Supplementary Material

A new method for the synthesis of 3-substituted indoles

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Experimental:

Instruments and materials.

All reactions were carried out in oven dried glassware. Solvents used for the experiments were distilled and dried by employing standard protocols. All starting materials were purchased from Sigma-Aldrich, Spectrochem Chemicals or from S. D. Fine Chemicals and were used without further purification. Progress of the reaction was monitored by thin layer chromatography using dried and activated silica gel TLC plates (aluminium sheets coated with silica gel, E. Merck). Visualization of TLC plates was done by exposure to iodine vapours or UV lamp. Separation and purification of compounds were done by column chromatography using silica gel (Spectrochem Chemicals, 60-120 mesh). The products were further purified by recrystallization from appropriate solvent systems. Solvent eluted from the column chromatography was concentrated using Heidolph, IKA or Buchi rotary evaporators. Melting points were determined on a Neolab melting point apparatus and are uncorrected. Infrared spectra were recorded on Jasco4100 and ABB Bomem (MB Series) FT-IR spectrometers. $^1$H and $^{13}$C NMR spectra were recorded on a 400 MHz BrukerAvanceIII FT-NMR spectrometer with tetramethylsilane (TMS) as internal standard. Chemical shifts (δ) are reported in parts per million (ppm) downfield of TMS. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), and multiplet (m). Elemental analysis was performed using ElementarSysteme (Vario EL III). Molecular mass was determined by electron impact (EI) method using GC-MS (Agilent GC-7890A, Mass-5975C) and fast atom bombardment (FAB) using JMS 600 JEOL mass spectrometer.

1. Preparation of Nitrones: $N$-(9H-fluoren-9-ylidene)aniline oxide (1a)$^{1a,b}$, $N$-(9H-fluoren-9-ylidene)-4-methylaniline oxide (10)$^{1c,d}$ and $N$-(9H-fluoren-9-ylidene)naphthalen-1-amine oxide (18)$^{4e}$ were prepared according to procedures available in literature. $N$-(9H-fluoren-9-ylidene)-2-methylaniline oxide (11) and $N$-(9H-fluoren-9-ylidene)-3-methylaniline oxide (12) were synthesised by the oxidation of corresponding imines, adapting the same procedure reported for nitrone 10.$^{1c,d}$

1a. General Procedure for the Synthesis of $N$-Fluorenylidene-$N$-arylamines

A mixture of flurenone (10 mmol), amine (16 mmol) and BF$_3$-etherate (1 mL) in 30 mL CHCl$_3$ containing EtOH (5 mL) was refluxed for 15 minutes. The resulting solution was then concentrated and cooled. The residue obtained was recrystallized from a 1:3 mixture of chloroform-ethanol to give yellow crystals of $N$-fluorenylidene-$N$-arylamines.

1b. General procedure for oxidation of $N$-fluorenylidene-$N$-arylamines to the corresponding fluorenylidene-$N$-arylnitrones

To a solution of imine (10 mmol) in 10 mL DCM at 0-5°C, $m$-CPBA (11 mmol) in 5 mL DCM was added with stirring. The reaction mixture was then stirred for 5h keeping the temperature below 5 °C. After completion of the reaction, excess $m$-CPBA was removed by filtration, and the filtrate was washed twice with NaHCO$_3$ solution and finally with water. Organic layer was separated, dried over anhydrous sodium sulfate and solvent was removed under reduced pressure. The residue obtained was recrystallized from a mixture (1:1) of DCM and hexanes to give $N$-fluorenylidene-$N$-arylnitrones in good yield.

Yellow solid. mp: 145 °C. IRνmax (KBr): 3061 cm⁻¹ (=C-H stretch), 1540 cm⁻¹ (C=N stretch), 1261 cm⁻¹ (N→O stretch). ¹H NMR (400 MHz, CDCl₃): δH 8.97-8.95 (m, 1H), 7.73-7.23 (m, 9H), 5.75 (d, J = 8 Hz, 2H), 2.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δC 146.3, 139.2, 139.1, 132.1, 132.0, 131.7, 131.2, 130.6, 130.1, 129.2, 128.9, 127.8, 127.6, 127.2, 123.8, 123.2, 120.2, 119.6, 16.4. MS: m/z 285 (M⁺).


