Stereoselective Construction of the Diterpene Part of Indole Alkaloids, Radarins, by Way of Intramolecular Diels–Alder Reaction

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The tricyclic diterpene part of the indole alkaloids, radarins A–D (**1-4**), was synthesized in a highly stereoselective manner by the exploitation of an intramolecular Diels–Alder reaction. (±)-5,6-Dimethyl-2,3,4,4a,5,6,7,8-octahydro-2-oxo-5-vinylnaphthalene (**7**) was converted into trienes **28** and **29**, possessing (1*E*,3*E*)- and (1*E*,3*Z*)-4-(phenylthio)butadiene moieties. Intramolecular [4 + 2] cycloadditions of **28** and **29** yielded tricyclic **32** selectively, producing the ABC carbon skeleton of radarins.

Radarins A–D (**1-4**) are indole alkaloids isolated from the sclerotia of *Aspergillus sulphureus*.[1] Among them, radarin A has the most potent activity against the corn earworm *Helicoverpa zea* and exhibits significant cytotoxicity in assays against three human solid tumor cell lines. Extensive high-field 2D NMR experiments have established the unique diterpene skeleton of the radarins.[1] As part of our continuing interest in the syntheses of polycyclic natural products,[2] we sought an efficient route to the tricyclic ring system and report herein the stereocontrolled construction of the ABC carbon framework, employing an intramolecular Diels–Alder reaction (IMDA).[3]

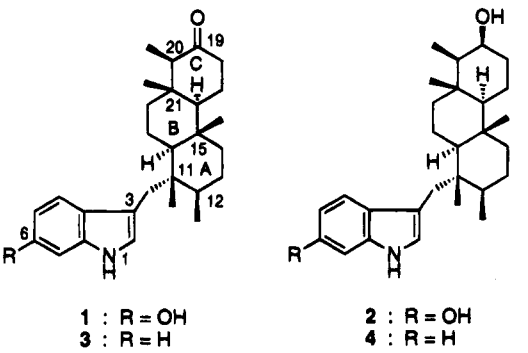
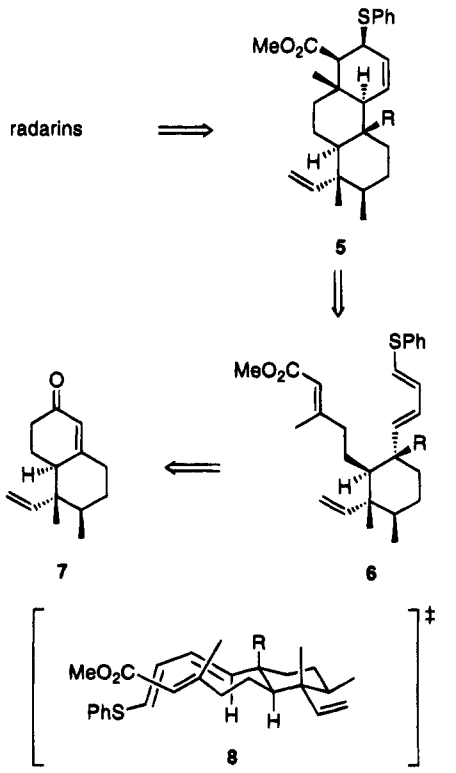


Figure 1.

Our retrosynthetic analysis is shown in Scheme 1. We envisioned the diastereoselective assembly of a potential intermediate **5** by the IMDA of **6**. The sulfenyl group would assist in the IMDA and would be useful for further functionalization.[4] Stereoselective construction of *trans-anti-trans* perhydrophenanthrenes had been performed by the IMDA of cyclohexane derivatives having ethenyl and hexa-3,5-dienyl side chains at contiguous positions.[5] However, to our knowledge, a selective synthesis of the desired framework by the IMDA of cyclohexanes such as **6**, carrying butadienyl and but-3-enyl groups, has not been reported.[6] We expected that the transition state **8**, leading to **5**, would be viable and preferred if the R group imposes only slight steric hindrance. The preparation of **6** would start with the known bicyclic enone **7**.[7] The vinyl group of **7** could be utilized in introducing the indole part of the radarins.

Scheme 1



[⊗] Abstract published in *Advance ACS Abstracts,* July 15, 1995.

(1) Laakso, J. A.; Gloer, J. B.; Wicklow, D. T.; Dowd, P. F. *J. Org. Chem.* **1992**, *57*, 138–141.

(2) (a) Ihara, M.; *J. Pharm. Soc. Jpn.* **1992**, *112*, 516–533. (b) Ihara, M.; Fukumoto, K. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1010–1022. (c) Fukumoto, K. *Syn. Org. Chem. Jpn.* **1994**, *52*, 2–18.

(3) Oppolzer, W. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 10–23; Brieger, G.; Bennett, J. N. *Chem. Rev.* **1980**, *80*, 63–97. Fallis, A. G. *Can. J. Chem.* **1984**, *62*, 183–234. Ciganek, E. *Organic Reactions*; Dauben, W. G., Ed.; Wiley and Sons: New York, 1984; Vol. 32, pp 1–374. Carruthers, W. *Cycloaddition Reactions in Organic Synthesis*; Pergamon Press: Oxford, 1990; pp 140–208. Roush, W. R. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Paquette, L. A., Eds.; Pergamon Press: Oxford, 1991; Vol. 5, pp 513–550.

(4) (a) Lavielle, G.; Sturtz, G. *Bull. Soc. Chim. Fr.* **1970**, 1369–1376. (b) Ihara, M.; Kawaguchi, A.; Ueda, H.; Chihiro, M.; Fukumoto, K.; Kametani, T. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1331–1337.

(5) Ihara, M.; Sudow, I.; Fukumoto, K.; Kametani, T. *J. Org. Chem.* **1985**, *50*, 144–145. Shing, T. K. M.; Tang, Y. *J. Chem. Soc., Chem. Commun.* **1992**, 341–342. Abad, A.; Agullo, C.; Arno, M.; Cunat, A. C.; Meseguer, B.; Zaragoza, R. J. *Synlett* **1994**, 733–735.

(6) Uguen and co-workers reported the selective formation of *cis-syn-trans* perhydrophenanthrene by IMDA of 1-(2-oxobut-3-enyl)-2-(1-methylbutadienyl)cyclohexane: Tahri, A.; Uguen, D.; Cinn, A. De; Fischer, J. *Tetrahedron Lett.* **1994**, *35*, 3945–3948.

