Supporting Information

Preparation of Distant Quaternary Carbon Stereocenters by Double Selective Ring-Opening of 1,1-Biscyclopropyl Methanol Derivatives

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Author Contributions

The manuscript was written through contributions of all the authors.
General experimental details

Unless stated otherwise, reactions were conducted in flame-dried glassware under a positive pressure of argon. Ether and THF were dried from Pure-Solv® Purification System (Innovative Technology©). All other commercially obtained reagents were used as received. Dichloromethane was distilled from CaH₂. Copper iodide, rhodium acetate dimer, AlMe₃ (2M in hexane), AlEt₃ (1M in hexane) were purchased from Aldrich. [Cu(MeCN)₄]PF₆, (R,S)-JOSIPHOS and dppf were purchased from Aldrich. All alkyl Grignard reagents were prepared from the corresponding alkyl bromides. Thin layer chromatography (TLC) was conducted with Merck silica gel 60 F254 pre-coated plates (0.25 mm) and visualized by exposure to UV light (254 nm) or stained with anisaldehyde, phosphomolybdic acid, or potassium permanganate. Purification by column chromatography was performed using Fluka silica gel 60Å (40-63mm, 230-400 mesh). ¹H-NMR and ¹³C-NMR spectra were recorded on a Bruker© spectrometers AVIII400, using CDCl₃ (unless otherwise specified) as solvent. Chemical shifts are reported in parts per million (ppm) with respect to the residual solvent signal CDCl₃ (¹H NMR: δ = 7.20 ppm; ¹³C NMR: δ = 77.00 ppm). Peak multiplicities are reported as follows: s = singlet, bs = broad singlet, d = doublet, t = triplet, dd = doublet of doublets, td = triplet of doublets, m = multiplet. The GC chromatograms were recorded using Varian© 3800 apparatus with Varian© CP-Sil 8CB® column. High-resolution mass spectra (HRMS) were obtained by the mass spectrometry facility at the Technion-Israel Institute of Technology. Reactions were monitored by gas chromatography spectrometry (GC) using an Agilent Technologies 7820A GC with an Agilent Technologies 19091J-413 (30 m × 0.3 mm) column or (GC-MS) Thermo Scientific TM Ion Trap GC/MS: ITQTM 900 with a Varian Factor Four Capillary column (VF-5 ms, 30m × 0.25mm). Crystal XRD data were collected on a diffractometer Nonius Kappa CCD at Schulich Faculty of Chemistry at Technion-Israel Institute of Technology. Enantiomeric excesses were determined by chiral-HPLC using Agilent© 1100 Series line with CHIRALCEL® OD (0.46 cm Ø×25 cm).
General procedure for the double carbometalation reaction leading to 10a<sub>1-5</sub> and 10b<sub>1-5</sub>

To a suspension of CuI (2 mmol, 1 equiv.) in 16 mL of THF, MeLi (1.6 M in diethyl ether, 2 mmol, 1 equiv.) was added dropwise at -45 °C. The reaction mixture was allowed to stir for 30 min after which cyclopropene ester 6 (2 mmol dissolved in 2 mL of THF, 1 equiv.) was added dropwise over a period of 5 min. The reaction mixture was stirred at -45 °C until TLC shows complete consumption of the starting cyclopropene 6 (the reaction was usually completed in 45 min). Then, methylphenyl cyclopropene (2.4 mmol, 1.2 equiv.) dissolved in 2 mL of THF was added over 15 min. Allow the reaction to slowly warm up from -45 °C to -20 °C for 1.5 h (until consumption of the second cyclopropene monitored by TLC). After cooling the reaction temperature to -30 °C, allyl bromide (5 equiv.) was added, and the reaction mixture was slowly warm up to -20 °C for 1 h. The reaction was hydrolyzed with a 3:1 aqueous saturated solution of ammonium chloride and ammonium hydroxide 20 mL (10 mL per mmol). The aqueous layer was extracted twice with diethyl ether and the combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. Products were isolated through column chromatography using 1% diethyl ether and petroleum ether as eluents to get the two products in 15-21% yield.

General procedure for the reduction of 10a<sub>1-5</sub> and 10b<sub>1-5</sub> into 4a<sub>1-5</sub> and 4b<sub>1-5</sub>

To a well stirred solution of 10a,b (0.5mmol, 1 equiv.) in diethyl ether (5 mL) at -35 °C was added DIBAL-H (2 equiv., 1 M solution in hexane) under argon atmosphere. The reaction was generally completed in 60 min and then hydrolyzed with a solution of ammonium chloride (10 mL per mmol). The formation of a white precipitate was observed after 10 min, which becomes clearer after the addition of 1 N HCl and further stirring. The aqueous layer was extracted twice with diethyl ether and the combined organic phases were washed with brine, dried over MgSO<sub>4</sub>, filtered, and concentrated under reduced pressure. The crude compound was then purified by column chromatography using 10-40% diethyl ether and petroleum ether to provide 4a,b in 70-80% yields.

General procedure for the isomerization (compounds 11a-c)

The alkene zipper catalyst (CAS Number: 930601-66-4) (5 mol%, CAUTION: the catalyst is air sensitive and thus should be handled under an inert atmosphere) was added into a flame dried round bottom flask under Ar atmosphere. 2 mL of dichloroethane was then added followed by a solution of alcohol 10 (0.5 mmol) in 0.5 mL of dichloroethane. The reaction mixture was stirred for 10 minutes at room temperature until apparition of an homogeneous solution and the flask was then placed on a pre-heated oil bath at 50 °C for 20-24 h. After completion of the reaction (as monitored by TLC), the reaction mixture was cooled down to room temperature, diluted with Et<sub>2</sub>O (15 mL) and filtered over a small bed of silica. The combined diethyl ether fractions were concentrated, and subjected to a column chromatography to provide the products 11a-c.

General procedure for the remote Heck arylation of ω-ene biscyclopropyl carbinol 4a<sub>1-5</sub>
A magnetic stirring bar was placed into a vial of 10 mL capacity that was charged with the alcohol (0.12 mmol), aryl iodide (1.5 equiv.), Pd(OAc)$_2$ (15 mol%), (p-CF$_3$C$_6$H$_4$)$_3$P (15 mol%), NaHCO$_3$ (2.5 equiv.), pre-activated molecular sieves (4Å size, powdered, 30 mg/mmol) and tetrabutylammonium chloride (TBACl) (2 equiv.) followed by addition of EtOAc (1 mL). The reaction mixture was then purged with argon and sealed with a Teflon cap. The reaction mixture was stirred for 10 min at room temperature to obtain a homogeneous solution and was then placed on a pre-heated oil bath at 85-90 °C for 20-24 h. After completion of the reaction (as monitored by TLC), the reaction mixture was cooled down to room temperature, diluted with Et$_2$O (15 mL) and filtered over a small bed of silica. The combined diethyl ether fractions were concentrated, and the crude reaction mixture was purified by column chromatography to provide the expected products.