1d. Characterization data for N-(9H-fluoren-9-ylidene)-3-methylaniline oxide (12)

Yellow solid. mp: 112 °C. IRνmax (KBr): 3050 cm⁻¹ (=C-H stretch), 1540 cm⁻¹ (C=N stretch), 1261 cm⁻¹ (N→O stretch). ¹H NMR (400 MHz, CDCl₃): δH 8.92 (d, J = 7.2 Hz, 1H), 7.72 -7.23 (m, 9H), 6.94-6.90 (m, 1H), 5.95 (d, J = 8 Hz, 1H), 2.46 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δC 140.6, 139.3, 132.4, 131.1, 131.0, 129.9, 129.1, 128.9, 127.3, 127.1, 124.3, 123.9, 120.8, 120.2, 119.6. 21.4. MS: m/z 285 (M⁺).

Elemental analysis calculated for C₂₀H₁₅NO: C: 84.19, H: 5.30, N: 4.91. Found: C: 84.24, H: 5.29, N: 4.94.

2. General procedure for indole synthesis: In all reactions, a 1:1 mixture (1mmol each) of nitrone and acetylene in 10 mL of acetonitrile was stirred under reflux for 4 h. After the complete consumption of starting materials, solvent was evaporated off and the residue was redissolved in dichloromethane (10 mL) in the same flask. Oxalic acid (1mmol) adsorbed on silica gel (1 g) was added to the same pot and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, solvent was removed and the products were isolated by column chromatography over silica gel using mixtures of hexane and ethyl acetate as eluents. In all reactions, fluorenone was formed as a by-product in yields comparable to those cited for indoles. Optimal consumption of starting materials was achieved by recycling fluorenone.

2a. Reaction of N-(9H-fluoren-9-ylidene)aniline oxide (1a) with benzozyphenylacetylene (2a)

N-(9H-Fluoren-9-ylidene)aniline oxide (1a) (0.271 g, 1mmol) and benzoylphenylacetylene (2a) (0.211 g, 1mmol) in acetonitrile (10 mL) was stirred at 82 °C for 4h. Progress of the reaction was monitored by TLC. After complete consumption of nitrone, solvent was removed under reduced pressure and the residue was redissolved in dichloromethane (10 mL) in the same flask. Oxalic acid (0.1 g, 1mmol) adsorbed on of silica gel (1 g) was added to the same pot and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, reaction mixture was filtered and solvent was removed under reduced pressure. The residue obtained was chromatographed over silica gel using a mixture of hexane and ethyl acetate to give fluorenone (0.120 g, 66%) followed by indole 6a (0.190g, 64%) and isoxazoline 5a (0.091 g, 19%). The products were further purified by recrystallization from hexane-dichloromethane mixture.
Characterization data:

phenyl(2-phenyl-1H-indol-3-yl)methanone (6a): White solid. mp: 202°C. IR\(\nu_{\text{max}}\) (KBr): 3149 cm\(^{-1}\) (N-H stretch), 3050 cm\(^{-1}\) (=C-H stretch), 1593 cm\(^{-1}\) (C=O stretch). \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta_H\) 8.57 (s, 1H), 7.96-7.94 (m, 1H), 7.66-7.64 (m, 2H), 7.47-7.16 (m, 11H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta_C\) 193.2, 143.54, 139.7, 135.5, 131.7, 131.6, 129.7, 129.2, 128.8, 128.7, 128.4, 127.8, 123.64, 122.2, 121.8, 110.9. MS: \(m/\text{z} \, 297\) (\(M^+\)). Elemental analysis calculated for C\(_{21}\)H\(_{15}\)NO: C: 84.82, H: 5.08, N: 4.71. Found: C: 84.77, H: 5.05, N: 4.69.

