Electronic Supporting Information

Palladium(II)-catalyzed coupling reactions with a chelating vinyl ether and arylboronic acids: A new Heck/Suzuki domino diarylation reaction

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Experimental

General comments

NMR spectra were recorded on a Varian Mercury plus spectrometer (CDCl₃ solution, 1H at 399.8 MHz and ¹³C at 100.5 MHz). Chemical shifts for ¹H and ¹³C are referenced to TMS via the solvent signals (¹H, CHCl₃ at 7.26 ppm; ¹³C, CDCl₃ at 77.0 ppm). ¹³C NMR signals are presented in 0.1 ppm accuracy except when the shifts are too close to avoid ambiguous interpretation; in such cases the ¹³C NMR signals will be presented in 0.01 ppm accuracy. Low resolution EI mass spectra were recorded on a GC-MS instrument equipped with a Varian Chrompack Capillary column CP-SIL 8 CB Low Bleed/MS (30 m x 0.22 mm, 0.25 µm) and utilizing an ion generation potential of 70 eV. The oven temperature was 40-300 °C (gradient 30 °C/min), unless stated otherwise. Analytical LC-MS (ESI+) was performed on a Gilson HPLC system with Finnigan AQA quadrupole mass spectrometer using a Chromolith SpeedROOD RP-18e 50 x 4.6 mm column, with gradient of MeOH/H₂O in 0.05% aqueous HCOOH as mobile phase at a flow rate of 4 mL/min. Analytical thin layer chromatography was performed using aluminium sheets precoated with silica 0.2 mm silica gel 60 F254. Visualization was performed by ultraviolet light and/or by staining with an ethanolic solution of phosphomolybdic acid (12 g
phosphomolybdic acid in 250 mL ethanol). Column chromatography was performed using commercially available silica (Merck grade 9385, 230-400 mesh, 60 Å) or aluminum oxide (Aldrich, activated, neutral, STD grade, 150 mesh, 58 Å). Heated reactions were performed in SUN-SRi vials (17 x 60 CLR S/N, 8 mL) or Microwave/safe vials (2-5 mL). The vials were heated in preheated metal blocks and magnetically stirred with Teflon-coated magnetic stirring bars. Balloons filled with molecular oxygen were mounted onto a syringe attached to a needle, providing oxygen to the reaction via penetration of the needle through a septum.

**Materials**

Palladium(II)acetate, palladium(II)trifluoroacetate, Pd$_2$(dba)$_3$, Pd(acac)$_2$ and dppp were obtained from Strem Chemicals. All boronic acids and $p$-benzoquinone were purchased from Sigma-Aldrich and used as received. All other reagents and solvents obtained from commercial sources were used as received.

**Method A: Procedure for oxidative Heck $\alpha$-arylation of $N,N$-dimethyl-2-(vinlyoxy)ethanamine (1) with $p$-tolylboronic acid yielding $N,N$-dimethyl-2-(1-$p$-tolylvinlyoxy)ethanamine (3a), Table 1**

To a thick wall glass vial equipped with a teflon-coated stirring bar, $p$-tolylboronic acid (118 mg, 0.87 mmol), 1 (49.5 mg, 0.43 mmol, 1 equiv) and 1,4-dioxane (3 mL) were added. The mixture was stirred until all material had dissolved whereafter Pd(O$_2$CCF$_3$)$_2$ (5 mol%) and dppp (18 mol%) were added. The vial was sealed with a septum, flushed with nitrogen followed by connection of oxygen balloon and stirred at room temperature for 6 hours. The reaction was stopped when GC-MS showed full consumption of the starting olefin (1). The mixture was diluted with EtOAc (20 mL) and washed three times with NaOH (20 mL, aq, 0.1M). The organic phase was dried with K$_2$CO$_3$ (s), concentrated under reduced pressure and purified by column chromatography (aluminium oxide, iso-hexane:EtOAc:Et$_3$N, 90:6:4) affording 3a (66.4 mg, 75%) as a colorless oil; The acquired spectroscopic data were in accordance with previous published results.$^1$ $^1$H NMR $\delta$ 7.51 (d, $J = 8.3$ Hz, 2H), 7.13 (d, $J = 8.3$ Hz, 2H), 4.62 (d, $J = 2.7$ Hz, 1H), 4.17 (d, $J = 2.7$ Hz, 1H), 3.98 (dd, $J = 5.8$, 11.5 Hz, 2H), 2.76 (dd, $J = 5.8$, 11.5 Hz, 2H), 2.36 (s, 6H), 2.34 (s, 3H); $^{13}$C NMR $\delta$ 160.0, 138.4, 133.8, 128.9, 125.4, 81.9, 66.3, 58.2, 46.1, 21.3; MS (70 eV) m/z (relative intensity) 205 (M$^+$, 1), 115 (11), 91 (10), 72 (12), 71 (40), 58 (100).

**Method B: Procedure for oxidative Heck $\beta$-arylation of $N,N$-dimethyl-2-(vinlyoxy)ethanamine (1), Table 1**

To a thick wall glass vial equipped with a teflon-coated stirring bar, the proper arylboronic acid (0.33 mmol), 1 (20 mg, 0.17 mmol, 1 equiv) and $N,N$-dimethylformamide (1.0 mL) were added. The mixture was stirred until
all material had dissolved whereafter Pd(OAc)$_2$ (1.9 mg, 5 mol%) was added. The vial was sealed with a septum, flushed with nitrogen followed by connection of an oxygen ballon and stirred at 60 °C. The reaction was stopped when GC-MS showed full consumption of the starting material dimethyl-(2-vinyloxy-ethyl)-amine (1). The mixture was diluted with EtOAc (10 mL) and washed three times with NaOH (10 mL, aq, 1M). The organic phase was dried with K$_2$CO$_3$ (s), concentrated under reduced pressure and purified by column chromatography (aluminium oxide).

