Supplementary Information

Selective Iron-catalyzed Transfer Hydrogenation of Terminal Alkynes

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General comments

All reactions were carried out under argon atmosphere. Chemicals were purchased from Aldrich, Fluka, Acros, Alfa Aesar and used without further purification. NMR data were recorded on Bruker ARX 400 and Bruker ARX 300 spectrometers. ^{13}C- and ^{1}H-NMR spectra were referenced to signals of the deutero solvents. The Gas chromatography analysis was performed on an Agilent HP-6890 instrument with a FID detector and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.32 mm i.d., 0.25 µm film thickness) using argon as carrier gas. Gas chromatography-mass analysis was carried out on an Agilent HP-5890 instrument with an Agilent HP-5973 Mass Selective Detector (EI) and HP-5 capillary column (polydimethylsiloxane with 5% phenyl groups, 30 m, 0.25 mm i.d., 0.25 µm film thickness) using helium carrier gas. HRMS was performed on MAT 95XP (EI) and Agilent 6210 Time-of-Flight LC/MS (ESI).

General procedure

$Fe(BF_4)_2 \cdot 6H_2O$ (1 mg; 0.003 mmol) and tetraphos (2 mg; 0.003 mmol) are placed in a Schlenk-tube under argon atmosphere. 1 mL dry tetrahydrofurane is added and the purple solution is stirred for 2 min. Phenylacetylene (55 µL; 0.5 mmol) and 100 µL *n*-hexadecane as an internal GC-standard are injected and a sample is taken for GC-analysis. The solution is heated to 40 °C and the reaction starts by addition of 2 equiv formic acid (40 µL; 0.1 mmol). After 2 hours, a second sample is taken for GC-analysis and conversion and yield are determined by comparison with authentic samples. For the isolation, the reaction is scaled up by the factor of 2. No standard is required. When the reaction is completed, the reaction solution is diluted with a mixture of *n*-hexane and ethyl acetate (3:1), filtered through a plug of silica and the solvent removed *in vacuo*.

Analytical Data

3-Vinylphenol

^{1}H NMR (300 MHz, CDCl3): δ = 7.21-7.33 (m, 1H), 7.02-7.08 (m, 1H), 6.94-6.98 (m, 1H), 6.75-6.85 (m, 1H), 6.72 (dd, 1 H, *J* ~ 17.65 Hz, 28.46 Hz), 5.78 (d, 1H, *J* ~ 17.51 Hz), 5.31 (d, 1H, *J* ~ 10.94 Hz), 5.09 (br, 1H).
^{13}C NMR (75 MHz, CDCl3): δ = 155.76, 139.45, 136.56, 129.88, 119.27, 114.96, 114.48, 112.88.
ATR-IR (cm^{-1}) (neat): 3285 (s), 3088 (m), 2979 (m), 2875 (m), 1706 (m), 1579 (s), 1491 (m), 1450 (s), 1414 (w), 1339 (s), 1257 (s), 1234 (s), 1155 (s), 1047 (s), 989 (s), 909 (s), 865 (s), 785 (s), 714 (s).
GC-MS (EI, 70eV): m/z(%) = 120 (M^+, 100), 119 (17), 94 (15), 92 (14), 91 (93), 65 (23), 63 (16), 51 (11), 39 (17).
HR-MS (EI): Calc. for $C_8H_8O_1$: 120.05697; found: 120.056954.

2-Vinylbenzylalcohol

^{1}H NMR (300 MHz, CDCl3): δ = 7.47-7.55 (m, 1H), 7.20-7.36 (m, 3H), 7.02 (dd, 1H, *J* ~ 17.40 Hz, 28.38 Hz), 5.67 (d, 1H, *J* ~ 17.36 Hz), 5.33 (d, 1H, *J* ~ 11.01 Hz), 4.72 (s, 2H), 1.83 (s, 1H).
^{13}C NMR (75 MHz, CDCl3): δ = 137.6, 136.7, 133.9, 128.4, 128.3, 128.0, 126.1, 116.6, 63.5.
ATR-IR (cm^{-1}) (neat): 3297 (s), 3065 (m), 3031 (w), 2885 (m), 1718 (w), 1627 (m), 1571 (w), 1483 (s), 1452 (m), 1415 (m), 1282 (w), 1210 (m), 1184 (m), 1102 (m), 1004 (s), 946 (w), 914 (s), 837 (w), 761 (s), 731 (s).
GC-MS (EI, 70eV): m/z(%) = 134 (M^+, 79), 133 (98), 117 (11), 116 (25), 115 (67), 106 (11), 105 (100), 103 (31), 102 (12), 91 (56), 89 (14), 79 (42), 78 (21), 77 (61), 74 (12), 65 (11), 63 (20), 51 (29), 50 (17), 39 (16).
HR-MS (EI): Calc. for $C_9H_{10}O_1$: 134.07262; found: 134.073353.

4-Vinylacetophenone

^{1}H NMR (300 MHz, CDCl3): δ = 7.92 (d, 2H, *J* = 8.38 Hz), 7.48 (d, 2H, *J* ~ 8.28 Hz), 6.76 (dd, 1H, *J* ~ 10.88 Hz, 17.64 Hz), 5.88 (d, 1H, *J* ~ 17.64 Hz), 5.40 (d, 1H, *J* ~ 10.89 Hz), 2.59 (s, 3H).
^{13}C NMR (75 MHz, CDCl3): δ = 197.7, 142.2, 136.4, 136.1, 128.8, 126.4, 116.9, 26.7.
ATR-IR (cm^{-1}) (neat): 2920 (s), 2851 (s), 1685 (s), 1604 (m), 1561 (w), 1462 (m), 1402 (m), 1377 (w), 1356 (m), 1307 (w), 1178 (m), 1119 (w), 1075 (w), 1012 (w), 990 (m), 954 (w), 930 (w), 914 (m), 844 (s), 721 (m).
GC-MS (EI, 70eV): m/z(%) = 146 (M^+, 34), 131 (100), 103 (46), 102 (12), 77 (30), 51 (13).
HR-MS (EI): Calc. for $C_{10}H_{10}O_1$: 146.07262; found: 146.072714.

