Olefination of α-Hydroxy- or α-Aminoaldehyde Derivatives via Reaction of their Arylsulfonylhydrazones with Sulfonyl Anions

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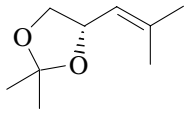
Supporting Information

Table of Contents

1. General Experimental Methods

NMR measurements were carried at 200 MHz (^{1}H) or at 50 MHz (^{13}C). The chemical shifts are reported on the δ scale downfield from tetramethylsilane (δ = 0.00 ppm) or relative to the resonance of $CDCl_3$ (δ 77.0 ppm for the central line of the triplet), or DMSO-d_6 (δ = 39.5 ppm for the central line of the septet) in the ^{13}C mode. DEPT sequence was used for assigning multiplicities in ^{13}C NMR spectra. THF was dried over Na-K alloy and distilled under argon. All reactions involving air- and moisture-sensitive compounds were performed in oven- or flame-dried glassware under argon. Organic extracts were dried over anhydrous $MgSO_4$ and the solvents were removed on a rotary evaporator under reduced pressure. Dry column vacuum chromatography (Pedersen, D. S.; Rosenbohm, C. *Synthesis* **2001**, 2431-2434) was performed on Merck silica gel 60 less than 0.063 mm with hexane – ethyl acetate (gradient elution). Merck silica gel 60 F_{254} plates were used for thin layer chromatography (TLC). *iso*-PrMgCl (2M in THF) was purchased from Fluka. HPLC was carried out with UV detector using a 250x4.6 mm Nucleosil 50/5 mμ column (flow 1 mL/min) for analytical purposes and two 250x20 mm Nucleosil 60/7 mμ columns connected in series (flow 15 mL/min) for preparative separations.

2. Preparation and characterization of compounds 4 – 21…… p. S2-S11



4b

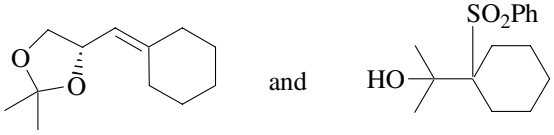
and

5a

(4*R*)-2,2-Dimethyl-4-(2-methylprop-1-enyl)-1,3-dioxolane (4b) and 2,3-dimethyl-3-(phenylsulfonyl)butan-2-ol (5a).

The general procedure was followed using: isopropyl phenyl sulfone **3b** (558 mg, 3.02 mmol, 2.8 equiv), *iso*-PrMgCl (2M in THF, 1.5 mL, 3.0 mmol) and tosylhydrazone (*S*)-**2** (319 mg, 1.07

mmol) in THF (10 mL). The mixture was stirred for 16 h, the reaction was quenched with concd. aqueous ammonia (0.4 mL). The product was isolated in the usual way and chromatographed on silica gel (15 g) to give **4b** (69 mg, 41%) and **5a** (36 mg, 15%); **4b**: colorless oil; $[\alpha]^{27}_{D}$ +3.13 (c 3.27, hexane)^{1}H NMR ($CDCl_3$) 1.40 (3H, s), 1.42 (3H, s), 1.73 (3H, d , *J* 1.4 Hz), 1.75 (3H, d, *J* 1.4 Hz), 3.49 (1H, t *J* 8.1 Hz), 4.06 (1H, dd *J* 8.0, 5.9 Hz), 4.70-4.85 (1H, m), 5.12-5.24 (1H, m) ppm; ^{13}C NMR ($CDCl_3$) 18.33 (3), 25.95 (3), 26.08 (3), 26.88 (3), 69.42 (2), 72.96 (1), 108.63 (0), 122.03 (1), 138.71 (0) ppm. HRMS (EI): calcd. for $C_9H_{16}O_2$, 156.11503; found, 156.11497. **5a**: m.p. 79-81 ^{0}C (hexane). ^{1}H NMR ($CDCl_3$) 1.30 (6H, s), 1.51 (6H, s), 3.85 (1H, bs), 7.52-7.73 (m, 3H), 7.85-7.95 (m, 2H); ^{13}C NMR ($CDCl_3$) 20.69 (3), 27.17 (3), 69.61 (0), 75.33 (0), 128.78 (1), 130.19 (1), 133.69 (1), 137.12 (0). HRMS liquid SIMS, calcd. for $C_{12}H_{18}O_3SNa$ $(M+Na)^+$ 265.0869; found: 265.0867.



