Pd-Catalysed Decarboxylative Suzuki Reactions and Orthogonal Cu-based *O*-Arylation of Aromatic Carboxylic Acids

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Supporting Information

Table of Contents

1. General Information
a. Materials b. Methods
2. Experimental Section
 a. Synthesis of the arylboron reagents b. Preparation of the catalysts c. Optimization of the reaction conditions d. General procedures for the Pd-catalysed decarboxylative Suzuki cross-coupling e. General procedures for the Cu-catalysed <i>O</i>-arylation of aromatic carboxylic acids
3. Characterization of the Products
NMR spectra data of compounds
4. Copies of ¹ H-NMR and ¹³ C-NMR Spectra

1. General Information.....

a. Materials

All reactions were carried out in oven-dried vials. The solvents, i.e. DMSO, NMP, DMF, DMAc, diglyme, were bought from Sigma-Aldrich (Sealed under argon) without further purification. All benzoic acids were purchased from Alfa Aesar, TCI or Sigma-Aldrich. All aryl boronic acids were purchased from Alfa Aesar, J&K or Sigma-Aldrich and used directly. All Ag and Cu salts were bought from Sigma-Aldrich, Strem, or Alfa Aesar. All the other reagents and solvents were bought from Sinopharm Chemical Reagent Co. Ltd or Alfa Aesar and were purified when necessary.

b. Methods

¹H-NMR, ¹³C-NMR, ¹⁹F-NMR spectra were recorded on a Bruker Advance 400 spectrometer at ambient temperature in CDCl₃ unless otherwise noted. Data for ¹H-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Data for ¹³C-NMR are reported in terms of chemical shift (δ ppm). Data for ¹⁹F-NMR are reported as follows: chemical shift (δ ppm), multiplicity, integration, and coupling constant (Hz). Gas chromatographic (GC) analysis was acquired on a Shimadzu GC-2014 Series GC System equipped with a flame-ionization detector. GC-MS analysis was performed on Thermo Scientific AS 3000 Series GC-MS System. High-resolution mass spectra (HRMS) were recorded on a BRUKER VPEXII spectrometer with EI mode. Elementary analysis was carried out on Elementar Vario EL III elemental analyzer. Organic solutions were concentrated under reduced pressure on a Buchi rotary evaporator. Flash column chromatographic purification of products was accomplished using forced-flow chromatography on Silica Gel (200-300 mesh).

2. Experimental Section.....

a. Synthesis of the arylboron reagents.

Table S1



b. Preparation of the catalyst:

Preparation of palladium (II) trifluoroacetate:

A 50 ml oven-dried flask was charged with $Pd(OAc)_2$ (1.0 g, 4.46 mmol). 25 ml trifluoroacetatic acid was added. The mixture was stirred and heated to reflux (at 90 °C) in an oil bath. A gray-brown solid was formed as the mixture was heated. The solid was isolated by filtration and washed with trifluoroacetic acid (*ca.* 10 ml). The residue was dried under vacuum at 40°C for 3 h offering a brownish powder.

Reference: Daniel P. Bancroft; F. Albert Cotton; Mark Verbruggen Acta Cryst. 1989, C45, 1289.

Preparation of bis(acetonitrile) palladium (II) *p*-toluenesulfonate:

To a clear dark orange solution of $Pd(OAc)_2$ (0.33 g, 1.47 mmol) in acetonitrile (30 ml) a solution of *p*-toluenesulfonic acid (1.5 g, 7.9 mmol) in acetonitrile (40 ml) was added dropwise with stirring. The color gradually changed to pale yellow. Subsequently diethyl ether (50 ml) was added, and this resulted in precipitation of fine pale yellow microcrystals. The suspension was set aside over night and the supematent liquid was decanted. The crystals were washed with diethyl ether, dried under a slight vacuum, and shown to be $Pd(MeCN)_2(OTs)_2$.

Reference: E. Drent; J. A. M. van Broekhoven; M. J. Doyle J. Organomet. Chem., 1991, 417, 235.

Preparation of bis(acetonitrile)dichloropalladium(II):

A suspension of $PdCl_2$ (1.00 g, 5.65 mmol) was heated to reflux in CH_3CN (50 ml) with vigorous stirring for 10 h under N₂. Hot filtration of the resultant wine-red coloured solution through a ceolite pad into stirred petroleum spirit (40–60 °C) at room temperature afforded a yellow-orange solid. Recrystallisation from CH_3CN (100 ml), DCM (150 ml) and hexane (50 ml) gave $(CH_3CN)_2PdCl_2$ as a bright yellow powdery solid.

Reference: Mathews, Christopher J.; Smith, Paul J.; Welton, Tom *J. Mol. Catal. A Chem.*, **2003**, *206*, 77.

c. Optimization of the reaction conditions:

General Procedure:

A 10ml oven-dried vial was charged with $Pd(TFA)_2$ (0.04 mmol), Ag_2CO_3 (0.6 mmol), 2,4,6-trimethoxybenzoic acid (0.2 mmol), benzeneboronic acid (0.4 mmol). DMSO (1.0 ml) was added by syringe at room temperature. The vial was then sealed and the mixture was allowed to stir at the appointed temperature (120 ± 5 °C) for 2 h. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with ethyl acetate, and analyzed by gas chromatography.

STable2

Decarboxylative Suzuki coupling between 2,4,6-trimethoxybenzoic acid and organoboron reagents^[a].



[a] Condition for this transformation: 0.2 mmol of, 0.4 mmol of benzeneboronic acid, 20% mol of catalyst, 3.0 equiv.Ag₂CO₃, 1ml DMSO, 120°C, 2 h. GC yields were determined with the use of benzophenone as an internal standard. [b]Yields were based on 2,4,5-trimethoxybenzoic acid.

STable 3

Various conditions towards the decarboxylative cross-coupling between 2,4,6-trimethoxybenzoic acid and benzeneboronic acid^[a]



Entry	Pd Source	Ag Source	Solvent	Yield [%] ^[b]
1	Pd(TFA) ₂	Ag ₂ CO ₃	DMF	10
2	Pd(TFA) ₂	Ag ₂ CO ₃	NMP	trace
3	Pd(TFA) ₂	Ag ₂ CO ₃	DMSO:DMF=1:9	69
4	Pd(TFA) ₂	Ag_2CO_3	DMSO:NMP=1:9	80
5	Pd(OAc) ₂	Ag ₂ CO ₃	DMSO	51
6	PdCl ₂	Ag ₂ CO ₃	DMSO	53
7	Pd(CH ₃ CN) ₂ Cl ₂	Ag ₂ CO ₃	DMSO	54
8	Pd(TFA) ₂	Ag ₂ CO ₃	DMSO	96
9 ^[c]	Pd(TFA) ₂	Ag_2CO_3	DMSO	95
10 ^[d]	Pd(TFA) ₂	Ag_2CO_3	DMSO	61
11 ^[e]	Pd(TFA) ₂	Ag ₂ CO ₃	DMSO	35
12	1	Ag ₂ CO ₃	DMSO	0
13	Pd(TFA) ₂	1	DMSO	trace
14	Pd(CH ₃ CN) ₄ (BF4) ₂	Ag_2CO_3	DMSO	74
15	Pd(CH ₃ CN) ₂ (OTS) ₂	Ag_2CO_3	DMSO	61
16	Pd(TFA) ₂	Ag ₃ PO ₄	DMSO	36
17	Pd(TFA) ₂	Ag ₂ O	DMSO	79
18	Pd(TFA) ₂	AgOAc	DMSO	22
19	Pd(TFA) ₂	AgTFA	DMSO	7
20	Pd(TFA) ₂	AgF ₂	DMSO	53
21	Pd(TFA) ₂	AgOTs	DMSO	5
22	Pd(TFA) ₂	AgOMs	DMSO	4
23	Pd(TFA) ₂	Ag_2SO_4	DMSO	6
24	Pd(TFA) ₂	AgBF ₄	DMSO	26
25	Pd(TFA) ₂	AgNO₃	DMSO	16

Table S3

[a]Condition for this transformation: 0.2 mmol of 2,4,6-trimethoxybenzoic acid, 0.4 mmol of benzeneboronic acid, 20% mol of catalyst, 3.0 equiv. [Ag], 1ml of solvent, 120°C, 30 min. GC yields were determined with the use of benzophenone as an internal standard. [b]Yields were based on 2,4,5-trimethoxybenzoic acid. [c] 10min. [d] 10 mol% $Pd(TFA)_{2.}$ [e] 5 mol% $Pd(TFA)_{2.}$

d. General Procedure for Pd-catalysed decarboxylative Suzuki cross-coupling:

General procedure :

Palladium(II) trifluoroacetate (0.04 mmol), Ag_2CO_3 (0.6 mmol), benzoic acid (0.2 mmol) and the aryl boronic reagent (0.4 mmol) were placed in an oven-dried 10 ml vial. Then DMSO (1 ml) was added with a syringe. The vial was sealed and stirred at $120\pm5^{\circ}C$ for the appointed time. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with diethyl ether (30 ml). It was then filtered through a short silica column to remove the deposition. The organic layers were washed with water (50 ml×2), and then with brine, dried over MgSO₄, and filtered. The solvents were removed. Purification of the residue by column chromatography (silica gel, ethyl acetate/petroleum ether) yielded the desired product.

