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Short communication

The polymer-supported sulfonic acid catalyzed one-step synthesis of diaminotriphenylmethanes

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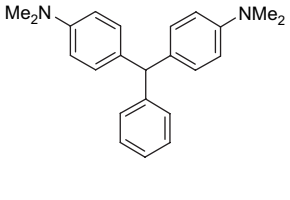
Abstract

A novel efficient method for the synthesis of diaminotriphenylmethanes (DTMs) in high yield through one-step condensation of arylaldehydes and *N*,*N*-dimethylaniline catalyzed by polymer-supported sulfonic acid (NKC-9) is described. This method offers the advantages of mild reaction condition, simplicity and reuse of the catalyst.

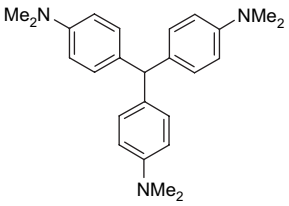
Keywords: Leuco-dye; Diaminotriphenylmethane; Polymer-supported sulfonic acid

1. Introduction

Diaminotriphenylmethanes (DTMs) can be used as dyes such as *Leucomalachite Green* and *Leucocrystal Violet* [1–3]. Inaddition, DTMs have other important chemical and biological utilities. They not only have antifungal activity [4–6], phototoxicity toward tumor cells [7], but also have been used as copper corrosion inhibitors [8]; furthermore, they have particular structural properties in solid and solution phases [9–12]. Hence, the development of new and more efficient synthetic methods for DTMs is important.



Leucocomalachite Green



Leucocrystal Violet

One of the most useful methods for the synthesis of DTMs is the reaction of arylaldehyde with *N*,*N*-dimethylaniline in the presence of an acid, such as sulfuric acid, HCl, and *p*-TSA, Lewis acids such as zinc chloride as well as zeolites and montmorillonite K-10 [13–19]. To the best of our knowledge, the use of polymer-supported sulfonic acid to catalyze the above-mentioned reaction is novel. This communication reports the synthesis of DTMs by the reaction of arylaldehydes with *N*,*N*-dimethylaniline catalyzed by a polystyrene-supported sulfonic acid (NKC-9) as depicted in Scheme 1.

2. Experimental

2.1. General synthetic procedure

A 25 mL three-necked flask equipped with a mechanical stirrer was charged with xylene (10 mL), arylaldehyde (1 mmol) and *N*,*N*-dimethylaniline (2 mmol) to which was added NKC-9 (0.5 g, >2.4 mmol H^+). The ensuing mixture was stirred at 110–120 °C for 6–8 h and cooled to room temperature. The catalyst was filtered off and washed three times

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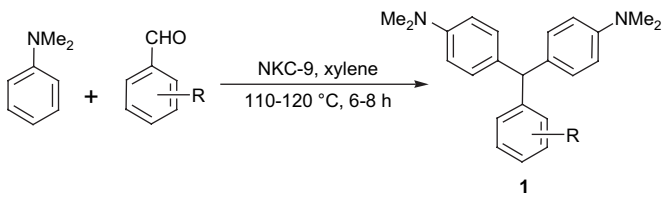

Scheme 1. **1a**, R = H; **1b**, R = 4-NO_2; **1c**, R = 3-NO_2; **1d**, R = 2-NO_2; **1e**, R = 4-Cl; **1f**, R = 4-Br; **1g**, R = 3-Br; **1h**, R = 4-CH_3; **1i**, R = 4-$N(CH_3)_2$; **1j**, R = 4-F.

with acetone (5 mL). The filtrate was collected and evaporated to dryness. The crude product was purified by recrystallization from petroleum ether to give **1**.

2.2. Analytical data for *1a–1j*

Compound **1a**: m.p. 91–92 °C, yield 80%; ^{1}H NMR ($CDCl_3$): δ 2.91 (s, 12H, 2N*(CH$_3$)$_2$*), 5.38 (s, 1H, Ph*CH*), 6.66–7.25 (m, 13H, *ArH*); IR (KBr, cm^{-1}): 3072 (w), 1611 (m), 1532 (s), 1459 (m), 1347 (m); HRMS: *m/z* calcd for $C_{23}H_{26}N_2$ 330.2096, found 330.2086.

