Synthesis of polynitrostilbenes from 2,4,6-trinitro-*m*-xylene and 2,4,6-trinitrotoluene by a microwave-assisted solvent free method

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A microwave-assisted method for the synthesis of polynitrostilbenes involving the condensation of 2,4,6-trinitro-*m*-xylene and 2,4,6-trinitrotoluene with aryl aldehydes in the presence of piperidine and silica-gel is reported. Compared with conventional methods, a shorter reaction time is required and this method has a lower environmental impact. A mechanism for the reaction is also proposed and supported by UV-Vis absorption spectroscopy.

Keywords: polynitrostilbenes, microwave irradiation, silica-gel supported, solvent-free reaction

Polynitrostilbenes, such as 2,2′,4,4′,6,6′-hexanitrostilbene (HNS)[1–3] are well known explosives with excellent thermal stability and detonation properties. Nitrostilbene-based compounds are also widely used as organic nonlinear optical materials[4–9] for high-performance electro-optical devices. The Mizoroki–Heck reaction, Negishi–Stille coupling and Wittig-type reactions have proved to be quite versatile in the preparation of different substituted stilbenes. However, they need transition-metal catalysis and complicated sequences to form halogen- and phosphorus-containing substrates.[10–15] More recently, transition metal catalysts especially palladium have been widely studied in stilbene syntheses. Other methods include the McMurry coupling and alkene cross-metathesis as well as one-pot multicatalytic processes.[16–19] These sometimes lacked stereoselectivity and the cost was increased by using noble metals. We have reported[20] that 2,4,6-trinitro-*m*-xylene (TNMX) will condense with two equivalents of aromatic aldehydes in boiling benzene with a piperidine catalyst. The whole process was time-consuming but proceeded with high stereoselectivity.

Recently, microwave-assisted organic synthesis (MAOS) has developed into a popular branch of synthetic organic chemistry,[21–25] as it helps in minimising the energy consumption required for heating as well as the time required for the reaction. However, a combination of microwave and solvent-free conditions are rare in polynitrostilbene chemistry. We now report a useful and solvent-free method for the synthesis of an array polynitrostilbenes based on TNMX and 2,4,6-trinitrotoluene (TNT) with piperidine catalysis utilising microwave irradiation. To make the system safer, silica-gel was used as an effective solid support. In order to shed more light on this reaction, the mechanism of the reaction was also studied by UV-Vis absorption.

Results and discussion

Initially, we performed the reaction using TNMX, benzaldehyde and silica-gel in the absence of piperidine with an irradiation power of 300 W at 120 °C for 15 min. Even though in some reports, the silica gel supporter was an effective catalyst for Knoevenagel reactions under microwave irradiation,[26–28] no catalytic effect was found with silica-gel which lacked the basic strength for this reaction. (Table 1, entries 1 and 2) The two starting materials were then mixed without silica-gel but in the presence of piperidine. The reaction was originally carried out in a domestic microwave oven for 15 min, affording the desired product **3** in 74% yield (Table 1, entry 3). However, in some cases, decomposition occurred and potential hazards were identified with this oven and a laboratory oven was used. Silica-gel was used as a security guard with economical and recyclable properties. Furthermore, by increasing the reaction temperature to 130 °C, the product **3** was obtained with 75% yield (Table 1, entry 5). When the reaction was carried out at 140 °C, no significant change in the yield was observed (Table 1, entry 6). Increasing the irradiation time to 20 min, enhanced the yield to 85% (Table 1, entries 6 and 7). On further increasing the irradiation time, the yield decreased (Table 1, entry 8). It was observed in this study that the temperature did not have much influence on the reaction (Table 1, entries 4, 5 and 6). High temperature (more than 150 °C) might cause the catalyst to evaporate and carbonise since some black substance appeared. On the other hand, the reaction time proved to have a great influence on the yield (Table 1, entries 4, 7 and 8). Screening these reaction parameters revealed that a time of 20 min was most appropriate and the temperature was controlled at 120 °C.

Finally, we examined the amount of piperidine loaded on the silica-gel. We carried out the reaction with different amounts of piperidine. (Table 2) The optimum amount amount of piperidine loaded on the silica-gel was 2.0 mmol for the synthesis of **3** (Table 1, entry 7). Moreover, to elucidate the importance of microwave irradiation, we also carried out the reaction under conventional heating (oil bath) and even after a long reaction time (100 min) only 45% yield of desired product was achieved (Table 1, entry 12).

