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A new palladium catalyzed protocol for atom-efficient cross-coupling reactions of triarylbismuths with aryl halides and triflates

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ABSTRACT

A new palladium catalyzed protocol for an atom-efficient cross-coupling reaction of triarylbismuths with aryl halides and triflates has been described. The palladium catalytic system with Cs_2CO_3 base was found to be very efficient in DMA solvent to furnish excellent yields of cross-coupled functionalized biaryls in short reaction times.

1. Introduction

The role of organoboron, organotin, organosilicon, and other organometallic reagents has been demonstrated to be vital to obtain biaryls in organic synthesis.[1–4] The importance of these methods led to the development of numerous new catalytic protocols and new reagents.[2,3] However, there is also a need for the development of atom-efficient organometallic reagents, which can react with more than 1 equiv of electrophilic coupling reagents[5] in order to reduce the organometallic loadings for industrial scale preparations.[1f] Triarylbismuth reagents with three aryl groups on bismuth have attracted our attention as viable atom-efficient organometallic coupling partners for C–C bond formations. Triarylbismuths are non-toxic, stable to air, and can be readily prepared by known procedures.[6]

Organobismuth compounds in general, are popular for N- and O-arylation reactions under metal mediated or catalyzed conditions.[7] However, application of organobismuth compounds to C–C bond formations are relatively scarce. The reactivity studies undertaken with triarylbismuths for the conversion of Bi–C to C–C under metal catalyzed cross-coupling conditions are very limited.[8–10] This is partly due to weak nature of the Bi–C bond and its facile cleavage to give biaryls in the presence of metal catalyst even at room temperature conditions.[8a,9a] In particular, promoting the triarylbismuths toward cross-coupling was found to be a delicate task and this could be one reason why triarylbismuths were untapped as atom-efficient reagents for organic synthesis. Thus, finding the right combination for general cross-coupling reactivity often demands a systematic study. Our recent efforts in this direction allowed us to realize the facile reactivity of triarylbismuth for cross-coupling reaction with electrophilic coupling partners to some extent.[11] However, the metal catalyzed protocols available are still limited toward the utilization of these reagents for C–C bond formations in organic synthesis.

From our earlier studies of palladium catalyzed conditions, it was also found that the role of catalyst precursor in combination with base, solvent, and temperature bear tremendous effect on the reactivity of triarylbismuths, hence play a decisive role for cross-coupling reaction with electrophilic coupling partners.[11] This was also known with other cross-coupling reactions using organoboron and other organometallic reagents.[4] In continuation of our interest in triarylbismuths for C–C bond formations, we now report a new and novel palladium catalyzed protocol for atom-efficient cross-coupling of triarylbismuths with aryl bromides, iodides, and triflates.

2. Results and discussion

To develop a new palladium catalyzed protocol, our initial attempts involved screening of palladium chloride as catalyst precursor in combination with triphenylphosphine (TPP) as a ligand. A

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systematic study was carried out using a variety of bases and solvents under different temperature conditions for the cross-coupling reaction of 4-acetylphenyl bromide with triphenylbismuth, and the results are given in Table 1.

This investigation provided varied combinations of base and solvent systems to obtain the desired cross-coupling in moderate conversions. Thus, the reactions carried out with Cs_2CO_3 as base in different solvents identified DMA (*N*,*N*-dimethylacetamide) furnishing 79% conversion (entry 4) while, NMP and DMF led to 44% and 71% conversions (entries 2 and 5). However, 1,4-dioxane and THF solvent systems were found to be inefficient and did not provide respectable conversions (entries 1 and 3). Further examination of DMA with different bases K_3PO_4, KOAc, and K_2CO_3 delivered moderate cross-coupling conversion (entries 6–8). Next, lowering the reaction temperature to 60 °C had no positive effect, giving only 36% conversion with Cs_2CO_3 in DMA (entry 9). Strikingly, the cross-coupling reaction carried out at 90 °C improved the conversion to 89% in 2 h with 85% isolated product (entry 10). Further study with varying Cs_2CO_3 base equivalents produced mixed conversions (entry 11–13) revealing that 4 equiv of base is necessary to furnish high cross-coupling conversion. A control reaction carried out without base delivered only 16% cross-coupling conversion indicating the role of base to activate triarylbismuth for cross-coupling reaction (entry 14). From this study, it was clear that Cs_2CO_3 (4 equiv) in DMA with $PdCl_2$ (0.09 equiv)/PPh_3 (0.18 equiv) at 90 °C is an optimized condition for high cross-coupling conversion. At this point, it is noteworthy to mention that the present protocol is highly efficient as 3 equiv of aryl bromide reacted with 1 equiv of triphenylbismuth cleanly to provide high yield of cross-coupling product in short reaction time. Thus, the atom-efficiency of triphenylbismuth where all the three phenyls were efficiently coupled with 3 equiv of electrophilic coupling partner was thoroughly established. This is an important aspect to note with triarylbismuths, which is not true with organoboron, organotin or organosilicon reagents.

The cross-coupling scope and generality of a variety of aryl bromides with different triarylbismuths was investigated using optimized conditions and the results are given in Table 2.

The reactions of electronically divergent phenyl bromides was found to be high yielding furnishing a variety of functionalized biphenyls with different triarylbismuths. Firstly, aryl bromides with 4-acetyl as an electron-withdrawing substituent furnished good yields of functionalized biphenyls (entries 1–3). The reactivity of *o*-, *m*- and *p*-nitro substituted phenyl bromides was remarkable furnishing corresponding biphenyls in good to excellent yields (entries 5–12). Notably, the poor cross-coupling reactivity reported with 2-nitrophenyl bromide due to sterics in the *ortho* position under Suzuki coupling conditions[12] was not operative in the present case, thus giving moderate to good yields of products (entries 10–12). The reaction of 4-cyano and 2-cyano substituted phenyl bromides also produced 55–85% yields of the substituted biphenyls (entries 13–16). Similarly, the reactivity of *para* substituted phenyl bromides containing trifluoromethyl, benzoyl, and carboethoxy groups was found to be good to excellent (entries 17–23). Thus, aryl bromides studied with electron-withdrawing groups showed good to high cross-coupling reactivity with different triarylbismuths. The cross-coupling reactions of electron-rich *p*-tolylbromide and *m*-tolylbromide furnished moderate yields of cross-coupled biphenyls (entries 24, 25). The reaction of *o*-tolylbromide produced 32% of the cross-coupled product with trianisylbismuth. Notably, electron-rich substrates, which are otherwise known to show poor reactivity in this type of reaction showed moderate reactivity with triarylbismuths.

