Synthesis of Functionalized 3,4-Diarylbenzophenones and 2,4-Diarylbenzophenones by Site-Selective Suzuki and Sonogashira Cross-Coupling Reactions of Bis(triflates) of 3,4- and 2,4-Dihydroxybenzophenone

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Abstract: Palladium(0)-catalyzed Suzuki and Sonogashira cross-coupling reactions of the bis(triflates) of 2,4- and 3,4-dihydroxybenzophenone afforded 2,4- and 3,4-diarylbenzophenones, respectively. The reactions proceeded with very good site-selectivity in favor of position 4.

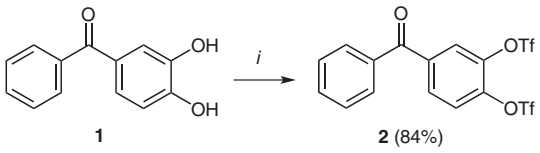
Key words: benzophenone, cross-coupling, palladium, site-selectivity, Suzuki reaction, Sonogashira reaction

Aryl-substituted benzophenones have been widely used in medicinal and agricultural chemistry and in material sciences. They show cytotoxic and antimicrobial activity, and enzyme inhibition.[2] Benzoylfluorenones contain the core structure of arylated benzophenones incorporated in the fluorenone system; they have been also reported to show interesting pharmacological properties.[3] Naturally occurring anthraquinones and tetracyclines are often very complex ring systems containing a hidden 4-arylbenzophenone unit.[4] 2-Hydroxy- and amino-substituted benzophenones have been reported to act as antitubulin agents and are, thus, interesting lead structures in the development of anticancer agents.[5] Benzophenones have found applications as sun cremes because of their activities as photosensitizers and UV-filters. Several benzophenone derivatives show fluorescence or phosphorescence, which allow useful applications in analytical chemistry.[6]

Benzophenones are available by Friedel–Crafts acylations[7] or by reaction of benzaldehydes with aromatic organometallic reagents and subsequent oxidation of the alcohol thus formed.[8] In the case of functionalized substrates, for example, containing a hydroxy, halide, or ester group, these methods often give unsatisfactory results, due to several side-reactions and low chemoselectivity. A more chemoselective strategy relies on the SmI_2-mediated reaction of benzaldehydes with benzyl halides and subsequent oxidation.[9] We reported the synthesis of 4-(2-hydroxybenzoyl)salicylates by cyclization of 1,3-bis(silyloxy)buta-1,3-dienes with 3-formylchromones.[10] In recent years, a number of site-selective palladium(0)-catalyzed cross-coupling reactions of polyhalogenated heterocycles[11] and of poly(triflates)[12] of carbacyclic substrates have been reported. We started a program directed to the application of this strategy to the site-selective synthesis of arylated benzophenones. Recently, we have reported[13] Suzuki–Miyauara reactions of the bis(triflate) of 3,4-dihydroxybenzophenone. Herein, we report full details of these studies, a comprehensive study of the scope, and an extension to the synthesis of alkynylated benzophenones by Sonogashira reactions. In addition, we report, for the first time, site-selective Suzuki–Miyaura and Sonogashira reactions of the bis(triflate) of parent 2,4-dihydroxybenzophenone. All reactions proceed with excellent site-selectivity in favor of position 4.

3,4-Dihydroxybenzophenone

Commercially available 3,4-dihydroxybenzophenone (**1**) was transformed into its bis(triflate) **2** in 84% yield (Scheme 1). 3,4-Diarylbenzophenones **3a–j** were prepared by Suzuki reaction of **2** with 2.6 equivalents of various aryl boronic acids (Scheme 2, Table 1). During the optimization, it proved to be important to use $Pd(PPh_3)_4$ (6 mol%) as the catalyst and to use an excess (2.6 equiv) of the arylboronic acid. 1,4-Dioxane was employed as the solvent (reflux, 4 h) and K_3PO_4 as the base.



1 2 (84%)

Scheme 1 Synthesis of **2**. *Reagents and conditions*: *i*) **1** (1.0 equiv), CH_2Cl_2, –78 °C, pyridine (4.0 equiv), Tf_2O (2.4 equiv), –78 → 0 °C, 4 h.

2 3a–j

Scheme 2 Synthesis of **3a–j**. *Reagents and conditions*: *i*) **2** (1.0 equiv), $ArB(OH)_2$ (2.6 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (6 mol%), 1,4-dioxane (5 mL per 1 mmol of **2**), 110 °C, 4 h.

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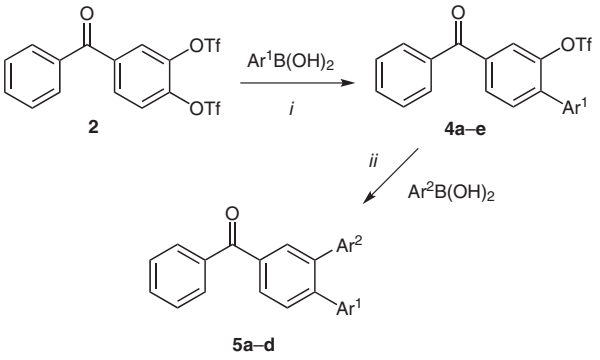
Table 1 Synthesis of **3a–j**

3	Ar	Yield (%)[a]
a	Ph	78
b	4-FC_6H_4	69
c	3,5-$Me_2C_6H_3$	75
d	3,5-$(MeO)_2C_6H_3$	74
e	2-$MeOC_6H_4$	67
f	4-$MeOC_6H_4$	54
g	2-$EtOC_6H_4$	76
h	3,4-$Me_2C_6H_3$	58
i	4-EtC_6H_4	78
j	2-ClC_6H_4	68

[a] Yields of isolated products.

The palladium-catalyzed Suzuki reaction of **2** with boronic acids (1.3 equiv) resulted in site-selective attack at carbon atom C-4 to give 4-aryl-3-(trifluoromethylsulfonyloxy)benzophenones **4a–e** (Scheme 3, Table 2). In the reactions, $Pd(PPh_3)_4$ (3 mol%) was used as the catalyst. The pure mono-coupled product had to be purified from bis-coupled products by chromatography. 3,4-Diarylbenzophenone **5a–d**, containing two different aryl groups, were prepared by reaction of **4a–e** with (4-vinylphenyl)boronic acid (1.3 equiv).



Scheme 3 Synthesis of **4a–e** and **5a–d**. *Reagents and conditions*: *i*) **2** (1.0 equiv), boronic acid (1.3 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 110 °C, 4 h; *ii*) **4a–e** (1.0 equiv), (4-vinylphenyl)boronic acid (1.3 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 110 °C, 4 h.

The structure of compound **4d** was unambiguously confirmed by 2D-NMR techniques (Figure 1). In the NOESY spectrum, an interaction was observed between the aromatic proton 5-H of ring A, to that of the aromatic protons of ring B attached to the carbons atoms C-2′ and C-6′. This confirmed that the first attack of boronic acid takes place at carbon C-4 of the bis(triflate).

Table 2 Synthesis of **4a–e** and **5a–d**

4	5	Ar[1]	Ar[2]	Yield (%)[a] **4a–e**	Yield (%)[a] **5a–d**
a	**a**	3-$MeOC_6H_4$	4-$(CH_2{=}CH)C_6H_4$	68	68
b		2,5-$(MeO)_2C_6H_3$		72	–[b]
c	**b**	4-MeC_6H_5	4-$(CH_2{=}CH)C_6H_4$	64	78
d	**c**	3,4,5-$(MeO)_3C_6H_2$	4-$(CH_2{=}CH)C_6H_4$	76	64
e	**d**	4-*t*-BuC_6H_4	4-$(CH_2{=}CH)C_6H_4$	70	62

[a] Yields of isolated products.
[b] Reaction was not carried out.

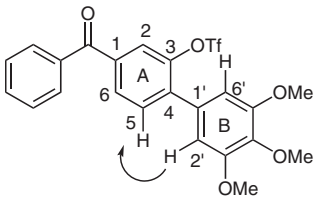


Figure 1 Relevant NOESY correlations for compound **4d**

The first attack of site-selective palladium(0)-catalyzed cross coupling reactions generally occurs at the sterically less encumbered and electronically more deficient position. The site-selective formation of **4a–e** can be explained by the fact that carbon atom C-4 (located *para* to the keto group) is more electron-deficient than C-3 (located *meta* to the keto group). In contrast, the steric environment of positions 3 and 4 is similar and should have no influence on the selectivity (Figure 2).

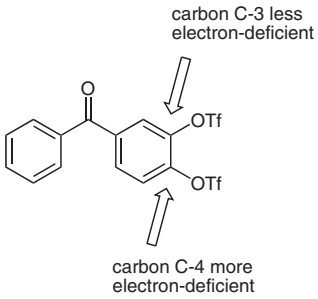


Figure 2 Possible explanation for the site-selective formation of products **4a–e**

We were interested in the question whether a high degree of site-selectivity can be also obtained for Sonogashira cross-coupling reactions. The Sonogashira reaction of **2** with various alkynes (2.6 equiv) afforded the 3,4-dialkynylbenzophenones **6a–f** in good yields (Scheme 4, Table 3). The best yields were obtained when $Pd(PPh_3)_2Cl_2$ (6 mol%) was used as the catalyst with 2.6 equivalents of the alkyne and when the reaction was carried out in DMF (reflux, 4 h) using Et_3N as the base.

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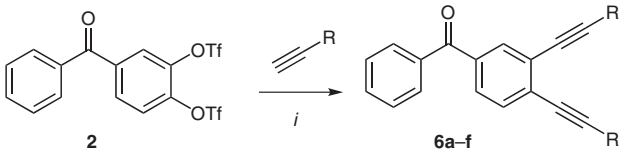


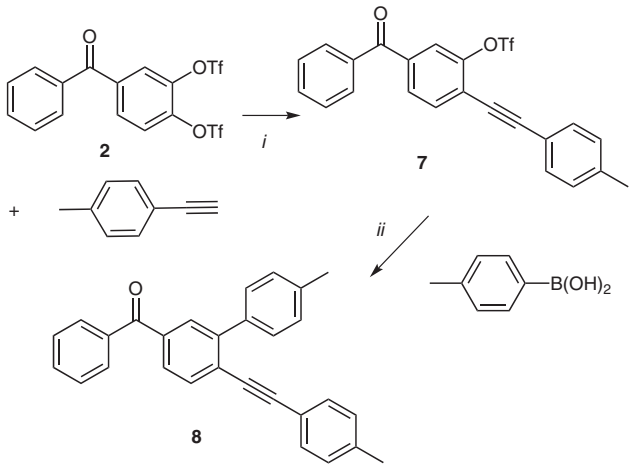
Scheme 4 Synthesis of **6a–f**. *Reagents and conditions*: *i*) **2** (1.0 equiv), alkyne (2.0 equiv), anhyd CuI (10 mol%), $Pd(PPh_3)_2Cl_2$ (6 mol%), Et_3N (1.25 equiv), DMF, 110 °C, 4 h.

Table 3 Synthesis of **6a–f**

6	R	Yield (%)[a]
a	4-*t*-BuC_6H_4	78
b	Ph	54
c	3-$MeOC_6H_4$	64
d	4-MeC_6H_4	66
e	4-FC_6H_4	60
f	3-MeC_6H_4	58

[a] Yields of isolated products.

The Sonogashira reaction of 3,4-bis(trifluoromethylsulfonyloxy)benzophenone (**2**) with *p*-tolylacetylene (1.3 equiv), in the presence of $Pd(PPh_3)_2Cl_2$ (3 mol%), proceeded with very good site-selectivity (attack at carbon atom C-4) to give product **7** (Scheme 5). Product **7** was treated with 4-methylphenylboronic acid (1.0 equiv), in the presence of K_3PO_4 as a base and $Pd(PPh_3)_4$ (3 mol%) as the catalyst in 1,4-dioxane at 90 °C, to give product **8** in good yield (64%). The structure of **8** was independently confirmed by X-ray crystal structure analysis (Figure 3).[14]



Scheme 5 Synthesis of **7** and **8**. *Reagents and conditions*: *i*) **2** (1.0 equiv), alkyne (1.0 equiv), anhyd CuI (10 mol%), $Pd(PPh_3)_2Cl_2$ (6 mol%), Et_3N (1.25 equiv), DMF, 90 °C, 8 h; *ii*) **7** (1.0 equiv), 4-methylphenylboronic acid (1.3 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 90 °C, 4 h.

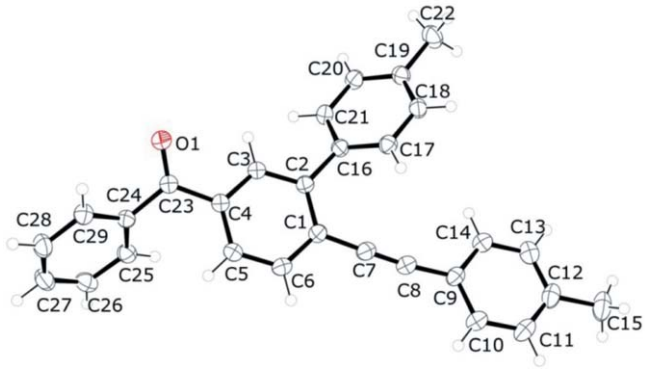
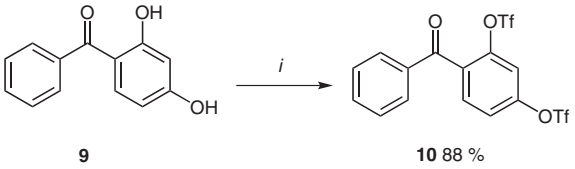


Figure 3 ORTEP plot of **8**

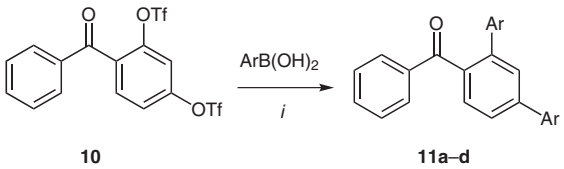
2,4-Dihydroxybenzophenone

We next decided to extend the scope of the study to the bis(triflate) derived from commercially available 2,4-dihydroxybenzophenone (**9**). The reaction of **9** with trifluoromethanesulfonic anhydride resulted in the formation of 2,4-bis(trifluoromethylsulfonyloxy)benzophenone (**10**) in 88% yield (Scheme 6).



