Supporting Information

One-Pot Method for Synthesis of 1-Aryl-2-Aminoalkanol Derivatives from the Corresponding Amides or Nitriles

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1. Optimization of the Reaction Conditions

1.1 Optimization of the Hydride Loading and the Reaction Temperature

Optimization experiments were performed as follows: A solution of 1a (0.3 g, 1.31 mmol) in an appropriate anhydrous solvent was treated with the corresponding hydride dropwise/portionwise at 0 °C (foaming). The resulting mixture was left to stir under the argon/air/oxygen-filled rubber balloon at ambient or slightly elevated temperature (55 °C) for 3–48 h (please, see Tab. S1–S3 for further details). The initially formed deep-red color gradually disappeared during the reaction time, leaving the light-yellow colored solution.

TLC (SiO₂) CH₂Cl₂–MeOH (90:10) or CHCl₃–MeOH–NH₄OH (79:20:1).

Then the reaction mixture was carefully quenched by a dropwise addition of an aqueous solution of NaOH (5 M, 1 mL) at 0 °C and further diluted with an aqueous solution of NaOH (5 M, 15 mL). The organic and aqueous layers were separated and the aqueous phase was reextracted with toluene (5 × 15 mL). The combined organic phase was dried over anhydrous Na₂SO₄, filtered, and evaporated in vacuo.

The yellow oily residue was dissolved in 5 mL of Et₂O–MeOH, and a solution of anhydrous oxalic acid (0.13 g, 1.1 equiv) in 5 mL of Et₂O–MeOH (5:1) was added dropwise. The resulting white precipitate was filtered off, washed several times with fresh Et₂O–MeOH (5:1), Et₂O, and dried in vacuo.

**Table S1. Optimization of the hydride loading and the reaction temperature**

| entry | hydride | solvent | atm. | temp. | time | yield | 3a/4a ratio | variable |
|-------|---------|---------|------|-------|------|-------|------------|----------|
| 1     | SMEAH [70% in MePh, 5 equiv] | MePh [5 mL] | Ar | 25 °C | 48 h | 30 mg | 74:26 | Hydride Load |
| 2     | SMEAH [70% in MePh, 10 equiv] | MePh [5 mL] | Ar | 25 °C | 48 h | 60 mg | 84:16 | Hydride Load |
| 3     | SMEAH [70% in MePh, 15 equiv] | MePh [5 mL] | Ar | 25 °C | 48 h | 145 mg | 84:16 | Hydride Load |
| 4     | SMEAH [70% in MePh, 20 equiv] | MePh [5 mL] | Ar | 25 °C | 48 h | 162 mg | 85:15 | Hydride Load |
| 5     | SMEAH [70% in MePh, 10 equiv] | MePh [5 mL] | Ar | 55 °C | 24 h | 79 mg | 58:42 | Temp. |

Footnotes: Experiments were performed at the 1.3 mmol scale; SMEAH = sodium bis(2-methoxyethoxy)aluminum hydride; †based on the isolated yields, ‡measured by ¹H NMR (400 MHz, DMSO-d₆, 35 °C) analyses of the isolated products (Fig. S1).
1.2 Alteration of the Hydride Type

![Chemical structure](image)

Table S2. Alteration of the Hydride Type

| entry | hydride          | solvent          | atm. | temp. | time | yield | 3a/4a ratio | variable |
|-------|------------------|------------------|------|-------|------|-------|-------------|----------|
| 6     | DIBAH [25% in MePh, 30 equiv] | MePh [5 mL]     | Ar   | 25 °C | 48 h | 252 mg | 1:99        |          |
| 7     | LAH [7.5 equiv]  | THF-MePh [1:1, 8 mL] | Ar   | 25 °C | 48 h | 74 mg  | 5:95        |          |
| 8     | LMAH [15 equiv]  | THF-MePh [1:1, 8 mL] | Ar   | 25 °C | 48 h | 214 mg | 48:52      |          |

Footnotes: Experiments were performed at the 1.3 mmol scale; DIBAH = diisobutylaluminum hydride, LAH = lithium aluminum hydride, LMAH = lithium dimethoxyaluminum hydride; a-based on the isolated yields, b-measured by 1H NMR (400 MHz, DMSO-d6, 35 °C) analyses of the isolated products (Fig. S1).

1.3 Optimization of the Solvent Type and the Reaction Atmosphere

![Chemical structure](image)

Table S3. Optimization of the Solvent Type

| entry | hydride          | solvent          | atm. | temp. | time | yield | 3a/4a ratio | variable |
|-------|------------------|------------------|------|-------|------|-------|-------------|----------|
| 9     | SMEAH [70% in MePh, 15 equiv] | THF [5 mL]     | Ar   | 25 °C | 48 h | 87 mg  | 92:8        |          |
| 10    | SMEAH [70% in MePh, 15 equiv] | Et2O [5 mL]    | Ar   | 25 °C | 48 h | 120 mg | 89:11       |          |
| 11    | SMEAH [70% in MePh, 15 equiv] | dioxane [5 mL] | Ar   | 25 °C | 48 h | 50 mg  | 93:7        |          |
| 12    | SMEAH [70% in MePh, 15 equiv] | DME [5 mL]     | Ar   | 25 °C | 48 h | 61 mg  | 92:8        |          |
| 13    | SMEAH [70% in MePh, 15 equiv] | DME [5 mL]     | Dry air | 25 °C | 3 h  | 75 mg  | 93:7        |          |
| 14    | SMEAH [70% in MePh, 15 equiv] | THF [5 mL]     | O2   | 25 °C | 3 h  | 182 mg | 94:6        |          |

