# **Supporting Information**

# Isonicotinate Ester-Catalyzed Decarboxylative Borylation of (Hetero)Aryl- and Alkenyl Carboxylic Acids through N-Hydroxyphthalimide Esters

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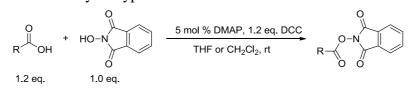
#### **1. General Information**

All reactions were carried out in oven-dried Schlenk tubes under argon atmosphere (purity≥99.999%) unless otherwise mentioned. Commercial reagents were purchased from Adamas-beta, TCI and Aldrich. Organic solutions were concentrated under reduced pressure on Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

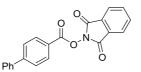
<sup>1</sup>H-NMR, <sup>11</sup>B-NMR and <sup>13</sup>C-NMR spectra were recorded on a Bruker Avance 400 spectrometer at ambient temperature. Data for <sup>1</sup>H-NMR are reported as follows: chemical shift (ppm, scale), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet and/or multiplet resonances, br = broad), coupling constant (Hz), and integration. Data for <sup>13</sup>C-NMR are reported in terms of chemical shift (ppm, scale), multiplicity, and coupling constant (Hz). HRMS analysis was performed on Finnigan LCQ advantage Max Series MS System. ESI-mass data were acquired using a Thermo LTQ Orbitrap XL Instrument equipped with an ESI source and controlled by Xcalibur software.

#### 2. Procedure for the Synthesis of Redox Active Esters

The redox active esters can be synthesized by the condensation of corresponding carboxylic acids with *N*-hydroxyphthalimide.



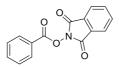
The corresponding aryl- or alkenyl carboxylic acid (12 mmol, 1.2 equiv.), *N*-hydroxyphthalimide (1.63 g, 10 mmol, 1.0 equiv.), and 4-dimethylaminopyridine (61 mg, 0.5 mmol, 5 mol %) were mixed in a flask with a magnetic stirring bar. 40 mL dry  $CH_2Cl_2$  was added, then a solution of *N*,*N* -dicyclohexylcarbodiimide (2.48 g, 12 mmol, 1.2 equiv.) in  $CH_2Cl_2$  (15 mL) was added slowly at room temperature. The reaction mixture was stirred at room temperature for 2 h. After *N*-hydroxyphthalimide was completely converted, the white precipitate was filtered off and the solution was concentrated under vacuum. Corresponding redox active esters were purified by column chromatography on silica gel ( $CH_2Cl_2$  or petroleum ether/ethyl acetate as eluent).



**1, 3-dioxoisoindolin-2-yl [1,1'-biphenyl]-4-carboxylate (S-1):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (3.05 g, 89%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.25 (d, J = 8.2 Hz, 2H), 7.92 (dd, J = 5.1, 3.2 Hz, 2H), 7.80 (dd, J = 5.1, 3.2 Hz, 2H), 7.75 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 7.2 Hz, 2H), 7.49 (t, J = 7.4 Hz, 2H), 7.45 – 7.38 (m, 1H).

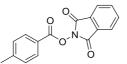
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.7, 162.1, 147.7, 139.5, 134.8, 131.2, 129.1, 128.7, 127.5, 127.4, 124.1, 123.9. (one carbon signal is overlapped)



**1, 3-dioxoisoindolin-2-yl benzoate (S-2):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.40 g, 90%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.19 (d, *J* = 7.7 Hz, 2H), 7.91 (dd, *J* = 4.6, 3.0 Hz, 2H), 7.81 (dd, *J* = 4.6, 3.0 Hz, 2H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H).

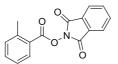
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.8, 162.1, 134.9, 134.8, 130.6, 129.0, 128.9, 125.3, 124.0.



**1, 3-dioxoisoindolin-2-yl 4-methylbenzoate (S-3):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.64 g, 94%).

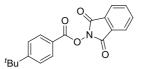
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.07 (d, *J* = 7.9 Hz, 2H), 7.94 – 7.89 (m, 2H), 7.83 – 7.77 (m, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 2.45 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.8, 162.2, 146.1, 134.8, 130.7, 129.6, 129.1, 124.0, 122.4, 21.9.



**1, 3-dioxoisoindolin-2-yl 2-methylbenzoate (S-4):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.61 g, 93%).

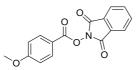
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (d, *J* = 7.8 Hz, 1H), 7.92 (dd, *J* = 4.4, 3.2 Hz, 2H), 7.81 (dd, *J* = 4.4, 3.2 Hz, 2H), 7.54 (t, *J* = 7.5 Hz, 1H), 7.37 – 7.31 (m, 2H), 2.64 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  163.1, 162.3, 142.1, 134.8, 134.0, 132.0, 131.4, 129.1, 126.1, 124.4, 124.0, 21.6.



**1, 3-dioxoisoindolin-2-yl 4-(tert-butyl)benzoate (S-5):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (3.01 g, 93%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.13 (d, *J* = 8.2 Hz, 2H), 7.96 – 7.86 (m, 2H), 7.84 – 7.77 (m, 2H), 7.55 (d, *J* = 8.1 Hz, 2H), 1.37 (s, 9H).

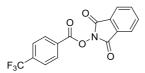
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.8, 162.2, 159.0, 134.8, 130.6, 129.1, 125.9, 124.0, 122.4, 35.34, 31.0.



**1, 3-dioxoisoindolin-2-yl 4-methoxybenzoate (S-6):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.67 g, 90%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.15 (d, *J* = 8.6 Hz, 2H), 7.97 – 7.88 (m, 2H), 7.84 – 7.77 (m, 2H), 7.00 (d, *J* = 8.6 Hz, 2H), 3.90 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.9, 162.4, 162.2, 134.8, 132.9, 129.0, 124.0, 117.2, 114.23, 55.6.

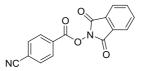


**1, 3-dioxoisoindolin-2-yl 4-(trifluoromethyl)benzoate (S-7):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.94 g, 88%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 (d, *J* = 8.2 Hz, 2H), 7.95 (dd, *J* = 5.5, 3.1 Hz, 2H), 7.86 – 7.80 (m, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.9, 161.8, 136.2 (q, *J* = 33.0 Hz), 135.0, 131.1, 129.0, 128.7, 126.0 (q, *J* = 3.7 Hz), 124.2, 123.3 (q, *J* = 273.1 Hz).

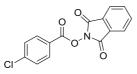
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.39.



**1, 3-dioxoisoindolin-2-yl 4-cyanobenzoate (S-8):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a orange solid (2.77 g, 95%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.31 (d, *J* = 8.1 Hz, 2H), 7.96 – 7.92 (m, 2H), 7.89 – 7.82 (m, 4H).

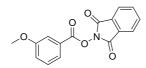
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.7, 161.5, 135.0, 132.6, 131.1, 129.2, 128.9, 124.2, 118.3, 117.4.



**1, 3-dioxoisoindolin-2-yl 4-chlorobenzoate (S-9):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.89 g, 95%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.14 (d, *J* = 8.2 Hz, 2H), 7.95 – 7.91 (m, 2H), 7.85 – 7.81 (m, 2H), 7.53 (d, *J* = 8.3 Hz, 2H).

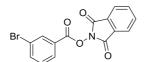
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.1, 162.0, 141.7, 134.9, 132.0, 129.4, 129.0, 124.1, 123.7.



**1, 3-dioxoisoindolin-2-yl 3-methoxybenzoate (S-10):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.82 g, 95%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 – 7.92 (m, 2H), 7.86 – 7.79 (m, 3H), 7.67 (s, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.24 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.89 (s, 3H).

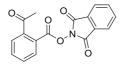
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.8, 162.1, 159.8, 134.8, 130.0, 129.0, 126.4, 124.0, 123.1, 121.7, 114.7, 55.6.



**1, 3-dioxoisoindolin-2-yl 3-bromobenzoate** (**S-11**): This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (3.11 g, 90%).

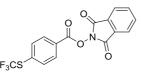
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.33 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.93 (dd, *J* = 4.2, 3.0 Hz, 2H), 7.87 – 7.80 (m, 3H), 7.43 (t, *J* = 7.9 Hz, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.8, 161.7, 137.9, 134.9, 133.5, 130.4, 129.2, 129.0, 127.2, 124.1, 122.9.



**1, 3-dioxoisoindolin-2-yl 2-acetylbenzoate (S-12):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.63 g, 85%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.10 (d, *J* = 7.7 Hz, 1H), 7.93 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.82 (dd, *J* = 5.3, 3.2 Hz, 2H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.67 – 7.56 (m, 2H), 2.60 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  201.0, 163.6, 161.8, 142.8, 134.9, 133.7, 130.7, 130.5, 129.0, 127.6, 124.4, 124.1, 29.5.

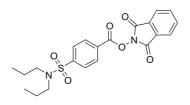


**1, 3-dioxoisoindolin-2-yl 4-((trifluoromethyl)thio)benzoate (S-13):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (3.30 g, 90%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.24 (d, J = 8.1 Hz, 2H), 7.96 – 7.92 (m, 2H), 7.86 – 7.79 (m, 4H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.0, 161.8, 135.6, 134.9, 132.6 (q, *J* = 2.0 Hz), 131.4, 129.2 (q, *J* = 308.6 Hz), 128.9, 127.3, 124.2.

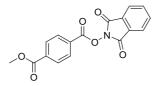
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -41.35.



**1, 3-dioxoisoindolin-2-yl 4-(N,N-dipropylsulfamoyl)benzoate (S-14):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (3.74 g, 87%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.33 (d, *J* = 8.1 Hz, 2H), 8.02 – 7.91 (m, 4H), 7.86 – 7.82 (m, 2H), 3.17 – 3.10 (m, 4H), 1.63 – 1.50 (m, 4H), 0.89 (t, *J* = 7.4 Hz, 6H).

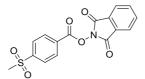
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.8, 161.7, 146.2, 135.0, 131.3, 128.9, 128.6, 127.4, 124.2, 49.9, 21.9, 11.2.



**1, 3-dioxoisoindolin-2-yl methyl terephthalate (S-15):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (3.12 g, 96%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.27 (d, *J* = 8.1 Hz, 2H), 8.20 (d, *J* = 8.2 Hz, 2H), 7.96 – 7.92 (m, 2H), 7.86 – 7.82 (m, 2H), 3.99 (s, 3H).

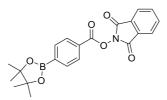
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 165.8, 162.2, 161.9, 135.6, 134.9, 130.6, 129.9, 129.0, 128.9, 124.1, 52.6.



**1, 3-dioxoisoindolin-2-yl 4-(methylsulfonyl)benzoate (S-16):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (3.21 g, 93%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.41 (d, *J* = 8.1 Hz, 2H), 8.14 (d, *J* = 8.0 Hz, 2H), 7.97 – 7.93 (m, 2H), 7.87 – 7.83 (m, 2H), 3.12 (s, 3H).

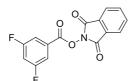
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.7, 161.5, 146.0, 135.0, 131.6, 130.2, 128.9, 128.0, 124.2, 44.3.



1, 3-dioxoisoindolin-2-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (S-17): This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (3.58 g, 91%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.17 (d, *J* = 7.6 Hz, 2H), 7.99 – 7.90 (m, 4H), 7.82 (dd, *J* = 4.3, 2.8 Hz, 2H), 1.38 (s, 12H).

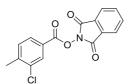
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.9, 162.0, 135.0, 134.8, 129.5, 129.1, 127.3, 124.0, 84.4, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**1, 3-dioxoisoindolin-2-yl 3,5-difluorobenzoate (S-18):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.61 g, 86%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 – 7.92 (m, 2H), 7.86 – 7.82 (m, 2H), 7.76 – 7.61 (m, 2H), 7.21 – 7.14 (m, 1H).

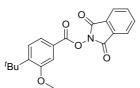
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.1 (d, J = 11.8 Hz), 161.7 (t, J = 5.9 Hz), 161.0, 135.0, 129.0, 128.3 (t, J = 9.7 Hz), 124.2, 114.2 – 113.5 (m), 110.5 (t, J = 25.1 Hz). <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -106.79.



**1, 3-dioxoisoindolin-2-yl 3-chloro-4-methylbenzoate (S-19):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.90 g, 92%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (s, 1H), 7.99 – 7.87 (m, 3H), 7.82 (dd, *J* = 4.8, 2.2 Hz, 2H), 7.40 (d, *J* = 7.9 Hz, 1H), 2.49 (s, 3H).

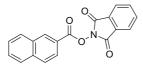
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.9, 161.8, 144.0, 135.1, 134.8, 131.4, 131.0, 128.9, 128.7, 124.3, 124.0, 20.6.



**1, 3-dioxoisoindolin-2-yl 4-(tert-butyl)-3-methoxybenzoate (S-20):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (3.18 g, 90%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (dd, *J* = 5.3, 2.9 Hz, 2H), 7.84 – 7.74 (m, 3H), 7.61 (s, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 3.92 (s, 3H), 1.40 (s, 9H).

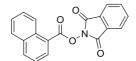
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.8, 162.1, 158.6, 146.2, 134.7, 129.0, 127.0, 124.0, 123.8, 123.2, 112.6, 55.3, 35.5, 29.3.



**1, 3-dioxoisoindolin-2-yl 2-naphthoate (S-21):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.95 g, 93%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.82 (s, 1H), 8.14 (d, *J* = 8.6 Hz, 1H), 8.04 – 7.90 (m, 5H), 7.83 (dd, *J* = 5.3, 2.2 Hz, 2H), 7.68 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.5 Hz, 1H).

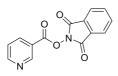
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.0, 162.1, 136.3, 134.8, 133.0, 132.3, 129.6, 129.3, 129.0, 128.8, 127.9, 127.2, 125.2, 124.0, 122.4.



**1, 3-dioxoisoindolin-2-yl 1-naphthoate (S-22):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.88 g, 91%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.85 (d, *J* = 8.6 Hz, 1H), 8.54 (d, *J* = 7.3 Hz, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 7.99 – 7.91 (m, 3H), 7.83 (dd, *J* = 5.0, 3.0 Hz, 2H), 7.67 (t, *J* = 7.7 Hz, 1H), 7.63 – 7.56 (m, 2H).

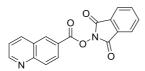
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.1, 162.3, 135.6, 134.8, 133.8, 131.9, 131.5, 129.1, 128.8, 128.7, 126.8, 125.4, 124.5, 124.1, 121.7.



**1, 3-dioxoisoindolin-2-yl nicotinate (S-23):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.36 g, 88%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 9.40 (s, 1H), 8.93 (d, *J* = 4.7 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.87 – 7.83 (m, 2H), 7.55 – 7.48 (m, 1H).

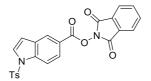
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 161.7, 161.7, 155.0, 151.5, 138.0, 135.0, 128.9, 124.1, 123.7, 121.9.



**1, 3-dioxoisoindolin-2-yl quinoline-6-carboxylate (S-24):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.99 g, 94%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.10 (d, *J* = 3.6 Hz, 1H), 8.82 (s, 1H), 8.40 (d, *J* = 8.9 Hz, 1H), 8.35 (d, *J* = 8.3 Hz, 1H), 8.27 (d, *J* = 8.8 Hz, 1H), 7.96 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.84 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.56 (dd, *J* = 8.2, 4.3 Hz, 1H).

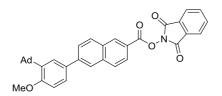
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.4, 162.0, 153.1, 150.1, 138.1, 134.9, 132.9, 130.2, 129.3, 129.0, 127.5, 124.2, 123.5, 122.4.



**1, 3-dioxoisoindolin-2-yl 1-tosyl-1H-indole-5-carboxylate (S-25):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (4.14 g, 90%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.43 (s, 1H), 8.14 – 8.09 (m, 2H), 7.96 – 7.88 (m, 2H), 7.85 – 7.75 (m, 4H), 7.69 (d, *J* = 3.2 Hz, 1H), 7.27-7.23 (m, 2H), 6.77 (d, *J* = 3.2 Hz, 1H), 2.36 (s, 3H).

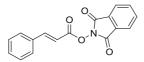
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.9, 162.1, 145.7, 138.2, 134.8, 134.7, 130.7, 130.2, 129.0, 128.2, 126.9, 126.5, 125.2, 124.0, 120.2, 113.8, 109.4, 21.6.



1,3-dioxoisoindolin-2-yl6-(3-((3s)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoate (S-26): This compound was prepared following general procedure for thesynthesis of redox active ester. It was isolated as a white solid (5.01 g, 90%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.81 (s, 1H), 8.14 (d, *J* = 8.5 Hz, 1H), 8.06 – 7.98 (m, 3H), 7.98 – 7.92 (m, 2H), 7.88 – 7.80 (m, 3H), 7.62 (s, 1H), 7.57 (d, *J* = 8.5 Hz, 1H), 7.01 (d, *J* = 8.4 Hz, 1H), 3.91 (s, 3H), 2.19 (s, 6H), 2.11 (s, 3H), 1.81 (s, 6H).

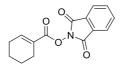
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.0, 162.2, 159.1, 142.5, 139.1, 136.8, 134.8, 132.8, 132.2, 131.0, 130.0, 129.1, 128.8, 127.0, 126.0, 125.8, 125.6, 124.8, 124.0, 121.7, 112.1, 55.2, 40.6, 37.2, 37.1, 29.1.



**1, 3-dioxoisoindolin-2-yl cinnamate (S-27):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.60 g, 89%).

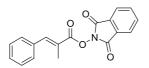
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.96 (d, J = 16.1 Hz, 1H), 7.91 (dd, J = 4.6, 3.3 Hz, 2H), 7.80 (dd, J = 4.6, 3.2 Hz, 2H), 7.60 (d, J = 7.2 Hz, 2H), 7.49 – 7.41 (m, 3H), 6.66 (d, J = 16.1 Hz, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 163.0, 162.1, 150.0, 134.8, 133.6, 131.6, 129.1, 129.0, 128.7, 124.0, 111.8.



**1, 3-dioxoisoindolin-2-yl cyclohex-1-ene-1-carboxylate (S-28):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.47 g, 91%).

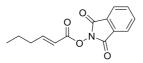
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 (dd, J = 4.9, 3.0 Hz, 2H), 7.79 (dd, J = 4.9, 3.1 Hz, 2H), 7.41 – 7.37 (m, 1H), 2.42 – 2.36 (m, 2H), 2.34 – 2.28 (m, 2H), 1.77 – 1.63 (m, 4H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  163.0, 162.3, 145.8, 134.7, 129.1, 126.2, 123.9, 26.3, 24.0, 21.7, 21.0.



**1, 3-dioxoisoindolin-2-yl (E)-2-methyl-3-phenylacrylate (S-29):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.70 g, 88%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.00 (s, 1H), 7.92 (dd, *J* = 4.8, 3.2 Hz, 2H), 7.81 (dd, *J* = 4.7, 3.0 Hz, 2H), 7.50 – 7.34 (m, 5H), 2.27 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 164.6, 162.2, 143.7, 134.8, 134.8, 130.0, 129.4, 129.1, 128.6, 124.0, 123.8, 14.3.



**1, 3-dioxoisoindolin-2-yl (E)-hex-2-enoate (S-30):** This compound was prepared following general procedure for the synthesis of redox active ester. It was isolated as a white solid (2.41 g, 93%).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.91 – 7.87 (m, 2H), 7.88 – 7.84 (m, 2H), 7.40 – 7.28 (m, 1H), 6.09 (d, *J* = 15.8 Hz, 1H), 2.34 – 2.29 (m, 2H), 1.62 – 1.49 (m, 2H), 0.99 (t, *J* = 7.4 Hz, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 162.4, 162.1, 155.9, 134.7, 129.0, 123.9, 115.6, 34.9, 20.9, 13.7.

