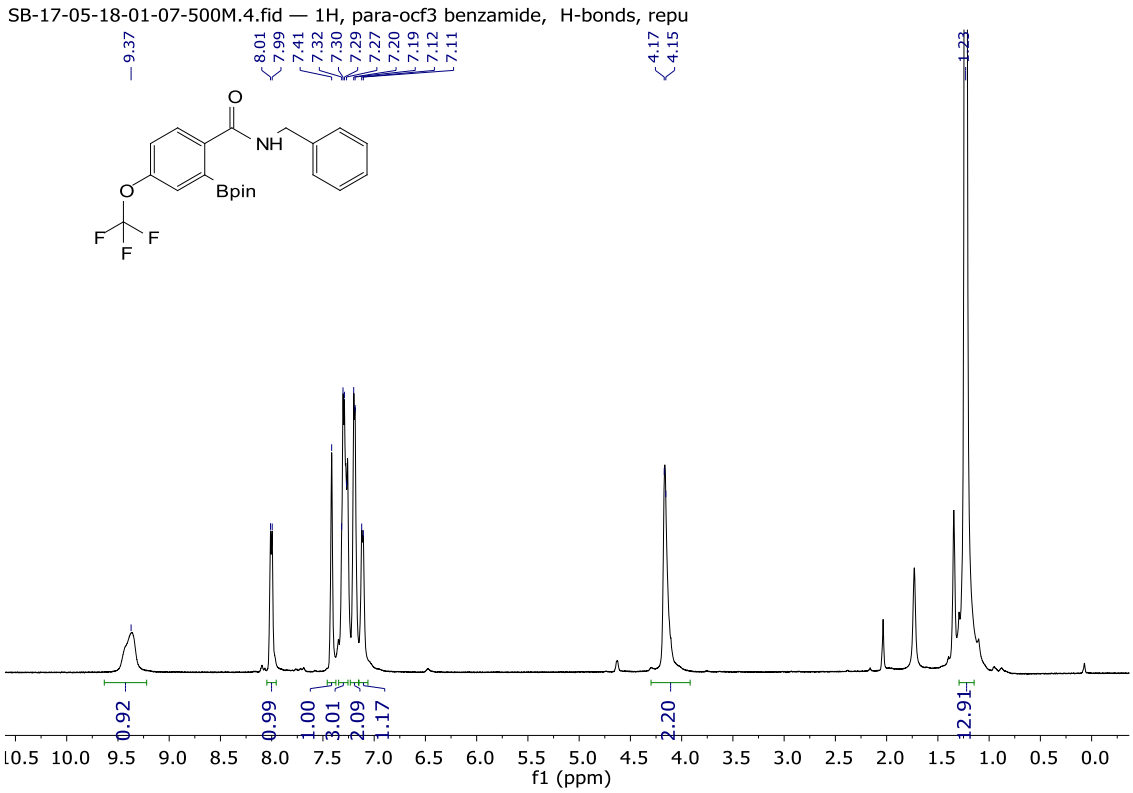


Figure S119. $^{1}HNMR$ spectra of borylated aromatic amide **20so**

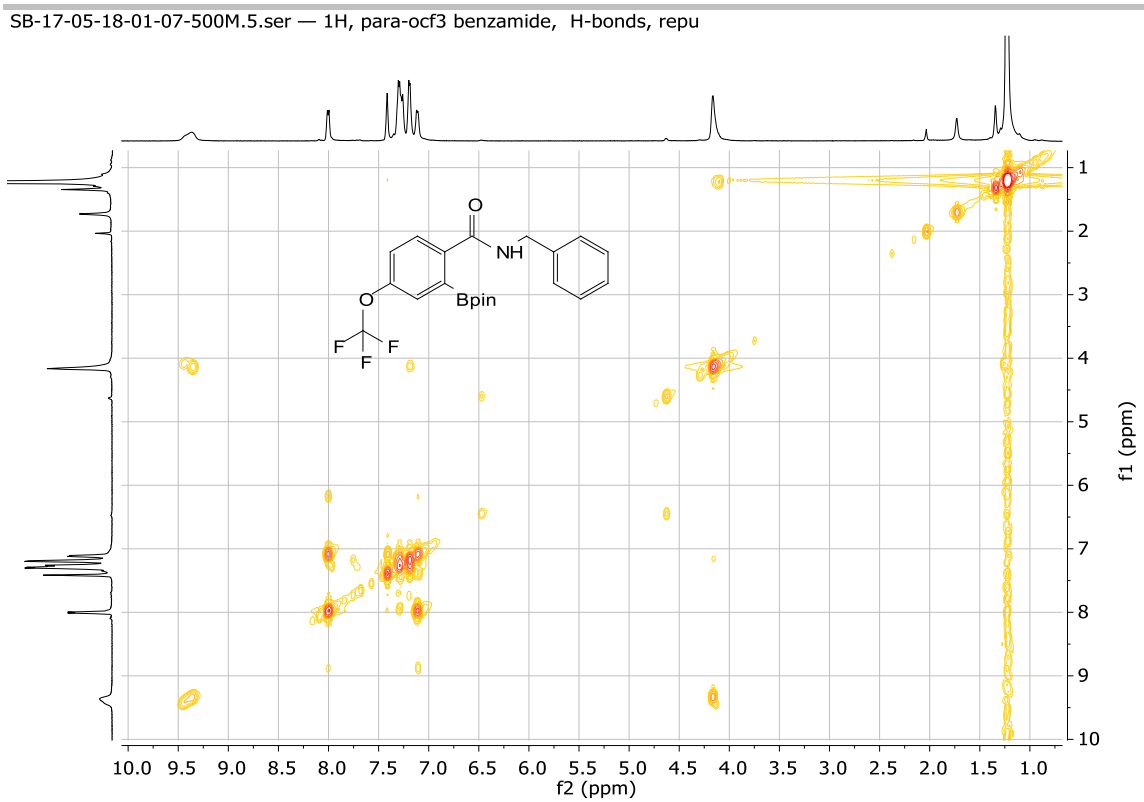


Figure S120. ^{1}H-^{1}H COSYNMR spectra of borylated aromatic amide **20so**

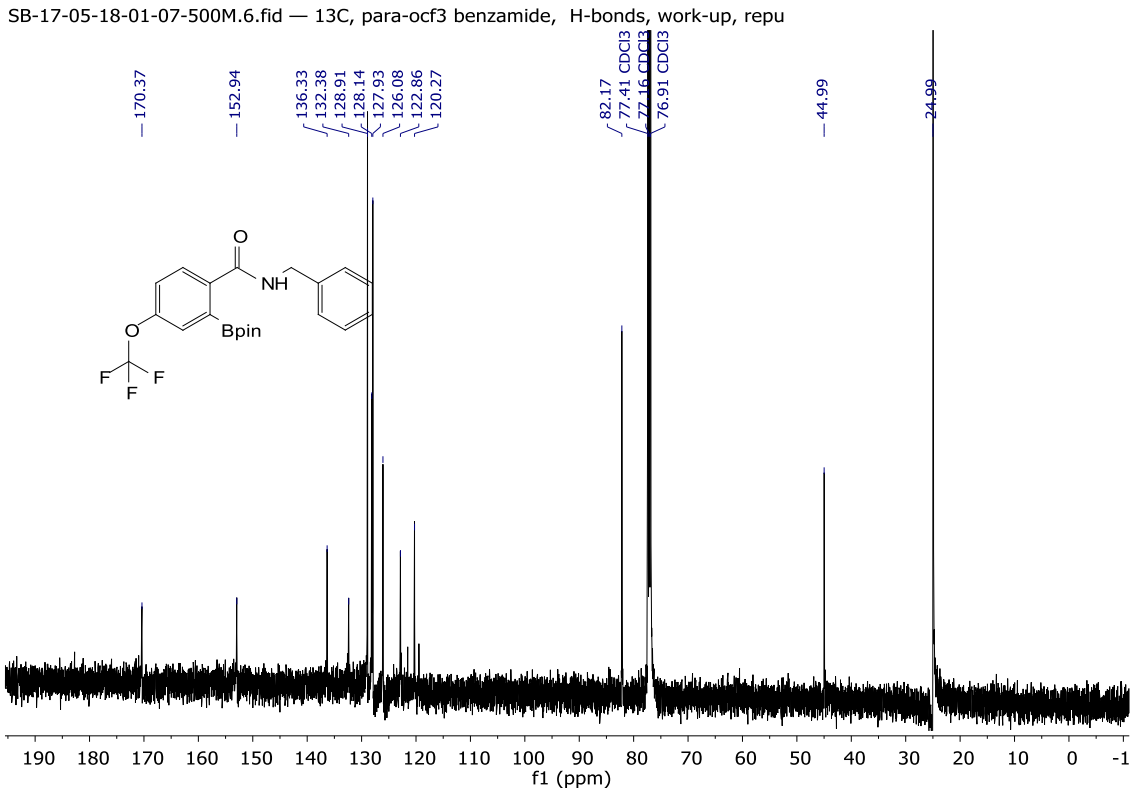


Figure S121. ^{13}C NMR spectra of borylated aromatic amide **20so**

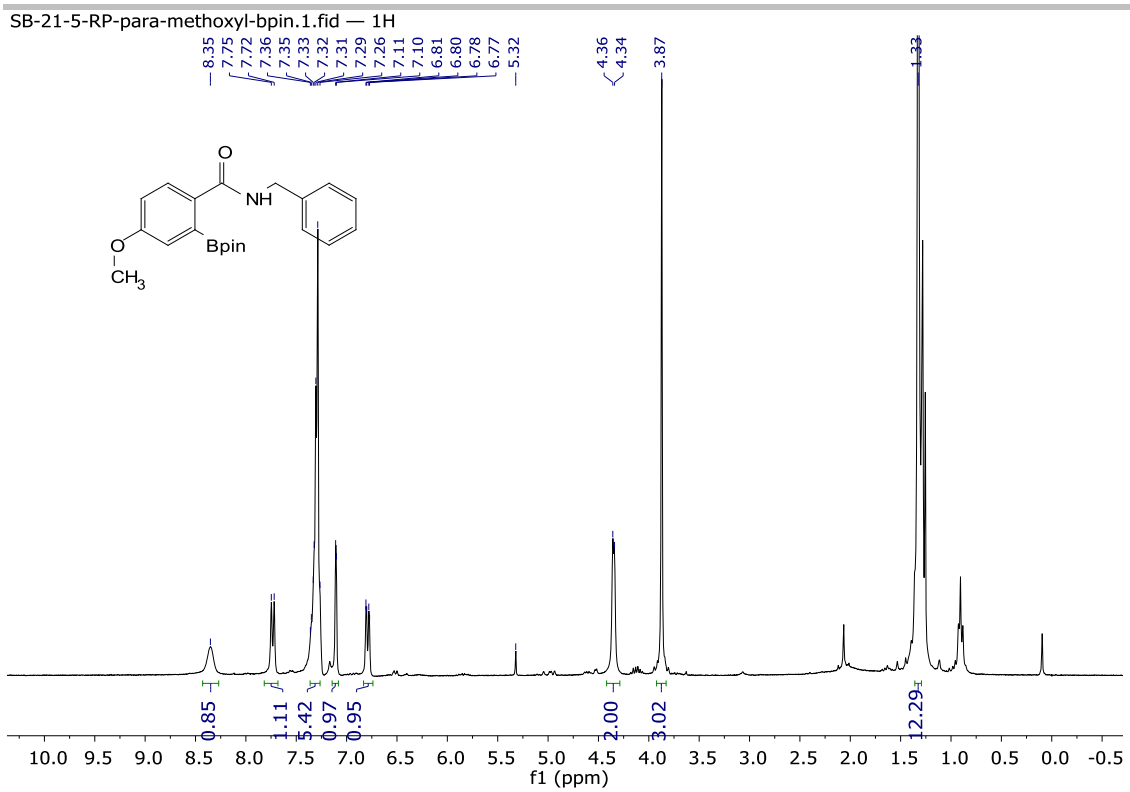


