Asymmetric Synthesis of 2,3-Dihydrobenzofurans by a [4+1] Annulation Between Ammonium Ylides and In Situ Generated o-Quinone Methides

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Asymmetric synthesis of 2,3-dihydrobenzofurans via a (4+1) annulation between ammonium ylides and in situ generated ortho-quinone methides

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1. General Information:

1.1. General Methods

$^1$H- and $^{13}$C-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 and on a Bruker Avance III 700 MHz spectrometer with an Ascend magnet and TCI cryoprobe, which are both 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 an Agilent 6520 Q-TOF mass spectrometer with an ESI source and an Agilent G1607A coaxial sprayer or 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.

IR spectra were recorded on a Bruker Tensor 27 FT-IR spectrometer with ATR unit.

Preparative column chromatography was carried out using Davisil LC 60A 70-200 MICRON silica gel. TLC probes were detected at 254 nm or stained with with an appropriate staining solution (compare section 3.1.3).

HPLC was performed using a Dionex Summit HPLC system consisting of a Dionex P-680 pump, an ASI-100 HPLC-autosampler, a STH-585 column oven and a PDA-100 detector or a Thermo Scientific Dionex Ultimate 3000 system with diode array detector with a Chiralcel OD-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-Kα radiation ($\lambda = 0.71073$ Å).

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. All reactions were carried out under Argon.

1.2. Computational Methods

Geometry optimization has been performed using the Jaguar 8.5 pseudospectral program package using the well-established B3LYP hybrid density functional with the D3 dispersion correction and the standard split valence polarized 6-31G* basis as implemented in Jaguar. All the optimization calculations include an implicit description of dichloromethane solvent using the Poisson–Boltzmann polarizable continuum method as incorporated in Jaguar, and parameters for dichloromethane.

Electronic energies were obtained by single point calculations at the B3LYP-D3/6-311+G**(dichloromethane) level of theory.
The correct nature of each stationary point as minima (zero imaginary frequencies) or transition states (one imaginary frequency) has been checked by performing frequency calculations at the B3LYP/6-31G*(dichloromethane) level of theory.

Thermal and entropic contributions to free energy (at 298.15 K) and zero-point energy have been obtained from these frequency calculations. In Jaguar, the translational partition function is computed for ideal gas standard conditions, corresponding to a pressure of 1 atmosphere at 298.15 K. For solution reactions, the standard condition is instead 1 mol/L. Accordingly, the free energy value computed in Jaguar was corrected by a concentration term, equal to $RT \ln \left( \frac{V_{\text{mol}_{\text{gas}_{\text{1atm}}}}}{V_{\text{mol}_{\text{1M}}}} \right)$, i.e. 1.89 kcal/mol at 298.15 K.

For the large reaction systems there are usually several local minima or saddle points corresponding to each intermediate or transition state. This is due to the possibility of multiple conformations of substituents. We have made a systematic attempt to locate all possible local minima and saddle points, with the data presented referring to the lowest energy form unless mentioned otherwise. All species have been fully geometry optimized, and the Cartesian coordinates are supplied in Section 3.
2. Syntheses

2.1 Syntheses of Starting Materials

2.1.1 Synthesis of Quinone Methide Precursors 1

General procedure (in analogy to literature\(^1\)):

1) The arylbromide (ArBr, 2.5 equiv.) is dissolved in THF (0.7 mL per mmol ArBr) and added dropwise to a mixture of Mg turnings (2.5 equiv.) and THF (0.35 mL per mmol Mg). After formation of the Grignard reagent has started, the mixture is stirred at room temperature for 30 min and then refluxed for 1 h. After cooling with an ice bath, the aldehyde (1 equiv.), which is solved in THF (1.1 mL per mmol aldehyde), is added dropwise and the solution is stirred at room temperature for 3 h. Afterwards the reaction is quenched with saturated NH\(_4\)Cl and the mixture extracted with DCM and washed with brine. The combined organic phases are dried over Na\(_2\)SO\(_4\), filtered, and evaporated to dryness. The crude product is purified by column chromatography (silica gel, heptane:EtOAc).

2) TolSO\(_2\)Na (1.15 equiv.) and TsOH (1.75 equiv.) are dissolved in DCM (3.4 mL per mmol TolSO\(_2\)Na) and stirred for 5 min. Then the afore synthesised alcohol (part 1) is dissolved in DCM (2.5 mL per mmol) and added to the mixture and then stirred at room temperature for 1.5 h. Afterwards the reaction mixture is extracted with DCM and washed with 1N HCl and brine. The combined organic layers are dried over Na\(_2\)SO\(_4\) and evaporated to dryness. The crude product is separated by column chromatography (silica gel, heptane:EtOAc) to give starting materials 1 in the reported yields.

Compound 1c: Obtained as a light orange powder in 55% over 2 steps (4.5 mmol scale), R\(_f\): 0.43 (heptane:EtOAc = 3:2). Analytical data match those reported in literature\(^1\). \(^1\)H NMR (300 MHz, \(\delta\), CDCl\(_3\), 298 K): 2.36 (s, 3H), 5.83 (s, 1H), 6.55 (s, 1H), 6.95 – 6.87 (m, 2H), 7.23 – 7.12 (m, 3H), 7.33 – 7.29 (m, 3H), 7.57 – 7.52 (m, 5H) ppm.

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1) Mu-Wang, C.; Liang-Liang, C.; Zhi-Shi, Y.; Guo-Fang, J.; Yong-Gui Z.; Chem. Commun., 2013, 49, 1660
Compound 1g: Obtained as a light yellow powder in 58% over 2 steps (4.5 mmol scale), Rf: 0.28 (heptane:EtOAc = 2:1). Analytical data match those reported previously\(^1\). \(^1\)H NMR (300 MHz, δ, CDCl\(_3\), 298 K): 2.37 (s, 3H), 3.78 (s, 3H), 5.76 (s, 1H), 6.94 – 6.80 (m, 4H), 7.23 – 7.16 (m, 3H), 7.57 – 7.43 (m, 5H) ppm.

Compound 1h: Obtained as a light yellow powder in 43% over two steps (4.5 mmol scale), Rf: 0.48 (heptane:EtOAc = 2:1). Analytical data match those reported previously\(^1\). \(^1\)H NMR (300 MHz, δ, CDCl\(_3\), 298 K): 2.38 (s, 3H), 5.92 (s, 1H), 6.07 (s, 1H), 6.84 – 6.81 (m, 1H), 6.98 – 6.92 (m, 1H), 7.24 – 7.17 (m, 3H), 7.62 – 7.55 (m, 5H), 7.71 – 7.68 (m, 2H) ppm.

Compound 1i: Obtained as a dark purple powder in 80% over 2 steps (4.5 mmol scale), Rf: 0.44 (heptane:EtOAc = 2.5:2). \(^1\)H NMR (300 MHz, δ, CDCl\(_3\), 298 K): 2.3 (s, 3H), 6.92 – 6.82 (m, 3H), 7.20 – 7.10 (m, 3H), 7.40 – 7.37 (m, 2H), 7.57 – 7.52 (m, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.87 – 7.74 (m, 3H), 8.47 (d, J = 7.5 Hz, 1H) ppm. \(^{13}\)C NMR (75 MHz, δ, CDCl\(_3\), 298 K): 21.6, 31.2, 34.6, 70.6, 118.0, 120.3, 121.4, 122.5, 125.1, 125.7, 126.8, 127.2, 128.9, 129.1, 129.3, 129.5, 130.1, 131.1, 131.7, 133.9, 135.6, 144.6, 154.2 ppm. HRMS (ESI): m/z calculated for C\(_{24}\)H\(_{20}\)O\(_3\)S: 411.1025 [M+Na]\(^+\); found: 411.1027.

Compound 1j: Obtained as an orange powder in 53% over 2 steps (4.5 mmol scale), Rf: 0.45 (heptane:EtOAc = 2:1). \(^1\)H NMR (300 MHz, δ, CDCl\(_3\), 298 K): 1.28 (s, 9H), 2.36 (s, 3H), 5.78 (s, 1H), 6.59 (s, 2H), 6.93 – 6.86 (m, 2H), 7.22 – 7.13 (m, 3H), 7.34 – 7.31 (m, 2H), 7.55 – 7.45 (m, 5H) ppm. \(^{13}\)C NMR (75 MHz, δ, CDCl\(_3\), 298 K): 21.6, 31.2, 34.6, 70.6, 118.0, 120.3, 121.4, 125.6, 128.9, 129.0, 129.2, 130.0, 130.1, 131.1, 135.0, 144.6, 151.8, 154.3 ppm. HRMS (ESI): m/z calculated for C\(_{24}\)H\(_{26}\)O\(_3\)S: 417.1495 [M+Na]\(^+\); found: 417.1495.

Compound 1p: Obtained as a white powder in 31% over 2 steps (4.5 mmol scale), Rf: 0.19 (heptane:EtOAc = 2.5:1). \(^1\)H NMR (300 MHz, δ, CDCl\(_3\), 298 K): 2.37 (s, 3H), 5.75 (s, 1H), 6.80 (d, J = 8.6 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.34 – 7.28 (m, 4H), 7.50 – 7.47 (m, 2H), 7.56 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 2.4 Hz, 1H) ppm. \(^{13}\)C NMR (75 MHz, δ, CDCl\(_3\), 298 K): 21.7, 70.2, 113.5, 119.8, 122.2, 128.8, 128.9, 129.5, 130.2, 131.7, 133.1, 133.4, 134.5, 145.1, 153.7 ppm. HRMS (ESI): m/z calculated for C\(_{20}\)H\(_{17}\)BrO\(_3\): 438.9979 [M+Na]\(^+\); found: 438.9972.
Compound **1q**: Obtained as a white powder in 64% over 2 steps (4.5 mmol scale), \( R_f \) 0.35 (heptane:EtOAc = 2:1). \(^1\)H NMR (300 MHz, \( \delta \), CDCl\(_3\), 298 K): 1.18 (s, 9H), 2.33 (s, 3H), 5.75 (s, 1H), 6.48 (s, 2H), 6.80 (d, \( J = 8.4 \) Hz, 1H), 7.20 – 7.11 (m, 3H), 7.32 – 7.28 (m, 3H), 7.37 – 7.36 (m, 1H), 7.58 – 7.51 (m, 4H) ppm. \(^{13}\)C NMR (75 MHz, \( \delta \), CDCl\(_3\), 298 K): 21.6, 31.3, 34.1, 71.7, 117.8, 119.2, 127.1, 128.2, 128.6, 128.7, 128.9, 129.3, 130.3, 132.0, 134.9, 144.1, 144.6, 152.1 ppm. HRMS (ESI): \( m/z \) calculated for C\(_{24}\)H\(_{26}\)O\(_3\)S: 417.1495 [M+Na]\(^+\); found: 417.1495.

[Image of Compound 1q]

Compound **1r**: Obtained as a light yellow powder in 63% over 2 steps (4.5 mmol scale), \( R_f \) 0.50 (heptane:EtOAc = 3:2). \(^1\)H NMR (300 MHz, \( \delta \), CDCl\(_3\), 298 K): 2.27 (s, 3H), 2.36 (s, 3H), 5.85 (s, 1H), 6.83 (t, \( J = 7.7 \) Hz, 1H), 7.18 – 7.10 (m, 3H), 7.35 – 7.28 (m, 4H), 7.57 – 7.50 (m, 4H) ppm. \(^{13}\)C NMR (75 MHz, \( \delta \), CDCl\(_3\), 298 K): 16.4, 21.6, 30.9, 70.0, 110.8, 121.0, 123.8, 127.2, 128.6, 128.9, 129.3, 130.3, 131.5, 132.4, 134.9, 144.7, 152.8 ppm. HRMS (ESI): \( m/z \) calculated for C\(_{21}\)H\(_{20}\)O\(_3\)S: 375.1025 [M+Na]\(^+\); found: 375.1023.

[Image of Compound 1r]

Compound **1s**: Obtained as a yellow powder in 76% over 2 steps (4.5 mmol scale), \( R_f \) 0.29 (heptane:EtOAc = 2.5:1). \(^1\)H NMR (300 MHz, \( \delta \), CDCl\(_3\), 298 K): 2.24 (s, 3H), 6.55 (s, 1H), 7.05 (d, \( J = 8.1 \) Hz, 2H), 7.28 – 7.20 (m, 2H), 7.39 – 7.32 (m, 4H), 7.74 – 7.63 (m, 7H), 8.89 (s, 1H) ppm. \(^{13}\)C NMR (75 MHz, \( \delta \), CDCl\(_3\), 298 K): 21.5, 30.9, 70.0, 110.8, 121.0, 123.8, 127.2, 128.6, 128.9, 129.3, 129.4, 129.8, 130.9, 131.7, 133.0, 134.2, 145.2, 154.6 ppm. HRMS (ESI): \( m/z \) calculated for C\(_{24}\)H\(_{20}\)O\(_3\)S: 411.1025 [M+Na]\(^+\); found: 411.1025.

[Image of Compound 1s]

Compound **1t**: Obtained as a white powder in 50% over 2 steps (3.2 mmol scale), \( R_f \) 0.39 (heptane:EtOAc = 2.5:1). \(^1\)H NMR (300 MHz, \( \delta \), CDCl\(_3\), 298 K): 2.40 (s, 3H), 6.45 (s, 1H), 6.81 (dd, \( J = 1.4 \) Hz, \( J = 7.9 \) Hz, 1H), 6.93 (dd, \( J = 1.2 \) Hz, \( J = 8.4 \) Hz, 1H), 7.10 (t, \( J = 8.0 \) Hz, 1H), 7.22 (d, \( J = 8.1 \) Hz, 2H), 7.36 (t, \( J = 3.2 \) Hz, 3H), 7.67 – 7.59 (m, 4H), 8.73 (s, 1H) ppm. \(^{13}\)C NMR (75 MHz, \( \delta \), CDCl\(_3\), 298 K): 21.7, 71.7, 118.4, 119.0, 122.0, 128.7, 128.8, 129.0, 129.6, 129.9, 130.0, 130.9, 133.9, 135.8, 145.6, 157.1 ppm. HRMS (ESI): \( m/z \) calculated for C\(_{20}\)H\(_17\)ClO\(_3\)S: 395.0479 [M+Na]\(^+\); found: 395.0481.
2.1.2 Syntheses of Ammonium Salts 6

General procedure for achiral ammonium salts (in analogy to literature\(^2\)):

To a solution of bromoacetophenone derivative (1 equiv.) in THF (3.3 mL per mmol starting material) trimethylamine (33% in EtOH – 1 equiv.) is added and the mixture is stirred overnight. The product is filtered off and washed twice with EtOAc and dried under vacuo.

Achiral ammonium salt 6c: Isolated as a white powder in 88% (15 mmol scale), \(^1\)H NMR (700 MHz, \(\delta\), CDCl\(_3\), 298 K): 3.70 (s, 9H), 5.95 (s, 2H), 7.51 (t, \(J = 7.8\) Hz, 2H), 7.64 (t, \(J = 7.4\) Hz, 1H), 8.12 (d, \(J = 7.5\) Hz, 2H) ppm. \(^{13}\)C NMR (176 MHz, \(\delta\), CDCl\(_3\), 298 K): 55.0, 68.4, 128.7, 129.5, 134.3, 135.3, 191.3 ppm. HRMS (ESI): \(^{m/z}\) calculated for C\(_{11}\)H\(_{16}\)NO: 178.1226 [M]\(^+\); found: 178.1225.

Achiral ammonium salt 6d: Obtained as a white powder in 97% (0.5 mmol scale), \(^1\)H NMR (300 MHz, \(\delta\), DMSO, 298 K): 2.52 (s, 3H), 3.40 (s, 9H), 5.35 (s, 2H), 7.54 (d, \(J = 7.9\) Hz, 2H), 7.99 (d, \(J = 7.9\) Hz, 2H) ppm. \(^{13}\)C NMR (75 MHz, \(\delta\), DMSO, 298 K): 21.3, 53.4, 67.0, 128.0, 129.6, 131.8, 145.5, 190.8 ppm. HRMS (ESI): \(^{m/z}\) calculated for C\(_{12}\)H\(_{18}\)NO: 192.1383 [M]\(^+\); found: 192.1381.

Achiral ammonium salt 6e: Isolated as a white powder in 69% (3 mmol scale), \(^1\)H NMR (300 MHz, \(\delta\), CDCl\(_3\), 298 K): 3.68 (s, 9H), 3.84 (s, 3H), 5.82 (s, 2H), 6.93 (d, \(J = 8.9\) Hz, 2H), 8.10 (d, \(J = 8.9\) Hz, 2H) ppm. \(^{13}\)C NMR (75 MHz, \(\delta\), DMSO, 298 K): 53.4, 55.8, 66.8, 114.3, 127.2, 130.5, 164.3, 189.6 ppm. HRMS (ESI): \(^{m/z}\) calculated for C\(_{12}\)H\(_{16}\)NO\(_2\): 208.1332 [M]\(^+\); found: 208.1333.

Achiral ammonium salt 6f: Obtained as a white powder in 99% (3 mmol scale), \(^1\)H NMR (300 MHz, \(\delta\), DMSO, 298 K): 3.44 (s, 9H), 5.44 (s, 2H), 7.84 (d, \(J = 7.9\) Hz, 2H), 8.13 (d, \(J = 8.2\) Hz, 2H) ppm. \(^{13}\)C NMR (75 MHz, \(\delta\), DMSO, 298 K): 53.5, 67.2, 129.2, 129.9, 133.1, 139.6, 190.4 ppm. HRMS (ESI): \(^{m/z}\) calculated for C\(_{11}\)H\(_{15}\)ClNO: 212.0837 [M]\(^+\); found: 212.0835.

