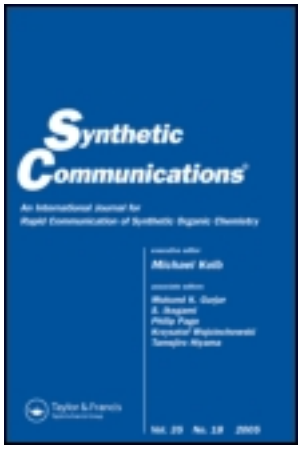

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Microwave-Assisted Wittig Reaction of Semistabilized Nitro-Substituted Benzyltriphenyl-Phosphorous Ylides with Aldehydes in Phase-Transfer Conditions

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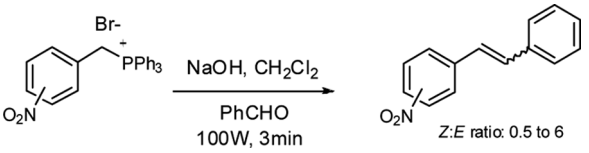
MICROWAVE-ASSISTED WITTIG REACTION OF SEMISTABILIZED NITRO-SUBSTITUTED BENZYLTRIPHENYL-PHOSPHOROUS YLIDES WITH ALDEHYDES IN PHASE-TRANSFER CONDITIONS

Tiago Rodrigues, Francisca Lopes, and Rui Moreira
Faculty of Pharmacy, University of Lisbon, Lisbon, Portugal

GRAPHICAL ABSTRACT



Abstract *We report here a simple entry into the nitrostilbene system in very short reaction times and good yields using the microwave-assisted Wittig reaction in phase-transfer conditions of nitro-substituted benzyltriphenylphosphonium ylides with aldehydes.*

Keywords Microwave; nitrostilbenes; phase-transfer catalysis; stereoselectivity; Wittig reaction

INTRODUCTION

(1*H*-Pyridin-4-ylidene)amines or 4-pyridonimines (**A**, Scheme 1) have recently been reported as a novel class of antimalarial compounds active against multidrug-resistant *Plasmodium falciparum* strains.[1] Diversity at the imine side-chain of **A** was incorporated via the nitrostilbenes precursors (**1**, Scheme 1), which were reduced to the corresponding phenethylanilines by Pd-C-catalyzed hydrogenation with triethylsilane in methanol and then reacted with the appropriate *N*-alkyl-4-chloropyridinium triflates to give the desired 4-pyridonimines. Nitrostilbenes **1** were synthesized using the Wittig reaction of the appropriate nitro-substituted benzyltriphenyl phosphorous ylides with aromatic aldehydes, in phase-transfer catalysis (PTC) conditions, which were usually complete in 2 to 3 h at room temperature. To extend the structure–activity relationship studies, a more expeditious synthesis of nitrostilbenes **1** was required. Furthermore, nitrostilbenes **1** are also key intermediates in the synthesis of the amyloid aggregation inhibitors **B**[2] and liver X receptor antagonists **C**.[3]

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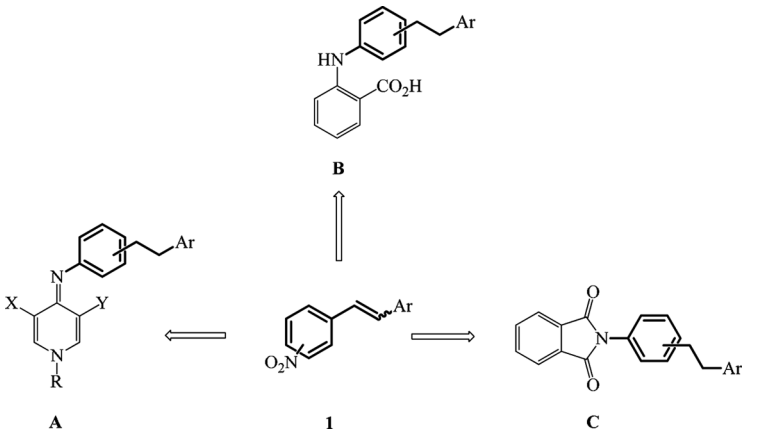


Scheme 1. 4-Pyridonimines (**A**), anthranilic acids (**B**), and phthalimides (**C**) with pharmacological interest and their stilbene precursors (**1**).