**N,N-dimethyl-2-(4-methylstyryloxy)ethanamine (4a)**

Using method B, the reaction mixture was stirred for 24 h and 4a was obtained as a mixture of isomers in 51% yield (19 mg, E:Z = 37:63) after column chromatography (aluminium oxide, iso-hexane:EtOAc:Et$_3$N gradient, 92:4:4 to 70:26:4) as a colorless oil. The acquired spectroscopic data was in accordance with previous published results.$^1$ $^1$H NMR $\delta$ 7.47 (d, $J = 8.15$ Hz, 2H, Z), 7.13-7.04 (m, E:Z mixture, 2H, Z, 4H, E), 6.98 (d, $J = 13.0$ Hz, 1H, E), 6.15 (d, $J = 7.0$ Hz, 1H, Z), 5.83 (d, $J = 13.0$ Hz, 1H, E), 5.21 (d, $J = 7.0$ Hz, 1H, Z), 4.03 (t, $J = 6.01$ Hz, 2H, Z), 3.93 (t, $J = 5.4$ Hz, 2H, E), 2.73-2.65 (m, E:Z mixture, 2H each), 2.35 (s, 6H, Z), 2.34 (s, 6H, E), 2.31 (s, 3H, Z), 2.30 (s, 3H, E); $^{13}$C NMR $\delta$ 147.2, 145.7, 135.3, 135.2, 133.3, 132.9, 129.3, 128.8, 128.1, 125.0, 105.91, 105.89, 71.7, 67.2, 58.6, 58.2, 45.9, 45.6, 21.2, 21.0; MS (70 eV) m/z (relative intensity) 205 (M$^+$, 15), 115 (7), 105 (9), 72 (93), 58 (100).

**2-(4-methoxystyryloxy)-N,N-dimethylethanamine (4b)**

Using method B, the reaction mixture was stirred for 24 h and 4b was obtained as a mixture of isomers in 53% yield (23 mg, E:Z = 14:86) after column chromatography (aluminium oxide, iso-hexane:EtOAc:Et$_3$N gradient, 92:4:4 to 70:26:4). The acquired spectroscopic data was in accordance with previous published results.$^1$ $^1$H NMR $\delta$ 7.51 (d, $J = 8.9$ Hz, 2H, Z), 7.14 (d, $J = 8.7$ Hz, 2H, E), 6.88 (d, $J = 12.9$ Hz, 1H, E), 6.84-6.81 (m, E:Z mixture, 2H each), 6.10 (d, $J = 7.1$ Hz, 1H, Z), 5.81 (d, $J = 12.9$ Hz, 1H, E), 5.19 (d, $J = 7.1$ Hz, 1H, Z), 4.04 (t, $J = 5.9$ Hz, 2H, Z), 3.93 (t, $J = 5.5$ Hz, 2H, E), 3.80 (s, 3H, Z), 3.79 (s, 3H, E), 2.73 (t, $J = 5.9$ Hz, Z), 2.69 (t, $J = 5.5$ Hz, E), 2.37 (s, 3H, Z), 2.35 (s, 3H, E); $^{13}$C NMR $\delta$ 157.8, 144.6, 129.4, 128.6, 113.6, 105.7, 71.2, 58.4, 55.2, 45.7 (signals from Z-isomer); MS (70 eV) m/z (relative intensity) 221 (M$^+$, 10), 121 (12), 72 (100), 58 (63).

**N,N-dimethyl-2-(2-methylstyryloxy)ethanamine (4c)**

Using method B, the reaction mixture was stirred for 24 h and 4c was obtained as a mixture of isomers in 56% yield (20 mg, E:Z = 38:62) after column chromatography (aluminium oxide, iso-hexane:EtOAc:Et$_3$N gradient, 92:4:4 to 70:26:4). The acquired spectroscopic data was in accordance with previous published results.$^1$ $^1$H NMR $\delta$ 7.47 (d, $J = 8.15$ Hz, 2H, Z), 7.13-7.04 (m, E:Z mixture, 2H, Z, 4H, E), 6.98 (d, $J = 13.0$ Hz, 1H, E), 6.15 (d, $J = 7.0$ Hz, 1H, Z), 5.83 (d, $J = 13.0$ Hz, 1H, E), 5.21 (d, $J = 7.0$ Hz, 1H, Z), 4.03 (t, $J = 6.01$ Hz, 2H, Z), 3.93 (t, $J = 5.4$ Hz, 2H, E), 2.73-2.65 (m, E:Z mixture, 2H each), 2.35 (s, 6H, Z), 2.34 (s, 6H, E), 2.31 (s, 3H, Z), 2.30 (s, 3H, E); $^{13}$C NMR $\delta$ 147.2, 145.7, 135.3, 135.2, 133.3, 132.9, 129.3, 128.8, 128.1, 125.0, 105.91, 105.89, 71.7, 67.2, 58.6, 58.2, 45.9, 45.6, 21.2, 21.0; MS (70 eV) m/z (relative intensity) 205 (M$^+$, 15), 115 (7), 105 (9), 72 (93), 58 (100).
oxide, iso-hexane:EtOAc:Et₃N gradient, 92:4:4 to 70:26:4) as a colorless oil; \(^1\)H NMR \(\delta \) 7.91 (dd, \(J = 1.7, 7.8 \) Hz, 1H, \(Z\)), 7.27-7.24 (m, 1H, \(E\)), 6.86 (d, \(J = 12.8 \) Hz, 1H, \(E\)), 6.25 (d, \(J = 7.2 \) Hz, 1H, \(Z\)), 5.97 (d, \(J = 12.8 \) Hz, 1H, \(E\)), 5.34 (t, \(J = 6.0 \) Hz, 2H, \(Z\)), 4.03 (t, \(J = 6.0 \) Hz, 2H, \(E\)), 3.95 (t, \(J = 5.6 \) Hz, 2H, \(E\)), 2.71-2.65 (m, 2H each), 2.34 (s, 6H, \(E\)), 2.33 (s, 6H, \(Z\)), 2.30 (s, 3H, \(Z\)), 2.29 (s, 3H, \(E\)); \(^{13}\)C NMR \(\delta \) 148.2, 146.3, 135.1, 134.8, 134.7, 134.1, 130.1, 129.8, 128.9, 126.0, 125.9, 125.8, 125.6, 124.8, 104.2, 102.8, 71.7, 67.4, 58.6, 58.2, 45.9, 45.7, 20.2, 20.0; MS (70 eV) m/z (relative intensity) 205 (M\(^+\), 7), 115 (9), 72 (76), 58 (100); Anal. Calcd for C\(_{13}\)H\(_{19}\)NO (%): C, 76.06; H, 9.33; N, 6.82. Found: C, 75.95; H, 9.09; N, 6.93.

