Silica-Supported Sodium with Ionic Liquid: A Neutral Catalyst System for Michael Reactions of Indoles in Water

Yanlong Gu, Chikako Ogawa, and Shū Kobayashi*

Graduate School of Pharmaceutical Sciences, The University of Tokyo, The HFRE Division, ERATO, Japan Science and Technology Agency (JST), Hongo, Bunkyo-ku, Tokyo 113-0033, Japan

Supporting Information

Experimental

General. ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA300, JNM-LA400, or ECX-400 spectrometer in CDCl_3 , and tetramethylsilane (TMS) was used as internal standard. IR spectra were measured on a JASCO FT/IR-610 spectrometer. Commercially available chemicals and dry solvents (ethyl acetate, hexane, toluene, THF, and ethanol), purchased from Aldrich, Kanto Chemical, Tokyo Chemical Industry, and Wako Pure Chemical Industry, were purified according to standard procedures before use. Column chromatography was conducted on Silica gel 60 (Merck) and preparative thin-layer chromatography (PTLC) was carried out using Wakogel B-5F. ICP analysis was performed using Shimadzu ICPS-7510. The structures of known compounds were confirmed by comparison with data shown in literature.

Preparation of silica gel-supported sodium. Preparation of silica-supported sodium catalysts was performed according to Scheme S-1. In this work, silica gel with large pore from Strem Chemicals Company was used. As shown in Scheme S-1, arylsulfonic acid-functionalized silica gel (Silica- PhSO_3H) was prepared according to a modified synthetic procedure using (chlorosulfonylphenyl) ethyltriethoxysilane (CSPTMS) as a precursor.¹⁻³ The detailed procedure is as follows: silica gel was activated before use over 2N HCl at 80 °C for 8 h. The obtained activated silica was filtrated off and washed with deionized water until the pH value became 7. After drying at air and reduced pressure, the activated silica gel (6.0 g) was mixed with a

dichloromethane solution of CSPTMS (5 g, 50 wt% in CH_2Cl_2) in a 100 mL round-bottom flask under Ar. Dried toluene was then added, and the mixture was refluxed at 130 °C for 24 h. After the reaction was complete, the reaction mixture was cooled to room temperature. The solid was filtrated off, and washed with dried toluene (20 mL $\times$ 5 times). The obtained silica gel material was then dried at 80 °C for 6 h under reduced pressure (1 mmHg). This silica gel was then treated with 2N H_2SO_4 (50 mL) for 12 h at 80 °C. After filtration, the obtained solid material was carefully washed with pure water to adjust the pH value of the solution to 6-7. After drying, ion exchange capacity was determined by a known method.¹

Scheme S-1. Preparation of Silica-Na materials

As a typical procedure, the Silica-PhSO₃H material (15.0 mg) was mixed with a NaCl aqueous solution (20 mL, 0.1 N) in a 30 mL flask, and the mixture was stirred for 24 h at room temperature. The solution was then titrated by a NaOH aqueous solution (0.01 N) to adjust the PH value to 7. From the consumption difference of the NaOH aqueous solution between the activated silica gel and the Silica-PhSO₃H material, the ion exchange capacity of Silica-PhSO₃H can be calculated. The obtained Silica-PhSO₃H material has 0.70 mmolH⁺/g of ion exchange capacity. Elemental analysis revealed that the sulfur content is 2.4 wt% in Silica-PhSO₃H. This is good agreement with the ion exchange capacity. Silica-PhSO₃H was then converted to the corresponding sodium salt using an aqueous solution of NaCl (1.0 N). For complete exchange of Silica-PhSO₃H to the corresponding sodium salt, an aqueous solution of NaOH (0.05 N) was used to neutralize the

produced H^+ during the ion exchange procedure.¹ For decreases of the Na loading, decreased amounts of CSPTMS (3 g and 1g) were used under the same conditions; thus, two Silica-Na catalysts with 0.57 and 0.35 mmol/g of Na loadings were obtained.

A typical procedure for Michael reaction of 1-methylindole. All reactions were conducted in a 10 mL V-type flask equipped with magnetic stirring. In a typical reaction, Silica-Na **3** (Na loading 0.70 mmol/g, 50 mg, 14 mol % Na) was mixed with 0.25 mL of the ethyl acetate solution of ionic liquid [DBIm]SbF₆ (12.5 mg of [DBIm]SbF₆ was contained, 25 wt% with regard to Silica-Na). After a few minutes stirring, ethyl acetate was evaporated and the residue solid material was dried under reduced pressure (1.0 mmHg) for 10 minutes at room temperature. Water (0.25 mL), 1-methylindole (32.8 mg, 0.25 mmol), and methyl vinyl ketone (MVK, 17.5 mg 0.25 mmol) were then introduced successively. The mixture was stirred for 12 h at 30 °C. After the reaction, the mixture was extracted with a mixture of ethyl acetate and hexane (1:1 v/v, 6 mL $\times$ 4). After concentration of the organic phase, the crude compounds were purified by PTLC to give 4-(1-methyl-3-indolyl)-2-butanone (47.8 mg, 95%). The residue solid was treated under reduced pressure to remove all the volatile components, and then reused in the next run.

In the case of a solid substrate, the silica material, ionic liquid, the solid substrate, and stirring bar were premixed in ethyl acetate before the reaction. After a few minutes stirring, ethyl acetate was evaporated, and the residue solid material was dried under reduced pressure (1 mmHg) at room temperature. Finally, water and a liquid substrate were introduced successively. The following procedure is analogous to that of liquid substrates.

4-(1-Methyl-3-indolyl)-2-butanone (1**):⁴**

(oil, Hexane/EtOAc = 4:1, 87%); ¹H NMR δ 2.05, (s, 3H), 2.74 (t, 2H, J = 7.3 Hz), 2.95 (t, 2H, J = 7.3 Hz), 3.63 (s, 3H), 6.75 (s, 1H), 7.03 (t, 1H, J = 11.5 Hz), 7.12-7.21 (m, 2H), 7.49, (d, 1H, J = 7.8 Hz); ¹³C NMR δ 19.2, 30.0, 32.5, 44.3, 109.2, 113.6, 118.6, 118.7, 121.5, 126.3, 127.5, 136.9, 208.7.

