Organic & Biomolecular Chemistry

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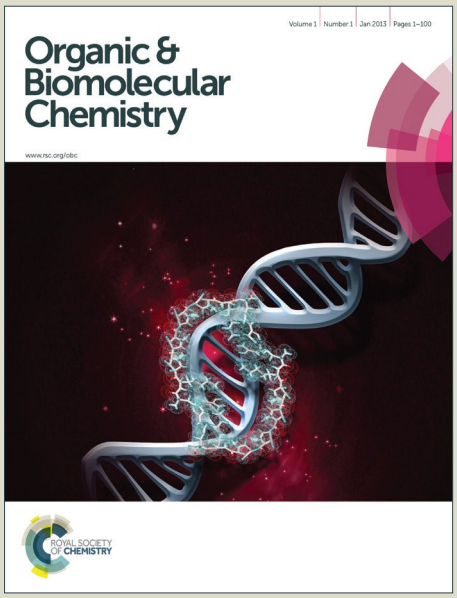

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DOI: 10.1039/C6OB01758D

Journal Name

ARTICLE

Carboxyl Radical-Assisted 1,5-Aryl Migration through Smiles Rearrangement

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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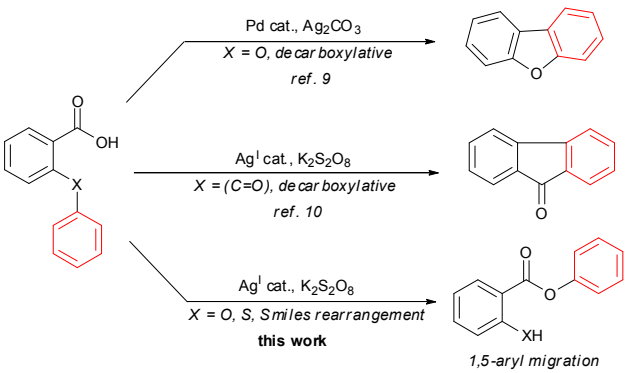
We report herein, a silver(I)-catalyzed Smiles rearrangement of 2-aryloxy- or 2-(arylthio)benzoic acids to provide aryl-2-hydroxybenzoate or aryl-2-mercaptobenzoate dimer respectively through 1,5-aryl migration from oxygen or sulfur to carboxylate oxygen. Mechanistically, the aryl ether moiety undergoes an intramolecular *ipso* attack by the carboxyl radical followed by a C-O or C-S bond cleavage. Aryl-2-mercaptobenzoates undergoes oxidative dimerization through thiol moiety *in situ*.

Introduction

The rearrangement reactions provide concise routes to the atom-economic synthesis in organic chemistry.[1] In this vein, the Smiles rearrangement offers a unique opportunity to the synthesis of privileged medicinal scaffolds originally through an intramolecular nucleophilic aromatic substitution.[2] Varieties of Smiles rearrangement such as Truce-Smiles,[3] Ugi-Smiles[4] have been explored for the multi-component reactions (MCR) in medicinal chemistry. However, the potential of radical-Smiles rearrangement has been realized recently.[5] Notably, the Zard group explored a peroxide-mediated radical-Smiles rearrangement to access aryl- or pyridylacetic acid derivatives from *N*-(α-xanthyl)acetanilides or *N*-(α-xanthyl)acetylaminopyridines respectively.[6] Recently, a photoredox-catalyzed synthesis of a difluoro-substituted spirocyclic ORL-1 antagonist through radical-Smiles rearrangement was reported by the Stephenson group which provides an alternative and practical route with easily available starting materials at industrially relevant scale and catalyst loading.[7]

Carboxylic acids have been explored as inexpensive, readily available, air and moisture stable cross-coupling partner.[8] The Glorius group reported a palladium-catalyzed decarboxylative intramolecular C-H arylation to afford dibenzofuran using 2-aryloxybenzoic acids.[9] Alternatively, silver(I)-catalyzed decarboxylative Pschorr-type cyclization to afford fluorenone was reported by the Greaney group.[10] The Baran group also employed this $Ag(I)/K_2S_2O_8$ catalytic system for the generation of aryl radicals from boronate counterpart which has been trapped intra- and intermolecularly.[11] Recently, similar catalytic system has been utilized for the decarboxylative Minisci-type arylation with benzoic acid derivatives.[12] Intrigued by these earlier reports we were interested to develop a silver-catalyzed decarboxylative dibenzofuran synthesis from 2-aryloxybenzoic acids in an intramolecular fashion. Interestingly, we observed 1,5-aryl migration through Smile-type rearrangement in lieu of expected decarboxylative dibenzofuran formation (Scheme 1). Since radical aryl migration is a useful tool in organic synthesis,[13] we were interested to develop this rearrangement reaction. From literature, a persulfate-mediated uncontrolled 1,5-aryl migration/oxidative dimerization cascade in water was reported.[14] Surprisingly, in our present study, the 1,5-aryl migratory product formed predominantly and a trace amount (<5%) of dimerization product was observed in electrospray ionization (ESI) mass spectrometry of the crude reaction mixture (see the Electronic Supplementary Information). A copper-catalyzed domino aryl migration/C-O/C-N bond formation for the synthesis of dibenzoxazepinones,[15] and a base-promoted 1,5-aryl migration through Smiles rearrangement were reported.[16] But, the later protocol is limited to the nicotinamides only where the phenolic hydroxyl group is stabilized by the *ortho* pyridinyl nitrogen. We report herein, a silver(I)-catalyzed 1,5-aryl migration of 2-aryloxybenzoic acids via C-O/C-S bond cleavage and C-O bond formation cascade. The corresponding

Scheme 1. Divergent syntheses from *ortho*-substituted benzoic acids



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Electronic Supplementary Information (ESI) available: Starting Meterials Preparation, Control Experiments, Optimization details, ^1H, ^{13}C NMR spectra for all synthesized compounds, and crystallographic data of **2t**. See DOI: 10.1039/c000000x/

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DOI: 10.1039/C6OB01758D

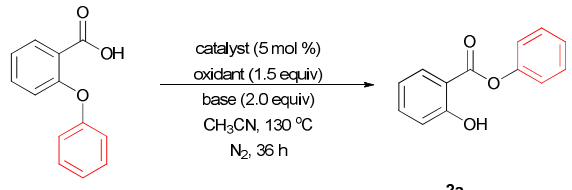
thioethers provided the rearranged product with disulfide bond formation under this oxidative condition.

Results and discussion

To optimize the reaction conditions, 2-phenoxybenzoic acid was chosen as a model substrate. Initially, catalytic amount of silver(I) nitrate in the presence of 3.0 equiv of $K_2S_2O_8$ afforded the Smiles rearrangement product in 34% yield. Decreasing the amount of oxidant to 1.5 equiv, the yield was further improved. However, other common oxidants such as aq. *tert*-butyl hydroperoxide, (diacetoxyiodo)benzene (PIDA), benzoyl peroxide even ammonium persulfate were not effective for this transformation. Similarly, other silver salts, palladium(II)triflate, iron(III)acetylacetonato, nickel(II)triflate, copper(II)acetate, tetrabutylammonium iodide were proved to be inferior catalysts compare to silver(I) nitrate Gratifyingly, the yield was improved with the addition of sodium trifluoroacetate as a base. After screening several bases, ultimately potassium trifluoroacetate provided the migratory product in good yields (for details see the Electronic Supplementary Information). Acetonitrile was the solvent of choice since other solvents such as dichloroethane, *N*,*N*-dimethylformamide, toluene etc. afforded no or inferior yields. A substantial amount of decomposition product formation was observed which we could not eliminate even after rigorous optimization. Interestingly, salicylic acid formation through hydrolysis of the Smiles rearrangement product was not observed under the reaction condition.

