Supporting Information for
A Recyclable Silica-Supported Iridium Bipyridine Catalyst for Aromatic C-H Borylation

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S1.Analysis of Reaction Yields from NMR spectra

The NMR spectra of crude products that were used to calculate the product yields. Reactions were run using $Cl_2CHCHCl_2$ as an internal standard, from which yields were calculated.

Example detailed calculation:

1.0 mmol arene + 0.25 mmol B_2pin_2 catalyzed by 1.4 mmol% Ir, after filtration and evaporation, 50 μL (0.4766 mmol) of $Cl_2CHCHCl_2$ was added as internal standard.

For example, for the NMR spectrum of 1,2-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene (1,2-dichlorobenzene as substrate, catalyzed by **Ir-1**), the peak at 5.95 ppm was assigned to the protons of the internal standard ($Cl_2CHCHCl_2$) and the peak at 1.34 ppm was assigned to the protons of the Bpin group in the product.

The internal standard has 2 protons, and 0.4766 moles were added, and a peak area of 2 was observed in the NMR;

The product has 12 protons, and the number of moles is an unknown, while a peak area of 12.66 was observed (n=12.66);

Product moles / Internal standard moles = (n/12) / (2/2); Product moles = 0.4766 * n / 12

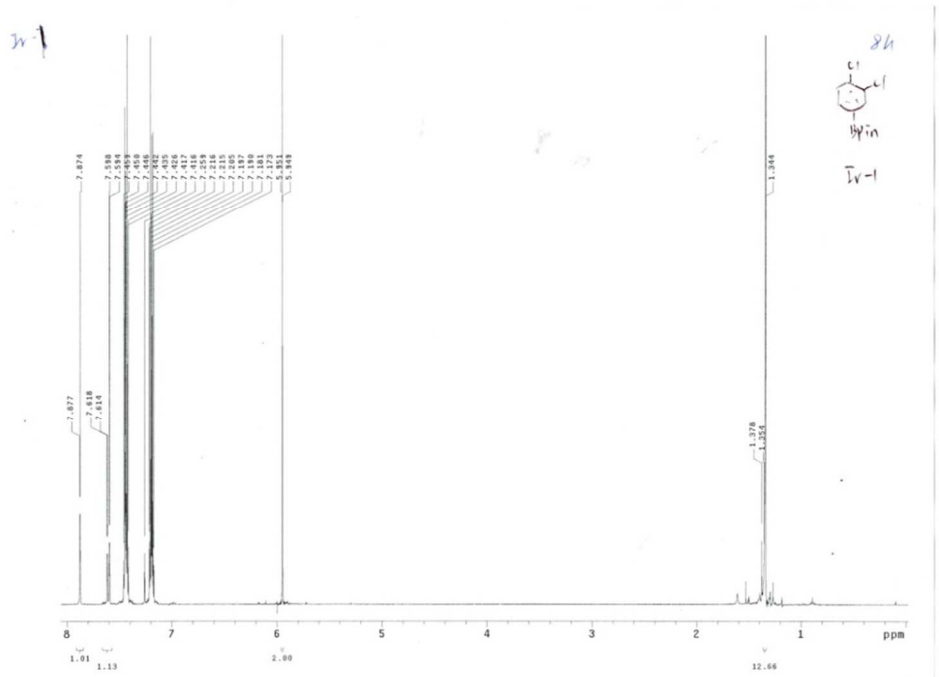
Yield % = (moles of product / (moles of B_2Pin_2 *2 equivalents of BPin per B_2Pin_2))*100

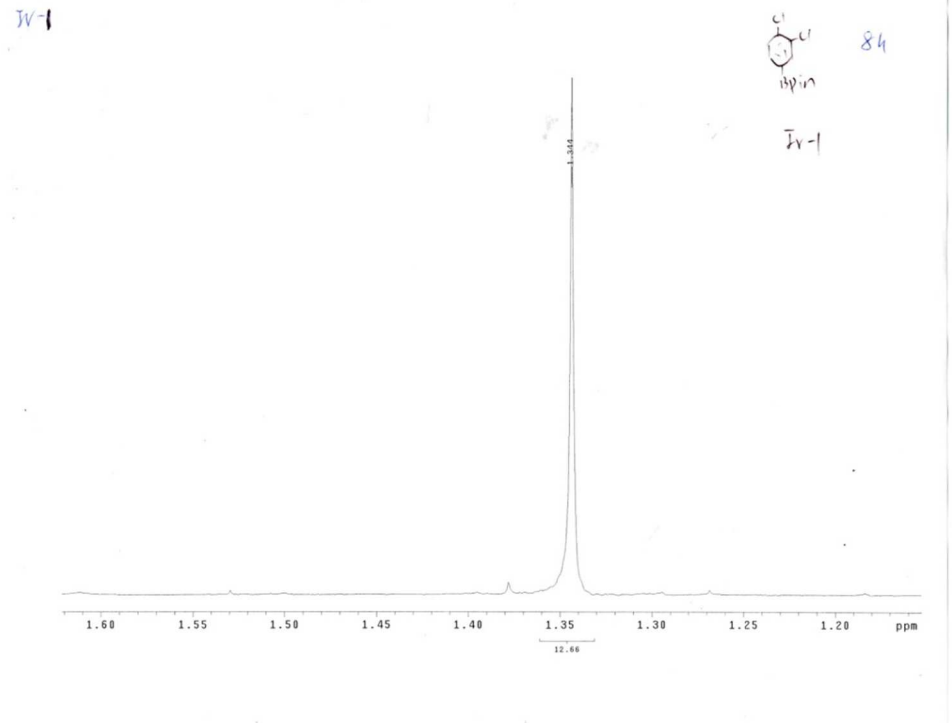
$\text{Yield\%} = \frac{0.4766 \times n}{12 \times 0.5} \times 100\%$ (n= peak area of Bpin in the product, = 12.66 in this case) = 100% yield.

Thus, from this single spectrum, the calculated product yield is 100%. From this spectrum, we can also find that the protons of the starting material (B_2pin_2, 1.25ppm) disappeared completely, again indicating 100% conversion of B_2pin_2. After repeated experiments for 1,2-dichlorobenzene three times, we obtained the average yield of 96%, as presented in paper.

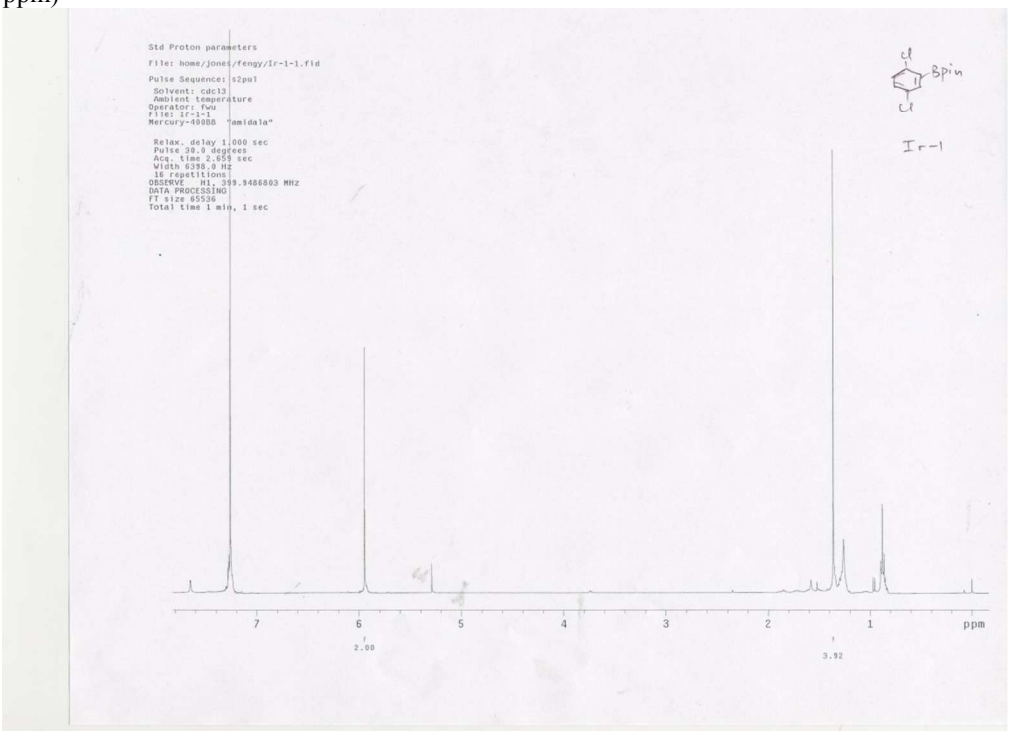
Raw NMR results are reported below using **Ir-1** as the catalyst for borylation:

