Supporting Information for

Palladium-Catalyzed [2+1+1] Annulation of Norbornenes with (Z)-Bromostyrenes: Synthesis of Bismethylenecyclobutanes via Twofold C(sp²)-H Bond Activation

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1 General information

Experimental: All bimethylene-cyclobutanation ([2+1+1] cycloaddition) reactions were carried out under an inert atmosphere of nitrogen in sealed tube. All solvents were dried by standard methods before use. All reactions were monitored by TLC with silica gel-coated plates. NMR spectra were recorded on Bruker Avance 400 (400 MHz for $^1$H; 100 MHz for $^{13}$C) instruments. Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard (for CDCl$_3$, $^1$H NMR: 7.26 ppm, $^{13}$C NMR: 77.16 ppm). Coupling constants ($J$) were reported in Hz. Mass spectra (EI, 70 eV) were recorded on an Agilent 5975 instrument. High resolution mass spectra (HRMS) were recorded on a Waters Micromass GCT instrument. All commercially available reagents were used as received.

2 Substrates Preparation

2.1 General Procedure for the Preparation of (Z)-Vinyl Bromides$^1$:

\[ 
\begin{align*}
\text{O} & \quad \text{CO}_2\text{H} \\
\text{H} & \quad \text{R}_1 \\
& \quad \text{CO}_2\text{H} \\
\text{Pyridine} & \quad \text{Br}_2 & \quad \text{NET}_3
\end{align*}
\]

Aldehydes (50 mmol), malonic acid (50 mmol), pyridine (150 mmol), and a few drops of piperidine were added in a 50 mL three-neck flask equipped with a reflux condenser. Firstly the reaction mixture was stirred at 100 °C for 8 h and 120 °C for 2 h, then transferred to a beaker containing 10 mL concentrated hydrochloric acid and 30 mL ice water. After the mixture was cooled, the resultant precipitate was filtered, washed three times with ice water, and recrystallized with ethanol to give pure propenoic acids.

To a mixture of propenoic acids (85 mmol) and chloroform (50 mL) cooled to 0 °C, was added bromine (5.3 mL, 102mmol) dropwise and the resulting solution was stirred at this temperature for 20 min. The solution was stored in refrigerator
overnight, filtered and washed twice with cold chloroform to give the crude product 2,3-dibromopropanoic acid derivatives which was used in the next step without further purification.

Triethylamine (160 mmol, 23 mL) was added to the mixture of 2,3-dibromopropanoic acid derivatives (80 mmol) and dry DMF (40mL) at 0 °C dropwise. The solution was stirred at 0 °C for 30 min, then at room temperature for 6 h. Water (20mL) was added. The mixture was extracted with ethoxyethane (3 x 40mL). The organic layers were combined, washed with saturated potassium carbonate (2 x 40mL) and saturated sodium chloride(2 x 40mL), dried over magnesium sulfate and concentrated in vacuo, purified by chromatography on a column of silica gel with PE/EA=100/1 to give (z)-vinyl bromides.

2.2 The Synthesis of Endo-Norbornenesuccinimides (2a, 2b):

Triethylamine (6.6 mmol, 0.92 mL) and the desired anhydride (6 mmol) were added to a solution of 4-amino acid 6 (6 mmol) in 5 mL of N, N-dimethylformamide (DMF). The solution was heated for 16 h at 120 °C. After it returned to room temperature, the resulting mixture was treated with water, and extracted with ethyl ether and washed with 1 N HCl (20 mL). The combined organic layer was washed with brine, dried over magnesium sulfate and concentrated in vacuo, purified by chromatography on a column of silica gel with PE/EA=3/1 to afford the pure products as white solid( 86% yield). \(^1\)H NMR (CDCl\(_3\), 400 MHz) \(\delta\) 7.25 (d, \(J = 8.0\) Hz, 2H), 7.03 (d, \(J = 8.0\) Hz, 2H), 6.28 (s, 2H), 3.52 (s, 2H), 3.43-3.44 (m, 2H), 2.38 (s, 3H), 1.80 (d, \(J = 8.8\) Hz, 2H), 1.62 (d, \(J = 8.8\) Hz, 2H).
3. Pd(OAc)$_2$-Catalyzed [2+1+1] Cycloaddition of (Z)-Vinyl Bromides and Norbornene Derivatives