## 3. Investigation of the Key Reaction Parameters

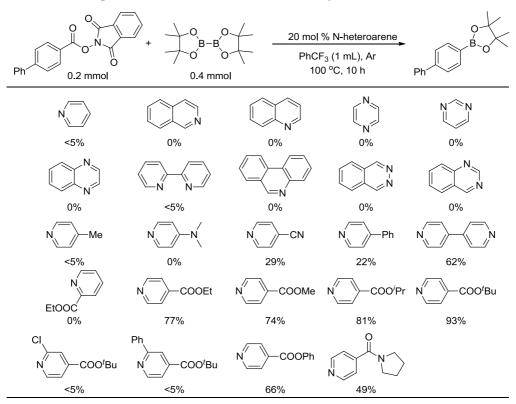
Ph	0 N + 0.2 mmol	$\begin{array}{c} 0 \\ 0 \\ 0 \\ 0 \\ 0.4 \text{ mmol} \end{array} \qquad \begin{array}{c} 20 \text{ mmol} \\ 20 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $	Solvent (1 mL), Ar 100 °C, 10 h
	entry	solvent	yield (%)
	1	DCE	20
	2	DMF	8
	3	MeCN	40
	4	Dioxane	13
	5	EtOAc	88
	6	Toluene	47
	7	PhCl	55
	8	PhCF <sub>3</sub>	93

#### **Table S1: Screening of different solvents**

Reaction conditions: 0.2 mmol redox active ester, 0.4 mmol B2pin2, 20 mol %

isonicotinate tert-butyl ester, 1 mL solvent, 100 °C, 10 h. Yield determined by GC.

# Table S2: Screening of different N-heteroarene catalysts



Reaction conditions: 0.2 mmol redox active ester, 0.4 mmol B<sub>2</sub>pin<sub>2</sub>, 20 mol % *N*-heteroarene, 1 mL PhCF<sub>3</sub>, 100 °C, 10 h. Yield determined by GC.

Ph 0.2 m	N = + + + + + + + + + + + + + + + + + +	mol % N COO <sup>t-</sup> Bu PhCF <sub>3</sub> (1 mL), Ar Additive, T, 10 h	Ph Bo
entry	additive	t (°C)	yield (%)
1	-	70	77
2	-	80	83
3	-	90	89
4	-	100	93
5	-	110	94
6	20 mol % potassium phthalimide	100	74
7	100 mol % NaOAc	100	58
8	100 mol % PhONa	100	trace

#### **Table S3: Screening of different temperature and additives**

Reaction conditions: 0.2 mmol redox active ester, 0.4 mmol B<sub>2</sub>pin<sub>2</sub>, 20 mol % isonicotinate *tert*-butyl ester, additive, 1 mL PhCF<sub>3</sub>, T, 10 h. Yield determined by GC.

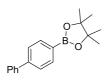
#### 4. Experimental procedures and spectral data

#### 4.1 Experimental procedures

General Procedure for Decarboxylative Borylation

A 10 mL Schlenk tube containing a stirring bar was charged with redox active ester (1.0 equiv., 0.2 mmol) and  $B_2pin_2$  (2.0 equiv., 0.4 mmol). The tube was then evacuated and back-filled with argon three times. Anhydrous trifluorotoluene (PhCF<sub>3</sub>, 1.0 mL) was added subsequently, then isonicotinate *tert*-butyl ester (15 mol %, 0.03 mmol) was added. The tube was sealed by a plastic screw cap and heated at 110 °C for 15 h. After cooling to room temperature, the organic layers were concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give the product.

#### 4.2 Spectral Data



**2-([1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1):** Following the general procedure, obtained in 85% yield as a white solid (47.6 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.* **2017**, *56*, 2482–2486).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.89 (d, *J* = 8.0 Hz, 2H), 7.64-7.59 (m, 4H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.35 (t, *J* = 7.4 Hz, 1H), 1.36 (s, 12H).

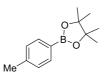
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.0, 141.1, 135.3, 128.8, 127.6, 127.3, 126.5, 83.8, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane** (2): Following the general procedure, obtained in 86% yield as a colorless liquid (35.1 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2017**, *139*, 607–610).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 – 7.79 (m, 2H), 7.49 – 7.43 (m, 1H), 7.39 – 7.35 (m, 2H), 1.35 (s, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  133.7, 130.2, 126.7, 82.8, 23.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane** (3): Following the general procedure, obtained in 91% yield as a colorless liquid (39.7 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2017**, *139*, 607–610).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (d, *J* = 7.5 Hz, 2H), 7.11 (d, *J* = 7.5 Hz, 2H), 2.29 (s, 3H), 1.26 (s, 12H).

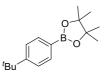
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  140.4, 133.8, 127.5, 82.6, 23.8, 20.7. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**4,4,5,5-tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane** (**4**): Following the general procedure, obtained in 62% yield as a colorless liquid (27.0 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.* **2017**, *56*, 2482–2486).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.76 (dd, J = 5.6, 2.4 Hz, 1H), 7.34 – 7.28 (m, 1H), 7.20 – 7.14 (m, 2H), 2.54 (s, 3H), 1.34 (s, 12H).

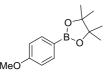
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  144.8, 135.8, 130.8, 129.8, 124.7, 83.4, 24.9, 22.2. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (5):** Following the general procedure, obtained in 82% yield as a colorless liquid (42.7 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2015**, *137*, 1593–1600).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 7.6 Hz, 2H), 1.26 (s, 12H), 1.25 (s, 9H).

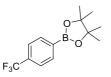
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  153.5, 133.7, 123.7, 82.6, 33.9, 30.2, 23.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (6): Following the general procedure, obtained in 62% yield as a colorless liquid (29.0 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.* **2017**, *56*, 2482–2486).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.75 (d, *J* = 8.2 Hz, 2H), 6.89 (d, *J* = 8.2 Hz, 2H), 3.82 (s, 3H), 1.33 (s, 12H).

 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  161.1, 135.5, 112.3, 82.5, 54.1, 23.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

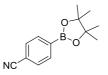


4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane(7):Following the general procedure, obtained in 74% yield as a white solid (40.3 mg, eluent:petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with theliterature (Ref: J. Am. Chem. Soc. 2017, 139, 607–610).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 7.7 Hz, 2H), 7.61 (d, *J* = 7.8 Hz, 2H), 1.36 (s, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  135.1, 132.9 (q, *J* = 32.1 Hz), 124.2 (q, *J* = 272.5 Hz), 124.4 (q, *J* = 3.7 Hz), 84.3, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

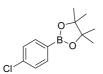
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.04.



**4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (8):** Following the general procedure, obtained in 86% yield as a white solid (39.4 mg, eluent: petroleum ether/ethyl acetate = 10/1). The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2017**, *139*, 607–610).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 1.35 (s, 12H).

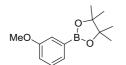
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  135.1, 131.2, 118.9, 114.5, 84.5, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (9): Following the general procedure, obtained in 75% yield as a colorless liquid (35.8 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2017**, *139*, 607–610).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.73 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.3 Hz, 2H), 1.34 (s, 12H).

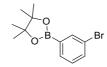
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  137.5, 136.1, 128.0, 84.0, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**2-(3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10):** Following the general procedure, obtained in 83% yield as a colorless liquid (38.8 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2017**, *139*, 607–610).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.40 (d, J = 7.2 Hz, 1H), 7.33 (s, 1H), 7.29 (t, J = 7.7 Hz, 1H), 7.01 (d, J = 8.2 Hz, 1H), 3.83 (s, 3H), 1.34 (s, 12H).

 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  159.0, 128.9, 127.2, 118.7, 118.0, 83.8, 55.2, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (11): Following the general procedure, obtained in 50% yield as a colorless liquid (28.3 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *Org. Lett.* **2014**, *16*, 2366–2369).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.93 (s, 1H), 7.71 (d, *J* = 7.4 Hz, 1H), 7.58 (d, *J* = 7.8 Hz, 1H), 7.26 – 7.22 (m, 1H), 1.34 (s, 12H).

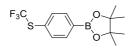
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  136.4, 133.2, 132.1, 128.5, 121.4, 83.1, 23.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**1-(2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)ethan-1-one** (12): Following the general procedure, obtained in 53% yield as a colorless liquid (26.1 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Ref: *Org. Biomol. Chem.* **2014**, *12*, 3604–3610).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, *J* = 7.7 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.43 (t, *J* = 7.3 Hz, 1H), 2.61 (s, 3H), 1.44 (s, 12H).

 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  199.8, 140.5, 132.5, 132.2, 128.9, 128.4, 83.7, 25.5, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

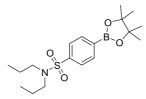


**4,4,5,5-tetramethyl-2-(4-((trifluoromethyl)thio)phenyl)-1,3,2-dioxaborolane** (13): Following the general procedure, obtained in 68% yield as a colorless liquid (41.4 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.* **2014**, *53*, 9311–9315).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84 (d, *J* = 7.6 Hz, 2H), 7.64 (d, *J* = 7.6 Hz, 2H), 1.35 (s, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  135.6, 135.2, 129.6 (q, *J* = 306.5 Hz), 127.5(q, *J* = 2.1 Hz), 84.3, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -42.28.



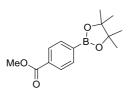
### N, N-dipropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) benzenesul fonamide

(14): Following the general procedure, obtained in 85% yield as a white solid (62.4 mg, eluent: petroleum ether/ethyl acetate = 5/1). The compound data was in agreement with

the literature (Ref: Angew. Chem. Int. Ed. 2017, 56, 2482-2486).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.92 (d, J = 7.8 Hz, 2H), 7.78 (d, J = 7.9 Hz, 2H), 3.10 – 3.03 (m, 4H), 1.59 – 1.48 (m, 4H), 1.36 (s, 12H), 0.86 (t, J = 7.4 Hz, 6H).

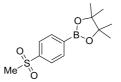
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.4, 135.2, 126.0, 84.4, 50.0, 24.9, 22.0, 11.2. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**Methyl 4-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)benzoate (15):** Following the general procedure, obtained in 88% yield as a white solid (46.1 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.* **2017**, *56*, 2482–2486).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.1 Hz, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 3.92 (s, 3H), 1.36 (s, 12H).

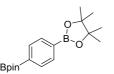
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  167.2, 134.7, 132.3, 128.6, 84.2, 52.2, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**4,4,5,5-tetramethyl-2-(4-(methylsulfonyl)phenyl)-1,3,2-dioxaborolane**(16):Following the general procedure for 24 h, obtained in 90% yield as a white solid (50.8mg, eluent: petroleum ether/ethyl acetate = 4/1). The compound data was in agreementwith the literature (Ref: *Org. Biomol. Chem.* **2014**, *12*, 3604–3610).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00 (d, *J* = 7.7 Hz, 2H), 7.93 (d, *J* = 7.7 Hz, 2H), 3.05 (s, 3H), 1.36 (s, 12H).

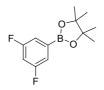
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.6, 135.6, 126.3, 84.5, 44.4, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene** (**17**): Following the general procedure, obtained in 84% yield as a white solid (55.4 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.* **2017**, *56*, 2482–2486).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80 (s, 4H), 1.35 (s, 24H).

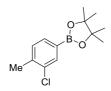
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  133.9, 83.9, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**2-(3,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18):** Following the general procedure, obtained in 70% yield as a colorless liquid (33.6 mg, eluent: petroleum ether/ethyl acetate = 20/1). The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2016**, *138*, 5250–5253).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.31 – 7.24 (m, 2H), 6.92 – 6.82 (m, 1H), 1.34 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  162.7 (dd, *J* = 249.7, 11.0 Hz), 116.9 – 116.7 (m), 106.5 (t, *J* = 25.1 Hz), 84.43, 24.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

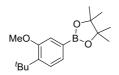
<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -110.77 - -110.90 (m).



**2-(3-chloro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (19): Following the general procedure, obtained in 75% yield as a colorless liquid (37.9 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2017**, *139*, 976–984).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.77 (s, 1H), 7.57 (dd, *J* = 7.4, 0.7 Hz, 1H), 7.23 (d, *J* = 7.5 Hz, 1H), 2.39 (s, 3H), 1.34 (s, 12H).

 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  139.3, 135.2, 134.2, 132.8, 130.5, 84.0, 24.8, 20.3. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

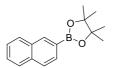


**2-(4-(tert-butyl)-3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane** (20): Following the general procedure, obtained in 66% yield as a white solid (38.3 mg, eluent: petroleum ether/ethyl acetate = 30/1).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.37 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.28 (m, 2H), 3.88 (s, 3H), 1.37 (s, 9H), 1.33 (s, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.1, 141.8, 127.3, 126.2, 117.1, 83.7, 55.1, 35.1, 29.6, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.

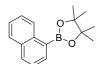
HRMS (ESI) Calcd for C<sub>17</sub>H<sub>28</sub>BO<sub>3</sub><sup>+</sup> [M+H]<sup>+</sup>: 291.2126, found: 291.2122.



**4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane** (**21**): Following the general procedure, obtained in 65% yield as a white solid (33.0 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.* **2017**, *56*, 2482–2486).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.38 (s, 1H), 7.88 (d, *J* = 7.7 Hz, 1H), 7.86 – 7.79 (m, 3H), 7.53 – 7.43 (m, 2H), 1.39 (s, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  136.3, 135.1, 132.8, 130.4, 128.7, 127.7, 127.0, 125.8, 84.0, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. (one carbon signal is overlapped)



**4,4,5,5-tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (22):** Following the general procedure, obtained in 57% yield as a white solid (28.9 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *Org. Lett.* **2014**, *16*, 2366–2369).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.76 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 6.8 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.55 – 7.45 (m, 3H), 1.42 (s, 12H).

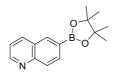
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 135.9, 134.6, 132.2, 130.6, 127.4, 127.3, 125.3, 124.4, 123.9, 82.7, 23.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (23):** Following the general procedure, obtained in 76% yield (determined by <sup>1</sup>H-NMR) as a white solid. The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2017**, *139*, 607–610).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.95 (s, 1H), 8.70 – 8.63 (m, 1H), 8.15 – 7.98 (m, 1H), 7.33 – 7.21 (m, 1H), 1.36 (s, 12H).

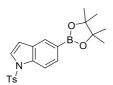
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  155.4, 151.9, 142.3, 123.1, 84.2, 24.9. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinolone (24):** Following the general procedure, obtained in 68% yield (determined by <sup>1</sup>H-NMR) as a white solid. The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2013**, *135*, 18730–18733).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.97 – 8.90 (m, 1H), 8.35 (s, 1H), 8.19 (d, *J* = 8.3 Hz, 1H), 8.10 – 8.08 (m, 2H), 7.43 – 7.34 (m, 1H), 1.39 (s, 12H).

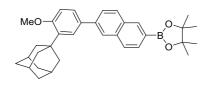
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  151.3, 149.7, 136.7, 136.1, 134.2, 128.5, 127.7, 121.1, 84.2, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1H-indole (25):** Following the general procedure for 24 h, obtained in 42% yield as a colorless liquid (79.4 mg, eluent: petroleum ether/ethyl acetate = 5/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.* **2017**, *56*, 2482–2486).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.01 (s, 1H), 7.98 (d, *J* = 8.3 Hz, 1H), 7.76 – 7.72 (m, 3H), 7.54 (d, *J* = 3.6 Hz, 1H), 7.19 (d, *J* = 8.1 Hz, 2H), 6.64 (dd, *J* = 7.7, 2.8 Hz, 1H), 2.32 (s, 3H), 1.34 (s, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 145.0, 136.8, 135.2, 130.7, 130.4, 129.9, 128.7, 126.8, 126.4, 112.9, 109.3, 83.8, 24.9, 21.5. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**2-(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-4,4,5,5tetramethyl-1,3,2-dioxaborolane (26):** Following the general procedure, obtained in 45% yield as a white solid (44.5 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *Angew. Chem. Int. Ed.* **2017**, 56, 2482–2486).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.37 (s, 1H), 7.99 – 7.95 (m, 1H), 7.92 (d, *J* = 8.5 Hz, 1H), 7.89 – 7.81 (m, 2H), 7.71 (d, *J* = 8.5 Hz, 1H), 7.60 (s, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 6.98 (d, *J* = 8.4 Hz, 1H), 3.89 (s, 3H), 2.18 (s, 6H), 2.10 (s, 3H), 1.80 (s, 6H), 1.40 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  158.7, 140.0, 138.9, 136.0, 135.4, 133.1, 131.6, 130.8, 129.0, 127.1, 126.0, 125.6, 124.8, 112.1, 83.9, 55.2, 40.6, 37.2, 37.1, 29.1, 25.0. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening. (one carbon signal is overlapped)



(E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (27): Following the general procedure, obtained in 48% yield as a colorless liquid (22.1 mg, eluent: petroleum ether/ethyl acetate = 30/1). The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2017**, *139*, 976–984).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.52 – 7.46 (m, 2H), 7.40 (d, *J* = 18.5 Hz, 1H), 7.36 – 7.28 (m, 3H), 6.17 (d, *J* = 18.4 Hz, 1H), 1.32 (s, 12H).

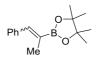
 $^{13}$ C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  149.5, 137.5, 128.9, 128.6, 127.0, 83.3, 24.8. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**2-(cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28):** Following the general procedure, obtained in 85% yield as a colorless liquid (35.4 mg, eluent: petroleum ether/ethyl acetate = 40/1). The compound data was in agreement with the literature (Ref: *J. Am. Chem. Soc.* **2017**, *139*, 607–610).

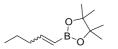
<sup>1</sup>H NMR (400 MHz, CDCl3) δ 6.69 – 6.36 (m, 1H), 2.28 – 1.91 (m, 4H), 1.81 – 1.50 (m, 4H), 1.26 (s, 12H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)  $\delta$  142.9, 83.0, 26.6, 26.1, 24.8, 22.5, 22.2. The carbon directly attached to the boron atom was not detected due to quadrupolar broadening.



**4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2-dioxaborolane (29):** Following the general procedure, obtained in 81% (Z/E = 3:1) yield as a colorless liquid (39.5 mg, eluent: petroleum ether/ethyl acetate = 40/1). The compound data was in agreement with the literature (Ref: *Chem. Commun.* **2014**, *50*, 2058–2060).

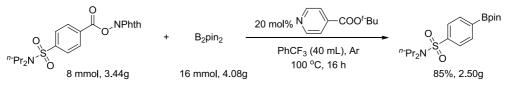
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.62 – 6.73 (m, 6H), 2.01 – 1.96 (m, 3H), 1.31 (s, 9H, *cisisomer*), 1.26 (s, 3H, *trans-isomer*).



**4,4,5,5-tetramethyl-2-(pent-1-en-1-yl)-1,3,2-dioxaborolane** (30): Following the general procedure, obtained in 53% (E/Z= 2.4:1) yield as a colorless liquid (20.8 mg, eluent: petroleum ether/ethyl acetate = 40/1). The compound data was in agreement with the literature (Ref: *Chem. Commun.* 2014, *50*, 2058–2060).

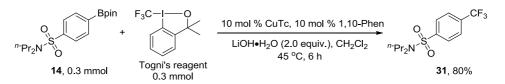
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.63 (dt, J = 18.0, 6.4 Hz, 0.7H, trans-isomer), 6.50 – 6.36 (m, 0.3H, cis-isomer), 5.43 (d, J = 18.0 Hz, 0.7H, trans-isomer), 5.34 (d, J = 13.6 Hz, 0.3H, cis-isomer), 2.44 – 2.06 (m, 2H), 1.54 – 1.33 (m, 2H), 1.27 (s, 12H), 0.91 (t, J = 7.3 Hz, 3H).