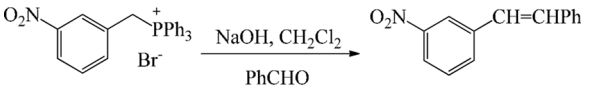
The Wittig reaction of an aldehyde with a phosphorus ylide is one of the most commonly used carbon–carbon double-bond-forming reactions in organic chemistry because of the unambiguous positioning of the double bond.[4,5] Typically, the reaction is carried out using a hydride or organometallic base in anhydrous aprotic solvents.[5,6] The use of water as solvent for Wittig reactions[7–11] and PTC[12–16] methods has been a successful alternative to classical organic solvents. Herein, we report the synthesis of nitrostilbenes via PTC Wittig reactions using the appropriate nitrobenzylphosphonium salts in either room temperature or microwave (MW)–assisted synthesis. As part of this work, we observed some interesting Z/E selectivity trends and found that these can be rationalized in terms of the electronic effect exerted by the nitro substituent on the acidity of the benzylphosphonium salts or by the substituent at the aldehyde. Furthermore, the MW-assisted sysnthesis provided shorter reaction times and greater reaction rates for stabilized phosphoranes.

RESULTS AND DISCUSSION

The PTC protocol previously reported,[1] which afforded the required stilbenes **1** after phase separation and flash chromatography purification, was optimized and then adapted for the MW-assisted conditions. The reaction of 3-nitrobenzyltriphenyl phosphonium bromide (1 molar equiv.) with benzaldehyde (1 molar equiv.) was performed in dichloromethane in the presence of NaOH 0.1 N (1.2 molar equiv.) at room temperature to give **1a** in 92% yield, with a Z/E ratio of 84:16 (Table 1, entry 1). The reaction extent and reaction time (2 h) were independent of the stirring rate, and no significant changes on the reaction extent were observed using benzaldehyde in the range of 1.0 to 1.5 molar equivalents. Thus, for an easier separation of the stilbene from the aldehyde, 1 molar equivalent of the latter was used in subsequent reactions.

The effect of MW irradiation (100 W, 3 min) on the PTC protocol was first studied at different temperatures (Table 1, entries 2 to 5). Interestingly, the conversion rate decreased with higher temperatures. Also, the stereocontrol was poorer when

Table 1. Temperature effect using the PTC/MW method and comparison with the traditional PTC method



2a **1a**

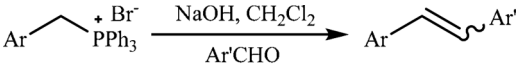
Entry	Method	Temperature	Time	Yield (%)	*Z*/*E* (ratio)
1	A: PTC	RT	2 h	92	84:16 (5.25)
2	B: PTC/MW/100 W	30	3 min	84	73:27 (2.70)
3	C: PTC/MW/100 W	50	3 min	88	71:29 (2.45)
4	D: PTC/MW/100 W	70	3 min	70	69:31 (2.23)
5	E: PTC/MW/100 W	90	3 min	64	68:32 (2.13)

compared to the reaction without microwaves. The selected temperature for further MW-assisted Wittig reactions, varying the substitution pattern of the benzyltriphenyl phosphonium salts and aldehydes, was 30 °C.

