First TDAE-Mediated Double Addition of Nitrobenzylic Anions to Aromatic Dialdehydes

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Abstract: We report herein the first tetrakis(dimethylamino)ethylene (TDAE)-mediated double addition of nitrobenzylic anions to aromatic dialdehydes such as terephthalaldehyde and isophthalaldehyde, and have developed a new methodology that allows us to observe the double addition. This TDAE-mediated approach is an original and mild method with which to generate tri-aromatic diols.

Key words: TDAE, dialdehydes, reduction, nucleophilic addition, nitrobenzyl anions

Since tetrakis(dimethylamino)ethylene (TDAE) was first discovered by Pruett[1] in 1950 (Figure 1), a large number of applications have been developed that use this powerful electron donor. In 1966, Carpenter[2] showed that TDAE can be used as a single electron transfer (SET) reagent in dehalogenation processes using $CF_3CCl_2CCl_3$ and $CF_3CCl_2CCl_2CF_3$ as substrates. Pawelke[3] later found that at low temperatures, TDAE and CF_3I form a charge-transfer complex that can act as a nucleophilic trifluoromethylating reagent in polar solvents. In 1998,[4] Médebielle showed that TDAE could generate stable anions derived from bromodifluoromethylated heterocycles. Later, in 1999[5] it was demonstrated that the CF_3I/TDAE reagent combination could promote nucleophilic trifluoromethylation of *p*-toluenesulfinimides with very good diastereoselectivities. Nishiyama confirmed that TDAE could be used in the reductive debromination of 1,2-bis(bromoethyl)arene and in the reductive dimerization of α-bromoesters.[6] Moreover, Tanaka[7,8] has discovered that TDAE could be used in several metal-mediated coupling reactions. Since 2005, Murphy and collaborators[9] focused their research on TDAE-analogs as super-electron-donors, and a range of tetraazaalkenes have be used to reduce sulfones, sulfonamides and enhanced iodoaryl compounds in order to generate indolines, bicyclic lactones and tetrahydrofurans.

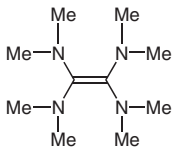

Figure 1 Tetrakis(dimethylamino)ethylene (TDAE)

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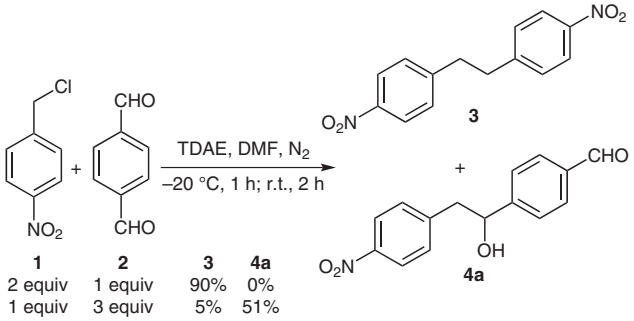
TDAE, an organic reducing agent, is able to react with halogenated derivatives to generate an anion, under mild conditions, via two sequential transfers of one electron.[10,11] According to this strategy, we have recently developed several useful reactions between nitrobenzylic substrates and various electrophiles such as aldehydes, ketones, α-keto esters, α-ketolactams, ketomalonates and diketone derivatives that led to the corresponding alcohol adducts.[12] In our research program directed toward the development of original synthetic methodologies using TDAE, the introduction of the double reactivity concept has been considered. We report herein the reaction between nitrobenzyl chloride derivatives and dialdehydes such as terephthalaldehyde (**2**) and isophthalaldehyde (**5**).

In order to explore this original reactivity, a first attempt was carried on with two equivalents of *p*-nitrobenzyl chloride (**1**) and one equivalent of dialdehyde **2** (Scheme 1). Unfortunately, we observed the formation of dimer **3** (4,4′-dinitrobibenzyl) in 90% yield.[12a] To reduce the extent of dimer formation, the reaction was then performed with one equivalent of chloride **1** and three equivalents of the dialdehyde **2**, with the TDAE added slowly to the mixture at –20 °C. However, only 51% of the desired aldol **4a** was isolated and no trace of the double addition adduct was been observed.



