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ARTICLE

Synthesis of functionalized *para*- and *meta*-terphenyls based on site-selective Suzuki cross-coupling reactions of bis(triflates) of methyl 2,5-dihydroxybenzoate and methyl 2,4-dihydroxybenzoate

Muhammad Nawaz, Ihsan Ullah, Obaid-ur-Rahman Abid, Asad Ali, Tamás Patonay, Ashot S. Saghyan, Tariel V. Ghochikan, Alexander Villinger, and Peter Langer

Abstract: The palladium(0)-catalyzed Suzuki cross-coupling reaction of the bis(triflates) of methyl 2,5-dihydroxybenzoate and methyl 2,4-dihydroxybenzoate afforded *para*- and *meta*-terphenyls, respectively. The reactions proceeded with very good site selectivity in favor of the sterically less hindered carbon atom.

Key words: terphenyls, cross-coupling, palladium, site selectivity, Suzuki reaction.

Résumé : La réaction de couplage croisé de Susuki des bis(triflates) de méthyl 2,5-dihydroxybenzoate et de méthyl 2,4-dihydroxybenzoate catalysée au palladium(0) a donné les *para*- et *méta*-terphényles, respectivement. Les réactions se sont déroulées avec une très bonne sélectivité de site en faveur de l'atome de carbone stériquement le moins encombré. [Traduit par la Rédaction]

Mots-clés : terphényles, couplage croisé, palladium, sélectivité de site, réaction de Suzuki.

Introduction

Functionalized *p*-terphenyls occur in a great variety of pharmacologically relevant natural products. Examples include terphenyllin,[1] terprenin,[2] curtisian A,[3] leucomentin-6,[4] thelephorin A,[5] ganbajunin D,[6] and thelephantin A.[7] Symmetrical and unsymmetrical terphenyls, functionalized with electron donor or acceptor groups, are the main constituents of a large number of natural products of mushrooms belonging to the Thelephoraceae family. Several synthetic *p*-terphenyl derivatives have been designed as selective inhibitors for dihydroortate dehydrogenase and cyclooxygenase enzymes.

In recent years, site-selective palladium-catalyzed reactions of polyhalogenated substrates have been studied.[8] We have reported site-selective reactions of various polyhalogenated heterocycles and of poly(triflates) of various arenes.[9] Polyhalogenated benzoic acid derivatives are interesting substrates for site-selective palladium(0)-catalyzed cross-coupling reactions. Tschierske and co-workers reported the synthesis of *p*-terphenyls by double Suzuki reactions of methyl 2,5-dibromobenzoate.[10] As two equivalents of the same boronic acid were employed in this study, no issue of site selectivity arose. Mioskowski et al. reported site-selective Sonogashira reactions of 2,5-diiodobenzoic acid.[11a] The scope of this approach is limited by the fact that polyhalogenated benzene derivatives are often not readily available. Reactions of the bis(triflate) of diethyl 2,5-bis-hydroxy-terephthalate have been previously reported.[11b] We envisaged that the bis(triflate) of methyl 2,5-dihydroxybenzoate, which represents a commercially available and inexpensive substrate, could be of considerable preparative usefulness in palladium-catalyzed cross-coupling reactions. Recently, we have reported preliminary results related to Suzuki–Miyaura reactions of this substrate.[12] Herein, we report full details of these studies related to the preparative scope. In addition, we report, for the first time, Suzuki–Miyaura reactions of the bis(triflate) of methyl 2,4-dihydroxybenzoate. These reactions result in the formation of *meta*-terphenyls. The chemical core structure of *meta*-terphenyls occurs in a great variety of pharmacologically relevant natural products. Examples include various simple hydroxylated and alkylated *meta*-terphenyls, such as trifucolnonaacetate, dunnianol, and mulberrofuran R.[13] Other derivatives, such as pusilatin A, are incorporated in cyclophanes.[14] The *meta*-terphenyl unit of various other natural products is incorporated in bis(anthracene)[15] or bis(carbazole)[16] frameworks. The *meta*-terphenyl substructure is also found in complex macrocyclic natural products, such as acutissimin B, castalagin, and roburin A.[17,18] Sonogashira reactions of the bis(triflate) of dimethyl 4,6-dihydroxy-isophthalate have been previously reported.[19]

Results and discussion

Methyl 2,5-dihydroxybenzoate (**1**) was transformed into bis(triflate) **2** in 84% yield (Scheme 1). The Suzuki reaction of **2** with different boronic acids (2.6 equiv.) afforded the novel 2,5-diarylbenzoates **3a–3f** in good yields (Scheme 2; Table 1). 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 was employed, and when the reaction was carried out in 1,4-dioxane (reflux, 4 h) using K_3PO_4 as the base. The structures of all products were established by spectroscopic methods. The structures of **1**, **2**, and **3d** were independently confirmed by X-ray crystal structure analyses

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M. Nawaz and A. Villinger. Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany.
I. Ullah and A. Ali. Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany; Department of Chemistry, Abdul Wali Khan University, Mardan, KPK, Pakistan.
O.-u.-R. Abid. Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany; Department of Chemistry, Hazara University, Mansehra, KPK, Pakistan.
T. Patonay. Department of Organic Chemistry, University of Debrecen, H-4032 Debrecen, Egyetem tér 1, Hungary.
A.S. Saghyan. Scientific and Production Center "Armbiotechnology" of NAS RA, Gyurjyan str. 14, 0056 Yerevan, Armenia; Department of Chemistry, Yerevan State University, Alex Manoogian 1, 0025 Yerevan, Armenia.
T.V. Ghochikan. Department of Chemistry, Yerevan State University, Alex Manoogian 1, 0025 Yerevan, Armenia.
P. Langer. Institut für Chemie, Universität Rostock, Albert-Einstein-Str. 3a, 18059 Rostock, Germany; Leibniz-Institut für Katalyse e. V. an der Universität Rostock, Albert-Einstein-Str. 29a, 18059 Rostock, Germany.
Corresponding author: P. Langer (e-mail: peter.langer@uni-rostock.de).

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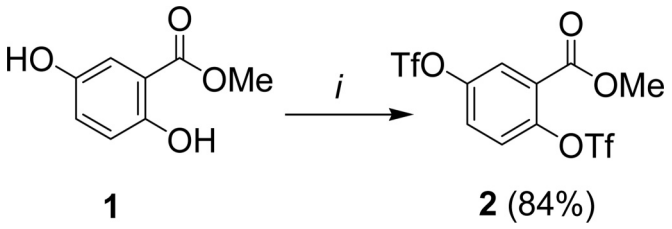
Scheme 1. Synthesis of **2**. Reagents and conditions: (*i*) CH_2Cl_2, 1 (1.0 equiv.), –78 °C, pyridine (4.0 equiv.), –78 °C, Tf_2O (2.4 equiv), 4 h.



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

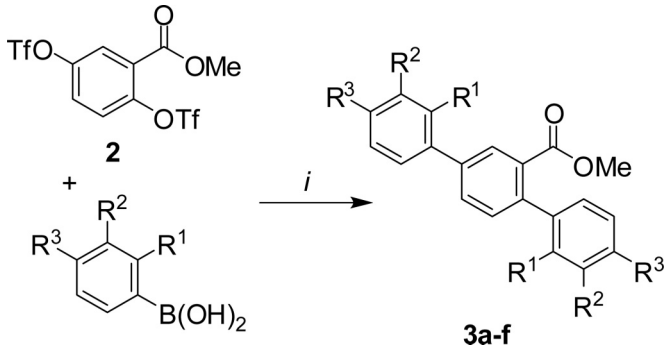


Table 1. Synthesis of **3a–3f**.

3	R^1	R^2	R^3	% (3)[a]
a	OMe	H	H	78
b	H	H	*t*Bu	75
c	H	OMe	OMe	56
d	H	H	Vinyl	77
e	H	Cl	H	67
f	H	H	H	54

[a]Yields of isolated products.

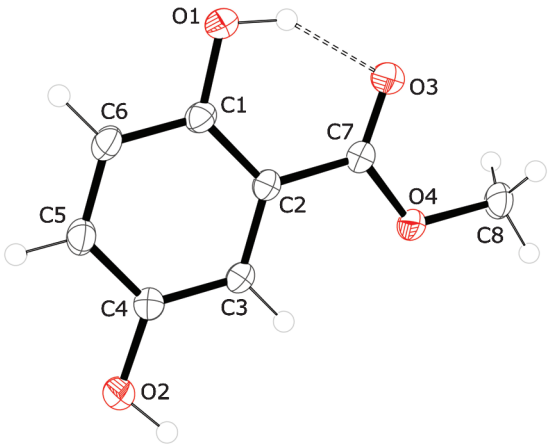
(Figs. 1–3) (see Supplementary material section). The X-ray crystal structure analysis of **3b** was already published in our preliminary communication.[12]

The Suzuki reaction of **2** with different boronic acids (1.3 equiv.) in the presence of $Pd(PPh_3)_4$ (3 mol%) occurred site selectively at carbon atom C-5 and afforded the biaryls **4a–4g** (Scheme 3; Table 2). The reaction of **4a–4g** with vinylphenyl boronic acid (1.3 equiv.) gave 2,5-diarylbenzoates **5a–5g** containing two different aryl groups.

In some cases, a small amount of the bis-coupled product and of the other regioisomer could be detected in the crude product (by ^{1}H NMR and GC–MS). For example, 10% of the bis-coupled product was detected by ^{1}H NMR in the crude product of **4a**. The pure monocoupled products were obtained after chromatographic purification. The oxidative addition of palladium usually occurs first at the less steric-hindered and more electron-deficient carbon atom. Carbon atom C-2 of bis(triflate) **2** is more electron deficient than C-5 due to the electronic influence of the ester group. On the other hand, carbon C-5 is less sterically hindered than C-2. Therefore, the site-selective formation of **4a–4g** seems to be mainly influenced by steric parameters (Scheme 4).

Extending the scope of our study, we have investigated Suzuki reactions of the bis(triflate) of commercially available methyl 2,4-dihydroxybenzoate to give *meta*-terphenyls. Methyl 2,4-dihydroxybenzoate (**6**) was transformed into its bis(triflate) **7** in 88% yield (Scheme 5). The Suzuki reaction of **7** with different boronic acids (2.6 equiv.) afforded the novel 2,5-diarylbenzoates **8a–8j** in good yields (Scheme 6; Table 3). The best yields were

Fig. 1. Ortep plot of **1**.



obtained when $Pd(PPh_3)_4$ (6 mol%) was used as the catalyst, when 2.6 equiv. of the boronic acid was employed, and when the reaction was carried out in 1,4-dioxane (reflux, 4 h) using K_3PO_4 as the base.

The Suzuki reaction of **7** with different boronic acids (1.3 equiv.) in the presence of $Pd(PPh_3)_4$ (3 mol%) proceeded with very good site selectivity at carbon atom C-4 and afforded the biaryls **9a–9e** (Scheme 7; Table 4). In some cases, a small amount of the bis-coupled product could be detected in the crude product (by ^{1}H NMR and GC-MS). The pure monocoupled products were again obtained after chromatographic purification. The reaction of **9a–9e** with vinyl phenyl boronic acid (1.3 equiv.) gave 2,4-diarylbenzoates **10a–10d** containing two different aryl groups. The structure of **9c** was independently confirmed by X-ray crystal structure analysis (Fig. 4).[20]

As mentioned above, the oxidative addition of palladium usually occurs first at the most electron-deficient carbon atom. Carbon atoms C-2 and C-4 of bis(triflate) **7** are equally electron deficient. The site-selective formation of **9a–9e** can be explained by the fact that carbon atom C-4 is less sterically hindered (Scheme 8).

In conclusion, we have reported the synthesis of *para*- and *meta*-terphenyls based on Suzuki cross-coupling reactions of the bis(triflates) of methyl 2,5- dihydroxybenzoate and methyl 2,4-dihydroxybenzoate, respectively. The reactions proceed with very good site selectivity.

Experimental section

General comments

All solvents were dried by standard methods and all reactions were carried out under an inert atmosphere. For ^{1}H and ^{13}C NMR spectra, the deuterated solvents indicated were used. MS data were obtained by electron ionization (EI, 70 eV), chemical ionization (isobutane), or electrospray ionization. For preparative scale chromatography, silica gel 60 (0.063–0.200 mm, 70–230 mesh) was used. X-ray crystal structure analysis: crystallographic data were collected on a Bruker X8Apex diffractometer with CCD-Kamera (MoKa und Graphit Monochromator, = 0.71073 Å). The structures were solved by direct methods using SHELXS-97 and refined against F2 on all data by full matrix least-squares with SHELXL-97.

