over sodium sulfate, and concentrated to afford 1.6 g of a mixture of diols. Recrystallization from water gave 1.03 g (56%) of the erythro isomer **2e** as colorless needles, mp 134–135 °C. ^{1}H-NMR ($CDCl_3$/DMSO-d_6): δ 7.45–8.31 (4 H, m, aromatic), 8.12 (1 H, d, J = 1.0 Hz, NH), 6.08 (1 H, s, $CHCl_2$), 5.50 (1 H, d, J = 5.3 Hz, benzylic OH), 4.99 (1 H, t, J = 5.7 Hz, benzylic), 4.42 (1 H, t, J = 5.7 Hz, primary OH), 4.08 (1 H, m, CHN), 3.91–3.63 (2 H, m, CH_2). ^{13}C-NMR: δ 163.63, 147.51, 143.80, 132.37, 128.70, 121.91, 121.11, 72.25, 66.05, 60.03, 55.97. Anal. Calcd for $C_{11}H_{12}Cl_2N_2O_5$: C, 40.86; H, 3.72; N, 8.67; Found, 41.00; H, 3.74; N, 8.63.

From the mother liquors of the erythro diol was obtained 0.08 g of the threo isomer **2t** as sugarlike cubes, mp 134–135 °C. ^{1}H-NMR ($CDCl_3$/DMSO-d_6): δ 7.42–8.32 (4 H, m, aromatic), 7.69 (1 H, s, NH), 6.00 (1 H, s, $CHCl_2$), 5.45 (1 H, d, J = 4.7 Hz, sec OH), 5.24 (1 H, dd, J = 6.5, 2.5 Hz, benzylic), 4.55 (1 H, t, J = 5.8 Hz, primary OH), 4.17 (1 H, m, CHN), 3.75 (2 H, m, CH_2O). ^{13}C-NMR: δ 163.96, 147.62, 143.95, 131.94, 128.65, 121.80, 120.86, 70.33, 66.00, 61.47, 56.04. Anal. Found: C, 40.99; H, 3.76; N, 8.63.

(b) To a solution of sodium borohydride (3.0 g, 79 mmol) in 100 mL of dry acetonitrile, kept under N_2 at 0 °C, was added 115 mL of glacial acetic acid dropwise, keeping the temperature below 5 °C, over a period of 15 min. A solution of **6** (10.0 g, 31.1 mmol) in 300 mL of acetonitrile was added in one portion, and the mixture was stirred at 25 °C for 24 h, at which time TLC showed the absence of **6**. The mixture was vigorously stirred with 450 mL of 0.5 N sodium potassium tartrate for 12 h, and the organic layer was salted out and separated. Workup as in part a gave, after recrystallization from water, 5.2 g (52%) of **2e**, mp 134–135 °C, and 0.43 g (4.3%) of **2t**, mp 134–135 °C.

(c) To a solution of **6** (1.0 g, 3.1 mmol) in 25 mL of dry CH_2Cl_2 at −78 °C was added a 1.5 M solution of diisobutylaluminum hydride in toluene (4.15 mL, 6.2 mmol) over 6 min. The mixture was stirred for 20 min at −78 °C and for 3 h at 25 °C and diluted with 60 mL of cold water, and the organic layer was separated. The aqueous layer was extracted with two 20-mL portions of $CHCl_3$, and the combined organic solutions were washed with saturated brine and dried over $MgSO_4$. Evaporation of the solvents left a yellow solid (0.40 g) which was recrystallized from water to afford 0.28 g (28%) of **2t**, mp 134–135 °C.

(d) To a solution of **6** (10.0 g, 31.1 mmol) in 200 mL of methanol and 10 mL of chloroform at 30 °C was added sodium borohydride (1.5 g, 39.6 mmol) in two portions. After the vigorous reaction ceased the solution was cooled, diluted with 100 mL of water, and heated at 60 °C for 20 min. Workup as in c left a residue of 9.3 g of mixed isomers, which was recrystallized from water to give 7.3 g (73%) of a 1:1 mixture of **2e** and **2t**, mp 121–126 °C.

(e) A mixture of aluminum isopropoxide (2.3 g, 11 mmol) and 2-propanol (25 mL) was heated to 60 °C and vigorously stirred in a three-neck flask equipped with a condenser and Dean–Stark trap. Ketone **6** (2.0 g, 6.2 mmol) was added, and the mixture was heated under reflux for 10 h, removing about 6 mL of distillate from the trap every 45 min and replacing it with 6 mL of 2-propanol. After cooling to 25 °C, 12 mL of water was added and the mixture was heated to reflux for 30 min, cooled, and extracted with two 30-mL portions of ethyl acetate. The extracts were worked up as in c, and the crude yellow solid was recrystallized from water to give 0.32 g (16%) of **2e**, light yellow needles, mp 133–134 °C.

The **erythro acetonide 7e** was prepared by stirring a mixture of the diol **2e** (0.10 g, 0.31 mmol) with 2,2-dimethoxypropane (2.0 mL, 16 mmol) and a trace of *p*-toluenesulfonic acid in 2 mL of dry THF for 12 h. Removal of the solvent left a brown solid, which was taken up in $CHCl_3$ and passed through a short column of silica gel. Concentration of the eluate and recrystallization of the residue from $CHCl_3$/hexane gave 0.10 g (89%) of the acetonide, mp 136–138 °C. ^{1}H-NMR ($CDCl_3$/DMSO-d_6): δ 7.33–8.27 (5 H, m, aromatic and NH), 5.79 (1 H, s, $CHCl_2$), 5.07 (1 H, d, J = 8.9 Hz, benzylic), 3.86–3.98 (3 H, m, CH_2O and CHN), 1.55 (3 H, s, CH_3), 1.53 (s, 3 H, CH_3). ^{13}C-NMR: δ 164.16, 147.56, 140.89, 132.99, 129.13, 122.88, 122.22, 99.17, 72.71, 66.10, 61.80, 49.76, 28.66, 19.02. Anal. Calcd for $C_{14}H_{16}Cl_2N_2O_5$: C, 46.28; H, 4.41; N, 7.71. Found: C, 46.32; H, 4.46; N, 7.69.

