SUPPORTING INFORMATION

THE HIYAMA CROSS-COUPPLING REACTION IN THE STEREOSPECIFIC SYNTHESIS OF RETINOIDS

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General Methods. Solvents were dried according to published methods and distilled before use.¹ All other reagents were commercial compounds of the highest purity available. Reactions were carried out under atmosphere of argon in flame-dried glassware with magnetic stirring. Visualization of analytical thin-layer chromatography (TLC) was accomplished with phosphomolybdic acid ethanolic solution (10%) stain followed by heating. Proton (¹H) and carbon (¹³C) magnetic resonance spectra (NMR) were recorded using CDCl₃ as solvent. Chemical shifts (δ) are expressed in parts per million (ppm) relative to tetramethylsilane as internal reference. ¹³C multiplicities were assigned with the aid of the DEPT pulse sequence.

Experimental Procedures

All the solutions employed were degassed by argon bubbling during 15 min. Cross-coupling reactions and purification of the retinoids were carried out in the absence of light.

(1*E*,3*E*)-1-Iodo-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**8**).² *p*-Toluensulphonic acid (5 mg, 0.027 mmol) and DHP (352 mL, 4.03 mmol) were sequentially added to a solution of (2*E*,4*E*)-5-iodo-3-methylpenta-2,4-dien-1-ol³ (615 mg, 2.74 mmol) in THF (10 mL) and the mixture was stirred for 2h at rt. The solution was quenched with NaHCO₃ (15 mL) and the aqueous phase was extracted with diethyl ether (2x15 mL). The combined organic phases were washed with water (2x15 mL) and brine (2x15 mL), dried with (anhydrous) sodium sulphate and filtered. The solvent was evaporated and the crude was purified by column chromatography (SiO₂, 80:20 hexane/AcOEt) to obtain compound **8** (776 mg, 92%) as a clear yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 1.5-1.8 (m, 6H), 1.71 (s, 3H), 3.3-3.5 (m, 1H), 3.7-3.8 (m, 1H), 4.07 (dd, *J* = 11.5, 6.7 Hz, 1H), 4.19 (dd, *J* = 11.5, 5.5 Hz, 1H), 4.55 (t, *J* = 3.2 Hz, 1H), 5.55 (t, *J* = 6.1 Hz, 1H), 6.23 (d, *J* = 14.6 Hz, 1H), 7.05 (d, *J* = 14.6 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 12.0 (CH₃), 19.2 (CH₂), 25.3 (CH₂), 30.4 (CH₂), 62.0 (CH₂), 62.9 (CH₂), 75.6 (CH), 97.7 (CH), 129.2 (CH), 136.7 (C), 148.7 (CH) ppm. MS (CI) *m/z* (%) 309 (*M*⁺+1, 10), 223 (10), 207 (100), 181 (36). HMRS (CI) calcd for C₁₁H₁₇IO₂, 308.0273; found, 308.0267.

(1*Z*,3*E*)-1-Iodo-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**10**). Following the same procedure as described for compound **8**, reaction of (2*E*,4*Z*)-5-iodo-3-methylpenta-2,4-dien-1-ol³ (45 mg, 0.20 mmol) with *p*-toluensulphonic acid (1 mg, 0.005 mmol) and DHP (27 μ L, 0.31 mmol) in THF (2 mL) for 2h at rt afforded, after column chromatography (SiO₂, 80:20 hexane/AcOEt), compound **10** (56 mg, 91%) as a clear yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 1.4-1.8 (m, 6H), 1.93 (s, 3H), 3.4-3.5 (m, 1H), 3.8-3.9 (m, 1H), 4.13 (dd, *J* = 13.1, 7.0 Hz, 1H), 4.19 (dd, *J* = 13.1, 6.2 Hz, 1H), 4.65 (t, *J* = 3.2 Hz, 1H), 5.81 (t, *J* = 6.6 Hz, 1H), 6.23 (d, *J* = 8.5 Hz, 1H), 6.76 (d, *J* = 8.5 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 15.8 (CH₃), 19.4 (CH₂), 25.4 (CH₂), 30.6 (CH₂), 62.2 (CH₂), 63.1 (CH₂), 76.6 (CH), 97.8 (CH), 129.8 (CH), 136.1 (C), 141.5 (CH) ppm. MS (CI) *m/z* (%) 309 (*M*⁺+1, 72), 206 (100), 181 (97). HMRS (CI) calcd for C₁₁H₁₈IO₂, 309.0351; found, 309.0349.

¹ Armarego, W. L. F.; Perrin, D. D. *Purification of Laboratory Chemicals*. 4th Ed; Butterworth-Heinemann: Oxford, **1996**.

² Negishi, E.; Owczarczyk, Z. *Tetrahedron Lett.* **1991**, 32, 6683.

³ a) de Lera, A. R.; Torrado, A.; Iglesias, B.; López, S. *Tetrahedron Lett.* **1992**, 33, 6205. b) Torrado, A.; Iglesias, B.; López, S.; de Lera, A. R. *Tetrahedron* **1995**, 51, 2435.

(1*E*,3*E*)-1-Ethoxydimethylsilyl-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**5a**). *Method A*: Ethoxydimethylsilane (439 μ L, 3.19 mmol) was added dropwise to a solution of Pt(DVDS) (0.1 M in xylenes, 90 μ L, 0.009 mmol) and *t*-Bu₃P (2 μ L, 0.008 mmol) in THF (4 mL), and the mixture was stirred for 30 min at rt. A solution of (*E*)-3-methyl-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**7**)⁴ (300 mg, 1.66 mmol) in THF (1 mL) was then added over 10 min. and the reaction mixture was stirred for 1h. The solvent was removed under vacuum and the crude was purified by column chromatography (SiO₂, 95:5 hexane/AcOEt) to yield compound **5a** (434 mg, 92%) as a clear yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.17 (s, 6H), 1.16 (t, *J* = 6.9 Hz, 3H), 1.5-1.9 (m, 6H), 1.80 (s, 3H), 3.4-3.5 (m, 1H), 3.63 (q, *J* = 6.9 Hz, 2H), 3.8-3.9 (m, 1H), 4.14 (dd, *J* = 12.9, 7.1 Hz, 1H), 4.34 (dd, *J* = 12.9, 6.6 Hz, 1H), 4.61 (t, *J* = 3.6 Hz, 1H), 5.71 (t, *J* = 6.8 Hz, 1H), 5.77 (d, *J* = 19.0 Hz, 1H), 6.64 (d, *J* = 19.0 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -1.8 (2xCH₃), 12.0 (CH₃), 18.4 (CH₃), 19.4 (CH₂), 25.4 (CH₂), 30.5 (CH₂), 58.3 (CH₂), 62.0 (CH₂), 63.5 (CH₂), 97.7 (CH), 124.9 (CH), 130.0 (CH), 137.7 (C), 149.5 (CH) ppm. MS (CI) *m/z* (%) 285 (M⁺+1, 7), 284 (3), 243 (15), 183 (100). HMRS (CI) calcd for C₁₅H₂₈O₃Si, 284.1807; found, 284.1813.

Dimethyl (1*E*,3*E*)-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-dienyl silanol (**5b**). *Method A*: Following the same procedure as described for compound **5a**, reaction of Pt(DVDS) (0.1 M in xylenes, 150 μ L, 0.015 mmol), *t*-Bu₃P (4 μ L, 0.015 mmol), ethoxydimethylsilane (755 μ L, 5.49 mmol), and (*E*)-3-methyl-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**7**) (500 mg, 2.77 mmol) in THF (5 mL) afforded, after acid hydrolysis [CH₃CN, 1.0 M HOAc/NaOAc buffer, pH=5, 12h] and column chromatography (SiO₂, 85:15 hexane/AcOEt), compound **5b** (632 mg, 89%) as a clear yellow oil. *Method C*: *n*-BuLi (2.5 M in hexanes, 256 μ L, 0.64 mmol) was added over 10 min to a solution of (1*E*,3*E*)-1-iodo-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**8**) (100 mg, 0.32 mmol) in diethyl ether (2 mL) cooled at -78 °C, and the reaction mixture was stirred at this temperature for 1h. A solution of hexamethylcyclotrisiloxane (24 mg, 0.11 mmol) in diethyl ether (1 mL) was added at the same temperature and the reaction was allowed to warm to rt for 6 h. The solution was then cooled to 0 °C and quenched with water (15 mL). The aqueous phase was extracted with diethyl ether (2x15 mL) and the combined organic phases were washed with water (2x15 mL) and brine (2x15 mL). The organic layer was dried with anhydrous sodium sulphate and filtered. The solvent was evaporated and the crude was purified by column chromatography (SiO₂, 85:15 hexane/AcOEt) to yield compound **5b** (65 mg, 80%) as a clear yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.19 (s, 6H), 1.4-1.7 (m, 6H), 1.75 (s, 3H), 3.5-3.6 (m, 1H), 3.7-3.8 (m, 1H), 4.16 (dd, *J* = 13.0, 7.2 Hz, 1H), 4.31 (dd, *J* = 13.0, 6.2 Hz, 1H), 4.62 (t, *J* = 3.4 Hz, 1H), 5.70 (t, *J* = 6.7 Hz, 1H), 5.80 (d, *J* = 19.0 Hz, 1H), 6.61 (d, *J* = 19.0 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ 0.1 (2xCH₃), 12.0 (CH₃), 19.3 (CH₂), 25.4 (CH₂), 30.5 (CH₂), 62.1 (CH₂), 63.6 (CH₂), 97.8 (CH), 126.3 (CH), 129.9 (CH), 137.7 (C), 148.9 (CH) ppm. MS (CI) *m/z* (%) 257 (M⁺+1, 1), 155 (81), 85 (100). HMRS (CI) calcd for C₁₃H₂₅O₃Si, 257.1572; found, 257.1570.

