

**The *N,N*-Diethyl *O*-Carbamate:  
Directed Metalation Group and Orthogonal Suzuki-Miyaura Cross  
Coupling Partner**

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**Supporting Information**

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## Experimental Procedures

### General Methods

Melting points are uncorrected and represent values obtained on recrystallized materials with a Fisher Scientific melting point apparatus. IR spectra were recorded as films prepared by evaporation of  $\text{CH}_2\text{Cl}_2$  solutions or as KBr pellets using a BONEM FT-IR spectrophotometer. NMR spectra were recorded on a Bruker Avance-300, 400 or 500 MHz. GC/MS were performed on an Agilent Technologies GC-MS system (6890N network GC system and 5973 Mass selective detector). High resolution mass spectra (HRMS) were recorded on a Kratos Mass Spectrometer or on a Micromass 70-250S Double Focusing Mass Spectrometer. Anhydrous toluene was obtained by forced passage through activated alumina in a Pure-Solv 400 solvent purification system (Innovative Technology, Inc.) whereas the anhydrous *o*-xylene was purchased from Sigma-Aldrich Chemical Co. Where appropriate, reactions were monitored by TLC and GC/MS. Flash column chromatography was carried out using Silicycle Silica-P Flash Silica Gel.  $\text{K}_3\text{PO}_4$  was dried by heating at 250°C under vacuum for 5 h and stored in glovebox.

### General Procedure A: Preparation of Aryl *O*-Carbamates

Flame dried glassware, under an atmosphere of Argon, was charged with a stir bar and  $\text{NaH}$  (60% in mineral oil). Anhydrous hexane of the requisite amount was then cannulated slowly in while stirring the solution. After stirring for 10 minutes stirring was halted and the resulting suspension left to settle. The hexanes were then carefully cannulated out of the flask

leaving behind crystalline NaH. To this solution THF with the corresponding phenol (0.1-0.2 M) was added at 0°C sequentially via cannula while stirring, the reaction was vented to allow for the release of the evolved hydrogen gas. After complete addition the reaction was allowed to warm to rt, and left for 2-3 hours. The reaction vessel was then cooled down to 0°C using an ice bath; the addition of ClCONEt<sub>2</sub> was then added dropwise. The reaction was monitored and typically left at rt for 24 h. Once complete disappearance of the starting material was observed by TLC and by GC/MS the reaction was carefully quenched with the minimum amount of aqueous NH<sub>4</sub>Cl at 0°C degrees to ensure complete neutralization of any excess NaH. The stir bar was then removed and washed with a minimum amount of ethyl acetate and THF was removed carefully under reduced pressure. Additional distilled water was then added to ensure complete solvation of any inorganic salts, and the reaction mixture extracted by CH<sub>2</sub>Cl<sub>2</sub> three times. The collected organic phases were dried under anhydrous sodium sulfate and solvent was removed under reduced pressure. In most cases purification was performed using Kruger Rohr distillation.

### **General Procedure B: Dehydration of Boronic Acids**

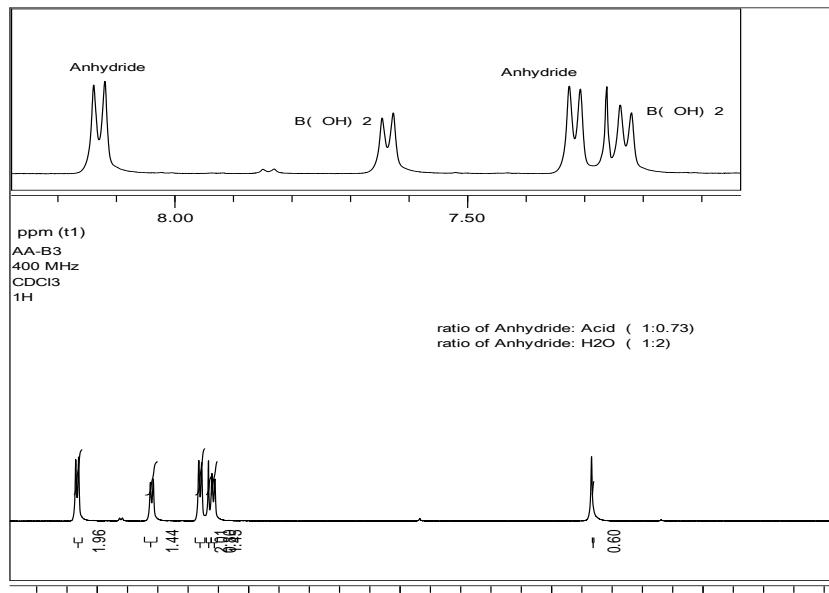
Boroxines were prepared from commercial or prepared boronic acids by heating at 60-80°C under vacuum for 1-12 h using a Kugelrohr apparatus. Prior to use of the boroxine, its <sup>1</sup>H NMR spectrum was recorded to determine the ratio of boroxine: water content. If the ratio was within the range of 1:0.08-1:0.11 (boroxine: water), and 1:0.06-1:0.1 (boroxine: boronic acid), then the boronic anhydride was deemed suitable for undertaking the cross-coupling reaction.

### **General Procedure C: Cross Coupling of OCONET<sub>2</sub>**

A 5 mL flame dried vial containing a Teflon coated stir bar was cooled to rt under nitrogen and capped. Reagents and reactants were weighed and added under an atmosphere of nitrogen. Solvents, stored in a Schlenk flask, were then added via septum cap syringe injection under nitrogen. The vial was then capped and stirred at rt for a short period of time (1 min) to ensure complete dissolution of catalyst. The solution was stirred at the indicated temperatures and the reaction was monitored periodically by GC/MS and TLC at the following time intervals: 0.5 h, 1h, 2 h, 5 h. The reaction was stopped when total disappearance of the starting material or no further conversion to the product was observed. The mixture was then cooled to rt and concentrated, Deionized H<sub>2</sub>O (1 mL) was added to the residue and the mixture was extracted with EtOAc (4 X 1.5 mL). The combined organic fractions were dried (Na<sub>2</sub>SO<sub>4</sub>), subjected to filtration, and concentrated to dryness under reduced pressure. The residue was dissolved in a minimum amount of CH<sub>2</sub>Cl<sub>2</sub> and purified by silica gel flash column chromatography column using the specified eluent to afford the product.

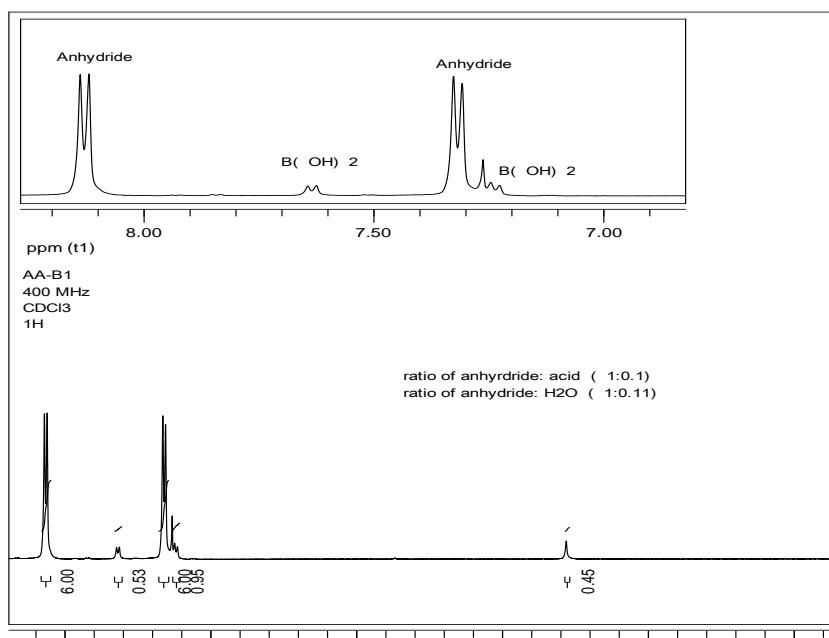
## Boronic Acid Study

<sup>1</sup>H NMR of **1b/a** used, (Table 1, Entry 6). 26% (GC/MS) Cross Coupling Product, 20 h  
Ratio of Boronic acid: Boroxine (1:1).

