Supporting Information

Incorporation of Carbon Dioxide into Phthalides via Ligand-Free Copper-Catalyzed Direct Carboxylation of Benzoxasiloles

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General Information

$^1$H and $^{13}$C NMR spectra were recorded on a JEOL ECX-400, JEOL ECX-500 and a JEOL ECX-600 in CDCl$_3$, DMSO-d$_6$, Acetone-d$_6$ or CD$_3$OD. Chemical shifts of $^1$H and $^{13}$C were reported in parts per million (ppm) from tetramethylsilane using the solvent resonance as the internal standard (For $^1$H NMR: CDCl$_3$: 7.27, DMSO-d$_6$: 2.50, Acetone-d$_6$: 2.05 and CD$_3$OD: 3.31; For $^{13}$C NMR: CDCl$_3$: 77.0, DMSO-d$_6$: 39.5, Acetone-d$_6$: 29.8 and CD$_3$OD: 49.0). IR spectra were measured on a JASCO FT/IR-610 spectrometer. High-resolution mass spectrometry was carried out using a JEOL JMS-T100TD (ESI and DART). HPLC analysis was performed on Shimadzu LC-20AB with chiral HPLC column. Column chromatography was carried out using silica gel obtained from Merck & Co.

Reagents: Unless stated otherwise, commercial organic chemicals were purchased from Tokyo Chemical Industry Co. Ltd and used as received. [Ir(cod)(OMe)]$_2$ and [Rh(nbd)Cl]$_2$ were purchased from Strem Chemical Inc and stored in glovebox. CuI was purchased from Wako Pure Chemical Industries, Ltd. and stored in glovebox. CsF was obtained from Tokyo Chemical Industry Co. Ltd, dried at 200 °C for 18 h under strong vacuum (0.1 mmHg) and stored in glovebox. Alcohols used for the preparation of starting materials were either purchased from Tokyo Chemical Industry Co. Ltd or synthesized by reduction of the corresponding aldehydes or ketones with NaBH$_4$.

Organic solvents for reactions were purified by distillation under dry argon atmosphere or purchased as anhydrous solvent from Wako Pure Chemical Industries, Ltd.

Part I: Preparation of Starting Materials

Synthesis of benzoxasiloles 1a-l

1,1-Diisopropyl-6-methoxy-1,3-dihydrobenzo[c][1,2]oxasilole 1a:
Step 1: To a 100 mL 2 neck round bottom flask was charged 4-methoxybenzyl alcohol (2.76 g, 20 mmol), imidazole (2.7 g, 20 mmol) and THF (40 mL). An argon balloon was attached and (iPr)_2SiHCl (3.64 g, 4.0 mL, 24 mmol) was added dropwise. The reaction was stirred overnight at room temperature and the solvent was removed under reduced pressure. Hexane (60 mL) was then added and the mixture was filtered through a Celite plug, affording a clear solution. Solvent was removed under reduced pressure to afford crude silyl ether which was directly used for the next step.

Step 2: Under air, to a 100 mL Schlenck tube was charged a solution of the silyl ether and 2-norbornene (3.8 g, 40 mmol) in THF (6 mL), a freshly prepared solution of [Rh(nbd)Cl]_2 (56 mg, 0.12 mmol) in THF (2 mL) and a freshly prepared solution of P(p-anisyl)_3 (250 mg, 0.72 mmol) in THF (2 mL). The tube was flushed with argon, sealed and heated at 120 °C for 4-5 h, when ^1H NMR analysis indicated the full conversion of the silyl ether. The solvent was then removed under reduced pressure and the crude mixture was purified by Kugelrohr distillation (135-140 °C, 0.1 mmHg) to afford 1a (3.8 g, 76 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.\(^1\)

\[^1\text{H NMR}\ (\text{CDCl}_3, 600 \text{ MHz}) \delta 7.15 (d, J = 8.2 \text{ Hz}, 1\text{H}), 7.06 (d, J = 2.7 \text{ Hz}, 1\text{H}), 6.97 (dd, J = 2.4, 8.6 \text{ Hz}, 1\text{H}), 5.10 (s, 2\text{H}), 3.84 (s, 3\text{H}), 1.26-1.21 (m, 2\text{H}), 1.04-1.00 (m, 12\text{H}).\]

\[^{13}\text{C NMR}\ (\text{CDCl}_3, 150 \text{ MHz}) \delta 158.4, 142.8, 133.4, 122.3, 116.1, 116.0, 72.1, 55.4, 17.0, 16.9, 13.0.\]

\(1,1\)-Diisopropyl-6-methyl-1,3-dihydrobenzo[\text{c}][1,2]oxasilole 1b:

\[\begin{align*}
\text{OH} &\text{THF, r.t. 12 h} \quad \text{OSiH}^{(\text{iPr})_2} \\
\text{Me} &\text{Me} \\
\end{align*}\]

The synthesis of 1b followed the synthesis of 1a in smaller scale. Step 1: 4-methylbenzyl alcohol (1.22 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (iPr)_2SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]_2 (28 mg, 0.06 mmol) in THF (1 mL) and P(p-anisyl)_3 (126 mg, 0.36 mmol) in
THF (1 mL). The crude mixture was purified by Kugelrohr distillation (120 °C, 0.1 mmHg) to afford \( 1\text{b} \) (1.8 g, 77 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.\(^1\)

\( ^{1}\text{H NMR} \) (CDCl\(_3\), 400MHz) \( \delta \) 7.38 (s, 1H), 7.22 (dd, \( J = 0.9, 7.8 \) Hz, 1H), 7.14-7.12 (m, 1H), 5.12 (s, 2H), 2.39 (s, 1H), 1.29-1.17 (m, 2H), 1.05-1.01 (m, 12H).

\( ^{13}\text{C NMR} \) (CDCl\(_3\), 101MHz) \( \delta \) 147.9, 135.8, 132.4, 131.8, 130.5, 121.2, 72.3, 21.2, 17.0, 13.1.

\( 1\text{,1-Diisopropyl-}N,N\text{-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilol-6-amine 1c:} \)

\[
\text{Me}_2\text{N} \quad \text{OH} \quad \text{OSiH} \left(\text{Pr}_2\right) \quad \text{Me}_2\text{N} \\
\left(\text{Pr}_2\right)\text{SiCl} \quad \text{imidazole} \quad \text{THF, r.t. 12 h} \quad \text{[Rh(nbd)Cl]}_{2} \quad \text{P(p-anisyl)}_{3} \\
\text{Me}_2\text{N} \quad \text{OSiH} \left(\text{Pr}_2\right) \quad \text{Me}_2\text{N} \\
2\text{-norbornene} \quad \text{THF, 120 °C, 4 h} \quad \text{1c}
\]

The synthesis of \( 1\text{c} \) followed the synthesis of \( 1\text{a} \) in smaller scale. Step 1: 4-dimethylaminobenzyl alcohol (1.5 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and \( \left(\text{Pr}_2\right)\text{SiHCl} \) (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), \[\text{[Rh(nbd)Cl]}_{2} \) (28 mg, 0.06 mmol) in THF (1 mL) and \( \text{P(p-anisyl)}_{3} \) (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (147 °C, 0.1 mmHg) followed by column chromatography to afford \( 1\text{c} \) (1.7 g, 65 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.\(^1\)

\( ^{1}\text{H NMR} \) (CDCl\(_3\), 600 MHz) \( \delta \) 7.11 (d, \( J = 8.2 \) Hz, 1H), 6.90 (d, \( J = 2.7 \) Hz, 1H), 6.86 (dd, \( J = 2.7, 8.2 \) Hz, 1H), 5.08 (s, 2H), 2.97 (s, 6H), 1.25-1.21 (m, 2H), 1.06-1.02 (m, 12H).

\( ^{13}\text{C NMR} \) (CDCl\(_3\), 150 MHz) \( \delta \) 149.5, 139.0, 132.6, 121.8, 115.3, 115.2, 72.1, 41.1, 17.1, 17.0, 13.1.

\( 6\text{-Fluoro-1,1-diisopropyl-1,3-dihydrobenzo[c][1,2]oxasilole 1d:} \)
The synthesis of 1d followed the synthesis of 1a in smaller scale. Step 1: 4-fluorobenzyl alcohol (1.1, 8.8 mmol), imidazole (1.23 g, 18 mmol), THF (20 mL) and (iPr)_2SiHCl (1.6 g, 1.8 mL, 10.6 mmol). Step 2: 2-norbornene (1.7 g, 17.6 mmol) in THF (3 mL), [Rh(nbd)Cl]_2 (25 mg, 0.05 mmol) in THF (1 mL) and P(p-anisyl)_3 (110 mg, 0.32 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (110 °C, 0.1 mmHg) to afford 1d (1.3 g, 60 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.¹

¹H NMR (CDCl₃, 400MHz) δ 7.22-7.17 (m, 2H), 7.09-7.06 (m, 1H), 5.11 (s, 2H), 1.28-1.19 (m, 2H), 1.07-0.97 (m, 12H).

¹³C NMR (CDCl₃, 101MHz) δ 162.0 (d, J = 246.4 Hz), 146.0 (d, J = 3.0 Hz), 134.5 (d, J = 5.8 Hz), 122.9 (d, J = 7.7 Hz), 117.8 (d, J = 19.2 Hz), 116.9 (d, J = 23 Hz), 72.0, 16.9, 16.8, 13.0.

6-Chloro-1,1-diisopropyl-1,3-dihydrobenzo[c][1,2]oxasilole 1e:

The synthesis of 1e followed the synthesis of 1a in smaller scale. Step 1: 4-chlorobenzyl alcohol (1.43 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (iPr)_2SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]_2 (28 mg, 0.06 mmol) in THF (1 mL) and P(p-anisyl)_3 (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (125 °C, 0.1 mmHg) followed by column chromatography (EtOAc:n-Hexane = 5:95) to afford 1e (1.3 g, 51 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.¹
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.51 (d, $J = 1.8$ Hz, 1H), 7.36 (dd, $J = 2.1$, 8.0 Hz, 1H), 7.17 (d, $J = 7.8$ Hz, 1H), 5.10 (s, 2H), 1.28-1.21 (m, 2H), 1.07-1.00 (m, 12 H).

