Electronic Supplementary Material (ESI) for New Journal of Chemistry. This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2017

Electronic Supplementary Information for

Metal-free denitrative arylation of β -nitrostyrenes using benzoyl peroxide: an easy access to *trans*-stilbenes

Arvind Kumar Yadav and Krishna Nand Singh*

Department of Chemistry (Center of Advanced Study), Institute of Science, Banaras Hindu University, Varanasi-221005, India. E-mail: knsinghbhu@yahoo.co.in; knsingh@bhu.ac.in; Fax: +91 5322460533; Tel:+91 5322500652

Contents	Page No.
I. General Information	1
II. General procedure for the synthesized compounds	2
III. Spectral data of synthesized compounds	2-9
IV. References	9
V. Copies of ¹ H and ¹³ C NMR spectra of the synthesized compounds	10-49

I. General Information: All commercially available reagents were used without further purification unless otherwise specified. Solvents were purified by the usual methods and were stored over molecular sieves. All the reactions were performed using oven-dried glassware including sealed tube. Organic solutions were concentrated using a Buchi rotary evaporator under diminished pressure. Column chromatography and TLC were performed using silica gel (Merck 100–200 mesh) and silica gel GF254 (Merck) plates respectively. Melting point (M.p.) was determined by open glass tube and is uncorrected. ¹H (500 MHz) and ¹³C (126 MHz) NMR spectra were recorded on a JEOL ECZ 500R FTNMR spectrometer in CDCl₃ using TMS as internal reference. The chemical shifts are reported in δ/ppm and coupling constants (*J*) in Hertz (Hz).

II. General procedure for the synthesis of Stilbene 2: β-Nitrostyrene 1 (1.0 mmol), benzoyl peroxide (BPO)/substituted benzoyl peroxide (0.5 mmol) and CH₃CN (3 mL) were placed in a dried sealed vessel. The contents were heated under stirring at 100 °C for 2-4 h. After the completion of reaction (as indicated by TLC), the contents were quenched with water (10 mL) and then extracted with ethyl acetate (3 × 10 mL). The combined organic phase was dried over anhydrous magnesium sulfate, filtered and concentrated under reduced pressure to give the crude product, which was purified by silica gel column chromatography using n-hexane to give the pure product **2** in high yields (MS, Table 2). The structures of the products were confirmed by comparison of M.p., ¹H, and ¹³C NMR spectral data with those reported in the literature.¹

III. Spectral data of compounds 2:



(E)-1,2-Diphenylethene (2a):¹ White solid (87% yield). M.p.: 121-122 °C (Lit. 121-122 °C).^{1a}
¹H NMR (500 MHz, CDCl₃): δ = 7.53 (d, J = 7.8 Hz, 1H, ArH), 7.52 (d, J = 7.2 Hz, 1H, ArH), 7.38-7.35 (m, 2H, ArH), 7.28-7.24 (m, 1H, ArH), 7.12 (s, 1H, CH). ¹³C NMR (126 MHz, CDCl₃): δ = 137.4, 128.7, 128.5, 127.7, 126.6.



(*E*)-1-Methyl-4-styrylbenzene (2b):¹ White solid (90% yield). M.p.: 114-115 °C (Lit. 114-116 °C).^{1*a*} ¹H NMR (500 MHz, CDCl₃): δ = 7.44 (d, *J* = 7.2 Hz, 2H, ArH), 7.42 (d, *J* = 8.4 Hz, 2H, ArH), 7.35 (t, *J* = 7.2 Hz, 2H, ArH), 7.28 (d, *J* = 7.2 Hz, 1H, ArH), 7.18 (d, *J* = 7.8 Hz, 2H, ArH), 7.00 (d, *J* = 4.8 Hz, 2H, CH), 2.29 (s, 3H, CH₃). ¹³C NMR (126 MHz, CDCl₃): δ = 137.5, 137.5, 134.6, 129.4, 128.7, 128.7, 127.7, 127.4, 126.5, 126.4, 21.2.



(*E*)-1-Methoxy-4-styrylbenzene (2c):¹ White solid (92% yield). M.p.: 134-135 °C (Lit. 134-135 °C). ¹*a* ¹H NMR (500 MHz, CDCl₃): δ = 8.15 (d, *J* = 7.8 Hz, 1H, ArH), 7.46-7.34 (m, 4H, ArH), 7.28 (t, *J* = 7.2 Hz, 2H, ArH), 7.18 (d, *J* = 16.2 Hz, 1H, ArH), 7.00 (d, *J* = 9.2 Hz, 1H, CH), 6.98 (d, *J* = 16.2 Hz, 1H, ArH), 6.88 (d, *J* = 9.0 Hz, 1H, CH), 3.75 (s, 3H, CH₃). ¹³C NMR (126 MHz, CDCl₃): δ = 159.3, 133.6, 130.1, 128.6, 128.2, 127.7, 127.2, 126.6, 126.2, 114.2, 55.4.



