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Synthesis of trifluoromethyl-substituted bi- and terphenyls by site-selective Suzuki–Miyaura reactions of various dihalogenated trifluoromethyl-benzene derivatives

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ABSTRACT

A variety of trifluoromethylated bi- and terphenyls were prepared by site-selective Suzuki–Miyaura cross-coupling reactions of various dihalogenated trifluoromethyl-substituted benzene derivatives. The reactions proceed with excellent site-selectivities.

1. Introduction

Palladium-catalyzed coupling reactions are effective synthetic tools for the formation of C–C bonds between nucleophilic and electrophilic substrates concluding into highly substituted arenes [1] which play a key role in total synthesis of bioactive compounds [2]. The regioselectivity of Pd-catalyzed cross-coupling reactions of polyhalogenated arenes has been broadly studied and can provide a versatile and feasible way for the design and synthesis of libraries of various functionalized scaffolds [3]. In particular, the Suzuki–Miyaura cross-coupling reaction has become one of the most widely used methods for the formation of carbon–carbon bonds because of the mild reaction conditions and compatibility with a broad range of functional groups [4]. The trifluoromethyl (CF_3) group is a significant structural motif in many pharmaceutically relevant molecules [5] having a wide range of interesting applications in medicinal and agricultural chemistry [6]. Various compounds with CF_3 motif have been reported to exhibit biologically interesting properties, such as antimalarial activity [7], antituberculosis agents (mafloquine) [8], and antiviral agents [9]. Similarly, boxidine is the most efficient nonsteroidal hypocholesteremic agent that is reported to inhibit the biosynthesis of cholesterol and lowers the cholesterol level (Fig. 1) [10]. Furthermore, fluorine is contained in many liquid crystals which include twisted nematic liquid crystal displays (TN-LCDs) and thin-film transistor liquid crystal displays (TFT-LCDs) (Fig. 1) [11].

Recently, we have reported a convenient synthesis of trifluoromethyl-substituted biaryls and teraryls by site-selective Suzuki–Miyaura reactions of 1,4-dibromo-2-trifluoromethylbenzene [12]. Herein, we report full details of these studies. We have greatly extended the scope of this approach and herein report what are, to the best of our knowledge, the first site-selective Suzuki–Miyaura cross-coupling reactions of 2,4-dichloro-1-(trifluoromethyl)benzene, 1-bromo-4-chloro-2-(trifluoromethyl)-benzene and 4-bromo-1-chloro-2-(trifluoromethyl)benzene. These reactions provide a convenient access to a great variety of trifluoromethylated arenes from simple starting materials. The products are pharmacologically relevant and are not readily available by other methods.

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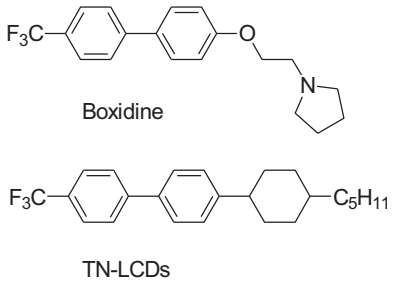


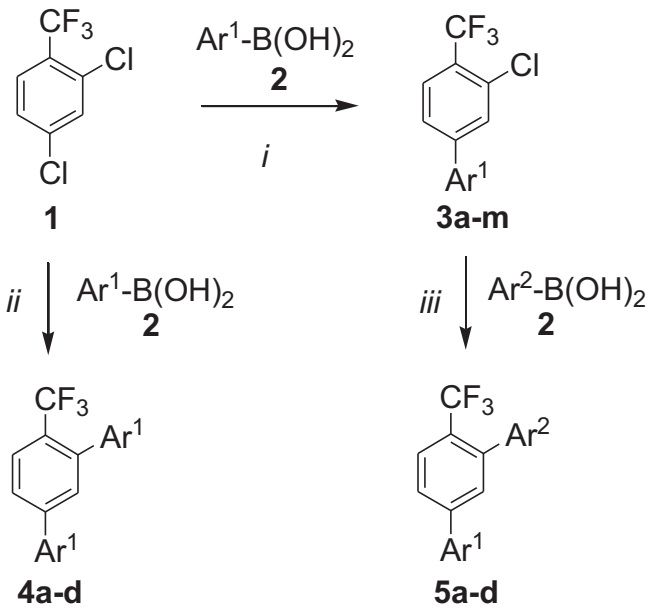
Fig. 1. Important trifluoromethyl-substituted arenes.

2. Results and discussion

2.1. 2,4-Dichloro-1-(trifluoromethyl)benzene

The Suzuki–Miyaura cross-coupling reactions of commercially available 2,4-dichloro-1-(trifluoromethyl)benzene (**1**) with 1.3 equiv. of arylboronic acids **2a**–**m** afforded the biphenyls **3a**–**m** in moderate to good yields (Scheme 1, Table 1) with excellent site-selectivity. The best yields were obtained using 1.3 equiv. of the arylboronic acid, $Pd(PPh_3)_4$ (0.05 equiv.) as the catalyst and 2 M aq. K_2CO_3 as the base (1,4-dioxane, 80 °C, 6 h). The formation of the other regioisomer was not observed. The low yield of **3d** can be explained by the steric hindrance of 2,6-dimethylphenylboronic acid. The low yields of **3j**–**m** can be explained by the presence of electron-withdrawing substituents Cl, F or CF_3 located at the phenylboronic acids. These substituents result in a decrease of the nucleophilicity of the boronic acid. In these reactions, the conversion was not complete and also some decomposition was observed. The structures of all products were established by NMR, MS and IR data. The structure of **3c** (Fig. 2) was independently confirmed by X-ray crystal structure analysis [13]. As expected, the two aryl groups are slightly twisted out of plane, due to steric reasons.

The Suzuki–Miyaura reactions of 2,4-dichloro-1-(trifluoromethyl)benzene (**1**) with 2.5 equiv. of arylboronic acids **2a**–**c**,**k** gave 2,4-diaryl-1-(trifluoromethyl)benzene derivatives **4a**–**d** in moderate yields. The reactions were carried out at 100 °C in 1,4-dioxane using 2.5 equiv. of the arylboronic acid, 5 mol% of $Pd(PPh_3)_4$ and an aqueous solution of K_2CO_3 (2 M) as the base (Scheme 1, Table 1). It is not surprising that the yields of **4a**–**d** are lower than the yields of mono-arylated products **3**, because two C–C bonds are formed. In case of **4d**, an electron poor (less nucleophilic) arylboronic acid was employed. In addition, the steric hindrance exerted by the CF_3 group might result in a decrease of the yield.



Scheme 1. Synthesis of **3a**–**m**, **4a**–**d**, and **5a**–**d**. Reagents and conditions: *i*, **1** (1.0 equiv.), **2** (1.3 equiv.), $Pd(PPh_3)_4$ (5 mol%), 2 M K_2CO_3, 1,4-dioxane, 80 °C, 6 h; *ii*, **1** (1.0 equiv.), Ar^1-$B(OH)_2$ (2.5 equiv.), $Pd(PPh_3)_4$ (5 mol%), 2 M K_2CO_3, 1,4-dioxane, 100 °C, 8 h; *iii*, **3c** (1.0 equiv), Ar^2-$B(OH)_2$ (1.3 equiv), $Pd(PPh_3)_4$ (5 mol%), aq. K_2CO_3 (2 M), 1,4-dioxane, 90 °C, 8 h.

The Suzuki–Miyaura reaction of 3-chloro-4′-methyl-4-(trifluoromethyl)biphenyl (**3c**) with 1.3 equiv. of arylboronic acids **2e**,**f**,**k**,**n** afforded the disubstituted products **5a**–**d**, containing two different aryl groups, in moderate to good yields (except for **5c**). The relatively low yields can be again explained by steric effects. The reactions were carried out in 1,4-dioxane using $Pd(PPh_3)_4$ (5 mol%) and an aqueous solution of K_2CO_3 (2 M) at 90 °C for 8 h (Scheme 1, Table 1). The reactions were carried out under optimized conditions as shown in Table 3 (vide infra). The use of other solvents (rather than dioxane) did not result in an increase of the yield.

2.2. 1,4-Dibromo-2-trifluoromethylbenzene

The Suzuki–Miyaura reaction of commercially available 1,4-dibromo-2-trifluoromethylbenzene (**6**) with arylboronic acids **2**

Table 1
Synthesis of **3a**–**m**, **4a**–**d**, and **5a**–**d**.

2,3	4	5	Ar^1	Ar^2	%[a] (**3**)	%[a] (**4**)	%[a] (**5**)
a	**a**		2-MeC_6H_4	–	93	57	
b	**b**		3-MeC_6H_4	–	95	39	
c	**c**	**a**	4-MeC_6H_4	3,5-$Me_2C_6H_3$	97	60	64
		b	4-MeC_6H_4	4-EtC_6H_4			40
		c	4-MeC_6H_4	4-FC_6H_4			25
		d	4-MeC_6H_4	4-(MeO)C_6H_4			59
d			2,6-$Me_2C_6H_3$	–	36		
e			3,5-$Me_2C_6H_3$	–	72		
f			4-EtC_6H_4	–	49		
g			2-(MeO)C_6H_4	–	56		
h			2,3-$(MeO)_2C_6H_3$	–	74		
i			2,3,4-$(MeO)_3C_6H_2$	–	60		
j			2-ClC_6H_4	–	47		
k	**d**		4-FC_6H_4	–	46		
l			4-$(CF_3)C_6H_4$	–	35		
m			3-$(CF_3)C_6H_4$	–	32		

[a] Yields of isolated products.

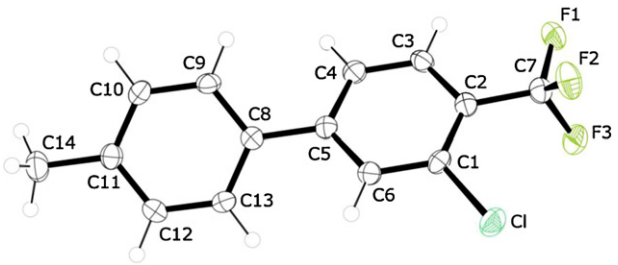
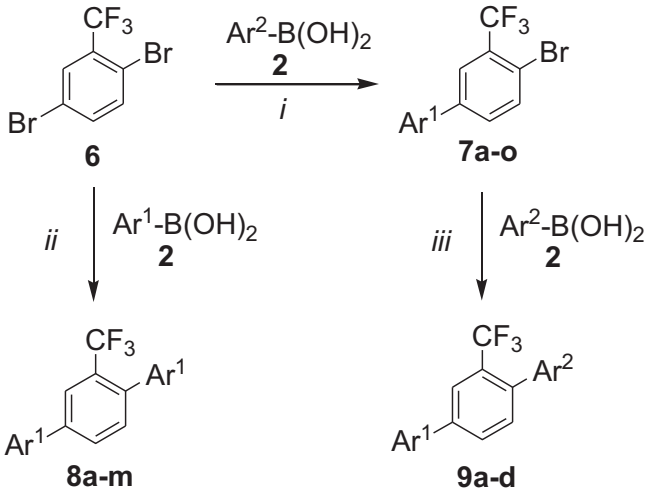


Fig. 2. ORTEP view of the crystal structure of **3c**.



Scheme 2. Synthesis of **7a–o**, **8a–m** and **9a–d**. *Conditions: i*, **6** (1.0 equiv.), **2** (1.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (H_2O, 2 M), 1,4-dioxane, 70 °C, 8 h; *ii*, **6** (1.0 equiv.), **2** (2.5 equiv.), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (H_2O, 2 M), dioxane, 90 °C, 8 h; *iii*, **7** (1.0 equiv.), **2** (1.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), K_2CO_3 (H_2O, 2 M), dioxane, 80 °C, 8 h.

(1.0 equiv.) afforded the 4-aryl-1-bromo-2-trifluoromethylbenzenes **7a–o** in 79–94% yields (Scheme 2, Table 2). All reactions proceeded with very good site-selectivity in favor of position 4. The products were pure after chromatography. Small amounts (approx. 5–10%) of diarylated products were detected in the crude product mixture (by ^1H NMR) before the separation. Very good yields were

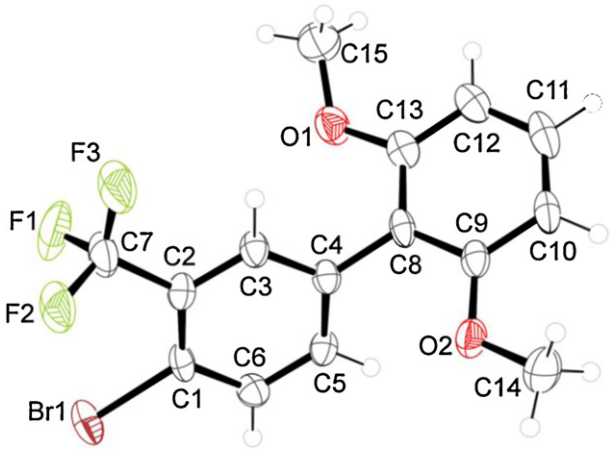


Fig. 3. Crystal structure of **7n**.

obtained for products derived from both electron rich and poor arylboronic acids. The best yields were obtained using exactly 1.0 equiv. of the arylboronic acid, $Pd(PPh_3)_4$ (5 mol%) as the catalyst, and K_2CO_3 (2 M aqueous solution) as the base. The temperature also played an important role and was adjusted to 70 °C (1,4-dioxane, 8 h) (Table 3). The employment of other solvents or bases resulted in the formation of only trace amounts of product or no conversion at all. The increase of the temperature resulted in the formation of mixtures, due to the formation of significant amounts of terphenyls. The reaction time had only a small effect on the yields. The structure of **7n** was independently confirmed by X-ray crystal structure analysis (Fig. 3) [13]. The aryl group are twisted out of plane, due to the steric effect of the methoxy groups.

The Suzuki–Miyaura reaction of **6** with 2.5 equiv. of various arylboronic acids **2** afforded the 2,5-diaryl-1-(trifluoromethyl)-benzene derivatives **8a–m** in good yields (Scheme 2, Table 2). The reactions had to be carried out at 90 °C instead of 70 °C to ensure a complete conversion. Very good yields were again obtained for products derived from both electron rich and poor arylboronic acids. The structure of **8l** was independently confirmed by X-ray crystal structure analysis (Fig. 4) [13]. The aryl groups are again twisted out of plane.

Table 2
Synthesis of **7a–o**, **8a–m** and **9a–d**.

7	8	9	Ar^1	Ar^2	% (**7**)[a]	% (**8**)[a]	% (**9**)[a]
a	**a**		2-MeC_6H_4	–	87	85	
	b		3-MeC_6H_4	–		86	
	c		4-MeC_6H_4	–		85	
b	**d**		3,5-$Me_2C_6H_3$	–	83	87	
c	**e**	**a**	4-EtC_6H_4	3,4-$(MeO)_2C_6H_3$	87	87	88
	f		2,3-$(MeO)_2C_6H_3$	–		87	
d	**g**		2,3,4-$(MeO)_3C_6H_2$	–	82	91	
	h		3-$(CF_3)C_6H_4$	–		82	
	i		4-$(MeO)C_6H_4$	–		93	
e			2-ClC_6H_4	–	84		
f			4-FC_6H_4	–	80		
g	**j**		C_6H_5	–	82	84	
h			3-ClC_6H_4	–	86		
i			3-$(Vinyl)C_6H_4$	–	84		
j			4-*t*-BuC_6H_4	–	88		
k			4-ClC_6H_4	–	83		
l		**b**	2-Naphthyl	3,4-$(MeO)_2C_6H_4$	79		85
m	**k**		2,5-$(MeO)_2C_6H_3$	–	92	79	
n			2,6-$(MeO)_2C_6H_3$	–	87		
o	**l**	**c**	3,4-$(MeO)_2C_6H_3$	4-FC_6H_4	94	95	80
		d	3,4-$(MeO)_2C_6H_3$	3,5-$Me_2C_6H_4$			86
	m		3-$(MeO)C_6H_4$	–		89	

[a] Yields of isolated products.

Table 3
Optimization of the synthesis of **7j** and **7o** ($Pd(PPh_3)_4$ was used as the catalyst).

Entry	Solvent	Base	T [°C]	t [h]	**7o**	**7j**
1	Dioxane	2 M K_2CO_3	60	8	–[a]	–[a]
2	THF	2 M K_2CO_3	60	8	–[a]	–[a]
3	DME	2 M K_2CO_3	70	8	–[a]	–[a]
4	Dioxane	3eq. Cs_2CO_3	70	8	Traces	Traces
5	Dioxane	3 eq. K_3PO_4	70	8	Traces	Traces
6	Toluene	3 eq. K_3PO_4	70	8	Traces	Traces
7	Toluene	2 M K_2CO_3	70	8	Traces	Traces
8	Toluene	2 M K_2CO_3	90	8	Traces	Traces
9	Dioxane	2 M K_2CO_3	90	6	–[b]	–[b]
10	Dioxane	2 M K_2CO_3	80	6	–[b]	–[b]
11	THF	2 M K_2CO_3	75	6	–[c]	–[c]
12	Dioxane	2 M K_2CO_3	70	3	87%	82%
13	Dioxane	2 M K_2CO_3	70	8	94%	88%

[a] No conversion;
[b] Unseparable mixture of mono- and diarylated products.
[c] Unseparable mixture, mainly diarylated product.

Table 4
Synthesis of 1-aryl-4-chloro-2-trifluoromethylbenzenes **11a–i**.

11	**2**	Ar	% (**11**)[a]
a	**a**	2-MeC_6H_4	33
b	**c**	4-MeC_6H_4	91
c	**i**	2,3,4-$(MeO)_3C_6H_2$	42
d	**k**	4-FC_6H_4	73
e	**m**	3-$(CF_3)C_6H_4$	69
f	**n**	4-$(MeO)C_6H_4$	61
g	**o**	C_6H_5	56
h	**r**	4-*t*BuC_6H_4	46
i	**w**	3,4-$(MeO)_2C_6H_3$	22

[a] Yields of isolated products.

The bromide group of biaryls **7** easily undergoes Suzuki–Miyaura reactions. The reaction of **7c**,**l**,**o** with arylboronic acids afforded terphenyls **9a–d** in high yields (Scheme 2, Table 2). A one-pot synthesis of **9a–d** starting with substrates **6** also proved to be possible (sequential addition of two different boronic acids). However, the yields proved to be lower as compared to the stepwise procedure. Therefore, this strategy was not further studied. The structure of **9b** was independently confirmed by X-ray crystal structure analysis (Fig. 5) [13]. The aryl groups are again twisted out of plane.

2.3. 1-Bromo-4-chloro-2-(trifluoromethyl)benzene and 4-bromo-1-chloro-2-(trifluoromethyl)-benzene

The Suzuki–Miyaura reaction of commercially available 1-bromo-4-chloro-2-(trifluoromethyl)benzene (**10**) with arylboronic acids **2** (1.0 equiv.) afforded the 1-aryl-4-chloro-2-(trifluoromethyl)

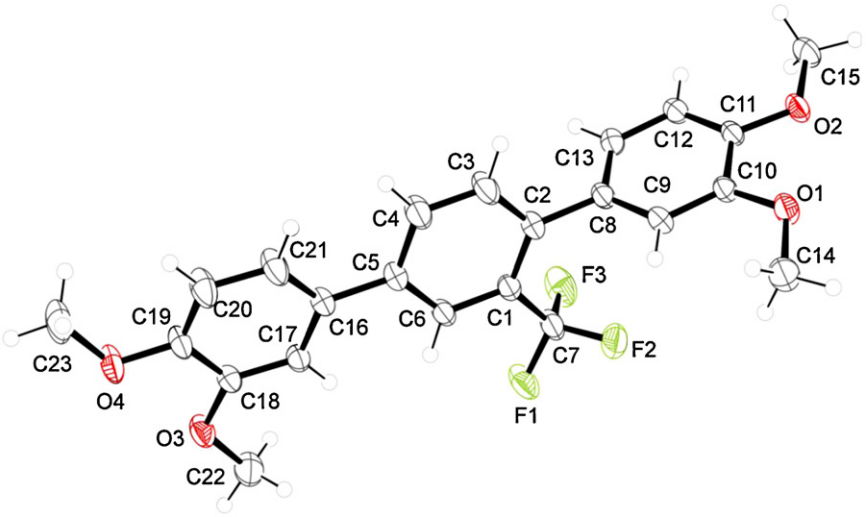


Fig. 4. Crystal structure of **8l**.

