# Supporting Information 

# Directed Ortho Borylation of Phenol Derivatives Catalyzed by a Silica-Supported Iridium Complex 

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## Table of Contents

Instrumentation and Chemicals ..... S1
Experimental Procedures ..... S2-S3
Compounds Characterization ..... S3-S12
References ..... S12-S13
NMR spectra ..... S14-S103

## Instrumentation and Chemicals

NMR spectra were recorded on a Varian Gemini 2000 spectrometer, operating at 300 MHz for ${ }^{1} \mathrm{H}$ NMR and 75.4 MHz for ${ }^{13} \mathrm{C}$ NMR. Chemical shift values for ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ are reference to $\mathrm{Me}_{4} \mathrm{Si}$ and the residual solvent resonances respectively. Chemical shifts are reported in $\delta \mathrm{ppm}$. Elemental analysis was performed at the Center for Instrument Analysis, Hokkaido University. High-resolution mass spectra were recorded on a Thermo Scientific Exactive or JEOL JMS-T100GC mass spectrometer at the Center for Instrument Analysis, Hokkaido University. TLC analyses were performed on commercial glass plates bearing $0.25-\mathrm{mm}$ layer of Merck Silica gel $60 \mathrm{~F}_{254}$. Silica gel (Kanto Chemical Co., Silica gel 60 N , spherical, neutral) was used for column chromatography. Gas chromatographic (GC) analyses were conducted on a Shimadzu GC-14B equipped with a flame ionization detector. Gel permeation chromatography (GPC) was performed by LC-908 (Japan Analytical Industry Ltd., two in-line JAIGEL-2H, $\mathrm{CHCl}_{3}, 3.5 \mathrm{~mL} / \mathrm{min}$, UV and RI detectors).

All reactions were carried out under nitrogen or argon atmosphere. Materials were obtained from commercial suppliers or prepared according to standard procedures unless otherwise noted. Silica-SMAP was prepared according to the reported procedure. ${ }^{1}$ All solvents for catalytic reactions were degassed via four freeze-pump-thaw cycles before use. $[\operatorname{Ir}(\mathrm{OMe})(\operatorname{cod})]_{2}$ was prepared according to the literature. ${ }^{2}$ Pinacolatoborane and bis(pinacolato)diboron were purchased from

## Experimental Procedures

## Typical Procedure for the Ortho-Borylation of Phenyl Diethylcarbamate (3aa) (Scheme 1).

In a glove box, Silica-SMAP (1, $\left.0.064 \mathrm{mmol} \mathrm{Pg}^{-1}, 40 \mathrm{mg}, 0.0025 \mathrm{mmol}\right)$, anhydrous, degassed hexane $(1.1 \mathrm{~mL})$, and $[\operatorname{Ir}(\mathrm{OMe})(\mathrm{cod})]_{2}(0.8 \mathrm{mg}, 0.00125 \mathrm{mmol})$ in hexane $(0.4 \mathrm{~mL})$ were placed in a 10 mL -glass tube containing a magnetic stirring bar, and the mixture was stirred for 1 min at $25^{\circ} \mathrm{C}$. 3aa ( $196.5 \mathrm{mg}, 1.0 \mathrm{mmol}$ ), and pinacolatoborane ( $\mathbf{2}, 62.8 \mathrm{mg}, 0.5 \mathrm{mmol}$ ) were added in the tube, which was then sealed with a screw cap. The tube was removed from the glove box. After the resulting mixture was stirred at $70{ }^{\circ} \mathrm{C}$ for 12 h , the mixture was filtered through a glass pipet equipped with a cotton filter. Solvent was removed under reduced pressure. An internal standard (1,1,2,2-tetrachloroethane) was added to the reaction mixture. The yield of the product was determined by ${ }^{1} \mathrm{H}$ NMR. The crude material was purified by GPC to give the borylation product 4aa ( $100.5 \mathrm{mg}, 0.32 \mathrm{mmol}$ ) in $64 \%$ isolated yield.

Suzuki-Miyaura Cross-Coupling/Deprotection of Carbamate (Scheme 2, upper side). 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-diethylcarbamate (4aa) ( $96.6 \mathrm{mg}, 0.30$ mmol), 2-bromothiophene ( $62.9 \mathrm{mg}, 0.36 \mathrm{mmol}$ ), $\mathrm{Na}_{2} \mathrm{CO}_{3}(256.0 \mathrm{mg}, 2.4 \mathrm{mmol})$ and $\mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}$ $(18.1 \mathrm{mg}, 0.015 \mathrm{mmol})$ in a mixed solvent consisting of DME ( 1.0 mL ) and $\mathrm{H}_{2} \mathrm{O}(0.1 \mathrm{~mL})$ were placed in 10 mL -glass tube containing a magnetic stirring bar. The tube was then sealed with a screw cap in argon. After being stirred at $90{ }^{\circ} \mathrm{C}$ for 24 h , the glass tube was cooled to rt . The reaction mixture was washed with water and brine, and was dried over $\mathrm{MgSO}_{4}$. Solvent was removed under reduced pressure. The crude material was dissolved in $\mathrm{Et}_{2} \mathrm{O}(5.0 \mathrm{~mL})$, and the solution was added to a suspension of $\mathrm{LiAlH}_{4}(34.1 \mathrm{mg}, 0.9 \mathrm{mmol})$ in $\mathrm{Et}_{2} \mathrm{O}(10.0 \mathrm{~mL})$ in a two-neck round-bottom flask equipped with a reflux condenser. After being stirred at reflux for 7 h , the flask was cooled to room temperature, and water $(5.0 \mathrm{~mL})$ and $1 \mathrm{M} \mathrm{HCl} \mathrm{aq}(5.0 \mathrm{~mL})$ were in turn added to the reaction mixture at $0{ }^{\circ} \mathrm{C}$. The mixture was extracted with EtOAc $(2 \times 20 \mathrm{~mL})$. The combined organic layers were washed with brine and dried over $\mathrm{MgSO}_{4}$. The solvent was evaporated. Flash silica gel column chromatography (hexane/EtOAc 90:10) of the crude product provided $\mathbf{6}$ ( 36.2 mg , 0.20 mmol ) in $68 \%$ yield. Spectral data match those previously reported. ${ }^{3}$