$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 148.9, 134.6, 132.8, 131.5, 129.6, 122.9, 72.1, 16.9, 13.0.

1,1-Diisopropyl-5-methoxy-1,3-dihydrobenzo[c][1,2]oxasilole 1f:

The synthesis of 1f followed the synthesis of 1a in smaller scale. Step 1: 3-methoxybenzyl alcohol (1.38 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (iPr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(p-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (130 °C, 0.1 mmHg) to afford 1e (1.7 g, 68 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.¹

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.47 (d, $J = 8.2$ Hz, 1H), 6.88 (d, $J = 7.6$ Hz, 1H), 6.76 (s, 1H), 5.11 (s, 2H), 3.83 (s, 3H), 1.24-1.12 (m, 2H), 1.03-0.99 (m, 12H).

$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 161.3, 153.0, 133.1, 122.5, 113.8, 106.2, 72.3, 55.1, 16.99, 16.97, 13.1.

1,1-Diisopropyl-4-methoxy-1,3-dihydrobenzo[c][1,2]oxasilole 1g:

The synthesis of 1g followed the synthesis of 1a in smaller scale. Step 1: 2-methoxybenzyl alcohol (1.38 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (iPr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL),
[Rh(nbd)Cl]₂ (28 mg, 0.06 mmol) in THF (1 mL) and P(p-anisyl)₃ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (125 °C, 0.1 mmHg) to afford 1e (1.5 g, 60 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.¹

¹H NMR (CDCl₃, 600 MHz) δ 7.30 (t, J = 7.6 Hz, 1H), 7.14 (d, J = 6.9 Hz, 1H), 6.87 (d, J = 7.6 Hz, 1H), 5.11 (s, 2H), 3.84 (s, 3H), 1.24-1.20 (m, 2H), 1.04-1.00 (m, 12H).

¹³C NMR (CDCl₃, 150 MHz) δ 154.2, 138.9, 133.7, 128.3, 123.7, 110.4, 70.4, 54.8, 16.9, 13.1.

1,1-Diisopropyl-4-methyl-1,3-dihydrobenzo[c][1,2]oxasilole 1h:

[Olefin, Alcohol, Imidazole, THF, rt. 12 h] → 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]₂ (28 mg, 0.06 mmol) in THF (1 mL) and P(p-anisyl)₃ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (120 °C, 0.1 mmHg) to afford 1b (1.4 g, 60 % yield, 2 steps) as a colorless oil.

¹H NMR (CDCl₃, 400MHz) δ 7.49 (d, J = 7.3 Hz, 1H), 7.34-7.25 (m, 2H), 5.17 (s, 2H), 2.30 (s, 3H), 1.36-1.28 (m, 2H), 1.15-1.09 (m, 12H).

¹³C NMR (CDCl₃, 150 MHz) δ 149.1, 131.4, 130.6, 129.5, 126.8, 71.8, 18.1, 17.0, 13.1.

DART-MS m/z cald for C₁₄H₂₃OSi [M+H]^+: 235.15182, found: 235.15219

IR (KBr, cm⁻¹) v: 2944, 284, 1462, 1211, 1074, 1049, 989, 881, 778, 694.

3,3-Diisopropyl-1,3-dihydronaphtho[2,1-c][1,2]oxasilole 1i:
The synthesis of 1i followed the synthesis of 1a in smaller scale. Step 1: 1-naphthalenemethanol (1.58 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (iPr)_2SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]_2 (28 mg, 0.06 mmol) in THF (1 mL) and P(p-anisyl)_3 (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by column chromatography (EtOAc:n-Hexane = 5:95) followed by Kugelrohr distillation (200 °C, 0.1 mmHg) to afford 1i (1.7 g, 63% yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.\(^1\)

\(^1\)H NMR (CDCl\(_3\), 600 MHz) \(\delta\) 7.94 - 7.92 (m, 1H), 7.80 (d, \(J = 8.2\) Hz, 1H), 7.73-7.71 (m, 1H), 7.64-7.62 (m, 1H), 7.57-7.54 (m, 2H), 5.61 (s, 2H), 1.34-1.29 (m, 2H), 1.08-1.04 (m, 12H).

\(^{13}\)C NMR (CDCl\(_3\), 150 MHz) \(\delta\) 148.3, 134.0, 129.3, 128.6, 127.9, 127.9, 127.1, 126.5, 126.2, 122.9, 71.9, 17.1, 17.0, 13.2.

1,1-Diisopropyl-3,6-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilole 1j:

The synthesis of 1j followed the synthesis of 1a in smaller scale. Step 1: 1-(4-methylphenyl)ethanol (1.36 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (iPr)_2SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]_2 (28 mg, 0.06 mmol) in THF (1 mL) and P(p-anisyl)_3 (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (130 °C,
0.1 mmHg) followed by column chromatography (EtOAc:n-Hexane = 5:95) to afford 1j (1.0 g, 40% yield, 2 steps) as a colorless oil.

\[ ^1H \text{NMR (CDCl}_3, 400 \text{ MHz)} \delta 7.34 (s, 1H), 7.22 (d, J = 7.8 \text{ Hz, 1H}), 7.10 (d, J = 8.2 \text{ Hz, 1H}), 5.30 (q, J = 6.3 \text{ Hz, 1H}), 2.39 (s, 3H), 1.50 (d, J = 6.9 \text{ Hz, 3H}), 1.26-1.15 (m, 2H), 1.07-0.96 (m, 12H). \]

\[ ^{13}C \text{NMR (CDCl}_3, 101\text{MHz)} \delta 152.5, 135.9, 132.3, 131.8, 130.6, 121.8, 78.1, 24.9, 21.2, 17.4, 17.3, 17.0, 17.0, 13.2, 12.5. \]

DART-MS m/z calcd for C\(_{15}\)H\(_{25}\)OSi [M+H]\(^+\): 249.16747, found: 249.16632

\[ \text{IR (KBr, cm}^{-1}\text{)} \nu: 2946, 2865, 1464, 1085, 925, 880, 792, 670, 635, 494 \]

The synthesis of 1k followed the synthesis of 1a in smaller scale. Step 1: 1-(3-methoxyphenyl)ethanol (1.50 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (iPr)_2SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]_2 (28 mg, 0.06 mmol) in THF (1 mL) and P(p-anisyl)_3 (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (130 °C, 0.1 mmHg) followed by column chromatography (EtOAc:n-Hexane = 5:95) to afford 1k (1.58 g, 60% yield, 2 steps) as a colorless oil.

\[ ^1H \text{NMR (CDCl}_3, 400\text{MHz)} \delta 7.45 (d, J = 8.2 \text{ Hz, 1H}), 6.87 (dd, J = 2.1, 8.0 \text{ Hz, 1H}), 6.73 (s, 1H), 5.28 (q, J = 6.4 \text{ Hz, 1H}), 3.84 (s, 3H), 1.51 (d, J = 6.4 \text{ Hz, 3H}), 1.22-1.17 (m, 2H), 1.06-0.97 (m, 12H). \]

\[ ^{13}C \text{NMR (CDCl}_3, 101\text{MHz)} \delta 161.3, 157.4, 133.0, 122.4, 113.5, 107.2, 78.1, 55.1, 24.8, 17.3, 17.2, 17.0, 16.9, 13.2, 12.5. \]

DART-MS m/z calcd for C\(_{15}\)H\(_{25}\)O\(_2\)Si [M+H]\(^+\): 265.16238, found: 265.16109
IR (KBr, cm\(^{-1}\)) v: 2945, 2864, 1600, 1465, 1306, 1239, 1071, 881, 786, 677.

(R)-1,1-Diisopropyl-5-methoxy-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole (R)-1k:

\[
\begin{align*}
\text{MeO} & \quad \text{O} & \quad \text{MeO} \\
\text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

Synthesis of chiral alcohol: In a 300 mL 3 neck round bottom flask was charged (R,R)-RuTsDPEN (127 mg, 0.2 mmol). An argon balloon was attached and isopropanol (200 mL) was added followed by 3’-methoxyacetophenone (3.0 g, 20 mmol) and a solution of KOH (28 mg) in isopropanol (20 mL). The reaction was stirred at room temperature for 3 days, then quenched with HCl (1N, 1 mL) and the solvent was removed. Brine (50 mL) was added and the mixture was extracted to EtOAc. Removal of solvent followed by column chromatography afforded the chiral alcohol (2 g, 66%) with 94% ee (HPLC, OD-H, iPrOH:n-Hexane = 2:98, 1 mL/min).

The chiral alcohol was then used for the synthesis of (R)-1k following the same procedure for the synthesis of 1k. Yield: 1.7 g (65%) colorless oil.

1,1-Diisopropyl-4-methoxy-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole 1l:

\[
\begin{align*}
\text{MeO} & \quad \text{O} & \quad \text{MeO} & \quad \text{MeO} \\
\text{OH} & \quad \text{OH} & \quad \text{OH} & \quad \text{OH}
\end{align*}
\]

The synthesis of 1l followed the synthesis of 1a in smaller scale. Step 1: 1-(2-methoxyphenyl)ethanol (1.50 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (iPr)\(_2\)SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]\(_2\) (28 mg, 0.06 mmol) in THF (1 mL) and P(p-anisyl)\(_3\) (126 mg, 0.36
mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (130 °C, 0.1 mmHg) followed by column chromatography (EtOAc:n-Hexane = 5:95) to afford 1I (2.0 g, 76% yield, 2 steps) as a colorless oil.

