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TETRAHEDRON

Application of the Pd-catalyzed heteroarylation to the synthesis of 5-(indol-2′-yl)pyridin-2-one and 5-(indol-2′-yl)pyran-2-one.

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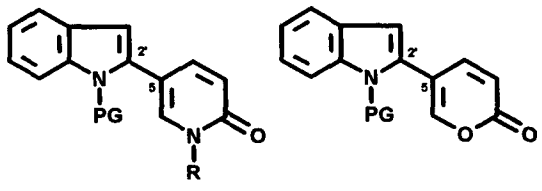
Abstract. The synthesis of 5-(indol-2′-yl)pyridin-2-ones and 5-(indol-2′-yl)pyran-2-one by Pd-catalyzed reactions is described. The best results are obtained using 2-indolylstannanes or 2-indolylzinc halides to be coupled with 5-bromopyridin-2-ones or 5-bromopyran-2-one in the presence of $Pd(PPh_3)_4$ as catalyst. Other Pd-catalyzed reactions are discussed.

Keywords: coupling reactions, palladium, indoles, pyridones, pyrones.

In connection with our program on the synthesis of some indole alkaloids by [4+2]π cycloadditions, we required a convenient method for preparation of unknown 5-(indol-2′-yl)pyridin-2-one and 5-(indol-2′-yl)pyran-2-one (Figure) to be used as dienes.



Figure

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In this report we describe an efficient method based on Pd-catalyzed cross-coupling reactions using different 2-functionalized indoles with 5-functionalized pyran-2-ones and pyridin-2-ones. Palladium cross-coupling reactions are largely used for the formation of the carbon-carbon bond[1], but apart from this palladium chemistry has also been investigated for the preparation and functionalization of indoles.[2]

First we investigated the reaction betwen 2-stannylindole and 5-brominated partners in the presence of Pd(0) according to the Palmisano methodology.[3] The 2-indolylstannanes **1a,b** were prepared by metalation of the corresponding protected *1H*-indoles, followed by quenching with Bu_3SnCl. The purified indolylstannanes were reacted with 5-bromopyridin-2-ones[4] (**2b,c**) and 5-bromopyran-2-one[5] (**2e**) in DMF (110 °C) using $Pd(PPh_3)_4$ as catalyst. When the indole was protected as the *N-p*-methoxybenzenesulfonyl (*N*-PMBS) derivative, only the dimeric compound 7 was detected (Table, entry 1). When the *N*-protecting group was (trimethylsilyl)ethoxymethyl)methyl (SEM) the desired products were obtained in good yields (**3**, 55%, **4**, 71%, **5**, 44%) (entry 2, 3, 10). As the toxicity of organotin compounds greatly limits the large scale development of the reaction, we considered the use of other 2-indolyl anion equivalents.

Our first choice was the 2-indolylzinc derivatives independently developed by Bosch[6] and Sakamoto.[7] The required 2-indolylzinc halides **1c** and **1d** were prepared by treating of the corresponding *N*-PMBS-indole and *N*-SEM-indole with BuLi, followed by lithium-zinc transmetallation with anhydrous $ZnCl_2$. The reaction of *N*-PMBS-indole (**1c**) with **2c** gave rise exclusively to the dimeric compound **7**. This result parallels that obtained in entry 1 and is probably due to the strong electron-withdrawing character of the *N*-PMBS protecting group which decreases the reactivity of the anion equivalent. We decided to enhance the reactivity of the indolylzinc halide by introducing SEM as the indole protecting group. The reaction of **1d** with pyridones **2b** and **2c** furnished the desired products **3** and **4** in 51% and 57% yields respectively (entries 5 and 6). The use of 5-bromopyran-2-one as electrophile resulted in the corresponding product **5** in poor yield (11%, entry 11).

