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Hexamethylenetetraamine-Bromine Catalyzed Rapid and Efficient Synthesis of Bis(indolyl)methanes

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Summary. Highly rapid and convenient syntheses of bis(indolyl)methanes in excellent yields were carried out using the inexpensive and easily available catalyst, hexamethylenetetraamine-bromine (*HMTAB*). Mild reaction conditions, short reaction times, and excellent yields are important features of this method.

Keywords. Aldehydes; Ketones; Indoles; Electrophilic substitution reactions.

Introduction

Bis(indolyl)alkanes and their derivatives constitute an important group of bioactive metabolites of terrestrial and marine origin [1]. During the last few years a large number of natural products containing bis(indolyl)methanes [2] and bis(indolyl) ethanes [3] have been isolated from marine sources. Indoles and their derivatives are used as antibiotics [4]. The acid catalyzed reaction of electron rich heterocyclic compounds with *p*-dimethylaminobenzaldehyde is known as the *Ehrlich* test [5] for π-electron rich heterocycles, such as pyrroles and indoles. The analogous reaction of indoles with other aromatic or aliphatic aldehydes and ketones produces azafulvenium salts. The azafulvenium salts can undergo further addition with a second indole molecule to afford bis(indolyl)methanes [6]. Protic acids [7] as well as *Lewis* acids [8, 9] are known to promote these reactions. Recently montmorillonite clay K-10 [10] and lanthanide triflates [11] have been also found to catalyze these reactions. However, many *Lewis* acids become deactivated or sometimes decomposed by nitrogen containing reactants. Even when the desired reactions proceed, more than stoichiometric amounts of the *Lewis* acids are required because the acids are trapped by nitrogen [12]. These problems can be somewhat circumvented by using expensive

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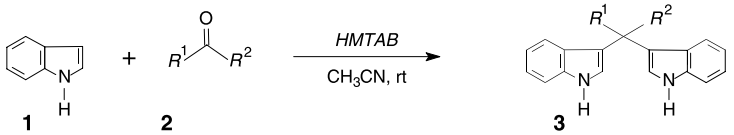
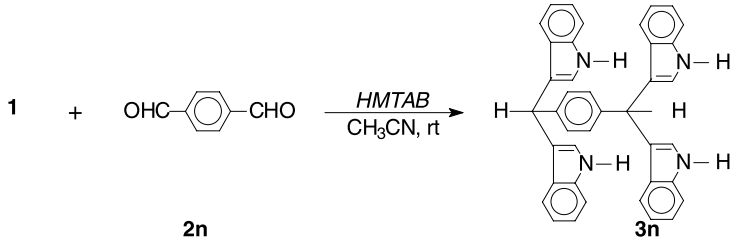
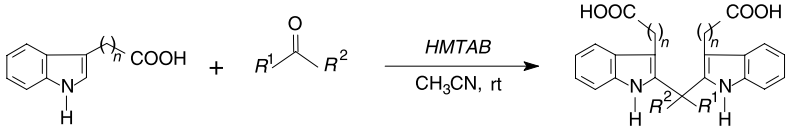


1 **2** **3**

	R^1	R^2		R^1	R^2
2a	*Et*	H	**3a**	*Et*	H
2b	*n*-Propyl	H	**3b**	*n*-Propyl	H
2c	*Ph*	H	**3c**	*Ph*	H
2d	4-Cl*Ph*	H	**3d**	4-Cl*Ph*	H
2e	4-CN*Ph*	H	**3e**	4-CN*Ph*	H
2f	4-NO_2*Ph*	H	**3f**	4-NO_2*Ph*	H
2g	4-OH*Ph*	H	**3g**	4-OH*Ph*	H
2h	4-N(*Me*)$_2$*Ph*	H	**3h**	4-N(*Me*)$_2$*Ph*	H
2i	4-NHCOCH$_3$*Ph*	H	**3i**	4-NHCOCH$_3$*Ph*	H
2j	*Ph*CH=CH	H	**3j**	*Ph*CH=CH	H
2k	2-Thiophene	H	**3k**	2-Thiophene	H
2l	2-Furyl	H	**3l**	2-Furyl	H
2m	3,4-Methylene-dioxyphenyl	H	**3m**	3,4-Methylene-dioxyphenyl	H
2o	α-Naphthyl	H	**3o**	α-Naphthyl	H
2p	*Me*	*Me*	**3p**	*Me*	*Me*
2q	–$(CH_2)_5$–		**3q**	–$(CH_2)_5$–	
2r	*Ph*	*Me*	**3r**	*Ph*	*Me*



