Catalytic Asymmetric Formal Total Synthesis of
(-)-Triptophenolide and (+)-Triptolide.

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General Experimental Procedures: All reactions were performed with dry solvents under anhydrous conditions, unless otherwise noted. Dry tetrahydrofuran (THF) were distilled over sodium. Dichloromethane were distilled over calcium hydride. Starting materials and reagents used in reactions were obtained commercially from Aladdin, Acros, Aldrich and were used without purification, unless otherwise indicated. Silica gel (200-300 mesh, Qingdao Marine Chemical Ltd., China), light petroleum ether (bp 60–90 °C) and ethyl acetate were used for product purification by flash column chromatography. Claisen rearrangement reaction was performed by CEM Discover microwave synthesizer. Proton nuclear magnetic resonance (1H-NMR) spectra were recorded on Bruker Avance 400 and 500 spectrometer at 400 and 500 MHz. Carbon-13 nuclear magnetic resonance (13C-NMR) was recorded at 100 and 125 MHz. IR spectra were recorded with KBr pellets on a Bruker Tensor 27 FT-IR spectrometer. Mass spectra were recorded on a VG-Auto-Spec-3000 spectrometer.

Experimental

To a solution of bromophenol (20 g, 8.0 mmol) in dry CH2Cl2 (39 mL) was added
pyridine (12 mL) at 0 °C, then AcCl (12 mL) was injected drop-wise slowly under argon. The mixture was stirred at room temperature for 3 h. The reaction was quenched with H2O and extracted with CH2Cl2 (3×100 mL). The combined organic phases were washed with H2O, brine, dried over Na2SO4 and concentrated under reduced pressure.

To a solution of the crude acetic 3-bromo benzoate (12.5 g) in dry CH2Cl2 (40 mL) was added AlCl3 (28 g, 0.21mol) portion-wise at room temperature. The reaction mixture was stirred at 130 °C for 3 h. The resulting mixture was cooled at room temperature and dissolved with CH2Cl2, the reaction was quenched with H2O, the aqueous layer was extracted with CH2Cl2 (3×100 mL). The combined organic phases were washed with H2O, brine, dried over Na2SO4 and concentrated under reduced pressure. The product was used directly in the next step.

To a suspension of phenol (25.2 g, 0.1mol), anhydrous Cs2CO3 (47 g, 0.15mol, 1.5eq) and KI (16.6 g, 0.1 mol, 1.0eq) in CH3CN (100 mL) was added BnBr (12 mL, 0.1mol, 1.0eq), and the mixture was stirred at room temperature until the starting phenol was completely consumed. The mixture was filtered and the solvent was removed by rotary evaporation. The crude product was purified by flash column silica gel chromatography (PET: EA = 15:1) to give ketone (24.8 g) as faint yellow solid in 93 % yield.

Methyl iodide (0.68 mL, 78.5 mmol, 1.3 eq) in ether (10 mL) under argon was added drop-wise to a suspension of magnesium turnings (260 mg, 10.86 mmol, 1.3eq) in dry ether (10 mL). After the magnesium turnings disappeared, a solution of methyl aryl ketone (2.55 g, 8.36 mmol) in dry THF (15 mL) was added slowly at 0 °C. The reaction mixture was then allowed to warm to room temperature. The reaction completed in 3 hrs . The reaction was quenched with saturated ammonium chloride, extracted with EtOAc (3×25 mL). The combined organic layers were washed with
brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure.

To a stirred solution of crude tertiary alcohol (5.2 g, 16.2 mmol) and triethylsilane (5.18 mL, 32.5 mmol, 2.0 eq) in CH₂Cl₂ (20 mL) at 0 °C was added drop-wise BF₃·Et₂O (1.62 mL, 16.2 mmol, 1.0 eq). The solution was allowed to warm to room temperature and stirred for 20 minutes. The reaction mixture was quenched with saturated aqueous NaHCO₃ (50 mL) and was extracted with CH₂Cl₂ (3 × 15 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (PET) to give bromobenzene (3.98 g) as colorless oil in 95% yield.