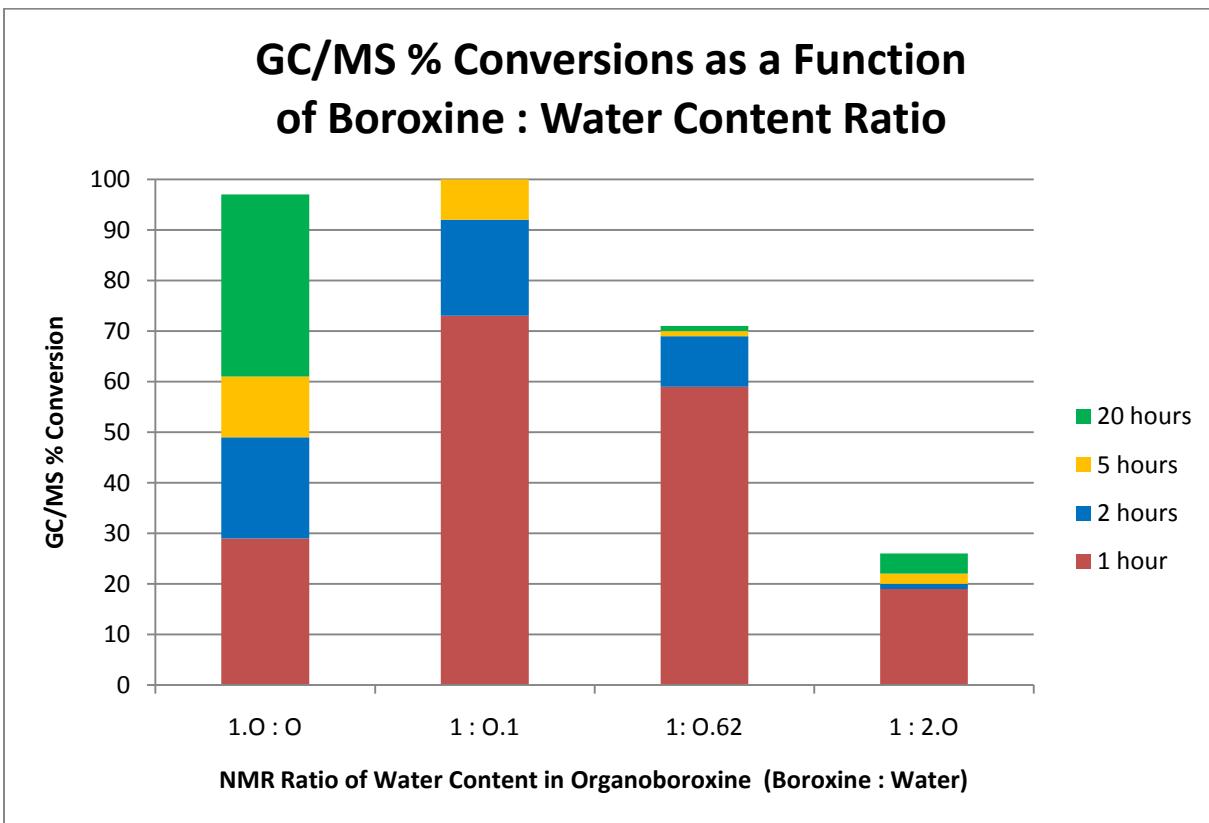


<sup>1</sup>H NMR of **1b/a** used, (Table 1, entries 1, 2, 4, 5, 8, 9, 10).

Ratio of Boronic acid: Boroxine (10:1)



## Rate Study



The ratio of water content (Boroxine: water) was obtained from proton NMR of each organoborane sample. This graph illustrates the GC/MS % Conversion yield at 1, 2, 5, and 20 hours for four samples with varying amounts of water.

NMR Ratio of Boroxine: water	Time (hours)	GCMS % Conversion
1.0 : 0	1	29
	2	49
	5	61
	20	97
1.0 : 0.1	1	73
	2	92
	5	100
1: 0.62	1	59
	2	69
	5	70
	20	71
1 : 2.0	1	19
	2	20
	5	22
	20	26

## Prepared Compounds

### Preparation of Aryl O-Carbamates

#### 2-Naphthyl *N,N*-diethyl *O*-carbamate

Preparation of this compound was carried out in accordance with

**General Procedure A** from 2-naphthol (2.88 g, 20 mmol), NaH (1.04

g, 26mmol, 60% dispersion in mineral oil), ClCONEt<sub>2</sub> (6.318 g, 26 mmol). Standard workup and

Kugelrohr distillation to give a clear oil which solidified to a colorless solid and recrystallized in

Hexanes to give the product (4.2 g ,17.4 mmol, 87%) as a colourless solid; IR (film)  $V_{\max}$  cm<sup>-1</sup>

2974, 2936, 1596, 1418, 1244, 1210, 1165, 970, 753 ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  ppm 7.86

(d,  $J$  = 8.55 Hz, 2H), 7.82 (d,  $J$  = 7.76 Hz, 1H), 7.61 (d,  $J$  = 1.33 Hz, 1H), 7.53-7.43 (m, 2H),

7.31 (dd,  $J = 8.81, 2.12$  Hz, 1H), 3.49 (dd,  $J = 35.41, 5.56$  Hz, 4H), 1.27 (t,  $J = 28.66, 28.66$  Hz, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 42.1 (1C), 13.8 (1C), 118.4 (1C), 121.7 (s, 1C), 125.3 (1C), 126.3 (1C), 127.5 (1C), 127.7 (1C), 129.1 (1C), 131.1 (1C), 133.9 (1C), 149.2 (1C), 154.3 (1C)

**1-Naphthyl  $N,N$ -diethyl  $O$ -carbamate (Table 2, Entry 1)**

Prepared according to method described in literature.<sup>1</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 7.71 (d,  $J = 8.19$  Hz, 1H), 7.94 (dd,  $J = 4.70, 4.04$  Hz, 1H), 7.91-7.83 (m, 1H), 7.50 (tdd,  $J = 15.81, 12.55, 4.96, 4.96$  Hz, 3H), 7.30 (dd,  $J = 11.15, 4.53$  Hz, 1H), 3.55 (dd,  $J = 64.33, 6.43$  Hz, 4H), 1.47-1.17 (m, 6H).

**Phenyl  $N,N$ -diethyl  $O$ -carbamate (Table 2, Entry 2)**

Prepared according to method described in literature.<sup>2</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 7.48-7.40 (m, 2H), 7.25-7.18 (m, 2H), 3.49 (dd,  $J = 16.09, 6.98$  Hz, 4H), 1.45-1.16 (m, 6H), 7.28 (s, 1H). Spectral data was found to be identical to those reported.<sup>2</sup>

**Benzo[d][1,3]dioxol-5-yl  $N,N$ -diethyl  $O$ -carbamate (Table 2, Entry 3)**

Prepared according to method described in literature.<sup>3</sup>

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 6.77-6.71 (m, 1H), 6.64 (d,  $J = 2.16$

Hz, 1H), 6.54 (dd,  $J$  = 8.36, 2.30 Hz, 1H), 3.38 (d,  $J$  = 6.44 Hz, 4H), 1.28-1.12 (m, 6H), 5.95 (s, 2H). Spectral data was found to be identical to those reported.<sup>3</sup>

**3-Fluorophenyl *N,N*-diethyl *O*-carbamate (Table 2, Entry 4)**

Prepared according to method described in literature.<sup>4</sup>

<sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>)  $\delta$  ppm 7.35-7.27 (m, 1H), 6.91 (ddd,  $J$  = 14.06, 9.79, 7.56 Hz, 3H), 3.40 (dd,  $J$  = 13.59, 6.86 Hz, 4H), 1.28-1.16 (m, 6H).