Once we had established the best conditions, we then examined the scope of the reaction (Table 3). At first, a variety of aromatic aldehydes were reacted with TNMX in order to synthesise different polynitrostilbenes. Furthermore, to reveal the advantages of a microwave-assisted synthesis of polynitrostilbenes, the traditional thermal assisted results were also examined. The electronic effects of substituents in aromatic aldehydes were evaluated and a remarkable effect on the reaction was discovered. For instance, when there was a chlorine substituent in the aldehyde, a significant increase in the reaction time ranging from 26 h to 45 h was observed and the yield of the products decreased compared to benzaldehyde in the traditional method. However, by using a microwave-assisted method the reaction time was controlled at only 20 min and the yield of the desired products was nearly the same as the traditional method (Table 2, entries 1–5).

If a strong electron-withdrawing nitro group was employed, the corresponding products were obtained in lower yields. About 5% of the product was achieved after 24 h with *ortho*-nitrobenzaldehyde using the traditional method. Notably, the yield increased to 50% by applying the microwave methodology in 20 min (Table 2, entry 6). It might be explained by "nonthermal" microwave effects.

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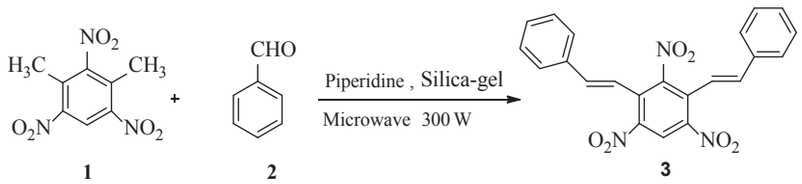
Table 1 Optimisation of silica-gel supported microwave-assisted condensation[a]

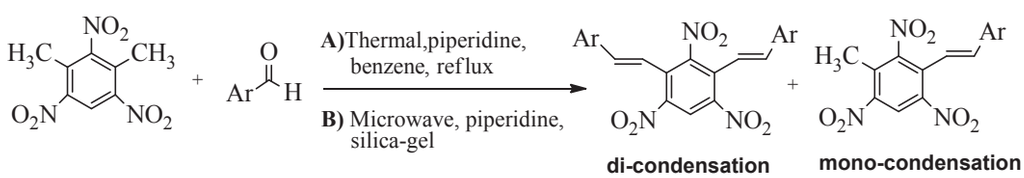


1 **2** **3**

Entry	Piperidine loading/mmol	Time/min	Temperature/°C	Yield/%[b]
1	0.0	15	120	0
2[c]	0.0	15	120	0
3[c]	2.0	15	120	74
4	2.0	15	120	73
5	2.0	15	130	75
6	2.0	15	140	76
7	2.0	15	120	85
8	2.0	25	120	83
9	1.5	20	120	77
10	2.5	20	120	85
11	3.0	20	120	84
12[d]	2.0	100	120	45

[a]Reactions were carried out with 2.0 mmol of TNMX and 4.2 mmol of benzaldehyde, 3.5 g of silica gel. Irradiations were carried out in a microwave oven operating at 300 W.
[b]Isolated yield after recrystallisation of via silica gel column.
[c]Without SiO_2.
[d]Conventional heating, oil bath.

Table 2 Diversification of polynitrostilbenes via substituted aldehydes[a]

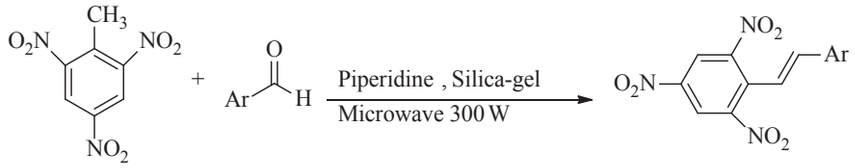


di-condensation **mono-condensation**

Entry	Ar	Method	Time	Yield of di-/%[b]	Yield of mono-/%[b]
1	C_6H_5-	**A**[c]	26 h	85	0
		B[d]	20 min	83	0
2	2-ClC_6H_4-	**A**	28 h	81	0
		B	20 min	80	0
3	3-ClC_6H_4-	**A**	26 h	82	0
		B	20 min	80	0
4	4-ClC_6H_4-	**A**	26 h	79	0
		B	20 min	77	0
5	2,4-$Cl_2C_6H_3$-	**A**	45 h	70	0
		B	20 min	70	0
6	2-$NO_2C_6H_4$-	**A**	24 h	5	0
		B	20 min	50	0
7	3-$NO_2C_6H_4$-	**A**	25 h	30	0
		B	20 min	55	0
8	4-$NO_2C_6H_4$-	**A**	19 h	0	0
		B	20 min	0	0
9	4-$CH_3C_6H_4$-	**A**	12 h	88	0
		B	20 min	86	0
10	4-$OCH_3C_6H_4$-	**A**	12 h	89	0
		B	20 min	87	0
11	3-OHC_6H_4-	**A**	40 h	55	14
		B	20 min	64	4
12	4-$N(CH_3)_2C_6H_4$-	**A**	24 h	75	20
		B	20 min	85	5

