Characterization of Novel Sulfonium Photoacid Generators and their Microwave-assisted Synthesis

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Materials.

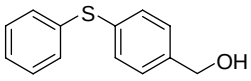
Compounds **1**,[1] **4**,[2] and **9**,[3] were synthesized according to methods reported in the literature. Thioanisole and phenyl sulfide were used as provided by suppliers. All glassware was flamed dried and cooled in a desicator over calcium chloride. All reactions were carried out under N_2 atmosphere. All sulfonium salt synthesis and purification were carried out under yellow light, red light, or in the dark. The sulfonium salt preparation, when carried out by conventional heating methods, was done according literature procedures using chlorobenzene as a solvent.[4]

Instrumentation.

Absorption spectra were recorded with an Agilent 8453 UV–visible spectrophotometer. Steady-state fluorescence spectra were measured with a PTI Quantamaster spectrofluorimeter in the photon counting regime of the PMT using an L-format configuration. The fluorescence spectra were corrected for the spectral dependence of the PMT. All measurements were performed at room temperature in 1 cm quartz cuvettes, with dye concentrations in the order of 10^{-6} M. Spectroscopic grade solvents, hexanes, THF, acetonitrile were obtained from Aldrich and used without any further

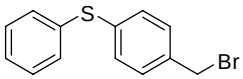
purification. Fluorescence quantum yields of were determined relative to 9, 10-diphenylanthracene in cyclohexane as a standard.[5] In steady-state photoacid quantum yield determinations, the excitation monochromator of the PTI spectrofluorimeter was used to selectively excite the sample at the desired wavelength, and the intensity of the incident radiation was measured with an Ophir Power Star power meter equipped with a UV 1.44 cm^2 detector head. Rhodamine B was used as a sensor of photoacid generation, observing the change in optical density of the sulfonium salt did not exceed 5% as suggested in the literature.[6] All microwave-assisted reactions were run in a CEM Discover unit in closed vessel mode.

Synthetic Procedures and Characterization.

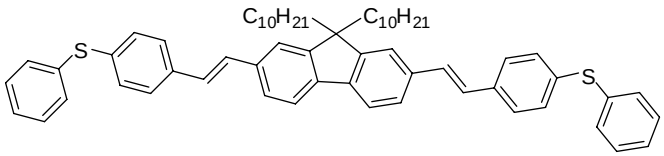


Preparation of (4-(phenylthio)phenyl)methanol. 4-(Phenylthio)benzadehyde **1** (2.00 g, 9.36 mmol), 0.36 g (9.42 mmol) $NaBH_4$, and 3.589 g of neutral alumina were placed in a 250 mL round bottom flask and stirred under. The reaction was followed by TLC (ethyl acetate:hexane 1:1) and stopped after 25.5 h, once the starting material was consumed entirely. The product was extracted with ethyl acetate and concentrated *in vacuo*. The crude product was purified by column chromatography (ethyl acetate:hexane 1:1) to obtain 1.77 g (88%) colorless needles. Mp 48.1-48.9 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) 7.27 (m, 9H), 4.65 (d, 5.7 Hz, 2H), 1.77 (t, 5.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) 141.2 (C), 136 (C), 135.2 (C), 132.8 (CH), 131.5 (CH), 129.8 (CH), 128.2 (CH), 127.3 (CH), 65.2 (CH_2), ^{13}C NMR DEPT 135 (75 MHz, $CDCl_3$) 132.8 (CH), 131.5 (CH), 129.8

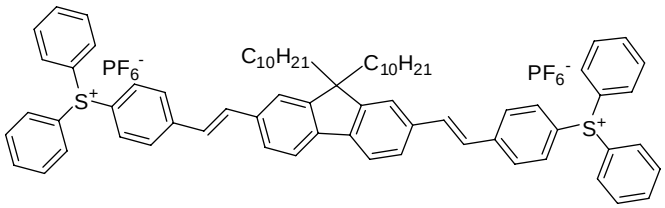
(CH), 128.2 (CH), 127.3 (CH), 65.2 (CH_2). Elemental Analysis Calcd. for ($C_{13}H_{12}OS$): C, 72.19; H, 5.59; S, 14.82, Found C, 72.25; H, 5.58; S, 14.83.