Spectral data was found to be identical to those reported.<sup>4</sup>

**4-Cyanophenyl *N,N*-diethyl *O*-carbamate (Table 2, Entry 5)**

<sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>)  $\delta$  ppm 1.23 (td,  $J$  = 14.63, 6.97, 6.97 Hz, 6H), 3.41 (qd,  $J$  = 20.76, 6.84, 6.84, 6.81 Hz, 4H), 7.27 (s, 1H), 7.25 (s, 1H), 7.66 (d,  $J$  = 8.65 Hz, 2H)

**2,4-Dimethylphenyl *N,N*-diethyl *O*-carbamate (Table 2, Entry 6)**

<sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>)  $\delta$  ppm 1.23 (d,  $J$  = 25.75 Hz, 6H), 3.57-3.28 (m, 4H), 2.29 (s, 3H), 2.17 (s, 3H), 7.05-6.89 (m, 3H)

**2-Benzylphenyl *N,N*-diethyl *O*-carbamate (Table 2, Entry 7)**

<sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>)  $\delta$  ppm 7.23-7.01 (m, 9H), 3.88 (s, 2H), 3.26 (dd,  $J$  = 12.27, 6.58 Hz, 4H), 1.08 (d,  $J$  = 4.90 Hz, 6H)

*(E)*-2-Styrylphenyl *N,N*-diethyl *O*-carbamate (**Table 2, Entry 8**)

Prepared according to method described in literature.<sup>5</sup>

<sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>) δ ppm 7.63-7.58 (m, 1H), 7.41 (d, *J* = 7.44 Hz, 1H), 7.28 (t, *J* = 7.54, 7.54 Hz, 1H), 7.22-7.11 (m, 6H), 7.04 (dd, *J* = 23.15, 12.25 Hz, 2H), 3.50-3.31 (m, 4H), 1.29-1.10 (m, 6H). Spectral data is identical to those reported.<sup>5</sup>

2-Methoxyphenyl *N,N*-diethyl *O*-carbamate (**Table 2, Entry 9**)

Prepared according to method described in literature.<sup>6</sup>

<sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>) δ ppm 7.15 (t, *J* = 7.78, 7.78 Hz, 1H), 7.09 (d, *J* = 7.55 Hz, 1H), 6.93 (dd, *J* = 12.68, 5.85 Hz, 2H), 3.83 (s, 3H), 3.52-3.34 (m, 4H), 1.24 (d, *J* = 27.15 Hz, 6H). Spectral data is identical to those reported.<sup>7</sup>

2-Biphenyl *N,N*-diethyl *O*-carbamate (**Table 2, Entry 10**)

Prepared according to method described in literature.<sup>8</sup>

<sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>) δ ppm 7.36 (tt, *J* = 8.33, 8.33, 4.51, 4.51 Hz, 6H), 7.28 (s, 1H), 7.22 (t, *J* = 7.77, 7.77 Hz, 1H), 3.24 (dd, *J* = 9.26, 3.93 Hz, 4H), 1.10-0.90 (m, 6H). Spectral data is identical to those reported.<sup>8</sup>

Pyridin-3-yl *N,N*-diethyl *O*-carbamate (**Table 2, Entries 11-15**)

Prepared according to method described in literature.<sup>9</sup>

<sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>) δ ppm 8.36 (s, 2H), 7.43 (ddd, *J* = 6.79, 5.34, 1.25 Hz, 1H), 7.23-7.16 (m, 1H), 1.24-1.05 (m, 6H), 3.33 (dd, *J* = 16.39, 7.64 Hz, 4H).

**Quinolin-2-yl *N,N*-diethyl *O*-carbamate (Table 2, Entry 16)**

Prepared according to method described in literature.<sup>10</sup>

<sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>) δ ppm 3.49 (ddd, *J* = 42.12, 13.95, 6.86 Hz, 4H), 8.29-7.47 (m, 5H), 1.37-1.18 (m, 6H), 7.24 (s, 1H). Spectral data is identical to those reported.<sup>10</sup>

**9*H*-carbazol-4-yl *N,N*-diethyl *O*-carbamate (Table 2, Entry 13)**

This compound was prepared according to **General Procedure A** from 9*H*-carbazol-4-ol (4.03 g, 18.4 mmol), NaH (108 mg, 4.5 mmol, 60% dispersion in oil) and ClCONEt<sub>2</sub> (608 mg, 4.5 mmol). Standard workup and flash silica gel chromatography, (isocratic elution with 2:1( hexanes: ethyl acetate )+ 2% NEt<sub>3</sub>) afforded the product (991 mg, 3.52 mmol, 86%) as a light brown solid, mp 148-154 °C (hexanes); IR (film CH<sub>2</sub>Cl<sub>2</sub>)  $\nu_{\text{max}}$  cm<sup>-1</sup> 2974, 2973, 2933, 1701, 1700, 1611, 1633, 1611, 1508, 1473, 1458, 1421, 1247, 1208, 1162, 1068, 1067, 957, 788, 773, 755, 723, 723; <sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>) δ ppm 1.42 (t, *J* = 6.80, 6.80 Hz, 3H), 1.29 (dd, *J* = 14.33, 7.37 Hz, 3H), 3.51 (td, *J* = 13.59, 3.53, 3.53 Hz, 2H), 3.75-3.67 (m, 2H), 6.98 (d, *J* = 7.83 Hz, 1H), 7.24-7.15 (m, 2H), 7.44-7.30 (m, 3H), 7.96 (d, *J* = 7.69 Hz, 1H), 8.16 (s, 1H); <sup>13</sup>C NMR (400 MHz, *CDCl*<sub>3</sub>) δ ppm 139.45 (1C), 141.2 (1C), 146.3 (1C), 154.4 (1C), 125.8 (1C), 125.4 (1C), 121.7 (1C), 121.1 (1C), 119.2 (1C), 115.8 (1C), 112.2 (1C), 110.6 (1C), 107.8 (1C), 42.31 (1C), 42.0 (1C), 14.4 (1C), 13.4 (1C); LRMS

(EI) (*m/z*) (%), 282[M<sup>+</sup>](9), 218(100), 69(98), 131(85), 263(38), 100(28), 149 (22); HRMS (EI) calculated for C<sub>17</sub>H<sub>18</sub>N<sub>2</sub>O<sub>2</sub> [M<sup>+</sup>] 82.1368: found 282.1375.

**2, 2, 7-Trimethyl-4a,8a-dihydro-2*H*-chromen-5-yl *N,N*-diethyl *O*-carbamate (5)**

Compound prepared according to method described in literature.<sup>11</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 3.53-3.35 (m, 4H), 1.23 (td, *J* = 23.86, 6.46, 6.46 Hz, 6H), 5.56 (d, *J* = 9.93 Hz, 1H), 6.34 (d, *J* = 9.93 Hz, 1H), 6.47 (s, 2H), 1.44 (d, *J* = 18.51 Hz, 6H), 2.25 (s, 3H). Spectral data is identical to those reported.<sup>11</sup>

**2-(Benzofuran-2-yl)-6-methoxyphenyl *N,N*-diethyl *O*-carbamate (7)**

Compound prepared according to method described in literature.<sup>12</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 1.22 (td, *J* = 42.98, 6.97, 6.97 Hz, 6H), 1.49 (s, 2H), 3.80 (s, 3H), 3.37 (dd, *J* = 2.57, 0.73 Hz, 4H), 7.24-7.12 (m, 4H), 6.97-6.87 (m, 2H), 7.51 (t, *J* = 9.05, 9.05 Hz, 2H), 7.42 (d, *J* = 8.12 Hz, 1H). Spectral data is identical to those reported.<sup>12</sup>

**4-(4-Methoxyphenyl)pyridin-3-yl *N,N*-diethyl *O*-carbamate (8)**

Prepared according to method described in literature.<sup>13</sup>

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 1.03 (td, *J* = 14.42, 7.09, 7.09 Hz, 6H), 3.24 (qd, *J* = 21.34, 7.07, 7.07, 6.96 Hz, 4H), 3.78 (s, 3H), 6.94-6.84

(m, 2H), 7.23 (d,  $J$  = 4.97 Hz, 1H), 7.36-7.30 (m, 2H), 8.39 (d,  $J$  = 6.06 Hz, 2H). Spectral data was found to be identical to those reported.<sup>13</sup>

### Preparation of Aryl Boroxines

#### Triphenyl Boroxine **1d** (Table 3, Entry 1)

Triphenyl boronic acid anhydride (boroxine) was prepared according to **General Method B**, and obtained by Kugelrohr distillation at 75 °C for 1 hour resulting in a colorless solid. <sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>) Boroxine: δ ppm 8.26 (d,  $J$  = 6.80 Hz, 6H), 7.61 (t,  $J$  = 7.33, 7.33 Hz, 3H), 7.52 (t,  $J$  = 7.32, 7.32 Hz, 6H). <sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>) Boronic acid: δ ppm 8.09-7.92 (m, 0.02H), 7.74 (d,  $J$  = 6.70 Hz, 0.07H), 7.42 (t,  $J$  = 7.20, 7.20 Hz, 0.08H), 4.62 (s, 0.03H). <sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>) Water: δ ppm 1.56 (s, 0.11H). The ratio of boronic acid: boroxine: water was determined to be 0.07:1: 0.11 by NMR spectral analysis.