1	2	3	4a
2 equiv	1 equiv	90%	0%
1 equiv	3 equiv	5%	51%

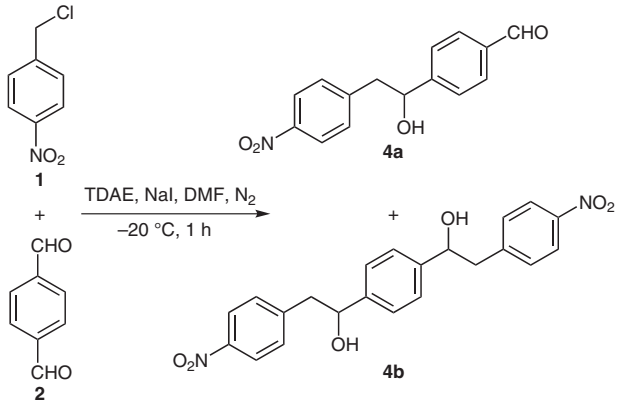
Scheme 1 Preliminary study

When chloride **1** is added slowly at –20 °C to a mixture of sodium iodide, dialdehyde **2** and TDAE in anhydrous DMF, the double addition product **4b** was obtained in 33% yield (Table 1, entry 1). The sodium iodide salt must facilitate the reaction by halogen-exchange activation.[13] In order to optimize the synthesis of derivative **4b**, we

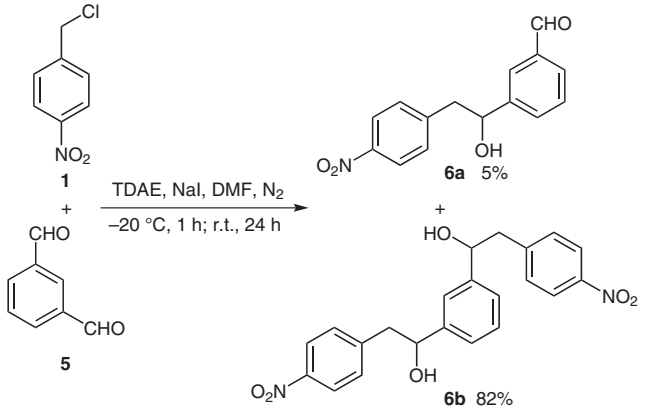
Table 1 Influence of Experimental Conditions on the Reaction of Chloride **1** and Dialdehyde **2**[a]

Entry	**1** (equiv)	TDAE (equiv)	Time (h)	Yield of **4a** (%)[b]	Yield of **4b** (%)[b]	Global yield (%)[b]
1	2.0	3.0	2	15	33	48
2	2.2	2.4	2	5	33	38
3	3.0	3.5	2	5	49	54
4	4.0	4.5	2	19	44	63
5	2.0	3.0	24	62	33	95
6	2.0	3.0	48	54	33	87
7	3.0	3.5	24	7	58	65
8	3.0	3.5	48	15	29	44

[a] Reagents and conditions: **1** was added to a mixture of NaI (0.4 equiv), **2** (1 equiv) and TDAE, N_2, at –20 °C for 1 h then at r.t. for 24 h.
[b] Yield refers to chromatographically isolated pure products and are relative to dialdehyde **2**.



Scheme 2 TDAE-initiated reactivity of *p*-nitrobenzyl chloride (**1**) and terephthalaldehyde (**2**)



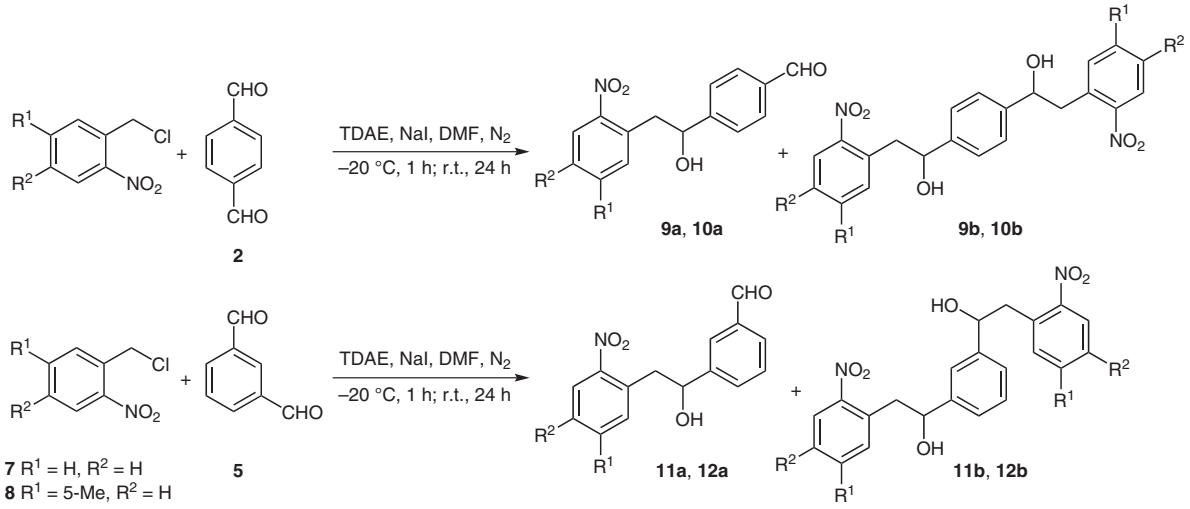
Scheme 3 TDAE-initiated reactivity of *p*-nitrobenzyl chloride **1** and isophthalaldehyde **5**

