Nucleophilic Aromatic Substitution of Polyfluoroarene to Access Highly Functionalized 10-Phenylphenothiazine Derivatives

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Abstract: Nucleophilic aromatic substitution (S_NAr) reactions can provide metal-free access to synthesize monosubstituted aromatic compounds. We developed efficient S_NAr conditions for p-selective substitution of polyfluoroarenes with phenothiazine in the presence of a mild base to afford the corresponding 10-phenylphenothiazine (PTH) derivatives. The resulting polyfluoroarene-bearing PTH derivatives were subjected to a second S_NAr reaction to generate highly functionalized PTH derivatives with potential applicability as photocatalysts for the reduction of carbon–halogen bonds.

Keywords: polyfluoroarene; phenothiazine; nucleophilic aromatic substitution; amination; photocatalyst

1. Introduction

Owing to the high electronegativity of fluorine atoms, polyfluoroarenes can undergo nucleophilic aromatic substitution (S_NAr) [1], wherein nucleophiles attack the low-electron-density arene core, and the fluoride anion is eliminated as a fluoride salt. Although transition-metal-catalyzed C-F and C-H bond functionalization of polyfluoroarenes have advanced considerably in recent years [2–6], S_NAr of polyfluoroarenes offers a transition-metal-free approach to substituted polyfluoroarenes. Polyfluoroarenes react with organometallic compounds, such as organolithium or organomagnesium reagents, to convert aromatic C-F bonds into C-C bonds without the use of transition metal catalysts [7,8]. The combination of a fluoride salt and organosilane compounds as nucleophiles has also been successful in the S_NAr of polyfluoroarenes, wherein the reaction proceeds with a catalytic amount of a fluoride anion [9–13]. The use of alcohols or amines as nucleophiles enables C-O and C-N bond formation to produce the corresponding aryl ether and aniline derivatives [8,14,15].

Functionalized arenes, such as arylamine derivatives, can be synthesized via transition-metal-catalyzed cross-coupling reactions [16–21]. However, the high cost of organometallic catalysts and contamination of the resulting products with metal traces represent major drawbacks of such methods. Alternative methods for transition-metal-free synthesis of arylamine derivatives have been achieved using hypervalent iodine reagents [22–27], sulfonium reagents [28], nitorarenes [29–33], or electrochemical conditions [34]. The S_NAr reaction also offers an alternative method without the use of transition metals, which is therefore potentially applicable in the facile synthesis of organic functional materials containing substituted arenes. For instance, 1,2,3,5-tetrakis(carbazolyl)-4,6-dicyanobenzene (4CzIPN), an organic photocatalyst, has been produced by multiple S_NAr reactions using carbazole and 1,3-dicyano-2,4,5,6-tetrafluorobenzene with NaH as the base [35]. In this context, we focused on the application of a sequential and controllable S_NAr reaction for the synthesis of 10-phenylphenothiazine (PTH) derivatives, which serve as organic photocatalysts that induce dehalogenative bond formation via processes such as atom transfer radical polymerization [36–46].
PTH derivatives are generally prepared via palladium- or copper-catalyzed coupling reactions of phenothiazine with aryl halides or arylboronic acids (Scheme 1a) [36–52]. Transition-metal-free methods for the synthesis of PTH derivatives include oxidative C-H amination in the presence of oxidants [53–57] or under electrolytic conditions [58,59], although starting materials are limited to phenols and anilines (Scheme 1b). In addition, S_NAr of triphenylsulfonium salts, nitroarenes, and fluoroarenes with phenothiazine have been demonstrated for the preparation of PTH derivatives (Scheme 1c) [28,60–67].

**Scheme 1.** Access to PTH derivatives under various conditions.

We envisioned that a reaction between phenothiazine and polyfluoroarenes would afford the corresponding polyfluoroarene-bearing PTH derivatives, which would then undergo a second S_NAr reaction for the introduction of other nucleophiles to afford highly functionalized PTH derivatives (Scheme 2). In addition to the synthetic utility of polyfluoroarenes, their introduction provides unique functionalities crucial in materials science, such as improvement of oxidation resistance, lowering of both HOMO and LUMO energy levels, and favorable stacking interactions with electron-rich aromatic rings [68–70]. However, S_NAr of polyfluoroarenes often suffers from uncontrollable substitution, resulting in a mixture of regioisomers and/or multisubstituted products. Therefore, it is necessary to establish appropriate conditions that suppress unselective substitution events and over-reactions, while being applicable to a wide range of polyfluoroarenes. Herein, we demonstrate S_NAr of various polyfluoroarenes resulting in mono-phenothiazination in the presence of an appropriate base to afford PTH derivatives bearing polyfluoroarenes, and further transformation of the resulting PTH derivatives to highly functionalized PTH derivatives via a second S_NAr reaction.

