Robust, scalable construction of an electrophilic deuterated methylthiolating reagent: Facile access to SCD$_3$-containing scaffolds with nucleophiles

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1. General information

All reactions were performed with dry glassware under atmosphere of nitrogen unless otherwise noted. Anhydrous CH\textsubscript{3}OH, EtOH, THF, N,N-dimethylformamide (DMF), Dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) were purchased from Energy-Chemical and directly used without further purification. All glassware was oven dried before use. Unless otherwise stated, reagents were commercially available and used as purchased without further purification. Chemicals were purchased from Adamas-beta, Macklin Reagent, Energy Chemicals, Aladdin, JiuDing Chemicals or Bide Pharmatech Ltd. All the reactions were monitored by thin layer chromatography (TLC, Silica gel). The spots were visualized by UV light. Purification of products was conducted by flash chromatography on silica gel.

All experiments were conducted under inert atmosphere unless otherwise noted. \textsuperscript{1}H and \textsuperscript{13}C NMR spectra were recorded on a Bruker Ascend\textsuperscript{TM} 400 (400 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and the residual solvent peak was used as an internal reference: \textsuperscript{1}H (chloroform $\delta$ 7.26; DMSO $\delta$ 2.50), \textsuperscript{13}C (chloroform $\delta$ 77.16; DMSO $\delta$ 39.5). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. Melting point (MP) was obtained on Hanon MP-430. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254nm. All GC-MS analyses were performed on an Agilent Technologies 8860 GC system equipped with a 5977B MS detector. High resolution mass spectra (HRMS) were obtained on Agilent 1290II-6545 spectrometer and Agilent GC-MS 7250 QTOF. Column chromatography was performed with silica gel (200-300 mesh ASTM).
2. Optimization of S-Methyl-$d_3$ Reagent$^{a,b}$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Electrophile</th>
<th>Base</th>
<th>Solvent</th>
<th>TBAI (mol%)</th>
<th>Time (h)</th>
<th>Temp (°C)</th>
<th>Yield (D inc.) $^b$ (%)</th>
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<td>Pyridine</td>
<td>DMF</td>
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<td>DMF</td>
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<td>Et$_3$N</td>
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<td>2,6-Lutidine</td>
<td>DMF</td>
<td>-</td>
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$^a$(1 mmol), electrophile (1.1 mmol, 1.1 equiv.), and base (1.2 mmol, 1.2 equiv.) in solvent (2 mL) at 0 °C under N$_2$ atmosphere for 1.5-24 h, then TsSNa (1.5 mmol, 1.5 equiv.) and TBAI were added to solvent at 40-80 °C under N$_2$ atmosphere for 4-8 h. $^b$Isolated yield. ND = Not determined.

3. General procedure for the the Synthesis of TsSCD$_3$

To a flame dried Schlenk tube equipped with a stirring bar were added CD$_3$OD (40.6 μL, 1 mmol, 1.0 equiv.), 2,6-lutidine (138.2 μL, 1.2 mmol, 1.2 equiv.), dry DMF (2 mL) and Tf$_2$O (185.0 μL, 1.1 mmol, 1.1 equiv.) added sequentially under N$_2$. The reaction mixture was stirred at 0 °C for 90 min. After that, TsSNa (315.0 mg, 1.5 mmol, 1.5 equiv.) and TBAI (18.5 mg, 0.05 mmol, 5 mol%) was added to the mixture. The reaction was stirred for a further 6 h at 60 °C. The reaction mixture was quenched with water (10 mL) and then extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (15 mL), dried over sodium sulfate, filtrated and concentrated. The crude product was purified by column chromatography (Ethyl Acetate/Hexane: 1/70 to 1/40) to afford 3 (172.2 mg, 84 yield%) as white solid.
4. Deuterated Methylthiolation with Arylboronic Acids as Nucleophiles

**General procedure A:** To a mixture of copper(II) sulfate (1.60 mg, 10.0 µmol, 5 mol%) and sodium bicarbonate (33.6 mg, 0.4 mmol, 2 equiv.) was added a solution of 3 (41.0 mg, 0.2 mmol, 1 equiv.) and Arylboronic Acids (4) (0.3 mmol, 1.5 equiv.) dissolved in methanol (2.0 mL) at room temperature. After stirring for 24 h at the same temperature, then the mixture was diluted with water and extracted with DCM (3×5 mL). The organic phase was dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford 5a-5i, 5k, 5l, 5m and 5p-5t.

**General procedure B:** To a mixture of copper(II) sulfate (1.6 mg, 10.0 µmol, 5 mol%) and sodium bicarbonate (33.6 mg, 0.4 mmol, 2 equiv.) was added a solution of 3 (41.0 mg, 0.2 mmol, 1 equiv.) and Arylboronic Acids (4) (0.3 mmol, 1.5 equiv.) dissolved in ethanol (2.0 mL) at room temperature. After stirring for 24 h at the same temperature, then the mixture was diluted with water and extracted with DCM (3×5 mL). The organic phase was dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford 5j, 5n.

