

Green Synthesis of Bis(indolyl)methane Derivatives using PEG-400

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Polyethylene glycol (PEG-400) has been considered as an effective and eco-friendly solvent cum activator for the one-pot coupling of indole and aldehydes to produce indole derivatives. The reaction was performed under mild conditions and the versatility of one-pot reaction was confirmed.

Keywords: 3,3'-(Phenylmethylene)bis(1H-indole), Indole, Aldehyde, Polyethylene glycol, Catalyst-free conditions.

INTRODUCTION

Green chemistry relates to the design of a process that minimizes the use and generation of hazardous substances. Green catalysis is one of the key areas of green chemistry. Now a days, the environmentally friendly solvents such as ionic liquids, super critical fluids and polyethylene glycol have been gaining importance as green reaction media in view of environmental regulations [1]. In this connection, polyethylene glycol (PEG) attain much more importance as an alternative reaction media to perform most of the organic reactions, because of its characteristic advantages such as recyclable, non-toxic in nature, thermally stable, inexpensive and easy to handle over the conventional solvents. Further, PEG also emerged as a powerful phase transfer catalyst and used in many organic transformations. In this perspective, PEG has been played a key role in the practice of green chemistry [2].

There are various methods for the synthesis of bis(indolyl)methanes available in literature. However, most of the methods involves protic acids and Lewis acids as catalysts to promote nucleophilic substitution reaction on various aldehydes and carbonyl compounds with indoles [3]. Further there are other acidic catalysts such as H-Y zeolite [4], sulfamidic acid [5], metaltriflates [6], LiClO₄ [7], bis(cyclopentadienyl) ZrCl₂ [8], CuBr₂ [9], ZrCl₄ [10] Zn(HSO₄)₂ [11], CAN [12] polyindole salt [13], N-tert ion exchange resin [14], butanesulfinyl aldimines [15], AcOH [16], InCl₃ [17], InF₃ [18], Ln(OTf)₃ [19], Dy(OTf)₃ [3c], FeCl₃·6H₂O [20], V(HSO₄)₃ [21], SBA-15/SO₃H [22], TBBDA [23], oxalic acid [24], silica bonded S-sulfonic acid [25], Bi(NO₃)₃ [26], Cu(BF₄)₂·SiO₂ [27], vanadium molybdophosphoric acid [28], Ph-PMO-SO₃H [29],

glycerol and CeCl₃ [30], B(C₆F₅)₃ [31], H₆P₂W₁₈O₆ [2,32] phosphated zirconia [33], Ph₃CCl [34] have also been utilized for the synthesis of bis(indolyl)methanes. These methods involves certain drawbacks, such as expensive catalysts, long reaction times, a harsh reaction conditions (e.g., high temperatures, pressure vessels), tedious work-up, high amount of catalyst loading and poor yield of desired product [35-37]. In this scenario, the necessity of an efficient and green reaction medium for the synthesis of bis(indolyl)methanes is highly desirable.

As we know that the inherent properties of polyethylene glycol (PEG) such as inexpensive, thermally stability, recyclability and non-toxic nature, in addition to them the high solubility in water and organic solvents alcohol and acetone [38] and insoluble in less polar solvents such as hexane makes it easy to recover [2,39-41]. Therefore from the past decade, the usage of PEG for various organic transformations is an area of growing interest. To the best of our knowledge, there is no report for the synthesis of bis(indolyl)methanes using PEG as a recyclable and mild reaction medium. Hence, as a part of our ongoing research in the field of PEG-mediated and catalyst free synthesis of heterocyclic compounds [42-44]. Herein, we report an green, simple and efficient method for the synthesis of bis(indolyl)methanes using PEG-400 as recyclable medium.

