

Electronic Supplementary Information

Synthesis of new styrylarenes *via* Suzuki-Miyaura coupling catalysed by highly active, well-defined palladium catalysts

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Experimental Part

Instruments

¹H NMR (300 MHz), ¹³C NMR (75 MHz), and ¹⁹F NMR (282 MHz) and DEPT spectra were recorded on a Varian XL 300 MHz spectrometer in CDCl₃ or DMSO solution. Chemical shifts are reported in δ (ppm) with reference to the residue solvents (¹H δ_H = 7.26 ppm, ¹³C δ_C = 77.0 ppm for CD₃Cl and ¹H δ_H = 2.16 ppm, ¹³C δ_C = 128.05 ppm for C₆D₆) peak for ¹H, ¹³C and to TMS (²⁹Si δ_H = 0.00 ppm). Analytical gas chromatographic (GC) analyses were performed on a Varian Star 3400CX with a DB-5 fused silica capillary column (30 m x 0.15 mm) and TCD. Mass spectra of the substrates and products were obtained by GCMS analysis (Varian Saturn 2100T, equipped with a BD-5 capillary column (30 m) and an ion trap detector. High-resolution mass spectroscopic (HRMS) analyses were performed on an AMD-402 mass spectrometer. Thin-layer chromatography (TLC) was made on plates pre-coated plastic sheet with 250 μm thick silica gel (Polygram SilG/UV₂₅₄, ROTH), and column chromatography was conducted with silica gel 60 (70-230 mesh, Fluka). Elementary analysis measurements were performed using by Elementar Analyser Vario EL III. UV-Vis spectra were measured using a Cary 300 Bio Varian spectrophotometer, and fluorescence spectra were measured on a Perkin Elmer LS 50B spectrofluorimeter.

Materials

The chemicals were obtained from the following sources: toluene, diethyl ether, dichloromethane, pentane and hexane, were purchased from Fluka, CDCl₃ from Dr Glaser A.G. Basel, 4-bromostyrene, 2-bromothiophene, 1-bromonaphtalene, bromopentafluorobenzene, bromobenzene, 1,4-dibromobenzene, 1,4-dibromotetrafluorobenzene, sodium carbonate (Na₂CO₃), potassium carbonate (K₂CO₃), magnesium sulphate, calcium hydride (CaH₂), sodium hydride (NaH), 1,2-dichloromethane, triphenylphosphine, ethanol, benzene-d₆ (C₆D₆, 99.6 atom% D), phenylboronic acid, 4-vinylphenylboronic acid, bis(dibenzylideneacetone)palladium(0) - [Pd(dba)₂] (**1**), Celite 545 from Aldrich and 9-bromoanthracene, 9,10-dibromoanthracene, 2,5-dibromothiophene, 1,4-dibromonaphtalene, tricyclohexylphosphine from ABCR. Toluene was distilled from sodium and hexane, ethanol from calcium hydride under argon. The above mentioned solvents were stored over molecular sieves type 4Å. All liquid substrates were also dried and degassed by bulb-to-bulb distillation. All the syntheses of catalysts, molecular compounds and catalytic tests were carried out under an inert argon or air atmosphere.

Procedure for Synthesis of Palladium(0) Complexes

The title compounds were synthesized according to the procedure presented below.²⁴

Bis(triphenylphosphine)(dibenzylideneacetone)palladium(0) - {Pd(η²-dba)(PPh₃)₂} (**2**): Pd(dba)₂ (**1**) (0.3 g, 5.22 x 10⁻⁴ mol), triphenylphosphine (0.275 g, 1.054 x 10⁻³ mol) were placed in a Schlenk flask (25 mL) and degassed for a one minute. Afterwards 4 mL toluene (0.125M) was introduced into a vigorously stirred solids of substrates and the final mixture was left

for 22h at room temperature to give a yellow-orange solution. The excess of solvent was evaporated under reduced pressure, followed by the addition of hexane and gave a deep yellow precipitate. Next, the latter was filtered ('canula' system), washed with cold hexane (3 x 15 mL) and dried in vacuum for 3h (0.42g, 98% yield).