\(\)N,N-dimethyl-2-(4-(trifluoromethyl)styryloxy)ethanamine (4d)

Using method B, the reaction mixture was stirred for 24 h and 4d was obtained as a mixture of isomers in 47% yield (23 mg, \(E:Z = 60:40\)) after column chromatography (aluminium oxide, iso-hexane:EtOAc:Et\(_3\)N gradient, 92:4:4 to 70:26:4) as a colorless oil; \(^1\)H NMR \(\delta \) 7.65 (d, \(J = 8.3 \) Hz, 2H, \(Z\)), 7.53-7.47 (m, \(E:Z\) mixture, 2H each), 7.29 (d, \(J = 8.3 \) Hz, 2H, \(E\)), 7.11 (d, \(J = 13.0 \) Hz, 1H, \(E\)), 6.31 (d, \(J = 7.0 \) Hz, 1H, \(E\)), 5.86 (d, \(J = 13.0 \) Hz, 1H, \(Z\)), 5.26 (d, \(J = 7.0 \) Hz, 1H, \(E\)), 4.08 (t, \(J = 5.9 \) Hz, 2H, \(Z\)), 3.98 (t, \(J = 5.5 \) Hz, 2H, \(E\)); \(^{13}\)C NMR \(\delta \) 149.6, 148.4, 139.9 (q, \(J = 1.5 \) Hz), 139.3 (q, \(J = 1.5 \) Hz), 128.1, 127.7 (q, \(J = 32 \) Hz, \(Z\)), 127.6 (q, \(J = 32 \) Hz, \(E\)) 125.5 (q, \(J = 3.8 \) Hz), 125.0 (q, \(J = 4.0 \)), 124.9, 124.1 (q, \(J = 272 \) Hz, Two close signals, \(E:Z\) carbons), 104.9, 104.7, 72.2, 67.5, 58.6, 58.1, 45.9, 45.6; MS (70 eV) m/z (relative intensity) 259 (M\(^+\), 15), 72 (37), 58 (100); Anal. Calcd for C\(_{13}\)H\(_{16}\)F\(_3\)NO (%): C, 60.22; H, 6.22; N, 5.40. Found: C, 60.48; H, 6.53; N, 5.34.

**Method C: General procedure for diarylation of N,N-dimethyl-2-(vinlyloxy)ethanamine (1), table 2**

To a 8 mL glass vial equipped with a teflon-coated stirring bar, corresponding boronic acid (1.04 mmol), p-benzoquinone (37.8 mg, 0.35 mmol), 1 (40 mg, 0.35 mmol), and 1,4-dioxane (2.4 mL) were added. The vial was stirred until all material had dissolved whereafter Pd(O\(_2\)CCF\(_3\))\(_2\) (5 mol%) was added. The vial was rapidly put in a preheated metalblock at 40 °C and the content was magnetically stirred for 8-24 h under open air. The reaction mixture was diluted on EtOAc (10 mL), thereafter put on an separation funnel and extracted with HCl (3-5 x 10 mL, aq, 2M). The acidic aqueous phases were combined and thereafter basified with NaOH (aq, 6M). The alkaline aqueous phase was then extracted with EtOAc (3 x 15 mL). The combined organic phases were thereafter washed with NaOH (3 x 15 mL, aq, 1M), dried with K\(_2\)CO\(_3\) (s), concentrated under reduced pressure and stored in a glovebox in vacuo. The product was obtained as a colorless solid.
and purified by column chromatography affording pure products 5a-5m. It is worthwhile to note that the majority of the products could be obtained in >95% purity after merely using the extraction procedure described above.

2-(1,2-di-p-tolylethoxy)-N,N-dimethylethanamine (5a)

Using method C, the reaction mixture was stirred for 8 h and 5a was obtained in 82% yield (85 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et3N, 80:16:4) as a colorless oil; 1H NMR δ 7.16-7.10 (m, 4H), 7.05-6.99 (m, 4H), 4.35 (dd, J = 5.9, 7.6 Hz, 1H), 3.42 (ddd, J = 5.4, 6.3, 10.1 Hz, 1H), 3.29 (ddd, J = 5.4, 6.2, 10.1 Hz, 1H), 3.10 (dd, J = 7.7, 13.7 Hz, 1H), 2.83 (dd, J = 5.9, 13.7 Hz, 1H), 2.49 (dd, J = 5.4, 6.3, 12.8 Hz, 1H), 2.34 (s, 3H), 2.30 (s, 3H), 2.20 (s, 6H); 13C NMR δ 139.0, 137.1, 135.6, 135.4, 129.4, 128.9, 128.6, 83.9, 66.9, 58.8, 45.7, 44.4, 21.1, 21.0; MS (70 eV) m/z (relative intensity) 298 (M+ 2), 224 (19), 105 (15), 72 (30), 58 (100); Anal. Calcd for C20H27NO (%): C, 80.76; H, 9.15; N, 4.71. Found: C, 80.37; H, 9.05; N, 4.83.

