Synthesis of Some New 1,4-Distyrylbenzenes Using Immobilized Palladium Nanoparticles on Silica Functionalized Morpholine as a Recyclable Catalyst

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Abstract: Some new 1,4-distyrylbenzene derivatives were synthesized by using immobilized palladium nanoparticles on silica-bonded *N*-propyl morpholine (PNP-SBNPM) as a heterogeneous catalyst. These one-pot reactions afforded a range of stereoselective, symmetrical (*E*)-1,4-distyrylbenzene derivatives with high yields (78–90%). The green catalyst system is recyclable and allows facile product isolation. The recycled catalyst could be reused six times without appreciable loss of catalytic activity.

Key words: synthesis, 1,4-distyrylbenzenes, heterogeneous catalyst, palladium nanoparticles, silica-bonded *N*-propylmorpholine

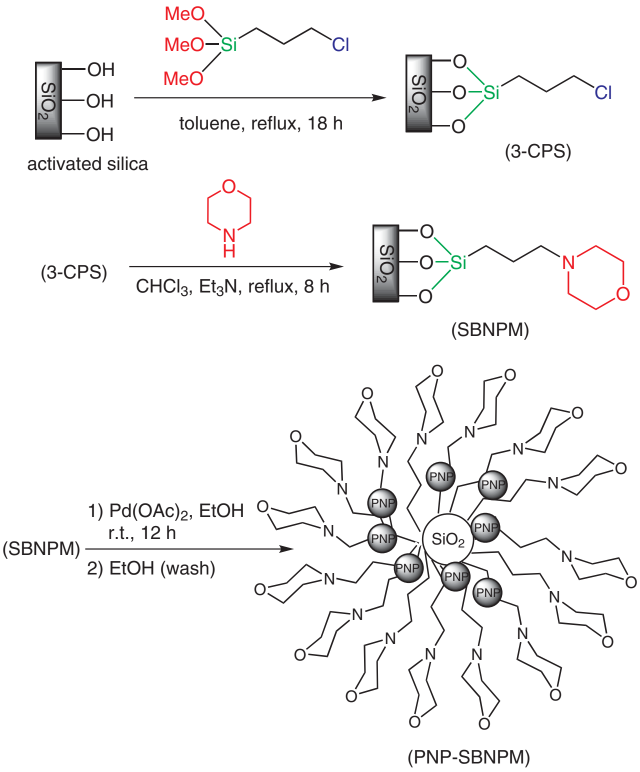
There is widespread interest in the use of conjugated organic materials in emerging optoelectronic technologies.[1–6] Conjugated materials, such as small molecules and polymers, have appeared that enable emission from organic-based light-emitting diodes (OLEDs) over the entire visible spectrum.[1,7,8] In contrast to conjugated polymers, conjugated small molecules are desirable because their relatively simple structure enables straightforward structure–property relationships to be determined. Such small molecule systems also allow regular structure films of specified thickness to be created in pure form by using evaporation techniques.[9]

To prepare these conjugated systems, two methods are routinely used. In the first method, predefined groups are attached to the carbon skeleton whereas in the second method predefined groups are attached to the starting materials. In order to build up the carbon framework in both methods, C–C coupling reactions are required. There are different strategies for C–C coupling, such as Wittig reaction,[2,10] Horner–Emmons,[3] Hiyama coupling,[11] and Heck reaction.[12–16] Palladium catalysts have proven to be good catalysts for a range of carbon–carbon and carbon–heteroatom coupling reactions, such as the Heck, Sonogashira, Suzuki, and Stille reactions.[17–22]

Considering the high cost of existing Pd catalysts and many of the ligands, preparing a high-performance Pd catalyst that can be recycled is very desirable. Recyclable Pd catalyst systems can be created by adsorbing a complex of palladium metal together with suitable ligands onto the surface of solid supports to form heterogeneous catalysts.[23–25] Pd nanoparticle catalyst systems have also been used[26–32] in a green catalytic system that does not need ligands.

In this study, palladium nanoparticles are laid on silica-functionalized morpholine. After characterization of the catalyst with respect to the catalyst amount and reaction conditions required, its use in the Heck reaction between 1,4-diiodobenzene and styrene was evaluated. Finally, new 1,4-distyrylbenzenes that can be used in OLEDs were synthesized under optimized conditions.

