Supplementary Material (ESI) for Chemical Communications
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Supporting Information

Amphiphilic photo-isomerisable phosphanes for aqueous organometallic catalysis

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General remarks

The ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded at 300.13, 75.47 and 121.49 MHz on a Bruker Avance DRX spectrometer, respectively. The processor tensiometer Sigma 70 (KSV) and the Wilhelmy plate method for air-water interface have been used for the surface tension measurements at 298 K. The precision of the force transducer of the surface tension apparatus was 0.1mN/m and before each measurement, the platinum plate was cleaned in red/orange colour flame. A syringe is filled with a concentrated solution of the studied compound and addition of small volumes to ultrapure water enhances the solution concentration. After addition, the solution is gently stirred for 30 s. Surface tension is measured for each concentration. The temperature stabilization can be estimated as better than ±0.05 K with a thermoregulated bath Lauda RC6.

Evaluation of the *trans* to *cis* isomerization: Ultrapure water was degassed by three freeze-pump-thaw cycles and used immediately under N_2. In a flamed schlenk tube under N_2 was introduced the *para*-$(Ph_2P)PhNNPhSO_3Na$ (resp. the *meta*-$(Ph_2P)PhNNPhSO_3Na$) and the appropriate volume of degassed deionized water in order to obtain the solution at a concentration of 10^{-4}mol.L^{-1}. The solution was transferred in a sealed quartz tube under N_2.

The UV/Vis spectra were performed in a JASCO V-630, optical length of 1 cm, scanning at 2000 nm.min^{-1}.

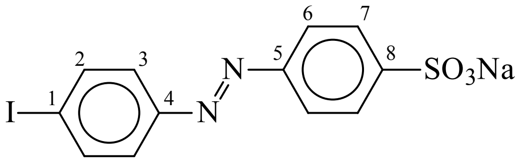
The irradiations were performed in a negatoscope with a 6 Watt 365 nm UV lamp at 22°C directly through the quartz tube. After an irradiation step, a fraction was injected in HPLC while the tube was placed in the UV / Vis spectrometer.

The quantification was performed in HPLC Shimadzu (C18 XTerra column, 0.7 mL / min with 0% up to 50% acetonitrile during 10 min and up to 100% at 15 min and to 30 min). Gas chromatographic analyses were carried out on a Shimadzu GC-17A gas chromatograph equipped with a methyl silicone capillary column (30 m x 0.25 mm; 0.25 μm) and a flame ionization detector (GC:FID). All reactants were purchased from Aldrich Chemicals or Fisher Scientific in their highest purity and used without further purification. Distilled deionized water was used in all experiments. All solvents and liquid reagents were degassed by bubbling N_2 for 15 min before each use or by two freeze-pump-thaw cycles before use.

Phosphane synthesis

***para*-IPhNNPh (1)** was prepared according to the literature and the analyses are in good agreement with those described (YU, B. C.; SHIRAI, Y.; TOUR, J. M. *Tetrahedron,* **2006**, *62*, 10303-10310).

***para*-IPhNNPhSO$_3$Na (2):** Commercial sulfuric oleum (65%, 4 mL) was added dropwise to a solution of **1** (1g, 3.2 mmol) in 10 mL of sulfuric acid (96%) cooled in an ice bath. The reaction mixture was kept at room temperature for 72 h. Excess SO_3 was then transformed to H_2SO_4 by addition of 20 mL water into the cooled solution. Meanwhile, a precipitate appeared. A 4 N sodium hydroxide aqueous solution was then added to the mixture, cooled in an ice bath, up to neutral pH (about 150 mL solution are needed). After addition of 100 mL water, boiling the solution results in a homogeneous phase. After cooling to 20 °C, a precipitate was isolated by filtration and washed with ice-cold water. **2** was obtained as an orange powder and dried under vacuum. Yield: 95%.



para-IPhNNPhSO$_3$Na (**2**)

^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ 7.69 (d, ^3J(H,H) = 8.4 Hz, 2H, H-3), 7.80 (d, ^3J(H,H) = 8.4 Hz, 2H, H-7), 7.87 (d, ^3J(H,H) = 8.4 Hz, 2H, H-6), 7.99 (d^3J(H,H) = 8.4 Hz, 2H, H-2); JMOD-^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ 99.73 (s, C-1), 122.81 (s, C-6), 124.92 (s, C-3), 127.28 (s, C-7), 138.94 (s, C-2), 151.09 (s, C-8), 151.62 (s, C-4), 152.00 (s, C-5).

