Synthesis of Biaryl Derivatives by Using Ruthenium-Mediated [2+2+2] Cyclotrimerization and Suzuki–Miyaura Cross-Coupling as Key Steps

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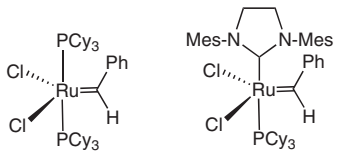
Abstract: Functionalized biaryl derivatives have been prepared by applying [2+2+2] cyclotrimerization with the aid of Grubbs' first-generation catalyst (G-I). The trimerized products were subjected to the Suzuki–Miyaura cross-coupling reaction sequence to generate highly functionalized biaryl derivatives.

Key words: terphenyl, quinquephenyl, [2+2+2] cyclotrimerization, Suzuki–Miyaura cross-coupling, metathesis

The biaryl unit occupies a unique position in synthetic organic chemistry. These compounds draw considerable attention due to their broad applications, such as key building blocks for pharmaceutically active molecules,[1] ligands for catalysis,[2] liquid crystals,[3] organic semiconductors,[4] polymers,[5] and sensors.[6] Various methods have been reported for aryl–aryl cross-coupling between two different aryl groups. Most of these developments are based on the transition-metal-catalyzed cross-coupling of aryl halides with arylmetal species through Stille, Suzuki, Negishi, Kharasch, and Hiyama coupling reactions.[7] Lately, attention has also been focused on strategies other than cross-coupling, such as the Diels–Alder reaction,[8] [2+2+2] cyclotrimerization,[9] oxidative coupling,[10] and radical chain reaction of arenediazonium salts.[11] Additionally, some other methodologies have also been reported for the preparation of biaryl[12] and terphenyl derivatives.[13] Various structurally related biaryl-containing cyclopeptide natural products such as biphenomycin[14] and arylomycin[15] represent interesting examples of biaryl compounds used in medicinal chemistry.

Metal-catalyzed cyclotrimerization of an alkyne is one of the most powerful methods for assembling substituted benzene derivatives.[16] In this regard, various transitional-metal derivatives (e.g., Co, Pd, Cr, Ni, Rh, and Ta)[17] have been used for this transformation.

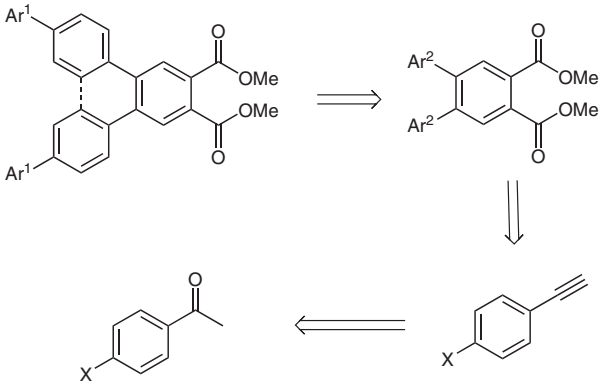
Ruthenium catalysts have broad application[18,19] in the synthesis of various natural and non-natural products.[20] Limited reports are available for [2+2+2] cyclotrimerization using ruthenium catalysts. Our group has extensively used ruthenium catalysts (Figure 1) for metathesis reactions.[21] Additionally, Suzuki–Miyaura cross-coupling[22] and [2+2+2] cyclotrimerization[23] have been used to generate diverse polycyclic compounds.[24] In continuation of our work in this area we are interested in designing biaryl derivatives by cyclotrimerization using a ruthenium-based catalyst.



1 (G-I) **2** (G-II)

Figure 1 Various Grubbs catalysts used in [2+2+2] cyclotrimerizations

Herein, we report the synthesis of biaryl derivatives based on [2+2+2] cyclotrimerization and Suzuki–Miyaura cross-coupling as key steps. The first step involves [2+2+2] cyclotrimerization of phenylacetylene derivatives with dimethyl acetylenedicarboxylate in the presence of Grubbs' catalyst to generate biaryl derivatives. Later on, these biaryl compounds were subjected to Suzuki–Miyaura cross-coupling with various boronic acids such as 4-formyl-, 4-acetoxy-, and 4-methoxyphenylboronic acids in the presence of $Pd(PPh_3)_4$ catalyst in tetrahydrofuran–toluene–water (1:1:1) to generate the terphenyl systems (Scheme 1).