#### Tri(*p*-tolyl) Boroxine **1a** (Table 3, Entry 2)

Sample of *p*-tolyl boronic acid anhydride (boroxine) was prepared according to **General Method B**, and obtained by Kugelrohr distillation at 75°C for 1 hour resulting in a colorless solid. <sup>1</sup>H NMR (300 MHz, *CDCl*<sub>3</sub>) Boroxine: δ ppm 2.45 (s, 9H), 8.13 (d,  $J$  = 7.69 Hz, 6H), 7.31 (d,  $J$  = 7.64 Hz, 6H). <sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>) Boronic acid: δ ppm 7.63 (d,  $J$  = 7.77 Hz, 0.07H), 7.23 (d,  $J$  = 7.73 Hz, 0.08H), 4.54 (s, 0.03H), 2.39 (s, 0.11H). <sup>1</sup>H NMR (300 MHz, *CDCl*<sub>3</sub>) Water: δ ppm 1.55(s,

0.01H). The ratio of boronic acid: boroxine: water was determined to be 0.09:1:0.1 by NMR spectral analysis.

#### Tris(4-methoxyphenyl) Boroxine (**Table 3, Entry 3**)

Sample of tris(4-methoxyphenyl) boronic acid anhydride (boroxine) was prepared in accordance with **General Method B**, and obtained by Kugelrohr distillation at 75°C for 4 hours gave the anhydride.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Boroxine:  $\delta$  ppm 8.16 (d,  $J$  = 8.51 Hz, 6H), 7.00 (t,  $J$  = 7.08, 7.08 Hz, 6H), 3.88 (s, 9H).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Boronic acid:  $\delta$  ppm 8.06 (d,  $J$  = 8.66 Hz, 0.03H), 7.69 (d,  $J$  = 8.23 Hz, 0.03H), 4.51 (s, 0.03H), 3.84 (s, 0.05H).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Water:  $\delta$  ppm 1.57 (s, 0.08H). The ratio of boronic acid: boroxine: water was determined to be 0.03: 1: 0.8 by NMR spectral analysis.

#### Tris(3-methoxyphenyl) Boroxine (**Table 3, Entry 4**)

Sample of tris(3-methoxyphenyl) boronic acid anhydride (boroxine) was obtained by dissolving in toluene and evaporated under reduced pressure and held under reduced pressure for 24 hours followed by sequential heating Kugelrohr distillation at 65°C for 12 hours.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Boroxine:  $\delta$  ppm 7.82 (d,  $J$  = 7.23 Hz, 3H), 7.74 (d,  $J$  = 2.55 Hz, 3H), 7.44 (t,  $J$  = 7.72, 7.72 Hz, 3H), 7.14

(dd,  $J = 8.19, 2.71$  Hz, 3H), 3.92 (s, 9H).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Boronic acid:  $\delta$  ppm 7.41-7.35 (m, 0.05H), 7.33 (d,  $J = 8.00$  Hz, 0.07H), 7.29 (d,  $J = 7.40$  Hz, 0.08H), 7.06-7.01 (m, 0.07H) 4.62 (s, 0.12H), 3.85 (d,  $J = 7.13$  Hz, 0.21H).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Water:  $\delta$  ppm 1.56 (s, 0.19H). The ratio of boronic acid: boroxine: water was determined to be 0.08: 1: 0.19 by NMR spectral analysis.

#### Tris(4-trifluoromethylphenyl) Boroxine (**Table 3, Entry 5**)

Sample of tris(4-trifluoromethylphenyl) boronic acid anhydride (boroxine) was prepared in accordance with **General Method B**, and obtained by Kugelrohr distillation at 95°C for 12 hours.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Boroxine:  $\delta$  ppm 8.35 (d,  $J = 7.65$  Hz, 6H), 7.75 (dd,  $J = 26.20, 4.46$  Hz, 6H).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Boronic acid:  $\delta$  ppm 7.85 (s, 0.06H), 7.66 (d,  $J = 7.35$  Hz, 0.06H), 4.70-4.56 (m, 0.06H).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) Water:  $\delta$  ppm 1.56 (s, 0.12H). The ratio of boronic acid: boroxine: water was determined to be 0.06: 1: 0.12 by NMR spectral analysis.

#### Synthesis of Biaryls and Heterobiaryls

#### 2-*p*-Tolylnaphthalene (**Table 1, Entry 1**)

Preparation of this compound was carried out in accordance with the **General Procedure C** using the following materials: 2-naphthyl diethylcarbamate (73 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015

mmol), anhydrous  $K_3PO_4$  (318 mg, 1.5 mmol), tri(*p*-tolyl) boroxine (101 mg, 0.32 mmol),  $PCy_3HBF_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until complete disappearance of the starting material was observed by GC/MS (5 h). Standard workup and preparatory TLC developed in hexanes afforded the product (54.8 mg, 0.25 mmol, 84%) as a colorless solid, mp 92-94 °C (hexanes), lit<sup>14</sup> 94-95 °C.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm 8.03 (s, 1H), 7.94-7.83 (m, 3H), 7.74 (dd,  $J$  = 8.50, 1.09 Hz, 1H), 7.63 (d,  $J$  = 7.94 Hz, 2H), 7.54-7.43 (m, 2H), 7.37-7.27 (m, 2H), 2.41 (d,  $J$  = 14.66 Hz, 3H). Physical and spectral data were found to be identical to those reported.<sup>15</sup>

### 1-Phenylnaphthalene (**Table 2, Entry 1**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 1-naphthyl diethylcarbamate (73 mg, 0.3 mmol),  $NiCl_2(PCy_3)_2$  (10 mg, 0.015 mmol), anhydrous  $K_3PO_4$  (318 mg, 1.5 mmol), triphenyl boroxine (90 mg, 0.29 mmol),  $PCy_3HBF_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until complete disappearance of the starting material was observed by GC/MS (5 h). Purification was performed using preparatory TLC developed in hexanes to afford the product (50 mg, 0.24 mmol, 82%) as a colorless oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm 7.91 (d,  $J$  = 8.40 Hz, 2H), 7.89-7.85 (m, 1H), 7.55 (d,  $J$  = 7.08 Hz, 1H), 7.47-7.41 (m, 3H), 7.51 (d,  $J$  = 2.26 Hz, 2H), 7.50 (d,  $J$  = 1.12 Hz, 2H), 7.49-7.47 (m, 1H). Spectral data was found to be identical to those reported.<sup>16</sup>

### 4-Methoxybiphenyl (**Table 2, Entry 2**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: phenyl diethylcarbamate (59 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5mmol), tris(*p*-Methoxyphenyl) boroxine (116 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until no further conversion to product (64%) was observed by GC/MS (5 h). Standard workup and flash silica gel chromatography, (isocratic elution with hexanes) afforded the product (32 mg, 0.17 mmol, 58%) as a colorless solid, mp 84 °C sharp (hexanes), lit<sup>17</sup> 87-88 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ ppm, 7.60-7.50 (m, 4H), 7.42 (t,  $J$  = 7.65, 7.65 Hz, 2H), 7.31 (t,  $J$  = 7.35, 7.35 Hz, 1H), 7.01-6.95 (m, 2H), 3.86 (s, 3H). Physical and spectral data were found to be identical to those reported.<sup>18</sup>

### 5-Phenylbenzo[d][1,3]dioxole (**Table 2, Entry 3**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: benzo[d][1,3]dioxol-5-yl diethylcarbamate (71 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5mmol), triphenyl boroxine (90 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until no further conversion to product (23%) was observed by GC/MS (5 h). Standard workup and flash silica gel chromatography, (isocratic elution with hexanes) afforded the product (19 mg, 0.095 mmol, 31%) as a clear yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ ppm 7.53 (d,  $J$  = 7.32 Hz, 2H), 7.42

(t,  $J = 7.52, 7.52$  Hz, 2H), 7.32 (t,  $J = 7.28, 7.28$  Hz, 1H), 7.08 (d,  $J = 8.54$  Hz, 2H), 6.90 (d,  $J = 7.82$  Hz, 1H), 6.01 (s, 2H). Spectral data was found to be identical to those reported.<sup>19</sup>