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2) Herchl, R.; Stiftinger, M.; Waser, M.; *Org. Biomol. Chem.*, 2011, 9, 7023.
General procedure for chiral ammonium salts:

To a solution of bromoacetophenone derivative (1 equiv.) in THF (12 mL per mmol starting material) quinidine (A2) is added and the mixture is stirred overnight. After evaporation to dryness the crude product is purified by column chromatography (silica gel, DCM:MeOH).

Chiral ammonium salt 6c-A2: Isolated as a light yellow powder in 89 % (3 mmol scale). Analytical data match to literature. \[^1^H\]NMR (300 MHz, δ, CDCl\(_3\), 298 K): 1.01 – 0.92 (m, 1H), 2.05 – 1.94 (m, 3H), 2.30 (t, J = 12.3 Hz, 1H), 2.90 (q, J = 8.4 Hz, 1H), 4.10 (s, 3H), 4.49 – 4.33 (m, 2H), 4.79 – 4.73 (t, J = 9.5 Hz, 1H), 4.99 (t, J = 10.4 Hz, 1H), 5.36 – 5.27 (m, 2H), 5.68 – 5.61 (d, J = 18.9 Hz, 1H), 6.01 – 5.89 (m, 2H), 6.34 (d, J = 5.9 Hz, 1H), 6.725 (d, J = 18.8 Hz, 1H), 7.07 (d, J = 2.6 Hz, 1H), 7.38 – 7.34 (m, 1H), 7.49 (t, J = 7.5 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.80 (d, J = 4.5 Hz, 1H), 8.00 (d, J = 9.3 Hz, 1H), 8.35 (d, J = 8.0 Hz, 2H), 8.75 (d, J = 4.6 Hz, 1H) ppm.

Chiral ammonium salt 6d-A2: Obtained as a beige powder in 99 % (1 mmol scale), R\(_f\): 0.40 (DCM:MeOH = 10:1). \[^1^H\]NMR (300 MHz, δ, CDCl\(_3\), 298 K): 0.98 – 0.93 (m, 1H), 2.05 – 1.96 (m, 3H), 2.32 – 2.28 (m, 1H), 2.38 (s, 3H), 2.88 (q, J = 8.3 Hz, 1H), 3.66 (q, J = 10.7 Hz, 1H), 4.09 (s, 3H), 4.25 (t, J = 11.2 Hz, 1H), 4.53 (t, J = 10.4 Hz, 1H), 4.76 (t, J = 9.6 Hz, 1H), 5.06 (t, J = 10.1 Hz, 1H), 5.46 – 5.28 (m, 3H), 6.02 – 5.91 (m, 2H), 6.37 (d, J = 5.8 Hz, 1H), 6.83 (d, J = 18.9 Hz, 1H), 7.05 (d, J = 2.6 Hz, 1H), 7.28 (d, J = 8.2 Hz, 2H), 7.36 (d, J = 2.6 Hz, J = 7.3 Hz, 1H), 7.82 (d, J = 4.5 Hz, 1H), 8.00 (d, J = 9.2 Hz, 1H), 8.26 (d, J = 8.1 Hz, 2H), 8.76 (d, J = 4.6 Hz, 1H) ppm. \[^1^C\]NMR (75 MHz, δ, MeOD, 298 K): 21.8, 22.1, 24.5, 28.5, 39.3, 57.2, 58.6, 63.3, 64.7, 68.2, 101.8, 118.1, 121.4, 124.2, 127.4, 129.8, 131.1, 131.7, 133.0, 137.0, 144.8, 145.5, 148.1, 148.5, 160.4, 194.1 ppm. HRMS (ESI): m/z calculated for C\(_{29}\)H\(_{33}\)N\(_2\)O\(_3\): 457.2486 [M]+; found: 457.2480.

3) Jian, L.; Yunbo, Q.; Tingting, L.; Yongmei, W.; Bioorg. Med. Chem. Lett., 2007, 17, 4102.
Chiral ammonium salt 6e-A2: Obtained as a light yellow powder in 99% (1 mmol scale). Analytical data match those reported before.\(^3\) \(\text{H} NMR (300 MHz, \delta, \text{CDCl}_3, 298 K): 0.98 – 0.89 (m, 1H), 2.02 – 1.91 (m, 3H), 2.27 (t, \(J = 12.1\) Hz, 1H), 2.90 (q, \(J = 8.4\) Hz, 1H), 3.80 (s, 3H), 4.10 (s, 3H), 4.51 – 4.44 (m, 2H), 4.74 (t, \(J = 9.4\) Hz, 1H), 4.95 (t, \(J = 10.4\) Hz, 1H), 5.35 – 5.26 (m, 2H), 5.70 (d, \(J = 18.3\) Hz, 1H), 6.00 – 5.88 (m, 2H), 6.34 (d, \(J = 5.9\) Hz, 1H), 6.59 (d, \(J = 18.3\) Hz, 1H), 6.90 (d, \(J = 9.0\) Hz, 2H), 7.09 (d, \(J = 2.6\) Hz, 1H), 7.35 (dd, \(J = 2.6\) Hz, \(J = 9.3\) Hz, 1H), 7.79 (d, \(J = 4.7\) Hz, 1H), 7.98 (d, \(J = 9.2\) Hz, 1H), 8.33 (d, \(J = 8.9\) Hz, 2H), 8.72 (d, \(J = 4.6\) Hz, 1H) ppm.

Chiral ammonium salt 6f-A2: Isolated as a light pink powder in quantitative yield (1 mmol scale), \(R_F: 0.30\) (DCM:MeOH = 10:1). Analytical data match those reported in literature.\(^3\) \(\text{H} NMR (300 MHz, \delta, \text{CDCl}_3, 298 K): 0.99 – 0.91 (m, 2H), 2.03 – 1.93 (m, 3H), 2.28 (t, \(J = 11.7\) Hz, 1H), 2.87 (q, \(J = 8.6\) Hz, 1H), 3.47 (d, \(J = 5.1\) Hz, 1H), 3.79 – 3.75 (m, 1H), 4.08 (s, 3H), 4.48 – 4.40 (m, 2H), 4.72 (t, \(J = 9.4\) Hz, 1H), 4.95 (t, \(J = 9.8\) Hz, 1H), 5.33 – 5.27 (m, 2H), 6.00 – 5.82 (m, 3H), 6.22 (d, \(J = 6.1\) Hz, 1H), 6.70 (d, \(J = 18.9\) Hz, 1H), 7.03 (d, \(J = 2.6\) Hz, 1H), 7.36 (dd, \(J = 2.6\) Hz, \(J = 9.2\) Hz, 1H), 7.48 (d, \(J = 8.6\) Hz, 2H), 7.79 (d, \(J = 4.7\) Hz, 1H) 8.00 (d, \(J = 9.2\) Hz, 1H), 8.35 (d, \(J = 8.6\) Hz, 2H), 8.74 (d, \(J = 4.6\) Hz, 1H) ppm.
2.2 (Asymmetric) (4+1) Cyclization Reaction

General procedure: Compound 1 (1 equiv.), ammonium salt 6 (1.2 equiv.) and Cs$_2$CO$_3$ (2.5 equiv.) are dissolved in DCM (15 mL per mmol 1). The reaction mixture is either stirred overnight (for achiral salts 6) or for 3 days (when using chiral salts 6) and afterwards extracted with DCM and brine. The combined organic phases are dried over Na$_2$SO$_4$, filtered and evaporated to dryness. The crude products are purified by column chromatography (silica gel, heptane:EtOAc first to obtain products 5 and DCM/MeOH then to recover the chiral amine A2).

Product 5c: Isolated as a white residue in the reported yields (1 mmol). [$\alpha$]$^2_0^0$ = -8.8 (c = 0.2, DCM, e.r. = 99:1), R$_\ell$: 0.53 (heptane:EtOAc = 5:1). $^1$H NMR (700 MHz, $\delta$, CDCl$_3$, 298 K): 4.99 (d, $J$ = 6.5 Hz, 1H), 5.82 (d, $J$ = 6.4 Hz, 1H), 6.90 (t, $J$ = 7.5 Hz, 1H), 7.01 – 6.98 (m, 2H), 7.24 – 7.20 (m, 3H), 7.30 – 7.28 (m, 1H), 7.35 – 7.33 (m, 2H), 7.46 (t, $J$ = 7.7 Hz, 2H), 7.60 (t, $J$ = 7.3 Hz, 1H), 7.96 (d, $J$ = 7.6 Hz, 2H) ppm. $^{13}$C NMR (176 MHz, $\delta$, CDCl$_3$, 298 K): 51.0, 90.7, 110.1, 121.8, 125.5, 127.6, 128.3, 128.8, 129.0, 129.1, 129.5, 133.9, 134.6, 142.4, 159.2, 194.8 ppm. HRMS (ESI): m/z calculated for C$_{21}$H$_{16}$O$_2$: 323.1043 [M+Na]$^+$; found: 323.1040.

The enantioselectivity is determined by HPLC (YMC Cellulose-SB, eluent: hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: $t_{\text{major}}$ (2R, 3R) = 15.7 min, $t_{\text{minor}}$ (2S, 3S) = 17.0 min).

Product 5d: Obtained as a yellow residue (0.1 mmol scale). [$\alpha$]$^2_0^0$ = -19.5 (c = 1.0, DCM, e.r. = 98.5:1.5), R$_\ell$: 0.35 (heptane:EtOAc = 10:1). $^1$H NMR (700 MHz, $\delta$, CDCl$_3$, 298 K): 4.97 (d, $J$ = 6.3 Hz, 1H), 5.81 (d, $J$ = 6.3 Hz, 1H), 6.89 (t, $J$ = 7.4 Hz, 1H), 7.01 – 6.98 (m, 2H), 7.30 – 7.20 (m, 6H), 7.34 (t, $J$ = 7.4 Hz, 2H), 7.86 (d, $J$ = 8.0 Hz, 2H) ppm. $^{13}$C NMR (176 MHz, $\delta$, CDCl$_3$, 298 K): 21.9, 51.1, 90.6, 110.1, 121.7, 125.5, 127.5, 128.3, 129.0, 129.1, 129.5, 132.0, 142.5, 145.0, 159.2, 194.4 ppm. HRMS (ESI): m/z calculated for C$_{22}$H$_{18}$O$_2$: 337.1199 [M+Na]$^+$; found: 337.1197. The enantioselectivity is determined by HPLC (Chiralcel OD-H, eluent: hexane:i-PrOH = 95:5, 0.8 mL/min, 10 °C, retention times: $t_{\text{major}}$ (2R, 3R) = 12.6 min, $t_{\text{minor}}$ (2S, 3S) = 10.8 min).
Product 5e: Obtained as a beige residue (0.1 mmol scale). $[\alpha]_{D}^{20} = -15.0$ (c = 0.5, DCM, e.r. = 97:3), Rf: 0.27 (heptane:EtOAc = 10:1). $^1$H NMR (700 MHz, δ, CDCl$_3$, 298 K): 3.87 (s, 3H), 4.99 (d, $J = 6.6$ Hz, 1H), 5.77 (d, $J = 6.6$ Hz, 1H), 6.80 (t, $J = 7.5$ Hz, 1H), 6.92 (d, $J = 8.7$ Hz, 2H), 7.01 – 6.97 (m, 2H), 7.02 (t, $J = 7.8$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 2H), 7.29 – 7.27 (m, 1H), 7.35 – 7.33 (m, 2H), 7.94 (d, $J = 8.9$ Hz, 2H) ppm. $^{13}$C NMR (176 MHz, δ, CDCl$_3$, 298 K): 51.1, 55.7, 90.7, 110.1, 114.1, 121.7, 125.5, 127.6, 128.4, 129.0, 129.2, 129.6, 131.9, 142.5, 159.3, 164.2, 193.3 ppm. HRMS (ESI): m/z calculated for C$_{22}$H$_{18}$O$_3$: 353.1148 [M+Na]$^+$; found: 353.1145. The enantiomeric purity is determined by HPLC (Chiralcel OD-H, eluent: hexane:i-ProOH = 100:1, 0.5 mL/min, 10 °C, retention times: $t_{major}$ (2R, 3R) = 41.5 min, $t_{minor}$ (2S, 3S) = 39.6 min).

Product 5f: Isolated as a white residue (0.1 mmol scale). $[\alpha]_{D}^{20} = -15$ (c = 0.5, DCM, e.r. = 99:1), Rf: 0.47 (heptane:EtOAc = 10:1). $^1$H NMR (300 MHz, δ, CDCl$_3$, 298 K): 4.99 (d, $J = 6.6$ Hz, 1H), 5.72 (d, $J = 6.6$ Hz, 1H), 7.00 – 6.85 (m, 3H), 7.23 – 7.16 (m, 3H), 7.35 – 7.26 (m, 3H), 7.42 – 7.39 (m, 2H), 8.18 (d, $J = 7.8$ Hz, 2H) ppm. $^{13}$C NMR (75 MHz, δ, CDCl$_3$, 298 K): 50.7, 90.7, 110.0, 121.8, 125.4, 127.6, 128.2, 129.0, 129.1, 129.2, 130.8, 132.9, 140.4, 142.1, 158.9, 193.6 ppm. HRMS (ESI): m/z calculated for C$_{23}$H$_{16}$ClO$_2$: 357.0653 [M+Na]$^+$; found: 357.0650. The enantiomeric purity is determined by HPLC (YMC Cellulose-SB, eluent: hexane:i-ProOH = 95:5, 0.5 mL/min, 10 °C, retention times: $t_{major}$ (2R, 3R) = 17.1 min, $t_{minor}$ (2S, 3S) = 15.8 min).

Product 5g: Isolated as a white residue (0.1 mmol scale). $[\alpha]_{D}^{20} = -16.5$ (c = 0.5, DCM, e.r. = 90:10), Rf: 0.48 (heptane:EtOAc = 5:1). $^1$H NMR (700 MHz, δ, CDCl$_3$, 298 K): 3.78 (s, 3H), 4.90 (d, $J = 6.2$ Hz, 1H), 5.76 (d, $J = 6.5$ Hz, 1H), 6.88 – 6.84 (m, 3H), 6.97 (t, $J = 7.8$ Hz, 2H), 7.13 (d, $J = 8.6$ Hz, 2H), 7.19 (t, $J = 7.8$ Hz, 1H), 7.44 (t, $J = 7.8$ Hz, 2H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.92 (d, $J = 7.7$ Hz, 2H) ppm. $^{13}$C NMR (176 MHz, δ, CDCl$_3$, 298 K): 50.5, 55.5, 90.9, 110.1, 114.5, 121.7, 125.4, 128.8, 129.0, 129.3, 129.4, 129.6, 133.9, 134.5, 134.6, 159.1, 195.0 ppm. HRMS (ESI): m/z calculated for C$_{22}$H$_{16}$O$_3$: 353.1148 [M+Na]$^+$; found: 353.1147. The enantiomeric purity is determined by HPLC (YMC Cellulose-SB, eluent: hexane:i-ProOH = 95:5, 0.5 mL/min, 10 °C, retention times: $t_{major}$ (2R, 3R) = 21.7 min, $t_{minor}$ (2S, 3S) = 24.7 min).