To a stirred -78 °C solution of bromobenzene (3.98 g, 13.1 mmol) in Toluene/THF (V:V=2:1, 30 mL) under argon was added drop-wise a solution of n-butyllithium (6.3 mL, 15.67 mmol, 1.2 eq, 2.5 M in hexane). The resulting mixture was stirred at -78 °C for 1 hour, then tri-isopropyl borate (4.56 mL, 19.65 mmol, 1.2 eq) was added slowly. The mixture was allowed to warm to room temperature and worked up with 3M HCl (20 mL). After stirring for 1 hour the resulted mixture was extracted with EtOAc (3 × 15 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (PET: EA = 1:1) to give aryl boronic acid (2.41 g) as white solid in 68% yield.
M.P.: 123-125°C. $^1$H NMR (400 MHz, DMSO) $\delta$ 6.90 (m, 3H), 6.85 – 6.79 (m, 3H), 6.76 (m, 1H), 6.60 (d, $J = 7.5$ Hz, 1H), 4.53 (s, 2H), 2.76 (m, 1H), 0.59 (d, $J = 6.9$ Hz, 6H). $^{13}$C NMR (100 MHz, DMSO) $\delta$ 155.28, 138.78, 138.09, 128.91, 128.12, 127.75, 127.45, 125.48, 117.70, 69.7, 26.95, 22.96, 22.96. IR (neat): $\nu$ 3440, 3431, 2961, 1606, 1503, 1455, 1408, 1342, 1268, 1232, 732, 694. HREIMS m/z: calcd. for C$_{16}$H$_{19}$BO$_3$ [M]$^+$: 270.1427, found: 270.1415.

Synthesis of compound 8: A screw-top dram vial was charged with a stir bar, Pd(OCOCF$_3$)$_2$ (12.5 mg, 0.0375 mmol, 5% eq), (S)-t-BuPyOX (9.2 mg, 0.045 mmol, 6% eq), NH$_4$PF$_6$ (37 mg, 0.225 mmol, 0.3 eq), and the aryl boronic acid 8 (405 mg, 1.5 mmol, 2.0 eq). The mixtures were suspended in CH$_2$Cl$_2$ (2 mL) and stirred for 2 min at room temperature. After a while a yellow suspension was formed. 3-methyl-2-cyclohexenone 7 (83 mg, 0.75 mmol, 1.0 eq) and water (68μL, 3.75 mmol, 5.0 eq) were added. The walls of the vial were rinsed with an additional portion of CH$_2$Cl$_2$ (0.5 mL). The mixture was stirred at 60°C in an oil bath for 24 hrs. Upon complete consumption of the starting material (monitored by TLC, 4:1 hexanes/EtOAc), the mixture was filtrated and the filtrate was further concentrated. The crude product was purified by flash column silica gel chromatography (PET: EA = 50:1) to give compound 9 (183 mg) as colorless oil in 73% yield and 80% ee by chiral HPLC analysis.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 7.3$ Hz, 2H), 7.38 (t, $J = 7.4$ Hz, 3H), 7.16 (d, $J = 8.0$ Hz, 1H), 6.89 – 6.84 (m, 2H), 5.08 (s, 2H), 3.35 (septet, $J = 6.9$ Hz, 1H), 2.84 (d, $J = 14.2$ Hz, 1H), 2.42 (d, $J = 14.2$ Hz, 1H), 2.29 (t, $J = 6.8$ Hz, 2H), 2.16 – 2.10 (m, 1H), 1.91 – 1.82 (m, 2H), 1.62 (m, 1H), 1.29 (s, 3H), 1.22 (d, $J = 6.9$ Hz, 6H). $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 211.67, 155.78, 145.94, 137.53, 135.19, 128.50, 128.50, 127.73, 127.27, 127.27, 126.11, 118.02, 109.72, 70.03 (s, 3H), 53.27 (s, 3H),
42.84 (s, 2H), 40.85 (s, 3H), 38.12 (s, 3H), 29.95, 26.62, 22.71, 22.69, 22.05. IR (neat): ν 2960, 2871, 1712, 1610, 1503, 1455, 1412, 1236, 1163, 1025, 821, 739, 698. HREIMS m/z: calcd. for C_{23}H_{28}O_{2} [M]^{+}: 336.2089, found: 336.2097