STable 4

Various conditions towards the Cu-catalysed cross-coupling between 2,4,6-trimethoxybenzoic acid and benzeneboronic acid^[a]



Entry	Cu Source	Base	Solvent	Yield [%] ^[b]
1 ^[c]	CuF ₂	Ag ₂ CO ₃	DMSO	87
2	CuF ₂	Ag ₂ CO ₃	DMSO	35
3	$Cu(OAc)_2$	Ag ₂ CO ₃	DMSO	78
4	CuCl ₂	Ag ₂ CO ₃	DMSO	82
5	Cul	Ag ₂ CO ₃	DMSO	85
6	Cu(OTf) ₂	Ag ₂ CO ₃	DMSO	93
7	/	Ag ₂ CO ₃	DMSO	0
8	Cu(OTf) ₂	1	DMSO	trace
9	Cu(OTf) ₂	AgOAc	DMSO	16
10	Cu(OTf) ₂	AgOTs	DMSO	trace
11	Cu(OTf) ₂	Ag ₂ O	DMSO	77
12	Cu(OTf) ₂	Ag ₂ CO ₃	DMF	74
13	Cu(OTf) ₂	Ag ₂ CO ₃	NMP	61
14	Cu(OTf) ₂	Ag ₂ CO ₃	Toluene	10
15	Cu(OTf) ₂	Ag ₂ CO ₃	Diglyme	0
16	Cu(OTf) ₂	Ag ₂ CO ₃	DMAc	75
17 ^[d]	Cu(OTf) ₂	K ₂ CO ₃	DMSO	trace
18 ^[d]	Cu(OTf) ₂	Na ₂ CO ₃	DMSO	trace
19 ^[d]	Cu(OTf) ₂	Prydine	DMSO	36

Table S4

[a] Condition for this transformation: 0.2 mmol of 2,4,6-trimethoxybenzoic acid, 0.4 mmol of benzeneboronic acid, 20% mol of catalyst, 2.0 equiv. base, 1ml of solvent, 120°C, 2 h. GC yields were determined with the use of benzophenone as an internal standard. [b] Yields were based on 2,4,5-trimethoxybenzoic acid. [c] 1.0 eq. CuF2. [d] 200 mg 4Å MS,1 atm O_2 as the oxidant.

e. General procedure for the Cu-catalysed O-arylation of aromatic carboxylic acids

General procedure :

Copper(II) trifluoromethanesulfonate (0.04 mmol), Ag_2CO_3 (0.4 mmol), benzoic acid (0.2 mmol) and the aryl boronic acid (0.4 mmol) were placed in an oven-dried 10 ml vial. Then DMSO (1 ml) was added with a syringe. The vial was sealed and stirred at $120\pm5^{\circ}C$ for the appointed time. Upon completion of the reaction, the mixture was cooled to room temperature and diluted with diethyl ether (30 ml). It was then filtered through a short silica column to remove the deposition. The organic layers were washed with water (50 ml×2), and then with brine, dried over MgSO₄, and filtered. The solvents were removed. Purification of the residue by column chromatography (silica gel, ethyl acetate/petroleum ether) yielded the desired product.

3. Characterization of the Products.....



2,4,6-trimethoxybiphenyl (3a). Spectral data corresponds to that previously reported. Colorless solid (45 mg, 92% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.71 (s, 6H), 3.86 (s, 3H), 6.23 (s, 2H), 7.33 (m, 5H). ¹³C-NMR (100 MHz, CDCl₃) δ 55.39, 55.90, 90.99, 112.62, 126.49, 127.63, 131.22, 134.14, 158.39, 160.53.

Reference: Ikuya Ban; Tomoko Sudo; Tadashi Taniguchi; Kenichiro Itami Org. Lett. 2008, 10, 3607.



2,4,6-trimethoxy-4'-methylbiphenyl (3b). Spectral data corresponds to that previously reported. Colorless solid (45 mg, 87% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.36 (s, 3H), 3.69 (s, 6H), 3.84 (s, 3H), 6.22 (s, 2H), 7.17-7.23 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ 21.39, 55.41, 55.92, 91.00, 112.54, 128.54, 128.91, 131.07, 136.04, 158.49, 160.45.

Reference: Ikuya Ban; Tomoko Sudo; Tadashi Taniguchi; Kenichiro Itami Org. Lett. 2008, 10, 3607.



4'-bromo-2,4,6-trimethoxybiphenyl (3c). Spectral data corresponds to that previously reported. Colorless solid (61 mg, 95% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.72 (s, 6H), 3.86 (s, 3H), 6.22 (s, 2H), 7.20 (d, 2H, *J*=8.0 Hz), 7.48 (d, 2H, *J*=8.0 Hz). ¹³C-NMR (100 MHz, CDCl₃): δ 55.40, 55.85, 90.94, 111.21, 120.50, 130.79, 133.00, 133.06, 158.22, 160.82.

Reference: Ikuya Ban; Tomoko Sudo; Tadashi Taniguchi; Kenichiro Itami Org. Lett. 2008, 10, 3607.



4'-phenyl-2,4,6-trimethoxybiphenyl (3d). Colorless solid (64 mg, 94% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.74 (s, 6H), 3.87 (s, 3H), 6.25 (s, 2H), 7.32 (m, 1H), 7.43 (m, 4H), 7.62 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃): δ 55.42, 55.95, 91.02, 112.07, 126.45, 126.98, 127.18, 128.67, 131.64,





2,4,6-trimethoxy-4'-(trifluoromethyl)biphenyl (3e). Colorless solid (56 mg, 89% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.71 (s, 6H), 3.85 (s, 3H), 6.23 (s, 2H), 7.44 (d, 2H, *J*=8.0 Hz), 7.60 (d, 2H, *J*=8.0 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 55.40, 55.83, 90.96, 111.05, 124.47(q, *J*=3.5 Hz), 124.57(q, *J*=271 Hz, CF₃), 128.32(q, *J*=32.1 Hz), 131.67, 138.20(d, *J*=1.4 Hz), 158.30, 161.17. ¹⁹F-NMR(377 MHz, CDCl₃): δ -62.29 (s). HRMS (EI) m/z calcd for C₁₆H₁₅F₃O₃: 312.0973; found: 312.0914.



2,4,4',6-tetramethoxybiphenyl (3f). Spectral data corresponds to that previously reported. Colorless solid (40 mg, 72% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.72 (s, 6H), 3.83 (s, 3H), 3.86 (s, 3H), 6.22 (S, 2H), 6.93 (d, 2H, *J*=8.8Hz), 7.26 (d, 2H, *J*=8.8Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 55.13, 55.39, 55.91, 90.89, 112.05, 113.25, 126.14, 132.20, 158.12, 158.43, 160.28.

Reference: Jean-Michel Becht; Cedric Catala; Claude Le Drian; Alain Wagner Org. Lett. 2007, 9, 1781.