General procedure for the remote Heck arylation of (E)-propenyl biscyclopropyl carbinol 11a-c

A magnetic stirring bar was placed into a vial of 10 mL capacity that was charged with the alcohol (0.15 mmol), aryl iodide (1.5 equiv.), Pd(OAc)$_2$ (15 mol%), (p-CF$_3$C$_6$H$_4$)$_3$P (15 mol%), NaHCO$_3$ (2.5 equiv.), pre-activated molecular sieves (4Å size, powdered, 30 mg/mmol) and tetrabutylammonium chloride (TBACl) (2 equiv.) followed by addition of toluene (1 mL). The reaction mixture was then purged with argon and sealed with a Teflon cap. The reaction mixture was stirred for 10 min at room temperature to obtain a homogeneous solution and was then placed on a pre-heated oil bath at 95-100 °C for 20-24 h. After completion of the reaction (as monitored by TLC), the reaction mixture was cooled down to room temperature, diluted with Et$_2$O (15 mL) and filtered over a small bed of silica. The combined diethyl ether fractions were concentrated, and the crude reaction mixture was purified by column chromatography to provide the expected products.
Characterization data for 4a₁⁻₅ and 4b₁⁻₅

Chemical formula: C₂₃H₃₅O₂; Exact mass: 342.2559. Pale-yellow oil. \( d_r > 99:01:0:0 \). \( R_f = 0.2 \) (hexane/Et₂O, 70:30, v/v).

\( ^{1}H \) NMR (400 MHz, CDCl₃) \( \delta \) 7.18 (d, \( J = 8.8 \) Hz, 2H), 6.82 (d, \( J = 8.8 \) Hz, 2H), 6.08 – 6.01 (m, 1H), 5.20 (dd, \( J = 17.2, 2.0 \) Hz, 1H), 5.07 (dd, \( J = 10.2, 1.8 \) Hz, 1H), 3.78 (s, 3H), 3.67 – 3.63 (m, 2H), 2.39 – 2.25 (m, 1H), 2.23 – 2.12 (m, 1H), 1.44 – 1.31 (m, 10H), 1.21 (s, 3H), 0.92 (t, \( J = 7.2 \) Hz, 3H), 0.86 – 0.81 (m, 2H), 0.25 (dd, \( J = 8.8, 5.2 \) Hz, 1H). \( ^{13}C \) NMR (100 MHz, CDCl₃) \( \delta \) 159.27, 159.04, 139.40, 130.74, 129.64, 114.05, 103.31, 102.59, 101.51, 114.51, 113.56, 63.34, 55.17, 35.84, 34.41, 29.19, 28.57, 26.79, 25.90, 25.80, 24.67, 24.20, 23.14, 20.35, 16.65, 14.08. HRMS (APCI): \( m/z \) calculated for C₂₃H₃₅O₂[\( \text{M}+\text{H}\)^+]: 343.2632, found 343.2621.

Chemical formula: C₂₁H₃₀O₂; Exact mass: 314.2246. Pale-yellow oil. \( d_r > 99:01:0:0 \). \( R_f = 0.2 \) (hexane/Et₂O, 70:30, v/v). \( ^{1}H \) NMR (400 MHz, CDCl₃) \( \delta \) 7.11 (t, \( J = 7.8 \) Hz, 1H), 6.78 – 6.72 (m, 2H), 6.63 – 6.60 (m, 1H), 6.00 – 6.90 (m, 1H), 5.14 – 5.08 (m, 1H), 5.0 – 4.97 (m, 1H), 3.71 (s, 3H), 3.62 – 3.52 (m, 2H), 2.33 – 2.26 (m, 1H), 2.19 – 2.11 (m, 1H), 1.38 – 1.31 (m, 2H), 1.26 (s, 3H), 1.22 – 1.15 (m, 1H), 1.11 (s, 3H), 0.92 (t, \( J = 7.6 \) Hz, 3H), 0.83 – 0.73 (m, 2H), 0.17 (dd, \( J = 8.8, 5.2 \) Hz, 1H). \( ^{13}C \) NMR (101 MHz, CDCl₃) \( \delta \) 159.47, 151.40, 138.56, 129.18, 119.41, 114.62, 113.30, 110.27, 63.31, 55.07, 34.59, 28.71, 28.51, 27.35, 26.48, 26.21, 25.64, 24.10, 19.70, 16.11, 11.26. HRMS (APCI): \( m/z \) calculated for C₂₁H₃₀O₂[M–OH]^+: 297.2213, found 297.2220.

Chemical formula: C₂₂H₃₃O₃; Exact mass: 344.2351. Pale-yellow oil. \( d_r > 99:01:0:0 \). \( R_f = 0.3 \) (hexane/Et₂O, 60:40, v/v). \( ^{1}H \) NMR (400 MHz, CDCl₃) \( \delta \) 7.01 (d, \( J = 8.0 \) Hz, 1H), 6.33 – 6.27 (m, 2H), 6.05 – 5.95 (m, 1H), 5.12 – 5.07 (m, 1H), 4.98 – 4.95 (m, 1H), 3.72 (s, 3H), 3.70 (s, 3H), 3.56 (s, 2H), 2.36 – 2.28 (m, 1H), 2.13 – 2.06 (m, 1H), 1.42 – 1.28 (m, 3H), 1.17 (s, 3H), 1.14 (s, 3H), 0.94 (t, \( J = 7.2 \) Hz, 3H), 0.81 – 0.77 (m, 1H), 0.72 – 0.67 (m, 1H), 0.15 (dd, \( J = 8.8, 5.2 \) Hz, 1H). \( ^{13}C \) NMR (101 MHz, CDCl₃) \( \delta \) 159.27, 159.04, 139.40, 130.74, 129.64, 114.05, 103.31, 98.46, 63.51, 55.28, 54.93, 34.19, 28.80, 28.72, 25.60, 25.16, 25.08, 24.13, 23.46, 19.68, 15.25, 11.27. HRMS (APCI): \( m/z \) calculated for C₂₂H₃₃O₃[M+H]^+: 345.2430, found 345.2442.

