

## Supporting information for

# Palladium-Catalyzed Desulfitative Hydroarylation of Alkynes with Sodium Sulfinates

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### General information:

All experiments were carried out under an atmosphere of argon. Flash column chromatography was performed over silica gel 48-75  $\mu\text{m}$ .  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to  $\text{SiMe}_4$  or chloroform signals. MS analyses were performed on Agilent 5975 GC-MS instrument (EI). The new compounds were characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, MS and HRMS. The structure of known compounds were further corroborated by comparing their  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR data and MS data with those of literature. Unless otherwise noted, all reagents were obtained from commercial suppliers and used without further purification. Aromatic sulfinic acid sodium salts **1a**, **1b**, **1h**, **1i**, and **1n** were purchased from Alfa Aesar, others were prepared according to the literature procedures. Solvents were used as received without further purification.

### General procedure: 1,1,2-triphenylethene (**3a**)

A pressure tube (10 mL) was charged with sodium benzenesulfinate (**1a**, 60.0 mg, 0.3 mmol), diphenylethyne (**2a**, 35.6 mg, 0.2 mmol),  $\text{Pd}(\text{OAc})_2$  (2.2 mg, 0.01 mmol), and 1,8-naphthalenediamine (4.3 mg, 0.02 mmol). The sealed reaction vessel was purged with argon three times. Trifluoroacetic acid (0.3 mmol) and a mixture of 1,4-dioxane (0.3 mL) and  $\text{H}_2\text{O}$  (0.1 mL) were added to the sealed reaction vessel by syringe. The resulting solution was heated to 120  $^\circ\text{C}$  for 24 h. After cooling to room temperature, the volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether) to give **3a** in 90% yield (46.1 mg) as colourless oil.

### Optimization of reaction conditions

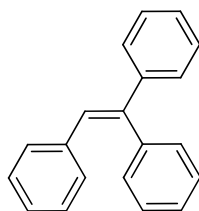
**Table 1.** Optimization of the reaction conditions.<sup>a</sup>

$\text{PhSO}_2\text{Na}$  (1a) +  $\text{Ph}-\text{C}\equiv\text{C}-\text{Ph}$  (2a)  $\xrightarrow[\text{120 }^\circ\text{C, argon}]{\text{catalyst}}$   $\text{Ph}-\text{CH}=\text{C}(\text{Ph})-\text{CH}=\text{CH}_2$  (3a)

Entry	Catalyst	Ligand	Additive	Solvent	Yield [%] <sup>b</sup>
1	PdCl <sub>2</sub>	1,8-naph	TFA	dioxane/H <sub>2</sub> O	90
2	Pd(OH) <sub>2</sub>	1,8-naph	TFA	dioxane/H <sub>2</sub> O	93
3	Pd(acac) <sub>2</sub>	1,8-naph	TFA	dioxane/H <sub>2</sub> O	89
4	Pd(TFA) <sub>2</sub>	1,8-naph	TFA	dioxane/H <sub>2</sub> O	88
5	Pd(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub>	1,8-naph	TFA	dioxane/H <sub>2</sub> O	95
6	Pd(OAc) <sub>2</sub>	1,8-naph	TFA	dioxane/H <sub>2</sub> O	96
7		1,8-naph	TFA	dioxane/H <sub>2</sub> O	8
8	Pd(OAc) <sub>2</sub>	DMAP	TFA	dioxane/H <sub>2</sub> O	72
9	Pd(OAc) <sub>2</sub>	1,10-Phen	TFA	dioxane/H <sub>2</sub> O	22
10	Pd(OAc) <sub>2</sub>	8-hydroxyquinoline	TFA	dioxane/H <sub>2</sub> O	70
11	Pd(OAc) <sub>2</sub>	2,2'-bipyridine	TFA	dioxane/H <sub>2</sub> O	24
12	Pd(OAc) <sub>2</sub>	DABCO	TFA	dioxane/H <sub>2</sub> O	82
13	Pd(OAc) <sub>2</sub>	1,8-naph	TFA	toluene/H <sub>2</sub> O	45
14	Pd(OAc) <sub>2</sub>	1,8-naph	TFA	anisole/H <sub>2</sub> O	54
15	Pd(OAc) <sub>2</sub>	1,8-naph	TFA	diglyme/H <sub>2</sub> O	79
16	Pd(OAc) <sub>2</sub>	1,8-naph	TFA	DMF/H <sub>2</sub> O	26
17	Pd(OAc) <sub>2</sub>	1,8-naph	TFA	H <sub>2</sub> O	45
18	Pd(OAc) <sub>2</sub>	1,8-naph	HOAc	dioxane/H <sub>2</sub> O	30
19	Pd(OAc) <sub>2</sub>	1,8-naph		dioxane/H <sub>2</sub> O	10

