Supporting Information (74 Pages)

Engaging electronic effects for atropselective [5+2]-photocycloaddition of maleimides.

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1. General methods

All commercially obtained reagents/solvents were used as received; chemicals were purchased from Alfa Aesar®, Sigma-Aldrich®, Acros organics®, TCI America®, Mallinckrodt®, and Oakwood® Products, and were used as received without further purification. Unless otherwise stated, reactions were conducted in oven-dried glassware under nitrogen atmosphere. $^1$H-NMR and $^{13}$C-NMR spectra were recorded on Varian 400 MHz (100 MHz for $^{13}$C) and on 500 MHz (125 MHz for $^{13}$C) spectrometers. Data from the $^1$H-NMR spectroscopy are reported as chemical shift ($\delta$ ppm) with the corresponding integration values. Coupling constants ($J$) are reported in hertz (Hz). Standard abbreviations indicating multiplicity are used as follows: s (singlet), b (broad), d (doublet), t (triplet), q (quartet), m (multiplet) and virt (virtual). Data for $^{13}$C NMR spectra are reported in terms of chemical shift ($\delta$ ppm). HPLC analyses were performed on Waters® HPLC equipped with 2525 pump or on Dionex® Ultimate 3000 HPLC. Waters® 2767 sample manager was used for automated sample injection on Waters® HPLC Ultimate 3000 sample injector was used for injection on Dionex® HPLC. All HPLC injections were monitored using a Waters® 2487 dual wavelength absorbance detector at 254 and 270 nm or on Dionex® HPLC were monitored using a diode array detector (DAD3000125). Analytical and semi-preparative injections were performed on chiral stationary phase using various columns as indicated below.

i) Regis® PIRKLE COVALENT (R,R) WHELK–01
   a) 25 cm x 4.6 mm column for analytical injections.
   b) 25 cm x 10 mm column for semi-preparative injections.

ii) CHIRALCEL® OD-H
    a) 0.46 cm x 25 cm column for analytical injections.
    b) 10 mm x 25 cm column for semi-preparative injections.

iii) CHIRALPAK® AD-H
     a) 0.46 cm x 25 cm column for analytical injections.
     b) 10 mm x 25 cm column for semi-preparative injections

iv) CHIRALPAK® IC
    a) 0.46 cm x 25 cm column for analytical injections.
    b) 10 mm x 25 cm column for semi-preparative injections

Masslynx software version 4.1 was used to monitor/analyze the HPLC injections on Waters® and to process HPLC traces. Chromeleon 7 software was used to monitor and process HPLC injections on Dionex® HPLC. Igor Pro® Software version 6.0 was used to process the HPLC graphics. Optical activity values were recorded on JASCO® DIP – 370 digital polarimeter. When necessary, the
compounds were purified by combiflash equipped with dual wavelength UV-Vis absorbance detector (Teledyne ISCO) using hexanes:ethyl acetate as the mobile phase and Redisep® cartridge filled with silica (Teledyne ISCO) as stationary phase. In some cases, compounds were purified by column chromatography on silica gel (Sorbent Technologies®, silica gel standard grade: porosity 60 Å, particle size: 230 x 400 mesh, surface area: 500 – 600 m²/g, bulk density: 0.4 g/mL, pH range: 6.5 – 7.5). Unless indicated, the Retardation Factor (Rf) values were recorded using a 5-50% hexanes: ethyl acetate as mobile phase and on Sorbent Technologies®, silica Gel TLC plates (200 mm thickness w/UV254). Absorbance measurements were performed using Agilent technologies® Cary 300 UV-Vis spectrophotometer.

2. Chemical structures of maleimides and synthetic protocol

2.1. Chemical structures of maleimides

![Chemical Structures](image_url)

- **1(a-i)**
  - a) R¹-R⁴ = H
  - b) R¹ = Me; R²-R⁴ = H
  - c) R¹ = Br; R²-R⁴ = H
  - d) R¹ = Ph; R²-R⁴ = H
  - e) R¹ = Ph; R² = H; R³-R⁴ = Me
  - f) R¹ = OMe; R²-R⁴ = H
  - g) R¹ = CF₃; R²-R⁴ = H
  - h) R¹ = Me; R² = Br; R³-R⁴ = H
  - i) R¹ = (Me)₂; R²-R⁴ = H

- **2(a-h)**
  - a) R¹ = H; b) R¹ = Me; c) R¹ = Br; d) R¹ = Ph; e) R¹ = CF₃

- **3(a-e), 3(g-h)**

- **4a-e**
  - a) R¹ = H; b) R¹ = Me; c) R¹ = Br; d) R¹ = Ph; e) R¹ = CF₃

- **4f**

- **4h**

- **5**

- **6**

- **7**

- **8**

- **9**

- **10**
2.2. Synthetic protocol for aniline derivatives 5 and maleimides 1a-i

![Diagram of synthetic protocol for aniline derivatives 5 and maleimides 1a-i]

(a) Toluene, 45 °C, 2 h; (b) CH$_3$COONa, CH$_3$COOH, reflux, 2 h
3. General procedure for the synthesis atropisomeric maleimide 1a-i and their precursors

3.1. Synthesis of 2-amino benzyl alcohol 7

The benzyl alcohol derivative was synthesized according to a procedure reported in the literature.\(^1\) To a slurry of lithium aluminum hydride (2.5 equiv.) in dry THF (50 mL) under N\(_2\) atmosphere at 0 °C, a solution anthranilic acid derivative 8 (4.0 g, 1.0 equiv.) in dry THF (50 mL) was added over a period of 15 min without allowing the internal temperature to rise above 5 °C. The resulting mixture was allowed to warm to room temperature over 12 h. After the reaction, the mixture was cooled to 0 °C and quenched with saturated Na\(_2\)SO\(_4\) solution over 15 min. To the resulting solid mixture DCM (CH\(_2\)Cl\(_2\), 75 mL) was added, stirred for 15 min, filtered and the filtered solid residue was washed with DCM (50 mL). The combined organic layer was dried over anhyd. Na\(_2\)SO\(_4\), filtered and the solvent was removed under reduced pressure to get the crude product. The crude product was directly taken to next step without further purification.

\[ \text{Rf} = 0.45 \text{ (50% hexanes: 50% ethyl acetate), Yield for 7 = 90\%} \]

\(^1\)H-NMR (400 MHz, CDCl\(_3\), δ ppm): 7.03-7.01 (m, 1H), 6.92-6.90 (m, 1H), 6.65-6.61 (m, 1H), 4.61 (s, 2H), 3.40 (bs, 3H) and 2.15 (m, 3H).

\(^{13}\)C-NMR (100 MHz, CDCl\(_3\), δ ppm): 144.3, 130.7, 127.3, 124.4, 122.9, 117.9, 64.7 and 17.5.
3.2. Synthesis of 2-methoxymethylaniline 6

\[
\begin{array}{c}
\text{NH}_2 \\
\text{MeOH, Concd. H}_2\text{SO}_4 \\
\text{Reflux, 7 h}
\end{array}
\rightarrow
\begin{array}{c}
\text{NH}_2 \\
\text{6}
\end{array}
\]

Scheme S2: Synthesis of 2-methoxymethylaniline derivative 6.