1H NMR (CDCl₃, 400MHz) δ 7.29-7.25 (m, 1H), 7.09 (d, J = 6.9 Hz, 1H), 6.86 (d, J = 7.8 Hz, 1H), 5.38 (q, J = 6.3 Hz, 1H), 3.82 (s, 3H), 1.53 (d, J = 6.4 Hz, 3H), 1.25-0.87 (m, 14H).

13C NMR (CDCl₃, 101MHz) δ 154.4, 142.9, 133.8, 128.5, 123.7, 111.1, 77.2, 54.8, 23.4, 17.4, 17.4, 17.0, 13.2, 12.6.

DART-MS m/z cald for C₁₅H₂₅O₂Si [M+H]⁺: 265.16238, found: 265.16170

IR (KBr, cm⁻¹) v: 2943, 2866, 1568, 1464, 1255, 1078, 1053, 1024, 927, 880, 803, 685.

Synthesis of benzoxasiloles 1n-w²

1,1,3-Trimethyl-1,3-dihydrobenzoxasiloles 1n:

Step 1: In a 200 mL 2 neck round bottom flask equipped with a 20 mL dropping funnel and an argon balloon, to the solution of ClMe₂SiH (2.8 g, 3.3 mL, 30 mmol) in Et₂O (70 mL) at 0 °C was added dropwise a solution of 1-phenylethanol (2.44 g, 20 mmol), Et₃N (4.0 g, 40 mmol) in Et₂O (20 mL). A white precipitate appeared immediately. The mixture was stirred at 0 °C for 20 mins and at room temperature for 16 h. Then, it was diluted with Et₂O (50 mL), washed quickly with saturated NaHCO₃ and brine, and dried over Na₂SO₄. Et₂O was then removed under reduced pressure to afford the silyl ether which was directly used for the next step.

Step 2: Inside and argon glovebox, a 100 mL Schlenck tube was successively charged with a solution of the silyl ether in THF (20 mL), 2-norbornene (2.3 g, 24 mmol) in THF (20 mL), [Ir(cod)(OMe)]₂ (60 mg, 0.092 mmol) and phenanthroline (48 mg, 0.25 mmol). The
flask was sealed, taken out of glovebox, stirred at room temperature for 1 h and 100 °C for 16 h upon which \(^1\)H NMR analysis showed full conversion of the silyl ether. The solvent was then removed under reduced pressure and the crude mixture was purified using Kugelrohr distillation (125-130 °C, 40 mmHg) to afford \(1n\) (2.6 g, 73 % yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.\(^3\)

\(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 7.57 (d, \(J = 7.4\) Hz, 1H), 7.41 (t, \(J = 7.4\) Hz, 1H), 7.31 (t, \(J = 7.5\) Hz, 1H), 7.22 (d, \(J = 8.0\) Hz, 1H), 5.34 (q, \(J = 6.6\) Hz, 1H), 1.52 (d, \(J = 6.9\) Hz, 3H), 0.42 (s, 3H), 0.38 (s, 3H).

\(^{13}\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 154.3, 135.0, 130.8, 129.6, 126.9, 122.1, 77.8, 25.2, 1.6, 0.4.

(R)-1,1,3-Trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole (R)-\(1n\):

The chiral alcohol was prepared via asymmetric transfer hydrogenation as described in the synthesis of (R)-\(1k\). Yield: 1.6 g (66%) colorless oil, 94% ee (HPLC: OD-H, 4PrOH/n-Hexane = 2:98, 1 mL/min).

\begin{center}
\begin{tikzpicture}
% TikZ code for the reaction diagram
\end{tikzpicture}
\end{center}

**Step 1:** The chiral alcohol (1.22 g, 10 mmol) was treated with (Me\(_2\)SiH)\(_2\)NH (1.14 mL, 6.6 mmol) at 60 °C overnight. Excess silylating reagent was removed under reduced pressure.

**Step 2:** Inside and argon glovebox, a 100 mL Schlenck tube was successively charged with a solution of the silyl ether in THF (10 mL), 2-norbornene (1.15 g, 12 mmol) in THF (10 mL), [Ir(cod)(OMe)]\(_2\) (30 mg, 0.046 mmol) and phenanthroline (24 mg, 0.125 mmol). The flask was sealed, taken out of glovebox, stirred at room temperature for 1 h and 100 °C for
16 h upon which $^1$H NMR analysis showed full conversion of the silyl ether. The solvent was then removed under reduced pressure and the crude mixture was purified using Kugelrohr distillation to afford (R)-7n (1.25 g, 70% yield, 2 steps) as a colorless oil.

6-Methoxy-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole 1n:

The synthesis of 1o followed the synthesis of (R)-1m. Step 1: 1-(4-methoxyphenyl)ethanol (1.50 g, 10 mmol), (Me$_2$Si)$_2$NH (1.14 mL, 6.6 mmol). Step 2: silyl ether in THF (10 mL), 2-norbornene (1.15 g, 12 mmol) in THF (10 mL), [Ir(cod)(OMe)$_2$] (30 mg, 0.046 mmol) and phenanthroline (23 mg, 0.125 mmol). The crude mixture was purified by Kugelrohr distillation (130 °C, 0.1 mmHg) to afford 1o (1.2 g, 57% yield, 2 steps) as a colorless oil.

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.14 (d, $J = 8.7$ Hz, 1H), 7.05 (d, $J = 2.7$ Hz, 1H), 6.99-6.96 (m, 1H), 5.30 (q, $J = 6.4$ Hz, 1H), 3.85 (s, 3H), 1.50 (d, $J = 6.4$ Hz, 3H), 0.42 (s, 3H), 0.38 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 158.7, 146.5, 136.6, 123.1, 116.6, 114.3, 77.4, 55.4, 25.4, 1.5, 0.3.

DART-MS m/z cald for C$_{11}$H$_{17}$O$_2$Si [M+H]$^+$: 209.09978, found: 209.09951

IR (KBr, cm$^{-1}$) v: 2968, 1471, 1286, 1082, 927, 880, 823, 789.

6-Chloro-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole 1p:
The synthesis of 1p followed the synthesis of (R)-1m. Step 1: 1-(4-chlorophenyl)ethanol (1.56 g, 10 mmol), (Me₂SiH)₂NH (1.14 mL, 6.6 mmol). Step 2: silyl ether in THF (10 mL), 2-norbornene (1.15 g, 12 mmol) in THF (10 mL), [Ir(cod)(OMe)]₂ (30 mg, 0.046 mmol) and phenanthroline (23 mg, 0.125 mmol). The crude mixture was purified by Kugelrohr distillation (110 °C, 0.1 mmHg) afford 1p (1.6 g, 76% yield, 2 steps) as a colorless oil.

¹H NMR (CDCl₃, 400 MHz) δ 7.51 (d, J = 1.8 Hz, 1H), 7.36 (dd, J = 1.8, 8.2 Hz, 1H), 7.14 (d, J = 8.2 Hz, 1H), 5.30 (q, J = 6.4 Hz, 1H), 1.49 (d, J = 6.4 Hz, 3H), 0.42 (s, 3H), 0.38 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ 152.5, 137.7, 133.1, 130.5, 129.7, 123.6, 77.5, 25.2, 1.4, 0.3.

DART-MS m/z cald for C₉H₁₄ClOSi [M+H]⁺: 213.05024, found: 213.05015.

IR (KBr, cm⁻¹) ν: 2972, 2871, 1451, 1254, 1091, 928, 791.

6-Iodo-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole 1q

The synthesis of 1q followed the synthesis of (R)-1m in a smaller scale. Step 1: 1-(4-iodophenyl)ethanol (1.24 g, 5 mmol), (Me₂SiH)₂NH (0.57 mL, 3.3 mmol). Step 2: silyl ether in THF (5 mL), 2-norbornene (0.57 g, 6 mmol) in THF (5 mL), [Ir(cod)(OMe)]₂ (15 mg, 0.023 mmol) and phenanthroline (12 mg, 0.063 mmol). The crude mixture was purified by Kugelrohr distillation (130-140 °C, 0.1 mmHg) afford 1q (0.9 g, 60% yield, 2 steps) as a colorless oil.

¹H NMR (CDCl₃, 400 MHz) δ 7.89 (s, 1H), 7.70 (d, J = 7.8 Hz, 1H), 6.99 (d, J = 8.2, 1H), 5.30-5.27 (m, 1H), 1.48 (d, J = 6.4 Hz, 3H), 0.41 (s, 3H), 0.37 (s, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ 153.7, 139.6, 138.8, 138.3, 124.3, 93.5, 77.5, 25.1, 1.5, 0.3.

DART-MS m/z cald for C₁₀H₁₄IOSi [M+H]⁺: 304.98586, found: 304.98595
**IR (KBr, cm⁻¹) v:** 2975, 2869, 1254, 1084, 1022, 927, 826, 790, 747.

6-Bromo-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole **1r:**

![Chemical diagram]

The synthesis of **1r** followed the synthesis of **1m.** Step 1: 1-(4-bromophenyl)ethanol (4.0 g, 20 mmol), ClMe₂SiH (2.8 g, 3.3 mL, 30 mmol), Et₃N (4 g, 40 mmol), Et₂O (70 + 20 mL). Step 2: silyl ether in THF (20 mL), 2-norbornene (2.3 g, 24 mmol) in THF (20 mL), [Ir(cod)(OMe)]₂ (60 mg, 0.092 mmol) and phenanthroline (46 mg, 0.25 mmol). The crude mixture was purified by Kugelrohr distillation (125-130 °C, 0.1 mmHg) to afford **1r** (3.4 g, 66% yield, 2 steps) as a colorless oil.

**¹H NMR (CDCl₃, 400 MHz) δ:** 7.66 (s, 1H), 7.51 (d, J = 8.2 Hz, 1H), 7.09 (d, J = 8.2 Hz, 1H), 5.28 (q, J = 6.4 Hz, 1H), 1.49 (d, J = 6.4 Hz, 3H), 0.42 (s, 3H), 0.38 (s, 3H).