1-(2',4',6'-trimethoxybiphenyl-4-yl)ethanone (3g). Colorless solid (48 mg, 84% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.61 (s, 3H), 3.72 (s, 6H), 3.87 (s, 3H), 6.23 (s, 2H), 7.44 (m, 2H, *J*=8.4 Hz), 7.97 (m, 2H, *J*=8.4Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 26.57, 55.42, 55.87, 90.95, 111.32, 127.69, 131.56, 135.14, 139.78, 158.27, 161.14, 197.98. HRMS (EI) m/z calcd for C₁₇H₁₈O₄: 286.1205; found: 286.1198.



2-(2,4,6-trimethoxyphenyl)naphthalene (3h). Spectral data corresponds to that previously reported. Colorless solid (54 mg, 92% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.78 (s, 6H), 3.94 (s, 3H), 6.34 (s, 2H), 7.53 (m, 3H), 7.90 (m, 4H). ¹³C-NMR(100 MHz, CDCl₃) δ 55.44, 55.96, 91.15, 112.57, 125.48, 125.53, 126.86, 127.68, 128.10, 128.90, 129.84, 129.99, 130.96, 131.80, 132.40, 133.43, 158.62,

160.74. HRMS (EI) m/z calcd for C₁₇H₁₈O₄: 294.1256; found: 294.1263. **Reference:** Ikuya Ban; Tomoko Sudo; Tadashi Taniguchi; Kenichiro Itami *Org. Lett.* **2008**, *10*, 3607.



2',4',6'-trimethoxybiphenyl-4-carbonitrile (3i). Colorless solid (39 mg, 72% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.72 (s, 6H), 3.86 (s, 3H), 6.22 (S, 2H), 7.44 (m, 2H, *J*=8.8 Hz), 7.63 (m, 2H, *J*=8.8 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 55.45, 55.82, 90.93, 109.82, 110.50, 119.49, 131.29, 132.20, 139.61, 158.15, 161.47. HRMS (EI) m/z calcd for C₁₆H₁₅NO₃: 269.1052; found: 269.1021.



Ethyl 2',4',6'-trimethoxybiphenyl-4-carboxylate (3j). Colorless solid (51 mg, 81% yield). ¹H-NMR (400 MHz, CDCl₃) δ 1.39 (t, 3H, *J*=7.2 Hz), 3.72 (s, 6H), 3.86 (s, 3H), 4.38 (q, 2H, *J*=7.2 Hz), 6.23 (S, 2H), 7.40 (d, 2H, *J*=8.4 Hz), 8.05 (d, 2H, *J*=8.4 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 14.40, 55.40, 55.85, 60.68, 90.96, 111.55, 128.40, 128.83, 131.31, 139.34, 158.28, 161.03, 166.80. HRMS (EI) m/z calcd for C₁₈H₂₀O₅: 316.1311; found: 316.1292.



3'-chloro-2,4,6-trimethoxybiphenyl (3k). Spectral data corresponds to that previously reported. Colorless solid (47 mg, 85% yield). ¹H-NMR (400 MHz, CDCl₃): δ 3.72 (s, 6H), 3.86 (s, 3H), 6.21 (s, 2H), 7.26 (m, 4H). ¹³C-NMR(100 MHz, CDCl₃) δ 55.41, 55.87, 90.81, 111.04, 126.58, 128.78, 129.53, 131.35, 133.34, 136.0, 158.27, 160.92.

Reference: Ikuya Ban; Tomoko Sudo; Tadashi Taniguchi; Kenichiro Itami Org. Lett. 2008, 10, 3607.



3'-fluoro-2,4,6-trimethoxybiphenyl (3l). Spectral data corresponds to that previously reported. Colorless solid (51 mg, 97% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.73 (s, 6H), 3.86 (s, 3H), 6.22 (s, 2H), 6.97 (t, 1H, *J*=8.4Hz), 7.05 (d, 1H, *J*=10.0Hz), 7.10 (d, 1H, *J*=7.6Hz), 7.32 (m, 1H). ¹³C-NMR(100 MHz, CDCl₃) δ 55.41, 55.87, 90.82, 111.19, 113.33 (d, *J*=21 Hz), 118.22 (d, *J*=21

Hz), 126.99 (d, *J*=2.5 Hz), 128.81 (d, *J*=8.1 Hz), 136.29 (d, *J*=8.6 Hz), 158.26, 160.85, 162.40 (d, *J*=239.1 Hz). ¹⁹F-NMR (377 MHz, CDCl₃): δ -115 (s, 1F).

Reference: Ikuya Ban; Tomoko Sudo; Tadashi Taniguchi; Kenichiro Itami Org. Lett. 2008, 10, 3607.



2,3',4,6-tetramethoxybiphenyl (3m). Spectral data corresponds to that previously reported. Colorless solid (40 mg, 73% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.72 (s, 6H), 3.81 (s, 3H), 3.86 (s, 3H), 6.22 (s, 2H), 6.84 (ddd, 1H, J_1 =8.4 Hz, J_2 =2.8 Hz, J_3 =0.8 Hz), 6.88 (m, 1H), 6.91 (m, 1H), 7.30 (t, 1H, J=8.0 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 55.14, 55.39, 55.92, 90.97, 112.1, 112.44, 117.01, 123.73, 128.47, 135.49, 158.40, 158.98, 160.58.

Reference: Ikuya Ban; Tomoko Sudo; Tadashi Taniguchi; Kenichiro Itami Org. Lett. 2008, 10, 3607.



5-(2,4,6-trimethoxyphenyl)benzo[d][1,3]dioxole (3n). Colorless solid (40 mg, 70% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.73 (s, 6H), 3.85 (s, 3H), 5.96 (s, 2H), 6.22 (s, 2H), 6.81(m, 3H). ¹³C-NMR(100 MHz, CDCl₃) δ 55.38, 55.92, 90.97, 100.80, 107.89, 111.81, 112.12, 124.44, 127.54, 146.11, 147.0, 158.47, 160.43. HRMS (EI) m/z calcd for C₁₆H₁₆O₅: 288.0998; found: 288.0918.



2,4,6-trimethoxy-2'-methylbiphenyl (30). Colorless solid (17 mg, 32% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.07 (s, 3H), 3.69 (s, 3H), 3.86 (s, 3H), 6.22 (s, 2H), 7.11 (m, 1H), 7.21 (m, 3H). ¹³C-NMR(100 MHz, CDCl₃) δ 19.77, 55.36, 55.83, 90.75, 111.87, 125.19, 127.08, 129.51, 131.29, 134.16, 137.81, 158.34, 160.64. HRMS (EI) m/z calcd for C₁₆H₁₈O₃: 258.1256; found: 258.1222.



3',5'-difluoro-2,4,6-trimethoxybiphenyl (3p). Colorless solid (48 mg, 85% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.74 (s, 6H), 3.86 (s, 3H), 5.99 (s, 2H), 6.21 (s, 2H), 6.72 (m, 1H), 6.86 (m, 2H).

¹³C-NMR(100 MHz, CDCl₃) δ 55.41, 55.84, 90.79, 101.85 (t, *J*=25 Hz), 110.19 (t, *J*=2.2 Hz), 114.18 (q, *J*=5.5 Hz), 137.39 (t, *J*=9.9 Hz), 158.15, 161.17 (t, *J*=5.7 Hz), 163.60 (d, *J*=13.2 Hz). ¹⁹F-NMR (377 MHz, CDCl₃): δ -112(s). HRMS (EI) m/z calcd for C₁₅H₁₄F₂O₃: 280.0911; found: 280.0893.



2,4,6-trimethoxy-3',5'-bis(trifluoromethyl)biphenyl (3q). Colorless solid (71 mg, 93% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.74 (s, 6H), 3.86 (s, 3H), 5.99 (s, 2H), 6.21 (s, 2H), 6.72 (m, 1H), 6.86 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ 55.45, 55.79, 90.83, 109.25, 120.05 (m), 123.73 (q, *J*=273.2 Hz), 130.57 (q, *J*=31.8 Hz), 131.695 (d, *J*=3.0 Hz), 136.26, 158.19, 161.65. ¹⁹F-NMR (377 MHz, CDCl₃): δ -62.7(s). HRMS (EI) m/z calcd for C₁₇H₁₄F₆O₃: 380.0847; found: 380.0842.