Scheme 6 Synthesis of **10**. *Reagents and conditions*: *i*) **9** (1.0 equiv), CH_2Cl_2, –78 °C, pyridine (4.0 equiv), Tf_2O (2.4 equiv), –78 °C, 4 h.

The Suzuki–Miyaura reaction of **10** with different aryl boronic acids (2.6 equiv) afforded the 2,4-diarylbenzophenones **11a–d** in good yields (Scheme 7, Table 4). The reactions were carried out under the conditions reported for the synthesis of **3a–j**.



Scheme 7 Synthesis of **11a–d**. *Reagents and conditions*: *i*) **10** (1.0 equiv), boronic acid (2.6 equiv), K_3PO_4 (3.0 equiv), $Pd(PPh_3)_4$ (6 mol%), 1,4-dioxane (5 mL per 1 mmol of **10**), 110 °C, 4 h.

Table 4 Synthesis of **11a–d**

11	Ar	Yield (%)[a]
a	Ph	82
b	4-MeC_6H_4	84
c	3-ClC_6H_4	75
d	4-$MeOC_6H_4$	71

[a] Yields of isolated products.

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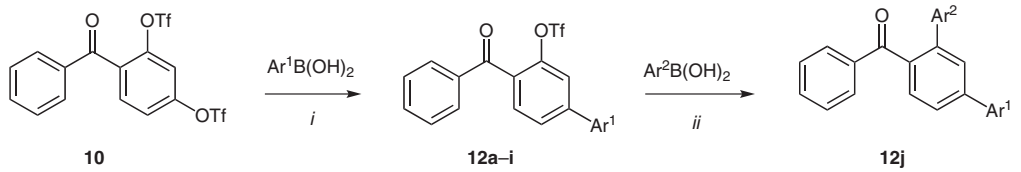


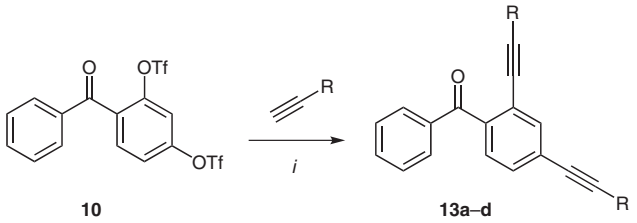
Scheme 8 Synthesis of **12a–i**. *Reagents and conditions*: *i*) **10** (1.0 equiv), boronic acid (2.6 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 90 °C, 4 h; *ii*) boronic acid (1.3 equiv), **12e** (1.0 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 90 °C, 4 h.

The Suzuki–Miyaura reaction of **10** with 1.3 equivalents of different arylboronic acids, in the presence of $Pd(PPh_3)_4$ (3 mol%), resulted in site-selective attack at carbon atom C-4 to give the 4-aryl-2-(trifluoromethylsulfonyloxy)benzophenones **12a–i** (Scheme 8, Table 5). The reaction of **12e** with 4-methoxyphenylboronic acid (1.3 equiv) gave the aryl substituted benzophenone **12j**, which have two different aryl substituents at the positions 2 and 4 (Scheme 8, Table 5).

Table 5 Synthesis of **12a–j**

12	Ar^1	Yield (%)[a] **12**	Ar^2	Yield (%)[a] **12j**
a	4-MeC_6H_4	73		
b	4-EtC_6H_4	75		
c	3,4-$(Me)_2C_6H_3$	68		
d	3,5-$Me_2C_6H_3$	67		
e	4-*t*-BuC_6H_4	76	4-$MeOC_6H_4$	71
f	3-ClC_6H_4	65		
g	3-$MeOC_6H_4$	64		
h	4-$MeOC_6H_4$	63		
i	3,4,5-$(MeO)_3C_6H_2$	58		

[a] Yields of isolated products.



Scheme 9 Synthesis of **13a–d**. *Reagents and conditions*: *i*) **10** (1.0 equiv), alkyne (2.2 equiv), anhyd CuI (10%), $Pd(PPh_3)_2Cl_2$ (6 mol%), Et_3N (1.25 equiv), NBu_4I (15 mol%), DMF, 90 °C, 4 h.

The Sonogashira reaction of **10** with different alkynes resulted in the formation of the 2,4-dialkynylbenzophenones **13a–d** (Scheme 9, Table 6). The reactions were accomplished using the catalyst $Pd(PPh_3)_2Cl_2$ (6 mol%), 2.2 equivalents of the terminal alkynes, anhydrous CuI (20 mol%), and NBu_4I (15 mol%) in DMF. All reactions proceeded in good yields.

Table 6 Synthesis of **13a–d**

13	R	Yield (%)[a]
a	Ph	78
b	3-MeC_6H_4	74
c	4-MeC_6H_4	77
d	*n*-C_8H_{17}	74

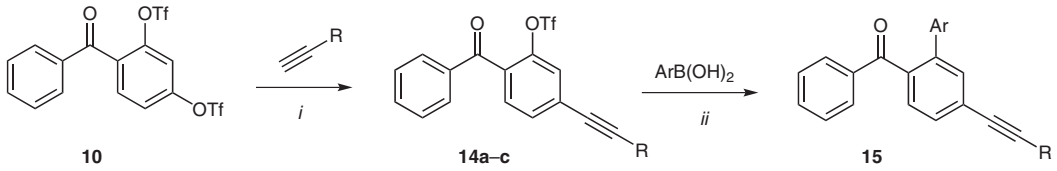
[a] Yields of isolated products.

Site-selective Sonogashira reactions of **10** were next studied. The reaction of **10** with aliphatic and aromatic alkynes afforded the 4-alkynyl-2-(trifluoromethylsulfonyloxy)benzophenones **14a–c** in good yields (Scheme 10, Table 7). The best yields were obtained with $Pd(PPh_3)_2Cl_2$ (3 mol%) as the catalyst using 1.1 equivalents of the terminal alkyne in the presence of CuI (10 mol%) and NBu_4I (15 mol%) in DMF. The Suzuki reaction of product **14c** with 4-*tert*-butylphenylboronic acid (1.2 equiv), in the presence of K_3PO_4 (1.5 equiv) and $Pd(PPh_3)_4$ (3 mol%),

Table 7 Synthesis of **14a–c** and **15**

14	R	Yield (%)[a] **14**	Ar	Yield (%)[a] **15**
a	*n*-Pr	78		
b	*n*-C_8H_{17}	81		
c	4-$MeOC_6H_4$	68	4-*t*-BuC_6H_4	73

[a] Yields of isolated products.



Scheme 10 Synthesis of **14a–c** and **15**. *Reagents and conditions*: *i*) **10** (1.0 equiv), alkyne (1.1 equiv), anhyd CuI (10%), $Pd(PPh_3)_2Cl_2$ (3%), Et_3N (1.25 equiv), DMF, 90 °C, 8 h; *ii*) **14c** (1.0 equiv), 4-*tert*-butylphenylboronic acid (1.3 equiv), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane, 90 °C, 4 h.

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gave product **15** in good yield (73%). The structure of **14c** was independently confirmed by X-ray crystal structure analysis (Figure 4).[14]

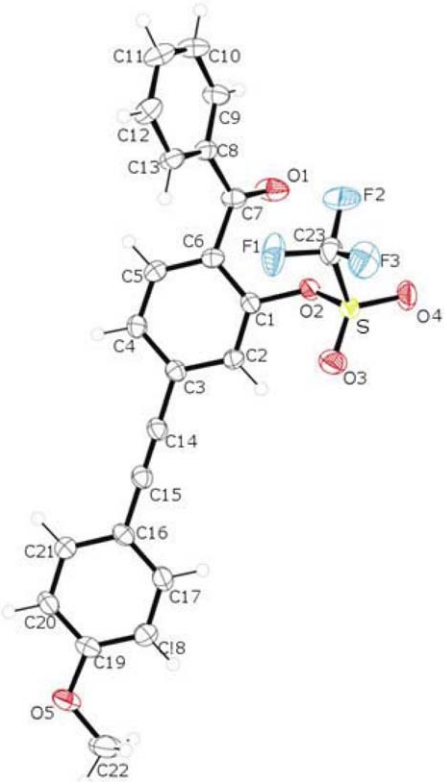

Figure 4 ORTEP plot of **14c** (50% probability level)

In conclusion, we have reported the synthesis of various substituted benzophenones by Suzuki and Sonogashira reactions of the bis(triflates) of 3,4- and 2,4-dihydroxybenzophenone. The reactions proceed with excellent site-selectivity in favor of position 4.

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^{1}H and ^{13}C NMR spectra, the deuterated solvents indicated were used. Mass spectrometric data were obtained by electron ionization (EI, 70 eV), chemical ionization (CI, isobutane), or electrospray ionization (ESI). For preparative scale chromatography, silica gel 60 (0.063–0.200 mm, 70–230 mesh) was used.

Triflates 2 and 10; General Procedure

To a stirred solution of **1** and/or **9** (1.0 equiv) in CH_2Cl_2 (10 mL/mmol) was added pyridine (4.0 equiv) at –78 °C under an argon atmosphere. After 10 min, Tf_2O (2.4 equiv) was added at –78 °C. The mixture was allowed to warm up to 0 °C and stirred for 4 h. The mixture was filtered and the filtrate was concentrated in vacuo. The products of the reaction mixture were isolated by rapid column chromatography (flash silica gel, heptanes–EtOAc).

3,4-Bis(trifluoromethylsulfonyloxy)benzophenone (2)

Starting from **1** (168 mg, 0.78 mmol), pyridine (0.25 mL, 3.12 mmol), and Tf_2O (0.30 mL, 1.8 mmol), **2** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil (318 mg, 84%).

IR (KBr): 3061 (w), 1598, 1589, 1580 (m), 1496, 1431, 1414, 1319, 1291 (m), 1265 (s), 1165, 1077, 1028, 989, 976, 932 (m), 887, 787, 757 (s), 680, 595, 572 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.44–7.60 (m, 5 H, ArH), 7.68–7.72 (m, 2 H, ArH), 7.86 (s, 1 H, ArH),

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 115.9 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 121.1 (q, $J_{F,C}$ = 321.3 Hz, CF_3), 123.6, 125.2, 128.7, 129.9, 130.9, 133.6 (CH_{Ar}), 135.7, 138.7, 140.2, 142.9 (C_{Ar}), 192.6 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3, 72.0 (2 CF).

GC-MS (EI, 70 eV): *m*/*z* (%) = 478 (M^+, 74), 401 (05), 345 (08), 253 (26), 225 (32), 204 (04), 167 (22), 156 (06), 128 (27), 105 (100), 77 (43), 69 (30), 51 (14).

HRMS (EI): *m*/*z* calcd for $C_{15}H_8F_6O_7S_2$ [M^+]: 477.96041; found: 477.960958.

2,4-Bis(trifluoromethylsulfonyloxy)benzophenone (10)

Starting from **9** (214 mg, 1.0 mmol), pyridine (0.32 mL, 4.0 mmol), and Tf_2O (0.40 mL, 2.4 mmol), **10** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a highly viscous oil (420 mg, 88%).

IR (KBr): 3303, 3092 (w), 1657 (s), 1600, 1597, 1493, 1433, 1427 (m), 1319 (w), 1295, 1274, 1242, 1216 (m), 1189, 1133 (s), 1087, 966, 936, 923, 892, 859, 854, 795, 752, 693, 664, 603, 584, 570 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.54–6.55 (m, 1 H, ArH), 6.59–6.69 (m, 3 H, ArH), 7.79–6.87 (m, 2 H, ArH), 6.93–6.96 (m, 2 H, ArH).

^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 114.0 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.9 (q, $J_{F,C}$ = 320 Hz, CF_3), 116.5, 121.2, 128.8, 130.1, 132.5 (CH_{Ar}), 132.7 (C_{Ar}), 134.3 (CH_{Ar}), 135.7, 147.0, 150.5 (C_{Ar}), 190.9 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.7, –73.0 (CF).

GC-MS (EI, 70 eV): *m*/*z* (%) = 478 (M^+, 50), 401 (22), 184 (19), 156 (10), 128 (8), 105 (100), 77 (34), 69 (27), 51 (10).

HRMS (EI, 70 eV): *m*/*z* calcd for $C_{15}H_8F_6O_7S_2$ [M^+]: 477.96101; found: 477.961098.

Suzuki Cross-Coupling Reactions; General Procedure

1,4-Dioxane solution of the arylboronic acid, K_3PO_4, $Pd(PPh_3)_4$, and the aromatic triflate was stirred in a pressure tube at the denoted temperature for 4 h under argon atmosphere. After cooling to 20 °C, sat. aq NH_4Cl (50 mL) was added, the organic and aqueous layers were separated, and the latter was extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried (Na_2SO_4), filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography.

Phenyl([1,1′;2′,1″]terphenyl-4′-yl)methanone (3a)

Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol%), phenylboronic acid (129 mg, 1.06 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **3a** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless solid; reaction temperature 110 °C; yield: 108 mg (78%); mp 138–140 °C.

IR (KBr): 3286, 3010, 2912, 2854, 2728 (w), 1728 (s), 1574, 1502 (m), 1492, 1452, 1436, 1386, 1328, 1294 (m), 1250 (s), 1198, 1116, 1064, 1036, 959, 902 (m), 882, 840, 793, 738 (s), 695, 648, 594, 563 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.00–7.12 (m, 10 H, ArH), 7.38–7.47 (m, 4 H, ArH), 7.72 (d, *J* = 6.5 Hz, 1 H, ArH), 7.74–7.80 (m, 3 H, ArH).