**Scheme 2.** Synthesis of highly functionalized PTH derivatives via sequential S_NAr reactions.

**2. Results and Discussion**

The reaction of phenothiazine with octafluorotoluene in the presence of K_2CO_3 in N,N-dimethylformamide (DMF) at 60 °C afforded the corresponding PTH derivative 3aa as the sole product in 96% yield (Scheme 3). The fluorine atom at the p-position of the trifluoromethyl group of octafluorotoluene was substituted by phenothiazine, without the
formation of regioisomers or multisubstituted products. The observed regioselectivity was in agreement with previously reported outcomes of octafluorotoluene SNAr [11,13], and it is governed by the electron density at the reactive carbons (ortho- and para-positions) on the aromatic ring and the steric repulsion between the trifluoromethyl group and bulky phenothiazine. The K$_2$CO$_3$/DMF system was found to be an efficient combination for mono SNAr between various phenothiazines and octafluorotoluene (Scheme 3). For example, phenothiazine derivatives bearing electron-deficient and electron-donating groups (1b–1e) were employed in the present reaction to give the corresponding PTH derivatives (3ba–3ea). Moreover, phenoxazine derivative 3fa was synthesized under similar conditions. Next, we examined various polyfluoroarenes for the SNAr reaction with phenothiazine.

Scheme 3. SNAr reaction of octafluorotoluene with phenothiazine derivatives or phenoxazine.

In contrast to octafluorotoluene, several other polyfluoroarenes exhibited decreased selectivities with the combination of K$_2$CO$_3$ and DMF, due to their inherently high reactivities, and the reaction of pentafluorobenzonitrile yielded complex mixtures including $p$- and $o$-substituted products, 3ab and 3ab', respectively (Scheme 4). Pentafluoronitrobenzene provided similar results, undergoing uncontrollable SNAr.

Scheme 4. Reaction of pentafluorobenzonitrile with phenothiazine using the K$_2$CO$_3$/DMF system.

Thus, optimization of the reaction conditions was performed for pentafluorobenzonitrile (2b) to suppress multiple substitution (Table 1). Using Li$_2$CO$_3$ or Na$_2$CO$_3$ instead of K$_2$CO$_3$ afforded the desired product 3ab in low yield along with unreacted 2b (entries 1 and 2). On the other hand, the use of Cs$_2$CO$_3$ led to high reactivity, and multiple substitutions occurred to give a complex mixture, containing 3ab in 13% (entry 3). Inorganic phosphate salts, such as Li$_3$PO$_4$ and Na$_3$PO$_4$, exhibited comparable results to those of carbonate salts (entries 4 and 5). On the other hand, the use of K$_3$PO$_4$ improved
the reaction yield of 3ab to 48% (entry 6). The use of Na$_3$PO$_4$ or K$_3$PO$_4$ at an elevated reaction temperature of 80 °C resulted in lower yields compared to those attained under the conditions in entry 6 (entries 7 and 8). Next, we surveyed reaction solvents. In the case of acetonitrile (MeCN) at 60 °C, the reaction yield improved to 76% (entry 9). N,N-Dimethylacetamide (DMA) and dimethyl sulfoxide (DMSO) were also suitable, albeit providing slightly decreased yields (entries 10 and 11). Chloroform, tetrahydrofuran (THF), and 1,4-dioxane were found to be inappropriate solvents (entries 12–14).

Table 1. Optimization of reaction conditions using pentafluorobenzonitrile a.

| Entry | Base       | Solvent | Temperature | 3ab Yield |
|-------|------------|---------|-------------|-----------|
| 1     | Li$_2$CO$_3$ | DMF     | 60 °C       | 0% b      |
| 2     | Na$_2$CO$_3$ | DMF     | 60 °C       | 7% b      |
| 3     | Cs$_2$CO$_3$ | DMF     | 60 °C       | 13% b,c   |
| 4     | Li$_3$PO$_4$ | DMF     | 60 °C       | 1% b      |
| 5     | Na$_3$PO$_4$ | DMF     | 60 °C       | 13% b      |
| 6     | K$_3$PO$_4$ | DMF     | 60 °C       | 48% d      |
| 7     | Na$_3$PO$_4$ | DMF     | 80 °C       | 32% d      |
| 8     | K$_3$PO$_4$ | DMF     | 80 °C       | 38% d      |
| 9     | K$_3$PO$_4$ | MeCN    | 60 °C       | 76% d      |
| 10    | K$_3$PO$_4$ | DMA     | 60 °C       | 43% d      |
| 11    | K$_3$PO$_4$ | DMSO    | 60 °C       | 38% d      |
| 12    | K$_3$PO$_4$ | CHCl$_3$| 60 °C       | 0%         |
| 13    | K$_3$PO$_4$ | THF     | 60 °C       | 0%         |
| 14    | K$_3$PO$_4$ | 1,4-dioxane | 60 °C   | 0%         |

a Reaction conditions: Phenothiazine 1a (0.50 mmol), pentafluorobenzonitrile 2b (1.0 mmol), and base (2.0 mmol) in solvent (5.0 mL, 0.1 M). b Determined by $^{19}$F-NMR using 4-fluorotoluene as an internal standard. c With multi-substitution products d Isolated yield.