^1H NMR (300 MHz, C_6D_6 , 298K) δ (ppm) = 7.85 (s, 1H, $-\text{HC}=\text{CH}-$), 7.79 (s, 1H, $-\text{HC}=\text{CH}-$), 7.49 (s, 4H, *m*-Ph, dba), 7.44 (s, 12H, *m*-Ph, PPh_3), 6.92 and 6.89 (d, 24H, *o*-, *p*-Ph, dba and PPh_3), 6.21 (m, 2H, $-\text{HC}=\text{CH}-$), 5.43 (m, 2H, $-\text{HC}=\text{CH}-$, coordinated). ^{13}C NMR (75.42 MHz, C_6D_6 , 298K, δ (ppm) = 187.51 (CO), 143.06, 137.20; 136.91, 134.38, 134.27, 132.82, 132.72, 130.59, 129.14, 129.01, 128.61, 128.57, 128.49, 126.16. ^{31}P NMR (121.47 MHz, C_6D_6 , 298K, δ (ppm) = 26.91 (d, $J_{\text{P-H}} = 8.99$ Hz). IR (KBr, cm^{-1}) 1925 (ν (CO)). Elemental analyses calcd. for $\text{C}_{54}\text{H}_{46}\text{OP}_2\text{Pd}$: C 73.76, H 5.27; found C 73.84, H 5.29.

Bis(tricyclohexylphosphine)(dibenzylideneacetone) palladium(0) – {Pd(η^2 -dba)(PCy₃)₂} (**3**)²⁵ was prepared essentially in a manner similar to that synthesis procedure of **2** complex. $\text{Pd}(\text{dba})_2$ (**1**) (0.3 g, 5.22×10^{-4} mol), tricyclohexylphosphine (0.294 g, 1.054×10^{-3} mol) were placed in a Schlenk flask (25 mL) and degassed for a one minute. Subsequently, 4 mL toluene (0.125M) was introduced into a vigorously stirred solids of substrates and the final mixture was left for 18h at room temperature to give a yellow-orange solution. The excess of solvent was evaporated under reduced pressure, followed by the addition of hexane and gave an orange precipitate. After that, the latter was filtered ('canula' system), washed with cold hexane (3 x 15 mL) and dried in vacuum for 3h (0.40g, 95% yield).

^1H NMR (300 MHz, C_6D_6 , 298 K, δ (ppm) = 7.85 (sb, 1H, $-\text{HC}=\text{CH}-$, dba), 7.82 (s, 1H, $-\text{HC}=\text{CH}-$, dba), 7.50 (sb, 4H, *m*-Ph, dba), 7.17 (m), 7.06 (d, 8H, *o*-, *p*-Ph-); 4.93 (m, 2H, $-\text{HC}=\text{CH}-$ coordinated), 2.02 (m), 1.72 (m), 1.66 (m), 1.35 (m), 1.21 (m) 66H, $-\text{C}_6\text{H}_{10}$). ^{13}C NMR (75.42 MHz, C_6D_6 , 298 K, δ (ppm) = 187.92 (CO), 143.08, 135.79, 130.60, 129.36, 128.96, 127.82, 126.53, 36.49, 36.01, 31.11, 28.35, 27.64, 27.49, 27.02. ^{31}P NMR (121.47 MHz, C_6D_6 , 298 K, δ (ppm) = 45.02. IR (KBr, cm^{-1}) = 1923 (ν (CO)). Elemental analyses calcd. for $\text{C}_{54}\text{H}_{82}\text{OP}_2\text{Pd}\cdot\text{C}_7\text{H}_8$: C 72.70, H 9.00; found C 72.81, H 8.99.

Synthesis of Organic Compounds

Catalytic Part

General procedure for catalytic test of new palladium complexes reactivity

A mixture of aryl bromine or 4-bromostyrene (0.5 mmol), phenylboronic acid or 4-vinylphenylboronic acid (0.5 mmol), 2M aq. base solution (0.7-1 mmol of Na_2CO_3 or K_2CO_3 depending on the combination of complex), ethanol (0.75 mL), toluene (0.5M solution concentration for bromoarene), $[\text{Pd}(\text{dba})(\text{PR}_3)_2]$ complex (**2** – R = Ph or **3** – R = Cy; 0.01-1 mol%) were placed in a two-necked glass-reactor equipped with a magnetic stirring bar and reflux condenser. The suspension was degassed and heated in an oil bath at 40-90°C for 0.5-24h. The reaction progress was monitored by TLC (eluent: hexane, $R_f = 0.6-0.8$ in relation to biphenyl) and GCMS to complete.