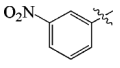
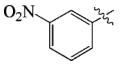
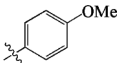
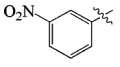
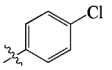
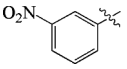
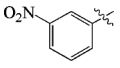
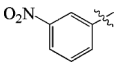
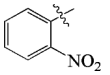
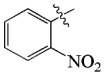
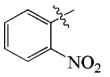
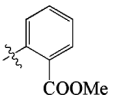
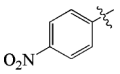
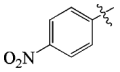
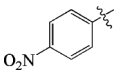
From Table 2 it can be seen that the stereoselectivity[17] using the standard PTC method depends significantly on the position of the nitro group in the phosphonium halide **2**. No isomerisation on chromatography from *Z* to *E* was detected for several cases. Additionally, no light sensitiveness was noted. The use of a solvent such as dichloromethane may favor *Z*-selectivity as reported by Hwang et al.[3]. For example, a high *Z*-stereoselectivity was observed for the reaction of 3- and 3,5-dinitrobenzylphosphonium salts with benzaldehyde (Table 2 entries 1 and 14, respectively). In contrast, placement of the nitro group in the 2- or 4-positions of **2** led to a significant increase in the proportion of the *E*-alkene and loss of stereoselectivity (entries 7 and 10, respectively). The reaction of 2,4-dinitrobenzylphosphonium chloride with benzaldehyde shifted the stereoselectivity toward the formation of the *E*-alkene (entry 13). Overall, this shift from *Z*- to *E*-stereoselectivity can be ascribed, at least in part, to the stabilizing effect of the nitro groups in the 2- or 4-positions on the phosphorous ylide and is consistent with the suggestion that the dominant structure of phosphonium ylides is the dipolar P^+-C^- zwitterion rather than the P=C double bond.[17] Indeed, the equilibrium acidities, pK_{HA} (in dimethylsulfoxide, DMSO), of 4-substituted $ArCH_2PPh_3^+$ cations correlate with the Hammett σ^- constants of the substituents in the aryl moiety, reflecting the direct conjugation of the negative in the conjugate base (ylide) with electron-withdrawing groups such as NO_2.[17] The MW-assisted Wittig reaction was performed in 3 min with total consumption of the aldehyde and resulted in a decrease of the *Z*-stereoselectivity (Table 2, e.g., entries 1/1′ and 14/14′). With the stabilized 4-nitrophosphorane, the reaction rate increased, and inversion on the stereoselectivity was observed (entries 10/10′). With 2,4-dinitrophosphorane, an untractable mixture was obtained (entries 13/13′).

Variation of the substitution pattern in the aldehyde did not affect significantly the PTC reaction yield, and although diastereoselection was variable, the *Z*-isomer was predominant. For reactions with 2-halobenzaldehydes, the expected *Z*-diastereoselectivity was observed even for the 2-nitro ylide (Table 2, e.g., entry 8). The cooperative *ortho* halo effect[18,19] may be responsible for these results and overrides the stabilizing effect of resonance to the nitro group. The MW-assisted Wittig

Table 2. Reaction of nitro-substituted benzyltriphenyl phosphonium salts with aldehydes under standard PTC conditions at room temperature (Method A) and microwave-assisted synthesis (Method B)

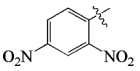
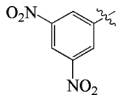


2 **1a-n**

			Method A: PTC, RT, 2 h			Method B: PTC, 100 W, 30 °C, 3 min		
Cpd	Ar	Ar′	Entry	Yield **1** (%)[a]	*Z*:*E* (ratio)[b]	Entry	Yield **1** (%)[a]	*Z*:*E* (ratio)[b]
1a			1	92	84:16 (5.25)	1′	84	73:27 (2.70)
1b			2	98	77:23 (3.35)	2′	79	77:23 (3.33)
1c			3	93	70:30 (2.33)	3′	96	70:30 (2.38)
1d			4	96	91:9 (10.11)	4′	49	86:14 (6.14)
1e			5	100	85:15 (5.67)	5′	46	83:17 (4.88)
1f			6	52	81:19 (4.26)	6′	45	80:20 (4.00)
1g			7	95	57:43 (1.33)	7′	24	69:31 (2.22)
1h			8	90	83:17 (4.88)	8′	88	76:24 (3.17)
1i			9	47	78:22 (3.54)	9′	39	63:37 (1.70)
1j			10	88	58:42 (1.37)	10′	93	34:66 (0.52)
1k			11	100	58:42 (1.37)	11′	77	74:26 (2.85)
1l			12	92	67:33 (2.00)	12′	96	80:20 (4.00)

(*Continued*)

Table 2. Continued

Cpd	Ar	Ar′	Method A: PTC, RT, 2 h Entry	Yield **1** (%)[a]	*Z*:*E* (ratio)[b]	Method B: PTC, 100 W, 30 °C, 3 min Entry	Yield **1** (%)[a]	*Z*:*E* (ratio)[b]
1m			13	34	17:83 (0.20)	13′	ND[c]	ND[c]
1n			14	76	88:12 (7.33)	14′	67	71:29 (2.45)