**¹³C NMR (CDCl₃, 100 MHz) δ:** 153.0, 138.3, 133.5, 132.5, 124.0, 121.5, 77.5, 25.1, 1.5, 0.3.

**DART-MS m/z cald for C₁₀H₁₄BrOSi [M+H]⁺:** 256.99973, found: 256.99873

**IR (KBr, cm⁻¹) v:** 2971, 2869, 1254, 1084, 1023, 928, 857, 827, 791, 420.

5-Bromo-1,1,3-trimethyl-1,3-dihydrobenzo[c][1,2]oxasilole **1s:**

![Chemical diagram]

The synthesis of **1s** followed the synthesis of (R)-**1m.** Step 1: 1-(3-bromophenyl)ethanol (2.0 g, 10 mmol), (Me₂SiH)₂NH (1.14 mL, 6.6 mmol). Step 2: silyl ether in THF (10 mL), 2-norbornene (1.15 g, 12 mmol) in THF (10 mL), [Ir(cod)(OMe)]₂ (30 mg, 0.046 mmol)
and phenanthroline (23 mg, 0.125 mmol). The crude mixture was purified by Kugelrohr distillation (130 °C, 0.1 mmHg) afford 1s (1.6 g, 62% yield, 2 steps) as a colorless oil.

1H NMR (CDCl₃, 400 MHz) δ 7.45-7.37 (m, 3H), 5.29 (q, J = 6.7 Hz, 1H), 1.50 (d, J = 6.4 Hz, 3H), 0.41 (s, 3H), 0.37 (s, 3H).

13C NMR (CDCl₃, 100 MHz) δ 156.6, 133.8, 132.3, 130.1, 125.5, 124.5, 77.3, 25.1, 1.5, 0.3.

DART-MS m/z cald for C₁₀H₁₄BrOSi [M+H]+: 256.99973, found: 256.99966

IR (KBr, cm⁻¹) ν: 2971, 2875, 1254, 1190, 1088, 1025, 931, 857, 824, 789.

3-Isopropyl-1,1-dimethyl-1,3-dihydrobenzo[c][1,2]oxasilole 1t

The synthesis of 1s followed the synthesis of 1m. Step 1: 2-methyl-1-phenylpropan-1-ol (3.0 g, 20 mmol), ClMe₂SiH (2.8 g, 3.3 mL, 30 mmol), Et₃N (4 g, 40 mmol), Et₂O (70 + 20 mL). Step 2: silyl ether in THF (20 mL), 2-norbornene (2.3 g, 24 mmol) in THF (20 mL), [Ir(cod)(OMe)₂] (60 mg, 0.092 mmol) and phenanthroline (46 mg, 0.25 mmol). The crude mixture was purified by Kugelrohr distillation (90 °C, 0.1 mmHg) to afford 1t (2.6 g, 63% yield, 2 steps) as a colorless oil. This is a known compound and the spectroscopic data is in agreement with the literature.³

1H NMR (CDCl₃, 400 MHz) δ 7.56 (d, J = 7.3 Hz, 1H), 7.40 (t, J = 7.4 Hz, 1H), 7.30 (t, J = 7.4 Hz, 1H), 7.21 (d, J = 7.8 Hz, 1H), 5.18 (s, 1H), 2.14-2.11 (m, 1H), 1.18 (d, J = 6.9 Hz, 3H), 0.60 (d, J = 6.9 Hz, 3H), 0.42 (s, 3H), 0.37 (s, 3H).

13C NMR (CDCl₃, 100 MHz) δ 152.3, 136.2, 130.7, 129.5, 126.8, 122.2, 86.3, 34.4, 20.3, 14.8, 0.8, 0.7.

1,1-Dimethyl-3-phenyl-1,3-dihydrobenzo[c][1,2]oxasilole 1u:
The synthesis of 1u followed the synthesis of (R)-1m with slight modification. Step 1: benzhydrol (1.84 g, 10 mmol), (Me₂SiH)₂NH (1.14 mL, 6.6 mmol). Step 2: silyl ether in THF (10 mL), 2-norbornene (1.15 g, 12 mmol) in THF (10 mL), [Ir(cod)(OMe)]₂ (30 mg, 0.046 mmol) and phenanthroline (23 mg, 0.125 mmol). The reaction was heated at 80 °C. The crude mixture was purified by Kugelrohr distillation (140 °C, 0.1 mmHg) afford 1u (1.4 g, 58% yield, 2 steps) as a white solid. This is a known compound and the spectroscopic data is in agreement with the literature.

1H NMR (CDCl₃, 500 MHz) δ 7.62-7.61 (m, 1H), 7.33-7.26 (m, 7H), 7.03-7.02 (m, 1H), 6.16 (s, 1H), 0.53 (s, 3H), 0.45 (s, 3H).

13C NMR (CDCl₃, 101 MHz) δ 152.4, 143.7, 135.1, 130.6, 129.8, 128.5, 127.8, 127.1, 127.1, 123.7, 84.0, 1.2, 0.5.

1,1,3,3-Tetramethyl-1,3-dihydrobenzo[c][1,2]oxasilole 1w

The synthesis of 1w followed the synthesis of 1m. Step 1: 2-phenyl-2-propanol (2.72 g, 20 mmol), ClMe₂SiH (2.8 g, 3.3 mL, 30 mmol), Et₃N (4 g, 40 mmol), Et₂O (70 + 20 mL). Step 2: silyl ether in THF (20 mL), 2-norbornene (2.3 g, 24 mmol) in THF (20 mL), [Ir(cod)(OMe)]₂ (60 mg, 0.092 mmol) and phenanthroline (46 mg, 0.25 mmol). The crude mixture was purified by Kugelrohr distillation (140 °C, 40 mmHg) to afford 1w (2.3 g, 60% yield, 2 steps) as a white solid. This is a known compound and the spectroscopic data is in agreement with the literature.³
**1H NMR** (CDCl$_3$, 400 MHz) δ 7.55 (d, $J = 6.9$ Hz, 1H), 7.43-7.40 (m, 1H), 7.33-7.29 (m, 1H), 7.24 (d, $J = 7.8$ Hz, 1H), 1.55 (s, 6 H), 0.40 (s, 6 H).

**13C NMR** (CDCl$_3$, 101 MHz) δ 157.9, 134.5, 130.7, 129.7, 126.8, 122.1, 83.4, 32.1, 1.2.

**Synthesis of 1x-y**

1,1-Diisopropyl-4,5,6-trimethoxy-3-methyl-1,3-dihydrobenzo[c][1,2]oxasilole 1x:

[Chemical structure image]

Synthesis of 1-(2,3,4-trimethoxyphenyl)ethanol: To a solution of the 2,3,4-trimethoxybenzaldehyde (2.9 g, 15 mmol) in Et$_2$O (10 mL) was added MeMgBr (3 M in Et$_2$O, 6.3 mL) dropwise. The mixture was then heated to reflux for 2 h, cooled to room temperature and quenched with saturated NH$_4$Cl solution. The mixture was extracted with Et$_2$O (3 x 20 mL). The combined organic phase was washed with NaHCO$_3$, brine, dried over Na$_2$SO$_4$ and the solvent was removed under reduced pressure. The alcohol was obtained after column chromatography. Yield 2.2 g (69%) colorless oil.

The synthesis of 1x followed the synthesis of 1a in smaller scale. Step 1: 1-(2,3,4-trimethoxyphenyl)ethanol (2.12 g, 10 mmol), imidazole (1.36 g, 10 mmol), THF (20 mL) and (iPr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(p-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by Kugelrohr distillation (170°C, 0.1 mmHg) to afford 1x (1.7 g, 52% yield, 2 steps) as a colorless oil.

**1H NMR** (CDCl$_3$, 600 MHz) δ 6.73 (s, 1H), 5.34 (q, $J = 6.2$ Hz, 1H), 3.91 (s, 3H), 3.90 (s, 3H), 3.89 (s, 3H), 1.52 (d, $J = 6.9$ Hz, 3H), 1.23-1.11 (m, 2H), 1.08 (dd, $J = 3.1$, 7.2 Hz, 6H), 0.97 (t, $J = 7.2$ Hz, 6H).

**13C NMR** (CDCl$_3$, 150 MHz) δ 153.5, 148.4, 143.4, 140.5, 127.0, 109.0, 60.7, 60.4, 56.2, 24.3, 17.4, 17.4, 17.0, 17.0, 13.2, 12.6.
**DART-MS** m/z cald for C$_{17}$H$_{29}$O$_4$Si [M+H]$^+$: 325.18351, found: 325.18327

**IR (KBr, cm$^{-1}$)** ν: 2942, 2865, 1588, 1557, 1468, 1398, 1296, 1238, 1193, 1120, 1093, 1050, 1022

1,1-Diisopropyl-4-methoxy-5-methyl-6-((tetrahydro-2H-pyran-2-yloxy)-1,3-dihydrobenzo[cd][1,2]oxasilole 1x:

![Chemical structure](image)

The aldehyde starting material was prepared according to literature.$^4$

Reduction of the aldehyde: A 50 mL round bottom flask was charged with the aldehyde (2.5 g, 10 mmol) and MeOH (20 mL) and cooled to 0 °C in an ice-water bath. NaBH$_4$ (760 mg, 20 mmol) was added in portions. After the addition was completed, the reaction was stirred at room temperature overnight before quenching with acetone. The solvent was removed and water (30 mL) was added and the mixture was extracted to EtOAc (3 x 15 mL). The combined organic solvent was washed with brine (2 x 20 mL), dried over Na$_2$SO$_4$. Removal of the solvent afforded the benzyl alcohol which was directly used in the next step.