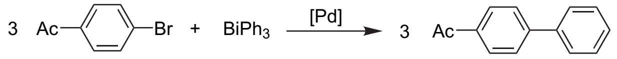
To further elaborate the general reactivity of the present protocol with other electrophilic coupling reagents, we have undertaken the cross-coupling study with functionalized aryl iodides and the results are given in Table 3.

The reactivity of various substituted aryl iodides with different triarylbismuths were found to be faster and efficient furnishing good to high yields of the cross-coupled biphenyls in a short period of 1 h. The cross-coupling reactivity with aryl iodides was found to be efficient even with a lower palladium catalyst (0.06 equiv) loading when compared to the corresponding reactivity with aryl bromides. As shown in Table 3, the reactions of electron-deficient aryl iodides afforded high yields of cross-coupling products with various triarylbismuths. For example, aryl iodides substituted with *p*-acetyl (entries 1–3), *p*-nitro (entries 4–6), *p*-cyano (entries 7–9), *p*-chloro (entries 10–12), *p*-trifluoromethyl (entries 13–15), and *m*-cyano (entry 16) produced high isolated yields of cross-coupled products with different triarylbismuths. The reactions of electron-rich *p*-methoxy and *p*-methyl substituted phenyl iodides furnished moderate to good yields of the products (entries 17–19). This improved reactivity of electron-rich aryl iodides is similar to that observed with aryl bromides with different triarylbismuths.

Further, to broaden the scope, cross-coupling reactions of aryl triflates with triphenylbismuth was studied. The cross-coupling reaction of 4-acetylphenyl triflate as model substrate was studied with triphenylbismuth in combination with various additives and the results are given in Table 4.

As shown, the initial cross-coupling reaction carried out at 90 °C for 3 h produced only 59% conversion of cross-coupled product (entry 1). So, attempts were made to improve reactivity of aryl triflates to obtain respectable cross-coupling conversion. Unfortunately, the reaction carried out lowering the temperature to 60 °C did not improve the cross-coupling conversion (entry 2). The observed lower reactivity with aryl triflate could be attributed to the unstable nature of the intermediate Pd(II) complex that is expected to form during initial oxidative addition of aryl triflate to Pd(0). The replacement of triflate ion with halides by salt additives was demonstrated in the literature to improve the stability and reactivity of Pd(II) intermediate.[13] Hence, we screened the reaction in the presence of various additives to check their effect for improving the cross-coupling conversion. As shown in Table 4, the presence of various additives showed a positive effect on the cross-coupling conversion. For example, the reactions carried out with the additives such as LiCl (entry 3), KCl (entry 4), KBr (entry 5), LiBr (entry 6), tetrabutylammonium iodide (TBAI) (entry 8), tetrabutylammonium

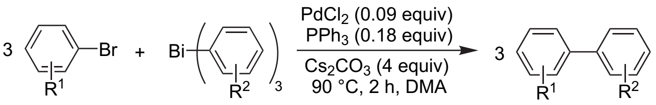
Table 1
Screening conditions[a,b]



Entry	Base	*T* (°C)	Solvent	*t* (h)	Conv[f] (%)
1	Cs_2CO_3	80	1,4-Dioxane	2	14
2	Cs_2CO_3	80	NMP	2	44
3	Cs_2CO_3	80	THF	2	02
4	Cs_2CO_3	80	DMA	3	79
5	Cs_2CO_3	80	DMF	3	71
6	K_3PO_4	80	DMA	3	56
7	KOAc	80	DMA	3	56
8	K_2CO_3	80	DMA	3	53
9	Cs_2CO_3	60	DMA	3	36
10	Cs_2CO_3	90	DMA	2	89[b]
11	Cs_2CO_3	90	DMA	2	54[c]
12	Cs_2CO_3	90	DMA	2	65[d]
13	Cs_2CO_3	90	DMA	2	76[e]
14	None	90	DMA	2	16

[a] Conditions: $BiPh_3$ (1 equiv), 4-acetylphenyl bromide (3.6 equiv), $PdCl_2$ (0.09 equiv), PPh_3 (0.18 equiv), base (4 equiv), and solvent (3 mL).
[b] 4-Acetylphenyl bromide (3.3 equiv) for entries 10–14.
[c] With base (1 equiv).
[d] With base (2 equiv).
[e] With base (3 equiv).
[f] Measured by GC analysis.