studied the influence of the chloride/dialdehyde/TDAE ratio and reaction time (Table 1). The best reaction conditions for the synthesis of compound **4b** were found to be: 3.5 equivalents of TDAE, 3.0 equivalents of **1** and 0.4 equivalents of sodium iodide at –20 °C for one hour followed by 24 hours at room temperature under an inert atmosphere (Scheme 2; Table 1, entry 7). In order to extend and validate this new methodology, we applied these optimized conditions for the TDAE-initiated reaction of *p*-nitrobenzyl chloride (**1**) with isophthalaldehyde (**5**; Scheme 3); under these conditions the derivative **6b**, corresponding to the double addition, was isolated with an excellent yield (82%). When the TDAE-initiated reactivity of *o*-nitrobenzyl chloride derivatives **7** and **8** toward terephthalaldehyde (**2**) and isophthalaldehyde (**5**) was investigated, we found that these conditions furnished a corresponding mixture of aldols **9a–12a** and diols **9b–12b** (Scheme 4, Table 2).

As for the *p*-nitrobenzyl chloride series, we could generate the diol derivatives under these new conditions (1 equiv of dialdehyde, 3 equiv of chloride, 3.5 equiv of TDAE). These results confirmed that this method could be extended to different chlorides and aromatic dialdehydes.

In conclusion, this study presents the first TDAE-mediated double addition of nitrobenzylic anions to aromatic dialdehydes. We have developed a new protocol by changing the order of addition of the reagents. This original process allows us to generate tri-aromatic diols that could be used as starting materials for dehydration and electrocyclization reactions in order to obtain polycyclic conjugated molecules. The synthesis of dissymetric diols via a 'one-pot' procedure is under investigation.

Melting points were determined on a Buchi capillary melting point apparatus and are uncorrected. Elemental analyses were performed by the Centre de Microanalyses of the spectropole (Aix-Marseille University). Both ^{1}H and ^{13}C NMR spectra were determined on a Brucker AC 200 spectrometer. The ^{1}H NMR chemical shifts (δ) are reported as parts per million downfield from tetramethylsilane (TMS), and the ^{13}C NMR chemical shifts were referenced to the solvents peaks: $CDCl_3$ (δ = 76.9 ppm) or DMSO-d_6 (δ = 39.6 ppm). Absorptions are reported with the following notations: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet or overlapping). The following adsorbents were used for column chromatography: silica gel 60 (Merck, particle size 0.063–0.200 mm, 70–230 mesh ASTM). TLC were performed on 5 × 10 cm aluminum plates coated with silica gel 60 F-254 (Merck) in an appropriate solvent system.



Scheme 4 Extension of the TDAE-initiated reactivity with dialdehyde **2** and **5**

Table 2 Reaction of Dialdehydes **2** and **5** with Chlorides **7** and **8** using TDAE

Entry	Chloride	R^1	R^2	Dialdehyde	Mono addition yield (%)[a]	Double addition yield (%)[a]	Global yield (%)[a]
1	**7**	H	H	**2**	32 (**9a**)	43 (**9b**)	75
2	**8**	Me	H	**2**	28 (**10a**)	68 (**10b**)	96
3	**7**	H	H	**5**	7 (**11a**)	76 (**11b**)	83
4	**8**	Me	H	**5**	11 (**12a**)	54 (**12b**)	65

[a] Yield refers to chromatographically isolated pure products and are relative to dialdehyde **2** or **5**.

