NBS-Catalyzed Hydroamination and Hydroalkoxylation of Activated Styrenes

Supporting Information

*Siva Kumar Talluri and A. Sudalai **

CE-PD Division, National Chemical Laboratory, Pashan Road, Pune,

India 411008

General information:

Solvents were purified and dried by standard procedures before use; petroleum ether of boiling range 60-80 °C was used. NBS was recrystallized before use. Melting points were uncorrected. ¹H NMR and ¹³C NMR were recorded on Bruker AC-200 and MSL-300 NMR spectrometers, respectively. Elemental analysis was done on a Carlo Erba CHNS-O analyzer. N-bromosuccinimide was recrystallized before use.

General experimental procedure for the Hydroamination of activated styrenes:

A mixture of olefin (2 mmol), N-bromosuccinimide (20 mol%), TsNH₂ (342 mg, 2 mmol) was taken in CH₂Cl₂ (4 ml) and was stirred at 25 °C. The reaction mixture was monitored by TLC. After completion of the reaction, the reaction mixture was concentrated under reduced pressure to give crude product, which was purified by column chromatography packed with silica gel (60-120 mesh) using pet. ether and EtOAc as eluents to afford pure product.

Hydroamination**1) 1-(4-Methoxyphenyl)-1-(p-toluenesulfonamido)ethane**

Yield: 502 mg (82 %); **mp:** 87-88 °C; ¹H NMR δ: 7.62 (2H, d, *J* = 8.31 Hz), 7.17 (2H, d, *J* = 8.30 Hz), 7.02 (2H, d, *J* = 8.80 Hz), 6.70 (2H, d, *J* = 8.79 Hz), 5.29 (1H, d, *J* = 6.84 Hz), 4.40 (1H, m), 3.73 (3H, s), 2.38 (3H, s), 1.38 (3H, d, *J* = 6.84 Hz); ¹³C NMR δ: 158.49, 142.61, 137.65, 134.23, 129.12, 127.14, 126.84, 113.5, 54.95, 52.89, 23.19, 23.16; **Analysis:** C₁₆H₁₉NO₃ S requires C, 62.93; H, 6.27; N, 4.59; S, 10.5; found C, 62.88; H, 6.21; N, 4.54; S, 10.44 %.

2) 1-(4-Methoxyphenyl)-1-(benzyloxycarbonylamino)ethane

Yield: 456 mg (80 %); **mp:** 78-79 °C; ¹H NMR δ: 7.32 (5H, m), 7.22 (2H, d, *J* = 8.30 Hz), 6.85 (2H, d, *J* = 8.79 Hz), 5.07 (2H, d, *J* = 4.4 Hz), 4.8 (1H, m), 3.77 (3H, s), 1.45 (3H, d, *J* = 6.84 Hz); ¹³C NMR δ: 158.31, 155.33, 136.33, 135.59, 128.02, 127.58, 126.73, 113.54, 66.08, 54.72, 49.76, 21.94; **Analysis:** C₁₇H₁₉NO₃ requires C, 71.56; H, 6.71; N, 4.91; found C, 71.51; H, 6.63; N, 4.85 %.

3) 1-(4-Methoxyphenyl)-1-(methoxycarbonylamino)ethane

Yield: 310 mg (74 %); **mp:** 42-43 °C; $^1\text{H NMR}$ δ : 7.20 (2H, d, $J = 8.22$ Hz), 6.83 (2H, d, $J = 8.61$ Hz), 4.98 (1H, d, $J = 6.27$ Hz), 4.76 (1H, m), 3.77 (3H, s), 3.63 (3H, s), 1.45 (3H, d, $J = 6.65$ Hz); $^{13}\text{C NMR}$ δ : 158.66, 156.09, 135.84, 127.05, 113.82, 54.97, 51.77, 49.97, 22.29; **Analysis:** $\text{C}_{11}\text{H}_{15}\text{NO}_3$ requires C, 63.14; H, 7.17; N, 6.69; found C, 63.07; H, 7.09; N, 6.60 %.

4) 1-(4-Ethoxyphenyl)-1-(*p*-toluenesulfonamido)ethane

Yield: 479 mg (75 %); **mp:** gum; $^1\text{H NMR}$ δ : 7.60 (2H, d, $J = 8.30$ Hz), 7.15 (2H, d, $J = 8.30$ Hz), 6.97 (2H, d, $J = 8.80$ Hz), 6.64 (2H, d, $J = 8.30$ Hz), 5.49 (1H, d, $J = 6.84$ Hz), 4.43-4.30 (1H, m), 4.06-3.88 (3H, m), 2.38 (3H, s), 1.44-1.34 (8H, m); $^{13}\text{C NMR}$ δ : 157.87, 142.58, 137.69, 134.05, 129.12, 127.10, 126.84, 114.13, 63.11, 52.92, 23.15, 23.12, 14.55; **Analysis:** $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}$ requires C, 63.92; H, 6.63; N, 4.39; S, 10.04; found C, 63.81; H, 6.58; N, 4.32; S, 9.98 %.

