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The reaction of *N*-tosyl imines with heteroaromatic compounds: a new access to triheteroarylmethanes

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ABSTRACT

Useful triheteroarylmethanes were prepared by the double Friedel–Crafts reaction of a wide variety of aromatic *N*-tosyl imines with furan, thiophene, and pyrrole in the presence of $Cu(OTf)_2$ and Montmorillonite K-10 clay catalysts.

1. Introduction

Triarylmethanes have attracted much attention as leuco dyes,[1] protecting groups[2] and photochromic agents.[3] Furthermore, the ring hydroxylated triarylmethanes show antitumor and antioxidant properties.[4] Within the context of wide-ranging applications of triarylmethanes, triheteroarylmethanes find many applications in non-linear optics and conducting polymers.[5] Diheteroarylmethanes are also used in the food industry as natural components of certain food and beverage items.[6] While many methods, such as the direct condensation of arenes with aldehydes and the reaction of benzhydroles with aromatic compounds[7] are available for the preparation of triarylmethanes, the synthesis of triheteroarylmethanes is less developed. These compounds have been prepared through the condensation of heteroaromatic compounds with (i) aldehydes,[8a–f] (ii) vinyl aromatic compounds[8g] and (iii) triethylorthoformate[8h,i] in the presence of different catalysts, such as P_2O_5,[8e] $AuCl_3$,[8d,f] $NaHSO_4$. SiO_2,[8c] Montmorillonite clays[8a,c,h] and ionic liquids.[8b] The quest for cheap, environmentally friendly catalysts and mild reaction conditions is still a major challenge for the synthesis of triheteroarylmethanes. Herein we report a convenient and practical method for the synthesis of these compounds by the condensation of heteroaromatic compounds with *N*-tosyl imines using two reusable and efficient catalysts, $Cu(OTf)_2$ and Montmorillonite K-10 clay.

Recent work in our laboratories have shown that metal triflates are effective reusable catalysts for the addition of pyrrole to α,β-unsaturated compounds and *N*-tosyl imines.[9] *meso*-Substituted dipyrromethanes were obtained by double Friedel–Crafts reaction of pyrrole with *N*-tosyl imines and these compounds were used in the synthesis of *meso*-substituted tetraphenylporphyrins.[10] In an effort to further broaden the repertoire of applications of metal triflates as environmentally benign catalysts for organic reactions, we decided to extend our studies to the synthesis of triheteroarylmethanes.

2. Results and discussion

The condensation of *N*-((1*H*-pyrrol-2-yl)methylene)-4-methylbenzenesulfonamide (**1a**) with pyrrole was selected as a model reaction to determine the optimum reaction conditions (Scheme 1). Our attempt was started by investigating the effect of different *N*-tosyl imine/pyrrole ratios on the yield of product **2a**. Reactions with 1–10 equiv of pyrrole were performed in THF in the presence of $Cu(OTf)_2$ (10 mol %) at room temperature and resulted in low yields (<20%). When the amount of pyrrole was increased and used as both reagent and solvent, the highest yield (85%) was obtained with 40 equiv of pyrrole. Further increasing the equivalents of pyrrole did not affect the yield of **2a**.

Then the activity of a number of catalysts was determined using the model reaction (Scheme 1). A control experiment showed that no reaction was observed in the absence of catalyst even after a long reaction time (48 h) (Table 1, entry 1). Screening of a series of

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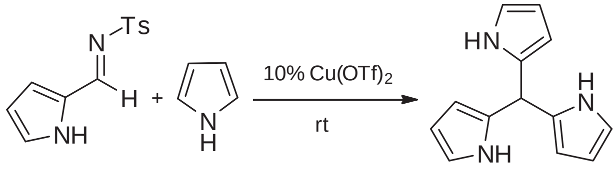


1a **2a**

Scheme 1. Synthesis of tri(1*H*-pyrrol-2-yl)methane.

metal triflate catalysts for the model reaction revealed that Nd and La-triflates catalyzed the reaction with low yields (Table 1, entries 8 and 9). Gd, Y, Yb, Sc, and Zn-triflates gave the product with moderate yields (Table 1, entries 3–7). The highest yield of **2a** (85%) was obtained with $Cu(OTf)_2$ (Table 1, entry 2).