1 **2n** **3n**



	n		R^1	R^2		*n*	R^1	R^2
1a	1	**2s**	*Et*	H	**3s**	1	*Et*	H
1b	1	**2t**	4-*MePh*	H	**3t**	1	4-*MePh*	H
1c	2	**2u**	*n*-Propyl	H	**3u**	2	*n*-Propyl	H
1d	2	**2v**	4-NO_2*Ph*	H	**3v**	2	4-NO_2*Ph*	H
1e	3	**2w**	*n*-Propyl	H	**3w**	3	*n*-Propyl	H
1f	3	**2x**	3,4-Methylene-dioxyphenyl	H	**3x**	3	3,4-Methylene-dioxyphenyl	H

Scheme 1

lithium perchlorate [13]. However, longer reaction times and moderate to poor yields for nitro-substituted aromatic aldehydes and ketones are the limitations.

The development of a method which allows the reaction under essentially mild conditions should heighten the synthetic potential of this conversion. Hexamethylenetetraamine-bromine (*HMTAB*) is an important reagent not only for bromination but also for a range of other reactions [14]. The reagent is transformed during reaction into easily removable products and presents a convenient alternative to other *N*-haloamines. We report here application of *HMTAB* as a catalyst for the synthesis of bis(indolyl)methanes under mild conditions (Scheme 1).

Results and Discussion

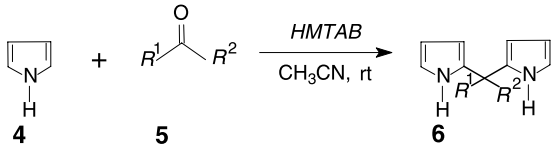
The electrophilic substitution reactions of indoles with aldehydes as well as ketones proceeded smoothly at room temperature. Bis(indolyl)methanes are formed in almost quantitative yields when indole was treated with various aldehydes or ketones in the presence of a catalytic amount (10%) of *HMTAB*. The results are summarized in Table 1. The methodology is found to be general as the reactions of aliphatic aldehydes (entries 1, 2), α,β-unsaturated aldehydes (entry 10), a variety of substituted aromatic aldehydes (entries 3–15, 20, 22, 24) as well as aliphatic, alicyclic, and aromatic ketones (entries 16–18) with indoles have furnished the corresponding bis(indolyl)methanes in excellent yields. Aromatic aldehydes with strong electron withdrawing substituents on the ring, α,β-unsaturated aldehydes, and ketones require longer reaction times giving low to moderate yields of the corresponding bis(indolyl)methanes. In this context, the present protocol is noteworthy because even nitro substituted aromatic aldehydes, α,β-unsaturated aldehydes, and ketones underwent smooth reactions with indoles giving excellent yields of products under mild and neutral conditions. It is also interesting to note that even the reaction of indole with terephthalaldehyde under this reaction condition furnished the corresponding tetra(indolyl)methane derivative in excellent yield in a very short time (15 min). It is important to note that heterocyclic aldehydes (entries 11, 12) underwent smooth reactions with indole giving excellent yields of the corresponding bis(indolyl)methanes under mild and neutral conditions, a reaction otherwise problematic under highly acidic conditions.

The present procedure is superior in comparison with $BF_3 \cdot Et_2O$ or $AlCl_3$ catalyzed reactions of acetone with indole, which generated several unexpected products [9a, 16], whereas expensive lanthanide triflate catalyzed reactions took a very long reaction time (24 h) [11]. 3-Substituted indoles such as indole-3-acetic acid (entries 19, 20), indole-3-propionic acid (entries 21, 22), and indole-3-butyric acid (entries 23, 24) were also examined for this reaction. Since the more active site C-3 was blocked in these cases electrophilic substitution took place at the C-2 giving the corresponding bis(indolyl)methanes (entries 19–24) in excellent yields in a short time. In comparison to the reported catalysts, *HMTAB* in acetonitrile is found to be an excellent catalyst in terms of yields and short reaction times under mild and almost neutral reaction conditions. Considering the importance of dipyrrylmethane synthesis with respect to the preparation of porphyrins and its analogs, some experiments have been carried out using pyrrole and aldehydes or ketones under similar reaction conditions (Scheme 2).