2-(1,2-bis(4-methoxyphenyl)ethoxy)-N,N-dimethylethanamine (5b)

Using method C, the reaction mixture was stirred for 18 h and 5b was obtained in 66% yield (76 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et3N, 70:26:4) as a colorless oil; 1H NMR δ 7.14 (dd, J = 2.2, 6.7 Hz, 2H), 6.99 (dd, J = 2.2, 6.6 Hz, 2H), 6.83 (dd, J = 2.2, 6.7 Hz, 2H), 6.75 (dd, J = 2.2, 6.6 Hz, 2H), 4.30 (dd, J = 6.3, 7.2 Hz, 1H), 3.79 (s, 3H), 3.76 (s, 3H), 3.40 (ddd, J = 5.4, 6.3, 10.1 Hz, 1H), 3.29 (ddd, J = 5.4, 6.3, 10.1 Hz, 1H), 3.08 (dd, J = 7.3, 13.7 Hz, 1H), 2.81 (dd, J = 6.3, 13.7 Hz, 1H), 2.53-2.40 (m, 2H), 2.20 (s, 6H); 13C NMR δ 159.0, 157.9, 134.0, 130.7, 130.4, 128.0, 113.6, 113.3, 83.7, 66.7, 58.8, 55.2, 55.1, 45.7, 43.8; MS (70 eV) m/z (relative intensity) 330 (M+ 11), 256 (25), 240 (19), 208 (10), 135 (10), 121 (14), 72 (71), 58 (100); Anal. Calcd for C20H27NO3 (%): C, 72.92; H, 8.26; N, 4.25. Found: C, 72.97; H, 8.41; N, 4.25.

2-(1,2-di-o-tolylethoxy)-N,N-dimethylethanamine (5c)

Using method C, the reaction mixture was stirred for 24 h and 5c was obtained in 66% yield (68 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et3N, 80:16:4) as a colorless oil; 1H NMR δ 7.48 (dd, J = 1.6, 7.7 Hz, 1H), 7.23 (ddt, J = 0.5, 1.5, 7.4 Hz, 1H), 7.15 (dt, J = 1.5, 7.4 Hz, 1H), 7.10-7.01 (m, 5H), 4.73 (dd, J = 6.1, 7.4 Hz, 1H), 3.41 (ddd, J = 5.5, 6.2, 10.0 Hz, 1H), 3.27 (ddd, J = 5.4, 6.2, 10.0 Hz, 1H), 3.15 (dd, J = 7.4, 13.8 Hz, 1H), 2.86 (dd, J = 6.1, 13.8 Hz, 1H), 2.52-2.14 (m, 2H), 2.23 (s, 3H), 2.19 (s, 6H), 2.08 (s, 3H); 13C NMR δ 140.3, 136.70, 136.68, 135.5, 130.3, 130.1, 129.9, 127.1, 126.24, 126.21, 126.18, 125.5, 79.2, 67.0, 58.9, 45.7, 41.2, 19.5, 18.8; MS (70 eV) m/z...
4,4'-[(1-(2-(dimethylamino)ethoxy)ethane-1,2-diyl)bis(N,N-dimethylaniline) (5e)

Using method C, the reaction mixture was stirred for 12 h and 5e was obtained in 49% yield (60 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et3N, 80:16:4) as a yellow oil; 1H NMR δ 7.13 (dd, J = 2.1, 6.7 Hz, 2H), 7.00 (dd, J = 2.2, 6.6 Hz, 2H), 6.69 (dd, J = 2.1, 6.7 Hz, 2H), 6.63 (dd, J = 2.2, 6.6 Hz, 2H), 4.27 (dd, J = 5.7, 7.9 Hz, 1H), 3.49-4.42 (m, 1H), 3.37-3.29 (m, 1H), 3.02 (dd, J = 7.6, 14 Hz, 1H), 2.94 (s, 6H), 2.89 (s, 6H), 2.80 (dd, J = 5.5, 14.0 Hz, 1H), 2.67-2.51 (m, 2H), 2.27 (s, 6H); 13C NMR δ 150.1, 149.1, 130.1, 129.5, 127.8, 127.2, 112.7, 112.3, 84.2, 65.5, 58.2, 45.0, 43.6, 40.9, 40.6; ESI+-MS m/z (relative intensity) 356.3 ([M+H]+, 32), 178.7 ([M+2H]2+, 100); Anal. Calcd for C20H27NO (%): C, 80.76; H, 9.15; N, 4.71. Found: C, 80.65; H, 9.02; N, 4.83.