The **threo acetonide 7t** was prepared from diol **2t** as described above; recrystallization from ethyl acetate/hexane gave the acetonide (39%), mp 182–184 °C. ^{1}H-NMR ($CDCl_3$/DMSO-d_6): δ 7.47–8.27 (5 H, m, aromatic and NH), 6.18 (1 H, s, $CHCl_2$), 5.35 (1 H, br s, benzylic), 4.39 (1 H, dd, J = 10, 2 Hz), 4.25 (1 H, dd, J = 8.0, 2.0 Hz, CHN), 3.84 (1 H, dd, J = 10, 2 Hz), 1.63 (6 H, s, CH_3). ^{13}C-NMR: δ 163.27, 147.36, 139.74, 131.59, 128.42, 121.88, 120.59, 99.30, 70.85, 65.35, 63.22, 46.58, 28.83, 18.05. Anal. Found: C, 46.11; H, 4.39; N, 7.66.

Crystallography. Crystals of **2e** and **2t** were mounted on a Syntex P3 automated diffractometer. Unit cell dimensions were determined by least-squares refinement of the best angular positions for 15 independent reflections ($2q$ > 15°) during normal alignment procedures using molybdenum radiation (I = 0.71069 Å). Data were collected at room temperature using a variable rate scan, a q–$2q$ scan mode and a scan width of 1.2° below Ka_1 and 1.2° above Ka_2 to a maximum $2q$ value of 45.0°. Backgrounds were measured at each side of the scan for a combined time equal to the total scan time. The intensities of three standard reflections were remeasured after every 97 reflections and, as the intensities of these reflections showed less than 6% variation, corrections for decomposition were deemed unnecessary. Data were corrected for Lorentz, polarization, and background effects. After removal of space group forbidden (**2e** only) and redundant data, observed data (**2e**, 1250; **2t**, 1557 points) were used for solution and refinement. The structures were solved for carbon, nitrogen, and oxygen positions using direct methods.[13] Least-squares refinement[14] converged with anisotropic thermal parameters. Hydrogen atoms (except for the hydroxyl hydrogens of **2e**) were located from a difference Fourier synthesis. These positions were included in the final refinement with isotropic thermal parameters but held invariant. A final difference Fourier revealed no electron density of interpretable level. Scattering factors were taken from Cromer and Mann.[15] The final cycle of refinement-function minimized $\Sigma(|F_o| - |F_c|)^2$, led to final agreement factor, R = 5.8% (**2e**), 5.2% (**2t**); $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| \times 100$. Unit weights were used until the final cycles of refinement, when weights equal to $1/sF$ were introduced. R_w = 7.6% (**2e**), 7.1% (**2t**).

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Registry No. 2e, 138125-71-0; **2t**, 138125-72-1; **3**, 2227-64-7; **4**, 36765-84-1; **4** acetyl deriv., 89260-48-0; **5**, 137965-23-2; **6**, 137965-24-3; **7e**, 137965-26-5; **7t**, 137965-27-6; *m*-nitroacetophenone, 121-89-1; 1-(*m*-nitrophenyl)-3,5,7-triaza-1-azoniaadamantane bromide, 7478-10-6; 2-(dichloroacetamido)-2-(*m*-nitrobenzoyl)-1,3-propanediol, 137965-25-4.

Supplementary Material Available: X-ray crystallographic data for diols **2e** and **2t**, including bond angles and distances, positional parameters, atomic thermal parameters, and ORTEP drawings (10 pages). This material is contained in many 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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Enantioselective Synthesis of PsiAβ, a Sporogenic Metabolite of *Aspergillus nidulans*

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Two novel hydroxy unsaturated C-18 fatty acids, psiAα (**1**) and psiAβ (**2**), have recently been identified as en-

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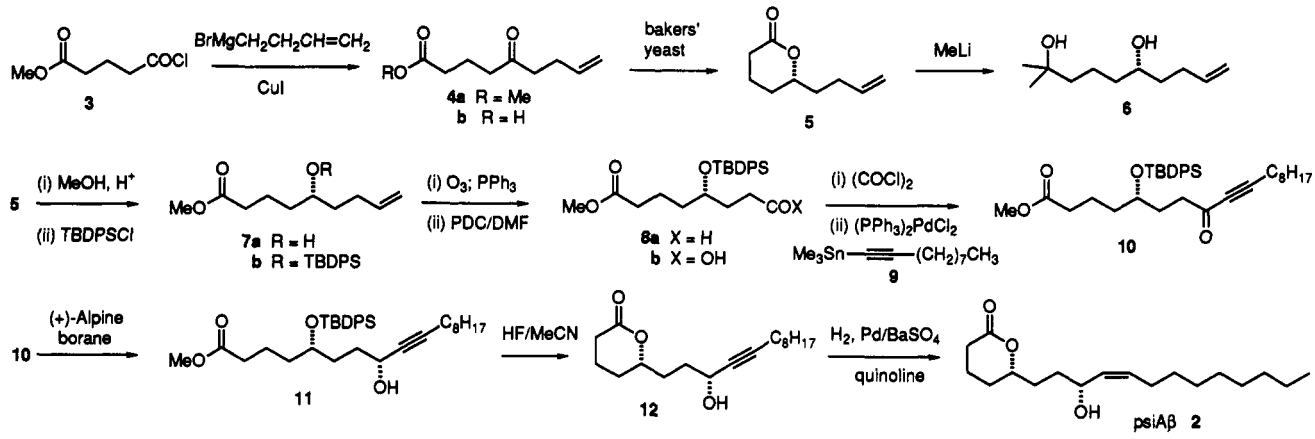
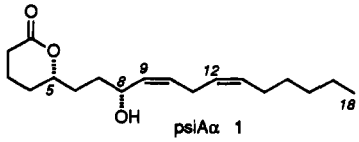
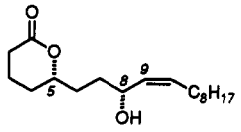
Scheme I



dogenous factors which induce premature sexual sporulation in the ascomycetous fungus *Aspergillus nidulans*.[1]



psiAα 1



psiAβ 2

It has been suggested that the psi factors may function in a "hormonal" role in regulating the sporulation cycle of *A. nidulans*, an organism used extensively in biochemical and genetic research.[2] We report here an enantioselective synthesis of psiAβ using asymmetric Alpine-borane and microbiological reductions as the key steps. Our synthetic strategy, which is outlined in Scheme I, was based on the recent employment of bakers' yeast (*Saccharomyces cerevisiae*) for the generation of saturated γ- and δ-lactones from the corresponding γ- and δ-keto acids in acceptable chemical yield and excellent optical yield.[3]