Suzuki-Miyaura Cross-Coupling/Ni-Catalyzed Cross-Coupling (Scheme 2, bottom side). 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-diethylcarbamate (4aa) ( $96.1 \mathrm{mg}, 0.30$ mmol ), 2-bromobenzene ( $58.1 \mathrm{mg}, 0.37 \mathrm{mmol}$ ), $\mathrm{Na}_{2} \mathrm{CO}_{3}(258.1 \mathrm{mg}, 2.4 \mathrm{mmol}), \mathrm{Pd}\left(\mathrm{PPh}_{3}\right)_{4}(17.7 \mathrm{mg}$, $0.015 \mathrm{mmol})$ in a mix solvent consisting of DME ( 1.0 ml ) and $\mathrm{H}_{2} \mathrm{O}(0.1 \mathrm{ml})$ were placed in a 10
mL -glass tube containing a magnetic stirring bar. The tube was then sealed with a screw cap under argon. After being stirred at $90{ }^{\circ} \mathrm{C}$ for 24 h , the glass tube was cooled to rt . The reaction mixture was washed with water and brine, and was dried over $\mathrm{MgSO}_{4}$. After filtration, the solvent was evaporated. Flash silica gel column chromatography (hexane/EtOAc 95:5) of the crude product provided $7(65.4 \mathrm{mg}, 0.24 \mathrm{mmol})$ in $81 \%$ yield. In a glove box, $7(65.4 \mathrm{mg}, 0.24 \mathrm{mmol}), \mathrm{Ni}(\mathrm{acac})_{2}$ ( $3.4 \mathrm{mg}, 0.013 \mathrm{mmol}$ ), 1-[2-(diphenylphosphino)phenyl]ethanol ( $3.7 \mathrm{mg}, 0.012 \mathrm{mmol}$ ) in $\mathrm{Et}_{2} \mathrm{O}$ ( 0.6 $\mathrm{mL})$ and anhydrous, degassed $\mathrm{Et}_{2} \mathrm{O}(0.9 \mathrm{~mL})$ were placed sequentially in a 10 mL -glass tube containing a magnetic stirring bar, which was then sealed with a screw cap. The tube was removed from the glove box, and 4-methoxyphenylmagnesium bromide ( $480 \mu \mathrm{~L}, 0.48 \mathrm{mmol}, 1.0 \mathrm{M}$ in $\mathrm{Et}_{2} \mathrm{O}$ ) was added to the tube. After being stirred at room temperature for $41 \mathrm{~h}, \mathrm{sat} . \mathrm{NH}_{4} \mathrm{Cl}$ was added to the reaction mixture. The mixture was extracted with EtOAc ( $2 \times 20 \mathrm{~mL}$ ). The combined organic layers were washed with brine and dried over $\mathrm{MgSO}_{4}$. The solvent was evaporated. Flash silica gel column chromatography (hexane/EtOAc 95:5) of the crude product provided 8 ( $50.8 \mathrm{mg}, 0.20 \mathrm{mmol}$ ) in $80 \%$ yield. Spectral data match those previously reported. ${ }^{4}$

## Compounds Characterization

The phenol derivatives 3ab, 3ac, 3ad, 3ae, 3af and 3ah are known compounds. The Starting materials 3aa, ${ }^{5} \mathbf{3 a g},{ }^{6} \mathbf{3 b},{ }^{7} \mathbf{3 c},{ }^{8} \mathbf{3 d},{ }^{8} \mathbf{3 g},{ }^{9} \mathbf{3 i}^{5}, \mathbf{3 1}^{10}$ and $\mathbf{3 m}{ }^{9}$ shown in Scheme 1 and Table 1 are known compounds. Compound $\mathbf{4 a} \mathbf{a}$ is found in the literature. ${ }^{11}$ The borylation products $\mathbf{4 a} \mathbf{a}$ and $\mathbf{4 b} \mathbf{~} \mathbf{4 s}$ were purified by GPC.

2-Methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-Diethylcarbamate (4b)


Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.18-1.33(\mathrm{~m}, 6 \mathrm{H}), 1.30(\mathrm{~s}, 12 \mathrm{H}), 2.21(\mathrm{~s}, 3 \mathrm{H}), 3.39(\mathrm{q}, J=7.2$ $\mathrm{Hz}, 2 \mathrm{H}), 3.52(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.10(\mathrm{t}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.28(\mathrm{~d}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.60(\mathrm{~d}, J=7.2$ $\mathrm{Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C} \mathbf{N M R}\left(\mathrm{CDCl}_{3}\right) \delta 13.32,14.05,16.16,24.70,41.53,41.90,83.32,124.92,130.56$, 133.84, 133.88, 154.29, 154.69. A signal for the carbon directly attached to the boron atom was not observed. Anal. Calcd for $\mathrm{C}_{18} \mathrm{H}_{28} \mathrm{BNO}_{4}$ : C, $64.88 \%$; H, $8.47 \%$; N, $4.20 \%$. Found: C, 64.65; H, 8.55\%; N, 4.22\%.


Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.17-1.33(\mathrm{~m}, 6 \mathrm{H}), 1.29(\mathrm{~s}, 12 \mathrm{H}), 2.34(\mathrm{~s}, 3 \mathrm{H}), 3.38(\mathrm{q}, J=6.9$ $\mathrm{Hz}, 2 \mathrm{H}), 3.50(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.90(\mathrm{~s}, 1 \mathrm{H}), 7.01(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.66(\mathrm{~d}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H})$. ${ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.20,13.79,21.16,24.60,41.40,41.72,83.16,122.87,125.65,136.11$, 142.77, 154.87, 156.33. A signal for the carbon directly attached to the boron atom was not observed. Anal. Calcd for $\mathrm{C}_{18} \mathrm{H}_{28} \mathrm{BNO}_{4}$ : C, $64.88 \%$; H, $8.47 \%$; N, $4.20 \%$. Found: C, $64.60 ; \mathrm{H}$, 8.54\%; N, 4.21\%.

## 5-Methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl N,N-Diethylcarbamate

 (4d)

4 d
Colorress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.18-1.31(\mathrm{~m}, 6 \mathrm{H}), 1.29(\mathrm{~s}, 12 \mathrm{H}), 3.38(\mathrm{q}, J=7.2, \mathrm{~Hz}, 2 \mathrm{H})$, $3.51(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 6.63(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}), 6.75(\mathrm{dd}, J=8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.70$ $(\mathrm{d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C} \mathbf{N M R}\left(\mathrm{CDCl}_{3}\right) \delta 13.25,13.86,24.68,41.48,41.79,55.18,83.13,108.02$, 111.11, 137.31, $154.70,157.92,163.09$. A signal for the carbon directly attached to the boron atom was not observed. HRMS-ESI $(\mathrm{m} / \mathrm{z})$ : $[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{18} \mathrm{H}_{28} \mathrm{O}_{5} \mathrm{NBNa}$, 372.19527; found, 372.19570 .

## 3-Trifluoromethylphenyl $N, N$-Diethylcarbamate (3e)



Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.19-1.29(\mathrm{~m}, 6 \mathrm{H}), 3,36-3.49(\mathrm{~m}, 4 \mathrm{H}), 7.34(\mathrm{~m}, 1 \mathrm{H}), 7.40(\mathrm{~s}$, $1 \mathrm{H}), 7.44-7.51(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.14,14.06,41.88,42.29,119.05(\mathrm{q}, J=4.0 \mathrm{~Hz})$, $121.87(\mathrm{q}, J=3.4 \mathrm{~Hz}), 123.71(\mathrm{q}, J=273.7 \mathrm{~Hz}), 125.45(\mathrm{~d}, J=1.1 \mathrm{~Hz}), 129.77,131.73(\mathrm{q}, J=32.6$ $\mathrm{Hz}), 151.72,153.70,156.23$. Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{14} \mathrm{~F}_{3} \mathrm{NO}_{2}$ : C, $55.17 \%$; $\mathrm{H}, 5.40 \%$; N, $5.36 \%$. Found: C, 55.07\%; H, 5.32\%; N, 5.34\%.

## 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-5-trifluoromethylphenyl

 $N, N$-Diethylcarbamate (4e)

Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.18-1.31(\mathrm{~m}, 6 \mathrm{H}), 1.31(\mathrm{~s}, 12 \mathrm{H}), 3.39(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H})$, $3.49(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.33(\mathrm{~s}, 1 \mathrm{H}), 7.44(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.88(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.20,13.84,24.70,41.59,41.97,83.92,119.23(\mathrm{q}, J=4.0 \mathrm{~Hz}), 121.36(\mathrm{q}, J=3.4 \mathrm{~Hz})$, $123.65(\mathrm{q}, J=273.1 \mathrm{~Hz}), 133.89(\mathrm{q}, J=33.2 \mathrm{~Hz}), 136.68,154.41,156.23$. A signal for the carbon directly attached to the boron atom was not observed. HRMS-ESI $(\mathrm{m} / \mathrm{z})$ : $[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{18} \mathrm{H}_{25}$ $\mathrm{O}_{4} \mathrm{BF}_{3} \mathrm{NNa}, 410.17209$; found, 410.17247. The regioselectivity was assigned on the basis of the $J_{\mathrm{C}-\mathrm{F}}$ values in the ${ }^{13} \mathrm{C}$ NMR spectrum.


## (1,1'-Biphenyl)-3-yl $N, N$-Diethylcarbamate (3f)


$3 f$
Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.20-1.30(\mathrm{~m}, 6 \mathrm{H}), 3.38-3.50(\mathrm{~m}, 4 \mathrm{H}), 7.12(\mathrm{~m}, 1 \mathrm{H}), 7.31-7.37$ $(\mathrm{m}, 2 \mathrm{H}), 7.40-7.45(\mathrm{~m}, 4 \mathrm{H}), 7.58-7.61(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.16,14.03,41.72,42.07$, 120.51, 120.55, 123.79, 127.16, 127.46, 128.69, 129.44, 140.43, 142.57, 151.94, 154.20. Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{19} \mathrm{NO}_{2}$ : C, $75.81 \%$; H, $7.11 \%$; N, 5.20\%. Found: C, $75.85 \%$; H, 7.17\%; N, 5.21\%.

