

Supporting Information for
A Simple and Efficient Protocol for the Synthesis of Functionalized
Styrenes from 1,2-Dibromoethane and Arylboronic Acids.

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General Methods

All reactions were carried out under argon atmosphere in oven dried resealable Schlenk tube. 1,2-Dibromoethane, (1,2-dibromoethyl)benzene were purchased from Aldrich. Methanol and tetrahydrofuran were purchased from Merck. Arylboronic acids were prepared according to the previously published procedure (Bean, F. R.; Johnson, K. R. J. Am. Chem. Soc. 1932, 54, 4415). Chemicals were used without further purification. NMR spectra were recorded on a Varian XL300 spectrometer. Infrared spectra were performed in a SHIMADZU FTIR-8300 spectrometer. Mass spectra were obtained on a GC/MS Shimadzu QP-5050 (EI, 70eV). Gas chromatography analyses were performed on a Varian 3400-CX GC with a FID and 30 meter capillary column with a dimethylsiloxane stationary phase.

Typical experiment for the Suzuki coupling of 1,2-dibromoethane and arylboronic acids

An oven-dried resealable Schlenk flask was evacuated and back-filled with argon and charged with KOH (225 mg, 4 mmol). The flask was evacuated and back-filled with argon, and then tetrahydrofuran (2.5 mL) and 1,2-dibromoethane (87 μ L, 1 mmol) were added. The reaction mixture was stirred at 100° for 1 h. The solution was then allowed to cool to

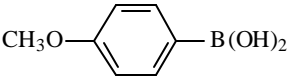
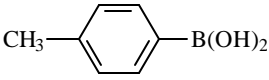
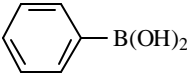
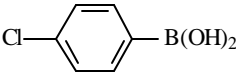
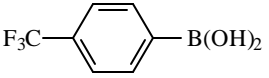
room temperature, and a solution of 1-naphthylboronic acid (258 mg, 1.5 mmol), PPh_3 (21 mg, 0.08 mmol), and $\text{Pd}(\text{OAc})_2$ (9.0 mg, 0.04 mmol) in methanol (2.5 mL) was added. The reaction mixture was stirred at 100°C for 1 h. The solution was then allowed to cool to room temperature, taken up in ether (20 mL) and washed with aqueous NaOH (1 M, 5 mL) and brine (2x5 mL). The organic layer was dried over MgSO_4 , filtered, concentrated in vacuo and then the crude material was purified by flash chromatography on silica gel. For volatile styrene derivatives the workup was: volatile fraction (composed of solvents and styrene derivative) was separated from the reaction mixture by a micro distillation under reduced pressure. The fraction obtained (composed of solvents and styrene derivative) were submitted to a fractional distillation to remove the solvents. The residue is composed of styrene derivative in >95% purity as checked by GC and ^1H NMR. GC yields were determined by using undecane as internal standard. Known styrene derivatives were characterized by comparison with authentic or commercial samples (GC-MS and ^1H NMR).

2,4,6-trimethylstyrene. The coupling of 1,2-dibromoethane with 2,4,6-trimethylphenylboronic acid was carried out using the general procedure to afford 78.8 mg (54% yield based on 1,2-dibromoethane) the title compound as a colorless oil. ^1H NMR (200 MHz, CDCl_3) δ 6.90 (s, 2H), 6.70 (dd, $J=11, 18$, 1H), 5.33 (dd, $J=2, 11$, 1H), 5.26 (dd, $J=2, 18$, 1H), 2.31 (s, 9H). ^{13}C NMR (50.3 MHz, CDCl_3) δ 136.4, 135.9, 135.2, 128.7, 119.3, 21.2, 21.1. IR (neat) ν (cm^{-1}) 2957, 2920, 2868, 1628, 1614, 1450, 1263, 1096, 1022, 907, 804, 731. GC-MS (IE, 70 eV) m/z (%): 146 (100, M^+), 131 (68), 91 (56), 115 (54), 129 (44), 51 (41), 116 (36), 128 (35).