Figure S122. ^{1}H NMR spectra of borylated aromatic amide **21so**

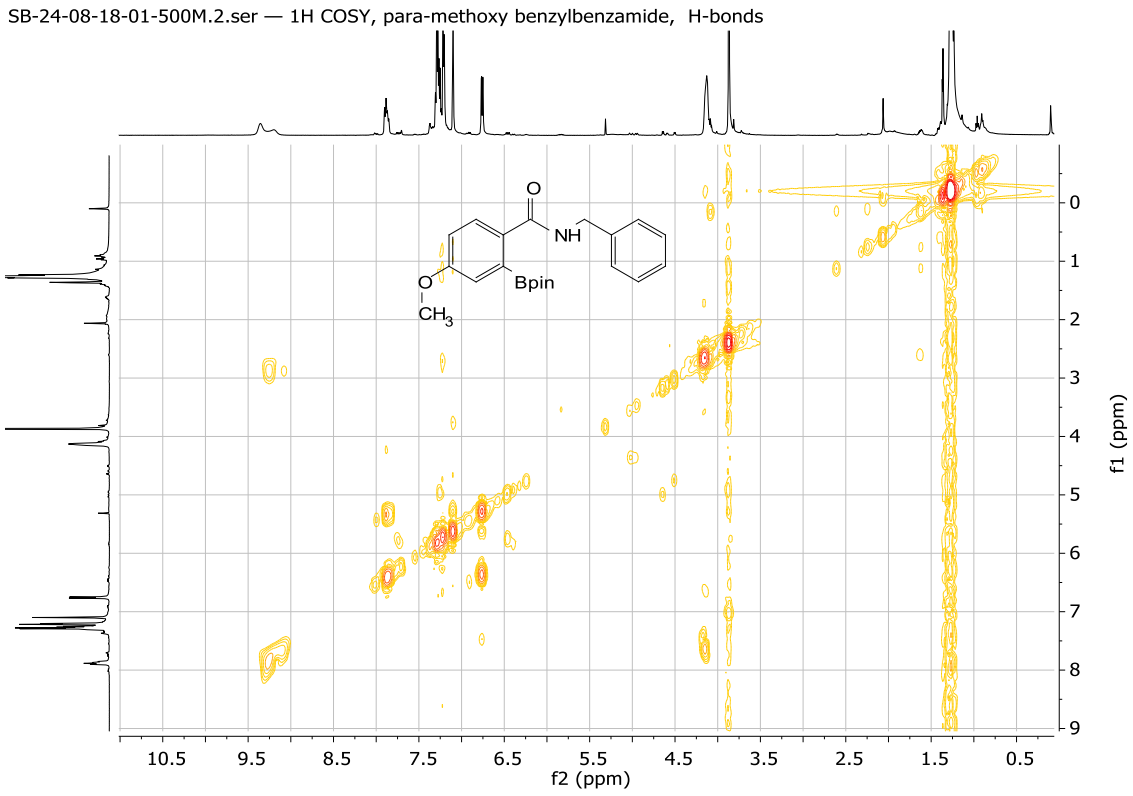


Figure S123. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **21so**

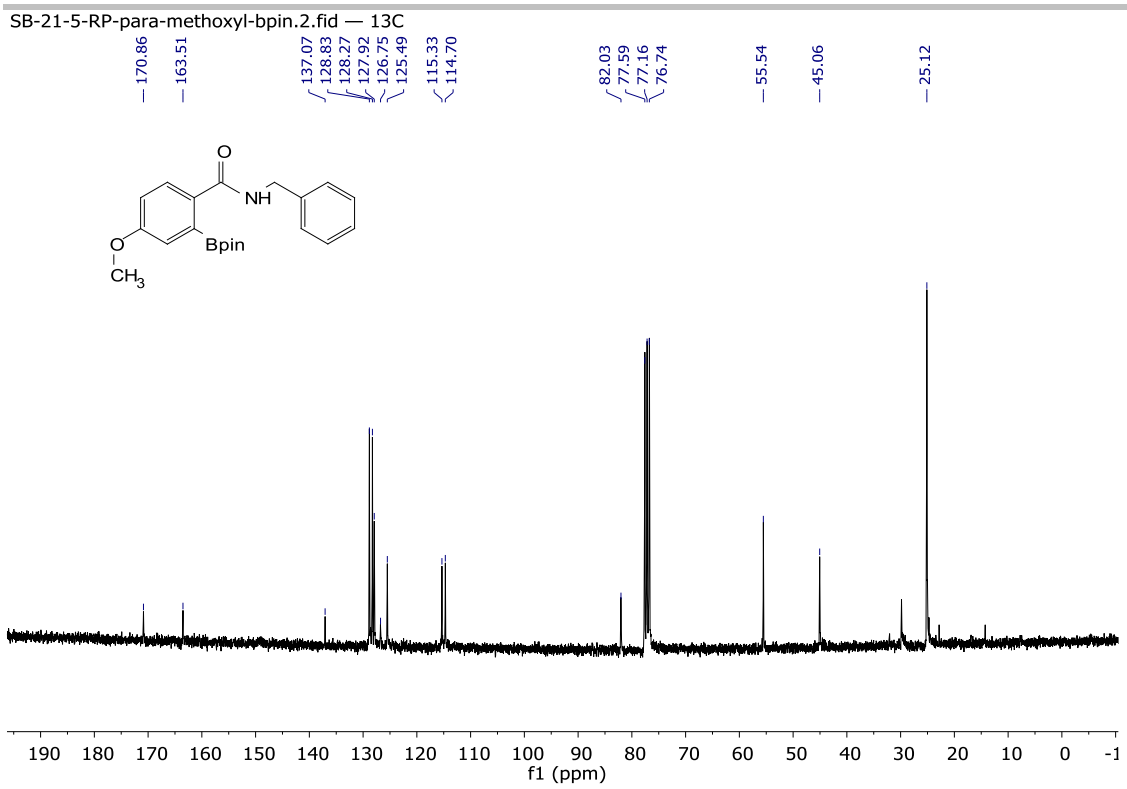


Figure S124. ^{13}C NMR spectra of borylated aromatic amide **21so**

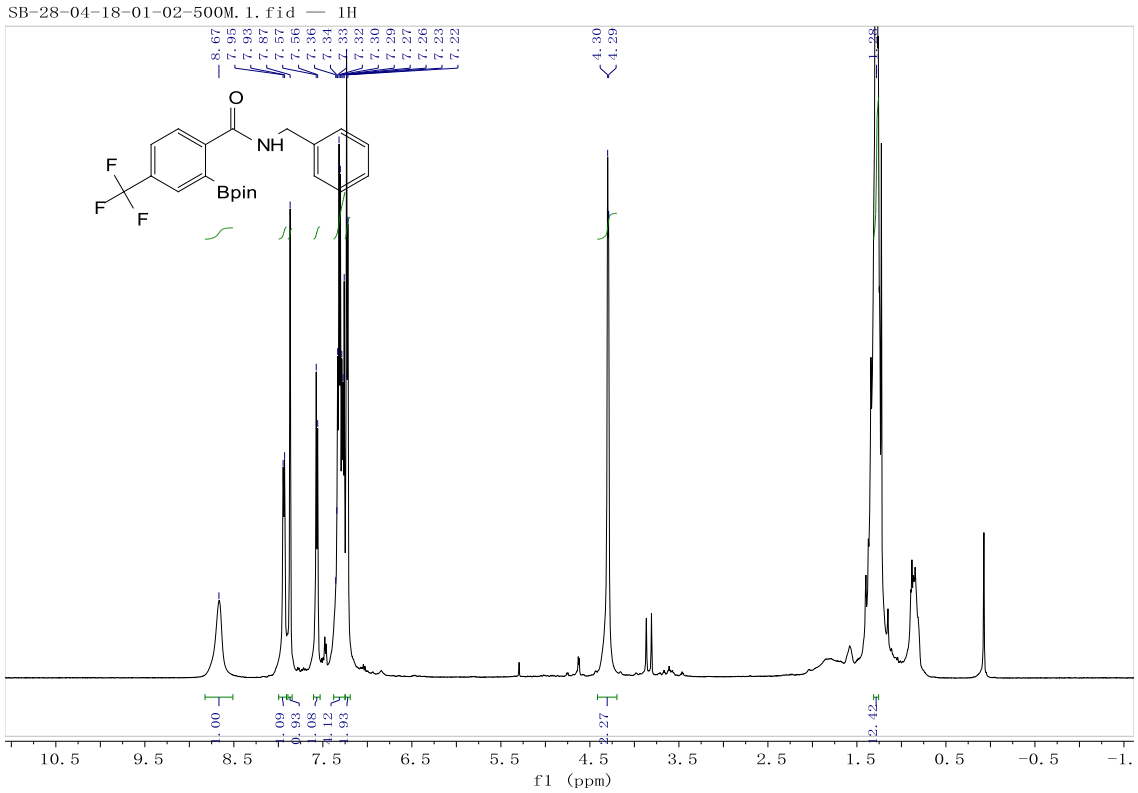


Figure S125. ^{1}H NMR spectra of borylated aromatic amide **22so**