An alternative approach could be to exchange the reactivity of the partners in the reaction exploiting the electrophilic character of 2-haloindoles. Thus we examined the preparation of the anion equivalent of pyridin-2-ones and pyran-2-one. In the event, attempts to generate the stannyl derivative of *N*-benzylpyridin-2-one by transmetallation[8] of the respective lithium derivative were unsuccessful, probably because of the slow conversion of the corresponding bromide **2c** to the lithium derivative. In any case, the lithium bromide exchange reaction of 5-bromo-pyran-2-one is known to give ring opening.[9]

The zinc organometallics **2d, f** derived from 5-iodopyridin-2-one and 5-bromopyran-2-one respectively were easily generated[10] using commercially available zinc dust previously activated with TMSCl and 1,2-dibromoethane in THF. The reaction is complete after 3 h. The subsequent cross-coupling reactions of **2d** and **2f** with 2-iodoindole **1e**, in the presence of $Pd(PPh_3)_4$, were sluggish and not suitable (entries 7 and 12).

The oxidative coupling[11] of pyridone **2a** with 2-stannylindole **1b** by $Pd(AcO)_2$ failed to give the desired product and only the dimeric compound **8** was obtained (entry 8). When *N*-PMBS-2-iodoindole **1f** (entry 9) was the electrophile in the cross-coupling reaction, the unexpected product **9** was obtained.

While the preparation of 5-(indol-2′-yl)pyridin-2-ones could be efficiently made by 2-indolylzinc halide methodology, this was not the case for 5-(indol-2′-yl)pyran-2-one. With the aim of preparing a pyrone derivative not requiring to the use of the 2-stannylindole, we investigated the coupling of indol-2-yl boron compounds.

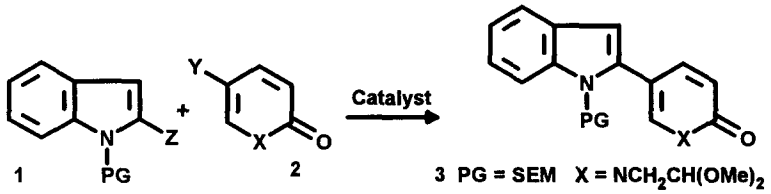
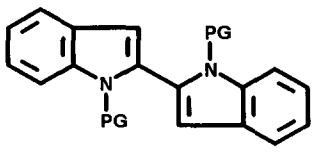


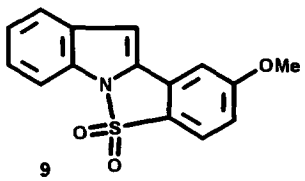
Table.

Entry		PG	Z		Y	X	Catalyst	Product	Yield %
1	**1a**	PMBS	$SnBu_3$	**2b**	Br	$NCH_2CH(OMe)_2$	$Pd(PPh_3)_4$	**7**	14
2	**1b**	SEM	$SnBu_3$	**2b**	Br	$NCH_2CH(OMe)_2$	$Pd(PPh_3)_4$	**3**	55
3	**1b**	SEM	$SnBu_3$	**2c**	Br	NCH_2Ph	$Pd(PPh_3)_4$	**4**	71
4	**1c**	PMBS	ZnCl	**2c**	Br	NCH_2Ph	$Pd(PPh_3)_4$	**7**	12
5	**1d**	SEM	ZnCl	**2b**	Br	$NCH_2CH(OMe)_2$	$Pd(PPh_3)_4$	**3**	51
6	**1d**	SEM	ZnCl	**2c**	Br	NCH_2Ph	$Pd(PPh_3)_4$	**4**	57
7	**1e**	SEM	I	**2d**	ZnI	NCH_2Ph	$Pd(PPh_3)_4$	**4**	10
8	**1b**	SEM	$SnBu_3$	**2a**	H	$NCH_2CH(OMe)_2$	$Pd(AcO)_2$	**8**	23
9	**1f**	PMBS	I	**2a**	H	$NCH_2CH(OMe)_2$	$Pd(AcO)_2$	**9**	12
10	**1b**	SEM	$SnBu_3$	**2e**	Br	O	$Pd(PPh_3)_4$	**5**	44
11	**1d**	SEM	ZnCl	**2e**	Br	O	$Pd(PPh_3)_4$	**5**	11
12	**1e**	SEM	I	**2f**	ZnBr	O	$Pd(PPh_3)_4$	**5**	10
13	**1g**	BOC	$B(OH)_2$	**2e**	Br	O	$Pd(PPh_3)_4$	**6**	12
14	**1h**	BOC	$B(Et)^-_3Li^+$	**2g**	Br	O	$Pd(PPh_3)_4$	**6**	5