2-(1,2-bis(2-methoxyphenyl)ethoxy)-N,N-dimethylethananine (5f)

Using method C, the reaction mixture was stirred for 24 h and 5f was obtained in 48% yield (55 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et3N, 70:26:4) as a colorless oil; 1H NMR δ 7.44 (dd, J = 1.9, 7.5 Hz, 1H), 7.20 (ddd, J = 1.8, 7.3, 8.2 Hz, 1H), 7.16-7.11 (m, 1H), 7.05 (dd, J = 1.9, 7.8 Hz, 1H), 6.96 (ddd, J = 0.4, 1.1, 7.4 Hz, 1H), 6.81-6.76 (m, 3H), 5.04 (dd, J = 5.5, 7.8 Hz, 1H), 3.76 (s, 3H), 3.64 (s, 3H), 3.47 (ddd, J = 5.7, 6.2, 11.8 Hz, 1H), 3.34 (ddd, J = 5.6, 6.2, 11.8 Hz, 1H), 3.08 (ddd, J = 7.8, 13.6 Hz, 1H), 2.92 (dd, J = 5.4, 13.6 Hz, 1H), 2.51-2.39 (m, 2H), 2.19 (6H); 13C NMR δ 157.8, 157.1, 131.1, 131.0, 127.9, 127.5, 127.0, 126.8, 120.6, 119.9, 110.2, 110.0, 75.4, 67.2, 58.8, 55.3, 55.2, 45.7, 37.6; MS (70 eV) m/z (relative intensity) 330 (M+, 3), 256 (45), 240 (15), 135 (32), 91 (24), 72 (48), 58 (100); Anal. Calcd for C22H23N3O (%): C, 72.92; H, 8.26; N, 4.25. Found: C, 72.97; H, 8.19; N, 4.36.

2-(1,2-di-m-tolylethoxy)-N,N-dimethylethanamine (5g)

Using method C, the reaction mixture was stirred for 8 h and 5g was obtained in 92% yield (95 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et3N, 80:16:4) as a colorless oil; 1H NMR δ 7.21 (dd, J = 0.8, 7.4 Hz, 1H), 7.13 (dd, J = 0.5, 7.4 Hz, 1H), 7.10-7.05 (m, 3H), 7.02-6.93 (m, 3H), 4.37 (dd, J = 5.2, 8.1 Hz, 1H), 3.45 (ddd, J = 5.4, 6.2, 10.0 Hz, 1H), 3.29 (ddd, J = 5.4, 6.3, 10.0 Hz, 1H), 3.09 (dd, J = 8.1, 13.7 Hz, 1H), 2.83 (dd, J = 5.3, 13.7 Hz, 1H), 5.51-2.39 (m, 2H), 2.35 (s, 3H), 2.31 (s, 3H), 2.19 (s, 6H); 13C NMR δ 142.2, 138.8, 137.8, 137.4, 130.4, 128.2, 128.1, 127.8,
127.3, 126.7, 126.5, 123.8, 84.0, 67.1, 58.9, 45.7, 44.8, 21.4, 21.3; MS (70 eV) m/z (relative intensity) 298 (M⁺, 10), 105 (12), 72 (21), 58 (100); Anal. Calcd for C₂₀H₂₇NO (%): C, 80.76; H, 9.15; N, 4.71. Found: C, 80.72; H, 8.99; N, 4.84.

2-(1,2-di(naphthalen-2-yl)ethoxy)-N,N-dimethylethanamine (5h)

Using method C, the reaction mixture was stirred for 24 h and 5h was obtained in 50% yield (64 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et₃N, 70:26:4) as a colorless oil; ¹H NMR δ 7.86-7.82 (m, 2H), 7.80-7.76 (m, 2H), 7.75-7.69 (m, 3H), 7.64 (s, 1H), 7.51-7.46 (m, 3H), 7.47-7.41 (m, 2H), 7.29 (dd, J = 1.7, 8.3 Hz, 1H), 4.69 (dd, J = 5.6, 7.7 Hz, 1H), 3.49 (ddd, J = 5.1, 6.3, 10.2 Hz, 1H), 3.43-3.35 (m, 2H), 3.16 (dd, J = 5.7, 13.8 Hz, 1H), 2.58-2.46 (m, 2H), 2.20 (s, 6H); ¹³C NMR δ 139.3, 136.1, 133.4, 133.2, 133.1, 132.0, 128.3, 128.1, 128.0, 127.9, 127.7, 127.5, 127.5 (2 overlapping signals), 126.1, 125.9, 125.8, 125.7, 125.2, 124.5, 84.2, 66.8, 58.7, 45.5, 44.8; MS (70 eV) m/z (relative intensity) 370 (M⁺, 15), 296 (16), 155 (11), 115 (10), 72 (32), 58 (100); Anal. Calcd for C₂₆H₂₇NO (%): C, 84.51; H, 7.37; N, 3.79. Found: C, 84.32; H, 7.66; N, 3.54.

2-(1,2-diphenylethoxy)-N,N-dimethylethanamine (5i)

Using method C, the reaction mixture was stirred for 12 h and 5i was obtained in 81% yield (76 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et₃N, 70:26:4) as a colorless oil; ¹H NMR δ 7.34-7.39 (m, 2H), 7.28-7.22 (m, 4H), 7.21-7.14 (m, 2H), 7.13-7.09 (m, 2H), 4.42 (dd, J = 5.8, 7.7 Hz, 1H), 3.44 (ddd, J = 5.3, 6.2, 10.2 Hz, 1H), 3.32 (dddd, J = 0.5, 5.3, 6.3, 10.2 Hz, 1H), 3.15 (ddd, J = 0.5, 7.7, 13.7 Hz, 1H), 2.89 (dd, J = 5.8, 13.7 Hz, 1H), 2.56-2.42 (m, 2H), 2.20 (s, 6H); ¹³C NMR δ 141.8, 138.5, 129.5, 128.2, 128.0, 127.6, 126.7, 126.0, 84.0, 66.9, 58.7, 45.6, 44.8; MS (70 eV) m/z (relative intensity) 270 (M⁺, 40), 178 (4), 72 (17), 58 (100); Anal. Calcd for C₁₈H₂₃NO (%): C, 80.26; H, 8.61; N, 5.20. Found: C, 80.13; H, 8.68; N, 5.33.