(*E*)-1-Methoxy-2-styrylbenzene (2d):¹ Colorless liquid (86% yield). ¹H NMR (500 MHz, CDCl₃): δ = 7.53 (d, J = 7.8 Hz, 1H, ArH), 7.51 (d, J = 7.2 Hz, 2H, ArH), 7.45 (d, J = 16.8 Hz, 1H, ArH), 7.35 (t, J = 7.2 Hz, 2H, ArH), 7.27-7.17 (m, 2H, ArH), 7.16 (d, J = 16.8 Hz, 1H, CH), 6.98 (t, J = 7.2 Hz, 1H, ArH), 6.90 (d, J = 8.4 Hz, 1H, CH), 3.82 (s, 3H, CH₃). ¹³C NMR (126 MHz, CDCl₃): δ = 156.9, 138.0, 129.1, 128.6, 128.6, 127.4, 126.6, 126.4, 126.4, 123.5, 120.8, 111.0, 55.6.



(E)-1-Chloro-4-styrylbenzene (2e):¹ Yellow solid (78% yield). M.p.: 129-130 °C (Lit. 129-131).^{1a} ¹H NMR (500 MHz, CDCl₃): δ = 7.43 (d, J = 7.8 Hz, 2H, ArH), 7.37 (t, J = 7.8 Hz, 2H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 7.2 Hz, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 7.2 Hz, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 7.2 Hz, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 7.2 Hz, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 7.2 Hz, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 7.2 Hz, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 7.2 Hz, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H, ArH), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 7.2 Hz, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 7.2 Hz, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 7.2 Hz, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H, ArH), 7.27 (d, J = 7.2 Hz, 2H, ArH), 7.24 (d, J = 7.2 Hz, 1H), 7.30 (d, J = 7.2 Hz, 2H), 7.30 (d, J = 7.2 Hz), 7.30

ArH), 7.02-6.95 (m, 2H, CH). ¹³C NMR (126 MHz, CDCl₃): δ = 137.0, 135.9, 133.2, 129.4, 128.9, 128.8, 127.9, 127.7, 127.4, 126.6.



(*E*)-1-Chloro-3-styrylbenzene (2f):¹ White solid (80% yield): M.p.: 72-73 °C (Lit. 71-72 °C).^{1a}
¹H NMR (500 MHz, CDCl₃): δ = 7.44 (d, J = 7.8 Hz, 3H, ArH), 7.23 (t, J = 7.8 Hz, 3H, ArH),
7.20 (t, J = 7.8 Hz, 2H, ArH), 7.16 (d, J = 8.4Hz, 1H, ArH), 7.06 (d, J = 16.2 Hz, 1H, CH), 6.98
(d, J = 16.2 Hz, 1H, CH). ¹³C NMR (126 MHz, CDCl₃): δ = 139.3, 136.8, 134.7, 130.2, 129.9,
128.8, 128.4, 127.5, 127.2, 126.7, 126.3, 124.8.



(*E*)-1-Chloro-2-styrylbenzene (2g):¹ White solid (73% yield). M.p.: 64-65 °C (Lit. 64-66 °C).^{1*a*} ¹H NMR (500 MHz, CDCl₃): δ = 7.62 (d, *J* = 8.0 Hz, 1H, ArH), 7.47 (dd, *J* = 7.6, 16.4 Hz, 3H, ArH), 7.32 (t, *J* = 7.6 Hz, 3H, ArH), 7.23 (d, *J* = 7.6 Hz, 1H, ArH and 1H, CH), 7.17-7.10 (m, 1H, ArH), 7.02 (d, *J* = 16.4 Hz, 1H, CH). ¹³C NMR (126 MHz, CDCl₃): δ = 137.1, 135.5, 133.5, 131.3, 129.9, 128.8, 128.6, 128.1, 126.9, 126.9, 126.5, 124.8.