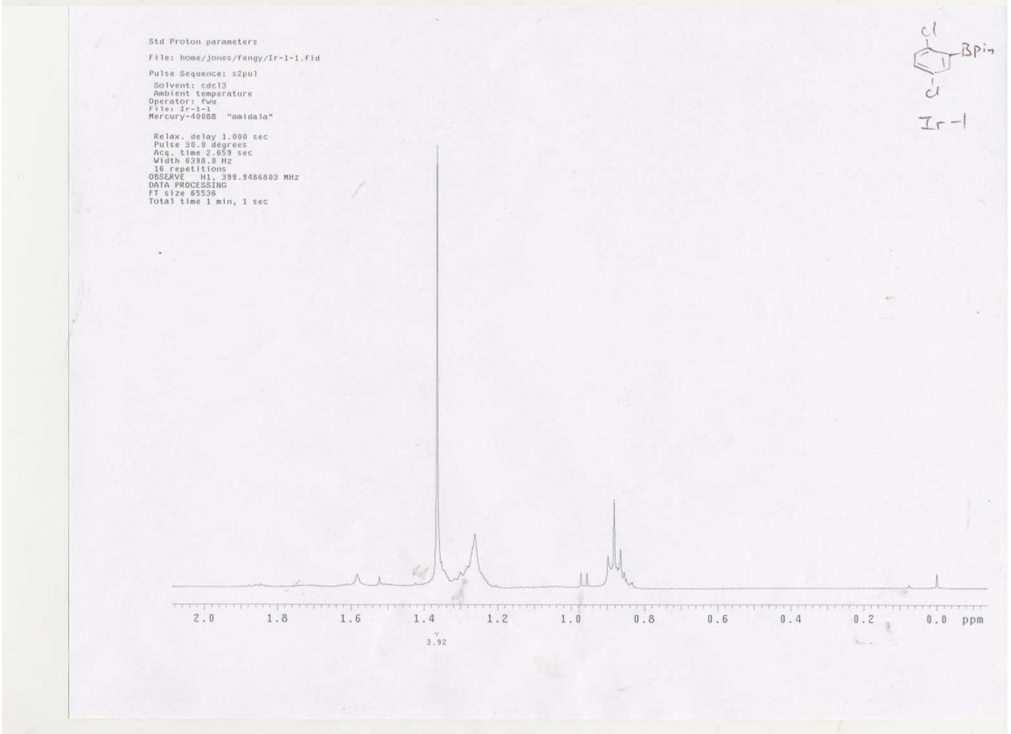
(1) 1,2-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene; ($Cl_2CHCHCl_2$: 5.95ppm; ArBpin: 1.344ppm)



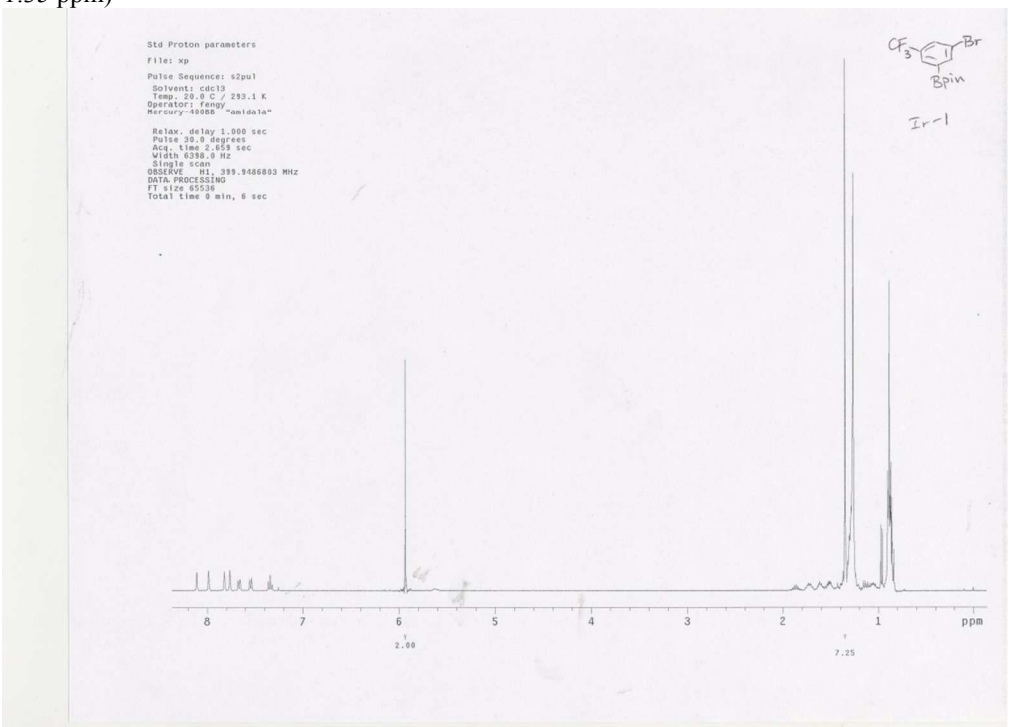


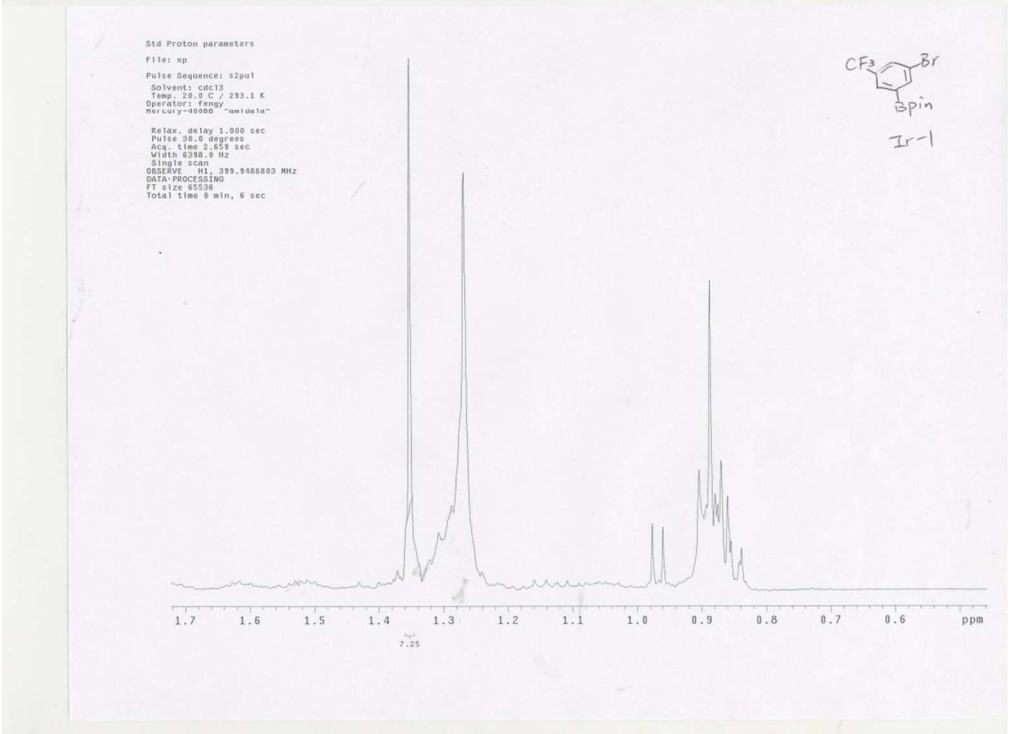
(2) 1,4-Dichloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene ($Cl_2CHCHCl_2$: 5.93 ppm; ArBpin: 1.35 ppm)