2b. Reaction of N-(9H-fluoren-9-ylidene)aniline oxide (1a) with cinnamoylphenylacetylene (2b)

N-(9H-Fluoren-9-ylidene)aniline oxide (1a) (0.274 g, 1 mmol) and cinnamoylphenylacetylene (2b) (0.230 g, 1 mmol) in acetonitrile (10 mL) was stirred at 82 °C for 4 h. Progress of the reaction was monitored by TLC. After the complete consumption of nitrone, solvent was removed under reduced pressure and the residue was redissolved in dichloromethane in the same flask. Oxalic acid (0.1 g, 1mmol) adsorbed on of silica gel (1g) was added to the same pot and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, solvent was removed under reduced pressure. The residue obtained was chromatographed over silica gel using a mixture of hexane and ethyl acetate to give fluorenone (0.119 g, 67%) followed by the indole 6b (0.220 g, 68%) and isoxazoline 5b (0.081 g, 16%). The products were further purified by recrystallization from hexane-dichloromethane mixture.

Characterization data:

\((E)-3\)-phenyl-1-(2-phenyl-1H-indol-3-yl)prop-2-en-1-one (6b, 67%): Light yellow solid. mp: 152°C. IR\(\nu_{\text{max}}\) (KBr): 3175 cm\(^{-1}\) (N-H stretch), 3057 cm\(^{-1}\) (=C-H stretch), 1634 cm\(^{-1}\) (C=O stretch). \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta_H\) 8.53 (s, 1H), 8.46-8.44 (m, 1H), 7.66-7.14 (m, 14H), 6.80 \((d, J = 15.6 \text{ Hz}, 1H)\). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta_C\) 187.3, 143.9, 140.3, 135.5, 135.4, 132.6, 130.1, 129.6, 129.6, 128.9, 128.7, 128.1, 128.0, 126.7, 123.9, 122.2, 122.7, 116.4, 110.9. MS: \(m/\text{z} \, 323\) (\(M^+\)). Elemental analysis calculated forC\(_{23}\)H\(_{17}\)NO: C: 85.42, H: 5.30, N: 4.33. Found: C: 85.39, H: 5.26, N: 4.31.

\((E)-1-(2',5'-\text{diphenyl}-2'H\text{-spiro}[\text{fluorene-9,3'-isoxazole}-4'-yl])-3\text{-phenylprop-2-en-1-one}\) (5b, 16%): Yellow solid. mp: 105°C. IR\(\nu_{\text{max}}\) (KBr): 3058 cm\(^{-1}\) (=C-H stretch), 1649 cm\(^{-1}\) (C=O stretch). \(^1\)HNMR (400 MHz, CDCl\(_3\)): \(\delta_H\) 7.89-7.86 \((m, 2H)\), 7.67 \((d, J = 7.6 \text{ Hz}, 2H)\), 7.64-7.60 \((m, 1H)\), 7.57-7.53 \((m, 4H)\), 7.36-7.32 \((m, 2H)\), 7.27-7.16 \((m, 6H)\), 6.99-6.91 \((m, 4H)\), 6.81-6.76 \((m, 1H)\), 6.61-6.58 \((m, 2H)\), 6.36 \((d, J = 15.6 \text{ Hz}, 1H)\). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta_C\) 183.9, 163.1, 145.9, 144.9, 140.8, 140.7, 134.9,131.7, 130.2, 129.8, 129.4, 128.8, 128.6, 128.1, 128.0, 127.9, 127.0, 125.4,
124.7, 123.6, 120.1, 118.3, 117.0, 84.9. **MS**: *m/z* 503 (*M*)'. Elemental analysis calculated for C_{31}H_{23}NO_2: C: 85.86, H: 5.00, N: 2.78. Found: C: 85.82, H: 4.98, N: 2.75.