(1*E*,3*E*)-3-Methyl-1-methylsilacyclobutyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**5c**). *Method C*: Following the same procedure as described for compound **5b**, treatment of a solution of (1*E*,3*E*)-1-iodo-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**8**) (200 mg, 0.65 mmol) in diethyl ether (2 mL) with *n*-BuLi (2.5 M in hexanes, 325 μ L, 0.81 mmol) at -78 °C, followed by trapping of the resulting anion with a solution of chloromethylsilacyclobutane (119 μ L, 0.97 mmol) in diethyl ether (1 mL) afforded, after column chromatography (SiO₂, 95:5 hexane/AcOEt), compound **5c** (148 mg, 86%) as a clear yellow oil.

⁴ Mori, K.; Fujioka, T. *Tetrahedron* **1984**, *40*, 2711.

^1H NMR (300 MHz, CDCl_3) δ 0.35 (s, 3H), 0.9-1.1 (m, 4H) 1.5-1.8 (m, 6H), 1.81 (s, 3H), 2.0-2.2 (m, 2H), 3.4-3.5 (m, 1H), 3.8-3.9 (m, 1H), 4.20 (dd, $J = 12.9, 7.2$ Hz, 1H), 4.40 (dd, $J = 12.9, 6.2$ Hz, 1H), 4.65 (t, $J = 3.5$ Hz, 1H), 5.74 (t, $J = 6.7$ Hz, 1H), 5.96 (d, $J = 18.9$ Hz, 1H), 6.71 (d, $J = 18.9$ Hz, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ -1.8 (CH_3), 12.1 (CH_3), 14.4 ($2\times\text{CH}_2$), 18.2 (CH_2), 19.4 (CH_2), 25.4 (CH_2), 30.6 (CH_2), 62.2 (CH_2), 63.7 (CH_2), 97.9 (CH), 125.9 (CH), 129.9 (CH), 137.8 (C), 149.3 (CH) ppm. MS (ESI) m/z (%) 289 ($\text{M}^+ + \text{Na}$, 100), 267 ($\text{M}^+ + 1$, 33), 165 (42). HMRS (ESI) calcd for $\text{C}_{15}\text{H}_{26}\text{O}_2\text{Si}$, 267.1780; found, 267.1770.

(1*E*,3*E*)-1-Benzyltrimethylsilyl-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**5d**). *Method A*: Following the same procedure as described for compound **5a**, reaction of Pt(DVDS) (0.1 M in xylenes, 50 μL , 0.005 mmol), *t*-Bu₃P (1 μL , 0.004 mmol), benzyltrimethylsilane (229 μL , 1.45 mmol), and (*E*)-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**7**) (200 mg, 1.11 mmol) in THF (2 mL) afforded compound **5d** (355 mg, 97%) as a clear yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 0.07 (s, 6H), 1.5-1.6 (m, 6H), 1.70 (s, 3H), 2.11 (s, 2H), 3.5-3.6 (m, 1H), 3.8-3.9 (m, 1H), 4.18 (dd, $J = 12.9, 7.2$ Hz, 1H), 4.38 (dd, $J = 12.9, 6.2$ Hz, 1H), 4.62 (t, $J = 3.6$ Hz, 1H), 5.70 (t, $J = 6.7$ Hz, 1H), 5.80 (d, $J = 18.9$ Hz, 1H), 6.55 (d, $J = 18.9$ Hz, 1H), 6.9-7.0 (m, 2xArH), 7.0-7.1 (m, ArH), 7.1-7.2 (m, 2xArH) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ -3.3 ($2\times\text{CH}_3$), 12.0 (CH_3), 19.3 (CH_2), 25.4 (CH_2), 26.1 (CH_2), 30.5 (CH_2), 62.1 (CH_2), 63.6 (CH_2), 97.8 (CH), 123.8 (ArCH), 125.8 (CH), 127.9 ($2\times\text{ArCH}$), 128.1 ($2\times\text{ArCH}$), 129.2 (CH), 137.8 (C), 139.8 (ArC), 148.6 (CH) ppm. MS (ESI) m/z (%) 353 ($\text{M}^+ + \text{Na}$, 44), 331 ($\text{M}^+ + 1$, 2), 149 (100). HMRS (ESI) calcd for $\text{C}_{20}\text{H}_{30}\text{NaO}_2\text{Si}$, 353.1912; found, 353.1907.

(1*E*,3*E*)-1-Diisopropylsilyl-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**5e**). *Method A*: Following the same procedure as described for compound **5a**, reaction of Pt(DVDS) (0.1 M in xylenes, 30 μL , 0.003 mmol), *t*-Bu₃P (1 μL , 0.004 mmol), diisopropylsilane (96 mg, 0.83 mmol), and (*E*)-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**7**) (100 mg, 0.55 mmol) in THF (2 mL) afforded compound **5e** (156 mg, 95%) as a clear yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 1.0-1.1 (m, 14H), 1.5-1.6 (m, 6H), 1.78 (s, 3H), 3.4-3.5 (m, 1H), 3.65 (d, $J = 4.5$ Hz, 1H), 3.8-3.9 (m, 1H), 4.16 (dd, $J = 12.8, 7.1$ Hz, 1H), 4.35 (dd, $J = 12.8, 6.3$ Hz, 1H), 4.64 (t, $J = 3.8$ Hz, 1H), 5.69 (t, $J = 6.7$ Hz, 1H), 5.74 (dd, $J = 18.8, 4.5$ Hz, 1H), 6.71 (d, $J = 18.8$ Hz, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 10.9 ($2\times\text{CH}$), 12.3 (CH_3), 18.8 ($2\times\text{CH}_3$), 19.0 ($2\times\text{CH}_3$), 19.7 (CH_2), 25.7 (CH_2), 30.9 (CH_2), 62.4 (CH_2), 63.9 (CH_2), 98.3 (CH), 120.3 (CH), 129.5 (CH), 138.2 (C), 151.9 (CH) ppm. MS (ESI) m/z (%) 297 ($\text{M}^+ + 1$, 30), 253 (44), 215 (100). HMRS (ESI) calcd for $\text{C}_{17}\text{H}_{33}\text{O}_2\text{Si}$, 297.2249; found, 297.2253.

(*E*)-3-Methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**9**). *Method C*: Following the same procedure as described for compound **5b**, treatment of a solution of (1*E*,3*E*)-1-iodo-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**8**) (200 mg, 0.65 mmol) in diethyl ether (2 mL) with *n*-BuLi (2.5 M in hexanes, 325 μL , 0.81 mmol) at -78 $^\circ\text{C}$, followed by trapping of the resulting anion with a solution of benzylchlorodimethylsilane (175 μL , 0.97 mmol) in diethyl ether (1 mL) afforded, after column chromatography (SiO_2 , 90:10 hexane/AcOEt), compound **9** (85 mg, 72%) as a clear yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 1.4-1.8 (m, 6H), 1.75 (s, 3H), 3.4-3.5 (m, 1H), 3.8-3.9 (m, 1H), 4.12 (dd, $J = 12.7, 7.2$ Hz, 1H), 4.33 (dd, $J = 12.7, 6.3$ Hz, 1H), 4.55 (t, $J = 3.7$ Hz, 1H), 5.00 (d, $J = 10.0$ Hz, 1H), 5.55 (d, $J = 17.4$ Hz, 1H), 5.61 (t, $J = 6.7$ Hz, 1H), 6.35 (dd, $J = 17.4, 10.0$ Hz, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 11.8 (CH_3), 19.4 (CH_2), 25.4 (CH_2), 30.5 (CH_2), 62.1 (CH_2), 63.4 (CH_2), 97.8 (CH), 112.6 (CH), 128.0 (CH_2), 130.8 (C),

140.7 (CH) ppm. MS (CI) m/z (%) 183 ($M^+ + 1$, 1), 182 (M^+ , 2), 149 (100). HMRS (ESI) calcd for $C_{11}H_{19}O_2$, 183.1285; found, 183.1384.