Product 5h: Obtained as a light yellow residue (0.1 mmol scale). $[\alpha]_{D}^{20} = -12.7$ (c = 0.8, DCM, e.r. = 98:2), Rf: 0.56 (heptane:EtOAc = 5:1). $^1$H NMR (300 MHz, δ, CDCl$_3$, 298 K): 5.12 (d, $J = 6.7$ Hz, 1H), 5.74 (d, $J = 6.5$ Hz, 1H), 7.00 –6.88 (m, 3H), 7.24 – 7.19 (m, 1H), 7.35 (d, $J = 8.1$ Hz, 2H), 7.46 (t, $J = 7.6$ Hz, 2H), 7.62 – 7.57 (m, 3H), 7.98 – 7.95 (m, 2H) ppm. $^{13}$C NMR (75 MHz, δ, CDCl$_3$, 298 K): 50.3, 90.3, 110.2, 121.9, 125.3, 126.0, 128.5, 128.6, 128.9, 129.3, 134.0, 134.4, 146.2, 159.0, 194.3 ppm. $^{19}$F NMR (282 MHz, δ, CDCl$_3$, 298 K): -62.5 ppm. HRMS (ESI): m/z calculated for C$_{22}$H$_{16}$F$_3$O$_2$: 391.0916 [M+Na]$^+$; found: 391.0919. The enantiomeric purity is determined by HPLC (YMC Cellulose-SB, eluent: hexane:i-ProOH = 95:5, 0.5 mL/min, 10 °C, retention times: $t_{major}$ (2R, 3R) = 21.7 min, $t_{minor}$ (2S, 3S) = 24.7 min).
PrOH = 250:1, 0.5 mL/min, 10 °C, retention times: 

\[ t_{\text{major}} \ (2R, 3R) = 49.8 \ \text{min}, \ t_{\text{minor}} \ (2S, 3S) = 56.9 \ \text{min}. \]

**Product 5i:** Obtained as a yellow residue (0.1 mmol scale), \([\alpha]_D^{20} = -15.9 \ \text{(c = 0.7, DCM, e.r. = 93:7)}, \ R\ell: 0.40 \ (\text{heptane:EtOAc = 5:1}). \)  
1H NMR (300 MHz, \( \delta \), CDCl\(_3\), 298 K): 6.05 – 5.86 (m, 2H), 6.99 – 6.89 (m, 2H), 7.12 – 7.07 (m, 1H), 7.23 – 7.20 (m, 1H), 7.59 – 7.38 (m, 7H), 7.80 (d, \( J = 8.2 \ \text{Hz}, \ 1H), 7.91 – 7.88 (m, 1H), 7.98 (d, \( J = 7.6 \ \text{Hz}, \ 2H), 8.12 \ (s, 1H) \ \text{ppm.} \) 13C NMR (75 MHz, \( \delta \), CDCl\(_3\), 298 K): 44.3, 90.0, 110.1, 121.8, 123.2, 125.7, 125.9, 126.6, 128.1, 128.6, 129.3, 129.9, 131.4, 133.8, 134.7, 159.0, 194.9 ppm. HRMS (ESI): \( m/z \) calculated for C\(_{25}\)H\(_{18}\)O\(_2\): 373.1199 \([\text{M+Na}^+]; \) found: 373.1198. The enantioselectivity is determined by HPLC (Chiralcel OD-H, eluent: hexane:i-PrOH:MeOH = 100:3:1, 0.8 mL/min, 10 °C, retention times: 

\[ t_{\text{major}} \ (2R, 3R) = 13.4 \ \text{min}, \ t_{\text{minor}} \ (2S, 3S) = 12.3 \ \text{min}. \]

**Product 5j:** Obtained as a light yellow residue (0.1 mmol scale), \([\alpha]_D^{20} = -12.7 \ \text{(c = 0.8, DCM, e.r. = 97:3)}, \ R\ell: 0.57 \ (\text{heptane:EtOAc = 10:1}). \)  
1H NMR (300 MHz, \( \delta \), CDCl\(_3\), 298 K): 1.32 (s, 9H), 4.98 (d, \( J = 6.4 \ \text{Hz}, \ 1H), 5.81 (d, \( J = 6.4 \ \text{Hz}, \ 1H), 6.93 – 6.87 (m, 1H), 7.05 – 6.97 (m, 2H), 7.24 – 7.14 (m, 3H), 7.37 – 7.34 (m, 2H), 7.49 – 7.44 (m, 2H), 7.63 – 7.57 (m, 1H), 7.98 – 7.95 (m, 2H) \ \text{ppm.} \) 13C NMR (75 MHz, \( \delta \), CDCl\(_3\), 298 K): 31.4, 34.6, 50.4, 90.7, 110.0, 121.6, 125.4, 125.9, 127.8, 128.7, 128.8, 129.4, 133.8, 134.5, 139.1, 150.4, 159.1, 194.8 ppm. HRMS (ESI): \( m/z \) calculated for C\(_{25}\)H\(_{24}\)O\(_2\): 379.1669 \([\text{M+Na}^+]; \) found: 379.1667. The enantioselectivity is determined by HPLC (YMC Cellulose-SB, eluent: hexane:i-PrOH = 99:1, 0.5 mL/min, 10 °C, retention times: 

\[ t_{\text{major}} \ (2R, 3R) = 20.8 \ \text{min}, \ t_{\text{minor}} \ (2S, 3S) = 24.0 \ \text{min}. \]

**Product 5k:** Obtained as a brown residue (0.1 mmol scale), \([\alpha]_D^{20} = -18.3 \ \text{(c = 0.6, DCM, e.r. = 93:7)}, \ R\ell: 0.45 \ (\text{heptane:EtOAc = 5:1}). \)  
1H NMR (300 MHz, \( \delta \), CDCl\(_3\), 298 K): 3.75 (s, 3H), 5.98 – 5.74 (m, 2H), 6.90 – 6.77 (m, 4H), 6.99 (m, 1H), 7.17 – 7.11 (m, 2H), 7.32 (t, \( J = 7.6 \ \text{Hz}, \ 1H), 7.41 – 7.39 (m, 2H), 7.70 (d, \( J = 8.5 \ \text{Hz}, \ 1H), 7.82 – 7.79 (m, 1H), 7.90 – 7.87 (m, 2H), 8.05 (s, 1H) \ \text{ppm.} \) 13C NMR (75 MHz, \( \delta \), CDCl\(_3\), 298 K): 44.4, 55.5, 90.0, 110.0, 113.9, 121.7, 113.4, 125.7, 125.9, 126.6, 127.6, 128.0, 128.9, 129.0, 131.5, 131.9, 134.1, 159.0, 164.0, 193.2 ppm. HRMS (ESI): \( m/z \) calculated for C\(_{26}\)H\(_{20}\)O\(_3\): 403.1305 \([\text{M+Na}^+]; \) found: 403.1301. The enantioselectivity is determined by HPLC (Chiralcel OD-H, eluent: hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: 

\[ t_{\text{major}} \ (2R, 3R) = 40.4 \ \text{min}, \ t_{\text{minor}} \ (2S, 3S) = 31.9 \ \text{min}. \]
**Product 5i**: Obtained as a light brown residue (0.1 mmol scale). $[\alpha]_D^{20} = -18.3$ (c = 0.8, DCM, e.r. = 93:7), R$e$ 0.64 (heptane:EtOAc = 5:1). $^1$H NMR (700 MHz, $\delta$, CDCl$_3$, 298 K): 2.38 (s, 3H), 6.08 – 5.79 (m, 2H), 6.96 – 6.88 (m, 2H), 7.22 – 7.19 (m, 4H), 7.39 (t, $J$ = 7.7 Hz, 1H), 7.49 – 7.48 (m, 2H), 7.89 – 7.78 (m, 5H), 8.16 (s, 1H) ppm. $^{13}$C NMR (176 MHz, $\delta$, CDCl$_3$, 298 K): 21.9, 44.4, 90.3, 110.1, 121.8, 123.4, 125.8, 126.0, 126.7, 128.0, 129.0, 129.5, 129.8, 131.6, 132.2, 144.9, 159.1, 194.5 ppm. HRMS (ESI): $m/z$ calculated for C$_{23}$H$_{26}$O$_5$: 387.1356 [M+Na]$^+$; found: 387.1355. The enantioselectivity is determined by HPLC (YMC Cellulose-SB, eluent: hexane:i-PrOH = 99:1, 0.5 mL/min, 10 °C, retention times: $t_{major}$ (2R, 3R) = 43.3 min, $t_{minor}$ (2S, 3S) = 32.4 min).

**Product 5m**: Obtained as a yellow residue (0.1 mmol scale). $[\alpha]_D^{20} = -13.2$ (c = 0.9, DCM, e.r. = 94:6), R$e$ 0.52 (heptane:EtOAc = 5:1). $^1$H NMR (300 MHz, $\delta$, CDCl$_3$, 298 K): 5.92 – 5.64 (m, 2H), 6.84 – 6.76 (m, 2H), 6.96 – 6.93 (m, 1H), 7.12 – 7.06 (m, 2H), 7.30 – 7.23 (m, 2H), 7.37 – 7.34 (m, 2H), 7.60 – 7.53 (m, 1H), 7.66 (d, $J$ = 8.3 Hz, 1H), 7.81 – 7.74 (m, 3H), 8.01 (s, 1H) ppm. $^{13}$C NMR (75 MHz, $\delta$, CDCl$_3$, 298 K): 44.2, 90.0, 110.1, 112.5, 121.9, 123.2, 124.1, 125.2, 125.7, 126.7, 128.1, 128.5, 129.0, 130.7, 131.0, 131.4, 133.0, 134.2, 140.3, 158.8, 193.9 ppm. HRMS (ESI): $m/z$ calculated for C$_{23}$H$_{27}$ClO$_5$: 407.0809 [M+Na]$^+$; found: 407.0806. The enantioselectivity is determined by HPLC (YMC Cellulose-SB, eluent: hexane:i-PrOH = 99:1, 0.5 mL/min, 10 °C, retention times: $t_{major}$ (2R, 3R) = 56.0 min, $t_{minor}$ (2S, 3S) = 35.1 min).

**Product 5n**: Isolated as a light yellow residue. $[\alpha]_D^{20} = -21.2$ (c = 0.3, DCM, e.r. = 93:7), R$e$ 0.55 (heptane:EtOAc = 5:1). $^1$H NMR (700 MHz, $\delta$, CDCl$_3$, 298 K): 3.80 (s, 3H), 4.94 (d, $J$ = 6.7 Hz, 1H), 5.70 (d, $J$ = 6.7 Hz, 1H), 6.91 – 6.87 (m, 3H), 6.96 (d, $J$ = 8.1 Hz, 1H), 7.00 (d, $J$ = 7.6 Hz, 1H), 7.15 (d, $J$ = 8.6 Hz, 2H), 7.21 (t, $J$ = 7.7 Hz, 1H), 7.44 (d, $J$ = 8.7 Hz, 2H), 7.90 (d, $J$ = 8.4 Hz, 2H) ppm. $^{13}$C NMR (176 MHz, $\delta$, CDCl$_3$, 298 K): 50.3, 55.5, 91.0, 110.1, 114.5, 121.9, 125.3, 129.0, 129.2, 129.4, 129.5, 130.9, 133.0, 134.2, 140.5, 158.9, 159.1, 194.0 ppm. HRMS (ESI): $m/z$ calculated for C$_{22}$H$_{27}$ClO$_5$: 387.0758 [M+Na]$^+$; found: 387.0756. The enantioselectivity is determined by HPLC (Chiralcel OD-H, eluent: hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: $t_{major}$ (2R, 3R) = 23.4 min, $t_{minor}$ (2S, 3S) = 19.9 min).

**Product 5o**: Isolated as a brown residue (0.1 mmol scale). $[\alpha]_D^{20} = -6.5$ (c = 1.0, DCM, e.r. = 98.5:1.5), R$e$ 0.21 (heptane:EtOAc = 5:1). $^1$H NMR (700 MHz, $\delta$, CDCl$_3$, 298 K): 3.76 (s, 3H), 3.83 (s, 3H), 4.88 (d, $J$ = 6.8 Hz, 1H), 5.69 (d, $J$ = 6.6 Hz, 1H), 6.85 – 6.82 (m, 3H), 6.88 (d, $J$ = 8.5 Hz, 2H), 6.95 – 6.92 (m, 2H), 7.11 (d, $J$ = 8.6 Hz, 2H), 7.15 (t, $J$ = 7.7 Hz, 1H), 7.89 (d, $J$ = 8.7 Hz, 2H) ppm. $^{13}$C NMR (176 MHz, $\delta$, CDCl$_3$, 298 K): 50.6, 55.5, 55.7, 90.8, 110.1, 114.1, 114.5, 121.7, 125.4, 127.6, 128.9, 129.4, 129.8, 131.8, 134.6, 159.1, 159.2, 164.2, 193.5 ppm. HRMS (ESI): $m/z$ calculated for C$_{23}$H$_{26}$O$_4$: 383.1254 [M+Na]$^+$; found: 383.1253. The enantioselectivity is determined by HPLC (YMC
Cellulose-SB, eluent: hexane:i-PrOH = 98:2, 0.5 mL/min, 10 °C, retention times: $t_{\text{major}}$ (2R, 3R) = 67.4 min, $t_{\text{minor}}$ (2S, 3S) = 73.7 min.

**Product 5p:** Obtained as a pale oil (0.1 mmol scale). $[\alpha]_{D}^{20} = -9.9$ (c = 1.0, DCM, e.r. = 99:1), R$_{e}$ 0.54 (heptane:EtOAc = 5:1). $^1$H NMR (300 MHz, δ, CDCl$_3$, 298 K): 4.97 (d, $J$ = 6.4 Hz, 1H), 5.84 (d, $J$ = 6.5 Hz, 1H), 6.86 (d, $J$ = 8.6 Hz, 1H), 7.11 – 7.10 (m, 1H), 7.24 – 7.20 (m, 2H), 7.39 – 7.28 (m, 4H), 7.49 – 7.44 (m, 2H), 7.63 – 7.58 (m, 1H), 7.95 – 7.92 (m, 2H) ppm. $^{13}$C NMR (75 MHz, δ, CDCl$_3$, 298 K): 50.6, 91.0, 111.6, 113.5, 127.8, 128.1, 128.3, 128.8, 129.2, 129.3, 131.8, 134.0, 134.2, 141.4, 158.2, 194.1 ppm. HRMS (ESI): $m/z$ calculated for C$_{21}$H$_{22}$BrO: 401.0148 [M+Na$^+$]; found: 401.0147. The enantioselectivity is determined by HPLC (YMC Cellulose-SB, eluent: hexane:i-PrOH = 98:2, 0.5 mL/min, 10 °C, retention times: $t_{\text{major}}$ (2R, 3R) = 24.4 min, $t_{\text{minor}}$ (2S, 3S) = 26.2 min).

**Product 5q:** Obtained as a light yellow residue (0.1 mmol scale). $[\alpha]_{D}^{20} = -8.4$ (c = 0.8, DCM, e.r. = 99:1), R$_{e}$ 0.52 (heptane:EtOAc = 10:1). $^1$H NMR (700 MHz, δ, CDCl$_3$, 298 K): 1.24 (s, 9H), 4.99 (d, $J$ = 6.3 Hz, 1H), 5.77 (d, $J$ = 6.6 Hz, 1H), 6.90 (d, $J$ = 8.7 Hz, 1H), 7.03 (s, 1H), 7.26 – 7.23 (m, 3H), 7.29 (t, $J$ = 7.4 Hz, 1H), 7.35 (t, $J$ = 7.4 Hz, 2H), 7.45 (t, $J$ = 7.8 Hz, 1H), 7.59 (t, $J$ = 7.4 Hz, 1H), 7.95 (d, $J$ = 7.6 Hz, 2H) ppm. $^{13}$C NMR (176 MHz, δ, CDCl$_3$, 298 K): 31.8, 34.5, 51.2, 91.0, 109.2, 122.3, 125.9, 127.5, 128.4, 128.8, 129.1, 129.5, 133.9, 134.7, 142.5, 144.9, 157.1, 195.0 ppm. HRMS (ESI): $m/z$ calculated for C$_{25}$H$_{24}$O$_2$: 379.1669 [M+Na$^+$]; found: 379.1667. The enantioselectivity is determined by HPLC (YMC Cellulose-SB, eluent: hexane:i-PrOH = 250:1, 0.5 mL/min, 10 °C, retention times: $t_{\text{major}}$ (2R, 3R) = 33.9 min, $t_{\text{minor}}$ (2S, 3S) = 31.2 min).

**Product 5r:** Isolated as an orange residue (0.1 mmol scale). $[\alpha]_{D}^{20} = -12.7$ (c = 0.4, DCM, e.r. = 97:3), R$_{e}$ 0.64 (heptane:EtOAc = 5:1). $^1$H NMR (300 MHz, δ, CDCl$_3$, 298 K): 2.32 (s, 3H), 5.01 (d, $J$ = 6.5 Hz, 1H), 5.79 (d, $J$ = 6.5 Hz, 1H), 6.86 – 6.78 (m, 2H), 7.05 – 7.02 (m, 1H), 7.37 – 7.23 (m, 5H), 7.46 (t, $J$ = 7.5 Hz, 2H), 7.63 – 7.57 (m, 1H), 8.00 – 7.97 (m, 2H) ppm. $^{13}$C NMR (75 MHz, δ, CDCl$_3$, 298 K): 15.3, 51.3, 90.5, 120.2, 121.5, 122.7, 127.4, 128.2, 128.5, 128.6, 129.0, 129.3, 130.1, 133.7, 134.6, 142.4, 157.6, 195.1 ppm. HRMS (ESI): $m/z$ calculated for C$_{22}$H$_{23}$O$_2$: 337.1199 [M+Na$^+$]; found: 337.1195. The enantioselectivity is determined by HPLC (YMC Cellulose-SB, eluent: hexane:i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: $t_{\text{major}}$ (2R, 3R) = 13.9 min, $t_{\text{minor}}$ (2S, 3S) = 17.1 min).
Product 5s: Obtained as a yellow residue (0.1 mmol scale). \([\alpha]_D^{20} = -5.3\) (c = 0.8, DCM, e.r. = 66:34), Rf: 0.47 (heptane:EtOAc = 5:1). \(^1^H\) NMR (300 MHz, δ, CDCl\(_3\), 298 K): 5.29 (d, J = 5.3 Hz, 1H), 5.91 (d, J = 5.4 Hz, 1H), 7.29 – 7.20 (m, 9H), 7.45 (t, J = 7.6 Hz, 2H), 7.59 (t, J = 7.4 Hz, 1H), 7.77 – 7.74 (m, 2H), 7.97 – 7.94 (m, 2H) ppm. \(^1^C\) NMR (75 MHz, δ, CDCl\(_3\), 298 K): 50.7, 91.6, 112.1, 119.9, 122.8, 123.2, 126.9, 127.5, 128.0, 128.8, 128.9, 129.1, 129.4, 130.1, 130.4, 130.6, 133.8, 134.3, 142.4, 157.2, 194.7 ppm. HRMS (ESI): \(m/z\) calculated for C\(_{25}\)H\(_{18}\)O\(_2\): 373.1199 [M+Na]\(^+\); found: 373.1198. The enantioselectivity is determined by HPLC (YMC Cellulose-SB, eluent: hexane/i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: \(t_{\text{major}}\) (2R, 3R) = 27.9 min, \(t_{\text{minor}}\) (2S, 3S) = 25.6 min).