4c **5b**

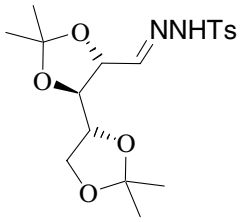
(4*R*)-4-(Cyclohexylidenemethyl)-2,2-dimethyl-1,3-dioxolane (4c) and 2-[1-(phenylsulfonyl)cyclohexyl]propan-2-ol (5b)

To cyclohexyl phenyl sulfone **3c** (543 mg, 2.42 mmol, 3.3 equiv), stirred under argon at rt, *iso*-PrMgCl (2M in THF, 1.8 mL, 3.6 mmol) was added. The mixture was stirred for 3 h and then tosylhydrazone (*S*)-**2** (219 mg, 0.734 mmol) in THF (2.5 mL) was added. After 16 h, the reaction was quenched with concd. aqueous ammonia solution (0.4 mL) and the product was isolated in the usual way. Chromatography of the crude product on silica gel (30 g) afforded **4c** (35 mg, 24%) and **5b** (56 mg, 26%);

4c: colorless oil; $[\alpha]_{D}^{22}$ +2.3 (c 1.6, hexane). ^{1}H NMR ($CDCl_3$) 1.39 (3H, s), 1.42 (3H, s), 1.4-1.7 (6H, m), 2.0-2.3 (4H, m), 3.48 (1H, t, *J* 8.1 Hz), 4.02 (1H, dd, *J* 8.0, 5.9 Hz), 4.76-4.90 (1H, dt, *J* 8.4, 6.0 Hz), 5.07-5.16 (1H, dt, *J* 8.8, 1.0 Hz) ppm. ^{13}C NMR ($CDCl_3$) 26.13 (3), 26.66 (2), 26.92

(3), 27.87 (2), 28.31 (2), 29.40 (2), 37.17 (2), 69.72 (2), 72.19 (1), 108.70 (0), 118.80 (1), 146.36 (0). HRMS (EI): calcd. for $C_{12}H_{20}O_2$, 196.14633; forund: 196.14641.

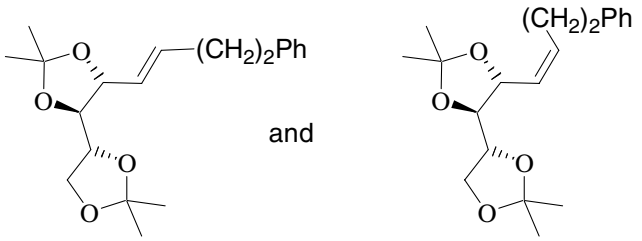
5b: m.p. 104-106 °C (CH_2Cl_2-hexane), ^{1}H NMR ($CDCl_3$) 1.0-1.2 (4H, m), 1.47 (6H, s), 1.3-1.5 (2H, m), 1.8-2.0 (2H, m), 1.2-1.4 (2H, m), 4.05 (1H, s), 7.5-7.7 (3H, m), 7.9-8.0 (2H, m) ppm. ^{13}C NMR ($CDCl_3$) 21.40 (2), 23.46 (2), 26.70 (2), 28.16 (3), 75.27 (0), 128.78 (1), 130.19 (1), 133.49 (1), 140.66 (0). HRMS (liquid sims): calcd. for $C_{15}H_{22}O_3SNa$ $(M+Na)^+$ 305.1182; found, 305.1204.