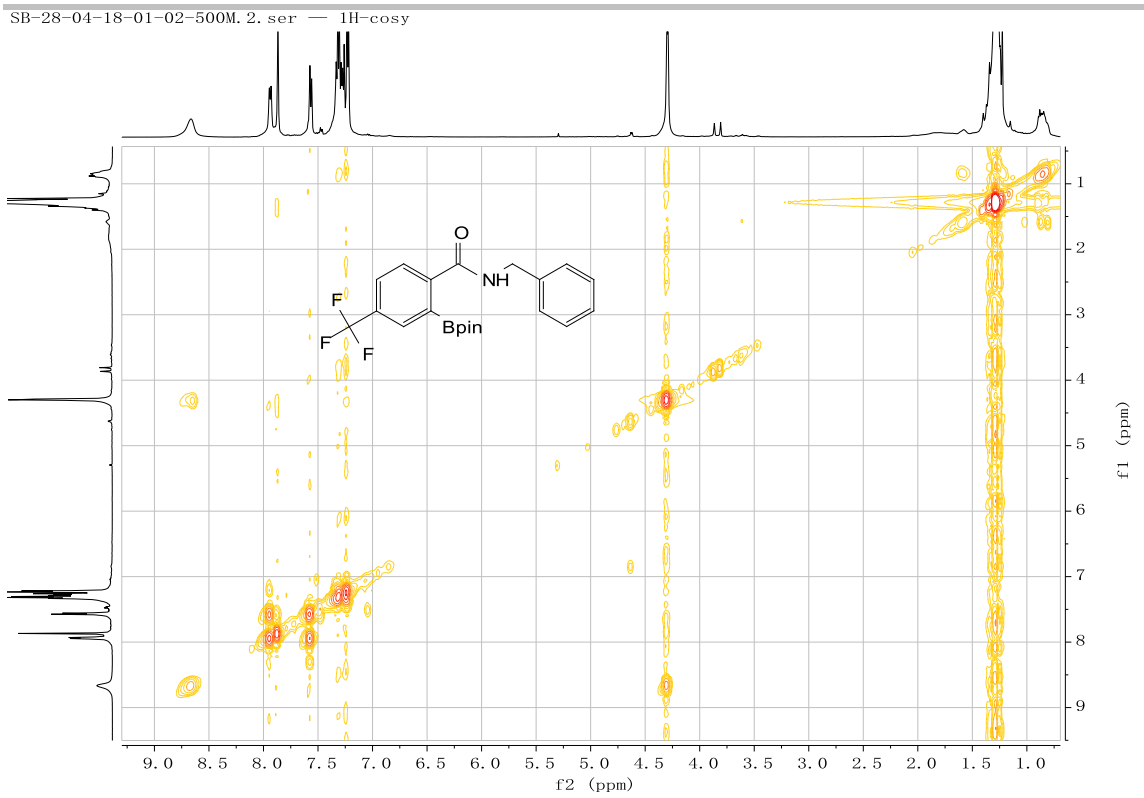


Figure S126. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **22so**

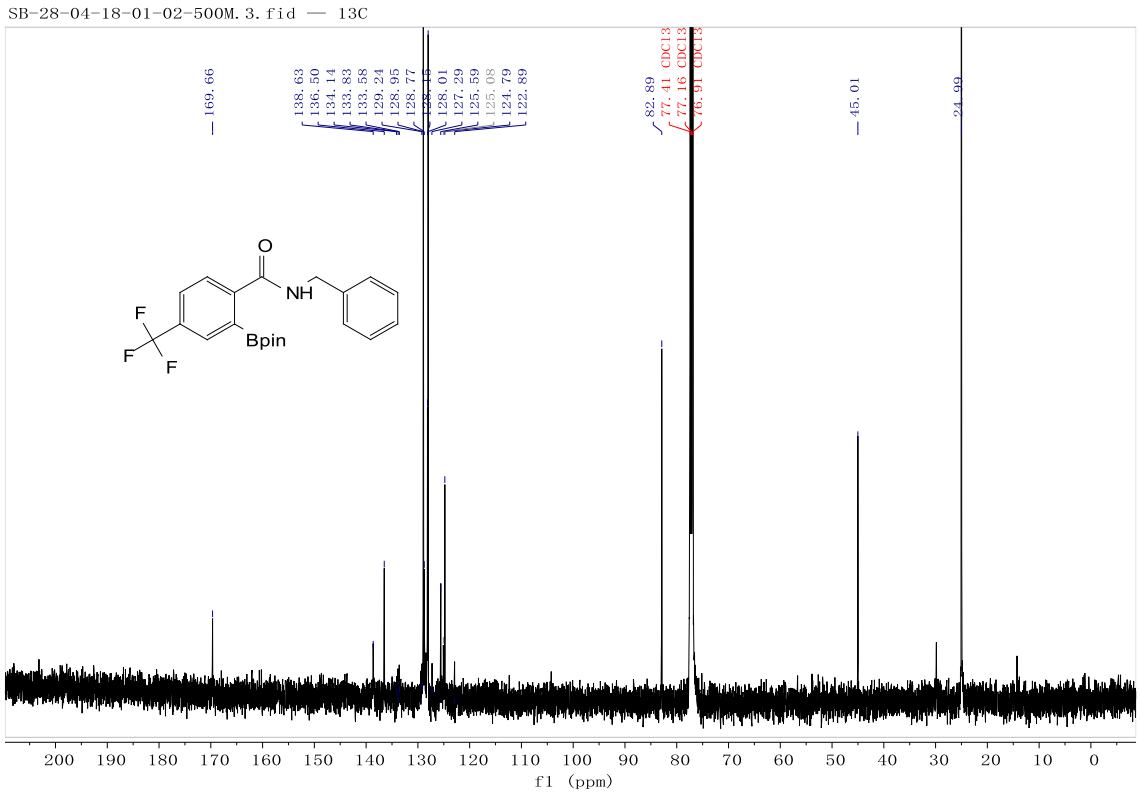


Figure S127. ^{13}C NMR spectra of borylated aromatic amide **22so**

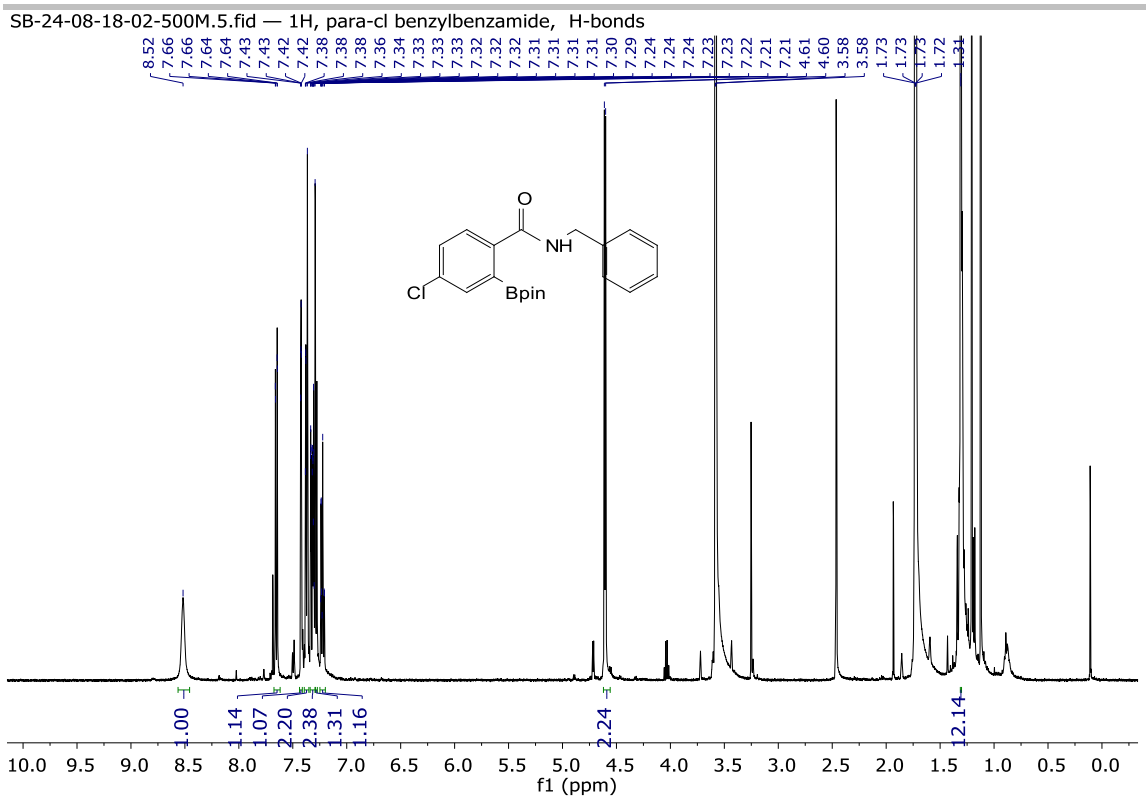


Figure S128. ^{1}H NMR spectra of borylated aromatic amide **23so**

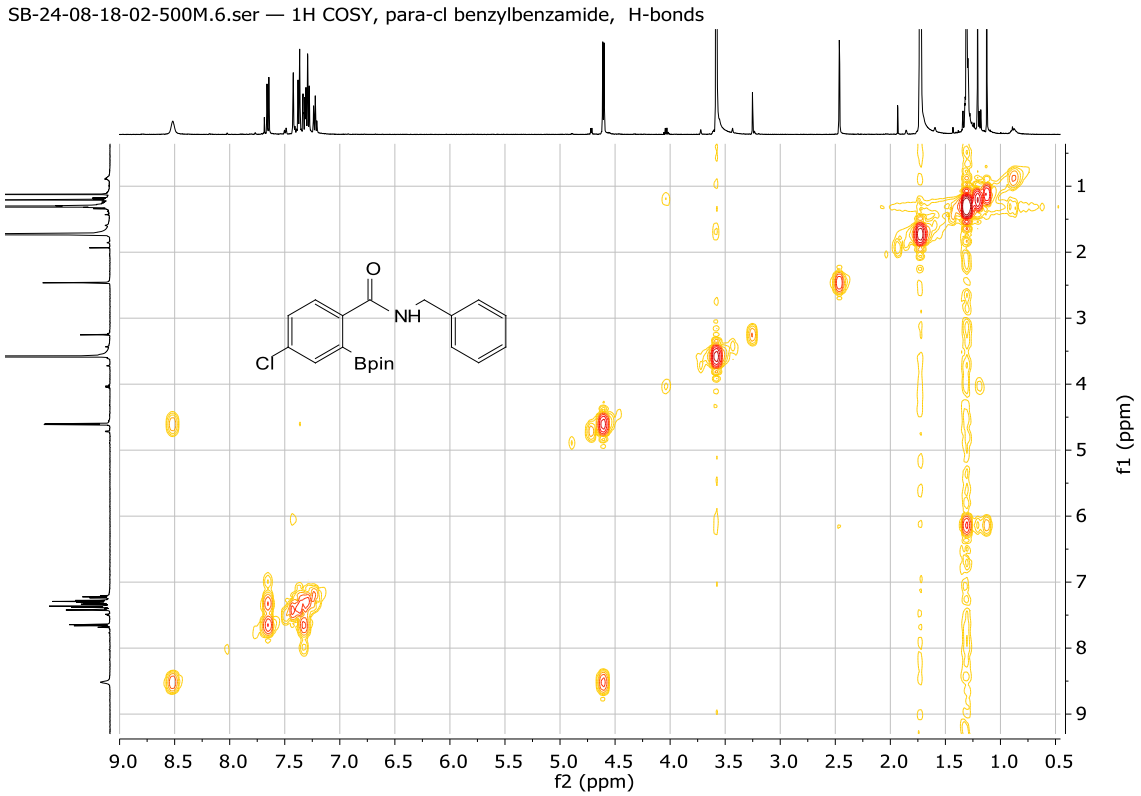