Table 1. *HMTAB* catalyzed synthesis of bis(indolyl)methanes

Entry	Indole	Aldehyde/Ketone	Product	Time	Yield[a,b]
				min	%
1	**1**	**2a**	**3a**	1	94
2	**1**	**2b**	**3b**	1	99
3	**1**	**2c**	**3c**	3	99
4	**1**	**2d**	**3d**	2	99
5	**1**	**2e**	**3e**	5	99
6	**1**	**2f**	**3f**	2	100
7	**1**	**2g**	**3g**	4	99
8	**1**	**2h**	**3h**	5	99
9	**1**	**2i**	**3i**	5	99
10	**1**	**2j**	**3j**	10	90
11	**1**	**2k**	**3k**	3	98
12	**1**	**2l**	**3l**	3	99
13	**1**	**2m**	**3m**	3	99
14	**1**	**2n**	**3n**	15	96
15	**1**	**2o**	**3o**	15	96
16	**1**	**2p**	**3p**	180	90
17	**1**	**2q**	**3q**	60	99
18	**1**	**2r**	**3r**	360	98
19	**1a**	**2a**	**3s**	2	97
20	**1b**	**2t**	**3t**	5	99
21	**1c**	**2b**	**3u**	6	96
22	**1d**	**2f**	**3v**	4	98
23	**1e**	**2b**	**3w**	2	99
24	**1f**	**2m**	**3x**	2	98

[a] Yield of isolated pure products; [b] products are characterized by IR, ^{1}H NMR, elemental analysis, and comparison with authentic samples



4 **5** **6**

	R^1	R^2		R^1	R^2
5a	H	H	**6a**	H	H
5b	*Me*	*Me*	**6b**	*Me*	*Me*
5c	*Ph*	*Me*	**6c**	*Ph*	*Me*
5d	4-Cl*Ph*	H	**6d**	4-Cl*Ph*	H
5e	4-NO_2*Ph*	H	**6e**	4-NO_2*Ph*	H

Scheme 2

It is interesting to note that excellent yields of the corresponding dipyrrylmethanes are obtained in a short time under mild conditions. The results are presented in Table 2.

Table 2. *HMTAB* catalyzed synthesis of dipyrrylmethanes

Entry	Pyrrole	Aldehyde/Ketone	Product	Time	Yield
				min	%
1	**4**	**5a**	**6a**	15	91
2	**4**	**5b**	**6b**	20	93
3	**4**	**5c**	**6c**	30	84
4	**4**	**5d**	**6d**	15	95
5	**4**	**5e**	**6e**	15	94

In conclusion, *HMTAB* in acetonitrile was found to be an effective catalyst for electrophilic substitution reactions of indoles with aldehydes and ketones giving bis(indolyl)methanes in almost quantitative yields. The use of this inexpensive and easily available catalyst under mild and neutral reaction and work-up conditions, the cleaner reactions and greater selectivity make this protocol practical and economically attractive. The procedure is found to be general as a variety of aldehydes and ketones react with indoles under mild reaction conditions.

Experimental

IR spectra were recorded on a Bomem MB-104 FTIR spectrometer whereas ^{1}H NMRs were scanned on a AC-300F NMR (300 MHz) instrument using $CDCl_3$ as solvent and *TMS* as internal standard. Elemental analyses were made by Carlo-Erba EA1110 CNNO-S analyzer and agreed favourably with the calculated values.

General Procedure

A mixture of 1 mmol of aldehyde, 2 mmol of indole, and 0.1 mmol of *HMTAB* in 5 cm^3 of acetonitrile was stirred at room temperature for the time specified in Table 1. After completion of the reaction (TLC), the solvent was removed under vacuum and the product was purified by column chromatography (silica gel, ethyl acetate:pet. ether = 3:7).

3,3′-Bisindolylethylmethane (**3a**, $C_{19}H_{18}N_2$)

Mp 89°C; IR ($CHCl_3$): $\bar{\nu} = 3420, 3165, 2970, 2916, 1664, 1590, 1328, 744\ cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 7.61$ (br s, 2H, NH), 7.0–7.3 (m, 8Ar–H), 6.63 (s, 2Ar–CH), 5.64 (t, CH), 2.11 (m, CH_2), 1.99 (t, CH_3) ppm.