Compound **1b**: m.p. 169–171 °C, yield 93%; ^{1}H NMR ($CDCl_3$): δ 2.94 (s, 12H, 2N*(CH$_3$)$_2$*), 5.46 (s, 1H, Ph*CH*), 6.67–8.13 (m, 12H, *ArH*); ^{13}C NMR ($CDCl_3$): δ 55.4, 113.0, 123.8, 130.3, 130.5, 131.4, 146.7, 149.8, 154.0; IR (KBr, cm^{-1}): 3071 (w), 1613 (m), 1520 (s), 1443 (m), 1342 (m); HRMS: *m/z* calcd for $C_{23}H_{25}N_3O_2$ 375.1947, found 375.1949.

Compound **1c**: m.p. 145–146 °C, yield 90%; ^{1}H NMR ($CDCl_3$): δ 2.95 (s, 12H, 2N*(CH$_3$)$_2$*), 5.48 (s, 1H, Ph*CH*), 6.69–8.04 (m, 12H, *ArH*); ^{13}C NMR ($CDCl_3$): δ 55.2, 113.1, 121.5, 124.5, 129.3, 130.2, 130.3, 131.5, 135.9, 148.4, 149.7; IR (KBr, cm^{-1}): 3087 (w), 1613 (m), 1520 (s), 1443 (m), 1350 (m); HRMS: *m/z* calcd for $C_{23}H_{25}N_3O_2$ 375.1947, found 375.1936.

Compound **1d**: m.p. 152–153 °C, yield 93%; ^{1}H NMR ($CDCl_3$): δ 2.93 (s, 12H, 2N$(CH_3)_2$), 6.09 (s, 1H, Ph*CH*), 6.65–7.82 (m, 12H, *ArH*); ^{13}C NMR ($CDCl_3$): δ 55.3, 122.8, 128.5, 129.4, 130.1, 130.3, 130.4, 130.5, 132.7, 148.4, 149.5; IR (KBr, cm^{-1}): 3071 (w), 1613 (m), 1520 (s), 1443 (m), 1350 (m); HRMS: *m/z* calcd for $C_{23}H_{25}N_3O_2$ 375.1947, found 375.1978.

Compound **1e**: m.p. 89–90 °C, yield 82%; ^{1}H NMR ($CDCl_3$): δ 2.91 (s, 12H, 2N*(CH$_3$)$_2$*), 5.33 (s, 1H, Ph*CH*), 6.64–7.24 (m, 12H, *ArH*); ^{13}C NMR ($CDCl_3$): δ 41.2, 55.3, 113.0, 113.1, 128.6, 130.3, 131.1, 132.0, 132.7, 149.5; IR (KBr, cm^{-1}): 3038 (w), 1613 (m), 1520 (s), 1443 (m), 1350 (m); HRMS: *m/z* calcd for $C_{23}H_{25}N_2Cl$ 366.1677, found 366.1689.

Compound **1f**: m.p. 117–118 °C, yield 80%; ^{1}H NMR ($CDCl_3$): δ 2.82 (s, 12H, 2N*(CH$_3$)$_2$*), 5.24 (s, 1H, Ph*CH*), 6.57–7.29 (m, 12H, *ArH*); ^{13}C NMR ($CDCl_3$): δ 41.2, 54.9, 113.0, 120.1, 130.3, 130.4, 131.6, 132.6, 146.1, 149.5. IR (KBr, cm^{-1}): 3033 (w), 1613 (m), 1520 (s), 1443 (m), 1350 (m).

Compound **1g**: m.p. 111–112 °C, yield 75%; ^{1}H NMR ($CDCl_3$): δ 2.95 (s, 12H, 2N*(CH$_3$)$_2$*), 5.36 (s, 1H, Ph*CH*), 6.70–7.34 (m, 12H, *ArH*); ^{13}C NMR ($CDCl_3$): δ 55.3, 113.1, 122.8, 128.5, 129.4, 130.1, 130.4, 130.5, 132.7, 148.4, 149.5; IR (KBr, cm^{-1}): 3071 (w), 1613 (m), 1520 (s), 1474 (m), 1443 (m), 1350 (m); HRMS: *m/z* calcd for $C_{23}H_{25}N_2Br$ 408.1201, found 408.1210.

Compound **1h**: m.p. 95–96 °C (lit 99–100 °C, Ref. [19]), yield 71%; ^{1}H NMR ($CDCl_3$): δ 2.32 (s, 3H, *CH$_3$*), 2.92 (s, 12H, 2N*(CH$_3$)$_2$*), 5.35 (s, 1H, Ph*CH*), 6.67–7.27 (m, 12H, *ArH*).