Preparation of (4-(bromomethyl)phenyl)(phenyl)sulfide, 2. The synthesis of (4-(bromomethyl)phenyl)(phenyl)sulfide was performed based on a modified procedure from Boekelheide *et al.*[7] (4-(Phenylthio)phenyl)methanol (0.532 g, 2.46 mmol) was refluxed in 10 mL of an HBr (33% in AcOH) for 2 h and later taken to room temperature. The reaction progress was followed by TLC every 15 min. Upon completion (12 h), the solution was extracted with chloroform (2x). The fractions were combined and washed with a sodium bicarbonate solution, rinsed with water (2x), and dried with anhydrous magnesium sulfate. After concentration, in vacuo, the crude was purified by column chromatography (ethyl acetate:hexane 1:1) to obtain 0.65 g (95%) of a colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) 7.088 (m, 9H), 4.23 (s, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) 137.3 (C), 136.3 (C), 134.8 (C), 132.2 (CH), 130.5 (CH), 130.0 (CH), 129.6 (CH), 127.9 (CH), 33.5 (CH_2), ^{13}C NMR DEPT 135 (75 MHz, $CDCl_3$) 132.3 (CH), 130.5 (CH), 130.2 (CH), 129.8 (CH), 128.0 (CH), 33.7 (CH_2). Elemental Analysis Calcd. for ($C_{13}H_{11}BrS$): C, 55.92; H, 3.97; S, 11.48, Found: C, 56.00; H, 4.06; S, 11.37.

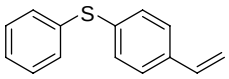


Preparation of (4,4'-(1E,1'E)-2,2'-(9,9-didecyl-9H-fluorene-2,7-diyl)bis(ethene-2,1-diyl)bis(4,1-phenylene))bis(phenylsulfane), 5. In a two-neck, 250 mL round bottom flask, 0.651 g (2.33 mmol of (4-(bromomethyl)phenyl)(phenyl)sulfide, **2**, were dissolved in 6 mL of dry, freshly distilled triethylphosphite. The mixture, was taken to reflux and monitored by TLC until complete conversion of the starting material was observed (6 h). The unreacted triethylphosphite was evaporated by vacuum distillation, affording a viscous, pale yellow oil which was used for the Horner-Emmons-Wadsworth reaction without further purification. The phosphonate, was dissolved in 10 mL of dry DMF and 1.11 g of NaH was added portion-wise to the solution. The mixture was stirred at room temperature for 1 h. A solution of 2,7-diformylflourene, **4**, (0.60 g, 1.2 mmol, in 5 mL of dry DMF) was added dropwise to the solution, which was then monitored by TLC until no 2,7-diformylflourene was observed (21 h). Once the reaction was complete, the solution was added dropwise to 150 mL of 0 ºC water. The resulting yellow oil was extracted with methylene chloride (2x) and washed (3x) with water, and dried with magnesium sulfate. The crude was purified by column chromatography on silica gel using an ethyl acetate:hexane mixture of 1:1 and run under N_2. The yellow oil obtained 0.96 g (48% in two steps) crystallized after several days. Mp 59.6-61.1ºC; ^{1}H NMR (300 MHz, $CDCl_3$) 7.66 (d, 4.8 Hz, 2H), 7.33 (m, 26H), 2.02 (m, 4H), 1.10 (m, 28H), .093(m, 42 H); ^{13}C NMR (75 MHz, $CDCl_3$) 151.8 (C), 140.9 (C), 136.7 (C), 136.3 (C), 136.0 (C), 134.9 (C), 131.5 (CH), 131.2 (CH), 129.9 (C), 129.4 (CH), 127.3 (CH), 127.3 (C), 126.0 (C), 121.0 (C), 120.2 (C). 109.1 (C), 55.3 (C), 40.8 (C), 32.2 (C), 30.4 (C), 30.0 (C), 29.9 (C), 29.7 (C), 24.1 (C), 23.0 (C), 14.5 (C). Elemental Analysis Calcd. for ($C_{61}H_{70}S_2$): C, 84.47; H, 8.13; S, 7.39, Found: C, 84.28; H, 8.24; S, 7.21.