1-(*p*-methoxyphenyl)-1-phenylethylene. The coupling of (1,2-dibromoethyl)benzene with 4-methoxyphenylboronic acid was carried out using the general procedure to afford 209.8 mg (100 % yield based on (1,2-dibromoethyl)benzene) the title compound as a white solid (95% pure as judged by GC), mp 115-117 °C. ¹H NMR (200 MHz, CDCl₃) δ 7.35-7.28 (m, 9H), 5.42 (dd, J=1, 9, 1H), 5.37 (dd, J=1,9, 1H), 3.85 (s, 3H). ¹³C NMR (50.3 MHz, CDCl₃) δ 159.5, 149.7, 142.0, 134.2, 129.6, 128.5, 128.3, 127.9, 128.0, 127.9, 114.4, 113.2, 55.6. IR (neat) ν (cm⁻¹) 2912, 2853, 1603, 1508, 1458, 1377, 1246, 1176, 1028, 905, 845, 781. GC-MS (IE, 70 eV) m/z (%): 51 (100), 50 (60), 63 (57), 210 (55, M⁺), 77 (50), 165 (45), 195 (41), 152 (34), 89 (23)..

Effect of substituents arylboronic acid

An oven-dried resealable Schlenk flask was evacuated and back-filled with argon and charged with KOH (140.97 mg, 2.5 mmol), 1,2-dibromoethane (140.9 mg, 0.75 mmol) and 1.5 mL of tetrahydrofuran. The reaction mixture was stirred at 100 °C for 1 h. An other oven-dried resealable Schlenk flask was evacuated and backfilled with argon and charged with aryl boronic acids (0.025 mmol of each one, phenylboronic acid, 4-methylphenylboronic acid, 4-methoxyphenylboronic acid), PPh₃ (1.6 mg, 0.006 mmol) and Pd(OAc)₂ (0.003 mmol, 4 mol % based on the total amount of arylboronic acid). The flask was evacuated, back filled with argon and then were added 1.5 mL of methanol. The solution was transferred for the reaction mixture and stirred at 100 °C. The reaction profile was monitored by CG. The same procedure was carried out using phenylboronic acid, 4-chlorophenylboronic acid, 4-trifluoromethylphenylboronic acid (0.025 mmol of each one).

Aryboronic acid	v (mmol/h)	log k _X /k _H	σ
	4,23 . 10 ⁻²	0.2980	- 0.28
	2,76 . 10 ⁻²	0.1125	- 0.14
	2,13 . 10 ⁻²	0	0
	1,11 . 10 ⁻²	- 0.3763	0.24
	0,51 . 10 ⁻²	- 0.7140	0.53

Entry 2; Table 2. GC analysis for the reaction mixture (undecane as internal standard)