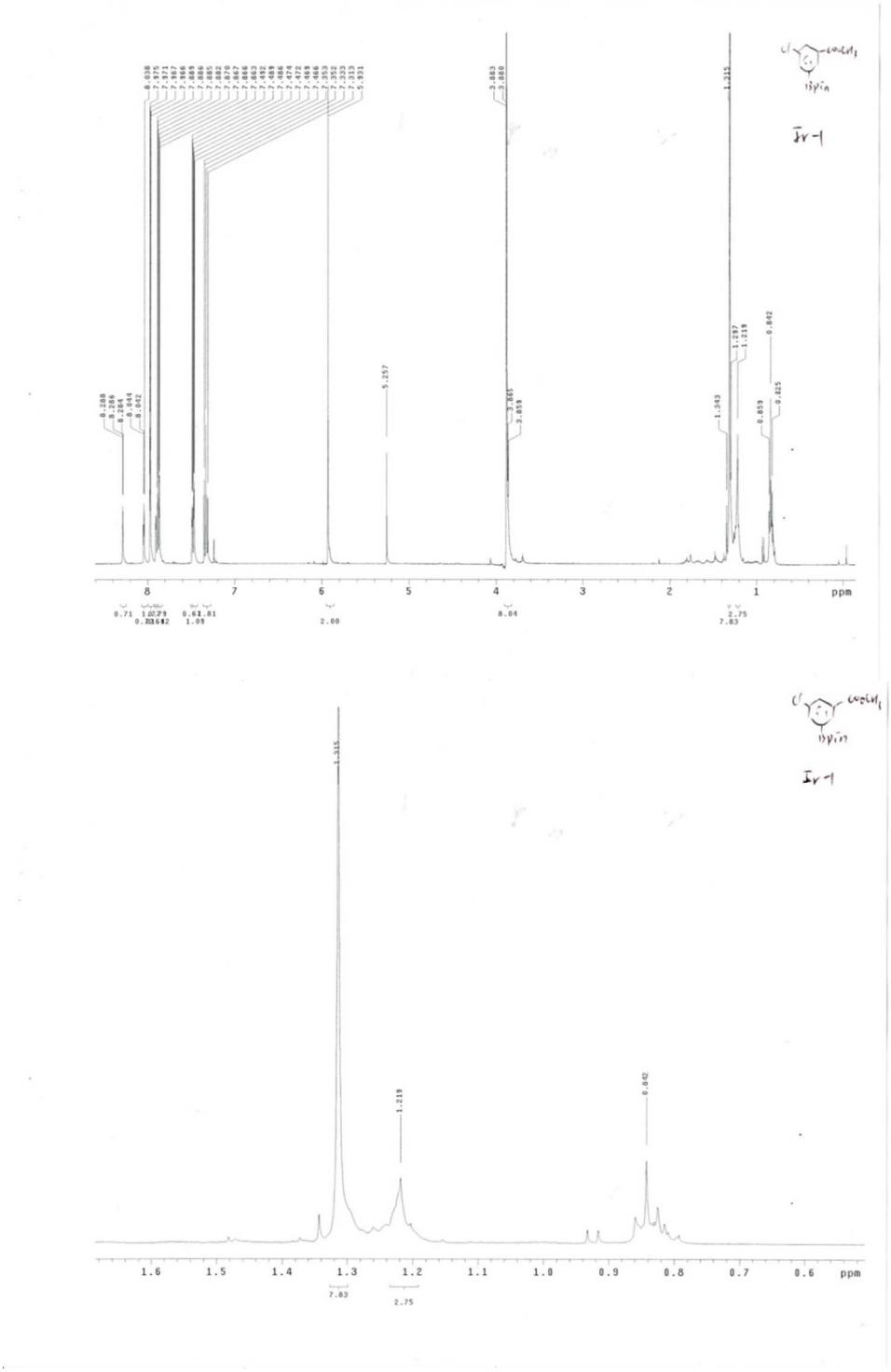


(3) 3-Bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrifluoride ($Cl_2CHCHCl_2$: 5.95 ppm; ArBpin: 1.35 ppm)

