

Synthesis of 2',4-Diarylbenzophenones through Site-Selective Suzuki–Miyaura Reactions of Bis(triflates) of 2',4-Dihydroxybenzophenones

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Palladium(0)-catalyzed Suzuki cross-coupling reactions of the bis(triflates) of 2',4-dihydroxybenzophenones afforded 2',4-diarylbenzophenones. The reactions proceeded with very good site selectivity in favour of the 4-position.

Introduction

Benzophenones show a variety of useful pharmacological and physical properties. 4-Arylbenzophenones, for instance, exhibit interesting pharmacological activities such as cytotoxic^[1] and antibacterial activities,^[2] as well as the inhibition of various enzymes.^[3] 4-(2-Hydroxybenzoyl)salicylic acids were reported to show good in vitro activity as selectin antagonists.^[4] Structurally related benzoylfluorones are also of biological relevance.^[5] 4-Arylbenzophenones are substructures of complex polycyclic frameworks, such as anthraquinone and tetracycline natural products.^[6] 2-Hydroxy- and 2-aminobenzophenones are of considerable importance in anticancer therapy, because they act as antitubulin agents.^[7] Benzophenones also have technical applications. Functionalized benzophenones are also widely used as photosensitizers and UV filters (sun creams).^[8] 2,2'-Dihydroxy-4,4'-dimethoxybenzophenone is used as a sensitive fluorimetric reagent for the determination of the nitrate anion. This method has been applied to the analysis of a variety of natural waters and sediments.^[9] Several substituted benzophenones display phosphorescence.^[10–12]

Classic syntheses of benzophenones are based on reactions of aryllithium or magnesium reagents with aldehydes and subsequent oxidation and on Friedel–Crafts acylations.^[7b,13] For the synthesis of *functionalized* benzophenones (e.g., containing hydroxy, halide or ester groups), these methods often give unsatisfactory results, due to competing side reactions. An alternative strategy is based on SmI₂-mediated reactions between benzaldehydes and benzyl halides and subsequent oxidation.^[14]

In recent years we have studied domino reactions between silyl enol ethers and chromones. In this context we developed a new approach to 4-(2-hydroxybenzoyl)salicylates through cyclizations of 1,3-bis(silyloxy)buta-1,3-dienes with 3-formylchromones.^[4] Recently we reported^[15] the synthesis of 2',4-diaryl-2-methoxycarbonylbenzophenones based on site-selective^[16] Suzuki–Miyaura cross-coupling reactions of bis(triflates) of 2',4-dihydroxy-2-methoxycarbonylbenzophenones. Here we report full details of these studies and a comprehensive study of the scope of this approach. In addition, we report for the first time on site-selective Suzuki–Miyaura reactions of the bis(triflate) of the parent 2',4-dihydroxybenzophenone.

Results and Discussion

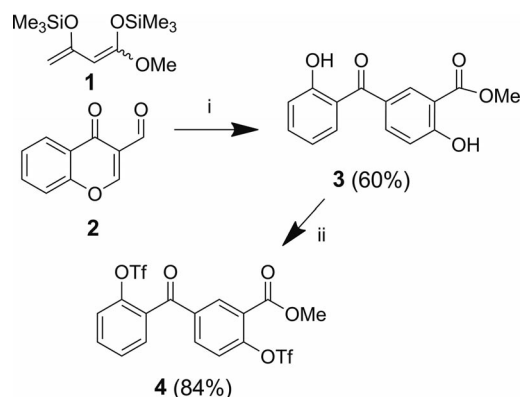
The TMSOTf-mediated domino “addition/retro-Michael/Mukaiyama-aldol” reaction between 3-formylchromone (**2**, Scheme 1) and 1,3-bis(trimethylsilyloxy)buta-1,3-diene (**1**) afforded the 2',4-dihydroxybenzophenone **3**, which was transformed into its bis(triflate) **4**. The structure of **4** was independently confirmed by X-ray crystal structure analysis (Figure 1).^[17]

Suzuki reactions between **4** and different boronic acids afforded the novel 2',4-diarylbenzophenones **5a–r** in good yields (Scheme 2, Table 1). The best yields were obtained when Pd(PPh₃)₄ (6 mol-%) was used as the catalyst, when 2.6 equiv. of the boronic acid were employed, and when the reaction was carried out in 1,4-dioxane (reflux, 4 h) with K₃PO₄ as the base. The benzophenones **5g** and **5r** were prepared from 4- and 3-bromophenylboronic acid, respectively, in good yields. These experiments show that the presence of the bromine moiety is compatible with the reaction conditions.

The structures of all products were confirmed by spectroscopic methods. The structure of **5a** was independently confirmed by an X-ray crystal structure analysis (Figure 2).^[17]

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Scheme 1. Synthesis of **3** and **4**. Reagents and conditions: (i) **1** (**2** (1.0 equiv.), Me₃SiOTf (0.3 equiv.), CH₂Cl₂, 0 °C, **2** **1** (1.1 equiv.), 0 → 20 °C, 12 h, **3**. HCl (10%); (ii) **1** **3** (1.0 equiv.), pyridine (4.0 equiv.), CH₂Cl₂, –78 °C, 10 min, **2**. Tf₂O (2.4 equiv.), –78 → 0 °C, 4 h.

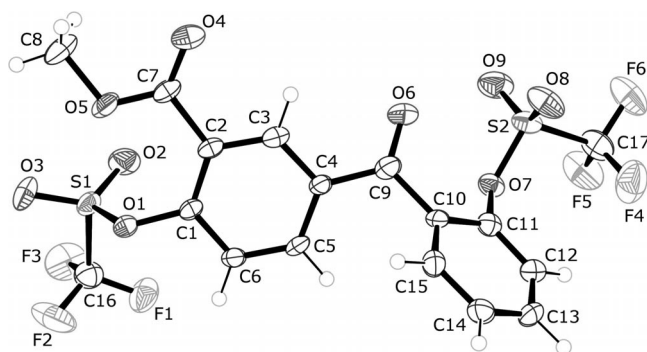
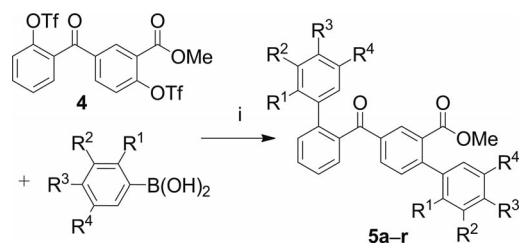


Figure 1. ORTEP plot of **4**.



Scheme 2. Synthesis of **5a–r**. Reagents and conditions: (i) 1,4-dioxane (5 mL per 1 mmol of triflate), **4** (1.0 equiv.), boronic acids (2.6 equiv.), K₃PO₄ (3.0 equiv.), Pd(PPh₃)₄ (6 mol-%), 110 °C, 4 h.

Suzuki reactions between **4** and only 1.3 equiv. of boronic acids afforded the 4-arylbenzophenones **6a–h** with very good site selectivity (Scheme 3, Table 2). Suzuki–Miyaura reactions between **6a**, **6c** or **6e–h** and 4-vinylphenylboronic acid gave the 2',4-diarylbenzophenones **7a–f**, each containing two different aryl groups (Scheme 3, Table 3). The configurations of all products were again studied by spectroscopic methods. The structures of **6d** and **6g** were independently confirmed by X-ray crystal structure analyses (Figures 3 and 4).^[17]

The site selectivities of palladium(0)-catalyzed reactions are generally controlled by electronic and steric parameters. Oxidative addition of the palladium(0) catalyst usually oc-

Table 1. Synthesis of **5a–r**.

5	R ¹	R ²	R ³	R ⁴	Yield of 5 ^[a] [%]
a	H	H	Me	H	84
b	H	H	H	H	75
c	H	H	C ₂ H ₅	H	62
d	H	Cl	H	H	77
e	H	H	vinyl	H	72
f	H	H	Cl	H	64
g	H	H	Br	H	74
h	H	OMe	OMe	H	62
i	H	H	OH	H	67
j	H	OMe	OMe	OMe	58
k	H	H	F	H	62
l	H	OH	H	H	65
m	H	H	CF ₃	H	76
n	OMe	H	H	OMe	67
o	OMe	H	H	H	69
p	H	H	<i>t</i> Bu	H	72
q	H	Me	H	Me	78
r	H	Br	H	H	64

[a] Yield of isolated product.

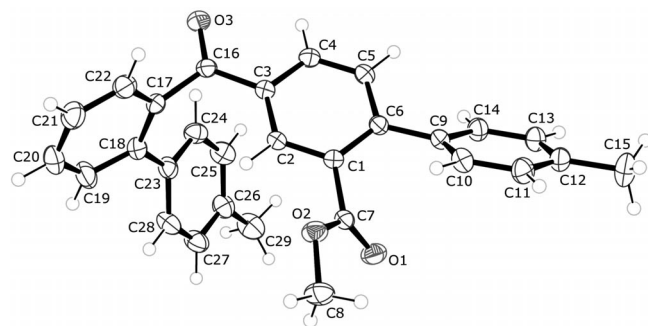
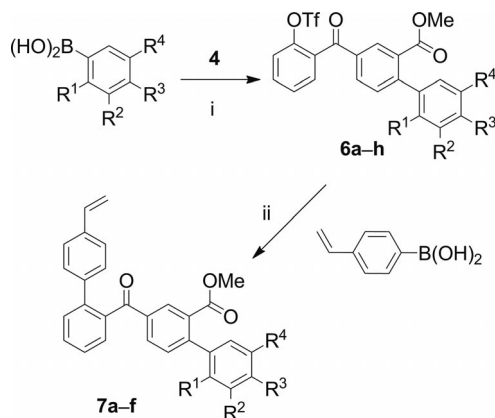


Figure 2. ORTEP plot of **5a**.



Scheme 3. Synthesis of **6a–h** and **7a–f**. Reagents and conditions: (i) **4** (1.0 equiv.), boronic acid (1.3 equiv.), K₃PO₄ (3.0 equiv.), Pd(PPh₃)₄ (3 mol-%), 1,4-dioxane, 110 °C, 4 h; (ii) **6a**, **6c** or **6e–h** (1.0 equiv.), 4-vinylphenylboronic acid (1.3 equiv.), K₃PO₄ (3.0 equiv.), Pd(PPh₃)₄ (3 mol-%), 1,4-dioxane, 110 °C, 4 h.

curs first at the most electron-deficient and sterically less hindered carbon atom. The site-selective formation of the products **6a–h** might therefore be explained by the fact that

Table 2. Synthesis of **6a–h**.

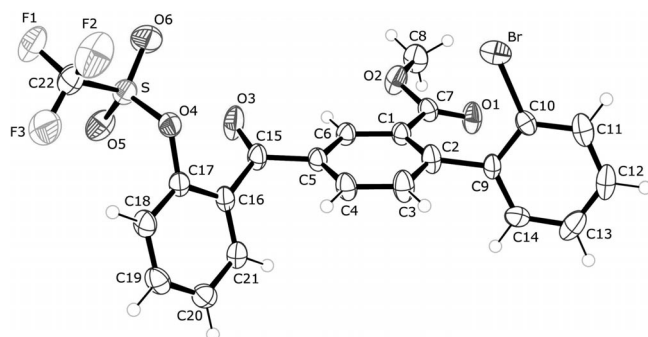
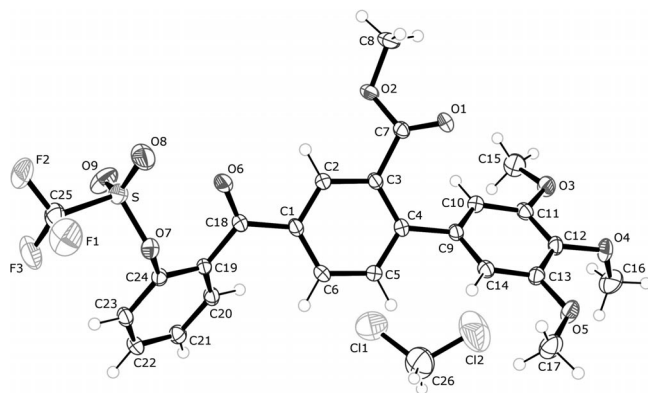
6	R ¹	R ²	R ³	R ⁴	Yield of 6 ^[a] [%]
a	H	Me	H	Me	78
b	H	H	Cl	H	45
c	OEt	H	H	H	89
d	Br	H	H	H	78
e	H	OMe	OMe	H	44
f	H	H	OH	H	63
g	H	OMe	OMe	OMe	43
h	H	OH	H	H	72

[a] Yield of isolated product.

Table 3. Synthesis of **7a–f**.

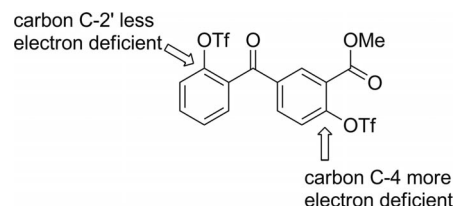
6	7	R ¹	R ²	R ³	R ⁴	Yield of 7 ^[a] [%]
a	a	H	Me	H	Me	60
f	b	H	H	OH	H	74
e	c	H	OMe	OMe	H	65
g	d	H	OMe	OMe	OMe	72
h	e	H	OH	H	H	64
c	f	OEt	H	H	H	68

[a] Yield of isolated product.

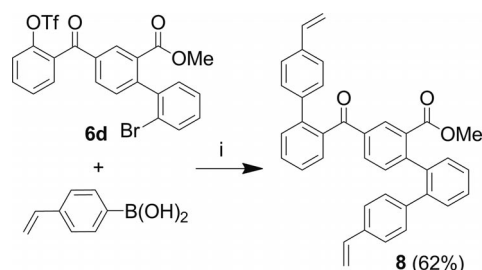
Figure 3. ORTEP plot of **6d**.Figure 4. ORTEP plot of **6g**.

carbon atom C-4 is more electron-deficient and less sterically hindered than C-2' (Scheme 4). One electron-withdrawing benzoyl group is located *ortho* to C-2'. In contrast,

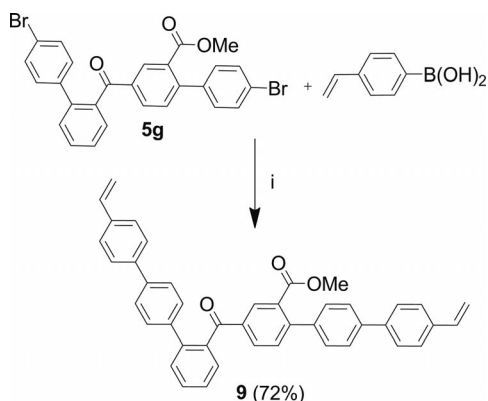
both an electron-withdrawing benzoyl group and an electron-withdrawing ester group are located *para* and *ortho*, respectively, to C-4.

Scheme 4. Possible explanation for the site-selective formation of the products **6a–h**.

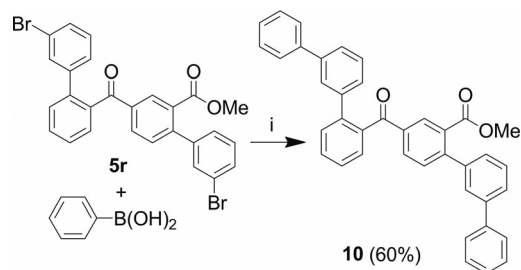
The Suzuki–Miyaura reaction between **6d**, containing a bromide and a triflate group both in *ortho* positions (Scheme 5), and 4-vinylphenylboronic acid (2.6 equiv.) afforded the bisdiphenyl ketone **8** in 62% yield.

Scheme 5. Synthesis of **8**. Reagents and conditions: (i) **6d** (1.0 equiv.), 4-vinylphenylboronic acid (2.6 equiv.), K₃PO₄ (3.0 equiv.), Pd(PPh₃)₄ (6 mol-%), 1,4-dioxane, 110 °C, 4 h.

The Suzuki–Miyaura reaction between 4-vinylphenylboronic acid (2.6 equiv.) and **5g**, containing two *para*-bromophenyl moieties (Scheme 6) afforded the diphenyl triphenyl ketone **9**.

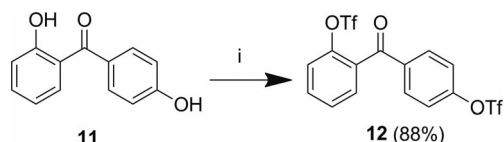
Scheme 6. Synthesis of **9**. Reagents and conditions: (i) **5g** (1.0 equiv.), 4-vinylphenylboronic acid (2.6 equiv.), K₃PO₄ (3.0 equiv.), Pd(PPh₃)₄ (6 mol-%), 1,4-dioxane, 110 °C, 4 h.

The Suzuki–Miyaura reaction between 4-vinylphenylboronic acid (2.6 equiv.) and **5r**, containing two *meta*-bromophenyl moieties (Scheme 7), afforded the diphenyl triphenyl ketone **10**.



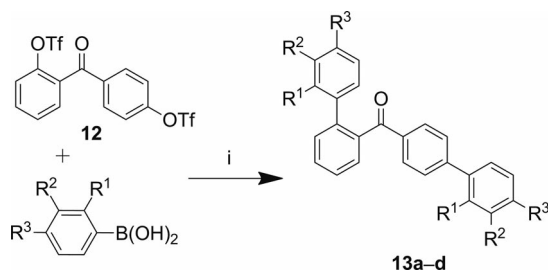
Scheme 7. Synthesis of **10**. Reagents and conditions: (i) **5r** (1.0 equiv.), 4-vinylphenylboronic acid (2.6 equiv.), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 110 °C, 4 h.

Extending the scope of our study, we investigated reactions of the bis(triflate) of the commercially available 2',4-dihydroxybenzophenone (**11**), which was transformed into the bis(triflate) **12** in 88% yield (Scheme 8).



Scheme 8. Synthesis of **12**. Reagents and conditions: (i) CH_2Cl_2 , **11** (1.0 equiv.), -78 °C, pyridine (4.0 equiv.), Tf_2O (2.4 equiv.), -78 → 0 °C, 4 h.

Suzuki reactions between **12** and different boronic acids (2.6 equiv.) afforded the novel 2',4-diarylbenzophenones **13a–d** in good yields (Scheme 9, Table 4). The best yields were obtained when $Pd(PPh_3)_4$ (6 mol-%) was used as the catalyst, when 2.6 equiv. of the boronic acid were employed, and when the reaction was carried out in 1,4-dioxane (reflux, 4 h) with K_3PO_4 as the base. The structures of all products were established by spectroscopic methods. The structure of **13b** was independently confirmed by X-ray crystallographic analysis (Figure 5).^[17]



Scheme 9. Synthesis of **13a–d**. Reagents and conditions: (i) 1,4-dioxane (5 mL per 1 mmol of triflate), **12** (1.0 equiv.), boronic acid (2.6 equiv.), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (6 mol-%), 110 °C, 4 h.

