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On the Route to the Photogeneration of Heteroaryl Cations. The Case of Halothiophenes

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Abstract. 2-Chloro-, bromo- and iodothiophenes undergo photochemical dehalogenation via the triplet state. In the presence of suitable π -bond nucleophiles, thienylation occurs with modest yield in chloro- and bromoderivatives (via photogenerated triplet 2-thienyl cation). Specific trapping by using oxygen along with computational analysis carried out by means of a density functional method support that in the case of iododerivatives homolytic thienyl-I bond fragmentation occurs first and heteroaryl cations are formed by electron transfer within the triplet radical pair, thus opening an indirect access to such cations.

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INTRODUCTION

The mild conditions of transition metal catalyzed cross-coupling arylations have been the basis of the enormous success of this class of reactions.¹ Transition metal catalytic reactions are generally depicted as involving oxidative addition of the starting compound to the metal that imparts an electrophilic character to the reactive complex, thus enabling the reaction with both n and π -nucleophiles (NuE in Scheme 1, path a). Metal-free alternatives conserving mild conditions are still a challenge² but photochemical reactions have proved to give a significant contribution to this field.³ Indeed, the high energy of excited states makes possible to confront the barrier of the Ar-X bond cleavage process and to generate convenient intermediates (e.g. aryl radicals or aryl cations) for organic synthesis.⁴ For example, our research group have developed photo-S_N1arylations⁵ through triplet phenyl cations (³Ar⁺) by photoheterolysis of the triplet state of phenyl halides (³Ar-X), ⁵ sulfonates, ⁶ phosphates^{6a} and sulfates.⁷ Contrary to their singlet counterpart, which behave as unselective electrophiles, ⁵ triplet cations attack selectively π -nucleophiles (NuE), thus leading to the arylation of alkenes, alkynes and (hetero)aromatics (Scheme 1, path b).

Scheme 1. Ar-X Activation via Metal Catalysis (path a) and by Photochemical Means (path b)



Cat = Transition metal catalyst ISC = Inter System Crossing NuE = n or π -bond nucleophiles.

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These photochemical reactions are efficient when irradiating, in polar protic solvents, aryl chlorides substituted with strong (NH₂, NMe₂, OH, OMe, CH₂SiMe₃)^{5,8} or mild (alkyl, SiMe₃) electron-donating groups.⁹ In highly ion stabilizing 2,2,2-trifluoroethanol (TFE), heterolysis of the Ar-Cl bond can likewise take place in parent chlorobenzene¹⁰ or in 4-chloro-benzaldehydes and acetophenones when protected as 1,3-dioxolanes.¹¹ Recently, we demonstrated that the likelihood of the photoheterolysis step was established through DFT calculations evaluating the geometry, the spin and charge distribution on the benzene ring of the aromatic in its triplet state (³ArX).¹² Indeed, the process is efficient where the triplet state showed an out of the plane deformation of the C atom bringing the nucleofugal group and, after stretching the Ar-X bond up to 4 Å, a negative charge must develop on the leaving atom with only a small fraction of the spin density. Another key parameter for the feasibility of the heterolytic step is the energy required for elongating the ³Ar-X bond (< 27 kcal mol⁻¹).¹²

We then deemed to extend this approach to the photogeneration of heteroaryl cations due to the pivotal role that substituted heterocycles have in bioactive compounds and drugs.¹³ This is a difficult task and only a couple of photoheterolytic cleavages were claimed to generate heteroaryl cations as shown in Scheme 2.^{14,15} An intriguing case was the photocyanation of substituted nitrothiophenes **Ia,b** and nitrofuran **Ic** (Scheme 2a).¹⁴ Another unusual leaving group was the fluorine anion in the methoxylation of (\pm)-*N*-formyl-4-fluorotryptophan methyl ester (**III**) to give (\pm)-*N*-formyl-4-methoxytryptophan methyl ester (**IV**, 45% yield, Scheme 2b).¹⁵