The palladium nanoparticles on silica-bonded *N*-propylmorpholine (PNP-SBNPM) were produced through the reaction of silica-bonded *N*-propylmorpholine (SBNPM)



Scheme 1 Preparation of PNP-SBNPM

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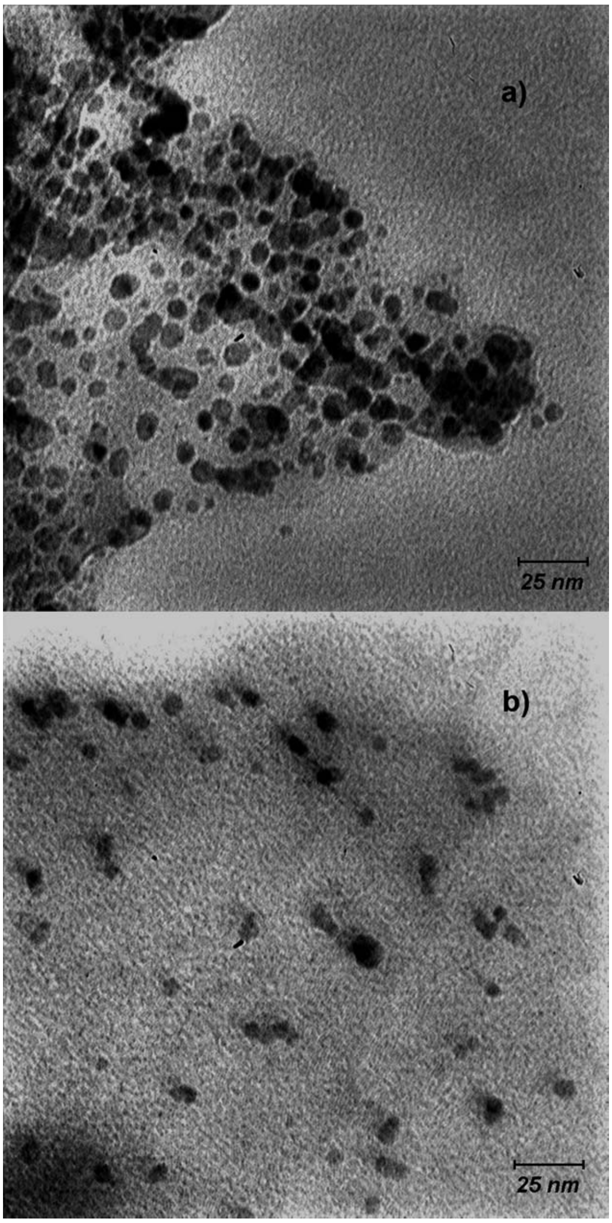


Figure 1 TEM images of Pd nanoparticles (a) before and (b) after five repeated reactions

with palladium acetate in ethanol.[27–30] To prepare SBNPM, 3-chloropropylsilica (3-CPS) was treated with morpholine; 3-CPS was, in turn, produced by the reaction of activated silica[33] with 3-chloropropyl trimethoxysilane (Scheme 1).

The EDX spectrum showed the presence of 0.0516 gram of palladium per gram of catalyst. It is possible to calculate the amount of used palladium in the reaction for one mole of the reactants. Here, 0.05 gram of catalyst was used per mole aryl halide, which is equivalent to 0.00258 gram of Pd metal. In other words, 2.4 mol% of catalyst per millimole of aryl halide was used.

Transmission electron microscopic (TEM) images of the PNP-SBNPM catalyst shows that Pd nanoparticles with near spherical morphology are assembled onto the silica-bonded *N*-propylmorpholine support, with a relatively good monodispersity (±0.8). The particles had an average size of 7 nm both before (Figure 1, a) and after five repeated reactions (Figure 1, b).

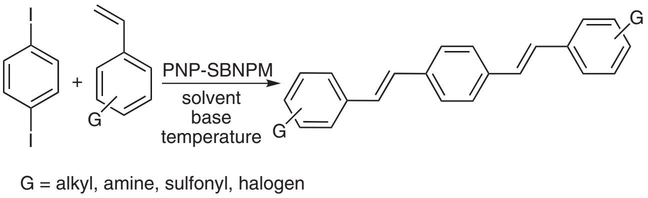
The XRD pattern of the PNP-SBNPM catalyst also showed that the palladium nanoparticles were held on the silica surface. The strongest peaks of the XRD pattern corresponded to the SiO_2 and other peaks were indexed as the (111), (200), (220), (311) and (222) planes of the palladium nanoparticles (Figure 2).[34]

The microscopic features of the catalyst were observed with SEM, and the morphology of the functionalized silica is shown in Figure 3.