Methyl 4-vinylbenzoate

^{1}H NMR (300 MHz, CDCl3): δ = 7.96-8.04 (m, 2H), 7.44-7.48 (m, 2H), 6.75 (dd, 1H, *J* ~ 17.61 Hz, 28.55 Hz), 5.86 (d, 1H, *J* ~ 17.62 Hz), 5.38 (d, 1H, *J* ~ 10.84 Hz), 3.91 (s, 3H).
^{13}C NMR (75 MHz, CDCl3): δ = 167.0, 142.1, 136.2, 130.0, 129.4, 126.3, 116.6, 52.2.
ATR-IR (cm^{-1}) (neat): 2979 (w), 2948 (m), 2847 (m), 1710 (s), 1629 (w), 1605 (m), 1563 (w), 1437 (s), 1403 (m), 1316 (w), 1275 (s), 1193 (w), 1180 (s), 1106 (s), 1014, 994, 961, 930, 860, 835, 783, 714.
GC-MS (EI, 70eV): m/z(%) = 162 (M^+, 44), 131 (100), 103 (36), 102 (12), 77 (30), 51 (13).
HR-MS (EI): Calc. for $C_{10}H_{10}O_2$: 162.06753; found: 162.067660.

1,4-Divinylbenzene

^{1}H NMR (300 MHz, CDCl3): δ = 7.38 (s, 4H), 6.71 (dd, 2 H, *J* ~ 17.64 Hz, 28.46 Hz), 5.75 (d, 2H, *J* ~ 17.65 Hz), 5.24 (d, 2H, *J* ~ 10.85 Hz).
^{13}C NMR (75 MHz, CDCl3): δ = 137.2, 136.6, 126.5, 113.9.
ATR-IR (cm^{-1}) (neat): 3087 (m), 3006 (m), 1820 (m), 1702 (m), 1628 (s), 1605 (w), 1558 (w), 1509 (s), 1400 (s), 1289 (m), 1210 (m), 1167 (w), 1118 (w), 1040 (w), 1013 (1013), 987 (s), 903 (s), 842 (s), 747 (w), 701 (m).

GC-MS (EI, 70eV): m/z(%) = 130 (M^+, 100), 129 (36), 128 (38), 127 (17), 115 (34), 103 (11), 77 (14), 51 (13).
HR-MS (EI): Calc. for $C_{10}H_{10}$: 130.07770; found: 130.077377.

3-Vinylthiophene

^{1}H NMR (300 MHz, CDCl3): δ = 7.22-7.33 (m, 2H), 7.14-7.20 (m, 1H), 6.71 (dd, 1H, *J* = 17.54 Hz, 28.41 Hz), 5.58 (d, 1H, *J* = 17.58 Hz), 5.19 (d, 1H, *J* = 10.95 Hz).
^{13}C NMR (75 MHz, CDCl3): δ = 140.6, 131.1, 126.1, 124.8, 122.4, 113.7.
ATR-IR (cm^{-1}) (neat): 3090 (m), 3008 (w), 1677 (w), 1630 (s), 1519 (w), 1428 (w), 1394 (w), 1354 (w), 1298 (w), 1244 (m), 1211 (w), 1152 (m), 1082 (m), 1023 (w), 986 (s), 900 (s), 862 (s), 826 (m), 785 (s).
GC-MS (EI, 70eV): m/z(%) = 110 (M^+, 100), 109 (41), 84 (42), 69 (11), 66 (28), 65 (13), 58 (15), 51 (11), 50 (11), 45 (24), 39 (26).
HR-MS (EI): Calc. for C_6H_6S: 110.01847; found: 110.01827.

1-Vinylcyclohexene

^{1}H NMR (300 MHz, CDCl3): δ = 6.34 (dd, 1H, *J* = 17.52 Hz, 28.19 Hz), 5.76 (s, 1H), 5.06 (d, 1H, *J* = 17.69 Hz), 4.88 (d, 1H, *J* = 10.8 Hz), 2.09-2.18 (m, 4H), 1.55-1.73 (m, 4H).
^{13}C NMR (75 MHz, CDCl3): δ = 140.4 136.2, 130.0, 109.7, 25.9, 23.9, 22.7, 22.5.
ATR-IR (cm^{-1}) (neat): 3088 (w), 3003 (w), 2926 (s), 2859 (m), 2835 (w), 1641 (m), 1605 (m), 1449 (w), 1436 (m), 1349 (w), 1314 (w), 1269 (w), 1186 (w), 1136 (m), 1080 (w), 1024 (w), 988 (s), 916 (w), 890 (s), 845 (s), 802 (m).
GC-MS (EI, 70eV): m/z(%) = 108 (M^+, 33), 93 (64), 91 (29), 80 (21), 79 (100), 78 (14), 77 (35), 67 (14), 65 (13), 51 (15), 41 (17), 39 (26).
HR-MS (EI): Calc. for C_8H_{12}: 108.09335; found: 108.092832.

1H-NMR of the partially deuterated 4-vinylacetophenone