Next, various polyfluoroarenes were subjected to S$_N$Ar with phenothiazine under the optimum conditions of K$_3$PO$_4$ in MeCN at 60 °C, as summarized in Scheme 5. Under these conditions, octafluorotoluene (2a) produced 3aa in 67% yield, which was lower than that obtained with the use of K$_2$CO$_3$ and DMF. Pentafluoronitrobenzene (2c) also underwent S$_N$Ar with high selectivity to afford $p$-substituted product 3ac in 78% yield. Ester-bearing PTH derivative 3ad was synthesized from methyl pentafluorobenzoate (2d) in 69% yield. Thus, the combination of K$_3$PO$_4$ and MeCN proved effective for achieving $p$-selective mono-substitution of a wide range of highly reactive polyfluoroarenes. Chloropentafluorobenzene (2e) underwent S$_N$Ar using K$_2$CO$_3$ in DMSO at 85 °C to afford the corresponding product 3ae, while the K$_3$PO$_4$/MeCN system resulted in low yield. The use of DMSO improved the reactivity of substitution presumably due to the higher solubility of the base. It should be noted that selective C–F bond functionalization occurred and the chlorine atom remained intact under these S$_N$Ar conditions, allowing for further product transformation via transition-metal-catalyzed cross-coupling reactions. In contrast to results obtained with electron-deficient groups, methyl-substituted pentafluorobenzene did not furnish the desired product even under K$_2$CO$_3$/DMSO conditions. When pentafluoropyridine (2f) was employed as the substrate, the S$_N$Ar reaction proceeded smoothly under K$_3$PO$_4$/MeCN conditions to produce fluorinated pyridylphenothiazine 3af in 92% yield. Simple polyfluoroarenes lacking other functional groups were also tested in the present S$_N$Ar protocol. The reaction of decafluorobiphenyl (2g) afforded the corresponding
mono-substituted product 3ag in 51% yield, along with a trace amount of the disubstituted compound (4aga). On the other hand, octafluoronaphthalene (2h) underwent double substitution to give 4aha in 22% yield, even with 2 equivalents of 2h. Hexafluorobenzene (2i) exhibited low reactivity under the K\textsubscript{2}PO\textsubscript{4}/MeCN system, as was the case with 2e. The combination of K\textsubscript{2}CO\textsubscript{3} and DMSO at 85 °C led to double substitution of 2i affording 4aia in 64% yield. In this case, 2i exists in the vapor phase as a result of its low boiling point (bp: ca. 80 °C); therefore, once the first S\textsubscript{N}Ar reaction occurs, the second is favored due to the monosubstituted product being in solution while the bulk of 2i remains in the vapor phase.

![Scheme 5. S\textsubscript{N}Ar reaction of phenothiazine with various polyfluoroarenes.](image)

Next, further transformations of obtained PTH derivatives 3 were performed (Scheme 6). Thus, S\textsubscript{N}Ar of 3ab with p-methoxyphenol proceeded in the presence of K\textsubscript{2}CO\textsubscript{3} to afford PTH derivative 4abb, bearing both cyano and phenoxy groups. Phthalimide, commonly used as a protecting group and photosensitizer, was also introduced onto 3ac via further S\textsubscript{N}Ar to obtain multifunctionalized 4acc. Transition-metal-free carbon–carbon bond formation was also examined using a combination of organosilanes and a catalytic amount of Bu\textsubscript{4}NSiF\textsubscript{2}Ph\textsubscript{3} (TBAT). Thiophene moieties, ubiquitous in functional organic materials owing to their high electron density, can be introduced onto 3af via the reaction with thienyl silane and TBAT to afford diheteroaromatic 4afd. Similarly, ethynylsilane participated in the carbon–carbon bond forming reaction with 3ag to produce linear analog 4age. Hence, PTH derivatives bearing various functional groups, connected through C–O,
C–N, and C–C bonds, were synthesized via sequential \( S_N \)Ar of polyfluoroarenes under transition-metal-free conditions.

**Scheme 6.** Synthesis of highly functionalized PTH derivatives via \( S_N \)Ar.

### 3. Materials and Methods

#### 3.1. General Information

\( ^{1}H, ^{13}C, \) and \( ^{19}F \) nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JMN-400 spectrometer at 25 °C unless otherwise noted. The data are reported as follows: chemical shift in part per million (\( \delta \)), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet), integration, and coupling constant (Hz). The chemical shifts in the \( ^{1}H \) NMR spectra were recorded relative to the residual solvent peaks (CDCl\(_3\): \( \delta \) 7.26). The chemical shifts in the \( ^{13}C \) NMR spectrum were also recorded relative to the residual solvent peaks (CDCl\(_3\): \( \delta \) 77.0). The chemical shifts in the \( ^{19}F \) NMR spectrum were recorded relative to that of the internal standard (4-fluorotoluene: \( \delta \) −121.0). High-resolution mass spectra (HRMS) were obtained using a Thermo Scientific Exactive Plus
3.2. S_N_Ar Reaction of Phenothiazines with Polyfluoroarenes

