Supporting Information for

Enantioconvergent Cu-Catalyzed Radical C–N Coupling of Racemic Secondary Alkyl Halides to Access α-Chiral Primary Amines

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Table S1. Reaction Condition Optimization with Benzyl Bromide

<table>
<thead>
<tr>
<th>entry</th>
<th>[Cu]</th>
<th>L*n</th>
<th>base</th>
<th>solvent</th>
<th>T (°C)</th>
<th>yield (%)</th>
<th>e.e. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuTc</td>
<td>L*1</td>
<td>Cs2CO3</td>
<td>Et2O</td>
<td>r. t.</td>
<td>trace b</td>
<td>–</td>
</tr>
<tr>
<td>2</td>
<td>CuTc</td>
<td>L*2</td>
<td>Cs2CO3</td>
<td>Et2O</td>
<td>r. t.</td>
<td>trace b</td>
<td>–</td>
</tr>
<tr>
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<td>15 b</td>
<td>61</td>
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<td>r. t.</td>
<td>trace</td>
<td>–</td>
</tr>
<tr>
<td>5</td>
<td>CuTc</td>
<td>L*5</td>
<td>Cs2CO3</td>
<td>Et2O</td>
<td>r. t.</td>
<td>67</td>
<td>83</td>
</tr>
<tr>
<td>6</td>
<td>CuTc</td>
<td>L*5</td>
<td>Cs2CO3</td>
<td>THF</td>
<td>r. t.</td>
<td>trace</td>
<td>–</td>
</tr>
<tr>
<td>7</td>
<td>CuTc</td>
<td>L*5</td>
<td>Cs2CO3</td>
<td>benzene</td>
<td>r. t.</td>
<td>&lt; 5</td>
<td>–</td>
</tr>
<tr>
<td>8</td>
<td>CuTc</td>
<td>L*6</td>
<td>Cs2CO3</td>
<td>Et2O</td>
<td>r. t.</td>
<td>91</td>
<td>91</td>
</tr>
<tr>
<td>9</td>
<td>CuI</td>
<td>L*6</td>
<td>Cs2CO3</td>
<td>Et2O</td>
<td>r. t.</td>
<td>trace</td>
<td>–</td>
</tr>
<tr>
<td>10</td>
<td>Cu(Ph3)3Br</td>
<td>L*6</td>
<td>Cs2CO3</td>
<td>Et2O</td>
<td>r. t.</td>
<td>37</td>
<td>78</td>
</tr>
<tr>
<td>11</td>
<td>Cu(PrCOO)2</td>
<td>L*6</td>
<td>Cs2CO3</td>
<td>Et2O</td>
<td>r. t.</td>
<td>14</td>
<td>92</td>
</tr>
<tr>
<td>12</td>
<td>CuTc</td>
<td>L*6</td>
<td>K2CO3</td>
<td>Et2O</td>
<td>r. t.</td>
<td>trace</td>
<td>–</td>
</tr>
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<td>CuTc</td>
<td>L*6</td>
<td>KOH</td>
<td>Et2O</td>
<td>r. t.</td>
<td>&lt; 5</td>
<td>67</td>
</tr>
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<td>14</td>
<td>CuTc</td>
<td>L*6</td>
<td>Cs2CO3</td>
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<td>40</td>
<td>49</td>
<td>78</td>
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<tr>
<td>15</td>
<td>CuTc</td>
<td>L*6</td>
<td>Cs2CO3</td>
<td>Et2O</td>
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<td>85</td>
<td>95</td>
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<tr>
<td>16</td>
<td>CuTc</td>
<td>L*7</td>
<td>Cs2CO3</td>
<td>Et2O</td>
<td>r. t.</td>
<td>81</td>
<td>97</td>
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aReaction conditions: (±)-E1 (0.025 mmol), N1 (1.0 equiv.), [Cu] (10 mol%), L*n (10 mol%), and base (4.0 equiv.) in solvent (0.5 mL) at room temperature for 72 h under argon; Yield of 1 was isolated; Ee was based on HPLC analysis.

bThe yield of S-B1 was based on ¹H NMR using 1,3,5-trimethoxybenzene as an internal standard: 10% yield by L*1, trace by L*2, 13% yield by L*3.
Table S2. Reaction Condition Optimization with α-Arylcarbonyl Alkyl Bromide

![Chemical Structure](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>[Cu]</th>
<th>L*n</th>
<th>Ar</th>
<th>solvent</th>
<th>T (°C)</th>
<th>yield (%)</th>
<th>e.e. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuTc</td>
<td>L*5</td>
<td>Ph</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>26</td>
<td>34</td>
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<tr>
<td>2</td>
<td>CuTc</td>
<td>L*5</td>
<td>Ph</td>
<td>THF</td>
<td>r. t.</td>
<td>41</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>CuTc</td>
<td>L*5</td>
<td>Ph</td>
<td>dioxane</td>
<td>r. t.</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>4</td>
<td>CuTc</td>
<td>L*5</td>
<td>Ph</td>
<td>benzene</td>
<td>r. t.</td>
<td>17</td>
<td>32</td>
</tr>
<tr>
<td>5</td>
<td>Cu(HFacac)₂</td>
<td>L*5</td>
<td>Ph</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>88</td>
<td>53</td>
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<tr>
<td>6</td>
<td>Cu(HFacac)₂</td>
<td>L*6</td>
<td>Ph</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>83</td>
<td>56</td>
</tr>
<tr>
<td>7</td>
<td>Cu(HFacac)₂</td>
<td>L*7</td>
<td>Ph</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>82</td>
<td>63</td>
</tr>
<tr>
<td>8</td>
<td>Cu(HFacac)₂</td>
<td>L*7</td>
<td>4-MeOPh</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>63</td>
<td>84</td>
</tr>
<tr>
<td>9</td>
<td>Cu(HFacac)₂</td>
<td>L*7</td>
<td>4-MeOPh</td>
<td>Et₂O</td>
<td>10</td>
<td>69</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>Cu(HFacac)₂</td>
<td>L*7</td>
<td>4-MeOPh</td>
<td>Et₂O</td>
<td>0</td>
<td>55</td>
<td>91</td>
</tr>
<tr>
<td>11</td>
<td>Cu(HFacac)₂</td>
<td>L*7</td>
<td>4-MeOPh</td>
<td>Et₂O</td>
<td>0</td>
<td>80</td>
<td>91</td>
</tr>
</tbody>
</table>

*aReaction conditions: (±)-SE41 (0.025 mmol), sulfoximine (1.1 equiv.), [Cu] (10 mol%), L*n (10 mol%) and base (4.0 equiv.) in solvent (0.5 mL) for 72 h under argon; Yield of 41 was isolated; Ee was based on HPLC analysis.
Table S3. Reaction Condition Optimization with α-Aminocarbonyl Alkyl Bromide

![Reaction scheme](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>[Cu]</th>
<th>L*ₙ</th>
<th>X</th>
<th>solvent</th>
<th>T (°C)</th>
<th>yield (%)</th>
<th>e.e. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CuTc</td>
<td>L*5</td>
<td>4.0</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>60</td>
<td>44</td>
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<tr>
<td>2</td>
<td>CuTc</td>
<td>L*5</td>
<td>4.0</td>
<td>CH₂Cl₂</td>
<td>r. t.</td>
<td>71</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>CuTc</td>
<td>L*5</td>
<td>4.0</td>
<td>Dioxane</td>
<td>r. t.</td>
<td>52</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>CuTc</td>
<td>L*5</td>
<td>4.0</td>
<td>Benzene</td>
<td>r. t.</td>
<td>36</td>
<td>13</td>
</tr>
<tr>
<td>5</td>
<td>CuTc</td>
<td>L*6</td>
<td>4.0</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>71</td>
<td>75</td>
</tr>
<tr>
<td>6</td>
<td>CuI</td>
<td>L*5</td>
<td>4.0</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>56</td>
<td>61</td>
</tr>
<tr>
<td>7</td>
<td>Cu(PPh₃)Br</td>
<td>L*5</td>
<td>4.0</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>70</td>
<td>44</td>
</tr>
<tr>
<td>8</td>
<td>Cu(PrCOO)₂</td>
<td>L*5</td>
<td>4.0</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>83</td>
<td>48</td>
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<tr>
<td>9</td>
<td>Cu(HFacac)₂</td>
<td>L*5</td>
<td>4.0</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>90</td>
<td>77</td>
</tr>
<tr>
<td>10</td>
<td>Cu(HFacac)₂</td>
<td>L*6</td>
<td>4.0</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>91</td>
<td>94</td>
</tr>
<tr>
<td>11</td>
<td>Cu(HFacac)₂</td>
<td>L*6</td>
<td>4.0</td>
<td>Et₂O</td>
<td>0</td>
<td>85</td>
<td>96</td>
</tr>
<tr>
<td>12</td>
<td>Cu(HFacac)₂</td>
<td>L*6</td>
<td>2.5</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>95</td>
<td>94</td>
</tr>
<tr>
<td>13</td>
<td>Cu(HFacac)₂</td>
<td>L*6</td>
<td>2.0</td>
<td>Et₂O</td>
<td>r. t.</td>
<td>83</td>
<td>93</td>
</tr>
</tbody>
</table>

*Reaction conditions: (±)-SE55 (0.025 mmol), N1 (1.0 equiv.), [Cu] (10 mol%), L*ₙ (10 mol%), and base (4.0 equiv.) in solvent (0.5 mL) for 72 h under argon; Yield of 55 was isolated; Ee was based on HPLC analysis.*
Scheme S1. The Attempt of Other Common Ammonia Surrogates

\[ \text{(±)-E1} \quad 1.0 \text{ equiv.} \quad + \quad [\text{N}] \quad 1.0 \text{ equiv.} \quad \rightarrow \quad \text{product} \]

- Benzylamine: No product
- Benzenesulfonylhydrazide: No product
- Dimethylformamide-2-carboxamide: No product
- 2,2-Dimethyl-1,3-dioxane-4,6-dione: No product
- 4-Norbornene-2,3-dicarboximide: No product
- 2-Naphthylamine: No product
- 2-Naphthalenesulfonylhydrazide: No product
- 2,2'-Bipyridine: <5% yield
- Bis(trimethylsilyl)amine: No product
Scheme S2. The Synthesis of Antipodes

\[
\begin{align*}
\text{E1} & \quad \text{1.0 equiv.} & \quad \text{Br} & \quad \text{Me} \\
+ & \quad \text{N1} & \quad \text{1.0 equiv.} & \quad \text{Ph} & \quad \text{SiNMMe}_2 \\
\text{CuTc}(10 \text{ mol\%; L}^7(10 \text{ mol\%; C }\text{CsCO}_3(4.0 \text{ equiv.})) & \quad \text{Et}_2\text{O, rt}} \\
\text{O}_2 \text{N} & \quad \text{Me} & \quad \text{O} & \quad \text{Me} & \quad \text{N} & \quad \text{Ph} \\
& & & \text{Ph} \\
\text{99\%, 88\% ee} \\
\text{SE41} & \quad \text{1.0 equiv.} & \quad \text{Br} & \quad \text{Me} \\
+ & \quad \text{N1} & \quad \text{1.1 equiv.} & \quad \text{Ph} & \quad \text{PMP} \\
\text{Cu(Facac)}(10 \text{ mol\%; L}^7(10 \text{ mol\%; C }\text{CsCO}_3(4.0 \text{ equiv.})) & \quad \text{Et}_2\text{O, 0 °C}} \\
\text{O}_2 \text{N} & \quad \text{Me} & \quad \text{N} & \quad \text{PMP} \\
& & & \text{PMP} \\
\text{99\%, 96\% ee} \\
\text{E2} & \quad \text{1.0 equiv.} & \quad \text{Br} & \quad \text{Me} \\
+ & \quad \text{N1} & \quad \text{1.2 equiv.} & \quad \text{Ph} & \quad \text{Ph} \\
\text{Cu(Facac)}(10 \text{ mol\%; L}^7(10 \text{ mol\%; C }\text{CsCO}_3(2.5 \text{ equiv.})) & \quad \text{Et}_2\text{O, rt}} \\
\text{O}_2 \text{N} & \quad \text{Me} & \quad \text{N} & \quad \text{Ph} & \quad \text{Ph} \\
& & & \text{Ph} \\
\text{99\%, 97\% ee} \\
\end{align*}
\]
Scheme S3. Radical Clock Experiments

\[ \text{Scheme S3. Radical Clock Experiments} \]

The complete loss of enantioselectivity indicates that 86 might have formed through facile direct substitution reactions between E3 and N1 due to the doubly activated nature of E3.
Figure S1. The time-course profile of the model reaction under the optimal conditions.
Figure S2. The X-ray structure of 26.
Figure S3. The X-ray structure of 58.
Figure S4. The X-ray structure of 83.
Figure S5. Cyclic voltammograms of compound 83 were measured in CH$_3$CN in the presence of TBAPF$_6$ (0.1 M) with scan rates of 100 mV s$^{-1}$. Potentials are given vs. the ferrocene/ferrocenium (Fc/Fc$^+$) couple. (a) and (b) are the scan spectra of corresponding oxidation and reduction, respectively. (c) is the whole scan spectrum of 83 with Fe/Fe$^+$ in CH$_3$CN.
General information

Most of reactions were carried out under argon atmosphere using Schlenk techniques. Reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. CH₂Cl₂, THF and DMF were purified and dried using a solvent-purification system that contained activated alumina under argon. Copper(I) thiophene-2-carboxylate (CuTc, CAS No. 68986-76-5) was purchased from Bide Pharmatech Ltd. Copper(II) hexafluoroacetylacetonate (Cu(HFacac)₂, CAS No. 14781-45-4) was purchased from TCI. Cs₂CO₃ was purchased from Bide Pharmatech Ltd. and treated by hot gun (approximate 500 to 600 °C) for 5 minutes in vacuum. Anhydrous diethyl ether (Et₂O) was purchased from Shanghai Lingfeng Chemical Reagent Co. Ltd, which was treated by 4 Å Molecular sieve and distilled after refluxing with sodium and benzophenone. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 60 GF254 plates. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 0.040–0.063 mm). As the eluent, the petroleum ether (PE), hexane, ethyl acetate (EtOAc), dichloromethane (CH₂Cl₂) and methanol were purchased from Shanghai Titan Scientific Co. Ltd without further purification. Visualization on TLC was achieved by use of UV light (254 nm), iodine on silica gel or basic KMnO₄ indicator. NMR spectra were recorded on Bruker DRX-400 and DPX-600 spectrometers at 400 or 600 MHz for ¹H NMR, 100 or 150 MHz for ¹³C NMR, 376 MHz for ¹⁹F NMR and 162 MHz or 243 MHz for ³¹P NMR, respectively, in CDCl₃, CD₂OD, C₆D₆, D₂O or DMSO-d₆ with tetramethylsilane (TMS) as internal standard. The chemical shifts are expressed in ppm and coupling constants are given in Hz. Data for ¹H NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; p, pentet, m, multiplet; br, broad), coupling constant (Hz), integration. Data for ¹³C NMR are reported in terms of chemical shift (δ, ppm). Mass spectrometric data were obtained using Bruker Apex IV RTMS. Enantiomeric excess (ee) value was determined using Agilent high-performance liquid chromatography (HPLC) with a Hatachi detector (at appropriate wavelength) or SHIMADZU LC-20AD with SPD-20AV detector. Column conditions are reported in
the experimental section below. Specific optical rotation was measured on a Rudolph-Autopol I. X-ray diffraction was measured on a 'Bruker APEX-II CCD' diffractometer with Cu–Kα radiation.
General procedure for reaction condition screening.

General procedure for Supplementary Table 1.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-$\lambda^6$-sulfanone N1 (5.4 mg, 0.025 mmol, 1.0 equiv.), [Cu] (0.0025 mmol, 10 mol%), chiral ligand $L^*n$ (0.0025 mmol, 10 mol%), base (0.10 mmol, 4.0 equiv.) and anhydrous solvent (0.5 mL). To this solution was added (1-bromoethyl)benzene (4.6 mg, 0.025 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 72 h. The precipitate was diluted with EtOAc, filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

General procedure for Supplementary Table 2.

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfoximine (0.028 mmol, 1.1 equiv.), [Cu] (0.0025 mmol, 10 mol%), chiral ligand $L^*n$ (0.0025 mmol, 10 mol%), Cs$_2$CO$_3$ (32.6 mg, 0.10 mmol, 4.0 equiv.) and anhydrous solvent (0.5 mL). To this solution was added 2-bromo-1-phenylpropan-1-one (5.3 mg, 0.025 mmol, 1.0 equiv.) and the reaction mixture was stirred for 72 h. The precipitate was diluted with EtOAc, filtered through
a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

**General procedure for Supplementary Table 3.**

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ⁶-sulfanone (6.5 mg, 0.030 mmol, 1.2 equiv.), [Cu] (0.0025 mmol, 10 mol%), chiral ligand L*n (0.0025 mmol, 10 mol%), Cs₂CO₃ (X equiv.) and anhydrous solvent (0.5 mL). Then, 2-bromo-1-(indolin-1-yl)propan-1-one (6.3 mg, 0.025 mmol, 1.0 equiv.) was added into the mixture and stirred at room temperature for 18 h. The precipitate was diluted with EtOAc, filtered off and washed with EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford the desired product.
The synthesis of starting materials.

All the benzylic halides were synthesized following the literatures.1

The Synthesis of sulfoximines.

General procedure SM A: To a solution of sulfide or sulfoxide (1.0 equiv.) in methanol were added PhI(OAc)₂ (2.5 equiv.) and ammonium carbamate (2.0 equiv.) at 0 °C. The reaction mixture was warmed up to room temperature and stirred overnight. After that, the solvent was removed by evaporator and the residue was dissolved in CH₂Cl₂. The organic phase was washed with water, dried over Na₂SO₄, filtered, and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel to afford the desired product.

Iminodiphenyl-λ⁶-sulfanone (N1)

According to General procedure SM A with sulfinyldibenzene (2.02 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product N1 as a white powder (1.87 g, 86% yield).

¹H NMR (400 MHz, CDCl₃) δ 8.21 – 7.91 (m, 4H), 7.67 – 7.37 (m, 6H), 2.74 (s, 1H).

¹³C NMR (100 MHz, CDCl₃) δ 143.4, 132.6, 129.1, 127.9.

HRMS (ESI) m/z calcd. for C₁₂H₁₂NOS [M + H]⁺ 218.0634, found 218.0633.
Iminobis(4-methoxyphenyl)-\(\lambda^6\)-sulfanone (SN2)

According to **General procedure SM A** with 4,4'-sulfinylbis(methoxybenzene) (2.62 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product **SN2** as a yellow powder (2.22 g, 80% yield).

\(^1\text{H NMR}\) (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.94 (d, \(J = 8.5\) Hz, 4H), 6.93 (d, \(J = 8.5\) Hz, 4H), 3.82 (s, 6H), 2.92 (brs, 1H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl\textsubscript{3}) \(\delta\) 162.8, 135.6, 129.8, 114.3, 55.6.

**HRMS** (ESI) \(m/z\) calcd. for C\textsubscript{14}H\textsubscript{16}NO\textsubscript{3}S [M + H]\(^+\) 278.0845, found 278.0844.

di([1,1'-Biphenyl]-4-yl)(imino)-\(\lambda^6\)-sulfanone (SN3)

According to **General procedure SM A** with 4,4''-sulfinyldi1,1'-biphenyl (3.54 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/3) to yield the product **SN3** as a white powder (2.44 g, 66% yield).

\(^1\text{H NMR}\) (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.16 (d, \(J = 8.5\) Hz, 4H), 7.81 – 7.65 (m, 4H), 7.65 – 7.53 (m, 4H), 7.53 – 7.36 (m, 6H), 3.16 (brs, 1H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl\textsubscript{3}) \(\delta\) 145.6, 142.1, 139.4, 129.0, 128.47, 128.46, 127.9, 127.4.

**HRMS** (ESI) \(m/z\) calcd. for C\textsubscript{24}H\textsubscript{20}NOS [M + H]\(^+\) 370.1260, found 370.1258.
bis(4-(tert-Butyl)phenyl)(imino)-λ6-sulfanone (SN4)

According to General procedure SM A with 4,4'-sulfinylbis(tert-butylbenzene) (3.14 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product SN4 as a white powder (2.66 g, 81% yield).

\[^1H\text{NMR}\text{(400 MHz, CDCl}_3\text{)} \delta 7.97 \text{(d, } J = 8.4 \text{ Hz, 4H)}, \text{ 7.47 \text{(d, } J = 8.5 \text{ Hz, 4H)}, \text{ 2.94 \text{(brs, 1H)}, \text{ 1.29 \text{(s, 18H)}}.\]

\[^{13}\text{C NMR}\text{(100 MHz, CDCl}_3\text{)} \delta 156.2, 140.6, 127.8, 126.1, 35.0, 31.1.\]

HRMS (ESI) \text{m/z calcd. for C}_{20}\text{H}_{28}\text{NOS }[M + H]^+ 330.1886, \text{ found 330.1883.}\]

bis(4-Cyclohexylphenyl)(imino)-λ6-sulfanone (SN5)

According to General procedure SM A with 4,4'-sulfinylbis(cyclohexylbenzene) (3.66 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product SN5 as a white powder (3.16 g, 83% yield).

\[^1H\text{NMR}\text{(400 MHz, CDCl}_3\text{)} \delta 7.95 \text{(d, } J = 8.1 \text{ Hz, 4H)}, \text{ 7.28 \text{(d, } J = 8.0 \text{ Hz, 4H)}, \text{ 2.86 \text{(brs, 1H)}, \text{ 1.77 \text{(dd, } J = 33.6, 10.8 \text{ Hz, 10H)}, \text{ 1.50 – 1.09 \text{(m, 10H)}}.\]

\[^{13}\text{C NMR}\text{(100 MHz, CDCl}_3\text{)} \delta 153.0, 140.9, \text{ 128.0, 127.6, 44.4, 34.09, 34.07, 26.7, 26.0.}\]

HRMS (ESI) \text{m/z calcd. for C}_{24}\text{H}_{32}\text{NOS }[M + H]^+ 382.2199, \text{ found 382.2195.}\]
bis(4-Fluorophenyl)(imino)-λ6-sulfanone (SN6)

According to General procedure SM A with bis(4-fluorophenyl)sulfane (2.22 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product SN6 as a yellow oil (2.28 g, 90% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.11 – 7.95 (m, 4H), 7.22 – 7.06 (m, 4H), 3.23 (brs, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.2 (d, $J = 255.1$ Hz), 139.3 (d, $J = 3.1$ Hz), 130.6 (d, $J = 9.5$ Hz), 116.4 (d, $J = 22.7$ Hz).

$^{19}$F NMR (376 MHz, CDCl$_3$) δ –105.6 (tt, $J = 8.2$, 4.8 Hz, 2F).

HRMS (ESI) $m/z$ calcd. for C$_{12}$H$_{10}$F$_2$NOS [M + H]$^+$ 254.0446, found 254.0444.

bis(4-Chlorophenyl)(imino)-λ6-sulfanone (SN7)

According to General procedure SM A with bis(4-chlorophenyl)sulfane (2.54 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product SN7 as a yellow powder (2.48 g, 87% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.01 – 7.92 (m, 4H), 7.49 – 7.42 (m, 4H), 3.15 (s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 141.6, 139.6, 129.6.

HRMS (ESI) $m/z$ calcd. for C$_{12}$H$_{10}$Cl$_2$NOS [M + H]$^+$ 285.9855, found 285.9854.
bis(4-Bromophenyl)(imino)-\(\lambda^6\)-sulfanone (SN8)

According to General procedure SM A with bis(4-bromophenyl)sulfane (3.42 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product SN8 as an orange powder (3.36 g, 90% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.85 (d, \(J = 8.3\) Hz, 4H), 7.58 (d, \(J = 8.3\) Hz, 4H), 3.27 (s, 1H).

\(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 142.1, 132.5, 129.5, 128.1.

HRMS (ESI) \(m/z\) calcd. for C\(_{12}\)H\(_{10}\)Br\(_2\)NOS [M + H]\(^+\) 373.8844, found 373.8844.

4,4'-Sulfonimidoyldibenzonitrile (N2)

According to General procedure SM A with 4,4'-sulfinyldibenzonitrile (2.52 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product N2 as a yellow powder (2.32 g, 87% yield).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.31 – 8.11 (m, 4H), 7.95 – 7.77 (m, 4H), 3.36 (s, 1H).

\(^1\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.6, 133.2, 128.8, 117.09, 117.05.

HRMS (ESI) \(m/z\) calcd. for C\(_{14}\)H\(_{10}\)N\(_3\)OS [M + H]\(^+\) 268.0539, found 268.0538.
Dimethyl 4,4'-sulfonimidoyldibenzoate (SN10)

According to General procedure SM A with dimethyl 4,4'-sulfinyldibenzoate (3.18 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product SN10 as a white powder (2.73 g, 82% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.19 – 8.06 (m, 8H), 3.94 (s, 6H), 3.28 (s, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.5, 146.7, 134.1, 130.5, 128.1, 52.7.

HRMS (ESI) $m/z$ calcd. for C$_{16}$H$_{16}$NO$_5$S [M + H]$^+$ 334.0744, found 334.0742.

bis(3,5-Dimethylphenyl)(imino)-λ6-sulfanone (SN11)

According to General procedure SM A with dimethyl 5,5'-sulfinylbis(1,3-dimethylbenzene) (2.58 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product SN11 as a white powder (1.97 g, 72% yield).

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (s, 4H), 7.11 (s, 2H), 2.98 (s, 1H), 2.34 (s, 12H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 143.2, 139.1, 134.2, 125.4, 21.2.

HRMS (ESI) $m/z$ calcd. for C$_{16}$H$_{20}$NO$_5$S [M + H]$^+$ 274.1260, found 274.1258.
The synthesis of SE40.

To a solution of "BuLi (5.0 mL, 12.0 mmol, 1.2 equiv., 2.4 M in hexane) in THF (5.0 mL) was added 3,3-dimethylbut-1-yne (984.0 mg, 12.0 mmol, 1.2 equiv.) dropwise with vigorously stirring at −78 °C under an argon atmosphere. After that, the mixture was warmed up to room temperature, stirred for another 30 min, and cooled down to −78 °C again. To this solution was added 3-phenylpropanal (1.34 g, 10.0 mmol, 1.0 equiv.) dropwise. The reaction mixture was warmed up to room temperature and stirred for another 2 h. The reaction was quenched with slow addition of ice. The organic phase was washed with brine, dried over Na2SO4, filtered, and concentrated to afford the crude product SE40-1 (2.05 g, 95% yield) as a colorless oil, which was immediately applied to the next step without further purification.

The crude SE40-1 (2.05 g) was dissolved in CH2Cl2 (20.0 mL) and cooled down to 0 °C. To this solution were added imidazole (775.2 mg, 11.4 mmol, 1.2 equiv.) and PPh3Br2 (4.79 g, 11.4 mmol, 1.2 equiv.) sequentially at that temperature and the reaction mixture was warmed up to room temperature and stirred for another 3 h. The mixture was filtered through a short pad of Celite and washed with Et2O. The combined organic phase was concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford the desired product SE40 (2.38 g, 90% yield) as a colorless oil.

6,6-Dimethyl-1-phenylhept-4-yn-3-ol (SE40-1)

\[ \text{SE40-1} \]

^1H NMR (400 MHz, CDCl3) δ 7.36 – 7.29 (m, 2H), 7.28 – 7.19 (m, 3H), 4.40 (q, \( J = 6.0 \text{ Hz}, 1\text{H} \)), 2.83 (t, \( J = 7.9 \text{ Hz}, 2\text{H} \)), 2.08 – 1.96 (m, 2H), 1.28 (s, 9H).
$^{13}$C NMR (100 MHz, CDCl$_3$) \( \delta \) 141.7, 128.5, 128.4, 125.9, 94.2, 79.5, 61.9, 39.8, 31.6, 31.1, 27.4.

(3-Bromo-6,6-dimethylhept-4-yn-1-yl)benzene (SE40)

![SE40](image)

$^1$H NMR (400 MHz, CDCl$_3$) \( \delta \) 7.39 – 7.30 (m, 2H), 7.28 – 7.18 (m, 3H), 4.53 (t, \( J = 6.7 \) Hz, 1H), 2.88 (t, \( J = 7.6 \) Hz, 2H), 2.44 – 2.22 (m, 2H), 1.27 (s, 9H).

$^{13}$C NMR (100 MHz, CDCl$_3$) \( \delta \) 140.4, 128.60, 128.55, 126.2, 96.7, 77.8, 41.8, 37.8, 33.5, 30.8, 27.6.

HRMS (ESI) \( m/z \) calcd. for C$_{15}$H$_{19}$ [M – Br]$^+$ 199.1481, found 199.1482.
The synthesis of α-bromo ketones.

**General procedure SM B:** To a solution of ketone (1.0 equiv.) in Et₂O was added bromine (10.0 equiv.) dropwise at room temperature and the reaction mixture was stirred for another 1 h. Upon completion (monitored by TLC), the reaction was quenched with saturated NaHCO₃ solution and extracted with Et₂O three times. The combined organic phase was washed with Na₂S₂O₃ solution and brine, then dried over Na₂SO₄ and concentrated to afford the residue. The residue was purified by flash column chromatography on silica gel to afford the desired product.

**2-Bromo-1-(3-methoxyphenyl)propan-1-one (SE44)**

![Structure of SE44](image)

According to **General procedure SM B** with 1-(3-methoxyphenyl)propan-1-one (1.64 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the product **SE44** as a colorless oil (2.01 g, 83% yield).

**¹H NMR** (400 MHz, CDCl₃) δ 7.64 – 7.59 (m, 1H), 7.57 (dd, J = 2.7, 1.6 Hz, 1H), 7.41 (t, J = 8.0 Hz, 1H), 7.15 (ddd, J = 8.2, 2.7, 0.9 Hz, 1H), 5.30 (q, J = 6.6 Hz, 1H), 3.88 (s, 3H), 1.92 (d, J = 6.6 Hz, 3H).

**¹³C NMR** (100 MHz, CDCl₃) δ 193.2, 159.9, 135.4, 129.7, 121.3, 120.2, 113.3, 55.5, 41.6, 20.2.

**HRMS** (ESI) m/z calcd. for C₁₀H₁₂BrO₂ [M + H]⁺ 243.0015, found 243.0015.

**1-(Benzo[d][1,3]dioxol-5-yl)-2-bromobutan-1-one (SE45)**

![Structure of SE45](image)
According to **General procedure SM B** with 1-(benzo[d][1,3]dioxol-5-yl)butan-1-one (1.92 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the product **SE45** as a colorless oil (1.92 g, 71% yield).

**1H NMR** (400 MHz, CDCl₃) δ 7.68 – 7.59 (m, 1H), 7.53 – 7.47 (m, 1H), 6.92 – 6.84 (m, 1H), 6.07 (s, 2H), 5.05 – 4.95 (m, 1H), 2.32 – 2.04 (m, 2H), 1.08 (t, J = 7.3 Hz, 3H).

**13C NMR** (100 MHz, CDCl₃) δ 191.5, 152.3, 148.4, 129.2, 125.2, 108.7, 108.1, 102.1, 49.0, 27.1, 12.2.

**HRMS** (ESI) m/z calcd. for C₁₁H₁₂BrO₃ [M + H]⁺ 270.9964 & 272.9944, found 270.9963 & 272.9942.

**2-Bromo-1-(3-(trifluoromethyl)phenyl)propan-1-one (SE46)**

![SE46](image)

According to **General procedure SM B** with 1-(3-(trifluoromethyl)phenyl)propan-1-one (2.02 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE46** as a colorless oil (2.49 g, 89% yield).

**1H NMR** (400 MHz, CDCl₃) δ 8.29 (s, 1H), 8.22 (d, J = 7.9 Hz, 1H), 7.86 (d, J = 7.8 Hz, 1H), 7.65 (t, J = 7.8 Hz, 1H), 5.30 (d, J = 6.8 Hz, 1H), 1.94 (d, J = 6.6 Hz, 3H).

**13C NMR** (100 MHz, CDCl₃) δ 192.0, 134.7, 132.0, 131.4 (q, J = 33.0 Hz), 130.0 (q, J = 3.6 Hz), 129.4, 125.8 (q, J = 3.8 Hz), 123.6 (q, J = 272.6 Hz), 41.2, 19.8.

**19F NMR** (376 MHz, CDCl₃) δ –62.9 (s, 3F).

**HRMS** (ESI) m/z calcd. for C₁₀H₉BrF₃O [M + H]⁺ 280.9783, found 280.9783.
2-Bromo-1-phenylpentan-1-one (SE50)

According to General procedure SM B with 1-phenylpentan-1-one (1.62 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product SE50 as a colorless oil (1.34 g, 56% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.10 – 7.99 (m, 2H), 7.68 – 7.58 (m, 1H), 7.57 – 7.46 (m, 2H), 5.18 (dd, $J$ = 7.8, 6.5 Hz, 1H), 2.27 – 2.08 (m, 2H), 1.70 – 1.36 (m, 2H), 1.01 (t, $J$ = 7.4 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 193.3, 134.5, 133.7, 128.9, 128.8, 47.1, 35.5, 20.8, 13.6.

HRMS (ESI) m/z calcd. for C$_{11}$H$_{14}$BrO [M + H]$^+$ 241.0223, found 241.0221.

2-Bromo-1-(thiophen-2-yl)propan-1-one (SE51)

According to General procedure SM B with 1-(thiophen-2-yl)propan-1-one (1.40 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the product SE51 as a colorless oil (1.70 g, 78% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.85 (dd, $J$ = 3.9, 1.2 Hz, 1H), 7.70 (dd, $J$ = 5.0, 1.1 Hz, 1H), 7.16 (dd, $J$ = 5.0, 3.9 Hz, 1H), 5.15 (q, $J$ = 6.7 Hz, 1H), 1.90 (d, $J$ = 6.7 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 186.9, 140.9, 134.9, 133.1, 128.3, 42.5, 20.4.

HRMS (ESI) m/z calcd. for C$_{7}$H$_{8}$BrOS [M + H]$^+$ 218.9474, found 218.9474.
2-Bromo-4-methylpentan-3-one (SE53)

\[
\begin{align*}
\text{SE53} & \quad \text{Me} \quad \text{O} \quad \text{Br} \\
\text{Me} & \quad \text{Me} \\
\end{align*}
\]

To a solution of lithium bis(trimethylsilyl)amide (LiHMDS) (2.0 mmol, 20 mol%) in THF was added 2-methylpentan-3-one (1.00 g, 10.0 mmol, 1.0 equiv.) dropwise at −78 °C. The reaction mixture was then warmed up to 0 °C and stirred for 10 min. After cooling down to −78 °C, bromine (1.60 g, 10.0 mmol, 1.0 equiv.) was added dropwise and the mixture was stirred for another 10 min at that temperature. Then the reaction mixture was quenched with saturated NaHCO₃ solution and extracted with Et₂O. The combined organic phase was washed with brine, dried over Na₂SO₄ and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/CH₂Cl₂ = 4/1) to yield the product SE53 as a colorless oil (1.37 g, 77% yield).

\[^1H\text{ NMR}\ (400 \text{ MHz, CDCl}_3) \delta 4.56 (d, J = 6.8 \text{ Hz, 1H}), 3.11 \text{ (hept, } J = 6.8 \text{ Hz, 1H),} 1.74 \text{ (d, } J = 6.8 \text{ Hz, 3H), 1.18 \text{ (d, } J = 6.7 \text{ Hz, 3H),} 1.14 \text{ (d, } J = 7.0 \text{ Hz, 3H).}
\]

\[^{13}C\text{ NMR}\ (100 \text{ MHz, CDCl}_3) \delta 207.9, 45.9, 37.5, 20.1, 19.5, 18.7.
\]

\[^\text{HRMS}\ (\text{ESI}) m/z \text{ calcd. for } \text{C}_6\text{H}_{11}\text{O} [\text{M – Br}]^+ 99.0804, \text{ found 99.0810.}\]
The synthesis of SE54.

To a mixture of cyclohexanecarbaldehyde (1.68 g, 15.0 mmol, 1.0 equiv.) and K₂CO₃ (0.41 g, 3.0 mmol, 0.2 equiv.) in Et₂O (30.0 mL) was added trimethylsilyl cyanide (1.63 g, 16.5 mmol, 1.1 equiv.) and the mixture was stirred at room temperature overnight. After completion (monitored by TLC), the reaction was quenched with saturated NaHCO₃ solution and extracted with Et₂O three times. The combined organic phase was washed with brine and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product SE54-1 as a colorless oil (1.90 g, 91% yield).

To a solution of SE54-1 (0.70 g, 5.0 mmol, 1.0 equiv.) in CH₂Cl₂ (25.0 mL) were added triphenylphosphine dibromide (2.53 g, 6.0 mmol, 1.2 equiv.) and imidazole (0.41 g, 6.0 mmol, 1.2 equiv.) with vigorous stirring at 0 °C under argon. Then the reaction mixture was allowed to warm to room temperature and stirred overnight. After completion (monitored by TLC), the reaction was quenched with saturated NH₄Cl solution and extracted with CH₂Cl₂ three times. The combined organic phase was washed with brine and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the product SE54 as a yellow oil (0.55 g, 55% yield).