(*E*)-1-Bromo-2-styrylbenzene (2h):¹ Yellow liquid (76% yield).^{1a} ¹H NMR (500 MHz, CDCl₃):
δ = 7.67 (d, J = 7.8 Hz, 1H, ArH), 7.57 (dd, J = 7.8, 7.8 Hz, 3H, ArH), 7.47 (d, J = 16.2 Hz, 1H, ArH), 7.38 (t, J = 7.8 Hz, 2H, ArH), 7.29-7.06 (m, 2H, ArH), 7.04 (t, J = 7.8 Hz, 1H, CH), 6.98 (d, J = 16.2 Hz, 1H, CH). ¹³C NMR (126 MHz, CDCl₃): δ = 137.2, 137.1, 133.1, 131.5, 128.8, 128.4, 128.1, 127.6, 127.5, 126.9, 126.8, 124.2.



(*E*)-1-Bromo-3-styrylbenzene (2i):¹ White solid (82% yield). M.p.: 72-73 °C (Lit. 72-73 °C).^{1*a*} ¹H NMR (500 MHz, CDCl₃): δ = 7.59 (s, 1H, ArH), 7.44 (d, *J* = 7.8 Hz, 2H, ArH), 7.35 (t, *J* = 7.8 Hz, 3H, ArH), 7.22 (t, *J* = 7.8 Hz, 2H, ArH), 7.14 (d, *J* = 8.4Hz, 1H, ArH), 7.04 (d, *J* = 16.2 Hz, 1H, CH). ¹³C NMR (126 MHz, CDCl₃): δ = 139.6, 136.8, 130.4, 130.2, 129.3, 128.8, 128.1, 127.1, 126.7, 125.2, 122.9.



(*E*)-1-Fluoro-4-styrylbenzene (2j):¹ White solid (78% yield). M.p.: 123-124 °C (Lit. 123-124 °C). ^{1*a*} ¹H NMR (500 MHz, CDCl₃): δ = 7.43-7.39 (m, 5H), 7.30 (t, *J* = 7.8 Hz, 1H), 7.19-7.18 (m, 1H), 6.99-6.96 (m, 4H). ¹³C NMR (126 MHz, CDCl₃): δ = 163.8 (¹*J*_{*C*-*F*} = 248.8 Hz), 137.2, 133.6 (³*J*_{*C*-*F*} = 3.8 Hz), 128.7, 128.5, 128.0, 128.0, 127.7, 127.5, 126.5, 115.7 (²*J*_{*C*-*F*} = 21.9 Hz).



(*E*)-1-Fluoro-2-styrylbenzene (2k):¹ White solid (74% yield). M.p.: 103-104 °C (Lit. 103-105 °C).^{1*a*} ¹H NMR (500 MHz, CDCl₃): $\delta = 7.54$ (t, J = 7.8 Hz, 1H, ArH), 7.46 (d, J = 7.8 Hz, 2H, ArH), 7.30 (t, J = 7.5 Hz, 2H, ArH), 7.33-7.04 (m, 4H, ArH), 7.00 (t, J = 7.8 Hz, 1H, CH), 6.98 (d, J = 16.2 Hz, 1H, CH). ¹³C NMR (126 MHz, CDCl₃): $\delta = 161.5$ (d, ¹ $J_{C-F} = 246.5$ Hz), 137.3, 131.0 (d, ³ $J_{C-F} = 3.8$ Hz), 128.7 (d, ³ $J_{C-F} = 3.8$ Hz), 128.0, 127.1(d, ³ $J_{C-F} = 3.8$ Hz), 126.7, 125.2, 125.1, 124.2 (d, ² $J_{C-F} = 21.4$ Hz), 121.0, 115.9 (d, ² $J_{C-F} = 21.4$ Hz).



(*E*)-1-Nitro-2-styrylbenzene (2l):¹ Yellow orange solid (70% yield). M.p.: 71-73 °C (Lit. 72-73 °C). ¹H NMR (500 MHz, CDCl₃): δ = 8.23 (d, J = 9.0 Hz, 1H), 7.98 (dd, J = 7.5 Hz, 9.0 Hz, 1H), 7.65 (t, J = 7.5 Hz, 2H), 7.62 (t, J = 7.5 Hz, 2H), 7.34-7.28 (m, 3H), 7.23 (d, J = 7.4 Hz, 1H), 7.11 (d, J = 16.0 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃): δ = 149.9, 135.4, 132.8, 132.0, 129.1, 128.4, 127.7, 126.0, 124.9, 123.7, 122.5, 120.6.