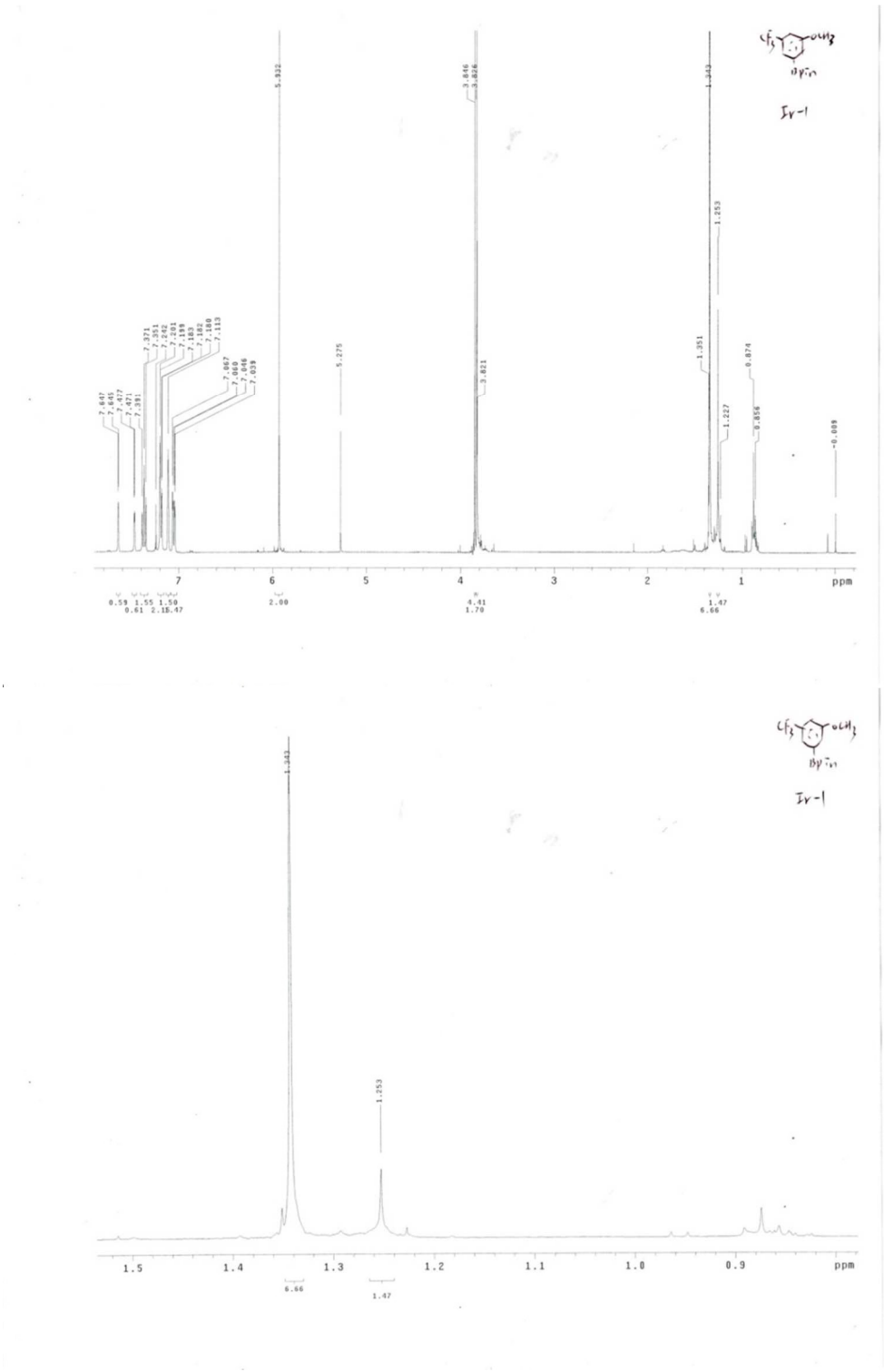




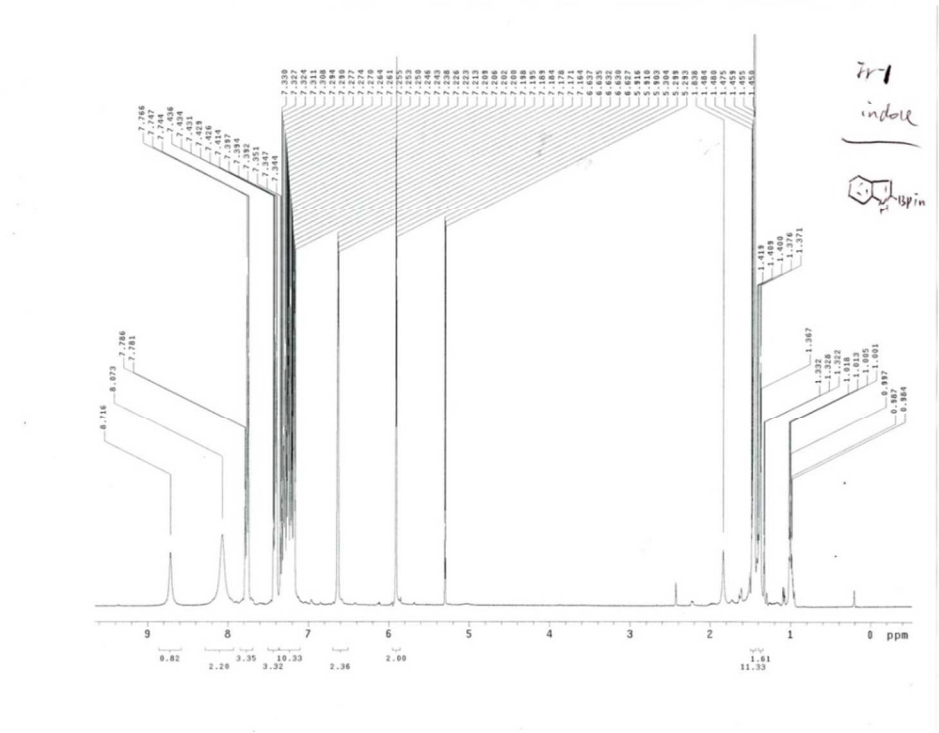
(4) Methyl 3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate ($Cl_2CHCHCl_2$: 5.93 ppm; ArBpin: 1.32 ppm)



(5) 3-Trifluoromethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anisole ($Cl_2CHCHCl_2$: 5.93 ppm; ArBpin: 1.34 ppm)

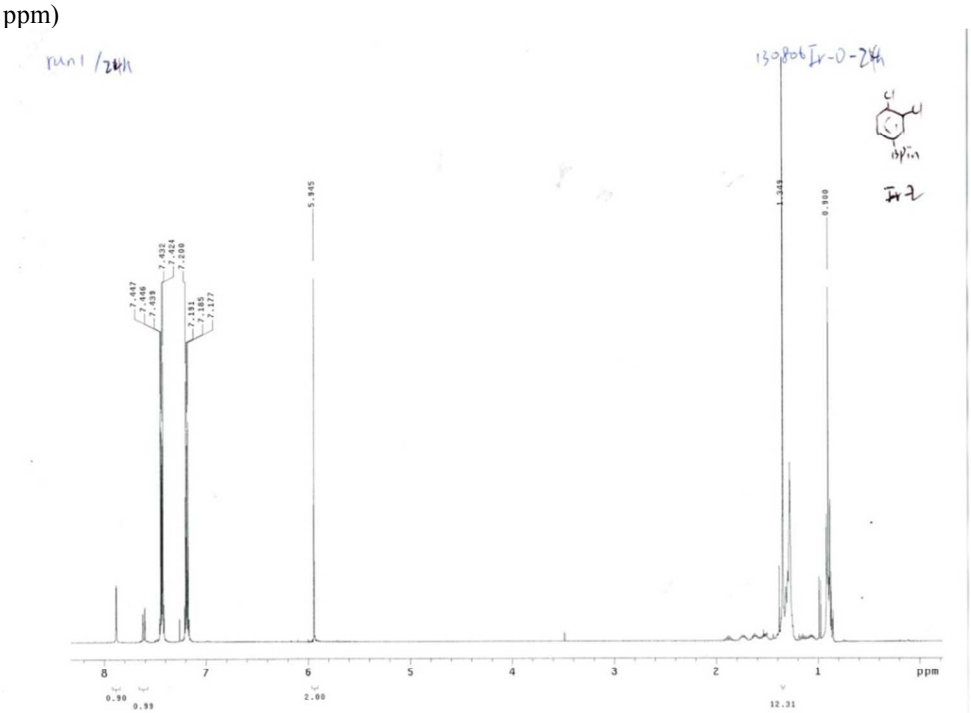


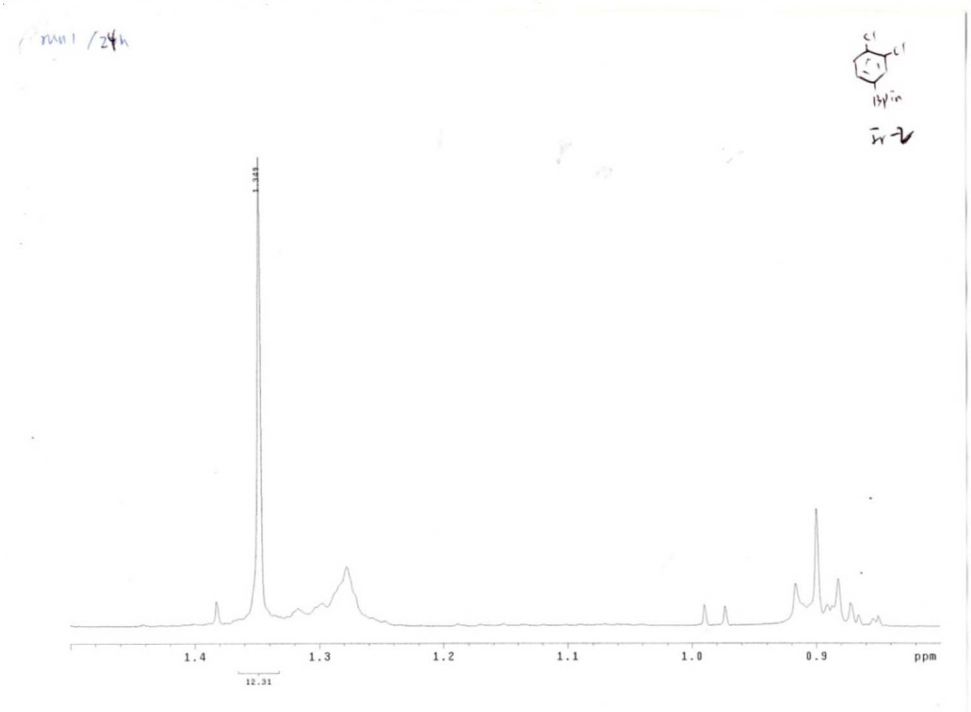
(6) 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)indole ($Cl_2CHCHCl_2$: 5.91 ppm; ArBpin: 1.48 ppm)



