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Regioselective preparation of functional aryl ethers and esters by stepwise nucleophilic aromatic substitution reaction

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ABSTRACT

Functional aryl ethers bearing mono- and di-substituted azo compounds, allyl functionalities, vinyl phenyl moieties, trifluoromethyl ($-CF_3$) groups, etc. were prepared by nucleophilic substitution reaction of 2,3,4,5,6-pentafluorobenzonitrile (PFBN) in a stepwise manner at room temperature in dipolar aprotic solvents in a regioselective manner. Mono substituted aryl ether further underwent two more substitutions at *ortho* and *ortho′* positions either with the same or different phenoxides. However, *para* substituted monoesters as well as *para*-ether-*ortho*-ester obtained by using carboxylates as (one of the) nucleophiles did not undergo any further displacement. The synthetic strategy described here is useful for making various functional materials such as lubricants, liquid crystals, curing agents, pigments and superhydrophobic materials.

1. Introduction

Organic compounds containing multiple fluorine atoms are high performance materials and applied in many areas such as hydrophobic materials [1], lubricants [2], thermally stable materials [3], dielectric materials [4], liquid crystals [5], etc. Due to the unique properties of fluorinated compounds, these are also used widely as drugs in various therapeutic areas such as antifungal agents [6], antibiotics [7], antimalarial compounds [8], antidepressants [9], anti-inflammatory agents [10], anesthetics [11], and in biomedical research as drug delivery systems [12]. Quite apart from these applications, fluorinated compounds are also valuable intermediates for preparing a variety of materials such as contrast agents for bio-imaging applications [13], electronic applications [14] and high performance coatings [15].

In aromatic compounds containing fluorine atoms, these atoms are either present on the aromatic ring substituting H atoms or attached as a pendant group such as perfluoroalkyl (e.g., $-CF_3$ or higher homologues). These fluorinated aromatic compounds of the first category readily undergo nucleophilic substitution reactions, particularly if the compound contains multiple F atoms on the aromatic ring or if it possesses electron withdrawing groups suitably positioned to activate the displacement of fluorine as fluoride (F^-). Indeed this ability to undergo nucleophilic substitution has been made use of for making various high performance engineering thermoplastics such as poly(arylene ether)s viz., poly(ether ether ketone)s, (PEEK), poly(ether sulfone)s, poly(ether imide)s, etc. which are well known for excellent properties such as high temperature stability, high glass transition temperature, anti-flammable nature, solvent resistance, etc. [16]. Fluorinated aromatic compounds are also often used as building blocks in the preparation of macrocycles [17], glycosyl donors [18], and fused ring systems [19].

2. Results and discussion

Perfluoro and difluoro organic compounds such as 2,3,4,5,6-pentafluorobenzonitrile [20] (PFBN) and 2,6-difluorobenzonitrile [21] (DFBN) are valuable starting materials, because of its ability to undergo nucleophilic substitution under mild conditions yielding various organic compounds and functional polymers with highly polar cyano (–CN) pendant groups [20d,21b].

The *para* F atom of PFBN readily undergoes nucleophilic substitution selectively even at room temperature or lower [20d]. This superior reactivity of *para* F atom as compared to those at *ortho*, *ortho′* positions enabled us to prepare linear poly(arylene ether)s with multiple pendant groups [20d]. As reported here, this reactivity difference has been exploited to prepare various symmetrically and unsymmetrically trisubstituted arylene ether and ester derivatives under mild reaction conditions. It is useful to

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note here that carboxylates have rarely been used as nucleophiles in nucleophilic aromatic substitution reactions. Previously we employed carboxylates as nucleophiles in nucelophilic aliphatic substitution reactions to make unsaturated poly(ether ester)s and polyesters [22].

In the first step of nucleophilic substitution reaction, the *para* fluorine atom was selectively displaced with one equivalent of (substituted) phenol in presence of base at room temperature or below, quantitatively. Subsequent reaction(s) with two more equivalents of similar or dissimilar nucleophiles displaces F atoms at *ortho* and *ortho′* positions as well. Thus this methodology offers a unique advantage of making symmetrical or differently trisubstituted benzonitriles in a facile manner.

In this study, we used four different phenols viz., phenol, 3-(trifluoromethyl)phenol, 3,5-bis(trifluoromethyl)phenol and 3-phenoxyphenol as nucleophile to displace the *para*-fluorine atom of PFBN. The nucleophilic aromatic substitution reaction proceeded smoothly in dipolar aprotic solvents in presence of base such as potassium carbonate at room temperature for 24 h. The preparation of various 4-phenoxy-2,3,5,6-tetrafluorobenzonitrile (PTFBN) is shown in Scheme 1.

The nuclear magnetic resonance spectrum of F nuclei, ^{19}F NMR spectra, of PTFBN clearly indicate that the complete disappearance of signal corresponding to the *para* fluorine atom at −141.75 ppm. Also, the ^{19}F NMR spectroscopic analysis of **2b** (Figs. 1 and S1) showed signals at −62.96 ppm, −131.5 ppm, and −150.42 ppm corresponding to $-CF_3$ group, *meta* and *ortho* F atoms respectively with the intensity ratio of 3:2:2, as expected. The facile mono substitution yielded analytically pure compounds as established by elemental analysis. The nature of compounds varied from solid to viscous liquid depending on the type of phenol used for nucleophilic substitution reaction. The mono substituted PTFBN were obtained in high yields (85–92%) after purification.

The mono substituted PTFBNs possess two more displaceable F atoms of equal reactivity at *ortho*, *ortho′* positions. Thus, trisubstituted arylene ethers were prepared by employing two equivalents of same or different phenols in a one or two step reaction at room temperature respectively.

The disubstituted phenoxy benzonitriles, TriFBNs were obtained by reacting PTFBN with one equivalent of phenol such as 3-(trifluoromethyl)phenol, and 3,5-bis(trifluoromethyl)phenol as shown in Scheme 2. These reactions usually yielded some impurities such as trisubstituted compounds because of the equal reactivity of fluorine atoms at *ortho*, *ortho′* positions. In spite of this side reaction, disubstituted compounds were obtained in high to very high yields depending on the reactivity of monohydroxy

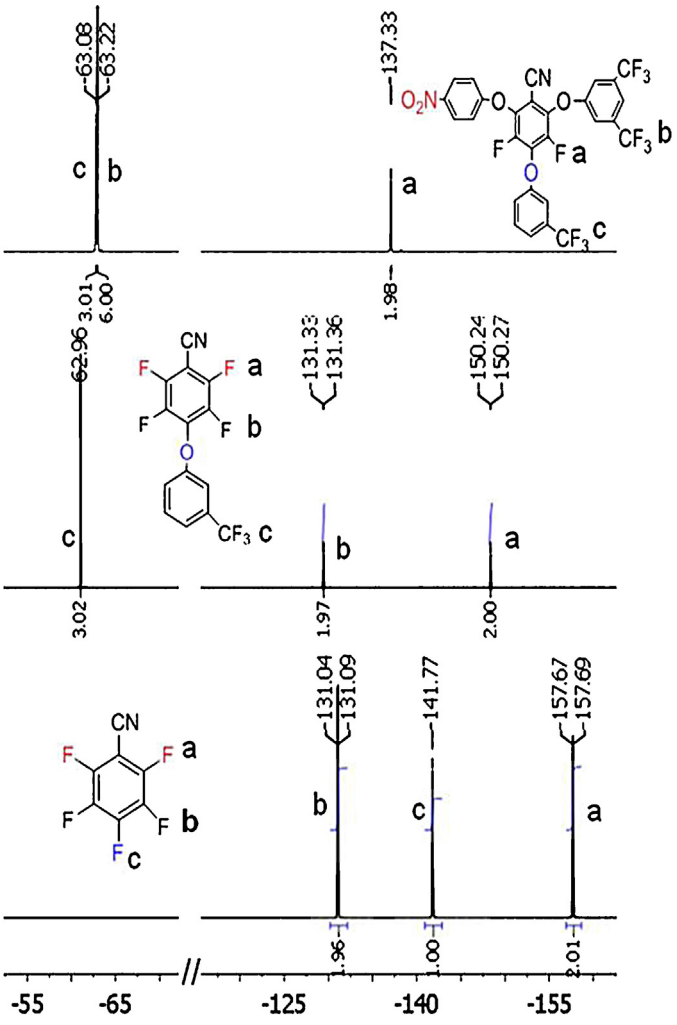
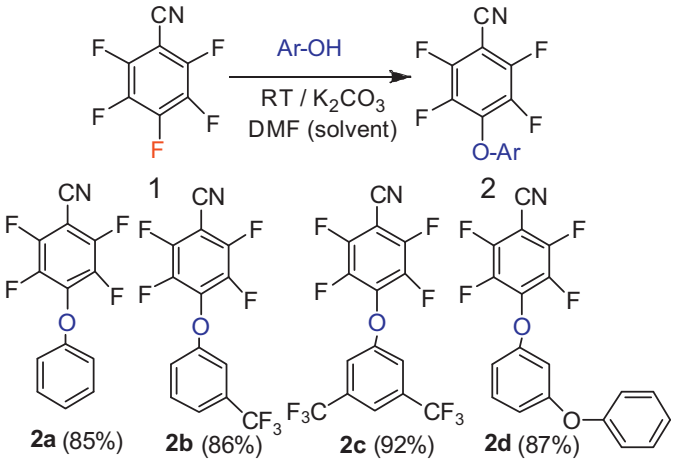
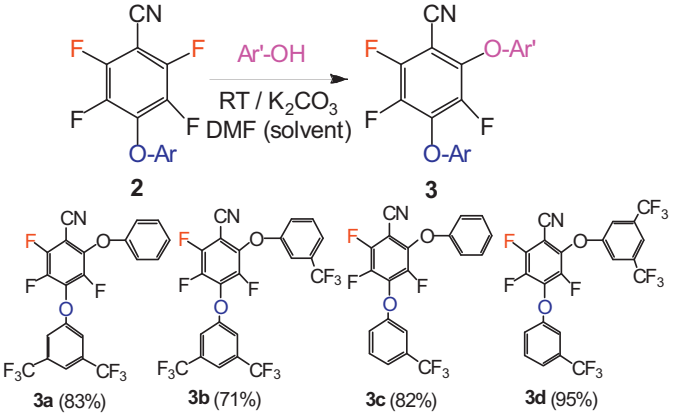


