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# Reactivity of 1,2,3- and 1,2,4-trifluorobenzenes in <br> Palladium-catalyzed direct arylation 

Xinzhe Shi, Shuxin Mao, Jean-François Soulé,* Henri Doucet*<br>Univ Rennes, CNRS, ISCR-UMR 6226, F-35000 Rennes, France.<br>jean-francois.soule@univ-rennes1.fr; henri.doucet@univ-rennes1.fr

## Graphical abstract




#### Abstract

The higher reactivity of $\mathrm{C} 4-\mathrm{H}$ bond as compared to $\mathrm{C} 5-\mathrm{H}$ bond of 1,2,3-trifluorobenzene in palladium-catalyzed direct arylation allows the selective synthesis of 4 -aryl-1,2,3-trifluorobenzenes in moderate to high yields. In most cases, phosphine-free $\operatorname{Pd}(\mathrm{OAc})_{2}$ catalyst and inexpensive KOAc base were employed. Then, from these 4-aryl-1,2,3trifluorobenzenes, the palladium-catalyzed C - H bond functionalization of the C6-position allows the synthesis of the corresponding 4,6-diarylated 1,2,3-trifluorobenzenes. We also applied these reaction conditions to the regioselective direct C3-arylation of 1,2,4-trifluorobenzene.


## Introduction

Several bioactive compounds contain a (poly)fluorobiphenyl motif, such as Diflunisal which exhibits analgesic and antiinflamatory activity. Therefore, the discovery of simple, but general routes to (poly)fluorobiphenyls has potential for medicinal chemistry. The Pd-catalyzed direct arylation of a wide variety of (hetero)aromatics, via a $\mathrm{C}-\mathrm{H}$ bond activation step, has brought a synthesis revolution in the preparation of bi(hetero)aryls in recent years. Such couplings are very
attractive, compared to the more classical Pd-catalysed reactions such as Stille, Suzuki or Negishi couplings as they do not require the preliminary synthesis of organometallic derivatives. ${ }^{1}$ Several examples of metal-catalyzed arylations via a C-H bond activation ${ }^{2}$ of polyfluorobenzenes with aryl halides have been reported. ${ }^{3}$ Fagnou et al. and a few other groups have already reported examples of Pd-catalyzed direct arylations of tetra-and penta-fluorobenzenes. ${ }^{4.6}$ They observed that the $\mathrm{C}-\mathrm{H}$ bonds flanked by two fluoro substituents such as in pentafluorobenzene, 1,2,4,5-tetrafluorobenzene or even 1,3,5trifluorobenzene, could be easily arylated with aryl halides. ${ }^{4 a-g}$ In contrast, to our knowledge, a single example of metalcatalyzed direct arylation of 1,2,3-trifluorobenzene has been reported (Scheme 1, top). ${ }^{7}$ For this reaction, Larrosa et al. employed $\left[\mathrm{Ru}(t-\mathrm{BuCN})_{6}\right]\left[\mathrm{BF}_{4}\right]_{2}$ as the catalyst and $\left(\mathrm{NMe}_{4}\right)\left(4-\mathrm{FC}_{6} \mathrm{H}_{4} \mathrm{CO}_{2}\right)$ ( 0.35 equiv.), ( $\mathrm{NMe}_{4}$ )OPiv ( 0.4 equiv.), $\left(\mathrm{NMe}_{4}\right)\left(\mathrm{OC}\left(\mathrm{CF}_{3}\right)_{3}\right)$ (2.5 equiv) as additives. The coupling product was obtained as a mixture of two regioisomers (C4:C5 77:23) in $29 \%$ yield. To our knowledge, the regioselective metal-catalyzed direct arylation of 1,2,3-trifluorobromobenzene has not yet been described (Scheme 1, bottom).


Scheme 1. Metal-catalyzed arylations of 1,2,3-trifluorobenzene

As the discovery of an effective method, for the arylation of such trifluorobenzene derivatives, especially using easily available catalyst and base is highly desirable, the reactivity and regioselectivity for direct arylation using 1,2,3trifluorobromobenzene in the presence of palladium catalysts needed to be investigated. Here, we report (i) on the regioselectivity of the palladium-catalyzed direct arylation of 1,2,3-trifluorobenzene using a low loading of a phosphine-free palladium catalyst; (ii) on the scope of the reaction; (iii) on the subsequent reactivity of these 4 -aryl-1,2,3-trifluorobenzenes in Pd-catalysed C-H bond functionalization; and (iv) on the reactivity in direct arylation of 1,2,4-trifluorobenzene using a phosphine-free catalyst.

The free energy of activation for direct arylation in the presence of palladium-catalysts via Concerted Metalation Deprotonation (CMD) ${ }^{8,9}$ pathway for several poly(fluoro)benzenes has been calculated by Gorelsky (Figure 1). C-H bonds flanked by two fluoro-substituents such as in pentafluorobenzene, 1,3,5-trifluorobenzene or even 1,3-difluorobenzene are generally very reactive, as their energy of activation is quite low ( $<26 \mathrm{kcal} \mathrm{mol}^{-1}$ ). Conversely, for $1,2,3$-trifluorobenzene, the energy of activation of the C-H bonds adjacent to one fluorine atom is higher ( $28.8 \mathrm{kcal} \mathrm{mol}^{-1}$ ), and the other C-H bond has an energy of activation of $31.7 \mathrm{kcal} \mathrm{mol}^{-1}$. Therefore, due to the lower energy of activation of the C-H bonds adjacent to one fluorine atoms of 1,2,3-trifluorobenzene, for reactions which proceed via a Pd-catalyzed CMD mechanism, we expected to be able to control the regioselectivity of their functionalization using Pd-catalysis instead of Ru-catalysis.


Figure 1. Free energy of activation ( $\Delta G_{298 \mathrm{~K}}^{\ddagger}$, kcal $\mathrm{mol}^{-1}$ ) for direct arylation via the CMD pathway involving an acetate ligand with the $\left[\mathrm{Pd}\left(\mathrm{C}_{6} \mathrm{H}_{5}\right)\left(\mathrm{PMe}_{3}\right)(\mathrm{OAc})\right]$ catalyst. ${ }^{8}$

## Results and discussion

4-Bromopropiophenone (1 equiv.) and 1,2,3-trifluorobenzene (1.5 equiv.) were employed as model substrates for our study (Table 1). We initially examined the influence of the nature of the base on the aryl bromide conversion and on the regioselectivity of the reaction using $2 \mathrm{~mol} \% \mathrm{Pd}(\mathrm{OAc})_{2}$ catalyst and DMA as the solvent. We had previously observed that
this catalyst precursor associated to this solvent promoted the coupling of several polyfluorobenzenes with aryl bromides in high yields. ${ }^{10} \mathrm{Cs}_{2} \mathrm{CO}_{3}, \mathrm{~K}_{2} \mathrm{CO}_{3}$ or NaOAc bases, led to high conversions of 4-bromopropiophenone, but the desired product 1a was only obtained in trace amount (Table 1, entries 1-3). The use of the acetate salts, KOAc or CsOAc, afforded $\mathbf{1 a}$ in higher yields; however, the yields remained moderate, even when an higher catalyst loading ( $5 \mathrm{~mol} \%$ ) or a palladiumdiphosphine catalyst were used (Table 1, entries 4-7). PivOK was found to be the most effective base for this reaction, as 1a was obtained in $41 \%$ yield (Table 1, entry 8 ). The good performance of pivalate as base/ligand is consistent with a CMD pathway. ${ }^{8,9}$ Finally, the use of 3 equiv. of 1,2,3-trifluorobenzene in the presence of $2 \mathrm{~mol} \% \mathrm{Pd}(\mathrm{OAc})_{2}$ catalyst and PivOK as base in DMA afforded 1a in 54\% yield (Table 1, entry 11). In all cases, the 4,6-diarylated 1,2,3-trifluorobenzene $\mathbf{1 b}$ was produced in very low yields ( $<10 \%$ ) and C5-arylated 1,2,3-trifluorobenzene was not detected.

## Table 1: Influence of the reaction conditions on the Pd-catalyzed C4-arylation

## of 1,2,3-trifluorobenzene with 4-bromopropiophenone



| Entry | Catalyst (mol\%) | Solvent | Base | Conv. (\%) | Ratio 1a:1b | Yield in 1a (\%) |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 1 | $\mathrm{Pd}(\mathrm{OAc})_{2}(2)$ | DMA | $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ | 100 | 0:0 | 0 |
| 2 | $\mathrm{Pd}(\mathrm{OAc})_{2}(2)$ | DMA | $\mathrm{K}_{2} \mathrm{CO}_{3}$ | 100 | 100:0 | <5 |
| 3 | $\mathrm{Pd}(\mathrm{OAc})_{2}(2)$ | DMA | NaOAc | 100 | 100:0 | $<5$ |
| 4 | $\mathrm{Pd}(\mathrm{OAc})_{2}(2)$ | DMA | KOAc | 100 | 93:7 | 31 |
| 5 | $\mathrm{Pd}(\mathrm{OAc})_{2}(5)$ | DMA | KOAc | 88 | 100:0 | 21 |
| 6 | $\mathrm{Pd}(\mathrm{OAc})_{2}(2)$ | DMA | CsOAc | 50 | 98:2 | 14 |
| 7 | $\mathrm{PdCl}\left(\mathrm{C}_{3} \mathrm{H}_{5}\right)(\mathrm{dppb})(2)$ | DMA | KOAc | 100 | 100:0 | 24 |
| 8 | $\mathrm{Pd}(\mathrm{OAc})_{2}(2)$ | DMA | KOPiv | 100 | 91:9 | 41 |
| 9 | $\mathrm{Pd}(\mathrm{OAc})_{2}(2)$ | DMF | KOAc | 100 | 100:0 | 8 |
| 10 | $\mathrm{Pd}(\mathrm{OAc})_{2}(2)$ | DMA | KOAc | 100 | 93:7 | $37^{\text {a }}$ |
| 11 | $\mathrm{Pd}(\mathrm{OAc})_{2}(2)$ | DMA | KOPiv | 100 | 95:5 | $54^{\text {a }}$ |

Conditions: 4-Bromopropiophenone (1 equiv.), 1,2,3-trifluorobenzene (1.5 equiv.), base (2 equiv.), $16 \mathrm{~h}, 150^{\circ} \mathrm{C}$, conversion of 4-bromopropiophenone, isolated yields. ${ }^{\text {a }} 3$ equiv. of 1,2,3-trifluorobenzene.