5-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-Diethylcarbamate (4f)

$4 f$
Colorress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.19-1.32(\mathrm{~m}, 6 \mathrm{H}), 1.32(\mathrm{~s}, 12 \mathrm{H}), 3.40(\mathrm{q}, J=6.9, \mathrm{~Hz}, 2 \mathrm{H})$, $3.53(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.31(\mathrm{~d}, J=1.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.36(\mathrm{dm}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.40(\mathrm{~m}, 1 \mathrm{H}), 7.61$ $(\mathrm{dm}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.84(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C} \mathbf{N M R}\left(\mathrm{CDCl}_{3}\right) \delta 13.26,13.88,24.69,41.51$, $41.82,83.41,120.90,123.44,127.19,127.73,128.70,136.64,140.22,145.28,154.82,156.72$. A signal for the carbon directly attached to the boron atom was not observed. HRMS-ESI $(\mathrm{m} / \mathrm{z})$ : $[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{23} \mathrm{H}_{30} \mathrm{O}_{4} \mathrm{NBNa}, 418.21601$; found, 418.21634.

## 5-Chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-Diethylcarbamate (4g)



4 g

Colorress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.17-1.33(\mathrm{~m}, 6 \mathrm{H}), 1.30(\mathrm{~s}, 12 \mathrm{H}), 3.38(\mathrm{q}, J=7.2, \mathrm{~Hz}, 2 \mathrm{H})$, $3.49(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.11(\mathrm{~d}, J=1.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.18(\mathrm{dd}, J=8.1,1.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.70(\mathrm{~d}, J=8.1 \mathrm{~Hz}$, $1 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.18,13.81,24.65,41.52,41.89,83.59,122.85,125.11,137.00,137.49$, 154.33, 156.79. A signal for the carbon directly attached to the boron atom was not observed. Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{25} \mathrm{BClNO}_{4}$ : C, $57.74 \%$; H, $7.13 \%$; N, $3.96 \%$. Found: C, $57.49 ; \mathrm{H}, 7.10 \%$; N, $3.88 \%$. The synthesis of known compound 4-chloro-4'-methoxy-[1,1'-biphenyl]-2-ol ${ }^{13}$ from $\mathbf{4 g}$ by Suzuki-Miyaura coupling followed by deprotection of the carbamate moiety confirmed the assignment for $\mathbf{4 g}$.


## 4-Methylphenyl Diethylcarbamate (3h)



Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.20-1.24(\mathrm{~m}, 6 \mathrm{H}), 2.33(\mathrm{~s}, 3 \mathrm{H}), 3.37-3.44(\mathrm{~m}, 4 \mathrm{H}), 6.99(\mathrm{dm}, J=$ $8.1 \mathrm{~Hz}, 2 \mathrm{H}), 7.15(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.13,13.93,20.52,41.58,41.93$, 121.37, 129.60, 134.45, 149.27, 154.42. Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{17} \mathrm{NO}_{2}: \mathrm{C}, 69.54 \% ; \mathrm{H}, 8.27 \%$; N , 6.76\%. Found: C, 69.52\%; H, 8.40\%; N, 6.75\%.

4-Methyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-Diethylcarbamate (4h)


4h
Colorress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.17-1.30(\mathrm{~m}, 6 \mathrm{H}), 1.30(\mathrm{~s}, 12 \mathrm{H}), 2.32(\mathrm{~s}, 3 \mathrm{H}), 3.37(\mathrm{q}, J=7.2$, $\mathrm{Hz}, 2 \mathrm{H}), 3.50(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.95(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.23(\mathrm{dd}, J=8.1,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.57(\mathrm{~d}, J$ $=2.4 \mathrm{~Hz}, 1 \mathrm{H}){ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.18,13.79,20.37,24.59,41.34,41.66,83.25,121.90,132.71$, 134.01, 136.48, 154.07, 154.95. A signal for the carbon directly attached to the boron atom was not observed. HRMS-ESI $(\mathrm{m} / \mathrm{z}):[\mathrm{M}+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{18} \mathrm{H}_{29} \mathrm{BNO}_{4}, 334.21896$; found, 334.21924.

## 4-Methoxy-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl

$N, N$-Diethylcarbamate (4i)


Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.17-1.30(\mathrm{~m}, 6 \mathrm{H}), 1.30(\mathrm{~s}, 12 \mathrm{H}), 3.37(\mathrm{q}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H})$, $3.49(\mathrm{q}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H}), 3.81(\mathrm{~s}, 3 \mathrm{H}), 6.96-6.97(\mathrm{~m}, 2 \mathrm{H}), 7.27(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathbf{C} \mathbf{N M R}\left(\mathrm{CDCl}_{3}\right) \delta 13.27$, $13.87,24.69,41.42,41.78,55.55,83.47,118.23,119.75,123.19,149.90,155.24,156.44$. A signal for the carbon directly attached to the boron atom was not observed. HRMS-ESI $(\mathrm{m} / \mathrm{z}):[\mathrm{M}+\mathrm{Na}]^{+}$ calcd for $\mathrm{C}_{18} \mathrm{H}_{28} \mathrm{BNO}_{5} \mathrm{Na}, 372.19527$; found, 372.19552 .