Figure S129. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **23so**

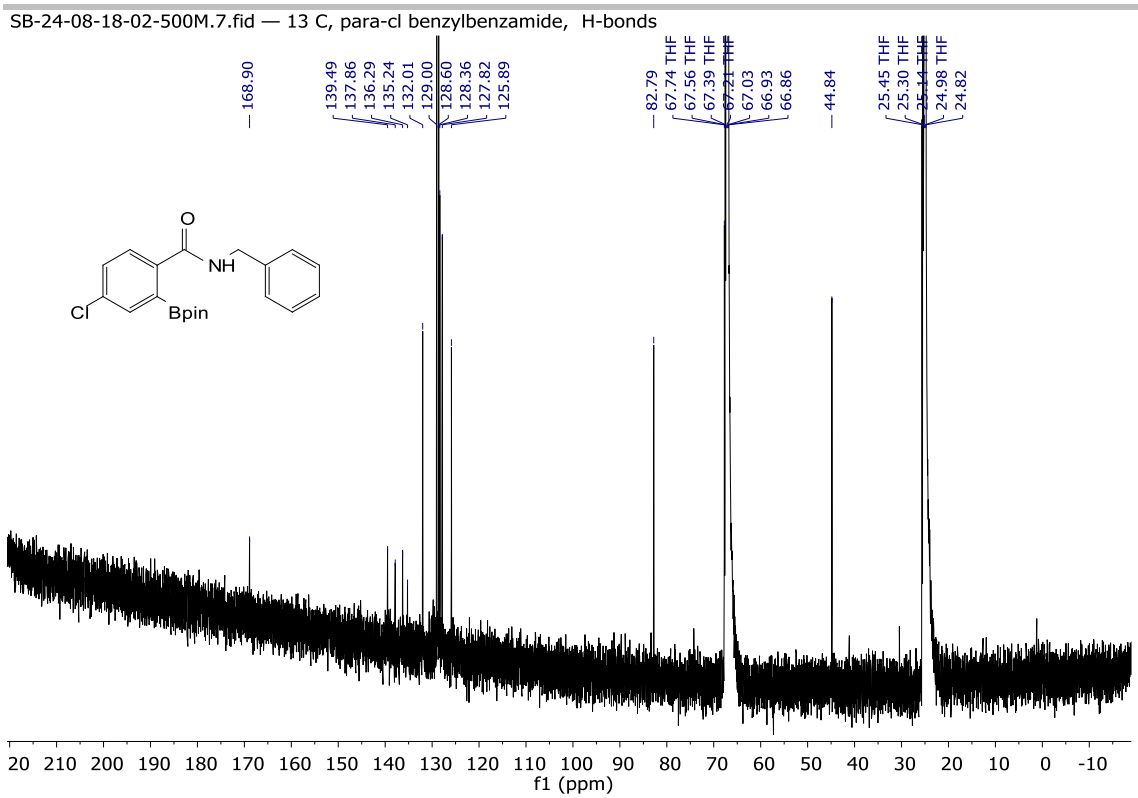


Figure S130. ^{13}C NMR spectra of borylated aromatic amide **23so**

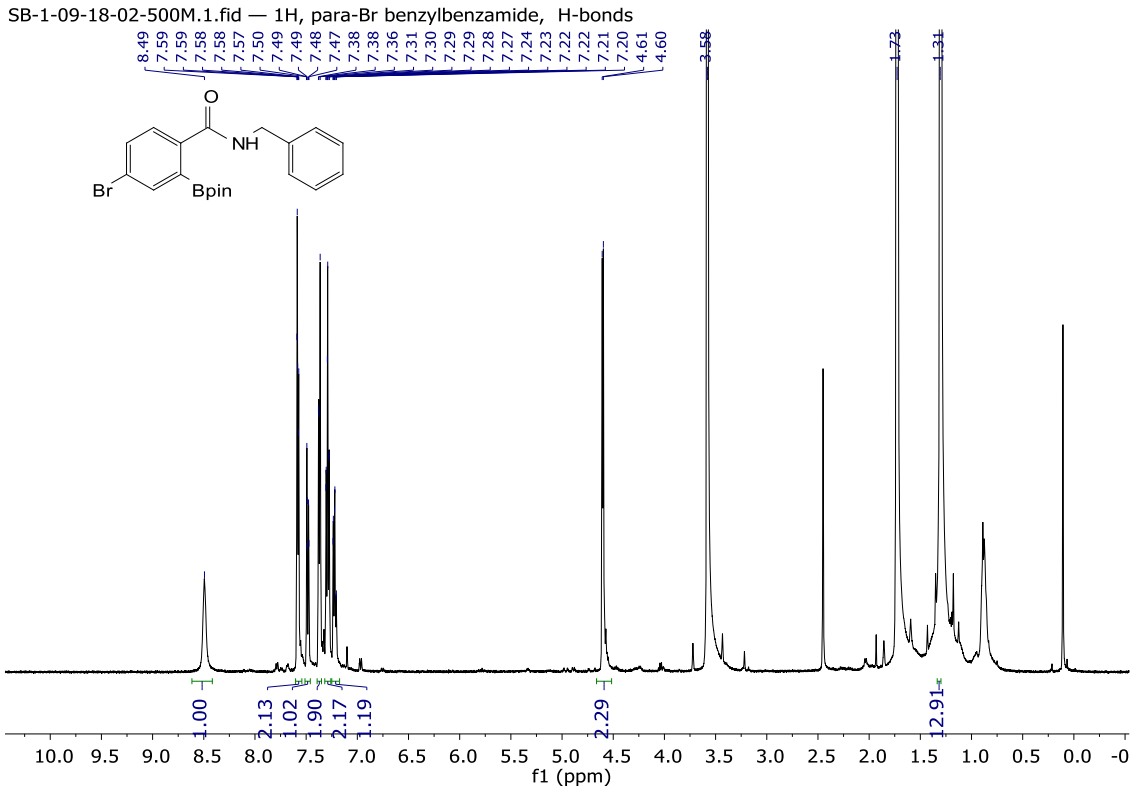


Figure S131. ^{1}H NMR spectra of borylated aromatic amide **24so**

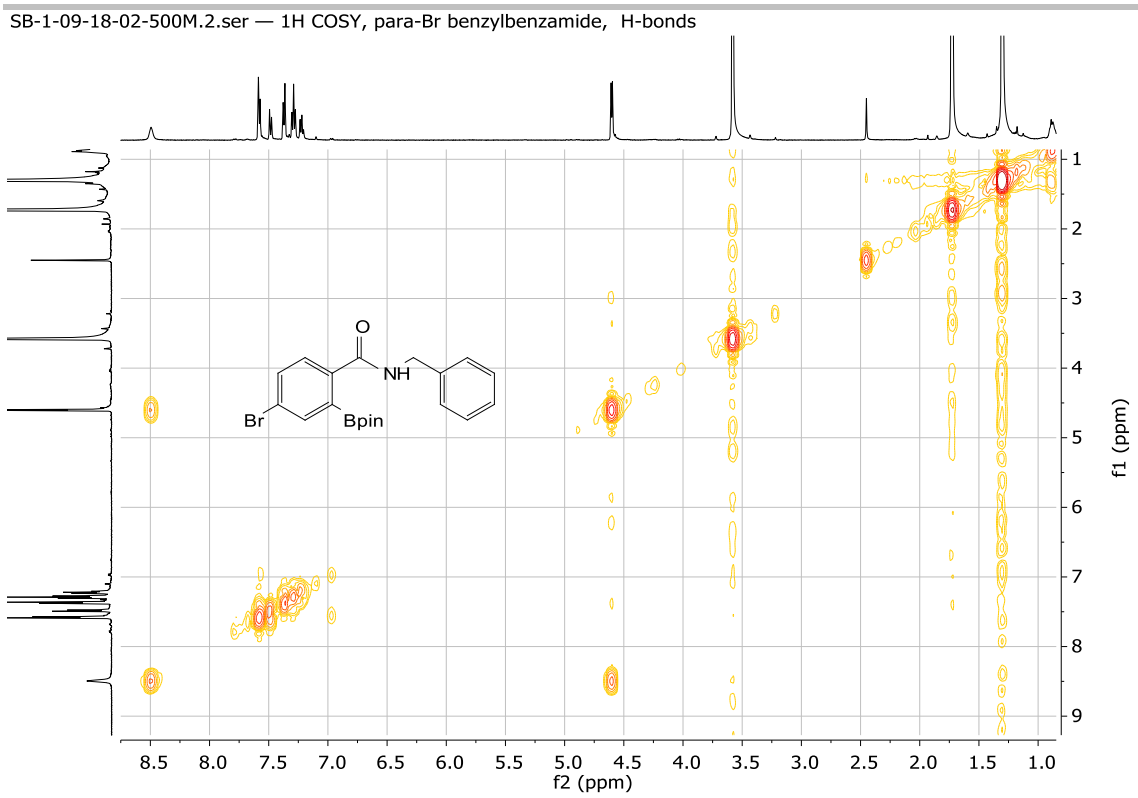