2-Cyclohexyl-2-hydroxyacetonitrile (SE54-1)

\[ \text{SE54-1} \]

\(^1\text{H NMR}\) (400 MHz, CDCl₃) δ 4.25 (d, \(J = 6.4\) Hz, 1H), 3.95 (brs, 1H), 1.96 – 1.63 (m, 6H), 1.34 – 1.02 (m, 5H).

\(^13\text{C NMR}\) (100 MHz, CDCl₃) δ 119.5, 66.1, 42.1, 28.2, 27.9, 25.9, 25.43, 25.41.
2-Bromo-2-cyclohexylacetonitrile (SE54)

\[
\text{SE54}
\]

**\[^{1}H\text{ NMR}\]** (400 MHz, CDCl\textsubscript{3}) \( \delta \) 4.21 (d, \( J = 5.7 \text{ Hz} \), 1H), 2.10 – 1.93 (m, 2H), 1.92 – 1.87 (m, 3H), 1.77 – 1.68 (m, 1H), 1.41 – 1.12 (m, 5H).

**\[^{13}C\text{ NMR}\]** (100 MHz, CDCl\textsubscript{3}) \( \delta \) 116.6, 42.7, 34.3, 30.4, 29.5, 25.6, 25.5.

**HRMS (ESI)** \( m/z \) calcd. for C\textsubscript{8}H\textsubscript{13}BrN [M + H]\textsuperscript{+} 202.0226, found 202.0225.
The synthesis of α-bromo amides.

**General procedure SM C:** To a solution of Et₃N (1.52 g, 15.0 mmol, 1.5 equiv.) and amine (10.0 mmol, 1.0 equiv.) in THF (5.0 mL) was added 2-bromopropanoyl bromide (2.59 g, 12.0 mmol, 1.2 equiv.) dropwise at 0 °C. Then the reaction mixture was warmed up to room temperature and stirred for 3 h. After completion (monitored by TLC), the reaction was quenched with saturated NH₄Cl solution and extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na₂SO₄, filtrated and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel to afford the desired product.

**General procedure SM D:** To a solution of 2-bromo aliphatic acid (5.0 mmol, 1.0 equiv.) and Et₃N (1.52 g, 15.0 mmol, 3.0 equiv.) in THF (10.0 mL) was added pivaloyl chloride (603.0 mg, 5.0 mmol, 1.0 equiv.) dropwise at 0 °C. The reaction mixture was stirred at that temperature for 4 h, and then LiCl (0.21 g, 5.0 mmol, 1.0 equiv.) and morpholine (0.44 g, 5.0 mmol, 1.0 equiv.) were added sequentially. The mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with 1.0 M aqueous HCl solution and extracted with EtOAc three times. The combined organic phase was washed with 1.0 M aqueous NaOH solution and brine, dried over Na₂SO₄, filtrated and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel to afford the desired product.

**General procedure SM E:** To a solution of aliphatic acid (10.0 mmol, 1.0 equiv.) and hexamethylphosphoramide (HMPA) (0.5 mL) in THF (30.0 mL) was added lithium diisopropylamide (LDA) (11.0 mL, 11.0 mmol, 1.1 equiv., 1.0 M in THF) at −10 °C. After being stirred for 2 h at −10 °C, the reaction mixture was cooled down to −78 °C and treated with a solution of carbon tetrabromide (7.30 g, 22.0 mmol, 2.2 equiv.) in THF (3.0 mL). The solution was warmed up to room temperature over 1 h and stirred for another 1 h at room temperature. The reaction was quenched with brine, acidified with 2.0 M aqueous HCl solution, and extracted with Et₂O three times. The combined organic phase was dried over magnesium sulfate, filtered and concentrated to afford the crude bromo acid, which was immediately used in the next step without further
To a solution of the above bromo acid in CH$_2$Cl$_2$ (10.0 mL) was added oxalyl chloride (2.52 g, 20.0 mmol, 2.0 equiv.) and a drop of DMF at room temperature. The reaction mixture was stirred for 2 h at room temperature. Then the solvent was removed under reduced pressure to afford the bromo acyl chloride, which was immediately used in the next step without further purification.

To a solution of morpholine (1.74 g, 20.0 mmol, 2.0 equiv.) and Et$_3$N (2.02 g, 20.0 mmol, 2.0 equiv.) in CH$_2$Cl$_2$ (20.0 mL) was added the above bromo acidic chloride at 0 °C. The mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with brine and extracted with EtOAc three times. The combined organic phase was dried over magnesium sulfate, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel to yield the product.

2-Bromo-1-(indolin-1-yl)propan-1-one (SE55)

According to General procedure SM C with indoline (1.19 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product SE55 as a pink amorphous powder (2.20 g, 87% yield).

$^{1}$H NMR (400 MHz, CDCl$_3$) δ 8.28 (d, $J = 8.1$ Hz, 1H), 7.36 – 7.17 (m, 2H), 7.09 (t, $J = 7.5$ Hz, 1H), 4.59 (q, $J = 6.6$ Hz, 1H), 4.40 (td, $J = 10.0, 6.8$ Hz, 1H), 4.08 (td, $J = 10.0, 6.9$ Hz, 1H), 3.38 – 3.17 (m, 2H), 1.94 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.0, 142.7, 131.5, 127.7, 124.6, 124.4, 117.6, 47.8, 40.9, 28.1, 21.3.

HRMS (ESI) $m/z$ calcd. for C$_{11}$H$_{13}$BrNO [M + H]$^+$ 254.0175, found 254.0175.
2-Bromo-1-(5-(trifluoromethyl)indolin-1-yl)propan-1-one (SE57)

According to General procedure SM C with 5-(trifluoromethyl)indoline (1.87 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product SE57 as a pink amorphous powder (2.73 g, 85% yield).

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 8.34 (d, \( J = 8.5 \) Hz, 1H), 7.51 (d, \( J = 9.3 \) Hz, 1H), 7.46 (s, 1H), 4.58 (q, \( J = 6.6 \) Hz, 1H), 4.48 (td, \( J = 10.1, 6.9 \) Hz, 1H), 4.17 – 4.11 (m, 1H), 3.40 – 3.18 (m, 2H), 1.93 (d, \( J = 6.5 \) Hz, 3H).

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 167.6, 145.6, 132.2, 126.2 (dd, \( J = 64.8, 32.2 \) Hz), 125.3 (dd, \( J = 7.7, 3.9 \) Hz), 124.2 (q, \( J = 270.0 \) Hz), 122.0 – 120.7 (m), 117.2, 48.1, 40.5, 27.8, 21.1.

\( ^{19}\text{F NMR} \) (376 MHz, CDCl\(_3\)) \( \delta \) –61.8 (s, 3F).

HRMS (ESI) \( m/z \) calcd. for C\(_{12}\)H\(_{12}\)BrF\(_3\)NO [M + H]\(^+\) 322.0049, found 322.0049.

2-Bromo-N-methyl-N-phenylpropanamide (SE59)

According to General procedure SM C with N-methylaniline (1.07 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product SE59 as a brown amorphous powder (1.88 g, 78% yield).

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 7.50 – 7.33 (m, 3H), 7.33 – 7.19 (m, 2H), 4.26 (q, \( J = 6.7 \) Hz, 1H), 3.27 (s, 3H), 1.71 (d, \( J = 6.7 \) Hz, 3H).

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 169.6, 142.9, 123.0, 128.5, 127.1, 39.1, 38.1, 21.9.

HRMS (ESI) \( m/z \) calcd. for C\(_{10}\)H\(_{13}\)BrNO [M + H]\(^+\) 242.0175, found 242.0174.
2-Bromo-N-phenylpropanamide (SE60)

According to **General procedure SM C** with aniline (0.93 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE60** as a white amorphous powder (1.88 g, 83% yield).

**1H NMR** (400 MHz, CDCl₃) δ 8.46 (s, 1H), 7.57 (d, J = 7.9 Hz, 2H), 7.40 – 7.30 (m, 2H), 7.17 (t, J = 7.4 Hz, 1H), 4.66 – 4.53 (m, 1H), 2.01 – 1.89 (m, 3H).

**13C NMR** (100 MHz, CDCl₃) δ 168.0, 137.2, 129.1, 125.1, 120.5, 44.8, 22.6.

**HRMS** (ESI) m/z calcd. for C₉H₁₁BrNO [M + H]+ 228.0019, found 228.0018.

2-Bromo-1-morpholinopropan-1-one (E2)

According to **General procedure SM C** with morpholine (0.87 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **E2** as a colorless oil (2.03 g, 92% yield).

**1H NMR** (400 MHz, CDCl₃) δ 4.57 – 4.46 (m, 1H), 3.88 – 3.54 (m, 6H), 3.53 – 3.37 (m, 2H), 1.81 (t, J = 6.1 Hz, 3H).

**13C NMR** (100 MHz, CDCl₃) δ 167.7, 66.6, 66.3, 46.5, 42.6, 37.7, 21.5.

**HRMS** (ESI) m/z calcd. for C₇H₁₃BrNO₂ [M + H]+ 222.0124, found 222.0124.
2-Bromo-1-morpholinohexan-1-one (SE62)

According to **General procedure SM D** with 2-bromohexanoic acid (0.97 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE62** as a colorless oil (0.82 g, 62% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.33 (t, $J = 7.1$ Hz, 1H), 3.86 – 3.39 (m, 8H), 2.24 – 1.97 (m, 2H), 1.49 – 1.25 (m, 4H), 0.90 (t, $J = 6.9$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 66.7, 66.3, 46.6, 43.5, 42.6, 34.4, 29.7, 22.2, 13.9.

**HRMS** (ESI) $m/z$ calcd. for C$_{10}$H$_{19}$BrNO$_2$ [M + H]$^+$ 264.0594, found 264.0594.

2-Bromo-4-methyl-1-morpholinopentan-1-one (SE63)

According to **General procedure SM D** with 2-bromo-4-methylpentanoic acid (0.97 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE63** as a colorless oil (0.68 g, 52% yield).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.43 (dd, $J = 8.0$, 6.6 Hz, 1H), 3.87 – 3.41 (m, 8H), 2.06 – 1.71 (m, 3H), 1.01 – 0.86 (m, 6H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 167.4, 66.7, 66.3, 52.2, 46.6, 43.1, 41.8, 26.1, 22.5, 21.8.

**HRMS** (ESI) $m/z$ calcd. for C$_{10}$H$_{19}$BrNO$_2$ [M + H]$^+$ 264.0594, found 264.0594.
**2-Bromo-4-chloro-1-morpholinobutan-1-one (SE64)**

![SE64](image)

A mixture of 4-chlorobutanoic acid (1.22 g, 10.0 mmol, 1.0 equiv.), PBr₃ (0.54 g, 2.0 mmol, 0.2 equiv.) and Br₂ (3.20 g, 20.0 mmol, 2.0 equiv.) was refluxed overnight. After concentration under reduced pressure, the crude bromo acetyl bromide was obtained and dissolved in CH₂Cl₂ (10.0 mL). To this solution were added morpholine (1.04 g, 12.0 mmol, 1.2 equiv.) and Et₃N (3.03 g, 30.0 mmol, 3.0 equiv.) sequentially at room temperature and the reaction mixture was stirred overnight. The reaction was quenched with saturated NH₄Cl solution and extracted with CH₂Cl₂ three times. The combined organic phase was washed with brine, dried over Na₂SO₄, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford the desired product **SE64** as a colorless oil (1.10 g, 41% yield).

**¹H NMR** (400 MHz, CDCl₃) δ 4.70 (t, J = 6.9 Hz, 1H), 3.85 – 3.44 (m, 10H), 2.57 – 2.43 (m, 2H).

**¹³C NMR** (100 MHz, CDCl₃) δ 166.5, 66.6, 66.3, 46.6, 42.7, 42.5, 39.8, 36.9.

**HRMS** (ESI) m/z calcd. for C₈H₁₄BrClNO₂ [M + H]⁺ 269.9891, found 269.9890.

**2-(3-Bromo-4-morpholino-4-oxobutyl)isoindoline-1,3-dione (SE65)**

![SE65](image)

According to **General procedure SM D** with 2-bromo-4-(1,3-dioxoisindolin-2-y1)butanoic acid (1.56 g, 5.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the
product SE65 as a brown amorphous powder (0.78 g, 41% yield).

$^1$H NMR (400 MHz, CDCl₃) δ 7.88 – 7.83 (m, 2H), 7.77 – 7.71 (m, 2H), 4.49 – 4.38 (m, 1H), 3.92 – 3.43 (m, 10H), 2.83 – 2.60 (m, 1H), 2.38 – 2.19 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl₃) δ 168.4, 166.2, 134.1, 132.0, 123.3, 66.6, 66.4, 46.3, 42.6, 39.4, 35.3, 33.8.

HRMS (ESI) m/z calculated for C₁₆H₁₈BrN₂O₄ [M + H]⁺ 381.0444, found 381.0442.

2-Bromo-1-morpholino-4-phenoxybutan-1-one (SE66)

According to General procedure SM E with 4-phenoxybutanoic acid (1.80 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product SE66 as a red oil (1.96 g, 60% yield).

$^1$H NMR (400 MHz, CDCl₃) δ 7.34 – 7.24 (m, 2H), 6.98 (tt, $J = 7.4, 1.1$ Hz, 1H), 6.91 (dt, $J = 7.8, 1.0$ Hz, 2H), 4.80 (dt, $J = 7.9, 5.9$ Hz, 1H), 4.25 – 4.02 (m, 2H), 3.87 – 3.41 (m, 8H), 2.68 – 2.35 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl₃) δ 166.9, 158.6, 129.6, 121.2, 114.5, 66.72, 66.69, 63.9, 46.5, 42.8, 42.7, 34.3.

HRMS (ESI) m/z calculated for C₁₄H₁₉BrNO₃ [M + H]⁺ 328.0543, found 328.0543.

Ethyl 4-bromo-5-morpholino-5-oxopentanoate (SE67)

According to General procedure SM E with 5-ethoxy-5-oxopentanoic acid (1.60 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product SE67 as a red oil (1.14...
g, 37% yield).

**1H NMR** (400 MHz, CDCl₃) δ 4.71 – 4.61 (m, 1H), 4.14 (q, J = 7.2 Hz, 2H), 3.86 – 3.45 (m, 8H), 2.61 – 2.48 (m, 2H), 2.44 – 2.31 (m, 2H), 1.27 (t, J = 7.2 Hz, 3H).

**13C NMR** (100 MHz, CDCl₃) δ 172.8, 167.0, 66.6, 60.6, 46.5, 42.7, 42.3, 31.4, 29.7, 14.2.

**HRMS** (ESI) m/z calcd. for C₁₁H₁₉BrNO₄ [M + H]⁺ 308.0492, found 308.0491.

### 2-Bromo-1-morpholino-4-phenylbutan-1-one (SE68)

![SE68](image)

According to **General procedure SM E** with 4-phenylbutanoic acid (1.64 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE68** as a colorless oil (1.87 g, 60% yield).

**1H NMR** (400 MHz, CDCl₃) δ 7.40 – 7.12 (m, 5H), 4.28 – 4.23 (m, 1H), 3.91 – 3.28 (m, 8H), 2.88 – 2.75 (m, 2H), 2.56 – 2.27 (m, 2H).

**13C NMR** (100 MHz, CDCl₃) δ 167.2, 140.2, 128.6, 126.4, 66.7, 66.2, 52.6, 46.5, 42.2, 36.0, 33.3.

**HRMS** (ESI) m/z calcd. for C₁₄H₁₉BrNO₂ [M + H]⁺ 312.0594, found 312.0593.

### 2-Bromo-1-morpholinohex-5-en-1-one (SE69)

![SE69](image)

According to **General procedure SM E** with hex-5-enoic acid (1.14 g, 10.0 mmol, 1.0 equiv.), the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **SE69** as a red oil (1.49 g, 57% yield).
yield).

$^1\text{H NMR}$ (400 MHz, CDCl$_3$) $\delta$ 5.81 – 5.63 (m, 1H), 5.09 – 4.93 (m, 2H), 4.38 – 4.28 (m, 1H), 3.82 – 3.32 (m, 8H), 2.26 – 2.07 (m, 4H).

$^{13}\text{C NMR}$ (100 MHz, CDCl$_3$) $\delta$ 167.2, 136.6, 116.2, 66.6, 66.3, 46.5, 42.6, 42.4, 33.5, 31.4.

HRMS (ESI) $m/z$ calcd. for C$_{10}$H$_{17}$BrNO$_2$ [M + H]$^+$ 262.0437, found 262.0437.
Enantioconvergent N-alkylation reactions.

All the racemic products were prepared by S_N2 reaction without further optimization.

**General procedure:**

\[
\text{Br/Cl} + \text{R'S-NH} \xrightarrow{\text{KOH (3.0 equiv.)}} \text{R^1-N=S-Ar} \]

To a mixture of alkyl halides (3.0 equiv.) and sulfoximine (1.0 equiv.) in DMF was added KOH (3.0 equiv.). The reaction mixture was then warmed up to 60 °C and stirred for 3–12 h. After cooling to room temperature, the solution was diluted with H_2O and extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na_2SO_4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired products.

**Enantioconvergent N-alkylation: scope of sulfoximines. (Figure 2B)**

**General procedure A:**

\[
\text{R^2=NHAr} + \text{R'Br/Cl} \xrightarrow{\text{CuTc (10 mol%), L*7 (10 mol%), Cs_2CO_3 (4.0 equiv.)}} \text{R^1-N=S-Ar} \]

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone (43.4 mg, 0.20 mmol, 1.0 equiv.), CuTc (3.9 mg, 0.020 mmol, 10 mol%), chiral ligand L*7 (27.3 mg, 0.020 mmol, 10 mol%), Cs_2CO_3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et_2O (2.0 mL). To this solution was added alkyl halide (0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 30 to 96 h. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc. The mixture was then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.
General procedure B:

\[
R^1\begin{array}{c}
\text{Br} \\
\end{array} + \begin{array}{c}
\text{SO} \\
\text{Ar} \\
\text{NH} \\
\end{array} \rightarrow \begin{array}{c}
\text{N} \\
\text{Ar} \\
\end{array}
\]

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfoximine (0.20 mmol, 1.0 equiv.), CuTc (3.9 mg, 0.020 mmol, 10 mol%), chiral ligand L*7 (27.3 mg, 0.020 mmol, 10 mol%), Cs2CO3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et2O (2.0 mL). To this solution was added benzyl bromide (0.30 mmol, 1.5 equiv.) and the reaction mixture was stirred at room temperature for 3 to 5 d. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, then filtered through a pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

\((S)-\text{Diphenyl((1-phenylethyl)imino)-}\lambda^6-\text{sulfanone (1)}\)

According to General procedure A with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 1 as a colorless oil (51.8 mg, 81% yield, 97% ee).

\([\alpha]_D^{20} = -37 (c 1.0, \text{CH}_2\text{Cl}_2).\)

HPLC analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, \(\lambda = 230\) nm), \(t_R\) (major) = 38.53 min, \(t_R\) (minor) = 49.20 min.

\(^1\text{H NMR}\) (400 MHz, CDCl3) \(\delta 8.13 – 8.04\) (m, 2H), 7.95 – 7.79 (m, 2H), 7.58 – 7.44 (m, 6H), 7.43 – 7.37 (m, 2H), 7.37 – 7.30 (m, 2H), 7.27 – 7.20 (m, 1H), 4.44 (q, \(J = 6.6\) Hz, 1H), 1.59 (d, \(J = 6.6\) Hz, 3H).
\[^{13}\text{C NMR}\ (100 \text{ MHz}, \text{CDCl}_3) \delta 147.5, 141.5, 140.8, 132.4, 132.3, 129.1, 129.0, 128.9, 128.5, 128.2, 126.4, 126.2, 54.2, 28.2.\]

HRMS (ESI) \(m/z\) calcd. for C\(_{20}\)H\(_{20}\)NOS [M + H]\(^{+}\) 322.1260, found 322.1258.

According to General procedure A with (1-chloroethyl)benzene (28.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product as a colorless oil (45.6 mg, 71% yield, 93% ee).

HPLC analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, \(\lambda = 254\) nm), \(t_R\) (major) = 29.91 min, \(t_R\) (minor) = 44.48 min.

\((R)\)-Diphenyl((1-phenylethyl)imino)-\(\lambda^6\)-sulfanone (\((R)-1\))

According to General procedure A with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand L*7' for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product \((R)-1\) as a colorless oil (63.6 mg, 99% yield, 98% ee).

HPLC analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, \(\lambda = 254\) nm), \(t_R\) (minor) = 24.87 min, \(t_R\) (major) = 27.64 min.

\((S)\)-bis(4-Methoxyphenyl)((1-phenylethyl)imino)-\(\lambda^6\)-sulfanone (2)

According to General procedure B with iminobis(4-methoxyphenyl)-\(\lambda^6\)-sulfanone (55.4 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column...
chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 2 as a colorless oil (75.6 mg, 99% yield, 98% ee).

$[\alpha]_{D}^{20} = -32$ (c 1.6, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel ID (hexane/PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 13.36 min, $t_R$ (minor) = 17.99 min.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.99 – 7.91 (m, 2H), 7.75 – 7.67 (m, 2H), 7.46 – 7.39 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 1H), 6.96 – 6.89 (m, 2H), 6.88 – 6.79 (m, 2H), 4.37 (q, $J = 6.6$ Hz, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 1.54 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.8, 162.7, 147.9, 133.7, 132.7, 130.9, 130.4, 128.3, 126.4, 114.4, 114.3, 55.7, 55.6, 54.2, 28.4.

**HRMS** (ESI) $m/z$ calcd. for C$_{22}$H$_{24}$NO$_3$S [M + H]$^+$ 382.1471, found 382.1467.

(S)-di([1,1'-Biphenyl]-4-yl)(1-phenylethyl)imino)-$\lambda^6$-sulfanone (3)

According to **General procedure B** with di([1,1'-biphenyl]-4-yl)(imino)-$\lambda^6$-sulfanone (73.8 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 3 as a colorless oil (55.8 mg, 59% yield, 97% ee).

$[\alpha]_{D}^{20} = -9$ (c 2.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel IE (hexane/PrOH = 80/20, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 12.65 min, $t_R$ (minor) = 16.82 min.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.20 – 8.11 (m, 2H), 7.95 – 7.88 (m, 2H), 7.73 – 7.66 (m, 2H), 7.63 – 7.52 (m, 6H), 7.50 – 7.42 (m, 6H), 7.42 – 7.37 (m, 2H), 7.36 – 7.30 (m, 2H), 7.26 – 7.20 (m, 1H), 4.50 (q, $J = 6.6$ Hz, 1H), 1.62 (d, $J = 6.6$ Hz, 3H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 147.7, 145.5, 145.3, 140.3, 139.62, 139.59, 129.6, 129.12, 129.10, 129.06, 128.48, 128.46, 128.3, 127.91, 127.89, 127.5, 127.4, 126.5, 126.4, 54.4, 28.4.

HRMS (ESI) \(m/z\) calcd. for C\(_{32}\)H\(_{28}\)NOS [M + H]\(^+\) 474.1886, found 474.1884.

\((S)-\text{bis}(4-(\text{tert-Butyl})\text{phenyl})((1\text{-phenylethyl})\text{imino})-\lambda^6\text{-sulfanone (4)}\)

According to **General procedure B** with bis(4-(tert-butyl)phenyl)(imino)-\(\lambda^6\)-sulfanone (65.8 mg, 0.20 mmol, 1.0 equiv.) at 0 °C for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 4 as a colorless oil (77.9 mg, 90% yield, 92% ee).

\([\alpha]_{D20} = -40\) (c 0.6, CH\(_2\)Cl\(_2\)).

**HPLC** analysis: Chiralcel IC (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, \(\lambda = 254\) nm), \(t_R\) (major) = 5.80 min, \(t_R\) (minor) = 7.26 min.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.01 – 7.93 (m, 2H), 7.76 – 7.69 (m, 2H), 7.51 – 7.45 (m, 2H), 7.45 – 7.40 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.16 (m, 1H), 4.41 (q, \(J = 6.6\) Hz, 1H), 1.55 (d, \(J = 6.6\) Hz, 3H), 1.30 (s, 9H), 1.28 (s, 9H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 156.0, 155.9, 147.9, 138.8, 137.9, 128.8, 128.4, 128.2, 126.4, 126.3, 126.2, 126.1, 54.1, 35.2, 35.1, 31.23, 31.21, 28.3.

HRMS (ESI) \(m/z\) calcd. for C\(_{28}\)H\(_{36}\)NOS [M + H]\(^+\) 434.2512, found 434.2508.
(S)-bis(4-Cyclohexylphenyl)((1-phenylethyl)imino)-λ⁶-sulfanone (5)

According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and bis(4-cyclohexylphenyl)(imino)-λ⁶-sulfanone (76.2 mg, 0.20 mmol, 1.0 equiv.) for 3 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 5 as a colorless oil (50.4 mg, 52% yield, 92% ee).

[α]D²⁰ = −17 (c 2.0, CH₂Cl₂).

**HPLC** analysis: Chiralcel IC (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), tₚ (major) = 7.41 min, tₚ (minor) = 9.35 min.

**¹H NMR** (400 MHz, CDCl₃) δ 7.97 – 7.90 (m, 2H), 7.75 – 7.66 (m, 2H), 7.44 – 7.38 (m, 2H), 7.29 (m, 4H), 7.23 – 7.15 (m, 3H), 4.39 (q, J = 6.6 Hz, 1H), 2.59 – 2.41 (m, 2H), 1.90 – 1.68 (m, 10H), 1.54 (d, J = 6.6 Hz, 3H), 1.44 – 1.13 (m, 10H).

**¹³C NMR** (100 MHz, CDCl₃) δ 152.9, 152.8, 147.9, 139.1, 138.3, 129.1, 128.6, 128.2, 127.6, 126.4, 126.3, 54.2, 44.61, 44.56, 34.3, 34.2, 28.3, 26.8, 26.1.

**HRMS** (ESI) m/z calcd. for C₃₂H₄₀NOS [M + H]⁺ 486.2825, found 486.2822.

(S)-bis(4-Fluorophenyl)((1-phenylethyl)imino)-λ⁶-sulfanone (6)

According to **General procedure B** with bis(4-fluorophenyl)(imino)-λ⁶-sulfanone (50.6 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column
chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 6 as a colorless oil (58.5 mg, 82% yield, 98% ee).

$[\alpha]_D^{20} = -44$ (c 0.3, CH$_2$Cl$_2$).

HPLC analysis: Chiralcel IG (hexane/iPrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 8.93 min, $t_R$ (minor) = 10.40 min.

$^1$H NMR (400 MHz, $\delta$ 8.08 – 7.99 (m, 2H), 7.82 – 7.72 (m, 2H), 7.42 – 7.34 (m, 2H), 7.30 (m, 2H), 7.24 – 7.19 (m, 1H), 7.18 – 7.11 (m, 2H), 7.08 – 7.00 (m, 2H), 4.37 (q, $J = 6.6$ Hz, 1H), 1.54 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 165.3 (d, $J = 254.7$ Hz), 165.2 (d, $J = 254.6$ Hz), 147.3, 137.5 (d, $J = 2.8$ Hz), 136.8 (d, $J = 3.2$ Hz), 131.7 (d, $J = 9.4$ Hz), 131.2 (d, $J = 9.4$ Hz), 128.4, 126.7, 126.3, 116.6, 116.3, 54.4, 28.3.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –106.0 (tt, $J = 8.2$, 5.2 Hz, 1F), –106.1 (tt, $J = 8.3$, 5.0 Hz, 1F).

HRMS (ESI) $m/z$ calcd. for C$_{20}$H$_{18}$F$_2$NOS [M + H]$^+$ 358.1072, found 358.1067.

(S)-bis(4-Chlorophenyl)((1-phenylethyl)imino)-$\lambda^6$-sulfanone (7)

According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and bis(4-chlorophenyl)(imino)-$\lambda^6$-sulfanone (57.0 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 7 as a colorless oil (56.0 mg, 72% yield, 94% ee).

$[\alpha]_D^{20} = -18$ (c 2.0, CH$_2$Cl$_2$).

HPLC analysis: Chiralcel IG (hexane/iPrOH = 95/5, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 10.20 min, $t_R$ (minor) = 13.26 min.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.99 – 7.91 (m, 2H), 7.74 – 7.65 (m, 2H), 7.47 – 7.41 (m, 2H), 7.40 – 7.34 (m, 3H), 7.33 – 7.27 (m, 3H), 7.24 – 7.18 (m, 1H), 4.38 (q, $J$ = 6.6 Hz, 1H), 1.54 (d, $J$ = 6.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.1, 139.9, 139.4, 139.27, 139.25, 130.4, 130.0, 129.5, 128.4, 126.7, 126.3, 54.4, 28.2.

HRMS (ESI) $m$/z calcd. for C$_{20}$H$_{18}$Cl$_2$NOS [M + H]$^+$ 390.0481, found 390.0477.

(S)-bis(4-Bromophenyl)((1-phenylethyl)imino)-$\lambda^6$-sulfanone (8)

According to General procedure A with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and bis(4-bromophenyl)(imino)-$\lambda^6$-sulfanone (74.6 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 8 as a colorless oil (44.8 mg, 47% yield, 96% ee).

$[\alpha]_{D}^{20} = -3$ (c 1.9, CH$_2$Cl$_2$).

HPLC analysis: Chiralcel IG (hexane/iPrOH = 90/10, flow rate 1.0 mL/min, $\lambda$ = 254 nm), $t_R$ (major) = 8.39 min, $t_R$ (minor) = 10.53 min.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.90 – 7.83 (m, 2H), 7.66 – 7.58 (m, 4H), 7.54 – 7.47 (m, 2H), 7.39 – 7.34 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.18 (m, 1H), 4.37 (q, $J$ = 6.6 Hz, 1H), 1.54 (d, $J$ = 6.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 147.1, 140.5, 139.8, 132.6, 130.6, 130.1, 128.4, 128.0, 127.9, 126.7, 126.3, 54.4, 28.2.

HRMS (ESI) $m$/z calcd. for C$_{20}$H$_{18}$Br$_2$NOS [M + H]$^+$ 477.9470, found 477.9469.
(S)-4,4’-((1-Phenylethyl)sulfonimidoyl)dibenzonitrile (9)

According to **General procedure B** with 4,4'-sulfonimidoyldibenzoate N2 (53.4 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product 9 as a colorless oil (33.4 mg, 45% yield, 90% ee).

\[ \alpha \]D\textsubscript{20} = −3 (c 1.7, CH\textsubscript{2}Cl\textsubscript{2}).

**HPLC** analysis: Chiralcel IA (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, \( \lambda \) = 254 nm), \( t_R \) (minor) = 12.02 min, \( t_R \) (major) = 14.15 min.

\(^1\text{H NMR}\) (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.18 – 8.10 (m, 2H), 7.89 – 7.82 (m, 2H), 7.83 – 7.75 (m, 2H), 7.69 – 7.62 (m, 2H), 7.35 – 7.25 (m, 4H), 7.26 – 7.17 (m, 1H), 4.41 (q, \( J \) = 6.6 Hz, 1H), 1.55 (d, \( J \) = 6.6 Hz, 3H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl\textsubscript{3}) \( \delta \) 146.3, 145.0, 144.8, 133.2, 133.1, 129.7, 129.3, 128.6, 127.1, 126.2, 117.3, 116.9, 116.7, 54.5, 27.9.

**HRMS** (ESI) \( m/z \) calcd. for C\textsubscript{22}H\textsubscript{18}N\textsubscript{3}OS [M + H]\textsuperscript{+} 372.1165, found 372.1161.

Dimethyl 4,4’-((1-phenylethyl)sulfonimidoyl)(S)-dibenzoate (10)

According to **General procedure B** with Dimethyl 4,4'-sulfonimidoyldibenzoate (66.6 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the product 10 as a colorless oil (40.2 mg, 46% yield, 97% ee).
\[ \alpha \]D^{20} = -30 \ (c \ 0.3, \ \text{CH}_2\text{Cl}_2). 

**HPLC** analysis: Chiralcel IC (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, \( \lambda = 254 \) nm), \( t_R \) (major) = 20.26 min, \( t_R \) (minor) = 26.54 min.

**H NMR** (400 MHz, CDCl\textsubscript{3}) \( \delta \) 8.18 – 8.07 (m, 4H), 8.02 (d, \( J = 8.5 \) Hz, 2H), 7.90 – 7.82 (m, 2H), 7.41 – 7.35 (m, 2H), 7.33 – 7.27 (m, 2H), 7.24 – 7.17 (m, 1H), 4.40 (q, \( J = 6.6 \) Hz, 1H), 3.93 (s, 3H), 3.91 (s, 3H), 1.55 (d, \( J = 6.6 \) Hz, 3H).

**C NMR** (100 MHz, CDCl\textsubscript{3}) \( \delta \) 165.8, 147.0, 145.1, 144.7, 134.0, 133.9, 130.5, 130.4, 129.1, 128.7, 128.4, 126.8, 126.3, 54.5, 52.8, 52.7, 28.1.

**HRMS** (ESI) \( m/z \) calcd. for C\textsubscript{24}H\textsubscript{24}NO\textsubscript{5}S [M + H]\(^+\) 438.1370, found 438.1367.

(S)-bis(3,5-Dimethylphenyl)((1-phenylethyl)imino)-\( \lambda^6 \)-sulfanone (11)

According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and bis(3,5-dimethylphenyl)(imino)-\( \lambda^6 \)-sulfanone (54.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 11 as a colorless oil (45.2 mg, 60% yield, 90% ee).

\[ \alpha \]D^{20} = -33 \ (c \ 2.0, \ \text{CH}_2\text{Cl}_2). 

**HPLC** analysis: Chiralcel IE (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, \( \lambda = 254 \) nm), \( t_R \) (major) = 7.99 min, \( t_R \) (minor) = 8.95 min.

**H NMR** (400 MHz, CDCl\textsubscript{3}) \( \delta \) 7.66 – 7.60 (m, 2H), 7.43 – 7.37 (m, 4H), 7.33 – 7.28 (m, 2H), 7.23 – 7.17 (m, 1H), 7.13 – 7.09 (m, 1H), 7.08 – 7.03 (m, 1H), 4.37 (q, \( J = 6.6 \) Hz, 1H), 2.35 (s, 6H), 2.24 (s, 6H), 1.56 (d, \( J = 6.6 \) Hz, 3H).

**C NMR** (100 MHz, CDCl\textsubscript{3}) \( \delta \) 147.9, 141.3, 140.7, 139.04, 138.97, 134.2, 134.0, 128.2, 126.6, 126.5, 126.4, 125.9, 54.3, 28.2, 21.4, 21.3.

**HRMS** (ESI) \( m/z \) calcd. for C\textsubscript{24}H\textsubscript{28}NOS [M + H]\(^+\) 378.1886, found 378.1882.
Enantioconvergent N-alkylation: scope of benzyl and propargyl halides. (Figure 2B)

**General procedure C:**

![Chemical structure](image)

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ⁶-sulfanone (43.4 mg, 0.20 mmol, 1.0 equiv.), CuTc (3.9 mg, 0.020 mmol, 10 mol%), chiral ligand L⁶* (27.3 mg, 0.020 mmol, 10 mol%), Cs₂CO₃ (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et₂O (2.0 mL). To this solution was added alkyl halide (0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at 0 °C for 30–96 h. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

**(S)-Diphenyl((1-(p-tolyl)ethyl)imino)-λ⁶-sulfanone (12)**

According to **General procedure A** with 1-(1-bromoethyl)-4-methylbenzene (39.6 mg, 0.20 mmol, 1.0 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 12 as a colorless oil (60.3 mg, 90% yield, >99% ee).

[α]D²₀ = −50 (c 1.0, CH₂Cl₂).

**HPLC** analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm),

$t_R$ (major) = 44.39 min, $t_R$ (minor) = 66.88 min.
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 – 7.98 (m, 2H), 7.89 – 7.77 (m, 2H), 7.52 – 7.40 (m, 4H), 7.40 – 7.34 (m, 2H), 7.31 (d, $J = 8.1$ Hz, 2H), 7.11 (d, $J = 7.8$ Hz, 2H), 4.36 (q, $J = 6.6$ Hz, 1H), 2.33 (s, 3H), 1.54 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 144.6, 141.6, 140.8, 135.8, 132.3, 132.2, 129.1, 129.03, 128.97, 128.9, 128.5, 126.1, 54.0, 28.3, 21.1.

HRMS (ESI) $m/z$ calcd. for C$_{21}$H$_{22}$NOS [M + H]$^+$ 336.1417, found 336.1415.

(S)-Diphenyl((1-(o-tolyl)ethyl)imino)-$\lambda^6$-sulfanone (13)

![Chemical Structure](image)

According to General procedure A with 1-(1-bromoethyl)-2-methylbenzene (39.6 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 13 as a colorless oil (61.0 mg, 91% yield, >99% ee).

$[\alpha]_{D}^{20} = 7$ (c 1.0, CH$_2$Cl$_2$).

HPLC analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, $\lambda = 230$ nm), $t_R$ (major) = 32.31 min, $t_R$ (minor) = 47.47 min.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.16 – 8.06 (m, 2H), 7.92 (dd, $J = 7.8$, 1.4 Hz, 1H), 7.83 – 7.74 (m, 2H), 7.58 – 7.42 (m, 4H), 7.40 – 7.27 (m, 3H), 7.15 (td, $J = 7.4$, 1.5 Hz, 1H), 7.05 (dd, $J = 7.7$, 1.4 Hz, 1H), 4.65 (q, $J = 6.5$ Hz, 1H), 2.04 (s, 3H), 1.54 (d, $J = 6.5$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 145.9, 141.5, 141.0, 133.4, 132.4, 132.2, 129.9, 129.02, 128.99, 128.9, 128.4, 126.6, 126.3, 126.1, 50.3, 27.3, 19.0.

