Supporting information

Examining the vinyl moiety as a protecting group for hydroxyl (-OH) functionality under basic conditions

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General information

All chemicals of the reagent grade or higher purity level were purchased from Sigma Aldrich, Alfa Aesar, and Acros Organics and used without further purification unless otherwise noted. Granulated CaC₂ of the technical grade purity (>75%) was purchased from Sigma Aldrich. NMR spectra were recorded on a Bruker Avance 400 (¹H 400 MHz; ¹³C 101 MHz) and a Bruker Avance 500 (¹H 500 MHz; ¹³C 126 MHz) spectrometers. Chemical shifts δ are reported in ppm relative to residual CHCl₃ (¹H, δ = 7.26) or DMSO (¹H, δ = 2.50) and CDCl₃ (¹³C, δ = 77.16) or DMSO-d₆ (¹³C, δ = 39.52) as internal standards. High-resolution mass spectra (HRMS) were recorded on a Bruker micrOTOF spectrometer using electrospray ionization (ESI). The reactions were monitored by TLC analysis using Merck UV-254 plates. Flash chromatography was performed using Merck silica gel 60 (230–400 Mesh). Before vinyl ethers purification, silica gel was neutralized with triethylamine.

Sequential Vinylation of 2l

A reaction tube was loaded with alcohol **11** (1.0 mmol), KOH (1.25 mmol, 69 mg), KF (4.0 mmol, 232 mg) and calcium carbide (2.0 mmol, 128 mg). DMSO (1.5 mL) and H₂O (4.0 mmol, 72 μ L) were added, the tube was immediately sealed, and the mixture was stirred at 130 °C for 3 h. After cooling to 25 °C, the mixture was extracted with hexane (6 × 3 mL), the collected hexane layers were concentrated under reduced pressure and the residue was placed in a reaction tube containing new portions of the reagents. DMSO and water were added, the tube was sealed and the mixture was stirred at 130 °C for 3 h. After cooling to 25 °C the action was repeated again. After three consecutive vinylations the product was purified from residual **11** by flash chromatography.

(4-Chlorophenyl)methyl Vinyl Ether 2b

Yield 152 mg (90%). Pale yellow oil. ¹H NMR (400 MHz, DMSO-d₆) δ = 7.43 (d, *J* = 8.6 Hz, 2H), 7.39 (d, *J* = 8.6 Hz, 2H), 6.58 (dd, *J* = 14.2, 6.7 Hz, 1H; OCH=), 4.77 (s, 2H, CH₂O), 4.30 (dd, *J* = 14.2, 1.9 Hz, 1H; =CH₂), 4.06 (dd, *J* = 6.7, 1.9 Hz, 1H; =CH₂). ¹³C NMR (101 MHz, DMSO-d₆) δ = 151.6 (OCH=), 136.1 (C), 132.3 (C), 129.3 (2CH), 128.3 (2CH), 87.9 (=CH₂), 68.7 (CH₂O). HRMS (ESI) *m/z* [M+Ag]⁺ calcd for C₉H₉ClOAg⁺: 276.9381, found: 276.9370.

(4-Bromophenyl)methyl Vinyl Ether 2c

Yield 189 mg (89%). Pale yellow oil. ¹H NMR (400 MHz, DMSO-d₆) δ = 7.57 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.5 Hz, 2H), 6.58 (dd, *J* = 14.2, 6.7 Hz, 1H; OCH=), 4.75 (s, 2H, CH₂O), 4.30 (dd, *J* = 14.2, 1.9 Hz, 1H; =CH₂), 4.06 (dd, *J* = 6.7, 1.9 Hz, 1H; =CH₂). ¹³C NMR (101 MHz, DMSO-d₆) δ = 151.5 (OCH=), 136.5 (C), 131.2 (2CH), 129.6 (2CH), 120.8 (C), 87.9 (=CH₂), 68.7 (CH₂O). HRMS (ESI) *m/z* [M+Ag]⁺ calcd for C₉H₉BrOAg⁺: 320.8865, found: 320.8880.