**General procedure C:** To a mixture of copper(II) sulfate (31.9 mg, 0.2 mmol, 1 equiv.) and sodium bicarbonate (33.6 mg, 0.4 mmol, 2 equiv.) was added a solution of 3 (41.0 mg, 0.2 mmol, 1 equiv.) and 4o (45.6 mg, 0.3 mmol, 1.5 equiv.) dissolved in ethanol (2.0 mL) at room temperature. After stirring for 24 h at the same temperature, then the mixture was diluted with water and extracted with DCM (3×5 mL). The organic phase was dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford 5o (23.5 mg, 75 %) as a colorless oil.
General procedure D: To a mixture of copper(II) sulfate (1.2 mg, 7.5 µmol, 5 mol%) and sodium bicarbonate (25.2 mg, 0.3 mmol, 2 equiv.) was added a solution of 3 (71.8 mg, 0.35 mmol, 2.3 equiv.) and 4u (24.9 mg, 0.15 mmol, 1 equiv.) dissolved in methanol (2.0 mL) at room temperature. After stirring for 24 h at the same temperature, then the mixture was diluted with water and extracted with DCM (3×5 mL). The organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford 5u (17.9 mg, 68%) as a colorless oil.
5. Deuterated Methylthiolation with Various Nucleophiles

Procedure for the synthesis of 7a, 7b, 7c:

\[
\text{TsSCD}_3 + \begin{align*}
6a & \quad R = \text{Me} \\
6b & \quad R = \text{t-Bu} \\
6c & \quad R = \text{Ad}
\end{align*}
\]

\[
\text{Cs}_2\text{CO}_3 (1.5 \text{ equiv.}) \quad \text{DCE, r.t., } \text{N}_2, 12 \text{ h}
\]

To a mixture of 3 (61.5 mg, 0.3 mmol, 1.5 equiv.), NuH (0.2 mmol) and Cs\(_2\)CO\(_3\) (97.7 mg, 0.3 mmol, 1.5 equiv.) was added DCE (1 mL) at room temperature under N\(_2\) atmosphere. The system was stirred at room temperature for 12 h. The reaction system was filtered and evaporated under reduced pressure. The mixture was purified by column chromatography to give 7a, 7b, and 7c.

### Reaction Optimization of Asymmetric Deuterated Methylthiolation\(^{a,b,3}\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Catalyst</th>
<th>R</th>
<th>Temp (°C)</th>
<th>ee (^b) (%)</th>
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<tbody>
<tr>
<td>1</td>
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<td>(DHQD)(_2)AQN</td>
<td>Me</td>
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<td>21</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>3</td>
<td>toluene</td>
<td>Cinconine</td>
<td>Me</td>
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<td>11</td>
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<tr>
<td>4</td>
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<td>Me</td>
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<tr>
<td>5</td>
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<td>19</td>
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<tr>
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<tr>
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<td>13</td>
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<tr>
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<td>t-Bu</td>
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<tr>
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<td>(DHQD)(_2)AQN</td>
<td>t-Bu</td>
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\(^a\)Reaction conditions: 3 (0.02 mmol), NuH (0.02 mmol), catalyst (20 mol%) in 0.5 mL of solvent at indicated temperature for 16 h. \(^b\)Determined by HPLC analysis on a chiral stationary phase.
Procedure for the synthesis of 7d, 7e

\[ \text{TsSCD}_3 + \begin{array}{c} \text{3} \\
6d \quad R = \text{Cl} \\
6e \quad R = \text{MeO}_2\text{C}
\end{array} \xrightarrow{\text{TBHP (2 equiv.)}} \begin{array}{c} \text{7d} \quad R = \text{Cl} \\
7e \quad R = \text{MeO}_2\text{C}
\end{array} \]

A 10 mL round bottomed flask equipped with a stirring bar was charged with 3 (TsSCD$_3$, 0.25 mmol, 51.2 mg, 1.0 equiv.), aldehydes (0.375 mmol, 1.5 equiv.), and CH$_3$CN (2.0 mL) followed by sequential addition of tert-butyl hydroperoxide (0.5 mmol, 64.5 mg, 2.0 equiv, 70 wt. % in H$_2$O). The reaction was stirred at 82 °C for 24 h. The solvent was filtered and the filtrate was evaporated in vacuo. The residue was purified by silica gel flash column chromatography to afford 7d and 7e.

Procedure for the synthesis of 7f, 7g

\[ \text{TsSCD}_3 + \begin{array}{c} \text{3} \\
6f \quad R = 3-\text{Me} \\
6g \quad R = 4-\text{Cl}
\end{array} \xrightarrow{\text{LiHMDS (1.1 equiv.)}} \begin{array}{c} \text{7f} \quad R = 3-\text{Me} \\
7g \quad R = 4-\text{Cl}
\end{array} \]

LiHMDS (0.22 mL, 1 M in THF, 1.1 equiv.) was slowly added to a stirred solution of alkyne (1 equiv.) in dry THF (2 mL) over 10 min at -78 °C. After 15 min, the lithium acetaminide was treated with 3 (TsSCD$_3$, 45.1 mg, 0.22 mmol, 1.1 equiv.) in dry THF (1.1 M) which was added drop-wise over 15 min and the solution was then stirred for a further 15 min at -78 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was quenched with satd. NH$_4$Cl(aq) and then extracted with diethyl ether (2 × 10 mL). The combined organic layers were dried over Na$_2$SO$_4$, filtered and concentrated under reduced pressure to give a residue which was purified by silica gel flash column chromatography to afford 7f and 7g.

Procedure for the synthesis of 7h

\[ \text{TsSCD}_3 + \begin{array}{c} \text{3} \\
6h \quad \text{Cl-SCD}_3
\end{array} \xrightarrow{\text{MgCl·LiCl (1.1 equiv.)}} \begin{array}{c} \text{7h} \quad \text{Cl-SCD}_3
\end{array} \]

A dry and argon flushed Schlenk-flask, equipped with a magnetic stirrer and a septum was charged with 6h (76.5 mg, 0.5 mmol, 1 equiv.) in THF (1 mL) and cooled to the appropriate temperature. TMPMgCl·LiCl (0.55 mL, 1 M in THF, 1.1 equiv.) was added dropwise at rt for 30 min. Then, 3 (128.1 mg, 0.625 mmol, 1.25 equiv.) was added and the reaction mixture stirred at rt for 30 min. The reaction mixture was quenched with half concentrated aqueous NH$_4$Cl solution, extracted with Et$_2$O (3 × 10 mL). The combined organic layers were dried over Na$_2$SO$_4$ and
concentrated in vacuo. Flash column chromatographical purification on silica gel (pentane) afforded 7h (85.4 mg, 85%) as a pale yellow oil.