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^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 126.9, 127.2, 128.0, 128.1, 128.4, 129.1, 129.7, 129.8, 130.0, 130.6, 132.2, 132.5 (CH_{Ar}), 136.5, 137.7, 138.3, 140.6, 140.7, 144.7 (C_{Ar}), 196.3 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 334 (M^+, 100), 257 (52), 228 (31), 202 (07), 128 (06), 105 (24), 77 (20).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{18}O$ [M^+]: 334.13522; found: 334.135837.

Phenyl(4,4″-difluoro[1,1′;2′,1″]terphenyl-4′-yl)methanone (3b)
Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-fluorophenylboronic acid (148 mg, 1.06 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **3b** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a yellow oil; reaction temperature 110 °C; yield: 107 mg (69%).

IR (KBr): 3052, 3020, 2996, 2830 (w), 1716 (s), 1656, 1596 (m), 1490, 1456, 1432, 1398, 1317, 1273 (m), 1178, 1118, 1072, 1054, 945, 936 (m), 843, 827, 796, 746 (s), 695, 642, 581, 532 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.82–6.90 (m, 3 H, ArH), 6.99–7.10 (m, 4 H, ArH), 7.40–7.55 (m, 5 H, ArH), 7.73–7.80 (m, 4 H, ArH).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 115.0, 115.3, 128.4, 129.3, 130.0, 130.5, 131.1, 131.4, 132.1, 132.5 (CH_{Ar}), 136.3, 136.8, 137.5, 138.2, 139.7, 143.5, 160.5, 163.7 (C_{Ar}), 196.1 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 370 (M^+, 100), 293 (58), 264 (17), 244 (19), 105 (22), 77 (16);

HRMS (EI): *m*/*z* calcd for $C_{25}H_{16}F_2O$ [M^+]: 370.11637; found: 370.116463.

Phenyl(3,5,3″,5″-tetramethyl[1,1′;2′,1″]terphenyl-4′-yl)methanone (3c)
Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol%), 3,5-dimethylphenylboronic acid (159 mg, 1.06 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **3c** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless crystalline solid; reaction temperature 110 °C; yield: 123 mg (75%); mp 140–142 °C.

IR (KBr): 3289, 3013, 2916, 2857, 2732 (w), 1732 (s), 1574, 1505 (m), 1495, 1455, 1436, 1386, 1328, 1296 (m), 1250 (s), 1199, 1118, 1067, 1036, 959, 902 (m), 882, 842, 793, 738 (s), 695, 648, 596, 567 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 2.09 (s, 6 H, 2 CH_3), 2.11 (s, 6 H, 2 CH_3), 6.68 (d, *J* = 4.45 Hz, 3 H, ArH), 6.75 (d, *J* = 6.55 Hz, 2 H, ArH), 7.38–7.48 (m, 5 H, ArH), 7.68, 7.72 (dd, *J* = 1.85, 9.8 Hz, 1 H, ArH), 7.75 (m, 3 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.2 (2 CH_3), 21.3 (2 CH_3), 125.1, 127.5, 127.7, 128.3, 128.6, 128.8, 130.0, 130.4, 132.1, 132.3 (CH_{Ar}), 136.3, 137.1, 137.8, 138.1, 140.4, 140.5, 140.9, 144.9 (C_{Ar}), 196.4 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 390 (M^+, 100), 313 (29), 270 (13), 239 (07), 148 (04), 105 (22), 77 (11).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{26}O$ [M^+]: 390.19782; found: 390.197629.

Phenyl(2,4,2″,4″-tetramethoxy[1,1′;2′,1″]terphenyl-4′-yl)methanone (3d)
Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol%), 2,4-dimethoxyphenylboronic acid (192 mg, 1.06 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **3d** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless solid; reaction temperature 110 °C; yield: 140 mg (74%); mp 136–138 °C.

IR (KBr): 3288, 3012, 2914, 2856, 2730 (w), 1731 (s), 1572, 1505 (m), 1495, 1455, 1436, 1386, 1328, 1296 (m), 1250 (s), 1199, 1118, 1067, 1036, 959, 902 (m), 882, 842, 793, 738 (s), 695, 648, 596, 567 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.53, 3.55, 3.77, 3.78 (s, 12 H, 4 OCH_3), 6.35–6.41 (m, 3 H, ArH), 6.93 (t, *J* = 8.9 Hz, 1 H, ArH), 7.48–7.57 (m, 5 H, ArH), 7.81–7.92 (m, 5 H, ArH).

^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 55.1, 55.3 (4 OCH_3), 98.2, 103.9, 104.0 (CH_{Ar}), 123.03, 123.07 (C_{Ar}), 128.1, 128.4, 130.0, 131.0, 131.5, 132.0, 133.1 (CH_{Ar}), 135.6, 138.0, 142.9, 157.1, 160.0 (C_{Ar}), 196.3 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 454 (M^+, 100), 377 (03), 227 (05), 105 (37).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{26}O_5$ [M^+]: 454.17748; found: 454.177627.

Phenyl(2,2″-dimethoxy-[1,1′;2′,1″]terphenyl-4′-yl)methanone (3e)
Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol%), 2-methoxyphenylboronic acid (161 mg, 1.06 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **3e** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless solid; reaction temperature 110 °C; yield: 110 mg (67%); mp 152–154 °C.

IR (KBr): 3055, 3024, 2998, 2832 (w), 1712 (s), 1654, 1597 (m), 1493, 1459, 1434, 1396, 1317, 1273 (m), 1178, 1118, 1074, 1051, 946, 932 (m), 843, 827, 796, 748 (s), 695, 642, 581, 531 cm^{-1} (m).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.39, 3.41 (s, 6 H, 2 OCH_3), 6.61–6.77 (m, 2 H, ArH), 6.94–7.09 (m, 5 H, ArH), 7.35–7.46 (m, 4 H, ArH), 7.75–7.82 (m, 5 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 54.9 (2 OCH_3), 110.3, 110.4, 119.9, 120.0, 128.2, 128.5, 128.7, 128.8 (CH_{Ar}), 130.0 (C_{Ar}) 130.1, 130.7, 131.2, 131.3, 132.1, 132.7 (CH_{Ar}), 135.9, 137.9, 138.4, 143.0, 156.0, 156.8 (C_{Ar}), 196.3 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 394 (M^+, 100), 363 (21), 317 (80), 289 (20), 274 (46), 259 (11), 202 (18), 158 (15), 105 (83), 77 (68).

HRMS (EI): *m*/*z* calcd for $C_{27}H_{22}O_3$ [M^+]: 394.15635; found: 394.156782.

Phenyl(4,4′-dimethoxy[1,1′;2′,1″]terphenyl-4′-yl)methanone (3f)
Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-methoxyphenylboronic acid (161 mg, 1.06 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **3f** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a yellow oil; reaction temperature 110 °C; yield: 90 mg (54%).

IR (KBr): 3052, 3022, 2996, 2830 (w), 1716 (s), 1652, 1596 (m), 1492, 1456, 1432, 1394, 1316, 1272 (m), 1176, 1116, 1072, 1050, 945, 932 (m), 843, 827, 796, 748 (s), 692, 642, 579, 529 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.68, 3.69 (s, 6 H, 2 OCH_3), 6.66–6.71 (m, 4 H, ArH), 6.96–7.04 (m, 4 H, ArH), 7.37–7.46 (m, 3 H, ArH), 7.68, 7.71 (d, *J* = 1.80, 9.75 Hz, 1 H, ArH), 7.74–7.79 (m, 4 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 55.1 (2 OCH_3), 113.5 (C_{Ar}), 113.6, 128.3, 128.8, 130.0, 130.5, 130.8, 131.0, 132.3, 132.4, 132.9 (CH_{Ar}), 133.0, 136.2, 137.8, 140.1, 144.2, 158.8 (C_{Ar}), 196.3 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 394 (M^+, 100), 317 (11), 289 (04), 258 (03), 202 (07), 105 (24).

HRMS (EI): *m*/*z* calcd for $C_{27}H_{22}O_3$ [M^+]: 394.15635; found: 394.156091.

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Phenyl(2,2′-diethoxy[1,1′;2′,1″]terphenyl-4′-yl)methanone (3g)
Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol%), 2-ethoxyphenylboronic acid (175 mg, 1.06 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **3g** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless solid; reaction temperature 110 °C; yield: 135 mg (76%); mp 168–170 °C.

IR (KBr): 3048, 3024, 2994, 2832 (w), 1718 (s), 1654, 1598 (m), 1494, 1452, 1430, 1396, 1318, 1274 (m), 1178, 1116, 1074, 1052, 947, 932 (m), 843, 823, 798, 748 (s), 690, 644, 577, 527 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.09–1.15 (m, 6 H, 2 CH_3), 3.64 (q, *J* = 6.8 Hz, 4 H, 2 CH_2), 6.59–6.70 (m, 4 H, ArH), 6.90–6.96 (m, 2 H, ArH), 7.00–7.10 (m, 2 H, ArH), 7.32–7.44 (m, 4 H, ArH), 7.72 (dd, *J* = 1.86, 7.89 Hz, 1 H, ArH), 7.77–7.81 (m, 3 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 14.5, 14.7 (2 CH_3), 63.1, 63.3 (2 CH_2), 111.3, 111.4, 119.6, 119.7, 128.2, 128.3, 128.6, 130.0 (CH_{Ar}), 130.1 (C_{Ar}), 131.0, 131.5, 131.7, 132.1, 132.9 (CH_{Ar}), 135.6, 138.0, 138.5, 143.1, 155.5, 155.6 (C_{Ar}), 196.5 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 422 (M^+, 100), 407 (07), 365 (06), 347 (04), 289 (08), 261 (11), 202 (08), 144 (05), 105 (89), 77 (33).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{26}O_3$ [M^+]: 422.18765; found: 422.187400.

Phenyl(3,4,3″,4″-tetramethyl[1,1′;2′,1″]terphenyl-4′-yl)methanone (3h)
Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol%), 3,4-dimethylphenylboronic acid (159 mg, 1.06 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **3h** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 110 °C; yield: 96 mg (58%).

IR (KBr): 3044, 3020, 2990, 2838 (w), 1716 (s), 1656, 1594 (m), 1492, 1450, 1432, 1396, 1318, 1270 (m), 1172, 1118, 1072, 1050, 945, 930 (m), 841, 821, 796, 746 (s), 692, 644, 575, 525 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.03, 2.05, 2.06, 2.08 (s, 12 H, 4 CH_3), 6.71–6.83 (m, 4 H, ArH), 6.90 (d, *J* = 6.8 Hz, 2 H, ArH), 7.30–7.41 (m, 5 H, ArH), 7.64, 7.66 (dd, *J* = 1.8, 7.9 Hz, 1 H, ArH), 7.72, 7.74 (dd, *J* = 1.9, 4.5 Hz, 2 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 19.4, 19.5, 19.7, 19.8 (4 CH_3), 126.7, 127.3, 128.3, 128.8, 129.2, 130.0, 130.6, 130.8, 130.9, 132.3 (CH_{Ar}), 135.0, 135.4, 136.1, 137.8, 138.2, 140.7, 144.7 (C_{Ar}), 196.4 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 390 (M^+, 100), 375 (04), 313 (15), 285 (04), 270 (18), 239 (08), 148 (05), 105 (42), 77 (13).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{26}O$ [M^+]: 390.19782; found: 390.197714.

Phenyl(4,4′-diethyl[1,1′;2′,1″]terphenyl-4′-yl)methanone (3i)
Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-ethylphenylboronic acid (159 mg, 1.06 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **3i** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless solid; reaction temperature 110 °C; yield: 128 mg (78%); mp 138–140 °C.

IR (KBr): 3046, 3026, 2992, 2834 (w), 1716 (s), 1652, 1596 (m), 1492, 1454, 1432, 1394, 1316, 1276 (m), 1176, 1114, 1072, 1054, 945, 934 (m), 841, 825, 796, 746 (s), 692, 642, 574, 524 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.06–1.13 (m, 6 H, 2 CH_3), 2.45–2.54 (m, 4 H, 2 CH_2), 6.95–7.02 (m, 8 H, ArH), 7.32–7.45 (m, 4 H, ArH), 7.69, 7.71 (dd, *J* = 1.8, 7.9 Hz, 1 H, ArH), 7.72–7.77 (m, 3 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 15.3 (2 CH_3), 28.4, 28.5 (2 CH_2), 127.5, 127.6, 128.3, 128.9, 129.6, 129.7 (CH_{Ar}), 127.9, 128.3 (C_{Ar}), 130.0, 130.7, 132.3, 132.4 (CH_{Ar}), 133.0, 136.6, 137.4, 138.6, 137.1 138.7, 142.7 (C_{Ar}), 196.3 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 390 (M^+, 100), 375 (06), 313 (16), 241 (12), 105 (58), 77 (17).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{26}O$ [M^+]: 390.19782; found: 390.197382.

Phenyl(2,2′-dichloro[1,1′;2′,1″]terphenyl-4′-yl)methanone (3j)
Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), Pd ($PPh_3)_4$ (6 mol%), 2-chlorophenylboronic acid (165 mg, 1.06 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **3j** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 110 °C; yield: 115 mg (68%).

IR (KBr): 3054, 2958, 2842 (w), 1662, 1594 (s), 1558, 1486 (m), 1442, 1428, 1396, 1312, 1276, 1242 (m), 1211 (s), 1160, 1132, 1096, 1024, 983 (m), 873, 816, 792, 761 (s), 692, 672, 571 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 6.96–7.06 (m, 5 H, ArH), 7.20–7.26 (m, 2 H, ArH), 7.39–7.50 (m, 5 H, ArH), 7.80–7.86 (m, 4 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 126.2, 127.2, 128.3, 128.9, 129.1, 129.7, 130.0, 130.1, 130.9, 131.2, 132.5, 132.8 (CH_{Ar}), 133.0, 136.6, 137.4, 138.6, 138.7, 142.7 (C_{Ar}), 196.0 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.4 (CF_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 402 (M^+, 100, ^{35}Cl), 367 (09), 325 (81), 291 (07), 262 (61), 226 (80), 200 (07), 150 (05), 113 (06), 105 (64), 77 (36), 51 (06).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{16}Cl_2O$ [M^+, ^{35}Cl]: 402.05782; found: 402.057942.