Table 1
Effects of catalysts on the synthesis of **2a**[a]

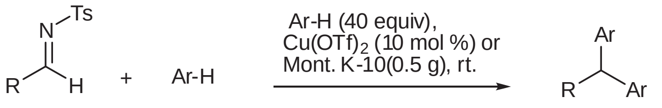
Entry	Catalyst	Time/h	Yield[b] (%) of **2a**
1	None	48	—
2	$Cu(OTf)_2$	1	85
3	$Gd(OTf)_3$	1	65
4	$Y(OTf)_3$	1	58
5	$Yb(OTf)_3$	1	77
6	$Sc(OTf)_3$	1	54
7	$Zn(OTf)_2$	1	65
8	$Nd(OTf)_3$	1	23
9	$La(OTf)_3$	1	24
10	H_2SO_4	0.5	65
11	HCl	0.5	55
12	TFA	0.5	82
13	TsOH	1	84
14	$CuBr_2$	3	82
15	$AlCl_3$	3	44
16	$FeCl_3$	2	80
17	Mont. KSF[c]	48	—
18	Mont. K-10[c]	2	85

[a] Reaction conditions: *N*-tosyl imine (0.5 mmol), pyrrole (20 mmol), catalyst (10 mol %), room temperature.
[b] Yield refers to pure product after column chromatography.
[c] Clay (0.5 g) was used.

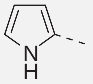
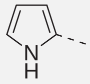
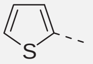
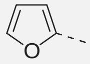
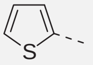
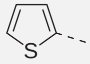
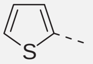
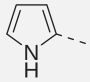
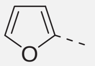
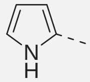
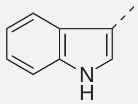
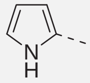
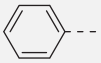
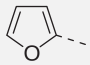
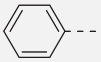
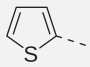
These variations in the product yields prompted us to examine other Lewis acids or protic acids and compare their activity with $Cu(OTf)_2$. Two liquid acid catalysts, H_2SO_4 and HCl, yielded the product with 65% and 55% yields, respectively (Table 1, entries 10 and 11). Some traditional catalysts, such as $CuBr_2$, $FeCl_3$, and *p*-toluenesulfonic acid catalyzed the reaction with comparable yields to $Cu(OTf)_2$ (80–84% yields). Two clays, KSF and K-10, having wide applications in organic synthesis were also tested. Although Montmorillonite K-10 clay gave the product with 85% yield, KSF clay did not provide any product at all (Table 1, entries 17 and 18).

Having found that two non-toxic, environmentally benign, reusable compounds, $Cu(OTf)_2$ and Montmorillonite K-10 clay, are the most effective catalysts in the synthesis of triheteroarylmethanes, we then tested the applicability of the current method to the reaction of different *N*-tosyl imines with heteroaromatic compounds. As shown in Table 2, $Cu(OTf)_2$ catalyst formed all products within a shorter time than Montmorillonite K-10 did. In all cases except **2e** and **2f**, the reactions gave higher yields with $Cu(OTf)_2$ than with Montmorillonite K-10. $Cu(OTf)_2$ promoted the reaction of phenyl substituted *N*-tosyl imine with thiophene in low yields, while Montmorillonite K-10 failed to catalyze this reaction (Table 2, entries 15 and 16).

Table 2
$Cu(OTf)_2$ and Mont. K-10 catalyzed reactions of *N*-tosyl imines with heteroaromatic compounds