4-(5-Bromo-3-indolyl)-2-butanone (2):⁵

(white solid, Hexane/EtOAc = 4:1, yield 92%); ¹H NMR δ 2.17 (s, 3H), 2.84 (t, 2H, *J* = 7.3 Hz), 3.01 (t, 2H, *J* = 7.3 Hz), 7.00 (d, 1H, *J* = 2.3 Hz), 7.22-7.30 (m, 2H), 7.72 (d, 1H, *J* = 1.4 Hz), 8.11 (br, 1H); ¹³C NMR δ 19.0, 30.1, 43.9, 112.5, 112.6, 114.9, 121.3, 122.8, 124.8, 128.9, 134.9, 208.5.

4-(5-Methyl-3-indolyl)-2-butanone (3):

(White solid, Hexane/EtOAc = 3:1, 94%); melting point: 94-95 °C. ¹H NMR δ 2.17 (s, 3H), 2.49 (s, 3H), 2.86 (t, *J* = 7.8 Hz, 2H), 3.05 (t, *J* = 7.4 Hz, 2H), 6.95 (d, *J* = 0.9 Hz, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 7.25 (d, *J* = 8.2 Hz, 1H), 7.39 (s, 1H), 7.93 (br, 1H); ¹³C NMR δ 19.4, 21.5, 30.0, 44.1, 110.8, 114.6, 118.2, 121.6, 123.6, 127.3, 128.4, 134.6, 208.9. IR (KBr) 3326, 1705, 1560, 1442, 1317, 1159, 804, 788 cm⁻¹. Anal. Calcd for C₁₃H₁₅NO: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.55; H, 7.64, N, 6.77.

4-(4-Methyl-3-indolyl)-2-butanone (4):⁶

(White solid, Hexane/EtOAc = 3:1, 83%); melting point: 116-117 °C; ¹H NMR δ 2.12 (s, 3H), 2.84 (t, *J* = 7.3 Hz, 2H), 3.14 (t, *J* = 7.6 Hz, 2H), 3.91 (s, 3H), 6.48 (d, *J* = 7.4 Hz, 1H), 6.81 (s, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 7.07 (t, *J* = 8.0 Hz, 1H), 8.02 (br, 1H); ¹³C NMR δ 21.4, 29.9, 45.7, 55.1, 99.3, 104.5, 115.5, 117.1, 120.4, 122.7, 138.1, 154.6, 209.7.

4-(1-1*H*-3-Indolyl)-2-butanone (5):⁴

(white solid, Hexane/EtOAc = 3:1, 96%); ^1H NMR δ 2.18 (*s*, 3H), 2.88 (*t*, 2H, $J = 7.3$ Hz), 3.10 (*t*, 2H, $J = 7.3$ Hz), 6.99 (*s*, 1H), 7.15-7.28 (*m*, 2H), 7.37 (*d*, 1H, $J = 8.2$ Hz), 7.63 (*d*, 1H, $J = 7.8$ Hz), 8.09 (*br*, 1H); ^{13}C NMR δ 19.28, 29.99, 44.00, 111.13, 114.97, 118.56, 119.18, 121.46, 121.93, 127.08, 136.23, 208.91.

4-(5-Methoxy-3-indolyl)-2-butanone (6):⁵

(White solid, Hexane/EtOAc = 3:1, yield 90%); ^1H NMR δ 2.17 (*s*, 3H), 2.86 (*t*, 2H, $J = 7.3$ Hz), 3.03 (*t*, 2H, $J = 7.3$ Hz), 3.89 (*s*, 3H), 6.87 (*d*, 1H, $J = 8.7$ Hz), 6.97 (*s*, 1H), 7.04 (*s*, 1H), 7.25 (*d*, 1H, $J = 8.7$ Hz), 7.98 (*br*, 1H); ^{13}C NMR δ 19.27, 30.03, 43.88, 55.92, 100.50, 111.85, 112.13, 114.80, 122.20, 127.50, 131.39, 153.87, 208.85.

4-(5-Chloro-3-indolyl)-2-butanone (7):

(White solid, Hexane/EtOAc = 3:1, 97%); melting point: 82-83 °C; ^1H NMR δ 2.15 (*s*, 3H), 2.83 (*t*, $J = 7.3$ Hz, 2H), 3.00 (*t*, $J = 7.3$ Hz, 2H), 6.99 (*s*, 1H), 7.14 (*dd*, $J_a = 8.7$ Hz, $J_b = 1.8$ Hz, 1H), 7.25 (*d*, $J = 8.2$ Hz, 1H), 7.55 (*d*, $J = 1.8$ Hz, 1H), 8.18 (*br*, 1H); ^{13}C NMR δ 19.1, 30.0, 43.8, 112.2, 114.8, 118.1, 122.2, 123.0, 124.9, 128.2, 134.6, 208.6; IR (KBr) 3352, 1700, 1457, 1358, 1166, 1058 cm^{-1} . Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{ClNO}$: C, 65.02; H, 5.46; N, 6.32. Found: C, 64.73; H, 5.37, N, 6.24.

3-(1-1H-3-Indolyl)-cyclopentanone (8):⁷

(oil, Hexane/EtOAc = 3:1, 70%); ^1H NMR δ 2.10-2.20 (*m*, 1H), 2.29-2.56 (*m*, 4H), 2.75-2.81 (*m*, 1H), 3.74 (*p*, 1H, $J = 7.8$ Hz), 6.99 (*s*, 1H), 7.16 (*t*, 1H, $J = 7.1$ Hz), 7.24 (*t*, 1H, $J = 7.6$ Hz), 7.39 (*d*, 1H, $J = 8.3$ Hz), 7.65 (*d*, 1H, $J = 7.8$ Hz), 8.07 (*br*, 1H); ^{13}C NMR δ 29.87, 33.71, 38.15, 45.28, 111.34, 118.59, 119.07, 119.46, 119.91, 122.33, 126.60, 136.68, 219.40.

