Supporting Information

for

Potassium Carbonate-Silica: A Highly Effective Stationary Phase for the Chromatographic Removal of Organotin Impurities.

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General Experimental

Reagents were obtained commercially and used without further purification unless indicated otherwise. All reactions were carried out in oven-dried glassware under an inert atmosphere of argon where appropriate. THF and diethyl ether were freshly distilled from a purple solution of sodium benzophenone ketyl radical. Chromatographic purification was performed using the K₂CO₃-silcia method (10% w/w anhydrous potassium carbonate in silica 60A Particle Size 30–70 micron). ¹H NMR spectra were recorded on either a Bruker AV-300 (300 MHz) or DPX-400 (400 MHz) spectrometer operating at 298 K. Chemical shifts are quoted in parts per million downfield of tetramethylsilane with residual solvent as the internal standard. Assignments were made on the basis of chemical shift, coupling constants, COSY and comparison of spectra with those of related compounds. Coupling constants (*J*) are reported in hertz and are round to the nearest 0.1 Hz. The NMR solvent CDCl₃ was taken from a stock containing anhydrous K₂CO₃ to remove residual HCl.

Experimental Procedures, ¹H NMR Data and Recorded ¹H NMR Spectra

5-[1,3]Dithian-2-ylbenzo[1,3]dioxole, 2¹



5-Bromo-6-[1,3]dithian-2-ylbenzo[1,3]dioxole (80 mg, 0.25 mmol), tributyltin hydride (134 μ L, 0.50 mmol) and TBAF (1 M in THF:H₂O (95:5), 1.0 mL, 1.0 mmol) were heated in toluene (5 mL) at 90 °C for 1 h. The resulting solution was cooled to RT and concentrated *in vacuo*. Purification by column chromatography (10% w/w anhydrous K₂CO₃-silica; 10% diethyl ether in petroleum ether) afforded the title compound as a white crystalline solid (59 mg, 99%).



(S)-3-(3-Bromo-4-vinyl-phenyl)-2-*tert*-butoxycarbonylaminopropionic acid methyl ester, 4



To a stirred solution of (*S*)-3-(3-bromo-4-trifluoromethanesulfonyloxyphenyl)-2-*tert*butoxycarbonylaminopropionic acid methyl ester (2.25 g, 4.45 mmol), tributylvinyltin (1.30 mL, 4.45 mmol) and LiCl (0.94 g, 22.2 mmol) in DMF (45 mL) was added Pd(dppf)Cl₂.CH₂Cl₂ (0.18 g, 0.22 mmol). The reaction mixture was stirred at RT for 16 h then partitioned between water (50 mL) and ethyl acetate (50 mL). The aqueous phase was separated and extracted with ethyl acetate (2 x 50 mL). The combined organic phases were washed with water (5 x 50 mL) and brine (50 mL), dried (MgSO₄) and concentrated *in vacuo*. Purification by column chromatography (10% w/w anhydrous K₂CO₃-silica; 10% ethyl acetate in petroleum ether) afforded the title compound as a colourless oil (1.39 g, 81%).



Indole-2-carboxaldehyde, 6



Following the procedure of Guibe *et al.*² To a stirred suspension of indole-2-carbonyl chloride (0.337 g, 1.88 mmol) and Pd(PPh₃)₄ (0.023 g, 0.02 mmol) in toluene (4 mL) was added tributyltin hydride (0.56 mL, 2.07 mmol) dropwise over 5 min. After 1 h at RT the reaction mixture was filtered through Celite[®] and concentrated *in vacuo*. Purification by column chromatography (10% w/w anhydrous K₂CO₃-silica; 10% ethyl acetate in petroleum ether) afforded the title compound as a white solid (0.087 g, 32%).



