Electronic Supplementary Information

**Trapping of chiral enolates generated by Lewis acid promoted conjugate addition of Grignard reagents to unreactive Michael acceptors by various electrophiles**

D. Vargová, J. M. Pérez, S. R. Harutyunyan, R. Šebesta*

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**General experimental information**

All reactions using oxygen- and/or moisture-sensitive materials were carried out with anhydrous solvents (vide infra) under a nitrogen atmosphere using oven-dried glassware and standard Schlenk techniques. Reactions were monitored by ¹H NMR and GC-MS. (GC, HP6890: MS HP5973) with an HP5 column (Agilent Technologies, Palo Alto, CA). Purification of the products was performed by column chromatography using Merck 60 A 230-400 mesh silica gel. Components were visualized by UV and KMnO₄ staining. NMR data was collected on Agilent MR 400 with Varian 5mm OneNMR probe (¹H at 400.0 MHz; ¹³C at 100.58 MHz) and or Varian Mercury Plus 300 with Varian 5 mm PFG AutoSW probe (¹H at 300.0 MHz; ¹⁹F at 282 MHz). Chemical shifts are reported in parts per million (ppm) relative to residual solvent peak (CDCl₃, ¹H: 7.26 ppm; ¹³C: 77.16 ppm). Coupling constants are reported in Hertz. Multiplicity is reported with the usual abbreviations (s: singlet, br s: broad singlet, d: doublet, dd: doublet of doublets, t: triplet, tdt: triplet doublet of triplets, tqp: triplet quartet of triplets, tqq: triplet triplet of quartets, q: quartet, quint: quintet, sex: sextet, hept: heptet, m: multiplet). When possible, signals of minor diastereomers are in italic. 1D ¹⁹F spectra were acquired with inverse-gated ¹H decoupling. Assignments of peaks were performed with the assistance of 2D NMR experiments including COSY, HSQC and HMBC. Exact mass spectra were recorded on a LTQ Orbitrap XL apparatus with ESI ionization. Enantiomeric excess (ee) were determined by chiral HPLC analysis using a Shimadzu LC-10AD VP HPLC equipped with a Shimadzu SPD-M10AVP diode array detector.
Unless otherwise indicated, reagents and substrates were purchased from commercial sources and used as received. Solvents not required to be dry were purchased as technical grade and used as received. Dry solvents were freshly collected from a dry solvent purification system prior to use. Diisopropyl amine was dried over CaH₂ and distilled prior to use. Inert atmosphere experiments were performed with standard Schlenk techniques with dried (P₂O₅) nitrogen gas. Grignard reagents were purchased from Sigma-Aldrich (EtMgBr, MeMgBr (3.0 M in Et₂O), iBuMgBr, cyclopentylMgBr (2.0 M in Et₂O). nBuLi was purchased from Sigma-Aldrich as a 1.6 M solution in hexanes. Enamides and heteroarene substrates were available from previous research.⁷⁻⁹ Chiral ligands (L₁, L₂) were purchased from Solvias. (R)-BINAP was purchased from TCI. The BF₄ salts of tropylium and benzo[1,3]dithiol-1-ium were purchased from TCI. The cations were characterized by ¹H and ¹⁹F NMR and compared with literature data. Benzo[1,3]dithiol-1-ium bis((trifluoromethyl)sulfonyl)amide is stable in a nitrogen-flushed flask at -23 °C for several months. 5,6-Dihydro-4H-1,3-dithiin-1-ium bis((trifluoromethyl)sulfonyl)amide was only used freshly prepared. Tropylium bis((trifluoromethyl)sulfonyl)amide was stored up to one week at -23 °C in a nitrogen flushed flask. After more than two weeks a drop in the yields was observed. All new compounds were fully characterized by ¹H and ¹³C NMR and HRMS techniques. Enantiomeric ratios of the conjugated addition products were determined, and are assumed to be the same, as for the tandem products. For the same CA products one representative HPLC chromatogram is shown.

Optimization of trapping reaction

Table S1: Screening of additives in the trapping reaction:

<table>
<thead>
<tr>
<th>Entry</th>
<th>Additive</th>
<th>4.4 equiv.</th>
<th>Conversion (%)</th>
<th>Yield 3a (%)</th>
<th>dr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>25</td>
<td>19⁺</td>
<td>59:41</td>
</tr>
<tr>
<td>2</td>
<td>DMF</td>
<td>32</td>
<td>32</td>
<td>nd</td>
<td></td>
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<tr>
<td>3</td>
<td>DMPU</td>
<td>37</td>
<td>9</td>
<td>nd</td>
<td></td>
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<tr>
<td>4</td>
<td>NMP</td>
<td>33</td>
<td>21</td>
<td>nd</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>DMEU</td>
<td>45</td>
<td>27</td>
<td>54:46</td>
<td></td>
</tr>
</tbody>
</table>

⁺1.1 equiv. of tropylium NTf₂ 4 added.
Table S2: Screening of solvents in the trapping reaction:

1. 6 mol% L1, 5 mol % CuBr.SMe₂
2 equiv. TMSOTf, 2 equiv. MeMgBr
DCM, -50°C

2. 1.3 equiv. Tropylium NTf₂ 4
solvent 2, NMP, r.t.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent 2</th>
<th>Additive</th>
<th>Conversion (%)</th>
<th>Yield 3a (%)</th>
<th>dr</th>
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<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>Y</td>
<td>28</td>
<td>19</td>
<td>53:47</td>
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<tr>
<td>2</td>
<td>THF</td>
<td>Y</td>
<td>11</td>
<td>0</td>
<td>n.d.</td>
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<tr>
<td>3</td>
<td>Trifluorotoluene</td>
<td>Y</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>4</td>
<td>2-Me-THF</td>
<td>Y</td>
<td>0</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>5</td>
<td>THF</td>
<td>N</td>
<td>37</td>
<td>15</td>
<td>53:47</td>
</tr>
</tbody>
</table>

Table S3: The effect of different silyl triflates on the dr of 3a in the trapping reaction:

1. 6 mol% L1, 5 mol % CuBr.SMe₂
2 equiv. R₃SiOTf, 2 equiv. MeMgBr
DCM, -50°C, o.n.

2. 1.1 equiv. Tropylium NTf₂ 4
0.6 mol% DMEU, r.t., o/n

<table>
<thead>
<tr>
<th>Entry</th>
<th>R₃SiOTf</th>
<th>Conversion (%)</th>
<th>Yield 3a (%)</th>
<th>dr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>TMSOTf</td>
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<td>59</td>
<td>56:44</td>
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<tr>
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<td>TBSOTf</td>
<td>56</td>
<td>23</td>
<td>55:45</td>
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<tr>
<td>5</td>
<td>TBDPSOTf</td>
<td>49</td>
<td>33</td>
<td>n.d.*</td>
</tr>
</tbody>
</table>

*aDue to the large amount of TBDPSOTf residue it is not clear from the crude.

Presumably, the ee of the reaction is also affected, the ee’s were not determined.

Table S4: Screening of conditions for trapping of Pd-allyl cation 9:

1. 6 mol% L1, 5 mol % CuBr.SMe₂,
2 equiv. LA, 2 equiv. MeMgBr
DCM, -50°C, o.n.

2. 3 equiv. additive, -50°C to r.t., o.n.
The cations were prepared according to the procedure reported previously.\textsuperscript{1}

Carbenium tetrafluoroborate (1.0 mmol) and LiNTf\textsubscript{2} (1.0 mmol, 287 mg) were combined in a mixture of H\textsubscript{2}O (2.5 mL) and EtOAc (2.5 mL) and then stirred for 2 h. After separation of layers, organic phase was dried over anhydrous MgSO\textsubscript{4}, filtered and solvent was evaporated under reduced pressure. The crude product was dried at high vacuum overnight.