The methoxyaniline derivative was synthesized according to a procedure reported in the literature.\(^2\) To a solution of aminobenzyl alcohol derivative 7 (5.0 g, 1.0 equiv.) in methanol (40 mL) at 0 °C, concd. H\(_2\)SO\(_4\) (1.1 equiv.) was added over 5 min. The resulting mixture was heated to 50 °C for 7 h. After the reaction, the mixture was cooled to 10 °C and neutralized with saturated Na\(_2\)CO\(_3\) solution carefully, during which a brisk effervescence was observed. The aqueous layer was extracted with DCM (3 × 40 mL). The combined organic layer was dried over anhyd. Na\(_2\)SO\(_4\), filtered and the solvent was removed under reduced pressure to get the crude product. The crude product was purified by combiflash using a hexanes: ethyl acetate mixture.

R\(_f\) = 0.80 (50% hexanes: 50% ethyl acetate), Yield for 6 = 77%

\(^1\)H-NMR (400 MHz, CDCl\(_3\), \(\delta\) ppm): 7.05-7.03 (m, 1H), 6.96-6.94 (m, 1H), 6.6-6.62 (m, 1H), 4.49 (s, 2H), 4.12 (bs, 2H), 3.33 (s, 3H) and 2.17 (s, 3H).

\(^13\)C-NMR (100 MHz, CDCl\(_3\), \(\delta\) ppm): 144.6, 130.7, 128.3, 122.5, 121.5, 117.5, 74.1, 57.6, and 17.5.
3.3. Synthesis of 2-(allyl)aniline 5

![Scheme S3: Synthesis of 2-(allyl)aniline derivative 5.](image)

To a solution methoxyaniline derivative 6 (5.3 g, 1.0 equiv.) in dry THF (40 mL) at 0 °C, allyl magnesium halide (2.0 M in THF, 2.2 equiv.) was added slowly over 15 min. The resulting mixture was allowed to warm to room temperature over 12 h. After the reaction, the mixture was cooled to 0 °C and quenched with dil. HCl. The aqueous layer was extracted with DCM (3 × 50 mL). The combined organic layer was dried over anhyd. Na₂SO₄, filtered and the solvent was removed under reduced pressure to get the crude product. The crude product was purified by combiflash using a hexanes: ethyl acetate mixture.

Rf = 0.40 (80% hexanes: 20% ethyl acetate), Yield for 5 = 55%

¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.03-6.95 (m, 2H), 6.69-6.66 (m, 1H), 6.12-5.94 (m, 1H), 5.20-5.12 (m, 2H), 3.68 (bs, 2H), 3.38-3.34(m, 2H) and 2.22 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃, δ ppm): 143.0,136.1,128.8,128.0,123.3,122.3,118.1,1,116.1,36.8 and 17.6.
3.4. Synthesis of atropisomeric maleimide derivatives 1a-d, 1g, 1i

Scheme S4: Synthesis of atropisomeric maleimide derivatives 1a-d, 1g-1h and 1i.

To a solution of aniline derivative 5 (500 mg, 1.1 equiv.) in toluene (5 mL) corresponding anhydride 4a-e, 4f, 4h (1.0 equiv.) was added and the resulting mixture was heated to 50 °C for 2 h. After the reaction, the solvent was concentrated and the residue was directly taken to next step. To the residue from the above reaction in glacial acetic acid (5 mL), anhyd. sodium acetate (236 mg, 2.88 mmol) was added. The resulting mixture was refluxed for 2 h. After the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The organic layer was washed with DI water (2 x 15 mL), saturated NaHCO₃ solution (2 x 15 mL), dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure to yield crude product. The crude product was purified by combiflash using a hexanes:ethyl acetate mixture.

TLC condition - Rf = 0.45 (80% hexanes:20% ethyl acetate) for 1a (Yield = 54 %)

1H-NMR (400 MHz, CDCl₃, δ ppm): 7.27-7.23 (m, 1H), 7.16-7.12 (m, 2H), 5.81-5.71 (m, 1H), 4.98-4.93 (m, 2H), 3.19-3.17 (d, J = 6.4 Hz, 2H) and 2.07 (s, 3H).

13C-NMR (100 MHz, CDCl₃, δ ppm): 169.9, 130.3, 137.6, 136.1, 134.5, 129.9, 129.4, 129.3, 128.3, 116.6, 36.9 and 18.1.

TLC condition - Rf = 0.65 (80% hexanes:20% ethyl acetate) for 1b (Yield = 60 %)

1H-NMR (400 MHz, CDCl₃, δ ppm): 7.28-7.24 (m, 1H), 7.17-7.12 (m, 2H), 6.46-6.45 (q, J = 5.2 Hz 1H), 5.82-5.72 (m, 1H), 4.98-4.93 (m, 2H), 3.19-3.17 (d, J = 6.8 Hz, 2H), 2.14-2.14 (d, J = 2 Hz, 2H) and 2.09 (s, 3H).

13C-NMR (100 MHz, CDCl₃, δ ppm): 170.9, 169.9, 146.1, 139.3, 137.5, 136.2, 129.7, 129.6, 129.3, 128.2, 127.8, 116.4, 36.9, 18.2 and 11.4.
TLC condition - \( R_f = 0.50 \) (80\% hexanes:20\% ethyl acetate) for 1c (Yield = 67\%)

\( ^1\text{H-NMR (400 MHz, CDCl}_3, \delta \text{ ppm): } 7.30-7.26 \text{ (m, 1H), 7.18-7.14 \text{ (m, 2H), 6.99 (s,1H), 5.81-5.71 \text{ (m, 1H), 5.00-4.94 \text{ (m, 2H), 3.20-3.19 (d, J = 6.8 Hz, 2H) and 2.10 (s, 3H).} \)

\( ^{13}\text{C-NMR (100 MHz, CDCl}_3, \delta \text{ ppm): } 167.7, 164.4, 139.2, 137.5, 136.0, 132.3, 131.9, 130.2, 129.5, 129.1, 128.4, 116.7, 37.1 \text{ and 18.1.} \)

TLC condition - \( R_f = 0.50 \) (80\% hexanes:20\% ethyl acetate) for 1d (Yield = 78\%)

\( ^1\text{H-NMR (400 MHz, CDCl}_3, \delta \text{ ppm): } 8.03-8.00 \text{ (m, 2H), 7.49-7.48 \text{ (m, 3H), 7.32-7.29 \text{ (m, 1H), 7.23-7.21 \text{ (m, 2H), 6.90 (s, 1H), 5.91-5.80 \text{ (m, 1H), 5.04-5.00 \text{ (m, 2H), 3.31-3.29 (d, J = 6.4 Hz, 2H) and 2.1 (s, 3H).} \)

\( ^{13}\text{C-NMR (100 MHz, CDCl}_3, \delta \text{ ppm): } 169.9, 169.5, 144.1, 139.4, 137.7, 136.3, 131.6, 129.8, 129.8, 129.4, 129.3, 129.1, 128.9, 128.3, 124.3, 116.6, 37.1 \text{ and 18.3.} \)

TLC condition - \( R_f = 0.60 \) (80\% hexanes:20\% ethyl acetate) for 1g (Yield = 40\%)

\( ^1\text{H-NMR (400 MHz, CDCl}_3, \delta \text{ ppm): } 7.32-7.28 \text{ (m, 1H), 7.21-7.15 \text{ (m, 2H), 7.09-7.08 (q, J = 5.2Hz, 1H), 5.79-5.69 \text{ (m, 1H), 4.99-4.92 \text{ (m, 2H), 3.22-3.20 (d, J = 6.8 Hz, 2H) and 2.10 (s, 3H).} \)