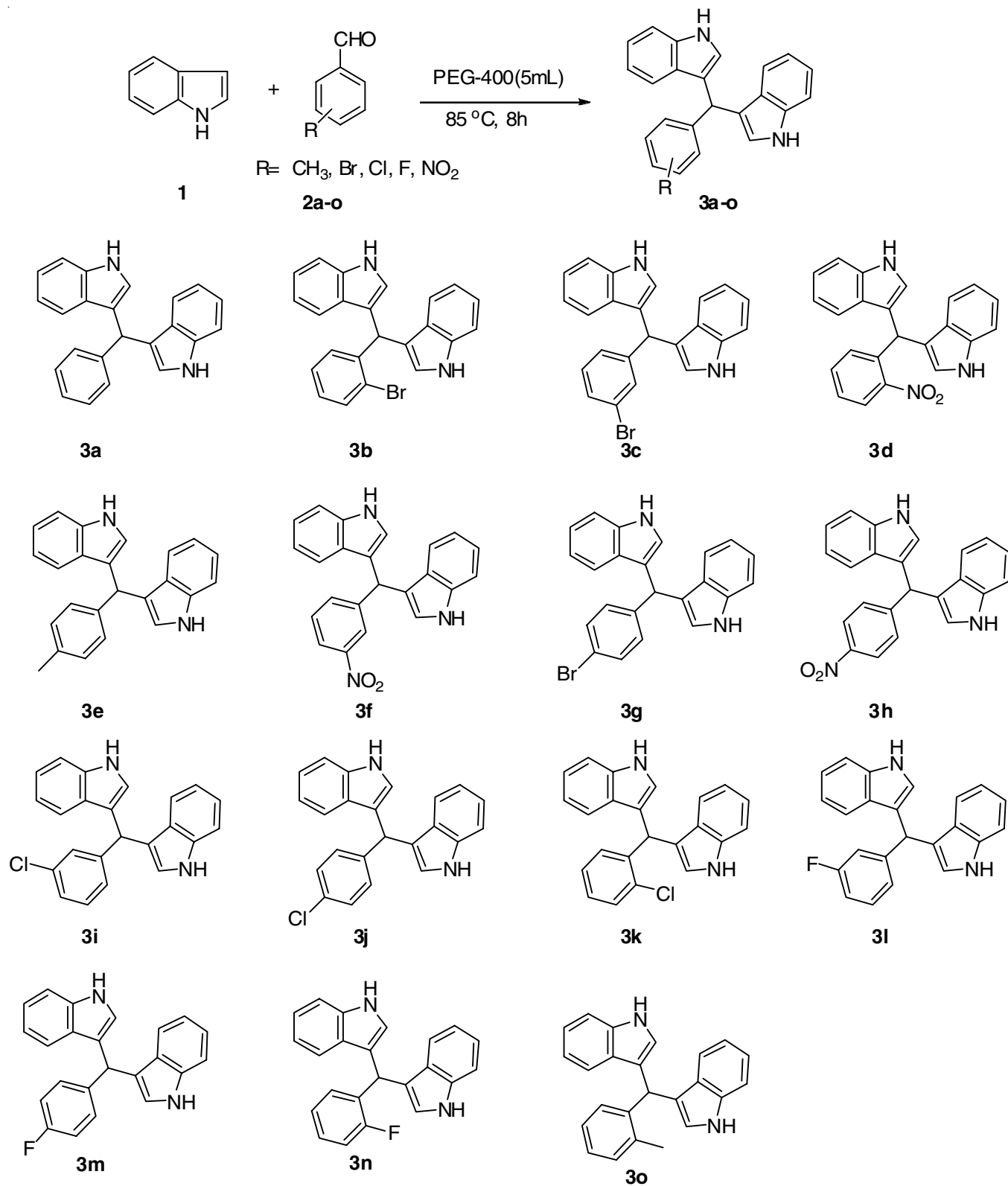
EXPERIMENTAL

All the chemicals were purchased from Sigma Aldrich with purity not less than 99.9%. Analytical thin layer chromatography (TLC) was carried out by using silica gel 60 F254 pre-coated plates. Visualization was accomplished with UV lamp

of I₂ stain. All the products were characterized by their NMR and HRMS spectra. ¹H NMR and ¹³C NMR were recorded on 400 or 100 MHz, in CDCl₃ and the chemical shifts were reported in parts per million (ppm, δ) downfield from the tetramethylsilane.