General procedure for catalytic test of S-M cross-coupling

A mixture of aryl bromine (0.5 mmol), 4-vinylphenylboronic acid (0.5 mmol), 2M aq. base solution (1 mmol of K_2CO_3 or Na_2CO_3 depending on the combination of substrate), ethanol (0.75 mL), toluene (0.5M solution concentration for bromoarene), $[\text{Pd}(\eta^2\text{-dba})(\text{PR}_3)_2]$ complex (**3** – R = Cy or **2** – R = Ph; 1-0.5 mol%) were placed in a two-necked glass-reactor equipped with a magnetic stirring bar and reflux condenser. The suspension was degassed and heated in an oil bath at 40-90°C for 2-6h. The reaction progress was monitored by TLC (eluent: hexane / DCM = 10:1, $R_f = 0.52-0.56$ in relation to biphenyl) and GCMS to complete. The correct structures of biphenyl or 4-vinylbiphenyl were identified and confirmed by NMR method.

Analytic Data

Biphenyl (**4**)²⁸

MS (EI) (m/z (relat. int. %)): 154 (M⁺) (100), 128 (7), 115 (5), 76 (15), 52 (6). ¹H NMR (CDCl₃; δ (ppm)): 7.35 (t, 4H, *J*_{HH} = 7.7 Hz), 7.44 (t, 4H, *J*_{HH} = 7.1 Hz), 7.57 (d, 4H, *J*_{HH} = 8.3 Hz).

4-vinylbiphenyl (**5**)²⁹

¹H NMR (300 MHz, CDCl₃; δ (ppm)): 5.27 (d, 1H, *J*_{HH} = 0.9, 10.8 Hz), 5.77 (dd, 1H, *J*_{HH} = 0.9, 17.7 Hz), 6.76 (dd, 1H, *J*_{HH} = 10.8, 17.4 Hz), 7.29-7.63 (m, 9H). MS (EI) (m/z (relat. int. %)): 180 (M⁺) (100), 165 (17), 152 (10), 129 (38), 102 (9), 76 (14), 51 (7). HRMS (m/z) calcd. for C₁₄H₁₂: 180.09390, found 180.09385.

Synthesis of New Styrylarenes

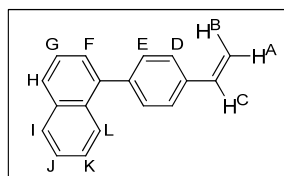
General procedure for synthesis of monostyryl derivatives via S-M cross-coupling²⁶

A mixture of aryl bromine (1 mmol), 4-vinylphenylboronic acid (1 mmol), alkali solution 2M (3 mL, Na₂CO₃, K₂CO₃ depending on the combination of complex reactivity), toluene (0.25M solution concentration for halide), ethanol (2 mL), {Pd(η²-dba)(PR₃)₂} complex (**2** or **3**, 0.2-1 mol%) were placed in a two-necked glass-reactor equipped with a magnetic stirring bar and reflux condenser. The suspension was heated in an oil bath at 60-90°C for 2-20h. After the reaction was completed (monitored by TLC and GCMS analysis), the resulting mixture was isolated by very quick 'flash' column system (glass filter G3, silica gel ±4 cm, celite) connected with membrane pump and dried over anhydrous MgSO₄ for 4h. The excess of solvent was evaporated under vacuum. The resulting olefins were dissolved in THF, DCM or CHCl₃, isolated and purified by repeated precipitation from DCM/hexane system (except of **6**). The final products were filtered off and dried under vacuum for 15 minutes. The isolated yields were from 73 to 95% (depending on the combination of starting bromoarene).

Analytic Data of Monostyryl-olefins

1-(4-vinylphenyl)naphthalene (**6**)