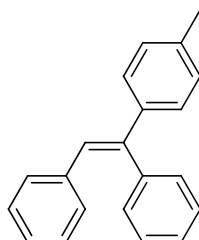
<sup>a</sup> Conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), catalyst (5 mol%), ligand (10 mol%), additive (0.3 mmol), solvent (0.3 mL), H<sub>2</sub>O (0.1 mL), 120 °C, 24 h under argon unless otherwise noted, 1,8-naph = 1,8-naphthalenediamine. <sup>b</sup> GC yield based on **2a**.

**1,1,2-Triphenylethene (3a, CAS: 58-72-0)**<sup>[1]</sup>



<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.26-7.32 (m, 8H), 7.12-7.21 (m, 5H), 7.03 (m, 2H), 6.97 (s, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  143.4, 142.6, 140.4, 137.4, 130.4, 129.5, 128.6, 128.2, 128.2, 127.9, 127.6, 127.5, 127.4, 126.7; MS (EI) *m/z* (%) 256 (100), 239, 178, 126, 77.

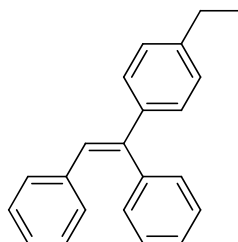
**(E)-(1-(4-Methylphenyl)-1,2-diphenyl)ethene (3b, CAS: 70603-14-4)**<sup>[1]</sup>



The reaction was conducted with sodium 4-methylbenzenesulfinate (**1b**, 53.4 mg, 0.3 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 47.5 mg, 88% yield of **3b** as white solid.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  7.32 (m, 3H), 7.21-7.26 (m, 4H), 7.11-7.13 (m, 5H), 7.02 (m, 2H), 6.94 (s, 1H), 2.36 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm)  $\delta$  142.5, 140.6, 140.5, 137.5, 137.3, 130.4, 129.5, 128.9, 128.6, 127.9, 127.5, 127.3, 127.3, 126.6, 21.1; MS (EI) *m/z* (%) 270 (100), 255, 239, 178, 126.

**(E)-(1-(4-Ethylphenyl)-1,2-diphenyl)ethene (3c, CAS: 86701-20-4)**<sup>[2]</sup>

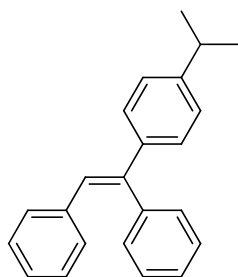


The reaction was conducted with sodium 4-ethylbenzenesulfinate (**1c**, 57.7 mg, 0.3 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column

chromatography on silica gel (petroleum ether) to provide 47.8 mg, 84% yield of **3c** as colourless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.11-7.32 (m, 12H), 7.02 (m, 2H), 6.95 (s, 1H), 2.66 (q,  $J$  = 7.2 Hz, 2H), 1.25 (t,  $J$  = 6.8 Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  143.7, 142.5, 140.8, 140.5, 137.5, 130.4, 129.5, 128.6, 127.9, 127.7, 127.5, 127.4, 127.3, 126.6, 28.5, 15.5; MS (EI)  $m/z$  (%) 284 (100), 255, 178, 126, 91.