Synthesis of triflates 2 and 7

To a stirred solution of **1** and **6** (1.0 equiv) in CH_2Cl_2 (10 mL/mmol) was added pyridine (4.0 equiv.) at –78 °C under an argon atmosphere. After 10 min, Tf_2O (2.4 equiv.) was added at –78 °C. The mixture was allowed to warm up to 0 °C and stirred for 4 h. The reaction mixture was filtered and the filtrate was concentrated in vacuo. The products of the reaction mixture were isolated

Fig. 2. Ortep plot of **2**.

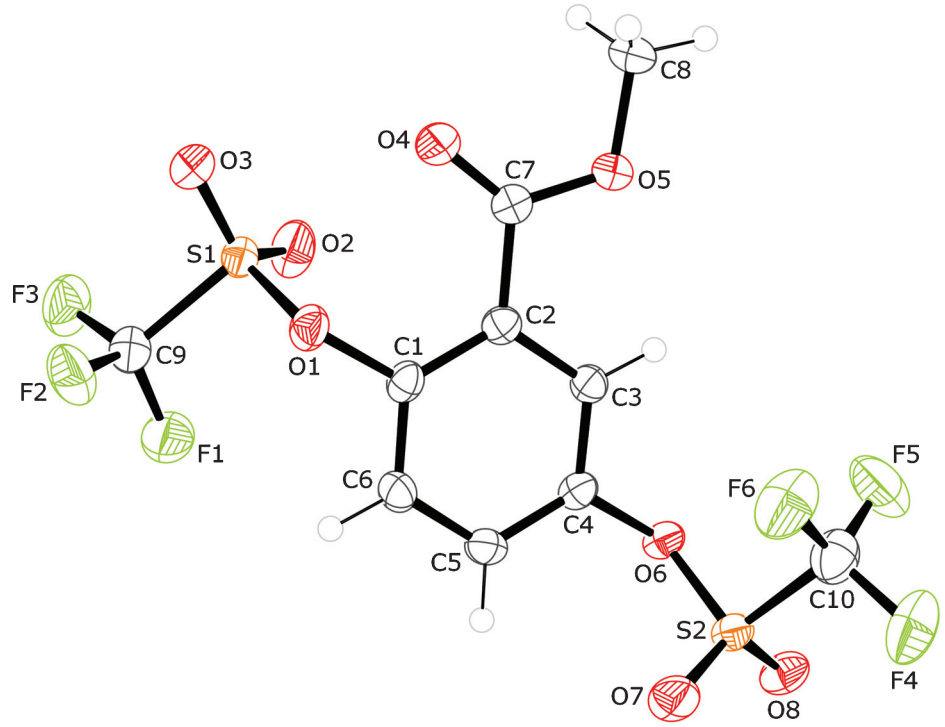
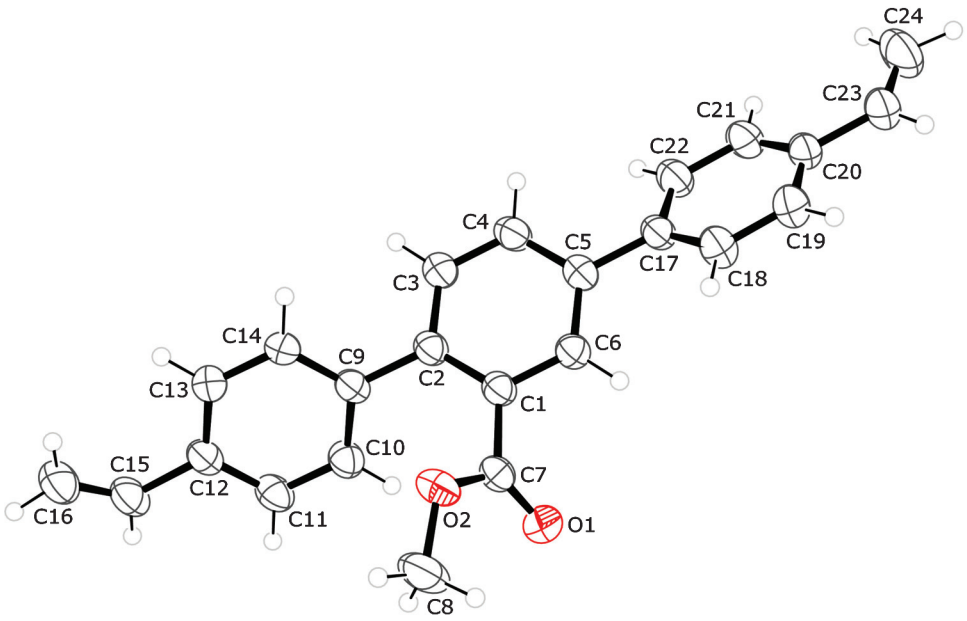


Fig. 3. Ortep plot of **3d**.



by rapid column chromatography (flash silica gel, heptanes/EtOAc).

Methyl 2,5-bis(trifluoromethylsulfonyloxy)benzoate (2)

Starting with **1** (168 mg, 1.0 mmol), pyridine (0.32 mL, 4.0 mmol), and Tf_2O (0.39 mL, 2.4 mmol), **2** was isolated as a colorless crystalline solid; yield 364 mg (84%), mp 152–154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 3H, OCH_3), 7.36 (s, 1H, ArH), 7.47 (d, 1H, J = 3.0 Hz, ArH), 7.92 (d, 1H, J = 3.2 Hz, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 53.2 (OCH_3), 116.5 (q, $J_{C,F}$ = 320.0 Hz, CF_3), 120.2 (q, $J_{C,F}$ = 318.0 Hz, CF_3), 125.0, 125.6, 127.0 (CH_{Ar}), 147.1, 147.9, 148.0 (C_{Ar}), 162.3 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.3 (CF). IR (KBr): $\tilde{\nu}$ = 3121, 3088, 2961 (w), 1736, 1618 (s), 1586, 1485, 1300, 1279 (m), 1244 (s), 1124, 1075, 977 (m), 875, 781, 759 (s), 698, 581, 543 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 432 (M^+, 70), 401(40), 363(06), 337(02), 299(32), 273(13), 235(98), 205(27), 179(24), 135(62), 107(33), 79(26), 69(100), 53(28). HRMS (EI) calcd. for $C_{10}H_6F_6O_8S_2$ [M^+]: 431.94028; found: 431.940891.

Methyl 2,4-bis(trifluoromethylsulfonyloxy)benzoate (7)

Starting with **6** (168 mg, 1.0 mmol), pyridine (0.32 mL, 4.0 mmol), and Tf_2O (0.39 mL, 2.4 mmol), **7** was isolated as a colorless oil (382 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 3H, OCH_3), 7.19 (s, 1H, ArH), 7.35 (d, 1H, J = 8.2 Hz, ArH), 8.17 (d, 1H,

Scheme 3. Synthesis of **4a–4g** and **5a–5g**. Reagents and conditions: (*i*) **2** (1.0 equiv.), boronic acids (1.3 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane (5 mL per 1 mmol of **2**), 110 °C, 4 h; (*ii*) **4a–4g** (1.0 equiv.), vinylphenyl boronic acids (1.3 equiv.), K_3PO_4 (1.5 equiv), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane (5 mL per 1 mmol of **2**), 110 °C, 4 h.

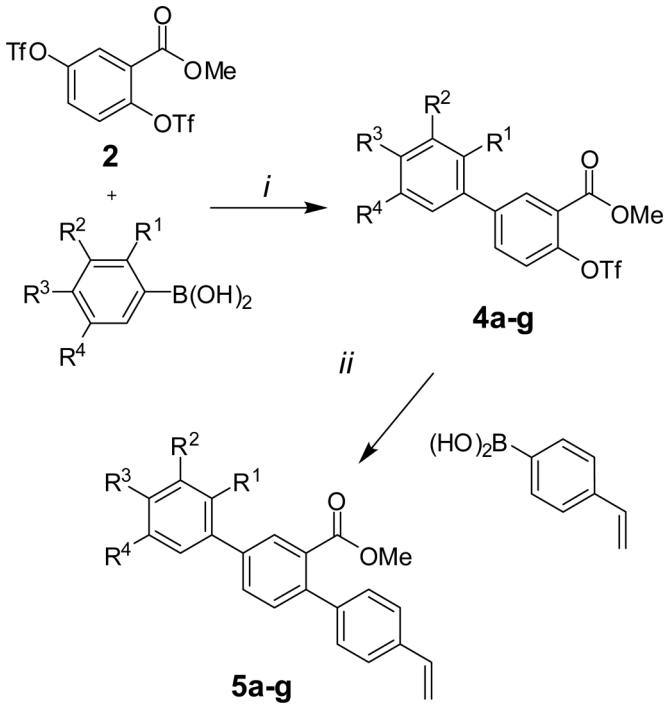
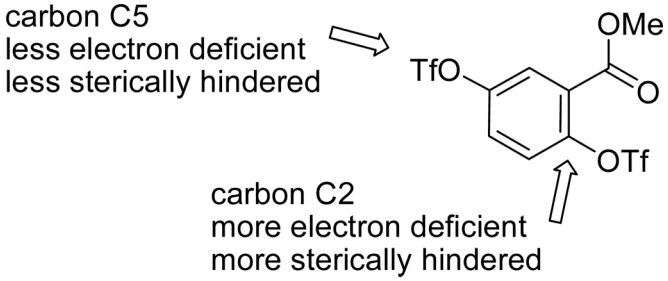


Table 2. Synthesis of **4a–4g** and **5a–5g**

4, 5	R^1	R^2	R^3	R^4	% (**4**)[a]	% (**5**)[a]
a	H	Me	H	Me	83	72
b	OMe	H	H	OMe	72	78
c	H	H	Me	H	64	68
d	H	OMe	OMe	H	67	64
e	H	H	Br	H	63	62
f	OMe	H	OMe	H	73	67
g	H	H	Cl	H	59	72

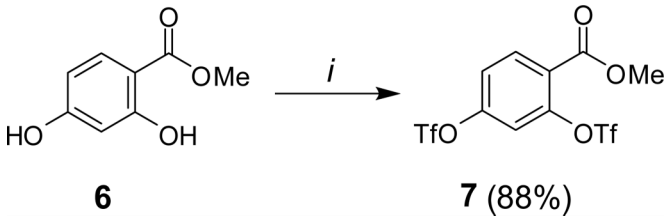
[a]Yields of isolated products.

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



J = 8.6 Hz, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 53.1 (OCH_3), 116.1 (CH_{Ar}), 116.8 (q, $J_{F,C}$ = 320.2 Hz, CF_3), 120.8 (CH_{Ar}), 121.4 (q, $J_{F,C}$ = 321.2 Hz, CF_3), 124.7 (C_{Ar}), 133.8 (CH_{Ar}), 148.6, 151.8 (C_{Ar}), 162.7 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –72.4, –73.1 ($2CF_3$). IR (KBr): $\tilde{\nu}$ = 3117, 3085, 2960 (w), 1733, 1617 (s), 1583 (m), 1481, 1302, 1277 (m), 1241 (s), 1123, 1073, 975 (m), 873, 780, 758 (s), 697, 580, 541 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 432 (M^+, 61), 401(61), 363(06), 337(52), 273(77), 207(53), 179(15), 138(10), 107(34), 95(06), 79(22), 69(100), 51(16), 39(03). HRMS (EI) calcd. for $C_{10}H_6F_6O_8S_2$ [M^+]: 431.94028; found: 431.941432.

Scheme 5. Synthesis of **7**. Reagents and conditions: (*i*) CH_2Cl_2, 6 (1.0 equiv.), –78 °C, pyridine (4.0 equiv.), –78 °C, Tf_2O (2.4 equiv.), 4 h.



Scheme 6. Synthesis of **8a–8j**. Reagents and conditions: (*i*) **7** (1.0 equiv.), boronic acids (2.6 equiv.), K_3PO_4 (3.0 equiv.), $Pd(PPh_3)_4$ (6 mol%), 1,4-dioxane (5 mL per 1 mmol of **7**), 110 °C, 4 h.

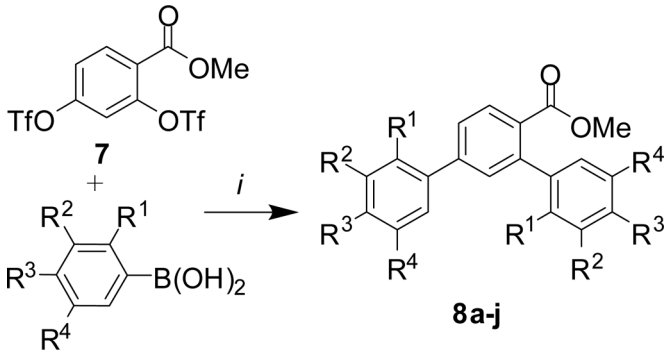


Table 3. Synthesis of **8a–8j**.