(*E*)-3-Methyl-1-methylsilacyclobutyl-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**11c**). *n*-BuLi (2.5 M in hexanes, 1.73 mL, 4.33 mmol) was added over 10 min to a solution of (*E*)-3-methyl-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**7**) (600 mg, 3.33 mmol) in diethyl ether (8 mL) cooled at $-78\text{ }^{\circ}\text{C}$, and the reaction mixture was stirred at this temperature for 1 h. A solution of chloromethylsilacyclobutane (608 μL , 5.00 mmol) in diethyl ether (2 mL) was added at the same temperature and the reaction was allowed to warm to rt for 4 h. The solution was then cooled to $0\text{ }^{\circ}\text{C}$ and quenched with water (25 mL). The aqueous phase was extracted with diethyl ether (3x30 mL) and the combined organic phases were washed with water (2x25 mL) and brine (2x25 mL). The organic layer was dried with anhydrous sodium sulphate and filtered. The solvent was evaporated and the crude was purified by column chromatography (SiO_2 , 95:5 hexane/AcOEt), to obtain compound **11c** (791 mg, 90%) as a yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 0.43 (s, 3H), 0.9–1.2 (m, 4H), 1.4–1.9 (m, 6H), 1.85 (s, 3H), 1.9–2.2 (m, 2H), 3.4–3.5 (m, 1H), 3.7–3.8 (m, 1H), 4.10 (dd, $J = 13.3, 7.2\text{ Hz}$, 1H), 4.26 (dd, $J = 13.3, 6.2\text{ Hz}$, 1H), 4.63 (t, $J = 3.2\text{ Hz}$, 1H), 6.08 (t, $J = 6.7\text{ Hz}$, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ -0.1 (CH_3), 15.4 ($2\times\text{CH}_2$), 17.4 (CH_3), 18.3 (CH_2), 19.2 (CH_2), 25.4 (CH_2), 30.5 (CH_2), 62.1 (CH_2), 63.0 (CH_2), 90.1 (C), 97.8 (CH), 109.4 (C), 120.9 (C), 135.2 (CH) ppm. MS (ESI) m/z (%) 287 ($M^+ + \text{Na}$, 19), 265 ($M^+ + 1$, 13), 245 (100), 163 ($M^+ - \text{OTHP}$, 24). HMRS (ESI) calcd for $\text{C}_{15}\text{H}_{25}\text{O}_2\text{Si}$, 265.1623; found, 265.1623.

(*E*)-1-Benzyltrimethylsilyl-3-methyl-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**11d**). Following the same procedure as described for compound **11c**, treatment of a solution of (*E*)-3-methyl-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**7**) (71 mg, 0.39 mmol) in diethyl ether (4 mL) with *n*-BuLi (1.6 M in hexanes, 317 μL , 0.51 mmol) at $-78\text{ }^{\circ}\text{C}$, followed by trapping of the resulting anion with a solution of benzylchlorodimethylsilane (106 μL , 0.58 mmol) in diethyl ether (2 mL) afforded, after column chromatography (SiO_2 , 95:5 hexane/AcOEt), compound **11d** (118 mg, 92%) as a yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 0.12 (s, 6H), 1.5–1.6 (m, 6H), 1.79 (s, 3H), 2.18 (s, 2H), 3.4–3.5 (m, 1H), 3.8–3.9 (m, 1H), 4.09 (dd, 1H, $J = 13.3, 7.2\text{ Hz}$), 4.24 (dd, 1H, $J = 13.3, 6.2\text{ Hz}$), 4.61 (t, 1H, $J = 3.1\text{ Hz}$), 6.05 (t, $J = 6.7\text{ Hz}$, 1H), 7.1–7.2 (m, 3xArH), 7.2–7.3 (m, 2xArH) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ -2.1 ($2\times\text{CH}_3$), 17.3 (CH_3), 19.3 (CH_2), 25.4 (CH_2), 26.2 (CH_2), 30.5 (CH_2), 62.1 (CH_2), 63.0 (CH_2), 90.2 (C), 97.8 (CH), 108.7 (C), 121.1 (C), 124.2 (ArCH), 128.0 ($2\times\text{ArCH}$), 128.3 ($2\times\text{ArCH}$), 134.7 (CH), 139.0 (ArC) ppm. MS (ESI) m/z (%) 329 ($M^+ + 1$, 22), 245 (100), 227 (80). HMRS (ESI) calcd for $\text{C}_{20}\text{H}_{29}\text{O}_2\text{Si}$, 329.1936; found, 329.1943.

(*E*)-1-Diisopropylsilyl-3-methyl-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**11e**). Following the same procedure as described for compound **11c**, treatment of a solution of (*E*)-3-methyl-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**7**) (100 mg, 0.55 mmol) in diethyl ether (4 mL) with *n*-BuLi (1.6 M in hexanes, 451 μL , 0.72 mmol) at $-78\text{ }^{\circ}\text{C}$, followed by trapping of the resulting anion with a solution of chlorodiisopropylsilane (1.6 M in hexanes, 141 μL , 0.83 mmol) in diethyl ether (2 mL) afforded, after column chromatography (SiO_2 , 95:5 hexane/AcOEt), compound **11e** (147 mg, 90%) as a yellow oil.

^1H NMR (300 MHz, CDCl_3) δ 1.1–1.2 (m, 14H), 1.4–1.7 (m, 6H), 1.79 (s, 3H), 3.4–3.5 (m, 1H), 3.69 (s, 1H), 3.7–3.8 (m, 1H), 4.03 (dd, $J = 13.2, 7.2\text{ Hz}$, 1H), 4.23 (dd, $J = 13.2, 6.3\text{ Hz}$, 1H), 4.57 (t, $J = 3.5\text{ Hz}$, 1H), 6.01 (t, $J = 6.7\text{ Hz}$, 1H) ppm. ^{13}C NMR (75 MHz, CDCl_3) δ 10.8 ($2\times\text{CH}$), 17.4 (CH_3), 18.2 ($2\times\text{CH}_3$), 18.4 ($2\times\text{CH}_3$), 19.2 (CH_2),

25.4 (CH₂), 30.5 (CH₂), 62.0 (CH₂), 63.0 (CH₂), 85.4 (C), 97.8 (CH), 110.1 (C), 121.0 (C), 134.7 (CH) ppm. MS (ESI) *m/z* (%) 295 (M⁺+1, 4), 195 (62), 179 (29), 101 (11). HMRS (ESI) calcd for C₁₇H₃₁O₂Si, 295.2093; found, 295.2087.

(1*Z*,3*E*)-3-Methyl-1-methylsilacyclobutyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**6c**). *Method D*: To a stirred suspension of Cp₂Zr(H)Cl⁵ (425 mg, 1.65 mmol) in THF (30 mL) was added dropwise a solution of (*E*)-3-methyl-1-(methylsilacyclobutyl)-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**11c**) (350 mg, 1.32 mmol) in THF (3 mL) and the mixture was stirred for 4h until the hydrozirconation was complete, as evidence by the disappearance of the insoluble hydride and the formation of a clear solution. It was then diluted with *n*-pentane (20 mL), stirred for a further 20 min, filtered through a short pad of neutral alumina, and concentrated. Flash chromatography of the crude (SiO₂, 95:5 hexane/AcOEt) afforded compound **6c** (273 mg, 77%) as a clear yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.39 (s, 3H), 0.9-1.2 (m, 4H), 1.4-1.7 (m, 6H), 1.78 (s, 3H), 1.9-2.1 (m, 2H), 3.4-3.5 (m, 1H), 3.8-3.9 (m, 1H), 4.12 (dd, *J* = 12.8, 7.2 Hz, 1H), 4.29 (dd, *J* = 12.8, 6.2 Hz, 1H), 4.64 (t, *J* = 3.5 Hz, 1H), 5.64 (t, *J* = 6.7 Hz, 1H), 5.69 (d, *J* = 14.7 Hz, 1H), 6.81 (d, *J* = 14.7 Hz, 1H) ppm. ¹³C NMR (75 MHz, CDCl₃) δ -1.8 (CH₃), 12.1 (CH₃), 14.4 (2xCH₂), 18.2 (CH₂), 19.4 (CH₂), 25.4 (CH₂), 30.6 (CH₂), 62.2 (CH₂), 63.7 (CH₂), 97.9 (CH), 127.9 (CH), 128.9 (CH), 138.8 (C), 149.9 (CH) ppm. MS (ESI) *m/z* (%) 289 (M⁺+Na, 55), 285 (5), 267 (M⁺+1, 23), 245 (100), 289 (35). HMRS (ESI) calcd for C₁₅H₂₇O₂Si, 267.1780; found, 267.1775.

