Supporting Information

Design of Chiral Urea-Quaternary Ammonium Salt Hybrid Catalysts for Asymmetric Reactions of Glycine Schiff Bases

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1. General Information:

$^1$H- and $^{13}$C-NMR spectra were recorded on a Bruker Avance III 300 MHz spectrometer, on a Bruker Avance III 700 MHz spectrometer with TCI cryoprobe or on Bruker DRX 400, 300, 250 MHz spectrometers. All NMR spectra were referenced on the solvent peak. High resolution mass spectra were obtained using an Agilent 6520 Q-TOF mass spectrometer with an ESI source and an Agilent G1607A coaxial sprayer or using a Thermo Fisher Scientific LTQ Orbitrap XL with an Ion Max API Source. Additional mass spectral analyses were carried out using an electrospray spectrometer, Waters 4 micro quadrupole. Elemental analyses were performed with a FLASHEA 1112 series-Thermo Scientific for CHNS-O apparatus. IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer with ATR unit. HPLC analysis were performed either by using a Waters instrument or using a Dionex Summit HPLC system with a Chiralcel OD-H (250 x 4.6 mm, 5 µm), a Chiralcel OD-R (250 x 4.6 mm, 10 µm), a Chiralpak AD-H (250 x 4.6 mm, 5 µm), or a Chiralpak IA-3 (250 x 4.6 mm, 3 µm) chiral stationary phase. Optical rotations were recorded on a Perkin Elmer Polarimeter Model 241 MC and on a Schmidt + Haensch Polarimeter Model UniPol L 1000. All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. All reactions were performed under an Ar-atmosphere.
2. Optimized Protocol for the Synthesis of Bifunctional Ammonium Salts:

Optimized protocol for quaternization with electron-withdrawing substituents:

![Chemical Structure](image)

**General Syntheses of 13 (via Steps A,B as depicted in Scheme 2 of the manuscript):**

**Step 1 (A):** The corresponding benzaldehyde (2 mmol) was added to a solution of 11 (428 mg, 2 mmol, 1 eq) (prepared from (S,S)-cyclohexanediamine-5-dihydrochloride\(^1\) according to literature\(^2\)) in THF/methanol = 1/1 (10 mL) and the solution was stirred at r.t. overnight. After the addition of NaBH\(_4\) (114 mg, 3 mmol, 1.5 eq) stirring was continued for another 2 h at r.t.. The reaction was quenched by addition of water and extracted with water/diethyl ether. The organic phase was washed with brine, dried over Na\(_2\)SO\(_4\), and evaporated to dryness to obtain the crude product 12 in quantitative yield which could be directly used without any purification.

**Compound 12c (R\(^1\) = 3,5-(CF\(_3\))\(_2\)-Ph):** Obtained in 95% yield (824 mg, 1.9 mmol). \(^1\)H NMR (300 MHz, δ, CDCl\(_3\), 298 K): 1.08-1.35 (m, 4H), 1.42 (s, 9H), 1.61-1.85 (m, 2H), 1.96 (s (b), 1H), 1.99-2.15 (m, 2H), 3.31-3.47 (m, 1H), 3.83 (d, 1H, J = 14.1 Hz), 4.00 (d, 1H, J = 14.1 Hz), 4.48 (d, 1H, J = 7.3 Hz), 7.73 (s, 1H), 7.82 (s, 2H) ppm.

**Step 2 (B):** The corresponding amine 12 (1.7 mmol) was dissolved in 3 ml DMF. After the addition of K\(_2\)CO\(_3\) (287 mg, 2.1 mmol, 1.2 eq) and methyl iodide (646 µl, 10.4 mmol, 6 eq) the suspension was stirred for 20-30 h at 60 °C. After removal of excess methyl iodide under reduced pressure, the suspension was extracted with dichloromethane/brine. The organic phase was dried over Na\(_2\)SO\(_4\) and removal of the solvent under reduced pressure gives 13, which was used without further purification.

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**Compound 13c (R<sup>1</sup> = 3,5-(CF<sub>3</sub>)<sub>2</sub>-Ph):** Obtained in 70% yield (1.13 g, 1.2 mmol). [α]<sub>D</sub> = -7.4°; <sup>1</sup>H NMR (700 MHz, δ, CDCl<sub>3</sub>, 298 K): 1.32-1.40 (m, 1H), 1.46 (s, 9H), 1.58-1.66 (m, 1H), 1.66-1.74 (m, 1H), 1.77-1.84 (m, 1H), 1.95-2.06 (m, 3H), 2.59-2.64 (m, 1H), 3.22 (s, 3H), 3.28 (s, 3H), 4.11-4.18 (m, 1H), 4.93-5.00 (m, 1H), 5.16 (d, 1H, J = 12.8 Hz), 5.36 (d, 1H, J = 12.8 Hz), 5.87 (d, 1H, J = 9.9 Hz), 8.01 (s, 1H), 8.13 (s, 2H) ppm; <sup>13</sup>C NMR (125 MHz, δ, CDCl<sub>3</sub>, 298 K): 24.8, 24.8, 27.7, 28.5, 35.7, 51.1, 51.7, 63.1, 77.8, 81.5, 122.8 (q, J = 273 Hz), 124.9, 130.3, 133.0 (q, J = 34 Hz), 133.6, 155.9 ppm; <sup>19</sup>F NMR (282 MHz, δ, CDCl<sub>3</sub>, 298 K): -62.8 ppm; IR (film): ν<sub>max</sub> = 3431, 3270, 3011, 2980, 2939, 2867, 1695, 1625, 1516, 1467, 1455, 1393, 1370, 1323, 1281, 1242, 1176, 1138, 1048, 1024, 904, 870, 844, 737, 709, 683 cm<sup>-1</sup>; HRMS (ESI) m/z calcld for C<sub>22</sub>H<sub>31</sub>F<sub>6</sub>N<sub>2</sub>O<sub>2</sub>+: 469.2284 [M<sup>+</sup>], found: 469.2281.

**Optimized protocol for quaternization with sterically demanding substituents:**

Step 1 (C): Amine 11 was prepared according to literature<sup>3</sup>. 11 (535 mg, 2.5 mmol) was dissolved in 40 ml 1,2-dichloroethane. After addition of formaldehyde (37w% aq. solution, 394 µl, 5 mmol, 2 eq) the solution was stirred at r.t. for 15 min. Then NaBH(OAc)<sub>3</sub> (1.25 g, 5.8 mmol, 2.3 eq) was added and the solution was stirred at r.t. overnight. The reaction was quenched with 50 ml saturated sodium bicarbonate solution and extracted with dichloromethane. The organic phase was dried over Na<sub>2</sub>SO<sub>4</sub> and removal of the solvent under reduced pressure gave 19 (581 mg, 2.4 mmol, 96%) which was directly used without further purification. Analytical data were in accordance with those reported in literature<sup>3</sup>. <sup>1</sup>H NMR (300 MHz, δ, CDCl<sub>3</sub>, 298 K): 0.96-1.34 (m, 4H), 1.44 (s, 9H), 1.60-1.70 (m, 1H), 1.72-1.86 (m, 2H), 2.11-2.28 (m, 1H), 2.21 (s, 6H), 2.40-2.52 (m, 1H), 3.12-3.24 (m, 1H), 5.28 (s, 1H) ppm.

Step 2 (D): A solution of 19 (50 mg, 0.2 mmol) and the corresponding benzyl bromide derivative (0.6 mmol, 1.5 eq) in 0.5 mL DMF was stirred at 60 °C overnight. Evaporation of the solvent under reduced pressure gave crude 13 which was used without further purification.

**Compound 13a (R¹ = α-Naphthyl):** Analytical data were found to be in accordance with literature\(^4\). \([\alpha]_D^{23}\) (c = 1.0, dichloromethane) = -5.2\(^\circ\); \(^1\)H NMR (300 MHz, δ, CDCl\(_3\), 298 K): 1.25-1.38 (m, 1H), 1.45 (s, 9H), 1.58-1.77 (m, 3H), 1.85-2.08 (m, 3H), 2.52-2.64 (m, 1H), 2.99 (s, 3H), 3.14 (s, 3H), 4.14-4.28 (m, 1H), 5.07-5.20 (m, 1H), 5.30 (d, 1H, J = 13.4 Hz), 5.47 (d, 1H, J = 13.4 Hz), 6.16 (d, 1H, J = 10.1 Hz), 7.40-7.53 (m, 2H), 7.54-7.63 (m, 1H), 7.67 (d, 1H, J = 7.0 Hz), 7.86 (d, 1H, J = 8.0 Hz), 7.94 (d, 1H, J = 8.3 Hz), 8.22 (d, 1H, J = 8.2 Hz) ppm; \(^13\)C NMR (75MHz, δ, CDCl\(_3\), 298 K): 24.5, 24.6, 27.6, 28.4, 35.6, 48.8, 50.6, 51.6, 62.3, 76.5, 80.7, 123.3, 123.6, 125.0, 126.6, 128.1, 129.3, 132.0, 133.1, 134.0, 134.1, 155.6 ppm; IR (film): \(3439, 3244, 3005, 2976, 2936, 2864, 1697, 1508, 1489, 1456, 1456, 1321, 1273, 1242, 1159, 1047, 1024, 870, 808, 783, 733 \text{ cm}^{-1}\); HRMS (ESI) \(m/z\) calcd for C\(_{24}\)H\(_{35}\)N\(_2\)O\(_2\): 383.2699 [M\(^+\)]\(^\circ\), found: 383.2693.

**Optimized protocol for deprotection and coupling with iso(thio)cyanates:**

**General Syntheses of 1 (E,F):**

**Step 1 (E):** The corresponding ammonium salt 13 (1.1 mmol) was dissolved in 12 ml dichloromethane and hydroiodic acid (57w% aq. solution, 1.45 ml, 11 mmol, 10 eq) was added. After stirring for 2 h at r.t. the reaction was basified with saturated sodium carbonate solution and extracted with dichloromethane. The organic phase was dried over Na\(_2\)SO\(_4\) and removal of the solvent under reduced pressure gave crude 14 in quantitative yield.