Table 4. Synthesis of **13a–d**.

13	R¹	R²	R³	Yield of 13 ^[a] [%]
a	H	OCH ₃	H	78
b	F	H	H	70
c	H	H	OCH ₃	68
d	H	H	vinyl	66

[a] Yield of isolated product.

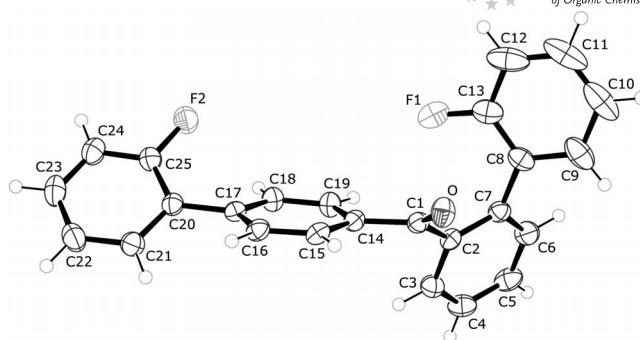
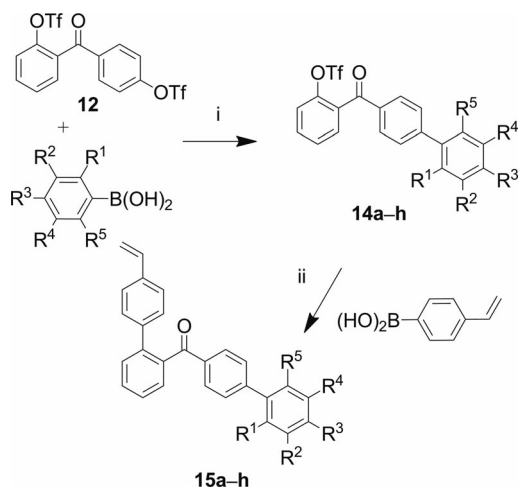


Figure 5. ORTEP plot of **13b**.

Suzuki reactions between **12** and smaller quantities of the different boronic acids (1.3 equiv.) in the presence of $Pd(PPh_3)_4$ (3 mol-%) proceeded with very good site selectivities in favour of carbon atom C-4 to give the benzophenones **14a–h** (Scheme 10, Table 5). The pure products were obtained after chromatographic purification. Treatment of **14a–h** with (4-vinylphenyl)boronic acid (1.3 equiv.) gave the 2',4-diarylbenzophenones **15a–h**, each containing two different aryl groups (Scheme 10, Table 5). The struc-



Scheme 10. Synthesis of **14a–h** and **15a–h**. Reagents and conditions: (i) **12** (1.0 equiv.), boronic acids (1.3 equiv.), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 110 °C, 4 h; (ii) **14a–h** (1.0 equiv.), 4-vinylphenylboronic acid (1.3 equiv.), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (3 mol-%), 1,4-dioxane, 110 °C, 4 h.

Table 5. Synthesis of **14a–h** and **15a–h**.

14,15	R¹	R²	R³	R⁴	R⁵	Yield [%]	
						14 ^[a]	15 ^[a]
a	H	OCH ₃	H	H	H	68	70
b	OCH ₃	H	H	OCH ₃	H	72	72
c	OCH ₃	H	H	H	OCH ₃	64	68
d	OE _t	H	H	H	H	76	62
e	H	vinyl	H	H	H	70	66
f	H	H	<i>t</i> Bu	H	H	66	64
g	H	CH ₃	H	CH ₃	H	78	76
h	H	H	Et	H	H	74	74

[a] Yield of isolated product.

tures of all products were verified by spectroscopic methods. The structures of **14f** and **14h** were independently confirmed by X-ray crystallography (Figures 6 and 7).^[17]

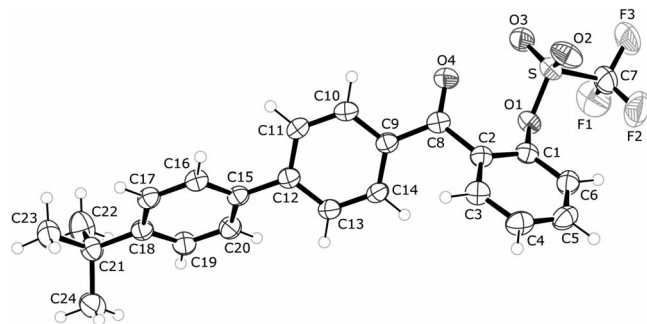


Figure 6. ORTEP plot of **14f**.

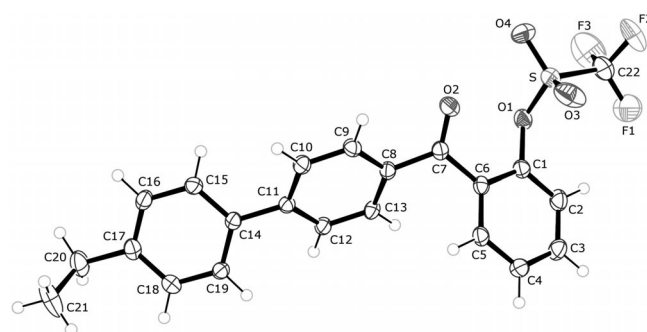
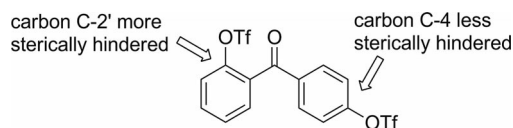


Figure 7. ORTEP plot of **14h**.

The site-selective formation of **14a–h** can be explained by the fact that carbon atom C-4' (located *para* to the keto group) is less sterically hindered than C-1 (located *ortho* to the keto group) (Scheme 11). Both centres are similar from the electronic viewpoint.



Scheme 11. Possible explanation for the site-selective formation of products **14a–h**.

Conclusion

In conclusion, we report the synthesis of various 2',4-diarylbenzophenones based on palladium(0)-catalyzed Suzuki cross-coupling reactions of the bis(triflates) of 2',4-dihydroxybenzophenones. These reactions proceed with very good site selectivities.

Experimental Section

General Comments: All solvents were dried by standard methods and all reactions were carried out under inert atmosphere. For ¹H and ¹³C NMR spectra the deuterated solvents indicated were used. Mass spectrometric data (MS) 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.

Synthesis of the Triflates 4 and 12: Pyridine (4.0 equiv.) was added at –78 °C under argon to a stirred solution of **3** or **11** (1.0 equiv.) in CH₂Cl₂ (10 mL mmol^{–1}). After 10 min, Tf₂O (2.4 equiv.) was added at –78 °C. The mixture was allowed to warm to 0 °C and stirred for 4 h. The reaction 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).

Methyl 2-(Trifluoromethanesulfonyloxy)-5-[2-(trifluoromethanesulfonyloxy)benzoyl]benzoate (4): Compound **4** was obtained from **3** (120 mg, 0.44 mmol), pyridine (0.14 mL, 1.76 mmol) and Tf₂O (0.17 mL, 1.05 mmol) as a crystalline colourless solid (200 mg, 84%). M.p. 124–126 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.90 (s, 3 H, OCH₃), 7.39 (d, *J* = 8.7 Hz, 2 H, ArH), 7.45–7.54 (m, 2 H, ArH), 7.66 (s, 1 H, ArH), 8.02 (dd, *J* = 2.4, 8.6 Hz, 1 H, ArH), 8.39 (d, *J* = 2.2 Hz, 1 H, ArH) ppm. ¹³C NMR (75.46 MHz, CDCl₃): δ = 53.0 (OCH₃), 116.2 (q, *J*_{FC} = 320.0 Hz, CF₃), 116.5 (C), 120.5 (q, *J*_{FC} = 321.2 Hz, CF₃), 120.8 (C), 122.8, 123.4, 128.5, 131.2, 133.7, 134.4, 135.3 (CH), 136.4, 146.7, 151.1, 163.2 (C), 190.1 (C=O) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = –73.28 (CF) ppm. IR (KBr): ν̄ = 3117, 3076, 3040 (w), 1671, 1624 (s), 1582 (m), 1479, 1341, 1237 (m), 1202 (s), 1164, 1087, 988 (m), 866, 793, 703 (s), 589, 537 (m) cm^{–1}. GC–MS (EI, 70 eV): *m/z* (%) = 536 [M]⁺ (89), 505 (40), 467 (06), 403 (09), 375 (23), 311 (100), 247 (61), 211 (20), 183 (30), 155 (34), 120 (29), 92 (16), 69 (50). HRMS (EI): calcd. for C₁₇H₁₀F₆O₅S₂ [M]⁺ 535.96649; found 535.966638.

2-[4-(Trifluoromethanesulfonyloxy)benzoyl]phenyl Trifluoromethanesulfonate (12): Compound **12** was obtained from **11** (168 mg, 0.78 mmol), pyridine (0.25 mL, 3.12 mmol) and Tf₂O (0.31 mL, 1.87 mmol) as a yellow oil (yield 330 mg, 88%). ¹H NMR (300 MHz, CDCl₃): δ = 7.31–7.38 (m, 3 H, ArH), 7.43–7.53 (m, 2 H, ArH), 7.58–7.64 (m, 1 H, ArH), 7.83 (d, *J* = 8.91 Hz, 2 H, ArH) ppm. ¹³C NMR (62.90 MHz, CDCl₃): δ = 115.8 (q, *J*_{FC} = 320.0 Hz, CF₃), 120.9 (q, *J*_{FC} = 321.3 Hz, CF₃), 121.6, 122.7, 128.3, 131.1, 132.2, 133.3 (CH_{Ar}), 133.3, 136.3, 146.6, 152.7 (C_{Ar}), 190.8 (C=O) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = –73.3, 72.6 (2 CF) ppm. IR (KBr): ν̄ = 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 (m) cm^{–1}. GC–MS (EI, 70 eV): *m/z* (%) = 478 [M]⁺ (58), 345 (06), 317 (13), 281 (09), 253 (100), 212 (12), 184 (28), 155 (07), 128 (12), 92 (10), 69 (17), 63 (06). HRMS (EI): calcd. for C₁₅H₈F₆O₇S₂ [M]⁺ 477.96101 found 477.961813.

General Procedure for the Synthesis of Benzophenones 5a–r and 13a–d: A 1,4-dioxane solution of the arylboronic acid, K₃PO₄, Pd(PPh₃)₄ and the triflate **4** or **12** was stirred at 110 °C under argon for 4 h. After the system had cooled to 20 °C, a saturated aqueous solution of NH₄Cl was added, the organic and aqueous layers were separated, and the latter was extracted with CH₂Cl₂. The combined organic layers were dried (Na₂SO₄) and filtered, and the filtrate was concentrated in vacuo. The residue was purified by column chromatography.

Methyl 2-Hydroxy-5-(2-hydroxybenzoyl)benzoate (3): Compound **3** was obtained from **2** (1740 mg, 10 mmol), 1,3-bis(silyloxy)buta-1,3-diene (**1**, 2860 mg, 11 mmol) and TMSOTf (0.54 mL, 3 mmol) as a yellowish oil (1650 mg, 60%). ¹H NMR (300 MHz, CDCl₃): δ = 3.89 (s, 3 H, OCH₃), 6.79–6.85 (m, 1 H, ArH), 6.94–6.98 (m, 1 H, ArH), 7.02 (s, 1 H, ArH), 7.39–7.43 (m, 1 H, ArH), 7.49 (dd, *J* = 1.6, 7.9 Hz, 1 H, ArH), 7.77 (dd, *J* = 2.2, 8.7 Hz, 1 H, ArH), 8.18 (d, *J* = 2.2 Hz, 1 H, ArH), 11.1 (s, 1 H, OH), 11.7 (s, 1 H,

OH) ppm. ^{13}C NMR (62.90 MHz, CDCl_3): δ = 52.7 (OCH_3), 117.8, 118.5, 118.7 (CH_{Ar}), 131.8 (C_{Ar}), 132.4, 132.9 (CH_{Ar}), 135.1, 135.6 (C_{Ar}), 136.1, 136.6 (CH_{Ar}), 161.9, 163.6 (C_{Ar}), 168.9 (COO), 197.9 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3117, 3076, 3040 (w), 1671, 1624 (m), 1582 (s), 1438, 1341, 1291 (m), 1237, 1202 (s), 1164, 1087, 988, 933, 819, 779 (m), 725, 678 (s), 537 (m) cm^{-1} . GC-MS (EI, 70 eV): m/z (%) = 272 (92) $[\text{M}]^+$, 239 (25), 212 (06), 196 (02), 184 (11), 147 (38), 128 (04), 121 (96), 120 (100), 92 (20), 79 (07), 65 (13), 53 (05), 39 (06). HRMS (EI): calcd. for $\text{C}_{15}\text{H}_{12}\text{O}_5$ $[\text{M} + \text{H}]^+$ 272.07575; found 273.075251.

Methyl 4'-Methyl-4-(4'-methylbiphenylcarbonyl)biphenyl-2-carboxylate (5a): Compound **5a** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (6 mol-%), *p*-tolylboronic acid (144 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless crystalline solid; yield 145 mg (84%). M.p. 114–116 °C. ^1H NMR (300 MHz, CDCl_3): δ = 2.17 (s, 3 H, CH_3), 2.30 (s, 3 H, CH_3), 3.56 (s, 3 H, OCH_3), 6.95 (d, J = 8.0 Hz, 2 H, ArH), 7.04–7.21 (m, 6 H, ArH), 7.35–7.53 (m, 5 H, ArH), 7.70 (dd, J = 2.9, 8.1 Hz, 1 H, ArH), 7.98 (d, J = 1.9 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.89 MHz, CDCl_3): δ = 21.0 (CH_3), 21.2 (CH_3), 52.1 (OCH_3), 126.9, 127.9, 128.8, 128.9, 129.0 (CH_{Ar}), 129.9 (C_{Ar}), 130.2, 130.6, 131.4, 132.1 (CH_{Ar}), 135.8, 137.1, 137.2, 137.7, 138.3, 141.3, 146.3 (C_{Ar}), 168.4 (COO), 197.4 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3080, 3057, 3025 (w), 1724, 1659 (s), 1613 (w), 1595 (m), 1574, 1518 (w), 1438, 1310, 1277 (m), 1231 (s), 1152, 1082, 972 (m), 819, 704 (s), 536 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 420 (100) $[\text{M}]^+$, 405 (21), 373 (09), 359 (23), 332 (07), 253 (26), 210 (07), 195 (40), 165 (39) 152 (25). HRMS (EI): calcd. for $\text{C}_{29}\text{H}_{24}\text{O}_3$ $[\text{M}]^+$ 420.17200; found 420.172525.

Methyl 4-(Biphenylcarbonyl)biphenyl-2-carboxylate (5b): Compound **5b** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (6 mol-%), phenylboronic acid (130 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless solid; yield 120 mg (75%). M.p. 124–126 °C. ^1H NMR (300 MHz, CDCl_3): δ = 3.51 (s, 3 H, OCH_3), 7.06–7.19 (m, 8 H, ArH), 7.23 (s, 1 H, ArH), 7.37–7.54 (m, 6 H, ArH), 7.69 (dd, J = 2.2, 8.4 Hz, 1 H, ArH), 7.97 (d, J = 1.9 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.89 MHz, CDCl_3): δ = 52.0 (OCH_3), 115.3 (C_{Ar}), 127.3, 127.4, 127.8, 128.0, 128.1, 128.3, 128.9, 129.0, 130.2, 130.6, 130.8, 131.5, 132.1 (CH_{Ar}), 136.1, 138.3, 140.1, 140.2, 141.3, 146.3 (C_{Ar}), 168.2 (COO), 197.3 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3056, 3024, 2849 (w), 1721, 1663 (s), 1596 (m), 1556 (w), 1433 (m), 1398 (w), 1303 (m), 1230 (s), 1151, 1086, 939, 967 (m), 742 (s), 539 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 392 (100) $[\text{M}]^+$, 359 (11), 331 (41), 305 (11), 239 (39), 181 (54), 165 (06), 152 (51) 139 (04). HRMS (EI): calcd. for $\text{C}_{27}\text{H}_{20}\text{O}_3$ $[\text{M}]^+$ 392.14070; found 392.140174.

Methyl 4'-Ethyl-4-(4'-ethylbiphenylcarbonyl)biphenyl-2-carboxylate (5c): Compound **5c** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (6 mol-%), 4-ethylphenylboronic acid (159 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a yellow solid; yield 115 mg (62%). M.p. 93–94 °C. ^1H NMR (300 MHz, CDCl_3): δ = 1.06 (t, J = 7.6 Hz, 3 H, CH_3 ethyl), 1.18 (t, J = 7.6 Hz, 3 H, CH_3 ethyl), 2.47 (q, J = 7.6 Hz, 2 H, CH_2 ethyl), 2.62 (q, J = 7.5 Hz, 2 H, CH_2 ethyl), 3.56 (s, 3 H, OCH_3), 6.96 (d, J = 8.1 Hz, 2 H, ArH), 7.02–7.12 (m, 4 H, ArH), 7.14–7.18 (m, 2 H, ArH), 7.21 (s, 1 H, ArH), 7.37–7.44 (m, 2 H, ArH), 7.48–7.54 (m, 2 H, ArH), 7.68 (dd, J = 1.8, 7.7 Hz, 1 H, ArH), 7.95 (d, J = 2.1 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.90 MHz, CDCl_3): δ = 15.3 (CH_3), 15.4 (CH_3), 28.4, 28.5 (2 CH_2 ethyl), 52.0 (OCH_3), 127.0, 127.6, 127.8, 128.0, 128.9, 129.0, 130.1, 130.5, 130.6 (CH_{Ar}), 130.7 (C_{Ar}), 131.4, 132.0 (CH_{Ar}), 135.9, 137.4, 138.3, 141.4, 143.5, 143.9, 146.2, 147.2 (C_{Ar}), 168.4 (COO), 197.5

(C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3055, 3021, 2962 (w), 1721, 1663 (s), 1597 (m), 1552, 1515 (w), 1434, 1303 (m), 1229 (s), 1150, 1085, 939 (m), 829, 760 (s), 584 (m) cm^{-1} . GC-MS (EI, 70 eV): m/z (%) = 448 (100) $[\text{M}]^+$, 419 (41), 387 (31), 359 (07), 267 (21), 209 (25), 165 (29), 152 (16). HRMS (EI): calcd. for $\text{C}_{31}\text{H}_{28}\text{O}_3$ $[\text{M}]^+$ 448.20330; found 448.203658.

