SUPPORTING INFORMATION

Enantioselective Spirocyclopropanation of Para-Quinone Methides Using Ammonium Ylides

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1 Experimental Section

1.1 GENERAL

$^1$H-, $^{13}$C- and $^{19}$F-NMR spectra were recorded on a Bruker Avance III 300 MHz spectrometer with a broad band observe probe and a sample changer for 16 samples which is property to the Austro-Czech NMR-Research Center “RERI-uasb”. All NMR spectra were referenced on the solvent peak.

High resolution mass spectra were obtained using a Thermo Fisher Scientific LTQ Orbitrap XL with an Ion Max API Source. Analyses were made in the positive ionization mode if not otherwise stated. Purine (exact mass for [$M+H]^+ = 121.050873$) and 1,2,3,4,5,6-hexakis(2,2,3,3-tetrafluoropropoxy)-1,3,5,2,4,6-triazatriphosphinane (exact mass for [$M+H]^+ = 922.009798$) were used for internal mass calibration.

Preparative column chromatography was carried out using Davisil LC 60A 70-200 MICRON silica gel or WoelmPharma Alumina N32-63 neutral aluminium oxide. TLC probes were detected at 254 nm or stained with an appropriate staining solution.

HPLC was performed using a Thermo Scientific Dionex Ultimate 3000 system with diode array detector with a Chiralpak AD-H (250 x 4.6 mm, 5 µm) or a YMC Cellulose-SB (250 x 4.6 mm, 5 µm) chiral stationary phase.

Optical rotations were recorded on a Schmidt + Haensch Polarimeter Model UniPol L 1000 (1 dm cuvette).

Single-crystal structure analyses were carried out on a Bruker Smart X2S diffractometer operating with Mo-$K_α$ radiation ($\lambda=0.71073$ Å).

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated THF was distilled from Na and benzophenone under Ar atmosphere and DCM was distilled from P$_2$O$_5$ under Ar atmosphere. All reactions were performed under an Ar atmosphere.
1.2 PRACTICAL EXPERIMENTAL

1.2.1 Synthesis of starting materials

1.2.1.1 Synthesis of quinone methides

\[
\text{Ar}^{-}\text{CHO} + \text{t-BuOH} \rightarrow \text{Ar}^{-}\text{CO} \text{t-Bu} \text{OH}
\]

**General procedure A:** According to literature\(^1\), 1 equiv of 2,6-di-t-butylphenol and 1 equiv of aldehyde were dissolved in toluene (0.25 M) and heated to reflux in a Dean-Stark apparatus. Piperidine (2 equiv) was added dropwise over 1 h and the reaction mixture was refluxed for 3 h. After cooling just below the boiling point of the mixture, acetic anhydride (2 equiv) was added and stirring continued for 15 min. Then the reaction mixture was poured on ice-water, extracted with DCM (3 times), dried over Na\(_2\)SO\(_4\), the solvent evaporated and the residue dried in vacuo. The resulting crude product was subjected to column chromatography and further recrystallized from n-heptane as stated below.

**Quinone methide 1a:** Prepared according to the general procedure A, using 2,6-di-t-butylphenol (5.16 g, 25.0 mmol) and benzaldehyde (2.66 g, 5.0 mmol) in toluene (100 ml), refluxing and adding piperidine (4.95 ml, 4.27 g, 50.1 mmol) over 1 h, refluxing for 3 h and afterwards adding acetic anhydride (4.70 ml, 5.08 g, 49.7 mmol) and stirring for 15 min, yielding 1a (5.08 g, 69%) after column chromatography (silica, heptanes:EtOAc = 50:1) and recrystallization from n-heptane as yellow solid. Analytical data were in accordance to literature\(^2\). \(^1\)H NMR (300 MHz, δ, CDCl\(_3\), 298 K): 1.34 (s, 9H), 1.38 (s, 9H), 7.06 (d, \(J = 2.4 \text{ Hz}\), 1H), 7.23 (s, 1H), 7.39-7.53 (m, 5H), 7.57 (d, \(J = 2.4 \text{ Hz}\), 1H) ppm.

**Quinone methide 1b:** Prepared according to the general procedure A, using 2,6-di-t-butylphenol (1.03 g, 5.0 mmol) and 4-(trifluoromethyl)benzaldehyde (871 mg, 5.0 mmol) in toluene (20 ml), refluxing and adding piperidine (0.99 ml, 853 mg, 10.0 mmol) over 1 h, refluxing for 3 h and afterwards adding acetic anhydride (1.00 ml, 1.02 g, 10.0 mmol) and stirring for 15 min, yielding 1b (399 mg, 22%) after column chromatography (silica, heptanes:EtOAc = 50:1) as orange solid. Analytical data were in accordance to literature\(^2\). \(^1\)H NMR (300 MHz, δ, CDCl\(_3\), 298 K): 1.29 (s, 9H), 1.38 (s, 9H), 7.02 (d, \(J = 2.3 \text{ Hz}\), 1H), 7.23 (s, 1H), 7.42 (d, \(J = 8.1 \text{ Hz}\), 1H), 7.55 (d, \(J = 8.1 \text{ Hz}\), 2H), 7.71 (d, \(J = 8.1 \text{ Hz}\), 2H) ppm.

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1) Chu, W.-D.; Zhang, L.-F.; Bao, X.; Zhao, X.-H; Zeng, C.; Du, J.-Y; Zhang, G.-B.; Wang, F.-X; Ma, X.-Y.; Fan, C.-A.; Angew. Chem. Int. Ed., 2013, 52, 9229-9233.
2) Reddy, V.; Anand, R. V.; Org. Lett., 2015, 17, 3390-3393.
**Quinone methide 1c**: Prepared according to the general procedure A, using 2,6-di-<i>t</i>-butylphenol (1.03 g, 5.0 mmol) and 4-<i>t</i>-butylbenzaldehyde (811 mg, 5.0 mmol) in toluene (20 ml), refluxing and adding piperidine (0.99 ml, 853 mg, 10.0 mmol) over 1 h, refluxing for 3 h and afterwards adding acetic anhydride (1.00 ml, 1.02 g, 10.0 mmol) and stirring for 15 min, yielding 1c (1.10 g, 63%) after column chromatography (silica, heptanes:EtOAc = 50:1) as yellow solid. Analytical data were in accordance to literature. <sup>1</sup>H NMR (300 MHz, δ, CDCl<sub>3</sub>, 298 K): 1.47 (s, 9H), 1.49 (s, 9H), 7.14 (d, J = 8.5 Hz, 2H), 7.75 (d, J = 2.9 Hz, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 2.3 Hz, 1H), 7.60 (d, J = 2.3 Hz, 1H), 7.39 (d, J = 2.3 Hz, 1H), 7.67 (d, J = 3.3 Hz, 2H), 7.14 (d, J = 2.2 Hz, 1H), 7.76 (d, J = 2.2 Hz, 1H), 7.30 (d, J = 2.3 Hz, 1H); 13C NMR (75 MHz, δ, CDCl<sub>3</sub>, 298 K): 146.0, 148.0, 150.9, 186.1 ppm; HRMS (ESI): m/z calcd. for C<sub>33</sub>H<sub>31</sub>NO: 461.2478 [M+H]<sup>+</sup>; found: 461.2475.

**Quinone methide 1d**: Prepared according to the general procedure A, using 2,6-di-<i>t</i>-butylphenol (1.03 g, 5.0 mmol) and 4-bromobenzaldehyde (925 mg, 5.0 mmol) in toluene (20 ml), refluxing and adding piperidine (0.99 ml, 853 mg, 10.0 mmol) over 1 h, refluxing for 3 h and afterwards adding acetic anhydride (1.00 ml, 1.02 g, 10.0 mmol) and stirring for 15 min, yielding 1d (803 mg, 43%) after column chromatography (silica, heptanes:EtOAc = 50:1) as yellow solid. Analytical data were in accordance to literature. <sup>1</sup>H NMR (300 MHz, δ, CDCl<sub>3</sub>, 298 K): 1.32 (s, 9H), 1.36 (s, 9H), 7.02 (d, J = 2.3 Hz, 1H), 7.10 (s, 1H), 7.33 (d, J = 8.4 Hz, 2H), 7.46 (d, J = 2.3 Hz, 1H), 7.60 (d, J = 8.4 Hz, 2H) ppm.

**Quinone methide 1e**: Prepared according to the general procedure A, using 2,6-di-<i>t</i>-butylphenol (1.03 g, 5.0 mmol) and 1-naphthaldehyde (781 mg, 5.0 mmol) in toluene (20 ml), refluxing and adding piperidine (0.99 ml, 853 mg, 10.0 mmol) over 1 h, refluxing for 3 h and afterwards adding acetic anhydride (1.00 ml, 1.02 g, 10.0 mmol) and stirring for 15 min, yielding 1e (1.03 g, 60%) after column chromatography (silica, heptanes:EtOAc = 50:1) as yellow solid. Analytical data were in accordance to literature. <sup>1</sup>H NMR (300 MHz, δ, CDCl<sub>3</sub>, 298 K): 1.35 (s, 9H), 1.39 (s, 9H), 7.20 (d, J = 2.3 Hz, 1H), 7.39 (d, J = 2.3 Hz, 1H), 7.46-7.51 (m, 1H), 7.53-7.61 (m, 3H), 7.78 (s, 1H), 7.89-7.96 (m, 2H), 8.00-8.07 (m, 1H) ppm.

**Quinone methide 1f**: Prepared according to the general procedure A, using 2,6-di-<i>t</i>-butylphenol (1.03 g, 5.0 mmol) and 4-(dimethylamino)benzaldehyde (746 mg, 5.0 mmol) in toluene (20 ml), refluxing and adding piperidine (0.99 ml, 853 mg, 10.0 mmol) over 1 h, refluxing for 3 h and afterwards adding acetic anhydride (1.00 ml, 1.02 g, 10.0 mmol) and stirring for 15 min, yielding 1f (810 mg, 48%) after column chromatography (silica, heptanes:EtOAc = 50:1) as intensively red solid. <sup>1</sup>H NMR (300 MHz, δ, CDCl<sub>3</sub>, 298 K): 1.35 (s, 9H), 1.35 (s, 9H), 3.08 (s, 6H), 6.75 (d, J = 8.9 Hz, 2H), 7.00 (d, J = 2.3 Hz, 1H), 7.11 (s, 1H), 7.45 (d, J = 8.9 Hz, 2H), 7.67 (d, J = 2.3 Hz, 1H) ppm; <sup>13</sup>C NMR (75 MHz, δ, CDCl<sub>3</sub>, 298 K): 29.5, 29.6, 34.8, 35.3, 40.0, 111.9, 123.8, 128.0, 128.2, 132.7, 135.8, 144.4, 146.0, 148.0, 150.9, 186.1 ppm; HRMS (ESI): m/z calcd. for C<sub>26</sub>H<sub>23</sub>NO: 388.1747 [M+H]<sup>+</sup>; found: 388.1745.

**Quinone methide 1g**: Prepared according to the general procedure A, using 2,6-di-<i>t</i>-butylphenol (1.03 g, 5.0 mmol) and 3-pyridinecarboxaldehyde (536 mg, 5.0 mmol) in toluene (20 ml), refluxing and adding piperidine (0.99 ml, 854 mg, 10.0 mmol) over 1 h, refluxing for 3 h and afterwards adding acetic anhydride (1.00 ml, 1.02 g, 10.0 mmol) and stirring for 15 min, yielding 1g (561 mg, 38%) after column chromatography (silica, heptanes:EtOAc = 50:1) as orange to red solid. <sup>1</sup>H NMR (300 MHz, δ, CDCl<sub>3</sub>, 298 K): 1.30 (s, 9H), 1.34 (s, 9H), 7.03 (d, J = 2.4 Hz, 1H),
7.11 (s, 1H), 7.35-7.45 (m, 2H), 7.77 (d, J = 8.0 Hz, 1H), 8.61 (dd, J = 4.7 Hz, J = 1.1 Hz, 1H), 8.71 (d, J = 1.3 Hz, 1H) ppm; \( ^{13} \text{C} \) NMR (75 MHz, δ, CDCl\(_3\), 298 K): 29.4, 29.4, 35.0, 35.4, 123.4, 126.7, 131.8, 133.5, 134.4, 136.8, 137.5, 148.4, 149.5, 150.1, 150.8, 186.4 ppm; HRMS (ESI): \( m/z \) calcd. for C\(_{20}\)H\(_{25}\)NO: 296.2009 [M]+; found: 296.2002.

**Quinone methide 1h**: Prepared according to the general procedure A, using 2,6-di-\( t \)-butylphenol (1.03 g, 5.0 mmol) and 2-methoxybenzaldehyde (1.03 g, 5.0 mmol) in toluene (20 ml), refluxing and adding piperidine (0.99 ml, 853 mg, 10.0 mmol) over 1 h, refluxing for 3 h and afterwards adding acetic anhydride (1.00 ml, 1.02 g, 10.0 mmol) and stirring for 15 min, yielding 1h (1.43 g, 88%) after column chromatography (silica, heptanes:EtOAc = 50:1) as yellow solid. Analytical data were in accordance to literature\(^3\). \( ^{1} \text{H} \) NMR (300 MHz, δ, CDCl\(_3\), 298 K): 1.29 (s, 9H), 1.34 (s, 9H), 2.41 (s, 3H), 7.01 (d, J = 8.5 Hz, 1H), 7.04 (t, J = 3.7 Hz, 1H), 7.08 (d, J = 2.3 Hz, 1H), 7.36-7.42 (m, 3H), 7.47 (d, J = 2.3 Hz, 1H) ppm.

**Quinone methide 1i**: Prepared according to the general procedure A, using 2,6-di-\( t \)-butylphenol (1.03 g, 5.0 mmol) and 4-methylbenzaldehyde (601 mg, 5.0 mmol) in toluene (20 ml), refluxing and adding piperidine (0.99 ml, 854 mg, 10.0 mmol) over 1 h, refluxing for 3 h and afterwards adding acetic anhydride (1.00 ml, 1.02 g, 10.0 mmol) and stirring for 15 min, yielding 1i (787 mg, 51%) after column chromatography (silica, heptanes:EtOAc = 50:1) as yellow solid. Analytical data were in accordance to literature\(^3\). \( ^{1} \text{H} \) NMR (300 MHz, δ, CDCl\(_3\), 298 K): 1.31 (s, 9H), 1.34 (s, 9H), 2.41 (s, 3H), 7.01 (d, J = 2.2 Hz, 1H), 7.16 (s, 1H), 7.26 (d, J = 8.1 Hz, 2H), 7.37 (d, J = 8.1 Hz, 2H), 7.56 (d, J = 2.2 Hz, 1H) ppm.

**Quinone methide 1j**: Prepared according to the general procedure A, using 2,6-di-\( t \)-butylphenol (1.03 g, 5.0 mmol) and 2-methoxybenzaldehyde (1.03 g, 5.0 mmol) in toluene (20 ml), refluxing and adding piperidine (0.99 ml, 853 mg, 10.0 mmol) over 1 h, refluxing for 3 h and afterwards adding acetic anhydride (1.00 ml, 1.02 g, 10.0 mmol) and stirring for 15 min, yielding 1j (1.22 g, 75%) after column chromatography (silica, heptanes:EtOAc = 50:1) as yellow solid. Analytical data were in accordance to literature\(^1\). \( ^{1} \text{H} \) NMR (300 MHz, δ, CDCl\(_3\), 298 K): 1.32 (s, 9H), 1.33 (s, 9H), 3.87 (s, 3H), 6.98 (d, J = 8.6 Hz, 2H), 7.00 (d, J = 2.3 Hz, 1H), 7.13 (s, 1H), 7.44 (d, J = 8.6 Hz, 2H), 7.56 (d, J = 2.3 Hz, 1H) ppm.

**Quinone methide 1k**: Prepared according to the general procedure A, using 2,6-di-\( t \)-butylphenol (1.03 g, 5.0 mmol) and 4-chlorobenzaldehyde (703 mg, 5.0 mmol) in toluene (20 ml), refluxing and adding piperidine (0.99 ml, 853 mg, 10.0 mmol) over 1 h, refluxing for 3 h and afterwards adding acetic anhydride (1.00 ml, 1.02 g, 10.0 mmol) and stirring for 15 min, yielding 1k (888 mg, 54%) after column chromatography (silica, heptanes:EtOAc = 50:1) as orange solid. Analytical data were in accordance to literature\(^4\). \( ^{1} \text{H} \) NMR (300 MHz, δ, CDCl\(_3\), 298 K): 1.30 (s, 9H), 1.33 (s, 9H), 7.00 (d, J = 2.4 Hz, 1H), 7.11 (s, 1H), 7.38 (d, J = 8.7 Hz, 2H), 7.41-7.46 (m, 3H) ppm.

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3) Wang, L.; Jia, Y.-X.; Zhang, J.M.; Qian, C.; Chen, X.-Z.; Monatsh. Chem., 2014, 145, 1941-1945.
4) Lou, Y.; Cao, P.; Jia, T.; Zhang, Y.; Wang, M.; Liao, J.; Angew. Chem. Int. Ed., 2015, 54, 12134-12138.
Quinone methide 11:

According to literature, SI1 (2.44 g, 20.0 mmol, 1.0 equiv) was dissolved in toluene (20 ml) and benzoyl chloride (4.15 ml, 5.06 g, 36.0 mmol, 1.8 equiv) was added dropwise. Then AlCl3 (3.34 g, 25 mmol, 1.25 equiv) was slowly added and the reaction mixture was stirred at rt for 7 h. Afterwards the solvent was evaporated and the crude product was purified by column chromatography (silica gel, heptanes:DCM = 1:1) to obtain SI2 as red residue (2.05 g, 45%).

To palladium on C (10 wt %, powder, 0.35 g, 0.05 equiv) under an atmosphere of H2 was added a solution of SI2 (2.05 g, 9.0 mmol, 1.0 equiv) in EtOH (14 ml). The reaction mixture was stirred overnight at rt and filtered through a pad of celite. The solvent was evaporated to yield SI3 as yellow oil (1.76 g, 92%) in sufficient purity for further reactions.

To a solution of KOH (1.73 g, 30.9 mmol, 4.2 equiv) and K3Fe(CN)6 (10.14 g, 30.8 mmol, 4.0 equiv) in water (28 ml) was added a solution of SI3 (1.76 g, 7.7 mmol, 1.0 equiv) in heptanes (28 ml). The biphasic reaction mixture was vigorously stirred for 2 h and extracted with DCM. The combined organic phases were dried over Na2SO4, the solvent evaporated and the residue dried in vacuo to yield 11 as yellow solid (761 mg, 47%) in sufficient purity for further reactions. 1H NMR (300 MHz, δ, CDCl3, 298 K): 2.07-2.12 (m, 6H), 7.06-7.11 (m, 1H), 7.20 (s, 1H), 7.39-7.52 (M, 5H), 7.53-7.57 (M, 1H) ppm.

Quinone methide 1m:

According to literature, SI4 (5.04 g, 18.0 mmol, 1.0 equiv) was dissolved in toluene (60 ml) and pTsOHxH2O (171.2 mg, 0.9 mmol, 5 mol %) and ethylene glycol (2.23 g, 35.9 mmol, 2.0 equiv) were added. The reaction mixture was refluxed in a Dean-Stark apparatus overnight. Afterwards, the

5) Gao, S.; Xu, X.; Yuan, Z.; Zhou, H; Yao, H.; Lin, A.; Eur. J. Org. Chem., 2016, 3006-3012.
6) Gai, K.; Fang, X.; Li, X.; Xu, J.; Wu, X.; Lin, A.; Yao, H.; Chem. Commun., 2015, 51, 15831-15834.
mixture was allowed to cool to rt and K₂CO₃ (498 mg, 3.6 mmol, 0.2 equiv) was added stirring continued for 1 h at rt. The mixture was filtered and the solvent was evaporated to yield SI₅ as colourless residue (5.71 g, 17.6 mmol, 98%) in sufficient purity for further reactions.

A mixture of SI₅ (5.71 g, 17.6 mmol, 1.0 equiv) and HMDS (5.68 g, 35.2 mmol, 2.0 equiv) was refluxed and anhydrous THF (44 ml) for 5 h. Afterwards the solvent was evaporated and the crude residue redissolved in anhydrous THF (44 ml) and cooled to -78 °C. To the stirred solution, a solution of n-BuLi (1.6 M in hexanes, 11 ml, 17.6 mmol 1.0 equiv) was added dropwise. The reaction was stirred at -78 °C for 1 h and then at rt for 2 h. Afterwards the reaction mixture was quenched with sat. NH₄Cl, extracted with EtOAc and the combined organic phases were washed with brine, dried over Na₂SO₄, the solvent evaporated and the residue dried in vacuo to yield SI₆ as slightly yellow residue (5.30 g, 16.7 mmol, 95%) in sufficient purity for further reactions.

A mixture of SI₆ (5.30 g, 16.7 mmol, 1.0 equiv) and TMSCl (2.72 g, 25.0 mmol, 1.5 equiv) and Et₃N (2.53 g, 25.0 mmol, 1.5 equiv) in anhydrous THF (56 ml) was stirred at rt for 1 h. Then the mixture was cooled to -78 °C and a solution of n-BuLi (1.6 M in hexanes, 10.4 ml, 16.7 mmol, 1.0 equiv) was added dropwise. The reaction was stirred at -78 °C overnight and then quenched with sat. NH₄Cl, extracted with EtOAc and the combined organic phases were washed with brine, dried over Na₂SO₄, the solvent evaporated and the residue dried in vacuo to yield SI₇ as slightly yellow residue (4.41 g, 14.2 mmol, 85%) in sufficient purity for further reactions.

