Supporting information for

Chiral Ion-Pair Organocatalyst Promotes Highly Enantioselective 3-exo Iodo-cycloetherification of Allyl Alcohols

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1. General information

Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Non-aqueous reaction were conducted under an inert atmosphere of nitrogen in flame-dried glassware. Anhydrous solvent were treated as follow: tetrahydrofuran and diethyl ether were distilled from sodium under nitrogen atmosphere, dimethylformamide were distilled over calcium hydride under reduced pressure, and dichloromethane and toluene was distilled distilled from calcium hydride under nitrogen atmosphere. Thin layer chromatography was conducted on Merck 60 F254 pre-coated silica gel plates. Column chromatography was carried out by normal silica gel (40-60 µm, 200-400 mesh, Silicycle P60). NMR data including $^1$H NMR or $^{13}$C NMR spectra were recorded on Agilent 500 and Agilent 400. $^1$H NMR Chemical shifts were reported in ppm from the solvent resonance as the internal standard (CDCl$_3$: 7.26 ppm, D$_2$O: 4.79). $^{13}$C NMR chemical shifts were reported in ppm relative to the solvent (CDCl$_3$:77 ppm). Infrared spectra were performed on a Nicolet 380FT-IR and are reported in terms of frequency of absorption (cm$^{-1}$). Low mass spectra were measured on a Shimadzu LCMS-2010EV mass spectrometer (ESI) and Agilent Technologies 5973N (EI). High resolution mass spectra were obtained from IonSpec 4.7 Tesla FTMS mass spectrometer (MALDI), Bruker APEXIII 7.0 TESLA FTMS (ESI) and Waters Micromass GCT Premier (EI).
2. Reaction conditions optimization

Table S1. Evaluation of chiral silver phosphate and ammonium salts

```
<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>silver salt (equiv)</th>
<th>additive (equiv)</th>
<th>yield (%)</th>
<th>ee (%)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>L1 (0.1)</td>
<td>A1 (0.12)</td>
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<td>30</td>
</tr>
<tr>
<td>2</td>
<td>DCM</td>
<td>L1 (0.1)</td>
<td>A2 (0.12)</td>
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<td>19</td>
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<td>L1 (0.1)</td>
<td>A3 (0.12)</td>
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<td>69</td>
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</tr>
<tr>
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<td>91</td>
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<tr>
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<td>DCM</td>
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<td>A8 (0.12)</td>
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<td>13</td>
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<td>67</td>
</tr>
<tr>
<td>15</td>
<td>DCM</td>
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<td>--</td>
<td>trace</td>
<td>ND</td>
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<tr>
<td>16</td>
<td>DCM</td>
<td>L1 (0.1)</td>
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<td>trace</td>
<td>ND</td>
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<tr>
<td>17</td>
<td>DCM</td>
<td>--</td>
<td>A8 (0.12)</td>
<td>trace</td>
<td>ND</td>
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</tbody>
</table>
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Reaction conditions: To a mixture of silver salt L1 (0.01 mmol), ammonium salt A (0.012 mmol) and NIS (0.12 mmol) was added DCM (1 mL) then the reaction mixture was cooled to 0 °C. Allyl alcohol 1a (0.1 mmol) in 0.5 mL DCM was added dropwise and the reaction was quenched after 40 h. \(^a\)Isolated yield. \(^b\)Determined by HPLC using Chiralpak AD column.
Table S2. Survey of other organocatalysts.

![Reaction Scheme](image)

Reaction conditions: To a mixture of catalyst L1 (0.01 mmol), NIS (0.12 mmol) was added DCM (1 mL) then the reaction mixture was cooled to 0 °C. Allyl alcohol 1a (0.1 mmol) in 0.5 mL DCM was added dropwise and the reaction was quenched after 40 h.

Other organocatalysts:

![Other Organocatalysts](image)
Table S3. Screening of halogen sources

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>silver salt</th>
<th>additive</th>
<th>halogenating reagent</th>
<th>yield&lt;sup&gt;a&lt;/sup&gt; (%)</th>
<th>ee&lt;sup&gt;b&lt;/sup&gt; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>DCM</td>
<td>L1 (0.1)</td>
<td>A8 (0.12)</td>
<td>NIS</td>
<td>65</td>
<td>91</td>
</tr>
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<td>2</td>
<td>DCM</td>
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<td>A8 (0.12)</td>
<td>I₂</td>
<td>NR</td>
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<tr>
<td>3</td>
<td>DCM</td>
<td>L1 (0.1)</td>
<td>A8 (0.12)</td>
<td>NCS</td>
<td>NR</td>
<td>--</td>
</tr>
<tr>
<td>4</td>
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<td>A8 (0.12)</td>
<td>NBS</td>
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<td>79</td>
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<tr>
<td>5</td>
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<td>L1 (0.1)</td>
<td>A8 (0.12)</td>
<td>H1</td>
<td>23</td>
<td>8</td>
</tr>
<tr>
<td>6</td>
<td>DCM</td>
<td>L1 (0.1)</td>
<td>A8 (0.12)</td>
<td>H2</td>
<td>46</td>
<td>31</td>
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<tr>
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<td>DCM</td>
<td>L1 (0.1)</td>
<td>A8 (0.12)</td>
<td>H3</td>
<td>68</td>
<td>78</td>
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</table>

Reaction conditions: To a mixture of silver salt L1 (0.01 mmol), ammonium salt A8 (0.012 mmol) and halogenating reagent (0.12 mmol) was added DCM (1 mL) then the reaction mixture was cooled to 0 °C. Allyl alcohol 1a (0.1 mmol) in 0.5 mL DCM was added dropwise and the reaction was quenched after 40 h. <sup>a</sup>Isolated yield. <sup>b</sup>Determined by HPLC using Chiralpak AD column.
Table S4. Effects of additive and temperature.

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst (equiv)</th>
<th>additive (equiv)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>yield(^a) (%)</th>
<th>ee(^b) (%)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>C1 (0.1)</td>
<td>--</td>
<td>0</td>
<td>40</td>
<td>42</td>
<td>83</td>
</tr>
<tr>
<td>2</td>
<td>C1 (0.1)</td>
<td>DABCO (0.1)</td>
<td>0</td>
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<tr>
<td>3</td>
<td>C1 (0.1)</td>
<td>(-)-CSA (0.1)</td>
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<td>38</td>
<td>80</td>
</tr>
<tr>
<td>4</td>
<td>C1 (0.1)</td>
<td>Ph3P=S (0.1)</td>
<td>0</td>
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<td>63</td>
<td>90</td>
</tr>
<tr>
<td>5</td>
<td>C1 (0.1)</td>
<td>A8 (0.1)</td>
<td>0</td>
<td>40</td>
<td>82</td>
<td>92</td>
</tr>
<tr>
<td>6</td>
<td>C1 (0.1)</td>
<td>A8 (0.1)</td>
<td>-20</td>
<td>107</td>
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<td>94</td>
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<tr>
<td>8</td>
<td>C1 (0.1)</td>
<td>A8 (0.1)</td>
<td>-40</td>
<td>121</td>
<td>83</td>
<td>94</td>
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</table>

Reaction conditions: To a mixture of silver salt C1 (0.01 mmol), additive (0.012 mmol) and NIS (0.12 mmol) was added DCM (1 mL) then the reaction mixture was cooled to 0 °C. Allyl alcohol 1a (0.1 mmol) in 0.5 mL DCM was added dropwise and the reaction was quenched at indicated time.

\(^a\)Isolated yield. \(^b\)Determined by HPLC using Chiralpak AD column.
Table S5. Screening of solvents.

![Chemical structure](image)

<table>
<thead>
<tr>
<th>entry</th>
<th>solvent</th>
<th>catalyst</th>
<th>additive</th>
<th>yield(^a) (%)</th>
<th>ee(^b) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CH(_2)Cl(_2)</td>
<td>C1 (0.1)</td>
<td>A8 (0.1)</td>
<td>82</td>
<td>92</td>
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<td>2</td>
<td>CHCl(_3)</td>
<td>C1 (0.1)</td>
<td>A8 (0.1)</td>
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<td>69</td>
</tr>
<tr>
<td>3</td>
<td>1,2-dichoroethane</td>
<td>C1 (0.1)</td>
<td>A8 (0.1)</td>
<td>76</td>
<td>19</td>
</tr>
<tr>
<td>4</td>
<td>Ethylene dibromide</td>
<td>C1 (0.1)</td>
<td>A8 (0.1)</td>
<td>49</td>
<td>55</td>
</tr>
<tr>
<td>5</td>
<td>CH(_3)CN</td>
<td>C1 (0.1)</td>
<td>A8 (0.1)</td>
<td>59</td>
<td>50</td>
</tr>
<tr>
<td>6</td>
<td>EtOAc</td>
<td>C1 (0.1)</td>
<td>A8 (0.1)</td>
<td>31</td>
<td>67</td>
</tr>
<tr>
<td>8</td>
<td>THF</td>
<td>C1 (0.1)</td>
<td>A8 (0.1)</td>
<td>73</td>
<td>85</td>
</tr>
<tr>
<td>9</td>
<td>Hexane</td>
<td>C1 (0.1)</td>
<td>A8 (0.1)</td>
<td>59</td>
<td>50</td>
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</table>

Reaction conditions: To a mixture of silver salt L1 (0.01 mmol), additive (0.012 mmol) and NIS (0.12 mmol) was added Solvent (1 mL) then the reaction mixture was cooled to 0 °C. Allyl alcohol 1a (0.1 mmol) in 0.5 mL DCM was added dropwise and the reaction was quenched after 40 h.

\(^a\) Isolated yield. \(^b\) Determined by HPLC using Chiralpak AD column.
Proposed transition states for the observed stereoselectivity.

![Diagram](image)

**Figure S1.** Rationale for the Observed Stereoselectivity.

To explain the stereoselectivity of this reaction, putative transition states are proposed based on previous working model for the chiral anionic phase-transfer catalyst (Figure S1). That is, the iodine of NIS may be first transferred to DABCO moiety of the ion-pair organocatalyst, which may be accelerated by ammonium A8. Subsequently, alkene exchanges with one of DABCO-derived ammonium to produce cyclization precursor. In the transition state, chiral phosphate functionalizes as Brønsted base for deprotonation of hydroxyl of allyl alcohol and meanwhile is hold tightly with DABCO-derived ammonium by Columbic interaction. Through these cooperative interactions, substrate and NIS are simultaneously activated by the ion-pair catalyst, which leads to a well-defined transition state for the 3-exo iodo-cycloetherification. As shown in Figure S1, iodonium complexing with Re face of alkene in TS1 suffers less steric repulsion between substrate and phosphate than that in TS2, which would favorably produce the observed stereoisomer (R)-2a.

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General procedure for preparation of substrates, ammonium salts and catalyst

3.1 General procedure for the synthesis of 2-Aryl-2-propen-1-ol

![Chemical Structure](image)

**General procedure A**[1a]
To a THF solution (20 ml) of alkene (4 mmol) was added t-BuLi (8 mmol) at -78 °C. After stirred at this temperature for 1.5 h, the lithium salt was quenched with ketone (4.8 mmol). The mixture stirred for a further 1 h, and slowly warmed to rt. Water (10 ml) was then added, and the organic product extracted with Et₂O, and dried over anhydrous Na₂SO₄. The alcohol were purified by flash column chromatography (ethyl acetate/petroleum ether = 1:25, v/v).

**General procedure B**
A 50 mL two-neck round-bottomed flask equipped with an addition funnel and a condenser was charged with Mg turnings (264 mg, 11 mmol). Anhydrous THF (3 mL) and 1,2-dibromoethane (91 mg, 43 µL, 0.05 mmol) were added via syringe, then the mixture was activated by heat with a hairdryer during which time there were bubbles emerging from the surface of Mg turnings. After stirring at rt for 0.5 min, corresponding alkene (10 mmol) in anhydrous THF (10 mL) was then added dropwise over 0.5 h via the addition funnel, during which time a significant exotherm was observed. The reaction was then placed in an oil bath and heated at reflux for 2 h. At which time, ketone (11 mmol) was added. After further stirring for 1.5 h at reflux, saturated NH₄Cl (aq.) (5 mL) was added. The organic layer was extracted with ethyl acetate and washed with brine, separated, dried over Na₂SO₄, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1:25, v/v) to afford the product.

**General procedure C**[1b]
Into a flame-dried 50 mL round-bottomed flask was added dry THF (15 mL) under a nitrogen atmosphere. After cooling to -78 °C (acetone/dry-ice bath), n-BuLi (8.3 mL, 2.5 M in hexane, 20.5 mmol) and dry CH₃CN (550 µL, 10.5 mmol) were slowly added respectively. After stirring for 20 min, aryl epoxide (10 mmol) was then added. The reaction mixture was gradually warmed up to room temperature overnight and quenched with saturated NaHCO₃ (15 mL). After the phase separation, the aqueous layer was extracted with Et₂O. The combined organics were washed with brine, dried over Na₂SO₄, and concentrated under reduced pressure. The crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1:25, v/v).

**2-Methyl-3-phenyl-but-3-en-2-ol (1a)**
1a, a known compound[1b], was prepared following the general procedure A by using acetone and α-bromostyrene as a colorless liquid (1.13 g, 61% yield on 11.4 mmol scale).

Analytical data for 1a: ¹H NMR (500 MHz, CDCl₃) δ 7.33-7.27 (m, 5H), 5.46 (d, J = 1.0 Hz, 1H), 4.99
(d, J = 1.0 Hz, 1H), 2.12 (brs, 1H), 1.44 (s, 6H); 13C NMR (126 MHz, CDCl₃) δ 157.1, 141.6, 128.9, 127.8, 127.0, 112.6, 73.0, 29.7; IR (film) 3388, 915, 703 cm⁻¹; HRMS(ESI+) exact mass calcd. for C₁₁H₁₄O requires m/z [M⁺]: 162.1045. Found m/z 162.1047.

2-Methyl-3-p-tolyl-but-3-en-2-ol (1aa)
1aa, a known compound[1a], was prepared following the general procedure A by using acetone and 1-(1-bromovinyl)-4-methylbenzene as a yellow liquid (454 mg, 60% yield on 4.3 mmol scale).
Analytical data for 1aa: 1H NMR (500 MHz, CDCl₃) δ 7.20 (d, J = 10.0 Hz, 1H), 7.13 (d, J = 10.0 Hz, 2H), 5.41 (d, J = 1.0 Hz, 1H), 4.96 (d, J = 1.0 Hz, 1H), 2.36 (s, 3H), 1.66 (brs, 1H), 1.42 (s, 6H); 13C NMR (126 MHz, CDCl₃) δ 157.0, 138.5, 136.7, 128.7, 128.5, 112.3, 73.1, 29.7, 21.1; IR (film) 3393, 2976, 910, 792 cm⁻¹; HRMS(ESI+) exact mass calcd. for C₁₅H₁₆O requires m/z 176.1201. Found m/z 176.1202.

3-(4-Butyl-phenyl)-2-methyl-but-3-en-2-ol (1ab)
1ab was prepared following the general procedure A by using acetone and 1-(1-bromovinyl)-4-butylbenzene as a yellow liquid (417 mg, 49% yield on 3.9 mmol scale).
Analytical data for 1ab: 1H NMR (500 MHz, CDCl₃) δ 7.21 (d, J = 7.5 Hz, 2H), 7.13 (d, J = 7.5 Hz, 2H), 5.10 (d, J = 1.5 Hz, 1H), 4.96 (d, J = 1.5 Hz, 1H), 2.61 (t, J = 7.5 Hz, 2H), 1.66 (brs, 1H), 1.65-1.58 (m, 2H), 1.41 (s, 6H), 1.40-1.34 (m, 2H), 0.94 (t, J = 7.5 Hz, 3H); 13C NMR (126 MHz, CDCl₃) δ 157.0, 141.7, 138.6, 128.7, 127.8, 112.3, 73.1, 35.3, 33.6, 29.7, 22.4, 14.0; IR (film) 3392, 2929, 1177, 913, 839 cm⁻¹; HRMS(ESI+) exact mass calcd for C₁₃H₂₅NaO₁ requires m/z [M+Na⁺]: 241.1563. Found m/z 241.1553.

3-(4-tert-Butyl-phenyl)-2-methyl-but-3-en-2-ol (1ac)
1ac was prepared following the general procedure B by using acetone and 1-(1-bromovinyl)-4-((tert-butyl)benzene as a pale yellow solid (412 mg, 42% yield on 4.5mmol scale).
Analytical data for 1ac: 1H NMR (500 MHz, CDCl₃) δ 7.32 (d, J = 7.5 Hz, 2H), 7.23 (d, J = 7.5 Hz, 2H), 5.39 (d, J = 1.5 Hz, 1H), 4.97 (d, J = 1.5 Hz, 1H), 1.63 (brs, 1H), 1.42 (s, 6H), 1.33 (s, 9H); 13C NMR (126 MHz, CDCl₃) δ 156.9, 149.9, 138.3, 128.5, 124.7, 112.3, 73.1, 34.5, 31.4, 29.7; IR (film) 3398, 1508, 913, 838 cm⁻¹; HRMS(ESI+) exact mass calcd for C₁₃H₂₅NaO₁ requires m/z [M+Na⁺]: 241.1563. Found m/z 241.1557.

3-Biphenyl-4-yl-2-methyl-but-3-en-2-ol (1ad)
1ad was prepared following the general procedure B by using acetone and 4-(1-bromovinyl)-1,1'-biphenyl as a pale yellow solid (324 mg, 34% yield on 4.0 mmol scale).
Analytical data for 1ad: 1H NMR (500 MHz, CDCl₃) δ 7.62 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz,
2-Methyl-3-m-toly-but-3-en-2-ol (1ae)

1ae was prepared following the general procedure B by using acetonone and 1-(1-bromovinyl)-3-methylbenzene as a pale yellow liquid (221 mg, 37% yield on 3.4 mmol scale).

Analytical data for 1ae: \( ^1H \text{NMR (500 MHz, } \text{CDCl}_3 \text{)} \delta 7.21 (t, J = 7.5 \text{ Hz, } 1H), 7.12-7.10 (m, 3H), 5.42 (s, 1H), 4.96 (s, 1H), 2.37 (s, 3H), 1.76 (brs, 1H), 1.43 (s, 1H); \(^{13}C \text{NMR (126 MHz, } \text{CDCl}_3 \text{)} \delta 157.2, 141.4, 137.3, 129.6, 127.8, 127.7, 125.9, 112.3, 73.0, 29.7, 21.5; IR (film) 3387, 911, 837 cm\(^{-1}\); HRMS(EI+) exact mass calcd for C\(_{12}\)H\(_{16}\)O requires m/z [M\(^+\)]: 238.1358. Found m/z 238.1360.