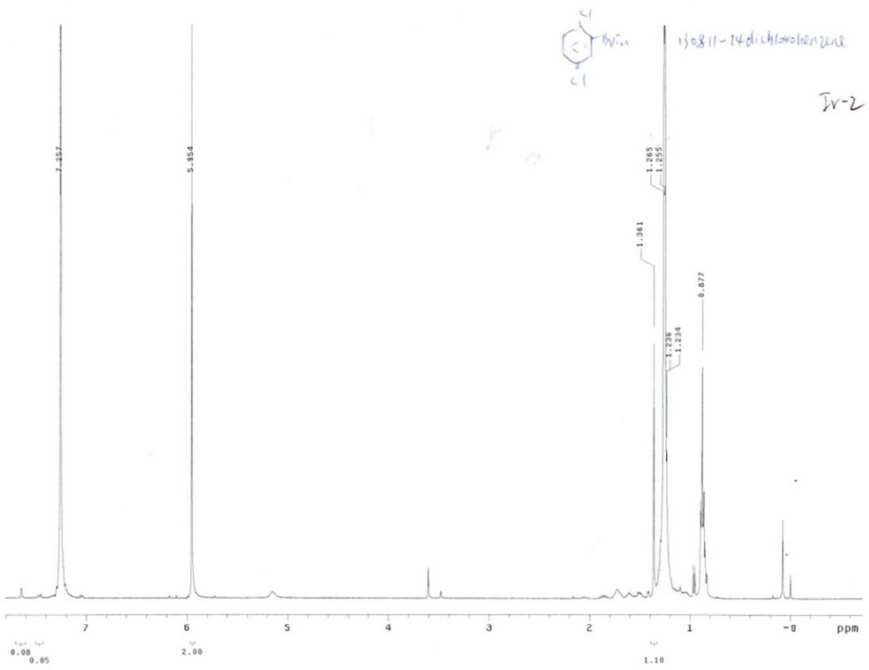
Raw NMR results are reported below using **Ir-2** as the catalyst for borylation:

(1) 1,2-Dichloro-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene ($Cl_2CHCHCl_2$: 5.94 ppm; ArBpin: 1.35 ppm)