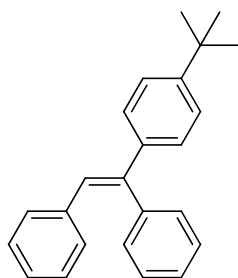
**(E)-1-(4-*iso*-Propylphenyl)-1,2-diphenylethene (3d)**



The reaction was conducted with sodium 4-isopropylbenzenesulfinate (**1d**, 61.8 mg, 0.3 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 47.7 mg, 80% yield of **3d** as colourless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.32 (m, 3H), 7.11-7.25 (m, 9H), 7.00-7.02 (m, 2H), 6.96 (s, 1H), 2.90-2.93 (m, 1H), 1.26 (d,  $J$  = 6.4 Hz, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  148.3, 142.5, 140.9, 140.5, 137.6, 130.4, 129.5, 128.6, 127.9, 127.5, 127.4, 127.3, 126.6, 126.2, 33.8, 23.9; MS (EI)  $m/z$  (%) 298 (100), 283, 255, 178, 91; HRMS calcd. for:  $\text{C}_{23}\text{H}_{22}$   $[\text{M}+\text{H}]^+$ : 298.1722, found 298.1726.

**(E)-1-(4-*tert*-Butylphenyl)-1,2-diphenylethene (3e, CAS: 104729-88-6)**<sup>[3]</sup>

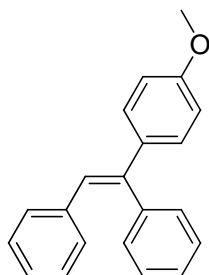


The reaction was conducted with sodium 4-*tert*-butylbenzenesulfinate (**1e**, 66.1 mg, 0.3 mmol)

and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 51.2 mg, 82% yield of **3e** as colourless oil. The ratio of **3e/4e** is 95:5.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.22-7.33 (m, 9H), 7.11-7.12 (m, 3H), 7.00-7.02 (m, 2H), 6.97 (s, 1H), 1.33 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 150.6, 142.4, 140.5, 140.4, 137.5, 130.4, 129.5, 128.6, 127.9, 127.5, 127.3, 127.2, 126.6, 125.1, 34.5, 31.3. MS (EI)  $m/z$  (%) 312, 297 (100), 178, 127, 91.

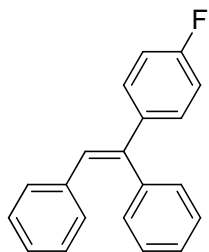
**(E)-(1-(4-Methoxyphenyl)-1,2-diphenyl)ethene (3f, CAS: 1233-23-4)**<sup>[4]</sup>



The reaction was conducted with sodium 4-methoxybenzenesulfinate (**1f**, 58.2 mg, 0.3 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 45.8 mg, 80% yield of **3f** as colourless oil. The ratio of **3f/4f** is 95:5.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.21-7.32 (m, 7H), 7.00-7.12 (m, 5H), 6.89 (s, 1H), 6.85 (d,  $J$  = 8.0 Hz, 2H), 3.82 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 159.3, 142.2, 140.6, 137.6, 136.1, 130.4, 129.4, 128.8, 128.6, 127.9, 127.3, 126.5, 126.4, 113.6, 55.3; MS (EI)  $m/z$  (%) 286 (100), 270, 178, 165, 77.

**(E)-(1-(4-Fluorophenyl)-1,2-diphenyl)ethene (3g, CAS: 70603-17-7)**<sup>[5]</sup>

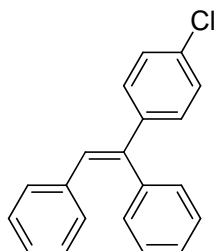


The reaction was conducted with sodium 4-fluorobenzenesulfinate (**1g**, 54.6 mg, 0.3 mmol) and

diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 47.1 mg, 86% yield of **3g** as colourless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.29-7.33 (m, 5H), 7.12-7.19 (m, 5H), 6.98-7.02 (m, 4H), 6.90 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 162.4 (d,  $J = 245.6$  Hz), 141.6, 140.2, 139.6 (d,  $J = 2.9$  Hz), 137.3, 130.3, 129.5, 129.2 (d,  $J = 7.9$  Hz), 128.7, 128.0, 128.0, 127.5, 126.8, 115.0 (d,  $J = 21.3$  Hz); MS (EI)  $m/z$  (%) 274 (100), 259, 196, 126, 77.