## 4-Trifluoromethylphenyl $N, N$-Diethylcarbamate (3j)



Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.19-1.29(\mathrm{~m}, 6 \mathrm{H}), 3.36-3.49(\mathrm{~m}, 4 \mathrm{H}), 7.25(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H})$, $7.63(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 12.72,13.63,41.62,42.01,121.94,123.94(\mathrm{q}, J=$ $272.0 \mathrm{~Hz}), 126.24(\mathrm{q}, ~ J=4.0 \mathrm{~Hz}), 126.89(\mathrm{q}, J=32.6 \mathrm{~Hz}), 153.25,154.14(\mathrm{~d}, J=1.1 \mathrm{~Hz})$. Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{14} \mathrm{~F}_{3} \mathrm{NO}_{2}$ : C, $55.17 \%$; H, 5.40\%; N, 5.36\%. Found: C, 55.13\%; H, 5.36\%; N, 5.36\%.

## 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-4-trifluoromethylphenyl

## $N, N$-Diethylcarbamate (4j)


$4 j$
White solid. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.18-1.32(\mathrm{~m}, 6 \mathrm{H}), 1.30(\mathrm{~s}, 12 \mathrm{H}), 3.39(\mathrm{q}, J=7.2, \mathrm{~Hz}, 2 \mathrm{H})$, $3.51(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.19(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.68(\mathrm{dd}, J=8.4,2.1 \mathrm{~Hz}, 1 \mathrm{H}), 8.04(\mathrm{~d}, J=2.1 \mathrm{~Hz}$, 1H). ${ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.18,13.84,24.70,41.59,41.95,83.93,122.70,124.20(\mathrm{q}, J=272.6 \mathrm{~Hz})$, $127.06(\mathrm{q}, J=32.6 \mathrm{~Hz}), 129.09(\mathrm{q}, J=3.4 \mathrm{~Hz}), 133.38(\mathrm{q}, J=4.0 \mathrm{~Hz}), 154.24,158.76(\mathrm{q}, J=1.7$ Hz ). A signal for the carbon directly attached to the boron atom was not observed. Anal. Calcd for $\mathrm{C}_{18} \mathrm{H}_{25} \mathrm{~F}_{3} \mathrm{NO}_{4}$ : C, $55.83 \% ; \mathrm{H}, 6.51 \%$; N, $3.62 \%$. Found: C, $55.47 \%$; H, $6.43 \% ; \mathrm{N}, 3.57 \%$. m.p. $63.5-64.5{ }^{\circ} \mathrm{C}$. The regioselectivity was assigned on the basis of the $J_{\mathrm{C}-\mathrm{F}}$ values in the ${ }^{13} \mathrm{C}$ NMR spectrum.



(1,1'-Biphenyl)-4-yl $N, N$-Diethylcarbamate (3k)


3k

Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.20-1.30(\mathrm{~m}, 6 \mathrm{H}), 3.40-3.48(\mathrm{~m}, 4 \mathrm{H}), 7.26(\mathrm{dm}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H})$, $7.34(\mathrm{tt}, J=7.2,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.44(\mathrm{tm}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.55-7.59(\mathrm{~m}, 4 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right)$ $\delta 13.16,14.01,41.72,42.08,121.99,127.05,127.12,127.91,128.71,138.15,140.60,151.02$, 154.22. Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{19} \mathrm{NO}_{2}$ : C, $75.81 \%$; $\mathrm{H}, 7.11 \%$; $\mathrm{N}, 5.20 \%$. Found: $\mathrm{C}, 75.63 ; \mathrm{H}, 7.15 \%$; N, 5.22\%.

## 4-Phenyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-Diethylcarbamate (4k)



4k
White solid. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.19-1.32(\mathrm{~m}, 6 \mathrm{H}), 1.32(\mathrm{~s}, 12 \mathrm{H}), 3.40(\mathrm{q}, J=7.2, \mathrm{~Hz}, 2 \mathrm{H})$, $3.53(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.15(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.32(\mathrm{tt}, J=7.5,1.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.42(\mathrm{t}, J=7.5 \mathrm{~Hz}$, $2 \mathrm{H}), 7.60(\mathrm{dd}, J=7.5,1.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.64(\mathrm{dd}, J=8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.99(\mathrm{~d}, J=2.4 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.20,13.82,24.64,41.44,41.77,83.41,122.51,126.99,127.14,128.58,130.78$, $134.94,137.78,140.63,154.80,155.73$. A signal for the carbon directly attached to the boron atom was not observed. Anal. Calcd for $\mathrm{C}_{23} \mathrm{H}_{30} \mathrm{BNO}_{4}: \mathrm{C}, 69.88 \% ; \mathrm{H}, 7.65 \%$; N, $3.54 \%$. Found: C, 69.76; $\mathrm{H}, ~ 7.75 \%$; N, $3.55 \%$. m.p. $154.7-156.0{ }^{\circ} \mathrm{C}$. The synthesis of known compound [ $1,1^{\prime}: 3^{\prime}, 1$ "-terphenyl]-4'-ol ${ }^{14}$ from $\mathbf{4 k}$ by Suzuki-Miyaura coupling followed by deprotection of the carbamate moiety confirmed the assignment for $\mathbf{4 k}$.