(2) 1,4-Dichloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene ($Cl_2CHCHCl_2$: 5.95 ppm; ArBpin: 1.36 ppm)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1.361
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5
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0
ppm
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2.00
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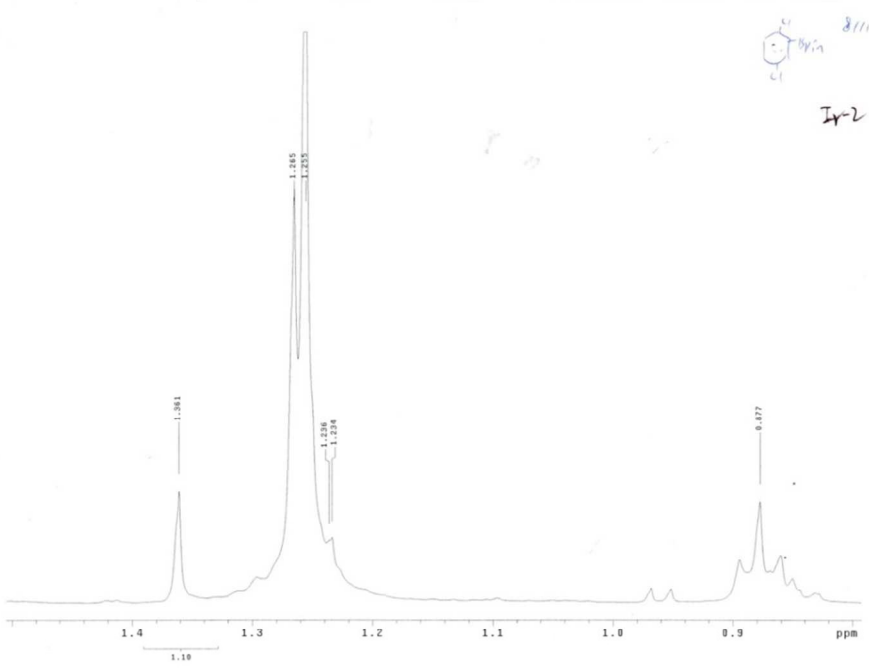
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1.361
1.236
1.234
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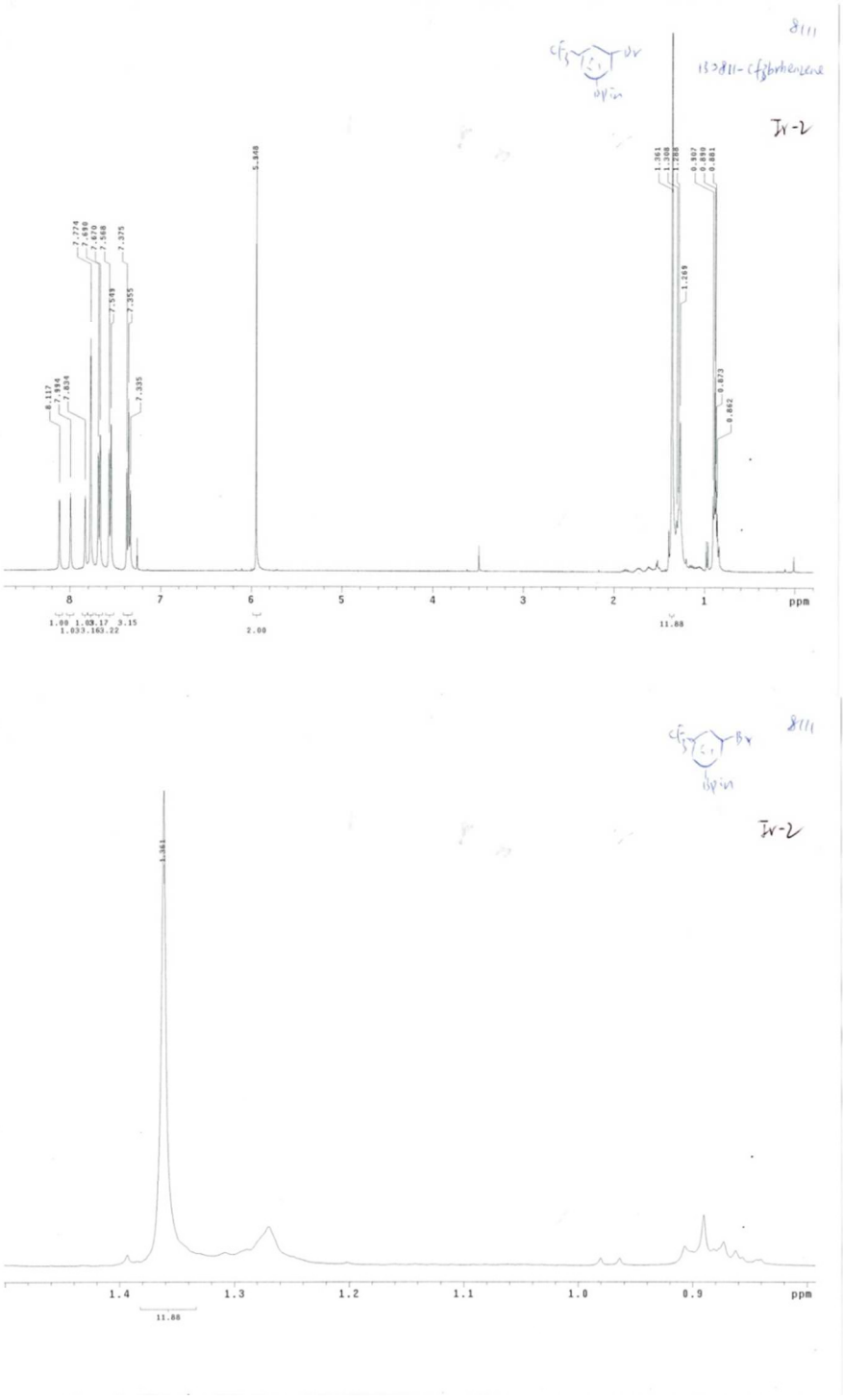
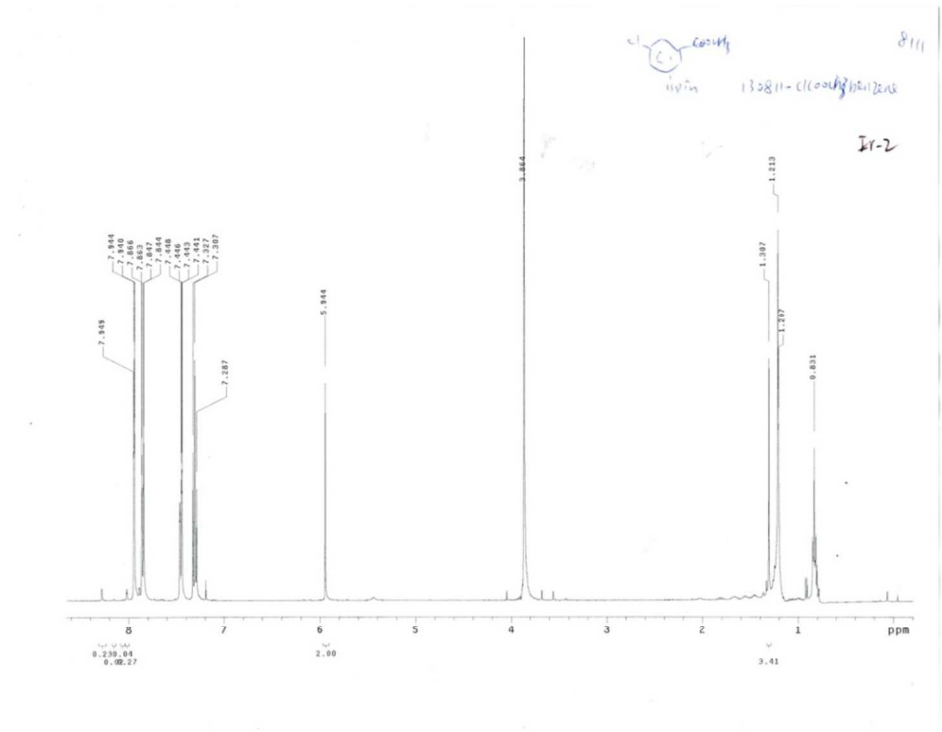
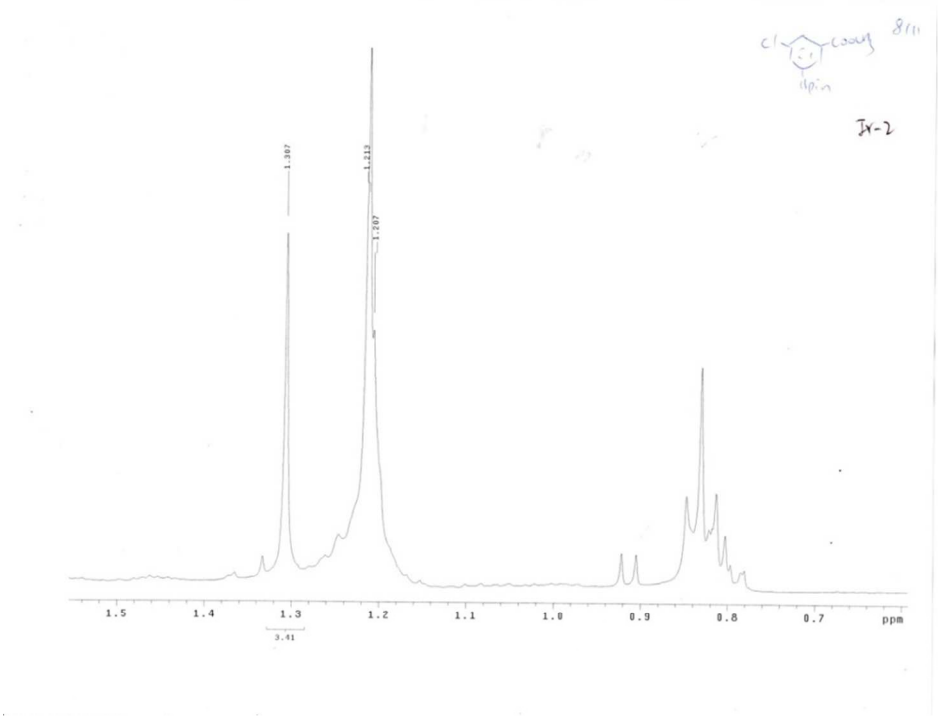
1.4
1.3
1.2
1.1
1.0
0.9
ppm
1.10

(3) 3-Bromo-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrifluoride ($Cl_2CHCHCl_2$: 5.94 ppm; ArBpin: 1.36 ppm)