SEM = 2-(trimethylsilyl)ethoxymethyl; PMBS = *p*-methoxybenzenesulfonyl; BOC = *tert*-butoxycarbonyl



7 PG = PMBS
8 PG = SEM



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The palladium-catalyzed cross-coupling between trivalent organoboron compounds and organic halides in the presence of a base is an effective method for C-C bond formation.[12] The cross-coupling reaction of indolyl boronic acid **1g**,[13] derived from *N*-BOC-indole by direct metallation, with 2-bromopyran-2-one, yielded the adduct **6** (12%). The reaction of triethyl-(*N*-BOC-indol-2′-yl)borate **1h** (derived from *N*-BOC-indole and BuLi, followed by treatment with triethylborane)[14] led to **6** in very low yield (5%).

In conclusion practical and efficient synthesis of 5-(indol-2′-yl)pyridin-2-ones and 5-(indol-2′-yl)pyran-2-one have been described. While 5-(indol-2′-yl)pyridin-2-ones could be prepared in appreciable yield using either 2-indolylstannane or 2-indolylzinc halide, the preparation of 5-(indol-2′-yl)pyran-2-one is possible only using 2-indolylstannane. Finally, this study has contributed to finding an efficient production[15] of new compounds belonging to the family of 5-substituted 2*H*-pyran-2-ones, whose other members are well-known as cardiotonic agents,[16] insect defense[17] and antiviral agents.[18]

EXPERIMENTAL[19]

Preparation of 2-(tributylstannyl)-1-(*p*-methoxybenzenesulfonyl)indole (1a). To a solution of 1-(*p*-methoxybenzensulfonyl)indole[13] (0.58 g, 2.0 mmol) in THF (5 ml) at -10 °C BuLi (1.5 ml, 1.6 M solution) was added. After 10 min at -10 °C, Bu_3SnCl (0.64 ml, 2.36 mmol) was added at -20 °C. After 30 min at r.t. the reaction mixture was poured into 25 ml of NH_4Cl 5% and extracted with AcOEt. The product was isolated by flash chromatography (hexane:Et_2O 4:1). Yield: 72%. Oil. R_f 0.42 (hexane:Et_2O 4:1). IR ($CHCl_3$) 1595, 1485, 1450, 1370, 1330 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.82 (1H, m), 7.62 (2H, AA′ part of AA′BB′ system), 7.50 (1H, m), 7.18 (2H, m), 6.84 (2H, BB′ part of AA′BB′ system), 6.80 (1H, s), 3.80 (3H, s), 1.80-0.80 (27H, m); ^{13}C-NMR ($CDCl_3$) δ 163.1, 143.4, 138.2, 131.9, 130.8, 128.5 (2C), 123.6, 122.7, 120.2, 114.1 (3C), 113.6, 55.5, 31.2 (3C), 14.3 (3C), 13.6 (3C), 11.9 (3C).

Preparation of 2-iodo-1-[2-(trimethylsilyl)ethoxymethyl]indole (1e). To a solution of 1-[2-(trimethylsilyl)-ethoxymethyl]indole[3a] (1.0 g, 4.04 mmol) in dry THF (7 ml) under N_2, BuLi 1.6M in hexane (2.75 ml, 4.4 mmol) was added dropwise at -15 °C. After 10 min stirring at this temperature, the resulting orange solution was cooled to -40 °C and solid NIS (1.03 g, 4.5 mmol) was added in small portions. The reaction mixture was stirred for 2 h at r.t., poured into 25 ml of NH_4Cl 5% and extracted with AcOEt.. The product was isolated by flash chromatography (hexane:CH_2Cl_2 3:1). Yield: 36%. Yellow oil, R_f 0.15 (hexane:CH_2Cl_2 3:1). IR ($CHCl_3$) 1460, 1295 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.52 (1H, d, J = 7.5 Hz), 7.48 (1H, d, J = 7.5 Hz), 7.18 (1H, t, J = 7.5 Hz), 7.10 (1H, t, J = 7.5 Hz), 6.72 (1H, s), 5.51 (2 H, s), 3.55 (2H, t, J = 8.0 Hz), 0.91 (2H, t, J = 8.0 Hz), 0.00 (9H, s); Anal. Calcd for $C_{14}H_{20}NOSiI$: C 45.04, H 5.40, N 3.75. Found: C 45.23, H 5.45, N 3.80.