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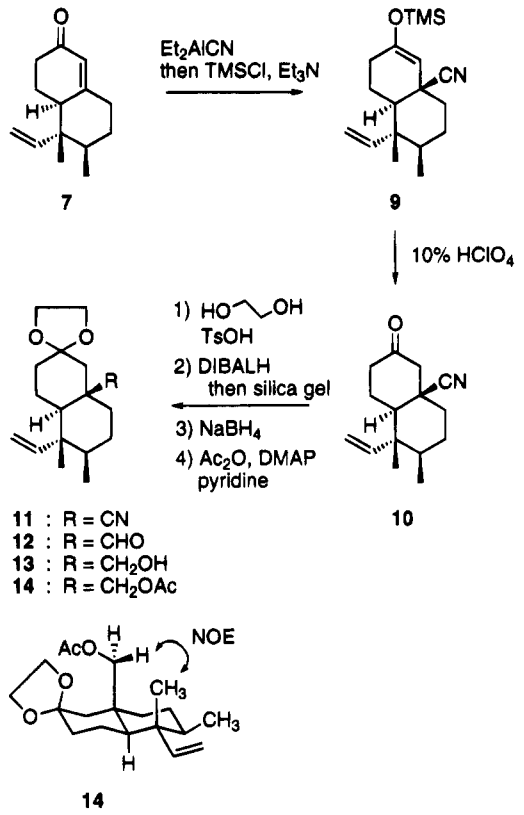
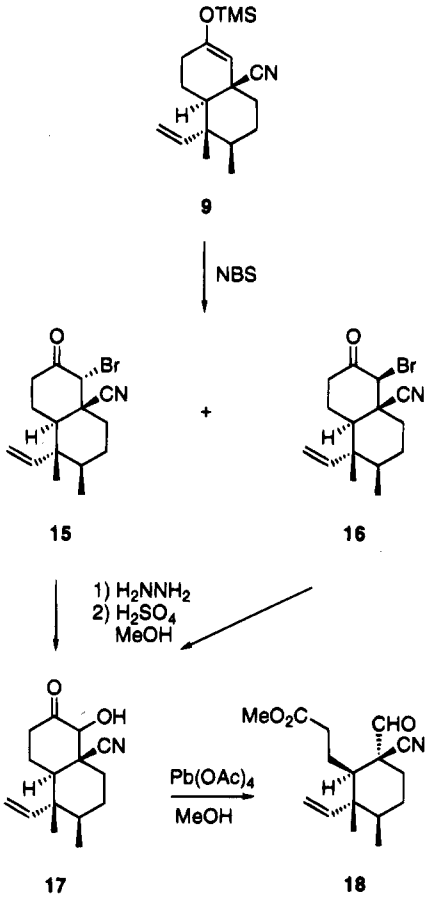
Scheme 2



A nitrile group was chosen to be the one-carbon unit at the angular position for the following reasons: (1) the necessity of introducing the functional group under thermodynamically controlled conditions in order to form the *trans* fused decalin system, (2) a small steric interaction in the transition state **8**, and (3) the facile conversion into a methyl group by standard methods. Thus, **7**[7] was treated with Et_2AlCN.[8] With the intention of regioselective cleavage of the bond between C(1) and C(2), the resulting enolate was quenched *in situ* with TMSCl in the presence of Et_3N.[9] The stereochemistry of **9**, obtained as a single stereoisomer, was determined by NOE experiments after its conversion into **14**, as depicted in Scheme 2. An NOE with 11.5% enhancement was observed between the hydrogen atoms of the methylene group at the angular C(8a) position and the hydrogen atoms of the methyl group at the C(5) position; the data firmly indicate the required *trans* fused configuration.

The selective cleavage of the double bond of the siloxy olefin was carried out as shown in Scheme 3. After the formation of **9** from **7**, treatment with NBS[10] produced **15** and **16** in 58% and 10% yields, respectively. Both bromides **15** and **16** were transformed into the same α-hydroxy ketone **17** upon treatment with H_2NNH_2[11] followed by acidic hydrolysis of the resulting α-hydroxy hydrazone. By this procedure, **17** was obtained in 89% overall yield from **15** and in 63% overall yield from **16**.

Scheme 3



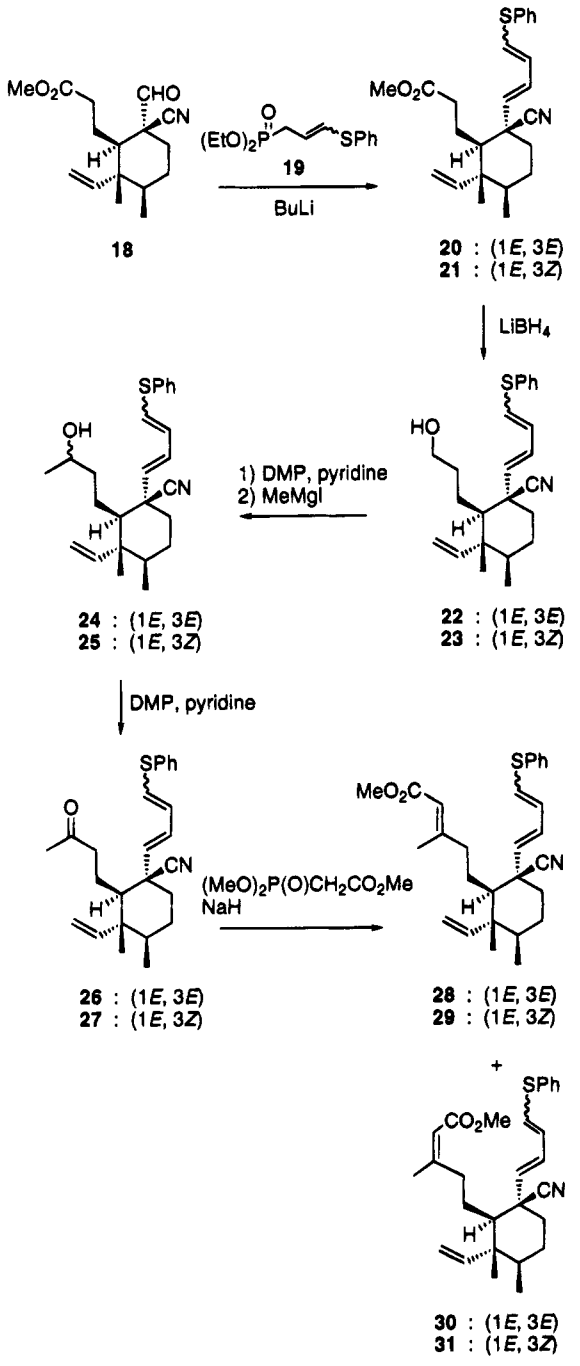
Oxidation of **17** with $Pb(OAc)_4$ in MeOH[12] gave a 73% yield of **18**.

With **18** in hand, we next examined construction of the diene part. According to our synthetic plan, **18** was treated with diethyl 3-(phenylthio)prop-2-enylphosphonate **19**[4] in the presence of BuLi. Two isolable dienes **20** and **21** were obtained in 23% and 38% yields, respectively (Scheme 4). Transformation of **20** into **26** *via* the corresponding carboxylic acid derivative gave poor results. Thus, the ester group of **20** was selectively reduced with $LiBH_4$ to give **22** in 81% yield, which was converted into **24** in 74% overall yield upon oxidation with the Dess–Martin periodinane (DMP),[13] followed by a Grignard reaction with MeMgI. Oxidation of **24** with DMP[13] produced **26** in 80% yield, which was then subjected to an Emmons reaction to furnish **28** in 72% yield and **30** in 12% yield. By the same method, diene **21** was transformed, *via* **23** (89% yield), **25** (49% yield), and **27** (89% yield), into **29** (54% yield) and **31** (15% yield).

The IMDAs of **28** in the presence of various Lewis acids were unsuccessful. The construction of the perhydrophenanthrene skeleton was achieved by heating in *o*-dichlorobenzene (ODB) at 180 °C in a sealed tube. After 10 h of heating, tricyclic **32** was obtained in 82% yield from **28** as the sole stereoisomer. The same compound **32** was produced in 55% yield from **29** (Scheme 5). It is assumed that **29** was transformed into **32** after isomerization to **28**.[14]

(7) Tokoroyama, T.; Fujimori, K.; Shimizu, T.; Yamagiwa, Y.; Monden, M.; Iio, H. *Tetrahedron* **1988**, *44*, 6607–6622.
(8) Nagata, W.; Yoshioka, M. *Organic Reactions*; Dauben, W. G., Ed.; Wiley and Sons: New York, 1984; Vol. 25, pp 225–476.
(9) Smith, A. B., III; Leenay, T. L. *J. Am. Chem. Soc.* **1989**, *111*, 5761–5768.
(10) Blanco, L.; Amice, P.; Conia, J. M. *Synthesis* **1976**, 194–196.
(11) Catsoulacos, P.; Hassner, A. *J. Org. Chem.* **1967**, *32*, 3723–3724.
(12) (a) Baer, E. *J. Am. Chem. Soc.* **1942**, *64*, 1416–1421. (b) Ihara, M.; Toyota, M.; Fukumoto, K.; Kametani, T. *J. Chem. Soc., Perkin Trans. 1* **1986**, 2151–2161.
(13) Dess, D. B.; Martin, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 7277–7287.