\( ^{13}\text{C-NMR (100 MHz, CDCl}_3, \delta \text{ ppm): } 166.2, 163.9, 139.0, 137.5, 136.0, 133.7, 130.3, 129.6, 128.7, 128.5, 120.8, 118.1, 116.5, 37.3 \text{ and 17.9.} \)

TLC condition - \( R_f = 0.50 \) (80\% hexanes:20\% ethyl acetate) for 1h (Yield = 60\%)

\( ^1\text{H-NMR (400 MHz, CDCl}_3, \delta \text{ ppm): } 7.29-7.25 \text{ (m, 1H), 7.18-7.15 \text{ (m, 2H), 5.81-5.71 \text{ (m, 1H), 4.99-4.93 \text{ (m, 2H), 3.20-3.18 (d, J = 6.8 Hz, 2H), 2.11 (s, 3H) and 2.09 (s, 3H).} \)

\( ^{13}\text{C-NMR (100 MHz, CDCl}_3, \delta \text{ ppm): } 168.5, 164.5, 142.8, 139.2, 137.6, 136.1, 129.9, 129.4, 128.3, 125.5, 116.5, 37.0, 18.2 \text{ and 11.2.} \)
3.5. Synthesis of atropisomeric maleimide derivative 1e

![Scheme S5: Synthesis of atropisomeric maleimide derivative 1e.](image)

To a solution of aniline derivative 9 (500 mg, 1.1 equiv.) in toluene (5 mL) corresponding anhydride 4d (1.0 equiv.) was added and the resulting mixture was heated to 50 °C for 2 h. After the reaction, the solvent was concentrated and the residue was directly taken to next step. To the residue from the above reaction in glacial acetic acid (5 mL), anhyd. sodium acetate (236 mg, 2.88 mmol) was added. The resulting mixture was refluxed for 2 h. After the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate (20 mL). The organic layer was washed with DI water (2 x 15 mL), saturated NaHCO₃ solution (2 x 15 mL), dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure to yield crude product. The crude product was purified by combiflash using a hexanes:ethyl acetate mixture.

TLC condition - Rf = 0.2 (95% hexanes:5% ethyl acetate) for 1e (Yield = 68 % )

¹H-NMR (400 MHz, CDCl₃, δ ppm): 7.98-7.96 (m, 2H), 7.48-7.46 (m, 3H), 7.02-6.98 (d, J = 16.4, 2H), 6.85 (s, 1H), 4.72 (s, 1H), 4.62 (s, 1H), 3.19 (s, 2H), 2.34 (s, 3H), 2.12 (s, 3H), and 1.59 (s, 3H).

¹³C-NMR (100 MHz, CDCl₃, δ ppm): 169.7, 169.6, 144.0, 139.5, 138.5, 137.3, 131.5, 130.2, 129.6, 129.2, 129.0, 128.9, 42.6, 22.1, 21.4 and 18.1.
3.6. Synthesis of atropisomeric maleimide derivative 1f

![Scheme S6: Synthesis of atropisomeric maleimide derivative 1f.](image)

To a solution of bromo maleimide derivative 1c (500 mg, 1.0 equiv.) in MeOH (5 mL) triethylamine in MeOH (1.1 equiv.) was added and the resulting mixture refluxed for 1 h. After the reaction, the solvent was concentrated and the reaction mixture was quenched with DI water. The aqueous layer is extracted with DCM (20 mL). The combined organic layer was dried over anhyd. Na₂SO₄, filtered and concentrated under reduced pressure to yield crude product. The crude product was purified by combiflash using a hexanes:ethyl acetate mixture.

TLC condition - Rf = 0.40 (50% hexanes:50% ethyl acetate) , Yield = 63 %

^1^H-NMR (400 MHz, CDCl₃, δ ppm): 7.27-7.23 (m, 1H), 7.15-7.11 (m, 2H), 5.83-5.72 (m, 1H), 5.54 (s, 1H), 4.99-4.95 (m, 2H), 3.96 (s, 3H), 3.20 (d, J = 6.8, 2H) and 2.10 (s, 3H).

^1^3^C-NMR (100 MHz, CDCl₃, δ ppm): 169.3, 164.7, 161.0, 139.4, 137.7, 137.1, 129.8, 129.3, 129.0, 128.2, 116.5, 96.7, 59.2, 36.9 and 18.2.
4. Racemization kinetics of non-biaryl axially chiral maleimides 1c-f

Racemization kinetics of optically pure atropisomeric maleimides 1c-f was performed at 100 °C in toluene. The racemization (% ee) was followed by HPLC analyses on a chiral stationary phase at different time intervals (Figures S1). The activation energy (Table S1) for racemization was computed from equations 1 and 2.

\[ k_{\text{rac}} = \kappa \left( \frac{k_B T}{h} \right) e^{-\Delta G_{\text{rac}}^\ddagger / RT} \]

\[ \Delta G_{\text{rac}}^\ddagger = -RT \ln \left( \frac{h k_{\text{rac}}}{\kappa T k_B} \right) \]

The half-life of racemization, \( \tau_{1/2} \), can be calculated using the rate constant of racemization \( k_{\text{rac}} \) (assuming \( 1-P_0 = 0 \) at \( t = 0 \)).

\[ \ln \left( \frac{x_{eq}}{x_{eq} - x} \right) = \ln \left( \frac{R_0}{2R - R_0} \right) = \ln \left( \frac{R + S}{R - S} \right) = 2k_{\text{enant}} t \]  
Equation 1.

\[ \ln \left( \frac{R_0}{R_0 - x} \right) = k_{\text{rac}} t \]  
Equation 2.

Where,

\( k_{\text{rac}} = 2k_{\text{enant}} \)

\( R_0 \) is the initial concentration of the \( (R) \)-enantiomer;

\( x = R_0 - R, S \) (concentration of the racemate at time \( t \)); and

\( k_{\text{rac}} \) is the rate constant for racemization

**Note:** \( R_0 = R + S \)

At 50% ee, the equation becomes:

\[ \tau_{1/2(\text{enant})} = \frac{\ln 2}{2k_{\text{enant}}} \quad \text{or} \quad \tau_{1/2(\text{rac})} = \frac{\ln 2}{k_{\text{rac}}} \]
**Figure S1:** Racemization kinetics of maleimides 1c-f in toluene at 100 °C.

**Table S1:** Half-life, activation energy and rate for racemization of maleimides 1c-f in toluene at 100 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>$\tau_{1/2\text{rac}}$ (days)</th>
<th>$\Delta G_{\text{rac}}^z$ (kcal-mol$^{-1}$)</th>
<th>$k_{\text{rac}}$ (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1c</td>
<td>23</td>
<td>33.0</td>
<td>3.5 X 10$^{-7}$</td>
</tr>
<tr>
<td>2</td>
<td>1d</td>
<td>32</td>
<td>33.3</td>
<td>2.5X 10$^{-7}$</td>
</tr>
<tr>
<td>3</td>
<td>1e</td>
<td>26</td>
<td>33.1</td>
<td>3.1 X 10$^{-7}$</td>
</tr>
<tr>
<td>4</td>
<td>1f</td>
<td>17</td>
<td>32.8</td>
<td>4.6 X 10$^{-6}$</td>
</tr>
</tbody>
</table>

Reported values carry an error of ±5%.
5. **UV-Vis Spectrum of atropisomeric maleimides and its photoproducts**

The UV-Vis spectra of atropisomeric maleimides and its photoproducts were measured in acetonitrile.