**Procedure for the synthesis of 7i**

\[
\text{TsSCD}_3 + \begin{array}{c}
\text{Ph}
\end{array}
\xrightarrow{\text{LiHMDS (1.1 equiv.)}} \begin{array}{c}
\text{Ph}
\end{array}
\]

LiHMDS (0.22 ml, 1 M in THF, 1.1 equiv.) was slowly added to a stirred solution of diphenylphosphine oxide (33.8 mg, 0.2 mmol, 1 equiv.) in dry CH₂Cl₂ (0.1 M) over 10 min at -78 °C. After 15 min, 3 (TsSCD₃, 45.1 mg, 0.22 mmol, 1.1 equiv.) in dry THF (1.1 M) which was added drop-wise over 15 min and the solution was then stirred for a further 15 min at -78 °C. The mixture was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was quenched with satd. NH₄Cl(aq) and then extracted with diethyl ether (2 × 10 mL). The combined organic layers were dried over Na₂SO₄, filtered and concentrated under reduced pressure to give a residue which was purified by silica gel flash column chromatography to afford 7i (30.1 mg, 60%) as yellow oil.

**Procedure for the synthesis of 7j**

\[
\text{TsSCD}_3 + \begin{array}{c}
\text{Ph}
\end{array}
\xrightarrow{n-\text{BuLi (1.1 equiv.)}} \begin{array}{c}
\text{Ph}
\end{array}
\]

n-BuLi (0.165 mmol, 2.5 M in THF, 1.1 equiv.) was slowly added to a stirred solution of diphenylamine (25.4 mg, 0.15 mmol, 1 equiv.) in dry THF (1.0 mL) over 10 min at -0 °C. The mixture was allowed to warm to ambient temperature for 1 h, and 3 (TsSCD₃, 46.1 mg, 0.225 mmol, 1.5 equiv.) was subsequently added to the mixture. After 12 h, the reaction mixture was quenched with saturated NH₄Cl aqueous solution. The aqueous layer was extracted with ether, and the combined organic layer was dried by Na₂SO₄. Filtration, concentration and flash column chromatography provided 7j (16.3 mg, 50%) as yellow oil.

**Procedure for the synthesis of 7k, 7l, 7m, 7n**

\[
\text{TsSCD}_3 + \begin{array}{c}
\text{Me}
\end{array}
\xrightarrow{\text{Et₃N (1 equiv.)}} \begin{array}{c}
\text{Me}
\end{array}
\]

3 (TsSCD₃, 45.1 mg, 0.22 mmol, 1.1 equiv.) was dissolved in dry DCM (1 mL) in the round bottom flask. Then a solution of 1-Dodecanethiol (40.5 mg, 0.2 mmol, 1 equiv.) and NEt₃ (20.2 mg, 28.0 μL, 0.2 mmol, 1 equiv.) in dry DCM (0.5 mL) was added. Reaction was stirred for 4 h. After this time, solvent was evaporated and purified using column chromatography to afford 7k (35.6 mg, 71%) as pale yellow oil.
3 (TsSCD$_3$, 45.1 mg, 0.22 mmol, 1.1 equiv.) was dissolved in dry DCM (1 mL) in the round bottom flask. Then a solution of thiol (0.2 mmol, 1 equiv.) and NEt$_3$ (20.2 mg, 0.2 mmol, 28.0 μL, 1 equiv.) in dry DCM (0.5 mL) was added. Reaction was stirred for 4 h. After this time, solvent was evaporated and purified using column chromatography to afford 7l, 7m.

3 (TsSCD$_3$, 45.1 mg, 0.22 mmol, 1.1 equiv.) was dissolved in dry DCM (1 mL) in the round bottom flask. Then a solution of N-Boc-L-Cysteine Methyl ester (47.0 mg, 0.2 mmol, 1 equiv.) and NEt$_3$ (20.2 mg, 0.2 mmol, 28.0 μL, 1 equiv.) in dry DCM (0.5 mL) was added. Reaction was stirred for 4 h. After this time, solvent was evaporated and purified using column chromatography to afford 7n (45.4 mg, 80%) as colorless oil.
6. Gram-Scale Operation and Further Transformation

![Chemical Reaction](attachment:image.png)

To a flame dried Schlenk tube equipped with a stirring bar were added CD₃OD (1.80 g, 2.10 mL, 50 mmol, 1.0 equiv.), 2,6-lutidine (6.42 g, 6.90 mL, 60 mmol, 1.2 equiv.), dry DMF (100 mL) and Tf₂O (15.51 g, 9.25 mL, 55 mmol, 1.1 equiv.) added sequentially under N₂. The reaction mixture was stirred at 0 °C for 90 min. After that, TsNa (15.77 g, 75 mmol, 1.5 equiv.) and TBAI (0.92 g, 2.5 mmol, 5 mol%) was added to the mixture. The reaction was stirred for a further 6 h at 60 °C. The reaction mixture was quenched with water (10 mL) and then extracted with ethyl acetate (3 × 80 mL). The combined organic layer was washed with brine (2 × 30 mL), dried over sodium sulfate, filtrated and concentrated. The crude product was purified by column chromatography (Ethyl Acetate/Hexane: 1/70 to 1/40) to afford 3 (8.71 g, 85 yield%) as white solid.

![Chemical Reaction](attachment:image.png)

To a mixture of copper(II) sulfate (63.8 mg, 0.4 mmol, 5 mol%) and sodium bicarbonate (1.34 g, 16 mmol, 2 equiv.) was added a solution of 3 (1.64 g, 8 mmol) and 4a (2.38 g, 12 mmol, 1.5 equiv.) dissolved in methanol (40 mL) at room temperature. After stirring for 24 h at the same temperature. After that, the mixture was diluted with brine (5 mL) and extracted with DCM (3×20 mL). The organic phase was dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by silica gel flash chromatography to afford 5a as white solid.