4-Benzoyl-3′-methoxybiphenyl-2-yl Trifluoromethanesulfonate (4a)
Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), Pd ($PPh_3)_4$ (3 mol%), 3-methoxyphenylboronic acid (80 mg, 0.53 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **4a** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless viscous oil; reaction temperature 110 °C; yield: 124 mg (68%).

IR (KBr): 3063, 3003, 2940 (w), 1660, 1598 (s), 1580, 1552, 1479 (m), 1447, 1421, 1396, 1317, 1278, 1244 (m), 1204 (s), 1179, 1167, 1047, 1020, 990 (m), 883, 841, 788, 762 (s), 695, 629, 597, 568 cm^{-1} (m).

^1H NMR (250 MHz, $CDCl_3$): δ = 3.76 (s, 3 H, OCH_3), 6.89–7.01 (m, 4 H, ArH), 7.28 (d, *J* = 7.8 Hz, 1 H, ArH), 7.40–7.54 (m, 4 H, ArH), 7.73–7.81 (m, 3 H, ArH).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 55.3 (OCH_3), 114.7, 114.8 (CH_{Ar}), 121.7 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.2, 123.8, 128.6, 129.8, 129.9, 130.0, 131.9, 133.1, 133.6 (CH_{Ar}), 135.9, 136.5, 138.2, 139.2, 146.4, 159.7 (C_{Ar}), 194.0 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.8 (CF_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 436 (M^+, 80), 303 (07), 225 (03), 202 (05), 183 (04), 155 (06), 127 (05), 105 (100), 77 (32).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{15}F_3O_5S$ [M^+]: 436.05868; found: 436.058307.

4-Benzoyl-2′,5′-dimethoxybiphenyl-2-yl Trifluoromethanesulfonate (4b)
Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), Pd ($PPh_3)_4$ (3 mol%), 2,5-dimethoxyphenylboronic acid (96 mg, 0.53 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **4b** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless solid; reaction temperature 110 °C; yield: 140 mg (72%); mp 138–140 °C.

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IR (KBr): 3061, 3005, 2929 (w), 1661, 1590 (s), 1554, 1472 (m), 1446, 1418, 1399, 1317, 1280, 1244 (m), 1204 (s), 1169, 1137, 1087, 1033, 985 (m), 880, 844, 794, 766 (s), 699, 671, 587 cm^{-1} (m).

^1H NMR (250 MHz, $CDCl_3$): δ = 3.69 (s, 6 H, 2 OCH_3), 6.61 (d, *J* = 8.4 Hz, 1 H, ArH), 7.18 (s, 1 H, ArH), 7.28–7.38 (m, 2 H, ArH), 7.42–7.56 (m, 3 H, ArH), 7.70–7.84 (m, 4 H, ArH).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 55.8 (2 OCH_3), 103.8, 104.0, 121.1 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.7, 128.3, 128.4, 129.0, 130.0, 130.1, 131.0, 132.8, 133.8 (CH_{Ar}), 136.1, 136.8, 137.1, 137.9, 148.0, 157.7 (C_{Ar}), 194.3 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –74.6 (CF_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 466 (M^+, 100), 333 (28), 302 (24), 225 (32), 197 (04), 105 (84), 77 (28).

HRMS (EI): *m*/*z* calcd for $C_{22}H_{17}F_3O_6S$ [M^+]: 466.06925; found: 466.069859.

4-Benzoyl-4′-methylbiphenyl-2-yl Trifluoromethanesulfonate (4c)

Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), Pd (PPh_3)$_4$ (3 mol%), 4-methoxyphenylboronic acid (80 mg, 0.53 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **4c** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a red viscous oil; reaction temperature 110 °C; yield: 112 mg (64%).

IR (KBr): 3060, 3027, 2922 (w), 1660, 1597 (s), 1549, 1484 (m), 1446, 1421, 1317, 1277, 1244 (m), 1204 (s), 1167, 1135, 1098, 1037, 985 (m), 876, 814, 788, 762 (s), 697, 669, 573 cm^{-1} (m).

^1H NMR (250 MHz, $CDCl_3$): δ = 2.33 (s, 3 H, OCH_3), 7.19 (d, *J* = 7.8 Hz, 3 H, ArH), 7.34 (d, *J* = 8.2 Hz, 1 H, ArH), 7.40–7.55 (m, 5 H, ArH), 7.72–7.77 (m, 3 H, ArH).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.3 (CH_3), 121.1 (q, $J_{F,C}$ = 321 Hz, CF_3), 123.8, 128.5, 129.1, 129.4, 129.9, 130.0, 131.9, 133.0 (CH_{Ar}), 137.6, 138.7, 139.1, 139.5, 146.5, 149.2 (C_{Ar}), 194.1 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.8 (CF_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 420 (M^+, 59), 209 (04), 181 (04), 139 (06), 105 (100), 77 (29).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{15}F_3O_4S$ [M^+]: 420.06377; found: 420.063160.

4-Benzoyl-3′,4′,5′-trimethoxybiphenyl-2-yl Trifluoromethanesulfonate (4d)

Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), Pd (PPh_3)$_4$ (3 mol%), 3,4,5-trimethoxyphenylboronic acid (112 mg, 0.53 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **4d** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a yellow solid; reaction temperature 110 °C; yield: 159 mg (76%); mp 152–154 °C.

IR (KBr): 3065, 2999, 2936 (w), 1660, 1609 (s), 1584, 1514, 1488 (m), 1463, 1418, 1393, 1317, 1291, 1278 (m), 1241 (s), 1170, 1104, 1063, 1001, 978 (m), 889, 831, 790, 745 (s), 675, 630, 598, 569 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 6 H, 2 OCH_3), 3.83 (s, 3 H, OCH_3), 6.62 (s, 2 H, ArH), 7.39–7.47 (m, 3 H, ArH), 7.56 (s, 1 H, ArH), 7.68–7.78 (m, 3 H, ArH), 7.88 (d, *J* = 6.4 Hz, 1 H, ArH).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 56.2 (2 OCH_3), 61.0 (OCH_3), 106.8 (CH_{Ar}), 120 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.0, 128.5, 130.0, 130.4, 133.1, 133.3 (CH_{Ar}), 135.8, 136.7, 137.7, 138.6, 149.0, 153.3 (C_{Ar}), 194.8 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.8 (CF_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 496 (M^+, 92), 363 (26), 332 (100), 317 (17), 255 (12), 227 (07), 185 (05), 105 (57), 77 (19).

HRMS (EI): *m*/*z* calcd for $C_{23}H_{19}F_3O_7S$ [M^+]: 496.07981; found: 496.079887.

4-Benzoyl-4′-*tert*-butylbiphenyl-2-yl Trifluoromethanesulfonate (4e)

Starting from **2** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), Pd (PPh_3)$_4$ (3 mol%), 4-*tert*-butylphenylboronic acid (94 mg, 0.53 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **4e** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless viscous oil; reaction temperature 110 °C; yield: 136 mg (70%).

IR (KBr): 3060, 2904, 2868 (w), 1713, 1610, 1579, 1518, 1462, 1446 (w), 1392, 1317, 1278, 1268, 1178, 1117, 1027, 1016, 1001, 973, 954, 854, 765 (m), 734, 698, 605 (w), 565 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.19, 1.21 (s, 6 H, 2 CH_3), 1.28 (s, 3 H, CH_3), 6.97–7.00 (dd, *J* = 1.80, 8.90 Hz, 1 H, ArH), 7.12–7.15 (dd, *J* = 2.1, 8.4 Hz, 1 H, ArH), 7.34–7.45 (m, 3 H, ArH), 7.48–7.54 (m, 3 H, ArH), 7.72–7.80 (m, 4 H, ArH).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 31.2 (2 CH_3), 31.3 (CH_3), 34.7 (C), 120 (q, $J_{F,C}$ = 320 Hz, CF_3), 123.9, 124.8, 125.6, 128.3, 129.0, 129.4, 130.0, 131.9, 133.0 (CH_{Ar}), 136.6, 137.9, 138.0, 141.0, 146.6, 152.3 (C_{Ar}), 194.8 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.8 (CF_3).

GC-MS (EI, 70 eV): *m*/*z* (%) = 462 (M^+, 39), 447 (100), 299 (35), 273 (07), 209 (05), 165 (06), 105 (30), 77 (15), 57 (09).

HRMS (EI): *m*/*z* calcd for $C_{24}H_{21}F_3O_4S$ [M^+]: 462.11072; found: 462.110624.

(3-Methoxy-4″-vinyl[1,1′;2′,1″]terphenyl-4′-yl)phenylmethanone (5a)

Starting from **4a** (70 mg, 0.16 mmol), K_3PO_4 (101 mg, 0.48 mmol), Pd (PPh_3)$_4$ (3 mol%), 4-vinylphenylboronic acid (29 mg, 0.20 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **5a** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless viscous oil; reaction temperature 110 °C; yield: 42 mg (68%).

IR (KBr): 3055, 3003, 2953, 2833 (w), 1655 (s), 1628 (w), 1595 (s), 1513 (w), 1494, 1464, 1427, 1389, 1294 (m), 1248 (s), 1177, 1114, 1074, 1018, 989, 947 (m), 869, 842, 783, 765 (s), 696, 638, 564, 540 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.53 (s, 3 H, OCH_3), 5.10 (dd, *J* = 1.4, 9.8 Hz, 1 H, CH_2), 5.58 (dd, *J* = 1.2, 8.1 Hz, 1 H, CH_2), 6.52 (dd, *J* = 1.3, 8.2 Hz, 1 H, CH), 6.52–6.72 (m, 3 H, ArH), 7.00–7.20 (m, 5 H, ArH), 7.37–7.50 (m, 4 H, ArH), 7.72–7.79 (m, 4 H, ArH).

^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 55.1 (OCH_3), 113.2 (CH_{Ar}), 113.9 (CH_{2vinyl}), 113.2, 115.1, 122.1, 125.9, 128.3, 129.1, 129.2, 129.9, 130.0, 132.1, 132.4, 136.3 ($CH_{Ar,}$ CH_{vinyl}), 136.7, 137.6, 140.0, 140.1, 140.3, 141.8, 144.4, 159.2 (C_{Ar}), 196.2 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 390 (M^+, 100), 349 (03), 313 (15), 285 (04), 239 (09), 105 (33), 77 (16).

HRMS (EI): *m*/*z* calcd for $C_{28}H_{22}O_2$ [M^+]: 390.16143; found: 390.161704.

(4-Methyl-4″-vinyl[1,1′;2′,1″]terphenyl-4′-yl)phenylmethanone (5b)

Starting from **4c** (70 mg, 0.16 mmol), K_3PO_4 (101 mg, 0.48 mmol), Pd (PPh_3)$_4$ (3 mol%), 4-vinylphenylboronic acid (29 mg, 0.20 mmol) and 1,4-dioxane (5 mL/mmol of triflate), **5b** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless solid; reaction temperature 110 °C; yield: 48 mg (78%); mp 148–150 °C.

IR (KBr): 3052, 3002, 2952, 2830 (w), 1654 (s), 1630 (w), 1596 (s), 1512 (w), 1496, 1462, 1428, 1390, 1296 (m), 1246 (s), 1178, 1116, 1072, 1016, 987, 945 (m), 869, 842, 781, 765 (s), 696, 634, 564, 542 cm^{-1} (m).

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^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 3 H, CH_3), 5.15 (d, *J* = 10.8 Hz, 1 H, CH_2), 5.66 (d, *J* = 9.6 Hz, 1 H, CH_2), 6.63 (dd, *J* = 1.3, 8.2 Hz, 1 H, CH), 6.96–7.00 (m, 2 H, ArH), 7.16–7.21 (m, 3 H, ArH), 7.41–7.51 (m, 6 H, ArH), 7.72–7.80 (m, 5 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 21.1 (CH_3), 113.8 (CH_{2vinyl}), 125.9, 128.3, 128.8, 129.1, 129.5, 130.0, 130.6, 132.2, 132.4, 136.4 ($CH_{Ar,}$ CH_{vinyl}), 136.9, 137.5, 137.8, 140.1, 140.3, 144.6, 144.4, 159.2 (C_{Ar}), 196.2 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 374 (M^+, 100), 359 (04), 297 (19), 253 (10), 148 (04), 105 (24), 77 (12).

HRMS (EI): *m*/*z* calcd for $C_{28}H_{22}O$ [M^+]: 374.16652; found: 374.166329.

Phenyl(3,4,5-trimethoxy-4″-vinyl[1,1′;2′,1″]terphenyl-4′-yl)methanone (5c)

Starting from **4d** (70 mg, 0.14 mmol), K_3PO_4 (89 mg, 0.42 mmol), Pd (PPh_3)$_4$ (3 mol%), 4-vinylphenylboronic acid (26 mg, 0.18 mmol), and 1,4-dioxane (5 mL/mmol of triflate), **5c** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless viscous oil; reaction temperature 110 °C; yield: 40 mg (64%).