Footnotes: Experiments were performed at the 1.3 mmol scale; SMEAH = sodium bis(2-methoxyethoxy)aluminum hydride, DME = dimethoxyethane; a-based on the isolated yields, b-measured by 1H NMR (400 MHz, DMSO-d6, 35 °C) analyses of the isolated products (Fig. S1).
Figure S1. \textsuperscript{1}H NMR (400 MHz, DMSO-\textit{d}_6, 35 °C) analysis of the isolated product mixtures of \textbf{Entries 6–8} and \textbf{14} (in detail).

**HPLC conditions:** an YMC-Triart C\textsubscript{18} column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH\textsubscript{4} (pH = 9.30), 40:60, 0.2 mL/min, 40 °C (\(\lambda = 230\) nm).

Figure S2. RP-HPLC analysis of the \textbf{4a} prepared according to the \textbf{Entry 6} (Tab. S2).
2. Substrate Scope

2.1 The reduction of 1a

\[
\begin{align*}
3a \cdot H_2C_2O_4 &+ 4a \cdot H_2C_2O_4 \\
\text{t} = 0 \ h & \quad \text{t} = 1.5 \ h & \quad \text{t} = 3 \ h
\end{align*}
\]

Figure S3. Visual progress and TLC analysis of the crude reaction mixture of 1a after 3 h (SiO\(_2\), CH\(_2\)Cl\(_2\)–MeOH, 9:1).
**HPLC conditions:** an YMC-Triart C$_{18}$ column (3 μm, 150 × 2.0 mm), MeCN–50mM HCOONH$_4$ (pH = 9.30), 40:60, 0.2 mL/min, 40 °C (λ = 230 nm).

**Figure S4.** RP-HPLC analysis of the precipitate from the reduction of 1a showing 3a/4a = 94:6 (external standard calibration method).

**Figure S5.** $^1$H NMR (400 MHz, DMSO-$d_6$, 35 °C) analysis of the precipitate from the reduction of 1a showing 3a/4a = 94:6.
2.2 The reduction of 1ad

HPLC conditions: an YMC-Triart C$_{18}$ column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH$_4$ (pH = 9.30), 40:60, 0.2 mL/min, 40 °C (λ = 230 nm).

Figure S6. RP-HPLC analysis of the precipitate from the reduction of 1ad showing 3a/4a = 63:37 (external standard calibration method).
Figure S7. $^1$H NMR (400 MHz, DMSO-$d_6$, 35 °C) analysis of the precipitate from the reduction of 1ad showing $3a/4a = 62:38$. 
2.3 The reduction of 1b

\[
\begin{align*}
3b \cdot H_2C_2O_4 & + 4b \cdot H_2C_2O_4 \\
\end{align*}
\]

**HPLC conditions:** an YMC-Triart C\textsubscript{18} column (3 µm, 150 \times 2.0 mm), MeCN–50mM HCOONH\textsubscript{4} (pH = 9.30), 20:80, 0.2 mL/min, 40 °C (λ = 210 nm).

**Figure S8.** HPLC analysis of the authentic sample of 3b.
Figure S9. HPLC analysis of the authentic sample of 4b. Note: the first peak corresponds to oxalic acid.

Figure S10. HPLC analysis of the precipitate from the reduction of 1b under O₂ atmosphere showing 3b/4b = 95:5 (external standard calibration method). Note: the first peak corresponds to oxalic acid.
Figure S11. HPLC analysis of the precipitate from the reduction of 1b under Ar atmosphere showing 3b/4b = 81:19 (external standard calibration method). Note: the first peak corresponds to oxalic acid.
2.4 The reduction of 1ba

\[
\begin{align*}
\text{3b} \cdot \text{H}_2\text{C}_2\text{O}_4
\end{align*}
\]

**HPLC conditions:** an YMC-Triart C\textsubscript{18} column (3 \textmu m, 150 \times 2.0 mm), MeCN–50mM HCOONH\textsubscript{4} (pH = 9.30), 20:80, 0.2 mL/min, 40 °C (\( \lambda = 210 \text{ nm} \)).

