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A water-soluble pyridyl-triazole ligand for aqueous phase palladium catalyzed Suzuki-Miyaura coupling

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ELECTRONIC SUPPLEMENTARY INFORMATION

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EXPERIMENTAL

Materials and Instrumentation

Phenylboronic acid, p-bromoacetophenone, 1-bromo-4-methoxybenzene, 1-bromo-4-methyl-benzene, 1-bromo-2-methylbenzene, 2-bromo-1,3,5-trimethylbenzene, 4-bromobenzaldehyde, 2-bromothiophene, 3-bromothiophene, bromonaphtalene, bromopyridine, bromopyrimidine, 4-chloroacetophenone, quaternary ammonium salts, analytical grade K_2CO_3 Na_2CO_3 and Cs_2CO_3 were purchased from Aldrich and used as received.

"Milli Q" purified water was employed in the catalytic experiments. Tetrahydrofuran, methanol, diethyl ether, and other commercial solvents (Aldrich) were purified as described in the literature.[1] But-3-ynyl sodium sulfate was prepared by a literature procedure;[2] $[Pd(\eta^3\text{-}C_3H_5)Cl]_2$ was prepared as described by Hartley.[3]

^1H and $^{13}C\{1H\}$ NMR spectra were recorded on a Bruker AVANCE 300 spectrometer. The chemical shift values of the spectra are reported in δ units with reference to the residual solvent signal. GC analyses were performed on an Agilent Technologies 6850 gas chromatograph fitted with an HP-5 column (30 m × 0.32 μm × 0.25 μm). GC-MS spectra were recorded on a Hewlett–Packard 5890 series II gas chromatograph interfaced to a HP 5971 quadrupole mass detector.

ESI-MS analyses were performed using an Agilent LC-MSD-Trap-SL operating in negative ion mode. Freshly prepared methanol solutions of **1** in were introduced into the ESI source by a syringe pump at 8 μL/min flow rate.

2.2. *Sodium 2-(1-((pyridin-2-yl)methyl)-1H-1,2,3-triazol-4-yl)ethyl sulfate* (**1**)

To a suspension of but-3-ynyl sodium sulfate (455 mg, 2.6 mmol) in a mixture of *t*-BuOH (15 mL) and H_2O (1 mL) were added a solution of 2-(azidomethyl)pyridine (3.57 mg, 2.7 mmol) in *t*-BuOH (5 mL), and, finally, a solution of $Cu(OAc)_2{\cdot}H_2O$ (26 mg, 0.13 mmol) in water (0.5 mL).

The mixture was stirred under inert atmosphere for 48 hours, then the liquid phase was taken to dryness to give a green solid. Flash-chromatography (silica gel, tetrahydrofuran/methanol 6:4) affords the title compound as a white solid which was dissolved in methanol and precipitated with diethylether (525 mg, 66%).

^1H NMR (300 MHz, 298 K, CD_3OD): δ 8.54 (d, 1H, J = 3.8 Hz), 7.96 (s, 1H), 7.84 (tt, 1H; J = 7.7 and 1.9 Hz), 7.38 (m, 1H), 7.28 (d, 1H, J = 7.9 Hz), 5.70 (s, 1H), 4.25 (t, 1H; J = 6.5 Hz), 3.09 (t, 1H; J = 6.5 Hz). $^{13}C\{^1H\}$ NMR (75 MHz, 298 K, CD_3OD): δ = 155.8, 150.4, 145.8, 139.1, 124.9, 124.7, 123.8. 67.6, 55.9, 26.8. ESI-MS in negative mode: 283.0 ($C_{10}H_{11}N_4O_4S^-$, 100%), 589 (**1**+$C_{10}H_{11}N_4O_4S^-$, 4%). Anal. Found: C, 39.3; H, 3.5. $C_{10}H_{11}N_4O_4SNa$ requires: C, 39.22; H, 3.62.