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Compound 14c (R_1 = 3,5-(CF_3)_2-Ph): Obtained in quantitative yield (689 mg, 1.1 mmol). \(^1\)H NMR (300 MHz, δ, CDCl_3, 298 K): 1.31-1.76 (m, 5H), 1.84-1.95 (m, 1H), 1.96-2.07 (m, 1H), 2.27-2.37 (m, 1H), 3.06 (s, 3H), 3.17 (s, 3H), 3.46 (s (b), 2H), 3.56-3.68 (m, 1H), 4.06-4.17 (m, 1H), 5.12 (d, 1H, J = 12.7 Hz), 5.48 (d, 1H, J = 12.7 Hz), 7.96 (s, 1H), 8.16 (s, 2H) ppm.

Step 2 (F): A solution of 14 (1 mmol) and the corresponding iso(thio)cyanate (1.2 mmol, 1.2 eq) in 20 ml dichloromethane was stirred for 2-6 h at r.t. Evaporation of the solvent under reduced pressure gave crude 1, which was further purified by column chromatography (dichloromethane/methanol = 50/1 to 10/1) to obtain pure catalysts 1.

Compound 1a: Obtained in 61% (over 4 steps, starting from 0.2 mmol 11) as a yellowish oil. Analytical data were found to be in accordance with literature\(^4\). [α]_D\(^{23}\) (c = 0.75, dichloromethane) = -49.1°; \(^1\)H NMR (300 MHz, δ, CDCl_3, 298 K): 1.25-1.48 (m, 2H), 1.62-1.90 (m, 2H), 1.91-2.08 (m, 2H), 2.15-2.28 (m, 1H), 2.58-2.70 (m, 1H), 2.90 (s, 3H), 3.17 (s, 3H), 3.94 (s, 6H), 4.45-4.70 (m, 2H), 5.42 (d, 1H, J = 13.1 Hz), 5.70 (d, 1H, J = 13.1 Hz), 7.15 (t, 2H, J = 7.6 Hz), 7.24 (d, 1H, J = 7.8 Hz), 7.45 (d, 1H, J = 7.1 Hz), 7.66 (t, 2H, J = 8.6 Hz), 7.97 (d, 1H, J = 9.7 Hz), 8.08 (d, 1H, J = 8.6 Hz), 8.42 (t, 1H, J = 1.4 Hz), 8.56 (d, 2H, J = 1.4 Hz), 9.05 (s, 1H) ppm; \(^13\)C NMR (75 MHz, δ, CDCl_3, 298 K): 24.5, 25.0, 27.4, 36.1, 48.0, 50.6, 51.4, 52.4, 63.5, 77.3, 122.9, 123.2, 123.8, 124.6, 125.0, 126.4, 127.8, 129.0, 131.2, 131.7, 132.8, 133.6, 133.9, 139.9, 155.2, 166.3 ppm; IR (film): \(\nu\) = 3244, 3028, 2943, 2866, 1717, 1684, 1558, 1541, 1508, 1437, 1346, 1317, 1242, 1047, 997, 876, 808, 783, 754 cm\(^{-1}\); HRMS (ESI): m/z calcd for C\(_{30}\)H\(_{36}\)N\(_3\)O\(_5\): 518.2655 [M\(^+\)]; found: 518.2662.

Compound 1c: Obtained in 65% (123.2 mg, 0.217 mmol) as a colourless oil. [α]_D\(^{21}\) (c = 1.3, CHCl_3) = 13.0°; \(^1\)H NMR (300 MHz, δ, CDCl_3, 298 K): 1.16 (t, J = 7.2 Hz 3H), 1.24-1.41 (m, 1H), 1.43-1.66 (m, 2H), 1.67-1.87 (m, 2H), 1.90-2.12 (m, 2H), 1.49-1.61 (m, 1H), 3.06 (s, 3H), 3.18-3.34 (m, 5H), 4.22-4.38 (m, 1H), 4.59-4.52 (m, 1H), 5.32-5.47 (m, 2H), 5.99 (s, 1H), 6.92 (d, J = 9.7 Hz, 1H), 7.97 (s, 1H), 8.00 (s, 2H), \(^13\)C NMR (75 MHz, δ, CDCl_3, 298 K): 15.5, 24.7, 25.1, 27.4, 35.2, 35.9, 48.1, 50.9, 51.0, 65.3, 78.0, 122.7 (q, J = 273Hz), 124.8, 130.5, 133.0 (q, J = 34 Hz), 133.4, 157.7 ppm; \(^19\)F NMR (282 MHz, δ, CDCl_3, 298 K):
-62.9 ppm IR (film): $\tilde{\nu} = 3295, 3021, 2988, 2936, 2864, 2349, 2288, 1656, 1546, 1449, 1373, 1278, 1174, 1130, 904, 843, 751, 719, 682, 663, 593, 463, \text{cm}^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{20}$H$_{28}$F$_6$N$_3$O$: 440.2131 [M$^+$]; found: 440.2118.

**Compound 1d:** Obtained in 67% (96 mg, 0.14 mmol) as an orange oil. $[\alpha]_D^{21}$ (c = 0.75, dichloromethane) = -29.3°; $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 1.29-1.46 (m, 1H), 1.56-2.06 (m, 5H), 2.11-2.23 (m, 1H), 2.55-2.67 (m, 1H), 3.19 (s, 3H), 3.28 (s, 3H), 3.8 (s, 2H), 7.39 (t, 1H, $J = 8.2$ Hz), 7.47 (d, 1H, $J = 9.2$ Hz), 7.73 (dd, 2H, $J_1 = 8.1$ Hz, $J_2 = 1.5$ Hz), 7.84 (dd, 1H, $J_1 = 8.1$ Hz, $J_2 = 1.8$ Hz), 7.94 (s, 1H), 8.03 (s, 2H), 8.69 (t, 1H, $J = 2.1$ Hz), 9.11 (s, 1H) ppm; $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 24.5, 25.0, 27.3, 36.0, 49.1, 50.6, 50.9, 65.0, 78.4, 113.0, 117.5, 122.5 (q, $J = 275$ Hz), 124.3, 124.9, 129.6, 130.2, 133.1 (q, $J = 33$ Hz), 133.3, 140.4, 148.6, 155.1 ppm; $^{19}$F NMR (282 MHz, $\delta$, CDCl$_3$, 298 K): -63.0 ppm; IR (film): $\tilde{\nu} = 3462, 3254, 3031, 2944, 2866, 1692, 1600, 1548, 1529, 1485, 1451, 1434, 1372, 1352, 1280, 1178, 1137, 904, 843, 830, 798, 737, 709, 683 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{24}$H$_{27}$F$_6$N$_4$O$_3$: 533.1982 [M$^+$]; found: 533.1998.

**Compound 1e:** Obtained in 79% over 2 steps (1.15 g, 1.53 mmol) as an orange oil. $[\alpha]_D^{21}$ (c = 0.75, dichloromethane) = -51.2°; $^1$H NMR (700 MHz, $\delta$, CDCl$_3$, 298 K): 1.36-1.44 (m, 1H), 1.55 (qd, 1H, $J_1 = 12.1$ Hz, $J_2 = 2.9$ Hz), 1.68-1.77 (m, 1H), 1.80-1.85 (m, 1H), 1.85-1.92 (m, 1H), 2.00-2.07 (m, 1H), 2.17-2.23 (m, 1H), 2.59-2.65 (m, 1H), 3.13 (s, 3H), 3.25 (s, 3H), 4.39 (qd, 1H, $J_1 = 10.5$ Hz, $J_2 = 3.4$ Hz), 4.67 (td, 1H, $J_1 = 10.8$ Hz, $J_2 = 2.7$ Hz), 5.36 (d, 1H, $J = 13.5$ Hz), 5.38 (d, 1H, $J = 13.5$ Hz), 7.50 (s, 1H), 7.58 (d, 1H, $J = 9.8$ Hz), 7.95 (s, 1H), 8.00 (s, 2H), 8.08 (s, 2H), 9.15 (s, 1H) ppm; $^{13}$C NMR (175 MHz, $\delta$, CDCl$_3$, 298 K): 24.7, 25.1, 27.4, 36.0, 48.5, 50.6, 50.9, 65.6, 78.0, 116.1, 118.3, 122.5 (q, $J = 273$ Hz), 123.4 (q, $J = 273$ Hz), 125.1, 130.1, 132.2 (q, $J = 33$ Hz), 133.2, 133.2 (q, $J = 34$ Hz), 140.6, 155.1 ppm; $^{19}$F NMR (282 MHz, $\delta$, CDCl$_3$, 298 K): -63.1, -63.1 ppm; IR (film): $\tilde{\nu} = 3462, 3273, 3091, 3048, 2945, 2867, 1696, 1624, 1567, 1474, 1443, 1387, 1318, 1278, 1176, 1131, 1042, 945, 904, 884, 845, 737, 704, 683, 648 cm$^{-1}$; HRMS (ESI): $m/z$ calcd for C$_{26}$H$_{27}$F$_{12}$N$_3$O$: 624.1879 [M$^+$]; found: 624.1880.
3. Asymmetric Michael Addition Reactions:

**General Procedure:** Degased toluene (5 mL) was added to a mixture of the Schiff base 5 (0.1 mmol), catalyst 1c (10 mol%), and Cs$_2$CO$_3$ (1.5 eq) in the Schlenk tube. Stirring rate was set to 1000 rpm and the corresponding electrophile 15 (1.5 eq.) was added. After 24 h at 25 °C the reaction mixture was filtrated over a plug of Na$_2$SO$_4$. The solvents were removed under reduced pressure. The crude products were purified by column chromatography (silica gel, heptanes:EtOAc = 20:1 to 2:1) giving the products 16 in the reported yields.

*R-(+)-16a.* Obtained as a colourless oil in 85% yield and with e.r. = 95:5 upon reacting Schiff base 5a with acrylate 15a in the presence of 10 mol% catalyst at 25 °C under the general reaction conditions. Analytical data are in full accordance with those reported in literature$^{5,6}$. $^1$H NMR (300 MHz, CDCl$_3$, 298 K): 1.44 (s, 9H), 2.16-2.27 (m, 2H), 2.33-2.41 (m, 2H), 3.59 (s, 3H), 3.93-3.99 (m, 1H), 7.14-7.21 (m, 2H), 7.28-7.47 (m, 6H), 7.60-7.68 (m, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$, 298 K): 28.2, 28.8, 30.5, 51.7, 64.9, 81.3, 127.9, 128.1, 128.6, 128.7, 128.9, 130.5, 136.6, 139.6, 170.8, 170.9, 173.7 ppm; IR (film): $\tilde{\nu} = 2978$, 2926, 1738, 1707, 1661, 1599, 1578, 1449, 1369, 1319, 1279, 1260, 1234, 1153, 943, 920, 849, 812 cm$^{-1}$; The enantioselectivity was determined by HPLC (Chiralcel AD-H, eluent: n-hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: 10.9 min (major; R-enantiomer), 12.3 min (minor; S-enantiomer)); Absolute configuration was determined by comparison of the retention times and the $[\alpha]_D$-value with reported data$^{5,6}$. HRMS (ESI): m/z calcd for C$_{23}$H$_{27}$NO$_4$: 382.2013 [M+H$^+$]; found: 382.2013.