**Figure S12.** HPLC analysis of the precipitate from the reduction of 1ba showing 3b. Note: the first peak corresponds to oxalic acid.
2.5 The reduction of 1bb

\[
\text{Fig. S13. HPLC analysis of the precipitate from the reduction of 1bb showing } 3b/4ba = 29:71 \text{ (external standard calibration method). Note: the first peak corresponds to oxalic acid.}
\]
Figure S14. $^1$H NMR (400 MHz, DMSO-$d_6$, 35 °C) analysis of the precipitate from the reduction of 1bb showing 3b/4ba = 30:70.
2.6 The reduction of 1bc

\[
\text{HPLC conditions: an YMC-Triart C}_{18}\text{ column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH}_4 (\text{pH = 9.30}), 20:80, 0.2 \text{mL/min, 40 °C (λ = 210 nm).}
\]

**Figure S15.** HPLC analysis of the precipitate from the reduction of 1bc showing 3b. Note: the first peak corresponds to oxalic acid.
2.7 The reduction of 1c

\[ \text{HPLC conditions: } \text{an YMC-Triart C}_{18} \text{ column (3 } \mu\text{m, 150 } \times \text{ 2.0 mm), MeCN–50mM HCOONH}_4 \text{ (pH = 9.30), 30:70, 0.2 mL/min, 40 } ^\circ\text{C (} \lambda = 210 \text{ nm).} \]

**Figure S16.** HPLC analysis of the precipitate from the reduction of 1c showing 3c/4c = 95:5 (external standard calibration method). Note: the first peak corresponds to oxalic acid.
Figure S17. $^1$H NMR (400 MHz, DMSO-$d_6$, 35 °C) analysis of the precipitate from the reduction of 1c showing 3c/4c = 95:5.
2.8 The reduction of 1ca

![Chemical structure of 3c](image)

**HPLC conditions:** an YMC-Triart C_{18} column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH_4 (pH = 9.30), 30:70, 0.2 mL/min, 40 °C (λ = 210 nm).

**Figure S18.** HPLC analysis of the precipitate from the reduction of 1ca showing 3c. Note: the first peak corresponds to oxalic acid.
2.9 The reduction of 1cb

![Chemical structure of 3ca • H₂C₂O₄](image)

**HPLC conditions:** an YMC-Triart C₁₈ column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH₄ (pH = 9.30), 30:70, 0.2 mL/min, 40 °C (λ = 210 nm).

**Figure S19.** HPLC analysis of the precipitate from the reduction of 1cb showing 3ca. Note: the first peak corresponds to oxalic acid.
2.10 The reduction of **1cc**

![Chemical structure of 3cb • H$_2$C$_2$O$_4$](image)

**HPLC conditions**: an YMC-Triart C$_{18}$ column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH$_4$ (pH = 9.30), 40:60, 0.2 mL/min, 40 °C (λ = 210 nm).

**Figure S20.** HPLC analysis of the precipitate from the reduction of **1cc** showing **3cb**. Note: the first peak corresponds to oxalic acid.
2.11 The reduction of 1d

HPLC conditions: an YMC-Triart C$_{18}$ column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH$_4$ (pH = 9.30), 40:60, 0.2 mL/min, 40 °C ($\lambda = 210$ nm).

**Figure S21.** HPLC analysis of the precipitate from the reduction of 1d showing 3d. Note: the first peak corresponds to oxalic acid.
2.12 The reduction of **1da**

![Chemical Structure](image)

**HPLC conditions:** an YMC-Triart C$_{18}$ column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH$_4$ (pH = 9.30), 40:60, 0.2 mL/min, 40 °C ($\lambda = 210$ nm).

**Figure S22.** HPLC analysis of the precipitate from the reduction of **1da** showing **3d**. Note: the first peak corresponds to oxalic acid.
2.13 The reduction of 1e

HPLC conditions: an YMC-Triart C₁₈ column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH₄ (pH = 9.30), 50:50, 0.2 mL/min, 40 °C (λ = 210 nm).

Figure S23. HPLC analysis of the precipitate from the reduction of 1e showing 3e.
Figure S24. $^1$H NMR (400 MHz, DMSO-$d_6$, 35 °C) analysis of the precipitate from the reduction of $1e$ showing $3e/4e = 97:3$. 
2.14 The reduction of 1f

\[ 3f \cdot H_2C_2O_4 + 4f \cdot H_2C_2O_4 \]

**HPLC conditions:** an YMC-Triart C\textsubscript{18} column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH\textsubscript{4} (pH = 9.30), 50:50, 0.2 mL/min, 40 °C (\( \lambda = 210 \) nm).

**Figure S25.** HPLC analysis of the precipitate from the reduction of 1f showing 3f/4f = 94:6 (external standard calibration method).
Figure S26. \(^1\)H NMR (400 MHz, DMSO-d\(_6\), 35 °C) analysis of the precipitate from the reduction of 1f showing 3f/4f = 93:7.
2.15 The reduction of 1g

\[
\begin{align*}
3g \cdot H_2C_2O_4 + 4g \cdot H_2C_2O_4
\end{align*}
\]

**HPLC conditions:** an YMC-Triart C\textsubscript{18} column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH\textsubscript{4} (pH = 9.30), 30:70, 0.2 mL/min, 40 °C (\(\lambda = 230\) nm).

**Figure S27.** HPLC analysis of the precipitate from the reduction of 1g showing 3g/4g = 95:5 (external standard calibration method).
2.16 The reduction of 1h

\[
\begin{align*}
3h \cdot H_2C_2O_4 & \quad + \quad 4h \cdot H_2C_2O_4 \\
\end{align*}
\]

**HPLC conditions:** an YMC-Triart C<sub>18</sub> column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH<sub>4</sub> (pH = 9.30), 20:80, 0.2 mL/min, 40 °C (λ = 230 nm).