General procedure for the synthesis of bis(indolyl)methane by using PEG as reaction medium: A mixture of the requisite aldehyde (2 mmol), indole (1.0 mmol) was taken

in PEG (5 mL) and stirred at 85 °C for the appropriate time. After completion of the reaction, as monitored by TLC, the reaction mixture was poured into water and extracted with ethyl acetate. The organic layer was removed under reduced pressure and the crude product was purified by column chromatography. The recovered PEG could be reused for a number of cycles without significant loss of activity (**Scheme-I**).



Scheme-I: PEG-400 mediated synthesis of bis(indolyl)methane derivatives

Spectral data

3,3'-(Phenylmethylene)bis(1H-indole) (3a): Red colour solid, m.f. $C_{23}H_{18}N_2$, m.w. 322.15, yield 90 %; m.p. 152 °C; Reported: 150-152 °C [45]. Elemental analysis: Calcd. (found): C 85.68 (85.62), H 5.63 (5.62), N 8.69 (8.65); IR (KBr, ν_{max} , cm^{-1}): 704, 740, 1004, 1086, 1216, 1262, 1340, 1417, 1453, 1494, 1593, 1624, 2848, 2924, 3054, 3416, 3416. 1H NMR (400 MHz, $CDCl_3$): δ 5.85 (s, 1H), 6.72 (s, 2H), 7.02 (t, 2H, J = 6.7 Hz), 7.12-7.20 (m, 3H), 7.25-7.30 (m, 2H), 7.34-7.40 (m, 6H), 7.90 (br, 2H). ^{13}C NMR (DMSO): δ 46.1, 111.0, 119.2, 119.7, 119.9, 121.9, 123.6, 126.1, 127.1, 128.2, 128.7, 136.7, 144.0. MS: m/z 321 (M^+).

3,3'-[(2-Bromophenyl)methylene]bis(1H-indole) (3b): Red colour solid, m.f. $C_{23}H_{17}N_2Br$, m.w. 400.06, yield 70 %; m.p. 76-77 °C [46]. Elemental analysis: Calcd. (found): C 68.84 (68.81), H 4.27 (4.22), N 6.98 (6.91), Br 19.91 (19.91); IR (KBr, ν_{max} , cm^{-1}): 740, 792, 1024, 1024, 1097, 1216, 1257, 1334, 1412, 1453, 1567, 1582, 2848, 2920, 2977, 3054, 3411; 1H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 2H), 7.46-7.27 (m, 5H), 7.19 (s, 1H), 7.15 (d, J = 5.8 Hz, 1H), 7.13-7.06 (m, 2H), 7.05-7.00 (m, 1H), 6.95 (t, J = 7.5 Hz, 2H), 6.56 (s, 2H), 6.27 (s, 1H); ^{13}C NMR (DMSO): δ 111.3, 118.1, 119.2, 119.8, 121.9, 124.1, 127.0, 127.3, 130.6, 132.8, 136.8, 143.2. MS: m/z 400 (M^+).

3,3'-[(3-Bromophenyl)methylene]bis(1H-indole) (3c): Red colour solid, m.f. $C_{23}H_{17}N_2Br$, m.w. 400.06, yield 70 %; m.p.: 104-106 °C [46]. Elemental analysis: Calcd. (found): C 68.84 (68.82), H 4.27 (4.25), N 6.98 (6.96), Br 19.91 (19.96); IR (KBr, ν_{max} , cm^{-1}): 740, 792, 1014, 1097, 1216, 1272, 1334, 1417, 1458, 1567, 1587, 1618, 2925, 2972, 3054, 3416; 1H NMR (400 MHz, $CDCl_3$): δ 7.97 (s, 2H), 7.49 (s, 1H), 7.41-7.34 (m, 5H), 7.31 (d, J = 21.5 Hz, 1H), 7.22-7.11 (m, 3H), 7.02 (t, J = 7.5 Hz, 2H), 6.65 (s, 2H), 5.85 (s, 1H); ^{13}C NMR (DMSO): δ 39.7, 111.1, 119.1, 119.3, 119.8, 119.9, 122.0, 123.6, 126.8, 130.5, 131.3, 136.7, 143.1. MS: m/z 435 (M^+).