3.1 General Procedures for the [2+1+1] Cycloaddition

**Synthesis of [2+1+1] Cycloaddition products 3**

To a flame-dried Teflon-screw-capped tube was equipped with a magnetic stir bar, (Z)-vinyl bromides 1 (1.1 mmol, 2.2 equiv.), norbornene derivants 2 (0.5 mmol, 1.0 equiv.), Pd(OAc)$_2$ (11.22 mg, 0.05 mmol, 10 mol%), PPh$_3$ (28.85 mg, 0.11 mmol, 22 mol%), Cs$_2$CO$_3$ (488.73 mg, 1.5 mmol, 3.0 equiv.) and toluene (2.0 mL) were added sequentially under nitrogen. The tube was sealed with a Teflon lined cap, the reaction mixture was stirred at 110°C for 12 h. After completion of the reaction, the resulting mixture was cooled down to room temperature, diluted with CH$_2$Cl$_2$ (10 mL), filtered through a short pad of silica gel and washed with EtOAc (30 mL). The filtrate was concentrated under vacuum and the residue was purified by silica gel column chromatography to afford the corresponding products 3.

3.2 Experimental Characterization of Products

(3$^R$4$^S$,4$^R$5$^Z$,6$^S$,7$^R$,7$^S$)-5,6-dibenzylidene-2-(p-tolyl)octahydro-1H-4,7-methanocyclobuta[f]isoindole-1,3(2H)-dione (3aa): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give white solid, 196.6 mg, 86% yield. **M.p:** 264-266°C; $^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.95 (t, J = 7.2 Hz, 2H), 6.75 (t, J = 7.6 Hz, 4H), 6.66 (d, J = 7.2 Hz, 4H), 6.33 (s, 2H), 3.38 (s, 2H), 3.24 (s, 2H), 3.05 (s, 2H), 2.41 (s, 3H), 2.36 (d, J = 11.2 Hz, 1H), 1.64 (d, J = 10.8 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 176.8, 140.3, 138.8, 136.8, 129.9, 129.0, 127.9, 126.6, 126.5, 126.5, 124.8, 48.0, 43.5, 43.2, 36.0, 21.2; HRMS (EI) calcd. for C$_{32}$H$_{27}$NO$_2$ [M$^+$]: 457.2042,
found: 457.2039.

(3^R,4^S,4^aR,5Z,6Z,6^aS,7R,7^aS)-5,6-bis(4-methylbenzylidene)-2-(p-tolyl)octahydro-1H-4,7-methanocyclobuta[f]isoindole-1,3(2H)-dione (3ba): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1 → 3/1) to give white solid, 201.4 mg, 83 % yield. **Mp:** 258-260°C; **^1H NMR** (400 MHz, CDCl\textsubscript{3}) δ 7.31 (d, J = 7.6 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 8.4 Hz, 4H), 6.51 (d, J = 8.4 Hz, 4H), 6.27 (s, 2H), 3.36 (s, 2H), 3.21 (s, 2H), 3.02 (s, 2H), 2.41 (s, 3H), 2.37 (d, J = 10.4 Hz, 1H), 2.18 (s, 6H), 1.62 (d, J = 10.0 Hz, 1H); **^13C NMR** (100 MHz, CDCl\textsubscript{3}) δ 176.8, 139.7, 138.7, 136.4, 134.2, 129.8, 129.2, 127.8, 127.1, 126.5, 124.4, 48.0, 43.3, 43.2, 36.0, 21.1, 21.0; **HRMS (EI)** calcd. for C\textsubscript{34}H\textsubscript{31}NO\textsubscript{2} [M\textsuperscript{+}]: 485.2355, found: 485.2358. The configuration was confirmed by X-ray analysis (Figure S3) and undoubtedly determined that bismethenylcyclobutane moiety was formed.

![Figure S1. ORTEP drawing of product 3ba](image_url)