\textit{Cyclohepta-2,4,6-trien-1-yl}ium bis((trifluoromethyl)sulfonyl)amide 4

\begin{align*}
\text{Entry} & \quad \text{LA} & \quad \text{Additive} & \quad \text{Solvent} 2 \\
1 & \text{TMSOTf} & \text{Pd(PPh\textsubscript{3})\textsubscript{4}} & \text{DCM} \\
2 & \text{TMSOTf} & \text{DMPU} & \text{DCM} \\
3 & \text{TMSOTf} & \text{DMPU} & \text{THF} \\
4 & \text{TMSOTf}\textsuperscript{b} & \text{DMPU} & \text{PhMe} \\
5 & \text{BF\textsubscript{3}.Et\textsubscript{2}O}\textsuperscript{c} & \text{DMEU} & \text{DCM} \\
6 & \text{BF\textsubscript{3}.Et\textsubscript{2}O}\textsuperscript{c} & - & \text{DCM} \\
7 & \text{TMSOTf} & \text{MeLi, LiCl, Pd(PPh\textsubscript{3})\textsubscript{4}} & \text{THF} \\
\end{align*}

\textsuperscript{a} 5 mol \% CuI was used; \textsuperscript{b} Reaction was performed without ligand; \textsuperscript{c} EtMgBr was used.

91\% yield, red-brown solid

\textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 9.32 (s, 7H).

\textsuperscript{19}F NMR (282 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) -79.5.

Spectral data are in agreement with literature data.\textsuperscript{1a}

\textit{Benzo[d][1,3]dithiol-1-ium} bis((trifluoromethyl)sulfonyl)amide 5

\begin{align*}
\text{Entry} & \quad \text{LA} & \quad \text{Additive} & \quad \text{Solvent} 2 \\
1 & \text{TMSOTf} & \text{Pd(PPh\textsubscript{3})\textsubscript{4}} & \text{DCM} \\
2 & \text{TMSOTf} & \text{DMPU} & \text{DCM} \\
3 & \text{TMSOTf} & \text{DMPU} & \text{THF} \\
4 & \text{TMSOTf}\textsuperscript{b} & \text{DMPU} & \text{PhMe} \\
5 & \text{BF\textsubscript{3}.Et\textsubscript{2}O}\textsuperscript{c} & \text{DMEU} & \text{DCM} \\
6 & \text{BF\textsubscript{3}.Et\textsubscript{2}O}\textsuperscript{c} & - & \text{DCM} \\
7 & \text{TMSOTf} & \text{MeLi, LiCl, Pd(PPh\textsubscript{3})\textsubscript{4}} & \text{THF} \\
\end{align*}

85\% yield, red solid

\textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 11.71 (s, 1H), 8.72 (dd, \(J = 5.9, 2.9\) Hz, 3H), 8.16 (dd, \(J = 6.4, 3.2\) Hz, 3H).

\textsuperscript{19}F NMR (282 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) -79.5.

Spectral data are in agreement with literature data.\textsuperscript{1a}

\textit{5,6-Dihydro-4H-1,3-dithiin-1-ium} bis((trifluoromethyl)sulfonyl)amide 6

\begin{align*}
\text{Entry} & \quad \text{LA} & \quad \text{Additive} & \quad \text{Solvent} 2 \\
1 & \text{TMSOTf} & \text{Pd(PPh\textsubscript{3})\textsubscript{4}} & \text{DCM} \\
2 & \text{TMSOTf} & \text{DMPU} & \text{DCM} \\
3 & \text{TMSOTf} & \text{DMPU} & \text{THF} \\
4 & \text{TMSOTf}\textsuperscript{b} & \text{DMPU} & \text{PhMe} \\
5 & \text{BF\textsubscript{3}.Et\textsubscript{2}O}\textsuperscript{c} & \text{DMEU} & \text{DCM} \\
6 & \text{BF\textsubscript{3}.Et\textsubscript{2}O}\textsuperscript{c} & - & \text{DCM} \\
7 & \text{TMSOTf} & \text{MeLi, LiCl, Pd(PPh\textsubscript{3})\textsubscript{4}} & \text{THF} \\
\end{align*}

55\% yield after two steps, orange slurry

\textsuperscript{1}H NMR (300 MHz, CD\textsubscript{2}Cl\textsubscript{2}) \(\delta\) 5.91 (br s, 1H), 3.84 – 2.91 (m, 2H), 2.86 – 1.80 (m, 4H).
19F NMR (282 MHz, CD$_2$Cl$_2$) δ -79.3.
Spectral data are in agreement with literature data.\textsuperscript{1b}

\textbf{Trapping of enamides}

\textbf{Procedure A: With tropylium cation}

In a flame-dried Schlenk tube equipped with septum and magnetic stirring bar, CuBr.SMe$_2$ (5 mol%) and L1 (6 mol%) were dissolved in DCM (1.0 mL), and stirred under nitrogen atmosphere for 20 min. The substrate (0.212 mmol, 1.0 equiv.) was added at once. After stirring for 5 min at r.t. the reaction mixture was cooled down to -50 °C (or -78 °C), and TMSOTf (2.0 equiv) was added. After 20 min, RMgBr (2.0 equiv, 3M or 2M in Et$_2$O) was added and stirred for 18 h at the same temperature. Cation (1.1 equiv) was dissolved in DCM (0.07 M), and DMEU (15 µL per 0.233 mmol of tropylium cation) \textit{(takes about 5 minutes to dissolve)} and added to the reaction mixture at -50 °C and stirred overnight at ambient temperature in the absence of light. The reaction was quenched by 2 mL of NH$_4$Cl, extracted to DCM (3 x 10 mL), dried over MgSO$_4$, filtered and the solvent was evaporated. The products were obtained after column chromatography on SiO$_2$ with pentane/Et$_2$O. All the trapping products stain yellow with KMnO$_4$, while the CA products stain white. The trapping product has always a higher R$_f$ value, than the CA product.

\textbf{Procedure B: With benzoditiolium cation}

The same procedure was used for CA as in procedure A. Benzo[d][1,3]dithiol-1-ium bis((trifluoromethyl)sulfonyl)amide 5 was dissolved in DCM (0.07M) and added to the reaction mixture at -50 °C and stirred overnight at ambient temperature in the absence of light. The work-up follows the same procedure as in A.

HPLC of the CA product isolated from the trapping reaction mixture was measured. The enantiomeric excesses were compared with the data reported in the literature.\textsuperscript{2} Since the values are comparable, within experimental error, it was shown, that the enantiomeric ratios do not change during the course of the trapping reaction. For products, where the conjugate addition step follows the same procedure one representative HPLC is given.

The absolute configurations on the carbons in position 3 were assigned configurations as reported previously. The relative stereochemistry was assigned by X-ray crystallography (see details below). The stereogenic center on carbon 2 for products with nearly 1:1 diastereomeric ratio is not indicated.

\textit{(3R)-2-(cyclohepta-2,4,6-trien-1-yl)-N,N,3-trimethylhexanamide 3a}

CA was performed at -50°C. Column chromatography on SiO$_2$ with pentane/Et$_2$O 5:1.
59% yield, *er* 99:1, yellow oil, major diastereomer was obtained pure, minor only as mixture inseparable from major.

**Major diastereomer:** $^1$H NMR (300 MHz, CDCl$_3$) δ 6.72 – 6.51 (m, 2H), 6.18 (ddd, $J = 9.9$, 6.0, 4.0 Hz, 2H), 5.54 (dd, $J = 9.5$, 6.4 Hz, 1H), 5.21 (dd, $J = 9.5$, 6.6 Hz, 1H), 3.08 (s, 3H), 3.00 (s, 3H), 2.89 (t, $J = 7.8$ Hz, 1H), 2.25 (q, $J = 7.1$ Hz, 1H), 2.03 (dd, $J = 9.6$, 6.8, 2.6 Hz, 1H), 1.44 – 1.31 (m, 2H), 1.22 – 1.03 (m, 2H), 0.91 – 0.81 (m, 6H).

