Full paper/Mémoire

An efficient ultrasound-promoted method for the synthesis of bis(indole) derivatives

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A B S T R A C T

In this paper, the reaction of indole with electron-deficient alkenes in aqueous media is reported. This procedure allows the synthesis of bis(indole) derivatives in good to high yields at 90 °C under silent and ultrasound irradiation conditions. Short reaction times and high yields of desired products are the main advantages of the presented procedure. This reaction catalyzed by 12-tungstophosphoric acid is operationally simple and considers environmental aspects by avoiding toxic catalysts and solvents.

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1. Introduction

Bis(indole)-based compounds have recently received much attention as important building blocks for the synthesis of various active biological compounds [1–7]. Bis(indole) derivatives have been prepared *via* condensation reactions of indole with various aldehydes or ketones in the presence of either protic or Lewis acids [8–12]. Ultrasound irradiation is a powerful technique in synthetic organic chemistry. Enhanced reaction rates, simple experimental procedures, and high yields are the notable features of the ultrasound approach as compared to established methods [13–15]. Organic synthesis in aqueous media is gaining importance in view of the fact that the use of many toxic and volatile organic solvents contributes to pollution. There have been profound

research activities in the development of organic reactions in aqueous media, offering key advantages such as rate enhancement and insolubility of final products, which facilitates their isolation by simple filtration [16]. Keggin-type heteropolyacids (HPAs) have been studied extensively for organic synthetic processes as acid or redox catalysts in homogeneous and heterogeneous media [17]. HPAs have catalyzed several organic transformations such as Diels–Alder reaction [18], oxidative dehydrogenation of alcohols and amines [19], olefin hydration [20], synthesis of dihydropyrimidinones [21], esterification reactions [22], preparation of oximes [23] and synthesis of oxazolines, imidazolines, and thiazolines [24]. In conjunction with an ongoing research program involving the synthesis of bis(indole) compounds, we report a simple method for the preparation of bis(indole) derivatives through the Michael reaction of indole with different electron-deficient alkenes. This reaction is catalyzed by 12-tungstophosphoric acid in aqueous media at 90 °C under silent and ultrasound irradiation conditions (Scheme 1).
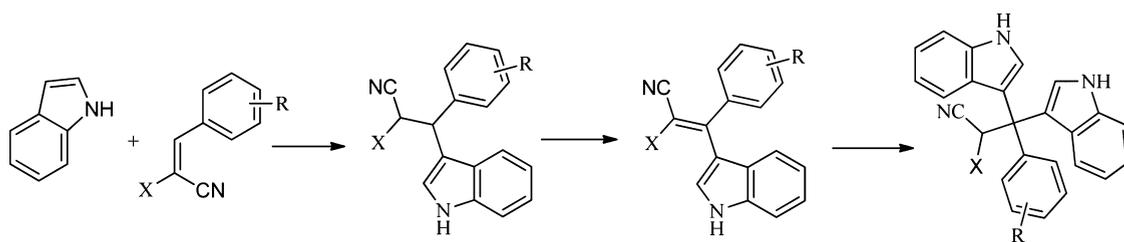
Scheme 1. Synthesis of bis(indole) derivatives catalyzed by 12-tungstophosphoric acid in aqueous media at 90 °C.

2. Results and discussion

In our initial study, the reaction of indole and 2-benzylidenemalononitrile was considered as a model one to optimize the conditions. The reaction was first carried out in H_2O in the absence of $H_3PW_{12}O_{40}$ and in reflux conditions. No reaction occurred under silent and ultrasound irradiation conditions (Table 1, entry 1). Similar reactions were then attempted in the presence of 2, 2.5, 3, and 3.5 mol-% of $H_3PW_{12}O_{40}$. The results in Table 1, entries 2–5, show that the use of 3 mol-% of $H_3PW_{12}O_{40}$ at reflux in H_2O is sufficient to push the reaction forward. Higher reaction loading of the catalyst had no significant influence on the reaction yield. To find the optimum reaction temperature, the reaction was carried out with 3 mol-% of $H_3PW_{12}O_{40}$ at room temperature, 60 °C, and at reflux temperature, which resulted in the isolation of the product in trace amounts and yields of 65% and 93% (Table 1, entries 7, 6, and 4), respectively. Thus, 3 mol-% of $H_3PW_{12}O_{40}$ and a reaction temperature at reflux were the optimal conditions. In addition, EtOH, MeCN, and $MeCO_2Et$ were also tested as solvents. In these cases,

2-((di(H1 indol-3-yl)(phenyl)methyl)malononitrile was formed in lower yields (Table 1, entries 8–10). When H_3NSO_3 and $C_{10}H_{16}O_4S$ were used as catalysts, 2-((di(H1 indol-3-yl)(phenyl)methyl)malononitrile was formed slightly in lower yields (Table 1, entries 13, 14).