HRMS (ESI) $m/z$ calcd. for C$_{21}$H$_{22}$NOS [M + H]$^+$ 336.1417, found 336.1415.
(S)-((1-(4-Fluorophenyl)ethyl)imino)diphenyl-λ₆-sulfanone (14)

According to General procedure A with 1-(1-bromoethyl)-4-fluorobenzene (40.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 14 as a colorless oil (63.1 mg, 93% yield, 96% ee).

[α]_D^{20} = −58 (c 1.0, CH₂Cl₂).

HPLC analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), t_R (major) = 40.70 min, t_R (minor) = 50.64 min.

_1^H NMR (400 MHz, CDCl₃) δ 8.12 – 8.00 (m, 2H), 7.91 – 7.81 (m, 2H), 7.58 – 7.45 (m, 4H), 7.44 – 7.34 (m, 4H), 7.00 (t, J = 8.6 Hz, 2H), 4.41 (q, J = 6.6 Hz, 1H), 1.56 (d, J = 6.6 Hz, 3H).

_1^3C NMR (100 MHz, CDCl₃) δ 161.5 (d, J = 243.7 Hz), 143.3 (d, J = 3.0 Hz), 141.3, 140.8, 132.4, 132.3, 129.09, 129.07, 128.8, 128.4, 127.7 (d, J = 7.8 Hz), 114.8 (d, J = 21.0 Hz), 53.5, 28.2.

_1^9F NMR (376 MHz, CDCl₃) δ –117.2 (td, J = 8.9, 4.4 Hz, 1F).

HRMS (ESI) m/z calcd. for C₂₀H₁₉FNOS [M + H]^+ 340.1166, found 340.1164.

(S)-((1-(4-Chlorophenyl)ethyl)imino)diphenyl-λ₆-sulfanone (15)

According to General procedure A with 1-(1-bromoethyl)-4-chlorobenzene (43.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 15 as a colorless oil (66.0 mg, 93% yield, >99% ee).

[α]_D^{20} = −118 (c 1.0, CH₂Cl₂).
HPLC analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm),
$t_R$ (major) = 41.11 min, $t_R$ (minor) = 55.00 min.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.06 (d, $J = 8.1$ Hz, 2H), 7.85 (d, $J = 7.9$ Hz, 2H), 7.57 – 7.45 (m, 4H), 7.46 – 7.32 (m, 4H), 7.29 (d, $J = 8.1$ Hz, 2H), 4.39 (q, $J = 6.6$ Hz, 1H), 1.56 (d, $J = 6.5$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.1, 141.3, 140.7, 132.5, 132.4, 131.9, 129.1, 128.8, 128.4, 128.3, 127.7, 53.6, 28.1.

HRMS (ESI) m/z calcd. for C$_{20}$H$_{19}$ClNOS [M + H]$^+$ 356.0870, found 356.0868.

$(S)$-((1-(4-Bromophenyl)ethyl)imino)diphenyl-$\lambda^6$-sulfanone (16)

According to General procedure A with 1-bromo-4-(1-bromoethyl)benzene (52.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 16 as a colorless oil (66.2 mg, 83% yield, 97% ee).

$[\alpha]_D^{20} = -123$ (c 1.0, CH$_2$Cl$_2$).

HPLC analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm),
$t_R$ (major) = 43.10 min, $t_R$ (minor) = 60.89 min.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.05 (d, $J = 8.0$ Hz, 2H), 7.85 (d, $J = 7.6$ Hz, 2H), 7.36 (m, 8H), 7.32 (dd, $J = 8.4$, 2.0 Hz, 2H), 4.38 (q, $J = 6.6$ Hz, 1H), 1.55 (d, $J = 6.7$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.6, 141.3, 140.7, 132.5, 132.4, 131.2, 129.1, 128.8, 128.4, 128.1, 120.0, 53.7, 28.1.

HRMS (ESI) m/z calcd. for C$_{20}$H$_{19}$BrNOS [M + H]$^+$ 400.0365 & 402.0345, found 400.0364 & 402.0341.
(S)-((1-(4-Iodophenyl)ethyl)imino)diphenyl-λ⁶-sulfanone (17)

According to General procedure A with 1-(1-bromoethyl)-4-iodobenzene (62.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 17 as a yellow oil (71.5 mg, 80% yield, 98% ee).

$[\alpha]_D^{20} = -76$ (c 1.0, CH₂Cl₂).

HPLC analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm),
$\tau_R$ (major) = 45.58 min, $\tau_R$ (minor) = 62.72 min.

$^1$H NMR (400 MHz, CDCl₃) δ 8.08 – 7.97 (m, 2H), 7.84 – 7.78 (m, 2H), 7.64 – 7.58 (m, 2H), 7.55 – 7.43 (m, 4H), 7.42 – 7.34 (m, 2H), 7.20 – 7.14 (m, 2H), 4.33 (q, $J = 6.6$ Hz, 1H), 1.51 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl₃) δ 147.3, 141.2, 140.7, 137.2, 132.5, 132.4, 129.1, 128.8, 128.4, 91.6, 53.8, 28.0.

HRMS (ESI) m/z calcd. for C₂₀H₁₉INOS [M + H]$^+$ 448.0227, found 448.0225.

(S)-((1-(3-Iodophenyl)ethyl)imino)diphenyl-λ⁶-sulfanone (18)

According to General procedure A with 1-(1-bromoethyl)-3-iodobenzene (62.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 18 as a yellow oil (71.5 mg, 80% yield, 97% ee).

$[\alpha]_D^{20} = -16$ (c 0.9, CH₂Cl₂).

HPLC analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, λ = 230 nm),
$\tau_R$ (major) = 39.88 min, $\tau_R$ (minor) = 46.09 min.
\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta 8.06\) (d, \(J = 6.4\) Hz, 2H), \(7.84\) (d, \(J = 7.4\) Hz, 2H), \(7.75\) (s, 1H), \(7.60 - 7.31\) (m, 8H), \(7.05\) (t, \(J = 7.7\) Hz, 1H), \(4.35\) (q, \(J = 6.6\) Hz, 1H), \(1.55\) (d, \(J = 6.6\) Hz, 3H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta 148.8, 140.1, 139.6, 134.4, 134.3, 131.5, 131.4, 129.0, 128.1, 128.0, 127.7, 127.3, 124.6, 93.3, 52.5, 26.9.

\text{HRMS} \text{ (ESI)} \ m/z \text{ calcd. for C}_{20}H_{19}INOS [M + H]\(^+\) 448.0227, found 448.0225.

\((S)-\text{Diphenyl((1-(4-(trifluoromethyl)phenyl)ethyl)imino)-}\lambda^6\text{-sulfanone (19)}\)

\[
\begin{align*}
\text{F}_3\text{C} & \quad \text{N} & \quad \text{S}\text{Ph} \\
\text{Ph} & \quad \text{Me} & \quad \text{O}
\end{align*}
\]

According to \textbf{General procedure A} with 1-(1-bromoethyl)-4-(trifluoromethyl)benzene (50.4 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 19 as a colorless oil (73.9 mg, 95% yield, 98% ee).

\(\left[\alpha\right]_{D}^{20} = -11\) (c 1.0, CH\(_2\)Cl\(_2\)).

\text{HPLC} \text{ analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.3 mL/min, } \lambda = 230 \text{ nm),}

\(t_R \) (major) = 49.46 min, \(t_R \) (minor) = 58.97 min.

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta 8.06\) (d, \(J = 7.6\) Hz, 2H), \(7.84\) (d, \(J = 8.0\) Hz, 2H), \(7.60 - 7.45\) (m, 8H), \(7.45 - 7.37\) (m, 2H), \(4.46\) (q, \(J = 6.6\) Hz, 1H), \(1.58\) (d, \(J = 6.5\) Hz, 3H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta 151.5\) (d, \(J = 1.1\) Hz), \(141.2, 140.6, 132.5, 132.4, 129.14, 129.12, 128.7, 128.4, 128.2\) (q, \(J = 24.0\) Hz), \(126.6, 125.2\) (q, \(J = 3.8\) Hz), \(124.4\) (q, \(J = 270.0\) Hz), \(53.8, 28.0\).

\(^{19}\text{F NMR}\) (376 MHz, CDCl\(_3\)) \(\delta -62.2\) (s, 3F).

\text{HRMS} \text{ (ESI)} \ m/z \text{ calcd. for C}_{21}H_{19}F_3NOS [M + H]\(^+\) 390.1134, found 390.1132.
(S)-Diphenyl((1-(3-(trifluoromethyl)phenyl)ethyl)imino)-λ6-sulfanone (20)

\[
\text{F}_3\text{C} \quad \begin{array}{c}
\text{N} \\
\text{S} \\
\text{Ph}
\end{array} \quad \text{Me} \quad \text{O}
\]

According to **General procedure A** with 1-(1-bromoethyl)-3-(trifluoromethyl)benzene (52.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **20** as a colorless oil (73.9 mg, 95% yield, 98% ee).

\[\alpha\]D\text{20}^20 = −23 (c 1.0, CH\text{2Cl}_2).

**HPLC** analysis: Chiralcel IA (hexane/PrOH = 99/1, flow rate 0.3 mL/min, λ = 230 nm), \(t_R\) (major) = 43.16 min, \(t_R\) (minor) = 50.19 min.

\(^1H\text{ NMR}\) (400 MHz, CDCl\text{3}) \(\delta \) 8.10 – 8.02 (m, 2H), 7.88 – 7.80 (m, 2H), 7.70 – 7.61 (m, 2H), 7.56 – 7.37 (m, 8H), 4.47 (q, \(J = 6.6\) Hz, 1H), 1.59 (d, \(J = 6.6\) Hz, 3H).

\(^13C\text{ NMR}\) (100 MHz, CDCl\text{3}) \(\delta \) 148.4, 141.2, 140.6, 132.5, 132.4, 130.3 (q, \(J = 31.9\) Hz), 129.8 (d, \(J = 1.4\) Hz), 129.14, 129.10, 128.7, 128.6, 128.4, 124.4 (q, \(J = 270.0\) Hz), 128.6, 123.2 (dq, \(J = 10.8, 3.8\) Hz), 53.8, 27.9.

\(^19\text{F NMR}\) (376 MHz, CDCl\text{3}) \(\delta \) –62.4 (s, 3F)

**HRMS** (ESI) \(m/z\) calcd. for C\text{21}H\text{19}F\text{3}N\text{OS} \[M + H\]^+ 390.1134, found 390.1132.

(S)-3-(1-((Oxodiphenyl-λ6-sulfaneylidene)amino)ethyl)benzaldehyde (21)

\[
\text{OHC} \quad \begin{array}{c}
\text{N} \\
\text{S} \\
\text{Ph}
\end{array} \quad \text{Me} \quad \text{O}
\]

According to **General procedure A** with 3-(1-bromoethyl)benzaldehyde (42.4 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **21** as a yellow oil (55.8 mg, 80% yield, 97% ee).

\[\alpha\]D\text{20}^20 = −59 (c 1.0, CH\text{2Cl}_2).

**HPLC** analysis: Chiralcel IA (hexane/PrOH = 98/2, flow rate 1.0 mL/min, λ = 254 nm),
$t_R$ (major) = 36.15 min, $t_R$ (minor) = 39.79 min.

$^1$H NMR (400 MHz, CDCl$_3$) δ 10.02 (s, 1H), 8.10 – 8.00 (m, 2H), 7.92 (s, 1H), 7.89 – 7.82 (m, 2H), 7.75 (dd, $J = 7.7$, 1.8 Hz, 2H), 7.58 – 7.44 (m, 5H), 7.44 – 7.36 (m, 2H), 4.49 (q, $J = 6.6$ Hz, 1H), 1.59 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 192.7, 148.7, 141.1, 140.7, 136.4, 132.7, 132.6, 132.4, 129.2, 129.1, 128.9, 128.7, 128.4, 127.8, 53.7, 27.9.

HRMS (ESI) $m/z$ calcd. for C$_{21}$H$_{20}$NO$_2$S [M + H]$^+$ 350.1209, found 350.1208.

(S)-((1-(3-Acetylphenyl)ethyl)imino)diphenyl-λ$_6$-sulfanone (22)

![Chemical Structure](image)

According to General procedure A with 1-(3-(1-bromoethyl)phenyl)ethan-1-one (45.2 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 22 as a colorless oil (63.2 mg, 87% yield, 98% ee).

$[\alpha]_{D}^{20} = -46$ (c 1.0, CH$_2$Cl$_2$).

HPLC analysis: Chiralcel IA (hexane/iPrOH = 97/3, flow rate 0.5 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 67.42 min, $t_R$ (minor) = 73.93 min.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.09 – 8.01 (m, 2H), 7.97 (s, 1H), 7.88 – 7.80 (m, 3H), 7.73 – 7.68 (m, 1H), 7.58 – 7.35 (m, 7H), 4.48 (q, $J = 6.6$ Hz, 1H), 2.61 (s, 3H), 1.59 (d, $J = 6.6$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 198.5, 148.1, 141.2, 140.7, 137.1, 132.5, 132.4, 131.2, 129.13, 129.10, 128.8, 128.5, 128.4, 126.5, 126.3, 53.9, 28.0, 26.8.

HRMS (ESI) $m/z$ calcd. for C$_{22}$H$_{22}$NO$_2$S [M + H]$^+$ 364.1366, found 364.1358.
(S)-3-(1-((Oxodiphenyl-\(\lambda^6\)-sulfaneylidene)amino)ethyl)benzonitrile (23)

According to **General procedure A** with 3-(1-bromoethyl)benzonitrile (41.8 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 23 as a colorless oil (65.7 mg, 95% yield, 92% ee).

\([\alpha]_{D}^{20} = -17 \text{ (c 1.0, CH}_2\text{Cl}_2\text{).} \]

**HPLC** analysis: Chiralcel IA (hexane/iPrOH = 98/2, flow rate 1.0 mL/min, \(\lambda = 230\) nm), \(t_R\) (major) = 28.68 min, \(t_R\) (minor) = 35.92 min.

\(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 8.02 (d, \(J = 8.1\) Hz, 2H), 7.83 (d, \(J = 8.3\) Hz, 2H), 7.73 (s, 1H), 7.64 (d, \(J = 7.9\) Hz, 1H), 7.58 – 7.45 (m, 5H), 7.45 – 7.34 (m, 3H), 4.41 (q, \(J = 6.6\) Hz, 1H), 1.53 (d, \(J = 6.6\) Hz, 3H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 149.0, 141.0, 140.6, 132.6, 132.5, 131.0, 130.2, 130.1, 129.21, 129.17, 129.0, 128.6, 128.4, 119.3, 112.1, 53.4, 27.9.

**HRMS** (ESI) \(m/z\) calcd. for C\(_{21}\)H\(_{19}\)N\(_2\)OS [M + H]\(^+\) 347.1213, found 347.1210.

According to **General procedure A** with 3-(1-chloroethyl)benzonitrile (33.0 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 23 as a colorless oil (62.3 mg, 90% yield, 96% ee).

**HPLC** analysis: Chiralcel IA (hexane/iPrOH = 98/2, flow rate 1.0 mL/min, \(\lambda = 230\) nm), \(t_R\) (major) = 28.29 min, \(t_R\) (minor) = 35.67 min.

Methyl (S)-3-(1-((oxodiphenyl-\(\lambda^6\)-sulfaneylidene)amino)ethyl)benzoate (24)
According to **General procedure A** with methyl 3-(1-bromoethyl)benzoate (48.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **24** as a yellow oil (70.5 mg, 93% yield, 96% ee).

$[\alpha]_{D}^{20} = -12$ (c 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel OZ3 (hexane/iPrOH = 98/2, flow rate 0.7 mL/min, $\lambda = 230$ nm), $t_R$ (minor) = 48.26 min, $t_R$ (major) = 58.05 min.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 8.10 – 8.02 (m, 3H), 7.94 – 7.87 (m, 1H), 7.87 – 7.80 (m, 2H), 7.73 – 7.67 (m, 1H), 7.57 – 7.43 (m, 4H), 7.43 – 7.34 (m, 3H), 4.47 (q, $J = 6.6$ Hz, 1H), 3.92 (s, 3H), 1.58 (d, $J = 6.6$ Hz, 3H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$ 167.3, 147.9, 141.3, 140.7, 132.5, 132.3, 131.0, 123.0, 129.10, 129.08, 128.8, 128.4, 128.3, 127.7, 127.5, 53.9, 52.0, 28.0.

**HRMS** (ESI) $m/z$ calcd. for C$_{22}$H$_{22}$NO$_3$S [M + H]$^+$ 380.1315, found 380.1312.

According to **General procedure A** with methyl 3-(1-chloroethyl)benzoate (39.6 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **24** as a yellow oil (58.4 mg, 77% yield, 97% ee).

**HPLC** analysis: Chiralcel OZ3 (hexane/iPrOH = 98/2, flow rate 0.7 mL/min, $\lambda = 230$ nm), $t_R$ (minor) = 52.88 min, $t_R$ (major) = 64.56 min.

**($S$)-((1-(Naphthalen-2-yl)ethyl)imino)diphenyl-$\lambda^6$-sulfanone (25)**

![25]

According to **General procedure A** with 2-(1-bromoethyl)naphthalene (46.8 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product **25** as a colorless oil (63.8 mg, 86% yield, 93% ee).
\[ [\alpha]^D_{20} = -8 \ (c \ 1.0, \ CH_2Cl_2). \]

**HPLC analysis:** Chiralcel IA (hexane/PrOH = 98/2, flow rate 1.0 mL/min, \( \lambda = 230 \) nm),

\( t_R \) (major) = 18.74 min, \( t_R \) (minor) = 34.32 min.

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \( \delta \) 8.12 (d, \( J = 7.6 \) Hz, 2H), 7.92 – 7.80 (m, 6H), 7.67 (d, \( J = 8.5 \) Hz, 1H), 7.58 – 7.41 (m, 6H), 7.41 – 7.32 (m, 2H), 4.62 (q, \( J = 6.6 \) Hz, 1H), 1.69 (d, \( J = 6.7 \) Hz, 3H).

**\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)) \( \delta \) 145.0, 141.5, 140.8, 133.5, 132.6, 132.4, 132.3, 129.10, 129.07, 129.0, 128.5, 127.94, 127.93, 127.6, 125.8, 125.3, 125.2, 124.3, 54.5, 28.2.

**HRMS** (ESI) \( m/z \) calcld. for C\(_{24}\)H\(_{22}\)NOS [M + H]\(^+\) 372.1417, found 372.1415.

According to **General procedure A** with 2-(1-chloroethyl)naphthalene (38.0 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 25 as a colorless oil (60.1 mg, 81% yield, 96% ee).

**HPLC analysis:** Chiralcel IA (hexane/PrOH = 98/2, flow rate 1.0 mL/min, \( \lambda = 230 \) nm),

\( t_R \) (major) = 28.38 min, \( t_R \) (minor) = 35.84 min.

**\((S)-((1-(Naphthalen-1-yl)ethyl)imino)diphenyl-\lambda^6\)-sulfanone (26)**

\[
\text{\includegraphics{image}}
\]

According to **General procedure A** with 1-(1-bromoethyl)naphthalene (46.8 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 26 as a colorless oil (53.4 mg, 72% yield, 95% ee).

X-ray quality crystals were obtained by slow evaporation of solvent from a saturated solution in a mixture of toluene/hexane.

\[ [\alpha]^D_{20} = 4 \ (c \ 1.0, \ CH_2Cl_2). \]

**HPLC analysis:** Chiralcel OD3 (hexane/PrOH = 99/1, flow rate 0.5 mL/min, \( \lambda = 254 \) nm, \( \lambda = 230 \) nm),

\( t_R \) (major) = 18.74 min, \( t_R \) (minor) = 34.32 min.
nm), $t_R$ (major) = 18.40 min, $t_R$ (minor) = 20.42 min.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.19 – 8.06 (m, 3H), 7.98 (d, $J$ = 7.2 Hz, 1H), 7.87 (d, $J$ = 7.9 Hz, 1H), 7.84 – 7.79 (m, 2H), 7.76 (d, $J$ = 8.1 Hz, 1H), 7.57 – 7.36 (m, 7H), 7.34 – 7.25 (m, 2H), 5.22 (q, $J$ = 6.6 Hz, 1H), 1.75 (d, $J$ = 6.6 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 143.3, 141.7, 140.8, 133.9, 132.4, 132.2, 130.3, 129.03, 129.00, 128.82, 128.76, 128.4, 127.0, 125.8, 125.4, 125.1, 123.8, 123.7, 51.3, 27.8.

HRMS (ESI) $m/z$ calcd. for C$_{24}$H$_{22}$NOS [M + H]$^+$ 372.1417, found 372.1414.

($S$)-Diphenyl((1-phenylpropyl)imino)-$\lambda^6$-sulfanone (27)

According to General procedure A with (1-bromopropyl)benzene (39.2 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 26 as a colorless oil (53.6 mg, 80% yield, 95% ee).

$[\alpha]_{D}^{20}$ = $-51$ (c 1.0, CH$_2$Cl$_2$).

HPLC analysis: Chiralcel OZ3 (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, $\lambda$ = 230 nm), $t_R$ (minor) = 21.76 min, $t_R$ (major) = 37.32 min.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.17 – 8.01 (m, 2H), 7.84 – 7.72 (m, 2H), 7.57 – 7.40 (m, 4H), 7.41 – 7.27 (m, 6H), 7.26 – 7.17 (m, 1H), 4.10 (t, $J$ = 6.7 Hz, 1H), 2.02 – 1.79 (m, 2H), 0.93 (t, $J$ = 7.3 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.2, 141.4, 141.0, 132.3, 132.2, 129.01, 128.99, 128.9, 128.5, 128.0, 126.9, 126.4, 60.5, 34.3, 11.0.

HRMS (ESI) $m/z$ calcd. for C$_{21}$H$_{22}$NOS [M + H]$^+$ 336.1417, found 336.1414.
(S)-((Cyclopentyl(phenyl)methyl)imino)diphenyl-\(\lambda^6\)-sulfanone (28)

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-\(\lambda^6\)-sulfanone (43.4 mg, 0.20 mmol, 1.0 equiv.), CuTc (15.4 mg, 0.080 mmol, 40 mol%), chiral ligand L*6 (81.9 mg, 0.080 mmol, 40 mol%), Cs2CO3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et2O (2.0 mL). To this solution was added (bromo(cyclopentyl)methyl)benzene (47.6 mg, 0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 5 d. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the desired product 28 as a colorless oil (61.5 mg, 82% yield, 92% ee).

\[ [\alpha]_{D}^{20} = -47 \quad (c \ 0.6, \ CH_{2}Cl_{2}). \]

**HPLC** analysis: Chiralcel OZ3 (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, \(\lambda = 254\) nm), \(t_R\) (minor) = 21.68 min, \(t_R\) (major) = 25.37 min.

\( ^{1}H\) NMR (400 MHz, CDCl3) \(\delta 8.08 – 7.93\) (m, 2H), \(7.77 – 7.63\) (m, 2H), \(7.53 – 7.35\) (m, 4H), \(7.31 – 7.13\) (m, 7H), \(3.88\) (d, \(J = 8.4\) Hz, 1H), \(2.32\) (h, \(J = 8.1\) Hz, 1H), \(1.98\) (td, \(J = 7.4, 6.4, 3.5\) Hz, 1H), \(1.75 – 1.38\) (m, 5H), \(1.39 – 1.05\) (m, 2H).

\( ^{13}C\) NMR (100 MHz, CDCl3) \(\delta 146.3, 141.3, 141.2, 132.2, 132.0, 129.03, 128.95, 128.7, 128.5, 127.9, 127.2, 126.2, 63.7, 49.7, 30.8, 30.0, 25.3, 25.1.

**HRMS** (ESI) \(m/z\) calcd. for C_{29}H_{26}NOS [M + H]^+ 376.1730, found 376.1727.
(S)-((2-Methyl-1-phenylpropyl)imino)diphenyl-λ⁶-sulfanone (29)

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ⁶-sulfanone (43.4 mg, 0.20 mmol, 1.0 equiv.), CuTc (15.4 mg, 0.080 mmol, 40 mol%), chiral ligand L*'6 (81.9 mg, 0.080 mmol, 40 mol%), Cs₂CO₃ (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et₂O (2.0 mL). To this solution was added (1-bromo-2-methylpropyl)benzene (42.4 mg, 0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 5 d. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the desired product 29 as a colorless oil (27.9 mg, 40% yield, 91% ee).

[H]D₂₀ = −7 (c 1.0, CH₂Cl₂).

HPLC analysis: Chiralcel OZ3 (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), tᵣ (major) = 16.71 min, tᵣ (minor) = 17.44 min.

^1H NMR (400 MHz, CDCl₃) δ 8.04 – 7.94 (m, 2H), 7.74 – 7.64 (m, 2H), 7.53 – 7.36 (m, 4H), 7.31 – 7.13 (m, 7H), 3.82 (d, J = 7.0 Hz, 1H), 2.02 (h, J = 6.8 Hz, 1H), 1.05 (d, J = 6.7 Hz, 3H), 0.79 (d, J = 6.8 Hz, 3H).

^13C NMR (100 MHz, CDCl₃) δ 145.3, 141.4, 141.2, 132.2, 132.0, 129.0, 128.9, 128.7, 128.5, 127.7, 127.6, 126.2, 65.1, 36.8, 19.8, 19.7.

HRMS (ESI) m/z calcd. for C₂₂H₂₄NOS [M + H]⁺ 350.1573, found 350.1571.

(S)-Diphenyl((1-phenylhex-5-en-1-yl)imino)-λ⁶-sulfanone (30)

According to General procedure C with (1-bromohex-5-en-1-yl)benzene (47.6 mg,
0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 30 as a colorless oil (39.1 mg, 52% yield, 92% ee).

$[\alpha]_{D20}^{20} = -5$ (c 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel IA (hexane/PrOH = 99/1, flow rate 0.5 mL/min, $\lambda = 230$ nm), $t_R$ (major) = 30.13 min, $t_R$ (minor) = 33.86 min.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.04 (d, $J = 8.0$ Hz, 2H), 7.77 (d, $J = 8.1$ Hz, 2H), 7.57 – 7.40 (m, 4H), 7.40 – 7.25 (m, 6H), 7.25 – 7.17 (m, 1H), 5.79 (ddt, $J = 16.7$, 8.9, 6.5 Hz, 1H), 5.04 – 4.85 (m, 2H), 4.17 (t, $J = 6.8$ Hz, 1H), 2.04 (q, $J = 7.3$ Hz, 2H), 2.00 – 1.76 (m, 2H), 1.62 – 1.31 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 146.4, 141.4, 141.0, 139.1, 132.3, 132.2, 129.0, 128.9, 128.5, 128.1, 126.8, 126.4, 114.3, 58.9, 41.0, 33.7, 25.8.

**HRMS** (ESI) $m/z$ calcd. for C$_{24}$H$_{26}$NOS [M + H]$^+$ 376.1730, found 376.1728.

(S)-(3-Chloro-1-phenylpropyl)imino)diphenyl-$\lambda^6$-sulfanone (31)

According to **General procedure C** with (1-bromo-3-chloropropyl)benzene (46.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 31 as a colorless oil (56.8 mg, 77% yield, 94% ee).

$[\alpha]_{D20}^{20} = -9$ (c 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel OZ3 (hexane/PrOH = 97/3, flow rate 0.7 mL/min, $\lambda = 230$ nm), $t_R$ (minor) = 18.62 min, $t_R$ (major) = 32.09 min.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.08 – 7.95 (m, 2H), 7.84 – 7.70 (m, 2H), 7.55 – 7.39 (m, 4H), 7.39 – 7.16 (m, 7H), 4.37 (dd, $J = 8.2$, 4.9 Hz, 1H), 3.93 – 3.75 (m, 1H), 3.67 – 3.51 (m, 1H), 2.44 – 2.25 (m, 1H), 2.25 – 2.08 (m, 1H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.3, 141.0, 140.6, 132.5, 132.4, 129.1, 129.0, 128.9, 128.5, 128.3, 126.8, 126.7, 56.1, 43.9, 42.6.
(S)-((3-(Benzyloxy)-1-phenylpropyl)imino)diphenyl-\(\lambda^6\)-sulfanone (32)

According to **General procedure C** with (3-(benzyloxy)-1-bromopropyl)benzene (60.8 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 32 as a colorless oil (68.8 mg, 78% yield, 92% ee).

\([\alpha]_D^{20} = -14\) (c 1.0, CH\(_2\)Cl\(_2\)).

**HPLC** analysis: Chiralcel IE (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, \(\lambda = 254\) nm), \(t_R\) (major) = 10.36 min, \(t_R\) (minor) = 11.36 min.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.09 – 8.01 (m, 2H), 7.82 – 7.73 (m, 2H), 7.56 – 7.41 (m, 4H), 7.40 – 7.26 (m, 11H), 7.26 – 7.19 (m, 1H), 4.60 (d, \(J = 11.7\) Hz, 1H), 4.49 (d, \(J = 11.7\) Hz, 1H), 4.43 (dd, \(J = 8.3, 5.4\) Hz, 1H), 3.88 – 3.74 (m, 1H), 3.63 – 3.50 (m, 1H), 2.29 – 2.17 (m, 1H), 2.17 – 2.03 (m, 1H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 146.2, 141.2, 140.8, 138.9, 132.3, 132.2, 129.03, 128.96, 128.9, 128.6, 128.2, 128.1, 127.7, 127.3, 126.8, 126.5, 72.8, 67.6, 55.9, 41.1.

**HRMS** (ESI) m/z calcd. for C\(_{21}\)H\(_{21}\)ClNOS [M + H]+ 370.1027, found 370.1021.

**HRMS** (ESI) m/z calcd. for C\(_{28}\)H\(_{28}\)NO\(_2\)S [M + H]+ 442.1835, found 442.1834.

(S)-bis(4-Methoxyphenyl)((5-oxo-1,5-diphenylpentyl)imino)-\(\lambda^6\)-sulfanone (33)

According to **General procedure C** with 5-bromo-1,5-diphenylpentan-1-one (63.4 mg, 0.20 mmol, 1.0 equiv.) and iminobis(4-methoxyphenyl)-\(\lambda^6\)-sulfanone (55.4 mg, 0.20
mmol, 1.0 equiv.) for 96 h at 0 °C, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product 33 as a yellow oil (57.5 mg, 56% yield, 84% ee).

\([\alpha]_{D}^{20} = -0.1 \) (c 1.0, CH2Cl2).

HPLC analysis: Chiralcel IA (hexane/PrOH = 75/25, flow rate 1.0 mL/min, \(\lambda = 254\) nm), \(t_R\) (major) = 16.69 min, \(t_R\) (minor) = 19.25 min.

\(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 7.94 – 7.86 (m, 4H), 7.69 – 7.63 (m, 2H), 7.54 – 7.48 (m, 1H), 7.45 – 7.37 (m, 2H), 7.35 – 7.30 (m, 2H), 7.30 – 7.23 (m, 2H), 7.22 – 7.15 (m, 1H), 6.94 – 6.87 (m, 2H), 6.83 – 6.74 (m, 2H), 4.17 (dd, \(J = 7.2, 5.1\) Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 2.97 – 2.87 (m, 2H), 2.01 – 1.72 (m, 4H).

\(^{13}\)C NMR (100 MHz, CDCl3) \(\delta\) 200.5, 162.6, 162.5, 146.4, 137.1, 133.3, 132.77, 132.76, 130.8, 130.3, 128.5, 128.1, 126.8, 126.4, 114.2, 114.1, 58.7, 55.54, 55.52, 41.0, 38.5, 21.3.

HRMS (ESI) \(m/z\) calcd. for C\(_{31}\)H\(_{32}\)NO\(_4\)S [M + H]\(^+\) 514.2047, found 514.2045.

Ethyl \([S]\)-5-\(((\text{bis}(4\text{-methoxyphenyl})\text{oxo}-\lambda^6\text{-sulfaneylidene})\text{amino})\)-5-phenylpentanoate (34)

According to General procedure C with ethyl 5-bromo-5-phenylpentanoate (56.8 mg, 0.20 mmol, 1.0 equiv.) and iminobis(4-methoxyphenyl)-\(\lambda^6\)-sulfanone (55.4 mg, 0.20 mmol, 1.0 equiv.) at room temperature for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product 34 as a yellow oil (76.0 mg, 79% yield, 87% ee).

\([\alpha]_{D}^{20} = -35 \) (c 0.3, CH2Cl2).

HPLC analysis: Chiralcel IE (hexane/PrOH = 50/50, flow rate 1.0 mL/min, \(\lambda = 254\) nm), \(t_R\) (major) = 16.69 min, \(t_R\) (minor) = 19.25 min.

\(^1\)H NMR (400 MHz, CDCl3) \(\delta\) 7.94 – 7.86 (m, 4H), 7.69 – 7.63 (m, 2H), 7.54 – 7.48 (m, 1H), 7.45 – 7.37 (m, 2H), 7.35 – 7.30 (m, 2H), 7.30 – 7.23 (m, 2H), 7.22 – 7.15 (m, 1H), 6.94 – 6.87 (m, 2H), 6.83 – 6.74 (m, 2H), 4.17 (dd, \(J = 7.2, 5.1\) Hz, 1H), 3.79 (s, 3H), 3.78 (s, 3H), 2.97 – 2.87 (m, 2H), 2.01 – 1.72 (m, 4H).

\(^{13}\)C NMR (100 MHz, CDCl3) \(\delta\) 200.5, 162.6, 162.5, 146.4, 137.1, 133.3, 132.77, 132.76, 130.8, 130.3, 128.5, 128.1, 126.8, 126.4, 114.2, 114.1, 58.7, 55.54, 55.52, 41.0, 38.5, 21.3.

HRMS (ESI) \(m/z\) calcd. for C\(_{31}\)H\(_{32}\)NO\(_4\)S [M + H]\(^+\) 514.2047, found 514.2045.
nm), \( t_R \) (major) = 14.61 min, \( t_R \) (minor) = 24.34 min.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 7.98 – 7.82 (m, 2H), 7.70 – 7.58 (m, 2H), 7.34 – 7.23 (m, 4H), 7.22 – 7.15 (m, 1H), 6.96 – 6.87 (m, 2H), 6.83 – 6.74 (m, 2H), 4.16 – 4.02 (m, 3H), 3.81 (s, 3H), 3.78 (s, 3H), 2.34 – 2.16 (m, 2H), 1.96 – 1.66 (m, 4H), 1.21 (t, \( J = 7.1 \) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 173.8, 162.6, 162.5, 146.4, 133.3, 132.8, 130.8, 130.3, 128.1, 126.8, 126.4, 114.2, 114.1, 60.1, 58.6, 55.6, 55.5, 40.9, 34.2, 21.9, 14.2.

HRMS (ESI) \( m/z \) calcd. for C\(_{27}\)H\(_{32}\)NO\(_5\)S \([M + H]^+\) 482.1996, found 482.1991.

\((S)-\text{Diphenyl}(1-(\text{pyridin-3-yl})\text{ethyl})i\text{mino})-\lambda^6\text{-sulfanone (35)}\)

According to General procedure C with 3-(1-bromoethyl)pyridine (37.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product 35 as a red oil (53.4 mg, 83% yield, 93% ee).

\([\alpha]_D^{20} = -9 \) (c 1.0, CH\(_2\)Cl\(_2\)).

HPLC analysis: Chiralcel OZ3 (hexane/iPrOH = 85/15, flow rate 0.7 mL/min, \( \lambda = 230 \) nm), \( t_R \) (major) = 19. 80 min, \( t_R \) (minor) = 24.55 min.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.59 (d, \( J = 2.3 \) Hz, 1H), 8.48 (dd, \( J = 4.8, 1.7 \) Hz, 1H), 8.11 – 7.99 (m, 2H), 7.93 – 7.75 (m, 3H), 7.58 – 7.45 (m, 4H), 7.45 – 7.37 (m, 2H), 7.30 – 7.21 (m, 1H), 4.44 (q, \( J = 6.6 \) Hz, 1H), 1.58 (d, \( J = 6.6 \) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 148.2, 147.9, 142.6, 141.1, 140.6, 133.9, 132.6, 132.5, 129.2, 129.1, 128.7, 128.4, 123.3, 51.9, 27.8.

HRMS (ESI) \( m/z \) calcd. for C\(_{19}\)H\(_{19}\)N\(_2\)OS \([M + H]^+\) 323.1213, found 323.1211.
(S)-(1-(Benzofuran-3-yl)ethyl)imino)diphenyl-λ⁶-sulfanone (36)

According to **General procedure A** with 3-(1-bromoethyl)benzofuran (44.8 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 36 as a colorless oil (62.0 mg, 86% yield, 97% ee).

\[\alpha\]D₂₀ = −70 (c 0.9, CH₂Cl₂).

**HPLC** analysis: Chiralcel OZ3 (hexane/iPrOH = 85/15, flow rate 0.3 mL/min, λ = 254 nm), \(t_R\) (major) = 21.07 min, \(t_R\) (minor) = 22.23 min.