**Major diastereomer:** $^{13}$C NMR (101 MHz, CDCl$_3$) δ 177.5, 133.5, 132.9, 127.7, 127.5, 126.9, 125.9, 48.9, 42.3, 40.8, 38.8, 38.2, 36.8, 23.2, 19.7, 16.9.


**(R)-N,N-Dimethyl-3-methyl-hexanamide**

\[ \text{HPLC: Chiracel-OBH, } n\text{-heptane/i-PrOH 95:5, 0.5 mL/min, 40 } ^\circ \text{C, detection at 210 nm. Retention time (min): 10.4 (minor) and 11.5 (major).} \]

**(3R)-2-(Benzo[d][1,3]dithiol-2-yl)-N,N,3-trimethylhexanamide 3b**

CA was performed at -50°C. Column chromatography on SiO$_2$ with pentane/Et$_2$O 10:1. 25% yield, *er* 99:1, red solid, inseparable mixture of diastereomers
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.28 – 7.15 (m, 2H), 7.12 – 6.95 (m, 2H), 5.23 (dd, $J = 17.7$, 10.8 Hz, 1H), 3.29 (ddd, $J = 10.9$, 4.0, 2.0 Hz, 1H), 3.01 – 2.93 (overlapping singlets, 6H), 2.13 (s, 1H), 1.53 – 1.25 (m, 2H), 1.25 – 1.05 (m, 2H), 1.01 – 0.81 (m, 6H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 174.9, 174.9, 140.2, 140.1, 139.8, 139.7, 128.2, 128.2, 128.1, 128.1, 125.3, 125.2, 125.1, 125.1, 58.3, 57.9, 55.6, 54.7, 40.9, 40.9, 39.9, 38.4, 36.9, 36.4, 23.5, 23.3, 20.3, 17.0, 16.8, 16.8.


(3S)-N,N-Diallyl-2-(cyclohepta-2,4,6-trien-1-yl)-3-methylpentanamide 3f

CA was performed at -50°C. Column chromatography on SiO$_2$ with pentane/Et$_2$O 3:1.

25% yield, er 79:21, yellow oil, inseparable mixture of diastereomers

Mixture of diastereomers: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.63 – 6.52 (m, 2H), 6.12 (dt, $J = 9.8$, 3.1 Hz, 2H), 5.80 – 5.63 (m, 2H), 5.52 – 5.39 (m, 1H), 5.22 – 5.05 (m, 5H), 4.08 – 3.83 (m, 4H), 2.81 (dt, $J = 11.6$, 7.2 Hz, 1H), 2.25 – 2.06 (m, 1H), 1.91 (ttdd, $J = 10.4$, 6.9, 3.7 Hz, 1H), 1.44 (ddddd, $J = 25.0$, 13.2, 7.4, 3.8 Hz, 1H), 1.04 (ddddd, $J = 17.2$, 8.6, 5.2 Hz, 1H), 0.88 – 0.74 (m, 6H).

Mixture of diastereomers: $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.0, 176.8, 136.19, 136.17, 136.12, 136.1, 133.6, 133.5, 133.0, 132.9, 127.7, 127.6, 127.5, 127.4, 127.1, 126.8, 125.9, 125.7, 120.5, 120.4, 120.18, 120.15, 52.5, 52.4, 50.3, 50.3, 48.9, 48.0, 47.2, 42.4, 39.0, 38.4, 30.0, 29.6, 19.1, 18.9, 14.9, 14.2.

HRMS (ESI+, m/Z): calcd for C$_{19}$H$_{27}$NO [M+H]$^+$: 286.2165, found: 286.2160.

(S)-N,N-Diallyl-3-methyl-pentanamide

HPLC: Chiracel-ODH, n-heptane/i-PrOH 99:01, 0.5 mL/min, 40 °C, detection at 211 nm. Retention time (min): 14.5 (minor) and 15.6 (major).
(3S)-2-(Cyclohepta-2,4,6-trien-1-yl)-1-(2,5-dihydro-1H-pyrrol-1-yl)-3-methylpentan-1-one 9

\[
\begin{align*}
\text{N} & \quad \text{O} \\
\text{Ru} & \quad \text{Cl} \\
\text{Cl} & \\
\end{align*}
\]

Hoveyda-Grubbs catalyst (1.7 mg, 0.003 mmol, 5.7 mol%) was dissolved in 1mL of dry DCM, and the substrate (15.0 mg, 0.053 mmol) was added in dry DCM (2 mL) and left to stir overnight. The solvent was evaporated, and the reaction mixture was filtered through a small pad of silica gel in hexane/Et\(_2\)O 1:1 to get rid of the catalyst. Evaporation of the solvent afforded the crude product.

95% yield, \(er\) 79:21, yellow oil

\(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 6.72 – 6.56 (m, 2H), 6.20 (dt, \(J = 10.7, 5.8\) Hz, 2H), 5.89 (dd, \(J = 5.3, 3.1\) Hz, 1H), 5.79 (dd, \(J = 6.5, 3.4\) Hz, 1H), 5.59 (ddd, \(J = 22.1, 9.5, 6.4\) Hz, 1H), 5.22 (td, \(J = 10.0, 6.6\) Hz, 1H), 4.39 – 4.20 (m, 4H), 2.67 (dt, \(J = 12.3, 7.6\) Hz, 1H), 2.35 (q, \(J = 6.9\) Hz, 1H), 2.21 (q, \(J = 6.9\) Hz, 1H), 2.08 – 1.91 (m, 1H), 1.57 – 1.31 (m, 1H), 1.24 – 1.01 (m, 1H), 0.94 – 0.80 (m, 6H).

HRMS (ESI+, m/Z): calcd for C\(_{17}\)H\(_{24}\)NO [M+H]\(^+\): 258.1852, found: 258.1850.

(2R,3S)-2-(Cyclohepta-2,4,6-trien-1-yl)-N,N-dimethyl-3-phenylpentanamide 3g

\[
\begin{align*}
\text{N} & \\
\text{O} & \\
\end{align*}
\]

CA was performed at -50°C. Column chromatography on SiO\(_2\) with pentane/Et\(_2\)O 3:1.
24% yield, er 77:23, white solid

Major diastereomer: $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.16 (t, $J$ = 7.2 Hz, 2H), 7.09 (t, $J$ = 7.2 Hz, 1H), 7.03 (d, $J$ = 7.0 Hz, 2H), 6.50 – 6.41 (m, 2H), 6.03 (dt, $J$ = 15.7, 5.8, 2.3 Hz, 2H), 5.47 – 5.39 (m, 1H), 5.08 – 4.99 (m, 1H), 3.09 (t, $J$ = 8.0 Hz, 1H), 2.93 (td, $J$ = 9.2, 7.6, 3.3 Hz, 1H), 2.86 (s, 3H), 2.57 (s, 3H), 2.24 (q, $J$ = 6.8 Hz, 1H), 1.66 (ddq, $J$ = 25.2, 13.5, 6.6 Hz, 2H), 0.59 (t, $J$ = 7.2 Hz, 3H).

Major diastereomer: $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 145.3, 133.3, 132.8, 131.1, 130.8 (2C), 129.0, 127.7, 127.7, 126.8, 125.7, 51.3, 49.4, 43.0, 40.2, 38.2, 26.3, 15.0.

HRMS (ESI+, m/z): calcd for C$_{20}$H$_{25}$NONa [M+Na]: 318.1828, found: 318.1828.

(S)-N,N-Dimethyl-3-phenylpentanamide

HPLC: Chiracel-ODH, n-heptane/i-PrOH 90:10, 0.5 mL/min, 40 °C, detection at 208 nm. Retention time (min): 12.1 (major) and 13.3 (minor).