IR (KBr): 3054, 3002, 2952, 2830 (w), 1654 (s), 1630 (w), 1596 (s), 1512 (w), 1496, 1462, 1428, 1390, 1296 (m), 1246 (s), 1178, 1116, 1072, 1016, 987, 945 (m), 869, 842, 781, 765 (s), 696, 634, 564, 542 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.54 (s, 6 H, 2 OCH_3), 3.75 (s, 3 H, OCH_3), 5.19 (dd, *J* = 1.3, 10.8 Hz, 1 H, CH_2), 5.69 (dd, *J* = 2.1, 9.6 Hz, 1 H, CH_2), 6.63 (dd, *J* = 1.3, 8.2 Hz, 1 H, CH), 7.09 (d, *J* = 8.2 Hz, 1 H, ArH), 7.24–7.36 (m, 4 H, ArH), 7.40–7.48 (m, 3 H, ArH), 7.50–7.65 (m, 3 H, ArH), 7.71 (dd, *J* = 1.8, 7.9 Hz, 1 H, ArH), 7.80–7.86 (m, 2 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 55.9 (2 OCH_3), 60.9 (OCH_3), 114.2 (CH_{2vinyl}), 125.9, 128.0, 128.3, 129.6, 130.0, 131.6, 135.0, 135.8, 136.4 ($CH_{Ar,}$ CH_{vinyl}), 136.9, 137.5, 137.8, 140.1, 140.3, 144.6, 144.4, 152.7 (C_{Ar}), 196.2 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 450 (M^+, 100), 435 (20), 332 (05), 207 (07), 105 (33), 77 (20).

HRMS (EI): *m*/*z* calcd for $C_{30}H_{26}O_4$ [M^+]: 450.18256; found: 450.182820.

(4-*tert*-Butyl-4″-vinyl[1,1′;2′,1″]terphenyl-4′-yl)phenylmethanone (5d)

Starting from **4e** (70 mg, 0.15 mmol), K_3PO_4 (95 mg, 0.45 mmol), Pd (PPh_3)$_4$ (3 mol%), 4-vinylphenylboronic acid (28 mg, 0.19 mmol) and 1,4-dioxane (5 mL/mmol of triflate), **5d** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless solid; reaction temperature 110 °C; yield: 39 mg (62%); mp 138–140 °C.

IR (KBr): 3052, 3006, 2956, 2832 (w), 1656 (s), 1632 (w), 1598 (s), 1516 (w), 1496, 1464, 1432, 1392, 1298 (m), 1246 (s), 1178, 1118, 1072, 1014, 985, 943 (m), 869, 842, 785, 765 (s), 694, 634, 562, 541 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.21 (s, 3 H, CH_3), 1.22 (s, 6 H, 2 CH_3), 5.13 (dd, *J* = 1.2, 10.6 Hz, 1 H, CH_2), 5.61 (dd, *J* = 2.4, 9.5 Hz, 1 H, CH_2), 6.55 (dd, *J* = 1.3, 8.2 Hz, 1 H, CH), 7.00–7.10 (m, 4 H, ArH), 7.15–7.23 (m, 4 H, ArH), 7.40–7.54 (m, 4 H, ArH), 7.72–7.81 (m, 4 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 31.3 (2 CH_3), 34.5 (CH_3), 113.8 (CH_{2vinyl}), 125.0, 125.8, 128.3, 129.1, 129.3, 129.6, 130.0, 130.7, 132.2, 132.3, 136.4 ($CH_{Ar,}$ CH_{vinyl}), 136.9, 137.1, 137.3, 137.7, 140.1, 140.2, 144.5, 150.2 (C_{Ar}), 196.2 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 416 (M^+, 87), 401 (100), 252 (06), 105 (53), 77 (23).

HRMS (EI): *m*/*z* calcd for $C_{31}H_{28}O$ [M^+]: 416.21347; found: 416.213534.

Sonogashira Cross-Coupling Reactions; General Procedure

In a pressure tube, a suspension of $Pd(PPh_3)_2Cl_2$, aromatic triflate, alkyne, $(Bu)_4NI$, CuI, Et_3N, and for the synthesis of compounds **13** and **14**, also Bu_4NI in DMF, was purged with argon and stirred at first at 20 °C for 10 min. Stirring was continued at the given temperature for the given time. The reaction mixture was cooled to 20 °C, poured into H_2O (25 mL) and CH_2Cl_2 (25 mL), and the organic and the aqueous layers were separated. The latter was extracted with CH_2Cl_2 (3 × 25 mL). The combined organic layers were washed with H_2O (3 × 20 mL), dried (Na_2SO_4), concentrated in vacuo, and the residue was purified by chromatography (flash silica gel, heptanes–EtOAc).

{3,4-Bis[(4-*tert*-butylphenyl)ethynyl]phenyl}phenylmethanone (6a)

Starting from **2** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (6 mol%), anhyd CuI (10 mol%), Et_3N (0.086 mL, 0.62 mmol), 4-*tert*-butylphenylacetylene (158 mg, 1.0 mmol) and DMF (5 mL per 1 mmol of **2**), **6a** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 110 °C; reaction time 4 h; yield: 192 mg (78%).

IR (KBr): 3083, 3060, 2959, 2866, 2211 (w), 1714 (s), 1659 (s), 1591, 1506, 1462, 1406, 1363, 1322 (m), 1268 (s), 1201, 1163, 1104, 1084, 982, 968, 882, 872, 792, 742, 651, 615, 528 cm^{-1} (w).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 1.26, 1.27 (s, 18 H, 6 CH_3), 7.16 (s, 1 H, ArH), 7.28–7.33 (m, 3 H, ArH), 7.41–7.48 (m, 3 H, ArH), 7.51–7.59 (m, 3 H, ArH), 7.64–7.75 (m, 5 H, ArH), 7.88 (d, *J* = 1.65 Hz, 1 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 30.9, 31.1 (6 CH_3), 87.0, 87.4, 94.6, 96.8 (C), 119.8, 119.9 (C_{Ar}), 125.4, 125.5 (CH_{Ar}), 126.0 (C_{Ar}), 128.4, 128.9 (CH_{Ar}), 129.7 (C_{Ar}), 129.9, 131.4, 131.6, 131.7, 132.6, 133.3 (CH_{Ar}), 136.4, 137.2, 152.0, 152.2 (C_{Ar}), 195.3 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 494 (M^+, 100), 479 (50), 262 (04), 232 (19), 204 (05), 105 (18), 77 (04).

HRMS (EI): *m*/*z* calcd for $C_{37}H_{34}O$ [M^+]: 494.26042; found: 494.260148.

[3,4-Bis(phenylethynyl)phenyl]phenylmethanone (6b)

Starting from **2** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (6 mol%), anhyd CuI (10 mol%), Et_3N (0.086 mL, 0.62 mmol), phenylacetylene (102 mg, 1.0 mmol), and DMF (5 mL per 1 mmol of **2**), **6b** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a light yellow oil; reaction temperature 110 °C; reaction time 4 h; yield: 103 mg (54%).

IR (KBr): 3081, 3062, 2958, 2864, 2210 (w), 1716 (s), 1658 (s), 1592, 1508, 1464, 1408, 1362, 1320 (m), 1266 (s), 1203, 1161, 1106, 1082, 981, 967, 881, 873, 792, 741, 653, 613, 523 cm^{-1} (w).

^{1}H NMR (250 MHz, $CDCl_3$): δ = 7.23–7.27 (m, 4 H, ArH), 7.37 (s, 1 H, ArH), 7.40–7.54 (m, 6 H, ArH), 7.57 (s, 1 H, ArH), 7.62 (d, *J* = 1.72 Hz, 1 H, ArH), 7.66 (d, *J* = 1.72 Hz, 1 H, ArH), 7.69–7.73 (m, 3 H, ArH), 7.88 (d, *J* = 1.62 Hz, 1 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 87.5, 87.9, 94.5, 96.6 (C), 120.4, 122.8 (C_{Ar}), 125.3, 128.2, 128.4, 128.5, 128.7, 128.9, 129.1, 129.9, 131.7, 131.8, 132.7, 133.3 (CH_{Ar}), 133.5, 136.7, 137.1 (C_{Ar}), 195.2 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 382 (M^+, 100), 352 (18), 305 (06), 276 (28), 250 (04), 176 (08), 77 (11).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{18}O$ [M^+]: 382.13522; found: 382.135497.

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{3,4-Bis[(3-methoxyphenyl)ethynyl]phenyl}phenylmethanone (6c)

Starting from **2** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (6 mol%), anhyd CuI (10 mol%), Et_3N (0.086 mL, 0.62 mmol), 3-methoxyphenylacetylene (132 mg, 1.0 mmol), and DMF (5 mL per 1 mmol of **2**), **6c** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a viscous oil; reaction temperature 110 °C; reaction time 4 h; yield: 142 mg (64%).

IR (KBr): 3061 (w), 2998, 2832 (m), 2203 (w), 1656 (m), 1591 (s), 1540, 1488, 1446, 1402, 1317 (m), 1279, 1219 (s), 1179, 1127, 1091, 985, 972, 869, 848 (m), 777, 710, 681 (s), 603, 562 cm^{-1} (w).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.68, 3.69 (s, 6 H, 2 OCH_3), 6.81–6.87 (m, 2 H, ArH), 7.00–7.06 (m, 2 H, ArH), 7.08–7.20 (m, 4 H, ArH), 7.41–7.46 (m, 2 H, ArH), 7.52–7.60 (m, 2 H, ArH), 7.66–7.69 (dd, *J* = 1.74, 8.07 Hz, 1 H, ArH), 7.72–7.75 (m, 2 H, ArH), 7.90 (d, *J* = 1.71 Hz, 1 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 55.2 (2 OCH_3), 87.3, 87.6, 94.4, 96.5 (4C), 115.6, 115.8, 116.2, 116.3 (CH_{Ar}), 123.7, 123.8 (C_{Ar}), 124.2, 124.3 (CH_{Ar}), 126.0 (C_{Ar}), 128.4, 129.2, 129.4, 129.5 (CH_{Ar}), 129.6 (C_{Ar}), 129.9, 131.6, 132.7, 133.2 (CH_{Ar}), 136.7, 137.1, 159.4 (C_{Ar}), 195.2 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 442 (M^+, 100), 427 (05), 399 (12), 365 (18), 337 (07), 250 (12), 105 (37), 77 (15), 57 (05), 44 (41).

HRMS (EI): *m*/*z* calcd for $C_{31}H_{22}O_3$ [M^+]: 442.15689; found: 442.156582.

[3,4-Bis(*p*-tolylethynyl)phenyl]phenylmethanone (6d)

Starting from **2** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (6 mol%), anhyd CuI (10 mol%), Et_3N (0.086 mL, 0.62 mmol), 4-methylphenylacetylene (116 mg, 1.0 mmol), and DMF (5 mL per 1 mmol of **2**), **6d** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a red viscous oil; reaction temperature 110 °C; reaction time 4 h; yield: 135 mg (66%).

IR (KBr): 3058, 3025, 2916, 2858, 2204 (w), 1651, 1587, 1514, 1444, 1404, 1317 (m), 1267, 1246 (m), 1177, 1104, 1040 (w), 981, 913, 871, 834, 787, 664 (m), 612, 586, 560 cm^{-1} (w).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.28, 2.29 (s, 6 H, 2 CH_3), 7.00–7.10 (m, 4 H, ArH), 7.36–7.44 (m, 6 H, ArH), 7.50–7.57 (m, 2 H, ArH), 7.63 (dd, *J* = 1.77 8.10 Hz, 1 H, ArH), 7.70–7.74 (m, 2 H, ArH), 7.87 (d, *J* = 1.71 Hz, 1 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 21.2, 21.5 (2 CH_3), 87.0, 87.4, 94.7, 96.9 (C), 123.8, 125.2, 126.0, 126.6 (C_{Ar}), 128.4, 128.9, 129.2, 129.3, 129.5, 129.9, 131.6, 131.7, 132.6, 133.2 (CH_{Ar}), 136.4, 137.2, 138.9, 139.2 (C_{Ar}), 195.3 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 410 (M^+, 100), 409 (33), 408 (15), 395 (29), 393 (12), 289 (16), 181 (10), 77 (10).

HRMS (EI): *m*/*z* calcd for $C_{31}H_{22}O$ [M^+]: 410.16652; found: 410.166081.

{3,4-Bis[(4-fluorophenyl)ethynyl]phenyl}phenylmethanone (6e)

Starting from **2** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (6 mol%), anhyd CuI (10 mol%), Et_3N (0.086 mL, 0.62 mmol), 4-flourophenylacetylene (120 mg, 1.0 mmol), and DMF (5 mL per 1 mmol of **2**), **6e** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a brown oil; reaction temperature 110 °C; reaction time 4 h; yield: 126 mg (60%).

IR (KBr): 3066, 2918, 2859, 2207, 1681 (w), 1648 (s), 1589, 1547, 1486, 1434, 1405, 1278, 1210, 1138, 1114, 1089, 1073, 937, 918, 867, 777, 695 (m), 605, 596, 546 cm^{-1} (w).

^1H NMR (250 MHz, $CDCl_3$): δ = 6.99–7.04 (m, 2 H, ArH), 7.14–7.23 (m, 4 H, ArH), 7.25–7.30 (m, 3 H, ArH), 7.42–7.47 (m, 2 H, ArH), 7.53–7.61 (m, 2 H, ArH), 7.66 (d, *J* = 1.47 Hz, 1 H, ArH), 7.70–7.75 (m, 1 H, ArH), 7.90 (d, *J* = 1.12 Hz, 1 H, ArH)).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 86.1, 86.9, 92.5, 96.9 (C), 120.4, 122.8 (C_{Ar}), 125.1, 127.2, 127.9, 128.2, 128.7, 129.1, 129.9, 131.7, 132.7, 133.3 (CH_{Ar}), 134.0, 135.0, 136.7, 137.0, 137.1 (C_{Ar}), 195.2 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 418 (M^+, 100), 389 (05), 341 (34), 312 (40), 293 (07), 216 (05), 187 (05), 147 (06), 105 (30), 77 (12).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{16}F_2O$ [M^+]: 418.11637; found: 418.116424.

[3,4-Bis(*m*-tolylethynyl)phenyl]phenylmethanone (6f)

Starting from **2** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (6 mol%), anhyd CuI (10 mol%), Et_3N (0.086 mL, 0.62 mmol), 3-methylphenylacetylene (116 mg, 1.0 mmol), and DMF (5 mL per 1 mmol of **2**), **6f** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a yellow oil, reaction temperature 110 °C; reaction time 4 h; yield: 120 mg (58%).