Octyl Vinyl Ether 2d

Yield 142 mg (91%). Pale yellow oil. ¹H NMR (400 MHz, CDCl₃) $\delta = 6.46$ (dd, J = 14.3, 6.8 Hz, 1H; OCH=), 4.17 (dd, J = 14.3, 1.8 Hz, 1H; =CH₂), 3.96 (dd, J = 6.8, 1.8 Hz, 1H; =CH₂), 3.67 (t, J = 6.6 Hz, 2H; CH₂O), 1.69-1.61 (m, 2H), 1.39-1.27 (m, 10H), 0.88 (t, J = 6.6 Hz, 3H; CH₃). ¹³C NMR (101 MHz, CDCl₃) $\delta = 152.2$ (OCH=), 86.3 (=CH₂), 68.3 (CH₂O), 32.0 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.2 (CH₂), 26.2 (CH₂), 22.8 (CH₂), 14.2 (CH₃). HRMS (ESI) m/z [M+Ag]⁺ calcd for C₁₀H₂₀OAg⁺: 263.0560, found: 263.0559.

Decyl Vinyl Ether 2e

Yield 175 mg (95%). Pale yellow oil. ¹H NMR (400 MHz, CDCl₃) $\delta = 6.46$ (dd, J = 14.3, 6.8 Hz, 1H; OCH=), 4.17 (dd, J = 14.3, 1.8 Hz, 1H; =CH₂), 3.96 (dd, J = 6.8, 1.8 Hz, 1H; =CH₂), 3.67 (t, J = 6.6 Hz, 2H; CH₂O), 1.69-1.61 (m, 2H), 1.39-1.22 (m, 14H), 0.88 (t, J = 6.8 Hz, 3H; CH₃). ¹³C NMR (101 MHz, CDCl₃) $\delta = 152.2$ (OCH=), 86.3 (=CH₂), 68.3 (CH₂O), 32.0 (CH₂), 29.72 (CH₂), 29.70 (CH₂), 29.54 (CH₂), 29.46 (CH₂), 29.2 (CH₂), 26.2 (CH₂), 22.8 (CH₂), 14.2 (CH₃). HRMS (ESI) m/z [M+Ag]⁺ calcd for C₁₂H₂₄OAg⁺: 291.0873, found: 291.0873.

1,10-Bis(vinyloxy)decane 2i

Yield 213 mg (94%). Pale yellow oil. ¹H NMR (400 MHz, CDCl₃) $\delta = 6.46$ (dd, J = 14.3, 6.8 Hz, 2H; 2OCH=), 4.17 (dd, J = 14.3, 1.8 Hz, 2H; 2=CH₂), 3.97 (dd, J = 6.8, 1.8 Hz, 2H; 2=CH₂), 3.67 (t, J = 6.6 Hz, 4H; 2CH₂O), 1.68-1.61 (m, 4H), 1.39-1.29 (m, 12H). ¹³C NMR (101 MHz, CDCl₃) $\delta = 152.2$ (2OCH=), 86.3 (2=CH₂), 68.3 (2CH₂O), 29.6 (2CH₂), 29.5 (2CH₂), 29.2 (2CH₂), 26.1 (2CH₂). HRMS (ESI) m/z [M+Ag]⁺ calcd for C₁₄H₂₆O₂Ag⁺: 333.0978, found: 333.0978.

Testing of 2a Stability under Various Conditions

71.5 mg of dry toluene and 153 mg of **2a** were added to 3.2 mL of the corresponding solvent. After stirring, an aliquot (200 μ L) of the solution was added to 0.083 mmol of an additive (see Table 2 for the list). After 24 h, 500 μ L of CDCl₃ was added to the mixture and checked.

