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A Green and Efficient Michael Addition of Indoles to α, β-unsaturated Electron-deficient Compounds and Synthesis of Bis-indolylmethanes Catalyzed by Gallium Dodecyl Sulfate [$Ga(DS)_3$] in Water

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Abstract: *α, β-unsaturated electron-deficient compounds and bis-indolylmethanes were successfully synthesized by gallium dodecyl sulfate ($Ga(DS)_3$) catalyzed Michael addition using indoles and α, β-unsaturated ketones(or aldehyde) as reactant, respectively. The samples were characterized by ^1H NMR (400 MHz), HRMS, and Electrothermal Digital Melting-point. The results showed that the α, β-unsaturated electron-deficient compounds and bis-indolylmethanes could be effectively catalyzed by using $Ga(DS)_3$ to give the corresponding adducts in good to excellent yields in water media.*

Keywords: indoles, Michael addition, α, β-unsaturated ketones, $Ga(DS)_3$

1. INTRODUCTION

Using water as the reaction solvent has attracted much attention in today's organic chemistry. In comparison with the common organic solvent, water is cheaper and safer. And using water instead of some harmful organic solvents can lead to a development of environmentally friendly chemical processes.

Michael additions promoted by Lewis acids is one of the important carbon-carbon bond-forming reaction in organic chemistry. And indole derivatives have received a great amount of attention in recent years due to their high biological activities [1-2]. Among them 3-substituted indoles are important because of their activities and as building blocks for the synthesis of biologically active compounds and natural products [3]. Therefore, it is very important to develop new and convenient synthetic methods for them. Up to date, some methods have been reported, in which the most useful method is using Lewis acid, such as Sm [4], $Ga(OTf)_3$ [5], I_2 [6], Cu [7], acidic ionic liquid [8-9], $Zr(NO_3)_3$ [10], $Cu(OTf)_2$ [11-12], $InBr_3$ [13], $InCl_3$ [14], $ZrOCl_2$ [15], LiBr [16-17] etc as catalyst for catalyzed the reaction of indoles and α,β-unsaturated carbonyl compounds. But some of these Lewis acids are moisture sensitive and require special care in handling and storage, and some of these examples need a long reaction time and more catalyst has to be used. Moreover, metal trifaltes are highly expensive. So the development of new reagents with great efficiency, convenient procedures and delivering better yields is of great interest.

In this article, we present the highly efficient Michael addition of indoles to α, β-unsaturated ketones and synthesis of bis-indolylmethanes in water media using gallium dodecyl sulfate [$Ga(DS)_3$] (Scheme 1) as a new Lewis acid surfactant catalyst (LASC) in water media.

2. EXPERIMENTAL

2.1. Preparation of $Ga(DS)_3$ from $GaCl_3$ and solium dodecyl sulfate

To a stirring solution of sodium dodecyl sufate (11.51g, 40mmol) in distilled water (300mL) was added a solution of $GaCl_3$ (1.76g, 10mmol) in water (75mL) at room temperature. A white precipitation appeeared immediately and the mixture was stirred

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for anothre 30min. The white solid was separated by filtration and washed with water (50mL×3). The isolated solid product was dried under reduced pressure and $Ga(DS)_3$ as a white powder was obtained.

2.2. General procedure for preparation of α, β-unsaturated electron-deficient compounds (3a-n)

The indoles (1.0mmol), α, β-unsaturated ketones (1.2mmol) and $Ga(DS)_3$ (10mol%) were added to water 10mL. The mixture was stirred at 80ºC for the appropriate time (Table 1, monitored by TLC). Ethyl acetate (20mL) was added to the mixture with stirring. The organic layer was separated and dried over Na_2SO_4. Evaporation of the solvent to give the crude corresponding product. Further purification was performed by column chromatography, eluting with the appropriate solvents to give the Michael adducts in 75% to 91% isolated yield.

2.3. General procedure for preparation of bis-indolylmethanes (6a-h)

In a 20-ml round-bottom f lask, a mixture of aldehyde (1 mmol) and indole (2 mmol) was stirred in the presence of $Ga(DS)_3$ (0.1 mmol) in water (2 ml) at 80ºC for the stipulated time (Table 2). After completion of the reaction, the product was extracted with EtOAc (3×10 ml). The organic layer was washed with brine (2×15 ml) and then water (2×10 ml), dried over anhydrous sodium sulfate, and concentrated under reduced pressure to give a crude product, Further purification was performed by column chromatography, eluting with the appropriate solvents to give the bis-indolylmethanes.