Preparation of 2-iodo-1-(*p*-methoxybenzenesulfonyl)indole (1f). To a solution of 1-(*p*-methoxybenzene sulfonyl)indole (1.0 g, 3.5 mmol) in dry THF (15 ml), BuLi 2.5M in hexane (1.8 ml) was added dropwise at -78 °C. After 20 min stirring at r.t., NIS (1.12 g, 5 mmol) was added in small portions at -78 °C. The reaction

mixture was stirred for 2 h at r.t., poured into 25 ml of NH_4Cl 5% and extracted with AcOEt. The product was isolated by flash chromatography (hexane:Et_2O 5:1). Yield: 60%. m.p. 125 °C; R_f 0.26 (hexane:Et_2O 5:1). IR ($CHCl_3$) 1585, 1480, 1370 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.28 (1H, d, J = 8.3 Hz), 7.83 (2H, AA′ part of AA′BB′ system), 7.45-7.21 (3H, m), 6.86 (2H, BB′ part of AA′BB′ system), 6.72 (1H, s), 3.80 (3H, s); ^{13}C-NMR ($CDCl_3$):δ 163.9, 139.4, 131.7, 130.9, 129.4 (2C), 124.8, 124.0, 123.6, 119.7, 115.4, 114.3 (2C), 71.7, 55.6; Anal. Calcd for $C_{15}H_{12}NO_3SI$: C 43.60, H 2.93, N 3.39. Found: C 43.73, H 2.98, N 3.44.

Cross-coupling reaction with indol-2-ylstannane (1a, 1b[3a]). To a dry and degassed solution of $Pd(PPh_3)_4$ (0.05 mmol, 5%) and halide **2b**, **2c**, **2e** (1.0 mmol) in DMF (5 ml), indol-2-ylstannane **1a**, **1b** (1.0 mmol) was added. The mixture was then heated to 110 °C with stirring. After the reaction was complete (TLC monitoring), the mixture was cooled to r.t., added to 20 ml of NH_4Cl 5% and extracted with AcOEt. The product was isolated by flash chromatography (silica gel).

Cross-coupling reaction with indol-2-ylzinc chloride (1c, 1d). To a dry solution of 1-(*p*-methoxybenzenesulfonyl)indole or 1-[2-(trimethylsilyl)ethoxymethyl]indole (1.2 mmol) in THF (3 ml), BuLi 1.6M in hexane (830 μl, 1.33 mmol, 1.1 eq) was slowly added at -15°C , and the mixture was stirred for 10 min at this temperature. The resulting orange solution was then cooled to -78°C and treated with a 0.6M solution of anhydrous $ZnCl_2$ (fused by flame-drying under reduced pressure for 5 min) in THF (2 ml, 1.2 mmol, 1.0 eq), and the stirring was continued for 5 min at this temperature: the solution assumed a pale yellow colour. In a separate flask, $Pd(PPh_3)_4$ (0.036 mmol, 3%) and halide **2b**, **2c**, **2e** (1.2 mmol) are dissolved in dry THF (2 ml). The resulting solution was then added to the solution of indol-2-ylzinc chloride **1c**, **1d** prepared above, at -78 °C. The mixture is allowed to stir at r.t. for 5 min and then refluxed. After the reaction was complete, the reaction mixture was cooled to r.t., added to 20 ml of NH_4Cl 5% and extracted with AcOEt. The product was isolated by flash chromatography (silica gel).