\(^1\)H NMR (400 MHz, CDCl₃) δ 8.08 (d, \(J = 6.3\) Hz, 2H), 7.92 (d, \(J = 7.6\) Hz, 2H), 7.74 (dd, \(J = 7.7, 1.4\) Hz, 1H), 7.64 (s, 1H), 7.56 – 7.44 (m, 5H), 7.44 – 7.36 (m, 2H), 7.34 – 7.19 (m, 2H), 4.70 (q, \(J = 6.6\) Hz, 1H), 1.73 (d, \(J = 6.6\) Hz, 3H).

\(^13\)C NMR (100 MHz, CDCl₃) δ 155.8, 141.3, 141.1, 140.7, 132.5, 132.4, 129.11, 129.10, 128.7, 128.4, 126.70, 126.66, 124.0, 122.2, 120.8, 111.5, 46.4, 26.2.

**HRMS** (ESI) \(m/z\) calcd. for C₂₂H₂₀NO₂S [M + H]^+ 362.1209, found 362.1207.

(S)-Diphenyl((1-(thiophen-3-yl)ethyl)imino)-λ⁶-sulfanone (37)

According to **General procedure A** with 3-(1-bromoethyl)thiophene (38.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 37 as a red oil (62.1 mg, 95% yield, 97% ee).

\[\alpha\]D₂₀ = −129 (c 1.0, CH₂Cl₂).

**HPLC** analysis: Chiralcel OZ3 (hexane/iPrOH = 90/10, flow rate 1.0 mL/min, λ = 254 nm), \(t_R\) (minor) = 6.92 min, \(t_R\) (major) = 9.09 min.

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\[^1\]H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.07 (d, \(J = 6.4\) Hz, 2H), 7.91 (d, \(J = 7.5\) Hz, 2H), 7.57 – 7.37 (m, 6H), 7.28 – 7.24 (m, 1H), 7.20 – 7.14 (m, 2H), 4.51 (q, \(J = 6.6\) Hz, 1H), 1.61 (d, \(J = 6.6\) Hz, 3H).

\[^13\]C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.7, 141.4, 140.7, 132.4, 132.3, 129.1, 128.8, 128.5, 126.6, 125.3, 119.6, 50.2, 27.0.

HRMS (ESI) \(m/z\) calcd. for C\(_{18}\)H\(_{18}\)NOS\(_2\) [M + H]\(^+\) 328.0824, found 328.0822.

According to General procedure A with 3-(1-chloroethyl)thiophene (29.2 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 37 as a red oil (39.2 mg, 60% yield, 93% ee).

HPLC analysis: Chiralcel ID (hexane/iPrOH = 90/10, flow rate 0.8 mL/min, \(\lambda = 254\) nm), \(t_R\) (major) = 11.94 min, \(t_R\) (minor) = 14.74 min.

\((S)\)-Diphenyl(1-(thiazol-4-yl)ethyl)imino)-\(\lambda^6\)-sulfanone (38)

\[\begin{align*}
\text{N} & \quad \text{N} \\
\text{S} & \quad \text{Ph}
\end{align*}\]

According to General procedure C with 4-(1-bromoethyl)thiazole (38.2 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product 38 as a colourless oil (55.8 mg, 85% yield, 82% ee).

\([\alpha]_{D}^{20} = -39\) (c 0.8, CH\(_2\)Cl\(_2\)).

HPLC analysis: Chiralcel AD3 (hexane/iPrOH = 95/5, flow rate 1.0 mL/min, \(\lambda = 230\) nm), \(t_R\) (minor) = 28.02 min, \(t_R\) (major) = 32.58 min.

\[^1\]H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.74 (d, \(J = 2.2\) Hz, 1H), 8.03 (dd, \(J = 20.5, 6.6\) Hz, 4H), 7.59 – 7.40 (m, 7H), 4.65 (q, \(J = 6.6\) Hz, 1H), 1.68 (d, \(J = 6.6\) Hz, 3H).

\[^13\]C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 163.2, 152.3, 141.1, 140.6, 132.50, 132.46, 129.17, 129.15, 128.8, 128.5, 113.3, 51.4, 25.6.
HRMS (ESI) m/z calcd. for C_{17}H_{17}N_{2}O_{2} [M + H]^+ 329.0777, found 329.0775.

\((S)-((1-(3-Methoxyphenyl)ethyl)imino)diphenyl-\lambda^6\text{-sulfanone (39)}\)

\[
\text{MeO} \quad \text{Ph} \quad \begin{array}{c}
\text{N} \\
\text{S} \\
\text{Ph}
\end{array}
\]

According to General procedure A with 1-(1-chloroethyl)-3-methoxybenzene (34.0 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product 39 as a colorless oil (51.2 mg, 73% yield, 98% ee). 
\([\alpha]_{D}^{20} = -37 (c 1.0, \text{CH}_2\text{Cl}_2)\).

HPLC analysis: Chiralcel IA (hexane/iPrOH = 98/2, flow rate 0.5 mL/min, \(\lambda = 230 \text{ nm}\)),

\(t_R\) (major) = 35.99 min, \(t_R\) (minor) = 41.71 min.

\(^1\text{H NMR}\) (400 MHz, CDCl₃) \(\delta 8.15 – 8.03\) (m, 2H), \(7.93 – 7.80\) (m, 2H), \(7.57 – 7.35\) (m, 6H), \(7.24\) (t, \(J = 7.9 \text{ Hz}\), 1H), \(7.09 – 7.03\) (m, 1H), \(7.03 – 6.98\) (m, 1H), 6.84 – 6.74 (m, 1H), 4.41 (q, \(J = 6.6 \text{ Hz}\), 1H), 3.83 (s, 3H), 1.58 (d, \(J = 6.6 \text{ Hz}\), 3H).

\(^{13}\text{C NMR}\) (100 MHz, CDCl₃) \(\delta 159.6, 149.3, 141.5, 140.8, 132.4, 132.3, 129.13, 129.0, 128.4, 118.7, 111.9, 111.8, 55.2, 54.2, 28.2\).

HRMS (ESI) m/z calcd. for C_{21}H_{22}NO_{2}S [M + H]^+ 352.1366, found 352.1364.

\((S)-((6,6\text{-Dimethyl-1-phenylhept-4-yn-3-yl})\text{imino})\text{bis(4-methoxyphenyl)}-\lambda^6\text{-sulfanone (40)}\)

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminobis(4-methoxyphenyl)-\(\lambda^6\)-sulfanone (55.4 mg, 0.20 mmol, 1.0 equiv.), Cu(PPh₃)₃Br (37.2 mg, 0.040 mmol, 20 mol%), chiral ligand

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L*4 (28.4 mg, 0.040 mmol, 20 mol%), Cs2CO3 (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et2O (2.0 mL). To this solution was added (3-bromo-6,6-dimethylhept-4-yn-1-yl)benzene (111.2 mg, 0.40 mmol, 2.0 equiv.) and the reaction mixture was stirred at room temperature for 7 d. The precipitate was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to afford the desired product 40 as a colorless oil (38.9 mg, 41% yield, 50% conversion, 80% ee).

\[ [\alpha]D^{20} = -10 \ (c \ 1.0, \ CH_2Cl_2). \]

**HPLC analysis:** Chiralcel IF (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, \( \lambda = 254 \text{ nm} \)), \( t_R \) (major) = 8.59 min, \( t_R \) (minor) = 9.77 min.

**\(^1\)H NMR** (400 MHz, CDCl3) \( \delta \) 8.03 – 7.87 (m, 4H), 7.30 – 7.22 (m, 4H), 7.20 – 7.14 (m, 1H), 7.00 – 6.90 (m, 4H), 3.98 (t, \( J = 6.7 \text{ Hz} \), 1H), 3.85 (s, 3H), 3.84 (s, 3H), 2.91 – 2.78 (m, 2H), 2.17 – 2.04 (m, 2H), 1.20 (s, 9H).

**\(^13\)C NMR** (100 MHz, CDCl3) \( \delta \) 162.7, 162.6, 142.5, 133.5, 133.2, 131.0, 130.0, 128.6, 128.2, 125.4, 114.17, 114.15, 91.3, 80.9, 55.6, 45.3, 41.5, 32.5, 31.2, 27.3.

**HRMS (ESI) \( m/z \)** calcd. for C29H34NO3S [M + H]^+ 476.2254, found 476.2263.
Enantioconvergent N-alkylation: scope of secondary α-bromoketones. (Figure 3A)

**General procedure D:**

\[
\begin{align*}
\text{R}_1\text{O} & \quad \text{R}_2\text{Br} \\
1.0 \text{ equiv.} & \quad 1.1 \text{ equiv.}
\end{align*}
\]

\[
\begin{align*}
\text{PMP} & \quad \text{NH} \\
\text{O} & \quad \text{PMP}
\end{align*}
\]

\[
\begin{align*}
\text{Cu(HFacac)}_2 & (10 \text{ mol\%}) \\
\text{L*7} & (10 \text{ mol\%}) \\
\text{Cs}_2\text{CO}_3 & (4.0 \text{ equiv.})
\end{align*}
\]

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminobis(4-methoxyphenyl)-$\lambda^6$-sulfanone (60.9 mg, 0.22 mmol, 1.1 equiv.), Cu(HFacac)$_2$ (8.8 mg, 0.020 mmol, 10 mol%), chiral ligand L*7 (27.3 mg, 0.020 mmol, 10 mol%), Cs$_2$CO$_3$ (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et$_2$O (4.0 mL). To this solution was added α-bromo ketone (0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at 0 °C for 72 h or more. Upon completion (monitored by TLC), the precipitate was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel to afford the desired product.

\((S)-\text{bis(4-Methoxyphenyl)((1-oxo-1-phenylpropan-2-yl)imino)-}\lambda^6\text{-sulfanone (41)}\)

According to **General procedure D** with 2-bromo-1-phenylpropan-1-one (42.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product 41 as a yellow oil (65.4 mg, 80% yield, 91% ee).

\[\alpha\]$_{D}^20 = -0.1 \ (c \ 1.0, \text{CH}_2\text{Cl}_2)\].

**HPLC** analysis: Chiralcel IE (hexane/iPrOH = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 29.03 min, $t_R$ (minor) = 36.90 min.
$^1$H NMR (400 MHz, CDCl₃) δ 8.06 – 8.00 (m, 2H), 7.98 – 7.90 (m, 2H), 7.79 – 7.71 (m, 2H), 7.57 – 7.49 (m, 1H), 7.45 – 7.38 (m, 2H), 6.98 – 6.90 (m, 2H), 6.90 – 6.82 (m, 2H), 4.72 (q, $J$ = 6.9 Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 1.54 (d, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl₃) δ 201.2, 162.8, 162.7, 135.8, 133.3, 132.60, 132.57, 130.4, 130.3, 129.2, 128.3, 114.32, 114.26, 55.6, 55.5, 55.4, 22.2.

HRMS (ESI) $m/z$ calcd. for C$_{23}$H$_{24}$NO$_4$S [M + H]$^+$ 410.1421, found 410.1419.

(R)-bis(4-Methoxyphenyl)((1-oxo-1-phenylpropan-2-yl)imino)-λ₆-sulfanone ((R)-41)

![Chemical structure of (R)-41](image)

According to General procedure D with 2-bromo-1-phenylpropan-1-one (42.6 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand L*7' for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product (R)-41 as a yellow oil (81.2 mg, 99% yield, 96% ee).

HPLC analysis: Chiralcel IE (hexane/iPrOH = 60/40, flow rate 1.0 mL/min, $\lambda$ = 254 nm), $t_R$ (minor) = 29.11 min, $t_R$ (major) = 36.78 min.

(S)-bis(4-Methoxyphenyl)((1-oxo-1-(p-tolyl)propan-2-yl)imino)-λ₆-sulfanone (42)

![Chemical structure of 42](image)

According to General procedure D with 2-bromo-1-(p-tolyl)propan-1-one (45.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product 42 as
a yellow oil (67.7 mg, 80% yield, 92% ee).

$\{\alpha\}^2_{D} = -70$ ($c$ 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel IE (hexane/PrOH = 50/50, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 31.44 min, $t_R$ (minor) = 38.38 min.

**H NMR** (400 MHz, CDCl$_3$) $\delta$ 7.94 (d, $J = 8.9$ Hz, 4H), 7.75 (d, $J = 8.9$ Hz, 2H), 7.21 (d, $J = 8.0$ Hz, 2H), 6.93 (d, $J = 8.9$ Hz, 2H), 6.85 (d, $J = 8.9$ Hz, 2H), 4.70 (q, $J = 6.8$ Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 2.39 (s, 3H), 1.52 (d, $J = 6.9$ Hz, 3H).

**C NMR** (100 MHz, CDCl$_3$) $\delta$ 200.7, 162.8, 162.6, 133.3, 133.3, 133.0, 132.6, 130.5, 130.3, 129.3, 129.0, 114.32, 114.31, 55.6, 55.5, 55.3, 22.4, 21.6.

**HRMS** (ESI) $m/z$ calcd. for C$_{26}$H$_{26}$NO$_4$S [M + H]$^+$ 424.1577, found 424.1575.

$\{S\}$-((1-(4-(Benzyloxy)phenyl)-1-oxopropan-2-yl)imino)bis(4-methoxyphenyl)-$\lambda^6$-sulfanone (43)

![Structure of 43]

According to **General procedure D** with 1-(4-(benzyloxy)phenyl)-2-bromopropan-1-one (63.8 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product 43 as a white amorphous solid (98.9 mg, 96% yield, 94% ee).

$\{\alpha\}^2_{D} = -72$ ($c$ 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel IA (hexane/PrOH = 70/30, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (minor) = 18.48 min, $t_R$ (major) = 20.31 min.

**H NMR** (400 MHz, CDCl$_3$) $\delta$ 8.08 (d, $J = 9.0$ Hz, 2H), 7.94 (d, $J = 9.0$ Hz, 2H), 7.75 (d, $J = 8.9$ Hz, 2H), 7.54 – 7.33 (m, 5H), 6.99 (d, $J = 8.9$ Hz, 2H), 6.94 (d, $J = 9.0$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 5.14 (s, 2H), 4.68 (q, $J = 6.8$ Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 1.53 (d, $J = 6.8$ Hz, 3H).
\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.6, 162.8, 162.7, 162.3, 136.3, 133.3, 132.6, 131.6, 130.5, 130.3, 128.7, 128.6, 128.2, 127.5, 114.33, 114.30, 114.27, 70.1, 55.60, 55.55, 55.3, 22.5.

HRMS (ESI) \(m/z\) calcd. for C\(_{30}\)H\(_{30}\)NO\(_5\)S [M + H]\(^+\) 516.1839, found 516.1838.

(S)-bis(4-Methoxyphenyl)((1-(3-methoxyphenyl)-1-oxopropan-2-yl)imino)-\(\lambda^6\)-sulfanone (44)

According to General procedure D with 2-bromo-1-(3-methoxyphenyl)propan-1-one (48.4 mg, 0.20 mmol, 1.0 equiv.) for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product 44 as a colorless oil (67.6 mg, 77% yield, 94% ee).

\([\alpha]_D^{20} = -16\) (c 1.0, CH\(_2\)Cl\(_2\)).

HPLC analysis: Chiralcel IE (hexane/iPrOH = 50/50, flow rate 1.0 mL/min, \(\lambda = 254\) nm), \(t_R\) (major) = 29.88 min, \(t_R\) (minor) = 37.45 min.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.96 – 7.90 (m, 2H), 7.77 – 7.70 (m, 2H), 7.61 – 7.53 (m, 2H), 7.30 (t, \(J = 7.9\) Hz, 1H), 7.11 – 7.01 (m, 1H), 6.94 – 6.89 (m, 2H), 6.88 – 6.79 (m, 2H), 4.69 (q, \(J = 6.9\) Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.78 (s, 3H), 1.51 (d, \(J = 6.9\) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 200.9, 162.8, 162.7, 159.6, 137.1, 133.3, 132.6, 130.4, 130.3, 129.2, 121.7, 119.3, 114.32, 114.25, 113.3, 55.6, 55.5, 55.4, 55.3, 22.2.

HRMS (ESI) \(m/z\) calcd. for C\(_{24}\)H\(_{26}\)NO\(_5\)S [M + H]\(^+\) 440.1526, found 440.1523.
(S)-((1-(Benzo[d][1,3]dioxol-5-yl)-1-oxobutan-2-yl)imino)bis(4-methoxyphenyl)-\(\lambda^6\)-sulfanone (45)

According to General procedure D with 1-(benzo[d][1,3]dioxol-5-yl)-2-bromobutan-1-one (54.0 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand L*6 for 5 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product 45 as a colorless oil (65.4 mg, 70% yield, 87% ee).

\[^{[\alpha]}D_{20} = -12\ (c\ 1.0,\ \text{CH}_2\text{Cl}_2)\].

HPLC analysis: Chiralcel IE (hexane/iPrOH = 50/50, flow rate 1.0 mL/min, \(\lambda = 254\) nm), \(t_R\) (major) = 39.80 min, \(t_R\) (minor) = 48.11 min.

\(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.95 – 7.88 (m, 2H), 7.75 – 7.67 (m, 3H), 7.54 (d, \(J = 1.7\) Hz, 1H), 6.95 – 6.88 (m, 2H), 6.86 – 6.80 (m, 2H), 6.78 (d, \(J = 8.2\) Hz, 1H), 6.01 (s, 2H), 4.29 (dd, \(J = 7.6, 6.3\) Hz, 1H), 3.81 (s, 3H), 3.77 (s, 3H), 2.02 – 1.80 (m, 2H), 0.97 (t, \(J = 7.4\) Hz, 3H).

\(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 199.4, 162.7, 162.6, 151.3, 147.8, 133.0, 132.8, 130.6, 130.5, 130.3, 125.4, 114.3, 109.1, 107.6, 101.7, 62.2, 55.6, 55.5, 29.6, 11.0.

HRMS (ESI) \(m/z\) calcd. for C\(_{25}\)H\(_{26}\)NO\(_6\)S \([\text{M + H}]^+\) 468.1475, found 468.1474.

(S)-bis(4-Methoxyphenyl)((1-oxo-1-(3-(trifluoromethyl)phenyl)propan-2-yl)imino)-\(\lambda^6\)-sulfanone (46)

According to General procedure D with 2-bromo-1-(3-(trifluoromethyl)phenyl)propan-1-one (56.0 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the
reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product 46 as a colorless oil (66.8 mg, 70% yield, 94% ee).

$[\alpha]_{D}^{20} = -6$ (c 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel IE (hexane/iPrOH = 50/50, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 11.29 min, $t_R$ (minor) = 12.15 min.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.43 – 8.36 (m, 1H), 8.34 – 8.24 (m, 1H), 7.91 – 7.83 (m, 2H), 7.80 – 7.75 (m, 1H), 7.75 – 7.67 (m, 2H), 7.59 – 7.52 (m, 1H), 6.98 – 6.90 (m, 2H), 6.89 – 6.79 (m, 2H), 4.60 (q, $J = 6.9$ Hz, 1H), 3.83 (s, 3H), 3.79 (s, 3H), 1.53 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 199.9, 162.9, 162.8, 136.2, 132.8, 132.7, 132.4, 130.7 (q, $J = 32.5$ Hz), 130.3, 130.2, 129.1 – 128.8 (m), 128.9, 126.54 – 126.24 (m), 123.9 (q, $J = 271.0$ Hz), 114.4, 114.3, 56.0, 55.60, 55.55, 21.8.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ –62.7 (s, 3F).

**HRMS** (ESI) $m/z$ calcd. for C$_{24}$H$_{23}$F$_3$NO$_4$S [M + H]$^+$ 478.1294, found 478.1294.

**HPLC** analysis: Chiralcel IE (hexane/iPrOH = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 22.57 min, $t_R$ (minor) = 24.84 min.

$(S)$-((1-(4-Fluorophenyl)-1-oxopropan-2-yl)imino)bis(4-methoxyphenyl)-$\lambda^5$-sulfanone (47)

According to **General procedure D** with 2-bromo-1-(4-fluorophenyl)propan-1-one (46.0 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product 47 as a yellow oil (60.6 mg, 71% yield, 91% ee).

$[\alpha]_{D}^{20} = -59$ (c 0.7, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel IE (hexane/iPrOH = 60/40, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 22.57 min, $t_R$ (minor) = 24.84 min.
\[^{1}\text{H} \text{NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 8.18 – 8.11 (m, 2H), 7.94 – 7.87 (m, 2H), 7.79 – 7.71 (m, 2H), 7.13 – 7.04 (m, 2H), 6.97 – 6.90 (m, 2H), 6.90 – 6.83 (m, 2H), 4.63 (q, \(J = 6.9\) Hz, 1H), 3.84 (s, 3H), 3.80 (s, 3H), 1.52 (d, \(J = 6.9\) Hz, 3H).

\[^{13}\text{C} \text{NMR}\] (100 MHz, CDCl\(_3\)) \(\delta\) 199.5, 165.4 (d, \(J = 254.1\) Hz), 162.8, 162.7, 133.1, 132.6, 132.0 (d, \(J = 9.1\) Hz), 131.9 (d, \(J = 3.0\) Hz), 130.33, 130.28, 115.3 (d, \(J = 21.6\) Hz), 114.33, 114.31, 55.7, 55.59, 55.55, 22.1.

\[^{19}\text{F} \text{NMR}\] (376 MHz, CDCl\(_3\)) \(\delta\) –106.0 (tt, \(J = 8.2, 5.5\) Hz, 1F).

HRMS (ESI) \(m/z\) calcd. for C\(_{23}\)H\(_{23}\)FNO\(_4\)S [M + H]\(^+\) 428.1326, found 428.1323.

\((S)-((1-(4-Bromophenyl)-1-oxopropan-2-yl)imino)bis(4-methoxyphenyl)\(\lambda^6\)-sulfanone (48)

![Image of compound 48]

According to General procedure D with 2-bromo-1-(4-bromophenyl)propan-1-one (58.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product 48 as a colorless oil (68.2 mg, 70% yield, 91% ee).

\([\alpha]_{D}^{20} = -253\) (c 0.4, CH\(_2\)Cl\(_2\)).

HPLC analysis: Chiralcel IC (hexane/iPrOH = 50/50, flow rate 1.0 mL/min, \(\lambda = 254\) nm), \(t_R\) (major) = 26.29 min, \(t_R\) (minor) = 50.81 min.

\[^{1}\text{H} \text{NMR}\] (400 MHz, CDCl\(_3\)) \(\delta\) 7.98 (d, \(J = 8.6\) Hz, 2H), 7.90 (d, \(J = 9.0\) Hz, 2H), 7.74 (d, \(J = 8.9\) Hz, 2H), 7.57 (d, \(J = 8.6\) Hz, 2H), 6.95 (d, \(J = 9.0\) Hz, 2H), 6.87 (d, \(J = 9.0\) Hz, 2H), 4.61 (q, \(J = 6.9\) Hz, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 1.51 (d, \(J = 6.9\) Hz, 3H).

\[^{13}\text{C} \text{NMR}\] (100 MHz, CDCl\(_3\)) \(\delta\) 200.1, 162.8, 162.7, 134.3, 133.0, 132.5, 131.5, 131.0, 130.31, 130.26, 127.7, 114.3, 55.7, 55.61, 55.58, 21.9.

HRMS (ESI) \(m/z\) calcd. for C\(_{23}\)H\(_{23}\)BrNO\(_4\)S [M + H]\(^+\) 488.0526 & 490.0505, found 488.0524 & 490.0499.
(S)-((1-(3-Chlorophenyl)-1-oxopropan-2-yl)imino)bis(4-methoxyphenyl)-λ6-sulfanone (49)

According to **General procedure D** with 2-bromo-1-(3-chlorophenyl)propan-1-one (49.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product 49 as a yellow oil (84.2 mg, 95% yield, 90% ee).

\[ [\alpha]^{20}_D = -70 \, (c \ 0.8, \text{CH}_2\text{Cl}_2). \]

**HPLC** analysis: Chiralcel IA (hexane/iPrOH = 60/40, flow rate 1.0 mL/min, λ = 254 nm), \( t_R \) (major) = 26.47 min, \( t_R \) (minor) = 33.30 min.

**1H NMR** (400 MHz, CDCl₃) \( \delta \): 8.01 (t, \( J = 1.8 \) Hz, 1H), 7.95 (dt, \( J = 7.8, 1.3 \) Hz, 1H), 7.90 (d, \( J = 9.0 \) Hz, 2H), 7.73 (d, \( J = 9.0 \) Hz, 2H), 7.53 – 7.44 (m, 1H), 7.36 (t, \( J = 7.8 \) Hz, 1H), 6.94 (d, \( J = 9.0 \) Hz, 2H), 6.87 (d, \( J = 9.0 \) Hz, 2H), 4.61 (q, \( J = 6.8 \) Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 1.52 (d, \( J = 6.8 \) Hz, 3H).

**13C NMR** (100 MHz, CDCl₃) \( \delta \): 199.9, 162.9, 162.7, 137.3, 134.4, 132.9, 132.5, 132.4, 130.31, 130.28, 129.6, 129.3, 127.4, 114.4, 114.3, 55.60, 55.56, 21.9.

**HRMS** (ESI) \( m/z \) calcd. for C₂₃H₂₃ClNO₄S [M + H]⁺ 444.1031, found 444.1031.

(S)-bis(4-Methoxyphenyl)((1-oxo-1-phenylpentan-2-yl)imino)-λ6-sulfanone (50)

According to **General procedure D** with 2-bromo-1-phenylpentan-1-one (48.0 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand \( \text{L}^*6 \) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product 50 as a white amorphous solid (68.2 mg, 78% yield, 92% ee).
$[\alpha]_D^{20} = 0.5$ (c 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel IE (hexane/iPrOH = 50/50, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 21.29 min, $t_R$ (minor) = 26.26 min.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 8.06 – 7.99 (m, 2H), 7.99 – 7.92 (m, 2H), 7.76 – 7.68 (m, 2H), 7.56 – 7.48 (m, 1H), 7.45 – 7.37 (m, 2H), 6.97 – 6.90 (m, 2H), 6.87 – 6.80 (m, 2H), 4.47 (t, $J = 6.9$ Hz, 1H), 3.84 (s, 3H), 3.78 (s, 3H), 1.95 – 1.81 (m, 2H), 1.65 – 1.54 (m, 1H), 1.47 – 1.37 (m, 1H), 0.90 (t, $J = 7.3$ Hz, 3H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$ 201.7, 162.8, 162.6, 136.1, 133.1, 132.7, 132.5, 130.6, 130.4, 129.1, 128.2, 114.3, 114.2, 60.5, 55.6, 55.5, 38.3, 19.7, 13.9.

**HRMS** (ESI) $m/z$ calcd. for C$_{25}$H$_{28}$NO$_4$S [M + H]$^+$ 438.1734, found 438.1733.

(S)-bis(4-Methoxyphenyl)((1-oxo-1-(thiophen-2-yl)propan-2-yl)imino)-$\lambda^6$-sulfanone (51)

![Structure of 51](image)

According to **General procedure D** with 2-bromo-1-(thiophen-2-yl)propan-1-one (43.8 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product 51 as a colorless oil (68.0 mg, 82% yield, 94% ee).

$[\alpha]_D^{20} = -63$ (c 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel IE (hexane/iPrOH = 50/50, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (major) = 24.03 min, $t_R$ (minor) = 27.76 min.

**$^1$H NMR** (400 MHz, CDCl$_3$) $\delta$ 8.01 (dd, $J = 3.9, 1.2$ Hz, 1H), 7.97 – 7.91 (m, 2H), 7.82 – 7.75 (m, 2H), 7.61 (dd, $J = 4.9, 1.2$ Hz, 1H), 7.10 (dd, $J = 4.9, 3.8$ Hz, 1H), 6.98 – 6.91 (m, 2H), 6.91 – 6.84 (m, 2H), 4.42 (q, $J = 6.8$ Hz, 1H), 3.83 (s, 3H), 3.80 (s, 3H), 1.55 (d, $J = 6.8$ Hz, 3H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$) $\delta$ 194.7, 162.8, 162.7, 141.0, 133.8, 133.6, 133.0, 132.3, 130.5, 130.3, 127.7, 114.4, 114.3, 57.5, 55.60, 55.57, 23.0.
HRMS (ESI) $m/z$ calcd. for C$_{21}$H$_{22}$NO$_4$S$_2$ [M + H]$^+$ 416.0985, found 416.0983.

(S)-bis(4-Methoxyphenyl)((3-oxobutan-2-yl)imino)-$\lambda^6$-sulfanone (52)

![Chemical structure of 52](image)

According to **General procedure D** with 3-bromobutan-2-one (45.0 mg, 0.30 mmol, 1.5 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product 52 as a yellow oil (42.3 mg, 61% yield, 72% ee).

$[\alpha]_{D}^{20} = -1$ ($c$ 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel IC (hexane/PrOH = 60/40, flow rate 1.0 mL/min, $\lambda$ = 254 nm), $t_R$ (minor) = 21.16 min, $t_R$ (major) = 22.89 min.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.31 – 7.64 (m, 4H), 7.09 – 6.78 (m, 4H), 3.85 (s, 3H), 3.84 (s, 3H), 3.69 (q, $J$ = 6.8 Hz, 1H), 2.35 (s, 3H), 1.37 (d, $J$ = 6.8 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 212.0, 162.9, 162.8, 132.5, 132.3, 130.4, 130.3, 114.5, 114.4, 59.6, 55.6, 25.9, 21.1.

HRMS (ESI) $m/z$ calcd. for C$_{18}$H$_{22}$NO$_4$S [M + H]$^+$ 348.1264, found 348.1262.

(S)-bis(4-Methoxyphenyl)((4-methyl-3-oxopentan-2-yl)imino)-$\lambda^6$-sulfanone (53)

![Chemical structure of 53](image)

According to **General procedure D** with 2-bromo-4-methylpentan-3-one (35.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product 52 as a colorless oil (58.5 mg, 78% yield, 89% ee).

$[\alpha]_{D}^{20} = -3$ ($c$ 1.0, CH$_2$Cl$_2$).
**HPLC** analysis: Chiralcel IC (hexane/iPrOH = 50/50, flow rate 1.0 mL/min, λ = 254 nm), \( t_R \) (minor) = 10.52 min, \( t_R \) (major) = 12.73 min.

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \( \delta \) 7.96 – 7.88 (m, 2H), 7.88 – 7.81 (m, 2H), 6.99 – 6.91 (m, 4H), 3.90 – 3.82 (m, 7H), 3.32 (p, \( J = 6.8 \) Hz, 1H), 1.37 (d, \( J = 6.9 \) Hz, 3H), 1.12 (d, \( J = 6.8 \) Hz, 3H), 1.08 (d, \( J = 6.9 \) Hz, 3H).

**\(^{13}\)C NMR** (100 MHz, CDCl\(_3\)) \( \delta \) 216.5, 162.8, 162.7, 133.0, 132.5, 130.39, 130.37, 114.4, 114.3, 57.9, 55.6, 35.7, 21.2, 19.1, 18.9.

**HRMS** (ESI) \( m/z \) calcd. for C\(_{20}\)H\(_{26}\)NO\(_4\)S [M + H]\(^+\) 376.1577, found 376.1575.
Enantioconvergent N-alkylation: scope of secondary α-bromonitrile. (Figure 3A)

\((S)-2-((\text{bis}(4\text{-}\text{methoxyphenyl})(\text{oxo})\text{-}\lambda^6\text{-sulfaneylidene})\text{amino})\text{-}2\text{-cyclohexylacetonitrile} \ (54)\)

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminobis(4-methoxyphenyl)-\(\lambda^6\)-sulfanone (60.9 mg, 0.22 mmol, 1.1 equiv.), Cu(PPh\(_3\))\(_3\)Br (18.6 mg, 0.020 mmol, 10 mol%), chiral ligand \(\text{L}^*\) (30.0 mg, 0.022 mmol, 11 mol%), Cs\(_2\)CO\(_3\) (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et\(_2\)O (4.0 mL). To this solution was added 2-bromo-2-cyclohexylacetonitrile (40.2 mg, 0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at 0 °C for 5 d. Upon completion (monitored by TLC), the precipitate was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to afford the desired product \(54\) as a colorless oil (54.1 mg, 68% yield, 90% ee).

\([\alpha]_{\text{D}}^{20} = 14 \ (c\ 1.0, \text{CH}_2\text{Cl}_2)\).

HPLC analysis: Chiralcel ID (hexane/iPrOH = 70/30, flow rate 1.0 mL/min, \(\lambda = 254\) nm), \(t_R\) (major) = 14.77 min, \(t_R\) (minor) = 16.93 min.

\(^1\text{H} \text{NMR} (400 \text{ MHz, CDCl}_3) \delta 7.92 \ (\text{dd}, J = 14.5, 8.9 \text{ Hz}, 4\text{H}), 6.98 \ (\text{dd}, J = 12.7, 9.0 \text{ Hz}, 4\text{H}), 3.85 \ (\text{s}, 6\text{H}), 3.80 \ (\text{d}, J = 6.4 \text{ Hz}, 1\text{H}), 2.12 – 2.03 \ (\text{m}, 1\text{H}), 1.96 \ (\text{d}, J = 12.3 \text{ Hz}, 1\text{H}), 1.82 – 1.68 \ (\text{m}, 3\text{H}), 1.36 – 1.09 \ (\text{m}, 6\text{H}).

\(^{13}\text{C} \text{NMR} (100 \text{ MHz, CDCl}_3) \delta 163.2, 163.1, 132.0, 131.4, 130.8, 130.1, 120.5, 114.7, 114.4, 55.7, 55.6, 50.4, 43.5, 29.4, 28.9, 26.2, 25.8.

HRMS (ESI) \(m/z\) calcd. for \(\text{C}_{22}\text{H}_{27}\text{N}_{2}\text{O}_{3}\text{S} [\text{M + H}]^+ 399.1737\), found 399.1735.
Enantioconvergent N-alkylation: scope of secondary α-bromo amides. (Figure 3A)

General procedure E:

\[
\begin{array}{c}
\text{R}^2 \quad \text{O} \quad \text{N} \quad \text{R}^3 \\
\text{R}^1 \quad \text{Br} \quad \text{1.0 equiv.}
\end{array}
\quad +
\quad
\begin{array}{c}
\text{Ph} \quad \text{S} \quad \text{NH} \\
\text{Ph} \quad \text{1.0 equiv.}
\end{array}
\quad \xrightarrow{\text{Cu(HFacac)}_2 (10 \text{ mol\%}) \quad \text{L}^*6 (10 \text{ mol\%}) \quad \text{Cs}_2\text{CO}_3 (2.5 \text{ equiv.}) \quad \text{Et}_2\text{O}, \text{rt}}
\quad \begin{array}{c}
\text{R}^2 \quad \text{O} \quad \text{N} \quad \text{S} \quad \text{Ph} \\
\text{R}^3 \quad \text{R}^1 \quad \text{Ph} \quad \text{1.0 equiv.}
\end{array}
\]

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ^6-sulfanone (43.4 mg, 0.20 mmol, 1.0 equiv.), Cu(HFacac)₂ (8.8 mg, 0.020 mmol, 10 mol%), chiral ligand L^*6 (20.5 mg, 0.020 mmol, 10 mol%), Cs₂CO₃ (163.0 mg, 0.50 mmol, 2.5 equiv.) and anhydrous Et₂O (4.0 mL). Then, α-bromo amide (0.20 mmol, 1.0 equiv.) was added into the mixture and stirred at room temperature for 36 h or more. Upon completion (monitored by TLC), the precipitate was filtered off and washed with EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford the desired product.

General procedure F:

\[
\begin{array}{c}
\text{R}^2 \quad \text{O} \quad \text{N} \quad \text{R}^3 \\
\text{R}^1 \quad \text{Br} \quad \text{1.0 equiv.}
\end{array}
\quad +
\quad
\begin{array}{c}
\text{Ar} \quad \text{S} \quad \text{NH} \\
\text{Ar} \quad \text{1.2 equiv.}
\end{array}
\quad \xrightarrow{\text{Cu(HFacac)}_2 (10 \text{ mol\%}) \quad \text{L}^*7 (10 \text{ mol\%}) \quad \text{Cs}_2\text{CO}_3 (2.5 \text{ equiv.}) \quad \text{Et}_2\text{O}, \text{rt}}
\quad \begin{array}{c}
\text{R}^2 \quad \text{O} \quad \text{N} \quad \text{S} \quad \text{Ar} \\
\text{R}^3 \quad \text{R}^1 \quad \text{Ar} \quad \text{1.0 equiv.}
\end{array}
\]

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with sulfoximine (0.24 mmol, 1.2 equiv.), Cu(HFacac)₂ (8.8 mg, 0.020 mmol, 10 mol%), chiral ligand L^*7 (27.3 mg, 0.020 mmol, 10 mol%), Cs₂CO₃ (163.0 mg, 0.50 mmol, 2.5 equiv.) and anhydrous Et₂O (4.0 mL). Then, α-bromo amide (0.20 mmol, 1.0 equiv.) was added into the mixture and stirred at room temperature for 36 h or more. Upon completion (monitored by TLC), the precipitate was filtered off and washed with EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to afford the desired product.
(S)-((1-(Indolin-1-yl)-1-oxopropan-2-yl)imino)diphenyl-\(\lambda^6\)-sulfanone (55)

According to **General procedure E** with 2-bromo-1-(indolin-1-yl)propan-1-one (50.6 mg, 0.20 mmol, 1.0 equiv.) for 36 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product 55 as a white amorphous solid (74.8 mg, 96% yield, 94% ee).

\([\alpha]_D^{20} = -114\) (c 1.0, CH₂Cl₂).