The synthesis of 1y followed the synthesis of 1a in smaller scale. Step 1: imidazole (1.36 g, 10 mmol), THF (20 mL) and ((Pr)$_2$SiHCl (1.82 g, 2.0 mL, 12 mmol). Step 2: 2-norbornene (1.9 g, 20 mmol) in THF (3 mL), [Rh(nbd)Cl]$_2$ (28 mg, 0.06 mmol) in THF (1 mL) and P(p-anisyl)$_3$ (126 mg, 0.36 mmol) in THF (1 mL). The crude mixture was purified by column chromatography to afford 1y (2.7 g, 74% yield, 3 steps) as a slight yellow oil.

**$^1$H NMR** (CDCl$_3$, 600 MHz) δ 7.04 (s, 1H), 5.44 (br. s., 1H), 5.14 (s, 2H), 3.94 (t, $J = 10.7$ Hz, 1H), 3.74 (s, 3H), 3.63-3.62 (m, 1H), 2.23 (s, 3H), 2.06-2.03 (m, 1H), 1.91-1.89 (m, 2H), 1.74-1.62 (m, 3H), 1.24-1.18 (m, 2H), 1.04-0.99 (m, 12H).

**$^{13}$C NMR** (CDCl$_3$, 150 MHz) δ 155.8, 153.5, 136.0, 130.8, 122.3, 112.7, 96.7, 70.0, 62.0, 60.0, 30.7, 25.3, 18.9, 17.0, 17.0, 16.9, 13.1, 13.1, 9.2.
**DART-MS** m/z cald for {C}_{20}{H}_{31}{O}_{4}{Si} [M-H]^{+}: 363.19916, found: 363.20035

**IR** (KBr, cm\(^{-1}\)) \(\nu:\) 2943, 2864, 1461, 1403, 1280, 1125, 1089, 1052, 1020, 961, 880, 787, 673.

**Part II: Optimization and Control Experiments**

*Experimental Procedure for the reaction of 1a and CO\(_2\) (Table 1):* In an argon glove box, a flame-dried 10 mL two neck tube was charged with CuI (7.6 mg, 0.04 mmol) and CsF (182 mg, 1.2 mmol). The tube was taken out and attached to a vacuum line and a CO\(_2\) balloon using a three-way stopcock. After three evacuation-CO\(_2\) refill cycles was conducted, DMSO (1.6 mL) and 1a (100 mg, 0.4 mmol) were added successively. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 20 h. After being cooled down, the reaction mixture was diluted with H\(_2\)O (5 mL), acidified using HCl 1N (4 mL), stirred for another 2 h and extracted to EtOAc (3 x 10 mL). The combined organic phase was washed with H\(_2\)O (2 x 15 mL), dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure. The crude mixture was analyzed by \(^1\)H NMR in CDCl\(_3\) using 1,3,5-trimethoxybenzene (22.4 mg) as the internal standard. The results were shown in Table 1.

**Screening different fluoride salts:**

\[
\begin{array}{|c|c|c|}
\hline
\text{Entry} & \text{Fluoride} & \text{Yield(\%)}^a \\
\hline
1 & CsF & 67 \\
2 & AgF & n.d. \\
3 & KF & 45 \\
4 & KF.2H\(_2\)O & n.d. \\
5 & TBAT\(^b\) & 28 \\
\hline
\end{array}
\]

\(^a\) Yields were determined by \(^1\)H NMR analysis

\(^b\) Tetrabutylammonium difluorotriphenylsilicate.

*Control Experiments for the carboxylation of PhSiMe\(_3\) and PhSi(OMe)\(_3\):* In an argon glove box, a flame-dried 10 mL two neck tube was charged with CuI (10 mg, 0.05 mmol) and
CsF (228 mg, 1.5 mmol). The tube was taken out and attached to a vacuum line and a CO₂ balloon using a three-way stopcock. After three evacuation-CO₂ refill cycles was conducted, DMSO (2 mL) and PhSiMe₃ (75 mg, 0.5 mmol) or PhSi(OMe)₃ were added successively. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 20 h. After being cooled down to 0 °C in an ice-water bath, the reaction mixture was diluted with H₂O (5 mL), acidified using HCl 1N (2 mL) and extracted to EtOAc (3 x 10 mL). The combined organic phase was washed with H₂O (2 x 15 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude mixture was analyzed by ¹H NMR in CDCl₃ using 1,3,5-trimethoxybenzene (22.4 mg) as the internal standard. The reaction using PhSi(OMe)₃ yielded benzoic acid (45%) while the reaction of PhSiMe₃ did not.

**Control Experiments for the carboxylation of benzoxaboroles**

In an argon glove box, a flame-dried 10 mL two neck tube was charged with CuI (10 mg, 0.05 mmol), CsF (228 mg, 1.5 mmol) and the substrate (75 mg, 0.5 mmol). The tube was taken out and attached to a vacuum line and a CO₂ balloon using a three-way stopcock. After three evacuation-CO₂ refill cycles was conducted, DMSO (2 mL) was added. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 20 h. After being cooled down to 0 °C in an ice-water bath, the reaction mixture was diluted with H₂O (5 mL), acidified using HCl 1N (2 mL), stirred for another 2 h and extracted to EtOAc (3 x 10 mL). The combined organic phase was washed with H₂O (2 x 15 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure. The crude mixture was analyzed by ¹H NMR in CDCl₃ using 1,3,5-trimethoxybenzene (22.4 mg) as the internal standard. The desired phthalide was not detected.

**Control Experiments for the carboxylation of benzoxaboroles under reported condition:**
To a 10 mL 2-neck tube was added the substrate (74 mg, 0.5 mmol) and IPrCuCl (2.4 mg, 0.005 mmol). THF (2 mL) was then added, followed by a solution of KO\textsubscript{t}Bu (60 mg, 0.525 mmol) in THF (0.5 mL). A CO\textsubscript{2} balloon was attached and the mixture was stirred at 70 °C for 18 h. The work-up was followed the above procedure. The desired phthalide was not detected.

**Part III: Substrate Scope for the Carboxylation of Benzosiloles**

**Carboxylation of substrate 1a-m**

6-Methoxyisobenzofuran-1(3H)-one 2a:

In an argon glove box, a flame-dried 20 or 30 mL two neck tube was charged with CuI (2 mg, 0.01 mmol) and CsF (228 mg, 1.5 mmol). The tube was taken out and attached to a vacuum line and a CO\textsubscript{2} balloon using a three-way stopcock. After three evacuation-CO\textsubscript{2} refill cycles was conducted, DMSO (4 mL) and 1a (250 mg, 1 mmol) were added successively. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 24 h. After being cooled down, the reaction mixture was diluted with H\textsubscript{2}O (5 mL), acidified using HCl 1N (8 mL), stirred for another 12 h and extracted to EtOAc (3 x 15 mL). The combined organic phase was washed with H\textsubscript{2}O (2 x 15 mL), dried over Na\textsubscript{2}SO\textsubscript{4} and the solvent was removed under reduced pressure. The pure product was obtained using pTLC in DCM (the use of DCM as the eluent was neccessary to separate the product from small amount of alcohol, the use of EtOAc:\textit{n}-Hexane system was not
effective). Yield: 134 mg (82%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.\textsuperscript{5a}

\textbf{\textsuperscript{1}H NMR} (CDCl\textsubscript{3}, 600MHz) $\delta$ 7.37 (d, $J = 8.2$ Hz, 1H), 7.34 (d, $J = 2.1$ Hz, 1H), 7.25-7.23 (m, 1H), 5.26 (s, 2H), 3.87 (s, 3H).

\textbf{\textsuperscript{13}C NMR} (CDCl\textsubscript{3} 151MHz) $\delta$ 171.1, 160.6, 138.8, 127.0, 123.0, 122.9, 107.5, 69.5, 55.7.

6-Methylisobenzofuran-1(3H)-one \textbf{2b}:

The synthesis of \textbf{2b} from \textbf{1b} (234 mg, 1 mmol) followed the synthesis of \textbf{2a}. Yield 114 mg (77%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.\textsuperscript{5b}

\textbf{\textsuperscript{1}H NMR} (CDCl\textsubscript{3}, 400MHz) $\delta$ 7.69 (s, 1H), 7.49 (d, $J = 7.8$ Hz, 1H), 7.38-7.36 (m, 1H), 5.27 (s, 2H), 2.46 (s, 3H).

\textbf{\textsuperscript{13}C NMR} (CDCl\textsubscript{3}, 101MHz) $\delta$ 171.2, 143.8, 139.2, 135.1, 125.8, 125.6, 121.7, 69.5, 21.2.

6-(Dimethylamino)isobenzofuran-1(3H)-one \textbf{2c}:

The synthesis of \textbf{2c} from \textbf{1c} (263 mg, 1 mmol) followed the synthesis of \textbf{2a} with slight modification. After the acidic quenching, the reaction was basified with NaOH 1N until pH > 10 before extraction. Yield 124 mg (72%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.\textsuperscript{5c}
$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.30 (d, $J = 8.2$ Hz, 1H), 7.11 (d, $J = 2.3$ Hz, 1H), 7.04 (dd, $J = 2.3$, 8.7 Hz, 1H), 5.22 (s, 2H), 3.01 (s, 6H).

$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 172.1, 151.2, 133.9, 126.6, 122.3, 118.9, 106.9, 69.5, 40.6.

6-Fluoroisobenzofuran-1(3H)-one 2d:

The synthesis of 2d from 1d (238 mg, 1 mmol) followed the synthesis of 2a. Yield 117 mg (77%) white solid. M.p: 109-111 °C.

$^1$H NMR (CDCl$_3$, 400MHz) $\delta$ 7.56 (dd, $J = 2.3$, 7.3 Hz, 1H), 7.49 (dd, $J = 4.4$, 8.5 Hz, 1H), 7.43-7.38 (m, 1H), 5.31 (s, 2H).

