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Synthesis and structure of an air-stable binuclear complex of bis(ethylcyclopentadienyl)zirconium perfluorooctanesulfonate and its catalytic application in one-pot three-component aza-Friedel–Crafts reactions

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An air-stable Lewis acidic binuclear complex of bis(ethylcyclopentadienyl)zirconium perfluorooctanesulfonate (**1a**) was successfully synthesized by the reaction of $(CH_3CH_2Cp)_2ZrCl_2$ with $C_8F_{17}SO_3Ag$. The complex **1a** was characterized by different techniques and found to have the nature of air-stability, water tolerance, thermal-stability, and strong Lewis-acidity. In addition, its solubility was higher than that of our previously reported uninuclear zirconocene bis(perfluorooctanesulfonate). This complex showed high catalytic efficiency, good recyclability, and reusability in the one-pot three-component aza-Friedel–Crafts reactions of indoles with aldehydes and *N*,*N*-dimethylaniline. The yields of the corresponding 3-diarylmethyl indoles are higher than those from the traditional Lewis acidic catalysts.

Introduction

Indoles are an important class of heterocycles that are found widely in many natural products.[1] Many natural and synthetic indoles are found to exhibit a broad range of biological activities, including anticancer,[2] antiangiogenic,[3] antiplasmodial,[4] and antitumor activites.[5] Consequently, the synthesis of indole derivatives have attracted great attention in organic chemistry over 50 years.[6] Among the various synthetic strategies, Lewis-acids catalyzed carbon–carbon bond forming reactions are of great importance. For example, the C3-alkylation of indoles with various reagents using $InCl_3$ ($In(OTf)_3$),[7] $Sc(OTf)_3$,[8] $FeCl_3$,[9] $CeCl_3$,[10] or $Al(OTf)_3$[11] as catalysts were continuously reported. However, most of them have one or more disadvantages such as air- or moisture-sensitive and the need of strictly anhydrous reaction conditions. Furthermore, most of these catalysts cannot be recycled owing to their decomposition or deactivation with the water generated in-situ. Therefore, it is still desirable to look for some air-stable, water-tolerant, strongly Lewis-acidic, and recyclable catalysts instead of the traditional Lewis-acid catalysts.

Recently, cationic group metallocene compounds have attracted increasing attention.[12] The metallocene triflates complexes of titanium, zirconium, and hafnocene ($Cp_2M(OTf)_2$, $Cp = C_5H_5$; M = Zr, Ti, Hf) were successfully applied to catalyze various C–C bond forming reactions.[13] Unfortunately, the application of these metallocene triflates was limited greatly owing to their facile hydrolysis and unstable features.[14] To overcome these shortcomings, Otera and co-workers found that the incorporation of perfluoroalkyl(aryl)sulfonate moieties into organometallic (ie., Sn, Zr, and Ti) cations could enhance acidity and stability.[15] With such understanding, several air-stable metallocene complexes bearing perfluorooctanesulfonate groups ($Cp_2M(OSO_2C_8F_{17})_2$, M = Ti, Zr) and $[\{CpHf(OH_2)_3\}_2(\mu^2\text{-}OH)_2][OSO_2C_8F_{17}]_4$ were synthesized successively in our group and were confirmed to show strong Lewis acidity and high catalytic activity in the C–C and C–O bond forming reactions.[16] However, their relatively low solubility in organic solvents owing to the strong lipophobic nature of C_8F_{17} group maybe declines the catalytic efficiency. We envisioned that alkyl group incorporated with Cp ring will maybe increase the solubility as well as the catalytic efficiency. Based on this idea and as part of our ongoing efforts devoted to metallocene complexes, ethyl was incorporated with cyclopentadiene group to afford an air-stable Lewis-acidic organometallic species. In this Letter, we wish to report the synthesis and characterization of μ^2-hydroxy bridged binuclear complex $[\{CH_3CH_2CpZr(OH_2)_3\}_2(\mu^2\text{-}OH)_2][OSO_2C_8F_{17}]_4\cdot 4H_2O\cdot 2THF$ (denoted as **1a**·$4H_2O\cdot 2THF$ hereafter) and its catalytic application in the one-pot three-component aza-Friedel–Crafts reactions of indoles, aldehydes, and *N*,*N*-dimethylaniline.