3,3'-[(2-Nitrophenyl)methylene]bis(1H-indole) (3d): Red colour solid, m.f. $C_{23}H_{17}N_3O_2$, m.w. 367.13, yield 85 %; m.p. 140-142 °C [46]. Elemental analysis: Calcd. (found): C 75.19 (75.15), H 4.66 (4.61), N 11.44 (11.42); IR (KBr, ν_{max} , cm^{-1}): 735, 1092, 1340, 1453, 1515, 1593, 1711, 2848, 2920, 2956, 3426; 1H NMR (400 MHz, DMSO): δ 10.93 (s, 2H), 7.88 (d, J = 7.9 Hz, 1H), 7.56 (t, J = 7.5 Hz, 1H), 7.46 (t, J = 7.3 Hz, 1H), 7.40 (d, J = 7.7 Hz, 1H), 7.36 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.06 (t, J = 7.5 Hz, 2H), 6.89 (t, J = 7.4 Hz, 2H), 6.78 (s, 2H), 6.40 (s, 1H). ^{13}C NMR (DMSO): δ 111.4, 116.9, 118.5, 118.9, 121.2, 123.1, 123.9, 126.4, 129.3, 126.4, 129.3, 136.7. MS: m/z 366 (M^+).

3,3'-(*p*-Tolylmethylene)bis(1H-indole) (3e): Dark pink colour solid, m.f. $C_{24}H_{20}N_2$, m.w. 336.16, yield 92 %; m.p. 94-95 °C; Reported: 94-96 °C [45]. Elemental analysis: Calcd. (found): C 85.68 (85.64), H 5.99 (5.97), N 8.33 (8.23); IR (KBr, ν_{max} , cm^{-1}): 740, 808, 952, 1045, 1159, 1200, 1340, 1453, 1515, 1608, 2853, 2920, 3411. 1H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H), 5.82 (s, 1H), 6.65 (s, 2H), 6.97 (t, 2H, J = 7.5 Hz), 7.2 (d, 2H, J = 7.3 Hz), 7.19-7.26 (m, 6H), 7.2 (d, 2H, J = 7.3 Hz), 7.91 (br, 2H). ^{13}C NMR (DMSO): δ 110.9, 119.2, 119.9, 121.8, 123.5, 127.1, 128.5, 128.9, 135.4, 136.7, 141.0. MS: m/z 335 (M^+).

3,3'-(3-Nitrophenyl)methylene]bis(1H-indole) (3f): Brown colour solid, m.f. $C_{23}H_{17}N_3O_2$, m.w. 367.13, yield 85 %;

m.p. 217-218 °C; Reported: 219 °C [46]. Elemental analysis: Calcd. (found): C 75.19 (75.22), H 4.66 (4.68), N 11.44 (11.41); IR (KBr, ν_{max} , cm^{-1}): 7835, 802, 1009, 1340, 1458, 1510, 1593, 1706, 1727, 2848, 2920, 2956, 3411. 1H NMR (400 MHz, $CDCl_3$): δ 6.18 (s, 1H), 6.76 (s, 2H), 7.0-7.05 (m, 3H), 7.42 (d, 3H, J = 7.8 Hz), 7.4 (d, 2H, J = 7.9 Hz), 7.49 (d, 2H, J = 8.6 Hz), 7.97 (br, 2H), 8.00 (d, 2H, J = 8.3 Hz). ^{13}C NMR (DMSO): δ 29.3, 111.4, 116.9, 118.5, 118.9, 121.1, 123.9, 126.4, 129.3, 136.7. MS: m/z 366 (M^+).