## 4-Chloro-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-Diethylcarbamate (4I)



41
Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.17-1.36(\mathrm{~m}, 6 \mathrm{H}), 1.30(\mathrm{~s}, 12 \mathrm{H}), 3.37(\mathrm{q}, J=7.5 \mathrm{~Hz}, 2 \mathrm{H})$, $3.49(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.01(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.38(\mathrm{dd}, J=8.4,2.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.73(\mathrm{~d}, J=2.7 \mathrm{~Hz}$, 1H). ${ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.26,13.89,24.74,41.54,41.92,83.82,123.77,130.47,131.98,135.76$, 154.62, 154.69. A signal for the carbon directly attached to the boron atom was not observed. HRMS-ESI $(\mathrm{m} / \mathrm{z}):[\mathrm{M}+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{17} \mathrm{H}_{26} \mathrm{BClNO}_{4}, 354.16434$; found, 354.16429.

5-Bromo-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-Diethylcarbamate (4m)


Wthie solid. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.17-1.33(\mathrm{~m}, 6 \mathrm{H}), 1.29(\mathrm{~s}, 12 \mathrm{H}), 3.37(\mathrm{q}, J=7.2, \mathrm{~Hz}, 2 \mathrm{H})$, $3.48(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.27(\mathrm{~d}, J=1.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.34(\mathrm{dd}, J=8.1,1.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.63(\mathrm{~d}, J=8.1$ $\mathrm{Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.22,13.84,24.69,41.55,41.93,83.64,125.65,125.74,128.07$, $137.19,154.36,156.72$. A signal for the carbon directly attached to the boron atom was not observed. Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{25} \mathrm{BBrNO}_{4}$ : C, $51.29 \%$; H, $6.33 \%$; N, $3.52 \%$. Found: C, $50.97 \%$; H , $6.28 \%$; N, $3.43 \%$. m.p. $84.5-85.4^{\circ} \mathrm{C}$.

## 4-(Methoxycarbonyl)phenyl $N, N$-Diethylcarbamate (3n)



Colorress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.19-1.28(\mathrm{~m}, 6 \mathrm{H}), 3.36-3.48(\mathrm{~m}, 4 \mathrm{H}), 3.91(\mathrm{~s}, 3 \mathrm{H}), 7.21(\mathrm{dm}$, $J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 8.23(\mathrm{dm}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 12.79 .13 .71,41.54,41.88,51.55$, 121.26, 126.46, 130.62, 153.08, 155.10, 166.11. HRMS-ESI $(m / z):[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{13} \mathrm{H}_{17} \mathrm{NO}_{4} \mathrm{Na}, 274.10498$; found, 274.10497.

## 4-(Methoxycarbonyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl

$N, N$-Diethylcarbamate (4n) and 4-(Methoxycarbonyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxa borolan-2-yl)phenyl $N, N$-Diethylcarbamate (4n')


Colorress oil. ${ }^{\mathbf{1}} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \mathbf{4 n} ; \delta 1.18-1.32(\mathrm{~m}, 6 \mathrm{H}), 1.32(\mathrm{~s}, 12 \mathrm{H}), 3.39(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H})$, $3.51(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.91(\mathrm{~s}, 3 \mathrm{H}), 7.15(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.12(\mathrm{dd}, J=8.4,2.4 \mathrm{~Hz}, 1 \mathrm{H}), 8.45$ (d, $J=2.4 \mathrm{~Hz}, 1 \mathrm{H}) .4 \mathrm{n}$ '; $\delta 3.90(\mathrm{~s}, 3 \mathrm{H}), 7.21-7.23(\mathrm{~m}, 2 \mathrm{H}), 7.95(\mathrm{~d}, J=9.3 \mathrm{~Hz}, 1 \mathrm{H})$ (only observed peaks). ${ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \mathbf{4 n + 4 n}$ '; $\delta 13.15,13.20,13.86,14.07,41.56,41.84,41.90,42.15,83.76$, 84.08, 122.15, 122.34, 125.02, 126.67, 129.96, 130.36, 133.65, 137.94, 154.23, 154.57, 159.87, 166.73 (only observed peaks). HRMS-ESI ( $\mathrm{m} / \mathrm{z}$ ): $[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{19} \mathrm{H}_{28} \mathrm{NO}_{6} \mathrm{BNa}, 400.19014$; found, 400.19046. The position of the boron atom was determined by comparison of the ${ }^{1} \mathrm{H}$ NMR chemical shifts with those of the isomer $\mathbf{4 n}$ ': the aromatic proton of $\mathbf{4 n}$ at C3 position was observed at a significantly lower magnetic field than the aromatic proton of $\mathbf{4 n}$ ' at C 2 position, which indicates that the $\mathbf{4 n}$ is a borylated at the ortho position of the carbamate moiety.

## 3-(2-Methoxy-2-oxoethyl)phenyl $N$,N-Diethylcarbamate (30)



Colorress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.18-1.27(\mathrm{~m}, 6 \mathrm{H}), 3.37-3.45(\mathrm{~m}, 4 \mathrm{H}), 3.63(\mathrm{~s}, 2 \mathrm{H}), 3.70(\mathrm{~s}$, $3 \mathrm{H}), 7.04-7.13(\mathrm{~m}, 3 \mathrm{H}), 7.31(\mathrm{t}, J=7.5 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.13,13.98,40.68,41.69$, $42.03,51.87,120.54,122.63,125.96,129.22,135.15,151.62,154.10,171.71$. Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{19} \mathrm{NO}_{4}: \mathrm{C}, 63.38 \% ; \mathrm{H}, 7.22 \%$; N, $5.28 \%$. Found: C, $63.02 \%$; H, $7.21 \%$; N, $5.24 \%$.