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Results and discussion

The synthesis of **1a** is shown in Scheme 1.[17] Treatment of bis(ethylcyclopentadienyl)zirconium dichloride [$(CH_3CH_2Cp)_2ZrCl_2$] (1 equiv) with silver perfluorooctanesulfonate ($AgOSO_2C_8F_{17}$) (2 equiv) in dry THF yielded **1a**·xH_2O·yTHF (after recrystallization from THF). The water molecules in the complex originated from air or the solvent, and the hydrate numbers x and solvating ligand THF y varied according to the reaction conditions. The result of ^1H NMR spectroscopy (in dry [D_6] acetone) showed that in the freshly prepared sample after recrystallization and vacuum treatment at 60 °C for 1 h, complex **1a·xH₂O·yTHF** became **1a** ($x = 0$, $y = 0$). It is notable that the samples remained as dry powder after being kept in open air over a month, and exhibited no sign of structural change by ^1H NMR spectroscopy analysis, showing a great advantage over zirconocene bis(triflate) and the traditional Lewis-acid catalysts from an operational point of view.

Though it is difficult to acquire the crystal structure owing to the large disorder of perfluorooctanesulfonate group, the cationic structure of **1a·4H_2O·2THF** was fortunately confirmed by X-ray analysis after a series of efforts. The crystals suitable for the X-ray diffraction were obtained by diffusion of hexane into saturated THF solution. The crystal structure together with selected bonds and angles are shown in Figure 1. It is clear that bis(ethyl) zirconocene in compound **1a** is cationic. Also, it is interesting to find that complex **1a** is binuclear structure, different from the uninuclear structure of $Cp_2Zr(OSO_2C_8F_{17})_2$[16d] even though their synthetic procedures are identical. And the zirconium atoms have a distorted octahedral coordination with the Cp group trans to the OH unit, similar to that of $[\{CpZr(OH_2)_3\}_2(\mu^2\text{-}OH)_2]$ $[C_6F_5SO_3]_4\cdot 6H_2O$.[18]

The Zr–O distances of **1a·4H_2O·2THF** are 2.110(5), 2.130(5), 2.170(5), 2.194(5), and 2.202(5) Å, respectively. The Zr(2)–O(16)–Zr(1) angle is 111.2(2)° and the Zr–Zr distance is 3.5315(15), showing that there is no Zr–Zr interaction. The $C_8F_{17}SO_3^-$ ions, the dissociated H_2O molecules, and the solvating ligand THF are packed around the complex cation in such a way that their oxygen atoms point toward the H_2O ligands. The C_8F_{17} chains of the anion, on the other hand, are clustered together to produce hydrophobic domains in the crystal structure.