Scheme 2. Rare Examples of Photogenerated Heteroaryl Cations



One of the main drawback in dealing with heteroaryl cations is that in most cases these underwent ring opening to more stable open chain cations. In fact, calculations showed that the heteroaryl cations deriving from the dediazoniation of adeninediazonium ion $(V^+$, Scheme 3a)^{16a} or cytosinediazonium ion $(VII^+$, Scheme 3b)^{16b} were in equilibrium with the more thermodynamically favored VI^+ and $VIIII^+$, respectively. Nonetheless, dediazoniation of some electron-rich five membered heterocycles (see the case of pyrazolyl cation intermediate IX^+ , Scheme 3c) has been postulated as a possible pathway for thermal formation of **X** via intramolecular arylation.¹⁷

Scheme 3



The obvious choice for photogenerating a heteroaryl cation was by photolysis of electron-rich five membered heterocycles, in particular highly aromatic thiophenes. Shelf stable halothiophenes were selected in place of more delicate thienyl diazonium salts¹⁸ as the cation precursors. The photosubstitution of thiophenes has been previously investigated mainly on derivatives bearing conjugating and electron-withdrawing substituents, such as nitro, carbonyl or carboxyl groups and a thienyl radical was invoked as the intermediate.¹⁹ Thus, as a first attempt to generate a triplet thienyl cation, we decided to explore the photochemical behavior of 2-halothiophenes (Th-X, **1a-e**, Chart 1). A combined computational and experimental investigation was carried out and the results were compared with those of an extended range of halobenzenes previously studied by our research group.

X=C Y=H Y=Me X=I

Chart 1. Substrates Examined in the Present Work

RESULTS

Computational Investigation. In order to clarify the course of the photoreaction a preliminary computational study on thiophenes **1a-d** was carried out. A detailed description of the theoretical approach is available in the Supporting Information. Briefly, density functional theory (DFT) at the (U)B3LYP/6-311+G(2d,p) level was adopted to optimize the absolute minimum of **1a-c** as in our previous studies on phenyl halides.¹² In the case of **1d**, since the above basis set is not defined for Iodine atom, a mixed set was employed, *viz.* 6-311+G(2d,p) for C, H, S atoms and LANL2DZ for the Iodine atom.¹² Solvent effects (MeOH and C₆H₁₂ bulk) were included at the same level of theory by single-point calculations using the CPCM method (conductor-like polarizable continuum model).²⁰

The energy (in the 50-60 kcal mol⁻¹ range, see Table S2) of the triplet halothiophenes ³**1a-d** in methanol and in cyclohexane bulk was calculated. As it is apparent from Figure 1 all triplet states were non planar and exhibited a marked out of the molecular plane displacement of the halogen atom (X) and (to a lower degree) of the carbon atom (C₂) bearing X (see also Figures S1-S5). The homolytic vs heterolytic character of the C₂-X bond cleavage in ³**1a-d** was evaluated by stretching the bond in the optimized configuration of these triplets¹² up to 4 Å (MeOH and C₆H₁₂ bulk) a distance where the bond can be considered broken.¹²



Figure 1. Geometries, ESP atomic charges, spin densities (*in italics*) (in parentheses after elongation of C₂-X bond up to 4.00 Å) calculated in MeOH at the CPCM-UB3LYP/gen//UB3LYP/gen level of theory for: (a) ${}^{3}1a$; (b) ${}^{3}1b$; (c) ${}^{3}1c$; (d) ${}^{3}1d$.