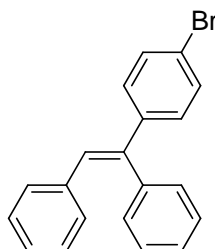
**(E)-(1-(4-Chlorophenyl)-1,2-diphenyl)ethene (3h, CAS: 84224-88-4)**<sup>[5]</sup>



The reaction was conducted with sodium 4-chlorobenzenesulfinate (**1h**, 59.6 mg, 0.3 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 51.0 mg, 88% yield of **3h** as colourless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.26-7.33 (m, 7H), 7.12-7.18 (m, 5H), 7.03 (m, 2H), 6.94 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 141.9, 141.4, 139.9, 137.1, 133.3, 130.3, 129.5, 128.8, 128.7, 128.5, 128.3, 128.0, 127.6, 126.9; MS (EI)  $m/z$  (%) 290 (100), 253, 239, 178, 126.

**(E)-(1-(4-Bromophenyl)-1,2-diphenyl)ethene (3i, CAS: 34699-27-9)**<sup>[6]</sup>

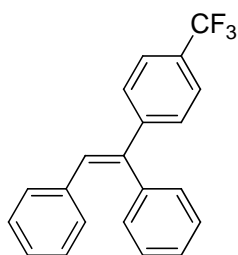


The reaction was conducted with sodium 4-bromobenzenesulfinate (**1i**, 72.9 mg, 0.3 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column

chromatography on silica gel (petroleum ether) to provide 50.4 mg, 75% yield of **3i** as colourless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.43 (d,  $J = 8.0$  Hz, 2H), 7.33 (m, 3H), 7.12-7.20 (m, 7H), 7.03 (m, 2H), 6.95 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 142.4, 141.5, 139.9, 137.1, 131.3, 130.3, 129.5, 129.2, 128.7, 128.6, 128.0, 127.6, 127.0, 121.5. MS (EI)  $m/z$  (%) 336 (100), 253, 239, 178, 126.

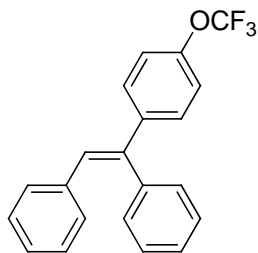
**(E)-(1-(4-Trifluoromethylphenyl)-1,2-diphenyl)ethene (3j)** <sup>[7]</sup>



The reaction was conducted with sodium 4-trifluoromethylbenzenesulfinate (**1j**, 69.6 mg, 0.3 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 44.1 mg, 68% yield of **3j** as colourless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.55-7.57 (m, 2H), 7.35-7.43 (m, 5H), 7.15-7.19 (m, 5H), 7.02-7.05 (m, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 147.0, 141.4, 139.7, 136.8, 130.9, 130.3, 130.0, 129.7, 128.9, 128.1, 128.0 (q,  $J = 25.3$  Hz), 127.8, 127.3, 125.2 (q,  $J = 3.8$  Hz), 124.3 (q,  $J = 270.2$  Hz); MS (EI)  $m/z$  (%) 324 (100), 309, 253, 178, 126.

**(E)-(1-(4-Trifluoromethoxyphenyl)-1,2-diphenyl)ethene (3k)**



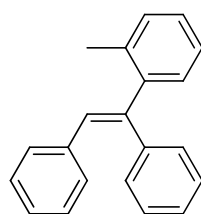
The reaction was conducted with sodium 4-trifluoromethoxybenzenesulfinate (**1k**, 74.4 mg, 0.3 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash



column chromatography on silica gel (petroleum ether) to provide 53.0 mg, 78% yield of **3k** as colourless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.34 (m, 5H), 7.14-7.19 (m, 7H), 7.03 (m, 2H), 6.95 (s, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 148.6 (d,  $J = 1.9$  Hz), 142.1, 141.3, 139.9, 137.0, 132.0, 130.3, 129.6, 128.9, 128.8, 128.0, 127.7, 127.0, 120.6, 120.5 (q,  $J = 255.7$  Hz); MS (EI)  $m/z$  (%) 340 (100), 325, 253, 165, 69; HRMS calcd. for:  $\text{C}_{21}\text{H}_{15}\text{OF}_3$   $[\text{M}+\text{H}]^+$ : 340.1075, found 340.1079.