![UV-Vis spectra of maleimides and photoproducts](image)

**Figure S2:** UV-Vis spectra of maleimides 1 and its photoproducts 2 and 3 in acetonitrile.
**Figure S3**: Molar absorptivity of 1 for the longest absorption wavelength.

**Solvatochromic effect**: The UV-Vis spectra of atropisomeric maleimide 1d in various solvent viz. Methyl cyclohexane (MCH), acetonitrile (MeCN) and methanol (MeOH).

![UV-Vis spectra of maleimides 1d in various solvents](image)

**Figure S4**: UV-Vis spectra of maleimides 1d in various solvents.
6. **General irradiation procedures and characterization of photoproducts.**

6.1. Solvent optimization for photoreaction of maleimides 1a

Several solvents were screened for the photoreaction of atropisomeric maleimide 1a. In a typical experiment, maleimide 1a in a given solvent (~3.9 mM concentration) was degassed with N₂ for 15 min and then sealed for photoreaction. This solution was irradiated in a Rayonet reactor (~300 nm or ~350 nm) for 3 h. After the reaction, a stock solution of internal standard (triphenylmethane) was added and this solution was concentrated under reduced pressure to obtain the crude reaction mixture. ¹H-NMR spectroscopy was recorded on the crude reaction mixture and from the integral values the conversion and mass balance were calculated (refer to section 7.3).

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>NMR Yield (%)</th>
<th>% mass balance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetonitrile</td>
<td>26 (60)</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ethyl acetate</td>
<td>Decomposed</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Dichloromethane</td>
<td>20 (59)</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Chloroform</td>
<td>Decomposed</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Benzene</td>
<td>33 (50)</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>MCH</td>
<td>35 (59)</td>
<td></td>
</tr>
</tbody>
</table>

*Note: The reported value carry an error of ±5%.

6.2. Photoreaction of atropisomeric maleimides 1a under various atmospheric conditions:

![Scheme 7: General irradiation procedure for maleimides 1a](image)

In a typical experiment, maleimide 1a in MeCN (~3.9 mM concentration) was bubbled with Nitrogen or Oxygen for 8-10 min. For irradiation under air, the reaction mixture was irradiated without bubbling. The resultant solution was irradiated in a Rayonet reactor (~300 nm or ~350 nm) for 3 h. After the reaction, a stock solution of internal standard (triphenylmethane) was added and this solution was concentrated under reduced pressure to obtain the crude reaction mixture. ¹H-NMR
spectroscopy was recorded on the crude reaction mixture and from the integral values the conversion and mass balance were calculated (refer to section 7.3).

**Table S3: Photoreaction of 1a at various atmospheric conditions**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Condition</th>
<th>NMR Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Nitrogen</td>
<td>23</td>
</tr>
<tr>
<td>2</td>
<td>Oxygen</td>
<td>22</td>
</tr>
<tr>
<td>3</td>
<td>Air</td>
<td>26</td>
</tr>
</tbody>
</table>

*Note:* The reported value carry an error of ±5%.

6.3. Process for photoreaction of atropisomeric maleimides 1a-l

**Scheme 8: General irradiation procedure for maleimides 1a-l**

**Enantiospecific reactions:** A solution of optically pure atropisomeric maleimides obtained from HPLC preparative separation on a chiral stationary phase (2.5-4.0 mM or 1 mg/1 mL) in appropriate solvent was irradiated in a Rayonet reactor fitted with bulb of desired wavelength. After the irradiation, the solvent was evaporated under reduced pressure and the photoproducts were isolated by preparative thin layer chromatography and characterized by NMR spectroscopy, mass spectrometry, single crystal XRD, [α]_D and by HPLC. HPLC analysis of the photoproduct(s) on a chiral stationary phase gave the optical purity of the photoproducts.

**Large-scale reactions:** Large-scale reactions were carried out on racemic maleimides as batches (4 × 20 mL test tubes per batch). After the irradiation the solutions were combined and the solvent was evaporated under reduced pressure. The residue was purified by combiflash using a hexanes:ethyl acetate mixture as mobile phase. Conversion and mass balance were obtained from NMR integration of the crude reaction mixture against triphenylmethane as an internal standard using the following formula
\[
\text{mol}_a = \text{mol}_i \times \left( \frac{\text{Integral of analyte}}{\text{Integral of Int. Std}} \right) \times \frac{N_a}{N_i}
\]

Where, \(N_a\) and \(N_i\) are the number of nuclei giving rise to the relevant analyte and internal standard signals respectively. Similarly \(\text{mol}_a\) and \(\text{mol}_i\) are the molarity of analyte and the internal standard in deuterated chloroform, respectively.

The \(dr\) of the photoproducts 2 and 3 were calculated from the crude reaction mixture after the photoreaction.

**Table S4**: Analysis of conversion and \(dr\) in the photoproducts

<table>
<thead>
<tr>
<th>Entry</th>
<th>Compound</th>
<th>% NMR Yield (% mass balance)</th>
<th>(dr) (2:3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1a</td>
<td>26 (60)</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>1b</td>
<td>16 (76)</td>
<td>60:40</td>
</tr>
<tr>
<td>3</td>
<td>1c</td>
<td>20 (60)</td>
<td>65:35</td>
</tr>
<tr>
<td>4</td>
<td>1d</td>
<td>50 (85)</td>
<td>70:30</td>
</tr>
<tr>
<td>5</td>
<td>1e</td>
<td>14 (86)</td>
<td>74:26</td>
</tr>
<tr>
<td>6</td>
<td>1f</td>
<td>18 (50)</td>
<td>99:1</td>
</tr>
<tr>
<td>7</td>
<td>1g</td>
<td>26 (98)</td>
<td>45:55</td>
</tr>
<tr>
<td>8</td>
<td>1h</td>
<td>18 (98)</td>
<td>69:31</td>
</tr>
<tr>
<td>9</td>
<td>1i</td>
<td>No reaction</td>
<td></td>
</tr>
</tbody>
</table>

*Note: The reported value carry an error of ±5%.*
TLC condition - $R_f = 0.30$ (80% hexanes:20% ethyl acetate) for **2a**

$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.05-7.01 (m, 3H), 6.58-6.65 (m, 1H), 6.39-6.36 (m, 1H), 5.08-5.02 (m, 1H), 3.66-3.59 (m, 1H), 3.08-2.99 (m, 1H), 2.78-2.72 (m, 2H) and 2.23 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 209.9, 172.5, 148.9, 146.3, 145.7, 141.5, 141.3, 138.2, 135.7, 132.4, 67.0, 60.9, 44.5 and 31.9.

---

TLC condition - $R_f = 0.15$ (80% hexanes:20% ethyl acetate) for **2b**

$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.03-6.99 (m, 3H), 6.46-6.45 (m, 1H), 5.01-4.96 (m, 1H), 3.61-3.54 (m, 1H), 3.07-3.00 (m, 1H), 2.80-2.73 (m, 2H), 2.22 (s, 3H) and 2.05-2.04 (d, J = 4 Hz 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 200.9, 162.9, 145.3, 139.1, 132.3, 131.4, 131.2, 127.9, 125.4, 122.3, 56.6, 51.3, 34.3, 21.9 and 20.6.