Fig. 1. Stacked ^{19}F NMR spectra of 2,3,4,5,6-pentaflourobenzo-nitrile (PFBN), 4-phenoxy-3-(trifluoromethyl)-2,3,5,6-tetraflouro benzonitrile (**2b**) and 2-[3,5-bis(trifluoromethyl)phenoxy]-3,5-difluoro-6-(4-nitrophenoxy)-4-[3-(trifluoromethyl)-phenoxy]benzonitrile (**4e**).



Scheme 1. Regioselective synthesis of 4-phenoxy(substituted)-2,3,5,6-tetraflurobenzonitriles (PTFB).

phenol moiety. The formation of trisubstituted product occurred even when the reaction was carried out at lower temperatures (5–10 °C) and with lower base concentration (0.75 equivalents). Surprisingly the reactions with 3,5-bis(trifluoromethyl)phenol proceeded with high yields for both mono (Scheme 1, **2c**) as well as disubstitution (Scheme 2, **3d**). Earlier we noticed that the PTFBN

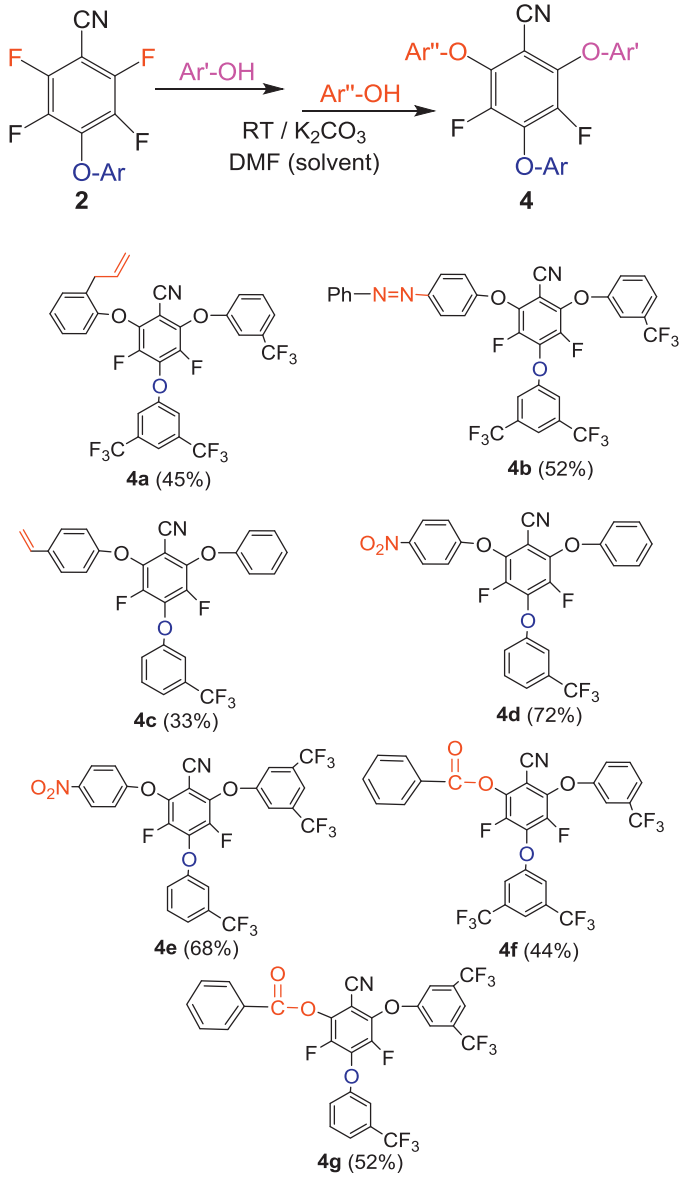


Scheme 2. Regioselective synthesis of disubstituted trifluorobenzonitrile ethers.

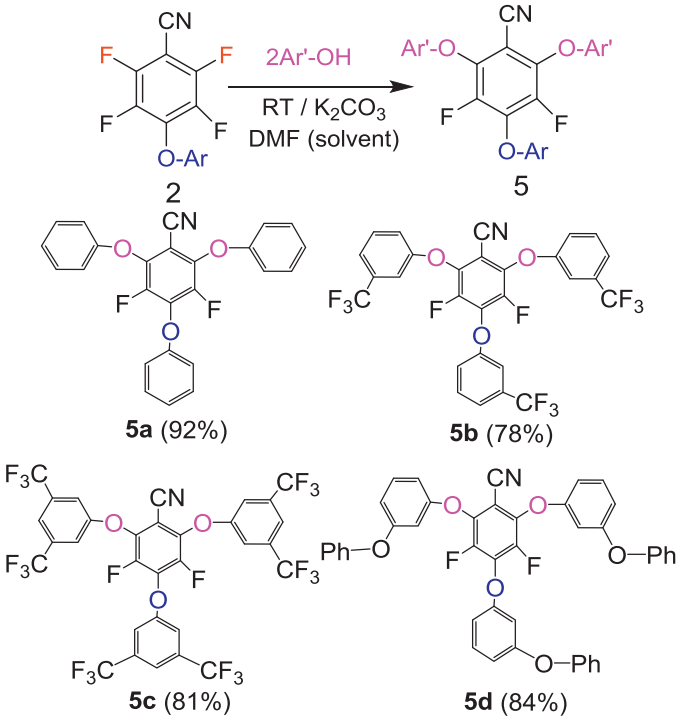
substituted with 3,5-bis(trifluoromethyl)phenoxy group yielded the arylene ether copolymers with the highest molecular weight among various substituted PTFBN [20d]. Thus the nucleophilic substitution of mono substituted PTFBN was influenced by the type of substituent present in the phenoxy moiety as well as the nature of nucleophiles. The ^{19}F NMR spectroscopic analysis of compound **3c** (Fig. S2) in Scheme 2, showed that the signal ratio of 3:1:1:1 (−62.98 ppm (3F, s), −131.26 to −131.35 ppm (1F, dd), −140.49 to −140.52 ppm (1F, d), −150.18 to −150.23 ppm (1F, d)) as expected thereby indicating the cleanliness of the reaction as well as the purity of product.

The versatility of the process can be noticed by the experiments described in subsequent sections. The remaining F atom at *ortho′* position of the diphenoxy substituted benzonitrile was displaced by several functional nucleophiles such as 2-allyl (–CH_2–CH=CH_2) phenol (Scheme 3, **4a**), 4-diazo (–N=N–) phenol (Scheme 3, **4b**), 4-vinyl (–CH=CH_2) phenol (Scheme 3, **4c**) and 4-nitro (–NO_2) phenol (Scheme 3, **4d**/**4e**). We believe that compounds similar to **4c** with four –CF_3 pendant groups would be useful for making highly fluorinated polymers and thus are capable of influencing the surface properties. The fluorine content of this polymer is about 10 wt% lower than that of pentafluoro styrene. However, the presence of pendant –CN group as well as the potential to form donor–acceptor complexes could add self assembly characteristics which may aid in the formation of super hydrophobic surfaces. Besides the various functional phenols, it was also possible to use benzoic acid as nucleophile to form ether esters (Scheme 3, **4f**/**4g**). The ^{19}F NMR spectrum of compound **4d** (Fig. S3) in Scheme 3, exhibited signals at −62.97 (3F, s), −137.47 to −137.48 (1F, d), −140.02 to −140.03 (1F, d) (signals corresponding to two *meta* fluorine atoms with equal intensity ratios) thereby confirming the formation of unsymmetrical trisubstituted product in a facile manner even with poor nucleophiles such as *p*-nitrophenoxide. The compound **4e** (Scheme 3) exhibited peaks corresponding to two *meta*-fluorine atoms as well as six fluorine atoms associated with the two –CF_3 groups [^{19}F NMR (ppm): −63.08 (3F, s), −63.22 (6F, s), −137.33 (2F, s)] (Fig. 1). Thus it is clear from the foregoing experimental results that it is convenient to form symmetrically as well as unsymmetrically substituted compounds by regioselective nucleophilic substitution involving PFBN even with poor nucleophiles.