*R-(+)-16b.* Obtained as a colourless oil in 74% yield and with e.r. = 92:8 upon reacting Schiff base 5b with acrylate 15b in the presence of 10 mol% catalyst at 25 °C under the general conditions. Analytical data are in full accordance with those reported in literature$^{7,8}$. $[\alpha]_D^{21}$ (c = 0.85, CHCl$_3$) = 17.9$^\circ$; $^1$H NMR (300 MHz, CDCl$_3$, 298 K): 2.23-2.32 (m, 2H), 2.33-2.40 (m, 2H), 3.57 (s, 3H), 4.11-4.17 (m, 1H), 5.16 (dd, $J = 7.0$ Hz, 12.5 Hz, 2H), 7.08-7.14 (m, 2H), 7.28-7.42 (m, 11H), 7.59-7.67 (m, 2H) ppm; $^{13}$C NMR (75 MHz, CDCl$_3$, 298 K): 28.5, 30.4, 51.5, 64.1, 66.6, 127.8, 128.0, 128.1, 128.2, 128.5, 128.7, 128.9, 130.5, 135.8, 136.1, 171.4, 173.4 ppm; IR (film): $\tilde{\nu} = 3063$, 2959, 2928, 2853, 1742, 1705, 1659, 1599, 1578, 1499, 1449, 1420, 1389, 1377, 1317, 1279, 1209, 1192, 1177, 1157, 922, 754, 706 cm$^{-1}$; The

enantioselectivity was determined by HPLC (Chiralcel AD-H, eluent: n-hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: 29.6 min (major; (R)-enantiomer), 36.1 min (minor; (S)-enantiomer)); Absolute configuration was determined by comparison of the retention times and the [α]D-value with reported data. HRMS (ESI): m/z calcd for C26H33NO4: 416.1856 [M+H]+; found: 416.1858.

(+)-16c. Obtained as a colourless oil in 90% yield and with e.r. = 92:8 upon reacting Schiff base 4c with acrylate 15c using 10 mol% catalyst at 25 °C under the general reaction conditions. Analytical data are in full accordance with those reported in literature. [α]D 21 (c = 0.9, CHCl3) = 63.1°; 1H NMR (300 MHz, δ, CDCl3, 298 K): 2.20-2.29 (m, 2H), 2.32-2.40 (m, 2H), 3.58 (s, 3H), 3.71 (s, 3H), 4.13 (t, J = 6.2 Hz, 1H), 7.14-7.21 (m, 2H), 7.29-7.48 (m, 6H), 7.60-7.67 (m, 2H) ppm; 13C NMR (75 MHz, δ, CDCl3, 298 K): 28.6, 30.4, 51.6, 52.2, 64.1, 127.8, 128.1, 128.6, 128.8, 128.9, 130.6, 172.0, 172.2, 173.4 ppm; IR (film): ν = 3057, 3051, 2992, 2955, 1736, 1624, 1576, 1445, 1437, 1316, 1265, 1204, 1172, 1074, 1028, 1001, 781, 731, 702 cm⁻¹; The enantioselectivity was determined by HPLC (Chiralcel AD-H, eluent: n-hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: 19.2 min (major; (+)-enantiomer), 21.6 min (minor; (-)-enantiomer)); HRMS (ESI): m/z calcd for C23H21NO4: 340.1543 [M+H]+; found: 340.1543.

R-(+)-16d. Obtained as a colourless oil in 63% yield and with e.r. = 95:5 upon reacting Schiff base 4c with acrylate (15d) using 10 mol% catalyst at 25 °C under the standard conditions. Analytical data are in full accordance with those reported in literature. [α]D 21 (c = 0.3, CHCl3) = 21.7°; 1H NMR (300 MHz, δ, CDCl3, 298 K): 0.90 (t, J = 7.3 Hz, 3H), 1.28-1.40 (m, 2H), 1.44 (s, 9H), 1.48-1.60 (m, 2H), 2.17-2.27 (m, 2H), 2.31-2.40 (m, 2H), 3.93-4.03 (m, 3H), 7.13-7.20 (m, 2H), 7.29-7.47 (m, 6H), 7.61-7.68 (m, 2H) ppm; 13C NMR (75 MHz, δ, CDCl3, 298 K): 13.8, 19.2, 28.2, 28.8, 30.7, 30.9, 64.4, 67.0, 81.3, 127.9, 128.1, 128.4, 128.6, 128.9, 130.2, 136.6, 139.6, 170.8, 170.9, 173.4 ppm; IR (film): ν = 2957, 2929, 2855, 2361, 2341, 1734, 1703, 1660, 1448, 1368, 1277, 1151, 920, 845, 764, 702, 639, 464 cm⁻¹; The enantioselectivity was determined by HPLC (Chiralcel AD-H, eluent: n-hexane: i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: 9.8 min (major; R-(+)-enantiomer), 10.5 min (minor; S-(-)-enantiomer)); HRMS (ESI): m/z calcd for C26H33NO4: 424.2488 [M+H]+; found: 424.2475.

**R-(+)-16e.** Obtained as a colourless oil in <10% yield and with e.r. = 83:17 upon reacting Schiff base 4c with acrylate (15e) using 10 mol% catalyst at 25 °C under the standard conditions and in 52% yield and with e.r. = 83:17 upon reacting Schiff base 4c with acrylate (15) using 10 mol% catalyst at 25 °C using 5 eq. of Cs₂CO₃. Analytical data are in full accordance with those reported in literature. \([\alpha]_D^{21} (c = 0.87, \text{CHCl}_3) = 14.4^\circ; \) \(^1\)H NMR (300 MHz, δ, CDCl₃, 298 K): 1.38 (s, 9H), 1.44 (s, 9H), 2.13-2.30 (m, 4H), 3.91-3.67 (m, 1H), 7.14-7.21 (m, 2H), 7.28-7.52 (m, 6H), 7.56-7.68 (m, 2H) ppm; \(^13\)C NMR (75 MHz, δ, CDCl₃, 298 K): 28.2, 29.0, 32.2, 80.3, 81.2, 128.0, 128.1, 128.6, 128.7, 129.0, 130.4, 136.7, 139.7, 170.8, 171.1, 172.6 ppm; IR (film): \(\tilde{\nu} = 2961, 2977, 2932, 1732, 1668, 1456, 1368, 1276, 1254, 1147, 1073, 1028, 919, 846, 751, 696, 638, 459 \text{cm}^{-1};\) The enantioselectivity was determined by HPLC (Chiralcel AD-H, eluent: n-hexane:i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: 15.3 min (major, \(R\)-(+) enantiomer), 16.3 min (minor; \(S\)-(−)-enantiomer)); HRMS (ESI): \(m/z\) calcd for \(C_{28}H_{33}NO_{4}\): 424.2488 \([\text{M+H}]^+\); found: 424.2473.

**R-(+)-16f.** Obtained as a colourless oil in 96% yield and with e.r. = 91:9 upon reacting Schiff base 4c with acrylate (15f) using 10 mol% catalyst at 25 °C under the standard conditions. Analytical data are in full accordance with those reported in literature. \([\alpha]_D^{21} (c = 1.44, \text{CHCl}_3) = 41.0^\circ; \) \(^1\)H NMR (300 MHz, δ, CDCl₃, 298 K): 1.44 (s, 9H), 2.20-2.30 (m, 2H), 2.38-2.47 (m, 2H), 3.95-4.01 (m, 1H), 5.04 (s, 2H), 7.12-7.19 (m, 2H), 7.27-7.45 (m, 11H), 7.61-7.67 (m, 2H) ppm; \(^13\)C NMR (75 MHz, δ, CDCl₃, 298 K): 28.2, 28.7, 30.9, 65.0, 66.3, 81.3, 127.9, 128.1, 128.3, 128.6, 128.7, 128.9, 130.5, 136.1, 136.6, 139.6, 170.8, 170.9, 173.1 ppm; IR (film): \(\tilde{\nu} = 3025, 2978, 2873, 2349, 1724, 1625, 1448, 1367, 1252, 1148, 845, 753, 697, 523 468 \text{cm}^{-1};\) The enantioselectivity was determined by HPLC (Chiralcel AD-H, eluent: n-hexane:i-PrOH = 100:1, 1 mL/min, 10 °C, retention times: 17.7 min (major, \(R\)-(+) enantiomer), 20.9 min (minor; \(S\)-(−)-enantiomer)); HRMS (ESI): \(m/z\) calcd for \(C_{29}H_{34}NO_{4}\): 458.2331 \([\text{M+H}]^+\); found: 458.2311.