[a]Reactions were carried out with 2.0 mmol of TNMX and 4.2 mmol of aromatic aldehyde, 2.0 mmol of piperidine.
[b]Isolated yield after recrystallisation of via silica column.
[c]Benzene as a solvent, the reflux rate was controlled at about 100 drops/min.
[d]Irradiations were carried out in a microwave oven operating at 300 W, temperature 120 °C, 3.5 g of silica gel.

Table 3 Condensation of TNT and aromatic benzaldehyde[a]



Entry	Ar	Yield/%[b]	Entry	Ar	Yield/%[b]
1	C_6H_5-	88	6	2-$NO_2C_6H_4$-	78
2	2-ClC_6H_4-	82	7	3-$NO_2C_6H_4$-	82
3	3-ClC_6H_4-	83	8	4-$NO_2C_6H_4$-	76
4	4-ClC_6H_4-	82	9	4-$CH_3C_6H_4$-	82
5	2,4,-$Cl_2C_6H_3$-	80	10	4-$N(CH_3)_2C_6H_4$-	80

[a]Reactions were carried out with 2.0 mmol of TNT and 2.1 mmol of aromatic aldehyde, piperidine, 2.0 mmol. Irradiations were carried out in a microwave oven operating at 300 W, temperature 120 °C, time 20 min, silica gel, 3.5 g.
[b]Isolated yield after recrystallisation.

Using *meta*-nitrobenzaldehyde as the aldehyde, the yield of the product was 30% by the traditional method while a 55% yield was obtained by the microwave irradiation (Table 2, entry 7). Interestingly, *para*-nitrobenzaldehyde did not undergo in this reaction at all using the either traditional method or the microwave (Table 2, entry 8).

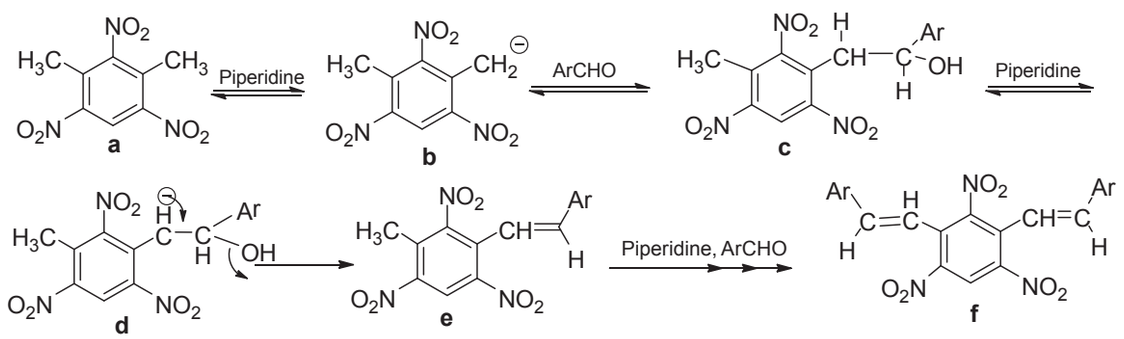
Using an electron-donating methyl and methoxyl group in the *para*-position in the aldehydes, the corresponding products were obtained in yields of 88% and 89% by the conventional method while nearly the same yield was obtained by microwave methodology (Table 2, entries 9 and 10). Furthermore, it was observed in this study that mono-condensation products could be isolated for *meta*-hydroxybenzaldehyde and *para*-dimethylamino-benzaldehyde by the traditional method (Table 2, entries 11 and 12). However, applying the microwave methodology, we found that the yield of mono-condensation products decreased while the di-condensation products increased.

To establish the generality and scope of the method, the procedure was successfully applied to TNT and afforded the desired condensation products in excellent yields, as the methyl group in TNT was more activated than TNMX (Table 3). Aromatic aldehydes substituted with a nitro-group also gave the corresponding products in an acceptable yield (Table 3, entries 6–8).