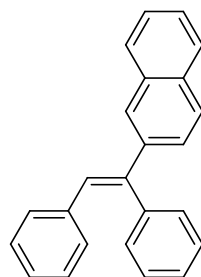
**(E)-(1-(2-Methylphenyl)-1,2-diphenyl)ethene (3l, CAS:1985-77-9)**<sup>[1]</sup>



The reaction was conducted with sodium 2-methylbenzenesulfinate (**1l**, 53.4 mg, 0.3 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 25.9 mg, 48% yield of **3l** as colourless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.14-7.32 (m, 14H), 6.62 (s, 1H), 2.12 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  144.1, 143.0, 140.3, 137.5, 136.2, 130.5, 130.2, 130.1, 129.9, 129.4, 128.2, 128.0, 127.4, 127.1, 126.8, 125.6, 20.4; MS (EI)  $m/z$  (%) 270, 255, 192, 179 (100), 91.

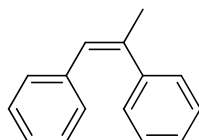
**(E)-2-(1,2-Diphenylvinyl)naphthalene (3m, CAS: 721929-17-5)**



The reaction was conducted with sodium naphthalene-2-sulfinate (**1l**, 64.2 mg, 0.3 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 42.8 mg, 70% yield of **3m** as colourless oil. The ratio of the addition product **3m/4m** is 93:7.

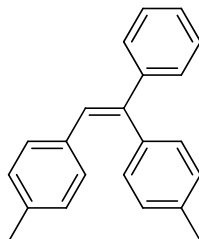
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.71-7.80 (m, 4H), 7.32-7.53 (m, 8H), 7.01-7.14 (m, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 142.6, 140.8, 140.4, 137.4, 133.4, 132.9, 130.5, 129.6, 128.7, 128.7, 128.3, 128.0, 127.7, 127.5, 127.5, 126.8, 126.8, 126.1, 125.9, 125.6; MS (EI)  $m/z$  (%) 306 (100), 289, 229, 215, 145.

**(Z)-1,2-Diphenylprop-1-ene (3n, CAS: 779-51-1)**



The reaction was conducted with sodium methanesulfinate (**1n**, 30.3 mg, 0.3 mmol) and diphenylethyne (**2a**, 35.6 mg, 0.2 mmol). No desired product was detected by GC-MS.

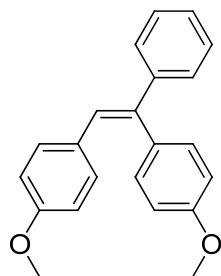
**(Z)-1-Methyl-3-(2-phenyl-2-*p*-tolylvinyl)benzene (3o, CAS: 66184-01-8)** <sup>[5]</sup>



The reaction was conducted with sodium benzenesulfinate (**1a**, 60.0 mg, 0.3 mmol) and 1,2-di(*p*-tolyl)ethyne (**2b**, 41.2 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 48.3 mg, 85% yield of **3o** as colourless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.28-7.31 (m, 5H), 7.08-7.15 (m, 4H), 6.90-6.95 (m, 5H), 2.38 (s, 3H), 2.27 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 143.9, 141.7, 137.6, 136.9, 136.4, 134.7, 130.3, 129.4, 129.3, 128.7, 128.1, 127.9, 127.6, 127.2, 21.3, 21.1; MS (EI)  $m/z$  (%) 282 (100), 269, 254, 172, 126.