Chemical formula: C₂₂H₃₂O₃; Exact mass: 344.2351. Pale-yellow oil. \( d_r > 99:01:0:0 \). \( R_f = 0.2 \) (hexane/Et₂O, 70:30, v/v). \( ^{1}H \) NMR (400 MHz, CDCl₃) \( \delta \) 6.73 – 6.68 (m, 3H), 6.02 – 5.92 (m, 1H), 5.15 – 5.01 (m, 1H), 5.0 – 4.98 (m, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.63 – 3.52 (m, 2H), 2.34 – 2.26 (m, 1H), 2.2 – 2.11 (m, 1H), 1.36 – 1.31 (m, 2H), 1.24 (s, 3H), 1.18 – 1.33 (m, 4H), 0.93 (t, \( J = 7.6 \) Hz, 3H), 0.78 – 0.73 (m, 2H), 0.16 (dd, \( J = 8.8, 5.2 \) Hz, 1H). \( ^{13}C \) NMR
(101 MHz, CDCl3) δ 148.60, 146.93, 142.67, 138.67, 119.04, 114.56, 110.99, 110.97, 63.28, 55.86, 55.72, 34.51, 28.70, 28.49, 26.99, 26.40, 25.76, 25.58, 24.09, 19.70, 16.69, 11.24.

**HRMS (APCI):** m/z calculated for C22H33O2[M-OH]+: 327.2319, found 327.2315.

![Chemical structure 1](image1)

Chemical formula: C23H34O2; Exact mass: 342.2559. Pale-yellow oil. 

**1H NMR (400 MHz, CDCl3) δ 7.11 (t, J = 7.8 Hz, 1H), 6.76 – 6.72 (m, 2H), 6.63 – 6.60 (m, 1H), 5.98 – 5.90 (m, 1H), 5.13 – 5.07 (m, 1H), 5.0 – 4.96 (m, 1H), 3.70 (s, 3H), 3.59 – 3.51 (m, 2H), 2.32 – 2.24 (m, 1H), 2.19 – 2.14 (m, 1H), 1.34 – 1.18 (m, 10H), 1.11 (s, 3H), 0.85 – 0.80 (m, 3H), 0.79 – 0.72 (m, 2H), 0.17 (dd, J = 8.8, 5.2 Hz, 1H).

**13C NMR (101 MHz, CDCl3) δ 159.48, 151.43, 138.58, 129.18, 119.43, 114.62, 113.32, 110.30, 63.39, 55.08, 35.87, 34.49, 29.22, 28.53, 27.28, 26.54, 24.76, 24.21, 23.16, 20.35, 16.17, 14.10. **HRMS (APCI):** m/z calculated for C23H33O[M-OH]⁺: 325.2526, found 325.2534.

![Chemical structure 2](image2)

Chemical formula: C23H34O2; Exact mass: 342.2559. Pale-yellow oil. 

**1H NMR (400 MHz, CDCl3) δ 7.16 – 7.14 (m, 2H), 6.82 – 6.80 (m, 2H), 6.02 – 5.93 (m, 1H), 5.17 – 5.12 (m, 1H), 5.06 – 5.02 (m, 1H), 3.80 – 3.77 (m, 4H), 3.64 – 3.59 (m, 1H), 2.28 – 2.18 (m, 2H), 1.40 – 1.24 (m, 10H), 0.91 (t, J = 7.2 Hz, 3H), 0.86 – 0.79 (m, 2H), 0.25 (dd, J = 8.0, 4.0 Hz, 1H).**

**13C NMR (100 MHz, CDCl3) δ 157.43, 142.19, 138.16, 128.39, 114.63, 113.60, 63.52, 55.25, 35.63, 34.47, 29.24, 29.06, 26.08, 26.05, 25.94, 24.70, 23.71, 23.16, 19.95, 16.54, 14.12. **HRMS (APCI):** m/z calculated for C23H33O2[M+H]⁺: 343.2632, found 343.2622.

![Chemical structure 3](image3)

Chemical formula: C21H30O2; Exact mass: 314.2246. Pale-yellow oil. 

**1H NMR (400 MHz, CDCl3) δ 7.12 (t, J = 7.8 Hz, 1H), 6.76 – 6.70 (m, 2H), 6.64 – 6.61 (m, 1H), 5.94 – 5.84 (m, 1H), 5.09 – 5.04 (m, 1H), 4.97 – 4.94 (m, 1H), 3.72 – 3.69 (m, 4H), 3.57 – 3.50 (m, 1H), 2.18 – 2.14 (m, 2H), 1.36 – 1.29 (m, 2H), 1.27 (s, 3H), 1.16 – 1.14 (m, 1H), 1.06 (s, 3H), 0.91 (t, J = 7.4 Hz, 3H), 0.80 – 0.76 (m, 2H), 0.17 (dd, J = 8.4, 5.2 Hz, 1H).**

**13C NMR (101 MHz, CDCl3) δ 159.49, 151.56, 137.98, 129.19, 119.61, 114.70, 113.56, 110.15, 63.41, 55.13, 34.52, 28.96, 28.47, 26.61, 26.48, 26.42, 25.63, 23.50, 19.26, 15.99, 11.26. **HRMS (APCI):** m/z calculated for C21H29O[M-OH]⁺: 297.2213, found 297.2218.

![Chemical structure 4](image4)

Chemical formula: C22H32O3; Exact mass: 344.2351. Pale-yellow oil. 

**1H NMR (400 MHz, CDCl3) δ 6.98 (d, J = 8.0 Hz, 1H), 6.33 – 6.28 (m, 2H), 5.98 – 5.88 (m, 1H), 5.10 – 5.04 (m, 1H), 4.97 – 4.93 (m, 1H), 3.74 (s, 3H), 3.69 (s, 3H), 3.66 – 3.57 (m, 2H), 2.17 – 2.13 (m, 2H), 1.36 – 1.28 (m, 3H), 1.15 (s, 3H), 1.025 – 0.97 (m, 4H), 0.88 (t, J = 7.4 Hz, 3H), 0.53 (t, J = 8.8 Hz, 1H), 0.16 (dd, J =...
8.8, 5.2 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.11, 159.07, 138.58, 130.61, 129.90, 114.24, 103.49, 98.47, 55.26, 54.97, 34.47, 29.21, 28.74, 25.81, 25.49, 24.98, 23.98, 23.05, 18.99, 15.16, 11.26. HRMS (APCI): m/z calculated for C$_{22}$H$_{33}$O$_3$[M+H]$^+$: 345.2430, found 345.2429.