Table 2
Cross-coupling of aryl bromides with triarylbismuths[a,b]



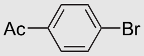
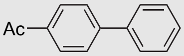
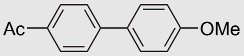
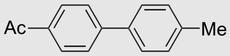
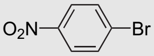
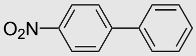
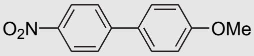
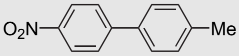
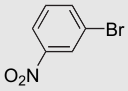
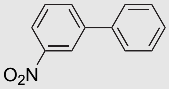
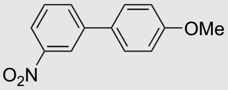
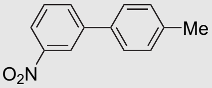
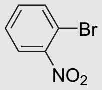
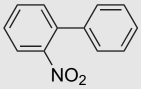
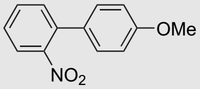
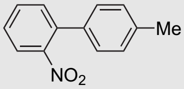
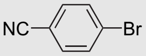
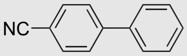
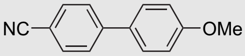
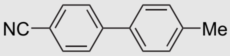
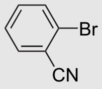
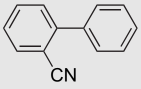
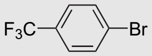
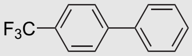
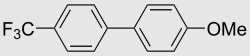
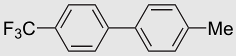
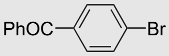
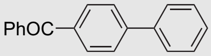
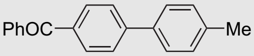
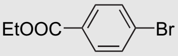
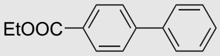
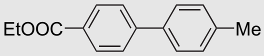
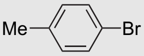
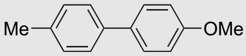
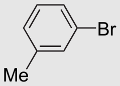
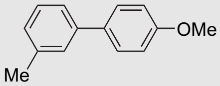
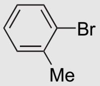
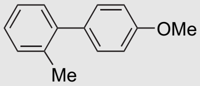
Entry	R^1–X	$BiAr_3$	Product		Yield[c] (%)
1		$BiPh_3$		**1a**	85
2		Bi(*p*-anisyl)$_3$		**1b**	76
3		Bi(*p*-tolyl)$_3$		**1c**	88
4		$BiPh_3$		**2a**	85
5		Bi(*p*-anisyl)$_3$		**2b**	75
6		Bi(*p*-tolyl)$_3$		**2c**	83
7		$BiPh_3$		**3a**	80
8		Bi(*p*-anisyl)$_3$		**3b**	67
9		Bi(*p*-tolyl)$_3$		**3c**	81
10		$BiPh_3$		**4a**	72
11		Bi(*p*-anisyl)$_3$		**4b**	63
12		Bi(*p*-tolyl)$_3$		**4c**	70
13		$BiPh_3$		**5a**	69
14		Bi(*p*-anisyl)$_3$		**5b**	79
15		Bi(*p*-tolyl)$_3$		**5c**	85
16		$BiPh_3$		**6a**	55
17		$BiPh_3$		**7a**	84
18		Bi(*p*-anisyl)$_3$		**7b**	72
19		Bi(*p*-tolyl)$_3$		**7c**	62
20		$BiPh_3$		**8a**	69
21		Bi(*p*-tolyl)$_3$		**8b**	72
22		$BiPh_3$		**9a**	70
23		Bi(*p*-tolyl)$_3$		**9b**	90

Table 2 (*continued*)

Entry	R^1–X	$BiAr_3$	Product		Yield[c] (%)
24		Bi(*p*-anisyl)$_3$		**10a**	52
25		Bi(*p*-anisyl)$_3$		**11a**	58
26		Bi(*p*-anisyl)$_3$		**12a**	32

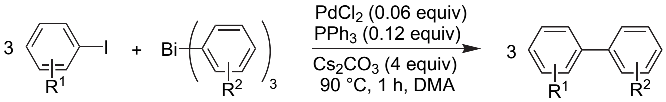
[a] Reaction conditions: $BiAr_3$ (1 equiv), aryl bromide (3.3 equiv), $PdCl_2$ (0.09 equiv), PPh_3 (0.18 equiv), Cs_2CO_3 (4 equiv), DMA (3 mL), 90 °C, and 2 h.

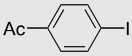
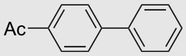
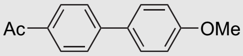
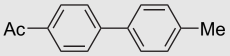
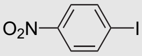
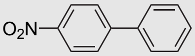
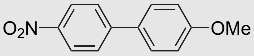
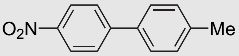
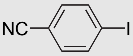
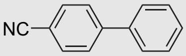
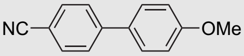
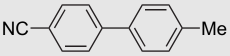
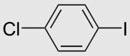
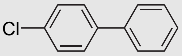
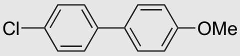
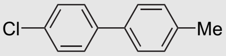
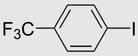
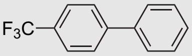
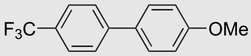
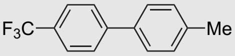
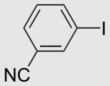
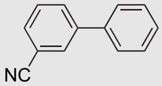
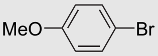
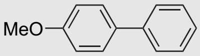
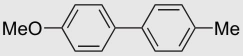
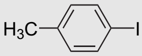
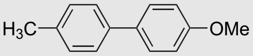
[b] Homo-coupling biaryls from triarylbismuths formed as minor side products.

[c] Isolated yields obtained after column chromatography. Yields are calculated based on the amount of triarylbismuth used.

Table 3

Cross-coupling of aryl iodides with triarylbismuths[a,b]



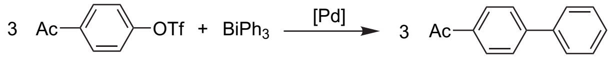
Entry	R^1–X	$BiAr_3$	Product		Yield[c] (%)
1		$BiPh_3$		**1a**	85
2		Bi(*p*-anisyl)$_3$		**1b**	76
3		Bi(*p*-tolyl)$_3$		**1c**	81
4		$BiPh_3$		**2a**	96
5		Bi(*p*-anisyl)$_3$		**2b**	74
6		Bi(*p*-tolyl)$_3$		**2c**	94
7		$BiPh_3$		**5a**	93
8		Bi(*p*-anisyl)$_3$		**5b**	72
9		Bi(*p*-tolyl)$_3$		**5c**	92
10		$BiPh_3$		**13a**	70
11		Bi(*p*-anisyl)$_3$		**13b**	74
12		Bi(*p*-tolyl)$_3$		**13c**	80
13		$BiPh_3$		**7a**	87
14		Bi(*p*-anisyl)$_3$		**7b**	85
15		Bi(*p*-tolyl)3		**7c**	92
16		$BiPh_3$		**14a**	87
17		$BiPh_3$		**15a**	52
18		Bi(*p*-tolyl)$_3$		**10a**	79
19		Bi(*p*-anisyl)$_3$		**10a**	71

[a] Reaction conditions: $BiAr_3$ (1 equiv), aryl iodide (3.3 equiv), $PdCl_2$ (0.06 equiv), PPh_3 (0.12 equiv), Cs_2CO_3 (4 equiv), DMA (3 mL), 90 °C, and 1 h.