Accordingly, the synthesis of psiAβ began with construction of a suitable δ-keto acid substrate, allowing for microbial reduction and subsequent elaboration at C-8. Hence, the δ-keto ester **4a** was prepared by copper-catalyzed coupling[4] of the Grignard reagent of 4-bromo-1-butene and the acid chloride of monomethylglutaric acid,[5] **3**. The ketone **4a** was hydrolyzed to the acid **4b** and subjected to reduction by fermenting bakers' yeast.[3] Azeotropic distillation of the culture broth extract in benzene with catalytic CSA furnished the 5(*S*)-δ-lactone[6] **5** in 35–50% yield after chromatography. The optical purity of **5** was determined following the protocol of Utaka et al.[3] Thus, lactone **5** was converted to the diol **6**, which was analyzed by an NMR shift reagent study; the opposite enantiomer (5*R*) could not be detected, indicating >98% ee for the lactone **5**. Various attempts at oxidative cleavage of the olefin in **5** to the carboxylic acid were unsuccessful due to hydrolysis of the lactone and oxidation of the C-5 alcohol, or transesterification of the desired lactone acid. Consequently, lactone **5** was converted to the TBDPS-protected hydroxy ester **7b**. Two-step oxidation of **7b** provided the carboxylic acid **8b** via the aldehyde **8a**.[7] The acetylenic ketone **10** was readily prepared by the palladium-catalyzed coupling[8] of 1-(trimethylstannyl)-1-decyne[9] **9** and the corresponding acid chloride of **8b** in 80% yield. The coupling reaction was observed to be solvent dependent, and the highest yields were obtained in 1,2-dichloroethane. The TBDPS protecting group was essential for the coupling reaction, as the corresponding TBDMS-protected alcohol was observed to undergo facile desilylation and γ-lactonization during acid chloride formation.[8b]

The alkynone **10** was subsequently reduced to the 8-(*R*)-propargylic alcohol **11** with neat Alpine-borane[10,11] (~97.5% ee) in good yields (74–86%) with very good stereoselectivity (~93.5% ee, uncorrected). Treatment of **11** with aqueous HF in acetonitrile[12] effected deprotection and concomitant lactonization to the acetylenic hydroxy lactone **12**. Catalytic hydrogenation of **12** furnished (+)-psiAβ, **2**. Spectral data (^{1}H-NMR, ^{13}C-NMR, IR, HRMS) of synthetic psiAβ and that of the authentic compound[13] were identical. Additionally, the comparison of the optical rotation of the synthetic psiAβ ($[\alpha]^{29}_D$ = +59.3 (c = 0.0076 g mL^{-1}, CH_3CN)) with that of the authentic compound ($[\alpha]^{30}_D$ = +63.7 (c = 0.0042 g mL^{-1}, CH_3CN)) confirmed that the absolute configuration of psiAβ had been correctly assigned and indicated that a high optical yield (ca. 93%) had been achieved in the synthesis. Furthermore, the synthetic psiAβ exhibited an identical "peripheral" induction of sexual sporulation as observed with the authentic compound.[2b]

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Experimental Section

NMR spectra were measured in $CDCl_3$, and chemical shift values are reported relative to the residual solvent signals (δ 7.24 and 77.0 for ^1H and ^{13}C measurements, respectively). Optical determinations by NMR shift studies were performed with tris[3-(heptafluoropropylhydroxymethylene-*d*)camphorato]europium(III) [Eu(hfc)$_3$]. Optical rotations were measured at the sodium D-line. Standard workup procedures included drying over anhydrous $MgSO_4$ and in vacuo concentration prior to purification. Flash chromatography[14] was performed on silica gel (ICN, 32–63 mesh). All solvents for isolation and chromatography were reagent or HPLC grade, and used as received. Dry solvents were obtained as follows: THF was freshly distilled from sodium benzophenone under argon; CH_2Cl_2, 1,2-dichloroethane, MeCN, pyridine, and DMF were distilled from CaH_2; Et_2O was obtained from Mallinckrodt, and used directly as received. Dry glassware for moisture-sensitive reactions was obtained either by oven-drying and assembly under N_2, or by flame-drying and cooling under N_2. Inert atmosphere was obtained with a stream of N_2 and glassware equipped with rubber septa; reagent transfer was performed by syringe or cannula techniques.

Glutaric Acid, Monomethyl Ester, Monochloride (3). In a round-bottom flask equipped with a $CaSO_4$ drying tube were combined monomethyl glutarate (2.57 mL, 20.6 mmol, 1.0 equiv), thionyl chloride (3.0 mL, 41.1 mmol, 2.0 equiv), and 2 drops of DMF; the mixture was stirred at rt for 12 h and purified by bulb-to-bulb distillation (~0.5 mmHg, oven temperature 100–125 °C) to give 2.71 g (80%) of acid chloride **3** as a light yellow liquid: ^1H-NMR (250 MHz, $CDCl_3$) δ 3.62 (3 H, s, CO_2CH_3), 2.95 (2 H, t, J = 7.2 Hz, CH_2COCl), 2.35 (2 H, t, J = 7.2 Hz, CH_2CO_2Me), 1.95 (2 H, tt, J = 7.2, 7.2 Hz, $CH_2CH_2CH_2$); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 173.2, 172.6, 51.6, 45.9, 32.0, 20.1; IR (film) 1798, 1737, 1438, 1371, 1203, 1165, 1039, 936, 870 cm^{-1}.