When optimizing the model reaction, bis(indole) derivatives were synthesized in high yields under silent and ultrasound irradiation conditions. Ultrasound irradiation accelerated such reactions. The results are summarized in Table 2. It can be observed that the process tolerates both electron-donating and electron-withdrawing substituents in benzaldehydes. In all the cases, the reactions proceeded efficiently at reflux under mild conditions to afford the corresponding products in high yields. All the products were characterized by ^{1}H- and ^{13}C-NMR, IR spectroscopy and elemental analyses.

As expected, the reaction could be extended to other electron-deficient alkenes. Under optimized conditions, 2-(pyridylmethylene)malononitriles, 3-(pyridyl)acrylates were also chosen as electron-deficient alkenes to react with indole and were found to generate the corresponding indolyl derivatives. The reaction proceeded smoothly as

Table 1
Optimization of reaction conditions on the reaction of indole and 2-benzylidenemalononitrile[a].

Entry	Temp (°C)	Solvent	Catalyst (mol %)	Yield (%)[b]
1	Reflux	H_2O	$H_3PW_{12}O_{40}$ (0)	0
2	Reflux	H_2O	$H_3PW_{12}O_{40}$ (2)	70
3	Reflux	H_2O	$H_3PW_{12}O_{40}$ (2.5)	87
4	Reflux	H_2O	$H_3PW_{12}O_{40}$ (3)	93
5	Reflux	H_2O	$H_3PW_{12}O_{40}$ (3.5)	92
6	60	H_2O	$H_3PW_{12}O_{40}$ (3)	65
7	Room temp	H_2O	$H_3PW_{12}O_{40}$ (3)	Trace
8	Reflux	EtOH	$H_3PW_{12}O_{40}$ (3)	30
9	Reflux	$MeCO_2Et$	$H_3PW_{12}O_{40}$ (3)	20
10	Reflux	MeCN	$H_3PW_{12}O_{40}$ (3)	28
11	Reflux	H_2O	$H_3PMo_{12}O_{40}$ (5.4)	91
12	Reflux	H_2O	$H_4SiW_{12}O_{40}$ (3.4)	92
13	Reflux	H_2O	$C_{10}H_{16}O_4S$ (42)	70
14	Reflux	H_2O	H_3NSO_3 (100)	75

[a] Reaction conditions: indole (1 mmol), 2-benzylidenemalononitrile (0.5 mmol), and solvent (4 mL).
[b] Isolated yields.

Table 2
Synthesis of bis(indole) derivatives in the presence of $H_3PW_{12}O_{40}$ under silent and ultrasonic conditions in aqueous media[a].
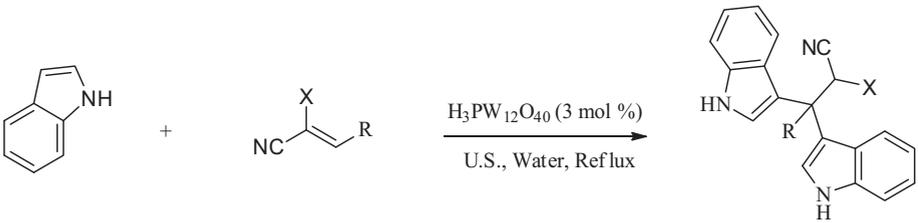
Entry	X	R	Time Silent/sonication[c]	Yield (%)[b] Silent/sonication	Mp (°C)
1	CN	C_6H_5	11 h/14 min	94/93	89–90
2	CN	$4\text{-}NO_2C_6H_4$	8 h/10 min	92/91	243–245
3	CN	$2\text{-}FC_6H_4$	10 h/12 min	87/85	128–129
4	CN	$4\text{-}FC_6H_4$	10 h/12 min	86/85	132–135
5	CN	$4\text{-}ClC_6H_4$	10 h/12 min	85/83	Oil
6	CN	$4\text{-}MeOC_6H_4$	12 h/17 min	85/82	126–128
7	CN	$3,4\text{-}diMeOC_6H_3$	12 h/17 min	81/80	168–169
8	CN	$4\text{-}HOC_6H_4$	12 h/20 min	80/78	87–88
9	CN	$4\text{-}MeC_6H_4$	11 h/15 min	82/80	174–176
10	CN	$4\text{-}iprC_6H_4$	11 h/15 min	79/77	181–183
11	CO_2Me	C_6H_5	12 h/13 min	92/91	Oil
12	CO_2Et	C_6H_5	12 h/13 min	91/90	Oil