[b] Homo-coupling biaryls from triarylbismuths formed as minor side products.

[c] Isolated yields obtained after column chromatography. Yields are calculated based on the amount of triarylbismuth used.

Table 4
Screening with different additives[a,b]



Entry	Additive (equiv)	T (°C)	t (h)	Conv[c] (%)
1	None	90	3	59
2	None	60	3	47
3	LiCl (9.9)	90	3	78
4	KCl (9.9)	90	3	70
5	KBr (9.9)	90	3	77
6	LiBr(9.9)	90	3	68
7	AgI (9.9)	90	3	03
8	TBAI (9.9)	90	3	80
9	TBAB (9.9)	90	3	72
10	NaBr (6.6)	90	3	62
11	KI (6.6)	90	3	74
12	TBAI (3.3)	90	3	83
13	TBAB (3.3)	80	5	85
14	TBAI (3.3)	80	5	83
15	TBAB (1.1)	90	1	79[d]

[a] Conditions: $BiPh_3$ (1 equiv), aryl triflate (3.3 equiv), $PdCl_2$ (0.09 equiv), PPh_3 (0.18 equiv), Cs_2CO_3 (4 equiv), additive, and DMA (3 mL).

[b] Homo-coupling product biphenyl from triphenylbismuth formed as minor side product.

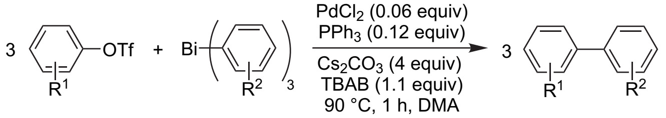
[c] Measured by GC analysis.

[d] With catalyst loading of $PdCl_2$ (0.06 equiv)/PPh_3 (0.12 equiv).

bromide (TBAB) (entry 9), NaBr (entry 10), and KI (entry 11) produced improved conversion in the range of 62–80% with the exception of silver iodide (entry 7). This also revealed that TBAB and TBAI were equally effective at producing good conversion (entries 12–15). Further, a cross-coupling reaction carried out with catalyst loading of $PdCl_2$ (0.06 equiv)/PPh_3 (0.12 equiv) and with TBAB (1.1 equiv) also produced excellent conversion (entry 15) and, hence, we decided to further investigate this reactivity with other triflates using these conditions. The reactivity of various functionalized aryl triflates with different triarylbismuths under optimized palladium protocol condition is shown in Table 5.

Thus, the reactions carried out using electronically divergent aryl triflates produced excellent cross-coupling yields with different triarylbismuths. For example, the reactions of variety of electron-deficient phenyl triflates substituted with *p*- and *m*-acetyl groups (entries 1–3 and 7–9), *p*-nitro (entries 4–6), *p*-cyano (entries 10–12), *m*-cyano (entries 13–15), *p*-chloro (entries 16–18), and *p*-fluoro (entry 19) produced good to high isolated yields of the functionalized biaryls with different triarylbismuths. The cross-coupling reaction of 2-naphthyl triflate with different triarylbismuths furnished good yields of the corresponding cross-coupling products (entries 20–22). Strikingly, the reactivity of various triarylbismuths was unaffected by the change in electronics of the aryl rings in triarylbismuths, thus furnishing consistently good to

Table 5
Cross-coupling of aryl triflates with triarylbismuths[a,b]



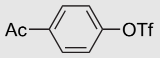
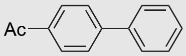
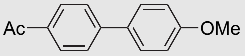
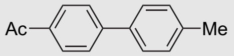
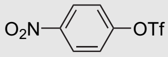
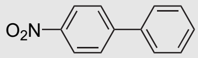
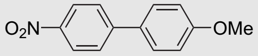
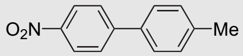
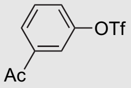
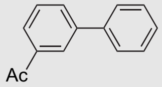
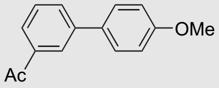
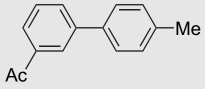
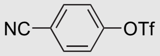
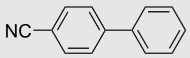
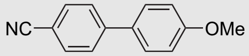
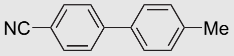
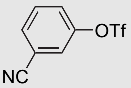
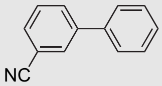
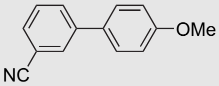
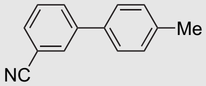
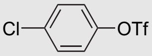
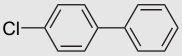
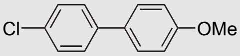
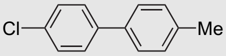
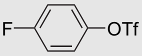
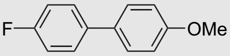
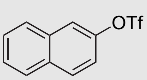
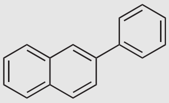
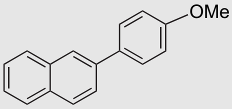
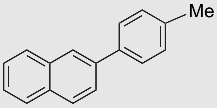
Entry	R^1–X	$BiAr_3$	Product		Yield[c] (%)
1		$BiPh_3$		**1a**	74
2		Bi(*p*-anisyl)$_3$		**1b**	75
3		Bi(*p*-tolyl)$_3$		**1c**	82
4		$BiPh_3$		**2a**	74
5		Bi(*p*-anisyl)$_3$		**2b**	77
6		Bi(*p*-tolyl)$_3$		**2c**	84
7		$BiPh_3$		**16a**	75
8		Bi(*p*-anisyl)$_3$		**16b**	82
9		Bi(*p*-tolyl)$_3$		**16c**	87
10		$BiPh_3$		**5a**	78
11		Bi(*p*-anisyl)$_3$		**5b**	73
12		Bi(*p*-tolyl)$_3$		**5c**	80