Gram-Scale Synthesis of 2c

A reaction tube was loaded with **1c** (1.496 g, 8.0 mmol), KOH (10.0 mmol, 560 mg), KF (32.0 mmol, 1.856 g) and calcium carbide (16.0 mmol, 1.024 g). DMSO (12 mL) and H₂O (32.0 mmol, 576 μ L) were added, the tube was immediately sealed, and the mixture was stirred at 130 °C for 3 h. After cooling to 25 °C, the mixture was extracted with hexane (6 × 10 mL), and the collected hexane layers were concentrated under reduced pressure to afford **2c**. Yellow oil, yield 1.380 g (81%).

Cross-Coupling Reactions with Vinyl Protected Bromide 2c



Suzuki cross-coupling reaction of 2c with phenylboronic acid was performed in accordance with the previously described procedure^[1] and afforded vinyl ether 3a in 91% yield. Sonogashira reaction was performed according to a modified protocol.^[2] A reaction tube was loaded with 14 mg (0.02 mmol) of PdCl₂(PPh₃)₂, 1 mg (0.005 mmol) of CuI, and 4 mL of triethylamine solution of 2c (213 mg, 1 mmol) under argon. After complete dissolution of the catalysts, 170 µL (1.2 mmol) of (trimethylsilyl)acetylene was added to the tube and the mixture was stirred at 80 °C for 24 h. The solids were removed by filtration and washed with triethylamine. The resulting mixture was analyzed by ¹H NMR spectroscopy; the NMR yield of 4a was 75%. Solvent was removed under reduced pressure to afford crude 4a, which was used in the next step without purification.

4-(Vinyloxymethyl)biphenyl 3a

White solid, m. p. 48-50 °C. ¹H NMR (400 MHz, CDCl₃) δ = 7.62-7.60 (m, 4H), 7.48-7.43 (m, 4H), 7.36 (t, *J* = 7.3 Hz, 1H), 6.61 (dd, *J* = 14.3, 6.8 Hz, 1H; OCH=), 4.83 (s, 2H; CH₂O), 4.35 (dd, *J* = 14.3, 2.1 Hz, 1H; =CH₂), 4.13 (dd, *J* = 6.8, 2.1 Hz, 1H; =CH₂). ¹³C NMR (101 MHz, CDCl₃) δ = 151.8 (OCH=), 141.1 (C), 141.0 (C), 136.0 (C), 128.9 (2CH), 128.2 (2CH), 127.5 (CH), 127.4 (2CH), 127.3 (2CH), 87.6 (=CH₂), 70.0 (CH₂O). HRMS (ESI) *m*/*z* [M+Ag]⁺ calcd for C₁₅H₁₄OAg⁺: 317.0090, found: 317.0087.

Biphenyl-4-ylmethanol³ 3

Compound **3** was obtained according to the general procedure for vinyl ethers hydrolysis. White solid, m. p. 95-97 °C (lit.³ 97-99 °C). Yield 166 mg (99%). ¹H NMR (400 MHz, CDCl₃) δ = 7.62-7.59 (m, 4H), 7.48-7.43 (m, 4H), 7.37 (t, *J* = 7.3 Hz, 1H), 4.74 (s, 2H; CH₂O), 1.95 (s, 1H; OH). ¹³C NMR (101 MHz, CDCl₃) δ = 141.0 (C), 140.8 (C), 140.0 (C), 128.9 (2CH), 127.6 (2CH), 127.4 (3CH), 127.2 (2CH), 65.2 (CH₂O). HRMS (ESI) *m*/*z* [M+Ag]⁺ calcd for C₁₃H₁₂OAg⁺: 290.9934, found: 290.9931.

(4-((trimethylsilyl)ethynyl)phenyl)methanol² 4

Compound **4** was obtained according to the general procedure for vinyl ethers hydrolysis. Yellow solid, m. p. 62-64 °C (lit.² 66 °C). Yield 149 mg (73% ower two steps). ¹H NMR (400 MHz, CDCl₃) δ = 7.44 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 4.62 (s, 2H; CH₂O), 2.21 (s, 1H; OH), 0.25 (s, 9H; TMS). ¹³C NMR (101 MHz, CDCl₃) δ = 141.4 (C), 132.2 (2CH), 126.7 (2CH), 122.4 (C), 105.1 (C=), 94.3 (C=), 64.9 (CH₂O), 0.1 (TMS). HRMS (ESI) *m*/*z* [M+Ag]⁺ calcd for C₁₂H₁₆OSiAg⁺: 311.0016, found: 311.0011.