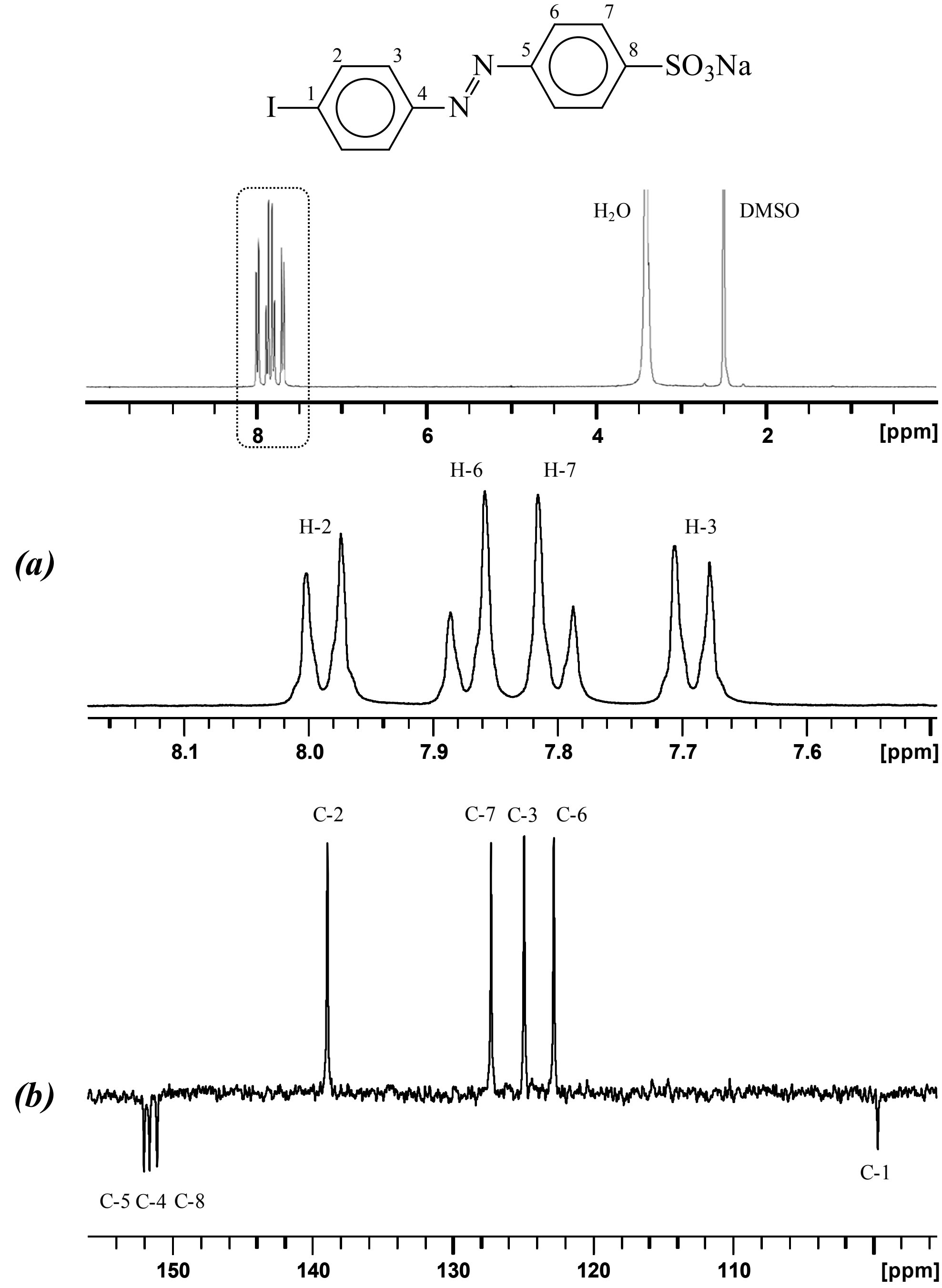
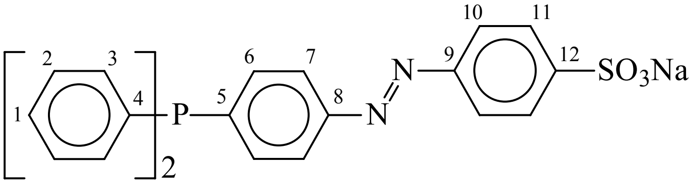


Figure S1: ^{1}H ***(a)*** and JMOD-^{13}C{^{1}H}***(b)*** NMR spectra of *para*-IPhNNPhSO$_3$Na (**2**).