SI₇ (4.41 g, 14.2 mmol, 1.0 equiv) was dissolved in acetone (142 ml) and pTsOH·H₂O (270 mg, 1.42 mmol, 0.1 equiv) was added. The reaction was stirred for 1 h at rt and then diluted with H₂O and EtOAc. After extraction with EtOAc the combined organic phases were washed with brine, dried over Na₂SO₄, the solvent evaporated and the residue dried in vacuo to yield SI₈ as slightly yellow residue (3.71 g, 14.2 mmol, 98%) in sufficient purity for further reactions.

To a cooled (0 °C) solution of SI₈ (3.71 g, 14.2 mmol, 1.0 equiv) in anhydrous THF (28 ml) was added a solution of PhMgBr (1.0 M in THF, 57 ml, 57 mmol, 4.0 equiv) and the reaction mixture was refluxed for 2 h and cooled to 0 °C again and quenched with sat. NH₄Cl. The mixture was filtered over a pad of celite and the solution extracted with Et₂O, the combined organic phases were dried over Na₂SO₄, the solvent evaporated and the residue dried in vacuo to yield SI₉ as slightly yellow residue (3.82 g, 11.1 mmol, 78%) in sufficient purity for further reactions.

To a cooled (0 °C) mixture of SI₉ (3.82 g, 11.1 mmol, 1.0 equiv) and Et₃N (2.47 g, 24.4 mmol, 2.2 equiv) in anhydrous DCM (111 ml) was added MeSO₂Cl (1.40 g, 12.2 mmol, 1.1 equiv) and the mixture was allowed to warm to rt and stirred for 1 h. The reaction mixture was diluted H₂O and DCM. After extraction with DCM the combined organic phases were washed with brine, dried over Na₂SO₄, the solvent evaporated and the residue dried in vacuo to yield 1m as yellow residue (3.55 g, 10.9 mmol, 98%) in sufficient purity for further reactions. ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 0.07 (s, 9H), 0.11 (s, 9H), 7.12 (s, 1H), 7.21 (d, J = 2.7 Hz, 1H), 7.24-7.36 (m, 5H), 7.73 (d, J = 2.7 Hz, 1H) ppm.
1.2.1.2 Synthesis of α-bromo acetamides

Acetamide SI10: According to literature, to a cooled to solution (-10 °C) of diethylamine (14.6 g, 200 mmol, 2 equiv) in DCM (90 ml) was added dropwise a solution of bromoacetyl bromide (20.2 g, 100 mmol, 1 equiv) in DCM (10 ml). The reaction mixture was continued to stir further at -10 °C for 15 min and then warmed to rt over 1 h. The resulting mixture was filtered, the filtrate was poured into water, extracted with DCM (3 times), dried over Na2SO4, the solvent evaporated and the residue dried in vacuo, yielding SI10 (16.9 g, 87 mmol, 87%) as orange liquid which was used without further purification. Analytical data were in accordance to literature. 1H NMR (300 MHz, δ, CDCl3, 298 K): 1.11 (t, J = 7.2 Hz, 3H), 1.23 (t, J = 7.2 Hz, 3H), 3.36 (q, J = 7.2 Hz, 2H), 3.78 (s, 3H).

Acetamide SI11: According to literature, to a cooled to solution (0 °C) of piperidine (508 mg, 6.0 mmol, 1 equiv) and triethylamine (607 mg, 6.0 mmol, 1 equiv) in DCM (30 ml) was added dropwise a solution of bromoacetyl bromide (1.21 g, 6.0 mmol, 1 equiv) in DCM (10 ml). The reaction mixture was continued to stir further at 0 °C for 1 h. The resulting mixture was poured into water, extracted with DCM (3 times), dried over Na2SO4, the solvent evaporated and the residue dried in vacuo, yielding SI11 (1.13 g, 5.5 mmol, 91%) as a brown oil which was used without further purification. Analytical data were in accordance to literature. 1H NMR (300 MHz, δ, CDCl3, 298 K): 1.43-1.63 (m, 6H), 3.33-3.40 (m, 4H), 3.47 (t, J = 5.3 Hz, 2H), 3.79 (s, 2H) ppm.

Acetamide SI12: In analogy to literature, to a cooled to solution (0 °C) of morpholine (440 mg, 5.1 mmol, 1 equiv) and triethylamine (512 mg, 5.1 mmol, 1 equiv) in DCM (10 ml) was added dropwise a solution of bromoacetyl bromide (1.03 g, 5.1 mmol, 1 equiv) in DCM (10 ml). The reaction mixture was continued to stir further at 0 °C for 2 h. The resulting mixture was poured into water, extracted with DCM (3 times), dried over Na2SO4, the solvent evaporated and the residue dried in vacuo, yielding SI12 (0.97 g, 4.6 mmol, 91%) as a brown oil which was used without further purification. Analytical data were in accordance to literature. 1H NMR (300 MHz, δ, CDCl3, 298 K): 3.44 (t, J = 4.6 Hz, 2H), 3.54 (t, J = 4.9 Hz, 2H), 3.57-3.68 (m, 4H), 3.79 (s, 2H) ppm.

Acetamide SI13: According to literature, to a cooled to solution (0 °C) of N,O-dimethylhydroxylamine hydrochloride (0.49 g, 5.0 mmol, 1 equiv) and triethylamine (504 mg, 5.0 mmol, 1 equiv) in DCM (20 ml) was added dropwise a solution of bromoacetyl bromide (1.01 g, 5.0 mmol, 1 equiv) in DCM (10 ml). The reaction mixture was continued to stir further at rt for 1 h. The resulting mixture was poured into water, extracted with DCM (3 times) and washed with 1 N HCl, sat. NaHCO3 solution and brine. The resulting organic phase was dried over Na2SO4, the solvent evaporated and the residue dried in vacuo, yielding SI13 (901 mg, 5.0 mmol, 99%) as orange oil which was used without further purification. Analytical data were in accordance to literature. 1H NMR (300 MHz, δ, CDCl3, 298 K): 3.23 (s, 3H), 3.78 (s, 3H), 4.00 (s, 2H) ppm.

7) Hama, T.; Liu, X.; Culkin, D. A.; Hartwig, J. F.; J. Am. Chem. Soc., 2003, 125, 11176-11177.
8) Leung, P. S.-W.; Teng, Y.; Toy, P. H.; Org. Lett., 2010, 12, 4996-4999.
9) Conrad, W. E.; Fukazawa, R.; Haddadin, M. J.; Kurth, M. J.; Org. Lett., 2011, 13, 3138-3141.
10) Leung, P. S.-W.; Teng, Y.; Toy, P. H.; Org. Lett., 2010, 12, 4996-4999.
Acetamide SI14: In analogy to literature\(^1\), to a cooled to solution (0 °C) of dibenzylamine (985 mg, 5.0 mmol, 1 equiv) and triethylamine (502 mg, 5.0 mmol, 1 equiv) in DCM (20 ml) was added dropwise a solution of bromoacetyl bromide (1.01 g, 5.0 mmol, 1 equiv) in DCM (10 ml). The reaction mixture was continued to stir further at 0 °C for 30 min. The resulting mixture was poured into water, extracted with DCM (3 times), dried over Na\(_2\)SO\(_4\), the solvent evaporated and the residue dried in vacuo, yielding SI14 in (1.56 g, 4.9 mmol, 98%) as a brown oil which was used without further purification. Analytical data were in accordance to literature\(^2\). \(^1\)H NMR (300 MHz, δ, CD\(_3\)OD, 298 K): 3.95 (s, 2H), 4.56 (s, 2H), 4.65 (s, 2H), 7.15-7.46 (m, 10H) ppm.

1.2.1.3 Synthesis of chiral amines

Amine Q2: In analogy to literature\(^3\), KH (0.96 g, 7.2 mmol, 1.2 equiv, 30% suspension in mineral oil) was washed three times with pentanes, cooled to 0 °C and suspended in DMF (6.7 ml). Quinine (1.95 g, 6.0 mmol, 1 equiv) was added and the mixture stirred at 0 °C for 1 h before MeI (937 mg, 6.6 mmol, 1.1 equiv) was added. The mixture was allowed to warm to rt and further stirred for 2 h. Excess MeI was removed under reduced pressure and the resulting mixture carefully quenched with ice-cold water. The obtained solution was extracted 4 times with EtOAc, dried over Na\(_2\)SO\(_4\), the solvent evaporated and the residue dried in vacuo, yielding Q2 after column chromatography (silica gel, EtOAc:MeOH = 3:2) as a colourless oil (1.38 g, 4.1 mmol, 68%). Analytical data were in accordance to literature\(^4\). \(^1\)H NMR (300 MHz, δ, CD\(_3\)OD, 298 K): 1.38-1.54 (m, 1H), 1.57-1.71 (m, 1H), 1.25-1.96 (m, 3H), 2.33-2.46 (m, 1H), 2.70-2.92 (m, 2H), 3.11-3.27 (m, 2H), 3.35 (s, 3H), 3.53-3.67 (m, 1H), 3.98 (s, 3H), 4.81-4.99 (m, 2H), 5.26-5.34 (m, 1H), 5.59 -5.75 (m, 1H), 1.47-1.67 (m, 2H), 7.36-7.49 (m, 2H), 7.55 (d, J = 4.6 Hz, 1H), 7.96 (d, J = 9.2 Hz, 1H), 8.68 (d, J = 4.6 Hz, 1H) ppm.

Amine QD2: In analogy to literature\(^3\), KH (802 mg, 6.0 mmol, 1.2 equiv, 30% suspension in mineral oil) was washed three times with pentanes, cooled to 0 °C and suspended in DMF (5.6 ml). Quinidine (1.62 g, 5.0 mmol, 1 equiv) was added and the mixture stirred at 0 °C for 1 h before MeI (746 mg, 5.3 mmol, 1.1 equiv) was added. The mixture was allowed to warm to rt and further stirred for 2 h. Excess MeI was removed under reduced pressure and the resulting mixture carefully quenched with ice-cold water. The obtained solution was extracted 4 times with EtOAc, dried over Na\(_2\)SO\(_4\), the solvent evaporated and the residue dried in vacuo, yielding QD2 after column chromatography (silica gel, EtOAc:MeOH = 3:2) as a colourless oil (1.59 g, 4.7 mmol, 93%). Analytical data were in accordance to literature\(^5\). \(^1\)H NMR (300 MHz, δ, CD\(_3\)OD, 298 K): 1.02-1.15 (m, 1H), 1.40-1.62 (m, 2H), 1.64-1.74 (m, 1H), 2.10-2.35 (m, 2H), 2.71-3.07 (m, 4H), 3.35 (s, 3H), 3.36-3.46 (m, 2H), 3.96 (s, 3H), 7.49 (m, 2H), 7.55 (d, J = 4.6 Hz, 1H), 7.96 (d, J = 9.2 Hz, 1H), 8.68 (d, J = 4.6 Hz, 1H) ppm.

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1) Gois, P. M. P.; Alfonso, C. A. M.; Eur. J. Org. Chem., 2003, 19, 3798-3810.
2) Miller, K. J.; Saherwala, A. A.; Webber, B. C.; Wu, Y.; Sherry, A. D.; Woods, M.; Inorg. Chem., 2010, 49, 8662-8664.
3) Papageorgiou, C. D.; Cubillo de Dios, M. A.; Ley, S. V.; Gaunt, M. J.; Angew. Chem. Int. Ed., 2004, 43, 4641-4644.
4) Riches, S. L.; Saha, C.; Filgueira, N. F.; Grange, E.; McCarrigle, E. M; Aggarwal, V. K.; J. Am. Chem. Soc., 2010, 132, 7626-7630.
5) Ishii, Y.; Fuji, oto, R.; Mikami, M.; Murakami, S.; Miki, Y.; Furukawa, Y.; Org. Process Res. Dev., 2007, 11, 609-615.
5.03-5.21 (m, 3H), 6.02-6.28 (m, 1H), 7.36-7.45 (m, 2H), 7.54 (d, J = 4.6 Hz, 1H), 7.96 (d, J = 7.8 Hz, 1H), 8.67 (d, J = 4.6 Hz, 1H) ppm.

Amine Q3: In analogy to literature\textsuperscript{16}, KH (1.10 g, 8.2 mmol, 1.4 equiv, 30\% suspension in mineral oil) was washed three times with pentanes, cooled to 0 °C and suspended in THF (25 ml). Cinchonidine (1.47 g, 5.0 mmol, 1 equiv) was added and the mixture stirred at 0 °C for 1 h, and further stirred at 50 °C for 2 h. The resulting orange suspension was cooled to 0 °C and MeI (746 mg, 5.3 mmol, 1.05 equiv) was added. The mixture was allowed to warm to rt and stirred overnight. Excess MeI was removed under reduced pressure and the resulting mixture carefully quenched with ice-cold water. The obtained solution was extracted 4 times with EtOAc, washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, the solvent evaporated and the residue dried \textit{in vacuo}, yielding Q3 as orange oil (1.52 g, 4.9 mmol, 98\%) in sufficient purity for further reactions. Analytical data were in accordance to literature\textsuperscript{17}. \textit{\textsuperscript{1}H NMR} (300 MHz, \textit{δ}, CD\textsubscript{3}OD, 298 K): 1.47-1.67 (m, 2H), 1.70-1.91 (m, 3H), 2.23-2.40 (m, 1H), 2.51-2.78 (m, 2H), 2.98-3.18 (m, 2H), 3.34 (s, 3H), 3.39-3.52 (m, 1H), 4.81-5.02 (m, 3H), 5.09-5.23 (m, 1H), 5.62-5.84 (m, 1H), 7.56-7.74 (m, 2H), 7.81 (t, J = 7.1 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.4 Hz, 1H), 8.86 (d, J = 4.5 Hz, 1H) ppm; HRMS (ESI): m/z calcd. for C\textsubscript{20}H\textsubscript{16}N\textsubscript{2}O: 309.1961 [M+H]\textsuperscript{+}; found: 309.1962.

Amine QD3 According to literature\textsuperscript{16}, KH (1.10 g, 8.2 mmol, 1.4 equiv, 30\% suspension in mineral oil) was washed three times with pentanes, cooled to 0 °C and suspended in THF (25 ml). Cinchonine (1.47 g, 5.0 mmol, 1 equiv) was added and the mixture stirred at 0 °C for 1 h, and further stirred at 50 °C for 2 h. The resulting orange suspension was cooled to 0 °C and MeI (746 mg, 5.3 mmol, 1.05 equiv) was added. The mixture was allowed to warm to rt and stirred overnight. Excess MeI was removed under reduced pressure and the resulting mixture carefully quenched with ice-cold water. The obtained solution was extracted 4 times with EtOAc, washed with brine, dried over Na\textsubscript{2}SO\textsubscript{4}, the solvent evaporated and the residue dried \textit{in vacuo}, yielding QD3 as orange oil (1.40 g, 4.5 mmol, 91\%) in sufficient purity for further reactions. Analytical data were in accordance to literature\textsuperscript{16}. \textit{\textsuperscript{1}H NMR} (300 MHz, \textit{δ}, CD\textsubscript{3}OD, 298 K): 1.10-1.24 (m, 1H), 1.43-1.6 (m, 2H), 1.68-1.76 (m, 1H), 2.09-2.22 (m, 1H), 2.25-2.38 (m, 1H), 2.71-2.98 (m, 3H), 3.01-3.13 (m, 1H), 3.35 (s, 3H), 3.37-3.43 (m, 1H), 5.06-5.17 (m, 2H), 5.22-5.30 (m, 1H), 6.04-6.20 (m, 1H), 7.62 (d, J = 4.6 Hz, 1H), 7.69 (t, J = 7.7 Hz, 1H), 7.80 (t, J = 7.7 Hz, 1H), 8.11 (d, J = 8.5 Hz, 1H), 8.22 (d, J = 8.1 Hz, 1H), 8.87 (d, J = 4.5 Hz, 1H) ppm; HRMS (ESI): m/z calcd. for C\textsubscript{20}H\textsubscript{16}N\textsubscript{2}O: 309.1961 [M+H]\textsuperscript{+}; found: 309.1964.

Amine Q4: According to literature\textsuperscript{18}, Quinine (1.62 g, 5.0 mmol, 1 equiv) was dissolved in dry DCM (170 ml) and cooled to -78 °C. A Solution of BB\textsubscript{3}r (1.0 M in DCM, 20 ml, 20 mmol, 4 equiv) was added dropwise, the reaction mixture was slowly warmed to rt and afterwards refluxed for 1 h. After cooling the mixture again to 5 °C, a 10 wt \% solution of aqueous NaOH (50 ml) was added and the resulting phases separated. The aqueous phase was washed 2 times with DCM and then acidified by addition of 4 N HCl to pH = 8.5. The resulting cloudy liquid was extracted 5 times with DCM and the combined organic phases dried over Na\textsubscript{2}SO\textsubscript{4}, the solvent evaporated and the residue dried \textit{in vacuo}, yielding Q4 as yellow solid (1.21 g, 3.9 mmol, 78\%) in sufficient purity for

16) Perron, Q.; Alexakis, A.; \textit{Adv. Synth. Catal.}, \textbf{2010}, 352, 2611-2620.
17) Diezi, S.; Szabo, A.; Mallat, T.; Baiker, A.; \textit{Tetrahedron: Asymmetry}, \textbf{2003}, 14, 2573-2577.
18) Small, LV. D.; Rosenberg; H.; Nwangwu, P. U.; Holeslaw, T. L.; Stohs, S. J.; \textit{J. Med. Chem.}, \textbf{1979}, 22, 1014-1016.
further reactions. Analytical data were in accordance to literature.\textsuperscript{19} $^1$H NMR (300 MHz, $\delta$, CDCl\textsubscript{3}, 298 K): 1.16-1.31 (m, 1H), 1.43-1.57 (m, 1H), 1.77-2.04 (m, 3H), 2.11-2.24 (m, 1H), 2.29-2.40 (m, 1H), 2.61-2.75 (m, 2H), 3.02-3.11 (m, 1H), 3.91-4.05 (m, 1H), 4.68-4.81 (m, 2H), 5.37-5.53 (m, 1H), 6.00 (s, 1H), 7.28-7.42 (m, 2H), 7.55 (d, $J = 4.2$ Hz, 1H), 7.97 (d, $J = 8.8$ Hz, 1H), 8.68 (d, $J = 4.2$ Hz, 1H) ppm.

Amine QD4: According to literature\textsuperscript{18}, Quinidine (1.62 g, 5.0 mmol, 1 equiv) was dissolved in dry DCM (170 ml) and cooled to -78 °C. A solution of BBr\textsubscript{3} (1.0 M in DCM, 20 ml, 20 mmol, 4 equiv) was added dropwise, the reaction mixture was slowly warmed to rt and afterwards refluxed for 1 h. After cooling the mixture again to 5 °C, a 10 wt% solution of aqueous NaOH (50 ml) was added and the resulting phases separated. The aqueous phase was washed 2 times with DCM and then acidified by addition of 4 N HCl to pH = 8.5. The resulting cloudy liquid was extracted 5 times with DCM and the combined organic phases dried over Na\textsubscript{2}SO\textsubscript{4}, the solvent evaporated and the residue dried in vacuo, yielding QD4 as yellow solid (1.21 g, 3.9 mmol, 78%) in sufficient purity for further reactions. Analytical data were in accordance to literature\textsuperscript{19}. $^1$H NMR (300 MHz, $\delta$, CDCl\textsubscript{3}, 298 K): 0.81-0.99 (m, 1H), 1.22-1.43 (m, 2H), 1.65-1.76 (m, 1H), 2.10-2.38 (m, 3H), 2.47-2.61 (m, 1H), 2.80-2.94 (m, 1H), 2.95-3.07 (m, 1H), 3.74-3.86 (m, 1H), 4.99-5.12 (m, 2H), 6.01-6.21 (m, 2H), 7.29-7.46 (m, 2H), 7.58 (d, $J = 4.3$ Hz, 1H), 7.98 (d, $J = 9.3$ Hz, 1H), 8.69 (d, $J = 4.3$ Hz, 1H) ppm.

1.2.1.4 Synthesis of ammonium salts

General procedure B (for achiral ammonium salts): In analogy to literature\textsuperscript{20}, 1.5 equiv of trimethylamine (33% solution in EtOH) was added to 1 equiv of $\alpha$-bromo amide in THF (10 ml/g amide) and stirred for 24 h at room temperature. The resulting suspension was filtered and the solid washed 3 times with ether and dried in vacuo to yield pure ammonium salt.

General procedure C (for chiral ammonium salts): According to literature\textsuperscript{21}, 1 equiv of amine was added to 1 equiv of $\alpha$-bromo amide in THF (10 ml/g amide) and stirred for 24 h at room temperature. The solvent evaporated, the residue dried in vacuo and the crude product was subjected to column chromatography as stated below.

Ammonium salt 5a: Prepared according to general procedure B, using SI10 (970 mg, 5.0 mmol) and trimethylamine (33% solution in EtOH, 1.85 ml, 7.5 mmol) in 10 ml THF stirring for 24 h at rt, yielding 5a (1.16 g, 4.6 mmol, 92%) as white solid in sufficient purity for further reactions. Analytical data were in accordance to literature\textsuperscript{21}. $^1$H NMR (300 MHz, $\delta$, CDCl\textsubscript{3}, 298 K): 1.15 (t, $J = 7.1$ Hz, 3H), 1.28 (t, $J = 7.2$ Hz, 3H), 3.38 (q, $J = 7.1$ Hz, 2H), 3.48 (q, $J = 7.2$ Hz, 2H), 3.63 (s, 9H), 5.01 (s, 2H) ppm.