(3^R,4^S,4^aR,5Z,6Z,6^aS,7R,7^aS)-5,6-bis(3-methylbenzylidene)-2-(p-tolyl)octahydro-1H-4,7-methanocyclobuta[f]isoindole-1,3(2H)-dione (3ca): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1 → 3/1) to give white solid, 201.4 mg, 83 % yield. **Mp:** 258-260°C; **^1H NMR** (400 MHz, CDCl\textsubscript{3}) δ 7.31 (d, J = 7.6 Hz, 2H), 7.19 (d, J = 8.4 Hz, 2H), 6.55 (d, J = 8.4 Hz, 4H), 6.51 (d, J = 8.4 Hz, 4H), 6.27 (s, 2H), 3.36 (s, 2H), 3.21 (s, 2H), 3.02 (s, 2H), 2.41 (s, 3H), 2.37 (d, J = 10.4 Hz, 1H), 2.18 (s, 6H), 1.62 (d, J = 10.0 Hz, 1H); **^13C NMR** (100 MHz, CDCl\textsubscript{3}) δ 176.8, 139.7, 138.7, 136.4, 134.2, 129.8, 129.2, 127.8, 127.1, 126.5, 124.4, 48.0, 43.3, 43.2, 36.0, 21.1, 21.0; **HRMS (EI)** calcd. for C\textsubscript{34}H\textsubscript{31}NO\textsubscript{2} [M\textsuperscript{+}]: 485.2355, found: 485.2358. The configuration was confirmed by X-ray analysis (Figure S3) and undoubtedly determined that bismethenylcyclobutane moiety was formed.
chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1 → 3/1) to give white solid, 186.8 mg, 77 % yield. **Mp:** 242-245°C; **IH NMR** (400 MHz, CDCl3) δ 7.31 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.0 Hz, 2H), 6.80 (d, J = 4.4 Hz, 4H), 6.65 (s, 2H), 6.37 (s, 2H), 6.29 (s, 2H), 3.37 (s, 2H), 3.23 (s, 2H), 3.04 (s, 2H), 2.41 (s, 3H), 2.35 (d, J = 11.2 Hz, 1H), 1.83 (s, 6H), 1.63 (d, J = 10.8 Hz, 1H); **13C NMR** (100 MHz, CDCl3) δ 176.8, 140.0, 138.7, 136.7, 136.5, 129.8, 129.2, 129.1, 127.4, 126.6, 126.5, 125.3, 124.9, 48.0, 43.5, 43.2, 36.0, 21.1, 20.7; **HRMS (EI)** calcd. for C34H31NO2 [M⁺]: 485.2355, found: 485.2354.

(3R,4S,4aR,5Z,6Z,6aS,7R,7aS)-5,6-bis(4-methoxybenzylidene)-2-(p-tolyloctahydro-1H-4,7-methanocyclobuta[f]isoindole-1,3(2H)-dione (3da): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1 → 3/1) to give white solid, 186.2 mg, 72 % yield. **Mp:** 255-257°C; **IH NMR** (400 MHz, CDCl3) δ 7.31 (d, J = 8.4 Hz, 2H), 7.19 (d, J = 8.0 Hz, 2H), 6.55 (d, J = 8.8 Hz, 4H), 6.31 (d, J = 8.4 Hz, 4H), 6.25 (s, 2H), 3.68 (s, 6H), 3.36 (s, 2H), 3.21 (s, 2H), 3.01 (s, 2H), 2.41 (s, 3H), 2.34 (d, J = 10.8 Hz, 1H), 1.62 (d, J = 10.8 Hz, 1H); **13C NMR** (100 MHz, CDCl3) δ 176.9, 158.9, 139.0, 138.8, 129.9, 129.8, 129.1, 129.1, 126.5, 123.5, 111.8, 54.9, 48.0, 43.3, 43.1, 36.0, 21.2; **HRMS (EI)** calcd. for C34H31NO2 [M⁺]: 517.2253, found: 517.2258.

(3R,4S,4aR,5Z,6Z,6aS,7R,7aS)-5,6-bis(4-chlorobenzylidene)-2-(p-tolyloctahydro-1H-4,7-methanocyclobuta[f]isoindole-1,3(2H)-dione (3ea): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1 → 3/1) to give white solid, 246.8 mg, 94 % yield. **Mp:** 298-301°C; **IH NMR** (400 MHz, CDCl3) δ 7.31 (d, J = 8.0 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.8 Hz, 4H), 6.57 (d, J = 8.4 Hz, 4H), 6.26 (s, 2H), 3.37 (s, 2H), 3.22 (s, 2H), 3.03 (s,
(3R,4S,4'R,5Z,6Z,6'S,7R,7'S)-5,6-bis(3-chlorobenzylidene)-2-(p-tolyl)octahydro-1H-4,7-methanocyclobuta[f]isoindole-1,3(2H)-dione (3fa): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1 → 3/1) to give white solid, 238.9 mg, 91% yield. Mp: 263-265°C; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, J = 7.6 Hz, 2H), 7.18 (d, J = 7.6 Hz, 2H), 6.97 (d, J = 8.0 Hz, 2H), 6.79 (t, J = 7.6 Hz, 2H), 6.65 (d, J = 7.6 Hz, 2H), 6.60 (s, 2H), 6.27 (s, 2H), 3.39 (s, 2H), 3.24 (s, 2H), 3.05 (s, 2H), 2.41 (s, 3H), 2.30 (d, J = 10.8 Hz, 1H), 1.67 (d, J = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 176.7, 141.4 138.9, 138.4, 133.1, 129.9, 129.0, 128.1, 127.8, 126.8, 126.4, 125.9, 123.8, 47.9, 43.5, 43.1, 36.0, 21.2; HRMS (EI) calcd. for C₂₃H₂₅Cl₂NO₂ [M⁺]: 525.1262, found: 525.1258.