Scheme 4



The configuration of the product was assigned to **32** on the basis of reaction mechanism and spectral analysis. MMX energies of four possible conformations **A**–**D** were calculated using the GMMX[15] program, followed by PCMODEL.[16] The transition state **A** leading to **32** has an energy of 183.34 kcal/mol, while **B** leading to **33**, **C** leading to **34**, and **D** leading to **35** have energies of 183.94, 192.02, and 191.29 kcal/mol, respectively. This suggests that conformation **A** is the most favorable, as expected. However, the calculated energy difference between conformations **A** and **B** is not large enough to explain the exclusive formation of **32**.

From the 500 MHz ^{1}H NMR spectrum, the coupling constant between hydrogens at the C(2) and C(3) positions are found to be 2.60 Hz, whereas $J_{4,5}$ and $J_{5,6}$ are 3.66 and 6.72 Hz, respectively. Estimated coupling constants for structures **32**-**35** are listed in Table 1. The coupling constants observed in the NMR spectra of the IMDA product are in good agreement with those calculated for **32**. The desired structure **32** was further supported by the observation of NOEs between hydrogens at the C(2) and C(6) positions as well as between the C(2) and C(10) positions.

The stereoselective construction of the ABC carbon skeleton of radarins A–D (**1**-**4**) was achieved utilizing the IMDA as the pivotal step.

Experimental Section

General Procedure. All reactions were carried out under a positive atmosphere of dry Ar unless otherwise indicated. Solvents were distilled prior to use: THF, Et_2O, and benzene were distilled from Sodium benzophenone; CH_2Cl_2, DME, and MeCN were distilled from CaH_2 and stored over 4-Å molecular sieves. Unless otherwise noted, all extracts were dried over $MgSO_4$, and the solvent was removed by rotary evaporation under reduced pressure. All new compounds are homogeneous on TLC, and their purities were further verified by 300 or 500 MHz ^{1}H NMR spectra.

(±)-(4a*R,5*S**,6*R**,8a*S**)-8a-Cyano-1,2,3,4,4a,5,6,7,8,8a-decahydro-5,6-dimethyl-2-oxo-5-vinylnaphthalene (10).** To a stirred solution of **7**[7] (53 mg, 0.26 mmol) in dry benzene (2 mL) was added at rt 1 M Et_2AlCN–toluene (0.79 mL, 0.79 mmol), and the mixture was stirred for 3 h at rt. After additions of Et_3N (0.18 mL, 1.29 mmol) and TMSCl (0.10 mL, 0.79 mmol), the mixture was further stirred for 12 h at rt. The reaction mixture was poured into saturated $NaHCO_3$ and the resulting mixture was extracted thoroughly with Et_2O. The extract was washed with brine, dried, and evaporated to give crude **9** as a yellowish oil: IR (neat, cm^{-1}) 2220, 1660, 1254; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.20 (s, 9H), 0.78 (d, J = 6.7 Hz, 3H), 1.04 (s, 3H), 4.72 (s, 1H), 5.00 (dd, J = 1.2, 17.7 Hz, 1H), 5.14 (dd, J = 1.2, 11.0 Hz, 1H), 5.39 (dd, J = 11.0, 17.7 Hz, 1H), which was used in the following reaction without purification.

A mixture of the above product **9** and 10% $HClO_4$ (1 mL) in THF (2.5 mL) was stirred for 30 min at rt. After addition of H_2O, the mixture was thoroughly extracted with Et_2O. The extract was washed with brine, dried, and evaporated to give a residue, which was subjected to chromatography on silica gel. Elution with hexane–AcOEt (9:1 v/v) afforded the starting **7** (6.8 mg, 13%). Further elution with hexane–AcOEt (4:1 v/v) provided **10** (32 mg, 53%) as a pale yellowish oil: IR (neat, cm^{-1}) 2260, 1720, 1634; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.83 (d, J = 6.7 Hz, 3H), 1.06 (s, 3H), 1.40–1.47 (m, 1H), 1.51 (dd, J = 2.4, 12.2 Hz, 1H), 1.52 (ddd, J = 4.3, 12.2, 14.0 Hz, 1H), 1.62–1.70 (m, 2H), 1.84–1.91 (m, 1H), 2.04–2.09 (m, 1H), 2.12 (ddd, J = 3.1, 3.1, 13.4 Hz, 1H), 2.25–2.30 (m, 1H), 2.32 (d, J = 14.7 Hz, 1H), 2.51–2.56 (m, 1H), 2.67 (dd, J = 2.4, 14.7 Hz, 1H), 5.05 (br d, J = 17.6 Hz, 1H), 5.20 (br d, J = 11.0 Hz, 1H), 5.28 (dd, J = 11.0, 17.6 Hz, 1H); HRMS (M^+) 231.1623 calcd for $C_{15}H_{21}NO$, found 231.1613.

(±)-(4a*R,5*S**,6*R**,8a*S**)-8a-Cyano-1,2,3,4,4a,5,6,7,8,8a-decahydro-5,6-dimethyl-2,2-(ethylenedioxy)-5-vinylnaphthalene (11).** A solution of **10** (17.4 mg, 0.075 mmol), ethylene glycol (1 mL), and a catalytic amount of TsOH in benzene (10 mL) was heated under reflux for 10 h in a Dean–Stark apparatus. After dilution with benzene, the mixture was washed with saturated $NaHCO_3$ and brine, dried, and evaporated to give a residue which was chromatographed on silica gel. Elution with hexane–AcOEt (17: 3 v/v) afforded **11** (13.8 mg, 67%), recrystallization of which from hexane provided colorless prisms: mp 88.0–90.5 °C; IR (neat, cm^{-1}) 2220, 1630; ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.78 (d, J = 6.9 Hz, 3H), 1.07 (s, 3H), 3.89–4.12 (m, 4H), 5.00 (dd, J = 1.2, 17.0 Hz, 1H), 5.14

(14) Grieco, P. A.; Lis, R.; Zelle, R. E.; Finn, J. *J. Am. Chem. Soc.* **1986**, *108*, 5908–5919.
(15) GMMX (Version 1.0), Serena Software, P. O. Box 3076, Bloomington, IN.
(16) PCMODEL (Version 4.0), Serena Software, P. O. Box 3076, Bloomington, IN.