**HPLC** analysis: Chiralcel OZ3 (hexane/PrOH = 80/20, flow rate 1.0 mL/min, \(\lambda = 254\) nm), \(t_R\) (minor) = 20.34 min, \(t_R\) (major) = 31.38 min.

**\(^1H\ NMR** (400 MHz, CDCl₃) \(\delta\) 8.28 (d, \(J = 8.2\) Hz, 1H), 8.05 (d, \(J = 6.9\) Hz, 2H), 7.96 (d, \(J = 6.7\) Hz, 2H), 7.56 – 7.33 (m, 6H), 7.23 – 7.09 (m, 2H), 7.00 (t, \(J = 7.4\) Hz, 1H), 4.31 (q, \(J = 6.6\) Hz, 1H), 4.16 – 3.95 (m, 2H), 3.17 – 2.92 (m, 2H), 1.46 (d, \(J = 6.5\) Hz, 3H).

**\(^{13}C\ NMR** (100 MHz, CDCl₃) \(\delta\) 172.0, 143.3, 141.7, 141.2, 132.6, 132.5, 131.4, 129.12, 129.09, 128.41, 128.35, 127.4, 124.4, 123.6, 117.6, 52.0, 47.7, 28.2, 20.9.

**HRMS** (ESI) \(m/z\) calcd. for C₂₃H₂₃N₂O₂S [M + H]⁺ 391.1475, found 391.1472.

(S)-(1-(5-Methoxyindolin-1-yl)-1-oxopropan-2-yl)imino)diphenyl-\(\lambda^6\)-sulfanone (56)

According to **General procedure E** with 2-bromo-1-(5-methoxyindolin-1-yl)propan-1-one (56.6 mg, 0.20 mmol, 1.0 equiv.) for 30 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to yield the product 56 as a yellow amorphous solid (78.1 mg, 93% yield, 93% ee).

\([\alpha]_D^{20} = -56\) (c 0.7, CH₂Cl₂).

**HPLC** analysis: Chiralcel OZ3 (hexane/PrOH = 70/30, flow rate 0.6 mL/min, \(\lambda = 254\) nm), \(\lambda = 254\) nm.
nm), \( t_R \) (minor) = 36.70 min, \( t_R \) (major) = 46.77 min.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.24 – 8.14 (m, 1H), 8.04 (d, \( J = 6.9 \) Hz, 2H), 7.95 (d, \( J = 6.8 \) Hz, 2H), 7.55 – 7.34 (m, 6H), 6.70 (s, 2H), 4.28 (q, \( J = 6.5 \) Hz, 1H), 4.12 – 3.92 (m, 2H), 3.77 (s, 3H), 3.11 – 2.87 (m, 2H), 1.45 (d, \( J = 6.6 \) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 171.3, 156.3, 141.6, 141.2, 136.9, 133.0, 132.6, 132.5, 129.12, 129.08, 128.39, 128.37, 118.2, 111.8, 110.6, 55.6, 51.8, 47.9, 28.4, 21.0.

HRMS (ESI) \( m/z \) calcd. for C\(_{24}\)H\(_{25}\)N\(_2\)O\(_3\)S [M + H]\(^+\) 421.1580, found 421.1574.

\((S)-((1\text{-oxo-1-(5-(Trifluoromethyl)indolin-1-yl)propan-2-yl} \text{imino})\text{diphenyl-1,6-sulfanone (57)}\)

According to General procedure E with 2-bromo-1-(5-(trifluoromethyl)indolin-1-yl)propan-1-one (64.4 mg, 0.20 mmol, 1.0 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/Et\(_2\)OAc = 3/1) to yield the product 57 as a white amorphous solid (83.3 mg, 91% yield, 94% ee).

\( [\alpha] \)\(_{D20}^2 \) = −425 (c 0.6, CH\(_2\)Cl\(_2\)).

HPLC analysis: Chiralcel OZ3 (hexane/iPrOH = 70/30, flow rate 0.6 mL/min, \( \lambda = 254 \) nm), \( t_R \) (minor) = 17.91 min, \( t_R \) (major) = 20.29 min.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 8.33 (d, \( J = 8.5 \) Hz, 1H), 8.02 (d, \( J = 6.7 \) Hz, 2H), 7.96 (d, \( J = 6.5 \) Hz, 2H), 7.56 – 7.32 (m, 8H), 4.31 (q, \( J = 6.6 \) Hz, 1H), 4.17 (t, \( J = 8.5 \) Hz, 2H), 3.21 – 3.00 (m, 2H), 1.45 (d, \( J = 6.6 \) Hz, 3H).

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \( \delta \) 172.6, 146.2, 141.5, 141.1, 132.7, 132. 6, 132.1, 129.2, 129.1, 128.4, 128.2, 125.4 (q, \( J = 32.0 \) Hz), 125.1 (q, \( J = 3.9 \) Hz), 124.4 (q, \( J = 270.0 \) Hz), 121.4 (d, \( J = 4.1 \) Hz), 117.2, 52.0, 48.1, 27.9, 20.6.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \( \delta \) −61.6 (s, 3F).

HRMS (ESI) \( m/z \) calcd. for C\(_{24}\)H\(_{22}\)F\(_3\)N\(_2\)O\(_2\)S [M + H]\(^+\) 459.1349, found 459.1342.
(S)-((1-(5-Bromoindolin-1-yl)-1-oxopropan-2-yl)imino)diphenyl-λ6-sulfanone (58)

According to General procedure E with 2-bromo-1-(5-bromoindolin-1-yl)propan-1-one (66.6 mg, 0.20 mmol, 1.0 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product 58 as a white amorphous solid (91.7 mg, 98% yield, 94% ee).

X-ray quality crystals were obtained by slow evaporation of solvent from a saturated solution in a mixture of CH2Cl2/hexane.

\[ [\alpha]^2_{D20} = -46 \ (c \ 0.5, \ CH2Cl2). \]

HPLC analysis: Chiralcel OZ3 (hexane/iPrOH = 70/30, flow rate 0.6 mL/min, \( \lambda = 254 \) nm), \( tR \) (minor) = 24.31 min, \( tR \) (major) = 29.96 min.

\(^1H\) NMR (400 MHz, CDCl3) \( \delta \) 8.14 (d, \( J = 8.6 \) Hz, 1H), 7.99 (dd, \( J = 27.4, 7.6 \) Hz, 4H), 7.61 – 7.36 (m, 6H), 7.32 – 7.14 (m, 2H), 4.28 (q, \( J = 6.6 \) Hz, 1H), 4.18 – 3.98 (m, 2H), 3.19 – 2.89 (m, 2H), 1.43 (d, \( J = 6.6 \) Hz, 3H).

\(^13C\) NMR (100 MHz, CDCl3) \( \delta \) 172.1, 142.5, 141.6, 141.1, 133.8, 132.6, 132.5, 130.2, 129.2, 129.1, 128.4, 128.3, 127.4, 118.9, 116.0, 51.9, 47.9, 28.0, 20.7.

HRMS (ESI) \( m/z \) calcd. for C\(_{23}\)H\(_{22}\)BrN\(_2\)O\(_2\)S [M + H]\(^+\) 469.0580, found 469.0577.

(S)-N-Methyl-2-(((oxodiphenyl-λ6-sulfaneylidene)amino)-N-phenylpropanamide (59)

According to General procedure F with 2-bromo-N-methyl-N-phenylpropanamide (48.2 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product 59 as an amorphous solid (55.2 mg, 73% yield, 93% ee).

\[ [\alpha]^2_{D20} = 0.1 \ (c \ 1.0, \ CH2Cl2). \]
**HPLC** analysis: Chiralcel OZ3 (hexane/iPrOH = 70/30, flow rate 0.6 mL/min, λ = 230 nm), $t_R$ (minor) = 34.32 min, $t_R$ (major) = 43.04 min.

**$^1$H NMR** (400 MHz, CDCl$_3$) δ 7.99 (d, $J = 7.2$ Hz, 2H), 7.89 (d, $J = 7.6$ Hz, 2H), 7.58 – 7.37 (m, 6H), 7.20 (s, 3H), 6.76 (s, 2H), 3.95 (q, $J = 6.8$ Hz, 1H), 3.19 (s, 3H), 1.34 (d, $J = 6.9$ Hz, 3H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$) δ 174.4, 143.4, 141.5, 141.0, 132.42, 132.38, 129.5, 129.1, 129.0, 128.9, 128.4, 127.6, 127.2, 49.2, 37.7, 22.4.

**HRMS** (ESI) $m/z$ calcd. for C$_{22}$H$_{23}$N$_2$O$_2$S [M + H]$^+$ 379.1475, found 379.1469.

(S)-2-((Oxodiphenyl-λ$_6$-sulfaneylidene)amino)-N-phenylpropanamide (60)

![Chemical Structure](image)

According to **General procedure F** with 2-bromo-N-methyl-N-phenylpropanamide (48.2 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the product 60 as a colorless oil (35.6 mg, 49% yield, 72% ee).

$\{\alpha\}$$_{D}^20 = -31$ (c 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel IA (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), $t_R$ (minor) = 10.04 min, $t_R$ (major) = 17.58 min.

**$^1$H NMR** (400 MHz, CDCl$_3$) δ 9.23 (s, 1H), 8.11 – 7.94 (m, 4H), 7.69 – 7.51 (m, 8H), 7.35 (t, $J = 7.9$ Hz, 2H), 7.13 (t, $J = 7.4$ Hz, 1H), 3.89 (q, $J = 6.9$ Hz, 1H), 1.55 (d, $J = 6.9$ Hz, 3H).

**$^{13}$C NMR** (100 MHz, CDCl$_3$) δ 172.9, 140.2, 139.7, 138.0, 133.11, 133.05, 129.6, 129.4, 129.0, 128.5, 128.3, 124.1, 119.7, 54.9, 22.7.

**HRMS** (ESI) $m/z$ calcd. for C$_{21}$H$_{21}$N$_2$O$_2$S [M + H]$^+$ 365.1318, found 365.1313.
(S)-((1-Morpholino-1-oxopropan-2-yl)imino)diphenyl-λ6-sulfanone (61)

\[ \text{61} \]

According to General procedure F with 2-bromo-1-morpholinopropan-1-one E2 (44.2 mg, 0.20 mmol, 1.0 equiv.) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product 61 as a colorless oil (68.0 mg, 95% yield, 95% ee).

\[ \alpha \]D20 = 27 (c 1.0, CH2Cl2).

**HPLC analysis:** Chiralcel OZ3 (hexane/iPrOH = 80/20, flow rate 0.8 mL/min, \( \lambda \) = 230 nm), \( t_R \) (minor) = 32.31 min, \( t_R \) (major) = 40.52 min.

\(^1H\) NMR (400 MHz, CDCl3) \( \delta \) 8.04 – 7.86 (m, 4H), 7.57 – 7.40 (m, 6H), 4.24 (q, \( J = 6.7 \) Hz, 1H), 3.88 – 3.45 (m, 8H), 1.39 (d, \( J = 6.7 \) Hz, 3H).

\(^13C\) NMR (100 MHz, CDCl3) \( \delta \) 172.5 141.2, 140.9, 132.6, 129.2 128.4 128.3, 66.9, 66.7, 51.6, 46.2, 42.6, 21.4.

**HRMS (ESI) m/z** calcd. for C19H23N2O3S \([M + H]^+\) 359.1424, found 359.1419.

(R)-((1-Morpholino-1-oxopropan-2-yl)imino)diphenyl-λ6-sulfanone ((R)-61)

\[ (R)-\text{61} \]

According to General procedure F with 2-bromo-1-morpholinopropan-1-one E2 (44.2 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand L*7' for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product (R)-61 as a colorless oil (68.1 mg, 99% yield, 97% ee).

**HPLC analysis:** Chiralcel OZ3 (hexane/iPrOH = 80/20, flow rate 0.8 mL/min, \( \lambda \) = 230 nm), \( t_R \) (major) = 31.16 min, \( t_R \) (minor) = 42.41 min.
(S)-((1-Morpholino-1-oxohexan-2-yl)imino)diphenyl-λ6-sulfanone (62)

According to General procedure F with 2-bromo-1-morpholinohexan-1-one (52.6 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product 62 as a colorless oil (68.1 mg, 85% yield, 89% ee).

$$[\alpha]_{D}^{20} = -20 \ (c \ 1.0, \text{CH}_2\text{Cl}_2).$$

HPLC analysis: Chiralcel OZ3 (hexane/iPrOH = 80/20, flow rate 0.8 mL/min, $\lambda = 230$ nm), $t_R$ (minor) = 15.98 min, $t_R$ (major) = 18.14 min.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.03 – 7.89 (m, 4H), 7.59 – 7.39 (m, 6H), 4.00 (t, $J = 7.2$ Hz, 1H), 3.88 – 3.74 (m, 1H), 3.71 – 3.39 (m, 7H), 1.91 – 1.70 (m, 2H), 1.53 – 1.39 (m, 1H), 1.38 – 1.16 (m, 3H), 0.87 (t, $J = 7.0$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 172.3, 141.1, 140.6, 132.60, 132.59, 129.1, 128.6, 128.4, 66.9, 66.6, 56.6, 46.2, 42.5, 35.3, 28.6, 22.5, 14.0.

HRMS (ESI) m/z calcd. for C$_{22}$H$_{29}$N$_2$O$_3$S [M + H]$^+$ 401.1893, found 401.1888.

(S)-((4-Methyl-1-morpholino-1-oxopentan-2-yl)imino)diphenyl-λ6-sulfanone (63)

According to General procedure F with 2-bromo-4-methyl-1-morpholinopentan-1-one (52.6 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product 63 as a colorless oil (63.2 mg, 79% yield, 91% ee).

$$[\alpha]_{D}^{20} = -13 \ (c \ 1.0, \text{CH}_2\text{Cl}_2).$$

HPLC analysis: Chiralcel AZ3 (hexane/iPrOH = 80/20, flow rate 0.6 mL/min, $\lambda = 230$ nm), $t_R$ (minor) = 35.34 min, $t_R$ (major) = 41.25 min.
$^1$H NMR (400 MHz, CDCl$_3$) δ 7.97 (dd, $J = 14.1$, 7.3 Hz, 4H), 7.62 – 7.38 (m, 6H), 4.08 (dd, $J = 8.7$, 5.7 Hz, 1H), 3.84 – 3.33 (m, 8H), 1.90 – 1.67 (m, 2H), 1.65 – 1.53 (m, 1H), 0.90 (d, $J = 6.6$ Hz, 3H), 0.85 (d, $J = 6.5$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.5, 141.1, 140.6, 132.62, 132.61, 129.2, 129.1, 128.6, 128.4, 66.9, 66.5, 54.4, 46.2, 44.4, 42.5, 24.7, 23.2, 21.9.

HRMS (ESI) m/z calcd. for C$_{22}$H$_{29}$N$_2$O$_3$S [M + H]$^+$ 401.1893, found 401.1888.

(S)-((4-Chloro-1-morpholino-1-oxobutan-2-yl)imino)diphenyl-λ$_6$-sulfanone (64)

According to General procedure F with 2-bromo-4-chloro-1-morpholinobutan-1-one (53.8 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product 64 as a yellow oil (62.5 mg, 77% yield, 93% ee).

$[\alpha]D^{20} = 5$ (c 1.0, CH$_2$Cl$_2$).

HPLC analysis: Chiralcel IF (hexane/iPrOH = 70/30, flow rate 0.8 mL/min, λ = 254 nm), $t_R$ (major) = 14.79 min, $t_R$ (minor) = 16.52 min.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.04 (d, $J = 7.2$ Hz, 2H), 7.96 (d, $J = 7.3$ Hz, 2H), 7.60 – 7.43 (m, 6H), 4.35 (dd, $J = 8.3$, 5.3 Hz, 1H), 3.88 – 3.78 (m, 1H), 3.72 – 3.25 (m, 9H), 2.33 – 2.13 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 171.3, 140.9, 140.5, 132.83, 132.76, 129.24, 129.21, 128.6, 128.4, 66.8, 66.5, 51.3, 46.1, 42.4, 42.3, 37.8.

HRMS (ESI) m/z calcd. for C$_{20}$H$_{24}$ClN$_2$O$_3$S [M + H]$^+$ 407.1191, found 407.1188.
(S)-2-(4-Morpholino-4-oxo-3-((oxodiphenyl-\(\lambda_6\)-sulfaneylidene)amino)butyl)
isoindoline-1,3-dione (65)

According to **General procedure F** with 2-(3-bromo-4-morpholino-4-oxobutyl)isoindoline-1,3-dione (76.0 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/5) to yield the product **65** as an amorphous solid (62.0 mg, 60% yield, 88% ee).

\[\text{[\alpha]}_D^{20} = -18 \ (c \ 0.9, \text{CH}_2\text{Cl}_2).\]

**HPLC** analysis: Chiralcel IA (hexane/iPrOH = 60/40, flow rate 0.8 mL/min, \(\lambda = 230\) nm), \(t_R\) (minor) = 19.59 min, \(t_R\) (major) = 27.62 min.

**\(^1H\) NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.97 (d, \(J = 7.7\) Hz, 2H), 7.90 (d, \(J = 7.2\) Hz, 2H), 7.80 (dd, \(J = 5.4, 3.1\) Hz, 2H), 7.70 (dd, \(J = 5.5, 3.1\) Hz, 2H), 7.64 – 7.32 (m, 6H), 4.13 (t, \(J = 7.0\) Hz, 1H), 3.93 – 3.36 (m, 10H), 2.35 (dt, \(J = 13.4, 6.8\) Hz, 1H), 2.11 – 1.99 (m, 1H).

**\(^1^3C\) NMR** (100 MHz, CDCl\(_3\)) \(\delta\) 170.8, 168.2, 140.8, 140.6, 133.9, 132.8, 132.6, 132.1, 129.2, 128.5, 128.2, 123.1, 66.7, 66.5, 53.4, 46.2, 42.5, 35.5, 33.6.

**HRMS** (ESI) \(m/z\) calcd. for C\(_{28}\)H\(_{28}\)N\(_3\)O\(_5\)S \([M + H]^+\) 518.1744, found 518.1741.

(S)-bis(4-Methoxyphenyl)((1-morpholino-1-oxo-4-phenoxybutan-2-yl)imino)-\(\lambda^6\)-sulfanone (66)
According to **General procedure F** with 2-bromo-1-morpholino-4-phenoxybutan-1-one (65.4 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **66** as a colorless oil (84.8 mg, 81% yield, 89% ee).

$[\alpha]_{D}^{20} = 3$ (c 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel ID (hexane/iPrOH = 50/50, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (minor) = 32.61 min, $t_R$ (major) = 56.48 min.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.83 (dd, $J = 8.9, 1.2$ Hz, 4H), 7.36 – 7.20 (m, 2H), 7.06 – 6.69 (m, 7H), 4.36 (dd, $J = 8.3, 5.7$ Hz, 1H), 4.39 – 4.19 (m, 1H), 4.11 – 4.01 (m, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.77 – 3.35 (m, 8H), 2.41 – 2.16 (m, 2H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 172.1, 162.8, 158.8, 132.9, 132.3, 130.4, 130.3, 129.4, 120.6, 114.5, 114.4, 114.3, 66.9, 66.5, 64.4, 55.60, 55.55, 52.0, 46.1, 42.5, 34.9.

**HRMS** (ESI) $m/z$ calcd. for C$_{28}$H$_{33}$N$_2$O$_6$S $[M + H]^+$ 525.2054, found 525.2048.

**Ethyl (S)-4-((bis(4-methoxyphenyl)(oxo)-$\lambda^5$-sulfaneylidene)amino)-5-morpholino-5-oxopentanoate (67)**

![67](image)

According to **General procedure F** with ethyl 4-bromo-5-morpholino-5-oxopentanoate (61.4 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product **67** as a colorless oil (66.6 mg, 66% yield, 88% ee).

$[\alpha]_{D}^{20} = 4$ (c 1.0, CH$_2$Cl$_2$).

**HPLC** analysis: Chiralcel ID (hexane/iPrOH = 50/50, flow rate 1.0 mL/min, $\lambda = 254$ nm), $t_R$ (minor) = 37.86 min, $t_R$ (major) = 75.79 min.
**1H NMR** (400 MHz, CDCl3) δ 7.90 (d, J = 8.9 Hz, 2H), 7.80 (d, J = 8.9 Hz, 2H), 6.92 (dd, J = 8.9, 6.3 Hz, 4H), 4.18 – 4.01 (m, 3H), 3.82 (s, 6H), 3.81 – 3.71 (m, 1H), 3.69 – 3.54 (m, 4H), 3.54 – 3.37 (m, 3H), 2.63 – 2.43 (m, 2H), 2.15 – 1.95 (m, 2H), 1.24 (t, J = 7.1 Hz, 3H).

**13C NMR** (100 MHz, CDCl3) δ 173.6, 172.2, 162.9, 162.8, 132.8, 132.4, 130.5, 130.4, 114.4, 114.3, 66.9, 66.6, 60.3, 55.61, 55.59, 54.7, 46.1, 42.5, 30.7, 29.9, 14.2.


(S)-bis(4-Methoxyphenyl)((1-morpholino-1-oxo-4-phenylbutan-2-yl)imino)-λ6-sulfanone (68)

![Chemical structure of 68](image)

According to **General procedure C** with 2-bromo-1-morpholino-4-phenylbutan-1-one (62.2 mg, 0.20 mmol, 1.0 equiv.) for 96 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product 68 as a colorless oil (65.0 mg, 65% yield, 89% ee).

[α]D20 = –0.4 (c 0.3, CH2Cl2).

**HPLC** analysis: Chiralcel IA (hexane/iPrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), tR (minor) = 12.69 min, tR (major) = 18.84 min.

**1H NMR** (400 MHz, CDCl3) δ 7.94 – 7.75 (m, 4H), 7.39 – 7.08 (m, 5H), 6.92 (dd, J = 9.0, 0.9 Hz, 4H), 3.99 (dd, J = 7.6, 6.4 Hz, 1H), 3.83 (s, 3H), 3.82 (s, 3H), 3.73 – 3.30 (m, 8H), 3.01 – 2.75 (m, 1H), 2.72 – 2.60 (m, 1H), 2.17 – 2.07 (m, 2H).

**13C NMR** (100 MHz, CDCl3) δ 172.2, 162.8, 141.8, 132.8, 132.5, 130.4, 130.3, 128.56, 128.3, 125.8, 114.4, 114.3, 66.9, 66.6, 55.8, 55.6, 46.1, 42.5, 37.0, 32.6.

**HRMS** (ESI) m/z calcd. for C28H33N2O5S [M + H]+ 509.2105, found 509.2103.
(S)-bis(4-Methoxyphenyl)((1-morpholino-1-oxohex-5-en-2-yl)imino)-λ6-sulfanone (69)

According to **General procedure F** with 2-bromo-1-morpholinohex-5-en-1-one (52.2 mg, 0.20 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product 69 as a colorless oil (71.4 mg, 78% yield, 90% ee).

\[ \alpha \]_D^20 = -3 (c 1.0, CH2Cl2).

**HPLC** analysis: Chiralcel IA (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, \( \lambda = 254 \) nm), \( t_R \) (minor) = 16.58 min, \( t_R \) (major) = 18.86 min.

\[^1\text{H} \text{NMR} \text{(400 MHz, CDCl}_3) δ\] 7.85 (dd, \( J = 11.5, 8.9 \) Hz, 4H), 6.92 (dd, \( J = 8.9, 1.8 \) Hz, 4H), 5.78 (ddt, \( J = 16.9, 10.2, 6.5 \) Hz, 1H), 5.24 – 4.70 (m, 2H), 4.00 (dd, \( J = 7.9, 6.4 \) Hz, 1H), 3.82 (s, 6H), 3.81 – 3.39 (m, 8H), 2.33 – 2.18 (m, 1H), 2.17 – 2.04 (m, 1H), 1.98 – 1.80 (m, 2H).

\[^{13}\text{C} \text{NMR} \text{(100 MHz, CDCl}_3) δ\] 172.3, 162.80, 162.78, 138.1, 133.0, 132.6, 130.4, 130.3, 115.0, 114.4, 114.3, 67.0, 66.7, 56.0, 55.6, 46.2, 42.5, 34.7, 30.6.

**HRMS** (ESI) \( m/z \) calcd. for C_{24}H_{31}N_{2}O_{5}S [M + H]^+ 459.1948, found 459.1942.
Demonstration of synthetic potentials. (Figure 4)

A gram-scale experiment. (Figure 4A)

According to General procedure F with 2-bromo-1-morpholinopropan-1-one E2 (1.11 g, 5.0 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the product 61 as a colorless oil (1.41 g, 79% yield, 93% ee).

Synthesis of the antipodes of products. (Figure 4B)

According to General procedure A with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand L*7' (27.3 mg, 0.020 mmol, 10 mol%) for 60 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product (R)-1 as a colorless oil (63.6 mg, 99% yield, 98% ee).

HPLC analysis: Chiralcel IA (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), 

Conversion of enantioenriched sulfoximines to chiral primary amines. (Figure 4C)

Deprotection of benzyl products to primary amine (90)

Procedure a:
To a flamed dried flask charged with a stir bar were added 1 (18.3 mg, 0.057 mmol, 1.0 equiv., 96% ee), Mg (13.7 mg, 0.57 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), HCl (0.31 mL, 1.25 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added to the mixture at 0 °C, and the mixture was warmed up to room temperature to afford a homogeneous solution in 10 min. The mixture was stirred for another 1 h, then concentrated under reduced pressure to afford the crude product 70 (8.1 mg, 91% crude yield, determined by 1H NMR using 1,3,5-trimethoxybenzene as an internal standard).

To a solution of the crude 70 (6.3 mg, 0.052 mmol, 1.0 equiv.) in CH2Cl2 (2.0 mL) were added Et3N (21.0 mg, 0.21 mmol, 4.0 equiv.) and Ac2O (21.4 mg, 0.21 mmol, 4.0 equiv.) sequentially. The reaction was stirred at room temperature for 12 h, and then quenched with saturated NH4Cl solution. The mixture was extracted with CH2Cl2 three times. The combined organic layer was dried over anhydrous Na2SO4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to afford the desired product 70-1 as a yellow oil (8.4 mg, 99% yield, 95% ee).

Procedure b:

To a solution of 1 (64.2 mg, 0.20 mmol, 1.0 equiv., 96% ee) in THF (5.0 mL) was added the freshly prepared Na/naphthalene reagent (4.0 mL, 2.0 mmol, 10.0 equiv., 0.5 M in THF) dropwise with vigorously stirring at −78 °C under argon. The reaction was stirred at −78 °C for 10 min and quenched with MeOH. Then, the mixture was concentrated in
vacuum and redissolved in HCl (1.1 mL, 4.4 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane). After stirring for another 3 h, the mixture was concentrated under reduced pressure to afford the crude product 70 (27.9 mg, 89% crude yield, determined by 1H NMR using 1,3,5-trimethoxybenzene as an internal standard).

To a solution of the crude 70 in CH₂Cl₂ (10.0 mL) were added Et₃N (80.8 mg, 0.80 mmol, 4.0 equiv.) and Ac₂O (81.6 mg, 0.80 mmol, 4.0 equiv.) sequentially. The mixture was stirred at room temperature for 12 h. Then the reaction was quenched with saturated NH₄Cl solution and extracted with CH₂Cl₂ three times. The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 2/1) to afford the desired product 70-1 as a yellow oil (28.7 mg, 99% yield, 95% ee).

(S)-Chloro(1-phenylethyl)-λ⁵-azane (70)

\[
\text{NH}_2\cdot\text{HCl}
\]

1H NMR (400 MHz, MeOD) \(\delta 7.48 – 7.27 (m, 5H), 4.39 (q, J = 6.9 Hz, 1H), 1.57 (d, J = 6.8 Hz, 3H)\).

13C NMR (100 MHz, MeOD) \(\delta 138.5, 128.9, 128.7, 126.5, 51.1, 19.7\).

(S)-N-(1-Phenylethyl)acetamide (70-1)

\[
\text{NHAc}
\]

\([\alpha]_D^{20} = -77 (c 0.4, \text{CH}_2\text{Cl}_2)\).

**HPLC** analysis: Chiralcel AD3 (hexane/iPrOH = 90/10, flow rate 0.5 mL/min, \(\lambda = 210\) nm), \(t_R\) (minor) = 11.15 min, \(t_R\) (major) = 13.16 min. (procedure a)

**HPLC** analysis: Chiralcel AD3 (hexane/iPrOH = 90/10, flow rate 0.5 mL/min, \(\lambda = 210\) nm), \(t_R\) (minor) = 11.52 min, \(t_R\) (major) = 14.12 min. (procedure b)
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.40 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 5.77 (brs, 1H), 5.22 – 5.07 (m, 1H), 2.00 (s, 3H), 1.51 (d, \(J = 6.9\) Hz, 3H).

\(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 169.1, 143.2, 128.7, 127.4, 126.2, 48.8, 23.5, 21.7.

HRMS (ESI) \(m/z\) calcd. for C\(_{10}\)H\(_{14}\)NO [M + H]\(^+\) 164.1070, found 164.1069.

**Deprotection of amide product to primary amine (71)**

**Procedure a:**

![Chemical structure](#)

To a flame-dried flask charged with a stir bar were added 59 (37.8 mg, 0.10 mmol, 1.0 equiv., 93% ee), Mg (24.0 mg, 1.0 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), HCl (0.55 mL, 2.2 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added to the mixture at 0 °C, and the reaction was warmed up to room temperature to afford a homogeneous solution in 10 min. After stirring for another 1 h, the solvent was removed under reduced pressure to afford the crude product 71 (17.3 mg, 81% crude yield, determined by \(^1\)H NMR using 1,3,5-trimethoxybenzene as an internal standard).

Then, CH\(_2\)Cl\(_2\) (5.0 mL), Et\(_3\)N (40.0 mg, 0.40 mmol, 4.0 equiv.), and Ac\(_2\)O (40.8 mg, 0.40 mmol, 4.0 equiv.) were added to the crude 71 sequentially. The mixture was stirred at room temperature for 12 h and quenched with saturated NH\(_4\)Cl solution. The mixture was extracted with CH\(_2\)Cl\(_2\) three times. The combined organic layer was dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated to afford the crude product, which was purified by column chromatography (petroleum ether/EtOAc = 1/1) to yield the desired product 71-1 as a yellow oil (17.8 mg, 99% yield, 88% ee).

**Procedure b:**

![Chemical structure](#)
To a solution of 59 (75.6 mg, 0.20 mmol, 1.0 equiv., 93% ee) in THF were added the freshly prepared Na/naphthalene reagent (4.0 mL, 2.0 mmol, 10.0 equiv., 0.5 M in THF) dropwise vigorously stirring at −78 °C under argon. The reaction mixture was stirred at −78 °C for 10 min and quenched with MeOH (The color was disappeared). Then, the mixture was concentrated in vacuum and redissolved in HCl (0.30 mL, 1.2 mmol, 6.0 equiv., 4.0 M in 1,4-dioxane). The reaction mixture was stirred for another 3 h. The mixture was concentrated under reduced pressure to afford the crude product 71 (29.5 mg, 68% crude yield, determined by 1H NMR using 1,3,5-trimethoxybenzene as an internal standard).

To a solution of the crude 71 (24.2 mg, 0.14 mmol, 1.0 equiv.) in CH2Cl2 (5.0 mL) were added Et3N (56.6 mg, 0.56 mmol, 4.0 equiv.) and Ac2O (57.4 mg, 0.56 mmol, 4.0 equiv.) sequentially. The reaction was stirred at room temperature for 12 h, then quenched with saturated NH4Cl solution and extracted with CH2Cl2 three times. The combined organic layer was dried over anhydrous Na2SO4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to afford the desired product 71-1 as a yellow oil (30.5 mg, 99% yield, 90% ee).

(S)-2-(Chloro-λ5-azaneyl)-N-methyl-N-phenylpropanamide (71)

\[
\text{Ph} \quad \text{O} \quad \text{NH}_2\text{HCl} \\
\text{Me} \quad \text{Me}
\]

1H NMR (400 MHz, MeOD) δ 7.60 – 7.52 (m, 2H), 7.51-7.43 (m, 3H), 3.97 (q, J = 6.9 Hz, 1H), 3.30 (s, 3H), 1.29 (d, J = 6.9 Hz, 3H).

13C NMR (100 MHz, MeOD) δ 169.4, 141.7, 130.2, 128.8, 127.4, 47.2, 37.3, 15.5.
(S)-2-Acetamido-N-methyl-N-phenylpropanamide (71-1)

\[\alpha\]D²⁰ = 73 (c 1.5, CH₂Cl₂).

**HPLC** analysis: Chiralcel ADH (hexane/iPrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), \( t_R \) (minor) = 4.42 min, \( t_R \) (major) = 5.54 min. (**Procedure a**)

**HPLC** analysis: Chiralcel ADH (hexane/iPrOH = 70/30, flow rate 1.0 mL/min, λ = 254 nm), \( t_R \) (minor) = 4.05 min, \( t_R \) (major) = 4.97 min. (**Procedure b**)

**¹H NMR** (400 MHz, CDCl₃) \( \delta \) 7.50 – 7.42 (m, 2H), 7.41 – 7.37 (m, 1H), 7.31 – 7.24 (m, 2H), 6.65 (brs, 1H), 4.59 (q, \( J = 7.0 \) Hz, 1H), 3.27 (s, 3H), 1.96 (s, 3H), 1.14 (d, \( J = 6.8 \) Hz, 3H).

**¹³C NMR** (100 MHz, CDCl₃) \( \delta \) 173.1, 169.5, 142.6, 130.1, 128.5, 127.4, 46.0, 37.9, 23.1, 18.7.

**HRMS** (ESI) m/z calcd. for C₁₂H₁₇N₂O₂ [M + H]⁺ 221.1285, found 221.1281.
Conversion of enantioenriched sulfoximines to valuable chiral building blocks. (Figure 4D)

The synthesis of 73.

To a solution of 61 (71.6 mg, 0.20 mmol, 1.0 equiv.) in THF (3.0 mL) was added DIBAL-H (0.22 mL, 0.22 mmol, 1.1 equiv., 1.0 M in hexane) dropwise at −78 °C. The reaction mixture was stirred for 1 h and another portion of DIBAL-H (60.0 μL, 0.060 mmol, 0.3 equiv., 1.0 M in hexane) was added to the above solution. Upon completion (monitored by TLC), the reaction was quenched with saturated NH₄Cl solution and extracted with CH₂Cl₂ three times. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated to afford the crude product, which was dissolved in MeOH (5.0 mL). To this solution was added NaBH₄ (15.2 mg, 0.40 mmol, 2.0 equiv.) at 0 °C. After stirring for 10 min, the reaction mixture was quenched with saturated aqueous NH₄Cl solution and extracted with CH₂Cl₂ three times. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the desired product 72 as a yellow oil (36.9 mg, 67% yield, 93% ee).

To a flamed flask charged with a stir bar were added 72 (36.9 mg, 0.13 mmol, 1.0 equiv., 93% ee), Mg (64.8 mg, 2.7 mmol, 20.0 equiv.) and anhydrous MeOH (2.0 mL) under argon. The mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), HCl (1.4 mL, 5.6 mmol, 44.0 equiv., 4.0 M in 1,4-dioxane) was added to the reaction mixture at 0 °C and the reaction was stirred at room temperature to afford a homogenous solution in 10 min.

Upon completion (monitored by TLC), the solvent was removed under reduced pressure. The residue was dissolved in EtOAc (2.0 mL), followed by the addition of a solution of Na₂CO₃ (42.4 mg, 0.40 mmol, 3.0 equiv.) in H₂O (5.0 mL) and CbzCl (34.0
μl, 0.16 mmol, 1.2 equiv.). The reaction was stirred for 1 h and quenched with H2O. The mixture was extracted with EtOAc three times. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to afford the desired product 73 as a light yellow oil (24.2 mg, 89% yield, 93% ee).

(S)-(1-Hydroxypropan-2-yl)iminodiphenyl-λ₆-sulfanone (72)

HPLC analysis: Chiralcel OD3 (hexane/iPrOH = 90/10, flow rate 0.8 mL/min, λ = 254 nm), \( t_R \) (major) = 10.77 min, \( t_R \) (minor) = 12.39 min.

\(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 8.10 – 8.02 (m, 2H), 7.99 – 7.90 (m, 2H), 7.59 – 7.44 (m, 6H), 3.56 (dd, \( J = 10.7, 3.7 \) Hz, 1H), 3.49 (dd, \( J = 10.7, 7.7 \) Hz, 1H), 3.39 – 3.28 (m, 1H), 2.93 (brs, 1H), 1.22 (d, \( J = 6.5 \) Hz, 3H).

\(^1\)C NMR (100 MHz, CDCl₃) \( \delta \) 140.6, 140.5, 132.6, 132.6, 129.3, 129.2, 128.7, 128.5, 68.7, 53.3, 20.5.

HRMS (ESI) \( m/z \) calcd. for C₁₅H₁₈NO₂S [M + H]⁺ 276.1053, found 276.1059.

Benzyl (S)-(1-hydroxypropan-2-yl)carbamate (73)

\([\alpha]\)D\(^{20}\) = −4 (c 1.2, CH₂Cl₂).

HPLC analysis: Chiralcel IA (hexane/iPrOH = 90/10, flow rate 0.8 mL/min, λ = 210 nm), \( t_R \) (major) = 17.73 min, \( t_R \) (minor) = 21.51 min.