Figure S132. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amide **24so**

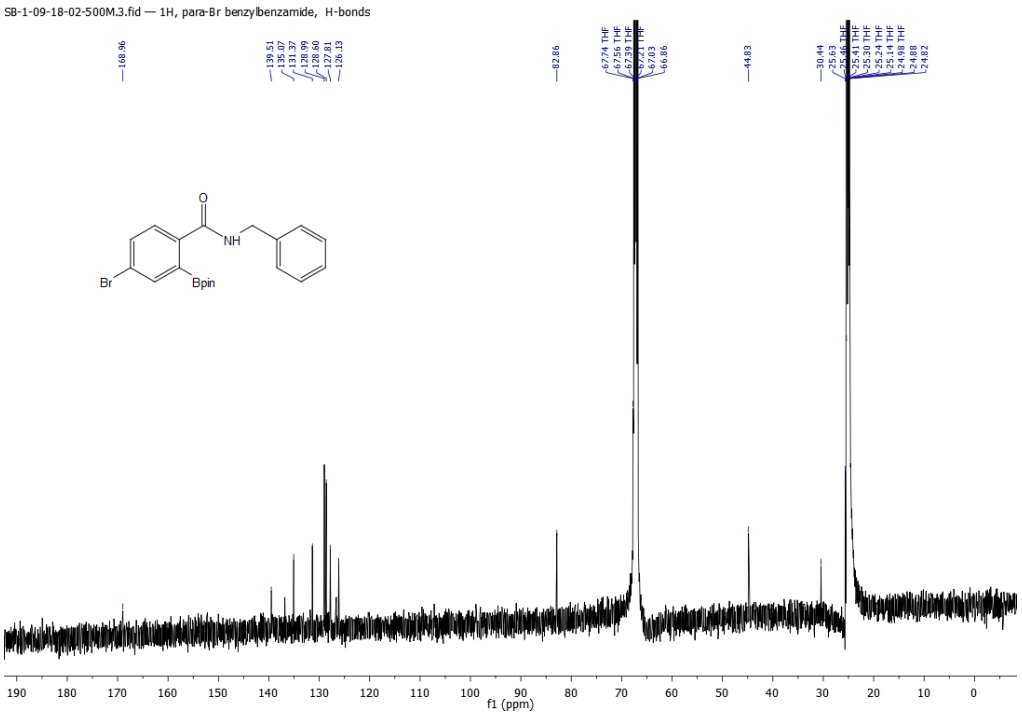


Figure S133. ^{13}C NMR spectra of borylated aromatic amide **24so**

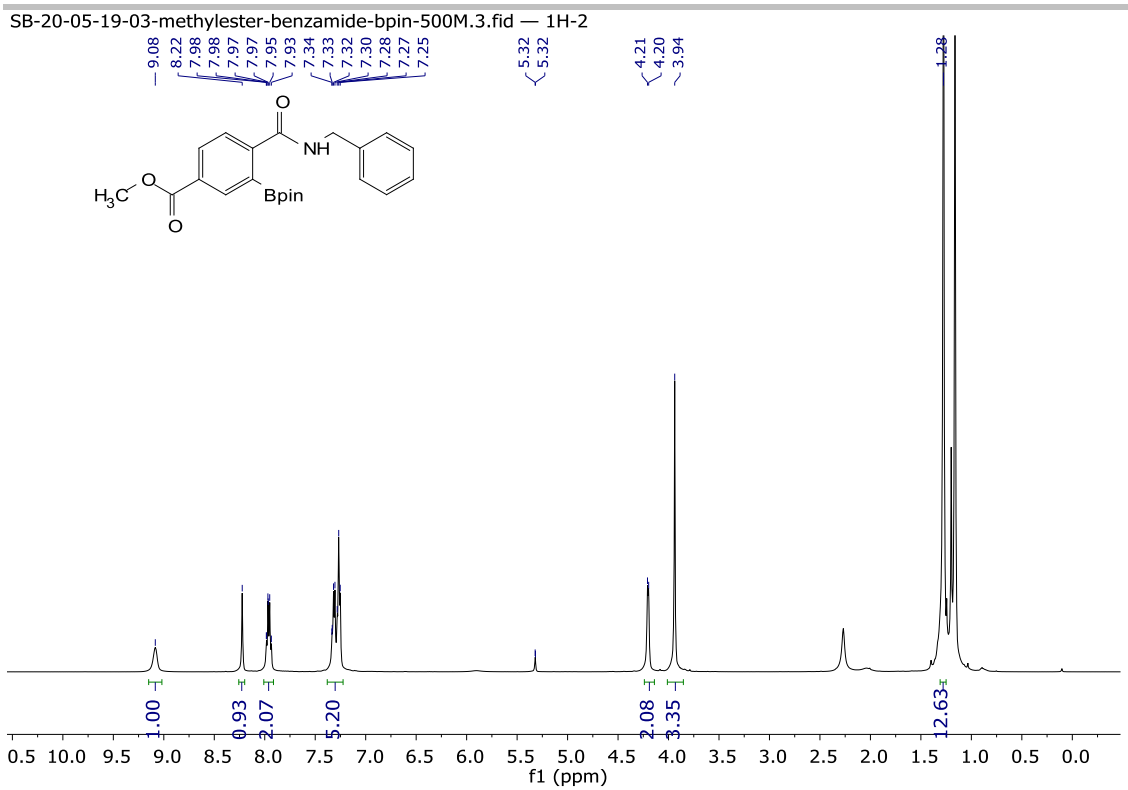


Figure S134. ^{1}H NMR spectra of borylated aromatic amide **25so**

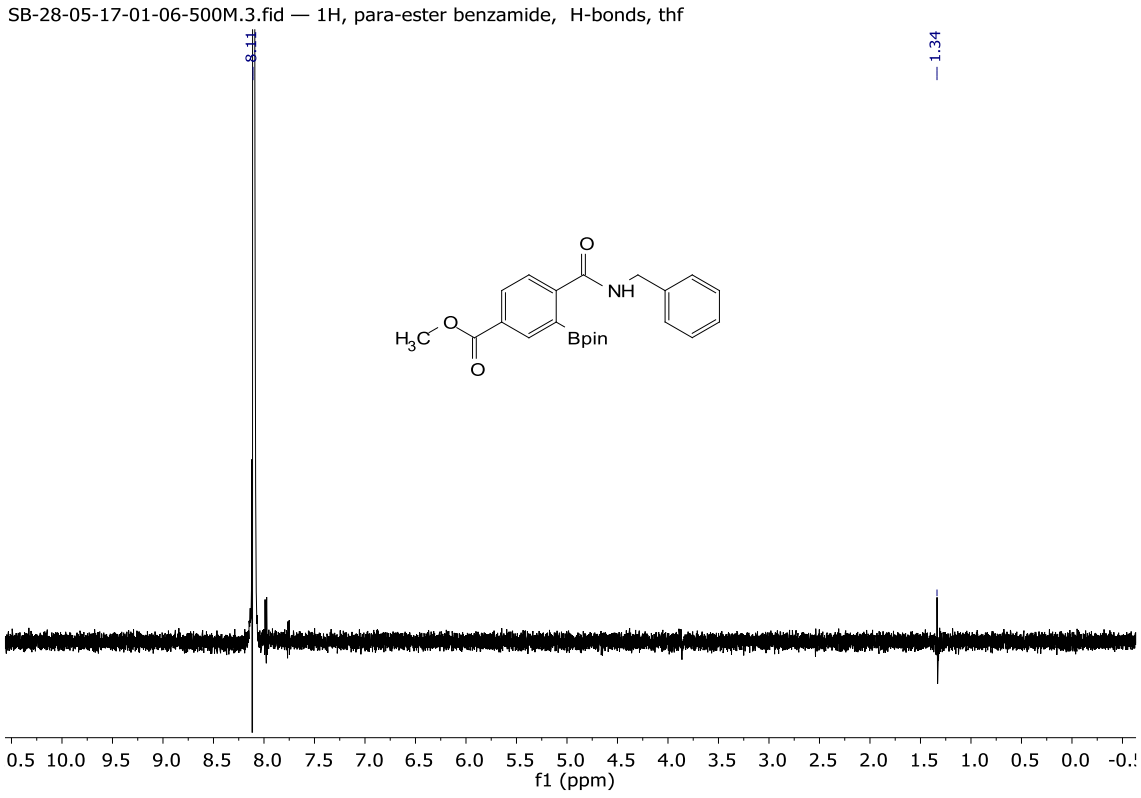


Figure S135. ^{1}H-^{1}H 1D NOESY NMR spectra of borylated aromatic amide **25so**