(2R,3S)-2-(Benzo[d][1,3]dithiol-2-yl)-3-(3-bromophenyl)-N,N-dimethylpentanamide 3h

CA was performed at -78°C, 2 equiv. of cation were used in this case. Column chromatography on SiO$_2$ with pentane/Et$_2$O 3:1.

40% yield, er 65:35, white crystals, inseparable mixture of diastereomers
$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.29 (d, $J = 7.7$ Hz, 1H), 7.24 (s, 1H), 7.19 – 7.09 (m, 2H), 7.07 (d, $J = 7.6$ Hz, 1H), 7.02 (d, $J = 7.5$ Hz, 1H), 7.00 – 6.94 (m, 2H), 5.20 (d, $J = 10.4$ Hz, 1H), 4.83 (d, $J = 10.0$ Hz, 1H), 3.49 (dd, $J = 9.9$, 7.2 Hz, 1H), 3.31 (dd, $J = 10.3$, 5.2 Hz, 1H), 3.15 (dt, $J = 11.7$, 4.4 Hz, 1H), 2.79 (s, 3H), 2.74 (s, 1H), 2.18 (s, 3H), 1.90 – 1.67 (m, 2H), 0.87 (t, $J = 7.3$ Hz, 3H), 0.64 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 173.5, 146.8, 142.3, 139.9, 139.4, 134.9, 134.0, 132.65, 132.61, 132.2, 130.9, 130.0, 128.3, 128.2, 125.3, 125.2, 125.1, 124.9, 124.9, 124.9, 58.1, 57.8, 56.5, 56.2, 51.5, 50.7, 40.8, 39.9, 38.2, 37.4, 24.0, 15.1, 14.9.


**(S)-N,N-Dimethyl-3-(3-bromophenyl)pentanamide**

![Chemical structure of (S)-N,N-Dimethyl-3-(3-bromophenyl)pentanamide](image)

HPLC: Chiracel-ODH, n-heptane/i-PrOH 97:2, 0.5 mL/min, 40 °C, detection at 210 nm. Retention time (min): 22.0 (major) and 26.0 (minor).

**(2S,3S)-2-(Cyclohepta-2,4,6-trien-1-yl)-N,N,5-trimethyl-3-propylhexanamide 3i**

![Chemical structure of (2S,3S)-2-(Cyclohepta-2,4,6-trien-1-yl)-N,N,5-trimethyl-3-propylhexanamide](image)

CA was performed at -50°C. Column chromatography on SiO$_2$ with pentane/Et$_2$O 10:1.
59% yield, er 97:3, yellow oil

**Major diastereomer:** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.67 – 6.55 (m, 2H), 6.22 (dd, $J = 9.4, 4.2$ Hz, 1H), 6.18 – 6.13 (m, 1H), 5.50 – 5.41 (m, 1H), 5.26 (q, $J = 7.5$ Hz, 1H), 3.02 (q, $J = 8.2, 7.2$ Hz, 1H), 3.00 (s, 3H), 2.96 (s, 3H), 2.63 – 2.54 (m, 1H), 1.89 – 1.76 (m, 1H), 1.66 – 1.58 (m, 1H), 1.57 – 1.46 (m, 1H), 1.34 – 1.15 (m, 2H), 1.06 (dt, $J = 13.4, 6.5$ Hz, 2H), 0.88 (overlapping t, $J = 7.2$ Hz, 3H), 0.84 (d, $J = 4.2$ Hz, 3H), 0.83 (d, $J = 4.4$ Hz, 3H).

**Mixture of diastereomers:** $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 177.07, 177.01, 133.35, 133.30, 132.93, 132.90, 128.02, 127.95, 127.73, 127.69, 127.63, 127.51, 126.48, 126.41, 44.92, 44.80, 43.86, 42.50, 42.23, 42.12, 40.66, 40.59, 38.88, 38.81, 38.28, 38.25, 36.24, 35.57, 28.34, 28.29, 26.74, 25.56, 25.46, 24.44, 23.22, 22.39, 17.12, 17.07.

HRMS (ESI+, m/z): calcd for C$_{19}$H$_{32}$NO $[M+H]^+$: 290.2478, found: 290.2479.

*(S)-N,N-Dimethyl-5-methyl-3-propyl-hexanamide*

HPLC: Chiracel-ADH, n-heptane/i-PrOH 95.5:0.5, 0.5 mL/min, 40 °C, detection at 219 nm. Retention time (min): 45.5 (major) and 59.2 (minor).

**(2S,3S)-2-(Cyclohepta-2,4,6-trien-1-yl)-3-cyclopentyl-N,N-dimethylhexanamide 3j**

CA was performed at -50°C. Column chromatography on SiO$_2$ with pentane/Et$_2$O 10:1.

44% yield, er 99:1, yellow oil, mixture of diastereomers
$^1$H NMR (400 MHz, CDCl$_3$) δ 6.61 – 6.51 (m, 2H), 6.11 (dd, $J$ = 14.5, 9.3, 4.8 Hz, 2H), 5.51 (dd, $J$ = 9.5, 6.5 Hz, 1H), 5.38 (dd, $J$ = 9.6, 6.7 Hz, 1H), 5.23 – 5.19 (m, 1H), 5.16 (dd, $J$ = 9.5, 6.8 Hz, 1H), 2.99 (s, 3H), 3.04 – 2.92 (m, 1H), 2.89 (s, 3H), 2.50 – 2.42 (m, 1H), 2.32 (q, $J$ = 7.2 Hz, 1H), 1.92 (ddt, $J$ = 17.2, 10.1, 7.1 Hz, 1H), 1.78 (p, $J$ = 5.4 Hz, 1H), 1.75 – 1.63 (m, 1H), 1.61 – 1.33 (m, 4H), 1.30 – 0.95 (m, 6H), 0.76 (t, $J$ = 6.9 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 177.4, 133.5, 133.3, 132.9, 132.8, 127.9, 127.8, 127.4, 127.1, 126.7, 125.9, 46.0, 45.9, 45.4, 44.9, 42.9, 42.5, 40.8, 40.7, 38.4, 38.3, 34.5, 34.3, 33.8, 32.0, 31.8, 28.3, 28.1, 28.0, 27.7, 26.1, 24.2, 17.4, 17.2.

HRMS (ESI+, $m/z$): calcd for C$_{20}$H$_{32}$NO [M+H]$^+$:302.2478, found: 302.2478.

(R)-N,N-Dimethyl-3-cyclopentyl-hexanamide

\[
\begin{align*}
\text{HPLC: Chiracel-OZH, } & \text{n-heptane/i-PrOH 98:2, 0.5 mL/min, 40 °C, detection at 205 nm.} \\
& \text{Retention time (min): 36.2 (minor) and 38.8 (major).}
\end{align*}
\]

Synthesis of 3a via Li-2:

\[
\begin{align*}
\text{1. LDA, THF, 1h, } & \text{-78 °C} \\
\text{2. } & \text{Diisopropyl amine (0.031 mL, 0.219 mmol, 1.15 equiv.) was dissolved in THF (0.1 mL) and cooled down to } -78 \text{ °C. } n\text{BuLi (0.131 mL, 0.210 mmol, 1.1 equiv, 1.6 M in hexane) was added dropwise, and the reaction was stirred for 30 min. (R)-N,N-Dimethyl-3-methyl-hexanamide}
\end{align*}
\]

S12
(30.0 mg, 0.191 mmol, 1.0 equiv) was dissolved in THF (0.3 mL) and added dropwise to the solution. The reaction was stirred at -78 °C for 1 h, before tropylium NTf₂ 4 (77.9 mg, 0.210 mmol, 1.1 equiv) dissolved in DCM (2.6 mL) and DMEU (15 µL) was added dropwise, and let to stir overnight at -78 °C. The reaction was quenched with 0.1 mL of MeOH, followed by 2 mL NH₄Cl and let to warm to room temperature. The reaction was extracted with DCM (3 x 10 mL), dried over MgSO₄, filtered, and the solvent was evaporated. The crude mixture was analyzed by GC-MS.