(3R,4S,4'R,5Z,6Z,6'S,7R,7'S)-5,6-bis(4-fluorobenzylidene)-2-(p-tolyl)octahydro-1H-4,7-methanocyclobuta[f]isoindole-1,3(2H)-dione (3ha): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1 → 3/1) to give white solid, 236.7 mg, 96% yield. Mp: 297-299°C; ¹H NMR (400 MHz, CDCl₃) δ 7.31 (d, J = 8.4 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 6.65 (dd, J₁ = 8.4 Hz, J₂ = 13.6 Hz, 4H), 6.51 (t, J = 8.8 Hz, 4H), 6.26 (s, 2H), 3.38 (t, J = 2.8 Hz, 2H), 3.22 (s, 2H), 3.03 (s, 2H), 2.41 (s, 3H), 2.31 (d, J = 10.8 Hz, 1H), 1.66 (d, J = 10.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 176.7, 162.0 (d, J_C,F = 247.3 Hz), 140.2, 138.9, 132.8 (d, J_C,F = 3.4 Hz), 129.9, 129.4 (d, J_C,F = 8.9 Hz), 129.0, 126.4, 123.5, 113.5 (d, J_C,F = 21 Hz), 47.9, 43.4, 43.1, 36.0, 21.2; HRMS (EI) calcd. for C₂₃H₂₅F₂NO₂ [M⁺]:
493.185, found: 493.185.

(3R,4S,4’S,6’S,7R,7’S)-5,6-bis(4-methylbenzylidene)-2-isobutyloctahydro-1H-4,7-methanocyclobuta[ff]isoindole-1,3(2H)-dione (3bb): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give white solid, 180.5 mg, 80 % yield. **Mp:** 200-203°C; **1H NMR** (400 MHz, CDCl₃) δ 6.53 (d, J = 8.4 Hz, 4H), 6.50 (d, J = 8.0 Hz, 4H), 6.24 (s, 2H), 3.34 (d, J = 6.0 Hz, 2H), 3.20 (s, 2H), 3.02 (s, 2H), 2.91 (s 2H), 2.30 (d, J = 10.4 Hz, 1H), 2.17 (s, 6H), 2.05-2.12 (m, 1H), 1.56 (d, J = 10.8 Hz, 1H), 0.95 (d, J = 6.8 Hz, 6H); **13C NMR** (100 MHz, CDCl₃) δ 178.7, 140.6, 137.1, 135.0, 128.5, 127.8, 125.0, 48.7, 46.8, 44.1, 43.3, 36.8, 27.9, 21.7, 21.1; **HRMS (EI)** calcd. for C₃₁H₅₃NO₂ [M⁺]: 451.2511, found: 451.2505.

(3R,4S,4’R,6’S,7R,7’S)-5,6-bis(4-chlorobenzylidene)-2-isobutyloctahydro-1H-4,7-methanocyclobuta[ff]isoindole-1,3(2H)-dione (3eb): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give light yellow solid, 221.0 mg, 90 % yield. **Mp:** 221-224°C; **1H NMR** (400 MHz, CDCl₃) δ 6.75 (d, J = 8.4 Hz, 4H), 6.54 (d, J = 8.4 Hz, 4H), 6.24 (s, 2H), 3.34 (d, J = 6.0 Hz, 2H), 3.21 (s, 2H), 3.03 (s, 2H), 2.92 (s, 2H), 2.25 (d, J = 10.4 Hz, 1H), 2.04-2.11 (m, 1H), 1.60 (d, J = 10.4 Hz, 1H), 0.95 (d, J = 6.4 Hz, 6H); **13C NMR** (100 MHz, CDCl₃) δ 177.7, 141.1, 135.2, 132.9, 128.9, 126.7, 123.5, 47.8, 46.1, 43.4, 42.5, 36.0, 27.1, 20.3; **HRMS (EI)** calcd. for C₂₉H₂₇Cl₂NO₂ [M⁺]: 491.1419, found: 491.1426.