(*E*)-1-Nitro-3-styrylbenzene (2m):¹ Yellow orange solid (72% yield). M.p.: 102-103 °C (Lit. 102-103 °C). ¹H NMR (500 MHz, CDCl₃): δ = 8.28 (s, 1H), 8.02 (dd, J = 8.2, 1.3 Hz, 1H), 7.71 (dd, J = 7.7 Hz, 1H), 7.45 (dd, J = 15.7, 7.7 Hz, 2H), 7.43-7.29 (m, 3H), 7.25 (t, J = 7.3 Hz, 1H),

7.17 (d, J = 5.3 Hz, 1H), 7.06 (d, J = 15.3 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃): $\delta = 147.7$, 138.1, 135.2, 131.2, 130.7, 128.5, 127.8, 127.5, 125.8, 125.0, 120.9, 119.8.



(*E*)-1-Nitro-4-styrylbenzene (2n):¹ Yellow orange solid (65% yield). M.p.: 148-150 °C (Lit. 150 °C). ¹H NMR (500 MHz, CDCl₃): δ = 8.14 (d, J = 8.8 Hz, 2H), 7.55 (d, J = 8.7 Hz, 2H), 7.47 (d, J = 7.3 Hz, 2H), 7.33 (t, J = 7.5 Hz, 2H), 7.32-24 (m, 1H), 7.17 (t, J = 4.4 Hz, 1H), 7.07 (d, J = 16.3 Hz, 1H). ¹³C NMR (126 MHz, CDCl₃) δ = 146.7, 143.8, 136.1, 133.2, 128.8, 128.8, 127.0, 126.8, 126.2, 124.1.



(*E*)-2-Styrylthiophene (2o):^{1d} Yellow solid (89% yield). M.p.: 127-128 °C (Lit. 72-73 °C).^{1a} ¹H NMR (500 MHz, CDCl₃): δ = 7.40 (d, *J* = 7.4 Hz, 2H, ArH), 7.28 (t, *J* = 7.4 Hz, 2H, ArH), 7.18-7.11 (m, 3H, ArH), 7.00 (d, *J* = 3.5 Hz, 1H, ArH), 6.94 (d, *J* = 16.1 Hz, 1H, CH), 6.87 (d, *J* = 3.7 Hz, 1H, CH). ¹³C NMR (126 MHz, CDCl₃): δ = 142.9, 137.0, 135.1, 128.7, 128.4, 127.6, 126.3, 126.1, 124.4, 121.8.



(E)-1,2-Dip-tolylethene (2p):¹ White solid (90% yield). M.p.: 179-180 °C (Lit. 180-182 °C).^{1a}
¹H NMR (500 MHz, CDCl₃): δ = 7.21 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.5 Hz, 2H), 6.55 (s, 1H),
2.35 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ = 136.8, 134.6, 129.6, 129.0, 126.4, 21.3.



(*E*)-1-Methoxy-4-(4-methylstyryl)benzene (2q):¹ White solid (92% yield). M.p.: 159-161 °C (Lit. 160-162 °C).^{1*a*} ¹H-NMR (500 MHz, CDCl₃): δ = 7.42 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.70 (d, *J* = 8.7 Hz, 2H), 3.69 (s, 3H), 2.32 (s, 3H). ¹³C-NMR (126 MHz, CDCl₃): δ = 160.0, 144.6, 135.1, 132.0, 130.1, 129.5, 128.7, 124.8, 120.2, 114.0, 55.3, 21.7.



(E)-1,2-Bis(4-methoxyphenyl)ethene (2r):¹ Yellowish solid (94% yield). M.p.: 212-214 °C (Lit. 212-213 °C).^{1a} ¹H NMR (500 MHz, CDCl₃): δ = 7.34-7.12 (m, 2H), 6.85-6.68 (m, 2H), 6.37 (s, 1H), 3.71 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ = 158.5, 130.1, 128.4 125.6, 114.1, 55.2.



(E)-1-Fluoro-2-(3-methylstyryl)benzene (2s):¹ Colorless oil (78% yield). ¹H NMR (500 MHz, CDCl₃): δ = 7.53 (d, J = 1.5 Hz, 1H), 7.29 (d, J = 14.0 Hz, 2H), 7.21-7.17 (m, 3H), 7.09-7.01 (m,

4H), 2.31 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): $\delta = 161.4$ (d, ¹ $J_{C-F} = 247.1$ Hz), 138.3, 137.2, 131.0 (d, ³ $J_{C-F} = 3.7$ Hz), 128.8 (d, ³ $J_{C-F} = 3.6$ Hz), 128.6, 128.1, 127.3 (d, ³ $J_{C-F} = 3.7$ Hz), 127.0, 125.4, 124.2 (d, ² $J_{C-F} = 21.3$ Hz), 123.9, 120.7, 115.9 (d, ² $J_{C-F} = 21.3$ Hz), 21.5.