---

TLC condition - $R_f = 0.2$ (80% hexanes:20% ethyl acetate) for **3b**

$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.07-7.02 (m, 3H), 6.37 (s, 1H), 5.05-4.98 (m, 1H), 3.64-3.57 (m, 1H), 2.98-2.90 (m, 1H), 2.78-2.65 (m, 2H), 2.22 (s, 3H) and 2.18 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 199.7, 163.7, 145.1, 138.9, 133.1, 131.6, 131.2, 128.3, 125.5, 122.4, 56.9, 50.6, 34.1, 21.9 and 21.3.

---

TLC condition - $R_f = 0.30$ (80% hexanes:20% ethyl acetate) for **2c**

$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.19 (s, 1H), 7.05-7.02 (m, 3H), 5.07-4.99 (m, 1H), 3.65-3.58 (m, 1H), 3.19-3.11 (m, 1H), 2.92-2.75 (m, 2H) and 2.22 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 192.7, 160.3, 138.5, 137.5, 132.9, 131.4, 131.3, 128.2, 125.9, 122.5, 56.5, 50.3, 34.2 and 21.9.
TLC condition - \( R_f = 0.2 \) (80% hexanes:20% ethyl acetate) for \( 3c \)

\(^1\)H-NMR (400 MHz, CDCl\(_3\), \( \delta \) ppm): 7.08 (s, 1H), 7.07-7.04 (m, 3H), 5.13-5.06 (m, 1H), 3.68-3.61 (m, 1H), 2.99-2.91 (m, 1H), 2.79-2.70 (m, 2H) and 2.23 (s, 3H).

\(^1\)C-NMR (100 MHz, CDCl\(_3\), \( \delta \) ppm): 196.5, 158.1, 138.3, 137.7, 135.6, 131.4, 128.7, 126.2, 122.6, 57.2, 50.0, 34.1 and 21.8.

TLC condition - \( R_f = 0.40 \) (80% hexanes:20% ethyl acetate) for \( 2d \) and \( 3d \) (single spot)

\(^1\)H-NMR (400 MHz, CDCl\(_3\), \( \delta \) ppm), (Major \( 2d \) + minor \( 3d \), 70:30): 7.50-7.27 (m, 16H), 7.06-7.04 (m, 9H), 6.67 (s, 2H), 6.62 (s, 1H), 5.23-5.13 (m, 3H), 3.64-3.58 (m, 3H), 3.18-3.11 (m, 2H), 3.01-2.95 (m, 3H), 2.82-2.71 (m, 4H), 2.26 (s, 6H) and 2.25 (s, 3H).

\(^1\)C-NMR (100 MHz, CDCl\(_3\), \( \delta \) ppm), (Major \( 2d \) + minor \( 3d \), 70:30): 201.9, 200.7, 163.7, 162.9, 148.6, 146.6, 138.9, 138.7, 136.8, 135.5, 132.3, 131.8, 131.4, 131.2, 130.1, 129.8, 129.1, 128.8, 128.7, 128.5, 128.1, 128.0, 125.8, 125.5, 122.6, 122.5, 57.1, 57.0, 53.5, 50.8, 36.9, 33.9, 33.7, 29.9, 22.2 and 21.8

TLC condition - \( R_f = 0.20 \) (80% hexanes:20% ethyl acetate) for \( 2e \) and \( 3e \) (single spot)

\(^1\)H-NMR (400 MHz, CDCl\(_3\), \( \delta \) ppm), (Major \( 2e \) + minor \( 3e \), 74:26): 7.57-7.54 (m, 2H), 7.41-7.38 (m, 10H), 7.06 (s, 1H), 6.89-6.87 (m, 5H), 6.48-6.47 (d, \( J = 2 \) Hz, 1H), 3.62-3.59 (d, \( J = 14 \) Hz, 2H), 3.48-3.45 (d, \( J = 15 \) Hz, 3H), 3.38-3.30 (m, 3H), 3.11-3.07 (d, \( J = 14 \) Hz, 2H), 2.99-2.92 (m, 2H), 2.86-2.82 (d, \( J = 15.2 \) Hz, 2H), 2.29-2.28 (m, 8H), 2.14 (s, 4H), 2.09 (s, 3H), 1.43 (s, 3H) and 1.33 (s, 4H).

\(^1\)C-NMR (100 MHz, CDCl\(_3\), \( \delta \) ppm), (Major \( 2e \) + minor \( 3e \), 74:26): 196.5, 195.4, 163.9, 161.7, 152.1, 142.5, 139.4, 138.6, 138.2, 137.8, 135.8, 135.4, 132.6, 131.6, 131.4, 131.2, 129.8, 129.2, 129.1, 128.9, 128.96, 128.7, 128.5, 128.48, 128.3, 122.96, 122.90, 64.84, 64.80, 54.2, 53.9, 47.6, 46.9, 23.2, 22.7, 21.8, 21.2, 21.1, 21.0

TLC condition - \( R_f = 0.20 \) (50% hexanes:50% ethyl acetate) for \( 2f \)

\(^1\)H-NMR (400 MHz, CDCl\(_3\), \( \delta \) ppm): 7.03-6.99 (m, 3H), 5.74 (s, 1H), 5.07-5.02 (m, 1H), 3.76 (s, 3H), 3.65-3.58 (m, 1H), 3.09-3.02 (m, 1H), 2.86-2.70 (m, 2H), and 2.22 (s, 3H).

\(^1\)C-NMR (100 MHz, CDCl\(_3\), \( \delta \) ppm): 194.8, 163.1, 158.9, 139.2, 131.2, 130.9, 131.3, 127.9, 125.2, 122.4, 106.3, 56.4, 56.38, 34.1 and 21.8.
TLC condition - Rf = 0.20 (80% hexanes:20% ethyl acetate) for 2g

$^1$H-NMR (400 MHz, CDCl$_3$, $\delta$ ppm): 7.13-7.09(m, 3H), 6.95 (s, 1H), 5.16-5.09 (m, 1H), 3.76-3.69 (m, 1H), 3.14-3.06 (m, 1H), 2.89-2.82 (m, 2H) and 2.29 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 197.7, 157.7, 137.9, 135.7, 135.6, 131.3, 131.1, 128.5, 126.1, 122.4, 56.9, 50.6, 33.6, 29.7 and 21.7.

---

TLC condition - Rf = 0.10 (80% hexanes:20% ethyl acetate) for 3g

$^1$H-NMR (400 MHz, CDCl$_3$, $\delta$ ppm): 7.12-7.09(m, 4H), 5.11-5.04 (m, 1H), 3.72-3.66 (m, 1H),3.22-3.15 (m, 1H), 2.99-2.85 (m, 2H) and 2.29 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 193.7, 159.9, 138.1, 135.9, 131.3, 131.2, 128.3, 126.2, 122.4, 119.8, 56.5, 51.6, 33.9, 29.7 and 21.7.

---

TLC condition - Rf = 0.40 (80% hexanes:20% ethyl acetate) for 2h

$^1$H-NMR (400 MHz, CDCl$_3$, $\delta$ ppm): 7.05-7.02(m, 3H), 5.09-5.02 (m, 1H), 3.63-3.37 (m, 1H), 2.99-2.92 (m, 1H), 2.84-2.73 (m, 2H), 2.24 (s, 3H) and 2.21 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 199.7, 159.4, 145.9, 138.4, 131.4, 129.3, 128.4, 125.9, 122.6, 56.6, 50.9, 33.5, 22.9 and 21.8.

