# Supplementary Material

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## A New Tandem Synthetic Routes to Angular Triquinanes. Synthesis of the Waihoensene Ring System

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The experimental details for the synthesis of the new compounds as well as the X-ray data for compounds **5a**,**12**, **13**, **16**, **17** and **21** are provided below.

### General Experimental Details

All reactions were conducted in oven-dried and/or flame-dried glassware under a positive pressure of dry nitrogen. Tetrahydrofuran (THF) was dried by passing it through two 2 x 36 inch columns of anhydrous neutral A-2 alumina, activated under a flow of argon at 350 °C for 3 h. Dichloromethane was distilled from calcium hydride immediately prior to use. Solvents were removed in vacuo at 20 Torr. All reactions were monitored by tlc using Merck silica gel 60 F-254 coated on glass. Flash chromatography was performed using Merck silica gel (230-400 Mesh), or Fisher Scientific Florisil®. $^1H$ NMR (300 and 500 MHz) and $^{13}C$ NMR (75 and 125 MHz) spectra were recorded in $CDCl_3$ as solvent. Coupling constants (*J* values) are given in Hertz (Hz). Melting points are uncoirrected.

1-Bromo-6-methoxy-cyclohexene and 1-bromo-5-methoxy-cyclopentene were prepared from 2-cyclohexenone and 2-cyclopentenone according to standard methods.[1]

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[1] 1. α-Bromination: C. J. Kowalski, A. D. Weber. K. W. Fields, *J. Org. Chem.* **1982**, *47*, 5088.
2. Luche-Reduction: S. E. Denmark, K. L. Habermas, G. A. Hite, *Helv. Chim. Acta* **1988**, *71*, 168.
3. Williamson ether synthesis: NaH, THF, MeI, 12 h r.t.

***cis*-13-Methyl-tricyclo[10.3.0.0$^{4,9}$]pentadeca-4(5),12(13)-diene-3,14-dione (5b).** A magnetically stirred solution of 6-methoxy-1-lithio-cyclohexene [prepared from 277 mg (1.45 mmol) of 1-bromo-6-methoxy-cyclohexene and 1.7 mL t-butyllithium (1.7 M, 2.9 mmol, 2.0 eq)] was added dropwise to 364 mg (1.45 mmol) *cis*-2-methyl-3-[(trimethylsilyl)oxy]-1-vinyl-bicyclo[3.2.0]hept-2-en-7-one (**8**) in THF (15 mL) at -78 °C. After 10 min, 0.28 mL (236 mg, 2.18 mmol, 1.5 eq) chlorotrimethylsilane were added *via* syringe and the solution allowed to warm to ambient temperature. After hydrolysis with 2 M HCl (5 mL) and extraction of the mixture with ether (3 x 20 mL), the combined organic layers were washed with saturated aqueous NaHCO$_3$ (10 mL), dried (MgSO$_4$), filtered, and concentrated. Flash chromatography (silica gel, hexanes/ethyl acetate 1 : 1) furnished the title compound (191 mg, 54 %) as a colorless solid: mp 121-122 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) $\delta$: 6.86 (t, *J* = 4.0 , 1H), 3.55 (dd, *J* = 11.7, 5.3, 1H), 3.09 (br. s, 1H), 2.94 (dt, *J* = 13.3, 2.9, 1H), 2.73 (d, *J* = 11.2, 1H), 2.53 (m, 2H), 2.42 (dt, *J* = 13.1, 2.9, 1H), 2.35 (dd, *J* = 11.8, 4.0, 1H), 2.30-2.12 (m, 2H), 1.96 (ddt, *J* = 13.6, 5.7, 2.5, 1H), 1.78-1.58 (m, 5H), overlapping with 1.64 (d, *J* = 1.9, 3H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 207.7, 199.2, 172.7, 140.3, 140.1, 138.4, 40.5, 38.4, 38.3, 36.1, 35.1, 31.2, 29.8, 25.7, 16.6, 8.0; IR (CHCl$_3$) 2926, 2865, 1696, 1640, 1599 cm$^{-1}$; HRMS (CI) calc'd for $C_{16}H_{20}O_2$ (M$^+$): 244.1463, found 244.1457.