![Chromatogram](image)

**Figure S28.** HPLC analysis of the precipitate from the reduction of 1h showing 3h/4h = 97:3 (external standard calibration method).
The reduction of 2a

HPLC conditions: an YMC-Triart C\textsubscript{18} column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH\textsubscript{4} (pH = 9.30), 40:60, 0.2 mL/min, 40 °C (λ = 230 nm).

Figure S29. RP-HPLC analysis of the precipitate from the reduction of 1a showing 3a/4a = 89:11 (external standard calibration method).
Figure S30. $^1$H NMR (400 MHz, DMSO-$d_6$, 35 °C) analysis of the precipitate from the reduction of 1a showing 3a/4a = 89:11.
2.18 The reduction of 2b

\[
\text{HPLC conditions: an YMC-Triart C}_{18}\text{ column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH}_4 (pH = 9.30), 20:80, 0.2 mL/min, 40 °C (λ = 210 nm).}
\]

Figure S31. HPLC analysis of the precipitate from the reduction of 2b showing 3b. Note: the first peak corresponds to oxalic acid.
2.19 The reduction of \(2ba\)

\[
\begin{align*}
\ce{\text{OH}} & \quad \ce{\text{NH}_3} \\
\ce{\text{O}} & \quad \ce{\text{O}} \\
\ce{\text{C}_6\text{H}_5} & \quad \ce{\text{OH}} \\
3b & \quad \ce{\text{H}_2\text{C}_2\text{O}_4}
\end{align*}
\]

**HPLC conditions:** an YMC-Triart C\textsubscript{18} column (3 \(\mu\)m, 150 \(\times\) 2.0 mm), MeCN–50mM HCOONH\(_4\) (pH = 9.30), 20:80, 0.2 mL/min, 40 °C (\(\lambda = 210\) nm).

**Figure S32.** HPLC analysis of the precipitate from the reduction of \(2ba\) showing 3b. Note: the first peak corresponds to oxalic acid.
2.20 The reduction of 2c

\[
\text{HPLC conditions: } \text{an YMC-Triart C}_{18} \text{ column (3 } \mu\text{m, 150 } \times \text{ 2.0 mm), MeCN–50mM HCOONH}_4 (\text{pH} = 9.30), 30:70, 0.2 mL/min, 40 ^\circ \text{C} (\lambda = 210 \text{ nm}).}
\]

Figure S33. RP-HPLC analysis of the precipitate from the reduction of 2c showing 3c/4c = 94:6 (external standard calibration method). Note: the first peak corresponds to oxalic acid.
Figure S34. $^1$H NMR (400 MHz, DMSO-$d_6$, 35 °C) analysis of the precipitate from the reduction of 1c showing $3c/4c = 94:6$. 
2.21 The reduction of 2d

\[ \text{HO} - \text{S} - \text{OH} + \text{NH}_3 \text{O} \text{O} \text{OH} \]

\[ 3d \cdot \text{H}_2\text{C}_2\text{O}_4 + 4d \cdot \text{H}_2\text{C}_2\text{O}_4 \]

**HPLC conditions:** an YMC-Triart C\textsubscript{18} column (3 \( \mu \)m, 150 \( \times \) 2.0 mm), MeCN–50mM HCOONH\textsubscript{4} (pH = 9.30), 40:60, 0.2 mL/min, 40 °C (\( \lambda = 210 \) nm).

**Figure S35.** RP-HPLC analysis of the precipitate from the reduction of 2d showing 3d/4d = 92:8 (external standard calibration method). Note: the first peak corresponds to oxalic acid.
Figure S36. $^1$H NMR (400 MHz, DMSO-d$_6$, 35 °C) analysis of the precipitate from the reduction of 2d showing 3d/4d = 92:8.

Figure S37. RP-HPLC analysis of the precipitate from the reduction of 2d with added NaCN (10 equiv) showing 3d/4d = 99:1 (external standard calibration method). Note: the first peak corresponds to oxalic acid.
2.22 The reduction of 2da

\[
3d \cdot H_2C_2O_4
\]

**HPLC conditions:** an YMC-Triart C\(_{18}\) column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH\(_4\) (pH = 9.30), 40:60, 0.2 mL/min, 40 °C (\(\lambda = 210\) nm).

**Figure S38.** RP-HPLC analysis of the precipitate from the reduction of 2da showing 3d. Note: the first peak corresponds to oxalic acid.
2.23 The reduction of 2e

\[ \text{HPLC conditions: an YMC-Triart C}_{18} \text{ column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH}_4 (pH = 9.30), 50:50, 0.2 mL/min, 40 °C (λ = 210 nm).} \]

Figure S39. RP-HPLC analysis of the precipitate from the reduction of 2e showing 3e/4e = 93:7 (external standard calibration method). Note: the first peak corresponds to oxalic acid.
Figure S40. $^1$H NMR (400 MHz, DMSO-$d_6$, 35 °C) analysis of the precipitate from the reduction of 1e showing 3e/4e = 91:9.

Figure S41. $^{19}$F NMR (376 MHz, DMSO-$d_6$, 35 °C) analysis of the precipitate from the reduction of 1e showing 3e/4e = 89:11.
2.24 The reduction of 2f

HPLC conditions: an YMC-Triart C18 column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH4 (pH = 9.30), 50:50, 0.2 mL/min, 40 °C (λ = 210 nm).