Then, $1,2,3$-trifluorobenzene was coupled with a set of (hetero)aryl bromides in the presence of $2 \mathrm{~mol} \% \mathrm{Pd}(\mathrm{OAc})_{2}$, KOPiv as the base in DMA (Scheme 2). Very regioselective C4-arylations and quite good yields in 2-7 were obtained using aryl bromides bearing nitro, cyano, formyl, acetyl, ester or trifluoromethyl para-substitutents. In all cases, a regioselective arylation at the C-H adjacent to a C-F bond was observed, and low amounts of diarylated 1,2,3-trifluorobenzene were observed by GC/MS and ${ }^{1} \mathrm{H}$ NMR analysis of the crude mixtures. Similar yields were obtained for the coupling of the electron-rich aryl bromides, 4-bromotoluene and 4-bromoanisole with 1,2,3-trifluorobenzene to give $\mathbf{8}$ and $\mathbf{9}$ in $48 \%$ and $64 \%$ yield, respectively. Nitro-, nitrile-, formyl-, acetyl- and ester-substituents at meta-position on the aryl bromides were also tolerated giving access to $\mathbf{1 0 - 1 4}$ in $40-67 \%$ yield. Reactions with the more hindered substrates, 2-bromobenzonitrile and 1bromonaphthalene were also successful. The use of the $N$-containing heterocycles, 3-bromopyridine and 3-bromoquinoline afforded the desired C4-arylated trifluorobenzene derivatives 17 and 18 in $64 \%$ and $72 \%$ yields, respectively. In all cases, no formation of the C5-arylated 1,2,3-trifluorobenzenes was detected by GC/MS analysis of the crude mixture. It should be noted that in a few cases such as for the preparation of $\mathbf{3 , 4}$ and $\mathbf{1 5}$, the use of KOAc as base led to higher yields than with PivOK, due to cleaner reactions.




18 72\%
*: KOAc (2 equiv.), 1,2,3-trifluorobenzene (1.5 equiv.)
**: KOAc (2 equiv.), 1,2,3-trifluorobenzene (3 equiv.)
Scheme 2. Scope of the C4-arylation of 1,2,3-trifluorobenzene

The one pot synthesis of 4,6-diarylated 1,2,3-trifluorobenzene from 1,2,3-trifluorobenzene was then examined (Scheme 3). As seen in the table 1 and in the scheme 2, the 4,6-diarylation of this trifluorobenzene derivative using only one equiv. of aryl bromide is generally observed in trace amount, revealing that the second arylation is much slower than the first one. The use of an excess of the electron-rich aryl bromides, 4-bromotoluene and 4-bromoanisole (3 equiv.) in the presence of $2 \mathrm{~mol} \%$ $\mathrm{Pd}(\mathrm{OAc})_{2}$ catalyst afforded the desired product $\mathbf{1 9}$ and $\mathbf{2 0}$ in $63 \%$ and $31 \%$ yields, respectively. Lower yields in $\mathbf{2 1}$ and $\mathbf{2 2}$ were obtained from 2-bromobenzonitrile and 1-bromonaphthalene. In all cases, no arylation at the C5-position of 1,2,3trifluorobenzene was detected.


Scheme 3. Scope of the one pot 4,6-diarylation of 1,2,3-trifluorobenzene

Then, the reactivity for C6-arylation, via a C-H bond activation of the trifluorobenzene moiety of some of the previously obtained C4-arylated trifluorobenzene derivatives was evaluated (Scheme 4). The reaction of 9 with 4-bromobenzonitrile using $5 \mathrm{~mol} \% \mathrm{PdCl}\left(\mathrm{C}_{3} \mathrm{H}_{5}\right)(\mathrm{dppb})$ catalyst and KOPiv as base afforded 23 in $48 \%$ yield; whereas the use of $\mathrm{Pd}(\mathrm{OAc})_{2}$ catalyst led to a low yield. From $\mathbf{8}$ and 4 -bromobenzonitrile, under the same conditions, the desired product $\mathbf{2 4}$ was obtained in $51 \%$ yield. Conversely, the reaction of $\mathbf{3}$ and 4 -bromotoluene was quite sluggish affording $\mathbf{2 4}$ in $<10 \%$ yield revealing that $1,2,3-$ trifluorobenzene derivatives bearing an electron-deficient benzene unit at C 4 -position are poorly reactive for C 6 -arylation. Therfore, for the preparation of non-symmetrically substituted 4,6-diaryl-1,2,3-trifluorobenzenes, the most electron-rich arene should be introduced in the first step.


## Scheme 4. Scope of the C6-arylation of 1,2,3-trifluoro-4-aryl-benzenes

The reactivity of two $1,2,3$-trifluorobenzene derivatives bearing a functional group at C4-position was also studied (Scheme 5). For the coupling reactions with 1-methoxy-2,3,4-trifluorobenzene, both C 5 and C 6 positions might have been arylated (Scheme 5, top). However, with both 2-bromobenzonitrile and 3-bromopyridine, only the $\mathrm{C}-\mathrm{H}$ bond adjacent to one fluorine atom was arylated to give 26 and 27 in $61 \%$ and $48 \%$ yields, respectively. This is certainly due to the higher acidity of this position. Conversely, the reaction of 2,3,4-trifluoroaniline, under the same reaction conditions, gave no coupling product; whereas, the use of the thermally more stable catalyst $\operatorname{PdCl}\left(\mathrm{C}_{3} \mathrm{H}_{5}\right)(\mathrm{dppb})^{12}$ associated to KOAc as base led exclusively to the amination product 28 in low yield (Scheme 5, bottom). This amination product 28 could be obtained in a higher yield of $62 \%$ using $\mathrm{Cs}_{2} \mathrm{CO}_{3}$ as base.


## Scheme 5. Reactivity of 1-methoxy-2,3,4-trifluorobenzene and 2,3,4-trifluoroaniline

Very few results concerning the Pd-catalyzed direct C3-arylation of 1,2,4-trifluorobenzene, ${ }^{9}$ especially using aryl halides as aryl source, ${ }^{9 \mathrm{c}}$ have been reported so far. A single example was reported by Cazin et al. in 2014. ${ }^{\text {9c }}$ They described that from this trifluorobenzene derivative and 4-bromotoluene, using a dual metal system involving $\mathrm{Cu}(\mathrm{Cl})(\mathrm{NHC})$ and $\mathrm{Pd}(\mathrm{Cl})$ (cinnamyl)(NHC) as catalyst, the C 3 -arylated trifluorobenzene could be obtained in good yield. As our "ligand-free" catalytic system was quite efficient for the regioselective C4-arylation of 1,2,3-trifluorobenzene, we also investigated its efficiency for the arylation of 1,2,4-trifluorobenzene (Scheme 6). In all cases, we observed a highly regioselective arylation at C3-position of 1,2,4-trifluorobenzene, as no other regioisomers could be detected by GC/MS analysis of the crude mixtures. Both electron-donating and electron-withdrawing sustituents on the aryl bromide were tolerated affording the desired products 29-34 in 53-70\% yields. From 3-bromopyridine and 3-bromoquinoline, the expected products $\mathbf{3 5}$ and $\mathbf{3 6}$ were also regioselectively obtained in good yields. For most of these reactions, the formation of side-products in low yields arising from the aryl-bromides homo-coupling and from the diarylation of $1,2,4$-trifluorobenzene was also observed by GC/MS analysis of the crude mixtures.


 DMA, $150{ }^{\circ} \mathrm{C}, 16 \mathrm{~h}$

| R |  | Yield (\%) |
| :--- | :--- | :--- |
| 4- $\mathrm{NO}_{2}$ | 29 | $53,66^{*}$ |
| $4-\mathrm{CN}$ | 30 | 70 |
| $4-\mathrm{CHO}$ | 31 | $56,53^{*}$ |
| 4-COMe | 32 | 60 |
| $4-\mathrm{Me}$ | 33 | 61 |
| $2-\mathrm{CN}$ | 34 | 59 |


$3572 \%$

*: KOPiv (2 equiv.), 1,2,4-trifluorobenzene (2 equiv.)

## Scheme 6. Scope of the C3-arylation of 1,2,4-trifluorobenzene

In summary, the use of a Pd-catalyst instead of a Ru-catalyst for the direct arylation of 1,2,3-trifluorobenzene allowed its regioselective functionalization at C4-position. We demonstrated that, using only $2 \mathrm{~mol} \%$ of easily available $\mathrm{Pd}(\mathrm{OAc})_{2}$ catalyst precursor and KOAc or KOPiv as inexpensive bases, a wide variety of 4-(hetero)arylated 1,2,3-trifluorobenzenes can be obtained with high regioselectivities and good yields. This strategy allowed the straightforward synthesis of C4-arylated 1,2,3-trifluorobenzenes in only one step from commercially available compounds. The access to a few symmetrical and nonsymmetrical 4,6-diaryl-1,2,3-trifluorobenzenes in moderate yields via successive C - H bond functionalizations is also described. This "phosphine-free" catalyst procedure was also successfully employed for the regioselective C3-arylation of 1,2,4-trifluorobenzene.