Interestingly, when piperidine was added to TNMX solution, the colour of the solution changed, which gave a better understanding of this type of reaction. In order to investigate the mechanism of the condensation, UV-Vis absorption spectra was used for detecting the changes. When we mixed TNMX with piperidine in an acetonitrile solution, a new absorption peak appeared around 330 nm. However, no changes happened in absorption when mixing of benzaldehyde and piperidine (ESI) It is proposed that the formation of a methylene anion occurs first with the piperidine catalyst. A plausible pathway for the synthesis of polynitrostilbenes is illustrated in Scheme 1. We assumed that initially one of the two methyl groups in TNMX **a** was deprotonated by the organocatalyst piperidine affording the intermediate carbanion **b**, which then reacted with the aromatic aldehyde in an aldol reaction and formed the product **c**. Subsequently, **c** was deprotonated to give **d** in another piperidine catalysed step and furnished the elimination product **e**. The final di-condensation product **f** was formed by a similar sequence.

Conclusion

In summary, we have described a new approach to the synthesis of polynitrostilbenes. The process takes place under silica-gel supported solvent-free conditions utilising microwave irradiation with a piperidine catalyst. Applying this new methodology, we obtained the desired compounds in good yields within a short time. Moreover, two mono-condensation products were separated successfully with TNMX. The mechanism of this reaction was also studied by UV-Vis absorption spectra. The extension of this approach to other polynitrostilbenes and more detailed work on the mechanisms are in progress in our laboratory.



Scheme 1 Possible mechanism of this type condensation catalysed by piperidine.

Experimental

CAUTION: Although no problems were encountered during the synthesis, all polynitrocompounds are explosive and great care must be taken in all the processes. Safety equipment such as Kevlar gloves, bar shields, and ear plugs are highly recommended especially when collecting the energetic materials. It is also advised to work on all small quantities (< 1.0 g). Large-scale reactions require other safety means.

All microwave reactions were carried out in specialised vessels in the microcomputer microwave chemical reactor WBFY-201. The temperature was monitored throughout the reaction by an infrared detector. All chemical reagents and solvents (analytical grade) were used as supplied unless otherwise stated. All experiments were monitored by TLC, TLC plates were visualised by exposure to UV light (254 nm). ^{1}H and ^{13}C spectra were recorded on a Bruker Avance III 500 MHz, using $CDCl_3$ or DMSO-d_6 as a solvent. Coupling constants are reported in Hz. IR spectra were recorded using Bruker Tensor 27 with the sample dispersed in a KBr pellet. Multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. Mass spectra were obtained using an electrospray (ESI-TOF) mass spectrometer 6500 Series and a Bruker Daltonics flexAnalysis instrument. The UV-Vis absorption was carried out on Shimadzu UV-1800 Series, wavelength range (nm) from 220.0 to 600.0, slit width is 1.0 nm and light source wavelength is 340.0 nm.

Traditional thermal synthesis

In a typical experiment, the polynitroaromatic (2.0 mmol), benzene (40 mL), aromatic aldehyde (4.2 mmol), piperidine (2.0 mmol) were placed in a 100 mL flask equipped with a Dean-Stark trap. The mixture was heated to reflux for 15 h or even more. The whole process was monitored by thin-layer chromatography (TLC). After evaporation of the benzene (25–30 mL), ethanol was added dropwise to the residue until a precipitate appeared. Then, the mixture was cooled to room temperature and placed in a refrigerator overnight. The precipitated product was collected, washed and dried. The solid was crystallised from an appropriate solvents. In some cases, when ethanol was added, no precipitate appeared and the product was isolated *via* silica gel column chromatography.

Microwave irradiation

In a typical experiment, the polynitroaromatic (2.0 mmol) together with aromatic aldehyde (4.2 mmol) and piperidine (2.0 mmol) were dissolved in methylene dichloride (15 mL). Then 3.5 g silica gel (48–75 um) was added and thoroughly mixed. The solution was evaporated slowly to dryness under normal atmospheric pressure. The solid was transferred into a specialised vessel and the glass vessel (Pyrex) was irradiated in a microwave oven during appropriate time at the indicated power (see Table 2). After cooling, the reaction product was isolated by extraction of the silica gel with methylene dichloride (2 × 20 mL) or acetone (2 × 20 mL).The organic layer was evaporated to dryness under reduced pressure to obtain crude product. The product was purified by recrystallisation or *via* silica gel column chromatography.