Figure S42. HPLC analysis of the precipitate from the reduction of 2f showing $3f/4f = 97:3$ (external standard calibration method). Note: the first peak corresponds to oxalic acid.

Figure S43. $^1$H NMR (400 MHz, DMSO-$d_6$, 35 °C) analysis of the precipitate from the reduction of 1f showing $3f:4f = 96:4$. 
2.25 The reduction of 2g

\[
\begin{align*}
\text{3g} \cdot \text{H}_2\text{C}_2\text{O}_4
\end{align*}
\]

**HPLC conditions:** an YMC-Triart C\textsubscript{18} column (3 \(\mu\)m, 150 \(\times\) 2.0 mm), MeCN–50mM HCOONH\textsubscript{4} (pH = 9.30), 30:70, 0.2 mL/min, 40 °C (\(\lambda = 230\) nm).

**Figure S44.** HPLC analysis of the precipitate from the reduction of 2g showing 3g.
2.26 The reduction of 2h

\[
\begin{align*}
3h \cdot H_2C_2O_4 &+ 4h \cdot H_2C_2O_4
\end{align*}
\]

**HPLC conditions**: an YMC-Triart C18 column (3 µm, 150 × 2.0 mm), MeCN–50mM HCOONH4 (pH = 9.30), 20:80, 0.2 mL/min, 40 °C (λ = 230 nm).

**Figure S45.** HPLC analysis of the precipitate from the reduction of 2h showing 3h/4h = 96:4 (external standard calibration method).
3. Determination of the Enantiomeric Purity of 8a, 8b, and 5a

HPLC conditions: a Hypersil silica column (3 µm, 100 × 4.6 mm used as a precolumn, which was connected via the standard blue PEEK capillary tubing (L 300 mm, ID 0.01”, OD 1/16”) to a Daicel Chiralpak IA column (5 µm, 250 × 4.6 mm), i-PrOH–n-heptane, 10:90, 0.5 mL/min, 25 °C (λ = 230 nm).

![Chiral HPLC chromatogram of 8a (0% ee).](image)

### Results

| Peak No. | Peak ID | Ret Time | Height     | Area          | Conc.   |
|---------|---------|----------|------------|---------------|---------|
| 1       |         | 36.360   | 246387.406 | 16595349.000 | 49.9440 |
| 2       |         | 49.382   | 143238.063 | 16632589.000 | 50.0560 |
| **Total** | **389625.469** | 33227938.000 | 100.0000 |              |         |

**Figure S46.** Chiral HPLC chromatogram of 8a (0% ee).
**Stereochemical assignment:** Absolute configuration of (R)-5 was established by comparison of the sign of specific rotation and the relative elution order of the resolved peaks with literature data.\(^1\)

**HPLC conditions:** A Hypersil silica column (3 µm, 100 × 4.6 mm) used as a precolumn, which was connected via the standard blue PEEK capillary tubing (L 300 mm, ID 0.01”, OD 1/16”) to a Daicel Chiralpak IB column (5 µm, 250 × 4.6 mm), i-PrOH–n-heptane, 5:95, 0.5 mL/min, 25 °C (λ = 230 nm).

**Figure S47.** Chiral HPLC chromatogram of rac-5a (0% ee).
Figure S48. Chiral HPLC chromatogram of (R)-5a (6% ee).

**Results**

| Peak No. | Peak ID | Ret Time | Height  | Area      | Conc.  |
|----------|---------|----------|---------|-----------|--------|
| 1        | 28.503  | 30436.004| 1223650.625 | 47.0368  |
| 2        | 34.070  | 27920.609| 1377261.525 | 52.9632  |
| **Total**|         | 58356.613| 2600412.250 | 100.0000 |

Figure S48. Chiral HPLC chromatogram of (R)-5a (6% ee).
Stereochemical assignment: Absolute configuration of (S)-8b was established by chemical correlation with (S)-1ba.

HPLC conditions: a Hypersil silica column (3 µm, 100 × 4.6 mm used as a precolumn, which was connected via the standard blue PEEK capillary tubing (L 300 mm, ID 0.01”, OD 1/16”) to a Daicel Chiralpak IA column (5 µm, 250 × 4.6 mm), i-PrOH–n-heptane, 10:90, 0.5 mL/min, 25 °C (λ = 230 nm).

Figure S49. Chiral HPLC chromatogram of rac-8b (0% ee).
Figure S50. Chiral HPLC chromatogram of (S)-8b (> 99% ee).
4. Identification of the Reaction Intermediates

The reduction of 1d (275 mg, 1.3 mmol) was performed according to GP. The precipitated salt was filtered off and afforded 101 mg of 3d·H₂C₂O₄ as a white hygroscopic powder (26% yield). The crude filtrate was treated according to GP and provided 130 mg of the yellowish waxy residue, which contained 5c as a major component (HPLC purity > 90%). Then the residue (120 mg) was subjected to column chromatography (120 × 15 mm), 10 g of SiO₂, n-heptane–EtOAc (9:1), and fractions of 10 mL each were collected.

