Support Information

Polymer-Assisted Solution-Phase (PASP) Suzuki Couplings Employing an Anthracene-Tagged Palladium Catalyst

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The suspension of 9-hydroxymethylantracene **A** (1.5 g, 7.2 mmol, 1 equiv) in toluene (40 mL) was cooled to 0°C followed by addition of phosphorus tribromide (0.8 mL, 8.4 mmol, 1.17 equiv) *via* syringe. The mixture was stirred at 0°C for 1 h and then warmed to room temperature, during which the reaction became homogeneous. Saturated Na₂CO₃ solution (15 mL) was added slowly and the reaction was stirred until it cooled to room temperature. The phases were separated, and the organic phase was washed with H₂O (10 mL), brine (10 mL) and dried over MgSO₄. The yellow filtrate was concentrated to minimum volume, then stored at 0°C for crystallization. The yellow needle-like solid was collected and dried *in vacuo* (1.24 g). The mother liquid was concentrated and purified using flash chromatography (0.6 g). The two parts were combined to afford the product **B** as yellow solid (total 1.84 g, 94%).

9-Azidomethylantracene (**C**).

The 9-bromomethylantracene **B** (1.04 g, 3.85 mmol, 1 equiv) was dissolved in DMSO and NaN₃ (257 mg, 3.95 mmol, 1.02 equiv) was added in one portion. The temperature of the solution was raised to 50°C and stirring was continued at 50°C for 3.5 h. LC-MS showed complete conversion of the starting material. The reaction was cooled to room temperature and H₂O (40 mL) was added, followed by addition of EtOAc (20 mL). The two phases were separated and the aqueous phase was extracted by EtOAc (2x20 mL). The combined organic phase was washed with brine (15 mL), dried over MgSO₄ and filtered. The filtrate was concentrated and purified with flash chromatography (EtOAc/hexane = 5/95) to afford the product **C** as yellow solid (0.9 g, 100% yield).

9-Aminomethylantracene (D).

The suspension of azide compound **C** (0.4 g, 1.93 mmol, 1 equiv) and 10% Pd/C (204 mg, 0.1 equiv) in methanol (20 mL) was charged with N₂ for three times and H₂ for 4 times, and then put under H₂ for 30 minutes. TLC showed completion of the reaction. The reaction was filtered through a Celite pad followed by washing with methanol. The filtrate was concentrated to give the product **D** as yellow solid (392 mg, 98% yield). LC-MS showed high purity of the product (>95%) and the product was used directly without further purification.

Anthracene-tagged phosphine (**1**).

Pd complex Pd(PAnPh₂)Cl₂ (**2**).

Light yellow powder (3.2 g, 80% yield).

N-(9-Anthrylmethyl)-4-bromobenzamide (**20**).

A yellow solid (2.5 g, 66%), HPLC purity (retention time): 98% (3.42 min); LRMS (ESI) for $C_{22}H_{16}BrNO$ (M+H) 390.

4-[[[9-Anthrylmethyl)amino]carbonyl}phenylboronic acid (**25**).

A pale yellow solid (2.52 g, 67% yield), HRMS m/z calcd for $C_{22}H_{19}BNO_3$ ($M+H$) 356.1457, found 356.1469.

4'-Nitro-1,1'-biphenyl-4-carbonitrile (**14aA**).

A yellow solid (30.0 mg, 89%), HRMS m/z calcd for $C_{13}H_8N_2O_2$ (M^+) 224.0586, found 224.0603.

Ethyl 4'-nitro-1,1'-biphenyl-4-carboxylate (**14aB**).

A yellow solid (42.0 mg, 100% yield), HRMS m/z calcd for $C_{15}H_{13}NO_4$ (M^+) 271.0845, found 271.0861.

4-Chloro-3-methyl-4'-nitro-1,1'-biphenyl (**14aC**).

A yellow solid (29.6 mg, 80% yield), HRMS m/z calcd for $C_{13}H_{10}ClNO_2$ (M^+) 247.0400, found 247.0380.

4-Isobutyl-4'-nitro-1,1'-biphenyl (**14aD**).

A brown oily residue (26.3 mg, 69%), HRMS m/z calcd for $C_{16}H_{17}NO_2$ (M^+) 255.1259, found 255.1239.