[a]Yield is given for the isolated isomer mixture;.
[b]Z/E ratios were determined by ^{1}H NMR;.
[c]Untractable mixture.

reaction with 2-halobenzaldehydes gave moderate (entry 4′) to excellent yields (entry 12′), although the cooperative *ortho* halo effect was not as pronounced when compared to standard PTC reactions. The PTC and MW-assisted reactions carried out with phenylacetaldehyde gave only moderate yields of the corresponding stilbene (entries 6/6′), and an increased rate of hydrolysis of the phosphorane into the 3-nitrotoluene was observed. Moreover, 3-nitrotoluene was the sole product when the reactions were carried out with aliphatic aldehydes. Instability of stabilized phosphoranes has already been reported while using MW-assisted synthesis.[20]

In conclusion, we have developed a very fast and efficient synthesis of nitro-substituted stilbenes relying on appropriately substituted nitrobenzyltriphenyl phosphonium salts and diverse aldehydes, based on a MW-assisted Wittig reaction in PTC conditions. From these experiments, we conclude that the PTC MW protocol was efficient for semistabilized ylides, at the expense of Z/E selectivity.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded as $CDCl_3$ or MeOD solutions in a Bruker AM 400 WB (Bruker Bioscience, Billerica, MA, USA); chemical shifts are given in parts per million (ppm), and coupling constants, *J*, are quoted in hertz (Hz). Fourier transform infrared (FTIR) spectra were recorded on a Nicolet Impact 400 spectrophotometer (Nicolet, Madison, WI, USA). Microwave-assisted synthesis was carried out in a CEM Corporation Discover Labmate. Melting points were determined using a Bock Monoscop M. instrument and are uncorrected. All chemicals were of reagent grade, used without further purification, and generally purchased from Sigma-Aldrich.

General Procedure for the Synthesis of Nitrostilbenes

The phosphonium salt (1 molar equiv.) and distilled or crystallized aldehyde (1 molar equiv.) were suspended in dichloromethane (3 mL). An aqueous solution of NaOH 0.1–0.5 N (1.2 molar equiv.) was added to the mixture. The ylidic

characteristic color was noted immediately and gradually faded with time. The biphasic mixture was stirred (1600 rpm) at room temperature (20–25 °C) for 2 h, after which the organic phase was separated and concentrated under reduced pressure, and the crude product was purified by column chromatography (hexane–ethyl ether 4:1) to afford, typically, yellowish oils corresponding to a diastereomer mixture. For most cases, the isomers were not separated, and the Z/E ratios were calculated by comparing the alkene ^{1}H NMR peaks of the isomers after flash chromatography. The Z/E ratio for **1i** was obtained from the ratio of the OMe signal. Quoted yields are given after purification. Generally, all aldehyde starting material was consumed, and little hydrolysis of the phosphonium salt or ylide, to the corresponding nitrotoluene, was noted. No other products were detected. Poor yield of **1e** is accounted for by the low solubility of the phosphonium salt in water.

Spectral Data

1-Nitro-3-styrylbenzene, 1a. Yellow oil. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 6.63 (1H, d, $J = 12.0$ Hz, C*H*), 6.81 (1H, d, $J = 12.0$ Hz, C*H*), 7.18–7.24 (2H, m, Ar-*H*), 7.27–7.30 (3H, m, Ar-*H*), 7.39 (1H, t, $J = 8.0$ Hz, Ar-*H*), 7.56 (1H, br. d, $J = 7.6$ Hz, Ar-*H*), 8.06 (1H, dd, $J = 8.4$ and 1.6 Hz, Ar-*H*), 8.12 (1H, dd, $J = 1.6$ Hz, Ar-*H*). *E* isomer: mp 92–95 °C. ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.16 (1H, d, $J = 16.4$ Hz, C*H*), 7.27 (1H, d, $J = 16.4$ Hz, C*H*), 7.35 (1H, d, $J = 6.4$ Hz, Ar-*H*), 7.42 (2H, t, $J = 7.2$ Hz, Ar-*H*), 7.55 (3H, m, Ar-*H*), 7.83 (1H, d, $J = 8.0$ Hz, Ar-*H*), 8.13 (1H, d, $J = 8.4$ Hz, Ar-*H*), 8.13 (1H, br. s, Ar-*H*).