Product 5t: Obtained as a white residue (0.1 mmol scale). \([\alpha]_D^{20} = 2.3\) (c = 0.8, DCM, e.r. = 73:27), Rf: 0.44 (heptane:EtOAc = 5:1). \(^1^H\) NMR (300 MHz, δ, CDCl\(_3\), 298 K): 4.94 (d, J = 4.5 Hz, 1H), 5.89 (d, J = 4.5 Hz, 1H), 6.86 (d, J = 8.1 Hz, 1H), 6.94 (d, J = 8.1 Hz, 1H), 7.17 (t, J = 8.0 Hz, 1H), 7.24 – 7.21 (m, 1H), 7.39 – 7.28 (m, 3H), 7.49 (t, J = 7.5 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.96 – 7.93 (m, 2H) ppm. \(^1^C\) NMR (75 MHz, δ, CDCl\(_3\), 298 K): 50.8, 90.6, 108.6, 122.2, 127.6, 128.0, 128.9, 129.0, 129.3, 130.4, 131.4, 133.8, 134.0, 140.9, 160.3, 194.1 ppm. HRMS (ESI): \(m/z\) calculated for C\(_{25}\)H\(_{15}\)ClO\(_2\): 357.0653 [M+Na]\(^+\); found: 357.0651. The enantioselectivity is determined by HPLC (YMC Cellulose-SB, eluent: hexane/i-PrOH = 95:5, 0.5 mL/min, 10 °C, retention times: \(t_{\text{major}}\) (2R, 3R) = 22.5 min, \(t_{\text{minor}}\) (2S, 3S) = 18.9 min).

Product 5u: Obtained as a white residue (0.1 mmol scale). Rf: 0.44 (heptane:EtOAc = 5:1). \(^1^H\) NMR (300 MHz, δ, CDCl\(_3\), 298 K): 3.69 (s, 3), 4.99 (d, J = 6.5 Hz, 1H), 5.78 (d, J = 6.5 Hz, 1H), 6.57 (d, J = 2.2 Hz, 1H), 6.76 (dd, J = 2.2, 8.7 Hz, 1H), 6.89 (d, J = 8.7 Hz, 1H), 7.22 – 7.28 (m, 2H), 7.29 – 7.39 (m, 3H), 7.41 – 7.50 (m, 2H), 7.55 – 7.63 (m, 1H), 7.92 – 7.99 (m, 2H) ppm. \(^1^C\) NMR (75 MHz, δ, CDCl\(_3\), 298 K): 51.1, 55.9, 90.8, 110.0, 110.8, 114.4, 127.4, 128.1, 128.6, 128.9, 129.3, 130.0, 133.7, 134.4, 141.9, 153.1, 154.9, 194.7 ppm. LRMS (ESI): \(m/z\) calculated for C\(_{22}\)H\(_{13}\)ClO\(_3\): 331.13 [M+H]\(^+\); found: 331.2. The enantioselectivity is determined by HPLC (YMC Cellulose-SB, eluent: hexane/i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: \(t_{\text{major}}\) (2R, 3R) = 34.0 min, \(t_{\text{minor}}\) (2S, 3S) = 45.9 min).

Product 5v: Obtained as a colourless residue (0.1 mmol scale). Rf: 0.49 (heptane:EtOAc = 5:1). \(^1^H\) NMR (300 MHz, δ, CDCl\(_3\), 298 K): 1.50 (d, J = 6.9 Hz, 3H), 3.84 (dq, J = 6.9, 6.9 Hz, 1H), 5.42 (d, J = 6.9 Hz, 1H), 6.86 – 6.97 (m, 2H), 7.12 – 7.22 (m, 2H), 7.45 – 7.56 (m, 2H), 7.58 – 7.66 (m, 1H), 8.01 – 8.07 (m, 2H) ppm. \(^1^C\) NMR (75 MHz, δ, CDCl\(_3\), 298 K): 20.0, 39.8, 90.4, 109.8, 121.2, 123.9, 128.4, 128.6, 129.1, 130.5, 133.6, 134.8, 158.4, 195.9 ppm. HRMS (ESI): \(m/z\) calculated for C\(_{10}\)H\(_{14}\)O\(_2\): 239.11 [M+H]\(^+\); found: 239.1. The enantioselectivity is determined by HPLC (YMC Cellulose-SB, eluent: hexane/i-PrOH = 100:1, 0.5 mL/min, 10 °C, retention times: \(t_{\text{major}}\) (2R, 3R) = 27.1 min, \(t_{\text{minor}}\) (2S, 3S) = 31.6 min).
3. Computational Details, Energies and Geometries

3.1 Conformational study of betaines

For trans pathway, addition occurs via a cisoid approach of reactants. The betaine formed initially is therefore in a cisoid conformation. In order for the second key step to occur, this betaine needs to undergo rotation around the newly formed carbon-carbon bond to give the corresponding transoid conformer (Figure S1). The computed free energy of the transition state for this rotational equilibrium is 6.3 kcal.mol\(^{-1}\), i.e. lower than TS to ring closure. It is thus not relevant for the reactivity and selectivity.

Addition to form cis betaine occurs via a transoid approach. The betaine formed is thus in a conformation allowing cyclization.

**Figure S1.** Computed free energy profile including conformational equilibrium for betaines.
3.2. Addition on the aromatic ring

Addition can potentially not only occur on the methylene position of the electrondeficient o-quinone methide but also onto electrophilic C3 and C5 carbon atoms of the quinone ring. Free energy barrier for these different addition mode are reported in Table S1. These data are in good agreement with the observed exclusive addition onto the methylene group.

| Table S1: Free energy barrier to addition (kcal.mol\(^{-1}\)) |
|-------------------------------------------------------------|
| Addition mode | TS\(_{\text{add-trans}}\) | TS\(_{\text{add-cis}}\) |
| Ph | | |
| O | 13.6 | 11.6 |
| Ph | 30.2 | 26.8 |
| O | 30.5 | 30.6 |

3.3. Benchmark calculations

Free energy of key transition states has been obtained at different levels of theory (Table S2).

| Table S2: Relative free energy (kcal.mol\(^{-1}\)) of key TSs. |
|-------------------------------------------------------------|
| B3LYP-3/6-31G* | B3LYP-D3/6-311+G** | B3LYP-D3/cc-pVTZ | M06-2X-D3/6-311+G** | SCS-MP2/6-31+G** |
| trans addition TS | 20.6 | 13.6 | 14.3 | 14.0 | 13.3 |
| cis addition TS | 9.0 | 11.6 | 12.5 | 12.3 | 11.3 |
| trans elimination TS | 3.1 | 7.9 | 8.8 | 6.4 | 2.5 |
| cis alimation TS | 6.7 | 11.7 | 12.2 | 11.2 | 7.8 |
3.4. Epimerization process

The full computed free energy profile for epimerization of cis-A via a fully intramolecular mechanism is depicted in Figure S2. It should be noted that protonation and/or deprotonation steps may also well occur via a pathway involving an intermolecular process (through cis-C or trans-C for instance).

Figure S2. Some potential pathways for the isomerization of cis-A into trans-A (free energies in kcal.mol\(^{-1}\)).\(^4\)

\(^4\) The free energy of cis-C and trans-C was computed taking 1a as proton source.
3.5. Computational results – Energies and Geometries

o-quinone methide

E(B3LYP-D3/6-31G*(dichloromethane)) = -576.628033
E(B3LYP-D3/6-311+G**(dichloromethane)) = -576.779513
Gtot(B3LYP/6-31G*(dichloromethane)) = -576.473748

Ylide

E(B3LYP-D3/6-31G*(dichloromethane)) = -558.160579
E(B3LYP-D3/6-311+G**(dichloromethane)) = -558.320133
Gtot(B3LYP/6-31G*(dichloromethane)) = -557.955608
$E_{\text{B3LYP-D3/6-31G}^*}\text{(dichloromethane)} = -1134.799245$

$E_{\text{B3LYP-D3/6-311+G}^{**}\text{(dichloromethane)}} = -1134.803474$

$G_{\text{tot}\text{(B3LYP/6-31G}^*\text{(dichloromethane)}} = -1134.415533$
C  -1.428701  0.636788   2.948235
C  -2.241188  1.781684   3.000275
C  -1.654877  3.032130   2.749264
C  -0.290188  3.136636   2.480469
H    1.577043  2.077808   2.252723
H    0.554065 -0.155355   2.664900
H  -1.889243 -0.332063   3.117624
H  -2.258490  3.933962   2.752895
H   0.147916  4.113833   2.291841

C  -2.241188  1.781684   3.000275
C  -1.654877  3.032130   2.749264
C  -0.290188  3.136636   2.480469
H    1.577043  2.077808   2.252723
H    0.554065 -0.155355   2.664900
H  -1.889243 -0.332063   3.117624
H  -2.258490  3.933962   2.752895
H   0.147916  4.113833   2.291841

Cis addition TS

E(B3LYP-D3/6-31G*(dichloromethane)) = -1134.803474
E(B3LYP-D3/6-311+G**(dichloromethane)) = -1135.108222
Gtot(B3LYP/6-31G*(dichloromethane)) = -1134.417990

C  -1.240343  5.182226   5.775009
C  -2.490073  4.689822   5.797970
C  -2.394501  3.247218   6.104897
C  -1.112506  2.667961   6.362216
C   0.035284  3.418044   6.341922
C  -0.039181  4.806778   6.033596
H   1.296324  6.480564   5.547297
O  -3.593422  5.254737   5.543457
H  -1.055348  1.616085   6.621941
H   0.996295  2.962128   6.567188
H   0.878687  5.393905   6.013042
C  -3.606718  2.536989   6.176509
H  -4.462690  3.179294   6.352333
C  -4.429010  2.629503   3.836128
H  -3.980032  3.610867   3.840698
C  -3.818703  1.534310   3.166506
O  -4.434147  0.497094   2.791524
N  -5.929168  2.750732   3.722040
C  -6.350650  4.056157   4.411521
H  -7.434366  4.151990   4.310146
H  -6.070407  4.050633   5.463415
H  -5.842965  4.880424   3.909431
C  -6.615988  1.619798   4.492020
H  -7.697288  1.741480   4.387050
H  -6.273682  0.690041   4.043603
H  -6.330356  1.657515   5.541742
C  -6.391562  2.778466   2.327035
Facetoid Trans-A

E(B3LYP-D3/6-31G*(dichloromethane)) = -1134.819257

E(B3LYP-D3/6-311+G**(dichloromethane)) = -1135.120907

Gtott(B3LYP/6-31G*(dichloromethane)) = -1134.432203
Transoid trans-A

E(B3LYP-D3/6-31G*(dichloromethane)) = -1134.826741
E(B3LYP-D3/6-311+G**(dichloromethane)) = -1135.133223
Gtot(B3LYP/6-31G*(dichloromethane)) = -1134.438629
TS rotation trans-A

E(B3LYP-D3/6-31G*(dichloromethane)) = -1134.815779
E(B3LYP-D3/6-311+G**(dichloromethane)) = -1135.120329
Gtot(B3LYP/6-31G*(dichloromethane)) = -1134.426275
Cis-A

$E_{\text{B3LYP-D3/6-31G}}(\text{dichloromethane}) = -1134.832488$

$E_{\text{B3LYP-D3/6-311+G**(dichloromethane)}} = -1135.137778$

$G_{\text{tot(B3LYP/6-31G*(dichloromethane))}} = -1134.444481$

$C - 1.073518 \quad 5.243341 \quad 6.104739$
$C - 2.334507 \quad 4.595269 \quad 5.916676$
$C - 2.370680 \quad 3.187780 \quad 6.256442$
$C - 1.230303 \quad 2.542454 \quad 6.738786$
$C - 0.015879 \quad 3.211681 \quad 6.904746$
$C \quad 0.047909 \quad 4.572714 \quad 6.578650$
TS proton transfer in cis-A

\[
E(\text{B3LYP-D3/6-31G* (dichloromethane)}) = -1134.81879
\]
\[
E(\text{B3LYP-D3/6-311+G** (dichloromethane)}) = -1135.120907
\]
\[
G_{\text{tot}}(\text{B3LYP/6-31G* (dichloromethane)}) = -1134.434101
\]
B (from cis-A)

\[ E(\text{B3LYP-D3/6-31G*(dichloromethane)}) = -1134.82399 \]
E(B3LYP-D3/6-311+G**(dichloromethane)) = -1135.128090 
Gtot(B3LYP/6-31G*(dichloromethane)) = -1134.435462 

C  -7.394214  0.731241  5.653845 
C  -6.114562  1.226726  5.369071 
C  -5.137429  1.347790  6.385599 
C  -5.491861  0.877501  7.661115 
C  -6.760009  0.374384  7.950686 
C  -7.722130  0.312127  6.939826 
H  -8.111692  0.670041  4.838832 
H  -4.748152  0.896706  8.452055 
H  -6.988755  0.029059  8.956532 
H  -8.717817  -0.074706  7.147106 
C  -3.682111  1.760414  6.090599 
H  -3.191911  0.796145  5.913432 
C  -3.378939  2.467006  4.745222 
C  -2.339509  1.966728  3.908434 
O  -1.645462  2.641028  3.092387 
C  -1.350544  -2.248823  4.008974 
C  -0.354624  -1.268786  4.072353 
C  -0.698675  0.082882  4.030709 
C  -2.042998  0.478150  3.955021 
C  -3.033742  -0.512765  3.873906 
C  -2.689682  -1.866441  3.898348 
H  -1.083755  -3.303231  4.040169 
H  0.690836  -1.559452  4.152798 
H  0.072793  0.848312  4.062487 
H  -4.078162  -0.227650  3.788945 
H  -3.469949  -2.621972  3.833161 
N  -3.638095  3.976877  4.617396 
C  -2.431742  4.791304  5.043170 
H  -2.650766  5.853406  4.901654 
H  -2.234531  4.581632  6.092992 
H  -1.592425  4.482625  4.422942 
C  -3.983002  4.324751  3.179455 
H  -4.144701  5.403945  3.116461 
H  -3.156093  4.017908  2.545964 
H  -4.897979  3.793769  2.912976 
C  -4.822159  4.419483  5.436385 
H  -4.987632  5.483221  5.249705 
H  -5.695673  3.847673  5.130445 
H  -4.614666  4.267348  6.489417 
C  -1.284710  3.388191  9.360718 
C  -0.719268  2.597106  8.355368 
C  -1.519230  2.089108  7.333052 
C  -2.898435  2.351491  7.282643 
C  -3.452342  3.135218  8.304674 
C  -2.654346  3.653146  9.330386 
H  -0.664861  3.784193  10.162240 
H  0.344813  2.369866  8.371823 
H  -1.069948  1.476287  6.554565 
H  -4.521622  3.325189  8.327909 
H  -3.112228  4.256004  10.112042 
O  -5.871116  1.570914  4.065378 
H  -4.900182  1.845441  4.028661
TS rotation B

\[
E(\text{B3LYP-D3/6-31G*(dichloromethane)}) = -1134.79831
\]
\[
E(\text{B3LYP-D3/6-311+G**(dichloromethane)}) = -1135.1064475
\]
\[
G_{\text{tot}}(\text{B3LYP/6-31G*(dichloromethane)}) = -1134.409009
\]

| Atom | X (Å) | Y (Å) | Z (Å) |
|------|-------|-------|-------|
| C    | -6.694940 | -0.332999 | 7.364158 |
| C    | -5.606614 | 0.098260  | 6.597271 |
| C    | -5.374171 | 1.470038  | 6.379591 |
| C    | -6.288342 | 2.375760  | 6.934568 |
| C    | -7.371233 | 1.956715  | 7.704360 |
| C    | -7.570134 | 0.591068  | 7.929814 |
| H    | -6.837002 | -1.402688 | 7.499459 |
| H    | -6.150070 | 3.434567  | 6.733656 |
| H    | -8.058095 | 2.690769  | 8.119446 |
| H    | -8.410499 | 0.244857  | 8.527728 |
| C    | -4.080226 | 1.952088  | 5.686840 |
| H    | -3.676390 | 1.104630  | 5.116638 |
| C    | -3.318404 | 3.123477  | 4.704707 |
| C    | -5.479029 | 3.219629  | 3.925729 |
| O    | -5.908806 | 4.251256  | 3.295529 |
| C    | -7.825972 | -0.362933 | 3.312622 |
| C    | -6.456149 | -0.371174 | 3.040943 |
| C    | -5.698937 | 0.784664  | 3.247606 |
| C    | -6.295564 | 1.958099  | 3.730558 |
| C    | -7.679369 | 1.970037  | 3.946437 |
| C    | -8.436720 | 0.815278  | 3.756926 |
| H    | -8.417254 | -1.265552 | 3.172769 |
| H    | -5.977355 | -1.276437 | 2.672702 |
| H    | -4.632358 | 0.782509  | 3.033010 |
| H    | -8.149161 | 2.885314  | 4.296798 |
| H    | -9.505259 | 0.828520  | 3.962172 |
| N    | -3.303558 | 4.250893  | 4.488842 |
| C    | -3.093302 | 4.458377  | 2.995019 |
| H    | -2.419304 | 5.307168  | 2.853971 |
| H    | -2.645339 | 3.545153  | 2.600082 |
| H    | -4.059735 | 4.648556  | 2.537069 |
| C    | -3.814901 | 5.537660  | 5.100238 |
| H    | -3.104148 | 6.346573  | 4.902003 |
| H    | -4.783345 | 5.743395  | 4.646111 |
| H    | -3.915402 | 5.380095  | 6.174656 |
| C    | -1.916271 | 3.992843  | 5.022467 |
| H    | -1.257290 | 4.760938  | 4.611802 |
| H    | -1.909037 | 4.050899  | 6.104910 |
| H    | -1.585098 | 3.007043  | 4.694644 |
| C    | -1.316426 | 2.226853  | 9.049540 |
| C    | -1.118237 | 1.291663  | 8.033364 |
| C    | -2.000510 | 1.234948  | 6.950046 |
| C    | -3.093050 | 2.105409  | 6.859372 |
| C    | -3.295185 | 3.024708  | 7.901391 |
| C    | -2.412249 | 3.094063  | 8.978012 |
| H    | -0.633160 | 2.275541  | 9.894550 |
| H    | -0.278424 | 0.601316  | 8.080919 |
\[\begin{align*}
\text{H} & \quad -1.833764 \quad 0.501807 \quad 6.162722 \\
\text{H} & \quad -4.154544 \quad 3.687503 \quad 7.877657 \\
\text{H} & \quad -2.586639 \quad 3.817899 \quad 9.770751 \\
\text{O} & \quad -4.785433 \quad -0.898177 \quad 6.109435 \\
\text{H} & \quad -4.361817 \quad -0.607723 \quad 5.283879 \\
\text{B } (\text{from } \text{trans}-\text{A}) \\
\text{E}(\text{B3LYP}-\text{D3}/6-31\text{G}*(\text{dichloromethane})) & \quad = -1134.821801 \\
\text{E}(\text{B3LYP}-\text{D3}/6-31\text{1}+\text{G}**(\text{dichloromethane})) & \quad = -1135.12720 \\
\text{G}_{\text{tot}}(\text{B3LYP}/6-31\text{G}*(\text{dichloromethane})) & \quad = -1134.434253 \\
\end{align*}\]
TS proton transfer in trans-A

\[ E(\text{B3LYP-D3/6-31G*(dichloromethane)}) = -1134.818765 \]
\[ E(\text{B3LYP-D3/6-31+G**(dichloromethane)}) = -1135.120876 \]
\[ G_{\text{tot}}(\text{B3LYP/6-31G*(dichloromethane)}) = -1134.434053 \]
Trans elimination TS