## Experimental section

## General procedure for palladium-catalyzed direct (di)arylations of trifluorobenzenes

The reaction of the aryl bromide, trifluorobenzene derivative and KOPiv or KOAc in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}$ or $\operatorname{PdCl}\left(\mathrm{C}_{3} \mathrm{H}_{5}\right)(\mathrm{dppb})^{12}$ (see schemes) at $150{ }^{\circ} \mathrm{C}$ during 16 h in DMA ( 4 mL ) under argon affords the coupling products 1-36 after evaporation of the solvent and purification on silica gel. Eluent heptane:ethyl acetate 9:1 for compounds 1-6, 10-15, 20, 21, 23-26, 28, 30-32, 34; heptane:ethyl acetate $4: 1$ for compounds 17, 18, 35, 36; heptane:ethyl acetate 1:1 for compound 27; heptane for compounds 7-9, 16, 19, 22, 29, 33.

From 4-bromopropiophenone ( $0.213 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2$ $\mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 1a was obtained in $54 \%$ yield $(0.142 \mathrm{~g})$ as a white solid: $\mathrm{mp} 89-92^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.05(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.60(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.23-7.02(\mathrm{~m}, 2 \mathrm{H}), 3.03(\mathrm{q}, J=7.6$ $\mathrm{Hz}, 2 \mathrm{H}), 1.25(\mathrm{t}, J=7.6 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 200.2,150.9$ (ddd, $J=251.8,10.0,3.0 \mathrm{~Hz}$ ), 148.8 (ddd, $J=252.6,10.7,3.3 \mathrm{~Hz}$ ), 140.2 (dt, $J=251.7,15.5 \mathrm{~Hz}$ ), 138.4, 136.4, $129.0(\mathrm{~d}, J=3.0 \mathrm{~Hz}$ ), 128.3, 125.6 (dd, $J=10.5,3.7 \mathrm{~Hz}), 123.8(\mathrm{~m}), 112.5(\mathrm{dd}, \mathrm{J}=17.5,4.0 \mathrm{~Hz}), 31.9,8.23$. Anal. Calcd for $\mathrm{C}_{15} \mathrm{H}_{11} \mathrm{~F}_{3} \mathrm{O}(264.25): \mathrm{C}$, 68.18; H, 4.20. Found: C, 67.98; H, 4.00.

4,4"-Di(propionyl)-4',5',6'-trifluoro-1,1':3',1"-terphenyl (1b) was also isolated in low yield: ${ }^{1} \mathrm{H}$ NMR (400 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 8.07(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 4 \mathrm{H}), 7.64(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 4 \mathrm{H}), 7.30(\mathrm{td}, J=7.7,2.3 \mathrm{~Hz}, 1 \mathrm{H}), 3.05(\mathrm{q}, J=7.5 \mathrm{~Hz}, 4 \mathrm{H})$, $1.26(\mathrm{t}, \mathrm{J}=7.5 \mathrm{~Hz}, 6 \mathrm{H})$.

## 2,3,4-Trifluoro-4'-nitro-1,1'-biphenyl (2)

From 4-bromonitrobenzene ( $0.202 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 2 was obtained in $37 \%$ yield ( 0.093 g ) as a yellow solid: $\mathrm{mp} 145-148^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.32(\mathrm{~d}, J=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.68(\mathrm{~d}, \mathrm{~J}=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.25-7.04(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 151.4(\mathrm{ddd}, J=253.1,10.0,3.1 \mathrm{~Hz}), 148.9(\mathrm{ddd}, J=253.0,10.0,3.4 \mathrm{~Hz}), 147.6(\mathrm{~m}), 140.5(\mathrm{dt}, J=$ 252.6, 15.5 Hz ), $140.4,129.7(\mathrm{~d}, ~ J=3.1 \mathrm{~Hz}), 124.5(\mathrm{dd}, J=10.5,3.9 \mathrm{~Hz}$ ), 123.9, $123.8(\mathrm{~m}), 112.8(\mathrm{dd}, J=17.6$, 4.0 Hz ). Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{6} \mathrm{~F}_{3} \mathrm{NO}_{2}$ (253.18): C, $56.93 ; \mathrm{H}, 2.39 ; \mathrm{N}, 5.53$. Found: $\mathrm{C}, 56.98 ; \mathrm{H}, 2.21 ; \mathrm{N}, 5.78$.

## 2',3',4'-Trifluoro-[1,1'-biphenyl]-4-carbonitrile (3)

From 4-bromobenzonitrile ( $0.182 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.198 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 3 was obtained in $57 \%$ yield $(0.133 \mathrm{~g})$ as a white solid: $\mathrm{mp} 132-135^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.75(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.61(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.22-7.03(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 $\mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 151.1$ (ddd, $J=251.3,10.1,3.0 \mathrm{~Hz}$ ), 148.8 (ddd, $J=252.6,10.7,3.3 \mathrm{~Hz}$ ), 140.4 (dt, $J=252.4$, 15.5 Hz ), $138.6,132.5,129.5(\mathrm{~d}, \mathrm{~J}=3.1 \mathrm{~Hz}), 124.8(\mathrm{dd}, J=10.4,3.7 \mathrm{~Hz}), 123.8(\mathrm{~m}), 118.4,112.7(\mathrm{dd}, J=17.5$, 4.1 Hz), 112.1. Anal. Calcd for $\mathrm{C}_{13} \mathrm{H}_{6} \mathrm{~F}_{3} \mathrm{~N}$ (233.19): C, 66.96; H, 2.59; N, 6.01. Found: C, 66.70; H, 2.41; N, 6.12.

## 2',3',4'-Trifluoro-[1,1'-biphenyl]-4-carbaldehyde (4)

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From 4-bromobenzaldehyde ( $0.185 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.198 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2$ $\mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 4 was obtained in $52 \%$ yield $(0.123 \mathrm{~g})$ as a white solid: $\mathrm{mp} 153-156{ }^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 10.08(\mathrm{~s}, 1 \mathrm{H}), 7.97(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.66(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.23-7.04(\mathrm{~m}, 2 \mathrm{H})$. ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 191.7,151.0(\mathrm{ddd}, J=252.2,10.3,3.0 \mathrm{~Hz}$ ), 148.9 (ddd, $J=252.9,10.7,3.3 \mathrm{~Hz}$ ), 140.3 (dt, $J=252.1,15.5 \mathrm{~Hz}$ ), 140.0, 135.9, 130.0, $129.5(\mathrm{~d}, J=3.0 \mathrm{~Hz}), 125.5(\mathrm{dd}, J=10.5,3.7 \mathrm{~Hz}), 123.9(\mathrm{~m})$, 112.5 (dd, $J=17.4,4.1 \mathrm{~Hz}$ ). Anal. Calcd for $\mathrm{C}_{13} \mathrm{H}_{7} \mathrm{~F}_{3} \mathrm{O}$ (236.19): C, 66.11; H, 2.99 66.30; H, 3.21.

4,4"-Di(formyl)-4',5',6'-trifluoro-1,1':3',1"-terphenyl was also isolated in low yield in an impure form: ${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 10.07(\mathrm{~s}, 2 \mathrm{H}), 7.98(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 4 \mathrm{H}), 7.71(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 4 \mathrm{H}), 7.32(\mathrm{td}, J=7.7,2.3 \mathrm{~Hz}, 1 \mathrm{H})$.

## 1-(2',3',4'-Trifluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (5)

From 4-bromoacetophenone ( $0.199 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2$ $\mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 5 was obtained in $52 \%$ yield $(0.130 \mathrm{~g})$ as a white solid: $\mathrm{mp} 69-72{ }^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.05(\mathrm{~d}, \mathrm{~J}=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.60(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.23-7.04(\mathrm{~m}, 2 \mathrm{H}), 2.65(\mathrm{~s}, 3 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 197.5,150.9$ (ddd, $J=251.8,10.0,3.0 \mathrm{~Hz}$ ), 148.8 (ddd, $J=252.6,10.7,3.3 \mathrm{~Hz}$ ), 140.4 (dt, $J=251.8,15.5 \mathrm{~Hz}$ ), 138.7, 136.6, $129.0(\mathrm{~d}, J=3.0 \mathrm{~Hz}), 128.7,125.6(\mathrm{dd}, J=11.0,3.7 \mathrm{~Hz}), 123.8(\mathrm{~m})$, 112.5 (dd, $J=17.4,4.0 \mathrm{~Hz}$ ), 26.7. Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{~F}_{3} \mathrm{O}$ (250.22): C, 67.20; H, 3.63; found: C, 67.34; $\mathrm{H}, 3.80$.

## Ethyl 2',3',4'-trifluoro-[1,1'-biphenyl]-4-carboxylate (6)

From ethyl 4-bromobenzoate ( $0.229 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2$ $\mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 6 was obtained in $53 \%$ yield $(0.148 \mathrm{~g})$ as a white solid: $\mathrm{mp} 81-84^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.12$ ( $\mathrm{d}, \mathrm{J}=8.4 \mathrm{~Hz}, 2 \mathrm{H}$ ), $7.57(\mathrm{~d}, J=8.4 \mathrm{~Hz}, 2 \mathrm{H}), 7.21-7.02(\mathrm{~m}, 2 \mathrm{H}), 4.41(\mathrm{q}, J=7.6$ $\mathrm{Hz}, 2 \mathrm{H}), 1.42(\mathrm{t}, \mathrm{J}=7.6 \mathrm{~Hz}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 166.2,150.9(\mathrm{ddd}, \mathrm{J}=251.5,10.2,2.9 \mathrm{~Hz}), 148.9$ (ddd, $J=252.5,10.6,3.4 \mathrm{~Hz}$ ), $140.3(\mathrm{dt}, J=251.7,15.5 \mathrm{~Hz}$ ), $130.2,129.9,128.8(\mathrm{~d}, J=3.0 \mathrm{~Hz}$ ), 125.7 (dd, $J=$ $10.5,3.8 \mathrm{~Hz}$ ), 123.9 (m), 112.4 (dd, $J=17.4,4.0 \mathrm{~Hz}$ ), 61.2, 14.3. Anal. Calcd for $\mathrm{C}_{15} \mathrm{H}_{11} \mathrm{~F}_{3} \mathrm{O}_{2}$ (280.25): C, 64.29; H, 3.96; found: C, 64.07; H, 4.11.