1-(4-Methoxystyryl)-3-nitrobenzene, 1b. Yellow gum. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 3.79 (1H, s, OCH_3), 6.51 (1H, d, $J = 12.0$ Hz, C*H*), 6.70 (1H, d, $J = 12.0$ Hz, C*H*), 6.79 (2H, d, $J = 8.4$ Hz, Ar-*H*), 7.15 (2H, d, $J = 8.4$ Hz, Ar-*H*), 7.37 (1H, t, $J = 8.0$ Hz, Ar-*H*), 7.58 (1H, t, $J = 8.0$ Hz, Ar-*H*), 8.03 (1H, m, Ar-*H*), 8.13 (1H, s, Ar-*H*). *E* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 3.85 (1H, s, OCH_3), 6.93 (2H, d, $J = 8.4$ Hz, Ar-*H*), 6.98 (1H, d, $J = 16.0$ Hz, C*H*), 7.02 (1H, m, Ar-*H*), 7.50 (3H, m, Ar-*H*), 7.76 (1H, d, $J = 7.6$ Hz, Ar-*H*), 8.03 (1H, m, Ar-*H*), 8.32 (1H, s, Ar-*H*).

1-(4-Chlorostyryl)-3-nitrobenzene, 1c. Yellow gum. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 6.65 (1H, d, $J = 12.0$ Hz, C*H*), 6.73 (1H, d, $J = 12.0$ Hz, C*H*), 7.10–7.59 (6H, m, Ar-*H*), 8.08 (1H, d, $J = 8.8$ Hz, Ar-*H*), 8.11 (1H, s, Ar-*H*). *E* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.12 (1H, d, $J = 16.0$ Hz, C*H*), 7.27 (1H, d, $J = 16.0$ Hz, C*H*), 7.10–7.59 (5H, m, Ar-*H*), 7.81 (1H, d, $J = 7.6$ Hz, Ar-*H*), 8.13 (1H, d, $J = 8.8$ Hz, Ar-*H*), 8.39 (1H, s, Ar-*H*).

1-Fluoro-2-(2-nitrostyryl)benzene, 1d. Yellow gum. *Z* isomer: ^{1}H NMR (MeOD, 400.13 MHz) δ 6.83 (1H, d, $J = 12.0$ Hz, C*H*), 6.79–6.96 (2H, m, Ar-*H*), 7.02 (1H, t, $J = 9.2$ Hz, Ar-*H*), 7.05 (1H, d, $J = 12.0$ Hz, C*H*), 7.15–7.26 (2H, m, Ar-*H*), 7.36–7.50 (2H, m, Ar-*H*), 8.08–8.18 (1H, m, Ar-*H*). *E* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 6.96–7.14 (1H, m, Ar-*H*), 7.15–7.26 (1H, m, Ar-*H*), 7.27–7.35 (2H, m, C*H* +Ar-*H*), 7.36–7.50 (1H, m, Ar-*H*), 7.64 (1H, d, $J = 16.4$ Hz, C*H*), 7.62–7.72 (2H, m, Ar-*H*), 7.82 (1H, d, $J = 7.6$, Ar-*H*), 8.01 (1H, d, $J = 8.0$, Ar-*H*).

1-Chloro-2-(3-nitrostyryl)benzene, 1e. Yellow solid, mp 44–50 °C. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 6.76 (1H, d, $J = 12.4$ Hz, C*H*), 6.89 (1H, d, $J = 12.4$ Hz, C*H*), 7.08–7.16 (2H, m, Ar-*H*), 7.23–7.28 (1H, m, Ar-*H*), 7.36 (1H, t, $J = 8.0$ Hz, Ar-*H*), 7.44–7.47 (2H, m, Ar-*H*), 8.00–8.10 (2H, m, Ar-*H*). *E* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.08–7.16 (1H, m, C*H*), 7.23–7.28 (1H, m, Ar-*H*), 7.32–7.40 (1H, m, Ar-*H*), 7.44–7.47 (1H, m, Ar-*H*), 7.58 (1H, t, $J = 8.0$ Hz, Ar-*H*), 7.66 (1H, d, $J = 16.4$ Hz, C*H*), 7.72 (1H, d, $J = 7.6$ Hz, Ar-*H*), 7.89 (1H, d, $J = 8.0$ Hz, Ar-*H*), 8.16 (1H, d, $J = 8.0$ Hz, Ar-*H*), 8.43 (1H, s, Ar-*H*).