As described above, due to the similarity in reactivity between F atoms at *ortho*, *ortho′* positions of PTFBN, obviously, it was possible to form aryl ethers with symmetrical substitution at 2,6-position (Scheme 4). The usefulness of this process can be noticed by the ability to make compounds such as 5 g, (Fig. 2) which is comparable to widely used crosslinkers such as 1,4-divinyl benzene. Because of the relatively larger size as well as due to the presence of multiple pendant groups (–CF_3) it may be possible to influence the size of void in such crosslinked structures and thereby the porosity of resulting materials. Such porous compounds have wide applications in gas separation and storage of hydrogen gas [23]. It was also possible to extend this methodology to prepare aryl ethers bearing photoactive *diazo* (–N=N–) moiety (Fig. 2, **5e**), and allyl (–CH_2–CH=CH_2) (Fig. 2, **5f**), functionality. Thus this is a facile approach for introducing highly reactive functionalities under very mild conditions. In the same way, the



Scheme 3. Regioselective synthesis of trisubstituted difluorobenzonitrile ethers and esters.



Scheme 4. Synthesis of symmetrically substituted benzonitriles.

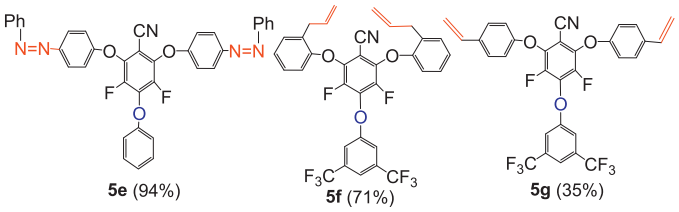


Fig. 2. Trisubstituted difluorobenzonitrile ethers containing various functional groups.

unsymmetrically trisubstituted compounds were prepared from various monohydroxy phenols such as phenol, 3-(trifluoromethyl)phenol, 3,5-bis(trifluoromethyl)phenol, and 3-phenoxyphenol and their combinations are presented in Fig. 3.

The unusual behavior of carboxyl substituted substrate for subsequent nucleophilic substitution reaction was further explored deeply in order to understand the limitation of this process. As briefly mentioned earlier, the nucleophilic substitution proceeded in a facile manner even with conjugated and thus weaker nucleophiles such as carboxylate anions (Scheme 5, compound **6**). However, the reaction did not proceed beyond the mono substitution stage either with carboxylates or phenoxides even when the reactions were attempted at high temperatures (120 °C). This may be due to the combination of reasons like disrupted planarity as well as competing reactions. Subsequently, we attempted to incorporate ester functionality into PTFBN (Scheme 6, **7a–d**). Once again, our attempts to displace both F atoms at *ortho*, *ortho*′ positions of PTFBN with two equivalents of

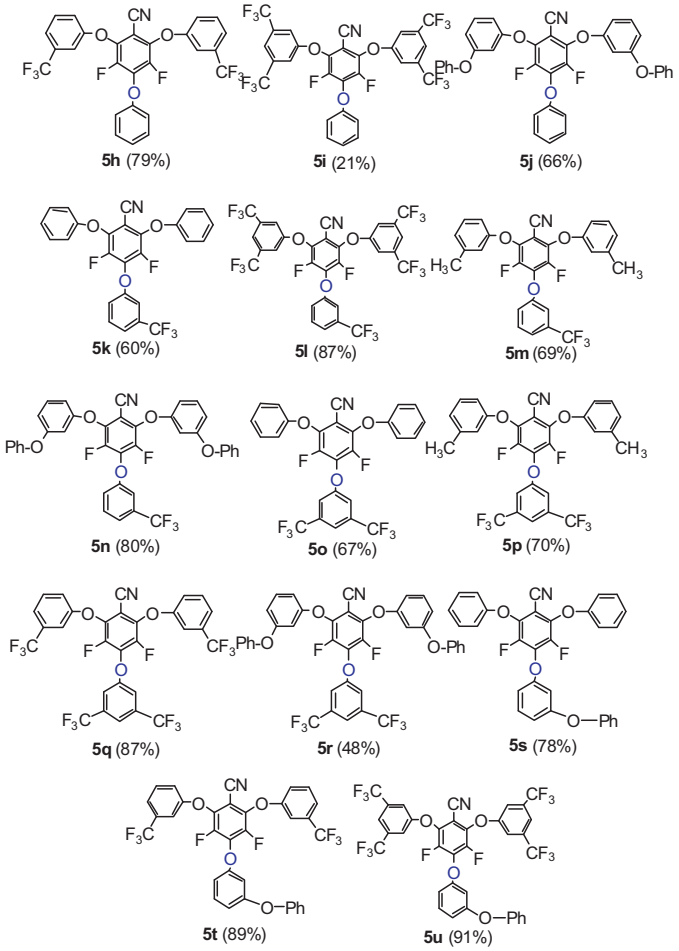
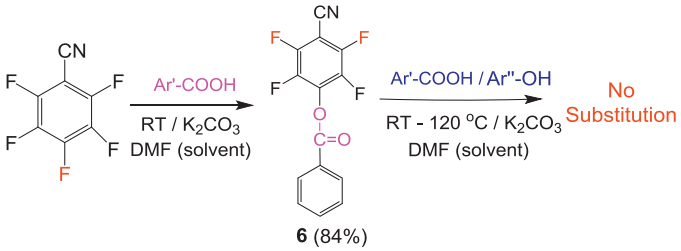
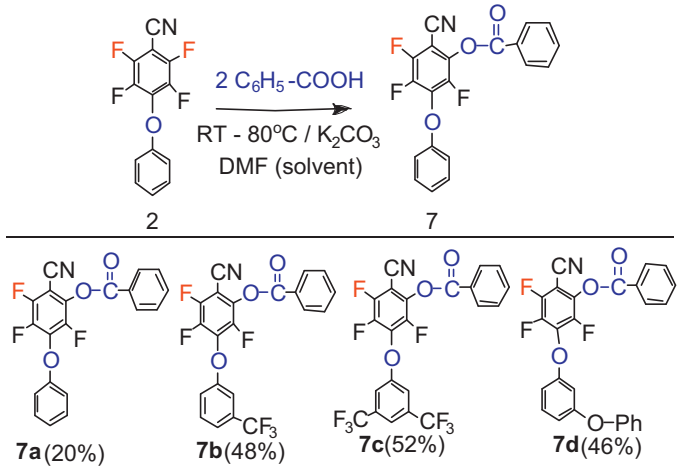


Fig. 3. Chemical structure of unsymmetrically trisubstituted benzonitrile ethers.



Scheme 5. The preparation of *para* substituted monobenzoxy tetrafluorobenzonitrile (**6**).



Scheme 6. Different monobenzoxy trifluorobenzonitriles synthesized from 4-phenoxy-2,3,5,6-tetrafluorobenzonitrile.

carboxylate yielded only the mono carboxylate substituted product even after heating the reaction mixture at 65 °C. Upon increasing the reaction temperature to 120 °C only charred mass was obtained. The above results indicate that formation of ester linkage either at the stage of mono substitution or at later stages completely suppress any further substitution reaction irrespective of the nature of nucleophile. This is most likely the result of steric effect. Unlike ether (–O–) formation with phenols, the ester (–COO–) formation likely leads to a bulkier substituted product. This increased bulkiness of carboxylates could twist electron withdrawing –CN group out of plane thereby affecting its activating ability for nucleophilic substitution. Due to this reason, the F atom at the *ortho*′ position is no longer activated for nucleophilic attack by the second carboxylate nucleophile.

Similar steric effect can be expected in the monocarboxylate product such as 4-benzoxy-2,3,5,6-tetrafluorobenzonitrile (Scheme 5, compound **6**). Here, the effect could be cascade in nature. Accordingly, the bulkiness of compound **6** could twist the two F atoms at 3,5-position which could in turn twist the two F atoms at 2,6-position thereby making the F atoms at *ortho*, *ortho*′ positions out of plane and thus rendering them unsuitable for further nucleophilic attack.