***para*-(Ph_2P)PhNNPhSO_3Na (3):** To a solution of *para*-IPhNNPhSO_3Na (**2**) (0.40 g, 1.0 mmol), sodium acetate (0.08g, 1.0 mmol) and palladium acetate (5.6 mg, 0.025 mmol) in anhydrous DMF (4 mL), was added diphenylphosphine (0.17 mL, 0.19 g, 1.0 mmol) under nitrogen. The mixture was then stirred and heated at 100 °C for 16 h. After cooling, the solution was transferred under nitrogen at the top of a silica column. An ethylacetate/methanol mixture (gradient from 100/0 to 80/20) was used as eluant. Each fraction was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy and fractions where a unique signal was observed were combined. **3** was obtained after rotary evaporation as an orange powder. Yield: 65%.



para-(Ph_2P)PhNNPhSO_3Na (**3**)

^1H NMR (300 MHz, D_2O, 25 °C): δ 6.50-6.80 (br m, 12H, H-1, H-2, H-6, H-3), 7.00 (br m, 4H, H-10, H-11), 7.38 (br d, ^3J(H,H) = 7.0 Hz, 2H, H-7); ^1H NMR (300 MHz, DMSO-D_6, 25°C): δ7.28-7.37 (m, 4H, H-3), 7.41 (t, ^3J(H,H) = ^3J(H,P) = 7.9 Hz, 2H, H-6), 7.43-7.48 (m, 6H, H-1, H-2), 7.79 (d, ^3J(H,H) = 8.5 Hz, 2H, H-11), 7.85 (d, ^3J(H,H) = 8.5 Hz, 2H, H-10), 7.92 (d, ^3J(H,H) = 7.0 Hz, 2H, H-7); JMOD-$^{13}C\{^1H\}$ NMR (75.5 MHz, CH_3OH, 25 °C): δ 122.72 (s, C-10), 122.82 (d, ^3J(P,C) = 10.0 Hz, C-7), 127.08 (s, C-11), 128.79 (d, ^3J(P,C) = 6.8 Hz, C-2), 129.26 (s, C-1), 133.94 (d, ^2J(P,C) = 20.0 Hz, C-3), 134.16 (d, $^2J_{P,C}$ = 13.7 Hz, C-6), 136.79 (d, ^1J(P,C) = 16.3 Hz, C-4), 142.71 (d, ^1J(P,C) = 16.3 Hz, C-5), 147.52 (s, C-12), 152.71 (s, C-8), 153.62 (s, C-9); $^{31}P\{^1H\}$ NMR (121.5 MHz, D_2O, 25 °C): δ -6.02 (s); $^{31}P\{^1H\}$ NMR (121.5 MHz, [D_6]DMSO, 25 °C): δ-6.33 (s).

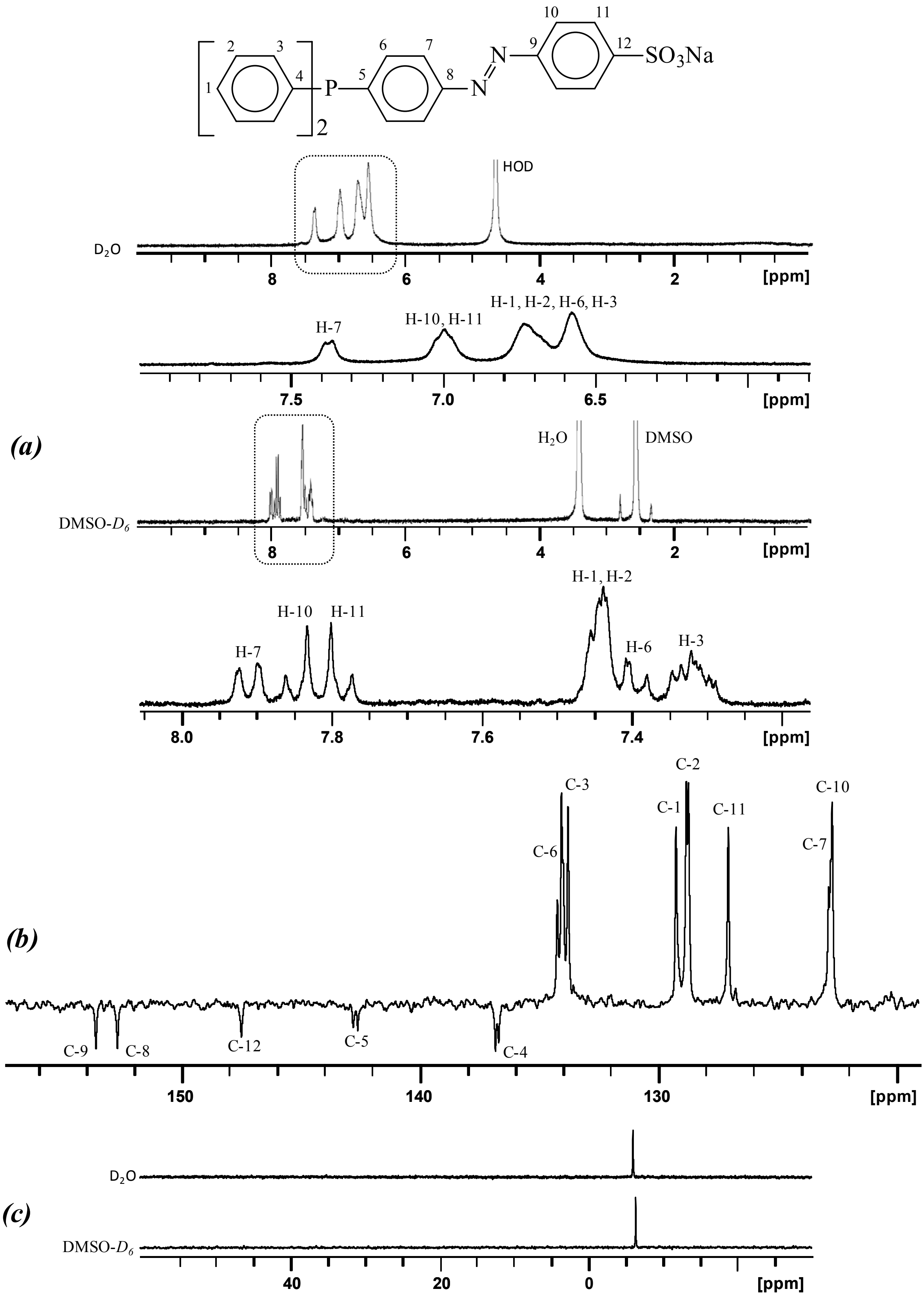
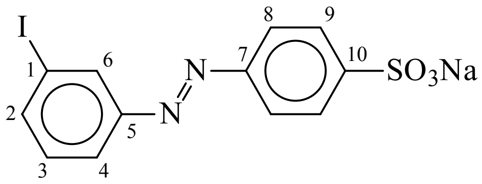