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

3-(3-Methoxy-phenyl)-2-methyl-but-3-en-2-ol (1af)

1af, a known compound\(^{[a]}\), was prepared following the general procedure A by using acetonone and 1-(1-bromovinyl)-3-methoxybenzene as a pale yellow liquid (438 mg, 57% yield on 4.0 mmol scale).

Analytical data for 1af: \( ^1H \text{NMR (500 MHz, C}_{6}H_{12} \text{)} \delta 7.21-7.24 (t, J = 8.0 \text{ Hz, } 1H), 6.83-6.89 (m, 3H), 5.42 (s, 1H), 4.98 (s, 1H), 3.81 (s, 3H), 1.68 (brs, 1H), 1.42 (s, 6H); \(^{13}C \text{NMR (500 MHz, C}_{6}H_{12} \text{)} \delta 156.9, 156.0, 142.9, 128.8, 121.3, 114.8, 112.5, 112.3, 73.0, 55.2, 29.7; IR (film) 3402, 911, 832 cm\(^{-1}\); HRMS (ESI+) exact mass calcd for C\(_{12}\)H\(_{16}\)Na\(_2\)O requires m/z [M+Na\(^+\)]: 215.1043. Found m/z 215.1042.

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

3-(4-Chloro-phenyl)-2-methyl-but-3-en-2-ol (1ag)

1ag, a known compound\(^{[a]}\), was prepared following the general procedure B by using acetonone and 1-(1-bromovinyl)-4-chlorobenzene as a pale yellow liquid (227 mg, 36% yield on 3.2 mmol scale).

Analytical data for 1ag: \( ^1H \text{NMR (500 MHz, C}_{6}H_{12} \text{)} \delta 7.129-7.24 (m, 4H), 5.43 (d, J = 1.0 \text{ Hz, } 1H), 4.97 (d, J = 1.0 \text{ Hz, } 1H), 1.64 (brs, 1H), 1.40 (s, 6H); \(^{13}C \text{NMR (126 MHz, C}_{6}H_{12} \text{)} \delta 155.8, 139.9, 133.0, 130.2, 127.9, 113.2, 72.9, 29.6; IR (film) 3392, 2978, 1560, 920, 790 cm\(^{-1}\); HRMS(EI+) exact mass calcd for C\(_{12}\)H\(_{16}\)OCl requires m/z [M\(^+\)]: 196.0655. Found m/z 196.0653.

\[
\begin{align*}
&\text{F} \\
&\text{Cl} \quad \text{OH}
\end{align*}
\]

3-(3-Fluoro-phenyl)-2-methyl-but-3-en-2-ol (1ah)

1ah was prepared following the general procedure B by using acetonone and 1-(1-bromovinyl)-3-fluorobenzene as a pale yellow liquid (173 mg, 26% yield on 3.7 mmol).

Analytical data for 1ah: \( ^1H \text{NMR (500 MHz, C}_{6}H_{12} \text{)} \delta ^1H \text{NMR (500 MHz, C}_{6}H_{12} \text{)} \delta 7.27 (q, J = 8.5 \text{ Hz, } 1H), 7.11-7.04 (m, 2H), 6.98 (td, J = 8.5, 2.5 \text{ Hz, } 1H), 5.44 (s, 1H), 5.00 (s, 1H), 1.65 (brs, 1H), 1.41 (s, 6H); \(^{13}C \text{NMR (126 MHz, C}_{6}H_{12} \text{)} \delta 162.1 (d, J = 247.0 \text{ Hz}, 155.8, 143.7 (d, J = 8.8 \text{ Hz, S11}}

129.2 (d, J = 8.8 Hz), 124.5 (d, J = 2.5 Hz), 115.9 (d, J = 21.4 Hz), 113.9 (d, J = 21.4 Hz), 113.2, 72.9, 29.6; 13C NMR (376 MHz, CDCl3) δ -113.84--113.90 (m); IR (film) 3396, 2961, 1223, 841 cm⁻¹; HRMS(El+) exact mass calcd for C₁₁H₁₅O requires m/z [M⁺]: 180.0950. Found m/z: 180.0949.

3-ethyl-2-phenylpent-1-en-3-ol (1b)

1b, a known compound[1c], was prepared following the general procedure A by using 3-pentanone and α-bromostyrene as a colorless liquid (504 mg, 53% yield on 5.0 mmol scale).

Analytical data for 1b: 1H NMR (500 MHz, CDCl3) δ 7.32-7.29 (m, 3H), 7.27-7.25 (m, 2H), 5.39 (d, J = 1.0 Hz, 1H), 5.14 (d, J = 1.0 Hz, 1H), 1.72-1.67 (m, 2H), 1.66-1.60 (m, 2H), 1.50 (brs, 1H), 0.95 (t, J = 7.5 Hz, 6H); 13C NMR (126 MHz, CDCl3) δ 153.7, 141.8, 128.4, 127.8, 127.0, 115.4, 78.1, 31.9, 7.8; IR (film) 3407, 906, 832 cm⁻¹; HRMS(El+) exact mass calcd for C₁₃H₁₈O requires m/z [M⁺+Na⁺]: 190.1358. Found m/z 190.1354.

1-(1-Phenyl-vinyl)-cyclopentanol (1c)

1c, a known compound[1d], was prepared following the general procedure B by using cyclopentanone and α-bromostyrene as a colorless liquid (4.29 g. 76% yield on 30 mmol scale).

Analytical data for 1c: 1H NMR (500 MHz, CDCl3) δ 7.41 (d, J = 5.0 Hz, 2H), 7.34-7.28 (m, 3H), 5.45 (s, 1H), 5.09 (s, 1H), 1.92-1.85 (m, 4H), 1.82-1.79 (m, 2H), 1.74-1.66 (m, 3H); 13C NMR (126 MHz, CDCl3) δ 154.9, 141.8, 128.5, 127.8, 127.1, 113.2, 84.1, 39.2, 23.3; IR (film) 3388, 915, 703 cm⁻¹; HRMS(ESI+) exact mass calcd for C₁₅H₂₀O requires m/z [M⁺+Na⁺]: 239.1406. Found m/z 239.1398.

1-(1-(m-tolyvinyl)cyclopentanol (1ca)

1ca was prepared following the general procedure B by using cyclopentanone and 1-(1-bromovinyl)-3-methylbenzene as a yellow liquid (286 mg, 41% yield on 3.2 mmol scale).

Analytical data for 1ca: 1H NMR (500 MHz, CDCl3) δ 7.22-7.17 (m, 3H), 7.10 (d, J = 10.0 Hz, 1H), 5.41 (d, J = 1.0 Hz, 1H), 5.05 (d, J = 1.0 Hz, 1H), 2.36 (s, 3H), 1.90-1.84 (m, 4H), 1.80-1.78 (m, 2H), 1.70-1.68 (m, 2H), 1.47 (brs, 1H); 13C NMR (126 MHz, CDCl3) δ 155.0, 141.6, 137.4, 129.2, 127.8, 127.7, 125.5, 113.0, 84.1, 39.2, 23.28, 23.27, 21.5; IR (film) 3420, 1601, 949, 911 cm⁻¹; HRMS(El+) exact mass calcd for C₁₄H₁₈O requires m/z [M⁺]: 202.1358. Found m/z 202.1359.

1-(1-(4-(tert-butylphenyl)vinyl) cyclopentanol (1cb)

1cb was prepared following the general procedure B by using cyclopentanone and 1-(1-bromovinyl)-4-(tert-butyl)benzene as a colorless liquid (708 mg, 63% yield on 4.6 mmol scale).

Analytical data for 1cb: 1H NMR (500 MHz, CDCl3) δ 7.35 (d, J = 1.0 Hz, 4H), 5.42 (d, J = 1.0 Hz, 1H), 5.09 (s, J = 1.0 Hz, 1H), 1.93-1.87 (m, 4H), 1.84-1.81 (m, 2H), 1.72-1.70 (m, 2H), 1.36 (s, 9H); 13C NMR (126 MHz, CDCl3) δ 154.8, 149.9, 138.7, 128.7, 128.2, 124.7, 112.9, 84.2, 39.3, 34.5, 31.4, 23.4; IR
(film) 3458, 999, 842 cm⁻¹; HRMS(EI⁺) exact mass calcd for C₁₅H₂₄O requires m/z [M⁺]: 244.1827. Found m/z 244.1830.

1-(1-(3-methoxyphenyl)vinyl)cyclopentanol (1cc)

1cc was prepared following the general procedure B by using cyclopentanone and 1-(1-bromovinyl)-3-methylbenzene as a yellow liquid (465 mg, 41% yield on 5.2 mmol scale).

Analytical data for 1cc: ¹H NMR (500 MHz, CDCl₃) δ 7.24-7.21 (m, 1H), 6.97-6.94 (m, 2H), 6.83 (d, J = 10.0 Hz, 1H), 5.42 (s, 1H), 5.08 (s, 1H), 3.81 (s, 3H), 1.89-1.84 (m, 4H), 1.80-1.77 (m, 2H), 1.70-1.65 (m, 2H), 1.49 (brs, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 159.0, 154.7, 143.2, 128.8, 121.0, 114.4, 113.2, 112.4, 84.0, 55.2, 39.2, 23.3; IR (film) 3420, 1601, 949, 911 cm⁻¹; HRMS(EI⁺) exact mass calcd for C₁₄H₁₃O₂ requires m/z [M⁺]: 218.1307. Found m/z 218.1309.

1-(1-(3-fluorophenyl)vinyl)cyclopentanol (1cd)

1cd was prepared following the general procedure B by using cyclopentanone and 1-(1-bromovinyl)-3-fluorobenzene as a yellow liquid (195 mg, 27% yield on 3.5 mmol scale).

Analytical data for 1cd: ¹H NMR (500 MHz, CDCl₃) δ 7.28-7.23 (m, 1H), 7.17-7.12 (m, 2H), 6.70 (t, J = 12.5 Hz, 1H), 5.43 (s, 1H), 5.09 (s, 1H), 1.89-1.78 (m, 6H), 1.74-1.68 (m, 2H), 1.42 (brs, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 162.34 (d, J = 244.5 Hz), 153.7 (d, J = 1.9 Hz), 143.9 (d, J = 7.6 Hz), 129.2 (d, J = 8.5 Hz), 124.1 (d, J = 2.9 Hz), 115.5 (d, J = 20.9 Hz), 114.0 (d, J = 6.6 Hz), 113.8, 83.9, 39.1, 23.2; ¹⁹F NMR (376MHz, CDCl₃) δ -113.1307. IR (film) 3347, 1508, 836 cm⁻¹; HRMS(EI⁺) exact mass calcd for C₁₄H₁₃OF requires m/z [M⁺]: 206.1107. Found m/z 206.1103.

1-(1-(4-fluorophenyl)vinyl)cyclopentanol (1ce)

1ce was prepared following the general procedure B by using cyclopentanone and 1-(1-bromovinyl)-4-fluorobenzene as a yellow liquid (286 mg, 42% yield on 3.3 mmol scale).

Analytical data for 1ce: ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.35 (m, 2H), 7.01-6.96 (m, 2H), 5.41 (d, J = 1.0 Hz 1H), 5.06 (d, J = 1.0 Hz 1H), 1.90-1.74 (m, 6H), 1.71-1.67 (m, 2H), 1.50 (brs, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 162.1 (d, J = 244.7 Hz), 153.8, 137.6 (d, J = 3.8 Hz), 130.0 (d, J = 7.6 Hz), 114.6 (d, J = 9.2 Hz), 113.5, 84.1, 39.1, 23.2; ¹⁹F NMR (376MHz, CDCl₃) δ -115.78--115.84; IR (film) 3397, 915, 841 cm⁻¹; HRMS(EI⁺) exact mass calcd for C₁₄H₁₃OF requires m/z [M⁺]: 206.1107. Found m/z 206.1104.

1-(1-(4-chlorophenyl)vinyl)cyclopentanol (1cf)

1cf was prepared following the general procedure B by using cyclopentanone and 1-(1-bromovinyl)-4-chlorobenzene as a yellow liquid (248 mg, 31% yield on 3.6 mmol scale).

Analytical data for 1cf: ¹H NMR (500 MHz, CDCl₃) δ 7.34-7.32 (m, 2H), 7.27-7.25 (m, 2H), 5.41 (d, J
1-(1-(naphthalen-2-ylvinyl)cyclopentanol (1cg)

1cg was prepared following the general procedure B by using cycloheptanone and 2-(1-bromovinyl) naphthalene as a yellow liquid (297 mg, 39% yield on 3.2 mmol scale).

Analytical data for 1cg: ¹H NMR (500 MHz, CDCl₃) δ 7.86 (s, 1H), 7.83 (d, J = 7.5 Hz, 2H), 7.79 (d, J = 7.5 Hz, 1H), 7.56 (d, J = 10.0 Hz, 1H), 7.49-7.47 (m, 2H), 5.52 (s, 1H), 5.20 (s, 1H), 1.94-1.84 (m, 6H), 1.73-1.70 (m, 2H), 1.64 (brs, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 154.9, 139.3, 133.1, 132.5, 128.1, 127.5, 127.2, 127.07, 127.05, 126.06, 125.8, 113.7, 84.3, 39.3, 23.3; IR (film) 3435, 951, 899 cm⁻¹; HRMS (EI⁺) exact mass calcd for C₁₇H₁₅OCl requires m/z [M⁺]: 222.0811. Found m/z 222.0812.

1-(1-(5,6,7,8-tetraydroxynaphthalen-2-ylvinyl)cyclopentanol (1ch)

1ch was prepared following the general procedure B by using cycloheptanone and 6-(1-bromovinyl)-1,2,3,4-tetraydroxynaphthalene as a yellow liquid (387 mg, 47% yield on 3.4 mmol scale).

Analytical data for 1ch: ¹H NMR (500 MHz, CDCl₃) δ 7.09 (d, J = 7.5 Hz, 2H), 7.07 (s, 1.0H) 7.01 (d, J = 7.5 Hz, 1H), 5.38 (s, 1H), 5.04 (s, 1H), 2.76, (m, 1H), 1.91-1.84 (m, 4H), 1.81-1.78 (m, 6H), 1.71-1.66 (m, 2H), 1.62 (brs, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 154.9, 138.8, 136.5, 136.0, 129.1, 128.5, 125.6, 112.7, 84.1, 39.3, 29.5, 29.1, 23.3, 23.2; IR (film) 3425, 952, 879 cm⁻¹; HRMS (EI⁺) exact mass calcd for C₁₇H₂₃O requires m/z [M⁺]: 238.1358. Found m/z 238.1362.

1-(1-Phenyl-vinyl)-cyclohexanol (1d)

1d, a known compound, was prepared following the general procedure B by using cyclohexanone and α-bromostyrene as a pale yellow liquid (2.10 g, 52% yield on 20.0 mmol scale).

Analytical data for 1d: ¹H NMR (500 MHz, CDCl₃) δ 7.31-7.27 (m, 5H), 5.43 (d, J = 5.0 Hz, 1H), 5.02 (d, J = 5.0 Hz, 1H), 1.69-1.56 (m, 8H), 1.53-1.50 (m, 2H), 1.44 (brs, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 156.7, 141.6, 129.0, 127.7, 126.9, 113.4, 73.6, 36.7, 25.5, 22.1; IR (film) 3388, 915, 703 cm⁻¹; HRMS (EI⁺) exact mass calcd for C₁₄H₁₅O requires m/z [M⁺]: 202.1358. Found m/z 202.1354.

1-(1-Phenyl-vinyl)-cycloheptanol (1e)

1e was prepared following the general procedure B by using cycloheptanone and α-bromostyrene in 56% yield as a yellow liquid Yellow liquid (1.22 g, 56% yield on 1.0 mmol scale).

Analytical data for 1e: ¹H NMR (500 MHz, CDCl₃) δ 7.32-7.29 (m, 5H), 5.40 (d, J = 1.0 Hz, 1H), 4.97 (d, J = 1.0 Hz, 1H), 1.99-1.94 (m, 2H), 1.99-1.94 (m, 2H), 1.79-1.74 (m, 2H), 1.67-1.61 (m, 4H), S14
1.56 (brs, 1H), 1.50-1.47 (m, 2H), 1.44-1.40 (m, 2H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 157.6, 141.8, 129.1, 127.7, 126.9, 112.7, 77.5, 40.6, 29.2, 22.4; IR (film) 3421, 973, 702 cm$^{-1}$; HRMS(EI+) exact mass calcd for C$_{11}$H$_{20}$O requires m/z [M]$^+$: 216.1514. Found m/z 216.1512.

2-phenylprop-2-en-1-ol (1f)

1f was prepared following the general procedure C by using 2-phenyloxirane as a yellow liquid (684 mg, 51% yield on 10 mmol scale).

Analytical data for 1f: $^1$H NMR (500 MHz, CDCl$_3$) δ 7.45 (d, J = 8.0 Hz, 2H ), 7.36 (t, J = 8.0 Hz, 2H ), 7.31 (t, J = 8.0 Hz, 1H), 5.48 (s, 1H), 5.36 (s, 1H), 4.55 (s, 2H), 1.79 (brs, 1H); $^{13}$C NMR (126 MHz, CDCl$_3$) δ 147.3, 138.5, 128.5, 127.9, 126.1, 112.6, 65.0; IR (film) 3367, 961, 715 cm$^{-1}$; HRMS(EI+) exact mass calcd for C$_9$H$_{10}$O requires m/z [M]$^+$: 134.0732 Found m/z 134.0729.

3-cyclohexyl-2-methylbut-3-en-2-ol (1g)

1g, a known compound[14], was prepared following the general procedure A by using acetone and (1-bromovinyl)cyclohexane as a colorless liquid (309 mg, 46% yield on 4.0 mmol scale).

Analytical data for 1g: $^1$H NMR (500 MHz, CDCl$_3$) δ 5.11 (s, 1H), 4.80 (s, 1H), 2.01 (t, J = 11.5 Hz, 1H), 1.75-1.67 (m, 5H), 1.55 (brs, 1H), 1.33 (s, 6H), 1.30-1.18 (m, 5H); $^{13}$C NMR (126 MHz, cde1) δ 162.2, 105.7, 73.8, 39.7, 35.5, 28.8, 27.1, 26.2; IR (film) 3401, 2874, 881 cm$^{-1}$; HRMS(EI+) exact mass calcd for C$_{11}$H$_{20}$O requires m/z [M]$^+$: 148.1514. Found m/z 148.1510.

3.2 Synthesis of ammonium salt

General procedure D

To a solution of DABCO (224 mg, 2.0 mmol) in 10 ml EA was added halogenated alkanes (2.0 mmol). The mixture was stirred at rt for 3 hours, filtrated then dried under reduced pressure getting the analytically pure quaternary ammonium salt.