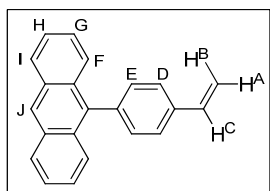
The product was isolated as a light yellowish solid with 83 % yield (191 mg). ¹H NMR (300 MHz, CDCl₃; δ (ppm)): 5.32 (dd, 1H, (A), *J*_{HH} = 10.8, 0.9 Hz), 5.83 (dd, 1H, (B), *J*_{HH} = 17.7, 0.9 Hz), 6.83 (dd, 1H, (C), *J*_{HH} = 17.7, 11.1 Hz), 7.41-7.57 (m, 7H, (E, F, G, I, J, K)), 7.90 (dd, 2H, (D), *J*_{HH} = 13.2, 8.1 Hz), 8.01 (d, 1H, (L), *J*_{HH} = 3.6 Hz), 8.21 (d, 1H, (H), *J*_{HH} = 8.1 Hz). ¹³C NMR (75.42 MHz, CDCl₃; δ (ppm)): 114.0, 125.4, 125.9, 125.9, 126.0, 126.1, 126.4, 126.8, 127.7, 128.3, 130.2, 130.3, 131.5, 133.8, 136.5, 139.9, 140.3. MS (EI) (m/z (relat. int. %)): 230 (M⁺) (100), 215 (19), 202 (31), 190 (5), 176 (2), 163 (2), 150 (3), 137 (1), 126 (2), 113 (7), 101 (10), 87 (4), 74 (6), 63 (7), 50 (9). HRMS (m/z) calcd. for C₁₈H₁₄: 230.10955, found 230.10937.



9-(4-vinylphenyl)anthracene (**7**)

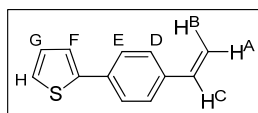
The product was isolated as a yellowish solid with 95 % yield (246 mg). ¹H NMR (300 MHz, CDCl₃; δ (ppm)): 5.38 (dd, 1H, (A), *J*_{HH} = 10.8, 0.6 Hz), 5.81 (dd, 1H, (B), *J*_{HH} = 17.6, 0.8 Hz), 6.75 (dd, 1H, (C), *J*_{HH} = 17.6, 10.9 Hz), 7.33-7.50 (m, 4H(G i H)), 7.41 (d, 2H, (D), *J*_{HH} = 8.1 Hz), 7.64 (d, 2H, (E), *J*_{HH} = 7.8 Hz), 7.70, (dd, 2H, (F), *J*_{HH} = 0.9, 0.9 Hz), 8.05 (d, 2H, (I),

$J_{HH} = 8.4$ Hz), 8.50 (s, 1H, (J)). ^{13}C NMR (75.42 MHz, CDCl_3 ; δ (ppm)): 114.1, 125.1, 125.3, 126.2, 126.6, 126.8, 128.3, 130.1, 131.3, 131.5, 136.6, 136.65, 136.7, 138.3. MS (EI) (m/z (relat. int. %)): 279 (M^+) (100), 264 (18), 252 (21), 240 (4), 227 (3), 200 (1), 187 (0), 175 (1), 150 (1), 138 (5), 126 (5), 113 (6), 98 (2), 87 (2), 74 (4), 63 (4), 50 (5). HRMS (m/z) calcd. for $\text{C}_{22}\text{H}_{16}$: 280.12520, found: 280.12511.



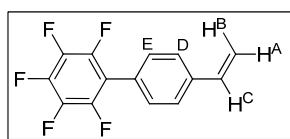
2-(4-vinylphenyl)thiophene (8)

The product was isolated as a yellow solid with 73 % yield (136 mg). ^1H NMR (300 MHz, CDCl_3 ; δ (ppm)): 5.28 (dd, 1H, (A), $J_{HH} = 10.9, 0.8$ Hz), 5.81 (dd, 1H, (B), $J_{HH} = 17.6, 0.8$ Hz), 6.75 (dd, 1H, (C), $J_{HH} = 17.6, 10.9$ Hz), 7.10 (dd, 1H, (F), $J_{HH} = 3.6, 5.1$ Hz), 7.28 (dd, 1H, (G), $J_{HH} = 0.9$ Hz), 7.33 (dd, 1H, (H), $J_{HH} = 1.2$ Hz), 7.45 (d, 2H, (D), $J_{HH} = 8.1$ Hz), 7.62 (d, 2H, (E), $J_{HH} = 8.4$ Hz). ^{13}C NMR (75.42 MHz, CDCl_3 ; δ (ppm)): 113.9, 123.0, 124.8, 125.9, 126.7, 128.0, 133.8, 136.2, 136.7, 144.1. MS (EI) (m/z (relat. int. %)): 186 (M^+) (100), 171 (9), 160 (3), 152 (14), 141 (11), 128 (3), 115 (17), 108 (2), 102 (5), 89 (5), 77 (6), 63 (8), 50 (9). HRMS (m/z) calcd. for $\text{C}_{12}\text{H}_{10}\text{S}$: 186.05032, found 186.05016.