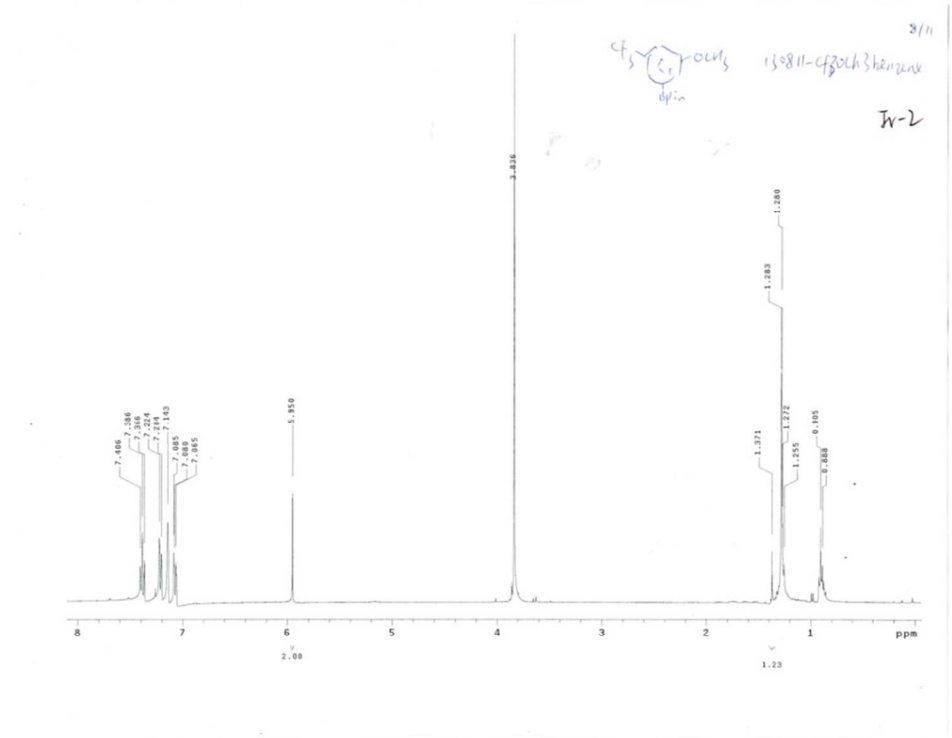


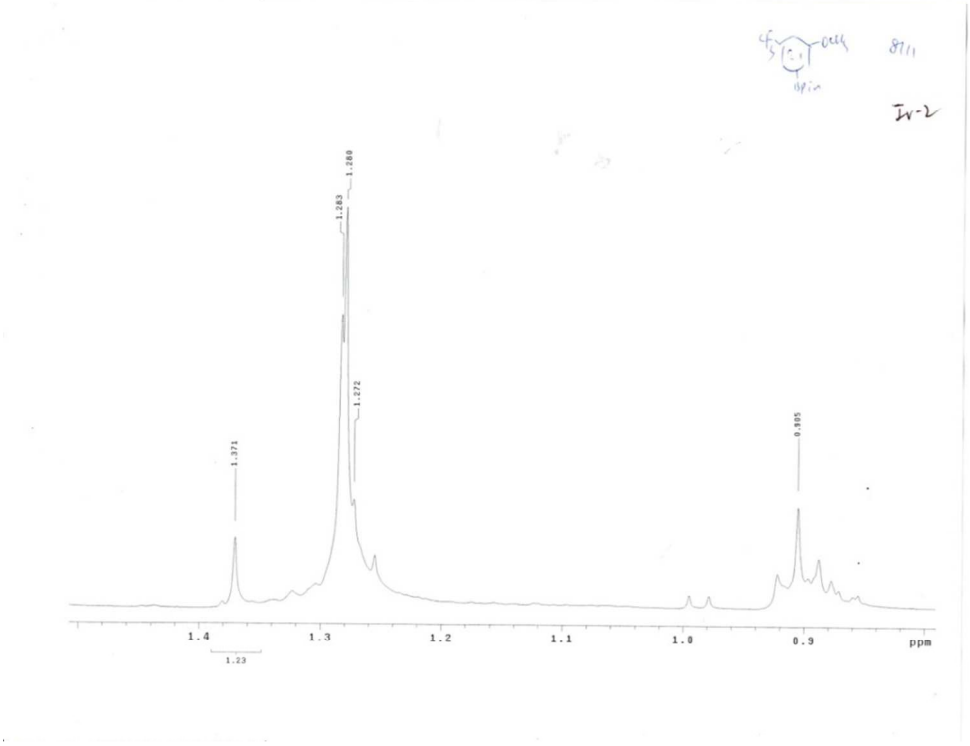
(4) Methyl 3-chloro-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate ($Cl_2CHCHCl_2$: 5.94 ppm; ArBpin: 1.31 ppm)



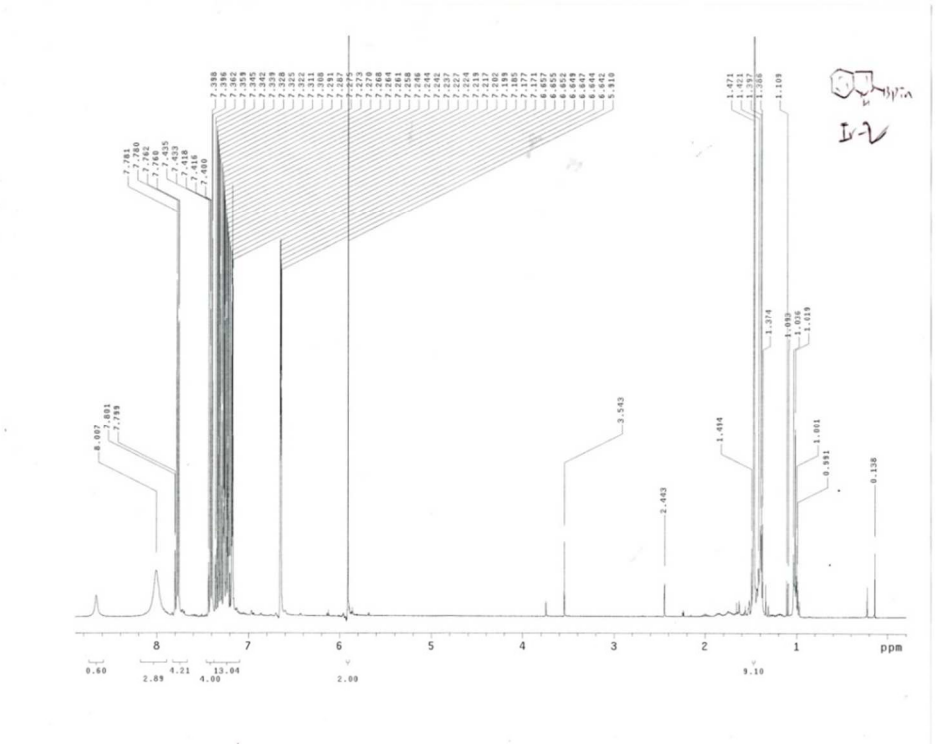


(5) 3-Trifluoromethyl-5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)anisole ($Cl_2CHCHCl_2$: 5.95 ppm; ArBpin: 1.37 ppm)





(7) 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)indole ($Cl_2CHCHCl_2$: 5.91 ppm; ArBpin: 1.47 ppm)