## 2,3,4-Trifluoro-4'-(trifluoromethyl)-1,1'-biphenyl (7) ${ }^{13}$

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From 4-bromobenzotrifluoride ( $0.225 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2$ $\mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 7 was obtained in $55 \%$ yield $(0.152 \mathrm{~g})$ as a white solid: $\mathrm{mp} 64-67^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.72(\mathrm{~d}, \mathrm{~J}=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.61(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 2 \mathrm{H}), 7.20-7.03(\mathrm{~m}, 2 \mathrm{H})$.
4,4"-Di(trifluoromethyl)-4',5',6'-trifluoro-1,1':3',1"-terphenyl was also isolated in low yield: ${ }^{1} \mathrm{H}$ NMR ( 400 MHz , $\mathrm{CDCl}_{3}$ ): $\delta 7.81(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 4 \mathrm{H}), 7.74(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 4 \mathrm{H}), 7.37(\mathrm{td}, J=7.7,2.3 \mathrm{~Hz}, 1 \mathrm{H})$.

## 2,3,4-Trifluoro-4'-methyl-1,1'-biphenyl (8) ${ }^{13}$

From 4-bromotoluene ( $0.171 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 8 was obtained in $48 \%$ yield $(0.106 \mathrm{~g})$ as a white oil.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.41$ (d, $\left.J=7.8 \mathrm{~Hz}, 2 \mathrm{H}\right), 7.28(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.18-6.97(\mathrm{~m}, 2 \mathrm{H}), 2.44(\mathrm{~s}, 3 \mathrm{H})$.

## 2,3,4-Trifluoro-4'-methoxy-1,1'-biphenyl (9) ${ }^{14}$

From 4-bromoanisole ( $0.187 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 9 was obtained in $64 \%$ yield $(0.152 \mathrm{~g})$ as a white solid: $\mathrm{mp} 73-76^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.43$ (d, $J=8.0 \mathrm{~Hz}, 2 \mathrm{H}$ ), 7.15-7.07 (m, 1H), 7.05-6.97 (m, 1H), 6.99 (d, J=8.0 Hz, $2 \mathrm{H}), 3.86(\mathrm{~s}, 3 \mathrm{H})$.

## 2,3,4-Trifluoro-3'-nitro-1,1'-biphenyl (10)

From 3-bromonitrobenzene ( $0.202 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 10 was obtained in $60 \%$ yield $(0.152 \mathrm{~g})$ as a yellow solid: $\mathrm{mp} 102-105^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.36(\mathrm{~s}, 1 \mathrm{H}), 8.25(\mathrm{~d}, J=8.2 \mathrm{~Hz}, 1 \mathrm{H}), 7.84(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.64(\mathrm{t}, J=8.0 \mathrm{~Hz}$, $1 \mathrm{H}), 7.24-7.05(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 151.1$ (ddd, $J=252.5,10.1,3.0 \mathrm{~Hz}$ ), 148.7 (ddd, $J=252.5$, 10.7, 3.4 Hz ), 148.5, $140.2(\mathrm{dt}, J=252.5,15.5 \mathrm{~Hz}), 135.6,134.8(\mathrm{~d}, J=3.3 \mathrm{~Hz}), 129.7,124.3(\mathrm{dd}, J=10.5,3.8$ $\mathrm{Hz}), 123.9(\mathrm{~m}), 123.7(\mathrm{~d}, \mathrm{~J}=2.7 \mathrm{~Hz})$, 123.1, $112.7(\mathrm{dd}, J=17.5,4.1 \mathrm{~Hz})$. Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{6} \mathrm{~F}_{3} \mathrm{NO}_{2}(253.18): \mathrm{C}$, 56.93; H, 2.39; N, 5.53. Found: C, 56.74; H, 2.24; N, 5.47.

2',3',4'-Trifluoro-[1,1'-biphenyl]-3-carbonitrile (11)
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From 3-bromobenzonitrile ( $0.182 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 11 was obtained in $67 \%$ yield $(0.156 \mathrm{~g})$ as a white solid: $\mathrm{mp} 92-95^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.78(\mathrm{~s}, 1 \mathrm{H}), 7.74(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.70(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.58(\mathrm{t}, J=7.8 \mathrm{~Hz}$, $1 \mathrm{H}), 7.20-7.04(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 151.0(\mathrm{ddd}, \mathrm{J}=252.3,10.1,3.0 \mathrm{~Hz}), 148.8$ (ddd, $J=252.5$, $10.7,3.4 \mathrm{~Hz}$ ), $140.1(\mathrm{dt}, J=252.5,15.5 \mathrm{~Hz}), 135.3,133.1(\mathrm{~d}, J=3.0 \mathrm{~Hz}), 132.3(\mathrm{~d}, J=2.8 \mathrm{~Hz}), 131.7,129.6$, $124.4(\mathrm{dd}, J=10.6,3.7 \mathrm{~Hz}), 123.7(\mathrm{~m}), 118.3,113.1,112.8(\mathrm{dd}, J=17.5,4.1 \mathrm{~Hz})$. Anal. Calcd for $\mathrm{C}_{13} \mathrm{H}_{6} \mathrm{~F}_{3} \mathrm{~N}$ (233.19): C, 66.96; H, 2.59; N, 6.01. Found: C, 66.78; H, 2.69; N, 5.92.

3,3'-Dicyano-4',5',6'-trifluoro-1,1':3',1"-terphenyl was also isolated in low yield: ${ }^{1} \mathrm{H}$ NMR (400 MHz, $\mathrm{CDCl}_{3}$ ): $\delta$ $7.90(\mathrm{~s}, 2 \mathrm{H}), 7.85(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.79(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.67(\mathrm{t}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.32(\mathrm{td}, J=7.7,2.3 \mathrm{~Hz}$, 1H).

## 2',3',4'-Trifluoro-[1,1'-biphenyl]-3-carbaldehyde (12)

From 3-bromobenzaldehyde ( $0.185 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2$ $\mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150{ }^{\circ} \mathrm{C}$ during 16 h , product 12 was obtained in $40 \%$ yield $(0.094 \mathrm{~g})$ as a white solid: $\mathrm{mp} 69-72{ }^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 10.08(\mathrm{~s}, 1 \mathrm{H}), 8.00(\mathrm{~s}, 1 \mathrm{H}), 7.92(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.77(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.64(\mathrm{t}$, $J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.25-7.14(\mathrm{~m}, 1 \mathrm{H}), 7.13-7.04(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 191.8,151.0(\mathrm{ddd}, \mathrm{J}=252.3$, $10.1,3.0 \mathrm{~Hz}), 148.8(\mathrm{ddd}, J=252.5,10.6,3.3 \mathrm{~Hz}), 140.4(\mathrm{dt}, J=252.0,15.5 \mathrm{~Hz}), 136.8,135.1,134.6(\mathrm{~d}, J=3.1$ $\mathrm{Hz}), 129.8(\mathrm{~d}, J=2.5 \mathrm{~Hz}), 129.5,129.4,125.3(\mathrm{dd}, J=10.7,3.7 \mathrm{~Hz}), 123.8(\mathrm{~m}), 112.5(\mathrm{dd}, J=17.4,4.1 \mathrm{~Hz})$. Anal. Calcd for $\mathrm{C}_{13} \mathrm{H}_{7} \mathrm{~F}_{3} \mathrm{O}$ (236.19): C, 66.11; H, 2.99. Found: C, 66.00; H, 2.87.

## 1-(2',3',4'-Trifluoro-[1,1'-biphenyl]-3-yl)ethan-1-one (13)

From 3-bromoacetophenone ( $0.199 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2$ $\mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150{ }^{\circ} \mathrm{C}$ during 16 h , product 13 was obtained in $54 \%$ yield $(0.135 \mathrm{~g})$ as a white solid: $\mathrm{mp} 92-95^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 8.07(\mathrm{~s}, 1 \mathrm{H}), 7.98(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.70(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.56(\mathrm{t}, \mathrm{J}=7.8 \mathrm{~Hz}$, $1 \mathrm{H}), 7.24-7.13(\mathrm{~m}, 1 \mathrm{H}), 7.13-7.01(\mathrm{~m}, 1 \mathrm{H}), 2.65(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 197.6,150.7$ (ddd, $\mathrm{J}=$ $251.3,10.1,3.0 \mathrm{~Hz}$ ), 148.8 (ddd, $J=251.8,10.5,3.3 \mathrm{~Hz}), 140.1(\mathrm{dt}, J=252.0,15.5 \mathrm{~Hz}), 137.5,134.6,133.3(\mathrm{~d}, \mathrm{~J}$ $=3.1 \mathrm{~Hz}), 129.0,128.6(\mathrm{~d}, J=2.5 \mathrm{~Hz}), 128.1,125.7(\mathrm{dd}, J=10.7,3.9 \mathrm{~Hz}), 123.9(\mathrm{~m}), 112.4(\mathrm{dd}, J=17.3,4.0 \mathrm{~Hz})$, 26.7. Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{~F}_{3} \mathrm{O}$ (250.22): C, 67.20; H, 3.63. Found: C, 67.40; H, 3.69.