2,4,6-trimethoxy-3',5'-dimethylbiphenyl (3r). Colorless solid (51 mg, 95% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.33 (s, 6H), 3.70 (s, 6H), 3.84 (s, 3H), 6.21 (s, 2H), 6.92 (s, 3H). ¹³C-NMR (100 MHz, CDCl₃) δ 21.50, 55.40, 55.95, 90.95, 112.86, 128.58, 128.98, 133.93, 136.93, 158.48, 160.43. HRMS (EI) m/z calcd for C₁₇H₂₀O₃: 272.1412; found: 272.1408.



2,3',6-trimethoxybiphenyl (4a). Spectral data corresponds to that previously reported. Colorless solid (26% and 91% yield respectively). ¹H-NMR (400 MHz, CDCl₃) δ 3.73 (s, 6H), 3.81 (s, 3H), 6.65 (d, 2H, *J*=8.8 Hz), 6.90 (m, 3H), 7.29 (m, 2H). ¹³C-NMR(100 MHz, CDCl₃) δ 55.16, 55.96, 104.23, 112.38, 116.69, 119.45, 123.39, 128.58, 128.73, 135.52, 157.73, 159.03.

Reference: Jean-Michel Becht; Arnaud Gissot; Alain Wagner; Charles Mioskowski. Chem. Eur. J. 2003, 9, 3209.



2',6'-difluorobiphenyl-4-carbonitrile (4b). Spectral data corresponds to that previously reported. Colorless solid (13% and 67% yield respectively). ¹H-NMR (400 MHz, CDCl₃) δ 3.76 (s, 6H), 6.67 (d, 2H, *J*=8.0 Hz), 6.99-7.05 (m, 1H), 7.07-7.11 (m, 1H), 7.13-7.16 (m, 1H), 7.31 (t, 1H, *J*=8.0 Hz),

7.36-7.39(m, 1H). ¹³C-NMR(100 MHz, CDCl₃) δ 111.96 (q, *J*=19.6 Hz), 116.72 (t, *J*=18.5 Hz), 118.62, 130.25 (t, *J*=9.9 Hz), 131.13 (t, *J*=1.2 Hz), 132.01, 134.10, 158.57 (d, *J*=6.3 Hz), 161.05 (d, *J*=6.5 Hz). ¹⁹F-NMR (377 MHz, CDCl₃): δ -114.34 (s, 2F).

Reference: Rui Shang; Yao Fu; Yan Wang; Qing Xu; Hai-Zhu Yu; Lei Liu Angew. Chem. Int. Ed. 2009, 48, 9350.



4'-phenyl-2-nitrobiphenyl (4c). Yellow solid (15% and 64% yield respectively). ¹H-NMR (400 MHz, CDCl₃) δ 7.38 (m, 3H), 7.47 (m, 4H), 7.64 (m, 5H), 7.87 (m, 1H). ¹³C-NMR(100 MHz, CDCl₃) δ 124.17, 127.17, 127.45, 127.61, 128.21, 128.37, 128.86, 131.98, 132.32, 136.02, 136.29, 140.42, 141.17, 149.37. HRMS (EI) m/z calcd for C₁₈H₁₃NO₂: 275.0946; found: 275.0914.



2,4,5-trimethoxy-4'-methylbiphenyl (5a). Colorless solid (34 mg, 65% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.42 (s, 3H), 3.79 (s, 3H), 3.90 (s, 3H), 3.97 (s, 3H), 6.66 (s, 1H), 6.91 (s, 1H), 7.25 (d, 2H, *J*=7.6 Hz), 7.44 (d, 2H, *J*=7.2 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 21.21, 56.21, 56.59, 56.76, 98.45, 114.49, 122.47, 128.86, 129.28, 135.46, 136.36, 143.29, 148.79, 150.75. HRMS (EI) m/z calcd for C₁₆H₁₈O₃: 258.1256; found: 258.1207.



2,6-dimethoxy-4'-methylbiphenyl (5b). Spectral data corresponds to that previously reported. Colorless solid (33 mg, 73% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.38 (s, 3H), 3.72 (s, 6H), 6.64 (d, 2H, *J*=8.8 Hz), 7.23 (m, 5H). ¹³C-NMR(100 MHz, CDCl₃) δ 21.41, 55.94, 104.26, 106.24, 128.47, 128.56, 130.77, 131.08, 136.33, 157.83.

Reference: Gupta, Arun Kumar; Rim, Chul Yun; Oh, Chang Ho. Synlett 2004, 12, 2227.



5-(2,6-dimethoxyphenyl)benzo[d][1,3]dioxole (5c). Spectral data corresponds to that previously reported. Colorless solid (42 mg, 81% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.73 (s, 6H), 5.96 (s, 2H), 6.63 (d, 2H, *J*=8.8 Hz), 6.83(m, 3H), 7.25(t, 3H, *J*=8.2 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 55.97, 100.87, 104.24, 107.96, 111.58, 119.16, 124.23, 127.52, 128.55, 146.35, 147.08, 157.84. **Reference:** Jean-Michel Becht; Arnaud Gissot; Alain Wagner; Charles Mioskowski. *Chem. Eur. J.* **2003**, *9*, 3209.



4'-bromo-2,6-dimethoxybiphenyl (5d). Colorless solid (42 mg, 72% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.73 (s, 6H), 6.64 (d, 2H, *J*=8.4 Hz), 7.22 (d, 2H, *J*=8.4 Hz), 7.28 (t, 1H, *J*=8.4 Hz), 7.51 (d, 2H, *J*=8.4 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 55.91, 104.24, 118.29, 120.85, 129.04, 130.86, 132.74, 133.08, 157.54.

Reference: Jean-Michel Becht; Claude Le Drian Org. Lett., 2008, 10, 3161.



4'-chloro-2,6-dimethoxybiphenyl (5e). Spectral data corresponds to that previously reported. Colorless solid (37 mg, 76% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.73 (s, 6H), 6.65 (d, 2H, *J*=8.4 Hz), 7.26-7.30 (m, 3H), 7.36 (d, 2H, *J*=8.8 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 55.90, 104.23, 118.30, 127.92, 129.0, 132.38, 132.56, 132.60, 157.60.

Reference: Jean-Michel Becht; Cedric Catala; Claude Le Drian; Alain Wagner Org. Lett., 2007, 9, 1781.



3'-chloro-2,6-dimethoxybiphenyl (5f). Colorless solid (32 mg, 64% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.73 (s, 6H), 6.64 (d, 2H, *J*=8.0 Hz), 7.21-7.34 (m, 5H). ¹³C-NMR(100 MHz, CDCl₃) δ 55.91, 104.19, 118.16, 126.86, 128.83, 129.18, 129.24, 131.08, 133.43, 136.03, 157.59. HRMS (EI) m/z calcd for C₁₄H₁₃O₂Cl: 248.0604; found: 248.0598.



4'-bromo-2,4-dimethoxybiphenyl (5g). Colorless solid (33 mg, 57% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.79 (s, 3H), 3.84 (s, 3H), 6.55 (s, 1H), 6.56 (m, 1H), 7.36 (d, 2H, *J*=9.2 Hz), 7.49 (d, 2H, *J*=9.2 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 55.45, 55.53, 99.08, 104.79, 120.55, 122.35, 131.04, 131.08, 131.10, 137.30, 157.38, 160.63. HRMS (EI) m/z calcd for C₁₄H₁₃BrO₂: 292.0099; found: 292.0097.



4'-tert-butyl-2,4-dimethoxybiphenyl (5h). Colorless solid (35 mg, 66% yield). ¹H-NMR (400 MHz,

CDCl₃) δ 1.27 (s, 9H), 3.71 (s, 3H), 3.76 (s, 3H), 6.47 (m, 2H), 7.17(d, 1H, *J*=9.6 Hz), 7.35 (m, 4H). ¹³C-NMR(100 MHz, CDCl₃) δ 30.37, 33.45, 54.36, 54.48, 97.93, 103.55, 122.43, 123.92, 127.99, 130.19, 134.32, 148.18, 156.47, 159.1. HRMS (EI) m/z calcd for C₁₈H₂₂O₂: 270.1620; found: 270.1614.