![Chemical Reaction](attachment:image.png)

To a Schlenk tube under air atmosphere were added 5a (40.6 mg, 0.2 mmol, 1 equiv.), m-CPBA (81.2 mg, 85%, 0.4 mmol, 2 equiv.), and DCM (2.0 mL). The system was heated to 50 °C for 6 h to afford 8a (43.7 mg, 93 %) as a white solid.

![Chemical Reaction](attachment:image.png)

To a Schlenk tube under air were added 5a (40.6 mg, 0.2 mmol, 1 equiv.), NaIO₄ (51.3, 0.24 mmol, 1.2 equiv.), and MeOH/H₂O (1:1, 2.0 mL). The system was heated to 50 °C for 6 h to afford 8b (36.4 mg, 83 %) as a white solid.
To a Schlenk tube under air were added 5a (20.3 mg, 0.1 mmol, 1 equiv.), NCNH₂ (5.0 mg, 0.12 mmol, 1.2 equiv.), Phl(OAc)₂ (35.4 mg, 0.11 mmol, 1.1 equiv.), and MeCN (2.0 mL). The system was stirred at 0 °C for 12 h to afford 8c (21.9 mg, 90 %) as a white solid.
7. Spectroscopic Data of Compounds

The title compound 3 was isolated as a white solid (172.2 mg, 84%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (70/1 to 50/1). (R, 0.7, petroleum ether/ethyl acetate = 10/1). D-inc. >99% (determined by $^1$H NMR). MP: 56.5 – 57.4 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J$ = 8.2 Hz, 2H), 7.35 (d, $J$ = 8.2 Hz, 2H), 2.45 (s, 3H).

To a flame dried Schlenk tube equipped with a stirring bar were added CH$_3$OH (40.4 μL, 1 mmol, 1.0 equiv.), 2,6-lutidine (138.2 μL, 1.2 mmol, 1.2 equiv.), dry DMF (2 mL) and Tf$_2$O (185.0 μL, 1.1 mmol, 1.1 equiv.) added sequentially under N$_2$. The reaction mixture was stirred at 0 °C for 90 min. After that, TsSNa (315.0 mg, 1.5 mmol, 1.5 equiv.) and TBAI (18.5 mg, 0.05 mmol, 5 mol%) was added to the mixture. The reaction was stirred for a further 6 h at 60 °C. The reaction mixture was quenched with water (10 mL) and then extracted with ethyl acetate (3 × 10 mL). The combined organic layer was washed with brine (15 mL), dried over sodium sulfate, filtered and concentrated. The title compound 3a was isolated as a white solid (163.6 mg, 81%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (70/1 to 50/1). (R, 0.7, petroleum ether/ethyl acetate = 10/1). D-inc. >99% (determined by $^1$H NMR). MP: 56.0 – 57.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.80 (d, $J$ = 8.1 Hz, 2H), 7.35 (d, $J$ = 8.1 Hz, 2H), 2.49 (s, 3H), 2.45 (s, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.9, 141.1, 129.9, 127.3, 21.8, 18.1. MS (EI) m/z 202.01 [M]+.

The title compound 5a was isolated as a white solid (36.5 mg, 90%) through flash chromatography on silica gel eluting with petroleum ether. (R, 0.5, petroleum ether). D-inc. >99% (determined by $^1$H NMR). MP: 88.7 – 90.1 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J$ = 8.2 Hz, 2H), 7.54 (d, $J$ = 8.2 Hz, 2H), 7.48 – 7.42 (m, 2H), 7.39 – 7.32 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 140.7, 138.1, 137.7, 128.9, 127.6, 127.3, 127.1, 127.0. MS (EI) m/z 203.08 [M]+.

The title compound 5b was isolated as a colorless oil (38.7 mg, 83%) through flash chromatography on silica gel eluting with petroleum ether. (R, 0.4, petroleum ether). D-inc. >99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.47 – 7.31 (m, 5H), 7.23 – 7.18 (m, 1H), 6.91 – 6.84 (m, 2H), 6.78 – 6.74 (m, 1H), 5.06 (s, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.2, 140.0, 136.9, 129.8, 128.7, 128.1, 127.6, 119.2, 113.2, 111.4, 70.13. HRMS (ESI-TOF) m/z Calcd for C$_{14}$H$_{12}$D$_7$OS 234.1032 [M+H]+, Found 234.1035.
The title compound 5c was isolated as a colorless oil (32.8 mg, 75%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.4, petroleum ether). D-inc. >99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.30 (m, 2H), 7.30 – 7.24 (m, 2H), 7.15 – 7.07 (m, 1H), 7.03 – 6.98 (m, 2H), 6.98 – 6.94 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.4, 155.3, 132.3, 129.9, 129.2, 123.4, 119.7, 118.8. HRMS (EI) m/z Calcd for C$_{13}$H$_8$D$_3$OS 219.0797 [M]+; Found 219.0802.

The title compound 5d was isolated as a colorless oil (31.9 mg, 73%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.4, petroleum ether). D-inc. >99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.36 – 7.30 (m, 2H), 7.29 – 7.25 (m, 1H), 7.18 – 7.11 (m, 2H), 7.11 – 7.06 (m, 1H), 7.00 – 6.96 (m, 2H), 6.92 – 6.88 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.3, 153.6, 130.8, 129.8, 126.8, 126.0, 124.5, 123.1, 119.4, 118.0. HRMS (EI) m/z Calcd for C$_{13}$H$_9$D$_3$OS 219.0793 [M]+, Found 219.0793.