Methyl 5-Oxo-8-nonenoate (4a). Grignard reagent was prepared from 4-bromo-1-butene (1.50 mL, 14.8 mmol, 1.04 equiv) and magnesium turnings (390 mg, 14.2 mmol) in 15 mL of dry THF. The resulting yellow Grignard solution was filtered and added (1.25 h) via an addition funnel to a solution of acid chloride **3** (2.34 g, 14.2 mmol), and catalytic copper(I) iodide (142 mg, 0.746 mmol, 0.05 equiv) in 40 mL of dry THF at −15 °C. The resulting yellow solution was stirred an additional 1 h at −15 to 0 °C and quenched with 50 mL of saturated NH_4Cl. The solution was extracted with 50 mL of hexane, washed with 50 mL each of saturated $NaHCO_3$, 20% sodium thiosulfate, and brine, dried, and concentrated. Bulb-to-bulb distillation (0.5 mmHg, oven temperature 150 °C) afforded 2.04 g (77%) of keto ester **4a** as a colorless liquid: ^1H-NMR (250 MHz, $CDCl_3$) δ 5.76 (1 H, ddt, J = 16.9, 10.2, 6.5 Hz, CH=CH_2), 5.10–4.90 (2 H, m, CH=CH_2), 3.64 (3 H, s, CO_2CH_3), 2.50–2.40 (4 H, m), 2.30 (4 H, t, J = 7.2 Hz), 1.87 (2 H, tt, J = 7.1, 7.1 Hz, 3-CH_2); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 209.0, 173.4, 136.9, 115.1, 51.4, 41.7, 41.4, 32.9, 27.6, 18.7; IR (film) 2951, 1736, 1714, 1641, 1437, 1415, 1371, 1315, 1252, 1199, 1176, 1096, 999 cm^{-1}; HRMS (EI) m/e 184.1107 (M$^+$; $C_{10}H_{16}O_3$, calcd 184.1099), 185.1190 (M$^+$ + 1; $C_{10}H_{17}O_3$, calcd 185.1178).

5-Oxo-8-nonenoic Acid (4b). To a solution of keto ester **4a** (1.03 g, 5.59 mmol) in 10 mL of methanol was added 10 mL of 1 M KOH, and the reaction mixture was stirred at rt for 3 h. The mixture was acidified with 50 mL of 10% HCl, extracted with 3 × 50 mL of Et_2O, dried, and concentrated to afford 950 mg (96%) of keto acid **4b** as a colorless solid: ^1H-NMR (250 MHz, $CDCl_3$) δ 5.76 (1 H, ddt, J = 17.1, 10.3, 6.4 Hz, CH=CH_2), 5.10–4.80 (2 H, m, CH=CH_2), 2.48 (4 H, t, J = 7.2 Hz, CH_2COCH_2), 2.35 (2 H, t, J = 7.2 Hz, CH_2CO_2H), 2.30–2.20 (2 H, m, CH_2CH=CH_2), 1.87 (2 H, tt, J = 7.2, 7.2 Hz, 3-CH_2); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 209.4, 179.1, 136.9, 115.2, 41.8, 41.4, 33.0, 27.7, 18.5; IR (film) 3077 (br), 1710, 1641, 1412, 1375, 1244, 1096, 998, 917 cm^{-1}; HRMS (EI) m/e 170.0914 (M$^+$; $C_9H_{14}O_3$, calcd 170.0943), 171.0998 (M$^+$ + 1; $C_9H_{15}O_3$, calcd 171.1021). Anal. Calcd for $C_9H_{14}O_3$: C, 63.51; H, 8.29. Found: C, 63.38; H, 8.32.

(+)-8-Nonen-5(*S*)-olide (5). An actively fermenting culture of bakers' yeast was prepared from 30 g of bakers' yeast, 37.5 g of glucose, 75 mg of KH_2PO_4, and 43 mg of $MgSO_4$, dissolved in 100 mL of deionized water in a 1-L Erlenmeyer flask. The culture was agitated for 40 min at 25 °C in a shaker bath, followed by addition of the keto acid **4b** (910 mg, 5.33 mmol) dissolved in 110 mL of 0.1 M KOH. The incubation proceeded at 25–28 °C (with constant agitation) while the pH of the broth was continually adjusted to pH 6–7 by addition of 1 M KOH. After 48 h, 44 g of Celite was added to the culture, and the viscous suspension was shaken at rt for 4 h, after which the mixture was filtered through a Celite pad on a large sintered-glass funnel and the pad rinsed with 100 mL of water. The filtrate was acidified with concd HCl to pH 2 and extracted with 3 × 400 mL of Et_2O; the combined extracts were washed with brine, dried, and concentrated. The residue was dissolved in 250 mL of benzene with 10 mg of camphorsulfonic acid, and the solution was heated at reflux for 3 h with a Dean–Stark trap and condenser; the solution was washed with 100 mL each saturated $NaHCO_3$ and brine, dried, and concentrated to give 620 mg of yellow liquid. The crude product was purified on 55 g of silica gel, eluted with 35% EtOAc/Hex which afforded 264 mg (35%) of lactone **5** as a light yellow liquid: ^1H-NMR (250 MHz, $CDCl_3$) δ 5.78 (1 H, ddt, J = 17.0, 10.3, 6.6 Hz, CH=CH_2), 5.10–4.90 (2 H, m, CH=CH_2), 4.28 (1 H, m, 5-H), 2.70–2.30 (2 H, m, 2-CH_2), 2.30–2.20 (2 H, m), 2.00–1.40 (6 H, m); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 171.4, 137.0, 114.9, 79.3, 34.5, 29.0, 28.7, 27.4, 18.0; IR (film) 2945, 1733, 1641, 1444, 1342, 1242, 1187, 1041, 915 cm^{-1}; HRMS (EI) m/e 154.1021 (M$^+$; $C_9H_{14}O_2$, calcd 154.0994), 155.1099 (M$^+$ + 1; $C_9H_{15}O_2$, calcd 155.1072); $[\alpha]^{23}_D$ = +47.3 (c = 0.135 g mL^{-1}, $CHCl_3$). The optical purity was determined as >98% ee by an NMR chemical shift study with the diol derivative **6**; see below.