We also studied the effect of nature of substituents of phenoxy moiety with three different *para* substituents such as 4-phenoxy- (Scheme 6, **7a**), 4-phenoxy-3-(trifluoromethyl)- (Scheme 6, **7b**), 4-phenoxy-3,5-bis(trifluoromethyl)- (Scheme 6, **7c**) and 4-(m-phenoxyphenol) (Scheme 6, **7d**) for further nucleophilic substitution with carboxylates. However, there was no influence of *para* substituents to form *ortho* and *ortho*′ substituted esters. The esterification reactions yields (Scheme 6, compounds **7a–d**) were invariably lower than that of etherification reactions yields (Scheme 2, compounds **3a–d**).

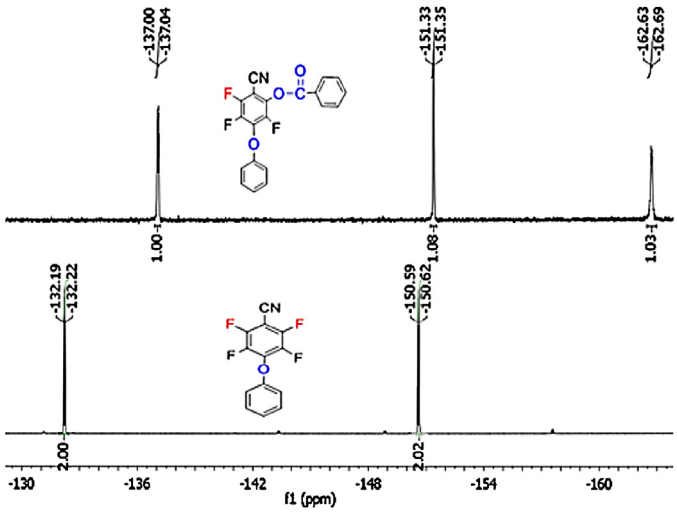


Fig. 4. Stacked ^{19}F NMR spectra of 4-phenoxy-2,3,5,6-tetra flourobenzonitrile (**2a**) and 2-cyano-3,4,6-trifluoro-5-phenoxy phenyl benzoate (**7a**).

The remaining F atom at the *ortho′* position of diphenoxy substituted benzonitrile (Scheme 2, compounds **3a–d**) could be conveniently displaced by carboxylate yielding bisaryl ether esters (Scheme 3, compounds **4f–g**). The esterfication reactions proceeded even at room temperature though the yields were moderate (45–52%). Increasing the reaction temperature (~80 °C) did not influence either the yield or further substitution. In general, barring mono esterification involving nucleophilic substitution at the *para* position, all other substitutions by carboxylate proceeded with low yields. This may be again due to the difficulty of formation of suitable transition states caused by the bulkiness which may have been induced by the conjugated nature of carboxylate anion as compared to phenoxide nucleophile (Fig. 4).

3. Conclusion

In conclusion, we have reported novel semifluorinated aryl ethers and esters prepared by step wise nucleophilic aromatic substitution reaction. We exploited this methodology to prepare several aryl ethers possessing reactive, polymerizable and photo-active functionalities. We believe this methodology is highly useful for making materials suitable for diverse variety of applications such as lubricants, super hydrophobic coatings, liquid crystals, gas separation membranes, hydrogen storage, curing agents, pigments, photosensitive materials and many others.

4. Experimental

4.1. Materials

Phenol, 4-vinylphenol (10 wt% in propylene glycol), and m-cresol were received from Sigma–Aldrich, USA. Pentafluorobenzonitrile (PFBN), 3-(trifluoromethyl)phenol, 3,5-bis(trifluoromethyl)phenol, 4-phenylazophenol, 3-phenoxyphenol and potassium carbonate were received from Alfa Aesar, USA and used without further purification. *o*-Allylphenol was purchased from Kanto Chemical Co. Inc., Japan. *N*,*N*-Dimethylformamide (DMF) was purified by Glass contour-6 solvent purification system. All other reagents were used as received.

4.2. Characterization

NMR (^1H, ^{13}C, and ^{19}F) spectra were recorded on Bruker UltraShield Avance 400 MHz NMR instrument using deuterated chloroform-d or DMSO-d_6 as a solvent at room temperature. Melting point measurement were carried out with pure samples using Buchi melting point apparatus B-450 at the heating rate of 20 °C/min. Thin layer chromatography (TLC) were performed on 0.2 mm silica gel coated plates purchased from Merck, Germany and visualization of the spots was accomplished by UV light (254 nm). Mass analyses were carried out using Agilent 1200 LC with 6210 MSD TOF (LC-TOF) instrument in negative mode electron spray ionization technique (ESI). The elemental analyses of samples were carried out using Thermo Scientific Flash 2000 CHNS/O Analyzer.

4.2.1. Synthesis of 2,3,5,6-tetrafluoro-4-[3-(trifluoromethyl) phenoxy]benzonitrile (**2b**)

In a 50 mL two-neck round bottom flask was charged with 25 mL of dry DMF followed by PFBN (1.0 mL, 8.11 mmol) and 3-(trifluoromethyl)phenol (0.986 mL, 8.11 mmol) under inert atmosphere. Potassium carbonate (1.68 g, 12.16 mmol) was added and the reaction mixture was stirred for 24 h at room temperature. After the reaction mixture was neutralized with acidified water and extracted with ether (yield: 95%). The compound was purified by column chromatography using ethylacetate/hexane to yields a pale yellow viscous liquid of 4-phenoxy-3-(trifluoromethyl)-2,3,5,6-tetrafluorobenzonitrile (yield: 86%).

^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.17–7.19 (*d*, 1H, *meta*-), 7.27 (s, 1H, *ortho*-), and 7.47–7.54 (*q*, 2H, *para*- and *ortho′*-); ^{19}F NMR (376 MHz, DMSO-d_6, δ ppm): −62.96 (3F, $-CF_3$), −131.5 (2F, *meta*-), and −150.42 (2F, *ortho*-). Anal. calcd for $C_{14}H_4F_7NO$: C, 50.17; H, 1.20; N, 4.18; Found: C, 50.60; H, 1.05; N, 4.30.

4.2.2. Synthesis of 3-[3,5-bis(trifluoromethyl)phenoxy]-6-cyano-2,4,5-trifluorophenyl benzoate (**7c**)

In a 50 mL two-neck round bottom flask containing 25 mL of dry DMF was charged with purified sample of 4-[3,5-bis(trifluoromethyl)phenoxy]-2,3,5,6-tetrafluorobenzonitrile (400 mg, 0.99 mmol) and two equivalents of benzoic acid (242 mg, 1.98 mmol) followed by potassium carbonate (411 mg, 2.97 mmol) and the reaction was continued 24 h at room temperature. The reaction mixture was neutralized with acidified water and extracted with ethyl acetate yields 64%. The compound was purified by column chromatography using ethyl acetate/hexane mixture yields brownish color solid of 3-[3,5-bis(trifluoromethyl)-phenoxy]-6-cyano-2,4,5-trifluorophenyl benzoate (yield: 52%).

^1H NMR (400 MHz, DMSO-d_6, δ ppm): 7.86 (2H, s), 7.90 (2H, s), 7.93–7.98 (4H, m); ^{19}F NMR (376 MHz, DMSO-d_6, δ ppm): −61.60 (6F, s), −137.18 to −137.26 (1F, m), −152.06 (1F, b), −165.44 (1F, b). ESI-TOF MS for $C_{22}H_8F_9NO_3$: Calcd: 505.28; found: 400.01 ($M-CO-C_6H_5$).

4.3. Spectroscopic data of new compounds

4.3.1. Compound **2a**. 2,3,5,6-tetrafluoro-4-phenoxybenzonitrile

Yield: 85% as white solid; mp: 63.5–66.6 °C; ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.92–6.94 (2H, d), 7.11–7.15 (1H, m), 7.28–7.32 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 107.45, 116.35, 125.15, 130.32, 147.13, 148.05, 149.59, 156.61; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −133.16 to −132.26 (2F, m), −150.56 to −150.66 (2F, m). Anal. calcd for $C_{13}H_5F_4NO$: C, 58.44; H, 1.89; N, 5.24; found: C, 58.40; H, 1.81; N, 5.01. ESI-TOF MS for $C_{13}H_5F_4NO$: Calcd: 267.03; found: 264.02 (M−3H).