Next we explored the substrate scope under the optimized reaction condition. The starting materials were synthesized through a copper-catalyzed cross-coupling of 2-halobenzoic acid and phenol or thiophenol derivatives. A wide range of substrates underwent Smiles rearrangement to provide 1,5-aryl migratory products. Several substituents on the phenol component such as alkyl (**2g**, **2k**, **2p**, Scheme 2), aryl (**2h**, Scheme 2), alkoxyl (**2e**, **2f**, **2l**, **2n**, Scheme 2), chloro (**2c**, **2m**, **2u**, Scheme 2), bromo (**2d**, Scheme 2), and fluoro (**2b**, Scheme 2), were well tolerated under the reaction conditions. Interestingly, substrates derived from 1-, and 2- naphthols (**2i**, **2j**, **2q**, Scheme 2) also furnished the migratory products in good yields. Similarly, substitutions on the benzoic acid moiety such as fluoro (**2o**-**2q**, Scheme 2), chloro (**2r**, Scheme 2), and nitro groups (**2s**-**2u**, Scheme 2) were also survived. A representative structure of the migratory product has been unambiguously characterized by X-ray crystallography also (**2t**). But, electron-rich benzoic acid such as 5-methoxy-2-phenoxybenzoic acid, **1v** was unreactive under the

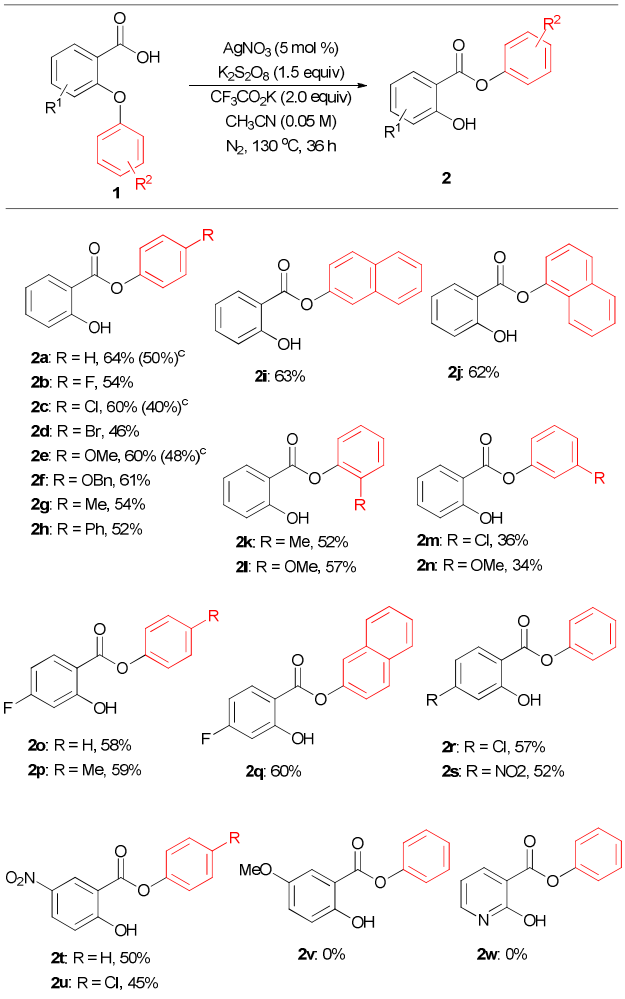
Table 1. Optimization of the reaction conditions[a,b]



entry	catalyst (5 mol %)	oxidant (1.5 equiv)	base (2.0 equiv)	yield (%)[b]
1[c]	$AgNO_3$	$K_2S_2O_8$	-	34
2	$AgNO_3$	$K_2S_2O_8$	-	44
3	$AgNO_3$	aq. TBHP	-	0
4	$AgNO_3$	$(NH_4)_2S_2O_8$	-	27
5	$AgNO_3$	$PhI(OAc)_2$	-	0
6	$AgNO_3$	$(PhCOO)_2$	-	trace
7	AgOAc	$K_2S_2O_8$	-	34
8	Ag_2CO_3	$K_2S_2O_8$	-	36
9	$Pd(TFA)_2$	$K_2S_2O_8$	-	trace
10	$Fe(acac)_3$	$K_2S_2O_8$	-	36
11	$Ni(OTf)_2$	$K_2S_2O_8$	-	35
12	Cu(OAc)	$K_2S_2O_8$	-	25
13	TBAI	$K_2S_2O_8$	-	30
14	$AgNO_3$	$K_2S_2O_8$	CF_3CO_2Na	50
15	**$AgNO_3$**	**$K_2S_2O_8$**	**CF_3CO_2K**	**64**
16	-	$K_2S_2O_8$	CF_3CO_2K	37
17	$AgNO_3$	-	CF_3CO_2K	0

[a]All reactions were carried out in 0.1 mmol scale. [b]Yields refer to here are overall isolated yields. [c]3.0 equiv of $K_2S_2O_8$ was used.

Scheme 2. Substrate scope with diarylethers[a,b]



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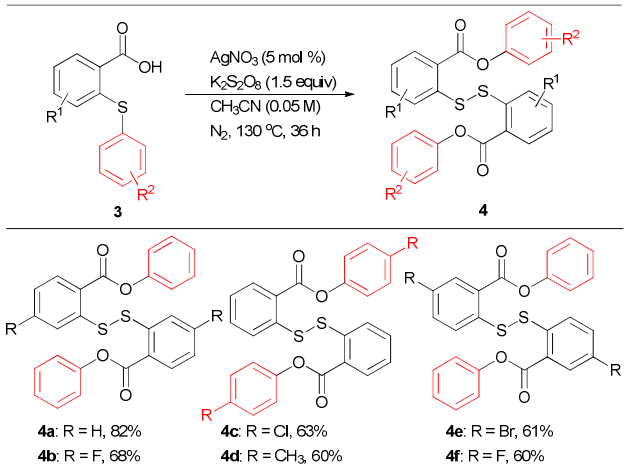
[a]The reaction was carried out in 0.1 mmol scale, 0.05 M. [b]Yield refer to here is the average isolated yield of at least two experiments. [c]The reaction was performed in 0.5 mmol scale.

reaction condition. However, it was difficult to predict the influence of the electronic nature of the substituents since a substantial amount of decomposition products was observed. Unfortunately, the yield of the products was decreased to some extent at higher scale. For example, in a reaction at 0.5 mmol scale, **1a** provided 50% yield of the desired product **2a** (Scheme 2). Similarly, **2c** and **2e** were isolated in 40% and 48% yields respectively at 0.5 mmol scale. Phenyl ether of nicotinic acid, **1w** also did not provide any desired product. Interestingly, the corresponding benzamide in place of benzoic acid did not afford any desired product which indicates a distinct reaction mechanism to the base-promoted anionic Smiles rearrangement.[16] The desired product was hydrolyzed to provide corresponding salicylic acid (**6a**) and phenol in an alcoholic sodium hydroxide solution (see the Electronic Supplementary Information).

On the accomplishment of Smiles rearrangement of 2-aryloxybenzoic acids, we were interested to examine the migratory event of the corresponding thioethers. Under the optimized conditions, the corresponding migratory product with disulfide bond **4a** was isolated albeit in moderate yield and a substantial amount of starting material was recovered. Gratifyingly, excellent to good yield of the corresponding Smiles rearrangement product was isolated by simply omitting the base from the standard reaction conditions. From ^{1}H NMR and mass spectroscopy it was also confirmed that the free thiol groups underwent oxidative homocoupling to furnish disulfide linkage *in situ*. This rearranged disulfide product was also observed as a byproduct (15%) in the persulfate mediated oxidation of diphenyl sulfide-2-carboxylic acids.[17] Gratifyingly, under our optimized condition, a number of 2-arylmarcapto benzoic acids with different substituents provided the 1,5-aryl migratory products followed by oxidative homocoupling products in good to high yields (Scheme 3). Unfortunately, 5-methoxy-2-(phenylthio)benzoic acid was unreactive under the reaction condition. The disulfide linkage was easily reduced to the corresponding thiols (**5a**) with triphenylphosphine (see the Electronic Supplementary Information).

Scheme 3. Substrate scope with diarylthioethers[ab]

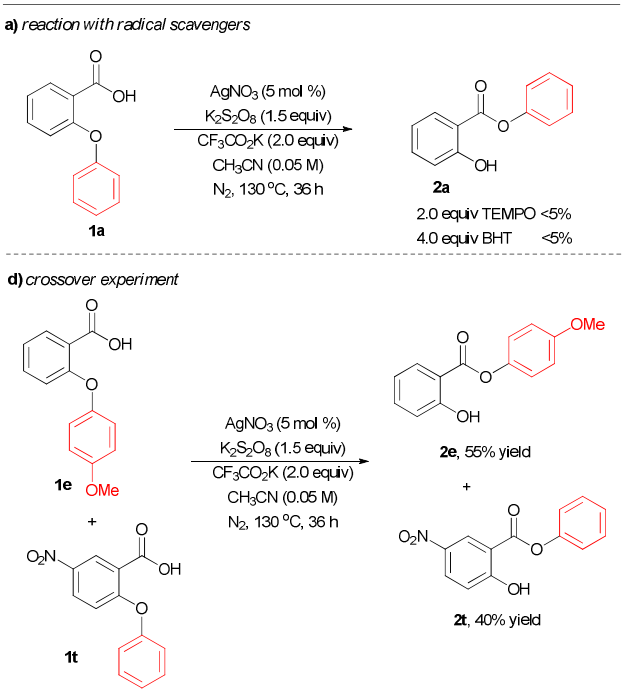


[a]The reaction was carried out in 0.2 mmol scale, 0.05 M. [b]Yield refer to here is the average isolated yield of at least two experiments.