E(B3LYP-D3/6-31G*(dichloromethane)) = -1134.813656
E(B3LYP-D3/6-311+G**(dichloromethane)) = -1135.113974
Gtot(B3LYP/6-31G*(dichloromethane)) = -1134.427576
| Atom | X     | Y     | Z    |
|------|-------|-------|------|
| H    | -5.712705 | 0.996857 | 7.536081 |
| C    | -6.707927  | 3.529907  | 7.621469  |
| H    | -7.739969  | 3.439143  | 7.259361  |
| H    | -6.624721  | 3.028506  | 8.586851  |
| H    | -6.457672  | 4.585451  | 7.739145  |
| C    | -5.981430  | 3.531110  | 5.316154  |
| H    | -7.015857  | 3.374229  | 4.983626  |
| H    | -5.791502  | 4.605876  | 5.388306  |
| H    | -5.294205  | 3.092034  | 4.594425  |
| C    | -2.259738  | 3.201694  | 2.305438  |
| C    | -2.778104  | 1.953910  | 2.656273  |
| C    | -3.050921  | 1.658823  | 3.996139  |
| C    | -2.812513  | 2.606915  | 4.998049  |
| C    | -2.277937  | 3.853715  | 4.638091  |
| C    | -2.007294  | 4.149789  | 3.301119  |
| H    | -2.046177  | 3.433080  | 1.264208  |
| H    | -2.969964  | 1.206502  | 1.889210  |
| H    | -3.447485  | 0.679710  | 4.261600  |
| H    | -2.054991  | 4.577709  | 5.417928  |
| H    | -1.590708  | 5.119999  | 3.039983  |

**Cis elimination TS**

E(B3LYP-D3/6-31G*(dichloromethane)) = -1134.805131  
E(B3LYP-D3/6-311+G**(dichloromethane)) = -1135.104716  
Gtot(B3LYP/6-31G*(dichloromethane)) = -1134.421755  

| Atom | X     | Y     | Z    |
|------|-------|-------|------|
| C    | -0.517448 | 4.414857 | 6.374076 |
| C    | -1.861888 | 4.054087 | 6.121868 |
| C    | -2.270711 | 2.741527 | 6.463174 |
| C    | -1.392748 | 1.828333 | 7.033806 |
| C    | -0.065165 | 2.199243 | 7.287571 |
| C    | 0.357580  | 3.491199 | 6.949606 |
| H    | -0.186810 | 5.418985 | 6.117314 |
| O    | -2.756207 | 4.864823 | 5.602831 |
| H    | -1.738064 | 0.823583 | 7.276437 |
| H    | 0.626155  | 1.493057 | 7.741472 |
| H    | 1.387979  | 3.786899 | 7.143860 |
| C    | -3.711900 | 2.436997 | 6.057945 |
| H    | -4.090043 | 1.697809 | 6.79284 |
| C    | -4.500592 | 3.728111 | 6.269740 |
| H    | -4.291823 | 4.223521 | 7.206611 |
| C    | -5.201353 | 4.527973 | 5.204756 |
| O    | -5.722119 | 3.951293 | 4.253354 |
| N    | -6.272137 | 3.023189 | 7.173577 |
| C    | -5.872550 | 2.545259 | 8.514585 |
| H    | -6.755042 | 2.212411 | 9.077706 |
| H    | -5.181740 | 1.702848 | 8.428277 |
| H    | -5.386491 | 3.355911 | 9.065946 |
| C    | -6.894829 | 1.941696 | 6.381135 |
| H    | -7.838843 | 1.624565 | 6.845917 |
| H    | -7.078911 | 2.303609 | 5.368599 |
| H    | -6.221961 | 1.085172 | 6.333227 |
| C    | -7.215430 | 4.156320 | 7.317009 |
Trans 2,3-dihydroquinone

E(B3LYP-D3/6-31G*(dichloromethane)) = -960.364263
E(B3LYP-D3/6-311+G**(dichloromethane)) = -960.611433
Gtot(B3LYP/6-31G*(dichloromethane)) = -960.098006
Cis 2,3-dihydroquinone

E(B3LYP-D3/6-31G*(dichloromethane)) = -960.364109
E(B3LYP-D3/6-311+G**(dichloromethane)) = -960.61051
Gtot(B3LYP/6-31G*(dichloromethane)) = -960.097744
Trans cyclization TS toward cyclopropane

E(B3LYP-D3/6-31G*(dichloromethane)) = -1134.794688
E(B3LYP-D3/6-311+G**(dichloromethane)) = -1135.0981663
Gtot(B3LYP/6-31G*(dichloromethane)) = -1134.411163
Cis cyclization TS toward cyclopropane

\[ \text{E(B3LYP-D3/6-31G*(dichloromethane))} = -1134.799895 \]
\[ \text{E(B3LYP-D3/6-311+G**(dichloromethane))} = -1135.101919 \]
\[ \text{Gtot(B3LYP/6-31G*(dichloromethane))} = -1134.418274 \]

H    -2.462792  6.299574  3.720097 
H    -3.734143  5.061584  3.532269 
H    -3.237369  5.587837  5.161716 
C    -2.357056  5.393218  9.559319 
C    -1.438881  4.345104  9.463764 
C    -1.567141  3.398333  8.445902 
C    -2.609898  3.475650  7.509026 
C    -3.530977  4.527475  7.617812 
C    -3.400705  5.774445  8.633736 
H    -2.262420  6.134007 10.350363 
H    -0.622472  4.262795 10.178593 
H    -0.843954  2.586490  8.379855 
H    -4.367551  4.567371  6.931293 
H    -4.127206  6.284074  8.705440 

O    -1.827307  4.619909  2.785645 
H    -1.882424  5.588419  2.460457 

C    -6.234965  1.184578  6.696222 
C    -5.050193  2.007707  6.613449 
C    -3.818923  1.296728  6.231332 
C    -3.834186 -0.097333  5.967094 
C    -4.999839 -0.823913  6.059916 
C    -6.204357 -0.163839  6.424999 
H    -7.160992  1.681770  6.976579 
O    -5.068674  3.256048  6.828600 
H    -2.908923 -0.599787  5.700194 
H    -5.000830 -1.892678  5.861829 
H    -7.123759 -0.744577  6.490614 
C    -2.546791  2.157194  6.185149 
C    -2.949607  2.433433  4.789049 
C    -2.624051  1.610714  3.569975 
O    -1.463344  1.276430  3.334210 
H    -3.817668  3.075105  4.712597 
C    -5.667839  0.516633  0.748076 
C    -4.312422  0.470871  0.399680 
C    -3.345183  0.838508  1.329035 
C    -3.718443  1.273059  2.615171 
C    -5.080553  1.311836  2.957893 
C    -6.047510  0.933080  2.026590 
H    -6.424674  0.221647  0.024474 
H    -4.014048  0.144355 -0.593941 
H    -2.289841  0.798277  1.075230 
H    -5.389626  1.598274  3.956985 
H    -7.098707  0.953258  2.303671 
N    -1.827230  4.267413  4.132184 
C    -0.377174  4.044132  4.177345 
H    0.171924  4.969201  3.939326 
H    -0.096518  3.706411  5.177981 
H    -0.107890  3.266051  3.461236 
C    -2.294285  4.619909  2.785645 
H    -1.882424  5.588419  2.460457
\[ \begin{align*}
H & \ -1.983023 \quad 3.849872 \quad 2.074777 \\
H & \ -3.387490 \quad 4.685630 \quad 2.783757 \\
C & \ -2.260399 \quad 5.260247 \quad 5.124667 \\
H & \ -1.918588 \quad 6.270097 \quad 4.849859 \\
H & \ -3.352823 \quad 5.262552 \quad 5.200114 \\
H & \ -1.844213 \quad 5.006721 \quad 6.102820 \\
H & \ -2.773076 \quad 3.041225 \quad 6.783934 \\
C & \ 1.163145 \quad 0.552039 \quad 7.756974 \\
C & \ 0.627265 \quad 0.007025 \quad 6.594792 \\
C & \ -0.553810 \quad 0.492738 \quad 6.042914 \\
C & \ -0.678835 \quad 2.117899 \quad 7.813524 \\
C & \ 0.502988 \quad 1.620488 \quad 8.366348 \\
H & \ 1.130975 \quad -0.007025 \quad 3.849872 \\
H & \ 0.924584 \quad 0.047854 \quad 5.129886 \\
H & \ 0.903629 \quad 2.066938 \quad 9.274017 \\
\end{align*} \]

**Trans addition TS onto C3**

\[ \begin{align*}
E(\text{B3LYP-D3}/6-31G*(\text{dichloromethane})) & = -1134.772215 \\
E(\text{B3LYP-D3}/6-311+G**(\text{dichloromethane})) & = -1135.080923 \\
G_{\text{tot}}(\text{B3LYP}/6-31G*(\text{dichloromethane})) & = -1134.387157 \\
\end{align*} \]
Cis addition TS onto C3

E(B3LYP-D3/6-31G*(dichloromethane)) = -1134.776230
E(B3LYP-D3/6-311+G**(dichloromethane)) = -1135.084280
Gtot(B3LYP/6-31G*(dichloromethane)) = -1134.392764
Trans addition TS onto C5

\[
E(\text{B3LYP-D3/6-31G*(dichloromethane)}) = -1134.773050 \\
E(\text{B3LYP-D3/6-311+G**(dichloromethane)}) = -1135.0782364 \\
G_{\text{tot}}(\text{B3LYP/6-31G*(dichloromethane)}) = -1134.387869
\]
H -2.421843 -3.480847 3.577204  
C -2.724463 -3.828483 6.947780  
H -2.174739 -4.772572 6.923642  
H -2.390735 -3.231910 7.795897  
H -3.798053 -3.994468 6.987147  
C -0.975663 -2.642282 5.699093  
H -0.353555 -3.515880 5.908202  
H -0.711071 -2.218779 4.727965  
H -0.837950 -1.891271 6.475158  
C -5.758880 -0.750246 7.991108  
C -6.107142 0.380945 7.243668  
C -5.139326 1.134032 6.525860  
C -3.718189 0.594034 6.583847  
C -3.475810 -0.773503 7.150849  
C -4.481288 -1.300597 8.017882  
H -6.532712 -1.214865 8.603765  
H -7.127035 0.757365 7.246328  
O -5.384016 2.209971 5.922153  
H -2.448294 -0.953242 7.449081  
H -4.271743 -2.169427 8.632051  
C -4.678497 -2.125891 5.042779  
O -5.299753 -3.091411 5.352226  
C -6.784471 0.443386 2.294186  
C -7.436500 -0.603235 2.960308  
C -6.731568 -1.410065 3.846609  
C -5.363609 -1.192052 4.091220  
C -4.720100 -0.146847 3.405662  
C -5.428762 0.667220 2.522411  
H -7.337197 1.078999 1.603398  
H -8.495507 -0.785132 2.789654  
H -7.228359 -2.216408 4.376625  
H -3.666549 0.056682 3.563511  
H -4.916475 1.479357 2.011780

\textbf{Cis addition TS onto C5}

\begin{align*}
\text{E(B3LYP-D3/6-31G*(dichloromethane))} & = -1134.774517 \\
\text{E(B3LYP-D3/6-311+G**(dichloromethane))} & = -1135.078692 \\
\text{Gtot(B3LYP/6-31G*(dichloromethane))} & = -1134.388563
\end{align*}

| C     | 0.217438 | 2.536388 | 4.331373 |
|-------|----------|----------|----------|
| C     | -1.128900| 2.221057 | 4.502684 |
| C     | -1.585715| 1.614599 | 5.688609 |
| C     | -0.654500| 1.379682 | 6.718202 |
| C     | 0.691874 | 1.705378 | 6.550433 |
| C     | 1.135079 | 2.276543 | 5.354201 |
| H     | 0.551906 | 2.992275 | 3.401855 |
| H     | -1.839188| 2.422182 | 3.704499 |
| H     | -0.996640| 0.978704 | 7.668422 |
| H     | 1.394708 | 1.525202 | 7.361223 |
| H     | 2.184732 | 2.532488 | 5.225582 |
| C     | -3.019210| 1.317001 | 5.818516 |
| H     | -3.692236| 2.042300 | 5.361036 |
| C     | -3.212290| -2.268418| 5.488492 |
| Element | X   | Y   | Z   |
|---------|-----|-----|-----|
| H       | -4.272263 | -2.160924 | 5.283876 |
| C       | -2.298277  | -1.849790  | 4.415472 |
| O       | -1.119511  | -2.261161  | 4.378553 |
| N       | -3.000902  | -3.716935  | 5.943089 |
| C       | -2.897908  | -4.639156  | 4.740826 |
| H       | -2.907164  | -5.672096  | 5.098736 |
| H       | -3.759587  | -4.456935  | 4.095216 |
| H       | -1.971643  | -4.429281  | 4.211000 |
| C       | -4.206951  | -4.164282  | 6.736210 |
| H       | -4.020199  | -5.175140  | 7.106572 |
| H       | -4.353526  | -3.472736  | 7.561870 |
| H       | -5.078895  | -4.162293  | 6.077970 |
| C       | -1.757679  | -3.899323  | 6.788176 |
| H       | -1.638519  | -4.965660  | 6.993952 |
| H       | -0.913096  | -3.513521  | 6.223127 |
| H       | -1.883761  | -3.355103  | 7.720396 |
| C       | -3.486710  | 0.924244   | 1.338315 |
| C       | -2.181273  | 0.422364   | 1.404468 |
| C       | -1.828109  | -0.466441  | 2.414531 |
| C       | -2.770456  | -0.883506  | 3.373506 |
| C       | -4.080210  | -0.378663  | 3.291172 |
| C       | -4.431250  | 0.522589   | 2.285360 |
| H       | -3.763341  | 1.626986   | 0.554938 |
| H       | -1.437923  | 0.735236   | 0.674259 |
| H       | -0.814050  | -0.845876  | 2.486859 |
| H       | -4.836005  | -0.645734  | 4.019059 |
| H       | -5.443733  | 0.917529   | 2.252525 |
| C       | -4.835012  | -1.118546  | 8.501847 |
| C       | -5.672508  | -0.388291  | 7.645899 |
| C       | -5.144553  | 0.332889   | 6.538340 |
| C       | -3.632854  | 0.264295   | 6.404936 |
| C       | -2.939523  | -0.921949  | 6.982436 |
| C       | -3.493954  | -1.373517  | 8.230746 |
| H       | -5.264831  | -1.526366  | 9.418106 |
| H       | -6.731404  | -0.272204  | 7.864472 |
| O       | -5.831697  | 1.055973   | 5.766763 |
| H       | -1.857011  | -0.908740  | 6.906863 |
| H       | -2.895714  | -1.967600  | 8.915885 |
4. Copies of HPLC Chromatograms

Operator: Admin  Timebase: U-3000_DAD  Sequence: WAS_20160621_NIK_YMC
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11.1.2017 10:19 AM

2 NIK-066-02 (95/5) flow 0,5

Sample Name: NIK-066-02 (95/5) flow 0,5
Vial Number: G46
Sample Type: unknown
Control Program: YMC_60Min_95_5_flow0_5
Quantif. Method: AD_H
Recording Time: 21.6.2016 10:37
Run Time (min): 60,00

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

![HPLC Chromatogram](image)

Ph

5c racemic

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU/min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 14.56        | n.a.      | 1949.083   | 844.441      | 47.09      | n.a.   | BM+  |
| 2   | 15.58        | n.a.      | 1930.108   | 1023.533     | 62.01      | n.a.   | MB+  |
| Total|              |           | 3670.191   | 1967.974     | 100.00     | 0.000  |      |

default/Integration

Chromleon (c) Dionex 1996-2006
Version 8.80 SR12 Build 3578 (207198)
3 NIK-137-02 (95/5) flow 0,5

