Improved Sommelet reaction catalysed by lanthanum triflate

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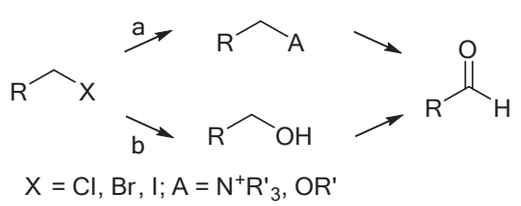
An improved Sommelet reaction for the synthesis of araldehydes from benzyl halides and hexamethylenetetramine was achieved employing lanthanum triflate (3 mol%) as catalyst in water with sodium dodecyl sulfate (SDS, 2 wt%) as solubiliser. Good to excellent yields were obtained in most of the 18 examples.

Keywords: Sommelet reaction, lanthanum triflate, hexamethylenetetramine, benzyl halides, araldehydes

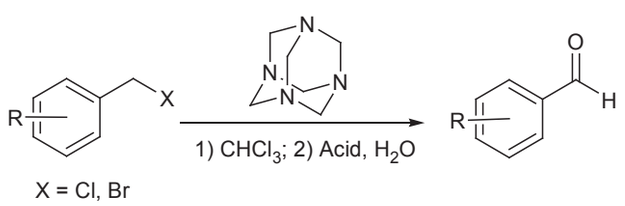
Aldehydes are versatile building blocks for the synthesis of heterocycles,[1–3] and useful functionalised compounds.[4–6] They are frequently used as intermediates in many useful drugs, *e.g.* Irbesartan and Valsartan.[7] Moreover, a number of aldehydes possess biological activities[8] and their properties have attracted considerable attention in medicinal chemistry.

As a ubiquitous synthetic transformation in synthetic pharmaceuticals[9,10] and natural products,[11,12] the conversion of halides to aldehydes has attracted considerable attention and it has been the subject of considerable research. A common approach for this transformation can be achieved by two different routes as shown in Scheme 1. Type (a) is exemplified by the Sommelet reaction, the Kröhnke reaction,[13] and the Kornblum reaction[14] in which halides are transformed into aldehydes *via* the formation of ammonium salts or esters prior to hydrolysis. For example, Moorthy and co-workers recently used IBX (2-iodoxybenzoic acid) in DMSO which allowed the direct conversion of benzyl halides to aldehydes and ketones in good yield.[15] In type (b), alcohol intermediates generated by hydrolysis of halides are oxidised *in situ* by MnO_2,[16] $NaNO_3$,[17] hydrogen peroxide,[18] or *N*-methyl morpholineoxide.[19]

As one of the most important methodologies, the Sommelet reaction is a well-established method for converting benzyl halides into the corresponding aldehydes in excellent yields (Scheme 2). Since it was first reported in 1913 by Marcel Sommelet,[20] applications of this reaction have been long associated with a number of disadvantages including: (i) organic solvents such as chloroform[21,22] and acetonitrile[23] are needed in order to avoid the interaction between hexamethylenetetramine and the Brønsted acid; (ii) some functional groups are incompatible with Brønsted acid; and (iii) more than stoichiometric amounts of Brønsted acid[24] have been employed in this reaction. Moreover, these Brønsted acids cannot be recovered and reused. Therefore, the development of new eco-friendly and facile synthetic methods is urgently needed to overcome the drawbacks of Sommelet reaction.



Scheme 1 Alternative routes (a, b) from a halide to corresponding aldehyde.



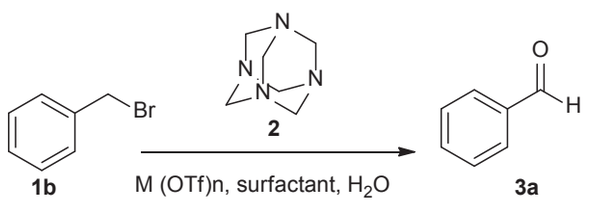
Scheme 2 Typical Sommelet reaction.