Phenothiazine derivatives (1.0 mmol) and base (4.0 mmol, 4.0 eq) were placed in a screw-capped test tube and dried under vacuum for 1 h. Backfilling with N_2, solvent (10 mL) and polyfluoroarenes (2.1 mmol, 2.1 eq) were added in this order. The reaction mixture was stirred at 60 °C for 24 h. The reaction was quenched with water (50 mL), and the mixture was transferred to a separatory funnel containing diethyl ether (50 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic fractions were washed with brine (50 mL), dried over Na_2SO_4, and all volatiles were removed under vacuum. The residue was purified by flash column chromatography (SiO_2) to yield the corresponding 10-phenylphenothiazine (PTH) derivatives.

3.2.2. 10-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)-10H-phenothiazine (3aa)

The title compound was prepared according to General Procedure A with phenothiazine (1a, 200 mg, 1.0 mmol), octafluorotoluene (2a, 300 µL, 2.1 mmol, 2.1 eq), and K_2CO_3 (554 mg, 4.0 mmol, 4.0 eq) in DMF (10 mL). 3aa was isolated by flash column chromatography (SiO_2, AcOEt/hexane = 1/100) in 96% yield (398 mg, 0.958 mmol) as a pale yellow solid. \(^1\)H NMR (400 MHz, CDCl_3, rt, δ/ppm): 7.12 (dd, J = 7.3, 2.0 Hz, 2H), 6.93–7.02 (m, 2H), 6.27 (dd, J = 7.8, 2.0 Hz, 2H). \(^19\)F NMR (376 MHz, CDCl_3, rt, δ/ppm): −85.0 (t, J = 22.0 Hz, 3F), −140.5–(−140.6) (m, 2F), −142.0–(−142.1) (m, 2F). HRMS (DART) m/z: ([M + H]^+) Calcd for C_{19}H_{19}F_{13}NS: 416.0338; Found 416.0342.

3.2.4. 10-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)-2-(trifluoromethyl)-10H-phenothiazine (3ca)

The title compound was prepared according to General Procedure A with 2-(trifluoromethyl)-10H-phenothiazine (1c, 133.6 mg, 0.50 mmol), octafluorotoluene (2a, 150 µL, 1.05 mmol, 2.1 eq), and K_2CO_3 (277 mg, 2.0 mmol, 4.0 eq) in DMF (5 mL). 3ca was isolated by flash column chromatography (SiO_2, AcOEt/hexane = 1/200) in 94% yield (220 mg, 0.455 mmol) as a pale yellow solid. \(^1\)H NMR (400 MHz, CDCl_3, rt, δ/ppm): 7.21 (s, 2H), 7.13–7.10 (m, 1H), 7.06–6.98 (m, 2H), 6.43 (s, 1H), 6.27 (d, J = 7.3 Hz, 1H). \(^19\)F NMR (376 MHz, CDCl_3, rt, δ/ppm): −58.5 (t, J = 22.0 Hz, 3F), −140.8–(−140.6) (m, 2F), −142.1–(−142.2) (m, 2F). HRMS (DART) m/z: ([M + H]^+) Calcd for C_{20}H_{19}F_{13}NS: 449.9949; Found 449.9946.

3.2.5. 2-Methoxy-10-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)-10H-phenothiazine (3da)

The title compound was prepared according to General Procedure A with 2-methoxy-10H-phenothiazine (1d, 114.6 mg, 0.50 mmol), octafluorotoluene (2a, 150 µL, 1.05 mmol, 2.1 eq), and K_2CO_3 (277 mg, 2.0 mmol, 4.0 eq) in DMF (5 mL). 3da was isolated by flash column chromatography (SiO_2, AcOEt/hexane = 1/150) in 89% yield (200 mg, 0.449 mmol) as a pale yellow solid. \(^1\)H NMR (400 MHz, CDCl_3, rt, δ/ppm): 7.05 (dd, J = 7.8, 2.0 Hz, 2H), 6.85 (dd, J = 22.0 Hz, 2H), 6.27 (dd, J = 7.8, 2.0 Hz, 2H).
3.2.6. 2-(Ethylthio)-10-(2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl)-10H-phenothiazine (3ea)

The title compound was prepared according to General Procedure A with 2-ethylthio-10H-phenothiazine (1e, 129.7 mg, 0.50 mmol), octafluorotoluene (2a, 150 µL, 1.05 mmol, 2.1 eq), and K$_2$CO$_3$ (277 mg, 2.0 mmol, 4.0 eq) in DMF (5 mL). 3ea was isolated by flash column chromatography (SiO$_2$, AcOEt/hexane = 1/100) in 55% yield (130 mg, 0.273 mmol) as a yellow oil. $^1$H NMR (400 MHz, CDCl$_3$, rt, $\delta$/ppm): 7.08–7.05 (m, 1H), 7.03–6.91 (m, 4H), 6.25–6.21 (m, 2H), 2.81 (q, $J$ = 7.3 Hz, 2H), 1.23 (t, $J$ = 7.3 Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$, rt, $\delta$/ppm): −58.5 (t, $J$ = 22.0 Hz, 3F), −191.2 (m, 2F), −140.2 (s, 3H). HRMS (DART) $m/z$: ([M + H$^+$]) Calcd for C$_{21}$H$_{13}$F$_7$NS$_2^+$ 476.0372; Found 476.0371.