1-butyl-1,4-diazabicyclo[2.2.2]octan-1-ium bromide (A1)

Analytical data for: $^1$H NMR (400 MHz, D$_2$O) δ 3.39 (t, J = 8.0 Hz, 6H), 3.27-3.23 (m, 2H), 3.18 (t, J = 8.0 Hz, 6H), 1.77-1.69 (m, 2H), 1.41-1.32 (m, 2H), 0.94 (t, J = 7.5 Hz, 3H); $^{13}$C NMR (101 MHz, D$_2$O) δ 64.39, 64.36, 64.32, 51.98, 51.94, 51.91, 44.1, 23.1, 19.2, 12.7; HRMS (ESI+) exact mass calcd for C$_{10}$H$_{18}$N$_2$ requires m/z [M-Br]$^+$: 169.1699. Found m/z 169.1697

1-butylquinuclidin-1-ium bromide (A2)

Analytical data for A2: $^1$H NMR (400 MHz, D$_2$O) δ 3.37 (t, J = 8.0 Hz, 6H), 3.11-3.07 (m, 2H), 2.18-2.15 (m, 1H), 2.10-1.92 (m, 6H), 1.72-1.66 (m, 2H), 1.36-1.31 (m, 2H), 0.92 (t, J = 8.0 Hz, 3H); $^{13}$C NMR (101 MHz, D$_2$O) δ 64.08, 64.04, 64.01, 54.4, 23.37, 23.27, 19.2, 19.03, 18.98, 18.98, 12.7; HRMS (ESI+) exact mass calcd for C$_{11}$H$_{22}$N requires m/z [M-Br]$^+$: 168.1747. Found m/z 168.1748.
Note: proton and carbon peak of NCH₂CO of A₃-A₇ are not found in the NMR spectra due to the rapid exchange with D₂O. Those two peaks could be detected by using CDCl₃ as solvent as exemplified by the spectra of A₈ in CDCl₃.

1-(2-oxo-2-phenylethyl)-1,4-diaza[2.2.2]octan-1-ium bromide (A3)
Analytical data for A³: ¹H NMR (500 MHz, D₂O) δ 7.99 (dd, J = 10.0, 1.0 Hz, 2H), 7.78 (dt, J = 10.0, 1.0 Hz, 1H), 7.62 (t, J = 10.0 Hz, 2H), 3.81 (t, J = 7.5 Hz, 6H), 3.32 (t, J = 7.5 Hz, 6H); ¹³C NMR (126 MHz, D₂O) δ 191.7, 135.2, 134.1, 129.1, 127.9, 52.9, 44.1. HRMS (ESI⁺) exact mass calced for C₁₄H₁₈N₂O requires m/z [M-Br]⁺: 231.1492. Found m/z 231.1490

1-(2-(4-cyanophenyl)-2-oxoethyl)-1,4-diaza[2.2.2]octan-1-ium bromide (A4)
Analytical data for A⁴: ¹H NMR (500 MHz, D₂O) δ 8.12 (dd, J = 7.5, 3.0 Hz, 2H), 7.98 (dd, J = 7.5, 3.0 Hz, 2H), 3.82 (t, J = 7.5 Hz, 6H), 3.33 (t, J = 7.5 Hz, 6H); ¹³C NMR (126 MHz, D₂O) δ 190.5, 137.3, 133.1, 128.2, 118.3, 116.7, 52.9, 44.0; HRMS (ESI⁺) exact mass calced for C₁₅H₁₈N₂O requires m/z [M-Br]⁺: 256.1444. Found m/z 256.1447.

1-(2-(4-methoxophenyl)-2-oxoethyl)-1,4-diaza[2.2.2]octan-1-ium bromide (A5)
Analytical data for A⁵: ¹H NMR (500 MHz, D₂O) δ 7.99 (d, J = 10.0 Hz, 2H), 7.13 (d, J = 10.0 Hz, 2H), 3.94 (s, 3H), 3.80 (t, J = 7.5 Hz, 6H), 3.31 (t, J = 7.5 Hz, 6H); ¹³C NMR (101 MHz, D₂O) δ 189.8, 164.5, 130.5, 127.1, 114.3, 55.6, 52.8, 44.0; HRMS (ESI⁺) exact mass calced for C₁₅H₂₀N₂O requires m/z [M-Br]⁺: 260.1525. Found m/z 260.1523.

1-(2-(3-methoxophenyl)-2-oxoethyl)-1,4-diaza[2.2.2]octan-1-ium bromide (A6)
Analytical data for A⁶: ¹H NMR (400 MHz, D₂O) δ 7.55 (d, J = 8.0, 1H), 7.50 (t, J = 8.0, 1H), 7.46 (s, 1H), 7.31 (dd, J = 8.0, 2.0 Hz, 1H), 3.86 (s, 3H), 3.77 (t, J = 8.0 Hz, 6H), 3.28 (t, J = 8.0 Hz, 6H); ¹³C NMR (101 MHz, D₂O) δ 191.2, 159.2, 135.4, 130.3, 121.1, 120.8, 112.4, 55.5, 52.8, 44.0; HRMS (ESI⁺) exact mass calced for C₁₅H₂₀N₂O requires m/z [M-Br]⁺: 260.1525. Found m/z 260.1524.

1-(2-(4-butoxyphenyl)-2-oxoethyl)-1,4-diaza[2.2.2]octan-1-ium bromide (A7)
Analytical data for A⁷: ¹H NMR (500 MHz, D₂O) δ 7.97 (d, J = 10.0 Hz, 2H), 7.11 (d, J = 10.0 Hz, 2H), 4.18 (t, J = 10.0 Hz, 2H), 3.79 (t, J = 7.5 Hz, 6H), 3.31 (t, J = 7.5 Hz, 6H), 1.82-1.76 (m, 2H), 1.50-1.45 (m, 2H), 0.96 (t, J = 7.5 Hz, 3H); ¹³C NMR (126 MHz, D₂O) δ 189.9, 164.1, 130.6, 127.1, 114.9, 68.7, 52.9, 44.1, 30.3, 18.5, 13.0; HRMS (ESI⁺) exact mass calced for C₁₈H₂₁N₂O requires m/z
1-(2-(4-(hexyloxy)phenyl)-2-oxoethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium bromide (A8)

Analytical data for A8: $^1$H NMR (500 MHz, D$_2$O) $\delta$ 7.88 (d, $J = 10.0$ Hz, 2H), 6.84 (d, $J = 10.0$ Hz, 2H), 3.88 (m, 2H), 3.75 (m, 6H), 3.23 (m, 6H), 1.63 (m, 2H), 1.36-1.30 (m, 6H), 0.92 (t, $J = 5.0$ Hz, 3H); $^{13}$C NMR (101 MHz, D$_2$O) $\delta$ 189.4, 163.8, 130.7, 127.0, 114.5, 68.4, 52.7, 44.0, 31.5, 28.7, 25.4, 22.4, 13.7; For comparison, NMR spectra were also measured by using CDCl$_3$ as solvent to find signals of $\text{NCH}_2\text{CO}$. H NMR (500 MHz, CDCl$_3$) $\delta$ 8.00 (d, $J = 8.5$ Hz, 3H), 6.84 (d, $J = 8.5$ Hz, 2H), 5.53 (s, 2H, NCH$_2$CO), 4.03 (s, 6H), 3.91 (t, $J = 6.0$ Hz, 2H), 3.22 (s, 6H), 1.80-1.67 (m, 2H), 1.46-1.36 (m, 2H), 1.37-1.26 (m, 4H), 0.93-0.85 (m, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 189.3, 164.5, 131.0, 127.0, 114.7, 68.5, 65.3 (NCH$_2$CO), 52.8, 45.2, 31.5, 29.0, 25.6, 22.5, 14.00; HRMS (ESI+) exact mass calced for C$_{25}$H$_{30}$N$_2$O$_2$ requires m/z [M-Br]$^+$: 330.2307. Found m/z 330.2307.

1-(2-(4-(octyloxy)phenyl)-2-oxoethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium bromide (A9)

Analytical data for A9: $^1$H NMR (500 MHz, D$_2$O) $\delta$ 7.87 (d, $J = 7.5$ Hz, 2H), 6.81 (d, $J = 7.5$ Hz, 2H), 3.84 (m, 2H), 3.74 (m, 6H), 3.20 (m, 6H), 1.61 (m, 2H), 1.41-1.23 (m, 10H), 0.95 (t, $J = 7.5$ Hz, 3H); $^{13}$C NMR (101 MHz, D$_2$O) $\delta$ 189.3, 163.8, 130.8, 127.0, 114.4, 68.3, 52.7, 44.0, 31.9, 29.5, 29.3, 29.0, 25.9, 22.6, 13.9; HRMS (ESI+) exact mass calced for C$_{22}$H$_{26}$N$_2$O$_2$ requires m/z [M-Br]$^+$: 359.2693. Found m/z 359.2695.

1-(2-(4-(methylsulfonyl)phenyl)-2-oxoethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium bromide (A10)

Analytical data for A10: $^1$H NMR (500 MHz, D$_2$O) $\delta$ 8.21 (d, $J = 10.0$ Hz, 2H), 8.13 (d, $J = 10.0$ Hz, 2H), 3.83 (t, $J = 7.5$ Hz, 6H), 3.33 (t, $J = 7.5$ Hz, 6H) and 3.33 (s, 3H); $^{13}$C NMR (126 MHz, D$_2$O) $\delta$ 190.4, 143.7, 138.3, 128.9, 127.8, 52.9, 44.0, 42.9; HRMS (ESI+) exact mass calced for C$_{13}$H$_{20}$N$_2$O$_2$S requires m/z [M-Br]$^+$: 308.1195. Found m/z 308.1196.

1-(2-(benzo[d][1,3]dioxol-5-yl)-2-oxoethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium bromide (A11)

Analytical data for A11: $^1$H NMR (500 MHz, D$_2$O) $\delta$ 7.63 (d, $J = 10.0$ Hz, 1H), 7.44 (s, 1H), 7.02 (d, $J = 10.0$ Hz, 1H), 6.13 (s, 2H), 3.78 (t, $J = 7.5$ Hz, 6H), 3.30 (t, $J = 7.5$ Hz, 6H); $^{13}$C NMR (101 MHz, D$_2$O) $\delta$ 189.3, 153.2, 148.1, 128.6, 125.3, 108.3, 107.1, 102.4, 52.8, 44.0; HRMS (ESI+) exact mass calced for C$_{15}$H$_{20}$N$_2$O$_3$ requires m/z [M-Br]$^+$: 274.1317. Found m/z 274.1319.

1-(2-(naphthalen-2-yl)-2-oxoethyl)-1,4-diazabicyclo[2.2.2]octan-1-ium bromide (A12)

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Analytical data for A12: 1H NMR (500 MHz, D2O) δ 8.48 (s, 1H), 8.05 (d, J = 5.0 Hz, 1H), 7.98 (dd, J = 10.0, 5.0 Hz, 2H), 7.88 (dd, J = 10.0, 1.5 Hz, 1H), 7.74 (dd, J = 7.5, 1.5 Hz, 1H), 7.67 (t, J = 7.5 Hz, 1H), 3.80 (t, J = 7.5 Hz, 6H), 3.31 (t, J = 7.5 Hz, 6H); 13C NMR (126 MHz, D2O) δ 191.2, 135.9, 131.8, 130.5, 129.82, 129.77, 128.9, 127.8, 127.4, 122.5, 52.9, 44.1; HRMS (ESI+) exact mass calced for C18H20N2O requires m/z [M-Br]+: 280.1576. Found m/z 280.1577.

3.3 preparation of catalyst

3.3.1 Synthesis of silver phosphate[2]

![Synthesis of silver phosphate](image)

To a solution of chiral phosphoric (140 mg, 0.25 mmol) in CH2Cl2 (1.5 mL) in the dark was added Ag2CO3 (34.5 mg, 0.125 mmol) followed by distilled water 1.5 mL. The resulting mixture was stirred for one hour. After this time, the mixture was diluted with water (3 mL) and CH2Cl2 (3mL). The aqueous layer extracted with CH2Cl2. The combined organic extracts were filtered through celite and concentrated to afford the product as a fluffy white solid (163 mg, 0.24 mmol, 95% yield).

3.3.2 Preparation of ion-pair catalyst

![Preparation of ion-pair catalyst](image)

A solution of quaternary ammonium salt A8 (1.0 mmol) and 707 anion exchange resin (4.0 g, 12.0 mmol, 3mmol/g) in 15 mL methanol was stirred at rt for 3 hours, then filtered. The filtrate was added 8H-TRIP phosphoric acid (1.0 mmol, 760 mg) and stirred for two hours at rt. Then concentrated to get the ion pair catalyst C1 quantitatively.

Analytical data for C1: 1H NMR (500 MHz, CDCl3) δ 7.90 (d, J = 8.5 Hz, 2H), 6.97 (s, 2H), 6.93 (s, 2H), 6.84 (s, 2H), 6.64 (d, J = 8.5 Hz, 2H), 6.05 (d, J = 15.0 Hz, 1H), 4.42 (d, J = 15.0 Hz, 1H), 3.97 (d, J = 2.4 Hz, 2H), 3.51 (m, 3H), 3.40 (m, 3H), 2.95-2.58 (m, 20H), 2.28 (d, J = 16.6 Hz, 2H), 1.85-1.70 (m, 10H), 1.47-1.45 (m, 2H), 1.35-1.34 (m, 4H), 1.26-1.24 (m, 12H), 0.98 (m, 11H), 0.91 (m, 8H), 0.86 (d, J = 6.8 Hz, 6H); 13C NMR (126 MHz, cdc13) δ 189.8, 164.5, 148.3, 147.1, 146.0, 135.9, 134.0, 132.2, 132.1, 131.2, 129.0, 128.1, 127.0, 120.9, 119.5, 114.4, 77.3, 68.3, 65.2, 52.0, 44.5, 33.9, 31.5, 30.7, 30.3, 29.2, 29.1, 27.8, 26.2, 25.7, 24.7, 24.3, 24.0, 23.5, 23.3, 23.1, 23.0, 22.6, 14.0; 31P NMR (162 MHz, CDCl3) δ 2.40; HRMS (ESI+) exact mass calced for C30H31N2O4 requires m/z [M-phosphate]+: 331.2380. Found m/z 331.2395. HRMS (ESI-) exact mass calced for C30H34O1P1 requires m/z [M-ammonium]-: 759.4548. Found m/z 759.4570.
4. General procedure for asymmetric 3-exo iodo-cycloetherification

**General procedure E**

In a Schlenk tube, ion pair catalyst **C1** (0.01 mmol), ammonium salt **A8** (0.01 mmol), NIS (0.12 mmol) and CH₂Cl₂ (1 mL) was added, then the reaction mixture was cooled to -20 °C. Allyl alcohol **I** (0.1 mmol) in 0.5 mL CH₂Cl₂ was added dropwise and the reaction was quenched by the addition of Na₂S₂O₃ aqueous solution at indicated time (monitored by TLC). The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. Then the organic layer combined washed with brine, dried over Na₂SO₄, filtered and then concentrated. The residue was purified by preparative TLC (ethyl acetate/petroleum ether = 1:30, v/v) to afford the product.

*Note: Racemic products were obtained by following general procedure E using rac-**C1** as catalyst.*

**Characterization of product**

(R)-2-(iodomethyl)-3,3-dimethyl-2-phenyloxirane (2a)

Prepared according to the general procedure E with **Ia** (16.2 mg, 0.1 mmol) over the course of 107 h at -20 °C as a yellow liquid (28.2 mg, 99% yield, 94% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak ID3 column, hexane/i-PrOH 98.5:1.5, 0.5 mL/min, t_major = 5.98 min, t_minor = 5.60 min). ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.30 (m, 5H), 3.61-3.51 (m, 2H), 1.54 (s, 3H), 1.02 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 138.6, 128.0, 127.8, 127.3, 68.2, 67.8, 22.8, 20.8, 11.6; IR (neat) 2961, 1447, 763, 700 cm⁻¹; HRMS (EI⁺) exact mass calcd for C₁₁H₁₃O: m/z 161.0965 ([M-I]⁺), found: m/z 161.0964. [α]D²⁵ = -23.5 (c 0.55, CHCl₃).

**Gram scale synthesis of 2a:** At nitrogen atmosphere, CH₂Cl₂ (40 ml) was added to a mixture of ion pair catalyst **C1** (335 mg, 0.31 mmol), ammonium salt **A8** (126 mg, 0.31 mmol) and NIS (1.7g, 7.56 mmol) under -20 °C. After the mixture stirred for one minute, **Ia** (1.0 g, 6.17 mmol) in CH₂Cl₂ (3.0ml) was added dropwise. After 127 h, the reaction was quenched by the addition of Na₂S₂O₃ aqueous solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. Then the organic layer combined washed with brine, dried over Na₂SO₄, filtered and then concentrated. The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1/100, v/v) to afford 1.47 g (83 %) yellow liquid. Enantiomeric excess was found to be 93% measured by chiral HPLC (ChiralPak AD-H column, hexane/i-PrOH 98.5:1.5 0.7 mL/min, t_major = 5.77 min, t_minor = 5.41 min).

(R)-2-(iodomethyl)-3,3-dimethyl-2-(p-tolyloxirane (2aa)

Prepared according to the general procedure E with **Ia** (17.6 mg, 0.1 mmol) over the course of 111 h at -20 °C as a yellow liquid (27.6 mg, 95% yield, 93% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak ID3 column, hexane/i-PrOH 98.5:1.5, 0.7 mL/min, t_major = 3.63 min, t_minor =
(R)-2-(4-butylphenyl)-2-(iodomethyl)-3,3-dimethyloxirane (2ab)

Prepared according to the general procedure E with 1ab (21.8 mg, 0.1 mmol) over the course of 111 h at -20 °C as a yellow liquid (28.2 mg, 91% yield, 93% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak AD-H column, hexane/i-PrOH 98.5:1.5, 0.4 mL/min, t_major = 10.98 min, t_minor = 10.31 min). \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.28 (d, \(J = 10.0\) Hz, 2H), 7.15 (d, \(J = 10.0\) Hz, 2H), 3.59-3.55 (m, 2H), 2.61 (t, \(J = 7.5\) Hz, 2H), 1.63-1.57 (m, 2H), 1.52 (s, 3H), 1.39-1.32 (m, 2H), 1.02 (s, 3H), 0.93 (t, \(J = 7.5\) Hz, 3H); \(^1^C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 142.4, 135.7, 128.0, 127.1, 68.1, 67.8, 35.4, 33.5, 22.8, 22.4, 20.8, 14.0, 11.9; IR (neat) 2956, 1456, 1010, 831, 573 cm\(^{-1}\); HRMS (EI\(^+\)) exact mass calcd for C\(_{12}\)H\(_{15}\)O: m/z 217.1592 ([M-I]\(^+\)), found: m/z 217.1594. \([\alpha]_D^{23.5} = -19.1\) (c 1.06, CHCl\(_3\)).