---

TLC condition - Rf = 0.2 (80% hexanes:20% ethyl acetate) for 3h

$^1$H-NMR (400 MHz, CDCl$_3$, $\delta$ ppm): 7.05-7.02 (m, 3H), 5.04-4.97 (m, 1H), 3.62-3.56 (m, 1H), 3.07-2.99 (m, 1H), 2.89-2.84 (m, 1H), 2.79-2.74 (m, 1H), 2.31 (s, 3H) and 2.19 (s, 3H).

$^{13}$C-NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 195.2, 161.9, 142.2, 138.3, 131.3, 131.32, 129.4, 128.3, 125.9, 122.6, 56.4, 50.5, 33.5, 21.8 and 21.5.
6.4. Synthesis of minor methoxy maleimides photoproduct 3f

Scheme S9: Synthesis of minor methoxy maleimides photoproduct 3f

To a solution of bromo maleimide derivative 2c (10 mg, 1.0 equiv.) in MeOH (5 mL) triethylamine in MeOH (1.1 equiv.) was added and the resulting mixture refluxed for 1 h. After the reaction, the solvent was concentrated and the reaction mixture was quenched with DI water. The aqueous layer is extracted with DCM (20 mL). The combined organic layer was dried over anhyd. Na$_2$SO$_4$, filtered and concentrated under reduced pressure to yield crude product. The crude product was purified by combiflash using a hexanes:ethyl acetate mixture. Since the yield was very low (>0.5 mg was isolated) the product was characterized by mass spectrometry and HPLC.

TLC condition - Rf = 0.10 (50% hexanes:50% ethyl acetate) for 3f
7. X-Ray crystal structure data for atropisomeric maleimides and its photoproducts

Structure determination: Single crystal X-ray diffraction data of the compounds 2 and 3 were collected on a Bruker Apex Duo diffractometer with a Apex 2 CCD area detector at T = 100K. Cu radiation was used. All structures were processed with Apex 2 v2010.9-1 software package (SAINT v. 7.68A, XSEEL v. 6.3.1). Direct method was used to solve the structures after multi-scan absorption corrections. Details of data collection and refinement are given in the table below.

<table>
<thead>
<tr>
<th>Formula</th>
<th>(10R)-2b (PkJ)</th>
<th>(10S)-2b (PkJ)</th>
<th>2c</th>
<th>3c</th>
<th>2f</th>
<th>2g</th>
<th>3g</th>
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</thead>
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<td>C₁₆H₁₂BrNO₂</td>
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<td>b [Å]</td>
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<td>90</td>
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<td>90</td>
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<td>β [Å]</td>
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<td>108.4870(10)</td>
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<td>γ [Å]</td>
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<td>90</td>
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<td>90</td>
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<tr>
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<td>ρcalc [g/mm³]</td>
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<td>0.84</td>
<td>0.84</td>
<td>0.84</td>
<td>0.84</td>
<td>0.84</td>
<td>0.84</td>
</tr>
<tr>
<td>R1/wR2 (I ≥ 2σ) [%]</td>
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<td>2.66/6.56</td>
<td>3.21/7.78</td>
<td>0.00/4.25</td>
<td>0.000/28.73</td>
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<td>R1/wR2 (all data) [%]</td>
<td>2.83/6.84</td>
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<td>5.08/11.69</td>
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</tbody>
</table>
7.1. Photoproduct (10R)-2b (crystallized from hexanes:CHCl₃)

7.2. Photoproduct (10S)-2b (crystallized from hexanes:CHCl₃)

7.3. Photoproduct 2c (crystallized from hexanes:CHCl₃)

7.4. Photoproduct 3c (crystallized from hexanes:CHCl₃)
7.5. Photoproduct 2f (crystallized from hexanes:CHCl$_3$)

7.6. Photoproduct 2g (crystallized from hexanes:CHCl$_3$)

7.7. Photoproduct 3g (crystallized from hexanes:CHCl$_3$)

8. References:

9. NMR spectra, HPLC and specific rotation data of maleimides and its photoproducts.

$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.27-7.23 (m, 1H), 7.16-7.12 (m, 2H), 5.81-5.71 (m, 1H), 4.98-4.93 (m, 2H), 3.19-3.17 (d, J = 6.4 Hz, 2H) and 2.07 (s, 3H).
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 169.9, 130.3, 137.6, 136.1, 134.5, 129.9, 129.4, 129.3, 128.3, 116.6, 36.9 and 18.1.

* = Solvent
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.28-7.24 (m, 1H), 7.17-7.12 (m, 2H), 6.46-6.45 (q, J = 5.2 Hz 1H), 5.82-5.72 (m, 1H), 4.98-4.93 (m, 2H), 3.19-3.17 (d, J = 6.8 Hz, 2H), 2.14-2.14 (d, J = 2 Hz, 2H) and 2.09 (s, 3H).
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 170.9, 169.9, 146.1, 139.3, 137.5, 136.2, 129.7, 129.6, 129.3, 128.2, 127.8, 116.4, 36.9, 18.2 and 11.4.

* = Solvent
$^{1}$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.30-7.26 (m, 1H), 7.18-7.14 (m, 2H), 6.99 (s, 1H), 5.81-5.71 (m, 1H), 5.00-4.94 (m, 2H), 3.20-3.19 (d, J = 6.8 Hz, 2H) and 2.10 (s, 3H).
$^{13}$C-NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 167.7, 164.4, 139.2, 137.5, 136.0, 132.3, 131.9, 130.2, 129.5, 129.1, 128.4, 116.7, 37.1 and 18.1.

* = Solvent
HPLC analysis conditions:
For analytical conditions,
I). Column : CHIRALPAK-IC
    Abs. detector wavelength : 254 nm and 270 nm
    Mobile phase : Hexanes:2-propanol = 98:2
    Flow rate : 1.0 mL/min
    Retention times (min) : ∼6.72 [(+)-1c] and ∼7.40 [(-)-1c]

For preparative conditions,
I). Column : CHIRALPAK-IC
    Abs. detector wavelength : 254 nm and 270 nm
    Mobile phase : Hexanes:2-propanol = 99:1
    Flow rate : 3.0 mL/min
    Retention times (min) : ∼13.05 [(+)-1c and ∼15.30 [(-)-1c]

Optical rotation [α]D²²:
HPLC retention time (CHIRALPAK-IC) at ∼ 6.72 min, (c ≈ 0.383 %, CHCl₃) = +8.33 deg
HPLC retention time (CHIRALPAK-IC) at ∼ 7.40 min, (c ≈ 0.383 %, CHCl₃) = -8.85 deg.
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 8.03-8.00 (m, 2H), 7.49-7.48 (m, 3H), 7.32-7.29 (m, 1H), 7.23-7.21 (m, 2H), 6.90 (s, 1H), 5.91-5.80 (m, 1H), 5.04-5.00 (m, 2H), 3.31-3.29 (d, J = 6.4 Hz, 2H) and 2.1 (s, 3H).
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 169.9, 169.5, 144.1, 139.4, 137.7, 136.3, 131.6, 129.8, 129.8, 129.4, 129.3, 129.1, 128.9, 128.3, 124.3, 116.6, 37.1 and 18.3.