## 5-(2-Methoxy-2-oxoethyl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl

 $N, N$-Diethylcarbamate (4o)

Colorress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.17-1.35(\mathrm{~m}, 6 \mathrm{H}), 1.29(\mathrm{~s}, 12 \mathrm{H}), 3.38(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H})$, $3.50(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.62(\mathrm{~s}, 2 \mathrm{H}), 3.67(\mathrm{~s}, 3 \mathrm{H}), 7.02(\mathrm{~s}, 1 \mathrm{H}), 7.12(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}), 7.73(\mathrm{~d}, J$ $=8.1 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.28,13.87,24.70,40.93,41.51,41.83,51.99,83.42,123.16$, $125.80,136.44,138.31,154.78,156.41,171.56$. Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{30} \mathrm{BNO}_{6}: \mathrm{C}, 61.39 \% ; \mathrm{H}$, $7.73 \%$; N, $3.58 \%$. Found: C, $61.06 \%$; H, $7.65 \%$; N, $3.59 \%$.

## 3-[\{(tert-Butoxycarbonyl)oxy\}methyl]phenyl $N, N$-Diethylcarbamate (3p)



Colorress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.18-1.29(\mathrm{~m}, 6 \mathrm{H}), 1.49(\mathrm{~s}, 9 \mathrm{H}), 3.35-3.47(\mathrm{~m}, 4 \mathrm{H}), 5.08(\mathrm{~s}$, $2 \mathrm{H}), 7.10(\mathrm{dm}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.15(\mathrm{~s}, 1 \mathrm{H}), 7.20(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.35(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.08,13.94,27.4841 .65,42.00,67.91,82.12,121.39,121.64,124.63,129.24$, 136.93, 151.60, 153.31, 153.98. Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{25} \mathrm{NO}_{5}: \mathrm{C}, 63.14 \%$; H, $7.79 \%$; N, $4.33 \%$. Found: C, 62.84; H, 7.80\%; N, 4.37\%.

5-[\{(tert-Butoxycarbonyl)oxy\}methyl]-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-Diethylcarbamate (4p)


Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.17-1.32(\mathrm{~m}, 6 \mathrm{H}), 1.30(\mathrm{~s}, 12 \mathrm{H}), 1.49(\mathrm{~s}, 9 \mathrm{H}), 3.37(\mathrm{q}, J=7.2$ $\mathrm{Hz}, 2 \mathrm{H}), 3.50(\mathrm{q}, J=6.9 \mathrm{~Hz}, 2 \mathrm{H}), 5.08(\mathrm{~s}, 2 \mathrm{H}), 7.09(\mathrm{~d}, J=1.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.19(\mathrm{dd}, J=7.8,1.2 \mathrm{~Hz}$, 1H) $7.76(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.24,13.85,24.69,27.60,41.50,41.83,67.81$, $82.28,83.47,121.57,124.08,136.42,140.07,153.39,154.73,156.40$. A signal for the carbon directly attached to the boron atom was not observed. HRMS-ESI $(\mathrm{m} / \mathrm{z}):[\mathrm{M}+\mathrm{Na}]^{+}$calcd for $\mathrm{C}_{23} \mathrm{H}_{36} \mathrm{BO}_{7} \mathrm{NNa}, 472.24770$; found, 472.24743.

## 3-(2-Methyl-1,3-dioxan-2-yl)phenyl $N, N$-Diethylcarbamate (3q)



Colorress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.19-1.29(\mathrm{~m}, 7 \mathrm{H}), 1.52(\mathrm{~s}, 3 \mathrm{H}), 2.12(\mathrm{~m}, 1 \mathrm{H}), 3.37-3.47(\mathrm{~m}$, 4H), 3.79-3.87 (m, 4H), 7.09 (ddd, $J=7.8,2.4,1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.18(\mathrm{t}, J=1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.27(\mathrm{~m}, 1 \mathrm{H})$, $7.39(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.18,14.05,25.14,32.12,41.72,42.06,61.18$, $100.15,120.38,121.00,123.44,129.49,142.84,152.07,154.18$. Anal. Calcd for $\mathrm{C}_{16} \mathrm{H}_{23} \mathrm{NO}_{4}: \mathrm{C}$, $65.51 \%$; H, $7.90 \%$; N, $4.77 \%$. Found: C, $65.20 \%$; H, $7.94 \%$; N, $4.76 \%$.

## 5-(2-Methyl-1,3-dioxan-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-Diethylcarbamate (4q)



White solid. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.18-1.34(\mathrm{~m}, 7 \mathrm{H}), 1.31(\mathrm{~s}, 12 \mathrm{H}), 1.49(\mathrm{~s}, 3 \mathrm{H}), 2.11(\mathrm{~m}, 1 \mathrm{H})$, $3.39(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.52(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.77-3.89(\mathrm{~m}, 4 \mathrm{H}), 7.13(\mathrm{~d}, J=1.5 \mathrm{~Hz}, 1 \mathrm{H}), 7.27$ $(\mathrm{m}, 1 \mathrm{H}), 7.82(\mathrm{~d}, J=8.1 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 13.21,13.85,24.66,25.12,32.01,41.43$, 41.76, 61.27, 83.42, 100.16, 120.86, 123.19, 136.66, 145.95, 154.74, 156.82. Anal. Calcd for $\mathrm{C}_{22} \mathrm{H}_{34} \mathrm{BNO}_{6}: \mathrm{C}, 63.02 \%$; H, 8.17\%; N, 3.34\%. Found: C, $62.74 \%$; H, $8.30 \%$; N, $3.32 \%$. m.p. $105.5-106.5^{\circ} \mathrm{C}$.

