$[Ru(\eta_4\text{-}C_8H_{12})(\eta_6\text{-}C_8H_{10})]$,[9] or $[RuH_2(H_2)_2(PCy_3)_2]$,[5, 10] and uses 1-alkynes instead of cyclopropenes, diazoalkanes, vinyl chlorides, or propargylic chlorides as carbene source. The complexes **7** and **8**, which display about the same catalytic activity as the hitherto most commonly used compound $[RuCl_2({=}CHPh)(PCy_3)_2]$, can now be prepared on a larger scale. Our method of using 1-alkynes also allows the synthesis of other carbene compounds such as $[RuCl(X)({=}CHCH_2R)(PCy_3)_2]$ ($X = CF_3CO_2$, CN), the catalytic properties of which are currently being investigated.[11]

Experimental Section

7: Mg (2 g, 82.3 mmol) in THF (100 mL) was activated with 1,2-dichloroethane (2 mL). Tricyclohexylphosphane (9 g, 32.1 mmol) and $RuCl_3 \cdot 3H_2O$ (2 g, 7.65 mmol) were then added . The mixture was warmed under an atmosphere of hydrogen and vigorously stirred first for 2 h at 65 °C and then for 2 h at 85 °C. A red solution formed and an orange solid precipitated. The reaction mixture was then cooled to −40 °C, and ethyne (380 mL, ca. 15.8 mmol) was introduced by gas burette. The solution was then stirred for 5 min at −40 °C, followed by the addition of H_2O (0.5 mL, 27.8 mmol). After the reaction mixture was warmed to room temperature the solvent was removed, the crude product was transfered to a soxhlet apparatus and extracted with pentane (250 mL) for 12 h. A pink solid was isolated, which was washed with pentane (20 mL) and dried in vacuo. Yield: 4.37 g (75 %). For spectroscopic data see ref. [2d].

8: As described for **7**, with $RuCl_3 \cdot 3H_2O$ (0.5 g, 1.91 mmol), THF (25 mL), Mg (0.5 g, 20.6 mmol), $ClCH_2CH_2Cl$ (0.5 mL), and PCy_3 (2.31 g, 8.2 mmol) as starting materials. After the reduction the reaction mixture was cooled to −40 °C and phenylacetylene (0.22 mL, 1.91 mmol) was added dropwise, which caused a vigorous evolution of gas. The solution was stirred for 20 min at −40 °C, and then warmed to 0 °C, and H_2O (0.13 mL, 7.2 mmol) was added. After further warming to room temperature and continuous stirring for another 10 min, the solvent was removed, and the residue extracted with toluene (60 mL). The extract was dried in vacuo, and the purple residue was washed four times with pentane (4 × 10 mL) and twice with methanol (2 × 40 mL). Yield: 1.21 g (76 %). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 19.40$ [t, $^3J(H,H) = 5$ Hz, 1 H, $C\mathit{H}CH_2Ph$], 7.30–7.12 (m, 5 H, Ph-H), 3.98 [d, $^3J(H,H) = 5$ Hz, 2 H, $CHC\mathit{H}_2Ph$]; ^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 316.5$ [t, $^2J(C,P) = 7$ Hz, $\mathit{C}HCH_2Ph$], 138.9, 128.3, 128.2, 126.3 (je s, C-Ph), 64.5 (s, $CH\mathit{C}H_2Ph$); ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 34.6$ (s).

9: Ethyne was passed through a stirred solution of **6** (102 mg, 0.146 mmol) in CH_2Cl_2 (10 mL) at −78 °C for 30 s. The solvent was removed under reduced pressure, and the brown residue was washed with pentane (5 mL) and dried in vacuo. Yield: 99 mg (94 %). ^1H NMR (400 MHz, C_6D_6): $\delta = 2.70$ [d, $^3J(P,H) = 3$ Hz, 2 H, $RuCCH_2$], −16.17 [t, $^2J(P,H) = 18$ Hz, 1 H, RuH]; ^{13}C NMR (100.6 MHz, C_6D_6): $\delta = 326.2$ [t, $^2J(P,C) = 15$ Hz, $Ru\mathit{C}CH_2$], 86.6 [t, $^3J(P,C) = 4$ Hz, $RuC\mathit{C}H_2$]; ^{31}P NMR (162 MHz, $CDCl_3$): $\delta = 41.5$ (s).