\textsuperscript{19} Xu, X.-H.; Kusuda, A.; Tokunaga, E.; Shibata, N.; \textit{Green Chem.}, 2011, 13, 46-50.
\textsuperscript{20} Roiser, L.; Robiette, R.; Waser, M.; \textit{Synlett}, 2016, 27, 1963-1968.
\textsuperscript{21} Herchl, R.; Stiftinger, M.; Waser, M.; \textit{Org. Biomol. Chem.}, 2011, 9, 7023-7027.
Ammonium salt 5b: Prepared according to general procedure B, using SI11 (213 mg, 1.0 mmol) and trimethylamine (33% solution in EtOH, 0.37 ml, 1.5 mmol) in 2 ml THF stirring for 24 h at rt, yielding 5b (241 mg, 0.9 mmol, 90%) as slightly brown solid in sufficient purity for further reactions. Analytical data were in accordance to literature.\(^{21}\) \(\text{^1H NMR} (300 \text{ MHz, } \delta, \text{CDCl}_3, 298 \text{ K}): 1.51-1.75 (m, 6H), 3.47-3.56 (m, 4H), 3.60 (s, 9H), 3.13 (s, 2H) \text{ ppm.}\)

Ammonium salt 5c: Prepared according to general procedure B, using SI12 (216 mg, 1.0 mmol) and trimethylamine (33% solution in EtOH, 0.37 ml, 1.5 mmol) in 2 ml THF stirring for 24 h at rt, yielding 5c (227 mg, 0.9 mmol, 85%) as brownish, hygroscopic solid in sufficient purity for further reactions. Analytical data were in accordance to literature.\(^{21}\) \(\text{^1H NMR} (300 \text{ MHz, } \delta, \text{CDCl}_3, 298 \text{ K}): 3.56-3.62 (m, 2H), 3.60 (s, 9H), 3.64-3.74 (m, 4H), 3.77-3.82 (m, 2H), 5.26 (s, 2H) \text{ ppm.}\)

Ammonium salt 5d: Prepared according to general procedure B, using SI13 (183 mg, 1.0 mmol) and trimethylamine (33% solution in EtOH, 0.37 ml, 1.5 mmol) in 2 ml THF stirring for 24 h at rt, yielding 5d (190 mg, 0.8 mmol, 79%) as brownish, hygroscopic solid in sufficient purity for further reactions. Analytical data were in accordance to literature.\(^{21}\) \(\text{^1H NMR} (300 \text{ MHz, } \delta, \text{CDCl}_3, 298 \text{ K}): 3.52 (s, 3H), 3.65 (s, 9H), 3.95 (s, 3H), 5.11 (s, 2H) \text{ ppm.}\)

Ammonium salt 5f: Prepared according to general procedure C, using SI10 (193 mg, 1.0 mmol) and quinine (326 mg, 1.0 mmol) in 2 ml THF stirring for 24 h at rt, yielding 5f after column chromatography (silica gel, DCM:MeOH = 10:1) as off-white solid (270 mg, 0.5 mmol, 52%). \([\alpha]_D^{20} = -111.4^\circ \ (c = 1.00, \text{MeOH}); \text{^1H NMR} (300 \text{ MHz, } \delta, \text{CD}_{2}\text{OD}, 298 \text{ K}): 0.92-1.04 (m, 1H), 1.24 (t, J = 7.1 Hz, 3H), 1.33 (t, J = 7.2 Hz, 3H), 1.90 (t, J = 12.4 Hz, 1H), 2.02-2.25 (m, 3H), 2.83-2.93 (m, 1H), 3.47-3.72 (m, 6H), 4.15 (s, 3H), 4.60 (d, J = 17.0 Hz, 1H), 4.71-4.82 (m, 2H), 4.92 (d, J = 17.0 Hz, 1H), 5.00-5.11 (m, 2H), 5.31-5.41 (m, 1H), 5.46-5.80 (m, 2H), 7.44 (dd, J = 9.3 Hz, J = 2.5 Hz, 1H), 7.55 (d, J = 2.5 Hz, 1H), 7.86 (d, J = 4.7 Hz, 1H), 7.96 (d, J = 9.3 Hz, 1H), 8.73 (d, J = 4.7 Hz, 1H) ppm; \text{^13C NMR} (75 \text{ MHz, } \delta, \text{CD}_{2}\text{OD}, 298 \text{ K}): 13.4, 14.3, 23.1, 26.5, 27.4, 38.8, 42.0, 43.1, 57.4, 59.6, 59.9, 61.3, 63.5, 68.3, 102.2, 116.3, 121.1, 124.3, 127.4, 131.6, 138.9, 144.7, 146.1, 148.1, 160.5, 165.3 ppm; HRMS (ESI): m/z calcd. for C_{36}H_{36}N_{3}O_{3}+: 438.2751 [M]^+; found: 438.2750.\)

Ammonium salt 5g: Prepared according to general procedure C, using SI10 (193 mg, 1.0 mmol) and quinidine (327 mg, 1.0 mmol) in 2 ml THF stirring for 24 h at rt, yielding 5g after column chromatography (silica gel, DCM:MeOH = 10:1) as off-white solid (373 mg, 0.7 mmol, 72%). \([\alpha]_D^{20} = 142.5^\circ \ (c = 1.00, \text{MeOH}); \text{^1H NMR} (300 \text{ MHz, } \delta, \text{CD}_{2}\text{OD}, 298 \text{ K}): 0.76-0.91 (m, 1H), 1.23 (t, J = 7.1 Hz, 3H), 1.34 (t, J = 7.1 Hz, 3H), 1.84-2.06 (m, 3H), 2.13 (t, J = 12.4 Hz, 1H), 2.92 (q, J = 8.5 Hz, 1H), 3.45-3.74 (m, 5H), 3.90 (t, J = 11.2 Hz, 1H), 4.15 (s, 3H), 4.50 (t, J = 10.7 Hz, 1H), 4.64 (t, J = 11.1 Hz, 1H), 4.75 (d, J = 17.0 Hz, 1H), 4.87-5.04 (m, 2H), 5.24-5.37 (m,
2H), 5.87-6.05 (m, 2H), 7.39 (dd, J = 9.3 Hz, J = 2.5 Hz, 1H), 7.66 (d, J = 2.5 Hz, 1H), 7.88 (d, J = 4.7 Hz, 1H), 7.92 (d, J = 9.2 Hz, 1H), 8.71 (d, J = 4.7 Hz, 1H) ppm; $^{13}$C NMR (75 MHz, δ, CD$_3$OD, 298 K): 13.4, 14.4, 22.1, 24.6, 28.5, 39.2, 41.9, 43.2, 57.3, 58.5, 59.9, 63.1, 64.7, 68.4, 102.7, 118.0, 121.2, 124.2, 127.6, 131.4, 137.0 144.7, 146.1, 148.0, 160.5, 165.2 ppm; HRMS (ESI): $m/z$ calcd. for C$_{26}$H$_{36}$N$_2$O$_5$*: 438.2751 [M$^+$]; found: 438.2749.

**Ammonium salt 5h:** Prepared according to general procedure C, using SI10 (737 mg, 3.8 mmol) and Q2 (1.29 g, 3.8 mmol) in 8 ml THF stirring for 24 h at rt, yielding 5h after column chromatography (silica gel, DCM:MeOH = 10:1) as off-white solid (1.54 g, 2.9 mmol, 76%). Analytical data were in accordance to literature$^{21}$. $^1$H NMR (300 MHz, δ, CD$_3$OD, 298 K): 1.00-1.12 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.36 (t, J = 7.1 Hz, 3H), 1.98 (t, J = 12.4 Hz, 1H), 2.04-2.26 (m, 3H), 2.82-2.95 (m, 1H), 3.49 (s, 3H), 3.52-3.64 (m, 4H), 3.64-3.75 (m, 2H), 4.15 (s, 3H), 4.53-4.69 (m, 4H), 4.96-5.10 (m, 2H), 5.27-5.37 (m, 1H), 5.38-5.44 (m, 1H), 5.63-5.77 (m, 1H), 7.46 (dd, J = 9.3 Hz, J = 2.6 Hz, 1H), 7.57 (d, J = 2.6 Hz, 1H), 7.67 (d, J = 4.7 Hz, 1H), 7.98 (d, J = 9.3 Hz, 1H), 8.76 (d, J = 4.7 Hz, 1H) ppm; HRMS (ESI): $m/z$ calcd. for C$_{12}$H$_{27}$NO$_5$*: 452.2908 [M$^+$]; found: 452.2902.

**Ammonium salt 5i:** Prepared according to general procedure C, using SI10 (195 mg, 1.0 mmol) and QD2 (331 mg, 1.0 mmol) in 2 ml THF stirring for 24 h at rt, yielding 5i after column chromatography (silica gel, DCM:MeOH = 10:1) as white solid (479 mg, 0.9 mmol, 92%). $[\alpha]_{D}^{20} = 145.2^\circ$ (c = 0.98, MeOH); $^1$H NMR (300 MHz, δ, CD$_3$OD, 298 K): 0.91-1.03 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.36 (t, J = 7.2 Hz, 3H), 1.89-2.06 (m, 3H), 2.19 (t, J = 12.8 Hz, 1H), 2.93 (q, J = 8.6 Hz, 1H), 3.50 (s, 3H), 3.52-3.65 (m, 5H), 3.81-3.92 (m, 1H), 4.16 (s, 3H), 4.34-4.53 (m, 2H), 4.63-4.71 (m, 1H), 4.85-4.96 (m, 4H), 5.27-5.37 (m, 2H), 5.47-5.51 (m, 2H), 5.92-6.08 (m, 1H), 7.45 (dd, J = 9.3 Hz, J = 2.6 Hz, 1H), 7.65-7.73 (m, 2H), 7.98 (d, J = 9.3 Hz, 1H), 8.77 (d, J = 4.6 Hz, 1H) ppm; $^{13}$C NMR (75 MHz, δ, CD$_3$OD, 298 K): 13.4, 14.5, 22.7, 24.3, 28.5, 39.1, 42.1, 43.2, 54.9, 57.3, 57.9, 58.6, 60.2, 63.4, 63.4, 65.1, 78.8, 102.7, 118.1, 121.2, 124.4, 128.5, 131.6, 136.9, 141.1, 145.3, 148.0, 160.6, 165.0 ppm; HRMS (ESI): $m/z$ calcd. for C$_{27}$H$_{38}$N$_2$O$_5$*: 452.2908 [M$^+$]; found: 452.2902.

**Ammonium salt 5j:** Prepared according to general procedure C, using SI10 (77 mg, 0.4 mmol) and Q3 (123 mg, 0.4 mmol) in 1 ml THF stirring for 24 h at rt, yielding 5j after column chromatography (silica gel, DCM:MeOH = 5:1) as beige solid (149 mg, 0.3 mmol, 74%). $[\alpha]_{D}^{20} = -82.0^\circ$ (c = 1.00, MeOH); $^1$H NMR (300 MHz, δ, CD$_3$OD, 298 K): 1.14-1.21 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.37 (t, J = 7.2 Hz, 3H), 2.05-2.29 (m, 4H), 2.84-2.95 (m, 1H), 3.49 (s, 3H), 3.54-3.69 (m, 4H), 3.71-3.87 (m, 2H), 4.48-4.78 (m, 4H), 4.87-5.01 (m, 2H), 5.21-5.32 (m, 1H), 5.45-5.53 (m, 1H), 5.59-5.73 (m, 1H), 7.67-7.78 (m, 2H), 7.84 (t, J = 7.2 Hz, 1H), 8.10 (d, J = 8.2 Hz, 1H), 8.25 (d, J = 8.5 Hz, 1H), 8.94 (d, J = 4.6 Hz, 1H) ppm; $^{13}$C NMR (75 MHz, δ, CD$_3$OD, 298 K): 13.4, 14.5, 23.0, 26.3, 27.4, 38.6, 42.1, 43.2, 57.9, 59.6, 60.0, 61.8, 64.3, 77.9, 116.6, 121.2, 124.4, 126.9, 128.8, 130.3, 131.3, 138.6, 142.7, 149.1, 151.0, 164.8 ppm; HRMS (ESI): $m/z$ calcd. for C$_{26}$H$_{38}$N$_2$O$_5$*: 422.2802 [M$^+$]; found: 422.2801.
Ammonium salt 5k: Prepared according to general procedure C, using SI10 (31 mg, 0.2 mmol) and QD3 (49 mg, 0.2 mmol) in 1 ml THF stirring for 24 h at rt, yielding 5k after column chromatography (silica gel, DCM:MeOH = 5:1) as beige solid (62 mg, 0.1 mmol, 77%). [α]D20 = 112.6° (c = 1.00, MeOH); 1H NMR (300 MHz, δ, CD2OD, 298 K): 1.03-1.14 (m, 1H), 1.31 (t, J = 7.1 Hz, 3H), 1.35 (t, J = 7.1 Hz, 3H), 1.88-2.07 (m, 3H), 2.31 (t, J = 12.3 Hz, 1H), 2.93 (q, J = 8.7 Hz, 1H), 3.47 (s, 3H), 3.52-3.71 (m, 6H), 3.74-3.85 (m, 1H), 4.41-4.52 (m, 1H), 4.53-4.64 (m, 1H), 4.64-4.70 (m, 2H), 5.27-5.38 (m, 2H), 5.45-5.51 (m, 1H), 5.96-6.10 (m, 1H), 7.69-7.80 (m, 2H), 7.86 (dd, J = 7.7 Hz, J = 1.2 Hz, 1H), 8.12 (dd, J = 8.4 Hz, J = 0.7 Hz, 1H), 8.34 (d, J = 8.3 Hz, 1H), 8.95 (d, J = 4.6 Hz, 1H) ppm; 13C NMR (75 MHz, δ, CD2OD, 298 K): 13.4, 14.4, 18.4, 22.4, 24.4, 28.5, 39.2, 42.1, 43.2, 57.9, 58.3, 58.8, 60.0, 63.3, 65.3, 78.5, 118.1, 121.2, 124.7, 127.2, 128.9, 130.3, 131.4, 137.0, 142.6, 149.2, 151.0, 164.8 ppm; HRMS (ESI): m/z calcd. for C26H38N3O7+: 422.2802 [M]+; found: 422.2798.

Ammonium salt 5l: Prepared according to general procedure C, using SI10 (147 mg, 0.8 mmol) and Q4 (236 mg, 0.8 mmol) in 2 ml THF stirring for 24 h at rt, yielding 5l after column chromatography (silica gel, DCM:MeOH = 1:1) as brown solid (275 mg, 0.6 mmol, 72%). [α]D20 = -82.6° (c = 1.00, MeOH); 1H NMR (300 MHz, δ, CD2OD, 298 K): 1.03-1.15 (m, 1H), 1.30 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 1.94-2.26 (m, 4H), 2.84-2.97 (m, 1H), 3.49-3.85 (m, 7H), 4.64-4.78 (m, 2H), 4.89-4.97 (m, 2H), 5.01-5.09 (m, 1H), 5.32-5.43 (m, 1H), 5.63-5.81 (m, 2H), 7.37-7.46 (m, 2H), 7.79 (d, J = 4.6 Hz, 1H), 7.93 (d, J = 8.9 Hz, 1H), 8.67 (d, J = 4.6 Hz, 1H) ppm; 13C NMR (75 MHz, δ, CD2OD, 298 K): 13.3, 14.3, 22.8, 26.5, 27.4, 38.9, 42.3, 43.4, 59.4, 59.6, 61.8, 63.7, 67.9, 105.4, 116.6, 121.1, 123.4, 127.7, 131.5, 138.8, 143.8, 145.4, 147.5, 158.1, 165.1 ppm; HRMS (ESI): m/z calcd. for C25H34N3O6+: 424.2600 [M]+; found: 424.2596.

Ammonium salt 5m: Prepared according to general procedure C, using SI10 (199 mg, 1.0 mmol) and QD4 (303 mg, 1.0 mmol) in 2 ml THF stirring for 24 h at rt, yielding 5m after column chromatography (silica gel, DCM:MeOH = 1:1) as brown solid (355 mg, 0.7 mmol, 72%). [α]D20 = 132.6° (c = 1.00, MeOH); 1H NMR (300 MHz, δ, CD2OD, 298 K): 0.84-0.96 (m, 1H), 1.19 (t, J = 7.1 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H), 1.86-1.97 (m, 3H), 2.14 (t, J = 12.3 Hz, 1H), 2.74-2.86 (m, 1H), 3.29-3.46 (m, 3H), 3.48-3.64 (m, 3H), 4.36-4.74 (m, 1H), 4.49-4.61 (m, 1H), 4.62-4.74 (m, 2H), 4.78-4.84 (m, 1H), 5.16-5.29 (m, 2H), 5.55-5.62 (m, 1H), 5.86-6.00 (m, 1H), 7.27-7.38 (m, 2H), 7.69 (d, J = 4.7 Hz, 1H), 7.84 (d, J = 9.1 Hz, 1H), 8.59 (d, J = 4.7 Hz, 1H) ppm; 13C NMR (75 MHz, δ, CD2OD, 298 K): 13.3, 14.3, 22.0, 24.6, 28.6, 39.3, 42.2, 43.3, 58.8, 59.6, 63.1, 64.6, 68.3, 105.8, 118.0, 121.1, 123.3, 127.9, 131.5, 137.0, 143.9, 145.4, 147.5, 158.2, 165.0 ppm; HRMS (ESI): m/z calcd. for C23H34N3O6+: 424.2600 [M]+; found: 424.2595.

Ammonium salt 5n: Prepared according to general procedure C, using SI11 (95 mg, 0.5 mmol) and Q2 (154 mg, 0.5 mmol) in 1 ml THF stirring for 24 h at rt, yielding 5n after column chromatography (silica gel, DCM:MeOH = 10:1) as off-white solid (137 mg, 0.3 mmol, 55%). [α]D20 = -121.8° (c = 1.00, MeOH); 1H NMR (300 MHz, δ, CD2OD, 298 K): 1.02-1.14 (m, 1H), 1.62-1.81 (m, 6H), 1.96-2.26 (m, 4H), 2.83-2.94 (m, 1H), 3.48 (s, 3H), 3.59-3.81 (m, 6H), 4.13 (s, 3H), 4.52-4.80 (m, 4H), 4.94-5.07 (m, 2H), 5.27-5.38 (m, 1H), 5.38-5.45 (m, 1H), 5.62-5.76 (m, 1H), 7.42-7.49 (m, 2H), 7.68 (d, J = 4.6 Hz, 1H), 7.95-8.01 (m, 1H), 8.76 (d, J = 4.6 Hz, 1H) ppm; 13C NMR (75 MHz, δ, CD2OD, 298 K): 23.6, 25.1, 26.4, 27.4, 27.5, 38.6, 44.3, 47.4, 57.3, 57.8,
Ammonium salt 5o: Prepared according to general procedure C, using S112 (98 mg, 0.5 mmol) and Q2 (157 mg, 0.5 mmol) in 1 ml THF stirring for 24 h at rt, yielding 5o after column chromatography (silica gel, DCM:MeOH = 10:1) as brown solid (98 mg, 0.2 mmol, 38%). [α]_D^{20} = -126.8° (c = 1.00, MeOH); 1H NMR (300 MHz, δ, CD3OD, 298 K): 1.05-1.17 (m, 1H), 1.96-2.27 (m, 4H), 2.83-2.95 (m, 1H), 3.50 (s, 3H), 3.58-3.89 (m, 10H), 4.12 (s, 3H), 4.55-4.72 (m, 3H), 4.79-4.89 (m, 2H), 4.92-5.07 (m, 2H), 5.24-5.36 (m, 1H), 5.47-5.53 (m, 1H), 5.62-5.77 (m, 1H), 7.41-7.51 (m, 2H), 7.68 (d, J = 4.6 Hz, 1H), 7.94-8.02 (m, 1H), 8.76 (d, J = 4.6 Hz, 1H) ppm; 13C NMR (75 MHz, δ, CD3OD, 298 K): 23.5, 26.4, 27.4, 38.6, 43.5, 46.9, 57.4, 57.7, 60.0, 61.7, 63.9, 67.4, 67.5, 78.0, 102.3, 116.4, 121.3, 124.4, 128.3, 131.6, 138.7, 141.3, 145.2, 148.0, 160.4, 164.7 ppm; HRMS (ESI): m/z calcd. for C25H34N3O7+: 464.2908 [M]+; found: 464.2898.