#### 5. Gram-scale Reaction



A 100 mL Schlenk tube containing a stirring bar was charged with redox active ester (1.0 equiv., 8 mmol) and  $B_2pin_2$  (2.0 equiv., 16 mmol). The tube was then evacuated and back-filled with argon three times. Anhydrous trifluorotoluene (PhCF<sub>3</sub>, 40 mL) was added subsequently, then isonicotinate *tert*-butyl ester (20 mol %, 1.6 mmol) was added. The tube was sealed by a plastic screw cap and heated at 100 °C for 16 h. After cooling to room temperature, the organic layers were concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give the product (2.5g, 85%).

#### 6. Diverse Transformation of Aryl Boronic Ester



**Trifluoromethylation**<sup>1</sup>: A 10 mL Schlenk tube containing a stirring bar was charged with aryl boronic ester **14** (0.3 mmol), Togni's reagent (0.3 mmol), CuTc (10 mol %, 0.03 mmol), 1,10-Phenanthroline (10 mol %, 0.03 mmol) and LiOH•H<sub>2</sub>O (2.0 equiv., 0.6 mmol). The tube was then evacuated and back-filled with argon three times. Anhydrous  $CH_2Cl_2$  (1.0 mL) was added subsequently, then the tube was sealed by a plastic screw cap and heated at 45 °C for 6 h. After cooling to room temperature, the organic layers were concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give the product (74.2 mg, 80%).

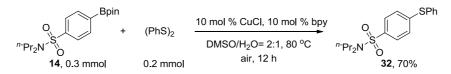
#### *N*,*N*-dipropyl-4-(trifluoromethyl)benzenesulfonamide (31)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.94 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.1 Hz, 2H), 3.16 – 3.08 (m, 4H), 1.64 – 1.49 (m, 4H), 0.88 (t, *J* = 7.3 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 143.8, 134.0 (q, *J* = 33.0 Hz), 127.5, 126.1 (q, *J* = 3.7 Hz), 123.3 (q, *J* = 272.9 Hz), 50.0, 22.0, 11.1.

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -63.07.

HRMS (ESI) Calcd for C<sub>13</sub>H<sub>19</sub>F<sub>3</sub>NO<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 310.1083, found: 310.1086.



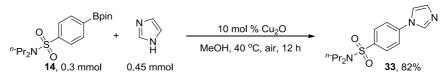
**Sulfenylation**<sup>2</sup>: A 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged with aryl boronic ester **14** (0.3 mmol), CuCl (10 mol %, 0.03 mmol), 2,2'-bipyridine (10 mol %, 0.03 mmol), disulfide (0.2 mmol) in a nitrogen-filled glove box. The Schlenk tube was then covered with a rubber septum and removed from the glove box. DMSO (0.6 mL) and H<sub>2</sub>O (0.3 mL) were added via syringe under air, and the tube was connected to an air-filled balloon and heated at 80 °C for 12 h. The mixture was cooled to room temperature and diluted with ethyl acetate (10 mL). The resulting solution was concentrated under reduced pressure. Finally, the crude mixture was purified by column chromatography on silica gel to give the product (73.4mg, 70%).

#### 4-(phenylthio)-*N*,*N*-dipropylbenzenesulfonamide (32)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.64 (d, J = 8.4 Hz, 2H), 7.49 (d, J = 4.4 Hz, 2H), 7.45 – 7.39 (m, 3H), 7.22 (d, J = 8.3 Hz, 2H), 3.08 – 3.01 (m, 4H), 1.66 – 1.47 (m, 4H), 0.86 (t, J = 7.4 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 144.1, 137.1, 134.0, 131.7, 129.8, 129.0, 127.7, 127.6, 50.1, 22.1, 11.2.

HRMS (ESI) Calcd for C<sub>18</sub>H<sub>24</sub>NO<sub>2</sub>S<sub>2</sub><sup>+</sup> [M+H]<sup>+</sup>: 350.1243, found: 350.1237.



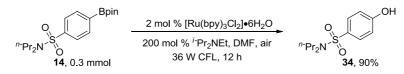
Amination<sup>3</sup>: A 10 mL Schlenk tube equipped with a magnetic stirrer bar was charged with aryl boronic ester **14** (0.3 mmol), Cu<sub>2</sub>O (10 mol %, 0.03 mmol) and imidazole (0.45 mmol). MeOH (1 mL) were added via syringe under air, and the tube was connected to an air-filled balloon and heated at 40 °C for 12 h. After cooling to room temperature, the organic layers were concentrated under reduced pressure. The crude mixture was purified by column chromatography on silica gel to give the product (75.5 mg, 82%).

#### 4-(1*H*-imidazol-1-yl)-*N*,*N*-dipropylbenzenesulfonamide (33)

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.21 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.2 Hz, 2H), 7.40 (s, 1H), 7.33 (s, 1H), 3.18 – 3.03 (m, 4H), 1.72 – 1.46 (m, 4H), 0.89 (t, *J* = 7.3 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 139.9, 139.5, 136.0, 130.2, 129.1, 121.6, 118.4, 50.0, 22.0, 11.2.

HRMS (ESI) Calcd for C<sub>15</sub>H<sub>22</sub>N<sub>3</sub>O<sub>2</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 308.1427, found: 308.1421.



**Hydroxylation**<sup>4</sup>: To a mixture of aryl boronic ester **14** (0.3 mmol),  $Ru(bpy)_3Cl_2 \cdot 6H_2O$  (2 mol %) in DMF (3.0 mL) was added <sup>*i*</sup>-Pr<sub>2</sub>NEt (0.6 mmol). The solution was stirred at room temperature under 36 W CFL irradiation in open to air for 12h, the reaction mixture was cooled to 0 °C and quenched carefully by aqueous solution of HCl (10%, 3 mL). The resultant mixture was extracted with Et<sub>2</sub>O (3 x 5 mL). The combined organic layers were

washed with brine (10 mL) and dried over  $Na_2SO_4$ . After removal of the solvent in vacuum, the residue was purified by column chromatography on silica gel to give the product (69.5 mg, 90%).

# 4-hydroxy-N,N-dipropylbenzenesulfonamide (34)

<sup>1</sup>H NMR (400 MHz, DMSO) δ 10.41 (s, 1H), 7.60 (d, J = 8.5 Hz, 2H), 6.91 (d, J = 8.4 Hz, 2H), 2.95 (t, J = 7.5 Hz, 4H), 1.54 – 1.35 (m, 4H), 0.80 (t, J = 7.3 Hz, 6H). <sup>13</sup>C NMR (101 MHz, DMSO) δ 161.1, 129.4, 129.2, 115.7, 49.7, 21.7, 11.1. HRMS (ESI) Calcd for C<sub>12</sub>H<sub>20</sub>NO<sub>3</sub>S<sup>+</sup> [M+H]<sup>+</sup>: 258.1158, found: 258.1154.

#### 7. References

1. Liu, T.; Shao, X.; Wu, Y.; Shen, Q. Angew. Chem. Int. Ed. 2012, 51, 540-543.

2. Cheng, J.-H.; Yi, C.-L.; Liu, T.-J.; Lee, C.-F. Chem. Commun. 2012, 48, 8440-8442.

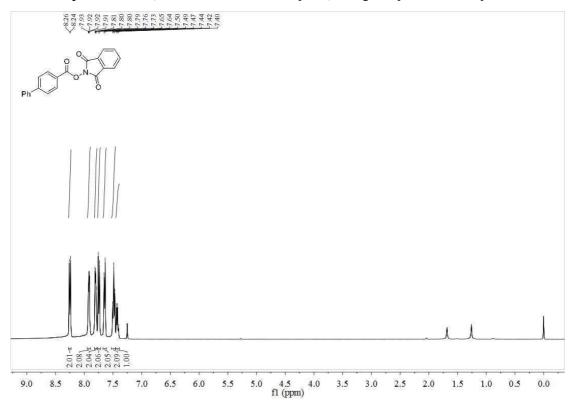
3. Sreedhar, B.; Venkanna, G. T.; Kumar, K. B. S.; Balasubrahmanyam, V. *Synthesis* **2008**, 795–799.

4. Zou, Y.-Q.; Chen, J.-R.; Liu, X.-P.; Lu, L.-Q.; Davis, R. L.; Jørgensen, K. A.; Xiao, W.-

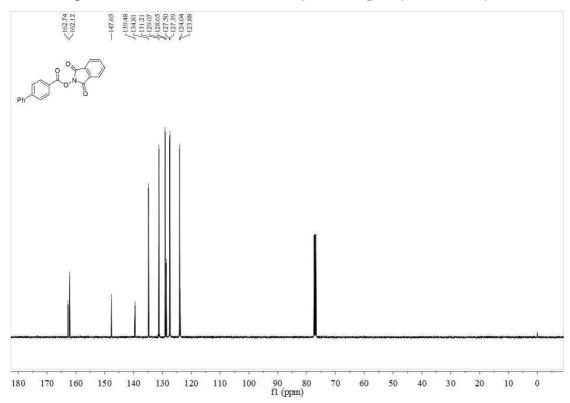
J. Angew. Chem. Int. Ed. 2012, 51, 784–788.

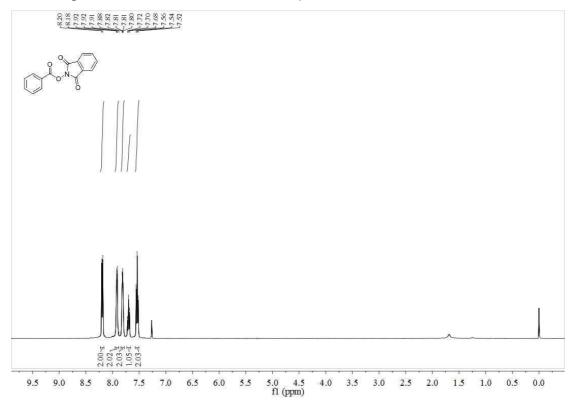
# 8. NMR Spectra

<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl [1,1'-biphenyl]-4-carboxylate (S-1)** 



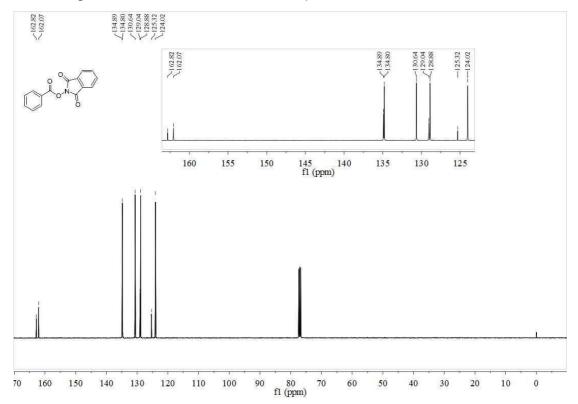
<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl [1,1'-biphenyl]-4-carboxylate (S-1)

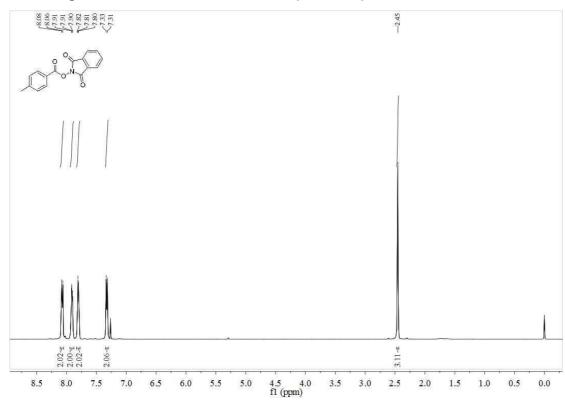




<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl benzoate** (S-2)

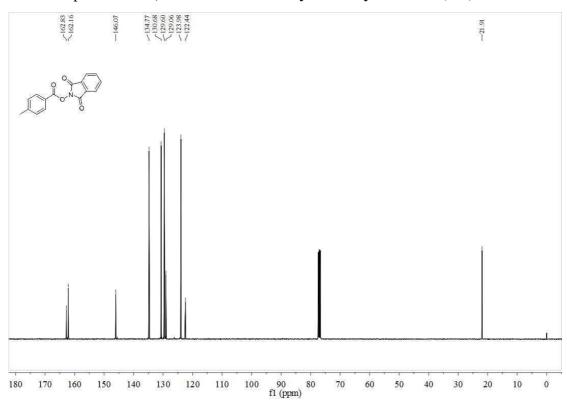
<sup>13</sup>C NMR spectrum of **1**, **3-dioxoisoindolin-2-yl benzoate** (S-2)

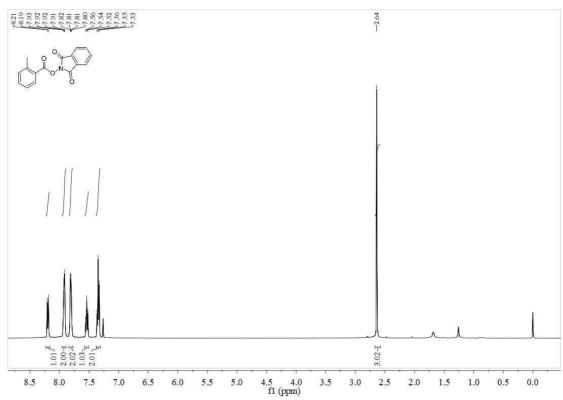




<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 4-methylbenzoate** (S-3)

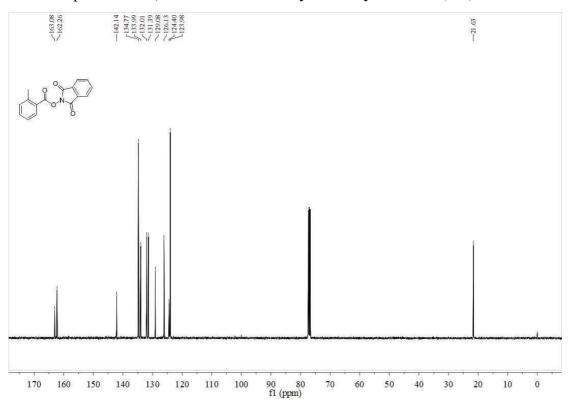
<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 4-methylbenzoate (S-3)

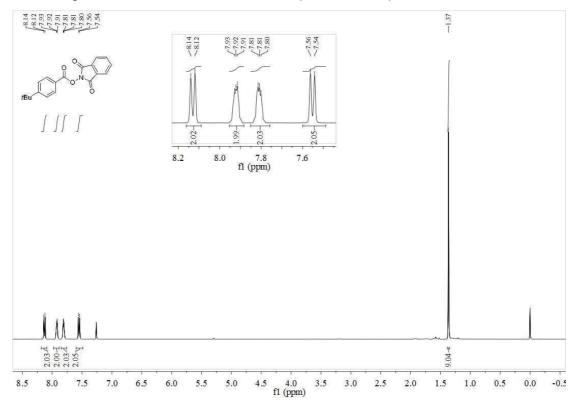




<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 2-methylbenzoate** (S-4)

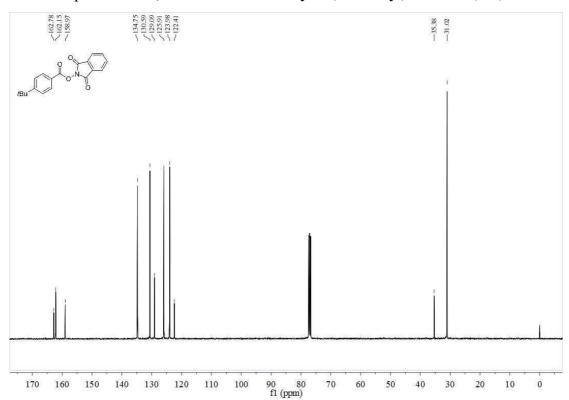
<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 2-methylbenzoate (S-4)

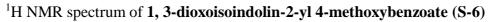


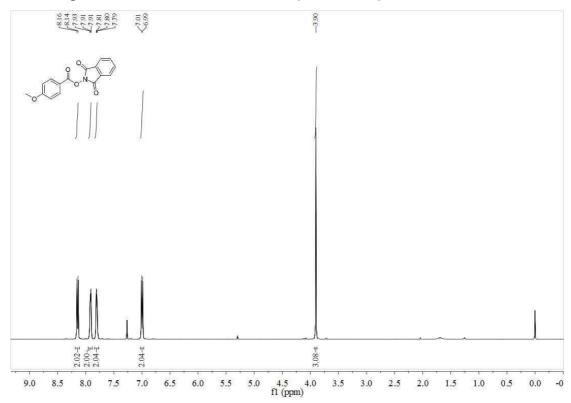


<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 4-(tert-butyl)benzoate (S-5)** 

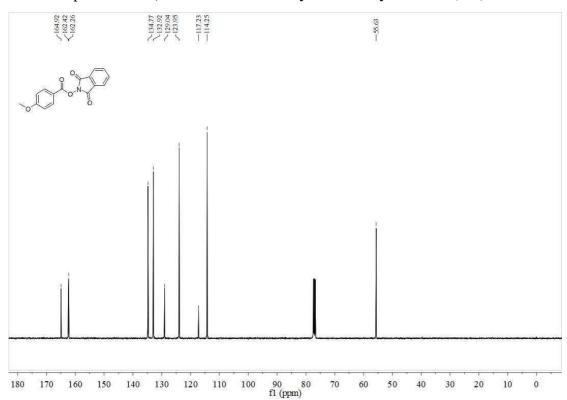
<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 4-(tert-butyl)benzoate (S-5)

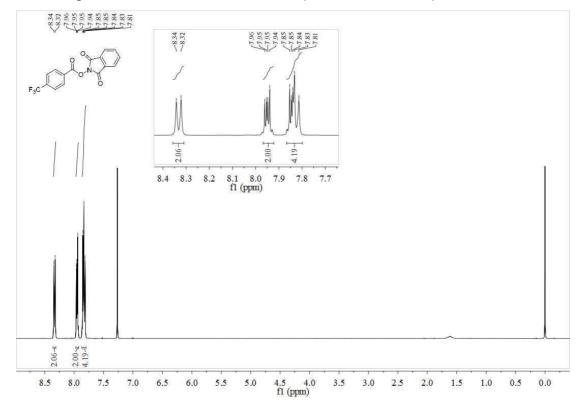






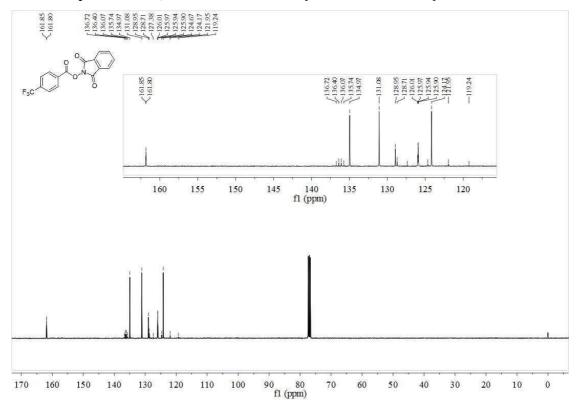
<sup>13</sup>C NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 4-methoxybenzoate** (S-6)

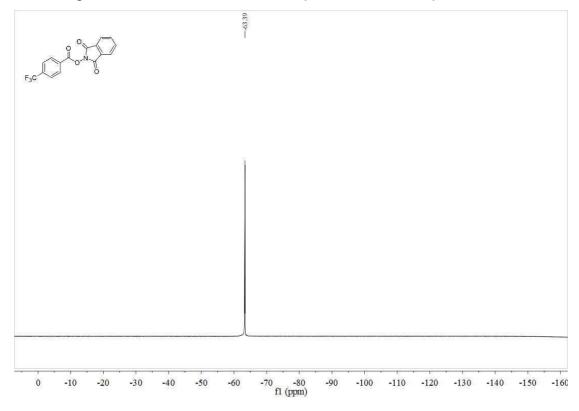




<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 4-(trifluoromethyl)benzoate (S-7)** 