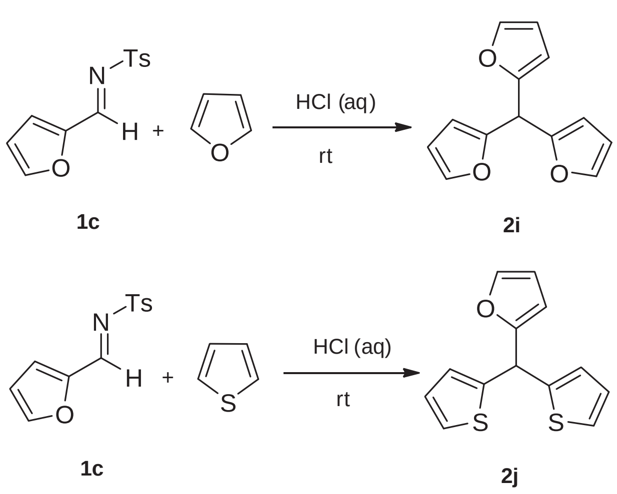
1 **2**

Entry	R	Ar	Product	Catalyst	Time (h)	Yield[a] (%)
1	1a 		**2a**	$Cu(OTf)_2$	1	85
2				Mont. K-10	2	85
3	1b 		**2b**	$Cu(OTf)_2$	1	60
4				Mont. K-10	4	40
5	1b 		**2c**	$Cu(OTf)_2$	1	62
6				Mont. K-10	2[b]	40
7	1b 		**2d**	$Cu(OTf)_2$	1	80
8				Mont. K-10	2	75
9	1c 		**2e**	$Cu(OTf)_2$	1	87
10				Mont. K-10	6	94
11	1d 		**2f**	$Cu(OTf)_2$	1	55
12				Mont. K-10	4	66
13	1e 		**2g**	$Cu(OTf)_2$	1	60
14				Mont. K-10	4	26
15	1e 		**2h**	$Cu(OTf)_2$	4[b]	30
16				Mont. K-10	24	—

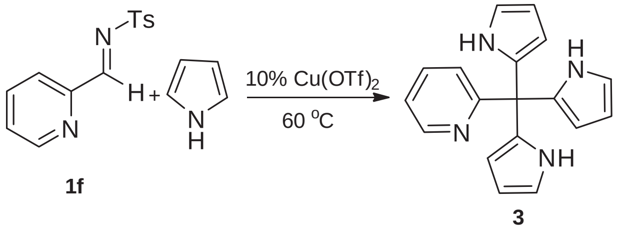
[a] Yield refers to pure product after column chromatography.
[b] The reaction was carried out at 60 °C.

The same method was applied to the addition of furane and thiophene to *N*-(furan-2-ylmethylene)-4-methylbenzenesulfonamide (**1c**). However, studies with $Cu(OTf)_2$ and Montmorillonite K-10 catalysts proved ineffective, providing recovered starting materials. Taking account of this failure, other catalysts and harsher reaction conditions were carried out. **2i** and **2j** were synthesized in the presence of aqueous HCl at room temperature in 89% and 30% yields, respectively (Scheme 2).

Moreover, we tested $Cu(OTf)_2$ and Montmorillonite K-10 clay on the reaction of 2-pyridyl substituted *N*-tosyl imine **1f** with pyrrole under the conditions given in Table 2. Montmorillonite K-10 did not provide any product and only the starting materials were recovered after long reaction times. Surprisingly, $Cu(OTf)_2$ catalyzed the reaction by affording a triple arylation product **3** at 60 °C in 25% yield (Scheme 3).



Scheme 2. Synthesis of triheteroarylmethanes **2i** and **2j**.



Scheme 3. Synthesis of tetraheteroarylmethane **3**.

3. Conclusion

In summary, we have described a new method for the preparation of triheteroarylmethanes through the double Friedel–Crafts reaction of a wide variety of aromatic *N*-tosyl imines with furan, thiophene, and pyrrole in the presence of $Cu(OTf)_2$ and Montmorillonite K-10 clay catalysts. The notable features of this method are the mild reaction conditions, cleaner reaction profiles, and the use of recoverable environmentally friendly catalysts.

4. Experimental

4.1. General

Commercially available reagents and solvents were used without further purification. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using $SiMe_4$ as an internal reference with Bruker 400 FT NMR spectrometer. Data for ^1H are reported as follows: chemical shift (ppm) and multiplicity (s=singlet, d=doublet, t=triplet, dd=doublet of doublet, m=multiplet, br s=broad singlet). Coupling constants are expressed as *J* values in hertz. Data for ^{13}C NMR are reported as parts per million. Infrared spectra were taken by ATR (Nicolet iS10) and are reported in cm^{-1}. Elemental analysis experiments were performed by Elementar Micro Vario CHNS. Melting points were recorded on Gallenkamp melting-point apparatus. Reactions were monitored by thin layer chromatography using 60F silica gel plates. Flash column chromatography was performed on silica gel 60 F_{254} (230–400 mesh). The spots were visualized with UV light (λ=254 nm). *N*-tosyl imines (**1a**–**f**) are synthesized in high yields by the reaction of *p*-toluenesulfonamide and aldehydes in the presence of *p*-toluenesulfonic acid.