[a] Reaction conditions: indole (1 mmol), electron deficient alkenes (0.5 mmol).
[b] Isolated yields.
[c] Constant frequency: 70 W.

expected in high yields, but while we wanted to obtain the expected bis(indole) derivatives, only indolyl derivatives were obtained (Table 3). A possible reason for this is that the oxidative dehydrogenation of 2-((indolyl)(pyridyl)-methylene)malononitriles and of 3-(indolyl)(pyridyl)acry-lates in the presence of $H_3PW_{12}O_{40}$ is less reactive than 2-((aryl)(indolyl)methyl)malonitriles and 3-(aryl)(indolyl)a-crylates, respectively. ^{1}H- and ^{13}C-NMR spectra of the crude mixture clearly indicate that the formation of the product leads to one enantiomer. Our attempts to detect

the second enantiomer in the reaction mixture were not successful. The results are summarized in Table 3. To explore the scope and limitations of this reaction further, we extended our studies to the reaction of pyrrole and 2-benzylidenemalonitrile in the presence of 12-tungstopho-sphoric acid as a catalyst in aqueous media at 90 °C under the established conditions. The reaction proceeded smoothly and a black sticky mixture was obtained after 3 h. In accordance with the literature, we think that pyrrole as an acid-sensitive compound undergoes polymerization

Table 3
Synthesis of 2-((indolyl)(pyridyl)methylene)malononitriles and 3-(indolyl)(pyridyl) acrylates in the presence of $H_3PW_{12}O_{40}$ under silent and ultrasonic conditions in aqueous media[a].
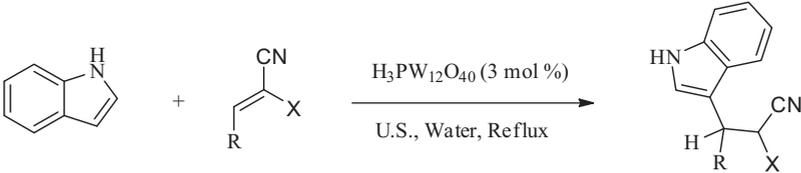
Entry	X	R	Time Silent/sonication[c]	Yield (%)[b] Silent/sonication	Mp (°C)
1	CN	3-pyridyl	9/10	92/91	159–161
2	CN	4-pyridyl	9/10	91/90	165–166
3	CO_2Me	3-pyridyl	10/11	88/86	144–145
4	CO_2Me	4-pyridyl	11/12	86/84	Oil
5	CO_2Et	3-pyridyl	10/11	87/85	147–148
6	CO_2Et	4-pyridyl	11/12	85/83	Oil

[a] Reaction conditions: indole (1 mmol), 2-(pyridylmethylene)malononitriles or 3-(pyridyl) acrylates (0.5 mmol).
[b] Isolated yields.
[c] Constant frequency: 70 W.

reactions without any occurrence of Michael addition reactions.

A plausible mechanism for the conjugate addition of indole to 2-benzylidenemalonitrile, oxidative dehydrogenation of Michael adducts and second conjugate addition of indole with dehydrogenation adducts is proposed in Scheme 2. $H_3PW_{12}O_{40}$ coordinated with nitrile groups of 2-benzylidenemalonitrile to give **1**. The electron-rich β-position of the indole ring then attacked the electron-deficient conjugated carbon–carbon double bond of **1**, followed by a hydrogen transfer, and was rearranged to give **2**. Then, $H_3PW_{12}O_{40}$ protonated the aromatic ring and got rearranged to give **4**. Finally, dehydrogenation of **4** resulted in 2-((indolyl)(phenyl)methylene)malononitriles (**5**). 2-(di(1H-indol-3-yl)-(phenyl)methyl)malononitrile was obtained by the second conjugate addition of indole with compound **5**, and $H_3PW_{12}O_{40}$ was released to catalyze the next cycle (Scheme 2).