(3R,4S,4’R,6’S,7R,7’S)-5,6-bis(3-chlorobenzylidene)-2-isobutyloctahydro-1H-4,7-methanocyclobuta[ff]isoindole-1,3(2H)-dione (3fb): The title compound was prepared according to the general
procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give white solid, 203.8 mg, 83 % yield. Mp: 217-221°C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.93 (s, 2H), 6.77 (s, 2H), 6.63 (s, 2H), 6.57 (s, 2H), 6.23 (s, 2H), 3.33 (d, J = 4.8 Hz, 2H), 3.21 (s, 2H), 3.04 (s, 2H), 2.93 (s 2H), 2.24 (d, J = 8.8 Hz, 1H), 2.06-2.08 (m, 1H), 1.56 (d, J = 7.6 Hz, 1H), 0.94 (d, J = 3.6 Hz, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 177.8, 141.6, 138.6, 133.2, 128.2, 127.9, 126.9, 126.0, 123.8, 48.0, 46.2, 43.7, 42.6, 36.2, 27.2, 20.4; HRMS (EI) calcd. for C\textsubscript{29}H\textsubscript{27}Cl\textsubscript{2}NO\textsubscript{2} [M\textsuperscript{+}]: 491.1419, found: 491.1424.

(3\textsuperscript{a}R,4\textsuperscript{a}S,4\textsuperscript{a}R,6\textsuperscript{a}S,7\textsuperscript{R},7\textsuperscript{S})-5,6-bis(4-fluorobenzylidene)-2-isobutoctahydro-1\textit{H}-4,7-methanocyclobuta[f]isoindole-1,3(2\textit{H})-dione (3gb): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a gradient eluent of petroleum ether/EtOAc (10/1→3/1) to give white solid, 195.2 mg, 85 % yield. Mp: 228-232°C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.61 (t, J = 7.2 Hz, 4H), 6.48 (t, J = 8.2 Hz, 4H), 6.22 (s, 2H), 3.33 (d, J = 7.2 Hz, 2H), 3.20 (s, 2H), 3.02 (s, 2H), 2.91 (s 2H), 2.25 (d, J = 10.8 Hz, 1H), 2.04-2.12 (m, 1H), 1.58 (d, J = 14.4 Hz, 1H), 0.94 (d, J = 14.4 Hz, 6H); \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ 177.8, 162.2 (d, J=\textit{CF} = 253.1 Hz), 140.4, 133.0 (d, J=\textit{CF} = 3.0 Hz), 129.5 (d, J=\textit{CF} = 7.7 Hz), 123.5, 113.6 (d, J=\textit{CF} = 22.1 Hz), 48.0, 46.2, 43.5, 42.7, 36.1, 27.2, 20.4; HRMS (EI) calcd. for C\textsubscript{29}H\textsubscript{27}Cl\textsubscript{2}NO\textsubscript{2} [M\textsuperscript{+}]: 459.2010, found: 459.2010.

(2\textsuperscript{a}R,3\textsuperscript{a}R,3\textsuperscript{a}S,6\textsuperscript{a}R,7\textsuperscript{S},7\textsuperscript{a}S)-1,2-bis((Z)-benzylidene)-2,2\textsuperscript{a},3,3\textsuperscript{a},4,6\textsuperscript{a},7,7\textsuperscript{a}-octahydro-1\textit{H}-3,7-methanocyclobuta[f]indene (3ac): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give white solid, 131.1 mg, 78 % yield. Mp: 132-135°C; \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ 6.81 (t, J = 7.2 Hz, 2H), 6.57-6.65 (m, 8H), 6.12 (s, 2H), 5.60 (s, 1H), 5.54 (s, 1H), 3.08-3.10 (m, 1H), 2.96 (d, J = 5.6 Hz, 1H), 2.83 (d, J = 6.0 Hz, 1H), 2.58-2.63 (m, 1H), 2.41 (d, J = 4.0 Hz, 1H), 2.01-2.30 (m, 3H), 1.98 (d, J = 10.4 Hz, 1H), 1.32 (d, J
= 10.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.7, 142.2, 136.7, 130.5, 129.9, 126.8, 126.8, 125.5, 125.0, 122.1, 121.9, 51.9, 44.1, 44.1, 42.3, 41.3, 41.1, 34.6, 30.7; HRMS (EI) calcd. for C$_{26}$H$_{24}$ [M$^+$]: 336.1878, found: 336.1874.