The thermal behavior of complex **1a** was investigated by thermogravimetric-differential scanning calorimetry (TG-DSC) in air (Fig. S1, see ESI). The TV-DSC curves indicate three stages of weight losses. The endothermic step below 100 °C can be attributed to the removal of water molecules. The material is stable up to about 250 °C, after which weight loss of exothermic nature emerges, possibly resulting from the oxidation of organic entities. The removal of perfluorooctanesulfuryl ligand at about 400 °C was observed, thus leaving zirconium dichloride compounds. Conductivity measurement was applied to investigate their ionic dissociation behavior in CH_3CN (Table S1, see ESI). The molar conductivity (Λ) of **1a·4H_2O·2THF**) is 670 $\mu S\ cm^{-1}$ in CH_3CN (1.0 $mmol\ L^{-1}$) at 25 °C. The large molar conductivity value is consistent with complete ionization into 1:4 electrolyte in CH_3CN, implying that these complexes are cationic in the solid state and in solution. Actually, owing to the existence of ethyl, it is more soluble in some polar organic solvents such as acetone, CH_3CN, THF, EtOAc, and MeOH (Table S2, see ESI) than the $Cp_2Zr(OSO_2C_8F_{17})_2$.[16e] Notably, it has a relatively strong acidity with acid strength of $0.8 < H_0 < 3.3$ (H_0 being the Hammett acidity function, see ESI), the same as that of $Cp_2Zr(OSO_2C_8F_{17})_2$.[16e] Accordingly, these features of complex **1a** encouraged us to evaluate its performance as Lewis acid catalyst in the one-pot three-component aza-Friedel–Crafts reactions of indoles with aldehydes and tertiary aromatic amines. The reactions generated the corresponding 3-diarylmethyl indoles in moderate to good yields (Scheme 2).

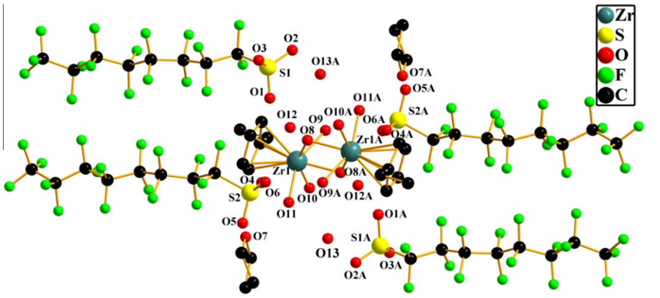
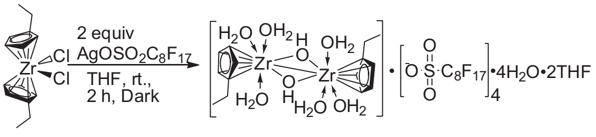


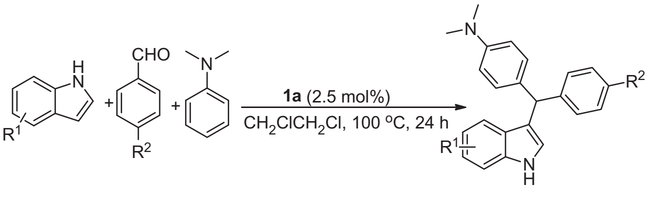
Figure 1. Crystal structure of $[CH_3CH_2CpZr(OH_2)_3\}_2(\mu^2\text{-}OH)_2][OSO_2C_8F_{17}]_4\cdot 4H_2O\cdot 2THF]$ (**1a**·$4H_2O$·2THF), Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Zr(1)–O(8), 2.110(5); Zr(1)–O(11), 2.130(5); Zr(1)–O(8A), 2.170(5); Zr(1)–O(10), 2.194(5); Zr(1)–O(9), 2.202(5); Zr(1)–C(3), 2.505(8); Zr(1)–C(4), 2.521(7); Zr(1)–Zr(1A), 3.5315(15); O(8)–Zr(1)–O(11), 94.8(2); O(8)–Zr(1)–O(8A), 68.8(2); O(8)–Zr(1)–O(10), 150.8(2); O(10)–Zr(1)–O(9), 80.1(2); O(8)–Zr(1)–C(3), 99.6(2); O(10)–Zr(1)–C(2), 131.0(2); C(2)–Zr(1)–C(4), 54.0(3); O(8)–Zr(1)–Zr(1A), 34.96(13); C(5)–Zr(1)–Zr(1A), 153.99(19); Zr(1)–O(8)–Zr(1A), 111.2(2); The planes of the two Cp rings are parallel.



Scheme 1. Synthesis of **1a·4H_2O·2THF**.