8	R^1	R^2	R^3	R^4	% (**8**)[a]
a	H	H	Cl	H	72
b	OMe	H	H	OMe	78
c	H	H	H	H	65
d	H	H	*t*Bu	H	79
e	H	OH	H	H	62
f	Br	H	H	H	74
g	F	H	H	H	68
h	H	H	F	H	77
i	H	CF_3	H	H	63
j	H	H	CF_3	H	69

[a]Yields of isolated products.

2,2″-Dimethoxy-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (3a)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 2-methoxyphenylboronic acid (180 mg, 1.19 mmol), and 1,4-dioxane (5 mL/mmol triflate), **3a** was isolated as a colorless viscous oil; yield 126 mg (78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.57 (s, 3H, OCH_3), 3.65 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 6.82 (d, 2H, *J* = 8.2 Hz, ArH), 6.90–6.99 (m, 3H, ArH), 7.20–7.29 (m, 3H, ArH), 7.32 (d, 1H, *J* = 6.9 Hz, ArH), 7.64 (dd, 1H, *J* = 1.9, 7.9 Hz, ArH), 7.95 (d, 1H, *J* = 1.7 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.6 (OCH_3), 55.2 (OCH_3), 55.5 (OCH_3), 110.0, 111.2, 120.7, 120.9, 128.7, 129.0 (CH_{Ar}), 129.4 (C_{Ar}), 130.0, 130.4 (CH_{Ar}), 130.5 (C_{Ar}), 130.8, 130.9 (CH_{Ar}), 131.3 (C_{Ar}), 132.6 (CH_{Ar}), 137.1, 137.4, 156.1, 156.5 (C_{Ar}), 168.7 (C=O). IR (KBr): $\tilde{\nu}$ = 3055, 3024, 2945, 2834 (w), 1720 (m), 1597, 1508 (w), 1492, 1479, 1433, 1311 (m), 1242 (s), 1179, 1120, 1086, 1053, 1003, 969, 910, 857, 789 (m), 748 (s), 686, 672, 576 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 348 (M^+, 72), 317(100), 302(16) 255(27), 231(06), 215(07), 166(08), 101(05). HRMS (EI) calcd. for $C_{22}H_{20}O_4$ [M^+]: 348.13561; found: 348.135865.

Scheme 7. Synthesis of **9a–9e** and **10a–10d**. Reagents and conditions: (*i*) **7** (1.0 equiv.), boronic acids (1.3 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane (5 mL per 1 mmol of **7**), 110 °C, 4 h; (*ii*) **9a–9e** (1.0 equiv.), vinylphenyl boronic acids (1.3 equiv.), K_3PO_4 (1.5 equiv.), $Pd(PPh_3)_4$ (3 mol%), 1,4-dioxane (5 mL per 1 mmol of **9**), 110 °C, 4 h.

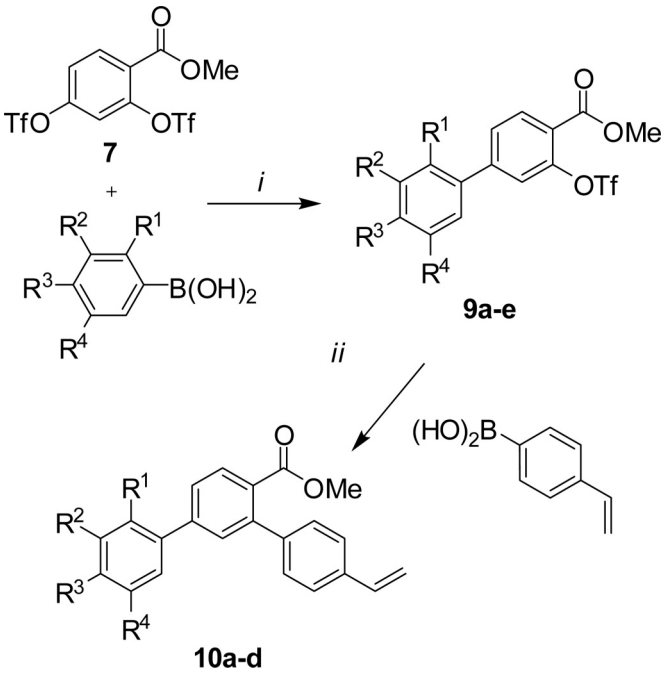


Table 4. Synthesis of **9a–9e** and **10a–10d**.

9, 10	R^1	R^2	R^3	R^4	% (**9**)[a]	% (**10**)[a]
a	OMe	H	H	OMe	78	76
b	H	OMe	OMe	H	72	72
c	OMe	H	H	H	76	64
d	OMe	H	OMe	H	67	69
e	H	Me	H	Me	60	—[b]

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

4,4″-Di-tert-butyl-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (3b)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-*tert*-butylphenylboronic acid (211 mg, 1.19 mmol), and 1,4-dioxane (5 mL/mmol triflate), **3b** was isolated as a colorless crystalline solid; yield 140 mg (75%), mp 148–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.28 (s, 18H, $6CH_3$), 3.58 (s, 3H, OCH_3), 7.15–7.25 (m, 4H, ArH), 7.28–7.42 (m, 4H, ArH), 7.49 (s, 1H, ArH), 7.63 (d, 1H, *J* = 5.0 Hz, ArH), 7.94 (d, 1H, *J* = 6.9 Hz, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 31.3 ($6CH_3$), 34.5 (2 C_{tBu}), 51.9 (OCH_3), 125.0, 125.8, 126.7, 127.0, 128.2, 129.2, 131.2 (CH_{Ar}), 131.7, 132.0, 135.3, 136.8, 137.9, 140.8, 150.8 (C_{Ar}), 168.9 (C=O). IR (KBr): $\tilde{\nu}$ = 3031, 2951, 2902 (w), 1727, 1605 (s), 1483 (m), 1461, 1362, 1267 (m), 1234 (s), 1180, 1085, 959 (m), 895, 788, 765 (s), 698, 572, 554 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 400 (M^+, 58), 385(100), 357(02), 297(03), 252(02), 185(14), 157(09), 141(04), 57(06), 41(03). HRMS (EI) calcd. for $C_{28}H_{32}O_2$ [M^+]: 400.23968; found: 400.239581.

3,4,3″,4″-Tetramethoxy-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (3c)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 3,4-dimethoxyphenylboronic acid (216 mg, 1.19 mmol), and 1,4-dioxane (5 mL/mmol triflate), **3c** was isolated as a reddish solid; yield 106 mg (56%), mp 140–142 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.62 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 3.87 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.81 (s, 1H, ArH), 6.85 (s, 2H, ArH), 6.90 (d, 1H, *J* = 8.3 Hz, ArH), 7.07 (d, 1H, *J* = 6.2 Hz, ArH), 7.12 (dd, 1H, *J* = 2.4, 8.6 Hz, ArH), 7.37 (d, 1H, *J* = 8.0 Hz, ArH), 7.63 (dd, 1H, *J* = 2.0, 8.0 Hz, ArH), 7.87 (d, 1H, *J* = 1.9 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 55.8 (OCH_3), 56.0 (OCH_3), 110.2, 111.9, 111.5, 111.7, 119.4, 120.6, 127.7, 129.2, 130.9 (CH_{Ar}), 131.5, 132.6, 133.5, 139.7, 140.1, 148.4, 148.6, 149.0, 149.6 (C_{Ar}), 169.7 (C=O). IR (KBr): $\tilde{\nu}$ = 2922, 2848 (w), 1724 (s), 1598, 1524, 1488, 1461, 1430, 1321, 1297 (m), 1240, 1215, 1174, 1137, 1090, 1020 (s), 960, 901, 864, 855, 807, 746, 671, 630, 578 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 408 (M^+, 100), 393(05), 333(04), 204(06), 145(05). HRMS (EI) calcd. for $C_{24}H_{24}O_6$ [M^+]: 408.15674; found: 408.157243.

4,4″-Divinyl-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (3d)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-vinylphenylboronic acid (176 mg, 1.19 mmol), and 1,4-dioxane (5 mL/mmol triflate), **3d** was isolated as a yellow solid; yield 121 mg (77%), mp 156–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 5.9 (dd, 1H, *J* = 1.8, 6.2 Hz, CH_{2vinyl}), 5.23 (dd, 1H, *J* = 1.6, 6.9 Hz, CH_{2vinyl}), 5.70 (dd, 1H, *J* = 1.9, 7.6 Hz, CH_{2vinyl}), 5.76 (dd, 1H, *J* = 1.8, 6.9 Hz, CH_{2vinyl}), 6.66 (d, 1H, *J* = 10.8 Hz, CH_{vinyl}), 6.72 (d, 1H, *J* = 10.2 Hz, CH_{vinyl}), 7.17 (s, 1H, ArH), 7.35–7.47 (m, 4H, ArH), 7.54 (d, 1H, *J* = 8.3 Hz, ArH), 7.66–7.72 (m, 4H, ArH), 7.98 (d, 1H, *J* = 1.8 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 114.4, 114.6 ($2CH_{2vinyl}$), 126.0, 126.7, 127.1, 128.2, 128.5, 129.5, 131.1, 136.2, 136.4 (CH_{Ar}, CH_{vinyl}), 136.8, 137.1, 138.9, 139.6, 140.3, 140.8, 141.3 (C_{Ar}), 169.2 (C=O). IR (KBr): $\tilde{\nu}$ = 3085, 3032, 2947, 2923 (w), 1719 (s), 1626, 1481, 1426, 1309, 1298 (m), 1237, 1139 (s), 1088, 1049, 991, 972, 898 (m), 823 (s), 783, 700, 672, 568 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 340 (M^+, 100), 309(09), 281(04), 265(12), 162(08), 133(05). HRMS (EI) calcd. for $C_{24}H_{20}O_2$ [M^+]: 340.14578; found: 340.146235.

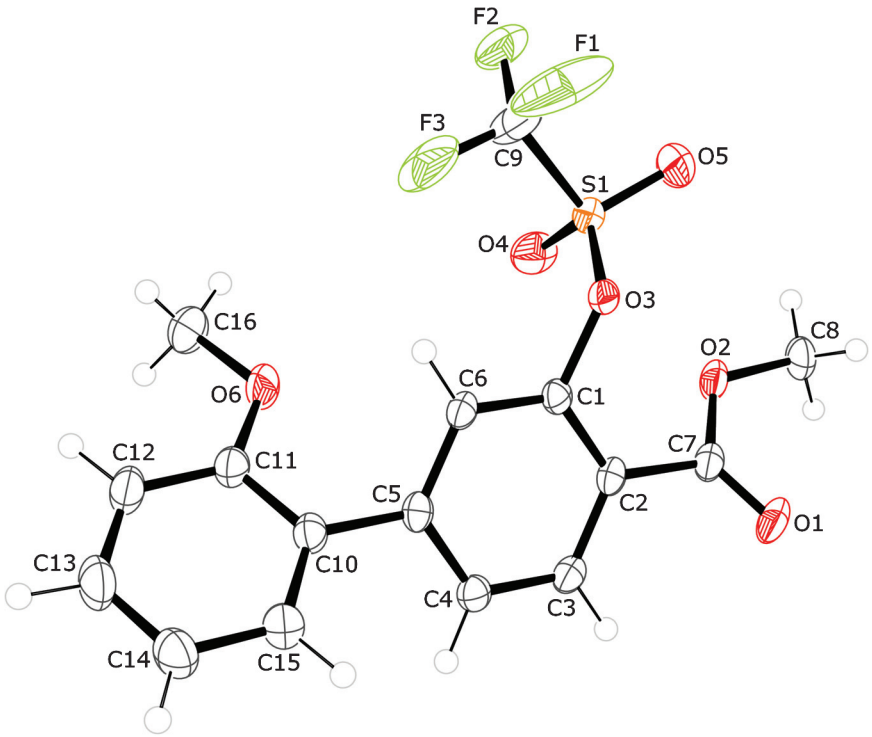
3,3″-Dichloro-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (3e)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), 3-chlorophenylboronic acid (185 mg, 1.19 mmol), and 1,4-dioxane (5 mL/mmol triflate), **3e** was isolated as a colorless viscous oil; yield 110 mg (67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 7.10–7.14 (m, 1H, ArH), 7.18–7.24 (m, 2H, ArH), 7.26 (s, 1H, ArH), 7.27–7.29 (m, 1H, ArH), 7.31 (d, 1H, *J* = 6.9 Hz, ArH), 7.42 (t, 1H, *J* = 1.8 Hz, ArH), 7.44 (t, 1H, *J* = 1.6 Hz, ArH), 7.52–7.55 (m, 1H, ArH), 7.63 (dd, 1H, *J* = 2.0, 8.0 Hz, ArH), 7.96 (d, 1 H, *J* = 1.95 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 125.2, 126.6, 127.2, 127.5, 128.4, 128.4, 129.2, 130.2, 131.2, 133.5, 133.8 (CH_{Ar}), 134.9, 135.2, 136.0 139.2, 140.5, 141.3, 142.5 (C_{Ar}), 168.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3057, 2947, 2848 (w), 1719 (s), 1594, 1566, 1463, 1435, 1311, 1294 (m), 1235 (s), 1192, 1146, 1092, 1054, 1022, 997, 970, 873 (m), 779, 691 (s), 673, 618, 559 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 356 (M^+, ^{35}Cl, ^{35}Cl)(100), 325(71), 290(20), 262(40), 200(04), 160(19), 131(05), 113(21), 75(03). HRMS (EI) calcd. for $C_{20}H_{14}Cl_2O_2$ [M^+, ^{35}Cl, ^{35}Cl]: 356.03654; found: 356.036229.