$^{13}$C NMR (CDCl$_3$, 101MHz) $\delta$ 169.9 (d, $J = 4.8$ Hz), 163.0 (d, $J = 246$ Hz), 141.9 (d, $J = 2.0$ Hz), 127.7 (d, $J = 8.6$ Hz), 123.8 (d, $J = 8.6$ Hz), 122.0 (d, $J = 24$ Hz), 112.0 (d, $J = 23$ Hz), 69.4.

DART-MS m/z cald for C$_8$H$_6$O$_2$F [M+H]$^+$: 153.03518, found: 153.03564

IR (KBr, cm$^{-1}$) ν: 2355, 1763, 1626, 1493, 1463, 1363, 1311, 1269, 1244, 1195, 1112, 1045.

6-Chloroisobenzofuran-1(3H)-one 2e:

The synthesis of 2e from 1e (255 mg, 1 mmol) followed the synthesis of 2a. Yield 135 mg (77%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.$^{5b}$
$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.86 (s, 1H), 7.65 (dd, $J = 1.8$, 7.8 Hz, 1H), 7.46 (d, $J = 8.2$ Hz, 1H), 5.31 (s, 2H).

$^{13}$C NMR (CDCl$_3$, 101 MHz) $\delta$ 169.6, 144.6, 135.3, 134.3, 127.5, 125.6, 123.4, 69.4.

5-Methoxyisobenzofuran-1(3H)-one 2f:

The synthesis of 2f from 1f (250 mg, 1 mmol) followed the synthesis of 2a. Yield 110 mg (68%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.$^b$

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.81 (d, $J = 8.9$ Hz, 1H), 7.04 (d, $J = 8.2$ Hz, 1H), 6.92 (s, 1H), 5.25 (s, 2H), 3.90 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 170.8, 164.7, 149.3, 127.2, 118.0, 116.5, 106.0, 69.1, 55.8.

4-Methoxyisobenzofuran-1(3H)-one 2g:

The synthesis of 2g from 1g (250 mg, 1 mmol) followed the synthesis of 2a. Yield 124 mg (76%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.$^d$

$^1$H NMR (CDCl$_3$, 600 MHz) $\delta$ 7.48-7.47 (m, 2H), 7.11-7.09 (m, 1H), 5.24 (s, 2H), 3.91 (s, 3H).

$^{13}$C NMR (CDCl$_3$, 150 MHz) $\delta$ 171.1, 154.2, 134.9, 130.7, 127.3, 117.1, 114.7, 68.0, 55.5.
4-Methylisobenzofuran-1(3H)-one 2h:

The synthesis of 2h from 1h (234 mg, 1 mmol) followed the synthesis of 2a. Yield 114 mg (77%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.5c

\(^1\)H NMR (CDCl\(_3\) 400MHz) \(\delta\) 7.73 (d, \(J = 6.9\) Hz, 1H), 7.45-7.41 (m, 2H), 5.24 (s, 2H), 2.36 (s, 3H).

\(^13\)C NMR (CDCl\(_3\), 101MHz) \(\delta\) 171.4, 145.4, 134.6, 132.3, 129.2, 125.3, 123.0, 69.0, 17.3.

Naphtho[1,2-c]furan-3(1H)-one 2i:

The synthesis of 2i from 1i (270 mg, 1 mmol) followed the synthesis of 2a, but use CuI (20 mg, 0.1 mmol). Yield 117 mg (64%) white solid. M.p 122-125 °C

\(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta\) 8.00 (d, \(J = 7.9\) Hz, 1H), 7.93 (d, \(J = 8.5\) Hz, 1H), 7.81 (d, \(J = 8.5\) Hz, 2H), 7.72 - 7.64 (m, 2H), 5.60 (s, 2H).

\(^13\)C NMR (CDCl\(_3\), 125 MHz) \(\delta\) 171.6, 146.9, 135.8, 130.0, 129.2, 129.1, 127.8, 126.7, 123.4, 123.0, 120.4, 69.0.

DART-MS m/z cald for C\(_{12}\)H\(_9\)O\(_2\) [M+H]: 185.06025, found: 185.06043

IR (KBr, cm\(^{-1}\)) ν: 3050, 1752, 1633, 1593, 1521, 1456, 1395, 1338, 1252, 1083, 1019.
3,6-Dimethylisobenzofuran-1(3H)-one 2j:

The synthesis of 2j from 1j (248 mg, 1 mmol) followed the synthesis of 2a, but use CuI (20 mg, 0.1 mmol). Yield 133 mg (82%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.\textsuperscript{5f}

\textbf{1H NMR} (CDCl\textsubscript{3}, 400MHz) \(\delta\) 7.69 (s, 1H), 7.49 (d, \(J = 7.8\) Hz, 1H), 7.32 (d, \(J = 7.8\) Hz, 1H), 5.53 (q, \(J = 6.4\) Hz, 1H), 2.47 (s, 3H), 1.61 (d, \(J = 6.9\) Hz, 3H).

\textbf{13C NMR} (CDCl\textsubscript{3}, 101MHz) \(\delta\) 170.6, 148.6, 139.3, 135.1, 125.9, 125.6, 121.2, 77.6, 21.2, 20.5.

5-Methoxy-3-methylisobenzofuran-1(3H)-one 2k:

The synthesis of 2k from 1k (278 mg, 1 mmol) followed the synthesis of 2a, but use CuI (20 mg, 0.1 mmol). Yield 148 mg (83%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.\textsuperscript{5f}

\textbf{1H NMR} (CDCl\textsubscript{3}, 400MHz) \(\delta\) 7.77 (d, \(J = 8.2\) Hz, 1H), 7.02-7.00 (m, 1H), 6.85 (d, \(J = 2.3\) Hz, 1H), 5.47 (q, \(J = 6.9\) Hz, 1H), 3.90 (s, 3H), 1.60 (d, \(J = 6.4\) Hz, 3H).

\textbf{13C NMR} (CDCl\textsubscript{3}, 101MHz) \(\delta\) 170.1, 164.7, 153.9, 127.1, 118.0, 116.2, 105.6, 77.0, 55.8, 20.3.

(R)-5-Methoxy-3-methylisobenzofuran-1(3H)-one (R)-2k:
Yield 142 mg (80%) yellow solid, 94% ee (HPLC, OD-H, iPrOH:n-Hexane = 2:98, 1 mL/min).

4-Methoxy-3-methylisobenzofuran-1(3H)-one 2l:

The synthesis of 2l from 1l (278 mg, 1 mmol) followed the synthesis of 2a. Yield 140 mg (79%) white solid. M.p. 115-117 °C

^1H NMR (CDCl₃, 400MHz) δ 7.48-7.43 (m, 2H), 7.10 (dd, J = 1.8, 6.9 Hz, 1H), 5.54 (q, J = 6.4 Hz, 1H), 3.91 (s, 3H), 1.64 (d, J = 6.4 Hz, 3H).

^13C NMR (CDCl₃, 101 MHz) δ 170.4, 154.2, 138.9, 130.8, 127.5, 117.0, 114.9, 77.0, 55.5, 19.0.

DART-MS m/z cald for C₁₀H₁₁O₃ [M+H]⁺: 179.07082, found: 179.07108

IR (KBr, cm⁻¹) ν: 2987, 2939, 2841, 1757, 1607, 1490, 1445, 1357, 1357, 1308, 1274, 1187, 1118, 1047.

3-Hydroxy-4-methylisobenzofuran-1(3H)-one 2m:
The synthesis of 2m from 1m (264 mg, 1 mmol)\textsuperscript{ib} followed the synthesis of 2a, with slight modification. The acidification step was conducted at 0 °C using HCl 2N (6 mL). PTLC was run using EtOAc:n-Hexane (1:1) as eluent. Yield 110 mg (68%) white solid. M.p. 123-126 °C

\textbf{1H NMR} (CD\textsubscript{3}OD, 600MHz) \(\delta\) 7.64-7.62 (m, 1H), 7.47-7.44 (m, 2H), 6.59 (s, 1H), 4.36 (s, 1H), 2.44 (s, 3H).

\textbf{13C NMR} (CD\textsubscript{3}OD, 151MHz) \(\delta\) 171.5, 146.9, 137.0, 136.3, 131.9, 128.1, 123.3, 99.7, 17.3.

\textbf{DART-MS} m/z cald for C\textsubscript{9}H\textsubscript{9}O\textsubscript{3} [M+H]+: 165.05517, found: 165.05589

\textbf{IR} (KBr, cm\textsuperscript{-1}) v: 3358, 2959, 1747, 1602, 1485, 1433, 1357, 1310, 1261, 1206, 1103, 1063, 1032.

\textit{Carboxylation of substrate 1n-w}

3-Methylisobenzofuran-1(3H)-one 2n:

In an argon glove box, a flame-dried 20 or 30 mL two neck tube was charged with Cul (2 mg, 0.01 mmol) and CsF (228 mg, 1.5 mmol). The tube was taken out and attached to a vacuum line and a CO\textsubscript{2} balloon using a three-way stopcock. After three evacuation-CO\textsubscript{2} refill cycles was conducted, DMSO (4 mL) and 1n (178 mg, 1 mmol) were added successively. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 24 h. After being cooled down, the reaction mixture was diluted with H\textsubscript{2}O
(20 mL), NaOH 1N (4 mL), stirred for 1 h and washed with Et₂O (3 x 10 mL). The aqueous phase was acidified using HCl 1N (12 mL), stirred for another 12 h and extracted to EtOAc (3 x 15 mL). The combined organic phase was washed with H₂O (2 x 15 mL), dried over Na₂SO₄ and the solvent was removed under reduced pressure to afford pure 2n. Yield: 112 mg (76%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.⁵f

¹H NMR (CDCl₃, 400 MHz) δ 7.90 (d, J = 7.3 Hz, 1H), 7.69 (t, J = 7.8 Hz, 1H), 7.54 (t, J = 7.6 Hz, 1H), 7.45 (d, J = 7.3 Hz, 1H), 5.58 (q, J = 6.6 Hz, 1H), 1.65 (d, J = 6.9 Hz, 3H).