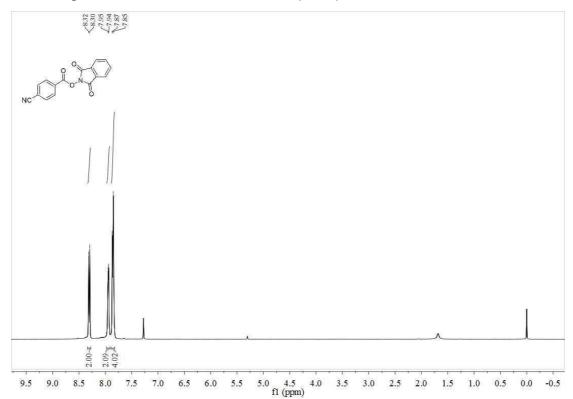
<sup>13</sup>C NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 4-(trifluoromethyl)benzoate (S-7)** 

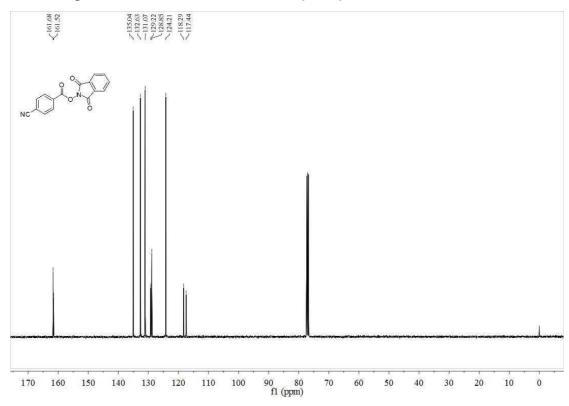




<sup>19</sup>F NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 4-(trifluoromethyl)benzoate (S-7)** 

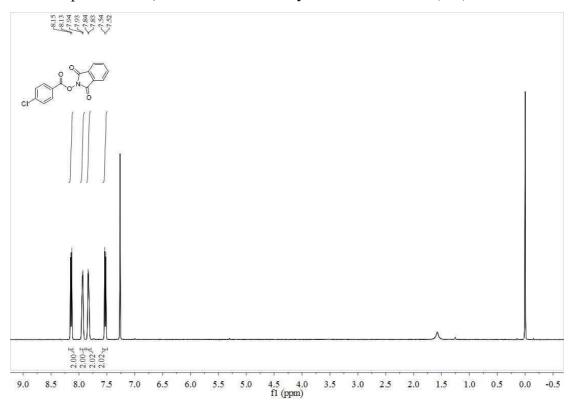
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 4-cyanobenzoate** (S-8)

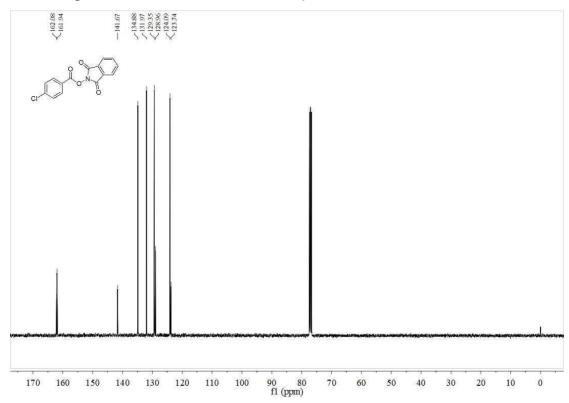




<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 4-cyanobenzoate (S-8)

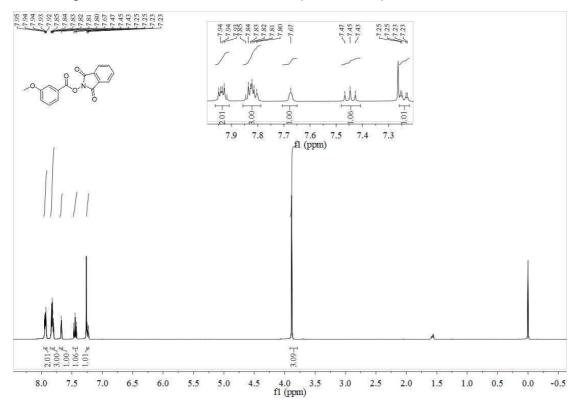
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 4-chlorobenzoate (S-9)** 

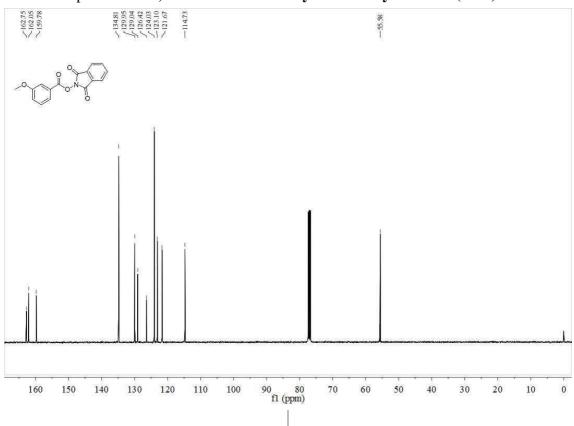




<sup>13</sup>C NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 4-chlorobenzoate (S-9)** 

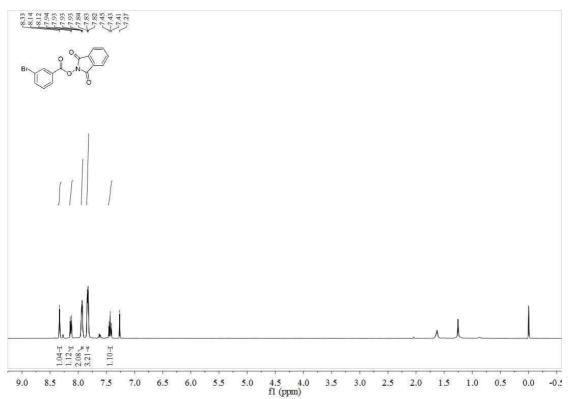
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 3-methoxybenzoate** (S-10)

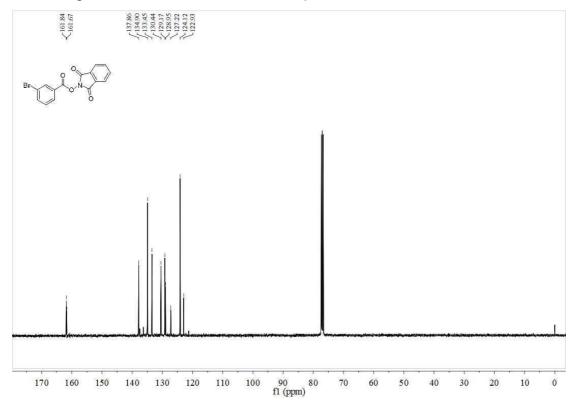




<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 3-methoxybenzoate (S-10)

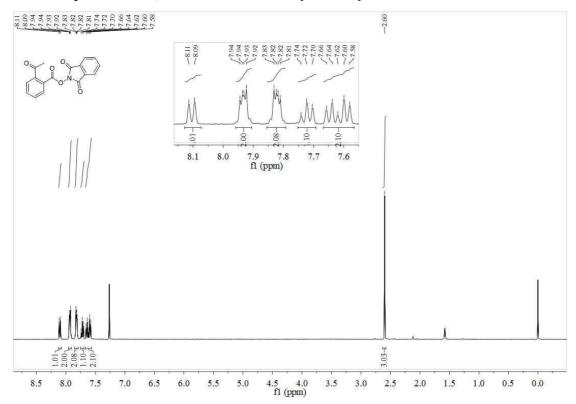
<sup>1</sup>H NMR spectrum of 1, 3-dioxoisoindolin-2-yl 3-bromobenzoate (S-11)

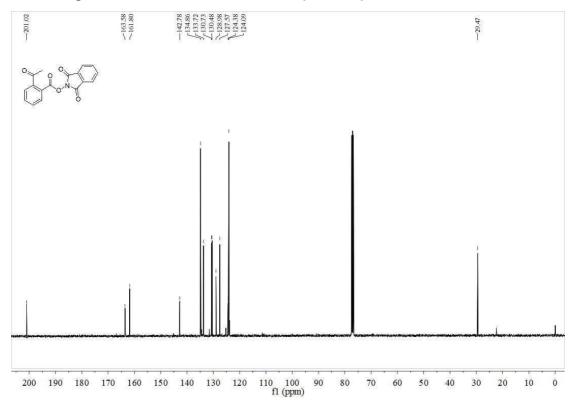




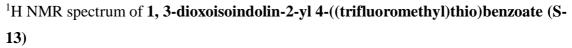
<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 3-bromobenzoate (S-11)

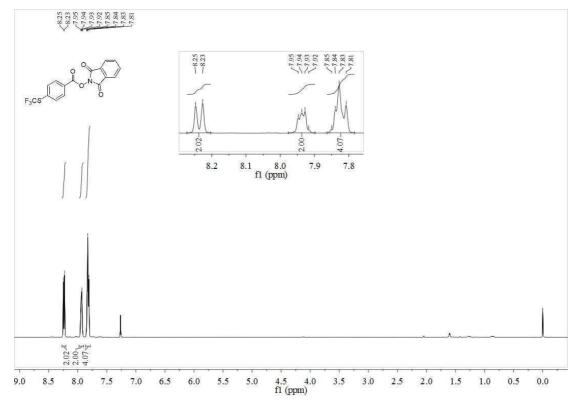
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 2-acetylbenzoate** (S-12)

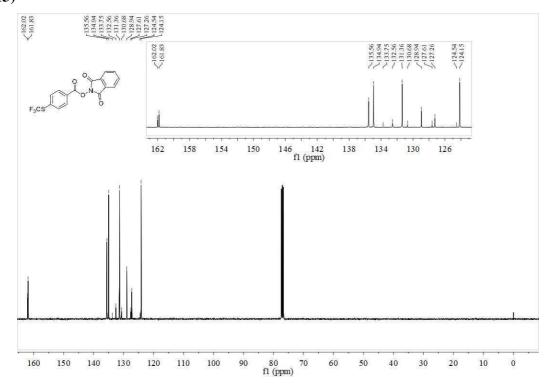




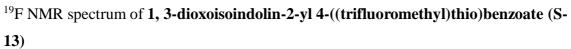
<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 2-acetylbenzoate (S-12)

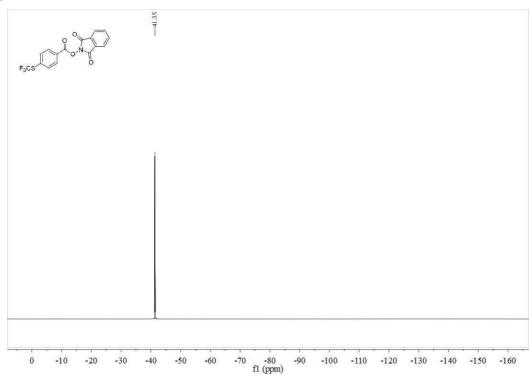




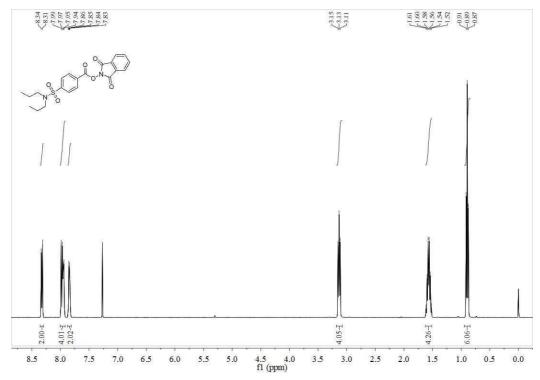


<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 4-((trifluoromethyl)thio)benzoate (S-13)

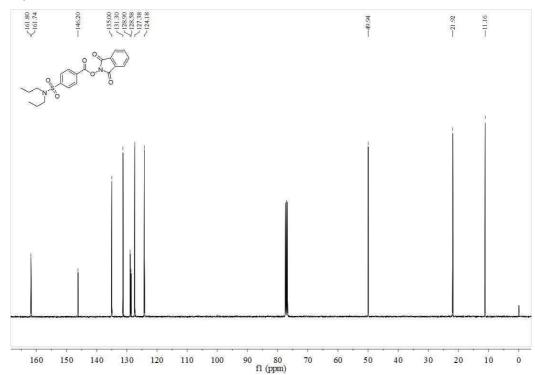




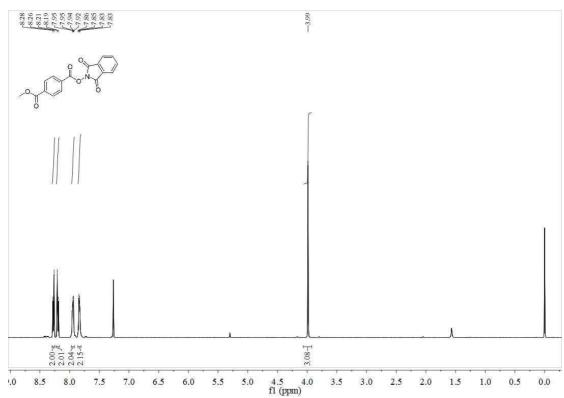
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 4-(N,N-dipropylsulfamoyl)benzoate** (S-14)



<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 4-(N,N-dipropylsulfamoyl)benzoate (S-14)

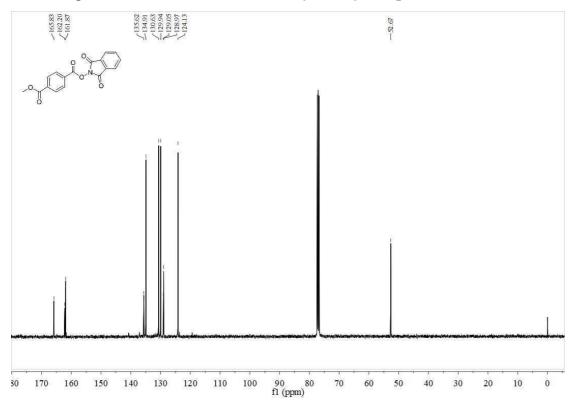


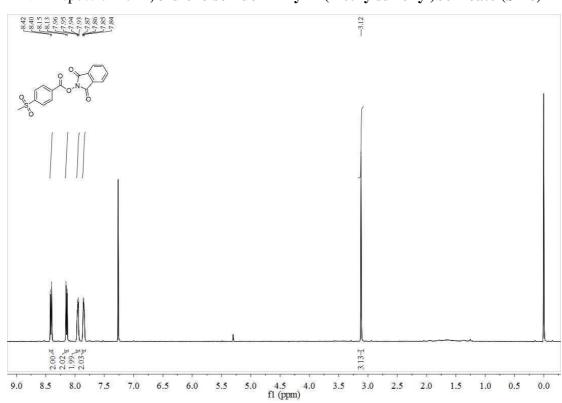
S46



<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl methyl terephthalate** (S-15)

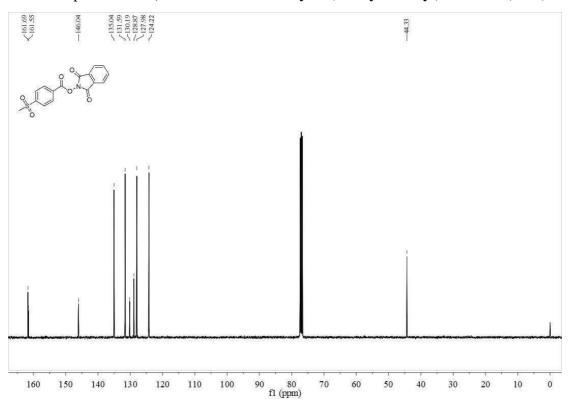
<sup>13</sup>C NMR spectrum of **1**, **3-dioxoisoindolin-2-yl methyl terephthalate** (S-15)



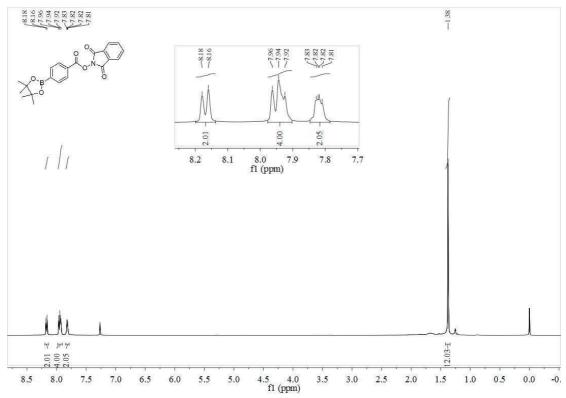


<sup>1</sup>H NMR spectrum of 1, 3-dioxoisoindolin-2-yl 4-(methylsulfonyl)benzoate (S-16)

<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 4-(methylsulfonyl)benzoate (S-16)

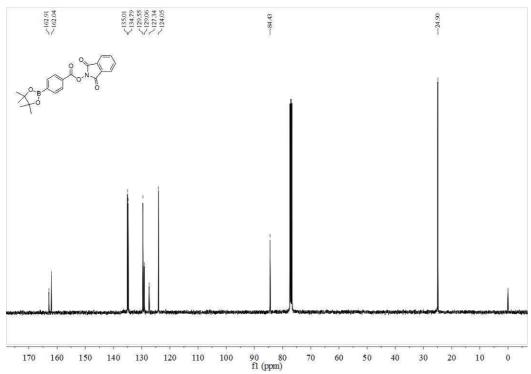


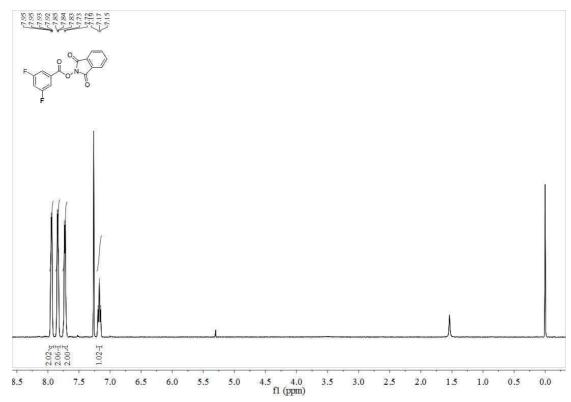
<sup>1</sup>H NMR spectrum of**1**, **3-dioxoisoindolin-2-yl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (S-17)** 



<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 4-(4,4,5,5-tetramethyl-1,3,2-

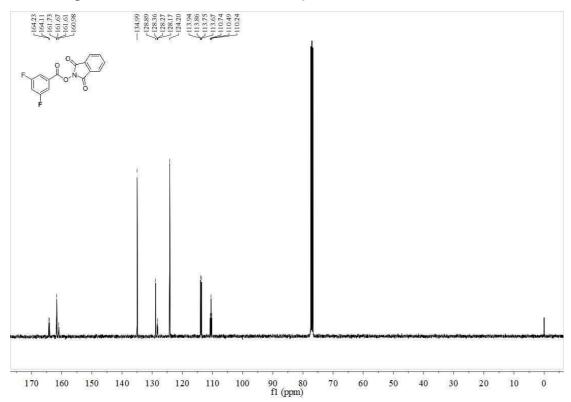
dioxaborolan-2-yl)benzoate (S-17)

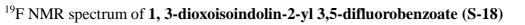


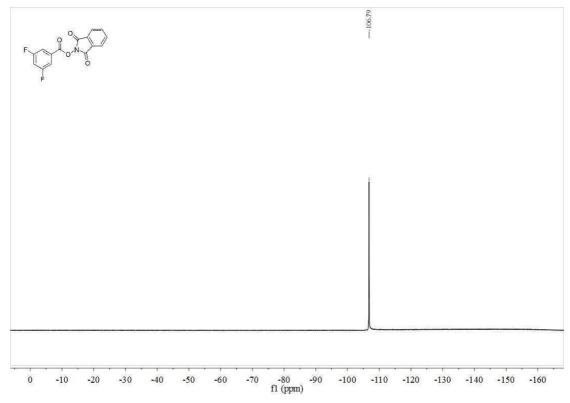


<sup>1</sup>H NMR spectrum of 1, 3-dioxoisoindolin-2-yl 3,5-difluorobenzoate (S-18)