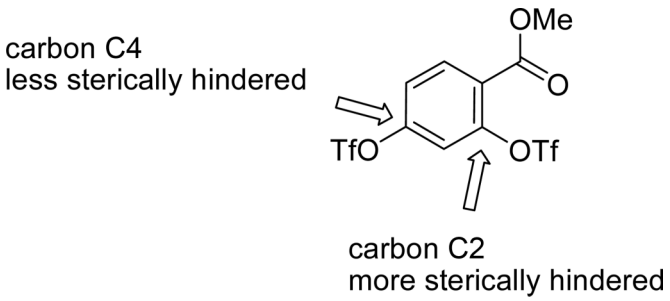
[1,1′;4′,1″]Terphenyl-2′-carboxylic acid methyl ester (3f)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (6 mol%), phenylboronic acid (145 mg, 1.19 mmol), and 1,4-dioxane (5 mL/mmol triflate), **3f** was isolated as a colorless viscous oil; yield 72 mg (54%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.51 (s, 3H, OCH_3), 7.22–7.25 (m, 4H, ArH), 7.26 (s, 1H, ArH), 7.27–7.30 (m, 3H, ArH), 7.46–7.50 (m, 4H, ArH), 7.79 (dd, 1H, *J* = 1.7, 7.7 Hz, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 125.7, 127.3, 127.4, 128.0, 128.1, 128.4, 128.9 (CH_{Ar}), 129.3 (C_{Ar}), 129.6, 130.6 (CH_{Ar}), 139.8, 141.5, 143.3, 144.1 (C_{Ar}), 168.8 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 2927, 2842 (w), 1716 (s), 1591, 1567, 1467, 1439, 1313, 1295 (m), 1231 (s), 1191, 1143, 1091, 1051, 1027, 993, 970, 873 (m), 779, 691 (s), 673, 618, 559 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 288 (M^+, 75), 257(100), 228(34), 202(08), 152(05), 128(04), 113(08). HRMS (EI) calcd. for $C_{20}H_{16}O_2$ [M^+]: 288.11448; found: 288.114296.

Fig. 4. Ortep plot of **9c**.



Scheme 8. Possible explanation for the site-selective formation of products **9a–9e**.



Methyl 3′,5′-dimethyl-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (4a)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,5-dimethylphenylboronic acid (88 mg, 0.59 mmol), and 1,4-dioxane (5 mL/mmol triflate), **4a** was isolated as a colorless solid; yield 150 mg (83%), mp 160–162 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.27 (s, 6H, $2CH_3$), 3.61 (s, 3H, OCH_3), 6.82 (s, 1H, ArH), 6.95 (s, 1H, ArH), 7.17 (s, 1H, ArH), 7.35 (d, 1H, *J* = 3.4 Hz, ArH), 7.36 (s, 1H, ArH), 7.63 (d, 1H, *J* = 3.4 Hz, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.2 ($2CH_3$), 52.3 (OCH_3), 120.0 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.4, 123.8, 126.1, 129.6, 132.6 (CH_{Ar}), 137.7, 139.2, 141.1, 143.0, 148.0 (C_{Ar}), 167.1 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.4 (CF). IR (KBr): $\tilde{\nu}$ = 3018, 2951, 2920 (w), 1723, 1601 (s), 1489 (m), 1467, 1328, 1271 (m), 1243 (s), 1137, 1099, 978 (m), 863, 785, 751 (s), 699, 577, 540 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 388 (M^+, 66), 357(07), 255(100), 227(12), 152(15), 115(03), 69(08). HRMS (EI) calcd. for $C_{17}H_{15}F_3O_5S$ [M^+]: 388.05868; found: 388.058373.

Methyl 2′,5′-dimethoxy-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (4b)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 2,5-dimethoxyphenylboronic acid (107 mg, 0.59 mmol), and 1,4-dioxane (5 mL/mmol triflate), **4b** was isolated as a yellow solid; yield 140 mg (72%), mp 148–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.69 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 3.90 (s, 3H, OCH_3), 6.81 (s, 1H, ArH), 6.83–6.86 (m, 2H, ArH), 7.24 (d, 1H, *J* = 8.5 Hz, ArH), 7.71 (dd, 1H, *J* = 2.4, 8.5 Hz, ArH), 8.14 (d, 1H, *J* = 2.3 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.6 (OCH_3), 55.8 (OCH_3), 56.1 (OCH_3), 112.6, 114.3, 116.4 (CH_{Ar}), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.2 (CH_{Ar}), 123.8, 128.3 (C_{Ar}), 133.5, 135.1 (CH_{Ar}), 138.9, 147.0, 150.5, 153.8 (C_{Ar}), 164.2 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.5 (CF). IR (KBr): $\tilde{\nu}$ = 3001, 2953, 2837 (w), 1728 (m), 1681, 1606, 1582 (w), 1504, 1464 (m), 1422 (s), 1307, 1248, 1171, 1074, 1051, 973, 905, 839, 804, 760, 693, 647, 572 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 420 (M^+, 100), 389(08), 287(46), 257(19), 227(14), 185(12), 162(06), 113(06), 69(08). HRMS (EI) calcd. for $C_{17}H_{15}F_3O_7S$ [M^+]: 420.04851; found: 420.049146.

Methyl 4′-methyl-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (4c)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-methylphenylboronic acid (80 mg, 0.59 mmol), and 1,4-dioxane (5 mL/mmol triflate), **4c** was isolated as a colorless solid; yield 112 mg (64%), mp 152–154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.26 (s, 3H, CH_3), 3.61 (s, 3H, OMe), 6.45 (dd, 2H, *J* = 8.3, 18.5 Hz, ArH), 7.24 (d, 1 H, *J* = 7.5 Hz, ArH), 7.27–7.31 (m, 1H, ArH), 7.47 (s, 1H, ArH), 7.52 (dd, 1H, *J* = 1.4, 8.1 Hz, ArH), 8.00 (d, 1H, *J* = 8.1 Hz, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.2 (CH_3), 52.3 (OCH_3), 111.7 (CH_{Ar}), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 123.0 (C_{Ar}), 124.1, 129.3, 130.7 (CH_{Ar}), 131.0 (C_{Ar}), 132.5 (CH_{Ar}), 145.2, 147.9, 156.3 (C_{Ar}), 167.1 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.4 (CF). IR (KBr): $\tilde{\nu}$ = 3012, 2952, 2926 (w), 1714, 1602 (s), 1493 (m), 1469, 1328, 1271 (m), 1243 (s), 1137, 1099, 978 (m), 863, 785, 751 (s), 699, 577, 540 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 374 (M^+, 66), 361(07), 257(100), 223(12), 148(15), 113(03), 69(08).

Methyl 3′,4′-dimethoxy-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (4d)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,4-dimethoxyphenylboronic acid (107 mg, 0.59 mmol), and 1,4-dioxane (5 mL/mmol triflate), **4d** was isolated

as a reddish solid; yield 131 mg (67%), mp 166–168 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.64 (s, 3H, OCH_3), 3.80 (s, 3H, OCH_3), 6.79 (s, 1H, ArH), 6.84–6.87 (m, 2H, ArH), 7.26 (d, 1H, *J* = 8.2 Hz, ArH), 7.671 (dd, 1H, *J* = 2.6, 8.2 Hz, ArH), 8.16 (d, 1H, *J* = 2.3 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.4 (OCH_3), 55.2 (OCH_3), 56.4 (OCH_3), 112.3, 114.6, 116.8 (CH_{Ar}), 121.0 (q, $J_{F,C}$ = 320.2 Hz, CF_3), 122.4 (CH_{Ar}), 123.4, 127.2 (C_{Ar}), 133.4, 136.1 (CH_{Ar}), 137.9, 146.0, 150.1, 152.4 (C_{Ar}), 168.2 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.2 (CF). IR (KBr): $\tilde{\nu}$ = 2999, 2952, 2849 (w), 1726 (m), 1603, 1588 (w), 1520, 1463 (m), 1421 (s), 1325, 1289, 1171, 1080, 1052, 974, 905, 883, 827, 806, 755, 684, 664, 573 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 420 (M^+, 51), 389(04), 287(100), 257(15), 229(17), 213(04), 185(05), 157(04), 114(05), 69(06).

Methyl 4′-bromo-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (4e)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-bromophenylboronic acid (118 mg, 0.59 mmol), and 1,4-dioxane (5 mL/mmol triflate), **4e** was isolated as a colorless viscous oil; yield 129 mg (63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.92 (s, 3H, OCH_3), 7.33–7.41 (m, 2H, ArH), 7.44 (d, 1H, *J* = 6.2 Hz, ArH), 7.48–7.52 (m, 2H, ArH), 7.59 (s, 1H, ArH), 7.93 (d, 1H, *J* = 6.2 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.7 (OCH_3), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 125.0, 125.6, 127.5, 128.6, 132.0 (CH_{Ar}), 133.0, 134.9, 136.0, 147.1, 147.8 (C_{Ar}), 168.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3119, 2959, 2872 (w), 1725 (s), 1613, 1586, 1479, 1461 (m), 1426 (s), 1300, 1278, 1244 (m), 1127 (s), 1076, 1001, 975, 921, 842, 782, 697, 665, 542 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 438 (M^+, ^{79}Br)(60), 383(71), 353(20), 307(100), 215(43), 170(08), 139(16), 69(05).

Methyl 2′,4′-dimethoxy-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (4f)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (146 mg, 0.69 mmol), $Pd(PPh_3)_4$ (3 mol%), 2,4-dimethoxyphenylboronic acid (107 mg, 0.59 mmol), and 1,4-dioxane (5 mL/mmol triflate), **4f** was isolated as a colorless solid; yield 142 mg (73%), mp 168–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.48–6.52 (m, 2H, ArH), 7.15–7.22 (m, 2H, ArH), 7.67 (dd, 1H, *J* = 2.4, 8.5 Hz, ArH), 8.1 (d, 1H, *J* = 2.3 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 55.4 (OCH_3), 55.5 (OCH_3), 99.0, 104.9 (CH_{Ar}), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.1 (CH_{Ar}), 123.7 (C_{Ar}), 131.1, 133.4 (CH_{Ar}), 134.9 (C_{Ar}), 135.0 (CH_{Ar}), 139.0, 146.6, 157.4, 161.2 (C_{Ar}), 168.4 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.5 (CF). IR (KBr): $\tilde{\nu}$ = 2921, 2871 (w), 1727 (m), 1677, 1609, 1578 (w), 1512, 1463 (m), 1422 (s), 1305, 1281, 1160, 1074, 1053, 967, 905, 890, 835, 797, 761, 686, 638, 571 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 420 (M^+, 38), 389(05), 287(100), 257(11), 229(04), 185(10), 128(06), 69(08). HRMS (EI) calcd. for $C_{17}H_{15}F_3O_7S$ [M^+]: 420.04851; found: 420.049231.