**(1aR*,4bS*,5aS*,9bR*)-9b-Hydroxy-4-methyl-1,1a,2,3,4b,5,5a,7,8,9b-decahydro-6*H*-pentaleno[2,1-a]inden-3-one (12).** As described for compound **5b**, a solution of 301 mg (1.58 mmol, 1.01 eq.) 1-bromo-6-methoxycyclohexene in THF (15 mL) was treated with 1.95 mL t-butyllithium (3.31 mmol, 1.7 M in pentane, 2.1 eq.) at -78 °C. After 45 min, the lithium reagent thus generated was added to 372 mg (1.57 mmol) bicycloheptenone **8** in 15 mL THF at -78 °C *via* cannula. Stirring was continued for 45 min, and then the cooling bath removed. After 15 min, 15 mL brine were added. The mixture was extracted with ether (3 x 20 mL), the combined organic layers were washed with brine (10 mL), dried (MgSO$_4$), and the solvents removed *en vacuo*. Flash chromatography (silica gel, hexanes/ethyl acetate 1 : 1) afforded 169 mg (44 %) of the title compound: colorless solid, mp 150-152 °C; $^1$H NMR (500 MHz, CDCl$_3$, TMS) $\delta$: 5.94 (dd, *J* = 6.6, 2.9, 1H), 3.01 (d, *J* = 9.0, 1H), 2.81 (m$_C$, 1H), 2.59 (dd, *J* = 17.8, 6.2, 1H), 2.38 (dd, *J* =11.5, 7.1, 1H), overlapping with 2.37 (m, 1H), 2.16 (m, 1H), 2.11-2.00 (m, 4H), 1.85 (m, 1H), 1.83 (s, 1H), 1.73 (dt, *J* = 12.2, 9.0, 1H), overlapping with 1.72 (d, *J* = 2.3, 3H), 1.61 (dd, *J* = 12.2, 12.0, 1H), 1.56 (s, 1H), 1.47 (m$_C$, 1H), 1.03 (ddt, *J* = 13.3, 10.5, 2.8, 1H); $^{13}$C NMR (125 MHz, CDCl$_3$) $\delta$: 209.8, 184.0, 151.9, 132.7, 120.1, 90.8, 50.8, 47.3, 43.0, 41.9, 40.6, 36.4, 29.4, 24.8, 22.0, 8.2; IR (CHCl$_3$) 3429, 2928, 1697, 1660 cm$^{-1}$; HRMS (CI) calc'd for $C_{16}H_{20}O_2$ (M$^+$) 244.1463, found 244.1461.

***cis*-7-Methyl-tricyclo[9.3.0.$0^{4,8}$]tetradeca-1(14),7-diene-2,6-dione (5a).** As described for **5b**, 356 mg (1.51 mmol) bicycloheptenone **8** in THF (10 mL) were treated at -78 °C with 5-methoxy-1-lithiocyclopentene [prepared by reacting 267 mg (1.51 mmol, 1.0 eq.) 1-bromo-5-methoxycyclopentene and 1.86 mL t-butyllithium (3.17 mmol, 1.7 M, 2.1 eq.) over a 45 min period] , followed by 0.29 mL chlorotrimethylsilane (246 mg, 2.27 mmol,1.5 eq.). After hydrolysis with 6 mL 2 M HCl and standard workup, flash chromatography (silica gel hexanes/ethyl acetate 1 : 1) yielded **5a** (206 mg, 62 %) as a colorless solid: mp 111 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 6.74 (m, 1H), 3.31 (dd, $J$ = 11.5, 5.3, 1H), 3.06 (br. s, 1H), 2.97 (m, 1H), 2.89 (dd, $J$ = 12.6, 5.3, 1H), 2.54-2.21 (m, 7H), 2.04 (ddt, $J$ = 13.7, 6.2, 3.2, 1H), 1.70 (m, 1H), 1.60 (d, $J$ = 2.0, 3H), 1.55 (m, 1H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$: 207.4, 197.0, 172.4, 147.6, 145.1, 138.7, 45.4, 40.6, 40.5, 38.2, 34.9, 34.4, 30.6, 29.4, 8.0; IR ($CHCl_3$) 2933, 2871, 1691, 1660, 1641, 1587 cm$^{-1}$; HRMS (CI) calc'd for $C_{15}H_{18}O_2$ ($M^+$): 230.1307, found 230.1306.