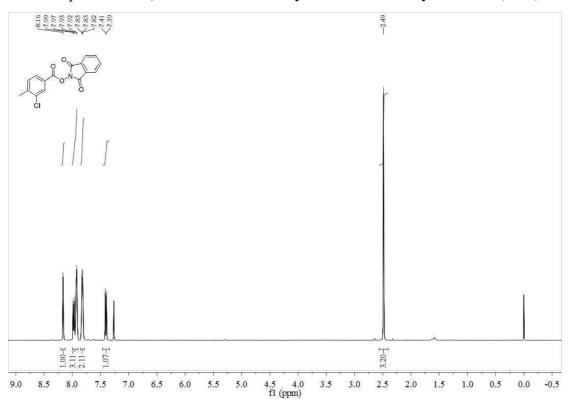
<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 3,5-difluorobenzoate (S-18)

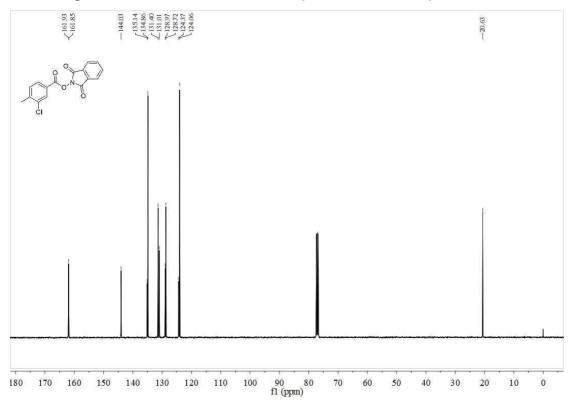






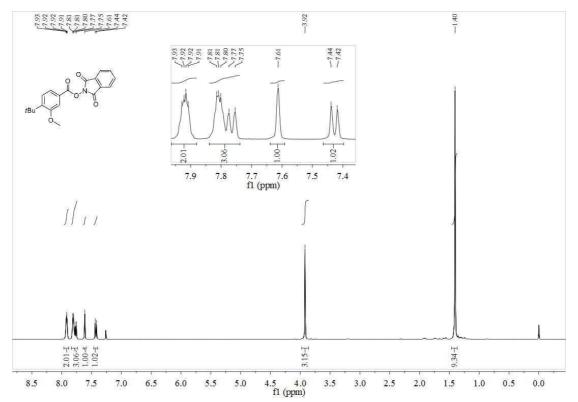
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 3-chloro-4-methylbenzoate** (S-19)



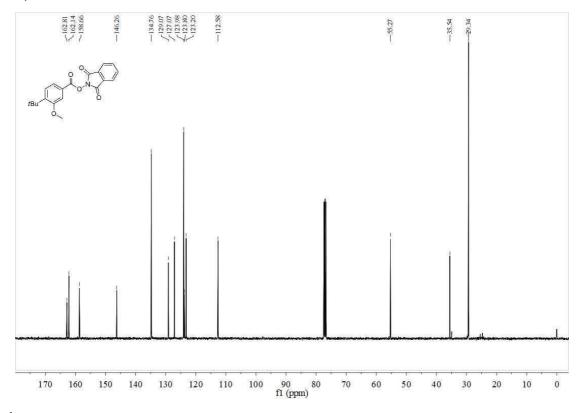


<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 3-chloro-4-methylbenzoate (S-19)

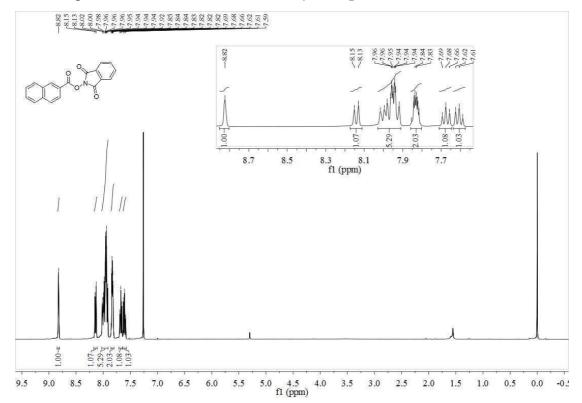
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 4-(tert-butyl)-3-methoxybenzoate (S-20)** 

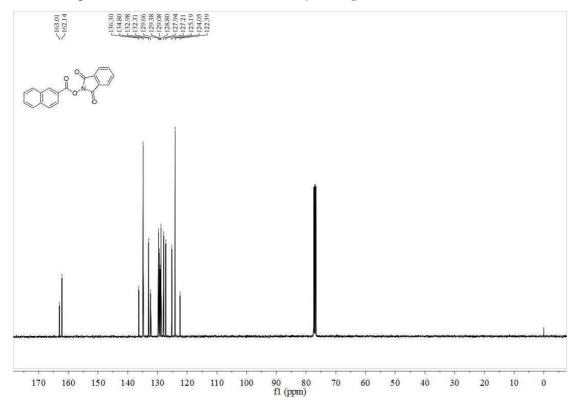


<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 4-(tert-butyl)-3-methoxybenzoate (S-20)



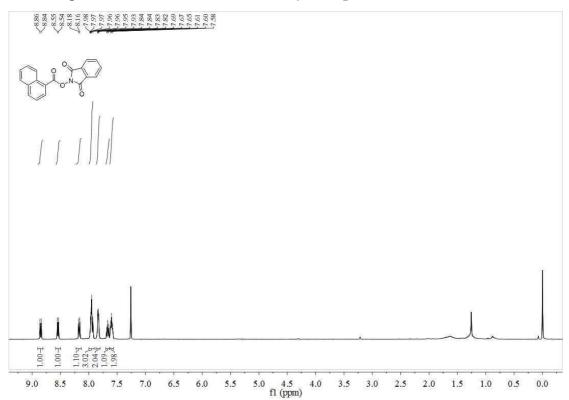
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 2-naphthoate** (S-21)

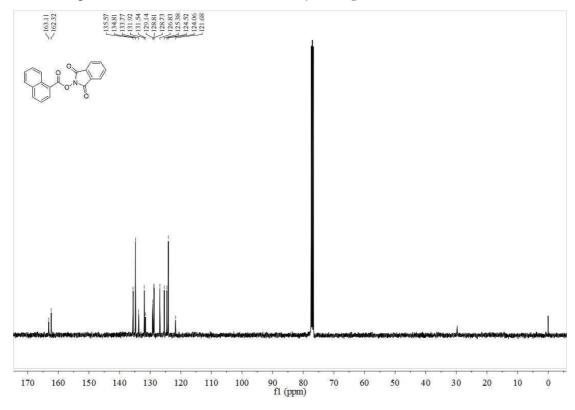




<sup>13</sup>C NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 2-naphthoate** (**S-21**)

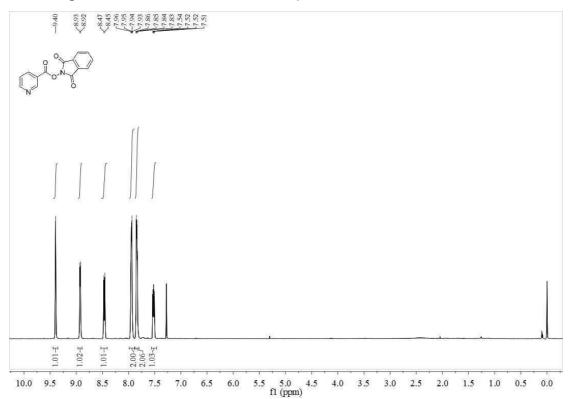
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 1-naphthoate** (S-22)

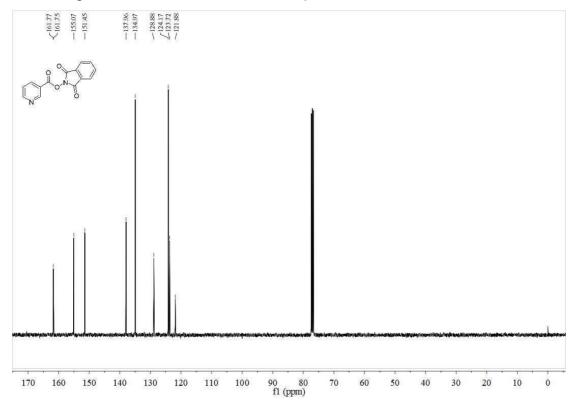




<sup>13</sup>C NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 1-naphthoate** (S-22)

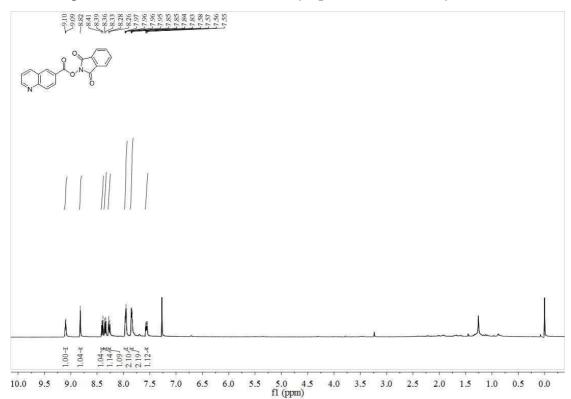
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl nicotinate** (S-23)

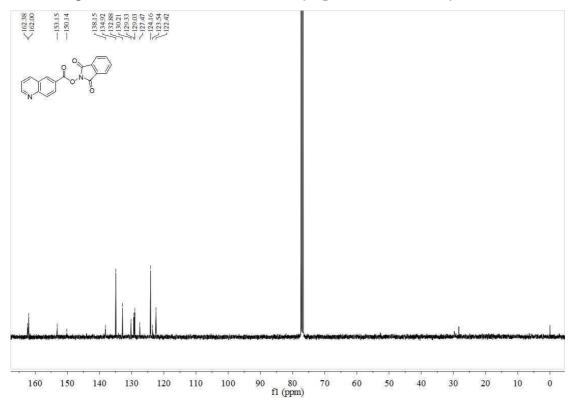




<sup>13</sup>C NMR spectrum of **1**, **3-dioxoisoindolin-2-yl nicotinate (S-23)** 

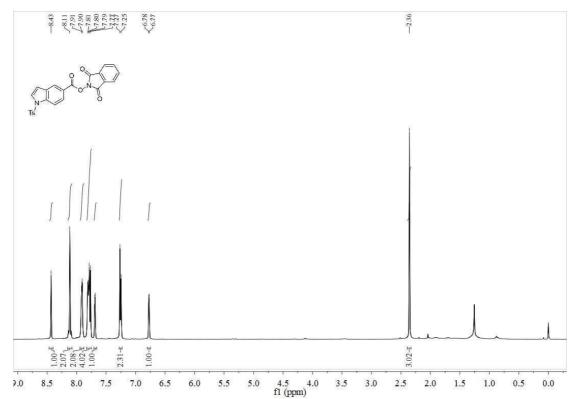
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl quinoline-6-carboxylate** (S-24)



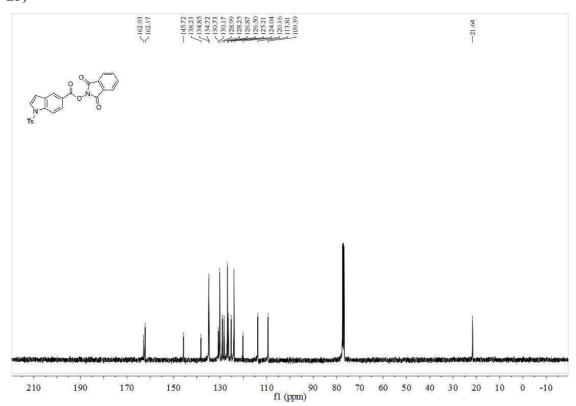


<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl quinoline-6-carboxylate (S-24)

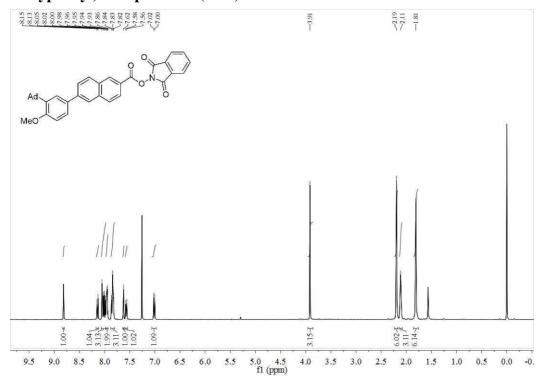
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 1-tosyl-1H-indole-5-carboxylate** (S-25)



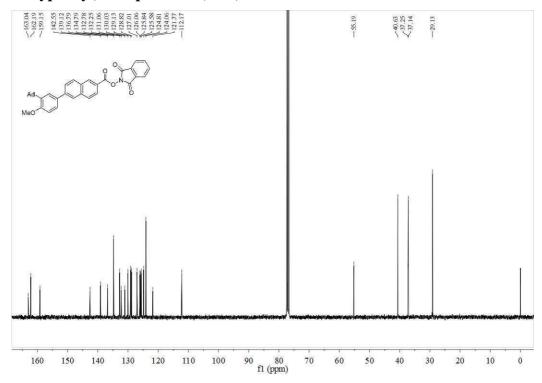
<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 1-tosyl-1H-indole-5-carboxylate (S-25)



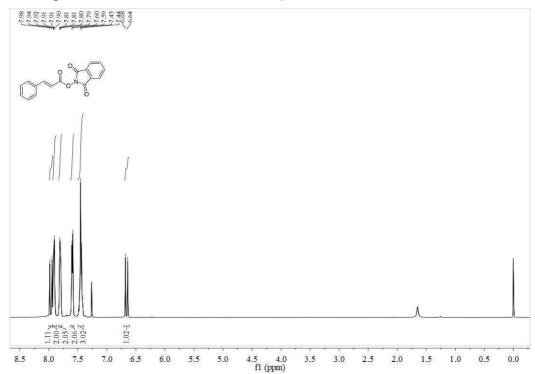
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl 6-(3-((3s)-adamantan-1-yl)-4**methoxyphenyl)-2-naphthoate (S-26)

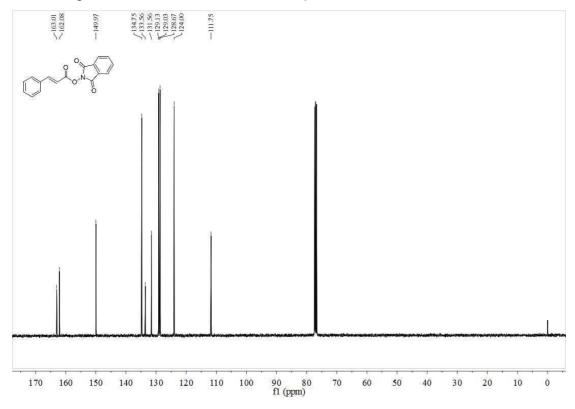


<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl 6-(3-((3s)-adamantan-1-yl)-4methoxyphenyl)-2-naphthoate (S-26)



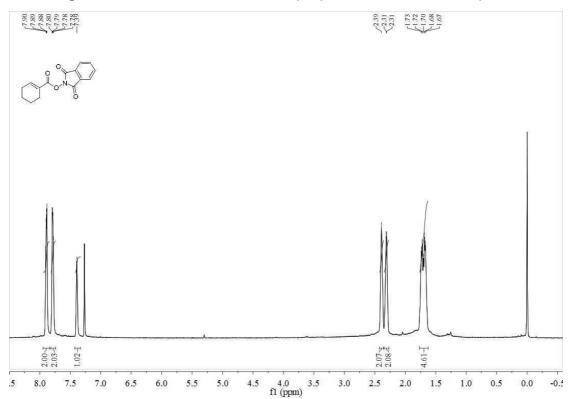
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl cinnamate (S-27)** 

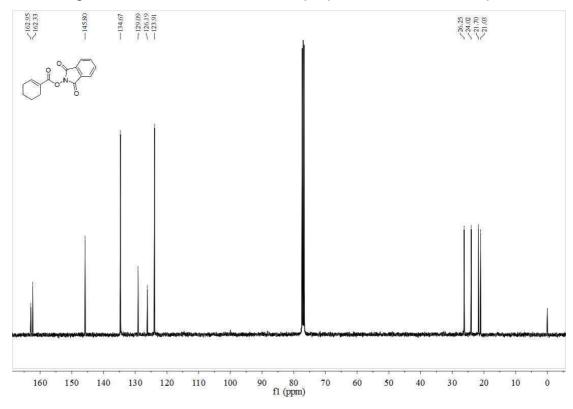




<sup>13</sup>C NMR spectrum of **1**, **3-dioxoisoindolin-2-yl cinnamate (S-27)** 

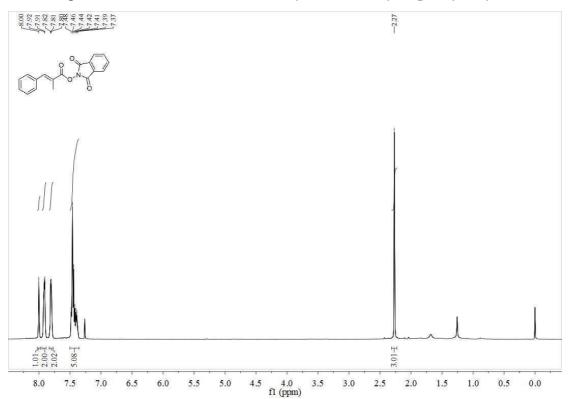
<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl cyclohex-1-ene-1-carboxylate** (S-28)

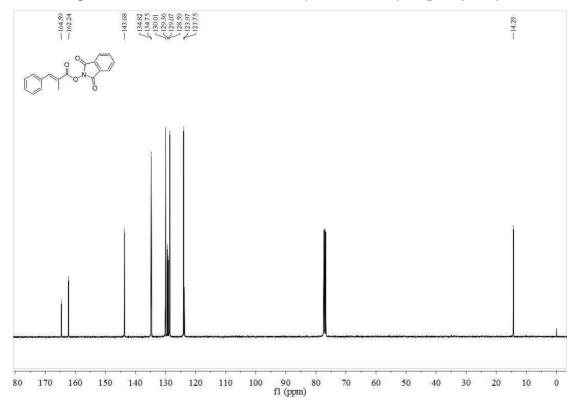




<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl cyclohex-1-ene-1-carboxylate (S-28)

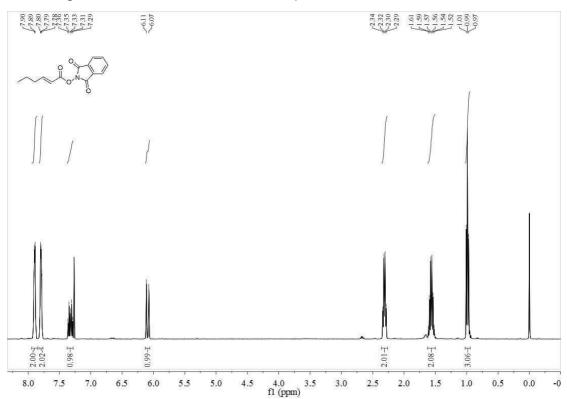
<sup>1</sup>H NMR spectrum of 1, 3-dioxoisoindolin-2-yl (E)-2-methyl-3-phenylacrylate (S-29)