The key parameters (ΔE , that is the energy required to stretch C₂-X bond up to 4.00 Å, charge and spin density at the X atom after C-X bond elongation) are summarily indicated in Figures 2a,b and reported in tabular way in the supplementary (See Table S5 in Supporting Information). The values calculated for 5-methyl-2-halothiophenes and 5-methoxy-2-halothiophenes were likewise reported for the sake of comparison. The barrier confronted decreased from 42 (for ³1a) to 13 kcal mol⁻¹ (for ³1d) in methanol bulk, with a much larger value in cyclohexane in the case of ³1a, while the energy involved in the Th-X bond stretching was independent of solvent polarity for the case of ³1b-d [ΔE (C₆H₁₂) $\approx \Delta E$ (MeOH) in Figure 2a]. Since the presence of an electron donating group (Me, OMe) was found to favor Ar-X heterolytic cleavage in aryl halides,¹² the effect of EDG substituents (in 5position) was also investigated in that case. Notably, a decrement of the ΔE required for the cleavage was observed in methanol when moving from unsubstituted to 5-methoxy-2halothiophene, except for the case of iodo-derivatives where such groups had no effect (Figure 2a).

In protic solvent bulk elongation of the C₂-X bond involved the localization of a full negative charge and a minor spin localization at the fluoro atom in ³1a (see Figure 2b and S1b) fully supporting heterolysis. With the other halides, however, charge localization was much lower and spin density increased suggesting a shift from heterolysis to the homolysis of Th-X bond (See figures 2b and S2-S5). The effect on charge separation and spin localization of a methyl or a methoxy group was negligible in fluoro and chlorothiophenes and small in bromo and iodo analogues. In contrast, homolysis was exclusive for all of the examined halothiophenes in cyclohexane (See Table S5 in Supporting Information).



Figure 2. (a) Calculated ΔE in MeOH and in C₆H₁₂ Bulk. \blacklozenge fluoroderivatives, \bullet chloroderivatives, \blacktriangle bromoderivatives, \blacksquare iododerivatives (halothiophene, 2-halo-5-methylthiophene, 2-halo-5-methylthiophene). (b) ESP charge distribution and spin density on the halogen (X, calculated in

MeOH or C_6H_{12} bulk). \blacklozenge fluoroderivatives, \blacklozenge chloroderivatives, \blacktriangle bromoderivatives, \blacksquare iododerivatives (halothiophene, 2-halo-5-methylthiophene, 2-halo-5-methoxythiophene).

For the sake of completeness, calculations on ³1a-d were also carried out by adopting the functional M06-2X (with def2TZVP as the basis set) which has been reported to be accurate in describing noncovalent interactions and bond dissociation processes.²¹ Solvation was carried out by using SMD model.²² In this case, geometries of ³1a-d at both the equilibrium and after stretching of the Th-X bond up to 4 Å have been optimized in solvent (MeOH bulk). The results observed with this method supported what already predicted by the former approach. Indeed, the ΔE values obtained are quite similar, while both spin and charge distribution (see Table S6 for further details) confirmed the heterolytic nature of the Th-Cl(Br) bond cleavage in ³1b-c and the homolysis of the Th-I bond in ³1d. In the latter case, however, the Th-I bond in the equilibrium geometry resulted already homolytically cleaved.

Photochemical results. 2-fluorothiophene (**1a**) was not experimentally studied because the calculated barrier to cleave the Th-F bond resulted too high (42 kcal mol⁻¹). 2-Bromo, and 2-iodothiophene (**1c,d**) are known to undergo reductive dehalogenation upon irradiation^{23,24} whereas the photochemistry of 2-chlorothiophene (**1b**) is so far unexplored. Whether a diagnostic heteroaryl cation intermediate was formed was investigated by irradiation in the presence of allyltrimethylsilane (ATMS, **4**).²⁵ Some significant data, concerning the irradiation of **1b-d** at a fixed time (6 h, 254 nm or 310 nm (for **1d**) centered lamps) are reported in Table 1. A base (caesium carbonate) was required in the experiments carried out in MeOH or TFE in order to avoid the formation of some filming on the walls and to buffer the acidity released. Reduction to thiophene **2** and arylation to allylthiophene **5** are the only observed pathways. **5** was formed in up to ca. 50% yield in the case of 2-iodothiophene **1d** in MeCN (Scheme 4), for which the measured quantum yield of photodecomposition (Φ_{-1}) is 0.12 (0.34 in MeOH).