5(*S*),9-Dihydroxy-9-methyl-1-decene (6). To a solution of the lactone **5** (~15 mg, ~0.1 mmol) in 2 mL of dry THF at −78 °C was added excess MeLi (1 mL of a 1 M solution in Et_2O, 1 mmol), and the reaction mixture was stirred at this temperature for 10 min and at rt for an additional 20 min. The reaction was quenched with 10 mL of saturated NH_4Cl, extracted with 20 mL of Et_2O, washed with 20 mL of brine, dried, and concentrated. Purification on silica gel eluted with 70% EtOAc/Hex afforded 11.4 mg (~70%) of **6** as a colorless oil: ^1H-NMR (250 MHz, $CDCl_3$) δ 5.84 (1 H, ddt, J = 16.9, 10.1, 6.7 Hz, CH=CH_2), 5.10–4.90 (2 H, m, CH=CH_2), 3.62 (1 H, m, 5-H), 2.15 (2 H, m, CH_2CH=CH_2), 1.70–1.30 (8 H, m), 1.19 (6 H, s, C(OH)(CH_3)$_2$); ^{13}C-NMR (50.0 MHz, $CDCl_3$) δ 138.6, 114.7, 71.4, 70.9, 43.9, 38.0, 36.8, 30.1, 29.4, 29.3, 20.4; IR (film) 3369 (br), 2975, 2938, 2869, 1644, 1375, 1219, 1150, 912 cm^{-1}. The optical purity was determined from an NMR shift study with Eu(hfc)$_3$. The *gem*-dimethyl group of *racemic* **6** appears as a singlet at δ 1.20; addition of the shift reagent results in a downfield shift (δ 2.20–2.00) and the resolution of the methyl group pair of each enantiomer. Similar analysis of *optically active* **6** derived from the bakers' yeast reaction revealed only one pair of singlets; signals corresponding to the opposite enantiomer, 5*R*, could not be detected. Thus the bakers' yeast reduction provided (5*S*)-**5** in >98% ee.

(−)-Methyl 5(*S*)-Hydroxy-8-nonenoate (7a). The lactone **5** (220 mg, 1.43 mmol) was dissolved in 10 mL of methanolic HCl and stirred at rt for 2 h. The reaction was diluted with 50 mL of Et_2O, washed with 25 mL of brine, dried, and concentrated. Chromatography on 20 g of silica gel eluted with 30% EtOAc/Hex provided 249 mg (94%) of the hydroxy ester **7a** as a light yellow oil: ^1H-NMR (250 MHz, $CDCl_3$) δ 5.72 (1 H, ddt, J = 16.9, 10.2, 6.7 Hz, CH=CH_2), 5.20–4.80 (2 H, m, CH=CH_2), 3.56 (3 H, s, CO_2CH_3), 3.51 (1 H, m, 5-H), 2.34 (1 H, br s, OH), 2.24 (2 H, t, J = 7.3 Hz, $CH_2CO_2CH_3$), 2.05 (2 H, m), 1.63 (2 H, m), 1.50–1.30 (4 H, m); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 174.1, 138.3, 114.5, 70.5, 51.3, 36.5, 36.3, 33.7, 29.8, 20.8; IR (film) 3447 (br), 2935, 1740, 1641, 1437, 1366, 1201, 1163, 1094, 996, 911 cm^{-1}; HRMS (EI) m/e 187.1307 (M$^+$ + 1; $C_{10}H_{19}O_3$, calcd 187.1334); $[\alpha]^{27}_D$ = −1.3 (c = 0.185 g mL^{-1}, $CHCl_3$).

(+)-Methyl 5(*S*)-[(*tert*-Butyldiphenylsilyl)oxy]-8-nonenoate (7b). To a solution of hydroxy ester **7a** (543 mg, 2.92 mmol) in 15 mL of dry DMF were added imidazole (600 mg, 8.81 mmol, 3.02 equiv) and *tert*-butyldiphenylsilyl chloride (1.21 g, 4.40 mmol, 1.51 equiv). The reaction was stirred 12 h, quenched with 10 mL of water, and diluted with 100 mL of Et_2O, and the organic layer washed with 50 mL each of 5% HCl, saturated $NaHCO_3$, and brine. The organic layer was dried, concentrated, and purified by chromatography on 50 g of silica gel eluted with 10% Et_2O/Hex which gave 1.08 g (87%) of **7b** as a colorless oil:

(14) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* 1978, *43*, 2923.

^{1}H-NMR (250 MHz, $CDCl_3$) δ 8.00–7.50 (4 H, m), 7.45–7.25 (6 H, m), 5.61 (1 H, ddt, J = 16.8, 10.2, 6.5 Hz, C*H*=CH_2), 4.90–4.75 (2 H, m, CH=CH_2), 3.72 (1 H, tt, J = 5.6, 5.6 Hz, 5-H), 3.61 (3 H, s, CO_2CH_3), 2.12 (2 H, t, J = 7.1 Hz, $CH_2CO_2CH_3$), 1.98 (2 H, m), 1.65–1.35 (6 H, m), 1.03 (9 H, s, Si(Ph)$_2$-t-C_4H_9); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 173.8, 138.5, 135.9, 134.5, 129.5, 127.4, 114.2, 72.3, 51.3, 35.5, 35.4, 34.0, 29.2, 27.1, 20.3, 19.4; IR (film) 3070, 2931, 2859, 1960, 1891, 1824, 1741, 1641, 1590, 1428, 1166, 1111, 911, 822, 741, 703 cm^{-1}; MS (CI, NH_3) m/e 425 (M^+ + 1), 442 ([M + NH_4]$^+$); HRMS (EI) m/e 393.2276 (M^+ – OMe; $C_{25}H_{33}O_2Si$, calcd 393.2250); $[\alpha]^{26}_D$ = +0.5 (c = 0.139 g mL^{-1}, $CHCl_3$). Anal. Calcd for $C_{26}H_{36}O_3Si$: C, 73.54; H, 8.55. Found: C, 73.42; H, 8.75.