(1*Z*,3*E*)-1-(Benzyldimethylsilyl)-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**6d**). *Method D*: Following the same procedure as described for compound **6c**, reaction of Cp₂Zr(H)Cl (98 mg, 0.37 mmol) and (*E*)-1-benzyldimethylsilyl-3-methyl-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**11d**) (49 mg, 0.15 mmol) in THF (15 mL) afforded, after treatment with *n*-pentane (15 mL) and purification, compound **6d** (37 mg, 76%) as a yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 0.08 (s, 6H), 1.4-1.9 (m, 6H), 1.74 (s, 3H), 2.19 (s, 2H), 3.5-3.6 (m, 1H), 3.8-3.9 (m, 1H), 4.07 (dd, *J* = 12.5, 7.1 Hz, 1H), 4.30 (dd, *J* = 12.5, 6.3 Hz, 1H), 4.65 (t, *J* = 3.7 Hz, 1H), 5.47 (d, *J* = 14.7 Hz, 1H), 5.57 (t, *J* = 6.7 Hz, 1H), 6.77 (d, *J* = 14.7 Hz, 1H), 7.0-7.1 (m, 2xArH), 7.1-7.2 (m, ArH), 7.3-7.4 (m, 2xArH) ppm. ¹³C RMN (75 MHz, CDCl₃) δ -1.3 (2xCH₃), 16.1 (CH₃), 19.4 (CH₂), 25.5 (CH₂), 27.1 (CH₂), 30.6 (CH₂), 62.1 (CH₂), 63.6 (CH₂), 97.9 (CH), 123.9 (ArCH), 125.5 (CH), 128.1 (2xArCH), 128.2 (2xArCH), 132.4 (CH), 139.3 (C), 140.2 (ArC), 150.9 (CH) ppm. MS (ESI) *m/z* (%) 331 (M⁺+1, 8), 315 (15), 229 (90). HMRS (ESI) calcd for C₂₀H₃₁O₂Si, 331.2093; found, 331.2095.

(1*Z*,3*E*)-1-Diisopropylsilyl-3-methyl-5-(tetrahydropyran-2-yloxy)penta-1,3-diene (**6e**). *Method D*: Following the same procedure as described for compound **6c**, reaction of Cp₂Zr(H)Cl (297 mg, 1.15 mmol) and (*E*)-1-diisopropylsilyl-3-methyl-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**11e**) (113 mg, 0.38 mmol) in THF (20 mL) afforded, after treatment with *n*-pentane (15 mL) and purification, compound **6e** (66 mg, 58 %) as a yellow oil.

¹H NMR (300 MHz, CDCl₃) δ 1.0-1.1 (m, 14H), 1.5-1.7 (m, 6H), 1.83 (s, 3H), 3.4-3.5 (m, 1H), 3.47 (d, *J* = 7.0 Hz, 1H), 3.8-3.9 (m, 1H), 4.14 (dd, *J* = 12.9, 7.0 Hz, 1H), 4.31 (dd, *J* = 12.9, 6.3 Hz, 1H), 4.65 (t, *J* = 3.2 Hz, 1H), 5.43 (dd, *J* = 15.1, 7.0 Hz, 1H), 5.66 (t, *J* = 6.7 Hz, 1H), 6.95 (d, *J* = 15.1 Hz, 1H). ¹³C NMR (75 MHz, CDCl₃) δ 11.6 (2xCH), 16.4 (CH₃), 18.8 (2xCH₃), 19.1 (2xCH₃), 19.7 (CH₂), 25.7 (CH₂), 30.9 (CH₂), 62.4 (CH₂), 63.7 (CH₂), 98.0 (CH), 122.5 (CH), 128.6 (CH), 139.5 (C), 152.5 (CH) ppm. MS (ESI) *m/z* (%) 297 (M⁺+1, 64), 295 (46), 211 (50), 196 (74), 195 (100). HMRS (ESI) calcd for C₁₇H₃₃O₂Si, 297.2249; found, 297.2247.

⁵ For preparation of Schwartz's reagent, see: a) Buchwald, S. L.; Lemaire, S. J.; Nielsen, R. B.; Watson, B. T.; King, S. M. *Tetrahedron Lett.* **1987**, 28, 3895. b) Lipshutz, B. H.; Keil, R.; Ellsworth, E. L. *Tetrahedron Lett.* **1990**, 31, 7257.

General procedure for coupling of organosilicon compounds **5 and **6** with trienyl iodide **3**:** TBAF (1.0 M in THF, 2-3 eq) was added dropwise to a solution of the organosilicon reagent **5-6** (1.5-2.5 eq) in THF (1-4 mL) and the mixture was stirred for 30 min (0 °C-rt). A solution of trienyl iodide **3**³ (1 eq) in THF and Pd₂(dba)₃·CHCl₃ (0.05-0.1 eq) were sequentially added at rt, and the mixture was stirred for 1-4h. Diethyl ether (5 mL) was added and the mixture was filtered through a short pad of silica gel. The solvent was removed under vacuum and the crude was purified by column chromatography (SiO₂, 95:5 hexane/AcOEt) to afford the corresponding retinyl ether (**12** or **13**) as a yellow oil.

trans-Tetrahydropyran-2-yl retinyl ether (**12**).²

Siloxane coupling: Following the general procedure, treatment of a solution of siloxane **5a** (40 mg, 0.14 mmol) in THF (2 mL) with TBAF (1.0 M in THF, 220 μL, 0.22 mmol) for 30 min at rt, followed by the addition of a solution of iodide **3** (30 mg, 0.095 mmol) in THF (1 mL) and Pd₂(dba)₃·CHCl₃ (5 mg, 0.005 mmol) afforded, after stirring for 4h, compound **12** in 86% yield (30 mg). **One-pot reaction:** 1,1,3,3 tetramethyl disiloxane (31 mg, 0.237 mmol) was added dropwise to a solution of Pt(DVDS) (0.1 M in xylenes, 15 μL, 0.0015 mmol) and *t*-Bu₃P (1 μL, 0.0016 mmol) in THF (1 mL) and the mixture was stirred for 30 min. A solution of (*E*)-3-methyl-5-(tetrahydropyran-2-yloxy)pent-3-en-1-yne (**7**) (52 mg, 0.28 mmol) in THF (1mL) was then added over 5 min. and the reaction mixture was stirred for 30 min. TBAF (1.0 M in THF, 632 μL, 0.632 mmol), Pd₂(dba)₃·CHCl₃ (8 mg, 0.008 mmol) and iodide **3** (50 mg, 0.16 mmol) were then sequentially added and the reaction mixture was stirred for 4h at rt, filtered through a pad of neutral alumina and concentrated. The crude was purified by column chromatography (SiO₂, 95:5 hexane/AcOEt) to afford compound **12** in a 74% yield (79 mg).

Silanol coupling: Following the general procedure, reaction of a solution of silanol **5b** (68 mg, 0.26 mmol) in THF (2 mL) with TBAF (1.0 M in THF, 190 μL, 0.19 mmol) at rt, followed by the addition of a solution of iodide **3** (35 mg, 0.11 mmol) in THF (1 mL) and Pd₂(dba)₃·CHCl₃ (6 mg, 0.006 mmol) afforded, after stirring for 4h, compound **12** in 89% yield (36 mg). **Ag₂O activation:** Silanol **5b** (63 mg, 0.24 mmol) and iodide **3** (39 mg, 0.12 mmol) were sequentially added to a suspension of Pd(PPh₃)₄ (7 mg, 0.006 mmol) and Ag₂O (28 mg, 0.12 mmol) in THF (2 mL). Temperature was raised to 50 °C and the reaction mixture was stirred for 8h, filtered through a pad of neutral alumina and concentrated. The crude was purified by column chromatography (SiO₂, 95:5 hexane/AcOEt) to afford compound **12** in 61% yield (28 mg). **TMSOK activation:** Silanol **5b** (36 mg, 0.15 mmol) was added to a stirred suspension of potassium trimethylsilanolate (25 mg, 0.19 mmol) in dioxane (2 mL) and the reaction mixture was stirred for 30 min. Iodide **3** (30 mg, 0.09 mmol) and Pd₂(dba)₃·CHCl₃ (5 mg, 0.005 mmol) were then sequentially added and the mixture was stirred for 3 h, filtered through a pad of neutral alumina and concentrated. The crude was purified by column chromatography (SiO₂, 95:5 hexane/AcOEt) to afford compound **12** in 74% yield (26 mg) as a clear yellow oil.

Silacyclobutane coupling: Following the general procedure, treatment of a solution of silacyclobutane **5c** (19 mg, 0.071 mmol) in THF (2 mL) with TBAF (1.0 M in THF, 150 μL, 0.150 mmol) for 30 min at 0 °C, followed by the addition of a solution of iodide **3** (15 mg, 0.048 mmol) in THF (1 mL) and Pd₂(dba)₃·CHCl₃ (3 mg, 0.003 mmol) afforded, after stirring for 2h at rt, compound **12** in 85% yield (15 mg).

Benzylsilane coupling: Following the general procedure, treatment of a solution of benzylsilane **5d** (31.6 mg, 0.096 mmol) in THF (2 mL) with TBAF (1.0 M in THF, 128 μL, 0.128 mmol) for 30 min at 0 °C, followed by the addition of a solution of iodide **3** (20 mg, 0.064 mmol) in THF (1 mL) and Pd₂(dba)₃·CHCl₃ (2 mg, 0.002 mmol) afforded, after stirring for 2h at rt, compound **12** in 77% yield (18 mg).