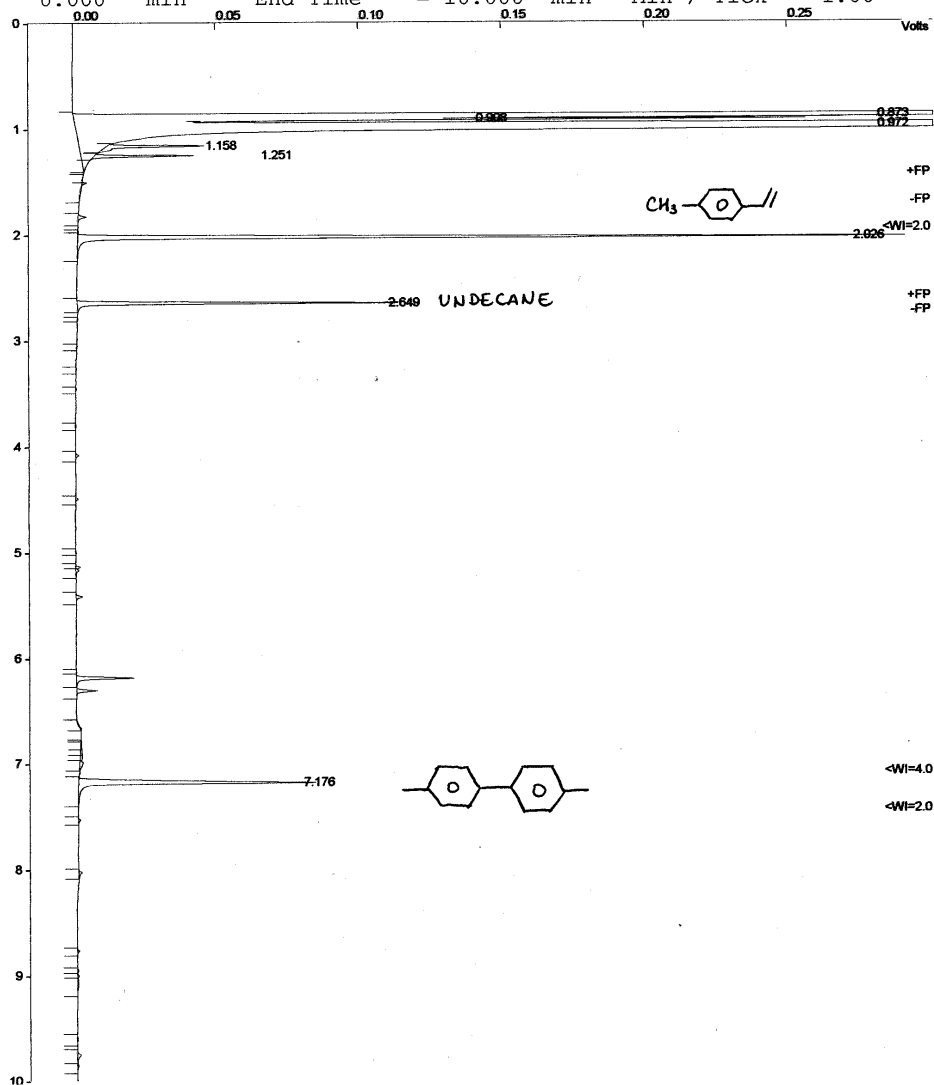
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Method File : C:\STAR\MODULE16\VANUSA.MTH
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Operator : Operator Detector Type: ADCB (1 Volt)
Workstation: Bus Address : 16
Instrument : Varian 16 Sample Rate : 10.00 Hz
Channel : A = A Run Time : 15.670 min

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Entry 3 ; Table 2. GC analysis for the reaction mixture (undecane as internal standard)