1-Nitro-3-(3-phenylprop-1-en-1-yl)benzene, 1f. Colorless oil. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 3.69 (2H, d, $J = 7.4$ Hz, CH_2), 6.07 (1H, dt, $J = 11.4$ and 7.6 Hz, C*H*), 6.64 (1H, d, $J = 11.4$ Hz, C*H*), 7.23–7.67 (7H, m, 7 Ar-*H*), 8.14 (1H, d, $J = 8.0$ Hz, Ar-*H*), 8.21 (1H, s, Ar-*H*). *E* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 3.62 (2H, d, $J = 5.5$ Hz, CH_2), 6.46–6.59 (1H, m, C*H*), 6.64 (1H, d, $J = 11.4$ Hz, C*H*), 7.23–7.67 (8H, m, C*H* + 7 Ar-*H*), 8.07 (1H, d, $J = 8.0$ Hz, Ar-*H*), 8.21 (1H, s, Ar-*H*).

1-Nitro-2-styrylbenzene, 1g. Yellow gum. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 6.80 (1H, d, $J = 12.0$ Hz, C*H*), 6.93 (1H, d, $J = 12.0$ Hz, C*H*), 7.08 (2H, dd, $J = 7.0$ and 3.2 Hz, Ar-*H*), 7.30 (1H, d, $J = 7.6$ Hz, Ar-*H*), 7.38–7.48 (3H, m, Ar-*H*), 7.54–7.67 (2H, m, Ar-*H*); 8.07–8.15 (1H, m, Ar-*H*). *E* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.12 (1H, d, $J = 16.4$ Hz, C*H*), 7.16–7.22 (3H, m, Ar-*H*), 7.26–7.34 (1H, m, Ar-*H*), 7.36 (1H, d, $J = 7.2$ Hz, Ar-*H*), 7.38–7.48 (2H, m, Ar-*H*), 7.63 (1H, d, $J = 16.4$ Hz, C*H*), 7.80 (1H, d, $J = 8.0$ Hz, Ar-*H*), 7.99 (1H, d, $J = 8.2$ Hz, Ar-*H*).

1-Fluoro-2-(3-nitrostyryl)benzene, 1h. Yellow gum. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 6.75 (1H, d, $J = 12.4$ Hz, C*H*), 6.81 (1H, d, $J = 12.4$ Hz, C*H*), 7.00 (1H, t, $J = 7.6$ Hz, Ar-*H*), 7.08 (1H, t, $J = 9.2$ Hz, Ar-*H*), 7.15 (1H, t, $J = 7.6$ Hz, Ar-*H*), 7.29 (1H, m, Ar-*H*), 7.39 (1H, m, Ar-*H*), 7.53 (1H, d, $J = 7.6$ Hz, Ar-*H*), 8.06 (1H, d, $J = 8.6$ Hz, Ar-*H*), 8.09 (1H, s, Ar-*H*). *E* isomer: ^{1}H-NMR ($CDCl_3$, 400.13 MHz) δ 7.15–7.30 (4H, m, C*H* + 3 Ar-*H*), 7.40 (1H, d, $J = 16.0$ Hz, C*H*), 7.56 (1H, d, $J = 8.2$ Hz, Ar-*H*), 7.63 (1H, t, $J = 7.6$ Hz, Ar-*H*), 7.85 (1H, d, $J = 7.6$ Hz, Ar-*H*), 8.13 (1H, d, $J = 8.0$ Hz, Ar-*H*), 8.39 (1H, s, Ar-*H*).