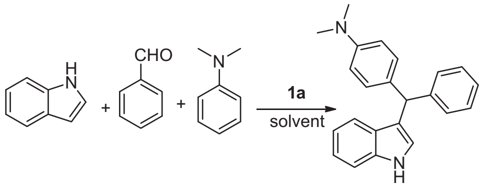
We choose to study the three-component reaction of indole with benzaldehyde and N,N-dimethylaniline as a model reaction to determine the optimal reaction conditions (Table 1).[19] In view of the binuclear structure, 2.5 mol % **1a** was used as catalyst. Firstly, different solvents were screened at 100 °C to find that $ClCH_2CH_2Cl$ was the most effective solvent, giving the corresponding product in 75% yield (entries 1–5). The yield was superior to that of $FeCl_3$,[20] its counterpart 5 mol % $Cp_2Zr(OSO_2C_8F_{17})_2$ and $[\{CpZr(OH_2)_3\}_2(\mu^2\text{-}OH)_2]$ $[C_6F_5SO_3]_4\cdot 6H_2O$ (entry 4). When the reaction temperature and time were decreased to 80 °C and 12 h, the yields were sharply decreased to 50% and 44%, respectively (entries 4 and 6), demonstrating that the reaction temperature and time were important to this system. Controlled experiments showed that no product can be obtained in the absence of **1a** (entry 7) and no obvious improvement of the yield was observed by increasing the catalyst loading to 5.0 mol % (entry 8).

Subsequently, the scope of indoles and benzaldehydes for the three-component aza-Friedel–Crafts reactions using **1a** as catalyst was evaluated (Table 2). It was found that indoles bearing electron-donating groups, such as methyl and methoxyl (entries 2, 3, 9 and 10), showed slightly higher reactivity than those with electron-withdrawing groups, like F, Cl, and Br (entries 4–6 and 8). It is worth to note that no reaction was observed when 5-nitroindole (bearing the strong electron-withdrawing group) was employed as the substrate (entry 7). On the contrary, benzaldehydes bearing electron-withdrawing groups (NO_2, CN, Cl, entries 13–15) gave



Scheme 2. The aza-Friedel–Crafts reactions of indoles with aldehydes and N,N-dimethylaniline catalyzed by complex **1a**.

Table 1
Screening optimal conditions[a]



Entry	Solvent	**1a** (mol %)	Temp (°C)	Yield[b] (%)
1	THF	2.5	100	46
2	DMSO	2.5	100	35
3	CH_3CN	2.5	100	24
4	$ClCH_2CH_2Cl$	2.5	100	75 (44[c], 70[d], 66[e])
5	Toluene	2.5	100	Trace
6	$ClCH_2CH_2Cl$	2.5	80	50
7	$ClCH_2CH_2Cl$	—	100	0
8	$ClCH_2CH_2Cl$	5	100	76

[a] Indole (0.5 mmol), benzaldehyde (0.55 mmol) and *N*,*N*-dimethylaniline (0.55 mmol), solvent (2 mL), 24 h.

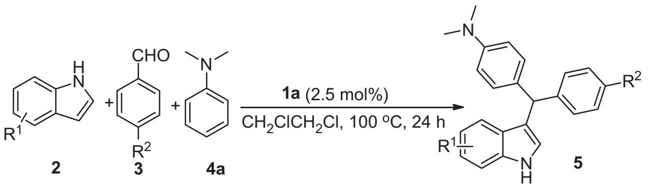
[b] Isolated yields.

[c] The reaction time was shorten to 12 h.

[d] Using 5 mol % $Cp_2Zr(OSO_2C_8F_{17})_2$ as catalyst.

[e] Using $[\{CpZr(OH_2)_3\}_2(\mu^2\text{-}OH)_2]\cdot[C_6F_5SO_3]_4\cdot 6H_2O$ as catalyst.