Cross-coupling reaction with 2-iodoindole (1e). Zn dust (65 mg, 1 mmol, 14.8 eq.; Aldrich, 325 mesh) was suspended in dry THF (1.5 ml). 1,2-Dibromoethane (5 ml, 0.058 mmol) was added under vigorous stirring, the mixture heated to 60 °C for 1 min and cooled to r.t.; then TMSCl (5 ml, 0.036 mmol) was added and the stirring was continued for 15 min at r.t. A solution of 5-iodo-1-benzylpyridin-2-one or 5-bromopyran-2-one **2e** (0.288 mmol, 1.5 eq.) in dry THF (1.5 ml) was added and the mixture was refluxed until the formation of the zinc derivative **2d**, **2f** was complete (TLC monitoring). The excess zinc dust was allowed to settle and the resulting clear solution of the zinc reagent was added at 0°C to a solution of 2-iodo-1-[2-(trimethylsilyl) ethoxymethyl]indole **1e** (0.187 mmol, 1 eq) and $Pd(PPh_3)_4$ (0.01 mmol, 5%) dissolved in dry THF (1.5 ml): the reaction mixture is stirred for 5 min at r.t. and then refluxed. After the reaction was complete, the reaction mixture was cooled to r.t., added to 10 ml of NH_4Cl 5% and extracted with AcOEt. The product was isolated by flash chromatography.

5-{1'-[2'-(Trimethylsilyl)ethoxymethyl]indol-2'-yl}-1-(2,2-dimethoxyethyl)pyridin-2-one (3). Yellow solid, m.p. 150 ^{0}C; R_f 0.25 (AcOEt : CH_2Cl_2 1:2). IR ($CHCl_3$) 1651, 1430 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.74 (1H, d, *J* = 3.0 Hz), 7.67 (1H, dd, *J* = 9.0 Hz, *J* = 3.0 Hz), 7.57 (1H, d, *J* = 7.5 Hz), 7.45 (1H, d, *J* = 7.5 Hz), 7.24 (1H, t, *J* = 7.5 Hz), 7.14 (1H, t, *J* = 7.5 Hz), 6.62 (1H, d, *J* = 9.0 Hz), 6.31 (1H, s), 5.38 (2H, s), 4.67 (1H, t, *J* = 5.8 Hz), 4.06 (2H, d, *J* = 5.8 Hz), 3.61 (2H, t, *J* = 7.5 Hz), 3.42 (6H, s), 0.91 (2H, t, *J* = 5.8 Hz), 0.0 (9 H, s); ^{13}C-NMR ($CDCl_3$): 161.9, 141.3, 139.1, 138.3, 136.9, 128.0, 122.5, 120.8, 120.5, 120.2, 111.2, 109.8, 102.8, 102.1, 72.6, 66.1, 55.4 (2C), 51.9, 18.1, -1.43 (3C); FABMS 429 (M+H); Anal. Calcd for $C_{23}H_{32}N_2O_4$ Si: C 64.45, H 7.53, N 6.54. Found: C 64.38, H 7.65 N 6.43.

5-{1'-[2'-(Trimethylsilyl)ethoxymethyl]indol-2'-yl}-1-benzylpyridin-2-one (4). Amorphous solid. R_f 0.23 (AcOEt:CH_2Cl_2 1:25).IR ($CHCl_3$) 1660, 1450 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.80 (1H, d, *J* = 3.0 Hz), 7.65 (1H,dd, *J* = 9.0 Hz, *J* = 3.0 Hz), 7.56 (1 H, d, *J* = 7.5 Hz), 7.45 (1H, d, *J* = 7.5 Hz), 7.35 - 7.21 (6H, m), 7.14 (1H, t, *J* = 7.5 Hz), 6.70 (1H, d, *J* = 9.0 Hz), 6.50 (1H, s), 5.38 (2H, s), 5.22 (2H, s), 3.61 (2 H, t, *J* = 7.5 Hz), 0.95 (2H, t, *J* = 5.8 Hz), 0.0 (9H,s); ^{13}C-NMR ($CDCl_3$) 161.7, 140.8, 137.2, 138.3, 136.1, 129.1, 128.8-128.2 (5C), 122.5, 120.8, 120.4, 120.2, 116.1, 111.7, 109.6, 102.7, 72.6, 66.1, 52.2, 8.0, 1.4 (3C); FABMS 431 (M+H); Anal. Calcd for $C_{26}H_{30}N_2O_2Si$: C 72.52, H 7.03, N 6.51. Found: C 72.68, H 7.18 N 6.71.