Investigation of the reaction mechanism

We performed several control experiments to understand the mechanism of this unexpected result. Generation of aryl radical through the decomposition of aryl diazonium salts and aryl boronates is energetically favourable process which occurs spontaneously at mild conditions.[18,11] But generation of aryl radical through decarboxylation is a high energetic process which occurs at elevated temperature.[12] In the case of 2-aroylbenzoic acid, the incipient radical generated through decarboxylation is stabilized by the *ortho*- ketone group.[10] In contrast, in this present study, the incipient radical is destabilized by the *ortho* ether moiety. This is consistent with our previous observation that *ortho, ortho* dimethoxy carboxylic acid does not decarboxylate with silver(I) catalyst whereas palladium catalyst is effective.[19] Previously, Ag(I)/$K_2S_2O_8$ catalytic system has been utilized for the C-H carboxylation in the biaryl system.[20] However, in this case C-H insertion of the carboxyl radical is not favoured due to the formation of seven membered ring. Instead, an *ipso* attack to the ether carbon is favoured and a concomitant homolytic C-O bond cleavage may occur. Typically, reductive cleavage of inert diarylether linkage is possible by nickel catalyst.[21] However, simple diarylether or 2-aryloxybenzamides did not furnish any product under this optimized condition. Therefore, 2-carboxylic acid was found to be crucial for the reaction to occur. The reaction was completely arrested with the addition of radical scavengers such as 2.0 equiv of 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) or 4.0 equiv of butylated hydroxytoluene (BHT) (Scheme 4a). Therefore, the reaction may proceed through a radical mechanism. The involvement of radical mechanism is further supported by the fact that the reaction also proceeds with persulfate in the absence of silver(I)nitrate to provide the desired product in moderate yield (entry 16, Table 1).[14,17] In order to gain insight further, we performed a cross-over experiment. While an equimolar mixture of **1e** and **1t** was subjected to the reaction conditions no cross-over products were detected in ^{1}H NMR as well as (ESI) mass spectrometry (Scheme 4b) (see the ESI). It suggests that the

Scheme 4. Control experiments



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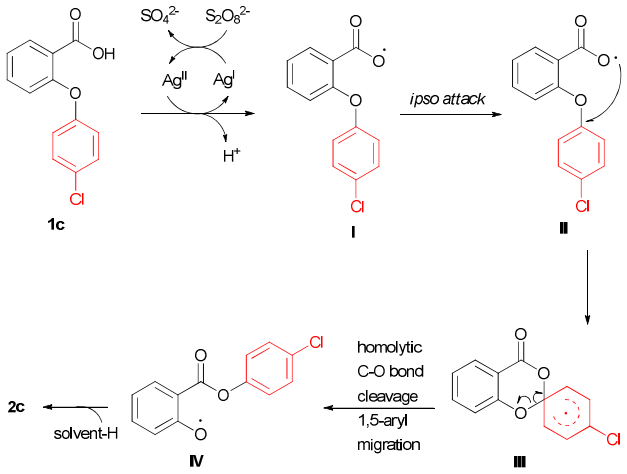
reaction may involve an intramolecular rearrangement for 1,5-aryl migration.

From the control experiments and substitution pattern of the observed products, we postulated the reaction mechanism. In the presence of catalytic silver(I) salt and stoichiometric persulfate anion the carboxyl radical **I** (Scheme 5) is generated. Instead of decarboxylation the carboxyl radical then undergoes an *ipso* attack to the arylether moiety **II** (Scheme 5). A concomitant homolytic C-O bond cleavage occurs which lead to the formation of aryl ester through 1,5 aryl migration **IV** (Scheme 5). The incipient phenoxyl radical may abstract a hydrogen atom from solvent or reaction medium to give the final migratory product **2c** (Scheme 5). This phenomenon is well-established in the previous literature.[14,22] Additionally, the reaction in nitromethane also provides the migratory product **2a** in lower (48%) yield. However, the exact nature of hydrogen whether it is a proton or hydride is not clear at this moment. In the case of thioethers, the homocoupling product may occur through the thiyl radical dimerization. The dimerization also may occur from the final migratory thiol product under the oxidative reaction conditions. To probe, when monomer of **4a** was subjected to the reaction conditions it furnished the dimerised product **4a** in quantitative yield. However, the possibility of thiyl radical dimerization is also plausible.

Scheme 5. Plausible mechanism of 1,5-aryl migration



Conclusions

In conclusion, we have developed a silver(I)-catalyzed selective 1,5-aryl migration of 2-aryloxy- or 2-(arylthio)benzoic acids through radical Smiles rearrangement. This unexpected aryl translocation occurs through an intramolecular *ipso* attack of the carboxyl radical to the arylether instead of expected intramolecular decarboxylative arylation to afford dibenzofuran. Subsequently, inert C-O bond cleavage of the diaryl ether occurs selectively. The corresponding thioethers also furnished the migratory products with disulfide linkage under this oxidative condition. We anticipate that the present catalytic system could be useful for the selective C-O bond cleavage in biomass conversion.

Experimental section

General information

Melting points were determined in open end-capillary tubes and are uncorrected. TLC was performed on silica gel plates (silica gel 60, f254), and the spots were visualized with UV light (254 and 365 nm) and $KMnO_4$ stain. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ using TMS as the internal standard. HRMS (m/z) were measured using EI (magnetic sector, positive ion) and ESI (Q-TOF, positive ion) techniques. Infrared (IR) spectra were recorded on Fourier transform infrared spectroscopy; only intense peaks were reported.

General experimental procedure for the preparation of 2-phenoxybenzoic acids, Scheme 2.[23]

To an oven-dried 100 mL round bottom flask equipped with magnetic stir bar, 2-halo benzoic acid (6.2 mmol, 1.0 equiv) was added in 50 mL of dimethylformamide (DMF), followed by phenol (12.4 mmol, 2.0 equiv), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (2.6 mL, 18.6 mmol, 3.0 equiv), pyridine (0.1 mL), copper(0) (52 mg, 0.81 mmol), and copper(I) iodide (53 mg, 0.28 mmol). The reaction mixture was heated to 160 ^oC under nitrogen atmosphere. After consumption of the starting materials as indicated by TLC (typically 2 h) the reaction mixture was cooled and acidified with 3N HCl until no more precipitate was formed. The resulting precipitates and reaction mixture were extracted with dichloromethane (60 mL) and cold water (70 mL). The organic layer was washed with cold water (20 mL x 3) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane as eluent to afford the desired white solid product.

2-Phenoxybenzoic acid, 1a, Scheme 2.[23] The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and Phenol (1.20 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (1.14 g, 86%), mp 107-109 ^oC. ^1H NMR (300 MHz, DMSO-d_6): δ 12.84 (brs, 1H), 7.81 (d, *J* = 7.8 Hz, 1H), 7.54 (td, *J* = 8.1 Hz, 1.8 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 2H), 7.24 (t, *J* = 7.5 Hz, 1H), 7.06 (t, *J* = 7.2 Hz, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.88 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.6, 157.5, 154.9, 133.5, 131.4, 129.9, 124.6, 124.0, 122.8, 121.0, 117.6.

2-(4-Fluorophenoxy)benzoic acid, 1b, Scheme 2.[9] The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and 4-fluorophenol (1.40 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (1.12 g, 78%), mp 142-144 ^oC. ^1H NMR (300 MHz, DMSO-d_6): δ 12.91 (brs, 1H), 7.82 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.56 (td, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.15-7.29 (m, 3H), 6.93-7.00 (m, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.6, 157.9 (d, *J* = 237.8 Hz), 155.2, 153.5 (d, *J* = 2.2 Hz), 133.6, 131.4, 124.3, 124.0, 120.6, 119.5 (d, *J* = 8.2 Hz), 116.4 (d, *J* = 23.2 Hz).