Methyl 4′-chloro-4-(trifluoromethylsulfonyloxy)biphenyl-3-carboxylate (4g)

Starting with **2** (200 mg, 0.46 mmol), K_3PO_4 (292 mg, 1.38 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-chlorophenylboronic acid (92 mg, 0.59 mmol), and 1,4-dioxane (5 mL/mmol triflate), **4g** was isolated as a yellow solid; yield 107 mg (59%), mp 140–142 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.91 (s, 3H, OCH_3), 7.12–7.15 (m, 1H, ArH), 7.27–7.33 (m, 1H, ArH), 7.36 (s, 1H, ArH), 7.47 (dd, 1H, *J* = 3.1, 9.0 Hz, ArH), 7.61–7.71 (m, 1H, ArH), 7.92 (d, 1H, *J* = 3.0 Hz, ArH), 8.16 (d, 1H, *J* = 2.4 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 53.1 (OCH_3), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 124.1, 125.6, 127.0, 128.3, 129.2 (CH_{Ar}), 133.0, 134.9, 136.0, 147.1, 147.8 (C_{Ar}), 168.4 (C=O). IR (KBr): $\tilde{\nu}$ = 3119, 2959, 2872 (w), 1725 (s), 1613, 1586, 1479, 1461 (m), 1426 (s), 1300, 1278, 1244 (m), 1127 (s), 1076, 1001, 975, 921, 842, 782, 697, 665, 542 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 394 (M^+, ^{35}Cl, 66), 363(11), 261(100), 233(20), 198(13), 175(06), 155(05)), 139(35), 113(05), 69(16), 63(05). HRMS (EI) calcd. for $C_{15}H_{10}ClF_3O_5S$ [M^+, ^{35}Cl]: 393.98841; found: 393.987890.

3″,5″-Dimethyl-4-vinyl-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (5a)

Starting with **4a** (100 mg, 0.25 mmol), K_3PO_4 (78 mg, 0.37 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (47 mg, 0.32 mmol), and 1,4-dioxane (5 mL/mmol triflate), **5a** was isolated as colorless solid; yield 64 mg (72%), mp 144–146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.28 (s, 6H, $2CH_3$), 3.60 (s, 3H, OCH_3), 5.20 (dd, 1H, *J* = 7.5, 3.2 Hz, CH_{2vinyl}), 5.24 (dd, 1H, *J* = 7.3, 4.2 Hz, CH_{2vinyl}), 5.71 (dd, 1H, *J* = 6.48, 3.2 Hz, CH_{vinyl}), 6.65 (d, 2H, *J* = 4.0 Hz, ArH), 6.90 (s, 1H, ArH), 7.18 (s, 1H, ArH), 7.45 (s, 2H, ArH), 7.65 (d, 2H, *J* = 2.4 Hz, ArH), 7.68 (d, 1H, *J* = 2.4 Hz, ArH), 7.94 (d, 1H, *J* = 2.4 Hz, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 21.3 ($2CH_3$), 52.0 (OCH_3), 113.9 (CH_{2vinyl}), 126.1, 126.7, 127.1, 127.9, 128.4, 129.3, 131.2, 130.1 (CH_{Ar}, CH_{vinyl}), 132.1, 133.6, 136.4, 137.0, 138.4, 139.4, 140.7 (C_{Ar}), 169.4 (C=O). IR (KBr): $\tilde{\nu}$ = 3029, 2947, 2900 (w), 1723, 1604 (s), 1479 (m), 1459, 1361, 1264 (m), 1231 (s), 1179, 1081, 957 (m), 893, 785, 762 (s), 693, 571, 551 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 342 (M^+, 100), 326(01), 311(22), 296(06), 267(08), 253(07), 202(01), 163(10), 133(05).

2″,5″-Dimethoxy-4-vinyl-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (5b)

Starting with **4b** (100 mg, 0.23 mmol), K_3PO_4 (72 mg, 0.34 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (42 mg, 0.29 mmol), and 1,4-dioxane (5 mL/mmol triflate), **5b** was isolated as colorless solid; yield 70 mg (78%), mp 156–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 5.52 (dd, 1H, *J* = 1.5, 7.2 Hz, CH_{2vinyl}), 5.62 (dd, 1H, *J* = 2.3, 6.2 Hz, CH_{2vinyl}), 5.72 (dd, 1H, *J* = 1.8, 6.2 Hz, CH_{vinyl}), 6.82–6.88 (m, 2H, ArH), 7.24 (d, 1H, *J* = 8.2 Hz, ArH), 7.30–7.40 (m, 4H, ArH), 7.60–7.66 (m, 2H, ArH), 7.92 (d, 1H, *J* = 1.8 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 55.8 (OCH_3), 56.3 (OCH_3), 113.8 (CH_{2vinyl}), 116.1, 116.5, 125.9, 128.0, 128.5, 130.4, 132.3, 133.0, 134.9 (CH_{Ar}, CH_{vinyl}), 135.0, 135.1, 136.4, 136.5, 137.4, 140.6, 150.8, 153.8 (C_{Ar}), 169.1 (C=O). IR (KBr): $\tilde{\nu}$ = 2922, 2850 (w), 1715, 1604, 1462, 1391, 1275 (m), 1227 (s), 1176, 1118, 1041, 1024, 998, 907, 877, 800, 788, 722, 639, 540 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 374 (M^+, 100), 327(07), 300(19), 285(07), 257(07), 228(04), 202(06), 150(06), 101(04), 59(06). HRMS (EI) calcd. for $C_{24}H_{22}O_4$ [M^+]: 374.15126; found: 374.150994.

4′-Methyl 4-vinyl-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (5c)

Starting with **4c** (100 mg, 0.26 mmol), K_3PO_4 (82 mg, 0.39 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (48 mg, 0.33 mmol), and 1,4-dioxane (5 mL/mmol triflate), **5c** was isolated as colorless solid; yield 60 mg (68%), mp 132–134 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.31 (s, 3H, CH_3), 3.60 (s, 3H, OCH_3), 5.19 (dd, 1H, *J* = 2.4, 9.4 Hz, CH_{2vinyl}), 5.71 (dd, 1 H, *J* = 3.8, 8.6 Hz, CH_{2vinyl}), 6.67 (dd, 1H, *J* = 10.8, 17.6 Hz, CH_{vinyl}), 7.15 (d, 2H, *J* = 6.2 Hz, ArH), 7.24 (s, 1H, ArH), 7.35–7.40 (m, 3H, ArH), 7.54–7.66 (m, 4H, ArH), 7.95 (d, 1H, *J* = 1.9 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 21.2 (CH_3), 52.0 (OCH_3), 113.9 (CH_{2vinyl}), 126.0, 126.8, 127.1, 128.1, 128.5, 129.5, 131.1, 136.2 (CH_{Ar}, CH_{vinyl}), 136.3, 136.5, 137.1, 137.9, 139.0, 139.4, 140.8 (C_{Ar}), 169.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 2946, 2920 (w), 1722, 1604 (s), 1482 (m), 1434, 1308, 1254 (m), 1234 (s), 1164, 1072, 971 (m), 854, 783, 750 (s), 694, 567 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 328 (M^+, 100), 297(24), 282(05), 253(11), 157(11), 126(06). HRMS (EI) calcd. for $C_{23}H_{20}O_2$ [M^+]: 328.14578; found: 328.146151.

3″,4″-Dimethoxy-4-vinyl-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (5d)

Starting with **4d** (100 mg, 0.23 mmol), K_3PO_4 (72 mg, 0.34 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (42 mg, 0.29 mmol), and 1,4-dioxane (5 mL/mmol triflate), **5d** was isolated as yellow solid; yield 57 mg (64%), mp 138–140 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.58 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 5.50 (dd, 1H, *J* = 2.6, 6.4 Hz, CH_{2vinyl}), 5.60 (dd, 1H, *J* = 2.4, 7.2 Hz, CH_{2vinyl}), 5.70 (dd, 1H, *J* = 1.4, 7.8 Hz, CH_{vinyl}), 6.80–6.86 (m, 2H, ArH), 7.22 (d, 1H, *J* = 6.2 Hz, ArH), 7.28–7.38 (m, 4H, ArH),

7.58–7.64 (m, 2H, ArH), 7.88 (d, 1H, J = 4.6 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 53.3 (OCH_3), 55.8 (OCH_3), 111.6, 113.4 (CH_{Ar}), 114.6 (CH_{2vinyl}), 126.7, 127.1, 128.0, 130.5, 134.6, 135.0, 135.1 (CH_{Ar}, CH_{vinyl}), 136.0, 136.1, 137.4, 138.5, 139.4, 140.6, 149.1, 151.4 (C_{Ar}), 168.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3050, 2922, 2851 (w), 1721, 1602 (s), 1461, 1433, 1390, 1240, 1215, 1171, 1093, 967, 888, 788, 722 (s), 665, 539 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 374 (M^+, 100), 325(03), 301(16), 281(05), 253(04), 226(06), 207(05), 153(08), 121(05), 57(10). HRMS (EI) calcd. for $C_{24}H_{22}O_4$ [M^+]: 374.15126; found: 374.151338.

4″-Bromo-4-vinyl-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (5e)

Starting with **4e** (100 mg, 0.22 mmol), K_3PO_4 (69 mg, 0.33 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (41 mg, 0.28 mmol), and 1,4-dioxane (5 mL/mmol triflate), **5e** was isolated as a colorless viscous oil; yield 56 mg (62%). ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 5.22 (dd, 1H, J = 2.4, 8.4 Hz, CH_{2vinyl}), 5.70 (dd, 1H, J = 2.8, 7.6 Hz, CH_{2vinyl}), 5.77 (dd, 1H, J = 2.4, 8.6 Hz, CH_{vinyl}), 7.24 (d, 2H, J = 6.2 Hz, ArH), 7.36–7.42 (m, 4H, ArH), 7.45 (s, 1H, ArH), 7.56 (d, 2H, J = 6.8 Hz, ArH), 7.66–7.70 (dd, 1H, J = 2.4, 9.6 Hz, ArH), 7.98 (d, 1H, J = 2.3 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 113.9 (CH_{2vinyl}), 126.0, 126.7, 127.1, 128.2, 128.5, 129.5, 131.1, 136.2 (CH_{Ar}, CH_{vinyl}), 136.4, 136.6, 137.1, 138.9, 139.6, 140.3, 140.8 (C_{Ar}), 169.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3084, 2946, 2921 (w), 1716 (s), 1604 (m), 1481 (m), 1455, 1389, 1256 (m), 1235 (s), 1185, 1090, 973 (m), 857, 781, 743 (s), 694, 653, 539 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 392 (M^+, ^{79}Br) (100) 319(03), 279(10), 231(05), 201(04), 173(06), 126(11), 107(08), 77(05), 57(10).

2″,4″-Dimethoxy-4-vinyl-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (5f)

Starting with **4f** (100 mg, 0.23 mmol), K_3PO_4 (72 mg, 0.34 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (42 mg, 0.29 mmol), and 1,4-dioxane (5 mL/mmol triflate), **5f** was isolated as a colorless viscous oil; yield 67 mg (67%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 5.20 (dd, 1H, J = 2.4, 10.8 Hz, CH_{2vinyl}), 5.72 (dd, 1H, J = 2.4, 9.6 Hz, CH_{2vinyl}), 6.69 (dd, 1H, J = 2.4, 10.6 Hz, CH_{vinyl}), 7.21–7.24 (m, 3H, ArH), 7.26 (s, 1H, ArH), 7.30–7.39 (m, 4H, ArH), 7.60 (dd, 1H, J = 1.9, 7.9 Hz, ArH), 7.88 (d, 1H, J = 1.6 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 55.4 (OCH_3), 55.6 (OCH_3), 99.0, 104.8 (CH_{Ar}), 113.8 (CH_{2vinyl}), 125.9, 128.6, 130.3 (CH_{Ar}), 130.4 (C_{Ar}), 130.7, 131.2, 132.0, 136.5 (CH_{Ar}, CH_{vinyl}), 136.6, 137.5, 138.9, 139.6, 140.0, 141.6, 142.0 (C_{Ar}), 169.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 2921, 2848 (w), 1716, 1608 (s), 1463, 1435, 1391 (m), 1242, 1217 (s), 1173, 1095, 965, 887, 783, 721, 663, 537(m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 374 (M^+, 100), 343(04), 285(06), 257(05), 179(06), 120(04). HRMS (EI) calcd. for $C_{24}H_{22}O_4$ [M^+]: 374.15126; found: 374.151040.