Table 5 (*continued*)

Entry	R^1–X	$BiAr_3$	Product		Yield[c] (%)
13		$BiPh_3$		**14a**	65
14		Bi(*p*-anisyl)$_3$		**14b**	84
15		Bi(*p*-tolyl)$_3$		**14c**	74
16		$BiPh_3$		**13a**	60
17		Bi(*p*-anisyl)$_3$		**13b**	63
18		Bi(*p*-tolyl)$_3$		**13c**	71
19		Bi(*p*-anisyl)$_3$		**17a**	51
20		$BiPh_3$		**18a**	74
21		Bi(*p*-anisyl)$_3$		**18b**	79
22		Bi(*p*-tolyl)$_3$		**18c**	76

[a] Reaction conditions: $BiAr_3$ (1 equiv), aryl triflate (3.3 equiv), $PdCl_2$ (0.06 equiv), PPh_3 (0.12 equiv), Cs_2CO_3 (4 equiv), TBAB (1.1 equiv), DMA (3 mL), 90 °C, and 1 h.

[b] Homo-coupling biaryls from triarylbismuths formed as a minor side products.

[c] Isolated yields obtained after column chromatography. Yields are calculated based on the amount of triarylbismuth used.

high yields of the cross-coupled products with different electrophilic coupling partners such as aryl bromides, iodides, and triflates.

3. Conclusion

We have disclosed an improved cross-coupling reactivity of triarylbismuths toward aryl bromides, iodides, and triflates under the present palladium catalyzed protocol. The simplicity associated with the present palladium catalyzed protocol comprises the utilization of routinely used palladium catalyst precursor and triphenylphosphine ligand. The efficient reactivity of the present catalytic protocol is evident from high yields obtained in short reaction times using different electrophilic coupling partners such as aryl bromides, iodides, and triflates with different triarylbismuths. The high atom-efficiency of triarylbismuths demonstrated by reacting with 3 equiv of electrophilic coupling partners further defines its breadth and versatility, which is not known with organoboron, organosilicon, organotin, and similar reagents. Thus, the present study and established new palladium protocol is expected to provide additional opportunity to exploit the inherent advantage associated with triarylbismuths as atom-efficient reagents for applications in organic synthesis.

4. Experimental section

4.1. General

All reactions were carried out in hot-oven-dried Schlenk tubes under nitrogen atmosphere using anhydrous solvents. All solvents were purified by standard purification procedures. Analytical thin layer chromatography (TLC) was performed using silica gel GF254 (Spectrochem) coated glass plates or using aluminum sheets precoated with silica gel 60 F_{254} (Merck). Visualization of TLC plate was accomplished with UV lamp or in iodine chamber. The column chromatography was performed using silica gel 100–200 mesh size (SD Fine-Chem Limited) with ethyl acetate/petroleum ether as an eluent system. Melting points were uncorrected and measured using JSGW melting point apparatus (Jain Scientific Glass Works, Ambala cantt, India). IR spectra were recorded on a Bruker vector 22 FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded on a JEOL-Lambda (400 MHz) spectrometer using $CDCl_3$ as a solvent and chemical shift values are expressed in parts per million (ppm) from tetramethylsilane (TMS) as an internal standard. Triarylbismuths were prepared by standard protocols.[6,8a,b] GC analysis of the crude reaction mixtures and also of the pure isolated products was performed using Perkin Elmer (Clarus 500 Gas Chromatograph) system. ESI-MS spectra were measured on Waters HAB213 Q-Tof Premier Micro mass spectrometer. All aryl halides were purchased from Acros Organics and triflates were prepared according to the reported procedure.[14]

4.1.1. *Representative procedure for cross-coupling reaction of aryl bromides with triarylbismuths*

A hot-oven-dried Schlenk tube was charged with 4-bromoacetophenone (0.825 mmol, 0.164 g) followed by triphenylbismuth (0.25 mmol, 0.11 g), Cs_2CO_3 (1 mmol, 0.326 g), triphenylphosphine (0.045 mmol, 0.012 g), $PdCl_2$ (0.0225 mmol, 0.004 g), and DMA (3 mL) solvent under nitrogen atmosphere. The reaction mixture was stirred at 90 °C for 2 h. The contents of the mixture were cooled to room temperature and quenched with dil. HCl (10 mL), extracted with ethyl acetate (3×10 mL). The combined organic extract was washed with water (2×10 mL) and brine (10 mL), dried over anhydrous $MgSO_4$ and was concentrated under vacuo to afford the crude product. The crude product was further purified on silica gel by column chromatography using 2% ethyl acetate in petroleum ether to afford 4-acetylbiphenyl, **1a** (0.125 g) in 85% yield based on the amount of triphenylbismuth used.