Table 2
Aza-Friedel–Crafts of indoles with aldehydes and *N*,*N*-dimethylaniline catalyzed by complex **1a**[a]



Entry	R¹	R²	Product	Yield[b]
1	H(**2a**)	H(**3a**)	**5a**	75
2	5-CH_3(**2b**)	H(**3a**)	**5b**	77
3	5-OCH_3(**2c**)	H(**3a**)	**5c**	80
4	5-F(**2d**)	H(**3a**)	**5d**	64
5	5-Cl(**2e**)	H(**3a**)	**5e**	65
6	5-Br(**2f**)	H(**3a**)	**5f**	66
7	5-NO_2(**2g**)	H(**3a**)	—	—
8	6-F(**2h**)	H(**3a**)	**5g**	63
9	7-CH_3(**2i**)	H(**3a**)	**5h**	68
10	2-CH_3(**2j**)	H(**3a**)	**5i**	69
11	H(**2a**)	4-CH_3(**3b**)	**5j**	70
12	H(**2a**)	4-OCH_3(**3c**)	**5k**	68
13	H(**2a**)	4-NO_2(**3d**)	**5l**	78
14	H(**2a**)	4-CN(**3e**)	**5m**	74
15	H(**2a**)	2,4-DiCl(**3f**)	**5n**	78
16	H(**2a**)	2-Naphthyl(**3g**)	**5o**	56
17	5-OCH_3(**2c**)	4-OCH_3(**3c**)	**5p**	71
18	5-OCH_3(**2c**)	4-NO_2(**3d**)	**5q**	82
19	5-F(**2d**)	4-OCH_3(**3c**)	**5r**	50
20	5-F(**2d**)	4-NO_2(**3d**)	**5s**	66

[a] Indole (0.5 mmol), benzaldehyde (0.55 mmol) and *N*,*N*-dimethylaniline (0.55 mmol), catalyst **1a** (28.5 mg, 2.5 mol %), solvent (2 mL), 24 h.

[b] Isolated yields.

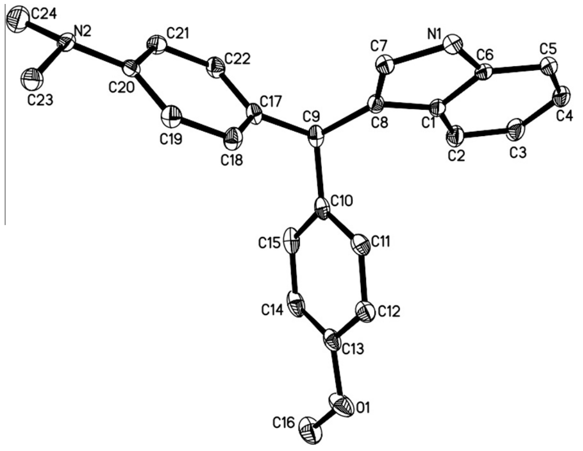
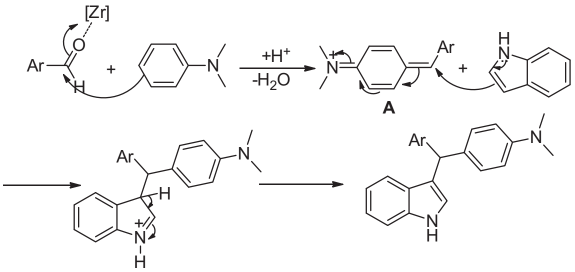


Figure 2. The X-ray crystal structure of compound **5k**.



Scheme 3. Plausible mechanism of the three-component aza-Friedel–Crafts reaction catalyzed by **1a**.

Table 3
Yield of the one-pot three-component aza-Friedel–Crafts reactions catalyzed by recovered **1a**[a]

Entry of cycle	1	2	3	4	5
Yield[b] (%)	75	72	71	73	72
Cat.[c] (%)	83	82	80	81	80

[a] Indole (0.5 mmol), benzaldehyde (0.55 mmol) and *N*,*N*-dimethylaniline (0.55 mmol), catalyst **1a** (28.5 mg, 2.5 mol %), solvent (2 mL), 24 h.

