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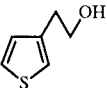
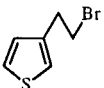

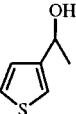

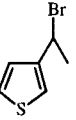
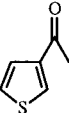
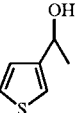


The synthesis of 3-vinylthiophene was efficiently achieved in two steps. 3-(2-bromoethyl)thiophene prepared from 3-(2-ethanol)thiophene was converted to the title compound (70% overall yield) using tetraglyme as a solvent and 1,8-diazabicyclo[5.4.0]undec-7-ene as a base.

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3-Substituted thiophenes have been largely used as starting monomers for the preparation of functionalized conjugated polymers [1]. Among the large palette of these compounds, 3-vinylthiophene appears to be a precursor particularly appropriate for grafting various specific groups from electrophilic (halogenation, oxymercuration, hydroboration) or radical addition reactions. In spite of the interest in this molecule, the literature procedures used for its preparation [2-11] were often inconvenient primarily due to poor or unsatisfactory yields (Table). We report

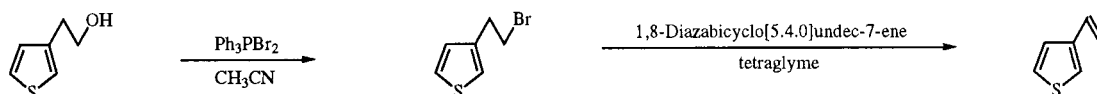
here a route which leads in two steps from 3-(2-bromoethyl)thiophene to 3-vinylthiophene in a good yield of pure product. The synthetic procedure is summarized in Scheme 1. The first step consists in the addition at 0° of 1 g (7.8 mmol) of 3-(2-ethanol)thiophene commercially available (Aldrich, 99%) to an anhydrous acetonitrile solution (15 ml) of triphenylphosphine dibromide as a bromination reagent, previously prepared *in situ* from triphenylphosphine (2.05 g, 7.8 mmol) and bromine (0.4 ml, 7.8 mmol). The solution was refluxed for 2-3 hours,

Table
Literature Procedures for the Two step Preparation of 3-Vinylthiophene

Starting Compound	First Step Product (isolated yield/%)	Overall Yield %	References
	 (95)	70	this work
	 (40-55)	22-33	[2]
	 (70)	– [c]	[3]
	 (86)	46 poor 39	[4] [5] [6]
	[a]	– [c]	[9-11]
	[b]	<30	[7,8]

[a] Synthesis *via* a Wittig reaction; [b] One step catalytic oxidation with sulfur dioxide; [c] Not indicated.

Scheme 1



then cooled to room temperature, diluted with diethyl ether and washed three times with water to eliminate triphenylphosphine oxide. The organic phase was dried over magnesium sulfate and the solvent was evaporated under vacuum. The crude product was chromatographed on silica gel (eluent, petroleum ether) to give 1.41 g (95%) of a clear yellow liquid. It must be noted that this compound was less efficiently obtained (about 50% yield) when phosphorus tribromide was used as the bromination reagent [12]; purity, 99.3% (monitored by gc); ¹H nmr 200 MHz (deuteriochloroform): δ/ppm (m, J (Hz)), 3.18 (t, J = 7.5, 2H), 3.55 (t, J = 7.5, 2H), 6.94-7.29 (m, 3H); ¹³C nmr 50 MHz (deuteriochloroform): δ/ppm 32.2, 33.8, 121.8, 125.8, 127.8, 139.1.

The conversion of the halogenated derivative to 3-vinylthiophene was accomplished in freshly distilled tetraglyme, a high boiling point solvent, in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene as a base. At room temperature, 1.2 equivalents of 1,8-diazabicyclo[5.4.0]undec-7-ene (0.90 ml, 6.0 mmoles) was poured dropwise into a tetraglyme solution (10 ml) containing 3-(2-bromoethyl)thiophene (0.95 g, 5.0 mmoles). After a few minutes, the white precipitate of the 1,8-diazabicyclo[5.4.0]undec-7-ene salt was visible and the mixture was stirred overnight. Completion of the reaction was checked by

thin-layer chromatography (eluent, petroleum ether). 3-Vinylthiophene was obtained as a colorless liquid by distillation under reduced pressure, isolated yield, 74%, purity, 99.5% (by gc); ¹H nmr data were in agreement with those given in the literature [4,6]; ¹³C nmr 50 MHz (deuteriochloroform): δ/ppm 113.6, 122.3, 124.7, 125.9, 131.0, 140.5.

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- [*] To whom correspondence should be addressed.
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