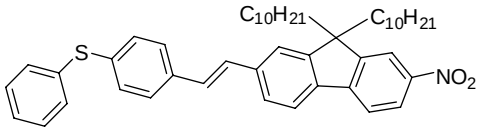


General procedure for the microwave-assisted preparation of sulfonium salts. Preparation of (4,4'-(1E,1'E)-2,2'-(9,9-didecyl-9H-fluorene-2,7-diyl)bis(ethene-2,1-diyl)bis(4,1-phenylene))bis(diphenylsulfonium) hexafluorophosphate(V), 7. In a 2 mL glass reaction vessel,[8] 0.21 g (0.24 mmol) of **5**, 0.21 g (0.48 mmol) of diphenyliodonium hexafluoro phosphate (V), **6**, and 0.006 g (5% molar) copper(II) benzoate were mixed in the dark in 2 mL of chlorobenzene while being purged with N_2. The microwave was set to closed vessel standard mode; maximum pressure 40 psi; maximum temperature 125 ºC, maximum power 100 W, high speed stirring. The run time (time at which the reaction reaches max temperature or pressure) was set for 30 s and the hold time for 1 min. The reaction was monitored by TLC until most of the starting material had disappeared.[9] Upon completion, 12 min hold time, the solvent was vacuum distilled affording a dark yellow crude. ^{1}H NMR revealed the presence of what appeared to mono-(45%) and bis-sulfonium (55%). The derivatives which were separated by column chromatography using hexane:ethyl acetate 6:4 as eluent, the faster eluting fraction (likely the mono-sulfonium) quickly decomposed and wasn't characterized. The second fraction was a dark yellow solid (0.239 g, 77%): Mp 63.5-65.8 ºC; ^{1}H NMR (500 MHz, acetone-d_6) 8.08 (d, 10 Hz, 4H), 7.93 (m, 28H), 7.70 (m, 4H), 7.53(d, 20 Hz, 2H), 2.15 (m, 4H), 1.14 (m, 28H), 0.78 (t, 5Hz, 6H), 0.65 (m, 4H). ^{13}C NMR (125 MHz, acetone-d_6) 151.8 (C), 144.4 (C), 141.7 (C), 136.0 (C), 134.7 (CH), 134.5 (C), 131.9 (CH), 131.6 (CH), 131.2 (CH), 129.0 (CH), 126.9 (C), 125.5 (C), 125.3

(CH), 121.8 (C), 120.5 (C), 120.4 (C), 55.1 (C), 40.0 (C), 31.7 (C), 23.6 (C), 22.3 (C), 13.5 (C). Elemental Analysis Calcd. for ($C_{73}H_{80}F_{12}P_2S_2$): C, 66.85; H, 6.15; S, 4.89, Found: C, 66.94; H, 6.28; S, 4.69.