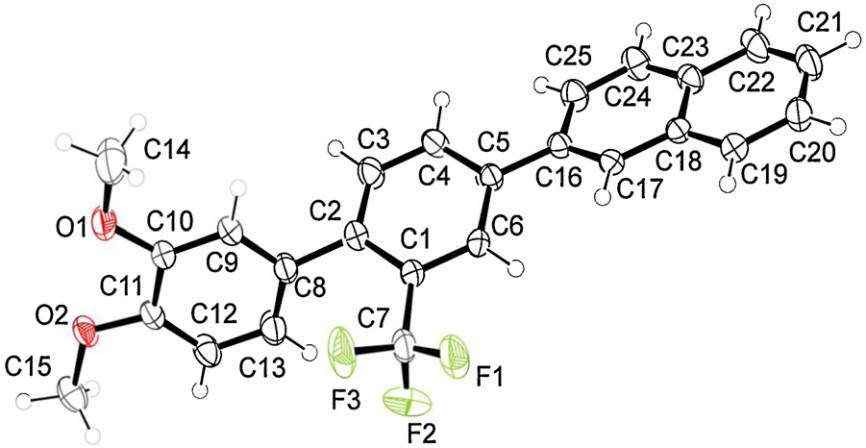
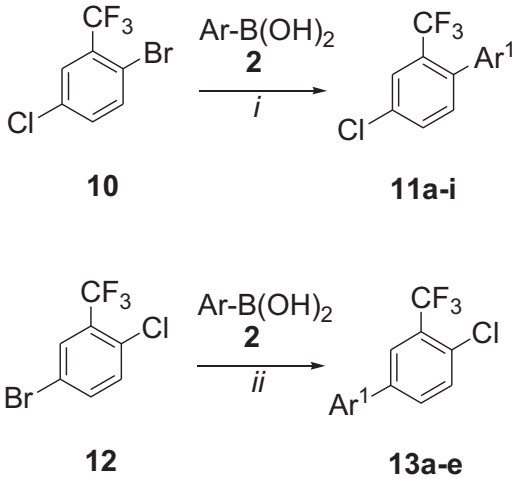


Fig. 5. Crystal structure of **9b**.

Table 5
Synthesis of 4-aryl-1-chloro-2-trifluoromethylbenzenes **13a–e**.

13	2	Ar	% (**13**)[a]
a	**a**	2-MeC_6H_4	96
b	**c**	4-MeC_6H_4	87
c	**e**	3,5-$Me_2C_6H_3$	37
d	**r**	4-$tBuC_6H_4$	87
e	**x**	4-BrC_6H_4	45

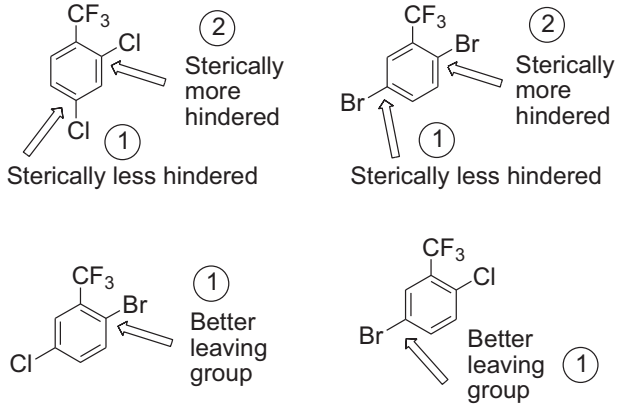
[a] Yields of isolated products.



Scheme 3. Synthesis of **11a–i** and **13a–e**. *Conditions: i*, **10** (1.0 equiv.), **2** (1.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4, 1,4-dioxane, 75 °C, 4 h; *ii*, **12** (1.0 equiv.), **2** (1.0 equiv.), $Pd(PPh_3)_4$ (5 mol%), K_3PO_4, 1,4-dioxane, 70 °C, 5 h.

benzenes **11a–i** in 22–91% yields (Scheme 3, Table 4). All reactions proceeded with very good chemoselectivity in favor of position 1. The best yields were obtained using exactly 1.0 equiv. of the arylboronic acid, $Pd(PPh_3)_4$ (5 mol%) as the catalyst, and K_3PO_4 as the base (1,4-dioxane, 75 °C, 4 h) (Table 4).

The Suzuki–Miyaura reaction of commercially available 4-bromo-1-chloro-2-(trifluoromethyl)benzene (**12**) with arylboronic acids **2** (1.0 equiv.) afforded the 4-aryl-1-chloro-2-(trifluoromethyl)benzenes **13a–e** in 37–96% yields (Scheme 3, Table 5). All reactions proceeded with very good chemoselectivity in favor of position 4. The best yields were obtained using exactly 1.0 equiv. of the arylboronic acid, $Pd(PPh_3)_4$ (5 mol%) as the catalyst, and K_3PO_4 as the base (1,4-dioxane, 70 °C, 5 h).



Scheme 4. Possible explanation for the site-selectivity of cross-coupling reactions of **1**.

3. Conclusion

The site-selective formation of **3a–m** can be explained by steric and electronic reasons. Generally, Suzuki–Miyaura reactions of polyhalogenated arenes proceed site-selectively by initial oxidative addition of the arylboronic acid at the more electron-deficient and less sterically-hindered position (Scheme 4) [3]. Position 4 of 2,4-dichloro-1-(trifluoromethyl)benzene **1** is sterically less hindered as compared to position 2 which is located close to the CF_3 moiety. The site-selective formation of **7a–o** can be explained as follows: Carbon atom C-4 is sterically less hindered than carbon C-1, due to its location *meta* to the CF_3 group. Therefore, the first oxidative addition occurs at position 4. The selective formation of **11a–i** and **13a–e** is based on the fact that bromine is a better leaving group than chlorine. The reactivity order of the Suzuki reaction is generally ArI > ArBr > ArOTf ≫ ArCl [14].

In conclusion, we have synthesized mono- and diarylated trifluoromethylbenzene derivatives by site-selective Suzuki–Miyaura cross-coupling reactions of 2,4-dichloro-1-(trifluoromethyl)benzene, 1,4-dibromo-2-trifluoromethyl-benzene, 1-bromo-4-chloro-2-(trifluoromethyl)benzene and 4-bromo-1-chloro-2-(trifluoromethyl)benzene. These reactions provide a convenient approach to trifluoromethyl-substituted bi- and terphenyls which are not readily available by other methods.

4. Experimental

4.1. General

Reactions were carried out under inert atmosphere (Argon). Solvents for reactions were dried and distilled by standard methods or purchased from Merck®, Aldrich®, Acros Organics®, and others whenever exclusion of water was desired. Solvents for liquid chromatography and extraction were always distilled prior to use and partly reused after fractional distillation (n-heptane, ethyl acetate). Bruker AC 250, Bruker ARX 300, Bruker ARX 500. For NMR characterization the one-dimensional ^1H NMR, proton-decoupled ^{13}C NMR, and DEPT 135 spectra were collected. If necessary other techniques (NOESY, COSY, HMQC, and HMBC) were applied as well. All NMR spectra presented in this work, were collected in DMSO-d_6 and $CDCl_3$solution. All chemical shifts were given in ppm. References (^1H NMR): TMS (δ = 0.00) or residual $CHCl_3$ (δ = 7.26) were taken as internal standard. References (^{13}C NMR): TMS (δ = 0.0) or residual $CHCl_3$ (δ = 77.0) were taken as internal standard. Multiplicities are given as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = Multiplet, br = broad signal. More complex coupling patterns are represented by combinations of the respective symbols. For example, td indicates a triplet of doublets with the larger coupling constant associated with the first symbol (here: triplet). Infrared Spectroscopy (IR): Nicolet 205 FT-IR, Nicolet Protége 460 FT-IR Peaks are given the following assignments: w = weak, m = medium, s = strong, br = broad. Mass Spectrometry (MS): AMD MS40, Varian MAT CH 7, MAT 731 (EI, 70 eV), Intecta AMD 402 (EI, 70 eV and CI), Finnigan MAT 95 (CI, 200 eV). High Resolution Mass Spectrometry (HRMS): Varian MAT 311, Intecta AMD 402. Elemental Analysis: LECO CHNS-932 Thermoquest Flash EA 1112. Melting Points: Micro heating table HMK 67/1825 Kuestner (Büchi Apparatus). Leitz Labolux 12 Pol with heating table Mettler FP 90. Melting points are uncorrected. Thin Layer Chromatography (TLC): Merck Kieselgel 60 F254 on aluminum foil from Macherey-Nagel. Detection was carried out under UV light at 254 nm and 365 nm. As colorizing reagent the following mixtures were used: 1–2/100 p-anisaldehyde or vanillin, 10/100 glacial acetic acid, 5/100 sulphuric acid, 83–84/100 methanol. Column chromatography: Column chromatography was performed with Merck Silica Gel 60 or Macherey-Nagel Silica

Gel 60 (0.063–0.200 mm, 70–230 mesh). The finer Merck Silica Gel 60 (0.040–0.063 mm, 230–400 mesh) was chosen when appropriate.

4.2. General procedure for the synthesis of **3a–m**

A 1,4-dioxane solution (8 mL) of **1** (1.0 mmol), arylboronic acid **2** (1.3 equiv.), 2 M K_2CO_3 (1 mL per cross coupling), and $Pd(PPh_3)_4$ (5 mol%) was heated at 80 °C for 6 h. After cooling to room temperature, H_2O was added and the reaction mixture was extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), filtered and concentrated in vacuo. The residue was purified by column chromatography (pure n-heptane).

4.2.1. 3′-Chloro-2-methyl-4′-(trifluoromethyl)biphenyl (**3a**)

Starting with **1** (0.215 g, 1 mmol), **2a** (0.176 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-dioxane (8 mL), **3a** was isolated as colorless oil (0.251 g, 93%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.31 (s, 3H, CH_3), 7.21–7.24 (m, 1H), 7.28–7.37 (m, 4H), 7.52 (s, 1H, ArH), 7.76 (d, ^3J = 7.93 Hz, 1H, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$), δ = 20.3 (CH_3), 123.1 (CF_3, q, $^1J_{CF}$ = 272.89 Hz), 126.1 (CH), 126.8 (C, q, $^2J_{CF}$ = 31.91 Hz), 127.3 (CH, q, $^3J_{CF}$ = 4.95 Hz), 127.6 (CH), 128.5 (CH), 129.4 (CH), 130.7 (CH), 132.1 (CH), 135.2 (2C), 139.1 (C), 147.2 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.27 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3214 (w), 3063 (w), 3021 (w), 2956 (w), 2926 (w), 2865 (w), 2741 (w), 1921 (w), 1804 (w), 1609 (m), 11,602 (m), 1556 (m), 1504 (w), 1481 (w), 1455 (w), 1383 (m), 1312 (s), 1280 (w), 1248 (m), 1173 (m), 1126 (s), 1102 (s), 1054 (w), 1027 (s), 964 (w), 945 (w), 892 (m), 867 (w), 838 (s), 786 (w), 760 (s), 738 (m), 724 (m), 681 (m), 661 (w), 641 (m), 599 (w), 594 (w), 565 (w), 551 (w), 536 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 270 (M^+, 100), 235 (11), 215 (27), 165 (80), 139 (3), 115 (3), 91 (3), 69 (5), 63 (3), 39 (2); HRMS (EI) calcd for $C_{14}H_{10}ClF_3$ [M^+]: 270.04176 found 270.042298.

4.2.2. 3-Chloro-3′-methyl-4-(trifluoromethyl)biphenyl (**3b**)

Starting with **1** (0.215 g, 1 mmol), **2b** (0.176 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3b** was isolated as colorless oil (0.257 g, 95%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.48 (s, 3H, CH_3), 7.27–7.30 (m, 1H), 7.39–7.43 (m, 3H), 7.56–7.59 (m, 1H), 7.75–7.78 (m, 2H); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 21.4 (CH_3), 123.1 (CF_3, q, $^1J_{CF}$ = 272.83 Hz), 124.3 (CH), 125.2 (CH), 126.8 (C, q, $^2J_{CF}$ = 31.59 Hz), 127.8 (CH, q, $^3J_{CF}$ = 5.04 Hz), 127.9 (CH), 129.0 (CH), 129.6 (CH), 129.9 (CH), 132.6 (C, q, $^4J_{CF}$ = 2.29 Hz), 138.2 (C), 138.9 (2C), 146.3 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.19 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3214 (w), 3027 (w), 2952 (w), 2923 (w), 2864 (w), 2736 (w), 1922 (w), 1883 (w), 1853 (w), 1791 (w), 1698(w), 1674 (w), 1605 (m), 1557 (m), 1503 (m), 1480 (w), 1456 (w), 1427 (w), 1377 (m), 1312 (s), 1299 (w), 1273(w), 1254 (w), 1175 (m), 1126 (s), 1104 (s), 999 (w), 961 (w), 910 (w), 880 (m), 835 (s), 781 (s), 736 (m), 721 (w), 698 (m), 684 (w), 633 (m), 596 (w), 569 (w), 540 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 270 (M^+, 100), 251 (5), 235 (12), 215 (9), 201 (6), 183 (2), 165 (33), 125 (1), 91 (2), 69 (2), 39 (1); HRMS (EI) calcd for $C_{14}H_{10}ClF_3$ [M^+]: 270.04176 found 270.041311.

4.2.3. 3-Chloro-4′-methyl-4-(trifluoromethyl)biphenyl (**3c**)

Starting with **1** (0.215 g, 1 mmol), **2c** (0.176 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3c** was isolated as white solid (0.262 g, 97%); mp 55–57 °C. ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.44 (s, 3H, CH_3), 7.31 (d, ^3J = 8.49 Hz, 2H, ArH), 7.50 (d, ^3J = 8.12 Hz, 2H, ArH), 7.56 (d, ^3J = 8.12 Hz, 1H, ArH), 7.74 (d, ^3J = 8.69 Hz, 2H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 21.2 (CH_3), 123.1 (CF_3, q, $^1J_{CF}$ = 275.65 Hz), 124.9 (CH), 126.6 (C, q, $^2J_{CF}$ = 31.36 Hz), 127.0 (2CH), 127.9 (CH, q, $^3J_{CF}$ = 5.50 Hz), 129.6 (CH), 129.9 (2CH), 132.6 (C, q, $^3J_{CF}$ = 1.65 Hz), 135.4 (C), 138.9 (C), 146.1 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.19 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3070 (w), 3040 (w), 3029 (m), 2921 (m), 2858 (w), 2739 (w), 1916 (w), 1797 (w), 1769 (w), 1602 (s), 1551 (m), 1520 (w), 1489 (m), 1413 (w), 1379 (m), 1356 (w), 1313 (s), 1290 (w), 1270 (w), 1254 (w), 1214 (w), 1187 (w), 1171 (m), 1121 (s), 1105 (s), 1040 (w), 1026 (m), 1014 (w), 959 (m), 904 (w), 887 (m), 845 (w), 836 (m), 808 (s), 785 (m), 740 (m), 717 (w), 676 (m), 643 (w), 624 (w), 588 (m), 561 (m), 547 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 270 (M^+, 100), 235 (14), 215 (8), 165 (32), 139 (2), 99 (1), 87 (1), 75 (1), 63 (1), 51 (1), 39 (1); HRMS (EI) calcd for $C_{14}H_{10}ClF_3$ [M^+]: 270.04176 found 270.041119.

4.2.4. 3′-Chloro-2,6-dimethyl-4′-(trifluoromethyl)biphenyl (**3d**)

Starting with **1** (0.215 g, 1 mmol), **2d** (0.194 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3d** was isolated as colorless oil (0.102 g, 36%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.95 (s, 6H, $2CH_3$), 7.03–7.15 (m, 4H, ArH), 7.25 (s, 1H, ArH), 7.66 (d, ^3J = 7.93 Hz, 1H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 20.7 ($2CH_3$), 123.0 (CF_3, q, $^1J_{CF}$ = 272.83 Hz), 126.8 (C, q, $^2J_{CF}$ = 31.59 Hz), 127.60 (2CH), 127.64 (CH), 127.7 (CH, q, $^3J_{CF}$ = 5.49 Hz), 128.0 (CH), 132.0 (CH), 132.4 (C, q, $^3J_{CF}$ = 1.83 Hz), 135.5 (2C), 138.9 (C), 146.6 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.28 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3064 (w), 3022 (w), 2953 (w), 2923 (w), 2855 (w), 2739 (w), 1928 (w), 1858 (w), 1787 (w), 1607 (m), 1559 (m), 1500 (w), 1464 (m), 1445 (w), 1384 (m), 1312 (s), 1285 (w), 1251 (m), 1240 (w), 1173 (m), 1126 (s), 1101 (s), 1054 (w), 1028 (s), 988 (w), 964 (w), 919 (w), 889 (m), 834 (s), 769 (s), 758 (w),752 (w), 718 (m), 667 (m), 646 (m), 595 (w), 566 (m), 553 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 284 (M^+, 100), 269 (25), 249 (73), 234 (28), 180 (22), 165 (38), 152 (4), 139 (1), 105 (1), 89 (2), 39 (1); HRMS (EI) calcd for $C_{15}H_{12}ClF_3$ [M^+]: 284.05741 found 284.056674.

4.2.5. 3-Chloro-3′,5′-dimethyl-4-(trifluoromethyl)biphenyl (**3e**)

Starting with **1** (0.215 g, 1 mmol), **2e** (0.194 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3e** was isolated as colorless oil (0.204 g, 72%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.43 (s, 6H, $2CH_3$), 7.11 (s, 1H, ArH), 7.22 (s, 2H, ArH), 7.56 (d, ^3J = 8.49 Hz, 1H, ArH), 7.73–7.76 (m, 2H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 21.3 ($2CH_3$), 123.1 (CF_3, q, $^1J_{CF}$ = 272.83 Hz), 125.1 (2CH), 125.2 (CH), 126.7 (C, q, $^2J_{CF}$ = 31.58 Hz), 127.7 (CH, q, $^3J_{CF}$ = 5.04 Hz), 129.9 (CH), 130.4 (CH), 132.5 (C, q, $^3J_{CF}$ = 1.83 Hz), 138.2 (C), 138.7 (2C), 146.4 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.19 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3016 (w), 2922 (w), 2856 (w), 1602 (m), 1562 (w), 1554 (m), 1501 (w), 1493 (w), 1479 (w), 1467 (w), 1443 (w), 1432 (w), 1409 (w), 1379 (w), 1315 (s), 1264 (w), 1212 (w), 1177 (m), 1132 (s), 1108 (m), 1040 (w), 1026 (m), 997 (w), 963 (w), 895 (w), 885 (w), 853 (w), 831 (m), 775 (w), 723 (w), 698 (w), 667 (w), 661 (w), 636 (w), 540 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 284 (M^+, 100), 269 (23), 249 (11), 234 (14), 165 (18), 152 (2), 105 (1), 51 (1); HRMS (EI) calcd for HRMS (EI) calcd for $C_{15}H_{12}ClF_3$ [M^+]: 284.05741 found 284.057528.

4.2.6. 3-Chloro-4′-ethyl-4-(trifluoromethyl)biphenyl (**3f**)

Starting with **1** (0.215 g, 1 mmol), **2f** (0.195 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3f** was isolated as colorless oil (0.14 g, 49%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.21 (t, J = 7.55 Hz, 3H, CH_3), 2.63 (q, J = 7.55 Hz, J = 15.11 Hz, 2H), 7.22 (d, ^3J = 8.50 Hz, 2H, ArH), 7.41–7.48 (m, 3H), 7.63–7.66 (m, 2H); ^{13}C NMR (75.46 MHz, $CDCl_3$), δ = 15.5 (CH_3), 28.6 (–CH_2–), 123.1 (CF_3, q, $^1J_{CF}$ = 272.90 Hz), 124.9 (CH), 127.0 (C, q, $^2J_{CF}$ = 34.66 Hz), 127.1 (2CH), 127.9 (CH, q, $^3J_{CF}$ = 5.50 Hz), 128.7 (2CH), 129.7 (CH), 132.6 (C, q, $^3J_{CF}$ = 1.65 Hz), 135.6 (C), 145.2 (C), 146.1 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.19 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3026 (w), 2966 (w), 2932

(w), 2874 (m), 1907 (w), 1579 (w), 1605 (m), 1576 (w), 1552 (m), 1523 (w), 1488 (w), 1461 (w), 1455 (w), 1420 (m), 1382 (m), 1312 (s), 1293 (w), 1254 (w), 1175 (m), 1127 (s), 1103(s), 1059 (w), 1042 (w), 1025 (m), 1015 (m), 962 (w), 887 (m), 820 (s), 772 (w), 736 (m), 699 (w), 674 (m), 644(w), 624 (w), 594 (m), 561 (m), 532 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 284 (M^+, 50), 271 (32), 269 (100), 249 (4), 233 (7), 165 (19), 117 (1), 77 (1), 63 (1), 39 (1); HRMS (EI) calcd for $C_{15}H_{12}ClF_3$ [M^+]: 284.05741 found 284.056982.