4.3.2. Compound **2b**. 2,3,5,6-tetrafluoro-4-[3-(trifluoromethyl)phenoxy] benzonitrile

Yield: 86% as colorless viscous liquid. ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.18–7.2 (1H, d), 7.28 (1H, s), 7.48–7.54 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 107.22, 109.81, 113.72, 119.55, 122.01,

131.06, 140.35, 142.80, 147.16, 149.77, 156.47; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): 62.96 (3F, s), −131.30 to −131.40 (2F, m), −150.20 to −150.31(2F, m). Anal. calcd for $C_{14}H_4F_7NO$: C, 50.17; H, 1.20; N, 4.18; found: C, 50.60; H, 1.05; N, 4.30. ESI-TOF MS for $C_{14}H_4F_7NO$: Calcd: 335.02; found: 332.02 (M−3H).

*4.3.3. Compound **2c**. 4-[3,5-bis(trifluoromethyl)phenoxy]-2,3,5,6-tetraflourobenzonitrile*

Yield: 92% as white solid; mp: 87.3–92.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.43 (2H, s), 7.73 (1H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 106.82, 109.77, 116.89, 119.11, 121.32, 123.14, 124.10, 134.11–134.41, 140.29, 156.59; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): 63.17 (6F, s), −130.33 to −130.44 (2F, m), −149.82 to −149.92 (2F, m). Anal. calcd for $C_{15}H_3F_{10}NO$: C, 44.69; H, 0.75; N, 3.47; found: C, 44.59; H, 0.82; N, 3.47. ESI-TOF MS for $C_{15}H_3F_{10}NO$: Calcd: 403.01; found: 400.00 (M−3H).

*4.3.4. Compound **2d**. 2,3,5,6-tetrafluoro-4-(3-phenoxyphenoxy)benzo-nitrile*

Yield: 87% as viscous liquid. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.69–6.71 (2H, b), 6.80–6.83 (1H, b), 7.04–7.06 (2H, d), 7.16–7.20 (1H, t), 7.28–7.32 (1H, m), 7.37–7.41 (2H, t); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 107.06, 107.38, 110.41, 114.80, 119.71, 124.44, 130.22, 131.00, 156.34, 157.54, 159.23; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −131.95 to −132.06 (2F, m), −150.44 to −150.54 (2F, m); Anal. calcd for $C_{19}H_9F_4NO_2$: C, 63.52; H, 2.52; N, 3.90; found: C, 63.54; H, 2.65; N, 3.95. ESI-TOF MS for $C_{19}H_9F_4NO_2$: Calcd: 359.06; found: 356.09 (M−3H).

*4.3.5. Compound **3a**. 4-[3,5-bis(trifluoromethyl)phenoxy]-2,3,5-trifluoro-6-phenoxybenzonitrile*

Yield: 83% as white sticky solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.97–6.99 (2H, d), 7.16–7.2 (1H, t), 7.34–7.38 (2H, t), 7.41 (2H, s), 7.70 (1H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −62.30 (6F, s), −130.34 to −130.42 (1F, dd), −139.93 to −139.96 (1F, d), −150.12 to −150.18 (1F, d). Anal. calcd for $C_{21}H_8F_9NO_2$: C, 52.85; H, 1.69; N, 2.93; found: C, 52.23; H, 1.64; N, 3.02. ESI-TOF MS for $C_{21}H_8F_9NO_2$: Calcd: 477.04; found: 474.03 (M−3H).

*4.3.6. Compound **3b**. 4-[3,5-bis(trifluoromethyl)phenoxy]-2,3,5-trifluoro-6-[3-(trifluoromethyl)phenoxy]benzonitrile*

Yield: 71% as white sticky solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.16–7.18 (1H, d), 7.23 (1H, s), 7.42 (2H, s), 7.47–7.51 (2H, t), 7.71 (1H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.05 (3F, s), −63.23 (6F, s), −129.42 to −129.50 (1F, dd), −139.99 to −140.02 (1F, d), −148.53 to −148.58 (1F, d). Anal. calcd for $C_{22}H_7F_{12}NO_2$: C, 48.46; H, 1.29; N, 2.57; found: C, 48.94; H, 1.63; N, 2.68. ESI-TOF MS for $C_{22}H_7F_{12}NO_2$: Calcd: 545.03; found: 542.02 (M−3H), 590.02 (M+2Na-H).

*4.3.7. Compound **3c**. 2,3,5-trifluoro-6-phenoxy-4-[3-(trifluoromethyl)-phenoxy]benzonitrile*

Yield: 82% as sticky solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.96–6.98 (2H, d), 7.14–7.18 (2H, m), 7.22 (1H, s), 7.33–7.35 (2H, t), 7.42–7.44 (1H, d), 7.47–7.50 (1H, t); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): 62.98 (3F, s), −131.26 to −131.35 (1F, dd), −140.49 to −140.52 (1F, d), −150.18 to −150.23 (1F, d). Anal. calcd for $C_{20}H_9F_6NO_2$: C, 58.69; H, 2.22; N, 3.42; found: C, 58.45; H, 2.55; N, 3.59. ESI-TOF MS for $C_{20}H_9F_6NO_2$: Calcd: 409.05; found: 454.05 (M+2Na-H).

*4.3.8. Compound **3d**. 2-[3,5-bis(trifluoromethyl)phenoxy]-3,5,6-trifluoro-4-[3-(trifluoromethyl)phenoxy]benzonitrile*

Yield: 95% as sticky solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.17–7.18 (1H, m), 7.27 (1H, s), 7.40–7.51 (4H, m), 7.71 (1H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.08 (3F, s), −63.25 (6F, s), −129.39 to −129.48 (1F, dd), −139.94 to −139.97 (1F, d), −147.34 to −147.40 (1F, d). Anal. calcd for $C_{22}H_7F_{12}NO_2$: C, 48.46; H, 1.29; N, 2.57; found: C, 48.62; H, 1.15; N, 2.66. ESI-TOF MS for $C_{22}H_7F_{12}NO_2$: Calcd: 545.03; found: 542.03 (M−3H).

*4.3.9. Compound **4a**. 4-[3,5-bis(trifluoromethyl)phenoxy]-3,5-difluoro-2-[2-(prop-2-en-1-yl)phenoxy]-6-[3-(trifluoromethyl)phenoxy]-benzonitrile*

Yield: 45% as sticky solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.50–3.52 (1H, d), 3.57–3.58 (1H, s), 5.04–5.12 (2H, m), 5.97–6.06 (1H, m), 6.66–6.68 (1H, m), 7.10–7.28 (6H, m), 7.39–7.51 (3H, m), 7.67 (1H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.01 (3F, s), −63.26 (6F, s), −139.04 (1F, s), −140.59 (1F, s). Anal. calcd for $C_{31}H_{16}F_{11}NO_3$: C, 56.46; H, 2.45; N, 2.12; found: C, 56.63; H, 2.53; N, 2.32. ESI-TOF MS for $C_{31}H_{16}F_{11}NO_3$: Calcd: 659.10; found: 704.09 (M+2Na-H).

*4.3.10. Compound **4b**. 4-[3,5-bis(trifluoromethyl)phenoxy]-3,5-difluoro-2-[4-(2-phenyldiazen-1-yl)phenoxy]-6-[3-(trifluoromethyl)phen-oxy]benzonitrile*

Yield: 52% as yellow solid; mp: 130.1–132.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.13–7.16 (2H, d), 7.26 (1H, s), 7.28 (1H, s), 7.41 (2H, s), 7.47–7.54 (5H, m), 7.69 (1H, s), 7.90–7.91 (2H, d), 7.96–7.99 (2H, d); ^{19}F NMR (376 MHz, $CDCl_3$, δppm): −63.00 (3F, s), −63.22 (6F, s),-138.34 (1F, s), −139.12 (1F, s). Anal. calcd for $C_{34}H_{16}F_{11}N_3O_3$: C, 56.44; H, 2.23; N, 5.81; found: C, 57.00; H, 2.77; N, 5.97. ESI-TOF MS for $C_{34}H_{16}F_{11}N_3O_3$: Calcd: 723.10; found: 768.09 (M+2Na-H).

*4.3.11. Compound **4c**. 2-(4-ethenylphenoxy)-3,5-difluoro-6-phenoxy-4-[3-(triflouromethyl)phenoxy]benzonitrile*

Yield: 33% as white solid; mp: 112.4–115.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 5.21–5.24 (1H, d), 5.65–5.70 (1H, d), 6.64–6.71 (1H, dd), 6.95–7.02 (4H, m), 7.15–7.18 (3H, m), 7.20 (1H, s), 7.34–7.41 (4H, m), 7.43–7.51 (1H, t) ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −62.94 (3F, s), −139.88 to −139.88 (1F, d), −140.06 to −140.07 (1F, d). Anal. calcd for $C_{28}H_{16}F_5NO_3$: C, 66.02; H, 3.17; N, 2.75; found: C, 66.58; H, 3.30; N, 3.03. ESI-TOF MS for $C_{28}H_{16}F_5NO_3$: Calcd: 509.11; found: 554.10 (M+2Na-H).