**R-(+)-16g.** Obtained as a colourless oil in 81% yield and with e.r. = 65:35 upon reacting Schiff base 4c with acrylate (15g) using 10 mol% catalyst at 25 °C under the general reaction conditions. Analytical data are in full accordance with those reported in literature. \([\alpha]_D^{21} (c = 0.92, \text{CHCl}_3) = 17.0^\circ; \) \(^1\)H NMR (300 MHz, δ, CDCl₃, 298 K): 1.38 (s, 9H), 2.08-2.32 (m, 2H), 3.14-3.37 (m, 2H), 3.97–4.04 (m, 1H), 7.08-7.16 (m, 2H), 7.28-7.47 (m, 6H), 7.51-7.60 (m, 4H), 7.61-7.69 (m, 1H), 7.86-7.93 (m, 2H) ppm; \(^13\)C NMR (75 MHz, δ, CDCl₃, 298 K): 27.2, 28.1, 53.0, 63.7, 81.9, 127.8, 128.2, 128.3, 128.8, 129.2, 129.4, 130.3, 133.8, 136.2, 139.0, 139.2, 170.0, 171.6 ppm; IR (film): \(\tilde{\nu} = 3060, 2977, 2932, 1768, 1622, 1446, 1393,
The enantioselectivity was determined by HPLC (Chiralcel AD-H, eluent: n-hexane/i-PrOH = 95:5, 1 mL/min, 10 °C, retention times: 18.6 min (major, \( R\-\))-enantiomer), 26.6 min (minor; \( S\-\))-enantiomer); HRMS (ESI): \( m/z \) calcd for \( \text{C}_{27}\text{H}_{35}\text{NO}_4\text{S} \): 464.1896 [M+H]\(^+\)\); found: 464.1884.

\[ \text{(+)-16h. Obtained as a colourless oil in around 10\% yield and with e.r. = 88:12} \]

\[ \text{S-(-)-16i. Obtained as a colourless oil in 95\% yield and with e.r. = 92:8} \]

10 G.N Gururaja, R. Herchl; A. Pichler; K. Gratzer; M. Waser; Molecules 2013, 18, 4357-4372.
(R,S)-(+)−16j. Obtained as a colourless oil in 85% yield and with d.r. = 20:1 and e.r. = 95:5 (major diastereomer) upon reacting Schiff base 4c with dimethylmaleat (15j) using 10 mol% catalyst at 25 °C under standard conditions. [α]D21 (c = 0.59, CHCl3) = 92.2°; 1H NMR (300 MHz, δ, CDCl3, 298 K): 1.43 (s, 9H), 2.58 (dd, J = 5.2, 16.9 Hz, 1H), 2.84 (dd, J = 9.3, 16.8 Hz, 1H), 3.51-3.59 (m, 1H), 3.64 (s, 3H), 3.70 (s, 3H), 4.20 (d, J = 3.7 Hz, 1H), 7.13-7.20 (m, 2H), 7.27-7.46 (m, 6H), 7.57-7.63 (m, 2H) ppm; 13C NMR (75 MHz, δ, CDCl3, 298 K): 28.0, 32.7, 45.1, 51.9, 52.0, 66.3, 81.9, 127.7, 128.1, 128.6, 128.9, 129.1, 130.7, 136.2, 139.2, 169.1, 172.0, 172.4, 172.7 ppm; IR (film): ν = 2979, 2952, 1732, 1626, 1437, 1368, 1148, 1001, 845, 782, 752, 696, 513 cm−1; E.r. was determined by HPLC (Chiralcel AD-H, eluent: n-hexane:i-PrOH = 98:2, 1.0 mL/min, 10 °C, retention times of the major diastereomer: 14.3 min (minor; (+)-enantiomer), 17.6 min (major, (+)-enantiomer); HRMS (ESI): m/z calc for C25H30NO6: 440.2073 [M+H]+; found: 440.2057.

(R,R)-(+)−16j'. Obtained as a colourless oil in 96% yield and with d.r. > 20:1 and e.r. = 88:12 (major diastereomer) upon reacting Schiff base 5a with dimethylfumarat (15j') using 10 mol% catalyst at 25 °C under the general conditions. Analytical data are in full accordance with those reported in literature9. [α]D21 (c = 0.82, CHCl3) = 73.7°; 1H NMR (300 MHz, δ, CDCl3, 298 K): 1.43 (s, 9H), 2.69 (dd, J = 3.9, 17.0 Hz, 1H), 3.10 (dd, J = 9.6, 17.0 Hz, 1H), 3.60 (s, 3H), 3.61-3.69 (s, 4H), 4.20 (d, J = 3.7 Hz, 1H, characteristic signal of the minor diastereomer), 4.42 (d, J = 5.0 Hz, 1H), 7.12-7.20 (m, 2H), 7.27-7.47 (m, 6H), 7.57-7.63 (m, 2H) ppm; 13C NMR (75 MHz, δ, CDCl3, 298 K): 28.1, 32.4, 44.7, 51.9, 52.1, 66.2, 82.1, 128.0, 128.1, 128.5, 128.9, 129.1, 130.6, 136.2, 139.4, 169.3, 172.2, 172.7, 172.9 ppm; IR (film): ν = 2979, 2952, 1732, 1626, 1437, 1368, 1148, 1001, 845, 782, 752, 696, 513 cm−1; E.r. was determined by HPLC (Chiralcel AD-H, eluent: n-hexane:i-PrOH = 98:2, 1.0 mL/min, 10 °C, retention times of the major diastereomer: 16.7 min (major, (+)-enantiomer), 39.4 min (minor; (-)-enantiomer)); HRMS (ESI): m/z calc for C25H30NO6: 440.2073 [M+H]+; found: 440.2062.

(2R,3S)-(+)−16k. Obtained as white solid in 25% yield and with d.r. = 3:1 and e.r. = 86:14 (major diastereomer) upon reacting Schiff base 4c with cyclohexenone (15k) using 10 mol% catalyst at 25 °C under standard conditions and in 36% yield and with d.r. = 3:1 and e.r. = 86:14 upon reacting Schiff base 4c with 5 eq. of cyclohexenone (15k) using 10 mol% catalyst. [α]D21 (c = 0.86, CHCl3) = 39.9°; 1H NMR (300 MHz, δ, CDCl3, 298 K): 1.43 (s, 9H), 1.55-1.74 (m, 3H), 1.95-2.56 (m, 5H), 2.60-2.44 (m, 1H), 3.79 (d, J = 5.0 Hz, 1H, minor), 3.90 (d, J = 4.3 Hz, 1H, major), 7.08-7.18 (m, 2H), 7.28-7.48 (m, 6H), 7.63-7.70 (m, 2H) ppm; 13C NMR (75 MHz, δ, CDCl3, 298 K): 25.5*, 26.3, 28.2, 38.3, 40.1*, 52.1, 54.6, 61.2, 124.2, 127.5, 129.0, 131.7, 135.6, 141.3, 144.6, 161.7, 169.3, 172.2, 172.7, 172.9 ppm; HRMS (ESI): m/z calc for C25H30NO6: 440.2073 [M+H]+; found: 440.2057.
40.3, 41.0, 42.2*, 68.0, 69.1*, 81.6, 127.9, 127.9*, 128.2, 128.4*, 128.7, 128.8, 128.8*, 128.9, 130.6, 136.5*, 136.7, 139.3, 139.4*, 170.3, 170.4*, 171.1, 171.5* ppm (*denotes minor diastereomer where observable); IR (film): $\bar{\nu} = 3059, 2976, 2931, 1727, 1685, 1597, 1447, 1367, 1147, 1002, 845, 750, 694, 546, 485, 403, 410, 422$, ppm.

The enantioselectivity was determined by HPLC (Chiralcel AD-H, eluent $n$-hexane:i-PrOH = 98:2, 0.5 mL/min, 10 °C, retention times of the major diastereomer: 26.5 min (major, (+)-enantiomer), 44.8 min (minor, (-)-enantiomer)); HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{30}$NO$_3$: 392.226 [M+H]$^+$; found: 392.2229.

**(+)-16l.** Obtained as a colourless oil in 82% yield and with d.r. = 4:1 and with e.r. = 95:5 (major diastereomer) upon reacting Schiff base 4c with cyclopentenone (15l) using 10 mol% catalyst at 25 °C under standard conditions. $[\alpha]_D^{21}$ (c = 1.15, CHCl$_3$) = 86.8°; $^1$H NMR (300 MHz, δ, CDCl$_3$, 298 K) of the major diastereomer:

$\delta$ (m, 1H), 2.56 (m, 1H), 6.75 (m, 5H), 7.12-7.50 (m, 6H), 7.59-7.66 (m, 2H) ppm; $^{13}$C NMR (75 MHz, δ, CDCl$_3$, 298 K): 25.5*, 26.4, 28.2, 38.3, 40.1*, 40.3, 41.0, 42.2*, 68.5, 69.1*, 81.6, 127.9, 128.2, 128.4*, 128.7, 128.8*, 128.8, 128.9, 130.6, 136.7, 139.3, 170.3, 170.4*, 171.1, 171.5* ppm (*denotes the minor diastereomer where observable); IR (film): $\bar{\nu} = 3059, 2976, 2931, 2864, 2349, 1709, 1624, 1422, 1367, 1282, 1224, 1146, 1107, 965, 846, 781, 752, 696, 637, 504$ cm$^{-1}$.

The enantioselectivity was determined by HPLC (Chiralcel AD-H, eluent n-hexane:i-PrOH = 100:3.5, 1.0 mL/min, 10 °C, retention times (major diastereomer): 7.1 min (major, (+)-enantiomer), 10.1 min (minor, (-)-enantiomer)); HRMS (ESI): $m/z$ calcd for C$_{25}$H$_{30}$NO$_3$: 378.2069 [M+H]$^+$; found: 378.2057.

**(2R, 3S)-(+) -16m.** Obtained as a colourless oil in 90% yield and with d.r. > 20:1 and e.r. = 93:7 (major diastereomer) upon reacting Schiff base 4c with chalcone (15m) using 10 mol% catalyst at 25 °C under standard conditions. Analytical data are in full accordance with those reported in literature$^{11}$. $[\alpha]_D^{21}$ (c = 0.65, CHCl$_3$) = 53.1°; $^1$H NMR (300 MHz, δ, CDCl$_3$, 298 K): 1.32 (s, 9H), 3.56-3.82 (m, 2H), 4.14-4.24 (m, 2H), 6.67-6.75 (m, 2H), 7.10-7.20 (m, 5H), 7.30-7.58 (m, 9H), 7.65-7.72 (m, 2H), 7.94-8.00 (m, 2H) ppm; $^{13}$C NMR (75 MHz, δ, CDCl$_3$, 298 K): 28.0, 40.2, 44.9, 71.1, 81.4, 126.7, 127.7, 128.2, 128.3, 128.5, 128.6, 128.7, 128.9, 130.5, 133.0, 136.4, 137.3, 139.5, 141.5, 170.2, 171.3, 198.8 ppm; IR (film): $\bar{\nu} = 3060, 3027, 2979, 2931, 1727, 1685, 1597, 1447, 1367, 1147, 1002, 845, 750, 694, 546, 531$ cm$^{-1}$; The enantioselectivity of the major diastereomer was determined by HPLC (Chiralcel AD-

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4. Asymmetric Aldol-Initiated Cascade Reactions:

**General Procedure:** In a round-bottom flask, 2-cyanbenzaldehydes 6 (0.10 mmol) were added at room temperature to a stirred solution of glycine Schiff base 5 (1.1 eq., 0.11 mmol), K$_2$CO$_3$ (1 eq.) and catalyst 1d (5% mol) in CH$_2$Cl$_2$ (3 mL). The mixture was stirred at r.t. for 24 h (1000 rpm). After, the mixture was purified directly by flash chromatography on silica gel with hexane:ethyl acetate = 8:2 to give the intermediates 7 as a mixture of diastereoisomers. The products 7 were dissolved in a cooled solution of 0.5 M HCl (1 mL) and THF (3 mL) (0 °C). The mixtures were stirred at the same temperature for 2 h and then concentrated under vacuum. The resulting residue was treated with saturated NaHCO$_3$ (20 mL), extracted with CH$_2$Cl$_2$ (4 x 30 mL) and purified by flash chromatography (silica gel, hexanes:EtOAc = 2:1).