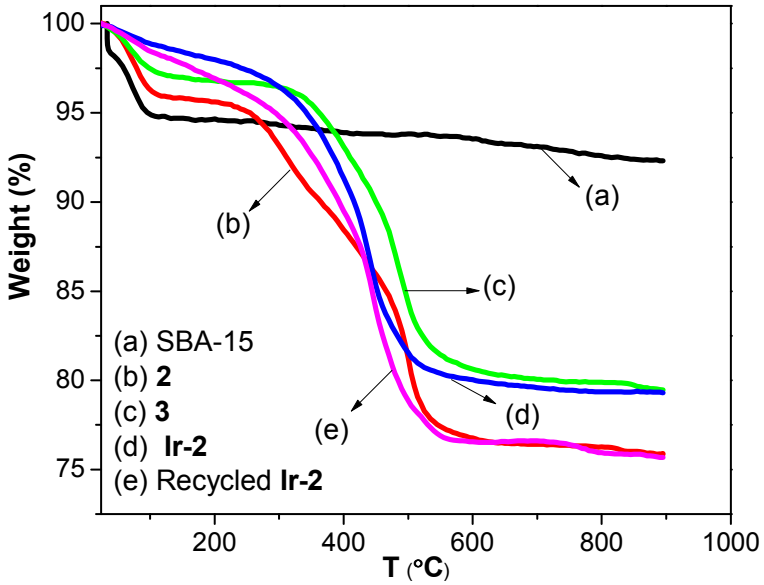


Figure S1. TGA curve for SBA-15, **2**, **3**, **Ir-2.**

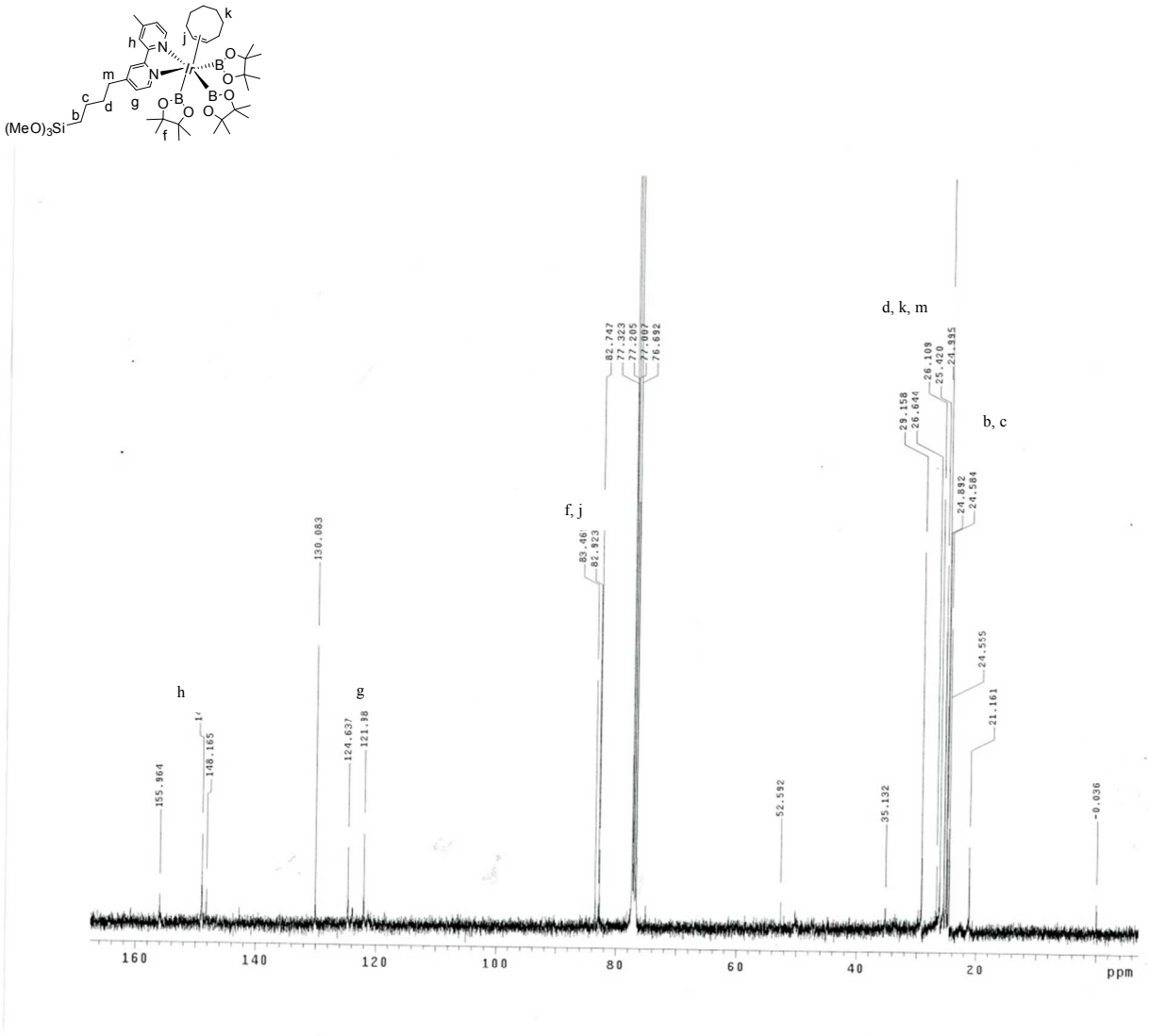
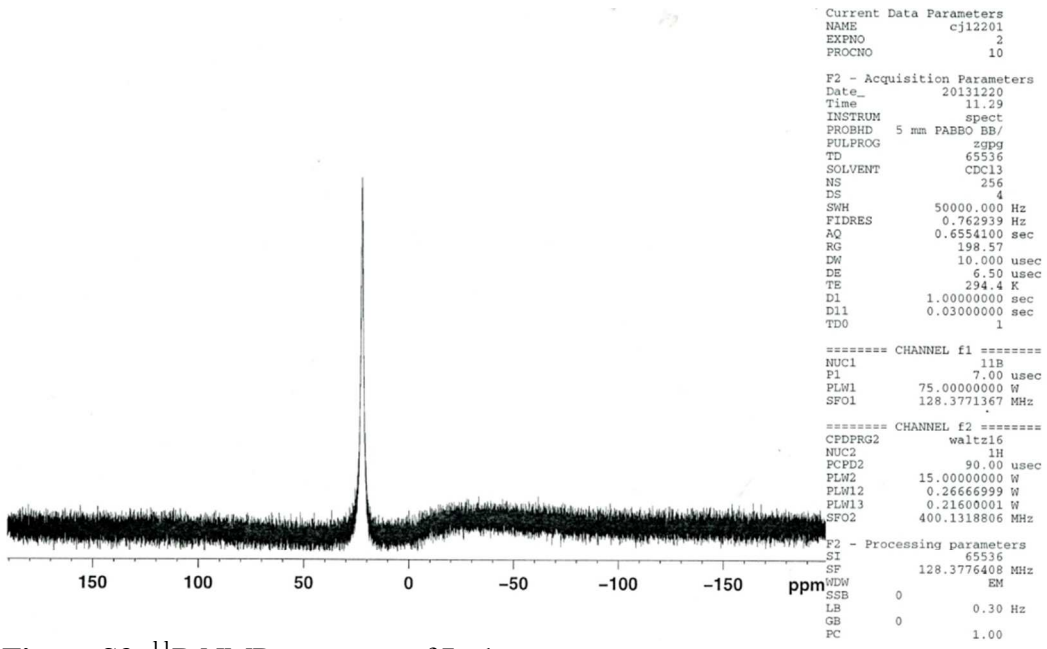


Figure S2. ^{13}C NMR spectrum of **Ir-1.**

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RG                     198.57
DW                     10.000 usec
DE                      6.50 usec
TE                     294.4 K
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D11                 0.03000000 sec
TD0                        1

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PLW1               75.00000000 W
SFO1              128.3771367 MHz

======== CHANNEL f2 ========
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PCPD2                   90.00 usec
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PLW13               0.21600001 W
SFO2              400.1318806 MHz

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Figure S3. ^{11}B NMR spectrum of **Ir-1.**

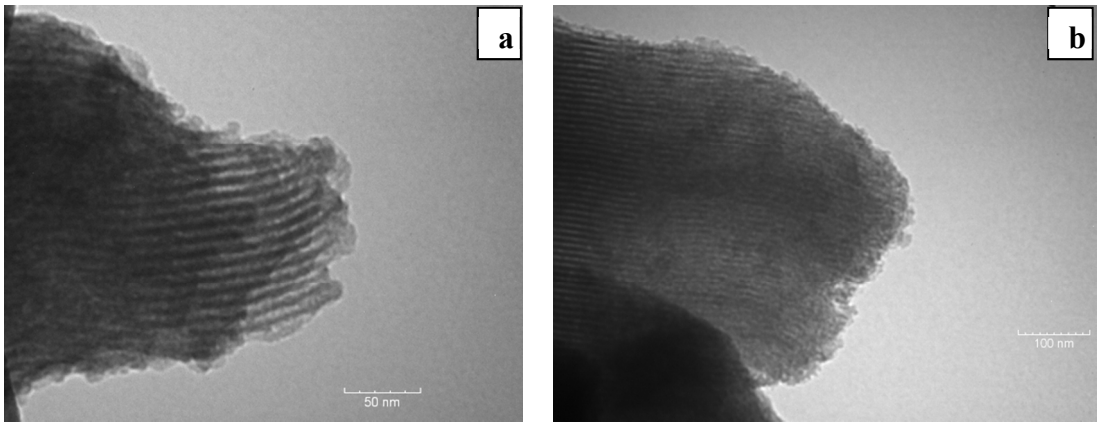

Figure S4. TEM images of fresh **Ir-2** (a) and used **Ir-2** (b).