3,3'-Bis(indolyl)-4-(bromophenyl)methane (3g): Red colour solid, m.f. $C_{23}H_{17}N_2Br$, m.w. 400.06, yield 70 %; m.p. 108-110 °C; Reported: 108-111 °C [47]. Elemental analysis: Calcd. (found): C 68.84 (68.82), H 4.27 (4.26), N 6.98 (6.99), Br 19.91 (19.89); IR (KBr, ν_{max} , cm^{-1}): 740, 1004, 1086, 1417, 1458, 1484, 2848, 2920, 2956, 3406. 1H NMR (400 MHz $CDCl_3$): δ 7.78 (1H, s, NH), 7.39 (2H, m, H-5 and H-11), 7.33 (1H, d, J = 8.8 Hz, H-8), 7.20 (2H, t, H-6, H-12, J = 8.2 Hz), 7.04 (1H, t, H-7, J = 8.2 Hz), 6.56 (1H, s, H-2), 5.85 (1H, s, H-3'). ^{13}C NMR (100 MHz ($CDCl_3$): δ 111.1, 119.1, 119.6, 119.8, 122.0, 126.8, 130.5, 131.2, 136.7, 143.1. MS: m/z 400 (M^+).

3,3'-[(4-Nitrophenyl)methylene]bis(1H-indole) (3h): Red colour solid, m.f. $C_{23}H_{17}N_3O_2$, m.w. 367.13, yield 85 %; m.p. 219-220 °C [46]. Elemental analysis: Calcd. (found): C 75.19 (75.21), H 4.66 (4.64), N 11.44 (11.41); IR (KBr, ν_{max} , cm^{-1}): 740, 1340, 1453, 1505, 1598, 1727, 2848, 2920, 2956, 3406. 1H NMR (400 MHz, DMSO): δ 10.95 (s, 2H), 8.15 (d, J = 8.7 Hz, 2H), 7.61 (d, J = 8.7 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.30 (d, J = 7.9 Hz, 2H), 7.06 (t, J = 7.5 Hz, 2H), 6.96-6.78 (m, 4H), 6.04 (s, 1H); ^{13}C NMR (100 MHz, DMSO): δ 29.3, 111.4, 116.9, 118.5, 118.9, 121.2, 123.1, 123.9, 126.4, 129.3, 136.7; MS: m/z 366 (M^+).

3,3'-(3-Chlorophenyl)methylene]bis(1H-indole) (3i): Red colour solid, yield 85 %; m.f. $C_{23}H_{17}N_2Cl$, m.w. 356.11, m.p. 77 °C; Reported: 76-77 °C. Elemental analysis: Calcd. (found): C 77.41 (77.34), H 4.80 (4.83), N 7.85 (7.81), Cl 9.97 (9.96); IR (KBr, ν_{max} , cm^{-1}): 740, 797, 1004, 1035, 1086, 1210, 1267, 1334, 1412, 1453, 1613, 2848, 2920, 3054, 3411. 1H NMR (400 MHz, $CDCl_3$): δ 6.02 (s, 1H), 6.67 (s, 2H), 7.12 (t, 3H, J = 8.5 Hz), 7.20 (t, 2H, J = 7.9 Hz), 7.27-7.40 (m, 8H), 7.97 (br, 2H). ^{13}C NMR (DMSO): δ 111.1, 118.3, 119.3, 119.8, 122.0, 123.8, 126.6, 127.0, 127.5, 129.5, 130.3, 134.0, 136.7, 141.3. MS: m/z 355 (M^+).