7

2,3:4,5-di-*O*-Isopropylidene-D-arabinose tosylhydrazone (**7**),

3,4:5,6-di-*O*-Isopropylidene-D-sorbitol (Jarosz, S.; Zamojski, A. *Carbohydr. Chem.* **1993**, *12*, 1223-1228) (901 mg, 3.43 mmol) was oxidized (Elder, J. S.; Mann, J.; Walsh, E. B. *Tetrahedron* **1985**, *41*, 3117-3125) with sodium periodate (903 mg) in THF (14 mL) and water (1.7 mL) to give 2,3:4,5-di-*O*-isopropylidene-D-arabinose **6** (756 mg, 96%) as a viscous oil. The latter product was dissolved in *tert*-butyl methyl ether (15 mL) and treated with tosylhydrazine (627 mg, 3.36 mmol). After 5 h, the precipitate was collected, washed with *tert*-butyl methyl ether and air-dried. Tosylhydrazone **7** (647 mg) was obtained; white crystals, m.p. 117-118 °C, $[\alpha]_D^{22}$ –14 (c 5.1, ethyl acetate). The filtrate was evaporated *in vacuo* and chromatographed on silica (15 g, hexane-ethyl acetate) to give additional **7** (255 mg, in total 69%yield). ^{1}H NMR (DMSO-d_6) 1.13 (3H, s), 1.19 (3H, s), 1.23 (3H, s), 1.30 (3H, s), 2.38 (3H, s), 3.6-3.8 (1H, m), 3.85-4.1 (3H, m), 4.28 (1H, t, *J* 6.5 Hz), 7.19 (1H, d, *J* 6.1 Hz), 7.39 (2H, d, *J* 8.0 Hz), 7.67 (2H, d, *J* 8.3 Hz) ppm. ^{13}C NMR (DMSO-d_6): 20.99 (3), 25.09 (3), 26.31 (3), 26.54 (3), 26.67 (3), 65.76 (2), 75.23(1), 77.37 (1), 77.91 (1), 108.64 (0), 109.60 (0), 126.99 (1), 129.45 (1), 135.91 (0), 143.22 (0), 146.86 (1) ppm.



E-**8** *Z*-**8**

***E*- and *Z*-(4*S*,4'*R*,5*R*)-2,2,2',2'-Tetramethyl-5[(1*E*)-4-phenylbut-1-enyl]-4,4'-bi-1,3-dioxolane (8).**

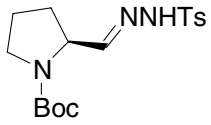
To sulfone **3a** (329 mg, 1.26 mmol, 2.96 equiv), stirred under argon at rt, *iso*-PrMgCl (2M in THF, 0.7 mL, 1.4 mmol) was added. The mixture was stirred for 1.5 h and then tosylhydrazone **7** (170 mg, 0.43 mmol) in THF (2 mL) was added. After 2 h, the reaction was quenched with concd. aqueous ammonia (0.2 mL). The product was isolated in the usual way and chromatographed on silica gel (15 g) to afford **8** (77 mg, 60%) as colorless oil; isomer ratio *Z*:*E* 11:89, by HPLC (hexane-ethyl acetate 9:1), t_R 6.2 min(*Z*-) and 6.8 min (*E*-isomer).

Samples of isomers were separated by preparative HPLC.

(*Z*)-**8**: ^{1}H NMR ($CDCl_3$) 1.33 (3H, s), 1.38 (3H, s), 1.40 (3H, s), 1.41 (3H, s), 2.4-2.6 (2H, m), 2.65-2.80 (2H, m), 3.65-3.75 (1H, m), 3.85-4.00 (1H, m), 4.00-4.15 (2H, m), 4.66 (1H, t, *J* 7.9-8.4 Hz), 5.3-5.55 (1H, m), 5.60-5.85 (1H, m), 7.2-7.4 (5H, m) ppm; on irradiation at δ 2.54 multiplet at δ 5.3-5.55 collapsed to a doublet of doublets, *J* 10.9, 8.7 Hz, and that at δ 5.60-5.85 to a doublet, *J* 10.8 Hz.

