A Convenient Synthesis of Symmetric 1,2-Diarylethenes from Arylmethyl Phosphonium Salts

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General Information

All organic solvents were distilled before being used. Commercially available reagents, obtained from Aldrich were used as received. DMF and MeCN were dried over CaH_2 , while DMSO was dried over molecular sieves. Methanol (99.9%) was used as obtained from Fisher Scientific. Reactions were followed with thin-layer chromatography (TLC) and visualized with a UV lamp. Reaction mixtures were purified on prep TLC plates using hexanes as the eluent. GC/MS analysis was done using HP 5890 Series II GC fitted with HP 5971 Series Mass Selective Detector, to confirm the purity of products. ^1H and proton decoupled ^{13}C NMR spectra were recorded on a Bruker AMX 500 MHz spectrometer at ambient temperature. Compounds **7** and **8** were synthesized as per procedures described previously.¹

3-Methyl-2-nitrothiophene.² 3-Methylthiophene (0.49 mL, 0.50 g, 5.1 mmols) was added to 10 mL of acetic anhydride and the solution was stirred at 0°C in an ice-salt bath. A pre-cooled

¹ (a) Lorimer, S. D.; Perry, N. B. *J. Nat. Prod.*, **1993**, *56*, 1444-1450. (b) Dupont, R.; Cotellet, P. *Tetrahedron*, **2001**, *57*, 5585-5589.

² (a) Threadgill, M. D.; Webb, P.; O'Neill, P.; Naylor, M. A.; Stephens, M. A.; Stratford, I. J.; Cole, S.; Adams, G. E.; Fielden, E. M. *J. Med. Chem.*, **1991**, *34*, 2112-2120. (b) Snyder, H. R.; Carpino, L. A.; Zack, J. F.; Mills, J. F. *J. Am. Chem. Soc.*, **1957**, *79*, 2556-2559.

mixture of 320 μL HNO_3 and 320 μL of H_2SO_4 was added to this solution dropwise. The solution turned dark green in the process. The reaction mixture was allowed to warm up to room temperature while stirring for two hours. The solution was cooled again and diluted with 10 mL of water, and neutralized with NaOH powder to a pH of 8. The resulting brown solution precipitated and was filtered. The brown residue was purified on column chromatography using hexane/ ethyl acetate mixtures (4:1) to obtain 0.301 g of the 3-methyl-2-nitrothiophene (43%).

^1H NMR (CDCl_3) δ 7.40 (d, J = 5.4 Hz, 1H), 6.91 (d, J = 5.4 Hz, 1H), 2.64 (s, 3H).

2-Bromomethylthiophene.³ 2-Methylthiophene (0.1 mL, 1 mmol) was added to 5 mL of dry 1,2-dichloroethane and the solution was heated to reflux. Benzoyl peroxide (0.002 g, 0.01 mmol) was added to the refluxing mixture, quickly followed by a mixture of benzoyl peroxide (0.002 g, 0.01 mmol) and *N*-bromosuccinimide (0.178 g, 1 mmol). The solution was refluxed for one hour. After cooling to room temperature, the succinimide was removed by dissolving in hexanes followed by filtration. The solvent was removed *in vacuo* at 40 $^\circ\text{C}$ to obtain 0.134 g of 2-bromomethylthiophene. ^1H NMR (CDCl_3) δ 7.32 (d, J = 5.0 Hz, 1H), 7.12 (d, J = 3.3 Hz, 1H), 6.95 (t, J = 3.6 Hz, 1H), 4.77 (s, 2H).

3-Bromomethylthiophene.⁴ 3-Methylthiophene (0.1 mL, 1 mmol) and benzoyl peroxide (0.002 g, 0.01 mmol) were added to 5 mL of dry benzene. After heating to reflux, a mixture of *N*-bromosuccinimide (0.178 g, 1 mmol) and benzoyl peroxide (0.002 g, 0.01 mmol) were slowly added. After refluxing for 30 min, the solution was cooled and distilled *in vacuo*. The residue was dissolved in hexanes and the byproduct (succinimide) was filtered by gravity. The solution was distilled *in vacuo* to obtain 0.143 g (88%) of 3-bromomethylthiophene. ^1H NMR (CDCl_3) δ 7.31-7.33 (m, 2H), 7.14 (d, J = 5.0 Hz, 1H), 4.54 (s, 2H).

³ Archer, W. J.; Cook, R.; Taylor, R. *J. Chem. Soc. Perkin Trans. 2*, **1983**, 813-819.

⁴ Campaigne, E. E.; Tullar, B. F. *Org. Synth.*, **1953**, 33, 96-98.

2-Bromo-3-bromomethylthiophene.³ Same procedure as for 2-bromomethylthiophene. Yield: 1.02 g from 1.00 g of 2-bromo-3-methylthiophene (71%). ¹H NMR (CDCl₃) δ 7.39 (d, *J* = 5.6 Hz, 1H), 7.14 (d, *J* = 5.7 Hz, 1H), 4.59 (s, 2H).