Sample Name: NIK-137-02 (95/5) flow 0,5
Injection Volume: 10,0
Vial Number: GC3
Channel: UV_VIS_2
Sample Type: unknown
Wavelength: 250
Control Program: YMC_50Min_55_5_flow0_5
Bandwidth: 4
Quantif. Method: AD_H
Temperature/Column: 10
Recording Time: 26.7.2016 12:27
Flow ml/min: 0,600
Run Time (min): 60,00
Sample Amount: 1,000

![Graph](image)

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU min) | Rel.Area (%) | Amount | Type |
|-----|---------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 15,69         | n.a.      | 500,487      | 154,281        | 98,75        | n.a.   | BM   |
| 2   | 16,96         | n.a.      | 5,479        | 1,952          | 1,25         | n.a.   | MB   |
| Total |              |           | 505,966      | 156,233        | 100,00       | 0,000  |      |

Chromatogram (c) Dionex 1996-2006
Version 6.80 SR12 Build 3878 (207/169)
NIK-078-02

Sample Name: NIK-078-02
Vial Number: BA3
Sample Type: unknown
Control Program: OD_H_90Min_95_5_flow08
Quantif. Method: default
Recording Time: 10.8.2016 23:30
Run Time (min): 90.00

Injection Volume: 10.0
Channel: UV_VIS_2
Wavelength: 290
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 0.800
Sample Amount: 1.0000

**Graphical Analysis**

**Table**

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 10.47        | n.a.      | 100,261    | 33,302       | 49.81      | n.a.   | SMB  |
| 2   | 12.38        | n.a.      | 91,017     | 33,556       | 50.19      | n.a.   | pMB  |
| Total|              |           | 191,278    | 66,859       | 100.00     | 0.00   |      |

**Chemical Structure**

5d racemic

Ph

 default/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
9 NIK-144-02

Sample Name: NIK-144-02
Vial Number: BA4
Sample Type: unknown
Control Program: OD_H_45Min_95_5_flow08
Quantfl. Method: default
Recording Time: 12.8.2016 12:03
Run Time (min): 29.06
Injection Volume: 10.0
Channel: UV_VIS_2
Wavelength: 250
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 0.800
Sample Amount: 1.000

![Graph and chemical structure with annotations]

| No. | Ret.Time | Peak Name | Height | Area | Rel.Area | Amount | Type |
|-----|----------|-----------|--------|------|----------|--------|------|
| 1   | 10.76    | n.a.      | 5.451  | 1.745| 1.49     | n.a.   | BMB* |
| 2   | 12.61    | n.a.      | 306.701| 115.230| 98.51 | n.a.   | BMB  |
| Total|          |           | 312.152| 116.075| 100.00| 0.000  |      |

Chromeleon (c) Dionex 1998-2006
Version 6.80 SR12 Build 3578 (207160)
6 NIK-077-02 (100/1MeOH) flow 0,5

Sample Name: NIK-077-02 (100/1MeOH) flow 0,5
Vial Number: GD1
Sample Type: unknown
Control Program: OD_HI_90Min_95_5_flow05
Quantif. Method: default
Recording Time: 17.8.2016 15:10
Run Time (min): 66,33

Injection Volume: 10,0
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*min | Rel.Area % | Amount | Type
---|--------------|-----------|------------|-------------|-----------|--------|-----
1 | 39,92        | n.a.      | 230,659    | 215,981     | 49,90     | n.a.   | BM
2 | 42,59        | n.a.      | 212,404    | 216,846     | 50,10     | n.a.   | MB
Total: |              |           | 443,062    | 432,827     | 100,00    | 0,000  |     

---

 Chromatogram: [Image of the chromatogram with peaks labeled 5e racemic]

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default/Integration

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Operator: Admin Timebase: U-3000_DAD Sequence: WAS_20160817_NIK

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Version 6.80 SR12 Build 3578 (207169)
7 NIK-149-02 (100/1MeOH) flow 0,5

Sample Name: NIK-149-02 (100/1MeOH) flow 0,5
Injection Volume: 10,0

Vial Number: GD2
Channel: UV_VIS_1

Sample Type: unknown
Wavelength: 220

Control Program: OD_H_90Min_95_5_flow05
Bandwidth: 4

Quant. Method: default
Temperature/Column: 10

Recording Time: 17.8.2016 16:17
Flow ml/min: 0,500

Run Time (min): 48,82
Sample Amount: 1,0000

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| No. | Ret. Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|---------------|-----------|------------|--------------|-----------|--------|------|
| 1   | 39,56         | n.a.      | 17,785     | 17,591       | 3,54      | n.a.   | BM   |
| 2   | 41,50         | n.a.      | 454,857    | 478,709      | 98,46     | n.a.   | MB   |
| Total|               |           | 472,642    | 498,300      | 100,00    | 0,00   |      |

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default/Integration
### 5 NIK-079-02 (95/5) flow 0,5

| Sample Name: | NIK-079-02 (95/5) flow 0,5 | Injection Volume: | 10.0 |
|--------------|----------------------------|-------------------|------|
| Vial Number: | GD5                        | Channel:          | UV_VIS_1 |
| Sample Type: | unknown                    | Wavelength:       | 220  |
| Control Program: | YMC_60Min_95_5_flow0_5 | Bandwidth:        | 4    |
| Quantl. Method: | AD_H                       | Temperature/Column: | 10  |
| Recording Time: | 2.8.2016 14:06           | Flow m/min:       | 0.500 |
| Run Time (min): | 60.00                      | Sample Amount:    | 10000 |

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![Chromatogram](attachment:chromatogram.png)

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| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 15.55        | n.a.      | 562,224    | 192,856      | 50.30      | n.a.   | BM * |
| 2   | 17.04        | n.a.      | 553,002    | 190,529      | 49.70      | n.a.   | MB * |
| Total|              |           | 1115,225   | 383,384      | 100.00     | 0.000  |

---

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
6 NIK-141-02 (95/5) flow 0.5

Sample Name: NIK-141-02 (95/5) flow 0.5
Injection Volume: 10.0
Vial Number: GD6
Channel: UV_VIS_1
Sample Type: unknown
Wavelength: 220
Control Program: YMC_60Min_95_5_flow0_5
Bandwidth: 4
Quantif. Method: AD_H
Temperature/Column: 10
Recording Time: 2.8.2016 15:07
Flow ml/min: 0.500
Run Time (min): 60.00
Sample Amount: 1,000.0

---

No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount n.a. | Type
---|-------------|-----------|------------|-------------|------------|-------------|--------
1  | 16.79       | n.a.      | 12,089     | 4,048       | 1.27       | n.a. BM*  |
2  | 17.11       | n.a.      | 863,301    | 313,963     | 98.73      | n.a. MB*  |
Total: |             |           | 875,371    | 318,012     | 100.00     | 0.000      |
4 NIK-111-02 (95/5) flow 0,5

Sample Name: NIK-111-02 (95/5) flow 0,5
Vial Number: GC4
Sample Type: unknown
Control Program: YMC_60Min_95_5_flow0_5
Quant. Method: AD_H
Recording Time: 26.7.2016 13:27
Run Time (min): 60,00

| No. | Rel.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 21,71        | n.a.      | 958,505    | 487,347      | 50,00      | n.a.   | BM   |
| 2   | 24,27        | n.a.      | 838,067    | 487,286      | 50,00      | n.a.   | MB   |

Total: 1754,562 974,613 100,00 0,000

default/integration
5 NIK-136-02 (95/5) flow 0.5

Sample Name: NIK-136-02 (95/5) flow 0.5
Vial Number: GC5
Sample Type: unknown
Control Program: YMC_50Min_95_5_flow0_5
Quantif. Method: AD_H
Recording Time: 26.7.2016 14:28
Run Time (min): 60.00

Injection Volume: 10.0
Channel: UV_VIS_2
Wavelength: 250
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 0.500
Sample Amount: 1.0000

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount (%) | Type |
|-----|----------------|-----------|--------------|----------------|--------------|------------|------|
| 1   | 21.74          | n.a.      | 1816810      | 974850         | 89.65        | n.a.       | BMB  |
| 2   | 24.67          | n.a.      | 189893       | 112697         | 10.35        | n.a.       | Rd   |
| Total|                |           | 2008803      | 1097447        | 100.00       | 0.000      |      |

default/integration

Chromeleon (c) Dionex 1996-2005
Version 6.80 SR12 Build 3578 (207169)
**NIK-140-02 (250/1) flow 0,5**

| Sample Name               | NIK-140-02 (250/1) flow 0,5 |
|---------------------------|-----------------------------|
| Vial Number               | BA6                         |
| Sample Type               | unknown                     |
| Control Program           | YMC_90Min_95_6_flow0_5      |
| Quantif. Method           | AD_H                        |
| Recording Time            | 11.10.2016 13:35            |
| Run Time (min)            | 90.00                       |
| Injection Volume          | 10.0                        |
| Channel                   | UV_VIS_1                    |
| Wavelength                | 220                         |
| Bandwidth                 | 4                           |
| Temperature/Column        | 19                          |
| Flow ml/min               | 0.50                        |
| Sample Amount             | 1,000                       |

![Graph](image)

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU'min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 51.16        | n.a.      | 213,592    | 307,402      | 49.99      | n.a.   | BM   |
| 2   | 56.16        | n.a.      | 168,204    | 307,522      | 50.01      | n.a.   | MB   |
| Total|              |           | 381,796    | 614,925      | 100.00     | 0.00   |      |

default/Integration

Chromeleon (c) Dionex 1998-2006
Version 6.80 SR12 Build 3576 (207169)
3 NIK-161-02 (250/1) flow 0,5

Sample Name: NIK-161-02 (250/1) flow 0,5  Injection Volume: 10.0
Vial Number: BB3  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: 220
Control Program: YMC_90Min_95_5_flow0_5  Bandwidth: 4
Quant. Method: AD_H  Temperature/Column: 10
Recording Time: 11.10.2016 15:53  Flow ml/min: 0.500
Run Time (min): 77.81  Sample Amount: 1.0000

No.  Ret.Time  Peak Name  Height  Area  Rel.Area  Amount  Type
   min    mAU    mAU*min  %      n.a.    n.a.        BMB
  1  49.79    n.a.    192.848  281.931  97.91    n.a.        BMB
  2  58.96    n.a.    3.955    6.009    2.09    n.a.        BMB*
Total: 196.803 287.940 100.00 0.000

5h e.r. = 98:2
3 NIK-123-02 (hexan/iPrOH/MeOH 100/3/1)

Sample Name: NIK-123-02 (hexan/iPrOH/MeOH 100/3/1)  Injection Volume: 10.0
Vial Number: GD1  Channel: UV_VIS_2
Sample Type: unknown  Wavelength: 290
Control Program: OD_H_90Min_95_5_flow08  Bandwidth: 4
Quantif. Method: default  Temperature/Column: 10
Recording Time: 11.8.2016 15:17  Flow ml/min: 0.800
Run Time (min): 15.06  Sample Amount: 1,000

No. | Ret.Time  | Peak Name | Height | Area | Rel.Area | Amount | Type  
--- | --- | --- | --- | --- | --- | --- | --- 
1  | 12.25 | n.a. | 414,906 | 144,266 | 49.94 | n.a. | BM  
2  | 13.35 | n.a. | 399,919 | 144,611 | 50.05 | n.a. | MB  
Total: | | | 806,825 | 288,877 | 100.00 | 0.000 |
5 NIK-139-02 (verdünnter, hexan/iPrOH/MeOH 100/3/1)

Sample Name: NIK-139-02 (verdünnter, hexan/iPrOH/MeOH) Injection Volume: 10,0
Vial Number: GD2 Channel: UV_VIS_2
Sample Type: unknown Wavelength: 290
Control Program: OD_H_25Min_95_5_flow08 Bandwidth: 4
Quantif. Method: default Temperature/Column: 10
Recording Time: 11.8.2016 15:49 Flow m/min: 0,800
Run Time (min): 17,65 Sample Amount: 1,0000

| No. | Ret.Time | Peak Name | Height | Area | Rel.Area | Amount | Type |
|-----|----------|-----------|--------|------|----------|--------|------|
| 1   | 12.34    | n.a.      | 17,358 | 6,115| 6,78     | n.a.   | BM   |
| 2   | 13.39    | n.a.      | 225,296| 84,097| 93.22    | n.a.   | MB   |
| Total|          |           | 242,654| 90,212| 100,00   | 0,000  |      |

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207109)
3  NIK-157-02 (99/1) flow 0,5

| Sample Name:             | NIK-157-02 (99/1) flow 0,5                  | Injection Volume: | 10,0 |
|--------------------------|--------------------------------------------|-------------------|------|
| Vial Number:             | GE3                                        | Channel:          | UV_VIS_1 |
| Sample Type:             | unknown                                    | Wavelength:       | 220  |
| Control Program:         | YMC_60Min_95_S_flow0_5                    | Bandwidth:        | 4    |
| Quantif. Method:         | AD_H                                       | Temperature/Column:| 10  |
| Recording Time:          | 14.9.2016 15:04                           | 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) | Rel.Area (%) | Amount | Type |
|-----|---------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 20,49         | n.a.      | 424,489      | 218,818        | 51,07        | n.a.   | BMB  |
| 2   | 23,24         | n.a.      | 353,796      | 209,670        | 49,93        | n.a.   | BMB  |
| Total:                           | 778,284   | 428,488      | 100,00        | 0,00          |        |      |

default/integration

Chromatogram

Chromarun (c) Dionex 1996-2006
Version 6.80 SR12 Build 3979 (207169)
4 NIK-158-02 (99/1) flow 0.5

| Sample Name:        | NIK-158-02 (99/1) flow 0.5 | Injection Volume: | 10,0 |
|---------------------|----------------------------|-------------------|------|
| Vial Number:        | GE4                        | Channel:          | UV_VIS_2 |
| Sample Type:        | unknown                    | Wavelength:       | 250  |
| Control Program:    | YMC_50Min_95_5_flow0_5     | Bandwidth:        | 4    |
| Quantif Method:     | AD_H                       | Temperature/Column:| 10  |
| Recording Time:     | 14.9.2016 16:05            | Flow ml/min:      | 0,500|
| Run Time (min):     | 60,00                      | Sample Amount:    | 1,000|

![Retention Time and Height Diagram]

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 20,83          | n.a.      | 462,756      | 259,502        | 96,91        | n.a.   | BMB  |
| 2   | 24,02          | n.a.      | 12,390       | 8,265          | 3,09         | n.a.   | BMB  |
| Total|                |           | 475,146      | 267,767        | 100,00       | 0,000  |      |

default/Integration
2  NIK-121-02 (95/5) flow 0,5

| Sample Name:         | NIK-121-02 (95/5) flow 0,5 | Injection Volume: 10.0 |
|----------------------|---------------------------|------------------------|
| Vial Number:         | GE2                       | Channel: UV_VIS_2      |
| Sample Type:         | unknown                   | Wavelength: 250        |
| Control Program:     | OD_H_90Min_95_5_flow05   | Bandwidth: 4           |
| Quantif. Method:     | default                   | Temperature/Column: 10 |
| Recording Time:      | 15.9.2016 11:52           | Flow ml/min: 0,500     |
| Run Time (min):      | 56,06                     | Sample Amount: 1,0000  |

![Chemical Structure]

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type   |
|-----|--------------|-----------|------------|--------------|------------|--------|--------|
| 1   | 30,34        | n.a.      | 26,439     | 42,359       | 49.33      | n.a.   | BMB*   |
| 2   | 39,03        | n.a.      | 32,462     | 43,510       | 50.67      | n.a.   | BMB    |

Total: 58,901 85,869 100.00 0.000

default/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
NIK-151-02 (95/5) flow 0,5

Sample Name: NIK-151-02 (95/5) flow 0,5
Vial Number: GE6
Sample Type: unknown
Control Program: OD_H_90Min_95_5_flow05
Quantif. Method: default
Recording Time: 15.9.2016 12:49
Run Time (min): 64,71

Injection Volume: 10.0
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 | Area | Rel.Area | Amount | Type
--- | --- | --- | --- | --- | --- | --- | ---
1 | 31,65 | n.a. | 49,667 | 88,060 | 6,94 | n.a. | BMB*
2 | 40,38 | n.a. | 819,625 | 1180,082 | 93,06 | n.a. | BMB*
Total: | | | | | | | 869,682 1266,122 100,00 0,000

---

Default/Integration

Chromeleon (c) Dionex 1998-2006
Version 6.80 SR12 Build 3578 (207169)
11 NIK-122-02 (99/1) flow 0,5

Sample Name: NIK-122-02 (99/1) flow 0,5
Vial Number: BA5
Sample Type: unknown
Control Program: YMC_60Min_95_5_flow0_5
Quantif. Method: AD_H
Recording Time: 9.8.2016 0:54
Run Time (min): 60,00

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

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**Fingerprint**

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| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|-------------|-----------|------------|-------------|------------|--------|------|
| 1   | 31,77       | n.a.      | 511,889    | 716,836     | 49,72      | n.a.   | BMB  |
| 2   | 43,63       | n.a.      | 488,546    | 724,844     | 50,28      | n.a.   | BMB* |
| Total|             |           | 1000,435   | 1441,681    | 100,00     | 0,000  |      |

---

Chromeleon (c) Dionex 1999-2006
Version 6.80 SR12 Build 3578 (297169)
12 NIK-145-02 (99/1) flow 0,5

Sample Name: NIK-145-02 (99/1) flow 0,5
Vial Number: BA8
Sample Type: unknown
Control Program: YMC_50Min_95.5_flow0.5
Quant. Method: AD_H
Recording Time: 9.8.2016 1:55
Run Time (min): 60,00
Injection Volume: 10,0
Channel: UV_VIS_2
Wavelength: 250
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 0,500
Sample Amount: 1,0000