Ammonium salt 5p: Prepared according to general procedure C, using S113 (84 mg, 0.5 mmol) and Q2 (152 mg, 0.5 mmol) in 1 ml THF stirring for 24 h at rt, yielding 5p after column chromatography (silica gel, DCM:MeOH = 10:1) as brown hygroscopic solid (194 mg, 0.4 mmol, 81%). [α]_D^{20} = -115.7° (c = 1.00, MeOH); 1H NMR (300 MHz, δ, CD3OD, 298 K): 1.06-1.20 (m, 1H), 1.97-2.30 (m, 4H), 2.86-2.98 (m, 1H), 3.40 (s, 3H), 3.51 (s, 3H), 3.61-3.78 (m, 2H), 3.95 (s, 3H), 4.14 (s, 3H), 4.55-4.68 (m, 2H), 4.70-4.74 (m, 1H), 4.82-4.92 (m, 2H), 5.04-5.11 (m, 1H), 5.28-5.38 (m, 1H), 5.50-5.56 (m, 1H), 5.65-5.80 (m, 1H), 7.38-7.54 (m, 2H), 7.70 (d, J = 4.6 Hz, 1H), 8.01 (d, J = 9.2 Hz, 1H), 8.79 (d, J = 4.6 Hz, 1H) ppm; 13C NMR (75 MHz, δ, CD3OD, 298 K): 23.5, 26.4, 27.3, 32.6, 38.6, 57.3, 57.5, 59.1, 59.9, 61.7, 62.6, 63.8, 77.9, 102.1, 116.5, 121.3, 124.5, 128.3, 131.7, 138.7, 141.1, 145.3, 148.0, 160.5, 166.5 ppm; HRMS (ESI): m/z calcd. for C25H34N3O7+: 440.2544 [M]+; found: 440.2538.

Ammonium salt 5q: Prepared according to general procedure C, using S114 (160 mg, 0.5 mmol) and Q2 (169 mg, 0.5 mmol) in 1 ml THF stirring for 24 h at rt, yielding 5q after column chromatography (silica gel, DCM:MeOH = 10:1) as brown solid (226 mg, 0.3 mmol, 69%). [α]_D^{20} = -141.3° (c = 0.93, MeOH); 1H NMR (300 MHz, δ, CD3OD, 298 K): 1.03-1.15 (m, 1H), 1.91-2.26 (m, 4H), 2.85-2.95 (m, 1H), 3.21 (s, 3H), 3.54-3.79 (m, 2H), 4.03 (s, 3H), 4.46-4.63 (m, 2H), 4.65-4.75 (m, 1H), 4.75-4.86 (m, 3H), 4.87-4.97 (m, 1H), 4.99-5.11 (m, 3H), 5.26-5.40 (m, 2H), 5.65-5.81 (m, 1H), 7.24-7.52 (m, 12H), 7.64 (d, J = 4.6 Hz, 1H), 8.01 (d, J = 9.7 Hz, 1H), 8.71 (d, J = 4.6 Hz, 1H) ppm; 13C NMR (75 MHz, δ, CD3OD, 298 K): 23.6, 26.3, 27.3, 38.6, 51.4, 51.8, 57.3, 57.6, 60.1, 60.5, 61.6, 63.9, 78.5, 102.1, 116.5, 121.2, 124.4, 128.2, 128.8, 129.4, 130.0, 130.5, 131.8, 136.9, 137.4, 138.6, 140.8, 145.3, 148.0, 160.6, 167.0 ppm; HRMS (ESI): m/z calcd. for C37H42N3O17+: 576.3221 [M]+; found: 576.3213.
1.2.2 Spirocyclopropanation reactions

General racemic procedure D: 1 equiv of achiral ammonium salt 5 (NR₃ = NMe₃) and 1.5 equiv of quinone methide 1 were placed in a Schlenk tube and pre-dried in vacuo. After suspension in anhydrous DCM (0.1 M), Cs₂CO₃ (5 equiv) was added and the mixture was stirred for 24 h at room temperature. Afterwards the mixture was filtered over a pad of Na₂SO₄, the solvent evaporated and the residue dried in vacuo. The resulting crude product was subjected to careful column chromatography as stated below.

General asymmetric procedure E: 1 equiv of chiral ammonium salt 5 (NR₃ = Q2) and 2.5 equiv of quinone methide 1 were placed in a pressure Schlenk tube and pre-dried in vacuo. After suspension in anhydrous DCM (0.1 M), Cs₂CO₃ (6 equiv) was added, the tube was sealed and the mixture was refluxed for 96 h. Afterwards the mixture was filtered over a pad of Na₂SO₄, the solvent evaporated and the residue dried in vacuo. The resulting crude product was subjected to careful column chromatography as stated below.

Cyclopropane 3b: Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1). Procedure D: Using 5a (26.5 mg, 0.11 mmol), 1a (44.7 mg, 0.15 mmol) and Cs₂CO₃ (163 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3b (36.3 mg, 0.09 mmol, 85%, trans:cis = 2.5:1, white solid); Procedure E: Using 5h (55.6 mg, 0.10 mmol). 1a (76.8 mg, 0.25 mmol) and Cs₂CO₃ (198 mg, 0.61 mmol) in 1 ml DCM, refluxing for 96 h, yielding 3b (42.3 mg, 0.10 mmol, 98%, dr > 40:1, er > 99.8:0.2 (major diastereomer), white solid). [α]D²⁰ = 184.3° (c = 0.99, CHCl₃); ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.02-1.12 (m, 12H), 1.14 (t, J = 7.2 Hz, 3H), 1.24 (s, 12H), 3.11 (d, J = 7.2 Hz, 1H), 3.14-3.35 (m, 3H), 3.66 (dq, J = 14.1 Hz, J = 7.2 Hz, 1H), 3.96 (d, J = 7.2 Hz, 1H), 5.92 (d, J = 2.7 Hz, 1H), 6.54 (d, J = 2.7 Hz, 1H), 7.20-7.37 (m, 5H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 13.1, 14.3, 29.3, 35.0, 35.1, 36.6, 37.2, 39.3, 41.0, 42.0, 127.4, 128.4, 129.0, 135.6, 138.9, 149.1, 166.5, 185.6 ppm; HRMS (ESI): m/z calcd. for C₂H₇NO₂: 430.2717 [M+Na]+; found: 430.2716; The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: tminor = 35.7 min, tmajor = 41.0 min).

Synthesis of the (-)-enantiomer of 3b was carried out in analogy to procedure E followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1), using 5i (55.5 mg, 0.10 mmol). 1a (76.6 mg, 0.25 mmol) and Cs₂CO₃ (196 mg, 0.60 mmol) in 1 ml DCM, refluxing for 96 h, yielding 3b (40.4 mg, 0.10 mmol, 95%, dr > 40:1, er > 0.2:99.8 (major diastereomer), white solid). [α]D²⁰ = -178.8° (c = 0.86, CHCl₃); The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: tminor = 35.8 min, tmajor = 41.8 min).

Catalytic and In Situ Ammonium Salt Formation Experiments for the Synthesis of 3b:

Procedure F: Amine Q2 (33.8 mg, 0.10 mmol, 1.0 equiv) and quinone methide 1a (72.9 mg, 0.25 mmol, 2.5 equiv) were placed in a pressure Schlenk tube and pre-dried in vacuo. After suspension in anhydrous DCM (1 ml), acetamide SI10 (19.4 mg, 0.1 mmol, 1 equiv) and Cs₂CO₃ (197 mg,
0.60 mmol, 6 equiv) were added, the tube was sealed and the mixture was refluxed for 72 h. Afterwards the mixture was filtered over a pad of Na₂SO₄, the solvent evaporated and the residue dried in vacuo. The resulting crude product was subjected to column chromatography (neutral alumina, heptanes:EtOAc = 1:10), yielding 3b (26.6 mg, 0.07 mmol, 65%, trans:cis = 3.5:1, er > 99.8:0.2 (major diastereomer), off-white solid).

Procedure G: Amine Q2 (10.1 mg, 0.03 mmol, 1.0 equiv) and quinone methide 1a (73.0 mg, 0.25 mmol, 2.5 equiv) were placed in a pressure Schlenk tube and pre-dried in vacuo. After suspension in anhydrous DCM (1 ml), acetamide SI10 (19.4 mg, 0.1 mmol, 1 equiv) and Cs₂CO₃ (197 mg, 0.60 mmol, 6 equiv) were added, the tube was sealed and the mixture was refluxed for 96 h. Afterwards the mixture was filtered over a pad of Na₂SO₄, the solvent evaporated and the residue dried in vacuo. The resulting crude product was subjected to column chromatography (neutral alumina, heptanes:EtOAc = 1:10), yielding 3b (9.8 mg, 0.02 mmol, 24%, dr > 40:1, er = 98.8:1.2 (major diastereomer), off-white solid).

**Cyclopropane 3c:** Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 5:1), Procedure D: Using 5a (26.8 mg, 0.11 mmol), 1I (33.4 mg, 0.16 mmol) and Cs₂CO₃ (173 mg, 0.53 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3c (23.6 mg, 0.07 mmol, 69%, dr > 20:1, white solid); Procedure E: Using 5h (54.9 mg, 0.10 mmol), 1I (54.1 mg, 0.25 mmol) and Cs₂CO₃ (200 mg, 0.62 mmol) in 1 ml DCM, refluxing for 96 h, yielding 3c (21.6 mg, 0.07 mmol, 65%, dr > 40:1, er = 99.8:0.2 (major diastereomer), white solid). [α]⁺²⁰ = 65.0° (c = 0.98, CHCl₃); ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.08-1.17 (m, 6H), 1.84 (d, J = 1.3 Hz, 3H), 1.96 (d, J = 1.3 Hz, 3H), 3.20 (d, J = 7.4 Hz, 1H), 3.22-3.39 (m, 3H), 3.55 (dq, J = 14.1 Hz, J = 7.1 Hz, 1H), 3.98 (d, J = 7.4 Hz, 1H), 6.04 (d, J = 1.3 Hz, 1H), 6.70 (d, J = 1.3 Hz, 1H), 7.20-7.25 (m, 2H), 7.29-7.36 (m, 3H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 12.9, 14.4, 16.2, 16.5, 36.1, 38.1, 39.5, 40.9, 42.0, 127.5, 128.6, 128.9, 135.3, 137.6, 142.4, 142.7, 166.3, 186.7 ppm; HRMS (ESI): m/z calcd. for C₁₁H₂₅NO₂: 324.1958 [M+H]⁺; found: 324.1957; The enantioselectivity was determined by HPLC (YMC Cellulose-SB, eluent: n-hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: t_major = 51.7 min, t_minor = 59.1 min).

**Cyclopropane 3d:** Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1), Procedure D: Using 5a (50.5 mg, 0.20 mmol), 1m (98.0 mg, 0.30 mmol) and Cs₂CO₃ (325 mg, 1.00 mmol) in 2 ml DCM, stirring for 24 h at rt, yielding 3d (65.9 mg, 0.15 mmol, 75%, dr = 6:1:1, white solid); Procedure E: Using 5h (26.6 mg, 0.05 mmol), 1m (40.8 mg, 0.13 mmol) and Cs₂CO₃ (97.5 mg, 0.30 mmol) in 0.5 ml DCM, refluxing for 96 h, yielding 3d (20.6 mg, 0.05 mmol, 94%, dr > 19:1, er > 99.8:0.2 (major diastereomer), white solid). [α]⁺²⁰ = 162.5° (c = 0.99, CHCl₃); ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 0.02 (s, 9H), 0.18 (s, 9H), 1.06-1.17 (m, 6H), 3.10-3.31 (m, 4H), 3.68 (dq, J = 14.1 Hz, J = 7.1 Hz, 1H), 4.04 (d, J = 7.3 Hz, 1H), 6.28 (d, J = 2.9 Hz, 1H), 6.92 (d, J = 2.9 Hz, 1H), 7.21-7.37 (m, 5H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): −1.7, −1.5, 13.0, 14.3, 37.6, 38.8, 40.6, 41.0, 42.0, 127.6, 128.5, 128.9, 135.1, 143.8, 144.0, 154.1, 154.3, 165.9, 191.6 ppm; HRMS (ESI): m/z calcd. for C₂₇H₃₇NO₂Si₂: 440.2436 [M+H]⁺; found: 440.2432; The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: t_major = 40.0 min, t_minor = 30.3 min).
Cyclopropane 3e: Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1), Procedure D: Using 5a (25.5 mg, 0.10 mmol), 1b (54.2 mg, 0.15 mmol) and Cs₂CO₃ (162 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3e (35.6 mg, 0.07 mmol, 73%), trans:cis = 2:1.1, white solid; Procedure E: Using 5h (26.5 mg, 0.05 mmol), 1b (59.3 mg, 0.13 mmol) and Cs₂CO₃ (98 mg, 0.30 mmol) in 0.5 ml DCM, refluxing for 96 h, yielding 3e (22.6 mg, 0.05 mmol, 95%), dr > 19:1, er = 99.7:0.3 (major diastereomer, white solid). [α]²⁰D = 144.9° (c = 1.00, CHCl₃);

¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.03-1.11 (m, 12H), 1.15 (t, J = 7.2 Hz, 3H), 1.24 (s, 9H), 3.09 (d, J = 7.3 Hz, 1H), 3.14-3.35 (m, 3H), 3.65 (dq, J = 14.1 Hz, J = 7.2 Hz, 1H), 3.97 (d, J = 7.2 Hz, 1H), 5.83 (d, J = 2.6 Hz, 1H), 6.51 (d, J = 2.6 Hz, 1H), 7.37 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 8.0 Hz, 1H), ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 13.1, 14.3, 29.1, 29.2, 35.1, 35.1, 36.5, 36.9, 38.5, 41.1, 42.0, 123.9 (q, J = 270.3 Hz), 125.4 (q, J = 3.8 Hz), 129.5 (q, J = 32.2 Hz), 129.5, 137.8, 138.5, 139.8, 150.1, 150.3, 166.0, 185.4 ppm; ¹⁹F NMR (282 MHz, δ, CDCl₃, 298 K): 62.53 ppm; HRMS (ESI): m/z calcd. for C₉H₈F₃NO₂: 428.2590 [M+Na]+; found: 428.2587; The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: t_major = 30.7 min, t_minor = 42.7 min).

Cyclopropane 3f: Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1), Procedure D: Using 5a (25.5 mg, 0.10 mmol), 1c (52.0 mg, 0.15 mmol) and Cs₂CO₃ (162 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3f (39.9 mg, 0.09 mmol, 85%), trans:cis = 2:8:1, white solid; Procedure E: Using 5h (54.0 mg, 0.10 mmol), 1c (87.6 mg, 0.25 mmol) and Cs₂CO₃ (200 mg, 0.61 mmol) in 1 ml DCM, refluxing for 96 h, yielding 3f (42.2 mg, 0.09 mmol, 91%), dr > 40:1, er = 99.6:0.4 (major diastereomer, white solid). [α]²⁰D = 145.3° (c = 0.97, CHCl₃);

¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.05 (t, J = 7.2 Hz, 3H), 1.09 (s, 9H), 1.13 (t, J = 7.1 Hz, 3H), 1.24 (s, 9H), 1.31 (s, 9H), 3.08 (d, J = 7.3 Hz, 1H), 3.11-3.33 (m, 3H), 3.66 (dq, J = 14.1 Hz, J = 7.1 Hz, 1H), 3.92 (d, J = 7.3 Hz, 1H), 5.94 (d, J = 2.7 Hz, 1H), 6.53 (d, J = 2.7 Hz, 1H), 7.15 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.2 Hz, 2H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 13.1, 14.3, 29.2, 29.3, 31.2, 34.5, 35.0, 35.1, 36.9, 37.3, 39.1, 41.0, 42.0, 125.2, 128.7, 132.6, 139.2, 139.3, 149.5, 166.6, 185.7 ppm; HRMS (ESI): m/z calcd. for C₁₃H₁₄NO₂: 464.3523 [M+H]+; found: 464.3518; The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: t_major = 18.4 min, t_minor = 39.7 min).

Cyclopropane 3g: Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1), Procedure D: Using 5a (25.3 mg, 0.10 mmol), 1i (30.9 mg, 0.15 mmol) and Cs₂CO₃ (163 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3g (27.0 mg, 0.06 mmol, 64%), trans:cis = 3:1:1, white solid; Procedure E: Using 5h (26.3 mg, 0.05 mmol), 1i (40.1 mg, 0.13 mmol) and Cs₂CO₃ (98 mg, 0.30 mmol) in 0.5 ml DCM, refluxing for 96 h, yielding 3g (19.8 mg, 0.05 mmol, 95%), dr > 40:1, er > 99.8:0.2 (major diastereomer, white solid). [α]²⁰D = 169.7° (c = 1.00, CHCl₃);

¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.05 (t, J = 7.2 Hz, 3H), 1.10 (s, 9H), 1.14 (t, J = 7.2 Hz, 3H), 1.24 (s, 9H), 2.34 (s, 3H), 3.07 (d, J = 7.2 Hz, 1H), 3.12-3.34 (m, 3H), 3.65 (dq, J = 14.1 Hz, J = 7.2 Hz, 1H), 3.91 (d, J = 7.3 Hz, 1H), 5.94 (d, J = 2.7 Hz, 1H), 6.53 (d, J = 2.7 Hz, 1H), 7.08-7.15 (m, 4H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 13.1, 14.3, 21.1, 29.2, 29.3, 29.6, 35.0, 35.1, 36.8, 37.3, 39.1, 41.0, 42.0, 128.9, 129.1, 132.5, 137.0, 139.1, 139.3, 149.5, 166.6, 185.3 ppm; HRMS (ESI): m/z
Cyclopropane 3h: Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1). Procedure D: Using 5a (25.5 mg, 0.10 mmol), 1k (49.1 mg, 0.15 mmol) and Cs₂CO₃ (164 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3h (39.5 mg, 0.09 mmol, 93%, trans: cis = 3.0:1, white solid); Procedure E: Using 5h (52.7 mg, 0.10 mmol), 1k (82.4 mg, 0.25 mmol) and Cs₂CO₃ (199 mg, 0.61 mmol) in 1 ml DCM, refluxing for 96 h, yielding 3h (40.9 mg, 0.10 mmol, 98%, dr > 40:1, er > 99.8:0.2 (major diastereomer), white solid). [α]²⁰ D = 189.8° (c = 0.98, CHCl₃); ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.05 (t, J = 7.2 Hz, 3H), 1.10 (s, 9H), 1.13 (t, J = 7.1 Hz, 3H), 1.23 (s, 9H), 3.03 (d, J = 7.3 Hz, 1H), 3.11-3.35 (m, 3H), 3.63 (dq, J = 14.1 Hz, J = 7.1 Hz, 1H), 3.89 (d, J = 7.3 Hz, 1H), 5.86 (d, J = 2.7 Hz, 1H), 6.49 (d, J = 2.7 Hz, 1H), 7.17 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.5 Hz, 2H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 13.1, 14.3, 29.2, 29.3, 35.1, 35.1, 36.7, 37.1, 38.4, 41.0, 42.0, 128.6, 130.4, 133.3, 134.2, 138.3, 138.7, 149.9, 150.1, 166.2, 185.5 ppm; HRMS (ESI): m/z calcd. for C₂₇H₅₃ClNO₅: 442.2507 [M+H]⁺; found: 442.2505. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: t_major = 36.3 min, t_minor = 47.5 min).

Cyclopropane 3i: Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1). Procedure D: Using 5a (26.3 mg, 0.10 mmol), 1h (48.9 mg, 0.15 mmol) and Cs₂CO₃ (162 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3i (35.0 mg, 0.08 mmol, 77%, trans: cis = 3.9:1, white solid); Procedure E: Using 5h (26.5 mg, 0.05 mmol), 1h (40.6 mg, 0.13 mmol) and Cs₂CO₃ (97 mg, 0.30 mmol) in 0.5 ml DCM, refluxing for 96 h, yielding 3i (20.0 mg, 0.05 mmol, 92%, dr > 40:1, er = 99.8:0.2 (major diastereomer), white solid). [α]²⁰ D = 71.4° (c = 1.00, CHCl₃); ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.03-1.10 (m, 12H), 1.14 (t, J = 7.1 Hz, 3H), 1.25 (s, 9H), 3.10 (d, J = 7.5 Hz, 1H), 3.13-3.32 (m, 3H), 3.58-3.73 (m, 4H), 3.81 (d, J = 7.5 Hz, 1H), 5.79 (d, J = 2.7 Hz, 1H), 6.60 (d, J = 2.7 Hz, 1H), 6.81 (d, J = 8.0 Hz, 1H), 6.91 (t, J = 7.3 Hz, 1H), 7.15 (d, J = 7.2 Hz, 1H), 7.21-7.29 (m, 1H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 13.2, 14.3, 29.3, 29.4, 34.9, 35.1, 35.8, 37.0, 37.2, 41.0, 42.1, 55.5, 110.4, 120.1, 124.6, 128.8, 129.1, 132.8, 139.6, 139.7, 149.3, 149.4, 154.9, 166.8, 185.8 ppm; HRMS (ESI): m/z calcd. for C₂₇H₅₃NO₅: 438.3003 [M+H]⁺; found: 438.3000. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: t_major = 22.7 min, t_minor = 12.7 min).