Metal triflates are a new type of strong Lewis acid. An outstanding feature of metal triflates lies in their stability in water. Only catalytic amounts of the metal triflates are required to complete the reactions in most cases. Furthermore, metal triflates can be recovered easily after reaction and reused without loss of activity. Thus many useful reactions including the aldol reaction[25,26] and the Mannich reaction[27,28] can be catalysed by them in aqueous medium. To the best of our knowledge, no uses of metal triflates in the Sommelet reaction have been published. We now report a novel method for carrying out the Sommelet reaction catalysed by metal triflates in water in the presence of a detergent, SDS.

Results and discussion

Because hexamethylenetetramine (HMT) is known to be stable with triflates in water, we aimed at optimising this reaction by using water alone as solvent. The results of our several experiments are listed in Table 1. In order to determine the optimum amount of HMT, we chose as a model the reaction of benzyl bromide **1b** (1 mmol) with varying amounts of HMT in the presence of zinc triflate (0.03 mmol) stirred in water (2 mL) at 100 °C (entries 1–4) (Scheme 3). It can be seen that 0.5 mol of **2** giving a yield of 76% is optimal (entry 2). Then we used the adopted reaction of **1b** (1 mmol) and **2** (0.5 mmol) as a model to study the influence of various metal triflates on the reaction, and the results are shown in entries 5–10. Lanthanum triflate was found to be the most suitable catalyst for this transformation, giving a yield of 84% (entry 10). A blank experiment without metal triflate afforded 25% yield (entry 11).

Because the solubility of halides and aldehydes in water is very low, the Sommelet reaction proceeded sluggishly in water, especially when the reactants were solid. For this reason we investigated the effect of some surfactants, hoping



Scheme 3 Sommelet reaction of benzyl bromide **1b** using a metal triflate as catalyst and a surfactant as a solubiliser.

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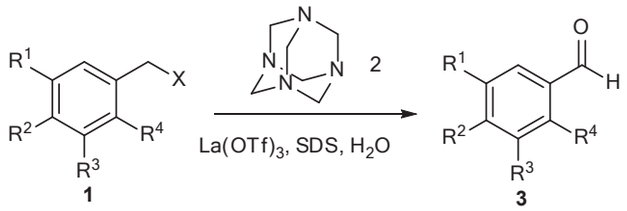
Table 1 Optimisation of the reaction conditions for converting benzyl bromide **1b** to benzaldehyde **3a** (Scheme 3)[a]

Entry	**2**/mmol	Catalyst	Surfactant	Time/h	Yield of **3a**/%[b]
1	0.25	$Zn(OTf)_2$	–	1.5	58
2	0.5	$Zn(OTf)_2$	–	1.5	76
3	1	$Zn(OTf)_2$	–	1.5	72
4	1.5	$Zn(OTf)_2$	–	1.5	74
5	0.5	$Mg(OTf)_2$	–	1.5	51
6	0.5	$Cu(OTf)_2$	–	1.5	48
7	0.5	$Bi(OTf)_3$	–	1.5	66
8	0.5	$Yb(OTf)_3$	–	1.5	67
9	0.5	$Y(OTf)_3$	–	1.5	79
10	0.5	$La(OTf)_3$	–	1.5	84
11	0.5	–	–	1.5	25
12	0.5	$La(OTf)_3$	PEG–400	1.5	74
13	0.5	$La(OTf)_3$	SDS	1.5	90
14	0.5	$La(OTf)_3$	CTAB	1.5	58
15	0.5	$La(OTf)_3$	CAB–35	1.5	65
16	0.5	$La(OTf)_3$	Triton X–100	1.5	85
17	0.5	$La(OTf)_3$	SDS	0.5	52
18	0.5	$La(OTf)_3$	SDS	1	75
19	0.5	$La(OTf)_3$	SDS	2	86
20	0.5	$La(OTf)_3$	SDS	2.5	73

[a]Reaction conditions: benzyl bromide **1b** (1 mmol) and hexamethylenetetramine in the presence of a metal triflate (0.03 mmol) and a surfactant (3.4 mg, 2 wt%) at 100 °C in water (2 mL).
[b]Isolated yield.

that they would speed up the reaction and increase the yield. Several kinds of surfactants were tried at 2 wt%): an anionic surfactant (sodium dodecyl sulfate; SDS), a cationic surfactant (cetyltrimethyl ammonium bromide; CTAB), a zwitterionic surfactant (cocoamido–propyl betaine; CAB-35), and two non-ionic surfactants (polyethyleneglycol; PEG and Triton X-100),[29] and the results are shown in entries 12–16. As can be seen, SDS proved to be superior to the others, giving a yield of 90% (entry 13).