2-(1,2-bis(4-iodophenyl)ethoxy)-N,N-dimethylethanamine (5j)

Using method C, the reaction mixture was stirred for 24 h and 5j was obtained in 11% yield (19 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et₃N, 60:36:4) as a colorless oil; ¹H NMR δ 7.43 (dd, J = 2.0, 6.6 Hz, 2H), 7.33 (dd, J = 1.8, 6.3 Hz, 2H), 7.07 (dd, J = 2.0, 6.6 Hz, 2H), 6.94 (dd, J = 1.8, 6.3 Hz, 2H), 4.33 (dd, J = 6.0, 7.4 Hz, 1H), 3.40 (ddd, J = 5.2, 6.3, 10.2 Hz, 1H), 3.31 (ddd, J = 5.1, 6.3, 10.2 Hz, 1H), 3.04 (dd, J = 7.4, 13.8 Hz, 1H), 2.79 (dd, J = 6.0, 13.8 Hz, 1H), 2.51 (ddd, J = 5.1, 6.3, 12.9 Hz, 1H), 2.46 (ddd, J = 5.1, 6.3, 12.9 Hz, 1H), 2.22 (s, 3H); ¹³C NMR δ
Using method C, the reaction mixture was stirred for 8 h and 5k was obtained in 66% yield (98 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et_3N, 70:26:4) as a colorless oil; ^1H NMR δ 7.43 (dd, J = 2.0, 6.6 Hz, 2H), 7.33 (dd, J = 1.8, 6.3 Hz, 2H), 7.07 (dd, J = 2.0, 6.6 Hz, 2H), 6.94 (dd, J = 1.8, 6.3 Hz, 2H), 4.33 (dd, J = 6.0, 7.4 Hz, 1H), 3.40 (ddd, J = 5.2, 6.3, 10.2 Hz, 1H), 3.31 (ddd, J = 5.1, 6.3, 10.2 Hz, 1H), 3.04 (dd, J = 7.4, 13.8 Hz, 1H), 2.79 (dd, J = 6.0, 13.8 Hz, 1H), 2.51 (ddd, J = 5.1, 6.3, 12.9 Hz, 1H), 2.46 (ddd, J = 5.1, 6.3, 12.9 Hz, 1H), 2.22 (s, 3H); ^13C NMR δ 140.5, 136.9, 131.5, 131.3, 131.1, 128.4, 121.5, 120.2, 83.0, 66.9, 58.7, 45.6, 44.0; MS (70 eV) m/z (relative intensity) 528 (M^+ 6), 258 (3), 178 (3), 72 (18), 58 (100); Anal. Calcd for C_18H_21Br_2NO (%): C, 50.61; H, 4.96; N, 3.28. Found: C, 50.29; H, 5.12; N, 3.48.

Using method C, the reaction mixture was stirred for 24 h and 5l was obtained in 28% yield (27 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et_3N, 70:26:4) as a colorless oil; ^1H NMR δ 7.27 (ddd, J = 0.6, 1.4, 4.8 Hz, 1H), 7.13 (dd, J = 1.2, 5.1 Hz, 1H), 6.95 (dd, J = 3.4, 4.8 Hz, 1H), 6.92 (ddd, J = 0.6, 1.4, 3.4 Hz, 1H), 6.89 (dd, J = 3.4, 5.1 Hz, 1H), 6.78 (ddd, J = 0.8, 2.1, 3.5 Hz, 1H), 4.70 (dd, J = 5.6, 7.8 Hz, 1H), 3.63-6.55 (m, 1H), 3.50-3.46 (m, 1H), 3.42 (dd, J = 1.1, 7.8, 14.8 Hz, 1H), 3.24 (dd, J = 0.9, 5.6, 14.8 Hz, 1H), 2.65-2.52 (m, 2H), 2.28 (s, 6H); ^13C NMR δ 145.1, 140.1, 126.4, 126.0 (2 overlapping signals), 125.7, 125.2, 124.1, 79.1, 66.8, 58.6, 45.4, 39.1; MS (70 eV) m/z (relative intensity) 282 (M^+ 2), 97 (15), 72 (19), 58 (100); Anal. Calcd for C_14H_19NOS_2 (%): C, 59.75; H, 6.80; N, 4.98. Found: C, 59.74; H, 6.87; N, 5.12.

Using method C, the reaction mixture was stirred for 24 h and 5m was obtained in 47% yield (46 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et_3N, 70:26:4) as a colorless oil; ^1H NMR δ 7.28 (ddd, J = 0.5, 3.0, 5.0 Hz, 1H), 7.18 (dd, J = 3.0, 4.9 Hz, 1H), 7.06 (ddd, J = 0.5, 1.3, 3.0 Hz, 1H), 7.03 (dd, J = 1.3, 5.0 Hz, 1H), 6.93-6.89 (m, 1H), 6.85 (dd, J = 1.3, 4.9 Hz, 1H), 4.52 (dd, J = 6.1, 7.4 Hz, 1H), 3.48 (ddd, J = 5.2, 6.3, 10.2 Hz, 1H), 3.42-3.35 (m, 1H), 3.18 (ddd, J = 140.5, 136.9, 131.5, 131.3, 131.1, 128.4, 121.5, 120.2, 83.0, 66.9, 58.7, 45.6, 44.0; MS (70 eV) m/z (relative intensity) 522 (M^+ 3), 433 (3), 306 (5), 178 (7), 72 (24), 58 (100); Anal. Calcd for C_18H_21I_2NO (%): C, 41.48; H, 4.06; N, 2.69. Found: C, 41.58; H, 4.05; N, 2.62.
0.9, 7.4, 14.3 Hz, 1H), 2.97 (ddd, J = 0.7, 6.1, 14.3 Hz, 1H), 2.58-2.45 (m, 2H), 2.24 (s, 6H); $^{13}$C NMR δ 143.2, 138.6, 128.9, 126.0, 125.9, 124.7, 122.1, 121.9, 79.0, 66.6, 58.7, 45.5, 38.1; MS (70 eV) m/z (relative intensity) 282 (M$^+$, 47), 72 (10), 58 (100); Anal. Calcd for C$_{14}$H$_{19}$NOS$_2$ (%): C, 59.75; H, 6.80; N, 4.98. Found: C, 59.53; H, 6.86; N, 5.07.