1-(1*H*-Indol-3-yl)-pentan-3-one (9):⁸

(White solid, Hexane/EtOAc = 3:1, 89%); ¹H NMR δ 0.96 (*t*, 3H, *J* = 7.3 Hz), 2.33 (*dd*, 2H, *J*_{*a*} = 7.4 Hz, *J*_{*b*} = 7.3 Hz), 2.74 (*t*, 2H, *J* = 7.3 Hz), 2.98 (*t*, 2H, *J* = 7.3 Hz), 6.88 (*d*, 1H, *J* = 2.3 Hz), 7.02-7.16 (*m*, 2H), 7.26 (*d*, 1H, *J* = 7.8 Hz), 7.52 (*d*, 1H, *J* = 7.8 Hz), 7.93 (*br*, 1H); ¹³C NMR δ 7.74, 19.40, 36.05, 42.75, 111.12, 115.25, 118.64, 119.22, 121.46, 121.96, 127.14, 136.27, 211.49.

3-(1*H*-3-Indolyl)-butyrophenone (10):⁹

(oil, Hexane/EtOAc = 3:1, 88%); ¹H NMR δ 1.51 (*d*, *J* = 6.9 Hz, 3H), 3.30 (*dd*, *J* = 7.3 Hz, *J* = 9.2 Hz, 1H), 3.53 (*dd*, *J* = 5.0 Hz, *J* = 11.5 Hz, 1H), 3.84-3.93 (*m*, 1H), 7.03 (*d*, *J* = 2.3 Hz, 1H), 7.14-7.29 (*m*, 2H), 7.39 (*d*, *J* = 8.2 Hz, 1H), 7.44-7.50 (*m*, 2H), 7.54-7.60 (*m*, 1H), 7.73 (*d*, *J* = 7.8 Hz, 1H), 7.99-8.01 (*m*, 2H); 8.08 (*br*, 1H); ¹³C NMR δ 20.97, 27.12, 46.42, 111.26, 119.16, 119.18, 120.18, 121.42, 121.95, 126.28, 128.06, 128.50, 132.88, 136.51, 137.26, 199.78.

3-(1*H*-3-Indolyl)-valerophenone (11):⁹

(Colorless oil, Hexane/EtOAc = 3:1, 43%); ¹H NMR δ 0.80 (*t*, *J* = 7.3 Hz, 3H), 1.78 (*m*, 2H), 3.31 (*m*, 2H), 3.52 (*m*, 1H), 6.92 (*d*, *J* = 2.3 Hz, 1H), 7.00-7.17 (*m*, 2H), 7.25 (*d*, *J* = 8.2 Hz, 1H), 7.30-7.35 (*m*, 2H), 7.41-7.45 (*m*, 1H), 7.61 (*d*, *J* = 7.8 Hz, 1H), 7.83 (*d*, *J* = 6.9 Hz, 2H), 7.89 (*br*, 1H); ¹³C NMR δ 12.2, 28.3, 34.5, 44.8, 111.2, 119.1, 119.4, 121.3, 121.8, 126.7, 128.1, 128.4, 132.8, 136.6, 137.3, 200.0.

Methyl 3-(3-oxobutyl)indole-5-carboxylate (12)

(White solid, Hexane/EtOAc = 1:1, 80%); melting point: 106-108 °C; ^1H NMR δ 2.12 (s, 3H), 2.82 (t, J = 7.3 Hz, 2H), 3.05 (t, J = 7.6 Hz, 2H), 3.92 (s, 3H), 7.02 (s, 1 H), 7.32 (d, J = 8.7 Hz, 1H), 7.87 (dd, J_a = 8.2 Hz, J_b = 1.4 Hz, 1H), 8.33 (s, 1H), 8.37 (br, 1H); ^{13}C NMR δ 19.1, 30.0, 43.9, 51.9, 110.8, 116.6, 121.3, 121.7, 122.9, 123.4, 126.8, 138.9, 168.2, 208.5; IR (KBr) 3317, 1712, 1618, 1350, 1282, 1217, 1110 cm^{-1} . Anal. Calcd for $\text{C}_{14}\text{H}_{15}\text{NO}_3$: C, 68.56; H, 6.16; N, 5.71. Found: C, 68.35; H, 6.08, N, 5.60.

3-(1-Phenyl-2-nitroethyl)-1-methyl-1H-indole (13): ¹⁰

(oil, Hexane/EtOAc = 3:1, 68%); ^1H NMR δ 3.62 (s, 3H), 4.80-4.86 (m, 1H), 4.92-4.97 (m, 1H), 5.08 (t, J = 8.3 Hz, 1H), 6.76, (s, 1H), 6.96-7.00 (m, 1H), 7.11-7.26 (m, 7H), 7.36 (d, J = 8.2 Hz, 1H); ^{13}C NMR δ 32.8, 41.5, 79.5, 109.5, 112.7, 118.9, 119.4, 122.2, 126.3, 126.5, 127.4, 127.7, 128.8, 137.2, 139.3.

3-[1-(4-Methoxyphenyl)-2-nitroethyl]-1-methyl-1H-indole (14): ¹⁰

(oil, Hexane/EtOAc = 2:1, 75%); ^1H NMR δ 3.73 (s, 3H), 3.76 (s, 3H), 4.88 (dd, J_a = 12.4 Hz, J_b = 8.7 Hz, 1H), 5.02 (dd, J_a = 12.4 Hz, J_b = 7.8 Hz, 1H), 5.13 (t, J = 7.8 Hz, 1H), 6.85, (d, J = 8.7 Hz, 3H), 7.07 (t, J = 7.4 Hz, 1H), 7.20-7.30 (m, 4H), 7.44 (d, J = 7.8 Hz, 1H); ^{13}C NMR δ 32.8, 40.8, 55.2, 79.7, 109.4, 113.1, 114.2, 119.0, 119.4, 122.1, 126.2, 126.5, 128.7, 131.3, 137.3, 158.8.