Scheme 1 Retrosynthetic analysis of biaryl derivatives

For the synthesis of biaryl derivatives, we started with commercially available acetophenone derivatives **3**. These acetophenones were converted into acetylene derivatives **5** using the Vilsmeier reaction as a key step. Thus, treatment of acetophenone **3** with phosphorus oxychloride and a slightly excess of *N*,*N*-dimethylformamide

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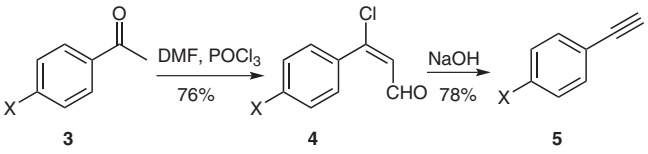
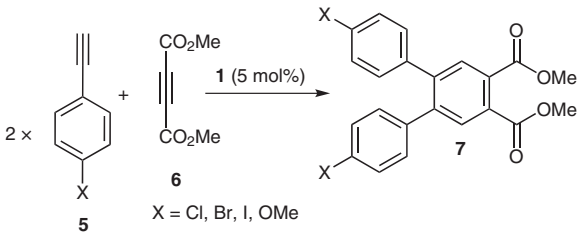
gave the corresponding β-chloro-α,β-unsaturated aldehyde **4** in 76% yield. Although we obtained two regioisomeric aldehydes, only one isomer is shown in Scheme 2. Hydrolysis of the β-chloro-α,β-unsaturated aldehyde intermediates with aqueous sodium hydroxide in dioxane gave the required acetylene derivatives **5** in 78% yield (Scheme 2).[25]



Scheme 2 Preparation of various phenylacetylene derivatives

The acetylenes **5** were subjected to [2+2+2] cyclotrimerization with dimethyl acetylenedicarboxylate (**6**) in the presence of Grubbs first-generation catalyst **1** (5 mol%) in toluene under reflux to deliver the terphenyl systems **7** (Scheme 3).



Scheme 3 [2+2+2] Cyclotrimerization with dimethyl acetylenedicarboxylate

When we replaced dimethyl acetylenedicarboxylate (**6**) with other acetylenic partners, such as 1,4-dibromobut-2-yne, 1,4-diacetylbut-2-yne, 1,4-dihydroxybut-2-yne, the desired [2+2+2] cyclotrimerized product was not observed. From the above reaction conditions we assumed that acetylene derivatives with electron-withdrawing groups like dimethyl acetylenedicarboxylate are required for the successful implementation of the [2+2+2] cyclotrimerization reaction with phenylacetylene derivatives.

The structures of the trimerized products **7a–d** were characterized using ^{1}H and ^{13}C NMR and HRMS data. ^{13}C NMR data clearly indicated the symmetrical nature of the product. Finally, an X-ray crystal structure of **7b** unambiguously established the structure of [2+2+2] trimerized product (Figure 2).[26] We also observed a minor amount of dimethyl acetylenedicarboxylate self-trimerized product (~15%).

Our detailed studies indicated that the catalyst G-I (**1**) is more suitable for cyclotrimerization than G-II (**2**). Various phenylacetylene derivatives **5** were subjected to [2+2+2] cyclotrimerization reaction with dimethyl acetylenedicarboxylate in presence of G-I (**1**) to deliver trimerized products **7a–d** in good yield (Table 1).