5) 1-(4-Ethoxyphenyl)-1-(benzyloxycarbonylamino)ethane

Yield: 359 mg (60 %); **mp:** 77-79 °C; $^1\text{H NMR}$ δ : 7.31 (5H, m), 7.20 (2H, d, $J = 8.61$ Hz), 6.82 (2H, d, $J = 8.61$ Hz), 5.07 (2H, d, $J = 3.14$ Hz), 4.98 (1H, d, $J = 9$ Hz), 4.79 (1H, m), 4.01 (2H, quartet, $J = 7.05$ Hz), 1.43 (6H, m); $^{13}\text{C NMR}$ δ : 158.01, 155.33, 136.51, 135.41, 128.28, 127.95, 127.8, 126.99, 114.35, 66.38, 63.11, 49.95, 22.19, 14.77; **Analysis:** $\text{C}_{18}\text{H}_{21}\text{NO}_3$ requires C, 72.22; H, 7.07; N, 4.68; found C, 72.18; H, 7.01; N, 4.53 %.

6) 1-(4-Benzyloxyphenyl)-1-(*p*-toluenesulfonamido)ethane

Yield: 595 mg (78 %); **mp:** 108-109 °C; $^1\text{H NMR}$ δ : 7.62 (2H, d, $J = 8.22$ Hz), 7.39 (5H, m), 7.17 (2H, d, $J = 8.22$ Hz), 7.01 (2H, d, $J = 8.60$ Hz), 6.76 (2H, d, $J = 8.61$ Hz), 5.24 (1H, d, $J = 7.04$ Hz), 4.99 (2H, s), 4.40 (1H, m), 3.73 (3H, s), 2.40 (3H, s), 1.40 (3H, d, $J = 6.65$ Hz); $^{13}\text{C NMR}$ δ : 157.94, 142.5, 138.09, 136.92, 134.64, 129.23, 128.46, 127.8, 127.32, 69.8, 53.03, 23.41, 21.42; **Analysis:** $\text{C}_{22}\text{H}_{23}\text{NO}_3\text{S}$ requires C, 69.27; H, 6.08; N, 3.67; S, 8.41; found C, 69.18; H, 6.01; N, 3.59; S, 8.38 %.

7) 1-(4-Methylthiophenyl)-1-(*p*-toluenesulfonamido)ethane

Yield: 534 mg (83 %); **mp:** 114-115 °C; **¹H NMR** δ: 7.57 (2H, d, *J* = 8.22 Hz), 7.13 (2H, d, *J* = 7.83 Hz), 6.99 (4H, m), 5.58 (1H, d, *J* = 7.04 Hz), 4.37 (1H, m), 2.40 (3H, s), 2.38 (3H, s), 1.37 (3H, d, *J* = 7.04 Hz); **¹³C NMR** δ: 142.58, 139.02, 137.94, 137.37, 129.22, 127.08, 126.68, 53.15, 23.36, 21.43, 15.8; **Analysis:** C₁₆H₁₉NO₂S₂ requires C, 59.78; H, 5.96; N, 4.36; S, 19.95; found C, 59.70; H, 5.89; N, 4.33; S, 19.88 %.

8) 1-(4-Methylthiophenyl)-1-(methoxycarbonylamino)ethane

Yield: 360 mg (80 %); **mp:** 53-54 °C; **¹H NMR** δ: 7.13 (4H, m), 4.86 (1H, m), 4.71 (1H, m), 3.57 (3H, s), 2.39 (3H, s), 1.37 (3H, d, *J* = 6.41 Hz); **¹³C NMR** δ: 155.95, 140.69, 137.22, 127.02, 126.35, 50.14, 29.54, 22.22, 15.90; **Analysis:** C₁₁H₁₅NO₂S requires C, 58.64; H, 6.71; N, 6.22; S, 14.23; found C, 58.57; H, 6.67; N, 6.16; S, 14.1 %.

9) 1-(2-Methyl-4-methoxyphenyl)-1-(*p*-toluenesulfonamido)ethane

Yield: 383 mg (60 %); **mp:** 92-93 °C; **¹H NMR** δ: 7.57 (2H, d, *J* = 8.60 Hz), 7.13 (2H, d, *J* = 8.23 Hz), 7.01 (1H, d, *J* = 9 Hz), 6.50 (2H, s), 5.12 (1H, m), 4.70-4.56 (1H, m), 3.71 (3H, s), 2.37 (3H, s), 2.15 (3H, s), 1.35 (3H, d, *J* = 6.65 Hz); **¹³C NMR** δ: 158.34, 142.46, 138.13, 135.73, 132.66, 129.18, 127.03, 126.77, 115.63, 111.48, 54.9, 49.24, 23.14, 21.44, 19.24; **Analysis:** C₁₇H₂₁NO₃S requires C, 63.92; H, 6.63; N, 4.39; S, 10.04; found C, 63.90; H, 6.59; N, 4.41; S, 9.97 %.