3.2.7. 10-(2,3,5,6-Tetrafluoro-4-(trifluoromethyl)phenyl)-10H-phenoxazine (3fa)

The title compound was prepared according to General Procedure A with 10H-phenoxazine (1f, 91.6 mg, 0.50 mmol), octafluorotoluene (2a, 150 µL, 1.05 mmol, 2.1 eq), and K$_2$CO$_3$ (277 mg, 2.0 mmol, 4.0 eq) in DMF (5 mL). 3fa was isolated by flash column chromatography (SiO$_2$, AcOEt/hexane = 1/100) in 80% yield (160 mg, 0.400 mmol) as a pale yellow solid. $^1$H NMR (400 MHz, CDCl$_3$, rt, $\delta$/ppm): 6.82–6.78 (m, 4H), 6.75–6.69 (m, 2H), 6.00 (dd, $J$ = 7.3, 1.5 Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$, rt, $\delta$/ppm): −58.5 (t, $J$ = 22.0 Hz, 3F), −140.3–(−140.5) (m, 2F), −142.0–(−142.1) (m, 2F). HRMS (DART) $m/z$: ([M + H$^+$]) Calcd for C$_{19}$H$_9$F$_3$ON$^+$ 400.0567; Found 400.0565.

3.2.8. 2,3,5,6-Tetrafluoro-4-(10H-phenothiazin-10-yl)benzonitrile (3ab)

The title compound was prepared according to General Procedure A with phenothiazine (1a, 399 mg, 2.0 mmol), pentafluorobenzonitrile (2b, 512 µL, 4.0 mmol, 2.0 eq), and K$_3$PO$_4$ (1.70 g, 8.0 mmol, 4.0 eq) in MeCN (20 mL). 3ab was isolated by flash column chromatography (SiO$_2$, AcOEt/hexane = 1/40) in 76% yield (568 mg, 1.53 mmol) as a pale yellow solid. $^1$H NMR (400 MHz, CDCl$_3$, rt, $\delta$/ppm): 7.13 (dd, $J$ = 7.3, 2.0 Hz, 2H), 7.08–6.95 (m, 4H), 6.27 (dd, $J$ = 7.8, 1.5 Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$, rt, $\delta$/ppm): −132.4–(−132.5) (m, 2F), −140.6–(−140.7) (m, 2F). HRMS (DART) $m/z$: ([M + H$^+$]) Calcd for C$_{17}$H$_9$F$_2$NS$^+$ 373.0417; Found 373.0415.

3.2.9. 10-(2,3,5,6-Tetrafluoro-4-nitrophenyl)-10H-phenothiazine (3ac)

The title compound was prepared according to General Procedure A with phenothiazine (1a, 399 mg, 2.0 mmol), pentafluorobenzonitrile (2c, 496 µL, 4.0 mmol, 2.0 eq), and K$_3$PO$_4$ (1.70 g, 8.0 mmol, 4.0 eq) in MeCN (20 mL). 3ac was isolated by flash column chromatography (SiO$_2$, AcOEt/hexane = 1/40) in 76% yield (613 mg, 1.53 mmol) as an orange solid. $^1$H NMR (400 MHz, CDCl$_3$, rt, $\delta$/ppm): 7.11 (dd, $J$ = 7.3, 1.5 Hz, 2H), 7.02–6.94 (m, 4H), 6.26 (dd, $J$ = 7.3, 1.5 Hz, 2H). $^{19}$F NMR (376 MHz, CDCl$_3$, rt, $\delta$/ppm): −132.4–(−132.5) (m, 2F), −140.6–(−140.7) (m, 2F). HRMS (DART) $m/z$: ([M + H$^+$]) Calcd for C$_{18}$H$_9$F$_2$NS$_2$O$_2$2$^+$ 393.0315; Found 393.0317.