¹³C NMR (CDCl₃, 100 MHz) δ 170.5, 151.2, 134.0, 129.0, 125.8, 125.7, 121.5, 77.7, 20.4.

(R)-3-Methylisobenzofuran-1(3H)-one (R)-2n:

Yield 113 mg (76%) yellow solid, 94% ee (HPLC, OJ, iPrOH:n-Hexane = 2:98, 1 mL/min).

6-Methoxy-3-methylisobenzofuran-1(3H)-one 2o:

The synthesis of 2o from 1o (208 mg, 1 mmol) followed the synthesis of 2n. Yield 134 mg (75%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.⁵h

¹H NMR (CDCl₃, 400 MHz) δ 7.33-7.31 (m, 2H), 7.24-7.22 (m, 1H), 5.52 (q, J = 6.6 Hz, 1H), 3.86 (s, 3H), 1.60 (d, J = 6.4 Hz, 3H).
$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 170.6, 160.6, 143.7, 127.1, 122.9, 122.4, 107.4, 77.6, 55.7, 20.5.

6-Chloro-3-methylisobenzofuran-1(3H)-one 2p:

The synthesis of 2p from 1b (212 mg, 1 mmol) followed the synthesis of 2n. Yield 152 mg (84%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.$^5f$

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 7.85 (d, $J = 1.8$ Hz, 1H), 7.64 (dd, $J = 1.8$, 8.2 Hz, 1H), 7.39 (d, $J = 8.2$ Hz, 1H), 5.56 (q, $J = 6.9$ Hz, 1H), 1.64 (d, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 168.9, 149.3, 135.4, 134.3, 127.6, 125.6, 122.9, 77.6, 20.3.

6-Iodo-3-methylisobenzofuran-1(3H)-one 2q:

The synthesis of 2q from 1q (304 mg, 1 mmol) followed the synthesis of 2a. Yield 195 mg (72%) white solid. M.p. 142-145 °C

$^1$H NMR (CDCl$_3$, 400 MHz) $\delta$ 8.22 (br. s., 1H), 7.98 (d, $J = 7.8$ Hz, 1H), 7.22 (d, $J = 7.8$ Hz, 1H), 5.52 (q, $J = 6.9$ Hz, 1H), 1.62 (d, $J = 6.4$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 100 MHz) $\delta$ 168.6, 150.4, 142.7, 134.6, 128.0, 123.3, 93.9, 77.7, 20.2.

DART-MS m/z cald for C$_9$H$_8$IO$_2$ [M+H]$^+$: 274.95690, found: 274.95773

IR (KBr, cm$^{-1}$) v: 2362, 1756, 1196.
6-Bromo-3-methylisobenzofuran-1(3H)-one \(2r\):

![Chemical structure](image)

The synthesis of \(2r\) from \(1r\) (257 mg, 1 mmol) followed the synthesis of \(2n\), but further purification by pTLC (EtOAc:n-Hexane = 4:6) was required for isolation of pure \(2r\). Yield 170 mg (75%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.\(^5\)

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta 8.01\) (s, 1H), \(7.79\) (d, \(J = 8.2\) Hz, 1H), \(7.34\) (d, \(J = 8.2\) Hz, 1H), \(5.54\) (q, \(J = 6.9\) Hz, 1H), \(1.63\) (d, \(J = 6.9\) Hz, 3H).

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta 168.8, 149.7, 137.1, 128.6, 127.8, 123.2, 123.0, 77.6, 20.2\).

5-Bromo-3-methylisobenzofuran-1(3H)-one \(2s\):

![Chemical structure](image)

The synthesis of \(2s\) from \(1s\) (257 mg, 1 mmol) followed the synthesis of \(2a\). Yield 160 mg (70%) white solid. M.p. 109 °C

\(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta 7.76-7.74\) (m, 1H), \(7.67-7.65\) (m, 1H), \(7.61\) (s, 1H), \(5.54\) (q, \(J = 6.9\) Hz, 1H), \(1.64\) (d, \(J = 6.9\) Hz, 4H).

\(^{13}\)C NMR (CDCl\(_3\), 100 MHz) \(\delta 169.4, 152.8, 132.7, 129.2, 127.0, 125.1, 124.7, 77.1, 20.2\).

DART-MS m/z cald for \(C_9H_8BrO_2\) [M+H]\(^+\): 226.97077, found: 226.97038

IR (KBr, cm\(^{-1}\)) \(\nu\): 2361, 1750, 1335, 1051.

3-Isopropylisobenzofuran-1(3H)-one \(2t\):
The synthesis of \( \text{2p} \) from \( \text{1p} \) (204 mg, 1 mmol) followed the synthesis of \( \text{2n} \). Yield 130 mg (74%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.\(^{5f}\)

\[ ^1H \text{ NMR (CDCl}_3, 400 MHz) \delta 7.90 (d, J = 7.3 \text{ Hz, 1H}), 7.67 (t, J = 7.3 \text{ Hz, 1H}), 7.53 (t, J = 7.3 \text{ Hz, 1H}), 7.45 (d, J = 7.8 \text{ Hz, 1H}), 5.38 (d, J = 3.7 \text{ Hz, 1H}), 2.33-2.25 (m, 1H), 1.13 (d, J = 6.9 \text{ Hz, 3H}), 0.81 (d, J = 6.9 \text{ Hz, 3H}). \]

\[ ^{13}C \text{ NMR (CDCl}_3, 100 MHz) \delta 170.8, 148.8, 133.8, 129.0, 126.7, 125.6, 122.1, 85.6, 32.3, 18.7, 15.6. \]

3-Phenylisobenzofuran-1(3H)-one \( \text{2u} \):

In an argon glove box, a flame-dried 20 or 30 mL two neck tube was charged with Cul (2 mg, 0.01 mmol), \( \text{1u} \) (240 mg, 1 mmol) and DMSO (4 mL). CsF (228 mg, 1.5 mmol) was added and the tube was taken out and attached to a CO\(_2\) balloon using a three-way stopcock. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 24 h. After being cooled down, the reaction mixture was diluted with H\(_2\)O (20 mL), NaOH 1N (4 mL), stirred for 1 h and washed with Et\(_2\)O (3 x 10 mL). The aqueous phase was acidified using HCl 1N (12 mL), stirred for another 12 h and extracted to EtOAc (3 x 15 mL). The combined organic phase was washed with H\(_2\)O (2 x 15 mL), dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure. Pure \( \text{2u} \) was obtained after pTLC using EtOAc:n-Hexane 1:1. Yield: 147 mg (70%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.\(^{5f}\)
$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.95 (d, $J = 7.9$ Hz, 1H), 7.63 (t, $J = 8.0$ Hz, 1H), 7.54 (t, $J = 7.5$ Hz, 1H), 7.37-7.32 (m, 3H), 7.33 (d, $J = 7.9$ Hz, 1H), 7.28-7.26 (m, 2H), 6.40 (s, 1H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 170.5, 149.6, 136.3, 134.3, 129.3, 129.2, 128.9, 126.9, 125.6, 125.5, 122.8, 82.7.

3-Butylisobenzofuran-1(3H)-one $^{2v}$:

![Chemical Structure](image)

The synthesis of $^{2v}$ from $^{1v}$ (220 mg, 1 mmol)$^3$ followed the synthesis of $^{2n}$. Yield 162 mg (85%) yellow oil. This is a known compound and the spectroscopic data is in agreement with the literature.$^5f$

$^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.91 (d, $J = 7.4$ Hz, 1H), 7.68 (t, $J = 7.4$ Hz, 1H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.44 (d, $J = 7.4$ Hz, 1H), 5.48 (dd, $J = 7.7$, 4.3 Hz, 1H), 2.09-2.02 (m, 1H), 1.81-1.74 (m, 1H), 1.53-1.34 (m, 4H), 0.92 (t, $J = 7.1$ Hz, 3H).

$^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 170.7, 150.1, 133.9, 129.0, 126.1, 125.7, 121.7, 81.4, 34.4, 26.9, 22.4, 13.8.

3,3-Dimethylisobenzofuran-1(3H)-one $^{2w}$:

![Chemical Structure](image)

The synthesis of $^{2w}$ from $^{1w}$ (192 mg, 1 mmol) followed the synthesis of $^{2n}$, with slight modification. Cul (20 mg, 0.1 mmol) was used and $^{1w}$ was dissolved in small amount of DMSO before being added to the reaction mixture. Yield 95 mg (59%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.$^5i$
\[ \text{H NMR (CDCl}_3, 400MHz) \delta 7.86 (dd, J = 0.9, 7.8 Hz, 1H), 7.68-7.64 (m, 1H), 7.52-7.48 (m, 1H), 7.42-7.39 (m, 1H), 1.66 (s, 6H). \]

\[ \text{13C NMR (CDCl}_3, 101MHz) \delta 169.8, 154.9, 134.1, 128.9, 125.7, 125.2, 120.6, 85.4, 27.3. \]

**Part IV: Gram-Scale Synthesis of 2p**

In an argon glove box, a flame-dried 100 mL two neck flask was charged with Cul (9 mg, 0.048 mmol) and CsF (1.09 g, 7.2 mmol). The flask was taken out and attached to a vacuum line and a CO\(_2\) balloon using a three-way stopcock. After three evacuation-CO\(_2\) refill cycles was conducted, DMSO (20 mL) and 1p (1.02 g, 4.8 mmol) were added successively. The tube was then immersed in a pre-heated oil bath at 60 °C and stirred vigorously for 24 h. After being cooled down, the reaction mixture was diluted with H\(_2\)O (50 mL), NaOH 1N (20 mL), stirred for 1 h and washed with Et\(_2\)O (3 x 30 mL). The aqueous phase was acidified using HCl 1N (60 mL), stirred for another 12 h and extracted to EtOAc (3 x 25 mL). The combined organic phase was washed with H\(_2\)O (3 x 50 mL), dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure to afford crude 2p (almost pure). The crude was further purified using column chromatography (EtOAc:n-Hexane = 3:7). Yield: 670 mg (77%) yellow oil.