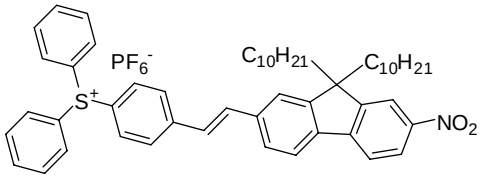


Preparation of phenyl(4-vinylphenyl)sulfane, 8. Methyl triphenyl phosphonium bromide (1.10 g, 3.1 mmol), was dissolved in methylene chloride while the vessel was purged with nitrogen. Sodium methoxide (1.46 g, 27 mmol) was quickly added and the vessel was nitrogen purged for another 15 min and subsequently stirred for 2 h. A solution of **1** (0.50 g, 2.35 mmol in 2.0 mL of methylene chloride) was added dropwise in the mixture. The reaction was kept at room temperature and followed to completion by TLC (18 h). Upon completion, the solvent was evaporated *in vacu*o and the resulting oil was redisolved in ethyl ether to precipitate triphenylphosphine oxide. The filtrate was concentrated and purified by column chromatography on silica gel using hexane as an eluent, affording a pale yellow oil, 0.21 g (42%).

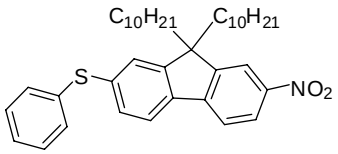


Preparation of (E)-(4-(2-(9,9-didecyl-7-nitro-9H-fluoren-2-yl)vinyl)phenyl)(phenyl)sulfane, 10. In a 2 mL glass reaction vessel[10] 9,9-didecyl-2-

iodo-7-nitro-9H-fluorene, **9** (0.49 g, 0.73 mmol) and phenyl(4-vinylphenyl)sulfane, **8** (0.12 g, 0.60 mmol) were dissolved in 2 mL of dry DMF with 0.01 g (0.06 mmol, 10% molar) of palladium acetate, and 0.80 g (7.9 mmol) of triethylamine. The mixture was purged with N_2 for 15 min while it was stirred. The microwave was set to closed vessel standard mode; maximum pressure 250 psi; maximum temperature 150 ºC, maximum power 60 W, high speed stirring. The run time (time at which the reaction reaches max temperature or pressure) was set for 30 s and the hold time for 30 min. The reaction was monitored by TLC every 30 s, and after 7.5 min the starting material was not observed. The mixture was cooled to room temperature and filtered through a celite plug. The filtrate was dissolved with methylene chloride, washed with water (4x), dried over anhydrous magnesium sulfate, and concentrated. The resulting dark brown oil was purified by column chromatography (hexane:ethyl acetate 9:1). A yellow oil 0.38 g (99%) was obtained, that crystallized on standing after several days. Mp 71.6-72.3 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) 8.25 (dd,3 Hz, 9Hz 1 H), 8.16 (d, 1.5Hz, 1H), 7.72 (dd, 3 Hz, 9Hz, 2 H), 7.52(d, 17 Hz, 1H), 7.46 (m, 3H), 7.30 (m, 7H), 7.17 (s, 2H), 2.04 (t, 6 Hz, 4H), 1.14 (m, 28H), 0.78 (t, 5Hz, 6H), 0.65 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) 153.1 (C), 152.3 (C), 147.4 (C), 147.2 (C), 138.6 (C), 138.5 (C), 136.1 (C), 135.8 (C), 135.6 (C), 131.5 (CH), 131.2 (CH), 129.5 (CH), 129.1 (C), 128.8 (C), 127.5 (CH), 126.2 (C), 123.6 (C), 121.7 (C), 121.2 (CH), 119.9 (C), 118.4 (C), 56.0 (C), 40.5 (C), 33.9(C), 32.2 (C), 30.2 (C), 29.9 (C), 29.6 (C), 29.6 (C), 24.1 (C), 23.0 (C), 14.5 (C). Elemental analysis calcd. $C_{47}H_{59}NO_2S$: C, 80.41; H, 8.47; S, 4.57; Found: C, 80.20; H, 8.32; S, 4.45.