3-(1-Furan-2-yl-2-nitroethyl)-1-methyl-1H-indole (15): ¹⁰

(oil, Hexane/EtOAc = 2:1, 81%); ^1H NMR δ 3.73 (s, 3H), 4.89 (dd, $J_a = 12.4$ Hz, $J_b = 7.4$ Hz, 1H), 5.03 (dd, $J_a = 12.4$ Hz, $J_b = 8.3$ Hz, 1H), 5.23 (t, $J = 7.8$ Hz, 1H), 6.16, (d, $J = 3.2$ Hz, 1H), 6.30 (dd, $J_a = 3.2$ Hz, $J_b = 1.8$ Hz, 1H), 6.97 (s, 1H), 7.12 (td, $J_a = 6.9$ Hz, $J_b = 0.9$ Hz, 1H), 7.22-7.31 (m, 2H), 7.37 (d, $J = 1.4$ Hz, 1H), 7.54 (d, $J = 8.2$ Hz, 1H); ^{13}C NMR δ 32.8, 35.6, 77.9, 107.2, 109.6, 109.9, 110.4, 118.7, 119.5, 122.1, 126.1, 127.3, 137.1, 142.2, 152.3.

1-Methyl-3-(2-nitro-1-thiophen-2-ylethyl)-1H-indole (16):¹⁰

(oil, Hexane/EtOAc = 2:1, 80%); ^1H NMR δ 3.74 (s, 3H), 4.99 (ddd, $J_a = 20.1$ Hz, $J_b = 12.8$ Hz, $J_c = 7.8$ Hz, 2H), 5.44 (t, $J = 7.8$ Hz, 1H), 6.92-6.98, (m, 3H), 7.10 (td, $J_a = 6.9$ Hz, $J_b = 0.9$ Hz, 1H), 7.18-7.31 (m, 3H), 7.50 (d, $J = 7.8$ Hz, 1H); ^{13}C NMR δ 32.9, 36.9, 80.1, 109.6, 112.4, 118.9, 119.6, 122.3, 124.8, 125.1, 126.2, 126.6, 126.9, 137.2, 143.1.

3-(2-Methylindol-3-yl)cyclohexanone (17):¹¹

(oil, Hexane/EtOAc = 3:1, 70%); ^1H NMR δ 1.71-1.82 (m, 1H), 1.96-2.02 (m, 1H), 2.15-2.33 (m, 2H), 2.34 (s, 3H), 2.35-2.50 (m, 3H), 2.93-2.99 (m, 1H), 3.14-3.21 (m, 1H), 7.01-7.10 (m, 2H), 7.22-7.26 (m, 1H), 7.62 (d, $J = 7.8$ Hz, 1H), 7.82 (brs, 1H); ^{13}C NMR δ 12.0, 26.1, 31.5, 37.3, 41.4, 48.1, 110.6, 113.8, 118.8, 119.1, 120.9, 126.8, 130.1, 135.4, 211.8.

Tert-butyl 3-(3-oxobutyl)indole-5-carbamate (18)

(White solid, Hexane/EtOAc = 1:1, 94%); melting point: 97-99 °C. ^1H NMR δ 1.58 (s, 9H), 2.14 (s, 3H), 2.82 (t, J = 7.3 Hz, 2H), 3.01 (t, J = 7.4 Hz, 2H), 6.61 (s, 1H), 6.93 (s, 1H), 7.10 (d, J = 8.3 Hz, 1H), 7.23 (d, J = 8.7 Hz, 1H), 7.66 (s, 1H), 8.22 (brs, 1H); ^{13}C NMR δ 19.2, 28.4, 29.9, 43.9, 79.9, 109.4, 111.3, 114.9, 115.7, 122.5, 127.3, 130.3, 133.2, 153.6, 209.0. IR (KBr) 3399, 3321, 2980, 1708, 1541, 1241, 1167, 668 cm^{-1} ; HRMS Calculated for $\text{C}_{17}\text{H}_{22}\text{N}_2\text{O}_3$ $[\text{M}+\text{Na}^+]$: 325.1523 Found: 325.1518.

4-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-indolyl)-2-butanone (19)

(White solid, Hexane/EtOAc = 3:1, 85%); melting point: 136-137 °C. ^1H NMR δ 1.32 (s, 12H), 2.06 (s, 3H), 2.76 (t, J = 7.3 Hz, 2H), 2.99 (t, J = 7.3 Hz, 2H), 6.87 (s, 1H), 7.26 (d, J = 8.2 Hz, 1H), 7.59 (d, J = 8.2 Hz, 1H), 8.06 (s, 1H), 8.20 (brs, 1H); ^{13}C NMR δ 19.2, 24.8, 29.9, 44.1, 83.4, 110.6, 115.6, 121.6, 126.3, 126.9, 128.2, 138.4, 208.9. IR (KBr) 3337, 3271, 2982, 1696, 1514, 1438, 1374, 1353, 1137, 1091, 962, 689 cm^{-1} ; HRMS Calculated for $\text{C}_{18}\text{H}_{24}\text{BNO}_3$ $[\text{M}+\text{H}^+]$: 314.1922 Found: 314.1931.