trans,trans-*1,3-Distyryl-2,4,6-trinitrobenzene (Table 2, entry 1)*: Yellow solid, recrystallisation from acetone, m.p. 149–150 °C, (lit.[20] 149.5–151.1 °C), IR (ν, cm^{-1}): 3095, 1634, 1588, 1541, 1451, 1395, 1344, 968. ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.72 (s, 1H), 7.50–7.37 (m, 10H), 7.20 (d, *J* = 16.60 Hz, 2H), 6.90 (d, *J* = 16.6 Hz, 2H).

trans,trans-*1,3-Di[2'-chlorostyryl]-2,4,6-trinitrobenzene (Table 2, entry 2)*: Yellow solid, recrystallisation from ethanol/acetone, m.p. 167–168 °C, IR (ν, cm^{-1}): 3099, 1631, 1582, 1552, 1534, 1511, 1468, 1386, 1334, 966. ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.82 (s, 1H), 7.66–7.64 (m, 2H), 7.42–7.40 (m, 2H), 7.33–7.32 (m, 4H), 7.29 (d, *J* = 16.60 Hz, 2H), 7.20 (d, *J* = 16.60 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), 151.01, 145.83, 134.10, 133.32, 132.25, 130.22, 129.83, 129.03, 126.40, 126.27, 120.80, 117.58. HRMS calcd for $C_{22}H_{13}Cl_2N_3O_6$ $(M+H)^+$: 485.9780, found 485.9776.

trans,trans-*1,3-Di[3'-chlorostyryl]-2,4,6-trinitrobenzene (Table 2, entry 3):* Yellow solid, recrystallisation from ethanol/acetone, m.p. 142–143 °C, (lit.[20] 142.5–143.1 °C), IR (ν, cm^{-1}): 3098, 1631, 1602, 1547, 1473, 1402, 1347, 979. ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.78 (s, 1H), 7.46 (s, 2H), 7.37–7.33 (m, 6H), 7.21 (d, *J* = 16.60 Hz, 2H), 6.81 (d, *J* = 16.60 Hz, 2H).

trans,trans-*1,3-Di[4'-chlorostyryl]-2,4,6-trinitrobenzene (Table 2, entry 4)*: Yellow solid, recrystallisation from ethanol/acetone, m.p. 158–160 °C, IR (ν, cm^{-1}): 3094, 1634, 1588, 1543, 1490, 1333, 972; ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.76 (s, 1H), 7.43–7.37 (m, 8H), 7.17 (d, *J* = 16.60 Hz, 2H), 6.84 (d, *J* = 16.60 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 145.70, 136.68, 135.02, 132.31, 129.89, 128.26, 127.68, 127.35, 120.78, 115.34. HRMS calcd for $C_{22}H_{13}Cl_2N_3O_6$ $(M+H)^+$: 485.9780, found 485.9749.

trans,trans-*1,3-Di[2',4'-dichlorostyryl]-2,4,6-trinitrobenzene (Table 2, entry 5)*: Yellow solid, recrystallisation from ethanol/acetone, m.p. 166–167 °C, IR (ν, cm^{-1}): 3095, 1633, 1545, 1383, 1339, 976; ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.81 (s, 1H), 7.56 (d, *J* = 2.00 Hz, 2H), 7.50 (d, *J* = 8.40 Hz, 2H), 7.32–7.30 (dd, J_1 = 2.00 Hz, J_2 = 8.40 Hz, 2H), 7.19 (d, *J* = 16.55 Hz, 2H), 6.77 (d, *J* = 16.55 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 150.74, 145.80, 135.30, 133.69, 133.10, 132.40, 129.98, 129.66, 128.11, 125.46, 120.94, 116.71. HRMS calcd for $C_{22}H_{11}Cl_4N_3O_6$ $(M+H)^+$: 555.9297, found 555.9294.

trans,trans-*1,3-Di[2'-nitrostyryl]-2,4,6-trinitrobenzene (Table 2, entry 6)*: Green yellow solid, recrystallisation from acetone, m.p. 212–213 °C, IR (ν, cm^{-1}): 3097, 1629, 1603, 1550, 1524, 1341, 975; ^{1}H NMR (500 MHz, DMSO-d_6), δ 9.07 (s, 1H) 8.09 (d, *J* = 8.15 Hz, 2H), 7.86 (d, *J* = 3.95 Hz, 2H), 7.69–7.66 (m, 4H), 7.50 (d, *J* = 16.45 Hz, 2H), 7.21 (d, *J* = 16.45 Hz, 2H); ^{13}C NMR (126 MHz, DMSO-d_6), δ 149.77, 147.23, 146.48, 133.59, 131.04, 129.89, 129.54, 128.33, 127.86, 124.23, 122.43, 121.96. HRMS calcd for $C_{22}H_{13}N_5O_{10}$ $(M+H)^+$: 508.0210, found (M + H) 508.0206, (M + Na) 530.0121, (M + K) 545.9988.