3,3'-(4-Chlorophenyl)methylene]bis(1H-indole) (3j): Red colour solid; m.f. $C_{23}H_{17}N_2Cl$, m.w. 356.11, yield 85 %; m.p. 77 °C; Reported: 76-77 °C [46]. Elemental analysis: Calcd. (found): C 77.41 (77.35), H 4.80 (4.82), N 7.85 (7.87), Cl 9.97 (9.90); IR (KBr, ν_{max} , cm^{-1}): 740, 797, 1004, 1035, 1086, 1210, 1267, 1334, 1412, 1453, 1613, 2848, 2920, 3054, 3411. 1H NMR (400 MHz, $CDCl_3$): δ 6.02 (s, 1H), 6.67 (s, 2H), 7.12 (t, 3H, J = 8.5 Hz), 7.20 (t, 2H, J = 7.9 Hz), 7.27-7.40 (m, 8H), 7.97 (br, 2H). ^{13}C NMR (DMSO): δ 111.1, 118.3, 119.3, 119.8, 122.0, 123.8, 126.6, 127.0, 127.5, 129.5, 130.3, 134.0, 136.7, 141.3. MS: m/z 355 (M^+).

3,3'-[(2-Chlorophenyl)methylene]bis(1H-indole) (3k): Red colour solid, m.f. $C_{23}H_{17}N_2Cl$, m.w. 356.11, yield 82 %; m.p. 71-72 °C [46]. Elemental analysis: Calcd. (found): C 77.41 (77.35), H 4.80 (4.82), N 7.85 (7.87), Cl 9.97 (9.90); IR (KBr, ν_{max} , cm^{-1}): 735, 792, 906, 1009, 1035, 1092, 1128, 1210, 1262,

1334, 1412, 1453, 1613, 2848, 2915, 3049, 3400; ^1H NMR (400 MHz, CDCl_3): δ 7.93 (s, 2H), 7.64 (d, J = 7.8 Hz, 1H), 7.44 (d, J = 7.9 Hz, 2H), 7.38 (d, J = 8.1 Hz, 2H), 7.23 (s, 1H), 7.21 (s, 1H), 7.17 (s, 2H), 7.14-7.10 (m, 1H), 7.06 (d, J = 15.0 Hz, 2H), 6.62 (s, 2H), 6.34 (s, 1H). ^{13}C NMR (100 MHz, CDCl_3): δ 111.1, 118.3, 119.3, 119.8, 122.0, 123.8, 126.6, 127.0, 127.7, 129.5, 130.3, 134.0, 136.7, 141.3. MS: m/z 355 (M^+).

3,3'-(3-Fluorophenyl)methylenebis(1H-indole) (3l): Red colour solid, m.f. $\text{C}_{23}\text{H}_{17}\text{N}_2\text{F}$, m.w. 340.14, yield 80 %; m.p. 73 °C; Reported: 74 °C. Elemental analysis: Calcd. (found): C 81.16 (81.02), H 5.03 (4.97), N 8.23 (8.20), F 5.58 (5.60); IR (KBr, ν_{max} , cm^{-1}): 740, 777, 875, 937, 1014, 1086, 1128, 1221, 1247, 1334, 1417, 1453, 1484, 1587, 1613, 2848, 2920, 3054, 3411. ^1H NMR (400 MHz, CDCl_3): δ 6.12 (s, 1H), 6.71 (s, 2H), 7.16 (t, 3H, J = 8.7 Hz), 7.22 (t, 2H, J = 8.0 Hz), 7.32-7.43 (m, 8H), 8.0 (br, 2H). ^{13}C NMR (DMSO): δ 40.0, 111.1, 113.0, 113.1, 115.5, 115.6, 119.0, 119.3, 119.8, 122.0, 123.6, 124.4, 124.4, 126.9, 129.5, 129.6, 136.7, 146.8, 146.8, 162.0, 164.0. MS: m/z 339 (M^+).