Compound **1i**: m.p. 167–168 °C (lit 175 °C, Ref. [16]), yield 66%; ^{1}H NMR ($CDCl_3$): δ 2.90 (s, 18H, 3*N(CH$_3$)$_2$*), 5.30 (s, 1H, Ph*CH*), 6.65–7.26 (m, 12H, *ArH*).

Compound **1j**: m.p. 99–100 °C, yield 85%; ^{1}H NMR ($CDCl_3$): δ 2.91 (s, 12H, 2N*(CH$_3$)$_2$*), 5.35 (s, 1H, Ph*CH*), 6.66–7.25 (m, 12H, *ArH*); ^{13}C NMR ($CDCl_3$): δ 41.2, 54.7, 113.0, 113.1, 115.1, 115.3, 130.3, 131.1, 131.2, 149.4; IR (KBr, cm^{-1}): 3063 (w), 1613 (m), 1512 (s), 1443 (m), 1350 (m); HRMS: *m/z* calcd for $C_{23}H_{25}N_2F$ 348.2002, found 348.1994.

3. Results and discussion

Initially, the reaction of benzaldehyde and *N*,*N*-dimethylaniline was conducted in the absence of NKC-9 at different temperatures, but no product was detected. Thus, the reaction was repeated in the presence of NKC-9 and, fortunately, the expected product **1a** was isolated from the reaction mixture and confirmed by IR, ^{1}H NMR, ^{13}C NMR and HRMS spectra. With these positive results, the reaction was carried out in different solvents from which it was established that no desired product was formed in $CHCl_3$ and cyclohexane (Table 1, entries 1 and 2) and only the trace amounts of product were detected using DMF (entry 3), and low yields of **1a** (entries 4–6) were obtained in benzene, toluene and chlorobenzene. It was obvious that xylene was the solvent of choice, it gave the highest yield (80%) at 110 °C in 8 h (entry 10).

The optimized condition for condensation of benzaldehyde and *N*,*N*-dimethylaniline was found to be as follows: to 10 mL xylene, benzaldehyde (1 mmol), *N*,*N*-dimethylaniline (2 mmol) and NKC-9 (0.5 g, >2.4 mmol H^+) were added. The mixture was stirred at 110–120 °C for 6–8 h. This

Table 1
Effect of different solvents on the yield of **1a**

Entry	Solvent	Temperature (°C)	Time (h)	Yield (%)[a]
1	$CHCl_3$	Reflux	8	Nr[b]
2	Cyclohexane	Reflux	8	Nr[b]
3	DMF	110	8	Trace
4	Benzene	Reflux	8	25
5	Toluene	110	8	35
6	Chlorobenzene	110	8	30
7	Xylene	60	8	20
8	Xylene	80	8	40
9	Xylene	100	8	70
10	Xylene	110	6	80

[a] Isolated yield.
[b] No reaction.

Table 2
The reusability of NKC-9 for the synthesis of compound **1a**

Run	Time (h)	Yield (%)[a]
1	6	80
2	6	80
3	7	79
4	7	78
5	8	76
6	8	75

[a] Yield of **1a**.

procedure was applied to the reactions of other arylaldehydes and *N*,*N*-dimethylaniline. The examination of benzaldehyde analogues revealed that the reaction was tolerant to substituents including methyl, halogen, nitro, and *N*,*N*-dimethylamino groups. It is worthy to note that the arylaldehyde with electron-withdrawing group is more favorable for the condensation. For example, 4-nitrobenzaldehyde gave 93% yield of **1b**. In contrast, the aldehyde with electron-donating substituent provided low yield, such as the case of formation of Leucocrystal Violet (**1i**) (66%).

Finally, the reusability of NKC-9 was investigated. The results showed that NKC-9 was stable; its activity remained unchanged after six runs (Table 2). If its activity is reduced, it can be reactivated by washing with acetone, dried in air and then kept in an oven at 100 °C for 2 h.

In summary, a new one-step synthesis of diaminotriphenylmethanes (DTMs) by the reaction of arylaldehydes and *N*,*N*-dimethylaniline catalyzed by polymer-supported sulfonic acid (NKC-9) has been developed. This method has the advantages of the cheap catalyst, mild condition, simple operation, good to excellent yields, and the reusability of NKC-9.

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