A BET surface area of 120 m^2g^{-1} and a total pore volume of 0.11 cm^3g^{-1} were measured for the catalyst.

Because the 1,4-distyrylbenzenes have fluorescence properties,[1–6] the synthesis of some of these compounds was assessed with palladium nanoparticle silica-bonded *N*-propyl morpholine as a new catalyst. For this purpose, we used the Heck reaction shown in Scheme 2.

Conditions were tested to optimize the above reaction with the PNP-SBNPM catalyst; the results are given in the Table 1. The reaction temperature was chosen to be 120 °C because poor conversion was observed at lower temperatures; no reaction was observed at room temperature. Carbonated bases were found to work well and we



Scheme 2 Synthesis of 1,4-distyryl-benzenes using PNP-SBNPM as catalyst

Table 1 Optimization of Reaction between 1,4-Diiodobenzene and Styrene in *N*,*N*-Dimethylformamide (5 mL)

Entry	Cat. (g)	Base (mmol)	Temp (°C)	Time (h)	Yield (%)[a]
1	0.05	Na_2CO_3 (2)	120	5	90
2	0.05	K_2CO_3 (2)	120	5	90
3	0.05	Cs_2CO_3 (1.2)	120	5	90
4	0.05	KO*t*-Bu (1.2)	120	12	70
5	0.05	Et_3N (3)	120	12	65
6	0.05	Na_2CO_3 (2)	90	5	80
7	0.05	Na_2CO_3 (2)	r.t.	24	0
8	0.03	Na_2CO_3 (2)	120	5	70
9	0.03	Na_2CO_3 (2)	120	24	75
10	0.075	Na_2CO_3 (2)	120	5	90

[a] Yield of isolated product.

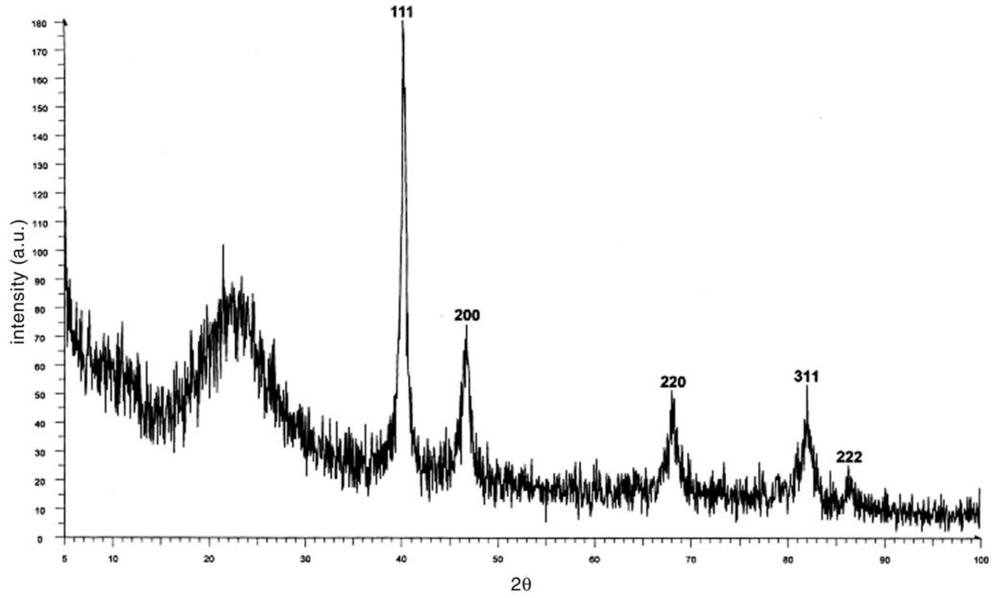
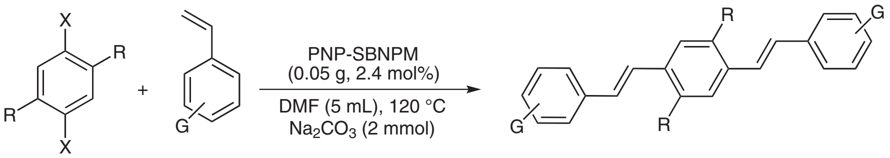