**(-)-8a.** Obtained according to the general procedure in 83% (22 mg, 0.083 mmol) as an amorphous solid. (dr = 4:1; e.r. (major) = 95:5). [α]$_D^{20}$ = -2.5 (c 0.5 in CHCl$_3$). $^1$H-NMR (300 MHz, CDCl$_3$): δ = 7.92 (d, $J$ = 7.6 Hz, 1H), 7.68 (t, $J$ = 6.48 Hz, 1H), 7.58 (t, $J$ = 7.42 Hz, 1H), 7.44 (d, $J$ = 7.6 Hz, 1H), 5.77 (d, $J$ = 3.5 Hz, 1H), 4.04 (d, $J$ = 3.6 Hz, 1H), 1.61 (br s, 2H), 1.40 (s, 9H) ppm. $^{13}$C-NMR (100 MHz, CDCl$_3$): δ = 171.5, 171.3, 147.5, 135.2, 130.8, 128.3, 126.9, 123.8, 83.9, 83.3, 58.7, 29.1 ppm. MS (ESI): m/z = 264.1 (M+H)$^+$ Anal. calcd for C$_{14}$H$_{17}$NO$_4$: C, 63.87; H, 6.51; N, 5.32. Found: C, 63.97; H, 6.41; N, 5.37%. HPLC separation of the major diastereomer: Chiralcel OD-H, hexane:i-PrOH = 9:1, 25 °C, 0.7 mL/min, (retention times: 25.3 min (minor); 34.3 min (major)).

**(-)-8b.** Obtained according to the general procedure in 80% (27 mg, 0.08 mmol) as an amorphous solid. (dr = 2.5:1; e.r. (major) = 91:9). [α]$_D^{20}$ = -4 (c 0.5 in CHCl$_3$). $^1$H-NMR (300 MHz, CDCl$_3$): δ = 8.04 (d, $J$ = 1.7 Hz, 1H), 7.78 (dd, $J_1$ = 8.1 Hz, $J_2$ = 1.7 Hz, 1H), 7.33 (d, $J$ = 8.1 Hz, 1H), 5.70 (d, $J$ = 3.8 Hz, 1H), 3.99 (d, $J$ = 3.7 Hz, 1H) 1.44 (s, 9H) ppm. $^{13}$C-NMR (75 MHz, CDCl$_3$): δ = 170.1, 168.3, 144.8, 136.9, 129.1, 128.5, 124.1, 123.4, 82.9, 81.7, 57.2, 27.8 ppm. MS (ESI): m/z = 343.2 (M+H)$^+$. Anal. calcd for C$_{14}$H$_{16}$BrNO$_4$: C, 43.14; H, 4.71; N, 4.09. Found: C, 43.39; H, 4.62; N, 4.23%. HPLC
separation of the major diastereomer: Chiralcel OD-H, hexane:i-PrOH = 9:1, 25 °C, 0.7 mL/min, (retention times: 27.1 min (minor); 35.0 min (major)).

(-)-8c. Obtained according to the general procedure in 78% (23 mg, 0.078 mmol) as an amorphous solid. (dr = 3.5:1; e.r. (major) = 88:12). [α]D20 = -11.8 (c 0.43 in CHCl3).

1H-NMR (300 MHz, CDCl3): δ = 7.87 (d, J = 1.8 Hz, 1H), 7.62 (dd, J1 = 8.1 Hz, J2 = 1.8 Hz, 1H), 7.39 (d, J = 7.8 Hz, 1H), 5.71 (d, J = 3.6 Hz, 1H), 3.99 (d, J = 3.6 Hz, 1H) ppm. 13C-NMR (75 MHz, CDCl3): δ = 170.2, 168.6, 145.1, 135.8, 134.4, 128.6, 125.5, 123.2, 82.8, 81.5, 56.7, 27.8 ppm. MS (ESI): m/z = 298.1 (M+H)+. Anal. calcd for C14H16ClNO4: C, 56.48, H, 5.42; N, 4.70. Found: C, 56.40; H, 5.62; N, 4.63%. HPLC separation of the major diastereomer: Chiralcel OD-H, hexane:i-PrOH = 9:1, 25 °C, 0.7 mL/min, (retention times: 11.7 min (minor); 14.6 min (major)).

(-)-8d. Obtained according to the general procedure in 75% (22 mg, 0.075 mmol) as an amorphous solid. (dr = 3:1; e.r. (major) = 87:13). [α]D20 = - 1.5 (c 0.35 in CHCl3).

1H-NMR (250 MHz, CDCl3): δ = 7.34-7.29 (m, 2H), 7.23-7.22 (m, 1H), 5.71 (d, J = 3.3 Hz, 1H), 4.00 (d, J = 3.3 Hz, 1H,) 3.86 (s, 3H), 1.42 (s, 9H) ppm. 13C-NMR (75 MHz, CDCl3): δ = 170.3, 170.0, 138.2, 128.5, 123.3, 123.0, 122.7, 107.5, 82.5, 81.6, 57.4, 55.7, 27.8 ppm. MS (ESI): m/z = 294.1 (M+H)+. Anal. calcd for C15H19NO5: C, 61.42; H, 6.53; N, 4.78. Found: C, 61.35; H, 6.63; N, 4.56%. HPLC separation of the major diastereomer: IA3 column, hexane:i-PrOH = 9:1, 25 °C, 0.6 mL/min, (retention times: 30.2 min (major); 33.4 min (minor)).
5. Copies of NMR Spectra of Key-Intermediates and Most Relevant Catalysts:

_Crude product_
Crude product
Nov-494-13
6. Copies of NMR Spectra of Selected Products 16 and Products 8:
Major diastereomer

\[
\begin{align*}
8a & \quad \text{O} \\
& \quad \text{CO}_2\text{tBu} \\
& \quad \text{NH}_2
\end{align*}
\]
Major diastereomer
Major diastereomer

8c

\[
\begin{align*}
&\text{Cl} \\
&\text{NH}_2 \\
&\text{CO}_2\text{Bu} \\
&\text{O} \\
&\text{O} \\
&\text{O} \\
&\text{O} \\
&\text{O} \\
&\text{O}
\end{align*}
\]
Major diastereomer

8d
7. Copies of HPLC Chromatograms of Products 16 and 8:

24 TIF-269-02

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![HPLC Chromatogram Graph]

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<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>Total:</td>
<td></td>
<td></td>
<td>451,964</td>
<td>104,409</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

Ph N CO₂fBu
Ph CO₂Me
16a (rac.)
14 TIF-256-02

Sample Name: TIF-256-02  Injection Volume: 5.0
Vial Number: RA1  Channel: UV_VIS_2
Sample Type: unknown  Wavelength: 250
Control Program: AD_H_100min_95-5_flow05  Bandwidth: 4
Quantif. Method: AD_H  Temperature/Column: 10
Recording Time: 13.3.2015 14:34  Flow ml/min: 0.500
Run Time (min): 17.88  Sample Amount: 1,000

---

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time min</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount n.a.</th>
<th>Type BM *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10.91</td>
<td>n.a.</td>
<td>903,789</td>
<td>192,805</td>
<td>94.81</td>
<td>n.a.</td>
<td>BM *</td>
</tr>
<tr>
<td>2</td>
<td>12.31</td>
<td>n.a.</td>
<td>44,727</td>
<td>10,545</td>
<td>5.19</td>
<td>n.a.</td>
<td>BM *</td>
</tr>
</tbody>
</table>

Total: | 948,516 | 203,350 | 100.00 | 0.00 |
37 TIF-282-02

Sample Name: TIF-282-02
Vial Number: RA1
Sample Type: unknown
Control Program: AD_H_100min_95-5_flow05
Quantif. Method: AD_H
Recording Time: 8.4.2015 16:33
Run Time (min): 66.12
Injection Volume: 5.0
Channel: UV_VIS_2
Wavelength: 250
Bandwidth: 4
Temperature/Column: 10
Flow m/min: 0.500
Sample Amount: 1.0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.27</td>
<td>n.a.</td>
<td>191,262</td>
<td>115,654</td>
<td>50.18</td>
<td>n.a.</td>
<td>M*</td>
</tr>
<tr>
<td>2</td>
<td>35.73</td>
<td>n.a.</td>
<td>153,953</td>
<td>114,842</td>
<td>49.82</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>345,205</td>
<td>230,496</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

Ph \begin{align*} & \text{Ph} \\ \text{N} & \text{CO}_2\text{Bn} \\ \text{CO}_3\text{Me} & \end{align*}

16b (rac.)