*4.2.7. 3′-Chloro-2-methoxy-4′-(trifluoromethyl)biphenyl (**3g**)*

Starting with **1** (0.215 g, 1 mmol), **2g** (0.198 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3g** was isolated as heavy oil (0.16 g, 56%). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.75 (s, 3H, OCH_3), 6.91–6.99 (m, 2H, ArH), 7.21 (dd, *J* = 7.55 Hz, *J* = 1.89 Hz, 1H, ArH), 7.28–7.34 (m, 1H, ArH), 7.42–7.45 (m, 1H, ArH), 7.60–7.64 (m, 2H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 55.5 (OCH_3), 111.4 (CH), 121.0 (CH), 123.1 (CF_3, q, $^1J_{CF}$ = 272.83 Hz), 126.5 (C, q, $^2J_{CF}$ = 31.59 Hz), 127.0 (CH, q, $^3J_{CF}$ = 5.49 Hz), 127.7 (CH, C), 130.0 (CH), 130.6 (CH), 131.7 (C, q, $^3J_{CF}$ = 1.83 Hz), 132.3 (CH), 143.7 (C), 156.4 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.25 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3069 (w), 3002 (w), 2941 (w), 2836 (w), 1605 (m), 1581 (w), 1555 (w), 1504 (m), 1482 (m), 1463 (m), 1435 (m), 1386 (m), 1311 (s), 1277 (w), 1251 (m), 1238 (m), 1175 (m), 1120 (s), 1103 (s), 1056 (w), 1025 (s), 1003 (w), 963 (w), 935 (w), 889 (m), 851 (w), 833 (m), 784 (m), 748 (s), 731 (w), 682 (m), 635 (m), 615 (w), 593 (w), 574 (w), 566 (w), 554 (m); GC–MS (EI, 70 eV): *m*/*z* (%): 286 (M^+, 100), 267 (7), 251 (19), 236 (59), 217 (13), 202 (21), 152 (4), 139 (12), 118 (19), 99 (3), 87 (7), 39 (2); HRMS (EI) calcd for $C_{14}H_{10}ClF_3O$ [M^+]: 286.03688 found 286.036464.

*4.2.8. 3′-Chloro-2,3-dimethoxy-4′-(trifluoromethyl)biphenyl (**3h**)*

Starting with **1** (0.215 g, 1 mmol), **2h** (0.237 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3h** was isolated as colorless oil (0.235 g, 74%). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.53 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 6.78–6.81 (m, 1H, ArH), 6.85 (dd, *J* = 8.31 Hz, *J* = 1.51 Hz, 1H, ArH, ArH), 6.98–7.03 (m, 1H, ArH), 7.42–7.45 (m, 1H, ArH), 7.59–7.61 (m, 2H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 55.9 (OCH_3), 60.8 (OCH_3), 112.9 (CH), 122.0 (CH), 123.1 (CF_3, q, $^1J_{CF}$ = 272.89 Hz), 124.5 (CH), 126.8 (C, q, $^2J_{CF}$ = 31.91 Hz), 127.2 (CH, q, $^3J_{CF}$ = 4.95 Hz), 127.6 (CH), 131.8 (C, q, $^3J_{CF}$ = 1.65 Hz), 132.1 (CH), 132.9 (C), 143.5 (C), 146.6 (C), 153.3 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.23 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3030 (w), 2966 (m), 2933 (w), 2874 (w), 1907 (w), 1606 (m), 1579 (w), 1516 (w), 1474 (m), 1415 (w), 1399 (m), 1377 (w), 1330 (s), 1283 (m), 1255 (m), 1167 (s), 1123 (s), 1087 (s), 1065 (w), 1029 (m), 1014 (m), 965 (w), 904 (m), 842 (w), 825 (s), 774 (w), 731 (w), 717 (m), 677 (w), 657 (m), 632 (m), 598 (m), 581 (w), 554 (m); GC–MS (EI, 70 eV): *m*/*z* (%): 316 (M^+, 100), 301 (17), 266 (92), 251 (12), 223 (10), 204 (8), 169 (6), 141 (2), 126 (2), 99 (1), 69 (3); HRMS (EI) calcd for $C_{15}H_{12}ClF_3O_2$ [M^+]: 316.04724 found 316.046783.

*4.2.9. 3′-Chloro-2,3,4-trimethoxy-4′-(trifluoromethyl)biphenyl (**3i**)*

Starting with **1** (0.215 g, 1 mmol), **2i** (0.276 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3i** was isolated as colorless oil (0.207 g, 60%). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 6.63 (d, *J* = 8.69 Hz, 1H, ArH), 6.89 (d, *J* = 8.69 Hz, 1H, ArH), 7.34 (d, *J* = 8.12 Hz, 1H, ArH), 7.56–7.59 (m, 2H, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$), δ = 55.9 (OCH_3), 60.9 (OCH_3), 61.1 (OCH_3), 107.7 (CH), 122.5 (CF_3, q, $^1J_{CF}$ = 272.89 Hz), 124.6 (CH), 125.6 (C), 126.2 (C, q, $^2J_{CF}$ = 31.36 Hz), 127.1 (CH, q, $^3J_{CF}$ = 5.50 Hz), 127.3 (CH), 131.8 (CH), 142.7 (C), 143.4 (C), 151.4 (C), 153.5 (C), 154.3 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.18 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2995 (w), 2938 (w), 2837 (w), 1740 (w), 1596 (s), 1552 (m), 1509 (m), 1484 (m), 1462 (m), 1434 (w), 1416 (m), 1378 (m), 1313 (w), 1304 (s), 1293 (w), 1257 (w), 1234 (m), 1211 (m), 1175 (s), 1127 (m), 1104 (s), 1084 (s), 1025 (w), 1009 (s), 927 (m), 883 (m), 838 (m), 794 (s), 759 (w), 737 (m), 697 (w), 689 (w), 654 (w), 621 (w), 603 (w), 585 (w), 539 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 346 (M^+, 100), 331 (16), 296 (31), 288 (19), 217 (29), 182 (6), 167 (2), 132 (1), 99 (2), 69 (2); HRMS (EI) calcd for $C_{16}H_{14}ClF_3O_3$ [M^+]: 346.05781 found 346.056833.

*4.2.10. 2,3′-Dichloro-4′-(trifluoromethyl)biphenyl (**3j**)*

Starting with **1** (0.215 g, 1 mmol), **2j** (0.202 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3j** was isolated as colorless oil (0.135 g, 47%). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.24–7.29 (m, 3H, ArH), 7.35–7.38 (m, 1H, ArH), 7.40–7.43 (m, 1H, ArH), 7.51 (s, 1H, ArH), 7.66 (d, ^3J = 8.12 Hz, 1H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 122.9 (CF_3, q, $^1J_{CF}$ = 273.29 Hz), 128.0 (C, q, $^2J_{CF}$ = 33.42 Hz), 127.1 (CH), 127.2 (CH, q, $^3J_{CF}$ = 5.49 Hz), 127.8 (CH), 129.7 (CH), 130.2 (CH), 130.9 (CH), 132.0 (C, q, $^3J_{CF}$ = 1.83 Hz), 132.2 (C), 132.3 (CH), 137.7 (C), 144.3 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.40 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3061 (w), 2924 (w), 2854 (w), 1923 (w), 1807 (w), 1607 (m), 1569 (m), 1556 (w), 1503 (m), 1468 (m), 1435 (m), 1385 (m), 1311 (s), 1264 (w), 1244 (w), 1174 (m), 1125 (s), 1103 (m), 1077 (m), 1050 (w), 1037(s), 1027 (m), 981 (w), 962 (w), 947 (w), 891 (m), 865 (w), 834 (s), 756 (m), 749 (m), 740 (w), 731 (w), 705(m), 671 (m), 636 (m), 598 (w), 562 (w), 557(w), 542 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 290 (M^+, 100), 271 (5), 255 (4), 235 (10), 220 (25), 201 (5), 186 (12), 170 (4), 150 (5), 123 (1), 99 (2), 50 (1); HRMS (EI) calcd for $C_{13}H_7Cl_2F_3$ [M^+]: 289.98714 found 289.987078.

*4.2.11. 3-Chloro-4′-fluoro-4-(trifluoromethyl)biphenyl (**3k**)*

Starting with **1** (0.215 g, 1 mmol), **2k** (0.181 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3k** was isolated as white solid (0.127 g, 46%); mp 67–69 °C. ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.02–7.11 (m, 2H, ArH), 7.37–7.48 (m, 3H, ArH), 7.58 (s, 1H, ArH), 7.63 (d, ^3J = 8.31 Hz, 1H, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$), δ = 116.2 (2CH, d, $^2J_{CF}$ = 22.01 Hz), 123.0 (CF_3, q, $^1J_{CF}$ = 272.90 Hz), 125.0 (CH), 128.0 (CH, q, $^3J_{CF}$ = 4.95 Hz), 128.9 (2CH, d, $^3J_{CF}$ = 8.25 Hz), 127.0 (C, q, $^2J_{CF}$ = 31.91 Hz), 129.8 (CH), 132.8 (C, q, $^3J_{CF}$ = 1.65 Hz), 134.4 (C, d, $^4J_{CF}$ = 3.30 Hz), 145.1 (C), 163.3 (CF, d, $^1J_{CF}$ = 249.24 Hz); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.28 ($ArCF_3$), −112.95 (ArF); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3075 (w), 3049 (w), 2924 (w), 2856 (w), 1890 (w), 1605 (m), 1598 (m), 1561 (w), 1521 (w), 1495 (m), 1489 (m), 1421 (w), 1383 (m), 1313 (s), 1290 (w), 1232 (s), 1179 (w), 1160 (w), 1126 (s), 1105 (s), 1059(w), 1038 (w), 1024 (m), 1014 (w), 959 (w), 884 (m), 839 (w), 820 (s), 804 (m), 764 (w), 738 (m), 712 (w), 701(w), 675 (m), 712 (w), 701 (w), 675 (m), 637 (w), 619 (w), 593 (m), 560 (m), 546 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 274 (M^+, 100), 238 (4), 219 (15), 170 (19), 120 (1), 94 (3), 85 (1), 75 (2), 69 (1); HRMS (EI) calcd for $C_{13}H_7ClF_4$ [M^+]: 274.01669 found 274.016090.

*4.2.12. 3-Chloro-4,4′-bis(trifluoromethyl)biphenyl (**3l**)*

Starting with **1** (0.215 g, 1 mmol), **2l** (0.246 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3l** was isolated as colorless oil (0.114 g, 35%). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.47–7.50 (m, 1H, ArH), 7.59–7.72 (m, 6H, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$), δ = 122.8 (CF_3, q, $^1J_{CF}$ = 272.90 Hz), 124.0 (CF_3, q, $^1J_{CF}$ = 271.80 Hz), 125.4 (CH), 127.6 (2CH), 126.1 (2CH, q, $^3J_{CF}$ = 3.85 Hz), 128.2 (CH, q, $^3J_{CF}$ = 5.50 Hz), 130.1 (CH), 130.9 (2C, q, $^2J_{CF}$ = 32.46 Hz), 133.0 (C, q, $^3J_{CF}$ = 1.65 Hz), 141.8 (C), 144.6 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.45 ($ArCF_3$), −62.69 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 2934 (w), 1924 (w), 1737 (w), 1607 (m), 1557 (m), 1492 (w), 1421 (w), 1381 (m), 1313 (s), 1257 (w), 1165 (w), 1105 (s), 1069 (s), 1038 (w), 1025 (m), 1014 (m), 964 (w), 956 (w), 890 (m), 850 (w), 824

(s), 771 (w), 742 (w), 732 (w), 693 (m), 653 (m), 625 (w), 598 (m), 558 (w), 543 (w); GC–MS (EI, 70 eV): *m/z* (%): 324 (M^+, 100), 305 (18), 274 (8), 220 (14), 170 (3), 144 (1), 112 (2), 99 (1), 75 (1), 69 (2); HRMS (EI) calcd for $C_{14}H_7ClF_6$ [M^+]: 324.01350 found 324.013171.

*4.2.13. 3-Chloro-3′,4-bis(trifluoromethyl)biphenyl (**3m**)*

Starting with **1** (0.215 g, 1 mmol), **2m** (0.246 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (8 mL), **3m** was isolated as colorless oil (0.103 g, 32%). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 7.49–7.61 (m, 3H, ArH), 7.64–7.74 (m, 4H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 122.8 (CF_3, q, $^1J_{CF}$ = 273.29 Hz), 123.9 (CF_3, q, $^1J_{CF}$ = 272.37 Hz), 123.9 (CH, q, $^3J_{CF}$ = 4.12 Hz), 124.7 (CH, q, $^3J_{CF}$ = 3.66 Hz), 125.3 (CH), 125.4 (CH, q, $^3J_{CF}$ = 3.66 Hz), 129.7 (CH), 130.0 (CH), 130.5 (CH), 131.5 (C, q, $^2J_{CF}$ = 32.04 Hz), 131.7 (C, q, $^2J_{CF}$ = 32.50 Hz), 133.1 (C, q, $^3J_{CF}$ = 1.83 Hz), 139.1 (C), 144.6 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.43 ($ArCF_3$), −62.72 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3071 (w), 3051 (w), 2926 (w), 1608 (m), 1565 (w), 1510 (w), 1503 (w), 1484 (w), 1443 (m), 1412 (w), 1385 (m), 1334 (m), 1314 (s), 1289 (w), 1267 (m), 1255 (m), 1167 (m), 1120 (s), 1104 (s), 1074 (m), 1049(m), 1026 (m), 1001 (w), 963 (w), 922 (w), 908 (w), 885 (m), 862 (m), 837 (m), 798 (s), 782 (w), 762 (w), 695(s), 674 (w), 665 (w), 659 (w), 636 (w), 620 (w), 591 (w), 557 (w), 544 (w); GC–MS (EI, 70 eV): *m/z* (%): 324 (M^+, 100), 305 (15), 274 (6), 220 (13), 170 (3), 145 (1), 109 (1), 99 (1), 75 (1), 69 (2); HRMS (EI) calcd for $C_{14}H_7ClF_6$ [M^+]: 324.01350 found 324.013577.

*4.3. General procedure for synthesis of **4a–d***

A 1,4-Dioxane solution (8 mL) of **1** (1.0 equiv.), arylboronic acid **2** (2.5 equiv.), 2 M K_2CO_3 (2 mL), and $Pd(PPh_3)_4$ (5 mol%) was heated at 110 °C for 8 h. After cooling to room temperature, H_2O was added and the reaction mixture was extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), filtered and concentrated in vacuo. The residue was purified by column chromatography (gradient elution n-heptane/ethyl acetate).

*4.3.1. 4-Trifluoromethyl-1,3-bis(2-methylphenyl)-benzene (**4a**)*

Starting with **1** (0.215 g, 1 mmol), **2a** (0.337 g, 2.5 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (2 mL), 1,4-Dioxane (8 mL), **4a** was isolated as colorless oil (0.186 g, 57%). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.01 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 7.09–7.19 (m, 9H), 7.34 (qd, J = 8.12 Hz, J = 0.94 Hz, 1H, ArH), 7.70 (d, ^3J = 7.93 Hz, 1H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 20.1 (CH_3), 20.4 (CH_3), 124.2 (CF_3, q, $^1J_{CF}$ = 273.74 Hz), 124.9 (CH), 125.9 (CH), 126.0 (CH, q, $^3J_{CF}$ = 5.04 Hz), 127.2 (C, q, $^2J_{CF}$ = 29.76 Hz), 127.91 (CH), 127.98 (CH), 128.0 (CH), 129.5 (CH), 129.6 (2CH), 130.6 (CH), 132.4 (CH), 135.2 (C), 135.9 (C), 138.9 (C), 140.2 (C), 140.5 (C, q, $^4J_{CF}$ = 2.29 Hz), 145.1 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −58.80 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3061 (w), 3020 (w), 2953 (w), 2923 (w), 2858 (w), 2738 (w), 2620 (w), 2576 (w), 1917 (w), 1806 (w), 1727 (w), 1609 (m), 1601 (m), 1564 (m), 1507 (w), 1479 (m), 1455 (m), 1390 (m), 1310 (s), 1256 (w), 1168 (s), 1116 (s), 1070 (m), 1044 (w), 1030 (m), 1009 (m), 985 (w), 964 (w), 943 (w), 908 (s), 866 (w), 839 (s), 768 (m), 754 (s), 739 (m), 724 (s), 692 (m), 653 (m), 639 (m), 630 (m), 597 (m), 557 (m), 539 (m); GC–MS (EI, 70 eV): *m/z* (%): 326 (M^+, 100), 311 (9), 285 (5), 257 (19), 242 (10), 215 (7), 165 (12), 105 (2), 91 (3), 65 (1); HRMS (EI) calcd for $C_{21}H_{17}F_3$ [M^+]: 326.12769 found 326.127047.

*4.3.2. 4-Trifluoromethyl-1,3-bis(3-methylphenyl)-benzene (**4b**)*

Starting with **1** (0.215 g, 1 mmol), **2b** (0.337 g, 2.5 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (2 mL), 1,4-Dioxane (8 mL), **4b** was isolated as colorless oil (0.126 g, 39%). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.32 (s, 3H, CH_3), 2.33 (s, 3H, CH_3), 7.05–7.14 (m, 4H), 7.19–7.35 (m, 4H), 7.46 (s, 1H), 7.54–7.58 (m, 1H), 7.69 (d, ^3J = 8.31 Hz, 1H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 21.4 (CH_3), 21.5 (CH_3), 124.3 (CF_3, q, $^1J_{CF}$ = 273.74 Hz), 124.4 (CH), 125.7 (CH), 126.1 (CH), 126.5 (CH, q, $^3J_{CF}$ = 5.04 Hz), 127.1 (C, q, $^2J_{CF}$ = 30.21 Hz), 127.7 (CH), 128.0 (CH), 128.4 (CH), 128.8 (CH), 128.9 (CH), 129.7 (CH), 130.7 (CH), 137.4 (C), 138.6 (C), 139.4 (C), 139.9 (C), 141.9 (C, q, $^4J_{CF}$ = 1.83 Hz), 144.2 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −56.54 ($ArCF_3$); IR (ATR, cm^{-1}): IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3030 (m), 2922 (m), 2853 (w), 2732 (w), 1943 (w), 1876 (w), 1788 (w), 1726 (w), 1603 (m), 1585 (w), 1567 (m), 1479 (m), 1454 (w), 1379 (m), 1309 (s), 1267 (w), 1165 (m), 1117 (s), 1096 (w), 1078 (m), 1031 (s), 999 (w), 962 (w), 895 (w), 881 (w), 835 (m), 783 (s), 758 (w), 734 (w), 703 (s), 694 (w), 643 (m), 611 (w), 589 (m), 563 (w); GC–MS (EI, 70 eV): *m/z* (%): 326 (M^+, 100), 305 (11), 291 (5), 257 (3), 165 (3), 128 (1), 91 (1); HRMS (EI) calcd for $C_{21}H_{17}F_3$ [M^+]: 326.12769 found 326.127119.

*4.3.3. 4-Trifluoromethyl-1,3-bis(4-methylphenyl)-benzene (**4c**)*

Starting with **1** (0.215 g, 1 mmol), **2c** (0.337 g, 2.5 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (2 mL), 1,4-Dioxane (8 mL), **4c** was isolated as colorless oil (0.196 g, 60%). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 2.29 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 7.11–7.20 (m, 6H, ArH), 7.37–7.44 (m, 3H, ArH), 7.51–7.55 (m, 1H, ArH), 7.66 (d, ^3J = 8.12 Hz, 1H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 21.2 (CH_3), 21.3 (CH_3), 124.4 (CF_3, q, $^1J_{CF}$ = 274.20 Hz), 125.4 (CH), 126.6 (CH, q, $^3J_{CF}$ = 5.49 Hz), 126.8 (CH), 127.0 (C, q, $^2J_{CF}$ = 30.21 Hz), 127.1 (2CH), 128.6 (CH), 128.89 (CH, q, $^5J_{CF}$ = 1.37 Hz), 129.5 (CH), 129.7 (2CH), 130.6 (CH), 136.6 (C), 136.7 (C), 137.0 (C), 138.2 (C), 141.9 (C), 144.0 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −56.47 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3024 (w), 2921 (m), 2856 (w), 2732 (w), 2620 (w), 2590 (w), 1904 (m), 1798 (w), 1732 (w), 1652 (w), 1607 (s), 1578 (w), 1561 (w), 1515 (m), 1500 (w), 1490 (m), 1455 (w), 1417 (w), 1383 (m), 1348 (w), 1307 (s), 1281 (w), 1264 (w), 1211 (w), 1170 (s), 1118 (s), 1111 (s), 1075 (s), 1029 (s), 1008 (m), 963 (w), 945 (w), 901 (m), 841 (m), 809 (s), 801 (m), 779 (w), 758 (m), 738 (w), 720 (m), 698 (w), 679 (w), 653 (w), 641 (w), 626 (w), 606 (w), 586 (m), 565 (w), 540 (m); GC–MS (EI, 70 eV): *m/z* (%): 326 (M^+, 100), 286 (1), 257 (4), 215 (2), 165 (3), 91 (2); HRMS (EI) calcd for $C_{21}H_{17}F_3$ [M^+]: 326.12769 found 326.127380.