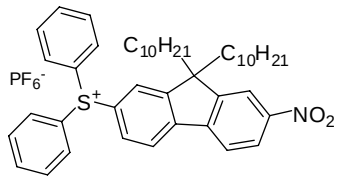
Preparation of (E)-(4-(2-(9,9-didecyl-7-nitro-9H-fluoren-2-yl)vinyl)phenyl)diphenylsulfonium hexaflourophosphate (V), 11. The preparation of sulfonium salt **11** was carried out according to the general procedure reported above. After purification, a yellow solid was obtained (0.23 g, 97%). Mp 62.4-64.5 ºC; ^{1}H NMR (300 MHz, DMSO-d_6) 8.26 (d, 2Hz 1 H), 8.18 (dd, 2 Hz, 8 Hz, 1H), 7.96 (m, 4 H), 7.74 (m, 14H), 7.58 (d, 16.2 Hz, 1H), 7.46 (d, 16.2 Hz, 1H), 7.17 (s, 2H), 2.04 (t, 6 Hz, 4H), 1.01 (m, 28H), 0.69 (t, 5Hz, 6H), 0.41 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$): 153.1 (C), 152.3 (C), 147.4 (C), 147.1 (C), 138.6 (C), 138.5 (C), 136.0, (C), 135.8 (C), 135.6 (C), 131.5 (CH), 131.1 (CH), 129.5 (CH), 129.1 (C), 128.8 (C), 127.5 (CH), 126.3 (C), 123.6 (C), 121.7 (C), 121.2 (CH), 119.9 (C), 118.4 (C), 56.0 (C), 40.5 (C), 33.9(C), 32.2 (C), 30.2 (C), 29.9 (C), 29.6 (C), 29.6 (C), 24.1 (C), 23.0 (C), 14.5 (C) Elemental analysis calcd. $C_{53}H_{64}F_6NO_2PS$: C, 68.88; H, 6.98; S, 3.47; Found: C, 68.60; H, 7.03; S, 3.47.



Preparation of 9,9-didecyl-7-nitro-9H-fluoren-2-yl)(phenyl)sulfane, 12.

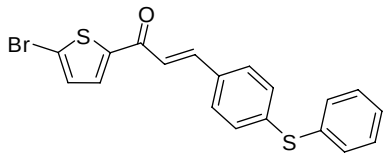
In a 2 mL glass reaction vessel 9,9-didecyl-2-iodo-7-nitro-9H-fluorene, **9** (0.52 g, 0.84 mmol) and thiophenol (0.11 g, 1.03 mmol) were dissolved in 2 mL of dry DMF with

copper iodide (0.01 g, 0.07 mmol, 8% molar), and cesium carbonate (0.62 g, 1.92 mmol). The mixture was purged with N_2 for 15 min while it was stirred. The microwave was set to closed vessel standard mode; maximum pressure 100 psi; maximum temperature 190 ºC, maximum power 150 W, and high speed stirring. The run time (time at which the reaction reaches max temperature or pressure) was set for 30 s and the hold time for 2 min. The reaction was monitored by TLC every 2 min, after 8 min the starting material had disappeared. The mixture was cooled to room temperature and was dissolved with methylene chloride, washed with water (4x), dried over anhydrous magnesium sulfate, and concentrated. The resulting light brown oil was purified by column chromatography (hexane:ethyl acetate 99:1). A light yellow oil 0.37 g (73%) was obtained. ^{1}H NMR (300 MHz, $CDCl_3$) 8.23 (d, 9Hz 1 H), 8.16 (s, 1H), 7.73 (d, 8 Hz, m, 1H), 7.66 (d, 8 Hz, m, 1H), 7.30 (m, 7H), 1.95 (m 4H), 1.10 (m, 28H), 0.85 (t, 6Hz, 6H), 0.57 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) 153.5 (C), 152.0 (C), 147.3 (C), 147.0 (C), 137.9 (C), 137.8(C), 131.3 (CH), 130.1 (C), 129.5 (CH), 127.6 (C), 125.7 (C), 123.6 (C), 122.0 (C), 120.0 (C), 118.5 (C), 56.1 (C), 40.3 (C), 32.3 (C), 30.2 (C), 29.9 (C), 29.7 (C), 24.2 (C), 23.1 (C), 14.5 (C). Elemental analysis calcd. $C_{39}H_{53}NO_2S$: C, 78.08; H, 8.90; S, 5.34: Found: C, 77.84; H, 8.65; S, 5.13.