## 5-Fluoro-2-methylphenyl Diethylcarbamate (3r)



Colorress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.19-1.29(\mathrm{~m}, 6 \mathrm{H}), 2.17(\mathrm{~s}, 3 \mathrm{H}), 3.36-3.50(\mathrm{~m}, 4 \mathrm{H})$, 6.80-6.88 (m, 2H), $7.14(\mathrm{tm}, J=7.2 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C} \mathbf{N M R}\left(\mathrm{CDCl}_{3}\right) \delta 13.01,13.89,15.34,41.69$, $42.07,109.86(\mathrm{~d}, J=24.0 \mathrm{~Hz}), 111.88(\mathrm{~d}, J=21.2 \mathrm{~Hz}), 126.02(\mathrm{~d}, J=3.4 \mathrm{~Hz}), 131.13(\mathrm{~d}, J=9.2$ $\mathrm{Hz}), 150.42(\mathrm{~d}, J=10.9 \mathrm{~Hz}), 153.32,161.03(\mathrm{~d}, J=244.5 \mathrm{~Hz})$. Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{16} \mathrm{FNO}_{2}: \mathrm{C}$, $63.98 \%$; H, $7.16 \%$; N, $6.22 \%$. Found: C, $63.87 \%$; H, $7.18 \%$; N, $6.26 \%$.

## 5-Fluoro-2-methyl-6-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl

 $N, N$-Diethylcarbamate (4r)

Coloress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.18-1.35(\mathrm{~m}, 6 \mathrm{H}), 1.33(\mathrm{~s}, 12 \mathrm{H}), 2.15(\mathrm{~s}, 3 \mathrm{H}), 3.39(\mathrm{q}, J=7.2$ $\mathrm{Hz}, 2 \mathrm{H}), 3.49(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.82(\mathrm{t}, J=8.4 \mathrm{~Hz}, 1 \mathrm{H}), 7.21(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathbf{C} \mathbf{N M R}\left(\mathrm{CDCl}_{3}\right) \delta 13.24$, $14.05,15.72,24.64,41.55,41.93,83.48,112.19(\mathrm{~d}, J=24.1 \mathrm{~Hz}), 126.22(\mathrm{~d}, J=4.0 \mathrm{~Hz}), 133.67(\mathrm{~d}$, $J=9.7 \mathrm{~Hz}), 153.80,154.22(\mathrm{~d}, J=10.9 \mathrm{~Hz}), 165.19(\mathrm{~d}, J=247.9 \mathrm{~Hz})$. A signal for the carbon directly attached to the boron atom was not observed. HRMS-ESI $(\mathrm{m} / \mathrm{z}):[\mathrm{M}+\mathrm{H}]^{+}$calcd for $\mathrm{C}_{18} \mathrm{H}_{28} \mathrm{O}_{4} \mathrm{NBF}, 352.20954$; found, 352.21046 . m.p. $112.6-115.2{ }^{\circ} \mathrm{C}$. The regioselectivity was assigned on the basis of the $J_{\mathrm{C}-\mathrm{F}}$ values in the ${ }^{13} \mathrm{C}$ NMR spectrum.




## 3,5-Dimethylphenyl Diethylcarbamate (3s)



Colorress oil. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.17-1.26(\mathrm{~m}, 6 \mathrm{H}), 2.30(\mathrm{~s}, 6 \mathrm{H}), 3.35-3.45(\mathrm{~m}, 4 \mathrm{H}), 6.74(\mathrm{t}, J$ $=0.9 \mathrm{~Hz}, 2 \mathrm{H}), 6.82(\mathrm{~d}, J=0.9 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathbf{C} \mathbf{N M R}\left(\mathrm{CDCl}_{3}\right) \delta 13.01,13.83,20.81,41.51,41.84$, 119.22, 126.62, 138.75, 151.30, 154.32. Anal. Calcd for $\mathrm{C}_{13} \mathrm{H}_{19} \mathrm{NO}_{2}$ : C, $70.56 \%$; H, $8.65 \%$; N , 6.33\%. Found: C, 70.47; H, 8.74\%; N, 6.26\%.

3,5-Dimethyl-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl $N, N$-Diethylcarbamate (4s)


White solid. ${ }^{1} \mathbf{H}$ NMR $\left(\mathrm{CDCl}_{3}\right) \delta 1.16-1.35(\mathrm{~m}, 6 \mathrm{H}), 1.31(\mathrm{~s}, 12 \mathrm{H}), 2.27(\mathrm{~s}, 3 \mathrm{H}), 2.44(\mathrm{~s}, 3 \mathrm{H}), 3.37$ $(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 3.46(\mathrm{q}, J=7.2 \mathrm{~Hz}, 2 \mathrm{H}), 6.68(\mathrm{~s}, 1 \mathrm{H}), 6.82(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathbf{C} \mathbf{N M R}\left(\mathrm{CDCl}_{3}\right) \delta 13.27$, 13.97, 21.01, 22.16, 24.74, 41.46, 41.73, 83.13, 119.99, 127.98, 141.09, 144.90, 155.02, 156.11. Anal. Calcd for $\mathrm{C}_{19} \mathrm{H}_{30} \mathrm{BNO}_{4}$ : C, 65.72; H, $8.71 \%$; N, $4.03 \%$. Found: C, $65.49 ; \mathrm{H}, 8.79 \% ; 3.92 \%$. m.p. $71.5-72.4^{\circ} \mathrm{C}$.

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