(4-(Vinyloxymethyl)phenyl)magnesium Bromide 5

Vinyl ether 2c was dried over calcium hydride before the reaction. Mg (216 mg, 9 mmol), anhydrous THF (3 mL), aryl bromide 2c (1.278 g, 6 mmol) and a crystal of iodine were placed in a dry round-bottom Schlenk flask under argon. The mixture was carefully heated with a heat gun until the reaction started and stirred under reflux for 30 min. After cooling to room temperature, solution of the Grignard reagent 5 was separated from the unreacted magnesium with a syringe and used in the next step.

4-Deuterobenzyl Vinyl Ether 6

The solution containing 1.2 mmol of **5** was added dropwise to 0.5 ml of D₂O under vigorous stirring at 0 °C. The resulting mixture was extracted with 2 mL of hexane and centrifuged. Extraction and centrifugation were repeated 6 times, and the collected hexane layers were concentrated under reduced pressure to give vinyl ether **6**. Pale yellow oil, yield 147 mg (91%). ¹H NMR (400 MHz, CDCl₃) δ = 7.40-7.35 (m, 4H), 6.58 (dd, *J* = 14.3, 6.8 Hz, 1H; OCH=), 4.78 (s, 2H; CH₂O), 4.33 (dd, *J* = 14.3, 2.1 Hz, 1H; =CH₂), 4.10 (dd, *J* = 6.8, 2.1 Hz, 1H; =CH₂). ¹³C NMR (101 MHz, CDCl₃) δ = 151.8 (OCH=), 137.0 (C), 128.5 (2CH), 127.7 (2CH), 87.5 (=CH₂), 70.2 (CH₂O). HRMS (ESI) *m*/*z* [M+H]⁺ calcd for C₉H₁₀DO⁺: 136.0867, found: 136.0865.

4-Deuterobenzyl Alcohol 7

Compound **7** was obtained according to the general procedure for vinyl ethers hydrolysis. Pale yellow oil, yield 98 mg (90%). ¹H NMR (400 MHz, CDCl₃) δ = 7.36 (s, 4H), 4.68 (s, 2H; CH₂O), 1.99 (br s, 1H; OH). ¹³C NMR (126 MHz, CDCl₃) δ = 141.0 (C), 128.6 (2CH), 127.5 (t, *J* = 24.4 Hz; CD), 127.1 (2CH), 65.4 (CH₂O). HRMS (ESI) *m*/*z* [M+Na]⁺ calcd for C₇H₇DONa⁺: 132.0530, found: 132.0532.

 $^1\mathrm{H}$ (400 MHz, DMSO-d_6) and $^{13}\mathrm{C}$ (101 MHz, DMSO-d_6) NMR spectra of 4-chlorobenzyl vinyl ether 2b



 $^1\mathrm{H}$ (400 MHz, DMSO-d_6) and $^{13}\mathrm{C}$ (101 MHz, DMSO-d_6) NMR spectra of 4-bromobenzyl vinyl ether 2c









¹H (400 MHz, CDCl₃) and ¹³C (101 MHz, CDCl₃) NMR spectra of 1,10-*bis*(vinyloxy)decane 2i



¹H (400 MHz, CDCl₃) and ¹³C (101 MHz, CDCl₃) NMR spectra of 4-(vinyloxymethyl)biphenyl 3a



 $^1\mathrm{H}$ (400 MHz, CDCl_3) and $^{13}\mathrm{C}$ (101 MHz, CDCl_3) NMR spectra of (4-((trimethylsilyl)ethynyl)-phenyl)methanol 4









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