3. Conclusions

In conclusion, we have developed a facile approach to prepare bis(indole) derivatives by reaction of indole with electron-deficient alkenes. This reaction is catalyzed by 12-tungstophosphoric acid as a highly stable, effective and readily available catalyst under silent and ultrasound irradiation conditions. The procedure reported here has the advantages of mild reaction conditions, short reaction time, high yields of products, operational simplicity, and avoidance of toxic catalysts and solvents.

4. Experimental

Melting points were determined by Büchi melting point B-540 B.V.CHI apparatus in open capillaries. They were uncorrected. IR spectra were recorded as KBr pellets on a Bruker Eqinox 55 spectrometer. ^{1}H- and ^{13}C-NMR spectra were obtained in CDCl$_3$ with Me$_4$Si as the internal standard with a Bruker Avance 500 MHz spectrometer. Elemental analyses were carried out with a Costech ECS 4010 CHN analyzer. Column chromatography was performed on a silica gel (230–400) mesh. Analytical TLC was performed on pre-coated plastic sheets of silica gel G/UV-254 with a thickness of 0.2 mm. Electron-deficient alkenes were prepared by treatment of benzaldehyde derivatives and active methylene compounds in aqueous media, at room temperature.

4.1. General procedure for the synthesis of bis(indole)

A mixture of indole (0.12 g, 1 mmol), electron-deficient alkenes (0.5 mmol) and catalyst (3 mol%) was refluxed at 90 °C in water (4 mL) under silent and ultrasound irradiation conditions for the appropriate time. The completion of the reaction was monitored by TLC. After cooling, the resulting precipitate was filtered, and the crude product was purified by column chromatography to
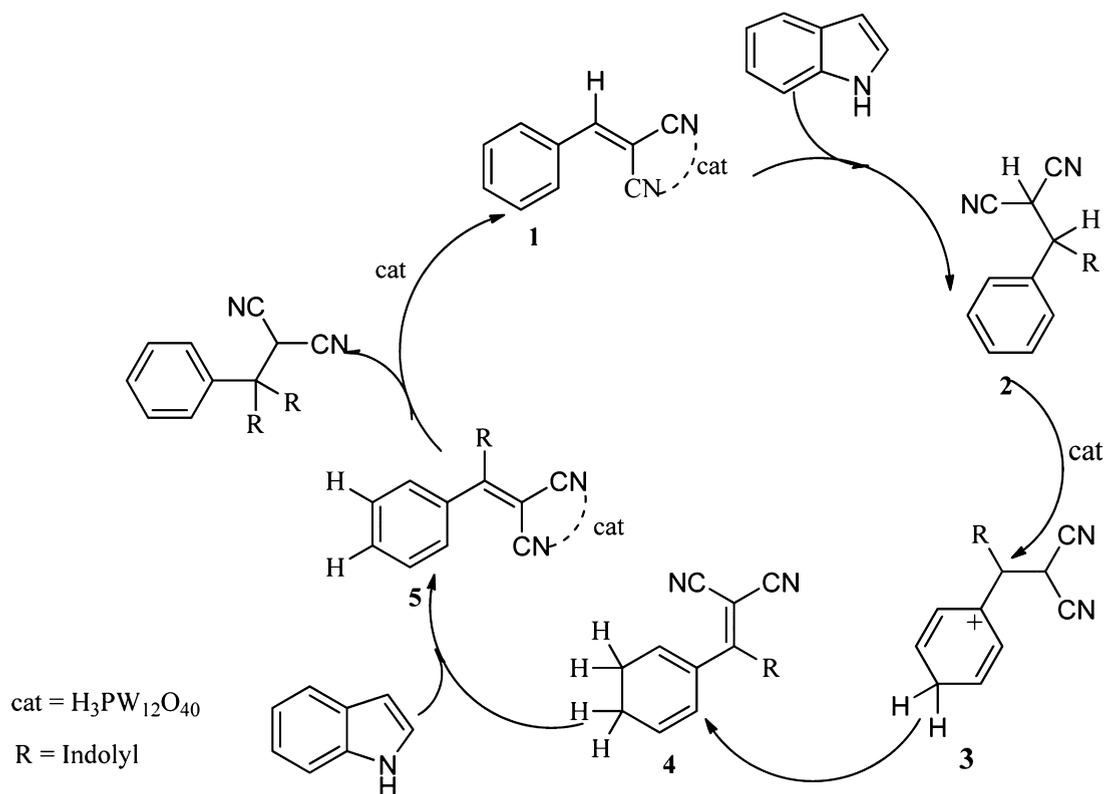
Scheme 2. The proposed mechanism for the synthesis of 2-(di(1H-indol-3-yl)-(phenyl)(methyl) malononitrile catalyzed by $H_3PW_{12}O_{40}$.