IR (KBr): 3056, 3021, 2914, 2857, 2206 (w), 1653, 1585, 1513, 1441, 1402, 1315 (m), 1265, 1245 (m), 1177, 1104, 1040 (w), 981, 913, 871, 834, 787, 664 (m), 612, 586, 560 cm^{-1} (w).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.17, 2.18 (s, 6 H, 2 CH_3), 7.02–7.10 (m, 4 H, ArH), 7.35–7.45 (m, 6 H, ArH), 7.52–7.59 (m, 2 H, ArH), 7.62 (dd, *J* = 1.77 8.10 Hz, 1 H, ArH), 7.68–7.72 (m, 2 H, ArH), 7.85 (d, *J* = 1.71 Hz, 1 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 21.2, 21.5 (2 CH_3), 87.1, 87.9, 94.8, 96.7 (C), 123.6, 125.3, 126.0, 126.8 (C_{Ar}), 128.3, 128.4, 128.8, 128.9, 129.1, 129.7, 129.9, 131.5, 132.4, 132.5, 132.7, 133.1, 133.5 (CH_{Ar}), 136.2, 137.6, 138.5, 139.6 (C_{Ar}), 195.1 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 410 (M^+, 100), 333 (23), 305 (08), 289 (34), 207 (07), 105 (15), 77 (15).

HRMS (EI): *m*/*z* calcd for $C_{31}H_{22}O$ [M^+]: 410.16652; found: 410.166081.

3-Trifluorosulfonyloxy-4-methylphenylaceylenebenzophenone (7)

Starting from **2** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (6 mol%), anhyd CuI (10 mol%), Et_3N (0.086 mL, 0.62 mmol), 4-methylphenylacetylene (58 mg, 0.50 mmol), and DMF (5 mL per 1 mmol of **2**), **7** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a light brown viscous oil; reaction temperature 90 °C; reaction time 8 h; yield: 156 mg (70%).

IR (KBr): 3305, 3062, 2922, 2867, 1909 (w), 1659, 1599 (m), 1515, 1446 (w), 1423 (s), 1319 (m), 1290, 1244 (m), 1171, 1076, 976 (m), 883, 844, 815 (s), 754, 733, 639, 532 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3 H, CH_3), 7.12 (d, *J* = 7.92 Hz, 2 H, ArH), 7.42–7.47 (m, 4 H, ArH), 7.55 (d, *J* = 7.13 Hz, 1 H, ArH), 7.63–7.67 (m, 2 H, ArH), 7.70–7.74 (m, 3 H, ArH).

^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.6 (CH_3), 81.7, 99.9 (C), 118.6 (C_{Ar}), 122.6 (q, $J_{C,F}$ = 320.0 Hz, CF_3), 123.1, 128.6, 129.3, 129.4, 129.9, 131.9, 133.1, 133.3 (CH_{Ar}), 136.4, 138.0, 140.0, 149.3 (C_{Ar}), 193.7 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 444 (M^+, 100), 311 (46), 255 (22), 176 (08), 115 (05), 105 (39), 77 (28), 51 (05).

HRMS (EI): *m*/*z* calcd for $C_{23}H_{15}F_3O_4S$ [M^+]: 444.06377; found: 444.063860.

[4′-Methyl-6-(*p*-tolylethynyl)biphenyl-3-yl]phenylmethanone (8)

Starting from **7** (100 mg, 0.22 mmol), K_3PO_4 (69 mg, 0.33 mmol), Pd (PPh_3)$_4$ (3 mol%), 4-methylphenylboronic acid (38 mg, 0.28 mmol), and 1,4-dioxane (5 mL/mmol of **7**), **8** was isolated by chro-

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matography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; yield: 55 mg (64%).

IR (KBr): 3078, 3057, 3028, 2916, 2858, 2209 (w), 1651, 1591 (s), 1512, 1442, 1412, 1394 (w), 1267, 1245 (m), 1182, 1143, 1075, 1040, 1016, 999 (w), 951 (m), 909, 857, 838 (w), 748, 697 (m), 610, 586 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.26, 2.33 (s, 6 H, 2 CH_3), 7.05 (d, *J* = 7.89 Hz, 2 H, ArH), 7.16–7.20 (m, 4 H, ArH), 7.40–7.52 (m, 5 H, ArH), 7.60–7.64 (m, 2 H, ArH), 7.73 (d, *J* = 1.53 Hz, 1 H, ArH), 7.76–7.80 (m, 2 H, ArH).

^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 21.2, 21.5 (2 CH_3), 88.4, 95.4 (2 C), 125.9 (C_{Ar}), 128.2, 128.3, 128.7, 129.1, 129.2, 129.9, 130.9, 131.4, 132.4, 132.7 (CH_{Ar}), 132.7, 136.7, 136.8, 137.5, 137.6, 138.8, 143.5 (C_{Ar}), 195.9 (C=O).

GC-MS (EI, 70 eV): *m*/*z* (%) = 386 (M^+, 100), 371 (05), 309 (27), 281 (12), 266 (36), 239 (05), 132 (05), 105 (39), 77 (22).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{22}O$ [M^+]: 386.16652; found: 386.166115.

[2,4-Bis(phenyl)phenyl]phenylmethanone (11a)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), phenylboronic acid (146 mg, 1.2 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **11a** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 110 °C; yield: 125 mg (82%).

IR (KBr): 3050, 3026, 2923, 2853 (w), 1657 (s), 1595 (m), 1552, 1496 (w), 1441, 1393, 1315 (m), 1279 (s), 1234, 1158, 1132, 1073, 1025, 960, 936, 922, 902, 843, 800, 773 (m), 760, 742, 690 (s), 638, 584 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.06–7.09 (m, 2 H, ArH), 7.11–7.15 (m, 2 H, ArH), 7.17–7.23 (m, 3 H, ArH), 7.27–7.33 (m, 3 H, ArH), 7.35–7.40 (m, 2 H, ArH), 7.49–7.51 (m, 1 H, ArH), 7.56–7.61 (m, 5 H, ArH).

^{13}C NMR (75.4 MHz, $CDCl_3$): δ = 125.7, 127.3, 127.4, 128.0, 128.1, 128.3, 128.9, 129.0, 129.1, 129.6, 129.9, 132.8 (CH_{Ar}), 137.5, 137.7, 140.1, 140.2, 141.9, 143.3 (C_{Ar}), 198.5 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 334 (M^+, 100), 333 (73), 258 (18), 257 (85), 229 (14), 228 (35), 227 (15), 226 (21), 105 (12), 77 (18).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{18}O$ [$M]^+$: 334.13522; found: 334.135618.

[2,4-Bis(*p*-tolyl)phenyl]phenylmethanone (11b)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-tolylboronic acid (163 mg, 1.2 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **11b** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 110 °C; yield: 139 mg (84%).

IR (KBr): 3079, 3032, 1661, 1596, 1490, 1445, 1426, 1314, 1283, 1242, 1178, 1138, 1069, 999, 914, 835, 751 (s), 698 (m), 785 (s) 621 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.16 (s, 3 H, CH_3), 2.33 (s, 3 H, CH_3), 6.93–6.96 (m, 2 H, ArH), 7.04–7.13 (m, 2 H, ArH), 7.19–7.25 (m, 4 H, ArH), 7.27–7.37 (m, 2 H, ArH), 7.45–7.51 (m, 3 H, ArH), 7.53–7.65 (m, 3 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.1 (CH_3), 21.2 (CH_3), 127.1, 128.1, 128.6, 128.7, 128.8, 129.0, 129.5, 129.6, 129.9, 130.0 (CH_{Ar}), 136.3, 137.5, 137.7, 140.1, 140.2, 141.9, 143.3 (C_{Ar}), 198.5 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 362 (M^+, 100), 333 (73), 258 (18), 257 (85), 229 (14), 228 (35), 227 (15), 226 (21), 105 (12), 77 (18).

HRMS (EI): *m*/*z* calcd for $C_{27}H_{22}O$ [$M]^+$: 362.13522; found: 362.134518.

[2,4-Bis(3-chlorophenyl)phenyl]phenylmethanone (11c)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 3-chlorophenylboronic acid (187 mg, 1.2 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **11c** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a white solid; reaction temperature 110 °C; yield: 138 mg (75%).

IR (KBr): 3080, 3034 (w), 1665 (s), 1595, 1545, 1494, 1443, 1430, 1316, 1285, 1244, 1180, 1135, 1071, 1002, 915, 837 (m), 753 (s), 700 (m), 787 (s), 671, 667, 624, 530 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.06–7.08 (m, 2 H, ArH), 7.23–7.40 (m, 6 H, ArH), 7.45–7.53 (m, 2 H, ArH), 7.54–7.61 (m, 6 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 125.4, 126.1, 127.2, 127.4, 127.6, 128.1, 128.2, 128.4, 128.7, 128.9, 129.5, 129.7, 130.2, 133.0 (CH_{Ar}), 133.0, 134.2, 134.9, 137.2, 137.7, 138.1, 140.5, 141.6, 142.0 (C_{Ar}), 197.9 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 404 ([M, $^{37}Cl_2$, 63]$^+$), 402 ([M, $^{35}Cl_2$, 100]$^+$), 401 (49), 369 (12), 368 (10), 367 (36), 329 (10), 328 (11), 327 (55), 326 (20), 325 (85), 290 (12), 264 (14), 263 (10), 262 (44), 227 (13), 226 (54), 225 (10), 224 (14), 184 (20), 105 (39), 77 (33).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{16}Cl_2O$ [(M^+, ^{35}Cl, ^{37}Cl)]$^+$: 402.05727; found: 402.056201.

[2,4-Bis(4-methoxyphenyl)phenyl]phenylmethanone (11d)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-methoxyphenylboronic acid (182 mg, 1.2 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **11d** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 110 °C; yield: 128 mg (71%).

IR (KBr): 3061, 2937 (w), 2842 (m), 1657, 1601 (s), 1526, 1490, 1443, 1425 (m), 1396 (s), 1296, 1246, 1211, 1139, 1062, 971, 910 (m), 832, 694 (s), 611, 539 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.65 (s, 3 H, OCH_3), 3.80 (s, 3 H, OCH_3), 6.66–6.69 (m, 1 H, ArH), 6.92–6.97 (m, 2 H, ArH), 7.13–7.18 (m, 2 H, ArH), 7.41–7.53 (m, 9 H, ArH), 7.75–7.78 (m, 2 H, ArH).

^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 55.3, 55.4 (OCH_3), 114.3, 114.6, 12.7, 128.0, 128.3, 129.4, 128.5, 130.1, 130.9, 133.6 (CH_{Ar}), 136.7, 137.5, 141.4, 142.7, 145.9, 147.4, 158.9, 159.6 (C_{Ar}), 197.8 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 394 (M^+, 100), 333 (73), 258 (18), 257 (85), 229 (14), 228 (35), 227 (15), 226 (21), 105 (12), 77 (18).

HRMS (EI): *m*/*z* calcd for $C_{25}H_{18}O$ [$M]^+$: 394.04522; found: 394.044518.

4-Benzoyl-4′-methylbiphenyl-3-yl Trifluoromethanesulfonate (12a)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-tolylboronic acid (81 mg, 0.6 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **12a** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; yield: 141 mg 73%).

IR (KBr): 3026, 2950, 2857 (w), 1657, 1615, 1598 (m), 1548, 1448 (w), 1422 (s), 1286, 1242 (m), 1206, 1136 (s), 1085 (m), 1018 (w), 945, 899 (m), 814 (s), 746, 703, 622, 604, 540 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.33 (s, 3 H, CH_3), 7.20–7.23 (m, 2 H, ArH), 7.39–7.43 (m, 4 H, ArH), 7.49–7.56 (m, 4 H, ArH), 7.74–7.77 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.2 (CH_3), 120.5 (q, *J* = 321 Hz, CF_3), 120.7, 126.1, 127.0, 128.5, 130.0, 130.1 (CH_{Ar}), 130.3 (C_{Ar}), 131.9, 133.6 (CH_{Ar}), 135.2, 136.7, 139.2, 146.3, 147.4 (C_{Ar}), 192.5 (C=O).

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^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3.

MS (EI, 70 eV): *m*/*z* (%) = 420 (M^+, 100), 343 (36), 287 (23), 210 (10), 105 (32), 77 (17).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{15}F_3O_4S$ $[M]^+$: 420.06377; found: 420.063866.

4-Benzoyl-4′-ethylbiphenyl-3-yl Trifluoromethanesulfonate (12b)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-ethylphenylboronic acid (90 mg, 0.6 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **12b** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; yield: 150 mg (75%).

IR (KBr): 3025, 2961, 2918, 2854 (w), 1655, 1615 (m), 1523, 1448 (w), 1422 (s), 1322, 1285, 1240 (m), 1205, 1137 (s), 1086 (m), 1018, 979 (w), 930, 898 (m), 828 (s), 798, 703, 603, 534 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.20 (t, *J* = 7.6 Hz, 3 H, CH_3), 2.64 (q, *J* = 7.6 Hz, 2 H, CH_2), 7.16–7.27 (m, 2 H, ArH), 7.38–7.47 (m, 4 H, ArH), 7.50–7.60 (m, 4 H, ArH), 7.75–7.78 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.4 (CH_3), 28.6 (CH_2), 118.5 (q, *J* = 319.1 Hz, CF_3), 120.7, 126.1, 127.1, 128.5, 128.8, 130.1 (CH_{Ar}), 131.6 (C_{Ar}), 131.8, 133.6 (CH_{Ar}), 135.4, 136.7, 145.5, 146.3, 147.3 (C_{Ar}), 192.5 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3.

MS (EI, 70 eV): *m*/*z* (%) = 434 (M^+, 100), 419 (10), 357 (31), 301 (16), 105 (33), 77 (16).