The title compound 5e was isolated as a white solid (28.6 mg, 81%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.6, petroleum ether). D-inc. >99% (determined by $^1$H NMR). MP: 55.4 – 56.7 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.80 (d, J = 8.1 Hz, 1H), 7.76 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 1.2 Hz, 1H), 7.52 – 7.46 (m, 1H), 7.46 – 7.38 (m, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 136.2, 134.0, 131.1, 128.3, 127.8, 126.9, 125.8, 125.3, 123.5. MS (EI) m/z 177.07 [M]+. 10

The title compound 5f was isolated as a white solid (32.2 mg, 71%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.6, petroleum ether). D-inc. >99% (determined by $^1$H NMR). MP: 91.8 – 93.7 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.74 – 8.67 (m, 1H), 8.67 – 8.60 (m, 1H), 8.43 – 8.36 (m, 1H), 7.86 – 7.79 (m, 1H), 7.74 – 7.66 (m, 2H), 7.64 – 7.56 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 134.5, 132.1, 130.6, 130.4, 129.0, 127.7, 127.1, 127.0, 126.9, 126.2, 125.0, 123.4, 123.2, 122.7. HRMS (EI) m/z Calcd for C$_{15}$H$_9$D$_3$S 227.0848 [M]+, Found 227.0844.

The title compound 5g was isolated as a yellow solid (35.1 mg, 70%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.4, petroleum ether). D-inc. >99% (determined by $^1$H NMR). MP: 69.9 – 71.0 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.56 (d, J = 9.2 Hz, 1H), 8.20 – 8.09 (m, 4H), 8.04 – 7.97 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 133.2, 131.6, 131.2, 129.5, 129.4, 127.7, 127.4, 127.0, 126.3, 125.4, 125.2, 125.1, 124.7, 123.9. HRMS (ESI-TOF) m/z Calcd for C$_{17}$H$_{10}$D$_3$S 252.0926 [M+H]+, Found 252.0921.

The title compound 5h was isolated as a colorless oil (24.5 mg, 76%, Yield

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was detected by $^1$H-NMR) through flash chromatography on silica gel eluting with petroleum ether. (R$_f$ 0.7, petroleum ether). D-inc. >99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.25 (d, $J = 8.7$ Hz, 2H), 7.18 (d, $J = 8.7$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.1, 131.0, 129.0, 128.1. MS (EI) m/z 161.01 [M]+. 

The title compound 5i was isolated as a colorless oil (29.5 mg, 72%), Yield was detected by $^1$H-NMR) through flash chromatography on silica gel eluting with petroleum ether. (R$_f$ 0.7, petroleum ether). D-inc. >99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39 (d, $J = 8.6$ Hz, 2H), 7.11 (d, $J = 8.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.8, 131.9, 128.2, 118.7. MS (EI) m/z 204.96 [M]+. 

The title compound 5j was isolated as a white solid (35.4 mg, 70%) through flash chromatography on silica gel eluting with petroleum ether. (R$_f$ 0.7, petroleum ether). D-inc. 99% (determined by $^1$H NMR). MP: 34.7 – 36.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.57 (d, $J = 8.6$ Hz, 2H), 6.98 (d, $J = 8.6$ Hz, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 138.7, 137.8, 128.4, 89.3. MS (EI) m/z 252.95 [M]+. 

The title compound 5k was isolated as a colorless oil (28.9 mg, 78%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (R$_f$ 0.5, petroleum ether/ethyl acetate = 10/1). D-inc. 99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.86 (d, $J = 8.5$ Hz, 2H), 7.17 (d, $J = 8.5$ Hz, 2H), 3.82 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.0, 145.5, 130.0, 126.4, 125.0, 52.1. HRMS (ESI-TOF) m/z Calcd for C$_9$H$_8$D$_3$O$_2$S 186.0668 [M+H]+, Found 186.0666. 

The title compound 5l was isolated as a colorless oil (31.8 mg, 80%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (R$_f$ 0.5, petroleum ether/ethyl acetate = 10/1). D-inc. 99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 8.5$ Hz, 2H), 7.25 (d, $J = 8.5$ Hz, 2H), 4.36 (q, $J = 7.1$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.5, 145.3, 130.0, 126.8, 61.0. MS (EI) m/z 199.07 [M]+. 

The title compound 5m was isolated as a yellow solid (26.8 mg, 78%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (50/1 to 30/1). (R$_f$ 0.6, petroleum ether/ethyl acetate = 10/1). D-inc. 99% (determined by $^1$H NMR). MP: 62.4 - 64.1 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.13 (d, $J = 9.1$ Hz, 2H), 1.39 (t, $J = 7.1$ Hz, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 148.9, 144.9, 125.1, 124.0. MS (EI) m/z 172.04 [M]+. 

The title compound 5n was isolated as a colorless oil (19.8 mg, 65%) through
flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 4/1). (Rf 0.4, petroleum ether/ethyl acetate = 4/1). D-inc. 99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 – 7.34 (m, 4H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.0, 130.6, 129.4, 129.0, 128.4, 118.6, 113.3. HRMS (ESI-TOF) m/z Calcd for C$_8$H$_5$DS 153.0566 [M+H]$^+$, Found 153.0560.

The title compound 5o was isolated as a colorless oil (23.5 mg, 75%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (12/1 to 4/1). (Rf 0.4, petroleum ether/ethyl acetate = 5/1). D-inc. 99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.29 (d, J = 8.5 Hz, 2H), 7.25 (d, J = 8.5 Hz, 2H), 4.65 (s, 2H), 1.68 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.9, 137.8, 127.8, 127.0, 65.1. HRMS (EI) m/z Calcd for C$_8$H$_7$D$_3$OS 157.0641 [M]$^+$, Found 157.0638.

The title compound 5p was isolated as a colorless oil (25.0 mg, 80%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (12/1 to 4/1). (Rf 0.4, petroleum ether/ethyl acetate = 5/1). D-inc. >99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38 – 7.34 (m, 1H), 7.29 – 7.24 (m, 2H), 7.19 – 7.14 (m, 1H), 4.74 (s, 2H), 2.43 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 139.0, 136.8, 128.5, 128.2, 126.7, 125.6, 63.7. HRMS (EI) m/z Calcd for C$_8$H$_7$D$_3$OS 157.0641 [M]$^+$, Found 157.0642.