*4.3.4. 4-Trifluoromethyl-1,3-bis(4-fluorophenyl)-benzene (**4d**)*

Starting with **1** (0.215 g, 1 mmol), **2k** (0.348 g, 2.5 equiv.), $Pd(PPh_3)_4$ (0.058 g, 0.05 equiv.), 2 M K_2CO_3 (2 mL), 1,4-Dioxane (8 mL), **4d** was isolated as colorless oil (0.165 g, 49%). ^1H NMR (300.13 MHz, $CDCl_3$): δ = 6.99–7.09 (m, 4H, ArH), 7.24–7.28 (m, 2H, ArH), 7.39 (s, 1H, ArH), 7.48–7.57 (m, 3H, ArH), 7.71 (d, ^3J = 8.12 Hz, 1H, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$), δ = 114.9 (2CH, d, $^2J_{CF}$ = 22.01 Hz), 116.0 (2CH, d, $^2J_{CF}$ = 21.46 Hz), 124.2 (CF_3, q, $^1J_{CF}$ = 273.45 Hz), 125.9 (CH), 126.8 (CH, q, $^3J_{CF}$ = 5.50 Hz), 127.4 (C, q, $^2J_{CF}$ = 30.26 Hz), 128.9 (2CH, d, $^3J_{CF}$ = 8.25 Hz), 130.6 (2CH), 130.7 (C, q, $^3J_{CF}$ = 1.65 Hz), 135.4 (C, d, $^4J_{CF}$ = 3.30 Hz), 135.6 (C, d, $^4J_{CF}$ = 3.30 Hz), 140.9 (C, q, $^3J_{CF}$ = 1.65 Hz), 143.2 (C), 162.6 (CF, d, $^1J_{CF}$ = 247.04 Hz), 163.1 (CF, d, $^1J_{CF}$ = 248.14 Hz); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −56.73 ($ArCF_3$), −113.77 (ArF), −114.50 (ArF); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3046 (w), 2923 (w), 2854 (w), 1894 (w), 1608 (m), 1568 (w), 1511 (m), 1490 (m), 1405 (w), 1384 (w), 1309 (s), 1264 (w), 1224 (m), 1174 (w), 1117 (s), 1095 (w), 1076 (m), 1030 (m), 1010 (w), 961 (w), 903 (w), 822 (s), 790 (m), 721 (m), 679 (m), 635 (w), 621 (w), 605 (w), 585 (w), 563 (m), 542 (m); GC–MS (EI, 70 eV): *m/z* (%): 334 (M^+, 100), 313 (7), 264 (9), 244 (6), 219 (7), 167 (6), 122 (2), 75 (1); HRMS (EI) calcd for $C_{19}H_{11}F_5$ [M^+]: 334.07754 found 334.077305.

4.4. General procedure for synthesis of **5a–d**

A 1,4-dioxane solution (8 mL) of **3** (1.0 equiv.), arylboronic acid **2** (1.3 equiv.), 2 M K_2CO_3 (1 mL), and $Pd(PPh_3)_4$ (5 mol%) was heated at 110 °C for 8 h. After cooling to room temperature, H_2O was added and the reaction mixture was extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), filtered and concentrated in vacuo. The residue was purified by column chromatography (gradient elution n-heptane/ethyl acetate).

4.4.1. 1-(4′-Methylphenyl)-3-(3″,5″-dimethylphenyl)-4-trifluoromethylbenzene (**5a**)

Starting with **3c** (0.08 g, 0.3 mmol), **2e** (0.058 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.017 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (4 mL), **5a** was isolated as colorless oil (0.065 g, 64%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.28 (s, 6H, $2CH_3$), 2.31 (s, 3H, CH_3), 6.92 (s, 2H, ArH), 6.96 (s, 1H, ArH), 7.17 (d, ^3J = 8.50 Hz, 2H, ArH), 7.42–7.45 (m, 3H, ArH), 7.53–7.56 (m, 1H, ArH), 7.68 (d, ^3J = 8.31 Hz, 1H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 21.1 (CH_3), 21.3 ($2CH_3$), 124.4 (CF_3, q, $^1J_{CF}$ = 271.91 Hz), 125.3 (CH), 126.4 (C, q, $^2J_{CF}$ = 30.67 Hz), 126.6 (CH, q, $^3J_{CF}$ = 5.49 Hz), 126.8 (2CH, q, $^5J_{CF}$ = 1.37 Hz), 127.1 (2CH), 129.3 (CH), 129.7 (2CH), 130.5 (CH), 136.6 (C), 137.2 (2C), 138.2 (C), 139.9 (C), 142.1 (C, q, $^3J_{CF}$ = 1.83 Hz), 143.9 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −56.51 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3023 (w), 2952 (w), 2919 (m), 2862 (w), 2735 (w), 1917 (w), 1598 (m), 1562 (w), 1470 (w), 1381 (w), 1307 (s), 1281 (m), 1192 (w), 1161 (m), 1119 (s), 1095 (w), 1027 (m), 964 (w), 900 (w), 858 (m), 811 (s), 772 (w), 717 (w), 704 (m), 659 (w), 646 (w), 633 (w), 589 (m), 541 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 340 (M^+, 100), 305 (7), 271 (4), 256 (5), 239 (5), 170 (4), 162 (5), 141 (1), 127 (3), 105 (3), 91 (2), 77 (1), 65 (1), 51 (1), 39 (1); HRMS (EI) calcd for $C_{22}H_{19}F_3$ [M^+]: 340.14334 found 340.143000.

4.4.2. 1-(4′-Methylphenyl)-3-(4″-ethylphenyl)-4-trifluoromethylbenzene (**5b**)

Starting with **3c** (0.08 g, 0.3 mmol), **2f** (0.059 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.017 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (4 mL), **5b** was isolated as colorless oil (0.04 g, 40%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.21 (t, *J* = 7.55 Hz, 3H, CH_3), 2.31 (s, 3H, CH_3), 2.63 (q, *J* = 7.74 Hz, *J* = 15.30 Hz, 2H, $-CH_2-$), 7.16–7.23 (m, 6H, ArH), 7.41–7.46 (m, 3H, ArH), 7.54–7.57 (m, 1H, ArH), 7.68 (d, ^3J = 8.31 Hz, 1H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 15.4 (CH_3), 21.1 (CH_3), 28.6 ($-CH_2-$), 124.4 (CF_3, q, $^1J_{CF}$ = 274.20 Hz), 125.3 (2CH), 126.6 (CH, q, $^3J_{CF}$ = 5.50 Hz), 127.1 (2CH), 127.3 (2CH), 128.5 (C), 128.9 (CH, q, $^4J_{CF}$ = 1.83 Hz), 129.6 (2CH), 126.9 (C, q, $^2J_{CF}$ = 30.21 Hz), 130.6 (CH), 136.5 (C), 137.3 (C), 141.9 (C, q, $^3J_{CF}$ = 1.83 Hz), 143.6 (C), 143.9 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −56.50 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3025 (w), 2928 (w), 2872 (w), 2731 (w), 2620 (w), 2431 (w), 2302 (w), 1905 (w), 1728 (w), 1665 (w), 1606 (m), 1514 (w), 1454 (w), 1384 (w), 1307 (s), 1265 (w), 1170 (m), 1112 (s), 1075 (m), 1029 (m), 1008 (w), 963 (w), 902 (w), 833 (w), 809 (s), 773 (w), 718 (w), 640 (w), 626 (w), 608 (w), 587 (w), 541 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 340 (M^+, 98), 325 (100), 305 (5), 270 (6), 241 (4), 189 (2), 162 (14), 127 (3), 105 (4), 91 (4), 65 (2), 51 (1), 39 (1); HRMS (EI) calcd for $C_{22}H_{19}F_3$ [M^+]: 340.14334 found 340.142981.

4.4.3. 1-(4′-Methylphenyl)-3-(4″-fluorophenyl)-4-trifluoromethylbenzene (**5c**)

Starting with **3c** (0.12 g, 0.4 mmol), **2k** (0.072 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.023 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (4 mL), **5c** was isolated as colorless oil (0.037 g, 25%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3), 6.99–7.07 (m, 2H, ArH), 7.17–7.29 (m, 4H, ArH), 7.43–7.46 (m, 3H, ArH), 7.59 (d, ^3J = 8.31 Hz, 1H, ArH), 7.70 (d, ^3J = 8.12 Hz, 1H, ArH); ^{13}C NMR (75.46 MHz, $CDCl_3$), δ = 21.2 (CH_3), 114.8 (2CH, d, $^2J_{CF}$ = 21.46 Hz), 124.3 (CF_3, q, $^1J_{CF}$ = 273.45 Hz), 125.8 (CH), 126.7 (CH, q, $^3J_{CF}$ = 4.95 Hz), 127.1 (2CH), 127.5 (C, q, $^2J_{CF}$ = 30.81 Hz), 129.7 (2CH), 130.5 (CH), 130.7 (2CH, d, $^3J_{CF}$ = 8.25 Hz), 135.8 (C, d, $^4J_{CF}$ = 3.30 Hz), 136.4 (C), 140.8 (C, q, $^3J_{CF}$ = 2.20 Hz), 138.3 (C), 144.2 (C), 162.5 (CF, d, $^1J_{CF}$ = 247.04 Hz); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −56.64 ($ArCF_3$), −114.74 (ArF); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3028 (w), 2923 (w), 2859 (w), 2733 (w), 1901 (w), 1741 (w), 1606 (m), 1563 (w), 1512 (m), 1490 (m), 1417 (w), 1308 (s), 1282 (w), 1224 (m), 1172 (m), 1117 (s), 1076 (m), 1030 (m), 1010 (w), 962 (w), 837 (m), 810 (s), 783 (w), 741 (w), 702 (w), 639 (w), 624 (w), 587 (w), 564 (w), 542 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 330 (M^+, 100), 289 (3), 261 (7), 246 (5), 220 (2), 183 (2), 165 (10), 144 (3), 109 (1), 91 (3), 89 (1), 75 (1), 63 (1), 51 (1), 39 (1); HRMS (EI) calcd for $C_{20}H_{14}F_4$ [M^+]: 330.10261 found 330.102661.

4.4.4. 1-(4′-Methylphenyl)-3-(4″-methoxyphenyl)-4-trifluoromethylbenzene (**5d**)

Starting with **3c** (0.08 g, 0.3 mmol), **2n** (0.059 g, 1.3 equiv.), $Pd(PPh_3)_4$ (0.017 g, 0.05 equiv.), 2 M K_2CO_3 (1 mL), 1,4-Dioxane (4 mL), **5d** was isolated as colorless oil (0.06 g, 59%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.31 (s, 3H, CH_3), 3.76 (s, 3H, OCH_3), 6.86 (d, ^3J = 8.69 Hz, 2H, ArH), 7.15–7.24 (m, 4H, ArH), 7.39–7.44 (m, 3H, ArH), 7.52–7.55 (m, 1H, ArH), 7.68 (d, ^3J = 8.12 Hz, 1H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 21.1 (CH_3), 55.3 (OCH_3), 113.3 (2CH), 124.4 (CF_3, q, $^1J_{CF}$ = 273.74 Hz), 125.3 (CH), 126.6 (CH, q, $^3J_{CF}$ = 5.49 Hz), 127.0 (C, q, $^2J_{CF}$ = 29.76 Hz), 127.1 (2CH), 129.7 (2CH), 130.2 (2CH, q, $^5J_{CF}$ = 1.37 Hz), 130.7 (CH), 132.3 (C), 136.5 (C), 138.2 (C), 141.6 (C, q, $^3J_{CF}$ = 1.83 Hz), 144.0 (C), 159.2 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −56.56 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3030 (w), 3000 (w), 2934 (w), 2836 (w), 1607 (m), 1562 (w), 1510 (m), 1463 (w), 1385 (w), 1307 (s), 1291 (w), 1243 (m), 1170 (m), 1116 (s), 1107 (s), 1076 (m), 1029 (s), 1004 (w), 962 (w), 930 (m), 809 (s), 762 (w), 679 (w), 624 (w), 606 (w), 587 (w), 573 (w), 545 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 342 (M^+, 100), 279 (5), 264 (6), 249 (3), 233 (2), 215 (2), 171 (4), 124 (1), 91 (2), 65 (1), 39 (1); HRMS (EI) calcd for $C_{21}H_{17}F_3O$ [M^+]: 342.12260 found 342.122754.

4.5. Typical procedure for the synthesis of 4-bromo-3-(trifluoromethyl)biphenyls (**7a–o**)

The reaction was carried out in a pressure tube. To a dioxane suspension (5 mL) of the 1,4-dibromo-2-(trifluoromethyl)benzene (**6**), $Pd(PPh_3)_4$ (3–5 mol%) and of the arylboronic acid (2) was added an aqueous solution of K_2CO_3 (2 M, 1–2 mL). The mixture was heated at the indicated temperature (70 °C) under Argon atmosphere for the indicated period of time (8 h). The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (5 mL each), and the organic and the aqueous layers were separated. The later was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with H_2O (3 × 10 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc) to give 4-bromo-3-(trifluoromethyl)-biphenyls (**7a–o**) (79–94%).

4.5.1. 4′-Bromo-2-methyl-3′-(trifluoromethyl)biphenyl (**7a**)

Starting from **6** (150 mg, 0.5 mmol), and **2a** (68 mg, 0.5 mmol), **7a** was obtained as a colorless oil (137 mg, 87%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 2.17 (s, 3H, CH_3), 7.09–7.26 (m, 5H, H_{Ar}), 7.56 (d, 1H, *J* = 2.1 Hz, H_{Ar}), 7.66 (d, 1H, *J* = 8.1 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.5; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 20.3 (CH_3), 118.4 ($J_{C,F}$ = 1.9 Hz, C_{Ar}), 122.9 ($J_{C,F}$ = 272 Hz, CF_3), 126.1, 128.2, 128.5 ($J_{C,F}$ = 5.3 Hz), 129.5 (CH_{Ar}), 129.9 ($J_{C,F}$ = 31.0 Hz, C_{Ar}), 130.6, 133.6, 134.7 (CH_{Ar}), 135.1, 139.2, 141.4 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3062, 3021, 2955, 1599 (w), 1470, 1399 (m), 1321 (s), 1248 (m), 1171, 1126, 1097, 1019 (s), 965, 906,

833 (m), 757, 724 (s), 659, 592, 555 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) 314 (M^+, ^{79}Br, 99), 235 (17), 234 (11), 233 (10), 215 (22), 214 (12), 166 (68), 165 (70), 115 (8), 107 (8), 91 (7). HRMS (EI): calcd. for $C_{14}H_{10}{}^{79}BrF_3$ $[M]^+$: 313.991250; Found: 313.991255.

*4.5.2. 4-Bromo-3′,5′-dimethyl-3-(trifluoromethyl)biphenyl (**7b**)*

Starting from **6** (150 mg, 0.5 mmol), and **2e** (75 mg, 0.5 mmol), **7b** was obtained as a colorless heavy oil (137 mg, 83%). ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ = 2.30 (s, 6H, $2CH_3$), 6.98 (s, 1H, H_{Ar}), 7.09 (s, 1H, H_{Ar}), 7.49 (dd, 1H, *J* = 1.9, 8.3 Hz, H_{Ar}), 7.66 (d, 1H, *J* = 8.3 Hz, H_{Ar}), 7.78 (d, 1H, *J* = 1.9 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.53; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 21.4 (CH_3), 118.4 ($J_{C,F}$ = 1.9 Hz, C_{Ar}), 122.9 ($J_{C,F}$ = 273 Hz, CF_3), 124.8, 126.4 ($J_{C,F}$ = 5.4 Hz, CH_{Ar}), 129.9 (CH_{Ar}), 130.9 ($J_{C,F}$ = 31.0 Hz, C_{Ar}), 131.3, 135.1 (CH_{Ar}), 138.6, 138.7, 138.9, 140.9 (C_{Ar}); IR (neat, cm^{-1}): $\tilde{\nu}$ = 3022 (w), 2921 (m), 2853 (w), 1604 (m), 1568 (w), 1468, 1391, 1334 (m), 1293 (s), 1251, 1207 (m), 1170 (m), 1128 (s), 1100, 1021 (m), 962, 892 (m), 825 (s), 760, 726 (w), 699, 659 (m), 597, 543 (w) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%) 328 (M^+, ^{79}Br, 100), 315 (19), 313 (19), 249 (11), 234 (17), 233 (12), 214 (5), 184 (5), 180 (12), 179 (9), 178 (9), 165 (25), 152 (5); HRMS (EI): calcd. for $C_{15}H_{12}{}^{79}BrF_3$ $[M]^+$: 328.006900; Found: 328.006512.

*4.5.3. 4-Bromo-4′-ethyl-3-(trifluoromethyl)biphenyl (**7c**)*

Starting from **6** (150 mg, 0.5 mmol), and **2f** (75 mg, 0.5 mmol), **7c** was obtained as a colorless oil (143 mg, 87%). ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ = 1.18 (t, 3H, *J* = 7.5 Hz, CH_3), 7.60 (q, 2H, *J* = 7.5 Hz, CH_2), 7.20 (d, 2H, *J* = 8.3 Hz, H_{Ar}), 7.39 (d, 2H, *J* = 8.3 Hz, H_{Ar}), 7.46 (dd, 1H, *J* = 8.2, 2.2 Hz, H_{Ar}), 7.64 (d, 1H, *J* = 8.3 Hz, H_{Ar}), 7.78 (d, 1H, *J* = 2.2 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.55; ^{13}C NMR (63 MHz, 300 K, $CDCl_3$): δ = 15.5 (CH_3), 28.5 (CH_2), 118.3 ($J_{C,F}$ = 1.8 Hz, C_{Ar}), 122.9 ($J_{C,F}$ = 273 Hz, CF_3), 126.2 ($J_{C,F}$ = 5.4 Hz), 126.8, 128.6 (CH_{Ar}), 130.3 ($J_{C,F}$ = 31.5 Hz, C_{Ar}), 131.3, 135.2 (CH_{Ar}), 136.0, 140.6, 144.7 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3027, 2965, 2873, 1602 (w), 1472, 1423 (m), 1323 (s), 1251 (m), 1171 (m), 1128, 1100 (s), 1014 (m), 964 (w), 902 (m), 817 (s), 773, 716, 660 (m), 612 (w), 548 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%) 328 (M^+, ^{79}Br, 72), 316 (15), 315 (100), 314 (16), 313 (99), 249 (8), 234 (13), 233 (9), 183 (8), 178 (6), 165 (28); HRMS (EI): calcd. for $C_{15}H_{12}{}^{79}BrF_3$ $[M]^+$: 328.006900; Found: 328.006104.

*4.5.4. 4′-Bromo-2,3,4-trimethoxy-3′-(trifluoromethyl)biphenyl (**7d**)*

Starting from **6** (150 mg, 0.5 mmol), and **2i** (106 mg, 0.5 mmol), **7d** was obtained as a colorless heavy oil (160 mg, 82%). ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.63, 3.82, 3.84 (s, 9H, 3 OCH_3), 6.67 (d, 1H, *J* = 8.7 Hz, H_{Ar}), 6.93 (d, 1H, *J* = 8.7 Hz, H_{Ar}), 7.45 (dd, 1H, *J* = 8.3, 2.1 Hz, H_{Ar}), 7.63 (d, 1H, *J* = 8.3 Hz, H_{Ar}), 7.75 (d, 1H, *J* = 2.1 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.51; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 56.0. 61.0, 61.1 (OCH_3), 107.7 (CH_{Ar}), 118.0 ($J_{C,F}$ = 1.9 Hz, C_{Ar}), 123.0 ($J_{C,F}$ = 272 Hz, CF_3), 124.4 (CH_{Ar}), 125.9 (C_{Ar}), 128.4 ($J_{C,F}$ = 5.4 Hz, CH_{Ar}), 129.8 ($J_{C,F}$ = 30.7 Hz, C_{Ar}), 133.5, 134.6 (CH_{Ar}), 137.7, 142.7, 151.2, 154.0 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 2936, 2837 (w), 1595, 1498, 1462, 1417, 1325, 1278, 1209, 1171 (m), 1128, 1082, 1008 (s), 927, 903, 884, 834, 794, 723, 664 (m), 586 (w), 529 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%) 390 (M^+, ^{79}Br, 100), 377 (9), 375 (9), 334 (14), 332 (14), 296 (25), 281 (22), 263 (22), 261 (22), 236 (10), 195 (5), 182 (11); HRMS (EI): calcd. for $C_{16}H_{14}O_3{}^{79}BrF_3$ $[M]^+$: 390.007290; Found: 390.006929.