trans,trans-*1,3-Di[3'-nitrostyryl]-2,4,6-trinitrobenzene (Table 2, entry 7)*: Pale yellow solid, recrystallisation from glacial acetic acid, m.p. 238–240 °C, IR (ν, cm^{-1}): 3084, 1636, 1585, 1529, 1391, 1348, 973; ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.89 (s, 1H), 8.34 (s, 2H), 8.27 (d, *J* = 8.15 Hz, 2H), 7.82 (d, *J* = 7.50 Hz, 2H),7.64–7.61 (dd, J_1 = 8.15 Hz, J_2 = 7.50 Hz, 2H), 7.34 (d, *J* = 16.45 Hz, 2H), 6.93 (d, *J* = 16.45 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 147.76, 145.97, 135.34, 135.14, 131.98, 129.56, 129.13, 127.94, 123.43, 121.13, 121.05, 118.09. HRMS calcd for $C_{22}H_{13}N_5O_{10}$ $(M+H)^+$: 508.2436, found 508.2439(M + H), 568.2878(M + Na + K).

trans,trans-*1,3-Di[4'-methylstyryl]-2,4,6-trinitrobenzene (Table 2, entry 9)*: Light yellow solid, recrystallisation from ethanol/acetone; m.p. 158–159 °C, (lit.[29] 158.4 °C), IR (ν, cm^{-1}): 3096, 1632, 1544, 1543, 1451, 1335, 974. ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.69 (s, 1H), 7.39(d, *J* = 8.00 Hz 4H), 7.22(d, *J* = 8.00 Hz, 4H), 7.13(d, *J* = 16.55 Hz, 2H), 6.86 (d, *J* = 16.55 Hz, 2H), 2.39(s, 6H).

trans,trans-*1,3-Di[4'-methoxystyryl]-2,4,6-trinitrobenzene (Table 2, entry 10)*: Orange yellow solid, recrystallisation from ethanol/acetone; m.p. 160–162 °C, IR (ν, cm^{-1}): 3094, 1631, 1606, 1585, 1511, 1385, 1329, 973; ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.65 (s, 1H), 7.42 (d, *J* = 8.40 Hz, 4H), 7.01 (d, *J* = 16.50 Hz, 2H), 6.91 (d, *J* = 8.40 Hz, 4H), 6.82 (d, *J* = 16.50 Hz, 2H), 3.84 (s, 6H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 160.15, 150.39, 145.23, 137.80, 130.26, 128.12, 126.75, 120.71, 113.39, 112.19, 54.47. HRMS calcd for $C_{24}H_{19}N_3O_8$ $(M+H)^+$: 478.2920, found 478.2924.

trans,trans-*1,3-Di[3'-hydroxystyryl]-2,4,6-trinitrobenzene (Table 2, entry 11)*: Yellow solid, the product was achieved *via* silica gel column with hexane/ethyl acetate (5 : 1); m.p. 194–196 °C, IR (ν, cm^{-1}): 3400, 3095, 1635, 1609, 1586, 1514, 1395, 1323, 972; ^{1}H NMR (500 MHz, DMSO-d_6), δ 9.60 (s, 2 H), 9.00(s, 1H), 7.29 (d, *J* = 16.60 Hz, 2 H), 7.23(t, *J* = 7.85 Hz, 2 H), 6.98 (d, *J* = 7.70 Hz, 2 H), 6.94 (s, 2 H), 6.81–6.78, (dd, J_1 = 8.10 Hz, J_2 = 1.75 Hz, 2H), 6.78 (d, *J* = 16.60 Hz, 2 H); ^{13}C NMR (126 MHz, DMSO-d_6), δ 157.26, 149.90, 145.98, 136.58, 135.74, 129.96, 129.49, 122.13, 117.87, 116.63, 116.31, 112.99. HRMS calcd for $C_{22}H_{15}N_3O_8$ $(M+H)^+$: 450.0968, found 450.0975, 511.0722(M + Na + K).