5-{1'-[2'-(Trimethylsilyl)ethoxymethyl]indol-2'-yl}pyran-2-one (5). White foam. R_f 0.38 (hexane:Et_2O 1:1). IR ($CHCl_3$) 1730, 1640 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 7.90 (1H, d, *J* = 3 Hz),7.68 (1H, dd, *J* = 10, 3 Hz), 7.61 (1H, d, *J* = 8 Hz), 7.45 (1H, d, *J* = 8 Hz), 7.28 (1H, t, *J* = 8 Hz), 7.16 (1H, t, *J* = 8 Hz), 6.58 (1H, s), 6.42 (1H, d, *J* = 10 Hz), 5.41 (2H, s), 3.55 (2H, t, *J* = 8 Hz), 0.94 (2H, t, *J* = 8 Hz), 0.01 (9H, s); ^{13}C-NMR ($CDCl_3$) δ 160.3, 145.5, 144.6, 138.3, 133.1, 127.4, 122.8, 120.7, 120.6, 115.8, 112.3, 109.5, 103.7, 72.3, 66.0, 17.4, -1.6 (3C). EIMS 341 (50%); 283 (45%); 224 (35%); Anal. Calcd for $C_{19}H_{23}NO_3Si$: C 66.83, H 6.79, N 4.10 Found: C 66.74, H 6.91 N 4.33.

Cross-coupling reaction with indol-2-ylboronic acid (1g). To a solution of 1-BOC-indole (300 mg, 1.46 mmol) in dry THF (20 ml), BuLi 2.5M in hexane (680 µl) was added dropwise at -78°C. After 20 min stirring at r.t. $B(OMe)_3$ (1.66 ml, 1.46 mmol) was added at -78°C. The reaction was stirred for 2 h at r.t., then it was poured into 10 ml of H_2O, extracted with AcOEt and evaporated to give boronic acid **1g** as a white cristaline solid. To a stirred mixture of 5-bromopyran-2-one (210 mg, 1.2 mmol), $Pd(PPh_3)_4$ (5 mmol/ 100 mmol 1-BOC-indole) in 15 ml of 1,4-dioxane was added **1g** (300 mg, 1.2 mmol) followed by Na_2CO_3 (2M solution, 600 µl) and LiCl (48 mg, 1.13 mmol). The mixture was then refluxed for 4 h and then was concentrated *in vacuo* and the residue was partitioned between H_2O and CH_2Cl_2. The aqueous phase was separated and extracted again with CH_2Cl_2.The product was isolated by flash chromatography (hexane:AcOEt 10:1). Yield:12%.

Cross-coupling reaction with triethyl indol-2-ylborate (1h) To a solution of 1-BOC-indole (168 mg, 0.65 mmol) in dry THF (5 ml), BuLi 2.5M in hexane (670 µl) was added dropwise at -20 °C. After stirring 15 min at -20 °C, BEt_3 (65 µl 0.65 mmol) was added, the reaction was stirred for 1 h at r.t. to give **1h**. 5-Bromopyran-2-

one (170 mg, 0.97 mmol) in 3 ml of THF was added followed by catalitic amount of $Pd(PPh_3)_4$. The reaction was heated to reflux for 2 h, cooled to r.t. and the solvent was evaporated. The residue was partitioned between CH_2Cl_2 and $NaHCO_3$ aqueous. After solvent removal under reduced pressure the residue was chromatographed on silica gel (AcOEt:hexane 2:3) to obtain the product. Yield 5 %.