(*E*)-**8**: $[\alpha]_D^{22}$ +4.1 (c 2.6, hexane). ^{1}H NMR ($CDCl_3$) 1.34 (3H, s), 1.39 (3H, s), 1.40 (6H, s), 2.30-2.45 (2H, m), 2.65-2.80 (2H, m), 3.68 (1H, dd, *J* 6.2 Hz, 1.6 Hz), 3.85-3.95 (1H, m), 3.95-4.20 (2H, m), 4.30 (1H, t, *J* 7.4 Hz), 5.54 (1H, ddt, *J* 15.4, 7.1, 1.3 Hz), 5.88 (1H, dt, *J* 15.6 Hz, 6.4 Hz), 7.10-7.35 (5H, m) ppm; on irradiation at δ 2.39 multiplet at δ 5.54 collapsed to a doublet of doublets, *J* 15.4, 7.1 Hz, and that at δ 5.88 to a doublet, *J* 15.2 Hz. ^{13}C NMR ($CDCl_3$) 25.34 (3), 26.71 (3), 26.96 (3), 27.12 (3), 34.17 (2), 35.45 (2), 66.67 (2), 80.03 (1), 80.93 (1), 109.08 (0),

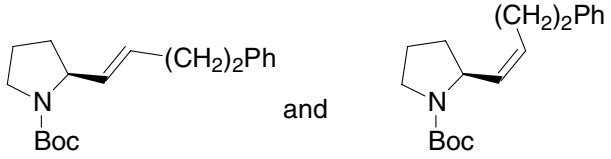
109.50 (0), 125.82 (1), 128.07 (1), 128.26 (1), 128.32 (1), 134.10 (1), 141.53 (0) ppm. HRMS (EI): calcd. for $C_{20}H_{28}O_4$, 332.19876; found, 332.19760.



11

***tert*-Butyl (2*S*)-2-((*E*)-{[(4-methylphenyl)sulphonyl]hydrazono}methyl)pyrrolidine-1-carboxylate (11).**

N-(*tert*-Butoxycarbonyl)-(S)-prolinol **9** (Aldrich) (262 mg, 1.3 mmol) in dichloromethane (11 mL) was oxidized with Dess-Martin periodinane (Dess, D. B.; Martin, J. C. *J. Org. Chem.* **1983**, *48*, 4155-4156) (682 mg, 1.61 mmol). The product was isolated in the usual way and purified by chromatography on silica gel. Thus obtained colorless oil was dissolved in diethyl ether (15 mL) and treated with tosylhydrazine (300 mg, 1.61 mmol). After 16 h, the precipitate was filtered off, washed with diethyl ether and dried to give **11** (358 mg, 73% from prolinol), m.p. 173-175 °C (dec.)); ^{1}H NMR (DMSO-d_6) 1.20 (9H, s), 1.5-2.1 (4H, m), 2.38 (3H), 3.2 (2H, m), 4.1 (1H, m), 7.17 (1H, m), 7.38 (2H, d, *J* 8.1 Hz), 7.66 (2H, d, *J* 8.2 Hz), 11.08 (1H, m) ppm. ^{13}C NMR (DMSO-d_6) 20.94 (3), 27.79 (3), 46.07 (2), 57.43 (2), 78.51 (0), 127.09 (1), 129.41 (1), 136.14 (0), 143.12 (0), 150.79 (1) ppm.

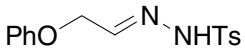


***E*-12** ***Z*-12**

(*E*)- and (*Z*)-*tert*-Butyl (2*S*)-2-[(1*E*)-4-phenylbut-1-enyl]pyrrolidine-1-carboxylate (12).