2c. Reaction of *N*(9H-fluoren-9-yldiene)aniline oxide (1a) with acetylphenylacetylene (2c)

*N*(9H-Fluoren-9-yldiene)aniline oxide (1a) (0.272 g, 1 mmol) and acetylphenylacetylene (2c) (0.140 g, 1 mmol) in acetonitrile (10 mL) was stirred at 82 °C for 4 h. Progress of the reaction was monitored by TLC. After the complete consumption of nitrone, solvent was evaporated off and the residue was redissolved in dichloromethane in the same flask. Oxalic acid (0.09 g, 1 mmol) adsorbed on of silica gel (0.5 g) was added to the *same pot* and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, reaction mixture was filtered and solvent was removed under reduced pressure. The residue obtained was chromatographed over silica gel using a mixture of hexane and ethyl acetate to give fluorenone (0.121 g, 67%) followed by the indole 6c (0.159 g, 66%) and isoxazoline 5c (0.075 g, 18%). The products were further purified by recrystallization from hexane-dichloromethane mixture.

**Characterization data:**

(2-methyl-1H-indol-3-yl)(phenyl)methanone (6c, 66%): 
White solid. 
mp: 168°C. 
\[\text{IR}_{\text{max}} (\text{KBr}) : 3174 \text{ cm}^{-1} (\text{N-H stretch}), 3058 \text{ cm}^{-1} (=\text{C-H stretch}), 1594 \text{ cm}^{-1} (\text{C=O stretch}).\] 
\[\text{^1H NMR} (400 \text{ MHz, CDCl}_3) : \delta_H 8.43 (s, 1H), 7.77-7.75 (m, 2H), 7.57-7.32 (m, 5H), 7.20-7.06 (m, 2H), 2.57 (s, 3H).\] 
\[\text{^13C NMR} (100 \text{ MHz, CDCl}_3) : \delta_C 193.0, 143.7, 141.3, 134.6, 131.5, 128.9, 128.3, 122.5, 121.6, 121.1, 110.5, 14.5. \] 
**MS**: *m/z* 235 (*M*'). Elemental analysis calculated for C_{16}H_{13}NO: C: 81.68, H: 5.57, N: 5.95. Found: C: 81.63, H: 5.56, N: 5.93.

1-(2',5'-diphenyl-2'H-spiro[fluorene-9,3'-isoxazole]-4'-yl)ethanone (5c, 18%):

Yellow solid. 
mp: 124°C. 
\[\text{IR}_{\text{max}} (\text{KBr}) : 3058 \text{ cm}^{-1} (=\text{C-H stretch}), 1649 \text{ cm}^{-1} (\text{C=O stretch}).\] 
\[\text{^1H NMR} (400 \text{ MHz, CDCl}_3) : \delta_H 7.84-7.81 (m, 2H), 7.69-7.65 (m, 2H), 6.93-6.89 (m, 2H), 6.74-6.69 (m, 1H), 6.56-6.53 (m, 2H), 2.28 (s, 3H).\] 
\[\text{^13C NMR} (100 \text{ MHz, CDCl}_3) : \delta_C 192.4, 163.4, 145.9, 144.9, 140.6, 131.4, 129.7, 129.4, 128.6, 128.3, 128.0, 127.9, 125.5, 123.6, 120.2, 117.3, 117.1, 84.5, 28.7. \] 
**MS**: *m/z* 415 (*M*'). Elemental analysis calculated for C_{29}H_{21}NO_2: C: 83.83, H: 5.09, N: 3.37. Found: C: 83.78, H: 5.05, N: 3.35.

2d. Reaction of *N*(9H-fluoren-9-yldene)aniline oxide (1a) with methyl propiolate (2d)

*N*(9H-Fluoren-9-yldene)aniline oxide (1a) (0.273 g, 1 mmol) and methyl propiolate (2d) (0.084 g, 1 mmol) in acetonitrile (10 mL) was stirred at 82 °C for 4 h. Progress of the reaction was monitored by TLC. After the complete consumption of nitrone, solvent was evaporated off and the residue was redissolved in dichloromethane in the same flask. Oxalic acid (0.1 g, 1 mmol) adsorbed on of silica gel (1 g) was added to
the same pot and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, solvent was removed under reduced pressure. The residue obtained was chromatographed over silica gel using a mixture of hexane and ethyl acetate to give fluorenone (0.160 g, 87%) followed by the indole 6d (0.151 g, 84%). The products were further purified by recrystallization from hexane-dichloromethane mixture.