* = Solvent
HPLC analysis conditions:

For analytical conditions,

I). Column: CHIRALPAK-ADH

Abs. detector wavelength: 254 nm and 270 nm
Mobile phase: Hexanes:2-propanol = 95:5
Flow rate: 1.0 mL/min
Retention times (min): ≈ 7.17 [(+)-1d] and ≈ 7.72 [(-)-1d]

For preparative conditions,

I). Column: CHIRALPAK-ADH
Abs. detector wavelength: 254 nm and 270 nm
Mobile phase: Hexanes:2-propanol = 99:1
Flow rate: 3.0 mL/min
Retention times (min): ≈ 31.95 [(+)-1d] and ≈ 36.02 [(-)-1d]

Optical rotation [α]_D

HPLC retention time (CHIRALPAK-ADH) at ≈ 7.17 min, (c ≈ 0.231 %, CHCl₃) = +7.10 deg
HPLC retention time (CHIRALPAK-ADH) at ≈ 7.72 min, (c ≈ 0.231 %, CHCl₃) = -7.45 deg.
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.98-7.96 (m, 2H), 7.48-7.46 (m, 3H), 7.02-6.98 (d, J = 16.4, 2H), 6.85 (s, 1H), 4.72 (s, 1H), 4.62 (s, 1H), 3.19 (s, 2H), 2.34 (s, 3H), 2.12 (s, 3H), and 1.59 (s, 3H).

* = Solvent
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 169.7, 169.6, 144.0, 139.5, 138.5, 137.3, 131.5, 130.2, 129.6, 129.2, 129.0, 128.9, 42.6, 22.1, 21.4 and 18.1.

* = Solvent
HPLC analysis conditions:

For analytical conditions,

I). Column : CHIRALPAK-IC
Abs. detector wavelength : 254 nm and 270 nm
Mobile phase : Hexanes:2-propanol = 90:10
Flow rate : 1.0 mL/min
Retention times (min) : ~ 6.12 [(+)\text{-}1\text{e}] and ~ 6.64 [(−)\text{-}1\text{e}]

For preparative conditions,

I). Column : CHIRALPAK-IC
Abs. detector wavelength : 254 nm and 270 nm
Mobile phase : Hexanes:2-propanol = 99:1
Flow rate : 3.0 mL/min
Retention times (min) : ~ 19.53 [(+)\text{-}1\text{e} and − 22.10 [(−)\text{-}1\text{e}]

Optical rotation $[\alpha]_{D}^{22}$:

HPLC retention time (CHIRALPAK-IC) at ~ 6.12 min, ($c = 1.364 \%$, CHCl$_3$) = +7.88 deg

HPLC retention time (CHIRALPAK-IC) at ~ 6.64 min, ($c = 1.364 \%$, CHCl$_3$) = -7.74 deg.
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.27-7.23 (m, 1H), 7.15-7.11 (m, 2H), 5.83-5.72 (m, 1H), 5.54 (s, 1H), 4.99-4.95 (m, 2H), 3.96 (s, 3H), 3.20 (d, J = 6.8, 2H) and 2.10 (s, 3H).
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 169.3, 164.7, 161.0, 139.4, 137.7, 137.1, 129.8, 129.3, 129.0, 128.2, 116.5, 96.7, 59.2, 36.9 and 18.2.

* = Solvent
HPLC analysis conditions:

For analytical conditions,

I). Column : CHIRALPAK-IC
         Abs. detector wavelength : 254 nm and 270 nm
         Mobile phase : Hexanes:2-propanol = 95:5
         Flow rate : 1.0 mL/min
         Retention times (min) : ~ 13.59 [(-)-1f] and ~ 15.34 [(+)-1f]

For preparative conditions,

I). Column : CHIRALPAK-IC
         Abs. detector wavelength : 254 nm and 270 nm
         Mobile phase : Hexanes:2-propanol = 99:1
         Flow rate : 3.0 mL/min
         Retention times (min) : ~ 5.64 [(-)1f] and ~ 18.89 (+)1f]

Optical rotation [α]D25:

HPLC retention time (CHIRALPAK-IC) at ~ 13.59 min, (c ≈ 0.408 %, CHCl₃) = - 3.69 deg
HPLC retention time (CHIRALPAK-IC) at ~ 15.35 min, (c ≈ 0.408 %, CHCl₃) = +1.89 deg.
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.32-7.28 (m, 1H), 7.21-7.15 (m, 2H), 7.09-7.08 (q, $J$ = 5.2Hz, 1H), 5.79-5.69 (m, 1H), 4.99-4.92 (m, 2H), 3.22-3.20 (d, $J$ = 6.8 Hz, 2H) and 2.10 (s, 3H).
$^{13}$C-NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 166.2, 163.9, 139.0, 137.5, 136.0, 133.7, 130.3, 129.6, 128.7, 128.5, 120.8, 118.1, 116.5, 37.3 and 17.9.

* = Solvent
HPLC analysis conditions:
For analytical conditions,

I). Column : CHIRALPAK-ADH  
Abs. detector wavelength : 254 nm and 270 nm  
Mobile phase : Hexanes:2-propanol = 95:5  
Flow rate : 1.0 mL/min  
Retention times (min) : ∼ 4.30 [(A)-1g] and ∼ 5.30 [(B)-1g]

For preparative conditions,

I). Column : CHIRALPAK-ADH  
Abs. detector wavelength : 254 nm and 270 nm  
Mobile phase : Hexanes:2-propanol = 99:1  
Flow rate : 3.0 mL/min  
Retention times (min) : ∼ 10.42 [(A)-1g] and ∼ 12.42 [(B)-1g]

Optical rotation $[\alpha]_D^{24}$:
HPLC retention time (CHIRALPAK-ADH) at ∼ 10.42 min, ($c \approx 0.283 \%$, CHCl$_3$) = +7.47 deg  
HPLC retention time (CHIRALPAK-ADH) at ∼ 12.42 min, ($c \approx 0.283 \%$, CHCl$_3$) = -7.21 deg.
$^1$H-NMR (400 MHz, CDCl$_3$, $\delta$ ppm): 7.29-7.25 (m, 1H), 7.18-7.15 (m, 2H), 5.81-5.71 (m, 1H), 4.99-4.93 (m, 2H), 3.20-3.18 (d, $J = 6.8$ Hz, 2H), 2.11 (s, 3H) and 2.09 (s, 3H).
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 168.5, 164.5, 142.8, 139.2, 137.6, 136.1, 129.9, 129.4, 128.3, 125.5, 116.5, 37.0, 18.2 and 11.2.
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.27-7.23 (m, 1H), 7.16-7.12 (m, 2H), 5.84-5.74 (m, 1H), 5.03-4.97 (m, 2H), 3.18 (d, J=6.8 Hz, 2H), 2.71 (s, 2H), 2.08 (s, 3H), 1.421 (s, 3H) and 1.42 (s, 3H).
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 182.2, 175.03, 137.97, 136.2, 136.1, 130.3, 129.8, 129.4, 128.3, 116.6, 44.2, 40.8, 36.5, 26.4, 25.6, and 17.9.

$*$ = solvent
${}^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.05-7.01 (m, 3H), 6.58-6.6.55 (m, 1H), 6.39-6.36 (m, 1H), 5.08-5.02 (m, 1H), 3.66-3.59 (m, 1H), 3.08-2.99 (m, 1H), 2.78-2.72 (m, 2H) and 2.23 (s, 3H).

*= Solvent
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 209.9, 172.5, 148.9, 146.3, 145.7, 141.5, 141.3, 138.2, 135.7, 132.4, 67.0, 60.9, 44.5 and 31.9.
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.03-6.99 (m, 3H), 6.46-6.45 (m, 1H), 5.01-4.96 (m, 1H), 3.61-3.54 (m, 1H), 3.07-3.00 (m, 1H), 2.80-2.73 (m, 2H), 2.22 (s, 3H) and 2.05-2.04 (d, J = 4 Hz, 3H).