2-(4-Chlorophenoxy)benzoic acid, 1c, Scheme 2. The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and 4-chlorophenol (1.60 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (1.3 g, 84%), mp 115-117 ^oC. ^1H NMR (300 MHz, DMSO-d_6): δ 7.85 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.60 (td, *J* = 8.1 Hz, 1.8 Hz, 1H), 7.36-7.41 (m, 2H), 7.31 (td, *J* = 8.1 Hz, 0.6 Hz, 1H), 7.08 (d, *J* = 8.1 Hz, 1H), 6.87-6.92 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.4, 156.7, 154.3, 133.8, 131.6, 129.7, 126.5, 124.74, 124.67, 121.6, 119.0; IR (neat): υ_{max} 1690, 1484, 1313, 1244, 1091, 826 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9ClO_3Na$ $[M + Na]^+$: 271.0138; found: 271.0130.

2-(4-Bromophenoxy)benzoic acid, 1d, Scheme 2.[9] The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and 4-bromophenol (1.2 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (1.27 g, 70%), mp 118-120 ^oC. ^1H NMR (300 MHz, DMSO-d_6): δ 12.94

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(brs, 1H), 7.86 (d, *J* = 6.9 Hz, 1H), 7.60 (t, *J* = 7.5 Hz, 1H), 7.50 (d, *J* = 8.7 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 1H), 7.09 (d, *J* = 8.1 Hz, 1H), 6.84 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.3, 157.2, 154.2, 133.8, 132.6, 131.6, 124.7, 121.7, 119.3, 114.2.

2-(4-Methoxyphenoxy)benzoic acid, 1e, Scheme 2.[9] The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and 4-methoxyphenol (1.54 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (1.29 g, 85%), mp 143-145 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.77 (dd, *J* = 7.5 Hz, 1.5 Hz, 1H), 7.48 (td, *J* = 8.4 Hz, 1.5 Hz, 1H), 7.17 (t, *J* = 7.5 Hz, 1H), 6.89-6.95 (m, 4H), 6.84 (d, *J* = 8.1 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.1, 156.4, 155.5, 150.3, 133.4, 131.3, 123.8, 123.1, 120.0, 119.2, 115.2, 55.6.

2-(4-(Benzyloxy)phenoxy)benzoic acid, 1f, Scheme 2. The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and 4-(benzyloxy)phenol (2.48 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (1.47 g, 74%), mp 153-155 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.85 (brs, 1H), 7.78 (dd, *J* = 7.5 Hz, 1.2 Hz, 1H), 7.31-7.52 (m, 6H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 8.4 Hz, 1H), 5.07 (s, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.8, 156.3, 154.5, 150.4, 137.1, 133.3, 131.3, 128.5, 127.9, 127.8, 123.7, 123.0, 119.9, 119.2, 116.0, 69.7; IR (neat): υ_{max} 1684, 1503, 1311, 1216, 1019, 784 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{16}O_4Na$ [M + Na]$^+$: 343.0946; found: 343.0950.

2-(*p*-Tolyloxy)benzoic acid, 1g, Scheme 2.[9] The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and *p*-cresol (1.34 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (1.13 g, 80%), mp 122-124 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.80 (dd, *J* = 7.8 Hz, 1.5 Hz, 1H), 7.52 (td, *J* = 8.4 Hz, 1.5 Hz, 1H), 7.22 (td, *J* = 7.5 Hz, 0.6 Hz, 1H), 7.16 (d, *J* = 8.1 Hz, 2H), 6.93 (d, *J* = 8.1 Hz, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.7, 155.5, 155.0, 133.4, 132.1, 131.3, 130.3, 124.2, 123.5, 120.3, 118.0, 20.3.

4-Diphenyl-2-phenoxybenzoic acid, 1h, Scheme 2. The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and 4-phenylphenol (2.11 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (1.48 g, 82%), mp 149-151 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.94 (brs, 1H), 7.86 (d, *J* = 7.5 Hz, 1H), 7.58-7.65 (m, 5H), 7.44 (t, *J* = 7.5 Hz, 2H), 7.28-7.35 (m, 2H), 7.10 (d, *J* = 8.1 Hz, 1H), 6.97 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.0, 157.8, 155.1, 140.0, 135.2, 134.2, 132.0, 129.4, 128.6, 127.6, 126.9, 125.2, 124.8, 122.0, 118.0; IR (neat): υ_{max} 1689, 1482, 1312, 1220, 758 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{19}H_{14}O_3Na$ [M + Na]$^+$: 313.0841; found: 313.0838.

2-(Naphthalen-3-yloxy)benzoic acid, 1i, Scheme 2.[9] The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and naphthalen-2-ol (1.79 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (1.31 g, 80%), mp 118-120 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.94 (d, *J* = 9.0 Hz, 1H), 7.89 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 7.8 Hz, 1H), 7.60 (t, *J* = 8.1 Hz, 1H), 7.39-7.49 (m, 2H), 7.25-7.35 (m, 2H), 7.20 (s, 1H), 7.12 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.6, 155.6, 154.8, 134.0, 133.8, 131.6, 130.0, 129.6, 127.7, 127.0, 126.7, 124.72, 124.67, 124.4, 121.5, 119.3, 112.1.

2-(*o*-Tolyloxy)benzoic acid, 1k, Scheme 2.[9] The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and *o*-cresol (1.3 mL, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (990 mg, 70%), mp 122-124 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.86 (brs, 1H), 7.81 (dd, *J* = 7.8 Hz, 1.5 Hz, 1H), 7.50 (td, *J* = 8.7 Hz, 1.8 Hz, 1H), 7.30 (d, *J* = 7.2 Hz, 1H), 7.15-7.22 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.80 (d, *J* = 8.1 Hz, 1H), 6.73 (d, *J* = 7.8 Hz, 1H), 2.30 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 167.1, 156.0, 155.0, 133.8, 131.8, 128.9, 127.7, 124.0, 123.8, 123.4, 119.2, 118.4, 16.2.

2-(2-Methoxyphenoxy)benzoic acid, 1l, Scheme 2. The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and 2-methoxyphenol (1.54 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (1.09 g, 72%), mp 114-116 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.82 (brs, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.43 (t, *J* = 7.2 Hz, 1H), 7.09-7.21 (m, 3H), 6.92-6.98 (m, 2H), 6.65 (d, *J* = 8.4 Hz, 1H), 3.74 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.8, 156.5, 151.0, 144.1, 133.2, 131.2, 125.3, 122.3, 122.2, 121.2, 120.8, 117.0, 113.5, 55.7; IR (neat): υ_{max} 1666, 1494, 1306, 1260, 749 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{14}H_{12}O_4Na$ [M + Na]$^+$: 267.0633; found: 267.0628.

2-(3-Chlorophenoxy)benzoic acid, 1m, Scheme 2. The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and 3-chlorophenol (1.33 mL, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (1.09 g, 71%), mp 98-100 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.97 (brs, 1H), 7.88 (d, *J* = 7.8 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.32-7.39 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 2H), 6.92 (s, 1H), 6.83 (dd, *J* = 8.4 Hz, 2.1 Hz, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.2, 158.9, 153.8, 133.9, 133.8, 131.6, 131.2, 125.0, 124.9, 122.5, 122.1, 117.0, 115.7; IR (neat): υ_{max} 1693, 1593, 1468, 1417, 1239, 913, 763 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9ClO_3Na$ [M + Na]$^+$: 271.0138; found: 271.0134.

2-(3-Methoxyphenoxy)benzoic acid, 1n, Scheme 2.[24] The same general procedure was followed by using 2-iodo benzoic acid (1.55 g, 6.2 mmol, 1.0 equiv) and 3-methoxyphenol (1.54 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (1.14 g, 75%), mp 118-120 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.82 (d, *J* = 7.5 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.21-7.30 (m, 2H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.67 (dd, *J* = 8.1 Hz, 1.2 Hz, 1H), 6.49 (s, 1H), 6.42 (d, *J* = 8.1 Hz, 1H), 3.72 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.6, 160.7, 158.7, 154.7, 133.4, 131.4, 130.4, 124.6, 124.1, 121.2, 109.6, 108.5, 103.9, 55.3.