[b] Isolated yield.

[c] Isolated yield of recovered catalyst.

their corresponding products in higher yields than those with electron-donating groups (entries 11 and12). The structure of compound **5k** was confirmed by X-ray crystallography (Fig. 2). Gratifyingly, 2-naphthaldehyde was also tolerated in this process, providing the compound **5o** in 56% yield (entry 16), demonstrating that the metallocene complex **1a** catalyzed-aza-Friedel–Crafts reaction is possible even in case where steric hindrance from the aldehyde is increased. Based on the results of electronic effects of indoles and benzaldehydes, treatment of 5-methoxylindole with 4-methoxybenzaldehyde and 4-nitrobenzaldehyde afforded compounds **5p**, **5q** in 71%, 82% yields, respectively (entries 17 and 18). Meanwhile, 5-fluoroindole reacted with 4-methoxybenzaldehyde and 4-nitrobenzaldehyde, giving **5r**, **5s** in 50%, 66% yields, respectively (entries 19 and 20).

According to the reported findings,[16b,e,20] the proposed mechanism of the three-component aza-Friedel–Crafts reaction of indole with benzaldehyde and *N*,*N*-dimethylaniline is shown in Scheme 3. When solid **1a** was added to the reaction system, the ligand OH groups dissociate immediately from the bis(ethyl) zirconocene cation. At this stage, there is frequent intra- and intermolecular exchange of substrate and organic solvent. The carbonyl group coordinates with the zirconium atoms and was activated. Then the activated benzaldehyde reacted with *N*,*N*-dimethylaniline to give an intermediate A. The β-carbon of the indole attacks the intermediate to produce the aimed product.

To test the reusability of the catalyst and the reproducibility of catalytic performance, **1a** was subjected to recycle in the three-component reaction of indole with benzaldehyde and *N*,*N*-dimethylaniline (Table 3). The detected change in product yield was minimal in a trial of five cycles, demonstrating that the catalyst is stable and suitable for reuse.

Conclusions

In conclusion, for the first time the novel air-stable Lewis acidic complex of $[\{CH_3CH_2CpZr(OH_2)_3\}_2(\mu^2\text{-}OH)_2][OSO_2C_8F_{17}]_4\cdot 4H_2\ O\cdot 2\ THF$ has been synthesized and its structure was determined by single-crystal X-ray. The complex was characterized by various techniques such as TG-DSC analysis, conductivity measurement, and acid strength (H_0). It can be used as an excellent catalyst for the three-component reactions of indoles with benzaldehydes and *N*,*N*-dimethylanilines. The novel complex has the advantages of air-stability, water tolerance, thermal-stability, highly catalytic efficiency, and reusability with better solubility and competitive yields as compared to its counterparts, such as $Cp_2Zr(OSO_2C_8F_{17})_2\cdot\ 3H_2O\cdot THF$ and the traditional Lewis-acid catalysts.

Acknowledgments

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Supplementary data

Supplementary data (CCDC 951169 and 951170 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ata_request/cif) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.2013.10.131.