The combined fractions 2–3 gave after evaporation 6 mg of the residue, which was subjected to NMR and GC-MS analysis. Therein, compounds 2d, 6, and 7 were successfully identified. The combined fractions 5–7 provided 81 mg of the pure 5c.

**HPLC conditions:** an YMC-Triart C₁₈ column (3 µm, 150 × 2.0 mm), MeCN–H₂O, 50:50 → 90:10, 0.2 mL/min, 40 °C (λ = 210 nm).

**Figure S51.** HPLC profile of the crude filtrate (210 nm).
Figure S52. $^1$H NMR (CDCl$_3$, 400 MHz) profile of the crude filtrate.

Figure S53. $^1$H NMR (CDCl$_3$, 400 MHz) profile of the crude filtrate (in detail).
**Figure S54.** $^{13}$C NMR (CDCl$_3$, 100 MHz) profile of the crude filtrate.

**Figure S55.** $^{13}$C NMR (CDCl$_3$, 100 MHz) profile of the crude filtrate (in detail).
**GC conditions:** a DB-5MS column (0.25 μm, 30 m × 0.25 mm), He (constant flow 1 mL/min), temperature program (50 °C | hold 2 min; 10 °C/min rate to 300°C | hold 15 min).

**Figure S56.** GC profile of the fractions 2–3.

**Figure S57.** MS spectrum of the peak 16.23 min corresponding to the compound 6.
Figure S58. MS spectrum of the peak 17.04 min corresponding to the compound 2d.

Figure S59. MS spectrum of the peak 31.65 min corresponding to the compound 7.
Figure S60. $^1$H NMR (CDCl$_3$, 400 MHz) profile of the fractions 2–3 in comparison with the authentic spectra of 6, 2d, and 7.

Figure S61. $^1$H NMR (CDCl$_3$, 400 MHz) profile of the fractions 2–3 in comparison with the authentic spectra of 6, 2d, and 7 (in detail).
Figure S62. $^{13}$C NMR (CDCl$_3$, 100 MHz) profile of the fractions 2–3 in comparison with the authentic spectra of 6, 2d, and 7.

Figure S63. $^{13}$C NMR (CDCl$_3$, 100 MHz) profile of the fractions 2–3 in comparison with the authentic spectra of 6, 2d, and 7 (in detail).
**GC conditions:** a DB-5MS column (0.25 µm, 30 m × 0.25 mm), He (constant flow 1 mL/min), temperature program (50 °C l hold 2 min; 10 °C/min rate to 300°C l hold 15 min).

**Figure S64.** GC profile of the fractions 5–7 corresponding to the compound 5c.

**Figure S65.** GC spectrum showing slow degradation of the sample containing 5c on the air.
Figure S66. MS spectrum of the peak 16.27 min corresponding to the compound 5c.

Figure S67. MS spectrum of the peak 25.66 min corresponding to the benzopinacol artifact.
**Figure S68.** $^1$H NMR (CDCl$_3$, 400 MHz) profile of the fractions 5–7 corresponding to the compound 5c.

**Figure S69.** $^1$H NMR (CDCl$_3$, 400 MHz) profile of the fractions 5–7 corresponding to the compound 5c (in detail).
**Figure S70.** $^{13}$C NMR (CDCl$_3$, 100 MHz) profile of the fractions 5–7 corresponding to the compound 5c.

**Figure S71.** $^{13}$C NMR (CDCl$_3$, 100 MHz) profile of the fractions 5–7 corresponding to the compound 5c (in detail).
5. References

(1) J. Xiao, Z. Z. Wong, Y. P. Lu and T. P. Loh, *Adv. Synth. Catal.* 2010, **352**, 1107.
6. HRMS and NMR Data

Figure S72. HRMS (ESI–Q-TOF) spectrum of 1aa [M+H]^+.

Figure S73. HRMS (ESI-Orbitrap) spectrum of 1ab [M+H]^+.

Figure S74. HRMS (ESI-Orbitrap) spectrum of 1ac [M+H]^+.
Figure S75. HRMS (ESI-Orbitrap) spectrum of 1ad [M−H]⁻.

Figure S76. HRMS (ESI-Orbitrap) spectrum of 1b [M+H]⁺.

Figure S77. HRMS (ESI-Orbitrap) spectrum of 1ba [M−H]⁻.
Figure S78. HRMS (ESI-Orbitrap) spectrum of 1bb [M+H]+.

Figure S79. HRMS (ESI-Orbitrap) spectrum of 1bc [M−H]−.

Figure S80. HRMS (ESI-Orbitrap) spectrum of 1bd [M+H]+.
Figure S81. HRMS (ESI-Orbitrap) spectrum of 1c [M+H]^+.

Figure S82. HRMS (ESI-Orbitrap) spectrum of 1ca [M−H]^−.

Figure S83. HRMS (ESI-Orbitrap) spectrum of 1cb [M−H]^−.
Figure S84. HRMS (ESI-Orbitrap) spectrum of 1cc [M+H]+.

Figure S85. HRMS (ESI-Orbitrap) spectrum of 1d [M+H]+.

Figure S86. HRMS (ESI-Orbitrap) spectrum of 1da [M−H]−.
Figure S87. HRMS (ESI-Orbitrap) spectrum of 1e [M+H]+.