**Characterization data:**

**Methyl 1H-indole-3-carboxylate (6d, 84%)**
- off-white solid. *mp:* 145-147 °C; IRνmax (KBr): 3229, 3005, 2936, 1664, 1525, 1440, 1201, 739 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δH 8.66 (br s, 1H), 7.17-8.14 (m, 5H), 3.857 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δC 184.4, 136.1, 131.1, 125.8, 123.2, 122.1, 121.5, 111.6, 51.2; MS: *m/z* 175 (*M*⁺). Elemental analysis calculated for C₁₀H₉NO₂: C: 68.54, H: 5.19, N: 8.01. Found: C: 68.49, H: 5.14, N: 8.03.

2e. Reaction of N-(9H-fluoren-9-ylidene)aniline oxide (1a) with methyl phenylpropionate (2e)

N-(9H-Fluoren-9-ylidene)aniline oxide (1a) (0.274 g, 1 mmol) and methyl phenylpropionate(2e) (0.162 g, 1 mmol) in acetonitrile (10 mL) was stirred at 82 °C for 4 h. Progress of the reaction was monitored by TLC. After the complete consumption of nitrone, solvent was evaporated off and the residue was redissolved in dichloromethane in the same flask. Oxalic acid (0.1 g, 1mmol) adsorbed on of silica gel (1 g) was added to the same pot and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, solvent was removed under reduced pressure. The residue obtained was chromatographed over silica gel using a mixture of hexane and ethyl acetate to give fluorenone (0.152 g, 84%) followed by the indole 6f (0.194 g, 82%). The products were further purified by recrystallization from hexane-dichloromethane mixture.

**Characterization data:**

(2-hydroxy-1H-indol-3-yl)(phenyl)methanone (6f, 82%)°: Off-white solid. *mp:* 179-180 °C; IRνmax (KBr): ν 3184, 3048, 1659, 1617, 1459, 1310, 1200. 964cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δH 8.87 ( br, s, 1H), 7.52-7.81 (m, 5H), 6.86-7.17 (m, 4H); ¹³C NMR (100 MHz, CDCl₃): δC 173.7, 171.8, 136.4, 134.1, 131.5, 128.7, 128.4, 126.0, 122.1, 121.9, 120.0, 110.3, 101.8; MS: *m/z* 237 (*M*⁺). Elemental analysis calculated for C₁₅H₁₁NO₂: C: 75.94, H: 4.67, N: 5.90. Found: C: 75.88, H: 4.63, N: 5.87.

2f. Reaction of N-(9H-fluoren-9-ylidene)-4-methylaniline oxide (10) with methyl propiolate (2d)

N-(9H-Fluoren-9-ylidene)-4-methylaniline oxide (10) (0.285g, 1 mmol) and methyl propiolate (2d) (0.085g, 1 mmol) in acetonitrile (10 mL) was stirred at 82 °C for 4 h. Progress of the reaction was monitored by TLC. After the complete consumption of nitroene, solvent was evaporated off and the residue was redissolved in dichloromethane in the same flask. Oxalic acid (0.09g, 1mmol) adsorbed on of silica
gel (1 g) was added to the same pot and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, solvent was removed under reduced pressure. The residue obtained was chromatographed over silica gel using a mixture of hexane and ethyl acetate to give fluorenone (0.161 g, 88%) followed by the indole 13 (0.158 g, 84%). The products were further purified by recrystallization from hexane-dichloromethane mixture.