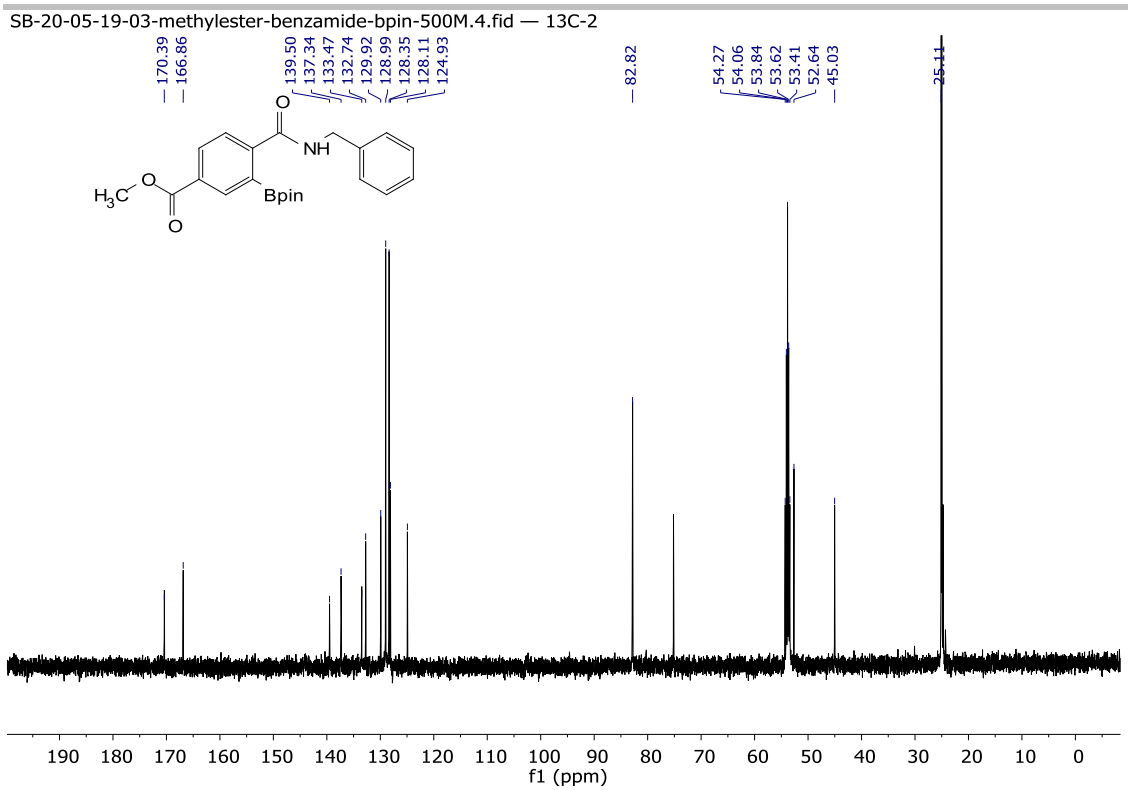


Figure S136. ^{13}C NMR spectra of borylated aromatic amide **25so**

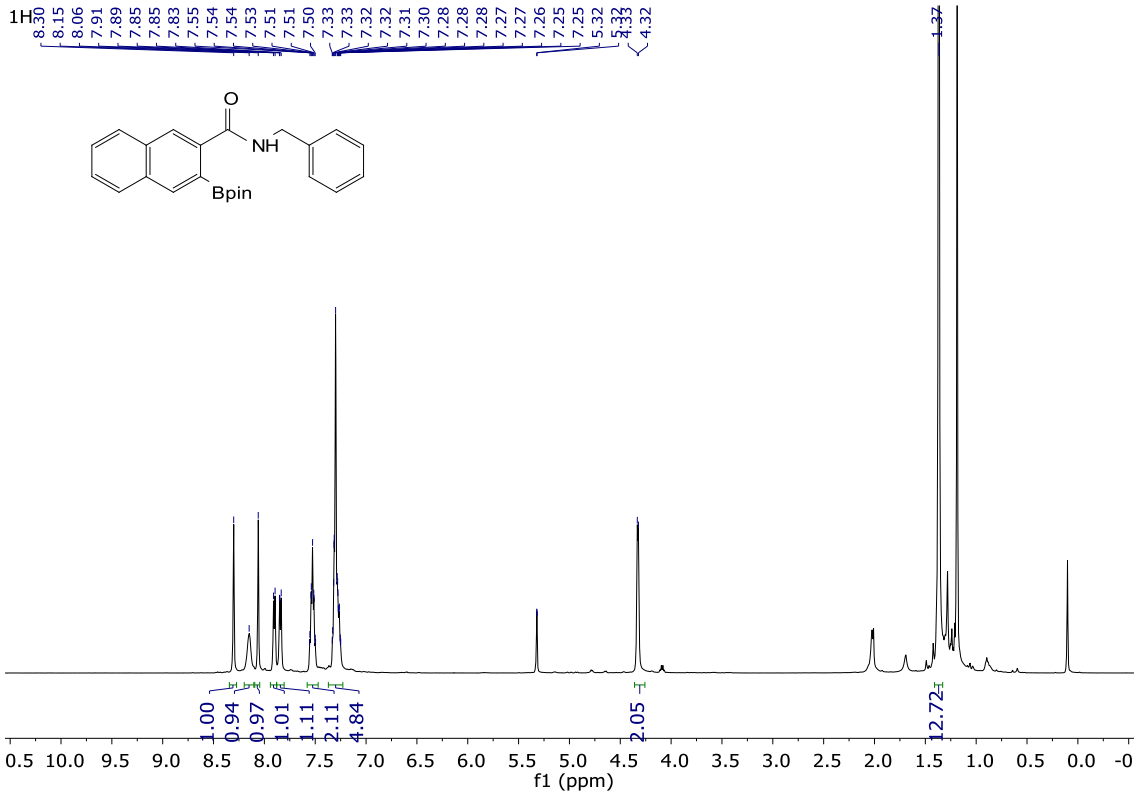


Figure S137. ^{1}H NMR spectra of borylated aromatic amides **26so**

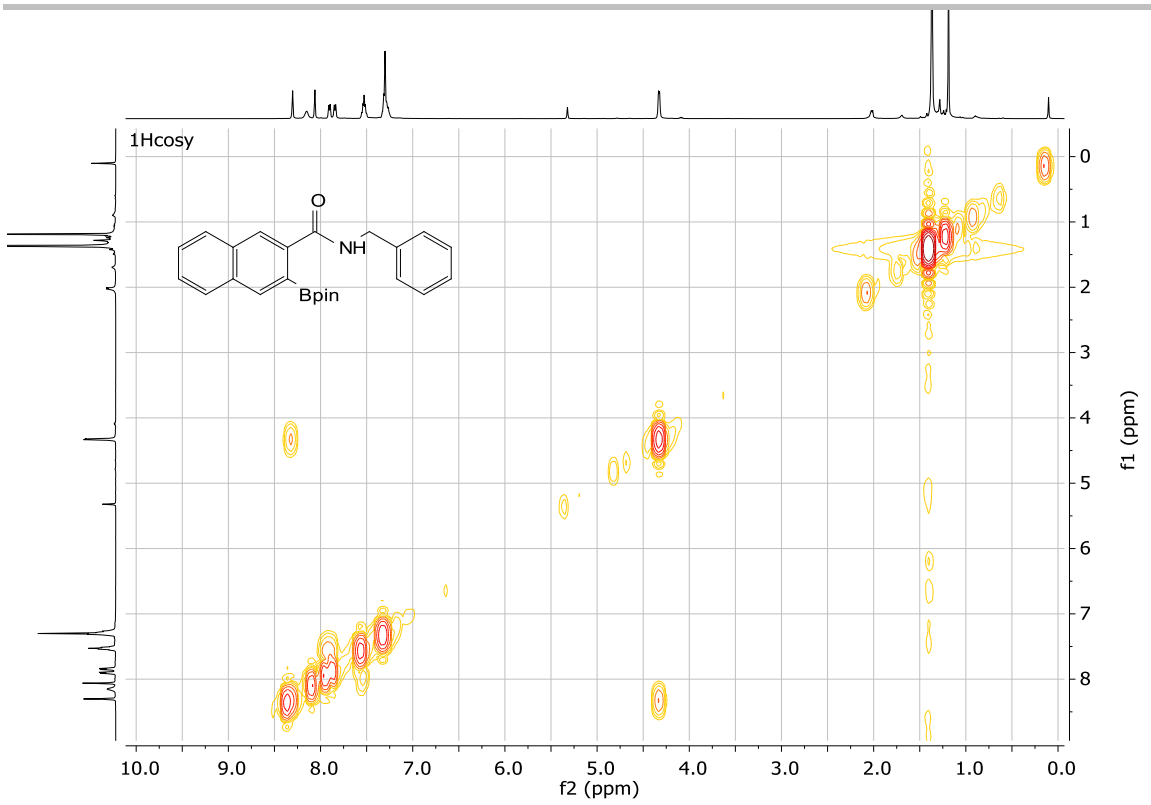


Figure S138. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amides **26so**

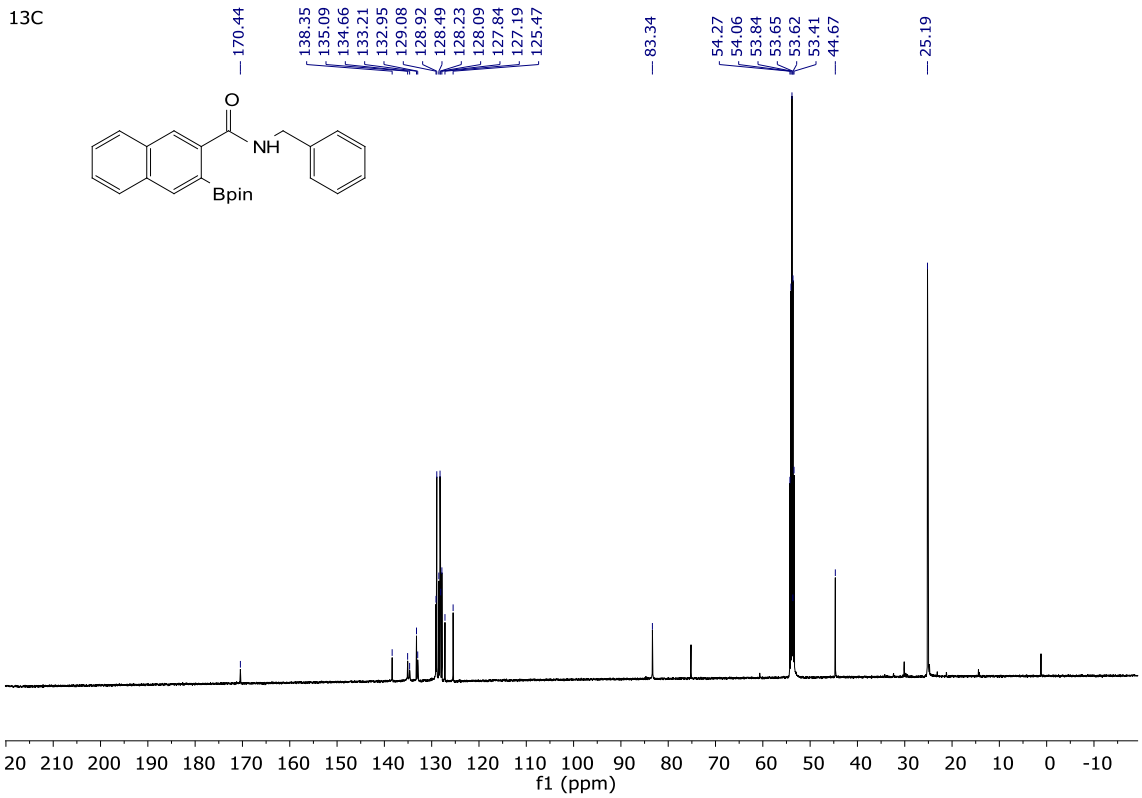


Figure S139. ^{13}C NMR spectra of borylated aromatic amides **26so**