**(3R*,3aS*,5aR*,9aR*,11aR*)-3-Methyl-1,2,3,5,5a,6,7,10,11,11a-decahydro-4*H*-pentaleno[6a,1-c]inden-2,10-dione (13).** A solution of 85 mg (0.35 mmol) dienedione **5a**, 5 mg (0.04 mmol) sodium thiophenolate, and 2 drops of thiophenol in 5 ml THF was heated at gentle reflux for 12 h. After cooling to ambient temperature and removal of the sovent *en vacuo*, flash chromatography (silica gel, hexanes/ethyl acetate 3 : 1) furnished 79 mg (93 %) of the title compound as a colorless solid: mp 102 °C; $^1$H NMR (500 MHz, $CDCl_3$, TMS) $\delta$: 6.12 (dt, $J$ = 10.2, 4.0, 1H), 5.30 (d, $J$ = 10.2, 1H), 2.85 (dd, $J$ = 18.8, 8.7, 1H), 2.66 (dq, $J$ = 10.9, 2.1, 1H), 2.55 (dd, $J$ = 19.4, 8.8, 1H), 2.43 (m, 1H), 2.38 (q, $J$ = 7.1, 1H), 2.29 (dt, $J$ = 19.4, 1.7, 1H), 2.19 (dd, $J$ = 18.8, 9.8, 1H), 2.07 (m$_C$, 2H), 1.95 (m$_C$, 1H), 1.84 (ddd, $J$ = 13.1, 9.7, 8.3, 1H), 1.67 (m, 2H), 1.53 (pseudo-q, $J$ = 5.1, 1H), 1.48 (m$_C$, 1H), 1.05 (d, $J$ = 7.1, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$: 219.1, 218.3, 132.5, 123.4, 64.5, 62.9, 46.4, 43.5, 41.1, 39.9, 37.4, 29.3, 27.6, 22.7, 20.8, 11.0; IR ($CHCl_3$) 3027, 2930, 1734 cm$^{-1}$; HRMS (CI) cal'd for $C_{16}H_{20}O_2$ ($M^+$): 244.1463, found 244.1454.

**(3R*,3aS*,5aS*,8S*,8aR*,10aR*)-3-Methyl-8-(phenylthio)-perhydropentaleno[6a,1-c]pentalen-2,9-dione (16).** A solution of 80 mg (0.35 mmol) dienedione **5b**, 0.035 ml (38 mg, 0.35 mmol) thiophenol, and 5 mg (0.04 mmol) sodium thiophenolate in 5 ml THF was stirred at ambient temperature for 1 h, and then heated at gentle reflux for 2 h. After cooling to ambient temperature and removal of the solvent, flash chromatography (silica gel, hexanes/ethyl acetate 3 : 1) provided 90 mg (76 %) of **16** as a colorless solid: mp 112 °C; $^1$H NMR (500 MHz, $CDCl_3$) $\delta$: 7.37 (m, 2H), 7.28 (m, 2H), 7.22 (m, 1H), 3.19 (q, $J$ = 7.3, 1H), overlapping with 3.18 (dd, $J$ = 11.5, 6.0, 1H), 2.71 (m, 1H), overlapping with 2.69 (dd, $J$ = 17.9, 7.7, 1H), 2.46 (m, 2H), 2.36 (dd, *J* = 17.9, 1.3, 1H), 2.31-2.07 (m, 4H), 1.89 (m, 2H), 1.56 (m, 1H), 1.46 (m, 1H), 1.24 (m, 1H), 0.93 (d, *J* = 7.1, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 219.3, 218.6, 136.6, 131.3, 129.1, 127.1, 61.8, 52.9, 51.9, 45.8, 44.8, 40.8, 37.8, 35.4, 32.8, 29.7, 28.7, 11.7; IR ($CHCl_3$): 2953, 2865, 1729, 1583, 748, 716 cm$^{-1}$; HRMS (CI) cal'd for $C_{21}H_{24}O_2S$ ($M^+$): 340.1497, found 340.1489.