Methyl 3'-Chloro-4-(3'-chlorobiphenylcarbonyl)biphenyl-2-carboxylate (5d): Compound **5d** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (6 mol-%), 3-chlorophenylboronic acid (165 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless oil; yield 146 mg (77%). ^1H NMR (300 MHz, CDCl_3): δ = 3.57 (s, 3 H, OCH_3), 7.00–7.06 (m, 4 H, ArH), 7.15–7.20 (m, 4 H, ArH), 7.26 (s, 1 H, ArH), 7.39–7.45 (m, 2 H, ArH), 7.52–7.58 (m, 2 H, ArH), 7.73 (dd, J = 1.9, 8.1 Hz, 1 H, ArH), 7.94 (d, J = 1.9 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.46 MHz, CDCl_3): δ = 52.2 (OCH_3), 126.3, 127.4, 127.5, 127.9, 128.1, 129.1, 129.2, 129.3, 129.5, 130.1 (CH_{Ar}), 130.5 (C_{Ar}), 130.7, 131.1, 131.7, 132.0 (CH_{Ar}), 134.0, 134.2, 136.5, 138.1, 140.0, 141.8, 141.9, 145.0 (C_{Ar}), 167.5 (COO), 196.8 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3059, 3024 (w), 1725, 1663, 1593 (s), 1557 (w), 1435 (m), 1303, 1231 (s), 1152, 1087 (m), 987 (w), 851 (m), 786 (s), 538 (m) cm^{-1} . GC-MS (EI, 70 eV): m/z (%) = 461 (47) $[\text{M}]^+$, 460 (97), 429 (18), 399 (70), 365 (12), 338 (10), 302 (09), 273 (74), 215 (88) 197 (36), 165 (28), 152 (100). HRMS (EI): calcd. for $\text{C}_{27}\text{H}_{18}\text{Cl}_2\text{O}_3$ $[\text{M}]^+$ 460.06275; found 460.062304.

Methyl 4'-Vinyl-4-(4'-vinylbiphenylcarbonyl)biphenyl-2-carboxylate (5e): Compound **5e** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (6 mol-%), 4-vinylphenylboronic acid (156 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a yellow solid; yield 132 mg (72%). M.p. 89–90 °C. ^1H NMR (300 MHz, CDCl_3): δ = 3.55 (s, 3 H, OCH_3), 5.16 (ddd, J = 0.8, 10.8, 24.2 Hz, 2 H, CH_2 vinyl), 5.65 (ddd, J = 0.8, 17.5, 33.0 Hz, 2 H, CH_2 vinyl), 6.59 (ddd, J = 10.9, 17.6, 28.5 Hz, 2 H, 2 CH_{vinyl}), 7.00–7.12 (m, 4 H, ArH), 7.14–7.18 (m, 2 H, ArH), 7.21 (s, 1 H, ArH), 7.34 (d, J = 8.1 Hz, 2 H, ArH), 7.40–7.50 (m, 4 H, ArH), 7.71 (dd, J = 1.8, 8.0 Hz, 1 H, ArH), 7.99 (d, J = 1.6 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.46 MHz, CDCl_3): δ = 52.1 (OCH_3), 114.2, 114.4, (2 CH_2 vinyl), 126.0, 126.2, 127.3, 128.3, 128.9, 129.2, 130.1, 130.6, 130.8, 131.6, 132.2, 136.2, 136.3 (CH_{Ar} , CH_{vinyl}), 136.7, 137.1, 138.2, 139.5, 139.6, 141.0, 146.1 (C_{Ar}), 168.2 (COO), 197.3 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3435, 3057, 3021, 2948 (w), 1721, 1663 (s), 1597 (m), 1548, 1514 (w), 1435, 1305 (m), 1230 (s), 1151, 1085, 939 (m), 838, 768 (s), 539 (m) cm^{-1} . GC-MS (EI, 70 eV): m/z (%) = 444 (100) $[\text{M}]^+$, 417 (05), 383 (08), 356 (04), 265 (19), 222 (11), 178 (30), 152 (07). HRMS (EI): calcd. for $\text{C}_{31}\text{H}_{24}\text{O}_3$ $[\text{M}]^+$ 444.17200; found 444.172615.

Methyl 4'-Chloro-4-(4'-chlorobiphenylcarbonyl)biphenyl-2-carboxylate (5f): Compound **5f** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (6 mol-%), 4-chlorophenylboronic acid (165 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless solid; yield 122 mg (64%). M.p. 49–50 °C. ^1H NMR (300 MHz, CDCl_3): δ = 3.56 (s, 3 H, OCH_3), 7.11 (s, 5 H, ArH), 7.20 (d, J = 8.4 Hz, 1 H, ArH), 7.30 (d, J = 8.6 Hz, 2 H, ArH), 7.38–7.50 (m, 5 H, ArH), 7.72 (dd, J = 1.8, 8.0 Hz, 1 H, ArH), 7.98 (d, J = 1.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.89 MHz, CDCl_3): δ = 52.2 (OCH_3), 127.6, 128.3, 128.5, 129.0, 129.4, 130.1, 130.3 (CH_{Ar}), 130.5 (C_{Ar}), 130.8, 130.9, 131.7, 132.2 (CH_{Ar}), 133.7, 134.1, 136.2, 138.1, 138.6, 140.1, 145.5 (C_{Ar}), 167.7 (COO), 196.9 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3058, 3027, 2949 (w), 1724, 1663 (s), 1599 (m), 1573, 1554 (w), 1472 (m), 1394 (w), 1230 (s), 1190 (w), 1152 (m), 1087 (s), 939 (m), 826 (s), 778, 535 (m) cm^{-1} . GC-MS (70 eV): m/z (%) = 460 $[\text{M}]^+$ (^{35}Cl), 461 (46), 460 (100), 429 (15),

401 (30), 372 (07), 273 (67), 215 (69), 197 (31), 180 (10) 165 (21), 152 (82). HRMS (EI): calcd. for $C_{27}H_{18}Cl_2O_3$ $[M]^+$ (^{35}Cl) 460.06275; found 460.062308.

Methyl 4'-Bromo-4-(4'-bromobiphenylcarbonyl)biphenyl-2-carboxylate (5g): Compound **5g** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol-%), 4-bromophenylboronic acid (212 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a yellow solid; yield 168 mg (74%). M.p. 49–51 °C. 1H NMR (300 MHz, $CDCl_3$): δ = 3.6 (s, 3 H, OCH_3), 7.12 (d, J = 5.9 Hz, 4 H, ArH), 7.43 (d, J = 6.1 Hz, 4 H, ArH), 7.40 (s, 1 H, ArH), 7.50–7.80 (m, 4 H, ArH), 7.91 (dd, J = 2.0, 5.9 Hz, 1 H, ArH), 8.19 (d, J = 1.7 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 52.3 (OCH_3), 122.7, 123.2, 126.7, 127.3, 128.2, 129.8, 130.2, 131.9, 132.5, 133.0, 133.7 (CH_{Ar}), 139.0, 139.3, 139.6, 146.3, 146.8, 147.0, 167.6 (C_{Ar}), 167.9, (COO), 191.3 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3063, 3031, 2951 (w), 1727, 1669 (s), 1477 (m), 1422 (s), 1307 (m), 1205 (s), 1167 (w), 1134 (m), 1086 (s), 944 (m), 884 (s), 781, 569 (m) cm^{-1} . MS (70 eV): m/z (%) = 550 (100) $[M]^+$ (^{81}Br), 513 (16), 410 (07), 379 (16), 319 (37), 298 (25), 215 (13), 181 (09), 151 (28) 121 (21), 82 (21), 69 (51). HRMS (EI): calcd. for $C_{27}H_{18}Br_2O_3$ $[M]^+$ (^{81}Br) 550.17200; found 550.172525.

Methyl 4-(3',4'-Dimethoxybiphenylcarbonyl)-3',4'-dimethoxybiphenyl-2-carboxylate (5h): Compound **5h** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol-%), 3,4-dimethoxyphenylboronic acid (192 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless solid; yield 132 mg (62%). M.p. 65–67 °C. 1H NMR (300 MHz, $CDCl_3$): δ = 3.54 (s, 3 H, OCH_3), 3.70 (s, 6 H, 2 OCH_3), 3.80 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 6.63 (d, J = 9.0 Hz, 1 H, ArH), 6.69–6.72 (m, 2 H, ArH), 6.73 (d, J = 2.7 Hz, 2 H, ArH), 6.80 (d, J = 7.7 Hz, 1 H, ArH), 7.19 (d, J = 2.2 Hz, 2 H, ArH), 7.22 (s, 1 H, ArH), 7.36–7.46 (m, 3 H, ArH), 7.69 (dd, J = 2.2, 8.2 Hz, 1 H, ArH), 7.86 (d, J = 1.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.1, 55.7, 55.8, 55.8, 55.9 ($SOCH_3$), 110.8, 111.0, 111.4, 112.3, 120.6, 121.6, 127.1, 128.6, 129.8, 130.4, 130.6 (CH_{Ar}), 130.8 (C_{Ar}), 131.2, 131.6, (CH_{Ar}), 132.6, 132.8, 135.6, 138.4, 140.7, 145.7, 148.4, 148.6, 148.7, 148.9 (C_{Ar}), 168.7 (COO), 197.7 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3057, 2998, 2950 (w), 1720 (m), 1662 (s), 1569 (w), 1518 (s), 1480 (m), 1437 (s), 1325 (m), 1243, 1214, 1171 (s), 1086, 941 (m), 881, 850, 756, 699 (s), 597 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 512 (100) $[M]^+$, 496 (04), 465 (02), 299 (03), 241 (09), 210 (04), 167 (01), 126 (02) 91 (01), 43 (05). HRMS (EI): calcd. for $C_{31}H_{28}O_7$ $[M]^+$ 512.18295; found 512.182285.

Methyl 4'-Hydroxy-4-(4'-hydroxybiphenylcarbonyl)biphenyl-2-carboxylate (5i): Compound **5i** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol-%), 4-hydroxyphenylboronic acid (146 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a yellow solid; yield 117 mg (67%). M.p. 134–136 °C. 1H NMR (300 MHz, $CDCl_3$): δ = 3.64 (s, 3 H, OCH_3), 6.52 (s, 1 H, OH), 6.55 (s, 1 H, OH), 6.66 (d, J = 7.9 Hz, 2 H, ArH), 6.97–7.02 (m, 4 H, ArH), 7.15 (s, 1 H, ArH), 7.19 (d, J = 2.2 Hz, 1 H, ArH), 7.39–7.41 (m, 3 H, ArH), 7.48–7.51 (m, 2 H, ArH), 7.66 (dd, J = 1.8, 8.0 Hz, 1 H, ArH), 7.90 (d, J = 1.7 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 115.4, 115.5, 126.8, 129.1, 129.5, 130.1, 130.4, 130.7, 131.0, 131.4 (CH_{Ar}), 131.7, 132.2 (C_{Ar}), 132.3 (CH_{Ar}), 135.5, 137.9, 141.3, 146.2, 155.6, 156.1 (C_{Ar}), 169.5 (COO), 198.4 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3352, 3060, 2951 (w), 1708, 1649 (m), 1589 (s), 1553 (w), 1517 (s), 1476 (m), 1398 (w), 1232, 1172 (s), 1153 (m), 1087 (s), 941 (m), 832 (s), 761, 660, 539 (m) cm^{-1} . GC–MS (70 eV): m/z (%) = 424 (96) $[M]^+$, 392 (100), 372 (24), 255 (18), 223 (35), 212 (16), 197 (58), 168 (14), 139 (23) 115 (13), 89 (02). HRMS (EI): calcd. for $C_{27}H_{20}O_5$ $[M]^+$ 424.13053; found 424.130645.

Methyl 3',4',5'-Trimethoxy-4-(3',4',5'-trimethoxybiphenylcarbonyl)biphenyl-2-carboxylate (5j): Compound **5j** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol-%), 3,4,5-trimethoxyphenylboronic acid (224 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a yellow solid; yield 136 mg (58%). M.p. 138–140 °C. 1H NMR (300 MHz, $CDCl_3$): δ = 3.52 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3), 3.69 (s, 6 H, 2 OCH_3), 3.78 (s, 6 H, 2 OCH_3), 3.81 (s, 3 H, OCH_3), 6.35 (s, 2 H, ArH), 6.39 (s, 2 H, ArH), 7.21 (dd, J = 1.1, 7.4 Hz, 1 H, ArH), 7.42–7.47 (m, 2 H, ArH), 7.52–7.56 (m, 2 H, ArH), 7.71 (d, J = 1.0 Hz, 2 H, ArH) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 55.9 (2 OCH_3), 56.1 (2 OCH_3), 60.6 (OCH_3), 60.9 (OCH_3), 105.2, 106.7, 127.6, 128.8, 129.4, 130.1, 130.8 (CH_{Ar}), 130.9 (C_{Ar}), 131.0, 131.1 (CH_{Ar}), 135.6, 135.8, 136.0, 137.3, 137.8, 138.4, 141.1, 145.6, 152.9, 153.0 (C_{Ar}), 168.7, (COO), 197.8 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3057, 2921, 2851 (w), 1722 (m), 1661 (s), 1583 (w), 1563 (s), 1461 (m), 1432 (s), 1377 (m), 1343, 1292, 1236, 1171 (s), 1067, 942 (m), 884, 875, 765, 679 (s), 532 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 572 (100) $[M]^+$, 556 (08), 525 (03), 286 (07), 240 (02), 197 (01), 127 (01), 69 (03). HRMS (EI): calcd. for $C_{33}H_{32}O_9$ $[M]^+$ 572.20408; found 572.204330.

Methyl 4'-Fluoro-4-(4'-fluorobiphenylcarbonyl)biphenyl-2-carboxylate (5k): Compound **5k** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 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 $^{-1}$ of triflate) as a yellow oil; yield 110 mg (62%). 1H NMR (300 MHz, $CDCl_3$): δ = 3.55 (s, 3 H, OCH_3), 6.82 (t, J = 8.7 Hz, 2 H, ArH), 6.9 (t, J = 8.6 Hz, 2 H, ArH), 7.10–7.17 (m, 4 H, ArH), 7.20 (s, 1 H, ArH), 7.38–7.50 (m, 4 H, ArH), 7.70 (dd, J = 2.2, 8.3 Hz, 1 H, ArH), 7.96 (d, J = 1.9 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 115.0 (d, $^3J_{C,F}$ = 7.5 Hz, CH_{Ar}), 115.4 (d, $^3J_{C,F}$ = 7.1 Hz, CH_{Ar}), 127.4, 128.9, 129.7, 129.8, 130.1, 130.6 (CH_{Ar}), 130.8 (d, $^3J_{C,F}$ = 4.4 Hz, CH_{Ar}), 131.6, 132.0 (CH_{Ar}), 136.1 (d, $^4J_{C,F}$ = 3.7 Hz, CF), 136.2, 138.2, 140.1, 145.5, 160.4 (d, $J_{C,F}$ = 20.1 Hz, CF), 164.3 (d, $J_{C,F}$ = 21.1 Hz, CF), 167.9 (COO), 197.1 (C=O) ppm. ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.34 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3062, 2950 (w), 1722, 1664 (s), 1557 (w), 1476, 1394, 1305, 1220 (m), 1154, 1085, 987 (m), 833, 760 (s), 657, 547 (m) cm^{-1} . GC–MS (EI, 70 eV): m/z (%) = 428 (100) $[M]^+$, 395 (09), 367 (30), 340 (10), 257 (51), 214 (10), 199 (59), 170 (47), 120 (02) 59 (02). HRMS (EI): calcd. for $C_{27}H_{18}F_2O_3$ $[M]^+$ 428.12185; found 428.121344.

Methyl 3'-Hydroxy-4-(3'-hydroxybiphenylcarbonyl)biphenyl-2-carboxylate (5l): Compound **5l** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), $Pd(PPh_3)_4$ (6 mol-%), 3-hydroxyphenylboronic acid (146 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless solid; yield 114 mg (65%). M.p. 48–49 °C. 1H NMR (300 MHz, $CDCl_3$): δ = 3.63 (s, 3 H, OCH_3), 6.75–6.88 (m, 5 H, ArH), 7.02 (dd, J = 1.1, 8.5 Hz, 1 H, ArH), 7.22 (d, J = 7.6 Hz, 2 H, ArH), 7.42–7.48 (m, 3 H, ArH), 7.54 (dd, J = 1.5, 8.0 Hz, 2 H, ArH), 7.75 (dd, J = 2.1, 7.7 Hz, 1 H, ArH), 8.02 (d, J = 1.8 Hz, 1 H, ArH), 11.84 (s, 2 H, OH) ppm. ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.4, (OCH_3), 115.0, 115.2, 116.2, 117.1, 118.5, 118.9, 119.2, 120.6, 129.5, 130.7, 131.1, 131.6, 132.2, 133.3, 136.7, (CH_{Ar}), 141.5, 142.2, 143.4, 144.2, 145.3, 147.2, 149.1, 155.6, 163.2 (C_{Ar}), 168.3 (COO), 197.5 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3071, 3048, 2962, 2839, 2831 (w), 1721, 1662 (s), 1593, 1582 (m), 1478, 1452 (m), 1391, 1343, 1301 (m), 1281, 1235, 1168 (s), 1092, 941 (s), 892, 863, 774, 694 (s), 591, 572, 530 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 424 (50) $[M]^+$, 410 (20), 390 (36), 380 (45), 341 (17), 312 (38), 285 (23), 249 (80), 221 (11), 134 (13), 110 (100), 91 (13), 64 (19). HRMS (EI): calcd. for $C_{27}H_{20}O_5$ $[M]^+$ 424.03841; found 424.038844.

Methyl 4'-(Trifluoromethyl)-4-[4'-(trifluoromethyl)biphenylcarbonyl]biphenyl-2-carboxylate (5m): Compound **5m** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd(PPh_3)₄ (6 mol-%), 4-(trifluoromethyl)phenylboronic acid (201 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless oil; yield 165 mg (76%). ¹H NMR (300 MHz, CDCl₃): δ = 3.55 (s, 3 H, OCH₃), 7.18–7.28 (m, 4 H, ArH), 7.31 (s, 1 H, ArH), 7.39–7.44 (m, 4 H, ArH), 7.48–7.50 (m, 1 H, ArH), 7.54–7.58 (m, 3 H, ArH), 7.74 (dd, J = 1.8, 8.0 Hz, 1 H, ArH), 8.02 (d, J = 1.8 Hz, 1 H, ArH) ppm. ¹³C NMR (75.46 MHz, CDCl₃): δ = 52.2 (OCH₃), 125.0 (q, ⁴ J_{FC} = 3.6 Hz, CH_{Ar}), 125.2 (q, ⁴ J_{FC} = 3.9 Hz, CH_{Ar}), 128.1, 128.4, 129.3, 129.4 (CH_{Ar}), 129.8 (C_{Ar}), 130.2 (CH_{Ar}), 130.4 (C_{Ar}), 130.8, 131.2, 131.8, 132.2 (CH_{Ar}), 136.7, 138.1, 140.1, 143.7, 143.9, 145.4, 146.2 (C_{Ar}), 167.7 (COO), 196.6 (C=O) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = –73.30 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3063, 2953, 2855 (w), 1727, 1666 (s), 1600 (w), 1437, 1321, 1233 (m), 1161, 1066, 940 (m), 838, 785, 705 (s), 671, 607, 539 (m) cm⁻¹. MS (EI, 70 eV): m/z (%) = 528 (10) [M]⁺, 291 (17), 290 (100), 271 (23), 240 (12), 201 (16), 162 (14), 97 (12), 84 (73) 71 (16), 57 (29). HRMS (EI): calcd. for C₂₉H₁₈F₆O₃ [M]⁺ 528.11547; found 528.115737.