HRMS (EI): *m*/*z* calcd for $C_{22}H_{17}F_3O_4S$ $[M]^+$: 434.07942; found: 434.078943.

4-Benzoyl-3′,4′-dimethylbiphenyl-3-yl Trifluoromethanesulfonate (12c)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,4-dimethylphenylboronic acid (90 mg, 0.60 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **12c** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; yield: 135 mg (68%).

IR (KBr): 3022, 2946, 2858, 2659 (w), 1655, 1614, 1598, 1513, 1447 (m), 1421 (s), 1319, 1280, 1242 (m), 1208, 1138 (s), 1084, 953, 862, 822, 742, 701, 651, 607, 572 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.23 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 7.14–7.27 (m, 3 H, ArH), 7.36–7.41 (m, 2 H, ArH), 7.48–7.58 (m, 4 H, ArH), 7.73–7.76 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 19.5 (CH_3), 19.9 (CH_3), 118.5 (q, *J* = 320.5 Hz, CF_3), 120.7, 124.5, 126.1, 128.3, 128.5, 130.1, 130.5, 131.8, 133.6 (CH_{Ar}), 135.6, 136.7, 137.6, 139.0, 146.5, 147.3, 153.8 (C_{Ar}), 192.5 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3.

MS (EI, 70 eV): *m*/*z* (%) = 434 (M^+, 100), 357 (29), 301 (22), 258 (10), 105 (29), 77 (15).

HRMS (EI): *m*/*z* calcd for $C_{22}H_{17}O_4F_3S$ $[M]^+$: 434.07942; found: 434.079871.

4-Benzoyl-3′,5′-dimethylbiphenyl-3-yl Trifluoromethanesulfonate (12d)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,5-dimethylphenylboronic acid (81 mg, 0.6 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **12d** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; yield: 133 mg (67%).

IR (KBr): 3028, 2952, 2859 (w), 1667, 1612, 1597 (m), 1553 (w), 1423 (s), 1389, 1315, 1285, 1246 (m), 1204, 1135 (s), 1069 (m), 1000 (w), 955, 899 (m), 836 (s), 755, 696, 602, 544 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.29 (s, 6 H, CH_3), 6.98 (s, 1 H, ArH), 7.11 (s, 2 H, ArH), 7.34–7.39 (m, 2 H, ArH), 7.48–7.56 (m, 4 H, ArH), 7.72–7.75 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.3 (2 CH_3), 120.6 (q, *J* = 319 Hz, CF_3), 121.0, 125.1, 126.4, 128.5, 130.1 (CH_{Ar}), 130.4 (C_{Ar}), 130.7, 131.8, 133.7 (CH_{Ar}), 136.7, 138.1, 138.9, 146.7, 147.3 (C_{Ar}), 192.5 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3.

MS (EI, 70 eV): *m*/*z* (%) = 434 (M^+, 100), 357 (37), 301 (23), 258 (10), 152 (10), 105 (33), 77 (17).

HRMS (EI): *m*/*z* calcd for $C_{22}H_{17}O_4F_3S$ $[M]^+$: 434.07942; found: 434.079065.

4-Benzoyl-4′-*tert*-butylbiphenyl-3-yl Trifluoromethanesulfonate (12e)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-*tert*-butylphenylboronic acid (106 mg, 0.60 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **12e** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; yield: 161 mg (76%).

IR (KBr): 3060, 2959, 2866 (w), 1660, 1614, 1596 (m), 1554 (w), 1462, 1415, 1318, 1241 (m), 1207, 1137 (s), 1089, 948, 895 (m), 810 (s), 696, 603, 569 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 9 H, CH_3), 7.37–7.42 (m, 3 H, ArH), 7.45–7.51 (m, 6 H, ArH), 7.52–7.60 (m, 3 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.2 (3CH_3), 34.7 (C), 120.7, 120.6 (q, *J* = 319 Hz, CF_3), 121.7, 126.2, 126.3, 126.9, 128.5, 130.1 (CH_{Ar}), 130.3 (C_{Ar}), 131.9, 133.6 (CH_{Ar}), 136.7, 146.2, 147.4, 152.4 (C_{Ar}), 192.5 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3.

MS (EI, 70 eV): *m*/*z* (%) = 462 (M^+, 33), 447 (100), 313 (15).

HRMS (EI): *m*/*z* calcd for $C_{24}H_{21}O_4F_3S$ $[M]^+$: 462.11072; found: 462.110339.

4-Benzoyl-3′-chlorobiphenyl-3-yl Trifluoromethanesulfonate (12f)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 3-chlorophenylboronic acid (93 mg, 0.60 mmol) and 1,4-dioxane (5 mL per 1 mmol of **10**), **12f** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; yield: 131 mg (65%).

IR (KBr): 3085, 3034 (w), 1665 (s), 1593, 1545, 1493, 1447, 1429, 1317, 1286, 1245, 1182, 1141, 1071, 997, 915, 833 (m), 746 (s), 696 (m), 783 (s), 671, 666, 621, 527 cm^{-1} (m).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.83–6.93 (m, 5 H, ArH), 6.98–7.07 (m, 5 H, ArH), 7.24–7.27 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 118.5 (q, *J* = 319.1 Hz, CF_3), 121.0, 125.4, 126.5, 127.3, 128.6, 129.0, 130.1, 130.5, 131.9, 133.8 (CH_{Ar}), 135.2, 136.5, 139.9, 144.7, 147.2, 160.2 (C_{Ar}), 192.3 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.9.

MS (EI, 70 eV): *m*/*z* (%) = 442 ([M, ^{37}Cl, 40]$^+$), 440 (M^+, 100), 365 (20), 363 (52), 309 (10), 307 (27), 244 (21), 230 (13), 215 (19), 139 (27), 105 (76), 77 (31).

HRMS (EI): *m*/*z* calcd for $C_{20}H_{12}ClF_3O_4S$ [M+, ^{35}Cl]: 440.00914; found: 440.00857.

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4-Benzoyl-3′-methoxybiphenyl-3-yl Trifluoromethanesulfonate (12g)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 3-methoxyphenylboronic acid (91 mg, 0.60 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **12g** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; yield: 128 mg (64%).

IR (KBr): 3078, 3030 (w), 1663 (s), 1596, 1540, 1492, 1443, 1428, 1316, 1285, 1244, 1180, 1140, 1071, 998, 913, 833 (m), 753 (s), 697 (m), 783 (s), 667, 529 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.79 (s, 3 H, OCH_3), 6.88–7.11 (m, 3 H, ArH), 7.30–7.42 (m, 3 H, ArH), 7.49–7.60 (m, 4 H, ArH), 7.74–7.77 (m, 1 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 113.2, 114.1, 119.6 (CH_{Ar}), 120.7 (q, *J* = 319.7 Hz, CF_3), 121.0, 126.5, 128.5, 130.1, 130.3 (CH_{Ar}), 130.8 (C_{Ar}), 131.8, 133.7 (CH_{Ar}), 136.6, 139.5, 146.2, 147.2, 160.2 (C_{Ar}), 192.4 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3.

MS (EI, 70 eV): *m*/*z* (%) = 436 (M^+, 100), 359 (24), 303 (14), 260 (14), 226 (11), 105 (28), 77 (16).

HRMS (EI): *m*/*z* calcd For $C_{21}H_{15}O_5S$ $[M]^+$: 436.05868; found: 436.058189.

4-Benzoyl-4′-methoxybiphenyl-3-yl Trifluoromethanesulfonate (12h)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methoxyphenylboronic acid (91 mg, 0.60 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **12h** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; yield: 126 mg (63%).

IR (KBr): 3082, 2962, 2867 (w), 1662, 1613, 1599 (m), 1556 (w), 1463, 1414, 1317, 1243 (m), 1209, 1136 (s), 1092, 947, 893 (m), 809 (s), 697, 605, 570 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.78 (s, 3 H, OCH_3), 6.92–6.96 (m, 2 H, ArH), 7.37–7.43 (m, 4 H, ArH), 7.46–7.52 (m, 4 H, ArH), 7.54–7.55 (m, 2 H, ArH).

^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 55.4 (OCH_3), 114.6 (CH_{Ar}), 118.4 (q, *J* = 319 Hz, CF_3), 120.3, 125.7, 128.4, 128.5 (CH_{Ar}), 129.8 (C_{Ar}), 130.1, 131.9, 133.6 (CH_{Ar}), 136.7, 145.9, 147.4, 160.5 (C_{Ar}), 192.5 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3.

MS (EI, 70 eV): *m*/*z* (%) = 436 (M^+, 100), 359 (14), 303 (15), 226 (15), 105 (35), 77 (16).

HRMS (EI): *m*/*z* calcd for $C_{21}H_{15}O_5F_3S$ $[M]^+$: 436.05868; found: 436.058078.

4-Benzoyl-3′,4′,5′-trimethoxybiphenyl-3-yl Trifluoromethanesulfonate (12i)

Starting from **10** (220 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,4,5-trimethoxyphenylboronic acid (127 mg, 0.60 mmol), and 1,4-dioxane (5 mL per 1 mmol of **10**), **12i** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; yield: 132 mg (58%).

IR (KBr): 3062 (w), 2923 (m), 2851 (w), 1665, 1611, 1585, 1515, 1487, 1412, 1316, 1272 (m), 1204, 1138, 1095, 965, 913, 854, 824, 756, 700, 646, 597 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H, OCH_3), 3.85 (s, 6 H, OCH_3), 6.70 (s, 2 H, ArH), 7.36–7.46 (m, 3 H, ArH), 7.50–7.55 (m, 3 H, ArH), 7.73–7.75 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 56.3 (2 OCH_3), 60.9 (OCH_3), 104.6 120.9 (CH_{Ar}), 122.5 (q, *J* = 319.5Hz, CF_3), 126.4, 128.5, 130.1, 131.8, 133.7 (CH_{Ar}), 133.9, 136.6, 139.0, 146.4, 147.2, 153.8 (C_{Ar}), 192.3 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3.

MS (EI, 70 eV): *m*/*z* (%) = 496 (M^+, 100), 481 (28), 105 (17), 77 (10).

HRMS (EI): *m*/*z* calcd for $C_{23}H_{19}F_3O_7S$ $[M]^+$: 496.07981; found: 496.079565.

Phenyl[4-(4-*tert*-butylphenyl)-2-(4-methoxyphenyl)phenyl]methanone (12j)

Starting from **12e** (161 mg, 0.35 mmol), K_3PO_4 (111 mg, 0.52 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methoxyphenylboronic acid (68 mg, 0.45 mmol), and 1,4-dioxane (5 mL per 1 mmol of **13b**), **12j** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; yield: 104 mg (71%).

IR (KBr): 3081, 3033 (w), 1663 (s), 1596, 1541, 1492, 1447, 1428, 1316, 1285, 1243, 1179, 1140, 1072, 1006, 913, 832, 698 (m), 785 (s), 670, 621, 529 cm^{-1} (m).

^1H NMR (250 MHz, $CDCl_3$): δ = 1.30 (s, 9 H, 3 CH_3), 3.65 (s, 3 H, OCH_3), 6.65–6.69 (m, 2 H, ArH), 7.13–7.24 (m, 5 H, ArH), 7.41–7.49 (m, 4 H, ArH), 7.53–7.65 (m, 7 H, ArH).

^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 31.3 (3 CH_3), 34.6 (C), 55.1 (OCH_3), 113.7, 125.1, 125.8, 126.9, 128.0, 128.6, 129.4, 129.9, 130.1, 132.7 (CH), 137.2, 137.3, 137.5, 139.1, 141.3, 143.0, 151.0, 158.9 (C), 198.3 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 421 (30), 420 (100), 419 (19), 406 (24), 405 (79), 443 (10), 105 (17).

HRMS (EI): *m*/*z* calcd for $C_{30}H_{28}O_2$ $[M]^+$: 421.07981; found: 421.079910.

[2,4-Bis(phenylethynyl)phenyl]phenylmethanone (13a)

Starting from **10** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (6 mol%), anhyd CuI (20 mol%), $(Bu)_4NI$ (15 mol%), and Et_3N (252 mg, 2.5 mmol), 1-ethynylbenzene (112 mg, 1.1 mmol) was added in DMF (5 mL per 1 mmol of **10**) to the reaction mixture. After completion of the reaction and workup, **13a** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; reaction time 4 h; yield: 149 mg (78%).

IR (KBr): 3079, 3032 (w), 1661, 1596, 1541, 1490, 1445, 1426, 1314, 1283, 1242, 1178, 1138, 1069, 999, 914, 835 (m), 751 (s), 698 (m), 785 (s), 669, 666, 621, 528 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 6.94–6.97 (m, 2 H, ArH), 7.08–7.15 (m, 3 H, ArH), 7.26–7.29 (m, 3 H, ArH), 7.34–7.48 (m, 7 H, ArH), 7.69–7.80 (m, 3 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 86.8, 87.9, 91.9, 95.7 (C), 122.4, 125.9 (C_{Ar}), 126.1, 128.4, 128.6, 128.8 (CH_{Ar}), 129.3 (C_{Ar}), 129.0, 130.2, 131.0 (CH_{Ar}), 131.3 (C_{Ar}), 131.5, 131.8, 131.9, 133.2, 135.5 (CH_{Ar}), 137.2, 140.6 (C_{Ar}), 196.4 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 382 (M^+, 100), 381 (57), 365 (19), 353 (13), 352 (20), 351 (11), 350 (14), 276 (28), 274 (19), 77 (10).

HRMS (EI): *m*/*z* calcd for $C_{29}H_{18}O$ $[M]^+$: 382.02323; found: 382.023235.

[2,4-Bis(3-tolylethynyl)phenyl]phenylmethanone (13b)

Starting from **10** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (6 mol%), anhyd CuI (20 mol%), $(Bu)_4NI$ (15 mol%), and Et_3N (252 mg, 2.5 mmol), 1-ethynyl-3-methylbenzene (128 mg, 1.1 mmol) was added in DMF (5 mL per 1 mmol of **10**) to the reaction mixture. After completion of the reaction and workup, **13b** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless

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oil; reaction temperature 90 °C; reaction time 4 h; yield: 151 mg (74%).