**(1R*,4R*,5R*,9S*)-5-Allyl-13-methyl-tricyclo[10.3.0.0$^{4,9}$]pentadec-12(13)-ene-3,14-dione (17).** A solution of 100 mg (0.41 mmol) **5a** and 0.65 mL (469 mg, 4.1 mmol, 10 eq.) allyltrimethylsilane in 6 mL $CH_2Cl_2$ was cooled to -78 °C, and 0.05 mL $TiCl_4$ (85 mg, 0.45 mmol, 1.1 eq.) were added dropwise. Stirring was continued for 30 min at -78 °C. The cooling bath was removed, and the dark red solution hydrolized with saturated aqueous $NaHCO_3$ (25 mL). The mixture was stirred for 45 min at ambient temperature, and then acidified with 2 M HCl. The layers were separated, and the aqueous layer extracted with $CH_2Cl_2$ (3 x 15 mL). The combined organic layers were washed with saturated aqueous $NH_4Cl$ (10 mL), dried ($MgSO_4$), filtered, and concentrated *en vacuo*. Flash chromatography (silica gel, hexanes/ethyl acetate 3 : 1) yielded product **17** (100 mg, 87 %) as a colorless solid: mp 120 °C; $^1$H NMR (500 MHz, TMS, $CDCl_3$) δ: 5.78 (dddd, *J* = 17.0, 10.2, 8.2, 6.0, 1H), 5.04 (ddd, *J* = 8.2, ≈3, ≈2, 1H), overlapping with 5.01 (ddd, *J* = 17.0, ≈3, ≈2, 1H), 3.55 ($m_C$, 1H), 3.39 (t, *J* = 4.0, 1H), 2.80 (dd, *J* = 15.2, 4.7, 1H), 2.68 (dd, *J* = 18.5, 6.7, 1H), 2.53 (dd, *J* = 17.0, 9.5, 1H), 2.37 ( dd *J* = 17.0, 9.5, 1H), 2.07-1.84 (m, 8H), 1.65 (s, 3H), overlapping with 1.62 (m, 3H), 1.46 (m, 1H), 1.41-1.25 (m, 2H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 215.0, 207.4, 174.8, 137.4, 136.6, 116.3, 54.2, 49.0, 42.2, 41.5 (2C), 38.8, 36.3, 31.0, 27.4, 26.5, 26.1, 24.7, 8.1; IR ($CHCl_3$) 2926, 1695, 1638 cm$^{-1}$; HRMS (CI) calc'd for $C_{19}H_{26}O_2$ ($M^+$): 286.1933, found 286.1932.