4-Chloro-2-phenoxybenzoic acid, 1r, Scheme 2. The same general procedure was followed by using 2,4-dichlorobenzoic acid (1.18 g, 6.2 mmol, 1.0 equiv) and Phenol (1.2 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 7:3 hexane/ethyl acetate) afforded the desired product as a white solid, (462 mg, 30%), mp 155-157 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.86 (d, *J* = 8.1 Hz, 1H), 7.32-7.42 (m, 3H), 7.15 (t, *J* = 7.2 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.0, 156.7, 156.6, 137.8, 133.8, 130.5, 124.4, 124.1, 120.7, 118.6, 100.0; IR (neat): υ_{max} 1675, 1591, 1482, 1308, 1229, 919 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9ClO_3Na$ [M + Na]$^+$: 271.0138; found: 271.0125.

5-Nitro-2-phenoxybenzoic acid, 1t, Scheme 2. The same general procedure was followed by using 2-bromo-5-nitrobenzoic acid (1.52 g, 6.2 mmol, 1.0 equiv) and Phenol (1.2 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl

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DOI: 10.1039/C6OB01758D

acetate) afforded the desired product as a white solid, (804 mg, 50%), mp 160-162 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.58 (d, *J* = 3.0 Hz, 1H), 8.33 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 2H), 7.27 (t, *J* = 7.8 Hz, 1H), 7.14 (t, *J* = 7.8 Hz, 2H), 7.00 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 165.3, 161.5, 155.3, 142.3, 130.9, 129.0, 127.4, 125.6, 123.8, 120.3, 119.2; IR (neat): υ_{max} 1691, 1614, 1479, 1348, 1257, 745 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9NO_5Na$ [M + Na]$^+$: 282.0378; found: 282.0401.

2-(4-Chlorophenoxy)-5-nitrobenzoic acid, 1u, Scheme 2. The same general procedure was followed by using 2-bromo-5-nitrobenzoic acid (1.52 g, 6.2 mmol, 1.0 equiv) and 4-chlorophenol (1.60 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (838 mg, 46%), mp 159-161 °C. ^{1}H NMR (600 MHz, DMSO-d_6): δ 8.60 (d, *J* = 2.4 Hz, 1H), 8.35 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 7.50-7.53 (m, 2H), 7.15-7.18 (m, 2H), 7.11 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, DMSO-d_6): δ 165.1, 160.9, 154.5, 142.7, 130.7, 129.3, 129.1, 127.5, 124.1, 121.8, 120.1; IR (neat): υ_{max} 1707, 1478, 1345, 845 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{13}H_8ClNO_5Na$ [M]$^+$: 315.9989; found: 315.9986.

5-methoxy-2-phenoxybenzoic acid, 1v, Scheme 2. The same general procedure was followed by using 2-bromo-5-methoxybenzoic acid (1.43 g, 6.2 mmol, 1.0 equiv) and Phenol (1.2 g, 12.4 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 6:4 hexane/ethyl acetate) afforded the desired product as a white solid, (760 mg, 50%), mp 142-144 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 7.26-7.31 (m, 3H), 7.15 (dd, *J* = 8.7 Hz, 2.4 Hz, 1H), 6.97-7.04 (m, 2H), 6.80 (d, *J* = 7.8 Hz, 2H), 3.78 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ 166.3, 158.8, 155.6, 147.6, 129.8, 126.0, 123.8, 122.1, 119.5, 116.5, 115.3, 55.7; IR (neat): υ_{max} 1692, 1598, 1482, 1275, 1218, 746 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{14}H_{12}O_4Na$ [M + Na]$^+$: 267.0633; found: 267.0635.

The experimental procedure for the preparation of compound **1o**, **1p**, **1q**, **1j**, **1s**, **1w**, **3a**, **3b**, **3c**, **3d**, **3e** and **3f** see the Electronic Supplementary Information (ESI).

General experimental Procedure for the carboxyl radical-assisted 1,5-aryl migration through Smiles rearrangement using 2-Phenoxybenzoic acids, Scheme 2.

To an oven-dried 15 mL sealed tube, a mixture of 2-phenoxybenzoic acids (0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv) was taken and dry MeCN (2.0 mL) was added to it. After flushing with nitrogen, the vessel was sealed with a screw cap. The reaction mixture was allowed to stir for 36 h at 130 °C. After completion (as indicated by TLC), the reaction mixture was cooled to room temperature. Then the reaction mixture was poured into water (20 mL) and extracted with ethyl acetate (20 mL). The organic layer was washed with water (10 mL) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane as eluent to afford the desired product.

Phenyl 2-hydroxybenzoate, 2a, Scheme 2.[25] The same general procedure was followed by using 2-phenoxybenzoic acid (21.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colourless oil, (14 mg, 64%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.53 (s, 1H), 8.10 (d, *J* = 7.8 Hz, 1H), 7.56 (t, *J* = 8.4 Hz, 1H), 7.48 (t, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.2 Hz, 1H),7.24 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 1H), 7.00 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.9, 162.2, 150.1, 136.5, 130.3, 129.6, 126.4, 121.6, 119.4, 117.8, 111.8.

4-Fluorophenyl 2-hydroxybenzoate, 2b, Scheme 2. The same general procedure was followed by using 2-(4-fluorophenoxy)benzoic acid (23.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colourless oil, (12.5 mg, 54%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.45 (s, 1H), 8.08 (dd, *J* = 7.8 Hz, 1.2Hz, 1H), 7.55-7.58 (m, 1H), 7.19-7.21 (m, 2H), 7.14-7.17 (m, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 7.00 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.9, 162.2, 160.5 (d, *J* = 244.5 Hz), 145.8 (d, *J* = 3.0 Hz), 136.6, 130.3, 123.1 (d, *J* = 7.5 Hz), 119.5, 117.9, 116.3 (d, *J* = 24.0 Hz), 111.6; IR (neat): υ_{max} 3230, 1692, 1504, 1300, 1182, 1064, 757 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9FO_3Na$ [M + Na]$^+$: 255.0433; found: 255.0451.

4-Chlorophenyl 2-hydroxybenzoate, 2c, Scheme 2.[26] The same general procedure was followed by using 2-(4-chlorophenoxy)benzoic acid (25.0 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a white solid, (15 mg, 60%), mp 98-100 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.39 (s, 1H), 8.05 (dd, *J* = 8.1 Hz, 1.5 Hz, 1H), 7.52-7.58 (m, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.16 (d, *J* = 9.0 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.97 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.6, 162.2, 148.5, 136.7, 131.8, 130.3, 129.7, 123.0, 119.6, 117.9, 111.5; IR (neat): υ_{max} 3256, 1686, 1486, 1304, 1195, 755 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9ClO_3Na$ [M + Na]$^+$: 271.0138; found: 271.0145.

4-Bromophenyl 2-hydroxybenzoate, 2d, Scheme 2. The same general procedure was followed by using 2-(4-bromophenoxy)benzoic acid (29.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a white solid, (13.5 mg, 46%), mp 67-69 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.40 (s, 1H), 8.07 (dd, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.55-7.60 (m, 3H), 7.13 (d, *J* = 9.0 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.99 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.5, 162.2, 149.1, 136.7, 132.7, 130.3, 123.4, 119.5, 117.9, 111.5; IR (neat): υ_{max} 3221, 1689, 1506, 1299, 1188, 1067, 755 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{13}H_9BrO_4$ [M]$^+$: 291.9735, 293.9715; found: 291.9738, 293.9727.

4-Methoxyphenyl 2-hydroxybenzoate, 2e, Scheme 2.[26] The same general procedure was followed by using 2-(4-methoxyphenoxy)benzoic acid (24.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a colourless oil, (14.5 mg, 60%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.56 (s, 1H), 8.09 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.54-7.57 (m, 1H), 7.13-7.16 (m, 2H), 7.06 (dd, *J* = 8.4 Hz, 0.6 Hz, 1H), 6.96-7.00 (m, 3H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.3, 162.1, 157.6, 143.4, 136.4, 130.3, 122.4, 119.4, 117.8, 114.6, 111.9, 55.6; IR (neat): υ_{max} 3221, 1689, 1506, 1299, 1188, 1067, 755 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{14}H_{12}O_4$ [M]$^+$: 244.0736; found: 244.0738.