Methyl 4-(2',5'-Dimethoxybiphenylcarbonyl)-2',5'-dimethoxybiphenyl-2-carboxylate (5n): Compound **5n** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd(PPh_3)₄ (6 mol-%), 2,5-dimethoxyphenylboronic acid (192 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless solid; yield 140 mg (67%). M.p. 150–152 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.27 (s, 3 H, OCH₃), 3.55 (s, 3 H, OCH₃), 3.57 (s, 3 H, OCH₃), 3.67 (s, 3 H, OCH₃), 3.72 (s, 3 H, OCH₃), 6.50 (d, J = 8.9 Hz, 1 H, ArH), 6.63 (dd, J = 3.6, 8.8 Hz, 1 H, ArH), 6.71–6.74 (m, 2 H, ArH), 6.78 (dd, J = 2.6, 7.7 Hz, 2 H, ArH), 7.23 (d, J = 7.9 Hz, 1 H, ArH), 7.37 (dd, J = 3.1, 7.3 Hz, 2 H, ArH), 7.46–7.52 (m, 2 H, ArH), 7.83 (dd, J = 1.8, 7.9 Hz, 1 H, ArH), 8.08 (d, J = 1.7 Hz, 1 H, ArH) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 51.8 (OCH₃), 54.8 (OCH₃), 55.7 (2 OCH₃), 55.8 (OCH₃), 111.1, 111.5, 113.5, 113.8, 116.0, 116.8, 127.0, 128.7, 130.9, 131.0, 131.1, 131.2, 132.5 (CH_{Ar}), 136.1, 137.8, 138.5, 142.3, 149.5, 150.2, 153.6, 153.7, 153.8, 156.0, 158.8 (C_{Ar}), 167.8 (COO), 195.7 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3070, 3050, 2970, 2842, 2832 (w), 1721, 1662 (s), 1594, 1582 (m), 1475, 1452 (m), 1391, 1341, 1301 (m), 1281, 1233, 1164 (s), 1091, 940 (s), 891, 862, 773, 691 (s), 592, 574, 530 (m) cm⁻¹. MS (EI, 70 eV): m/z (%) = 512 (40) [M]⁺, 448 (19), 409 (31), 385 (04), 340 (15), 323 (33), 288 (20), 250 (81), 195 (01), 182 (38), 167 (40), 151 (10), 138 (25), 123 (36), 94 (68), 84 (100), 65 (10), 47 (21), 43 (44). HRMS (EI): calcd. for C₃₁H₂₉O₇ [M + H]⁺ 513.19078; found 513.190802.

Methyl 2'-Methoxy-4-(2'-methoxybiphenylcarbonyl)biphenyl-2-carboxylate (5o): Compound **5o** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 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⁻¹ of triflate) as a colourless solid; yield 128 mg (69%). M.p. 139–140 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.32 (s, 3 H, OCH₃), 3.56 (s, 3 H, OCH₃), 3.61 (s, 3 H, OCH₃), 6.58 (d, J = 7.2 Hz, 1 H, ArH), 6.80–6.89 (m, 3 H, ArH), 6.92–6.98 (m, 2 H, ArH), 7.08–7.14 (m, 2 H, ArH), 7.16 (s, 1 H, ArH), 7.20–7.30 (m, 2 H, ArH), 7.37 (dd, J = 3.0, 7.7 Hz, 1 H, ArH), 7.46–7.52 (m, 1 H, ArH), 7.82 (dd, J = 2.0, 8.4 Hz, 1 H, ArH), 8.10 (d, J = 1.86 Hz, 1 H, ArH) ppm. ¹³C NMR (62.90 MHz, CDCl₃): δ = 51.8 (OCH₃), 54.4 (OCH₃), 55.2 (OCH₃), 109.9, 110.1, 110.3, 126.8, 128.6, 129.1, 129.4, 129.7, 130.8, 131.0, 131.1, 131.2, 132.5, 132.8 (CH_{Ar}), 135.1 (C_{Ar}), 136.8 (CH_{Ar}), 138.0, 138.5, 142.6, 144.2, 146.8, 155.2, 155.9, 164.5 (C_{Ar}), 167.9 (COO), 195.8 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3072, 3049, 2968, 2842, 2832 (w), 1719, 1664 (s), 1593, 1581 (m), 1475,

1452 (m), 1389, 1341, 1301 (m), 1281, 1231, 1164 (s), 1092, 941 (s), 891, 864, 779, 693 (s), 591, 573, 538 (m) cm⁻¹. MS (EI, 70 eV): m/z (%) = 452 (12) [M]⁺, 421 (100), 405 (01), 375 (01), 347 (08), 269 (03), 195 (09), 168 (05), 139 (05). HRMS (EI): calcd. for C₂₉H₂₄O₅ [M]⁺ 452.16183; found 452.161882.

Methyl 2'-Methoxy-4-(2'-methoxybiphenylcarbonyl)biphenyl-2-carboxylate (5p): Compound **5p** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd(PPh_3)₄ (6 mol-%), 4-*tert*-butylphenylboronic acid (188 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless solid; yield 150 mg (72%). M.p. 131–133 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.13 (s, 9 H, 3 CH₃), 1.26 (s, 9 H, 3 CH₃), 3.53 (s, 3 H, OCH₃), 7.06 (d, J = 8.6 Hz, 2 H, ArH), 7.10 (d, J = 4.2 Hz, 2 H, ArH), 7.14 (s, 1 H, ArH), 7.16 (d, J = 2.0 Hz, 1 H, ArH), 7.30 (d, J = 8.8 Hz, 2 H, ArH), 7.38–7.44 (m, 3 H, ArH), 7.48–7.53 (m, 2 H, ArH), 7.63 (dd, J = 1.9, 8.1 Hz, 1 H, ArH), 7.89 (d, J = 1.8 Hz, 1 H, ArH) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 31.3 (6 CH₃), 34.6 (2 C_tBu), 52.0 (OCH₃), 125.1, 125.2 (CH_{Ar}), 126.3 (C_{Ar}), 127.0, 127.8, 128.9, 129.0, 130.0, 130.4 (CH_{Ar}), 130.6 (C_{Ar}), 130.8, 131.3, 131.9 (CH_{Ar}), 136.1, 137.2, 138.4, 141.4, 145.9, 150.4, 150.8 (C_{Ar}), 168.5 (COO), 197.7 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3068, 3049, 2969, 2842, 2829 (w), 1721, 1663 (s), 1592, 1581 (m), 1472, 1452 (m), 1390, 1339, 1301 (m), 1279, 1235, 1162 (s), 1090, 941 (s), 891, 862, 771, 692 (s), 590, 572, 533 (m) cm⁻¹. MS (EI, 70 eV): m/z (%) = 504 (100) [M]⁺, 490 (32), 489 (89), 457 (42), 447 (14), 401 (12), 359 (01), 295 (03), 252 (02), 237 (39), 181 (24), 152 (09), 126 (03), 57 (24), 41 (10). HRMS (EI): calcd. for C₃₅H₃₆O₃ [M]⁺ 504.26590; found 504.265979.

Methyl 4-(3',5'-Dimethylbiphenylcarbonyl)-3',5'-dimethylbiphenyl-2-carboxylate (5q): Compound **5q** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 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⁻¹ of triflate) as a colourless solid; yield 144 mg (78%). M.p. 109–111 °C. ¹H NMR (300 MHz, CDCl₃): δ = 2.11 (s, 6 H, 2 CH₃), 2.26 (s, 6 H, 2 CH₃), 3.55 (s, 3 H, OCH₃), 6.69 (s, 1 H, ArH), 6.77 (d, J = 3.0 Hz, 2 H, ArH), 6.92 (s, 1 H, ArH), 7.16 (s, 1 H, ArH), 7.19 (d, J = 2.8 Hz, 1 H, ArH), 7.40 (d, J = 1.9 Hz, 1 H, ArH), 7.42 (s, 2 H, ArH), 7.49–7.54 (m, 2 H, ArH), 7.66 (dd, J = 1.9, 7.8 Hz, 1 H, ArH), 7.84 (d, J = 2.7 Hz, 1 H, ArH) ppm. ¹³C NMR (62.90 MHz, CDCl₃): δ = 21.0 (2 CH₃), 21.2 (2 CH₃), 52.0 (OCH₃), 125.8, 127.1, 128.9, 129.0, 129.5, 129.9, 130.3, 130.7, 131.1, 131.5 (CH_{Ar}), 136.1, 137.6, 137.7, 138.3, 139.9, 140.1, 141.7, 146.1 (C_{Ar}), 168.5 (COO), 197.6 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3068, 3048, 2969, 2837, 2821 (w), 1721, 1659 (s), 1593, 1579 (m), 1481, 1461 (m), 1389, 1331, 1301 (m), 1282, 1239, 1164 (s), 1090, 941 (s), 893, 863, 776, 691 (s), 593, 575, 530 (m) cm⁻¹. MS (EI, 70 eV): m/z (%) = 448 (87) [M]⁺, 433 (100), 401 (32), 387 (17), 267 (12), 209 (37), 179 (19), 165 (36), 115 (01), 77 (01). HRMS (EI): calcd. for C₃₁H₂₈O₃ [M]⁺ 448.20330; found 448.203841.

Methyl 3'-Bromo-4-(3'-bromobiphenylcarbonyl)biphenyl-2-carboxylate (5r): Compound **5r** was obtained from **4** (220 mg, 0.41 mmol), K_3PO_4 (261 mg, 1.23 mmol), Pd(PPh_3)₄ (6 mol-%), 3-bromophenylboronic acid (212 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless oil; yield 144 mg (64%). ¹H NMR (300 MHz, CDCl₃): δ = 3.57 (s, 3 H, OCH₃), 6.80 (d, J = 7.1 Hz, 2 H, ArH), 6.90 (t, J = 6.2 Hz, 2 H, ArH), 7.06 (d, J = 5.1 Hz, 2 H, ArH), 7.26 (s, 1 H, ArH), 7.39–7.58 (m, 6 H, ArH), 7.73 (dd, J = 2.5, 8.3 Hz, 1 H, ArH), 7.94 (d, J = 1.9 Hz, 1 H, ArH) ppm. ¹³C NMR (75.46 MHz, CDCl₃): δ = 52.2 (OCH₃), 126.3, 127.9, 128.1, 128.7, 129.1, 129.3, 129.5, 130.1, 130.7, 131.1, 131.6, 131.7, 132.0 (CH_{Ar}), 134.0, 135.2, 136.5, 137.1, 138.1, 139.9, 141.8, 141.9, 145.0 (C_{Ar}), 167.5 (COO), 196.8 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3059, 3024 (w), 1725, 1663, 1593 (s), 1557 (w), 1435 (m), 1303, 1231 (s), 1152,

1087 (m), 987 (w), 851 (m), 786 (s), 538 (m) cm^{-1} . GC–MS (EI, 70 eV): m/z (%) = 550 (47) [M^+ (^{81}Br , ^{79}Br)], 510 (46), 489 (48), 456 (21), 461 (92), 427 (16), 398 (72), 362 (10), 336 (12), 302 (09), 271 (72), 212 (86), 195 (32), 162 (26), 150 (100), 120 (45), 102 (36), 89 (42), 62 (46), 48 (28). HRMS (EI): calcd. for $\text{C}_{27}\text{H}_{18}\text{Br}_2\text{O}_3$ [M^+ (^{81}Br , ^{79}Br)] 550.24062; found 550.240120.

Methyl 3',5'-Dimethyl-4-[2-(trifluoromethanesulfonyloxy)benzoyl]biphenyl-2-carboxylate (6a): Compound **6a** was obtained from **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), 3,5-dimethylphenylboronic acid (52 mg, 0.35 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless oil; yield 107 mg (78%). ^1H NMR (300 MHz, CDCl_3): δ = 2.28 (s, 6 H, 2 CH_3), 3.58 (s, 3 H, OCH_3), 6.88 (s, 2 H, ArH), 6.96 (s, 1 H, ArH), 7.36 (s, 1 H, ArH), 7.47–7.61 (m, 4 H, ArH), 7.89 (dd, J = 2.1, 8.3 Hz, 1 H, ArH), 8.11 (d, J = 2.4 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.90 MHz, CDCl_3): δ = 21.2 (2 CH_3), 52.2 (OCH_3), 110.8 (C), 121.0 (q, J_{FC} = 320.7 Hz, CF_3), 122.6, 125.9, 128.1, 129.8, 131.0, 131.1, 131.3 (CH_{Ar}), 131.5, 132.0 (C_{Ar}), 132.2, 132.9 (CH_{Ar}), 135.0, 137.1, 139.8, 146.8, 147.6 (C_{Ar}), 168.4 (COO), 191.4 (C=O) ppm. ^{19}F NMR (282 MHz, CDCl_3): δ = –73.34 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3065, 3004, 2950 (w), 1724 (m), 1669 (s), 1560 (w), 1422 (s), 1308 (m), 1245, 1205, 1135 (s), 1092, 944 (m), 886, 855, 593 (s) cm^{-1} . MS (EI, 70 eV): m/z (%) = 492 (100) [M^+], 461 (19), 359 (03), 327 (31), 300 (14), 267 (19), 255 (07), 209 (03), 165 (09). HRMS (EI): calcd. for $\text{C}_{24}\text{H}_{19}\text{F}_3\text{O}_6\text{S}$ [M^+] 492.08490; found 492.084987.

Methyl 4'-Chloro-4-[2-(trifluoromethanesulfonyloxy)benzoyl]biphenyl-2-carboxylate (6b): Compound **6b** was obtained from **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), 4-chlorophenylboronic acid (54 mg, 0.35 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a yellow solid; yield 63 mg (45%). M.p. 105–106 °C. ^1H NMR (300 MHz, CDCl_3): δ = 3.61 (s, 3 H, OCH_3), 7.21 (d, J = 8.5 Hz, 2 H, ArH), 7.32 (s, 1 H, ArH), 7.35–7.42 (m, 3 H, ArH), 7.48 (dd, J = 1.0, 7.3 Hz, 1 H, ArH), 7.53–7.63 (m, 2 H, ArH), 7.90 (dd, J = 1.9, 8.0 Hz, 1 H, ArH), 8.20 (d, J = 1.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.46 MHz, CDCl_3): δ = 52.3 (OCH_3), 116.3 (C_{Ar}), 120.5 (q, J_{FC} = 321.1 Hz, CF_3), 122.7, 123.0, 128.2, 128.5, 129.5, 131.1, 131.8 (CH_{Ar}), 131.9 (C_{Ar}), 132.5, 133.1, (CH_{Ar}), 134.3, 135.5, 138.5, 146.3, 146.8 (C_{Ar}), 167.6 (COO), 191.3 (C=O) ppm. ^{19}F NMR (282 MHz, CDCl_3): δ = –73.29 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3066, 3033, 2952 (w), 1727, 1670 (s), 1603 (m), 1573, 1554 (w), 1475, 1308 (m), 1245, 1134, 1084 (s), 1040 (w), 944 (m), 827, 767, 592 (s) cm^{-1} . GC–MS (70 eV): m/z (%) = 498 (100) [M^+], 467 (30), 333 (26), 306 (14), 273 (32), 253 (07), 215 (06), 151 (07), 69 (06). HRMS (EI): calcd. for $\text{C}_{22}\text{H}_{14}\text{ClF}_3\text{O}_6\text{S}$ [M^+ (^{35}Cl)] 498.01462; found 498.014917.

Methyl 2'-Ethoxy-4-[2-(trifluoromethanesulfonyloxy)benzoyl]biphenyl-2-carboxylate (6c): Compound **6c** was obtained from **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), 2-ethoxyphenylboronic acid (58 mg, 0.35 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a yellow oil; yield 127 mg (89%). ^1H NMR (300 MHz, CDCl_3): δ = 1.32 (t, J = 3.1 Hz, 3 H, CH_3), 3.89 (s, 1 H, OCH_3), 4.05 (q, J = 4.1 Hz, 2 H, OCH_2), 6.82 (s, 1 H, ArH), 6.90–7.76 (m, 8 H, ArH), 7.91 (dd, J = 1.8, 8.1 Hz, 1 H, ArH), 8.21 (d, J = 1.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.46 MHz, CDCl_3): δ = 14.8 (CH_3), 51.8 (OCH_3), 63.9 (OCH_2), 111.2 (CH), 120.8 (q, J_{FC} = 320.1 Hz, CF_3), 122.6, 128.2, 129.6, 129.7, 131.1, 131.3, 131.8, 132.6, 132.9, 133.0 (CH_{Ar}), 135.0, 136.8, 137.5, 144.5, 146.8, 155.3, 163.9 (C_{Ar}), 167.6 (COO), 191.6 (C=O) ppm. ^{19}F NMR (282 MHz, CDCl_3): δ = –73.34 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3497, 3067, 3032 (w), 1725, 1669 (s), 1599 (m), 1575, 1500 (w), 1445, 1309, 1282 (m), 1245, 1206 (s), 1083, 945 (m), 884, 751 (s), 569 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 508 (100) [M^+], 477 (04),

463 (38), 448 (64), 415 (38), 315 (78), 287 (18), 271 (42), 253 (18), 223 (46), 139 (28), 121 (14), 69 (10). HRMS (EI): calcd. for $\text{C}_{24}\text{H}_{19}\text{F}_3\text{O}_7\text{S}$ [M^+] 508.07981; found 508.079693.