**Characterization data:**

Methyl 5-methyl-1H-indole-3-carboxylate (13, 84%)\(^{3d,e}\): pale yellow solid. mp: 163-164 °C; IR\(\nu_{\text{max}}\) (KBr): 3242, 2920, 2848, 1671, 1531, 1448, 1359, 1152, 731 cm\(^{-1}\); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta_{H} 8.52\) (br s, 1H), 7.91 (s, 1H), 7.79 (s, 1H), 7.21 (d, \(J = 8.4\) Hz, 1H), 7.02 (dd, \(J = 1.6, 8.4\) Hz, 1H), 3.85 (s, 3H), 2.42 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \(\delta_{C} 164.7, 133.4, 130.6, 129.9, 125.1, 123.8, 120.2, 110.1, 107.3, 49.9, 20.5\); MS: \(m/z\) 189 (M\(^{+}\)). Elemental analysis calculated for C\(_{11}\)H\(_{11}\)NO\(_2\): C: 69.84, H: 5.85, N: 7.41. Found: C: 69.88, H: 5.87, N: 7.44.

2g. Reaction of N-(9H-fluoren-9-ylidene)-2-methylaniline oxide (11) with methyl propiolate (2d)

N-(9H-Fluoren-9-ylidene)-2-methylaniline oxide (11) (0.283 g, 1 mmol) and methyl propiolate (2d) (0.082 g, 1 mmol) in acetonitrile (10 mL) was stirred at 82 °C for 4 h. Progress of the reaction was monitored by TLC. After the complete consumption of nitrone, solvent was evaporated off and the residue was redissolved in dichloromethane in the same flask. Oxalic acid (0.1 g, 1 mmol) adsorbed on silica gel (1 g) was added to the same pot and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, solvent was removed under reduced pressure. The residue obtained was chromatographed over silica gel using a mixture of hexane and ethyl acetate to give fluorenone (0.150 g, 85%) followed by the indole 14 (0.159 g, 82%). The products were further purified by recrystallization from hexane-dichloromethane mixture.

**Characterization data:**

Methyl 7-methyl-1H-indole-3-carboxylate (14, 82%)\(^{3d,f}\): Pale yellow solid. mp: 161-163 °C; IR\(\nu_{\text{max}}\) (KBr): 3289, 3019, 2952, 1697, 1614, 1531, 1442, 1318, 1204, 1131, 783, 711 cm\(^{-1}\); \(^{1}H\) NMR (400 MHz, CDCl\(_3\)): \(\delta_{H} 8.62\) (brs, 1H), 7.94 (d, \(J = 8\) Hz, 1H), 7.83 (s, 1H), 7.11 (t, \(J = 8\) Hz, 1H), 6.98 (d, \(J = 7.2\) Hz, 1H), 3.84 (s, 3H), 2.42 (s, 3H); \(^{13}C\) NMR (100 MHz, CDCl\(_3\)): \(\delta_{C} 164.8, 134.7, 129.7, 124.4, 122.7, 121.2, 119.6, 118.2, 108.2, 50.0, 15.5\); MS: \(m/z\) 189 (M\(^{+}\)). Elemental analysis calculated for C\(_{11}\)H\(_{11}\)NO\(_2\): C: 69.83, H: 5.86, N: 7.40. Found: C: 69.77, H: 5.80, N: 7.43.

2h. Reaction of N-(9H-fluoren-9-ylidene)-3-methylaniline oxide (12) with methyl propiolate (2d)

N-(9H-Fluoren-9-ylidene)-3-methylaniline oxide (12) (0.286 g, 1 mmol) and methyl propiolate (2d) (0.086 g, 1 mmol) in acetonitrile (10 mL) was stirred at 82 °C for 4 h. Progress of the reaction was monitored by TLC. After the complete consumption of nitrone, solvent was evaporated off and the residue was redissolved in
dichloromethane in the same flask. Oxalic acid (0.1 g, 1mmol) adsorbed on of silica gel (1 g) was added to the *same pot* and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, solvent was removed under reduced pressure. The residue obtained was chromatographed over silica gel using a mixture of hexane and ethyl acetate to give fluorenone (0.155 g, 86%) followed by the indoles 15 (0.120 g, 63%) and 16 (0.041 g, 21%). The products were further purified by recrystallization from hexane-dichloromethane mixture.