4.2. General procedure for $Cu(OTf)_2$ and Montmorillonite K-10 clay catalyzed synthesis of triarylmethanes (2a–h)

N-Tosyl imine (0.5 mmol) was dissolved in excess heteroaromatic compound (20 mmol) and catalyst (0.05 mmol $Cu(OTf)_2$ or 0.5 g Montmorillonite K-10) was added to the reaction mixture at the temperature indicated in Table 2. The reaction was monitored with TLC and completed at the appropriate time indicated in Table 2. The catalyst was removed from the reaction medium by subjecting the mixture to a short flash silica gel chromatography using ethyl acetate as an eluent. The eluent was removed under reduced pressure and the residue was purified by flash silica gel chromatography.

4.3. General procedure for HCl (aq) catalyzed synthesis of triarylmethanes (2i and 2j)

N-(Furan-2-ylmethylene)-4-methylbenzenesulfonamide (**1c**) (0.5 mmol) was dissolved in excess heteroaromatic compound (20 mmol) and then 1 mL of concd HCl (aq) was added to the reaction mixture at room temperature. The reaction was monitored with TLC and completed after 24 h. The mixture was subjected to a short flash silica gel chromatography using ethyl acetate as an eluent. The eluent was removed under reduced pressure and the residue was purified by flash silica gel chromatography.

4.4. Experimental procedure for the synthesis of 2-(tri(1*H*-pyrrol-2-yl)methyl)pyridine (3)

4-Methyl-*N*-(pyridin-2-ylmethylene)benzenesulfonamide (**1f**) (0.5 mmol) was dissolved in excess pyrrole (20 mmol) and then Cu $(OTf)_2$ (0.05 mmol) was added to the reaction mixture at room temperature. The reaction was heated at 60 °C by monitoring with TLC. After 6 h, the mixture was cooled to room temperature and subjected to a short flash silica gel chromatography using ethyl acetate as an eluent. The eluent was removed under reduced pressure and the residue was purified by flash silica gel chromatography.

4.5. Spectroscopic data of the products

*4.5.1. Tri(1H-pyrrol-2-yl)methane (**2a**)*[8g]. Pale yellow crystals; mp 133–134 °C; yield: 90 mg, 85%; R_f 0.34 (1:3 EtOAc/hexane); IR (ATR): 3449, 3369, 3106, 1559, 1464, 1403, 1315, 1258, 1125, 1087, 1030, 973, 878, 821, 772, 722, 661 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.35 (s, 1H), 5.92 (br s, 3H), 6.06 (dd, *J*=2.8, 5.6, 3H), 6.50–6.52 (m, 3H), 7.68 (br s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 37.3, 106.9, 108.6, 117.3, 131.1. Anal. Calcd for $C_{13}H_{13}N_3$: C, 73.91; H, 6.20; N, 19.89. Found: C, 73.60; H, 6.42; N, 19.98.

*4.5.2. 2,2′-(Thiophen-2-ylmethylene)difuran (**2b**).* Brown viscous oil; yield: 69 mg, 60%; R_f 0.77 (1:3 EtOAc/hexane); IR (ATR): 3118, 2963, 2927, 2852, 1731, 1592, 1501, 1434, 1378, 1228, 1164, 1147, 1073, 1009, 946, 885, 760, 731, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.65 (s, 1H), 6.07 (d, *J*=3.2, 2H), 6.26 (dd, *J*=1.6, 3.2, 2H), 6.82–6.83 (m, 1H), 6.85–6.89 (m, 1H), 7.13 (dd, *J*=1.2, 5.2, 1H), 7.29–7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 40.0, 107.3, 110.3, 124.8, 125.8, 126.7, 142.0, 142.3, 153.7. Anal. Calcd for $C_{13}H_{10}O_2S$: C, 67.80; H, 4.38; S, 13.92. Found: C, 67.55; H, 4.42; S, 14.06.