4.1.2. Representative procedure for cross-coupling reaction of aryl iodides with triarylbismuths

A hot-oven-dried Schlenk tube was charged with 4-iodoacetophenone (0.825 mmol, 0.203 g) followed by triphenylbismuth (0.25 mmol, 0.11 g), Cs_2CO_3 (1 mmol, 0.326 g), triphenylphosphine (0.03 mmol, 0.0078 g), $PdCl_2$ (0.015 mmol, 0.0027 g), and DMA (3 mL) solvent under nitrogen atmosphere. The reaction mixture was stirred at 90 °C for 1 h. The contents of the mixture were cooled to room temperature and quenched with dil HCl (10 mL), extracted with ethyl acetate (3×10 mL). The combined organic extract was washed with water (2×10 mL) and brine (10 mL), dried over anhydrous $MgSO_4$ and was concentrated under vacuo to afford the crude product. The crude product was further purified on silica gel by column chromatography (2% ethyl acetate in petroleum ether) to afford 4-acetylbiphenyl, **1a** (0.125 g) in 85% yield based on the amount of triphenylbismuth used.

4.1.3. Representative procedure for cross-coupling reaction of aryl triflates with triarylbismuths

A hot-oven-dried Schlenk tube was charged with 4-acetylphenyl triflate (0.825 mmol, 0.221 g) followed by triphenylbismuth (0.25 mmol, 0.11 g), Cs_2CO_3 (1 mmol, 0.326 g), tetrabutylammoniumbromide (0.275 mmol, 0.088 g), triphenylphosphine (0.03 mmol, 0.0078 g), $PdCl_2$ (0.015 mmol, 0.0027 g), and DMA (3 mL) solvent under nitrogen atmosphere. The reaction mixture was stirred at 90 °C for 1 h. The contents of the mixture were cooled to room temperature and quenched with dil HCl (10 mL), extracted with ethyl acetate (3×10 mL). The combined organic extract was washed with water (2×10 mL) and brine (10 mL), dried over anhydrous $MgSO_4$, and was concentrated under vacuo to get crude product. The crude product was further purified on silica gel by column chromatography (2% ethyl acetate in petroleum ether) to afford 4-acetylbiphenyl, **1a** (0.109 g) in 74% yield based on the amount of triphenylbismuth used.

4.2. Spectral data

4.2.1. 4-Acetylbiphenyl[15a] *(**1a**)*

The crude product was purified on SiO_2 by column chromatography (2% ethyl acetate in petroleum ether) to give **1a** as a white solid; Mp 117–118 °C (lit. 115–118 °C); R_f (10% ethyl acetate in petroleum ether) 0.25; δ_H (400 MHz, $CDCl_3$): 8.02 (d, 2H, J=8.3 Hz, CH_{ar}), 7.67 (d, 2H, J=8.1 Hz, CH_{ar}), 7.61 (d, 2H, J=7.3 Hz, CH_{ar}), 7.46 (t, 2H, J=7.6 Hz, CH_{ar}), 7.39 (t, 1H, J=7.3 Hz, CH_{ar}), 2.62 (s, 3H, $COCH_3$); δ_C (100 MHz, $CDCl_3$): 197.7, 145.7, 139.8, 135.8, 128.9, 128.9, 128.2, 127.2, 127.1, 26.6; ν_{max} (KBr): 3075, 2996, 2919, 1678, 1598, 1400, 1360, 1262, 1005, 837, 764, 686, 593 cm^{-1}.

4.2.2. 4-Acetyl-4′-methoxybiphenyl[15b] *(**1b**)*

The crude product was purified on SiO_2 by column chromatography (10% ethyl acetate in petroleum ether) to give **1b** as a pale yellow solid; Mp 145–146 °C (lit. 154–155 °C); R_f (10% ethyl acetate in petroleum ether) 0.15; δ_H (400 MHz, $CDCl_3$): 7.98 (d, 2H, J=7.8 Hz, CH_{ar}), 7.62 (d, 2H, J=8.0 Hz, CH_{ar}), 7.56 (d, 2H, J=8.1 Hz, CH_{ar}), 6.98 (d, 2H, J=8.3 Hz, CH_{ar}), 3.84 (s, 3H, OCH_3), 2.60 (s, 3H, $COCH_3$); δ_C (100 MHz, $CDCl_3$): 197.7, 159.9, 145.3, 135.2, 132.2, 128.9, 128.3, 126.6, 114.4, 55.3, 26.6; ν_{max} (KBr): 2924, 2851, 1675, 1599, 1527, 1494, 1461, 1442, 1398, 1360, 1291, 1265, 1199, 1134, 1031, 1012, 958, 817, 710, 641, 590 cm^{-1}.

4.2.3. 4-Acetyl-4′-methylbiphenyl[15b] *(**1c**)*

The crude product was purified on SiO_2 by column chromatography (2% ethyl acetate in petroleum ether) to give **1c** as a white solid; Mp 117–118 °C (lit. 119–120 °C); R_f (10% ethyl acetate in petroleum ether) 0.25; δ_H (400 MHz, $CDCl_3$): 8.00 (d, 2H, J=8.3 Hz, CH_{ar}), 7.65 (d, 2H, J=8.3 Hz, CH_{ar}), 7.51 (d, 2H, J=8.0 Hz, CH_{ar}), 7.26 (d, 2H, J=8.6 Hz, CH_{ar}), 2.61 (s, 3H, $COCH_3$), 2.39 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$): 197.7, 145.7, 138.2, 136.9, 135.5, 129.6, 128.9, 127.0, 126.9, 26.6, 21.1; ν_{max} (KBr): 2921, 1679, 1599, 1527, 1493, 1422, 1397, 1360, 1325, 1264, 1199, 1134, 1003, 960, 849, 807, 751, 636 cm^{-1}.

4.2.4. 4-Nitrobiphenyl[15b] *(**2a**)*

The crude product was purified on SiO_2 by column chromatography (1% ethyl acetate in petroleum ether) to give **2a** as a pale yellow solid; Mp 107–108 °C(lit. 108 °C); R_f (10% ethyl acetate in petroleum ether) 0.43; δ_H (400 MHz, $CDCl_3$): 8.28 (d, 2H, J=8.8 Hz, CH_{ar}), 7.72 (d, 2H, J=8.8 Hz, CH_{ar}), 7.61 (d, 2H, J=7.1 Hz, CH_{ar}), 7.41–7.50 (m, 3H, CH_{ar}); δ_C (100 MHz, $CDCl_3$): 147.6, 147.0, 138.7, 129.1, 128.8, 127.7, 127.3, 124.1; ν_{max} (KBr): 3074, 2925, 2835, 1685, 1592, 1512, 1344, 1104, 851, 738, 693, 468 cm^{-1}.