(\(R\))-2-(4-(tert-butyl)phenyl)-2-(iodomethyl)-3,3-dimethyloxirane (2ac)

Prepared according to the general procedure E with 1ac (21.8 mg, 0.1 mmol) over the course of 111 h at -20 °C as a white solid (28.2 mg, 86% yield, 91% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5μ cellulose-3 column, hexane/i-PrOH 98:2, 0.5 mL/min, t_major = 7.68 min, t_minor = 8.25 min). \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.35 (d, \(J = 8.5\) Hz, 2H), 7.31 (d, \(J = 8.5\) Hz, 2H), 3.58 (d, \(J = 10.0\) Hz, 1H), 3.55 (d, \(J = 10.0\) Hz, 1H), 1.53 (s, 3H), 1.32 (s, 9H), 1.02 (s, 3H); \(^1^C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 150.5, 135.3, 126.9, 124.9, 68.1, 67.7, 34.6, 31.4, 22.8, 20.8, 11.8; IR (neat) 2962, 1270, 1008, 830, 619 cm\(^{-1}\); HRMS (EI\(^+\)) exact mass calcd for C\(_{17}\)H\(_{21}\)O: m/z 217.1592 ([M-I]\(^+\)), found: m/z 217.1590. \([\alpha]_D^{23.5} = -13.6\) (c 0.93, CHCl\(_3\)).

(\(R\))-2(11,1’-biphenyl)-4-yl)-2-(iodomethyl)-3,3-dimethyloxirane (2ad)

Prepared according to the general procedure E with 1ad (23.8 mg, 0.1 mmol) over the course of 62 h at -20 °C as a yellow liquid (33.5 mg, 92% yield, 94% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak ID3 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 4.79 min, t_minor = 4.15 min). \(^1^H\) NMR (500 MHz, CDCl\(_3\)) \(\delta\) 7.61 (d, \(J = 10.0\) Hz, 2H), 7.59 (d, \(J = 10.0\) Hz, 2H), 7.43-7.47 (m, 4H), 7.35 (t, \(J = 7.5\) Hz, 1H), 3.63 (d, \(J = 10.0\) Hz, 1H), 3.61 (d, \(J = 10.0\) Hz, 1H), 1.56 (s, 3H), 1.07 (s, 3H); \(^1^C\) NMR (126 MHz, CDCl\(_3\)) \(\delta\) 140.6, 140.5, 137.6, 128.8, 127.7, 127.4, 127.1, 126.7, 68.3, 67.7, 22.9, 20.8, 11.5; IR (neat) 2922, 1487, 829, 755, 580 cm\(^{-1}\); HRMS (EI\(^+\)) exact mass calcd for C\(_{17}\)H\(_{17}\)O:
m/z 364.0324 ([M]+), found: m/z 364.0326. \([\alpha]D^{23.5} = -9.3 (c 1.34, CHCl_3)\).

(R)-2-(iodomethyl)-3,3-dimethyl-2-(m-tolyl)oxirane (2ae)

Prepared according to the general procedure E with 1ae (17.2 mg, 0.1 mmol) over the course of 134 h at -20 °C as a yellow liquid (27.3 mg, 93% yield, 90% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5μ cellulose-4 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_{major} = 5.89 min, t_{minor} = 5.51 min). \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 7.23 (t, J = 5.0 Hz, 1H), 7.18 (s, 1H), 7.17 (d, J = 5.0 Hz, 1H), 7.11 (d, J = 5.0 Hz, 1H), 3.59 (d, J = 10.0 Hz, 1H), 3.56 (d, J = 10.0 Hz, 1H), 2.37 (s, 3H), 1.53 (s, 3H), 1.03 (s, 3H); \(^{13}\)C NMR (126 MHz, CDCl₃) \(\delta\) 138.4, 137.7, 128.5, 127.9, 124.4, 68.2, 67.8, 22.8, 21.5, 20.8, 11.7; IR (neat) 2924, 1456, 1376, 785 cm⁻¹; HRMS (EI+) exact mass caleld for C₁₂H₁₃O: m/z 175.1123 ([M-I]+), found: m/z 175.1119. \([\alpha]D^{23.5} = -25.7 (c 0.84, CHCl₃)\).

(R)-2-(iodomethyl)-2-(3-methoxyphenyl)-3,3-dimethylxirane (2af)

Prepared according to the general procedure E with 1af (16.2mg, 0.1 mmol) over the course of 120 h at -20 °C as a yellow liquid (18.7 mg, 57% yield, 91% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak OD-H column, hexane/i-PrOH 98:2, 0.4 mL/min, t_{major} = 7.75 min, t_{minor} = 9.12 min). \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 7.26 (t, J = 10.0 Hz, 1H), 6.96 (d, J = 10.0 Hz, 1H), 6.93 (s, 1H), 6.84 (d, J = 5.0 Hz, 1H), 3.82 (s, 3H), 3.60-3.55 (m, 2H), 1.5 (s, 3H), 1.04 (s, 3H); \(^{13}\)C NMR (126 MHz, ) \(\delta\) 159.3, 140.2, 129.1, 119.5, 113.2, 113.0, 68.3, 67.8, 55.3, 22.7, 20.8, 11.3; IR (neat) 2917, 1109, 813, 555 cm⁻¹; HRMS (EI+) exact mass caleld for C₁₂H₁₃O₂: m/z 191.1072 ([M-I]+), found: m/z 191.1074. \([\alpha]D^{23.5} = -30.8 (c 1.21, CHCl₃)\).

(R)-2-(4-chlorophenyl)-2-(iodomethyl)-3,3-dimethylxirane (2ag)

Prepared according to the general procedure E with 1ag (20.2 mg, 0.1 mmol) over the course of 120 h at -20 °C as a yellow liquid (18.1 mg, 55% yield, 93% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak AD-H column, hexane/i-PrOH 98.5:1.5, 0.4 mL/min, t_{major} = 12.17 min, t_{minor} = 11.49 min). \(^1\)H NMR (500 MHz, CDCl₃) \(\delta\) 7.33 (s, 4H), 3.54 (s, 2H), 1.53 (s, 3H), 1.0 (s, 3H); \(^{13}\)C NMR (126 MHz, CDCl₃) 137.1, 133.6, 128.7, 128.3, 68.3, 67.4, 22.8, 20.7, 10.9; IR (neat) 2957, 1376, 1142, 814, 603 cm⁻¹; HRMS (EI+) exact mass caleld for C₁₁H₁₂OCl: m/z 195.0577 ([M-I]+), found: m/z 195.0581. \([\alpha]D^{23.5} = -19.2 (c 0.58, CHCl₃)\).

(R)-2-(3-fluorophenyl)-2-(iodomethyl)-3,3-dimethylxirane (2ah)

Prepared according to the general procedure E with 1ah (18.3 mg, 0.1 mmol) over the course of 107 h at -20 °C as a yellow liquid (10.1 mg, 32% yield, 86% ee). The enantiomeric purity was determined by

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HPLC analysis (ChiralPak ID3 column, hexane/i-PrOH 98:2, 0.7 mL/min, t\textsubscript{major} = 6.73 min, t\textsubscript{minor} = 6.33 min). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.32 (dt, \(J = 10.0, 5.0\) Hz, 1H), 7.17 (d, \(J = 10.0\) Hz, 1H), 7.11 (d, \(J = 10.0\) Hz, 1H), 7.01 (td, \(J = 10.0, 5.0\) Hz, 1H), 3.57 (d, \(J = 10.0\) Hz, 2H), 3.54 (d, \(J = 10.0\) Hz, 2H), 1.53 (s, 3H), 1.03 (s, 3H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 162.4 (d, \(J = 272.4\) Hz), 141.2 (d, \(J = 5.0\) Hz), 129.7 (d, \(J = 7.6\) Hz), 122.8, 114.8 (d, \(J = 21.4\) Hz), 114.5 (d, \(J = 22.7\) Hz), 68.5, 67.4, 22.7, 20.7, 10.6; \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) \(\delta\) -112.8; IR (neat) 2957, 1437, 763, 573 cm\(^{-1}\); HRMS (EI\textsuperscript{+}) exact mass calcd for \(\text{C}_{11}\text{H}_{13}\text{O}:\) m/z 161.0966 ([M-I]\textsuperscript{+}), found: m/z 161.0964. \([\alpha]\textsubscript{D}\textsuperscript{23.5} = -23.9 (c 0.43, CHCl\textsubscript{3}).

(R)-2,2-diethyl-3-(iodomethyl)-3-phenyloxirane (2b)

Prepared according to the general procedure E with 1b (19.3 mg, 0.1 mmol) over the course of 115 h at -20 °C as a yellow liquid (19.0 mg, containing about 9% rearrangement product, 60% yield, 95% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak IC column, hexane/i-PrOH 98:2, 0.7 mL/min, t\textsubscript{major} = 6.34 min, t\textsubscript{minor} = 5.72 min). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.36-7.30 (m, 5H), 3.64-3.59 (m, 2H), 1.95-1.87 (m, 1H), 1.74-1.71 (m, 1H), 1.25-1.20 (m, 2H), 1.11 (t, \(J = 7.5\) Hz, 3H), 0.82 (t, \(J = 7.5\) Hz, 3H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 138.8, 128.9, 127.9, 127.6, 57.8, 69.0, 24.8, 23.4, 12.2, 10.0, 8.8; IR (neat) 2956, 1447, 701, 577 cm\(^{-1}\); HRMS (EI\textsuperscript{+}) exact mass calcd for \(\text{C}_{13}\text{H}_{17}\text{O}:\) m/z 189.1279 ([M-I]\textsuperscript{+}), found: m/z 189.1278. \([\alpha]\textsubscript{D}\textsuperscript{23.5} = -65.7 (c 0.47, CHCl\textsubscript{3}).

(R)-2-(iodomethyl)-2-phenyl-1-oxaspiro[2.4]heptanes (2c)

Prepared according to the general procedure E with 1c (19.2 mg, 0.1 mmol) over the course of 44 h at -20 °C as a yellow liquid (32.1 mg, 99% yield, 97% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak OD-H column, hexane/i-PrOH 98:2, 0.7 mL/min, t\textsubscript{major} = 7.18 min, t\textsubscript{minor} = 7.81 min). \textsuperscript{1}H NMR (500 MHz, CDCl\textsubscript{3}) \(\delta\) 7.36 (d, \(J = 5.0\) Hz, 4H), 7.32-7.30 (m, 1H), 3.70 (d, \(J = 10.0\) Hz, 1H), 3.45 (d, \(J = 10.0\) Hz, 1H), 2.16-2.11 (m, 1H), 1.91-1.71 (m, 4H), 1.58-1.52 (m, 2H, 1H), 1.45-1.39 (m, 1H), 1.30-1.26 (m, 1H); \textsuperscript{13}C NMR (126 MHz, CDCl\textsubscript{3}) \(\delta\) 128.1, 127.7, 126.7, 80.0, 66.3, 32.6, 30.7, 25.4, 25.1, 12.0; IR (neat) 2960, 1447, 762, 572 cm\(^{-1}\); HRMS (EI\textsuperscript{+}) exact mass calcd for \(\text{C}_{15}\text{H}_{19}\text{O}:\) m/z 187.1123 ([M-I]\textsuperscript{+}), found: m/z 187.1125. \([\alpha]\textsubscript{D}\textsuperscript{23.5} = -38.5 (c 1.03, CHCl\textsubscript{3}).

Gram scale synthesis of 2c: At nitrogen atmosphere, CH\textsubscript{2}Cl\textsubscript{2} (30 mL) was added to a mixture of ion pair catalyst C1 (290 mg, 0.27 mmol), ammonium salt A8 (109 mg, 0.27 mmol) and NIS (1.46 g, 6.38 mmol) under -20 °C. After the mixture stirred for 5 min, 1c (1.0 g) in CH\textsubscript{2}Cl\textsubscript{2} (3.0 mL) was added dropwise. After 47 h, the reaction was quenched by the addition of Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} aqueous solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. Then the organic layer combined, washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and then concentrated. The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:100, v/v) to afford 1.54 g (92%) yellow liquid. Enantiomeric excess was found to be 98% measured by chiral HPLC (ChiralPak OD-H column, hexane/i-PrOH 98:2 0.7 mL/min, t\textsubscript{major} = 6.56 min, t\textsubscript{minor} = 7.04 min).

Synthesis of 2c using 1 mol% C1 on 3 mmol scale:

Following gram scale synthesis of 2c, synthesis of 2c on 3 mmol scale was carried out using 1 mol% C1 (32 mg, 0.03 mmol) under -40 °C. After 72 h, most of 1c was consumed and work-up of the reaction afforded 2c (820 mg,
(R)-2-(iodomethyl)-2-(m-toly)-1-oxaspiro[2.4]heptane (2ca)

Prepared according to the general procedure E with 1ca (20.8 mg, 0.1 mmol) over the course of 70 h at -20 °C as a yellow liquid (28.3 mg, 84 % yield, 95% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5µ cellulose-4 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 7.16 min, t_minor = 7.79 min).

\[
\begin{align*}
\text{t-Bu} & \\
\text{O} & \\
\text{O} & \\
\end{align*}
\]

(R)-2-(4-(tert-buty)phenyl)-2-(iodomethyl)-1-oxaspiro[2.4]heptane (2cb)

Prepared according to the general procedure E with 1cb (24.5 mg, 0.1 mmol) over the course of 21 h at -20 °C as a yellow liquid (31.1 mg, 82% yield, 92% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5µ cellulose-4 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 6.02 min, t_minor = 5.61 min). ¹H NMR (500 MHz, CDCl₃) δ 7.24 (t, J = 7.5 Hz, 1H), 7.15 (s, 1H), 7.14 (d, J = 7.5 Hz, 1H), 7.12 (d, J = 7.5 Hz, 1H), 3.69 (d, J = 10.0 Hz, 1H), 3.44 (d, J = 10.0 Hz, 1H), 2.37 (s, 3H), 2.15-2.10 (m, 1H), 1.90-1.84 (m, 1H), 1.80-1.72 (m, 3H), 1.60-1.51 (m, 1H), 1.46-1.40 (m, 1H), 1.31-1.26 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 138.5, 137.7, 128.5, 127.9, 127.3, 123.8, 80.0, 66.3, 32.7, 30.7, 25.4, 25.1, 21.5, 12.3; IR (neat) 2961, 1447, 763, 700 cm⁻¹; HRMS (EI⁺) exact mass calcd for C₁₅H₁₇O₁: m/z 328.0324 ([M⁺]⁺), found: m/z 328.0322. [α]D²¹⁺⁵ = -29.8 (c 1.13, CHCl₃)

\[
\begin{align*}
\text{t-Bu} & \\
\text{O} & \\
\text{O} & \\
\end{align*}
\]

(R)-2-(iodomethyl)-2-(3-methoxyphenyl)-1-oxaspiro[2.4]heptane (2ce)

Prepared according to the general procedure E with 1ce (22.0 mg, 0.1 mmol) over the course of 45 h at -20 °C as a yellow liquid (28.2 mg, 81% yield, 96.5% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5µ cellulose-4 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 8.45 min, t_minor = 7.95 min). ¹H NMR (500 MHz, CDCl₃) δ 7.27 (t, J = 7.5 Hz, 1H), 6.93 (d, J = 7.5 Hz, 1H), 6.90 (s, 1H), 6.84 (dd, J₁ = 7.5, 2.5 Hz, 1H), 3.82 (s, 3H), 3.69 (d, J = 10.0 Hz, 1H), 3.43 (d, J = 10.0 Hz, 1H), 2.15-2.09 (m, 1H), 1.88-1.86 (m, 1H), 1.83-1.70 (m, 3H), 1.58-1.51 (m, 1H), 1.47-1.41 (m, 1H), 1.33-1.27 (m, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 159.4, 140.1, 129.2, 119.0, 113.2, 112.5, 80.1, 66.3, 55.3, 32.6, 30.8, 25.4, 25.1, 11.9; IR (neat) 2961, 1447, 763, 700 cm⁻¹; HRMS (EI⁺) exact mass calcd for C₁₅H₁₃O₂: m/z 344.0273 ([M⁺]⁺), found: m/z 344.0269. [α]D²¹⁺⁵ = -35.3 (c 1.09, CHCl₃).
(R)-2-(3-fluorophenyl)-2-(iodomethyl)-1-oxaspiro[2.4]heptane (2cd)
Prepared according to the general procedure E with 1cd (20.5 mg, 0.1 mmol) over the course of 42 h at -20 °C as a yellow liquid (26.7 mg, 81% yield, 96.5% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5μ cellulose-4 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 6.56 min, t_minor = 6.27 min). 1H NMR (500 MHz, CDCl3) δ 7.33 (dt, J = 10.0, 7.5 Hz, 1H), 7.1 (d, J = 7.5 Hz, 1H), 7.07 (dd, J = 10.0, 1.5 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 3.67 (d, J = 10.5 Hz, 1H), 3.42 (d, J = 10.5 Hz, 1H), 2.15-2.09 (m, 1H), 1.89-1.85 (m, 1H), 1.81-1.71 (m, 3H), 1.57-1.54 (m, 1H), 1.44-1.38 (m, 1H), 1.32-1.28 (m, 1H); 13C NMR (126 MHz, CDCl3) δ 162.4 (d, J = 255.5 Hz), 141.3, 129.8 (d, J = 7.7 Hz), 122.3 (d, J = 2.9 Hz), 114.7 (d, J = 21.0 Hz), 114.0 (d, J = 22.8 Hz), 80.3, 65.9, 32.5, 30.7, 25.3, 25.1, 11.1; 19F NMR (376 MHz, CDCl3) δ -112.7; IR (neat) 2961, 1447, 763, 700 cm⁻¹; HRMS (EI+) exact mass caled for C13H14OF: m/z 332.0073 ([M]+), found: m/z 332.0070. [α]D23.5 = -48.4 (c 1.03, CHCl3).