3,3′-Bisindolylpropylmethane (**3b**, $C_{20}H_{20}N_2$)

Mp 109°C; IR ($CHCl_3$): $\bar{\nu} = 3414, 3160, 2970, 2922, 1644, 1596, 1407, 744\ cm^{-1}$; ^{1}H NMR ($CDCl_3$): $\delta = 7.60$ (br s, 2H, NH), 6.99–7.2 (m, 8Ar–H), 6.61 (s, 2Ar–CH), 5.62 (t, CH), 2.09 (m, $2CH_2$), 1.97 (t, CH_3) ppm.

3,3′-Bisindolylphenylmethane (**3c**)

Mp 123°C (Ref. [15] 125–126°C); spectroscopic data agree with those previously reported [15].

3,3′-Bisindolyl(4-chlorophenyl)methane (**3d**)

Mp 104°C (Ref. [16] 104–105°C); spectroscopic data agree with those previously reported [16].

3,3′-Bisindolyl(4-cyanophenyl)methane (**3e**, $C_{24}H_{17}N_3$)

Mp 211°C; IR ($CHCl_3$): $\bar{\nu} = 3396$, 3165, 2940, 2253, 1602, 1407, 757 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.96$ (br s, 2H, NH), 7.56 (d, $J = 8.18$ Hz, 2Ar–H), 7.44 (d, $J = 8.18$ Hz, 2Ar–H), 7.1–7.5 (m, 8Ar–H), 6.63 (s, 2Ar–CH), 5.92 (s, CH) ppm.

3,3′-Bisindolyl(4-nitrophenyl)methane (**3f**)

Mp 219°C (Ref. [17] 220–222°C); spectroscopic data agree with those previously reported [17].

3,3′-Bisindolyl(4-hydroxyphenyl)methane (**3g**, $C_{23}H_{18}N_2O$)

Mp 198°C; IR ($CHCl_3$): $\bar{\nu} = 3475$, 3378, 3031, 2995, 1638, 1584, 1377, 757 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.96$ (br s, 2H, NH), 7.67 (s, OH), 7.56 (d, $J = 8.18$ Hz, 2Ar–H), 7.44 (d, $J = 8.18$ Hz, 2Ar–H), 7.30 (m, 8Ar–H), 6.71 (s, 2Ar–CH), 5.52 (s, CH) ppm.

3,3′-Bisindolyl(4-(dimethylamino)phenyl)methane (**3h**, $C_{25}H_{23}N_3$)

Mp 226°C; IR ($CHCl_3$): $\bar{\nu} = 3408$, 3049, 2922, 1638, 1602, 1413, 1340, 738, 696 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 10.56$ (br s, 2H), 7.34–7.37 (d, $J = 8.18$ Hz, 2Ar–H), 7.25–7.26 (d, $J = 8.18$ Hz, 2Ar–H), 7.0–7.5 (m, 8Ar–H), 6.64 (s, 2Ar–CH), 5.66 (s, CH), 3.14 (s, $2CH_3$) ppm.

3,3′-Bisindolyl(4-acetamidophenyl)methane (**3i**, $C_{25}H_{21}N_3O$)

Mp 85°C; IR ($CHCl_3$): $\bar{\nu} = 3420$, 3305, 3055, 2934, 1657, 1596, 1322, 744 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 8.1$ (s, NHCO), 7.99 (br s, 2H, NH), 7.00–7.37 (m, 12Ar–H), 6.50 (s, 2Ar–CH), 5.6 (s, CH), 2.95 (s, $COCH_3$) ppm.

3,3′-Bisindolylcinnamylmethane (**3j**, $C_{25}H_{20}N_2$)

Mp 107°C; IR ($CHCl_3$): $\bar{\nu} = 3420$, 3305, 3055, 2927, 1657, 1596, 1402, 781 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.94$ (br s, 2H, NH), 7.44–7.68 (m, 13Ar–H), 6.54 (s, 2Ar–CH), 6.3 (d, $J = 15.2$, =CH), 6.1–6.19 (m, =CH), 5.52 (s, CH) ppm.

3,3′-Bisindolyl(2-thienyl)methane (**3k**)

Mp 153°C (Ref. [17] 149–156°C); spectroscopic data agree with those previously reported [17].