Table 1. Products from the Irradiation of 2-Halothiophenes (1b-d) 0.05 M in the Presence of)f
Allyltrimethylsilane (1 M)	

2-Halothiophene	Solvent	Conversion, %	Products	
			(yield %) ^a	
1b, X=Cl	MeCN	68	2, traces	
			5 , 10	
1b	MeOH ^b	78	2 , 12	
			5 , 10	
1b	TFE^{b}	68	2,>5	
			5 , 10	
1c , X = Br	MeCN	100	5 , 12	
1c	MeOH ^b	95	2 , 27	
			5, 9	
1c	TFE ^b	77	2, 9	
			5 , 16	
1d, X = I	MeCN	67	5 , 49 ^c	
1d	MeOH ^b	100	2 , 41	
			5 , 10	
1d	TFE ^b	100	2 , 20	
			5 , 35	

^{*a*} Yield based on the consumption of the 2-halothiophenes and determined by GC or GC/MS analysis; ^{*b*} Cs₂CO₃, 0.05 M added; ^{*c*} Isolated yield.

Since 2-iodothiophene 1d gave allylated product 5 in a satisfactory yield, reactions in solvents and in the presence of π nucleophiles were more extensively investigated for the case of 5-methyl-2-iodothiophene (1e), analytically more expedient (Table 2).

Table 2. Product Distribution by Irradiation (310 nm, 6h) of 5-Methyl-2-Iodothiophene (1e)

(0.05 M) in Solvents and in the Presence of π -Bond Nucleophiles

Conditions	Conversion, (%)	2e (yield %) ^a	Further products (yield %) ^a
Cyclohexane	100	79	3 , 15
CH ₃ COOMe	27	100	-
MeCN	27	95	-
MeOH	54	86	-
MeOH, Cs ₂ CO ₃ 0.05 M	100	98	-
TFE	73	62	2e' , 12 ^b
TFE, Cs ₂ CO ₃ 0.05 M	76	72	2e' , 12 ^b
TFE, Cs ₂ CO ₃ 0.05 M, O ₂	88	19	2e' <5 ^{<i>b</i>}
C ₆ H ₁₂ , 4 (1 M)	88	56	3 , 43; 5e , <5 ^b ; 6 , <5 ^b
MeCN, 4 (1 M)	63	18	5 e, 62
TFE, Cs ₂ CO ₃ 0.05 M 4 (1 M)	100	18	5e , 37 ^c
MeCN, 4' (0.2 M)	65	13	5 e, <5
MeCN, 4" (0.2 M)	62	-	5e' , <5 ^b
7 (neat)	62	35	9e , 65
7 /TFE (1/3), Cs ₂ CO ₃ 0.05 M	64	25	9e , 48 ^c ; 2e' , <5 ^b
TFE, Cs ₂ CO ₃ 0.05 M 8 1 M	90	16	10e , 44 ^c
TFE, Cs ₂ CO ₃ 0.05 M, 11 0.2 M	79	43	2e' , 8; ^{<i>b</i>} 12e , $<5^{b}$; 13e , $<5^{b}$

^{*a*}Yield based on the consumption of **1e** and determined by means of GC analyses. ^{*b*} Detected by GC-MS analysis. ^{*c*} Isolated yield.

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In solvent, reduction was the main process also with iodide 1e, with best yields in cyclohexane (with cyclohexyl iodide 3 as byproduct) and in methanol (with caesium carbonate). In TFE, however, 5-methyl-2-trifluoroethoxythiophene 2e' was formed in up to 10% yield. The allylation in the presence of 4 occurred with modest yield, at best in MeCN (62% yield). In contrast, the use of allylsulfones 4' and 4'' afforded the corresponding allylthiophenes only in traces. Phenylation was obtained both in benzene and in benzene/CF₃CH₂OH (1/3) mixture. A 40% arylation likewise, occurred with mesitylene. On contrast hexamethylbenzene had a limited effect on the product mixture, with a small amount of triene 12e and pentamethylbenzene 13e observed on the basis of GC/MS analysis. In order to obtain mechanistic evidence, the effect of oxygen (saturated solution) was tested, resulting in the quenching of both reductive alkylation and iodine substitution.