The title compound 5q was isolated as a colorless oil (20.8 mg, 73%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15/1 to 5/1). (Rf 0.3, petroleum ether/ethyl acetate = 5/1). D-inc. >99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, J = 8.6 Hz, 2H), 6.78 (d, J = 8.6 Hz, 2H), 5.04 (brs, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.2, 130.5, 128.9, 116.2. HRMS (EI) m/z Calcd for C$_7$H$_5$D$_3$OS 143.0484 [M]$^+$, Found 143.0482.

The title compound 5r was isolated as a yellow oil (41.6 mg, 86%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (30/1 to 10/1). (Rf 0.5, petroleum ether/ethyl acetate = 10/1). D-inc. >99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 (d, J = 8.7 Hz, 2H), 6.52 (s, 1H), 1.54 (s, 9H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 152.8, 136.3, 131.9, 128.7, 119.3, 80.7, 28.4. HRMS (ESI-TOF) m/z Calcd for C$_{12}$H$_{14}$D$_3$NO$_2$SNa 265.1066 [M+H]$^+$, Found 265.1063.

The title compound 5s was isolated as a colorless oil (28.0 mg, 82%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 6.84 – 6.73 (m, 3H), 5.94 (s, 2H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 148.2, 146.3, 130.6, 122.0, 109.5, 108.9, 101.3. HRMS (EI) m/z Calcd for C$_8$H$_5$D$_3$O$_2$S 171.0433 [M]$^+$, Found 171.0434.
The title compound 5t was isolated as a colorless oil (29.5 mg, 68%) through flash chromatography on silica gel eluting with petroleum ether. (R<sub>f</sub> 0.2, petroleum ether). D-inc. >99% (determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.94 (d, J = 7.6 Hz, 1H), 7.79 (d, J = 7.6 Hz, 1H), 7.65 (d, J = 8.2 Hz, 1H), 7.50 – 7.44 (m, 1H), 7.40 – 7.33 (m, 2H), 7.33 – 7.28 (m, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 156.1, 154.2, 127.4, 126.1, 124.2, 123.4, 123.0, 121.5, 120.9, 118.2, 112.1. HRMS (EI) m/z Calcd for C<sub>13</sub>H<sub>7</sub>D<sub>3</sub>OS 217.0644 [M]+, Found 217.0641.

The title compound 5u was isolated as a colorless oil (17.9 mg, 68%) through flash chromatography on silica gel eluting with petroleum ether. (R<sub>f</sub> 0.8, petroleum ether). D-inc. >99% (determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.20 (s, 4H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 135.2, 127.8. HRMS (EI) m/z Calcd for C<sub>8</sub>H<sub>4</sub>D<sub>6</sub>S 176.0601 [M]+, Found 176.0599.

The title compound 7a was isolated as a colorless oil (43.0 mg, 90%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (50/1 to 20/1). (R<sub>f</sub> 0.5, petroleum ether/ethyl acetate = 20/1). D-inc. >99% (determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, J = 7.8 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.46 – 7.40 (m, 2H), 3.89 (d, J = 17.8 Hz, 1H), 3.80 (s, 3H), 3.14 (d, J = 17.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.3, 169.9, 150.5, 135.5, 134.0, 128.4, 126.3, 125.7, 58.0, 53.4, 40.1. HRMS (ESI-TOF) m/z Calcd for C<sub>12</sub>H<sub>9</sub>D<sub>3</sub>O<sub>3</sub>S 262.0588 [M+Na]<sup>+</sup>, Found 262.0590.

The title compound 7b was isolated as a colorless oil (53.3 mg, 95%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (50/1 to 15/1). (R<sub>f</sub> 0.5, petroleum ether/ethyl acetate = 15/1). D-inc. >99% (determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.80 (d, J = 7.5 Hz, 1H), 7.62 – 7.58 (m, 1H), 7.43 – 7.38 (m, 2H), 3.82 (d, J = 17.7 Hz, 1H), 3.08 (d, J = 17.7 Hz, 1H), 1.46 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.8, 168.3, 150.5, 135.2, 134.2, 128.1, 126.2, 125.4, 83.2, 58.6, 40.1, 28.0. HRMS (ESI-TOF) m/z Calcd for C<sub>15</sub>H<sub>15</sub>D<sub>3</sub>O<sub>3</sub>SNa 304.1062 [M+Na]<sup>+</sup>, Found 304.1060. The enantioselectivity (58% ee) was determined by HPLC analysis: Daicel Chiralcel OD-H, hexane/iPrOH: 95/5, 1.0 mL/min, 25 °C, 254 nm, TR (major) = 7.2 min, TR (minor) = 9.2 min; [α]<sub>D</sub><sup>20</sup> = -150.3 (c = 1, CHCl<sub>3</sub>).

The title compound 7c was isolated as a colorless oil (66.5 mg, 93%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (50/1 to 15/1). (R<sub>f</sub> 0.5, petroleum ether/ethyl acetate = 15/1). D-inc. >99% (determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.20 (s, 4H). D-inc. >99% (determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, J = 7.8 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.46 – 7.40 (m, 2H), 3.89 (d, J = 17.8 Hz, 1H), 3.80 (s, 3H), 3.14 (d, J = 17.8 Hz, 1H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.3, 169.9, 150.5, 135.5, 134.0, 128.4, 126.3, 125.7, 58.0, 53.4, 40.1. HRMS (ESI-TOF) m/z Calcd for C<sub>12</sub>H<sub>9</sub>D<sub>3</sub>O<sub>3</sub>S 262.0588 [M+Na]<sup>+</sup>, Found 262.0590.