Figure 2 XRD of PNP-SBNPM



1 mmol 2.4 mmol **1a–h**

X = Br, I R = H, Me

G = amine, sulfonyl, halogen

Scheme 3 Synthesis of new 1,4-distyrylbenzenes under optimized conditions

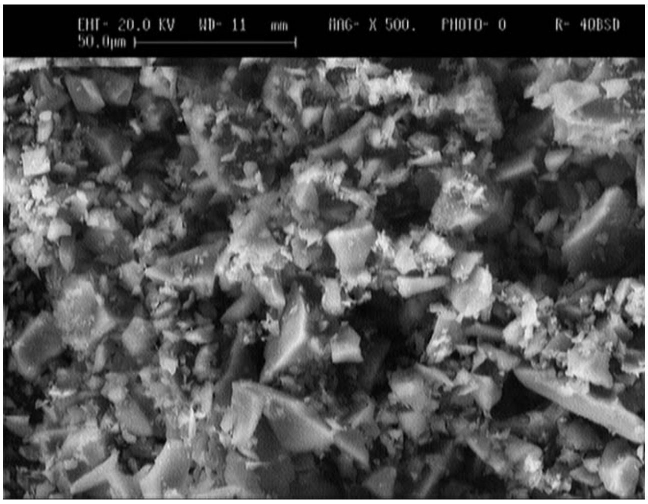


Figure 3 SEM of PNP-SBNPM

opted for Na_2CO_3 because of its low cost. Thus, the conditions give in Scheme 3 were selected.

Under the above conditions, aryl iodide reacts faster than other aryl halides (aryl chloride and bromide) and gave a higher conversion (Table 2).

Table 2 Effect of Halide on the Reaction of Styrene with Aryl Halides in the Presence of PNP-SBNPM

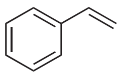
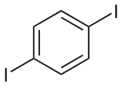
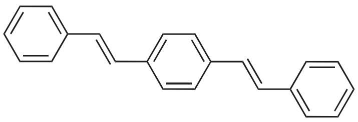
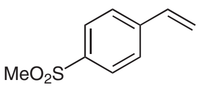
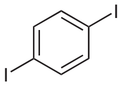
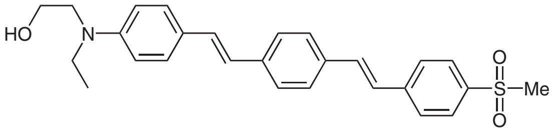
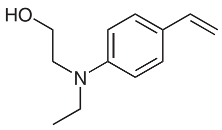
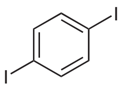
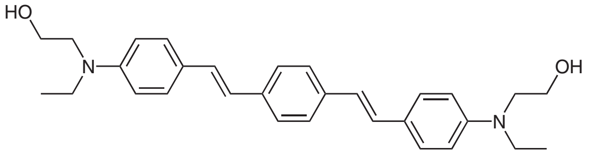
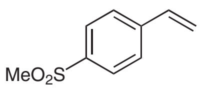
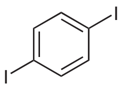
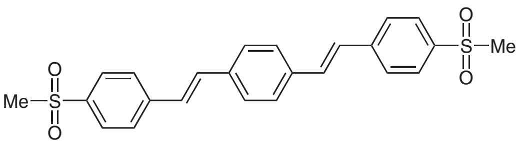
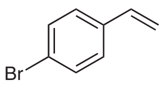
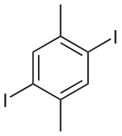
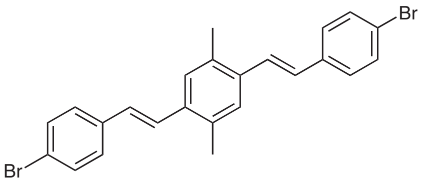
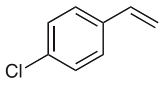
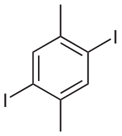
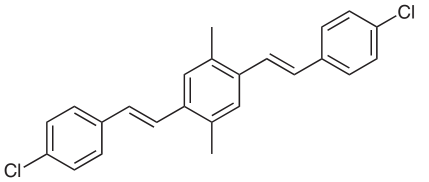
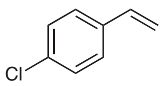
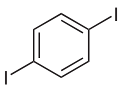
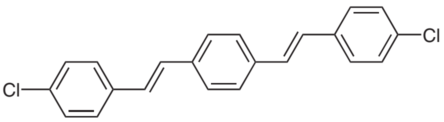
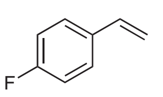
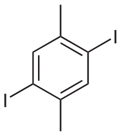
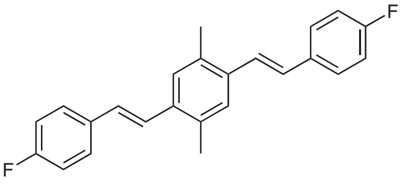
X	Time (h)	Yield (%)[a]
Cl	12	55
Br	12	75
I	5	90

[a] Yield of isolated product.