(R)-2-(4-fluorophenyl)-2-(iodomethyl)-1-oxaspiro[2.4]heptane (2ce)
Prepared according to the general procedure E with 1ce (20.2 mg, 0.1 mmol) over the course of 51 h at -20 °C as a yellow liquid (33.2 mg, 97% yield, 96.5% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak PA-2 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 7.54 min, t_minor = 8.31 min). 1H NMR (500 MHz, CDCl3) δ 7.35-7.32 (m, 2H), 7.06-7.02 (m, 2H), 3.64 (d, J = 10.0 Hz, 1H), 3.43 (d, J = 10.0 Hz, 1H), 2.15-2.10 (m, 1H), 1.89-1.84 (m, 1H), 1.80-1.71 (m, 3H), 1.58-1.54 (m, 1H), 1.44-1.38 (m, 1H), 1.28-1.22 (m, 1H); 13C NMR (126 MHz, CDCl3) δ 162.2 (d, J = 246.1 Hz), 134.4, 128.5 (d, J = 8.5 Hz), 115.1 (d, J = 21.0 Hz), 80.0, 65.8, 32.6, 30.7, 25.4, 25.1, 11.9; 19F NMR (376 MHz, CDCl3) δ -114.3; IR (neat) 2961, 1447, 763, 700 cm⁻¹; HRMS (EI+) exact mass calcd for C13H14OF: m/z 332.0073 ([M]+), found: m/z 332.0070. [α]D23.5 = -7.1 (c 1.20, CHCl3).

(R)-2-(4-chlorophenyl)-2-(iodomethyl)-1-oxaspiro[2.4]heptane (2cf)
Prepared according to the general procedure E with 1cf (22.5 mg, 0.1 mmol) over the course of 51 h at -20 °C as a yellow liquid (32.5 mg, 92% yield, 98% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak PA-2 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 8.17 min, t_minor = 9.39 min). 1H NMR (500 MHz, CDCl3) δ 7.34-7.29 (m, 4H), 3.65 (d, J = 10.0 Hz, 1H), 3.42 (d, J = 10.0 Hz, 1H), 2.15-2.09 (m, 1H), 1.89-1.85 (m, 1H), 1.79-1.71 (m, 3H), 1.58-1.55 (m, 1H), 1.43-1.37 (m, 1H), 1.29-1.23 (m, 1H); 13C NMR (126 MHz, CDCl3) δ 137.2, 133.6, 128.4, 128.1, 80.1, 65.9, 32.6, 30.7, 25.3, 25.1, 11.4; IR (neat) 2961, 1447, 763, 700 cm⁻¹; HRMS (EI+) exact mass calcd for C13H14OC1l2: m/z 347.9778 ([M]+), found: m/z 347.9781. [α]D23.5 = -5.2 (c 1.22, CHCl3).
(R)-2-(iodomethyl)-2-(naphthalen-2-yl)-1-oxaspiro[2.4]heptane (2cg)
Prepared according to the general procedure E with 1cg (23.6 mg, 0.1 mmol) over the course of 45 h at -20 °C as a yellow liquid (27.7 mg, 75% yield, 94% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5µ cellulose-4 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 7.93 min, t_minor = 7.07 min). 1H NMR (500 MHz, CDCl3) δ 7.87-7.84 (m, 4H), 7.51-7.46 (m, 3H), 3.83 (d, J = 10.0 Hz, 1H), 3.53 (d, J = 10.0 Hz, 1H), 2.20-2.16 (m, 1H), 1.94-1.71 (m, 4H), 1.60-1.51 (m, 1H), 1.47-1.41 (m, 1H), 1.34-1.27 (m, 1H); 13C NMR (126 MHz, CDCl3) δ 136.1, 133.0, 132.9, 128.1, 127.9, 127.7, 126.3, 126.1, 126.0, 124.4, 80.3, 66.5, 32.7, 30.8, 25.4, 25.1, 12.0; IR (neat) 2959, 1422, 816, 654 cm⁻¹; HRMS (EI+) exact mass calcd for C17H17O: m/z 364.0324 ([M⁺], found: m/z 364.0328. [α]D²⁵ = -6.5 (c 1.24, CHCl3).

(R)-2-(iodomethyl)-2-(5,6,7,8-tetrahydronaphthalen-2-yl)-1-oxaspiro[2.4]heptane (2ch)
Prepared according to the general procedure E with 1ch (23.9 mg, 0.1 mmol) over the course of 45 h at -20 °C as a yellow liquid (27.7 mg, 76% yield, 91% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5µ cellulose-4 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 6.95 min, t_minor = 6.25 min). 1H NMR (500 MHz, CDCl3) δ 7.06-7.01 (m, 3H), 3.67 (d, J = 10.0 Hz, 1H), 3.44 (d, J = 10.0 Hz, 1H), 2.80-2.72 (m, 4H), 2.14-2.10 (m, 1H), 1.88-1.85 (m, 1H), 1.81-1.72 (m, 6H), 1.58-1.53 (m, 2H), 1.49-1.42 (m, 1H), 1.32-1.26 (m, 1H); 13C NMR (126 MHz, CDCl3) δ 136.9, 136.5, 135.4, 128.7, 127.2, 123.8, 79.9, 66.2, 32.7, 30.8, 29.5, 29.2, 25.4, 25.1, 23.2, 12.6; IR (neat) 2926, 1434, 825, 603 cm⁻¹; HRMS (EI+) exact mass calcd for C17H21O: m/z 368.0637 ([M⁺], found: m/z 368.0633. [α]D²⁵ = -5.5 (c 1.27, CHCl3).

(R)-2-(iodomethyl)-2-phenyl-1-oxaspiro[2.5]octane (2d)
Prepared according to the general procedure E with 1d (20.4 mg, 0.1 mmol) over the course of 44 h at -20 °C as a yellow liquid (32.7 mg, 98% yield, 92% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak OD-H column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 6.56 min, t_minor = 7.01 min). 1H NMR (500 MHz, CDCl3) δ 7.39-7.29 (m, 5H), 3.63-3.59 (m, 2H), 1.89-1.70 (m, 4H), 1.53-1.47 (m, 3H), 1.44-1.39 (m, 1H), 1.22-1.19 (m, 2H); 13C NMR (126 MHz, CDCl3) δ 138.5, 132.8, 127.6, 72.8, 68.8, 32.6, 30.8, 25.4, 25.3, 24.4, 11.5; IR (neat) 2930, 1447, 703, 576 cm⁻¹; HRMS (EI+) exact mass calcd for C15H17O: m/z 201.1279 ([M⁺], found: m/z 201.1275. [α]D²⁵ = -36.9 (c 0.64, CHCl3).

**Gram scale synthesis of 2d**: At nitrogen atmosphere, CH₂Cl₂ (30 mL) was added to a mixture of ion pair catalyst C1 (269 mg, 0.25 mmol), ammonium salt A8 (101 mg, 0.25 mmol) and NIS (1.34 g, 6.0 mmol) under -20 °C. After the mixture stirred for 5 min, 1d (1.0 g) in CH₂Cl₂ (3.0 mL) was added dropwise. After 48 h, the reaction was quenched by the addition of Na₂S₂O₃ aqueous solution. The organic layer
was separated, and the aqueous layer was extracted with ethyl acetate for three times. Then the organic layer combined washed with brine, dried over Na₂SO₄, filtered and then concentrated. The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:100, v/v) to afford 1.47 g (90% yield) yellow liquid. Enantiomeric excess was found to be 90% measured by chiral HPLC (ChiralPak OD-H column, hexane/i-PrOH 98:2 0.7 mL/min, t_major = 6.02 min, t_minor = 6.38 min).

(R)-2-(iodomethyl)-2-phenyl-1-oxaspiro[2.6]nonane (2e)

Prepared according to the general procedure E with 1e (21.7 mg, 0.1 mmol) over the course of 44 h at -20 °C as a yellow liquid (31.2 mg, 91% yield, 98% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak IC column, hexane/i-PrOH 95:5, 0.7 mL/min, t_major = 6.72 min, t_minor = 5.92 min). ¹H NMR (500 MHz, CDCl₃) δ 7.37-7.30 (m, 5H), 3.64 (d, J = 10.0 Hz, 1H), 3.59 (d, J = 10.0 Hz, 1H), 2.09-2.04 (m, 1H), 1.97-1.92 (m, 1H), 1.84-1.79 (m, 1H), 1.65-1.59 (m, 4H), 1.50-1.44 (m, 2H); 1.38-1.26 (m, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 138.8, 128.0, 127.6, 127.2, 74.6, 68.7, 34.2, 33.2, 29.2, 28.8, 24.7, 24.0, 12.5; IR (neat) 2924, 1447, 703, 573 cm⁻¹; HRMS (EI⁺) exact mass calcd for C₁₅H₁₈O: m/z 214.1346 ([M⁺]), found: m/z 215.1440. [α]D²⁵ = -54.5 (c, 0.70, CHCl₃).

Gram scale synthesis of 2e: At nitrogen atmosphere, CH₂Cl₂ (25 mL) was added to a mixture of ion pair catalyst C1 (252 mg, 0.23 mmol), ammonium salt A8 (95 mg, 0.23 mmol) and NIS (1.25 g, 5.54 mmol) under -20 °C. After the mixture stirred for one minute, 1e (1.0 g) in CH₂Cl₂ (3.0 mL) was added dropwise. After 50 h, the reaction was quenched by the addition of Na₂S₂O₃ aqueous solution. The organic layer was separated, and the aqueous layer was extracted with ethyl acetate for three times. Then the organic layer combined washed with brine, dried over Na₂SO₄, filtered and then concentrated. The residue was purified by column chromatography (ethyl acetate/petroleum ether = 1:100, v/v) to afford 1.40 g (89% yield) yellow liquid. Enantiomeric excess was found to be 98% measured by chiral HPLC (ChiralPak IC column, hexane/i-PrOH 95:5 0.7 mL/min, t_major = 6.63 min, t_minor = 5.86 min).

(R)-2-(iodomethyl)-2-phenyloxirane (2f)

Prepared according to the general procedure E with 1f (13.5 mg, 0.1 mmol) over the course of 56 h at -20 °C as a yellow liquid (10.7 mg, 41% yield, 63% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak AD-H column, hexane/i-PrOH 98:2:1.5 0.7 mL/min, t_major = 23.06 min, t_minor = 20.66 min). ¹H NMR (500 MHz, CDCl₃) δ 7.38 (d, J = 7.5 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.29 (d, J = 7.5 Hz, 1H), 4.09 (d, J = 10.0 Hz, 1H), 4.04 (d, J = 10.0 Hz, 1H), 3.90 (d, J = 10.0 Hz, 1H), 3.56 (d, J = 10.0 Hz, 1H); ¹³C NMR (126 MHz, CDCl₃) δ 138.5, 128.6, 128.1, 126.0, 73.7, 65.8, 12.9; IR (neat) 2961, 1447, 765, 574 cm⁻¹; HRMS (EI⁺) exact mass calcd for C₆H₁₂O: m/z 133.1672 ([M⁺]), found: m/z 133.1674. [α]D²⁵ = -4.6 (c 0.31, CHCl₃).

(R)-2-cyclohexyl-2-(iodomethyl)-3,3-dimethylxirane (2g)

Prepared according to the general procedure E with 1g (16.8 mg, 0.1 mmol) over the course of 74 h at
-20 °C as a yellow liquid (20.9 mg, 71% yield, 37% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak AD-H column, hexane/i-PrOH 98:2, 0.7 mL/min, t_{major} = 5.87 min, t_{minor} = 6.37 min). \(^1\)H NMR (500 MHz, CDCl\(_3\)) \(\delta\) 3.56 (d, \(J = 10.0\) Hz, 1H), 3.02 (d, \(J = 10.0\) Hz, 1H), 1.89-1.60 (m, 5H), 1.50 (tt, \(J = 10.0, 2.5\) Hz, 1H), 1.39 (s, 3H), 1.37 (s, 3H), 1.36-1.35 (m, 1H), 1.27-1.19 (m, 3H); \(^13\)C NMR (126 MHz, CDCl\(_3\)) \(\delta\) 66.6, 66.0, 43.5, 31.3, 28.6, 27.1, 26.5, 26.3, 22.3, 20.3, 2.6; IR (neat) 2961, 1447, 763, 633 cm\(^{-1}\); HRMS (EI+) exact mass calcd for C\(_{11}\)H\(_{19}\)OI: m/z 294.0481 ([M-I]\(^+\)), found: m/z 294.0479; \([\alpha]\)\(_D\)^{23.5} = -10.5 (c 0.52, CHCl\(_3\)).
5. Wagner-Meerwein Rearrangement of epoxide and one-pot procedure

5.1 Wagner-Meerwein Rearrangement of 2c.

![Image](image-url)

Table S6. Optimization of the rearrangement of 2c[a]

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<th>entry</th>
<th>Cat</th>
<th>solvent</th>
<th>C (mmol/ml)</th>
<th>T (°C)</th>
<th>t (h)</th>
<th>ee (%)[b]</th>
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<td>1.5</td>
<td>91</td>
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</table>

[a] Reactions were performed with 2c in solvent at indicated concentration by addition of Lewis acid at indicated temperature (0.1 mmol). [b] Determined by HPLC using Lux 5μ cellulose-4 column. [b] Entry 8 was selected as the optimal condition.

(S)-2-(iodomethyl)-2-phenylcyclohexanone (3c)

To a stirred solution of 2c (31.4 mg, 0.1 mmol) in 2ml CH₂Cl₂ under nitrogen atmosphere at 0°C was added boron trifluoride etherate (10 ul, 0.1 mmol). Two hours later, saturated aqueous NaHCO₃ was added to the solution, and the resulting mixture was extracted with CH₂Cl₂. The organic layer was washed with brine, dried over Na₂SO₄, and evaporated in vacuo[36]. The residue was purified by preparative column chromatography (ethyl acetate/petroleum ether = 1/30, v/v) and gave 3c as a red brown liquid (29.1 mg, 93% yield, 93% ee for 0.1 mmol scale). The enantiomeric purity was determined by HPLC analysis (Lux 5μ cellulose-4 column, hexane/-PrOH 98:2, 0.7 mL/min, t_major = 10.21 min, t_minor = 11.52 min). ¹H NMR (500 MHz, CDCl₃) δ 7.37 (t, J = 7.5 Hz, 2H), 7.31 (d, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 2H), 3.61 (d, J = 10.0 Hz, 1H), 3.37 (d, J = 10.0 Hz, 1H), 2.81 (dq, J = 15.0, 3.0 Hz, 1H), 2.34-2.25 (m, 2H), 1.96-1.87 (m, 2H), 1.80-1.74 (m, 2H), 1.74-1.68 (m, 3H).[36] ¹³C NMR (126 MHz, CDCl₃) δ 210.2, 138.2, 129.1, 127.7, 126.8, 56.2, 40.2, 36.3, 27.8, 21.8, 19.5; IR (neat) 2939, 1704, 1448, 701 cm⁻¹; HRMS (ESI⁺) exact mass calcd for C₁₃H₁₄IO: m/z 315.0246 ([M+H]⁺), found: m/z 315.0247; [α]D²³.⁵ = 104.7 (c 0.44, CHCl₃).
(S,E)-1-(2,4-dinitrophenyl)-2-(2-iodomethyl)-2-phenylcyclohexylidene)hydrazine (4)

To a solution of 3c (31.3 mg, 0.1 mmol) in EtOH/H2O (1.8 mL/0.6 mL), 2,4-dinitrophenylhydrazine (36.4 mg, 0.12 mmol, wetted with 50% water) and con.H2SO4 (0.2 mL) were added. The mixture was stirred at rt for 4 h. Then H2O (3 mL) was added. The organic layer was extracted with ethyl acetate and washed with saturated NaHCO3 (aq.), brine, dried over Na2SO4, filtered and then concentrated. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1:15, v/v) to afford the title product as a yellow solid (42.9 mg, 87% yield, 94% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak ID3 column, hexane/i-PrOH 9:1, 0.7 mL/min, t_major = 12.51 min, t_minor = 11.34 min). 1H NMR (500 MHz, CDCl3) δ 11.41 (s, 1H), 9.17 (s, 1H), 8.39 (d, J = 10.0 Hz, 1H), 8.22 (d, J = 10.0 Hz, 1H), 7.38 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 1H), 7.38 (d, J = 7.5 Hz, 2H), 3.84 (d, J = 10.0 Hz, 1H), 3.48 (d, J = 10.0 Hz, 1H), 2.82 (d, J = 15.0 Hz, 1H), 2.68 (d, J = 15.0 Hz, 1H), 2.09-2.03 (m, 1H), 1.98-1.91 (m, 2H), 1.85-1.78 (m, 1H), 1.73-1.66 (m, 1H), 1.59-1.57 (m, 1H); 13C NMR (126 MHz, CDCl3) δ 160.1, 145.6, 139.8, 138.1, 130.3, 129.2, 127.7, 127.0, 123.5, 117.0, 50.3, 36.3, 29.7, 26.2, 25.1, 21.7, 19.8; IR (neat) 3323, 2934, 1617, 1336, 7442 cm⁻¹; HRMS (ESI+) exact mass calced for C19H20O6N4I: m/z 495.0518 ([M+H]+), found: m/z 495.0524. [α]D²³.₅ = 126.4 (c 0.55, CHCl₃).

To a flask charged with NaN₃ (7.8 mg, 0.12 mmol, in 1mL DMSO) was added a solution of 5 (31.2mg, 0.1 mmol) in 1mL DMSO under nitrogen. The mixture was stirred at 80 °C for 5 hours and cooled to room temperature. Then the reaction was washed with water for 3 times, dried under reduced pressure. The residue was purified by preparative column chromatography (ethyl acetate/petroleum ether = 1:30, v/v) and gave 6 as a colorless liquid (20.3 mg, 86% yield, 92% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5μ cellulose-4 column, hexane/iPrOH 98:2, 0.7 mL/min, t_major = 10.45 min, t_minor = 11.46 min). 1H NMR (500 MHz, CDCl₃) δ 7.39 (t, J = 7.5 Hz, 2H), 7.34-7.28 (m, 1H), 7.22 (d, J = 7.5 Hz, 2H), 3.63 (d, J = 12.5 Hz, 1H), 3.34 (d, J = 12.5 Hz, 1H), 2.74 (dd, J = 14.4, 2.5 Hz, 1H), 2.39-2.26 (m, 2H), 2.00-1.86 (m, 2H), 1.82-1.66 (m, 3H); 13C NMR (126 MHz, CDCl₃) δ 211.8, 137.9, 129.2, 127.7, 126.9, 59.9, 58.0, 39.9, 32.8, 27.9, 21.2; HRMS (ESI+) exact mass calced for C₁₂H₁₀N₂O: m/z 230.1293 ([M+H]+), found: m/z 230.1297; IR (neat) 2939, 2102, 1708, 702 cm⁻¹; [α]D²³.₅ = 136.1 (c 0.34, CHCl₃).