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU·min) | Rel.Area (%) | Amount (µg) | Type |
|-----|---------------|-----------|--------------|----------------|--------------|-------------|------|
| 1   | 32.41         | n.a.      | 16,623       | 23,736         | 7.18         | n.a.        | BMB  |
| 2   | 43.28         | n.a.      | 202,538      | 300,624        | 92.82        | n.a.        | BMB  |
| Total|               |           | 219,161      | 330,561        | 100.00       | 0.000       |      |

---

Operator: Admin
Timebase: U-3000_DAD
Sequence: WAS_20160808_NIK_YMC
Page 1/2
12.1.2017 1:41 PM

[Graph showing a chromatogram with peak 5I, e.r. = 93.7]

Chromeleon (c) Dionex 1996-2005
Version 6.80 SR12 Build 3578 (207169)
7 NIK-124-02 (99/1) flow 0,5

Sample Name: NIK-124-02 (99/1) flow 0,5
Sample Type: unknown
Control Program: YMC_60Min_95_5_flow0_5
Quantif. Method: AD_H
Recording Time: 8.8.2016 20:52
Run Time (min): 60,00

Injection Volume: 10,0
Channel: UV_VIS_2
Wavelength: 250
Bandwidth: 4
Temperature/Column: 10
Flow ml/min: 0,500
Sample Amount: 1,000

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU'min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 34,32        | n.a.      | 187,036    | 254,176      | 51,43      | n.a.   | BMB  |
| 2   | 58,45        | n.a.      | 139,999    | 240,052      | 49,57      | n.a.   | BMB  |
| Total|              |           | 327,035    | 494,228      | 100,00     | 0,00   |      |

default/Integration
8  NIK-143-02 (99/1) flow 0,5

Sample Name:  NIK-143-02 (99/1) flow 0,5  Injection Volume:  10,0
Vial Number:  BA2  Channel:  UV_VIS_2
Sample Type:  unknown  Wavelength:  250
Control Program:  YMC_60Min_95_5_flow0_5  Bandwidth:  4
Quantif. Method:  AD_H  Temperature/Column:  10
Recording Time:  8.8.2016 21:52  Flow ml/min:  0,500
Run Time (min):  60,00  Sample Amount:  1,000

| No. | Ret.Time | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|----------|-----------|------------|--------------|------------|--------|------|
| 1   | 35,06    | n.a.      | 16,605     | 23,138       | 6,97       | n.a.   | BMB  |
| 2   | 56,03    | n.a.      | 199,786    | 359,117      | 93,93      | n.a.   | BMB  |
| Total|          |           | 216,290    | 381,315      | 100,00     | 0,000  |      |

default/Integration

Chromeleon (c) Dionex 1995-2006
Version 6.80 SR12 Build 3578 (207169)
NIK-110-02 (95/5) flow 0,5

Sample Name: NIK-110-02 (95/5) flow 0,5
Val Number: GD7
Sample Type: unknown
Control Program: OD_H_60Min_95_5_flow05_25grad
Quantif. Method: default
Recording Time: 17.8.2016 12:01
Run Time (min): 33,97

Injection Volume: 10,0
Channel: UV_VIS_1
Wavelength: 220
Bandwidth: 4
Temperature/Column: 25
Flow ml/min: 0,500
Sample Amount: 1,0000

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| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 19.86        | n.a.      | 418,034    | 194,064      | 48.26      | n.a.   | BMB  |
| 2   | 23.53        | n.a.      | 372,204    | 208,092      | 51.74      | n.a.   | BMB  |
| Total|              |           | 790,238    | 402,156      | 100.00     | 0.000  |      |

default/Integration

Chromeleon (c) Dionex 1996-2006
Version 8.80 SR12 Build 3578 (207169)
NIK-142-02 (95/5) flow 0.5

Sample Name: NIK-142-02 (95/5) flow 0.5
Injection Volume: 10.0

Vial Number: OD8
Channel: UV_VIS_1

Sample Type: unknown
Wavelength: 220

Control Program: OD_H_60Min_95_5_flow05_25grad
Bandwidth: 4

Quantif. Method: default
Temperature/Column: 25

Recording Time: 17.8.2016 12:36
Flow ml/min: 0.500

Run Time (min): 49.88
Sample Amount: 1,0000

No. | Ret.Time  | Peak Name | Height  | Area   | Rel.Area  | Amount | Type
--- | --------- | --------- | ------- |-------- |---------- |------- |-----
    | min      |          | mAU    | mAU*min| %        |        |      
1   | 19.91    | n.a.     | 70,079 | 32,127 | 7.26     | n.a.  | BMB  
2   | 23.41    | n.a.     | 739,086| 410,303| 92.74    | n.a.  | BMB  
Total: |          |          | 809,165| 442,430| 100.00   | 0.000 |      

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default/Integration
8 NIK-113-02 (98/2) flow 0,5

Sample Name: NIK-113-02 (98/2) flow 0,5
Vial Number: BD1
Sample Type: unknown
Control Program: YMC_90Min_95_5_flow0_5
Quantif. Method: AD_H
Recording Time: 21.12.2016 16:00
Run Time (min): 90,00

Injection Volume: 10.0
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*min | Rel.Area % | Amount | Type |
|-----|----------------|-----------|------------|--------------|------------|--------|------|
| 1   | 71.23          | n.a.      | 135,349    | 297,273      | 50.70      | n.a.   | BM*  |
| 2   | 76.57          | n.a.      | 111,011    | 279,327      | 49.30      | n.a.   | MB*  |
| Total|                |           | 246,360    | 566,500      | 100.00     |        |      |

Chromleon (c) Dionex 1998-2006
Version 6.80 SR12 Build 3578 (207/169)
9 NIK-150-02 (98/2) flow 0,5

Sample Name: NIK-150-02 (98/2) flow 0,5
Sample Type: unknown
Control Program: YMC_90Min_95_5_flow0_5
Quantif. Method: AD_H
Recording Time: 21.12.2016 17:30
Run Time (min): 90,00

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

![Chemical Structure](image)

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 67,44        | n.a.      | 85,692     | 185,342      | 96,78      | n.a.   | BMB  |
| 2   | 73,74        | n.a.      | 2,256      | 2,293        | 1,22       | n.a.   | SM * |
| Total|              |           | 88,349     | 187,634      | 100,00     | 0.000  |      |

default/Integration
2 NIK-186-02 (98/2) flow 0,5

Sample Name: NIK-186-02 (98/2) flow 0,5  Injection Volume: 10,0
Vis No.: BA1  Channel: UV_VIS_2
Sample Type: unknown  Wavelength: 250
Control Program: YMC_50Min_55_5_flow9_6  Bandwidth: 4
Quantif. Method: AD_H  Temperature/Column: 10
Recording Time: 5.10.2016 13:26  Flow ml/min: 0,500
Run Time (min): 60,00  Sample Amount: 1,0000

![Chemical Structure]

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area % | Amount | Type |
|-----|----------------|-----------|--------------|----------------|------------|--------|------|
| 1   | 28,16          | n.a.      | 301,414      | 173,979        | 49,66      | n.a.   | BM   |
| 2   | 29,79          | n.a.      | 278,842      | 176,210        | 50,32      | n.a.   | MB   |
| Total|                |           | 580,256      | 350,189        | 100,00     | 0,000  |      |

default/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207'169)
3 NIK-187-02 (98/2) flow 0,5

| Sample Name: | NIK-187-02 (98/2) flow 0,5 | Injection Volume: | 10,0 |
|--------------|-----------------------------|-------------------|------|
| Vial Number: | BA2                         | Channel:          | UV_VIS_2 |
| Sample Type: | unknown                     | Wavelength:       | 250  |
| Control Program: | YMC_60Min_95_5_flow0_5     | Bandwidth:        | 4    |
| Quantif. Method: | AD_H                       | Temperature/Column: | 10 |
| Recording Time: | 5.10.2016 15:22            | Flow ml/min:      | 0,500|
| Run Time (min): | 60,00          | Sample Amount:    | 1,000|

![Graph](image)

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 24,39        | n.a.      | 626,669    | 338,631      | 98,89      | n.a.   | BM   |
| 2   | 26,24        | n.a.      | 6,071      | 3,804        | 1.11       | n.a.   | MB   |
| Total: |              |           | 632,740    | 342,435      | 100,00     | n.a.   |      |

**5p**

e.r. = 99:1

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
2  NIK-171-02 (250/1) flow 0,5

Sample Name: NIK-171-02 (250/1) flow 0,5  Injection Volume: 10,0
Vial Number: BA3  Channel: UV_VIS_1
Sample Type: unknown  Wavelength: 220
Control Program: YMC_95Min_95_5_flow3_5  Bandwidth: 4
Quantif. Method: AD,I  Temperature/Column: 10
Recording Time: 11.10.2016 15:06
Run Time (min): 45,66  Flow ml/min: 0,500
Sample Amount: 1,0000

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**Chart Analysis**

- **Compound Identification**
  - Ph: Phenyl
  - COPh: Carboxyphenyl
  - 5q: Racemic

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**Table**

| No. | Ret.Time (min) | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|----------------|-----------|------------|--------------|------------|--------|------|
| 1   | 32,75          | n.a.      | 223,450    | 202,189      | 49,89      | n.a.   | BM   |
| 2   | 36,55          | n.a.      | 190,929    | 203,117      | 50,11      | n.a.   | MB   |
| Total |                |            | 414,379    | 405,306      | 100,00     | 0,000  |      |

---

Chromeleon (c) Dionex 1995-2006
Version 6.80 SR12 Build 3578 (207109)
4 NIK-172-02 (250/1) flow 0,5

Sample Name: NIK-172-02 (250/1) flow 0,5
Injection Volume: 10.0
Vial Number: BA4
Channel: UV_VIS_2
Sample Type: unknown
Wavelength: 250
Control Program: YMC_90Min_95_6_flow0_5
Bandwidth: 4
Quantif. Method: AD_H
Temperature/Column: 10
Recording Time: 11.10.2016 17:11
Flow rate/min: 0.500
Run Time (min): 42.70
Sample Amount: 1,0000

---

No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
--- | --- | --- | --- | --- | --- | --- | --- |
1 | 31.19 | n.a. | 5,489 | 4,068 | 1.27 | n.a. | BMB |
2 | 33.87 | n.a. | 304,804 | 316,491 | 98.73 | n.a. | BMB |
Total: | 310,293 | 321,569 | 100.00 | 0.000 |

---

NIK-172-02 (250/1) flow 0,5

Ph

rBu

5q

e.r. = 99:1

---

Chromeleon (c) Dionex 1995-2006
Version 5.80 SR12 Build 3578 (207169)
6 NIK-197-02 (95/5) flow 0,5

Sample Name: NIK-197-02 (95/5) flow 0,5
Vial Number: BD4
Sample Type: unknown
Control Program: YMC_60Min_95_5_flow0_5
Quant. Method: AD_H
Recording Time: 21.12.2016 14:16
Run Time (min): 20.85

Injection Volume: 10.0
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 | 13.59 | n.a. | 768.966 | 191,652 | 49.98 | n.a. | BMB*
2 | 16.52 | n.a. | 540.119 | 191,808 | 50.02 | n.a. | BMB

Total: | | | 1308.485 | 383.470 | 100,00 | 0,000 |
7  NIK-196-02 (95/5) flow 0.5

Sample Name:  NIK-196-02 (95/5) flow 0.5
Vial Number:  BE4
Sample Type:  unknown
Control Program:  YMC_60Min_95_5_flow0.5
Quants Method:  AD_H
Recording Time:  21.12.2016 14:37
Run Time (min):  33.93
Injection Volume:  10.0
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 | Rel.Area % | Amount | Type |
|-----|----------|-----------|------------|--------------|------------|--------|------|
| 1   | 13.94    | n.a.      | 1107.759   | 298.218      | 95.68      | n.a.   | BMB* |
| 2   | 17.08    | n.a.      | 282202     | 9890         | 3.32       | n.a.   | BMB* |
| Total|          |           | 1135961    | 298108       | 100.00     | 0.000  |      |

NIK-196-02 (95/5) flow 0.5

Ph

\[ \text{5r} \]

e.r. = 97.3

[Graph and data analysis]

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
## 2 NIK-191-02 (95/5) flow 0.5

| Sample Name: | NIK-191-02 (95/5) flow 0.5 | Injection Volume: | 10.0 |
|--------------|---------------------------|-------------------|------|
| Val Number:  | BD2                       | Channel:          | UV_VIS_1 |
| Sample Type: | unknown                   | Wavelength:       | 220  |
| Control Program: | YMC_60Min_95_5_flow0_5 | Bandwidth:        | 4    |
| Quantif. Method: | AD_H                      | Temperature/Column: | 10 |
| Recording Time: | 21.12.2016 12:03         | Flow ml/min:      | 0.500 |
| Run Time (min): | 37.79                    | Sample Amount:    | 1,0000 |

![Chromatogram](image)

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type |
|-----|----------------|-----------|--------------|----------------|--------------|--------|------|
| 1   | 24.90          | n.a.      | 556,639      | 375,300        | 49.98        | n.a.   | BM*  |
| 2   | 27.25          | n.a.      | 486,641      | 375,635        | 50.02        | n.a.   | MB*  |
| Total: |               |           | 1043,480     | 750,936        | 100.00       | 0.000  |      |

(default/Integration)

Chromleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
3 NIK-190-02 (95/5) flow 0,5

Sample Name: NIK-190-02 (95/5) flow 0,5  Injection Volume: 10,0  
Vial Number: BE2  Channel: UV_VIS_2  
Sample Type: unknown  Wavelength: 250  
Control Program: YMC_60Min_95_5_flow0_5  Bandwidth: 4  
Quantif. Method: AD_H  Temperature/Column: 10  
Recording Time: 21.12.2016 12:42  Flow ml/min: 0,500  
Run Time (min): 37,46  Sample Amount: 1,0000

---

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 25.57        | n.a.      | 152,557    | 100,848      | 34.29      | n.a.   | BM*  |
| 2   | 27.66        | n.a.      | 254,579    | 193,233      | 65.71      | n.a.   | MB*  |
| Total|              |           | 407,136    | 294,081      | 100.00     | -      | 0.000|

---

default/Integration

Chromeleon (c) Dionex 1998-2006
Version 6.80 SR12 Build 3578 (207169)
### 4 NiK-201-02 (95/5) flow 0,5

| Sample Name:          | NIK-201-02 (95/5) flow 0,5 | Injection Volume: | 10,0 |
|-----------------------|---------------------------|-------------------|------|
| Vial Number:          | BD3                       | Channel:          | UV_VIS_1 |
| Sample Type:          | unknown                   | Wavelength:       | 220  |
| Control Program:      | YMC_60Min_95_5_flow0.5    | Bandwidth:        | 4    |
| Quantif Method:       | AD_H                      | Temperature/Column: | 10   |
| Recording Time:       | 21.12.2016 13:20          | Flow ml/min:      | 0,500|
| Run Time (min):       | 27,67                     | Sample Amount:    | 1,000|

![Chemical Structure Image](image)

| No. | Ret.Time (min) | Peak Name | Height (mAU) | Area (mAU*min) | Rel.Area (%) | Amount | Type  |
|-----|----------------|-----------|--------------|----------------|--------------|--------|-------|
| 1   | 18.97          | n.a.      | 556,663      | 207,683        | 50,06        | n.a.   | BMB   |
| 2   | 22.50          | n.a.      | 451,122      | 207,203        | 49,94        | n.a.   | BMB   |
| Total|                |           | 1000,785     | 414,887        | 100,00       | 0,000  |       |

**Note:** default/Integration

*Chromeleon (c) Dionex 1996-2006*  
*Version 6.90 SR12 Build 3578 (207160)*
5 NIK-202-02 (95/5) flow 0,5

Sample Name: NIK-202-02 (95/5) flow 0,5
Injection Volume: 10,0
Vial Number: 8E3
Channel: UV_VIS_2
Sample Type: unknown
Wavelength: 250
Control Program: YMC_60Min_95_5_flow0.5
Bandwidth: 4
Quantif. Method: AD_H
Temperature/Column: 10
Recording Time: 21.12.2016 13:49
Flow ml/min: 0,500
Run Time (min): 25,98
Sample Amount: 1,000

---

**5t**

\[
\text{e.r.} = 73:27
\]

---

| No. | Ret.Time | Peak Name | Height mAU | Area mAU/min | Rel.Area % | Amount | Type |
|-----|----------|-----------|------------|--------------|------------|--------|------|
| 1   | 18,93    | n.a.      | 58,515     | 21,224       | 26,99      | n.a.   | BMB  |
| 2   | 22,45    | n.a.      | 127,182    | 57,415       | 73,01      | n.a.   | BMB  |
| Total|          |           | 185,697    | 78,639       | 100,00     | 0,000  |      |

---

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
### Sample Information

| Sample Name          | Injection Volume |
|----------------------|------------------|
| ROI-1244-02_100_1_flo5 | 10.0             |

| Vial Number | Channel |
|-------------|---------|
| BD8         | UV_VIS_1 |

| Sample Type       | Wavelength |
|-------------------|------------|
| unknown           | 220        |

| Control Program   | Bandwidth  |
|-------------------|------------|
| AD_H_90Min_100A_flow0_5 | 4          |

| Quantif. Method   | Temperature/Column |
|-------------------|--------------------|
| default           | 10                 |

| Recording Time    | Flow ml/min |
|-------------------|-------------|
| 31.1.2017 13:41   | 0.500       |

| Run Time (min)    | Sample Amount |
|-------------------|---------------|
| 60,14             | 1,000         |