3-Bromomethylbenzothiophene. Same procedure as with 3-bromomethylthiophene. The crude yield was 80 % (0.121 g from 0.099 g of 3-methylbenzothiophene). The product decomposes on silica gel column during purification. ¹H NMR (CDCl₃) δ 7.93 (d, *J* = 8.0 Hz, 1H), 7.89 (d, *J* = 8.1 Hz, 1H), 7.52 (s, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 1H), 4.78 (s, 2H). ¹³C NMR (CDCl₃) δ 140.7, 137.4, 132.1, 126.6, 125.1, 124.6, 123.2, 122.3, 26.2.

Bromomethyl-2-nitrothiophene.^{2b} 3-Methyl-2-nitrothiophene (0.029 g, 0.203 mmols), *N*-Bromosuccinimide (0.038 g, 0.213 mmols), and Benzoyl peroxide (0.001 g, 4.128 μmol) were added to 5 mL of dried 1,2-dichloroethane. The solution was refluxed gently and monitored by TLC for 21 h. The solution was concentrated at 40 °C in vacuo and then dissolved in hexane to precipitate out the succinimide. Filtration by gravity followed by concentration in vacuo and purification on column chromatography using hexane/ ethyl acetate (9:1) gave 0.009 g of 3-bromomethyl-2-nitrothiophene (20%). ¹H NMR (CDCl₃) δ 7.48 (d, *J* = 5.5 Hz, 1H), 7.19 (d, *J* = 5.5 Hz, 1H), 4.90 (s, 2H).

2-Bromo-3-thienylmethyltriphenylphosphonium bromide 1.³ Triphenylphosphane (3.9 g, 14.9 mmol) was dissolved in 30 mL of dry CCl₄ and refluxed under nitrogen. 2-Bromo-3-bromomethylthiophene (3.8 g, 14.9 mmol) was dissolved in 3 mL of dry CCl₄ and added to the refluxing mixture. The solution was refluxed for 12 h. After cooling to room temperature, the white precipitate was filtered off, washed with CCl₄, and the solvent was removed under reduced pressure. Yield: 5.9 g from 3.8 g of 2-bromo-3-bromomethylthiophene (77%). ¹H NMR

(CDCl₃) δ 7.60-7.79 (m, 15H), 7.17 (d, $J = 5.7$, 1H), 6.86 (dd, $J_1 = 5.7$ Hz, $J_2 = 1.2$ Hz, 1H), 5.39 (d, $J = 13.7$ Hz, 2H).

3-Thienylmethyltriphenylphosphonium bromide 2. Same procedure as **1**, but with dry benzene as solvent. Yield: 0.279 g from 0.163 g of 3-bromomethylthiophene (69%). ¹H NMR (CDCl₃) δ 7.78-7.74 (m, 9H), 7.66-7.63 (m, 6H), 7.37 (s, 1H), 7.13 (d, $J = 4.9$ Hz, 1H), 6.71 (d, $J = 5.0$ Hz, 1H), 5.55 (d, $J = 22.0$ Hz, 2H).

3-Benzothienylmethyltriphenylphosphonium bromide 3. Same procedure as **1**. 55 % yield (0.052 g from 0.044 g of 3-bromomethylbenzothiophene. ¹H NMR (CDCl₃) δ 7.83-7.78 (m, 6H), 7.75-7.70 (m, 4H), 7.59-7.55 (m, 7H), 7.22-7.15 (m, 2H), 6.98 (t, $J = 7.5$ Hz, 1H), 5.76 (d, $J = 13.6$ Hz, 2H). ¹³C NMR (CDCl₃) δ 139.4, 138.4 (d, $J = 12.0$ Hz), 135.1 (d, $J = 11.5$ Hz), 134.5 (d, $J = 39$ Hz), 130.3 (d, $J = 49.5$ Hz), 129.7 (d, $J = 33.5$ Hz), 124.4 (d, $J = 88.5$ Hz), 122.6, 121.8, 121.0 (d, $J = 37.5$ Hz), 118.4, 117.8, 24.8 (d, $J = 194.5$ Hz).

2-Nitro-3-thienylmethyltriphenylphosphonium bromide 4. Same procedure as **1**. 55 % yield (0.045 g from 0.034 g of 3-Bromomethyl-2-nitrothiophene. ¹H NMR (CDCl₃) δ 7.80-7.76 (m, 9H), 7.68-7.66 (m, 7H), 7.27 (d, $J = 5.5$ Hz), 1H, 6.18 (d, $J = 15.3$ Hz, 2H). ¹³C NMR (CDCl₃) δ 135.5 (d, $J = 11.5$ Hz), 134.2, (d, $J = 39.5$ Hz), 132.5 (d, $J = 14.5$ Hz), 131.8 (d, $J = 11.5$ Hz), 130.7 (d, $J = 37.5$ Hz), 130.5 (d, $J = 50.5$ Hz), 117.1 (d, $J = 344$ Hz), 25.5 (d, $J = 196$ Hz).