3.2.10. Methyl 2,3,5,6-tetrafluoro-4-(10H-phenothiazin-10-yl)benzoate (3ad)

The title compound was prepared according to General Procedure A with phenothiazine (1a, 100 mg, 0.50 mmol), methyl pentafluorobenzonitrile (2d, 146 µL, 1.0 mmol, 2.0 eq), and K$_3$PO$_4$ (424.5 mg, 2.0 mmol, 4.0 eq) in MeCN (5 mL). 3ad was isolated by flash column chromatography (SiO$_2$, AcOEt/hexane = 1/200) in 69% yield (140 mg, 0.345 mmol) as a pale yellow solid. $^1$H NMR (400 MHz, CDCl$_3$, rt, $\delta$/ppm): 7.10 (dd, $J$ = 7.3, 1.5 Hz, 2H), 7.00–6.91 (m, 4H), 6.25 (dd, $J$ = 7.8, 1.0 Hz, 2H), 4.05 (s, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$, rt,
δ/ppm): −143.2−(−143.3) (m, 2F), −139.7−(−139.8) (m, 2F). HRMS (DART) m/z: ([M + H]+) Calcd for C_{20}H_{12}F_{4}NO_{2}S\textsuperscript{2+} 406.0519; Found 406.0520.

3.2.11. 10-(4-Chloro-2,3,5,6-tetrafluorophenyl)-10H-phenothiazine (3ae)

The title compound was prepared according to General Procedure A with phenothiazine (1a, 100 mg, 0.50 mmol), chloropentafluorobenzene (2e, 129 μL, 1.0 mmol, 2.0 eq), and K2CO3 (277 mg, 2.0 mmol, 4.0 eq) in DMSO (5 mL) at 80 °C. 3ae was isolated by flash column chromatography (SiO2, AcOEt/hexane = 1/200) in 62% yield (118 mg, 0.309 mmol) as a pale yellow solid. 1H NMR (400 MHz, CDCl3, rt, δ/ppm): 7.09 (dd, J = 7.3, 1.5 Hz, 2H), 7.00–6.91 (m, 4H), 6.26 (dd, J = 7.8, 1.5 Hz, 2H). 19F NMR (376 MHz, CDCl3, rt, δ/ppm): −141.0−(−141.0) (m, 2F), −143.8−(−143.8) (m, 2F). HRMS (DART) m/z: ([M + H]+) Calcd for C_{16}H_{9}ClF_{5}NS\textsuperscript{2+} 382.0075; Found 382.0075.

3.2.12. 10-(Perfluoropyridin-4-yl)-10H-phenothiazine (3af)

The title compound was prepared according to General Procedure A with phenothiazine (1a, 399 mg, 2.0 mmol), pentafluoropyridine (2f, 430 μL, 4.0 mmol, 2.0 eq), and K3PO4 (1.70 g, 8.0 mmol, 4.0 eq) in MeCN (20 mL). 3af was isolated by flash column chromatography (SiO2, AcOEt/hexane = 1/50) in 92% yield (640 mg, 1.84 mmol) as a pale yellow solid. 1H NMR (400 MHz, CDCl3, rt, δ/ppm): 7.04–6.94 (m, 4H), 6.34 (d, J = 7.8 Hz, 2H). 19F NMR (376 MHz, CDCl3, rt, δ/ppm): −88.9−(−89.0) (m, 2F), −144.5−(−144.7) (m, 2F). HRMS (DART) m/z: ([M + H]+) Calcd for C_{17}H_{9}F_{4}N_{2}S\textsuperscript{2+} 349.0417; Found 349.0420.

3.2.13. 10-(Perfluoro-[1,1′-biphenyl]-4-yl)-10H-phenothiazine (3ag)

The title compound was prepared according to General Procedure A with phenothiazine (1a, 100 mg, 0.50 mmol), decarboxylopyridobiphenyl (2g, 334 mg, 1.0 mmol, 2.0 eq), and K3PO4 (424.5 mg, 2.0 mmol, 4.0 eq) in MeCN (5 mL). 3ag was isolated by flash column chromatography (SiO2, AcOEt/hexane = 1/100) in 51% yield (130 mg, 0.253 mmol) as a pale yellow solid. 1H NMR (400 MHz, CDCl3, rt, δ/ppm): 7.12 (dd, J = 7.8, 1.5 Hz, 2H), 7.06–6.92 (m, 4H), 6.33 (d, J = 7.8 Hz, 2H). 19F NMR (376 MHz, CDCl3, rt, δ/ppm): −143.2−(−143.4) (m, 2F), −139.1−(−139.2) (m, 2F), −143.4−(−143.5) (m, 1F), −151.4−(−151.6) (m, 2F), −162.2−(−162.3) (m, 2F). HRMS (DART) m/z: ([M + H]+) Calcd for C_{24}H_{9}F_{4}N_{2}S\textsuperscript{2+} 514.0307; Found 514.0303.

3.2.14. 10,10′-(Perfluoronaphthalene-2,6-diyl)bis(10H-phenothiazine) (4aha)

The title compound was prepared according to General Procedure A with phenothiazine (1a, 100 mg, 0.50 mmol), octafluoronaphthalene (2h, 270 mg, 1.0 mmol, 2.0 eq), and K3PO4 (424.5 mg, 2.0 mmol, 4.0 eq) in MeCN (5 mL). 4aha was isolated by flash column chromatography (SiO2, AcOEt/hexane = 1/10) in 22% yield (70 mg, 0.111 mmol) as a pale yellow solid. 1H NMR (400 MHz, CDCl3, rt, δ/ppm): 7.12 (dd, J = 7.8, 1.5 Hz, 2H), 6.99–6.96 (m, 4H), 6.32 (d, J = 7.8 Hz, 2H). 19F NMR (376 MHz, CDCl3, rt, δ/ppm): −123.5−(−123.8) (m, 2F), −140.9−(−140.9) (m, 2F), −144.5−(−144.8) (m, 2F). HRMS (DART) m/z: ([M + H]+) Calcd for C_{34}H_{17}F_{6}N_{2}S\textsuperscript{2+} 631.0732; Found 631.0733.