2,3,4,5,6-pentafluoro-4'-vinylbiphenyl (9)

The product was isolated as a light-yellow solid with 92 % yield (248 mg). ^1H NMR (300 MHz, CDCl_3 ; δ (ppm)): 5.28 (dd, 1H, (A), $J_{HH} = 10.9, 0.8$ Hz), 5.77 (dd, 1H, (B), $J_{HH} = 17.6, 0.8$ Hz), 6.69 (dd, 1H, (C), $J_{HH} = 17.6, 10.9$ Hz), 7.32 (d, 2H, (D), $J_{HH} = 8.3$ Hz), 7.45 (d, 2H, (E), $J_{HH} = 8.2$ Hz). ^{13}C NMR (75.42 MHz, CDCl_3 ; (except for C_6F_5), δ (ppm)): 115.4, 125.6, 126.5, 126.7, 130.3, 136.4, 138.5. ^{19}F NMR (282 MHz, CDCl_3 ; δ (ppm)): -163.4 (m, 2F), -156.8 (t, $J = 20.9$ Hz, 1F), -144.6 (dd, $J = 7.2, 23.4$ Hz, 2F). MS (EI) (m/z (relat. int. %)): 270 (M^+) (100), 250 (16), 231 (4), 219 (22), 201 (15), 181 (2), 147 (2), 123 (3), 103 (3), 93 (3), 78 (4), 69 (4), 50 (5). HRMS (m/z) calcd. for $\text{C}_{14}\text{H}_7\text{F}_5$: 270.04679, found 270.04664.



General procedure for synthesis of distyryl derivatives via S-M cross-coupling²⁷

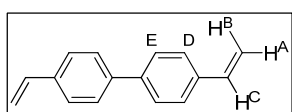
A mixture of aryl dibromide or aryl bromide for 10 (2 mmol), 4-vinylphenylboronic acid (4 mmol or 2 mmol for 10), 2M aq. base solution (2 mL, K_2CO_3 , ethanol (3 mL), toluene (0.25M solution concentration, olefin), $\text{Pd}(\eta^2\text{-dba})(\text{PCy}_3)_2$ (**3**) (0.2-0.4 mol%) were placed in a two-necked glass-reactor equipped with a magnetic stirring bar and reflux condenser. The suspension was degassed and heated in an oil bath at 70-80°C for 1-18h. After the reaction was completed (monitored by TLC and GCMS), the resulting mixture was concentrated and extracted with DCM and washed with water (three times). Then, the organic layer was collected and passed through by very quick 'flash system' (glass filter G3, silica gel, celite) and dried over anhydrous MgSO_4 for 4h. The excess of solvent was evaporated to dryness under vacuum. The resulting olefins were dissolved in DCM or CHCl_3 (quite good or weakly soluble), isolated and purified by repeated precipitation from

DCM/hexane system. The final products were filtered off and dried under vacuum for 20 minutes. The isolated yields were from 66 to 98% (depending on the combination of starting dibromoarene).

Analytic Data of Distyryl-olefins

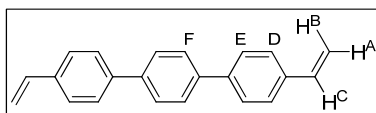
4,4'-divinylbiphenyl (**10**)

The product was isolated as a white solid with 90 % yield (371 mg). ^1H NMR (300 MHz, CDCl_3 ; δ (ppm)): 5.27 (dd, 2H, (A), $J_{\text{HH}} = 10.8, 0.9$ Hz), 5.77 (dd, 2H, (B), $J_{\text{HH}} = 17.7, 0.9$ Hz), 6.76 (dd, 2H, (C), $J_{\text{HH}} = 17.4, 10.8$ Hz), 7.48 (d, 4H, (E), $J_{\text{HH}} = 8.4$ Hz), 7.57 (d, 4H, (D), $J_{\text{HH}} = 8.4$ Hz). ^{13}C NMR (75.42 MHz, CDCl_3 ; δ (ppm)): 113.9, 126.6, 127.0, 136.3, 136.6, 140.1. MS (EI) (m/z (relat. int. %): 206 ($\text{M}^{+\bullet}$) (100), 190 (13), 178 (14), 165 (7), 152 (7), 139 (3), 128 (3), 115 (3), 102 (4), 89 (6), 76 (8), 63 (6), 51 (10). HRMS (m/z) calcd. for $\text{C}_{16}\text{H}_{14}$: 206.10955, found 206.10948. Elemental analyses calcd. for $\text{C}_{16}\text{H}_{14}$: C 93.16, H 6.84; found C 93.13, H 6.83. UV-Vis (CH_2Cl_2) $\lambda_{\text{max}} = 299$ nm; FL (CH_2Cl_2) $\lambda_{\text{max}} = 373$ nm.