### Chromatogram

![Chromatogram](image)

### Retention Time Table

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 33.49        | n.a.      | 120,784    | 134,800      | 50.52      | n.a.   | BMB  |
| 2   | 43.43        | n.a.      | 78,120     | 132,009      | 49.48      | n.a.   | BMB* |

**Total:**

| 198,905 | 266,809 | 100.00 | 0.000  |

---

Chromatogram [modified by Admin] using UV_VIS_1 with wavelength 220 nm.
### ROI-1243-02_100_1_flo5

| Sample Name:     | ROI-1243-02_100_1_flo5                                                                 |
|------------------|----------------------------------------------------------------------------------------|
| Vial Number:     | BE8                                                                                     |
| Sample Type:     | unknown                                                                                 |
| Control Program: | AD_H_90Min_100A_flow0_5                                                                 |
| Quantif. Method: | default                                                                                 |
| Recording Time:  | 31.1.2017 15:25                                                                        |
| Run Time (min):  | 80.02                                                                                   |
| Injection Volume:| 10.0                                                                                     |
| Wavelength:      | 220                                                                                     |
| Bandwidth:       | 4                                                                                       |
| Temperature/Column: | 10                                                                                      |
| Flow ml/min:     | 0.500                                                                                   |
| Sample Amount:   | 1,000                                                                                   |

**Chemical Structure:**

![Chemical Structure](image)

**Table:**

| No. | Ret.Time min | Peak Name | Height mAU | Area mAU*min | Rel.Area % | Amount | Type |
|-----|--------------|-----------|------------|--------------|------------|--------|------|
| 1   | 34.08        | n.a.      | 37,865     | 44,488       | 99.24      | n.a.   | BMB* |
| 2   | 45.91        | n.a.      | 0.228      | 0.339        | 0.76       | n.a.   | BMB* |
| Total|              |           | 38.094     | 44.827       | 100.00     | 0.000  |      |

**Note:**

- mAU: Milli-Angle Units
- mAU*min: Milli-Angle Units per Minute
- Rel.Area: Relative Area
- Amount: Amount
- Type: Type

This data was generated using Chromeleon (c) Dionex 1996-2006, Version 6.80 SR12 Build 3578 (207169).
2  ROI-1236-02_100_1_flo5

Sample Name: ROI-1236-02_100_1_flo5  Injection Volume: 10.0
Vial Number: BD7  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: 31.1.2017 12:24  Flow ml/min: 0.500
Run Time (min): 76.50  Sample Amount: 1.0000

---

Default/Integration

---

Chromatogram

| No. | Ret.Time  | Peak Name | Height mAU | Area mAU’min | Rel.Area % | Amount | Type |
|-----|-----------|-----------|------------|--------------|------------|--------|------|
| 1   | 26.73     | n.a.      | 125,901    | 74,849       | 50.09      | n.a.   | BMB  |
| 2   | 31.03     | n.a.      | 107,107    | 74,583       | 49.91      | n.a.   | BMB  |
| Total|           |           | 233,007    | 149,432      | 100.00    | 0.000  |      |

---

Chromelon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207169)
Sample Name: ROI-1235-02_100_1_flo5
Injection Volume: 10.0
Val Number: BE7
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: 31.1.2017 14:44
Flow ml/min: 0.500
Run Time (min): 36.66
Sample Amount: 1.0000

No. | Ret.Time min | Peak Name | Height mAU | Area mAU/ min | Rel.Area % | Amount | Type
--- | ------------ | --------- | ---------- | ------------ | ---------- | ------ | ----
1   | 27.08       | n.a.      | 40.979     | 23.748       | 64.99      | n.a.   | BMB  
2   | 31.57       | n.a.      | 19.773     | 12.793       | 35.01      | n.a.   | BMB  
Total: | 60.753      | 36.541    | 100.00     | 0.000        |           |       |     

WAS_20170131_ROI_YMC #1 [modified by Admin]
UV_VIS_1
WVL: 220 nm

default/Integration

Chromeleon (c) Dionex 1996-2006
Version 6.80 SR12 Build 3578 (207199)
5. Copies of NMR-Spectra of new Compounds

![NMR Spectra Diagram]

**Current Data Parameters**
- **NAME**: NMR-131-12
- **NDATA**: 21

**F2 - Acquisition Parameters**
- **Data Type**: 20161230
- **Time**: 0:53 h
- **FIDID**: 2062701.00264
- **FIDFO1**: 300.1318533 MHz
- **TD0**: 1
- **D1**: 1.00000000 sec
- **TE**: 298.0 K
- **DE**: 6.50 usec
- **DW**: 83.200 usec
- **RG**: 512
- **AQ**: 5.4525952 sec
- **FIDRES**: 0.183399 Hz
- **SWH**: 6009.615 Hz
- **NS**: 16
- **SOLVENT**: CDCl3

**F2 - Processing parameters**
- **S**: 65536
- **P**: 0.0000000 W
- **EB**: 0.0000000 W
- **PL**: 50.0000000 W
- **PLFo2**: 300.1312000 MHz
- **FTMo2**: 10
- **PCDMo2**: 50.0000000 W
- **PLMo2**: 0.0000000 W
- **K**: 75.475344 MHz
- **PC**: 500.0000000 W
- **PLP**: 0.0000000 W
- **PLP**: 0.0000000 W
- **PLP**: 0.0000000 W
- **K**: 75.475344 MHz
- **K**: 65536
- **LB**: 1.00 Hz
- **PC**: 1.00

**Acquisition Parameters**
- **PROCNO**: 1
- **EXPNO**: 10
- **NAME**: NIK-131-02
- **Current Data Parameters**
- **1f**: OH
- **Ts**: tBu
- **tBu**: OH
- **Ts**: tBu
- **INSTRUM**: spect
- **Time**: 10.10 h
- **Date**: 20161108
### Processing Parameters

#### PLW
- PLW1: 20.00000000 W

#### NUC
- NUC1: 1H

#### SFO
- SFO1: 300.1318533 MHz

#### TD
- TD0: 1
- D1: 1.00000000 sec

#### TE
- TE: 298.0 K

#### DE
- DE: 6.50 usec

#### DW
- DW: 83.200 usec

#### RQ
- RG: 456

#### AQ
- AQ: 5.4525952 sec

#### FIDRES
- FIDRES: 0.183399 Hz

#### SWH
- SWH: 6009.615 Hz

#### DS
- DS: 2

#### NS
- NS: 16

#### SOLVENT
- SOLVENT: CDCl3

#### TD
- TD: 65536

#### PULPROG
- PULPROG: zg30

#### PROBHD
- PROBHD: Z862701_0064

#### INSTRUM
- INSTRUM: spect

#### Time
- Time: 13:25 h

#### Date
- Date: 20161109

#### Acquisition Parameters

| Parameter   | Value                  |
|-------------|------------------------|
| PROCNO      | 1                      |
| EXPNO       | 10                     |
| NAME        | NIR-199-02             |
| PROCNO      | 1                      |

### Processing Parameters

#### TIME
- Time: 3:13 h

#### PROCNO
- PROCNO: 2642701_0044

#### TD
- TD: 1

#### DE
- DE: 6.50 usec

#### DW
- DW: 83.200 usec

#### RG
- RG: 456

#### AQ
- AQ: 5.4525952 sec

#### FIDRES
- FIDRES: 0.183399 Hz

#### SWH
- SWH: 6009.615 Hz

#### DS
- DS: 2

#### NS
- NS: 16

#### SOLVENT
- SOLVENT: CDCl3

#### TD
- TD: 65536

#### PULPROG
- PULPROG: zg30

#### PROBHD
- PROBHD: Z862701_0064

#### INSTRUM
- INSTRUM: spect

#### Time
- Time: 13:25 h

#### Date
- Date: 20161109

### Current Data Parameters

| Parameter   | Value                  |
|-------------|------------------------|
| NAME        | NIR-199-02             |
| PROCNO      | 1                      |

### Processing Parameters

#### TIME
- Time: 3:13 h

#### PROCNO
- PROCNO: 2642701_0044

#### TD
- TD: 1

#### DE
- DE: 6.50 usec

#### DW
- DW: 83.200 usec

#### RG
- RG: 456

#### AQ
- AQ: 5.4525952 sec

#### FIDRES
- FIDRES: 0.183399 Hz

#### SWH
- SWH: 6009.615 Hz

#### DS
- DS: 2

#### NS
- NS: 16

#### SOLVENT
- SOLVENT: CDCl3

#### TD
- TD: 65536

#### PULPROG
- PULPROG: zg30

#### PROBHD
- PROBHD: Z862701_0064

#### INSTRUM
- INSTRUM: spect

#### Time
- Time: 13:25 h

#### Date
- Date: 20161109

### Current Data Parameters

| Parameter   | Value                  |
|-------------|------------------------|
| NAME        | NIR-199-02             |
| PROCNO      | 1                      |

### Processing Parameters

#### TIME
- Time: 3:13 h

#### PROCNO
- PROCNO: 2642701_0044

#### TD
- TD: 1

#### DE
- DE: 6.50 usec

#### DW
- DW: 83.200 usec

#### RG
- RG: 456

#### AQ
- AQ: 5.4525952 sec

#### FIDRES
- FIDRES: 0.183399 Hz

#### SWH
- SWH: 6009.615 Hz

#### DS
- DS: 2

#### NS
- NS: 16

#### SOLVENT
- SOLVENT: CDCl3

#### TD
- TD: 65536

#### PULPROG
- PULPROG: zg30

#### PROBHD
- PROBHD: Z862701_0064

#### INSTRUM
- INSTRUM: spect

#### Time
- Time: 13:25 h

#### Date
- Date: 20161109

### Current Data Parameters

| Parameter   | Value                  |
|-------------|------------------------|
| NAME        | NIR-199-02             |
| PROCNO      | 1                      |

### Processing Parameters

#### TIME
- Time: 3:13 h

#### PROCNO
- PROCNO: 2642701_0044

#### TD
- TD: 1

#### DE
- DE: 6.50 usec

#### DW
- DW: 83.200 usec

#### RG
- RG: 456

#### AQ
- AQ: 5.4525952 sec

#### FIDRES
- FIDRES: 0.183399 Hz

#### SWH
- SWH: 6009.615 Hz

#### DS
- DS: 2

#### NS
- NS: 16

#### SOLVENT
- SOLVENT: CDCl3

#### TD
- TD: 65536

#### PULPROG
- PULPROG: zg30

#### PROBHD
- PROBHD: Z862701_0064

#### INSTRUM
- INSTRUM: spect

#### Time
- Time: 13:25 h

#### Date
- Date: 20161109
| PC  | 1.00 |
|-----|------|
| GB  | 0    |
| LB  | 0.30 Hz |
| SSB | 0    |
| WDW | EM   |
| SF  | 300.1299705 MHz |
| SI  | 65536 |
| F2− | Processing parameters |
| ST  | 10532 |
| AP  | 300.1318533 MHz |
| WDN | EM   |
| SO  | 6.30 Hz |
| GR  | 1.00 |

Current Data Parameters
NAME: B18-073-01
EXPNO: 1

F3 - Acquisition Parameters
Date: 20161029
Time: 22:00 h
Instruments: spect
PROBNO: 284731_0041
TD: 4000
Diluent: DMSO
Solvent: DMSO

Acquisition Parameters
PROCNO: 1
EXPNO: 10
NAME: NIK-073-01_2

Current Data Parameters
NAME: B18-073-01
EXPNO: 1

F3 - Acquisition Parameters
Date: 20161029
Time: 22:00 h
Instruments: spect
PROBNO: 284731_0041
TD: 4000
Diluent: DMSO
Solvent: DMSO

Acquisition Parameters
PROCNO: 1
EXPNO: 10
NAME: NIK-073-01_2
Current Data Parameters
NAME: NMR-201-02
INSTRUM: spec
SPECIAL: spec
PDINC: 1

F1 - Acquisition Parameters
Date: 20161115
Time: 11:15 h
DEVIATION: spec
FREQUENCY: spec
TD: 65394
DGENT: 0
NS: 18
BS: 5

F1: 600.135 MHz
FIDRES: 0.00539 Hz
DG: 5046 Hz
DF: 83.406 usec
TE: 20.0 ms
DI: 0.0050200 sec
TD: 300.1310131 MHz
SF: 0.25 usec
PS1: 20.0000000 W

F1: Processing parameters
SF: 300.13107 MHz
MS: 0 MHz
SB: 0.30 Hz
GB: 0
PC: 0.002

Current Data Parameters
NAME: NMR-251-02
INSTRUM: spec
SPECIAL: spec
PDINC: 2

F3 - Acquisition Parameters
Date: 20161125
Time: 10:52 h
DEVIATION: spec
FREQUENCY: spec
TD: 65394
DGENT: 0
NS: 18
BS: 5

F3: 600.135 MHz
FIDRES: 0.00539 Hz
DG: 5046 Hz
DF: 83.406 usec
TE: 20.0 ms
DI: 0.0050200 sec
TD: 300.1310131 MHz
SF: 0.25 usec
PS1: 20.0000000 W

F3: Processing parameters
SF: 300.13107 MHz
MS: 0 MHz
SB: 0.30 Hz
GB: 0
PC: 0.002

Current Data Parameters
NAME: NMR-251-02
INSTRUM: spec
SPECIAL: spec
PDINC: 2

F1 - Acquisition Parameters
Date: 20161115
Time: 11:15 h
DEVIATION: spec
FREQUENCY: spec
TD: 65394
DGENT: 0
NS: 18
BS: 5

F1: 600.135 MHz
FIDRES: 0.00539 Hz
DG: 5046 Hz
DF: 83.406 usec
TE: 20.0 ms
DI: 0.0050200 sec
TD: 300.1310131 MHz
SF: 0.25 usec
PS1: 20.0000000 W

F1: Processing parameters
SF: 300.13107 MHz
MS: 0 MHz
SB: 0.30 Hz
GB: 0
PC: 0.002

Current Data Parameters
NAME: NMR-251-02
INSTRUM: spec
SPECIAL: spec
PDINC: 2

F3 - Acquisition Parameters
Date: 20161125
Time: 10:52 h
DEVIATION: spec
FREQUENCY: spec
TD: 65394
DGENT: 0
NS: 18
BS: 5

F3: 600.135 MHz
FIDRES: 0.00539 Hz
DG: 5046 Hz
DF: 83.406 usec
TE: 20.0 ms
DI: 0.0050200 sec
TD: 300.1310131 MHz
SF: 0.25 usec
PS1: 20.0000000 W

F3: Processing parameters
SF: 300.13107 MHz
MS: 0 MHz
SB: 0.30 Hz
GB: 0
PC: 0.002

Current Data Parameters
NAME: NMR-251-02
INSTRUM: spec
SPECIAL: spec
PDINC: 2

F1 - Acquisition Parameters
Date: 20161115
Time: 11:15 h
DEVIATION: spec
FREQUENCY: spec
TD: 65394
DGENT: 0
NS: 18
BS: 5

F1: 600.135 MHz
FIDRES: 0.00539 Hz
DG: 5046 Hz
DF: 83.406 usec
TE: 20.0 ms
DI: 0.0050200 sec
TD: 300.1310131 MHz
SF: 0.25 usec
PS1: 20.0000000 W

F1: Processing parameters
SF: 300.13107 MHz
MS: 0 MHz
SB: 0.30 Hz
GB: 0
PC: 0.002

Current Data Parameters
NAME: NMR-251-02
INSTRUM: spec
SPECIAL: spec
PDINC: 2

F3 - Acquisition Parameters
Date: 20161125
Time: 10:52 h
DEVIATION: spec
FREQUENCY: spec
TD: 65394
DGENT: 0
NS: 18
BS: 5

F3: 600.135 MHz
FIDRES: 0.00539 Hz
DG: 5046 Hz
DF: 83.406 usec
TE: 20.0 ms
DI: 0.0050200 sec
TD: 300.1310131 MHz
SF: 0.25 usec
PS1: 20.0000000 W

F3: Processing parameters
SF: 300.13107 MHz
MS: 0 MHz
SB: 0.30 Hz
GB: 0
PC: 0.002

Current Data Parameters
NAME: NMR-251-02
INSTRUM: spec
SPECIAL: spec
PDINC: 2

F1 - Acquisition Parameters
Date: 20161115
Time: 11:15 h
DEVIATION: spec
FREQUENCY: spec
TD: 65394
DGENT: 0
NS: 18
BS: 5

F1: 600.135 MHz
FIDRES: 0.00539 Hz
DG: 5046 Hz
DF: 83.406 usec
TE: 20.0 ms
DI: 0.0050200 sec
TD: 300.1310131 MHz
SF: 0.25 usec
PS1: 20.0000000 W

F1: Processing parameters
SF: 300.13107 MHz
MS: 0 MHz
SB: 0.30 Hz
GB: 0
PC: 0.002

Current Data Parameters
NAME: NMR-251-02
INSTRUM: spec
SPECIAL: spec
PDINC: 2

F3 - Acquisition Parameters
Date: 20161125
Time: 10:52 h
DEVIATION: spec
FREQUENCY: spec
TD: 65394
DGENT: 0
NS: 18
BS: 5

F3: 600.135 MHz
FIDRES: 0.00539 Hz
DG: 5046 Hz
DF: 83.406 usec
TE: 20.0 ms
DI: 0.0050200 sec
TD: 300.1310131 MHz
SF: 0.25 usec
PS1: 20.0000000 W

F3: Processing parameters
SF: 300.13107 MHz
MS: 0 MHz
SB: 0.30 Hz
GB: 0
PC: 0.002