Figure S2: ^{1}H ***(a)***, JMOD-^{13}C{^{1}H}***(b)*** and ^{31}P{^{1}H}***(c)*** NMR spectra of *para*-(Ph_2P)PhNNPhSO_3Na (**3**).

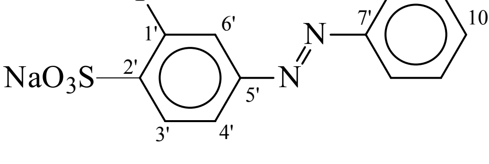
***meta*-IPhNNPh (4)** was prepared according to the literature (PRIEWISH, B.; RÜCK-BRAUN, K. *J. Org. Chem.,* **2005**, *70*, 2350-2352) and the analyses are in good agreement with those described (ROLING, P. V. *J. Org. Chem.,* **1975**, *40*, 2421-2425).

***meta*-IPhNNPhSO$_3$Na (5):** Commercial sulfuric oleum (65%, 12 mL) was added dropwise to a solution of **4** (3g, 3.2 mmol) in 30 mL of sulfuric acid (96%) cooled in an ice bath. The reaction mixture was kept at room temperature for 144 h. Excess SO$_3$ was then transformed to H$_2$SO$_4$ by addition of 60 mL water into the cooled solution. Meanwhile, a precipitate appeared. A 4 N sodium hydroxide aqueous solution was then added to the mixture, cooled in an ice bath, up to neutral pH (about 450 mL solution are needed). After addition of 300 mL water, boiling the solution results in a homogeneous phase. After cooling to 20 °C, a precipitate was isolated by filtration and washed with ice-cold water. This precipitate was a 70/30 mixture of **5** and **6**. This solid was recrystallized from a water/methanol mixture (100 mL/25 mL) to give **5** (orange powder). Yield: 45%.



meta-IPhNNPhSO$_3$Na (**5**)

^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ 7.44 (t, ^3J(H,H) = 7.8 Hz, 1H, H-3), 7.81 (d, ^3J(H,H) = 8.4 Hz, 2H, H-9), 7.89 (d, ^3J(H,H) = 8.4 Hz, 2H, H-8), 7.95 (d, ^3J(H,H) = 8.4 Hz, 1H, H-4), 7.98 (d, ^3J(H,H) = 8.4 Hz, 1H, H-2), 8.20 (t, ^4J(H,H) = 1.5 Hz, 1H, H-6); JMOD-^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ 96.03 (s, C-1), 122.87 (s, C-8), 124.04 (s, C-4), 127.24 (s, C-9), 129.99 (s, C-6), 132.06 (s, C-3), 140,32 (s, C-2), 151.75 (s, C-7), 151.80 (s, C-5), 153.22 (s, C-10).



meta-I(SO$_3$Na)PhNNPh (**6**)