9,10-Dimethoxy[7]helicene, 8³



A solution of *bis*-stilbene 7 (175 mg, 0.25 mmol), tributyltin hydride (170 μ L, 0.63 mmol) and VAZO (12 mg, 0.05 mmol) in toluene (5 mL) was heated at 90 °C, with further tributyltin hydride (170 μ L, 0.63 mmol) and VAZO (12 mg, 0.05 mmol) added after 4 h. After 24 h the reaction mixture was cooled to RT and concentrated *in vacuo*. Purification by column chromatography (10% w/w anhydrous K₂CO₃-silica; 10% diethyl ether in petroleum ether) afforded the title compound as orange needles (83 mg, 75%).



8,9-Dimethoxy-5-((E)-3-tributylstannylallyl)-5H-phenanthridin-6-one, 10



A solution of alkyne **9** (0.27 mmol, 0.10 g), tributyltin hydride (0.56 mmol, 0.16 mL) and VAZO (3 mg) in toluene (30 mL) was heated at reflux under nitrogen for 16 h then cooled to RT. Further tributyltin hydride (0.56 mmol, 0.16 mL) and VAZO (3 mg) were added. After 48 h at reflux the reaction mixture was cooled to RT, concentrated, re-dissolved in ether (30 mL) and stirred vigorously with a saturated aqueous solution of KF (50 mL) for 30 min. The organic phase was separated, washed with water (50 mL) and brine (50 mL) and dried (MgSO₄). Purification by column chromatography (10% w/w anhydrous K₂CO₃-silica; 25% diethyl ether in petroleum ether) gave the title compound as a colourless oil (55 mg, 32%).



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Tributylstannyl(trimethyl)silane, 11⁴

To a stirred solution of diisopropylamine (4.29 mL, 30.6 mmol) in THF (54 mL) at -78 °C was added *n*-butyllithium (10.5 mL, 2.5 M in hexanes, 26.8 mmol) dropwise over 15 min. The solution was warmed to RT and tributyltin hydride (5.38 mL, 20 mmol) added dropwise over 15 min. After 20 min, trimethylsilyl chloride (4 mL, 31.8 mmol) was added over 5 min, the solution was stirred for a further 10 min then the solvent was removed *in vacuo*. Purification by column chromatography (10% w/w anhydrous K₂CO₃-silica; petroleum ether) afforded the title compound as a colourless oil (8.69 g, 100%).

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¹H NMR (CDCl₃, 300 MHz): $\delta =$ 1.41–1.58 (6 H, m, 3 x CH₂) 1.23–1.38 (6 H, m, 3 x CH₂) 0.89 (9 H, t, J=7.3 Hz, 3 x CH₃) 0.79–0.91 (6 H, m, 3 x CH₂) 0.25 (9 H, s + d, J_{119117SnH}=26.4 Hz, 3 x SiCH₃)



10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 Chemical Shift (ppm) 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0 -0.5

N-Methyl-3-(tributylstannyl)indole-2-carboxaldehyde, 13



Following a modified procedure of Roschanger *et al.*⁵ To a stirred solution of *N*,*O*-dimethylhydroxylamine (0.147 g, 1.51 mmol) in THF (7 mL) at -78 °C was added *n*-butyllithium (1.18 mL, 2.56 M, 3.02 mmol). After 1 h a solution of *N*-methylindole-2-carboxaldehyde (0.300 g, 1.26 mmol in THF 3 mL) was added, followed after 15 min by *n*-butyllithium (1.13 mL, 2.56 M, 2.90 mmol). The solution was warmed to -40 °C and after 3 h tributyltin chloride (0.41 mL, 1.51 mmol) was added. The solution was warmed to RT and after 16 h, water (5 mL) and diethyl ether (10 mL) were added. The aqueous phase was washed with diethyl ether (10 mL) and the combined organic phases were washed with brine (20 mL), dried (MgSO₄) and concentrated *in vacuo*. Purification by column chromatography (10% w/w anhydrous K₂CO₃-silica; 5%–10% diethyl ether in petroleum ether) afforded the title compound as a pale yellow oil (0.245 g, 44%).