Silylhydride coupling: Following the general procedure, treatment of a solution of silylhydride **5d** (28 mg, 0.096 mmol) with TBAF (1.0 M in THF, 96 μL, 0.96 mmol) in THF (2 mL) for 30 min at 0 °C, followed by the

addition of a solution of iodide **3** (15 mg, 0.05 mmol) in THF (1 mL) and $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (2 mg, 0.002 mmol) afforded, after stirring for 2h at rt, compound **12** in 85% yield (15 mg).

^1H NMR (400 MHz, CDCl_3) δ 1.02 (s, 6H), 1.4-1.5 (m, 2H), 1.5-1.6 (m, 8H), 1.71 (s, 3H), 1.86 (s, 3H), 1.95 (s, 3H), 2.01 (t, J = 6.2 Hz, 2H), 3.4-3.5 (m, 1H), 3.8-3.9 (m, 1H), 4.19 (dd, J = 12.8, 7.4 Hz, 1H), 4.37 (dd, J = 12.8, 6.5 Hz, 1H), 4.64 (t, J = 3.2 Hz, 1H), 5.66 (t, J = 6.9 Hz, 1H), 6.07 (d, J = 11.2 Hz, 1H), 6.08 (d, J = 16.2 Hz, 1H), 6.13 (d, J = 16.2 Hz, 1H), 6.32 (d, J = 15.1 Hz, 1H), 6.59 (dd, J = 15.1, 11.2 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 12.7 (2x CH_3), 19.2 (CH_2), 19.5 (CH_2), 21.7 (CH_3), 25.4 (CH_2), 28.9 (2x CH_3), 30.6 (CH_2), 33.0 (CH_2), 34.2 (C), 39.6 (CH_2), 62.3 (CH_2), 63.7 (CH_2), 97.9 (CH), 124.8 (CH), 126.6 (CH), 127.7 (CH), 129.2 (C), 130.2 (CH), 135.9 (C), 136.5 (CH), 137.4 (C), 137.6 (CH), 137.8 (C) ppm. MS (ESI) m/z (%) 393 ($\text{M}^+\text{+Na}$, 12), 371 ($\text{M}^+\text{+1}$, 8), 269 (89), 245 (100). HMRS (ESI) calcd for $\text{C}_{25}\text{H}_{39}\text{O}_2$, 371.2950; found, 371.2958.

11-*cis*-Tetrahydropyran-2-yl retinyl ether (**13**).

Silacyclobutane coupling: Following the general procedure, treatment of a solution of silacyclobutane **6c** (21 mg, 0.08 mmol) in THF (2 mL) with TBAF (1.0 M in THF, 189 μL , 0.189 mmol) for 30 min at 0 °C, followed by the addition of a solution of the iodide **3** (15 mg, 0.05 mmol) in THF (1 mL) and $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (4 mg, 0.004 mmol) afforded, after stirring for 1h at rt, compound **13** in 85% yield (15 mg).

Benzylsilane coupling: Following the general procedure, treatment of a solution of benzylsilane **6d** (80 mg, 0.242 mmol) in THF (5 mL) with TBAF (1.0 M in THF, 322 μL , 0.322 mmol) for 30 min at 0 °C, followed by the addition of a solution of iodide **3** (50 mg, 0.16 mmol) in THF (1 mL) and $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (4 mg, 0.004 mmol) afforded, after stirring for 2h at rt, compound **13** in 62% yield (36 mg).

Silylhydride coupling: Following the general procedure, treatment of a solution of silylhydride **6d** (28 mg, 0.10 mmol) with TBAF (1.0 M in THF, 96 μL , 0.96 mmol) in THF (5 mL) for 30 min at 0 °C, followed by the addition of a solution of iodide **3** (15 mg, 0.05 mmol) in THF (1 mL) and $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$ (2 mg, 0.002 mmol) afforded, after stirring for 2h at rt, compound **13** in 73 % yield (13 mg).

^1H NMR (400 MHz, CDCl_3) δ 1.01 (s, 6H), 1.4-1.5 (m, 2H), 1.5-1.6 (m, 8H), 1.70 (s, 3H), 1.89 (s, 3H), 1.92 (s, 3H), 2.01 (t, J = 6.2 Hz, 2H), 3.5-3.6 (m, 1H), 3.8-3.9 (m, 1H), 4.18 (dd, J = 12.7, 6.3 Hz, 1H), 4.36 (dd, J = 12.7, 6.3 Hz, 1H), 4.65 (t, J = 3.7 Hz, 1H), 5.68 (t, J = 6.3 Hz, 1H), 5.90 (d, J = 11.7 Hz, 1H), 6.07 (d, J = 16.0 Hz, 1H), 6.18 (d, J = 16.0 Hz, 1H), 6.33 (t, J = 11.7 Hz, 1H), 6.53 (d, J = 11.7 Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 12.2 (CH_3), 17.3 (CH_3), 19.3 (CH_2), 19.5 (CH_2), 21.7 (CH_3), 25.4 (CH_2), 28.9 (2x CH_3), 30.7 (CH_2), 33.0 (CH_2), 34.2 (C), 39.6 (CH_2), 62.3 (CH_2), 63.7 (CH_2), 97.9 (CH), 124.9 (CH), 126.5 (CH), 126.9 (CH), 127.9 (CH), 129.1 (C), 132.7 (CH), 137.0 (C), 137.6 (C), 137.8 (C), 138.0 (CH) ppm. MS (ESI) m/z (%) 393 ($\text{M}^+\text{+Na}$, 10), 371 ($\text{M}^+\text{+1}$, 8), 269 (44), 245 (100). HMRS (ESI) calcd for $\text{C}_{25}\text{H}_{39}\text{O}_2$, 371.2950; found, 371.2947.

trans-Retinol (**1**).⁶ Water (72 μL , 4.00 mmol) and trimethylsilyl chloride (50 μL , 0.39 mmol) were sequentially added to a solution of tetrahydropyran-2-yl retinyl ether (**12**) (25 mg, 0.07 mmol) in MeOH (3 mL), and the reaction was stirred open to air for 10 minutes. NaHCO_3 saturated aqueous solution (10 mL) was then added and the aqueous phase was extracted with diethyl ether (2x15 mL). The combined organic phases were washed with water (2x15 mL) and brine (2x15 mL), dried with (anhydrous) sodium sulphate and filtered. The solvent was evaporated and the crude was purified by column chromatography (SiO_2 , 80:20 hexane/AcOEt) to yield compound **1** (14 mg, 74%) as a yellow oil.

⁶ Zeng, F.; Negishi, E. *Organic Lett.* **2001**, 3, 719.

^1H NMR (400 MHz, CDCl_3) 1.02 (s, 6H), 1.4-1.5 (m, 2H), 1.5-1.6 (m, 2H), 1.71 (s, 3H), 1.86 (s, 3H), 1.96 (s, 3H), 2.01 (t, $J = 5.9$ Hz, 2H), 4.30 (d, $J = 6.8$ Hz, 2H), 5.69 (t, $J = 6.8$ Hz, 1H), 6.08 (d, $J = 16.1$ Hz, 1H), 6.12 (d, $J = 11.0$ Hz, 1H), 6.16 (d, $J = 16.1$ Hz, 1H), 6.28 (d, $J = 15.2$ Hz, 1H), 6.59 (dd, $J = 15.2, 11.0$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 12.6 (CH_3), 12.7 (CH_3), 19.2 (CH_2), 21.7 (CH_3), 28.9 ($2\times\text{CH}_3$), 33.0 (CH_2), 34.2 (C), 39.6 (CH_2), 59.5 (CH_2), 125.2 (CH), 126.8 (CH), 129.2 (C), 129.9 (CH), 130.0 (CH), 136.2 (C), 136.3 (CH), 136.9 (C), 137.6 (CH), 137.8 (C) ppm. IR (CHCl_3) ν 3429 (s, O-H), 2930 (s, CH) cm^{-1} . MS (ESI) m/z (%) 309 ($\text{M}^+ + \text{Na}$, 3), 285 (30), 269 (60), 245 (100). HMRS (ESI) calcd for $\text{C}_{20}\text{H}_{30}\text{NaO}$, 309.2194; found, 309.2195.

11-*cis*-Retinol (**14**).⁷ Following the same procedure as described for compound **1**, treatment of a solution of tetrahydropyran-2-yl retinyl ether (**13**) (15 mg, 0.04 mmol) in MeOH (2 mL) with water (50 μL , 2.77 mmol) and trimethylsilyl chloride (30 μL , 0.24 mmol) for 10 min afforded, after column chromatography (SiO_2 , 80:20 hexane/AcOEt), compound **14** in 83 % yield (9.5 mg).