*4.5.5. 4′-Bromo-2-chloro-3′-(trifluoromethyl)biphenyl (**7e**)*

Starting from **6** (150 mg, 0.5 mmol), and **2j** (78 mg, 0.5 mmol), **7e** was obtained as a yellowish heavy oil (141 mg, 84%). ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ = 7.22–7.27 (m, 3H, H_{Ar}), 7.37–7.42 (m, 2H, H_{Ar}), 7.67–7.69 (m, 2H, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.5; ^{13}C NMR (63 MHz, 300 K, $CDCl_3$): δ = 119.3 ($J_{C,F}$ = 1.9 Hz, C_{Ar}), 122.8 ($J_{C,F}$ = 274 Hz, CF_3), 127.2, 128.8 ($J_{C,F}$ = 5.4 Hz), 129.4 ($J_{C,F}$ = 31.7 Hz, C_{Ar}), 129.5, 130.2, 131.0 (CH_{Ar}), 132.3 (C_{Ar}), 133.9, 134.6 (CH_{Ar}), 137.9, 138.7 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3060, 1924, 1604, 1561 (w), 1464, 1389 (m), 1324 (s), 1283, 1242, 1173 (m), 1125 (s), 1074 (m), 1017 (s), 964 (w), 906, 831 (m), 753 (s), 696, 657 (m), 590 (w), 550 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) 334 (M^+, ^{79}Br + ^{35}Cl, 76), 255 (9), 220 (23), 219 (15), 201 (8), 186 (8), 170 (7), 150 (9), 110 (7); HRMS (EI): calcd. for $C_{13}H_7{}^{79}Br{}^{35}ClF_3$ $[M]^+$: 333.936630; Found: 333.936584.

*4.5.6. 4-Bromo-4′-fluoro-3-(trifluoromethyl)biphenyl (**7f**)*

Starting from **6** (150 mg, 0.5 mmol), and **2k** (70 mg, 0.5 mmol), **7f** was obtained as a yellowish heavy oil (128 mg, 80%). ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ = 7.04–7.10 (m, 2H, H_{Ar}), 7.41–7.46 (m, 2H, H_{Ar}), 7.67 (d, 1H, *J* = 8.2 Hz, H_{Ar}), 7.75 (d, 1H, *J* = 2.2 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.61, −113.65; ^{13}C NMR (63 MHz, 298 K, $CDCl_3$): δ = 116.1 ($J_{C,F}$ = 21.7 Hz, CH_{Ar}), 118.7 ($J_{C,F}$ = 1.8 Hz, C_{Ar}), 122.8 ($J_{C,F}$ = 274 Hz, CF_3), 126.2 ($J_{C,F}$ = 5.4 Hz), 128.2 ($J_{C,F}$ = 8.2 Hz) (CH_{Ar}), 130.6 ($J_{C,F}$ = 31.2 Hz, C_{Ar}), 131.1 (CH_{Ar}), 134.8 ($J_{C,F}$ = 3.3 Hz, C_{Ar}) 135.4 (CH_{Ar}), 139.7, 163.0 ($J_{C,F}$ = 248.9 Hz) (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3045, 1892 (w), 1600, 1513 (m), 1473 (s), 1424, 1391 (m), 1325 (s), 1249 (m), 1173, 1099 (s), 1020 (m), 961 (w), 903 (m), 819 (s), 722, 659 (m), 612 (w), 570 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%) 318 (M^+, ^{79}Br, 100), 299 (10), 239 (17), 237 (8), 219 (35), 188 (6), 170 (28), 169 (9), 120 (8); HRMS (EI): calcd. for $C_{13}H_7{}^{79}BrF_4$ $[M]^+$: 317.966180; Found: 317.966583.

*4.5.7. 4-Bromo-3-(trifluoromethyl)biphenyl (**7g**)*

Starting from **6** (150 mg, 0.5 mmol), and **2o** (61 mg, 0.5 mmol), **7g** was obtained as a colorless oil (123 mg, 82%). ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ = 7.30–7.38 (m, 3H, H_{Ar}), 7.44–7.49 (m, 3H, H_{Ar}), 7.66 (d, 1H, *J* = 8.2 Hz, H_{Ar}), 7.78 (d, 1H, *J* = 8.2 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.5; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 118.7 ($J_{C,F}$ = 8.2 Hz, C_{Ar}), 122.9 ($J_{C,F}$ = 271 Hz, CF_3), 126.4 ($J_{C,F}$ = 5.5 Hz), 126.9, 128.4, 129.1 (CH_{Ar}), 130.4 ($J_{C,F}$ = 32.3 Hz, C_{Ar}), 131.3. 135.3 (CH_{Ar}), 138.6, 140.7 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3064, 3033, 1603 (w), 1470, 1401 (m), 1322 (s), 1251 (m), 1171, 1125, 1100, 1017 (s), 964, 898, 830 (m), 757, 694 (s), 617 (w), 545 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%) 300 (M^+, ^{79}Br, 100), 221 (13), 219 (7), 201 (29), 170 (5), 152 (25), 151 (10), 150 (9), 111 (8); HRMS (EI): calcd. for $C_{13}H_8{}^{79}BrF_3$ $[M]^+$: 299.975600; Found: 299.975571.

*4.5.8. 4-Bromo-3′-chloro-3-(trifluoromethyl)biphenyl (**7h**)*

Starting from **6** (150 mg, 0.5 mmol), and **2p** (78 mg, 0.5 mmol), **7h** was obtained as a colorless oil (144 mg, 86%). ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ = 7.28–7.33 (m, 3H, H_{Ar}), 7.43–7.46 (m, 2H, H_{Ar}), 7.67 (d, 1H, *J* = 8.3 Hz, H_{Ar}), 7.75 (d, 1H, *J* = 2.2 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.64; ^{13}C NMR (75 MHz, 300 K, $CDCl_3$): δ = 119.5 ($J_{C,F}$ = 1.8 Hz, C_{Ar}), 122.8 ($J_{C,F}$ = 272 Hz, CF_3), 125.1, 126.3 ($J_{C,F}$ = 5.4 Hz), 127.1, 128.4, 130.4 (CH_{Ar}), 130.6 ($J_{C,F}$ = 31.1 Hz, C_{Ar}), 131.2 (CH_{Ar}), 135.1 (C_{Ar}), 135.5 (CH_{Ar}), 139.2, 140.4 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3060, 1924, 1807, 1604, 1562 (w), 1464, 1398 (m), 1324 (s), 1242 (m), 1173, 1126 (s), 1074 (m), 1017 (s), 964, 906, 831 (m), 753 (s), 696, 657 (m), 590 (w), 550 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%) 334 (M^+, ^{79}Br + ^{35}Cl, 78), 255 (10), 220 (22), 219 (14), 201 (7), 186 (8), 170 (5), 169 (6), 150 (5); HRMS (EI): calcd. for $C_{13}H_7{}^{79}Br{}^{35}ClF_3$ $[M]^+$: 333.936630; Found: 333.936717.

*4.5.9. 4-Bromo-3-(trifluoromethyl)-3′-vinylbiphenyl (**7i**)*

Starting from **6** (150 mg, 0.5 mmol), and **2q** (74 mg, 0.5 mmol), **7i** was obtained as a colorless oil (137 mg, 84%). ^1H NMR (300 MHz, 298 K, $CDCl_3$): δ = 5.21 (d, 1H, *J* = 10.8 Hz, =CH_2), 5.71 (d, 1H, *J* = 17.5 Hz, =CH_2), 6.65 (dd, 1H, *J* = 17.5, 10.8 Hz, =CH), 7.28–7.33 (m, 3H, H_{Ar}), 7.42–7.46 (m, 2H, H_{Ar}), 7.63 (d, 1H, *J* = 8.2 Hz, H_{Ar}), 7.76 (d, 1H, *J* = 2.1 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$):

δ = −62.51; ^{13}C NMR (63 MHz, 300 K, $CDCl_3$): δ = 114.8 (=CH_2), 118.8 ($J_{C,F}$ = 1.8 Hz, C_{Ar}), 122.9 ($J_{C,F}$ = 274 Hz, CF_3), 124.9, 126.0, 126.3, 126.4 ($J_{C,F}$ = 5.4 Hz), 129.3 (CH_{Ar}), 130.4 ($J_{C,F}$ = 31.2 Hz, C_{Ar}), 131.3, 135.3 (CH_{Ar}), 136.0 (=CH), 138.4, 138.9, 140.5 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3045, 2927, 1892 (w), 1600, 1513, 1473, 1424 (m), 1324 (s), 1266, 1236, 1173 (m), 1126 (s), 1020 (m), 903, 843 (m), 819 (s), 722, 659, 570 (m) cm^{-1} GC–MS (EI, 70 eV): *m*/*z* (%) 326 (M$^+$, ^{79}Br, 100), 247 (8), 246 (12), 227 (6), 225 (5), 178 (25), 176 (11), 152 (6), 152 (6); HRMS (EI): calcd. for $C_{15}H_{10}{}^{79}BrF_3$ [M]$^+$: 325.991250; Found: 325.990805.

*4.5.10. 4-Bromo-4′-tert-butyl-3-(trifluoromethyl)biphenyl (**7j**)*

Starting from **6** (150 mg, 0.5 mmol), and **2r** (90 mg, 0.5 mmol), **7j** was obtained as a yellowish heavy oil (158 mg, 88%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 1.28 (s, 9H, $(CH_3)_3$), 7.42 (s, 4H, H_{Ar}), 7.50 (dd, 1H, *J* = 2.1, 8.3 Hz, H_{Ar}), 7.67 (d, 1H, *J* = 8.2 Hz, H_{Ar}), 7.80 (d, 1H, *J* = 2.1 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.61; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 31.2 ($(CH_3)_3$), 34.6 ($C(CH_3)_3$), 118.3 ($J_{C,F}$ = 1.9 Hz, C_{Ar}), 123.0 ($J_{C,F}$ = 272 Hz, CF_3), 126.1, 126.3 ($J_{C,F}$ = 5.4 Hz), 126.6 (CH_{Ar}), 130.4 ($J_{C,F}$ = 31.7 Hz, C_{Ar}), 131.1, 135.2 (CH_{Ar}), 135.7, 140.6, 151.6 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3034, 2961, 2868, 1601 (w), 1473, 1418 (m), 1325 (s), 1251, 1172 (m), 1129, 1100 (s), 1021 (m), 962 (w), 902 (m), 818 (s), 743, 697, 659 (m), 603 (w), 566 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 356 (M$^+$, ^{79}Br, 28), 344 (18), 343 (98), 342 (19), 341 (100), 315 (20), 313 (20), 262 (10), 233 (7), 222 (8), 165 (7), 157 (8), 156 (9); HRMS (EI): calcd. for $C_{17}H_{16}{}^{79}BrF_3$ [M]$^+$: 356.038200; Found: 356.038994.

*4.5.11. 4-Bromo-4′-chloro-3-(trifluoromethyl)biphenyl (**7k**)*

Starting from **6** (150 mg, 0.5 mmol), and **2s** (78 mg, 0.5 mmol), **7k** was obtained as a white solid (139 mg, 83%), mp = 50–52 °C. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 7.35–7.42 (m, 4H, H_{Ar}), 7.46 (dd, 1H, *J* = 2.0, 8.1 Hz, H_{Ar}), 7.69 (d, 1H, *J* = 8.1 Hz, H_{Ar}), 7.76 (d, 1H, *J* = 2.0 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.61; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 119.1 ($J_{C,F}$ = 1.9 Hz, C_{Ar}), 122.8 ($J_{C,F}$ = 272 Hz, CF_3), 126.2 ($J_{C,F}$ = 5.4 Hz), 128.2, 129.3 (CH_{Ar}), 130.6 ($J_{C,F}$ = 31.0 Hz, C_{Ar}), 131.1 (CH_{Ar}), 134.6 (C_{Ar}) 135.5 (CH_{Ar}), 137.1, 139.5 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3037, 2926, 1899, 1596 (w), 1470, 1417 (m), 1324 (s), 1248, 1171 (m), 1127, 1094, 1010 (s), 961 (w), 903 (m), 812 (s), 746, 695, 658 (m), 597 (w), 544 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 334 (M$^+$, ^{79}Br + ^{35}Cl, 76), 255 (11), 235 (8), 220 (18), 219 (16), 201 (8), 186 (9), 151 (6), 150 (5), 128 (7); HRMS (EI): calcd. for $C_{13}H_7{}^{79}Br{}^{35}ClF_3$ [M]$^+$: 333.936630; Found: 333.936462.

*4.5.12. 2-(4-Bromo-3-(trifluoromethyl)phenyl)naphthalene (**7l**)*

Starting from **6** (150 mg, 0.5 mmol), and **2t** (86 mg, 0.5 mmol), **7l** was obtained as a white crystalline solid (139 mg, 79%), mp = 206–208 °C. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 7.40–7.44 (m, 2H, H_{Ar}), 7.54–7.59 (m, 2H, H_{Ar}), 7.67 (d, 1H, *J* = 8.3 Hz, H_{Ar}), 7.75–7.88 (m, 5H, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.4; ^{13}C NMR (63 MHz, 298 K, $CDCl_3$): δ = 118.8 ($J_{C,F}$ =1.8 Hz, C_{Ar}), 123.0 ($J_{C,F}$ = 274 Hz, CF_3), 124.7, 126.0, 126.5 ($J_{C,F}$ = 5.4 Hz), 126.6, 126.7, 127.7, 128.2, 128.9 (CH_{Ar}), 130.3, 130.8 (C_{Ar}), 131.5 (CH_{Ar}), 132.2 ($J_{C,F}$ = 34.4 Hz, C_{Ar}) 135.4 (CH_{Ar}), 135.9, 140.6 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3048, 2916, 1586 (w), 1479, 1433, 1382, 1301 (m), 1230 (w), 1158, 1091, 1017 (m), 969, 885 (w), 814 (m), 743, 689 (s), 617 (m), 541 (w) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 350 (M$^+$, ^{79}Br, 100), 271 (13), 270 (9), 269 (9), 251 (12), 220 (5), 202 (27), 200 (9), 176 (6); HRMS (EI): calcd. for $C_{17}H_{10}{}^{79}BrF_3$ [M]$^+$: 349.991250; Found: 349.990657.

*4.5.13. 4′-Bromo-2,5-dimethoxy-3′-(trifluoromethyl)biphenyl (**7m**)*

Starting from **6** (150 mg, 0.5 mmol), and **2u** (91 mg, 0.5 mmol), **7 m** was obtained as a slight yellowish dense oil (166 mg, 92%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.65, 3.69 (s, 6H, 2 OCH_3), 6.76–6.79 (m, 3H, H_{Ar}), 7.43 (dd, 1H, *J* = 1.9, 8.2 Hz, H_{Ar}), 7.61 (d, 1H, *J* = 8.2 Hz, H_{Ar}), 7.75 (d, 1H, *J* = 1.9 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.48; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 55.7, 55.8 (OCH_3), 112.7, 114.0, 116.4 (CH_{Ar}), 118.4 ($J_{C,F}$ = 1.8 Hz, C_{Ar}), 123.0 ($J_{C,F}$ = 274 Hz, CF_3), 128.8 ($J_{C,F}$ = 5.4 Hz, CH_{Ar}), 128.9, 129.7 ($J_{C,F}$ = 31.0 Hz, C_{Ar}), 133.9, 134.5 (CH_{Ar}), 137.9, 150.5, 153.9 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3067, 2995, 2937, 2832, 1586 (w), 1515, 1474, 1401, 1327, 1286 (m), 1245, 1166, 1097, 1015 (s), 969, 910, 855 (m), 812 (s), 762, 671, 620, 582, 531 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 360 (M$^+$, ^{79}Br, 99), 347 (12), 345 (12), 267 (15), 266 (95), 252 (5), 251 (33), 223 (18), 218 (6), 207 (5), 206 (6), 195 (12), 188 (8), 175 (8), 169 (11); HRMS (EI): calcd. for $C_{15}H_{12}O_2{}^{79}BrF_3$ [M]$^+$: 359.996730; Found: 359.996175.

*4.5.14. 4′-Bromo-2,6-dimethoxy-3′-(trifluoromethyl)biphenyl (**7n**)*

Starting from **6** (150 mg, 0.5 mmol), and **2v** (91 mg, 0.5 mmol), **7n** was obtained as a colorless dense oil (157 mg, 87%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.65 (s, 6H, 2 OCH_3), 6.39–6.43 (m, 1H, H_{Ar}), 7.20–7.30 (m, 4H, H_{Ar}), 7.62 (d, 1H, *J* = 8.2 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.35; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 55.8 (2 OCH_3), 104.1 (CH_{Ar}), 117.9 ($J_{C,F}$ = 1.7 Hz, C_{Ar}), 123.2 ($J_{C,F}$ = 275.1 Hz, CF_3), 128.9, 129.5 ($J_{C,F}$ = 31.2 Hz, C_{Ar}), 129.7 ($J_{C,F}$ = 5.3 Hz), 129.8, 134.1, 135.7 (CH_{Ar}), 137.8, 157.9 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3065, 2999, 2935, 2830, 1587 (w), 1517, 1475, 1402, 1325, 1288 (m), 1245, 1165, 1098, 1015 (s), 971, 912, 855 (m), 811 (s), 762, 671, 615, 581, 530 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 360 (M$^+$, ^{79}Br, 100), 343 (5), 341 (5), 267 (5), 266 (30), 265 (5), 252 (5), 251 (24), 250 (7), 237 (6), 236 (9), 223 (16), 207 (8), 206 (7), 195 (10), 175 (7), 169 (8); HRMS (EI): calcd. for $C_{15}H_{12}O_2{}^{79}BrF_3$ [M]$^+$: 359.996730; Found: 359.995736.

*4.5.15. 4-Bromo-3′,4′-dimethoxy-3-(trifluoromethyl)biphenyl (**7o**)*

Starting from **6** (150 mg, 0.5 mmol), and **2w** (91 mg, 0.5 mmol), **7o** was obtained as a colorless heavy oil (170 mg, 94%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.85, 3.87 (s, 6H, 2 OCH_3), 6.87 (d, 1H, *J* = 8.2 Hz, H_{Ar}), 6.96 (d, 1H, *J* = 2.1 Hz, H_{Ar}), 7.02 (dd, 1H, *J* = 2.1, 8.2 Hz, H_{Ar}), 7.45 (dd, 1H, *J* = 2.2, 8.3 Hz, H_{Ar}), 7.64 (d, 1H, *J* = 8.3 Hz, H_{Ar}), 7.75 (d, 1H, *J* = 2.2 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −62.48; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 55.7, 55.8 (OCH_3), 112.7, 114.0, 116.4 (CH_{Ar}), 118.4 ($J_{C,F}$ = 1.8 Hz, C_{Ar}), 123.0 ($J_{C,F}$ = 274 Hz, CF_3), 128.8 ($J_{C,F}$ = 5.4 Hz, CH_{Ar}), 128.9, 129.7 ($J_{C,F}$ = 31.0 Hz, C_{Ar}), 133.9, 134.5 (CH_{Ar}), 137.9, 150.5, 153.9 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3066, 2998, 2937, 2833, 1588 (w), 1516, 1474, 1400, 1328, 1289 (m), 1244, 1166, 1099, 1016 (s), 970, 911, 856 (m), 810 (s), 761, 670, 619, 583, 532 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 360 (M$^+$, ^{79}Br, 100), 347 (14), 345 (14), 319 (16), 317 (17), 281 (7), 239 (8), 238 (56), 236 (8), 220 (11), 219 (5), 207 (8), 195 (15), 175 (6), 169 (8); HRMS (EI): calcd. for $C_{15}H_{12}O_2{}^{79}BrF_3$ [M]$^+$: 359.996730; Found: 359.996658.

*4.6. Typical procedure for the synthesis of 1,4-diaryl-3-(trifluoromethyl)benzene (**8a**–**m**)*

The reaction was carried out in a pressure tube. To a dioxane suspension (5 mL) of the 1,4-dibromo-2-(trifluoromethyl)benzene (**6**), $Pd(PPh_3)_4$ (3–5 mol%) and of the arylboronic acid (**2**) was added an aqueous solution of K_2CO_3 (2 M, 1–2 mL). The mixture was heated at the indicated temperature (90 °C) under Argon atmosphere for the indicated period of time (8 h). The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (5 mL each), and the organic and the aqueous layers were separated. The latter was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with H_2O (3 × 10 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc) to give 1,4-diaryl-3-(trifluoromethyl)-benzene (**8a**–**m**) (79–95%).