Trapping of heteroarenes

Conditions A: In a heat-dried Schlenk tube equipped with septum and magnetic stirring bar, CuBr SMe₂ (5 mol %), and ligand L₂ (6 mol %) were dissolved in Et₂O (0.1 M) and stirred under nitrogen atmosphere for 15 min. The substrate (1.0 equiv.) was added at once. After stirring for 5 min. at r.t. the reaction mixture was cooled to -78 °C and BF₃·Et₂O (1.2 equiv.) was added followed by EtMgBr (1.2 equiv.). The reaction was stirred at -78 °C for 4 h. Cation (1.5 equiv.) was dissolved in DCM (0.07 M), and DMEU (only for tropylium cation) (15 µL per 0.233 mmol of tropylium cation) (takes about 5 minutes to dissolve) and added to the reaction mixture at -78 °C and stirred overnight at ambient temperature in the absence of light. The reaction was quenched by 2 mL of NH₄Cl, extracted to DCM (3x10 mL), dried over MgSO₄, filtered and the solvent was evaporated. The products were obtained after column chromatography on SiO₂ with pentane/Et₂O. All the trapping products stain yellow with KMnO₄, while the CA products stain white. The trapping product has a higher Rf value, than the CA product in most cases.

Conditions B: In a heat dried Schlenk tube equipped with septum and magnetic stirring bar, CuBr SMe₂ (10 mol %), and ligand L₂ (12 mol %) were dissolved in DCM (0.1 M) and stirred under nitrogen atmosphere for 15 min. The substrate (1.0 equiv) was added at once. After stirring for 5 min. at r.t. the reaction mixture was cooled to -78 °C and TMSOTf (3.0 equiv) was added followed by RMgBr (3.0 equiv). The reaction was stirred at -78 °C for 16 h. The addition of cation and work-up follows the same procedure are in A.

2-((1R,2S)-1-(Cyclohepta-2,4,6-trien-1-yl)-2-phenylbutyl)benzo[d]oxazole 12a

Prepared using conditions A. Column chromatography on SiO₂ with pentane/Et₂O 20:1.

64% yield, er 99:1, colorless crystals.

Major diastereomer: ¹H NMR (400 MHz, CDCl₃) δ 7.78 – 7.71 (m, 1H), 7.58 – 7.50 (m, 1H), 7.39 – 7.29 (m, 2H), 7.24 (ddd, J = 7.6, 5.2, 1.6 Hz, 3H), 7.16 – 7.11 (m, 2H), 6.54 – 6.43 (m, 2H), 6.14 (dt, J = 9.6, 4.7 Hz, 1H), 6.00 (dd, J = 9.6, 5.0 Hz, 1H), 5.69 (dd, J = 9.6, 5.9 Hz, 1H), 5.12 (dd, J = 9.5, 5.9 Hz, 1H), 3.64 (dd, J = 10.3, 6.1 Hz, 1H), 3.34 (td, J = 10.8, 3.6 Hz,
1H), 1.78 (q, J = 6.0 Hz, 1H), 1.65 (ddd, J = 13.6, 6.7, 4.3 Hz, 1H), 1.50 (dqd, J = 14.4, 7.3, 3.5 Hz, 1H), 0.64 (t, J = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 165.64, 166.61, 149.6, 149.4, 140.6, 140.0, 139.9, 130.2, 129.8, 129.6, 129.5, 127.38, 127.36, 127.2, 126.9, 125.7, 125.5, 124.27, 124.25, 124.1, 123.62, 123.61, 123.3, 123.2, 122.9, 122.2, 122.1, 122.0, 121.1, 118.9, 118.7, 109.5, 109.3, 48.1, 47.4, 47.2, 45.7, 39.4, 38.5, 25.7, 25.3, 11.2, 11.0.

HRMS (ESI+, m/z): calcd for C$_{24}$H$_{24}$NO [M+H]$^+$: 342.1852, found: 342.1858.

(S)-2-(2-phenylbutyl)benzoxazole

HPLC: Chiracel-OZH, n-heptane/i-PrOH 99.5:0.5, 0.5 mL/min, 40 °C, detection at 237 nm. Retention time (min): 31.2 (major) and 36.0 (minor).

2-((1R,2S)-1-(Benzo[d][1,3]dithiol-2-yl)-2-phenylbutyl)benzo[d]oxazole 12b

Prepared using conditions B. Column chromatography on SiO$_2$ with pentane/Et$_2$O 10:1.
46% yield, er 55: 45, white solid.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.56 – 7.48 (m, 1H), 7.35 – 7.26 (m, 2H), 7.23 – 7.12 (m, 6H), 7.02 (d, $J$ = 7.7 Hz, 1H), 6.79 (d, $J$ = 7.7 Hz, 1H), 6.65 (t, $J$ = 7.6 Hz, 1H), 6.53 (t, $J$ = 7.6 Hz, 1H), 4.80 (d, $J$ = 4.8 Hz, 1H), 3.57 (dd, $J$ = 9.8, 5.1 Hz, 1H), 3.44 (td, $J$ = 10.3, 3.8 Hz, 1H), 1.62 – 1.40 (m, 2H), 0.59 (t, $J$ = 7.3 Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 166.9, 152.9, 143.4, 143.3, 139.7, 139.0, 131.7, 130.9, 129.9, 127.8, 127.5, 127.2, 126.6, 124.7, 124.6, 122.3, 112.9, 57.6, 56.9, 50.8, 28.9, 14.5.

HRMS (ESI+, m/z): calcd for C$_{24}$H$_{22}$NOS$_2$ [M+H]$^+$: 404.1137, found: 404.1130.

$(S)$-2-(2-phenylbutyl)benzoxazole

![](image1.png)

HPLC: Chiracel-OZH, n-heptane/i-PrOH 99.5:0.5, 0.5 mL/min, 40 °C, detection at 237 nm. Retention time (min): 31.2 (major) and 36.0 (minor).

2-((1R,2S)-1-(1,3-Dithian-2-yl)-2-phenylbutyl)benzo[d]oxazole 12c

![](image2.png)

Prepared using conditions B. Column chromatography on SiO$_2$ with pentane/Et$_2$O 2:1.
32% yield, *er* 55: 45, yellow solid.

$^1$H NMR (300 MHz, CDCl$_3$) δ 7.83 – 7.74 (m, 1H), 7.57 (ddd, $J = 8.0, 5.0, 3.3$ Hz, 1H), 7.39 – 7.24 (m, 7H), 3.92 (d, $J = 4.7$ Hz, 1H), 3.70 (dd, $J = 10.4, 4.7$ Hz, 1H), 3.48 (td, $J = 11.0, 3.3$ Hz, 1H), 2.79 – 2.60 (m, 4H), 2.56 – 2.45 (m, 1H), 1.92 (d, $J = 14.3$ Hz, 1H), 1.79 – 1.66 (m, 1H), 1.58 (tdd, $J = 7.3, 5.2, 2.7$ Hz, 1H), 0.62 (t, $J = 8.0$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 167.5, 153.3, 143.7, 143.6, 131.3, 131.0, 129.6, 127.5, 126.9, 122.9, 113.4, 54.1, 52.4, 50.5, 33.5, 33.0, 32.3, 28.9, 28.2, 14.5.

HRMS (ESI+, m/z): calcd for C$_{21}$H$_{24}$NOS$_2$ [M+H]$^+$: 370.1294, found: 370.1291.

4-((2S)-1-(Cyclohepta-2,4,6-trien-1-yl)-2-phenylbutyl)pyridine 12d

Prepared using conditions B. Column chromatography on SiO$_2$ with pentane/Et$_2$O 10:1.