(+)-Methyl 5(*S*)-[(*tert*-Butyldiphenylsilyl)oxy]-8-oxooctanoate (8a). The alkene **7b** (970 mg, 2.28 mmol) was dissolved in 15 mL of CH_2Cl_2, cooled to –78 °C, and ozonized until the solution turned light blue in color. Excess ozone was removed with a stream of N_2, and triphenylphosphine (900 mg, 3.45 mmol, 1.51 equiv) was added; the solution was allowed to warm to rt and stirred for 12 h under N_2. The solution was concentrated in vacuo, and the residue was purified on 50 g of silica gel eluted with a 0–5% Et_2O/CH_2Cl_2 gradient which afforded 775 mg (80%) of aldehyde **8a** as a colorless oil: ^{1}H-NMR (250 MHz, $CDCl_3$) δ 9.59 (1 H, t, J = 1.5 Hz, C*H*O), 7.70–7.60 (4 H, m), 7.45–7.30 (6 H, m), 3.77 (1 H, tt, J = 5.4, 5.4 Hz, 5-H), 3.60 (3 H, s, CO_2CH_3), 2.40 (2 H, dt, 1.5, 7.5 Hz, CH_2CHO), 2.10 (2 H, t, J = 7.2 Hz, $CH_2CO_2CH_3$), 1.90–1.60 (2 H, m), 1.60–1.35 (4 H, m), 1.03 (9 H, s, Si(Ph)$_2$-t-C_4H_9); ^{13}C-NMR (62.9 MHz, $CDCl_3$) δ 201.9, 173.5, 135.7, 134.0, 129.6, 127.5, 71.6, 51.3, 39.2, 35.5, 33.7, 28.0, 27.0, 20.2, 19.3; IR (film) 2953, 2857, 1963, 1894, 1737, 1590, 1427, 1111, 822, 741, 704 cm^{-1}; HRMS (EI) m/e 427.2312 (M^+ + 1; $C_{25}H_{35}O_4Si$, calcd 427.2305); $[\alpha]^{27}_D$ = +12.5 (c = 0.118 g mL^{-1}, $CHCl_3$).

(+)-Methyl 5(*S*)-[(*tert*-Butyldiphenylsilyl)oxy]-7-carboxyheptanoate (8b). To a solution of the aldehyde **8a** (752 mg, 1.76 mmol) in 5 mL of dry DMF was added pyridinium dichromate (3.3 g, 8.8 mmol, 5.0 equiv), and the mixture was stirred under N_2 at rt for 5 h. The mixture was diluted with 30 mL of water and extracted with 5 × 30 mL of Et_2O; the combined Et_2O extracts were dried and concentrated. The residue was purified by column chromatography on 25 g of silica gel eluted with a 0–5% MeOH/$CHCl_3$ gradient which afforded 790 mg (100%) of acid **8b** as a faint yellow oil: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.70–7.50 (4 H, m), 7.45–7.25 (6 H, m), 3.78 (1 H, tt, J = 5.4, 5.4 Hz, 5-H), 3.59 (3 H, s, CO_2CH_3), 2.35 (2 H, t, J = 7.8 Hz, CH_2CO_2H), 2.07 (2 H, t, J = 7.1 Hz, $CH_2CO_2CH_3$), 1.90–1.60 (2 H, m), 1.55–1.30 (4 H, m), 1.03 (9 H, s, Si(Ph)$_2$-t-C_4H_9); ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 177.9, 173.8, 135.8, 134.2, 133.9, 129.59, 129.54, 127.53, 127.46, 71.6, 51.4, 35.4, 33.8, 30.7, 29.4, 27.0, 20.2, 19.3; IR (film) 3500–2500, 2953, 2859, 1740, 1709, 1589, 1427, 1172, 1111, 822, 741, 703 cm^{-1}; HRMS (EI, isobutane) m/e 443.2276 (M^+ + 1; $C_{25}H_{35}O_5Si$, calcd 443.2254); $[\alpha]^{27}_D$ = –2.0 (c = 0.168 g mL^{-1}, $CHCl_3$).

1-(Trimethylstannyl)-1-decyne (9). In a round-bottom flask equipped with a condenser and $CaSO_4$ drying tube were combined 1-decyne (3.50 g, 25.0 mmol) and (dimethylamino)trimethyltin (5.25 g, 25.0 mmol) at rt, and the solution was heated to 100–140 °C over 2.5 h. The reaction was accompanied by the evolution of $HNMe_2$ and formation of a fine white precipitate. The liquid was filtered and distilled in vacuo to give 6.85 g (91%) of alkynylstannane **9** as a colorless liquid: ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.21 (2 H, t, J = 7.0 Hz), 1.50 (2 H, m), 1.40–1.10 (10 H, m), 0.86 (3 H, t, J = 6.6 Hz), 0.24 (9 H, s, SnCH_3); ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 111.2, 81.9, 31.8, 29.2, 29.1, 29.0, 28.8, 22.7, 20.1, 14.1; IR (film) 2956, 2927, 2856, 2153 (alkyne) 1465, 776, 723 cm^{-1}; MS (CI, NH_3) m/e 182 (M^+ – Me_3Sn + NH_3), 304 (M^+ – CH_3 + NH_3); MS (FAB) m/e 287 (M^+ – CH_3).

(–)-Methyl 5(*S*)-[(*tert*-Butyldiphenylsilyl)oxy]-8-oxooctadec-9-ynoate (10). The acid **8b** (204 mg, 0.461 mmol) was dried by azeotropic distillation with benzene and dissolved in 2 mL of dry CH_2Cl_2, to which was added oxalyl chloride (81 μL, 0.92 mmol, 2.0 equiv). The reaction was stirred for 2 h in flask equipped with a $CaSO_4$ drying tube, evaporated under astream of N_2, and dried in vacuo. The resulting acid chloride was redissolved in 2 mL of dry 1,2-dichloroethane to which was added the alkynylstannane **9** (208 mg, 0.691 mmol, 1.50 equiv) and catalytic bis(triphenylphosphine) palladium(II) chloride (6.5 mg, 0.02 equiv). The mixture was heated at reflux under N_2 for 30 min, cooled to rt, diluted with 40 mL of Et_2O, washed with 25 mL each of 0.5 M KF and brine, dried, and concentrated. The residue was purified by chromatography on 20 g of silica gel eluted with a 5–20% Et_2O/Hex gradient which afforded 212 mg (82%) of alkynone **10** as a yellow oil: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.70–7.55 (4 H, m), 7.45–7.25 (6 H, m), 3.73 (1 H, tt, J = 5.5, 5.5 Hz, 5-H), 3.57 (3 H, s, CO_2CH_3), 2.51 (2 H, t, J = 7.6 Hz), 2.29 (2 H, t, J = 7.1 Hz), 2.05 (2 H, t, J = 7.3 Hz, $CH_2CO_2CH_3$), 1.80–1.65 (2 H, m), 1.60–1.45 (4 H, m), 1.45–1.30 (4 H, m), 1.24 (8 H, br s), 1.02 (9 H, s, Si(Ph)$_2$-t-C_4H_9), 0.85 (3 H, t, J = 7.0 Hz, 18-CH_3); ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 187.9, 173.7, 135.8, 134.2, 133.9, 129.62, 129.58, 127.6, 127.5, 94.4, 80.8, 71.6, 51.4, 40.9, 35.6, 33.8, 31.8, 30.0, 29.1, 29.0, 28.9, 27.7, 27.0, 22.6, 20.3, 19.3, 18.9, 14.1; IR (film) 2929, 2857, 2211, 1962, 1893, 1742, 1673, 1590, 1461, 1428, 1248, 1168, 1111, 703 cm^{-1}; HRMS (CI, isobutane) m/e 563.3574 (M^+ + 1; $C_{35}H_{51}O_4Si$, calcd 563.3557); $[\alpha]^{27}_D$ = –7.5 (c = 0.109 g mL^{-1}, $CHCl_3$). Anal. Calcd for $C_{35}H_{50}O_4Si$: C, 74.68; H, 8.95. Found: C, 74.66; H, 8.89.