4″-Chloro-4-vinyl-[1,1′;4′,1″]terphenyl-2′-carboxylic acid methyl ester (5g)

Starting with **4g** (100 mg, 0.25 mmol), K_3PO_4 (78 mg, 0.37 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (47 mg, 0.32 mmol), and 1,4-dioxane (5 mL/mmol triflate), **5g** was isolated as a reddish solid; yield 64 mg (72%), mp 152–154 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 5.22 (dd, 1H, J = 4.6, 10.8 Hz, CH_{2vinyl}), 5.72 (dd, 1H, J = 4.3, 17.6 Hz, CH_{2vinyl}), 6.69 (dd, 1H, J = 10.8, 17.5 Hz, CH_{vinyl}), 7.21–7.25 (m, 2H, ArH), 7.35–7.41 (m, 2H, ArH), 7.44 (s, 1H, ArH), 7.54 (d, 2H, J = 8.2 Hz, ArH), 7.58–7.62 (m, 2 H, ArH), 7.68 (dd, 1H, J = 1.9, 8.6 Hz, ArH), 7.98 (d, 1H, J = 1.9 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 114.0 (CH_{2vinyl}), 126.0, 126.8, 127.1, 128.2, 129.5, 130.0, 131.1, 136.2 (CH_{Ar}, CH_{vinyl}), 136.5, 137.1, 138.9, 139.7, 140.3, 140.8, 141.0 (C_{Ar}), 169.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3054, 2922, 2852 (w), 1715, 1604 (m), 1501, 1462, 1391, 1306, 1275, 1241 (m), 1227 (s), 1176, 11181092, 1024, 998, 907, 877, 800, 788, 722, 639, 540 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 348 [M^+], ^{35}Cl, 100), 317(13), 282(31), 254(18), 226(07), 156(16), 126(10). HRMS (EI) calcd. for $C_{22}H_{17}ClO_2$ [M^+]: 348.09116; found: 348.091376.

4,4″-Dichloro-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (8a)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (438 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-chlorophenylboronic acid (280 mg, 1.80 mmol), and 1,4-dioxane (5 mL/mmol triflate), [8a] was isolated as a yellow oil; yield 180 mg (72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.56 (s, 3H, OCH_3), 7.06–7.09 (m, 1H, ArH), 7.19–7.23 (m, 4H, ArH), 7.32–7.34 (m, 2H, ArH), 7.37 (d, 1H, J = 3.2 Hz, ArH), 7.44 (d, 1H, J = 1.9 Hz, ArH), 7.45–7.47 (m, 1H, ArH), 7.82 (d, 1H, J = 8.1 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.2 (OCH_3), 125.4, 126.7, 127.5, 128.2, 129.3 (CH_{Ar}), 129.6 (C_{Ar}), 130.2, 130.9 (CH_{Ar}), 133.9, 134.9, 141.3, 142.0, 142.8, 143.0 (C_{Ar}), 168.0 (C=O). IR (KBr): $\tilde{\nu}$ = 3053, 2945, 2847 (w), 1716 (s), 1593, 1567, 1461, 1432, 1317, 1291 (m), 1231 (s), 1193, 1147, 1091, 1053, 1021, 996, 971, 875 (m), 773, 693 (s), 671, 617, 541 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 356 (M^+, ^{35}Cl, ^{35}Cl)(73), 325(100), 290(11), 262(38), 226(36), 200(04), 161(22), 131(05), 113(19). HRMS (EI) calcd. for $C_{20}H_{14}O_2Cl_2$ [M^+, ^{35}Cl, ^{35}Cl]: 356.03654; found: 356.036629.

2,5,2″,5″-Tetramethoxy-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (8b)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (438 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 2,5-dimethoxyphenylboronic acid (327 mg, 1.80 mmol), and 1,4-dioxane (5 mL/mmol triflate), **8b** was isolated as colorless solid; yield 222 mg (78%), mp 148–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 6H, $2OCH_3$), 3.66 (s, 3H, OCH_3), 3.70 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 6.74 (d, 1H, J = 2.3 Hz, ArH), 6.76 (s, 1H, ArH), 6.78 (d, 1H, J = 2.9 Hz, ArH), 6.82–6.83 (m, 2H, ArH), 6.85 (d, 1H, J = 2.8 Hz, ArH), 7.43 (d, 1H, J = 1.6 Hz, ArH), 7.50 (dd, 1H, J = 1.8, 8.0 Hz, ArH), 7.82 (d, 1H, J = 7.9 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.6 (OCH_3), 55.7 (OCH_3), 55.8 (OCH_3), 56.3 (OCH_3), 111.1, 112.7, 113.0, 113.8, 116.1, 116.5, 128.3, 129.1 (CH_{Ar}), 130.0, 130.3, 131.5 (C_{Ar}), 132.2 (CH_{Ar}), 138.2, 141.7, 150.4, 150.8, 153.6, 153.8 (C_{Ar}), 168.4 (C=O). IR (KBr): $\tilde{\nu}$ = 2928, 2831 (w), 1721, 1601, 1585, 1498, 1461, 1378,1250 (m), 1213 (s), 1175, 1092, 1040, 964, 904, 860, 821, 789 (m), 723 (s), 694, 605, 539 (m) cm^{-1}; GC–MS (EI, 70 eV): m/z (%): 408 (M^+, 100), 393(05), 377(71), 346(20), 204(08). HRMS (EI) calcd. for $C_{24}H_{24}O_6$ [M^+]: 408.15674; found: 408.156969.

[1,1′;3′,1″]Terphenyl-4′-carboxylic acid methyl ester (8c)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (438 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), phenylboronic acid (219 mg, 1.80 mmol), and 1,4-dioxane (5 mL/mmol triflate), **8c** was isolated as a reddish solid; yield 130 mg (65%), mp 150–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.51 (s, 3H, OCH_3), 7.22–7.25 (m, 4H, ArH), 7.26 (s, 1H, ArH), 7.27–7.30 (m, 3H, ArH), 7.46–7.50 (m, 4H, ArH), 7.79 (dd, 1H, J = 1.7, 7.7 Hz, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 125.7, 127.3, 127.4, 128.0, 128.1, 128.4, 128.9 (CH_{Ar}), 129.3 (C_{Ar}), 129.6, 130.6 (CH_{Ar}), 139.8, 141.5, 143.3, 144.1 (C_{Ar}), 168.8 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 2927, 2842 (w), 1716 (s), 1591, 1567, 1467, 1439, 1313, 1295 (m), 1231 (s), 1191, 1143, 1091, 1051, 1027, 993, 970, 873 (m), 779, 691 (s), 673, 618, 559 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 288 (M^+, 75), 257(100), 228(34), 202(08), 152(05), 128(04), 113(08). HRMS (EI) calcd. for $C_{20}H_{16}O_2$ [M^+]: 288.11448; found: 288.114296.

*4,4″-Di-*tert*-butyl-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (8d)*

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (438 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-*tert*-butylphenylboronic acid (320 mg, 1.80 mmol), and 1,4-dioxane (5 mL/mmol triflate), **8d** was isolated as a colorless solid; yield 220 mg (79%), mp 168–170 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.48 (s, 9H, $3CH_3$), 1.50 (s, 9H, $3CH_3$), 3.78 (s, 3H, OCH_3), 7.44 (d, 1H, J = 8.3 Hz, ArH), 7.55–7.60 (m, 4H, ArH), 7.68 (s, 1H, ArH), 7.70–7.75 (m, 4H, ArH), 8.00 (d, 1H, J = 8.1 Hz, ArH). ^{13}C NMR (75.46 MHz, $CDCl_3$): δ = 31.4 ($3CH_3$), 31.5 ($3CH_3$), 34.5 (2 C_{tBu}), 51.9 (OCH_3), 125.0, 125.4, 125.9, 127.0, 128.2, 129.5, 130.6 (CH_{Ar}), 133.9, 137.0, 138.5, 143.2, 143.9, 150.1, 151.2 (C_{Ar}), 169.0 (C=O). IR (KBr): $\tilde{\nu}$ = 3031, 2951, 2902 (w), 1727, 1605 (s), 1483 (m), 1461, 1362,

1267 (m), 1234 (s), 1180, 1085, 959 (m), 895, 788, 765 (s), 698, 572, 554 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%): 400 (M^+, 36), 385(100), 357(05), 313(03), 252(04), 185(11), 157(07), 141(04), 57(04). HRMS (EI) calcd. for $C_{28}H_{32}O_2$ [M^+]: 400.23968; found: 400.239954.

3,3″-Dihydroxy-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (8e)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (438 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 3-hydroxyphenylboronic acid (248 mg, 1.80 mmol), and 1,4-dioxane (5 mL/mmol triflate), **8e** was isolated as a colorless viscous oil; yield 138 mg (62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.56 (s, 3H, OCH_3), 6.02 (s, 2H, 2OH), 6.68 (s, 1H, ArH), 6.70.6.75 (m, 3H, ArH), 6.90 (t, 1H, *J* = 1.8 Hz, ArH), 6.98 (d, 1H, *J* = 7.9 Hz, ArH), 7.08 (d, 1H, *J* = 7.5 Hz, ArH), 7.11 (m, 1H, ArH), 7.34 (s, 1H, ArH), 7.37 (d, 1H, *J* = 1.7 Hz, ArH), 7.68 (d, 1H, *J* = 7.9 Hz, ArH). ^{13}C NMR (75.47 MHz, $CDCl_3$): δ = 52.3 (OCH_3), 114.2, 114.5, 115.2, 115.4, 119.6, 120.8, 125.7, 129.2, 129.3, 130.1, 130.3 (CH_{Ar}), 139.0, 141.2, 142.5, 142.6, 143.7, 155.4, 156.0 (C_{Ar}), 169.9 (C=O). IR (KBr): $\tilde{\nu}$ = 3058, 2941, 2927 (w), 1721, 1607 (s), 1481 (m), 1462, 1357, 1243 (m), 1221 (s), 1179, 1081, 957 (m), 891, 787, 761 (s), 697, 571, 541 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%): 320 (M^+, 100), 289(75), 260(13), 231(08), 215(09), 202(08), 189(05), 152(06), 101(05). HRMS (EI) calcd. for $C_{20}H_{16}O_4$ [M^+]: 320.10431; found: 320.104231.

2,2″-Dibromo-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (8f)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (438 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 2-bromophenylboronic acid (360 mg, 1.80 mmol), and 1,4-dioxane (5 mL/mmol triflate), **8f** was isolated as a yellow solid; yield 230 mg (74%), mp 138–140 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.60 (s, 3H, OCH_3), 7.10–7.15 (m, 2H, ArH), 7.22 (d, 1H, *J* = 1.9 Hz, ArH), 7.24 (d, 1H, *J* = 1.5 Hz, ArH), 7.26–7.30 (m, 2H, ArH), 7.43 (dd, 1H, *J* = 1.8, 8.1 Hz, ArH), 7.52–7.59 (m, 3H, ArH), 8.00 (d, 1H, *J* = 8.0 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 122.3, 122.9 (C_{Ar}), 127.0, 127.5, 128.7, 128.8 (CH_{Ar}), 129.0 (C_{Ar}), 129.3, 130.0, 130.1, 131.1, 132.1, 132.6, 133.3 (CH_{Ar}), 141.1, 141.9, 142.4, 144.4 (C_{Ar}), 167.0 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 2946, 2839 (w), 1716 (s), 1605, 1562, 1474, 1430, 1387 (m), 1286 (s), 1189, 1118, 1060, 1004, 962, 904, 827, 788 (m), 749 (s), 697, 660, 587 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%): 446 (M^+, ^{79}Br, ^{81}Br)(69), 370(12), 289(10), 257(100), 231(30), 202(08), 148(05), 128(04), 113(08).

2,2″-Difluoro-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (8g)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (438 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 2-flourophenylboronic acid (252 mg, 1.80 mmol), and 1,4-dioxane (5 mL/mmol triflate), **8g** was isolated as a reddish solid; yield 154 mg (68%), mp 144–146 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.60 (s, 3H, OCH_3), 6.95–7.10 (m, 4H, ArH), 7.18–7.26 (m, 3H, ArH), 7.35 (dt, 1H, *J* = 1.8, 7.7 Hz, ArH), 7.43 (t, 1H, *J* = 1.5 Hz, ArH), 7.53 (dt, 1H, *J* = 1.7, 8.1 Hz, ArH), 7.95 (d, 1H, *J* = 8.1 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 115.0 (d, $^2J_{C,F}$ = 22.2 Hz, CH_{Ar}), 116.2 (d, $^2J_{C,F}$ = 22.5 Hz, CH_{Ar}), 124.0 (d, $^4J_{C,F}$ = 3.5 Hz, CH_{Ar}), 124.5 (d, $^4J_{C,F}$ = 3.7 Hz, CH_{Ar}), 127.5 (d, $^2J_{C,F}$ = 13.0 Hz, CF), 128.4 (d, $^4J_{C,F}$ = 3.3 Hz, CH_{Ar}), 128.9 (C_{Ar}), 129.1 (C_{Ar}), 129.3 (d, $^3J_{C,F}$ = 8.1 Hz, CH_{Ar}), 129.9 (d, $^3J_{C,F}$ = 8.3 Hz, CH_{Ar}), 130.4 (CH_{Ar}), 130.5 (d, $^4J_{C,F}$ = 3.3 Hz, CH_{Ar}), 130.6 (d, $^4J_{C,F}$ = 3.1 Hz, CH_{Ar}), 132.0 (d, $^4J_{C,F}$ = 2.9 Hz, CH_{Ar}), 136.3 (C_{Ar}), 139.4 (d, $^4J_{C,F}$ = 1.0 Hz, CF), 157.7 (d, $^2J_{C,F}$ = 11.5 Hz, CF), 161.6 (d, $^2J_{C,F}$ = 14.3 Hz, CF), 167.5 (C=O). IR (KBr): $\tilde{\nu}$ = 3030, 2950, 2850 (w), 1722 (s), 1614, 1604, 1579, 1494, 1433, 1392, 1284, 1220, 1190, 1109, 1049, 1011, 960, 915, 842 (m), 817, 758 (s), 692, 638, 541 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%): 324 (M^+, 81), 293(100), 264(17), 244(35), 170(04), 146(05), 122(12). HRMS (EI) calcd. for $C_{20}H_{14}F_2O_2$ [M^+]: 324.09564; found: 324.095647.