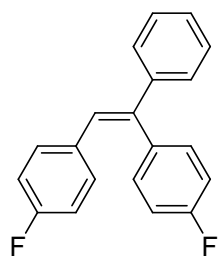
**(Z)-1-(2-Phenyl-2-*p*-methoxyphenylvinyl)-4-methoxybenzene (3p, CAS: 26326-61-4)** <sup>[5]</sup>



The reaction was conducted with sodium benzenesulfinate (**1a**, 60.0 mg, 0.3 mmol) and 1,2-bis(4-methoxyphenyl)ethyne (**2c**, 47.7 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 50.6 mg, 80% yield of **3p/4p** as white solid. The ratio of the addition product **3p/4p** is 2.5:1.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.26-7.31 (m, 4H), 6.65-7.23 (m, 10H), 3.81-3.85 (s, 3H), 3.76 (s, 3H); MS (EI)  $m/z$  (%) 316 (100), 301, 239, 165, 77.

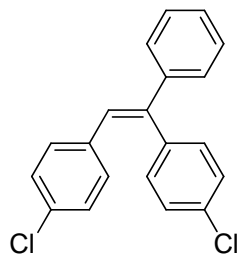
**(Z)-1-(2-Phenyl-2-*p*-fluorophenylvinyl)-4-fluorobenzene (3q)** <sup>[5]</sup>



The reaction was conducted with sodium benzenesulfinate (**1a**, 60.0 mg, 0.3 mmol) and 1,2-bis(4-fluorophenyl)ethyne (**2d**, 42.8 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 55.5 mg, 95% yield of **3q** as colourless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.30 (m, 5H), 7.15 (m, 2H), 6.99-7.05 (m, 4H), 6.91 (s, 1H), 6.82-6.86 (m, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 162.3 (d,  $J = 245.5$  Hz), 161.6 (d,  $J = 246.0$  Hz), 143.1, 141.5 (d,  $J = 1.5$  Hz), 136.0 (d,  $J = 3.6$  Hz), 133.4 (d,  $J = 3.4$  Hz), 132.1 (d,  $J = 7.9$  Hz), 131.1 (d,  $J = 7.8$  Hz), 128.3, 127.7, 127.5, 127.3, 115.7 (d,  $J = 21.2$  Hz), 115.0 (d,  $J = 21.3$  Hz); MS (EI)  $m/z$  (%) 292 (100), 270, 196, 135, 109.

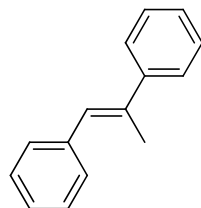
**(Z)-1-(2-Phenyl-2-*p*-chlorophenylvinyl)-4-chloro benzene (3r)** <sup>[5]</sup>



The reaction was conducted with sodium benzenesulfinate (**1a**, 60.0 mg, 0.3 mmol) and 1,2-bis(4-chlorophenyl)ethyne (**2e**, 49.4 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 58.5 mg, 90% yield of **3r** as colourless oil.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.26-7.31 (m, 7H), 7.12-7.13 (m, 4H), 6.95-6.97 (m, 2H), 6.90 (s, 1H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 142.7, 142.2, 138.5, 135.6, 133.6, 132.7, 131.8, 130.7, 129.0, 128.4, 128.3, 127.9, 127.6, 127.4; MS (EI)  $m/z$  (%) 324 (100), 288, 254, 176, 126.

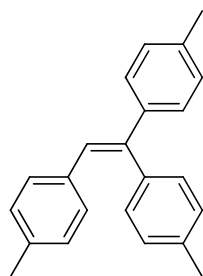
**(E)-1,2-Diphenylprop-1-ene (3s, CAS: 833-81-8)**<sup>[8]</sup>



The reaction was conducted with sodium benzenesulfinate (**1a**, 60.0 mg, 0.3 mmol) and 1-phenyl-1-propyne (**2f**, 27  $\mu\text{L}$ , 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 21.3 mg, 55% yield of **3s** as white solid.