4-[1-(2-Hydroxyethyl)-3-indolyl]-2-butanone (20):

(Oil, Hexane/EtOAc = 1:2, 85%); ^1H NMR δ 2.06 (brs, 1H), 2.16 (s, 3H), 2.85 (t, J = 7.8 Hz, 2H), 3.05 (t, J = 7.8 Hz, 2H), 3.90 (t, J = 5.0 Hz, 2H), 4.20 (t, J = 5.5 Hz, 2H), 6.96 (s, 1H), 7.14 (t, J = 8.2 Hz, 1H), 7.24 (t, J = 6.9 Hz, 1H), 7.35 (d, J = 8.2 Hz, 1H), 7.61 (d, J = 7.8 Hz, 1H); ^{13}C NMR δ 19.1, 29.9, 44.0, 48.4, 61.8, 109.3, 114.0, 118.8, 118.9, 121.7, 125.6, 127.8, 136.4, 208.9. IR (KBr) 3447, 2928, 1712, 1469, 1361, 1168, 1057, 774 cm^{-1} ; HRMS Calculated for $\text{C}_{14}\text{H}_{17}\text{NO}_2$

[M+Na⁺]: 232.1332 Found: 232.1339.

4-(5-Benzyloxy-3-indolyl)-2-butanone (21)

(White solid, Hexane/EtOAc = 2:1, 91%); melting point: 119-120 °C, ¹H NMR δ 2.12 (s, 3H), 2.79 (t, J = 7.8 Hz, 2H), 2.98 (t, J = 7.8 Hz, 2H), 5.10 (s, 2H), 6.91-6.94 (m, 2H), 7.09 (s, 1H), 7.22-7.24 (m, 2H), 7.27-7.32 (m, 1H), 7.35-7.39 (m, 2H), 7.47 (d, J = 7.8 Hz, 2H), 7.81 (brs, 1H); ¹³C NMR δ 19.3, 30.0, 43.9, 71.0, 102.3, 111.8, 112.8, 114.8, 122.3, 127.5, 127.6, 127.7, 128.5, 131.6, 137.6, 153.0, 208.9. IR (KBr) 3386, 2916, 1709, 1482, 1186, 1005, 714 cm⁻¹; Anal. Calcd for C₁₉H₁₉NO₂: C, 77.79; H, 6.53; N, 4.77. Found: C, 77.99; H, 6.73; N, 4.70.

4-(5-Dibenzylamino-1H-indol-3-yl)-butan-2-one (22): ⁶

(White solid, Hexane/EtOAc = 2:1, 74%); ¹H NMR δ 2.03 (s, 3H), 2.63 (t, J = 7.8 Hz, 2H), 2.87 (t, J = 6.8 Hz), 4.60 (s, 4H), 7.81-7.86 (m, 3H), 7.14-7.30 (m, 11H), 7.68 (brs, 1H); ¹³C NMR δ 19.4, 29.9, 43.7, 55.9, 102.9, 111.6, 112.3, 114.3, 121.9, 126.7, 127.2, 127.8, 128.4, 130.4, 139.4, 143.6, 208.9.

3-(3-Oxocyclopentyl)-1H-indole-5-carbonitrile (23): ¹²

(Oil, Hexane/EtOAc = 2:1, 85%); ¹H NMR δ 2.03-2.12 (m, 1H), 2.28-2.46 (m, 3H), 2.51-2.57 (m, 1H), 2.75 (dd, J_a = 18.3, J_b = 7.8 Hz, 1H), 3.68 (m, 1H), 7.11 (d, J = 2.3 Hz, 1H), 7.39-7.45 (m, 2H), 7.95 (s, 1H), 8.87 (brs, 1H); ¹³C NMR δ 29.9, 33.3, 38.0, 45.0, 102.2, 112.3, 119.3, 120.7, 122.3, 124.7, 125.1, 126.5, 138.4, 218.7.

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DFILE ¥Eca¥data¥Gu¥333.1
 COMNT
 DATIM 02-03-2006 15:20:41
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 24.3 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 32

4-(1-Methyl-3-indolyl)-2-butanone (1)

DFILE ¥Eca¥data¥Gu¥333-13C.1
 COMNT 02-03-2006 15:27:46
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 88
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 24.6 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 56

4-(1-Methyl-3-indolyl)-2-butanone (1)

DFILE ¥Eca¥data¥Gu¥335.1
 COMNT
 DATIM 01-03-2006 15:05:36
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 24.3 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 34

4-(5-Bromo-3-indolyl)-2-butanone (2)

DFILE ¥¥Eca¥data¥Gu¥335-13C.1
 COMNT
 DATIM 01-03-2006 15:10:38
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 58
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 24.5 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 56

4-(5-Bromo-3-indolyl)-2-butanone (2)

DFILE ¥Eca¥data¥Gu¥579.1
 COMNT
 DATIM 20-06-2006 17:47:29
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 26.0 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 32

4-(5-Methyl-3-indolyl)-2-butanone (3)

DFILE ¥Eca¥data¥Gu¥579-13C.1
 COMNT
 DATIM 20-06-2006 17:54:31
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 118
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 26.3 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 56

4-(5-Methyl-3-indolyl)-2-butanone (3)

DFILE ¥¥Eca¥data¥Gu¥329.1
COMNT
DATIM 24-02-2006 20:09:08
OBNUC 1H
EXMOD single_pulse.ex2
OBFRQ 399.78 MHz
OBSET 4.19 KHz
OBFIN 7.29 Hz
POINT 20480
FREQU 9378.89 Hz
SCANS 8
AQTM 2.1837 sec
PD 2.0000 sec
PW1 5.50 usec
IRNUC 1H
CTEMP 25.0 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 32

4-(4-Methyl-3-indolyl)-2-butanone (4)

DFILE ¥Eca¥data¥Gu¥329-13C.1
 COMNT
 DATIM 24-02-2006 20:18:40
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 90
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PWI 3.33 usec
 IRNUC 1H
 CTEMP 25.3 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 56

4-(4-Methyl-3-indolyl)-2-butanone (4)

DFILE ¥¥Eca¥data¥Gu¥320.1
 COMNT
 DATIM 16-02-2006 20:44:41
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 23.5 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 1.20 Hz
 RGAIN 28

4-(1-1H-3-Indolyl)-2-butanone (5)