## Methyl 2',3',4'-trifluoro-[1,1'-biphenyl]-3-carboxylate (14)

From methyl 3-bromobenzoate ( $0.215 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2$ $\mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 14 was obtained in $60 \%$ yield $(0.160 \mathrm{~g})$ as a yellow solid: $\mathrm{mp} 64-67^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.16(\mathrm{~s}, 1 \mathrm{H}), 8.07(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.70(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.54(\mathrm{t}, J=7.8 \mathrm{~Hz}$, 1H), 7.23-7.14 (m, 1H), 7.12-7.03 (m, 1H), 3.95 (s, 3H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 166.6,150.7$ (ddd, $J=$ $251.0,10.1,3.0 \mathrm{~Hz}$ ), 148.7 (ddd, $J=251.9,10.5,3.3 \mathrm{~Hz}$ ), 140.1 (dt, $J=251.7,15.5 \mathrm{~Hz}), 134.4,133.2(\mathrm{~d}, J=3.1$ $\mathrm{Hz}), 130.8,129.9(\mathrm{~d}, \mathrm{~J}=2.3 \mathrm{~Hz}), 129.3,128.8,125.7(\mathrm{dd}, J=10.7,3.9 \mathrm{~Hz}), 123.9(\mathrm{~m}), 112.4(\mathrm{dd}, J=17.3,4.0$ Hz ), 52.3. Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{~F}_{3} \mathrm{O}_{2}$ (266.22): $\mathrm{C}, 63.16$; $\mathrm{H}, 3.41$. Found: $\mathrm{C}, 63.08 ; \mathrm{H}, 3.34$.

## 2',3',4'-Trifluoro-[1,1'-biphenyl]-2-carbonitrile (15)

From 2-bromobenzonitrile ( $0.182 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 15 was obtained in $68 \%$ yield $(0.158 \mathrm{~g})$ as a yellow solid: $\mathrm{mp} 121-124^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.80(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.69(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.53(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.48(\mathrm{~d}, J=$ $8.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 7.22-7.06 (m, 2H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 151.5$ (ddd, $J=252.6,10.1,3.0 \mathrm{~Hz}$ ), 148.7 (ddd, $J$ $=252.3,10.7,3.5 \mathrm{~Hz}), 140.2(\mathrm{dt}, J=252.9,15.5 \mathrm{~Hz}), 137.5,133.4,132.8,130.9(\mathrm{~d}, J=1.2 \mathrm{~Hz}), 128.9,124.8(\mathrm{~m})$, 123.4 (dd, $J=12.3,3.7 \mathrm{~Hz}$ ), 117.6, 112.8, 112.5 (dd, $J=17.6,4.0 \mathrm{~Hz}$ ). Anal. Calcd for $\mathrm{C}_{13} \mathrm{H}_{6} \mathrm{~F}_{3} \mathrm{~N}$ (233.19): C , 66.96; H, 2.59; N, 6.01. Found: C, 67.05; H, 2.75; N, 5.80.

## 1-(2,3,4-Trifluorophenyl)naphthalene (16)

From 1-bromonaphthalene ( $0.207 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\operatorname{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 16 was obtained in $56 \%$ yield $(0.144 \mathrm{~g})$ as a white solid: $\mathrm{mp} 63-66^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.95(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.65(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.60-7.46(\mathrm{~m}, 3 \mathrm{H}), 7.44(\mathrm{~d}, J=7.8$ $\mathrm{Hz}, 1 \mathrm{H}), 7.18-7.06(\mathrm{~m}, 2 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 150.8$ (ddd, $J=250.1,10.1,2.9 \mathrm{~Hz}$ ), 149.1 (ddd, $J=$ $250.1,10.0,3.4 \mathrm{~Hz}), 140.1(\mathrm{dt}, J=251.9,15.5 \mathrm{~Hz}), 133.6,131.9(\mathrm{~d}, J=1.8 \mathrm{~Hz}), 131.6,129.1,128.5,127.9,126.6$, 125.7, $125.6(\mathrm{~m}), 125.3,125.2,112.0\left(\mathrm{dd}, \mathrm{J}=17.3,4.0 \mathrm{~Hz}\right.$ ). Anal. Calcd for $\mathrm{C}_{16} \mathrm{H}_{9} \mathrm{~F}_{3}(258.24)$ : C, $74.42 ; \mathrm{H}, 3.51$. Found: C, 74.61; H, 3.34.

## 3-(2,3,4-Trifluorophenyl)pyridine (17)

From 3-bromopyridine ( $0.158 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 17 was obtained in $64 \%$ yield $(0.134 \mathrm{~g})$ as a yellow solid: $\mathrm{mp} 94-97^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR (400 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 8.77(\mathrm{~s}, 1 \mathrm{H}), 8.68(\mathrm{~s}, 1 \mathrm{H}), 7.84(\mathrm{~d}, \mathrm{~J}=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.43(\mathrm{bs}, 1 \mathrm{H}), 7.21-7.04(\mathrm{~m}, 2 \mathrm{H})$.
${ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 151.0$ (ddd, $J=251.8,10.1,2.9 \mathrm{~Hz}$ ), 149.4 (bs), 148.8 (ddd, $J=251.5,10.0,3.6$ $\mathrm{Hz}), 140.5(\mathrm{dt}, \mathrm{J}=252.2,15.5 \mathrm{~Hz}), 136.1,130.1,123.8(\mathrm{~m}), 123.4(\mathrm{bs}), 112.6(\mathrm{dd}, \mathrm{J}=17.5,4.0 \mathrm{~Hz})$. Anal. Calcd for $\mathrm{C}_{11} \mathrm{H}_{6} \mathrm{~F}_{3} \mathrm{~N}$ (209.17): C, 63.16; H, 2.89; $\mathrm{N}, 6.70$. Found: C, 63.27; H, 2.74; N, 6.57 .

## 3-(2,3,4-Trifluorophenyl)quinoline (18)

From 3-bromoquinoline ( $0.208 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.396 \mathrm{~g}, 3 \mathrm{mmol}$ ), KOPiv ( $0.280 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150{ }^{\circ} \mathrm{C}$ during 16 h , product 18 was obtained in $72 \%$ yield $(0.186 \mathrm{~g})$ as a yellow solid: $\mathrm{mp} 158-161^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR (400 MHz, CDCl $)_{3}$ : $\delta 9.04(\mathrm{~s}, 1 \mathrm{H}), 8.28(\mathrm{~s}, 1 \mathrm{H}), 8.15(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.87(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.77(\mathrm{t}, \mathrm{J}$ $=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.60(\mathrm{t}, \mathrm{J}=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.32-7.22(\mathrm{~m}, 1 \mathrm{H}), 7.16-7.06(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 151.0$ (ddd, $J=250.8,10.1,2.9 \mathrm{~Hz}$ ), $150.8(\mathrm{~m}), 148.9(\mathrm{ddd}, J=252.2,10.5,3.6 \mathrm{~Hz}), 140.3(\mathrm{dt}, J=252.2,15.5 \mathrm{~Hz})$, $147.5,135.6(d, J=3.2 \mathrm{~Hz}), 130.2,129.3,128.1,127.5,127.3,127.0,124.0(\mathrm{~m}), 123.5(\mathrm{dd}, \mathrm{J}=11.0,3.7 \mathrm{~Hz})$, 112.7 (dd, $J=17.5,4.0 \mathrm{~Hz}$ ). Anal. Calcd for $\mathrm{C}_{15} \mathrm{H}_{8} \mathrm{~F}_{3} \mathrm{~N}$ (259.23): C, 69.50; H, 3.11; $\mathrm{N}, 5.40$. Found: C, 69.42; H , 3.04; N, 5.24.

## 4',5',6'-Trifluoro-4,4'-dimethyl-1,1':3',1"-terphenyl (19)

From 4-bromotoluene ( $0.513 \mathrm{~g}, 3 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.132 \mathrm{~g}, 1 \mathrm{mmol}$ ), KOPiv ( $0.420 \mathrm{~g}, 3 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150{ }^{\circ} \mathrm{C}$ during 16 h , product 19 was obtained in $63 \%$ yield $(0.196 \mathrm{~g})$ as a white solid: $\mathrm{mp} 90-93^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 7.43(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.28(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.23(\mathrm{td}, J=7.7,2.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.40$ $(\mathrm{s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CD}_{2} \mathrm{Cl}_{2}$ ): $\delta 147.5(\mathrm{ddd}, J=250.2,10.6,2.9 \mathrm{~Hz}), 140.4(\mathrm{dt}, J=249.0,16.3 \mathrm{~Hz}), 138.4$, 131.1, 129.4, $128.7(\mathrm{~m}), 126.3(\mathrm{dd}, J=9.6,5.5 \mathrm{~Hz}), 124.4(\mathrm{~m}), 20.9$. Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{15} \mathrm{~F}_{3}$ (312.34): C, 76.91; H, 4.84. Found: C, 76.74; H, 5.04.