4,4″-Difluoro-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (8h)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (438 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-flourophenylboronic acid (252 mg, 1.80 mmol), and 1,4-dioxane (5 mL/mmol triflate), **8h** was isolated as a colorless solid; yield 174 mg (77%), mp 156–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.58 (s, 3H, OCH_3), 6.97–7.06 (m, 4H, ArH), 7.19–7.23 (m, 2H, ArH), 7.40 (d, 1H, *J* = 1.8 Hz, ArH), 7.46–7.51 (m, 3H, ArH), 7.84 (d, 1H, *J* = 8.1 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 114.9 (d, $^2J_{C,F}$ = 21.5 Hz, CH_{Ar}), 115.8 (d, $^2J_{C,F}$ = 21.5 Hz, CH_{Ar}), 125.7 (CH_{Ar}), 128.9 (d, $^3J_{C,F}$ = 8.2 Hz, CH_{Ar}), 129.1 (C_{Ar}), 129.4 (CH_{Ar}), 129.9 (d, $^3J_{C,F}$ = 8.1 Hz, CH_{Ar}), 130.8 (CH_{Ar}), 135.7 (d, $^4J_{C,F}$ = 3.2 Hz, CF), 137.2 (d, $^4J_{C,F}$ = 3.3 Hz, CF), 142.4 (C_{Ar}), 143.1 (C_{Ar}), 162.3 (d, $^1J_{C,F}$ = 246.4 Hz, CF), 162.9 (d, $^1J_{C,F}$ = 247.9 Hz, CF), 168.3 (C=O). IR (KBr): $\tilde{\nu}$ = 3043, 2927, 2843 (w), 1721 (s), 1617, 1603, 1573, 1497, 1431, 1389, 1277, 1221, 1189, 1117, 1051, 1011, 957, 923, 839 (m), 817, 757 (s), 689, 638, 543 (m) cm^{-1}; GC–MS (EI, 70 eV): *m/z* (%): 324 (M^+, 81), 293(100), 264(20), 244(25), 170(04), 122(08). HRMS (EI) calcd. for $C_{20}H_{14}F_2O_2$ [M^+]: 324.09564; found: 324.095444.

3,3″-Bis-trifluoromethyl-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (8i)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (438 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 3-trifluoromethylphenylboronic acid (342 mg, 1.80 mmol), and 1,4-dioxane (5 mL/mmol triflate), **8i** was isolated as a colorless viscous oil; yield 187 mg (63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 7.44–7.48 (m, 4H, ArH), 7.54 (d, 2H, *J* = 7.6 Hz, ArH), 7.59 (dd, 2H, *J* = 1.8, 8.1 Hz, ArH), 7.72 (d, 1H, *J* = 7.6 Hz, ArH), 7.77 (s, 1H, ArH), 7.94 (d, 1H, *J* = 8.1 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 121.9 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.0 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 124.0 (dq, $J_{C,F}$ = 3.8 Hz, CH_{Ar}), 124.2 (dq, $J_{F,C}$ = 3.9 Hz, CH_{Ar}), 124.9 (q, $J_{C,F}$ = 3.7 Hz, CH_{Ar}), 125.3 (q, $J_{C,F}$ = 3.7 Hz, CH_{Ar}), 126.5, 128.4, 129.5 (CH_{Ar}), 129.8, 130.2 (C_{Ar}), 130.6 (CH_{Ar}), 130.7 (C_{Ar}), 131.2, 131.7, 132.0 (CH_{Ar}), 140.3, 141.9, 142.1, 142.9 (C_{Ar}), 167.8 (C=O). IR (KBr): $\tilde{\nu}$ = 3075, 2952, 2843 (w), 1725 (s), 1606, 1564, 1583, 1428, 1341, 1298 (m), 1244 (s), 1157 (m), 1125, 1071, 1035 (s), 965, 903, 844 (m), 803, 700 (s), 661, 612 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%): 424 (M^+, 57), 405(09), 393(100), 373(10), 345(13), 325(07), 296(13), 275(05), 226(05). HRMS (EI) calcd. for $C_{22}H_{14}F_6O_2$ [M^+]: 424.08925; found: 424.088866.

4,4″-Bis-trifluoromethyl-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (8j)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (438 mg, 2.07 mmol), $Pd(PPh_3)_4$ (6 mol%), 4-trifluoromethylphenylboronic acid (342 mg, 1.80 mmol), and 1,4-dioxane (5 mL/mmol triflate), **8j** was isolated as a yellow solid; yield 204 mg (69%), mp 142–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.61 (s, 3H, OCH_3), 7.38 (d, 2H, *J* = 7.9 Hz, ArH), 7.46 (d, 1H, *J* = 1.7 Hz, ArH), 7.58 (d, 1H, *J* = 1.7 Hz, ArH), 7.62 (d, 2H, *J* = 1.8 Hz, ArH), 7.64 (m, 4H, ArH), 7.95 (d, 1H, *J* = 8.1 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.0 (OCH_3), 121.9 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.0 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 124.0 (q, $J_{C,F}$ = 250.2 Hz, CF_3), 124.9 (q, $J_{C,F}$ = 3.8 Hz, CH_{Ar}), 125.9 (q, $J_{F,C}$ = 3.8 Hz, CH_{Ar}), 126.6, 127.6, 128.7, 129.6 (CH_{Ar}), 129.7, 129.8, 130.6 (C_{Ar}), 131.1 (CH_{Ar}), 142.3, 142.9, 143.0, 144.8 (C_{Ar}), 167.8 (C=O). IR (KBr): $\tilde{\nu}$ = 3071, 2947, 2841 (w), 1717 (s), 1607, 1563, 1579, 1421, 1343, 1293 (m), 1241 (s), 1161 (m), 1131, 1077, 1031 (s), 967, 907, 844 (m), 805, 703 (s), 661, 613 (m) cm^{-1}. GC–MS (EI, 70 eV): *m/z* (%): 424 (M^+, 56), 405(10), 393(100), 373(07), 345(11), 325(07), 296(20), 275(05), 226(05). HRMS (EI) calcd. for $C_{22}H_{14}F_6O_2$ [M^+]: 424.08925; found: 424.089297.

2′,5′-Dimethoxy-3-trifluoromethanesulfonyloxy-biphenyl-4-carboxylic acid methyl ester (9a)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (218 mg, 1.03 mmol), $Pd(PPh_3)_4$ (3 mol%), 2,5-dimethoxyphenylboronic acid (161 mg, 0.89 mmol), and 1,4-dioxane (5 mL/mmol triflate), [9a] was isolated as a colorless viscous oil; yield 228 mg (78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.67 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.88 (s, 3H, OCH_3),

6.80–6.84 (m, 3H, ArH), 7.47 (s, 1H, ArH), 7.52 (dd, 1H, J = 1.6, 8.3 Hz, ArH), 8.00 (d, 1H, J = 8.1 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 55.8 (OCH_3), 56.0 (OCH_3), 112.8, 114.8, 116.3 (CH_{Ar}), 121.3 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.2 (C_{Ar}), 123.8 (CH_{Ar}), 127.9 (C_{Ar}), 129.0, 132.2 (CH_{Ar}), 145.0, 147.9, 150.6, 153.8 (C_{Ar}), 164.1 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.4 (CF). IR (KBr): $\tilde{\nu}$ = 3001, 2953, 2837 (w), 1725, 1614, 1553, 1510, 1464 (m), 1421 (s), 1387, 1270, 1246 (m), 1202, 1135, 1072 (s), 1022, 893, 824, 778, 730, 664, 571 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 420 (M^+, 100), 389(06), 255(11), 240(15), 187(17), 162(05), 114(04), 69(05). HRMS (EI) calcd. for $C_{17}H_{15}F_3O_7S$ [M^+]: 420.04851; found: 420.048583.

3′,4′-Dimethoxy-3-trifluoromethanesulfonyloxy-biphenyl-4-carboxylic acid methyl ester (9b)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (218 mg, 1.03 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,4-dimethoxyphenylboronic acid (161 mg, 0.89 mmol), and 1,4-dioxane (5 mL/mmol triflate), **9b** was isolated as a colorless solid; yield 210 mg (72%); mp 148–150 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.86 (s, 3H, OCH_3), 6.97 (d, 1H, J = 2.1 Hz, ArH), 7.05 (dd, 1H, J = 2.1, 8.3 Hz, ArH), 7.20 (s, 1H, ArH), 7.33 (d, 1H, J = 1.3 Hz, ArH), 7.52 (d, 1H, J = 1.7, 8.1 Hz, ArH), 8.00 (d, 1H, J = 8.2 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.4 (OCH_3), 55.2 (OCH_3), 56.4 (OCH_3), 110.1, 111.6, 119.9 (CH_{Ar}), 120.2 (q, $J_{F,C}$ = 320.2 Hz, CF_3), 120.6, 126.1 (CH_{Ar}), 127.7, 131.6 (C_{Ar}), 133.0 (CH_{Ar}), 147.5, 148.6, 149.5, 150.2 (C_{Ar}), 168.2 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.2 (CF). IR (KBr): $\tilde{\nu}$ = 2999, 2952, 2849 (w), 1726 (m), 1603, 1588 (w), 1520, 1463 (m), 1421 (s), 1325, 1289, 1171, 1080, 1052, 974, 905, 883, 827, 806, 755, 684, 664, 573 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 420 (M^+, 100), 389(07), 259(62), 228(09), 185(05), 157(04), 114(06), 69(06). HRMS (EI) calcd. for $C_{17}H_{15}F_3O_7S$ [M^+]: 420.04851; found: 420.048645.

2′-Methoxy-3-trifluoromethanesulfonyloxy-biphenyl-4-carboxylic acid methyl ester (9c)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (218 mg, 1.03 mmol), $Pd(PPh_3)_4$ (3 mol%), 2-methoxyphenylboronic acid (135 mg, 0.89 mmol), and 1,4-dioxane (5 mL/mmol triflate), **9c** was isolated as a colorless crystalline solid; yield 206 mg (76%); mp 150–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.74 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.91–7.00 (m, 2H, ArH), 7.22–7.32 (m, 2H, ArH), 7.47 (s, 1H, ArH), 7.53 (dd, 1H, J = 1.6, 8.7 Hz, ArH), 8.03 (d, 1H, J = 8.1 Hz, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 55.4 (OCH_3), 111.4, 121.1 (CH_{Ar}), 122.0 (q, $J_{F,C}$ = 321.0 Hz, CF_3), 123.8, 129.0 (CH_{Ar}), 127.1 (C_{Ar}), 130.4, 130.6, 132.2 (CH_{Ar}), 145.2, 146.1, 147.9, 156.3 (C_{Ar}), 164.2 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.5 (CF_3). IR (KBr): $\tilde{\nu}$ = 3072, 2954, 2918 (w), 1726 (s), 1687 (w), 1615 (m), 1582 (w), 1483 (m), 1422 (s), 1397, 1292 (m), 1245 (s), 1136, 1073 (s), 969 (w), 914 (s), 858 (w), 826 (s), 783 (m), 752 (s), 695, 568 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 390 (M^+, 100), 359(19), 225(27), 197(11), 169(21), 155(10), 69(07). HRMS (EI) calcd. for $C_{16}H_{13}F_3O_6S$ [M^+]: 390.03794; found: 390.037761.