*4.5.3. Trithiophen-2-ylmethane (**2c**).* Brown viscous oil; yield: 81 mg, 62%; R_f 0.80 (1:3 EtOAc/hexane); IR (ATR): 3102, 2963, 2927, 2852, 1735, 1457, 1378, 1271, 1231, 1104, 1016, 862, 806, 691 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 6.04 (s, 1H), 6.86–6.88 (m, 6H), 7.14

(dd, J=1.6, 4.8, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 42.5, 124.8, 125.8, 126.6, 147.2. Anal. Calcd for $C_{13}H_{10}S_3$: C, 59.50; H, 3.84; S, 36.66. Found: C, 59.29; H, 4.15; S, 36.56.

*4.5.4. 2,2′-(Thiophen-2-ylmethylene)bis(1H-pyrrole) (**2d**)*[11a,b]. Brown crystals; mp 119–120 °C; yield: 91 mg, 80%; R_f 0.56 (1:3 EtOAc/hexane); IR (ATR): 3349, 3106, 2959, 2915, 2844, 1716, 1561, 1461, 1263, 1235, 1112, 1096, 1023, 798, 733, 710, 675 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.60 (s, 1H), 5.94 (br s, 2H), 6.06 (dd, J=2.8, 6.0, 2H), 6.54–6.56 (m, 2H), 6.77–6.78 (m, 1H), 6.84–6.86 (m, 1H), 7.10–7.11 (m, 1H), 7.78 (br s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 39.1, 107.1, 108.5, 117.4, 124.5, 125.5, 126.7, 131.9, 145.7. Anal. Calcd for $C_{13}H_{12}N_2S$: C, 68.39; H, 5.30; N, 12.27; S, 14.04. Found: C, 68.51; H, 5.18; N, 12.07; S, 14.24.

*4.5.5. 2,2′-(Furan-2-ylmethylene)bis(1H-pyrrole) (**2e**)*[11b,c]. Pale yellow oil; yield: 100 mg, 94%; R_f 0.56 (1:3 EtOAc/hexane); IR (ATR): 3388, 3094, 2967, 2923, 2852, 1708, 1569, 1509, 1461, 1430, 1406, 1259, 1092, 1028, 1012, 893, 711 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.45 (s, 1H), 5.94 (br s, 2H), 6.08–6.11 (m, 3H), 6.29–6.31 (m, 1H), 6.61 (br s, 2H), 7.36 (br s, 1H), 7.95 (br s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 37.8, 106.9, 107.0, 108.5, 110.3, 117.5, 129.9, 141.9, 154.5. Anal. Calcd for $C_{13}H_{12}N_2O$: C, 73.56; H, 5.70; N, 13.20. Found: C, 73.88; H, 5.67; N, 13.24.

*4.5.6. 3-(Di(1H-pyrrol-2-yl)methyl)-1H-indole (**2f**).* Pale yellow oil; yield: 86 mg, 66%; R_f 0.55 (1:3 EtOAc/hexane); IR (ATR): 3404, 3110, 3058, 2959, 2923, 2856, 1676, 1561, 1461, 1414, 1342, 1259, 1227, 1092, 1024, 885, 778, 718 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.71 (s, 1H), 6.00 (br s, 2H), 6.11 (br s, 2H), 6.57 (br s, 2H), 6.86 (br s, 1H), 7.00 (t, J=7.2, 1H), 7.14 (t, J=7.2, 1H), 7.28–7.30 (m, 2H), 7.92 (br s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 35.5, 106.6, 108.6, 111.2, 116.6, 117.5, 119.7, 120.0, 122.5, 123.0, 126.7, 132.5, 136.7. Anal. Calcd for $C_{17}H_{15}N_3$: C, 78.13; H, 5.79; N, 16.08. Found: C, 77.88; H, 5.92; N, 16.20.