A flask charged with AgBF₄ (0.13 mmol) in CH₃NO₂ (1mL) under nitrogen atmosphere was added 5 (31.4mg, 0.1mmol, in 0.4 mL DMF). Then stirred at 40 °C for 4.5 h in dark and filtered through a short
pad of celite. The filtrate was washed successively with water, brine, and then dried. The obtained residue was dissolved in methanol, added Na₂CO₃ and stirred at room temperature for 1h. After the addition of water (2 ml), the solution was extracted with DCM. The organic layers were washed with water, brine and dried over Na₂SO₄. Evaporation of the solvent gave the corresponding alcohol, which could be purified by chromatography (ethyl acetate/petroleum ether = 1:6, v/v) as a colorless liquid (23.2 mg, 74% yield, 91% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5μ cellulose-4 column, hexane/iPrOH 4:1, 0.7 mL/min, t_major = 9.14 min, t_minor = 8.19 min). ³¹H NMR (500 MHz, CDCl₃) δ 7.31-7.16 (m, 5H), 3.85 (s, 1H), 3.14 (d, J = 13.5 Hz, 1H), 2.1 (d, J = 13.5 Hz, 1H), 2.73-2.66 (m, 1H), 2.66-2.53 (m, 1H), 2.26-2.11 (m, 2H), 1.91-1.86 (m, 2H), 1.69-1.65 (m, 2H); ¹³C NMR (126 MHz, CDCl₃) δ 213.2, 135.3, 130.0, 128.2, 127.0, 79.3, 43.3, 40.4, 38.6, 28.0, 22.8; HRMS (ESI+) exact mass calc'd for C₁₃H₁₂O₂: m/z 227.1048 ([M+Na]⁺), found: m/z 227.1049; IR (neat) 3448, 2920, 1709, 702, 669 cm⁻¹; [α]D²³.⁵ = 50.0 (c 0.42, CHCl₃)

5.2 one-pot iodo-etherification/Wagner-Meerwein rearrangement reaction

![Reaction Scheme]

**General procedure F:** In a Schlenk tube, ion pair catalyst C1 (0.01 mmol), ammonium salt A8 (0.01 mmol), NIS (0.12 mmol) and CH₂Cl₂ (1 mL) was added, then the reaction mixture was cooled to -20 °C. Allyl alcohol I (0.1 mmol) in 1 mL CH₂Cl₂ was added dropwise. As the substrate disappeared indicated by TLC, boron trifluoride etherate (0.1 mmol) was added dropwise to the mixture at 0 °C. After 2.5 h, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1:25, v/v) to afford the product.

![Product](attachment:image.png)

**(S)-2-(iodomethyl)-2-phenylcyclohexanone (3c)**

Prepared according to the general procedure F with 2c (31.4 mg, 0.1 mmol) as a pale yellow liquid (24.8 mg, 79% yield, 93% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5μ cellulose-4 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 10.59 min, t_minor = 12.38 min). The product shows no difference in spectra with those of 3c obtained by stepwise reaction.

2.7 mmol scale synthesis of 3c: In a Schlenk tube, ion pair catalyst C1 (150 mg, 0.014 mmol), ammonium salt A8 (58 mg, 0.014 mmol), NIS (720 mg, 3.2 mmol) and CH₂Cl₂ (50 mL) was added, then the reaction mixture was cooled to -20 °C. Allyl alcohol I (500 mg, 2.66 mmol) in 5 mL CH₂Cl₂ was added dropwise. After 3h boron trifluoride etherate (120 mg, 104 ul, 0.9 mmol), was added dropwise to the mixture at 0 °C. After 2.5 h the reaction was quenched with saturated Na₂S₂O₃. The organic layer was separated and organic layer washed with CH₂Cl₂ for two times. Combined the organic layer, washed with brine, dried over Na₂SO₄ and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (ethyl acetate/petroleum ether = 1:100, v/v) to afford the product (685 mg, 2.18 mmol, 82% yield, 92% ee). Enantiomeric excess was found to be 92%
measured by chiral HPLC (Lux 5μ cellulose-4 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_{major} = 10.47 min, t_{minor} = 12.18 min).

(S)-2-(4-fluorophenyl)-2-(iodomethyl)cyclohexanone (3d)
Prepared according to the general procedure F with 2ce (22.3 mg, 0.1 mmol) as a white solid (32.2 mg, 92% yield, 89% ee). The enantiomeric purity was determined by HPLC analysis (ChiralPak IF-3 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_{major} = 9.96 min, t_{minor} = 13.29 min). 1H NMR (500 MHz, CDCl₃) δ 7.18 -7.16 (m, 2H), 7.08-7.04 (m, 2H), 3.57 (dd, J = 10.0, 1.5 Hz, 1H), 3.37 (dd, J = 10.0, 1.5 Hz, 1H), 2.82-2.75 (m, 1H), 2.31-2.26 (m, 2H), 1.96-1.68 (m, 5H); 13C NMR (126 MHz, CDCl₃) δ 210.1, 162.2 (d, J = 247.7 Hz), 134.1 (d, J = 3.4 Hz), 128.7 (d, J = 8.1 Hz), 116.1 (d, J = 21.4 Hz), 55.6, 40.1, 36.5, 27.8, 21.8, 19.7; 19F NMR (376 MHz, CDCl₃) δ -114.3; IR (neat) 2942, 1721, 1443, 678 cm⁻¹; HRMS (ESI⁺) exact mass calcd for C₁₃H₁₉FIO⁻: m/z 333.0152 ([M⁺H⁻]⁻), found: m/z 333.0152. [α]D²⁵ = 87.3 (c 0.94, CHCl₃).

(S)-2-(4-(tert-butyl)phenyl)-2-(iodomethyl)cyclohexanone (3e)
Prepared according to the general procedure F with 2cb (37.0 mg, 0.1 mmol) as a white solid (31.5 mg, 85% yield, 86% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5μ cellulose-4 column, hexane/i-PrOH 99:1, 0.7 mL/min, t_{major} = 7.79 min, t_{minor} = 9.01 min). 1H NMR (500 MHz, CDCl₃) δ 7.36 (d, J = 7.5 Hz, 2H), 7.11 (d, J = 7.5 Hz, 2H), 3.63 (d, J = 10.0 Hz, 1H), 3.29 (d, J = 10.0 Hz, 1H), 2.81-2.71 (m, 1H), 2.35-2.26 (m, 2H), 2.00-1.87 (m, 2H), 1.82-1.74 (m, 2H), 1.74-1.64 (m, 2H), 1.30 (s, 9H); 13C NMR (126 MHz, CDCl₃) δ 210.2, 150.7, 134.9, 126.4, 126.0, 55.8, 40.0, 36.2, 34.5, 31.3, 27.7, 21.8, 19.2; IR (neat) 2933, 1692, 1447, 683 cm⁻¹; HRMS (ESI⁺) exact mass calcd for C₁₇H₂₃IO⁻: m/z 371.0872 ([M⁺H⁻]⁻), found: m/z 371.0876. [α]D²⁵ = 69.5 (c 0.97, CHCl₃).

(S)-2-(iodomethyl)-2-(3-methoxyphenyl)cyclohexanone (3f)
Prepared according to the general procedure F with 2ce (34.4 mg, 0.1 mmol) as a white solid (27.3 mg, 85% yield, 88% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5μ cellulose-4 column, hexane/i-PrOH 99:1, 0.7 mL/min, t_{major} = 13.31 min, t_{minor} = 16.75 min). 1H NMR (500 MHz, CDCl₃) δ 7.28 (t, J = 8.0 Hz, 1H), 6.84 (d, J = 8.0 Hz, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.74 (s, 1H), 3.80 (s, 3H), 3.59 (d, J = 10.0 Hz, 1H), 3.36 (d, J = 10.0 Hz, 1H), 2.81-2.74 (m, 1H), 2.35-2.27 (m, 2H), 1.98-1.86 (m, 2H), 1.83-1.77 (m, 2H), 1.74-1.63 (m, 1H); 13C NMR (126 MHz, CDCl₃) δ 210.0, 160.1, 139.7, 130.1, 119.1, 113.2, 112.5, 56.1, 55.3, 40.2, 36.4, 27.7, 21.8, 19.2; IR (neat) 2937, 1712, 1437, 692 cm⁻¹; HRMS (ESI⁺) exact mass calcd for C₁₃H₁₃O₂⁻: m/z 345.0351 ([M⁺H⁻]⁻), found: m/z 345.0352. [α]D²⁵ = 79.7 (c 0.92, CHCl₃).
(S)-2-(iodomethyl)-2-phenylcycloheptanone (3g)
Prepared according to the general procedure F with 2d (20.2 mg, 0.1 mmol) as a pale yellow liquid (27.2 mg, 83% yield, 91% ee). The enantiomeric purity was determined by HPLC analysis (Lux 5μ cellulose-4 column, hexane/i-PrOH 98:2, 0.7 mL/min, t_major = 8.37 min, t_minor = 10.50 min). 1H NMR (500 MHz, CDCl₃) δ 7.35 (t, J = 7.5 Hz, 2H), 7.29 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 7.5 Hz, 2H), 3.81 (d, J = 10.0 Hz, 1H), 3.54 (d, J = 10.0 Hz, 1H), 2.59-2.51 (m, 2H), 2.35-2.33 (m, 1H), 2.13-2.18 (m, 1H), 1.96-1.93 (m, 1H), 1.86-1.81 (m, 2H), 1.62-1.44 (m, 3H), 1.27-1.22 (m, 1H); 13C NMR (126 MHz, CDCl₃) δ 210.8, 140.5, 128.7, 127.7, 126.8, 58.6, 41.6, 33.1, 30.4, 26.8, 24.2, 19.3; IR (neat) 2936, 1702, 1048, 706 cm⁻¹; HRMS (ESI+) exact mass calcd for C₁₉H₁₆IO: m/z 329.0402 ([M+H]+), found: m/z 329.0405. [α]D²³.⁵ = 94.7 (c 0.53, CHCl₃).
6. References


7. Copies of spectrum

[Diagram showing 1H and 13C NMR spectra of compound 1a]
n-Bu

1ab

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n-Bu

1ab

157.01  141.97  128.78  112.26  77.28  77.28  73.98  35.30  35.30  22.43  13.97
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Bandwidth: 4
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2   | 3.86          | n.a.     | 132.083      | 19.137         | 49.99       | n.a.   | MR *
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Wavelength: 214
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Bandwidth: n.a.
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2066 XZL-4-10-2 AD-H 98515 214 0.4
2090 SZG-3-79-1+- PC-3 982 214 0.5

Sample Name:  SZG-3-79-1+- PC-3 982 214 0.5  Injection Volume:  1.0
Vial Number:  GB5  Channel:  UV_VIS_2
Sample Type:  unknown  Wavelength:  214.0
Control Program:  test-dad2  Bandwidth:  4
Quantf. Method:  WXL  Dilution Factor:  1.0000
Run Time (min):  13.11  Sample Amount:  1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount (n.a.)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.69</td>
<td>n.a.</td>
<td>365.988</td>
<td>58.532</td>
<td>49.77</td>
<td>n.a.</td>
<td>MB*</td>
</tr>
<tr>
<td>2</td>
<td>8.27</td>
<td>n.a.</td>
<td>345.874</td>
<td>59.082</td>
<td>50.23</td>
<td>n.a.</td>
<td>BMB</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>711.863</td>
<td>117.614</td>
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</table>

21310-DAD #2090 [modified by Administrator]
2091 SZG-4-10-3 PC-3 982 214 0.5

Sample Name: SZG-4-10-3 PC-3 982 214 0.5
Vial Number: GB6
Sample Type: unknown
Control Program: test-dad2
Quantif. Method: WXL
Recording Time: 2014-5-28 10:10
Run Time (min): 11.29
Injection Volume: 1.0
Channel: UV_VIS_2
Wavelength: 214.0
Bandwidth: 4
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>n.a.</td>
<td>227.619</td>
<td>36.677</td>
<td>96.38</td>
<td>n.a.</td>
<td>M</td>
</tr>
<tr>
<td>2</td>
<td>6.25</td>
<td>n.a.</td>
<td>10.869</td>
<td>1.779</td>
<td>46.2</td>
<td>n.a.</td>
<td>BMB</td>
</tr>
<tr>
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<tr>
<td>Total</td>
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<td>238.508</td>
<td>38.455</td>
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<td>0.000</td>
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</table>

Diagram of compound 2ac.
775 SXG-4-4-2-1+- ID3 982 214 0.7

Sample Name: SXG-4-4-2-1+- ID3 982 214 0.7
Injection Volume: 1.0
Vial Number: R83
Channel: UV_VIS_1
Sample Type: unknown
Wavelength: 214
Control Program: WXL-2014-1
Bandwidth: n.a.
Quantif. Method: WXL
Dilution Factor: 1.0000
Recording Time: 2014/6/9 12:03
Sample Weight: 1.0000
Run Time (min): 11.69
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.15</td>
<td>n.a.</td>
<td>204.836</td>
<td>17.718</td>
<td>49.76</td>
<td>n.a.</td>
<td>BM8'</td>
</tr>
<tr>
<td>2</td>
<td>4.79</td>
<td>n.a.</td>
<td>170.788</td>
<td>17.892</td>
<td>50.24</td>
<td>n.a.</td>
<td>BM8'</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>375.624</td>
<td>35.610</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>
Sample Name: SXG-4-20-2 ID3 982 214 0.7
Injection Volume: 1.0
Channel: UV_VIS_1
Sample Type: unknown
Control Program: WXL-2014-1
Wavelength: 214
Bandwidth: n.a.
Quantif. Method: WXL
Dilution Factor: 1.0000
Recording Time: 2014/6/9 12:20
Sample Weight: 1.0000
Run Time (min): 6.39
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.15</td>
<td>s.a.</td>
<td>11532</td>
<td>0.995</td>
<td>3.04</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>4.79</td>
<td>s.a.</td>
<td>301235</td>
<td>31703</td>
<td>96.96</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>Total</td>
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<td>312767</td>
<td>32698</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>
669 SZG-4-10.4 PC-4 982 214 0.7

Sample Name: SZG-4-10.4 PC-4 982 214 0.7
Vial Number: GE1
Sample Type: unknown
Control Program: WXL-2014-1
Quantf Method: WXL
Recording Time: 2014/5/26 19:10
Run Time (min): 25.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height</th>
<th>Area</th>
<th>Ret.Area</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.51</td>
<td>n.a.</td>
<td>21.627</td>
<td>1932</td>
<td>5.25</td>
<td>n.a</td>
<td>MB*</td>
</tr>
<tr>
<td>2</td>
<td>5.89</td>
<td>n.a.</td>
<td>339.385</td>
<td>34870</td>
<td>94.75</td>
<td>n.a</td>
<td>MB*</td>
</tr>
</tbody>
</table>

Total: 361.013 36.802 100.00 0.000
**2163 SZG-4-15-5 OD-H 982 214 0.7**

- **Sample Name:** SZG-4-15-5 OD-H 982 214 0.7
- **Injection Volume:** 1.0
- **Channel:** UV_VIS_2
- **Wavelength:** 214.0
- **Bandwidth:** 4
- **Control Program:** test-dad
- **Quantif. Method:** WXL
- **Recording Time:** 2014-6-4 13:34
- **Kern Time (min):** 15.47
- **Dilution Factor:** 1.0000
- **Sample Weight:** 1.0000
- **Sample Amount:** 1.0000

### Retention Time and Peak Analysis

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU'·min)</th>
<th>Rel. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.75</td>
<td>n.a.</td>
<td>1043.776</td>
<td>144.473</td>
<td>95.58</td>
<td>n.a.</td>
<td>BMB'</td>
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<tr>
<td>2</td>
<td>9.12</td>
<td>n.a.</td>
<td>40.516</td>
<td>6.680</td>
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<td>n.a.</td>
<td>BMB</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Total:</strong></td>
<td><strong>1064.292</strong></td>
<td><strong>151.153</strong></td>
<td>100.00</td>
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</tbody>
</table>

- **%:** 91%
732 3-75-1+- AD-H 98515 214 0.4 18

Sample Name: 3-75-1+- AD-H 98515 214 0.4 18  Injection Volume: 1.0
Vial/Number: GA1  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: 214
Control Program: WXL-2014-1  Bandwidth: n.a.
Quantif. Method: WXL  Dilution Factor: 1.0000
Recording Time: 2014/6/4 11:12  Sample Weight: 1.0000
Run Time (min): 25.01  Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time min</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.47</td>
<td>n.a.</td>
<td>276.569</td>
<td>56.874</td>
<td>49.99</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>12.16</td>
<td>n.a.</td>
<td>263.009</td>
<td>57.091</td>
<td>50.18</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>Total</td>
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<td>113.965</td>
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</table>

WXL-2 #372 [modified by GC]  3-75-1+- AD-H 98515 214 0.4 18

UIV_VIS_1  WXL 214 nm
733 SZG-4-15-2 AD-H 98515 214 0.4 18

Sample Name: SZG-4-15-2 AD-H 98515 214 0.4 18
Vial Number: GAS
Sample Type: unknown
Control Program: WXL-2014-1
Quartef. Method: WXL
Recording Time: 2014/6/4 12:04
Run Time (min): 25.00

Injection Volume: 1.0
Channel: UV_VIS_1
Wavelength: 214
Bandwidth: n.a.
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
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<td>19735</td>
<td>4111</td>
<td>3.48</td>
<td>n.a.</td>
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<tr>
<td>2</td>
<td>12.17</td>
<td>n.a.</td>
<td>537.701</td>
<td>113.855</td>
<td>96.52</td>
<td>n.a.</td>
<td>8MB*</td>
</tr>
</tbody>
</table>

Total: 557.436 117.976 100.00 0.000

Graphical representation of the chromatogram.
Sample Name: 3-88-5+ ID3 982 214 0.4 18
Via Number: GA3
Sample Type: unknown
Control Program: WXL-2014-1
Quant. Method: WXL
Recording Time: 2014/6/3 19:41
Run Time (min): 25.00

Injection Volume: 2.0
Channel: UV_VIS_1
Wavelength: 214
Bandwidth: n.a.
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height</th>
<th>Area</th>
<th>Rel.Area</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>492.835</td>
<td>68.150</td>
<td>50.73</td>
<td>n.a</td>
<td>BM*</td>
</tr>
<tr>
<td>2</td>
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<td>n.a</td>
<td>456.294</td>
<td>66.197</td>
<td>49.27</td>
<td>n.a</td>
<td>MB*</td>
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<tr>
<td>Total</td>
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<td>949.129</td>
<td>134.347</td>
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</table>
1031 SZG-4-5-1-1+- OD-H 982 214 0.7

Sample Name: SZG-4-5-1-1+- OD-H 982 214 0.7
Vial Number: GB2
Sample Type: unknown
Control Program: WXL-2014-1
Quantif. Method: WXL
Recording Time: 2014/7/4 17:46
Run Time (min): 23.11

Injection Volume: 1.0
Channel: UV_VIS_1
Wavelength: 214
Bandwidth: n.a.