Finally, various reaction times were investigated and the results are shown as entries 17–20. The optimal reaction time was found to be 1.5 h which gave a yield of 90% (entry 13).



Scheme 4 Application of the new Sommelet reaction to the preparation of various benzaldehydes **3** from the corresponding benzyl halides **1** using lanthanum triflate as catalyst in water with SDS as a solubiliser.

However, after 1.5 h, it was observed that the yield began to decrease. This was presumably due to the oxidation of the aldehyde at high temperature over a prolonged period. The optimal set of conditions were finally obtained as benzyl bromide **1b** (1 mmol) and hexamethylenetetramine (0.5 mmol) in the presence of lanthanum triflate (0.03 mmol) and sodium dodecyl sulfate (SDS) (3.4 mg, 2 wt%) in water (2 mL) at reflux temperature for 1.5 h, which gave benzaldehyde **3a** in a very good yield of 90% (entry 13).

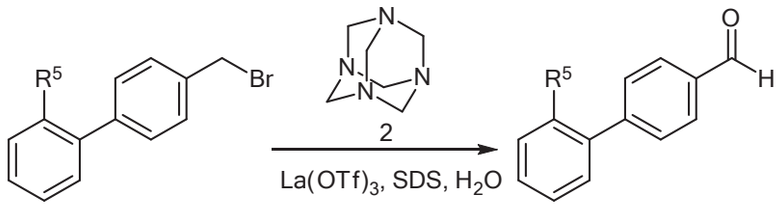
With suitable conditions to hand, we examined a variety of halides to check the versatility of the new method (Scheme 4). First, variously substituted benzyl halides with different halogen groups in the α position were investigated and the yields are shown in Table 2 (entries 1–3, 6–9, 12–13). In contrast to benzyl chlorides with/without substituent, the benzyl bromides and the single benzyl iodide showed positive activation in the reaction, presumably because Br and I are better leaving groups than Cl. The results of our limited study provide some understanding of the electronic/steric factors governing the performance of the reaction. Electron-donating groups favour the reaction. Compared with yields of 52–69% of those benzyl halides containing strong electron-withdrawing groups (entries 11–14), better yields of 72–92% were obtained for those with electron–donating groups (entries 1–10).

As an extension of our work, we chose to investigate three Ang-II receptor antagonist intermediates **1o–q** to see whether these diphenyl-4-methyl bromides would react under the optimal condition (Scheme 5). The results showed that all three reactions proceeded successfully

Table 2 Yields and reaction times for the conversion of various benzyl halides **1a–n** to the corresponding benzaldehydes **3a–n** by the new Sommelet reaction (Scheme 4)[a]

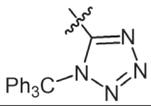
Entry		Halides					Product	Time/h	Yield/%[b]
		R^1	R^2	R^3	R^4	X			
1	**1a**	H	H	H	H	Cl	**3a**	1.5	78
2	**1b**	H	H	H	H	Br	**3a**	1.5	90
3	**1c**	H	H	H	H	I	**3a**	1.5	92
4	**1d**	H	CH_3	H	H	Br	**3d**	1.5	84
5	**1e**	CH_3	H	CH_3	H	Br	**3e**	1.5	78
6	**1f**	H	OCH_3	H	H	Cl	**3f**	1.5	82
7	**1g**	H	OCH_3	H	H	Br	**3f**	1.5	84
8	**1h**	H	Br	H	H	Cl	**3h**	2.5	75
9	**1i**	H	Br	H	H	Br	**3h**	2	80
10	**1j**	H	I	H	H	Br	**3j**	2	72
11	**1k**	H	NO_2	H	H	Br	**3k**	2.5	69
12	**1l**	H	H	H	NO_2	Cl	**3l**	2.5	55
13	**1m**	H	H	H	NO_2	Br	**3l**	2.5	61
14	**1n**	H	COOH	H	H	Cl	**3n**	4	52

[a]Reaction conditions: benzyl halide **1a–n** (1 mmol) and hexamethylenetetramine (0.5 mmol) in the presence of lanthanum triflate (0.03 mmol) and SDS (3.4 mg, 2 wt%) at 100 °C in water (2 mL).
[b]Isolated yield.