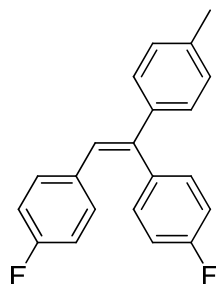
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.50-7.54 (m, 2H), 7.37 (m, 6H), 7.29-7.31 (m, 2H), 6.84 (s, 1H), 2.29 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 144.0, 138.4, 137.4, 129.1, 128.3, 128.2, 127.7, 127.2, 126.5, 126.0, 17.5; MS (EI)  $m/z$  (%) 194 (100), 179, 165, 115, 77.

**4,4',4''-(Ethene-1,1,2-triyl)tris(methylbenzene) (3t, CAS: 6629-83-0)**<sup>[6]</sup>



The reaction was conducted with sodium 4-methylbenzenesulfinate (**1b**, 53.4 mg, 0.3 mmol) and 1,2-di(*p*-tolyl)ethyne (**2b**, 41.2 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 48.3 mg, 81% yield of **3t** as white solid.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.20-7.22 (m, 2H), 7.10-7.12 (m, 6H), 6.93 (m, 4H), 6.87 (s, 1H), 2.38 (s, 3H), 2.35 (s, 3H), 2.26 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 141.6, 141.0, 137.7, 137.1, 136.8, 136.2, 134.9, 130.2, 129.4, 129.3, 128.8, 128.6, 127.5, 127.1, 21.3, 21.1, 21.1; MS (EI)  $m/z$  (%) 298 (100), 283, 253, 191, 126.

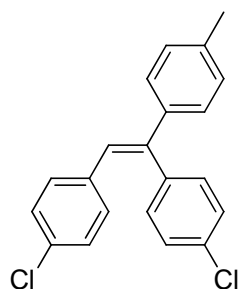
**(Z)-4,4'-(1,2-Tolyethene-1,2-diyl)bis(fluorobenzene) (3u)**



The reaction was conducted with sodium 4-methylbenzenesulfinate (**1b**, 53.4 mg, 0.3 mmol) and 1,2-bis(4-fluorophenyl)ethyne (**2d**, 42.8 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 49.0 mg, 80% yield of **3u** as white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.14-7.19 (m, 6H), 6.95-7.04 (m, 4H), 6.81-6.88 (m, 3H), 2.4 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 162.2 (d,  $J = 245.4$  Hz), 161.5 (d,  $J = 245.8$  Hz), 141.4 (d,  $J = 1.5$  Hz), 140.3, 137.6, 136.1 (d,  $J = 3.5$  Hz), 133.5 (d,  $J = 3.3$  Hz), 132.1 (d,  $J = 7.8$  Hz), 131.0 (d,  $J = 7.7$  Hz), 129.0, 127.4, 126.5, 115.7 (d,  $J = 21.2$  Hz), 115.0 (d,  $J = 21.3$  Hz), 21.1; MS (EI)  $m/z$  (%) 306 (100), 291, 270, 196, 135; HRMS calcd. for:  $\text{C}_{21}\text{H}_{16}\text{F}_2$   $[\text{M}+\text{H}]^+$ : 306.1220, found 306.1223.

**(Z)-4,4'-(1-*p*-Tolyethene-1,2-diyl)bis(chlorobenzene) (3v)**



The reaction was conducted with sodium 4-methylbenzenesulfinate (**1b**, 53.4 mg, 0.3 mmol) and 1,2-bis(4-chlorophenyl)ethyne (**2e**, 49.4 mg, 0.2 mmol). The crude mixture was purified by flash column chromatography on silica gel (petroleum ether) to provide 52.7 mg, 78% yield of **3v** as white solid.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm)  $\delta$  7.29-7.31 (m, 2H), 7.10-7.18 (m, 8H), 6.93-6.95 (m, 2H), 6.87 (s, 1H), 2.36 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , ppm) 142.1, 139.9, 138.6, 137.9, 135.7, 133.5, 132.5, 131.8, 130.7, 129.1, 129.0, 128.3, 127.5, 126.5, 21.1; MS (EI)  $m/z$  (%) 338 (100), 288, 252, 176, 126; HRMS calcd. for:  $\text{C}_{21}\text{H}_{16}\text{Cl}_2$   $[\text{M}+\text{H}]^+$ : 338.0629, found 338.0633.

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### $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