2-(4-methoxyphenyl)-5-nitrofuran (5i). Yellow solid (37 mg, 85% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.87 (s, 3H), 6.70 (d, 1H, *J*=3.6 Hz), 6.98 (d, 2H, *J*=8.8 Hz), 7.40 (d, 1H, *J*=3.6 Hz), 7.74 (d, 2H, *J*=8.8 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 55.47, 106.38, 114.53, 114.66, 120.68, 127.03, 157.1, 161.46, 167.72. HRMS (EI) m/z calcd for C₁₁H₉NO₄: 219.0532; found: 219.0454.



1-(2'-nitrobiphenyl-4-yl)ethanone (5j). Spectral data corresponds to that previously reported. Yellow solid (15 mg, 32% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.64 (s, 3H), 7.43(m, 3H), 7.54 (m, 1H), 7.66 (m, 1H), 7.94 (d, 1H, *J*=8.4 Hz), 8.02 (d, 2H, *J*=8.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 26.67, 124.43, 128.25, 128.68, 128.91, 130.92, 131.74, 132.62, 135.52, 136.68, 142.35, 197.49. **Reference:** Lukas J. Goossen; Nuria Rodriguez; Bettina Melzer; Christophe Linder; Guojun Deng;

Laura M. Levy. J. Am. Chem. Soc. 2007, 129, 4824.



4,4',5-trimethoxy-2-nitrobiphenyl (5k). Spectral data corresponds to that previously reported. Yellow solid (26 mg, 43% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.85 (s, 3H), 3.95 (s, 3H), 3.97 (s, 3H), 6.77 (s, 1H), 6.95 (d, 2H, *J*=8.8 Hz), 7.22 (d, 2H, *J*=8.8 Hz), 7.51 (s, 1H). ¹³C-NMR (100 MHz, CDCl₃) δ 55.32, 56.42, 56.45, 107.85, 113.73, 114.04, 129.25, 130.45, 130.92, 141.22, 147.86, 152.18, 159.42.

Reference: Becht, Jean-Michel; Catala, Cedric; Drian, Claude Le; Wagner, Alain Org. Lett. 2007, 9, 1781.



2,3,4,5,6-pentafluoro-3'-methoxybiphenyl (5l). Spectral data corresponds to that previously reported. Colorless solid (39 mg, 72% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.84 (s, 3H), 6.94 (s, 1H), 6.99 (m, 1H), 7.40 (t, 1H, *J*=8.0 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 55.4, 114.96, 115.95, 115.95 (dt, *J*=4.1 Hz, *J*=18.0 Hz), 122.56, 127.58, 129.81, 137.93 (dm, *J*=250.4 Hz), 140.55 (dm,

J=246.8 Hz), 144.26 (dm, *J*=246.8 Hz), 159.8. ¹⁹F-NMR (377 MHz, CDCl₃) δ -162.29 (m, 2F), -155.63 (t, 1F, *J*=21.5 Hz), -142.80 (dd, 2F, *J*=23.4 Hz, *J*=8.3 Hz). **Reference:** Lafrance, M.; Rowley, C. N.; Woo, T. K.; Fagnou, K. *J. Am. Chem. Soc.* **2006**, *128*, 8754.



2,3,4,5,6-pentafluoro-3'-nitrobiphenyl (5m). Spectral data corresponds to that previously reported. Yellow solid (47 mg, 81% yield). ¹H-NMR (400 MHz, CDCl₃) δ 7.71 (m, 1H),7.78 (m, 1H), 8.35 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ 113.59 (dt, *J*=3.6 Hz, *J*=16.9 Hz), 124.23, 125.26, 128.06, 129.89, 136.09, 138.02 (dm, *J*=254.9 Hz), 141.26 (dm, *J*=255 Hz), 144.16 (dm, *J*=248.3 Hz), 148.47. ¹⁹F-NMR (377 MHz, CDCl₃) δ -160.83 (m, 2F), -152.76 (t, 1F, *J*=21.1 Hz), -142.84 (dd, 2F, *J*=22.2 Hz, *J*=8.3 Hz).

Reference: Rui Shang; Yao Fu; Yan Wang; Qing Xu; Hai-Zhu Yu; Lei Liu Angew. Chem. Int. Ed. 2009, 48, 9350.



1-(2',3',4',5',6'-pentafluorobiphenyl-4-yl)ethanone (5n). Spectral data corresponds to that previously reported. Colorless solid (49 mg, 85% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.66 (s, 3H), 7.55 (d, 2H, J=8.4 Hz), 8.08 (d, 2H, J=8.0 Hz). ¹³C-NMR (100 MHz, CDCl₃): δ 26.61, 114.89 (dt, J=4.1 Hz, J=16.1 Hz), 128.56, 130.48, 131.06, 137.52, 137.93 (dm, J=244.9 Hz), 140.87 (dm, J=253.6 Hz), 144.09 (dm, J=247.4 Hz), 197.29. ¹⁹F-NMR (377 MHz, CDCl₃) δ -161.54 (m, 2F), -154.03 (t, 1F, J=20.4 Hz), -142.78 (dd, 2F, J=22.2 Hz, J=8.3 Hz).

Reference: Lafrance, M.; Shore, D.; Fagnou, K. Org. Lett. 2006, 8, 5097.



2',3',4',5',6'-pentafluorobiphenyl-4-carbonitrile (50). Spectral data corresponds to that previously reported. Colorless solid (53 mg, 98% yield). ¹H-NMR (400 MHz, CDCl₃) δ 7.59 (d, 2H, *J*=7.6 Hz), 7.82 (d, 2H, *J*=7.6 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 113.46, 114.18 (dt, *J*=3.5 Hz, *J*=16.7 Hz), 118.15, 130.97, 131.06, 132.54, 138.08 (dm, *J*=252.0 Hz), 141.29 (dm, *J*=254.6 Hz), 144.14 (dm, *J*=252.4 Hz). ¹⁹F-NMR (377 MHz, CDCl₃) δ -161.01 (m, 2F), -152.94 (t, 1F, *J*=21.3 Hz), -142.76 (dd, 2F, *J*=21.9 Hz, *J*=8.3 Hz).

Reference: Lafrance, M.; Shore, D.; Fagnou, K. Org. Lett. 2006, 8, 5097.



1-(2',6'-difluorobiphenyl-4-yl)ethanone (5p). Colorless solid (23 mg, 50% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.65 (s, 3H), 7.01 (m, 2H), 7.33 (m, 1H), 7.58 (d, 2H, J=8.0 Hz), 8.05 (d, 2H, J=8.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 55.29, 111.6 (dd, J=7.4 Hz, J=19.7 Hz), 117.49 (t, J=19.4 Hz), 128.20, 129.71 (t, J=10.0 Hz), 130.63, 134.13, 136.63, 159.98 (dd, J=6.1 Hz, J=247.6 Hz). ¹⁹F-NMR (377 MHz, CDCl₃) δ -114.21 (s, 2F). HRMS (EI) m/z calcd for C₁₄H₁₀OF₂: 232.0700; found: 232.0643.



2,6-difluoro-4'-methoxybiphenyl (5q). Spectral data corresponds to that previously reported. Colorless solid (23 mg, 52% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.85 (s, 3H), 6.97 (m, 4H), 7.23 (m, 1H), 7.41 (d, 2H, *J*=8.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 55.29, 111.6 (dd, *J*=7.4 Hz, *J*=19.7 Hz), 113.81, 118.19 (t, *J*=18.4 Hz), 121.28, 128.34 (t, *J*=10.1 Hz), 131.52, 159.49, 160.21 (dd, *J*=7.5 Hz, *J*=246.7 Hz). ¹⁹F-NMR (377 MHz, CDCl₃) δ -114.77 (s, 2F).

Reference: Wei, Ye; Kan, Jian; Wang, Min; Su, Weiping; Hong, Maochun Org. Lett. 2009, 11, 3346.