Cyclopropane 3j: Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1). Procedure D: Using 5a (25.5 mg, 0.10 mmol), 1j (49.1 mg, 0.15 mmol) and Cs₂CO₃ (163.9 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3j (31.9 mg, 0.07 mmol, 73%, trans: cis = 3.8:1, white solid); Procedure E: Using 5h (533 mg, 1.00 mmol), 1j (813 mg, 2.51 mmol) and Cs₂CO₃ (1.95 g, 5.98 mmol) in 10 ml DCM, refluxing for 96 h, yielding 3j (381 mg, 0.87 mmol, 87%, dr > 40:1, er = 99.8:0.2 (major diastereomer), white solid). [α]²⁰ D = 208.4° (c = 0.99, CHCl₃); ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.05 (t, J = 7.2 Hz, 3H), 1.08-1.16 (m, 12H), 1.23 (s, 9H), 3.05 (d, J = 7.2 Hz, 1H), 3.10-3.32 (m, 3H), 3.63 (dq, J = 14.1 Hz, J = 7.2 Hz, 1H), 3.81 (s, 3H), 3.89 (d, J = 7.2 Hz, 1H), 5.93 (d, J = 2.7 Hz, 1H), 6.51 (d, J = 2.7 Hz, 1H), 6.85 (d, J = 8.6 Hz, 2H), 7.15 (d, J = 8.6 Hz, 2H) ppm;
13C NMR (75 MHz, δ, CDCl3, 298 K): 13.1, 14.3, 29.2, 29.3, 35.0, 35.1, 37.0, 37.4, 38.8, 41.0, 42.0, 113.8, 127.6, 130.1, 139.1, 139.3, 149.5, 149.6, 158.8, 166.6, 185.6 ppm; HRMS (ESI): m/z calcd. for C29H39NO3: 438.3003 [M+H]+; found: 438.2997. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: tmajor = 16.9 min, tminor = 21.9 min).

Cyclopropane 3k: See 6h for yields. HRMS of crude product (ESI): m/z calcd. for C29H32N2O2: 451.3319 [M+H]+; found: 451.3315.

Cyclopropane 3l Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1), Procedure D: Using 5a (25.7 mg, 0.10 mmol), 1d (55.1 mg, 0.15 mmol) and Cs2CO3 (161 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3l (32.0 mg, 0.06 mmol, 64%, trans:cis = 2.2:1, white solid); Procedure E: Using 5h (55.1 mg, 0.10 mmol), 1d (96.7 mg, 0.25 mmol) and Cs2CO3 (203 mg, 0.62 mmol) in 1 ml DCM, refluxing for 96 h, yielding 3l (49.6 mg, 0.10 mmol, 98%, dr > 40:1, er > 99.8:0.2 (major diastereomer), colourless crystals after crystallization from DCM/heptanes). [α]D20 = 233.5° (c = 0.55, CHCl3); 1H NMR (300 MHz, δ, CDCl3, 298 K): 1.05 (t, J = 7.2 Hz, 3H), 1.10 (s, 9H), 1.13 (t, J = 7.1 Hz, 3H), 1.23 (s, 9H), 3.03 (d, J = 7.3 Hz, 1H), 3.11-3.34 (m, 3H), 3.64 (dq, J = 14.1 Hz, J = 7.1 Hz, 1H), 3.87 (d, J = 7.3 Hz, 1H), 4.58 (d, J = 2.7 Hz, 1H), 6.49 (d, J = 2.7 Hz, 1H), 7.12 (d, J = 8.1 Hz, 2H), 7.45 (d, J = 8.1 Hz, 2H) ppm; 13C NMR (75 MHz, δ, CDCl3; 298 K): 13.1, 14.3, 29.2, 29.3, 35.1, 35.1, 36.6, 37.0, 38.5, 41.1, 42.0, 121.4, 130.8, 131.6, 134.7, 138.2, 138.7, 149.9, 150.1, 166.2, 185.5 ppm; HRMS (ESI): m/z calcd. for C27H36BrNO2: 508.1822 [M+Na]+; found: 508.1817. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: tmajor (1S,2R) = 37.4 min, tminor (1R,2S) = 50.2 min).

Cyclopropane 3m: Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 1:1), Procedure D: Using 5a (25.2 mg, 0.10 mmol), 1g (44.2 mg, 0.15 mmol) and Cs2CO3 (160 mg, 0.49 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3m (40.0 mg, 0.10 mmol, 98%, trans:cis = 2.0:1, yellow solid); Procedure E: Using 5h (55.5 mg, 0.10 mmol), 1g (74 mg, 0.25 mmol) and Cs2CO3 (198 mg, 0.61 mmol) in 1 ml DCM, refluxing for 96 h, yielding 3m (32.5 mg, 0.08 mmol, 80%, dr > 40:1, er > 99.8:0.2 (major diastereomer), yellow-white solid). [α]D20 = 180.6° (c = 1.00, CHCl3); 1H NMR (300 MHz, δ, CDCl3, 298 K): 1.03-1.11 (m, 12H), 1.15 (t, J = 7.1 Hz, 3H), 1.24 (s, 9H), 3.10 (d, J = 7.2 Hz, 1H), 3.15-3.36 (m, 3H), 3.66 (dq, J = 14.1 Hz, J = 7.1 Hz, 1H), 3.91 (d, J = 7.2 Hz, 1H), 5.83 (d, J = 2.7 Hz, 1H), 6.52 (d, J = 2.7 Hz, 1H), 7.22-7.33 (m, 1H), 7.47 (d, J = 7.9 Hz, 1H), 8.45-8.62 (m, 2H) ppm; 13C NMR (75 MHz, δ, CDCl3, 298 K): 13.1, 14.3, 29.2, 29.2, 35.1, 35.2, 36.0, 36.5, 41.1, 42.1, 123.2, 123.5, 131.5, 136.8, 137.6, 138.4, 148.8, 152.0, 150.4, 165.9, 185.4 ppm; HRMS (ESI): m/z calcd. for C29H36N2O3: 409.2850 [M+H]+; found: 409.2851. The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 9:1, 0.5 mL/min, 10 °C, retention times: tmajor = 28.5 min, tminor = 14.6 min).
**Cyclopropane 3n:** Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1), Procedure D: Using 5a (26.3 mg, 0.10 mmol), 1e (52.4 mg, 0.15 mmol) and Cs₂CO₃ (163 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3n (38.5 mg, 0.08 mmol, 81%, trans: cis = 2.9:1, white solid); Procedure E: Using 5h (28.6 mg, 0.05 mmol), 1e (46.3 mg, 0.13 mmol) and Cs₂CO₃ (98 mg, 0.30 mmol) in 0.5 ml DCM, refluxing for 96 h, yielding 3n (20.9 mg, 0.05 mmol, 85%, dr > 40:1, er = 99.7:0.3 (major diastereomer), white solid). \([ \alpha ]_{D}^{20} = -108.4^\circ \text{ (c = 0.96, CHCl}_3 \); \[ \text{H NMR (300 MHz, } \delta , \text{ CDCl}_3, 298 K): 0.79 (s, 9H), 1.07 (t, J = 7.2 Hz, 3H), 1.15 (t, J = 7.1 Hz, 3H), 1.28 (s, 9H), 3.12-3.34 (m, 4H), 3.70 (dq, J = 14.1 Hz, J = 7.2 Hz, 1H), 4.18 (d, J = 7.2 Hz, 1H), 5.62 (d, J = 2.6 Hz, 1H), 6.70 (d, J = 2.6 Hz, 1H), 7.22 (s, 1H), 7.31-7.46 (m, 4H), 7.58 (d, J = 8.2 Hz, 1H), 7.70-7.84 (m, 2H) ppm; \[ ^{13} \text{C NMR (75 MHz, } \delta , \text{ CDCl}_3, 298 K): 13.2, 14.3, 28.8, 29.4, 34.7, 35.3, 37.1, 37.4, 41.0, 42.1, 124.1, 124.8, 126.1, 126.3, 126.4, 128.3, 132.8, 132.9, 133.4, 133.7, 139.2, 149.7, 150.5, 166.6, 185.4 ppm; HRMS (ESI): m/z calcd. for C_{31}H_{39}NO_{5}: 480.2873 \text{ [M+Na}^+; found: 480.2867; The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: t_{major} = 44.6 min, t_{minor} = 33.9 min).

**Cyclopropane 3o:** Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 5:1), Procedure D: Using 5b (27.0 mg, 0.10 mmol), 1a (44.3 mg, 0.15 mmol) and Cs₂CO₃ (163 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3o (39.3 mmg, 0.09 mmol, 92%, trans: cis = 3.2:1, colourless crystals); Procedure E: Using 5n (39.4 mg, 0.11 mmol), 1a (79.8 mg, 0.27 mmol) and Cs₂CO₃ (214 mg, 0.66 mmol) in 1 ml DCM, refluxing for 96 h, yielding 3o (44.4 mg, 0.11 mmol, 97%, dr > 18:1, er = 99.1:0.9 (major diastereomer), colourless crystals). \([ \alpha ]_{D}^{20} = 175.9^\circ \text{ (c = 0.98, CHCl}_3 \); \[ \text{H NMR (300 MHz, } \delta , \text{ CDCl}_3, 298 K): 1.09 (s, 9H), 1.25 (s, 9H), 1.38-1.70 (m, 6H), 3.09-3.18 (m, 2H), 3.18-3.26 (m, 1H), 3.34-3.46 (m, 1H), 3.97 (d, J = 7.4 Hz, 1H), 3.97-4.09 (m, 1H), 5.92 (d, J = 2.7 Hz, 1H), 6.44 (d, J = 2.7 Hz, 1H), 7.20-7.36 (m, 5H) ppm; \[ ^{13} \text{C NMR (75 MHz, } \delta , \text{ CDCl}_3, 298 K): 24.3, 25.7, 26.6, 29.2, 29.3, 30.9, 35.0, 35.1, 37.0, 37.4, 39.7, 43.4, 46.6, 127.4, 128.4, 129.0, 135.5, 138.7, 139.6, 149.5, 149.8, 165.7, 185.4, 206.9 ppm; HRMS (ESI): m/z calcd. for C_{21}H_{22}NO: 420.2897 \text{ [M+H}^+; found: 420.2896; The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: t_{major} = 15.5 min, t_{minor} = 17.6 min).

**Cyclopropane 3p:** Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 10:1), Procedure D: Using 5c (27.1 mg, 0.10 mmol), 1a (44.2 mg, 0.15 mmol) and Cs₂CO₃ (164 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3p (40.3 mg, 0.10 mmol, 95%, trans: cis = 2.9:1, colourless crystals); Procedure E: Using 5o (54.7 mg, 0.10 mmol), 1a (72.5 mg, 0.25 mmol) and Cs₂CO₃ (198 mg, 0.61 mmol) in 1 ml DCM, refluxing for 96 h, yielding 3p (44.4 mg, 0.11 mmol, 97%, dr > 18:1, er > 99.8:0.2 (major diastereomer), colourless crystals). \([ \alpha ]_{D}^{20} = 148.8^\circ \text{ (c = 0.97, CHCl}_3 \); \[ \text{H NMR (300 MHz, } \delta , \text{ CDCl}_3, 298 K): 1.08 (s, 9H), 1.26 (s, 9H), 3.27 (s, 3H), 3.49 (s, 3H), 3.58 (d, J = 7.3 Hz, 1H), 3.89 (d, J = 7.3 Hz, 1H), 5.93 (d, J = 2.7 Hz, 1H), 6.70 (d, J = 2.7 Hz, 1H), 7.21-7.38 (m, 5H) ppm; \[ ^{13} \text{C NMR (75 MHz, } \delta , \text{ CDCl}_3, 298 K): 29.3, 29.6, 35.2, 35.3, 37.0, 37.1, 39.6, 42.8, 46.1, 66.9, 67.1, 128.7, 128.7, 129.2, 135.3, 138.5, 139.1, 150.1, 150.3, 166.4, 185.5 ppm; HRMS (ESI): m/z calcd. for C_{25}H_{33}NO_{5}: 444.2509 \text{ [M+Na}^+; found: 444.2502; The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: t_{major} = 18.7 min, t_{minor} = 24.1 min).
**Cyclopropane 3q**: Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 5:1), Procedure D: Using 5d (29.0 mg, 0.12 mmol), 1a (44.9 mg, 0.15 mmol) and Cs₂CO₃ (163 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt. Yielding 3q (42.3 mg, 0.09 mmol, 89%, trans:cis = 9:7:1, colourless crystals); Procedure E: Using 5p (51.5 mg, 0.10 mmol), 1a (74.0 mg, 0.25 mmol) and Cs₂CO₃ (196 mg, 0.60 mmol) in 1 ml DCM, refluxing for 96 h. Yielding 3q (33.6 mg, 0.09 mmol, 85%, dr > 40:1, er > 99.8:0.2 (major diastereomer), colourless crystals). [α]D²⁰ = 178.9° (c = 0.97, CHCl₃); ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.10 (s, 9H), 1.29 (s, 9H), 3.11 (d, J = 7.3 Hz, 1H), 3.22-3.49 (m, 4H), 3.49-3.59 (m, 1H), 3.64-3.72 (m, 1H), 3.74-3.85 (m, 1H), 3.88-4.05 (m, 2H), 5.92 (d, J = 2.7 Hz, 1H), 6.44 (d, J = 2.7 Hz, 1H), 7.21-7.40 (m, 5H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 29.2, 29.3, 32.6, 34.5, 35.0, 35.1, 37.7, 39.0, 61.7, 127.5, 128.4, 129.0, 135.3, 138.7, 139.2, 149.4, 149.6, 168.5, 185.7 ppm; HRMS (ESI): m/z calcd. for C₂₅H₃₃NO₃: 396.2533 [M+H]⁺; found: 396.2534; The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: t_major (2R, 1S) = 25.0 min, t_minor (2S, 1R) = 30.5 min).

**Cyclopropane 3r**: Prepared according to general procedures followed by column chromatography (neutral alumina, heptanes:EtOAc = 15:1), Procedure D: Using 5e (38.3 mg, 0.10 mmol), 1a (44.0 mg, 0.15 mmol) and Cs₂CO₃ (163 mg, 0.50 mmol) in 1 ml DCM, stirring for 24 h at rt, yielding 3r (46.1 mg, 0.09 mmol, 85%, trans:cis = 1:2:1, white solid); Procedure E: Using 5q (65.3 mg, 0.10 mmol), 1a (75.0 mg, 0.25 mmol) and Cs₂CO₃ (197 mg, 0.61 mmol) in 1 ml DCM, refluxing for 96 h, yielding 3r (41.5 mg, 0.08 mmol, 78%, dr > 40:1, er > 99.8:0.2 (major diastereomer), white solid). [α]D²⁰ = 61.6° (c = 0.99, CHCl₃); ¹H NMR (300 MHz, δ, CDCl₃, 298 K): 1.02 (s, 9H), 1.28 (s, 9H), 3.16 (d, J = 7.3 Hz, 1H), 4.04 (d, J = 7.3 Hz, 1H), 4.21 (d, J = 14.6 Hz, 1H), 4.42 (s, 2H), 5.19 (d, J = 14.6 Hz, 1H), 5.73 (d, J = 2.7 Hz, 1H), 6.75 (d, J = 2.7 Hz, 1H), 7.07-7.17 (m, 4H), 7.22-7.41 (m, 11H) ppm; ¹³C NMR (75 MHz, δ, CDCl₃, 298 K): 29.1, 29.3, 34.9, 35.1, 36.1, 38.0, 39.7, 49.4, 50.0, 126.1, 127.4, 127.6, 127.8, 128.3, 128.4, 128.7, 128.8, 129.1, 135.3, 136.0, 136.8, 138.3, 149.5, 149.8 ppm; HRMS (ESI): m/z calcd. for C₃₇H₄₁NO₃: 532.3210 [M+H]⁺; found: 532.3205; The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: n-hexane:i-PrOH = 98:2, 0.5 mL/min, 10 °C, retention times: t_major = 100.0 min, t_minor = 86.5 min).
1.2.3 Ring opening reactions

**General procedure F:** 1 equiv of cyclopropane was dissolved in DCM (0.5 M), and 4 equiv of nucleophile were added. The mixture was stirred for the stated reaction times and after completion, the solvent was evaporated and the product dried *in vacuo.*

**Opened Cyclopropane 6a:** Prepared according to general procedure F, pure product was obtained without any purification, using 3b (20.5 mg, 0.05 mmol), and MeOH (6.4 mg, 0.20 mmol) in 0.1 ml DCM, stirring for 120 h at rt, yielding 6a (22.0 mg, 0.05 mmol, 99%, \( \text{dr} > 40:1, \text{er} > 99.8:0.2 \) (major diastereomer), colourless residue). \([\alpha]_D^{20} = 97.8^\circ \text{ (c = 1.01, CHCl}_3\text{)}; ^1\text{H NMR (300 MHz, }\delta, \text{ CDCl}_3\text{, 298 K): 1.07-1.14 (m, 6H), 1.25 (s, 18H), 3.04-3.22 (m, 2H), 3.23-3.39 (m, 4H), 3.63-3.78 (m, 2H), 4.72 (d, } J = 9.6 \text{ Hz, 1H), 4.96 (s, 3H), 6.65 (s, 2H), 6.84-6.95 (m, 2H), 7.06-7.15 (m, 3H) ppm; ^13\text{C NMR (75 MHz, }\delta, \text{ CDCl}_3\text{, 298 K): 12.8, 14.4, 30.1, 30.2, 34.0, 34.1, 40.7, 42.0, 56.3, 57.1, 86.1, 125.5, 125.5, 126.3, 127.0, 127.5, 135.3, 135.3, 140.2, 152.4, 171.0 ppm; HRMS (ESI): }m/z \text{ calcld. for C}_{38}\text{H}_{35}\text{NO}_2: 517.2599 [M+H]^{+}; \text{ found: 517.2597}; \text{ The enantioselectivity was determined by HPLC (YMC Cellulose-SB, eluent: } n\text{-hexane:i-PrOH = 50:1, 0.5 mL/min, 10 °C, retention times: } t_{\text{major}} = 37.4 \text{ min, } t_{\text{minor}} = 34.9 \text{ min).}

**Opened Cyclopropane 6b:** Prepared according to general procedure F, pure product was obtained without any purification, using 3j (22.0 mg, 0.05 mmol), and MeOH (6.4 mg, 0.20 mmol) in 0.1 ml DCM, stirring for 72 h at rt, yielding 6b (23.4 mg, 0.05 mmol, 99%, \( \text{dr} > 40:1, \text{er} = 99.7:0.3 \) (major diastereomer), colourless residue). \([\alpha]_D^{20} = 93.9^\circ \text{ (c = 1.00, CHCl}_3\text{)}; ^1\text{H NMR (300 MHz, }\delta, \text{ CDCl}_3\text{, 298 K): 1.06-1.14 (m, 6H), 1.26 (s, 18H), 3.06-3.20 (m, 2H), 3.24 (s, 3H), 3.26-3.39 (m, 1H), 3.61-3.77 (m, 5H), 3.23-3.39 (m, 4H), 3.63-3.78 (m, 2H), 4.67 (d, } J = 9.6 \text{ Hz, 1H), 4.96 (s, 1H), 6.61-6.69 (m, 4H), 6.81 (d, } J = 8.6 \text{ Hz, 2H) ppm; ^13\text{C NMR (75 MHz, }\delta, \text{ CDCl}_3\text{, 298 K): 12.8, 14.4, 30.2, 34.1, 40.6, 41.9, 55.1, 56.3, 56.9, 85.6, 112.9, 125.5, 126.5, 128.5, 132.3, 135.3, 152.4, 158.7, 171.1 ppm; HRMS (ESI): }m/z \text{ calcld. for C}_{38}\text{H}_{35}\text{NO}_2: 492.3084 [M+Na]^{+}; \text{ found: 492.3080}; \text{ The enantioselectivity was determined by HPLC (Chiralpak AD-H, eluent: } n\text{-hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: } t_{\text{major}} = 21.5 \text{ min, } t_{\text{minor}} = 10.4 \text{ min).}

**Opened Cyclopropane 6c:** Prepared according to general procedure F, pure product was obtained without any purification, using 3j (22.2 mg, 0.05 mmol), and EtOH (9.2 mg, 0.20 mmol) in 0.1 ml DCM, stirring for 96 h at rt, yielding 6c (24.3 mg, 0.05 mmol, 99%, \( \text{dr} > 40:1, \text{er} = 99.7:0.3 \) (major diastereomer), colourless residue). \([\alpha]_D^{20} = 99.2^\circ \text{ (c = 1.00, CHCl}_3\text{)}; ^1\text{H NMR (300 MHz, }\delta, \text{ CDCl}_3\text{, 298 K): 1.08-1.18 (m, 9H), 1.27 (s, 18H), 3.14-3.56 (m, 6H), 3.68 (d, } J = 9.6 \text{ Hz, 1H), 3.71 (s, 3H), 4.76 (d, } J = 9.6 \text{ Hz, 1H), 4.95 (s, 1H), 6.64 (d, } J = 8.7 \text{ Hz, 1H), 6.72 (s, 2H), 6.82 (d, } J = 8.7 \text{ Hz, 1H) ppm; ^13\text{C NMR (75 MHz, }\delta, \text{ CDCl}_3\text{, 298 K): 12.9, 14.5, 15.3, 30.2, 34.1, 40.9, 42.3, 55.1, 56.2, 64.4, 84.0, 112.8, 125.6, 126.6, 128.3, 133.1, 135.2, 152.4, 158.5, 171.4 ppm; HRMS (ESI): }m/z \text{ calcld. for C}_{38}\text{H}_{35}\text{NO}_2: 506.3241 [M+Na]^{+}; \text{ found: 506.3235}; \text{ The enantioselectivity was determined by HPLC (YMC Cellulose-SB, eluent: } n\text{-hexane:i-PrOH = 300:1, 0.5 mL/min, 10 °C, retention times: } t_{\text{major}} = 22.2 \text{ min, } t_{\text{minor}} = 20.6 \text{ min).}
Opened Cyclopropane 6d: Prepared according to general procedure F, pure product was obtained without any purification, using 3h (22.2 mg, 0.05 mmol), and MeOH (6.4 mg, 0.20 mmol) in 0.1 ml DCM, stirring for 120 h at rt, yielding 6d (23.6 mg, 0.05 mmol, 99%, dr > 40:1, er > 99.8:0.2 (major diastereomer), yellow residue). \( [\alpha]^{20}_D = 105.9^\circ \) (c = 1.00, CHCl3); \(^1\)H NMR (300 MHz, δ, CDCl3, 298 K): 1.05-1.14 (m, 6H), 1.27 (s, 18H), 3.03-3.20 (m, 2H), 3.23-3.36 (m, 4H), 3.62 (d, J = 9.5 Hz, 1H), 3.65-3.78 (m, 1H), 4.73 (d, J = 9.5 Hz, 1H), 5.00 (s, 1H), 6.63 (s, 2H), 6.82 (d, J = 8.4 Hz, 1H), 7.08 (d, J = 8.4 Hz, 1H) ppm; \(^13\)C NMR (75 MHz, δ, CDCl3, 298 K): 12.7, 14.4, 30.1, 34.1, 40.6, 41.9, 56.4, 57.2, 85.4, 125.4, 125.6, 127.6, 128.7, 132.7, 135.6, 139.0, 152.6, 170.7 ppm; HRMS (ESI): m/z calcd. for C\(_{28}\)H\(_{41}\)ClNO: 474.2770 [M+H]\(^+\); found: 474.2767.