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17. *Synthesis of complex **1a**:* To a solution of $(CH_3CH_2Cp)_2ZrCl_2$ (174 mg, 0.5 mmol) in 5 mL THF was added a solution of $AgOSO_2C_8F_{17}$ (605 mg, 1 mmol) in 10 mL THF. After the mixture was stirred at 25 °C for 12 h in the absence of light, it was filtrated. The filtrate was added into acetone and placed in a small jar and then put into a larger jar which was added 20 mL dry hexane and then the larger jar was obdurate. After keeping in the refrigerator for 24 h, the white crystal was obtained (445 mg, 70%). mp 166–167 °C. ^1H NMR (400 MHz, [D_6] acetone) $\delta = 6.61–6.60$ (m, 8H, Cp), 2.69 (q, 4H, $J = 7.5$ Hz), 1.15 (t, 6H, $J = 7.6$ Hz); ^{19}F NMR (288 MHz, [D_6] acetone): −76.07 to −76.12 (m, 3F, CF_3^-), −109.38 to 109.41 (m, 2F, $-CF_2^-$), −115.50 to −115.55 (m, 2F, $-CF_2^-$), −116.61 to −116.90 (m, 6F, $-CF_2^-$), −117.73 to −117.75 (m, 2F, $-CF_2^-$), −121.17 to −121.24 (m, 2F, $-CF_2^-$). Crystallographic data for $[\{CH_3CH_2CpZr(OH_2)_3\}_2(\mu^2\text{-}OH)_2][OSO_2C_8F_{17}]_4\cdot 4H_2O\cdot 2THF$: $C_{54}H_{56}F_{68}O_{26}S_4Zr_2$, white prism, formula weight 2723.66, Triclinic, $P-1$, $a = 10.498(2)$ Å, $b = 10.929(2)$ Å, $c = 20.659(4)$ Å, $V = 2277.4(8)$ Å^3, $Z = 2$, $D_{calcd} = 1.986$ g cm^{-3}, $R_{(int)} = 0.0631$, $R_1 = 0.0911$, $wR_2 = 0.2266$, GOF = 1.005, CCDC no. 951169.
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19. *Typical procedure for the aza-Friedel–Crafts of indoles with aldehydes and N,N-dimethylaniline catalyzed by complex **1a**:* To a 10 mL sealed tube was added indole (0.5 mmol), 4-methoxybenzaldehyde (0.55 mmol) and *N*,*N*-dimethylaniline (0.55 mmol), CH_2ClCH_2Cl (2 mL) and catalyst (34.0 mg, 2.5 mol %). The mixture was stirred at 100 °C for 24 h. Then the reaction mixture was evaporated in vacuum, CH_2Cl_2 (3 × 10 ml) was added to the reaction mixture and the catalyst was filtered for the next cycle of the reaction. The combined CH_2Cl_2 solution was removed by evaporation in vacuum and was then subjected to silica gel column chromatograph; the one-pot three-component aza-Friedel–Crafts product (**5k**) was obtained: 121.0 mg, isolated yield 68%. *N*,*N*-Dimethyl-4-((1*H*-indol-3-yl)(4-methoxyphenyl)methyl)aniline (**5k**). White solid, mp 160–162 °C (lit.[20] 162–164 °C). ^1H NMR (500 MHz, $CDCl_3$) δ 7.90 (s, 1H), 7.32 (d, $J = 8.0$ Hz, 1H), 7.25–7.23 (m, 1H), 7.14–7.13 (m, 3H), 7.08 (d, $J = 9.0$ Hz, 2H), 6.68 (d, $J = 8.5$ Hz, 2H), 6.98–6.95 (m, 1H), 6.81–6.79 (m, 2H), 6.57–6.56 (m, 1H), 5.52 (s, 1H), 3.77 (s, 3H), 2.91 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 157.8, 149.0, 137.0, 136.8, 132.9, 129.8, 129.5, 127.2, 123.8, 121.9, 121.0, 120.1, 119.2, 113.6, 112.8, 110.9, 55.2, 47.0, 40.8; *Crystallographic data for **5k**:* $C_{24}H_{23}N_2O$, white prism, formula weight 355.44, Monoclinic, P 21/c, $a = 16.4165(9)$ Å, $b = 5.8444(3)$ Å, $c = 21.0166(11)$ Å, $V = 1904.33(17)$ Å^3, $Z = 4$, $D_{calcd} = 1.240$ g cm^{-3}, $R_{(int)} = 0.0183$, $R_1 = 0.0691$, $wR_2 = 0.1935$, GOF = 1.092, CCDC no. 951170.
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