A range of compounds were synthesized with PNP-SBNPM catalyst under the above conditions (Table 3). Among all the compounds examined, only amine–sulfone-distilbene **1b** required a two-step synthesis; the others could be generated in a single step. In the former case, 4-[(methansulfonylphenyl)vinyl]-4-bromobenzene (MSPVBB) was prepared in 90% yield under the optimized conditions, and then, in a second step, **1b** was synthesized in 85% yield (Scheme 4).

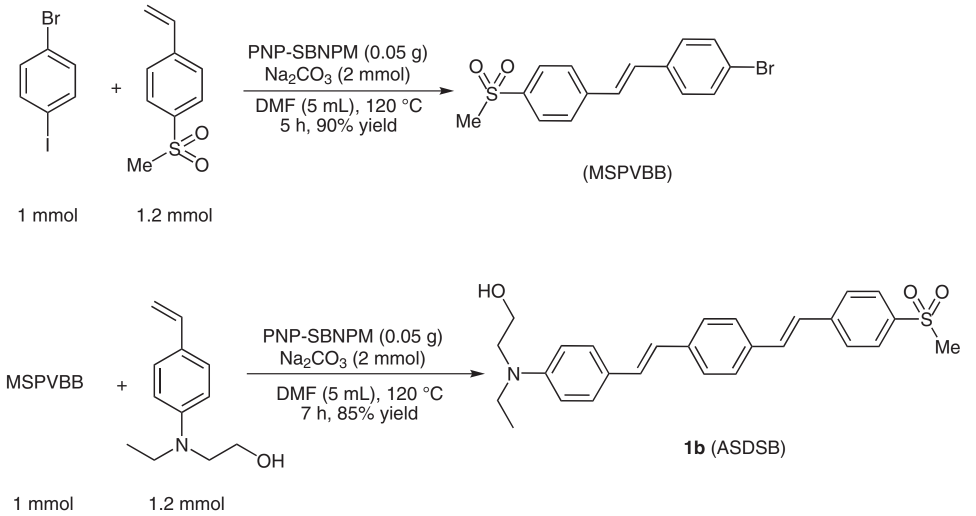
4-Bromostyrene, 4-chlorostyrene, and 4-fluorostyrene were reacted with 2,5-dimethyl-1,4-diiodobenzene to afford **1e**, **1f**, and **1h**, respectively, in very good yields (Table 3). Amine–amine distyrylbenzene **1c**, sulfone–sulfone distyrylbenzene **1d**, and chloro–chloro distyrylbenezene **1g** were synthesized from the reaction of dialkylaminostyrene, methylsulfonstyrene, and 4-chlorostyrene, respectively, with 1,4-diiodobenzene under the optimized conditions, in very good yields (Table 3). This is an efficient and highly stereoselective, one-pot synthetic methodology for the construction of (*E*)-poly(arylene-vinylene)s based on palladium-catalyzed Heck reaction of 4-substituted styrene derivatives with aryl dihalides.

Table 3 Synthesis of New 1,4-Distyrylbenzene Compounds

Entry	Alkene	Aryl Halide	Product	Time (h)	Yield (%)[a]
1			 **1a**	5	90
2			 **1b**	5 + 7	77[b]
3			 **1c**	7	87
4			 **1d**	6	90
5			 **1e**	5	87
6			 **1f**	5.5	83
7			 **1g**	4.5	85
8			 **1h**	6	78

[a] Yield of isolated product.

[b] Overall yield for two steps, see Scheme 4.