*4.5.7. 2,2′-(Phenylmethylene)difuran (**2g**)*[11d]. Pale brown oil; yield: 67 mg, 60%; R_f 0.86 (1:3 EtOAc/hexane); IR (ATR): 3126, 3027, 2967, 2935, 2860, 1728, 1596, 1502, 1453, 1374, 1227, 1175, 1144, 1084, 1010, 953, 889, 780, 725, 697 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.41 (s, 1H), 5.98 (d, J=2.8, 2H), 6.28 (dd, J=1.6, 2.8, 2H), 7.20–7.29 (m, 5H), 7.33 (br s, 2H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 45.1, 107.6, 110.3, 127.2, 128.5, 128.6, 139.6, 141.9, 154.5. Anal. Calcd for $C_{15}H_{12}O_2$: C, 80.34; H, 5.39. Found: C, 80.57; H, 5.21.

*4.5.8. 2,2′-(Phenylmethylene)dithiophene (**2h**)*[11d]. Pale yellow crystals; mp 67–68 °C; yield: 38 mg, 30%; R_f 0.84 (1:3 EtOAc/hexane); IR (ATR): 3068, 3027, 2959, 2919, 2848, 1728, 1457, 1374, 1231, 1076, 1024, 854, 802, 695 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.82 (s, 1H), 6.78 (d, J=3.6, 2H), 6.90 (dd, J=3.6, 5.2, 2H), 7.17 (d, J=5.2, 2H), 7.21–7.31 (m, 5H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 47.6, 124.6, 126.1, 126.6, 127.2, 128.4, 128.6, 143.7, 147.7. Anal. Calcd for $C_{15}H_{12}S_2$: C, 70.27; H, 4.72; S, 25.01. Found: C, 69.92; H, 4.95; S, 25.13.

*4.5.9. Trifuran-2-ylmethane (**2i**)*[11e]. Colorless viscous oil; yield: 95 mg, 89%; R_f 0.85 (1:3 EtOAc/hexane); IR (ATR): 3114, 2927, 2852, 1728, 1596, 1502, 1381, 1235, 1147, 1009, 946, 881, 773, 726 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.43 (s, 1H), 5.99–6.00 (m, 3H), 6.20–6.22 (m, 3H), 7.24–7.26 (m, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 39.0, 107.4, 110.4, 141.9, 152.0. Anal. Calcd for $C_{13}H_{10}O_3$: C, 72.89; H, 4.71. Found: C, 73.10; H, 4.55.

*4.5.10. 2-(Dithiophen-2-ylmethyl)furan (**2j**).* Pale brown oil; yield: 37 mg, 30%; R_f 0.76 (1:3 EtOAc/hexane); IR (ATR): 3106, 2955, 2922, 2856, 1728, 1616, 1509, 1457, 1414, 1229, 1144, 1076, 1010, 929, 853, 756, 732, 693 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.79 (s, 1H), 6.09 (d, J=3.2, 1H), 6.26 (dd, J=2.0, 3.2, 1H), 6.83–6.84 (m, 2H), 6.88 (dd, J=3.6, 4.8, 2H), 7.14–7.15 (m, 2H), 7.31 (br s, 1H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 41.2, 107.4, 110.3, 124.8, 125.8, 126.6, 142.1, 144.8, 155.4. Anal. Calcd for $C_{13}H_{10}OS_2$: C, 63.38; H, 4.09; S, 26.03. Found: C, 63.12; H, 4.23; S, 26.24.

*4.5.11. 2-(Tri(1H-pyrrol-2-yl)methyl)pyridine (**3**).* White powder; mp 172–173 °C; yield: 36 mg, 25%; R_f 0.61 (1:3 EtOAc/hexane); IR (ATR): 3444, 3399, 3330, 2962, 2929, 2860, 1712, 1540, 1426, 1266, 1209, 1091, 1029, 886, 800, 719 cm^{-1}; ^{1}H NMR (400 MHz, CDCl$_3$): δ 5.73 (br s, 3H), 6.08 (dd, J=2.8, 6.0, 3H), 6.67 (br s, 4H), 7.11–7.14 (m, 1H), 7.50–7.52 (m, 1H), 8.57–8.58 (m, 1H), 8.90 (br s, 3H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 51.6, 107.8, 108.3, 117.5, 122.0, 122.9, 134.1, 136.9, 148.3, 164.6. Anal. Calcd for $C_{18}H_{16}N_4$: C, 74.98; H, 5.59; N, 19.43. Found: C, 74.66; H, 5.73; N, 19.61.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2010.06.070.

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