## 4',5',6'-Trifluoro-4,4'-dimethoxy-1,1':3',1'-terphenyl (20)

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From 4-bromoanisole ( $0.561 \mathrm{~g}, 3 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.132 \mathrm{~g}, 1 \mathrm{mmol}$ ), KOPiv ( $0.420 \mathrm{~g}, 3 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 20 was obtained in $31 \%$ yield $(0.106 \mathrm{~g})$ as a white solid: $\mathrm{mp} 131-134{ }^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR (400 MHz, CDCl $\left.)_{3}\right): \delta 7.47(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 4 \mathrm{H}), 7.19(\mathrm{td}, J=8.0,2.2 \mathrm{~Hz}, 1 \mathrm{H}), 6.99(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 4 \mathrm{H}), 3.86$ $(\mathrm{s}, 6 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 159.6,147.2$ (ddd, $J=250.4,10.6,2.9 \mathrm{~Hz}$ ), 140.6 (dm, $J=250.0 \mathrm{~Hz}$ ), $130.0(\mathrm{~m}), 126.5,125.8$ (dd, $J=9.2,5.8 \mathrm{~Hz}$ ), $123.9(\mathrm{~m}), 114.2$, 55.4. Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{15} \mathrm{~F}_{3} \mathrm{O}_{2}$ (344.33): C, 69.76; H, 4.39. Found: C, 69.58; H, 4.31.

## 2,2'-Dicyano-4',5',6'-trifluoro-1,1':3',1"-terphenyl (21)

From 2-bromobenzonitrile ( $0.546 \mathrm{~g}, 3 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.132 \mathrm{~g}, 1 \mathrm{mmol}$ ), KOPiv ( $0.420 \mathrm{~g}, 3 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150{ }^{\circ} \mathrm{C}$ during 16 h , product 21 was obtained in $16 \%$ yield $(0.053 \mathrm{~g})$ as a yellow solid: $\mathrm{mp} 192-195^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.81(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.72(\mathrm{t}, J=8.0 \mathrm{~Hz}, 2 \mathrm{H}), 7.59(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.56(\mathrm{t}, J=$ $7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{td}, J=7.7,2.3 \mathrm{~Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 148.9$ (ddd, $J=255.6,10.8,3.6 \mathrm{~Hz}$ ), $140.5(\mathrm{dt}, J=254.6,15.7 \mathrm{~Hz}), 137.0,133.4,133.1,131.1,129.2,126.3(\mathrm{~m}), 123.2(\mathrm{dd}, J=10.4,6.4 \mathrm{~Hz}), 117.7$, 112.8. Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{9} \mathrm{~F}_{3} \mathrm{~N}_{2}$ (334.30): C, 71.86 ; H, 2.71; N, 8.38. Found: C, 71.99; H, 2.59; N, 8.40.

## 1,1'-(4,5,6-Trifluoro-1,3-phenylene)dinaphthalene (22)

From 1-bromonaphthalene ( $0.621 \mathrm{~g}, 3 \mathrm{mmol}$ ), 1,2,3-trifluorobenzene ( $0.132 \mathrm{~g}, 1 \mathrm{mmol}$ ), KOPiv ( $0.420 \mathrm{~g}, 3 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150{ }^{\circ} \mathrm{C}$ during 16 h , product 22 was obtained in $23 \%$ yield $(0.088 \mathrm{~g})$ as a yellow solid: $\mathrm{mp} 182-185^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 7.94(\mathrm{~d}, \mathrm{~J}=8.0 \mathrm{~Hz}, 4 \mathrm{H}), 7.82-7.78(\mathrm{~m}, 2 \mathrm{H}), 7.60-7.48(\mathrm{~m}, 8 \mathrm{H}), 7.26(\mathrm{td}, J=7.7,2.3$ $\mathrm{Hz}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 148.5$ (ddd, $\left.J=250.9,10.1,2.9 \mathrm{~Hz}\right), 140.1(\mathrm{dt}, J=253.9,17.0 \mathrm{~Hz}), 133.6$, 131.7 (m), 131.6, 129.1, 128.5, 128.1, 127.9, 126.7, 126.2, 125.3, 125.2. Anal. Calcd for $C_{26} H_{15} F_{3}$ (384.40): C, 81.24; H, 3.93. Found: C, 81.40; H, 3.98.

## 4',5',6'-Trifluoro-4"-methoxy-[1,1':3',1"-terphenyl]-4-carbonitrile (23)

From 4-bromobenzonitrile ( $0.273 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), 2,3,4-trifluoro-4'-methoxy-1,1'-biphenyl 9 ( $0.238 \mathrm{~g}, 1 \mathrm{mmol}$ ), KOPiv $(0.280 \mathrm{~g}, 2 \mathrm{mmol})$ in the presence of $\mathrm{PdCl}\left(\mathrm{C}_{3} \mathrm{H}_{5}\right)(\mathrm{dppb})(30.5 \mathrm{mg}, 0.05 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150{ }^{\circ} \mathrm{C}$ during 16 h , product 23 was obtained in $48 \%$ yield $(0.163 \mathrm{~g})$ as a white solid: $\mathrm{mp} 151-154{ }^{\circ} \mathrm{C}$.

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${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.76(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.66(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.46(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.23(\mathrm{td}, J$ $=7.8,2.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.00(\mathrm{~d}, \mathrm{~J}=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 3.87(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 159.9,148.3$ (ddd, $\mathrm{J}=$ 253.1, 10.6, 2.8 Hz ), 147.4 (ddd, $J=252.7,11.2,2.7 \mathrm{~Hz}$ ), $140.7(\mathrm{dt}, J=251.7,16.1 \mathrm{~Hz}), 138.7,132.5,130.0(\mathrm{~d}, \mathrm{~J}$ $=2.8 \mathrm{~Hz}), 129.5(\mathrm{~d}, J=2.9 \mathrm{~Hz}), 126.7(\mathrm{dd}, J=11.0,4.1 \mathrm{~Hz}), 125.8,124.2(\mathrm{dd}, \mathrm{J}=11.3,4.2 \mathrm{~Hz}), 124.1(\mathrm{~m}), 118.5$, 114.3, 112.1, 55.4. Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{12} \mathrm{~F}_{3} \mathrm{NO}$ (339.32): C, 70.80; H, 3.56; N, 4.13. Found: C, 71.07; H, 3.39; N, 4.40.

## 4',5',6'-Trifluoro-4"-methyl-[1,1':3',1"-terphenyl]-4-carbonitrile (24)

From 4-bromobenzonitrile ( $0.273 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), 2,3,4-trifluoro-4'-methyl-1,1'-biphenyl 8 ( $0.222 \mathrm{~g}, 1 \mathrm{mmol}$ ), KOPiv $(0.280 \mathrm{~g}, 2 \mathrm{mmol})$ in the presence of $\mathrm{PdCl}\left(\mathrm{C}_{3} \mathrm{H}_{5}\right)(\mathrm{dppb})(30.5 \mathrm{mg}, 0.05 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150{ }^{\circ} \mathrm{C}$ during 16 h , product 24 was obtained in $51 \%$ yield $(0.164 \mathrm{~g})$ as a white solid: $\mathrm{mp} 167-170^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR (400 MHz, CDCl $\left.)_{3}\right): \delta 7.76(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.66(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.42(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.27(\mathrm{~d}, J$ $=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.24(\mathrm{td}, J=7.8,2.3 \mathrm{~Hz}, 1 \mathrm{H}), 2.42(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 148.5(\mathrm{ddd}, \mathrm{J}=253.4$, $10.6,2.9 \mathrm{~Hz}), 147.6$ (ddd, $J=253.0,10.2,2.9 \mathrm{~Hz}$ ), $140.7(\mathrm{dt}, J=251.9,16.0 \mathrm{~Hz}), 138.7(\mathrm{~m}), 132.5,130.6,129.5$ $(m), 128.6(d, J=2.7 \mathrm{~Hz}), 127.0(\mathrm{dd}, J=11.0,4.1 \mathrm{~Hz}), 124.3(\mathrm{~m}), 118.5,112.2,21.2$. Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{12} \mathrm{~F}_{3} \mathrm{~N}$ (323.32): C, 74.30; H, 3.74; N, 4.33. Found: C, 74.41; H, 3.78; N, 4.60.

## 4',5',6'-Trifluoro-4-methyl-4'-nitro-1,1':3',1'-terphenyl (25)

From 4-bromonitrobenzene ( $0.303 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), 2,3,4-trifluoro-4'-methyl-1,1'-biphenyl 8 ( $0.222 \mathrm{~g}, 1 \mathrm{mmol}$ ), KOPiv $(0.280 \mathrm{~g}, 2 \mathrm{mmol})$ in the presence of $\mathrm{PdCl}\left(\mathrm{C}_{3} \mathrm{H}_{5}\right)(\mathrm{dppb})(30.5 \mathrm{mg}, 0.05 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150{ }^{\circ} \mathrm{C}$ during 16 h , product 25 was obtained in $37 \%$ yield $(0.127 \mathrm{~g})$ as a yellow solid: $\mathrm{mp} 150-153{ }^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR (400 MHz, CD $\mathrm{Cl}_{2}$ ): $\delta 8.30(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.73(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.43(\mathrm{~d}, J=8.5 \mathrm{~Hz}, 2 \mathrm{H}), 7.35-7.27$ $(\mathrm{m}, 3 \mathrm{H}), 2.40(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CD}_{2} \mathrm{Cl}_{2}\right): \delta 148.6(\mathrm{ddd}, \mathrm{J}=253.9,10.6,2.9 \mathrm{~Hz}), 147.6,147.5(\mathrm{ddd}, \mathrm{J}=$ $252.3,11.0,2.9 \mathrm{~Hz}), 140.6(\mathrm{dt}, \mathrm{J}=250.9,16.0 \mathrm{~Hz}), 140.5,138.8,130.6,129.8(\mathrm{~d}, \mathrm{~J}=3.0 \mathrm{~Hz}), 129.5,128.6(\mathrm{~d}, \mathrm{~J}=$ $2.2 \mathrm{~Hz}), 127.0(\mathrm{dd}, J=11.0,4.2 \mathrm{~Hz}), 124.6(\mathrm{~m}), 124.0(\mathrm{dd}, J=10.4,4.4 \mathrm{~Hz}), 123.8,20.9$. Anal. Calcd for $\mathrm{C}_{19} \mathrm{H}_{12} \mathrm{~F}_{3} \mathrm{NO}_{2}$ (343.31): $\mathrm{C}, 66.47$; $\mathrm{H}, 3.52$; $\mathrm{N}, 4.08$. Found: $\mathrm{C}, 66.57 ; \mathrm{H}, 3.41 ; \mathrm{N}, 3.79$.