**Characterization data:**

**Methyl 4-methyl-1H-indole-3-carboxylate (15, 63%)**
White solid. mp: 160-163 °C; IR*ν* max (KBr): 3289, 2920, 2853, 1673, 1614, 1442, 1406, 1354, 1178, 1053 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δH 8.64 (br s, 1H), 7.94 (s, 1H), 7.26 (t, J = 6.4 Hz, 1H), 7.17 (t, J = 6.4 Hz, 1H), 7.05 (d, J = 5.6Hz, 1H), 3.87 (s, 3H), 2.87 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δC 165.2, 136.9, 132.5, 131.9, 124.5, 124.0, 123.4, 109.7, 109.2, 51.1, 30.9; MS: m/z 189 (M⁺). Elemental analysis calculated for C₁₁H₁₁NO₂: C: 69.85, H: 5.85, N: 7.41. Found: C: 69.89, H: 5.87, N: 7.44.

**Methyl 6-methyl-1H-indole-3-carboxylate (16, 21%)**
White solid. mp: 158-161 °C; IR*ν* max (KBr): 3247, 2920, 1675, 1540, 1437, 1364, 1198, 1147, 1043 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δH 8.41 (br s, 1H), 8.06 (d, J = 8.4Hz, 1H), 7.09 (d, J = 8 Hz, 1H), 3.91 (s, 3H), 2.47 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δC 162.0, 142.0, 141.1, 134.1, 133.4, 130.3, 123.8, 121.2, 111.3, 51.0, 21.63; MS: m/z 189 (M⁺). Elemental analysis calculated for C₁₁H₁₁NO₂: C: 69.83, H: 5.85, N: 7.40. Found: C: 69.75, H: 5.80, N: 7.36.

2i. Reaction of N-(9H-fluoren-9-ylidene)naphthalen-1-amine oxide (18) with methyl propiolate (2d)

N-(9H-Fluoren-9-ylidene)naphthalene-1-amine oxide (18) (0.324 g, 1 mmol) and methyl propiolate (2d) (0.083 g, 1 mmol) in acetonitrile (10 mL) was stirred at 82 °C for 4 h. Progress of the reaction was monitored by TLC. After the complete consumption of nitrone, solvent was evaporated off and the residue was redissolved in dichloromethane in the same flask. Oxalic acid (0.1 g, 1mmol) adsorbed on of silica gel (1 g) was added to the *same pot* and the mixture was stirred at room temperature for 1 h. After the completion of the reaction, solvent was removed under reduced pressure. The residue obtained was chromatographed over silica gel using a mixture of hexane and ethyl acetate to give fluorenone (0.164 g, 91%) followed by the benzo[g]indole 19 (0.201 g, 89%). The products were further purified by recrystallization from hexane-dichloromethane mixture.

**Characterization data:**

**Methyl 1H-benzo[g]indole-3-carboxylate (19, 89%)**
Pale brown solid. mp: 202-205 °C; IR*ν* max (KBr): ν 3346, 2937, 2853, 1598, 1406, 1376, 1115, 1074, 991 cm⁻¹; ¹H NMR (400 MHz, CDCl₃): δH 9.67 ( br, s, 1H), 8.10 (d, J = 8 Hz, 1H), 7.91 (d, J = 7.6 Hz, 1H), 7.67 (d, J = 8.8 Hz, 1H), 7.32-7.60 (m, 4H), 3.98 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δC 162.4, 132.7, 132.0, 129.0, 126.1, 125.7, 125.5, 123.8, 122.2, 121.8,
121.26, 120.3, 110.2, 52.0; **MS**: $m/z$ 225 ($M^+$). Elemental analysis calculated for $C_{14}H_{11}NO_2$: C: 74.65, H: 4.92, N: 6.23. Found: C: 74.61, H: 4.88, N: 6.20.