Scheme 5 Application of the new Sommelet reaction to the preparation of various biphenyl-4-carboxaldehydes from the corresponding diphenyl-4-methyl bromides using lanthanum triflate as catalyst in water with SDS as a solubiliser.

Table 3 Yields and reaction times for the preparation of various biphenyl-4-carboxaldehydes **3o–q** from the corresponding diphenyl-4-methyl bromides **1o–q** by the new Sommelet reaction (Scheme 5)[a]

Entry	Bromide	R^5	Product	Time/h	Yield/%[b]
1	**1o**	CN	**3o**	4	71
2	**1p**	COO-t-Bu	**3p**	4.5	80
3	**1q**		**3q**	10	73

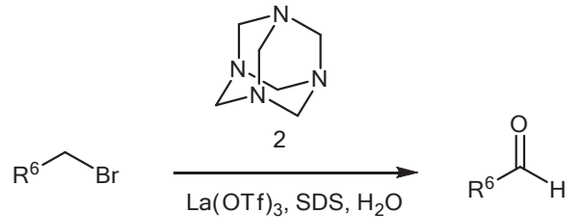
[a]Reaction conditions: bromide **1o–q** (1 mmol) and hexamethylenetetramine **2** (0.5 mmol) in the presence of lanthanum triflate (0.03 mmol) and SDS (3.4 mg, 2 wt%) at 100 °C in water (2 mL).
[b]Isolated yield.

Table 4 Yields and reaction times for the preparation of various aldehydes **3r–t** from the corresponding bromides **1r–t** by the new Sommelet reaction (Scheme 6)[a]

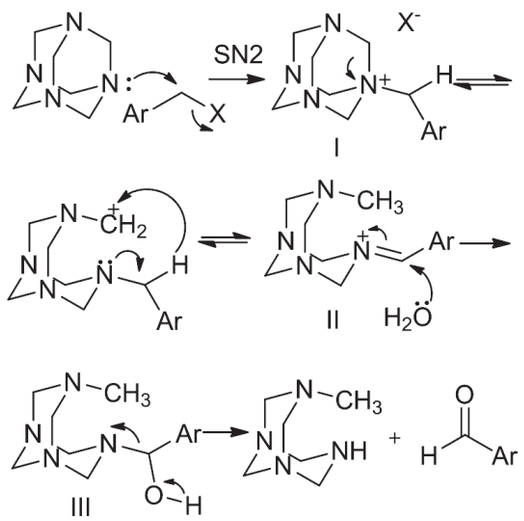
Entry	Bromide	R^6	Product	Time/h	Yield/%[a]
1	**1r**	2-Naphthyl	**3r**	1.5	94
2	**1s**	*n*-Butyl	**3s**	4	10[b]
3	**1t**	Allyl	**3t**	1.5	35[b]

[a]Reaction conditions: bromide **1r–t** (1 mmol) and hexamethylenetetramine **2** (0.5 mmol) in the presence of lanthanum triflate (0.03 mmol) and SDS (3.4 mg, 2 wt%) at 100 °C in water (2 mL).
[b]Isolated yield.