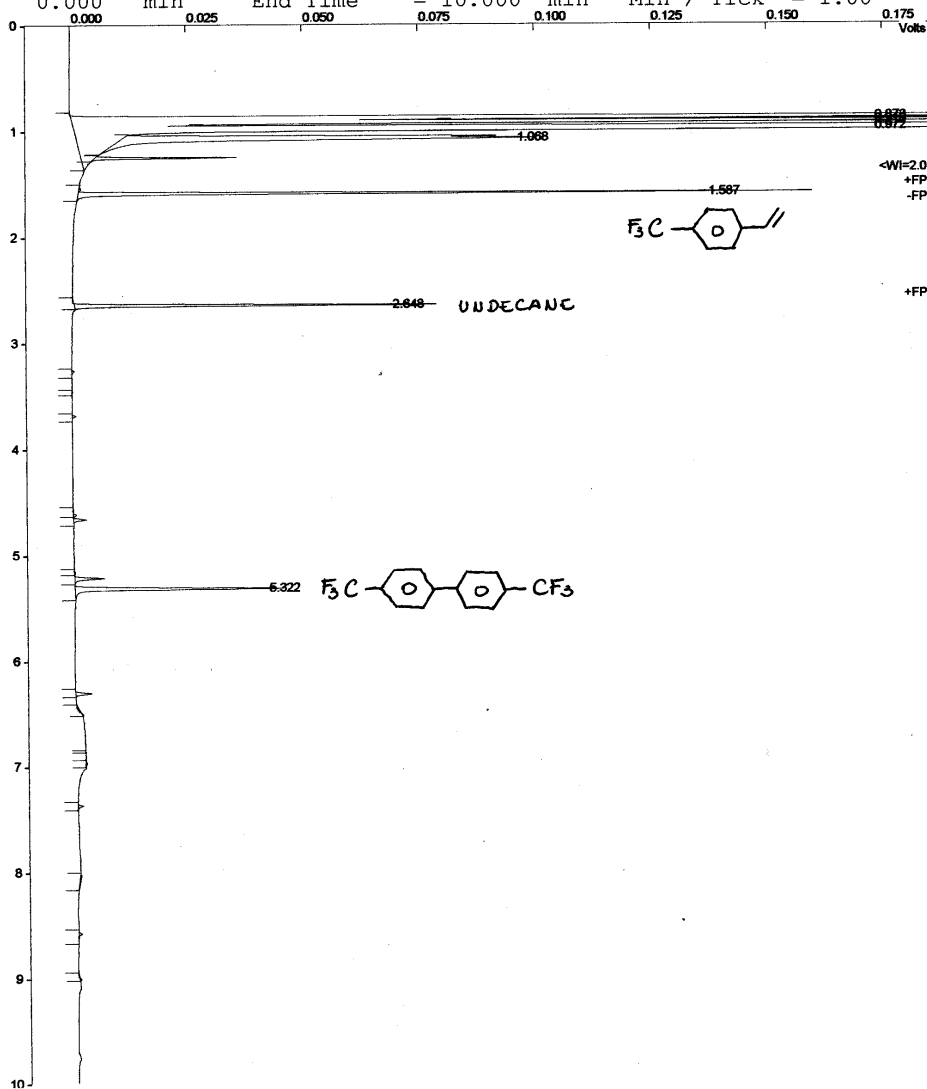
Title : 4-(Trifluoromethyl)styrene
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Method File : C:\STAR\MODULE16\VANUSA.MTH
Sample ID : Manual Sample

Injection Date: 14-MAY-3 3:04 PM Calculation Date: 14-MAY-3 3:22 PM

Operator : Operator Detector Type: ADCB (1 Volt)
Workstation: Bus Address : 16
Instrument : Varian 16 Sample Rate : 10.00 Hz
Channel : A = A Run Time : 17.553 min