2.4. Characterization

Melting points were recorded on an electrothermal digital melting-point qpparatus and are uncorrected. 1H NMR (400 MHz) spectra were recorded on a Varian Mercury MHz spectrometer in $CDCl_3$ or DMSO-d6. High-resolution mass spectra (HRMS) were obtained using a GCT-TOF instrument. IR spectra were obtained on a Nicolet FT-IR500 spectrophotometer using KBr pellets.

3. RESULTS AND DISCUSSION

In order to show the good catalytic effect of [$Ga(DS)_3$] a series of substituted indoles and α, β- unsaturated ketones were used to evaluate the scope of these Michael addition(Scheme 2). The result

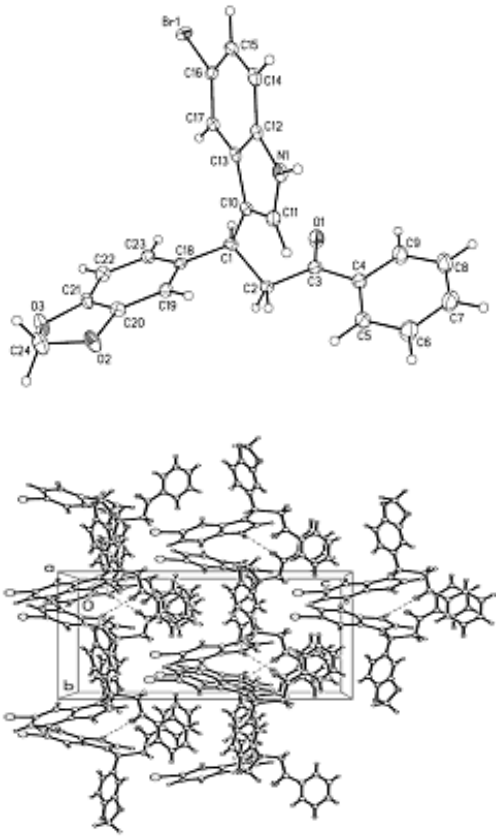
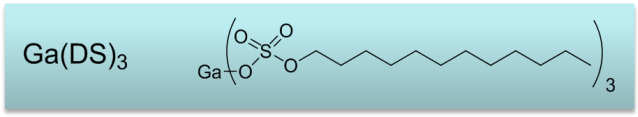


Figure 1. Molecular structure and packing diagram in a unit cell of the compound 3j

are summarized in Table 1. Addition of indole and indole with-monosubstitution at 1-, 2-, 5-, or 7-position were studied which

Scheme 1. Chemical structural formula of $Ga(DS)_3$



Scheme 2. $Ga(DS)_3$ catalyzed the typical Michael addition reaction

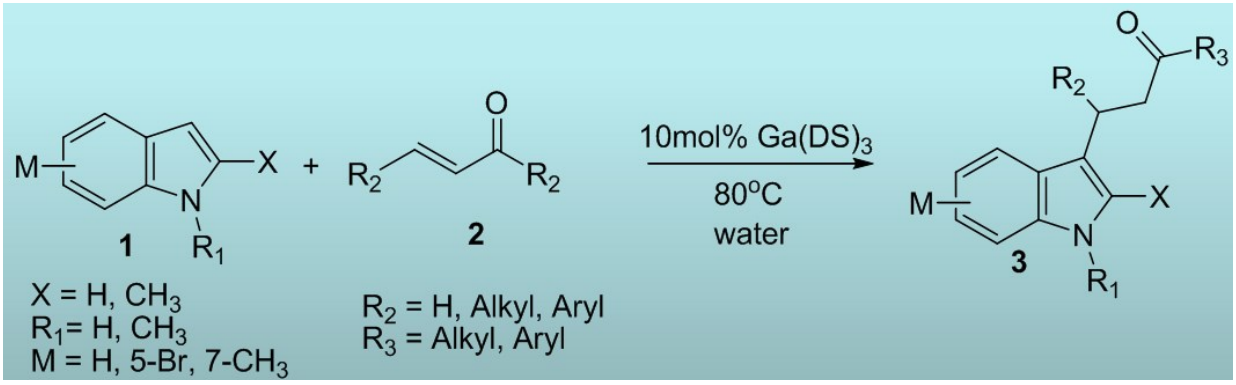
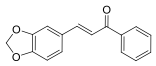
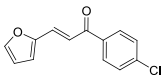
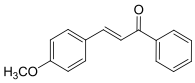
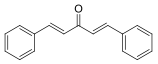
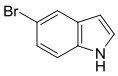
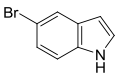
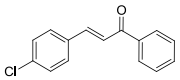
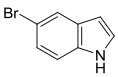
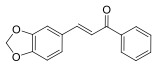
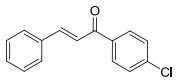
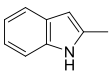