10: To a solution of **6** (96 mg, 0.137 mmol) in CH_2Cl_2 (10 mL) phenylacetylene (28.0 µL, 0.274 mmol) was added at −78 °C. After warming to room temperature, the solution was concentrated under reduced pressure to ca. 2 mL. Upon addition of pentane a green solid precipitated, which was removed by filtration and dried in vacuo. Yield: 80 mg (73 %). ^1H NMR (200 MHz, C_6D_6): $\delta = 4.41$ (br s, $RuCC\mathit{H}Ph$), −12.88 [t, $^2J(P,H) = 17$ Hz, 1 H, RuH]; ^{31}P NMR (162 MHz, C_6D_6): $\delta = 41.3$ (s).

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Exceptionally Simple Enantioselective Syntheses of Chiral Hexa- and Tetracyclic Polyprenoids of Sedimentary Origin**

Elias J. Corey,* Guanglin Luo, and
Linus Shouzhong Lin

A recent publication described the isolation of a series of four novel chiral polycyclic hydrocarbons from Eocene Messel shale (Germany), which appear to be remnants of an ancient family of cyclopolyprenoids.[1] This series includes the hexacyclic and tetracyclic hydrocarbons **1** and **2** as well as their pentacyclic analogue. In addition, GC-MS evidence was obtained for the occurrence in other sediments of the hepta- and octacyclic homologues of **1** and **2** in small amounts.[1] We report here the first syntheses of **1** and **2** by relatively short routes that take advantage of several recently introduced synthetic methods, especially regio- and enantioselective catalytic dihydroxylation of polyprenol esters,[2–4] stereospecific two-component synthesis of tri- and tetrasubstituted olefins,[3–5] and stereoselective Lewis acid catalyzed polycyclization of chiral polyunsaturated oxiranes.[3, 4, 6, 7]

The synthesis of the benzoperhydropicene derivative **1** is outlined in Scheme 1. α-Deprotonation of sulfone **3** with *n*BuLi generated the corresponding α-lithio derivative, which upon treatment with chiral acylsilane **4**[4] provided stereospecifically the coupling product **5** in a reaction that proceeds

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[*] Professor E. J. Corey, Dr. G. Luo, Dr. L. S. Lin
Department of Chemistry and Chemical Biology
Harvard University
12 Oxford Street, Cambridge, Massachusetts, 02138 (USA)
Fax: (+1) 617-495-0376
E-mail: corey@chemistry.harvard.edu