*4.3.12. Compound **4d**. 3,5-difluoro-2-(4-nitrophenoxy)-6-phenoxy-4-[3-(triflouromethyl)phenoxy]benzonitrile*

Yield: 72% as white sticky solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.97–6.99 (3H, d), 7.14–7.18 (3H, m), 7.23 (1H, s), 7.33–7.37 (3H, t), 7.43–7.51 (3H, m); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −62.97 (3F, s), −137.47 to −137.48 (1F, d), −140.02 to −140.03 (1F, d); Anal. calcd for $C_{26}H_{13}F_5N_2O_5$: C, 59.10; H, 2.48; N, 5.30; found: C, 59.25; H, 2.20; N, 5.68. ESI-TOF MS for $C_{26}H_{13}F_5N_2O_5$: Calcd: 528.38; found: 528.38.

*4.3.13. Compound **4e**. 2-[3,5-bis(trifluoromethyl)phenoxy]-3,5-difluoro-6-(4-nitrophenoxy)-4-[3-(trifluoromethyl)phenoxy]benzonitrile*

Yield: 68% as white solid; mp: 110.5–114.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.10–7.13 (4H, dd), 7.22 (1H, s), 7.44–7.46 (1H, d), 7.49–7.52 (1H, t), 8.26–8.29 (4H, dd); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.08 (3F, s), −63.22 (6F, s), −137.33 (2F, s). Anal. calcd for $C_{28}H_{11}F_{11}N_2O_5$: C, 50.62; H, 1.67; N, 4.22; found: C, 50.88; H, 1.97; N, 4.56. ESI-TOF MS for $C_{28}H_{11}F_{11}N_2O_5$: Calcd: 664.05; found: 709.05 (M+2Na-H).

*4.3.14. Compound **4f**. 3-[3,5-bis(trifluoromethyl)phenoxy]-6-cyano-2,4-difluoro-5-[3-(trifluoromethyl)phenoxy]phenylbenzoate*

Yield: 44% as white sticky solid; ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 7.43–7.47 (5H, m), 7.55–7.57 (2H, t), 7.79 (3H, s), 7.81 (2H, s); ^{19}F NMR (376 MHz, DMSO-d_6, δ ppm): −61.50 (3F, s), −61.68 (6F, s), −152.00 (2F, s). Anal. calcd for $C_{29}H_{12}F_{11}NO_4$: C, 53.80; H,

1.87; N, 2.16; found: C, 53.31; H, 2.20; N, 2.64. ESI-TOF MS for $C_{29}H_{12}F_{11}NO_4$: Calcd: 647.06; found: 542.02 (M−CO-C_6H_5).

*4.3.15. Compound **4g**. 3-[3,5-bis(trifluoromethyl)phenoxy]-2-cyano-4,6-difluoro-5-[3-(trifluoromethyl)phenoxy]phenylbenzoate*

Yield: 52% as white sticky solid; ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 7.02–7.04 (1H, d), 7.13 (2H, s), 7.33–7.37 (7H, m), 7.59 (2H, s); ^{19}F NMR (376 MHz, DMSO-d_6, δ ppm): −61.47 (3F, s), −61.63 (6F, s), −152.17 (2F, s). Anal. calcd for $C_{29}H_{12}F_{11}NO_4$: C, 53.80; H, 1.87; N, 2.16; found: C, 53.21; H, 2.32; N, 2.81. ESI-TOF MS for $C_{29}H_{12}F_{11}NO_4$: Calcd: 647.06; found: 542.02 (M−CO-C_6H_5).

*4.3.16. Compound **5a**. 3,5-difluoro-2,4,6-triphenoxybenzonitrile*

Yield: 92% as white solid; mp: 125.1–130.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.95–7.00 (6H, t), 7.10–7.15 (3H, m), 7.31–7.36 (6H, m); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): 140.19 (2F, s). Anal. calcd for $C_{25}H_{15}F_2NO_3$: C, 72.29; H, 3.64; N, 3.37. Found: C, 72.38; H, 3.59; N, 3.42. Anal. calcd for $C_{25}H_{15}F_2NO_3$: C, 72.29; H, 3.64; N, 3.37; found: C, 72.11; H, 3.93; N, 3.80. ESI-TOF MS for $C_{25}H_{15}F_2NO_3$: Calcd: 415.38; found: 415.39.

*4.3.17. Compound **5b**. 3,5-difluoro-2,4,6-tris[3-(trifluoromethyl)phen-oxy]benzonitrile*

Yield: 78% as white solid; mp: 110.5–113.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.11–7.22 (6H, m), 7.39–7.44 (3H, m), 7.46–7.50 (3H, t); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 109.76–109.83, 113.09–113.28, 119.13, 119.36, 121.45–121.63, 122.08, 122.64, 124.79, 130.34, 132.70, 133.02, 145.03–145.06, 147.58–147.62, 156.55, 156.76, 159.23; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −62.98 (6F, s), −63.05 (3F, s), −138.62 (2F, s). Anal. calcd for $C_{28}H_{12}F_{11}NO_3$: C, 54.30; H, 1.95; N, 2.26; found: C, 54.52; H, 2.35; N, 2.21. ESI-TOF MS for $C_{28}H_{12}F_{11}NO_3$: Calcd: 619.06; found: 664.07 (M+2Na-H).

*4.3.18. Compound **5c**. 2,4,6-tris[3,5-bis(trifluoromethyl)phenoxy]-3,5-diflourobenzonitrile*

Yield: 81% as pale yellow solid; mp: 154.0–160.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.42 (3H, s), 7.45 (6H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.27 (12F, s), −63.35 (6F, s), −137.40 (2F, s). Anal. calcd for $C_{31}H_9F_{20}NO_3$: C, 45.22; H, 1.10; N, 1.70; found: C, 45.55; H, 1.46; N, 1.62. ESI-TOF MS for $C_{31}H_9F_{20}NO_3$: Calcd: 823.03; found: 868.02 (M+2Na-H).

*4.3.19. Compound **5d**. 3,5-difluoro-2,4,6-tris(3-phenoxyphenoxy)benzo-nitrile*

Yield: 84% as colorless viscous liquid; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.60–6.65 (6H, m), 6.72–6.76 (3H, m), 7.00–7.05 (6H, m), 7.12–7.16 (3H, m), 7.23–7.26 (3H, ss), 7.33–7.37 (6H, t); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −139.91 (2F, s). Anal. calcd for $C_{43}H_{27}F_2NO_6$: C, 74.67; H, 3.93; N, 2.03; found: C, 74.40; H, 4.08; N, 2.04. ESI-TOF MS for $C_{43}H_{27}F_2NO_6$: Calcd: 691.18; found: 736.17 (M+2Na-H).

*4.3.20. Compound **5e**. 3,5-difluoro-4-phenoxy-2,6-bis[4-(2-phenyl-diazen-1-yl)phenoxy]benzonitrile*

Yield: 94% as yellow solid; mp: 169.8–175.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.84–6.90 (1H, d), 6.99–7.01 (2H, d), 7.10–7.16 (4H, m), 7.32–7.36 (2H, t), 7.44–7.52 (6H, m), 7.89–7.90 (4H, d), 7.95–7.97 (4H, d); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −139.12 (2F, s). Anal. calcd for $C_{37}H_{23}F_2N_5O_3$: C, 71.26; H, 3.72; N, 11.23; found: C, 71.27; H, 3.68; N, 11.08. ESI-TOF MS for $C_{37}H_{23}F_2N_5O_3$: Calcd: 623.18; found: 668.17 (M+2Na-H).

*4.3.21. Compound **5f**. 4-[3,5-bis(trifluoromethyl)phenoxy]-3,5-difluoro-2,6-bis[2-(prop-2-en-1-yl)phenoxy]benzonitrile*

Yield: 71% as white solid; mp: 80.6–85.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 3.57–3.58 (4H, d), 5.09–5.11 (4H, t), 5.98–6.08 (2H, m), 6.65–6.67 (2H, d), 7.11–7.13 (2H, m), 7.16–7.19 (2H, m), 7.26–7.29 (2H, t), 7.37 (2H, s), 7.68 (1H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.22 (6F, s), −140.85 (2F, s). Anal. calcd for $C_{33}H_{21}F_8NO_3$: C, 62.76; H, 3.35; N, 2.22; found: C, 62.46; H, 3.57; N, 2.53. ESI-TOF MS for: $C_{33}H_{21}F_8NO_3$: Calcd: 631.14; found: 676.13 (M+2Na-H).