Chemical formula: C$_{22}$H$_{32}$O$_3$; Exact mass: 344.2351. Pale-yellow oil. $\textit{dr} > 99:01:0:0$. Rf = 0.1 (hexane/Et$_2$O, 70:30, v/v). $^1$H NMR (400 MHz, CDCl$_3$) $^1$H NMR (400 MHz, CDCl$_3$) δ 6.70 – 6.69 (m, 3H), 5.96 – 5.86 (m, 1H), 5.11 – 5.05 (m, 1H), 4.99 – 4.95 (m, 1H), 3.80 (s, 3H), 3.77 (s, 3H), 3.75 – 3.70 (m, 1H), 3.56 – 3.51 (m, 1H), 2.19 – 2.14 (m, 2H), 1.37 – 1.29 (m, 2H), 1.25 (s, 3H), 1.15 – 1.11 (m, 1H), 1.05 (s, 3H), 0.93 (t, $J = 7.6$ Hz, 3H), 0.81 – 0.73 (m, 2H), 0.16 (dd, $J = 8.4$, 5.2 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 148.63, 147.00, 142.75, 138.08, 119.22, 114.64, 111.04, 77.32, 77.00, 76.68, 63.43, 55.90, 55.84, 34.59, 28.95, 28.45, 26.39, 26.26, 26.10, 25.60, 23.50, 19.29, 16.54, 11.24. HRMS (APCI): m/z calculated for C$_{22}$H$_{33}$O$_3$[M-OH]$^+$: 327.2319, found 327.2324.

Chemical formula: C$_{23}$H$_{34}$O$_2$; Exact mass: 342.2559. Pale-yellow oil. $\textit{dr} > 99:01:0:0$. Rf = 0.1 (hexane/Et$_2$O, 70:30, v/v). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.11 (t, $J = 7.8$ Hz, 1H), 6.76 – 6.69 (m, 2H), 6.63 – 6.60 (m, 1H), 5.94 – 5.84 (m, 1H), 5.09 – 5.03 (m, 1H), 4.98 – 4.94 (m, 1H), 3.72 – 3.67 (m, 4H), 3.54 – 3.49 (m, 1H), 2.21 – 2.11 (m, 2H), 1.33 – 1.13 (m, 10H), 1.06 (s, 3H), 0.83 (t, $J = 7.2$ Hz, 3H), 0.80 – 0.73 (m, 2H), 0.17 (dd, $J = 8.4$, 5.2 Hz, 1H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 159.46, 151.53, 137.96, 129.16, 119.57, 114.67, 113.52, 110.13, 63.40, 55.08, 35.56, 34.36, 29.20, 28.96, 26.49, 26.43, 24.68, 23.60, 23.13, 19.93, 15.98, 14.10. HRMS (APCI): m/z calculated for C$_{23}$H$_{33}$O$_3$[M-OH]$^+$: 325.2526, found 325.2530.

Chemical formula: C$_{23}$H$_{34}$O$_2$; Exact mass: 342.2559. Pale-yellow oil. $\textit{dr} > 99:01:0:0$. Rf = 0.3 (hexane/Et$_2$O, 70:30, v/v). $^1$H NMR (400 MHz, CDCl$_3$) δ 7.09 (d, $J = 8.8$ Hz, 2H), 6.73 (d, $J = 8.8$ Hz, 2H), 5.67 – 5.59 (m, 1H), 5.40 – 5.33 (m, 1H), 3.70 (s, 3H), 3.65 – 3.60 (m, 1H), 3.55 – 3.50 (m, 1H), 1.72 – 1.67 (m, 4H), 1.36 – 1.18 (m, 9H), 1.11 (s, 3H), 0.94 – 0.89 (m, 1H), 0.86 – 0.82 (m, 3H), 0.77 – 0.73 (m, 1H), 0.29 (dd, $J = 8.8$, 5.2 Hz, 1H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 157.51, 141.70, 128.20, 127.65, 126.91, 113.63, 63.25, 55.22, 35.81, 34.47, 30.37, 29.21, 29.05, 28.82, 25.14, 24.85, 23.11, 20.19, 18.39, 17.44, 14.11; HRMS (APCI): m/z calculated for C$_{23}$H$_{35}$O$_2$[M+H]$^+$: 343.2632, found 343.2605.

Chemical formula: C$_{22}$H$_{32}$O$_3$; Exact mass: 344.2351. Colorless oil. $\textit{dr} > 99:01:0:0$. Rf = 0.4 (hexane/Et$_2$O, 50:50, v/v). $^1$H NMR (400 MHz, CDCl$_3$) δ 6.72 – 6.69 (m, 3H), 5.70 – 5.61 (m, 1H), 5.42 – 5.34 (m, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 3.67 – 3.61 (m, 1H), 3.56 – 3.51 (m, 1H), 1.75 – 1.69 (m, 4H), 1.40 – 1.33 (m,
Chemical formula: C_{23}H_{34}O_2; Exact mass: 342.2559. Colorless oil. 

\[ \text{HRMS (APCI): } m/z \text{ calculated for C}_{22}H_{33}O_3[M+H]^+: 345.2430, \text{ found 345.2421.} \]

The compounds 5a:6a was obtained as a pale-yellow oil in a ratio of 85:15. Yield 31 mg (61%). E:Z > 99:01. Rf = 0.3 (hexane/Et_2O, 70:30, v/v). 

\[ \text{HRMS (APCI): } m/z \text{ calculated for C}_{23}H_{34}O_2[M+H]^+: 419.2950, \text{ found 419.2957.} \]

The compounds 5b:6b was obtained as a pale-yellow oil in a ratio of 85:15. Yield 32 mg (61%). E:Z > 99:01. Rf = 0.4 (hexane/Et_2O, 95:05, v/v). 

\[ \text{HRMS (APCI): } m/z \text{ calculated for C}_{30}H_{39}O_2[M+H]^+: 431.2956, \text{ found 431.2953.} \]
The compounds 5c:6e was obtained as a pale-yellow oil in a ratio of 82:18. Yield 34 mg (65%). $E:Z > 99:01$. $Rf = 0.4$ (hexane/Et$_2$O, 95:05, v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.70 (t, $J = 3.2$ Hz, 1H), 7.24 – 7.03 (m, 6H), 6.88 – 6.80 (m, 2H), 5.74 – 5.56 (m, 2H), 5.45 – 5.27 (m, 2H), 3.81 (s, 3H), 2.69 (t, $J = 7.6$ Hz, 2H), 2.40 – 2.29 (m, 7H), 1.46 – 1.37 (m, 5H), 1.31 – 1.20 (m, 4H), 1.15 – 1.14 (m, 3H), 0.93 – 0.89 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 203.75, 157.65, 139.18, 138.74, 138.34, 136.51, 135.03, 134.70, 128.92, 128.42, 128.13, 127.51, 113.26, 55.15, 53.83, 45.98, 41.75, 38.10, 35.45, 34.46, 26.69, 26.14, 24.07, 23.18, 20.99, 14.06. HRMS (APCI): m/z calculated for C$_{30}$H$_{41}$O$_2$[M+H]+: 433.3101, found 433.3077.