3,3′-Bisindolyl(2-furfuryl)methane (**3l**)

Mp 322°C (Ref. [17] 325°C); spectroscopic data agree with those previously reported [17].

3,3′-Bisindolyl(3,4-methylenedioxyphenyl)methane (**3m**)

Mp 99°C (Ref. [17] 90–91°C); spectroscopic data agree with those previously reported [17].

3,3′,3″,3‴-Tetraindolyl(terepthalyl)dimethane (**3n**)

Mp 136°C (Ref. [17] 138–140°C); spectroscopic data agree with those previously reported [17].

3,3′-Bisindolyl(1-napthyl)methane (**3o**, $C_{27}H_{20}N_2$)

Mp 220°C; IR ($CHCl_3$): $\bar{\nu} = 3414$, 2928, 2855, 1638, 1602, 1383, 755 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.64$ (br s, 2H, NH), 7.38–7.45 (m, 8Ar–H), 7.26–7.34 (m, 7Ar–H), 6.59 (s, 2Ar–CH), 5.61 (s, CH) ppm.

3,3′-Bisindolyldimethylmethane (**3p**, $C_{19}H_{18}N_2$)

Mp 97°C; IR ($CHCl_3$): $\bar{\nu} = 3418$, 2964, 1602, 1328, 744 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.67$ (br s, 2H, NH), 7.39–7.42 (m, 8H), 6.52 (s, 2Ar–CH), 2.0 (s, $2CH_3$) ppm.

1,1-(3,3′-Bisindolyl)cyclohexane (**3q**)

Mp 119°C (Ref. [18] 118–120°C); spectroscopic data agree with those previously reported [18].

3,3′-Bisindolylmethylphenylmethane (**3r**, $C_{24}H_{20}N_2$)

Mp 117°C; IR ($CHCl_3$): $\bar{\nu} = 3414$, 3062, 2922, 1636, 1602, 1450, 751, 696 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.71$ (br s, 2H, NH), 7.41–7.46 (m, 13Ar–H), 6.58 (s, Ar–CH), 2.23 (s, CH_3) ppm.

2,2′-Bis(3-(carboxymethyl)indolyl)ethylmethane (**3s**, $C_{26}H_{28}N_2O_4$)

Mp 208°C; IR ($CHCl_3$): $\bar{\nu} = 3420$, 3347, 2958, 1730, 1596, 1268, 702 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 11.3$ (s, 2H, COOH), 7.89 (br s, 2H, NH), 7.60–7.63 (m, 8Ar–H), 5.8 (t, CH), 3.8 (s, 4H, CH_2COO), 2.89 (m, 2CH), 1.94 (t, 3CH) ppm.

2,2′-Bis(3-(carboxymethyl)indolyl)(4-methylphenyl)methane (**3t**, $C_{23}H_{24}N_2O_4$)

Mp 221°C; IR ($CHCl_3$): $\bar{\nu} = 3475$, 3131, 2995, 1730, 1608, 1584, 1377, 575 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 12.1$ (s, 2H, COOH), 7.8 (br s, 2H, NH), 7.55–7.61 (m, 8Ar–H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.0$ Hz, 2H), 6.58 (s, Ar–CH), 2.91 (s, 4H, CH_2COO), 2.23 (s, Ar–CH_3) ppm.

2,2′-Bis(3-(carboxyethyl)indolyl)propylmethane (**3u**, $C_{26}H_{28}N_2O_4$)

Mp 115°C; IR ($CHCl_3$): $\bar{\nu} = 3447$, 3347, 3068, 2964, 1724, 1602, 1377, 708 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 11.1$ (s, 2H, COOH), 7.68 (br s, 2H, NH), 7.40–7.43 (m, 8Ar–H), 6.0 (t, CH), 2.91 (m, 8H, CH_2COO), 1.89–1.94 (m, 4CH), 1.82 (s, CH_3) ppm.

2,2′-Bis(3-(carboxyethyl)indolyl)(4-nitrophenyl)methane (**3v**, $C_{29}H_{25}N_2O_4$)

Mp 223°C; IR ($CHCl_3$): $\bar{\nu} = 3475$, 3327, 2940, 2867, 1736, 1638, 1584, 927 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 12.4$ (s, 2H, COOH), 7.9 (br s, 2H, NH), 7.10–7.36 (m, 12Ar–H), 6.54 (s, Ar–CH), 2.87–2.99 (m, 8H, CH_2COO) ppm.