The trimerized products **7b** and **7c** were subjected to Suzuki–Miyaura cross-coupling reaction with different

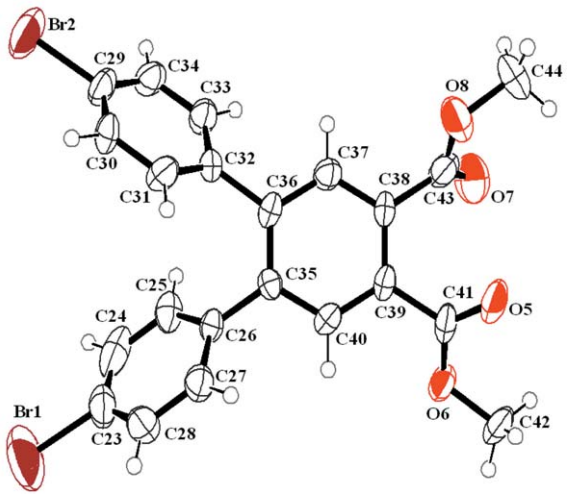
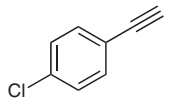
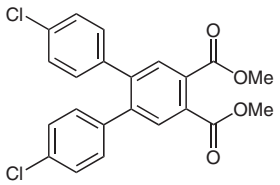
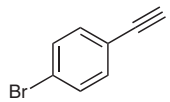
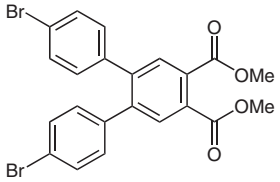
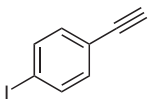
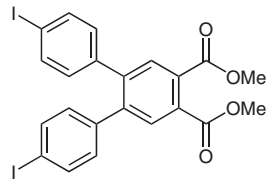
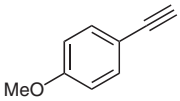
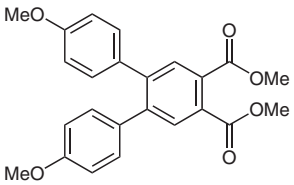


Figure 2 ORTEP diagram of **7b** at 50% probability

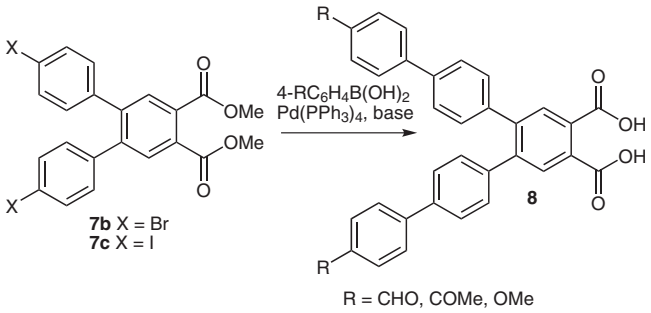
Table 1 List of Various [2+2+2] Cyclotrimerized Products Prepared

Entry	Substrate	Product[a]	Yield (%)
1	 **5a**	 **7a**	75
2	 **5b**	 **7b**	67
3	 **5c**	 **7c**	62
4	 **5d**	 **7d**	64

[a] Reaction conditions: **5**, DMAD (1.25 equiv), **1** (5 mol%), toluene, reflux, 36 h.

boronic acids such as 4-acetyl-, 4-formyl-, and 4-methoxyphenylboronic acid using $Pd(PPh_3)_4$ catalyst (5–9 mol%) in tetrahydrofuran–toluene–water (1:1:1) and using sodium carbonate as a base. We found that Suzuki–Miyaura

cross-coupling products were hydrolyzed in the course of the coupling sequence (Scheme 4). The presence of two aromatic rings in the *para* positions may be responsible for facial hydrolysis of the ester functionalities under mild reaction conditions