The compounds 5d:6d was obtained as a pale-yellow oil in a ratio of 90:10. Yield 26 mg (48%). $E:Z > 99:01$. $Rf = 0.4$ (hexane/Et$_2$O, 95:05, v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.69 (t, $J = 3.2$ Hz, 1H), 7.21 – 7.08 (m, 4H), 6.91 – 6.79 (m, 4H), 5.75 – 5.55 (m, 2H), 5.40 – 5.27 (m, 2H), 3.83 (s, 3H), 3.80 (s, 3H), 2.72 (t, $J = 7.6$ Hz, 2H), 2.40 – 2.25 (m, 4H), 1.45 – 1.36 (m, 5H), 1.33 – 1.19 (m, 5H), 1.14 – 1.13 (m, 3H), 0.92 – 0.88 (m, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 203.87, 157.63, 157.46, 139.32, 137.94, 136.62, 134.62, 130.20, 129.99, 128.17, 127.99, 126.95, 120.25, 113.26, 110.17, 55.18, 53.86, 45.97, 41.79, 38.11, 32.77, 30.27, 26.72, 26.15, 24.14, 23.20, 14.07. HRMS (APCI): m/z calculated for C$_{30}$H$_{41}$O$_2$[M+H]+: 449.3050, found 449.3038.

The compounds 5e:6e was obtained as a pale-yellow oil in a ratio of 90:10. Yield 31 mg (58%). $E:Z > 99:01$. $Rf = 0.4$ (hexane/Et$_2$O, 95:05, v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.61 (t, $J = 3.2$ Hz, 1H), 7.15 – 6.99 (m, 3H), 6.76 – 6.66 (m, 5H), 5.65 – 5.47 (m, 2H), 5.38 – 5.18 (m, 2H), 3.72 – 3.71 (m, 6H), 2.63 – 2.59 (m, 2H), 2.35 – 2.17 (m, 4H), 1.36 – 1.28 (m, 5H), 1.23 – 1.10 (m, 4H), 1.06 – 1.05 (m, 3H), 0.84 – 0.80 (m, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 203.80, 159.57, 157.68, 143.51, 139.16, 138.45, 136.50, 134.75, 129.18, 128.14, 127.39, 120.99, 114.28, 113.30, 111.02, 55.19, 55.07, 53.85, 46.00, 41.77, 38.13, 35.96, 34.25, 26.72, 26.15, 24.10, 23.19, 14.07; HRMS (APCI): m/z calculated for C$_{30}$H$_{41}$O$_2$[M+H]+: 449.3050, found 449.3040.

The compounds 5f:6f was obtained as a pale-yellow oil in a ratio of 80:20. Yield 29 mg (53%). $E:Z > 99:01$. $Rf = 0.4$ (hexane/Et$_2$O, 95:05, v/v). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 9.69 (t, $J = 3.2$ Hz, 1H), 7.22 – 7.05 (m, 4H), 6.89 – 6.75 (m, 4H), 5.72 – 5.54 (m, 2H), 5.41 – 5.25 (m, 2H), 3.80 – 3.77 (m, 6H), 2.66 (t, $J = 8$ Hz, 2H), 2.39 – 2.25 (m, 4H), 1.44 – 1.31 (m, 5H), 1.29 – 1.20 (m, 4H),
The compounds 5g:6g was obtained as a pale-yellow oil in a ratio of 95:05. Yield 37 mg (67%). E:Z > 99:01. Rf = 0.4 (hexane/Et2O, 95:05, v/v). 1H NMR (400 MHz, CDCl3) δ 9.62 (t, J = 4 Hz, 1H), 7.27 – 7.25 (m, 1H), 7.14 – 7.06 (m, 3H), 7.01 – 6.99 (m, 2H), 6.75 – 6.72 (m, 2H), 5.66 – 5.47 (m, 2H), 5.34 – 5.18 (m, 2H), 3.72 (s, 3H), 2.78 – 2.74 (m, 2H), 2.35 – 2.21 (m, 4H), 1.20 – 1.12 (m, 4H), 1.05 (s, 3H), 0.83 – 0.80 (m, 3H). 13C NMR (101 MHz, CDCl3) δ 203.81, 157.67, 139.19, 138.42, 134.70, 133.92, 129.43, 128.14, 127.46, 113.65, 113.27, 55.18, 53.85, 45.99, 41.77, 38.12, 34.98, 34.60, 26.69, 26.15, 24.09, 23.19, 14.07. HRMS (APCI): m/z calculated for C30H41O3[M+H]+: 449.3050, found 449.3070.

The compounds 5h:6h was obtained as a pale-yellow oil in a ratio of 95:05. Yield 30 mg (58%). E:Z > 99:01. Rf = 0.4 (hexane/Et2O, 95:05, v/v). 1H NMR (400 MHz, CDCl3) δ 9.69 (t, J = 4 Hz, 1H), 7.21 – 7.17 (m, 2H), 7.15 – 7.0 (m, 4H), 6.84 – 6.79 (m, 2H), 5.73 – 5.54 (m, 2H), 5.45 – 5.25 (m, 2H), 3.79 (s, 3H), 2.75 (t, J = 7.6 Hz, 2H), 2.41 – 2.25 (m, 4H), 1.44 – 1.36 (m, 5H), 1.29 – 1.16 (m, 5H), 1.12 (s, 3H), 0.90 (t, J = 7.2 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ 203.76, 157.68, 139.34, 139.08, 138.71, 136.46, 134.76, 133.99, 130.64, 129.41, 128.13, 127.23, 127.00, 126.59, 113.29, 55.19, 53.85, 45.99, 41.78, 38.13, 33.50, 32.75, 26.66, 26.15, 24.13, 23.20, 14.07. HRMS (APCI): m/z calculated for C29H38ClO2[M+H]+: 437.2850, found 437.2840.