Table 1. Michael addition of indoles to α, β-unsaturated ketones catalyzed by Ga(DS)$_3$ in water media

Entry	indoles	α, β-unsaturated ketones	Product[a]	t/h	Yield % [b]
1			3a	7	81
2			3b	5	80
3			3c	8	90
4			3d	8	83
5			3e	6	89
6			3f/3g	8	81/19
7			3h	6	90
8			3i	8	87
9			3j	8	90
10			3k	5	79
11			3l	7	82
12			3m	8	91
13			3n	8	90

[a]All compounds were characterized by ^{1}H NMR and HRMS spectra; [b] Isolated yield

Scheme 3. Ga(DS)$_3$ catalyzed the typical Michael addition reaction in water media

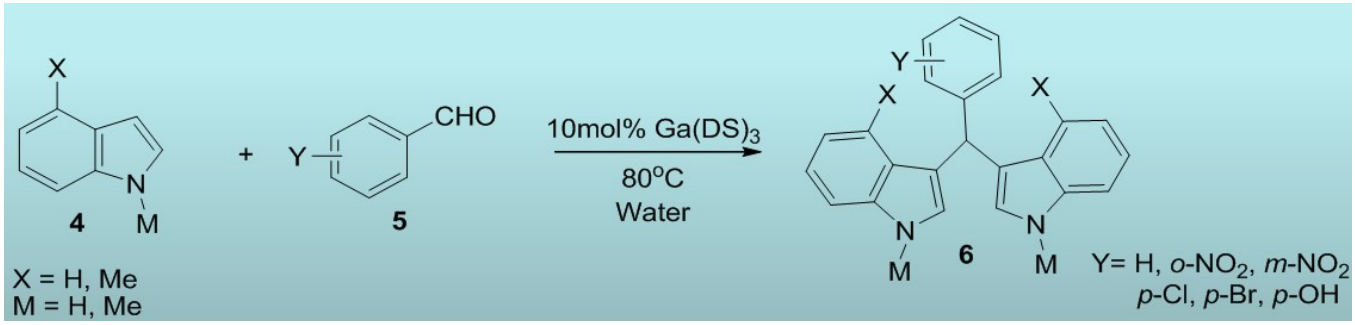
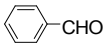
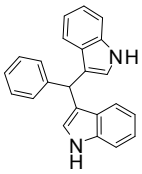
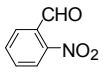
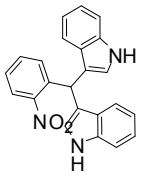
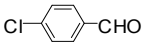
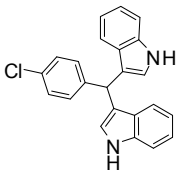
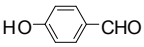
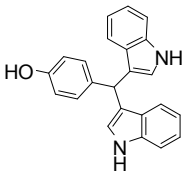
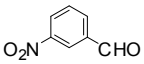
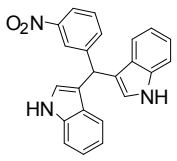
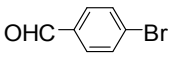
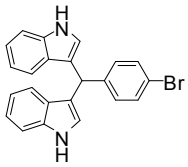
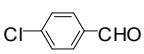
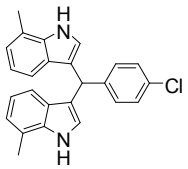
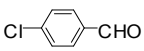
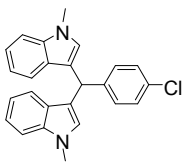