Scheme 4 Preparation of **1b** in two steps

These stereoselective, one-pot reactions afforded a range of symmetrical (*E*)-1,4-distyrylbenzene derivatives with high yields (78–90%).[11,35] The known products were characterized and their analytical data were compared to those given in the literature.[2,3,10,11]

The possibility of recycling the catalyst was examined by using the reaction of 1,4-diiodobenzene with styrene under the optimized conditions. Upon completion, the reaction mixture was filtered while hot, the solid was washed with hot DMF, and the recycled catalyst was used in the next reaction. The recycled catalyst could be reused six times without any treatment (Figure 4). The reaction time was five hours for each run. No appreciable loss in the catalytic activity of the PNP-SBNPM was observed, which was demonstrated further by ICP analysis of the original PNP-SBNPM and the six-fold reused catalyst, which showed less than 2% Pd loss had occurred during the recycling.

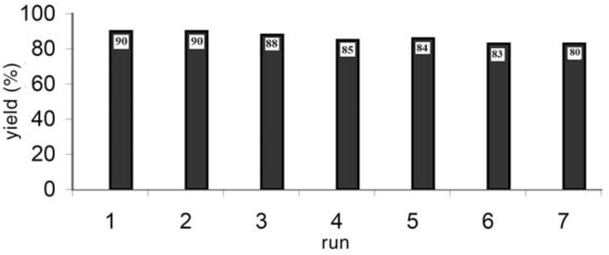


Figure 4 Recyclability of PNP-SBNPM in the reaction of 1,4-diiodobenzene with styrene under the optimized conditions; reaction time = 5 h

In summary, a new and high-performance recyclable catalyst has been introduced to synthesize conjugated small molecules such as 1,4-distrylbenzene derivatives for optophotonic purposes. By using this catalyst, some new 1,4-distrylbenzene derivatives were synthesized in high yield in short reaction times.

Chemicals were purchased from Fluka, Merck, or Aldrich Chemical Companies. The products were characterized by comparison of their spectral and physical data with those reported in the literature. ^1H NMR spectra were recorded with a Bruker (250 MHZ) or a Bruker (500 MHZ) Avance DRX spectrometer in pure DMSO-d_6 or $CDCl_3$ solvents with tetramethylsilane (TMS) as internal standard. Mass spectra were recorded with a FINNIGAN-MAT 8430 mass spectrometer operating at 70 eV. X-ray diffraction (XRD, D8, Advance, Bruker, axs) and FTIR spectroscopy (Shimadzu FT-IR 8300 spectrophotometer) were employed for characterization of the PNP-SBNPM catalyst. Melting points were determined in open capillary tubes in a Barnstead Electrothermal 9100 BZ circulating oil melting point apparatus. The reactions were monitored by TLC analysis on silica gel PolyGram SILG/UV254 plates. Column chromatography was carried out on columns of silica gel 60 (70–230 mesh).

1,4-Distyrylbenzenes 1; General Procedure

In a 50-mL, three-necked flask equipped with reflux condenser, under nitrogen gas, catalyst (0.05 g, 2.4 mol%) was added to a mixture of styrene (2.4 mmol), aryl halide (1 mmol), and Na_2CO_3 (2 mmol) in DMF (5 mL) and the mixture was stirred at 120 °C. The reactions were monitored by TLC. Stirring was continued for the time specified in Table 3 or until the consumption of the starting materials was observed. After completion of the reaction, the mixture was filtered while hot and the remaining catalyst was washed with hot DMF (2×3 mL). H_2O (20 mL) was added to the filtrate to form a precipitate. The product was purified by silica gel column chromatography (*n*-hexane–EtOAc).

It should be noted, in a separate reaction for the synthesis of distyrylbenzene **1a**, after completion of the reaction, hot filtration and precipitation of the product, ICP analysis of the remaining DMF solution showed the amount of leached palladium to be about 4.3 ppm. Furthermore, when the remaining DMF was used as catalyst in a new reaction, no product was obtained.

Distyrylbenzene (1a)

Pale-green crystalline solid; mp 264–266 °C (Lit.[10] 268–268.5 °C).

^1H NMR (250 MHz, DMSO-d_6): $\delta = 7.05–7.45$ (m, 8 H), 7.47–7.55 (m, 10 H).

^{13}C NMR (62.5 MHz, DMSO-d_6): $\delta = 124.3$, 125.5, 126.1, 126.9, 127.2, 128.0, 128.9, 129.4.