3,3'-(4-Fluorophenyl)methylenebis(1H-indole) (3m): Red colour solid, m.f. $\text{C}_{23}\text{H}_{17}\text{N}_2\text{F}$, m.w. 340.14, yield 85 %; m.p. 77 °C; yield 88 %; m.p. 77 °C; Reported: 76-77 °C [45]. Elemental analysis: Calcd. (found): C 81.16 (81.01), H 5.03 (4.99), N 8.23 (8.21), F 5.58 (5.56); IR (KBr, ν_{max} , cm^{-1}): 735, 849, 1009, 1086, 1159, 1210, 1267, 1340, 1417, 1453, 1500, 1598, 2848, 2920, 2956, 3054, 3406. ^1H NMR (400 MHz, CDCl_3): δ 6.02 (s, 1H), 6.67 (s, 2H), 7.12 (t, 3H, J = 8.5 Hz), 7.20 (t, 2H, J = 7.9 Hz), 7.27-7.40 (m, 8H), 7.97 (br, 2H). ^{13}C NMR (DMSO): δ 111.0, 114.8, 115.0, 119.3, 119.6, 119.8, 122.0, 123.5, 126.9, 130.0, 130.1, 136.7. MS: m/z 339 (M^+).

3,3'-(2-Fluorophenyl)methylenebis(1H-indole) (3n): Red colour solid, m.f. $\text{C}_{23}\text{H}_{17}\text{N}_2\text{F}$, m.w. 340.14, yield 85 %; m.p. 77 °C; Reported: 76-77 °C. Elemental analysis: Calcd. (found): C 81.16 (81.02), H 5.03 (4.97), N 8.23 (8.20), F 5.58 (5.60); IR (KBr, ν_{max} , cm^{-1}): 736, 850, 1010, 1088, 1161, 1211, 1268, 1341, 1418, 1454, 1501, 1599, 2849, 2921, 2957, 3055, 3407. ^1H NMR (400 MHz, CDCl_3): δ 6.02 (s, 1H), 6.67 (s, 2H), 7.12 (t, 3H, J = 8.5 Hz), 7.20 (t, 2H, J = 7.9 Hz), 7.27-7.40 (m, 8H), 7.97 (br, 2H). ^{13}C NMR (DMSO): δ 111.1, 114.9, 115.1, 119.4, 119.7, 119.6, 122.1, 123.6, 126.9, 130.0, 130.0, 136.8. MS: m/z 339 (M^+).

3,3'-(2-Methylphenyl)methylenebis(1H-indole) (3o): Dark pink colour solid, m.f. $\text{C}_{24}\text{H}_{17}\text{N}_2$, m.w. 336.16, yield 80 %; m.p. 94-95 °C; Reported: 94-96 °C. Elemental analysis: Calcd. (found): C 85.68 (85.62), H 5.99 (5.97), N 8.33 (8.30); IR (KBr, ν_{max} , cm^{-1}): 741, 809, 953, 1046, 1160, 1201, 1341, 1454, 1516, 1609, 2855, 2921, 3412. ^1H NMR (400 MHz, CDCl_3): δ 2.38 (s, 3H), 5.82 (s, 1H), 6.65 (s, 2H), 6.97 (t, 2H, J = 7.5 Hz), 7.2 (d, 2H, J = 7.3 Hz), 7.19-7.26 (m, 6H), 7.2 (d, 2H, J = 7.3 Hz), 7.91 (br, 2H). ^{13}C NMR (DMSO): δ 110.9, 119.3, 119.8, 121.9, 123.6, 127.2, 128.6, 128.9, 135.5, 136.8, 142.0. MS: m/z 335 (M^+).

RESULTS AND DISCUSSION

The versatility of this reaction by the synthesis of various *bis*(indolyl)methane derivatives using a variety of aldehydes and indoles has been investigated. Further all the reactions with various aldehydes are smoothly going and good yielding towards *bis*(indolyl)methane derivatives. Especially electron

rich aldehydes that are aldehydes with electron donating groups reacted efficiently and with less reaction time whereas aldehydes with electron withdrawing groups takes slighter more reaction time. The structures of all the final compounds were confirmed by their analytical and spectroscopic data and also comparing with already available reported values.

Conclusion

An efficient, inexpensive, high yielding and green synthetic method of *bis*(indolyl)methane derivatives from various aldehydes and indole under mild reaction conditions using PEG-400 is reported.

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