(2$^a$R,3$^R$,3$^a$R,6$^R$,7$^S$,7$^a$S)-1,2-bis((Z)-4-methylbenzylidene)-2,2$^a$-3,3$^a$-4,6$^a$-7,7$^a$-octahydro-1H-3,7-methanocyclobutulenylindene (3bc): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give pale yellow solid, 97.8 mg, 74% yield. Mp: 138-142°C; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.43 (t, J = 15.2 Hz, 8H), 6.06 (s, 2H), 5.59 (dd, J = 5.2 Hz, J = 1.6 Hz, 1H), 5.53 (dd, J = 4.8 Hz, J = 1.6 Hz, 1H), 3.06-3.09 (m, 1H), 2.92 (d, J = 6.0 Hz, 1H), 2.80 (d, J = 6.0 Hz, 1H), 2.55-2.62 (m, 1H), 2.38 (d, J = 4.0 Hz, 1H), 2.19-2.27 (m, 3H), 2.07 (s, 6H), 1.98 (d, J = 10.0 Hz, 1H), 1.30 (d, J = 10.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.1, 141.6, 134.7, 134.7, 134.0, 130.5, 129.8, 126.7, 126.0, 121.7, 121.5, 51.9, 44.1, 44.0, 42.3, 41.2, 41.1, 34.5, 30.7, 20.0; HRMS (EI) calcd. for C$_{28}$H$_{28}$ [M$^+$]: 364.2191, found: 364.2192.

(2$^a$R,3$^R$,3$^a$R,6$^R$,7$^S$,7$^a$S)-1,2-bis((Z)-3-methylbenzylidene)-2,2$^a$-3,3$^a$-4,6$^a$-7,7$^a$-octahydro-1H-3,7-methanocyclobutulenylindene (3cc): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give pale yellow solid, 91.2 mg, 69% yield. Mp: 135-139°C; $^1$H NMR (400 MHz, CDCl$_3$) δ 6.65-6.72 (m, 4H), 6.56 (d, J = 7.2 Hz, 2H), 6.30 (s, 2H), 6.09 (s, 2H), 5.61 (d, J = 3.6 Hz, 1H), 5.54 (d, J = 1.6 Hz, 1H), 3.07-3.10 (m, 1H), 2.94 (d, J = 6.0 Hz, 1H), 2.82 (d, J = 4.8 Hz, 1H), 2.56-2.63 (m, 1H), 2.41 (d, J = 4.8 Hz, 1H), 2.20-2.27 (m, 3H), 1.73 (s, 6H), 1.97 (d, J = 10.4 Hz, 1H), 1.31 (d, J = 10.0 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 142.5, 142.0, 136.6, 135.4, 130.5, 129.9, 128.2, 128.2, 125.8, 125.5, 124.2, 124.2, 122.2, 122.0, 51.9, 44.1, 44.1, 42.3, 41.3, 41.1, 34.5, 30.7, 19.9; HRMS (EI) calcd. for C$_{28}$H$_{28}$ [M$^+$]: 264.2191, found: 264.2197.
(2R,3R,3'S,6'R,7S,7'S)-1,2-bis((Z)-4-chlorobenzylidene)-2',2',3',3',4,6,7,7'-octahydro-1H-3,7-methanocyclobuta[f]indene (3ec): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether to give pale yellow solid, 161.6 mg, 80% yield. Mp: 174-179°C; 1H NMR (400 MHz, CDCl₃) δ 6.72 (d, J = 8.4 Hz, 4H), 6.55 (d, J = 8.4 Hz, 4H), 6.12 (s, 2H), 5.67 (dd, J = 5.6 Hz, J = 1.6 Hz, 1H), 5.60 (dd, J = 4.8 Hz, J = 1.6 Hz, 1H), 3.15-3.16 (m, 1H), 3.01 (d, J = 6.0 Hz, 1H), 2.89 (d, J = 6.0 Hz, 1H), 2.63-2.70 (m, 1H), 2.47 (d, J = 4.0 Hz, 1H), 2.28-2.31 (m, 3H), 1.99 (d, J = 10.4 Hz, 1H), 1.81 (d, J = 10.0 Hz, 1H); 13C NMR (100 MHz, CDCl₃) δ 144.5, 144.0, 136.1, 132.3, 132.3, 131.4, 131.0, 128.9, 128.9, 126.8, 122.0, 121.8, 52.8, 45.2, 45.1, 43.3, 42.3, 42.1, 35.6, 31.7; HRMS (EI) calcd. for C₂₅H₂₂Cl₂ [M⁺]: 404.1099, found: 404.1101.