## 2',3',4'-Trifluoro-5'-methoxy-[1,1'-biphenyl]-2-carbonitrile (26)

From 2-bromobenzonitrile ( $0.182 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluoro-4-methoxybenzene ( $0.243 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOPiv ( 0.280 $\mathrm{g}, 2 \mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA ( 4 mL ) at $150{ }^{\circ} \mathrm{C}$ during 16 h , product 26 was obtained in $61 \%$ yield $(0.160 \mathrm{~g})$ as a white solid: $\mathrm{mp} 128-131^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.80(\mathrm{~d}, J=8.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.67(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.53(\mathrm{t}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.50(\mathrm{~d}, J=$ $8.2 \mathrm{~Hz}, 1 \mathrm{H}$ ), 6.78 (td, $J=6.3,2.4 \mathrm{~Hz}, 1 \mathrm{H}$ ), $3.93(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 144.8$ ( m ), 142.8 (ddd, $J=$ $245.5,11.2,1.7 \mathrm{~Hz}$ ), 142.3 (ddd, $J=253.1,11.7,1.9 \mathrm{~Hz}$ ), 141.2 (ddd, $J=251.3,16.7,13.0 \mathrm{~Hz}$ ), 137.5, 133.5, 132.8, $131.0(\mathrm{~m}), 128.9,121.1(\mathrm{dd}, \mathrm{J}=12.7,4.5 \mathrm{~Hz}), 117.7,112.8,108.5(\mathrm{~m})$, 57.1. Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{8} \mathrm{~F}_{3} \mathrm{NO}$ (263.22): C, 63.88; H, 3.06; N, 5.32. Found: C, 64.11; H, 3.00; N, 5.07.

## 3-(2,3,4-Trifluoro-5-methoxyphenyl)pyridine (27)

From 3-bromopyridine ( $0.158 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,3-trifluoro-4-methoxybenzene ( $0.243 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOPiv ( 0.280 g , $2 \mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 27 was obtained in $48 \%$ yield $(0.115 \mathrm{~g})$ as a yellow solid: $\mathrm{mp} 142-145{ }^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.77(\mathrm{bs}, 1 \mathrm{H}), 8.67(\mathrm{bs}, 1 \mathrm{H}), 7.84(\mathrm{~d}, \mathrm{~J}=7.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.42(\mathrm{bs}, 1 \mathrm{H}), 6.75(\mathrm{t}, J=6.3$ $\mathrm{Hz}, 1 \mathrm{H}), 3.94(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 149.3,145.1(\mathrm{dt}, J=8.2,2.8 \mathrm{~Hz}$ ), 143.1 (ddd, $J=245.5,11.6$ $\mathrm{Hz}), 141.7$ (ddd, $J=252.5,11.7,2.7 \mathrm{~Hz}), 141.2$ (ddd, $J=251.3,17.0,13.0 \mathrm{~Hz}), 136.3,130.4,123.5,121.1(\mathrm{~d}, J=$ 10.5, 2.9 Hz ), 107.6, 57.1. Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{8} \mathrm{~F}_{3} \mathrm{NO}$ (239.20): C, 60.26; H, 3.37; N, 5.86. Found: C, 60.07; H, 3.24; N, 5.68.

## 2-((2,3,4-Trifluorophenyl)amino)benzonitrile (28)

From 2-bromobenzonitrile ( $0.182 \mathrm{~g}, 1 \mathrm{mmol}$ ), 2,3,4-trifluoroaniline ( $0.220 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\operatorname{PdCl}\left(\mathrm{C}_{3} \mathrm{H}_{5}\right)(\mathrm{dppb})(12.2 \mathrm{mg}, 0.02 \mathrm{mmol})$, in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 28 was obtained in $24 \%$ yield $(0.059 \mathrm{~g})$ as a yellow solid: $\mathrm{mp} 123-126^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.54(\mathrm{dd}, J=8.2,1.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.42(\mathrm{t}, J=7.6 \mathrm{~Hz}, 1 \mathrm{H}), 7.10-6.96(\mathrm{~m}, 3 \mathrm{H}), 6.93(\mathrm{~d}, J$ $=7.1 \mathrm{~Hz}, 1 \mathrm{H}), 6.13(\mathrm{~s}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \operatorname{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 148.0(\mathrm{ddd}, J=248.0,10.2,2.5 \mathrm{~Hz}), 146.2,145.2$ (ddd, $J=250.1,11.1,3.2 \mathrm{~Hz}$ ), 140.6 ( $\mathrm{ddd}, J=252.6,16.0,13.9 \mathrm{~Hz}$ ), 134.1, 133.2, $125.5(\mathrm{dd}, J=9.4,3.6), 120.5,117.4$ (ddd, $J=7.5,3.7,0.8 \mathrm{~Hz}$ ), 117.0, 114.4, 111.8 (dd, $J=18.2,4.1 \mathrm{~Hz}$ ), 99.6. Anal. Calcd for $\mathrm{C}_{13} \mathrm{H}_{7} \mathrm{~F}_{3} \mathrm{~N}_{2}(248.21): \mathrm{C}$, 62.91; H, 2.84; N, 11.29. Found: C, 62.99; H, 2.90; N, 11.47.

## 2,3,6-Trifluoro-4'-nitro-1,1'-biphenyl (29) ${ }^{15}$

From 4-bromonitrobenzene ( $0.202 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,4-trifluorobenzene ( $0.198 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2$ $\mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 29 was obtained in $53 \%$ yield $(0.134 \mathrm{~g})$ as a white solid: $\mathrm{mp} 127-130^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR (400 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 8.34(\mathrm{~d}, \mathrm{~J}=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.67(\mathrm{~d}, \mathrm{~J}=8.7 \mathrm{~Hz}, 2 \mathrm{H}), 7.30-7.17(\mathrm{~m}, 1 \mathrm{H}), 7.06-6.94(\mathrm{~m}$, 1H). ${ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 154.8$ (ddd, $J=247.0,4.5,3.0 \mathrm{~Hz}$ ), 147.9, $147.6(\mathrm{dm}, J=252.2 \mathrm{~Hz}), 147.5$ (dm, $J=246.1 \mathrm{~Hz}), 135.0(\mathrm{~d}, J=1.9 \mathrm{~Hz}), 131.3(\mathrm{t}, J=2.1 \mathrm{~Hz}), 123.6,118.1(\mathrm{dd}, J=20.2,14.0 \mathrm{~Hz}), 117.3(\mathrm{ddd}, J$ $=19.5,10.0,1.6 \mathrm{~Hz}), 111.4$ (ddd, $J=25.0,6.6,4.2 \mathrm{~Hz})$.

## 2',3',6'-Trifluoro-[1,1'-biphenyl]-4-carbonitrile (30) ${ }^{14}$

From 4-bromobenzonitrile ( $0.182 \mathrm{~g}, 1 \mathrm{mmol}$ ), $1,2,4$-trifluorobenzene ( $0.198 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in $\mathrm{DMA}(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 30 was obtained in $70 \%$ yield $(0.163 \mathrm{~g})$ as a white solid: $\mathrm{mp} 143-146{ }^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 7.76(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.59(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.27-7.16(\mathrm{~m}, 1 \mathrm{H}), 7.04-6.94(\mathrm{~m}$, 1 H ). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 154.8$ (ddd, $J=246.8,4.4,2.9 \mathrm{~Hz}$ ), $147.6(\mathrm{dm}, J=252.2 \mathrm{~Hz}$ ), $147.5(\mathrm{dm}, J=$ $246.1 \mathrm{~Hz}), 133.1(\mathrm{~d}, J=1.8 \mathrm{~Hz}), 132.2,131.0(\mathrm{t}, J=2.2 \mathrm{~Hz}), 118.4,118.3(\mathrm{dd}, J=20.1,14.6 \mathrm{~Hz}), 117.1(\mathrm{ddd}, J=$ $19.5,10.0,1.5 \mathrm{~Hz}$ ), 112.6, 111.4 (ddd, $J=25.1,6.7,4.3 \mathrm{~Hz}$ ).

## 2',3',6'-Trifluoro-[1,1'-biphenyl]-4-carbaldehyde (31)

From 4-bromobenzaldehyde ( $0.185 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,4-trifluorobenzene ( $0.198 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2$ $\mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 31 was obtained in $56 \%$ yield $(0.132 \mathrm{~g})$ as a white solid: $\mathrm{mp} 100-103^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 10.07(\mathrm{~s}, 1 \mathrm{H}), 7.98(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.64(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.24-7.11(\mathrm{~m}, 1 \mathrm{H})$, 7.00-6.92 (m, 1H). ${ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 191.7,155.0$ (ddd, $J=247.5,4.4,2.9 \mathrm{~Hz}$ ), 147.6 (ddd, $J=251.8$, $14.5,7.1 \mathrm{~Hz}), 147.5(\mathrm{ddd}, J=245.6,13.5,3.7 \mathrm{~Hz}), 136.2,134.5(\mathrm{~d}, J=1.6 \mathrm{~Hz}), 130.9(\mathrm{t}, J=2.1 \mathrm{~Hz}), 129.6,119.0$ (dd, $J=20.2,14.7 \mathrm{~Hz}$ ), 116.8 (ddd, $J=19.4,10.0,1.3 \mathrm{~Hz}$ ), 111.2 (ddd, $J=25.3,6.7,4.3 \mathrm{~Hz}$ ). Anal. Calcd for $\mathrm{C}_{13} \mathrm{H}_{7} \mathrm{~F}_{3} \mathrm{O}$ (236.19): C, 66.11; H, 2.99. Found: C, 66.00; H, 3.19.