2',4',6'-trifluorobiphenyl-4-carbonitrile (5r). Colorless solid (29 mg, 64% yield). ¹H-NMR (400 MHz, CDCl₃) δ 6.80 (m, 2H), 7.55 (m, 2H), 7.75 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ 99.89 (m), 111.26, 117.47, 130.05, 131.11, 132.25, 157.84 (dd, *J*=9.1 Hz, *J*=14.7 Hz), 160.29 (m), 162.80 (t, *J*=15.1 Hz). ¹⁹F-NMR (377 MHz, CDCl₃) δ -111.06 (d, 2F), -106.43 (t, 1F). HRMS (EI) m/z calcd for C₁₃H₆NF₃: 233.0452; found: 233.0428.



2,3,4,5-tetrafluoro-4'-methoxybiphenyl (5s). Colorless solid (35 mg, 68% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.85 (s, 3H), 6.97-7.05 (m, 3H), 7.40-7.43 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ 55.36, 110.47 (dt, *J*=3.2 Hz, *J*=19.7 Hz), 114.31, 125.13(m), 125.39, 129.30 (d, *J*=0.8 Hz), 139.32 (dm, *J*=252.9 Hz), 141.25 (dm, *J*=251.2 Hz), 144.79 (dm, *J*=242.4 Hz), 147.04 (dm, *J*=244.4 Hz), 160.4. ¹⁹F-NMR (377 MHz, CDCl₃) δ -158.11 (m, 1F), -155.50 (m, 1F), -144.12 (m, 1F), -139.92 (m, 1F). HRMS (EI) m/z calcd for C₁₃H₈FO₄: 256.0511; found: 256.0465.



2,3,6-trifluoro-4'-methoxybiphenyl (5t). Spectral data corresponds to that previously reported. Colorless solid (46 mg, 98% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H), 6.89 (m, 1H, *J*=2.4 Hz, *J*=3.6 Hz, *J*=9.2 Hz), 7.00 (d, 2H, *J*=9.2 Hz), 7.40 (m, 2H, *J*=8.8 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 99.89 (m), 111.26, 117.47, 130.05, 131.11, 132.25, 157.84 (dd, *J*=9.1 Hz, *J*=14.7 Hz), 160.29 (m), 162.80 (t, *J*=15.1 Hz). ¹⁹F-NMR (377 MHz, CDCl₃) δ -142.20 (dd, *J*=15.1 Hz, *J*=21.1 Hz 1F), -138.16 (dd, *J*=4.5 Hz, *J*=20.7 Hz, 1F), -120.0 (dd, *J*=4.1 Hz, *J*=15.1 Hz, 1F). HRMS (EI) m/z calcd for C₁₃H₉OF₃: 238.0605; found: 238.0604.

Reference: Rui Shang; Yao Fu; Yan Wang; Qing Xu; Hai-Zhu Yu; Lei Liu Angew. Chem. Int. Ed. 2009, 48, 9350.



Ethyl 2',3',5',6'-tetrafluoro-4'-methylbiphenyl-4-carboxylate (5u). Spectral data corresponds to that previously reported. Colorless solid (45 mg, 72% yield). ¹H-NMR (400 MHz, CDCl₃) δ 1.42 (t, 3H, J=7.2 Hz), 2.33 (t, 3H, J=2.4 Hz), 4.41 (q, 2H, J=7.2 Hz), 7.53 (dm, 2H, J=8.4 Hz), 8.15 (dm, 2H, J=8.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 7.68, 14.34, 61.24, 116.61 (t, J=18.6 Hz), 117.06 (t, J=15.6 Hz), 129.71, 130.27 (t, J=1.8 Hz), 130.91, 132.28, 143.57 (dm, J=239.2 Hz), 145.42 (dm, J=245.8 Hz), 166.11. ¹⁹F-NMR (377 MHz, CDCl₃) δ -145.26 (dd, J=12.8 Hz, J=22.2 Hz 2F), -143.58 (dd, J=12.1 Hz, J=21.5 Hz, 2F).

Reference: Rui Shang; Yao Fu; Yan Wang; Qing Xu; Hai-Zhu Yu; Lei Liu Angew. Chem. Int. Ed. 2009, 48, 9350.



4-bromo-2,3,5,6-tetrafluoro-4'-methoxybiphenyl (5v). Colorless solid (62 mg, 92% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H), 7.01 (d, 2H, *J*=8.8 Hz), 7.39 (d, 2H, *J*=8.8 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 55.33, 97.94 (t, *J*=22.6 Hz), 114.22, 118.95, 120.10 (t, *J*=16.2 Hz), 131.36, 144.10 (dm, *J*=247.2 Hz), 145.35 (dm, *J*=245.8 Hz), 160.38. ¹⁹F-NMR (377 MHz, CDCl₃) δ -142.43 (m, 2F), -133.90 (m, 2F). HRMS (EI) m/z calcd for C₁₃H₇OF₄Br: 333.9616; found: 333.9616.



2,3,5,6-tetrafluoro-4'-methoxybiphenyl (5w). Spectral data corresponds to that previously reported. Colorless solid (32 mg, 62% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.86 (s, 3H), 7.01 (m, 3H), 7.40 (m, 2H). ¹³C-NMR (100 MHz, CDCl₃) δ 55.31, 104.27 (t, *J*=22.6 Hz), 114.13, 119.56 (t, *J*=1.8 Hz), 121.26 (t, *J*=16.1 Hz), 131.43 (t, *J*=1.5 Hz), 143.78 (dm, *J*=242.5 Hz), 146.29 (dm, *J*=245.6 Hz), 160.23. ¹⁹F-NMR (377 MHz, CDCl₃) δ -144.26 (m, 2F), -139.44 (m, 2F).

Reference: Rui Shang; Yao Fu; Yan Wang; Qing Xu; Hai-Zhu Yu; Lei Liu Angew. Chem. Int. Ed. 2009, 48, 9350.



phenyl 2,4,6-trimethoxybenzoate (6a). Colorless solid (51 mg, 90% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.84 (s, 3H), 3.86 (s, 6H), 6.15 (s, 2H), 7.23-7.25 (m, 3H), 7.38-7.41 (m, 2H). ¹³C-NMR(100 MHz, CDCl₃) δ 55.48, 55.09, 90.75, 105.45, 121.88, 125.64, 129.30, 151.31, 159.14, 163.05, 164.82. HRMS (EI) m/z calcd for C₁₆H₁₆O₅: 288.0998; found: 288.0990.



phenyl 2,6-dimethoxybenzoate (6b). Colorless solid (49 mg, 95% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.86 (s, 6H), 6.59 (d, 2H, *J*=8.4 Hz), 7.21-7.27 (m, 3H), 7.32 (t, 1H, *J*=8.4 Hz), 7.37-7.42 (m, 2H). ¹³C-NMR(100 MHz, CDCl₃) δ 56.16, 104.06, 112.53, 121.88, 125.85, 129.40, 131.63, 151.18, 157.69, 165.05. HRMS (EI) m/z calcd for C₁₅H₁₄O₄: 258.0892; found: 258.0899.



4-bromophenyl 2,6-dimethoxybenzoate (6c). Colorless solid (45 mg, 68% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.86 (s, 6H), 6.59 (d, 2H, *J*=8.4 Hz), 7.15 (d, 2H, *J*=8.4 Hz), 7.33 (t, 1H, *J*=8.4 Hz), 7.51 (d, 2H, *J*=8.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 56.14, 104.04, 112.06, 118.91, 123.71, 131.85, 132.43, 150.18, 157.69, 164.68. HRMS (EI) m/z calcd for C₁₅H₁₃BrO₄: 335.9997; found: 335.9992.



p-tolyl 2,6-dimethoxybenzoate (6d). Colorless solid (44 mg, 81% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.34 (s, 3H), 3.85 (s, 6H), 6.58 (d, 2H, *J*=8.4 Hz), 7.11-7.20 (m, 4H), 7.30 (t, 1H, *J*=8.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 20.92, 56.51, 104.06, 112.65, 121.54, 129.92, 131.56, 135.44, 148.93, 157.66, 165.26. HRMS (EI) m/z calcd for C₁₆H₁₆O₄: 272.1049; found: 272.1045.