4-tert-Butoxy-3-tri-n-butylstannylcyclobut-3-ene-1,2-dione, 15



Following the procedure of Liebeskind *et al.*⁶ To a stirred solution of 3,4-di-*tert*butoxycyclobut-3-ene-1,2-dione (453 mg, 2.00 mmol) in THF (15 mL) at RT was added *n*-Bu₃SnSiMe₃ (1.10 g, 3.00 mmol). The solution was cooled to -23 °C and a solution of *n*-Bu₄NCN (11 mg, 0.04 mmol) in THF (2 mL) was added dropwise over 3 min. The reaction was warmed to RT then after 2 h was concentrated *in vacuo*. Purification by column chromatography (10% w/w anhydrous K₂CO₃-silica; 5% diethyl ether in petroleum ether) afforded the title compound as a yellow oil (248 mg, 28%).



3-Methoxy-6-tributylstannylstyrene, 17



To a stirred solution of 2-bromo-5-methoxystyrene (213 mg, 1 mmol) in THF at -78 °C was added *n*-butyllithium (0.5 mL, 2.2 M, 1.1 mmol) dropwise over 5 min. After 30 min tributyltin chloride (325 mg, 1 mmol) was added. The solution was warmed to RT and after 24 h was concentrated *in vacuo*. Purification by column chromatography (10% w/w anhydrous K₂CO₃-silica; 10% ethyl acetate in petroleum ether) afforded the title compound as a colourless oil (306 mg, 80%).



(Z)-1,2-bis-(Trimethylstannyl)ethene, 18⁷



Acetylene (generated by the dropwise addition of water onto CaC_2 solid and dried by passing successively through conc. H_2SO_4 , $NaOH_{(s)}$, $CaCl_{2(s)}$ and Drierite) was bubbled through a solution of hexamethylditin (556 mg, 1.70 mmol), $Pd(PPh_3)_4$ (154 mg, 0.13 mmol) and 1,4-dioxane (10 mL, purged with argon for 45 min prior to use) at 65 °C for 4 h. The solution was cooled to RT over 20 min then filtered. Purification by column chromatography (10% w/w anhydrous K₂CO₃-silica; hexane) gave the title compound (294 mg, 49%) as an orange oil.



The compound was assigned as having the *cis* geometry through comparison of the data with the literature. Using the satellites associated with the NMR active isotopes of tin, namely ¹¹⁹Sn and ¹¹⁷Sn, *J* values for the proton-proton and tin-proton coupling constants were obtained (see Figure below). The NMR shows a small amount of impurity (~5%), thought to be the corresponding *trans*-alkene.



Behaviour of Various Organotin Reagents on the K₂CO₃-silica Stationary Phase

General method: the reagent was subjected to column chromatography using 30% ethyl acetate in petroleum ether as eluent and 10% w/w K₂CO₃-silica as the stationary phase. Reagents were either eluted close to the solvent front or retained on the stationary phase. The mass recovery of the eluted reagents was recorded and in each case was adjudged to be free of solvent residue or decomposition products by ¹H NMR (See Figures below).

Tributylvinyltin – 98% recovery.







Phenyltributyltin – 97% recovery.



Notably, the technique proved valuable for the purification of 'aged' samples of hexabutylditin and tributyltin hydride. These 'aged' samples gave modest mass recovery (53% and 80% respectively) while the purified samples eluted with excellent mass recovery (97% and 100% respectively). ¹H NMR spectra recorded on the 'aged' and purified reagents are given below.



Hexabutylditin – 97% recovery from a pure sample (53% recovery from the 'aged' reagent above).



'Aged' tributyltin hydride (unpurified, from a reagent bottle >9 years old).



Tributyltin hydride – 100% recovery from a pure sample (80% recovery from the 'aged' reagent above).



References

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