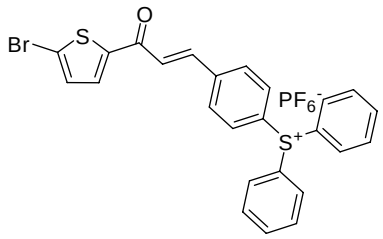


Preparation of (9,9-didecyl-7-nitro-9H-fluoren-2-yl)diphenylsulfonium hexafluorophosphate(V), 13. The preparation of sulfonium salt **11** was performed

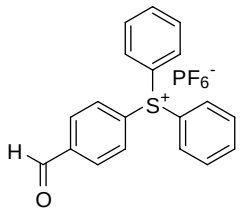
according to the general procedure reported above. After purification, a light yellow solid was obtained (0.08 g, 51%). Mp 42.7-44.6 ºC; ^{1}H NMR (300 MHz, $CDCl_3$) 8.33 (dd, 3Hz, 6Hz, 1 H), 8.25 (d, 3 Hz, 1H), 8.14 (d, 6Hz, 1 H), 7.97 (d, 6Hz, 1 H), 7.72 (m, 12H), 2.04 (t, 3 Hz, 4H), 1.10 (m, 28H), 0.85 (t, 5Hz, 6H), 0.51 (m, 4H). ^{13}C NMR (75 MHz, $CDCl_3$) Elemental analysis calcd. $C_{45}H_{58}F_6NO_2PS$: C, 65.75; H, 7.11; S, 3.90 ; Found: C, 65.90; H, 7.11; S, 4.11.



Preparation of (E)-1-(5-bromothiophen-2-yl)-3-(4-(phenylthio)phenyl)prop-2-en-1-one, 15. To a solution of acetylthiophene **16** (0.40 g, 2.00 mmol) in methanol at room temperature was added 0.11 g of powdered KOH. The mixture was stirred for 30 min then formyl phenyl phenyl sulfide **1** (0.43g, 2.0 mmol) was added. The reaction was let stir 10 h, resulting in a solid that was crystallized from an acetone water solution, yielding 0.6507 g (81%).of a colorless solid. Mp 149.8-150.2 ºC; ^{1}H NMR (500 MHz, $CDCl_3$) 7.78 (d, 15Hz, 1 H), 7.57 (d, 5 Hz, 1H), 7.52 (d, 9Hz, 2 H), 7.47 (m, 2 H), 7.39 (m, 2H), 7.26 (m, 4H), 7.15 (d, 5 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 180.7 (CHO), 152.0 (C), 147.3 (C), 147.0 (C), 143.8 (CH), 141.0 (C), 133.1 (CH), 133.3 (C), 131.7 (CH), 131.3 (CH), 129.6(CH), 129.1 (CH). 129.0 (CH), 128.3 (CH), 123.1 (C), 120.0 (CH). Elemental analysis calcd. $C_{19}H_{13}BrOS_2$ C, 56.86; H, 3.26; S, 15.98: Found: C, 57.01; H, 3.28; 16.04.