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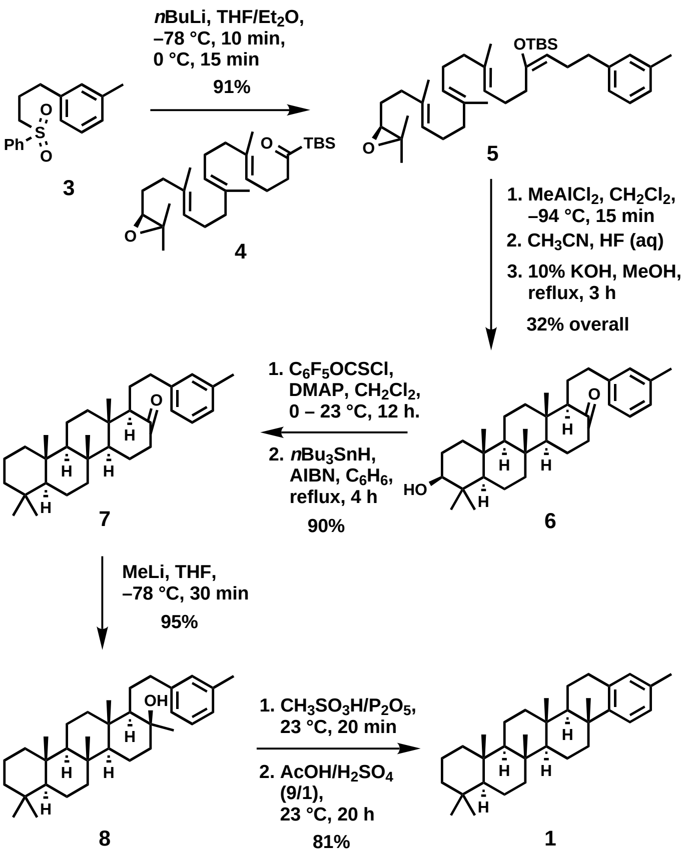
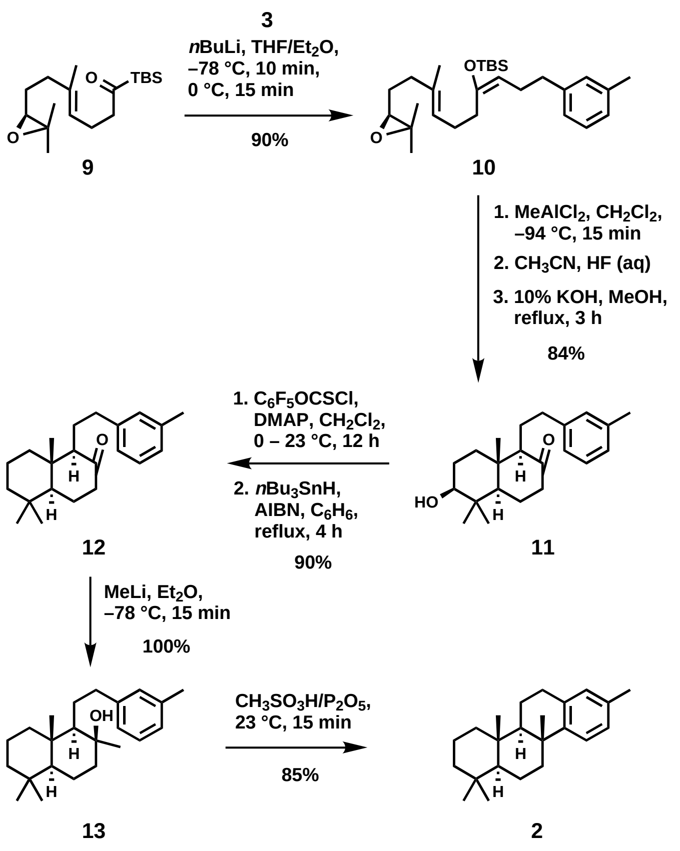


Scheme 1. Synthesis of **1**. TBS = tBuMe$_2$Si, DMAP = 4-dimethylaminopyridine, AIBN = 2,2′-azobisisobutyronitrile.



Scheme 2. Synthesis of **2**.

by 1) carbonyl addition, 2) Brook rearrangement, and 3) β-elimination of benzenesulfinate.[4] The efficiency and power of this fragment coupling are particularly noteworthy. Stereoselective tetracyclization of the epoxy tetraene **5** was induced by methylaluminum dichloride in CH_2Cl_2 at −94 °C to give, after sequential treatment of the crude product with HF in H_2O/CH_3CN (to effect desilylation of the 3-hydroxyl group) and 10% KOH in MeOH (to effect $\alpha \rightarrow \beta$ equilibration of the 3-methylphenylethyl sidechain), hydroxy ketone **6** as the only detectable pentacyclic product. Barton–McCombie deoxygenation at C(3) of **6**[8] to give **7** followed by reaction with methyllithium produced the tertiary alcohol **8**. Exposure of **8** to Eaton's acid (CH_3SO_3H/P_2O_5, 10/1)[9] afforded a mixture of **1** and olefinic dehydration products of **8**. Therefore, the resulting mixture was further treated with H_2SO_4/HOAc, which effected cyclization of the olefinic components to give **1** in good yield. The identity of synthetic and naturally derived **1** was rigorously established by comparison of ^{1}H and ^{13}C NMR spectra, infrared and mass spectra, optical rotation, and thin layer chromatographic mobility in two different solvent systems.[1, 10]