*4.6.1. 2-Trifluoromethyl-1,4-bis(2-methylphenyl)-benzene (**8a**)*

Starting from **6** (150 mg, 0.5 mmol), and **2a** (170 mg, 1.25 mmol), **8a** was obtained as a colorless heavy oil (139 mg, 85%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 2.02, 2.52 (s, 6H, 2 CH_3), 7.13–7.24 (m, 9H, H_{Ar}), 7.44 (m, 1H, H_{Ar}), 7.64 (d, 1H, J = 1.8 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −59.05; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 20.1, 20.4 (CH_3), 124.0 ($J_{C,F}$ = 270 Hz, CF_3), 124.8, 126.7 ($J_{C,F}$ = 5.1 Hz), 127.9 (CH_{Ar}), 128.5 ($J_{C,F}$ = 30.9 Hz, C_{Ar}), 129.5, 129.6, 129.7, 130.6, 131.4, 131.9 (CH_{Ar}), 135.3, 136.1, 138.7, 139.0, 140.2 ($J_{C,F}$ = 1.9 Hz), 141.1 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3021, 2924 (w), 1477, 1404 (m), 1321 (s), 1288, 1244 (m), 1167, 1117 (s), 1068, 1026, 1006 (m), 943 (w), 907, 846 (m), 753, 723 (s), 663, 583, 543 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 327 (24), 326 (M$^+$, 100), 311 (17), 285 (15), 271 (13), 270 (19), 258 (15), 257 (65), 242 (38), 241 (33), 239 (29), 215 (14), 165 (25); HRMS (EI): calcd. for $C_{21}H_{17}F_3$ [M]$^+$: 326.127690; Found: 326.127240.

*4.6.2. 2-Trifluoromethyl-1,4-bis(3-methylphenyl)-benzene (**8b**)*

Starting from **6** (150 mg, 0.5 mmol), and **2b** (170 mg, 1.25 mmol), **8b** was obtained as a yellowish heavy oil (140 mg, 86%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 2.32, 2.36 (s, 6H, 2 CH_3), 7.07–7.36 (m, 9H, H_{Ar}), 7.66 (dd, 1H, J = 7.9, 1.6 Hz, H_{Ar}), 7.86 (d, 1H, J = 1.6 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.72; ^{13}C NMR (75 MHz, 299 K, $CDCl_3$): δ = 21.4, 21.5 (CH_3), 123.2 (CH_{Ar}), 123.6 ($J_{C,F}$ = 275 Hz, CF_3), 123.7 ($J_{C,F}$ = 5.4 Hz), 125.0, 126.6, 126.8, 127.3, 127.7, 127.9, 128.2, 128.6 ($J_{C,F}$ = 1.6 Hz) (CH_{Ar}), 131.5 ($J_{C,F}$ = 29.7 Hz, C_{Ar}), 131.7 (CH_{Ar}), 136.3, 137.6, 138.4, 138.5, 139.1 ($J_{C,F}$ = 1.8 Hz), 139.4 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3030, 2921 (w), 1605, 1477 (m), 1393 (w), 1325, 1273, 1244, 1163 (m), 1118 (s), 1073, 1054, 1033 (m), 971 (w), 894, 840 (m), 779, 700 (s), 665, 609 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 327 (23), 326 (M$^+$, 100), 305 (17), 291 (35), 271 (23), 270 (49), 257 (37), 242 (49), 241 (56), 239 (42), 215 (24), 165 (31), 163 (46); HRMS (EI): calcd. for $C_{21}H_{17}F_3$ [M]$^+$: 326.127690; Found: 326.127298.

*4.6.3. 2-Trifluoromethyl-1,4-bis(4-methylphenyl)-benzene (**8c**)*

Starting from **6** (150 mg, 0.5 mmol), and **2c** (170 mg, 1.25 mmol), **8c** was obtained as a heavy oil (139 mg, 85%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 2.34 (s, 6H, 2 CH_3), 7.12–7.30 (m, 7H, H_{Ar}), 7.46 (d, 2H, J = 8.1 Hz, H_{Ar}), 7.65 (dd, 1H, J = 7.8, 1.5 Hz, H_{Ar}), 7.67 (d, 1H, J = 1.5 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.78; ^{13}C NMR (63 MHz, 300 K, $CDCl_3$): δ = 21.1, 21.2 (CH_3), 124.2 ($J_{C,F}$ = 275 Hz, CF_3), 124.5 ($J_{C,F}$ = 5.4 Hz), 126.9, 128.5 (CH_{Ar}), 128.7 ($J_{C,F}$ = 29.7 Hz, C_{Ar}), 128.8, 129.5, 129.7, 132.7 (CH_{Ar}), 136.6, 136.7, 137.3, 137.8, 139.9, 140.2 ($J_{C,F}$ = 1.9 Hz) (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3024, 2964, 1913, 1613 (w), 1487, 1423, 1323, 1265 (m), 1168, 1109 (s), 1068, 1004, 966, 902 (m), 811 (s), 757, 719, 666, 587 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 327 (23), 326 (M$^+$, 100), 305 (28), 291 (35), 271 (28), 270 (47), 257 (61), 256 (25), 242 (49), 241 (56), 239 (42), 215 (24), 207 (31), 200 (55), 165 (39), 163 (46), 152 (41), 135 (63), 121 (60), 119 (82), 105 (71), 91 (84), 69 (86); HRMS (EI): calcd. for $C_{21}H_{17}F_3$ [M]$^+$: 326.127690; Found: 326.127367.

*4.6.4. 2-Trifluoromethyl-1,4-bis(3,5-dimethylphenyl)-benzene (**8d**)*

Starting from **6** (150 mg, 0.5 mmol), and **2e** (187 mg, 1.25 mmol), **8d** was obtained as a white crystalline solid (154 mg, 87%), mp = 108–109 °C. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 2.41, 2.43, 2.45, 2.46 (s, 12H, 4CH_3), 7.03 (s, 2H, H_{Ar}), 7.08–7.10 (m, 2H, H_{Ar}), 7.28–7.30 (m, 2H, H_{Ar}), 7.41 (d, 1H, J = 7.9 Hz, H_{Ar}), 7.77 (dd, 1H, J = 7.9, 1.8 Hz, H_{Ar}), 7.97 (d, 1H, J = 1.8 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.70; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 21.3, 21.4 (CH_3), 124.2 ($J_{C,F}$ = 274 Hz, CF_3), 124.7 ($J_{C,F}$ = 5.4 Hz), 125.0 (CH_{Ar}), 125.1 (C_{Ar}), 126.8 ($J_{C,F}$ = 1.5 Hz, CH_{Ar}), 128.6 ($J_{C,F}$ = 29.5 Hz, C_{Ar}), 129.2, 129.6, 132.5 (CH_{Ar}), 137.2, 138.6, 139.5, 139.6, 140.2, 140.3, 140.5 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3020, 2916 (w), 1601, 1505, 1454, 1376, 1335 (m), 1293 (s), 1249 (m), 1199 (w), 1124 (s), 1088, 1048, 996 (m), 946 (w), 900 (m), 836 (s), 761, 701, 651, 580 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 355 (40), 354 (M$^+$, 100), 339 (15), 319 (32), 283 (22), 270 (44), 269 (30), 255 (39), 253 (41), 252 (36), 239 (33), 215 (19), 177 (39), 169 (24), 162 (48); HRMS (EI): calcd. for $C_{23}H_{21}F_3$ [M]$^+$: 354.158990; Found: 354.158570.

*4.6.5. 2-Trifluoromethyl-1,4-bis(4-ethylphenyl)-benzene (**8e**)*

Starting from **6** (150 mg, 0.5 mmol), and **2f** (187 mg, 1.25 mmol), **8e** was obtained as a white heavy oil (154 mg, 87%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 1.20 (t, 6H, J = 7.6 Hz, CH_3), 2.61 (q, 4H, J = 7.6 Hz, CH_2), 7.13–7.29 (m, 7H, H_{Ar}), 7.46 (d, 2H, J = 8.2 Hz, H_{Ar}), 7.64 (dd, 1H, J = 7.8, 1.6 Hz, H_{Ar}), 7.85 (d, 1H, J = 1.6 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.72; ^{13}C NMR (63 MHz, 300 K, $CDCl_3$): δ = 15.4 (CH_3), 28.6 (CH_2), 124.2 ($J_{C,F}$ = 275 Hz, CF_3), 124.5 ($J_{C,F}$ = 5.4 Hz), 127.0, 127.3, 128.5, 128.9 ($J_{C,F}$ = 1.6 Hz), (CH_{Ar}), 129.0 ($J_{C,F}$ = 31.2 Hz, C_{Ar}), 129.5, 132.7 (CH_{Ar}), 136.9, 137.0, 139.9 ($J_{C,F}$ = 1.8 Hz), 140.2, 143.6, 144.2 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3024, 2964, 1905, 1796, 1613 (w), 1487, 1426 (m), 1323 (s), 1264 (m), 1166, 1114 (s), 1069, 1005 (m), 964 (w), 903 (m), 821 (s), 718, 667, 588 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 355 (25), 354 (M$^+$, 100), 340 (18), 339 (78), 324 (13), 270 (14), 252 (11), 241 (9), 239 (22), 169 (14), 162 (32); HRMS (EI): calcd. for $C_{23}H_{21}F_3$ [M]$^+$: 354.195640; Found: 354.195231.

*4.6.6. 2-Trifluoromethyl-1,4-bis(2,3-dimethoxyphenyl)-benzene (**8f**)*

Starting from **6** (150 mg, 0.5 mmol), and **2h** (227 mg, 1.25 mmol), **8f** was obtained as a colorless heavy oil (182 mg, 87%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.55, 3.60, 3.84, 3.85 (s, 12H, 4 OCH_3), 6.79–7.10 (m, 6H, H_{Ar}), 7.29 (d, 1H, J = 7.9 Hz, H_{Ar}), 7.66 (dd, 1H, J = 7.9, 1.4 Hz, H_{Ar}), 7.87 (d, 1H, J = 1.4 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 299 K, $CDCl_3$): δ = −57.9; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 55.8, 55.9, 60.5, 60.7 (OCH_3), 112.2, 112.3, 122.4, 122.9 (CH_{Ar}), 123.8 ($J_{C,F}$ = 275.1 Hz, CF_3), 124.3, 126.8 ($J_{C,F}$ = 5.4 Hz) (CH_{Ar}), 128.6 ($J_{C,F}$ = 29.4 Hz, C_{Ar}), 131.6, 132.0 (CH_{Ar}), 133.7, 134.2, 135.8, 135.9, 137.5, 146.6, 152.5, 153.2 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3075, 2935, 2835, 1679 (w), 1579 (m), 1511 (w), 1465 (s), 1402, 1328, 1300 (m), 1260 (s), 1166 (m), 1119 (s), 1060 (m), 1001 (s), 907, 841, 786, 744, 674, 592, 541 (m) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 419 (27), 418 (M$^+$, 100), 388 (13), 369 (5), 368 (43), 363 (14), 353 (17), 252 (29), 325 (15), 304 (24), 209 (32); HRMS (EI): calcd. for $C_{23}H_{21}O_4F_3$ [M]$^+$: 418.138650; Found: 418.137837.

*4.6.7. 2-Trifluoromethyl-1,4-bis(2,3,4-trimethoxyphenyl)-benzene (**8g**)*

Starting from **6** (150 mg, 0.5 mmol), and **2i** (265 mg, 1.25 mmol), **8g** was obtained as a white crystalline solid (218 mg, 91%), mp = 85–87 °C. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.73, 3.79 (s, 6H, 2 OCH_3), 3.94 (s, 9H, 3 OCH_3), 3.97 (s, 3H, OCH_3), 6.72 (d, 1H, J = 8.6 Hz, H_{Ar}), 6.81 (d, 1H, J = 8.6 Hz, H_{Ar}), 6.95 (d, 1H, J = 8.5 Hz, H_{Ar}), 7.13 (d, 1H, J = 8.5 Hz, H_{Ar}), 7.36 (d, 1H, J = 7.9 Hz, H_{Ar}), 7.71 (dd, 1H, J = 7.9, 1.7 Hz, H_{Ar}), 7.91 (d, 1H, J = 1.7 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.78; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 55.9, 56.0, 60.8, 60.9, 61.0, 61.1 (OCH_3), 106.3, 107.6 (CH_{Ar}), 124.2 ($J_{C,F}$ = 273 Hz, CF_3), 124.7, 125.0 ($J_{C,F}$ = 1.4 Hz) (CH_{Ar}), 126.1 (C_{Ar}), 126.6 ($J_{C,F}$ = 5.3 Hz, CH_{Ar}), 126.9, 128.9 ($J_{C,F}$ = 29.2 Hz, C_{Ar}), 131.5, 132.4 (CH_{Ar}), 135.3 ($J_{C,F}$ = 2.0 Hz), 137.4, 141.9, 142.6, 151.4, 151.5, 153.6, 151.7 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 2936, 2837 (w), 1597 (m), 1555 (w), 1481, 1412, 1325, 1287, 1208, 1165 (m), 1108, 1078, 1003 (s), 920, 866, 793, 727, 695, 655 (m), 570 (w) cm^{-1}; GC–MS (EI, 70 eV): *m*/*z* (%) 479 (29), 478 (M$^+$, 100), 448 (28), 428 (25), 420 (43), 413 (36), 412 (45), 397 (14), 349 (35), 239 (52), 224 (22), 167 (25), 146 (24), 110 (9); HRMS (EI): calcd. for $C_{25}H_{25}O_6F_3$ [M]$^+$: 478.159770; Found: 478.159508.

*4.6.8. 2-Trifluoromethyl-1,4-bis(3-trifluoromethylphenyl)-benzene (**8h**)*

Starting from **6** (150 mg, 0.5 mmol), and **2m** (237 mg, 1.25 mmol), **8h** was obtained as a colorless heavy oil (178 mg, 82%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 7.37 (d, 1H, J = 5.3 Hz, H_{Ar}), 7.48 (m, 2H, H_{Ar}), 7.55–7.62 (m, 4H, H_{Ar}), 7.72–7.75 (m, 2H, H_{Ar}), 7.80 (s, 1H, H_{Ar}), 7.90 (d, J = 1.0 Hz, H_{Ar}); ^{19}F NMR (283 MHz, 300 K, $CDCl_3$): δ = −62.65, −56.91; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 123.9 ($J_{C,F}$ = 274.5 Hz, CF_3), 124.2 ($J_{C,F}$ = 275.2 Hz, CF_3), 123.9 ($J_{C,F}$ = 4.4 Hz), 124.7 ($J_{C,F}$ = 4.5 Hz), 125.1 ($J_{C,F}$ = 5.4 Hz), 125.8 ($J_{C,F}$ = 1.9 Hz), (CH_{Ar}), 129.3 ($J_{C,F}$ = 29.6 Hz, C_{Ar}), 129.6, 130.0 (CH_{Ar}), 130.0 ($J_{C,F}$ = 19.2 Hz, C_{Ar}), 130.5 (CH_{Ar}), 131.5 ($J_{C,F}$ = 19.4 Hz, C_{Ar}), 132.2, 132.6, 132.7 (CH_{Ar}), 139.2, 139.8, 139.9, 140.0 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3074, 3043 (w), 1481, 1431, 1398, 1332, 1313, 1245, 1164 (m), 1115, 1068, 1044 (s), 1001, 896, 845 (m), 799 (s), 759, 699, 653, 593, 561 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%) 435 (23), 434 (M$^+$, 100), 416 (12), 415 (27), 413 (15), 395 (23), 364 (13), 346 (24), 345 (47), 325 (19), 296 (25), 275 (14), 269 (24), 219 (18), 201 (16); HRMS (EI): calcd. for $C_{21}H_{11}F_9$ [M]$^+$: 434.071160; Found: 434.070626.

*4.6.9. 2-Trifluoromethyl-1,4-bis(4-methoxyphenyl)-benzene (**8i**)*

Starting from **6** (150 mg, 0.5 mmol), and **2n** (190 mg, 1.25 mmol), **8i** was obtained as a heavy oil (167 mg, 93%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.77, 3.78 (s, 6H, 2 OCH_3), 6.86 (d, 2H, J = 8.7 Hz, H_{Ar}), 6.93 (d, 2H, J = 8.7 Hz, H_{Ar}), 7.18–7.27 (m, 3H, H_{Ar}), 7.48 (d, 2H, J = 8.8 Hz, H_{Ar}), 7.62 (dd, 1H, J = 8.8, 1.6 Hz, H_{Ar}), 7.82 (d, 1H, J = 1.6 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.83; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 55.2, 55.4 (OCH_3), 113.3, 114.5, 124.2 ($J_{C,F}$ = 4.5 Hz) (CH_{Ar}) 124.3 ($J_{C,F}$ = 275 Hz, CF_3), 128.1, 129.2, 130.1 ($J_{C,F}$ = 1.4 Hz), (CH_{Ar}), 130.8 ($J_{C,F}$ = 30.9 Hz, C_{Ar}), 132.0 (CH_{Ar}), 132.8, 139.2, 139.3, 139.8 ($J_{C,F}$ = 1.9 Hz), 159.1, 159.7 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3028, 2922 (w), 1605, 1475 (m), 1395 (w), 1321, 1270, 1241, 1165 (m), 1118 (s), 1074, 1050, 1032 (m), 972 (w), 895, 839 (m), 778, 705 (s), 663, 607 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%) 359 (22), 358 (M$^+$, 100), 344 (12), 243 (32), 315 (14), 300 (14), 271 (17), 251 (41), 207 (15), 202 (22), 179 (49), 157 (28); HRMS (EI): calcd. for $C_{21}H_{17}O_2F_3$ [M]$^+$: 358.117520; Found: 358.116616.

*4.6.10. 1,4-Diphenyl-3-(trifluoromethyl)-benzene (**8j**)*

Starting from **6** (150 mg, 0.5 mmol), and **2o** (152 mg, 1.25 mmol), **8j** was obtained as a colorless heavy oil (127 mg, 85%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 7.26–7.58 (m, 11H, H_{Ar}), 7.68 (dd, 1H, J = 1.6, 7.9 Hz, H_{Ar}), 7.87 (d, 1H, J = 1.6 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.77; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 124.2 ($J_{C,F}$ = 273.1 Hz, CF_3), 124.8 ($J_{C,F}$ = 5.2 Hz), 127.1, 127.7, 128.8, 128.0, 128.9, 129.0 (CH_{Ar}), 129.3 ($J_{C,F}$ = 31.1 Hz, C_{Ar}), 129.7, 132.6 (CH_{Ar}), 139.5, 139.6, 140.2 ($J_{C,F}$ = 1.9 Hz), 140.5 (C_{Ar}); IR (neat, cm^{-1}): $\tilde{\nu}$ = 3346 (br.), 2973, 1581 (w), 1451, 1403, 1320, 1243, 1172 (m), 1124, 1071, 1044 (s), 1006, 977, 903, 879, 857, 837 (m), 761, 691 (s), 665, 597, 530 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%) 299 (49, M + 1), 298 (M$^+$, 100), 278 (7), 277 (16), 259 (7), 257 (12), 229 (5), 228 (15), 227 (8), 226 (13), 202 (8), 201 (14), 149 (5); HRMS (EI): calcd. for $C_{19}H_{13}F_3$ [M]$^+$: 298.096390; Found: 298.096115.

*4.6.11. 2-Trifluoromethyl-1,4-bis(2,5-dimethoxyphenyl)-benzene (**8k**)*

Starting from **6** (150 mg, 0.5 mmol), and **2u** (227 mg, 1.25 mmol), **8k** was obtained as a slight yellowish dense oil (165 mg, 79%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.61, 3.68, 3.70, 3.72 (s, 12H, 4 OCH_3), 6.72–6.88 (m, 6H, H_{Ar}), 7.23 (d, 1H, J = 7.9 Hz, H_{Ar}), 7.64 (d, 1H, J = 7.9 Hz, H_{Ar}), 7.64 (dd, 1H, J = 7.9, 1.3 Hz, H_{Ar}), 7.82 (d, 1H, J = 1.3 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −58.81; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 55.7, 55.8, 56.1, 56.2 (OCH_3), 111.7, 112.6, 113.8, 113.9, 116.6, 116.8 ($J_{C,F}$ = 1.3 Hz), 117.2 (CH_{Ar}), 124.2 ($J_{C,F}$ = 272.5 Hz, CF_3), 127.1 ($J_{C,F}$ = 5.4 Hz, CH_{Ar}), 128.8 ($J_{C,F}$ = 29.5 Hz), 129.4, 129.8 (C_{Ar}), 131.8, 132.1 (CH_{Ar}), 135.9 ($J_{C,F}$ = 1.8 Hz), 137.7, 150.7, 151.1, 152.9, 153.9 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 2934, 2835 (w), 1593 (m), 1551 (w), 1480, 1413, 1321, 1289, 1209, 1163 (m), 1105, 1077, 1001 (s), 925, 868, 792, 725, 697, 654 (m), 573 (w) cm^{-1}; GC–MS (EI, 70 eV): m/z (%) 419 (25), 418 (M$^+$, 100), 388 (18), 369 (7), 368 (46), 363 (17), 353 (37), 352 (45), 325 (28), 297 (13), 209 (31), 194 (20); HRMS (EI): calcd. for $C_{23}H_{21}O_4F_3$ [M]$^+$: 418.138650; Found: 418.139359.