4-methoxyphenyl 2,6-dimethoxybenzoate (6e). Colorless solid (51 mg, 89% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.79 (s, 3H), 3.86 (s, 6H), 6.58 (d, 2H, *J*=8.0Hz), 6.91 (dt, 2H, *J*=3.0 Hz, *J*=9.2 Hz), 7.17 (dt, 2H, *J*=3.0 Hz, *J*=9.2 Hz), 7.31 (t, 1H, *J*=8.4 Hz). ¹³C-NMR (100 MHz, CDCl₃) δ 55.61, 56.14, 104.05, 112.06, 114.45, 112.60, 114.45, 122.60, 131.56, 144.67, 157.34, 157.63, 165.43. HRMS (EI) m/z calcd for C₁₆H₁₆O₅: 288.0998; found: 288.0992.



4-acetylphenyl 3-bromo-2,6-dimethoxybenzoate (6f). Colorless solid (50 mg, 66% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.62 (s, 3H), 3.89 (s, 3H), 3.98 (s, 3H), 6.68 (d, 1H, *J*=9.2 Hz), 7.35 (dt, 2H, *J*=2.4 Hz, *J*=8.8 Hz), 7.59 (d, 1H, *J*=9.2 Hz), 8.05 (dt, 2H, *J*=2.8 Hz, *J*=8.8 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 26.62, 56.46, 62.39, 107.86, 108.61, 118.77, 121.87, 130.08, 135.07, 135.35, 154.47, 155.04, 156.97, 163.35, 196.85. HRMS (EI) m/z calcd for C₁₇H₁₅BrO₅: 378.0103; found: 378.0097.



phenyl 2,6-difluoro-4-methoxybenzoate (6g). Colorless solid (33 mg, 62% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.87 (s, 3H), 6.56 (d, 2H, *J*=10.4 Hz), 7.28 (m, 3H), 7.45 (t, 2H, *J*=7.6 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 56.12, 98.80 (dd, *J*=3.0 Hz, *J*=26.4 Hz), 102.54 (t, *J*=16.4 Hz), 121.69, 126.09, 129.49, 150.51, 159.96 (t, *J*=2.7 Hz), 162.76 (dd, *J*=9.2 Hz, *J*=247.2 Hz), 164.12. ¹⁹F-NMR (377 MHz, CDCl₃) δ -106.59 (s, 2F). HRMS (EI) m/z calcd for C₁₄H₁₀F₂O₃: 264.0598; found: 264.0594.



phenyl benzoate (6h). Spectral data corresponds to that previously reported. Colorless solid (28 mg, 70% yield). ¹H-NMR (400 MHz, CDCl₃) δ 7.22 (d, 2H, *J*=7.2 Hz), 7.27 (t, 1H, *J*=7.6 Hz), 7.43 (t, 2H, *J*=8.0 Hz), 7.51 (t, 2H, *J*=7.6 Hz), 7.64 (t, 1H, *J*=7.6 Hz), 8.21 (d, 2H, *J*=7.2 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 121.74, 125.91, 128.59, 129.52, 129.62, 130.19, 133.60, 151.0, 165.22.

Reference: Jessica Salvadori; Evita Balducci; Silvia Zaza; Elena Petricci; Maurizio Taddei J. Org. Chem., 2010, 75, 1841.



phenyl 4-methoxybenzoate (6i). Spectral data corresponds to that previously reported. Colorless solid (45 mg, 93% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.88 (s, 3H), 6.98 (d, 2H, *J*=9.2 Hz), 7.23 (m, 3H), 7.41 (t, 2H, *J*=7.6 Hz), 8.15 (d, 2H, *J*=8.8 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 55.52, 113.87, 121.83, 125.73, 129.45, 132.31, 151.14, 163.94, 164.93.

Reference: Changming Qin; Huayue Wu; Jiuxi Chen; Miaochang Liu; Jiang Cheng; Weike Su; Jinchang Ding *Org. Lett.* **2008**, *10*, 1537.



4-methoxyphenyl 4-methoxybenzoate (6j). Spectral data corresponds to that previously reported. Colorless solid (36 mg, 71% yield).¹H-NMR (400 MHz, CDCl₃) δ 3.81 (s, 3H), 3.88 (s, 3H), 6.92 (d, 2H, *J*=8.8 Hz), 6.97 (d, 2H, *J*=8.8 Hz), 7.11 (d, 2H, *J*=8.8 Hz), 8.14 (d, 2H, *J*=8.8 Hz). ¹³C-NMR (100MHz, CDCl₃) δ 55.51, 55.62, 113.83, 114.50, 121.98, 122.56, 132.26, 144.56, 157.24, 163.86, 165.30.

Reference: Helmi Neuvonen; Kari Neuvonen; Paavo Pasanen J. Org. Chem., 2004, 69, 3794.



4-methoxyphenyl 4-nitrobenzoate (6k). Spectral data corresponds to that previously reported. Colorless solid (25 mg, 46% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.83 (s, 3H), 6.96 (dt, 2H, *J*=3.2 Hz, *J*=9.2 Hz), 7.15 (dt, 2H, *J*=3.2 Hz, *J*=9.2 Hz), 8.36 (m, 4H). ¹³C-NMR (100 MHz, CDCl₃) δ 55.65, 114.68, 122.19, 123.71, 131.26, 135.11, 144.02, 150.89, 157.70, 163.68.

Reference: Helmi Neuvonen; Kari Neuvonen; Paavo Pasanen J. Org. Chem., 2004, 69, 3794.



phenyl 1-naphthoate (6l). Spectral data corresponds to that previously reported. Colorless solid (30 mg, 62% yield). ¹H-NMR (400 MHz, CDCl₃) δ 7.27-7.32 (m, 3H), 7.44-7.48 (m, 2H), 7.54-7.58 (m, 2H), 7.61-7.66 (m, 1H), 7.91 (d, 1H, *J*=8.0 Hz), 8.09 (d, 1H, *J*=8.0 Hz), 8.47 (dd, 1H, *J*=1.2 Hz, *J*=7.2 Hz), 9.04 (d, 1H, *J*=8.0 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 120.87, 123.51, 124.74, 124.90, 125.39, 127.14, 127.66, 128.53, 130.17, 130.68, 132.92, 133.27, 144.99, 164.80.

Reference: Ramesh, Chinnasamy; Nakamura, Ryo; Kubota, Yoshihiro; Miwa, Minoru; Sugi, Yoshihiro *Synthesis* **2003**, *4*, 501.



phenyl 2-naphthoate (6m). Colorless solid (33 mg, 66% yield). ¹H-NMR (400 MHz, CDCl₃) δ 7.24-7.30 (m, 3H), 7.45 (t, 2H, *J*=8.4 Hz), 7.55-7.59 (m, 2H), 7.60-7.64 (m, 2H), 7.94 (td, 3H, *J*=22.4 Hz, *J*=8.0 Hz), 8.19 (dd, 1H, *J*=8.8 Hz, *J*=1.6 Hz), 8.79 (s, 1H). ¹³C-NMR(100 MHz, CDCl₃) δ 121.81, 125.51, 125.95, 126.84, 126.88, 127.88, 128.43, 128.66, 129.53, 129.56, 135.87, 131.96, 132.56, 151.13, 165.40. HRMS (EI) m/z calcd for C₁₇H₁₂O₂: 248.0837; found: 248.0839.



phenyl cinnamate (6n). Spectral data corresponds to that previously reported. Colorless solid (40 mg, 89% yield). ¹H-NMR (400 MHz, CDCl₃) δ 6.63 (d, 1H, *J*=16.4 Hz) 7.16-7.18 (m, 2H), 7.22-7.26 (m, 1H), 7.38-7.42 (m, 5H), 7.56-7.59 (m, 2H), 7.87 (d, 1H, *J*=16.0 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 117.37, 121.68, 125.82, 128.34, 129.04, 129.48, 130.73, 134.23, 146.60, 150.87, 165.42.