Table 2. $Ga(DS)_3$ catalyzed synthesis of bis(indol-3-yl)methanes in water media

Entry	Indole	Aldehyde	Product [a]	Time	Yield(%)[b]
1			 **6a**	3.5 h	89
2			 **6b**	2.5 h	85
3			 **6c**	3 h	90
4			 **6d**	3 h	87
5			 **6e**	2.5 h	92
6			 **6f**	2.5 h	83
7			 **6g**	2.5 h	89
8			 **6h**	2.5 h	60

[a] All compounds were characterized by ^1H NMR and HRMS spectra; [b] Isolated yield

both obtianed the desired products in good yields. From the aspect of α, β- unsaturated ketones, but-3-en-2-one, 4-methyl-3-penten-2-one and 1, 4-diaryl-α, β- unsaturated ketones all gave the corresponding adduct with the indoles in good yields (entries 1-5, 7-13). Interestingly, compound (entry 6) have two conjugated double bonds, both monoadduct and diadduct were obtianed: the former was major one in a yield (81%). The structure of all the product were characterized by ^{1}H NMR, ^{13}C NMR and HRMS analyses. The structure of 3j was also characterized by X-ray single crystal diffraction (Figure 1).

Bis(indolyl)methanes are found widely distributed in the bioactive metabolites of terrestrial and marine organisms [18]. Some compounds have potent pharmaceutical activities such as tranquilizers [19]or anticarcinogen [20]. The good results above (Table 1) prompted us to explore if $Ga(DS)_3$ could also catalyze the synthesis of bis-indolylmethanes in water media. Fortunately, we found that only 10mol% $Ga(DS)_3$ can also efficiently catalyzed this reaction in water media to give exciting results (Scheme 3, Table 2).

4. CONCLUSION

In conclusion, in this study we have introductd a new cataylst $Ga(DS)_3$, which is a green and effective combined Leiws acid sufactant catalyst for the Michael addition of indoles to structurally diverse α,β-unsaturated ketones and synthesis of bis-indolylmethanes in water media.

Spectral data of products

4-(1H-Indol-3-yl)butan-2-one (**3a**): M.p. 71-72°C. ^{1}H NMR (400 MHz, $CDCl_3$): d 7.98 (s, 1H, NH), 7.60-7.11(m, 4H, C_6H_4), 6.96 (s, 1H, CH, indole ring), 3.07-3.03 (m, 2H, CH_2), 2.87-2.84(m, 2H, CH_2), 2.13 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): d 19.3, 30.0, 44.1, 111.1, 115.1, 118.6, 119.2, 121.4, 122.0, 127.1, 136.3, 208.8.

4-(1H-Indol-3-yl)-4-methylpentan-2-one (**3b**): M.p. 70-71°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (s, 1H, NH), 7.82-7.11 (m, 4H, ArH), 6.92 (s, 1H, CH, indole ring), 2.96 (s, 2H, CH_2), 1.72 (s, 3H, CH_3), 1.54 (s, 6H, 2×CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 29.0, 34.7, 55.3, 111.9, 119.4, 120.8, 120.9, 121.9, 123.8, 125.7, 137.4, 209.8; HRMS: *m/z* (%) cald. for $C_{14}H_{18}NO$ (M^+) 216.1388, found 216.1380 (M^+, 20.08).

3-(Benzo[d][1,3]dioxol-5-yl)-3-(1H-indol-3-yl)-1-phenylpropan-1-one (**3c**): M.p. 130-131°C**.** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H, NH), 7.94-6.79 (m, 11H, ArH), 6.79 (s, 1H, indole ring), 6.71-6.68 (m, 1H, ArH), 5.85 (m, 2H, CH_2), 4.98 (m, 1H, CH), 3.79-3.63 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.4, 45.7, 101.3, 108.5, 108.8, 111.6, 119.8, 119.9, 121.2, 121.6, 122.6, 126.9, 128.6, 129.1, 133.6, 137.0, 137.4, 138.7, 148.0, 199.0. HRMS: *m/z* (%) cald. for $C_{24}H_{19}NO_3$ (M^+) 369.1359, found 369.1356 (M^+ 25.81).