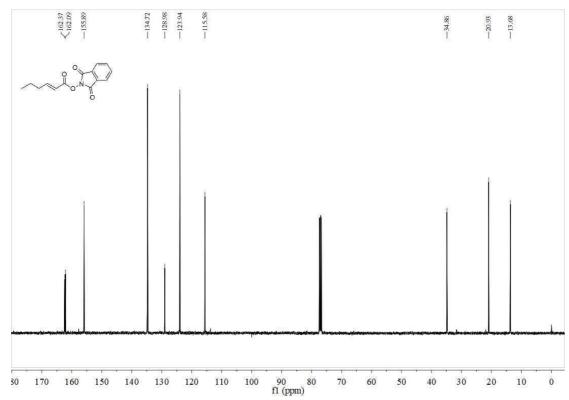




<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl (E)-2-methyl-3-phenylacrylate (S-29)

<sup>1</sup>H NMR spectrum of **1**, **3-dioxoisoindolin-2-yl** (**E**)-hex-2-enoate (**S-30**)

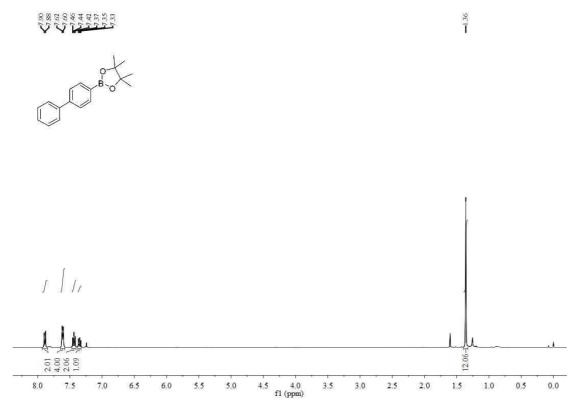




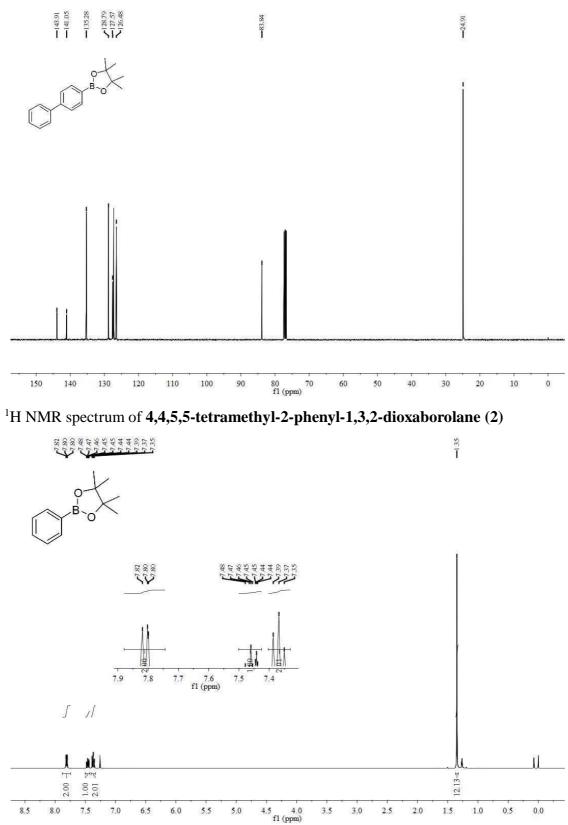
<sup>13</sup>C NMR spectrum of 1, 3-dioxoisoindolin-2-yl (E)-hex-2-enoate (S-30)

<sup>1</sup>H NMR spectrum of 2-([1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-

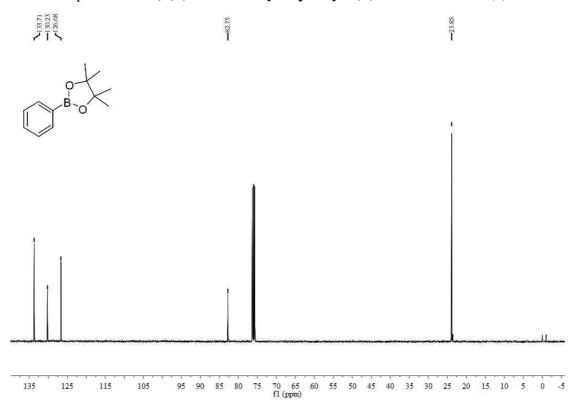
## dioxaborolane (1)



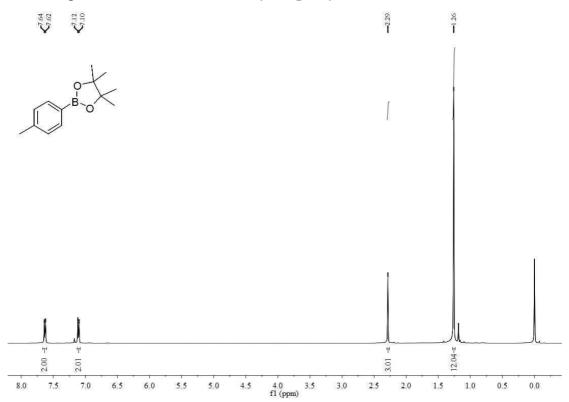
<sup>13</sup>C NMR spectrum of 2-([1,1'-biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (1)



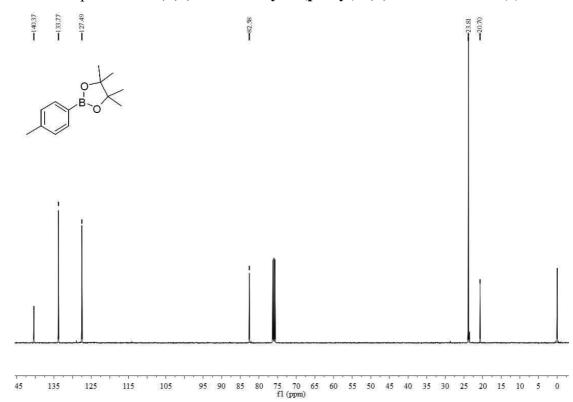
<sup>13</sup>C NMR spectrum of **4,4,5,5-tetramethyl-2-phenyl-1,3,2-dioxaborolane** (2)

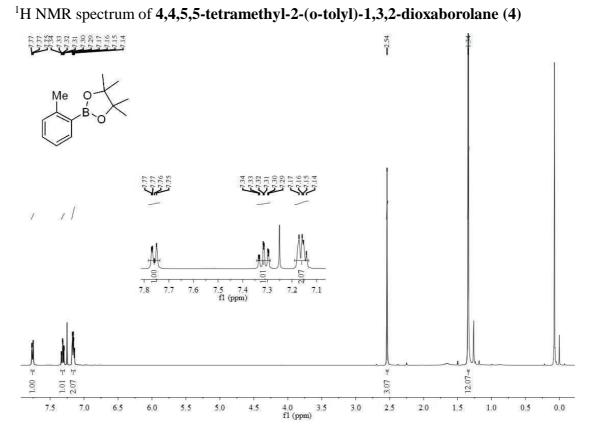


<sup>1</sup>H NMR spectrum of **4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (3)** 

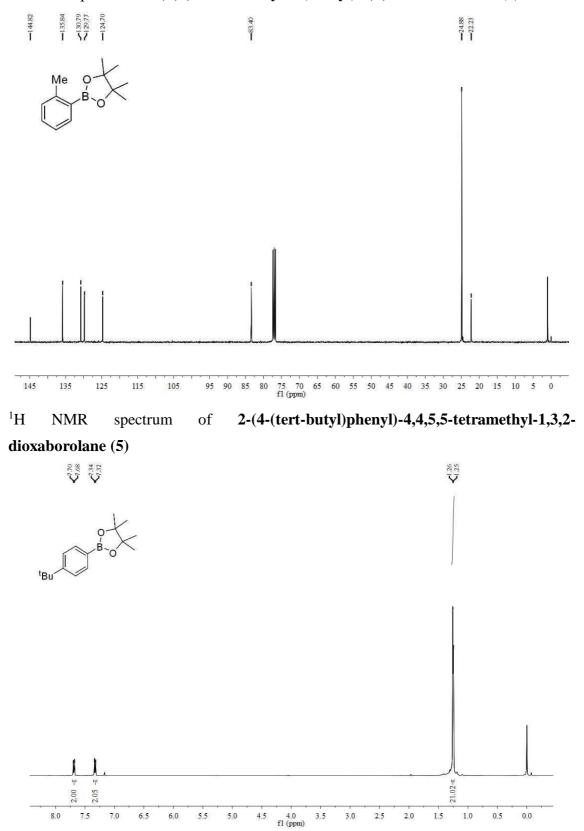


<sup>13</sup>C NMR spectrum of 4,4,5,5-tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (3)

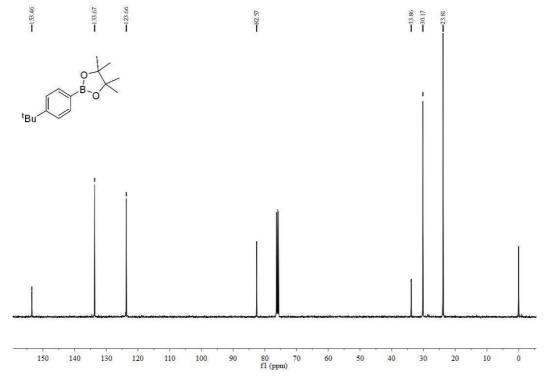


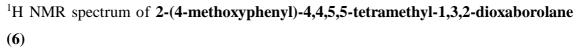


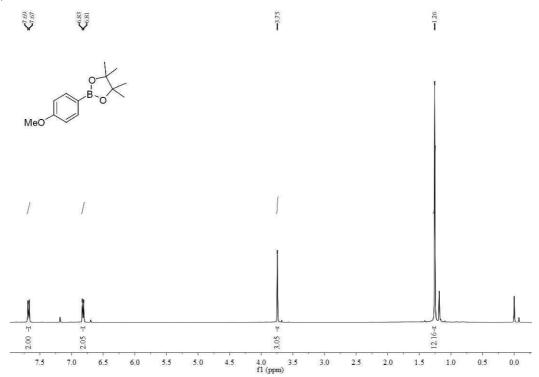
<sup>13</sup>C NMR spectrum of 4,4,5,5-tetramethyl-2-(o-tolyl)-1,3,2-dioxaborolane (4)



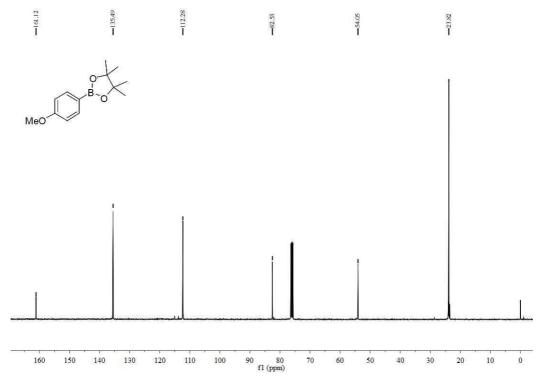
<sup>13</sup>C NMR spectrum of 2-(4-(tert-butyl)phenyl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (5)



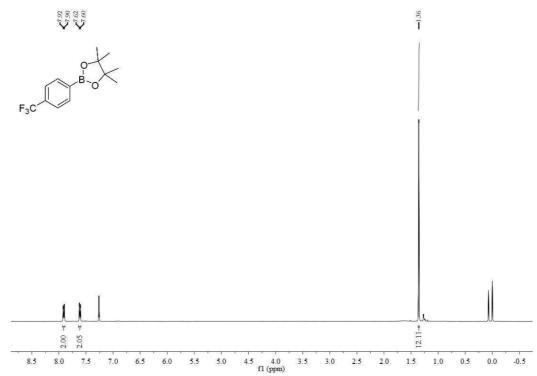




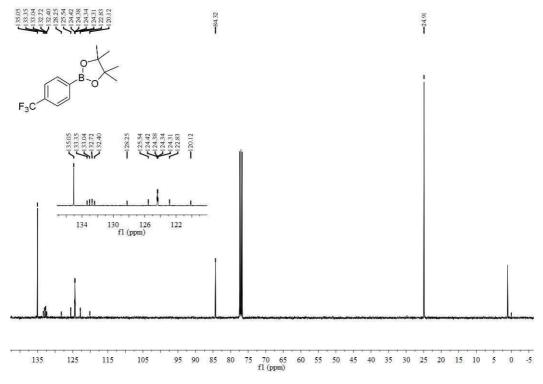
<sup>13</sup>C NMR spectrum of 2-(4-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane
(6)



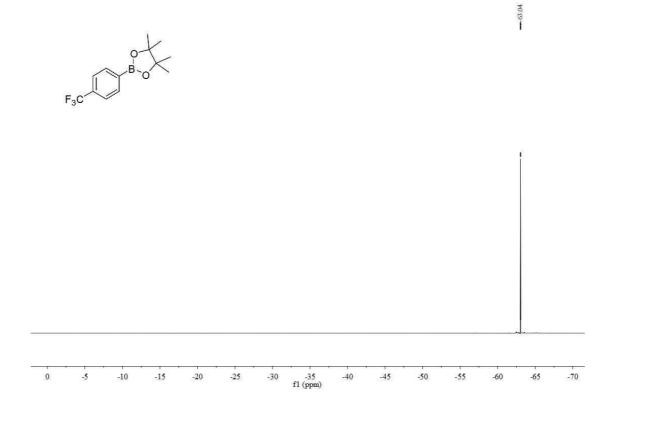
<sup>1</sup>H NMR spectrum of **4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2dioxaborolane (7)** 



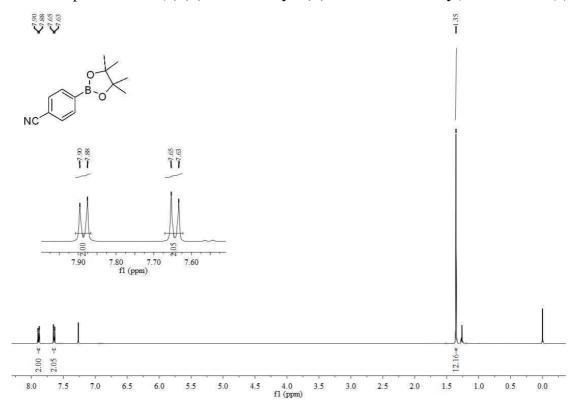
<sup>13</sup>C NMR spectrum of **4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2dioxaborolane (7)** 



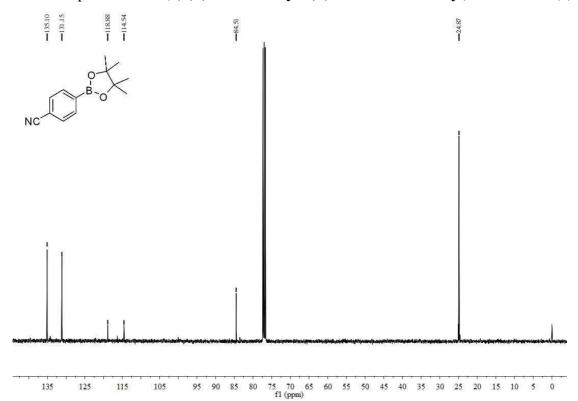
<sup>19</sup>F NMR spectrum of **4,4,5,5-tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2dioxaborolane (7)** 



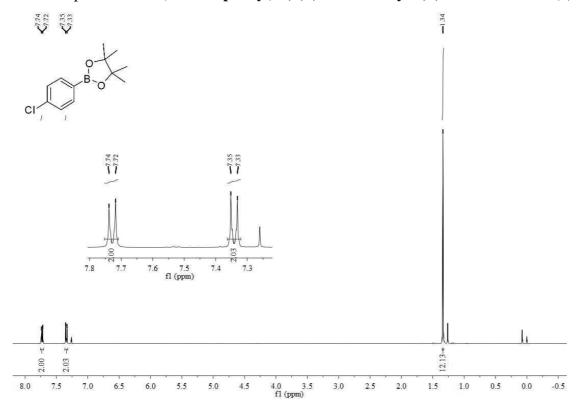
<sup>1</sup>H NMR spectrum of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (8)



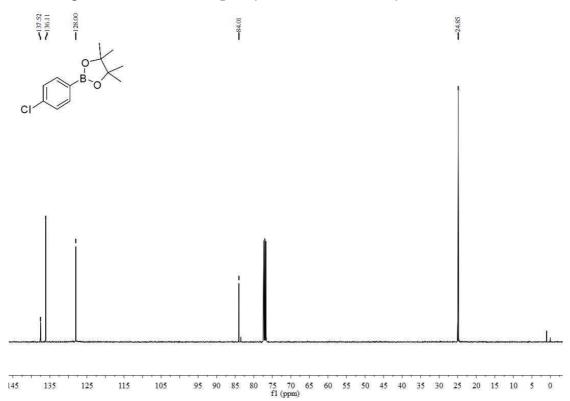
<sup>13</sup>C NMR spectrum of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (8)



<sup>1</sup>H NMR spectrum of 2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9)

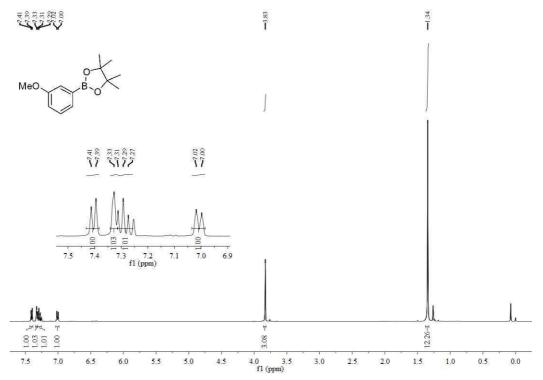


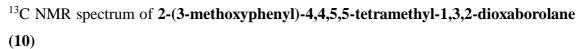
<sup>13</sup>C NMR spectrum of **2-(4-chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (9)** 

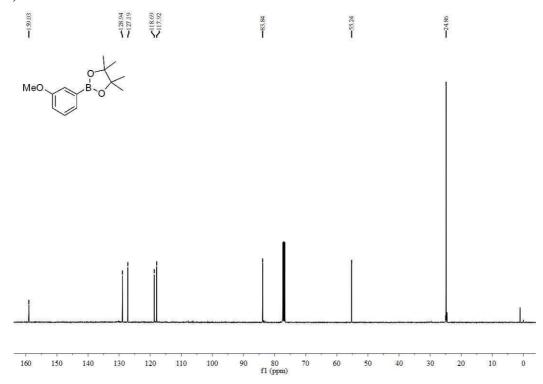


S72

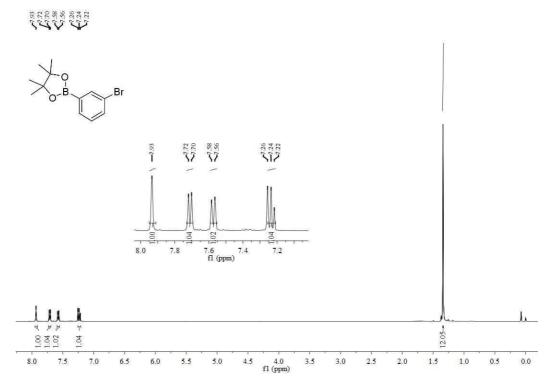
<sup>1</sup>H NMR spectrum of 2-(3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (10)

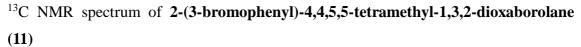


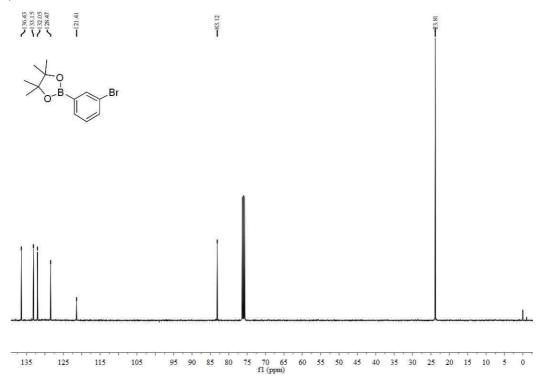




<sup>1</sup>H NMR spectrum of 2-(3-bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (11)