The compounds 5i:6i was obtained as a pale-yellow oil in a ratio of 82:18. Yield 30 mg (58%). E:Z > 99:01. Rf = 0.4 (hexane/Et2O, 95:05, v/v). 1H NMR (400 MHz, CDCl3) δ 9.69 (t, J = 3.2 Hz, 1H), 7.21 – 6.88 (m, 6H), 6.84 – 6.80 (m, 2H), 5.71 – 5.53 (m, 2H), 5.41 – 5.24 (m, 2H), 3.80 (s, 3H), 2.68 (t, J = 7.6 Hz, 2H), 2.38 – 2.25 (m, 4H), 1.44 – 1.36 (m, 5H), 1.29 – 1.17 (m, 5H), 1.14 – 1.13 (m, 3H), 0.91 – 0.87 (m, 3H). 13C NMR (101 MHz, CDCl3) δ 203.70, 161.2 (d, J = 241 Hz), 157.71, 139.04, 138.78, 137.4 (d, J = 3 Hz), 136.43, 134.75, 129.88 (d, J = 8 Hz), 128.09, 127.05, 114.95 (d, J = 21 Hz), 113.29, 55.18, 53.83, 45.99, 41.78, 38.13, 35.02, 34.44, 26.66,
The compounds 5j:6j was obtained as a pale-yellow oil in a ratio of 70:30. Yield 29 mg (54%). E:Z > 99:01. Rf = 0.4 (hexane/Et₂O, 95:05, v/v). ¹H NMR (400 MHz, CDCl₃) δ 9.62 (t, J = 3.2 Hz, 1H), 7.51 – 7.40 (m, 2H), 7.24 – 7.11 (m, 2H), 7.07 – 6.93 (m, 2H), 6.77 – 6.72 (m, 2H), 5.62 – 5.44 (m, 2H), 5.34 – 5.17 (m, 2H), 3.73 (s, 3H), 2.69 (t, J = 7.6 Hz, 2H), 2.37 – 2.19 (m, 4H), 1.35 – 1.28 (m, 5H), 1.22 – 1.09 (m, 4H), 1.07 – 1.05 (m, 3H), 0.84 – 0.79 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 203.55, 157.75, 147.49, 139.36, 138.79, 136.23, 134.84, 132.07, 129.40, 127.99, 126.29, 119.06, 113.30, 109.63, 55.19, 53.80, 45.97, 41.77, 38.14, 35.95, 33.76, 26.58, 26.13, 24.06, 23.16, 14.07. HRMS (APCI): m/z calculated for C₂₉H₃₈FO₂[M+H]+: 437.2850, found 437.2831.

The compounds 5k:6k was obtained as a pale-yellow oil in a ratio of 75:25. Yield 37 mg (65%). E:Z > 99:01. Rf = 0.4 (hexane/Et₂O, 95:05, v/v). ¹H NMR (400 MHz, CDCl₃) δ 9.61 – 9.56 (m, 1H), 8.08 – 7.96 (m, 1H), 7.79 – 7.72 (m, 1H), 7.65 – 7.58 (m, 1H), 7.45 – 7.22 (m, 4H), 7.17 – 6.97 (m, 2H), 6.75 – 6.71 (m, 2H), 5.63 – 5.45 (m, 3H), 5.36 – 5.16 (m, 2H), 3.71 (s, 3H), 3.09 (t, J = 7.6 Hz, 2H), 2.49 – 2.44 (m, 2H), 2.29 – 2.04 (m, 2H), 1.34 – 1.26 (m, 5H), 1.22 – 1.09 (m, 4H), 1.03 – 1.01 (m, 3H), 0.82 – 0.76 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 203.77, 157.67, 139.07, 138.46, 137.90, 136.48, 134.84, 132.07, 129.40, 127.99, 126.29, 119.06, 113.30, 109.63, 55.19, 53.82, 45.99, 41.77, 38.11, 33.79, 32.96, 26.67, 26.14, 24.13, 23.19, 14.07. HRMS (APCI): m/z calculated for C₃₀H₃₈NO₂[M+H]+: 444.2897, found 444.2888.

The compounds 5l:6l was obtained as a pale-yellow oil in a ratio of 90:10. Yield 31 mg (60%). E:Z > 99:01. Rf = 0.4 (hexane/Et₂O, 95:05, v/v). ¹H NMR (400 MHz, CDCl₃) δ 9.63 – 9.61 (m, 1H), 7.26 – 7.24 (m, 1H), 7.14 – 7.0 (m, 4H), 6.7 – 6.64 (m, 3H), 5.67 – 5.48 (m, 2H), 5.37 – 5.12 (m, 2H), 3.70 (s, 3H), 2.75 (t, J = 7.6 Hz, 2H), 2.36 – 2.17 (m, 4H), 1.38 – 1.33 (m, 5H), 1.05 (s, 3H), 0.75 (t, J = 5.6 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 203.61, 159.31, 148.89, 139.29, 138.20, 136.40, 134.57, 133.94, 130.57, 129.39, 128.91, 127.28, 127.25, 126.59, 119.57, 113.35, 110.90, 55.09, 53.50, 46.66, 38.38, 34.47, 33.52, 32.72, 26.41, 23.52, 8.37. HRMS (APCI-MS ES+) [M+H]+, calculated for C₂₇H₃₄ClO₂; 425.2242; found 425.2246.
The compounds 5m:6m was obtained as a pale-yellow oil in a ratio of 95:05. Yield 33 mg (61%). E:Z > 99:01. Rf = 0.4 (hexane/EtO, 95:05, v/v). ^1H NMR (400 MHz, CDCl₃) δ 9.73 (dd, J = 3.8, 2.8 Hz, 1H), 7.38 (dd, J = 7.2 1.8 Hz, 1H), 7.31 – 7.15 (m, 3H), 7.07 (d, J = 8.4 Hz, 1H), 6.49 (d, J = 2.5 Hz, 1H), 6.43 (dd, J = 8.5, 2.5 Hz, 1H), 5.79 (d, J = 16.0 Hz, 1H), 5.68 (d, J = 16.0 Hz, 1H), 5.41 (dt, J = 15.6, 6.8 Hz, 1H), 5.22 (d, J = 16.0 Hz, 1H), 3.85 (s, 3H), 3.74 (s, 3H), 2.89 – 2.84 (m, 2H), 2.48 – 2.42 (m, 2H), 2.40 – 2.24 (m, 2H), 1.55 – 1.39 (m, 5H), 1.13 (s, 3H), 0.85 (t, J = 7.6 Hz, 3H). ^13C NMR (101 MHz, CDCl₃) δ 204.49, 159.35, 158.57, 139.49, 138.69, 136.89, 133.94, 132.99, 130.51, 129.34, 128.33, 127.81, 127.14, 126.55, 103.11, 99.45, 55.20, 54.66, 53.55, 44.97, 38.12, 34.59, 33.66, 32.75, 25.57, 23.48, 8.22. HRMS (APCI-MS ES+) [M+H]^+, calculated for C₂₈H₃₆ClO₃; 455.2353; found 455.2368.