2-Thienylmethyltriphenylphosphonium bromide 5.³ Same procedure as **1**, but with dry benzene as solvent. Yield: 0.176 g (50%) from 0.142 g 2-bromomethylthiophene. ¹H NMR (DMSO) δ 7.92 (d, $J = 5.7$ Hz, 3H), 7.78-7.74 (m, 7H), 7.70-7.68 (m, 5H), 7.39-7.36 (m, 2H), 7.25-7.23 (m, 1H), 5.55 (d, $J = 14.6$ Hz, 2H).

Synthesis of Homocoupling Products.

General Procedure: The corresponding phosphonium salt was dissolved in 10 mL dry MeCN (or other solvents for Table 2), and cooled in an ice-water bath while stirring. In case of **7**, 200 mL acetonitrile was used in order to dissolve the phosphonium salt. One equivalent of base (NaH or *t*-BuOK) was gradually added. Upon completion, the solution was stirred at room temperature for 1 h. The solvent was evaporated in vacuo. The residue was suspended in ethyl acetate, and the product was isolated by preparative TLC with hexanes as the eluent. When DMSO or DMF were used as solvents, about 10 mL water was added to the reaction mixture and the products were extracted with ethyl acetate. The organic layer was washed a few times with water, dried over anhydrous Na₂SO₄ and the solvent was removed under reduced pressure. The product mixture was then subjected to a silica gel column using hexanes as the eluent.

1,2-Di(2-bromo-3-thienyl)ethene (*E* and *Z* isomers). Yield: 0.014 g from 0.066 g of **1** (64%) with NaH as the base in MeCN; 0.014 g from 0.070 g of **1** (61%) with *t*-BuOK as the base in MeCN; 0.008 g from 0.071 g of **1** (34%) with *t*-BuOK as the base in THF; 0.007 g from 0.070 g of **1** (29%) with *t*-BuOK as the base in benzene; 0.017 g from 0.070 g of **1** (71%) with *t*-BuOK as the base in DMSO; 0.008 g from 0.070 g of **1** (34%) with *t*-BuOK as the base in DMF. ¹H NMR (CDCl₃) δ 7.28 (s, 2H), 7.26 (s, 2H), 7.13 (d, *J* = 5.7 Hz, 2H), 6.72 (s, 2H), 6.72 (d, *J* = 5.7 Hz, 2H), 6.51 (s, 2H).

1,2-Di(3-thienyl)ethene (*E* isomer). Yield: 0.008 g from 0.050 g of **2** (68%) with *t*-BuOK as the base; 0.010 g from 0.050 g of **2** (91%) with NaH as the base. ¹H NMR (CD₃CN) δ 7.41 (dd, *J*₁ = 2.9 Hz, *J*₂ = 5.1 Hz, 2H), 7.37 (dd, *J*₁ = 1.2 Hz, *J*₂ = 5.1 Hz, 2H), 7.34 (dd, *J*₁ = 1.3 Hz, *J*₂ = 2.9 Hz, 2H), 7.08 (s, 2H). ¹³C NMR (CD₃CN) δ 141.4, 127.6, 125.9, 123.9, 123.3.

1,2-Bis(3,3'-benzo[b]thienyl)ethene (*E* and *Z* isomers). Yield: 0.013 g from 0.055 g of **3** (78%: 75% *E* & 3% *Z*) with *t*-BuOK as the base; 0.014 g from 0.104 g of **3** (47%: 23% *E* & 24% *Z*) using NaH as the base. ¹H NMR (CDCl₃) δ 8.05 (d, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.87-7.85 (m, 2H), 7.78-7.76 (m, 2H), 7.63 (s, 2H), 7.50-7.46 (m, 4H), 7.42 (t, *J* = 7.3 Hz, 2H), 7.37-7.35 (m, 4H), 7.20 (s, 2H), 6.96 (s, 2H). ¹³C NMR (CDCl₃) δ 140.8, 140.0, 138.3, 138.0, 134.5, 132.4, 124.9, 124.7, 124.6, 124.5, 124.4, 124.1, 123.2, 123.0, 122.6, 122.4, 122.2.

1,2-Di(2-thienyl)ethene (*E* isomer). Yield: 0.002 g from 0.050 g of **5** (21%). ¹H NMR (CDCl₃) δ 7.19 (d, *J* = 4.8 Hz, 2H), 7.06 (s, 2H), 7.05 (dd, *J*₁ = 1.1 Hz, *J*₂ = 3.5 Hz, 2H), 7.00 (dd, *J*₁ = 3.6 Hz, *J*₂ = 5.0 Hz, 2H). ¹³C NMR (CDCl₃) δ 142.4, 127.6, 126.0, 124.3, 121.5.