3. **CCDC numbers for key compounds:**

**3a. phenyl(2-phenyl-1H-indol-3-yl)methanone (6a)**

\[
\text{CCDC 1403832}
\]

Summary of Data CCDC 1403832

Compound Name:
Formula: C21 H15 N1 O1
Unit Cell Parameters: a 14.570(11) b 11.855(19) c 19.092(17) P21/c

**3b. \((E)-3\text{-phenyl-1-(2-phenyl-1H-indol-3-yl)}\text{prop-2-en-1-one (6b)}**

\[
\text{CCDC 1403833}
\]

Summary of Data CCDC 1403833

Compound Name:
Formula: C23 H17 N1 O1
Unit Cell Parameters: a 20.452(3) b 6.5017(8) c 12.9195(13) Pca21
3c. (2-hydroxy-1H-indol-3-yl)(phenyl)methanone (6f)$^{2h}$

CCDC 1403834

Summary of Data CCDC 1403834

Compound Name:
Formula: C15 H11 N1 O2
Unit Cell Parameters: a 4.0513(3) b 20.7985(18) c 13.5547(12) P21/c
4. GC traces for the mixture of $15^{2d}$ and $16^{2g}$ obtained from the reaction between 12 and 2d:
5. Copies of $^1$H and $^{13}$C NMR spectra for reported compounds:

phenyl(2-phenyl-$^{1}$H-indol-3-yl)methanone (6a)$_{2a}$

$^1$H NMR
$^{13}$C NMR
$^{13}$C NMR (aromatic region expanded) of 6a
(E)-3-phenyl-1-(2-phenyl-1H-indol-3-yl)prop-2-en-1-one (6b)²b

¹H NMR

[Chemical structure image]

[1H NMR spectrum image]
$^{13}$C NMR
(E)-1-(2',5'-diphenyl-2'H-spiro[fluorene-9,3'-isoxazole]-4'-yl)-3-phenylprop-2-en-1-one (5b)

$^{1}H$ NMR
$^{13}$C NMR
(2-methyl-1H-indol-3-yl)(phenyl)methanone (6c) 2c

$^1$H NMR
$^{13}$C NMR
1-(2',5'-diphenyl-2'H-spiro[fluorene-9,3'-isoxazole]-4'-yl)ethanone (5c)

\[ \text{1H NMR} \]
$^{13}$C NMR
Methyl 1H-indole-3-carboxylate (6d)\textsuperscript{2d-g}

\[ \text{MeO} \]

\[ \text{H NMR} \]
$^{13}$C NMR

![13C NMR spectrum and chemical structure](image-url)
(2-hydroxy-1H-indol-3-yl)(phenyl)methanone (6f)\textsuperscript{2h}

\[ \text{HNMR} \]
$^{13}$C NMR
$N$-(9$H$-fluoren-9-ylidene)-2-methylaniline oxide (11)

$^1$H NMR

![NMR spectrum](image-url)
$^{13}$C NMR
N-(9H-fluoren-9-ylidene)-3-methylaniline oxide (12)

\[ \text{NMR spectrum image} \]
Methyl 5-methyl-1H-indole-3-carboxylate (13)\textsuperscript{2d,e}

\textsuperscript{1}H NMR
Methyl 7-methyl-1\textit{H}-indole-3-carboxylate (14)\textsuperscript{2d,f}

\textsuperscript{1}H NMR
Methyl 4-methyl-1H-indole-3-carboxylate (15)\textsuperscript{2d}

\textsuperscript{1}H NMR (acetone is present as an impurity)
\[ ^{13}C\text{ NMR (acetone is present as an impurity)} \]
Methyl 6-methyl-1H-indole-3-carboxylate (16)\textsuperscript{2g}

\(^1\text{H} \text{NMR}\)
$^{13}$C NMR
Methyl 1H-benzo[g]indole-3-carboxylate (19)\textsuperscript{2i,j}

\[ \text{H NMR} \]
$^{13}$C NMR
References