TDAE Reaction; General Procedure

In a two-necked flask equipped with a silica gel drying tube and a nitrogen inlet under nitrogen at –20 °C, TDAE (1.04 mL, 4.47 mmol, 3.0 equiv or 1.21 mL, 5.21 mmol, 3.5 equiv) was added dropwise (via a syringe) to a solution of dialdehyde (0.2 g, 1.49 mmol, 1 equiv) and NaI (0.09 g, 0.60 mmol, 0.4 equiv) in anhydrous DMF (5 mL). A solution of corresponding benzyl chloride **1**, **7** or **8** (2 equiv or 3 equiv) in anhydrous DMF (2 mL) was added dropwise over 1 h. The solution was vigorously stirred at –20 °C for 1 h and then warmed to r.t. for 24 h. A solution of aq HCl (0.1 N, 100 mL) was slowly added in order to quench the reaction, then the aqueous solution was extracted with CH_2Cl_2 (3 × 50 mL), and the combined organic layers were washed with H_2O (3 × 100 mL), dried over $MgSO_4$ and the solvent removed under reduce pressure. Purification of the crude product by gradient chromatography (CH_2Cl_2–EtOAc, 1:0→2:1) gave the corresponding aldols (**4a**, **6a**, **9a**, **10a**, **11a**, and **12a**) and diols (**4b**, **6b**, **9b**, **10b**, **11b**, and **12b**).

4-[1-Hydroxy-2-(4-nitrophenyl)ethyl]benzaldehyde (4a)

Orange solid; mp 131 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 3.14 (d, *J* = 6.4 Hz, 2 H, CH_2), 5.05 (t, *J* = 6.4 Hz, 1 H, CH), 7.31 (d, *J* = 8.8 Hz, 2 H, Ar-H), 7.47 (d, *J* = 8.2 Hz, 2 H, Ar-H), 7.84 (d, *J* = 8.2 Hz, 2 H, Ar-H), 8.12 (d, *J* = 8.8 Hz, 2 H, Ar-H), 9.98 (s, 1 H, CHO).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 45.3, 74.3, 123.5, 126.4, 130.0, 130.4, 136.0, 145.2, 146.9, 150.0, 191.8.

Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.32; H, 4.86; N, 5.78.

1,1′-(1,4-Phenylene)bis[2-(4-nitrophenyl)ethanol] (4b)

Yellow solid; mp 222 °C.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 3.01 (m, 4 H, 2 × CH_2), 4.80 (m, 2 H, 2 ×CH), 5.38 (d, *J* = 5.4 Hz, 2 H, 2 ×OH), 7.25 (s, 4 H, ArH), 7.43 (d, *J* = 8.8 Hz, 4 H, ArH), 8.09 (d, *J* = 8.8 Hz, 4 H, ArH).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 45.1, 72.7, 122.8, 125.5, 130.7, 143.7, 145.8, 147.6.

Anal. Calcd for $C_{22}H_{20}N_2O_6$: C, 64.70; H, 4.94; N, 6.86. Found: C, 64.37; H, 4.15; N, 6.67.

3-[1-Hydroxy-2-(4-nitrophenyl)ethyl]benzaldehyde (6a)

Yellow solid; mp 131 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.86 (br s, 1 H, OH), 3.15 (d, *J* = 6.5 Hz, 2 H, CH_2), 5.06 (t, *J* = 6.5 Hz, 1 H, CH), 7.34 (d, *J* = 8.7 Hz, 2 H, ArH), 7.49–7.61 (m, 2 H, ArH), 7.80–7.88 (m, 2 H, ArH), 8.15 (d, *J* = 8.7 Hz, 2 H, ArH), 10.02 (s, 1 H, CHO).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 45.5, 74.2, 123.6, 126.5, 129.3, 129.6, 130.4, 131.9, 136.6, 144.4, 145.3, 146.9, 192.0.

Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.16; H, 4.93; N, 5.39.

1,1′-(1,3-Phenylene)bis[2-(4-nitrophenyl)ethanol] (6b)

Yellow solid; mp 132 °C.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 2.98 (d, *J* = 6.5 Hz, 4 H, 2 × CH_2), 4.82 (m, 2 H, 2 × CH), 5.42 (d, *J* = 4.6 Hz, 2 H, 2 × OH), 7.21 (m, 3 H, ArH), 7.33 (s, 1 H, ArH), 7.44 (d, *J* = 8.4 Hz, 4 H, ArH), 8.12 (d, *J* = 8.4 Hz, 4 H, ArH).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 45.4, 73.1, 123.0, 123.6, 124.6, 127.7, 130.9, 145.0, 146.1, 147.8.