2′,4′-Dimethoxy-3-trifluoromethanesulfonyloxy-biphenyl-4-carboxylic acid methyl ester (9d)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (218 mg, 1.03 mmol), $Pd(PPh_3)_4$ (3 mol%), 2,4-dimethoxyphenylboronic acid (161 mg, 0.89 mmol), and 1,4-dioxane (5 mL/mmol triflate), **9d** was isolated as a colorless crystalline solid; yield 196 mg (67%), mp 150–152 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.73 (s, 3H, OCH_3), 3.78 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 6.48–6.52 (m, 2H, ArH), 7.15–7.22 (m, 2H, ArH), 7.67 (dd, 1H, J = 2.4, 8.5 Hz, ArH), 8.1 (d, 1H, J = 2.3 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.5 (OCH_3), 55.4 (OCH_3), 55.5 (OCH_3), 99.0, 104.9 (CH_{Ar}), 120.0 (q, $J_{F,C}$ = 320.0 Hz, CF_3), 122.1 (CH_{Ar}), 123.7 (C_{Ar}), 131.1, 133.4 (CH_{Ar}), 134.9 (C_{Ar}), 135.0 (CH_{Ar}), 139.0, 146.6, 157.4, 161.2 (C_{Ar}), 168.4 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.5 (CF). IR (KBr): $\tilde{\nu}$ = 2921, 2871 (w), 1727 (m), 1677, 1609, 1578 (w), 1512, 1463 (m), 1422 (s), 1305, 1281, 1160, 1074, 1053, 967, 905, 890, 835, 797, 761, 686, 638, 571 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 420 (M^+, 38), 389(05), 287(100), 257(11), 229(04), 185(10), 128(06), 69(08). HRMS (EI) calcd. for $C_{17}H_{15}F_3O_7S$ [M^+]: 420.04851; found: 420.048507.

Methyl 3′,5′-dimethyl-3-(trifluoromethyl-sulfonyloxy)biphenyl-4-carboxylate (9e)

Starting with **7** (300 mg, 0.69 mmol), K_3PO_4 (218 mg, 1.03 mmol), $Pd(PPh_3)_4$ (3 mol%), 3,5-dimethylphenylboronic acid (133 mg, 0.89 mmol), and 1,4-dioxane (5 mL/mmol triflate), **9e** was isolated as colorless oil; yield 162 mg (60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (s, 6H, $2CH_3$), 3.59 (s, 3H, OCH_3), 6.81 (s, 1H, ArH), 6.92 (s, 1H, ArH), 7.15 (s, 1H, ArH), 7.34 (d, 1H, J = 3.4 Hz, ArH), 7.36 (s, 1H, ArH), 7.61 (d, 1H, J = 3.4 Hz, ArH). ^{13}C NMR (62.89 MHz, $CDCl_3$): δ = 21.1 ($2CH_3$), 52.4 (OCH_3), 120.0 (q, $J_{F,C}$ = 320 Hz, CF_3), 122.6, 123.4, 126.0, 129.3, 132.4 (CH_{Ar}), 137.7, 139.2, 141.1, 143.0, 148.0 (C_{Ar}), 167.1 (C=O). ^{19}F NMR (282 MHz, $CDCl_3$): δ = –73.4 (CF). IR (KBr): $\tilde{\nu}$ = 3016, 2948, 2920 (w), 1723, 1600 (s), 1485 (m), 1462, 1324, 1268 (m), 1241 (s), 1136, 1099, 975 (m), 861, 785, 753 (s), 699, 577, 540 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 388 (M^+, 66), 357(07), 255(100), 227(12), 152(15), 115(03), 69(08). HRMS (EI) calcd. for $C_{17}H_{15}F_3O_5S$ [M^+]: 388.05868; found: 388.058632.

2,5-Dimethoxy-4″-vinyl-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (10a)

Starting with [9a] (150 mg, 0.35 mmol), K_3PO_4 (110 mg, 0.52 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (66 mg, 0.45 mmol), and 1,4-dioxane (5 mL/mmol triflate), [10a] was isolated as yellow solid; yield 102 mg (76%), mp 156–158 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.71 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 5.19 (d, 1H, J = 10.8 Hz, CH_{2vinyl}), 5.71 (d, 1H, J = 17.5 Hz, CH_{2vinyl}), 6.67 (d, 1H, J = 6.3 Hz, CH_{vinyl}), 6.82 (d, 3H, J = 6.4 Hz, ArH), 7.24 (d, 2H, J = 7.3 Hz, ArH), 7.36 (d, 2H, J = 7.3 Hz, ArH), 7.46 (s, 1H, ArH), 7.50 (d, 1H, J = 7.8 Hz, ArH), 7.80 (d, 1H, J = 7.7 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 55.8 (OCH_3), 56.3 (OCH_3), 112.7 (CH_{Ar}), 113.8 (CH_{2vinyl}), 113.9, 116.5, 125.8, 128.3, 128.6, 129.7 (CH_{Ar}), 130.2 (C_{Ar}), 131.7 (CH_{Ar}), 136.4 (C_{Ar}), 136.5 (CH_{vinyl}), 135.0, 140.9, 141.6, 142.0, 150.7, 153.8 (C_{Ar}), 168.9 (C=O). IR (KBr): $\tilde{\nu}$ = 2996, 2832 (w), 1716 (s), 1600, 1553, 1483, 1431, 1379 (m), 1266, 1211 (s), 1138 (m), 1095, 1021, 1012 (s), 989, 906, 877 (m), 843 (s), 827, 752, 688, 631, 542 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 374 (M^+, 100), 343(04), 327(06), 300(15), 285(10), 257(06), 227(04), 202(07), 180(04), 150(06), 101(04), 59(06). HRMS (EI) calcd. for $C_{24}H_{22}O_4$ [M^+]: 374.15126; found: 374.151271.

3,4-Dimethoxy-4″-vinyl-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (10b)

Starting with **9b** (150 mg, 0.35 mmol), K_3PO_4 (110 mg, 0.52 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (66 mg, 0.45 mmol), and 1,4-dioxane (5 mL/mmol triflate), [10b] was isolated as white solid; yield 96 mg (72%), mp 142–144 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.57 (s, 3H, OCH_3), 3.81 (s, 3H, OCH_3), 3.83 (s, 3H, OCH_3), 5.17 (d, 1H, J = 11.1 Hz, CH_{2vinyl}), 5.69 (d, 1H, J = 17.5 Hz, CH_{2vinyl}), 6.66 (dd, 1H, J = 10.9, 17.6 Hz, CH_{vinyl}), 6.84 (d, 1H, J = 8.3 Hz, ArH), 7.03 (d, 1H, J = 1.8 Hz, ArH), 7.10 (dd, 1H, J = 2.0, 8.3 Hz, ArH), 7.22 (d, 2H, J = 8.1 Hz, ArH), 7.36 (d, 1H, J = 8.1 Hz, ArH), 7.44 (d, 2H, J = 1.5 Hz, ArH), 7.48 (dd, 1H, J = 1.7, 8.0 Hz, ArH), 7.82 (d, 1H, J = 8.0 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 52.1 (OCH_3), 55.9 (OCH_3), 56.0 (OCH_3), 111.3, 111.5 (CH_{Ar}), 113.9 (CH_{2vinyl}), 119.7 125.4, 125.9, 128.6, 129.0, 130.7 (CH_{Ar}), 132.6 (C_{Ar}), 136.4 (CH_{vinyl}), 136.6, 137.0, 138.2, 141.0, 142.9, 143.9, 149.3 (C_{Ar}), 168.6 (C=O). IR (KBr): $\tilde{\nu}$ = 2998, 2835 (w), 1715 (s), 1600, 1518, 1485, 1462, 1432, 1379, 1283 (m), 1246 (s), 1212, 1170, 1097, 1041, 990, 905, 843, 808, 784, 732, 682, 620, 541 (m) cm^{-1}. GC–MS (EI, 70 eV): m/z (%): 374 (M^+, 100), 359(04), 331(07), 301(12), 281(06), 253(08), 226(06), 207(05), 153(08), 121(05), 57(10). HRMS (EI) calcd. for $C_{24}H_{22}O_4$ [M^+]: 374.15126; found: 374.151281.

2-Methoxy-4″-vinyl-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (10c)

Starting with **9c** (150 mg, 0.38 mmol), K_3PO_4 (120 mg, 0.57 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (72 mg, 0.49 mmol),

and 1,4-dioxane (5 mL/mmol triflate), 10c was isolated as off white solid; yield 85 mg (64%), mp 160–162 °C. ^{1}H NMR (250 MHz, $CDCl_3$): δ = 3.58 (s, 3H, OCH_3), 3.72 (s, 3H, OCH_3), 5.17 (d, 1H, *J* = 10.9 Hz, CH_{2vinyl}), 5.68 (d, 1H, *J* = 17.6 Hz, CH_{2vinyl}), 6.67 (dd, 1H, *J* = 10.9, 17.6 Hz, CH_{vinyl}), 6.94 (dd, 2H, *J* = 7.9, 14.0 Hz, ArH), 7.22–7.29 (m, 4H, ArH), 7.36 (d, 1H, *J* = 8.1 Hz, ArH), 7.46 (d, 1H, *J* = 1.2 Hz, ArH), 7.50 (dd, 1H, *J* = 1.6, 8.0 Hz, ArH), 7.42 (s, 1H, ArH), 7.80 (d, 1H, *J* = 8.0 Hz, ArH). ^{13}C NMR (62.90 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 55.5 (OCH_3), 111.3 (CH_{Ar}), 113.8 (CH_{2vinyl}), 120.9, 125.8, 128.3, 128.6 (CH_{Ar}), 128.8 (C_{Ar}), 129.4, 129.7, 130.7, 131.8 (CH_{Ar}), 136.4 (C_{Ar}), 136.5 (CH_{vinyl}), 141.0, 141.8, 141.9, 142.6, 156.4 (C_{Ar}), 168.9 (C=O). IR (KBr): $\tilde{\nu}$ = 3002, 2947, 2835 (w), 1716 (s), 1627, 1580, 1513, 1498, 1461, 1386 (m), 1243 (s), 1180, 1137, 1120, 1055, 1024, 1005, 904, 786 (m), 750 (s), 715, 637, 574, 541 (m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 344 (M^+, 100), 313(24), 285(06), 270(10), 239(10), 164(06), 119(04). HRMS (EI) calcd. for $C_{23}H_{20}O_3$ [M^+]: 344.14070; found: 344.140881.

2,4-Dimethoxy-4″-vinyl-[1,1′;3′,1″]terphenyl-4′-carboxylic acid methyl ester (10d)

Starting with 9d (150 mg, 0.35 mmol), K_3PO_4 (110 mg, 0.52 mmol), $Pd(PPh_3)_4$ (3 mol%), 4-vinylphenylboronic acid (66 mg, 0.45 mmol), and 1,4-dioxane (5 mL/mmol triflate), **10d** was isolated as a colorless solid; yield 92 mg (69%), mp 160–162 °C. ^{1}HNMR (300 MHz, $CDCl_3$): δ = 3.59 (s, 3H, OCH_3), 3.75 (s, 3H, OCH_3), 3.79 (s, 3H, OCH_3), 5.20 (dd, 1H, *J* = 2.4, 10.8 Hz, CH_{2vinyl}), 5.72 (dd, 1H, *J* = 2.4, 9.6 Hz, CH_{2vinyl}), 6.69 (dd, 1H, *J* = 2.4, 10.6 Hz, CH_{vinyl}), 7.21–7.24 (m, 3H, ArH), 7.26 (s, 1H, ArH), 7.30–7.39 (m, 4H, ArH), 7.60 (dd, 1H, *J* = 1.9, 7.9 Hz, ArH), 7.88 (d, 1H, *J* = 1.6 Hz, ArH). ^{13}CNMR (75.47 MHz, $CDCl_3$): δ = 51.9 (OCH_3), 55.4 (OCH_3), 55.6 (OCH_3), 99.0, 104.8 (CH_{Ar}), 113.8 (CH_{2vinyl}), 125.9, 128.6, 130.3 (CH_{Ar}), 130.4 (C_{Ar}), 130.7, 131.2, 132.0, 136.5 (CH_{Ar}, CH_{vinyl}), 136.6, 137.5, 138.9, 139.6, 140.0, 141.6, 142.0 (C_{Ar}), 169.1 (C=O). IR (KBr): $\tilde{\nu}$ = 3052, 2921, 2848 (w), 1716, 1608 (s), 1463, 1435, 1391 (m), 1242, 1217 (s), 1173, 1095, 965, 887, 783, 721, 663, 537(m) cm^{-1}. GC–MS (EI, 70 eV): *m*/*z* (%): 374 (M^+, 100), 343(04), 285(06), 257(05), 179(06), 120(04). HRMS (EI) calcd. for $C_{24}H_{22}O_4$ [M^+]: 374.15126; found: 374.151040.

Supplementary material

Supplementary material is available with the article through the journal Web site at http://nrcresearchpress.com/doi/suppl/10.1139/cjc-2013-0201. CCDC 894261–894264 contain all crystallographic details of this publication and are available, free of charge, via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, GB-Cambridge CB21EZ; Fax: (+44)1223-336-033 or e-mail: deposit@ccdc.cam.ac.uk.

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