The title compound 7c was isolated as a colorless oil (66.5 mg, 93%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (50/1 to 15/1). (R<sub>f</sub> 0.5, petroleum ether/ethyl acetate = 15/1). D-inc. >99% (determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.20 (s, 4H). D-inc. >99% (determined by <sup>1</sup>H NMR). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (d, J = 7.8 Hz, 1H), 7.66 – 7.60 (m, 1H), 7.46 – 7.38 (m, 2H), 3.82 (d, J = 17.7 Hz, 1H), 3.08 (d, J = 17.7 Hz, 1H), 1.46 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 196.8, 168.3, 150.5, 135.2, 134.2, 128.1, 126.2, 125.4, 83.2, 58.6, 40.1, 28.0. HRMS (ESI-TOF) m/z Calcd for C<sub>15</sub>H<sub>15</sub>D<sub>3</sub>O<sub>3</sub>SNa 304.1062 [M+Na]<sup>+</sup>, Found 304.1060. The enantioselectivity (58% ee) was determined by HPLC analysis: Daicel Chiralcel OD-H, hexane/iPrOH: 95/5, 1.0 mL/min, 25 °C, 254 nm, TR (major) = 7.2 min, TR (minor) = 9.2 min; [α]<sub>D</sub><sup>20</sup> = -150.3 (c = 1, CHCl<sub>3</sub>).
ether/ethyl acetate (50/1 to 15/1). (Rf 0.5, petroleum ether/ethyl acetate = 15/1). D-inc. >99% (determined by \textsuperscript{1}H NMR). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.81 – 7.78 (m, 1H), 7.62 – 7.57 (m, 1H), 7.43 – 7.37 (m, 2H), 3.83 (d, \(J = 17.7\) Hz, 1H), 3.08 (d, \(J = 17.7\) Hz, 1H), 2.15 (s, 3H), 2.11 (s, 6H), 1.63 (s, 6H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 196.8, 167.9, 150.6, 135.2, 134.2, 128.1, 126.2, 125.4, 83.2, 58.6, 41.2, 40.2, 36.1, 31.0. HRMS (ESI-TOF) m/z Calcd for C\textsubscript{21}H\textsubscript{21}D\textsubscript{3}O\textsubscript{3}S 381.1532 [M+Na]\textsuperscript{+}, Found 381.1528.

The title compound \(7d\) was isolated as a colorless oil (33.1 mg, 70%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.6, petroleum ether) D-inc. >99% (determined by \textsuperscript{1}H NMR). \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.91 (d, \(J = 8.6\) Hz, 2H), 7.43 (d, \(J = 8.6\) Hz, 2H).

The title compound \(7e\) was isolated as a colorless oil (30.9 mg, 58%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.5, petroleum ether). D-inc. >99% (determined by \textsuperscript{1}H NMR).

The title compound \(7f\) was isolated as a colorless oil (28.7 mg, 87%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by \textsuperscript{1}H NMR).

The title compound \(7g\) was isolated as a pale yellow oil (25.1 mg, 68%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by \textsuperscript{1}H NMR).

The title compound \(7h\) was isolated as a pale yellow oil (85.4 mg, 85%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.5, petroleum ether). D-inc. >99% (determined by \textsuperscript{1}H NMR).

The title compound \(7i\) was isolated as a yellow oil (30.1 mg, 60%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.5, petroleum ether). D-inc. >99% (determined by \textsuperscript{1}H NMR).
flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (10/1 to 5/1). (Rf 0.5, petroleum ether/ethyl acetate = 5/1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.84 (m, 4H), 7.56 – 7.51 (m, 2H), 7.50 – 7.44 (m, 4H); ¹³C NMR (100 MHz, CDCl₃) δ 132.8 (d, ¹J_C-P = 106.7 Hz), 132.5 (d, ⁴J_C-P = 3.0 Hz), 131.6 (d, ³J_C-P = 10.5 Hz), 128.8 (d, ²J_C-P = 13.0 Hz); ³¹P NMR (162 MHz, CDCl₃) δ 44.30.

HRMS (ESI-TOF) m/z Calcd for C₁₃H₁₂D₃OPS 252.0686 [M+H]+, Found 252.0686.

The title compound 7j was isolated as a yellow oil (16.3 mg, 50%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, DMSO) δ 7.35 – 7.29 (m, 2H), 7.16 – 7.12 (m, 2H), 7.09 – 7.01 (m, 1H);

¹³C NMR (100 MHz, CDCl₃) δ 148.2, 129.4, 122.9, 121.9.


The title compound 7k was isolated as a pale yellow oil (35.6 mg, 71%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 2.69 (q, J = 8.0 Hz, 2H), 1.73 – 1.64 (m, 2H), 1.45 – 1.34 (m, 2H), 1.27 (s, 16H), 0.88 (t, J = 6.8 Hz, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 39.3, 38.5, 32.1, 29.8, 29.7, 29.6, 29.5, 29.4, 29.3, 28.7, 22.8, 14.2. HRMS (ESI-TOF) m/z Calcd for C₁₃H₂₆D₃S₂ 252.1899 [M+H]+, Found 252.1900.

The title compound 7l was isolated as a colorless oil (28.3 mg, 75%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 7.27 – 7.22 (m, 1H), 7.12 – 7.08 (m, 2H), 6.79 – 6.75 (m, 1H), 3.83 (s, 3H);

¹³C NMR (100 MHz, CDCl₃) δ 160.3, 138.4, 130.0, 119.7, 112.6, 55.5. HRMS (EI) m/z Calcd for C₈H₇D₃OS 189.0361 [M]⁺, Found 189.0359.

The title compound 7m was isolated as a yellow oil (32.6 mg, 80%) through flash chromatography on silica gel eluting with petroleum ether. (Rf 0.8, petroleum ether). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 8.19 (d, J = 9.0 Hz, 2H), 7.65 (d, J = 9.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 146.6, 146.4, 125.9, 124.3. HRMS (EI) m/z Calcd for C₇H₄D₃NOS 204.0107 [M⁺]⁺, Found 204.0104.