3.2.15. 10,10′-(Perfluoro-1,4-phenylene)bis(10H-phenothiazine) (4ai)

The title compound was prepared according to General Procedure A with phenothiazine (1a, 100 mg, 0.50 mmol), hexafluorobenzene (2i, 177 μL, 1.0 mmol, 2.0 eq), and K2CO3 (277 mg, 2.0 mmol, 4.0 eq) in DMSO (5 mL) at 80 °C. 4ai was isolated by flash column chromatography (SiO2, AcOEt/hexane = 1/50) in 64% yield (174 mg, 0.320 mmol) as a pale yellow solid. 1H NMR (400 MHz, CDCl3, rt, δ/ppm): 7.14 (dd, J = 7.3, 1.5 Hz, 2H), 7.06–6.98 (m, 4H), 6.39 (d, J = 8.3 Hz, 2H). 19F NMR (376 MHz, CDCl3, rt, δ/ppm): −143.0 (s, 2F). HRMS (DART) m/z: ([M + H]+) Calcd for C_{39}H_{17}F_{6}N_{2}S\textsuperscript{2+} 545.0764; Found 545.0766.
3.3. Sequential S_{NH}Ar Reaction with 3ab, 3ac, 3af, and 3ag

3.3.1. 3,5-Difluoro-2,6-bis(4-methoxyphenoxyl)-4-(10H-phenothiazin-10-yl)benzonitrile (4abb)

Phenothiazine derivative 3ab (0.10 mmol), 4-methoxyphenol (0.40 mmol, 4.0 eq), and K₂CO₃ (0.80 mmol, 8.0 eq) were placed in a screw-capped test tube and dried under vacuum for 1 h. After backfilling with N₂, DMF (1.5 mL) was added to the test tube. The reaction mixture was stored at room temperature for 24 h. The reaction was quenched with water (20 mL) and the mixture was transferred to a separatory funnel containing diethyl ether (20 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 20 mL). The combined organic fractions were washed with brine (20 mL), dried over Na₂SO₄, and all volatiles were removed under vacuum. 4abb was isolated by flash column chromatography (SiO₂, AcOEt/hexane = 1/10) in 86% yield (50 mg, 0.0862 mmol) as a pale yellow solid. ¹H NMR (400 MHz, CDCl₃, rt, δ/ppm): 8.07 (s, 1H), 7.95–7.82 (m, 2H), 7.43–7.37 (m, 2H), 7.14 (dd, J = 7.3, 1.5 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm): −132.2 (s, 2F). HRMS (DART) m/z: ([M + H]⁺) Calcd for C₂₃H₂₃F₂N₂S⁺ 581.1341; Found 581.1342.

3.3.2 2-(2,4,5-Trifluoro-6-nitro-3-(10H-phenothiazin-10-yl)phenyl)isoindoline-1,3-dione (4acc)

In a well-dried screw-capped test tube, 3ac (78.5 mg, 0.20 mmol) was dissolved in DMF. Phthalimide (40.7 mg, 0.22 mmol, 1.1 eq) was added to the mixture and the test tube was sealed with a cap, and the reaction mixture was stirred at 60 °C for 20 h. The reaction was quenched with water (20 mL) and the mixture was then transferred to a separatory funnel with diethyl ether (20 mL). The organic layer was separated, and the aqueous layer was extracted with diethyl ether (2 × 10 mL). The combined organic fractions were washed with brine (20 mL) and then dried over Na₂SO₄, and all the volatiles were removed under vacuum. 4acc was isolated by flash column chromatography (SiO₂, AcOEt/hexane = 1/10) in 69% yield (72.3 mg, 0.139 mmol) as a white solid. ¹H NMR (400 MHz, CDCl₃, rt, δ/ppm): 8.07 (s, 1H), 7.95–7.82 (m, 2H), 7.43–7.37 (m, 2H), 7.14 (dd, J = 7.3, 1.5 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm): −120.6–(−120.7) (m, 1F), −131.0–(−131.1) (m, 1F), −144.8–(−144.9) (m, 1F). HRMS (DART) m/z: ([M + H]⁺) Calcd for C₂₆H₁₃F₂O₃N₃S⁺ 520.0573; Found 520.0572.