obtain a pure one. The results are summarized in Tables 2 and 3. All the products are unknown compounds, which were characterized by mp, IR, elemental analyses, ^{1}H-, and ^{13}C-NMR spectra.

4.1.1. 2-(di(1H-indol-3-yl)(phenyl)methyl) malononitrile

Red crystals; mp 89–90 °C. IR (KBr): ν = 3409, 3050, 2923, 2160, 1606, 1475 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 5.94 (s, 1H, CH), 6.67 (s, 2H, CH), 7.07 (t, J = 6.4 Hz, 2H, ArH), 7.23 (t, J = 6.4, 2H, ArH), 7.27–7.35 (m, 7H, ArH), 7.45 (d, J = 6.9 Hz, 2H, ArH), 7.88 (s, 2H, NH) ppm; ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 40.61, 77.70, 111.41, 112.69, 119.58, 120.11, 120.30, 122.27, 124.00, 126.50, 127.51, 128.60, 129.11, 137.10, 144.40 ppm; anal. calc. for C$_{26}$H$_{18}$N$_4$: C 80.81, H 4.69, N 14.50. Found: C 80.51, H 4.49, N 14.20 (Table 2, entry 1).

4.1.2. 2-(di(1H-indol-3-yl)(4-nitrophenyl)methelyl)malononitrile

Yellow crystals; mp 243–245 °C. IR (KBr): ν = 3422, 3052, 2923, 2187, 1610, 1507, 1456, 1341 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 5.93 (s, 1H, CH), 6.64 (s, 2H, CH), 6.92 (t, J = 7.4 Hz, 2H, ArH), 7.09 (t, J = 7.4 Hz, 2H, ArH), 7.26 (d, J = 7.9 Hz, 2H, ArH), 7.34 (d, J = 8.1 Hz, 2H, ArH), 7.46 (d, J = 8.3 Hz, 2H, ArH), 8.06 (d, J = 8.7 Hz, 2H, ArH), 9.30 (s, 2H, NH) ppm; ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 36.01, 48.90, 111.01, 113.00, 113.28, 119.78, 120.10, 122.01, 123.78, 124.00, 128.01, 130.05, 138.50, 148.01, 149.11 ppm; anal. calc. for C$_{26}$H$_{17}$N$_5$O$_2$: C 72.38, H 3.97, N 16.23. Found: C 72.15, H 3.65, N 16.43 (Table 2, entry 2).

4.1.3. 2-((2-fluorophenyl)di(1H-indol-3-yl) methyl)malononitrile

Light pink crystals; mp 128–129 °C. IR (KBr): ν = 3392, 3050, 2930, 2165, 1580, 1438, 1219 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 6.28 (s, 1H, CH), 6.73 (s, 2H,CH), 7.09 (m, 3H, ArH), 7.13 (t, J = 9.1 Hz, 1H, ArH), 7.28 (m, 4H, ArH), 7.39 (d, J = 8.1 Hz, 2H, ArH), 7.46 (d, J = 7.9 Hz, 2H, ArH), 7.89 (s, 2H, NH) ppm; ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 36.00, 42.11, 111.40, 112.20, 113.01, 116.01, 118.68, 119.71, 120.20, 122.39, 124.01, 127.31, 128.01, 129.01, 130.68, 137.10, 159.01 ppm; anal. calc. for C$_{26}$H$_{17}$N$_4$F: C 77.21, H 4.24, N 13.85. Found: C 77.50, H 4.51, N 13.55 (Table 2, entry 3).