To sulfone **3a** (311 mg, 1.19 mmol, 3.07 equiv), stirred under argon at rt, *iso*-PrMgCl (2M in THF, 2 mL, 4 mmol) was added. The mixture was stirred for 1.5 h and then tosylhydrazone **11**

(143 mg, 0.39 mmol) in THF (5 mL) was added. After 16 h, the reaction was quenched with concd. aqueous ammonia (0.3 mL). The product was isolated in the usual way and chromatographed on silica gel (15 g) to afford **12** (103 mg, 88%) containing minor contaminations. Isomer ration *Z*:*E* 44:56 by HPLC (hexane-ethyl acetate 9:1), t_R 7.1 min *Z*-and 8.3 min *E*-isomer. Finally, a sample of **12** (80 mg) was chromatography using a preparative HPLC column to give (***Z***)**-12**-isomer (33 mg) and (*E*)-**12**-isomer (27 mg). (***Z***)**-12**: ^{1}H NMR ($CDCl_3$) 1.43 (9H, s), 1.6-2.0 (4H, m), 2.30-2.85 (4H, m), 3.25-3.45 (2H, m), 4.35-4.50 (1H, m), 5.24-5.48 (2H, m); 7.10-7.35 (5H, m) ppm; on irradiation at δ 2.51 the left part of the multiplet at δ 5.24-5.48 collapsed to a doublet, *J* 11.0 Hz. ^{13}C NMR ($CDCl_3$): 23.82 (2), 28.60 (3), 29.38 (2), 33.21 (2), 35.93 (2), 46.41 (2), 54.31 (1), 79.02 (0), 125.78 (1), 128.21 (1), 128.45 (1), 141.81 (0), 154.52 (0) ppm. (***E***)**-12**: ^{1}H NMR ($CDCl_3$) 1.43 (9H, s), 1.5-2.0 (4H, m), 2.25-2.45 (2H, m), 2.55-2.75 (3H, m), 3.25-3.45 (2H, m), 4.22 (1H, bs), 5.27-5.42 (1H, m), 5.43-5.61 (1H, m), 7.0-7.4 (5H, m) ppm; on irradiation at δ 2.33 multiplet at δ 5.27-5.42 collapsed to a doublet of doublets, *J* 15.2, 5.9 Hz, and that at 5.43-5.61 to a doublet, *J* 15.2 Hz. ^{13}C NMR ($CDCl_3$): 23.09 (2), 25.82 (2), 28.56 (3), 33.98 (2), 35.87 (2), 46.21 (2), 53.38 (1), 78.92 (0), 125.71 (1), 128.20 (1), 129.15 (1), 131.21 (0), 141.87 (0). HRMS (EI): calcd. for $C_{19}H_{27}NO_2$, 301.20418; found, 301.20514.

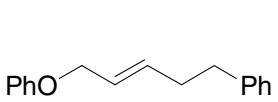


15

4-Methyl-*N'*-[(1*E*)-2-phenoxyethylidene]benzenesulfonohydrazide (15).

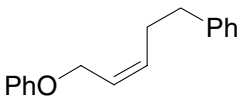
Phenyl glycidyl ether (1.0 g, 6.66 mmol) was cleaved with periodic acid (1.535 g, 6.73 mmol) in diethyl ether (50 mL), following the literature procedure (Fieser, L. F.; Fieser, M. *Fieser and Fieser's Reagents for Organic Synthesis*; Wiley: New York, 1992; Vol. 1, p. 817). The product was purified by chromatography on silica gel to give phenoxyacetaldehyde **13** (764 mg, 84%). The latter was dissolved in diethyl ether (25 mL) and tosylhydrazine (1.110 g, 5.96 mmol) was added. After 2.5 h the suspension was cooled in ice bath and filtered. Crystals were collected and washed with cold diethyl ether, and air-dried. Tosylhydrazone **15** (811 mg) was obtained, mp

123-124 0^0 C. The filtrate was evaporated and the residue was chromatographed on silica gel (30 g) to give additional portion of **15** (581 mg, 79% total yield). ^{1}H NMR (DMSO-d_6): 2.39 (3H), 4.56 (2H, d, *J* 4.9 Hz), 6.8-7.0 (3H, m), 7.1-7.3 (2H, m), 7.3-7.5 (3H, m), 7.68 (2H, d, *J* 8.2 Hz), 11.44 (1H, s, NH) ppm. ^{13}C NMR (DMSO-d_6) 21.00 (3), 66.56 (2), 114.53 (1), 120.90 (1), 127.08 (1), 129.39 (1), 129.64 (1), 135.99 (0), 143.40 (0), 145.67 (1), 157.66 (0) ppm. MS: 304 (M^+).