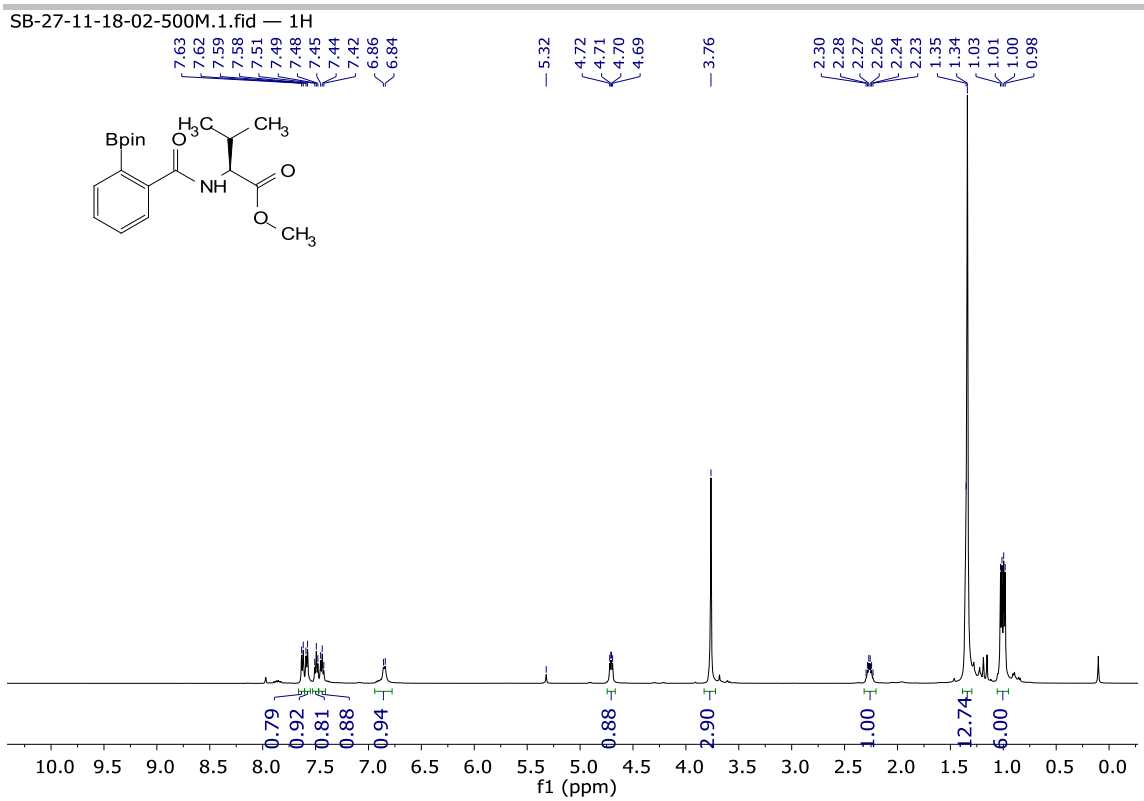


Figure S140. ^{1}H NMR spectra of borylated aromatic amides **27so**

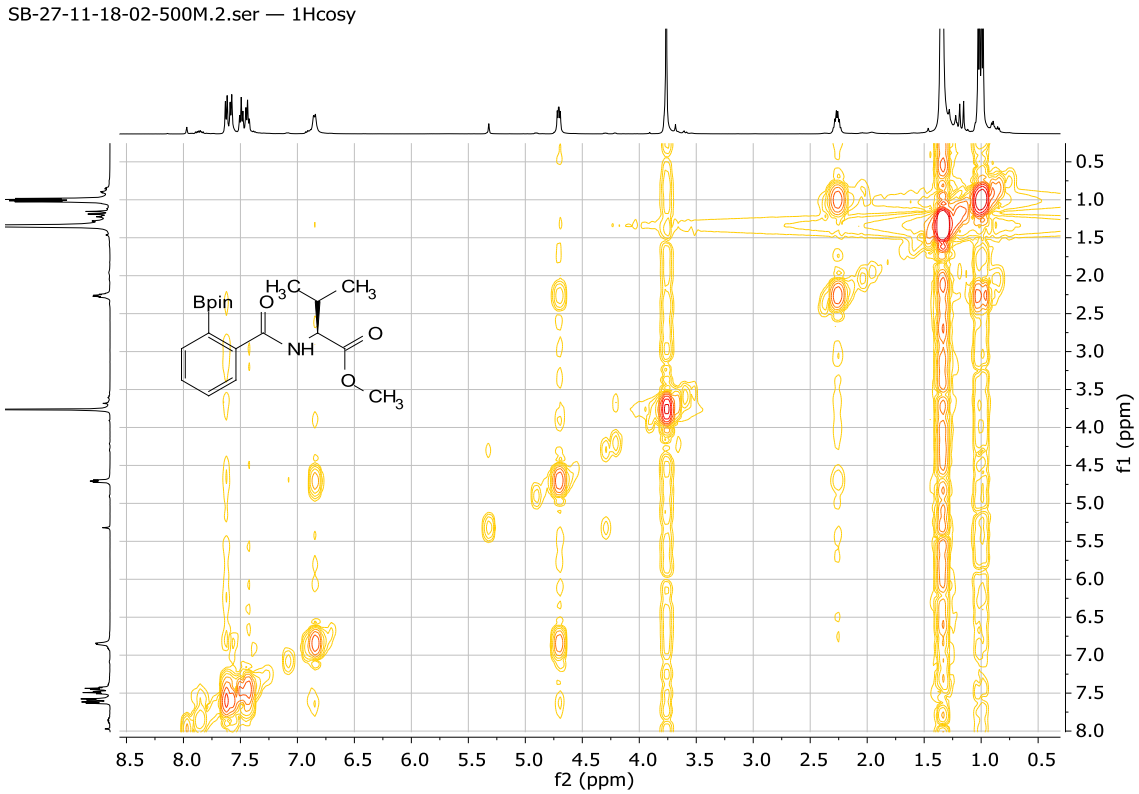


Figure S141. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amides **27so**

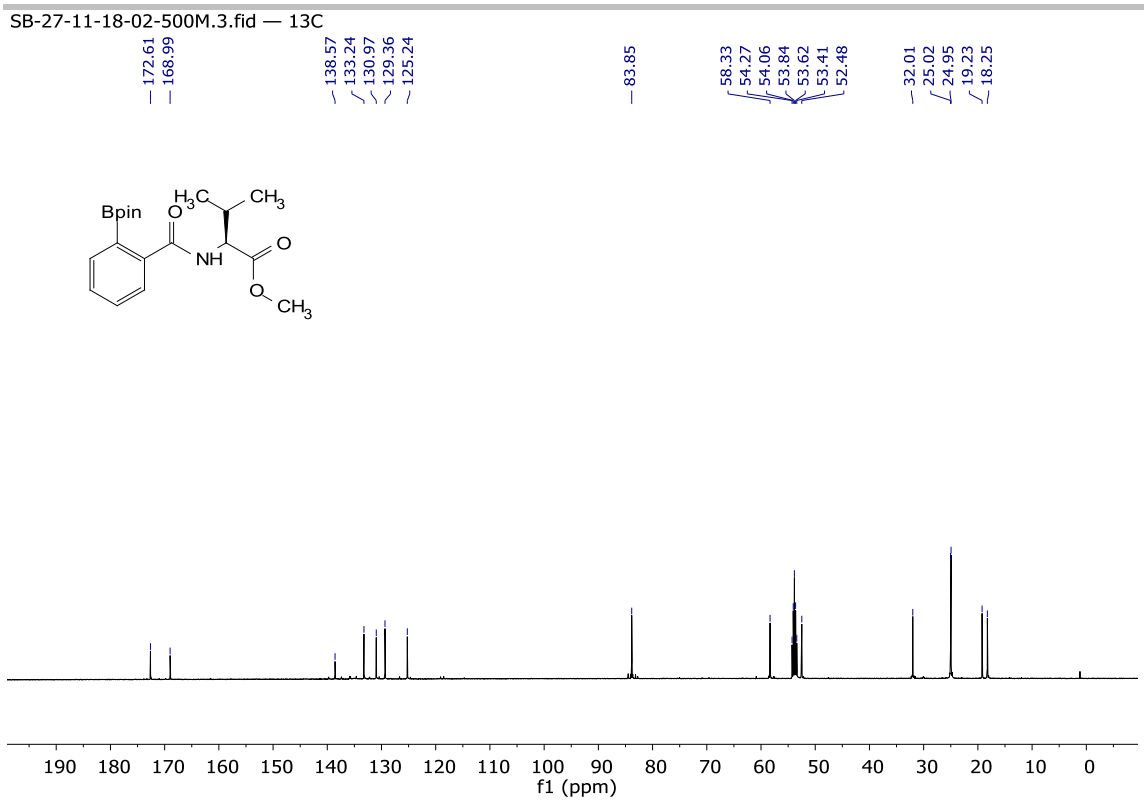


Figure S142. ^{13}C NMR spectra of borylated aromatic amides **27so**

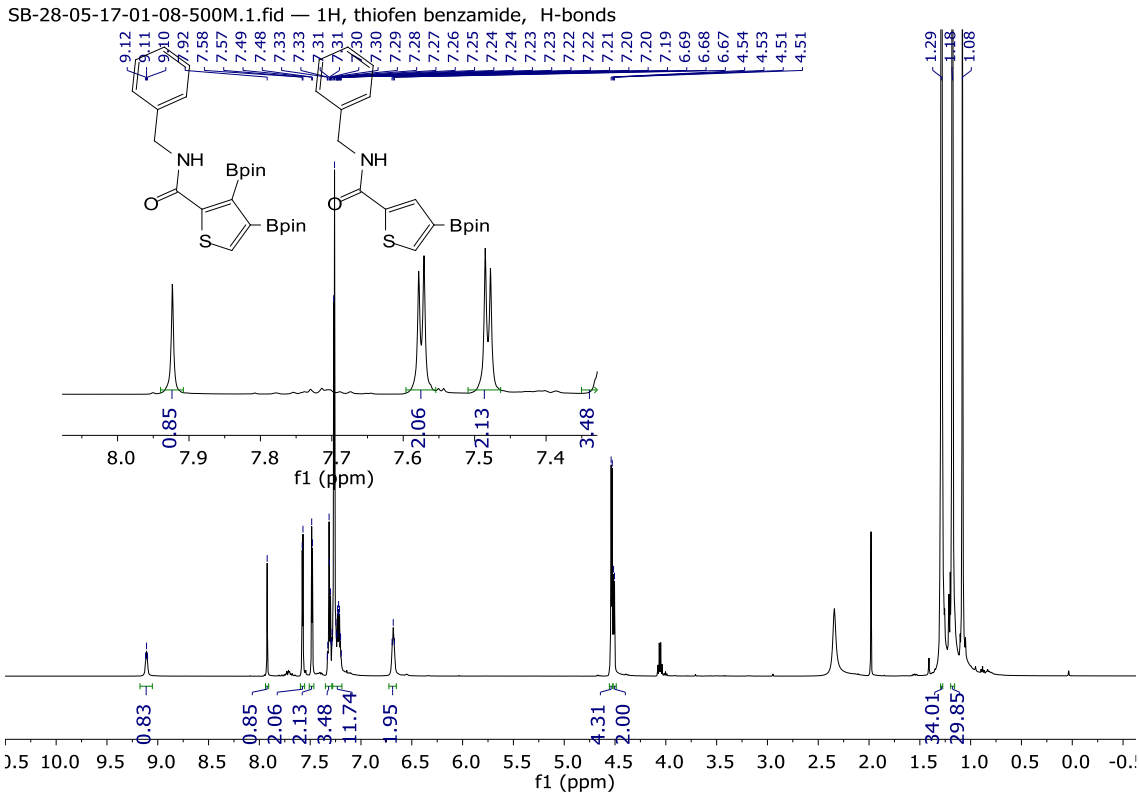


Figure S143. ^{1}H NMR spectra of borylated aromatic amides **28so** and **28sm** (1:2 ratio)