*4.3.22. Compound **5g**. 4-[3,5-bis(trifluoromethyl)phenoxy]-2,6-bis(4-ethenyl-phenoxy)-3,5-difluorobenzonitrile*

Yield: 35% as white solid; mp: 131.2–135.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 5.22–5.25 (2H, d), 5.66–5.70 (2H, dd), 6.64–6.71 (2H, dd), 6.95–6.97 (4H, d), 7.38–7.41 (6H, m), 7.67 (1H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.20 (6F, s), −139.75 (2F, s). Anal. calcd for $C_{31}H_{17}F_8NO_3$: C, 61.70; H, 2.84; N, 2.32; found: C, 62.04; H, 3.39; N, 2.64. ESI-TOF MS for $C_{31}H_{17}F_8NO_3$: Calcd: 603.11; found: 648.10 (M+2Na-H).

*4.3.23. Compound **5h**. 3,5-difluoro-4-phenoxy-2,6-bis[3-(trifluoro methyl)phenoxy]benzonitrile*

Yield: 79% as white solid; mp: 114.9–119.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.96–6.98 (2H, d), 7.13–7.22 (5H, m), 7.31–7.36 (2H, m), 7.41–7.43 (2H, d), 7.47–7.51 (2H, t); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −62.95 (6F, s), −138.64 (2F, s). Anal. calcd for $C_{27}H_{13}F_8NO_3$: C, 58.81; H, 2.38; N, 2.54; found: C, 59.40; H, 2.72; N, 2.58. ESI-TOF MS for $C_{27}H_{13}F_8NO_3$: Calcd: 551.08; found: 596.07 (M+2Na-H).

*4.3.24. Compound **5i**. 2,6-bis[3,5-bis(trifluoromethyl)phenoxy]-3,5-di-fluoro-4-phenoxybenzonitrile*

Yield: 21% as white solid; mp: 138.5–143.1 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.98–7.00 (2H, d), 7.16–7.20 (1H, t), 7.34–7.38 (2H, t), 7.43 (4H, s), 7.70 (2H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.21 (12F, s), −137.04 (2F, s). Anal. calcd for $C_{29}H_{11}F_{14}NO_3$: C, 50.67; H, 1.61; N, 2.04; found: C, 50.96; H, 1.73; N, 2.03. ESI-TOF MS for $C_{29}H_{11}F_{14}NO_3$: Calcd: 687.05; found: 732.05 (M+2Na-H).

*4.3.25. Compound **5j**. 3,5-difluoro-4-phenoxy-2,6-bis(3-phenoxyphen-oxy)benzonitrile*

Yield: 66% as colorless sticky solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.60–6.67 (4H, m), 6.73–6.76 (2H, d), 6.93–6.95 (2H, d), 7.00–7.04 (4H, d), 7.21–7.15 (3H, t), 7.21–7.28 (3H, m), 7.32–7.37 (5H, m); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −139.85 (2F, s). Anal. calcd for $C_{37}H_{23}F_2NO_5$: C, 74.12; H, 3.87; N, 2.34; found: C, 73.82; H, 4.05; N, 2.73. ESI-TOF MS for $C_{37}H_{23}F_2NO_5$: Calcd: 599.15; found: 644.15 (M+2Na-H).

*4.3.26. Compound **5k**. 3,5-difluoro-2,6-diphenoxy-4-[3-(trifluoromethyl) phenoxy]benzonitrile*

Yield: 60% as white solid; mp: 131.4–133.8 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.91–6.93 (4H, d), 7.04–7.08 (3H, t), 7.11 (1H, s), 7.25–7.32 (5H, m), 7.35–7.39 (1H, t); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 101.60, 110.40–110.44, 111.19, 112.94–113.05, 116.21, 119.35, 121.28–121.39, 124.60, 130.26, 130.95, 132.61, 132.94, 137.98–138.24, 142.83–142.99, 144.97–145, 147.52–147.55, 156.81, 157.14, 159.23; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −62.94 (3F, s), −140.00 (2F, s). Anal. calcd for $C_{26}H_{14}F_5NO_3$: C, 64.60; H, 2.92; N, 2.90; found: C, 64.52; H, 2.83; N, 2.72. ESI-TOF MS for $C_{26}H_{14}F_5NO_3$: Calcd: 483.09; found: 528.08 (M+2Na-H).

*4.3.27. Compound **5l**. 2,6-bis[3,5-bis(trifluoromethyl)phenoxy]-3,5-difluoro-4-[3-(trifluoromethyl)phenoxy]benzonitrile*

Yield: 87% as white solid; mp: 156.8–159.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.34–7.38 (3H, t), 7.43–7.47 (1H, t), 7.71 (2H, s), 7.75 (4H, s); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 113.59–113.63, 117.83–117.86, 118.89–119.04, 120.55, 122.20, 122.45, 125.14, 132.32, 134.03, 134.37, 146.70, 149.26, 158.43; ^{19}F NMR

(376 MHz, $CDCl_3$, δ ppm): −63.38 (3F, s), −63.45 (12F, s), −141.33 (2F, s). Anal. calcd for $C_{30}H_{10}F_{17}NO_3$: C, 47.70; H, 1.33; N, 1.85; found: C, 47.69; H, 0.89; N, 1.85. ESI-TOF MS for $C_{30}H_{10}F_{17}NO_3$: Calcd: 755.04; found: 800.03 (M+2Na-H).

*4.3.28. Compound **5m**. 3,5-difluoro-2,6-bis(3-methylphenoxy)-4-[3-(tri-fluoromethyl)phenoxy]benzonitrile*

Yield: 69% as white solid; mp: 107.0–110.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.35 (6H, s), 6.76–6.78 (2H, dd), 6.82 (2H, s), 6.95–6.98 (2H, d), 7.15 7.45–7.49 (1H, d), 7.20–7.26 (4H, m), 7.39–7.41 (1H, d); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 21.66, 101.74, 110.51, 113.01, 116.91, 119.41, 121.29–121.31, 125.39, 129.90, 130.94, 142.82–143.07, 145.01, 147.52, 156.89, 157.18; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −62.96 (3F, s), −140.26 (2F, s). Anal. calcd for $C_{28}H_{18}F_5NO_3$: C, 65.76; H, 3.55; N, 2.74; found: C, 65.38; H, 3.76; N, 2.69. ESI-TOF MS for $C_{28}H_{18}F_5NO_3$: Calcd: 511.12; found: 556.12 (M+2Na-H).

*4.3.29. Compound **5n**. 3,5-difluoro-2,6-bis(3-phenoxyphenoxy)-4-[3-(tri fluoromethyl)phenoxy]benzonitrile*

Yield: 80% as white solid; mp: 76.4–87.3 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.64–6.67 (3H, m), 6.74–6.77 (2H, m), 7.04–7.06 (3H, m), 7.12–7.16 (2H, t), 7.22–7.92 (4H, m), 7.33–7.38 (6H, t), 7.40–7.47 (2H, m); ^{13}C NMR ($CDCl_3$, 100 MHz, δ): 106.98, 110.31, 111.84, 113.36, 114.34, 119.17, 119.71, 121.38–121.53, 124.28, 130.18, 130.96, 156.47, 158.08, 159.27; ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −62.94 (3F, s), −139.71 (2F, s). Anal. calcd for $C_{38}H_{22}F_5NO_5$: C, 68.37; H, 3.32; N, 2.10; found: C, 68.75; H, 3.15; N, 2.12. ESI-TOF MS for $C_{38}H_{22}F_5NO_5$: Calcd: 667.14; found: 712.14 (M+2Na-H).

*4.3.30. Compound **5o**. 4-[3,5-bis(trifluoromethyl)phenoxy]-3,5-difluoro-2,6-diphenoxybenzonitrile*

Yield: 67% as white solid; mp: 101.4–104.7 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.00–7.02 (4H, d), 7.15–7.19 (2H, t), 7.35–7.39 (6H, m), 7.66 (1H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.21 (6F, s), −139.81(2F, s) Anal. calcd for $C_{27}H_{13}F_8NO_3$: C, 58.81; H, 2.38; N, 2.54; found: C, 59.00; H, 2.66; N, 2.59. ESI-TOF MS for $C_{27}H_{13}F_8NO_3$: Calcd: 551.08; found: 596.08 (M+2Na-H).

*4.3.31. Compound **5p**. 4-[3,5-bis(trifluoromethyl)phenoxy]-3,5-difluoro-2,6-bis(3-methylphenoxy)benzonitrile*

Yield: 70% as white solid; mp: 111.9–117.0 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 2.35 (6H, s), 6.77–6.82 (4H, t), 6.96–6.98 (2H, d), 7.21–7.26 (2H, t), 7.38 (2H, s), 7.66 (1H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.30 (6F, s), −137.11 (1F, s), −138.90 (1F, s). Anal. calcd for $C_{29}H_{17}F_8NO_3$: C, 60.11; H, 2.96; N, 2.42; found: C, 59.93; H, 2.47; N, 3.02. ESI-TOF MS for $C_{29}H_{17}F_8NO_3$: Calcd: 579.11; found: 642.11 (M+2Na-H).