(1R,2S,5R,6S)-3,4-bis((Z)-benzylidene)tricyclo[4.2.1.0²⁵]nonane (3ad): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether to give pale yellow solid, 108.8 mg, 73% yield. Mp: 88-92°C; 1H NMR (400 MHz, CDCl₃) δ 6.82 (t, J = 6.8 Hz, 2H), 6.59-6.66 (m, 8H), 6.17 (s, 2H), 2.83 (s, 2H), 2.29 (s, 2H), 1.81 (d, J = 10.0 Hz, 1H), 1.49 (d, J = 8.4 Hz, 2H), 1.14 (d, J = 8.4 Hz, 2H), 1.07 (d, J = 10.0 Hz, 1H); 13C NMR (100 MHz, CDCl₃) δ 142.1, 136.6, 126.9, 125.5, 125.0, 122.4, 47.8, 39.6, 31.3, 27.1; HRMS (EI) calcd. for C₂₃H₂₂ [M⁺]: 298.1722, found: 298.1725.

(1R,2S,5R,6S)-3,4-bis((Z)-4-methylbenzylidene)tricyclo[4.2.1.0²⁵]nonane (3bd): The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with an eluent of petroleum ether to give pale yellow solid, 114.2 mg, 70% yield. Mp: 102-106°C; 1H NMR (400 MHz, CDCl₃) δ 6.45 (t, J = 8.4 Hz, 8H), 6.12 (s, 2H), 2.80 (s, 2H), 2.26 (s, 2H), 2.08 (s, 6H), 1.81 (d, J = 10.0 Hz, 1H), 1.48 (d, J = 8.4 Hz, 2H), 1.10 (dd, J = 7.2...
Hz, $J = 1.6$ Hz, 2H), 1.06 (d, $J = 10.0$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃) δ 141.6, 134.8, 134.0, 126.7, 126.1, 122.0, 47.7, 39.6, 31.3, 27.1, 20.0; HRMS (EI) calcd. for C_{25}H_{26} [M^+]: 326.2035, found: 326.2036.

(1R,2S,5R,6S)-3,4-bis((Z)-3-methylbenzylidene)tricyclo[4.2.1.0²,5]nonane  (3cd):

The title compound was prepared according to the general procedure and purified by flash column chromatography on silica gel with a eluent of petroleum ether to give pale yellow solid, 106.0 mg, 65% yield. Mp: 95-99°C; $^1$H NMR (400 MHz, CDCl₃) δ 6.66-6.72 (m, 4H), 6.58 (d, $J = 7.2$ Hz, 2H), 6.32 (s, 2H), 6.15 (s, 2H), 2.82 (s, 2H), 2.28 (s, 2H), 1.80 (d, $J = 10.4$ Hz, 1H), 1.74 (s, 6H), 1.50 (d, $J = 10.0$ Hz, 2H), 1.14 (dd, $J = 7.2$ Hz, $J = 1.6$ Hz, 2H), 1.07 (d, $J = 10.4$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃) δ 141.9, 136.5, 135.4, 128.3, 125.9, 125.6, 124.3, 122.5, 47.8, 39.6, 31.3, 27.1, 19.9; HRMS (EI) calcd. for C_{25}H_{26} [M^+]: 326.2035, found: 326.2032.

4 References


5 Copies for $^1$H NMR and $^{13}$C NMR
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Nuts - $pdata

spect, CDCl₃, F1: 100.623 F2: 1.000  SW1: 24038 OF1: 9958.7  PTS1d: 32768   EX: zgdc30 PW: 9.5  usec PD: 1.2  sec NA: 512   LB: 0.0
3cd