E-**16**

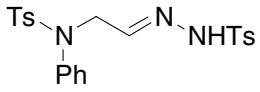
and



Z-**16**

(*E*)- and (*Z*)-5-Phenoxypent-3-enyl]benzene (16).

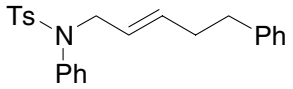
To sulfone **3a** (391 mg, 1.5 mmol, 3.0 equiv), stirred under argon at rt, *iso*-PrMgCl (2M in THF, (0.8 mL, 1.6 mmol) was added. The mixture was stirred for 1.5 h and then tosylhydrazone **15** (152 mg, 0.5 mmol) in THF (2.5 mL) was added. After 2 h, the reaction was quenched with concd. aqueous ammonia (0.2 mL). The product was isolated in the usual way and chromatographed on silica gel (30 g) to afford **16** (54 mg, 45%) as colorless oil. Isomer ratio *Z*:*E* 36:64 by HPLC (0.1% ethyl acetate in hexane), t_R 20.7 min (*Z*-) and 22.1 min (*E*-isomer). Samples of the isomers were separated by preparative HPLC. (*Z*)-**16**: ^{1}H NMR($CDCl_3$) 2.35-2.55 (2H, m), 2.65-2.80 (2H, m), 4.44 (2H, d , *J* 4.0 Hz), 5.60-5.80 (2H, m), 6.75-7.00 (3H, m), 7.10-7.35 (7H, m) ppm; on irradiation at δ 2.50 multiplet at δ 5.60-5.80 collapsed to an apparent triplet, *J* 3.5 Hz. HRMS (EI): calcd. for $C_{17}H_{18}O$, 238.13577; found, 238.13477. (*E*)-**16**: ^{1}H NMR ($CDCl_3$) 2.3-2.5 (2H, m), 2.65-2.80 (2H, m), 4.47 (2H, d *J* 5.6 Hz), 5.65-6.00 (2H, m), 6.8-7.0 (3H, m), 7.10-7.35 (5H, m) ppm; on irradiation at δ 2.43 the left part of the multiplet at δ 5.65-5.90 collapsed to a doublet, *J* 15.3 Hz. (*Z*)-**16 +** (*E*)-**16**: ^{13}C NMR ($CDCl_3$) 29.78 (2), 34.16 (2), 35.44 (2), 35.63 (2), 63.77 (2), 68.53 (2), 114.70 (1), 120.65 (1), 125.51 (1), 125.75 (1), 125.83 (1), 125.95 (1), 128.28 (1), 128.37 (1), 128.45 (1), 129.34 (1), 132.76 (1), 134.28 (1), 141.55 (0), 158.59 (0) ppm. HRMS (EI) calcd. for $C_{17}H_{18}O$: 238.13577; found 238.13624.



17

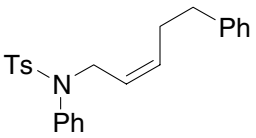
4-Methyl-N-((2*E*)-2-{[(4-methylphenyl)sulfonyl]hydrazono}ethyl)-N-phenylbenzenesulfonamide (17).

N-Phenyl-*N*-tosyl-2-aminoethanol (2.118 g, 7.27 mmol) was oxidized with PCC on alumina following the reported procedure (Cheng, Y.-S., Liu, W.-L., Chen, S.-H. *Synthesis* **1980**, 223-224) and the product was purified by chromatography. Thus obtained aldehyde **14** (433 mg, 1.496 mmol) was dissolved in diethyl ether (15 mL) and tosylhydrazine (312 mg, 1.675 mmol) was added. After 16 h, crystals were collected, washed with diethyl ether and dried to give crude **17** (557 mg). This product was purified by chromatography on silica gel (30 g) to give TLC-pure **17** (290 mg, 42%) and a contaminated fraction (129 mg). Pure **17**, mp 156-158 ^{0}C (hexane-ethyl acetate). ^{1}H NMR (DMSO-d$_6$) 2.39 (6H, s), 4.24 (2H, d, *J* 5.1 Hz), 6.9 (2H, m), 7.1-7.6 (12H, m), 11.24 (1H, s, NH) ppm. ^{13}C NMR (DMSO-d$_6$) 20.99 (3), 51.79 (2), 126.84 (1), 127.27 (1), 127.65 (1), 127.98 (1), 128.86 (1), 129.53 (1), 129.67 (1), 134.69 (0), 135.95 (0), 138.68 (0), 143.14 (0), 143.65 (0), 145.32 (1) ppm.