*4.3.32. Compound **5q**. 4-[3,5-bis(trifluoromethyl)phenoxy]-3,5-difluoro-2,6-bis[3-(trifluoromethyl)phenoxy]benzonitrile*

Yield: 87% as white sticky solid; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.19–7.22 (1H, m), 7.25–7.27 (3H, m), 7.41 (2H, s), 7.45 (2H, s), 7.47–7.55 (2H, m), 7.71–7.72 (1H, d); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.21 (6F, s), −63.30 (6F, s), −140.17(2F, s). Anal. calcd for $C_{29}H_{11}F_{14}NO_3$: C, 50.67; H, 1.61; N, 2.04; found: C, 50.70; H, 1.74; N, 2.21. ESI-TOF MS for $C_{29}H_{11}F_{14}NO_3$: Calcd: 687.05; found: 732.05 (M+2Na-H).

*4.3.33. Compound **5r**. 4-[3,5-bis(trifluoromethyl)phenoxy]-3,5-difluoro-2,6-bis(3-phenoxyphenoxy)benzonitrile*

Yield: 48% as white solid; mp: 84.7–89.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.63–6.66 (2H, dd), 6.69 (2H, b), 6.75–6.78 (2H, dd), 7.03–7.05 (4H, d), 7.13–7.16 (2H, t), 7.25–7.29 (2H, t), 7.34–7.38 (6H, m), 7.66 (1H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.16 (6F, s), −139.57(2F, s). Anal. calcd for $C_{39}H_{21}F_8NO_5$: C, 63.68; H, 2.88; N, 1.90; found: C, 63.17; H, 3.12; N, 1.95. ESI-TOF MS for $C_{39}H_{21}F_8NO_5$: Calcd: 735.13; found: 780.13 (M+2Na-H).

*4.3.34. Compound **5s**. 3,5-difluoro-2,6-diphenoxy-4-(3-phenoxyphenoxy) benzonitrile*

Yield: 78% as white solid; mp: 116.4–120.5 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.64–6.68 (2H, m), 6.73–6.75 (1H, dd), 6.97–7.03 (6H, m), 7.13–7.17 (3H, m), 7.24–7.28 (1H, dd), 7.33–7.38 (6H, m); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −140.23 (2F, s). Anal. calcd for $C_{31}H_{19}F_2NO_4$: C, 73.37; H, 3.77; N, 2.76; found: C, 73.42; H, 3.58; N, 2.80. ESI-TOF MS for $C_{31}H_{19}F_2NO_4$: Calcd: 507.13; found: 552.13 (M+2Na-H).

*4.3.35. Compound **5t**. 3,5-difluoro-4-(3-phenoxyphenoxy)-2,6-bis[3-(trifluoromethyl)phenoxy]benzonitrile*

Yield: 89% as white solid; mp: 107.9–110.2 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.62–6.68 (2H, m), 6.73–6.75 (2H, dd) 7.00–7.02 (2H, d), 7.13–7.17 (3H, m), 7.23–7.25 (2H, m), 7.33–7.37 (2H, t), 7.42–7.44 (2H, d), 7.47–7.51 (2H, t); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −62.94 (6F, s), −138.73 (2F, s). Anal. calcd for $C_{33}H_{17}F_8NO_4$: C, 61.60; H, 2.66; N, 2.18; found: C, 61.69; H, 2.70; N, 2.16. ESI-TOF MS for $C_{33}H_{17}F_8NO_4$: Calcd: 643.10; found: 688.10 (M+2Na-H).

*4.3.36. Compound **5u**. 2,6-bis[3,5-bis(trifluoromethyl)phenoxy]-3,5-di-fluoro-4-(3-phenoxyphenoxy)benzonitrile*

Yield: 91% as white solid; mp: 103.4–106.4 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 6.60–6.63 (1H, m), 6.71–6.72 (1H, t), 6.75–6.78 (1H, dd), 7.01–7.03 (2H, m), 7.14–7.18 (1H, t), 7.26 (1H, s), 7.34–7.38 (2H, m), 7.43 (4H, s), 7.71 (2H, s); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −63.19 (12F, s), −137.20 (2F, s). Anal. calcd for $C_{35}H_{15}F_{14}NO_4$: C, 53.93; H, 1.94; N, 1.80; found: C, 54.32; H, 2.28; N, 1.80. ESI-TOF MS for $C_{35}H_{15}F_{14}NO_4$: Calcd: 779.08; found: 824.07 (M+2Na-H).

*4.3.37. Compound **6**. 4-cyano-2,3,5,6-tetrafluorophenyl benzoate*

Yield: 84% as off-white solid; mp: 132.4–138.6 °C; ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 7.47–7.51 (2H, t), 7.61–7.65 (1H, t), 7.61–7.65 (2H, t); ^{19}F NMR (376 MHz, $CDCl_3$, δ ppm): −134.24 to −134.36 (2F, m), −159.71 to −159.84 (2F, m). Anal. calcd for $C_{14}H_5F_4NO_2$: C, 56.96; H, 1.71; N, 4.75; found: C, 57.20; H, 1.78; N, 4.98. ESI-TOF MS for $C_{14}H_5F_4NO_2$: Calcd: 297.04; found: 191.77 (M−CO-C_6H_5).

*4.3.38. Compound **7a**. 2-cyano-3,4,6-trifluoro-5-phenoxyphenylbenzoate*

Yield: 20% as off-white solid; mp: 175.7–180.2 °C; ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 7.11–7.18 (6H, m), 7.37–7.41(4H, t); ^{19}F NMR (376 MHz, DMSO-d_6, δ ppm): −136.98 to −137.06 (1F, dd), −151.33 to −151.35 (1F, d), −162.63 to −162.69 (1F, d). Anal. calcd for $C_{20}H_{10}F_3NO_3$: C, 65.05; H, 2.73; N, 3.79; found: C, 65.88; H, 2.83; N, 3.58. ESI-TOF MS for $C_{20}H_{10}F_3NO_3$: Calcd: 369.29; found: 264.02 (M−CO-C_6H_5).

*4.3.39. Compound **7b**. 2-cyano-3,4,6-trifluoro-5-[3-(trifluoromethyl) phenoxy]phenylbenzoate*

Yield: 48% as pale brownish solid; mp: 112.8–124.3 °C; ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 7.4–7.51 (3H, m), 7.54–7.57 (4H, m), 7.61–7.65 (2H, m); ^{19}F NMR (376 MHz, DMSO-d_6, δ ppm): −61.25 (3F, s), −136.59 to −136.68 (1F, dd), −151.20 to −151.24 (1F, dd), −162.46 to −162.51 (1F, d). Anal. calcd for $C_{21}H_9F_6NO_3$: C, 57.68; H, 2.07; N, 3.20; found: C, 57.10; H, 1.90; N, 3.29. ESI-TOF MS for $C_{21}H_9F_6NO_3$; Calcd: 437.29; found: 332.01(M−CO-C_6H_5).

*4.3.40. Compound **7c**. 3-[3,5-bis(trifluoromethyl)phenoxy]-6-cyano-2,4,5-triflourophenylbenzoate*

Yield: 52% as brownish solid; mp: 161.0–171.9 °C; ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 7.86 (2H, s), 7.90 (2H, s), 7.93–7.98 (4H, m); ^{19}F NMR (376 MHz, DMSO-d_6, δ ppm): −61.60 (6F, s), −137.18 to −137.26 (1F, m), −152.06 (1F, b), −165.44 (1F, b). Anal. calcd for $C_{22}H_8F_9NO_3$: C, 52.29; H, 1.60; N, 2.77; found: C, 52.20; H, 2.08; N, 2.98. ESI-TOF MS for $C_{22}H_8F_9NO_3$: Calcd: 505.28; found: 400.01(M−CO-C_6H_5).

*4.3.41. Compound **7d**. 2-cyano-3,4,6-trifluoro-5-(3-phenoxyphenoxy) phenylbenzoate*

Yield: 46% as pale brownish sticky solid; ^{1}H NMR (400 MHz, DMSO-d_6, δ ppm): 6.72–6.74 (1H, dd), 6.84–6.89 (2H, m), 7.03–7.05 (3H, d), 7.16–7.19 (2H, t), 7.34–7.43 (6H, m); ^{19}F NMR (376 MHz, DMSO-d_6, δ ppm): −136.84 to −136.93 (1F, dd), −151.37 (1F, b), −162.68 (1F, b). Anal. calcd for $C_{26}H_{14}F_3NO_4$: C, 67.68; H, 3.06; N, 3.04; found: C, 67.82; H, 3.15; N, 3.34. ESI-TOF MS for $C_{26}H_{14}F_3NO_4$; Calcd: 461.38; found: 356.05 (M−CO-C_6H_5).

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jfluchem.2014.03.005.

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