## 1-(2',3',6'-Trifluoro-[1,1'-biphenyl]-4-yl)ethan-1-one (32)

From 4-bromoacetophenone ( $0.199 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,4-trifluorobenzene ( $0.198 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2$ $\mathrm{mmol})$ in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 32 was obtained in $60 \%$ yield $(0.150 \mathrm{~g})$ as a white solid: $\mathrm{mp} 127-130^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 8.06(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.58(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 2 \mathrm{H}), 7.22-7.11(\mathrm{~m}, 1 \mathrm{H}), 6.99-6.92(\mathrm{~m}$, 1H), $2.65(\mathrm{~s}, 3 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 197.5,155.1$ (ddd, $J=246.1,4.4,2.9 \mathrm{~Hz}$ ), 147.7 (ddd, $J=251.8$, $14.5,7.1 \mathrm{~Hz}), 147.6(\mathrm{ddd}, J=245.6,13.5,3.7 \mathrm{~Hz}), 137.0,133.1(\mathrm{~d}, J=1.6 \mathrm{~Hz}), 130.5(\mathrm{t}, J=2.1 \mathrm{~Hz}), 128.3,119.2$
(dd, $J=20.3,14.8 \mathrm{~Hz}), 116.5(\mathrm{ddd}, J=19.4,10.0,1.3 \mathrm{~Hz}), 111.1$ (ddd, $J=25.3,6.7,4.2 \mathrm{~Hz})$, 26.7. Anal. Calcd for $\mathrm{C}_{14} \mathrm{H}_{9} \mathrm{~F}_{3} \mathrm{O}$ (250.72): C, 67.20; H, 3.63. Found: C, 66.97; H, 3.47.

## 2,3,6-Trifluoro-4'-methyl-1,1'-biphenyl (33) ${ }^{16}$

From 4-bromotoluene ( $0.171 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,4-trifluorobenzene ( $0.198 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 33 was obtained in $61 \%$ yield $(0.135 \mathrm{~g})$ as a white oil.
${ }^{1} \mathrm{H}$ NMR (400 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 7.36(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.29(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 2 \mathrm{H}), 7.15-7.05(\mathrm{~m}, 1 \mathrm{H}), 6.95-6.85(\mathrm{~m}$, 1H), 2.42 (s, 3H). ${ }^{13} \mathrm{C}$ NMR (100 MHz, $\mathrm{CDCl}_{3}$ ): $\delta 155.3$ (ddd, $J=245.0,4.6,2.8 \mathrm{~Hz}$ ), 147.8 (ddd, $J=249.6,14.3$, $7.5 \mathrm{~Hz}), 147.6(\mathrm{ddd}, J=244.5,13.8,3.7 \mathrm{~Hz}), 138.7,130.0(\mathrm{t}, \mathrm{J}=2.0 \mathrm{~Hz}), 129.2,125.3(\mathrm{~d}, J=2.0 \mathrm{~Hz}), 120.2(\mathrm{dd}, \mathrm{J}$ $=20.7,15.1 \mathrm{~Hz}), 115.3(\mathrm{ddd}, J=19.4,10.0,1.4 \mathrm{~Hz}), 110.8(\mathrm{ddd}, J=25.5,6.6,4.2 \mathrm{~Hz}), 21.3$.

## 2',3',6'-Trifluoro-[1,1'-biphenyl]-2-carbonitrile (34)

From 2-bromobenzonitrile ( $0.182 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,4-trifluorobenzene ( $0.198 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 34 was obtained in $59 \%$ yield $(0.137 \mathrm{~g})$ as a yellow oil.
${ }^{1} \mathrm{H}$ NMR (400 MHz, CDCl $\left.)_{3}\right): \delta 7.78(\mathrm{~d}, J=8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.72(\mathrm{t}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.57(\mathrm{t}, J=7.9 \mathrm{~Hz}, 1 \mathrm{H}), 7.49(\mathrm{~d}, J=$ $8.3 \mathrm{~Hz}, 1 \mathrm{H}), 7.33-7.19(\mathrm{~m}, 1 \mathrm{H}), 7.06-6.95(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 155.0(\mathrm{ddd}, \mathrm{J}=246.7,4.0,2.8$ $\mathrm{Hz}), 147.6(\mathrm{ddd}, \mathrm{J}=252.0,14.2,6.8 \mathrm{~Hz}), 147.4(\mathrm{ddd}, \mathrm{J}=246.2,13.0,3.7 \mathrm{~Hz}), 133.2,132.7,132.2(\mathrm{~d}, \mathrm{~J}=1.9 \mathrm{~Hz})$, $131.6,129.4,117.8$ (ddd, $J=19.3,9.9,1.4 \mathrm{~Hz}), 117.3,116.9(\mathrm{dd}, \mathrm{J}=21.9,16.0 \mathrm{~Hz}), 113.9,111.3(\mathrm{ddd}, \mathrm{J}=24.6$, 6.6, 4.3 Hz ). Anal. Calcd for $\mathrm{C}_{13} \mathrm{H}_{6} \mathrm{~F}_{3} \mathrm{~N}$ (233.19): C, 66.96; H, 2.59; N, 6.01. Found: C, 66.88; H, 2.40; N, 5.68.

## 3-(2,3,6-Trifluorophenyl)pyridine (35) ${ }^{15}$

From 3-bromopyridine ( $0.158 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,4-trifluorobenzene ( $0.198 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150{ }^{\circ} \mathrm{C}$ during 16 h , product 35 was obtained in $72 \%$ yield $(0.150 \mathrm{~g})$ as a white solid: $\mathrm{mp} 53-56^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 8.73(\mathrm{bs}, 1 \mathrm{H}), 8.66(\mathrm{~d}, J=3.7 \mathrm{~Hz}, 1 \mathrm{H}), 7.80(\mathrm{~d}, J=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.42(\mathrm{dd}, J=7.8$, $4.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.25-7.12(\mathrm{~m}, 1 \mathrm{H}), 7.02-6.93(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C}$ NMR (100 MHz, $\left.\mathrm{CDCl}_{3}\right): \delta 155.3$ (ddd, $J=246.3,4.6,2.8$ $\mathrm{Hz}), 150.6(\mathrm{~m}), 149.7,147.7(\mathrm{ddd}, \mathrm{J}=251.5,14.6,7.2 \mathrm{~Hz}), 147.5(\mathrm{ddd}, \mathrm{J}=245.5,13.4,3.7 \mathrm{~Hz}), 137.5(\mathrm{t}, \mathrm{J}=2.0$ $\mathrm{Hz}), 124.8,123.3 ; 116.9(\mathrm{dd}, \mathrm{J}=20.7,15.1 \mathrm{~Hz}), 116.8(\mathrm{ddd}, J=19.4,10.1,1.4 \mathrm{~Hz}), 111.2(\mathrm{ddd}, J=25.1,6.6,4.2$ Hz ).

## 3-(2,3,6-Trifluorophenyl)quinoline (36) ${ }^{17}$

From 3-bromoquinoline ( $0.208 \mathrm{~g}, 1 \mathrm{mmol}$ ), 1,2,4-trifluorobenzene ( $0.198 \mathrm{~g}, 1.5 \mathrm{mmol}$ ), KOAc ( $0.196 \mathrm{~g}, 2 \mathrm{mmol}$ ) in the presence of $\mathrm{Pd}(\mathrm{OAc})_{2}(2.4 \mathrm{mg}, 0.02 \mathrm{mmol})$ in DMA $(4 \mathrm{~mL})$ at $150^{\circ} \mathrm{C}$ during 16 h , product 36 was obtained in $58 \%$ yield $(0.150 \mathrm{~g})$ as a white solid: $\mathrm{mp} 109-112^{\circ} \mathrm{C}$.
${ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ): $\delta 9.00(\mathrm{~s}, 1 \mathrm{H}), 8.30(\mathrm{~s}, 1 \mathrm{H}), 8.17(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.88(\mathrm{~d}, J=8.0 \mathrm{~Hz}, 1 \mathrm{H}), 7.77(\mathrm{t}, J$ $=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.59(\mathrm{t}, \mathrm{J}=7.8 \mathrm{~Hz}, 1 \mathrm{H}), 7.25-7.17(\mathrm{~m}, 1 \mathrm{H}), 7.05-6.97(\mathrm{~m}, 1 \mathrm{H}) .{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right): \delta 155.4$ (ddd, $J=246.1,4.6,3.8 \mathrm{~Hz}$ ), 150.8 (m), 148.1 (ddd, $J=251.3,14.6,7.2 \mathrm{~Hz}$ ), 147.7 ( $\mathrm{ddd}, J=245.5,13.5,3.7 \mathrm{~Hz}$ ), $147.6,137.5(\mathrm{t}, J=2.0 \mathrm{~Hz}), 130.4,129.4,128.2,127.5,127.2,121.9,117.0(\mathrm{dd}, J=20.5,15.0 \mathrm{~Hz}), 116.7(\mathrm{ddd}, J$ $=19.4,10.1,1.4 \mathrm{~Hz}$ ), 111.3 (ddd, $J=25.0,6.6,4.2 \mathrm{~Hz})$.

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## Supporting Information Available ${ }^{1} \mathrm{H}$ and ${ }^{13} \mathrm{C}$ NMR spectra of new compounds and ${ }^{1} \mathrm{H}$ NMR spectra of known

 compounds. This material is available free of charge via the Internet at http://pubs.acs.org.
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