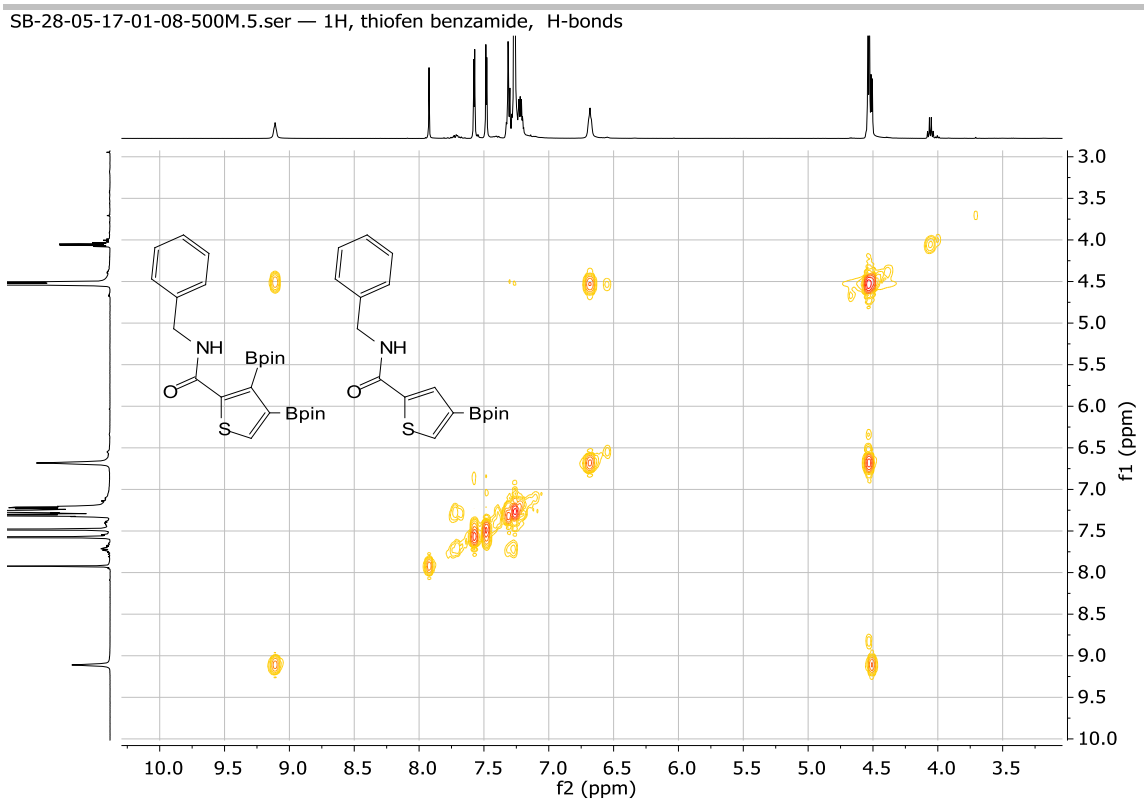


Figure S144. ^{1}H-^{1}H COSY NMR spectra of borylated aromatic amides **28so** and **28sm** (1:2 ratio)

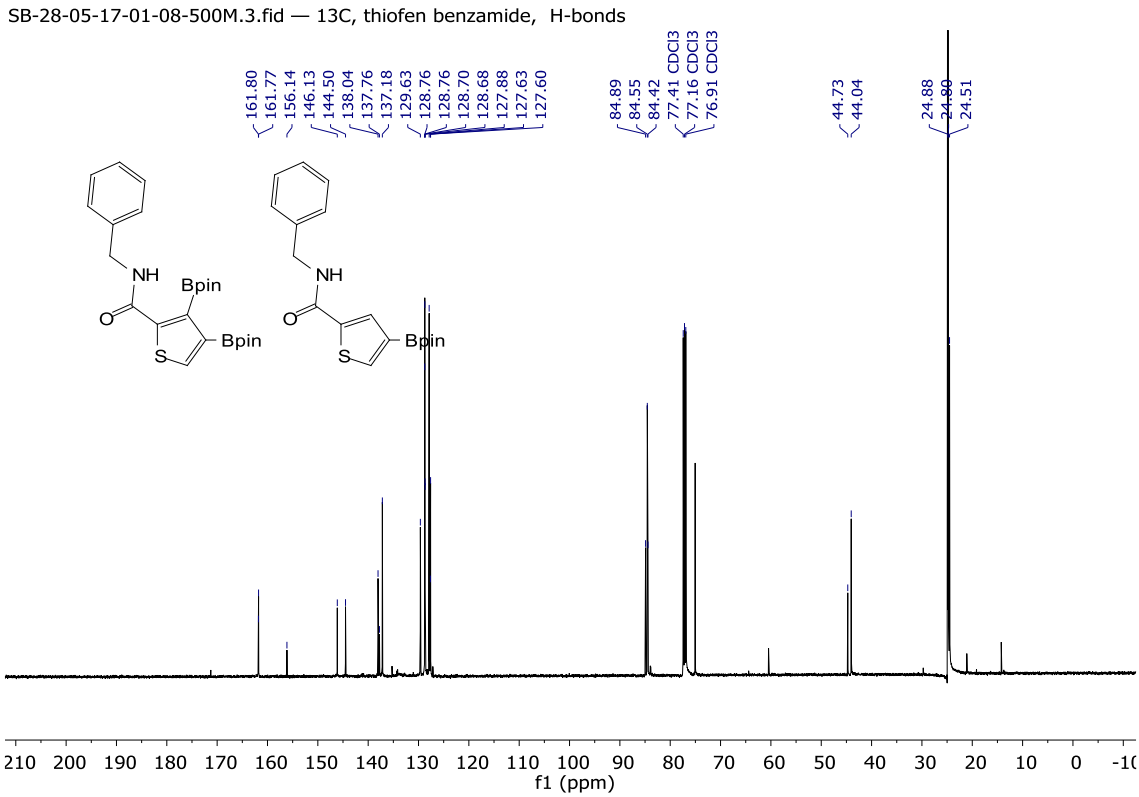


Figure S145. ^{13}C NMR spectra of borylated aromatic amides **28so** and **28sm** (1:2 ratio)

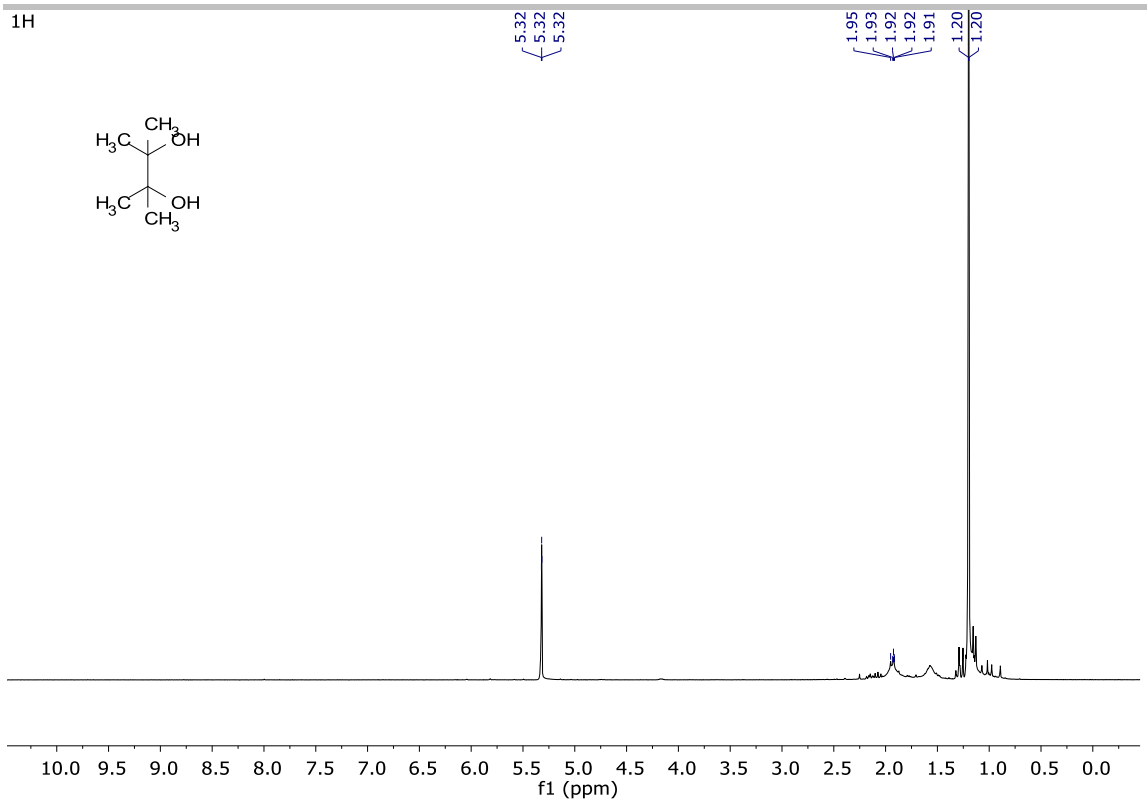


Figure S146. ^{1}H NMR spectra of **pinacol**

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