Scheme 4. Photolysis of 2-iodothiophenes (1d-e) in Solvents and in the Presence of π Nucleophiles



DISCUSSION

In order to obtain a more complete picture, the same calculations carried out for 2-halothiophenes were performed for 4-halotoluenes, 4-haloanisoles and 4-haloanilines, and are likewise reported in Figure 3. It appears that 2-halothiophenes encounter the highest barrier to heterolytic fragmentation in the series (independent of the medium, Figure 2a) even higher than 4-halotoluenes. On the contrary, the barrier strongly decreases while the ESP charge at the halogen atom strongly increases in the case of methoxy and aminobenzenes. When an heterolytic fragmentation is involved, the charge on the halogen atom is close to -1 (see Figure 1a). Only fluorinated or chlorinated thiophenes reach this region, along with all of the haloanilines and anisoles examined (see the lower charge with the iodoanisole, though). Moreover, with thiophenes, introducing substituents had only

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a minor effect on barrier and charge localization (see also Figures 2a and 2b) On the other hand, the presence of electron donating groups on benzene derivatives reduced the barrier in methanol, indeed heterolysis was an exothermic process for chloro and bromoanilines, and encountered a low barrier with the other 4-haloanilines and the 4-haloanisoles. It appears that with thiophene derivatives the aryl cation was not sufficiently stabilized to make this path dominating (high energy barrier for Th-X cleavage when X = F, Cl and low ESP charge in the case of bromides and iodides, Figure 1), while this was the case for phenyl derivatives. Triplet cations, which have a $\pi^5\sigma^1$ radical cation structure, are more stabilized by electron donating substituents for six-membered aromatics with respect to the corresponding five-membered heterocycles such as thiophenes (and expectedly with other electron rich heterocycles).



Figure 3. Energy required to stretch C-X bond up to 4.00 Å in the triplet state of some (hetero)aromatic halides vs ESP charge distribution on X atom (calculated in MeOH bulk). \blacklozenge fluoroderivatives, \blacklozenge chloroderivatives, \blacktriangle bromoderivatives, \blacksquare iododerivatives (halothiophene, 4-halo-*N*,*N*-dimethylanilines, 4-halotoluenes, 4-haloanisoles).

As shown in Figure 3, three groups of aromatic and heteroaromatic halides have been recognized on the basis of the nature of the (Het)Ar-X bond cleavage. In the group 1 a negative ESP charge (> - 15

0.75) developed at the halogen atom, while only a small fraction of the spin density (< 10%, see Table S5) became localized there, and heterolysis takes place with a small energy barrier (\leq 10 kcal mol⁻¹). These are necessary, but not sufficient conditions for the generation of an aryl cation. In fact, with iododerivatives, heavy atom effects (e.g. in iodoanilines) may promote ISC to the ground state and reducing the lifetime of the triplet excited state. Thus, a fast cleavage is mandatory to avoid disexcitation.^{8a} With less donating substituents (group 2), the barrier was higher (15-30 kcal mol⁻¹) with less charge (> -0.6) and more spin (10-20%) at the halogen. In this class the experimentally observed outcome still involved phenylation reactions via photogenerated aryl cations deriving from them, but only when irradiated in a protic, ion-solvating solvent. Finally, in the group 3 the required energy was relatively low but the charge at the halogen negligible, the spin larger (> 30%) and homolysis took place as primary process.