The enantioselectivity was determined by HPLC (YMC Cellulose-SB, eluent: n-hexane:i-PrOH = 500:1, 0.5 mL/min, 10 °C, retention times: \( t_{major} = 36.0 \text{ min}, t_{minor} = 38.3 \text{ min} \)).

Opened Cyclopropane 6e: Prepared according to general procedure F, pure product was obtained without any purification, using 3f (23.3 mg, 0.05 mmol), and MeOH (6.4 mg, 0.20 mmol) in 0.1 ml DCM, stirring for 72 h at rt, yielding 6e (24.7 mg, 0.05 mmol, 99%, dr > 40:1, er = 98.7:1.3 (major diastereomer), colourless residue). \( [\alpha]^{20}_D = 84.6^\circ \) (c = 0.99, CHCl3); \(^1\)H NMR (300 MHz, δ, CDCl3, 298 K): 1.08-1.14 (m, 6H), 1.25 (s, 18H), 1.26 (s, 9H), 3.03-3.21 (m, 2H), 3.21-3.38 (m, 4H), 3.62-3.80 (m, 2H), 4.65 (d, J = 9.9 Hz, 1H), 4.96 (s, 1H), 6.65 (s, 2H), 6.81 (d, J = 8.3 Hz, 2H), 7.14 (d, J = 8.3 Hz, 2H) ppm; \(^13\)C NMR (75 MHz, δ, CDCl3, 298 K): 12.8, 14.4, 30.2, 31.4, 34.1, 34.3, 40.6, 42.0, 56.3, 57.1, 85.9, 124.4, 125.6, 126.3, 127.2, 135.2, 137.1, 149.7, 152.4, 171.1 ppm; HRMS (ESI): m/z calcd. for C\(_{28}\)H\(_{40}\)NO: 496.3785 [M+H]\(^+\); found: 496.3778.

The enantioselectivity was determined by HPLC (YMC Cellulose-SB, eluent: n-hexane:i-PrOH = 300:1, 0.5 mL/min, 10 °C, retention times: \( t_{major} = 22.0 \text{ min}, t_{minor} = 20.5 \text{ min} \)).

Opened Cyclopropane 6f: Prepared according to general procedure F, pure product was obtained without any purification, using 3j (21.0 mg, 0.05 mmol), and MeOH (6.4 mg, 0.20 mmol) in 0.1 ml DCM, stirring for 120 h at rt, yielding 6f (22.5 mg, 0.05 mmol, 99%, dr > 35:1, er > 99.8:0.2 (major diastereomer), colourless crystals). \( [\alpha]^{20}_D = 51.3^\circ \) (c = 0.76, CHCl3); \(^1\)H NMR (300 MHz, δ, CDCl3, 298 K): 1.25 (s, 18H), 2.99-3.10 (m, 1H), 3.27 (s, 3H), 3.32-3.38 (m, 1H), 3.41-3.55 (m, 4H), 3.68-3.77 (m, 2H), 3.84-3.94 (m, 1H), 4.77 (d, J = 9.5 Hz, 1H), 4.99 (s, 1H), 6.58 (s, 2H), 6.88-6.95 (m, 2H), 7.08-7.15 (m, 3) ppm; \(^13\)C NMR (75 MHz, δ, CDCl3, 298 K): 30.1, 34.1 42.6, 46.1, 56.1, 57.0, 66.3, 66.8, 85.5, 125.3, 125.6, 127.2, 127.6, 135.7, 139.7, 152.6, 170.6 ppm; HRMS (ESI): m/z calcd. for C\(_{28}\)H\(_{40}\)NO: 454.2952 [M+H]\(^+\); found: 454.2950; The enantioselectivity was determined by HPLC (YMC Cellulose-SB, eluent: n-hexane:i-PrOH = 500:1, 0.5 mL/min, 10 °C, retention times: \( t_{major} = 68.0 \text{ min}, t_{minor} = 74.1 \text{ min} \)).

Opened Cyclopropane 6g: Prepared according to general procedure F, pure product was obtained without any purification, using 3j (22.2 mg, 0.05 mmol), and MeOH (6.4 mg, 0.20 mmol) in 0.1 ml DCM, stirring for 96 h at rt, yielding 6g (23.5 mg, 0.05 mmol, 99%, dr > 40:1, er > 99.8:0.2 (major diastereomer), colourless residue). \( [\alpha]^{20}_D = 56.1^\circ \) (c = 0.99, CHCl3); \(^1\)H NMR (300 MHz, δ, CDCl3, 298 K): 1.02-1.15 (m, 6H), 1.25 (s, 18H), 3.00-3.16 (m, 2H), 3.16-3.32 (m, 7H), 3.62 (d, J = 9.5 Hz, 1H), 3.66-3.85 (m, 2H), 4.92 (s, 1H), 5.28 (d, J = 9.4 Hz, 1H), 6.49 (d, J = 6.5 Hz, 1H), 6.67 (s, 2H), 6.93 (t, J = 7.5 Hz, 1H), 7.06-7.16 (m, 1H), 7.34-7.46 (m, 1H) ppm; \(^13\)C NMR (75 MHz, δ, CDCl3, 298 K): 12.7, 14.3, 30.2, 34.0, 40.5, 41.9, 54.9, 57.0, 109.8, 120.2, 125.6, 126.1, 128.1, 128.9, 134.5, 152.2, 157.9, 171.2 ppm; HRMS (ESI): m/z calcd. for C\(_{28}\)H\(_{43}\)NO: 549.1032 [M+H]\(^+\); found: 549.1038.
492.3084 [M+Na]⁺; found: 492.3078; The enantioselectivity was determined by HPLC (YMC Cellulose-SB, eluent: n-hexane:i-PrOH = 300:1, 0.5 mL/min, 10 °C, retention times: t\textsubscript{major} = 33.2 min, t\textsubscript{minor} = 36.3 min).

**Opened Cyclopropane 6h:** Prepared according to general procedure E, full conversion to 6h during column chromatography (neutral alumina, heptanes:EtOAc = 50:1): Using 5h (53.0 mg, 0.10 mmol), 1f (84.3 mg, 0.25 mmol) and Cs\textsubscript{2}CO\textsubscript{3} (195.2 mg, 0.60 mmol) in 1 ml DCM, refluxing for 96 h, yielding 6h (34.3 mg, 0.08 mmol, 76%, dr > 40:1, er > 99.8:0.2 (major diastereomer), yellow oil). \(\left[\alpha\right]_{D}^{20} = 89.9^\circ\) (c = 0.52, CHCl\textsubscript{3}); \textsuperscript{1}H NMR (300 MHz, \(\delta\), CDCl\textsubscript{3}, 298 K): 1.08-1.16 (m, 6H), 1.27 (s, 18H), 2.85 (s, 6H), 3.14-3.57 (m, 4H), 3.70 (d, \(J = 9.5\) Hz, 1H), 4.70 (d, \(J = 9.5\) Hz, 1H), 4.93 (s, 1H), 6.49 (d, \(J = 8.9\) Hz, 2H), 6.72 (s, 2H), 6.77 (d, \(J = 8.9\) Hz, 2H) ppm; \textsuperscript{13}C NMR (75 MHz, \(\delta\), CDCl\textsubscript{3}, 298 K): 12.7, 13.5, 30.2, 34.1, 40.2, 40.8, 41.9, 57.7, 112.4, 125.0, 127.2, 127.4, 130.0, 135.5, 150.1, 152.5, 173.0 ppm; HRMS (ESI): \(m/z\) calcd. for C\textsubscript{29}H\textsubscript{44}N\textsubscript{2}O\textsubscript{3}: 469.3425 [M+H]\(^+\); found: 469.3420; The enantioselectivity was determined by HPLC (YMC Cellulose-SB, eluent: n-hexane:i-PrOH = 300:1, 0.5 mL/min, 10 °C, retention times: t\textsubscript{major} = 46.4 min, t\textsubscript{minor} = 40.5 min).
2 X-Ray Analysis of 3l

Single-crystal structure analyses were carried out on a Bruker Smart X2S diffractometer operating with Mo-Kα radiation (λ= 0.71073 Å). Further crystallographic and refinement data can be found in Table 1. The structures were solved by direct methods (SHELXS-97)22 and refined by full-matrix least squares on $F^2$ (SHELXL-97).23 The H atoms were calculated geometrically, and a riding model was applied in the refinement process. The presence of the bromine atom allowed for the determination of the absolute configuration of 3l by refining the Flack parameter [0.041(10)]. CCDC 1513618 contains the supplementary crystallographic data for compound 3l. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk.

Table 1: Crystal Data and Data Collection and Structure Refinement Details for Compound 3l

| Crystal Data          | 3l               |
|-----------------------|------------------|
| Empirical formula     | C27H36BrNO2      |
| Formula weight        | 486.48           |
| Crystal size (mm)     | 0.67 × 0.49 × 0.40 |
| Crystal system        | orthorhombic     |
| Space group           | P2_12_2_1_2_1    |
| a (Å)                 | 10.5792(7)       |
| b (Å)                 | 12.2534(9)       |
| c (Å)                 | 20.4903(16)      |
| V (Å³)                | 2656.2(3)        |
| D_calcd (g cm⁻³)      | 1.217            |
| Z                     | 4                |
| μ (mm⁻¹)              | 1.57             |
| T (K)                 | 300              |
| θ range (°)           | 1.9 – 24.8       |
| No. of reflections measured | 28521          |
| No. of independent reflections | 4544          |
| Parameters refined/restraints | 288/0          |
| R_int                 | 0.057            |
| Absorption correction | multi-scan       |
| Tmin, Tmax            | 0.42, 0.57       |
| Largest diff. peak and hole (e Å⁻³) | 0.27 / -0.39 |
| Flack parameter       | 0.041(10)        |
| R₁ [I ≥ 2σ(I)]        | 0.036            |
| wR₂                   | 0.095            |
| CCDC no.              | 1513618          |

22) G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Göttingen, Germany, 1997. See also: G. M. Sheldrick, Acta Crystallographica, 1990, A46, 467-473.
23) G. M. Sheldrick, SHELXL-97, Program for crystal structure refinement, Göttingen, Germany, 1997. See also: G. M. Sheldrick, Acta Crystallographica, 2008, A64, 112-122
3 Copies of HPLC Chromatograms

Sample Name: ROI-1010_100_1_flo5  
Injection Volume: 30,0

Vial Number: BB3  
Channel: UV_VIS_1

Sample Type: unknown  
Wavelength: 220

Control Program: AD_H_90Min_100A_flow_5  
Bandwidth: 4

Quanif. Method: default  
Temperature/Column: 10

Recording Time: 20.1.2017 20:27  
Flow mL/min: 0,500

Run Time (min): 90,00  
Sample Amount: 1,0000

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU\*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|---------------|------------|--------|------|
| 1   | 12,81        | n.a.      | 186,667    | 92,562        | 8,47       | n.a.   | BMB  |
| 2   | 22,92        | n.a.      | 106,200    | 92,186        | 8,43       | n.a.   | BMB  |
| 3   | 35,12        | n.a.      | 318,767    | 453,400       | 41,46      | n.a.   | BM   |
| 4   | 40,92        | n.a.      | 270,787    | 454,779       | 41,61      | n.a.   | MB   |

Total: 862,421 1092,926 100,00 0,000

27
## 3 ROI-1086_100_1_flo5

**Sample Name:** ROI-1086_100_1_flo5  
**Injection Volume:** 30.0 µL  
**Vial Number:** GB1  
**Channel:** UV_VIS_2  
**Sample Type:** unknown  
**Wavelength:** 250 nm  
**Control Program:** AD_H_90Min_100A_flow0_5  
**Bandwidth:** 4  
**Quantif. Method:** default  
**Temperature/Column:** 10 °C  
**Recording Time:** 20.1.2017 21:58  
**Flow mL/min:** 0.500  
**Run Time (min):** 90.00  
**Sample Amount:** 1,0000 µL

![Safety and Operational Instructions Diagram](image_url)

### Table 1: Chromatography Data

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|---------------|-----------|--------------|----------------|-------------|--------|------|
| 1   | 35.72         | n.a       | 0.037        | 0.011          | 0.04        | n.a    | BMB* |
| 2   | 41.03         | n.a       | 18,510       | 27,074         | 99.98       | n.a    | BMB* |
| **Total:** |             |           | 16,545       | 27,085         | 100.00      | 0.000  |      |

---

*default/integration*  
*Chromeleon (c) Dionex 1996-2006*  
*Version 6.8 SR12 Build 3578 (207169)*
| No. | Ret.Time (min) | Peak Name  | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount (μl) | Type  |
|-----|---------------|------------|--------------|----------------|--------------|-------------|-------|
| 1   | 35.70         | n.a        | 0.268        | 0.363          | 1.24         | n.a         | BMB*  |
| 2   | 41.66         | n.a        | 17.776       | 28.871         | 98.76        | n.a         | BMB*  |
| Total|               |            | 18.044       | 29.235         | 100.00       | 0.000       |       |

WAS_20170120_2 ROI #20 [modified by Admin]
UV_VIS_2
VWL: 250 nm

Operator: Admin
Timebase: U-3000_DAD
Sequence: WAS_20170120_2 ROI

29
21 ROI-1191_100_1_flo5

Sample Name: ROI-1191_100_1_flo5
Injection Volume: 30.0
Vial Number: BB8
Channel: UV_VIS_1
Sample Type: unknown
Wavelength: 220
Control Program: AD_H_90Min_100A_flow0_5
Bandwidth: 4
Quantif. Method: default
Temperature/Column: 10
Recording Time: 22.1.2017 1:09
Flow m/min: 0.500
Run Time (min): 90.00
Sample Amount: 1.000

![Graph](image)

| No. | Ret.Time | Peak Name | Height mAU | Area mAU/min | Rel.Area % | Amount | Type |
|-----|----------|-----------|------------|--------------|------------|--------|------|
| 1   | 23.34    | n.a.      | 3.038      | 2.529        | 0.85       | n.a.   | BMB* |
| 2   | 35.76    | n.a.      | 201.474    | 294.433      | 98.57      | n.a.   | BMB  |
| 3   | 41.78    | n.a.      | 0.457      | 0.532        | 0.18       | n.a.   | BMB* |
| Total|          |           | 204.969    | 297.404      | 100.00     | 0.000  |      |

Chromleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207109)
1 ROI-1142-02_95_5_flo5

Sample Name: ROI-1142-02_95_5_flo5
Vial Number: GD3
Sample Type: unknown
Control Program: YMC_90Min_95_5_flow0_5
Quantif. Method: AD_H
Recording Time: 4.1.2017 17:08
Run Time (min): 90.00

Injection Volume: 20.0
Channel: UV_VIS_1
Wavelength: 220
Bandwidth: 4
Temperature/Column: 10
Flow m/min: 0.500
Sample Amount: 1,000

---

| No. | Ret. Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel. Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 53.45          | n.a.      | 38,504       | 78,907         | 50.07        | n.a.   | BMB* |
| 2   | 58.19          | n.a.      | 32,285       | 78,662         | 49.93        | n.a.   | BMB* |
|     |                |           |              |                |              |        |      |
| Total|                |           | 70,790       | 157,599        | 100.00       | 0.000  |      |

---

(default/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
### ROI-1179-03_95_5_flo5

| Sample Name         | ROI-1179-03_95_5_flo5 |
|---------------------|-----------------------|
| Vial Number         | GA3                   |
| Sample Type         | unknown               |
| Control Program     | YMC_90Min_95_5_flow0_5|
| Quantif. Method     | AD_H                  |
| Recording Time      | 4.1.2017 20:09        |
| Run Time (min)      | 90.00                 |

**Injection Volume:** 30.0

**Channel:** UV_VIS_1

**Wavelength:** 220

**Bandwidth:** 4

**Temperature/Column:** 10

**Flow m/min:** 0.500

**Sample Amount:** 1,000

---

**Chromatogram**

| No. | Ret.Time | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|----------|-----------|------------|--------------|------------|--------|------|
| 1   | 51.69    | n.a.      | 106.855    | 248.265      | 99.80      | n.a.   | BMB* |
| 2   | 59.14    | n.a.      | 0.628      | 0.494        | 0.20       | n.a.   | BMB* |
| Total|          |           | 107.483    | 248.759      | 100.00     | 0.000  |      |

---

**Remarks:**

- Chromatogram (c) Dionex 1996-2006
- Version 6.80 SR12 Build 3578 (207169)

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**default/Integration**
17 ROI-1203_100_1_fio5

Sample Name: ROI-1203_100_1_fio5  Injection Volume: 30.0
Vial Number: BC3  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: 220
Control Program: AD_H_90Min_100A_flow0_5  Bandwidth: 4
Quantif. Method: default  Temperature/Column: 10
Recording Time: 21.1.2017 19:06  Flow ml/min: 0.500
Run Time (min): 90.00  Sample Amount: 1,000

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 11.68          | n.a.      | 158.381      | 60.005         | 6.52         | n.a.   | BMB* |
| 2   | 18.63          | n.a.      | 87.180       | 61.273         | 6.66         | n.a.   | BMB  |
| 3   | 29.87          | n.a.      | 300.886      | 399.274        | 43.41        | n.a.   | BMB  |
| 4   | 39.84          | n.a.      | 225.863      | 399.124        | 43.40        | n.a.   | BMB  |
| Total|                |           | 772.309      | 919.676        | 100.00       | 0.000  |      |

default/integration

Chromleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
18 ROI-1206_100_1_fio5

| Sample Name                  | ROI-1206_100_1_fio5 |
|------------------------------|---------------------|
| Vial Number                  | BC4                 |
| Sample Type                  | unknown             |
| Control Program              | AD_H_90Min_100A_flow0_5 |
| Quantif. Method              | default             |
| Recording Time               | 21.1.2017 20:37     |
| Run Time (min)               | 90,00               |

| Injection Volume             | 30,0                |
| Channel                      | UV_VIS_1            |
| Wavelength                   | 220                 |
| Bandwidth                    | 4                   |
| Temperature/Column           | 10                  |
| Flow ml/min                  | 0,500               |
| Sample Amount                | 1,000               |

**Graph:**

- **Peak 1:** Rel. Time = 11.88 min, Height = 15,505 mAU, Area = 4,945 mAU·min, Rel.Area % = 4.87, n.a., BMB*
- **Peak 2:** Rel. Time = 18.67 min, Height = 0.018 mAU, Area = 0.037 mAU·min, Rel.Area % = 0.04, n.a., BMB*
- **Peak 3:** Rel. Time = 30.31 min, Height = 0.122 mAU, Area = 0.088 mAU·min, Rel.Area % = 0.09, n.a., BMB*
- **Peak 4:** Rel. Time = 40.00 min, Height = 56.562 mAU, Area = 96.406 mAU·min, Rel.Area % = 95.00, n.a., BMB

**Total:**

- Height = 72,206 mAU
- Area = 101,476 mAU·min
- Rel.Area % = 100.00
- Amount = 0.000

**Column:**

- 3d
- er > 99.5:0.2
5 ROI-1147_100_1_flo5

Sample Name: ROI-1147_100_1_flo5  Injection Volume: 30.0
Vial Number: GB7  Channel: UV_VIS_2
Sample Type: unknown  Wavelength: 250
Control Program: AD_H_90Min_100A_flow0_5  Bandwidth: 4
Quantif Method: default  Temperature/Column: 10
Recording Time: 21.1.2017 0:59  Flow ml/min: 0.500
Run Time (min): 90.00  Sample Amount: 1,0000

---

![Graph](image)

3e  er = 99.7 ± 0.3

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 12.28          | n.a.      | 11.747       | 5.284          | 4.80         | n.a.   | MIB* |
| 2   | 30.66          | n.a.      | 82.877       | 104.471        | 94.87        | n.a.   | BMB* |
| 3   | 42.67          | n.a.      | 0.270        | 0.360          | 0.33         | n.a.   | BMB* |
| Total |                |           | 94.895       | 110.115        | 100.00       | 0.00   |