2-((1E,5E)-1,6-diphenylhexa-1,5-dien-3-yloxy)-N,N-dimethylethanamine (5n)

Using method C, the reaction mixture was stirred for 12 h and 5n was obtained in 65% yield (76 mg) after column chromatography (silica gel, iso-hexane:EtOAc:Et$_3$N, 80:16:4) as a colorless oil; $^1$H NMR δ 7.42 (ddd, J = 0.5, 1.5, 3.6 Hz, 1H), 7.40-7.38 (m, 1H), 7.37-7.25 (m, 6H), 7.24-7.18 (m, 2H), 6.58 (d, J = 16.0 Hz, 1H), 6.47 (dt, J = 1.5, 15.8 Hz, 1H), 6.27 (dt, J = 7.1, 15.8 Hz, 1H), 6.16 (dd, J = 7.9, 16.0 Hz, 1H), 3.98-3.92 (m, 1H), 3.70 (ddd, J = 5.5, 6.3, 10.0 Hz, 1H), 3.48 (ddd, J = 5.5, 6.3, 10.0 Hz, 1H), 2.69-2.48 (m, 4H), 2.29 (s, 6H); $^{13}$C NMR δ 137.6, 136.5, 132.3, 132.1, 130.0, 128.5, 128.4, 127.7, 127.0, 126.5, 126.4, 126.0, 81.2, 66.7, 59.0, 45.9, 39.5; MS (70 eV) m/z (relative intensity) 322 (M$^+$, 7), 232 (8), 204 (5), 147 (5), 115 (12), 72 (52), 58 (100); Anal. Calcd for C$_{22}$H$_{27}$NO (%): C, 82.20; H, 8.47; N, 4.36. Found: C, 82.03; H, 8.36; N, 4.39.

References

N,N-dimethyl-2-(1-p-tolylvinloxy)ethanamine 3a

Chemical Formula: C_{10}H_{13}NNO
Molecular Weight: 205.30
$N,N$-dimethyl-2-(4-methylstyryloxy)ethanamine 4a

Chemical formula: C$_9$H$_{13}$NO
Molecular weight: 205.30

Chromatogram Plot
File: h:\gc\at05122_26165_flash001.sms
Sample: at05122_26165_Flash Operator: Operator
Scan Range: 1 - 1352 Time Range: 0.00 - 12.98 min. Date: 06/10/2009 10:56
Sample Notes: ROUTINE

Supplementary Material (ESI) for Chemical Communications
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2-(4-methoxystyryloxy)-N,N-dimethylethanamine 4b

Chemical Formula: C_{12}H_{15}NO_{2}
Molecular Weight: 221.30

Chromatogram Plot

Supplementary Material (ESI) for Chemical Communications
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**N,N-dimethyl-2-(2-methylstyryloxy)ethanamine 4c**

Chemical Formula: C_{12}H_{20}NO
Molecular Weight: 206.30

Chromatogram Plot

File: m:\synthesis\at051\gc_02\at05106 och fra\at05121_26155.smr
Sample: at05121_26155 Operator: Operator
Scan Range: 1 - 1325 Time Range: 0.00 - 12.98 min. Date: 06/05/2009 14:46
Sample Notes: ROUTINE

  - MZs: 58, 115, 173, 205, 324

- Spect 2: 7.178 min. Scan: 680 Chan: 1 Ion: 734 us RIC: 572730 BC
  - MZs: 58, 115, 174, 205, 281, 379

- Spect 1 - Spect 2 Normalized
  - MZs: 58, 115, 174, 205, 281, 379

- MCounts RIC all at05121_26155.smr

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$N,N$-dimethyl-2-(4-(trifluoromethyl)styryloxy)ethanamine 4d

Chemical Formula: C$_{13}$H$_{20}$F$_{3}$NO
Molecular Weight: 269.27

Chromatogram Plot

File: h:\gc\at05120_26163_fr23.sms
Sample: at05120_26163_fr23                Operator: Operator
Scan Range: 1 - 1351 Time Range: 0.00 - 12.98 min. D ate: 06/08/2009 16:17
Sample Notes: ROUTINE

Supplementary Material (ESI) for Chemical Communications
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2-(1,2-di-p-tolylethoxy)-N,N-dimethylethanamine 5a

Chemical Formula: C_{20}H_{24}NO
Molecular Weight: 297.43

Chromatogram Plot

File: m:\...\at05 oxidativ heck\synthesis\at051\gc\at05101_26065\_S-B-O.sms
Sample: at05101_26065\_S-B-O  Operator: Operator
Scan Range: 1 - 1309 Time Range: 0.00 - 12.98 min.  Date: 03/06/2009 09:15
Sample Notes: ROUTINE

Supplementary Material (ESI) for Chemical Communications
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2-(1,2-bis(4-methoxyphenyl)ethoxy)-N,N-dimethylethanamine 5b