The enantioselective total synthesis of the hydrochrysene derivative **2** was carried out in a way completely analogous to that described above for the hexacyclic homologue **1** starting with sulfone **3** and acylsilane **9** (Scheme 2).[11] Uniformly fine yields were obtained, which resulted in a remarkably direct synthesis of **2** in 58% overall yield. The physical properties of **2** matched exactly those previously reported.[1]

The short, efficient syntheses of **1** and **2**, together with previously described syntheses of dammarenediol II[3] and scalarenedial,[4] clearly demonstrate the effectiveness of the underlying strategy and methodology for enantioselective synthesis of many polycyclic polyprenols, including the natural precursors of shale components **1** and **2**.

Experimental Section

5: To a solution of sulfone **3** (168.6 mg, 0.614 mmol) in THF (2.8 mL) at −78 °C was added dropwise nBuLi (1.6 M in hexane, 0.385 mL, 0.614 mmol). The resulting yellow solution was stirred for 5 min at −78 °C and then added dropwise through a cannula to a solution of acylsilane **4** (183 mg, 0.41 mmol) in ether (2.8 mL). The mixture was stirred at −78 °C for 10 min, allowed to warm to 0 °C, and stirred for 15 min. The reaction was quenched by addition of a saturated aqueous solution of NH_4Cl, and the mixture was extracted with hexane (3 × 10 mL). The combined organic phases were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. Column chromatography of the residue (silica gel, hexane/ether/Et_3N, 100/10/1) provided enolsilane **5** (216 mg, 91%) as a colorless oil: $[\alpha]_D^{23} = -4.39$ ($c = 1.48$ in C_6H_6); IR (neat): $\tilde{\nu} = 2955$, 2929, 2921, 1666, 1462, 1454, 1252, 1140, 839 cm^{-1}; ^{1}H NMR (500 MHz, C_6D_6): $\delta = 7.16-6.90$ (4H, m), 5.31–5.20 (3H, m), 4.72 (1H, t, $J = 5.7$ Hz), 2.59–1.99 (21H, m), 2.17 (3H, s), 1.63 (3H, s), 1.57 (3H, s), 1.53 (3H, s), 1.14 (3H, s), 1.09 (3H, s), 0.98 (9H, s), 0.13 (6H, s); ^{13}C NMR (125 MHz, C_6D_6): $\delta =$ 152.1, 142.2, 137.7, 135.4, 134.9, 134.3, 129.8, 128.5, 126.8, 126.0, 125.1, 124.9, 124.4, 106.5, 63.4, 57.3, 40.2, 40.1, 37.5, 36.9, 32.0, 29.6, 28.0, 27.13, 27.08, 26.1, 26.0, 25.0, 21.5, 18.9, 18.3, 16.2, 16.12, 16.07, −4.3.