16% yield, *er* 99:1, white solid, mixture of diastereomers dr 1:1

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.45 (d, $J = 5.5$ Hz, 2H), 8.36 (d, $J = 5.6$ Hz, 2H), 7.20 (dq, $J = 12.1, 6.8$ Hz, 6H), 7.13 – 7.03 (m, 2H), 6.94 (d, $J = 6.5$ Hz, 1H), 6.84 (d, $J = 6.0$ Hz, 2H), 6.75 (dd, $J = 10.9, 5.6$ Hz, 1H), 6.62 (dd, $J = 9.8, 5.9$ Hz, 3H), 6.57 (d, $J = 5.3$ Hz, 2H), 6.38 (dd, $J = 9.3, 5.6$ Hz, 1H), 6.13 (dd, $J = 9.4, 5.3$ Hz, 1H), 6.00 (ddd, $J = 14.2, 9.3, 5.5$ Hz, 2H), 5.48 (dd, $J = 9.3, 5.9$ Hz, 1H), 5.18 (dd, $J = 9.4, 6.0$ Hz, 1H), 4.85 (dd, $J = 9.3, 6.1$ Hz, 1H), 4.78 (dd, $J = 9.3, 6.0$ Hz, 1H), 3.30 – 3.19 (m, 2H), 3.17 – 3.05 (m, 2H), 1.94 (dt, $J = 11.0, 6.0$ Hz, 1H), 1.89 – 1.72 (m, 2H), 1.67 (ddd, $J = 13.3, 9.4, 7.0$ Hz, 1H), 1.54 (ddt, $J = 14.7, 7.4, 4.0$ Hz, 1H), 1.47 – 1.31 (m, 1H), 0.86 (t, $J = 7.3$ Hz, 3H), 0.64 (t, $J = 7.3$ Hz, 3H).

$^{13}$C NMR (101 MHz, CDCl$_3$) δ 153.0, 151.9, 151.5, 145.0, 142.2, 133.7, 133.4, 133.34, 133.33, 132.0, 131.3, 130.8, 130.2, 129.1, 129.1, 128.4, 127.8, 127.7, 127.2, 127.1, 127.0, 126.7, 126.6, 125.7, 125.5, 56.8, 54.8, 52.9, 51.7, 43.8, 43.3, 29.1, 25.7, 15.1, 14.9.

HRMS (ESI+, m/z): calcd for C$_{22}$H$_{24}$N [M+H]$^+$: 302.1903, found: 302.1901.

(S)-4-(2-phenylbutyl)pyridine
HPLC: (254 nm, Chiralcel OZ-H, n-heptane:iPrOH = 95:5, 40 °C, 1.0 ml/min.), $t_R = 9.47$ min (major), $t_R = 10.11$ min (minor).

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**Trapping of enamides by activated alkenes**

The conjugate addition step was performed in the same way, as described for the trapping of enamides above. Alkene (2.0 equiv) was dissolved in DCM (0.1M) and added to the reaction and stirred overnight at -50 °C. (Similar outcome was achieved, if the reaction was stirred at ambient temperature after the addition of alkene). The reaction was quenched by aq. NH$_4$Cl (2 mL), extracted to DCM (3 x 10 mL) and dried over MgSO$_4$, filtered and the solvent was evaporated.

*(3R)-2-(2,2-bis(phenylsulfonyl)ethyl)-N,N,3-trimethylhexanamide 15a*

Column chromatography on SiO$_2$ with pentane/Et$_2$O 5:1.

65% yield, $er$ 99:1, yellow solid.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.01 – 7.95 (m, 2H), 7.91 – 7.82 (m, 2H), 7.73 – 7.63 (m, 2H), 7.61 – 7.49 (m, 4H), 4.68 (dd, $J = 11.0$, 2.6 Hz, 1H), 4.57 (dd, $J = 10.6$, 2.6 Hz, 1H), 3.47 – 3.27 (m, 1H), 3.08 (2 s, 3H), 2.91 (s, 3H), 2.45 (ddt, $J = 14.0$, 11.2, 2.8 Hz, 1H), 2.22 – 2.01 (m, 1H), 1.66 (m, 1H), 1.38 – 1.20 (m, 3H), 1.24 – 1.05 (m, 1H), 0.93 – 0.80 (m, 3H), 0.75 (d, $J = 6.8$ Hz, 3H).
13C NMR (101 MHz, CDCl₃) δ 175.91, 175.89, 140.7, 140.62, 140.5, 140.3, 137.3, 137.2, 137.1, 137.0, 132.6, 132.5, 131.95, 131.93, 131.84, 131.83, 131.77, 131.73, 131.61, 131.59, 84.5, 84.4, 46.4, 45.4, 40.4, 40.1, 39.7, 38.5, 38.42, 38.37, 37.7, 37.3, 28.1, 26.3, 23.3, 22.8, 20.0, 17.7, 16.84, 16.80.

HRMS (ESI+, m/z): calcd for C₂₃H₃₁NO₅S₂ [M+H]⁺: 466.1716, found: 466.1715.

\( (3R)-2-(2,2\text{-Dicyano-1-phenylethyl})-N,N,3\text{-trimethylhexanamide 15b} \)

Trapping reaction performed at -78 °C. Column chromatography on SiO₂ with pentane/Et₂O 5:1.

20% yield, er 99:1, white solid.

1H NMR (400 MHz, CDCl₃, signals of diastereomers are in italic) δ 7.42 – 7.24 (m, 5H), 4.39 (d, J = 5.4 Hz), 4.32 (d, J = 5.2 Hz), 4.11 (d, J = 5.1 Hz), 4.06 (d, J = 5.1 Hz), 3.68 (dddd, J = 20.6, 15.5, 10.8, 5.2 Hz, 1H), 3.48 – 3.32 (m, 1H), 3.10 (s, 1H), 3.09 (s, 1H), 2.97 (s, 1H), 2.83 (s, 2H), 2.80 (s, 1H), 2.59 (s, 2H), 2.57 (s, 1H), 1.73 (tt, J = 6.7, 3.0 Hz, 1H), 1.61 – 1.10 (m, 4H), 1.01 (dd, J = 28.1, 6.8 Hz, 3H), 0.93 – 0.62 (m, 3H).

13C NMR (101 MHz, CDCl₃) δ 205.4, 174.5, 173.0, 138.9, 138.4, 131.9, 131.8, 131.6, 131.6, 131.1, 131.0, 114.6, 114.4, 114.3, 50.6, 50.5, 49.4, 48.8, 48.7, 48.4, 41.0, 40.6, 40.6, 40.1, 38.6, 38.1, 38.1, 37.0, 36.6, 36.4, 35.9, 32.3, 30.5, 29.5, 29.4, 23.7, 23.3, 23.2, 20.5, 20.4, 17.0, 16.9, 16.7, 16.5.


\( (3R)-2\text{-Bromo-N,N,3\text{-trimethylhexanamide 15c} } \)

The conjugate addition step was performed in the same way, as described above. NBS (41.5 mg, 0.233 mmol, 1.1 equiv.) was dissolved in DCM (3.0 mL) and added to the reaction mixture at -50 °C and stirred overnight at ambient temperature. The reaction was quenched with saturated NH₄Cl, and extracted to DCM, dried over anhydrous MgSO₄, and filtered through a pad of Celite, and the solvent was evaporated.

(Using 3 equiv. of NBS led to a less clean reaction, with 40% conversion.)

Column chromatography on SiO₂ with pentane/Et₂O 5:1.

22% yield, er 99:1, yellow oil.
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 4.20 (d, \(J = 8.9\) Hz, 1H), 3.02 (s, 3H), 2.93 (s, 3H), 2.22 – 2.07 (m, 1H), 1.40 – 1.29 (m, 2H), 1.29 – 1.16 (m, 2H), 1.07 (d, \(J = 6.6\) Hz, 3H), 0.82 (t, \(J = 6.9\) Hz, 3H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 171.6, 54.3, 40.3, 39.0, 39.0, 38.9, 23.0, 20.3, 16.8.