10) 1-(3-Chloro-4-methoxyphenyl)-1-(*p*-toluenesulfonamido)ethane

Yield: 530 mg (78 %); gum; **¹H NMR** δ: 7.57 (2H, d, *J* = 8.22 Hz), 7.14 (2H, d, *J* = 8.22 Hz), 6.95(2H, s), 6.68 (1H, d, *J* = 8.22 Hz), 5.72 (1H, d, *J* = 7.44 Hz), 4.35 (1H, m), 3.81 (3H, s), 2.39 (3H, s), 1.36 (3H, d, *J* = 6.65 Hz); **¹³C NMR** δ: 153.99, 142.75, 137.7, 135.26, 129.2, 128.15, 126.99, 125.51, 122.15, 111.72, 55.85, 52.66, 23.21, 21.37; **Analysis:** C₁₆H₁₈ClNO₃S requires C, 56.55; H, 5.34; N, 4.12; S, 9.44; Cl, 10.43; found C, 56.43; H, 5.30; N, 4.09; S, 9.47; Cl, 10.36 %.

11) 1-(3-Chloro-4-methoxyphenyl)-1-(methoxycarbonylamino)ethane

Yield: 390 mg (80 %); gum; $^1\text{H NMR}$ δ : 7.42 (1H, s), 7.24 (1H, d, $J = 8.61$ Hz), 6.93 (1H, d, $J = 8.22$ Hz), 5.70 (1H, d, $J = 5.78$ Hz), 4.84 (1H, m), 3.94 (3H, s), 3.73 (3H, s), 1.52 (3H, d, $J = 7.04$ Hz); **Analysis:** $\text{C}_{11}\text{H}_{14}\text{ClNO}_3$ requires C, 54.22; H, 5.79; N, 5.75; Cl, 14.55; found C, 54.14; H, 5.84; N, 5.69; Cl, 14.51 %.

12) 1-(4-Isopropoxyphenyl)-1-(*p*-toluenesulfonamido)ethane

Yield: 456 mg (66 %); gum; $^1\text{H NMR}$ δ : 7.64 (2H, d, $J = 8.06$ Hz), 7.16 (2H, d, $J = 8.06$ Hz), 7.01 (2H, d, $J = 8.80$ Hz), 6.66 (2H, d, $J = 8.06$ Hz), 5.79 (1H, d, $J = 7.33$ Hz), 4.4 (2H, m), 2.39 (3H, s), 1.41-1.31 (9H, m); $^{13}\text{C NMR}$ δ : 157.08, 142.37, 138.31, 134.61, 129.15, 127.26, 127.11, 115.63, 69.58, 53.07, 23.4, 22.0, 21.33; **Analysis:** $\text{C}_{19}\text{H}_{23}\text{NO}_3\text{S}$ requires C, 66.06; H, 6.71; N, 4.05; S, 9.28; found C, 65.94; H, 6.77; N, 4.02; S, 9.21 %.

13) 1-(4-Cyclopentyloxyphenyl)-1-(*p*-toluenesulfonamido)ethane

Yield: 446 mg (62%); gum; $^1\text{H NMR}$ δ : 7.62 (2H, d, $J = 8.21$ Hz), 7.13 (2H, d, $J = 8.22$ Hz), 6.94 (2H, d, $J = 8.61$ Hz), 6.59 (2H, d, $J = 8.61$ Hz), 5.35 (1H, m), 4.64 (1H, m), 4.43-4.29 (1H, m), 2.38 (3H, s), 1.80 (8H, m), 1.38 (3H, d, $J = 6.65$ Hz); **Analysis:** $\text{C}_{20}\text{H}_{25}\text{NO}_3\text{S}$ requires C, 66.82; H, 7.01; N, 3.90; S, 8.92; found C, 66.70; H, 7.08; N, 3.81; S, 8.90 %.

Hydroalkoxylation

General experimental procedure for the Hydroalkoxylation of activated styrenes:

A mixture of olefin (2 mmol), N-bromosuccinimide (20 mol%), alcohol (2 mmol) was taken in CH₂Cl₂ (4 ml) and stirred at 25 °C. The reaction was monitored by TLC. After completion of the reaction, the reaction mixture was concentrated under reduced pressure to give crude product, which was purified by column chromatography packed with silica gel (60-120 mesh) using pet. ether and EtOAc as eluents to afford pure product.