Scheme 5

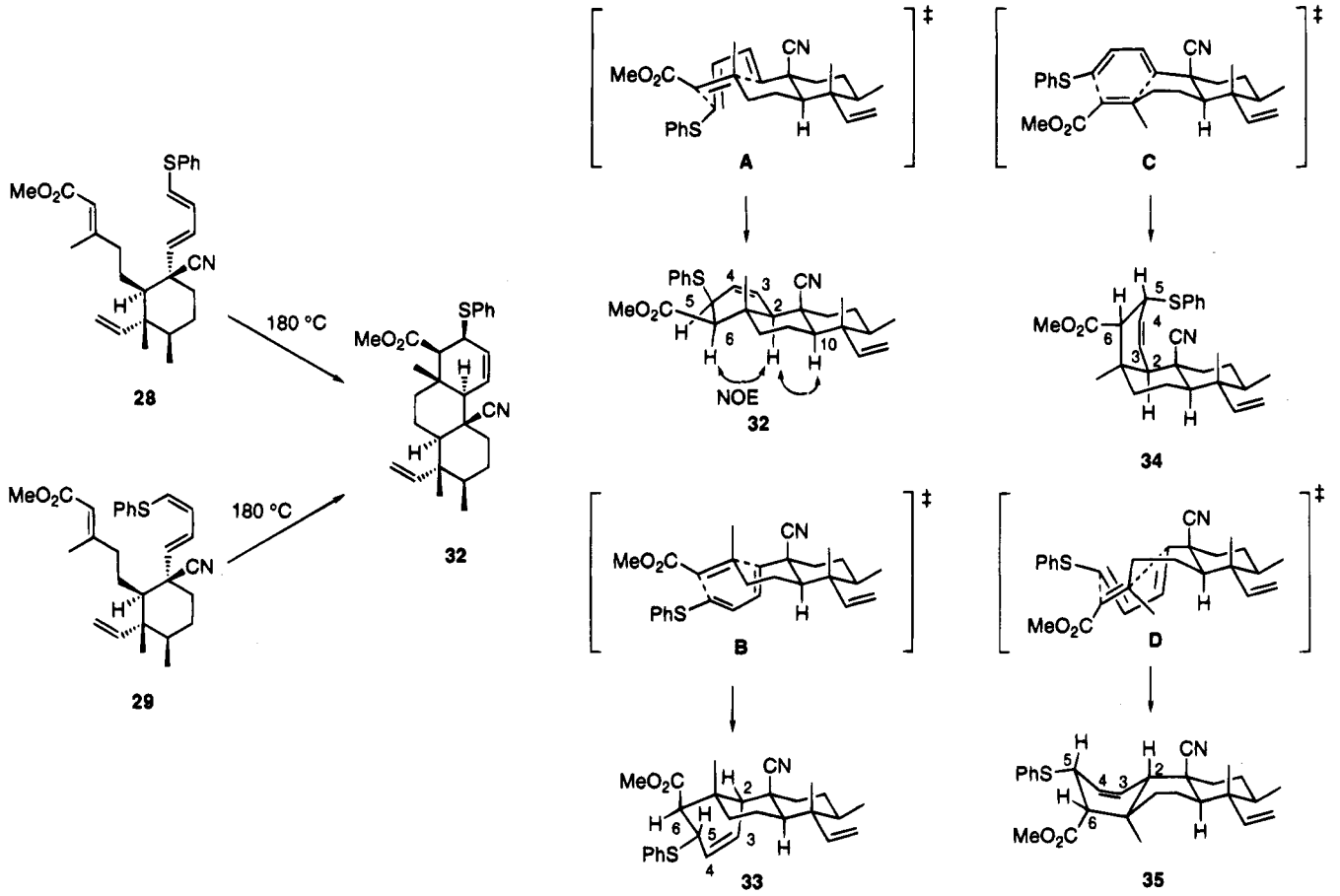


Table 1. Coupling Constants in ^{1}H NMR Spectroscoy[a]

	$J_{2,3}$	$J_{4,5}$	$J_{5,6}$
Diels–Alder product	2.60	3.66	6.72
calcd for **32**	2.70	3.64	6.98
calcd for **33**	2.75	4.17	0.37
calcd for **34**	4.79	3.46	11.39
calcd for **35**	2.60	5.77	3.28

[a] Coupling constants are calculated using PCMODEL.[15]

(dd, J = 1.2, 10.4 Hz, 1H), 5.39 (dd, J = 10.4, 17.0 Hz, 1H); HRMS (M^+) 275.1885 calcd for $C_{17}H_{25}NO_2$, found 275.1882.

(±)-(4a*R,5*S**,6*R**,8a*S**)-1,2,3,4,4a,5,6,7,8,8a-Decahydro-5,6-dimethyl-2,2-(ethylenedioxy)-8a-formyl-5-vinylnaphthalene (12).** To a stirred solution of **11** (13.7 mg, 0.05 mmol) in dry CH_2Cl_2 (1 mL) was slowly added at −78 °C 0.93 M DIBALH–hexane (60 μL, 0.06 mmol), and the mixture was stirred for 2.5 h at 0 °C. After additions of Et_2O and H_2O (60 μL), the mixture was stirred for 1 h at rt and then filtered through Celite. The filtrate was dried and evaporated to give a residue, which was treated for 1.5 h with silica gel. Elution with hexane–AcOEt (9:1 v/v) yielded **12** (8.1 mg, 58%) as a colorless oil: IR ($CHCl_3$, cm^{-1}) 1700, 1630; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.70 (d, J = 6.7 Hz, 3H), 0.77 (s, 3H), 0.92–0.99 (m, 1H), 1.07–1.16 (m, 1H), 1.30–1.39 (m, 3H), 1.44 (br d, J = 12.8 Hz, 1H), 1.62–1.66 (m, 1H), 1.77–1.80 (m, 1H), 1.83–1.88 (m, 2H), 1.94–2.03 (m, 1H), 2.20–2.25 (m, 1H), 3.79–3.93 (m, 4H), 4.94 (dd, J = 1.2, 17.0 Hz, 1H), 5.12 (dd, J = 1.2, 10.4 Hz, 1H), 5.47 (dd, J = 10.4, 17.0 Hz, 1H), 10.07 (d, J = 1.2 Hz, 1H); HRMS (M^+) 278.1882 calcd for $C_{17}H_{26}O_3$, found 278.1880.

(±)-(4a*R,5*S**,6*R**,8a*S**)-8a-(Acetoxymethyl)-1,2,3,4,4a,5,6,7,8,8a-decahydro-5,6-dimethyl-2,2-(ethylenedioxy)-5-vinylnaphthalene (14).** To a stirred solution of **12** (8.1 mg, 0.03 mmol) in MeOH (0.5 mL) was added at 0 °C $NaBH_4$ (1.1 mg, 0.03 mmol), and the mixture was stirred for 30 min at 0 °C. After being poured into H_2O, the mixture was thoroughly extracted with Et_2O. The extract was washed with brine, dried, and evaporated to afford crude **13**: IR ($CHCl_3$, cm^{-1}) 3420, 1630, which was used in the next reaction without purification.

A mixture of the above product, Ac_2O (0.4 mL), and a catalytic amount of DMAP in pyridine (1 mL) was stirred for 12 h at rt. After dilution with benzene, the resulting mixture was washed with H_2O, 10% aqueous $KHSO_4$, and brine, and dried. Evaporation of solvent gave a residue, which was chromatographed on silica gel with hexane–AcOEt (9:1 v/v) as eluent to provide **14** (8.4 mg, 90%). Recrystallization from hexane yielded colorless prisms: mp 123.5–124.0 °C; IR ($CHCl_3$, cm^{-1}) 1730, 1630; ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.73 (d, J = 6.1 Hz, 3H), 0.80 (s, 3H), 0.96–1.03 (m, 1H), 1.05–1.08 (m, 1H), 1.15–1.18 (m, 1H), 1.72–1.76 (m, 1H), 1.78–1.81 (m, 1H), 2.06 (s, 3H), 2.14–2.18 (m, 1H), 3.82–3.98 (m, 4H), 4.35 (dd, J = 1.2, 10.4 Hz, 1H), 4.40 (br d, J = 10.4 Hz, 1H), 4.91 (dd, J = 1.2, 17.1 Hz, 1H), 5.08 (dd, J = 1.2, 11.0 Hz, 1H), 5.42 (dd, J = 11.0, 17.1 Hz, 1H); HRMS (M^+) 322.2144 calcd for $C_{19}H_{30}O_4$, found 322.2179.