4-(Benzyloxy)phenyl 2-hydroxybenzoate, 2f, Scheme 2. The same general procedure was followed by using 2-(4-(benzyloxy)phenoxy)benzoic acid (32.0 mg, 0.1 mmol, 1.0 equiv),

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DOI: 10.1039/C6OB01758D

silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a white solid, (19.5 mg, 61%), mp 98-100 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.56 (s, 1H), 8.09 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.56 (td, *J* = 8.4 Hz, 1.2 Hz, 1H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.43 (t, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.14-7.16 (m, 2H), 7.05-7.07 (m, 3H), 6.99 (t, *J* = 7.8 Hz, 1H), 5.11 (s, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.2, 162.1, 156.9, 143.6, 136.7, 136.4, 130.3, 128.6, 128.1, 127.5, 122.4, 119.4, 117.8, 115.6, 111.9, 70.4; IR (neat): υ_{max} 3264, 1693, 1505, 1299, 1196, 749 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{20}H_{16}O_4Na$ $[M + Na]^+$: 343.0946; found: 343.0938.

***p*-Tolyl 2-hydroxybenzoate, 2g, Scheme 2.**[26] The same general procedure was followed by using 2-(*p*-tolyloxy)benzoic acid (23.0 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colourless oil, (12.5 mg, 54%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.56 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 8.4 Hz, 1H), 7.26-7.28 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.06 (d, *J* = 8.4 Hz, 1H), 6.99 (t, *J* = 7.8 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.1, 162.1, 147.8, 136.4, 136.1, 130.3, 130.1, 121.3, 119.4, 117.8, 111.9, 20.9; IR (neat): υ_{max} 3216, 1690, 1482, 1300, 1193, 757 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{14}H_{12}O_3$ $[M]^+$: 228.0786; found: 228.0778.

4-Diphenyl 2-hydroxybenzoate, 2h, Scheme 2. The same general procedure was followed by using 2-(4-phenylphenoxy)benzoic acid (29.0 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a white solid, (15 mg, 52%), mp 100-102 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.53 (s, 1H), 8.12 (d, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.62 (d, *J* = 7.8 Hz, 2H), 7.58 (t, *J* = 7.8 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.2 Hz, 1H), 7.31 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 1H), 7.01 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0, 162.2, 149.4, 140.2, 139.6, 136.5, 130.4, 128.8, 128.3, 127.5, 127.1, 121.9, 119.5, 117.8, 111.8; IR (neat): υ_{max} 3208, 1688, 1483, 1301, 1178, 757, 691 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{19}H_{14}O_3Na$ $[M + Na]^+$: 313.0841; found: 313.0856.

Naphthalen-2-yl 2-hydroxybenzoate, 2i, Scheme 2. The same general procedure was followed by using 2-(naphthalen-3-yloxy)benzoic acid (26.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a white solid, (16.5 mg, 63%), mp 86-88 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.55 (s, 1H), 8.17 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.71 (d, *J* = 2.4 Hz, 1H), 7.52-7.60 (m, 3H), 7.37 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 7.02 (t, *J* = 7.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.1, 162.2, 147.7, 136.5, 133.7, 131.7, 130.4, 129.6, 127.8, 127.7, 126.8, 126.0, 120.9, 119.5, 118.8, 117.9, 111.8; IR (neat): υ_{max} 3252, 1688, 1479, 1297, 1156, 756 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{17}H_{12}O_3Na$ $[M + Na]^+$: 287.0684; found: 287.0675.

Naphthalen-1-yl 2-hydroxybenzoate, 2j, Scheme 2. The same general procedure was followed by using 2-(naphthalen-1-yloxy)benzoic acid (26.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colourless oil, (16.4 mg, 62%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.52 (s, 1H), 8.32 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.93-7.96 (m, 2H), 7.86 (d, *J* = 8.4 Hz, 1H), 7.62-7.64 (m, 1H), 7.54-7.59 (m, 3H), 7.40 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.12 (dd, *J* = 8.4 Hz, 0.6 Hz, 1H), 7.08 (td, *J* = 7.8 Hz, 1.2 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 169.0, 162.3, 146.0, 136.7, 134.7, 130.4, 128.1, 126.8, 126.72, 126.67, 126.6, 125.4, 121.0, 119.6, 118.2, 118.0, 111.7; IR (neat): υ_{max} 3231, 2927, 1693, 1481, 1296, 1205, 761 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{17}H_{12}O_3Na$ $[M + Na]^+$: 287.0684; found: 287.0669.

***o*-tolyl 2-hydroxybenzoate, 2k, Scheme 2.**[26] The same general procedure was followed by using 2-(*o*-tolyloxy)benzoic acid (23.0 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colourless oil, (12 mg, 52%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.56 (s, 1H), 8.13 (dd, *J* = 7.8 Hz, 1.8 Hz, 1H), 7.57 (td, *J* = 9.0 Hz, 1.8 Hz, 1H), 7.31-7.33 (m, 1H), 7.29 (d, *J* = 7.8 Hz, 1H), 7.24 (td, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.15 (d, *J* = 7.8 Hz, 1H), 7.07 (dd, *J* = 8.4 Hz, 0.6 Hz, 1H), 7.01 (td, *J* = 7.8 Hz, 0.6 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.7, 162.2, 148.7, 136.4, 131.3, 130.29, 130.26, 127.1, 126.5, 121.8, 119.5, 117.8, 111.7, 16.2; IR (neat): υ_{max} 3214, 2926, 1689, 1584, 1486, 1299, 1165, 753 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{14}H_{12}O_3Na$ $[M + Na]^+$: 251.0684; found: 251.0672.

2-Methoxyphenyl 2-hydroxybenzoate, 2l, Scheme 2.[26] The same general procedure was followed by using 2-(2-methoxyphenoxy)benzoic acid (24.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a white solid, (14 mg, 57%), mp 64-66 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.51 (s, 1H), 8.13 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.54-7.57 (m, 1H), 7.30 (td, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.18 (dd, *J* = 7.8 Hz, 1.2 Hz, 1H), 7.02-7.06 (m, 3H), 6.99 (t, *J* = 7.8 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.4, 162.0, 151.1, 139.0, 136.3, 130.6, 127.4, 122.8, 120.8, 119.4, 117.7, 112.5, 111.8, 55.9; IR (neat): υ_{max} 3212, 1692, 1499, 1296, 754 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{14}H_{12}O_4Na$ $[M + Na]^+$: 267.0633; found: 267.0625.

3-Chlorophenyl 2-hydroxybenzoate, 2m, Scheme 2. The same general procedure was followed by using 2-(3-chlorophenoxy)benzoic acid (25.0 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colourless oil, (9.0 mg, 36%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.38 (s, 1H), 8.05 (d, *J* = 8.1 Hz, 1.8 Hz, 1H), 7.56 (td, *J* = 8.7 Hz, 1.8 Hz, 1H), 7.39 (t, *J* = 7.8 Hz, 1H), 7.27-7.32 (m, 2H), 7.12-7.15 (m, 1H), 7.05 (d, *J* = 8.4 Hz, 1H), 6.98 (td, *J* = 8.4 Hz, 1.2 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 148.5, 162.2, 150.5, 136.7, 134.9, 130.32, 130.27, 126.7, 122.4, 120.1, 119.6, 117.9, 111.4; IR (neat): υ_{max} 3216, 1675, 1587, 1479, 1304, 753 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9ClO_3Na$ $[M + Na]^+$: 271.0138; found: 271.0153.

3-Methoxyphenyl 2-hydroxybenzoate, 2n, Scheme 2. The same general procedure was followed by using 2-(3-methoxyphenoxy)benzoic acid (24.5 mg, 0.1 mmol, 1.0 equiv), silver

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DOI: 10.1039/C6OB01758D

nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 95:5 hexane/ethyl acetate) afforded the desired product as a colourless oil, (8.5 mg, 34%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 10.53 (s, 1H), 8.09 (dd, *J* = 8.1 Hz, 1.5 Hz, 1H), 7.56 (td, *J* = 8.7 Hz, 1.8 Hz, 1H), 7.37 (t, *J* = 8.1 Hz, 1H), 7.07 (dd, *J* = 7.8 Hz, 0.6 Hz, 1H), 7.00 (td, *J* = 8.1 Hz, 0.9 Hz, 1H), 6.87-6.90 (m, 1H), 6.83 (dd, *J* = 8.1 Hz, 1.2 Hz, 1H), 6.79 (t, *J* = 2.1 Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 168.8, 162.2, 160.6, 151.0, 136.5, 130.3, 130.0, 119.5, 117.8, 113.8, 112.2, 111.8, 107.7, 55.5; IR (neat): υ_{max} 3224, 2927, 1691, 1610, 1486, 1143, 760 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{14}H_{12}O_4Na$ [M + Na]$^+$: 267.0633; found: 267.0635.