Stilbene (*E* isomer). Yield: 0.006 g from 0.100 g of **6** (29%); Yield: 0.020 g from 0.152 g of **6** with 200 mL CH₃CN and 0.076 g *t*-BuOK (64%, *E/Z* ratio, 1:1.3). ¹H NMR (CD₃CN) δ 7.58 (dd, *J*₁ = 1.4 Hz, *J*₂ = 7.5 Hz, 4H), 7.38 (t, *J* = 6.9 Hz, 4H), 7.28 (tt, *J*₁ = 1.2 Hz, *J*₂ = 7.4 Hz, 2H), 7.22 (s, 2H). EI-MS, *m/z* (rel. intensity) 181 (*M*+1, 11.3), 180 (*M*+, 97.2), 179 (100), 178 (58.9), 165 (54.8), 152 (18.1), 115 (5.6), 102 (28.9), 90 (19), 89 (69.3), 77 (31.1), 76 (43.6), 63 (22.7), 51 (31.7).

(*E/Z*)-3,3'-Dimethoxystilbene.⁵ Yield: 0.023 g from 0.151 g of **7** (59 %, *E/Z* ratio, 1:1) with 0.036 g *t*-BuOK as base in 200 mL CH₃CN. Yield: 0.013 g from 0.151 g of **7** (33 %, *E/Z* ratio, 1:1.2) with 0.009 g NaH as base in 200 mL CH₃CN. Yield: 0.040 g from 0.153 g of **7** (100 %, *E/Z* ratio, 1:1.1) with 0.017 g NaH (1 equiv.) as base in 200 mL CH₃CN. ¹H NMR (CDCl₃) δ 7.30 (d, *J* = 7.9 Hz, 1H), 7.16 (t, *J* = 7.9 Hz, 2H), 7.13 (bd, *J* = 7.7 Hz, 2H), 7.10 (s, 2H), 7.06 (bt, *J* = 2.3 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 2H), 6.83 (dd, *J*₁ = 2.5 Hz, *J*₂ = 8.2 Hz, 2H), 6.81 (bt, *J*

⁵ Wyatt, P.; Warren, S.; McPartlin, M.; Woodroffe, T. *J. Chem. Soc. Perkin Trans. I*, **2001**, 279-297.

= 2.4 Hz, 2H), 6.76 (ddd, $J_1 = 0.7$ Hz, $J_2 = 5.1$ Hz, $J_3 = 10.5$ Hz, 3H), 6.59 (s, 2H), 3.82 (2, 3H), 3.68 (s, 3H).

(*E/Z*)-2,2'-Dimethoxystilbene.⁶ Yield: 0.015 g from 0.150 g of **8** (39 %, *E/Z* ratio, 1:3.4) with *t*-BuOK as base in 200 mL CH₃CN. Yield: 0.013 g from 0.151 g of **8** (33 %, *E/Z* ratio, 1:3.4) with NaH as base in 200 mL CH₃CN. ¹H NMR (CDCl₃) δ 7.67 (dd, $J_1 = 1.5$ Hz, $J_2 = 7.6$ Hz, 2H), 7.49 (s, 2H), 7.25 (dt, $J_1 = 1.6$ Hz, $J_2 = 8.0$ Hz, 2H), 7.18 (dt, $J_1 = 1.6$ Hz, $J_2 = 8.1$ Hz, 2H), 7.14 (dd, $J_1 = 1.6$ Hz, $J_2 = 7.6$ Hz, 2H), 7.98 (t, $J = 7.4$ Hz, 2H), 6.91 (d, $J = 8.5$ Hz, 2H), 6.89 (d, $J = 8.2$ Hz, 2H), 6.79 (s, 2H), 6.72 (dt, $J_1 = 0.6$ Hz, $J_2 = 7.8$ Hz, 2H), 3.89 (s, 3H), 3.85 (s, 3H).

Wittig Reactions

Reaction of 2-bromo-3-thienylmethyltriphenylphosphonium bromide and benzaldehyde.

0.532 g (1.03 mmol) of compound **1** was placed in a round bottom flask and to it was added 6 mL of acetonitrile. The solution was stirred magnetically until all solid dissolved. The reaction flask was placed in an ice bath and 0.1 mL (0.109 g, 1.03 mmol) of benzaldehyde was introduced into it while stirring. 0.116 g (1.03 mmol) of potassium *tert*-butoxide was added to the reaction mixture in small aliquots over 1 min. The mixture was allowed to warm up to room temperature while stirring continued for 1 h. The solvent was removed under reduced pressure. The crude product containing a mixture of the *E* and *Z* isomers was purified and the isomers were separated by column chromatography over neutral alumina (150 mesh, 58 Å, 155 m²/g) using petroleum ether (from bulk solution) as eluent. Total yield was 0.166 g (61 %).

⁶ (a) Ali, M. A.; Kondo, K.; Tsuda, Y. *Chem. Pharm. Bull.*, **1992**, *40*, 1130-1136. (b) Wallace, T. W.; Wardell, I.; Li, K.-D.; Leeming, P.; Redhouse, A. D.; Challand, S. R. *J. Chem. Soc. Perkin Trans. 1*, **1995**, 2293-2308.