(*E*)-1-[2-(4-Methansulfonylphenyl)vinyl]-4-bromobenzene (MSPVBB)

White solid; mp 151–154 °C.[36]

IR (KBr): 3010 (C–H), 2920 (C–H), 1590 (C=C), 1290 (SO_2), 1140 (SO_2) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 3.10 (s, 3 H, CH_3), 7.14 (d, J = 16.3 Hz, 1 H), 7.21 (d, J = 16.3 Hz, 1 H), 7.43 (d, J = 8.5 Hz, 2 H), 7.55 (d, J = 8.5 Hz, 2 H), 7.69 (d, J = 8.4 Hz, 2 H), 7.95 (d, J = 8.4 Hz, 2 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 45.0, 123.0, 127.5, 127.7, 128.3, 128.8, 131.8, 132.4, 135.7, 139.5, 142.9.

2-(*N*-{4-[4-(4-Methylsulfonyl)styryl]styryl}phenyl)-*N*-ethylaminoethanol (1b)

Orange solid; mp 274–276 °C.

IR (KBr): 3500 (O–H), 3020 (C–H), 1585 (C=C), 1519 (C=C), 1292 (SO_2), 1145 (SO_2) cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 1.09 (t, J = 6.9 Hz, 3 H, CH_3), 3.22 (s, 3 H, CH_3), 3.36–3.43 (m, 4 H, CH_2N), 3.53–3.56 (m, 2 H, CH_2O), 4.72 (t, J = 5.4 Hz, 1 H, OH), 6.67 (d, J = 8.8 Hz, 2 H), 6.95 (d, J = 16.3 Hz, 1 H), 7.17 (d, J = 16.3 Hz, 1 H), 7.35 (d, J = 16.4 Hz, 1 H), 7.40 (d, J = 8.7 Hz, 2 H), 7.46 (d, J = 16.4 Hz, 1 H), 7.55 (d, J = 8.3 Hz, 2 H), 7.62 (d, J = 8.3 Hz, 2 H), 7.84 (d, J = 8.4 Hz, 2 H), 7.90 (d, J = 8.3 Hz, 2 H).

MS (EI, 70 eV): m/z (%) = 447 (7.08) $[M]^+$, 416 (17.32), 342 (81.88), 285 (7.87), 236 (12.59), 178 (20.47), 149 (18.89), 111 (22.04), 97 (43.30), 83 (56.69), 57 (94.48), 43 (100).

Anal. Calcd for $C_{27}H_{29}NO_3S$: C, 72.45; H, 6.53; N, 3.12; S, 7.16. Found: C, 72.28; H, 6.66; N, 2.98, S, 6.97.

1,4-Bis{2-[*N*-ethyl-*N*-(4-vinylphenyl)amino]ethanol}benzene (1c)

Yellow solid; mp 215–217 °C.

IR (KBr): 2922, 1160, 1520, 1360, 1267, 1180, 1051, 964, 823 (C–H) cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 1.09 (t, J = 7.0 Hz, 6 H, CH_3), 3.35–3.42 (m, 8 H, CH_2N), 3.52–3.56 (m, 4 H, CH_2O), 4.71 (t, J = 5.4 Hz, 2 H, OH), 6.67 (d, J = 8.8 Hz, 4 H), 6.9 (d, J = 16.3 Hz, 2 H), 7.08 (d, J = 16.3 Hz, 2 H), 7.38 (d, J = 8.7 Hz, 4 H), 7.47 (s, 4 H).

MS (EI, 70 eV): m/z (%) = 456 (94.49) $[M]^+$, 426 (38.58), 425 (100), 412 (35.43), 381 (47.24), 365 (36.22), 352 (24.41), 313 (27.56), 264 (25.19), 236 (24.41), 197 (51.97), 183 (24.41), 169 (25.98), 109 (16.53), 97 (25.19), 83 (25.98), 69 (25.98), 57 (32.28), 43 (24.41).

Anal. Calcd for $C_{30}H_{36}N_2O_2$: C, 78.91; H, 7.95; N, 6.13. Found: C, 78.74; H, 8.06; N, 5.97.

1,4-Bis[4-(methylsulfonyl)styryl]benzene (1d)

Yellow-greenish solid; mp >300 (dec.).

IR (KBr): 3020 (C–H), 2921 (C–H), 1591 (C=C), 1506 (C=C), 1305 (SO_2), 1144 (SO_2) cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 3.23 (s, 6 H, CH_3), 7.43 (d, J = 16.4 Hz, 2 H), 7.51 (d, J = 16.4 Hz, 2 H), 7.71 (s, 4 H), 7.87 (d, J = 8.2 Hz, 4 H), 7.92 (d, J = 7.9 Hz, 4 H).