3-Methyl-trans-*3'-hydroxy-2,4,6-trinitrostilbene (Table 2, entry 11)*: Yellow solid, the product was achieved *via* silica gel column with hexane/ethyl acetate (5 : 1); m.p. 160–162 °C, IR (ν, cm^{-1}): 3408, 3092, 1633, 1605, 1576, 1524, 1394, 1313, 975; ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.71 (s, 1 H), 7.29 (t, *J* = 9.3 Hz, 1H), 7.16 (d, *J* = 16.60 Hz, 1 H),

7.05(d, J=7.65 Hz, 1 H), 6.95 (t, J=2.05 Hz, 1H), 6.87(dd, J_1=8.05 Hz, J_2=1.90 Hz, 1H), 6.80 (d, J=16.60 Hz, 1H), 2.60(s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6), δ 157.25, 151.25, 147.39, 145.42, 136.23, 135.76, 129.94, 129.65, 129.44, 122.03, 117.82, 116.89, 116.25, 112.95, 14.14. HRMS calcd for $C_{15}H_{11}N_3O_7$ $(M+H)^+$: 346.0597, found 346.0592.

trans,trans-*1,3-Di[4'-dimethylaminostyryl]-2,4,6-trinitrobenzene (Table 2, entry 12)*: Black solid, recrystallisation from ethanol/acetone; m.p. 199–200 °C, IR (ν, cm^{-1}): 3089, 2894, 1606, 1606, 1575, 1525, 1439, 1365, 1327, 1185, 969; ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.56 (s, 1H), 7.38 (d, J=8.80 Hz, 4 H), 6.94(d, J=16.40 Hz, 2H), 6.84 (d, J=16.40 Hz, 2H), 6.72 (d, J=6.50 Hz,4 H), 3.03 (s, 12H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 150.44, 150.00, 144.41, 138.71, 130.42, 128.16, 122.43, 120.81, 111.11, 109.27, 39.32. HRMS calcd for $C_{26}H_{25}N_5O_6$ $(M+H)^+$: 504.1805, found 504.1811.

3-Methyl-trans-*4'-dimethylamino-2,4,6-trinitrostilbene (Table 2, entry 12)*: Dark green solid, the product was achieved *via* silica gel column with hexane/ethyl acetate (6 : 1); m.p. 204–205 °C, IR (ν, cm^{-1}): 3078, 2896, 1580, 1526, 1362, 1332, 1170, 973; ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.62 (s, 1H), 7.39 (d, J=8.70 Hz, 2H), 6.94 (d, J=16.45 Hz, 1H), 6.84 (d, J=16.45 Hz, 1H), 6.74 (d, J=6.50 Hz, 2H), 3.04 (s, 6H), 2.57 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 151.63, 150.54, 145.64, 145.22, 139.16, 130.17, 129.42, 128.78, 128.27, 120.81, 111.15, 108.85, 39.33, 14.04. HRMS calcd for $C_{17}H_{16}N_4O_6$ $(M+H)^+$: 373.1070, found 373.1066.

trans-*2,4,6-Trinitrostilbene (Table 3, entry 1)*: Yellow solid, recrystallisation from ethanol/acetone, m.p. 155–156 °C (lit.[11] 156 °C), IR (ν, cm^{-1}): 3104, 3074, 1629, 1600, 1532, 1450, 1402, 1086, 975. ^{1}HNMR (500 MHz, $CDCl_3$), δ 8.86 (s, 2H), 7.49–7.36 (m, 5H), 7.36 (d, J=16.60 Hz, 1H), 6.79 (d, J=16.60 Hz, 1H).

trans-*2'-Chloro-2,4,6-trinitrostilbene (Table 3, entry 2)*: Yellow solid, recrystallisation from ethanol/acetone; m.p. 146–147 °C, (lit.[30] 145.5–146 °C), IR (ν, cm^{-1}): 3084, 1630, 1604, 1542, 1469, 1403, 1343, 974; ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.93 (s, 2H), 7.70–7.68 (m, 1H), 7.43–7.41 (m, 1H), 7.36–7.32 (m, 3H), 7.17 (d, J=16.60 Hz, 1H).

trans-*3'-Chloro-2,4,6-trinitrostilbene (Table 3, entry 3)*: Yellow solid, recrystallisation from ethanol/acetone, m.p. 141–142 °C, IR (ν, cm^{-1}): 3106, 3075, 1636, 1598, 1548, 1473, 1425, 1346, 981; ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.91 (s, 2H), 7.48(s, 1H), 7.38–7.33 (m, 4H), 6.70 (d, J=16.60 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 149.30, 145.27, 135.98, 135.53, 134.10, 132.42, 129.28, 128.98, 126.29, 124.65, 121.31, 117.13. HRMS calcd for $C_{14}H_8ClN_3O_6$ $(M+H)^+$: 350.0102, found 350.0105.