1 - 29.270
2 - 35.727

mAU

220

UV_VIS_2

WVL 250 nm

min

22.0

26.0

28.0

30.0

32.0

34.0

36.0

38.0

40.0

42.5

20

25

30

35

40

45

50

55

60

65

70

75

80

85

90

95

100
Sample Name: TIF-281-02  Injection Volume: 5.0
Vial Number: RA3  Channel: UV_VIS_2
Sample Type: unknown  Wavelength: 250
Control Program: AD_H_100min_95-5_flow05  Bandwidth: 4
Quantif. Method: AD_H  Temperature/Column: 10
Recording Time: 9.4.2015 11:08  Flow ml/min: 0.500
Run Time (min): 40.00  Sample Amount: 1,0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29,56</td>
<td>n.a.</td>
<td>288,527</td>
<td>175,217</td>
<td>91,73</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>36,08</td>
<td>n.a.</td>
<td>21,100</td>
<td>15,791</td>
<td>8,27</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>309,627</td>
<td>191,008</td>
<td>100,00</td>
<td>0,000</td>
<td></td>
</tr>
</tbody>
</table>

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
**40 TIF-287-02**

- **Sample Name:** TIF-287-02
- **Injection Volume:** 5.0
- **Vial Number:** RB4
- **Channel:** UV_VIS_2
- **Sample Type:** unknown
- **Wavelength:** 250
- **Control Program:** AD_H_100min_95-5_flow05
- **Bandwidth:** 4
- **Quantif. Method:** AD_H
- **Temperature/Column:** 10
- **Recording Time:** 9.4.2015 16:20
- **Flow ml/min:** 0.500
- **Run Time (min):** 26.65
- **Sample Amount:** 1,0000

---

### Chromatogram

- **Retention Time:**
  - **Peak Name:** 16c (rac.)
  - **Wavelength:** 250 nm

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.20</td>
<td>n.a.</td>
<td>521.987</td>
<td>197,204</td>
<td>50.00</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>21.52</td>
<td>n.a.</td>
<td>457.950</td>
<td>197,195</td>
<td>50.00</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
</tbody>
</table>

**Total:**
- **Height:** 979.937
- **Area:** 394.398
- **Rel.Area:** 100.00
- **Amount:** 0.000

---

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
41 TIF-285-02

Sample Name: TIF-285-02  Injection Volume: 5.0
Val Number: RB1  Channel: UV_VIS_2
Sample Type: unknown  Wavelength: 250
Control Program: AD_H_100min_95-5_flow05  Bandwidth: 4
Quantif. Method: AD_H  Temperature/Column: 10
Recording Time: 9.4.2015 17:16  Flow ml/min: 0.500
Run Time (min): 25.00  Sample Amount: 1,000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height</th>
<th>Area</th>
<th>Ret.Area</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>19.20</td>
<td>n.a.</td>
<td>875.758</td>
<td>332,098</td>
<td>91.99</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>21.56</td>
<td>n.a.</td>
<td>67.865</td>
<td>28,932</td>
<td>8.01</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>943,623</td>
<td>361,031</td>
<td>100.00</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
**43  TIF-291-02**

<table>
<thead>
<tr>
<th>Sample Name:</th>
<th>TIF-291-02</th>
<th>Injection Volume:</th>
<th>5,0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vial Number:</td>
<td>RC1</td>
<td>Channel:</td>
<td>UV_VIS_2</td>
</tr>
<tr>
<td>Sample Type:</td>
<td>unknown</td>
<td>Wavelength:</td>
<td>250</td>
</tr>
<tr>
<td>Control Program:</td>
<td>AD_H_100min_95-5_flow05</td>
<td>Bandwidth:</td>
<td>4</td>
</tr>
<tr>
<td>Quantif. Method:</td>
<td>AD_H</td>
<td>Temperature/Column:</td>
<td>10</td>
</tr>
<tr>
<td>Recording Time:</td>
<td>13.4.2015 14:03</td>
<td>Flow ml/min:</td>
<td>0,500</td>
</tr>
<tr>
<td>Run Time (min):</td>
<td>63,33</td>
<td>Sample Amount:</td>
<td>1,0000</td>
</tr>
</tbody>
</table>

**Chemical Structure**

![Chemical Structure](image)

**Table: Chromatographic Data**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount (n.a.)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.72</td>
<td>n.a.</td>
<td>672,398</td>
<td>128,319</td>
<td>50.06</td>
<td>n.a. BM*</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>10.48</td>
<td>n.a.</td>
<td>612,655</td>
<td>128,060</td>
<td>49.95</td>
<td>n.a. MB*</td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>1285,241</td>
<td>256,379</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

**Software Details**

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3978 (207169)
44 TIF-289-02

Sample Name: TIF-289-02  Injection Volume: 5.0
Vial Number: RC2  Channel: UV_VIS_2
Sample Type: unknown  Wavelength: 250
Control Program: AD_H_100min_95-5_flow05  Bandwidth: 4
Quantif. Method: AD_H  Temperature/Column: 10
Recording Time: 13.4.2015 15:07  Flow ml/min: 0.500
Run Time (min): 22.46  Sample Amount: 1,0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9.77</td>
<td>n.a.</td>
<td>330,788</td>
<td>62,823</td>
<td>94.90</td>
<td>n.a.</td>
<td>BM *</td>
</tr>
<tr>
<td>2</td>
<td>10.53</td>
<td>n.a.</td>
<td>15,837</td>
<td>3,374</td>
<td>5.10</td>
<td>n.a.</td>
<td>M *</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>346,626</td>
<td>66,197</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

default/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
**66  TIF-303-02**

- **Sample Name:** TIF-303-02
- **Injection Volume:** 5.0 µL
- **Vial Number:** RB3
- **Channel:** UV_VIS_2
- **Sample Type:** unknown
- **Wavelength:** 250 nm
- **Control Program:** AD_H_80min_100-1_flow05
- **Bandwidth:** 4 Å
- **Quantif. Method:** AD_H
- **Temperature/Column:** 10°C
- **Recording Time:** 24.4.2015 9:23
- **Flow ml/min:** 0.500
- **Run Time (min):** 25.38
- **Sample Amount:** 1,000 ppm

![Graph showing chromatogram with peaks labeled](image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount (%)</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.16</td>
<td>n.a.</td>
<td>274,994</td>
<td>87,626</td>
<td>49.87</td>
<td>n.a.</td>
<td>BM*</td>
</tr>
<tr>
<td>2</td>
<td>16.14</td>
<td>n.a.</td>
<td>255,833</td>
<td>88,098</td>
<td>50.13</td>
<td>n.a.</td>
<td>MB*</td>
</tr>
</tbody>
</table>

**Total:** 530,827 175,724 100.00 0.000
Sample Name: TIF-301-02

Injection Volume: 5,0

Vial Number: RA4

Channel: UV_VIS_2

Sample Type: unknown

Wavelength: 250

Control Program: AD_H_80min_100-1_flow05

Bandwidth: 4

Quantif. Method: AD_H

Temperature/Column: 10

Recording Time: 24.4.2015 9:50

Flow m/min: 0,500

Run Time (min): 80,00

Sample Amount: 1,000

---

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.33</td>
<td>n.a.</td>
<td>70,872</td>
<td>21,150</td>
<td>82.94</td>
<td>n.a.</td>
<td>BM*</td>
</tr>
<tr>
<td>2</td>
<td>16.30</td>
<td>n.a.</td>
<td>12,818</td>
<td>4,351</td>
<td>17.06</td>
<td>n.a.</td>
<td>MB*</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>83,690</td>
<td>25,501</td>
<td>100,00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

---

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
### 60 TIF-292-02

<table>
<thead>
<tr>
<th>Sample Name:</th>
<th>TIF-292-02</th>
<th>Injection Volume:</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vial Number:</td>
<td>RD1</td>
<td>Channel:</td>
<td>UV_VIS_1</td>
</tr>
<tr>
<td>Sample Type:</td>
<td>unknown</td>
<td>Wavelength:</td>
<td>220</td>
</tr>
<tr>
<td>Control Program:</td>
<td>AD_H_80min_100-1_flow1</td>
<td>Bandwidth:</td>
<td>4</td>
</tr>
<tr>
<td>Quantification Method:</td>
<td>AD_H</td>
<td>Temperature/Column:</td>
<td>10</td>
</tr>
<tr>
<td>Recording Time:</td>
<td>17.4.2015 16:29</td>
<td>Flow ml/min:</td>
<td>1,000</td>
</tr>
<tr>
<td>Run Time (min):</td>
<td>32.16</td>
<td>Sample Amount:</td>
<td>1,000</td>
</tr>
</tbody>
</table>

![Graph](image)

**16f (rac.)**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17.78</td>
<td>n.a.</td>
<td>125,380</td>
<td>57,801</td>
<td>49.97</td>
<td>n.a.</td>
<td>BMB</td>
</tr>
<tr>
<td>2</td>
<td>20.95</td>
<td>n.a.</td>
<td>104,763</td>
<td>57,872</td>
<td>50.03</td>
<td>n.a.</td>
<td>BMB</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>230,144</td>
<td>115,673</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

(No further information available from the image.)
58 TIF-294-02

Sample Name: TIF-294-02
Val Number: RD3
Sample Type: unknown
Control Program: AD_H_80min_100-1_flow1
Quantif. Method: AD_H
Recording Time: 17.4.2015 15:23
Run Time (min): 30.09
Injection Volume: 5.0
Channel: UV_VIS_2
Wavelength: 250
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 1,000
Sample Amount: 1,000

No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type
--- | ------------- | ---------- | ------------ | -------------- | ----------- | ------ | ---
1   | 17.68        | n.a.      | 359,414      | 165,197        | 90.92       | n.a.   | BM *
2   | 20.92        | n.a.      | 30,151       | 16,500         | 9.08        | n.a.   | MB*
Total: |              |            | 389,565      | 181,697        | 100.00      | 0.000

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
**Sample Name:** TIF-298-02  
**Injection Volume:** 5.0 μL  
**Vial Number:** RD4  
**Channel:** UV_VIS_2  
**Sample Type:** unknown  
**Wavelength:** 250 nm  
**Control Program:** AD_H_100min_95-5_flow05  
**Bandwidth:** 4  
**Quantif. Method:** AD_H  
**Temperature/Column:** 10 °C  
**Recording Time:** 23.4.2015 12:24  
**Flow ml/min:** 0.500  
**Run Time (min):** 58.76  
**Sample Amount:** 1,0000

**Peak Summary**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height</th>
<th>Area</th>
<th>Rel.Area</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>35.18</td>
<td>n.a.</td>
<td>173.671</td>
<td>147.978</td>
<td>50.13%</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>51.18</td>
<td>n.a.</td>
<td>120.671</td>
<td>147.209</td>
<td>49.87%</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>294.342</td>
<td>295.188</td>
<td>100.00%</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

16g (rac.)
64 TIF-299-03

Sample Name: TIF-299-03  Injection Volume: 5.0
Vial Number: RC4  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: 220
Control Program: AD_H_80min_100-1_flow1  Bandwidth: 4
Quantif. Method: AD_H  Temperature/Column: 10
Recording Time: 23.4.2015 16:14  Flow ml/min: 1,000
Run Time (min): 44,07  Sample Amount: 1,000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time min</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>18.60</td>
<td>n.a.</td>
<td>198,293</td>
<td>101,521</td>
<td>65.01</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>26.56</td>
<td>n.a.</td>
<td>72,672</td>
<td>54,653</td>
<td>34.99</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td></td>
<td>Total:</td>
<td></td>
<td>270,965</td>
<td>156,174</td>
<td>100.00</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
**10 TIF-304-03**