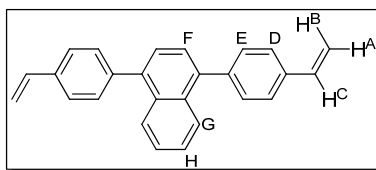
4,4'-divinyl-*p*-terphenyl (**11**)

The product was isolated as a white solid with 89 % yield (502 mg). ^1H NMR (300 MHz, CDCl_3 ; δ (ppm)): 5.29 (d, 2H, (A), $J_{\text{HH}} = 11.1$ Hz), 5.80 (d, 2H, (B), $J_{\text{HH}} = 17.7$ Hz), 6.77 (dd, 2H, (C), $J_{\text{HH}} = 17.5, 11.2$ Hz), 7.51 (d, 4H, (E), $J_{\text{HH}} = 8.4$ Hz), 7.62 (d, 4H, (D), $J_{\text{HH}} = 8.4$ Hz), 7.69 (s, 4H, (F)). ^{13}C NMR (75.42 MHz, CDCl_3 ; δ (ppm)): 113.9, 126.7, 127.1, 127.3, 136.4, 136.5, 136.7, 139.6. MS (EI) (m/z (relat. int. %): 282 ($\text{M}^{+\bullet}$) (100), 266 (4), 252 (6), 239 (7), 226 (2), 203 (3), 178 (8), 165 (3), 150 (2), 141 (4), 127 (3), 103 (3), 87 (3), 74 (3), 63 (5), 50 (4). HRMS (m/z) calcd. for $\text{C}_{22}\text{H}_{18}$: 282.14085, found 282.14077. Elemental analyses calcd. for $\text{C}_{22}\text{H}_{18}$: C 93.57, H 6.43; found C 93.60, H 6.45. UV-Vis (CH_2Cl_2) $\lambda_{\text{max}} = 311$ nm; FL (CH_2Cl_2) $\lambda_{\text{max}} = 380$ nm.



1,4-bis(4-vinylphenyl)naphthalene (**12**)

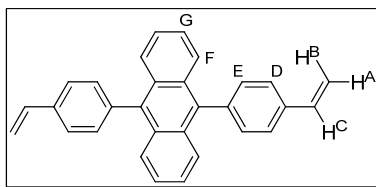
The product was isolated as a yellowish solid with yield 98% (651 mg). ^1H NMR (300 MHz, CDCl_3 ; δ (ppm)): 5.33 (dd, 2H, (A), $J_{\text{HH}} = 10.8, 0.9$ Hz), 5.86 (dd, 2H, (B), $J_{\text{HH}} = 17.4, 1.2$ Hz), 6.84 (dd, 2H, (C), $J_{\text{HH}} = 17.7, 10.8$ Hz), 7.43-7.59 (m, 4H, (D, E, F, G)), 8.01 (dd, 2H, (G), $J_{\text{HH}} = 6.6, 3.3$ Hz). ^{13}C NMR (75.42 MHz, CDCl_3 ; δ (ppm)): 114.0, 125.9, 126.1, 126.3, 126.4, 130.3, 131.9, 136.5, 136.6, 139.5, 140.3. MS (EI) (m/z (relat. int. %): 333 ($\text{M}^{+\bullet}$) (100), 316 (24), 303 (14), 290 (11), 277 (7), 264 (2), 250 (3), 228 (15), 202 (6), 188 (1), 151 (6), 139 (5), 113 (2), 77 (8), 63 (6), 50 (8). HRMS (m/z) calcd. for $\text{C}_{26}\text{H}_{20}$: 332.15650, found 332.15640. Elemental analyses calcd. for $\text{C}_{26}\text{H}_{20}$: C 93.94, H 6.06; found C 93.89, H 6.05. UV-Vis (CH_2Cl_2) $\lambda_{\text{max}} = 313$ nm; FL (CH_2Cl_2) $\lambda_{\text{max}} = 404$ nm.