Anal. Calcd for $C_{22}H_{20}N_2O_6$: C, 64.70; H, 4.94; N, 6.86. Found: C, 64.58; H, 5.21; N, 6.89.

4-[1-Hydroxy-2-(2-nitrophenyl)ethyl]benzaldehyde (9a)
Brown solid; mp 103 °C.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 2.26 (br s, 1 H, OH), 3.17 (dd, *J* = 8.8, 13.6 Hz, 1 H, CH_2), 3.42 (dd, *J* = 8.8, 13.6 Hz, 1 H, CH_2), 5.16 (dd, *J* = 3.8, 8.8 Hz, 1 H, CH), 7.29–7.54 (m, 3 H, ArH), 7.58 (d, *J* = 8.1 Hz, 2 H, ArH), 7.88 (d, *J* = 8.1 Hz, 2 H, ArH), 7.96–8.00 (m, 1 H, ArH), 10.01 (s, 1 H, CHO).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 41.5, 72.4, 124.3, 126.5, 127.9, 129.6, 132.8, 132.9, 133.5, 135.4, 143.4, 150.2, 152.3, 192.9.

Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.38; H, 4.89; N, 5.25.

1,1′-(1,4-Phenylene)bis[2-(2-nitrophenyl)ethanol] (9b)
Orange solid; mp 219 °C.

^{1}H NMR (200 MHz, DMSO-d_6): δ = 3.15 (d, *J* = 6.4 Hz, 4 H, 2 × CH_2), 4.72 (m, 2 H, 2 × CH), 5.38 (d, *J* = 4.7 Hz, 2 H, 2 × OH), 7.26 (s, 4 H, ArH), 7.43–7.50 (m, 4 H, ArH), 7.57–7.64 (m, 2 H, ArH), 7.89 (d, *J* = 7.5 Hz, 2 H, ArH).

^{13}C NMR (50 MHz, DMSO-d_6): δ = 42.0, 72.5, 124.2, 125.5, 127.7, 132.7, 133.4, 144.3, 150.2.

Anal. Calcd for $C_{22}H_{20}N_2O_6$: C, 64.70; H, 4.94; N, 6.86. Found: C, 64.74; H, 5.17; N, 6.72.

4-[1-Hydroxy-2-(5-methyl-2-nitrophenyl)ethyl]benzaldehyde (10a)
Brown solid; mp 126 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.40 (s, 3 H, CH_3), 3.10 (dd, *J* = 9.0, 13.5 Hz, 1 H, CH_2), 3.43 (dd, *J* = 3.6, 13.5 Hz, 1 H, CH_2), 5.14 (dd, *J* = 3.6, 9.0 Hz, 1 H, CH), 7.12 (s, 1 H, ArH), 7.21 (d, *J* = 8.4 Hz, 1 H, ArH), 7.60 (d, *J* = 8.2 Hz, 2 H, ArH), 7.88 (d, *J* = 8.2 Hz, 2 H, ArH), 7.92 (d, *J* = 8.4 Hz, 1 H, ArH), 10.01 (s, 1 H, CHO).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.4, 43.2, 73.7, 125.3, 126.2, 128.6, 130.0, 133.0, 134.2, 135.8, 144.3, 147.3, 150.7, 191.9.

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.16; H, 5.45; N, 4.91.

1,1′-(1,4-Phenylene)bis[2-(5-methyl-2-nitrophenyl)ethanol] (10b)
Beige solid; mp 193 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.88 (br s, 2 H, 2 × OH), 2.41 (s, 6 H, 2 × CH_3), 3.16 (dd, *J* = 9.1, 13.5 Hz, 2 H, CH_2), 3.40 (dd, *J* = 3.6, 13.5 Hz, 2 H, CH_2), 5.04 (dd, *J* = 3.6, 9.1 Hz, 2 H, 2 × CH), 7.17 (s, 2 H, ArH), 7.19 (d, *J* = 8.0 Hz, 2 H, ArH), 7.43 (s, 4 H, ArH), 7.91 (d, *J* = 8.0 Hz, 2 H, ArH).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.0, 42.4, 72.6, 124.5, 125.5, 128.1, 133.9, 134.0, 143.4, 144.5, 147.8.