Chemical Formula: C_{32}H_{27}NO_{3}
Molecular Weight: 329.43

Chromatogram Plot
File: \at05 oxidativ heck\synthesis\at051\gc_02\at05102_ptlc_r03.sms
Sample: at05102_PTLC_r03                  Operator: Operator
Scan Range: 1 - 1320 Time Range: 0.00 - 12.98 min. Date: 03/19/2009 12:03
Sample Notes: ROUTINE

Supplementary Material (ESI) for Chemical Communications
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2-(1,2-di-o-tolylethoxy)-N,N-dimethylethanamine 5c

Chemical Formula: C_{12}H_{19}NO
Molecular Weight: 297.43

Chromatogram Plot
File: \\...\at05116_260105_sbo.sms
Sample: at05116_260105_SBO                Operator: Operator
Scan Range: 1 - 1309 Time Range: 0.00 - 12.99 min.    Date: 04/27/2009 10:30
Sample Notes: ROUTINE

Supplementary Material (ESI) for Chemical Communications
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4,4'-(1-(2-(dimethylamino)ethoxy)ethane-1,2-diyl)bis(N,N-dimethylaniline) 5e
2-(1,2-bis(2-methoxyphenyl)ethoxy)-N,N-dimethylethanamine 5f

Chemical Formula: C_{20}H_{26}NO_{3}
Molecular Weight: 339.43

Chromatogram Plot

File: \...\at051\gc\_02\at05106 och framåt\at05113\_26099\_fr10.sms
Sample: at05116\_260105\_fr10
Operator: Operator
Scan Range: 1 - 1347 Time Range: 0.00 - 12.98 min.
Date: 04/29/2009 11:41
Sample Notes: ROUTINE

Supplementary Material (ESI) for Chemical Communications
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2-(1,2-di-\textit{m}-tolylethoxy)-\textit{N},\textit{N}-dimethylethanamine 5g

Chemical Formula: C_{16}H_{24}NO
Molecular Weight: 257.43

Chromatogram Plot
File: \ldots at05114_02\at05106 och framåt\at05114_260101_sbo.sms
Sample: at05114_260101_SBO Operator: Operator
Scan Range: 1 - 1306 Time Range: 0.00 - 12.99 min. Date: 04/27/2009 12:41
Sample Notes: ROUTINE
2-(1,2-di(naphthalen-2-yl)ethoxy)-N,N-dimethylethanamine 5h

Chemical Formula: C_{26}H_{20}NO
Molecular Weight: 389.40
2-(1,2-diphenylethoxy)-N,N-dimethylethanamine Si

Chemical Formula: C_{21}H_{25}NO
Molecular Weight: 290.36

Chromatogram Plot

File: \...\at05 oxidativ_heck\synthesis\at051\gci\at05104_26071_s-b-o.sms
Sample: at05104_26071_S-B-O Operator: Operator
Scan Range: 1 - 1321 Time Range: 0.00 - 12.99 min.
Sample Notes: ROUTINE

Supplementary Material (ESI) for Chemical Communications
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2-(1,2-bis(4-iodophenyl)ethoxy)-N,N-dimethylethanamine 5j

Chemical Formula: C_{26}H_{21}I_N_O
Molecular Weight: 521.17

Chromatogram Plot
File: .../at05115_26103_tr005.sms
Sample: at05115_26103_tr005
Operator: Operator
Scan Range: 1 - 1347 Time Range: 0.00 - 12.99 min.
Date: 04/29/2009 09:24
Sample Notes: ROUTINE

MCounts
Segment 1
Segment 2
Scans 157 447 735 1023 1294

Supplementary Material (ESI) for Chemical Communications
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2-(1,2-bis(4-bromophenyl)ethoxy)-N,N-dimethylethanamine 5k

Chemical Formula: C_{16}H_{12}Br_{2}NO
Molecular Weight: 427.17

Chromatogram Plot
File: C:\...@at05 oxidativ Heck\synthesis\at051\gc_02\at05105_ptlc_r03.sms
Sample: at05105_PTLC_r03 Operator: Operator
Scan Range: 1 - 1330 Time Range: 0.00 - 12.99 min. Date: 03/20/2009 12:55
Sample Notes: ROUTINE

Spect 1
10.113 min. Scan: 1015 Chan: 1 Ion: 105 us RIC: 3561302 BC

Segment 1
Scans 151 429 715 1003 1276

Segment 2
2-(1,2-di(thiophen-2-yl)ethoxy)-N,N-dimethylethanamine 5l

Chemical Formula: C_{14}H_{26}NOS
Molecular Weight: 281.44

Chromatogram Plot

File: ...
Sample: at05107_fr06
Operator: Org Farm Kemi
Scan Range: 1 - 1273 Time Range: 0.00 - 12.99 min.
Date: 05/05/2009 12:31
Sample Notes: Routine

(Supplementary Material (ESI) for Chemical Communications
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2-(1,2-di(thiophen-3-yl)ethoxy)-N,N-dimethylethanamine 5m

Chemical Formula: C_{14}H_{20}NOS_2
Molecular Weight: 281.44

Chromatogram Plot
File: ...
Sample: at05112_26095_fr07
Operator: Operator
Scan Range: 1 - 1318 Time Range: 0.00 - 12.99 min.
Sample Notes: ROUTINE

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Supplementary Material (ESI) for Chemical Communications
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2-((1E,5E)-1,6-diphenylhexa-1,5-dien-3-yloxy)-N,N-dimethylethanamine 5n

Chemical Formula: C_{27}H_{26}NO
Molecular Weight: 321.46

Chromatogram Plot

File: \...\synthesis\at051\gc_02\at05106 och framat05108_ptlc_r03.sms
Sample: at05108_PTLC_R03                  Operator: Operator
Scan Range: 1 - 1318 Time Range: 0.00 - 12.98 min. Date: 03/25/2009 11:31
Sample Notes: ROUTINE