(±)-(1*R,4a*R**,5*S**,6*R**,8a*R**)-(15) and (±)-(1*S**,4a*R**,5*S**,6*R**,8a*R**)-1-Bromo-8a-cyano-1,2,3,4,4a,5,6,7,8,8a-decahydro-5,6-dimethyl-2-oxo-5-vinylnaphthalene (16).** To a stirred solution of **7** (2.64 g, 12.92 mmol) in dry benzene (60 mL) was slowly added at rt 1 M Et_2AlCN–toluene (38.8 mL, 38.8 mmol), and the mixture was stirred for 8.5 h at rt. After additions of Et_3N (9 mL, 64.6 mmol) and TMSCl (4.9 mL, 38.8 mmol) at 0 °C, the mixture was further stirred for 12 h at 0 °C. The reaction mixture was diluted with Et_2O and then poured into saturated $NaHCO_3$. The mixture was thoroughly extracted with Et_2O. The extract was washed with brine, dried, and evaporated to give a residue, which was used in the next reaction.

To a solution of the above product in dry THF (50 mL) was added at 0 °C NBS (3.0 g, 16.8 mmol), and the mixture was stirred for 3 h at 0 °C. After addition of saturated $NaHCO_3$, the resulting mixture was thoroughly extracted with Et_2O. The extract was washed with brine, dried, and evaporated to give a residue, which was subjected to silica gel chromatography.

Elution with hexane–AcOEt (19:1 v/v) afforded **15** (2.34 g, 58%) as a pale yellowish solid: IR ($CHCl_3$, cm^{-1}) 2220, 1720; ^1H NMR (500 MHz, $CDCl_3$) δ 0.83 (d, J = 6.1 Hz, 3H), 1.05 (s, 3H), 1.41–1.48 (m, 1H), 1.66–1.78 (m, 2H), 1.81–1.90 (m, 2H), 1.96–2.04 (m, 2H), 2.12–2.18 (m, 1H), 2.39–2.44 (m, 1H), 3.06–3.14 (m, 1H), 4.21 (d, J = 1.8 Hz, 1H), 5.05 (br d, J = 17.1 Hz, 1H), 5.21 (br d, J = 11.0 Hz, 1H), 5.52 (dd, J = 11.0, 17.1 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 200.08, 146.77, 118.75, 115.25, 57.35, 44.01, 43.65, 42.38, 40.32, 35.04, 34.71, 26.27, 24.78, 16.28, 9.93; MS m/z (M^+) 309. Anal. Calcd for $C_{15}H_{20}BrNO$: C, 58.07; H, 6.50; N, 4.51; Br, 25.76. Found: C, 57.74; H, 6.48; N, 4.49; Br, 25.95.

Further elution with hexane–AcOEt (4:1 v/v) provided **16** (402 mg, 10%), which was recrystallized from hexane–$CHCl_3$ to yield pale yellowish prisms: mp 139–140 °C; IR ($CHCl_3$, cm^{-1}) 2213, 1720, 1634; ^1H NMR (300 MHz, $CDCl_3$) δ 0.84 (d, J = 6.7 Hz, 3H), 1.05 (s, 3H), 1.85–2.00 (m, 1H), 2.10–2.17 (m, 1H), 2.33–2.45 (m, 1H), 2.60–2.67 (m, 1H), 2.78–2.86 (m, 1H), 4.48 (s, 1H), 5.07 (br d, J = 17.6 Hz, 1H), 5.23 (br d, J = 11.0 Hz, 1H), 5.52 (dd, J = 11.0, 17.6 Hz, 1H); HRMS (M^+) 309.0728 calcd for $C_{15}H_{20}BrNO$, found 309.0739.

(±)-(4a*R,5*S**,6*R**,8a*S**)-8a-Cyano-1,2,3,4,4a,5,6,7,8,8a-decahydro-5,6-dimethyl-1-hydroxy-2-oxo-5-vinylnaphthalene (17).** (A) A mixture of **15** (273 mg, 0.88 mmol) and 98% $H_2NNH_2{\cdot}H_2O$ (3.3 mL, 68 mmol) in EtOH (6.6 mL) was heated for 6 h under reflux. After being poured into H_2O, the resulting mixture was thoroughly extracted with Et_2O. The extract was washed with brine, dried (Na_2SO_4), and evaporated to give a crude hydrazone as a pale yellowish oil: IR ($CHCl_3$, cm^{-1}) 3400–3250, 2210, 1630, 1618, which was used in the following reaction without purification.

A mixture of the above product and 6 N H_2SO_4 (0.8 mL) in MeOH (8 mL) was heated for 2 h under reflux. After filtration through Celite, the filtrate was diluted with Et_2O. The mixture was washed with brine, dried, and evaporated to give a residue, which was subjected to chromatography on silica gel. Elution with hexane–AcOEt (4:1 v/v) provided **17** (195 mg, 89%) as a solid, which was recrystallized from hexane–Et_2O to afford colorless needless: mp 131–134 °C; IR ($CHCl_3$, cm^{-1}) 3420, 2210, 1720, 1620; ^1H NMR (500 MHz, $CDCl_3$) δ 0.83 (d, J = 7.1 Hz, 3H), 1.06 (s, 3H) 1.38–1.48 (m, 1H), 1.58–1.72 (m, 3H), 1.83–1.92 (m, 1H), 2.08–2.13 (m, 1H), 2.33–2.40 (m, 1H), 2.54–2.60 (m, 1H), 2.67 (ddd, J = 2.4, 4.3, 14.0 Hz, 1H), 3.90 (br d, J = 4.9 Hz, 1H), 3.93 (d, J = 4.9 Hz, 1H), 5.05 (br d, J = 17.1 Hz, 1H), 5.21 (br d, J = 11.0 Hz, 1H), 5.49 (dd, J = 11.0, 17.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.09, 146.89, 119.63, 115.16, 80.73, 48.65, 47.77, 43.92, 40.44, 38.22, 35.04, 26.47, 25.52, 16.25, 10.24; MS m/z (M^+) 247. Anal. Calcd for $C_{15}H_{21}NO_2$: C, 72.84; H, 8.56; N, 5.66. Found: C, 72.95; H, 8.58; N, 5.68.

(B) By the same procedure as above, **16** (120 mg, 0.39 mmol) was converted to **17** (60 mg, 63%), which was identical with the above sample in all respects.

Methyl (±)-3-[(1*R,2*S**,3*S**,4*R**)-1-Cyano-3,4-dimethyl-1-formyl-3-vinylcyclohex-2-yl]propionate (18).** A mixture of **17** (540 mg, 2.18 mmol) and $Pb(OAc)_4$ (1.07 g, 2.41 mmol) in MeOH (22 mL) was stirred for 20 min at 0 °C and for 1 h at rt. After addition of saturated $NaHCO_3$, the mixture was filtered through Celite, and the filtrate was thoroughly extracted with Et_2O. The extract was washed with brine, dried, and evaporated to give a residue, which was chromatographed on silica gel. Elution with hexane–AcOEt (4:1 v/v) afforded **18** (444 mg, 73%) as a powder, which was recrystallized from hexane–AcOEt to provide colorless needles; mp 65–67 °C; IR ($CHCl_3$, cm^{-1}) 2220, 1730, 1620; ^1H NMR (300 MHz, $CDCl_3$) δ 0.82 (d, J = 6.6 Hz, 3H), 1.10 (s, 3H), 3.65 (s, 3H), 5.07 (dd, J = 1.1, 17.2 Hz, 1H), 5.22 (dd, J = 1.1, 10.6 Hz, 1H), 5.45 (dd, J = 10.6, 17.2 Hz, 1H), 9.39 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 194.42, 172.73, 146.13, 118.84, 115.34, 54.39, 51.58, 44.79, 44.39, 39.73, 33.64, 31.08, 25.19, 24.26, 16.36, 10.15; MS m/z (M^+) 277. Anal. Calcd for $C_{16}H_{23}NO_3$: C, 69.29; H, 8.36; N, 5.05. Found: C, 69.07; H, 8.46; N, 5.02.