Anal. Calcd for $C_{24}H_{24}N_2O_6$: C, 66.04; H, 5.54; N, 6.42. Found: C, 65.74; H, 5.67; N, 6.46.

3-[1-Hydroxy-2-(2-nitrophenyl)ethyl]benzaldehyde (11a)
Brown solid; mp 97.5 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.22 (br s, 1 H, OH), 3.19 (dd, *J* = 8.9, 13.6 Hz, 1 H, CH_2), 3.42 (dd, *J* = 3.8, 13.6 Hz, 1 H, CH_2), 5.15 (dd, *J* = 3.8, 8.9 Hz, 1 H, CH), 7.31–7.57 (m, 4 H, ArH), 7.67–7.71 (m, 1 H, CH), 7.79–7.84 (m, 1 H, CH), 7.92–8.00 (m, 2 H, ArH), 10.02 (s, 1 H, CHO).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.9, 73.4, 124.8, 126.9, 127.9, 128.9, 129.2, 131.8, 132.8, 133.6, 136.5, 145.1, 149.7, 165.1, 192.2.

Anal. Calcd for $C_{15}H_{13}NO_4$: C, 66.41; H, 4.83; N, 5.16. Found: C, 66.35; H, 4.97; N, 5.32.

1,1′-(1,3-Phenylene)bis[2-(2-nitrophenyl)ethanol] (11b)
Brown oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.88 (br s, 2 H, 2 × OH), 3.05–3.28 (m, 4 H, 2 × CH_2), 4.82–4.89 (m, 2 H, 2 × CH), 7.18–7.48 (m, 10 H, ArH), 7.84 (d, *J* = 7.8 Hz, 2 H, ArH).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 42.3, 73.8, 124.4, 124.9, 127.4, 128.4, 132.6, 133.1, 133.4, 143.8, 149.5.

Anal. Calcd for $C_{22}H_{20}N_2O_6$: C, 64.70; H, 4.94; N, 6.86. Found: 64.46; H, 5.31; N, 6.78.

3-[1-Hydroxy-2-(5-methyl-2-nitrophenyl)ethyl]benzaldehyde (12a)
Brown solid; mp 105.5 °C.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.39 (s, 3 H, CH_3), 3.13 (dd, *J* = 9.1, 13.4 Hz, 1 H, CH_2), 3.43 (dd, *J* = 3.7, 13.4 Hz, 1 H, CH_2), 5.14 (dd, *J* = 3.7, 9.1 Hz, 1 H, CH), 7.13 (s, 1 H, ArH), 7.20 (d, *J* = 8.4 Hz, 1 H, ArH), 7.53 (t, *J* = 7.6 Hz, 1 H, ArH), 7.71 (d, *J* = 7.6 Hz, 1 H, ArH), 7.81 (d, *J* = 7.6 Hz, 1 H, ArH), 7.92 (d, *J* = 8.4 Hz, 1 H, ArH), 7.94 (s, 1 H, ArH), 10.02 (s, 1 H, CHO).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 21.3, 43.3, 73.6, 125.3, 126.9, 128.6, 128.9, 129.2, 131.8, 133.1, 134.2, 136.6, 144.3, 145.1, 147.3, 192.2.

Anal. Calcd for $C_{16}H_{15}NO_4$: C, 67.36; H, 5.30; N, 4.91. Found: C, 67.44; H, 5.64; N, 4.77.

1,1′-(1,3-Phenylene)bis[2-(5-methyl-2-nitrophenyl)ethanol] (12b)
Brown oil.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.37 (s, 6 H, 2 × CH_3), 2.66 (br s, 2 H, 2 × OH), 2.89–3.37 (m, 4 H, 2 × CH_2), 4.95 (dd, *J* = 3.9, 8.8 Hz, 2 H, 2 × CH), 7.13–7.16 (m, 4 H, ArH), 7.29 (m, 3 H, ArH), 7.36 (m, 1 H, ArH), 7.82–7.86 (m, 2 H, ArH).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 38.5, 42.9, 74.1, 122.7, 124.9, 128.1, 128.5, 133.6, 134.1, 143.9, 144.2, 147.3.

Anal. Calcd for $C_{24}H_{24}N_2O_6$: C, 66.04; H, 5.54; N, 6.42. Found: C, 66.57; H, 5.98; N, 6.15.

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