Methyl 2'-Bromo-4-[2-(trifluoromethanesulfonyloxy)benzoyl]biphenyl-2-carboxylate (6d): Compound **6d** was obtained from **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), 2-bromophenylboronic acid (70 mg, 0.35 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless solid; yield 119 mg (78%). M.p. 124–126 °C. ^1H NMR (300 MHz, CDCl_3): δ = 3.58 (s, 3 H, OCH_3), 7.13 (s, 1 H, ArH), 7.28–7.40 (m, 4 H, ArH), 7.48–7.62 (m, 4 H, ArH), 7.94 (dd, J = 2.1, 8.1 Hz, 1 H, ArH), 8.36 (d, J = 2.1 Hz, 1 H, ArH) ppm. ^{13}C NMR (75.46 MHz, CDCl_3): δ = 52.3 (OCH_3), 122.7 (q, J_{FC} = 321.4 Hz, CF_3), 127.1, 128.3, 129.2, 129.7, 129.8, 130.2, 131.3, 131.8, 132.3, 132.9, 133.2, (CH_{Ar}), 134.9, 135.0, 136.0, 141.5, 146.7, 146.8, 147.2 (C_{Ar}), 166.2 (COO), 191.4 (C=O) ppm. ^{19}F NMR (282 MHz, CDCl_3): δ = –73.29 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3053, 2953, 2923 (w), 1728, 1672 (s), 1567 (m), 1482 (w), 1309, 1294 (m), 1241, 1203 (s), 1168 (m), 1087 (s), 948 (m), 887, 769, 592 (s) cm^{-1} . MS (EI, 70 eV): m/z (%) = 543 (100) [M^+], 489 (19), 462 (21), 402 (13), 389 (29), 347 (31), 331 (12), 301 (48), 271 (24), 242 (75), 215 (7), 183 (5), 151 (11), 69 (15). HRMS (EI): calcd. for $\text{C}_{22}\text{H}_{14}\text{BrF}_3\text{O}_6\text{S}$ [M^+ (^{79}Br)] 543.96471; found 543.964520.

Methyl 3',4'-Dimethoxy-4-[2-(trifluoromethanesulfonyloxy)benzoyl]biphenyl-2-carboxylate (6e): Compound **6e** was obtained from **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), 3,4-dimethoxyphenylboronic acid (63 mg, 0.35 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a yellow solid; yield 65 mg (44%). M.p. 116–118 °C. ^1H NMR (300 MHz, CDCl_3): δ = 3.61 (s, 3 H, OCH_3), 3.83 (s, 3 H, OCH_3), 3.86 (s, 3 H, OCH_3), 6.81 (s, 1 H, ArH), 6.86 (d, J = 6.2 Hz, 1 H, ArH), 7.19 (s, 1 H, ArH), 7.37 (d, J = 6.9 Hz, 1 H, ArH), 7.45–7.85 (m, 4 H, ArH), 7.91 (dd, J = 3.9, 7.2 Hz, 1 H, ArH), 8.1 (d, J = 1.9 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.89 MHz, CDCl_3): δ = 52.3, 55.8, 55.9, (3 OCH_3), 110.9, 111.4 (CH_{Ar}), 120.7 (q, J_{FC} = 320.1 Hz, CF_3), 122.6, 123.0, 128.1, 130.9, 131.1, 131.4, 132.2, 132.9, (CH_{Ar}), 133.9, 134.3, 134.8, 144.8, 146.8, 146.9, 148.7, 149.1 (C_{Ar}), 168.6 (COO), 191.3 (C=O) ppm. ^{19}F NMR (282 MHz, CDCl_3): δ = –73.30 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3064, 2994, 2924 (w), 1726 (s), 1668, 1520, 1482 (m), 1421 (s), 1308 (m), 1243, 1206, 1170, 1086 (s), 944 (m), 891 (s), 830 (m), 763 (s), 732, 655 (m), 602 (s), 592 (m) cm^{-1} . MS (EI, 70 eV): m/z (%) = 524 (100) [M^+], 493 (03), 392 (11), 359 (29), 332 (07), 289 (04), 218 (02), 189 (02), 121 (04), 69 (05). HRMS (EI): calcd. for $\text{C}_{24}\text{H}_{19}\text{F}_3\text{O}_8\text{S}$ [M^+] 524.07472; found 524.074184.

Methyl 4'-Hydroxy-4-[2-(trifluoromethanesulfonyloxy)benzoyl]biphenyl-2-carboxylate (6f): Compound **6f** was obtained from **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), 4-hydroxyphenylboronic acid (48 mg, 0.35 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless oil; yield 85 mg (63%). ^1H NMR (300 MHz, CDCl_3): δ = 3.60 (s, 3 H, OCH_3), 6.78 (d, J = 6.9 Hz, 2 H, ArH), 7.13 (d, J = 6.2 Hz, 2 H, ArH), 7.18 (s, 1 H, OH), 7.37 (s, 1 H, ArH), 7.40–7.62 (m, 4 H, ArH), 7.89 (dd, J = 4.6, 6.9 Hz, 1 H, ArH), 8.13 (d, J = 5.8 Hz, 1 H, ArH) ppm. ^{13}C NMR (62.89 MHz, CDCl_3): δ = 52.3 (OCH_3), 115.3 (CH_{Ar}), 122.7 (q, J_{FC} = 321.2 Hz, CF_3), 128.1, 129.6, 131.0, 131.1, 131.6, 132.4, 132.9, 133.0 (CH_{Ar}), 133.8, 134.2, 134.8, 145.1, 146.8, 147.1, 155.9 (C_{Ar}), 168.5 (COO), 191.4 (C=O) ppm. ^{19}F NMR (282 MHz, CDCl_3): δ = –73.71 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3377, 3060, 2952 (w), 1715, 1667 (s), 1599 (m), 1555, 1520 (w), 1480, 1310 (m), 1245, 1134, 1086 (s), 1040 (w), 944 (m), 884, 767, 656, 592 (s) cm^{-1} . GC–MS (70 eV): m/z (%) = 480 (22) [M^+], 449 (05), 348 (100), 315 (45), 289 (87), 272 (22), 255 (57), 228 (24), 197

(16), 139 (22), 121 (88), 93 (18), 65 (13). HRMS (EI): calcd. for $C_{22}H_{15}F_3O_7S[M]^+$ 480.04851; found 480.048783.

Methyl 3',4',5'-Trimethoxy-4-[2-(trifluoromethanesulfonyloxy)benzoyl]biphenyl-2-carboxylate (6g): Compound **6g** was obtained from **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol-%), 3,4,5-trimethoxyphenylboronic acid (74 mg, 0.35 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a crystalline yellow solid; yield 68 mg (43%). M.p. 103–104 °C. ¹H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 9 H, 3 OCH₃), 3.83 (s, 3 H, OCH₃), 6.49 (s, 2 H, ArH), 7.40 (s, 1 H, ArH), 7.45–7.63 (m, 4 H, ArH), 7.91 (dd, J = 4.2, 6.4 Hz, 1 H, ArH), 8.08 (d, J = 6.2 Hz, 1 H, ArH) ppm. ¹³C NMR (75.46 MHz, $CDCl_3$): δ = 52.4 (OCH₃), 56.2 (2 OCH₃), 60.9 (OCH₃), 105.5 (CH_{Ar}), 122.7 (q, J_{FC} = 320.1 Hz, CF₃), 128.2, 129.0, 130.8, 131.1, 131.2, 132.2, 133.0 (CH_{Ar}), 134.1, 135.1, 135.9, 136.8, 137.6, 138.0, 146.8, 153.1 (C_{Ar}), 168.5 (COO), 191.3 (C=O) ppm. ¹⁹F NMR (282.40 MHz, $CDCl_3$): δ = -73.27 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3074, 3052, 2972, 2846, 2835 (w), 1723, 1667 (s), 1597, 1586 (m), 1479, 1454 (m), 1394, 1344, 1300 (m), 1287, 1237, 1169 (s), 1093, 942 (s), 890, 865, 776, 696 (s), 593, 579, 532 (m) cm⁻¹. MS (EI, 70 eV): m/z (%) = 554 (100) [M]⁺, 539 (08), 422 (04), 389 (17), 347 (09), 319 (04), 203 (03), 69 (07). HRMS (EI): calcd. for $C_{25}H_{21}F_3O_9S[M]^+$ 554.08529; found 554.085710.

Methyl 3'-Hydroxy-4-[2-(trifluoromethanesulfonyloxy)benzoyl]biphenyl-2-carboxylate (6h): Compound **6h** was obtained from **4** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol-%), 3-hydroxyphenylboronic acid (48 mg, 0.35 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a yellow oil; yield 97 mg (72%). ¹H NMR (300 MHz, $CDCl_3$): δ = 3.62 (s, 3 H, OCH₃), 6.91 (s, 1 H, ArH), 7.11 (s, 1 H, ArH), 7.32 (d, J = 6.2 Hz, 1 H, ArH), 7.34 (t, J = 2.2 Hz, 1 H, ArH), 7.53 (d, J = 7.0 Hz, 1 H, ArH), 7.54 (m, 4 H, ArH), 7.81 (dd, J = 6.4, 2.1 Hz, 1 H, ArH), 8.15 (d, J = 6.2 Hz, 1 H, ArH), 11.80 (s, 1 H, OH) ppm. ¹³C NMR (62.90 MHz, $CDCl_3$): δ = 52.4, (OCH₃), 118.8, (C_{Ar}), 118.6, 119.0 (CH_{Ar}), 120.6 (q, J_{FC} = 320.1 Hz, CF₃), 121.3, 128.2, 130.0, 130.9, 131.0, 131.8, 132.0, 133.2, 136.8, (CH_{Ar}), 137.6 141.1, 142.9, 143.6, 144.2, 149.2 (C_{Ar}), 168.5 (COO), 199.8 (C=O) ppm. ¹⁹F NMR (282.40 MHz, $CDCl_3$): δ = -73.27 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3071, 3049, 2965, 2832, 2826 (w), 1716, 1654 (s), 1582, 1578 (m), 1462, 1448 (m), 1389, 1339, 1301 (m), 1282, 1234, 1164 (s), 1091, 940 (s), 897, 862, 771, 692 (s), 591, 575, 531 (m) cm⁻¹. MS (EI, 70 eV): m/z (%) = 480 (40) [M]⁺, 448 (19), 421 (31), 387 (04), 347 (15), 315 (33), 287 (20), 255 (81), 226 (15), 139 (14), 121 (100), 93 (18), 69 (19), 44 (04). HRMS (EI): calcd. for $C_{22}H_{15}F_3O_7S[M]^+$ 480.04851; found 480.048846.

Methyl 3',5'-Dimethyl-4-[2-(trifluoromethanesulfonyloxy)benzoyl]biphenyl-2-carboxylate (7a): Compound **7a** was obtained from **6a** (100 mg, 0.20 mmol), K_3PO_4 (127 mg, 0.60 mmol), $Pd(PPh_3)_4$ (3 mol-%), 4-vinylphenylboronic acid (38 mg, 0.26 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless solid; yield 54 mg (60%). M.p. 123–125 °C. ¹H NMR (300 MHz, $CDCl_3$): δ = 2.24 (s, 6 H, 2 CH₃), 3.54 (s, 3 H, OCH₃), 5.14 (dd, J = 2.3, 6.8 Hz, 1 H, CH₂ vinyl), 5.63 (dd, J = 1.5, 8.1 Hz, 1 H, CH₂ vinyl), 6.59 (dd, J = 1.2, 6.8 Hz, 1 H, CH₂ vinyl), 6.76 (s, 2 H, ArH), 6.91 (s, 1 H, ArH), 7.13 (s, 1 H, ArH), 7.21 (d, J = 7.2 Hz, 2 H, ArH), 7.37 (d, J = 6.2 Hz, 2 H, ArH), 7.54–7.65 (m, 4 H, ArH), 7.71 (dd, J = 1.9, 8.0 Hz, 1 H, ArH), 7.95 (d, J = 1.8 Hz, 1 H, ArH) ppm. ¹³C NMR (75.47 MHz, $CDCl_3$): δ = 21.3 (2 CH₃), 52.0 (OCH₃), 113.1 (CH₂ vinyl), 124.8, 125.0, (C_{Ar}), 125.9, 126.2, 127.2, 128.9, 129.6, 130.6, 131.3, 132.2, 133.4, 134.3, 136.3 (CH_{Ar}, CH_{vinyl}), 137.1, 137.3, 138.5, 139.0, 139.9, 145.6 (C_{Ar}), 167.4 (COO), 196.3 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3057, 3019, 2948 (w), 1720, 1663 (s), 1596 (m), 1556, 1513 (w), 1435, 1306 (m), 1231 (s), 1151, 1099, 940

(m), 864, 786 (s), 694, 647, 575, 540 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 446 (100) [M]⁺, 414 (16), 385 (16), 358 (08), 267 (29), 207 (20), 194 (08), 178 (49), 152 (14), 77 (01). HRMS (EI): calcd. for $C_{31}H_{26}O_3[M]^+$ 446.18765; found 446.187064.

Methyl 4'-Hydroxy-4-(4'-vinylbiphenylcarbonyl)biphenyl-2-carboxylate (7b): Compound **7b** was obtained from **6f** (150 mg, 0.31 mmol), K_3PO_4 (197 mg, 0.93 mmol), $Pd(PPh_3)_4$ (3 mol-%), 4-vinylphenylboronic acid (59 mg, 0.40 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless oil; yield 100 mg (74%). ¹H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3 H, OCH₃), 5.15 (dd, J = 3.9, 7.2 Hz, 1 H, CH₂ vinyl), 5.63 (dd, J = 2.2, 8.2 Hz, 1 H, CH₂ vinyl), 6.60 (dd, J = 1.6, 6.8 Hz, 1 H, CH_{vinyl}), 6.72 (d, J = 6.2 Hz, 2 H, ArH), 6.90 (d, J = 6.8 Hz, 2 H, ArH), 7.01 (d, J = 6.4 Hz, 2 H, ArH), 7.14 (d, J = 6.7 Hz, 2 H, ArH), 7.31–7.56 (m, 4 H, ArH), 6.73 (dd, J = 1.4, 8.2 Hz, 2 H, ArH), 7.97 (d, J = 1.9 Hz, 1 H, ArH), 9.43 (s, 1 H, OH) ppm. ¹³C NMR (62.89 MHz, $CDCl_3$): δ = 52.1 (OCH₃), 114.1 (CH₂ vinyl), 115.2, 126.2, 127.2 (CH_{Ar}), 127.9, 128.0, 128.1 (C_{Ar}), 128.8, 129.2, 130.1, 130.6, 130.7, 131.5, 132.1, 135.2, 136.2 (CH_{Ar}, CH_{vinyl}), 136.7, 138.2, 139.5, 140.9, 146.1, 155.7 (C_{Ar}), 168.6 (COO), 197.4 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3417, 3060, 3022, 2946 (w), 1715, 1692 (s), 1597 (m), 1555, 1519 (w), 1434, 1306 (m), 1233 (s), 1153, 1087, 987, 939 (m), 831, 769 (s), 699, 607, 571, 539 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 434 (100) [M]⁺, 401 (07), 373 (09), 347 (04), 255 (20), 212 (09), 178 (30), 152 (07), 91 (03). HRMS (EI): calcd. for $C_{29}H_{22}O_4[M]^+$ 434.15126; found 434.151613.

Methyl 3',4'-Dimethoxy-4-(4'-vinylbiphenylcarbonyl)biphenyl-2-carboxylate (7c): Compound **7c** was obtained from **6e** (150 mg, 0.28 mmol), K_3PO_4 (178 mg, 0.84 mmol), $Pd(PPh_3)_4$ (3 mol-%), 4-vinylphenylboronic acid (53 mg, 0.36 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a yellow solid; yield 90 mg (65%). M.p. 75–76 °C. ¹H NMR (300 MHz, $CDCl_3$): δ = 3.57 (s, 3 H, OCH₃), 3.79 (s, 3 H, OCH₃), 3.84 (s, 3 H, OCH₃), 5.15 (dd, J = 1.6, 7.2 Hz, 1 H, CH₂ vinyl), 5.64 (dd, J = 3.2, 6.2 Hz, 1 H, CH_{vinyl}), 6.60 (dd, J = 7.2, 6.4 Hz, 1 H, CH₂ vinyl), 6.69 (d, J = 6.4 Hz, 1 H, ArH), 6.83 (d, J = 7.2 Hz, 1 H, ArH), 6.90 (d, J = 6.4 Hz, 2 H, ArH), 7.00 (s, 1 H, ArH), 7.12, (d, J = 6.1 Hz, 2 H, ArH), 7.21 (s, 1 H, ArH), 7.38–7.56 (m, 4 H, ArH), 7.73 (dd, J = 1.8, 8.0 Hz, 1 H, ArH), 7.94 (d, J = 1.6 Hz, 1 H, ArH) ppm. ¹³C NMR (75.47 MHz, $CDCl_3$): δ = 52.2, 55.9, 55.9 (3 OCH₃), 111.4 (CH_{vinyl}), 114.1 (CH₂ vinyl), 120.7, 126.2, 127.2, 128.8, 129.2, 130.1, 130.5, 130.7, 131.3, 132.0, 135.2, 136.2 (CH_{Ar}, CH_{vinyl}), 136.7, 138.3, 139.5, 140.9, 141.1, 142.3, 143.6, 145.9, 148.6, 149.0 (C_{Ar}), 168.7 (COO), 197.2 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3056, 2999 (w), 1720, 1663 (s), 1596 (m), 1554, 1519 (w), 1436, 1306 (m), 1232 (s), 1140, 1086, 940 (m), 843, 765 (s), 699, 606, 539 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 478 (100) [M]⁺, 418 (02), 387 (03), 300 (05), 225 (12), 178 (20), 145 (06), 96 (03), 74 (02). HRMS (ESI⁺): calcd. for $C_{31}H_{26}O_5[M]^+$ 478.18539; found 478.185821.

Methyl 3',4',5'-Trimethoxy-4-(4'-vinylbiphenylcarbonyl)biphenyl-2-carboxylate (7d): Compound **7d** was obtained from **6g** (150 mg, 0.27 mmol), K_3PO_4 (171 mg, 0.81 mmol), $Pd(PPh_3)_4$ (3 mol-%), 4-vinylphenylboronic acid (51 mg, 0.35 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless oil; yield 100 mg (72%). ¹H NMR (300 MHz, $CDCl_3$): δ = 3.57 (s, 3 H, OCH₃), 3.77 (s, 6 H, 2 OCH₃), 3.81 (s, 3 H, OCH₃), 5.15 (dd, J = 5.9, 6.2 Hz, 1 H, CH₂ vinyl), 5.64 (dd, J = 4.6, 7.5 Hz, 1 H, CH₂ vinyl), 6.37 (s, 2 H, ArH), 6.60 (dd, J = 7.1, 6.7 Hz, 1 H, CH_{vinyl}), 7.14 (d, J = 7.5 Hz, 2 H, ArH), 7.30 (d, J = 6.2 Hz, 2 H, ArH), 7.41–7.61 (m, 4 H, ArH), 7.73 (dd, J = 4.2, 7.2 Hz, 2 H, ArH), 7.93 (d, J = 6.2 Hz, 1 H, ArH) ppm. ¹³C NMR (75.46 MHz, $CDCl_3$): δ = 52.2, 56.1, 60.9 (3 OCH₃), 114.1 (CH₂ vinyl), 127.2 (CH_{Ar}), 127.9, 128.5 (C_{Ar}),

128.9, 129.2, 130.1, 130.4, 130.8, 131.2, 131.9, 134.9, 135.0, 136.2 (CH_{Ar}, CH_{vinyl}), 136.1, 136.7, 138.2, 139.5, 140.9, 141.7, 145.9, 153.0 (C_{Ar}), 168.6 (COO), 197.2 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3055, 2925, 2850 (w), 1722, 1663 (s), 1583 (m), 1556, 1512 (w), 1433, 1397, 1342 (m), 1296, 1233 (s), 1151, 1122, 1094, 1028, 940 (m), 880, 831, 769 721, (s), 693, 644, 539 (m) cm⁻¹. GC–MS (EI, 70 eV): *m/z* (%) = 508 (100) [M]⁺, 493 (35), 277 (09), 262 (21), 219 (35), 201 (11), 183 (31), 152 (13), 108 (19), 57 (18), 44 (29). HRMS (EI): calcd. for C₃₂H₂₈O₆ [M]⁺ 508.18704; found 508.187819.