and the corresponding biphenyl-4-carboxaldehydes **3o–q** were obtained in very good yield (Table 3, entries 1–3). Finally we hoped to extend the new Sommelet reaction to nonbenzenoid aromatic, aliphatic and allyl bromides (Scheme 6). Unfortunately, although an excellent yield of the corresponding aldehyde **3r** was obtained from 2-naphthylmethyl bromide **1r**, low yields of aldehyde **3s**, **3t** were observed from butyl **1s** and allyl bromide **1t** (Table 4, entries 1–3). The mechanism of the Sommelet reaction has long been known[30] to involve three steps, as shown in Scheme 7. The reaction starts with a S_N2 reaction in which hexamethylenetetramine acts as the nucleophilic moiety displacing the halogen leaving group of the benzyl halide to give a hexaminium salt **I**. Then the salt undergoes a ring-opening with hydrogen transfer giving an imide intermediate **II**. In the aqueous medium, a hydrolysis process converts the imide into an aminol intermediate **III** which breaks down to the aldehyde. Since strong electron-withdrawing groups would decrease the electron cloud density of the benzene ring, such groups would reduce the stability of the imide intermediate **II**. This would explain the lower yields observed for these types of substituent. Substituent groups on the para position have lower steric hindrance than those on the ortho position; this would explain why the reaction on 4-nitrobenzyl bromide **1k** gave a higher yield than 2-nitrobenzyl bromide **1l** (Table 2, entries 11 and 12). Moreover, greater steric hindrance led to a longer reaction time. For example substrate **1q** needed nearly 10 h to give a 73% yield (Table 3).



Scheme 6 Application of the new Sommelet reaction to the preparation of various aldehydes from the corresponding bromides using lanthanum triflate as catalyst in water with SDS as a solubiliser.



Scheme 7 Mechanism of the Sommelet reaction.

In summary, we have developed a novel procedure for carrying out the Sommelet reaction under eco-friendly conditions. Advantages of the present process are good yields, replacement of an organic solvent by water and a decrease in the amount of Brønsted acid.

Experimental

All solvents and reagents were commercially available and used without further purification. Deionised water was used as solvent for the reaction. The flash column chromatography used using silica gel (200–400 mesh), purchased from Qingdao Haiyang Chemical Co., Ltd. Melting points were recorded on a Büchi B-540 apparatus and are uncorrected. Mass spectra were obtained on a Finnigan LCQ-Advantage. NMR spectra were obtained on a Varian-400 spectrometer (^{1}H NMR at 400 Hz, ^{13}C NMR at 100 Hz) in $CDCl_3$ or DMSO-*d6* using tetramethylsilane as internal standard. Chemical shifts (δ) are given in ppm and coupling constants (*J*) in Hz.

Synthesis of **3o***; typical procedure*

Hexamethylenetetramine **1** (70.1 mg), SDS (3.4 mg) and lanthanum triflate (17.6 mg) were dissolved in water (0.5 mL). Then **1o** (271 mg)

was added to the flask. The mixture was refluxed for 4 h to complete the reaction, which was monitored by TLC. The reaction mixture was extracted with EtOAc three times and the combined organic phases were distilled under reduced pressure. The crude product was purified by column chromatography on silica gel using hexane: EtOAc (5 : 1) as eluent to give **3o**, recrystallisation of which from EtOH gave white crystals, 147 mg (71%) (Table 3, entry 1).

Benzaldehyde (**3a**): Colourless oil; ^{1}H NMR ($CDCl_3$) δ 9.99 (s, 1H, CHO), 7.86 (d, J=8.0 Hz, 2H, ArH), 7.64–7.58 (m, 1H, ArH), 7.51 (m, 2H, ArH); MS(ESI): 129.2, $[M+23]^-$ (lit.[18]).

4-Methylbenzaldehyde (**3d**): Colourless oil; ^{1}H NMR ($CDCl_3$) δ 9.93 (s, 1H, CHO), 7.75 (d, J=8.0 Hz, 2H, ArH), 7.31 (d, J=8.0 Hz, 2H, ArH), 2.43 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 191.6, 145.3, 134.0, 129.6, 129.5, 21.9; MS(APCI): 241.1, $[2M+1]^+$ (lit.[18]).

3,5-Dimethylbenzaldehyde (**3e**): Colourless oil; ^{1}H NMR ($CDCl_3$) δ 9.92 (s, 1H, CHO), 7.47 (s, 2H, ArH), 6.98 (s, 1H, ArH), 2.38 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$) δ 192.4, 138.5, 136.4, 136.0, 127.4, 21.1; MS(APCI): 135.8, $[M+1]^+$ (lit.[34]).