^1H NMR (400 MHz, CDCl_3) δ 1.02 (s, 6H), 1.4-1.5 (m, 2H), 1.5-1.6 (m, 2H), 1.71 (s, 3H), 1.89 (s, 3H), 1.93 (s, 3H), 2.01 (t, $J = 6.3$ Hz, 2H), 4.29 (t, $J = 6.8$ Hz, 2H), 5.72 (t, $J = 6.8$ Hz, 1H), 5.87 (d, $J = 11.8$ Hz, 1H), 6.08 (d, $J = 16.1$ Hz, 1H), 6.17 (d, $J = 16.1$ Hz, 1H), 6.35 (t, $J = 11.8$ Hz, 1H), 6.56 (d, $J = 11.8$ Hz, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 12.2 (CH_3), 17.2 (CH_3), 19.3 (CH_2), 21.8 (CH_3), 28.9 ($2\times\text{CH}_3$), 33.0 (CH_2), 34.2 (C), 39.6 (CH_2), 59.5 (CH_2), 125.3 (CH), 126.2 (CH), 127.1 (CH), 129.2 (C), 130.1 (CH), 132.4 (CH), 136.5 (C), 137.3 (C), 137.9 (C), 138.0 (CH) ppm. IR (CHCl_3) ν 3417 (s, O-H), 2925 (s, CH) cm^{-1} . MS (ESI) m/z (%) 286 ($\text{M}^+ + 1$, 55), 285 (1), 199 (36), 179 (63), 79 (100). HRMS (ESI): calcd for $\text{C}_{20}\text{H}_{30}\text{O}$, 286.2297; found, 286.2290.

11-*cis*-Retinal (**2**).⁷ To a suspension of BaMnO_4 (28 mg, 0.11 mmol) in CH_2Cl_2 (2 mL) was added, dropwise, a solution of 11-*cis*-retinol (**14**) (10 mg, 0.03 mmol) in CH_2Cl_2 (0.5 mL). The resulting mixture was stirred for 6h, filtered through a short pad of neutral alumina (IV, hexane), and concentrated. Flash chromatography of the crude (Al_2O_3 , hexane) afforded 11-*cis*-retinal (**2**) as an unstable yellow oil (9 mg, 90% yield).

^1H NMR (400 MHz, CDCl_3) δ 1.02 (s, 6H), 1.4-1.5 (m, 2H), 1.5-1.6 (m, 2H), 1.71 (s, 3H), 1.99 (s, 3H), 2.02 (t, $J = 5.8$ Hz, 2H), 2.35 (s, 3H), 5.91 (d, $J = 11.8$ Hz, 1H), 6.08 (d, $J = 8.0$ Hz, 1H), 6.13 (d, $J = 16.0$ Hz, 1H), 6.34 (d, $J = 16.0$ Hz, 1H), 6.53 (d, $J = 12.4$ Hz, 1H), 6.68 (dd, $J = 12.4, 11.8$ Hz, 1H), 10.01 (d, $J = 8.0$ Hz, 1H) ppm. ^{13}C NMR (100 MHz, CDCl_3) δ 12.4 (CH_3), 18.0 (CH_3), 19.2 (CH_2), 21.8 (CH_3), 29.0 ($2\times\text{CH}_3$), 33.0 (CH_2), 34.3 (C), 39.5 (CH_2), 125.7 (CH), 129.7 ($2\times\text{CH}$), 130.1 (CH), 130.2 (C), 131.5 (CH), 137.4 (CH), 137.6 (C), 141.7 (C), 155.9 (C), 191.2 (CHO) ppm. IR (CHCl_3) ν 1727 (s), 1661 (s, CHO) cm^{-1} . MS (CI) m/z (%) 285 ($\text{M}^+ + 1$, 68), 284 (20), 149 (26), 29 (100). HRMS (CI) calcd. for $\text{C}_{20}\text{H}_{29}\text{O}$, 285.2218; found, 285.2219.

⁷ López, S.; Montenegro, J.; Saa, C. *J. Org. Chem.* **2007**, *72*, 9572.

¹ H NMR (CDCl ₃ , 300 MHz)	H ₁	H ₂	H ₄	H ₅	Me-C ₃	Si-R	OTHP H _{1'}	OTHP 2H _{2'} , 2H _{3'} , 2H _{4'}	OTHP H _{5'}
<p>5a</p>	5.77 d, 1H <i>J</i> = 19.0	6.64 d, 1H <i>J</i> = 19.0	5.71 t, 1H <i>J</i> = 6.8	4.14, dd, 1H <i>J</i> = 12.9, 7.1 4.34, dd, 1H <i>J</i> = 12.9, 6.6	1.80 s, 3H	0.17, s, 6H 1.16, t, 3H, <i>J</i> = 6.9 3.63, q, 2H, <i>J</i> = 6.9	4.61 t, 1H <i>J</i> = 3.6	1.5-1.9 m, 6H	3.4-3.5 m, 1H 3.8-3.9 m, 1H
<p>5b</p>	5.80 d, 1H <i>J</i> = 19.0	6.61 d, 1H <i>J</i> = 19.0	5.70 t, 1H <i>J</i> = 6.7	4.16, dd, 1H <i>J</i> = 13.0, 7.2 4.31, dd, 1H <i>J</i> = 13.0, 6.2	1.75 s, 3H	0.19, s, 6H	4.62 t, 1H <i>J</i> = 3.4	1.4-1.7 m, 6H	3.5-3.6 m, 1H 3.7-3.8 m, 1H
<p>5c</p>	5.96 d, 1H <i>J</i> = 18.9	6.71 d, 1H <i>J</i> = 18.9	5.74 t, 1H <i>J</i> = 6.7	4.20, dd, 1H <i>J</i> = 12.9, 7.2 4.40, dd, 1H <i>J</i> = 12.9, 6.2	1.81 s, 3H	0.35, s, 3H 0.9-1.1, m, 4H 2.0-2.2, m, 2H	4.65 t, 1H <i>J</i> = 3.5	1.5-1.8 m, 6H	3.4-3.5 m, 1H 3.8-3.9 m, 1H
<p>5d</p>	5.80 d, 1H <i>J</i> = 18.9	6.55 d, 1H <i>J</i> = 18.9	5.70 t, 1H <i>J</i> = 6.7	4.18, dd, 1H <i>J</i> = 12.9, 7.2 4.38, dd, 1H <i>J</i> = 12.9, 6.2	1.70 s, 3H	0.07, s, 6H 2.11, s, 2H 6.9-7.0, m, 2H 7.0-7.1, m, 1H 7.1-7.2, m, 2H	4.65 t, 1H <i>J</i> = 3.5	1.5-1.6 m, 6H	3.5-3.6 m, 1H 3.8-3.9 m, 1H
<p>5e</p>	5.74 dd, 1H <i>J</i> = 18.8, 4.5	6.71 d, 1H <i>J</i> = 18.8	5.69 t, 1H <i>J</i> = 6.7	4.16, dd, 1H <i>J</i> = 12.8, 7.1 4.35, dd, 1H <i>J</i> = 12.8, 6.3	1.78 s, 3H	1.0-1.1, m, 14H 3.65, d, 1H, <i>J</i> = 4.5	4.64 t, 1H <i>J</i> = 3.8	1.5-1.6 m, 6H	3.4-3.5 m, 1H 3.8-3.9 m, 1H
<p>8</p>	6.23 d, 1H <i>J</i> = 14.6	7.05 d, 1H <i>J</i> = 14.6	5.55 t, 1H <i>J</i> = 6.1	4.07, dd, 1H <i>J</i> = 11.5, 6.7 4.19, dd, 1H <i>J</i> = 11.5, 5.5	1.71 s, 3H	--	4.55 t, 1H <i>J</i> = 3.2	1.5-1.8 m, 6H	3.3-3.5 m, 1H 3.7-3.8 m, 1H
<p>9</p>	5.00, d, 1H <i>J</i> = 10.0 5.55, d, 1H <i>J</i> = 17.4	6.35 dd, 1H <i>J</i> = 17.4, 10.0	5.61 t, 1H <i>J</i> = 6.7	4.12, dd, 1H <i>J</i> = 12.7, 7.2 4.33, dd, 1H <i>J</i> = 12.7, 6.3	1.75 s, 3H	--	4.55 t, 1H <i>J</i> = 3.7	1.4-1.8 m, 6H	3.4-3.5 m, 1H 3.8-3.9 m, 1H