Figure S88. HRMS (ESI-Orbitrap) spectrum of 1f [M+H]+.

Figure S89. HRMS (ESI-Orbitrap) spectrum of 1g [M+H]+.
Figure S90. HRMS (ESI-Orbitrap) spectrum of 1h [M+H]⁺.

Figure S91. HRMS (ESI-Orbitrap) spectrum of 2a [M−H]⁻.

Figure S92. HRMS (ESI-Orbitrap) spectrum of 2ba [M+H]⁺.
Figure S93. HRMS (ESI-Orbitrap) spectrum of 2c \([M+H]^+\).

Figure S94. HRMS (ESI-Orbitrap) spectrum of 2da \([M-H]^−\).

Figure S95. HRMS (ESI-Orbitrap) spectrum of 2e \([M+H]^+\).
Figure S96. HRMS (ESI-Orbitrap) spectrum of 2f [M+H]^+.

Figure S97. HRMS (ESI-Orbitrap) spectrum of 2g [M+H]^+.

Figure S98. HRMS (ESI-Orbitrap) spectrum of 2h [M+H]^+.
Figure S99. HRMS (ESI–Q-TOF) spectrum of 3a [M+H]+.

Figure S100. HRMS (ESI-Obritrap) spectrum of 3b [M+H]+.

Figure S101. HRMS (ESI–Q-TOF) spectrum of 3c [M+H]+.
Figure S102. HRMS (ESI–Q-TOF) spectrum of 3ca [M+H]+.

Figure S103. HRMS (ESI–Q-TOF) spectrum of 3cb [M+H]+.

Figure S104. HRMS (ESI–Q-TOF) spectrum of 3d [M+H]+.
Figure S105. HRMS (ESI–Q-TOF) spectrum of 3e [M+H]^+.

Figure S106. HRMS (ESI–Q-TOF) spectrum of 3f [M+H]^+.

Figure S107. HRMS (ESI–Q-TOF) spectrum of 3g [M+H]^+.
Figure S108. HRMS (ESI-Orbitrap) spectrum of 3h [M+H]^+.

Figure S109. HRMS (ESI–Q-TOF) spectrum of 4a [M+H]^+.

Figure S110. HRMS (ESI–Q-TOF) spectrum of 4aa [M+H]^+.
Figure S111. HRMS (ESI–Q-TOF) spectrum of 4ba [M+H]\(^+\).

Figure S112. HRMS (ESI-Orbitrap) spectrum of 4bb [M+H]\(^+\).

Figure S113. HRMS (ESI–Q-TOF) spectrum of 4f [M+H]\(^+\).
**Figure S114.** HRMS (ESI-Orbitrap) spectrum of 5a [M+H]$^+$. 

**Figure S115.** HRMS (ESI-Orbitrap) spectrum of 5c [M+H]$^+$. 

**Figure S116.** HRMS (ESI-Orbitrap) spectrum of 5d [M−H$_2$O+H]$^+$. 
Figure S117. HRMS (ESI-Orbitrap) spectrum of 5e [M+H]+.

Figure S118. HRMS (ESI-Orbitrap) spectrum of 8a [M−H].

Figure S119. HRMS (ESI-Orbitrap) spectrum of 8b [M−H].
Figure S120. HRMS (ESI-Orbitrap) spectrum of 9 [M+H]+.

Figure S121. HRMS (ESI-Orbitrap) spectrum of 10 [M–H]−.
Figure S122. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1aa.

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Figure S123. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 1aa.
Figure S124. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1ab.
Figure S125. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 1ab.
Figure S126. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1ac.
Figure S127. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 1ac.
Figure S128. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1ad.
Figure S129. $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 1ad.
Figure S130. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1b.
Figure S131. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectrum of 1b.
Figure S132. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1ba.
Figure S133. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectrum of 1ba.
Figure S134. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1bb.
Figure S135. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectrum of 1bb.
Figure S136. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1bc.
Figure S137. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 1bc.
Figure S138. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1bd.

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Figure S139. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 1bd.
Figure S140. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of $1c$. 
Figure S141. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectrum of 1c.
Figure S142. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1ca.
Figure S143. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 1ca.

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Figure S144. $^{19}F$ NMR (376 MHz, DMSO-$d_6$) spectrum of 1ca.
Figure S145. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1cb.
Figure S146. $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 1cb.
Figure S147. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 1cb.
Figure S148. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1cc.