E-**18**

and



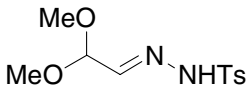
Z-**18**

(*E*)- and (*Z*)-4-Methyl-*N*-[(2*E*)-2-phenylpent-2-enyl)ethyl]-*N*-phenylbenzenesulfonamide (18).

To sulfone **3a** (391 mg, 1.5 mmol, 3.0 equiv), stirred under argon at rt, *iso*-PrMgCl (2M in THF, 0.8 mL, 1.6 mmol) was added. The mixture was stirred for 1.5 h and then tosylhydrazone **17** (229 mg, 0.5 mmol) in THF (1.8 mL) After 2 h, the reaction was quenched with concd. aqueous ammonia (0.2 mL). The product was isolated in the usual way and chromatographed on silica gel (20 g) to afford **18** (107 mg, 55%) as colorless oil. Isomer ratio *Z*:*E* 28:72 by HPLC (hexane-

ethyl acetate 19:1), t_R 12.2 min (*Z*-) and 13.0 min (*E*-isomer). Samples of isomers were prepared by preparative HPLC.

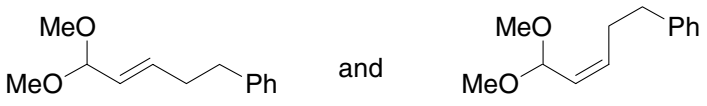
(*Z*)-**18**: ^{1}H NMR ($CDCl_3$) 2.10-2.25 (2H, m), 2.35-2.50 (2H, m), 2.43 (3H, s), 4.08 (2H, d, *J* 6.2 Hz), 5.25-5.55 (2H, m), 6.95-7.10 (4H, m), 7.15-7.35 (8H, m), 7.44-7.52 (2H, m) ppm; on irradiation at δ 2.18 the left part of the multiplet at δ 5.25-5.55 collapsed to a doublet, *J* 11.2 Hz. ^{13}C NMR ($CDCl_3$) 21.59 (3), 29.14 (2), 35.42 (2), 47.46 (2), 124.50 (1), 125.89 (1), 127.70 (1), 128.28 (1), 128.37 (1), 128.82 (1), 128.96 (1), 129.37 (1), 132.94 (1), 135,48 (0), 139.16 (0), 141.36 (0), 143.31 (0) ppm. (*E*)-**18**: mp 67-69 ^{0}C (dichloromethane – hexane). ^{1}H NMR ($CDCl_3$) 2.13-2.27 (2H, m), 2.42 (3H, s), 2.42-2.56 (2H, m), 4.10 (2H, d, *J* 5.1 Hz), 5.28-5.56 (2H, m), 6.95-7.10 (3H), 7.10-7.35 (9H), 7.42-7.52 (2H, m) ppm; on irradiation at δ 2.20 the left part of the multiplet at δ 5.28-5.56 collapsed to a doublet, *J* 15.4 Hz. ^{13}C NMR ($CDCl_3$) 21.54 (3), 33.72 (2), 35.36 (2), 52.90 (2), 124.86 (1), 125.72 (1), 127.64 (1), 128.18 (1), 128.27 (1), 128.72 (1), 128.95 (1), 129.30 (1), 134.61 (1), 135,65 (0), 139.08 (0), 141.35 (0), 143.22 (0) ppm. HRMS (ESI/APCI) calcd. for $C_{24}H_{25}O_2NS$: 391.16060, found 391.16198.