*4.6.12. 2-Trifluoromethyl-1,4-bis(3,4-dimethoxyphenyl)-benzene (**8l**)*

Starting from **6** (150 mg, 0.5 mmol), and **2w** (227 mg, 1.25 mmol), **8l** was obtained as a yellowish crystalline solid (198 mg, 95%), mp = 110–112 °C. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.80, 3.85, 3.86, 3.89 (s, 12H, 4 OCH_3), 6.84–7.12 (m, 6H, H_{Ar}), 7.32 (d, 1H, J = 7.9 Hz, H_{Ar}), 7.65 (dd, 1H, J = 7.9, 1.8 Hz, H_{Ar}), 7.81 (d, 1H, J = 1.8 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.78; ^{13}C NMR (63 MHz, 300 K, $CDCl_3$): δ = 55.8, 55.9, 56.1, 56.2 (OCH_3), 110.2, 110.5, 111.6, 112.5 ($J_{C,F}$ = 1.6 Hz), 119.5, 121.3 (CH_{Ar}), 124.2 ($J_{C,F}$ = 275.2 Hz, CF_3), 124.4 ($J_{C,F}$ = 5.3 Hz, CH_{Ar}), 128.8 ($J_{C,F}$ = 29.5 Hz, C_{Ar}), 129.4 (CH_{Ar}), 132.1, 132.4 (C_{Ar}), 132.7 (CH_{Ar}), 139.4 ($J_{C,F}$ = 1.8 Hz), 140.1, 148.1, 148.9, 149.2, 149.4 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 2935, 2836 (w), 1596 (m), 1555 (w), 1482, 1413, 1322, 1285, 1205, 1160 (m), 1107, 1074, 1002 (s), 923, 865, 792, 726, 693, 651 (m), 571 (w) cm^{-1}; GC–MS (EI, 70 eV): m/z (%) 419 (24), 418 (M$^+$, 100), 403 (25), 375 (30), 360 (48), 335 (31), 324 (23), 249 (19), 220 (15), 209 (49); HRMS (EI): calcd. for $C_{23}H_{21}O_4F_3$ [M]$^+$: 418.138650; Found: 418.138754.

*4.6.13. 2-Trifluoromethyl-1,4-bis(3-methoxyphenyl)-benzene (**8m**)*

Starting from **6** (150 mg, 0.5 mmol), and **2x** (190 mg, 1.25 mmol), **8m** was obtained as a heavy oil (159 mg, 89%). ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.76, 3.81 (s, 6H, 2 OCH_3), 6.84–6.89 (m, 4H, H_{Ar}), 7.06–7.31 (m, 5H, H_{Ar}), 7.66–7.69 (dd, 1H, J = 8.0, 1.6 Hz, H_{Ar}), 7.86 (d, 1H, J = 1.6 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.84; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 55.2, 55.3 (OCH_3), 112.9, 113.3, 113.5, 114.7, 119.6, 121.5 (CH_{Ar}), 123.1 ($J_{C,F}$ = 273 Hz, CF_3), 124.8 ($J_{C,F}$ = 5.3 Hz, CH_{Ar}), 128.7 ($J_{C,F}$ = 30.3 Hz, C_{Ar}), 128.8, 130.0, 132.4 (CH_{Ar}), 14.0, 140.4 ($J_{C,F}$ = 1.9 Hz), 140.8, 140.9, 158.9, 160.1 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3032, 2919 (w), 1603, 1477 (m), 1392 (w), 1324, 1272, 1243, 1161 (m), 1116 (s), 1073, 1055, 1034 (m), 972 (w), 894, 842 (m), 779, 702 (s), 664, 607 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%) 359 (33), 358 (M$^+$, 100), 339 (27), 328 (39), 315 (53), 285 (21), 272 (17), 271 (14), 265 (15), 251 (42), 245 (24), 233 (23), 202 (26), 179 (52); HRMS (EI): calcd. for $C_{21}H_{17}O_2F_3$ [M]$^+$: 358.117520; Found: 358.117099.

*4.7. Typical procedure for the synthesis of 1,4-diaryl-3-(trifluoromethyl)benzene (**9a–d**)*

The reaction was carried out in a pressure tube. To a dioxane suspension (5 mL) of the 4-aryl-1-bromo-2-trifluoromethylbenzenes (**7**), $Pd(PPh_3)_4$ (3–5 mol%) and of the arylboronic acid (**2**) was added an aqueous solution of K_2CO_3 (2 M, 1–2 mL). The mixture was heated at the indicated temperature (80 °C) under Argon atmosphere for the indicated period of time (8 h). The solution was cooled to 20 °C, poured into H_2O and CH_2Cl_2 (5 mL each), and the organic and the aqueous layers were separated. The later was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were washed with H_2O (3 × 10 mL), dried (Na_2SO_4), and concentrated in vacuo. The residue was purified by chromatography (flash silica gel, heptanes/EtOAc) to give 1,4-diaryl-3-(trifluoromethyl)-benzene (**9a–d**) (80–88%).

*4.7.1. 1-(3′,4′-Dimethoxy)-phenyl-4-(4″-ethyl)-phenyl-2-trifluoromethylbenzene (**9a**)*

Starting from **7c** (82 mg, 0.25 mmol), and **2w** (45 mg, 0.25 mmol), **9a** was obtained as a yellowish crystalline solid (85 mg, 88%), mp = 185–186 °C. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 1.21 (t, 3H, J = 7.6 Hz, CH_3), 2.64 (q, 2H, J = 7.6 Hz, CH_2), 3.81, 3.85 (s, 6H, 2 OCH_3), 6.82–6.85 (m, 3H, H_{Ar}), 7.24 (d, 2H, J = 8.3 Hz, H_{Ar}), 7.33 (dd, 1H, J = 7.9 Hz, H_{Ar}), 7.48 (d, 2H, J = 8.3 Hz, H_{Ar}), 7.66 (dd, 1H, J = 7.9, 1.8 Hz, H_{Ar}), 7.85 (d, 1H, J = 1.8 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.81; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 15.5 (CH_3), 28.5 (CH_2), 55.9 (2 OCH_3), 110.5, 112.6, 121.4 (CH_{Ar}), 124.2 ($J_{C,F}$ = 278 Hz, CF_3), 124.6 ($J_{C,F}$ = 5.3 Hz), 127.0, 128.5 (CH_{Ar}), 128.6 ($J_{C,F}$ = 28.7 Hz, C_{Ar}), 129.5 (CH_{Ar}), 132.2 (C_{Ar}), 132.7 (CH_{Ar}) 136.8, 139.7, 140.3, 144.3. 148.1, 148.6 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3062, 2966, 2869, 1604, 1551 (w), 1488, 1454, 1409, 1322, 1248, 1216, 1164 (m), 1115 (s), 1071 (m), 1024 (s), 969 (m), 933 (w), 904, 868 (m), 817 (s), 764, 719, 646, 609, 541 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%) 387 (25), 386 (M$^+$, 100), 371 (31), 343 (25), 313 (39), 303 (25), 285 (22), 275 (30), 259 (41), 215 (16), 186 (49), 164 (13), 144 (29); HRMS (EI): calcd. for $C_{23}H_{21}O_2F_3$ [M]$^+$: 386.148820; Found: 386.148894.

*4.7.2. 1-(3′,4′-Dimethoxy)-phenyl-4-naphthyl-2-trifluoromethylbenzene (**9b**)*

Starting from **7l** (88 mg, 0.25 mmol), and **2w** (45 mg, 0.25 mmol), **9b** was obtained as a yellowish crystalline solid (87 mg, 85%), mp = 212–214 °C. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.81, 3.84 (s, 6H, 2 OCH_3), 6.82–6.86 (m, 3H, H_{Ar}), 7.36–7.45 (m, 3H, H_{Ar}), 7.67 (dd, 1H, J = 8.5, 1.8 Hz, H_{Ar}), 7.77–7.87 (m, 4H, H_{Ar}), 8.00 (s, 2H, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.72; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 55.9, 56.0 (OCH_3), 110.4, 112.6, 121.4 (CH_{Ar}), 122.8 ($J_{C,F}$ = 275.2 Hz, CF_3), 125.0, 125.1, 126.0, 126.4, 126.6 (CH_{Ar}), 127.1, 127.3 (C_{Ar}), 127.7, 128.3 (CH_{Ar}), 128.5 ($J_{C,F}$ = 29.7 Hz, C_{Ar}), 128.8, 129.9 (CH_{Ar}), 132.1 (C_{Ar}), 132.9 (CH_{Ar}), 133.6, 136.7, 140.0, 140.2, 148.2, 148.7 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3052, 2954, 2834, 1602 (w), 1495, 1462, 1407 (m), 1369 (w), 1314 (m), 1244, 1217, 1164, 1118 (s), 1071 (m), 1022 (s), 952, 886, 857 (m), 811, 748 (s), 719, 644, 607, 553 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%) 409 (27), 408 (M$^+$, 100), 393 (13), 365 (32), 350 (29), 326 (23), 325 (47), 322 (30), 305 (14), 297 (16), 296 (44), 253 (14), 252 (39), 204 (59), 163 (52), 162 (36); HRMS (EI): calcd. for $C_{25}H_{19}O_2F_3$ [M]$^+$: 408.133170; Found: 408.133547.

*4.7.3. 1-(4′-Fluoro)-phenyl-4-(3″,4″-dimethoxy)-phenyl-2-trifluoromethylbenzene (**9c**)*

Starting from **7o** (90 mg, 0.25 mmol), and **2k** (35 mg, 0.25 mmol), **9c** was obtained as a yellowish crystalline solid (75 mg, 80%) mp = 79–81 °C. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 3.94, 4.02 (s, 6H, 2 OCH_3), 6.98–7.81 (m, 10H, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.82, −114.69; ^{13}C NMR (63 MHz, 300 K, $CDCl_3$): δ = 55.8, 56.0 (OCH_3), 110.2, 110.6, 114.7 ($J_{C,F}$ = 21.5 Hz), 119.6 (CH_{Ar}), 124.1 ($J_{C,F}$ = 274.5 Hz, CF_3), 124.5 ($J_{C,F}$ = 5.4 Hz) 128.7 ($J_{C,F}$ = 8.2 Hz, CH_{Ar}), 128.3, 129.3 ($J_{C,F}$ = 30.2 Hz) (C_{Ar}), 129.5 (CH_{Ar}), 130.7 (C_{Ar}), 132.6 (CH_{Ar}), 132.8, 140.6, 149.3, 149.4, 162.3 (J_{C-F} = 247.2) (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3063, 2969, 2845, 1602 (w), 1525, 1488, 1428, 1332, 1294 (m), 1244, 1171, 1109 (s), 1055, 1021 (m), 970, 925 (w), 837, 806 (s), 764, 724, 670, 648 (m), 595 (w), 537 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%) 377 (23), 376 (M$^+$, 100), 361 (23), 333 (30), 293 (39), 290 (20), 269 (14), 233 (20), 221 (24), 220 (46), 188 (44); HRMS (EI): calcd. for $C_{21}H_{16}O_2F_4$ [M]$^+$: 376.108090; Found: 376.107788.

*4.7.4. 1-(3′,5′-Dimethyl)-phenyl-4-(3″,4″-dimethoxy)-phenyl-2-trifluoromethylbenzene (**9d**)*

Starting from **7o** (90 mg, 0.25 mmol), and **2e** (38 mg, 0.25 mmol), **9d** was obtained as a yellowish crystalline solid (83 mg, 86%), mp = 154–156 °C. ^{1}H NMR (300 MHz, 298 K, $CDCl_3$): δ = 2.28 (s, 6H, 2CH_3), 3.86, 3.90 (s, 6H, 2 OCH_3), 6.89–6.95 (m, 4H, H_{Ar}), 7.06 (d, 1H, J = 2.1 Hz, H_{Ar}), 7.12 (dd, 1H, J = 8.2, 2.1 Hz, H_{Ar}), 7.28 (d, 1H, J = 7.9 Hz, H_{Ar}), 7.63 (dd, 1H, J = 7.9, 1.8 Hz, H_{Ar}), 7.81 (d, 1H, J = 1.8 Hz, H_{Ar}); ^{19}F NMR (282 MHz, 298 K, $CDCl_3$): δ = −56.74; ^{13}C NMR (75 MHz, 298 K, $CDCl_3$): δ = 56.0. 61.0, 61.1 (OCH_3), 107.7 (CH_{Ar}), 118.0 ($J_{C,F}$ = 1.9 Hz, C_{Ar}), 123.0 ($J_{C,F}$ = 272 Hz, CF_3), 124.4 (CH_{Ar}), 125.9 (C_{Ar}), 128.4 ($J_{C,F}$ = 5.4 Hz, CH_{Ar}), 129.8 ($J_{C,F}$ = 30.7 Hz, C_{Ar}), 133.5, 134.6 (CH_{Ar}), 137.7, 142.7, 151.2, 154.0 (C_{Ar}); IR (neat): $\tilde{\nu}$ = 3000, 2916, 2843 (w), 1600, 1520, 1465 (m), 1389 (w), 1331, 1293 (m), 1244, 1112, 1047 (s), 966, 899 (m), 837 (s), 763, 708, 658, 616, 574 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%) 387 (36), 386 (M$^+$, 100), 371 (28), 367 (20), 343 (59), 303 (29), 285 (25), 283 (31), 259 (25), 239 (26), 216 (14), 215 (36), 193 (28), 185 (33), 164 (41); HRMS (EI): calcd. for $C_{23}H_{21}O_2F_3$ [M]$^+$: 386.148820; Found: 386.148991.

*4.8. General procedure for the synthesis of **11a–i***

A 1,4-Dioxane solution (8 mL) of **10** (1.0 mmol), arylboronic acid **2** (1.0 equiv.), K_3PO_4, and $Pd(PPh_3)_4$ (5 mol%) was heated at 75 °C for 4 h. After cooling to room temperature, H_2O was added and the reaction mixture was extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), filtered and concentrated in vacuo. The residue was purified by column chromatography (pure n-heptane).

*4.8.1. 4-Chloro-2′-methyl-2-(trifluoromethyl)biphenyl (**11a**)*

Starting from **10** (259 mg, 1.0 mmol), and **2a** (136 mg, 1.0 equiv.), **11a** was obtained as a slight yellowish dense oil (90 mg, 33%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.94 (s, 3H, CH_3), 7.01 (d, ^3J = 7.93 Hz, 1H), 7.08–7.24 (m, 4H), 7.43 (dd, J = 8.12 Hz, J = 2.26 Hz, 1H), 7.66 (d, J = 2.26 Hz, 1H): ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 20.0 (CH_3), 123.1 (CF_3, q, J_{CF} = 274.20 Hz), 125.0 (CH), 126.3 (q, J_{CF} = 5.49 Hz, CH), 127.2 (CH), 128.2 (CH), 129.7 (CH), 130.3 (C, q, J_{CF} = 30.21 Hz), 131.4 (CH), 133.1 (CH), 135.9 (C), 137.7 (C), 139.2 (C, q, J_{CF} = 2.29 Hz), 141.6 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −59.62 ($ArCF_3$); IR (ATR, cm^{-1}): (= 3063 (s), 3021 (s), 2956 (s), 2925 (s), 2857 (s), 1915 (s), 1599 (s), 1566 (s), 1493 (s), 1476 (m), 1453 (s), 1405 (m), 1381 (s), 1303 (w), 1275 (s), 1246 (m), 1168 (w), 1125 (w), 1105 (s), 1063 (w), 1047 (s), 1005 (m), 986 (s), 963 (s), 943 (s), 889 (m), 866 (s), 833 (w), 797 (s), 762 (w), 727 (w), 675 (m), 654 (s), 624 (s), 601 (m), 567 (m), 553 (s), 533 (s); MS (GC, 70 eV): m/z (%): 270 (M$^+$, [^{35}Cl], 100), 250 (6), 235 (18), 215 (33), 201 (17), 183 (4), 165 (58), 139 (2), 107 (3), 91 (5), 63 (3), 51 (2), 39 (1); HRMS (EI) calcd for $C_{14}H_{10}ClF_3$ [M$^+$]: 270.04176 found 270.041702.

*4.8.2. 4-Chloro-4′-methyl-2-(trifluoromethyl)biphenyl (**11b**)*

Starting *from* **10** (259 mg, 1.0 mmol), and **2c** (135 mg, 1.0 equiv.), **11b** was obtained as a colorless dense oil (245 mg, 91%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.30 (s, 3H, CH_3), 7.06–7.17 (m, 4H), 7.36–7.42 (m, 2H), 7.62 (d, J = 2.27 Hz, 1H); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 21.2 (CH_3), 123.4 (CF_3, q, J_{CF} = 274.20 Hz), 126.4 (CH, q, J_{CF} = 5.49 Hz), 126.8 (CH), 128.7 (CH), 128.8 (CH, q, J_{CF} = 1.37 Hz), 129.5 (CH), 130.0 (C, q, J_{CF} = 30.67 Hz), 131.4 (CH), 133.3 (C), 133.6 (CH), 135.7 (C), 137.8 (C), 140.1 (C, q, J_{CF} = 1.83 Hz). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −57.30 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3025 (s), 2923 (s), 2856 (s), 2733 (s), 1905 (s), 1777 (s), 1657 (s), 1600 (s), 1562 (s), 1500 (s), 1479 (w), 1402 (m), 1302 (w), 1266 (s), 1251 (s), 1239 (s), 1214 (s), 1166 (w), 1123 (w), 1111 (s), 1062 (w), 1024 (s), 1005 (m), 963 (s), 945 (s), 889 (m), 834 (m), 814 (w), 801 (m), 755 (s), 726 (w), 698 (s), 664 (m), 643 (s), 629 (m), 617 (s), 581 (m), 549 (s), 530 (m); MS (GC, 70 eV): m/z (%): 270 (M$^+$, [^{35}Cl], 100), 249 (5), 235 (9), 215 (22), 201 (5), 183 (3), 165 (20), 134 (2), 115 (3), 91 (4), 75 (1), 63 (1); HRMS (EI) calcd for $C_{14}H_{10}ClF_3$ [M$^+$]: 270.04176 found 270.041731.

*4.8.3. 4′-Chloro-2,3,4-trimethoxy-2′-(trifluoromethyl)biphenyl (**11c**)*

Starting from **10** (259 mg, 1.0 mmol), and **2n** (212 mg, 1.0 equiv.), **11f** was obtained as a slight yellowish solid (145 mg, 42%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 6.60 (d, 1H, J = 8.69 Hz), 6.76 (dd, J = 8.49 Hz, J = 0.75 Hz, 1H), 7.17 (d, 1H, J = 8.30 Hz), 7.43 (dd, J = 8.30 Hz, J = 2.26 Hz, 1H), 7.64 (d, 1H, J = 2.26 Hz). ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 55.95 (OCH_3), 60.74 (OCH_3), 60.86 (OCH_3), 106.28 (CH), 123.36 (CF_3, q, J_{CF} = 274.65 Hz), 124.8 (CH), 126.3 (CH, q, J_{CF} = 5.49 Hz), 127.9 (C), 130.5 (C, q, J_{CF} = 30.21 Hz), 131.1 (CH), 134.1 (CH), 134.6 (C), 135.8 (C), 141.9 (C), 151.2 (C), 153.9 (C). ^{19}F NMR (282.40 MHz, DMSO-d_6): δ = −58.66 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3069 (m), 2961 (s), 2939 (m), 2910 (s), 2837 (s), 1847 (s), 1596 (w), 1574 (s), 1567 (s), 1504 (s), 1482 (w), 1462 (w), 1445 (s), 1435 (m), 1415 (m), 1407 (m), 1306 (w), 1293 (s), 1270 (m), 1250 (m), 1235 (m), 1209 (m), 1173 (w), 1131 (s), 1115 (w), 1101 (s), 1085 (w), 1053 (w), 1014 (m), 998 (w), 974 (s), 923 (s), 914 (m), 882 (m), 845 (m), 813 (s), 799 (w), 788 (s), 756 (s), 743 (s), 726 (m), 704 (s), 689 (m), 673 (s),658 (s), 646 (s), 611 (m), 589 (s), 572 (s), 536 (m); MS (GC, 70 eV): m/z (%): 346 (M^+, 100), 333 (8), 331 (24), 296 (27), 262 (6), 247 (4), 217 (20), 182 (16), 162 (2), 132 (1), 69 (1), 53 (2); HRMS (EI) calcd for $C_{16}H_{14}ClF_3O_3$ [M^+]: 346.05781 found 346.058121.