5-(1'-*tert*-Butoxycarbonylindol-2'-yl)pyran-2-one (6). m.p. 140 °C; R_f 0.4 (hexane:AcOEt 3:2). IR ($CHCl_3$) 1715, 1480, 1360, 1320, 1150, 1120 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ 8.15 (1H, d, J = 8 Hz), 7.59 (1H, d, J = 3Hz), 7.56 (1H, d, J = 8 Hz), 7.48 (1H, dd, J = 10, 3 Hz), 7.39-7.21 (2H, m), 6.59 (1H, s), 6.39 (1H, d, J = 10 Hz), 1.56 (9H, s); ^{13}C-NMR ($CDCl_3$) δ 160.7, 149.7, 149.3, 145.6, 137.1, 132.2, 128.5, 125.1, 123.3, 120.1, 115.8, 115.3, 114.5, 111.3, 84.8, 29.0 (3C); EIMS 311 (100%), 238 (11%), 266 (20%); Anal. Calcd for $C_{18}H_{17}NO_4$: C 69.44, H 5.51, N 4.50 Found: C 69.64, H 5.76 N 4.33.

1,1'-Bis(p-methoxybenzenesulfonyl)-2,2'-bi(1H-indole) (7). m.p. 176 °C; R_f 0.18 (CH_2Cl_2:hexane 3:1). IR ($CHCl_3$) 1585, 1490, 1430, 1375 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 8.25 (2H, d, J = 8 Hz), 7.61 (4H, AA' part of AA'BB' system), 7.41 (2H, t, J = 8 Hz), 7.36 (2H, d, J = 8 Hz), 7.29 (2H, t, J = 8 Hz), 6.86 (4H, AA' part of AA'BB'system), 6.61 (2H, s), 3.80 (6H, s); ^{13}C-NMR ($CDCl_3$) δ 165.6 (2C), 137.3 (2C), 130.5 (2C), 130.2 (2C), 129.2 (4C), 128.3 (2C), 125.4 (2C), 123.5 (2C), 121.1 (2C), 115.1 (2C), 114.7 (2C), 114.0 (4C), 55.5 (2C); EIMS 572 (20%); 337 (100%); 229 (70%); Anal. Calcd for $C_{30}H_{24}N_2O_6S_2$: C 62.92, H 4.23, N 4.89 Found: C 62.83, H 4.34 N 4.36.

1,1'-Bis[2-(trimethylsilyl)ethoxymethyl]-2,2'-bi(1H-indole) (8). m.p. 103 °C; R_f 0.5 (Et_2O:hexane 1:1). IR ($CHCl_3$) 1380, 1285, 1240, 1020 cm^{-1}; ^{1}H-NMR ($CDCl_3$, 300 MHz) δ 7.67 (2H, d, J = 8 Hz), 7.55 (2H, d, J = 8 Hz), 7.30 (2H, t, J = 8 Hz), 7.21 (2H, t, J = 8 Hz), 6.82 (2H, s), 5.43 (4H, s), 3.49 (4H, t, J = 8 Hz), 0.88 (4H, t, J = 8 Hz), 0.00 (18H, s); ^{13}C-NMR ($CDCl_3$) δ 138.01 (2C), 131.02 (2C), 128.12 (2C), 122.88 (2C), 120.94 (2C), 120.79 (2C), 110.51 (2C), 106.63 (2C), 73.16 (2C), 65.91 (2C), 17.97 (2C), -1.40 (6C). FABMS 493 (M+H); Anal. Calcd for $C_{28}H_{40}N_2O_2Si_2$: C 68.24, H 8.19, N 5.68 Found: C 68.32, H 8.23 N 5.73.

Compound 9. m.p. (dec.) 80 °C; R_f 0.4 (CH_2Cl_2); ^{1}H-NMR ($CDCl_3$) 7.72 (1H, d, J = 9 Hz), 7.70 (1H, d, J = 8 Hz), 7.60 (1H, d, J = 8 Hz), 7.37 (1H, t, J = 8 Hz), 7.22 (1H, t, J = 8 Hz), 7.16 (1H, d, J = 2 Hz), 6.97 (1H, dd, J = 8, 2 Hz), 6.81 (1H, s), 3.95 (3H, s); ^{13}C-NMR ($CDCl_3$) δ 162.5, 140.1, 135.0 (2C), 131.2, 130.1, 125.9, 124.0, 123.3, 122.5, 115.4, 111.7, 106.9, 100.8, 56.0; EIMS: 285 (100%); Anal. Calcd for $C_{15}H_{11}NO_3S$: C 63.14, H 3.89, N 4.90 Found: C 63.20, H 3.77 N 4.86.

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