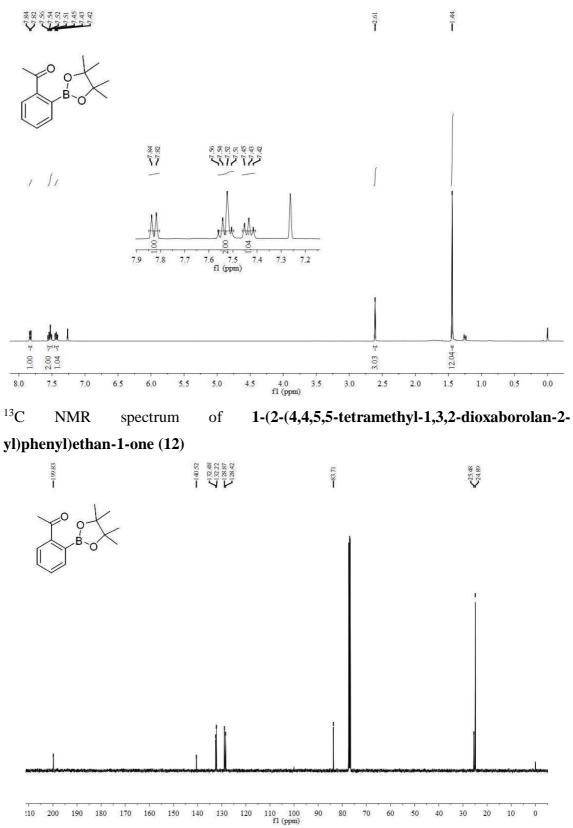




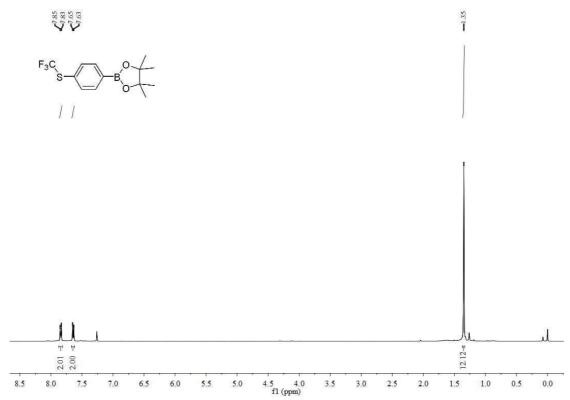


S74

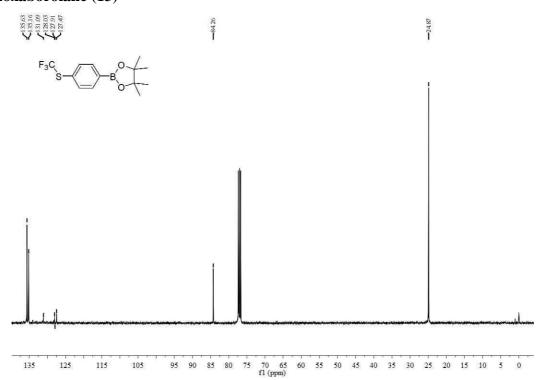
yl)phenyl)ethan-1-one (12)



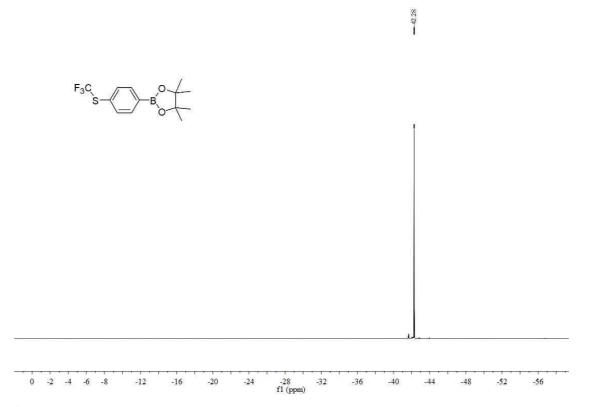
<sup>1</sup>H NMR spectrum of **4,4,5,5-tetramethyl-2-(4-((trifluoromethyl)thio)phenyl)-1,3,2dioxaborolane (13)** 



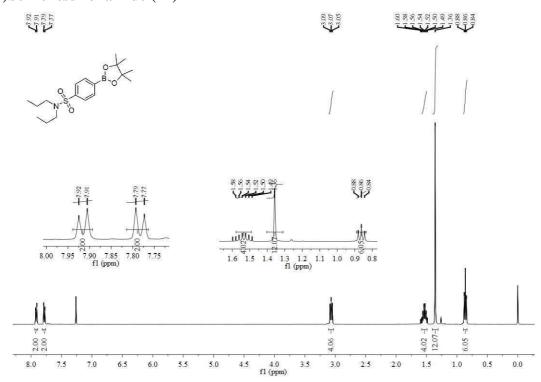
<sup>13</sup>C NMR spectrum of **4,4,5,5-tetramethyl-2-(4-((trifluoromethyl)thio)phenyl)-1,3,2dioxaborolane (13)** 



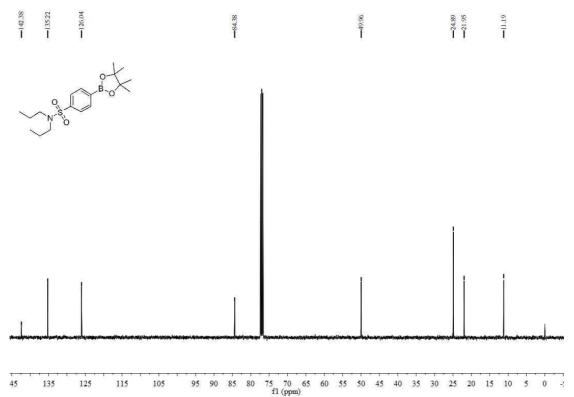
<sup>19</sup>F NMR spectrum of **4,4,5,5-tetramethyl-2-(4-((trifluoromethyl)thio)phenyl)-1,3,2dioxaborolane (13)** 



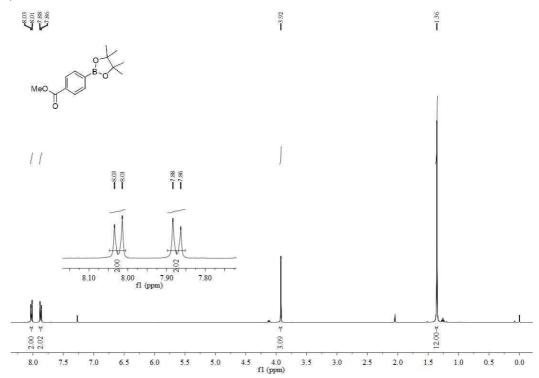
<sup>1</sup>H NMR spectrum of **N,N-dipropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonamide (14)** 



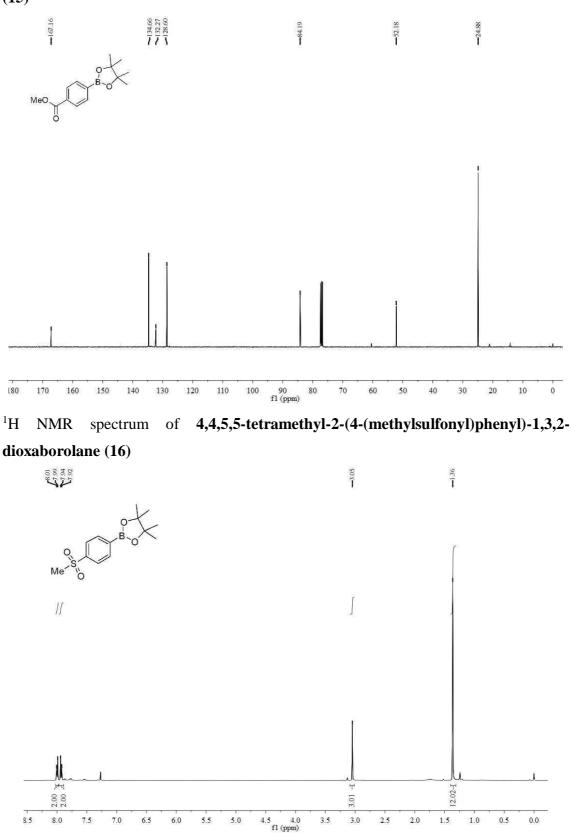
<sup>13</sup>C NMR spectrum of **N,N-dipropyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonamide (14)** 



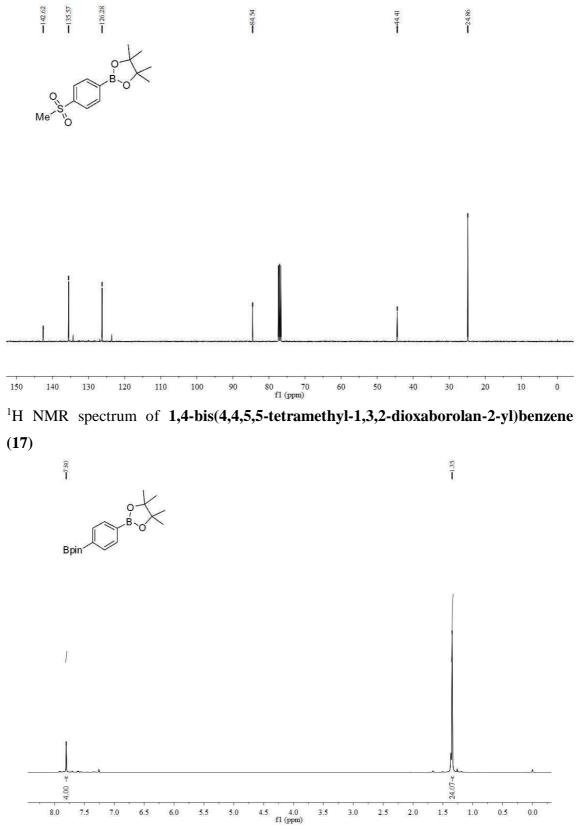
<sup>1</sup>H NMR spectrum of methyl 4-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)benzoate (15)



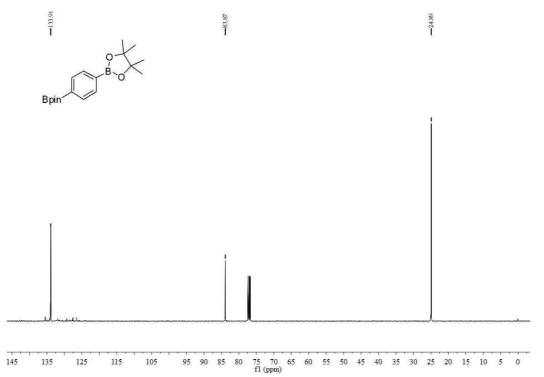
<sup>13</sup>C NMR spectrum of methyl 4-(4,4,5-trimethyl-1,3,2-dioxaborolan-2-yl)benzoate (15)



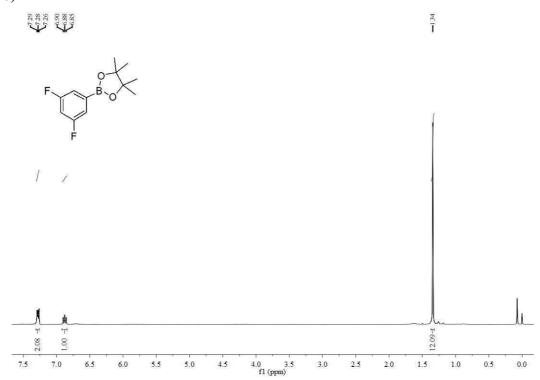
<sup>13</sup>C NMR spectrum of **4,4,5,5-tetramethyl-2-(4-(methylsulfonyl)phenyl)-1,3,2dioxaborolane (16)** 



<sup>13</sup>C NMR spectrum of 1,4-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene(17)



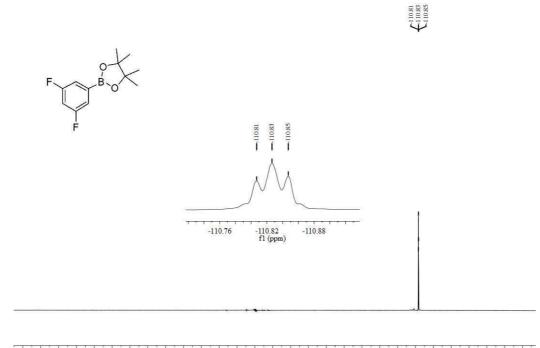
<sup>1</sup>H NMR spectrum of 2-(3,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (18)



<sup>13</sup>C NMR spectrum of **dioxaborolane (18)** 

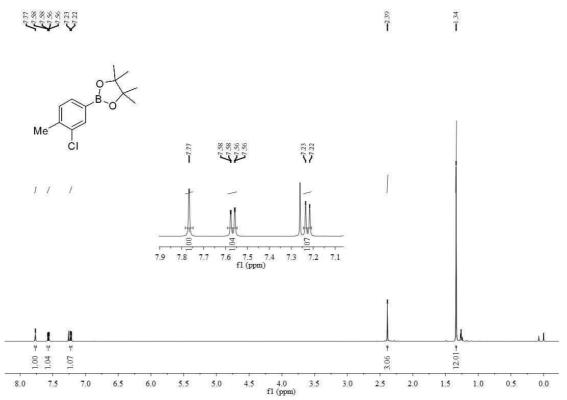
 $\frac{Z_{163,91}^{164,02}}{\chi_{161,54}^{161,54}}$  $\underbrace{ \{ \begin{array}{c} 116.91 \\ 116.69 \\ 116.69 \\ 116.69 \\ 106.27 \\ 106.27 \\ 106.27 \\ 106.27 \end{array} }$ -24.83 90 80 f1 (ppm) 160 150 140 130 120 110 100 70 60 50 40 30 20 10 0

<sup>19</sup>F NMR spectrum of 2-(3,5-difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane(18)

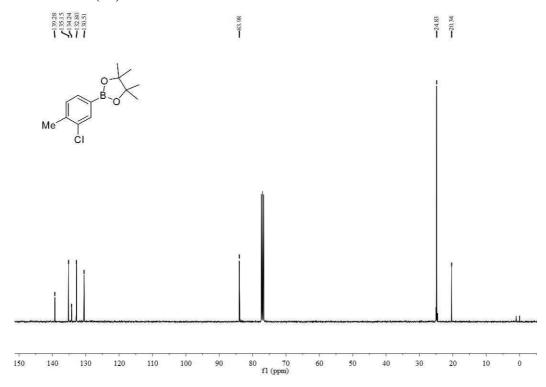


0 -5 -15 -25 -35 -45 -55 -65 -75 -85 -95 -105 -115 -125 -135 f1 (ppm)

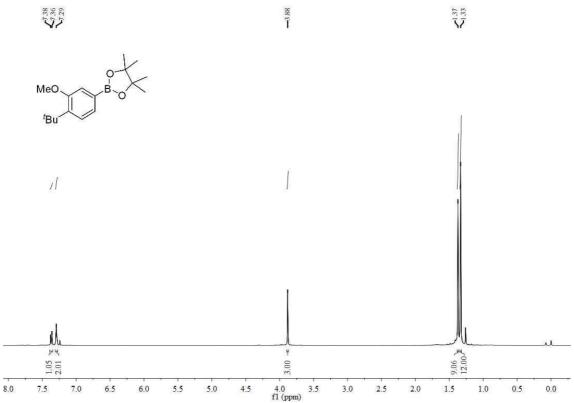
<sup>1</sup>H NMR spectrum of 2-(3-chloro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (19)



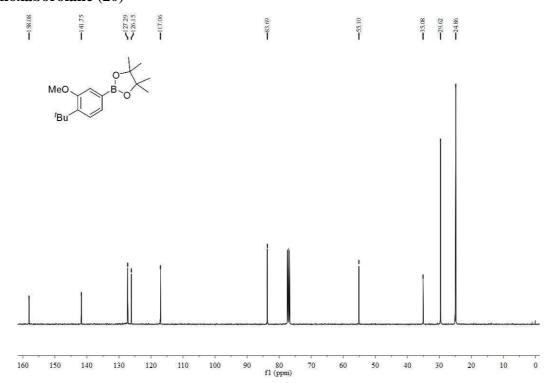
<sup>13</sup>C NMR spectrum of 2-(3-chloro-4-methylphenyl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (19)



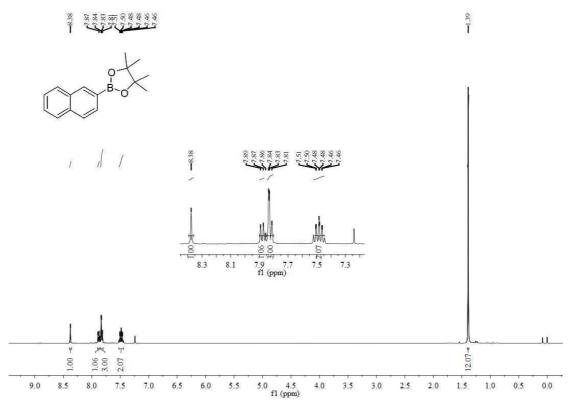
<sup>1</sup>H NMR spectrum of 2-(4-(tert-butyl)-3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (20)



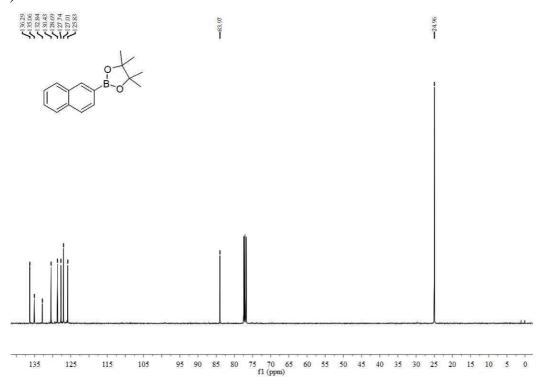
<sup>13</sup>C NMR spectrum of 2-(4-(tert-butyl)-3-methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2dioxaborolane (20)



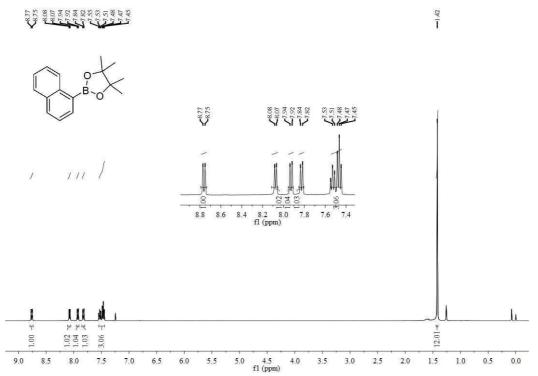
<sup>1</sup>H NMR spectrum of **4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane** (21)

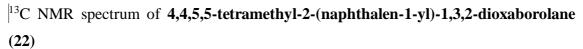


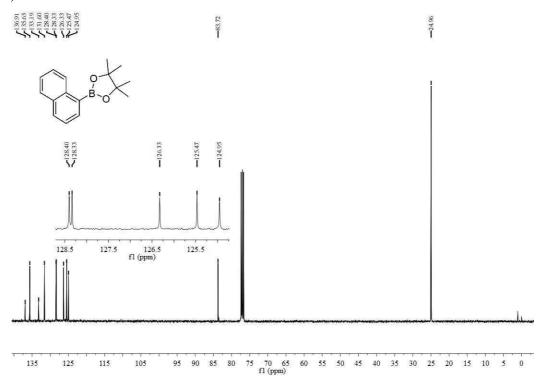
<sup>13</sup>C NMR spectrum of 4,4,5,5-tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane(21)