<table>
<thead>
<tr>
<th>Sample Name:</th>
<th>TIF-304-03</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vial Number:</td>
<td>RA1</td>
</tr>
<tr>
<td>Sample Type:</td>
<td>unknown</td>
</tr>
<tr>
<td>Control Program:</td>
<td>OD_R_80Min_46_55_flow07</td>
</tr>
<tr>
<td>Quantif. Method:</td>
<td>OD_R</td>
</tr>
<tr>
<td>Recording Time:</td>
<td>4.5.2015 14:35</td>
</tr>
<tr>
<td>Run Time (min):</td>
<td>55.96</td>
</tr>
</tbody>
</table>

**Retention Time Table**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height</th>
<th>Area</th>
<th>Rel.Area</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11.03</td>
<td>n.a.</td>
<td>446,048</td>
<td>185,719</td>
<td>49.83</td>
<td>n.a.</td>
<td>BM</td>
</tr>
<tr>
<td>2</td>
<td>12.51</td>
<td>n.a.</td>
<td>291,605</td>
<td>186,975</td>
<td>50.17</td>
<td>n.a.</td>
<td>MB</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>737,653</td>
<td>372,694</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

**Diagram**

Ph\[N\]CO₂Bu
Ph
CONMe₂
16h (rac.)

**UV_VIS_2**

WAX_20151501_TIF_ODR #10 [modified by Admin]
11 TIF-305-03

Sample Name: TIF-305-03
Vial Number: RA2
Sample Type: unknown
Control Program: OD_R_80Min_45_55_flow07
Quantif. Method: OD_R
Recording Time: 4.5.2015 15:32
Run Time (min): 41,41
Injection Volume: 10,0
Channel: UV_VIS_2
Wavelength: 250
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 0,700
Sample Amount: 1,0000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time min</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>11,09</td>
<td>n.a.</td>
<td>108,191</td>
<td>45,189</td>
<td>88,27</td>
<td>n.a.</td>
<td>M*</td>
</tr>
<tr>
<td>2</td>
<td>12,90</td>
<td>n.a.</td>
<td>11,641</td>
<td>6,006</td>
<td>11,73</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>119,832</td>
<td>51,195</td>
<td>100,00</td>
<td>0,000</td>
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</tr>
</tbody>
</table>

WAS_20151501_TIF_ODR #11 [modified by Admin]
59 TIF-297-02

Sample Name: TIF-297-02
Injection Volume: 5.0
Vial Number: RE1
Channel: UV_VIS_2
Sample Type: unknown
Wavelength: 250
Control Program: AD_H_80min_100-1_flow1
Bandwidth: 4
Quantif. Method: AD_H
Temperature/Column: 10
Recording Time: 17.4.2015 15:55
Flow m/min: 1,000
Run Time (min): 32.46
Sample Amount: 1,000

---

Ph
\[\text{N} \quad \text{CO}_2\text{fBu} \quad \text{COMe}\]
\(16\text{i (rac.)}\)

---

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.89</td>
<td>n.a.</td>
<td>209,925</td>
<td>77,705</td>
<td>50.19</td>
<td>n.a</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>17.01</td>
<td>n.a.</td>
<td>181,888</td>
<td>77,104</td>
<td>49.81</td>
<td>n.a</td>
<td>BMB*</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>391,813</td>
<td>154,810</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

---

default/Integration
Sample Name: TIF-296-02
Vial Number: RE3
Sample Type: unknown
Control Program: AD_H_80min_100-1_flow1
Quantif. Method: AD_H
Recording Time: 17.4.2015 14:27
Run Time (min): 25,43
Injection Volume: 5.0
Channel: UV_VIS_1
Wavelength: 220
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 1,000
Sample Amount: 1,000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.76</td>
<td>n.a.</td>
<td>352,084</td>
<td>131,976</td>
<td>92.35</td>
<td>n.a.</td>
<td>BM *</td>
</tr>
<tr>
<td>2</td>
<td>16.95</td>
<td>n.a.</td>
<td>26,215</td>
<td>19,937</td>
<td>7.65</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total:</td>
<td></td>
<td></td>
<td>378,298</td>
<td>142,913</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
### 8 TIF-342-02

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Injection Volume</th>
<th>Vial Number</th>
<th>Channel</th>
<th>Sample Type</th>
<th>Wavelength</th>
<th>Quantif. Method</th>
<th>Temperature/Column</th>
<th>Recording Time</th>
<th>Flow ml/min</th>
<th>Sample Amount</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIF-342-02</td>
<td>10.0</td>
<td>RC1</td>
<td>UV_VIS_1</td>
<td>unknown</td>
<td>220</td>
<td>AD_H</td>
<td>10</td>
<td>5.6.2015 15:28</td>
<td>1,000</td>
<td>1,0000</td>
</tr>
<tr>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### Chromatogram

![Chromatogram Image]

#### Table

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>14.24</td>
<td>n.a.</td>
<td>266,031</td>
<td>105,264</td>
<td>46.89</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>16.37</td>
<td>n.a.</td>
<td>13,653</td>
<td>6,488</td>
<td>2.69</td>
<td>n.a.</td>
<td>MB*</td>
</tr>
<tr>
<td>3</td>
<td>17.73</td>
<td>n.a.</td>
<td>197,516</td>
<td>106,457</td>
<td>47.42</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>4</td>
<td>33.89</td>
<td>n.a.</td>
<td>6,733</td>
<td>6,266</td>
<td>2.79</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>483,933</td>
<td>224,476</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

*Chromleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
9 TIF-344-02

Sample Name: TIF-344-02
Val Number: RC2
Sample Type: unknown
Control Program: AD_H_120min_98-2_flow1
Quantif. Method: AD_H
Recording Time: 5.6.2015 16:18
Run Time (min): 93.74
Injection Volume: 10.0
Channel: UV_VIS_1
Wavelength: 220
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 1,000
Sample Amount: 1,000

No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type
--- | ------------ | ---------- | ---------- | ------------ | ---------- | ------ | ----
1   | 14.29        | n.a.      | 46,331     | 16,941       | 4.81       | n.a.   | BMB* 
2   | 16.21        | n.a.      | 30,448     | 12,778       | 3.63       | n.a.   | BMB* 
3   | 17.58        | n.a.      | 568,620    | 319,457      | 90.78      | n.a.   | BMB* 
4   | 34.37        | n.a.      | 3,117      | 2,733        | 0.78       | n.a.   | BMB* 
Total: | | | 649,516 | 351,909 | 100.00 | 0.000 |

Chromleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
11 TIF-346-02

Sample Name: TIF-346-02
Vial Number: RE1
Sample Type: unknown
Control Program: AD_H_120min_98-2_flow1
Quantif Method: AD_H
Recording Time: 19.6.2015 15:46
Run Time (min): 120.00

Injection Volume: 20.0
Channel: UV_VIS_2
Wavelength: 250
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 1.000
Sample Amount: 1.0000

---

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height</th>
<th>Area</th>
<th>Rel.Area</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>15.18</td>
<td>n.a.</td>
<td>7.382</td>
<td>2.847</td>
<td>0.79</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>2</td>
<td>16.68</td>
<td>n.a.</td>
<td>659.226</td>
<td>310.585</td>
<td>86.45</td>
<td>n.a.</td>
<td>BM*</td>
</tr>
<tr>
<td>3</td>
<td>19.05</td>
<td>n.a.</td>
<td>9.560</td>
<td>5.668</td>
<td>1.58</td>
<td>n.a.</td>
<td>BMB*</td>
</tr>
<tr>
<td>4</td>
<td>39.36</td>
<td>n.a.</td>
<td>36.445</td>
<td>40.176</td>
<td>11.18</td>
<td>n.a.</td>
<td>BM*</td>
</tr>
</tbody>
</table>

Total: 712.612 359.277 100.00 0.000

---

default/Integration

Chromeleon (c) Dionex 1996-2006
Version 8.80 SR12 Build 3578 (207199)
### 82 TIF-310-03

| Sample Name: | TIF-310-03 | Injection Volume: | 5.0 |
| Vial Number: | RE1 | Channel: | UV_VIS_2 |
| Sample Type: | unknown | Wavelength: | 250 |
| Control Program: | AD_H_60min_98-2_flow05 | Bandwidth: | 4 |
| Quantif. Method: | AD_H | Temperature/Column: | 10 |
| Recording Time: | 29.5.2015 10:34 | Flow mL/min: | 0.500 |
| Run Time (min): | 60.00 | Sample Amount: | 1,0000 |

![Graph](image)  
16k (rac.)