The compounds 5n:6n was obtained as a pale-yellow oil in a ratio of 90:10. Yield 36 mg (66%). E:Z > 99:01. Rf = 0.4 (hexane/EtO, 95:05, v/v). ^1H NMR (400 MHz, CDCl₃) δ 9.64 – 9.62 (m, 1H), 7.26 – 7.24 (m, 1H), 7.15 – 7.0 (m, 3H), 6.79 – 6.63 (m, 3H), 5.66 – 5.48 (m, 2H), 5.33 – 5.18 (m, 2H), 2.36 – 2.17 (m, 4H), 1.37 – 1.33 (m, 5H), 1.05 (s, 3H), 0.75 (t, J = 7.6 Hz, 3H). ^13C NMR (101 MHz, CDCl₃) δ 203.46, 148.34, 147.17, 139.60, 139.28, 138.47, 136.73, 134.40, 133.92, 130.50, 128.33, 127.81, 127.14, 126.55, 125.86, 103.11, 99.45, 55.20, 54.66, 53.55, 44.97, 38.12, 34.59, 33.66, 32.75, 25.57, 23.48, 8.22. HRMS (APCI-MS ES+) [M+H]^+, calculated for C₂₈H₃₆ClO₃; 455.2353; found 455.2368.

Yield 29 mg (47%). Pale yellow oil. E/Z > 99:1. dr 92:08:0:0. ^1H NMR (400 MHz, CDCl₃) δ 9.67 – 9.60 (m, 1H), 7.25 – 7.24 (m, 1H), 7.15 – 7.0 (m, 3H), 6.78 – 6.74 (m, 2H), 5.74 – 5.43 (m, 3H), 5.27 (d, J = 16.0 Hz, 1H), 3.96 – 3.92 (m, 1H), 3.71 (s, 5H). 1H NMR (400 MHz, CDCl₃) δ 9.72 – 9.69 (m, 1H), 7.37 – 7.29 (m, 5H), 7.17 – 7.09 (m, 5H), 6.77 – 6.74 (m, 2H), 3.72 (s, 3H), 3.47 – 3.40 (m, 1H), 2.31 – 2.17 (m, 2H), 1.36 (s, 3H), 1.23 – 1.15 (m, 5H), 1.06 (s, 3H), 0.80 (t, J = 7.1 Hz, 4H). ^13C NMR (101 MHz, CDCl₃) δ 203.68, 157.72, 146.22, 139.34, 136.63, 136.49, 134.91, 133.05, 128.34, 128.08, 127.12, 125.96, 113.38, 55.20, 53.88, 45.87, 42.16, 41.83, 38.15, 26.77, 26.15, 24.16, 23.18, 21.51, 14.05. HRMS (APCI): m/z calculated for C₁₉H₁₃O₂[M+H]^+: 419.2949, found 419.2949.

Yield 34 mg (51%). Pale yellow oil. E/Z > 99:1. dr 98:2:0:0. 1H NMR (400 MHz, CDCl₃) δ 9.69 – 9.62 (m, 1H), 7.28 – 7.25 (m, 1H), 7.17 – 7.03 (m, 5H), 6.77 – 6.74 (m, 2H), 5.61 (dd, J = 16, 1.2 Hz, 1H), 5.52 (d, J = 16 Hz, 1H), 5.41 (dd, J = 16, 6.4 Hz, 1H), 5.28 (d, J = 16 Hz, 1H), 3.96 – 3.92 (m, 1H), 3.71 (s,
3H), 2.31 – 2.16 (m, 2H), 1.36 (s, 3H), 1.31 – 1.27 (m, 5H), 1.19 – 1.08 (m, 4H), 1.05 (s, 3H), 0.79 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 203.62, 157.75, 143.37, 139.20, 137.40, 136.41, 135.04, 133.56, 131.48, 129.54, 128.09, 127.84, 127.17, 126.91, 113.40, 55.19, 53.88, 45.93, 41.81, 38.14, 38.13, 26.78, 26.13, 24.16, 23.17, 20.23, 14.03. HRMS (APCI): m/z calculated for C$_{29}$H$_{38}$ClO$_2$[M+H]+: 453.2555, found 453.2561.

Yield 32 mg (50%). Pale yellow oil. $E/Z > 99:1$. $dr$ 90:10:0:0. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.61 (t, J = 3.2 Hz, 1H), 7.10 – 7.08 (m, 2H), 7.03 (s, 4H), 6.75 (d, J = 8.8 Hz, 2H), 5.60 – 5.41 (m, 3H), 5.26 (d, J = 16.0 Hz, 1H), 3.71 (s, 3H), 3.43 – 3.36 (m, 1H), 2.26 – 2.20 (m, 5H), 1.36 (s, 3H), 1.32 – 1.26 (m, 5H), 1.21 – 1.10 (m, 4H), 1.05 (s, 3H), 0.80 (t, J = 7.2 Hz, 3H); $^{13}$C NMR (101 MHz, CDCl$_3$) δ 203.67, 157.70, 143.18, 139.38, 136.52, 136.39, 135.38, 134.87, 133.22, 129.02, 128.07, 126.98, 113.36, 55.17, 53.86, 45.84, 41.82, 41.74, 38.14, 26.76, 26.14, 24.16, 23.17, 21.57, 20.94, 14.03. HRMS (APCI): m/z calculated for C$_{30}$H$_{41}$O$_3$[M+H]+: 433.3101, found 433.3104.