DFILE ¥Eca¥data¥Gu¥320-13C.1
 COMNT 16-02-2006 20:53:53
 DATIM 13C
 OBNUC single_pulse_dec
 EXMOD 100.53 MHz
 OBFRQ 5.35 KHz
 OBSET 5.86 Hz
 OBFIN 40961
 POINT 39259.39 Hz
 FREQU 113
 SCANS 1.0433 sec
 ACQTM 2.0000 sec
 PD 3.33 usec
 PW1 1H
 IRNUC 24.0 c
 CTEMP ODCL3
 SLVNT 77.00 ppm
 EXREF 1.20 Hz
 BF 56
 RGAIN

4-(1-1H-3-Indolyl)-2-butanone (5)

DFILE ¥Eca¥data¥Gu¥334.1
 COMNT
 DATIM 02-03-2006 09:08:04
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 16384
 FREQU 7503.00 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 23.7 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 32

4-(5-Methoxy-3-indolyl)-2-butanone (6)

S-22

DFILE ¥¥Eca¥data¥334-13C.1
 COMNT
 DATIM 02-03-2006 09:19:06
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 156
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 24.0 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 50

4-(5-Methoxy-3-indolyl)-2-butanone (6)

DFILE ¥Eca¥data¥Gu¥372.1
 COMNT
 DATIM 16-03-2006 09:12:52
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 24.3 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 1.20 Hz
 RGAIN 32

4-(5-Chloro-3-indolyl)-2-butanone (7)

S-24

DFILE \\Eca\data\Gu\372-13C.1
COMNT
DATIM 16-03-2006 09:16:50
OBNUC 13C
EXMOD single_pulse_dec
OBFRQ 100.53 MHz
OBSET 5.35 KHz
OBFIN 5.86 Hz
POINT 40961
FREQU 39259.39 Hz
SCANS 38
ACQTM 1.0433 sec
PD 2.0000 sec
PW1 3.33 usec
IRNUC 1H
CTEMP 24.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 1.20 Hz
RGAIN 56

4-(5-Chloro-3-indolyl)-2-butanone (7)

DFILE ¥¥Eca¥data¥Gu¥323.1
 COMNT 21-02-2006 13:43:26
 DATIM 1H
 OBNUC single_pulse.ex2
 EXMOD 399.78 MHz
 OBFRQ 4.19 KHz
 OBSET 7.29 Hz
 OBFIN 20480
 POINT 9378.89 Hz
 FREQU 8
 SCANS 2.1837 sec
 ACQTM 2.0000 sec
 PD 5.50 usec
 PW1 1H
 IRNUC 25.1 c
 CTEMP CDCL3
 SLVNT 7.24 ppm
 EXREF 0.12 Hz
 BF 34
 RGAIN

3-(1H-3-Indolyl)-cyclopentanone (8)

DFILE ¥¥Eca¥data¥Gu¥323-13C.1
 COMNT 21-02-2006 13:56:50
 DATIM 13C
 OBNUC single_pulse_dec
 EXMOD 100.53 MHz
 OBFRQ 5.35 KHz
 OBSET 5.86 Hz
 OBFIN 40961
 POINT 39259.39 Hz
 FREQU 132
 SCANS 1.0433 sec
 ACQTM 2.0000 sec
 PD 3.33 usec
 PW1 1H
 IRNUC 25.5 c
 CTEMP CDCL3
 SLVNT 77.00 ppm
 EXREF 0.12 Hz
 BF 54
 RGAIN

3-(1H-3-Indolyl)-cyclopentanone (8)

DFILE ¥Eca¥data¥Gu¥340.1
 COMNT
 DATIM 02-03-2006 18:10:51
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 24.4 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 32

1-(1H-Indol-3-yl)-pentan-3-one (9)

DFILE ¥¥Eca¥data¥Gu¥340-13C.1
 COMNT
 DATIM 02-03-2006 18:15:03
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 59
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 24.6 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 56

1-(1H-Indol-3-yl)-pentan-3-one (9)

DFILE ¥¥Eca¥data¥Gu¥345.1
 COMNT 08-03-2006 15:38:17
 DATIM 1H
 OBNUC single_pulse.ex2
 EXMOD 399.78 MHz
 OBFRQ 4.19 KHz
 OBSET 7.29 Hz
 OBFIN 20480
 POINT 9378.89 Hz
 FREQU 8
 SCANS 2.1837 sec
 ACQTM 2.0000 sec
 PD 5.50 usec
 PW1 1H
 IRNUC 25.3 c
 CTEMP CDCL3
 SLVNT 7.24 ppm
 EXREF 1.20 Hz
 BF 28
 RGAIN

3-(1H-3-Indolyl)-butyrophenone (10)

DFILE ¥¥Eca¥data¥Gu¥345-13C.1
 COMNT
 DATIM 08-03-2006 15:45:07
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRO 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 109
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 25.6 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 1.20 Hz
 RGAIN 54

3-(1H-3-Indolyl)-butyrophenone (10)

DFILE ¥¥Eca¥data¥Gu¥539.1
 COMNT
 DATIM 06-06-2006 16:33:48
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 25.5 c
 SLVNT CDCL3
 EXREF 0.00 ppm
 BF 0.12 Hz
 RGAIN 34

3-(1H-3-Indolyl)-valerophenone (11)

DFILE ¥Eca¥data¥Gu¥539-13C.1
 COMNT 06-06-2006 16:39:05
 DATIM 13C
 OBNUC single_pulse_dec
 EXMOD 100.53 MHz
 OBFRQ 5.35 KHz
 OBSET 5.86 Hz
 OBFIN 40961
 POINT 39259.39 Hz
 FREQU 81
 SCANS 1.0433 sec
 ACQTM 2.0000 sec
 PD 3.33 usec
 PW1 1H
 IRNUC 25.8 c
 CTEMP CDCL3
 SLVNT 77.00 ppm
 EXREF 0.12 Hz
 BF 56
 RGAIN