^{1}H NMR (300 MHz, [D$_6$]DMSO, 25 °C): δ7.68-7.75 (m, 3H, H-9’, H-10’), 8.00-8.10 (m, 3H, H-8’, H-4’), 8.20 (d, ^3J(H,H) = 8.4 Hz, 1H, H-3’), 8.42 (d, ^4J(H,H) = 1.8 Hz, 1H, H-6’); JMOD-^{13}C{^{1}H} NMR (75.5 MHz, [D$_6$]DMSO, 25 °C): δ 94.36 (s, C-1’), 122.96 (s, C-4’), 123.27 (s, C-8’), 129.31 (s, C-3’), 129.96 (s, C-9’), 132.54 (s, C-10’), 133,99 (s, C-6’), 151.96 (s, C-7’), 152.22 (s, C-5’), 152.72 (s, C-2’).

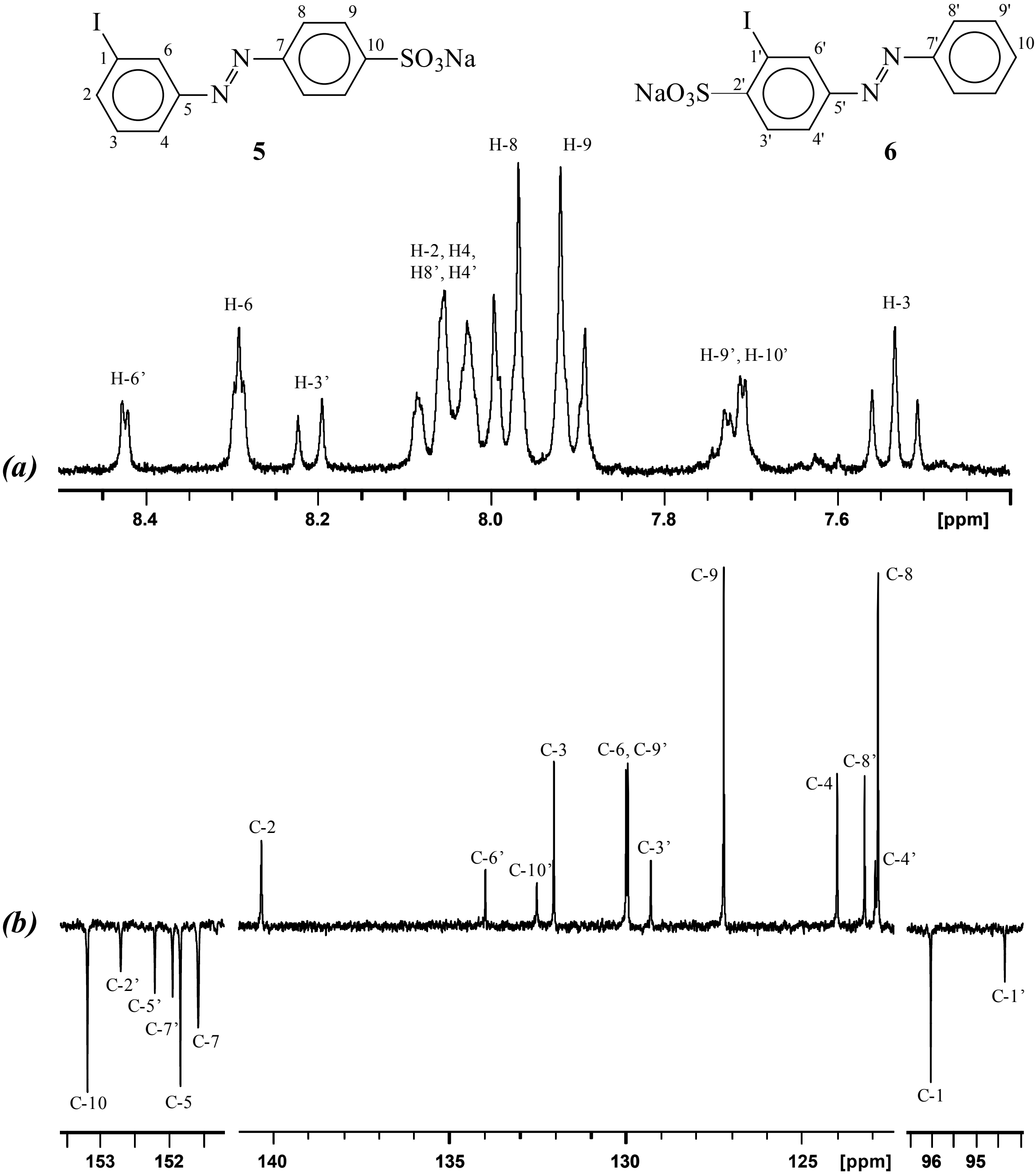


Figure S3: ^{1}H ***(a)*** and JMOD-^{13}C{^{1}H}***(b)*** NMR spectra of the 70/30 meta-IPhNNPhSO$_3$Na (**5**) / *meta*-I(SO$_3$Na)PhNNPh (**6**) mixture.