The title compound 7n was isolated as a colorless oil (45.4 mg, 80%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (15/1 to 5/1). (Rf 0.5, petroleum ether/ethyl acetate = 5/1). D-inc. >99% (determined by ¹H NMR). ¹H NMR (400 MHz, CDCl₃) δ 5.36 (d, J = 5.7 Hz, 1H), 4.60 (d, J = 5.7 Hz, 1H), 3.75 (s, 3H), 3.21 – 3.04 (m, 2H), 1.43 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 171.4, 155.2, 80.3, 52.9, 52.7, 40.3, 28.4. HRMS (ESI-TOF) m/z Calcd for C₁₀H₁₆D₃NO₃S₂ 307.0836 [M+Na]⁺, Found 307.0838.
The title compound 8a was isolated as a white solid (43.7 mg, 93%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (1/3 to 1/1). (Rf 0.5, petroleum ether/ethyl acetate = 1/2). D-inc. >99% (determined by $^1$H NMR). MP: 132.0 – 133.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 (d, J = 8.5 Hz, 2H), 7.77 (d, J = 8.5 Hz, 2H), 7.63 – 7.59 (m, 2H), 7.52 – 7.47 (m, 2H), 7.46 – 7.41 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.9, 139.3, 139.2, 129.2, 128.8, 128.1, 128.0, 127.5. HRMS (ESI-TOF) m/z Calcd for C$_{13}$H$_{10}$D$_3$O$_2$S 236.0825 [M+H]$^+$, Found 236.0823.

The title compound 8b was isolated as a white solid (36.3 mg, 83%) through flash chromatography on silica gel eluting with ethyl acetate. (Rf 0.6, ethyl acetate). D-inc. >99% (determined by $^1$H NMR). MP: 137.4 – 139.0 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.74 (d, J = 8.6 Hz, 2H), 7.70 (d, J = 8.6 Hz, 2H), 7.62 – 7.58 (m, 2H), 7.49 – 7.44 (m, 2H), 7.42 – 7.36 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.4, 144.2, 139.8, 129.1, 128.2, 128.1, 127.3, 124.1. HRMS (ESI-TOF) m/z Calcd for C$_{15}$H$_{10}$D$_3$OS 220.0875 [M+H]$^+$, Found 220.0870.

The title compound 8c was isolated as a colorless oil (21.9 mg, 90%) through flash chromatography on silica gel eluting with petroleum ether/ethyl acetate (1/3 to 1/1). (Rf 0.4, petroleum ether/ethyl acetate = 1/2). D-inc. >99% (determined by $^1$H NMR). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.86 (d, J = 8.6 Hz, 2H), 7.79 (d, J = 8.6 Hz, 2H), 7.60 – 7.55 (m, 2H), 7.52 – 7.46 (m, 2H), 7.46 – 7.40 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.5, 139.0, 134.6, 129.3, 129.0, 128.9, 127.4, 126.7, 124.1. HRMS (ESI-TOF) m/z Calcd for C$_{14}$H$_9$D$_3$NS 266.0802 [M+Na]$^+$, Found 266.0807.
8. References

9. Copies of $^1$H, $^{13}$C, and $^{31}$P NMR Spectra for Compounds

$^1$H NMR Spectrum of TsSMe (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of TsSMe (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 3 (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 3 (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5a (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5a (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of $5b$ (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of $5b$ (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5c (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5c (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5d (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 3d (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5e (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5e (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5f (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5f (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5g (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5g (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5h (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5h (100 MHz, CDCl$_3$)
$^{1}$H NMR Spectrum of 5i (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5i (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5j (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5j (100 MHz, CDCl$_3$)
$^1\text{H NMR Spectrum of 5k (400 MHz, CDCl}_3\text{)}$

$^{13}\text{C NMR Spectrum of 5k (100 MHz, CDCl}_3\text{)}$
$^1$H NMR Spectrum of 51 (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 51 (100 MHz, CDCl$_3$)
$^{1}$H NMR Spectrum of $5m$ (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of $5m$ (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of $5n$ (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of $5n$ (100 MHz, CDCl$_3$)
\textbf{^1H NMR Spectrum of 5o (400 MHz, CDCl\textsubscript{3})}

\textbf{^13C NMR Spectrum of 5o (100 MHz, CDCl\textsubscript{3})}
$^1$H NMR Spectrum of 5p (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5p (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5q (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5q (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5r (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5r (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5s (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5s (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of $5t$ (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of $5t$ (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 5u (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 5u (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 7a (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 7a (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 7b (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 7b (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 7c (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 7c (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 7d (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 7d (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 7e (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 7e (100 MHz, CDCl$_3$)
$^{1}H$ NMR Spectrum of 7f (400 MHz, CDCl$_3$)

$^{13}C$ NMR Spectrum of 7f (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 7g (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 7g (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 7h (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 7h (100 MHz, CDCl$_3$)
$^1$H NMR Spectrum of 7i (400 MHz, CDCl$_3$)

$^{13}$C NMR Spectrum of 7i (100 MHz, CDCl$_3$)
$^{31}P$ NMR Spectrum of 7i (162 MHz, CDCl$_3$)

$^1$H NMR Spectrum of 7j (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of 7j (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of 7k (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of 7k (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of 7l (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of 7l (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of 7m (400 MHz, CDCl$_3$)
$^{13}\text{C}$ NMR Spectrum of $7\text{m}$ (100 MHz, CDCl$_3$)

$^1\text{H}$ NMR Spectrum of $7\text{n}$ (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of 7n (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of 8a (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of 8a (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of 8b (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of $8b$ (100 MHz, CDCl$_3$)

$^1$H NMR Spectrum of $8c$ (400 MHz, CDCl$_3$)
$^{13}$C NMR Spectrum of 8c (100 MHz, CDCl$_3$)