Methyl (±)-1-{(1*R,2*R**,3*S**,4*R**)-1-Cyano-3,4-dimethyl-1-[(1*E*,3*E*)-4-(phenylthio)butadien-1-yl]-3-vinylcyclohex-2-yl}propionate (20) and Methyl (±)-3-{(1*R**,2*R**,3*S**,4*R**)-1-Cyano-3,4-dimethyl-1-[(1*E*,3*E*)-4-(phenylthio)-butadien-1-yl]-3-vinylcyclohex-2-yl}propionate (21).** To a stirred solution of **19**[4] (3.2 g, 11.2 mmol) in dry THF (60 mL) was added at −78 °C 1.56 M BuLi–hexane (5.77 mL, 9.0 mmol), and the mixture was stirred for 2 h at −78 °C. After addition of a solution of **18** (2.1 g, 7.5 mmol) in dry THF (40 mL), the mixture was stirred for 1 h at −78 °C and then diluted with Et_2O. The mixture was washed with H_2O. The aqueous solution was thoroughly extracted with Et_2O. The combined Et_2O layers were washed with brine, dried, and evaporated. Chromatography on silica gel with hexane–AcOEt (20:1 v/v) as eluent afforded **20** (0.71 g, 23%) as a yellowish oil: IR ($CHCl_3$, cm^{-1}) 2230, 1733, 1630; ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (d, J = 6.6 Hz, 3H), 1.09 (s, 3H), 1.92–2.01 (m, 1H), 2.13–2.38 (m, 2H), 3.63 (s, 3H), 5.02 (br d, J = 17.2 Hz, 1H), 5.15 (br d, J = 11.0 Hz, 1H), 5.26 (d, J = 15.8 Hz, 1H), 5.46 (dd, J = 11.0, 17.2 Hz, 1H), 6.29 (dd, J = 10.3, 14.7 Hz, 1H), 6.48–6.60 (m, 2H), 7.24–7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.30, 146.97, 134.44, 132.92, 130.06, 129.62, 129.24, 129.04, 127.23, 121.81, 114.69, 51.55, 50.53, 45.36, 45.25, 40.28, 38.46, 35.32, 26.81, 24.37, 16.65, 10.30; HRMS (M^+) 409.2076 calcd for $C_{25}H_{31}NO_2S$, found 409.2058.

Further elution with hexane–AcOEt (20:1 v/v) yielded **21** (1.16 g, 38%) as a yellowish oil: IR ($CHCl_3$, cm^{-1}) 2230, 1733, 1632; ^1H NMR (300 MHz, $CDCl_3$) δ 0.79 (d, J = 7.0 Hz, 3H), 1.11 (s, 3H), 1.97–2.06 (m, 1H), 2.35–2.42 (m, 2H), 3.64 (s, 3H), 5.02 (br d, J = 17.6 Hz, 1H), 5.16 (br d, J = 10.6 Hz, 1H), 5.39 (dd, J = 10.6, 17.6 Hz, 1H), 5.47 (d, J = 15.4 Hz, 1H), 6.22–6.36 (m, 2H), 6.89 (dd, J = 9.5, 15.4 Hz, 1H), 7.24–7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.28, 146.98, 135.85, 135.53, 129.38, 129.12, 127.44, 127.26, 126.82, 126.14, 121.63, 114.69, 51.55, 50.57, 45.42, 45.28, 40.28, 38.34, 35.33, 26.78, 24.43, 16.63, 10.32; MS m/z (M^+) 409. Anal. Calcd for $C_{25}H_{31}NO_2S$: C, 73.31; H, 7.63; N, 3.42; S, 7.83. Found: C, 73.35; H, 7.70; N, 3.33; S, 7.82.

(±)-3-{(1*S,2*R**,3*S**,4*R**)-1-Cyano-3,4-dimethyl-1-[(1*E*,3*E*)-4-(phenylthio)butadien-1-yl]-3-vinylcyclohex-2-yl}-1-propanol (22).** To a stirred solution of **20** (148 mg, 0.36 mmol) in dry THF (20 mL) was added at 0 °C $LiBH_4$ (47.2 mg, 2.16 mmol), and the mixture was stirred for 3 h at 50 °C. After neutralization by addition of 10% HCl at 0 °C, followed by addition of H_2O, the resulting mixture was thoroughly extracted with CH_2Cl_2. The extract was washed with brine, dried, and evaporated to afford a residue, which was purified by chromatography on silica gel. Elution with hexane–AcOEt (4:1 v/v) provided **22** (111 mg, 81%) as a yellowish oil; IR ($CHCl_3$, cm^{-1}) 3600–3400, 2250; ^1H NMR (300 MHz, $CDCl_3$) δ 0.79 (d, J = 7.0 Hz, 3H), 1.11 (s, 3H), 1.93–2.02 (m, 1H), 3.42–3.54 (m, 2H), 5.02 (br d, J = 16.5 Hz, 1H), 5.16 (br d, J = 10.6 Hz, 1H), 5.26 (br d, J = 15.0 Hz, 1H), 5.46 (dd, J = 10.6, 16.5 Hz, 1H), 6.30 (dd, J = 10.6, 14.7 Hz, 1H), 6.51 (d, J = 14.7 Hz, 1H), 6.52 (dd, J = 10.6, 14.7 Hz, 1H), 7.24–7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.33, 134.50, 133.24, 129.97, 129.23, 128.75, 127.18, 122.06, 114.43, 62.67, 51.53, 45.51, 45.37, 40.32, 38.28, 34.65, 26.82, 25.05, 16.71, 10.38; HRMS (M^+) 381.2125 calcd for $C_{24}H_{31}NOS$, found 381.2109.

(±)-3-{(1*S,2*R**,3*S**,4*R**)-1-Cyano-3,4-dimethyl-1-[(1*E*,3*Z*)-4-(phenylthio)butadien-1-yl]-3-vinylcyclohex-2-yl}-1-propanol (23).** Reduction of **21** (1.16 g, 2.84 mmol) with $LiBH_4$ (185 mg, 8.51 mmol) in dry THF (50 mL) was carried out as above to give **23** (0.97 g, 89%) as a yellowish oil: IR (neat, cm^{-1}) 3600–3200, 2235; ^1H NMR (300 MHz, $CDCl_3$) δ 0.79 (d, J = 7.0 Hz, 3H), 1.10 (s, 3H), 1.98–2.07 (m, 1H), 3.43–3.56 (m, 2H), 5.02 (br d, J = 17.2 Hz, 1H), 5.16 (br d, J = 11.0 Hz, 1H), 5.43 (dd, J = 11.0, 17.2 Hz, 1H), 5.46 (br d, J = 15.0 Hz, 1H), 6.22–6.36 (m, 2H), 6.88 (dd, J = 9.5, 15.0 Hz, 1H), 7.23–7.45 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 147.38, 136.04, 135.53, 129.39, 129.13, 127.53, 127.11, 126.85, 125.92, 121.90, 114.47, 62.72, 51.66, 45.61, 45.45, 40.40, 38.14, 34.72, 26.84, 25.04, 16.75, 10.44; HRMS (M^+) found 381.2110.