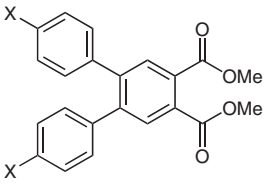
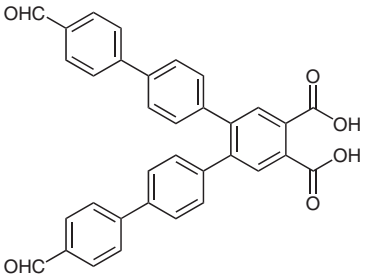
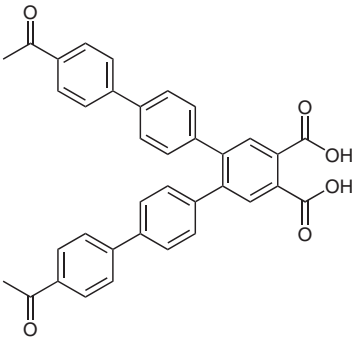
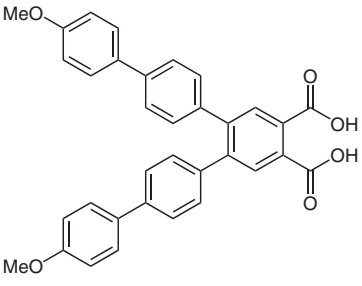
Scheme 4 Suzuki–Miyaura cross-coupling reactions

Table 2 Various Reaction Conditions Studied for the Suzuki–Miyaura Cross-Coupling Reaction[a]

Entry	Solvents[a]	Base	Product	Yield[b] (%)
1	THF–toluene–H_2O (1:1:1)	Na_2CO_3	**8b**	64
2	THF–toluene–H_2O (1:1:1)	K_2CO_3	**8c**	63
3	toluene	K_2CO_3	**8a**	66
4	toluene	Cs_2CO_3	**8c**	49
5	DME	K_2CO_3	**8b**	63
6	DMF	K_2CO_3	**8a**	58
7	THF	Na_2CO_3	**8c**	48
8	DMF	K_3PO_4	**8b**	52

[a] Reaction conditions: **7b** or **7c**, 4-$RC_6H_4B(OH)_2$, $Pd(PPh_3)_4$ (5–9 mol%), 90–120 °C, 6–12 h.
[b] Cross-coupling products isolated as the products of hydrolysis of the ester groups.

Table 3 Suzuki–Miyaura Cross-Coupling Reaction of Trimerized Products

Starting compound	Products[a]	Yield
 X = Br (**7b**) X = I (**7c**)	 **8a**	X = I, 74% X = Br, 63%
	 **8b**	X = I, 83% X = Br, 68%
	 **8c**	X = I, 53% X = Br, 48%

[a] Reaction conditions: **7b**,**c**, 4-$RC_6H_4B(OH)_2$, $Pd(PPh_3)_4$ (5–9 mol%), THF–toluene–H_2O (1:1:1), Na_2CO_3, 90 °C, 6 h.

To avoid the hydrolysis of the ester functionality, we studied the coupling reaction with substrate **7b** and **7c** with various solvents and bases (Table 2); all reaction conditions gave the ester-hydrolyzed Suzuki coupling products **8**.

We have prepared biaryl derivatives **7a–d** via [2+2+2] cyclotrimerization reaction by using Grubbs first-generation catalyst under toluene at reflux. The trimerized products **7b**,**c** were subjected Suzuki–Miyaura cross-coupling reaction to generate highly functionalized biaryl derivatives **8a–c** (Table 3). This methodology may be useful for the preparation of carbon-rich polycyclic derivatives with oxidative coupling as a key step.[27]

Analytical TLC was performed on 10 × 5 cm glass plates coated with silica gel g or GF_{254} (containing 13% $CaSO_4$ as a binder). Visualization was achieved by exposure to either iodine vapor or UV light. Column chromatography was performed using silica gel (100–200 mesh) and the column was usually eluted with a mixture of EtOAc and PE (petroleum ether; bp 60–80 °C). ^{1}H NMR and ^{13}C NMR spectral data were recorded on a Varian VXR 400 spectrometer using TMS as an internal standard and $CDCl_3$ as a solvent. Coupling constants (*J*) are given in hertz (Hz). HRMS data were recorded on a Q-ToF micro mass instrument. Boronic acids were purchased from Lancaster Chemical Company (UK) and Aldrich Chemical Company (USA). $(PPh_3)_4Pd$ catalyst was purchased from Strem Chemicals, Inc. (USA).