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default/Integration

Chromelon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
### 6 ROI-1024_100_1_flo5

| Sample Name       | ROI-1024_100_1_flo5  |
|-------------------|----------------------|
| Injection Volume  | 30.0                 |
| Vial Number       | BB5                  |
| Channel           | UV_VIS_1             |
| Sample Type       | unknown              |
| Wavelength        | 220                  |
| Control Program   | AD_H_90Min_100A_flow0_5 |
| Bandwidth         | 4                    |
| Quanif. Method    | default              |
| Temperature/Column| 10                   |
| Recording Time    | 21.1.2017 2:30       |
| Flow m/min        | 0.500                |
| Run Time (min)    | 90,00                |
| Sample Amount     | 1,000                |

![Graph showing a chromatogram with peak areas and retention times for compounds labeled as 1, 2, 3, and 4.](attachment:chromatogram.png)

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 12.57        | n.a.      | 94,786     | 49,397       | 6.25       | n.a.   | BMB  |
| 2   | 17.86        | n.a.      | 481,903    | 345,815      | 43.74      | n.a.   | MB*  |
| 3   | 22.50        | n.a.      | 50,106     | 51,560       | 6.52       | n.a.   | BMB  |
| 4   | 39.19        | n.a.      | 200,740    | 343,826      | 43.49      | n.a.   | BMB  |
| Total|              |           | 827,574    | 790,569      | 100.00     | 0.000  |      |

**Notes:**
- Chromelon (c) Dionex 1996-2006
- Version 6.80 SR12 Build 3578 (207169)
Sample Name: ROI-1114_100_1_flo5
Vial Number: GB3
Sample Type: unknown
Control Program: AD_H_120Min_100A_flow0_5
Quantif. Method: default
Recording Time: 31.1.2017 23:11
Run Time (min): 120,00
Injection Volume: 30.0
Channel: UV_VIS_2
Wavelength: 250
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 0.500
Sample Amount: 1.0000

No. | Ret.Time | Peak Name | Height mAU | Area mAU min | Rel.Area % | Amount | Type
---|---------|-----------|------------|-------------|----------|--------|-------
1  | 18.35   | n.a.      | 24.794     | 17,475      | 96.58    | n.a.   | MB*   
2  | 38.74   | n.a.      | 0.076      | 0.074       | 0.42     | n.a.   | BMB*  
Total: | 24.871 | 17,549 | 100.00 | 0.000

default/integration

defaultIntegration

Chromeleon (c) Dionex 1998-2006
Version 6.80 SR12 Build 3578 (207169)
13 ROI-1028_100_1_fio5

Sample Name: ROI-1028_100_1_fio5  
Injection Volume: 30.0
Vial Number: BB6  
Channel: UV_VIS
Sample Type: unknown  
Wavelength: 250
Control Program: AD_H_90Min_100A_flow0.5  
Bandwidth: 4
Quantif. Method: default  
Temperature/Column: 10
Recording Time: 21.1.2017 13:04  
Flow m/min: 0.500
Run Time (min): 90.00  
Sample Amount: 1,0000

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 12.59        | n.a.      | 6,180      | 4,212        | 6.20       | n.a.   | BMB* |
| 2   | 23.57        | n.a.      | 4,400      | 4,376        | 6.44       | n.a.   | BMB* |
| 3   | 38.31        | n.a.      | 18,370     | 29,492       | 43.42      | n.a.   | BMB* |
| 4   | 53.83        | n.a.      | 12,795     | 29,839       | 48.83      | n.a.   | BMB* |
| Total: |             |           | 41,745     | 67,919       | 100.00     | 0,000  |      |

default/integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
14 ROI-1095_100_1_flo5

Sample Name: ROI-1095_100_1_flo5
Injection Volume: 30.0
Vial Number: GD1
Channel: UV_VIS_2
Sample Type: unknown
Wavelength: 250
Control Program: AD_H_90Min_100A_flow0_5
Bandwidth: 4
Quantif. Method: default
Temperature/Column: 10
Recording Time: 21.1.2017 14:35
Flow ml/min: 0.500
Run Time (min): 90.00
Sample Amount: 1,000

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area % | Amount (n.a.) | Type |
|-----|---------------|-----------|--------------|----------------|------------|--------------|------|
| 1   | 38.48         | n.a       | 83.201       | 132,298        | 99.88      | n.a          | BMB  |
| 2   | 54.30         | n.a       | 0.150        | 0.164          | 0.12       | n.a          | BMB* |
| Total|               |           | 83.351       | 132,462        | 100.00     | 0.000        |      |

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
10 ROI-1135_100_1_flo5

Sample Name: ROI-1135_100_1_flo5  
Injection Volume: 30,0
Vial Number: GE3  
Channel: UV_VIS_1
Sample Type: unknown  
Wavelength: 220
Control Program: AD_H_120Min_100A_flow0_5  
Bandwidth: 4
Quantif. Method: default  
Temperature/Column: 10
Recording Time: 30.1.2017 9:25  
Flow m/min: 0,500
Run Time (min): 94,80  
Sample Amount: 1,0000

| No. | Ret. Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 36,15          | n.a.      | 30,858       | 45,017         | 51,44        | n.a.   | BMB* |
| 2   | 47,14          | n.a.      | 22,092       | 42,503         | 48,56        | n.a.   | BMB* |
| Total|                |           | 52,950       | 87,520         | 100,00       | 0,000  |

default/Integration

Chromleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
11 ROI-1139_100_1_flo5

Sample Name: ROI-1139_100_1_flo5  Injection Volume: 30,0
Vial Number: BA1  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: 220
Control Program: AD_H_120Min_100A_flow0_5  Bandwidth: 4
Quantif. Method: default  Temperature/Column: 10
Recording Time: 30.1.2017 11:00  Flow ml/min: 0,500
Run Time (min): 52,47  Sample Amount: 1,0000

![Graph with peak analysis details]

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 36,25        | n.a.      | 228,528    | 334,482      | 99,86      | n.a.   | BMB  |
| 2   | 47,51        | n.a.      | 0,450      | 0,462        | 0,14       | n.a.   | BMB* |
| Total|              |           | 228,978    | 334,944      | 100,00     | 0,000  |      |

Chromatogram (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
8 ROI-1144_95_5_flo5

Sample Name: ROI-1144_95_5_flo5  
Injection Volume: 20.0
Vial Number: GE7  
Channel: UV_VIS_1
Sample Type: unknown  
Wavelength: 220
Control Program: AD_H_90Min_100A_flow0_5  
Bandwidth: 4
Quant. Method: default  
Temperature/Column: 10
Recording Time: 18.1.2017 12:04  
Flow ml/min: 0.500
Run Time (min): 59.69  
Sample Amount: 1,0000

```
| No. | Rel. Time min | Peak Name | Height mAU | Area mAU | Rel. Area % | Amount n.a. | Type BMB |
|-----|---------------|-----------|------------|----------|-------------|-------------|--------|
| 1   | 12.83         | n.a.      | 285,164    | 127,235  | 50.10       | n.a.        | 8MB    |
| 2   | 22.76         | n.a.      | 138,151    | 126,742  | 49.00       | n.a.        | 8MB    |
| Total|               |           | 423,316    | 253,576  | 100.00      | 0.000       |        |
```

default/integration

Chromeleon (c) Dionex 1996-2006  
Version 6.80 SR12 Build 3578 (207169)
9 ROI-1113_95_5_flo5

Sample Name: ROI-1113_95_5_flo5  
Injection Volume: 20.0
Vial Number: GB5  
Channel: UV_VIS_1
Sample Type: unknown  
Wavelength: 220
Control Program: AD_H_90Min_100A_flow0_5  
Bandwidth: 4
Quantif. Method: default  
Temperature/Column: 10
Recording Time: 18.1.2017 13:05  
Flow ml/min: 0.500
Run Time (min): 29.37  
Sample Amount: 1,000

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 12.71        | n.a.      | 1,240      | 0.379        | 0.20       | n.a.   | BMB* |
| 2   | 22.66        | n.a.      | 206,913    | 191,129      | 99.80      | n.a.   | BMB  |
|     |              |           | 208,153    | 191,508      | 100.00     | 0.000  |      |

default/integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
## 10 ROI-1133_95_5_flo5

| Sample Name       | ROI-1133_95_5_flo5                  | Injection Volume: 20.0 |
|-------------------|-------------------------------------|------------------------|
| Val Number        | GE1                                 | Channel: UV_VIS_1      |
| Sample Type       | unknown                             | Wavelength: 220        |
| Control Program   | AD_H_60Min_100A_flow0_5             | Bandwidth: 4           |
| Quantif. Method   | default                             | Temperature/Column: 10 |
| Recording Time    | 18.1.2017 13:35                      | Flow ml/min: 0.500     |
| Run Time (min)    | 60.00                               | Sample Amount: 1000    |

![UV_VIS_1](image)

**WAS_20170118_ROI #10 [modified by Admin]**

| No. | Rel.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type  |
|-----|--------------|-----------|------------|--------------|------------|--------|-------|
| 1   | 9.77         | n.a.      | 7,132      | 2,283        | 1.77       | n.a.   | BMB** |
| 2   | 15.21        | n.a.      | 4,085      | 2,190        | 1.70       | n.a.   | BMB** |
| 3   | 16.01        | n.a.      | 100,379    | 62,191       | 48.19      | n.a.   | BMB   |
| 4   | 21.90        | n.a.      | 74,797     | 62,387       | 48.34      | n.a.   | BMB   |

**Total:**

| 186,393 | 129,051 | 100.00 | 0.00 |

Default/Integration

**Chromeleon (c) Dionex 1996-2006**

Version 6.80 SR 12 Build 3578 (207169)
11 ROI-1130_95_5_flo5

| Sample Name         | ROI-1130_95_5_flo5 | Injection Volume | 20.0          |
|---------------------|--------------------|-----------------|---------------|
| Vial Number         | GE4                | Channel         | UV_VIS_1      |
| Sample Type         | unknown            | Wavelength      | 220           |
| Control Program     | AD_H_60Min_100A_flow0_5 | Bandwidth      | 4             |
| Quantif Method      | default            | Temperature/Column | 10           |
| Recording Time      | 18.1.2017 14:35    | Flow ml/min     | 0.500         |
| Run Time (min)      | 60.00              | Sample Amount   | 1,000         |

![Chemical Structure](image)

- er = 99.8:0.2

| No. | Ret Time min | Peak Name | Height mAU | Area mAU|min | RelArea % | Amount | Type  |
|-----|--------------|-----------|------------|-------------|-----------|--------|-------|
| 1   | 16.92        | n.a.      | 290.008    | 182.707     | 99.77     | n.a.   | BMB   |
| 2   | 21.92        | n.a.      | 0.665      | 0.428       | 0.23      | n.a.   | BMB*  |
| Total|              |           | 290.703    | 183.135     | 100.00    | 0.00   |

Chromatograms

default/integration

Chromatogram:

Chromatogram (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
8 ROI-1022_100_1_flo5

Sample Name: ROI-1022_100_1_flo5  Injection Volume: 30,0
Vial Number: GC2  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: 220
Control Program: AD_H_90Min_100A_flow0_5  Bandwidth: 4
Quanif. Method: default  Temperature/Column: 10
Recording Time: 21.01.2017 5:31  Flow ml/min: 0,500
Run Time (min): 90,00  Sample Amount: 1,000

---

**Table:**

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU | Rel.Area % | Amount | Type |
|-----|-------------|-----------|------------|----------|------------|--------|------|
| 1   | 14,42       | n.a.      | 38,133     | 22,097   | 8,04       | n.a.   | BMB  |
| 2   | 37,36       | n.a.      | 106,889    | 183,882  | 50,28      | n.a.   | BMB* |
| 3   | 50,08       | n.a.      | 79,067     | 159,737  | 43,68      | n.a.   | BMB  |
|     | Total:      |           | 226,080    | 386,716  | 100,00     | 0,000  |      |

---

Chromlech (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
10 ROI-1148_100_1_flo5

| Sample Name          | ROI-1148_100_1_flo5 | Injection Volume | 30.0 |
|----------------------|----------------------|-----------------|------|
| Vial Number          | GB8                  | Channel         | UV_VIS_2 |
| Sample Type          | unknown              | Wavelength      | 250  |
| Control Program      | AD_H_90Min_100A_flow0_5 | Bandwidth      | 4    |
| Quantif. Method      | default              | Temperature/Column | 10   |
| Recording Time       | 21.1.2017 8:32       | Flow m/min      | 0.500 |
| Run Time (min)       | 90.00                | Sample Amount   | 1,000 |

```
WAS_20170120_2_ROI #10 [modified by Admin] UV_VIS_2
WVL:250 nm

3I
er > 99.8:0.2
```

| No. | Ret.Time | Peak Name | Height | Area   | Rel.Area | Amount | Type  |
|-----|----------|-----------|--------|--------|----------|--------|-------|
|     | min      |           | mAU    | mAU*min| %        |        |       |
| 1   | 14.52    | n.a.      | 0.410  | 0.197  | 0.34     | n.a.  | BMB*  |
| 2   | 37.39    | n.a.      | 38.259 | 57.961 | 99.50    | n.a.  | BMB*  |
| 3   | 50.20    | n.a.      | 0.091  | 0.036  | 0.16     | n.a.  | BMB*  |

Total:
38.761 58.253 100.00 0.000

default/Integration

Chromleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
**1 ROI-1134_9_1_flo5**

| Sample Name       | ROI-1134_9_1_flo5 |
|-------------------|-------------------|
| Vial Number       | GE2               |
| Sample Type       | unknown           |
| Control Program   | AD_H_90Min_100A_flow0_5 |
| Quantif. Method   | default           |
| Recording Time    | 1.2.2017 10:23    |
| Run Time (min)    | 90.00             |
| Injection Volume  | 30.0              |
| Channel           | UV_VIS_1          |
| Wavelength        | 220               |
| Bandwidth         | 4                 |
| Temperature/Column| 10                |
| Flow ml/min       | 0.500             |
| Sample Amount     | 1.0000            |

![Graph](image)

| No. | Rel.Time | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|----------|-----------|------------|--------------|------------|--------|------|
| 1   | 14.55    | n.a.      | 71,998     | 44,979       | 50.22      | n.a.   | BMB  |
| 2   | 32.57    | n.a.      | 14,135     | 44,562       | 49.78      | n.a.   | BMB* |
| Total|          |           | 86,133     | 89,560       | 100.00     | 0.000  |      |

default/Integration

Chromleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
2 ROI-1166_9_1_flo5

Sample Name: ROI-1166_9_1_flo5
Vial Number: BA8
Sample Type: unknown
Control Program: AD_H_90Min_100A_flow0_5
Quantif. Method: default
Recording Time: 1.2.2017 11:54
Run Time (min): 90.00
Injection Volume: 30.0
Channel: UV_VIS_1
Wavelength: 220
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 0.500
Sample Amount: 1,0000

| No. | Ret.Time | Peak Name | Height mAU | Area mAU*min | Ret.Area % | Amount | Type       |
|-----|----------|-----------|------------|--------------|------------|--------|------------|
| 1   | 14.60    | n.a.      | 0.983      | 0.278        | 0.07       | n.a.   | BMB*       |
| 2   | 28.53    | n.a.      | 116.440    | 390,626      | 99.93      | n.a.   | BMB        |
| Total|          |           | 117.423    | 390,505      | 100.00     | 0.000  |            |

default/integration

Chromelone (c) Dionex 1990-2006
Version 6.80 SR12 Build 3578 (207169)
11 ROI-1012_100_1_flo5

Sample Name: ROI-1012_100_1_flo5  Injection Volume: 30.0
Val Number: BB4  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: 220
Control Program: AD_H_90Min_100A_flow0_5  Bandwidth: 4
Quantif. Method: default  Temperature/Column: 10
Recording Time: 21.1.2017 10:03  Flow m/min: 0.500
Run Time (min): 90.00  Sample Amount: 1,000

| No. | Ret.Time | Peak Name | Height  | Area   | Rel.Area | Amount | Type     |
|-----|----------|-----------|---------|--------|----------|--------|----------|
| 1   | 17.99    | n.a.      | 357,835 | 328,991| 6.88     | n.a.   | BMB*     |
| 2   | 22.54    | n.a.      | 357,493 | 331,031| 6.92     | n.a.   | BMB*     |
| 3   | 33.84    | n.a.      | 1409,948| 2051,552| 42.89    | n.a.   | BMB*     |
| 4   | 44.44    | n.a.      | 928,781 | 2071,556| 43.31    | n.a.   | BMB*     |

Total: 3054.056 4753,129 100.00 0.000

default/integration  Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
12 ROI-1112_100_1_flo5

Sample Name: ROI-1112_100_1_flo5  Injection Volume: 30.0
Wial Number: GB4  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: 220
Control Program: AD_H_90Min_100A_flow0_5  Bandwidth: 4
Quantif. Method: default  Temperature/Column: 10
Recording Time: 21.1.2017 11:33  Flow m/min: 0.500
Run Time (min): 90.00  Sample Amount: 1,000

| No. | Ret Time min | Peak Name | Height mAU | Area mAU | Rel Area % | Amount | Type |
|-----|--------------|-----------|------------|----------|------------|--------|------|
| 1   | 18.77        | n.a.      | 8.549      | 6.990    | 0.43       | n.a.   | BMB* |
| 2   | 23.49        | n.a.      | 0.080      | 0.091    | 0.01       | n.a.   | BMB* |
| 3   | 33.95        | n.a.      | 3.994      | 5.316    | 0.32       | n.a.   | BMB* |
| 4   | 44.60        | n.a.      | 735.766    | 1623.776 | 99.24      | n.a.   | BMB* |
| Total|              |           | 748.421    | 1636.174 | 100.00     | 0.000  |      |

Chromleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
3 ROI-1052_95_5_flo5

Sample Name: ROI-1052_95_5_flo5
Vial Number: BA7
Sample Type: unknown
Control Program: AD_H_60Min_100A_flow0_5
Quantif. Method: default
Recording Time: 19.1.2017 16:17
Run Time (min): 33.78
Injection Volume: 20.0
Channel: UV_VIS_1
Wavelength: 220
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 0.500
Sample Amount: 1,0000

---

**Table of Results**

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU/min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 9.80         | n.a.      | 79,946     | 24,039       | 4.19       | n.a.   | BMB  |
| 2   | 12.48        | n.a.      | 58,019     | 25,077       | 4.37       | n.a.   | BMB  |
| 3   | 15.53        | n.a.      | 467,005    | 246,414      | 46.71      | n.a.   | BM   |
| 4   | 17.59        | n.a.      | 411,051    | 262,587      | 45.74      | n.a.   | MB   |
| Total: |             |           | 1016,061   | 574,117      | 100.00     | 0.000  |      |

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Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
12 ROI-1105_95_5_flo5

Sample Name: ROI-1105_95_5_flo5
Injection Volume: 20.0
Vial Number: GA4
Channel: UV_VIS_1
Sample Type: unknown
Wavelength: 220
Control Program: AD_H_60Min_100A_flow0_5
Bandwidth: 4
Quantif. Method: default
Temperature/Column: 10
Recording Time: 18.1.2017 15:36
Flow ml/min: 0.500
Run Time (min): 60.00
Sample Amount: 1,000

| No. | Ret Time min | Peak Name | Height mAU | Area mAU*min | RelArea % | Amount n.a. | Type BMB* |
|-----|--------------|-----------|------------|--------------|-----------|-------------|----------|
| 1   | 9.59         | n.a.      | 12,259     | 3,791        | 5.08      | n.a.        | BMB*     |
| 2   | 15.46        | n.a.      | 127,185    | 70,265       | 94.07     | n.a.        | BMB*     |
| 3   | 17.58        | n.a.      | 1,256      | 0.636        | 0.85      | n.a.        | BMB*     |

Total: 140.740 74.692 100.00 0.000

default/integration

Chromleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
13 ROI-1054_95_5_flo5

Sample Name: ROI-1054_95_5_flo5  
Injection Volume: 20.0  
Vial Number: GC4  
Channel: UV_VIS_1  
Sample Type: unknown  
Wavelength: 220  
Control Program: AD_H_60Min_100A_flow0_5  
Bandwidth: 4  
Quantif Method: default  
Temperature/Column: 10  
Recording Time: 18.1.2017 16:37  
Flow ml/min: 0.500  
Run Time (min): 60.00  
Sample Amount: 1.0000

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 13.49          | n.a.      | 6.749        | 3.453          | 1.87         | n.a.   | BM*  |
| 2   | 15.40          | n.a.      | 5.899        | 3.477          | 1.88         | n.a.   | MB*  |
| 3   | 18.72          | n.a.      | 124.944      | 89.363         | 48.35        | n.a.   | BMB  |
| 4   | 24.02          | n.a.      | 91.233       | 89.567         | 47.91        | n.a.   | BMB  |
| Total|                |           | 228.824      | 184.881        | 100.00       | 0.000  |      |

Chromleon (c) Dionex 1995-2006
Version 6.80 SR12 Build 3578 (207169)
14 ROI-1137_95_5_flo5

Sample Name: ROI-1137_95_5_flo5  
Injection Volume: 20.0

Val Number: GE6  
Channel: UV_VIS_1

Sample Type: unknown  
Wavelength: 220

Control Program: AD_H_60Min_100A_flow0_5  
Bandwidth: 4

Quantif. Method: default  
Temperature/Column: 10

Recording Time: 18.1.2017 17:37  
Flow ml/min: 0.500

Run Time (min): 60.00  
Sample Amount: 1,000

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**Chemical Structure**

3p  
er > 99.8.0.2

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| No. | Rel.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 13.48        | n.a.      | 14,703     | 6,930        | 2.75       | n.a.   | BMB* |
| 2   | 18.67        | n.a.      | 337,234    | 244,796      | 97.14      | n.a.   | BMB  |
| 3   | 24.10        | n.a.      | 0,525      | 0,280        | 0.11       | n.a.   | BMB* |
| Total|              |           | 352,462    | 252,008      | 100.00     | 0.000  |      |