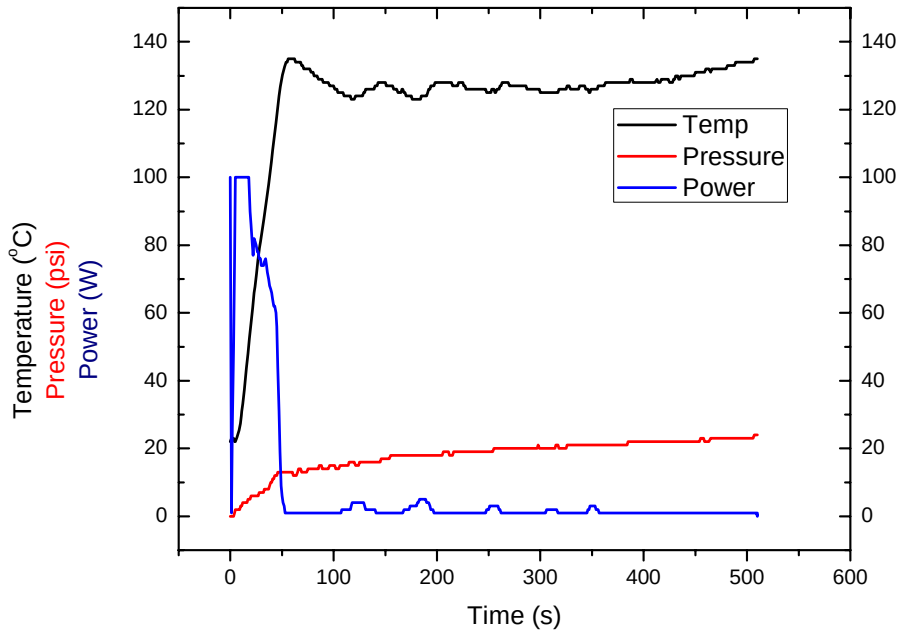
Preparation of (E)-(4-(3-(5-bromothiophen-2-yl)-3-oxoprop-1-enyl)phenyl)diphenylsulfonium hexafluorophosphate(V), 16. The preparation of sulfonium salt **11** was accomplished according to the general procedure reported above. After purification, a light yellow solid was obtained (0.225 g, 83%). Mp 72.1-73.9ºC; ^{1}H NMR (500 MHz, $CDCl_3$) 8.25 (d, 9Hz, 2 H), 8.06 (d, 5 Hz, 1H), 7.89 (m, 14H), 7.35 (d, 5Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 180.2 (CHO), 147.2 (C), 140.8 (C), 140.6 (C), 134.9 (CH), 134.2 (C), 132.5 (C), 131.8 (CH), 131.7 (CH), 131.4 (CH), 131.2 (CH), 126.0 (C), 125.1(C). 124.8 (C), 123.0 (C). $C_{25}H_{18}BrF_6OPS_2$: C, 48.17; H, 2.91; S, 10.29, Found: C, 48.25; H, 3.03; S, 10.17.



Preparation of (4-formylphenyl)diphenylsulfonium hexafluorophosphate(V), 22. The preparation of sulfonium salt **22** was carried out according to the general procedure reported above from the commercially available sulfide **21**. After purification, a colorless solid was obtained (0.378 g, 88%). ^{1}H NMR (500 MHz, acetone-d_6) 10.24 (s, 1 H), 8.34

(d, 9 Hz, 2H), 8.15 (d, 9 Hz, 2H), 8.08 (m, 6H), 7.91 (t, 9Hz, 4H) ^{13}C NMR (125 MHz, acetone-d_6) 191.2 (CHO), 140.3 (C), 135.0 (CH), 131.9 (CH), 131.7 (CH), 131.6 (CH), 131.5 (CH), 130.8 (C), 124.4 (CH). $C_{19}H_{15}F_6OPS$: C, 52.30; H, 3.46; S, 7.35, Found: C, 52.47; H, 3.43; S, 7.25.

Temperature vs. Time profile of the synthesis of sulfonium salt 11.



References and Notes

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(8) The high pressure reaction vessels were used were purchased from the microwave reactor manufacturer. Glass, 2 mL or 10 mL, heavy walled vessels with corresponding septum designed to withstand up to 300 psi inside the reation chamber.
(9) Rarely did the sulfides convert entirely. In the cases in which the reaction time was extended to try to achieve full conversion side products seriously complicated the purification hindering the overall yield of the sulfonium salt.
(10) The high pressure reaction vessels were used were purchased from the microwave reactor manufacturer. Glass, 2 mL or 10 mL, heavy walled vessels with corresponding septum designed to withstand up to 300 psi inside the reaction chamber.