trans-*4'-Chloro-2,4,6-trinitrostilbene (Table 3, entry 4)*: Yellow solid, recrystallisation from ethanol/acetone; m.p. 156–157 °C, (lit.[31] 154–155 °C), IR (ν, cm^{-1}): 3103, 3072, 1633, 1597, 1543, 1472, 1421, 1342, 978; ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.89 (s, 2H), 7.43–7.38(dd, J_1=19.05 Hz, J_2=8.60 Hz, 4H), 7.34 (d, J=16.60 Hz, 1H), 6.73 (d, J=16.60 Hz, 1H).

trans-*2',4'-Dichloro-2,4,6-trinitrostilbene (Table 3, entry 5)*: Yellow solid, recrystallisation from ethanol/acetone, m.p. 165–166 °C, IR (ν, cm^{-1}): 3073, 1635, 1593, 1535, 1469, 1390, 1345, 980; ^{1}H NMR (500 MHz, $CDCl_3$), δ 8.92 (s, 2H), 7.57(d, J=2.05 Hz, 1H) 7.50(d, J=8.35 Hz, 1H), 7.36–7.31 (m, 2H), 6.66 (d, J=16.60 Hz, 1H); ^{13}C NMR (126 MHz, $CDCl_3$), δ 149.28, 145.39, 134.75, 133.71, 133.12, 132.45, 132.17, 130.01, 128.09, 125.42, 121.36, 117.60. HRMS calcd for $C_{14}H_7Cl_2N_3O_6$ $(M+H)^+$: 383.9712, found 383.9720.

trans-*2'-Nitro-2,4,6-trinitrostilbene (Table 3, entry 6)*: Yellow solid, recrystallisation from acetone, m.p. 179–180 °C, (lit.[32] 181 °C), IR (ν, cm^{-1}): 3112, 3090, 1606, 1541, 1439, 1405, 1347, 969; ^{1}H NMR (500 MHz, $CDCl_3$), 8.99 (s, 2H), 8.15(d, J=8.20 Hz, 1H), 7.75(d, J=3.70 Hz, 2H), 7.60–7.57 (m, 1H), 7.32 (d, J=16.40 Hz, 1H), 7.26(d, J=16.40 Hz, 1H).

trans-*3'-Nitro-2,4,6-trinitrostilbene (Table 3, entry 7)*: Yellow solid, recrystallisation from ethanol/acetone; m.p. 159–160 °C, (lit.[32] 159 °C), IR (ν, cm^{-1}): 3090, 1635, 1600, 1534, 1438, 1410, 1352, 973. ^{1}H NMR (500 MHz, $CDCl_3$), 8.96 (s, 2H), 8.34 (s, 1H), 8.25(t, J=8.0 Hz, 1H), 7.82(d, J=8.0 Hz, 1H), 7.62 (t, J=8.0 Hz, 1H), 7.52 (d, J=16.60 Hz, 1H), 6.78(d, J=16.60 Hz, 1H).

trans-*4'-nitro-2,4,6-trinitrostilbene (Table 3, entry 8)*: Yellow solid, recrystallisation from ethanol/acetone; m.p. 195–196 °C, (lit.[33] 196 °C), IR (ν, cm^{-1}): 3099, 1698, 1539, 1509, 1401, 1344, 967. ^{1}H NMR (500 MHz, $CDCl_3$), 8.97 (s, 2H), 8.29(d, J=8.70 Hz, 2H), 7.66(d, J=8.70 Hz, 2H), 7.53 (d, J=16.65 Hz, 1H), 6.78(d, J=16.65 Hz, 1H).

trans-*4'-Methyl-2,4,6-trinitrostilbene (Table 3, entry 9)*: Light yellow solid, recrystallisation from ethanol/acetone; m.p. 162–163 °C, (lit.[34] 162.3 °C), IR (ν, cm^{-1}): 3083, 1628, 1597, 1536, 1407, 1342, 974.

trans-*4'-Dimethylamino-2,4,6-trinitrostilbene (Table 3, entry 10)*:Yellow solid, recrystallisation from ethanol/acetone; m.p. 232–233 °C, (lit.[34] 232–233 °C), IR (ν, cm^{-1}): 3092, 3078, 1631, 1580, 1526, 1443, 1362, 1332, 1235, 1170, 962.

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