#### 3-Fluoro-4'-methoxybiphenyl (**Table 2, Entry 4**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 3-fluorophenyl diethylcarbamate (66 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5 mmol), tris(*p*-Methoxyphenyl) boroxine (116 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until no further conversion to product (80%) was observed by GC/MS (5 h). Standard workup and flash silica gel chromatography, (isocratic elution with hexanes). Further purification was performed using preparatory TLC developed in 7:1 (hexanes:CH<sub>2</sub>Cl<sub>2</sub>) to afford the product (42 mg, 0.21 mmol, 69%) as a colorless solid, mp 65-67 °C (hexanes), lit<sup>20</sup> 67-67.5 °C. <sup>1</sup>H NMR (400 MHz, *CDCl*<sub>3</sub>) δ ppm 7.46 (d,  $J = 8.66$  Hz, 2H), 7.36-7.27 (m, 2H), 7.19 (d,  $J = 10.92$  Hz, 1H), 6.99-6.89 (m, 3H), 3.83-3.77 (m, 3H). Physical and spectral data were found to be identical to those reported.<sup>21</sup>

#### Biphenyl-4-carbonitrile (**Table 2, Entry 5**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 4-cyanophenyl diethylcarbamate (65 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$ , (10 mg, 0.015 mmol),

anhydrous  $K_3PO_4$  (318 mg, 1.5 mmol), triphenyl boroxine (90 mg, 0.29 mmol),  $PCy_3HBF_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until no further conversion to product (36%) was observed by GC/MS (5 h). Standard workup and flash silica gel chromatography, (isocratic elution with hexanes) afforded the product (15 mg, 0.08 mmol, 28%) as a light orange oil.  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  ppm 7.70 (td,  $J$  = 16.83, 8.33, 8.33 Hz, 4H), 7.59 (d,  $J$  = 7.05 Hz, 2H), 7.49 (t,  $J$  = 7.29, 7.29 Hz, 2H), 7.43 (d,  $J$  = 7.21 Hz, 1H). Spectral data was found to be identical to those reported.<sup>22</sup>

#### 2, 4-Dimethylbiphenyl (**Table 2, Entry 6**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 4-cyanophenyl diethylcarbamate (65 mg, 0.3 mmol),  $NiCl_2(PCy_3)_2$ , (10 mg, 0.015 mmol), anhydrous  $K_3PO_4$  (318 mg, 1.5 mmol), triphenyl boroxine (90 mg, 0.29 mmol),  $PCy_3HBF_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until no further conversion to product (8%) was observed by GC/MS (20 h). Isolation was not attempted. LRMS (EI) (*m/z*) (%) 182[ $M^+$ ] (70), 167(100), 51(60), 62(55), 77(50), 115(48), 152(45). Mass spectra match those previously reported.<sup>23</sup>

#### 2-Benzylbiphenyl (**Table 2, Entry 7**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 2-benzylphenyl diethylcarbamate

(85 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5 mmol), triphenylboroxine (90 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until no further conversion to product (60%) was observed by GC/MS (5 h). Standard workup and flash silica gel chromatography, (isocratic elution with hexanes) afforded the product (52 mg, 0.21 mmol, 70%) as a light brown oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 7.59 (d,  $J$  = 8.07 Hz, 1H), 7.43 (dd,  $J$  = 13.65, 6.57 Hz, 1H), 7.34 (t,  $J$  = 8.45, 8.45 Hz, 4H), 7.25-7.06 (m, 7H), 6.97 (d,  $J$  = 7.31 Hz, 1H), 3.97 (d,  $J$  = 12.11 Hz, 2H). Spectral data was found to be identical to those reported.<sup>24</sup>

#### (*E*)-2-Styrylbiphenyl (**Table 2, Entry 8**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: (*E*)-2-styrylphenyl diethylcarbamate (58 mg, 0.184 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (6.3 mg, 0.0091 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (194 mg, 0.914 mmol), triphenyl boroxine (55 mg, 0.175 mmol),  $\text{PCy}_3\text{HBF}_4$  (6.7 mg, 0.0183 mmol), *o*-xylene (0.75 mL, 0.2M). The reaction was stirred at 150 °C, until no further conversion to product (99%) was observed by GC/MS (5 h). Standard workup and flash silica gel chromatography, (isocratic elution with hexanes) afforded the product (44 mg, 0.17 mmol, 93%) as a light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 7.68 (d,  $J$  = 7.48 Hz, 1H), 7.36 (t,  $J$  = 4.21, 4.21 Hz, 1H), 7.34 (d,  $J$  = 2.97 Hz, 2H), 7.31 (d,  $J$  = 6.46 Hz, 3H), 7.29-7.26 (m, 3H), 7.22 (t,  $J$  = 7.51, 7.51 Hz, 2H), 7.19-7.11 (m, 2H), 7.09-7.01 (m, 1H), 7.01-6.93 (m, 1H). Spectral data was found to be identical to those reported.<sup>25</sup>

### 2-Methoxybiphenyl (**Table 2, Entry 9**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 2-methoxyphenyl diethylcarbamate (63 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5 mmol), triphenyl boroxine (90 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until no further conversion to product (40%) was observed by GC/MS (5 h). Standard workup and flash silica gel chromatography, (isocratic elution with 5:1 (hexanes: ethyl acetate)) afforded the product (20 mg, 0.11 mmol, 36%) as a light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ ppm 7.59 (d,  $J=7.2$  Hz, 2 H), 7.45 (t,  $J=7.3$  Hz, 2 H), 7.32–7.41 (m, 3H), 7.07 (t,  $J=7.4$  Hz, 1H), 7.02 (d,  $J=8.0$  Hz, 1H), 3.88 (s, 3 H). Spectral data was found to be identical to those reported.<sup>26</sup>

### *O*-Terphenyl (**Table 2, Entry 10**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 2-biphenyl diethylcarbamate (43 mg, 0.16 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (5.5 mg, 0.008 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (170 mg, 8 mmol), triphenyl boroxine (48 mg, 0.153 mmol),  $\text{PCy}_3\text{HBF}_4$  (5.9 mg, 0.016 mmol), *o*-xylene (0.8 mL, 0.2M). The reaction was stirred at 150 °C, until no further conversion to product (69%) was observed by GC/MS (5 h). Standard workup and flash silica gel chromatography, (isocratic elution with hexanes with addition of 2% ethyl acetate). Further purification by preparatory TLC was performed using isocratic hexanes with the addition of 2% EtOAc to afford the product

(18.3 mg, 0.08 mmol, 50%) as a clear oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 7.37-7.31 (m, 4H), 7.17-7.09 (m, 6H), 7.09-7.02 (m, 4H). Spectral data was found to be identical to those reported.<sup>27</sup>

### 3-Phenylpyridine (**Table 2, Entry 11**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 3-pyridinyl diethylcarbamate (58 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5 mmol), triphenylboroxine (90 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until no further conversion to product (100%) was observed by GC/MS (5 h). Standard workup and flash silica gel chromatography, (isocratic gradient elution of 1:1 to 1:3 (hexanes: ethyl acetate) + 2%  $\text{NEt}_3$ ) afforded the product (40 mg, 0.26 mmol, 85%) as a light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 8.85 (s, 1H), 8.59 (d,  $J$  = 4.67 Hz, 1H), 7.88 (d,  $J$  = 7.82 Hz, 1H), 7.59 (d,  $J$  = 8.16 Hz, 2H), 7.48 (t,  $J$  = 7.59, 7.59 Hz, 2H), 7.44-7.40 (m, 1H), 7.37 (dd,  $J$  = 7.80, 4.88 Hz, 1H). Spectral data was found to be identical to those reported.<sup>28</sup>

### 3-*p*-Tolylpyridine (**Table 2, Entry 12**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 3-pyridyl diethylcarbamate (58 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5mmol), tri(*p*-tolyl) boroxine (103 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-

xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, after 5 hours complete conversion was observed by TLC. Standard workup and flash silica gel chromatography, (isocratic elution with 5:1 to 2:1 (hexanes: ethyl acetate) + 2% NEt<sub>3</sub>) afforded the product (44 mg, 0.26 mmol, 87%) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 8.75 (d, *J* = 1.31 Hz, 1H), 8.47 (d, *J* = 3.76 Hz, 1H), 7.80-7.70 (m, 1H), 7.39 (d, *J* = 8.10 Hz, 2H), 7.25-7.22 (m, 1H), 7.22-7.16 (m, 2H), 2.33 (d, *J* = 9.59 Hz, 3H). Spectral data was found to be identical to those reported.<sup>29</sup>