Both experimental and computational data above support a mechanistic scheme depicted in Scheme 5, where halothiophene triplets ³**1b-e** are the reacting states.^{19b,e,26} In fluorothiophenes, however, that are expected to cleave heterolytically, the high barrier makes the process too slow to compete with physical decay even if the ions would be stabilized in a polar medium (see Figures 2 and 3). The process occurring in chloro- and bromothiophenes **1b,c** is an inefficient heterolytic cleavage of the Ar-X bond (Scheme 5, path a) to form the corresponding triplet thienyl cation (³**14**⁺, see structure in Figure S6). On the contrary, iodothiophenes **1d,e** underwent a photohomolytic C-X bond cleavage (paths b,c), a thermodynamically viable process (Figure 2). Thus, a triplet radical pair [**14**⁺ **X**⁺]³ was generated^{27,28} rather than cation ³**14**⁺. Diffusional separation of the radical center formed a solvated radical pair [**14**⁺ **X**⁺]_{solv} (path d).²⁹ The 2-thienyl radical (**14**⁺) is the intermediate involved both in the reduction to thiophenes **2** and **2e** (path e) and addition to π -nucleophiles in non-hydrogen donating solvents (path f, see also the experiment in benzene, Table 2).

Scheme 5. Pathways and Intermediates Involved in the Photochemistry of Halothiophenes 1b-e



The homolytic cleavage of the Th-X bond in ³1d,e was supported by experimental evidence as the specific quenching of the radical by oxygen, the formation of iodopropylsilane 6 from alkene 4 and the formation of iodocyclohexane 3. On contrast, the role of aryl radicals in arylations in polar solvents is excluded, since the presence of typical radical traps namely allyl phenyl sulfone 4' or sulfone 4'' did not lead to appreciable amounts of allylated derivatives (Table 2).³⁰ Furthermore, the products of the reaction with allyltrimethylsilane and those with hexamethylbenzene are typical markers of a triplet aryl cation and are best rationalized as resulting from electron transfer (ET) within the thienyl and halogen radical pair $[14^{\circ} X^{\bullet}]^3$. This leads indirectly to ion ³14⁺ (Scheme 5, path g)^{10,31} which is trapped by π -bond nucleophiles³² to give the arylated products (path h). The formation of aryl cations from an ET mechanism within a radical pair has been sparsely documented, providing that it takes place in a high polar medium (e.g. water).^{28,31b,33} Notice further

that 5-uracyl and 5-citosyl cations have been invoked when investigating the reactivity of 5fluorouracile³⁴ and 5-bromocitosine³⁵ respectively, where the heteroaryl radical intermediate was oxidized by the radical cation of N^{α} -acetyl-*L*-tryptophan *N*-ethylamide.^{34,35} More relevant to the present case, the formation of the parent triplet phenyl cations from the corresponding aryl radical has been previously postulated in the photodechlorination of chlorobenzene.¹⁰ The formation of a small amount of trifluoroethoxythiophene (**2e'**) in TFE is best justified via ISC from triplet to singlet thienyl cation (¹**14**⁺, Scheme 5, path i).³⁶ Despite calculations support that triplet thienyl cations are slightly more stable than the corresponding singlets (by 8-10 kcal mol⁻¹, Figures S6-S10), such small energy difference may be overestimated, as previously observed.³⁴ Indeed, solvolysis to **2e'** took place as a minor process and is fully suppressed when a reactive π -bond trap is used, supporting that singlet cation arises from the formerly generated ³**14**⁺.

In conclusion, the generation of triplet phenyl cations from halobenzenes is a highly efficient process, which is hardly extended to thiophenes. However, we demonstrated that heteroaryl cations are formed from thienyl iodides in polar and protic solvents via a homolytic cleavage of the Th-I bond followed by intramolecular electron transfer within the photogenerated triplet radical pair. The cleavage occurs with reasonable efficiency (see Table 1-2), though solvation of the radical pair before ET competes significantly, making reactions less clean. This work suggests that access to aryl cations is viable also via paths different than cleavage of the Ph-X bond encountered in electron-donating phenyl halides and further shows that a simply implemented functional method allows to predict the viability of either type of cleavage (homolytic or heterolytic) for a specific case.