\(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.47 – 7.27 (m, 5H), 5.09 (s, 2H), 5.03 – 4.86 (m, 1H), 3.93 – 3.74 (m, 1H), 3.64 (dd, \( J = 11.0, 3.9 \) Hz, 1H), 3.51 (dd, \( J = 11.0, 5.9 \) Hz, 1H), 2.57 (brs, 1H), 1.16 (d, \( J = 6.8 \) Hz, 3H).
13C NMR (100 MHz, CDCl3) δ 156.6, 136.4, 128.6, 128.2, 128.1, 77.1, 66.9, 49.0, 17.3.

HRMS (ESI) m/z calcd. for C11H16NO3 [M + H]^+ 210.1125, found 210.1131.

The synthesis of 75.

To a flamed flask charged with a stir bar were added 61 (358.0 mg, 1.0 mmol, 1.0 equiv., 93% ee), Mg (240.0 mg, 10.0 mmol, 10.0 equiv.) and anhydrous MeOH (10.0 mL) under argon. The reaction mixture was stirred at room temperature until Mg disappeared (Note: Ice bath needed if the reaction was too violent!). Upon completion (monitored by TLC), HCl (5.5 mL, 22.0 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added dropwise to the mixture at 0 °C, then the mixture was warmed up to room temperature to afford a homogeneous solution in 30 min. Upon completion (monitored by TLC), the solvent was removed under reduced pressure to afford the crude 74.

To the crude 74, CH2Cl2 (20.0 mL), Et3N (505.0 mg, 5.0 mmol, 5.0 equiv.) and (Boc)2O (654.0 mg, 3.0 mmol, 3.0 equiv.) were added sequentially. The mixture was stirred at room temperature for 3 h. Then the reaction was quenched with saturated NH4Cl solution and extracted with CH2Cl2 three times. The combined organic layer was dried over anhydrous Na2SO4, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the desired product 74-1 as a colorless oil (218.0 mg, 84% yield in three steps, 91% ee).

To a solution of LiAlH4 (11.3 mg, 0.30 mmol, 2.0 equiv.) in Et2O (4.0 mL) was added the solution of 74-1 (38.7 mg, 0.15 mmol, 1.0 equiv.) in Et2O (2.0 mL) dropwise at 0 °C under argon. The resulting mixture was slowly warmed up to room temperature and stirred for 3 h. Upon completion (monitored by TLC), the reaction was quenched with
Na₂SO₄•10H₂O, dried with Na₂SO₄, filtered and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the desired product 75 as a yellow oil (32.8 mg, 90% yield). To the solution of 75 (32.8 mg, 0.13 mmol, 1.0 equiv.) in 1,4-dioxane (2.0 mL) was added HCl (0.33 mL, 1.3 mmol, 10.0 equiv., 4.0 M HCl in 1,4-dioxane) and the resulting mixture was stirred at room temperature. Upon completion (monitored by TLC), the mixture was concentrated to afford the residue, which was directly used in the next step without further purification.

The residue and Et₃N (72.0 μL, 0.52 mmol, 4.0 equiv.) were dissolved in CH₂Cl₂ (5.0 mL) and cooled down to 0 °C. To this solution was added CbzCl (73.0 μL, 0.52 mmol, 4.0 equiv.) and the reaction mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with brine and extracted with CH₂Cl₂ three times. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the desired product 75-1 as a light yellow oil (29.6 mg, 82% yield, 91% ee).

(S)-2-Amino-1-morpholinopropan-1-one hydrochloride (74)

\[
\text{74} \\
\text{NH}_2\text{HCl}
\]

\(^1\text{H NMR}\ (400\text{ MHz, CD}_3\text{OD})\ \delta 4.41 - 4.29 (m, 1H), 3.63 - 3.55 (m, 5H), 3.50 - 3.41 (m, 3H), 1.37 (d, J = 6.8 Hz, 3H).

\(^1\text{C NMR}\ (100\text{ MHz, CD}_3\text{OD})\ \delta 168.1, 66.2, 46.7, 45.6, 42.4, 15.5.

\text{tert-Butyl (S)-(1-morpholino-1-oxopropan-2-yl)carbamate (74-1)}

\[
\text{74-1}
\]
[α]D20 5 (c 5.7, CH2Cl2).

**HPLC** analysis: Chiralcel IC (hexane/iPrOH = 90/10, flow rate 1.0 mL/min, λ = 214 nm), tR (major) = 17.35 min, tR (minor) = 21.74 min.

**1H NMR** (400 MHz, CDCl3) δ 5.57 (d, J = 7.7 Hz, 1H), 4.60 (p, J = 7.0 Hz, 1H), 3.78 – 3.63 (m, 5H), 3.63 – 3.53 (m, 2H), 3.53 – 3.43 (m, 1H), 1.44 (s, 9H), 1.30 (d, J = 6.9 Hz, 3H).

**13C NMR** (100 MHz, CDCl3) δ 171.3, 155.1, 79.6, 66.8, 66.6, 45.9, 42.4, 28.3, 19.2.

**HRMS** (ESI) m/z calcd. for C12H23N2O4 [M + H]+ 259.1652, found 259.1658.

**tert-Butyl (S)-(1-morpholinopropan-2-yl)carbamate (75)**

![tert-Butyl (S)-(1-morpholinopropan-2-yl)carbamate (75)](image)

[α]D20 2 (c 0.2, CH2Cl2).

**1H NMR** (400 MHz, CDCl3) δ 4.70 (brs, 1H), 3.86 – 3.42 (m, 5H), 2.59 – 2.46 (m, 2H), 2.45 – 2.36 (m, 2H), 2.35 – 2.27 (m, 1H), 2.27 – 2.18 (m, 1H), 1.45 (s, 9H), 1.15 (d, J = 6.5 Hz, 3H).

**13C NMR** (100 MHz, CDCl3) δ 155.8, 79.2, 67.0, 64.2, 53.8, 43.5, 28.5, 19.6.

**HRMS** (ESI) m/z calcd. for C12H25N2O3 [M + H]+ 245.1860, found 245.1856.

**Benzyl (S)-(1-morpholinopropan-2-yl)carbamate (75-1)**

![Benzyl (S)-(1-morpholinopropan-2-yl)carbamate (75-1)](image)

[α]D20 12 (c 1.5, CH2Cl2).

**HPLC** analysis: Chiralcel IC (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, λ = 210 nm), tR (minor) = 10.10 min, tR (major) = 13.92 min.

**1H NMR** (400 MHz, CDCl3) δ 7.42 – 7.28 (m, 5H), 5.19 – 5.00 (m, 3H), 3.89 – 3.73 (m, 1H), 3.72 – 3.57 (m, 4H), 2.60 – 2.44 (m, 2H), 2.43 – 2.21 (m, 4H), 1.19 (d, J = 6.4 Hz, 3H).
**HRMS** (ESI) *m/z* calcd. for C_{15}H_{23}N_{2}O_{3} [M + H]^+ 279.1703, found 279.1699.

**The synthesis of 76.**

To a solution of 74-1 (773.0 mg, 3.0 mmol, 1.0 equiv.) in anhydrous THF (15.0 mL) was added phenylmagnesium bromide (9.0 mL, 9.0 mmol, 3.0 equiv., 1.0 M in THF) dropwise at 0 °C under argon. Then the reaction mixture was stirred at 0 °C for 2 h. Upon completion (monitored by TLC), the reaction was quenched with saturated NH₄Cl solution and extracted with CH₂Cl₂ three times. The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to yield the desired product 76 as a colorless oil (709.0 mg, 95% yield, 91% ee).

**tert-Butyl (S)-(1-oxo-1-phenylpropan-2-yl)carbamate (76)**

[α]_{D}^{20} = −4 (c 4.8, CH₂Cl₂).

**HPLC** analysis: Chiralcel IA (hexane/iPrOH = 95/5, flow rate 1.0 mL/min, λ = 254 nm),

<table>
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<th>Compartment</th>
<th>Retention Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Minor</td>
<td>7.04</td>
</tr>
<tr>
<td>Major</td>
<td>8.54</td>
</tr>
</tbody>
</table>

**1H NMR** (400 MHz, CDCl₃) δ 7.99 (d, *J* = 7.3 Hz, 2H), 7.64 – 7.55 (m, 1H), 7.50 (t, *J* = 7.6 Hz, 2H), 5.60 (d, *J* = 6.5 Hz, 1H), 5.38 – 5.24 (m, 1H), 1.47 (s, 9H), 1.41 (d, *J* = 7.1 Hz, 3H).

**13C NMR** (100 MHz, CDCl₃) δ 199.5, 155.2, 134.2, 133.7, 128.8, 128.7, 79.7, 51.1, 28.4, 19.9.
HRMS (ESI) \( m/z \) calcd. for C\(_{14}H_{19}NO_3Na \) [M + Na]\(^+\) 272.1257, found 272.1262.

The synthesis of 77.

![Chemical Reaction](image)

To a flamed tube charged with a stir bar and rubber plug were added Lithium tri-\( \text{tert}-\)butoxyaluminum hydride (406.0 mg, 1.6 mmol, 8.0 equiv.), anhydrous EtOH (2.0 mL) under argon and the mixture was cooled down to \(-78 \, ^\circ\text{C}\). To this solution was added a solution of 76 (49.8 mg, 0.20 mmol, 1.0 equiv.) in anhydrous EtOH (1.0 mL) dropwise. The reaction mixture was stirred at \(-78 \, ^\circ\text{C}\) for 0.5 h. Upon completion (monitored by TLC), the reaction was quenched with 10% citric acid, and extracted with EtOAc three times. The combined organic layer was dried over anhydrous Na\(_2\)SO\(_4\), filtered and concentrated to afford crude product (the dr was determined by \(^1\)H NMR). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product 77 as a colorless oil (36.6 mg, 73% yield, 91% ee, dr > 20:1).

*tert*-Butyl ((1\(R\),2\(S\))-1-hydroxy-1-phenylpropan-2-yl)carbamate (77)

![Chemical Structure](image)

[\(\alpha\)]\(_{D}^{20}\) = \(-54\) (c 1.8, CH\(_2\)Cl\(_2\)).

**HPLC** analysis: Chiralcel OD-H (hexane/iPrOH = 92/8, flow rate 0.8 mL/min, \(\lambda = 214\) nm), \(t_R\) (minor) = 7.21 min, \(t_R\) (major) = 7.84 min.

**\(^1\)H NMR** (400 MHz, CDCl\(_3\)) \(\delta\) 7.38 – 7.32 (m, 4H), 7.32 – 7.25 (m, 1H), 4.85 (d, \(J = 2.2\) Hz, 1H), 4.77 (d, \(J = 7.9\) Hz, 1H), 4.00 (brs, 1H), 3.49 (brs, 1H), 1.47 (s, 9H), 0.99 (d, \(J = 6.9\) Hz, 3H).
The assignment of relative configuration was determined by 2D NMR analysis of the cyclization product.

To an oven dried round bottom flask was added sodium hydride (60% dispersion in mineral oil, 7.4 mg, 0.18 mmol, 1.2 equiv.). To this flask was added a solution of Boc-protected amino alcohol 77 (38.9 mg, 0.15 mmol, 1.0 equiv.) in THF (2.0 mL) slowly at 0 °C under argon. Then the flask was equipped with a reflux condenser and the reaction mixture was heated to reflux with stirring until the starting material was completely consumed (monitored by TLC). The mixture was cooled down to room temperature, quenched with saturated aqueous NH₄Cl solution, and transferred to a separatory funnel. The mixture was extracted with CH₂Cl₂ three times. The combined organic layer was dried over anhydrous Na₂SO₄, filtered, and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum/EtOAc = 3/1) to afford the pure product 77-1 as a yellow oil (23.1 mg, 87% yield).

(4S,5R)-4-Methyl-5-phenyloxazolidin-2-one (77-1)

1H NMR (400 MHz, CDCl₃) δ 7.45 – 7.34 (m, 3H), 7.34 – 7.29 (m, 2H), 6.28 (s, 1H), 5.73 (d, J = 8.0 Hz, 1H), 4.32 – 4.13 (m, 1H), 0.83 (d, J = 6.5 Hz, 3H).
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.6, 134.9, 128.53, 128.50, 126.0, 81.0, 52.4, 17.5.

HRMS (ESI) $m/z$ calcd. for C$_{10}$H$_{12}$NO$_2$ [M + H]$^+$ 170.0863, found 170.0861.

The synthesis of 78.

![Chemical structure of 76 and 78](image)

To a solution of 76 (49.8 mg, 0.20 mmol, 1.0 equiv.) in anhydrous THF (2.0 mL) was added methyl magnesium bromide (0.80 mL, 2.4 mmol, 12.0 equiv., 3.0 M in THF) dropwise at 0 °C under argon and then the mixture was stirred at 0 °C for 2 h. Upon completion (monitored by TLC), the reaction was quenched with saturated NH$_4$Cl solution, and extracted with CH$_2$Cl$_2$ three times. The combined organic layer was dried over anhydrous Na$_2$SO$_4$, filtered and concentrated to afford crude product (the dr was determined by $^1$H NMR). The residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 10/1) to yield the desired product 78 as a colorless oil (43.8 mg, 83% yield, 91% ee).

**tert-Butyl ((2S,3R)-3-hydroxy-3-phenylbutan-2-yl)carbamate (78)**

![Chemical structure of 78](image)

$[\alpha]_{D}^{20} = -3$ (c 2.2, CH$_2$Cl$_2$).

HPLC analysis: Chiralcel IC (hexane/iPrOH = 93/7, flow rate 0.8 mL/min, $\lambda$ = 214 nm), $t_R$ (major) = 7.69 min, $t_R$ (minor) = 8.29 min.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.45 (d, $J = 7.6$ Hz, 2H), 7.39 – 7.32 (m, 2H), 7.28 – 7.23 (m, 1H), 4.89 (d, $J = 9.3$ Hz, 1H), 4.07 – 3.96 (m, 1H), 2.80 (bs, 1H), 1.59 (s, 3H), 1.49 (s, 9H), 0.91 (d, $J = 6.8$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.4, 145.5, 128.2, 126.7, 125.1, 79.5, 77.1, 54.6, 28.5, 28.3, 16.1.

HRMS (ESI) $m/z$ calcd. for C$_{15}$H$_{23}$NO$_3$Na [M + Na]$^+$ 288.1570, found 288.1576.
The assignment of relative configuration was determined by 2D NMR analysis of the cyclization product.

\[
\begin{align*}
\text{Ph} \quad \text{OH} \\
\text{Me} \quad \text{NHboc} \\
\text{78} \quad \xrightarrow{\text{NaH, THF}} \\
\text{Me} \quad \text{Ph} \quad \text{NH} \\
\text{Me} \quad \text{78-1, 70%}
\end{align*}
\]

To an oven dried round bottom flask was added sodium hydride (60% dispersion in mineral oil, 3.6 mg, 0.090 mmol, 1.2 equiv.). To this flask was added a solution of Boc-protected amino alcohol 78 (19.8 mg, 0.075 mmol, 1.0 equiv.) in THF (1.0 mL) slowly at 0 °C under argon. Then the flask was equipped with a reflux condenser and the reaction mixture was heated to reflux with stirring until the starting material had been completely consumed (monitored by TLC). The mixture was cooled down to room temperature, quenched with saturated aqueous NH₄Cl solution, and transferred to a separatory funnel. The mixture was extracted with CH₂Cl₂ three times. The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 4/1) to afford the pure product 78-1 as a yellow oil (10.0 mg, 70% yield).

\((4S,5R)-4,5\text{-Dimethyl-5-phenyloxazolidin-2-one (78-1)}\)

\[
\begin{align*}
\text{78-1}
\end{align*}
\]

\(^1\text{H NMR}\) (400 MHz, CDCl₃) \(\delta\) 7.43 – 7.29 (m, 5H), 5.91 (s, 1H), 3.98 – 3.79 (m, 1H), 1.83 (s, 3H), 0.77 (d, \(J = 6.5\) Hz, 3H).

\(^13\text{C NMR}\) (100 MHz, CDCl₃) \(\delta\) 158.6, 139.5, 128.3, 127.8, 125.2, 86.5, 58.3, 27.6, 19.0.

HRMS (ESI) \(m/z\) calcd. for C₁₁H₁₄NO₂ [M + H]⁺ 192.1019, found 192.1016.
The synthesis of 79.

\[
\begin{align*}
\text{Ph} & \text{O} \quad \text{NHBOc} \\
\text{Me} & \\
76, \text{91\% ee} & \rightarrow \text{TsNHNH}_2 \quad \text{MeOH, 60°C} \\
\text{N} & \quad \text{NHBOc} \\
79-1 & \rightarrow \text{ZnF}_2, \text{NaBH}_3\text{CN} \quad \text{PhCH}_3, 80°C \\
\text{Ph} & \text{O} \quad \text{NHBOc} \\
\text{Me} & \\
79, \text{33\%, 88\% ee}
\end{align*}
\]

To a flask charged with a stir bar were added 76 (49.8 mg, 0.20 mmol, 1.0 equiv.), 4-methylbenzenesulfonylhydrazide (44.6 mg, 0.24 mmol, 1.2 equiv.) and MeOH (2.0 mL). The reaction mixture was stirred at 60 °C for 12 h. Upon completion (monitored by TLC), the reaction was concentrated to afford the crude product 79-1, which was directly used in the next step without further purification.

To a flask charged with a stir bar were added the above crude product 79-1, ZnF₂ (82.4 mg, 0.80 mmol, 4.0 equiv.), NaBH₃CN (100.8 mg, 1.6 mmol, 8.0 equiv.) and toluene (2.0 mL). Then the reaction mixture was stirred at 80 °C for 24 h. Upon completion (monitored by TLC), the reaction was quenched with 10% aqueous NaOH solution and extracted with CH₂Cl₂ three times. The combined organic layer was dried over anhydrous Na₂SO₄, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 20/1) to yield the desired product 79 as a white solid (15.4 mg, 33% yield in two steps, 88% ee).

**tert-Butyl (S)-(1-phenylpropan-2-yl)carbamate (79)**

\[
\begin{align*}
\text{HPLC analysis: Chiralcel OD3 (hexane/iPrOH = 99/1, flow rate 1.0 mL/min, λ = 214 nm), } & \\
\text{t}_R \text{ (major) = 8.53 min, } \text{t}_R \text{ (minor) = 9.14 min.} \\
\textbf{1H NMR} \ (400 \text{ MHz, CDCl}_3) & \delta \ 7.31 – 7.25 (m, 2H), 7.24 – 7.15 (m, 3H), 4.40 (brs, 1H), \\
& 3.91 (brs, 1H), 2.84 (dd, J = 13.2, 5.3 Hz, 1H), 2.65 (dd, J = 13.3, 7.4 Hz, 1H), 1.42 (s, 9H), 1.08 (d, J = 6.7 Hz, 3H).
\end{align*}
\]

\[\{\alpha\}_D^{20} = -3 \text{ (c 0.5, CH}_2\text{Cl}_2\].\]
$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 155.2, 138.3, 129.5, 128.3, 126.3, 79.1, 47.5, 43.0, 28.4, 20.2.

HRMS (ESI) $m/z$ calcd. for C$_{14}$H$_{21}$NO$_2$Na [M + Na]$^+$ 258.1465, found 258.1470.

The synthesis of 80.

To a solution of 74 (31.0 mg, 0.16 mmol, 1.0 equiv.) in CH$_2$Cl$_2$ was added CH$_2$Cl$_2$ (5.0 mL), Et$_3$N (0.11 mL, 0.80 mmol, 4.0 equiv.) and the mixture was cooled to 0 °C. To this solution was added CbzCl (136.0 mg, 0.80 mmol, 4.0 equiv.) and the reaction mixture was warmed up to room temperature and stirred overnight. The reaction was quenched with brine and extracted with CH$_2$Cl$_2$ three times. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated to afford the crude product, which was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to yield the desired product 80-1 as a yellow oil (45.6 mg, 98% yield, 90% ee).

To a solution of 80-1 (45.6 mg, 0.16 mmol, 1.0 equiv., 90% ee) in MeOH (0.3 mL) was added SOCl$_2$ (56.0 μL, 0.80 mmol, 5.0 equiv.) at 0 °C under argon. The reaction mixture was refluxed at 100 °C for 48 h, then cooled down to room temperature. The solvent was removed under reduced pressure. The residue was diluted with CH$_2$Cl$_2$, saturated aqueous NaHCO$_3$ solution and extracted with CH$_2$Cl$_2$ three times. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the desired product 80 as a yellow oil (19.0 mg, 50% yield, 89% ee).
Benzyl (S)-(1-morpholino-1-oxopropan-2-yl)carbamate (80-1)

\[\alpha\]_D^{20} = 13 (c 2.0, CH₂Cl₂).

**HPLC** analysis: Chiralcel AD (hexane/iPrOH = 75/25, flow rate 0.8 mL/min, λ = 210 nm), \(t_R\) (major) = 14.97 min, \(t_R\) (minor) = 16.92 min.

**¹H NMR** (400 MHz, CDCl₃) δ 7.45 – 7.29 (m, 5H), 6.01 – 5.80 (m, 1H), 5.11 (s, 2H), 4.77 – 4.58 (m, 1H), 3.77 – 3.44 (m, 8H), 1.34 (d, \(J = 6.8\) Hz, 3H).

**¹³C NMR** (100 MHz, CDCl₃) δ 171.0, 155.6, 136.4, 128.5, 128.1, 128.0, 66.79, 66.76, 66.5, 46.5, 45.9, 42.4, 19.2.

**HRMS** (ESI) \(m/z\) calcd. for C₁₅H₂₁N₂O₄ \([M + H]^+\) 293.1496, found 293.1491.

Methyl ((benzyloxy)carbonyl)-L-alaninate (80)

\[\alpha\]_D^{20} = −4 (c 0.5, CH₂Cl₂).

**HPLC** analysis: Chiralcel IB (hexane/iPrOH = 90/10, flow rate 0.8 mL/min, λ = 210 nm), \(t_R\) (major) = 10.36 min, \(t_R\) (minor) = 12.70 min.

**¹H NMR** (400 MHz, CDCl₃) δ 7.42 – 7.27 (m, 5H), 5.41 (brs, 1H), 5.10 (s, 2H), 4.47 – 4.30 (m, 1H), 3.73 (s, 3H), 1.40 (d, \(J = 7.2\) Hz, 3H).

**¹³C NMR** (100 MHz, CDCl₃) δ 173.5, 155.6, 136.3, 128.5, 128.2, 128.1, 66.9, 52.5, 49.6, 18.6.

**HRMS** (ESI) \(m/z\) calcd. for C₁₂H₁₆NO₄ \([M + H]^+\) 238.1074, found 238.1075.

The hydrolysis of 80
To a solution of 80 (16.6 mg, 0.070 mmol, 1.0 equiv.) in co-solvent of THF (1.0 mL) and H2O (1.0 mL) was added LiOH (3.4 mg, 0.14 mmol, 20.0 equiv.) in one portion at room temperature. The mixture was stirred at room temperature for 3 h. After completion (monitored by TLC), 3.0 M aqueous HCl solution was added and the mixture was extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na2SO4, filtered and concentrated to afford the product 80-2 as a colorless oil (10.0 mg, 61% yield).

((Benzyloxy)carbonyl)-L-alanine (80-2)

\[ \text{HO-} \text{NH} \text{Me} \]

\[ \text{80-2} \]

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.43 – 7.27 (m, 5H), 5.33 (d, $J$ = 7.8 Hz, 1H), 5.20 – 5.01 (m, 2H), 4.50 – 4.34 (m, 1H), 1.46 (d, $J$ = 7.2 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 177.6, 155.9, 136.1, 128.6, 128.3, 128.2, 67.2, 49.5, 18.4.

HRMS (ESI) $m/z$ calcd. for C$_{11}$H$_{13}$NO$_4$Na [M + Na]$^+$ 246.0737, found 246.0742.
Synthesis of novel chiral ligands. (Figure 4E)

The synthesis of 81 (Pyrox).

The compound 78 (110.0 mg, 0.42 mmol, 1.0 equiv.) was dissolved in HCl (0.53 mL, 2.1 mmol, 5.0 equiv., 4.0 M in 1,4-dioxane) and the reaction mixture was stirred at room temperature for 3 h. The solvent was removed by evaporator to afford the crude product 81-1, which was directly used in next step without further purification.

To the residue were added methyl picolinimidate (57.1 mg, 0.42 mmol, 1.0 equiv.), TsOH (7.2 mg, 0.042 mmol, 10 mol%) and toluene (1.0 mL) and the reaction mixture was refluxed for 5 h. After cooling down to room temperature, 1.0 M aqueous NaOH solution was added and the product was extracted with EtOAc three times. The combined organic phase was washed with brine, dried over Na₂SO₄, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (MeOH/CH₂Cl₂ = 1/20) to afford 81 as a colorless oil (87.8 mg, 83% yield in two steps, 98% ee).

(4S,5R)-4,5-Dimethyl-5-phenyl-2-(pyridin-2-yl)-4,5-dihydrooxazole (81)

\[ [\alpha]_{D}^{20} = -303 \ (c \ 5.0, \ CH_{2}Cl_{2}) \].

**HPLC** analysis: Chiralcel IF (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, λ = 260 nm), tR (minor) = 6.87 min, tR (major) = 8.49 min.
$^1$H NMR (400 MHz, CDCl$_3$) δ 8.71 (dd, $J = 3.6$, 1.1 Hz, 1H), 8.05 (d, $J = 7.9$ Hz, 1H), 7.73 (td, $J = 7.8$, 1.8 Hz, 1H), 7.38 – 7.16 (m, 6H), 4.25 (q, $J = 7.0$ Hz, 1H), 1.80 (s, 3H), 0.79 (d, $J = 7.0$ Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 160.9, 150.0, 147.0, 140.9, 136.6, 128.0, 127.2, 125.5, 125.4, 123.8, 90.2, 72.2, 27.9, 19.0.

HRMS (ESI) $m/z$ calcd. for C$_{16}$H$_{17}$N$_2$O [M + H]$^+$ 253.1335, found 253.1340.

The synthesis of 82 (N, P-ligand).

To a flame-dried flask charged with a stir bar were added 26 (30.0 mg, 0.081 mmol, 1.0 equiv., 98% ee), Mg (19.4 mg, 0.81 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The reaction mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), HCl (0.45 mL, 1.8 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added at 0 °C and the reaction mixture was stirred at room temperature to afford a homogenous solution in 10 min. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous Na$_2$CO$_3$ solution and extracted with CH$_2$Cl$_2$ three times. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated to afford the crude product.

Without further purification, the obtained crude product, 2-(diphenylphosphanylidene)benzoic acid (25.0 mg, 0.081 mmol, 1.0 equiv.), EDCI (18.6 mg, 0.097 mmol, 1.2 equiv.) and DMAP (0.99 mg, 0.0081 mmol, 0.1 equiv.) were dissolved in CH$_2$Cl$_2$ (5.0 mL) and the reaction mixture was stirred overnight. Upon completion, the reaction mixture was concentrated and purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to afford the desired product 82 as a white solid (30.0 mg, 81% yield, 97% ee).
(S)-2-(Diphenylphosphany1)-N-(1-(naphthalen-1-yl)ethyl)benzamide (82)

\[ \alpha \]_D^{20} = 15 (c 1.5, CH₂Cl₂).

**HPLC** analysis: Chiralcel ID (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), \( t_R \) (minor) = 16.82 min, \( t_R \) (major) = 22.78 min.

**^1H NMR** (400 MHz, CDCl₃) \( \delta \) 8.22 (d, \( J = 8.4 \) Hz, 1H), 7.89 (d, \( J = 8.0 \) Hz, 1H), 7.81 (d, \( J = 7.9 \) Hz, 1H), 7.61 – 7.55 (m, 2H), 7.55 – 7.50 (m, 1H), 7.45 – 7.39 (m, 1H), 7.39 – 7.26 (m, 11H), 7.26 – 7.19 (m, 2H), 7.00 – 6.91 (m, 1H), 6.25 (d, \( J = 8.2 \) Hz, 1H), 6.11 – 5.99 (m, 1H), 1.59 (d, \( J = 6.7 \) Hz, 3H).

**^13C NMR** (100 MHz, CDCl₃) \( \delta \) 168.5, 142.2, 142.1, 141.8, 137.74, 137.69, 137.62, 137.57, 136.8, 136.6, 134.3, 134.0, 133.9, 133.8, 133.7, 129.9, 128.7, 128.54, 128.53, 128.48, 128.4, 128.2, 127.7, 127.3, 127.2, 126.9, 64.9, 50.8, 39.0, 17.0, 12.1.

**^31P NMR** (162 MHz, CDCl₃) \( \delta \) –10.7.

**HRMS** (ESI) m/z calcd. for C₃₁H₂₇NOP [M + H]^+ 460.1825, found 460.1827.
Expedient synthesis of highly enantioenriched commercial drugs. (Figure 4F)

The synthesis of cinacalcet.

According to **General procedure A** with 1-(1-bromoethyl)naphthalene (23.4 mg, 0.10 mmol, 1.0 equiv.) and chiral ligand $L^*7'$ for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to afford the product (R)-26 as a white solid (27.1 mg, 73% yield, 99% ee).

To a flame-dried flask charged with a stir bar were added (R)-26 (27.1 mg, 0.073 mmol, 1.0 equiv., 99% ee), Mg (17.5 mg, 0.73 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), HCl (0.40 mL, 1.6 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added to the mixture at 0 °C and the reaction mixture was stirred at room temperature to afford a homogeneous solution in 10 min. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous Na$_2$CO$_3$ solution and extracted with CH$_2$Cl$_2$ three times. The combined organic layer was washed with brine, dried over Na$_2$SO$_4$, filtered and concentrated in vacuum. Without further purification, the residue was dissolved in MeCN (1.0 mL). To this solution were added K$_2$CO$_3$ (30.2 mg, 0.22 mmol, 3.0 equiv.) and 1-(3-iodopropyl)-3-(trifluoromethyl)benzene (22.9 mg, 0.073 mmol, 1.0 equiv.) under argon, and then the reaction mixture was refluxed at 70 °C for 24 h. Upon completion (monitored by TLC), the reaction was diluted with EtOAc and filtered through a short pad of Celite. The filtrate was evaporated to afford the crude product, which was purified by column chromatography on silica gel (MeOH/CH$_2$Cl$_2$ = 1/10) to afford the desired product **cinacalcet** as a yellow oil (25.8 mg, 99% yield, 97% ee).
(R)-((1-(Naphthalen-1-yl)ethyl)imino)diphenyl-λ₆-sulfanone ((R)-26)

\[
\begin{array}{c}
\text{(R)-26} \\
\end{array}
\]

**HPLC** analysis: Chiralcel OD3 (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), \(t_R\) (minor) = 19.50 min, \(t_R\) (major) = 21.47 min.

(R)-N-(1-(Naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (cinacalcet)

\[
\begin{array}{c}
\text{cinacalcet} \\
\end{array}
\]

\[\alpha\]D₂₀ = 4.7 (c 2.5, CH₂Cl₂).

**HPLC** analysis: Chiralcel IG (hexane/iPrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), \(t_R\) (major) = 10.97 min, \(t_R\) (minor) = 12.41 min.

**1H NMR** (400 MHz, CDCl₃) \(\delta\) 8.12 (d, \(J = 8.2\) Hz, 1H), 7.88 (dd, \(J = 7.8, 1.8\) Hz, 1H), 7.79 (t, \(J = 8.1\) Hz, 2H), 7.59 – 7.45 (m, 3H), 7.42 – 7.34 (m, 2H), 7.33 – 7.20 (m, 2H), 4.78 (q, \(J = 6.6\) Hz, 1H), 2.77 – 2.55 (m, 4H), 2.07 – 1.87 (m, 2H), 1.62 (d, \(J = 6.6\) Hz, 3H).

**13C NMR** (100 MHz, CDCl₃) \(\delta\) 142.5, 134.0, 131.7 (d, \(J = 1.0\) Hz), 131.2, 130.6 (q, \(J = 32.0\) Hz), 129.2, 128.7, 127.9, 126.2, 125.8, 125.6, 125.0 (q, \(J = 3.8\) Hz), 124.2 (q, \(J = 271.0\) Hz), 123.3, 122.8 (q, \(J = 4.5, 3.9\) Hz), 123.3, 122.5, 53.7, 46.8, 33.2, 30.6, 23.0.

**19F NMR** (376 MHz, CDCl₃) \(\delta\) –62.5 (s, 3F).

**HRMS** (ESI) \(m/z\) calcd. for CₙH₂₃F₃N [M + H]\(^+\) 358.1777, found 358.1779.

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S121
The synthesis of \((S)\)-cinacalcet.

According to **General procedure A** with 1-(1-bromoethyl)naphthalene (23.4 mg, 0.10 mmol, 1.0 equiv.) and Cu(HFacac)\(_2\) (4.4 mg, 0.10 mmol, 10 mol%) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to afford the product \((S)\)-26 as a white solid (31.9 mg, 86% yield, 98% ee).

To a flamed dried flask charged with a stir bar were added \((S)\)-26 (31.9 mg, 0.086 mmol, 1.0 equiv., 98% ee), Mg (20.6 mg, 0.86 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The reaction mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), HCl (0.47 mL, 1.9 mmol, 22.0 equiv., 4.0 M in 1,4-dioxane) was added to the reaction mixture at 0 °C and then the mixture was warmed up to room temperature to afford a homogeneous solution in 10 min. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous Na\(_2\)CO\(_3\) solution and extracted with CH\(_2\)Cl\(_2\) three times. The combined organic layer was washed with brine, dried over Na\(_2\)SO\(_4\), filtered and concentrated in vacuum. Without further purification, the residue was dissolved in MeCN (1.0 mL). To this solution were added K\(_2\)CO\(_3\) (35.9 mg, 0.26 mmol, 3.0 equiv.) and 1-(3-iodopropyl)-3-(trifluoromethyl)benzene (27.0 mg, 0.086 mmol, 1.0 equiv.) under argon, and then the reaction mixture was refluxed at 70 °C for 24 h. Upon completion (monitored by TLC), the reaction was diluted with EtOAc and filtered through a short pad of Celite. The filtrate was concentrated to afford the crude product, which was purified by column chromatography on silica gel (MeOH/CH\(_2\)Cl\(_2\) = 1/10) to afford the desired product \((S)\)-cinacalcet as a yellow oil (22.7 mg, 74% yield, 98% ee).
(S)-((1-(Naphthalen-1-yl)ethyl)imino)diphenyl-λ6-sulfanone ((S)-26)

HPLC analysis: Chiralcel OD3 (hexane/iPrOH = 99/1, flow rate 0.5 mL/min, λ = 254 nm), $t_R$ (major) = 19.20 min, $t_R$ (minor) = 21.64 min.

(S)-N-(1-(Naphthalen-1-yl)ethyl)-3-(3-(trifluoromethyl)phenyl)propan-1-amine (((S)-cinacalcet)

[α]D20 = −23 (c 1.3, CH2Cl2).

HPLC analysis: Chiralcel IG (hexane/iPrOH = 98/2, flow rate 0.5 mL/min, λ = 254 nm), $t_R$ (minor) = 11.33 min, $t_R$ (major) = 12.91 min.

The synthesis of dapoxetine.

According to General procedure C with 1-(3-bromo-3-phenylpropoxy)naphthalene (34.0 mg, 0.10 mmol, 1.0 equiv.) and iminobis(4-methoxyphenyl)-λ6-sulfanone (27.7 mg, 0.10 mmol, 1.0 equiv.) at 0 °C for 5 d and room temperature for another 2 d, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the dapoxetine-1 as a white solid (34.0 mg, 63% yield, 92% ee).

To a solution of the above sulfoximine (34.0 mg, 0.063 mmol, 1.0 equiv., 92% ee) in THF (3.0 mL) was added the freshly prepared Na/naphthalene reagent (1.30 mL, 0.63
mmol, 10.0 equiv., 0.5 M in THF) dropwise with vigorously stirring at −78 °C under argon. The reaction mixture was stirred at −78 °C for another 10 min and quenched with MeOH (The color was disappeared). Then, the mixture was warmed up to 0 °C, followed by the addition of HCl (0.16 mL, 0.63 mmol, 10.0 equiv., 4.0 M in 1,4-dioxane) and the reaction mixture was stirred for another 3 h. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous Na2CO3 solution and extracted with CH2Cl2 three times. The combined organic layer was washed with brine, dried over Na2SO4, filtered and concentrated in vacuum.

The residue was transferred to a Schlenk tube. Then HCHO (0.023 mL, 0.32 mmol, 5.0 equiv., 37% in water) and HCO2H (1.0 mL) were added under argon. The reaction mixture was refluxed at 100 °C for 24 h. Upon completion (monitored by TLC), the reaction was cooled down to room temperature and treated with 2.0 M aqueous NaOH solution. The mixture was extracted with CH2Cl2 three times. The combined organic layer was washed with brine, dried over Na2SO4, filtered and concentrated in vacuum. The residue was purified by column chromatography on silica gel (MeOH/CH2Cl2 = 1/10) to afford the desired product **dapoxetine** as a brown oil (13.6 mg, 71% yield, 93% ee).

**(S)-bis(4-Methoxyphenyl)((3-(naphthalen-1-yloxy)-1-phenylpropyl)imino)-λ6-sulfanone (dapoxetine-1)**

![dapoxetine-1](image)

**HPLC** analysis: Chiralcel IA (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), tR (minor) = 10.42 min, tR (major) = 13.60 min.