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.51</td>
<td>n.a.</td>
<td>344,715</td>
<td>193,815</td>
<td>42.86</td>
<td>n.a.</td>
<td>BM*</td>
</tr>
<tr>
<td>2</td>
<td>28.18</td>
<td>n.a.</td>
<td>51,680</td>
<td>31,015</td>
<td>6.88</td>
<td>n.a.</td>
<td>MB*</td>
</tr>
<tr>
<td>3</td>
<td>32.21</td>
<td>n.a.</td>
<td>45,356</td>
<td>32,167</td>
<td>7.11</td>
<td>n.a.</td>
<td>BM*</td>
</tr>
<tr>
<td>4</td>
<td>44.50</td>
<td>n.a.</td>
<td>195,224</td>
<td>195,238</td>
<td>43.17</td>
<td>n.a.</td>
<td>BM*</td>
</tr>
<tr>
<td>Total:</td>
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<td></td>
<td>639,955</td>
<td>452,235</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

*Chromeleon (c) Dionex 1998-2006  
Version 6.80 SR12 Build 3578 (207169)*
84 TIF-327-02

Sample Name: TIF-327-02  Injection Volume: 20.0
Vial Number: RB1  Channel: UV_VIS_2
Sample Type: unknown  Wavelength: 250
Control Program: AD_H_60min_96-2_flow05  Bandwidth: 4
Quantif. Method: AD_H  Temperature/Column: 10
Recording Time: 29.5.2015 13:02  Flow ml/min: 0.500
Run Time (min): 58.30  Sample Amount: 1.0000

---

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>26.50</td>
<td>n.a.</td>
<td>192,499</td>
<td>108,767</td>
<td>86.09</td>
<td>n.a.</td>
<td>M*</td>
</tr>
<tr>
<td>2</td>
<td>44.76</td>
<td>n.a.</td>
<td>17,948</td>
<td>17,574</td>
<td>13.91</td>
<td>n.a.</td>
<td>MB*</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>210,447</td>
<td>126,341</td>
<td>100.00</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

default/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
7 TIF-340-02

Sample Name: TIF-340-02
Vial Number: RE1
Sample Type: unknown
Control Program: AD_H_40Min_100_3,5_flow1
Quantif. Method: AD_H
Recording Time: 5.6.2015 14:16
Run Time (min): 28.88

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

---

**WAS_20150306_TIF_95-5-05 #7 [modified by Admin]**

![Graph of chromatogram](image)

- **Ph**
- **CO₂tBu**
- **16l (rac.)**

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height (mAU)</th>
<th>Area (mAU*min)</th>
<th>Rel.Area (%)</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.10</td>
<td>n.a.</td>
<td>405,634</td>
<td>92,964</td>
<td>43.59</td>
<td>n.a.</td>
<td>BM</td>
</tr>
<tr>
<td>2</td>
<td>7.71</td>
<td>n.a.</td>
<td>87,262</td>
<td>14,964</td>
<td>7.02</td>
<td>n.a.</td>
<td>M</td>
</tr>
<tr>
<td>3</td>
<td>8.22</td>
<td>n.a.</td>
<td>57,090</td>
<td>14,864</td>
<td>6.97</td>
<td>n.a.</td>
<td>M</td>
</tr>
<tr>
<td>4</td>
<td>10.04</td>
<td>n.a.</td>
<td>230,618</td>
<td>90,464</td>
<td>42.42</td>
<td>n.a.</td>
<td>BM</td>
</tr>
<tr>
<td>Total</td>
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<td>213,256</td>
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</tr>
</tbody>
</table>

---

*BM* stands for baseline material.
## TIF-341-02

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>TIF-341-02</th>
<th>Injection Volume</th>
<th>20.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vial Number</td>
<td>RA2</td>
<td>Channel</td>
<td>UV_VIS_1</td>
</tr>
<tr>
<td>Sample Type</td>
<td>unknown</td>
<td>Wavelength</td>
<td>220</td>
</tr>
<tr>
<td>Control Program</td>
<td>AD_H_40Min_100_3,5_flow1</td>
<td>Bandwidth</td>
<td>4</td>
</tr>
<tr>
<td>Quantif. Method</td>
<td>AD_H</td>
<td>Temperature/Column</td>
<td>10</td>
</tr>
<tr>
<td>Recording Time</td>
<td>5.6.2015 13:40</td>
<td>Flow m/min</td>
<td>1,000</td>
</tr>
<tr>
<td>Run Time (min)</td>
<td>14,12</td>
<td>Sample Amount</td>
<td>1,000</td>
</tr>
</tbody>
</table>

### Chromatogram:

![Chromatogram](image)

### Table:

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time min</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU*min</th>
<th>Rel.Area %</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.08</td>
<td>n.a.</td>
<td>1887,742</td>
<td>471,113</td>
<td>76.17</td>
<td>n.a.</td>
<td>BM</td>
</tr>
<tr>
<td>2</td>
<td>7.71</td>
<td>n.a.</td>
<td>208,414</td>
<td>51,107</td>
<td>8.26</td>
<td>n.a.</td>
<td>M</td>
</tr>
<tr>
<td>3</td>
<td>8.21</td>
<td>n.a.</td>
<td>253,420</td>
<td>71,146</td>
<td>11.60</td>
<td>n.a.</td>
<td>M</td>
</tr>
<tr>
<td>4</td>
<td>10.05</td>
<td>n.a.</td>
<td>63,082</td>
<td>25,111</td>
<td>4.66</td>
<td>n.a.</td>
<td>BM</td>
</tr>
</tbody>
</table>

**Total:**

2412,658 mAU, 618,477 mAU*min, 100.00 %, 0.000
79 TIF-317-02

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>TIF-317-02</th>
<th>Injection Volume</th>
<th>5.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vial Number</td>
<td>RD2</td>
<td>Channel</td>
<td>UV_VIS_2</td>
</tr>
<tr>
<td>Sample Type</td>
<td>unknown</td>
<td>Wavelength</td>
<td>250</td>
</tr>
<tr>
<td>Control Program</td>
<td>AD_H_60min_95-5_flow1</td>
<td>Bandwidth</td>
<td>4</td>
</tr>
<tr>
<td>Quantif. Method</td>
<td>AD_H</td>
<td>Temperature/Column</td>
<td>10</td>
</tr>
<tr>
<td>Recording Time</td>
<td>15.5.2015 15:46</td>
<td>Flow ml/min</td>
<td>1000</td>
</tr>
<tr>
<td>Run Time (min):</td>
<td>30.00</td>
<td>Sample Amount</td>
<td>10000</td>
</tr>
</tbody>
</table>

![Graph](attachment:image)

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time</th>
<th>Peak Name</th>
<th>Height</th>
<th>Area</th>
<th>Rel.Area</th>
<th>Amount</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.09</td>
<td>n.a.</td>
<td>211,544</td>
<td>80,628</td>
<td>50.21</td>
<td>n.a.</td>
<td>BM*</td>
</tr>
<tr>
<td>2</td>
<td>16.59</td>
<td>n.a.</td>
<td>148,099</td>
<td>79,839</td>
<td>49.79</td>
<td>n.a.</td>
<td>BM*</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>359,642</td>
<td>160,467</td>
<td>100.00</td>
<td>0.000</td>
<td></td>
</tr>
</tbody>
</table>

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
80 TIF-316-02

Sample Name: TIF-316-02  Injection Volume: 5.0
Vial Number: RD3  Channel: UV_VIS_2
Sample Type: unknown  Wavelength: 250
Control Program: AD_H_60min_95-5_flow1  Bandwidth: 4
Quantif. Method: AD_H  Temperature/Column: 10
Recording Time: 15.5.2015 16:16  Flow ml/min: 1,000
Run Time (min): 24.59  Sample Amount: 1,000

<table>
<thead>
<tr>
<th>No.</th>
<th>Ret.Time (min)</th>
<th>Peak Name</th>
<th>Height mAU</th>
<th>Area mAU’min</th>
<th>Rel.Area %</th>
<th>Amount n.a.</th>
<th>Type BM *</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.09</td>
<td>n.a.</td>
<td>435,656</td>
<td>168,067</td>
<td>92.69</td>
<td>n.a.</td>
<td>BM *</td>
</tr>
<tr>
<td>2</td>
<td>16.61</td>
<td>n.a.</td>
<td>25,038</td>
<td>13,260</td>
<td>7.31</td>
<td>n.a.</td>
<td>BM *</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td>460,693</td>
<td>181,326</td>
<td>100.00</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>

default/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
HPLC trace of the racemic mixture of diastereomers

![HPLC trace of the racemic mixture of diastereomers](image1)

<table>
<thead>
<tr>
<th>RT (min)</th>
<th>Area (V sec)</th>
<th>% Area</th>
<th>Height (V)</th>
<th>% Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.197</td>
<td>11092420</td>
<td>24.41</td>
<td>162742</td>
</tr>
<tr>
<td>2</td>
<td>25.496</td>
<td>11540725</td>
<td>25.40</td>
<td>177423</td>
</tr>
<tr>
<td>3</td>
<td>34.944</td>
<td>11546820</td>
<td>25.42</td>
<td>132294</td>
</tr>
<tr>
<td>4</td>
<td>45.920</td>
<td>11254379</td>
<td>24.77</td>
<td>104026</td>
</tr>
</tbody>
</table>

HPLC trace of enantioenriched major diastereomer

![HPLC trace of enantioenriched major diastereomer](image2)

<table>
<thead>
<tr>
<th>RT (min)</th>
<th>Area (V sec)</th>
<th>% Area</th>
<th>Height (V)</th>
<th>% Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.349</td>
<td>2846528</td>
<td>4.54</td>
<td>38554</td>
</tr>
<tr>
<td>2</td>
<td>34.385</td>
<td>59793862</td>
<td>95.48</td>
<td>632962</td>
</tr>
</tbody>
</table>

HPLC trace of enantioenriched mixture of diastereomers

![HPLC trace of enantioenriched mixture of diastereomers](image3)

<table>
<thead>
<tr>
<th>RT (min)</th>
<th>Area (V sec)</th>
<th>% Area</th>
<th>Height (V)</th>
<th>% Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>24.247</td>
<td>2081918</td>
<td>6.40</td>
<td>26038</td>
</tr>
<tr>
<td>2</td>
<td>25.685</td>
<td>1517109</td>
<td>4.56</td>
<td>22001</td>
</tr>
<tr>
<td>3</td>
<td>34.283</td>
<td>23134264</td>
<td>71.05</td>
<td>241268</td>
</tr>
<tr>
<td>4</td>
<td>48.623</td>
<td>5822709</td>
<td>17.89</td>
<td>40000</td>
</tr>
</tbody>
</table>
HPLC trace of rac- major diastereomer

HPLC trace of enantioenriched major diastereomer

### Table 1: Rac-mixture

<table>
<thead>
<tr>
<th>RT (min)</th>
<th>Area (V*sec)</th>
<th>% Area</th>
<th>Height (V)</th>
<th>% Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.451</td>
<td>2310447</td>
<td>48.16</td>
<td>41894</td>
</tr>
<tr>
<td>2</td>
<td>35.671</td>
<td>2496237</td>
<td>51.84</td>
<td>35427</td>
</tr>
</tbody>
</table>

### Table 2: Enantioenriched mixture

<table>
<thead>
<tr>
<th>RT (min)</th>
<th>Area (V*sec)</th>
<th>% Area</th>
<th>Height (V)</th>
<th>% Height</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>27.156</td>
<td>7852923</td>
<td>8.93</td>
<td>139689</td>
</tr>
<tr>
<td>2</td>
<td>35.095</td>
<td>80047741</td>
<td>91.07</td>
<td>1011375</td>
</tr>
</tbody>
</table>
HPLC trace of rac- major diastereomer