EXPERIMENTAL SECTION

Materials and Methods. ¹H NMR spectra were recorded with a 300 MHz spectrometer, while ¹³C NMR spectra were recorded with a 75 MHz spectrometer. The attributions were made on the basis

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of ¹H and ¹³C NMR, as well as DEPT-135 experiments; chemical shifts are reported in ppm downfield from TMS. GC-MS analyses were carried out using a GC-DSQ single quadrupole GC/MS system. A Rtx-5MS (30 m × 0.25 mm × 0.25 μ m) capillary column was used for analytes separation with helium as carrier gas at 36 mL min⁻¹. The injection in the GC system was performed in split mode and the injector temperature was 250 °C. The GC oven temperature was held at 40°C for 6 min, increased to 250 °C by a temperature ramp of 10 °C min⁻¹ and held for five min. The transfer line temperature was 280 °C and the ion source temperature 250 °C. For **2** mass spectral analyses were carried out in SIM mode, monitoring m/z 84, 58, 45 at the same time. To improve the quality of the integration of the peaks of interest the Base Peak function was applied to the chromatogram. This action afforded a new chromatogram that showed only the signals with m/z 84 as base peak. On contrast for **2e**', **5e**', **6**, **12e**, **13e** mass spectral analyses were carried out in full scan mode.

2-Halothiophenes **1a-1d**, thiophene (**2**), 2-methylthiophene (**2e**) and all of the employed π -bond nucleophiles were commercially available and used as received. 5-methyl-2-iodothiophene (**1e**) was obtained by iodination of **2e**.³⁷ 2-(Tosylmethyl)acrylate (**4**") was synthesized according to a literature procedure.³⁸

Photochemical experiments. The photochemical reactions were performed by using nitrogenpurged solutions in quartz tubes in a multilamp reactor fitted with ten 15 W Hg phosphor coated lamps (emission maximum 310 nm) or 4×15 W Hg lamps (emission centred at 254 nm). The reaction course was followed by GC analyses and the products formed were identified and quantified by comparison with authentic samples. Workup of the photolytes involved concentration in vacuo (80-100 Torr) and chromatographic separation. Solvent of HPLC purity were employed in the photochemical reactions. Quantum yields were measured at 254 nm (1 Hg lamp, 15W). The amount of 2-methylthiophene (**1e**) and iodocyclohexane (**3**) was determined by GC analysis on the basis of calibration curves by comparison with commercial standard. Products **2** (m/z: 84 (M⁺, 100),

58 (38), 45 (32)), **2e**' (m/z: 196 (M⁺, 72), 113 (96), 85 (68)), **5e**' (m/z: 196 (M⁺, 100), 136 (94), 111 (34)) **6** (m/z: 185 (34), 115 (16),72 (100)), **12e** (258 (M⁺, 30), 161(100)), **13e** (245 (M⁺, 100), 229 (98)) were determined by means of GC-MS analyses. In a typical experiment, a solution of **1b-e** (1.5 mmol, 0.05M), a π -bond nucleophile (1.0 M except where otherwise indicated), Cs₂CO₃ (0.05 M, 1.5 mmol except where indicated) in the chosen solvent (30 mL) was nitrogen purged in quartz tubes and irradiated. The reaction course was followed for GC analysis. The photolyzed solutions were concentrated in vacuo (80-100 Torr) and purified by column cromatography.

2-(2-Propenyl)thiophene (5). From 166 μ L (0.05 M, 1.5 mmol) of (1d), 4.77 mL (1M, 30 mmol) of allyltrimethylsilane (ATMS) in 30 mL of MeCN, irradiated at 310 nm for 6 hours (67% consumption of 1d). Purification by column chromatography (aluminium oxide neutral; eluant: pentane) afforded 61 mg of 5 (oil, 49% yield based on the consumption of 1d). Spectroscopic data of 5 were in accordance with the literature.³⁹ Anal. Calcd for C₇H₈S: C, 67.69; H, 6.49. Found: C, 67.7; H, 6.5.