Reference: Suman De Sarkar; Stefan Grimme; Armido Studer J. Am. Chem. Soc., 2010, 132, 1190.



p-tolyl cinnamate (60). Spectral data corresponds to that previously reported. Colorless solid (31 mg, 65% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.38 (s, 3H), 6.65 (d, 1H, *J*=16.0Hz), 7.07 (d, 2H, *J*=8.0Hz), 7.22 (d, 2H, *J*=8.0Hz), 7.43 (m, 3H), 7.59 (m, 2H), 7.88 (d, 1H, *J*=16.0Hz). ¹³C-NMR (100MHz, CDCl₃) δ 20.92, 117.46, 121.34, 128.32, 129.01, 129.99, 130.68, 134.26, 135.44, 146.42, 148.60, 165.64

Reference: Kaitner, B.; Stilinovic, V. Acta Cryst. 2007, E63, 04347.



phenyl 3-methylbenzofuran-2-carboxylate (6p). Colorless solid (26 mg, 52% yield). ¹H-NMR (400 MHz, CDCl₃) δ 2.67 (s, 3H), 7.25-7.36 (m, 4H), 7.42-7.51 (m, 3H), 7.59 (d, 1H, *J*=7.6 Hz), 7.68 (d, 1H, *J*=8.0 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 9.61, 112.35, 121.29, 121.78, 123.38, 126.17, 127.75, 128.35, 129.02, 129.57, 140.13, 150.25, 154.75, 158.85. HRMS (EI) m/z calcd for C₁₆H₁₂O₃: 252.0786; found: 252.0780.



phenyl 1-methyl-1H-pyrrole-2-carboxylate (6q). Colorless solid (30 mg, 74% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.95 (s, 3H), 6.19 (dd, 1H, *J*=2.4 Hz, *J*=4.0 Hz), 6.87 (t, 1H, *J*=2.4 Hz), 7.16 (t, 1H, *J*=2.4 Hz), 7.17-7.19 (m, 2H), 7.21-7.25 (m, 1H), 7.37-7.42 (m, 2H). ¹³C-NMR(100 MHz, CDCl₃) δ 35.83, 107.31, 118.17, 120.60, 120.97, 124.57, 128.36, 129.56, 149.65, 158.64. HRMS (EI) m/z calcd for C₁₂H₁₁NO₂: 201.0790; found: 201.0787.



phenyl 1-phenyl-1H-indole-2-carboxylate (6r). Colorless solid (40 mg, 64% yield). ¹H-NMR (400 MHz, CDCl₃) δ 7.11 (t, 3H, *J*=9.2 Hz), 7.18-7.23 (m, 2H), 7.28-7.39 (m, 5H), 7.41-7.51 (m, 3H), 7.69 (s, 1H), 7.77 (d, 1H, *J*=8.0 Hz), 8.09 (d, 1H, *J*=8.0 Hz), 8.47 (dd, 1H, *J*=1.2 Hz, *J*=7.2 Hz), 9.04 (d, 1H, *J*=8.0 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 111.72, 113.06, 121.55, 121.70, 122.71, 125.77, 126.08, 126.18, 128.01, 128.12, 128.29, 129.16, 129.38, 138.30, 141.19, 150.53, 159.57. HRMS (EI) m/z calcd for C₂₁H₁₅NO₂: 313.1103; found: 313.1098.



(E)-styryl 2,6-dimethoxybenzoate (6s). Colorless solid (53 mg, 95% yield). ¹H-NMR (400 MHz, CDCl₃) δ 3.83 (s, 6H), 6.47 (d, 1H, *J*=12.8 Hz), 6.58 (d, 2H, *J*=8.4 Hz), 7.21-7.37 (m, 6H), 8.08 (d, 1H, *J*=12.8 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 56.12, 104.03, 111.85, 115.79, 126.32, 127.39, 128.72, 131.84, 134.32, 136.87, 157.82, 163.61.

HRMS (EI) m/z calcd for C₁₇H₁₆O₄: 284.1049; found: 284.1041.



MeC

(E)-styryl 2,6-dichlorobenzoate (6t). Colorless solid (21 mg, 36% yield). ¹H-NMR (400 MHz, CDCl₃) δ 6.50 (d, 1H, *J*=12.8 Hz), 7.18-7.33 (m, 8H), 7.98 (d, 1H, *J*=12.4 Hz). ¹³C-NMR(100 MHz, CDCl₃) δ 116.35, 125.46, 126.84, 126.99, 127.77, 130.42, 131.34, 132.52, 135.08, 160.83. HRMS (EI) m/z calcd for C₁₅H₁₀Cl₂O₂: 292.0058; found: 292.0054



(E)-styryl 4-methoxybenzoate (6u). Yellow solid (31 mg, 62% yield). ¹H-NMR (400 MHz, CDCl₃)

δ 3.88 (s, 3H), 6.55 (d, 1H, *J*=12.8 Hz), 6.96 (d, 2H, *J*=8.8 Hz), 7.22-7.26 (m, 1H), 7.30-7.40 (m, 4H), 8.06-8.12 (m, 3H). ¹³C-NMR(100 MHz, CDCl₃) δ 55.51, 113.92, 115.39, 121.20, 126,26, 127.37, 128.75, 132.19, 134.40, 136.67, 163.40, 164.02. HRMS (EI) m/z calcd for C₁₆H₁₄O₃: 254.2806; found: 254.2802

Spectra Data (¹H, ¹³C, ¹⁹F) of all products

2,4,6-trimethoxybiphenyl (3a).



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2,4,6-trimethoxy-4'-methylbiphenyl (3b).



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4'-bromo-2,4,6-trimethoxybiphenyl (3c).





4'-phenyl-2,4,6-trimethoxybiphenyl (3d).





2,4,6-trimethoxy-4'-(trifluoromethyl)biphenyl (3e).



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2,4,4',6-tetramethoxybiphenyl (3f).



1-(2',4',6'-trimethoxybiphenyl-4-yl)ethanone (3g).

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2-(2,4,6-trimethoxyphenyl)naphthalene (3h).



2',4',6'-trimethoxybiphenyl-4-carbonitrile(3i).



Ethyl 2',4',6'-trimethoxybiphenyl-4-carboxylate (3j).



3'-chloro-2,4,6-trimethoxybiphenyl(3k).



3'-fluoro-2,4,6-trimethoxybiphenyl (3l).
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5-(2,4,6-trimethoxyphenyl)benzo[d][1,3]dioxole (3n).



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3',5'-difluoro-2,4,6-trimethoxybiphenyl (3p).





2,4,6-trimethoxy-3',5'-bis(trifluoromethyl)biphenyl (3q).

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2,4,6-trimethoxy-3',5'-dimethylbiphenyl (3r).



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2',6'-difluorobiphenyl-4-carbonitrile (4b).









4'-phenyl-2-nitrobiphenyl (4c).





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2,6-dimethoxy-4'-methylbiphenyl (5b).



5-(2,6-dimethoxyphenyl)benzo[d][1,3]dioxole (5c).











3'-chloro-2,6-dimethoxybiphenyl (5f).







4'-tert-butyl-2,4-dimethoxybiphenyl (5h).

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2-(4-methoxyphenyl)-5-nitrofuran (5i).

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1-(2'-nitrobiphenyl-4-yl)ethanone (5j).



4,4',5-trimethoxy-2-nitrobiphenyl (5k).



2,3,4,5,6-pentafluoro-3'-methoxybiphenyl (5l).





2,3,4,5,6-pentafluoro-3'-nitrobiphenyl (5m).







1-(2',3',4',5',6'-pentafluorobiphenyl-4-yl)ethanone (5n).

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1-(2',6'-difluorobiphenyl-4-yl)ethanone (5p).

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2',4',6'-trifluorobiphenyl-4-carbonitrile (5r).







2,3,4,5-tetrafluoro-4'-methoxybiphenyl (5s).





2,3,6-trifluoro-4'-methoxybiphenyl (5t).






4-bromo-2,3,5,6-tetrafluoro-4'-methoxybiphenyl (5v).







phenyl 2,4,6-trimethoxybenzoate (6a).



phenyl 2,6-dimethoxybenzoate (6b).



4-bromophenyl 2,6-dimethoxybenzoate (6c).

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p-tolyl 2,6-dimethoxybenzoate (6d).



4-methoxyphenyl 2,6-dimethoxybenzoate (6e).



4-acetylphenyl 3-bromo-2,6-dimethoxybenzoate (6f).



phenyl 2,6-difluoro-4-methoxybenzoate (6g).









4-methoxyphenyl 4-methoxybenzoate (6j).



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