20

***N'*-[(1*E*)-2,2-Dimethoxyethylidene]-4-methylbenzenesulfonohydrazide (20).**

Glyoxal 1,1-dimethyl acetal **19** (45% solution in *tert*-butyl methyl ether) (Fluka) (463 mg, 2.0 mmol) was diluted with *tert*-butyl methyl ether (2 mL) and to this solution tosylhydrazine (377 mg, 2.02 mmol) was added. After 16 h, the solvent was evaporated and the residue was chromatographed on silica gel (20 g) to give **20** (331 mg, 61%) as a viscous oil. ^{1}H NMR (DMSO-d_6) 2.38 (3H, s), 3.16 (6H, s), 4.60 (1H, d, *J* 5.6 Hz), 7.06 (1H, d, *J* 5.6 Hz), 7.43 (2H, d, *J* 8.6 Hz), 7.67 (2H, d, *J* 8.2 Hz), 11.42 (1H, s) ppm. ^{13}C NMR (DMSO-d_6) 20.99 (3), 53.24 (3), 101.43 (1), 127.07 (1), 129.61 (1), 135.77 (0), 143.50 (0), 145.63 (1) ppm.



E-**21** *Z*-**21**

(*E*)- and (*Z*)- 5,5-Dimethoxypent-3-enyl]benzene (21).

To sulfone **3a** (555 mg, 2.13 mmol, 3.12 equiv), stirred under argon at rt, *iso*-PrMgCl (2M in THF, 1.6 mL, 3.2 mmol) was added. The mixture was stirred for 1.5 h and then tosylhydrazone **20** (186 mg, 0.68 mmol) in THF (3 mL) was added. After 2 h, the reaction was quenched with concd. aqueous ammonia (0.2 mL). The product was isolated in the usual way and chromatographed on silica gel (30 g) to afford **21** (92 mg, 65%) as colorless oil. Isomer ratio *Z*:*E* 52:48 by HPLC (hexane-ethyl acetate 19:1) t_R 8.5 min (*Z*-) and 9.6 min (*E*-isomer). Samples of isomers were prepared by preparative HPLC. (*Z*)-**21**: ^{1}H NMR ($CDCl_3$) 2.38-2.55 (2H, m), 2.63-2.78 (2H,m), 3.26 (6H, s), 4.98 (1H, dd, *J* 6.3, 1.1 Hz), 5.44 (1H, ddt, *J* 11.2, 6.4, 1.4 Hz), 5.70 (1H, ddt, J =11.2, 7.5, 1.1 Hz), 7.1-7.4 (5H, m) ppm; on irradiation at δ 2.48 multiplet at 5.70 collapsed to a doublet, *J* 11.3 Hz. ^{13}C NMR ($CDCl_3$) 29.94 (2), 35.57 (2), 52.28 (3), 99.44 (1), 125.90 (1), 127.08 (1), 128.29 (1), 128.42 (1), 134.26 (1), 141.39 (0) ppm. HRMS (EI): calcd. for $C_{17}H_{18}O$, 238.13577; found, 238.13477. (*E*)-**21**: ^{1}H NMR ($CDCl_3$) 2.33-2.48 (2H, m), 2.66-2.79 (2H, m), 3.28 (6H, s), 4.71 (1H, d, *J* 5.4 Hz), 5.48 (1H, ddt, *J* 15.7, 5.3, 1.4 Hz), 5.87 (1H, ddt, *J* 15.7, 6.5, 0.8 Hz), 7.1-7.4 (5H, m) ppm; on irradiation at δ 2.41 multiplet at δ 5.48 collapsed to a doublet of doublets, *J* 15.6, 5.3 Hz, and that at δ 5.60-5.85 to a doublet of doublets, *J* 15.7, 0.8 Hz. ^{13}C NMR ($CDCl_3$) 33.87 (2), 35.27 (2), 52.68 (3), 103.27 (1), 125.86 (1), 127.11 (1), 128.31 (1), 128.36(1), 134.60 (1), 141.50 (0) ppm.

3. NMR spectra of new compounds