6: To a solution of **5** (214 mg, 0.37 mmol) in anhydrous CH_2Cl_2 (90 mL) at −95 °C was added a precooled solution of $MeAlCl_2$ (1 M in hexane, 0.45 mL, 0.45 mmol) in 20 mL of anhydrous CH_2Cl_2 (−95 °C); the addition was carried out along the side of the flask through a cannula. The reaction mixture was stirred at −95 °C for 15 min, and then the reaction was quenched by successive addition of Et_3N (1.6 mL) and a $MeOH/H_2O$ solution (4/1, 1.6 mL); introduction was again along the side of the flask at −95 °C. The resulting mixture was then poured into a half-saturated aqueous solution of NH_4Cl (40 mL), the organic phase was separated, and the aqueous phase was extracted with ether (2 × 20 mL). The combined organic phases were washed with brine, dried (Na_2SO_4), and concentrated in vacuo. The diastereomeric α and β sidechain isomers were separated by chromatography and treated individually with aqueous HF (48 %) in CH_3CN at 23 °C for 1.5 h to effect desilylation. The α isomer was dissolved in 10 % KOH in MeOH and heated under reflux for 3 h under argon to generate the thermodynamically more stable β diastereomer **6**. After chromatography (silica gel), pure **6** (55 mg, 32 %) was obtained as a colorless oil: $[\alpha]_D^{23} = +15.38$ ($c = 1.45$ in $CHCl_3$); IR (neat): $\tilde{\nu} = 3456, 2938, 2855, 1708, 1451, 1389, 1028, 909\ cm^{-1}$; ^1H NMR (500 MHz, $CDCl_3$): $\delta = 7.20-6.92$ (4H, m), 3.20 (1H, dd, $J = 4.8, 11.6$ Hz), 2.70–2.60 (1H, m), 2.48–1.00 (23H, m), 2.32 (3H, s), 0.97 (3H, s), 0.84 (3H, s), 0.82 (3H, s), 0.77 (3H, s), 0.70 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$): $\delta = 212.2$, 142.6, 137.9, 129.3, 128.2, 126.5, 125.4, 78.9, 63.6, 60.8, 59.2, 55.4, 43.0, 42.5, 42.1, 40.6, 38.9, 38.3, 38.1, 35.1, 28.0, 27.4, 23.9, 23.0, 21.4, 18.0, 17.8, 17.3, 16.3, 15.5, 15.2, 14.2; HR-MS (CI) calcd for $[C_{32}H_{48}O_2+NH_4]^+$: 482.3998, found: 482.4004.

1: To freshly distilled CH_3SO_3H (0.18 mL) under argon was added P_2O_5 (29 mg) in one portion, and the mixture was stirred at 23 °C for 2 h until a homogeneous solution was obtained. Alcohol **8** (4.9 mg, 10.5 µmol) was dissolved in ether (0.1 mL plus 0.1 mL for rinsing) and added dropwise to the acid mixture through a cannula. The resulting cloudy mixture was stirred at 23 °C for 15 min, at which point thin-layer chromatography indicated complete conversion into a single spot suggestive of a very nonpolar substance. Crushed ice was then added, and the mixture was extracted with ether (3 × 10 mL). The ethereal extracts were washed with water, aqueous $NaHCO_3$, and brine, dried (Na_2SO_4), and concentrated in vacuo. Since ^1H NMR analysis indicated that two olefinic products (70 %) were present in addition to the desired product **1** (30 %), the mixture was treated with CH_3COOH (0.9 mL) and concentrated H_2SO_4 (0.1 mL) in the form of a suspension at 23 °C for 20 h. The acidic mixture was then diluted with water and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic solution was washed with saturated solution of $NaHCO_3$ and then brine, dried (Na_2SO_4), and concentrated in vacuo. The ^1H NMR spectrum of the residue now indicated a homogeneous final product, which was crystallized from $CH_2Cl_2/MeOH$ to afford pure **1** (3.8 mg, 81 %) as very fine thin plates: $[\alpha]_D^{23} = -35.38$ ($c = 0.26$ in $CHCl_3$) [ref.[1] $[\alpha]_D^{23} = -38$ ($c = 0.37$ in $CHCl_3$)]; m.p. 268–270 °C (ref.[1] m.p. 268–269 °C); IR (neat): $\tilde{\nu} = 2942, 2924\ cm^{-1}$; ^1H NMR (500 MHz, CD_2Cl_2): $\delta = 7.10$ (1H, d, $J = 8.0$ Hz), 6.89 (1H, d, $J = 8.0$ Hz), 6.81 (1H, s), 2.85 (1H, dd, $J = 6.5, 16.5$ Hz), 2.76 (1H, dd, $J = 7.1, 11.4$ Hz), 2.35 (1H, dt, $J = 3.2, 12.4$ Hz), 2.23 (3H, s), 1.90–1.00 (23H, m), 1.14 (3H, s), 0.91 (3H, s), 0.86 (3H, s), 0.83 (6H, s), 0.80 (3H, s); ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta = 147.90$, 135.34, 134.65, 129.51, 126.74, 124.80, 61.58, 61.50, 56.88, 56.24, 42.50, 42.11, 42.08, 41.14, 40.13, 38.10, 38.07, 38.06, 37.81, 33.53, 33.38, 31.22, 26.23, 21.45, 20.81, 19.06, 18.70, 18.27, 18.20, 17.57 (two peaks in $CDCl_3$: 17.52, 17.49), 17.43, 16.29; HR-MS (EI) calcd for $[C_{33}H_{50}]^+$: 446.3913, found: 446.3921. All data matched those of the authentic natural product. The synthetic material coeluted with the authentic natural product on thin-layer chromatography: $R_f = 0.41$ (hexane), 0.67 (benzene/pentane, 1/10).