(–)-Methyl 5(*S*)-[(*tert*-Butyldiphenylsilyl)oxy]-8(*R*)-hydroxyoctadec-9-ynoate (11). Neat Alpine-borane (*B*-3-pinanyl-9-borabicyclo[3.3.1]nonane) was prepared in a dry round-bottom flask under N_2 from solid 9-borabicyclo[3.3.1]nonane dimer (1 equiv) and α-pinene (1.1 equiv) [97.5% ee, $[\alpha]^{26}_D$ = +50.3 (neat)] heated at 65 °C for 5 h to yield neat (+)-Alpine-borane as a viscous oil (density 0.93 g mL^{-1}).[10] Freshly prepared neat Alpine-borane (85 μL, 0.31 mmol, 3.2 equiv) was added to the neat alkynone **10** (55 mg, 0.098 mmol) in a dry 1-dram vial under N_2 at 0 °C, and the viscous mixture was subsequently stirred at rt for 12 h. The reduction was quenched by the addition of propionaldehyde (22 μL, 0.31 mmol); after stirring at rt for 1 h, the mixture was diluted with 5 mL of THF and 1.5 mL of 3 M KOH, followed by slow dropwise addition of 1 mL of 30% H_2O_2. The solution was stirred an additional 3 h, diluted with 40 mL of Et_2O, and washed with 25 mL each of water, saturated NH_4Cl, and brine. The organic layer was dried, concentrated, and purified by silica gel (10 g) column chromatography eluted with 20% EtOAc/Hex to give 45.5 mg (83%) of propargylic alcohol **11** as a faint yellow oil: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 7.70–7.60 (4 H, m), 7.45–7.30 (6 H, m), 4.22 (1 H, br s, 5-H), 3.76 (1 H, t, J = 4.6 Hz, 5-H), 3.59 (3 H, s, CO_2CH_3), 2.15 (2 H, dt, J = 1.8, 7.0 Hz, 11-CH_2), 2.08 (2 H, t, J = 7.3 Hz, $CH_2CO_2CH_3$), 1.70–1.20 (20 H, m), 1.04 (9 H, s, Si(Ph)$_2$-t-C_4H_9), 0.86 (3 H, t, J = 7.0 Hz, 18-CH_3); ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 173.8, 135.9, 134.3, 134.2, 129.6, 127.5, 85.6, 81.1, 72.3, 62.6, 51.4, 35.3, 33.9, 33.1, 31.8, 31.2, 29.2, 29.1, 28.9, 28.7, 27.1, 22.6, 20.3, 19.3, 18.7, 14.1; IR (film) 3430 (br), 2929, 2856, 2233 (wk), 1741, 1428, 1362, 1166, 1110, 1039, 822, 740 cm^{-1}; HRMS (CI, CH_4) m/e 565.3725 (M^+ + 1; $C_{35}H_{53}O_4Si$, calcd 565.3713); $[\alpha]^{27}_D$ = –7.7 (c = 0.092 g mL^{-1}, $CHCl_3$). The optical purity was determined as ~93.5% ee from an NMR shift study with Eu(hfc)$_3$ as per Midland and Graham.[10c]

(+)-8(*R*)-Hydroxyoctadec-9-yn-5(*S*)-olide (12). The mono-TBDPS protected dihydroxy ester **11** (92 mg, 0.16 mmol) was dissolved in 3 mL of CH_3CN in a plastic vial, to which was added 48% aqueous HF (250 μL, ~8% v/v). The reaction mixture was heated to 70 °C for 3 h, cooled to rt, diluted with 40 mL of Et_2O, and washed with 25 mL each of water, saturated $NaHCO_3$, and brine. The organic layer was dried, concentrated, and purified by chromatography on 5 g of silica gel eluted with 50% EtOAc/Hex which furnished 33 mg (69%) of acetylenic lactone **12** as a colorless viscous oil: ^{1}H-NMR (300 MHz, $CDCl_3$) δ 4.39 (1 H, m, 8-H), 4.31 (1 H, m, 5-H), 2.62–2.52 (1 H, m, 2-H), 2.48–2.37 (1 H, m, 2-H'), 2.17 (2 H, dt, J = 1.9, 7.2 Hz, 11-CH_2), 2.00–1.65 (8 H, m), 1.65–1.40 (3 H, m), 1.40–1.20 (9 H, m), 0.86 (3 H, t, J = 6.9 Hz, 18-CH_3); ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 171.8, 86.1, 80.6, 80.1, 62.1, 33.3, 31.8, 31.3, 29.4, 29.14, 29.04, 28.8, 28.6, 27.8, 22.6, 18.6, 18.4, 14.1; IR (film) 3424 (br), 2927, 2856, 2230 (wk), 1732, 1463, 1337, 1247, 1181, 1050, 932 cm^{-1}; HRMS (EI) m/e 294.2176 (M^+; $C_{18}H_{30}O_3$, calcd 294.2195; $[\alpha]^{27}_D$ = +34.5 (c = 0.095 g mL^{-1}, $CHCl_3$).