9,10-bis(4-vinylphenyl)anthracene (**13**)

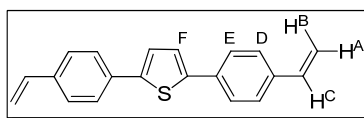
The product was isolated as a yellowish solid with 79% yield (604 mg). ^1H NMR (300 MHz, CDCl_3 ; δ (ppm)): 5.35 (dd, 2H, (A), $J_{\text{HH}} = 11.4, 0.6$ Hz), 5.93 (dd, 2H, (B), $J_{\text{HH}} = 17.4, 0.6$ Hz), 6.91 (dd, 2H, (C), $J_{\text{HH}} = 17.4, 11.1$ Hz), 7.33 (dd, 4H, (E),

$J_{HH} = 6.9, 3.3$ Hz), 7.45 (d, 4H (G), $J_{HH} = 8.1$ Hz), 7.67 (dd, 4H, (F), $J_{HH} = 6.9, 3.3$ Hz), 7.74 (d, 4H, (D), $J_{HH} = 10.2$ Hz). ^{13}C NMR (75.42 MHz, CDCl_3 ; δ (ppm)): 114.2, 125.0, 126.3, 126.9, 129.8, 131.5, 136.6, 136.7, 136.8, 138.6. MS (EI) (m/z (relat. int. %): 382 (M^+) (100), 365 (8), 339 (8), 312 (2), 278 (16), 263 (6), 236 (1), 206 (1), 176 (8), 125 (1), 104 (2), 77 (3), 50 (4). HRMS (m/z) calcd. for $\text{C}_{30}\text{H}_{22}$: 382.17215, found 382.17207. Elemental analyses calcd. for $\text{C}_{30}\text{H}_{22}$: C 94.20, H 5.80; found C 94.28, H 5.78. UV-Vis (CH_2Cl_2) $\lambda_{\text{max}} = 261, 358, 376, 396$ nm; FL (CH_2Cl_2) $\lambda_{\text{max}} = 432$ nm.



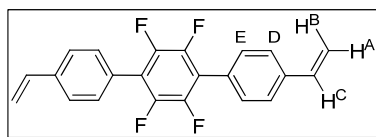
2,5-bis(4-vinylphenyl)thiophene (**14**)

The product was isolated as a yellow solid with 66% yield (380 mg). ^1H NMR (300 MHz, CDCl_3 ; δ (ppm)): 5.20 (dd, 2H, (A), $J_{HH} = 10.8, 2.4$ Hz), 5.71 (dd, 2H, (B), $J_{HH} = 17.4, 11.4$ Hz), 6.65 (dd, 2H, (C), $J_{HH} = 17.4, 10.5$ Hz), 7.19 (s, 2H, (F)), 7.36 (dd, 2H, (E), $J_{HH} = 18.0, 9.9$ Hz), 7.52 (dd, 4H, (D), $J_{HH} = 5.4, 1.2$ Hz). ^{13}C NMR (75.42 MHz, CDCl_3 ; δ (ppm)): 110.1, 111.8, 124.0, 125.6, 126.7, 136.2, 144.6. MS (EI) (m/z (relat. int. %): 289 (M^+) (100), 272 (12), 254 (9), 239 (12), 226 (19), 215 (5), 203 (3), 184 (7), 160 (7), 147 (19), 128 (7), 115 (26), 103 (16), 77 (13), 63 (14), 50 (14). HRMS (m/z) calcd. for $\text{C}_{20}\text{H}_{16}\text{S}$: 288.09727, found 288.09716. Elemental analyses calcd. for $\text{C}_{20}\text{H}_{16}\text{S}$: C 83.29, H 5.59, S 11.12; found C 83.17, H 5.57, S 11.08. UV-Vis (CH_2Cl_2) $\lambda_{\text{max}} = 363$ nm; FL (CH_2Cl_2) $\lambda_{\text{max}} = 432$ nm.