Methyl 3'-Hydroxy-4-(4'-vinylbiphenylcarbonyl)biphenyl-2-carboxylate (7e): Compound **7e** was obtained from **6h** (150 mg, 0.31 mmol), K₃PO₄ (197 mg, 0.93 mmol), Pd(PPh₃)₄ (3 mol-%), 4-vinylphenylboronic acid (59 mg, 0.40 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a yellow oil; yield 87 mg (64%). ¹H NMR (300 MHz, CDCl₃): δ = 3.61 (s, 3 H, OCH₃), 4.12 (dd, *J* = 2.6, 8.1 Hz, 1 H, CH₂ vinyl), 5.19 (dd, *J* = 2.8, 8.6 Hz, 1 H, CH₂ vinyl), 5.77 (dd, *J* = 2.4, 8.2 Hz, 1 H, CH_{vinyl}), 6.72 (d, *J* = 6.2 Hz, 1 H, ArH), 6.90 (d, *J* = 6.8 Hz, 1 H, ArH), 7.11 (s, 1 H, ArH), 7.20 (t, *J* = 6.7 Hz, 1 H, ArH), 7.30 (s, 1 H, ArH), 7.35–7.45 (m, 4 H, ArH), 7.54–7.65 (m, 4 H, ArH), 7.73 (dd, *J* = 5.4, 6.2 Hz, 1 H, ArH), 7.97 (d, *J* = 2.9 Hz, 1 H, ArH) ppm. ¹³C NMR (62.89 MHz, CDCl₃): δ = 51.5 (OCH₃), 114.3 (CH₂ vinyl), 115.2, 117.2, 118.3, 126.2, 127.2 (CH_{Ar}), 127.9, 128.0, 128.1 (C_{Ar}), 128.8, 129.2, 130.1, 130.6, 130.7, 131.5, 132.1, 136.2 (CH_{Ar}, CH_{vinyl}), 136.5, 138.1, 139.2, 140.4, 146.0, 155.2 (C_{Ar}), 168.2 (COO), 197.2 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3415, 3029, 3021, 2943 (w), 1719, 1691 (s), 1596 (m), 1553, 1517 (w), 1431, 1303 (m), 1231 (s), 1159, 1083, 981, 938 (m), 833, 767 (s), 691, 605, 573, 534 (m) cm⁻¹. GC–MS (EI, 70 eV): *m/z* (%) = 434 (100) [M]⁺, 401 (16), 375 (40), 341 (07), 314 (09), 281 (33), 255 (33), 207 (87), 191 (09), 133 (06), 121 (46), 93 (10), 65 (09), 44 (15). HRMS (EI): calcd. for C₂₉H₂₂O₄ [M]⁺ 434.15180; found 434.151680.

Methyl 2'-Ethoxy-4-(4'-vinylbiphenylcarbonyl)biphenyl-2-carboxylate (7f): Compound **7f** was obtained from **6c** (150 mg, 0.29 mmol), K₃PO₄ (184 mg, 0.87 mmol), Pd(PPh₃)₄ (3 mol-%), 4-vinylphenylboronic acid (55 mg, 0.37 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless solid; yield 93 mg (68%). M.p. 143–145 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.32 (t, *J* = 3.1 Hz, 3 H, CH₃), 3.54 (s, 1 H, OCH₃), 3.82 (q, *J* = 4.1 Hz, 2 H, OCH₂), 6.82 (s, 1 H, ArH), 6.907.12 (m, 4 H, ArH), 7.20–7.30 (m, 4 H, ArH), 7.42 (d, *J* = 2.4, 8.2 Hz, 2 H, ArH), 7.52–7.62 (m, 2 H, ArH), 7.91 (dd, *J* = 2.8, 7.2 Hz, 1 H, ArH), 8.21 (d, *J* = 6.8 Hz, 1 H, ArH) ppm. ¹³C NMR (75.46 MHz, CDCl₃): δ = 14.4 (CH₃), 51.7 (OCH₃), 63.8 (OCH₂), 111.3 (CH_{vinyl}), 114.0 (CH₂ vinyl), 120.7, 126.2, 127.2 (CH_{Ar}), 128.0 (C_{Ar}), 128.9, 129.2, 129.7, 130.1, 131.0, 131.4, 132.3, 133.2, 134.6, 136.2 (CH_{Ar}, CH_{vinyl}), 136.6, 137.2, 138.4, 139.5, 140.9, 141.1, 143.4, 144.2, 155.2 (C_{Ar}), 167.7 (COO), 197.5 (C=O) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.34 (CF) ppm. IR (KBr): $\tilde{\nu}$ = 3491, 3062, 3029 (w), 1723, 1661 (s), 1592 (m), 1571, 1504 (w), 1442, 1307, 1281 (m), 1241, 1202 (s), 1081, 942 (m), 883, 750 (s), 567 (m) cm⁻¹. MS (EI, 70 eV): *m/z* (%) = 462 (100) [M]⁺, 430 (07), 417 (21), 401 (46), 373 (30), 357 (04), 313 (04), 283 (06), 223 (21), 201 (27), 178 (67), 139 (19). HRMS (EI): calcd. for C₃₁H₂₆O₄ [M]⁺ 462.18256; found 462.182193.

Methyl 4'-Vinyl-4-(4'-vinylbiphenyl-2-carbonyl)[1,1';2',1'']terphenyl-2-carboxylate (8): Compound **8** was obtained from **6d** (150 mg, 0.27 mmol), K₃PO₄ (171 mg, 0.81 mmol), Pd(PPh₃)₄ (6 mol-%), 4-vinylphenylboronic acid (103 mg, 0.70 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a yellow oil; yield 90 mg (62%). ¹H NMR (300 MHz, CDCl₃): δ = 3.45 (s, 3 H, OCH₃), 5.15 (ddd, *J* = 0.8, 5.7, 10.9 Hz, 2 H, CH₂ vinyl), 5.62 (ddd, *J* = 0.8, 5.0, 17.6 Hz, 2 H, CH₂ vinyl), 6.57 (ddd, *J* = 1.9, 10.9, 17.6 Hz, 2 H, 2

CH_{vinyl}), 6.86 (d, *J* = 6.4 Hz, 4 H, ArH), 6.95 (d, *J* = 6.9 Hz, 4 H, ArH), 7.12 (d, *J* = 5.7 Hz, 2 H, ArH), 7.20 (t, *J* = 4.9 Hz, 2 H, ArH), 7.31 (s, 1 H, ArH), 7.40 (dd, *J* = 4.5, 6.7 Hz, 1 H, ArH), 7.43–7.52 (m, 4 H, ArH), 7.94 (d, *J* = 6.8 Hz, 1 H, ArH) ppm. ¹³C NMR (62.89 MHz, CDCl₃): δ = 52.0 (OCH₃), 113.8, 114.3 (2 CH₂ vinyl), 115.4 (C_{Ar}), 125.7, 126.1, 127.3, 128.9, 129.2, 129.8, 130.0, 130.7, 131.3, 131.9, 132.0, 133.2, 134.6, 136.2, 136.4 (CH_{Ar}, CH_{vinyl}), 136.6, 138.2, 138.9, 139.5, 139.8, 140.0, 140.7, 141.2, 143.4, 146.9 (C_{Ar}), 167.2 (COO), 197.4 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3056, 3019, 2948 (w), 1724, 1662 (s), 1596 (m), 1555, 1514 (w), 1435, 1399, 1305 (m), 1258, 1230 (s), 1152, 1085, 988, 941 (m), 843, 765 (s), 694, 633, 596, 540 (m) cm⁻¹. GC–MS (EI, 70 eV): *m/z* (%) = 520 (16) [M]⁺, 488 (100), 417 (14), 386 (32), 357 (07), 309 (20), 262 (48), 207 (50), 179 (77), 152 (20), 108 (13). HRMS (EI): calcd. for C₃₇H₂₈O₃ [M]⁺ 520.20330; found 520.203889.

Methyl 4'-Vinyl-4-(4'-vinyl[1,1';4',1'']terphenyl-2-carbonyl)-[1,1';4',1'']terphenyl-2-carboxylate (9): Compound **9** was obtained from **5g** (150 mg, 0.27 mmol), K₃PO₄ (171 mg, 0.81 mmol), Pd(PPh₃)₄ (6 mol-%), 4-vinylphenylboronic acid (103 mg, 0.70 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless solid; yield 118 mg (72%). M.p. 169–171 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.58 (s, 3 H, OCH₃), 5.05 (dd, *J* = 6.2, 5.4 Hz, 2 H, CH₂ vinyl), 5.16 (dd, *J* = 5.2, 6.4 Hz, 2 H, CH₂ vinyl), 5.23 (d, *J* = 6.4, 5.8 Hz, 2 H, CH_{vinyl}), 5.48 (d, *J* = 6.4 Hz, 8 H, ArH), 7.44 (d, *J* = 6.4 Hz, 4 H, ArH), 7.59 (d, *J* = 6.2 Hz, 4 H, ArH), 7.65–8.00 (m, 7 H, ArH) ppm. ¹³C NMR (62.89 MHz, CDCl₃): δ = 52.1 (OCH₃), 114.1 (CH₂ vinyl), 126.2, 127.0, 127.9, 128.0, 128.9, 129.2, 130.1, 130.7, 131.1, 131.8, 132.2, 133.0 (CH_{Ar}, CH_{vinyl}), 134.9, 135.0, 136.1, 136.8, 138.2, 139.7, 140.1, 141.0, 146.0 (C_{Ar}), 168.2 (COO), 197.3 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3427, 2948 (w), 1722, 1666 (s), 1596 (m), 1556, 1514 (w), 1434, 1305 (m), 1231 (s), 1152, 1093, 999, 939 (m), 843, 818, 768 (s), 726, 691, 649, 540 (m) cm⁻¹. GC–MS (EI, 70 eV): *m/z* (%) = 596 (10) [M]⁺, 540 (30), 502 (12), 480 (21), 439 (15), 414 (16), 385 (16), 358 (08), 267 (29), 207 (20), 194 (08), 178 (49), 152 (14), 77 (10). HRMS (EI): calcd. for C₄₃H₃₂O₃ [M]⁺ 596.71216; found 596.712403.

Methyl 4-(1,1';3',1'')Terphenyl-2-carbonyl[1,3';1',1'']terphenyl-2-carboxylate (10): Compound **10** was obtained from **5r** (150 mg, 0.27 mmol), K₃PO₄ (171 mg, 0.81 mmol), Pd(PPh₃)₄ (6 mol-%), phenylboronic acid (85 mg, 0.70 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a yellow oil; yield 90 mg (60%). ¹H NMR (300 MHz, CDCl₃): δ = 3.46 (s, 3 H, OCH₃), 7.10 (s, 1 H, ArH), 7.23 (s, 2 H, ArH), 7.25–7.50 (m, 17 H, ArH), 7.57 (t, *J* = 5.9 Hz, 1 H, ArH), 7.65 (d, *J* = 6.2 Hz, 2 H, ArH), 7.73 (dd, *J* = 6.2, 4.6 Hz, 1 H, ArH), 7.94 (d, *J* = 6.8 Hz, 1 H, ArH) ppm. ¹³C NMR (62.89 MHz, CDCl₃): δ = 52.0 (OCH₃), 126.2, 127.0, 127.5, 127.9, 128.1, 128.7, 129.0, 130.9, 131.5, 131.8, 134.9, 135.0, 135.8 (CH_{Ar}), 136.3, 138.5, 140.6, 141.1, 142.0, 143.0, 146.2, 166.3 (C_{Ar}), 168.1 (COO), 197.5 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3055, 3028, 2947 (w), 1720, 1662 (s), 1595 (m), 1572, 1487, (w), 1434, 1303 (m), 1210 (s), 1151, 1086, 1031, 940 (m), 896, 783 (s), 696, 628, 539 (m) cm⁻¹. GC–MS (EI, 70 eV): *m/z* (%) = 544 (20) [M]⁺, 520 (20), 490 (10), 465 (12), 430 (19), 414 (16), 385 (16), 358 (08), 267 (29), 207 (20), 194 (08), 178 (49), 152 (14), 77 (01). HRMS (EI): calcd. for C₃₉H₂₈O₃ [M]⁺ 544.29380; found 544.293634.

(3'-Methoxybiphenyl-2-yl)(3'-methoxybiphenyl-4-yl)methanone (13a): Compound **13a** was obtained from **12** (200 mg, 0.41 mmol), K₃PO₄ (260 mg, 1.23 mmol), Pd(PPh₃)₄ (6 mol-%), 3-methoxyphenylboronic acid (162 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless solid; yield 128 mg (78%). M.p. 152–154 °C. ¹H NMR (300 MHz, CDCl₃): δ = 3.61, 3.78 (s, 6 H, 2 OCH₃), 6.61–6.64 (m, 2 H, ArH), 6.75–6.86 (m, 3 H, ArH), 6.99–

7.07 (m, 2 H, ArH), 7.26 (t, $J = 7.95$ Hz, 1 H, ArH), 7.39–7.51 (m, 6 H, ArH), 7.63–7.66 (m, 2 H, ArH) ppm. ^{13}C NMR (75.47 MHz, CDCl_3): $\delta = 55.1, 55.3$ (2 OCH_3), 113.0, 113.2, 113.4, 114.4, 119.7, 121.5, 126.8, 127.1, 128.5, 129.3, 129.9, 130.2, 130.4, 131.0 (CH_{Ar}), 136.2, 139.0, 140.8, 141.3, 141.5, 145.2, 159.3, 160.0 (C_{Ar}), 198.2 ($\text{C}=\text{O}$) ppm. IR (KBr): $\tilde{\nu} = 3058, 2998, 2834$ (w), 1725 (w), 1661, 1581, 1477, 1435, 1398, 1307 (m), 1278, 1210 (s), 1170, 1150, 1049, 1027, 1019 (m), 929 (s), 844, 775 (m), 757, 689 (s), 672, 617, 565, 531 (m cm^{-1}). GC–MS (EI, 70 eV): m/z (%) = 394 (100) [$\text{M}]^+$, 363 (15), 281 (04), 211 (47), 168 (23), 139 (19), 44 (05). HRMS (EI): calcd. for $\text{C}_{27}\text{H}_{22}\text{O}_3$ [$\text{M}]^+$ 394.15689; found 394.156780.

(2'-Fluorobiphenyl-2-yl)(2'-fluorobiphenyl-4-yl)methanone (13b):

Compound **13b** was obtained from **12** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (6 mol-%), 2-fluorophenylboronic acid (148 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless crystalline solid; yield 108 mg (70%). M.p. 146–148 °C. ^1H NMR (300 MHz, CDCl_3): $\delta = 6.80$ (t, $J = 8.67$ Hz, 1 H, ArH), 6.93–7.00 (m, 2 H, ArH), 7.04–7.12 (m, 3 H, ArH), 7.17–7.23 (m, 3 H, ArH), 7.34–7.42 (m, 3 H, ArH), 7.46–7.50 (m, 2 H, ArH), 7.67 (d, $J = 8.25$ Hz, 2 H, ArH) ppm. ^{13}C NMR (75.47 MHz, CDCl_3): $\delta = 115.5$ (d, $^2J_{\text{C,F}} = 22.3$ Hz, CH_{Ar}), 116.3 (d, $^2J_{\text{C,F}} = 22.6$ Hz, CH_{Ar}), 124.2 (d, $^4J_{\text{C,F}} = 3.6$ Hz, CH_{Ar}), 124.5 (d, $^4J_{\text{C,F}} = 3.6$ Hz, CH_{Ar}), 127.5 (CH_{Ar}), 128.7 (d, $^4J_{\text{C,F}} = 3.1$ Hz, CH_{Ar}), 129.2 (CH_{Ar}), 129.5 (d, $^3J_{\text{C,F}} = 8.1$ Hz, CH_{Ar}), 129.7 (d, $^3J_{\text{C,F}} = 8.3$ Hz, CH_{Ar}), 130.1, 130.6, 131.2 (CH_{Ar}), 131.4 (d, $^4J_{\text{C,F}} = 3.2$ Hz, CH_{Ar}), 135.3, 136.3, 139.1, 140.1, 157.4, 158.1, 160.7, 161.4 (C_{Ar}), 197.0 ($\text{C}=\text{O}$) ppm. ^{19}F NMR (282 MHz, CDCl_3): $\delta = -117.3, -115.6$ (2 CF) ppm. IR (KBr): $\tilde{\nu} = 3310, 3039, 2954, 2852, 1728$ (w), 1665 (s), 1606, 1593, 1567, 1447, 1404, 1313, 1280, 1260, 1201, 1187, 1156, 1103, 1079, 1036, 975, 963, 945, 883, 844, 790 (m), 728, 719 (s), 694, 638, 614, 559 (w) cm^{-1} . GC–MS (EI, 70 eV): m/z (%) = 370 (100) [$\text{M}]^+$, 351 (26), 199 (72), 170 (48), 151 (10). HRMS (EI): calcd. for $\text{C}_{25}\text{H}_{16}\text{F}_2\text{O}$ [$\text{M}]^+$ 370.11637; found 370.116915.