¹³ C NMR (CDCl ₃ , 75 MHz)	C ₁	C ₂	C ₃	C ₄	C ₅	Me-C ₃	Si-R	OTHP C _{1'}	OTHP C _{2'}	OTHP C _{3'}	OTHP C _{4'}	OTHP C _{5'}
5a	124.9 CH	149.5 CH	137.7 C	130.0 CH	63.5 CH ₂	12.0 CH ₃	-1.8, 2CH ₃ 18.4, CH ₃ 58.3, CH ₂	97.7 CH	30.5 CH ₂	19.4 CH ₂	25.4 CH ₂	62.0 CH ₂
5b	126.3 CH	148.9 CH	137.7 C	129.9 CH	63.6 CH ₂	12.0 CH ₃	0.1, 2CH ₃	97.8 CH	30.5 CH ₂	19.3 CH ₂	25.4 CH ₂	62.1 CH ₂
5c	125.9 CH	149.3 CH	137.8 C	129.9 CH	63.7 CH ₂	12.1 CH ₃	-1.8, CH ₃ 14.4, 2CH ₂ 18.2, CH ₂	97.9 CH	30.6 CH ₂	19.4 CH ₂	25.4 CH ₂	62.2 CH ₂
5d	125.8 CH	148.6 CH	137.8 C	129.2 CH	63.6 CH ₂	12.0 CH ₃	-3.3, 2CH ₃ 26.1, CH ₂ 123.8, CH 127.9, 2CH 128.1, 2CH 139.8, C	97.8 CH	30.5 CH ₂	19.3 CH ₂	25.4 CH ₂	62.1 CH ₂
5e	120.3 CH	151.9 CH	138.2 C	129.5 CH	63.9 CH ₂	12.3 CH ₃	10.9, 2CH 18.8, 2CH ₃ 19.0 2CH ₃	98.3 CH	30.9 CH ₂	19.7 CH ₂	25.7 CH ₂	62.4 CH ₂
8	75.6 CH	148.7 CH	136.7 C	129.2 CH	62.9 CH ₂	12.0 CH ₃	--	97.7 CH	30.4 CH ₂	19.2 CH ₂	25.3 CH ₂	62.0 CH ₂
9	128.0 CH ₂	140.7 CH	130.8 C	112.6 CH	63.4 CH ₂	11.8 CH ₃	--	97.8 CH	30.5 CH ₂	19.4 CH ₂	25.4 CH ₂	62.1 CH ₂

¹ H NMR (CDCl ₃ , 300 MHz)	H ₄	H ₅	Me-C ₃	Si-R	OTHP H _{1'}	OTHP 2H _{2'} , 2H _{3'} , 2H _{4'}	OTHP H _{5'}
<p>11c</p>	6.08 t, 1H <i>J</i> = 6.7	4.10, dd, 1H <i>J</i> = 13.3, 7.2 4.26, dd, 1H <i>J</i> = 13.3, 6.2	1.85 s, 3H	0.43, s, 3H 0.9-1.2, m, 4H 1.9-2.2, m, 2H	4.63 t, 1H <i>J</i> = 3.2	1.4-1.9 m, 6H	3.4-3.5 m, 1H 3.7-3.8 m, 1H
<p>11d</p>	6.05 t, 1H <i>J</i> = 6.7	4.09, dd, 1H <i>J</i> = 13.3, 7.2 4.24, dd, 1H <i>J</i> = 13.3, 6.2	1.79 s, 3H	0.12, s, 6H 2.18, s, 2H 7.1-7.2, m, 3H 7.2-7.3, m, 2H	4.61 t, 1H <i>J</i> = 3.1	1.5-1.6 m, 6H	3.4-3.5 m, 1H 3.8-3.9 m, 1H
<p>11e</p>	6.01 t, 1H <i>J</i> = 6.7	4.03, dd, 1H <i>J</i> = 13.2, 7.2 4.23, dd, 1H <i>J</i> = 13.2, 6.3	1.79 s, 3H	1.02, m, 14H 3.69, s, 1H	4.57 t, 1H <i>J</i> = 3.5	1.4-1.7 m, 6H	3.4-3.5 m, 1H 3.7-3.8 m, 1H

¹³ C NMR (CDCl ₃ , 75 MHz)	C ₁	C ₂	C ₃	C ₄	C ₅	Me-C ₃	Si-R	OTHP C _{1'}	OTHP C _{2'}	OTHP C _{3'}	OTHP C _{4'}	OTHP C _{5'}
<p>11c</p>	90.1 C	109.4 C	120.9 C	135.2 CH	63.0 CH ₂	17.4 CH ₃	-0.1, CH ₃ 15.4, 2CH ₂ 18.3, CH ₂	97.8 CH	30.5 CH ₂	19.2 CH ₂	25.4 CH ₂	62.1 CH ₂
<p>11d</p>	90.2 C	108.7 C	121.1 C	134.7 CH	63.0 CH ₂	17.3 CH ₃	-2.1, 2CH ₃ 26.2, CH ₂ 124.2, CH 128.0, 2CH 128.3, 2CH 139.0, C	97.8 CH	30.5 CH ₂	19.3 CH ₂	25.4 CH ₂	62.1 CH ₂
<p>11e</p>	85.4 C	110.1 C	121.0 C	134.7 CH	63.0 CH ₂	17.4 CH ₃	10.8, 2CH 18.2, 2CH ₃ 18.4, 2CH ₃	97.8 CH	30.5 CH ₂	19.2 CH ₂	25.4 CH ₂	62.0 CH ₂

¹ H NMR (CDCl ₃ , 300 MHz)	H ₁	H ₂	H ₄	H ₅	Me-C ₃	Si-R	OTHP H _{1'}	OTHP 2H _{2'} , 2H _{3'} , 2H _{4'}	OTHP H _{5'}
<p>6c</p>	5.69 d, 1H <i>J</i> = 14.7	6.81 d, 1H <i>J</i> = 14.7	5.64 t, 1H <i>J</i> = 6.7	4.12, dd, 1H <i>J</i> = 12.8, 7.2 4.29, dd, 1H <i>J</i> = 12.8, 6.2	1.78 s, 3H	0.39, s, 3H 0.9-1.2, m, 4H 1.9-2.1, m, 2H	4.64 t, 1H <i>J</i> = 3.5	1.4-1.7 m, 6H	3.4-3.5 m, 1H 3.8-3.9 m, 1H
<p>6d</p>	5.47 d, 1H <i>J</i> = 14.7	6.77 d, 1H <i>J</i> = 14.7	5.57 t, 1H <i>J</i> = 6.7	4.07, dd, 1H <i>J</i> = 12.5, 7.1 4.30, dd, 1H <i>J</i> = 12.5, 6.3	1.74 s, 3H	0.08, s, 6H 2.19, s, 2H 7.0-7.1, m, 2H 7.1-7.2, m, 1H 7.3-7.4, m, 2H	4.65 t, 1H <i>J</i> = 3.7	1.4-1.9 m, 6H	3.5-3.6 m, 1H 3.8-3.9 m, 1H
<p>6e</p>	5.43 dd, 1H <i>J</i> = 15.1, 7.0	6.95 d, 1H <i>J</i> = 15.1	5.66 t, 1H <i>J</i> = 6.7	4.14, dd, 1H <i>J</i> = 12.9, 7.0 4.31, dd, 1H <i>J</i> = 12.9, 6.3	1.83 s, 3H	1.0-1.1, m, 14H 3.47, d, 1H, <i>J</i> = 7.0 Hz	4.65 t, 1H <i>J</i> = 3.2	1.5-1.7 m, 6H	3.4-3.5 m, 1H 3.8-3.9 m, 1H
<p>10</p>	6.23 d, 1H <i>J</i> = 8.5	6.76 d, 1H <i>J</i> = 8.5	5.81 t, 1H <i>J</i> = 6.6	4.13, dd, 1H <i>J</i> = 13.1, 7.0 4.19, dd, 1H <i>J</i> = 13.1, 6.2	1.93 s, 3H	--	4.65 t, 1H <i>J</i> = 3.2	1.4-1.8 m, 6H	3.4-3.5 m, 1H 3.8-3.9 m, 1H

¹³ C NMR (CDCl ₃ , 75 MHz)	C ₁	C ₂	C ₃	C ₄	C ₅	Me-C ₃	Si-R	OTHP C _{1'}	OTHP C _{2'}	OTHP C _{3'}	OTHP C _{4'}	OTHP C _{5'}
6c	128.9 CH	149.9 CH	138.8 C	127.9 CH	63.7 CH ₂	12.1 CH ₃	-1.8, CH ₃ 14.4, 2CH ₂ 18.2, CH ₂	97.9 CH	30.6 CH ₂	19.4 CH ₂	25.4 CH ₂	62.2 CH ₂
6d	125.5 CH	150.9 CH	139.3 C	132.4 CH	63.6 CH ₂	16.1 CH ₃	-1.3, 2CH ₃ 27.1, CH ₂ 123.9, CH 128.1, 2CH 128.2, 2CH 140.2, C	97.9 CH	30.6 CH ₂	19.4 CH ₂	25.5 CH ₂	62.1 CH ₂
6e	122.5 CH	152.5 CH	139.5 C	128.6 CH	63.7 CH ₂	16.4 CH ₃	11.6, 2CH 18.8, 2CH ₃ 19.1, 2CH ₃	98.0 CH	30.9 CH ₂	19.7 CH ₂	25.7 CH ₂	62.4 CH ₂
10	76.6 CH	141.5 CH	136.1 C	129.8 CH	63.1 CH ₂	15.8 CH ₃	--	97.8 CH	30.6 CH ₂	19.4 CH ₂	25.4 CH ₂	62.2 CH ₂