#### 3-(4-Methoxyphenyl)pyridine (**Table 2, Entry 13**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 3-pyridyl diethylcarbamate (58 mg, 0.3 mmol), NiCl<sub>2</sub>(PCy<sub>3</sub>)<sub>2</sub> (10 mg, 0.015 mmol), anhydrous K<sub>3</sub>PO<sub>4</sub> (318 mg, 1.5mmol), tri(*p*-Methoxyphenyl) boroxine (116 mg, 0.29 mmol), PCy<sub>3</sub>HBF<sub>4</sub> (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, after 5 hours complete conversion was observed by TLC. Standard workup and flash silica gel chromatography, (isocratic elution with 5:1 to 3:1 (hexanes: ethyl acetate) + 2% NEt<sub>3</sub>) afforded the product (47 mg, 0.25 mmol, 84%) as a light yellow oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ ppm 8.81 (d, *J* = 1.74 Hz, 1H), 8.54 (dd, *J* = 4.78, 1.51 Hz, 1H), 7.83 (ddd, *J* = 7.91, 2.27, 1.69 Hz, 1H), 7.54-7.50 (m, 2H), 7.33 (ddd, *J* = 7.89, 4.81, 0.69 Hz, 1H), 7.03-6.98 (m, 2H), 3.86 (s, 3H). Spectral data was found to be identical to those reported.<sup>29</sup>

3-(3-Methoxyphenyl)pyridine (**Table 2, Entry 14**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 3-pyridyl diethylcarbamate (58 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5 mmol), tris(3-methoxyphenyl) boroxine (117 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, after 5 hours complete conversion was observed by TLC. Standard workup and flash silica gel chromatography, (isocratic elution with 5:1 to 3:1 (hexanes: ethyl acetate) + 2%  $\text{NEt}_3$ ) afforded the product (36 mg, 0.19 mmol, 65%) as light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 8.84 (s, 1H), 8.58 (d,  $J$  = 3.99 Hz, 1H), 7.91-7.81 (m, 1H), 7.43-7.30 (m, 2H), 7.15 (d,  $J$  = 8.02 Hz, 1H), 7.11 (dd,  $J$  = 11.37, 9.26 Hz, 1H), 6.93 (td,  $J$  = 12.63, 6.31, 6.31 Hz, 1H), 3.86 (s, 3H). Spectral data was found to be identical to those reported.<sup>30</sup>

3-(4-(Trifluoromethyl)phenyl)pyridine (**Table 3, Entry 15**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 3-pyridyl diethylcarbamate (58 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5 mmol), tris(4-trifluoromethylphenyl) boroxine (150 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, after 20 hours complete conversion was observed by TLC. Standard workup and flash silica gel chromatography, (isocratic elution with 7:1 to 5:1 (hexanes: ethyl acetate) + 2%  $\text{NEt}_3$ ) afforded the product (47 mg, 0.21 mmol, 70%) as a light yellow oil.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm

8.85 (d,  $J = 1.40$  Hz, 1H), 8.64 (d,  $J = 3.76$  Hz, 1H), 7.92-7.84 (m, 1H), 7.73 (d,  $J = 8.32$  Hz, 2H), 7.70-7.63 (m, 2H), 7.39 (dd,  $J = 7.72, 4.82$  Hz, 1H). Spectral data was found to be identical to those reported.<sup>29</sup>

#### 2-Phenylquinoline (**Table 2, Entry 16**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 2-quinolinyl diethylcarbamate (72 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5 mmol), triphenylboroxine (90 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until complete conversion to product (100%) was observed by GC/MS (5 h). Standard workup and flash silica gel chromatography, (isocratic elution with 5:1 (hexanes: ethyl acetate) + 2%  $\text{NEt}_3$ ) afforded the product (31 mg, 0.15 mmol, 51%) as light yellow solid, 83-84 °C (hexanes), lit<sup>31</sup> 84-85 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) δ ppm 8.23 (d,  $J = 8.53$  Hz, 1H), 8.17 (d,  $J = 6.31$  Hz, 2H), 7.89 (d,  $J = 8.57$  Hz, 1H), 7.84 (d,  $J = 8.16$  Hz, 1H), 7.74 (t,  $J = 7.67, 7.67$  Hz, 1H), 7.60 (d,  $J = 7.36$  Hz, 1H), 7.54 (t,  $J = 7.23, 7.23$  Hz, 2H), 7.46 (dd,  $J = 16.64, 7.55$  Hz, 2H). Physical and spectral data were found to be identical to those reported.<sup>28</sup>

#### 4-Phenyl-9*H*-carbazole (**Table 2, Entry 17**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 9*H*-carbazol-4-yl

diethylcarbamate (85. mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5 mmol), triphenyl boroxine (90 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, until no further conversion to product (45%) was observed by GC/MS (5 h). Standard workup and flash silica gel chromatography, (isocratic elution with hexanes). Further purification was performed using preparatory TLC developed in toluene to afford the product (26 mg, 0.108 mmol, 36%) as colorless solid, mp 105-111 °C (hexanes). IR (film  $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3415, 2928, 1602, 1456, 1386, 1334, 1323, 757, 728, 701;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 7.97 (s, 1H), 7.92 (d,  $J$  = 7.79 Hz, 1H), 7.47 (dd,  $J$  = 8.07, 1.35 Hz, 1H), 7.40-7.34 (m, 1H), 7.34-7.28 (m, 2H), 7.27 (s, 1H), 7.26-7.22 (m, 2H), 7.21-7.15 (m, 1H) 7.11-7.05 (m, 1H), 6.95 (dd,  $J$  = 6.85, 1.36 Hz, 1H), 6.86-6.78 (m, 1H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 139.8 (1C), 139.6 (1C), 129.1 (2C), 128.3 (2C), 127.4 (1C), 125.8 (1C), 125.6 (1C), 125.5 (1C), 122.4 (1C), 121.09 (1C), 120.3 (1C), 119.4 (1C), 119.0 (1C), 110.5 (1C), 110.3 (1C), 109.4 (1C); LRMS (EI)  $m/z$  (%) 243[ $\text{M}^+$ ] (100), 242 (51), 68 (52), 241 (48), 130 (30). HRMS (EI) calculated for  $\text{C}_{18}\text{H}_{13}\text{N}$  [ $\text{M}^+$ ] 243.1048: found 243.1042.

### 2,2,7-Trimethyl-5-phenyl-4a,8a-dihydro-2*H*-chromene (**6**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 2,2,7-trimethyl-4a,8a-dihydro-2*H*-chromen-5-yl diethylcarbamate (87 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5 mmol), triphenylboroxine (90 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, after 5 hours no further conversion to the product (67%) was observed by

GC/MS. Standard workup and flash silica gel chromatography, (isocratic elution with hexanes) afforded the product (42 mg, 0.17 mmol, 56%) as a light yellow oil. IR (film  $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3028, 2974, 2923, 1607, 1561, 1496, 1453, 1388, 1274, 1360, 1323, 1295, 1215, 1137, 1110, 1017, 895, 868, 847, 7834, 767, 702, 650, 602;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 7.31 (d,  $J$  = 6.85 Hz, 2H), 7.25 (s, 1H), 6.59 (d,  $J$  = 8.77 Hz, 2H), 6.21 (t,  $J$  = 9.70, 9.70 Hz, 2H), 5.41 (dd,  $J$  = 19.89, 9.98 Hz, 2H), 2.23 (s, 3H), 1.37 (s, 6H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 140.0 (1C), 139.4 (1C), 138.7 (1C), 129.6 (2C), 129.3 (2C), 128.0 (2C), 127.0 (2C), 122.9 (1C), 120.7 (1C), 116.4 (1C), 116.1 (1C), 75.2 (1C), 27.7 (3C), 21.4 (1C); LRMS (EI) ( $m/z$ ) (%), 250[ $\text{M}^+$ ](15), 236(20), 235(100), 165(12); HRMS (EI) calculated for  $\text{C}_{18}\text{H}_{18}\text{O}$  [ $\text{M}^+$ ] 250.1358: found 250.1354.