2,2′-Bis(3-(carboxypropyl)indolyl)propylmethane (**3w**, $C_{28}H_{32}N_2O_4$)

Mp 215°C; IR ($CHCl_3$): $\bar{\nu} = 3414$, 3344, 3116, 2922, 1724, 1645, 1602, 781, 690 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 11.2$ (s, 2H, COOH), 7.71 (br s, 2H, NH), 7.02–7.21 (m, 8Ar–H), 5.9 (t, CH), 2.83–2.90 (m, 12H, CH_2COO), 1.8–1.7 (m, 4H, CH_2COO), 1.66 (t, CH_3) ppm.

2,2′-Bis(3-(carboxypropyl)indolyl)(3,4-methylenedioxyphenyl)methane (**3x**, $C_{32}H_{30}N_2O_4$)

Mp 168°C; IR ($CHCl_3$): $\bar{\nu} = 3408$, 3362, 3062, 2934, 1711, 1596, 1243, 933, 744 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 12.4$ (s, 2H, COOH), 7.89 (br s, 2H, NH), 7.41 (d, Ar–H), 7.38 (dd, Ar–H), 7.35 (s, Ar–H) 7.22–7.38 (m, 8H, Ar–H), 6.12 (s, OCH_2O), 5.96 (s, Ar–CH), 3.1–3.4 (m, 12H, CH_2COO) ppm.

2,2′-Dipyrrylmethane (**6a**, $C_9H_{10}N_2$)

Mp 75°C; IR ($CHCl_3$): $\bar{\nu} = 3418$, 3322, 3062, 2934, 1608, 1596, 1243, 933, 744 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.90$ (br s, 2H, NH), 6.70 (m, 2pyrrole-H), 6.16 (q, 2pyrrole-H), 5.90 (m, 2pyrrole-H), 5.40 (s, CH_2) ppm.

2,2′-Dipyrryldimethylmethane (**6b**, $C_{11}H_{14}N_2$)

Mp 108°C; IR ($CHCl_3$): $\bar{\nu} = 3428$, 3325, 3162, 3034, 1608, 1598, 1143, 933, 742 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.80$ (br s, 2H, NH), 6.62 (m, 2pyrrole-H), 6.06 (q, 2pyrrole-H), 5.83 (m, 2pyrrole-H), 2.8 (s, $2CH_3$) ppm.

2,2′-Dipyrryl(methylphenyl)methane (**6c**, $C_{16}H_{16}N_2$)

Mp 176°C; IR ($CHCl_3$): $\bar{\nu} = 3438$, 3325, 3160, 3134, 1609, 1602, 1223, 764 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 7.95$ (br s, 2H, NH), 7.41–7.50 (m, 5Ar–H), 6.81 (m, 2pyrrole-H), 6.30 (q, 2pyrrole-H), 5.94 (m, 2pyrrole-H), 3.1 (s, CH_3) ppm.

2,2′-Dipyrryl(4-chlorophenyl)methane (**6d**, $C_{15}H_{13}N_2Cl$)

Mp 201°C; IR ($CHCl_3$): $\bar{\nu} = 3441$, 3326, 3060, 3132, 1608, 1598, 1323, 767 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 8.06$ (d, $J = 8.9$ Hz, 2Ar–H), 7.98 (s br, 2H, NH), 7.26 (d, $J = 8.9$ Hz, 2Ar–H), 6.76 (m, 2pyrrole-H), 6.15 (q, 2pyrrole-H), 5.84 (m, 2pyrrole-H), 5.56 (s, CH) ppm.

2,2′-Dipyrryl(4-nitrophenyl)methane (**6e**, $C_{15}H_{13}N_3O_2$)

Mp 228°C; IR ($CHCl_3$): $\bar{\nu} = 3442$, 3327, 3160, 3032, 1608, 1602, 1324, 926, 749 cm^{-1}; ^1H NMR ($CDCl_3$): $\delta = 8.16$ (d, $J = 9.0$ Hz, 2Ar–H), 8.01 (s br, 2H, NH), 7.36 (d, $J = 9.0$ Hz, 2Ar–H), 6.8 (m, 2pyrrole-H), 6.18 (q, 2pyrrole-H), 5.87 (m, 2pyrrole-H), 5.58 (s, CH) ppm.

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