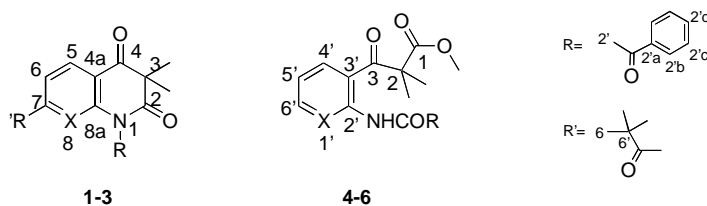


ONE STEP SYNTHESIS FOR THE PREPARATION OF QUINOLINE ALKALOID ANALOGS.

Supporting Information

Experimental Section

All reactions were performed in an oven-dried glassware under argon. Dichloromethane was distilled from sodium hydride under argon. Trimethylsilyl chloride and titanium chloride were freshly distilled and were kept under argon. Column chromatography was performed using Merck Silica gel 60 (70-230 mesh ASTM). NMR data were obtained using a Varian Gemini 2000 spectrometer (300 MHz ^1H , 75 MHz ^{13}C). Chemical shifts are quoted in ppm (s=singlet, d=doublet, dd=doublet of doublets, br=broad). J values are given in Hz. IR spectra were recorded on a Perkin-Elmer 267 photometer. All compounds characterized below are newly obtained.



General procedure for the preparation of 1-6: In a solution of **8** or **9** (1.5mmol) (Scheme 2) in anhydrous dichloromethane, the silyl ketene acetal (**10**) (1.5mmol) was added. The mixture was stirred at room temperature under argon, after which titanium tetrachloride was added in a dropwise manner. Stirring continued for 3 hours. The mixture was quenched by water and extracted with dichloromethane. The extract was evaporated *in vacuo* and the residue was purified by column chromatography (chloroform-methanol 5:0.15) to afford the desired product.

Properties of 1 (X=CH, R=CH₃, R'=H): IR ν_{max} (Nujol)/cm⁻¹: 1700, 1670 (C=O); NMR ^1H (CDCl₃): 7.95 (1H, dd, $J=2$ $J=8$, 5-H), 7.59 (1H, pseudotriplet, 7-H), 7.17 (1H, pseudotriplet, 8-H), 7.15 (1H, d, $J=8$, 6-H), 3.43 (3H, s, N-CH₃), 1.44 (6H, s, CH₃ at position 3); NMR ^{13}C (CDCl₃): 171.6 (C-4), 170.8 (C-8), 141.2 (C-8a), 134.1 (C-7), 124.5 (C-5), 115.3 (C-8), 114.3 (C-4a), 51.4 (C-3), 49.1 (N-CH₃), 23.5 (CH₃ at position 3); yield 48%.

Properties of 2 [X=CH, R=CH₃, R'=C(CH₃)₂CO₂CH₃]: IR ν_{max} (Nujol)/cm⁻¹: 1710 , 1680 (C=O); NMR ¹H (CDCl₃): 7.95 (1H, d, *J*=8, 5-H), 7.14 (1H, dd, *J*=2 *J*=8, 6-H), 7.08 (1H, d, *J*=2, 8-H), 3.68 (3H, s, CO₂CH₃), 3.46 (3H, s, N-CH₃), 1.62 (6H, s, CH₃ at position 7), 1.47 (6H, s, CH₃ at position 3); NMR ¹³C (CDCl₃): 197.4 (C-4), 176.3 (CO₂CH₃), 174.6 (C-4), 153.2 (C-6), 143.4 (C-8a), 128.5 (C-7), 120.7 (C-5), 118.6 (C-4a), 112.1 (C-8), 53.0 (C-3), 52.4 (CO₂CH₃), 47.2 (N-CH₃), 29.7 (C-6'), 26.2 (CH₃ at position 6'), 23.9 (CH₃ at position 3); yield 12%.

Properties of 3 (X=N, R=H, R'=H): IR ν_{max} (Nujol)/cm⁻¹: 3200 (NH), 1710 , 1670 (C=O); NMR ¹H (CDCl₃): 10.22 (1H, br, NH), 8.65 (1H, dd, *J*=2 *J*=8, 7-H), 8.26 (1H, dd, *J*=2 *J*=8, 5-H), 7.17 (1H, dd, *J*=5 *J*=8, 6-H), 1.53 (6H, s, CH₃); NMR ¹³C (CDCl₃): 175.0 (C-4), 174.1 (C-2), 154.6 (C-7), 153.6 (C-8a), 137.5 (C-5), 119.5 (C-6), 113.9 (C-4a), 53.2 (C-3), 23.3 (CH₃ at position 3); final yield 58%.

Properties of 4 (X=N, R=Ph): NMR ¹H (CDCl₃): 12.02 (1H, br, NH), 8.65 (1H, dd, *J*=2 *J*=8, 6'-H), 7.93 (1H, dd, *J*=2 *J*=8, 4'-H), 8.01-7.49 (5H, m, Ph), 7.06(1H, dd, *J*=5 *J*=8, 5'-H), 3.63 (3H, s, CO₂CH₃), 1.55 (6H, s, CH₃ at position 2); NMR ¹³C (CDCl₃): 200.8 (C-3), 175.0 (C-1), 164.8 (COPh), 153.2 (C-6'), 138.4 (C-4'), 152.7 (C-2'), 127.6 (C-3'), 117.8 (C-5'), 134.7 (C-2'a), 132.3 (C-2'd), 128.8 (C-2'b), 127.7 (C-2'c), 54.2 (C-2), 52.7 (CO₂CH₃), 24.1 (CH₃ at position 2); yield 65%.

Properties of 5 (X=N, R=CH₃): NMR ¹H (CDCl₃): 10.94 (1H, br, NH), 8.54 (1H, dd, *J*=2 *J*=8, 7'-H), 7.85 (1H, dd, *J*=2 *J*=8, 5'-H), 7.00 (1H, dd, *J*=2 *J*=8, 6'-H), 3.64 (3H, s, CO₂CH₃), 2.36 (3H, s, COCH₃), 1.53 (6H, s, CH₃ at position 2); NMR ¹³C (CDCl₃): 201.4 (C-3), 177.6 (C-1), 164.8 (COCH₃), 153.2 (C-6'), 138.4 (C-4'), 152.7 (C-2'), 127.6 (C-3'), 117.8 (C-5'), 132.3 (C-2'd), 54.2 (C-2), 52.7 (CO₂CH₃), 24.1 (CH₃ at position 2); yield 67%.

Properties of 6 (X=CH, R=CH₃): NMR ¹H (CDCl₃): 11.26 (1H, br, NH), 8.43 (1H,d, *J*=8, C-1'), 7.69 (1H, dd, *J*=2 *J*=8, C-4'), 7.46 (1H, pseudotriplet, C-6'), 7.17 (1H, pseudotriplet, C-5'), 3.62 (3.62, s, COCH₃), 1.54 (1H, s, CH₃ at position 2); yield 59%.