4.2.5. 4-Methoxy-4′-nitrobiphenyl[15c] *(**2b**)*

The crude product was purified on SiO_2 by column chromatography (0.5% ethyl acetate in petroleum ether) to give **2b** as a yellow solid; Mp 104–105 °C (lit. 107–108 °C); R_f (10% ethyl acetate in petroleum ether) 0.50; δ_H (400 MHz, $CDCl_3$): 8.24 (d, 2H, J=8.5 Hz, CH_{ar}), 7.66 (d, 2H, J=8.5 Hz, CH_{ar}), 7.55 (d, 2H, J=8.5 Hz, CH_{ar}), 7.00 (d, 2H, J=8.8 Hz, CH_{ar}), 3.85 (s, 3H, OCH_3); δ_C (100 MHz, $CDCl_3$): 160.4, 147.2, 146.5, 131.0, 128.5, 127.0, 124.1, 114.5, 55.4; ν_{max} (KBr): 3058, 2921, 2839, 1598, 1511, 1341, 1246, 1180, 1106, 1023, 836, 755, 719, 694 cm^{-1}.

4.2.6. 4-Methyl-4′-nitrobiphenyl[15d] *(**2c**)*

The crude product was purified on SiO_2 by column chromatography (0.5% ethyl acetate in petroleum ether) to give **2c** as a pale yellow solid; Mp 134–135 °C (lit. 140–141 °C);[15e] R_f (10% ethyl acetate in petroleum ether) 0.55; δ_H (400 MHz, $CDCl_3$): 8.25 (d, 2H, J=8.8 Hz, CH_{ar}), 7.69 (d, 2H, J=8.8 Hz, CH_{ar}), 7.51 (d, 2H, J=8.0 Hz, CH_{ar}), 7.28 (d, 2H, J=8.0 Hz, CH_{ar}), 2.41 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$): 147.5, 146.8, 139.0, 135.8, 129.8, 127.4, 127.2, 124.0, 21.2; ν_{max} (KBr): 3078, 2924, 2852, 1595, 1513,1483, 1397, 1338, 1294, 1189, 1107, 1004, 853, 824, 753, 720, 696 cm^{-1}.

4.2.7. 3-Nitrobiphenyl[16a] *(**3a**)*

The crude product was purified on SiO_2 by column chromatography (1% ethyl acetate in petroleum ether) to give **3a** as a pale yellow solid; Mp 54–56 °C (lit. 58.5–59.5 °C);[16b] R_f (10% ethyl acetate in petroleum ether) 0.43; δ_H (400 MHz, $CDCl_3$): 8.43 (s, 1H, CH_{ar}), 8.18 (d, 1H, J=7.8 Hz, CH_{ar}), 7.91 (d, 1H, J=7.6 Hz, CH_{ar}), 7.57–7.62 (m, 3H, CH_{ar}), 7.40–7.50 (m, 3H, CH_{ar}); δ_C (100 MHz, $CDCl_3$): 148.7, 142.8, 138.6, 133.0, 129.6, 129.1, 128.5, 127.1, 122.0; ν_{max} (KBr): 3081, 2922, 2851, 1577, 1528, 1499, 1472, 1349, 1291, 1043, 993, 897, 873, 812, 767, 731, 695, 675 cm^{-1}.

4.2.8. 4-Methoxy-3′-nitrobiphenyl[16a] *(**3b**)*

The crude product was purified on SiO_2 by column chromatography (1% ethyl acetate in petroleum ether) to give **3b** as a pale yellow solid; Mp 76–77 °C (lit.79–81 °C); R_f (10% ethyl acetate in petroleum ether) 0.35; δ_H (400 MHz, $CDCl_3$): 8.37–8.38 (m, 1H, CH_{ar}), 8.11 (d, 1H, J=8.3 Hz, CH_{ar}), 7.84 (d, 1H, J=7.8 Hz, CH_{ar}), 7.52–7.56 (m, 3H, CH_{ar}), 6.97–7.01 (m, 2H, CH_{ar}), 3.85 (s, 3H, OCH_3); δ_C (100 MHz, $CDCl_3$): 160.0, 148.7, 142.4, 132.4, 131.0, 129.6, 128.2, 121.3, 114.5, 55.4; ν_{max} (KBr): 3082, 3017, 2961, 2929, 2837, 1607, 1511, 1348, 1299, 1246, 1177, 1111, 1021, 876, 831, 804, 740, 719, 679 cm^{-1}.

4.2.9. *4-Methyl-3′-nitrobiphenyl*[16c,d] (**3c**)

The crude product was purified on SiO$_2$ by column chromatography (0.5% ethyl acetate in petroleum ether) to give **3c** as a pale yellow solid; Mp 75–76 °C (lit. 76–77 °C); R_f (10% ethyl acetate in petroleum ether) 0.55; δ_H (400 MHz, CDCl$_3$): 8.41 (s, 1H, CH$_{ar}$), 8.15 (d, 1H, J=8.1 Hz, CH$_{ar}$), 7.88 (d, 1H, J=7.8 Hz, CH$_{ar}$), 7.57 (t, 1H, J=7.8 Hz, CH$_{ar}$), 7.50 (d, 2H, J=8.1 Hz, CH$_{ar}$), 7.28 (d, 2H, J=8.1 Hz, CH$_{ar}$), 2.40 (s, 3H, CH_3); δ_C (100 MHz, CDCl$_3$): 148.7, 142.8, 138.5, 135.8, 132.8, 129.8, 129.6, 126.9, 121.7. 21.1; ν_{max} (KBr): 3087, 3025, 2922, 2854, 1582, 1529, 1380, 1346, 1293, 1260, 1186, 1084, 1037, 967, 899, 874, 804, 739, 681 cm^{-1}.