### 2-(6-Methoxybiphenyl-2-yl)benzofuran (**8**)

Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 2-(benzofuran-2-yl)-6-methoxyphenyl diethylcarbamate (102 mg, 0.3 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (10 mg, 0.015 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (318 mg, 1.5 mmol), triphenyl boroxine (90 mg, 0.29 mmol),  $\text{PCy}_3\text{HBF}_4$  (11 mg, 0.03 mmol), *o*-xylene (1.5 mL, 0.2M). The reaction was stirred at 150 °C, after 5 hours no further conversion to the product (52%) was observed by GC/MS. Purification of the crude was performed using preparatory TLC developed in hexanes to afford the product (19 mg, 0.06 mmol, 21%) as a colorless waxy solid, mp 130°C sharp (hexanes); IR ( $\text{CHCl}_2$  film)  $\nu_{\text{max}}$   $\text{cm}^{-1}$  3053, 3011, 2958, 2926, 2921, 2836, 1578, 1145, 1432, 1309, 1262, 1240, 1172, 1117, 1103, 1031, 934, 822, 796, 755, 703;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$

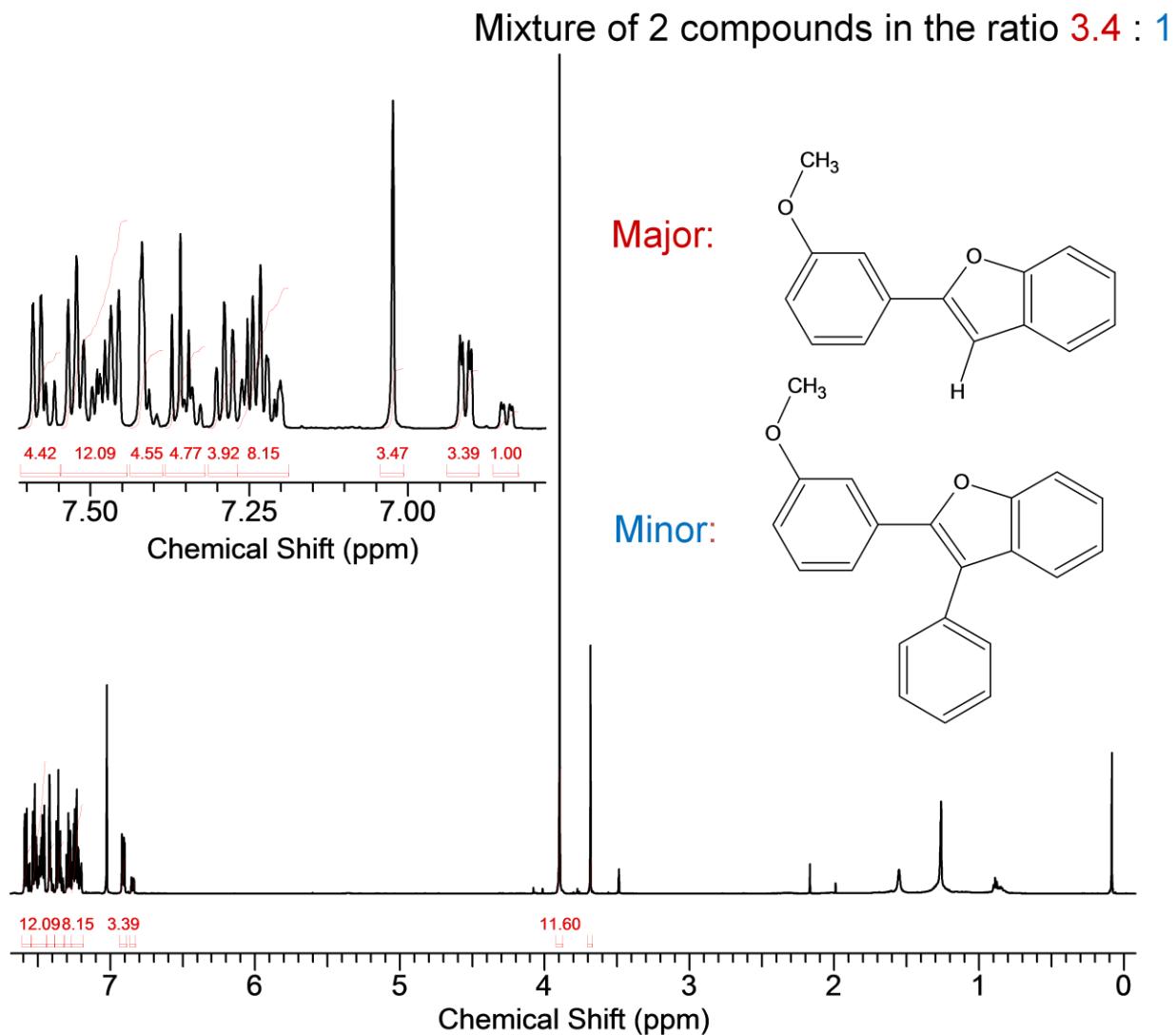
3)  $\delta$  ppm 7.63 (d,  $J$  = 7.92 Hz, 1H), 7.42-7.29 (m, 5H), 7.23-7.16 (m, 3H), 7.13 (dd,  $J$  = 15.30, 7.87 Hz, 1H), 7.03 (t,  $J$  = 7.45, 7.45 Hz, 1H), 6.92 (d,  $J$  = 8.20 Hz, 1H), 5.51 (s, 1H), 3.68 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 157.2 (1C), 154.4 (1C), 153.9 (1C), 137.3 (1C), 130.0 (3C), 128.6 (1C), 128.4 (2C), 127.3 (1C), 124.1 (1C), 122.5 (1C), 120.9 (1C), 119.8 (1C), 111.0 (2C), 110.82 (2C), 105.91 (1C), 55.98 (1C); LRMS (EI) ( $m/z$  (%)) 300[M $^+$ ] (100), 239(25), 301(270), 269(21); HRMS (EI) calculated for  $\text{C}_{21}\text{H}_{16}\text{O}_2$  [M $^+$ ] 300.1150: found 300.1151;