*4.8.4. 4-Chloro-4′-fluoro-2-(trifluoromethyl)biphenyl (**11d**)*

Starting from **10** (259 mg, 1.0 mmol), and **2k** (139 mg, 1.0 equiv.), **11d** was obtained as a colorless dense oil (200 mg, 73%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.09–7.15 (m, 2H, ArH), 7.27–7.32 (m, 3H, ArH), 7.56 (dd, J = 2.27, J = 8.68 Hz, 1H, ArH), 7.76 (d, J = 2.08 Hz, 1H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 114.9 (2CH, d, J_{CF} = 21.52 Hz), 123.2 (CF_3, q, J_{CF} = 274.20 Hz), 126.4 (CH, q, J_{CF} = 5.95 Hz), 130.6 (2CH, qd, J_{CF} = 1.83 Hz, J_{CF} = 8.24 Hz), 130.1 (C, q, J_{CF} = 30.67 Hz), 131.4 (CH), 133.5 (CH), 133.7 (C), 138.8 (C, q, J_{CF} = 1.83 Hz), 134.4 (C, d, J_{CF} = 3.20 Hz), 162.6 (CF, d, J_{CF} = 247.24 Hz); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −57.46 ($ArCF_3$), −114.13 (ArF); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3075 (w), 2856 (w), 1777 (w), 1600 (m), 1479 (s), 1402 (m), 1302 (s), 1230 (m), 1123 (s), 1062 (s), 1007 (m), 940 (w), 891 (m), 825 (s), 809 (s), 762 (w), 727 (s), 664 (m), 617 (w), 580 (m), 534 (m); GC–MS (EI, 70 eV): m/z (%): 274 (M^+, 100), 219 (29), 200 (1), 188 (4), 170 (10), 109 (3), 99 (2), 75 (1); HRMS (EI) calcd for $C_{13}H_7ClF_4$ [M^+]: 274.01669 found 274.015125.

*4.8.5. 4-Chloro-2,3′-bis(trifluoromethyl)biphenyl (**11e**)*

Starting from **10** (259 mg, 1.0 mmol), and **2 m** (189 mg, 1.0 equiv.), **11e** was obtained as a colorless dense oil (225 mg, 69%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.15–7.19 (m, 1H), 7.38–7.48 (m, 5H), 7.66 (d, J = 1.89 Hz, 1H); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 123.1 (CF_3, q, J_{CF} = 274.20 Hz), 123.9 (CF_3, q, J_{CF} = 272.40 Hz), 124.8 (CH, q, J_{CF} = 3.66 Hz), 125.7 (CH, q, J_{CF} = 1.83 Hz), 126.5 (CH, q, $^5J_{CF}$ = 5.49 Hz), 128.4 (CH), 130.1 (C, q, J_{CF} = 30.67 Hz), 130.5 (C, q, J_{CF} = 32.50 Hz), 131.6 (CH), 132.2 (CH), 133.2 (CH), 134.3 (C), 138.1 (C, q, J_{CF} = 1.83 Hz), 139.2 (C). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.71 ($ArCF_3$), −57.39 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3076 (s), 2929 (s), 2855 (s), 1602 (s), 1567 (s), 1512 (s), 1499 (s), 1479 (m), 1433 (m), 1405 (m), 1331 (w), 1300 (w), 1277 (m), 1250 (w), 1165 (w), 1118 (w), 1094 (m), 1076 (m), 1063 (w), 1024 (w), 1002 (s), 984 (s), 962 (s), 893 (m), 847 (m), 834 (m), 803 (w), 753 (s), 734 (w), 704 (w), 695 (m), 667 (s), 653 (s), 648 (s), 619 (s), 592 (s), 547 (m), 532 (s); MS (GC, 70 eV): m/z (%): MS (GC, 70 eV): m/z (%): 324 (M^+, [^{35}Cl], 100), 305 (8), 285 (3), 269 (13), 255 (1), 235 (13), 219 (11), 201 (4), 169 (2), 150 (1), 125 (1), 109 (1), 169 (2), 99 (1), 75 (1); HRMS (EI) calcd for $C_{14}H_7ClF_6$ [M^+]: 324.01350 found 324.013094.

*4.8.6. 4-Chloro-4′-methoxy-2-(trifluoromethyl)biphenyl (**11f**)*

Starting from **10** (259 mg, 1.0 mmol), and **2n** (152 mg, 1.0 equiv.), **11f** was obtained as a white solid (155 mg, 61%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.88 (s, 3H, OCH_3), 6.95 (d, J = 8.87 Hz, 2H), 7.23–7.30 (m, 3H), 7.53 (dd, J = 8.30 Hz, J = 2.26 Hz, 1H), 7.74 (d, J = 2.26 Hz, 1H); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 55.2 (OCH_3), 113.3 (2CH), 123.3 (CF_3, q, J_{CF} = 274.20 Hz), 126.4 (CH, q, J_{CF} = 5.49 Hz), 130.01 (C, q, J_{CF} = 30.21 Hz), 130.03 (CH, q, J_{CF} = 1.37 Hz), 130.9 (C), 131.3 (CH), 133.2 (C), 133.7 (2CH), 139.7 (C, q, J_{CF} = 1.83 Hz), 159.4 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −57.43 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3078 (s), 3040 (s), 3020 (s), 2967 (m), 2939 (m), 2914 (s), 2842 (m), 1882 (m), 1634 (s), 1611 (w), 1578 (s), 1562 (s), 1516 (m), 1481 (w), 1465 (s), 1455 (s), 1443 (m), 1403 (m), 1351 (s), 1332 (s), 1301 (w), 1247 (w), 1178 (w), 1133 (s), 1105 (w), 1063 (w), 1034 (w), 1018 (s), 1000 (m), 967 (s), 951 (m), 934 (s), 886 (w), 843 (m), 834 (s), 822 (w), 809 (s), 795 (m), 764 (s), 755 (s), 726 (w), 698 (s), 662 (m), 636 (m),618 (s), 585 (w), 550 (m), 535 (w); MS (GC, 70 eV): m/z (%): 286 (M^+, 100), 271 (11), 243 (3), 223 (6), 208 (21), 188 (18), 169 (2), 139 (4), 99 (1), 87 (1), 75 (1), 63 (1); HRMS (EI) calcd for $C_{14}H_{10}ClF_3O$ [M^+]: 286.03668 found 286.036392.

*4.8.7. 4-Chloro-2-(trifluoromethyl)biphenyl (**11g**)*

Starting from **10** (259 mg, 1.0 mmol), and **2o** (121 mg, 1.0 equiv.), **11g** was obtained as a colorless dense oil (215 mg, 84%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.17–7.21 (m, 3H), 7.29–7.35 (m, 3H), 7.41–7.52 (m, 1H), 7.64 (d, J = 2.08 Hz, 1H); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 123.3 (CF_3, q, J_{CF} = 274.66 Hz), 126.3 (CH, q, J_{CF} = 5.49 Hz), 127.2 (CH), 127.9 (CH), 128.8 (CH), 128.9 (CH), 129.9 (C, q, J_{CF} = 30.67 Hz), 131.4 (CH), 133.5 (CH), 136.1 (CH), 138.6 (C), 139.9 (C, q, J_{CF} = 1.83 Hz), 141.3 (C). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −57.32 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3064 (s), 3030 (s), 2926 (s), 2854 (s), 1605 (s), 1565 (s), 1476 (m), 1444 (s), 1432 (s), 1405 (m), 1336 (s), 1302 (w), 1246 (m), 1168 (m), 1123 (w), 1074 (s), 1063 (w), 1036 (s), 1024 (s), 1008 (m), 998 (s), 965 (s), 917 (s), 890 (m), 830 (w), 768 (w), 746 (s), 737 (m), 725 (s), 699 (w), 684 (m), 655 (m), 615 (s), 609 (s), 596 (m), 550 (m), 532 (s); MS (GC, 70 eV): m/z (%):MS (GC, 70 eV): m/z (%): 256 (M^+, [^{35}Cl], 100), 235 (6), 219 (6), 201 (38), 181 (2), 170 (3), 152 (9), 125 (1), 100 (4), 85 (1), 75 (2), 51 (1); HRMS (EI) calcd for $C_{13}H_8ClF_3$ [M^+]: 256.02611 found 256.026429.

*4.8.8. 4′-tert-Butyl-4-chloro-2-(trifluoromethyl)biphenyl (**11h**)*

Starting from **10** (259 mg, 1.0 mmol), and **2r** (178 mg, 1.0 equiv.), **11h** was obtained as a colorless dense oil (145 mg, 46%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.39 (s, 9H, $3CH_3$), 7.25 (d, J = 8.12, 2H, ArH), 7.44 (d, J = 8.49, 2H, ArH), 7.54 (dd, J = 1.89, J = 8.12 Hz, 1H, ArH), 7.69–7.76 (m, 2H, ArH); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 31.3 ($3CH_3$), 34.6 (C), 122.1 (CF_3, q, J_{CF} = 273.74 Hz), 124.8 (2CH), 126.3 (CH, q, J_{CF} = 5.49 Hz), 128.5 (2CH, q, J_{CF} = 1.83 Hz), 129.9 (C, q, J_{CF} = 30.67 Hz), 131.3 (CH), 133.6 (CH), 133.7 (C), 135.6 (2C), 150.8 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −57.30 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3073 (w), 2963 (m), 1777 (w), 1600 (w), 1480 (m), 1364 (w), 1302 (s), 1243 (w), 1169 (m), 1125 (s), 1061 (s), 1004 (m), 923 (w), 890 (m), 824 (s), 751 (w), 711 (m), 641 (w), 585 (s), 543 (m); GC–MS (EI, 70 eV): m/z (%): 312 (M^+, 22), 297 (100), 269 (17), 217 (4), 201 (3), 134 (4), 41 (4); HRMS (EI) calcd for $C_{17}H_{16}ClF_3$ [M^+]: 312.08871 found 312.088232.

*4.8.9. 4-Chloro-3′,4′-dimethoxy-2-(trifluoromethyl)biphenyl (**11i**)*

Starting from **10** (259 mg, 1.0 mmol), and **2w** (182 mg, 1.0 equiv.), **11i** was obtained as a slight yellowish solid (120 mg, 38%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 3.80 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.75–6.84 (m, 3H, ArH), 7.22 (d, J = 8.30 Hz, 1H), 7.43 (dd, J = 8.30 Hz, J = 1.70 Hz, 1H), 7.64 (d, J = 2.26 Hz, 1H): ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 55.8 ($2OCH_3$), 110.5 (CH), 112.4 (q, J_{CF} = 1.83 Hz, CH), 121.3 (q, J_{CF} = 1.83 Hz, CH), 123.3 (CF_3, q, J_{CF} = 274.20 Hz), 126.3 (q, J_{CF} = 5.49 Hz, CH), 129.9 (C, q, J_{CF} = 30.21 Hz), 131.1 (C), 131.3 (CH), 133.3 (C), 133.6 (CH),

139.7 (q, J_{CF} = 1.83 Hz, C), 148.2 (C), 148.8 (C). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −57.37 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3075 (s), 3015 (s), 2996 (s), 2962 (s), 2938 (s), 2909 (s), 2867 (s), 2838 (s), 1831 (s), 1606 (m), 1583 (m), 1567 (s), 1517 (w), 1485 (w), 1465 (w), 1453 (s), 1441 (m), 1411 (w), 1328 (s), 1304 (w), 1265 (s), 1249 (w), 1214 (w), 1189 (s), 1171 (w), 1120 (w), 1068 (w), 1048 (w), 1025 (w), 975 (s), 917 (s), 905 (m), 886 (m), 850 (w), 815 (s), 805 (w), 771 (m), 751 (m), 724 (w), 692 (s), 671 (s), 641 (w), 604 (m), 581 (s),539 (m); MS (GC, 70 eV): *m*/*z* (%): 316 (M^+, [^{35}Cl], 100), 301 (11), 273 (8), 258 (1), 233 (17), 218 (15), 195 (10), 169 (6), 126 (1), 99 (1), 87 (1), 75 (1), 63 (1), 51 (1); HRMS (EI) calcd for $C_{15}H_{12}ClF_3O_2$ [M^+]: 316.0427 found 316.047470.

4.9. General procedure for synthesis of **13a–e**

A 1,4-dioxane solution (8 mL) of **1** (1.0 mmol), arylboronic acid **2** (1.0 equiv.), K_3PO_4, and $Pd(PPh_3)_4$ (5 mol%) was heated at 70 °C for 5 h. After cooling to room temperature, H_2O was added and the reaction mixture was extracted with CH_2Cl_2. The organic layer was dried (Na_2SO_4), filtered and concentrated in vacuo. The residue was purified by column chromatography (pure n-heptane).

4.9.1. 4′-Chloro-2-methyl-3′-(trifluoromethyl)biphenyl (**13a**)

Starting from **12** (259 mg, 1.0 mmol), and **2a** (135 mg, 1.0 equiv.), **13a** was obtained as a colorless dense oil (260 mg, 96%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.17 (s, 3H, CH_3), 7.09–7.23 (m, 4H, ArH), 7.34 (dd, *J* = 2.64 Hz, *J* = 8.12 Hz, 1H, ArH), 7.46 (d, *J* = 8.31 Hz, 1H, ArH), 7.57 (d, *J* = 2.08 Hz, 1H); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 20.3 (CH_3), 122.9 (CF_3, q, J_{CF} = 273.29 Hz), 126.2 (CH), 128.1 (C, q, J_{CF} = 31.13 Hz), 128.2 (CH), 128.3 (CH, q, J_{CF} = 5.49 Hz), 129.6 (CH), 130.7 (CH), 130.8 (C, q, J_{CF} = 1.83 Hz), 131.2 (CH), 133.5 (CH), 135.2 (C), 139.3 (C), 140.9 (C). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.51 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3063 (w), 2862 (w), 1607 (w), 1474 (m), 1403 (m), 1322 (s), 1247 (m), 1128 (s), 1053 (w), 964 (w), 907 (m), 834 (m), 757 (s), 660 (m), 594 (w), 532 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 270 (M^+, 100), 235 (22), 215 (12), 165 (49), 139 (2), 91 (2), 63 (1); HRMS (EI) calcd for $C_{14}H_{10}ClF_3$ [M^+]: 270.04176 found 270.041299.

4.9.2. 4-Chloro-4′-methyl-3-(trifluoromethyl)biphenyl (**13b**)

Starting from **12** (259 mg, 1.0 mmol), and **2c** (135 mg, 1.0 equiv.), **13b** was obtained as a colorless dense oil (265 mg, 98%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.33 (s, 3H, CH_3), 7.19 (d, *J* = 8.31 Hz, 2H, ArH), 7.38 (d, *J* = 8.12 Hz, 2H, ArH), 7.46 (d, *J* = 8.49 Hz, 1H, ArH), 7.57 (dd, *J* = 2.27 Hz, *J* = 8.31 Hz, 1H, ArH), 7.79 (d, *J* = 2.27 Hz, 1H); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 21.1 (CH_3), 123.0 (CF_3, q, J_{CF} = 273.29 Hz), 125.8 (CH, q, J_{CF} = 5.49 Hz), 126.8 (2CH), 128.7 (C, q, J_{CF} = 31.13 Hz), 129.8 (2CH), 130.8 (C, q, J_{CF} = 1.83 Hz), 130.9 (CH), 131.7 (CH), 135.7 (C), 138.4 (CH), 140.1 (C). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.56 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3030 (w), 2865 (w), 2607 (w), 1478 (m), 1396 (w), 1327 (s), 1174 (m), 1136 (s), 1033 (m), 903 (w), 809 (s), 728 (w), 665 (m), 547 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 270 (M^+, 100), 235 (13), 215 (4), 165 (28), 135 (1), 91 (1), 63 (1); HRMS (EI) calcd for $C_{14}H_{10}ClF_3$ [M^+]: 270.04176 found 270.041748.

4.9.3. 4-Chloro-3′,5′-dimethyl-3-(trifluoromethyl)biphenyl (**13c**)

Starting from **12** (259 mg, 1.0 mmol), and **2e** (149 mg, 1.0 equiv.), **13c** was obtained as a colorless dense oil (205 mg, 72%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 2.42 (s, 6H, $2CH_3$), 7.08 (1H, ArH), 7.20 (2H, ArH), 7.57 (d, *J* = 8.49 Hz, 1H, ArH), 7.68 (dd, *J* = 1.89 Hz, *J* = 8.31 Hz, 1H, ArH), 7.90 (d, *J* = 2.27 Hz, 1H); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 21.3 ($2CH_3$), 122.9 (CF_3, q, J_{CF} = 273.29 Hz), 124.8 (2CH), 126.1 (CH, q, J_{CF} = 5.49 Hz), 128.6 (C, q, J_{CF} = 31.13 Hz), 129.9 (CH), 130.8 (C, q, J_{CF} = 1.83 Hz), 131.2 (CH), 131.6 (CH), 138.6 (C), 138.7 (2C), 140.4 (C). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.53 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3023 (w), 2734 (w), 1604 (m), 1394 (m), 1334 (s), 1294 (s), 1171 (m), 1128 (s), 1033 (s), 950 (w), 892 (m), 826 (s), 701 (m), 541 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 284 (M^+, 100), 269 (24), 233 (10), 165 (14), 125 (1), 77 (1), 69 (1); HRMS (EI) calcd for $C_{15}H_{12}ClF_3$ [M^+]: 284.05741 found 284.056637.

4.9.4. 4′-tert-Butyl-4-chloro-3-(trifluoromethyl)biphenyl (**13d**)

Starting from **12** (259 mg, 1.0 mmol), and **2r** (178 mg, 1.0 equiv.), **13d** was obtained as a colorless dense oil (270 mg, 87%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 1.29 (s, 9H, $3CH_3$), 7.42 (s, 4H, ArH), 7.47 (d, *J* = 8.31, 1H, ArH), 7.59 (dd, *J* = 1.89, *J* = 8.31 Hz, 1H, ArH), 7.81 (d, *J* = 2.08 Hz, 1H); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 31.2 ($3CH_3$), 34.6 (C), 122.9 (CF_3, q, J_{CF} = 273.29 Hz), 125.9 (CH, q, J_{CF} = 5.49 Hz), 126.1 (2CH), 126.7 (2CH), 128.7 (C, q, J_{CF} = 31.13 Hz), 130.8 (C, q, J_{CF} = 1.83 Hz), 131.0 (CH), 131.8 (CH), 135.7 (C), 140.0 (C), 151.6 (C); ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.57 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3034 (w), 2962 (m), 1787 (w), 1579 (w), 1477 (m), 1364 (w), 1325 (s), 1250 (m), 1174 (m), 1131 (s), 1111 (s), 1033 (s), 962 (w), 903 (m), 819 (s), 744 (m), 664 (m), 615 (w), 563 (w), 536 (m); GC–MS (EI, 70 eV): *m*/*z* (%): 312 (M^+, 26), 297 (100), 269 (21), 217 (1), 201 (2), 135 (6), 41 (4); HRMS (EI) calcd for $C_{17}H_{16}ClF_3$ [M^+]: 312.08871 found 312.088893.

4.9.5. 4′-Bromo-4-chloro-3-(trifluoromethyl)biphenyl (**13e**)

Starting from **12** (259 mg, 1.0 mmol), and **2x** (200 mg, 1.0 equiv.), **13e** was obtained as a white solid (150 mg, 45%). ^{1}H NMR (300.13 MHz, $CDCl_3$): δ = 7.43–7.50 (m, 2H, ArH), 7.57–7.69 (m, 4H, ArH), 7.88 (d, *J* = 2.08 Hz, 1H); ^{13}C NMR (62.89 MHz, $CDCl_3$), δ = 122.7 (C), 122.8 (CF_3, q, J_{CF} = 273.74 Hz), 125.9 (CH, q, J_{CF} = 5.49 Hz), 128.6 (2CH), 128.9 (C, q, J_{CF} = 31.59 Hz), 130.9 (CH), 131.6 (C, q, J_{CF} = 1.37 Hz), 131.9 (CH), 132.3 (2CH), 137.5 (C), 138.9 (C). ^{19}F NMR (282.40 MHz, $CDCl_3$): δ = −62.64 ($ArCF_3$); IR (ATR, cm^{-1}): $\tilde{\nu}$ = 3064 (w), 2853 (w), 1587 (w), 1474 (m), 1325 (s), 1250 (m), 1114 (s), 1030 (m), 905 (m), 846 (w), 812 (s), 730 (w), 663 (m), 599 (w), 526 (w); GC–MS (EI, 70 eV): *m*/*z* (%): 334 (M^+, 74), 220 (28), 170 (3), 150 (5), 100 (1), 85 (2), 50 (1); HRMS (EI) calcd for $C_{13}H_7BrClF_3$ [M^+]: 333.93663 found 333.936439.

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