Dimethyl 4,4″-Dichloro-1,1′:2′,1″-terphenyl-4′,5′-dicarboxylate (7a); Typical Procedure

4-Chlorophenylacetylene (**5a**, 100 mg, 0.73 mmol) in anhyd toluene was degassed with N_2 for 10 min. Then, Grubbs catalyst **1** (30 mg, 5 mol%) was added and the mixture was stirred for 15 min. DMAD (**6**, 259 mg, 1.82 mmol) in toluene was added to the mixture and it was refluxed under N_2 for 36 h. When the reaction was complete (TLC monitoring), the mixture was cooled to r.t. and the solvent was removed under reduced pressure and the residue was purified by column chromatography (EtOAc–PE) to give **7a** (228 mg, 75%); mp 180–182 °C.

IR (KBr): 836, 1247, 1594, 1736, 2954 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.94 (s, 6 H), 7.05 (d, *J* = 4.4 Hz, 4 H), 7.24 (d, *J* = 4.4 Hz, 4 H), 7.75 (s, 2 H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 52.9, 128.8, 131.0, 131.3, 134.1, 137.8, 142.2, 167.7.

HRMS (Q-ToF): *m*/*z* [M + Na]$^+$ calcd for $C_{22}H_{16}Cl_2NaO_4$: 437.0322; found: 437.0323.

Dimethyl 4,4″-Dibromo-1,1′:2′,1″-terphenyl-4′,5′-dicarboxylate (7b)

Following the typical procedure for **7a** using **5b** (100 mg, 0.55 mmol), Grubbs catalyst **1** (22 mg, 5 mol%), and DMAD (**6**, 195 mg, 1.37 mmol) gave **7b** (186 mg, 67%) as a solid; mp 158–160 °C.

IR (KBr): 596, 1247, 1431, 1590, 1736, 2953 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.94 (s, 6 H), 6.99 (d, *J* = 8.4 Hz, 4 H), 7.40 (d, *J* = 8.4 Hz, 4 H), 7.74 (s, 2 H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 52.8, 122.2, 131.1, 131.2, 131.5, 138.1, 142.0, 167.4.

HRMS (Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{17}Br_2O_4$: 505.1825; found: 505.1842.

Dimethyl 4,4″-Diiodo-1,1′:2′,1″-terphenyl-4′,5′-dicarboxylate (7c)

Following the typical procedure for **7a** using **5c** (100 mg, 0.43 mmol), Grubbs catalyst **1** (18 mg, 5 mol%), and DMAD (**6**, 152 mg, 1.07 mmol) gave **7c** (160 mg, 62%) as a solid; mp 149–150 °C.

IR (KBr): 1350, 1594, 1726, 2924 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 6 H), 6.86 (d, *J* = 4.8 Hz, 4 H), 7.60 (d, *J* = 4.8 Hz, 4 H), 7.73 (s, 2 H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 53.0, 94.1, 131.3, 131.4, 131.5, 137.7, 138.8, 142.2, 167.7.

HRMS (Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{17}I_2O_4$: 421.1627; found: 421.1646.

Dimethyl 4,4″-Dimethoxy-1,1′:2′,1″-terphenyl-4′,5′-dicarboxylate (7d)

Following the typical procedure for **7a** using **5d** (100 mg, 0.73 mmol), Grubbs catalyst **1** (30 mg, 5 mol%), and DMAD (**6**, 266 mg, 1.87 mmol) gave **7d** (195 mg, 64%) as a liquid.

IR (neat): 1265, 1602, 1725, 2953, 3056 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 6 H), 3.92 (s, 6 H), 6.78 (d, *J* = 4.4 Hz, 4 H), 7.06 (d, *J* = 4.8 Hz, 4 H), 7.73 (s, 2 H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 52.8, 55.4, 113.8, 130.5, 130.6, 130.9, 131.3, 132.3, 159.1, 168.1.