***** Star Chromatography Workstation ***** Version 4.5 *****

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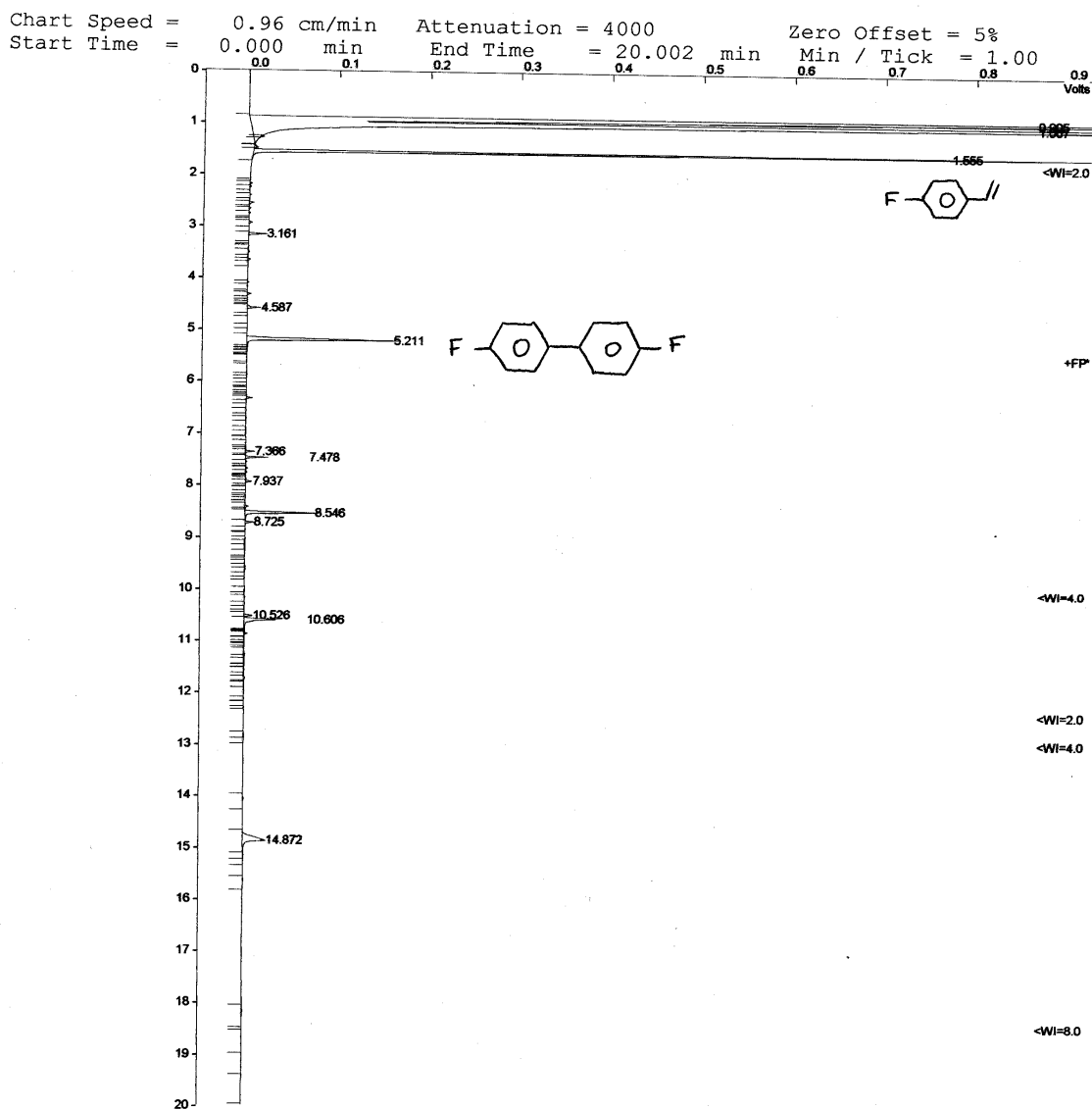
Entry 4 ; Table 2. GC analysis for the reaction mixture (undecane as internal standard)

Title : 4-Fluorostyrene (crude reaction)
Run File : C:\STAR\MODULE16\VL436.RUN
Method File : C:\STAR\MODULE16\VANUSA.MTH
Sample ID : Manual Sample

Injection Date: 27-JUN-3 2:09 PM Calculation Date: 27-JUN-3 2:29 PM

Operator : Operator Detector Type: ADCB (1 Volt)
Workstation: Bus Address : 16
Instrument : Varian 16 Sample Rate : 10.00 Hz
Channel : A = A Run Time : 20.002 min

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Entry 4 ; Table 2. GC analysis after workup