1-(4-Chlorophenyl)-3-(furan-2-yl)-3-(1H-indol-3-yl)propan-1-one (**3d**): M.p. 61-62 °C. ^{1}H NMR (400MHz, $CDCl_3$): δ 8.03 (s, 1H, NH), 7.86-7.06 (m, 10H, ArH), 6.26 (s, 1H, CH), 6.06 (s, 1H, CH), 5.11 (m, 1H, CH), 3.86-3.62 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 32.4, 43.2, 105.9, 110.5, 111.5, 116.6, 119.5, 119.8, 122.3, 122.4, 126.3, 129.1, 129.8, 135.4, 136.6, 139.7, 141.5, 156.8, 197.3. HRMS: *m/z* (%) cald. for $C_{21}H_{16}NO_2Cl$ (M^+) 349.0870, found 349.0842 (M^+, 94.25).

3-(1H-Indol-3-yl)-3-(4-methoxyphenyl)-1-phenylpropan-1-one (**3e**): M.p. 124-125 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (s, 1H, NH), 7.94-6.99 (m, 11H, ArH), 6.96 (s, 1H, CH, indole ring), 6.81-6.70 (m, 2H, ArH), 5.01 (m, 1H, CH), 3.81-3.66 (m, 5H, CH_2+CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.8, 45.8, 55.6, 111.6, 114.2, 119.8, 120.0, 121.7, 122.6, 128.6, 129.0, 129.2, 133.5, 136.7, 137.1, 137.5, 158.4, 198.2. HRMS: *m/z* (%) cald. for $C_{24}H_{21}NO_2$ (M^+) 355.1594, found 355.1580 (M^+,43.28).

5-(1H-Indol-3-yl)-1,5-diphenylpent-1-en-3-one (**3f**): M.p. 160-161 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (s, 1H, NH), 7.95-6.79 (m, 14H, ArH), 6.70 (d, 1H, *J* = 8Hz, CH), 5.87-5.85 (m, 2H, CH=CH), 5.00 (m, 1H, CH), 3.79-3.63 (m, 2H, CH_2). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.4, 45.7, 101.3, 108.6, 108.8, 111.6, 119.8, 119.9, 121.2, 121.6, 122.6, 126.9, 128.6, 129.1, 133.6, 137.0, 137.4, 138.7, 148.0, 199.0. HRMS: *m/z* (%) cald. for $C_{25}H_{21}NO$ (M^+) 351.1580, found 351.1579 (M^+, 19.88).

1,5-Di(1H-indol-3-yl)-1,5-diphenylpentan-3-one (**3g**): M.p. 60-61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84 (s, 1H, NH), 7.82 (s, 1H, NH), 7.95-6.99 (m, 18H, ArH), 6.69 (s, 1H, CH, indole ring), 6.64 (s, H, CH, indole ring), 4.78 (m, 2H, 2CH), 3.24-3.02 (m, 4H, $2CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 38.4, 50.1, 111.6, 115.7, 119.1, 119.9, 122.0(2C), 122.5, 126.7, 128.1, 128.2, 128.8, 138.9, 144.3, 231.9. HRMS: *m/z* (%) cald. for $C_{33}H_{28}N_2O$ (M^+) 468.2202, found 468.2224 (M^+, 100).

4-(5-Bromo-1H-indol-3-yl)butan-2-one (**3h**): M.p. 70-71 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04 (s, 1H, NH), 7.70-7.20 (m, 3H, ArH), 6.96 (s, 1H, CH, indole ring), 3.01-2.96 (m, 2H, CH_2), 2.84-2.79 (m, 2H, CH_2), 2.14 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 19.5, 30.6, 44.3, 112.3, 113.1, 115.3, 121.7, 123.3, 125.3, 129.4, 135.3, 209.0.

3-(5-Bromo-1H-indol-3-yl)-1-(4-chlorophenyl)-3-phenylpropan-1-one (**3i**): M.p. 189-190 °C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.04 (s, 1H, NH), 7.87- 7.19 (m, 12H, ArH), 7.01 (s, 1H, CH, indole ring), 4.97 (m, 1H, CH), 3.77-3.63 (m, 2H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 37.4, 44.4, 111.2, 113.6, 117.9, 121.0, 123.7, 123.8, 126.2, 127.9, 128.4, 128.9, 130.1, 135.1, 135.5, 138.3, 144.9, 197.5. HRMS: *m/z* (%) cald. for $C_{23}H_{17}NOClBr$ (M^+) 437.0182, found 437.0180 (M^+, 9.06).