**(3aR*,5aS*,8R*,8aS*,10aS*)-3-Methyl-9-oxo-2-[(trimethylsilyl)oxy]-1,4,5,5a,6,7,8,9,10,10a-decahydropentaleno[6a,1-c]pentalen-8-yl cyanide (19).** To a solution of 0.09 mL (0.65 mmol, 1.3 eq.) trimethylsilyl cyanide and 0.55 mL triethylaluminum (1.1 eq., 1.0 M solution in hexanes) in 5 mL THF was added a solution of 115 mg (0.5 mmol) **5b** in 3 mL THF *via* syringe at ambient temperature. The resulting yellow solution was heated at reflux for 5 h. After cooling to ambient temperature, the reaction was quenched by adding 5 mL saturated aqueous $NaHCO_3$. The mixture was transferred to a separatory funnel, and 40 mL ether and 15 mL saturated aqueous $NH_4Cl$ were added. The layers were separated and the aqueous layer was extracted with ether (3 x 20 mL). The combined organic layers were washed with brine (1 x 10 mL), dried ($MgSO_4$), filtered through celite, and concentrated. Flash chromatography (florisil®, hexanes/ethyl acetate 5 : 1) yielded 99 mg (60 %) of the title compound as a yellow oil: $^1$H NMR (500 MHz, $CDCl_3$) δ: 2.70 (dd, $J$ = 19.1, 9.1, 1H), 2.69 (dd, $J$ = 11.9, 6.5, 1H), 2.59 (m, 2H), 2.42 (m, 1H), 2.30-2.16 (m, 3H), 2.14-2.03 (m, 3H), 1.90 (m, 1H), 1.65 (t, $J$ = 2.1, 3H), 1.56 (m, 1H), 1.47 (m, 1H), 1.28 (m, 1H), 0.19 (s, 9H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 219.3, 148.7, 119.9, 113.8, 72.0, 65.4, 52.4, 43.9, 39.4, 37.9, 36.7, 34.0, 33.2, 32.9, 31.1, 10.2, 0.5 (3C); IR (thin film) 2955, 2238, 1732, 1671, 1253, 850 cm$^{-1}$; HRMS (EI) calc'd for $C_{19}H_{27}NO_2Si$ ($M^+$): 329.1811, found 329.1810.

**(3R*,3aS*,5aR*,8S*,8aS*,10aR*)-8-Ethyl-3-methyl-perhydropentaleno[6a,1-c]pentalen-2,9-dione (21).** A solution of 50 mg (0.22 mmol) dienedione **5b** in 4 mL $CH_2Cl_2$ was cooled to 0 °C and treated with 0.24 mL $AlEt_3$ (0.24 mmol, 1.1 eq., 1.0 M solution in hexanes). After 20 min of stirring, the reaction mixture was quenched by dropwise addition of 5 mL 2 M HCl. The mixture was transferred to a separatory funnel, and the aqueous layer extracted with ether (2 x 10 mL), and $CH_2Cl_2$ (10 mL). The combined organic layers were washed with saturated aqueous $NaHCO_3$ (10 mL), dried ($Na_2SO_4$), filtered through celite, and concentrated *en vacuo*. Purification by flash chromatography (silica gel, hexanes/ethyl acetate 5 : 1) furnished the title compound (31 mg, 55 %) as a colorless solid: mp 62 °C; $^1$H NMR (500 MHz, $CDCl_3$) δ: 2.60 (m, 2H), overlapping with 2.56 (dd $J$ = 17.6, 7.8, 1H), 2.50 (dd $J$ = 19.2, 8.5, 1H), 2.40 (m, 1H), 2.32 ( d, $J$ = 19.2, 1H), 2.08 (dd, $J$ = 17.6, 12.5, 1H), 1.98 (m, 2H), 1.92-1.75 ( m, 3H), 1.56-1.39 (m, 4H), 1.21 ( m, 2H), 1.16 (d, $J$ = 7.2, 3H), 0.90 (t, $J$ = 7.4, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) δ: 220.9, 219.6, 72.6, 62.0, 52.7, 48.4, 46.3, 45.4, 40.5, 35.4, 33.7, 33.2, 29.5, 28.9, 24.0, 14.0, 11.5); IR (thin film) 2948, 2872, 1738, 1727 cm$^{-1}$; HRMS (EI) calc'd for $C_{17}H_{24}O_2$ ($M^+$): 260.1776, found 260.1775.