IR (KBr): 3055, 2918, 2858, 1660, 1594, 1579, 1539, 1485, 1447, 1314, 1283, 1243, 1192, 1154, 1093, 1039, 999, 962, 922, 834 (m), 780 (s), 748, 700, 686 (s), 669, 624, 584 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.14 (s, 3 H, CH_3), 2.26 (s, 3 H, CH_3), 6.71–6.78 (m, 2 H, ArH), 6.93–7.18 (m, 4 H, ArH), 7.26–7.50 (m, 7 H, ArH), 7.66–7.80 (m, 3 H, ArH).

^{13}C NMR (62.8 MHz, $CDCl_3$): δ = 21.1, 21.2 (2 CH_3), 86.5, 87.6, 92.1, 96.0 (C), 122.2, 122.4, 126.0 (C_{Ar}), 128.0 (CH_{Ar}), 128.1 (C_{Ar}), 128.4, 128.8, 129.0, 129.5, 129.7, 130.1, 130.2, 130.9, 132.1, 132.3, 133.2, 135.4 (CH_{Ar}), 137.2, 137.8, 138.1, 140.5 (C_{Ar}), 196.4 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 410 (M^+, 100), 409 (33), 408 (15), 395 (29), 393 (12), 289 (16), 181 (10), 77 (10).

HRMS (EI): *m*/*z* calcd for $C_{31}H_{22}O$ $[M]^+$: 410.16652; found: 410.16873.

[2,4-Bis(*p*-tolylethynyl)phenyl]phenylmethanone (13c)

Starting from **10** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (6 mol%), anhyd CuI (20 mol%), $(Bu)_4NI$ (15 mol%), and Et_3N (252 mg, 2.5 mmol), 1-ethynyl-4-methylbenzene (128 mg, 1.1 mmol) was added in DMF (5 mL per 1 mmol of **10**) to the reaction mixture. After completion of the reaction and workup, **13c** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; reaction time 4 h; yield: 159 mg (77%).

IR (KBr): 3055, 3025, 2916, 2860 (w), 1659, 1591, 1555, 1477, 1445, 1406, 1316, 1286, 1241, 1178, 1116, 1088, 1037, 999, 917, 836 (m), 812 (s), 699 (m), 686 (s), 651, 621, 596 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 2.22 (s, 3 H, CH_3), 2.31 (s, 3 H, CH_3), 6.84–6.95 (m, 4 H, ArH), 7.10–7.18 (m, 3 H, ArH), 7.37–7.51 (m, 6 H, ArH), 7.68–7.82 (m, 3 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.4, 21.5 (2 CH_3), 86.2, 86.8, 87.3, 92.1 (C), 119.3, 119.5, 122.5, 126.0 (C_{Ar}), 128.4, 128.8, 129.0, 129.2, 130.1, 130.7, 131.3, 131.6, 133.1, 135.3 (CH_{Ar}), 137.3, 138.7, 139.0, 140.3 (C_{Ar}), 196.5 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 410 (M^+, 100), 409 (17), 408 (15), 396 (12), 395 (28), 366 (14), 204 (14), 197 (10), 196 (23), 191 (10), 190 (18), 182 (59), 181 (16), 176 (33), 170 (17), 123 144 (13), 143 (14), 131 (12), 77 (13).

HRMS (EI): *m*/*z* calcd for $C_{31}H_{22}O$ $[M]^+$: 410.16652; found: 410.16813.

[2,4-Di(dec-1-ynyl)phenyl]phenylmethanone (13d)

Starting from **10** (144 mg, 0.30 mmol), $Pd(PPh_3)_2Cl_2$ (6 mol%), anhyd CuI (10 mol%), $(Bu)_4NI$ (15 mol%), and Et_3N (151 mg, 1.49 mmol), dec-1-yne (45 mg, 0.33 mmol) was added in DMF (5 mL per 1 mmol of **10**) to the reaction mixture. After completion of the reaction and workup, **13d** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; reaction time 4 h; yield: 100 mg (74%).

IR (KBr): 3059 (w), 2952 (m), 2922 (s), 2852 (m), 2224 (w), 1659, 1593, 1543, 1481, 1446, 1404, 1317, 1292, 1264, 1239, 1177, 1159, 1123, 1027, 939, 841, 793, 744 (m), 713 (s), 694, 666 (m), 615 (w), 594 cm^{-1} (m).

^1H NMR (500 MHz, $CDCl_3$): δ = 0.78–0.82 (m, 6 H, 2 CH_3), 1.16–1.28 (m, 20 H, 10 CH_2), 1.36–1.44 (m, 4 H, 2 CH_2), 1.51–1.60 (m, 4 H, 2 CH_2), 7.37–7.41 (m, 3 H, ArH), 7.48–7.54 (m, 3 H, ArH), 7.67–7.71 (m, 2 H, ArH).

^{13}C NMR (125 MHz, $CDCl_3$): δ = 14.0 (2 CH_3), 19.6, 19.8, 22.6, 28.6, 28.7, 28.9, 29.1, 29.2, 31.8 (CH_2), 78.8, 79.3, 95.3, 97.7 (C), 126. 5 (C_{Ar}), 128.3, 128.4, 129.9 (CH_{Ar}), 130.4 (C_{Ar}), 131.7, 132.4 133.3 (CH_{Ar}), 135.9, 137.3 (C_{Ar}), 195.4 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 454 (M^+, 6), 285 (10), 105 (100), 77 (15).

HRMS (EI): *m*/*z* calcd for $C_{33}H_{42}O$ $[M]^+$: 454.32302; found: 454.313394.

2-Benzoyl-5-(hept-1-ynyl)phenyl Trifluoromethanesulfonate (14a)

Starting from **10** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), anhyd CuI (10 mol%), $(Bu)_4NI$ (27 mg, 15mol%), and Et_3N (126 mg, 1.25 mmol), hept-1-yne (53 mg, 0.55 mmol) was added in DMF (5 mL per 1 mmol of **10**) to the reaction mixture. After completion of the reaction and workup, **14a** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; reaction time 8 h; yield: 165 mg (78%).

IR (KBr): 3065 (w), 2931 (m), 2860 (w), 1668 (s), 1608, 1598 (m), 1493 (w), 1448 (s), 1317, 1283, 1236 (m), 1205, 1136 (s), 1086 (m), 1000 (w), 941, 970, 839, 803, 762, 697, 602 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.85 (t, *J* = 7.2 Hz, 3 H, CH_3), 1.25–1.36 (m, 4 H, 2 CH_2), 1.51–1.58 (m, 2 H, CH_2), 2.36 (t, *J* = 7.2 Hz, 2 H, CH_2), 7.31 (s, 1 H, ArH), 7.38–7.41(m, 4 H, ArH), 7.50–7.53 (m, 1 H, ArH), 7.68–7.72 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 19.4, 22.1, 28.0, 31.1 (CH_2), 78.4, 95.9 (C), 118.4 (q, *J* = 320 Hz, CF_3), 125.2, 128.5 (CH_{Ar}), 129.3 (C_{Ar}), 130.1, 130.9 (CH_{Ar}), 131.0 (C_{Ar}), 131.1, 133.7 (CH_{Ar}), 136.4, 146.6 (C_{Ar}), 192.2 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.4.

MS (EI, 70 eV): *m*/*z* (%) = 424 (M^+, 6), 295 (10), 105 (100), 77 (15), 29 (10).

HRMS (EI): *m*/*z* calcd For $C_{21}H_{19}F_3O_4S$ $[M]^+$: 424.09507; found: 424.09464.

2-Benzoyl-5-(dec-1-ynyl)phenyl Trifluoromethanesulfonate (14b)

Starting from **10** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), anhyd CuI (10 mol%), $(Bu)_4NI$ (27 mg, 15 mol%), and Et_3N (126 mg, 1.25 mmol), dec-1-yne (76 mg, 0.55 mmol) was added in DMF (5 mL per 1 mmol of **10**) to the reaction mixture. After completion of the reaction and workup, **14b** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; reaction time 8 h; yield: 188 mg (81%).

IR (KBr): 2924 (m), 2854 (w), 1669 (s), 1608, 1542, 1465 (m), 1426 (s), 1316, 1283, 1235 (m), 1206, 1138 (s), 1087, 1013, 970, 939, 884, 798, 698, 661, 603 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 0.80 (t, *J* = 7.3 Hz, 3 H, CH_3), 1.17–1.26 (m, 8 H, 4 CH_2), 1.33–1.38 (m, 2 H, CH_2), 1.50–1.55 (m, 2 H, CH_2), 2.36 (t, *J* = 6.9 Hz, 2 H, CH_2), 7.32 (s, 1 H, ArH), 7.37–7.42 (m, 4 H, ArH), 7.51–7.55 (m, 1 H, ArH), 7.69–7.72 (m, 2 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.5, 22.6, 28.3, 28.9, 29.0, 29.1, 31.8 (CH_2), 78.4, 95.9 (C), 114.2 (q, *J* = 320 Hz, CF_3), 125.2, 128.5 (CH_{Ar}), 129.3 (C_{Ar}), 130.1, 130.9 (CH_{Ar}), 131.0 (C_{Ar}), 131.1, 133.7 (CH_{Ar}), 136.5, 146.6 (C_{Ar}), 192.2 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.4.

MS (EI, 70 eV): *m*/*z* (%) = 466 (M^+, 9), 410 (14), 396 (10), 395 (10), 105 (100), 77 (16).

HRMS (EI): *m*/*z* calcd for $C_{24}H_{25}F_3O_4S$ $[M]^+$: 466.14202; found: 466.14314.

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2-Benzoyl-5-[(4-methoxyphenyl)ethynyl]phenyl Trifluoromethanesulfonate (14c)

Starting from **10** (238 mg, 0.50 mmol), $Pd(PPh_3)_2Cl_2$ (3 mol%), anhyd CuI (10 mol%), $(Bu)_4NI$ (27 mg, 15 mol%), and Et_3N (126 mg, 1.25 mmol), 4-methoxyphenylacetylene (72 mg, 0.55 mmol) was added in DMF (5 mL per 1 mmol of **10**) to the reaction mixture. After completion of the reaction and workup, **14c** was isolated by chromatography (flash silica gel, heptanes–EtOAc, 10:1) as a colorless oil; reaction temperature 90 °C; reaction time 8 h; yield: 156 mg (68%).

IR (KBr): 3085 (w), 2958 (m), 2837 (w), 1665 (s), 1596, 1539, 1513 (m), 1428 (s), 1394, 1282, 1246 (m), 1207, 1139 (s), 1076, 1025, 968, 912, 849 (m), 829 (s), 801, 745, 695, 653 (m), 600 cm^{-1} (s).

^1H NMR (300 MHz, $CDCl_3$): δ = 3.71 (s, 3 H, OCH_3), 6.78–6.81 (m, 2 H, ArH), 7.34–7.50 (m, 8 H, ArH), 7.68–7.71 (m, 2 H, ArH).

^{13}C NMR ($CDCl_3$, 75 MHz): δ = 55.3 (OCH_3), 85.7, 94.3 (C), 114.2 (CH_{Ar}), 117.5 (q, *J* = 320 Hz, CF_3), 124.8, 128.6 (CH_{Ar}), 128.8 (C_{Ar}), 130.1, 130.7 (CH_{Ar}), 131.0 131.2 (C_{Ar}), 131.3, 133.4, 133.8 (CH_{Ar}), 136.4, 146.7, 160.4 (C_{Ar}), 192.2 (C=O).

^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3.

MS (EI, 70 eV): *m*/*z* (%) = 460 (M^+, 100), 327 (21), 312 (12), 105 (16), 77 (11).

HRMS (EI): *m*/*z* calcd for $C_{23}H_{15}F_3O_5S$ $[M]^+$: 460.32357; found: 460.323471.

{4′-*tert*-Butyl-5-[(4-methoxyphenyl)ethynyl]biphenyl-2-yl}phenylmethanone (15)

Starting from **14c** (92 mg, 0.20 mmol), K_3PO_4 (63 mg, 0.30 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-*tert*-butylphenylboronic acid (46 mg, 0.26 mmol), and 1,4-dioxane (5 mL per 1 mmol of **14c**), **15** was isolated as a white solid; reaction temperature 90 °C; yield: 65 mg (73%); mp 131 °C.

IR (KBr): 3057, 3031 (w), 2957 (m), 2903, 2866, 2837 (w), 2220, 2201, 1713 (m), 1663 (s), 1593, 1543 (m), 1509 (s), 1462 (m), 1446 (w), 1412, 1362, 1280, 126 (m), 1245 (s), 1217, 1173, 1105, 1027, 927, 887 (m), 829 (s), 802, 762 (m), 701 (s), 655, 621, 536 cm^{-1} (m).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.14 (s, 9 H, 3 CH_3), 3.77 (s, 3 H, OCH_3), 6.81–6.84 (m, 2 H, ArH), 7.11–7.31 (m, 6 H, ArH), 7.40–7.56 (m, 8 H, ArH).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 31.1 (3 CH_3), 34.3 (C), 55.3 (OCH_3), 87.5, 91.2 (C), 114.0 (CH_{Ar}), 114.9 (C_{Ar}), 125.1 (CH_{Ar}), 125.8 (C_{Ar}), 127.9, 128.6, 129.0, 129.7, 132.6, 132.9, 133.2 (CH_{Ar}), 136.4, 137.4, 138.0, 141.5, 150.4, 159.9 (C_{Ar}), 198.3 (C=O).

MS (EI, 70 eV): *m*/*z* (%) = 444 (M^+, 100), 430 (17), 429 (42), 387 (10), 105 (24), 77 (13).

HRMS (EI): *m*/*z* calcd for $C_{32}H_{28}O_2$ $[M]^+$: 444.20838; found: 444.208616.

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