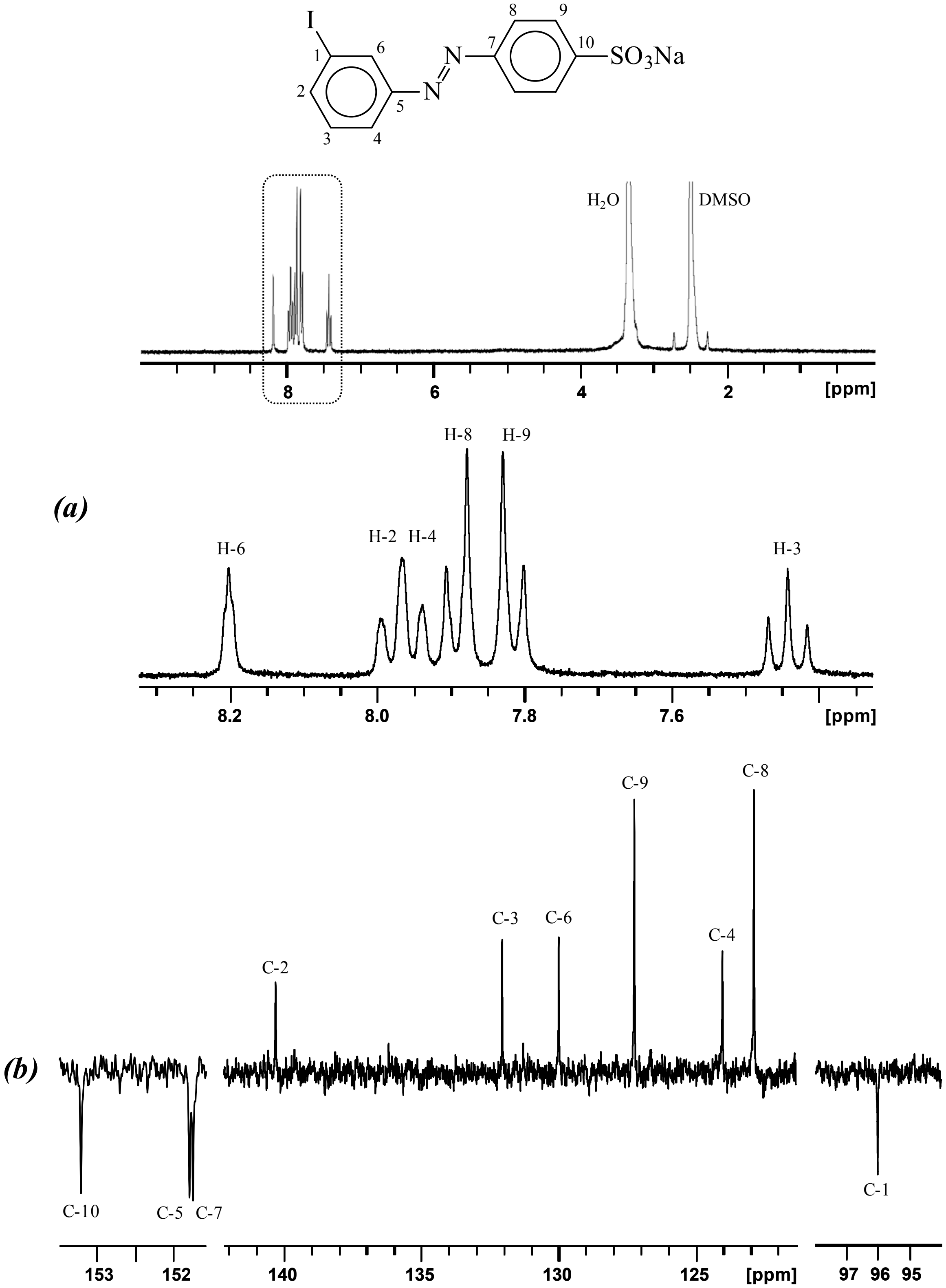
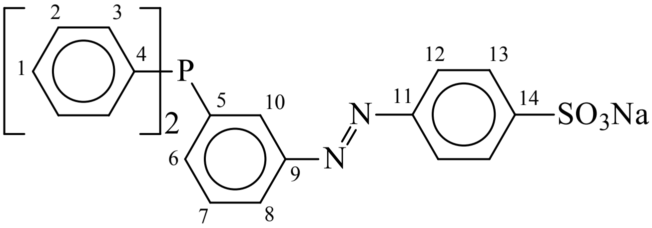


Figure S4: ^{1}H ***(a)*** and JMOD-^{13}C{^{1}H}***(b)*** NMR spectra of meta-IPhNNPhSO$_3$Na (**5**).