(4'-Methoxybiphenyl-2-yl)(3'-methoxybiphenyl-4-yl)methanone (13c):

Compound **13c** was obtained from **12** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (6 mol-%), 4-methoxyphenylboronic acid (161 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a yellow solid; yield 112 mg (68%). M.p. 138–140 °C. ^1H NMR (300 MHz, CDCl_3): $\delta = 3.61, 3.78$ (s, 6 H, 2 OCH_3), 6.61–6.64 (m, 2 H, ArH), 6.75–6.86 (m, 3 H, ArH), 6.99–7.07 (m, 2 H, ArH), 7.26 (t, $J = 7.95$ Hz, 1 H, ArH), 7.39–7.51 (m, 6 H, ArH), 7.63–7.66 (m, 2 H, ArH) ppm. ^{13}C NMR (75.47 MHz, CDCl_3): $\delta = 55.1, 55.3$ (2 OCH_3), 113.0, 113.4, 114.4, 119.7, 121.5, 126.8, 127.1, 128.5, 129.9, 130.4 (CH_{Ar}), 136.1, 139.2, 140.6, 141.4, 141.8, 145.6, 159.8, 160.3 (C_{Ar}), 198.3 ($\text{C}=\text{O}$) ppm. IR (KBr): $\tilde{\nu} = 3033, 2965, 2839$ (w), 1671, 1594, 1526, 1480, 1442, 1399, 1297, 1267 (m), 1248, 1226, 1189, 1133, 1090, 1030 (m), 1010, 936, 876, 824, 768 (s), 743, 717, 690, 627, 616, 542 (m) cm^{-1} . GC–MS (EI, 70 eV): m/z (%) = 394 (100) [$\text{M}]^+$, 363 (15), 281 (04), 211 (47), 168 (23), 139 (19), 44 (05). HRMS (EI): calcd. for $\text{C}_{27}\text{H}_{22}\text{O}_3$ [$\text{M}]^+$ 394.15689; found 394.156342.

(4'-Vinylbiphenyl-2-yl)(4'-vinylbiphenyl-4-yl)methanone (13d):

Compound **13d** was obtained from **12** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (6 mol-%), 4-vinylphenylboronic acid (157 mg, 1.06 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless oil; yield 107 mg (66%). ^1H NMR (300 MHz, CDCl_3): $\delta = 5.01$ – 5.11 (dd, $J = 1.7, 10.8$ Hz, 1 H, CH_2 vinyl), 5.19–5.24 (dd, $J = 1.7, 11.2$ Hz, 1 H, CH_2 vinyl), 5.54–5.61 (dd, $J = 1.7, 17.5$ Hz, 1 H, CH_2 vinyl), 5.68–5.74 (dd, $J = 1.6, 17.5$ Hz, 1 H, CH_2 vinyl), 6.47–6.57 (dd, $J = 10.8, 17.5$ Hz, 1 H, CH_{vinyl}), 6.62–6.72 (dd, $J = 10.8, 17.5$ Hz, 1 H, CH_{vinyl}), 7.18 (m, 4 H, ArH),

7.31–7.38 (m, 4 H, ArH), 7.40–7.48 (m, 4 H, ArH), 7.54 (s, 1 H, ArH), 7.66 (d, $J = 8.5$ Hz, 2 H, ArH) ppm. ^{13}C NMR (75.47 MHz, CDCl_3): $\delta = 114.2, 114.8$ (2 CH_2 vinyl), 125.3, 125.7, 126.3, 126.6, 126.9, 127.2, 128.6, 129.2, 129.7, 130.0, 130.3, 130.7 (CH_{Ar}), 136.1 (C_{Ar}), 136.3, 136.5 (CH_{Ar} , CH_{vinyl}), 136.8, 138.3, 138.9, 139.7, 140.2, 140.7, 146.4 (C_{Ar}), 198.2 ($\text{C}=\text{O}$) ppm. IR (KBr): $\tilde{\nu} = 3043, 3029, 2952, 2847, 1721$ (w), 1657, 1597 (s), 1579, 1513, 1475, 1447, 1403, 1317 (m), 1266, 1253, 1235 (s), 1187, 1153, 1041, 987 (m), 925 (s), 861, 803, 783, 708, 665, 627, 543 (m) cm^{-1} . GC–MS (EI, 70 eV): m/z (%) = 386 (100) [$\text{M}]^+$, 369 (8), 281 (07), 253 (04), 207 (56), 193 (08), 178 (51), 152 (16). HRMS (EI): calcd. for $\text{C}_{29}\text{H}_{22}\text{O}$ [$\text{M}]^+$ 386.16652; found 386.166535.

2-(3'-Methoxybiphenylcarbonyl)phenyl Trifluoromethanesulfonate (14a):

Compound **14a** was obtained from **12** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), 3-methoxyphenylboronic acid (80 mg, 0.53 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless oil; yield 124 mg (68%). ^1H NMR (300 MHz, CDCl_3): $\delta = 3.77$ (s, 3 H, OCH_3), 6.86 (dd, $J = 1.8, 8.10$ Hz, 1 H, ArH), 7.07–7.14 (m, 2 H, ArH), 7.27–7.38 (m, 2 H, ArH), 7.43 (d, $J = 7.11$ Hz, 1 H, ArH), 7.50–7.54 (m, 3 H, ArH), 7.61 (d, $J = 8.31$ Hz, 1 H, ArH), 7.80 (d, $J = 8.28$ Hz, 2 H, ArH) ppm. ^{13}C NMR (62.90 MHz, CDCl_3): $\delta = 55.3$ (OCH_3), 113.1, 113.7, 119.8 (CH_{Ar}), 121.0 (q, $J_{\text{FC}} = 320$ Hz, CF_3), 122.5, 127.2, 128.0, 130.0, 130.7, 131.1, 132.6 (CH_{Ar}), 135.2, 141.1, 146.3, 146.7, 147.2, 160.0 (C_{Ar}), 198.2 ($\text{C}=\text{O}$) ppm. ^{19}F NMR (282 MHz, CDCl_3): $\delta = -73.3$ (CF_3) ppm. IR (KBr): $\tilde{\nu} = 3066, 2921, 1727$ (w), 1665 (m), 1599 (s), 1479 (m), 1421 (s), 1400, 1309, 1293, 1274, 1247 (m), 1205, 1135 (s), 1086, 1051, 1028, 1013 (m), 936, 879, 845, 765 (s), 748, 691, 618, 568 (m) cm^{-1} . GC–MS (EI, 70 eV): m/z (%) = 436 (100) [$\text{M}]^+$, 303 (40), 287 (08), 260 (18), 231 (07), 211 (22), 168 (06), 139 (13), 69 (04). HRMS (EI): calcd. for $\text{C}_{21}\text{H}_{15}\text{F}_3\text{O}_5\text{S}$ [$\text{M}]^+$ 436.05868; found 436.058091.

2-(2',5'-Dimethoxybiphenylcarbonyl)phenyl Trifluoromethanesulfonate (14b):

Compound **14b** was obtained from **12** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), 2,5-dimethoxyphenylboronic acid (96 mg, 0.53 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a reddish solid; yield 140 mg (72%). M.p. 138–140 °C. ^1H NMR (300 MHz, CDCl_3): $\delta = 3.66$ (s, 6 H, 2 OCH_3), 6.60 (d, $J = 8.4$ Hz, 2 H, ArH), 7.17–7.26 (m, 2 H, ArH), 7.35–7.43 (m, 3 H, ArH), 7.52–7.58 (m, 2 H, ArH), 7.77 (d, $J = 8.37$ Hz, 2 H, ArH) ppm. ^{13}C NMR (75.47 MHz, CDCl_3): $\delta = 55.9$ (2 OCH_3), 104.2 (CH_{Ar}), 118.2 (C_{Ar}), 120.6 (q, $J_{\text{FC}} = 320$ Hz, CF_3), 122.4, 127.8, 129.5, 129.6, 130.0, 131.3, 131.4, 132.3 (CH_{Ar}), 132.7, 133.0, 134.5, 140.6, 146.9, 157.5 (C_{Ar}), 192.3 ($\text{C}=\text{O}$) ppm. ^{19}F NMR (282 MHz, CDCl_3): $\delta = -74.6$ (CF_3) ppm. IR (KBr): $\tilde{\nu} = 3068, 3002, 2839, 1726$ (w), 1665, 1603, 1588 (m), 1471 (s), 1402, 1294, 1272 (m), 1204, 1135, 1103, 1087 (s), 1036, 935 (m), 878, 782, 725 (s), 693, 620, 569 (m) cm^{-1} . GC–MS (EI, 70 eV): m/z (%) = 466 (100) [$\text{M}]^+$, 317 (25), 287 (15), 241 (12), 198 (05), 155 (04), 69 (04). HRMS (EI): calcd. for $\text{C}_{22}\text{H}_{17}\text{F}_3\text{O}_6\text{S}$ [$\text{M}]^+$ 466.06825; found 466.068720.

2-(2',6'-Dimethoxybiphenylcarbonyl)phenyl Trifluoromethanesulfonate (14c):

Compound **14c** was obtained from **12** (200 mg, 0.41 mmol), K_3PO_4 (260 mg, 1.23 mmol), $\text{Pd}(\text{PPh}_3)_4$ (3 mol-%), 2,6-dimethoxyphenylboronic acid (96 mg, 0.53 mmol) and 1,4-dioxane (5 mL mmol $^{-1}$ of triflate) as a colourless solid; yield 124 mg (64%). M.p. 162–164 °C. ^1H NMR (300 MHz, CDCl_3): $\delta = 3.65$ (s, 6 H, 2 OCH_3), 6.57 (d, $J = 8.4$ Hz, 2 H, ArH), 7.21 (t, $J = 8.37$ Hz, 1 H, ArH), 7.33–7.41 (m, 4 H, ArH), 7.50–7.56 (m, 2 H, ArH), 7.75 (d, $J = 8.37$ Hz, 2 H, ArH) ppm. ^{13}C NMR (62.90 MHz, CDCl_3): $\delta = 55.8$ (2 OCH_3), 104.2 (CH_{Ar}), 118.2 (C_{Ar}), 120.6 (q, $J_{\text{FC}} = 320$ Hz, CF_3), 122.4, 127.8, 129.5, 129.6, 131.3, 131.4, 132.3

(CH_{Ar}), 132.6, 134.5, 140.6, 146.9, 157.4 (C_{Ar}), 192.2 (C=O) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.5 (CF₃) ppm. IR (KBr): $\tilde{\nu}$ = 3065, 3004, 2841, 1721 (w), 1667, 1605, 1587 (m), 1473 (s), 1403, 1295, 1273 (m), 1205, 1137, 1105, 1081 (s), 1033, 931 (m), 877, 781, 722 (s), 693, 620, 569 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 466 (100) [M]⁺, 317 (23), 287 (14), 241 (11), 198 (05), 155 (04), 69 (04). HRMS (EI): calcd. for C₂₂H₁₇F₃O₆S [M]⁺ 466.06925; found 466.069423.

2-(2'-Ethoxybiphenylcarbonyl)phenyl Trifluoromethanesulfonate (14d): Compound **14d** was obtained from **12** (200 mg, 0.41 mmol), K₃PO₄ (260 mg, 1.23 mmol), Pd(PPh₃)₄ (3 mol-%), 2-ethoxyphenylboronic acid (88 mg, 0.53 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless solid; yield 144 mg (76%). M.p. 150–152 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.25 (t, J = 6.99 Hz, 3 H, CH₃), 3.97 (q, J = 6.9 Hz, 2 H, OCH₂), 6.89–6.98 (m, 2 H, ArH), 7.23–7.28 (m, 2 H, ArH), 7.34–7.44 (m, 2 H, ArH), 7.51–7.61 (m, 4 H, ArH), 7.76 (d, J = 8.52 Hz, 2 H, ArH) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 14.7 (CH₃), 64.1 (OCH₂), 112.6 (CH_{Ar}), 120.6 (q, J_{FC} = 321.0 Hz, CF₃), 120.9, 122.4, 128.0 (CH_{Ar}), 129.3 (C_{Ar}), 129.6, 129.7, 129.8, 130.7, 131.2, 132.4 (CH_{Ar}), 132.7, 134.6, 144.5, 146.8, 155.9 (C_{Ar}), 192.3 (C=O) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.4 (CF₃) ppm. IR (KBr): $\tilde{\nu}$ = 3068, 3034, 2925, 1722 (w), 1665, 1602 (m), 1581, 1511, 1446 (w), 1422 (s), 1312, 1264 (m), 1204, 1135 (s), 1086, 1039, 935 (m), 879, 750 (s), 693, 668, 646, 590 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 450 (100) [M]⁺, 422 (28), 289 (30), 215 (08), 197 (21), 168 (13), 121 (17), 92 (04), 69 (05). HRMS (EI): calcd. for C₂₂H₁₇F₃O₅S [M]⁺ 450.07433; found 450.074512.

2-(3'-Vinylbiphenylcarbonyl)phenyl Trifluoromethanesulfonate (14e): Compound **14e** was obtained from **12** (200 mg, 0.41 mmol), K₃PO₄ (260 mg, 1.23 mmol), Pd(PPh₃)₄ (3 mol-%), 3-vinylphenylboronic acid (78 mg, 0.53 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a yellow oil; yield 127 mg (70%). ¹H NMR (300 MHz, CDCl₃): δ = 5.23 (d, J = 10.95 Hz, 1 H, CH₂ vinyl), 5.74 (d, J = 17.55 Hz, 1 H, CH₂ vinyl), 6.65–6.74 (dd, J = 10.8, 17.5 Hz, 1 H, CH₂ vinyl), 7.33–7.38 (m, 3 H, ArH), 7.40–7.43 (m, 2 H, ArH), 7.50–7.55 (m, 3 H, ArH), 7.61 (d, J = 8.43 Hz, 2 H, ArH), 7.80 (d, J = 8.40 Hz, 2 H, ArH) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 114.7 (CH₂ vinyl), 120.6 (q, $J_{C,F}$ = 322.20 Hz, CF₃), 122.5, 125.3, 126.1, 126.8, 127.2, 128.1, 129.2, 130.8, 131.2, 132.6 (CH_{Ar}), 135.2 (C_{Ar}), 136.5 (CH_{Ar}), 138.3, 139.4, 140.0, 146.4, 146.8 (C_{Ar}), 192.1 (C=O) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.3 (CF₃) ppm. IR (KBr): $\tilde{\nu}$ = 3085, 3060, 2957, 2854 (w), 1665, 1601 (m), 1579, 1559, 1480 (w), 1421 (s), 1294, 1274, 1246 (w), 1204, 1134 (s), 1087 (m), 1039, 1014, 955 (w), 878, 866, 778, 766 (s), 747, 710, 670, 617, 568, 545 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 432 (100) [M]⁺, 299 (35), 284 (14), 255 (09), 207 (42), 178 (23), 152 (09), 69 (05). HRMS (EI): calcd. for C₂₂H₁₅F₃O₄S [M]⁺ 432.06377; found 432.063610.

2-(4'-tert-Butylbiphenylcarbonyl)phenyl Trifluoromethanesulfonate (14f): Compound **14f** was obtained from **12** (200 mg, 0.41 mmol), K₃PO₄ (260 mg, 1.23 mmol), Pd(PPh₃)₄ (3 mol-%), 4-tert-butylphenylboronic acid (94 mg, 0.53 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless crystalline solid; yield 128 mg (66%). M.p. 140–142 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.27 (s, 9 H, 3 CH₃), 7.32–7.42 (m, 4 H, ArH), 7.48–7.52 (m, 4 H, ArH), 7.60 (d, J = 8.28 Hz, 2 H, ArH), 7.78 (d, J = 8.25 Hz, 2 H, ArH) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 31.3 (3 CH₃), 34.6 (C_{tBu}), 120.0 (q, J_{FC} = 320 Hz, CF₃), 122.5, 126.0, 127.0, 127.1, 128.0, 130.8, 131.2, 132.5 (CH_{Ar}), 132.6, 134.9, 136.7, 146.4, 146.8, 151.7 (C_{Ar}), 192.1 (C=O) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.4 (CF₃) ppm. IR (KBr): $\tilde{\nu}$ = 3070, 3030, 2929 (w), 1660, 1600 (m), 1550, 1521, 1495, 1443 (w), 1425 (s), 1393, 1366,

1300 (w), 1278, 1269 (m), 1197, 1142 (s), 1112, 1040, 1003, 937, 882, 864 (m), 831, 767, 735 (s), 700, 645, 596, 567 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 462 (43) [M]⁺, 447 (100), 313 (43), 299 (09), 273 (04), 178 (04), 69 (04). HRMS (EI): calcd. for C₂₄H₂₁F₃O₄S [M]⁺ 462.11172; found 462.111365.

2-(3',5'-Dimethylbiphenylcarbonyl)phenyl Trifluoromethanesulfonate (14g): Compound **14g** was obtained from **12** (200 mg, 0.41 mmol), K₃PO₄ (260 mg, 1.23 mmol), Pd(PPh₃)₄ (3 mol-%), 3,5-dimethylphenylboronic acid (79 mg, 0.53 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless oil; yield 142 mg (78%). ¹H NMR (300 MHz, CDCl₃): δ = 2.28 (s, 6 H, 2 CH₃), 6.94 (s, 1 H, ArH), 7.14 (s, 2 H, ArH), 7.35 (dd, J = 8.25, 19.6 Hz, 2 H, ArH), 7.47–7.51 (m, 2 H, ArH), 7.56 (d, J = 8.3 Hz, 2 H, ArH), 7.75 (d, J = 8.3 Hz, 2 H, ArH) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 21.3 (2 CH₃), 120.6 (q, J_{FC} = 321.0 Hz, CF₃), 122.5, 125.2, 127.2, 128.0, 130.1, 130.7, 131.2, 132.6 (CH_{Ar}), 133.0, 135.0, 138.5, 139.6, 146.8, 146.9, (C_{Ar}), 192.2 (C=O) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.4 (CF₃) ppm. IR (KBr): $\tilde{\nu}$ = 3032, 2850, 2850, 1725 (w), 1665, 1600 (m), 1560, 1480 (w), 1422 (s), 1294, 1246 (m), 1203, 1135 (s), 1084, 1038, 1016 (m), 936 (m), 879, 850, 779 (s), 742, 639, 618, 568 (w) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 434 (100) [M]⁺, 301 (57), 285 (06), 258 (07), 209 (30), 165 (19), 69 (05). HRMS (EI): calcd. for C₂₂H₁₇F₃O₄S [M]⁺ 434.07942; found 434.079488.