1,4-bis(4-vinylphenyl)-2,3,5,6-tetrafluorobenzene (**15**)

The product was isolated as a yellow solid with 76% yield (538 mg). ^1H NMR (300 MHz, CDCl_3 ; δ (ppm)): 5.36 (dd, 2H, (A), $J_{HH} = 10.8, 0.6$ Hz), 5.86 (dd, 2H, (B), $J_{HH} = 17.7, 0.9$ Hz), 6.78 (dd, 2H, (C), $J_{HH} = 17.7, 10.8$ Hz), 7.49 (d, 4H, (E), $J_{HH} = 8.4$ Hz), 7.56 (d, 4H, (D), $J_{HH} = 6.3$ Hz). ^{13}C NMR (75.42 MHz, CDCl_3 ; (without of C_6F_4) δ (ppm)): 115.3, 126.4, 126.7, 130.4, 136.1, 138.3. ^{19}F NMR (282 MHz, CDCl_3 ; δ (ppm)): -144.79. MS (EI) (m/z (relat. int. %): 355 (M^+) (100), 335 (7), 307 (6), 284 (3), 250 (7), 232 (2), 201 (2), 178 (2), 154 (3), 123 (1), 103 (4), 77 (15), 51 (11). HRMS (m/z) calcd. for $\text{C}_{22}\text{H}_{14}\text{F}_4$: 354.10316, found 354.10308. Elemental analyses calcd. for $\text{C}_{22}\text{H}_{14}\text{F}_4$: C 74.54, H 3.98; found C 74.51, H 3.97.



X-Ray structure determination

Diffraction data were collected at room temperature by the ω -scan technique on an Agilent Technologies Excalibur four-circle diffractometer with Eos CCD-detector, using MoK_α radiation source ($\lambda = 0.7107\text{\AA}$). The data were corrected for Lorentz-polarization as well as for absorption effects.³⁰ Accurate unit-cell parameters were determined by a least-squares fit of 2523 (**3**) and 6692 (**2**) reflections of highest intensity, chosen from the whole experiment. The structures were solved with SIR92³¹ and refined with the full-matrix least-squares procedure on F^2 by SHELXL97.³² Scattering factors incorporated in SHELXL97 were used. The function $\Sigma w(|F_o|^2 - |F_c|^2)^2$ was minimized, with $w^{-1} = [\sigma^2(F_o)^2 + (A \cdot P)^2 + B \cdot P]$ ($P = [\text{Max}(F_o^2, 0) + 2F_c^2]/3$). The final values of A and B are listed in Table 1. All non-hydrogen atoms were refined anisotropically. The

hydrogen atoms were placed geometrically, in idealized positions, and refined as rigid groups with their U_{iso} 's as 1.2 times U_{eq} of the appropriate carrier atom. In the crystal structure of **3** the voids are filled with disordered solvent – toluene (methyl group is probably distributed all over the ring so we were not able to locate it) molecules; weak constraints for both geometry and ADP's of these disordered fragments were applied. Relevant crystal data are listed in Table 3, together with refinement details.

Table 3. Crystal data collection and structure refinement

Compound	2	3
Formula	C ₅₃ H ₄₄ OP ₂ Pd	C ₅₃ H ₇₈ OP ₂ Pd • C ₇ H ₉
Formula weight	865.22	992.60
Crystal system	triclinic	triclinic
Space group	P-1	P-1
a(Å)	10.8591(6)	10.6036(7)
b(Å)	11.7884(4)	15.6718(11)
c(Å)	17.5860(7)	16.8115(13)
α(°)	100.507(3)	90.300(6)
β(°)	96.062(4)	97.933(6)
γ(°)	94.798(4)	98.049(6)
V(Å ³)	2188.86(17)	2738.8(3)
Z	2	2
D _x (g cm ⁻³)	1.31	1.19
F(000)	892	1044
μ(mm ⁻¹)	0.53	0.43
Θ range (°)	3.19 – 25.00	2.92– 25.00
hkl range	-12≤h≤12 -14≤k≤12 -20≤l≤20	-12≤h≤12 -18≤k≤18 -19≤l≤17
Reflections:		
collected	16172	18598
unique (R _{int})	7667 (0.027)	9629 (0.074)
with I>2σ(I)	6757	4997
No. of parameters	524	605
Weighting scheme:		
A	0.0305	0.04
B	8.2883	0
R(F) [I>2σ(I)]	0.051	0.068
wR(F ²) [I>2σ(I)]	0.142	0.112
R(F) [all data]	0.047	0.153
wR(F ²) [all data]	0.144	0.137
Goodness of fit	1.161	0.921
max/min Δρ (e Å ⁻³)	1.26/-0.65	0.69/-0.56

Supplementary material

Crystallographic data (excluding structure factors) for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, Nos. CCDC-844578 (**3**) and CCDC-844579 (**2**). Copies of this information may be obtained free of charge from: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Fax: +44(1223)336-033, e-mail: deposit@ccdc.cam.ac.uk, or www: www.ccdc.cam.ac.uk.

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