Phenyl 4-fluoro-2-hydroxybenzoate, 2o, Scheme 2. The same general procedure was followed by using 4-fluoro-2-phenoxybenzoic acid (23.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colourless oil, (13.5 mg, 58%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.76 (d, *J* = 1.2 Hz, 1H), 8.11 (dd, *J* = 9.0 Hz, 6.6 Hz, 1H), 7.48 (t, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.8 Hz, 1H), 7.22 (d, *J* = 7.8 Hz, 2H), 6.75 (dd, *J* = 10.2 Hz, *J* = 2.4 Hz, 1H), 6.72 (td, *J* = 8.4 Hz, 2.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.3, 167.7 (d, *J* = 255.0 Hz), 164.3 (d, *J* = 13.5 Hz), 149.9, 132.6 (d, *J* = 12.0 Hz), 129.6, 126.5, 121.6, 108.6 (d, *J* = 3.0 Hz), 107.8 (d, *J* = 22.5 Hz), 104.6 (d, *J* = 24.0 Hz); IR (neat): υ_{max} 3180, 1691, 1596, 1500, 1259, 1192, 771 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9FO_3Na$ [M + Na]$^+$: 255.0433; found: 255.0455.

***p*-Tolyl 4-fluoro-2-hydroxybenzoate, 2p, Scheme 2.** The same general procedure was followed by using 2-(p-tolyloxy)-4-fluorobenzoic acid (25.0 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a white solid, (14.5 mg, 59%), mp 68-70 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.79 (d, *J* = 1.8 Hz, 1H), 8.10 (dd, *J* = 9.0 Hz, 6.6 Hz, 1H), 7.26 (d, *J* = 8.4 Hz, 2H), 7.10 (d, *J* = 8.4 Hz, 2H), 6.74 (dd, *J* = 10.2 Hz, 2.4 Hz, 1H), 6.71 (td, *J* = 8.4 Hz, 2.4 Hz, 1H), 2.40 (s, 3H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.5, 167.6 (d, *J* = 253.5 Hz), 164.3 (d, *J* = 15.0 Hz), 147.6, 136.2, 132.6 (d, *J* = 12.0 Hz), 130.1, 121.2, 108.6 (d, *J* = 3.0 Hz), 107.7 (d, *J* = 24.0 Hz), 104.6 (d, *J* = 24.0 Hz), 20.9; IR (neat): υ_{max} 3082, 1685, 1600, 1509, 1265, 1188, 767 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{14}H_{11}FO_3Na$ [M + Na]$^+$: 269.0590; found: 269.0556.

Naphthalen-2-yl 4-fluoro-2-hydroxybenzoate, 2q, Scheme 2. The same general procedure was followed by using 4-fluoro-2-(naphthalen-3-yloxy)benzoic acid (28.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a white solid, (17 mg, 60%), mp 78-80 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.77 (s, 1H), 8.17 (dd, *J* = 9.0 Hz, 6.6 Hz, 1H), 7.95 (d, *J* = 9.0 Hz, 1H), 7.91 (d, *J* = 7.2 Hz, 1H), 7.86 (d, *J* = 7.8 Hz, 1H), 7.70 (d, *J* = 2.4 Hz, 1H), 7.52-7.57 (m, 2H), 7.36 (dd, *J* = 9.0 Hz, 2.4 Hz, 1H), 6.77 (dd, *J* = 10.2 Hz, 2.4 Hz, 1H), 6.74 (td, *J* = 8.4 Hz, 2.4 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.5, 167.8 (d, *J* = 255.0 Hz), 164.4 (d, *J* = 13.5 Hz), 147.5, 133.7, 132.6 (d, *J* = 10.5 Hz), 131.7, 129.7, 127.8, 127.7, 126.8, 126.1, 120.8, 118.8, 108.6 (d, *J* = 1.5 Hz), 107.8 (d, *J* = 22.5 Hz), 104.7 (d, *J* = 2.4 Hz); IR (neat): υ_{max} 1677, 1506, 1262, 1205, 1152, 808 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{17}H_{11}FO_3Na$ [M + Na]$^+$: 305.0590; found: 305.0598.

Phenyl 4-chloro-2-hydroxybenzoate, 2r, Scheme 2. The same general procedure was followed by using 4-chloro-2-phenoxybenzoic acid (25.0 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 96:4 hexane/ethyl acetate) afforded the desired product as a colourless oil, (14 mg, 57%). ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.62 (s, 1H), 8.02 (d, J = 9.0 Hz, 1H), 7.46-7.49 (m, 2H), 7.34 (t, J = 7.2 Hz, 1H), 7.21-7.23 (m, 2H), 7.09 (d, J = 2.4 Hz, 1H), 6.98 (dd, J = 8.4 Hz, 1.8 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 168.4, 162.7, 149.9, 142.3, 131.3, 129.7, 126.5, 121.5, 120.2, 118.0, 110.5; IR (neat): υ_{max} 3202, 1693, 1487, 1192, 1081, 771 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9ClO_3Na$ [M + Na]$^+$: 271.0138; found: 271.0151.

Phenyl 2-hydroxy-4-nitrobenzoate, 2s, Scheme 2. The same general procedure was followed by using 4-nitro-2-phenoxybenzoic acid (26.0 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a yellowish solid, (13.5 mg, 52%), mp 146-148 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 10.75 (s, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.90 (d, *J* = 1.8 Hz, 1H), 7.81 (dd, *J* = 8.4 Hz, 1.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 1H), 7.24-7.26 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.6, 162.5, 152.5, 149.6, 131.7, 129.8, 126.9, 121.3, 116.6, 113.7, 113.3; IR (neat): υ_{max} 1690, 1527, 1208, 781 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_9NO_5Na$ [M + Na]$^+$: 282.0378; found: 282.0354.

Phenyl 2-hydroxy-5-nitrobenzoate, 2t, Scheme 2. The same general procedure was followed by using 5-nitro-2-phenoxybenzoic acid (26.0 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a yellowish solid, (13 mg, 50%), mp 149-151 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 11.19 (s, 1H), 9.05 (d, *J* = 2.4 Hz, 1H), 8.43 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.26 (d, *J* = 7.8 Hz, 2H), 7.18 (d, *J* = 9.6 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.7, 166.6, 149.6, 140.2, 131.1, 129.8, 127.0, 126.9, 121.3, 118.9, 111.7; IR (neat): υ_{max} 1697, 1624, 1514, 1333, 1194, 751 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{13}H_{10}NO_5$ [M + H]$^+$: 260.0559; found: 260.0574.

4-Chlorophenyl 2-hydroxy-5-nitrobenzoate, 2u, Scheme 2. The same general procedure was followed by using 2-(4-chlorophenoxy)-5-nitrobenzoic acid (29.5 mg, 0.1 mmol, 1.0 equiv), silver nitrate (0.9 mg, 0.005 mmol), potassium persulfate (40.5 mg, 0.15 mmol, 1.5 equiv) and potassium trifluoroacetate (30.5 mg, 0.2 mmol, 2.0 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (13 mg, 45%), mp 148-150 °C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 11.07 (brs, 1H), 9.02 (d, *J* = 2.4 Hz, 1H), 8.44 (dd, *J* = 9.0 Hz, 3.0 Hz, 1H), 7.46-7.48 (m, 2H), 7.20-7.23 (m, 2H), 7.18 (d, *J* = 9.0 Hz, 1H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 167.4, 166.6, 148.0, 140.2, 132.4, 131.3, 129.9, 127.0, 122.7, 119.0, 111.4; IR (neat): υ_{max} 1696, 1482, 1340, 1196, 723 cm^{-1}; HRMS (EI, m/z) calcd. for $C_{13}H_8ClNO_5$ [M]$^+$: 295.0061; found: 295.0059.

General experimental procedure for the carboxyl radical-assisted 1,5-aryl migration through Smiles rearrangement using 2-(phenylthio)benzoic acids, Scheme 3.