4-Methoxybenzaldehyde (**3f**): Colourless oil; ^{1}H NMR ($CDCl_3$) δ 9.85 (s, 1H, CHO), 7.81 (d, J=8.0 Hz, 2H, ArH), 6.98 (d, J=8.0 Hz, 2H, ArH), 3.86 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 190.7, 164.6, 132.0, 130.0, 114.4, 55.8; MS(ESI): 136.9, $[M+1]^+$ (lit.[31]).

4-Bromobenzaldehyde (**3h**): White crystal, m.p. 67.0–68.4 °C (MeOH) (lit.[40] 66–68 °C); ^{1}H NMR ($CDCl_3$) δ 9.96 (s, 1H, CHO), 7.74 (d, J=8.0 Hz, 2H, ArH), 7.67 (d, J=8.0 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 190.7, 134.9, 132.3, 130.8, 129.6; MS(ESI): 182.9, 184.9, $[M-1]^-$ (lit.[31]).

4-Iodobenzaldehyde (**3j**): White crystals; m.p. 76.3–77.8 °C (MeOH) (lit.[41] 77–78 °C); ^{1}H NMR ($CDCl_3$) δ 9.86 (s, 1H, CHO), 7.83 (d, J=8.0 Hz, 2H, ArH), 7.50 (d, J=8.0 Hz, 2H, ArH). ^{13}C NMR ($CDCl_3$) δ 191.1, 138.2, 130.6, 130.5, 92.3; MS(APCI): 254.2, $[M+23]^+$ (lit.[32]).

4-Nitrobenzaldehyde (**3k**): Yellow crystals; m.p. 104.3–107.3 °C (MeOH) (lit.[33] 105.3–106.2 °C); ^{1}H NMR ($CDCl_3$) δ 10.17 (s, 1H, CHO), 8.39 (d, J=8.0 Hz, 2H, ArH), 8.08 (d, J=8.0 Hz, 2H, ArH); ^{13}C NMR ($CDCl_3$) δ 190.0, 150.8, 139.8, 130.3, 124.1; MS(ESI): 150.9, $[M-1]^-$ (lit.[33]).

2-Nitrobenzaldehyde (**3l**): Yellow crystals; m.p. 37.6–42.7 °C (MeOH) (lit.[42] 42–44 °C); ^{1}H NMR ($CDCl_3$) δ 10.41 (s, 1H, CHO), 8.11 (m, 1H, ArH), 7.95 (m, 1H, ArH), 7.79 (m, 1H, ArH), 7.77–7.72 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$) δ 186.4, 149.3, 133.0, 132.7, 130.9, 128.1, 124.3; MS(APCI): 150.4, $[M]^+$ (lit.[33]).

4-Formylbenzoic acid (**3n**): Light yellow crystal (water); m.p. 245.1–248.3 °C (MeOH) (lit.[43] 221–222 °C); ^{1}H NMR (DMSO) δ 13.28 (s, 1H, COOH), 10.09 (s, 1H, CHO), 8.12 (d, J=8.0 Hz, 2H, ArH), 8.01 (d, J=8.0 Hz, 2H, ArH); ^{13}C NMR (DMSO) δ 221.0, 194.7, 167.1, 163.9, 158.1, 157.7; MS(ESI): 148.9, $[M-1]^-$ (lit.[35]).

2-Cyano-4'-formylbiphenyl (**3o**): White crystals (EtOH); ^{1}H NMR ($CDCl_3$) δ 10.08 (s, 1H, CHO), 8.00 (d, J=8.0 Hz, 2H, ArH), 7.80 (d, J=8.0 Hz, 1H, ArH), 7.72 (d, J=8.0 Hz, 1H, ArH), 7.68 (d, J=8.0 Hz, 2H, ArH), 7.53 (d, J=8.0 Hz, 1H, ArH), 7.50 (d, J=8.0 Hz, 1H, ArH); ^{13}C NMR ($CDCl_3$) δ 191.4, 143.8, 143.7, 136.0, 133.7, 132.9, 129.9, 129.8, 129.4, 128.3, 118.1, 111.2; MS(ESI): 208.0, $[M+1]^+$ (lit.[7]).