HRMS (Q-ToF): *m*/*z* [M + H]$^+$ calcd for $C_{24}H_{23}O_6$: 407.1495; found: 407.1507.

4,4‴-Diformyl-1,1′:2′,1″;4‴,1⁗-quinquephenyl-4″,5″-dicarboxylic Acid (8a); Typical Procedure

To a soln of **7c** (100 mg, 0.16 mmol) in THF–toluene–H_2O (1:1:1) mixture, 4-formylphenylboronic acid (118 mg, 0.79 mmol), aq Na_2CO_3 (83 mg, 0.78 mmol, degassed with N_2 for 20 min), and $Pd(PPh_3)_4$ (9.3 mg, 4 mol%) were added; the mixture was heated at 90 °C for 6 h. When the reaction was complete (TLC monitoring), the mixture was diluted with H_2O and extracted with CH_2Cl_2 (4 × 50 mL). The combined organic layers were washed with H_2O and brine and dried (Na_2SO_4). The solvent was evaporated and the crude product was charged on a column (silica gel, EtOAc–PE, 1:4) to give **8a** (62 mg, 74%) as a white solid; mp 155–158 °C.

IR (KBr): 960, 1352, 1384, 1601, 1677, 2811, 3428 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.44–7.51 (m, 6 H), 7.62–7.68 (m, 4 H), 7.74–7.77 (m, 4 H), 7.94–7.97 (m, 4 H), 10.06 (s, 2 H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 127.4, 127.5, 127.5, 128.4, 129.1, 130.9, 136.0, 136.1, 140.1, 146.6, 171.1, 198.1.

Anal. Calcd for $C_{34}H_{20}O_6$: C, 77.85; H, 3.84. Found: C, 78.68; H, 4.14.

4,4‴-Diacetyl-1,1′:2′,1″;4‴,1⁗-quinquephenyl-4″,5″-dicarboxylic Acid (8b)

Following the typical procedure for **8a** using **7c** (50 mg, 0.08 mmol), 4-acetylphenylboronic acid (58 mg, 0.20 mmol), aq Na_2CO_3 (34 mg, 0.32 mmol degassed with N_2 for 20 min), and $Pd(PPh_3)_4$ (9.7 mg, 4 mol%) gave **8b** (37 mg, 83%) as a white solid; mp 160–162 °C.

IR (KBr): 960, 1355, 1384, 1600, 2918, 3433 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.64 (s, 6 H), 7.40–7.49 (m, 6 H), 7.64–7.68 (m, 4 H), 7.68–7.70 (m, 4 H), 8.03–8.05 (m, 4 H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 26.7, 127.3, 127.4, 128.3, 129.0, 129.1, 135.9, 139.9, 145.8, 147.8, 178.4, 197.9.

Anal. Calcd for $C_{36}H_{24}O_6$: C, 78.25; H, 4.38. Found: C, 78.82; H, 3.67.

4,4‴″-Dimethoxy-1,1′:2′,1″;4‴,1‴″-quinquephenyl-4″,5″-dicarboxylic Acid (8c)

Following the typical procedure for **8a** using **7c** (50 mg, 0.08 mmol), 4-methoxyphenylboronic acid (58 mg, 0.33 mmol), aq Na_2CO_3 (35 mg, 0.33 mmol, degassed with N_2 for 20 min), and $Pd(PPh_3)_4$ (8.7 mg, 9 mol%) gave **8c** (23 mg, 54%) as a white solid; mp 179–181 °C.

IR (KBr): 1351, 1384, 1605, 2924, 3432 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 3.65 (s, 6 H), 6.95–7.00 (m, 4 H), 7.28–7.32 (m, 4 H), 7.39–7.43 (m, 4 H), 7.46–7.49 (m, 2 H), 7.51–7.56 (m, 4 H).

^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 52.8, 55.4, 113.8, 130.5, 130.6, 130.9, 131.3, 132.3, 159.1.

HRMS (ESI): *m/z* $[M]^+$ calcd for $C_{34}H_{26}O_6$: 530.5666; found: 530.6921.

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