(+)-PsiAβ [8(*R*)-Hydroxyoctadec-9(*Z*)-en-5(*S*)-olide] (2). To a mixture of 5% Pd–$BaSO_4$ (3.6 mg) and quinoline (1.5 mg) was added a solution of the propargylic alcohol **11** (32 mg, 3 mL MeOH). The vessel was evacuated and flushed with H_2 three times, and the hydrogenation was allowed to proceed for 1.5 h, at which time TLC indicated completion. The suspension was filtered over Celite, evaporated in vacuo, redissolved in 20 mL

of EtOAc, and washed with 3 × 10 mL of 10% HCl and 10 mL each of saturated $NaHCO_3$ and brine. The organic layer was dried, concentrated, and purified on a 20 × 20 cm 250 μm silica gel prep-TLC plate eluted with 50% EtOAc/CH_2Cl_2 which afforded 30 mg (94%) of psiAβ **2** as a colorless oil: ^{1}H-NMR (400 MHz, $CDCl_3$) δ 5.48 (1 H, ddt, J = 0.5, 11.0, 7.5 Hz, 10-H), 5.35 (1 H, ddt, J = 10.8, 8.8, 1.5 Hz, 9-H), 4.44 (1 H, ddd, J = ~8.0, 6.0, 6.0 Hz, 8-H), 4.30 (1 H, m, 5-H), 2.57 (1 H, m, 2-H), 2.44 (1 H, m, 2-H′), 2.06 (2 H, m, 11-H, H′), 1.95–1.45 (8 H, m), 1.40–1.20 (12 H, m), 0.86 (3 H, t, J = 6.9 Hz, 18-CH_3); ^{13}C-NMR (75.4 MHz, $CDCl_3$) δ 171.8, 132.9, 131.9, 80.3, 67.2, 32.6, 31.8, 31.5, 29.7, 29.4, 29.3, 29.2, 27.8, 27.7, 22.6, 18.5, 14.1; IR (film) 3430 (br), 2924, 2854, 1732, 1463, 1378, 1246, 1181, 1047, 932, 724 cm^{-1}; HRMS (EI) m/e 296.2357 (M^+; $C_{18}H_{32}O_3$, calcd 296.2351); $[\alpha]^{29}_D$ = +59.3 (c = 0.0076 g mL^{-1}, CH_3CN).

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Supplementary Material Available: ^{1}H NMR spectra of **4a,b**, **5**, **7a,b**, **8a,b**, **10**, **11**, **12**, and **2** (11 pages). Ordering information is given on any current masthead page.

Carboxylation of Carbenes in Low-Temperature Matrices

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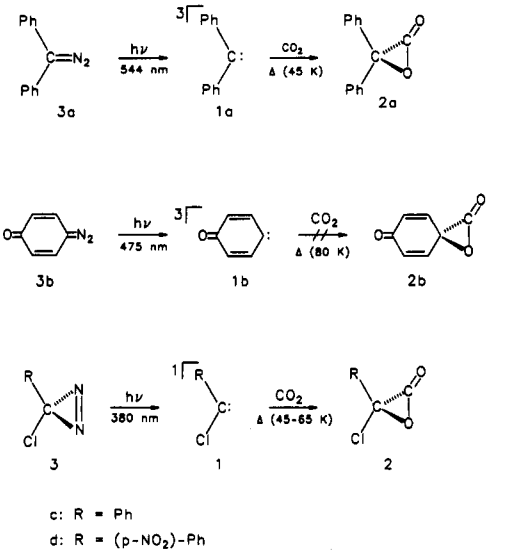
Oxiranones (α-lactones) are low-temperature species that can be generated by photodecarboxylation of malonyl peroxides[1,2] or by epoxidation of ketenes.[3,4] Two derivatives have been reported to be stable at ambient temperature (one of them in solution, only).[4,5] A matrix isolation study of the reaction of methylene with carbon dioxide has been described by Milligan and Jacox.[6]

Recently we reported on the carboxylation of diphenylcarbene **1a** in carbon dioxide doped argon and xenon matrices (0–10% CO_2).[7] The thermal reaction at low temperature (25–70 K) as well as the photochemical reaction at 10 K lead to diphenyloxiranone **2a**, which was characterized spectroscopically and through its subsequent photochemistry. The reaction between a triplet carbene and CO_2 is remarkable because it can be classified as formally "spin-forbidden". Thus, intersystem crossing (ISC) must occur on one of three possible pathways: (i) on the reactant side, which means thermal population of excited singlet diphenylmethylene (S-**1a**), (ii) on the product side, which means formation of triplet **2a**, or (iii) somewhere along the reaction coordinate (nonequilibrium surface crossing[8,9] or formation of a short-lived intermediate, e.g., a diradical with rapid spin equilibration). To study the influence of the spin state of carbenes on their reactivity, we have now investigated the kinetics of carboxylation of two triplet carbenes and two singlet carbenes in solid carbon dioxide: diphenylcarbene (**1a**), 4-oxo-2,5-cyclohexadienylidene (**1b**), phenylchlorocarbene (**1c**), and

Scheme I



(*p*-nitrophenyl)chlorocarbene (**1d**). The formally "spin-allowed" reactions of the singlet carbenes **1c** and **1d** are expected to be fast compared to the carboxylation of triplet carbenes **1a** and **1b**.

Triplet Carbenes 1a and 1b. Matrix isolation of **1a** in CO_2-doped argon matrices has already been described.[7] The IR spectra in solid CO_2 are similar to those in argon, the major difference being line broadening and small shifts of several absorptions. The thermal reaction of **1a** in solid CO_2 is described below. Irradiation (λ = 543 nm) of quinone diazide **3b**, matrix-isolated in CO_2 at 10 K, produced carbene **1b** which has been identified by comparison of its IR spectra with the argon spectra.[10–12] The C=O str vibration shows large line broadening, indicating a strong interaction of the C=O bond and CO_2 molecules in the matrix cage. Other bands are much less perturbed and were used to monitor the carbene concentration. In the temperature range between 45 and 80 K, **1b** is, unlike **1a**, unreactive toward CO_2.

Singlet Carbenes 1c and 1d. On irradiation (λ = 380 nm) of chlorophenyldiazirine (**3c**) in CO_2 (or CO_2-doped Ar matrices) at 10 K, carbene **1c** was formed as the major product.[13–17] A minor product with a predominant IR

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(12) **1b**: IR (CO_2, 10 K) 1503.7 (41.4), 1497.4 (100), 1491.1 (96.5), 1384.1 (42.7), 1371.6 (26.8), 1257.8 (62.3), 1081.3 (14.1), 939.6 (16.7), 828.2 (93.4) cm^{-1} (rel intensity).
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