t-butyl 4'-formylbiphenyl-2-carboxylate (**3p**): Colourless oil; ^{1}H NMR ($CDCl_3$) δ 10.05 (s, 1H, CHO), 7.91 (d, J=8.0 Hz, 2H, ArH), 7.84 (d, J=8.0 Hz, 1H, ArH), 7.54–7.40 (m, 4H, ArH), 7.30 (d, J=8.0 Hz, 1H, ArH), 1.26 (s, 9H, CH_3); ^{13}C NMR ($CDCl_3$) δ 191.7, 167.0, 148.2, 140.7, 134.8, 132.3, 130.8, 130.1, 129.9, 129.3, 129.2, 127.8, 81.6, 27.7; MS(APCI): 282.7, $[M+1]^+$ (lit.[36]).

2'-(2-Trityl-2H-tetrazol-5-yl)biphenyl-4-carboxyaldehyde (**3q**): White crystals; m.p. 154.1–156.2 °C (EtOH) (lit.[37] 154–156 °C); ^{1}H NMR ($CDCl_3$) δ 9.88 (s, 1H), 8.04 (m, 1H), 7.59 (d, J=8.0 Hz, 2H, CHO), 7.54–7.49 (m, 2H, ArH), 7.37 (m, 1H, ArH), 7.33 (s, 1H, ArH), 7.31 (s, 1H, ArH), 7.29 (s, 1H, ArH), 7.27 (s, 1H, ArH), 7.24 (s, 2H, ArH), 7.22 (s, 3H, ArH), 7.20 (s, 1H, ArH), 6.86 (d, J=8.0 Hz, 7H, ArH); ^{13}C NMR ($CDCl_3$) δ 191.5, 163.3, 147.3, 140.8, 140.5, 134.6, 130.2, 130.1, 130.0, 129.86, 129.7, 129.1, 128.2, 128.1, 127.5, 126.0, 83.0; MS(APCI): 468.3, $[M-24]^-$ (lit.[37]).

2-Naphthaldehyde (**3r**): White tabular crystals; m.p. 58.1–61.1 °C (lit.[44] 60.5–61.0 °C); ^{1}H NMR ($CDCl_3$) δ 10.15 (s, 1H, CHO), 8.32 (s, 1H, ArH), 7.99 (d, J=8.0 Hz, 1H, ArH), 7.93 (d, J=1.4 Hz, 1H, ArH), 7.92 (s, 1H, ArH), 7.89 (d, J=8.0 Hz, 1H, ArH), 7.67–7.60 (m, 1H, ArH), 7.60–7.53 (m, 1H, ArH); ^{13}C NMR ($CDCl_3$) δ 191.8, 136.2, 134.3, 133.9, 132.4, 129.3, 128.9, 127.9, 126.9, 122.5, 119.3; MS(APCI): 156.7, $[M+1]^+$ (lit.[31]).

Butyraldehyde (**3s**): Colourless oil; ^{1}H NMR ($CDCl_3$) δ 9.74 (s, 1H, CHO), 2.42 (m, 2H, CH_2), 1.67 (m, 2H, CH_2), 0.96 (t, J=8.0 Hz, 3H, CH_3); MS(ESI): 72.0, $[M]^+$ (lit.[38]).

Acrylaldehyde (**3t**): Light yellow oil; ^{1}H NMR ($CDCl_3$) δ 9.56 (d, J=8.0 Hz, 1H, CHO), 6.57–6.45 (m, 1H, CH), 6.44–6.31 (m, 2H, CH_2); MS(ESI): 57.0, $[M+1]^+$ (lit.[39]).

We thank the National Natural Science Foundation of China (21176222) and Zhejiang Natural Science Foundation (Y4090346) for financial support.

Received 26 October 2014; accepted 5 November 2014
Paper 1402974 doi: 10.3184/174751914X14175125259964
Published online: 19 December 2014

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