3-(1H-3-Indolyl)-valerophenone (11)

DFILE ¥¥Eca¥data¥Gu¥558.1
 COMNT 12-06-2006 10:32:03
 DATIM 1H
 OBNUC single_pulse.ex2
 EXMOD 399.78 MHz
 OBFRQ 4.19 KHz
 OBSET 7.29 Hz
 OBFIN 20480
 POINT 9378.89 Hz
 FREQU 8
 SCANS 2.1837 sec
 ACQTM 2.0000 sec
 PD 5.50 usec
 PW1 1H
 IRNUC 25.9 c
 CTEMP CDCL3
 SLVNT 7.24 ppm
 EXREF 0.12 Hz
 BF 34
 RGAIN

Methyl 3-(3-oxobutyl)indole-5-carboxylate (12)

DFILE ¥Eca¥data¥Gu¥558-13C.1
COMNT 12-06-2006 10:47:35
DATIM 13C
OBNUC single_pulse_dec
EXMOD 100.53 MHz
OBFRQ 5.35 KHz
OBSET 5.86 Hz
OBFIN 40961
POINT 39259.39 Hz
FREQU 287
SCANS 1.0433 sec
ACQTM 2.0000 sec
PD 3.33 usec
PW1 1H
IRNUC 26.4 c
CTEMP CDCL3
SLVNT 77.00 ppm
EXREF 0.12 Hz
BF 50
RGAIN

Methyl 3-(3-oxobutyl)indole-5-carboxylate (12)

DFILE ¥¥Eca¥data¥Gu¥584-1H.1
 COMNT 23-06-2006 18:02:47
 DATIM 1H
 OBNUC single_pulse.ex2
 EXMOD 399.78 MHz
 OBFRQ 4.19 KHz
 OBSET 7.29 Hz
 OBFIN 20480
 POINT 9378.89 Hz
 FREQU 8
 SCANS 2.1837 sec
 ACQTM 2.0000 sec
 PD 5.50 usec
 PW1 1H
 IRNUC 26.1 c
 CTEMP CDCL3
 SLVNT 0.00 ppm
 EXREF 0.12 Hz
 BF 32
 RGAIN

3-(1-Phenyl-2-nitroethyl)-1-methyl-1H-indole (13)

DFILE \\Eca\data\Gu\584-13C.1
 COMNT
 DATIM 23-06-2006 18:07:32
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 67
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 26.2 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 52

3-(1-Phenyl-2-nitroethyl)-1-methyl-1H-indole (13)

DFILE
 COMNT
 DATIM 16-06-2006 14:30:04
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 26.0 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 32

3-[1-(4-Methoxyphenyl)-2-nitroethyl]-1-methyl-1H-indole (14)

DFILE ¥Eca¥data¥Gu¥653-13C.1
 COMNT
 DATIM 16-06-2006 14:35:58
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 91
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 26.5 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 52

S-39

3-[1-(4-Methoxyphenyl)-2-nitroethyl]-
1-methyl-1H-indole (14)

DFILE
 COMNT
 DATIM 14-06-2006 09:27:30
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 25.8 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 32

3-(1-Furan-2-yl-2-nitroethyl)-
1-methyl-1H-indole (15)

DFILE ¥Eca¥data¥Gu¥559-13C.1
 COMNT 13-06-2006 14:08:21
 DATIM 13C
 OBNUC single_pulse_dec
 EXMOD 100.53 MHz
 OBFRQ 5.35 KHz
 OBSET 5.86 Hz
 OBFIN 40961
 POINT 39259.39 Hz
 FREQU 159
 SCANS 1.0433 sec
 ACQTM 2.0000 sec
 PD 3.33 usec
 PW1 1H
 IRNUC 25.8 c
 CTEMP CDCL3
 SLVNT 77.00 ppm
 EXREF 0.12 Hz
 BF 56
 RGAIN

3-(1-Furan-2-yl-2-nitroethyl)-
1-methyl-1H-indole (15)

DFILE ¥Eca¥data¥Gu¥560-1H.1
 COMNT 14-06-2006 09:37:02
 DATIM 1H
 OBNUC single_pulse,ex2
 EXMOD 399.78 MHz
 OBFRQ 4.19 KHz
 OBSET 7.29 Hz
 OBFIN 20480
 POINT 9378.89 Hz
 FREQU 8
 SCANS 2.1837 sec
 ACQTM 2.0000 sec
 PD 5.50 usec
 PW1 1H
 IRNUC 25.7 c
 CTEMP CDCL3
 SLVNT 7.24 ppm
 EXREF 0.12 Hz
 BF 34
 RGAIN

1-Methyl-3-(2-nitro-1-thiophen-2-ylethyl)-1H-indole (16)

DFILE ¥¥Eca¥data¥Gu¥560-H13C.1
 COMNT 14-06-2006 09:42:13
 DATIM 13C
 OBNUC single_pulse_dec
 EXMOD 100.53 MHz
 OBFRQ 5.35 KHz
 OBSET 5.86 Hz
 OBFIN 40961
 POINT 39259.39 Hz
 FREQU 83
 SCANS 1.0433 sec
 ACQTM 2.0000 sec
 PD 3.33 usec
 PW1 1H
 IRNUC 26.1 c
 CTEMP CDCL3
 SLVNT 77.00 ppm
 EXREF 0.12 Hz
 BF 50
 RGAIN

1-Methyl-3-(2-nitro-1-thiophen-2-ylethyl)-1H-indole (16)

3-(2-Methylindol-3-yl)cyclohexanone (17)

DFILE ¥Eca¥data¥Gu¥580-m-13C.1
 COMNT
 DATIM 20-06-2006 18:11:59
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 113
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 26.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 56

3-(2-Methylindol-3-yl)cyclohexanone (17)