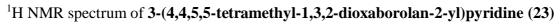


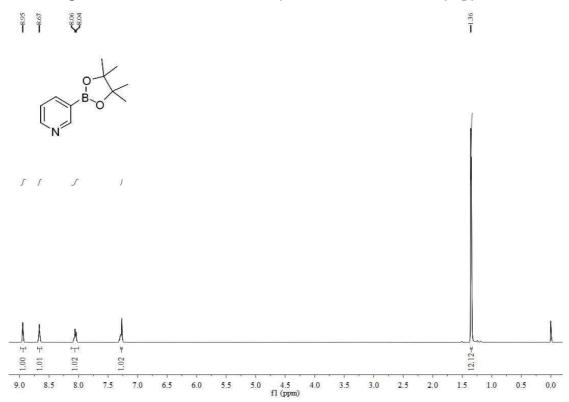
<sup>1</sup>H NMR spectrum of 4,4,5,5-tetramethyl-2-(naphthalen-1-yl)-1,3,2-dioxaborolane (22)



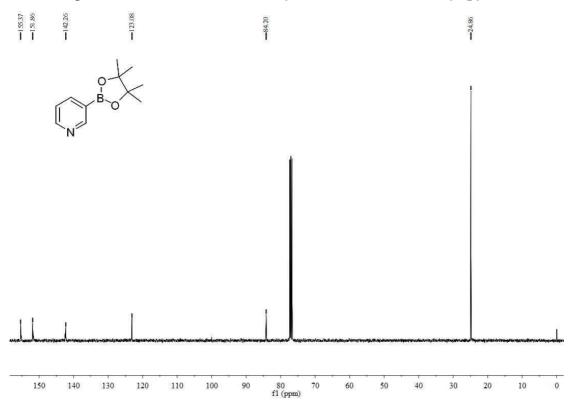


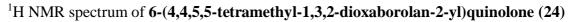


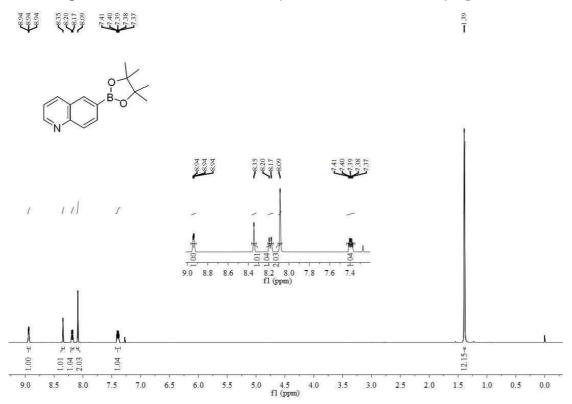




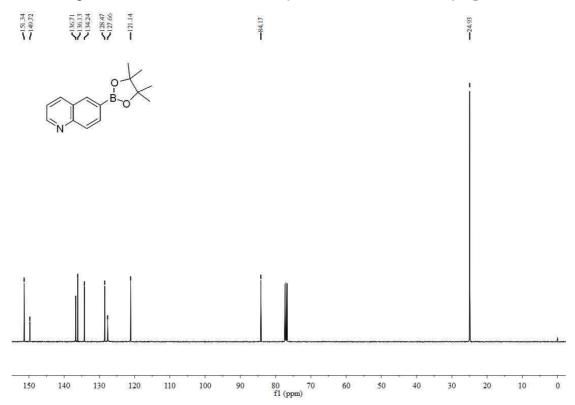
<sup>13</sup>C NMR spectrum of **3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (23)** 



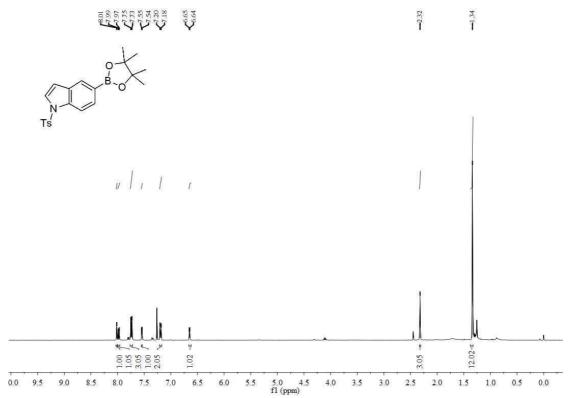




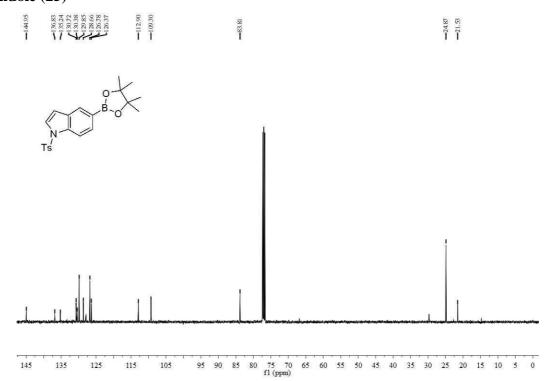
<sup>13</sup>C NMR spectrum of 6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)quinoline (24)



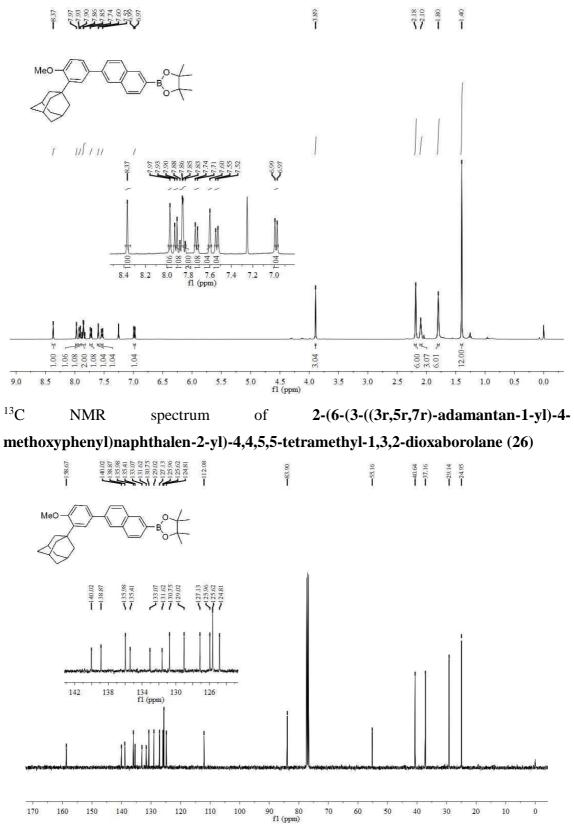
<sup>1</sup>H NMR spectrum of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1Hindole (25)

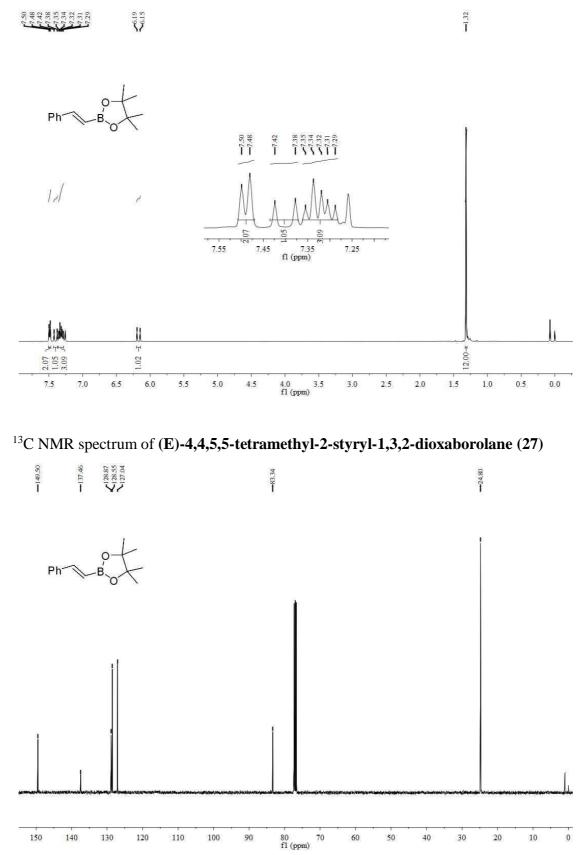


<sup>13</sup>C NMR spectrum of 5-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-tosyl-1Hindole (25)



 $\label{eq:hardenergy} {}^{1}\text{H} \qquad \text{NMR} \qquad \text{spectrum} \qquad \text{of} \qquad \textbf{2-(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (26)}$ 

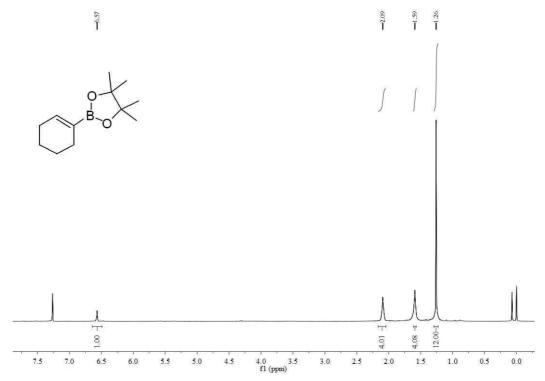




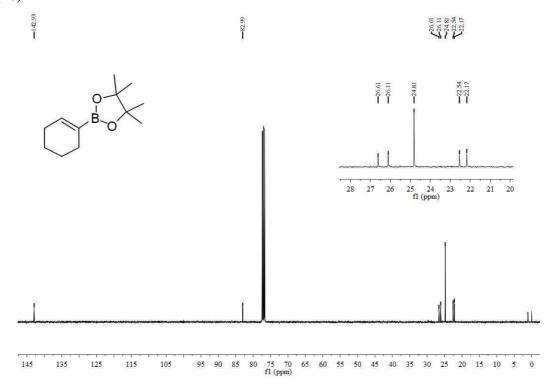
## <sup>1</sup>H NMR spectrum of (E)-4,4,5,5-tetramethyl-2-styryl-1,3,2-dioxaborolane (27)

S91

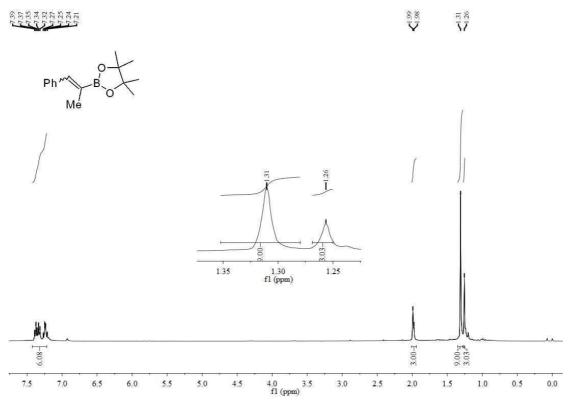
<sup>1</sup>H NMR spectrum of 2-(cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28)



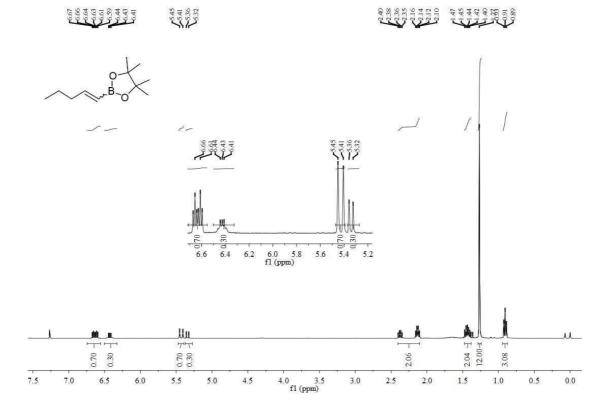
<sup>13</sup>C NMR spectrum of 2-(cyclohex-1-en-1-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (28)

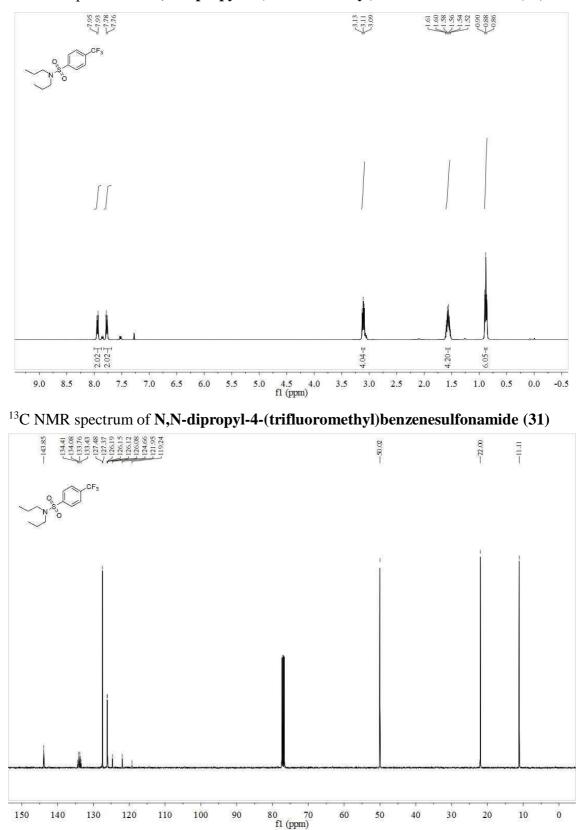


<sup>1</sup>H NMR spectrum of **4,4,5,5-tetramethyl-2-(1-phenylprop-1-en-2-yl)-1,3,2dioxaborolane (29)** 

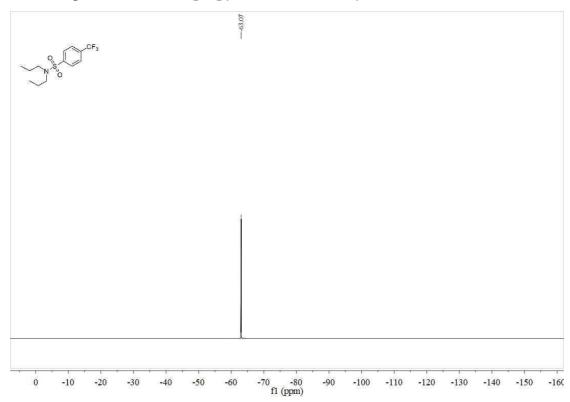


<sup>1</sup>H NMR spectrum of 4,4,5,5-tetramethyl-2-(pent-1-en-1-yl)-1,3,2-dioxaborolane (30)



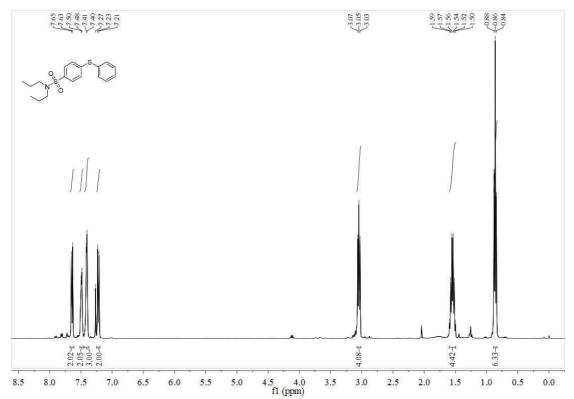


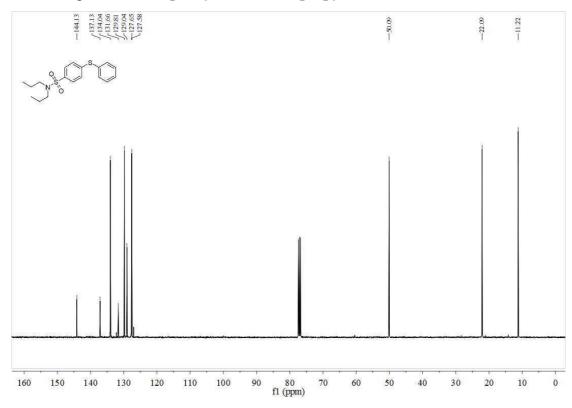
<sup>1</sup>H NMR spectrum of **N,N-dipropyl-4-(trifluoromethyl)benzenesulfonamide (31)** 



<sup>19</sup>F NMR spectrum of **N,N-dipropyl-4-(trifluoromethyl)benzenesulfonamide (31)** 

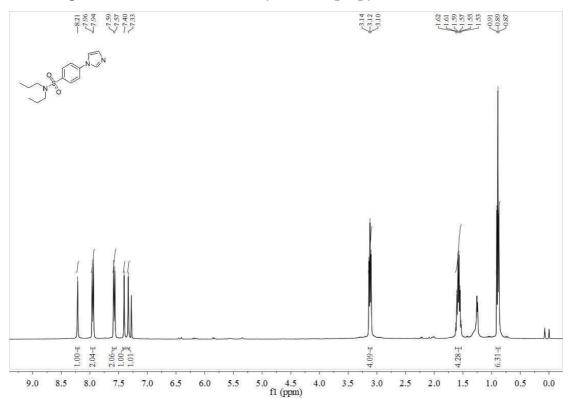
<sup>1</sup>H NMR spectrum of **4-(phenylthio)-N,N-dipropylbenzenesulfonamide (32)** 

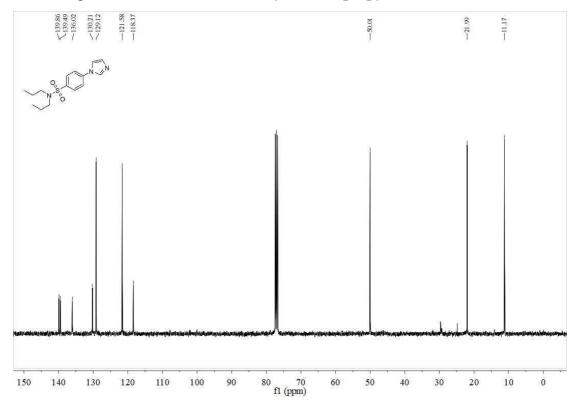




<sup>13</sup>C NMR spectrum of **4-(phenylthio)-N,N-dipropylbenzenesulfonamide (32)** 

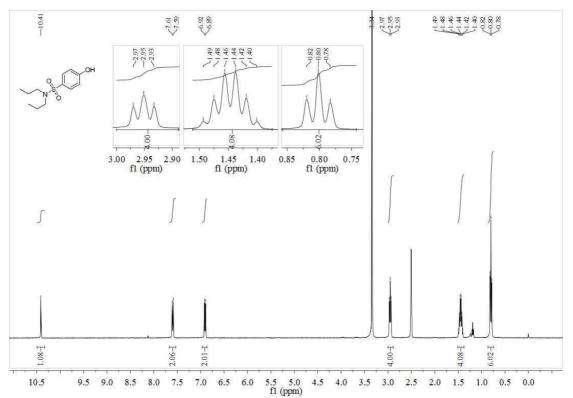
<sup>1</sup>H NMR spectrum of 4-(1H-imidazol-1-yl)-N,N-dipropylbenzenesulfonamide (33)

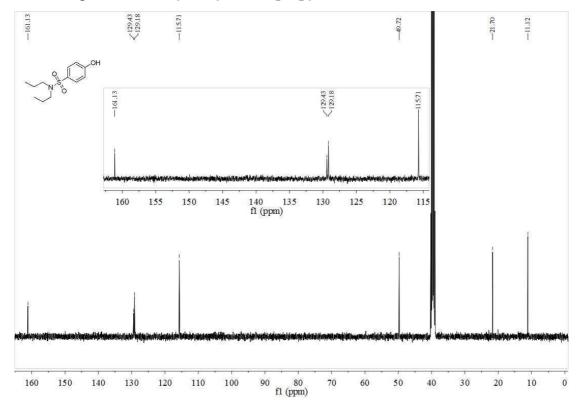




<sup>13</sup>C NMR spectrum of 4-(1H-imidazol-1-yl)-N,N-dipropylbenzenesulfonamide (33)

<sup>1</sup>H NMR spectrum of **4-hydroxy-N,N-dipropylbenzenesulfonamide (34)** 





<sup>13</sup>C NMR spectrum of **4-hydroxy-N,N-dipropylbenzenesulfonamide (34)**