4.1.4. 2-((4-fluorophenyl)di(1H-indol-3-yl) methyl)malononitrile

Red crystals; mp 132–135 °C. IR (KBr): ν = 3403, 3052, 2928, 2185, 1601, 1416, 1217 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 5.90 (s, H, CH), 6.33 (s, 2H, CH), 7.00 (m, 2H, ArH), 7.19–7.27 (m, 4H, ArH), 7.30 (m, 2H, ArH), 7.80 (d, J = 8.1 Hz, 2H, ArH), 8.00 (d, J = 7.9 Hz, 2H, ArH), 9.30 (s, 2H, NH) ppm; ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 39.90, 48.00, 112.01, 112.78, 113.01, 116.00, 119.01, 120.69, 121.20, 123.79, 128.41, 130.00, 136.78, 138.00, 159.11 ppm; anal. calc. for C$_{26}$H$_{17}$N$_4$F: C77.21, H 4.24, N 13.58. Found: C 77.00, H 4.60, N 13.44 (Table 2, entry 4).

4.1.5. 2-((4-chlorophenyl)di(1H-indol-3-yl)methyl)malononitrile

Viscous oil; IR (KBr): ν = 3411, 3052, 2923, 2165, 1616, 1415, 744 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 5.89 (s, 1H, CH), 6.66 (s, 2H, CH), 6.93–7.04 (m, J = 8.1 Hz, 4H, ArH), 7.21 (d, J = 7.9 Hz, 2H, ArH), 7.44 (d, J = 7.3 Hz, 2H, ArH), 7.80 (d, J = 8.1 Hz, 2H, ArH), 8.00 (d, 2H, ArH), 8.60 (s, 2H, NH) ppm; ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 37.60, 50.01, 112.00, 113.01, 113.79, 118.49, 120.01, 121.49, 121.68, 125.50, 128.29, 130.01, 131.87, 138.00, 140.01 ppm; anal. calc. for C$_{26}$H$_{17}$N$_4$Cl: C 74.19, H 4.07, N 13.31. Found: C 74.45, H 4.34, N 13.52 (Table 2, entry 5).

4.1.6. 2((3,4-di methoxyphenyl)di(1H-indol-3-yl)methyl)malononitrile

Light yellow crystals; mp 168–169 °C. IR (KBr): ν = 3399, 3055, 2926, 2250, 1593, 1456 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 3.80 (s, 3H, CH$_3$), 3.89 (s, 3H, CH$_3$), 5.88 (s, 1H, CH), 6.67 (d, J = 1.8 Hz, 1H, ArH), 6.71 (s, 2H, CH), 6.81 (d, J = 8.2 Hz, 1H, ArH), 6.88 (dd, J_1 = 8.4 Hz, J_2 = 1.8 Hz, 1H, ArH), 7.05 (t, J = 7.5 Hz, 2H, ArH), 7.21 (t, J = 7.5 Hz, 2H, ArH), 7.4 (d, J = 8.1 Hz, 2H, ArH), 7.45 (d, J = 7.9 Hz, 2H, ArH), 7.96 (s, 2H, NH) ppm; ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 38.01, 50.00, 57.30, 57.38, 110.01, 112.00, 112.78, 115.00, 117.68, 119.70, 120.01, 122.00, 123.01, 123.67, 128.71, 133.00, 136.48, 148.00, 150.00 ppm; anal. calc. for C$_{28}$H$_{22}$N$_4$O$_2$: C 75.32, H 4.97, N 12.55. Found: C75.52, H 4.63, N 12.22 (Table 2, entry 7).