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default/integration

Chromeleon (c) Dionex 1996-2006  
Version 8.80 SR12 Build 3578 (207169)
4 ROI-1163_N_100_1_flo5

Sample Name: ROI-1163_N_100_1_flo5  Injection Volume: 20,0
Vial Number: GC1  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: 220
Control Program: AD_H_120Min_100A_flow0_5  Bandwidth: 4
Quantiﬁ Method: default  Temperature/Column: 10
Recording Time: 7.3.2017 9:04  Flow mL/min: 0,500
Run Time (min): 42,99  Sample Amount: 1,0000

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 24,98          | n.a.      | 59,665       | 66,920         | 50,18        | n.a.   | BMB* |
| 2   | 30,50          | n.a.      | 21,849       | 66,447         | 49,82        | n.a.   | BMB* |
| Total |                |           | 81,514       | 133,367        | 100,00       | 0,000  |      |

default/integration  Chromatography (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
1 ROI-1136_N_100_1_flo5

Sample Name: ROI-1136_N_100_1_flo5
Injection Volume: 30.0
Vial Number: GC3
Channel: UV_VIS_1
Sample Type: unknown
Wavelength: 220
Control Program: AD_H_120Min_100A_flow0_5
Bandwidth: 4
Quantif. Method: default
Temperature/Column: 10
Recording Time: 7.3.2017 11:13
Flow ml/min: 0.500
Run Time (min): 42.02
Sample Amount: 1.0000

![Graph of compound 3q with R>99.8:0.2 and retention times 24.597, 27.593]

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area % | Amount | Type |
|------|---------------|-----------|--------------|----------------|-----------|--------|------|
| 1    | 24.70         | n.a.      | 0.388        | 0.219          | 0.15      | n.a.   | BMB* |
| 2    | 27.59         | n.a.      | 68.312       | 150.977        | 99.85     | n.a.   | BMB* |
| Total|               |           | 68.700       | 150.977        | 100.00    | 0.000  |      |

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
8 ROI-1162_98_2_flo5

Sample Name: ROI-1162_98_2_flo5
Vial Number: GD7
Sample Type: unknown
Control Program: AD_H_120Min_100A_flow0.5
Quantif. Method: default
Recording Time: 31.1.2017 4:35
Run Time (min): 120.00

Injection Volume: 20.0
Channel: UV_VIS_1
Wavelength: 220
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 0.500
Sample Amount: 1,0000

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|----------|------------|--------|------|
| 1   | 12.56        | n.a.      | 24.373     | 11,408   | 5.76       | n.a.   | BMB* |
| 2   | 58.02        | n.a.      | 4,456      | 11,496   | 5.81       | n.a.   | BMB* |
| 3   | 86.15        | n.a.      | 20,554     | 87,801   | 44.33      | n.a.   | BMB* |
| 4   | 100.33       | n.a.      | 15,421     | 87,354   | 44.10      | n.a.   | BMB* |

Total: 67,803 198,062 100.00 0.000

Chromleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3678 (207169)
7 ROI-1241_98_2_flo5

Sample Name: ROI-1241_98_2_flo5  
Injection Volume: 30.0

Vial Number: GD6  
Channel: UV_VIS_1

Sample Type: unknown  
Wavelength: 220

Control Program: AD_H_120Min_100A_flow0_5  
Bandwidth: 4

Quantif. Method: default  
Temperature/Column: 10

Recording Time: 31.1.2017 2:34  
Flow ml/min: 0.500

Run Time (min): 120.00  
Sample Amount: 1,0000

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| No. | Ret.Time | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type   |
|-----|----------|-----------|------------|--------------|------------|--------|--------|
| 1   | 12.60    | n.a.      | 0.958      | 0.474        | 0.24       | n.a.   | BMB*   |
| 2   | 86.50    | n.a.      | 0.137      | 0.206        | 0.10       | n.a.   | BMB*   |
| 3   | 100.02   | n.a.      | 41.266     | 199.302      | 99.88      | n.a.   | BMB*   |
| Total|          |           | 42.361     | 200.042      | 100.00     | 0.000  |        |

Chromatogram Image

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default/integration  

Chromelon (c) Dionex 1996-2006  
Version 6.80 SR12 Build 3578 (207169)
6 ROI-1230_500_1_flo5

Sample Name: ROI-1230_500_1_flo5  
Injection Volume: 20.0
Vial Number: BD6  
Channel: UV_VIS_1
Sample Type: unknown  
Wavelength: 220
Control Program: AD_H_90Min_100A_flow0_5  
Bandwidth: 4
Quantif. Method: default  
Temperature/Column: 10
Recording Time: 2.2.2017 4:21  
Flow ml/min: 0.500
Run Time (min): 90.00  
Sample Amount: 1.0000

---

![Graph](image)

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| No. | Ret.Time | Peak Name | Height | Area | Rel.Area | Amount | Type |
|-----|----------|-----------|--------|------|----------|--------|------|
| 1   | 34.06    | n.a.      | 22.509 | 28,850 | 51.54    | n.a. Mb* |
| 2   | 39.16    | n.a.      | 13,227 | 25,241 | 48.46    | n.a. bMb* |
| Total: | 35,736 | 52,091 | 100.00 | 0.00 |

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default/Integration  
Chromeleon (c) Dionex 1996-2006  
Version 6.80 SR12 Build 3578 (207169)
### 7 ROI-1231_500_1_flo5

| Sample Name          | ROI-1231_500_1_flo5       | Injection Volume: | 20.0 |
|----------------------|---------------------------|-------------------|------|
| Vial Number          | BE6                       | Channel:          | UV_VIS_1 |
| Sample Type          | unknown                   | Wavelength:       | 220  |
| Control Program      | AD_H_90Min_100A_flow0.5  | Bandwidth:        | 4    |
| Quantif. Method      | default                   | Temperature/Column: | 10   |
| Recording Time       | 2.2.2017 5:51             | Flow ml/min:      | 0.500|
| Run Time (min)       | 90.00                     | Sample Amount:    | 1,000|

![Graph Image]

| No. | Ret.Time (min) | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|---------------|-----------|------------|--------------|------------|--------|------|
| 1   | 34.88         | n.a.      | 0.773      | 0.611        | 0.19       | n.a.   | BMB* |
| 2   | 37.44         | n.a.      | 165.823    | 315.122      | 99.81      | n.a.   | BMB* |
| Total|               |           | 167.595    | 315.733      | 100.00     | 0.000  |      |

default/Integration

Chromleon (c) Dionex 1990-2006
Version 6.80 SR12 Build 3578 (207169)
2 ROI-1161_95_5_flo5

Sample Name: ROI-1161_95_5_flo5  
Injection Volume: 20.0
Val Number: GB6  
Channel: UV_VIS_1
Sample Type: unknown  
Wavelength: 220
Control Program: AD_H_60Min_100A_flow0_5  
Bandwidth: 4
Quantif. Method: default  
Temperature/Column: 10
Recording Time: 19.1.2017 15:38  
Flow ml/min: 0.500
Run Time (min): 38.42  
Sample Amount: 1,0000

No.  Rel.Time  Peak Name  Height  Area  Rel.Area  Amount  Type
      min       mAU   mAU*min %     
1      8.80     n.a.   36,146  10,736  1.40     n.a.     BMB*
2      10.43    n.a.   906,488 371,188 48.55    n.a.     BMB
3      13.65    n.a.   16,665  9,484  1.24     n.a.     BMB*
4      21.72    n.a.   322,961 373,153 48.61    n.a.     BMB

Total: 1282,250 764,561 100.00 0.000

default/integration
7 ROI-1091_95_5_flo5

Sample Name: ROI-1091_95_5_flo5  Injection Volume: 20.0  
Vial Number: GD4  Channel: UV_VIS_1  
Sample Type: unknown  Wavelength: 220  
Control Program: AD_H_60Min_100A_flow0_5  Bandwidth: 4  
Quantif Method: default  Temperature/Column: 10  
Recording Time: 19.1.2017 1:16  Flow ml/min: 0.500  
Run Time (min): 60.00  Sample Amount: 1,0000

No.  | Ret.Time | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type  
---|----------|-----------|------------|--------------|------------|--------|-------
1   | 9.00     | n.a.      | 1,084      | 0,225        | 0.07       | n.a.   | BMB*  
2   | 10.42    | n.a.      | 2,760      | 1,034        | 0.33       | n.a.   | BMB*  
3   | 13.59    | n.a.      | 13,350     | 7,542        | 2.41       | n.a.   | BMB   
4   | 21.54    | n.a.      | 272,669    | 308,699      | 97.20      | n.a.   | BMB*  
Total: |          |           | 289,884    | 317,599      | 100.00     | 0,000  

default/integration
**ROI-1196_300_1_flo5**

| Sample Name: | ROI-1196_300_1_flo5 |
|-------------|---------------------|
| Vial Number: | BA3                 |
| Sample Type: | unknown             |
| Control Program: | AD_H_90Min_100A_flow0_5 |
| Quantif. Method: | default            |
| Recording Time: | 29.1.2017 2:26 |
| Run Time (min): | 90,00              |

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU/min | Rel.Area % | Amount n.a. | Type BMB* |
|-----|--------------|-----------|------------|--------------|------------|------------|-----------|
| 1   | 20.31        | n.a.      | 1360,715   | 728,733      | 50.21      | n.a.       | BMB*      |
| 2   | 21.81        | n.a.      | 1102,656   | 722,608      | 49.79      | n.a.       | BMB*      |
| Total: |            |           | 2483,371   | 1451,342     | 100,00     | 0,000      |           |

**6c racemic**

*default/integration*
3 ROI-1214_300_1_flo5

Sample Name: ROI-1214_300_1_flo5
Injection Volume: 30.0

Vial Number: BA4
Channel: UV_VIS_1

Sample Type: unknown
Wavelength: 220

Control Program: AD_H_90Min_100A_flow95
Bandwidth: 4

Quantif. Method: default
Temperature/Column: 10

Recording Time: 29.1.2017 3:57
Flow ml/min: 0.500

Run Time (min): 90.00
Sample Amount: 1.0000

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount (n.a) | Type |
|-----|----------------|-----------|--------------|----------------|--------------|-------------|------|
| 1   | 20.56          | n.a.      | 0.528        | 0.266          | 0.30         | n.a.        | BMB  |
| 2   | 22.23          | n.a.      | 121,616      | 89,713         | 99.70        | n.a.        | BMB  |
|     |                |           |              |                |              |             |      |
| Total|                |           | 122,144      | 89,979         | 100.00       | 0.000       |      |
4 ROI-1224_500_1_flo5

Sample Name: ROI-1224_500_1_flo5
Vial Number: BD4
Sample Type: unknown
Control Program: AD_H_90Min_100A_flow0_5
Quantif. Method: default
Recording Time: 2,2.2017 1:20
Run Time (min): 90,00

Injection Volume: 20,0
Channel: UV_VIS_1
Wavelength: 220
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 0,500
Sample Amount: 1,0000

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**Chemical Structure**

![Chemical Structure](image)

**Retention Time**

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|---------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 35.98         | n.a.      | 10,733       | 11,485         | 46.61        | n.a.   | BMB  |
| 2   | 38.29         | n.a.      | 9,886        | 13,158         | 53.39        | n.a.   | BMB* |
| Total|               |           | 20,419       | 24,643         | 100.00       | 0.00   |      |

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default/integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
5 ROI-1225_500_1_flo5

Sample Name: ROI-1225_500_1_flo5
Injection Volume: 20.0
Vial Number: BE4
Channel: UV_VIS_1
Sample Type: unknown
Wavelength: 220
Control Program: AD_H_90Min_100A_flow9_5
Bandwidth: 4
Quantif. Method: default
Temperature/Column: 10
Recording Time: 2.2.2017 2:50
Flow ml/min: 0.500
Run Time (min): 90.00
Sample Amount: 1.0000

| No. | Ret.Time | Peak Name | Height | Area | Rel.Area | Amount | Type |
|-----|----------|-----------|--------|------|----------|--------|------|
| 1   | 36.73    | n.a.      | 250.143| 386.045| 100.00   | n.a.   | BMR  |

Total: 250.143 386.045 100.00 0.000

default/integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
**12 ROI-1226_300_1_flo5**

| Sample Name: | ROI-1226_300_1_flo5 | Injection Volume: | 20.0 |
|--------------|---------------------|------------------|------|
| Vial Number: | BD5                 | Channel:         | UV_VIS_1 |
| Sample Type: | unknown             | Wavelength:      | 220  |
| Control Program: | AD_H_120Min_100A_flow0_5 | Bandwidth: | 4 |
| Quantif. Method: | default             | Temperature/Column: | 10 |
| Recording Time: | 29.1.2017 20:32     | Flow ml/min:     | 0.500 |
| Run Time (min): | 120,00             | Sample Amount:   | 1,000 |

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**Chromatogram**

![Chromatogram](image)

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 20.34          | n.a.      | 200,806      | 90,358         | 49.92        | n.a.   | BM   |
| 2   | 22.18          | n.a.      | 136,180      | 99,665         | 50.08        | n.a.   | MB   |
| Total|                |           | 337,075      | 181,024        | 100.00       | 0.000  |      |

Default/Integration

Chromatogram (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)

69
13  ROI-1227_300_1_flo5

Sample Name: ROI-1227_300_1_flo5  Injection Volume: 20.0
Vial Number: BE5  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: 220
Control Program: AD_H_120Min_100A_flow0_5  Bandwidth: 4
Quantif. Method: default  Temperature/Column: 10
Recording Time: 29.1.2017 22:33  Flow m/min: 0.500
Run Time (min): 120.00  Sample Amount: 1,0000

No.  Ret.Time  Peak Name  Height  Area  Rel.Area  Amount  Type
min  mAU  mAU*min  %
1  20.50  n.a.  8.375  3.616  1.33  n.a.  BMB*
2  22.04  n.a.  409.495  268.322  98.67  n.a.  BM3
Total:  417.870  271.938  100.00  0.000

default/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207189)
6 ROI-1220_300_1_flo5

Sample Name: ROI-1220_300_1_flo5
Injection Volume: 20.0
Vial Number: BD2
Channel: UV_VIS_1
Sample Type: unknown
Wavelength: 220
Control Program: AD_H_120Min_100A_flow0_5
Bandwidth: 4
Quantif. Method: default
Temperature/Column: 10
Recording Time: 29.1.2017 8:29
Flow m/min: 0.500
Run Time (min): 120.00
Sample Amount: 1.0000

![Graph](image)

| No. | Ret.Time | Peak Name | Height | Area | Rel.Area | Amount | Type |
|-----|----------|-----------|--------|------|----------|--------|------|
| 1   | 68.01    | n.a.      | 28.077 | 77,612 | 56.31    | n.a.   | BMB* |
| 2   | 74.09    | n.a.      | 14,123 | 60,224 | 43.69    | n.a.   | BMB* |
| Total: |        |           | 42,199 | 137,836 | 100.00 | 0.000 |

default/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
### 7 ROI-1221_300_1_flo5

**Sample Name:** ROI-1221_300_1_flo5  
**Injection Volume:** 20.0  
**Vial Number:** BE2  
**Channel:** UV_VIS_1  
**Sample Type:** unknown  
**Wavelength:** 220  
**Control Program:** AD_H_120Min_100A_flow0_5  
**Bandwidth:** 4  
**Quantif. Method:** default  
**Temperature/Column:** 10  
**Recording Time:** 28.1.2017 10:29  
**Flow ml/min:** 0.500  
**Run Time (min):** 120.00  
**Sample Amount:** 1,0000

![Graph of the compound 6f with retention time and area data]

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount (n. a.) | Type |
|-----|---------------|-----------|--------------|----------------|--------------|---------------|------|
| 1   | 71.14         | n.a.      | 45,012       | 255,084        | 100.00       | n.a.          | BMS* |
| Total|               |           | 45,012       | 255,084        | 100.00       | 0.000         |      |
### ROI-1222_300_1_flo5

| Sample Name         | Injection Volume | Vial Number | Channel       | Wavelength |
|---------------------|------------------|-------------|---------------|------------|
| ROI-1222_300_1_flo5 | 20.0             | BD3         | UV_VIS_1      | 220        |
| Sample Type         |                  |             |               |            |
| unknown             |                  |             |               |            |
| Control Program     |                  |             |               |            |
| AD_H_120Min_100A_flow0_5 |          |             |               |            |
| Quantif. Method     |                  |             |               |            |
| default             |                  |             |               |            |
| Recording Time      |                  |             |               |            |
| 29.1.2017 12:30     |                  |             |               |            |
| Run Time (min)      |                  |             |               |            |
| 120.00              |                  |             |               |            |

#### Chromatogram
![Chromatogram](chart.png)

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | RelArea % | Amount | Type |
|-----|--------------|-----------|------------|--------------|-----------|--------|------|
| 1   | 33.19        | n.a.      | 73.961     | 92.324       | 49.32     | n.a.   | BM   |
| 2   | 36.31        | n.a.      | 54.975     | 94.889       | 50.68     | n.a.   | MB   |
| Total|              |           | 128.936    | 187.213      | 100.00    | 0.000  |

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Chromelbox (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207159)
9 ROI-1223_300_1_flo5

| Sample Name:       | ROI-1223_300_1_flo5                  | Injection Volume: | 20.0 |
|--------------------|--------------------------------------|-------------------|------|
| Visit Number:      | BE3                                  | Channel:          | UV_VIS_1 |
| Sample Type:       | unknown                              | Wavelength:       | 220  |
| Control Program:   | AD_H_120Min_100A_flow5_5            | Bandwidth:        | 4    |
| Quantif. Method:   | default                              | Temperature/Column: | 10 |
| Recording Time:    | 29.1.2017 14:30                      | Flow ml/min:      | 0.500 |
| Run Time (min):    | 120.00                               | Sample Amount:    | 1.0000 |

![Chromatogram Image]

| No. | Ret.Time (min) | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount n.a. | Type BMB |
|-----|---------------|-----------|------------|--------------|------------|-------------|----------|
| 1   | 34.85         | n.a       | 291,476    | 536,976      | 98.75      | n.a         | BMB      |
| 2   | 45.05         | n.a       | 4,271      | 6,785        | 1.25       | n.a         | BMB      |
| Total: |              |           | 295,747    | 543,761      | 100.00     | 0.00        |          |

Chromatogram (© Dionex 1996-2006)
Version 6.80 SR12 Build 3578 (207166)
### 9 ROI-1210_300_1_flo5

| Sample Name           | Injection Volume | Vial Number | Channel   | Sample Type | Wavelength | Quantif. Method | Recording Time | Run Time (min) | Flow m/min | Sample Amount |
|-----------------------|------------------|-------------|-----------|-------------|-------------|----------------|----------------|----------------|-------------|--------------|
| ROI-1210_300_1_flo5   | 30.0             | BA2         | UV_VIS_1  | unknown     | 220         | AD_H           | 2.2.2017 8:53  | 70.83         | 0.500       | 1,000        |

#### Chromatogram
![Chromatogram](image-url)

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type  |
|-----|----------------|-----------|--------------|----------------|--------------|--------|-------|
| 1   | 38.93          | n.a.      | 3.683        | 7.001          | 49.84        | n.a.   | BMB*  |
| 2   | 49.50          | n.a.      | 2.446        | 7.047          | 50.16        | n.a.   | BMB*  |

**Total:**

- Height (mAU): 6.129
- Area (mAU*min): 14.048
- Rel.Area (%): 100.00
- Amount: 0.000

**Ret. Time (min):**

- 34.1, 37.0, 40.0, 42.5, 45.0, 47.5, 50.0, 52.5, 55.0, 57.5, 60.1

**Mass Spectrometry**

- Mass: 677.5
- Charge: 1
- Precursor Mass: 677.5
- Spectral Curves: [Spectral Data]

**References:**

- Chromatogram (c) Dionex 1996-2005
- Version 6.80 SR12 Build 3578 (207169)
8 ROI-1193_300_1_flo5

Sample Name: ROI-1193_300_1_flo5
Injection Volume: 30.0
Vial Number: BD1
Channel: UV_VIS_1
Sample Type: unknown
Wavelength: 220
Control Program: AD_H_90Min_100A_flow0_5
Bandwidth: 4
Quanif. Method: AD_H
Temperature/Column: 10
Recording Time: 2.2.2017 7:22
Flow ml/min: 0.500
Run Time (min): 90.00
Sample Amount: 1.0000

WAS_20170201_2_ROI_YMC #8 [modified by Admin]

UV_VIS_1

![Chemical structure diagram]

6h
er > 99.6:0.2

| No. | Ret.Time | Peak Name | Height | Area | Rel.Area | Amount | Type  |
|-----|----------|-----------|--------|------|----------|--------|-------|
| 1   | 40.51    | n.a.      | 0.111  | 0.139| 0.19     | n.a.   | BMB*  |
| 2   | 46.36    | n.a.      | 25.990 | 72.716| 99.81    | n.a.   | BMB*  |
|     |          |           | 26.101 | 72.716| 100.00   | 0.000  |       |

default/integration
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Version 6.80 SR12 Build 3576 (207166)
4 Copies of NMR-Spectra