(±)-4-{(1*S,2*R**,3*S**,4*R**)-1-Cyano-3,4-dimethyl-1-[(1*E*,3*E*)-4-(phenylthio)butadien-1-yl]-3-vinylcyclohex-2-yl}-2-butanol (24).** To a stirred solution of DMP[13] (1.06 g, 2.50 mmol) and pyridine (0.5 mL, 6.24 mmol) in dry CH_2Cl_2 (70 mL) was slowly added at rt a solution of **22** (476 mg, 1.25 mmol) in CH_2Cl_2 (30 mL), and the mixture was stirred for 1 h at rt. After dilution with Et_2O, followed by addition of a

mixture (1:7 v/v) of saturated $NaHCO_3$ and 0.1 N aqueous $Na_2S_2O_3$, the resulting mixture was stirred for 30 min at rt. The aqueous layer was extracted with Et_2O. The combined organic layers were washed with saturated $NaHCO_3$ and brine. After being dried, the mixture was evaporated to give the corresponding aldehyde, which was subjected to the following reaction without purification.

To a stirred solution of the above product in dry Et_2O (40 mL) was slowly added at 0 °C 1 M MeMgI–Et_2O (5 mL, 5 mmol), and the mixture was stirred for 5 h at 0 °C. After addition of saturated NH_4Cl, the resulting mixture was thoroughly extracted with Et_2O. The extract was washed with brine, dried (Na_2SO_4), and evaporated to give a residue, which was chromatographed on silica gel. Elution with hexane–AcOEt (2:1 v/v) provided **24** (365 mg, 74%) as a yellowish oil: IR ($CHCl_3$, cm^{-1}) 3600–3200, 2225; ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (d, J = 6.6 Hz, 3H), 1.08–1.12 (m, 6H), 1.93–2.02 (m, 1H), 3.55–3.70 (m, 1H), 4.96–5.07 (m, 1H), 5.14–5.18 (m, 1H), 5.21–5.30 (m, 1H), 5.35–5.47 (m, 2H), 6.30 (dd, J = 10.6, 15.0 Hz, 1H), 6.48–6.56 (m, 2H), 7.24–7.42 (m, 5H); HRMS (M^+) 395.2281 calcd for $C_{25}H_{33}NOS$, found 395.2289.

(±)-4-{(1S*,2R*,3S*,4R*)-1-Cyano-3,4-dimethyl-1-[(1E,3Z)-4-(phenylthio)butadien-1-yl]-3-vinylcyclohex-2-yl}-2-butanol (25). By the same procedure as above, **23** (34.5 mg, 0.09 mmol) was transformed to **25** (17.4 mg, 49%) as a yellowish oil: IR (neat, cm^{-1}) 3600–3200, 2235; ^1H NMR (300 MHz, $CDCl_3$) δ 0.79 (d, J = 6.6 Hz, 3H), 1.10–1.12 (m, 6H), 1.98–2.08 (m, 1H), 3.55–3.73 (m, 1H), 5.02 (br d, J = 17.2 Hz, 0.5H), 5.03 (br d, J = 17.2 Hz, 0.5H), 5.16 (br d, J = 10.6 Hz, 0.5H), 5.17 (br d, J = 10.7 Hz, 0.5H), 5.37–5.47 (m, 2H), 6.23–6.35 (m, 2H), 6.89 (dd, J = 9.5, 15.4 Hz, 1H), 7.23–7.46 (m, 5H); HRMS (M^+) found 395.2267.

(±)-4-{(1S*,2R*,3S*,4R*)-1-Cyano-3,4-dimethyl-1-[(1E,3E)-4-(phenylthio)butadien-1-yl]-3-vinylcyclohex-2-yl}-2-butanone (26). To a stirred solution of DMP[13] (150 mg, 0.35 mmol) and pyridine (72 μL, 0.89 mmol) in CH_2Cl_2 (2.5 mL) was slowly added at rt a solution of **24** (70 mg, 0.18 mmol) in CH_2Cl_2 (2 mL), and the mixture was stirred for 2 h at rt. After additions of Et_2O and a mixture (1:7 v/v) of saturated $NaHCO_3$ and 0.1 N aqueous $Na_2S_2O_3$, the mixture was stirred for 30 min at rt. The aqueous layer was thoroughly extracted with Et_2O. The combined organic layers were washed with saturated $NaHCO_3$ and brine, dried, and evaporated. Chromatography on silica gel with hexane–AcOEt (6:1 v/v) as eluent gave **26** (56 mg, 80%) as a colorless oil: IR ($CHCl_3$, cm^{-1}) 2225, 1710; ^1H NMR (500 MHz, $CDCl_3$) δ 0.78 (d, J = 6.7 Hz, 3H), 1.09 (s, 3H), 1.94–1.99 (m, 1H), 2.05 (s, 3H), 2.24–2.32 (m, 1H), 2.41–2.49 (m, 1H), 5.02 (br d, J = 17.1 Hz, 1H), 5.14 (br d, J = 11.6 Hz, 1H), 5.26 (d, J = 15.3 Hz, 1H), 5.38 (dd, J = 11.6, 17.1 Hz, 1H), 6.29 (dd, J = 10.4, 14.7 Hz, 1H), 6.52 (d, J = 14.7 Hz, 1H), 6.53 (dd, J = 10.4, 15.3 Hz, 1H), 7.24–7.42 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.18, 147.18, 134.34, 133.07, 130.10, 129.50, 129.24, 129.20, 128.86, 127.27, 121.78, 114.61, 50.42, 45.37, 45.26, 44.97, 40.28, 38.43, 29.81, 26.76, 23.30, 16.60, 10.25; HRMS (M^+) 393.2125 calcd for $C_{25}H_{31}NOS$, found 393.2097.

(±)-4-{(1S*,2R*,3S*,4R*)-1-Cyano-3,4-dimethyl-1-[(1E,3Z)-4-(phenylthio)butadien-1-yl]-3-vinylcyclohex-2-yl}-2-butanone (27). Oxidation of **25** (353 mg, 0.89 mmol) as above provided **27** (312 mg, 89%) as a colorless oil: IR (neat, cm^{-1}) 2240, 1715; ^1H NMR (300 MHz, $CDCl_3$) δ 0.79 (d, J = 7.0 Hz, 3H), 1.11 (s, 3H), 2.05 (s, 3H), 2.22–2.35 (m, 1H), 2.42–2.55 (m, 1H), 5.02 (d, J = 17.2 Hz, 1H), 5.15 (d, J = 10.6 Hz, 1H), 5.40 (dd, J = 10.6, 17.2 Hz, 1H), 5.47 (d, J = 15.0 Hz, 1H), 6.22–6.36 (m, 2H), 6.89 (dd, J = 9.5, 15.0 Hz, 1H), 7.23–7.38 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 208.40, 147.26, 136.07, 135.48, 129.47, 129.16, 127.50, 127.23, 126.91, 126.08, 121.66, 114.67, 50.51, 45.48, 45.34, 45.00, 40.35, 38.40, 29.78, 26.81, 23.56, 16.65, 10.33; HRMS (M^+) found 393.2106.