Ketone 9 (174 mg, 0.52 mmol) and palladium on carbon (18 mg) were added to a round bottom flask and were dried under high vacuum. Then, 1 mL of EtOAc and 1 mL of EtOH were added. The mixture were degassed twice and stirred overnight at room temperature with H_{2} balloon. The crude was filtered through celite and eluted with EtOAc. The filtrate was concentrated and the crude product was purified by flash column silica gel chromatography (PET: EA = 100:1) to give phenol 10 (124 mg) as colourless oil in 97 % yield.

\[ ^{1}H \text{ NMR (400 MHz, CDCl}_3) \delta 7.12 (d, J = 8.1 \text{ Hz, 1H}), 6.83 (d, J = 8.1 \text{ Hz, 1H}), 6.74 (s, 1H), 5.84 (br.s, 1H), 3.31 – 3.08 (septet, J = 6.9 \text{ Hz, 1H}), 2.86 (d, J = 14.3 \text{ Hz, 1H}), 2.40 (d, J = 14.3 \text{ Hz, 1H}), 2.31 (t, J = 6.9 \text{ Hz, 2H}), 2.18 – 2.12 (m, 1H), 1.85 (m, 2H), 1.69 – 1.57 (m, 1H), 1.29 (s, 3H), 1.22 (d, J = 6.9 \text{ Hz, 6H}). \]

\[ ^{13}C \text{ NMR (100 MHz, CDCl}_3) \delta 212.88, 152.99, 145.91, 132.24, 126.50, 117.77, 113.05, 53.10, 42.61, 40.82, 38.05, 30.28, 26.69, 22.56, 22.54, 22.02. IR(neat): v 3380, 3359, 2960, 2822, 1697, 1616, 1580, 1418, 1309, 1235, 1159, 936, 817. \]

HREIMS m/z: calcd. for C_{16}H_{22}O_{2} [M]^{+}: 246.1620, found: 246.1618.

To a suspension of phenol 10 (249 mg, 1.0 mmol), anhydrous Cs_{2}CO_{3} (2.02 mmol, 2.0 eq) and KI (1.01 mmol, 1.0 eq) in CH_{3}CN (3 mL) was added allyl bromide (1.11
mol, 1.1eq), and the mixture was stirred at room temperature until the starting ketone was completely consumed. The mixture was filtered, and the solvent was removed by rotary evaporation. The crude product was purified by flash column silica gel chromatography (PET: EA = 50:3) to give compound 6 (257 mg) as colourless oil in 89 % yield.

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta: \]

- 7.16 (d, J = 8.0 Hz, 1H)
- 6.87 (d, J = 8.0, 1H)
- 6.78 (s, 1H)
- 6.16 – 6.01 (m, 1H)
- 5.45 (d, J = 17.3, 1H)
- 5.28 (d, J = 10.6, 1H)
- 4.55 (d, J = 5.0 Hz, 2H)
- 3.32 (sept, J = 6.9 Hz, 1H)
- 2.86 (d, J = 14.2 Hz, 1H)
- 2.43 (d, J = 14.2 Hz, 1H)
- 2.31 (t, J = 6.8 Hz, 2H)
- 2.16 (m, 1H)
- 1.94 – 1.84 (m, 2H)
- 1.71 – 1.65 (m, 1H)
- 1.32 (s, 3H)
- 1.22 (d, J = 6.9 Hz, 6H)

\[ \text{C NMR (100 MHz, CDCl}_3\text{) } \delta: \]

- 211.67
- 155.72
- 145.89
- 135.06
- 133.71
- 126.07
- 117.89
- 116.83
- 109.62
- 68.84
- 53.27
- 42.82
- 40.84
- 38.13
- 29.96
- 26.65
- 22.62
- 22.62
- 22.04

IR (neat): \( \nu \) 2960, 2871, 1713, 1611, 1571, 1544, 1413, 1236, 1165, 1026, 927, 821.