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>n.a.</td>
<td>223.051</td>
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<td>50.10</td>
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<tr>
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<td>n.a.</td>
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<td>49.96</td>
<td>n.a.</td>
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</table>
### 2189 SZG-4-19-3 OD-H 982 214 0.7

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>SZG-4-19-3 OD-H 982 214 0.7</th>
<th>Injection Volume: 1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vial Number:</td>
<td>GD3</td>
<td>Channel: UV_VIS_2</td>
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<tr>
<td>Sample Type:</td>
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<td>Wavelength: 2140</td>
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<td>Control Program:</td>
<td>test-dad</td>
<td>Bandwidth: 4</td>
</tr>
<tr>
<td>Quant. Method:</td>
<td>WXL</td>
<td>Dilution Factor: 1.0000</td>
</tr>
<tr>
<td>Recording Time:</td>
<td>2014-6-5 14:30</td>
<td>Sample Weight: 1.0000</td>
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<tr>
<td>Run Time (min):</td>
<td>14.95</td>
<td>Sample Amount: 1.0000</td>
</tr>
</tbody>
</table>

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**Graph**

- UV_VIS_2
- WVL 214 nm
- Ret. Time: 1.7183
- Ret. Time: 7.807

---

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel. Area (%)</th>
<th>Amount (n.a.)</th>
<th>Type</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>7.18</td>
<td>n.a.</td>
<td>805.280</td>
<td>99.745</td>
<td>98.69</td>
<td>n.a.</td>
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<td>9.842</td>
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<td>1.31</td>
<td>n.a.</td>
<td>BMS*</td>
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<td>Total</td>
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<td>815.122</td>
<td>101.007</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

---

S128
### 5134 SZG-8-29-1 OD-H 982 214 0.7

<table>
<thead>
<tr>
<th>Sample Name:</th>
<th>SZG-8-29-1 OD-H 982 214 0.7</th>
<th>Injection Volume:</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vial Number:</td>
<td>RD4</td>
<td>Channel:</td>
<td>UV_VIS_2</td>
</tr>
<tr>
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<td>Wavelength:</td>
<td>214.0</td>
</tr>
<tr>
<td>Control Program:</td>
<td>test-dad</td>
<td>Bandwidth:</td>
<td>4</td>
</tr>
<tr>
<td>Quantif. Method:</td>
<td>WXXL</td>
<td>Dilution Factor:</td>
<td>1.0000</td>
</tr>
<tr>
<td>Recording Time:</td>
<td>2015-5-4 10:46</td>
<td>Sample Weight:</td>
<td>1.0000</td>
</tr>
<tr>
<td>Run Time (min):</td>
<td>14.01</td>
<td>Sample Amount:</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

![Graph with peaks](chart.png)

**Table:**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
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<td>n.a.</td>
<td>1199.808</td>
<td>151.440</td>
<td>98.83</td>
<td>n.a.</td>
<td>BM *</td>
</tr>
<tr>
<td>2</td>
<td>7.79</td>
<td>n.a.</td>
<td>12.715</td>
<td>1.788</td>
<td>1.17</td>
<td>n.a.</td>
<td>M *</td>
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</tbody>
</table>

**Total:**

1212.523 153.228 100.00 3.000
### Sample Information

**Sample Name:** SZG-4-39-3+- PC-4 955 214 0.7  
**Injection Volume:** 2.0  
**Channel:** UV_VIS_2  
**Sample Type:** unknown  
**Wavelength:** 214.6  
**Control Program:** test-adv2  
**Bandwidth:** 4  
**Quantif. Method:** VXL  
**Dilution Factor:** 1.0000  
**Recording Time:** 2014-6-27 15:33  
**Sample Weight:** 1.0000  
**Run Time (min):** 11.82  
**Sample Amount:** 1.0000

### Chromatogram

![Chromatogram Image]

### Peak Table

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.90</td>
<td>n.a.</td>
<td>338.831</td>
<td>38.413</td>
<td>51.36</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>6.41</td>
<td>n.a.</td>
<td>310.429</td>
<td>36.375</td>
<td>48.64</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td></td>
<td></td>
<td><strong>649.060</strong></td>
<td><strong>74.787</strong></td>
<td><strong>100.00</strong></td>
<td>0.000</td>
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</tr>
</tbody>
</table>

---

*S131*
2357 SZ-4-40-3 PC-4 955 214 0.7

Sample Name: SZ-4-40-3 PC-4 955 214 0.7  Injection Volume: 2.0
Vial Number: GD4  Channel: UV_VIS_2
Sample Type: unknown  Wavelength: 214.0
Control Program: test-dad2  Bandwidth: 4
Quantif. Method: WXL  Dilution Factor: 1.0000
Recording Time: 2014-6-27 15:46  Sample Weight: 1.0000
Run Time (min): 11.33  Sample Amount: 1.0000

---

**Peak Name**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount (n.a.)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
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<td>5.86</td>
<td>n.a.</td>
<td>17.726</td>
<td>2.107</td>
<td>2.56</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>6.32</td>
<td>n.a.</td>
<td>720.618</td>
<td>80.155</td>
<td>97.44</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>738.344</td>
<td>82.262</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

---

**Diagram:**

- Compound 2ca with retention time 6.32 min and peak area 720.618 mAU.
### HPLC Analysis Details

**Sample Name:** SZG-4-40-2 PC-4 982 214 0.7  
**Injection Volume:** 1.0  
**Channel:** UV_VIS_2  
**Wavelength:** 214.0  
**Bandwidth:** 4  
**Dilution Factor:** 1.0000  
**Sample Weight:** 1.0000  
**Sample Amount:** 1.0000

### Chromatogram

- **Peak Name:** 1-Br 2cb
- **Retention Time (min):** 5.61
- **Height (mAU):** 47.990
- **Area (mAU*min):** 6.116
- **Relative Area (%):** 4.07
- **Type:** BN0

### Table

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.61</td>
<td>n.a.</td>
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<td>144.196</td>
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<td>n.a.</td>
<td>bMB*</td>
</tr>
</tbody>
</table>

**Total:** 1384.576, 150.312, 100.00, 0.000

---

S134
2366 SZG-4-50-5+- PC-4 982 214 0.7

Sample Name: SZG-4-50-5+- PC-4 982 214 0.7
Val Number: GD6
Sample Type: unknown
Control Program: test-dad2
Quantif. Method: WXXL
Recording Time: 2014-6-30 10:56
Run Time (min): 12.00

Injection Volume: 2.6
Channel: UV_VIS_2
Wavelength: 214.0
Bandwidth: 4
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time min</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.95</td>
<td>r.a.</td>
<td>542.318</td>
<td>77.025</td>
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<td>n.a.</td>
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<tr>
<td>2</td>
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<td>476.972</td>
<td>73.503</td>
<td>48.67</td>
<td>n.a.</td>
<td>MB</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1019.289</td>
<td>151.228</td>
<td>100.00</td>
<td>0.000</td>
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</tr>
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</table>

S135
Sample Name: SZG-4-85-5 PC-4 982 214 0.7
Injection Volume: 1.0
Channel: UV_VIS_2
Wavelength: 214.0
Bandwidth: 4
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

Run Time (min): 12.80

Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area % | Amount (n) | Type
--- | --- | --- | --- | --- | ---
1 | n.a. | n.a. | n.a. | n.a. | BM
2 | 451.872 | 71.398 | 98.24 | n.a. | MB
Total: 470.874 | 72.680 | 100.00 | 0.000

---

S136
2343 SZG-4-39-4- PC-4 982 214 0.7

Sample Name: SZG-4-39-4- PC-4 982 214 0.7
Vial Number: G03
Sample Type: unknown
Control Program: test-dad2
Quantif. Method: UV
Recording Time: 2014-6-26 11:40
Run Time (min): 11.00
Injection Volume: 1.0
Channel: UV_VIS_2
Wavelength: 214.0
Bandwidth: 4
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Ret.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>6.29</td>
<td>n.a.</td>
<td>422.662</td>
<td>48.066</td>
<td>n.a.</td>
<td>BM*</td>
<td></td>
</tr>
<tr>
<td>2</td>
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<td>n.a.</td>
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<td>43.228</td>
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<tr>
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<td>807.131</td>
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<td>0.000</td>
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S137
2344 SZG-4-40-4 PC-4 982 214 0.7

Sample Name: SZG-4-40-4 PC-4 982 214 0.7
Injection Volume: 1.0
Vial Number: G04
Channel: UV_VIS_2
Sample Type: unknown
Wavelength: 214.0
Control Program: test-dad2
Bandwidth: 4
Gerent Method: WKL
Dilution Factor: 1.0000
Recording Time: 2014-6-26 12:12
Sample Weight: 1.0000
Run Time (min): 15.00
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.27</td>
<td>n.a.</td>
<td>13.988</td>
<td>1.448</td>
<td>1.77</td>
<td>n.a.</td>
<td>MB*</td>
</tr>
<tr>
<td>2</td>
<td>6.58</td>
<td>n.a.</td>
<td>716.116</td>
<td>30.334</td>
<td>98.23</td>
<td>n.a.</td>
<td>MB*</td>
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<tr>
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<td>730.104</td>
<td>31.782</td>
<td>100.00</td>
<td>0.000</td>
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</table>
Sample Name: SGZ-4-26-2+. PA-2 982 214 0.7
Val Number: GD1
Sample Type: unknown
Control Program: test-dad
Quantif. Method: WXL
Recording Time: 2014-6-16 14:25
Run Time (min): 13.44

Injection Volume: 3.0
Channel: UV_VIS_2
Wavelength: 214.0
Bandwidth: 4
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

No.    Ret.Time Peak Name Height Area Rel.Area Amount Type
      min       mAU mAU*min %
1     7.58    n.a.   586.983   87.337   47.45   n.a.   BMB*
2     8.38    n.a.   496.722   96.711   52.55   n.a.   BMB*
Total: 1083.705 184.048 100.00 0.000

2ce  
/\C

WVL 214 nm
## Table 1: HPLC Analysis Results

<table>
<thead>
<tr>
<th>No</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.54</td>
<td>n.a.</td>
<td>958.690</td>
<td>148.033</td>
<td>98.27</td>
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<tr>
<td>2</td>
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<td>n.a.</td>
<td>11.152</td>
<td>2.500</td>
<td>1.73</td>
<td>n.a.</td>
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<tr>
<td></td>
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<tr>
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<td>959.841</td>
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<td>100.00</td>
<td>0.000</td>
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</tbody>
</table>

### Notes:
- *BMB*: Benzamidobenzocarbonyls
- Ret. Time: Retention Time
- Height: Height of the peak
- Area: Area under the peak
- Rel. Area: Relative Area
- Amount: Amount of the compound

**Graph:**
- UV_VIS_2 Chromatogram
- Time interval: 0.0 to 12.4 minutes
- Wavelength: 214 nm
- Sample Type: unknown
**Sample Information**

- **Sample Name:** SGZ-4-50-2-1+-PC-4 982 214 0.7
- **Injection Volume:** 2.0
- **Vial Number:** GD1
- **Sample Type:** unknown
- **Channel:** UV_VIS_2
- **Control Program:** test-dad2
- **Wavelength:** 214.0
- **Quant. Method:** WXL
- **Recording Time:** 2014-6-30 10:05
- **Run Time (min):** 12.00
- **Sample Weight:** 1.0000
- **Sample Amount:** 1.0000

**Graph and Data Table**

![Graph](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Ret. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.99</td>
<td>n.a.</td>
<td>377.565</td>
<td>47.152</td>
<td>51.43</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>7.81</td>
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<td>311.745</td>
<td>44.523</td>
<td>48.57</td>
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<tr>
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<td>91.675</td>
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</table>
**Sample Name:** SZG-4-48-2-1 PC-4 982 214 0.7  
**Injection Volume:** 2.0  
**Channel:** UV_VIS_2  
**Wavelength:** 214.0  
**Bandwidth:** 4  
**Dilution Factor:** 1.0000  
**Sample Weight:** 1.0000  
**Sample Amount:** 1.0000  
**Run Time (min):** 12.30

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU/min)</th>
<th>Ret.Area %</th>
<th>Amount</th>
<th>Type</th>
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<tbody>
<tr>
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<td>60.426</td>
<td>7.754</td>
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<tr>
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<td><strong>Total</strong></td>
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</tbody>
</table>

**Graph:**

- UV_VIS_2
- 2.0 mAU
- 12.30 min
2364 SZG-4-50-3+- PC-4 982 214 0.7

Sample Name: SZG-4-50-3+- PC-4 982 214 0.7
Injection Volume: 2.0

Vial Number: G03
Channel: UV_VIS_2

Sample Type: unknown
Wavelength: 214.0

Control Program: test-4ad2
Bandwidth: 4

Quant. Method: WX1
Dilution Factor: 1.0000

Recording Time: 2014-6-30 10:32
Sample Weight: 1.0000

Run Time (min): 10.41
Sample Amount: 1.0000

No. | Ret.Time | Peak Name | Height | Area | Rel.Area | Amount | Type
---|----------|-----------|--------|------|----------|--------|-------
1  | 6.19     | n.a.      | 283.671| 30.700| 51.40    | n.a.   | BMB*  
2  | 6.85     | n.a.      | 236.691| 29.023| 48.60    | n.a.   | BMB*  
Total: 520.361 | 59.722 | 100.00 | 0.300 |
Sample Name: SZG-4-48-3 PC-4 982 214 0.7
Injection Volume: 2.0
Channel: UV_VIS_2
Wavelength: 214.0
Bandwidth: 4
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU·min)</th>
<th>Rel. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
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<tr>
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<td>n.a.</td>
<td>3098430</td>
<td>399031</td>
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<td>BMB*</td>
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<td>Total</td>
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<td>3177703</td>
<td>417707</td>
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</table>
2191 SZG-3-79-2+- OD-H 982 214 0.7

Sample Name: SZG-3-79-2+- OD-H 982 214 0.7
Injection Volume: 1.0
Vial Number: G23
Channel: UV_VIS_2
Sample Type: unknown
Wavelength: 214.0
Control Program: test-dad
Bandwidth: 4
Quantif. Method: WDL
Dilution Factor: 1.0000
Recording Time: 2014-6-5 14:46
Sample Weight: 1.0000
Run Time (min): 12.54
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time min</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
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<td>131.402</td>
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<td>n.a.</td>
<td>BM*</td>
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<td>14.833</td>
<td>50.06</td>
<td>n.a.</td>
<td>BM*</td>
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<td>Total</td>
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<td>252.653</td>
<td>29.632</td>
<td>100.00</td>
<td>0.000</td>
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</tr>
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</table>

2d rac
Sample Name: SZG-4-19-4 OD-H 982 214 0.7
Injection Volume: 1.0
Vial Number: GD1
Channel: UV_VIS_2
Sample Type: unknown
Wavelength: 214.0
Control Program: test-dad
Bandwidth: 4
Quartz Method: WXL
Dilution Factor: 1.0000
Recording Time: 2014-6-5 15:00
Sample Weight: 1.0000
Run Time (min): 16.62
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
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<td>6.56</td>
<td>n.a.</td>
<td>229.120</td>
<td>25.943</td>
<td>n.a</td>
<td>BM**</td>
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</tr>
<tr>
<td>2</td>
<td>7.01</td>
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<td>7.268</td>
<td>4.09</td>
<td>1.106</td>
<td>n.a</td>
<td>MB*</td>
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<tr>
<td>Total</td>
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<td>236.388</td>
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</tr>
</tbody>
</table>

*BM** and MB* denote specific peaks or substances.
### 1241 SZG-4-86 OD-H 982 214 0.7

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
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<td>94.93</td>
<td>n.a</td>
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</tr>
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<td>12.439</td>
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<td>5.07</td>
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<td>tMB*</td>
</tr>
</tbody>
</table>

**Total:** 278.095, 29.464, 100.00, 0.000
1932 SZG-4-2-2- IC 955 214 0.7

Sample Name: SZG-4-2-2- IC 955 214 0.7
Injection Volume: 1.0

Vial Number: R06
Channel: UV_VIS_2

Sample Type: unknown
WaveLength: 214.0

Control Program: test-dad2
Bandwidth: 4

Quantif. Method: VXXL
Dilution Factor: 1.0000

Recording Time: 2014-5-13 11:16
Sample Weight: 1.0000

Run Time (min): 12.00
Sample Amount: 1.0000

---

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Ret. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.95</td>
<td>n.a.</td>
<td>304.751</td>
<td>304.751</td>
<td>51.64</td>
<td>n.a.</td>
<td>BMB^*</td>
</tr>
<tr>
<td>2</td>
<td>6.78</td>
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<td>244.028</td>
<td>244.028</td>
<td>48.36</td>
<td>n.a.</td>
<td>BMB^*</td>
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<td>548.779</td>
<td>55.902</td>
<td>100.00</td>
<td>0.000</td>
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</tr>
</tbody>
</table>

---
Sample Name: 2194 SZG-4-19-5 IC 955 214 0.7
Injection Volume: 0.8
Vial Number: 2194
Channel: UV_VIS_1
Sample Type: unknown
Wavelength: 214.0
Control Program: test-dad
Bandwidth: 4
Quantif. Method: WXL
Dilution Factor: 1.0000
Recording Time: 2014-6-5 15:49
Sample Weight: 1.0000
Run Time (min): 10.60
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>7.144</td>
<td>0.960</td>
<td>0.94</td>
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<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>6.72</td>
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<td>90.54</td>
<td>99.05</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>Total</td>
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<td>809.720</td>
<td>91.404</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
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</tbody>
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### 2648 SZG-4-87 IC 955 214 0.7

<table>
<thead>
<tr>
<th>Sample Name:</th>
<th>SZG-4-87 IC 955 214 0.7</th>
<th>Injection Volume:</th>
<th>1.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vial Number:</td>
<td>EE3</td>
<td>Channel:</td>
<td>UV_VIS_2</td>
</tr>
<tr>
<td>Sample Type:</td>
<td>unknown</td>
<td>Wavelength:</td>
<td>214.0</td>
</tr>
<tr>
<td>Control Program:</td>
<td>test-dad2</td>
<td>Bandwidth:</td>
<td>4</td>
</tr>
<tr>
<td>Quantif. Method:</td>
<td>WXL</td>
<td>Dilution Factor:</td>
<td>1.0000</td>
</tr>
<tr>
<td>Recording Time:</td>
<td>2014-8-11 11:15</td>
<td>Sample Weight:</td>
<td>1.0000</td>
</tr>
<tr>
<td>Run Time (min):</td>
<td>12.00</td>
<td>Sample Amount:</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

![Graph](image)

2e gram scale

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.86</td>
<td>r.a.</td>
<td>12.885</td>
<td>1.238</td>
<td>0.77</td>
<td>n.a.</td>
<td>8MB*</td>
</tr>
<tr>
<td>2</td>
<td>6.63</td>
<td>r.a.</td>
<td>1423.477</td>
<td>159.318</td>
<td>99.23</td>
<td>n.a.</td>
<td>8MB*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td></td>
<td></td>
<td>1436.362</td>
<td>160.556</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

---

S152
2066 SZG-3-100-2-- AD-H 98515 214 0.7

Sample Name: SZG-3-100-2-- AD-H 98515 214 0.7
Vial Number: GE4
Sample Type: unknown
Control Program: test-dad2
Guard Method: WGL
Recording Time: 2014-5-26 15:55
Run Time (min): 30.88
Injection Volume: 5.0
Channel: UV_VIS_2
Wavelength: 214.0
Bandwidth: 4
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

No. Ret.Time Peak Name Height Area Rel.Area Amount Type
min mAU mAUmin %
1 20.74 n.a. 41.701 17.237 50.52 n.a. BMB
2 23.21 n.a. 36.116 16.880 49.48 n.a. BMB
Total: 77.817 34.117 100.00 0.000

rac
Zf
1894 SZG-3-95-1 AD-H 982 214 0.7

Sample Name: SZG-3-95-1 AD-H 982 214 0.7
Val Number: RA2
Sample Type: unknown
Control Program: test-dad2
Quantif. Method: WXL
Recording Time: 2014-5-6 15:51
Run Time (min): 14.77

Injection Volume: 1.0
Channel: UV_VIS_2
Wavelength: 214.0
Bandwidth: 6
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.87</td>
<td>n.a.</td>
<td>364.521</td>
<td>40.126</td>
<td>58.56</td>
<td>n.a.</td>
<td>BMD*</td>
</tr>
<tr>
<td>2</td>
<td>6.37</td>
<td>n.a.</td>
<td>161.802</td>
<td>18.400</td>
<td>31.44</td>
<td>n.a.</td>
<td>BMD**</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>526.423</td>
<td>58.525</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

S156
**Sample Name:** SZG-4-51+- PC-4 982 214 0.7

**Injection Volume:** 0.8

**Channel:** UV_VIS 2

**Waveband:** 214.0

**Bandwidth:** 4

**Dilution Factor:** 1.0000

**Recording Time:** 2014-7-3 11:34

**Sample Weight:** 1.0000

**Sample Amount:** 1.0000

---

**Retention Time**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU.min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.28</td>
<td>n.a.</td>
<td>245.623</td>
<td>46.523</td>
<td>48.67</td>
<td>n.a.</td>
<td>BMB</td>
</tr>
<tr>
<td>2</td>
<td>11.64</td>
<td>n.a.</td>
<td>223.466</td>
<td>49.373</td>
<td>51.33</td>
<td>n.a.</td>
<td>BMB</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td></td>
<td></td>
<td>469.094</td>
<td>95.196</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

---

**Diagram:**

Chemical structure of 3c rac

---

S157
<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Ret. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.21</td>
<td>n.a.</td>
<td>9.19</td>
<td>174.638</td>
<td>99.33</td>
<td>n.a.</td>
<td>BMB</td>
</tr>
<tr>
<td>2</td>
<td>11.52</td>
<td>n.a.</td>
<td>30.743</td>
<td>6.663</td>
<td>3.67</td>
<td>n.a.</td>
<td>BMB</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>950.567</td>
<td>181.201</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>
Sample Name: SZG-4-93-1+- PC-4 982 214 0.7
Injection Volume: 2.0
Channel: UV_VIS_1
Sample Type: unknown
Wavelength: 214
Control Program: WIL-2014-2
Bandwidth: n.a.