3-(Benzo[d][1,3]dioxol-5-yl)-3-(5-bromo-1H-indol-3-yl)-1-phenylpropan-1-one (**3j**): M.p. 160-161°C. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.04 (s, 1H, NH), 7.93-6.80 (m, 10H, ArH), 6.75 (s, 1H, indole ring), 6.69-6.72 (m, 1H, ArH), 5.88 (m, 2H, CH_2) 4.91 (t, 1H, *J* = 7.2Hz, CH), 3.75-3.59 (m, 2H, CH_2). ^{13}C NMR (100 MHz, DMSO-d_6): δ 37.1, 44.5, 100.78, 107.93, 108.36, 111.13, 113.51, 118.24, 120.81, 121.06 (2C), 123.6, 128.2, 128.4, 128.8, 133.3, 135.1, 137.0, 139.2, 145.4, 147.2, 198.4. HRMS: *m/z* (%) cald. for $C_{24}H_{18}NO_3Br$ (M^+) 447.0470, found 447.0468(M^+, 12.24).

4-Methyl-4-(7-methyl-1H-indol-3-yl)pentan-2-one (**3k**): M.p.

74-75 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (s, 1H, NH), 7.67-6.99 (m, 3H, ArH), 6.92 (s, 1H, CH, indole ring), 2.96 (s, 2H, CH_2), 2.46 (s, 3H, CH_3), 1.72 (s, 3H, CH_3), 1.53 (s, 6H, 2×CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 17.9, 29.3, 32.3, 35.3, 55.9, 119.3, 120.2, 121.1, 121.2, 123.0, 124.8, 125.8, 137.5, 210.6; HRMS: *m/z* (%)cald. for $C_{15}H_{19}NO$ (M^+) 229.1467, found 229.1460 (M^+, 25.07).

4-(7-Methyl-1H-indol-3-yl)butan-2-one (**3l**): M.p. 102-103 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H, NH), 7.46- 6.90 (m, 4H), 2.94-2.91 (m, 2H, CH_2), 2.69-2.68 (m, 2H, CH_2), 2.22 (s, 3H, CH_3), 2.10 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) : δ 17.1, 19.9, 30.6, 44.6, 116.0, 116.8, 119.9, 120.9, 121.6, 122.9, 127.0, 136.3, 209.5.

1-(4-Chlorophenyl)-3-(1-methyl-1H-indol-3-yl)-3-phenylpropan-1-one (**3m**): M.p. 142-143 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85-6.99 (m, 13H, ArH), 6.81 (s, 1H, CH, indole ring), 5.03 (t, 1H, *J* = 7.2 Hz, CH), 3.79-3.66 (m, 5H, CH_2+CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 33.2, 38.6, 45.7, 109.7, 118.0, 119.4, 119.9, 122.2, 126.6, 126.8, 127.3, 128.2, 128.9, 129.3, 129.9, 135.8, 137.7, 139.9, 144.6, 199.8. HRMS: *m/z* (%) calcd. for $C_{24}H_{20}ClNO$ (M^+) 373.1233, found 373.1227 (M^+, 31.89).

4-(2-Methyl-1H-indol-3-yl)butan-2-one (**3n**): oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H, NH), 7.44-7.06 (m, 4H, ArH), 6.99 (s, 1H, CH, indole ring), 3.07-3.03 (m, 2H, CH_2), 2.87-2.83 (m, 2H, CH_2), 2.48 (s, 3H, CH_3), 2.14 (s, 3H, CH3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 11.5, 19.8, 41.5, 79.5, 111.4, 114.5. 118.9, 119.9, 121.6, 122.7, 126.1, 127.5, 127.4, 128.9, 136.5, 139.2, 208.5.