Methyl (E)-(±)-5-{(1S*,2R*,3S*,4R*)-1-Cyano-3,4-dimethyl-1-[(1E,3E)-4-(phenylthio)butadien-1-yl]-3-vinylcyclohex-2-yl}-3-methyl-2-pentenoate (28) and Methyl (Z)-(±)-5-{(1S*,2R*,3S*,4R*)-1-Cyano-3,4-dimethyl-1-[(1E,3E)-4-(phenylthio)butadien-1-yl]-3-vinylcyclohex-2-yl}-3-methyl-2-pentenoate (30). After a mixture of 60% NaH (10 mg, 0.25 mmol) and $(MeO)_2P(O)CH_2CO_2Me$ (52 μL, 0.32 mmol) in dry DME (2 mL) was stirred for 20 min at rt, to the resulting mixture was added at rt a solution of **26** (50 mg, 0.13 mmol) in dry DME (1 mL). The mixture was stirred for 30 min at rt for 1.5 h at 50 °C, and for 1 h under refluxing. After dilution with Et_2O, the mixture was washed with H_2O and brine and dried. Evaporation of the solvents gave a residue, which was chromatographed on silica gel. Elution with hexane–AcOEt (10:1 v/v) afforded **30** (7 mg, 12%) as a colorless oil: IR ($CHCl_3$, cm^{-1}) 2220, 1705; ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (d, J = 6.6 Hz, 3H), 1.08 (s, 3H), 1.77 (d, J = 1.1 Hz, 3H), 1.93–2.03 (m, 1H), 2.52–2.61 (m, 2H), 3.64 (s, 3H), 5.01 (dd, J = 0.9, 17.4 Hz, 1H), 5.15 (dd, J = 0.9, 10.4 Hz, 1H), 5.45 (dd, J = 10.4, 17.4 Hz, 1H), 5.47 (d, J = 15.4 Hz, 1H), 5.58 (br s, 1H), 6.35–6.56 (m, 3H), 7.24–7.42 (m, 5H); HRMS (M^+) 449.2387 calcd for $C_{28}H_{35}NO_2S$, found 449.2423.

Further elution with hexane–AcOEt (4:1 v/v) provided **28** (41 mg, 72%) as a colorless oil: IR ($CHCl_3$, cm^{-1}) 2220, 1705; ^1H NMR (300 MHz, $CDCl_3$) δ 0.78 (d, J = 7.0 Hz, 3H), 1.08 (s, 3H), 2.06 (d, J = 0.7 Hz, 3H), 3.68 (s, 3H), 5.02 (br d, J = 17.2 Hz, 1H), 5.17 (br d, J = 10.6 Hz, 1H), 5.23 (d, J = 15.4 Hz, 1H), 5.38 (dd, J = 10.6, 17.2 Hz, 1H), 5.54 (br s, 1H), 6.29 (dd, J = 10.6, 14.7 Hz, 1H), 6.53 (dd, J = 10.6, 15.4 Hz, 1H), 6.54 (d, J = 14.7 Hz, 1H), 7.24–7.42 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.13, 159.61, 147.01, 134.41, 132.84, 130.19, 129.64, 129.39, 129.27, 128.86, 127.30, 121.90, 115.62, 114.69, 51.12, 50.91, 45.46, 45.39, 42.66, 40.40, 38.19, 27.23, 26.78, 18.83, 16.77, 10.38; HRMS (M^+) 449.2387 calcd for $C_{28}H_{35}NO_2S$, found 449.2412.

Methyl (E)-(±)-5-{(1S*,2R*,3S*,4R*)-1-Cyano-3,4-dimethyl-1-[(1E,3Z)-4-(phenylthio)butadien-1-yl]-3-vinylcyclohex-2-yl}-3-methyl-2-pentenoate (29) and Methyl (Z)-(±)-5-{(1S*,2R*,3S*,4R*)-1-Cyano-3,4-dimethyl-1-[(1E,3Z)-4-(phenylthio)butadien-1-yl]-3-vinylcyclohex-2-yl}-3-methyl-2-pentenoate (31). By the same procedure as above, **27** (354 mg, 0.90 mmol) was transformed to **31** (62.5 mg, 15%) as a colorless oil: IR ($CHCl_3$, cm^{-1}) 2230, 1710; ^1H NMR (300 MHz, $CDCl_3$) δ 0.79 (d, J = 6.6 Hz, 3H), 1.09 (s, 3H), 1.78 (d, J = 0.7 Hz, 3H), 3.66 (s, 3H), 5.02 (br d, J = 17.2 Hz, 1H), 5.16 (d, J = 10.3 Hz, 1H), 5.46 (dd, J = 10.3, 17.2 Hz, 1H), 5.62 (d, J = 15.0 Hz, 1H), 5.69 (br s, 1H), 6.30 (dd, J = 9.2, 9.5 Hz, 1H), 6.38 (d, J = 9.2 Hz, 1H), 6.89 (dd, J = 9.5, 15.0 Hz, 1H), 7.22–7.36 (m, 5H); HRMS (M^+) 449.2401, and **29** (217 mg, 54%) as a colorless oil: IR ($CHCl_3$, cm^{-1}) 2250, 1710; ^1H NMR (300 Mz, $CDCl_3$) δ 0.79 (d, J = 7.0 Hz, 3H), 1.10 (s, 3H), 2.06 (br d, J = 0.7 Hz, 3H), 3.66 (s, 3H), 5.03 (d, J = 17.6 Hz, 1H), 5.17 (d, J = 9.9 Hz, 1H), 5.38 (dd, J = 9.9, 17.6 Hz, 1H), 5.42 (d, J = 15.0 Hz, 1H), 5.56 (br s, 1H), 6.26 (dd, J = 9.5, 9.9 Hz, 1H), 6.35 (d, J = 9.5 Hz, 1H), 6.90 (dd, J = 9.9, 15.0 Hz, 1H), 7.24–7.40 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 167.09, 159.64, 147.03, 135.66, 135.48, 129.47, 129.12, 127.67, 127.11, 126.86, 126.22, 121.71, 115.65, 114.66, 51.11, 50.88, 45.51, 45.40, 42.67, 40.40, 38.05, 27.17, 26.73, 18.75, 16.71, 10.45; HRMS (M^+) found 449.2387.

(±)-1-(1S*,2R*,5S*,6S*,7S*,10R*,11S*,12R*)-1-Cyano-11,12-dimethyl-6-(methoxycarbonyl)-5-(phenylthio)-11-vinyltricyclo[8.4.0.0^{2,7}]tetradec-3-ene (32). (A) A solution of **28** (18 mg, 0.04 mmol) in dry ODB (2 mL) was heated for 10 h at 180 °C in a sealed tube. After evaporation of the solvent, the residue was purified by chromatography on silica gel. Elution with hexane–AcOEt (10:1 v/v) provided **32** (14.8 mg, 82%) as an oil, which was recrystallized from Et_2O–hexane to give colorless needles: mp 175–176 °C; IR (neat, cm^{-1}) 2210, 1735; ^1H NMR (500 MHz, $CDCl_3$) δ 0.78 (d, J = 7.32 Hz, 3H), 1.10 (s, 3H), 1.49 (s, 3H), 1.81 (dd, J = 2.60, 3.05 Hz, 1H, 2-H), 2.85 (d, J = 6.72 Hz, 1H, 6-H), 3.53 (s, 3H), 4.09 (dd, J = 3.66, 6.72 Hz, 1H, 5-H), 4.99 (d, J = 17.09 Hz, 1H), 5.14 (d, J = 10.99 Hz, 1H), 5.33 (dd, J = 10.99, 17.09 Hz, 1H), 5.80 (dd, J = 2.60, 10.38 Hz, 1H, 3-H), 6.02 (ddd, J = 3.05, 3.66, 10.38 Hz, 1H, 4-H), 7.21–7.42 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.22, 147.75, 137.10, 131.38, 130.38, 128.98, 127.13, 123.51, 123.23, 114.30, 56.47, 55.11, 53.41, 51.05, 48.25, 44.08, 40.49, 37.73, 36.88, 36.26, 35.80, 26.64, 20.34, 16.26, 14.21, 9.98; MS m/z (M^+) 449. Anal. Calcd for $C_{28}H_{35}NO_2S$: C, 74.79; H, 7.85; N, 3.12. Found: C, 74.87; H, 7.98; N, 2.95.

(B) By the same procedure as above, **29** (27 mg, 0.06 mmol) was converted to **32** (15 mg, 55%), which was identical with the above compound, prepared by method A in all respects.

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Supporting Information Available: ^{1}H NMR spectra of **10**–**12**, **14**, **16**, **20**, and **22**–**31** (16 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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