2-Methyl-5-(2-propenyl)thiophene (5e). From 181 μL (0.05 M, 1.5 mmol) of 1e, 489 mg (0.05 M, 1.5 mmol) of Cs₂CO₃, 4.77 mL (1M, 30 mmol) of allyltrimethylsilane in 30 mL of TFE, irradiated 6 hours (100% consumption of 1e). Purification by column chromatography (aluminium oxide neutral; eluant: pentane) gave 77 mg of 5e (oil, 37% yield). 2-methyl-thiophene (2e) was likewise formed in 18% yield (determined on the basis of calibration curve). 5e:¹H NMR (CDCl₃) δ 2.45 (s, 3H), 3.50-3.55 (d, 2H, J = 6.6 Hz), 5.10-5.20 (m, 2H), 5.95-6.10 (m, 1H), 6.55-6.60 (m, 2H); ¹³C NMR (CDCl₃) δ 15.1 (CH₃), 34.6 (CH₂), 115.8 (CH), 124.1 (CH), 124.7 (CH), 136.8 (CH₂), 137.9, 140.3; IR (KBr) v_{max} 2921, 1638, 1420, 909, 790 cm⁻¹. Anal. Calcd for C₈H₁₀S: C, 69.51; H, 7.29. Found: C, 69.5; H, 7.3.

2-Methyl-5-phenylthiophene (9e). From 181 μ L (0.05 M, 1.5 mmol) of 1e, 489 mg (0.05 M, 1.5 mmol) of Cs₂CO₃, 7.5 mL (2.8M, 0.1 mmol) of benzene in 30 mL of TFE, irradiated 6 hours (64%)

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consumption of **1e**). Purification by column chromatography (silica; eluant: hexane) gave 80 mg of **9e** (white solid, 48% yield based on the consumption of **1e**), mp = 42-43°C , lit.⁴⁰ = 39-41°C). Compound **2e** was likewise formed in the reaction (25% yield based on the consumption of **1e** and determined on the basis of calibration curve). GC-MS analyses revealed also the presence of 2-(3,3,3-trifluoroethoxy)-5-methylthiophene (< 5%). Spectroscopic data of **9e** were in accordance with the literature.⁴¹ Anal. Calcd for C₁₁H₁₀S: C, 75.82; H, 5.78. Found: C, 75.8; H, 5.8.

2-(2,4,5-Trimethylphenyl)-5-methylthiophene (10e). From 181 μL (0.05 M, 1.5 mmol) of 1e, 489 mg (0.05 M, 1.5 mmol) of Cs₂CO₃, 4.17 mL (1 M, 30 mmol) of mesitylene in 30 mL of TFE, irradiated 6 hours (90% consumption of 1e). Purification by column chromatography (silica; eluant: hexane) gave 129 mg of 10e (colorless oil, 44% yield based on the consumption of 1e. Compound 2e was also formed in the reaction (16% yield based on the consumption of 1e and determined on the basis of calibration curve). 10e: ¹HNMR (CDCl₃) δ 2.20 (s, 6H), 2.40 (s, 3H), 2.55-2.60 (d, 3H, J = 0.9 Hz), 6.60-6.65 (d, 1H, J = 3.5 Hz), 6.75-6.80 (m, 1H), 6.97 (s, 2H). ¹³C NMR (CDCl₃) δ 15.2 (CH₃), 20.6 (CH₃), 21.0 (CH₃), 124.9 (CH), 126.1 (CH), 127.9 (CH), 131.4, 137.5, 138.2, 139, 139.4. IR (KBr) v_{max} 2911, 1454, 845, 791 cm⁻¹. Anal. Calcd for C₁₄H₁₆S: C, 77.72; H, 7.45. Found: C, 77.7; H, 7.4.

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Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: Absorption parameters measured for compounds **1b-1e**; ¹H and ¹³C NMR spectra of compounds **1e**, **5**, **5e**, **9e**, **10e**; details of the calculations on intermediates.

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