**Part V: Synthesis of Natural Products 4, 5 and 6**

4,5,6-Trimethoxy-3-methylisobenzofuran-1(3H)-one 2w:
The synthesis of \( 2w \) from \( 1w \) (324 mg, 1 mmol) followed the synthesis of \( 2a \), with slight modification. \( 1w \) was dissolved in a small amount of DMSO before being added to the reaction mixture. Yield 139 mg (58%) yellow oil.

\[ 1^1H \text{ NMR} \ (\text{CDCl}_3, 500 \text{ MHz}) \delta 7.10 \ (s, 1H), 5.49 \ (q, J = 6.2 \text{ Hz}, 1H), 3.97 \ (s, 3H), 3.92 \ (s, 3H), 3.90 \ (s, 3H), 1.62 \ (d, J = 6.8 \text{ Hz}, 3H). \]

\[ 1^3C \text{ NMR} \ (\text{CDCl}_3, 125 \text{ MHz}) \delta 170.2, 155.5, 147.5, 146.8, 136.6, 121.0, 102.5, 76.3, 61.0, 60.8, 56.3, 19.6. \]

\[ \text{DART-MS m/z cald for } C_{12}H_{15}O_5 \ [M+H]^+: 239.09195, \text{ found: 239.09226} \]

\[ \text{IR (KBr, cm}^{-1}\text{)} \nu: 2941, 1761, 1614, 1478, 1421, 1341, 1253, 1196, 1116, 1074, 1041. \]

4,5,6-Trihydroxy-3-methylisobenzofuran-1(3H)-one 4:

In a 20 mL 2-neck tube, attached with an argon balloon, was charged 2x (120 mg, 0.5 mmol) and DCM (2 mL). The solution was cooled to -78 °C in a dry ice-acetone bath. Then, BBr\(_3\) (1 M solution in DCM, 2.3 mL) was added dropwise. The reaction mixture was stirred at -78 °C for 30 minutes and at room temperature for 3 h. After that, it was again cooled to -78 °C and carefully quenched with saturated NaHCO\(_3\) (1 mL), diluted with brine and extracted to EtOAc (3 x 15 mL). The combined organic solution was washed once with brine, dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure to afford compound 6 as brown solid. Yield: 97 mg (quant.). This is a known compound and the spectroscopic data is in agreement with the literature.\(^6\)

\[ 1^1H \text{ NMR} \ (\text{DMSO-d}_6, 400 \text{ MHz}) \delta 9.89 \ (s, 1H), 9.38 \ (br. s., 1H), 9.31 \ (s, 1H), 6.69 \ (s, 1H), 5.46 \ (q, J = 6.4 \text{ Hz}, 1H), 1.48 \ (d, J = 6.4 \text{ Hz}, 3H). \]

\[ 1^3C \text{ NMR} \ (\text{DMSO-d}_6, 100 \text{ MHz}) \delta 170.2, 147.4, 139.9, 139.6, 130.6, 115.1, 101.5, 75.5, 19.4. \]
6-Hydroxy-4-methoxy-5-methylisobenzofuran-1(3H)-one 2x:

\[
\begin{align*}
\text{THPO} & \quad \text{Cul (1 mol\%)} \quad \text{CO}_2 \text{ (balloon)} \quad \text{CsF (1.5 eq), DMSO} \quad 60 ^\circ \text{C, 24 h} \quad \text{HCl} \quad \text{r.t., 12 h} \\
1y & \quad \text{2y}
\end{align*}
\]

The synthesis of 2x from 1x (364 mg, 1 mmol) followed the synthesis of 2u. Yield: 125 mg (65%) white solid. This is a known compound and the spectroscopic data is in agreement with the literature.\(^7\)

\(^1^H\ NMR\ (\text{CD}_3\text{OD, 600 MHz}) \delta 6.93 \text{ (s, 1H)}, 5.47 \text{ (s, 2H)}, 3.91 \text{ (s, 3H)}, 2.16 \text{ (s, 3H)}.

\(^1^C\ NMR\ (\text{CD}_3\text{OD, 150 MHz}) \delta 173.7, 159.3, 154.8, 127.8, 125.8, 124.9, 105.3, 70.2, 59.6, 9.8.

4-Methoxy-5-methyl-6-((3-methylbut-2-en-1-yl)oxy)isobenzofuran-1(3H)-one 4:

\[
\begin{align*}
\text{HO} & \quad \text{Prenyl bromide} \\
\text{OMe} & \quad \text{K}_2\text{CO}_3, \text{KI} \quad \text{Acetone, reflux} \\
2y & \quad 5
\end{align*}
\]

To a 10 mL 2-neck tube was added 2y (97 mg, 0.5 mmol), K\(_2\)CO\(_3\) (345 mg, 2.5 mmol) and KI (250 mg, 1.5 mmol). The tube was attached to an argon balloon. Acetone (1.5 mL) and prenyl bromide (223 mg, 1.5 mmol) was added \textit{via} syringes. The reaction was refluxed for 24 h. Then, it was diluted to H\(_2\)O (10 mL) and extracted to EtOAc (3 x 15 mL). The combined organic solution was washed with brine, dried over Na\(_2\)SO\(_4\) and the solvent was removed under reduced pressure. Compound 5 was obtained as white solid after column chromatography. Yield: 130 mg (quant.). This is a known compound and the spectroscopic data is in agreement with the literature.\(^7\)

\(^1^H\ NMR\ (\text{CDCl}_3, 600 MHz) \delta 7.08 \text{ (s, 1H)}, 5.49 \text{ (br. s., 1H)}, 5.38 \text{ (s, 2H)}, 4.58 \text{ (d, } J = 5.5 \text{ Hz, 2H)}, 3.89 \text{ (s, 3H)}, 2.21 \text{ (s, 3H)}, 1.80 \text{ (s, 3H)}, 1.75 \text{ (s, 3H)}.
^{13}C\ NMR\ (CDCl_3,\ 150\ MHz)\ \delta\ 171.3,\ 159.2,\ 152.9,\ 138.2,\ 128.0,\ 125.7,\ 124.7,\ 119.2,\ 101.9,\ 68.2,\ 65.8,\ 59.3,\ 25.7,\ 18.3,\ 9.7.

(E)-6-((3,7-Dimethylocta-2,6-dien-1-yl)oxy)-4-methoxy-5-methylisobenzofuran-1(3H)-one 5 (Marilone C):

Following the above procedure, using geranyl bromide (325 mg, 1.5 mmol) instead of prenyl bromide, compound 5 was obtained as colorless oil after column chromatography. Yield: 130 mg (78%). This is a known compound and the spectroscopic data is in agreement with the literature.\(^8\)

^{1}H\ NMR\ (Acetone-d_6,\ 600\ MHz)\ \delta\ 7.04\ (s,\ 1H),\ 5.53-5.50\ (m,\ 3H),\ 5.11\ (t,\ J = 6.5\ Hz,\ 1H),\ 4.71\ (d,\ J = 6.2\ Hz,\ 2H),\ 3.97\ (s,\ 3H),\ 2.14-2.09\ (m,\ 7H),\ 1.79\ (s,\ 3H),\ 1.64\ (s,\ 3H),\ 1.60\ (s,\ 3H).

^{13}C\ NMR\ (Acetone-d_6,\ 150\ MHz)\ \delta\ 171.2,\ 159.9,\ 154.0,\ 141.7,\ 132.2,\ 128.6,\ 126.0,\ 125.0,\ 124.8,\ 120.7,\ 102.2,\ 69.0,\ 66.6,\ 59.4,\ 40.2,\ 27.1,\ 25.9,\ 17.8,\ 16.8,\ 9.9.

Part VI: References


Part VII: NMR Spectra of Starting Materials and Products

![NMR Spectrum](image)
Part VIII: HPLC Traces of Chiral Alcohols and Phthalides

HPLC condition: OD-H, iPrOH:n-Hexane = 2:98, 1 mL/min, \( t_1 = 24.993 \), \( t_2 = 29.911 \)

HPLC chart of racemic alcohol

HPLC chart of chiral alcohol
HPLC condition: OD-H, iPrOH:n-Hexane = 2:98, 1 mL/min, \( t_1 = 14.994 \), \( t_2 = 18.731 \)

HPLC chart of racemic alcohol:

<table>
<thead>
<tr>
<th>Peak</th>
<th>Ret Time</th>
<th>Area</th>
<th>Height</th>
<th>Area%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.994</td>
<td>551402</td>
<td>28339</td>
<td>49.02%</td>
</tr>
<tr>
<td>2</td>
<td>18.731</td>
<td>555251</td>
<td>23085</td>
<td>50.73%</td>
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HPLC chart of chiral alcohol:

<table>
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<th>Ret Time</th>
<th>Area</th>
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<th>Area%</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>15.146</td>
<td>4207920</td>
<td>187356</td>
<td>97.770</td>
</tr>
<tr>
<td>2</td>
<td>19.250</td>
<td>135860</td>
<td>4153</td>
<td>2.2300</td>
</tr>
</tbody>
</table>
HPLC Condition: OD-H, iPrOH:n-Hexane = 2:98, 1 mL/min, $t_1 = 24.167$, $t_2 = 26.835$

HPLC chart of racemic phthalide:

HPLC chart of chiral phthalide:
HPLC Condition: OD-H, PrOH:n-Hexane = 2:98, 1 mL/min, $t_1 = 24.167$, $t_2 = 26.835$

HPLC chart of racemic phthalide:

![HPLC chart of racemic phthalide]

HPLC chart of chiral phthalide:

![HPLC chart of chiral phthalide]