1) 1-(4-Methoxyphenyl)-1-(benzyloxy)ethane

Yield: 392 mg (81%); liquid; ¹H NMR δ: 7.25 (7H, m), 6.85 (2H, m), 4.53-4.18 (3H, m), 3.73 (3H, s), 1.44 (3H, d, *J* = 6.26 Hz); **Analysis:** C₁₆H₁₈O₂ requires C, 79.31; H, 7.49; found C, 79.2; H, 7.44.

2) 1-(4-Methoxyphenyl)-1-(methoxy)ethane

Yield: 279 mg (84%); liquid; ¹H NMR δ: 7.17 (2H, d, *J* = 8.79 Hz), 6.82 (2H, d, *J* = 8.79 Hz), 4.19 (1H, quartet, *J* = 6.35 Hz), 3.78 (3H, s), 3.15 (3H, s), 1.39 (3H, d, *J* = 6.84 Hz); ¹³C NMR δ: 158.73, 135.27, 126.97, 113.43, 78.77, 55.59, 54.50, 23.67; **Analysis:** C₁₀H₁₄O₂ requires C, 72.26; H, 8.49; found C, 72.20; H, 8.39 %.

3) 1-(4-Methylthiophenyl)-1-(benzyloxy)ethane

Yield: 439 mg (85%); liquid; ¹H NMR δ: 7.28 (5H, m), 7.24 (4H, m), 4.45-4.22 (3H, m), 2.47 (3H, s), 1.45 (3H, d, *J* = 6.26 Hz); ¹³C NMR δ: 140.73, 138.63, 137.50, 128.19, 127.48, 127.30, 126.97, 126.78, 76.66, 70.13, 24.01, 15.92; **Analysis:** C₁₆H₁₈OS requires C, 74.38; H, 7.02; S, 12.41; found C, 74.41; H, 7.01; S, 12.30 %.

4) 1-(4-Methylthiophenyl)-1-(methoxy)ethane

Yield: 314 mg (86%); liquid; $^1\text{H NMR}$ δ : 7.18 (4H, m), 4.20 (1H, quartet, $J = 6.10$ Hz), 3.17 (3H, s), 2.45 (3H, s), 1.39 (3H, d, $J = 6.11$ Hz); **Analysis:** $\text{C}_{10}\text{H}_{14}\text{OS}$ requires C, 65.89; H, 7.74; S, 17.52; found C, 65.80; H, 7.81; S, 17.52 %.

5) 1-(3-Chloro-4-methoxyphenyl)-1-(benzyloxy)ethane

Yield: 459 mg (83%); liquid; $^1\text{H NMR}$ δ : 7.34-7.14 (8H, m), 6.88 (1H, d, $J = 8.21$ Hz), 4.45-4.21 (3H, m), 3.89 (3H, s), 1.44 (3H, d, $J = 6.26$ Hz); **Analysis:** $\text{C}_{16}\text{H}_{17}\text{ClO}_2$ requires C, 69.44; H, 6.19; Cl, 12.81; found C, 69.32; H, 6.10; Cl, 12.93 %.

6) 1-(4-Methoxyphenyl)-1-(allyloxy)ethane

Yield: 326 mg (85%); liquid; $^1\text{H NMR}$ δ : 7.20 (2H, d, $J = 8.60$ Hz), 6.83 (2H, d, $J = 8.61$ Hz), 5.94-5.77 (1H, m), 5.26-5.09 (2H, m), 4.38 (1H, q, $J = 6.26$ Hz), 4.16-3.89 (2H, m), 3.79 (3H, s), 1.42 (3H, d, $J = 6.26$ Hz); $^{13}\text{C NMR}$ δ : 158.98, 135.23, 127.91, 127.24, 116.0, 113.75, 76.63, 68.94, 54.90, 23.99; **Analysis:** $\text{C}_{10}\text{H}_{14}\text{O}_2$ requires C, 74.97; H, 8.39; found C, 74.83; H, 8.31 %.

7) 1-(4-Methoxyphenyl)-1-(propargyloxy)ethane

Yield: 289 mg (76%); liquid; $^1\text{H NMR}$ δ : 7.22 (2H, d, $J = 8.61$ Hz), 6.84 (2H, d, $J = 8.61$ Hz), 4.59 (1H, quartet, $J = 6.65$ Hz), 4.07-3.98 (1H, m), 3.86-3.82 (1H, m), 3.79 (3H, s), 2.34 (1H, m), 1.45 (3H, d, $J = 6.65$ Hz); **Analysis:** $\text{C}_{10}\text{H}_{14}\text{O}_2$ requires C, 75.76; H, 7.42; found C, 75.62; H, 7.31 %.

Spectra

UV Spectra

NMR studies:

¹H Spectrum of reaction mixture of 4-methoxystyrene and TsNHBr