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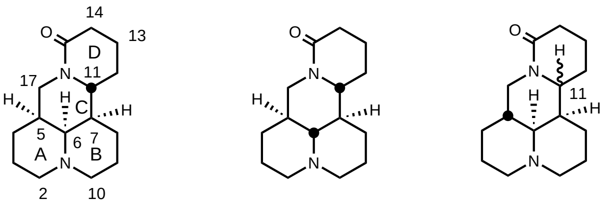
[10] We are indebted to Dr. Pierre Albrecht (Université Louis Pasteur, Strasbourg) for an authentic specimen of **1**.

[11] Prepared from (6*S*)-6,7-oxidogeranyl bromide as described previously for the farnesyl[3] and geranylgeranyl[4] homologues.

A Short Synthesis of (±)-Matrine**

Laurent Boiteau, Jean Boivin, Annie Liard, Béatrice Quiclet-Sire, and Samir Z. Zard*

Matrine (**1**) is the main alkaloid found in *Sophora flavenscens* Ait. and belongs to a family of about two dozen members with the same basic tetracyclic skeleton (Figure 1).[1] Some of these compounds (such as allomatrine, sophoridine, and darvasamine) differ only in the relative stereochemistry at the ring junctions; others contain one or more double bonds (leontalbinine, sophoramine) or a hydroxyl group (sophoranol or 5α-hydroxymatrine). Matrine has been claimed to have antiulcerogenic and anticancer activities, but information on these biological aspects is still scant.[1] Here we describe a short, convergent synthesis of (±)-matrine involving a radical cascade reaction of a xanthate as the key step.



matrine **1**
sophocarpine ($\Delta^{13,14}$)
leontalbinine ($\Delta^{7,11}$)
sophoramine ($\Delta^{11,12}$ and $\Delta^{13,14}$)

allomatrine

darvasamine (11α)
sophoridine (11β)

Figure 1. Some alkaloids of the matrine family.

The three earlier total syntheses of matrine[2] rely on traditional ionic chemistry; the most recent by Chen and coworkers[2a] is biomimetic in its conception and is based on an

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[*] Dr. S. Z. Zard,[+] A. Liard, Dr. B. Quiclet-Sire
Institut de Chimie des Substances Naturelles
F-91198 Gif-Sur-Yvette (France)
Fax: (+33) 1 69-07-72-47

Dr L. Boiteau, Dr. J. Boivin
Laboratoire de Synthèse Organique associé au CNRS
Ecole Polytechnique
91128 Palaiseau Cedex (France)
Fax: (+33) 1 69-33-30-10

[+] Can be reached at both addresses.

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