HREIMS m/z: calcd. for C\(_{19}\)H\(_{26}\)O\(_2\) [M]\(^+\): 286.1933, found: 286.1927

To a solution of carbonyl compound 6 (280 mg, 0.98 mmol) and absolute methanol (1 mL), sodium borohydride (74 mg, 1.96 mmol, 2.0eq) was added in ports at 0 °C. The solution was then stirred at room temperature and the progress of the reaction was monitored by TLC. The reaction was quenched with saturated ammonium chloride, extracted with EtOAc (3×5 mL). The combined organic layers were washed with brine, dried over Na\(_2\)SO\(_4\), filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (PET: EA = 6:1) to give corresponding alcohol 14 (256 mg) as colourless oil in 93 % yield.

\[ \text{H NMR (400 MHz, CDCl}_3\text{) } \delta: \]

- 7.15 (d, J = 8.0 Hz, 1H)
- 6.93 (d, J = 8.0, 1H)
- 6.82 (s, 1H)
- 6.15 – 6.02 (m, 1H)
- 5.44 (d, J = 17.3, 1H)
- 5.27 (d, J = 10.5, 1H)
- 4.59 – 4.53 (m, 2H)
- 3.96 – 3.58 (m, 1H)
- 3.31 (J = 6.9 Hz, 1H)
- 2.55 (d, J = 12.8 Hz, 1H)
- 2.24 (d,
\[ J = 12.8 \text{ Hz, 1H}, 2.04 - 1.26 \text{ (m, 6H)}, 1.22 \text{ (d, } J = 6.9 \text{ Hz, 6H)}, 1.18 \text{ (s, 3H)}. \]

\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 155.92, 149.93, 145.38, 133.91, 125.96, 118.37, 116.76, 109.92, 68.99, 67.56, 46.99, 39.93, 36.90, 35.87, 35.26, 26.64, 22.69, 22.69, 21.06. \]

\[ \text{IR (neat): } \nu 3338, 2934, 2864, 1610, 1560, 1502, 1455, 1410, 1242, 1106, 1015, 926, 820. \]

\[ \text{HREIMS } m/z: \text{ calcd. for C}_{19}\text{H}_{28}\text{O}_2 [M]^+: 288.2089, \text{ found: 288.2090} \]

\[ \text{A mixture of compound 14 (275 mg, 4.26 mmol) and N,N-diethylaniline (1 mL) was added to a Microwave test tube (10 mL) equipped with a magnetic stirring bar and a rubber cap. The test tube was subjected to microwave reactor (CEM, Discover) at 250^\circ \text{C (power 300 W)} \text{ for 40 minutes. After completion of the reaction, the tube was removed, cooled to room temperature, neutralized with hydrochloric acid (3 molL}^{-1}\text{)} \text{ and then extracted with (3×25 mL). The combined organic layer was washed successively with water (25 mL) and brine (25 mL), dried over Na}_2\text{SO}_4, \text{ filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (PET to give phenol 15 (195 mg) as yellow solid in 71% yield.} \]

\[ ^{1}\text{H NMR (400 MHz, CDCl}_3\text{)} \delta 7.05 \text{ (d, } J = 8.3 \text{ Hz, 1H)}, 6.94 \text{ (d, } J = 8.3 \text{ Hz, 1H)}, 6.26 - 5.98 \text{ (m, 1H)}, 5.26 \text{ (d, } J = 17.3 \text{ Hz, 1H)}, 5.13 \text{ (d, } J = 17.3 \text{ Hz, 1H)}, 3.81 - 3.48 \text{ (m, 3H)}, 3.21 \text{ (septet, } J = 6.9 \text{ Hz, 1H)}, 2.63 \text{ (d, } J = 13.1 \text{ Hz, 1H)}, 2.39 \text{ (d, } J = 13.1 \text{ Hz, 1H)}, 1.95 - 1.71 \text{ (m, 2H)}, 1.74 - 1.52 \text{ (m, 3H)}, 1.33 \text{ (s, 3H)}, 1.18 \text{ (d, } J = 6.9 \text{ Hz, 6H}). \]