*= Solvent
$^{13}$C-NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 200.9, 162.9, 145.3, 139.1, 132.3, 131.4, 131.2, 127.9, 125.4, 122.3, 56.6, 51.3, 34.3, 21.9 and 20.6.
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.07-7.02 (m, 3H), 6.37 (s, 1H), 5.05-4.98 (m, 1H), 3.64-3.57 (m, 1H), 2.98-2.90 (m, 1H), 2.78-2.65 (m, 2H), 2.22 (s, 3H) and 2.18 (s, 3H).

* = Solvent
$^{13}$C-NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 199.7, 163.7, 145.1, 138.9, 133.1, 131.6, 131.2, 128.3, 125.5, 122.4, 56.9, 50.6, 34.1, 21.9 and 21.3.
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.19 (s, 1H), 7.05-7.02 (m, 3H), 5.07-4.99 (m, 1H), 3.65-3.58 (m, 1H), 3.19-3.11 (m, 1H), 2.92-2.75 (m, 2H) and 2.22 (s, 3H).
$^{13}$C-NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 192.7, 160.3, 138.5, 137.5, 132.9, 131.4, 131.3, 128.2, 125.9, 122.5, 56.5, 50.3, 34.2 and 21.9.

* = Solvent
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.08 (s, 1H), 7.07-7.04 (m, 3H), 5.13-5.06 (m, 1H), 3.68-3.61 (m, 1H), 2.99-2.91 (m, 1H), 2.79-2.70 (m, 2H) and 2.23 (s, 3H).

* = Solvent
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 196.5, 158.1, 138.3, 137.7, 135.6, 131.4, 128.7, 126.2, 122.6, 57.2, 50.0, 34.1 and 21.8.
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm), (Major 2d + minor 3d, 70:30): 7.50-7.27 (m, 16H), 7.06-7.04 (m, 9H), 6.67 (s, 2H), 6.62 (s, 1H), 5.23-5.13 (m, 3H), 3.64-3.58 (m, 3H), 3.18-3.11 (m, 2H), 3.01-2.95(m, 3H), 2.82-2.71 (m, 4H), 2.26 (s, 6H) and 2.25 (s, 3H).

* = Solvent
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm), (Major 2d + minor 3d, 70:30): 201.9, 200.7, 163.7, 162.9, 148.6, 146.6, 138.9, 138.7, 136.8, 135.5, 132.3, 131.8, 131.4, 131.2, 130.1, 129.8, 129.1, 128.9, 128.7, 128.5, 128.1, 128.0, 125.8, 125.5, 122.6, 122.54, 57.1, 57.0, 53.5, 50.8, 36.9, 33.9, 33.7, 29.9, 22.2 and 21.8
\[^1\text{H-NMR}\ (400 \text{ MHz, CDCl}_3, \delta \text{ ppm}), (\text{Major } 2e + \text{ minor } 3e, 74:26): 7.57-7.54 (m, 2H), 7.41-7.38 (m, 10H), 7.06 (s, 1H), 6.89-6.87 (m, 5H), 6.48-6.47 (d, J = 2 \text{ Hz}, 1H), 3.62-3.59 (d, J = 14 \text{ Hz}, 2H), 3.48-3.45 (d, J = 15 \text{ Hz}, 3H), 3.38-3.30 (m, 3H), 3.11-3.07 (d, J = 14 \text{ Hz}, 2H), 2.99-2.92 (m, 2H), 2.86-2.82 (d, J = 15.2 \text{ Hz}, 2H), 2.29-2.28 (m, 8H), 2.14 (s, 4H), 2.09 (s, 3H), 1.43 (s, 3H) and 1.33 (s, 4H).\]
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm), (Major 2e + minor 3e, 74:26): 196.5, 195.4, 163.9, 161.7, 152.1, 142.5, 139.4, 138.6, 138.2, 137.8, 135.8, 135.4, 132.6, 131.6, 131.4, 131.2, 129.8, 129.2, 129.1, 128.9, 128.96, 128.7, 128.5, 128.48, 128.3, 122.96, 122.90, 64.84, 64.80, 54.2, 53.9, 47.6, 46.9, 23.2, 22.7, 21.8, 21.2, 21.1, 21.0

* = Solvent
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.03-6.99 (m, 3H), 5.74 (s, 1H), 5.07-5.02 (m, 1H), 3.76 (s, 3H), 3.65-3.58 (m, 1H), 3.09-3.02 (m, 1H), 2.86-2.70 (m, 2H), and 2.22 (s, 3H).

$\star$ = Solvent
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 194.8, 163.1, 158.9, 139.2, 131.2, 130.9, 131.3, 127.9, 125.2, 122.4, 106.3, 56.4, 56.38, 34.1 and 21.8.

*= Solvent
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.13-7.09 (m, 3H), 6.95 (s, 1H), 5.16-5.09 (m, 1H), 3.76-3.69 (m, 1H), 3.14-3.06 (m, 1H), 2.89-2.82 (m, 2H) and 2.29 (s, 3H).
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 197.7, 157.7, 137.9, 135.7, 135.6, 131.3, 131.1, 128.5, 126.1, 122.4, 56.9, 50.6, 33.6, 29.7 and 21.7.

* = Solvent
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.12-7.09 (m, 4H), 5.11-5.04 (m, 1H), 3.72-3.66 (m, 1H), 3.22-3.15 (m, 1H), 2.99-2.85 (m, 2H) and 2.29 (s, 3H).

* = Solvent
$^{13}$C-NMR (100 MHz, CDCl$_3$, $\delta$ ppm): 193.7, 159.9, 138.1, 135.9, 131.3, 131.2, 128.3, 126.2, 122.4, 119.8, 56.5, 51.6, 33.9, 29.7 and 21.7.
$^1$H-NMR (400 MHz, CDCl$_3$, δ ppm): 7.05-7.02 (m, 3H), 5.09-5.02 (m, 1H), 3.63-3.37 (m, 1H), 2.99-2.92 (m, 1H), 2.84-2.73 (m, 2H), 2.24 (s, 3H) and 2.21 (s, 3H).

* = Solvent
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 199.7, 159.4, 145.9, 138.4, 131.4, 129.3, 128.4, 125.9, 122.6, 56.6, 50.9, 33.5, 22.9 and 21.8.

* = Solvent
**H-NMR (400 MHz, CDCl₃, δ ppm):** 7.05-7.02 (m, 3H), 5.04-4.97 (m, 1H), 3.62-3.56 (m, 1H), 3.07-2.99 (m, 1H), 2.89-2.84 (m, 1H), 2.79-2.74 (m, 1H), 2.31 (s, 3H) and 2.19 (s, 3H).

* = Solvent
$^{13}$C-NMR (100 MHz, CDCl$_3$, δ ppm): 195.2, 161.9, 142.2, 138.3, 131.3, 131.32, 129.4, 128.3, 125.9, 122.6, 56.4, 50.5, 33.5, 21.8 and 21.5.

* = Solvent
HRMS-ESI (m/z) ([M + Na]⁺): Calculated: 280.0950; Observed: 280.0913; |Δm|: 11 ppm.
Figure S5: HPLC trace of A) Pure major methoxy maleimide photoproduc 2f, B) Crude photoreaction of 1f and C) HPLC trace of thermally synthesized 3f.