Quantif. Method: WIL
Dilution Factor: 1.0000
Sample Weight: 1.0000
Run Time (min): 13.89
Sample Amount: 1.0000

---

![Chemical Structure](image)

**Peak Table**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU²/min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.55</td>
<td>n.a.</td>
<td>696.479</td>
<td>102.863</td>
<td>48.79</td>
<td>n.a.</td>
<td>BMB⁺</td>
</tr>
<tr>
<td>2</td>
<td>9.67</td>
<td>n.a.</td>
<td>581.812</td>
<td>101.458</td>
<td>51.21</td>
<td>n.a.</td>
<td>bMB⁺</td>
</tr>
</tbody>
</table>

**Total:**

<p>| | | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>1188.291</td>
<td>201.921</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---
2726 SZG-5.7 PC-4 982 214 0.7

Sample Name: SZG-5.7 PC-4 982 214 0.7
Injection Volume: 1.0
Channel: UV_VIS_2
Wavelength: 214.0
Bandwidth: 4
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000
Run Time (min): 20.00

Peak Name | Ret. Time (min) | Height (mAU) | Area (mAU·min) | Rel.Area (%) | Amount | Type
---|---|---|---|---|---|---
5 | 10.45 | 450.431 | 86.456 | 96.10 | n.a. | BMB
2 | 11.49 | 16.622 | 3.055 | 3.90 | n.a. | BMB

Total: 467.053 89.971 100.00 0.000
**Sample Name:** SZG-5-31 PC-4 82 214 0.7  
**Injection Volume:** 8.0  
**Sample Type:** unknown  
**Channel:** UV_VIS_2  
**Wavelength:** 214.0  
**Bandwidth:** 4  
**Quant. Method:** WXL  
**Recording Time:** 2014-9-9 11:33  
**Sample Weight:** 1.0000  
**Sample Amount:** 1.0000

### Retention Time Table

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.19</td>
<td>n.a.</td>
<td>38.636</td>
<td>5.591</td>
<td>4.84</td>
<td>n.a.</td>
<td>BMB</td>
</tr>
<tr>
<td>2</td>
<td>9.14</td>
<td>n.a.</td>
<td>649484</td>
<td>114886</td>
<td>95.36</td>
<td>n.a.</td>
<td>BMB</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>628120</td>
<td>120457</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

**Diagram:**

[Chemical structure diagram image]

**Notes:**
- Sample details and chromatographic analysis results for compound 2844 SZG-5-31 PC-4 82 214 0.7.
**Sample Information**

- **Sample Name:** SZG-7-56-1+- PC-4 982 214 0.7
- **Vial Number:** GB4
- **Sample Type:** unknown
- **Control Program:** test-dad
- **Quantf. Method:** WXL
- **Recording Time:** 2015-2-3 20:33
- **Run Time (min):** 15.00

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.63</td>
<td>n.a.</td>
<td>691.829</td>
<td>139.396</td>
<td>49.45</td>
<td>n.a</td>
<td>BMB</td>
</tr>
<tr>
<td>2</td>
<td>12.60</td>
<td>n.a.</td>
<td>676.657</td>
<td>142.669</td>
<td>50.55</td>
<td>n.a</td>
<td>BMB</td>
</tr>
</tbody>
</table>

**Total:** 1268.486 282.881 100.00 0.000
### 4167 SZG-7-56-1 PC-4 982 214 0.7

<table>
<thead>
<tr>
<th>Sample Name:</th>
<th>Injection Volume:</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Val. Number:</td>
<td>Channel:</td>
<td>UV_VIS_2</td>
</tr>
<tr>
<td>Sample Type:</td>
<td>Wavelength:</td>
<td>214.0</td>
</tr>
<tr>
<td>Control Program:</td>
<td>Bandwidth:</td>
<td>4</td>
</tr>
<tr>
<td>Quantif. Method:</td>
<td>Dilution Factor:</td>
<td>1.0000</td>
</tr>
<tr>
<td>Recording Time:</td>
<td>Sample Weight:</td>
<td>1.0000</td>
</tr>
<tr>
<td>Run Time (min):</td>
<td>Sample Amount:</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

---

**Graph:**

- Compound: Ph
- Retention Time: 10.59 min
- Area: 172,897
- Height: 868,349
- Relative Area: 96.47%

**Peaks:**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel. Area (%)</th>
<th>Amount (n.a.)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.59</td>
<td>n.a.</td>
<td>868,349</td>
<td>172,897</td>
<td>96.47</td>
<td>n.a.</td>
<td>BM*</td>
</tr>
<tr>
<td>2</td>
<td>12.38</td>
<td>n.a.</td>
<td>26,696</td>
<td>6,330</td>
<td>3.53</td>
<td>n.a.</td>
<td>MB*</td>
</tr>
</tbody>
</table>

**Total:**

- Height: 895,045
- Area: 179,227
- Percent: 100.00
- Amount: 0.000

---

*Ph: Phenyl*
Sample Name: SZG-7-78 PC-4 982 214 0.7  
Vial Number: 082  
Sample Type: unknown  
Control Program: test-dad  
Quantif. Method: WXL  
Recording Time: 2015-3-17 14:03  
Run Time (min): 25.12  
Injection Volume: 1.0  
Channel: UF_VIS_2  
Wavelength: 224.0  
Bandwidth: 4  
Dilution Factor: 1.0000  
Sample Weight: 1.0000  
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height</th>
<th>Area</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.47</td>
<td>n.a.</td>
<td>1062.300</td>
<td>209.737</td>
<td>96.65</td>
<td>n.a.</td>
<td>BM *</td>
</tr>
<tr>
<td>2</td>
<td>12.18</td>
<td>n.a.</td>
<td>31.676</td>
<td>7.280</td>
<td>3.35</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td></td>
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<td></td>
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<tr>
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<td></td>
<td>1083.975</td>
<td>217.017</td>
<td>100.06</td>
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</tr>
</tbody>
</table>

3c one pot 2.0 mmol
## 2895 SZG-7-55-1 IF3 982 214 0.7

**Sample Name:** SZG-7-55-1 IF3 982 214 0.7  
**Injection Volume:** 5.0  
**Sample Type:** unknown  
**Control Program:** WJL-2014-1  
**Quantif. Method:** WJL  
**Recording Time:** 2015/2/7 11:13  
**Run Time (min):** 18.21  
**Wavelength:** UV_VIS_1  
**Dilution Factor:** 1.0000  
**Sample Weight:** 1.0000  
**Sample Amount:** 1.0000

---

**Table:**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU/min)</th>
<th>Rel.Area %</th>
<th>Amount (mg)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.99</td>
<td>n.a</td>
<td>531.138</td>
<td>77.547</td>
<td>50.28</td>
<td>n.a</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>13.21</td>
<td>n.a</td>
<td>330.888</td>
<td>76.685</td>
<td>49.72</td>
<td>n.a</td>
<td>MB**</td>
</tr>
<tr>
<td><strong>Total:</strong></td>
<td></td>
<td></td>
<td>868.025</td>
<td>154.231</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

---

**Graph:**

[Graph of the chromatogram with peaks labeled as 3d and rtC.]
Sample Name: SZG-7-58-2 PC-4 991 214 0.7
Vial Number: BC1
Sample Type: unknown
Control Program: WX1-2014
Quantitative Method: WX1
Recording Time: 2015/2/6 18:19
Run Time (min): 36.00
Injection Volume: 5.0
Channel: UV_VIS_1
Wavelength: 214
Bandwidth: n.a.
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret. Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU/min)</th>
<th>Rel. Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.93</td>
<td>n.a.</td>
<td>1222.615</td>
<td>195.036</td>
<td>50.68</td>
<td>n.a.</td>
<td>BM</td>
</tr>
<tr>
<td>2</td>
<td>9.18</td>
<td>n.a.</td>
<td>1007.291</td>
<td>189.790</td>
<td>49.32</td>
<td>n.a.</td>
<td>M</td>
</tr>
<tr>
<td>Total</td>
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<td>2229.906</td>
<td>384.827</td>
<td>100.00</td>
<td>0.000</td>
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</tr>
</tbody>
</table>

rac

3e
### 2892 SZG-7-55-2 PC-4 991 214 0.7

<table>
<thead>
<tr>
<th>Sample Name:</th>
<th>SZG-7-55-2 PC-4 991 214 0.7</th>
<th>Injection Volume:</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Val Number:</td>
<td>BC2</td>
<td>Channel:</td>
<td>UV_VIS_1</td>
</tr>
<tr>
<td>Sample Type:</td>
<td>unknown</td>
<td>Wavelength:</td>
<td>214</td>
</tr>
<tr>
<td>Quantif. Method:</td>
<td>WXL</td>
<td>Dilution Factor:</td>
<td>1.0000</td>
</tr>
<tr>
<td>Recording Time:</td>
<td>2015/2/6 20:22</td>
<td>Sample Weight:</td>
<td>1.0000</td>
</tr>
<tr>
<td>Run Time (min):</td>
<td>11.01</td>
<td>Sample Amount:</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

### Chromatogram

![Chromatogram](image)

### Table

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.79</td>
<td>n.a.</td>
<td>1759.955</td>
<td>278938</td>
<td>93.12</td>
<td>n.a.</td>
<td>BM*</td>
</tr>
<tr>
<td>2</td>
<td>9.01</td>
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<td>n.a.</td>
<td>MB*</td>
</tr>
<tr>
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<td>299533</td>
<td>100.00</td>
<td>0.00</td>
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</tr>
</tbody>
</table>

S171
2889 SZG-7-57 PC-4 991 214 0.7

Sample Name: SZG-7-57 PC-4 991 214 0.7
Vial Number: BD1
Sample Type: unknown
Control Program: WXL-2014
Quantif. Method: WXL
Recording Time: 2015/2/6 16:23
Run Time (min): 22.95

Injection Volume: 5.0
Channel: UV_VIS_1
Wavelength: 214
Bandwidth: n.a.
Dilution Factor: 1.0000
Sample Weight: 1.0000
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height</th>
<th>Area</th>
<th>Rel.Area</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>13.56</td>
<td>n.a.</td>
<td>200.590</td>
<td>58.299</td>
<td>49.99</td>
<td>n.a.</td>
<td>BM *</td>
</tr>
<tr>
<td>2</td>
<td>17.04</td>
<td>n.a.</td>
<td>156.760</td>
<td>55.228</td>
<td>50.01</td>
<td>n.a.</td>
<td>BM *</td>
</tr>
<tr>
<td>Total</td>
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<td></td>
<td>357.350</td>
<td>110.437</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

**Image Description:**
- The image contains a chromatogram with peak identifiers 1 and 2.
- Peak 1 has a retention time of 13.56 minutes and an area of 200.590 mAU.
- Peak 2 has a retention time of 17.04 minutes and an area of 156.760 mAU.
- The total area is 357.350 mAU.

**Chemical Structure:**
- The chemical structure shown includes a MeO group and a ketone group.
- The structure is annotated with peaks 1 and 2, indicating specific retention times and areas.
4342 SZG-4-89 PC-4 982 214 0.7

Sample Name: SZG-4-89 PC-4 982 214 0.7
Injection Volume: 5.9

Val Number: BC6
Channel: UV_VIS_2

Sample Type: unknown
Wavelength: 214.0

Control Program: test-dad
Bandwidth: 4

Quantif. Method: WX1
Dilution Factor: 1.0000

Recording Time: 2015-3-10 18:50
Sample Weight: 1.0000

Run Time (min): 15.00
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU•min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8.39</td>
<td>n.a.</td>
<td>221.806</td>
<td>34.096</td>
<td>49.53</td>
<td>n.a.</td>
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</tr>
<tr>
<td>2</td>
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<td>34.748</td>
<td>50.47</td>
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Total: 397.560 68.844 100.00 0.000

Ph

Ph

3g
rac

1: 8.387
2: 10.407
**4309 SZG-7-60-4B PC-4 982 214 0.7**

- **Sample Name:** SZG-7-60-4B PC-4 982 214 0.7
- **Injection Volume:** 3.0
- **Vial Number:** RB1
- **Channel:** UV_VIS_2
- **Sample Type:** unknown
- **Wavelength:** 214.0
- **Control Program:** test-dad
- **Bandwidth:** 4
- **Quantif. Method:** WXl
- **Dilution Factor:** 1.0000
- **Recording Time:** 2015-3-9 9:24
- **Sample Weight:** 1.0000
- **Run Time (min):** 17.04
- **Sample Amount:** 1.0000

---

![Chromatogram](image)

**Table:**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
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<td><strong>Total:</strong></td>
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<td></td>
<td>1747.963</td>
<td>284.122</td>
<td></td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

---

**Legend:**

- **Ph+**: Phenyl group
- **3g one pot**: 3 grams in one pot
8. VCD and IR experimental of 2c.

BioTools ChiralIR-2X FT-VCD spectrometer, equipped with a single photoelastic modulation (PEM) and a mercury cadmium tellurium (MCT) detector, was used to record the VCD and IR spectra. A solution of 2c (79 mg) in CDCl$_3$ (150μL) was placed in a BaF$_2$ cell with a path length of 75μm. Data were acquired at a resolution of 4 cm$^{-1}$ for 3 h. The racemic sample was measured under the same conditions to obtain VCD baseline.

VCD and IR calculations

Conformational analysis of (R)-2c was performed with Compute VOA (BioTools Inc., Jupiter, FL) using the Monte Carlo protocol at the molecular mechanic force field MMFF94 level. Within a 20 kcal/mol window, four energetically distinct conformers were predicted. Geometry optimization and frequencies calculation were carried out using the B3PW91 hybrid density functional and LANL2DZ basis set with Gaussian 09 (Gaussian Inc., Wallingford, CT). Boltzmann-population-weighted composite VCD and IR spectra were then generated by Compute VOA.

Comparisons of experimental and calculated VCD and IR spectra can be seen in Figure S2. A scaling factor of 0.96, obtained from Compare VOA (BioTools Inc., Jupiter, FL), has been applied to the calculated VCD and IR frequencies. The comparisons establish the absolute configuration of 2c as (R).

The assignment was evaluated by Compare VOA. Table S7 shows the related result, including spectral similarities and enantiomeric similarity index (the difference between the VCD spectral similarity of the correct and the incorrect enantiomers, ESI). The confidence level of the (R) assignment is 93%, based on the current Compare VOA database consisting of 105 previous correct assignments for different chiral structures.
**Figure S2.** VCD and IR spectra observed for 2c compared with the corresponding calculated spectra of $(R)$-2c.

**Table S7.** Compare VOA result for VCD and IR spectra of 2c

<table>
<thead>
<tr>
<th>Calculation Method</th>
<th>$^aS_{IR}$</th>
<th>$^bS_{IR}$</th>
<th>$^cS_{IR}$</th>
<th>$^dESI$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DFT/B3PW91/LANL2DZ</td>
<td>74.0</td>
<td>65.8</td>
<td>9.3</td>
<td>56.5</td>
</tr>
</tbody>
</table>

$^a$ IR spectral similarity  
$^b$ VCD spectral similarity for the $(R)$-configuration  
$^c$ VCD spectral similarity for the $(S)$-configuration  
$^d$ Enantiomeric similarity index.
9. X-ray crystallography of 2ac and 4

Figure S3. ORTEP drawing of 2ac
Figure S5. X-ray crystallography of 2ac
Figure S6. X-ray crystallography of 4