HRMS (ESI\(^+\), m/Z): calcd for C\(_9\)H\(_{19}\)BrNO [M+H]\(^+\): 236.0645, found: 236.0646.

**Trapping of carboxylic acids**

In a flame-dried Schlenk tube equipped with septum and magnetic stirring bar, \((E)\)-hexenoic acid (30.0 mg, 0.263 mmol, 1.0 equiv), CuBr·SMe\(_2\) (2.7 mg, 0.013 mmol, 5 mol\%) and ligand \((R)\)-Tol-Binap L\(_3\) (10.7 mg, 0.016 mmol, 6 mol\%) were dissolved in MTBE (2.6 mL) and stirred under nitrogen atmosphere for 20 min. at r.t. The mixture was cooled to \(-78\) °C and \(n\)BuLi (0.164 mL, 0.263 mmol, 1.0 equiv) was added. After 5 min., TMSOTf (0.1 mL, 0.578 mmol, 2.2 equiv) was added, and the mixture was allowed to stir for 5 min before EtMgBr (0.13 mL, 0.394 mmol, 1.5 equiv) was added dropwise. The reaction mixture was stirred under nitrogen atmosphere for 2 h. A solution of tropylium NTf\(_2\) (107.0 mg, 0.288 mmol, 1.1 equiv) in DCM (3.8 mL) and DMEU (20 µL) was added dropwise. After stirring for 16 h at ambient temperature, the reaction mixture was quenched by HCl aqueous solution (2.0 mL, 1.0 M) and extracted with DCM (3 x 10 mL). The combined organic phase was dried over MgSO\(_4\), filtered and evaporated. The products were obtained after column chromatography on SiO\(_2\) pentane to pentane/Et\(_2\)O 10:1. Precipitation by pentane followed by filtration removed most of the catalyst.

**(3R)-2-(Benzo[d][1,3]dithiol-2-yl)-3-ethylhexanoic acid 18a**

![Structure of 18a](image)

Yellow oil, \(er\) 99:1, 20% (small amount of BINAP present in the product)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.17 – 7.11 (m, 2H), 7.00 – 6.94 (m, 2H), 5.00 (d, \(J = 11.2\) Hz, 1H), 2.99 (td, \(J = 11.5, 2.4\) Hz, 1H), 1.92 – 1.81 (m, 1H), 1.58 – 1.45 (m, 1H), 1.42 – 1.33 (m, 2H), 1.17 – 1.13 (m, 2H), 1.12 – 0.93 (m, 1H), 0.90 – 0.79 (m, 6H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 177.3, 137.2, 136.2, 125.8, 125.7, 122.8, 122.6, 55.0, 53.5, 32.3, 31.1, 25.2, 23.0, 14.4, 14.1.

(3R)-2-(Cyclohepta-2,4,6-trien-1-yl)-3-ethylhexanoic acid 18b

Yellow oil, \( \text{er} \) 99:1, 15% yield, the product was obtained as a mixture with the conjugate addition product.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 6.66 – 6.55 (m, 2H), 6.16 (dd, \(J = 8.4, 3.9\) Hz, 2H), 5.38 – 5.30 (m, 1H), 5.18 (dd, \(J = 9.2, 6.4\) Hz, 1H), 2.77 (dt, \(J = 10.8, 5.6\) Hz, 1H), 2.05 (dt, \(J = 15.9, 6.5\) Hz, 1H), 1.38 – 1.14 (m, 5H), 0.85 – 0.77 (m, 6H).

\(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta\) 178.4, 129.9, 129.5, 124.1, 123.9, 122.6, 121.3, 47.3, 37.2, 33.4, 31.1, 29.8, 18.5, 13.1, 9.6.

HRMS (ESI-, \(m/z\)): calcd for \(\text{C}_{15}\text{H}_{21}\text{O}_2\) [M-H]: 233.1536, found: 233.1553.

\((R)\)-3-Ethylhexanoic acid

The \(\text{ee}\) of this compound was determined from the corresponding \(N, N\)-dimethyl amide derivate.

HPLC: Chiracel-OBH, \(n\)-heptane/i-PrOH 98:2, 0.5 mL/min., 40 °C, detection at 206 nm. Retention time (min): 14.6 (minor) and 16.3 (major).

Synthesis of TBS-ester intermediate

In a flame-dried Schlenk tube equipped with septum and magnetic stirring bar, hexenoic acid (70.0 mg, 0.613 mmol, 1.0 equiv.), CuBr·SMe\(_2\) (6.3 mg, 0.031 mmol, 5 mol%) and THF (6.1
mL) were added. The mixture was cooled to -20 °C and TBSOTf (0.313 mL, 1.363 mmol, 2.2 equiv.) was added. After 20 min., EtMgBr (0.613 mL, 1.840 mmol, 3.0 eq) was added dropwise, and the reaction mixture was allowed to stir for 2 h. The reaction was quenched with saturated NaHCO$_3$ aqueous solution (4.3 mL) and warmed to room temperature. The mixture was extracted with Et$_2$O (10.0 mL × 3). The combined organic phase was dried over MgSO$_4$, filtered and evaporated. Product was obtained as a colorless oil after column chromatography (SiO$_2$, pentane:Et$_2$O = 100:1) 30 mg, 19% yield.

$^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 2.23 (d, $J = 6.8$ Hz, 2H), 1.84-1.72 (m, 1H), 1.43-1.18 (m, 6H), 0.93 (s, 9H), 0.91-0.85 (m, 6H), 0.26 (s, 6H).

Spectral data are in agreement with literature data.$^{2d}$

Synthesis of 18b via lithiation of TBS-ester intermediate:

Diisopropyl amine (0.019 mL, 0.133 mmol, 1.15 equiv.) was dissolved in THF (0.1ml) and cooled down to -78 °C. nBuLi (0.080 mL, 0.128 mmol, 1.1 equiv., 1.6 M in hexane) was added dropwise, and the reaction was stirred for 30 min. TBS-ester intermediate (30.0 mg, 0.116 mmol, 1.0 equiv.) was dissolved in THF (0.4 ml) and added dropwise to the solution. The reaction was stirred at -78 °C for 1 h, before tropylium 4 (47.4 mg, 0.128 mmol, 1.1 equiv.) dissolved in DCM (1.6 mL) and DMEU (9 µL) was added dropwise, and let to stir overnight. The reaction was quenched with 0.1ml of MeOH, followed by 2 ml NH$_4$Cl and let to warm to room temperature. The reaction was extracted with DCM (3x10 mL), dried over MgSO$_4$, filtered, and the solvent was evaporated. The crude mixture was analyzed by GC-MS.
A suitable crystal of compound 12b was mounted on top of a cryoloop and transferred into the cold (100 K) nitrogen stream of a Bruker D8 Venture diffractometer. Data collection and reduction was done using the Bruker software suite APEX3. The final unit cell was obtained from the xyz centroids of 9944 reflections after integration. A multiscan absorption correction was applied, based on the intensities of symmetry-related reflections measured at different angular settings (SADABS). The structures were solved by dual space methods using SHELXT and refinement of the structure was performed using SHELXL. During the refinement, warning signs of twinning appeared and this was checked using PLATON/TWINROT. Data reduction was repeated using two components of which the orientation matrices were identified with program CELL_NOW. Integration was done using SAINT and the data was corrected for absorption using TWINABS. The structure was refined as described above (hklf4), except for the final refinements which were done using the hklf5 routine, which resulted in a BASF value of 0.134. The hydrogen atoms were generated by geometrical considerations, constrained to idealized geometries and allowed to ride on their carrier atoms with an isotropic displacement parameter related to the equivalent displacement parameter of their carrier atoms. The absolute configuration at C8 (R) was inferred from

the known configuration at C16 (S). Crystal data and details on data collection and refinement are presented in Table S1.