1-Nitro-4-styrylbenzene, 1j. Yellow gum. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 6.64 (1H, d, $J = 12.0$ Hz, C*H*), 6.84 (1H, d, $J = 12.0$ Hz, C*H*), 7.23–7.72 (7H, m, Ar-*H*), 8.09 (2H, d, $J = 8.4$ Hz, Ar-*H*). *E* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.17 (1H, d, $J = 16.4$ Hz, C*H*), 7.38 (1H, m, C*H*), 7.23–7.72 (7H, m, Ar-*H*), 8.25 (2H, d, $J = 8.4$ Hz, Ar-*H*).

1-Fluoro-2-(4-nitrostyryl)benzene, 1k. Yellow oil. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 6.67 (1H, d, $J = 12.0$ Hz, C*H*), 6.84 (1H, d, $J = 12.0$ Hz, C*H*), 7.00 (1H, t, $J = 7.6$ Hz, Ar-*H*), 7.04–7.32 (3H, m, Ar-*H*), 7.38 (2H, d, $J = 8.6$ Hz, Ar-*H*), 8.10 (2H, d, $J = 8.6$ Hz, Ar-*H*). *E* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.04–7.32 (5H, m, C*H* + 4 Ar-*H*), 7.45 (1H, d, $J = 16.4$ Hz, C*H*), 8.68 (2H, d, $J = 8.6$ Hz, Ar-*H*), 8.25 (2H, d, $J = 8.6$ Hz, Ar-*H*).

1-Chloro-2-(4-nitrostyryl)benzene, 1l. Yellow oil. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 6.67 (1H, d, $J = 12.0$ Hz, C*H*), 6.92 (1H, d, $J = 12.0$ Hz,

C*H*), 7.05–7.13 (2H, m, Ar-*H*), 7.21–7.37 (3H, m, Ar-*H*), 7.46 (1H, d, $J = 8.2$ Hz, Ar-*H*), 8.07 (2H, d, $J = 8.6$ Hz, Ar-*H*). *E* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.15 (1H, d, $J = 16.4$ Hz, C*H*), 7.21–7.37 (2H, m, C*H* +Ar-*H*), 7.45 (1H, d, $J = 8.0$ Hz, Ar-*H*), 7.66–7.76 (4H, m, Ar-*H*), 8.26 (2H, d, $J = 8.6$ Hz, Ar-*H*).

2,4-Dinitro-1-styrylbenzene, 1m. Yellow gum. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 6.90 (1H, d, $J = 12.0$ Hz, C*H*), 6.99 (1H, d, $J = 12.0$ Hz, C*H*), 7.06–7.12 (2H, m, Ar-*H*), 7.21–7.27 (3H, m, Ar-*H*), 7.38–7.51 (1H, m, Ar-*H*), 8.21 (1H, dd, $J = 8.6$ and 2.2 Hz, Ar-*H*), 8.96 (1H, d, $J = 2.2$ Hz, Ar-*H*). *E* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.32 (1H, d, $J = 16.4$ Hz, C*H*), 7.38–7.51 (3H, m, Ar-*H*), 7.61 (2H, d, $J = 8.0$ Hz, Ar-*H*), 7.66 (1H, d, $J = 16.4$ Hz, C*H*), 8.02 (1H, d, $J = 8.8$ Hz, Ar-*H*), 8.46 (1H, dd, $J = 8.8$ and 2.2 Hz, Ar-*H*), 8.86 (1H, d, $J = 2.2$ Hz, Ar-*H*).

3,5-Dinitro-1-styrylbenzene, 1n. Yellow gum. *Z* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 6.67 (1H, d, $J = 12.0$ Hz, C*H*), 7.02 (1H, d, $J = 12.0$ Hz, C*H*), 7.18–7.25 (2H, m, Ar-*H*), 7.30–7.37 (3H, m, Ar-*H*), 8.38 (2H, d, $J = 1.8$ Hz, Ar-*H*), 8.85 (1H, t, $J = 1.8$ Hz, Ar-*H*). *E* isomer: ^{1}H NMR ($CDCl_3$, 400.13 MHz) δ 7.36–7.50 (5H, m, 2 C*H* + 3 Ar-*H*), 7.61 (2H, d, $J = 7.2$ Hz, Ar-*H*), 8.68 (2H, d, $J = 2.0$ Hz, Ar-*H*), 8.91 (1H, t, $J = 7.2$ Hz, Ar-*H*).

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