\[ ^{13}\text{C NMR (100 MHz, CDCl}_3\text{)} \delta 153.36, 142.28, 136.22, 133.32, 124.87, 124.01, 120.68, 116.94, 67.88, 48.68, 41.37, 38.85, 35.98, 33.01, 32.25, 32.19, 22.69, 22.63, 21.56. \]

\[ \text{IR (neat): } \nu 3537, 3359, 2957, 2866, 1555, 1407, 1295, 1239, 1192, 1099, 1056, 1013, 939. \]

\[ \text{HREIMS } m/z: \text{ calcd. for C}_{19}\text{H}_{28}\text{O}_2 [M]^+: 288.2089, \text{ found: 288.2082} \]
Compound 15 (195 mg, 0.68 mmol, 1.0eq) was dissolved in dry Me₂CO (2.0 mL), and to the solution was added powdered potassium carbonate (169 mg, 1.22 mmol, 1.8eq) and methyl iodide (63 µL, 1.01 mmol, 1.5eq). The reaction mixture was stirred at 40°C for 7 h under Ar atmosphere and light-protecting condition. The solvent was evaporated under reduced pressure. Ice cooled H₂O (10 mL) was added to the residue and the aqueous phase was extracted with EtOAc (20 mL×3). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure afforded the corresponding compound 16 (203 mg), which was immediately used in the next step without further purification.

PCC (288 mg, 1.34 mmol, 2.0eq) and Celite (600 mg) were added to a solution of 16 (203 mg, mmol) in CH₂Cl₂ (2 mL). The mixture was stirred at room temperature overnight and then filtered through silica gel. pad. Removal of the solvent under reduced pressure to give crude product. It was then purified by flash column silica gel chromatography (PET: EA = 50:1) to give ketone 5 (178 mg) as colourless oil in 87% yield in 2 steps.

¹H NMR (400 MHz, CDCl₃) δ 7.08 (d, J = 8.5 Hz, 1H), 7.04 (d, J = 8.5 Hz, 1H), 5.99 (m, 1H), 5.02 (d, J = 9.9 Hz, 1H), 4.80 (d, J = 9.9 Hz, 1H), 3.71 (s, 3H), 3.65 (s, 2H), 3.32 – 3.21 (m, 1H), 2.94 (d, J = 14.3 Hz, 1H), 2.41 (d, J = 12.0 Hz, 2H), 2.29 (s, 2H), 1.94 – 1.76 (m, 3H), 1.41 (s, 3H), 1.21 (d, J = 6.9 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ 211.90, 157.76, 143.33, 140.19, 137.95, 130.94, 124.80, 123.35, 114.78, 61.69, 55.93, 44.18, 40.84, 36.98, 32.54, 28.66, 26.33, 24.00,
23.82,22.10. IR (neat): ν 2962,2872,1712,1457,1400,1317,1288,1228,1029,910,823. HREIMS m/z: calcd. for C_{20}H_{28}O_{2} [M]^{+}:300.2089, found:300.2081

To a stirred mixture of olefin 5 (117 mg, 0.39 mmol) and RuCl₃ (3mg, 3.5 mol %) in CH₃CN (1.2 mL) and distilled water (0.2 mL) was added in portions NaIO₄ (164 mg, 0.765 mmmol,2.0eq) over a period of 5 min at room temperature. The color turned from black to yellow immediately. The reaction was monitored by TLC. After completion in 0.5 h, the reaction was quenched with saturated aqueous solution of Na₂S₂O₃, extracted with EtOAc (3×10 mL). The combined organic layers were washed with water and brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (PET: EA = 10:1) to give desired aldehyde 17 (88 mg) as colourless oil in 75% yield.