4-Ethoxy-4'-nitro-1,1'-biphenyl (**14aE**).

A yellow solid (35.2 mg, 97% yield), HRMS m/z calcd for $C_{14}H_{13}NO_3$ (M^+) 243.0895, found 243.0871.

4'-Acetyl-1,1'-biphenyl-4-carbonitrile (**14bA**)

A white solid (29.5 mg, 89% yield), HRMS m/z calcd for $C_{15}H_{11}NO$ (M^+) 221.0841, found 221.0820.

Ethyl 4'-acetyl-1,1'-biphenyl-4-carboxylate (**14bB**).

A white solid (39.8 mg, 99%), HRMS m/z calcd for $C_{17}H_{16}O_3$ (M^+) 268.1099, found 268.1116.

1-(4'-Chloro-3'-methyl-1,1'-biphenyl-4-yl)ethanone (**14bC**).

A white solid (30.2 mg, 82% yield), HRMS m/z calcd for $C_{15}H_{13}ClO$ (M^+) 244.0655, found 244.0654.

1-(4'-Isobutyl-1,1'-biphenyl-4-yl)ethanone (**14bD**).

A white solid (24.9 mg, 66% yield), HRMS m/z calcd for $C_{18}H_{20}O$ (M^+) 252.1514, found 252.1510.

1-(4'-Ethoxy-1,1'-biphenyl-4-yl)ethanone (**14bE**)

A white solid (35.8 mg, 99% yield), HRMS m/z calcd for $C_{16}H_{16}O_2$ (M^+) 240.1150, found 240.1133.

2'-[(2-Methylphenoxy)methyl]-1,1'-biphenyl-4-carbonitrile (**14cA**).

A yellow oil (32.4 mg, 72% yield), HRMS m/z calcd for $C_{21}H_{18}NO$ ($M+H$) 300.1383, found 300.1388.

Ethyl 2'-[(2-methylphenoxy)methyl]-1,1'-biphenyl-4-carboxylate (**14cB**).

A yellow solid (44.6 mg, 86% yield), HRMS m/z calcd for $C_{23}H_{23}O_3$ ($M+H$) 347.1642, found 347.1621.

4'-Chloro-3'-methyl-2-[(2-methylphenoxy)methyl]-1,1'-biphenyl (**14cC**).

A yellow oily residue (41.9 mg, 86% yield), HRMS m/z calcd for $C_{21}H_{20}ClO$ ($M+H$) 323.1197, found 323.1215.

4'-Isobutyl-2-[(2-methylphenoxy)methyl]-1,1'-biphenyl (**14cD**).

A yellow oily residue (41.9 mg, 84% yield), HRMS m/z calcd for $C_{24}H_{27}O$ ($M+H$) 331.2056, found 331.2083.

4'-Ethoxy-2-[(2-methylphenoxy)methyl]-1,1'-biphenyl (**14cE**).

A yellow solid (33.4 mg, 70% yield), HRMS m/z calcd for $C_{22}H_{23}O_2$ ($M+H$) 319.1693, found 319.1722.

4'-Methoxy-1,1'-biphenyl-4-carbonitrile (**14dA**).

A white solid (26.3 mg, 84% yield), HRMS m/z calcd for $C_{14}H_{11}NO$ (M^+) 209.0841, found 209.0834.

Ethyl 4'-methoxy-1,1'-biphenyl-4-carboxylate (**14dB**).

A white solid (30.7 mg, 80% yield), HRMS m/z calcd for $C_{16}H_{16}O_3$ (M^+) 256.1099, found 256.1078.

4'-Chloro-3'-methyl-1,1'-biphenyl-4-yl methyl ether (**14dC**).

A white solid (27.1 mg, 78% yield), HRMS m/z calcd for $C_{14}H_{13}ClO$ (M^+) 232.0655, found 232.0644.

4'-Isobutyl-1,1'-biphenyl-4-yl methyl ether (**14dD**).

A white solid (28.9 mg, 80% yield), HRMS m/z calcd for $C_{17}H_{20}O$ (M^+) 240.1514, found 240.1515.

4-Ethoxy-4'-methoxy-1,1'-biphenyl (**14dE**).

A white solid (28.0 mg, 82% yield), HRMS m/z calcd for $C_{15}H_{16}O_2$ (M+H) 228.1150, found 228.1139.