Yield 29 mg (44%). Pale yellow oil. $E/Z > 99:1$. $dr$ 92:08:0:0. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.61 (t, J = 3.2 Hz, 1H), 7.17 – 7.08 (m, 3H), 6.77 – 6.64 (m, 5H), 5.62 – 5.41 (m, 3H), 5.27 (d, J = 16 Hz, 1H), 3.71 (m, 6H), 3.43 – 3.37 (m, 1H), 2.30 – 2.17 (m, 2H), 1.36 (d, J = 2.8 Hz, 3H), 1.31 – 1.27 (m, 4H), 1.22 – 1.08 (m, 5H), 1.05 (s, 3H), 0.79 (t, J = 6.8 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 203.66, 159.61, 157.73, 147.95, 139.32, 136.70, 136.47, 134.96, 132.87, 129.27, 128.07, 119.57, 113.38, 113.09, 111.00, 55.19, 55.06, 53.86, 45.86, 42.17, 41.79, 38.15, 26.76, 26.14, 24.15, 23.16, 21.44, 14.03. HRMS (APCI): m/z calculated for C$_{30}$H$_{41}$O$_3$[M+H]+: 449.3050, found 449.3026.

Yield 32 mg (47%). Pale yellow oil. $E/Z > 99:1$. $dr$ 98:2:0:0. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.55 – 9.54 (m, 1H), 8.07 (dd, J = 8.4, 1.2 Hz, 1H), 7.78 (dd, J = 8.0, 1.6 Hz, 1H), 7.65 – 7.62 (m, 1H), 7.42 – 7.28 (m, 4H), 7.09 – 7.06 (m, 2H), 6.75 – 6.72 (m, 2H), 5.64 – 5.53 (m, 2H), 5.49 (d, J = 16 Hz, 1H), 5.16 (d, J = 16 Hz, 1H), 4.27 – 4.20 (m, 1H), 3.71 (s, 3H), 2.22 – 2.10 (m, 2H), 1.44 (d, J = 6.8 Hz, 3H), 1.34 (s, 3H), 1.22 – 1.10 (m, 4H), 1.05 – 0.99 (m, 5H), 0.75 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 203.67, 157.72, 141.96, 139.20, 137.16, 136.41, 134.93, 133.96, 133.03, 131.44, 128.86, 128.13, 126.69, 125.61, 125.56, 125.28, 123.75, 123.37, 113.36, 55.19, 53.82, 45.95, 41.74, 38.07, 37.21, 26.75, 26.05, 24.04, 23.12, 21.05, 14.01. HRMS (APCI): m/z calculated for C$_{33}$H$_{44}$O$_2$[M+H]+: 469.3101, found 469.3126.

Yield 33 mg (50%). Pale yellow oil. $E/Z > 99:1$. $dr$ 98:2:0:0. $^1$H NMR (400 MHz, CDCl$_3$) δ 9.61 (t, J = 3.2 Hz, 1H), 7.27 (d, J = 8.0 Hz, 1H), 7.18 – 7.12 (m, 3H), 7.07 – 7.03 (m, 1H), 6.80 – 6.65 (m, 3H), 5.63 (dd, J = 16.0, 1.2 Hz, 1H), 5.54 (d, J = 16.0 Hz, 1H), 5.45 (dd, J = 16.0, 6.4 Hz, 1H), 5.31 (d, J = 16.0 Hz, 1H), 3.98 – 3.92 (m, 1H), 3.69 (s, 3H), 2.31 – 2.17 (m, 2H), 1.38 (s, 3H), 1.30 – 1.28 (m, 4H), 1.21 – 1.08 (m, 5H), 1.05 (s, 3H), 0.79 (t, J = 6.8 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ 203.56, 159.35, 149.05, 143.32, 136.92, 135.96, 135.22, 133.57, 131.75, 129.55, 128.99, 127.84, 127.20, 126.93, 119.47, 113.11, 111.28, 55.06,
Yield 30 mg (44%). Pale yellow oil. E/Z > 99:1. \( \text{dr} \) 98:2:0:0.

\( {}^1\text{H NMR} \) (400 MHz, CDCl\(_3\)) \( \delta \) 9.62 (t, \( J = 3.2 \) Hz, 1H), 7.27 – 7.25 (m, 1H), 7.18 – 7.12 (m, 2H), 7.07 – 7.02 (m, 1H), 6.73 – 6.68 (m, 3H), 5.61 (d, \( J = 16.0 \) Hz, 1H), 5.53 (d, \( J = 16.0 \) Hz, 1H), 5.44 (dd, \( J = 16.0, 6.4 \) Hz, 1H), 5.26 (d, \( J = 16.0 \) Hz, 1H), 3.98 – 3.91 (m, 1H), 3.78 (s, 3H), 3.71 (s, 3H), 2.31 – 2.17 (m, 2H), 1.37 – 1.33 (m, 5H), 1.29 (d, \( J = 7.0 \) Hz, 3H), 1.05 (s, 3H), 0.74 (t, \( J = 7.6 \) Hz, 3H).

\( {}^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 203.35, 148.36, 147.18, 143.28, 139.72, 137.20, 136.61, 134.65, 133.52, 131.70, 129.53, 127.77, 127.17, 126.89, 118.78, 110.94, 110.63, 55.79, 55.61, 53.51, 46.32, 38.37, 38.12, 34.51, 26.76, 23.53, 20.20, 8.31.

HRMS (APCI): m/z calculated for C\(_{28}\)H\(_{36}\)ClO\(_{3}\)[M+H\(^+\)]: 455.2353, found 455.2344.
$5a:6a = 85:15$
5b:6b = 85:15
$5\text{c:6c} = 82:18$
5d:6d = 90:10

\[
\text{MeO} \quad \text{MeOH} \\
\text{Bu}^\text{Me} \quad \text{H}
\]

5d:6d = 90:10

\[
\text{MeO} \quad \text{MeOH} \\
\text{Bu}^\text{Me} \quad \text{H}
\]

5d:6d = 90:10
5h:6h = 95:05

MeOH 4°C

6MeBuO

H Bu' Me

5h:6h = 95:05

MeOH 4°C

6MeBuO

H Bu' Me
5i:6i = 82:18

\[
\text{MeOH} \quad 4^\circ \text{C} \quad \text{6 MeBuO} \quad \text{F}
\]

5i:6i = 82:18

\[
\text{MeOH} \quad 4^\circ \text{C} \quad \text{6 MeBuO} \quad \text{F}
\]
5k:6k = 75:25

[Chemical structures and spectra]
5m:6m = 95:05

MeO,p(MeO)2H3C6Me

MeO,p(MeO)2H3C6Me

5m:6m = 95:05

MeO,p(MeO)2H3C6Me

MeO,p(MeO)2H3C6Me