#### 4-(4-Methoxyphenyl)-3-phenylpyridine (**10**)

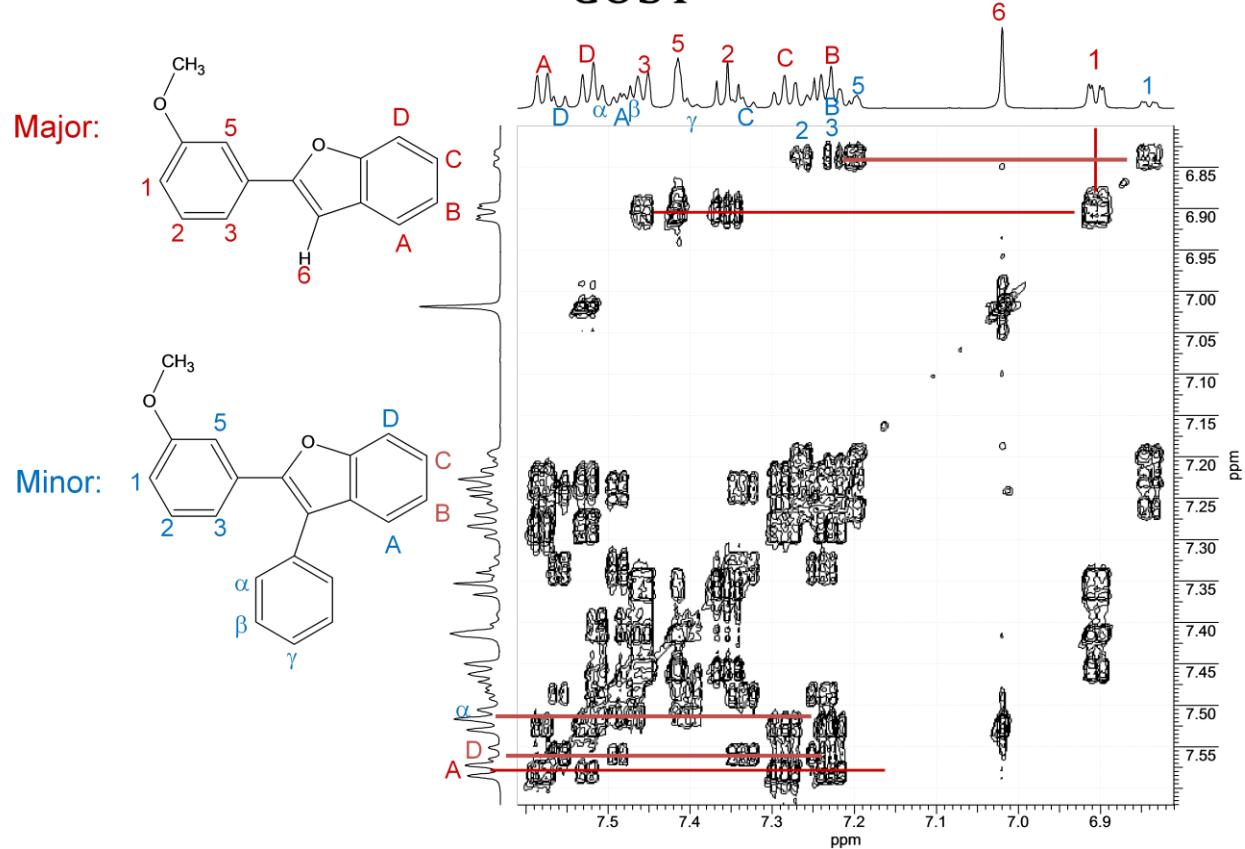
Preparation of this compound was carried out in accordance with **General Procedure C** using the following materials: 4-(4-methoxyphenyl)pyridin-2-yl diethylcarbamate (64 mg, 0.21 mmol),  $\text{NiCl}_2(\text{PCy}_3)_2$  (7.59 mg, 0.011 mmol), anhydrous  $\text{K}_3\text{PO}_4$  (227.9 mg, 1.07 mmol), triphenyl boroxine (64 mg, 0.20 mmol),  $\text{PCy}_3\text{HBF}_4$  (7.9 mg, 0.021 mmol), *o*-xylene (1.07 mL, 0.2M), stirred at 150°C for 2 hours. Reaction was stopped when starting material was no longer observed by TLC. Standard workup and flash silica gel chromatography, (isocratic elution with 5:1 to 2:1 (hexanes: ethyl acetate) + 2%  $\text{NEt}_3$ ) afforded the product (48 mg, 0.18 mmol, 91%) as a light orange oil. IR (film  $\text{CH}_2\text{Cl}_2$ )  $\nu_{\text{max}}$   $\text{cm}^{-1}$  2836, 1608, 1586, 1515, 1496, 1474, 1444, 1398, 1295, 1250, 1178, 1110, 1042, 1023, 1006, 827, 808, 781, 756, 701;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 8.57-8.53 (m, 2H), 7.28 (d,  $J$  = 5.03 Hz, 1H), 7.23 (td,  $J$  = 10.30, 5.18, 5.18 Hz, 3H), 7.17-7.09 (m, 2H), 7.09-7.00 (m, 2H), 6.75 (d,  $J$  = 8.78 Hz, 2H), 3.74 (s, 3H);  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  ppm 159.3 (1C), 150.9 (1C), 148.6 (1C), 147.3 (1C), 137.9 (1C), 135.6 (1C), 130.7 (1C), 130.5 (2C), 129.7 (C), 128.3 (2C), 127.2 (1C), 124.4 (1C), 113.7 (2C), 55.1 (1C); EIMS ( $m/z$  (%)) 218[M $^+$ ](100),

69(99), 131(87), 263(45), 100(28), 501(15), 217(17), 169(12); HRMS (EI) calculated for  $C_{18}H_{15}NO$   $[M^+]$  261.1154: found 261.1142.

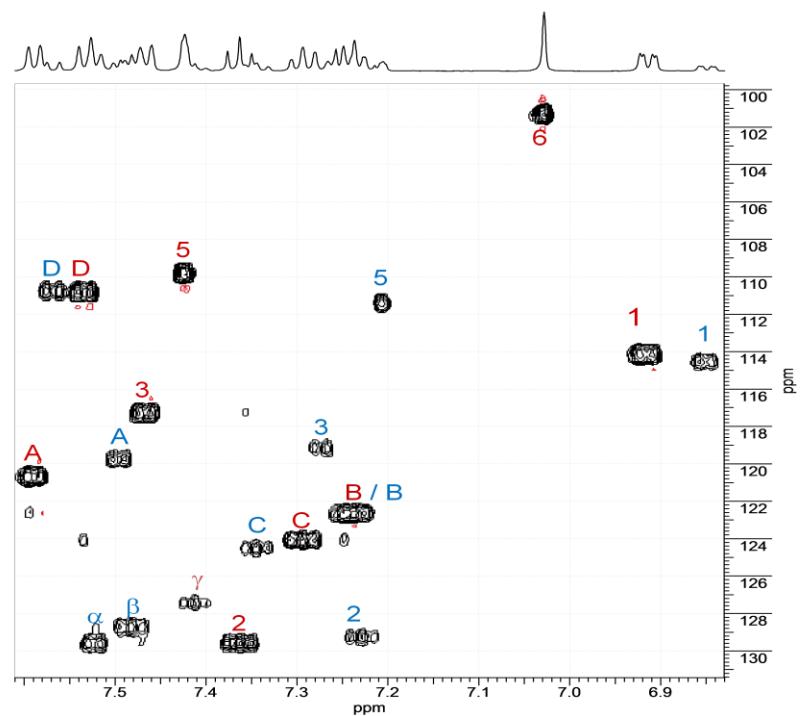
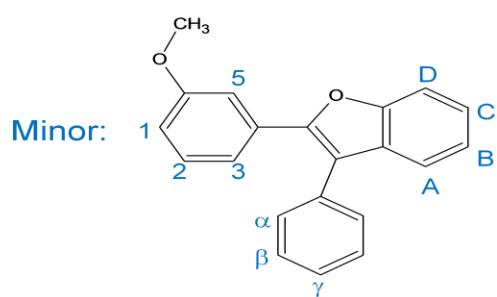
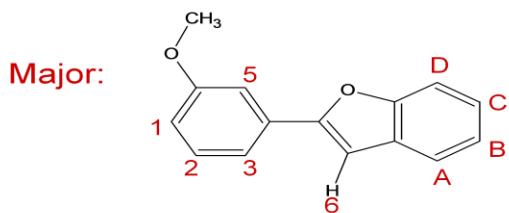
### NMR Analysis of Impurities for the Reaction of (7)



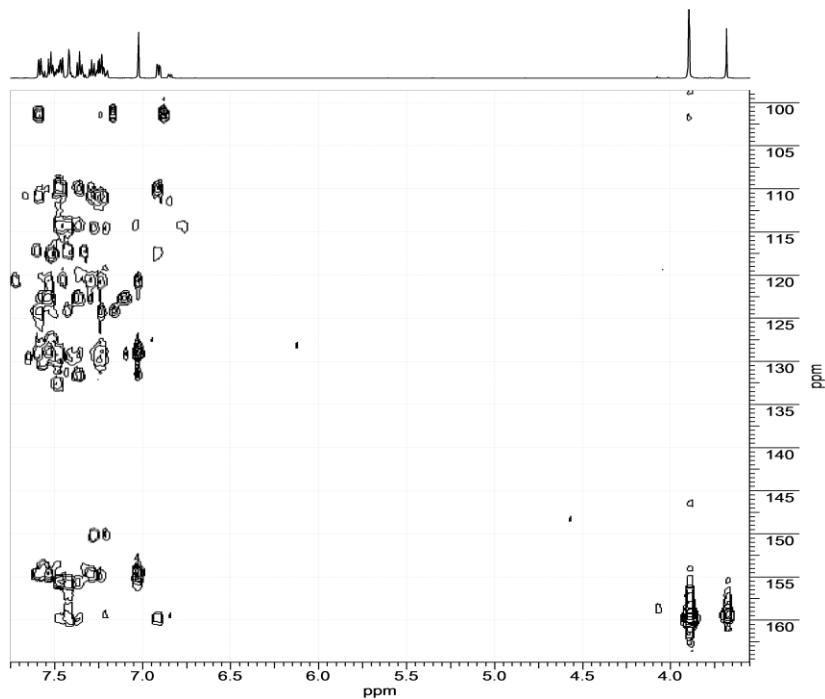
## COSY



## HSQC



## HMBC



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## **I Attached Spectra**