DFILE ¥Eca¥data¥Gu¥564-1.1
 COMNT 15-06-2006 14:28:12
 DATIM 1H
 OBNUC single_pulse.ex2
 EXMOD 399.78 MHz
 OBFRQ 4.19 KHz
 OBSET 7.29 Hz
 OBFIN 20480
 POINT 9378.89 Hz
 FREQU 8
 SCANS 2.1837 sec
 ACQTM 2.0000 sec
 PD 5.50 usec
 PW1 1H
 IRNUC 26.0 c
 CTEMP CDCL3
 SLVNT 7.24 ppm
 EXREF 0.12 Hz
 BF 28
 RGAIN

Tert-butyl 3-(3-oxobutyl)indole-5-carbamate (18)

DFILE ¥¥Eca¥data¥Gu¥564-1-13C.1
 COMNT 15-06-2006 14:41:53
 DATIM 13C
 OBNUC single_pulse_dec
 EXMOD 100.53 MHz
 OBFRQ 5.35 KHz
 OBSET 5.86 Hz
 OBFIN 40961
 POINT 39259.39 Hz
 FREQU 250
 SCANS 1.0433 sec
 ACQTM 2.0000 sec
 PD 3.33 usec
 PW1 1H
 IRNUC 26.4 c
 CTEMP CDCL3
 SLVNT 77.00 ppm
 EXREF 0.12 Hz
 BF 50
 RGAIN

Tert-butyl 3-(3-oxobutyl)indole-5-carbamate (18)

DFILE ¥Eca¥data¥Gu¥574.1
 COMNT 17-06-2006 18:46:28
 DATIM 1H
 OBNUC single_pulse.ex2
 EXMOD 399.78 MHz
 OBFRQ 4.19 KHz
 OBSET 7.29 Hz
 OBFIN 20480
 POINT 9378.89 Hz
 FREQU 8
 SCANS 2.1837 sec
 ACQTM 2.0000 sec
 PD 5.50 usec
 PW1 1H
 IRNUC 25.7 c
 CTEMP CDCL3
 SLVNT 7.24 ppm
 EXREF 0.12 Hz
 BF 28
 RGAIN

4-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-indolyl)-2-butanone (19)

DFILE ¥Eca¥data¥Gu¥574-13C.1
 COMNT
 DATIM 17-06-2006 18:51:29
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 73
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 26.0 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 54

4-(5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-3-indolyl)-2-butanone (19)

DFILE ¥¥Eca¥data¥Gu¥613.1
 COMNT
 DATIM 05-07-2006 22:00:46
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 25.6 °C
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 28

S-50

4-[1-(2-Hydroxyethyl)-3-indolyl]-2-butanone (20)

DFILE ¥Eca¥data¥Gu¥613-13C.1
 COMNT
 DATIM 05-07-2006 22:07:06
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 41
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 26.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 54

S-51

4-[1-(2-Hydroxyethyl)-3-indolyl]-2-butanone (2)

DFILE ¥¥Eca¥data¥Gu¥615.1
 COMNT
 DATIM 07-07-2006 11:51:20
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 25.9 c
 SLVNT ODCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 38

4-(5-Benzyloxy-3-indolyl)-2-butanone (21)

DFILE ¥Eca¥data¥Gu¥616-13C.1
 COMNT 07-07-2006 14:11:07
 DATIM 13C
 OBNUC single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 187
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 26.0 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 52

4-(5-Benzoyloxy-3-indolyl)-2-butanone (21)

DFILE ¥¥Eca¥data¥Gu¥678.1
 COMNT
 DATIM 02-08-2006 16:55:41
 OBNUC 1H
 EXMOD single_pulse.ex2
 OBFRQ 399.78 MHz
 OBSET 4.19 KHz
 OBFIN 7.29 Hz
 POINT 20480
 FREQU 9378.89 Hz
 SCANS 8
 ACQTM 2.1837 sec
 PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTEMP 23.8 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 34

4-(5-Dibenzylamino-1H-indol-3-yl)-
butan-2-one (22)

DFILE ¥Eca¥data¥Gu¥678-13C.1
 COMNT
 DATIM 02-08-2006 17:13:25
 OBNUC 13C
 EXMOD single_pulse_dec
 OBFRQ 100.53 MHz
 OBSET 5.35 KHz
 OBFIN 5.86 Hz
 POINT 40961
 FREQU 39259.39 Hz
 SCANS 327
 ACQTM 1.0433 sec
 PD 2.0000 sec
 PW1 3.33 usec
 IRNUC 1H
 CTEMP 24.2 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 0.12 Hz
 RGAIN 56

4-(5-Dibenzylamino-1H-indol-3-yl)-
butan-2-one (22)

DFILE \\Eca\data\Gu\666.1
 COMNT 18-07-2006 21:57:58
 DATIM 1H
 OBNUC single_pulse.ex2
 EXMOD 399.78 MHz
 OBFRQ 4.19 KHz
 OBSET 7.29 Hz
 OBFIN 20480
 POINT 9378.89 Hz
 FREQU 8
 SCANS 2.1837 sec
 ACQTM PD 2.0000 sec
 PW1 5.50 usec
 IRNUC 1H
 CTMP 21.3 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 32

3-(3-Oxocyclopentyl)-1H-indole-5-carbonitrile (23)

DFILE ¥¥Eca¥data¥Gu¥666-13C.1
 COMNT 18-07-2006 22:01:17
 DATIM 13C
 OBNUC single_pulse_dec
 EXMOD 100.53 MHz
 OBFRQ 5.35 KHz
 OBSSET 5.86 Hz
 OBFIN 40961
 POINT 39259.39 Hz
 FREQU 40
 SCANS 1.0433 sec
 ACQTM 2.0000 sec
 PD 3.33 usec
 PW1 1H
 IRNUC 21.8 c
 CTEMP CDCL3
 SLVNT 77.00 ppm
 EXREF 0.12 Hz
 BF 54
 RGAIN

3-(3-Oxocyclopentyl)-1H-indole-5-carbonitrile (23)