3,3′-(phenylmethylene)bis(1H-indole) (**6a**): m.p. 126-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *d* 5.88 (s, 1H, CH), 6.54-7.13 (m, 13H, ArH), 7.78 (s, 2H, 2NH); ^{13}C NMR (100 MHz, $CDCl_3$): *d* 40.6, 111.5, 119.6, 120.0, 120.3, 122.3, 124.1, 126.6, 127.4, 128.7, 129.1, 137.0, 144.4. HRMS (EI): calcd for $C_{23}H_{18}N_2$, 322.1470 [M^+], found 322.1484.

3,3′-((2-nitrophenyl)methylene)bis(1H-indole) (**6b**): m.p. 137-140 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *d* 6.60 (s, 1H, CH), 6.64 (s, 2H, indole ring), 7.24-7.47 (m, 9H, ArH), 7.88-7.90 (m, 1H, ArH), 8.04 (s, 2H, 2NH). HRMS (EI): calcd for $C_{23}H_{15}Br_2N_3O_2$, 522.9531 [M^+], found 522.9539.

3,3′-((4-chlorophenyl)methylene)bis(1H-indole) (**6c**): m.p. 89-91°C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 5.84 (s, 1H, CH), 6.59 (s, 2H, indole ring), 6.99-7.36 (m, 12H, ArH), 7.87(s, 2H, 2NH) ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 40.0, 111.5, 119.6., 119.8, 120.3, 122.5, 124.0, 127.3, 128.89, 130.5, 132.2, 137.1, 143.0.

4-(di(1H-indol-3-yl)methyl)phenol (**6d**): m.p. 76-78 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *d* 4.89 (brs, 1H, -OH), 5.78 (s, 1H, CH), 6.52-7.40 (m, 14H, ArH), 7.73 (s, 2H, 2NH). ^{13}C NMR(100 MHz, $CDCl_3$): *δ* 39.6, 108.4, 111.4, 115.3, 119.5, 120.1, 122.2, 123.9, 127.3, 136.9, 153.9.

3,3′-((3-nitrophenyl)methylene)bis(1H-indole) (**6e**): m.p. 85-87 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 5.99 (s, 1H, CH), 6.63 (s, 2H, indole ring), 7.01-8.21 (m, 12H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 39.6, 108.4, 111.5, 115.3., 119.5, 120.2, 120.3, 122.2, 124.0, 127.3, 130.1, 137.0, 154.0.1.

3,3′-((4-bromophenyl)methylene)bis(1H-indole) (**6f**): m.p. 112-113°C. ^{1}H NMR (400 MHz, $CDCl_3$): *d* 5.82 (s, 1H, CH), 6.56 (s, 2H, indole ring), 6.99-7.03 (m, 2H, ArH), 7.15-7.38 (m, 10H, ArH), 7.82 (s, 2H, 2NH). ^{13}C NMR (100 MHz, $CDCl_3$): *d* 40.0, 111.6, 119.2, 119.7, 120.1, 120.3, 122.4, 124.1, 127.1, 130.8, 131.7, 136.9, 143.4. HRMS: (EI) calcd for $C_{23}H_{17}BrN_2$, 400.0575 [M^+], found 400.0589.

3,3′-((4-chlorophenyl)methylene)bis(7-methyl-1H-indole) (**6g**): m.p. 156-158 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *d* 2.25 (s, 6H, 2CH_3), 5.66 (s, 1H, CH), 6.23 (s, 2H, indole ring), 7.07-6.80 (m, 10H, ArH), 7.34 (s, 2H, 2NH). ^{13}C NMR (100 MHz, $CDCl_3$): *d* 16.9, 40.1, 118.0, 119.9, 120.0, 120.7, 123.0, 123.8, 126.8. 128.7, 130.4, 132.0, 136.6, 143.0.

3,3′-((4-chlorophenyl)methylene)bis(1-methyl-1H-indole) (**6h**): m.p. 185-187°C. ^{1}H NMR (400 MHz, $CDCl_3$): *d* 3.76 (s, 6H, 2CH_3), 6.00 (s, 1H, CH), 6.65 (s, 2H, indole ring), 7.13-7.16 (m, 2H, ArH), 7.32-7.52 (m, 10H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): *d* 33.0, 39.9, 109.6, 118.1, 119.2, 120.3, 122.0, 127.7, 128.8, 130.5, 132.1, 137.8, 143.5.

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