(*E*)-1-Chloro-4-(4-methylstyryl)benzene (2t):¹ White solid (70% yield). M.p.: 201-203 °C (Lit. 202-203 °C).^{1*a*} ¹H NMR (500 MHz, CDCl₃): δ = 7.36-7.32 (m, 4H), 7.24 (d, *J* = 9.0, 2H), 7.10 (d, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 16.5 Hz, 2H), 2.29 (s, 3H). ¹³C NMR (126 MHz, CDCl₃): δ = 137.9, 136.1, 134.2, 133.0, 129.5, 129.3, 128.8, 127.6, 126.5, 126.4, 21.3.

IV. References: 1 (*a*) J. J. Heynekamp, M. W. Waylon, L. A. Hunsaker, A. M. Gonzales, R. A. Orlando, M. D. Lorraine and D. L. Vander Jagt, *J. Med. Chem.*, 2006, 49, 7182; (*b*) P. Schroll, D. P. Hari and B. König, *ChemistryOpen*, 2012, 1, 130; (*c*) N. Zhang, Z.-J. Quan, Z. Zhang, Y.-X. Da and X.-C. Wang, *Chem. Commun.*, 2016, 52, 14234; (*d*) P. Puthiyaraj and K. Pitchumani, *Green Chem.*, 2014, 16, 4223.

V. Copies of ¹H and ¹³C NMR spectra.

Compound 2a. ¹H NMR Spectrum (CDCl₃).





Compound 2a. ¹³C NMR Spectrum (CDCl₃).



Compound 2b. ¹H NMR Spectrum (CDCl₃).





Compound 2b. ¹³C NMR Spectrum (CDCl₃).





Compound 2c. ¹H NMR Spectrum (CDCl₃).





Compound 2c. ¹³C NMR Spectrum (CDCl₃).



Page 15 Compound 2d. ¹H NMR Spectrum (CDCl₃).





Compound 2d. ¹³C NMR Spectrum (CDCl₃).





Compound 2e. ¹H NMR Spectrum (CDCl₃).





Compound 2e. ¹³C NMR Spectrum (CDCl₃).





Compound 2f. ¹H NMR Spectrum (CDCl₃).





Compound 2f. ¹³C NMR Spectrum (CDCl₃).





Compound 2g. ¹H NMR Spectrum (CDCl₃).





Compound 2f. ¹³C NMR Spectrum (CDCl₃).





Compound 2h. ¹H NMR Spectrum (CDCl₃).





Compound 2h. ¹³C NMR Spectrum (CDCl₃).





Compound 2i. ¹H NMR Spectrum (CDCl₃).





Compound 2i. ¹³C NMR Spectrum (CDCl₃).



Compound 2j. ¹H NMR Spectrum (CDCl₃).





Compound 2j. ¹H NMR Spectrum (CDCl₃).



Compound 2k. ¹H NMR Spectrum (CDCl₃).





Compound 2k. ¹H NMR Spectrum (CDCl₃).



Compound 21. ¹H NMR Spectrum (CDCl₃).





Compound 21. ¹³C NMR Spectrum (CDCl₃).



Page 33

Compound 2m. ¹H NMR Spectrum (CDCl₃).





Compound 2m. ¹³C NMR Spectrum (CDCl₃).



Compound 2n. ¹H NMR Spectrum (CDCl₃).





Compound 2n. ¹³C NMR Spectrum (CDCl₃).



Compound 20. ¹H NMR Spectrum (CDCl₃).





Compound 20. ¹³C NMR Spectrum (CDCl₃).





Compound 2p. ¹H NMR Spectrum (CDCl₃).





Compound 2p. ¹³C NMR Spectrum (CDCl₃).





Compound 2q. ¹H NMR Spectrum (CDCl₃).





Compound 2q. ¹³C NMR Spectrum (CDCl₃).





Compound 2r. ¹H NMR Spectrum (CDCl₃).





Compound 2r. ¹³C NMR Spectrum (CDCl₃).





Compound 2s. ¹H NMR Spectrum (CDCl₃).





Compound 2s. ¹³C NMR Spectrum (CDCl₃).



Compound 2t. ¹H NMR Spectrum (CDCl₃).



Compound 2t. ¹³C NMR Spectrum (CDCl₃).