2-bromo-3-[(E)-2-phenylvinyl]thiophene.⁷ Isolated yield 0.049 g (35 % of mixture), white solid; ¹H NMR (CD₃COCD₃) δ 7.16 (d, *J* = 16.4 Hz, 1H), 7.24 (d, *J* = 16.4 Hz, 1H), 7.30 (t, *J* = 6.0 Hz, 1H), 7.39 (t, *J* = 7.7 Hz, 2H) 7.46 (d, *J* = 5.8 Hz, 1H), 7.57 (d, *J* = 5.9 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 2H); ¹³C NMR (CD₃COCD₃) δ 111.7, 121.7 126.3, 127.8, 128.2, 129.3, 130.0, 132.4, 138.4, 139.8.

2-bromo-3-[(Z)-2-phenylvinyl]thiophene. Isolated yield 0.089 g (65 % of mixture), almost colorless liquid; ¹H NMR (CD₃COCD₃) δ 6.43 (d, *J* = 12.1 Hz, 1H), 6.64 (d, *J* = 5.7 Hz, 1H), 6.77 (d, *J* = 12.1 Hz, 1H), 7.25–7.31 (m, 5H), 7.35 (d, *J* = 5.7 Hz, 1H); ¹³C NMR (CD₃COCD₃) δ 112.7, 123.2 127.0, 128.5, 128.6, 129.3, 129.6, 132.7, 137.9, 138.6.

2-bromo-3-[(1E/Z)-2-(3-nitrophenyl)prop-1-en-1-yl]thiophene. The compound **1** (0.155 g, 0.3 mmol) was placed in a dry round bottom flask and 4 mL of *t*-BuOH added to it. The mixture was stirred at room temperature until all solid dissolved. 0.049 g (0.3 mmol) of *m*-nitroacetophenone dissolved in 2 mL of *t*-BuOH were introduced into the reaction flask and stirred at room temperature for 1 h. Purification by column chromatography gave a mixture of *E/Z* isomers gave an yield of 0.037 g (38 %). ¹H NMR (CDCl₃) δ 8.37 (t, *J* = 3.0 Hz, 1H), 8.12 (s, 1H), 8.14 (d, *J* = 5.1 Hz, 1H), 8.10 (t, *J* = 1.9 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.49-7.46 (m, 2H), 7.33 (d, *J* = 5.7 Hz, 1H), 7.13 (d, *J* = 5.7 Hz, 1H), 6.94 (d, *J* = 5.7 Hz, 1H), 6.73 (s, 1H), 6.49 (s, 1H), 6.05 (d, *J* = 5.8 Hz, 1H), 2.31 (s, 3H), 2.27 (s, 3H).

GC-MS of some of the Isolated Homocoupling Products(base: *t*-BuOK; solvent: MeCN):

1,2-Di(2-bromo-3-thienyl)ethene From **1:**
GC

⁷ Munro, D. P.; Sharp, J. T. *J. Chem. Soc. Perkin Trans. I*, **1980**, 1718-1723.

MS

1,2-Di(3-thienyl)ethene From 2:

GC

MS

1,2-Di(2-thienyl)ethene From 5: GC

Abundance

MS

Abundance

Stilbene From 6:

GC

Abundance

MS

Abundance

Rf = 16.1 min

Abundance

Rf = 18.4 min

SpinWorks 2.5: Wittig Reaction - Step 2 (solid part)

1 + PhCHO + t-BuOK in CH3CN

Solvent: Acetone-d6

Product: 2-bromo-3-[(E)-2-phenylvinyl]thiophene

PPM 200 180 160 140 120 100 80 60 40 20 0

file: F:\New Folder\WALLY027A\31\fid expt: <zpgg30>

transmitter freq.: 125.771572 MHz

time domain size: 65536 points

width: 31446.54 Hz = 250.029004 ppm = 0.479836 Hz/pt

number of scans: 1024

freq. of 0 ppm: 125.757626 MHz

processed size: 32768 complex points

LB: 1.000 GB: 0.0000

Hz/cm: 1179.115 ppm/cm: 9.37505

SpinWorks 2.5: Wittig Reaction - Step 2 (solid part)

7.6145
7.6119
7.6086
7.5973
7.5963
7.5676
7.5665
7.5561
7.5551
7.4539
7.4423
7.4047
7.3742
7.3027
7.2991
7.2954
7.2868
7.2845
7.2821
7.2514
7.2187
7.1744
7.1417

1 + PhCHO + t-BuOK in CH₃CN
Solvent: Acetone-d₆
Product: 2-bromo-3-[(E)-2-phenylvinyl]thiophene

2.8000
2.7678
2.7658
2.7638
2.0595
2.0551
2.0507
2.0463
2.0419

PPM 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

file: F:\New Folder\WALLY027A\30\fid exp: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
freq. of 0 ppm: 500.130010 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 200.052 ppm/cm: 0.40000

SpinWorks 2.5: Wittig step 2.

file: F:\New Folder\WALLY027A\71\fid expt: <zpgg30>
transmitter freq.: 125.771572 MHz
time domain size: 65536 points
width: 31446.54 Hz = 250.029004 ppm = 0.479836 Hz/pt
number of scans: 1024

freq. of 0 ppm: 125.757671 MHz
processed size: 32768 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 1131.819 ppm/cm: 8.99901

SpinWorks 2.5: Wittig step 2.