^1^H NMR (400 MHz, CDCl₃) δ 9.58 (s, 1H), 7.15 (d, J = 8.4 Hz, 1H), 7.07 (d, J = 8.4 Hz, 1H), 3.83 (s, 2H), 3.62 (s, 3H), 3.24 (septet, J = 6.9 Hz, 1H), 2.93 (d, J = 14.4 Hz, 1H), 2.41 (d, J = 14.4 Hz, 1H), 2.29 (t, J = 6.9 Hz, 2H), 1.95 – 1.81 (m, 2H), 1.75 – 1.42 (m, 2H), 1.38 (s, 3H), 1.21 (d, J = 6.9, Hz, 6H). ^1^C NMR (100 MHz, CDCl₃) δ 211.19, 199.59, 157.38, 143.93, 140.23, 126.09, 124.89, 123.80, 60.10, 55.68, 43.81, 43.74, 40.66, 37.10, 28.30, 26.37, 23.80, 23.75,21.75. IR (neat): ν 2959, 2873, 1965, 1714, 1613, 1570, 1461, 1407, 1252,1036, 953, 821. HREIMS m/z: calcd. for C_{19}H_{26}O_{3} [M]^{+}:302.1882, found:302.1876

Compound 17 (45 mg, 0.15 mmol) was dissolved in dry Toluene (2.0 mL), the solution was stirred at 100°C and then added catalytic amount of p-TsOH (5 mg), the
progress of the reaction was monitored by TLC. The reaction was quenched with H₂O, extracted with EtOAc (3×5 mL). The combined organic layers were washed with brine, dried over Na₂SO₄, filtered, and concentrated under reduced pressure. The crude product was purified by flash column silica gel chromatography (PET: EA = 20:1) to give corresponding 19 (22 mg) as colourless oil in 51% yield. ¹H NMR (400 MHz, CDCl₃) δ 7.14 (d, J = 8.1 Hz, 1H), 7.05 (d, J = 8.1 Hz, 1H), 6.85 (dd, J = 9.9, 2.8 Hz, 1H), 6.44 (dd, J = 9.9, 2.3 Hz, 1H), 3.72 (s, 3H), 3.41 (s, 1H), 3.31 (septet, J = 6.9 Hz, 1H), 2.23 (m, 6H), 1.23 (d, J = 6.8 Hz, 6H), 0.97 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 209.60, 153.92, 143.41, 139.92, 125.76, 125.63, 123.76, 122.36, 118.73, 62.39, 55.06, 42.65, 40.73, 34.53, 26.22, 23.80, 23.76, 22.71, 20.16. IR (neat): ν 2958, 1716, 1668, 1569, 1583, 1547, 1463, 1327, 1139, 903. HREIMS m/z: calcd. for C₁₉H₂₄O₂ [M]+: 284.1776, found: 284.1779

19 (15 mg, 0.05 mmol) and palladium on carbon (3 mg) were added to a round bottom flask and were dried under high vacuum. Then, 1 mL of EtOAc and 1 mL of EtOH were added. The resulting mixture were equipped with a H₂ balloon and purged twice. The mixture was stirred overnight at room temperature. The crude was filtered off over celite and eluted with EtOAc. The filtrate was concentrated. The crude product was purified by flash column silica gel chromatography (PET: EA = 100:1) to give product 4 (11 mg) as colourless amorphphs in 93% yield and 83% ee by chiral HLPC.

¹H NMR (400 MHz, CDCl₃) δ 7.08 (d, J = 3.9 Hz, 2H), 3.72 (s, 3H), 3.29 (septet, 6.8 Hz, 1H), 3.06 (dd, J = 17.7, 6.0 Hz, 1H), 2.67 – 2.35 (m, 5H), 2.12 – 1.72 (m, 5H), 1.56 (s, 3H), 1.22 (dd, J = 6.7, 3.4 Hz, 6H), 1.05 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 212.54, 155.12, 144.65, 138.93, 128.52, 124.04, 121.03, 60.54, 55.10, 42.42, 40.88, 37.20, 26.14, 23.92, 23.87, 23.66, 23.10, 22.59, 17.05. IR (neat): ν 2960, 1714, 1478,
1437, 1424, 1307, 1300, 1291, 1116, 1054, 1032, 1008, 948, 816. HREIMS m/z: calcd.
for C_{10}H_{26}O_{2} [M]^+:, found: 286.1936

NOTE: Spectra of cis-isomer of 4 were loaded for the reason that after established the
structure cis-isomer of 4 by HMQC and ROESY 2D NMR analysis, it will indirectly
prove the correct assignment of 18 and trans isomer of 4.
Spectra for compounds