3.3.3. 10-(2-(Benzol[b]thiophen-2-yl)-3,5,6-trifluoropyridin-4-yl)-10H-phenothiazine (4afd)

In a well-dried screw-capped test tube, tetrabutylammonium difluorotriphenylsilicate (TBAT, 10.8 mg, 0.02 mmol, 20 mol%) and 4-methoxyphenol (0.40 mmol, 4.0 eq) were placed in a screw-capped test tube and dried under vacuum for 1 h. After backfilling with N₂, THF (1.0 mL) and benzo[b]thiophen-2-yltrimethylsilane (24.8 mg, 0.12 mmol, 1.2 eq) were added to the mixture in this order. Phenothiazine (0.10 mmol), 4-methoxyphenol (0.40 mmol, 4.0 eq), and TBAT (5.4 mg, 0.01 mmol, 10 mol%) were added and dried under vacuum for 1 h. After backfilling with N₂, THF (1.0 mL) and benzo[b]thiophen-2-yltrimethylsilane (24.8 mg, 0.12 mmol, 1.2 eq) were added to the mixture in this order. The test tube was sealed with a cap, and the reaction mixture was stirred at 60 °C for 20 h. The reaction was quenched with water (20 mL) and the mixture was then transferred to a separatory funnel with AcOEt (20 mL). The organic layer was separated, and the aqueous layer was extracted with AcOEt (2 × 10 mL). The combined organic fractions were washed with brine (20 mL) and then dried over Na₂SO₄, and all the volatiles were removed under vacuum. 4afd was isolated by flash column chromatography (SiO₂, AcOEt/hexane = 1/30) in 65% yield (30.0 mg, 0.0649 mmol) as a white solid. ¹H NMR (400 MHz, CDCl₃, rt, δ/ppm): 8.07 (s, 1H), 7.95–7.82 (m, 2H), 7.43–7.37 (m, 2H), 7.14 (dd, J = 7.3, 1.5 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm): −85.5–(−85.6) (m, 1F), −126.9–(−126.9) (m, 1F), −141.8–(−141.9) (m, 1F). HRMS (DART) m/z: ([M + H]⁺) Calcd for C₂₅H₁₃F₃N₂S⁺ 463.0545; Found 463.0544.

3.3.4.10-(2,2',3,3',5,5',6,6'-octafluoro-4'-(phenylethynyl)-[1,1'-biphenyl]-4-yl)-10H-phenothiazine (4age)

In a well-dried screw-capped test tube, tetrabutylammonium difluorotriphenylsilicate (TBAT, 10.8 mg, 0.02 mmol, 20 mol%) and 3ag (51.3 mg, 0.10 mmol) were added and
dried under vacuum for 1 h. After backfilling with N₂, THF (1.0 mL) and 1-phenyl-2-(trimethylsilyl)acetylene (24 µL, 0.12 mmol, 1.2 eq) were added to the mixture in this order. The test tube was sealed with a cap, and the reaction mixture was stirred at 60 °C for 20 h. The reaction was quenched with water (20 mL) and the mixture was then transferred to a separatory funnel with AcOEt (20 mL). The organic layer was separated, and the aqueous layer was extracted with AcOEt (2 × 10 mL). The combined organic fractions were washed with brine (20 mL) and then dried over Na₂SO₄, and all the volatiles were removed under vacuum. 4age was isolated by flash column chromatography (SiO₂, AcOEt/hexane = 1/19) in 73% yield (43.3 mg, 0.0727 mmol) as a white solid. ¹H NMR (400 MHz, CDCl₃, rt, δ/ppm): 7.64 (dd, J = 8.0, 1.7 Hz, 2H), 7.47–7.42 (m, 3H), 7.12 (dd, J = 7.3, 1.5 Hz, 2H), 7.04 (dt, J = 7.8, 1.4 Hz, 2H), 6.96 (dt, J = 7.3, 1.5 Hz, 2H), 6.35 (d, J = 7.8 Hz, 2H). ¹⁹F NMR (376 MHz, CDCl₃, rt, δ/ppm): −137.7–(−137.8) (m, 2F), −138.0–(−138.1) (m, 2F), −140.4–(−140.5) (m, 2F), −143.6–(−143.7) (m, 2F). HRMS (DART) m/z: ([M + H]+) Calcd for C₃₂H₁₄F₈NS⁺ 596.0714; Found 596.0715.

4. Conclusions

In conclusion, we demonstrated a controllable S₅Ar reaction of polyfluoroarenes with phenothiazine for the transition-metal-free synthesis of PTH derivatives. The combination of K₃PO₄ as the base and MeCN as the solvent was found to be widely applicable for the regioselective monosubstitution of highly reactive polyfluoroarenes, whereas the combination of K₂CO₃ and DMF resulted in multisubstitution. Various functional groups, including cyano, nitro, ester, and chlorine atoms, tolerated to the present conditions, thus enabling further transformations of the S₅Ar products. The obtained fluorine-containing PTH derivatives were employed in a sequential S₅Ar reaction to afford highly functionalized PTH derivatives. Further investigation of the optical characteristics of these compounds and their photocatalytic capabilities is currently underway.

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