7.3563
7.3554
7.3448
7.3441
7.3225
7.3186
7.3099
7.3059
7.3021
7.2977
7.2912
7.2809
7.2777
7.2676
7.2645
7.2608
7.2560
7.2523
7.2485
6.7844
6.7602
6.6408
6.6293
6.4467
6.4225

2.8574
2.0547
2.0503
2.0460
1.2847

1 + PhCHO + t-BuOK in CH₃CN
Solvent: Acetone-d₆
Product: 2-bromo-3-[(Z)-2-phenylvinyl]thiophene

PPM 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 0.0 -0.4

file: F:\New Folder\WALLY027A\70\fid exp: <zg30>
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16

freq. of 0 ppm: 500.130010 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 200.052 ppm/cm: 0.40000

SpinWorks 2.5: JWB-Judy-1: Wittig product from 1 and m-Nitroacetophenone using t-BuOK in BuOH.

1 + PhCHO + t-BuOK in t-BuOH

Solvent: Chloroform-d

Product: 2-bromo-3-[-(-2-(3-nitrophenyl)prop-1-en-1-yl)thiophene
E + Z isomer

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JWB-Judy-1\11\fid expfreq. of 0 ppm: 125.757763 MHz
transmitter freq.: 125.771572 MHz
time domain size: 65536 points
width: 31446.54 Hz = 250.029004 ppm = 0.479836 Hz/pt
processed size: 32768 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 1131.820 ppm/cm: 8.99901
number of scans: 1024

SpinWorks 2.5: JWB-Judy-1: Wittig product from 1 and m-Nitroacetophenone using t-BuOK in BuOH.

1 + PhCHO + t-BuOK in t-BuOH

Solvent: Chloroform-d

Product: 2-bromo-3-[-(2-(3-nitrophenyl)prop-1-en-1-yl)]thiophene
E + Z isomer

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JWB-Judy-1\10\fid expfreq. of 0 ppm: 500.130008 MHz
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 200.052 ppm/cm: 0.40000

SpinWorks 2.5: Wittig reaction with m-nitroacetophenone

7.2927
7.2810
7.2735
7.2703
7.2619
7.1398
7.1283
6.9810
6.7227
6.7112
6.5087

1 + PhCHO + t-BuOK in CH₃CN

Solvent: Chloroform-d

Product: 1,2-Di(2-bromo-3-thienyl)ethene

E + Z isomer

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\WALL Y028B\50\fid expfreq. of 0 ppm: 500.130008 MHz
transmitter freq.: 500.133089 MHz processed size: 32768 complex points
time domain size: 65536 points LB: 0.300 GB: 0.0000
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
Hz/cm: 200.052 ppm/cm: 0.40000

SpinWorks 2.5: JWB1-7. Coupling product from 2-bromo3-thienylmethylphosphonium bromide.

Homocoupling of 1
Product: 1,2-Di(2-bromo-3-thienyl)ethene
Solvent: Chloroform-d
E + Z isomer

PPM 200 180 160 140 120 100 80 60 40 20 0

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JWB1-7\1\fid expt <zfreq. of 0 ppm: 125.757761 MHz
transmitter freq.: 125.771572 MHz processed size: 32768 complex points
time domain size: 65536 points LB: 1.000 GB: 0.0000
width: 31446.54 Hz = 250.029004 ppm = 0.479836 Hz/pt Hz/cm: 1131.820 ppm/cm: 8.99901
number of scans: 1024

SpinWorks 2.5: JWB-7. Coupling product from 2-bromo-3-thienylmethyltriphenylphosphonium bromni

7.2699
7.2624
7.2581
7.1280
7.1165
6.9686
6.7104
6.6990
6.4960

Homocoupling of 1
Product: 1,2-Di(2-bromo-3-thienyl)ethene
Solvent: Chloroform-d
E + Z isomer

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JWB-7-DMF10\fid expfreq. of 0 ppm: 500.130014 MHz
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 200.052 ppm/cm: 0.40000

SpinWorks 2.5: JWB-6D. Rex with NaH.

Homocoupling of 2
Product: 1,2-Di(3-thienyl)ethene
Solvent: Acetonitrile-d₃
E isomer

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JWB-6D\11fid exp: <zfreq. of 0 ppm: 125.757653 MHz
transmitter freq.: 125.771572 MHz processed size: 32768 complex points
time domain size: 65536 points LB: 1.000 GB: 0.0000
width: 31446.54 Hz = 250.029004 ppm = 0.479836 Hz/pt
number of scans: 530
Hz/cm: 1131.819 ppm/cm: 8.99900

7.4187
7.4129
7.4085
7.4028
7.3769
7.3744
7.3667
7.3642
7.3458
7.3431
7.3400
7.3374
7.0824

file: C:\Documents and Settings\Owner\ANAMITRO-939D\A9\Desktop\AB4 NMR\JWB-6D\10fid
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.656569 ppm = 0.157632 Hz/pt
number of scans: 16
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 160.042 ppm/cm: 0.32000
expt: <freq. of 0 ppm: 500.130015 MHz

SpinWorks 2.5: JWB-6D. Reaction with NaH.