**Table S1. Crystallographic data for compound 12b**

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The trapping reaction of tropylium cation should be bright yellow in most cases. A black, or
darker color is usually a sign of a failed experiment and is mostly due to a problem with the
conjugate addition step, if older chemicals were used. a) Reaction with tropylium cation after
work-up. b) Reaction with benzoditiolium. c) Reaction with ditianium.
Cations.
Pictures of $^1$H, $^{13}$C, and $^{19}$F NMR spectra

$^1$H-NMR (300 MHz, CD$_2$Cl$_2$) of 4

$^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$) of 4
\(^1\)H-NMR (282 MHz, CD\(_2\)Cl\(_2\)) of 5

\(^{19}\)F-NMR (282 MHz, CD\(_2\)Cl\(_2\)) of 5
$^1$H-NMR (282 MHz, CD$_2$Cl$_2$) of 6

$^{19}$F-NMR (282 MHz, CD$_2$Cl$_2$) of 6
$^1$H-NMR (300 MHz, CDCl$_3$) of major diastereomer of 3a

$^{13}$C-NMR (101 MHz, CDCl$_3$) of major diastereomer of 3a
$^{13}$C-NMR (101 MHz, CDCl$_3$) of mixture of diastereomers of 3a

$^1$H-NMR (300 MHz, CDCl$_3$) of the crude mixture for dr determination of 3a
$^1$H-NMR (300 MHz, CDCl$_3$) of mixture of diastereomers of 3b

$^{13}$C-NMR (101 MHz, CDCl$_3$) of mixture of diastereomers of 3b
$^1$H-NMR (300 MHz, CDCl$_3$) of the crude mixture for dr determination of 3b

$^1$H-NMR (300 MHz, CDCl$_3$) of mixture of diastereomers of 3k
$^{13}$C-NMR (101 MHz, CDCl$_3$) of mixture of diastereomers of 3k

$^1$H-NMR (300 MHz, CDCl$_3$) of mixture of diastereomers of 10
$^1$H-NMR (300 MHz, CDCl$_3$) of the crude mixture for dr determination of 10

$^1$H-NMR (400 MHz, CDCl$_3$) of major diastereomer of 3g
$^{13}$C-NMR (101 MHz, CDCl$_3$) of mixture of diastereomers of 3g

$^1$H-NMR (400 MHz, CDCl$_3$) of the crude mixture for dr determination of 10
$^1$H-NMR (300 MHz, CDCl$_3$) of mixture of diastereomers of 3h

$^{13}$C-NMR (101 MHz, CDCl$_3$) of mixture of diastereomers of 3h
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$^1$H-NMR (400 MHz, CDCl$_3$) of major diastereomer of 3i
$^{13}$C-NMR (101 MHz, CDCl$_3$) of mixture of diastereomers of 3i

$^1$H-NMR (300 MHz, CDCl$_3$) of the crude mixture for dr determination of 3i
\(^{1}\)H-NMR (400 MHz, CDCl\(_3\)) of mixture of diastereomers of 3j

\(^{13}\)C-NMR (101 MHz, CDCl\(_3\)) of mixture of diastereomers of 3j
\( {^1}H\text{-NMR (300 MHz, CDCl}_3 \text{)} \) of the crude mixture for dr determination of \( \text{3j} \)

\( {^1}H\text{-NMR (400 MHz, CDCl}_3 \text{)} \) of mixture of diastereomers of \( \text{12a} \)
$^{13}$C-NMR (101 MHz, CDCl$_3$) of mixture of diastereomers of 12a

$^1$H-NMR (300 MHz, CDCl$_3$) of the crude mixture for dr determination of 12a
$^1$H-NMR (300 MHz, CDCl$_3$) of major diastereomer of 12b
$^{13}$C-NMR (101 MHz, CDCl$_3$) of major diastereomer of 12b

$^1$H-NMR (300 MHz, CDCl$_3$) of the crude mixture for dr determination of 12b
$^1$H-NMR (300 MHz, CDCl$_3$) of major diastereomer of 12c

$^{13}$C-NMR (101 MHz, CDCl$_3$) of major diastereomer of 12c
$^1$H-NMR (400 MHz, CDCl$_3$) of mixture of diastereomers of $12d$

$^{13}$C-NMR (101 MHz, CDCl$_3$) of mixture of diastereomers of $12d$
$^1$H-NMR (300 MHz, CDCl$_3$) of the crude mixture for dr determination of **12d**

| 1.02 | 1.28 | 1.30 | 1.32 | 1.33 | 1.34 | 1.35 | 1.83 | 2.19 | 3.01 | 3.31 |
|      |      |      |      |      |      |      |      |      |      |      |

$^1$H-NMR (400 MHz, CDCl$_3$) of mixture of diastereomers of **15a**

| 1.02 | 1.28 | 1.30 | 1.32 | 1.33 | 1.34 | 1.35 | 1.83 | 2.19 | 3.01 | 3.31 |
|      |      |      |      |      |      |      |      |      |      |      |
$^{13}$C-NMR (101 MHz, CDCl$_3$) of mixture of diastereomers of 15a

$^1$H-NMR (400 MHz, CDCl$_3$) of the crude mixture for dr determination of 15a
$^1$H-NMR (400 MHz, CDCl$_3$) of mixture of diastereomers of 15b

$^{13}$C-NMR (101 MHz, CDCl$_3$) of mixture of diastereomers of 15b
$^1$H-NMR (300 MHz, CDCl$_3$) of the crude mixture for dr determination of 15b

$^1$H-NMR (400 MHz, CDCl$_3$) of mixture of diastereomers of 15c
$^{13}$C-NMR (101 MHz, CDCl$_3$) of mixture of diastereomers of 15c

$^1$H-NMR (300 MHz, CDCl$_3$) of the crude mixture for dr determination of 15c
$^1$H-NMR (300 MHz, CDCl$_3$) of the crude mixture of 18a

$^1$H-NMR (300 MHz, CDCl$_3$) of 18a

3H-NMR (400 MHz, CDCl$_3$) of 18a
$^{13}$C-NMR (101 MHz, CDCl$_3$) of 18a

$^1$H-NMR (300 MHz, CDCl$_3$) of the crude mixture for dr determination of 18b
$^1$H-NMR (400 MHz, CDCl$_3$) of 18b

$^{13}$C-NMR (101 MHz, CDCl$_3$) of 18b
Computational details

The molecular models were build and optimized by AM1 method in Spartan 18 program package.\textsuperscript{3} From the conformer distribution, ten most stable conformers were selected and pre-optimized in Spartan at HF/3-21G level and then fully geometrically optimized at ωB97X-D/6-31G* level and energies were then refined by single point calculations at M06-2X/6-311+G** level.\textsuperscript{4}

**Z-Me-Li(diglyme)-ketene-aminal**

Geometry optimization: ωB97X-D/6-31G*
Single point energy calculation: M06-2X/6-311+G**
Energy: -796.702572 hartrees
HOMO energy: -5.35 eV

Cartesian coordinates
Z-Me-TMS-ketene-acetal
Geometry optimization: oB97X-D/6-31G*
Single point energy calculation: M06-2X/6-311+G**
Energy: -716.287318 hartrees
HOMO energy: -7.02 eV

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Z-Me-TMS-ketene-aminal

Geometry optimization: ωB97X-D/6-31G*
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Z-Me-TMS-N-benzoxazol

Geometry optimization: ωB97X-D/6-31G*
Single point energy calculation: M06-2X/6-311+G**
Energy: -886.912213 hartrees
HOMO energy: -6.13 eV

Cartesian coordinates

C  -0.678782 -0.000000  -3.954912
C  -0.954709 -0.000000  -2.479071
C   0.004561 -0.000000  -1.548384
O   1.337016  0.000000  -1.919376
N  -0.065640 -0.000000  -0.136370
Si  -1.464833  0.000000   0.972288
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C  -1.359076  1.552207   2.025331
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References