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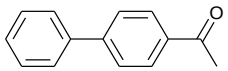
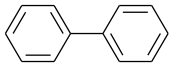
NMR characterization of the coupling products

4-Acetylbiphenyl[4]



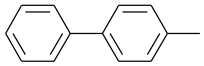
^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.02 (m, 2H), 7.67 (m, 2H), 7.64 (m, 2H), 7.53-7.30 (m, 3H), 2.64 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 197.7, 145.9, 139.9, 136.80, 129.07, 129.05, 128.3 , 127.38, 127.33, 26.8.

biphenyl[5]



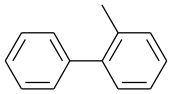
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47 (t, *J* = 7.0 Hz, 2H), 7.56 (t, J = 7.4 Hz, 4H), 7.71 (d, J = 7.6 Hz, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 127.2, 127.3, 128.8, 141.3.

4-methylbiphenyl[4]



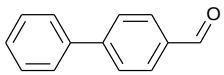
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.59 (m, 2H), 7.49 (m, 2H), 7.44-7.40 (m, 2H), 7.32 (m, 1H), 7.24-7.20 (m, 2H) 2.40 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 144.2, 138.3, 136.9, 129.4, 128.7, 126.9, 126.7, 21.1.

2-methylbiphenyl[4]



^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44-7.35 (m, 2H), 7.34-7.27 (m, 3H), 7.26-7.18 (m, 4H), 2.26 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 142.0, 141.90, 135.4, 130.4, 129.9, 129.3, 128.2, 127.4, 127.0, 125.9, 20.6.

4-biphenylcarbaldehyde[6]



^{1}H NMR (300 MHz, $CDCl_3$) δ: 10.06 (s, 1H, CHO), 7.95 (m, 2H), 7.75 (m, 2H), 7.62 (m, 2H), 7.50-7.40 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 191.9, 147.1, 139.7, 135.2, 130.2, 129.0, 128.4, 127.6, 127.3.

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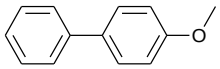
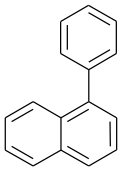
4-Methoxybiphenyl[4]



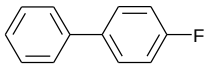
^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.44-7.40 (m, 4H) 7.32-7.28(m, 2H),6.98 (m, 2H), 3.86 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.1, 55.3.

1-Phenylnaphthalene[7]



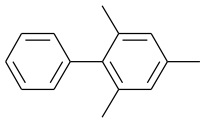
^{1}H NMR (300MHz, $CDCl_3$) δ): 7.96 (m, 2H), 7.91 (m, 1H), 7.59-7.44 (m, 9H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 140.9, 140.4, 133.9, 131.7, 130.2, 128.4, 127.7, 127.3, 127.0, 126.13, 125.9, 125.5.

4-Fluorobiphenyl[7]



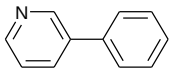
^{1}H NMR (300MHz, $CDCl_3$) δ: 7.54 (m,4H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 8.7 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 162.7 (d, *J* = 245.2 Hz), 140.4, 137.5, 129.02, 128.89, 128.79, 127.5, 127.2, ; 115.8 (d, *J* = 21.3 Hz).

2,4,6-trimethylbiphenyl[8]



^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.48-7.45 (m, 1H), 7.24-7.19 (m, 2H), 7.10-7.05 (m, 2H), 6.96 (s, 2H), 2.30 (s, 3H, CH_3), 2.03 (s, 6H).

3-Phenylpyridine[9]



^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.85 (s, 1H), 8.54 (d, *J* = 4 Hz, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.52-7.48 (m, 2H), 7.40-7.25 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 148.1, 148.0, 137.6, 136.5, 134.3, 129.0, 128.1, 127.0, 123.5.

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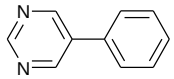
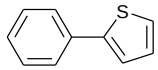
5-**Phenylpyrimidine**[9]



^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.20 (s, 1H), 8.93 (s, 2H), 7.57-7.44 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 157.3, 154.7, 134.1, 134.0, 129.3, 128.9, 126.8.

2-Phenylthiophene[9]



^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.67-7.64 (m, 2H), 7.44-7.41(m, 2H), 7.36-7.30 (m, 3H), 7.10 (m, 1H) ^{13}C NMR (75 MHz, $CDCl_3$) δ: 144.3, 134.2, 128.9, 128.0, 127.4, 125.9, 124.8, 122.9.

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