7.4187
7.4129
7.4085
7.4028
7.3769
7.3744
7.3667
7.3642
7.3458
7.3431
7.3400
7.3374

7.0824

Homocoupling of 2 (aromatic region expanded)
Product: 1,2-Di(3-thienyl)ethene
Solvent: Acetonitrile-d3
E isomer

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JWB-6D\10\fid exp: <zfreq. of 0 ppm: 500.130015 MHz
transmitter freq.: 500.133089 MHz processed size: 32768 complex points
time domain size: 65536 points LB: 0.300 GB: 0.0000
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
Hz/cm: 41.725 ppm/cm: 0.08343

SpinWorks 2.5: JWB-23. Spots 2-3.

Homocoupling of 3
Product: 1,2-Bis(3,3'-benzo[b]thienyl)ethene
Solvent: Chloroform-d
E + Z isomer

0.2306

77.4982
77.4530
77.3402
77.3263
77.2442
77.1526
77.0687
76.9908

140.7941
140.0236
138.3457
137.9828
134.5150
132.7521
128.6866
124.8780
124.6789
124.6481
124.6099
124.4261
124.1429
123.2488
122.9256
122.6285
122.4127
122.1893

PPM 200 180 160 140 120 100 80 60 40 20 0

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JWB-23sps2-3\13fid efreq. of 0 ppm: 125.757762 MHz
transmitter freq.: 125.771572 MHz processed size: 32768 complex points
time domain size: 65536 points LB: 1.000 GB: 0.0000
width: 31446.54 Hz = 250.029004 ppm = 0.479836 Hz/pt Hz/cm: 1131.820 ppm/cm: 8.99901
number of scans: 1024

SpinWorks 2.5: JWB-23. Spots 2-3. Homocoupling of benzothiophene using NaH.

Homocoupling of 3
Product: 1,2-Bis(3,3'-benzo[b]thienyl)ethene
Solvent: Chloroform-d
E + Z isomer

```

file: C:\Documents and Settings\Owner\ANAMITRO-939D\A9\Desktop\AB4 NMR\JWB-23\sp2-3\10\fid
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
efreq. of 0 ppm: 500.130008 MHz
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 200.052 ppm/cm: 0.40000

```

SpinWorks 2.5: JWB-23. Spots 2-3. Homocoupling of benzothiophene using NaH.

Homocoupling of 3 (aromatic region expanded)
Product: 1,2-Bis(3,3'-benzo[b]thienyl)ethene
Solvent: Chloroform-d
E + Z isomer

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JWB-23sps2-3\10fid
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 63.298 ppm/cm: 0.12656

SpinWorks 2.5: JWB-03 Spot 1. After 24 h in CDCl3 then Prep. TLC.

Homocoupling of 5
Product: 1,2-Di(2-thienyl)ethene
Solvent: Chloroform-d
E isomer

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JWB-03-spt1\1fid expfreq. of 0 ppm: 125.757759 MHz
transmitter freq.: 125.771572 MHz processed size: 32768 complex points
time domain size: 65536 points LB: 1.000 GB: 0.0000
width: 31446.54 Hz = 250.029004 ppm = 0.479836 Hz/pt
number of scans: 1024
Hz/cm: 1131.820 ppm/cm: 8.99901

SpinWorks 2.5: Homocoupling product from 2-ThienylMethylphosphonium bromide.

7.2699
7.1942
7.1845
7.0616
7.0529
7.0507
7.0457
7.0437
7.0092
7.0021
6.9991
6.9920

Homocoupling of 5
Product: 1,2-Di(2-thienyl)ethene
Solvent: Chloroform-d
E isomer

0.999
1.2085
1.2085

PPM 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JWB-03-spt1\10fid expfreq. of 0 ppm: 500.130008 MHz
transmitter freq.: 500.133089 MHz processed size: 32768 complex points
time domain size: 65536 points LB: 0.300 GB: 0.0000
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
Hz/cm: 200.052 ppm/cm: 0.40000

SpinWorks 2.5: JWB-03. Homocoupling product from 2-ThienylMethylphosphonium bromide.

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JWB-03-spt1\10fid expfreq. of 0 ppm: 500.130008 MHz
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 15.021 ppm/cm: 0.030003

SpinWorks 2.5: JWB-8. Coupling of Benzyltriphenylphosphonium bromide. Spot 1.

7.5704
7.4000
7.3965
7.3850
7.3725
7.3693
7.3012
7.2988
7.2964
7.2875
7.2842
7.2806
7.2717
7.2694
7.2672
7.2193

Homocoupling of 6
Product: Stilbene
Solvent: Chloroform-d
E isomer

[illegible]

file:	F:\AB4 NMR\JWB-8-Spot1\10\fid	expt: <zg30>

transmitter freq.: 500.133089 MHz

time domain size: 65536 points

width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt

number of scans: 16

freq. of 0 ppm: 500.130015 MHz

processed size: 32768 complex points

LB: 0.300 GB: 0.0000

Hz/cm: 150.039 ppm/cm: 0.30000

SpinWorks 2.5: JCB-39. Coupling product from benzylphosphonium bromide.