4.1.7. 2-((4-hydroxyphenyl)di(1H-indol-3-yl)methelyl)malononitrile

Red crystals; mp 87–88 °C. IR (KBr): ν = 3407, 3055, 2922, 1611, 1455 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 5.40 (s, 1H, CH), 5.30 (s, 1H, OH), 6.67 (s, 2H, NH), 6.8 (d, J = 8.2 Hz, 2H, ArH), 7.00 (m, 2H, ArH), 7.14 (d, J = 7.9 Hz, 2H, ArH), 7.6 (m, 2H, ArH), 7.90 (d, J = 8.2 Hz, 2H, ArH), 7.97 (d, J = 8.2 Hz, 2H, ArH), 8.30 (s, 2H, NH) ppm; ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 39.00, 49.01, 111.01, 113.00, 116.01, 119.58, 121.11, 123.01, 128.20, 129.01, 129.28, 132.69, 136.50, 138.01, 155.50 ppm; anal. calc. for C$_{26}$H$_{18}$N$_4$O: C 77.59, H 4.51, N 13.92. Found: C 77.65 H 4.71, N 13.62 (Table 2, entry 8).

4.1.8. 2-((1H-indol-3-yl)(pyridine-3-yl) methyl)malononitrile

White crystals; mp 159–161 °C. IR (KBr): ν = 3407, 3075, 2902, 2258 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 4.80 (d, J = 6.9 Hz, 1H, CH), 4.99 (d, J = 6.9 Hz, 1H, CH), 7.00–7.90 (m, 7H, ArH), 8.42 (s, 1H, CH), 8.61 (s, 1H, CH), 10.37 (s, 1H, NH) ppm; ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 29.50, 42.01, 110.90, 112.21, 112.89, 116.10, 118.61, 120.01, 122.68, 123.29, 124.00, 134.12, 136.10, 136.88, 150.01, 150.10; anal. calc. for C$_{17}$H$_{12}$N$_4$: C 74.98, H 4.44, N 20.58. Found: C 74.55, H 4.61, N 20.55 (Table 3, entry 1).

4.1.9. Ethyl 2-cyano-3-(1H-indol-3-yl)-3-(pyridine-3-yl)propanoate

Light pink crystals; mp 147–148 °C; IR (KBr): ν = 3411, 3040, 2980, 2252, 1732, 1580, 1440, 1260 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 1.06 (t, J = 7.1 Hz, 3H, CH$_3$), 4.08 (q, J = 7.1 Hz, 2H, CH$_2$), 4.34 (d, J = 6.2 Hz, 1H, CH), 5.01 (d, J = 6.2 Hz, 1H, CH), 6.80–7.90 (m, 7H, ArH), 8.45 (d, J = 3.9 Hz, 1H, CH), 8.63 (s, 1H, CH), 10.04 (s, 1H, NH) ppm; ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 14.10, 38.01, 40.88, 63.39, 111.11, 112.79, 116.10, 118.59, 119.90, 122.11, 122.59, 123.00,

124.01, 133.20, 135.29, 136.90, 148.21, 149.89, 165.19 ppm; anal. calc. for $C_{19}H_{17}N_3O_2$: C 71.46, H 5.37, N 13.16. Found: C 71.16, H 5.67, N 13.36 (Table 3, entry 5).

4.1.10. Ethyl 2-cyano-3-(1H-indol-3-yl)-3-(pyridine-4-yl)propanoate

Viscous oil. IR (KBr): ν = 3402, 2981, 2250, 1741, 1599, 1458 cm^{-1}; ^{1}H-NMR (500 MHz, CDCl$_3$): δ = 1.06 (t, J = 7.1 Hz, 3H, CH$_3$), 4.08 (q, J = 7.1 Hz, 2H, CH$_2$), 4.34 (d, J = 6.2 Hz, 1H, CH), 5.01 (d, J = 6.2 Hz, 1H, CH), 7.18 (m, 4H, ArH), 8.6 (d, J = 7.9, 2H, ArH), 7.28 (d, J = 8.2 Hz, 2H, ArH), 8.63 (s, 1H, CH), 10.04 (s, 1H, NH) ppm; ^{13}C-NMR (125 MHz, CDCl$_3$): δ = 14.10, 38.11, 40.10, 63.39, 112.01, 117.40, 120.69, 121.71, 122.59, 123.20, 124.51, 124.69, 137.11, 141.10, 150.01, 153.41, 164.69 ppm; anal. calc. for $C_{19}H_{17}N_3O_2$: C 71.46, H 5.37, N 13.16. Found: C 71.23, H 5.14, N 13.54 (Table 3, entry 6).

Acknowledgments

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