2-(4'-Ethylbiphenylcarbonyl)phenyl Trifluoromethanesulfonate (14h): Compound **14h** was obtained from **12** (200 mg, 0.41 mmol), K₃PO₄ (260 mg, 1.23 mmol), Pd(PPh₃)₄ (3 mol-%), 4-ethylphenylboronic acid (79 mg, 0.53 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless crystalline solid; yield 134 mg (74%). M.p. 170–172 °C. ¹H NMR (300 MHz, CDCl₃): δ = 1.17 (t, J = 7.5 Hz, 3 H, CH₃ ethyl), 2.59 (q, J = 7.5 Hz, 2 H, CH₂ ethyl), 7.19 (d, J = 8.1 Hz, 2 H, ArH), 7.35 (dd, J = 8.2, 18.5 Hz, 2 H, ArH), 7.44–7.51 (m, 4 H, ArH), 7.57 (d, J = 8.4 Hz, 2 H, ArH), 7.77 (d, J = 8.4 Hz, 2 H, ArH) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 14.4 (CH₃), 28.6 (CH₂), 120.6 (q, J_{FC} = 321.0 Hz, CF₃), 122.5, 127.0, 127.2, 128.0, 128.5, 130.8, 131.2, 132.6 (CH_{Ar}), 133.0, 134.8, 137.0, 144.8, 146.5, 146.8 (C_{Ar}), 192.1 (C=O) ppm. ¹⁹F NMR (282 MHz, CDCl₃): δ = -73.4 (CF₃) ppm. IR (KBr): $\tilde{\nu}$ = 3065, 3031, 2923, 1721 (w), 1663, 1605 (m), 1583, 1511, 1443 (w), 1421 (s), 1312, 1264 (m), 1203, 1137 (s), 1083, 1037, 931 (m), 877, 751 (s), 691, 667, 645, 591 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 434 (100) [M]⁺, 419 (08), 301 (41), 273 (17), 209 (21), 165 (13), 69 (05). HRMS (EI): calcd. for C₂₂H₁₇F₃O₄S [M]⁺ 434.07942; found 434.079081.

(3'-Methoxybiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (15a): Compound **15a** was obtained from **14a** (100 mg, 0.23 mmol), K₃PO₄ (146 mg, 0.69 mmol), Pd(PPh₃)₄ (3 mol-%), 4-vinylphenylboronic acid (44 mg, 0.30 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a yellow oil; yield 63 mg (70%). ¹H NMR (300 MHz, CDCl₃): δ = 3.76 (s, 3 H, OCH₃), 5.08–5.12 (dd, J = 1.7, 10.8 Hz, 1 H, CH₂ vinyl), 5.55–5.61 (dd, J = 1.2, 17.6 Hz, 1 H, CH₂ vinyl), 6.48–6.57 (dd, J = 10.8, 17.6 Hz, 1 H, CH₂ vinyl), 6.81–6.85 (m, 1 H, ArH), 6.99 (t, J = 1.7 Hz, 1 H, ArH), 7.03–7.07 (m, 1 H, ArH), 7.18 (s, 4 H, ArH), 7.24 (t, J = 7.9 Hz, 1 H, ArH), 7.40–7.47 (m, 6 H, ArH), 7.66 (d, J = 8.4 Hz, 2 H, ArH) ppm. ¹³C NMR (75.47 MHz, CDCl₃): δ = 55.3 (OCH₃), 113.0, 113.5 (CH_{Ar}), 114.0 (CH₂ vinyl), 119.7, 126.2, 126.9, 127.0, 128.7, 129.1, 129.9, 130.0, 130.3, 130.5 (CH_{Ar}), 136.2 (C_{Ar}), 136.3 (CH₂ vinyl), 136.6, 138.9, 139.6, 140.7, 141.3, 145.4, 160.0 (C_{Ar}), 198.1 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3054, 3001, 2953, 2851, 1725 (w), 1660, 1582, 1512, 1477, 1464, 1398, 1308 (m), 1212, 1170, 1116, 1050, 1012, 1003, 992 (m), 927, 842, 767, 743, 690 (s), 667, 641, 568 (m) cm⁻¹. GC-MS (EI, 70 eV): m/z (%) = 390 (100) [M]⁺, 373 (09), 283 (04), 211

(42), 178 (24), 152 (13), 101 (05). HRMS (EI): calcd. for $C_{28}H_{22}O_2$ $[M]^+$ 390.16143; found 390.161279.

(2',5'-Dimethoxybiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (15b): Compound **15b** was obtained from **14b** (100 mg, 0.21 mmol), K_3PO_4 (133 mg, 0.63 mmol), $Pd(PPh_3)_4$ (3 mol-%), 4-vinylphenylboronic acid (40 mg, 0.27 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless oil; yield 65 mg (72%). ¹H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 6 H, 2 OCH₃), 5.12 (d, J = 11.3 Hz, 1 H, CH₂ vinyl), 5.58–5.64 (dd, J = 1.4, 17.6 Hz, 1 H, CH₂ vinyl), 6.56 (d, J = 8.4 Hz, 1 H, CH_{vinyl}), 7.17 (s, 1 H, ArH), 7.22 (s, 4 H, ArH), 7.24–7.27 (m, 3 H, ArH), 7.34–7.48 (m, 5 H, ArH), 7.68 (d, J = 8.3 Hz, 2 H, ArH) ppm. ¹³C NMR (75.47 MHz, $CDCl_3$): δ = 55.9 (2 OCH₃), 104.2, 104.4 (CH_{Ar}), 113.8 (CH₂ vinyl), 118.5 (C_{Ar}), 126.1, 126.8, 128.8, 128.9, 129.2, 129.3, 129.4, 130.1, 130.6, 130.9 (CH_{Ar}), 135.5 (C_{Ar}), 136.4 (CH_{vinyl}), 136.6, 139.0, 139.5, 139.8, 141.0, 157.5 (C_{Ar}), 198.1 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3056, 3002, 2954, 2851, 1724 (w), 1661, 1601, 1587, 1514, 1441, 1432, 1401, 1330, 1277 (m), 1244 (s), 1183, 1171, 1033, 1001, 953, 879, 798, 768, 755, 693, 638, 611, 572 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 420 (100) $[M]^+$, 403 (07), 241 (40), 198 (10), 178 (23), 152 (07), 127 (05). HRMS (EI): calcd. for $C_{29}H_{24}O_3$ $[M]^+$ 420.17200; found 420.172846.

(2',6'-Dimethoxybiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (15c): Compound **15c** was obtained from **14c** (100 mg, 0.21 mmol), K_3PO_4 (133 mg, 0.63 mmol), $Pd(PPh_3)_4$ (3 mol-%), 4-vinylphenylboronic acid (40 mg, 0.27 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a yellow oil; yield 62 mg (68%). ¹H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 6 H, 2 OCH₃), 5.08–5.12 (dd, J = 1.7, 10.8 Hz, 1 H, CH₂ vinyl), 5.57–5.63 (dd, J = 1.8, 17.6 Hz, 1 H, CH₂ vinyl), 6.54 (d, J = 8.4 Hz, 1 H, CH_{vinyl}), 7.14–7.21 (m, 6 H, ArH), 7.24 (d, J = 8.4 Hz, 2 H, ArH), 7.33–7.36 (m, 1 H, ArH), 7.41–7.46 (m, 4 H, ArH), 7.66 (d, J = 8.4 Hz, 2 H, ArH) ppm. ¹³C NMR (62.90 MHz, $CDCl_3$): δ = 55.9 (2 OCH₃), 104.4 (CH_{Ar}), 113.8 (CH₂ vinyl), 118.5 (C_{Ar}), 126.1, 126.7, 128.9, 129.2, 129.3, 129.4, 130.1, 130.6, 130.9 (CH_{Ar}), 135.5 (C_{Ar}), 136.4 (CH_{vinyl}), 136.5, 139.0, 139.5, 139.8, 141.0, 157.5 (C_{Ar}), 198.1 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3054, 3029, 2951, 2857, 1726 (w), 1667, 1623, 1593, 1517, 1443, 1435, 1403, 1332, 1279 (m), 1245 (s), 1187, 1173, 1035, 1003, 957, 881, 783, 761, 757, 689, 632, 609, 571 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 420 (100) $[M]^+$, 403 (08), 241 (35), 198 (09), 178 (23), 152 (07), 127 (05). HRMS (EI): calcd. for $C_{29}H_{24}O_3$ $[M]^+$ 420.17200; found 420.172372.

(2'-Ethoxybiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (15d): Compound **15d** was obtained from **14d** (100 mg, 0.22 mmol), K_3PO_4 (139 mg, 0.66 mmol), $Pd(PPh_3)_4$ (3 mol-%), 4-vinylphenylboronic acid (42 mg, 0.29 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a pink oil; yield 56 mg (62%). ¹H NMR (300 MHz, $CDCl_3$): δ = 1.21 (t, J = 6.9 Hz, 3 H, CH₃), 3.92 (q, J = 6.9 Hz, 2 H, OCH₂), 5.09–5.13 (dd, J = 1.7, 10.8 Hz, 1 H, CH₂ vinyl), 5.56–5.62 (dd, J = 1.8, 17.6 Hz, 1 H, CH₂ vinyl), 6.49–6.59 (dd, J = 10.8, 17.6 Hz, 1 H, CH_{vinyl}), 6.86–6.59 (m, 2 H, ArH), 7.15–7.21 (m, 6 H, ArH), 7.40–7.46 (m, 6 H, ArH), 7.65 (d, J = 8.5 Hz, 2 H, ArH) ppm. ¹³C NMR (75.47 MHz, $CDCl_3$): δ = 14.7 (CH₃), 64.1 (OCH₂), 112.8 (CH_{Ar}), 113.9 (CH₂ vinyl), 118.5 (C_{Ar}), 120.9, 126.1, 126.9, 128.8, 129.1, 129.3, 129.4, 129.7, 130.0, 130.2, 130.7 (CH_{Ar}), 135.5 (C_{Ar}), 136.3 (CH_{vinyl}), 136.5, 139.1, 139.7, 140.8, 143.5, 155.8 (C_{Ar}), 198.3 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3056, 3031, 2954, 2850, 1724 (w), 1661, 1599 (s), 1580, 1511, 1473, 1446, 1401, 1311 (m), 1277, 1260, 1237 (s), 1185, 1150, 1039, 988 (m), 927 (s), 860, 803, 785, 708, 666, 628, 541 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 404 (100) $[M]^+$, 375 (18), 357 (10), 225 (23), 197 (14), 178 (44), 168 (13), 139 (12), 115 (06). HRMS (EI): calcd. for $C_{29}H_{24}O_2$ $[M]^+$ 404.17708; found 404.177499.

(4'-Vinylbiphenyl-2-yl)(3'-vinylbiphenyl-4-yl)methanone (15e): Compound **15e** was obtained from **14e** (100 mg, 0.23 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol-%), 4-vinylphenylboronic acid (44 mg, 0.30 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless oil; yield 59 mg (66%). ¹H NMR (300 MHz, $CDCl_3$): δ = 5.01–5.11 (dd, J = 1.7, 10.8 Hz, 1 H, CH₂ vinyl), 5.19–5.24 (dd, J = 1.7, 11.2 Hz, 1 H, CH₂ vinyl), 5.54–5.61 (dd, J = 1.7, 17.5 Hz, 1 H, CH₂ vinyl), 5.68–5.74 (dd, J = 1.6, 17.5 Hz, 1 H, CH₂ vinyl), 6.47–6.57 (dd, J = 10.8, 17.5 Hz, 1 H, CH_{vinyl}), 6.62–6.72 (dd, J = 10.8, 17.5 Hz, 1 H, CH_{vinyl}), 7.18 (s, 4 H, ArH), 7.31–7.38 (m, 4 H, ArH), 7.40–7.48 (m, 5 H, ArH), 7.66 (d, J = 8.5 Hz, 2 H, ArH) ppm. ¹³C NMR (75.47 MHz, $CDCl_3$): δ = 114.0, 114.6 (2 CH₂ vinyl), 125.2, 125.9, 126.2, 126.7, 126.9, 127.0, 128.7, 129.0, 129.1, 130.0, 130.3, 130.5 (CH_{Ar}), 136.1 (C_{Ar}), 136.3, 136.5 (CH_{vinyl}), 136.6, 138.2, 138.9, 139.6, 140.2, 140.7, 145.4 (C_{Ar}), 198.2 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3043, 3029, 2952, 2847, 1721 (w), 1657, 1597 (s), 1579, 1513, 1475, 1447, 1403, 1317 (m), 1266, 1253, 1235 (s), 1187, 1153, 1041, 987 (m), 925 (s), 861, 803, 783, 708, 665, 627, 543 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 386 (100) $[M]^+$, 359 (10), 281 (04), 207 (50), 193 (07), 178 (53), 152 (16). HRMS (EI): calcd. for $C_{29}H_{22}O$ $[M]^+$ 386.16652; found 386.166803.

(4'-tert-Butylbiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (15f): Compound **15f** was obtained from **14f** (100 mg, 0.21 mmol), K_3PO_4 (133 mg, 0.63 mmol), $Pd(PPh_3)_4$ (3 mol-%), 4-vinylphenylboronic acid (41 mg, 0.28 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a yellow oil; yield 58 mg (64%). ¹H NMR (300 MHz, $CDCl_3$): δ = 1.26 (s, 9 H, 3 CH₃), 5.07–5.11 (dd, J = 1.8, 10.8 Hz, 1 H, CH₂ vinyl), 5.54–5.60 (dd, J = 1.8, 17.5 Hz, 1 H, CH₂ vinyl), 6.47–6.57 (dd, J = 10.8, 17.6 Hz, 1 H, CH_{vinyl}), 7.17 (s, 4 H, ArH), 7.35–7.39 (m, 4 H, ArH), 7.42–7.49 (m, 6 H, ArH), 7.66 (d, J = 10.2 Hz, 2 H, ArH) ppm. ¹³C NMR (62.90 MHz, $CDCl_3$): δ = 31.2 (3 CH₃), 34.6 (C), 125.8, 126.2, 126.6, 126.9, 127.0, 128.6, 129.1, 130.0, 130.2, 130.5 (CH_{Ar}), 135.8 (C_{Ar}), 136.3 (CH_{vinyl}), 136.5, 136.9, 139.0, 139.6, 140.7, 145.3, 151.4 (C_{Ar}), 198.2 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3055, 3030, 2956 (w), 1724, 1661, 1600 (m), 1573, 1514, 1476, 1440, 1392, 1311 (w), 1276 (s), 1242, 1183, 1150, 1112, 1070, 1018, 987, 951 (w), 927 (s), 907, 861, 842, 781 (m), 756, 722 (s), 696, 649, 570 (w) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 416 (100) $[M]^+$, 401 (92), 383 (05), 281 (05), 237 (10), 207 (20), 178 (37), 152 (09), 41 (05). HRMS (EI): calcd. for $C_{31}H_{28}O$ $[M]^+$ 416.21247; found 416.212861.

(3',5'-Dimethylbiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (15g): Compound **15g** was obtained from **14g** (100 mg, 0.23 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol-%), 4-vinylphenylboronic acid (44 mg, 0.30 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless viscous oil; yield 68 mg (76%). ¹H NMR (250 MHz, $CDCl_3$): δ = 2.28 (s, 6 H, 2 CH₃), 5.10 (d, J = 11.5 Hz, 1 H, CH₂ vinyl), 5.54–5.62 (dd, J = 1.6, 17.6 Hz, 1 H, CH₂ vinyl), 6.47–6.58 (dd, J = 10.8, 17.6 Hz, 1 H, CH_{vinyl}), 6.93 (s, 1 H, ArH), 7.08 (s, 2 H, ArH), 7.18 (s, 4 H, ArH), 7.36–7.48 (m, 6 H, ArH), 7.64 (d, J = 8.4 Hz, 2 H, ArH) ppm. ¹³C NMR (62.90 MHz, $CDCl_3$): δ = 21.3 (2 CH₃), 113.9 (CH₂ vinyl), 125.1, 126.2, 126.8, 127.0, 128.6, 129.1, 129.8, 130.0, 130.2, 130.4 (CH_{Ar}), 135.8 (C_{Ar}), 136.3 (CH_{vinyl}), 136.5, 138.4, 139.0, 139.6, 139.8, 140.7, 145.8 (C_{Ar}), 198.2 (C=O) ppm. IR (KBr): $\tilde{\nu}$ = 3019, 2916, 1724 (w), 1661 (m), 1598 (s), 1556, 1475, 1440, 1397, 1313 (m), 1277 (s), 1209, 1184, 1150, 1117, 1071, 1033, 1002, 987 (m), 928 (s), 907, 781, 768, 695, 646, 581 (m) cm⁻¹. GC–MS (EI, 70 eV): m/z (%) = 388 (100) $[M]^+$, 371 (10), 209 (28), 194 (05), 178 (21), 165 (22), 152 (06). HRMS (EI): calcd. for $C_{29}H_{24}O$ $[M]^+$ 388.18217; found 388.182014.

(4'-Ethylbiphenyl-4-yl)(4'-vinylbiphenyl-2-yl)methanone (15h): Compound **15h** was obtained from **14h** (100 mg, 0.23 mmol), K_3PO_4

(146 mg, 0.69 mmol), Pd(PPh₃)₄ (3 mol-%), 4-vinylphenylboronic acid (44 mg, 0.30 mmol) and 1,4-dioxane (5 mL mmol⁻¹ of triflate) as a colourless oil; yield 66 mg (74%). ¹H NMR (250 MHz, CDCl₃): δ = 1.16 (t, *J* = 7.6 Hz, 3 H, CH₃), 2.58 (q, *J* = 7.6 Hz, 2 H, CH₂CH₃), 5.06 (d, *J* = 11.5 Hz, 1 H, CH₂_{vinyl}), 5.52–5.60 (dd, *J* = 1.7, 17.6 Hz, 1 H, CH₂_{vinyl}), 6.45–6.56 (dd, *J* = 10.8, 17.5 Hz, 1 H, CH_{vinyl}), 7.17 (s, 4 H, ArH), 7.32 (d, *J* = 6.2 Hz, 2 H, ArH), 7.37 (d, *J* = 6.8 Hz, 2 H, ArH), 7.39–7.49 (m, 6 H, ArH), 7.64 (d, *J* = 8.4 Hz, 2 H, ArH) ppm. ¹³C NMR (62.90 MHz, CDCl₃): δ = 15.5 (CH₃), 28.5 (CH₂_{ethyl}), 114.0 (CH₂_{vinyl}), 126.2, 126.6, 127.0, 127.1, 128.4, 128.6, 129.1, 130.0, 130.2, 130.5 (CH_{Ar}), 135.8 (C_{Ar}), 136.3 (CH_{vinyl}), 136.5, 137.1, 139.0, 139.6, 140.7, 144.5, 145.5 (C_{Ar}), 198.1 (C=O) ppm. IR (KBr): ν̄ = 3053, 2926, 1725 (w), 1660, 1598 (s), 1574, 1523, 1514, 1476, 1440, 1399, 1310 (m), 1277 (s), 1189, 1118, 1060, 1032, 1003, 987 (m), 928 (s), 908, 842, 780 (m), 735 (s), 700, 654, 539 (m) cm⁻¹. GC–MS (EI, 70 eV): *m/z* (%) = 388 (100) [M]⁺, 371 (09), 209 (28), 178 (20), 152 (17). HRMS (EI): calcd. for C₂₉H₂₄O [M]⁺ 388.18217; found 388.182058.

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