Homocoupling of 6 (optimized w/2 equiv. base)

Product: Stilbene

Solvent: Chloroform-d

E + Z isomer

0.2284

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JCB-38\1\fid exp: <zfreq. of 0 ppm: 125.757765 MHz
transmitter freq.: 125.771572 MHz processed size: 32768 complex points
time domain size: 65536 points LB: 1.000 GB: 0.0000
width: 31446.54 Hz = 250.029004 ppm = 0.479836 Hz/pt
number of scans: 1024
Hz/cm: 1131.820 ppm/cm: 8.99901

SpinWorks 2.5: JCB-38. Coupling product from benzylphosphonium bromide using 3 equiv. of tBuOK

7.5240
7.5093
7.3734
7.3583
7.3427
7.2577
7.2540
7.2401
7.2342
7.2188
7.2035
7.1978
7.1941
7.1809
7.1123
6.5963

Homocoupling of 6 (optimized w/2 equiv. base)

Product: Stilbene

Solvent: Chloroform-d

E + Z isomer

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JCB-38\10fid exp: <zfreq. of 0 ppm: 500.130023 MHz
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 200.052 ppm/cm: 0.40000

SpinWorks 2.5: JCB-18. Coupling from 3-Methylanisolephosphonium bromide using t-BuOK.

Homocoupling of 7
Product: 3,3'-Dimethoxystilbene
Solvent: Chloroform-d
E + Z isomer

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JCB-18\13fid exp: <zfreq. of 0 ppm: 125.757765 MHz
transmitter freq.: 125.771572 MHz processed size: 32768 complex points
time domain size: 65536 points LB: 1.000 GB: 0.0000
width: 31446.54 Hz = 250.029004 ppm = 0.479836 Hz/pt
number of scans: 1024
Hz/cm: 1131.820 ppm/cm: 8.99901

SpinWorks 2.5: JCB-18. Coupling product from 3-Methylanisolephosphonium bromide, using NaH.

Homocoupling of 7
Product: 3,3'-Dimethoxystilbene
Solvent: Chloroform-d
E + Z isomer

7.3308
7.3262
7.2858
7.2700
7.2542
7.2462
7.1589
7.1431
7.1273
7.1144
7.0992
7.0677
7.0409
6.8392
6.8294
6.8244
6.8131
6.8079
6.8028
6.7986
6.7495
6.7443
6.7329
6.7279
6.5718

3.8438
3.6567
3.6160

0.500
0.500
0.833
0.833
1.204
0.999

2.600
2.966

PPM 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JCB-18\10fid expt: <zfreq. of 0 ppm: 500.130020 MHz
transmitter freq.: 500.133089 MHz processed size: 32768 complex points
time domain size: 65536 points LB: 0.300 GB: 0.0000
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
Hz/cm: 200.052 ppm/cm: 0.40000

SpinWorks 2.5: JCB-23. Coupled product from 2-Methylanisolephosphonium bromide.

Homocoupling of 8
Product: 2,2'-Dimethoxystilbene
Solvent: Chloroform-d
E + Z isomer

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JCB-23\12fid exp: <zfreq. of 0 ppm: 125.757790 MHz
transmitter freq.: 125.771572 MHz
time domain size: 65536 points
width: 31446.54 Hz = 250.029004 ppm = 0.479836 Hz/pt
number of scans: 1024
processed size: 32768 complex points
LB: 1.000 GB: 0.0000
Hz/cm: 1131.820 ppm/cm: 8.99901

SpinWorks 2.5: JCB-23. Coupling product from 2-methylanisolephosphonium bromide using 1 equiv

6.7011
6.7025
6.7161
6.7311
6.7322
6.7449
6.7852
6.8764
6.8928
6.8992
6.9163
6.9670
7.1290
7.1333
7.2001
7.2290
7.2321
7.2456
7.2601
7.2633
7.2703
7.4946
7.6614
7.6645
7.6767
7.6797

3.8958
3.8849
3.8553
3.8453
3.8051

Homocoupling of 8
Product: 2,2'-Dimethoxystilbene
Solvent: Chloroform-d
E + Z isomer

0.913
0.999
1.374
6.227
0.824
3.886
3.947
3.009

2.793
2.793

PPM 8.8 8.4 8.0 7.6 7.2 6.8 6.4 6.0 5.6 5.2 4.8 4.4 4.0 3.6 3.2 2.8 2.4 2.0 1.6 1.2 0.8 0.4 0.0 -0.4

file: C:\Documents and Settings\Owner\ANAMITRO-939DA9\Desktop\AB4 NMR\JCB-23\10fid exp: <zfreq. of 0 ppm: 500.130008 MHz
transmitter freq.: 500.133089 MHz
time domain size: 65536 points
width: 10330.58 Hz = 20.655659 ppm = 0.157632 Hz/pt
number of scans: 16
processed size: 32768 complex points
LB: 0.300 GB: 0.0000
Hz/cm: 200.052 ppm/cm: 0.40000