***meta*-(Ph_2P)PhNNPhSO_3Na (7):** To a solution of **5** (0.40 g, 1.0 mmol), sodium acetate (0.08g, 1.0 mmol) and palladium acetate (5.6 mg, 0.025 mmol) in anhydrous DMF (4 mL), was added diphenylphosphine (0.17 mL, 0.19 g, 1.0 mmol) under nitrogen. The mixture was then stirred and heated at 100°C for 16 h. After cooling, the solution was transferred under nitrogen at the top of a silica column. An ethylacetate/methanol mixture (gradient from 100/0 to 80/20) was used as eluant. Each fraction was analyzed by $^{31}P\{^1H\}$ NMR spectroscopy and fractions where a unique signal was observed were combined. **7** was obtained after rotary evaporation as an orange powder. Yield: 77%.



meta-(Ph_2P)PhNNPhSO_3Na (**7**)

^{1}H NMR (300 MHz, D_2O, 25 °C): δ 6.50-7.15 (br m, 13H, H-10, H-7, H-1, H-2, H-6, H-3), 7.30-7.50 (br m, 5H, H-8, H-12, H-13); ^{1}H NMR (300 MHz, [D_6]DMSO, 25 °C): δ 7.28-7.38 (m, 4H, H-3), 7.42 (t, ^3J(H,H) = ^3J(H,P) = 6.3 Hz, 1H, H-6), 7.43-7.50 (m, 6H, H-1, H-2), 7.66 (t, ^3J(H,H) = 7.8 Hz, 1H, H-7), 7.73 (d, ^3J(H,P) = 7.2 Hz, 1H, H-10), 7.77 (d, ^3J(H,H) = 8.7 Hz, 2H, H-13), 7.81 (d, ^3J(H,H) = 8.7 Hz, 2H, H-12), 7.92 (d, ^3J(H,H) = 8.2 Hz, 1H, H-8); JMOD-$^{13}C\{^1H\}$ NMR (75.5 MHz, CH_3OH, 25 °C): δ 122.71 (s, C-12), 122.77 (s, C-8), 127.05 (s, C-13), 128.24 (d, ^2J(P,C) = 19.9 Hz, C-10), 128.77 (d, ^3J(P,C) = 7.0 Hz, C-2), 129.19 (s, C-1), 129.52 (d, ^3J(P,C) = 6.5 Hz, C-7), 133.81 (d, ^2J(P,C) = 20.0 Hz, C-3), 136.45 (d, ^2J(P,C) = 19.6 Hz, C-6), 136.89 (d, ^1J(P,C) = 11.0 Hz, C-4), 139.78 (d, ^1J(P,C) = 13.7 Hz, C-5), 147.52 (s, C-14), 152.76 (d, ^3J(P,C) = 7.0 Hz, C-9), 153.46 (s, C-11); $^{31}P\{^1H\}$ NMR (121.5 MHz, [D_6]DMSO, 25 °C): δ -6.69 (s).