**1H NMR** (400 MHz, CDCl3) δ 8.04 (dd, J = 8.4, 1.2 Hz, 1H), 7.87 – 7.78 (m, 3H), 7.73 – 7.64 (m, 2H), 7.51 – 7.31 (m, 8H), 7.28 – 7.23 (m, 1H), 6.86 (dd, J = 7.0, 1.6 Hz, 1H),
6.81 – 6.75 (m, 2H), 6.75 – 6.70 (m, 2H), 4.60 (dd, \( J = 8.2, 5.4 \) Hz, 1H), 4.51 (ddd, \( J = 9.3, 7.9, 4.9 \) Hz, 1H), 4.17 (dt, \( J = 9.4, 5.5 \) Hz, 1H), 3.79 (s, 3H), 3.70 (s, 3H), 2.54 – 2.31 (m, 2H).

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 162.5, 154.8, 146.4, 134.5, 132.7, 132.5, 130.6, 130.5, 128.3, 127.3, 126.8, 126.6, 126.2, 126.1, 125.7, 124.8, 122.3, 119.8, 114.2, 114.1, 104.6, 65.0, 56.0, 55.5, 55.4, 40.9.

HRMS (ESI) \( m/z \) calcd. for C\(_{33}\)H\(_{32}\)NO\(_4\)S [M + H]\(^+\) 538.2047, found 538.2060.

\( (S)\)-N,N-Dimethyl-3-(naphthalen-1-yloxy)-1-phenylpropan-1-amine (Dapoxetine)

\( \left[ \alpha \right] \text{D}_{20} = -1 \) (c 0.5, CH\(_2\)Cl\(_2\)).

HPLC analysis: Chiralcel OD3 (hexane/iPrOH = 95/5, flow rate 1.0 mL/min, \( \lambda = 240 \) nm), \( t_R \) (major) = 5.61 min, \( t_R \) (minor) = 7.10 min.

\( ^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 8.57 (dd, \( J = 8.1, 1.7 \) Hz, 1H), 7.86 (dd, \( J = 7.6, 1.9 \) Hz, 1H), 7.66 – 7.54 (m, 2H), 7.54 – 7.47 (m, 2H), 7.47 – 7.35 (m, 3H), 7.35 – 7.23 (m, 2H), 6.74 (d, \( J = 7.7 \) Hz, 1H), 5.55 (dd, \( J = 8.2, 4.7 \) Hz, 1H), 2.62 (t, \( J = 7.3 \) Hz, 2H), 2.52 – 2.38 (m, 1H), 2.34 (s, 6H), 2.25 – 2.14 (m, 1H).

\( ^{13}\text{C NMR} \) (100 MHz, CDCl\(_3\)) \( \delta \) 153.7, 142.0, 134.6, 128.7, 127.6, 126.4, 126.1, 125.93, 125.86, 125.2, 122.2, 120.1, 107.0, 78.4, 56.2, 45.7, 37.3.

HRMS (ESI) \( m/z \) calcd. for C\(_{21}\)H\(_{24}\)NO [M + H]\(^+\) 306.1852, found 306.1859.

The synthesis of rivastigmine.

According to General procedure A with 3-(1-bromoethyl)phenyl
ethyl(methyl)carbamate (28.5 mg, 0.10 mmol, 1.0 equiv.) for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to yield the rivastigmine-1 as a yellow solid (36.7 mg, 87% yield, 96% ee).

To a flamed dried flask charged with a stir bar were added the above sulfoximine (27.4 mg, 0.065 mmol, 1.0 equiv., 96% ee), Mg (15.0 mg, 0.65 mmol, 10.0 equiv.) and anhydrous MeOH (1.0 mL) under argon. The reaction mixture was stirred at room temperature until Mg disappeared. Upon completion (monitored by TLC), the reaction mixture was cooled down to at 0 °C and HCl (0.36 mL, 22.0 equiv., 1.4 mmol, 4.0 M in 1,4-dioxane) was added. The mixture was stirred at room temperature to afford a homogeneous solution in 10 min. Upon completion (monitored by TLC), the reaction was quenched with saturated aqueous Na₂CO₃ solution and extracted with CH₂Cl₂ three times. The combined organic layer was washed with brine, dried over Na₂SO₄, filtered and concentrated in vacuum.

The residue was transferred to a Schlenk tube. Then HCHO (0.025 mL, 0.33 mmol, 5.0 equiv., 37% in water) and HCO₂H (1.0 mL) were added under argon. The mixture was refluxed at 100 °C for 24 h. Upon completion (monitored by TLC), the reaction was cooled down to room temperature and treated with 2.0 M aqueous NaOH solution. The mixture was extracted with CH₂Cl₂ three times, washed with brine, dried over Na₂SO₄, filtered and concentrated to afford the crude product, which was purified by column chromatography on silica gel (MeOH/CH₂Cl₂ = 1/10) to afford the desired product rivastigmine as a colorless oil (14.6 mg, 90% yield, 97% ee).

(S)-3-(1-((Oxodiphenyl-λ₆-sulfaneylidene)amino)ethyl)phenyl ethyl(methyl)carbamate (rivastigmine-1)

\[
\text{rivastigmine-1}
\]

HPLC analysis: Chiralcel ID (hexane/iPrOH = 80/20, flow rate 1.0 mL/min, λ = 254 nm), \( t_R \) (major) = 18.91 min, \( t_R \) (minor) = 22.14 min.
\textbf{1H NMR} (400 MHz, CDCl$_3$) δ 8.09 – 8.01 (m, 2H), 7.87 – 7.78 (m, 2H), 7.53 – 7.33 (m, 6H), 7.26 (t, \(J = 7.9\) Hz, 1H), 7.20 (dd, \(J = 6.6, 1.9\) Hz, 2H), 7.02 – 6.94 (m, 1H), 4.39 (q, \(J = 6.6\) Hz, 1H), 3.44 (dq, \(J = 21.9, 7.2\) Hz, 2H), 3.02 (d, \(J = 27.4\) Hz, 3H), 1.55 (d, \(J = 6.6\) Hz, 3H), 1.30 – 1.12 (m, 3H).

\textbf{13C NMR} (100 MHz, CDCl$_3$) δ 154.7, 154.5, 151.5, 149.0, 141.5, 140.6, 132.39, 132.3, 129.12, 129.05, 129.0, 128.8, 128.4, 122.9, 119.7, 119.5, 53.9, 44.1, 34.2, 33.9, 28.1, 13.3, 12.5.

\textbf{HRMS (ESI)} \(m/z\) calcd. for C$_{24}$H$_{27}$N$_2$O$_3$S [M + H]$^+$ 423.1737, found 423.1745.

\((S)-3-(1-(Dimethylamino)ethyl)phenyl ethyl(methyl)carbamate (Rivastigmine)\)

\(\delta = -12\ (c 0.7, \text{CH}_2\text{Cl}_2)\).

\textbf{HPLC} analysis: Chiralcel ODH (hexane/iPrOH/TFA/DEA = 80/20/2/1, flow rate 1.0 mL/min, \(\lambda = 210\) nm), \(t_R\) (minor) = 9.56 min, \(t_R\) (major) = 16.01 min.

\textbf{1H NMR} (600 MHz, CDCl$_3$) δ 7.43 (t, \(J = 7.9\) Hz, 1H), 7.34 (d, \(J = 7.8\) Hz, 1H), 7.25 – 7.20 (m, 1H), 7.19 – 7.12 (m, 1H), 4.05 (q, \(J = 7.2\) Hz, 1H), 3.49 (q, \(J = 7.1\) Hz, 1H), 3.41 (q, \(J = 7.2\) Hz, 1H), 3.04 (d, \(J = 53.1\) Hz, 3H), 2.58 (s, 6H), 1.82 – 1.68 (m, 3H), 1.30 – 1.16 (m, 3H).

\textbf{13C NMR} (150 MHz, CDCl$_3$) δ 154.2, 154.1, 151.9, 136.9, 130.0, 125.43, 125.41, 122.9, 122.8, 122.31, 122.28, 65.8, 44.20, 44.15, 41.0, 34.3, 33.9, 17.84, 17.81, 13.3, 12.5.

\textbf{HRMS (ESI)} \(m/z\) calcd. for C$_{14}$H$_{23}$N$_2$O$_2$ [M + H]$^+$ 251.1754, found 251.1755.
**Mechanistic investigations. (Figure 5)**

**Synthesis of the sulfoximiato complex of Cu(I). (Figure 5A)**

To a mixture of sulfoximine \( \textbf{N1} \) (21.7 mg, 0.10 mmol, 1.0 equiv.) and CuMes (Mesityl Copper) (18.2 mg, 0.10 mmol, 1.0 equiv.) were added \( \text{C}_6\text{D}_6 \) (benzene-\(d_6\)) (1.0 mL) under argon atmosphere, and the mixture was stirred at 66 °C overnight. After completion (monitored by \(^1\)H NMR), the mixture was filtered in argon atmosphere and washed with anhydrous benzene. Next, the mixture thus obtained was transferred to a flask and volatiles were evaporated under reduced pressure to afford analytically pure \( \textbf{83} \) (~80% yield) as a crystalline solid.

The thus obtained product \( \textbf{83} \) was mixed with anhydrous DMSO at 100 °C in a glovebox and filtered to remove any remaining solids. The resulting solution was transferred to an NMR tube, and then stayed at 70 °C for 1 month to afford the X-ray quality crystals.

**((Oxodiphenyl-\( \lambda^6 \)-sulfaneylidene)amino)copper (83)**

\[
\begin{align*}
\text{Ph}-\text{S}^\text{N} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\text{Ph} & \quad \text{Ph} \\
\overset{\text{O}}{\text{S}} & \quad \text{NCu}_4
\end{align*}
\]

\(^1\)H NMR (600 MHz, DMSO-\(d_6\), 100 °C) \( \delta \) 7.97 – 7.75 (m, 16H), 7.50 – 7.22 (m, 24H)

\(^{13}\)C NMR (150 MHz, DMSO-\(d_6\), 100 °C) \( \delta \) 147.8, 132.1, 129.2, 127.1.

HRMS (ESI) \( m/z \) calcd. for C\(_{12}\)H\(_{11}\)CuNOS \([M + H]^+\) 279.9852, found 279.9838.
The effect of chiral ligand in the stoichiometric reaction of the sulfoximinato complex with alkyl bromide. (Figure 5B)

To the 83 (14.0 mg, 0.013 mmol, 0.25 equiv.) was added (1-bromoethyl)benzene (9.2 mg, 0.050 mmol, 1.0 equiv.), chiral ligand L*7 (6.8 mg, 0.0050 mmol, 10 mol%), Cs2CO3 (32.6 mg, 0.10 mmol, 2.0 equiv.) and anhydrous Et2O (1.0 mL) and stirred at room temperature for 72 h. The mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product and purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 1 as a colorless oil (12.5 mg, 78% yield, 96% ee).

The effect of sulfoximine on the reaction initiation. (Figure 5C)

To the 83 (14.0 mg, 0.013 mmol, 0.25 equiv.) was added (1-bromoethyl)benzene (9.2 mg, 0.050 mmol, 1.0 equiv.), Cs2CO3 (32.6 mg, 0.10 mmol, 2.0 equiv.) and anhydrous Et2O (1.0 mL) and stirred at room temperature for 72 h. The mixture was filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated to afford the crude product and determined by 1H NMR spectra. There is no reaction happened without the chiral ligand.
According to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand L*7 at 0 °C for 72 h, the reaction mixture was purified by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) to yield the product 1 as a colorless oil (44.3 mg, 69% yield, 96% ee).

![Chemical structure](image)

In absence of sulfoximine N1, according to **General procedure A** with (1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand L*7 at 0 °C for 72 h, there is no conversion of E1.

**The stereochemistry of alkyl bromide during the reaction. (Figure 5D)**

**Racemic benzylic bromide**

![Chemical structure](image)

According to **General procedure A** with rac-(1-bromoethyl)benzene E1 (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand L*7 at room temperature for 12 h, the reaction mixture was diluted with EtOAc and filtrated through a pad of Celite, then concentrated in vacuum. The yield of E1 was determined by 1H NMR spectra with 1,3,5-trimethoxybenzene as an internal standard, the product 1 as a colorless oil was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 5/1) as a colorless oil (16.6 mg, 26% yield, 96% ee).

**Chiral benzylic bromide**
According to General procedure A with (R)-(1-bromoethyl)benzene (36.8 mg, 0.20 mmol, 1.0 equiv.) and chiral ligand L*7 at room temperature for 12 h, the reaction mixture was diluted with EtOAc and filtrated through a pad of Celite, then concentrated in vacuum. The yield of (R)-E1 was determined by ¹H NMR spectra with 1,3,5-trimethoxybenzene as an internal standard, the product 1 (13.5 mg, 21% yield, 96% ee) as a colorless oil was obtained by column chromatography on silica gel (petroleum ether/EtOAc = 5/1).

Radical trap experiment with TEMPO. (Figure 5E)

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-λ⁶-sulfanone N1 (26.0 mg, 0.12 mmol, 1.2 equiv.), Cu(Hfacac)₂ (4.4 mg, 0.010 mmol, 10 mol%), chiral ligand L*7 (13.6 mg, 0.010 mmol, 10 mol%), Cs₂CO₃ (65.2 mg, 0.20 mmol, 2.0 equiv.), TEMPO (31.3 mg, 0.20 mmol, 2.0 equiv.) and anhydrous Et₂O (2.0 mL). To this solution was added (R)-(1-bromoethyl)benzene (18.4 mg, 0.10 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 96 h. The precipitate was diluted with EtOAc, and then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated under reduce pressure and the residue was purified by column chromatography on neutral alumina (petroleum) to afford 84 as a yellow oil (4.4 mg, 17% yield).
2,2,6,6-Tetramethyl-1-(1-phenylethoxy)piperidine (84)

\[
\text{S132}
\]

**1H NMR** (400 MHz, CDCl₃) δ 7.38 – 7.30 (m, 4H), 7.27 – 7.20 (m, 1H), 4.80 (q, \(J = 6.7\) Hz, 1H), 1.53 – 1.02 (m, 18H), 0.68 (s, 3H).

**13C NMR** (100 MHz, CDCl₃) δ 145.9, 128.0, 126.8, 126.6, 83.1, 59.7, 53.4, 40.4, 34.5, 34.1, 23.6, 20.4, 17.2.

**HRMS** (ESI) \(m/z\) calcd. for C₁₇H₂₈NO \([M + H]^+\) 262.2165, found 262.2161.

### Radical clock experiment. (Supplementary Scheme S3)

**Benzyl chloride**

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a magnetic stir bar was charged with iminodiphenyl-\(\lambda^6\)-sulfanone N₁ (52.0 mg, 0.24 mmol, 1.2 equiv.), CuTc (3.8 mg, 0.020 mmol, 10 mol%), chiral ligand L*₇ (27.3 mg, 0.020 mmol, 10 mol%), Cs₂CO₃ (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et₂O (2.0 mL). To this solution was added (chloro(cyclopropyl)methyl)benzene E₃ (33.2 mg, 0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 96 h. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, and then filtered through Celite and washed with EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 3/1) to afford the desired product 8₅ as a yellow oil (6.0 mg, 9% yield) and 8₆ as a yellow oil (19.1 mg, 28% yield, 0% ee).
(E)-Diphenyl((4-phenylbut-3-en-1-yl)imino)-$\lambda^6$-sulfanone (85)

\[
\text{\begin{align*}
\text{H NMR} & \ (400 \text{ MHz, CDCl}_3) \ \delta \ 8.05 - 7.91 \ (m, \ 4H), \ 7.53 - 7.41 \ (m, \ 6H), \ 7.39 - 7.32 \\
& \ \ (m, \ 2H), \ 7.32 - 7.27 \ (m, \ 2H), \ 7.22 - 7.15 \ (m, \ 1H), \ 6.51 - 6.41 \ (m, \ 1H), \ 6.30 \ (dt, \ J = \\
& \ 15.9, \ 6.9 \ Hz, \ 1H), \ 3.19 \ (t, \ J = 7.2 \ Hz, \ 2H), \ 2.62 - 2.51 \ (m, \ 2H).
\end{align*}}
\]

\[
\text{\begin{align*}
\text{13C NMR} & \ (100 \text{ MHz, CDCl}_3) \ \delta \ 140.8, \ 137.8, \ 132.4, \ 131.1, \ 129.1, \ 128.9, \ 128.6, \ 128.5, \\
& \ 128.4, \ 127.6, \ 126.9, \ 126.03, \ 125.99, \ 43.9, \ 36.6.
\end{align*}}
\]

HRMS (ESI) $m/z$ calcd. for C$_{22}$H$_{22}$NOS [M + H]$^+$ 348.1417, found 348.1411.

((Cyclopropyl(phenyl)methyl)imino)diphenyl-$\lambda^6$-sulfanone (86)

\[
\text{\begin{align*}
\text{HPLC} \ \text{analysis: Chiralcel ID (hexane/iPrOH = 90/10, flow rate 1.0 mL/min, \lambda = 254} \\
& \ \text{nm)}, \ \tau_R1 = 8.17 \text{ min, } \tau_R2 = 9.82 \text{ min.}
\end{align*}}
\]

\[
\text{\begin{align*}
\text{H NMR} & \ (400 \text{ MHz, CDCl}_3) \ \delta \ 8.09 - 8.00 \ (m, \ 2H), \ 7.80 - 7.70 \ (m, \ 2H), \ 7.53 - 7.37 \\
& \ (m, \ 6H), \ 7.36 - 7.27 \ (m, \ 4H), \ 7.25 - 7.19 \ (m, \ 1H), \ 3.61 \ (d, \ J = 7.6 \ Hz, \ 1H), \ 1.36 - 1.17 \\
& \ (m, \ 1H), \ 0.58 - 0.50 \ (m, \ 1H), \ 0.50 - 0.39 \ (m, \ 2H), \ 0.39 - 0.30 \ (m, \ 1H).
\end{align*}}
\]

\[
\text{\begin{align*}
\text{13C NMR} & \ (100 \text{ MHz, CDCl}_3) \ \delta \ 146.2, \ 141.7, \ 140.9, \ 132.3, \ 132.2, \ 128.94, \ 128.92, \ 128.6, \\
& \ 128.1, \ 126.8, \ 126.5, \ 62.9, \ 21.1, \ 4.8, \ 4.1.
\end{align*}}
\]

HRMS (ESI) $m/z$ calcd. for C$_{22}$H$_{22}$NOS [M + H]$^+$ 348.1417, found 348.1411.

$\alpha$-Bromo ketone

\[
\text{\begin{align*}
\text{\begin{array}{c}
\text{Cu(HFacac)}_2 \ (10 \text{ mol\%})
\end{array}}
\text{\begin{array}{c}
\text{L7} \ (10 \text{ mol\%})
\end{array}}
\text{\begin{array}{c}
\text{Cs$_2$CO$_3$} \ (4.0 \text{ equiv.})
\end{array}}
\text{\begin{array}{c}
\text{Et$_2$O, 0°C}
\end{array}}
\text{\begin{array}{c}
\text{E4, 1.0 equiv.}
\end{array}}
\text{\begin{array}{c}
\text{PMP-Sulforhamine}
\end{array}}
\text{\begin{array}{c}
\text{PMP-Sulforhamine}
\end{array}}
\text{\begin{array}{c}
\text{PMP-Sulforhamine}
\end{array}}
\text{\begin{array}{c}
\text{PMP-Sulforhamine}
\end{array}}
\text{\begin{array}{c}
\text{PMP-Sulforhamine}
\end{array}}
\end{align*}}
\]

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a
magnetic stir bar was charged with iminobis(4-methoxyphenyl)-\(\lambda^6\)-sulfanone (60.9 mg, 0.22 mmol, 1.1 equiv.), Cu(HFacac)\(_2\) (8.8 mg, 0.020 mmol, 10 mol%), chiral ligand L*7 (27.3 mg, 0.020 mmol, 10 mol%), Cs\(_2\)CO\(_3\) (260.8 mg, 0.80 mmol, 4.0 equiv.) and anhydrous Et\(_2\)O (4.0 mL). To this solution was added 2-bromo-2-cyclopropyl-1-phenylethan-1-one \(\text{E4}\) (47.6 mg, 0.20 mmol, 1.0 equiv.) and the reaction mixture was stirred at 0 °C for 72 h. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, and then filtered through a short pad of Celite and washed with EtOAc. The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/1) to yield the product \(\text{87}\) as a colorless oil (48.7 mg, 56% yield).

\(\text{(E)-bis(4-Methoxyphenyl)((5-oxo-5-phenylpent-3-en-1-yl)imino)-}\lambda^6\text{-sulfanone (87)}\)

\[
\text{87}
\]

\(\text{1H NMR (400 MHz, CDCl}_3\text{)} \delta 8.00 - 7.91 (m, 2H), 7.91 - 7.83 (m, 4H), 7.59 - 7.52 (m, 1H), 7.52 - 7.44 (m, 2H), 7.20 - 7.10 (m, 1H), 7.02 - 6.95 (m, 1H), 6.95 - 6.89 (m, 4H), 3.82 (s, 6H), 3.24 (t, } J = 6.9 \text{ Hz, 2H), 2.73 - 2.61 (m, 2H).} \)

\(\text{13C NMR (100 MHz, CDCl}_3\text{)} \delta 191.0, 162.7, 148.3, 138.0, 132.6, 130.4, 128.6, 128.5, 127.1, 114.4, 55.6, 42.7, 36.3. \)

\(\text{HRMS (ESI) m/z calcd. for C}_{25}\text{H}_{26}\text{NO}_4\text{S }[\text{M + H}]^+ 436.1577, \text{ found 436.1575.} \)

**\(\alpha\)-Bromo amide**

\[
\begin{align*}
\text{E5, 1.0 equiv.} \quad \text{Cu(HFacac)}_2 \quad (10 \text{ mol\%}) \quad \text{L*7} \quad (10 \text{ mol\%}) \quad \text{Cs}_2\text{CO}_3 \quad (2.5 \text{ equiv.}) \\
\text{N1, 1.2 equiv.} \quad \text{Et}_2\text{O, rt}
\end{align*}
\]

\(\text{89, 52\%}\)

Under argon atmosphere, an oven-dried resealable Schlenk tube equipped with a
A magnetic stir bar was charged with iminodiphenyl-\(\lambda^6\)-sulfanone N1 (13.0 mg, 0.060 mmol, 1.2 equiv.), Cu(HFacac)\(_2\) (2.39 mg, 0.0050 mmol, 10 mol%), chiral ligand L*7 (6.8 mg, 0.0050 mmol, 10 mol%), Cs\(_2\)CO\(_3\) (65.2 mg, 0.20 mmol, 4.0 equiv.) and anhydrous Et\(_2\)O (1.0 mL). To this solution was added alkyl halide 2-bromo-2-cyclopropyl-1-morpholinoethan-1-one E5 (12.4 mg, 0.050 mmol, 1.0 equiv.) and the reaction mixture was stirred at room temperature for 96 h. Upon completion (monitored by TLC), the precipitate was diluted with EtOAc, and then filtered through a short pad of Celite and washed with EtOAc. The filtrate was concentrated and the residue was purified by column chromatography on silica gel (petroleum ether/EtOAc = 1/2) to afford the desired product 89 as a yellow oil (10.0 mg, 52% yield).

\[(E)-((5-Morpholino-5-oxopent-3-en-1-yl)imino)diphenyl-\(\lambda^6\)-sulfanone (89)\]

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

\(^1H\) NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.06 – 7.93 (m, 4H), 7.59 – 7.42 (m, 6H), 6.95 (dt, \(J = 15.2, 6.9\) Hz, 1H), 6.32 (d, \(J = 15.2\) Hz, 1H), 3.81 – 3.45 (m, 8H), 3.21 (t, \(J = 7.0\) Hz, 2H), 2.65 – 2.53 (m, 2H).

\(^{13}C\) NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.9, 144.7, 140.6, 132.5, 129.2, 128.5, 121.0, 66.9, 46.2, 42.7, 36.0.

HRMS (ESI) \(m/z\) calcd. for C\(_{21}\)H\(_{25}\)N\(_2\)O\(_3\)S [M + H]\(^+\) 385.1580, found 385.1575.
NMR spectra
**NMe₂**

**Ph**

**dapoxetine⁻¹H**

**NMe₂**

**Ph**

**dapoxetine⁻¹³C**

S238
HPLC spectra

Signal 4: DAD1 D, Sig=230.4 Ref=360,100

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Totals: 5.30594e4 714.74118

Signal 4: DAD1 D, Sig=230.4 Ref=360,100

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Totals: 9.72873e4 1363.45988
The chloro substrate

Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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Totals: 3927.71960 38.75799

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 2363.46196 34.88321
### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Total: 3153.52234 74.81970

### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Total: 1.58439e4 333.82623
### Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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**Totals:**

4501.24731  738.27731

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### Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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**Totals:**

4997.32269  1116.91720

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Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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Totals: 3.22084e4 339.07188

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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Totals: 2.12171e4 257.58499
Signal 4: DAD1 D, Sig=230.4 Ref=360,100

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Signal 4: DAD1 D, Sig=230.4 Ref=360,100

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Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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Totals: 4103.88989 53.34387

Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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Totals: 1.75803e5 2545.18359
Signal 4: DAD1 D, Sig=230.4 Ref=360.100

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Totals: 1.03796e5 1135.43768

Signal 4: DAD1 D, Sig=230.4 Ref=360.100

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Totals: 1.27491e5 1592.59117
**Signal 4: DAD1 D, Sig=230,4 Ref=360,100**

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Totals: 8.96224e4 968.01822

**Signal 4: DAD1 D, Sig=230,4 Ref=360,100**

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Totals: 1.21539e5 1599.42526
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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Totals: 1.14477e5 1711.33785
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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<td>733.16608</td>
<td>6.47184</td>
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<td>6.61728e4</td>
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</table>
Signal 4: DAD1 D, Sig=230.4 Ref=360.100

Peak RetTime Type Width Area Height Area %
--- | ----- | ---- | --- | --- | --- |
 1  41.795 BB  1.0321 4.64648e4 677.55920  49.9437
 2  48.116 BB  1.1927 4.65696e4 585.01495  50.0563

Totals: 9.30345e4 1262.57416

Signal 4: DAD1 D, Sig=230.4 Ref=360.100

Peak RetTime Type Width Area Height Area %
--- | ----- | ---- | --- | --- | --- |
 1  43.156 BB  1.1629 4.45228e4 583.03094  98.8820
 2  50.186 BB  1.1637 503.37344  5.60514  1.1180

Totals: 4.50262e4 588.63609
### Signal 2: DAD1 B, Sig=254,4 Ref=360,100

<table>
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<th>Area %</th>
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<tr>
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<td>35.876 BB</td>
<td>1.0115</td>
<td>1953.82703</td>
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<td>2</td>
<td>39.568 BB</td>
<td>0.9743</td>
<td>1947.72913</td>
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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<th>Width</th>
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<th>Height</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>67.408</td>
<td>BB</td>
<td>1.5413</td>
<td>1.06781e4</td>
<td>102.50818</td>
<td>50.0453</td>
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<td>2</td>
<td>73.142</td>
<td>BB</td>
<td>1.7148</td>
<td>1.06588e4</td>
<td>92.47124</td>
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<td>2.13369e4</td>
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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<tr>
<td>1</td>
<td>67.416</td>
<td>BB</td>
<td>1.5810</td>
<td>5.09481e4</td>
<td>469.87244</td>
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<td>2</td>
<td>73.933</td>
<td>MM R</td>
<td>1.9635</td>
<td>616.10785</td>
<td>5.22972</td>
<td>1.1948</td>
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<td>5.15642e4</td>
<td>475.10215</td>
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Signal 4: DAD1 D, Sig=230.4 Ref=360,100

Peak RetTime Type Width Area Height Area %
#   [min]      [min] [mAU*s]   [mAU]  
--- |--------|--------|--------|--------|--------|
 1  28.857 FM R 0.8307 5726.69385 114.89928 49.8968  
 2  36.042 BB   1.1223 5750.37793  75.69331 50.1032  

Totals :  1.14771e4  190.59259

Signal 4: DAD1 D, Sig=230.4 Ref=360,100

Peak RetTime Type Width Area Height Area %
#   [min]      [min] [mAU*s]   [mAU]  
--- |--------|--------|--------|--------|-------|
 1  28.675 MM R 0.8402 5.73416e4 1137.46777 96.1699  
 2  35.924 MM R 0.9996 2283.73438  38.07840  3.8301  

Totals :  5.96253e4  1175.54618
The chloro substrates

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

<table>
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<th>Height</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>28.351</td>
<td>MM</td>
<td>0.6905</td>
<td>6129.36133</td>
<td>147.93439</td>
<td>50.5681</td>
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<td>2</td>
<td>35.981</td>
<td>MM</td>
<td>0.7676</td>
<td>5991.64551</td>
<td>130.09331</td>
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Totals: 1.21210e4 278.02769

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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<th>Height</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>28.293</td>
<td>BB</td>
<td>0.6580</td>
<td>5021.50195</td>
<td>116.23598</td>
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<tr>
<td>2</td>
<td>35.671</td>
<td>MM</td>
<td>0.9252</td>
<td>111.86822</td>
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Totals: 5133.37017 118.25111
### Signal 4: DAD1 D, Sig=230.4 Ref=360,100

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<th>Height [mAU]</th>
<th>Area %</th>
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<tbody>
<tr>
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<td>48.272</td>
<td>BB</td>
<td>0.9574</td>
<td>2136.25806</td>
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<td>2</td>
<td>59.716</td>
<td>BB</td>
<td>1.2536</td>
<td>2135.43652</td>
<td>25.74644</td>
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**Totals:** 4271.69458 | 58.82693

### Signal 4: DAD1 D, Sig=230.4 Ref=360,100

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<th>Width [min]</th>
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<th>Height [mAU]</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>48.256</td>
<td>BB</td>
<td>0.9586</td>
<td>1555.43750</td>
<td>25.61066</td>
<td>1.9405</td>
</tr>
<tr>
<td>2</td>
<td>58.046</td>
<td>BB</td>
<td>1.4289</td>
<td>7.86011e4</td>
<td>768.74951</td>
<td>98.0595</td>
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**Totals:** 8.01566e4 | 794.36017
The chloro substrates

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

<table>
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<th>Ret Time</th>
<th>Type</th>
<th>Width</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>52.060</td>
<td>BB</td>
<td>1.0606</td>
<td>4097.68799</td>
<td>59.12556</td>
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<tr>
<td>2</td>
<td>64.527</td>
<td>VB</td>
<td>1.2186</td>
<td>4087.59766</td>
<td>51.68767</td>
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</table>

Totals: 8185.28564 110.81322

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

<table>
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<th>Type</th>
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<th>Height [mAU*]</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>52.879</td>
<td>BB</td>
<td>1.1448</td>
<td>197.45909</td>
<td>2.70134</td>
<td>1.7432</td>
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<tr>
<td>2</td>
<td>64.555</td>
<td>MM R</td>
<td>1.6012</td>
<td>1.11300e4</td>
<td>115.84959</td>
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Totals: 1.13274e4 118.55094
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU*s] [mAU] %
---|--------|------|--------|------|-----|-----|
1 18.749 BB 0.4716 1.55100e4 486.97626 49.7060
2 34.035 BB 1.0074 1.56935e4 226.75638 50.2940
Totals : 3.12035e4 713.73264

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU*s] [mAU] %
---|--------|------|--------|------|-----|-----|
1 18.737 BB 0.5158 6.94171e4 2015.63318 96.4782
2 34.315 MM R 0.9429 2533.97803 44.78920 3.5218
Totals : 7.19511e4 2060.42238
The chloro substrates

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

<table>
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<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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<td>[min]</td>
<td>[min]</td>
<td>[mAU*]</td>
<td>[mAU]</td>
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<tr>
<td>1</td>
<td>28.283</td>
<td>BB</td>
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<td>6109.99902</td>
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<tr>
<td>2</td>
<td>35.910</td>
<td>MM</td>
<td>0.7831</td>
<td>6118.59473</td>
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Totals: 1.22286e4 273.54662

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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<tbody>
<tr>
<td></td>
<td>[min]</td>
<td>[min]</td>
<td>[mAU*]</td>
<td>[mAU]</td>
<td>%</td>
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<tr>
<td>1</td>
<td>28.384</td>
<td>BB</td>
<td>0.6669</td>
<td>5033.23438</td>
<td>114.93758</td>
<td>98.1808</td>
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<tr>
<td>2</td>
<td>35.839</td>
<td>MM</td>
<td>0.8933</td>
<td>93.26212</td>
<td>1.74008</td>
<td>1.8192</td>
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Totals: 5126.49649 116.67767

S276
**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

<table>
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<th>Area%</th>
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<tbody>
<tr>
<td>1</td>
<td>18.404</td>
<td>BB</td>
<td>0.3829</td>
<td>2473.65405</td>
<td>97.85881</td>
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<tr>
<td>2</td>
<td>20.062</td>
<td>BB</td>
<td>0.4221</td>
<td>2673.05542</td>
<td>96.21078</td>
<td>51.9372</td>
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**Totals:**

5146.70947 194.06960

**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

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<th>Height</th>
<th>Area%</th>
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<tbody>
<tr>
<td>1</td>
<td>18.402</td>
<td>BB</td>
<td>0.4603</td>
<td>1.8037e4</td>
<td>587.29456</td>
<td>97.7450</td>
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<tr>
<td>2</td>
<td>20.420</td>
<td>BB</td>
<td>0.4677</td>
<td>416.12219</td>
<td>13.49546</td>
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**Totals:**

1.84531e4 600.79001
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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<th>Area (mAU*s)</th>
<th>Height</th>
<th>Area (mAU)</th>
<th>%</th>
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<tbody>
<tr>
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<td>BB</td>
<td>0.4553</td>
<td>1823.32922</td>
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<tr>
<td>2</td>
<td>37.694</td>
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<td>0.8559</td>
<td>1832.67224</td>
<td>32.89739</td>
<td>50.1278</td>
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Totals: 3656.00146 95.23259

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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<th>Height</th>
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<tbody>
<tr>
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<td>BB</td>
<td>0.4681</td>
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<tr>
<td>2</td>
<td>37.315</td>
<td>BB</td>
<td>0.9319</td>
<td>4.34174e4</td>
<td>713.48608</td>
<td>97.4588</td>
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Totals: 4.45495e4 750.78482
### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<th>Height</th>
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<tr>
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<td>0.4792</td>
<td>258.25525</td>
<td>8.16025</td>
<td>50.1547</td>
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<tr>
<td>2</td>
<td>25.284</td>
<td>BB</td>
<td>0.6283</td>
<td>256.66193</td>
<td>5.84520</td>
<td>49.8453</td>
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**Totals:** 514.91718 14.00546

### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<th>Height</th>
<th>Area %</th>
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<td>0.4986</td>
<td>259.50281</td>
<td>8.12478</td>
<td>3.9846</td>
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<tr>
<td>2</td>
<td>25.373</td>
<td>BB</td>
<td>0.6991</td>
<td>6253.09863</td>
<td>136.85159</td>
<td>96.0154</td>
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**Totals:** 6512.60144 144.97638
### Signal 4: DAD1 D, Sig=230,4 Ref=360,100

<table>
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<tr>
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<td>VB</td>
<td>0.2171</td>
<td>2982.91162</td>
<td>213.39357</td>
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<td>BV</td>
<td>0.2514</td>
<td>3024.26807</td>
<td>184.36650</td>
<td>50.3442</td>
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**Totals:**

- 6007.17969
- 397.76007

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### Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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<th>Peak</th>
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<th>Area %</th>
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<tr>
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<td>VV</td>
<td>0.2203</td>
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<td>156.41428</td>
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<td>12.615</td>
<td>BV</td>
<td>0.2109</td>
<td>105.55209</td>
<td>6.31776</td>
<td>4.5202</td>
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**Totals:**

- 2335.11728
- 162.73204
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

Peak RetTime Type Width Area Height Area
# [min] [min] [mAU*s] [mAU] %
--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|--|
**Signal 4: DAD1 D, Sig=230,4 Ref=360,100**

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Totals: 217.76246 6.97301

**Signal 4: DAD1 D, Sig=230,4 Ref=360,100**

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Totals: 3973.80057 98.06646
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 5356.46094 292.49324

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Totals: 1.31869e4 736.22415
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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Totals: 1677.74719 48.00175

Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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Totals: 4065.39404 115.94804
### Signal 2: DAD1 B, Sig=254.4 Ref=360,100

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**Totals:** 1.91769e4 488.09717

### Signal 2: DAD1 B, Sig=254.4 Ref=360,100

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**Totals:** 7014.66418 224.14538
Signal 4: DAD1 D, Sig=230.4 Ref=360.100

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Totals: 1.11133e4 259.39566

Signal 4: DAD1 D, Sig=230.4 Ref=360.100

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Totals: 3.49291e4 999.37724
**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

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**Totals:**

|       | 6306.70166 | 234.90115 |

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**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

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**Totals:**

|       | 9.97787e4 | 3153.55377 |
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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### Signal 2: DAD1 B, Sig=230,4 Ref=360,100

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**Totals:** 2.24120e4 297.76402

### Signal 2: DAD1 B, Sig=230,4 Ref=360,100

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**Totals:** 2.11848e4 256.27059
### Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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**Totals:**

4.64394e4 733.36295

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### Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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**Totals:**

3.83877e4 799.64740
### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<td>8.775</td>
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**Totals:** 2.50666e4 1920.11963

### Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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<td>375.26151</td>
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**Totals:** 3710.97025 280.08615
**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

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**Totals:** 2.19802e4 243.61384

**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

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<td>5300.26172</td>
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**Totals:** 1.19758e5 1488.75009
Signal 1: DAD1 A, Sig=254.4 Ref=360,100

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Totals: 1.62894e4 258.82657

Signal 1: DAD1 A, Sig=254.4 Ref=360,100

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Signal 2: DAD1 B, Sig=254.4 Ref=360,100

Peak RetTime Type Width Area Height Area %
--- | ------- | ------- | ------- | ------- | ------- | ------- |
1   31.851 MM R  1.0371  3421.27783  54.98359  49.6998
2   38.536 BB    1.1333  3462.61279  46.25860  50.3002

Totals: 6883.89063 101.24219

Signal 2: DAD1 B, Sig=254.4 Ref=360,100

Peak RetTime Type Width Area Height Area %
--- | ------- | ------- | ------- | ------- | ------- | ------- |
1   31.444 MM R  1.0545  2.60207e4  411.25116  95.8009
2   38.384 BB    1.0603  1140.54004  15.21855  4.1991

Totals: 2.71612e4  426.46971
### Table 1

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<td>2645.55542</td>
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<td>2670.70923</td>
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**Totals:** 5316.26465 135.58151

### Table 2

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<tr>
<td>1</td>
<td>18.482</td>
<td>BB</td>
<td>0.5492</td>
<td>570.25281</td>
<td>15.72108</td>
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<td>2</td>
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<td>BBA</td>
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**Totals:** 1.99571e4 472.77296
Signal 2: DAD1 B, Sig=254.4 Ref=360,100

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<td>MM</td>
<td>1.0364</td>
<td>4920.84277</td>
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<td>BB</td>
<td>1.1316</td>
<td>4885.63672</td>
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Totals: 9806.47949 145.44650

Signal 2: DAD1 B, Sig=254.4 Ref=360,100

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<td>BB</td>
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<td>2</td>
<td>37.453</td>
<td>BB</td>
<td>0.9753</td>
<td>639.57898</td>
<td>8.70349</td>
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Totals: 2.23978e4 367.65930
### Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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<tr>
<td>1</td>
<td>39.911</td>
<td>BB</td>
<td>1.3251</td>
<td>6002.48193</td>
<td>67.13322</td>
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<td>2</td>
<td>47.849</td>
<td>BB</td>
<td>1.5796</td>
<td>6022.32422</td>
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**Totals:** 1.20248e4  123.44753

### Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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<td>2.05143e4</td>
<td>226.62315</td>
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<td>2</td>
<td>48.107</td>
<td>BB</td>
<td>1.2723</td>
<td>1443.66357</td>
<td>13.47137</td>
<td>6.5747</td>
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**Totals:** 2.19580e4  240.09452
Signal 2: DAD1 B, Sig=254.4 Ref=360.100

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<tr>
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<td>11.329</td>
<td>BV</td>
<td>0.3120</td>
<td>1088.28418</td>
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<td>2</td>
<td>12.168</td>
<td>VB</td>
<td>0.3343</td>
<td>1087.86206</td>
<td>50.29762</td>
<td>49.9903</td>
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Totals: 2176.14624 104.56111

Signal 2: DAD1 B, Sig=254.4 Ref=360.100

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<tr>
<td>1</td>
<td>11.290</td>
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<td>0.3108</td>
<td>1.58914e4</td>
<td>796.49493</td>
<td>96.9539</td>
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<td>0.3487</td>
<td>499.27292</td>
<td>21.67608</td>
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Totals: 1.63907e4 818.17102
**Signal 2: DAD1 B, Sig=254,4 Ref=360,100**

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<td>6511.51270</td>
<td>143.14381</td>
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<td>24.861</td>
<td>0.8381</td>
<td>6294.13281</td>
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Totals: 1.28056e4 268.30644

**Signal 2: DAD1 B, Sig=254,4 Ref=360,100**

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Totals: 2.19470e4 492.70068
### Signal 2: DAD1 B, Sig=254.4 Ref=360,100

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<td>1.0654</td>
<td>1.64059e4</td>
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<tr>
<td>2</td>
<td>50.747</td>
<td>MM R</td>
<td>2.1406</td>
<td>1.61219e4</td>
<td>125.52304</td>
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**Totals:**

3.25278e4  382.16208

### Signal 2: DAD1 B, Sig=254.4 Ref=360,100

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<tr>
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<td>1.5019</td>
<td>1530.70703</td>
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**Totals:**

3.38126e4  526.80809
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU*s] [mAU] %
--|--|--|--|--|--|
1 26.466 BB 1.0199 1884.78296 29.24394 49.8201
2 33.204 BB 1.2652 1898.39380 20.37167 50.1799

Totals: 3783.17676 49.61562

Signal 2: DAD1 B, Sig=254,4 Ref=360,100

Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU*s] [mAU] %
--|--|--|--|--|--|
1 26.470 BB 1.0425 1.12698e4 171.99257 95.2291
2 33.300 BB 1.1026 564.61102 6.05098 4.7709

Totals: 1.18344e4 178.04355
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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<td>1174.72986</td>
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Totals : 2284.77197 44.28176

Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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<td>26.255</td>
<td>BB</td>
<td>0.8477</td>
<td>1098.22229</td>
<td>19.48231</td>
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Totals : 2.77122e4 596.38636
**Signal 2: DAD1 B, Sig=254,4 Ref=360,100**

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<td>1 23.643 BB</td>
<td>1950.66357</td>
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<td>2 27.257 BB</td>
<td>1965.32861</td>
<td>34.94857</td>
<td>50.1872</td>
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**Totals:** 3915.99219 75.80798
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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<td>43.05470</td>
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Totals: 3715.53601 91.94841

Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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<td>22.888</td>
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<td>0.7123</td>
<td>1.75379e4</td>
<td>410.34650</td>
<td>85.7634</td>
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Totals: 2.04492e4 486.14286

S305
### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<td>[min]</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>10.536</td>
<td>0.3258</td>
<td>368.51419</td>
<td>17.63574</td>
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<tr>
<td>2</td>
<td>12.763</td>
<td>0.4030</td>
<td>377.31476</td>
<td>14.24509</td>
</tr>
</tbody>
</table>

**Totals:**

- 745.82895
- 31.88083

### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
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<tr>
<th>Peak RetTime Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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<tbody>
<tr>
<td>#</td>
<td>[min]</td>
<td></td>
<td></td>
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<tr>
<td>1</td>
<td>10.523</td>
<td>0.3275</td>
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<tr>
<td>2</td>
<td>12.727</td>
<td>0.4129</td>
<td>1.4611e4</td>
<td>548.26465</td>
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</table>

**Totals:**

- 1.54347e4
- 587.38988
### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>20.185</td>
<td>BB</td>
<td>0.6327</td>
<td>6343.5527</td>
<td>152.69914</td>
<td>50.0737</td>
</tr>
<tr>
<td>2</td>
<td>31.731</td>
<td>BB</td>
<td>1.0440</td>
<td>6324.86963</td>
<td>92.00576</td>
<td>49.9263</td>
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Totals: 1.26684e4  244.70490

### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>20.343</td>
<td>BB</td>
<td>0.6215</td>
<td>919.85565</td>
<td>22.95653</td>
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<tr>
<td>2</td>
<td>31.377</td>
<td>BBA</td>
<td>1.0759</td>
<td>3.16047e4</td>
<td>448.60132</td>
<td>97.1718</td>
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Totals: 3.25245e4  471.55785
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>35.874</td>
<td>BB</td>
<td>1.1008</td>
<td>2.29967e4</td>
<td>313.88516</td>
<td>50.0245</td>
</tr>
<tr>
<td>2</td>
<td>46.221</td>
<td>BB</td>
<td>1.3728</td>
<td>2.29742e4</td>
<td>250.30614</td>
<td>49.9755</td>
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</table>

**Totals:**
4.59708e4 564.19130

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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<th>Height</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>36.696</td>
<td>MM R</td>
<td>1.3398</td>
<td>139.82149</td>
<td>1.73928</td>
<td>3.2541</td>
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<tr>
<td>2</td>
<td>46.772</td>
<td>BB</td>
<td>1.4236</td>
<td>4156.90283</td>
<td>43.86626</td>
<td>96.7459</td>
</tr>
</tbody>
</table>

**Totals:**
4296.72432 45.60554
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU*s] [mAU] %
---|--------|--------|--------|--------|---
1 17.778 BB 0.4894 2.18919e4 683.92426 49.9939 |
2 20.270 BB 0.5687 2.18972e4 590.33777 50.0061 |

Totals : 4.37892e4 1274.26202

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type Width Area Height Area %
# [min] [min] [mAU*s] [mAU] %
---|--------|--------|--------|--------|---
1 17.907 BB 0.5053 479.34879 14.51269 3.1842 |
2 20.288 BB 0.5704 1.45744e4 391.46890 96.8158 |

Totals : 1.50538e4 405.98159
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
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<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>24.824</td>
<td>BB</td>
<td>0.7283</td>
<td>2.25128e4</td>
<td>468.75302</td>
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<tr>
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<td>31.333</td>
<td>BB</td>
<td>0.9383</td>
<td>2.25833e4</td>
<td>367.82880</td>
<td>50.0782</td>
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Totals: 4.50962e4  836.58182

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
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<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>24.307</td>
<td>BB</td>
<td>0.6759</td>
<td>3803.23779</td>
<td>86.00909</td>
<td>3.2335</td>
</tr>
<tr>
<td>2</td>
<td>29.962</td>
<td>BB</td>
<td>0.9036</td>
<td>1.13816e5</td>
<td>1903.54834</td>
<td>96.7665</td>
</tr>
</tbody>
</table>

Totals: 1.17620e5  1989.55743
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

<table>
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<tr>
<th>Peak RetTime Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>34.089</td>
<td>1.0990 3.1739e4</td>
<td>438.23398</td>
<td>50.1479</td>
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<tr>
<td>2</td>
<td>44.146</td>
<td>1.3293 3.15526e4</td>
<td>359.74316</td>
<td>49.8521</td>
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<tr>
<td>Totals</td>
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<td>6.32925e4 797.97714</td>
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Signal 4: DAD1 D, Sig=230,4 Ref=360,100

<table>
<thead>
<tr>
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<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>34.322</td>
<td>1.1008 6925.98096</td>
<td>94.96967</td>
<td>3.2618</td>
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<tr>
<td>2</td>
<td>43.038</td>
<td>1.5221 2.05411e5</td>
<td>1996.93567</td>
<td>96.7382</td>
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<tr>
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<td>2.12337e5 2091.90533</td>
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Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
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<th>Width [min]</th>
<th>Area [mAU*s]</th>
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<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>9.776</td>
<td>0.2733</td>
<td>304.83850</td>
<td>16.67424</td>
<td>49.6669</td>
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<tr>
<td>2</td>
<td>17.433</td>
<td>0.5366</td>
<td>308.92709</td>
<td>9.59446</td>
<td>50.3331</td>
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Totals: 613.76559 26.26871

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
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<tr>
<th>Peak</th>
<th>Ret Time [min]</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
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<td>10.038</td>
<td>0.2495</td>
<td>3579.75122</td>
<td>213.58316</td>
<td>14.0347</td>
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<tr>
<td>2</td>
<td>17.576</td>
<td>0.4462</td>
<td>2.19267e4</td>
<td>743.28137</td>
<td>85.9653</td>
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</table>

Totals: 2.55064e4 956.86453
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>31.859</td>
<td>BB</td>
<td>0.8262</td>
<td>3821.35596</td>
<td>69.63688</td>
<td>50.1127</td>
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<tr>
<td>2</td>
<td>41.126</td>
<td>BB</td>
<td>1.2262</td>
<td>3804.16870</td>
<td>45.55674</td>
<td>49.8873</td>
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</table>

Totals: 7625.52466 115.19362

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

<table>
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<th>RetTime</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>32.305</td>
<td>BB</td>
<td>0.8846</td>
<td>435.88144</td>
<td>7.27951</td>
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<tr>
<td>2</td>
<td>40.524</td>
<td>BB</td>
<td>1.2470</td>
<td>1.79486e4</td>
<td>211.29892</td>
<td>97.6291</td>
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</tbody>
</table>

Totals: 1.83844e4 218.57843
Signal 4: DAD1 D, Sig=230.4 Ref=360,100

Peak RetTime Type Width  Area       Height      Area  %
   #  [min]        [min]  [mAU*s]   [mAU]          |
-------------------|-----------------|-----------|-----------|
  1  31.953 BB  0.8065  5487.00049 101.52797 50.3826
  2  41.840 BB  1.1660  5403.65625  63.68179 49.6174

Totals:  1.08907e4  165.20976

Signal 4: DAD1 D, Sig=230.4 Ref=360,100

Peak RetTime Type Width  Area       Height      Area  %
   #  [min]        [min]  [mAU*s]   [mAU]          |
-------------------|-----------------|-----------|-----------|
  1  31.157 BB  0.9566  1.14461e5 1693.32275  98.3787
  2  42.409 BB  1.0001  1886.37891  22.54610  1.6213

Totals:  1.16347e5  1715.86886
### Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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<tr>
<td>1</td>
<td>15.718</td>
<td>BB</td>
<td>0.4477</td>
<td>2.84080e4</td>
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<td>49.9325</td>
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<tr>
<td>2</td>
<td>18.225</td>
<td>BB</td>
<td>0.7223</td>
<td>2.84848e4</td>
<td>570.66528</td>
<td>50.0675</td>
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**Totals:** 5.68928e4 1529.37085

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### Signal 4: DAD1 D, Sig=230,4 Ref=360,100

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<tbody>
<tr>
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<td>BB</td>
<td>0.4512</td>
<td>2303.86816</td>
<td>77.87305</td>
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</tr>
<tr>
<td>2</td>
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<td>BB</td>
<td>0.7341</td>
<td>3.96186e4</td>
<td>777.97815</td>
<td>94.5045</td>
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**Totals:** 4.19224e4 855.85120
Signal 1: DAD1 A, Sig=254.4 Ref=360.100

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<th>Width [min]</th>
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<tbody>
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<td>BB</td>
<td>1.2847</td>
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<td>41.689</td>
<td>BB</td>
<td>1.5054</td>
<td>4234.07715</td>
<td>42.02741</td>
<td>49.8163</td>
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Totals: 8499.37988 91.45770

Signal 4: DAD1 D, Sig=230.4 Ref=360.100

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<tbody>
<tr>
<td>1</td>
<td>35.339</td>
<td>BB</td>
<td>1.2765</td>
<td>3862.34229</td>
<td>44.07092</td>
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<tr>
<td>2</td>
<td>41.253</td>
<td>BB</td>
<td>1.6708</td>
<td>8.23952e4</td>
<td>772.25165</td>
<td>95.5223</td>
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</tbody>
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Totals: 8.62575e4 816.32257
### Signal 3: DAD1 C, Sig=254, Ref=360,100

**Peak** | **RetTime** | **Type** | **Width** | **Area** | **Height** | **Area %**
---|---|---|---|---|---|---|
1 | 15.034 | BB | 0.3481 | 1467.87512 | 63.41177 | 49.1827 |
2 | 16.456 | BB | 0.3975 | 1516.65771 | 57.17370 | 50.8173 |

**Totals:** 2984.53284 120.58548

### Signal 3: DAD1 C, Sig=254, Ref=360,100

**Peak** | **RetTime** | **Type** | **Width** | **Area** | **Height** | **Area %**
---|---|---|---|---|---|---|
1 | 14.788 | MM R | 0.3944 | 1.32235e4 | 558.75153 | 96.6281 |
2 | 16.516 | MM R | 0.4690 | 461.44833 | 16.39979 | 3.3719 |

**Totals:** 1.36849e4 575.15131
Signal 4: DAD1 D, Sig=230,4 Ref=360,100

<table>
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<th>Height</th>
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<tr>
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<td>BB</td>
<td>0.6596</td>
<td>2.15415e4</td>
<td>476.30225</td>
<td>50.0235</td>
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<tr>
<td>2</td>
<td>25.774</td>
<td>BB</td>
<td>0.8526</td>
<td>2.15213e4</td>
<td>380.09293</td>
<td>49.9765</td>
</tr>
</tbody>
</table>

Totals: 4.30627e4 856.39517

Signal 4: DAD1 D, Sig=230,4 Ref=360,100

<table>
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<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>19.594</td>
<td>MM R</td>
<td>0.8162</td>
<td>4.951.76563</td>
<td>101.10960</td>
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</tr>
<tr>
<td>2</td>
<td>27.617</td>
<td>MM R</td>
<td>1.0835</td>
<td>8.05810e4</td>
<td>1239.46155</td>
<td>94.2107</td>
</tr>
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Totals: 8.55328e4 1340.57115
### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
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<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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<tbody>
<tr>
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<td>BB</td>
<td>0.5149</td>
<td>4212.57129</td>
<td>121.39346</td>
<td>50.0658</td>
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<tr>
<td>2</td>
<td>18.888</td>
<td>BB</td>
<td>0.6893</td>
<td>4201.50000</td>
<td>90.55860</td>
<td>49.9342</td>
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**Totals:**

8414.07129 211.95206

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### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
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<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
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<td>BB</td>
<td>0.5434</td>
<td>413.00174</td>
<td>11.16825</td>
<td>5.3754</td>
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</tr>
<tr>
<td>2</td>
<td>18.835</td>
<td>MM R</td>
<td>0.7810</td>
<td>7270.23926</td>
<td>155.13843</td>
<td>94.6246</td>
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</tr>
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**Totals:**

7683.24100 166.30668

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S322
70-1 Procedure a:

Signal 2: DAD1 B, Sig=210.4 Ref=360,100

<table>
<thead>
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<th>RetTime</th>
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<th>Width</th>
<th>Area</th>
<th>Height</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>11.464</td>
<td>BB</td>
<td>0.4172</td>
<td>2.31839e4</td>
<td>874.91003</td>
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</tr>
<tr>
<td></td>
<td>13.669</td>
<td>BB</td>
<td>0.5023</td>
<td>2.34533e4</td>
<td>742.92719</td>
<td>50.2888</td>
</tr>
</tbody>
</table>

Totals : 4.66372e4 1617.83722

Signal 2: DAD1 B, Sig=210.4 Ref=360,100

<table>
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<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
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<th>Area %</th>
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<tbody>
<tr>
<td></td>
<td>11.145</td>
<td>BB</td>
<td>0.3908</td>
<td>579.53302</td>
<td>22.62584</td>
<td>2.6287</td>
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<tr>
<td></td>
<td>13.160</td>
<td>BB</td>
<td>0.4706</td>
<td>2.14666e4</td>
<td>730.92181</td>
<td>97.3713</td>
</tr>
</tbody>
</table>

Totals : 2.20461e4 753.54766
70-1 Procedure b:

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

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<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
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<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>11.803</td>
<td>MM R</td>
<td>0.5035</td>
<td>9622.04785</td>
<td>318.52432</td>
<td>50.7779</td>
</tr>
<tr>
<td>2</td>
<td>14.619</td>
<td>FM R</td>
<td>0.2890</td>
<td>9327.25293</td>
<td>537.85400</td>
<td>49.2221</td>
</tr>
</tbody>
</table>

Totals: 1.89493e4 856.37833

Signal 2: DAD1 B, Sig=210,4 Ref=360,100

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<th>RetTime</th>
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<th>Width</th>
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<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.518</td>
<td>BV R</td>
<td>0.3523</td>
<td>329.84317</td>
<td>12.01479</td>
<td>2.7470</td>
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<tr>
<td>2</td>
<td>14.118</td>
<td>VB</td>
<td>0.2047</td>
<td>1.16775e4</td>
<td>780.02032</td>
<td>97.2530</td>
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</tbody>
</table>

Totals: 1.20074e4 792.03511
71-1 procedure a:

Signal 2: DAD1 B, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
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<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.364</td>
<td>VV</td>
<td>0.1529</td>
<td>1263.34778</td>
<td>126.13493</td>
<td>49.8266</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>5.595</td>
<td>BB</td>
<td>0.2146</td>
<td>1272.14270</td>
<td>89.09251</td>
<td>50.1734</td>
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</tr>
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Totals: 2535.49048 215.22743

Signal 2: DAD1 B, Sig=254,4 Ref=360,100

<table>
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<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.416</td>
<td>VV</td>
<td>0.1779</td>
<td>94.88505</td>
<td>7.80298</td>
<td>5.9097</td>
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</tr>
<tr>
<td>2</td>
<td>5.541</td>
<td>VB</td>
<td>0.2187</td>
<td>1510.70288</td>
<td>103.27180</td>
<td>94.0903</td>
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</tr>
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</table>

Totals: 1605.58793 111.07478
### 71-1 procedure b:

![Chemical structure of rac-71-1](image)

**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

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<tr>
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<th>RetTime</th>
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<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>4.016</td>
<td>0.0944</td>
<td>744.98492</td>
<td>119.97974</td>
<td>49.7860</td>
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<tr>
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<td>4.986</td>
<td>0.1268</td>
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<td>88.73402</td>
<td>50.2140</td>
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</tr>
</tbody>
</table>

**Totals:** 1496.37323  208.71376

![Chemical structure of (S)-71-1](image)

**Signal 1: DAD1 A, Sig=254,4 Ref=360,100**

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime</th>
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<th>Area</th>
<th>Height</th>
<th>Area</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.051</td>
<td>0.1086</td>
<td>61.60689</td>
<td>8.70290</td>
<td>5.2014</td>
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<tr>
<td>2</td>
<td>4.969</td>
<td>0.1275</td>
<td>1122.81873</td>
<td>131.60585</td>
<td>94.7986</td>
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</tr>
</tbody>
</table>

**Totals:** 1184.42562  140.30875
### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

<table>
<thead>
<tr>
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<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>10.967</td>
<td>BB</td>
<td>0.3470</td>
<td>1197.34814</td>
<td>49.35469</td>
<td>50.0541</td>
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<tr>
<td>2</td>
<td>12.475</td>
<td>BB</td>
<td>0.4105</td>
<td>1194.76099</td>
<td>41.91695</td>
<td>49.9459</td>
</tr>
</tbody>
</table>

Totals: 2392.10913 91.27163

### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>10.768</td>
<td>BB</td>
<td>0.3610</td>
<td>4674.11084</td>
<td>186.11456</td>
<td>96.6247</td>
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<tr>
<td>2</td>
<td>12.390</td>
<td>BB</td>
<td>0.3648</td>
<td>163.27538</td>
<td>6.41850</td>
<td>3.3753</td>
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</tbody>
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Totals: 4837.38622 192.53306
Signal 3: DAD1 C, Sig=210.4 Ref=360.100

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
<th>Area [%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>17.879</td>
<td>BB</td>
<td>0.5361</td>
<td>9619.58008</td>
<td>262.16507</td>
<td>50.0112</td>
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</tr>
<tr>
<td>2</td>
<td>21.451</td>
<td>BB</td>
<td>0.6099</td>
<td>9615.27930</td>
<td>230.85823</td>
<td>49.9888</td>
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</tr>
</tbody>
</table>

Totals: 1.92349e4 493.02330

Signal 3: DAD1 C, Sig=210.4 Ref=360.100

<table>
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<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
<th>Area [%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>17.733</td>
<td>BB</td>
<td>0.5624</td>
<td>4.39897e4</td>
<td>1149.79004</td>
<td>96.6062</td>
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<tr>
<td>2</td>
<td>21.510</td>
<td>BB</td>
<td>0.5807</td>
<td>1545.38208</td>
<td>39.64761</td>
<td>3.3938</td>
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</table>

Totals: 4.55351e4 1189.43765
### rac-74-1

**Signal 2: DAD1 B, Sig=214,4 Ref=360,100**

<table>
<thead>
<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.468</td>
<td>BB</td>
<td>0.6521</td>
<td>3776.80518</td>
<td>87.75518</td>
<td>49.8942</td>
</tr>
<tr>
<td>2</td>
<td>21.642</td>
<td>MM R</td>
<td>0.8907</td>
<td>3792.81567</td>
<td>70.97343</td>
<td>50.1058</td>
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</table>

**Totals:**

7569.62085 158.72861

### (S)-74-1

**Signal 2: DAD1 B, Sig=214,4 Ref=360,100**

<table>
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<tr>
<th>Peak</th>
<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.348</td>
<td>BB</td>
<td>0.6713</td>
<td>2.15294e4</td>
<td>497.04449</td>
<td>95.6299</td>
</tr>
<tr>
<td>2</td>
<td>21.743</td>
<td>BB</td>
<td>0.6155</td>
<td>983.86243</td>
<td>18.89479</td>
<td>4.3701</td>
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</table>

**Totals:**

2.25133e4 515.93929
Signal 2: DAD1 B, Sig=210.4 Ref=360,100

<table>
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<th>Peak</th>
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<th>Area</th>
<th>Height</th>
<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>10.094</td>
<td>BB</td>
<td>0.3651</td>
<td>1.22806e4</td>
<td>506.03769</td>
<td>48.7944</td>
</tr>
<tr>
<td>2</td>
<td>13.943</td>
<td>MM</td>
<td>0.5663</td>
<td>1.28874e4</td>
<td>379.29300</td>
<td>51.2056</td>
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Totals: 2.51680e4 885.33069

Signal 2: DAD1 B, Sig=210.4 Ref=360,100

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<th>RetTime</th>
<th>Type</th>
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<th>Height</th>
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<tbody>
<tr>
<td>1</td>
<td>10.099</td>
<td>BB</td>
<td>0.3491</td>
<td>199.66264</td>
<td>8.28641</td>
<td>4.3393</td>
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<tr>
<td>2</td>
<td>13.921</td>
<td>BB</td>
<td>0.4980</td>
<td>4401.57178</td>
<td>133.03854</td>
<td>95.6607</td>
</tr>
</tbody>
</table>

Totals: 4601.23442 141.32495
### Peak RetTime Type Width Area Height Area %

<table>
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<th>RetTime [min]</th>
<th>Type</th>
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<th>Height [mAU]</th>
<th>Area [%]</th>
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<tbody>
<tr>
<td>1</td>
<td>7.093</td>
<td>BV</td>
<td>0.2510</td>
<td>1.23022e4</td>
<td>735.97424</td>
<td>49.3968</td>
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<tr>
<td>2</td>
<td>8.640</td>
<td>VB</td>
<td>0.2814</td>
<td>1.26027e4</td>
<td>670.08380</td>
<td>50.6032</td>
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</table>

**Totals:**

- 2.49049e4
- 1406.05804

### Peak RetTime Type Width Area Height Area %

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<tr>
<th>#</th>
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<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area [%]</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>7.037</td>
<td>BB</td>
<td>0.2389</td>
<td>1142.35095</td>
<td>72.09510</td>
<td>4.6600</td>
</tr>
<tr>
<td>2</td>
<td>8.543</td>
<td>BB</td>
<td>0.2877</td>
<td>2.33717e4</td>
<td>1218.81848</td>
<td>95.3400</td>
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</tbody>
</table>

**Totals:**

- 2.45140e4
- 1290.91358
### Signal 3: DAD1 C, Sig=214.4 Ref=360,100

<table>
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<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>7.312</td>
<td>BV</td>
<td>0.1792</td>
<td>3813.89136</td>
<td>329.09067</td>
<td>49.2725</td>
</tr>
<tr>
<td>2</td>
<td>7.981</td>
<td>MM R</td>
<td>0.2260</td>
<td>3926.50757</td>
<td>289.60992</td>
<td>50.7275</td>
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</table>

**Totals:** 7740.39893 618.70059

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### Signal 3: DAD1 C, Sig=214.4 Ref=360,100

<table>
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<th>RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area</th>
<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.213</td>
<td>BB</td>
<td>0.1655</td>
<td>155.55150</td>
<td>14.45717</td>
<td>4.5762</td>
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<tr>
<td>2</td>
<td>7.840</td>
<td>BB</td>
<td>0.1879</td>
<td>3243.57764</td>
<td>266.63788</td>
<td>95.4238</td>
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**Totals:** 3399.12914 281.09505

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S333
**Signal 1: DAD1 A, Sig=214,4 Ref=360,100**

<table>
<thead>
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<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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<tbody>
<tr>
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<td>7.792</td>
<td>0.1819</td>
<td>3095.37964</td>
<td>265.76370</td>
<td>50.1003</td>
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<tr>
<td>2</td>
<td>8.400</td>
<td>0.1819</td>
<td>3082.98071</td>
<td>260.90656</td>
<td>49.8997</td>
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**Totals:** 6178.36035 526.67026

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**Signal 1: DAD1 A, Sig=214,4 Ref=360,100**

<table>
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<tr>
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<th>Width [min]</th>
<th>Area [mAU*s]</th>
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<tbody>
<tr>
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<td>2.18047e4</td>
<td>1812.46399</td>
<td>95.3332</td>
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<td>2</td>
<td>8.285</td>
<td>0.1811</td>
<td>1067.38721</td>
<td>98.22916</td>
<td>4.6668</td>
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**Totals:** 2.28720e4 1910.69315
**Signal 3: DAD1 C, Sig=214.4 Ref=360,100**

<table>
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<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.529</td>
<td>BV</td>
<td>0.1831</td>
<td>8572.78613</td>
<td>729.68750</td>
<td>49.7934</td>
</tr>
<tr>
<td>2</td>
<td>9.148</td>
<td>VB</td>
<td>0.1922</td>
<td>8643.93066</td>
<td>699.47711</td>
<td>50.2066</td>
</tr>
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</table>

**Totals:**

1.72167e4 1429.16461

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**Signal 3: DAD1 C, Sig=214.4 Ref=360,100**

<table>
<thead>
<tr>
<th>#</th>
<th>RetTime [min]</th>
<th>Type</th>
<th>Width [min]</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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</thead>
<tbody>
<tr>
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<td>8.531</td>
<td>MM R</td>
<td>0.1893</td>
<td>2705.58447</td>
<td>238.17113</td>
<td>94.0151</td>
</tr>
<tr>
<td>2</td>
<td>9.141</td>
<td>MM R</td>
<td>0.1908</td>
<td>172.23415</td>
<td>15.04331</td>
<td>5.9849</td>
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</table>

**Totals:**

2877.81862 253.21444
### Peak RetTime Type Width Area Height Area %

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<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
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<tbody>
<tr>
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<td>BB</td>
<td>0.4606</td>
<td>1007.38684</td>
<td>32.59061</td>
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**Totals:**
2.00503e4 694.14194
### Signal 2: DAD1 B, Sig=210,4 Ref=360,100

<table>
<thead>
<tr>
<th>Peak RetTime</th>
<th>Type</th>
<th>Width</th>
<th>Area [mAU*s]</th>
<th>Height [mAU]</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.414</td>
<td>BB</td>
<td>0.2596 8253.10645</td>
<td>472.80496</td>
<td>49.7137</td>
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<tr>
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<td>12.643</td>
<td>BB</td>
<td>0.3499 8348.16602</td>
<td>355.62445</td>
<td>50.2863</td>
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**Totals:**
- **1.66013e4**
- **828.42941**

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### Signal 2: DAD1 B, Sig=210,4 Ref=360,100

<table>
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<tbody>
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<td>12.703</td>
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**Totals:**
- **2.51106e4**
- **1315.65819**
### Signal 5: DAD1 E, Sig=260,4 Ref=360,100

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<tr>
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<td>8.680</td>
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<td>50.0317</td>
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**Totals:**

1.64584e4 1211.65375

### Signal 5: DAD1 E, Sig=260,4 Ref=360,100

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**Totals:**

1944.01531 95.65957
### Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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<tbody>
<tr>
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<td>16.927</td>
<td>BB</td>
<td>0.4460</td>
<td>2238.84741</td>
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<td>2</td>
<td>22.919</td>
<td>BB</td>
<td>0.6580</td>
<td>2090.74072</td>
<td>48.98307</td>
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**Totals:** 4329.58813 126.25945

### Signal 2: DAD1 B, Sig=254,4 Ref=360,100

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<td>0.4647</td>
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<td>2</td>
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<td>BV</td>
<td>0.6651</td>
<td>3180.30957</td>
<td>73.46073</td>
<td>98.3971</td>
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**Totals:** 3232.11574 75.15510
### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<td>1</td>
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<td>BB</td>
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<td>21.709</td>
<td>BB</td>
<td>0.6496</td>
<td>4855.00000</td>
<td>106.15434</td>
<td>50.8373</td>
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**Totals:**

9550.06787 221.04159

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### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<tr>
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<td>0.4310</td>
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<td>2</td>
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<td>1.37202e4</td>
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**Totals:**

1.38175e4 284.12412
### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<tr>
<td>1</td>
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<td>0.2603</td>
<td>1.58807e4</td>
<td>943.72546</td>
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<tr>
<td>2</td>
<td>12.392</td>
<td>VB</td>
<td>0.2778</td>
<td>1.59274e4</td>
<td>894.22443</td>
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**Totals:**
- **Area:** $3.18081e4$
- **Height:** $1837.94989$

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### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<tr>
<td>1</td>
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<td>BB</td>
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<td>2</td>
<td>12.408</td>
<td>BB</td>
<td>0.2321</td>
<td>70.74434</td>
<td>4.20884</td>
<td>1.3040</td>
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**Totals:**
- **Area:** $5425.21944$
- **Height:** $269.94477$
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<th>Area %</th>
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<tbody>
<tr>
<td>1</td>
<td>19.314</td>
<td>BB</td>
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<td>5479.00537</td>
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<tr>
<td>2</td>
<td>21.635</td>
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<td>0.6429</td>
<td>5658.46143</td>
<td>125.29555</td>
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Totals: 1.11375e4 259.77968

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<th>Width</th>
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<tbody>
<tr>
<td>1</td>
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<td>BB</td>
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<tr>
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<td>21.644</td>
<td>BB</td>
<td>0.3911</td>
<td>126.33920</td>
<td>3.90864</td>
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Totals: 1.06072e4 253.15336
### rac-cinacalcet

Signal 1: DAD1 A, Sig=254.4 Ref=360,100

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<th>Height</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.255</td>
<td>BB</td>
<td>0.2685</td>
<td>1.63785e4</td>
<td>943.45209</td>
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<tr>
<td>2</td>
<td>12.830</td>
<td>BB</td>
<td>0.2847</td>
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**Totals:**

3.28332e4  1837.76581

### (S)-cinacalcet

Signal 1: DAD1 A, Sig=254.4 Ref=360,100

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<tr>
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<td>0.2238</td>
<td>46.54716</td>
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<td>2</td>
<td>12.912</td>
<td>BB</td>
<td>0.3006</td>
<td>4552.39404</td>
<td>232.29883</td>
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**Totals:**

4598.94120  234.88728
### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<th>Height [mAU]</th>
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<tr>
<td>1</td>
<td>10.430</td>
<td>MF R</td>
<td>0.3324</td>
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<td>13.615</td>
<td>BB</td>
<td>0.4160</td>
<td>8416.61035</td>
<td>304.95752</td>
<td>50.0231</td>
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**Totals:**

1.68254e4 726.60681

### Signal 1: DAD1 A, Sig=254,4 Ref=360,100

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<tbody>
<tr>
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<td>165.50771</td>
<td>8.41813</td>
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<td>13.602</td>
<td>BB</td>
<td>0.4154</td>
<td>3879.13306</td>
<td>140.79268</td>
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**Totals:**

4044.64076 149.21081
Signal 5: DAD1 F, Sig=240,4 Ref=360,100

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<tbody>
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<tr>
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<td>5.315</td>
<td>MF</td>
<td>0.1363</td>
<td>8028.58691</td>
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<td>48.7460</td>
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<tr>
<td>2</td>
<td>6.795</td>
<td>MM</td>
<td>0.1823</td>
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Totals: 1.64703e4 1753.67566

Signal 5: DAD1 F, Sig=240,4 Ref=360,100

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<td>5.610</td>
<td>FM</td>
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<td>788.99292</td>
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Totals: 817.56070 99.51093
Signal 2: DAD1 B, Sig=254.4 Ref=360,100

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<tbody>
<tr>
<td>1</td>
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<td>0.4722</td>
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<td>6748.38721</td>
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Totals: 1.35401e4 387.78673

Signal 2: DAD1 B, Sig=254.4 Ref=360,100

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<td>0.6112</td>
<td>55.39318</td>
<td>1.31574</td>
<td>1.8255</td>
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Totals: 3034.41320 98.86923
### rac-rivastigmine

**Signal 2: DAD1 B, Sig=210,4 Ref=360,100**

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<td>BV</td>
<td>0.4819</td>
<td>2.73700e4</td>
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<td>BB</td>
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<td>2.76650e4</td>
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**Totals:**

- **Area:** 5.50350e4
- **% Area:** 1428.84637

### rivastigmine

**Signal 2: DAD1 B, Sig=210,4 Ref=360,100**

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<td>363.49234</td>
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**Totals:**

- **Area:** 1.81201e4
- **% Area:** 373.40255
Signal 2: DAD1 B, Sig=254,4 Ref=360,100

### Peak RetTime Type Width Area Height Area %

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<tbody>
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<td>0.1593</td>
<td>732.68152</td>
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<td>0.2149</td>
<td>733.66266</td>
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<td>50.0335</td>
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**Totals:**

1466.34418 125.56197

Signal 2: DAD1 B, Sig=254,4 Ref=360,100

### Peak RetTime Type Width Area Height Area %

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<td>BV</td>
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<td>88.53080</td>
<td>49.6564</td>
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**Totals:**

2404.48169 207.83914
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