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DOI: 10.1039/C6OB01758D

To an oven-dried 15 mL sealed tube, a mixture of 2-(phenylthio)benzoic acids (0.2 mmol, 1.0 equiv), silver nitrate (1.7 mg, 0.01 mmol) and potassium persulfate (81 mg, 0.3 mmol, 1.5 equiv) was taken and dry MeCN (4.0 mL) was added to it. After flushing with nitrogen, the vessel was sealed with a screw cap. The reaction mixture was allowed to stir for 36 h at 130 ^{o}C. After completion (as indicated by TLC), the reaction mixture was cooled to room temperature. Then the reaction mixture was poured into water (30 mL) and extracted with ethyl acetate (40 mL). The organic layer was washed with water (10 mL x 2) and brine (10 mL), dried over anhydrous Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography using ethyl acetate/hexane as eluent to afford the desired product.

Diphenyl 2,2'-disulfanediyldibenzoate, 4a, Scheme 3. The same general procedure was followed by using 2-(phenylthio)benzoic acid (46.0 mg, 0.2 mmol, 1.0 equiv), silver nitrate (1.7 mg, 0.01 mmol), potassium persulfate (81 mg, 0.3 mmol, 1.5 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (37.5 mg, 82%), mp 104-106 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.34 (dd, *J* = 7.8 Hz, 1.8 Hz, 2H), 7.86 (dd, *J* = 8.4 Hz, 0.6 Hz, 2H), 7.53 (td, *J* = 8.4 Hz, 1.8 Hz, 2H), 7.46-7.49 (m, 4H), 7.29-7.36 (m, 8H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.9, 150.6, 141.4, 133.7, 132.0, 129.6, 126.6, 126.14, 126.07, 125.7, 121.7; IR (neat): υ_{max} 1718, 1488, 1246, 1194, 1036, 743 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{26}H_{18}O_4S_2Na$ [M + Na]$^+$: 481.0544; found: 481.0548.

Diphenyl 2,2'-disulfanediylbis(4-fluorobenzoate), 4b, Scheme 3. The same general procedure was followed by using 4-fluoro-2-(phenylthio)benzoic acid (50.0 mg, 0.2 mmol, 1.0 equiv), silver nitrate (1.7 mg, 0.01 mmol), potassium persulfate (81 mg, 0.3 mmol, 1.5 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (33.5 mg, 68%), mp 122-124 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.37 (dd, *J* = 8.4 Hz, 6.0 Hz, 2H), 7.55 (dd, *J* = 9.6 Hz, 2.4 Hz, 2H), 7.45-7.48 (m, 4H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.26-7.27 (m, 4H), 7.02-7.05 (m, 2H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 166.1 (d, *J* = 256.5 Hz), 164.1, 150.4, 144.8 (d, *J* = 9.0 Hz), 134.8 (d, *J* = 9.0 Hz), 129.6, 126.3, 122.8 (d, *J* = 3.0 Hz), 121.7, 113.4 (d, *J* = 22.5 Hz), 113.1 (d, *J* = 27.0 Hz); IR (neat): υ_{max} 1720, 1578, 1481, 1250, 1189, 1075, 746 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{26}H_{16}F_2O_4S_2Na$ [M + Na]$^+$: 517.0356; found: 517.0336.

Bis(4-chlorophenyl) 2,2'-disulfanediyldibenzoate, 4c, Scheme 3. The same general procedure was followed by using 2-(4-chlorophenylthio)benzoic acid (53.0 mg, 0.2 mmol, 1.0 equiv), silver nitrate (1.7 mg, 0.01 mmol), potassium persulfate (81 mg, 0.3 mmol, 1.5 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (33 mg, 63%), mp 160-162 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.31 (dd, *J* = 7.8 Hz, 1.2 Hz, 2H), 7.85 (d, *J* = 8.4 Hz, 2H), 7.53 (td, *J* = 8.4 Hz, 1.2 Hz, 2H), 7.43 (d, *J* = 9.0 Hz, 4H), 7.35 (t, *J* = 7.2 Hz, 2H), 7.24 (d, *J* = 8.4 Hz, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 164.6, 149.0, 141.4, 133.9, 132.1, 131.6, 129.6, 126.2, 126.1, 125.8, 123.1; IR (neat): υ_{max} 1720, 1485, 1248, 1199, 1036, 736 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{26}H_{16}Cl_2O_4S_2Na$ [M + Na]$^+$: 548.9765; found: 548.9767.

Di-*p*-tolyl 2,2'-disulfanediyldibenzoate, 4d, Scheme 3. The same general procedure was followed by using 2-(*p*-tolylthio)benzoic acid (49.0 mg, 0.2 mmol, 1.0 equiv), silver nitrate (1.7 mg, 0.01 mmol), potassium persulfate (81 mg, 0.3 mmol, 1.5 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (29 mg, 60%), mp 147-149 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.32 (dd, *J* = 7.8 Hz, 1.2 Hz, 2H), 7.85 (dd, *J* = 8.4 Hz, 0.6 Hz, 2H), 7.51 (td, *J* = 8.4 Hz, 1.2 Hz, 2H), 7.34 (td, *J* = 8.4 Hz, 1.2 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 4H), 7.17 (d, *J* = 9.0 Hz, 4H), 2.40 (s, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 165.1, 148.3, 141.3, 135.8, 133.6, 132.0, 130.0, 126.7, 126.1, 125.6, 121.4, 20.9; IR (neat): υ_{max} 1717, 1504, 1247, 1193, 1031, 736 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{28}H_{22}O_4S_2Na$ [M + Na]$^+$: 509.0857; found: 509.0851.

Diphenyl 6,6'-disulfanediylbis(3-bromobenzoate), 4e, Scheme 3. The same general procedure was followed by using 5-bromo-2-(phenylthio)benzoic acid (62.0 mg, 0.2 mmol, 1.0 equiv), silver nitrate (1.7 mg, 0.01 mmol), potassium persulfate (81 mg, 0.3 mmol, 1.5 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (37.5 mg, 61%), mp 210-212 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.45 (d, *J* = 2.4 Hz, 2H), 7.68 (d, *J* = 9.0 Hz, 2H), 7.62 (dd, *J* = 9.0 Hz, 2.4 Hz, 2H), 7.47-7.50 (m, 4H), 7.34 (t, *J* = 7.2 Hz, 2H), 7.27-7.29 (m, 4H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.8, 150.3, 140.1, 136.6, 134.7, 129.6, 128.0, 127.7, 126.4, 121.5, 119.6; IR (neat): υ_{max} 1726, 1454, 1289, 1241, 1193, 1077 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{26}H_{16}Br_2O_4S_2Na$ [M + Na]$^+$: 636.8754; found: 636.8748.

Diphenyl 6,6'-disulfanediylbis(3-fluorobenzoate), 4f, Scheme 3. The same general procedure was followed by using 5-fluoro-2-(phenylthio)benzoic acid (50.0 mg, 0.2 mmol, 1.0 equiv), silver nitrate (1.7 mg, 0.01 mmol), potassium persulfate (81 mg, 0.3 mmol, 1.5 equiv). Column chromatography (SiO_2, eluting with 9:1 hexane/ethyl acetate) afforded the desired product as a white solid, (29.5 mg, 60%), mp 153-155 ^{o}C. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.02 (dd, *J* = 8.4 Hz, 2.4 Hz, 2H), 7.79 (dd, *J* = 9.0 Hz, 4.8 Hz, 2H), 7.45-7.48 (m, 4H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.23-7.27 (m, 6H); ^{13}C NMR (150 MHz, $CDCl_3$): δ 163.9 (d, *J* = 1.5 Hz), 160.8 (d, *J* = 246.0 Hz), 150.3, 136.2 (d, *J* = 3.0 Hz), 129.6, 128.0 (d, *J* = 7.5 Hz), 127.9 (d, *J* = 6.0 Hz), 126.4, 121.5, 121.2 (d, *J* = 22.5 Hz), 118.7 (d, *J* = 24.0 Hz); IR (neat): υ_{max} 1727, 1460, 1243, 1193, 1029, 739 cm^{-1}; HRMS (ESI, m/z) calcd. for $C_{26}H_{16}F_2O_4S_2Na$ [M + Na]$^+$: 517.0356; found: 517.0360.

Acknowledgements

RJ thanks DST, SERB, Govt. of India for Ramanujan fellowship; award no. SR/S2/RJN-97/2012 and extra mural research grant no. EMR/2014/000469 for financial support. AH thanks CSIR, for his fellowship.

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