¹ H NMR (CDCl ₃ , 400 MHz)	H ₂	H ₃	H ₄	H ₇	H ₈	H ₁₀	H ₁₁	H ₁₂	H ₁₄	H ₁₅	2Me-C ₁	Me-C ₅	Me-C ₉	Me-C ₁₃	OTHP H _{1'}	OTHP 2H _{2'} , 2H _{3'} , 2H ₄	OTHP H _{5'}
<i>trans</i> -Tetrahydro pyran-2-yl retinyl ether (12)	1.5-1.6 m, 2H	1.4-1.5 m, 2H	2.01 t, 2H <i>J</i> = 6.2	6.08 d, 1H <i>J</i> = 16.2	6.13 d, 1H <i>J</i> = 16.2	6.07 d, 1H <i>J</i> = 11.2	6.59 dd, 1H <i>J</i> = 15.1, 11.2	6.32 d, 1H <i>J</i> = 15.1	5.66 t, 1H <i>J</i> = 6.9	4.19, dd, 1H <i>J</i> = 12.8, 7.4 4.37, dd, 1H <i>J</i> = 12.8, 6.5	1.02 s, 6H	1.71 s, 3H	1.95 s, 3H	1.86 s, 3H	4.64 t, 1H <i>J</i> = 3.2	1.5-1.6 m, 6H	3.4-3.5 m, 1H 3.8-3.9 1H, m
<i>trans</i> -Retinol (1)	1.4-1.5 m, 2H	1.5-1.6 m, 2H	2.01 t, 2H <i>J</i> = 5.9	6.08 d, 1H <i>J</i> = 16.1	6.16 d, 1H <i>J</i> = 16.1	6.12 d, 1H <i>J</i> = 11.0	6.59 dd, 1H <i>J</i> = 15.2, 11.0	6.28 d, 1H <i>J</i> = 15.2	5.69 t, 1H <i>J</i> = 6.8	4.30, d, 2H <i>J</i> = 6.8	1.02 s, 6H	1.71 s, 3H	1.96 s, 3H	1.86 s, 3H	--	--	--
11- <i>cis</i> -Tetrahydro pyran-2-yl retinyl ether (13)	1.4-1.5 m, 2H	1.5-1.6 m, 2H	2.01 t, 2H <i>J</i> = 6.2	6.18 d, 1H <i>J</i> = 16.0	6.07 d, 1H <i>J</i> = 16.0	6.53 d, 1H <i>J</i> = 11.7	6.33 t, 1H <i>J</i> = 11.7	5.90 d, 1H <i>J</i> = 11.7	5.68 t, 1H <i>J</i> = 6.3	4.18, dd, 1H <i>J</i> = 12.7, 6.3 4.36, dd, 1H <i>J</i> = 12.7, 6.3	1.01 s, 6H	1.70 s, 3H	1.92 s, 3H	1.89 s, 3H	4.65 t, 1H <i>J</i> = 3.7	1.5-1.6 m, 6H	3.5-3.6 m, 1H 3.8-3.9 m, 1H
11- <i>cis</i> -Retinol (14)	1.4-1.5 m, 2H	1.5-1.6 m, 2H	2.01 t, 2H <i>J</i> = 6.3	6.17 d, 1H <i>J</i> = 16.1	6.08 d, 1H <i>J</i> = 16.1	6.56 d, 1H <i>J</i> = 11.8	6.35 t, 1H <i>J</i> = 11.8	5.87 d, 1H <i>J</i> = 11.8	5.72 t, 1H <i>J</i> = 6.8	4.29, t, 2H <i>J</i> = 6.8	1.02 s, 6H	1.71 s, 3H	1.93 s, 3H	1.89 s, 3H	--	--	--
11- <i>cis</i> -Retinal (2)	1.4-1.5 m, 2H	1.5-1.6 m, 2H	2.02 t, 2H <i>J</i> = 5.8	6.34 d, 1H <i>J</i> = 16.0	6.13 d, 1H <i>J</i> = 16.0	6.53 d, 1H <i>J</i> = 12.4	6.68 dd, 1H <i>J</i> = 12.4, 11.8	5.91 d, 1H <i>J</i> = 11.8	6.08 d, 1H <i>J</i> = 8.0	10.01, d, 1H <i>J</i> = 8.0	1.02 s, 6H	1.71 s, 3H	1.99 s, 3H	2.35 s, 3H	--	--	--

¹³ C NMR (CDCl ₃ , 100 MHz)	C ₁	C ₂	C ₃	C ₄	C ₅	C ₆	C ₇	C ₈	C ₉	C ₁₀	C ₁₁	C ₁₂	C ₁₃	C ₁₄	C ₁₅	2Me- C ₁	Me- C ₅	Me- C ₉	Me- C ₁₃	C _{1'}	C _{2'}	C _{3'}	C _{4'}	C _{5'}
<i>trans</i> -Tetrahydro pyran-2-yl retinyl ether (12)	34.2 C	39.6 CH ₂	19.5 CH ₂	33.0 CH ₂	129.2 C	137.8 C	126.6 CH	137.6 CH	137.4 C	130.2 CH	124.8 CH	136.5 CH	135.9 C	127.7 CH	63.7 CH ₂	28.9 2CH ₃	21.7 CH ₃	12.7 CH ₃	12.7 CH ₃	97.9 CH	30.6 CH ₂	19.2 CH ₂	25.4 CH ₂	62.3 CH ₂
<i>trans</i> -Retinol (1)	34.2 C	39.6 CH ₂	19.2 CH ₂	33.0 CH ₂	129.2 C	137.8 C	126.8 CH	137.6 CH	136.9 C	129.9 CH	125.2 CH	136.3 CH	136.2 C	130.0 CH	59.5 CH ₂	28.9 2CH ₃	21.7 CH ₃	12.6 CH ₃	12.7 CH ₃	--	--	--	--	--
11- <i>cis</i> -Tetrahydro pyran-2-yl retinyl ether (13)	34.2 C	39.6 CH ₂	19.5 CH ₂	33.0 CH ₂	129.1 C	137.6 C	126.9 CH	138.0 CH	137.8 C	126.5 CH	124.9 CH	132.7 CH	137.0 C	127.9 CH	63.7 CH ₂	28.9 2CH ₃	21.7 CH ₃	12.2 CH ₃	17.3 CH ₃	97.9 CH	30.7 CH ₂	19.3 CH ₂	25.4 CH ₂	62.3 CH ₂
11- <i>cis</i> -Retinol (14)	34.2 C	39.6 CH ₂	19.3 CH ₂	33.0 CH ₂	129.2 C	137.9 C	127.1 CH	138.0 CH	137.3 C	126.2 CH	125.3 CH	132.4 CH	136.5 C	130.1 CH	59.5 CH ₂	28.9 2CH ₃	21.8 CH ₃	12.2 CH ₃	17.2 CH ₃	--	--	--	--	--
11- <i>cis</i> -Retinal (2)	34.3 C	39.5 CH ₂	19.2 CH ₂	33.0 CH ₂	130.2 C	137.6 C	131.5 CH	137.4 CH	141.7 C	125.7 CH	129.7 CH	130.1 CH	155.9 C	129.7 CH	191.2 CH	29.0 2CH ₃	21.8 CH ₃	12.4 CH ₃	18.0 CH ₃	--	--	--	--	--

5a¹H NMR (300 MHz, CDCl₃), Method A ¹³C NMR (75 MHz, CDCl₃), Method A

5b¹H NMR (300 MHz, CDCl₃), Method C ¹³C NMR (75 MHz, CDCl₃), Method C

5c ^1H NMR (300 MHz, CDCl_3), *Method C* ^{13}C NMR (75 MHz, CDCl_3), *Method C*

5d¹H NMR (300 MHz, CDCl₃), Method A ¹³C NMR (75 MHz, CDCl₃), Method A

5e ^1H NMR (300 MHz, CDCl_3), *Method A* ^{13}C NMR (75 MHz, CDCl_3), *Method A*

8 ^1H NMR (300 MHz, CDCl_3) ^{13}C NMR (75 MHz, CDCl_3)

9 ^1H NMR (300 MHz, CDCl_3) ^{13}C NMR (75 MHz, CDCl_3)

¹H NMR (300 MHz, CDCl₃) ^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (300 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

11d¹H NMR (300 MHz, CDCl₃) ¹³C NMR (75 MHz, CDCl₃)

11e ^1H NMR (300 MHz, CDCl_3) ^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (300 MHz, CDCl_3), Method D

^{13}C NMR (75 MHz, CDCl_3), Method D

^1H NMR (300 MHz, CDCl_3), Method D

^{13}C NMR (75 MHz, CDCl_3), Method D

^1H NMR (300 MHz, CDCl_3), Method D

^{13}C NMR (75 MHz, CDCl_3), Method D

12¹H NMR (400 MHz, CDCl₃) ¹³C NMR (100 MHz, CDCl₃)

S33

1 (Vitamin A, *trans*-retinol) ^1H NMR (400 MHz, CDCl_3) ^{13}C NMR (100 MHz, CDCl_3)

¹H NMR (400 MHz, CDCl₃)

¹³C NMR (100 MHz, CDCl₃)

14 (11-*cis*-Retinol) ^1H NMR (400 MHz, CDCl_3) ^1H NMR (100 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (100 MHz, CDCl_3)