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Figure S149. $^{13}$C APT NMR (100 MHz, CDCl$_3$) spectrum of 1cc.
Figure S150. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1d.
Figure S151. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1d.
Figure S152. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectrum of 1d.
Figure S153. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 1da.
Figure S154. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1da.
Figure S155. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 1da.
Figure S156. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1e.
Figure S157. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectrum of 1e.
Figure S158. $^{19}$F NMR (376 MHz, DMSO-$d_6$) spectrum of 1e.
Figure S159. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1f.
Figure S160. $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectrum of 1f.
Figure S161. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 1g.
Figure S162. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 1g.
Figure S163. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of $1h$. 
Figure S164. $\text{^{13}C NMR APT (100 MHz, DMSO-$d_6$)}$ spectrum of 1h.
Figure S165. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 2a.
Figure S166. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 2a.
Figure S167. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2ba.
Figure S168. $^{13}$C APT NMR (100 MHz, CDCl$_3$) spectrum of 2ba.
Figure S169. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2c.
Figure S170. $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 2c.
Figure S171. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2da.
Figure S172. $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 2da.
Figure S173. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2e.
Figure S174. $^{13}$C APT NMR (100 MHz, CDCl$_3$) spectrum of 2e.
Figure S175. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 2e.
Figure S176. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2f.
Figure S177. $^{13}$C APT NMR (100 MHz, CDCl$_3$) spectrum of 2f.
Figure S178. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2g.
Figure S179. $^{13}$C APT NMR (100 MHz, CDCl$_3$) spectrum of 2g.
Figure S180. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 2h.
Figure S181. $^{13}$C APT NMR (100 MHz, CDCl$_3$) spectrum of 2h.
Figure S182. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3a·H$_2$C$_2$O$_4$. 

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Figure S183. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 3a·H$_2$C$_2$O$_4$. 
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Figure S184. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of $3b\cdot H_2C_2O_4$. 
Figure S185. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of $3b \cdot H_2C_2O_4$. 

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Figure S186. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3c·H$_2$C$_2$O$_4$. 

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Figure S187. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of $3c \cdot H_2C_2O_4$. 

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Figure S188. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3ca·H$_2$C$_2$O$_4$. 

S-144
Figure S189. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 3ca·$\text{H}_2\text{C}_2\text{O}_4$. 

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Figure S190. $^{19}$F NMR (376 MHz, DMSO-$d_6$) spectrum of 3ca·H$_2$C$_2$O$_4$. 

S-146
Figure S191. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3cb·H$_2$C$_2$O$_4$. 

S-147
Figure S192. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 3cb·H$_2$C$_2$O$_4$. S-148
Figure S193. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3d·$\text{H}_2\text{C}_2\text{O}_4$. 

S-149
Figure S194. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 3d·$\text{H}_2\text{C}_2\text{O}_4$.

S-150
Figure S195. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3e·H$_2$C$_2$O$_4$. 

S-151
Figure S196. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 3e·H$_2$C$_2$O$_4$. S-152
Figure S197. $^{19}$F NMR (376 MHz, DMSO-$d_6$) spectrum of 3e·H$_2$C$_2$O$_4$. 

3e·H$_2$C$_2$O$_4$
Figure S198. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3f·H$_2$C$_2$O$_4$. 

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Figure S199. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 3f·$H_2C_2O_4$. 

3f·$H_2C_2O_4$
Figure S200. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 3g·H$_2$C$_2$O$_4$. 

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Figure S201. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 3g·H$_2$C$_2$O$_4$. 
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Figure S202. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of $3h\cdot H_2C_2O_4$. 

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Figure S203. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 3h·H$_2$C$_2$O$_4$. S-159
Figure S204. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 4a·H$_2$C$_2$O$_4$. 

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Figure S205. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 4a·H$_2$C$_2$O$_4$.
Figure S206. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 4aa·H$_2$C$_2$O$_4$. 
Figure S207. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 4aa•H$_2$C$_2$O$_4$. 

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Figure S208. Comparison of $^1$H NMR (400 MHz, DMSO-$d_6$) spectra of the pure 3b·H$_2$C$_2$O$_4$ and the mixture of 3b·H$_2$C$_2$O$_4$ and 4ba·H$_2$C$_2$O$_4$ (29:71).
Figure S209. Comparison of $^{13}$C NMR (100 MHz, DMSO-$d_6$) spectra of the pure $3b\cdot H_2C_2O_4$ and the mixture of $3b\cdot H_2C_2O_4$ and $4ba\cdot H_2C_2O_4$ (29:71). S-165
Figure S210. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of $4bb \cdot \text{H}_2\text{C}_2\text{O}_4$. 

S-166
Figure S211. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 4bb $\cdot$ H$_2$C$_2$O$_4$.
Figure S212. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 4f·H$_2$C$_2$O$_4$. 

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Figure S213. $\textsuperscript{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 4f·H$_2$C$_2$O$_4$. 

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Figure S214. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5a.
Figure S215. $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 5a.
Figure S216. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5b.
Figure S217. $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 5b.
Figure S218. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5c.
**Figure S219.** $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 5c.
Figure S220. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5d.
Figure S221. $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 5d.
Figure S222. \(^{19}F\) NMR (376 MHz, CDCl\(_3\)) spectrum of 5d.

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Figure S223. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 5e.
Figure S224. $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 5e.
Figure S225. $^1$H NMR (400 MHz, DMSO-$d_6$) spectrum of 8a.
Figure S226. $^{13}$C NMR APT (100 MHz, DMSO-$d_6$) spectrum of 8a.
Figure S227. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 8b.
Figure S228. $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 8b.
Figure S229. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 9.
Figure S230. $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 9.
Figure S231. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 9.
Figure S232. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of 10.
Figure S233. $^{13}$C NMR APT (100 MHz, CDCl$_3$) spectrum of 10.
Figure S234. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of 10.