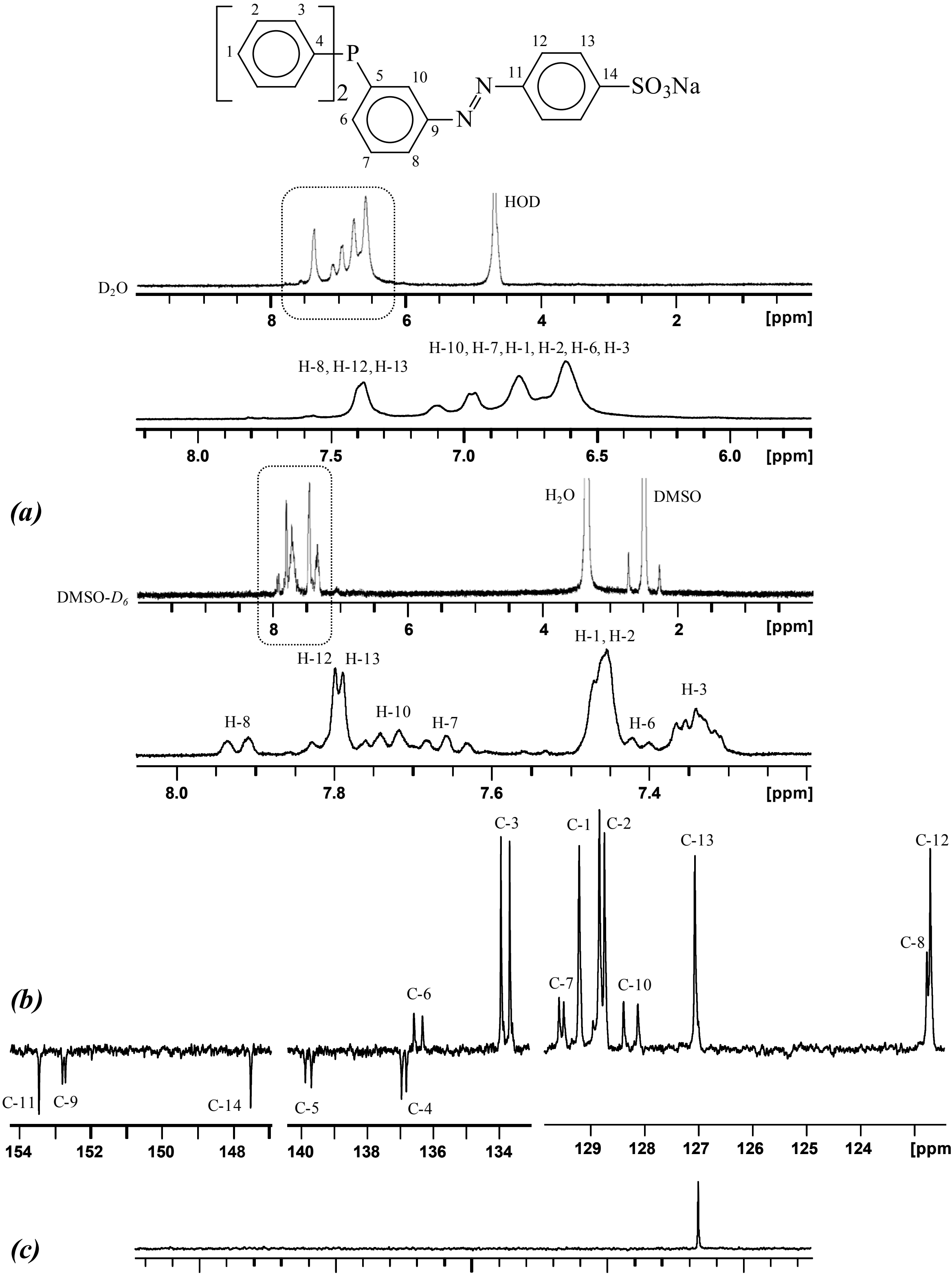


Figure S5: ^{1}H ***(a)***, JMOD-$^{13}C\{^{1}H\}$***(b)*** and $^{31}P\{^{1}H\}$***(c)*** NMR spectra of *meta*-(Ph_2P)PhNNPhSO_3Na (**7**).

Phosphane basicity

Phosphanes selenides were synthesized by refluxing excess selenium (10 equiv) with the phosphine (250 mg) in ethanol (15 mL) under nitrogen for 15 h. The resulting mixture was directly analyzed by $^{31}P\{^{1}H\}$ NMR without any purification. Comparison of the $^{1}J_{P=Se}$ values allow determining the relative basicity of the studied phosphanes.

Evaluation of the *trans*-to-*cis* isomerisation

Ultrapure water was degassed by three freeze-pump-thaw cycles and used immediately under nitrogen. In a flamed Schlenk tube under nitrogen was introduced **3** (or **7**) and the appropriate volume of degassed water in order to obtain the solution at a concentration of 10^{-4} M. The solution was transferred in a sealed quartz tube. The UV/vis spectra were performed in a JASCO V-630, optical length of 1 cm, scanning at 2000 nm.min^{-1}.

General procedure for catalysis experiments

$Pd(OAc)_2$ (4.5 µmol, 1 mg) and phosphane (40 µmol) were introduced under a nitrogen atmosphere into a Schlenk tube containing degassed water (4 g). After stirring with a magnetic bar for 16 h, the orange solution was separated under nitrogen into two equal fractions. The first fraction was put in a quartz Schlenk tube and the second one in a glass Schlenk tube. The two tubes were placed in a completely opaque box equipped with a UV lamp and a stirring agitator. The glass tube was enveloped with aluminium paper and the box was closed. The two aqueous solutions were then stirred with a magnetic bar at 365 nm for 90 min, 120 min and 150 min for **3**, **8** and **7** respectively. Only the solution placed in the quartz tube received the UV radiation. After irradiation, two equivalent mixtures of allyl undecyl carbonate (225 µmol; 100 equiv./Pd), diethylamine (450 µmol; 200 equiv./Pd), heptane (2 g) and dodecane (110 µmol; internal standard) were transferred under nitrogen into the two Schlenk tubes in the opaque box. The two biphasic media were stirred at 1250 rpm and the reactions were monitored by quantitative gas chromatographic analysis of the organic layers. The UV lamp stayed on continuously during the process. During the reaction, the temperature of the two media increased from 20 to 30 °C due to the heat generated by the UV lamp.