MS (EI, 70 eV): m/z (%) = 440 (23.53), 439 (44.70), 438 (100) $[M]^+$, 368 (22.35), 339 (17.64), 313 (36.47), 299 (30.59), 264 (43.53), 236 (40.00), 97 (53.00), 83 (60.00), 69 (69.90), 57 (95.29), 43 (91.77).

Anal. Calcd for $C_{24}H_{22}O_4S_2$: C, 65.73; H, 5.06; S, 14.62. Found: C, 65.54; H, 5.25; S, 14.45.

1,4-Bis(4-bromostyryl)-2,5-dimethylbenzene (1e)

Yellow solid; mp 238–240 °C.

IR (KBr): 3005 (C–H), 2910 (C–H), 1520 (C=C), 1480 (C=C), 960 (C–H), 805 (C–H) cm^{-1}.

^1H NMR (500 MHz, DMSO-d_6): δ = 2.41 (s, 6 H, CH_3), 7.15 (d, J = 16.2 Hz, 2 H), 7.41 (d, J = 16.2 Hz, 2 H), 7.54–7.63 (m, 10 H).

MS (EI, 70 eV): m/z (%) = 450 (1.90), 468 (3.70), 466 (1.95) $[M]^+$, 414 (37.03), 412 (35.18), 269 (38.88), 248 (100), 189 (50.92), 149 (49.74), 95 (12.96), 76 (10.16), 57 (15.74).

Anal. Calcd for $C_{24}H_{20}Br_2$: C, 61.56; H, 4.31; Br, 34.13. Found: C, 61.38; H, 4.46.

1,4-Bis(4-chlorostyryl)-2,5-dimethylbenzene (1f)

Yellow solid; mp 187–190 °C.

IR (KBr): 3010 (C–H), 1480 (C=C), 800 (C–H).

^1H NMR (250 MHz, DMDO-d_6): δ = 2.41 (s, 6 H, CH_3), 7.18 (d, J = 16.3 Hz, 1 H), 7.33 (d, J = 16.3 Hz, 1 H), 7.43 (d, J = 8.4 Hz, 2 H), 7.62–7.66 (m, 4 H), 7.67–7.76 (m, 6 H).

MS (EI, 70 eV): m/z (%) = 380 (92.70) $[M^+ +2]$, 379 (36.45) $[M^+ +1]$, 378 (100) $[M]^+$, 328 (26.04), 189 (17.70), 139 (12.50), 115 (6.24), 97 (3.12), 77 (6.24), 57 (4.16).

Anal. Calcd for $C_{24}H_{20}Cl_2$: C, 75.99; H, 5.32; Cl, 18.69. Found: C, 75.81; H, 5.50.

1,4-Bis(4-chlorostyryl)benzene (1g)

Yellow-green solid; mp 296–299 °C (Lit.[10] 294–295 °C).

IR (KBr): 3000 (C–H), 1580 (C=C), 1480 (C=C), 820 (C–H) cm^{-1}.

^1H NMR (250 MHz, DMSO-d_6): δ = 7.30 (m, 4 H), 7.41–7.46 (m, 8 H), 7.63–7.65 (m, 4 H).

MS (EI, 70 eV): m/z (%) = 352 (82.35) $[M^+ + 2]$, 351 (31.76) $[M^+ + 1]$, 350 (100) $[M]^+$, 202 (34.11), 178 (67.05), 149 (91.76), 113 (17.32), 89 (22.33), 71 (25.98), 57 (37.64).

1,4-Bis(4-fluorostyryl)-2,5-dimethylbenzene (1h)

Pale-yellow solid; mp 196–198 °C.

IR (KBr): 3015 (C–H), 1485, 1375, 1060, 1000, 960, 845, 800 (C–H) cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 2.46 (s, 6 H, CH_3), 7.02 (d, J = 16.1 Hz, 2 H), 7.09 (t, J = 8.6 Hz, 4 H), 7.25 (d, J = 16.1 Hz, 2 H), 7.44 (s, 2 H), 7.51–7.54 (m, 4 H).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 20.0, 116.0, 116.1, 126.3, 127.6, 128.4, 128.5, 128.7, 133.9, 135.1 (d, J_{C-F} = 186.8 Hz).

Anal. Calcd for $C_{24}H_{20}F_2$: C, 83.21; H, 5.82; F, 10.97. Found: C, 83.05; H, 6.01.

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