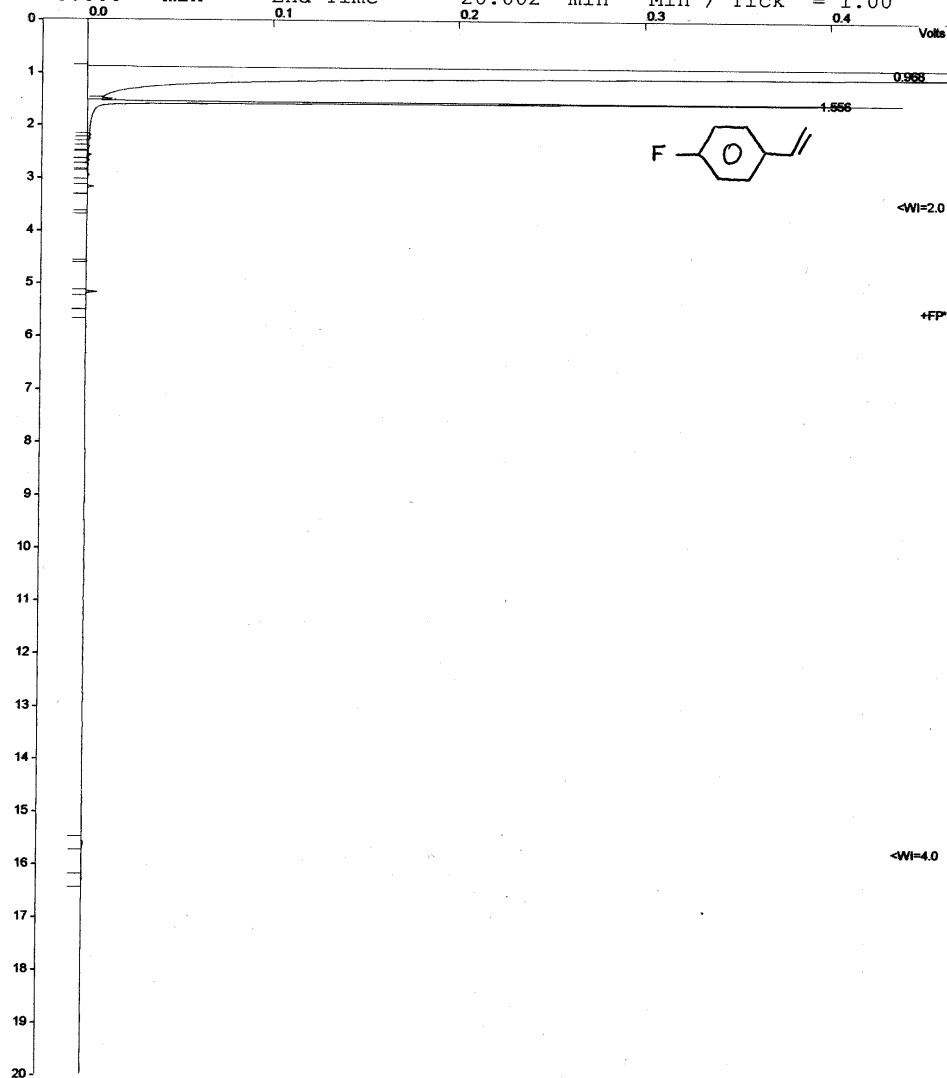
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Run File : C:\STAR\MODULE16\VL437.RUN
Method File : C:\STAR\MODULE16\VANUSA.MTH
Sample ID : Manual Sample

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Operator : Operator Detector Type: ADCB (1 Volt)
Workstation: Bus Address : 16
Instrument : Varian 16 Sample Rate : 10.00 Hz
Channel : A = A Run Time : 20.002 min

***** Star Chromatography Workstation ***** Version 4.5 *****

Chart Speed = 0.96 cm/min Attenuation = 2000 Zero Offset = 5%
Start Time = 0.000 min End Time = 20.002 min Min / Tick = 1.00



Entry 5; Table 2. GC analysis for the reaction mixture (undecane as internal standard)

Title : 4-Chlorostyrene
Run File : C:\STAR\MODULE16\VL336.RUN
Method File : c:\star\module16\vanusa.mth
Sample ID : Manual Sample

Injection Date: 14-MAY-3 3:32 PM Calculation Date: 14-MAY-3 4:04 PM

Operator : Operator Detector Type: ADCB (1 Volt)
Workstation: Bus Address : 16
Instrument : Varian 16 Sample Rate : 10.00 Hz
Channel : A = A Run Time : 20.002 min

***** Star Chromatography Workstation ***** Version 4.5 *****

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