4.2.10. *2-Nitrobiphenyl*[16c] (**4a**)

The crude product was purified on SiO$_2$ by column chromatography (1% ethyl acetate in petroleum ether) to give **4a** as a yellow liquid; R_f (10% ethyl acetate in petroleum ether) 0.40; δ_H (400 MHz, CDCl$_3$): 7.84 (dd, 1H, J=8.0, 1.2 Hz, CH$_{ar}$), 7.60 (td, 1H, J=7.6, 1.2 Hz, CH$_{ar}$), 7.38–7.48 (m, 5H, CH$_{ar}$), 7.29–7.32 (m, 2H, CH$_{ar}$); δ_C (100 MHz, CDCl$_3$): 149.3, 137.3, 136.3, 132.2, 131.9, 128.6, 128.2, 128.1, 127.8, 124.0; ν_{max} (liquid film): 3062, 3031, 2868, 1605, 1568, 1525, 1472, 1452, 1354, 1306, 1162, 1142, 1093, 1075, 917, 852, 782, 770, 740, 698, 666 cm^{-1}.

4.2.11. *4-Methoxy-2′-nitrobiphenyl*[15c] (**4b**)

The crude product was purified on SiO$_2$ by column chromatography (1% ethyl acetate in petroleum ether) to give **4b** as a yellow liquid; R_f (10% ethyl acetate in petroleum ether) 0.30; δ_H (400 MHz, CDCl$_3$): 7.80 (d, 1H, J=7.8 Hz, CH$_{ar}$), 7.57–7.61 (m, 1H, CH$_{ar}$), 7.42–7.46 (m, 2H, CH$_{ar}$), 7.24–7.27 (m, 2H, CH$_{ar}$), 6.94–6.97 (m, 2H, CH$_{ar}$), 3.85 (s, 3H, OCH_3); δ_C (100 MHz, CDCl$_3$): 159.6, 149.4, 135.8, 132.1, 131.9, 129.4, 129.1, 127.7, 124.0, 114.2, 55.3; ν_{max} (liquid film): 3065, 3034, 2959, 2934, 1612, 1579, 1522, 1476, 1441, 1412, 1356, 1295, 1254, 1091, 1017, 1000, 853, 832, 804, 781, 752, 728 cm^{-1}.

4.2.12. *4-Methyl-2′-nitrobiphenyl*[16c] (**4c**)

The crude product was purified on SiO$_2$ by column chromatography (1% ethyl acetate in petroleum ether) to give **4c** as a yellow liquid; R_f (10% ethyl acetate in petroleum ether) 0.43; δ_H (400 MHz, CDCl$_3$): 7.83 (d, 1H, J=8.1 Hz, CH$_{ar}$), 7.59–7.63 (m, 1H, CH$_{ar}$), 7.43–7.48 (m, 2H, CH$_{ar}$), 7.21–7.26 (m, 4H, CH$_{ar}$), 2.41 (s, 3H, CH_3); δ_C (100 MHz, CDCl$_3$): 149.3, 138.1, 136.2, 134.3, 132.2, 131.9, 129.4, 127.9, 127.7, 124.0, 21.2; ν_{max} (liquid film): 3027, 2921, 2867, 1613, 1566, 1525, 1475, 1355, 1305, 1283, 1041, 853, 819, 781, 749, 721, 704, 656, 639 cm^{-1}.

4.2.13. *4-Cyanobiphenyl*[16e] (**5a**)

The crude product was purified on SiO$_2$ by column chromatography (1% ethyl acetate in petroleum ether) to give **5a** as a white solid; Mp 84–85 °C (lit. 86–87 °C); R_f (10% ethyl acetate in petroleum ether) 0.35; δ_H (400 MHz, CDCl$_3$): 7.65–7.72 (m, 4H, CH$_{ar}$), 7.56–7.58 (m, 2H, CH$_{ar}$), 7.38–7.48 (m, 3H, CH$_{ar}$); δ_C (100 MHz, CDCl$_3$): 145.6, 139.1, 132.5, 129.0, 128.6, 127.6, 127.2, 118.9, 110.8; ν_{max} (KBr): 3064, 2220, 1687, 1598, 1478, 1399, 1176, 1115, 1076, 1005, 843, 768, 696 cm^{-1}.

4.2.14. *4-Cyano-4′-methoxybiphenyl*[15c] (**5b**)

The crude product was purified on SiO$_2$ by column chromatography (2% ethyl acetate in petroleum ether) to give **5b** as a white solid; Mp 97–98 °C (lit. 103–104 °C); R_f (10% ethyl acetate in petroleum ether) 0.20; δ_H (400 MHz, CDCl$_3$): 7.60–7.68 (m, 4H, CH$_{ar}$), 7.51 (d, 2H, J=8.8 Hz, CH$_{ar}$), 6.98 (d, 2H, J=8.8 Hz, CH$_{ar}$), 3.85 (s, 3H, OCH_3); δ_C (100 MHz, CDCl$_3$): 160.2, 145.2, 132.5, 131.4, 128.3, 127.1, 119.1, 114.5, 110.0, 55.4; ν_{max} (KBr): 3039, 2962, 2840, 2219, 1602, 1517, 1490, 1396, 1292, 1239, 1173, 1109, 1035, 855, 824, 737, 629 cm^{-1}.

4.2.15. *4-Cyano-4′-methylbiphenyl*[16f] (**5c**)

The crude product was purified on SiO$_2$ by column chromatography (1% ethyl acetate in petroleum ether) to give **5c** as a white solid; Mp 104–105 °C (lit. 104–106 °C); R_f (10% ethyl acetate in petroleum ether) 0.40; δ_H (400 MHz, CDCl$_3$): 7.63–7.70 (m, 4H, CH$_{ar}$), 7.47 (d, 2H, J=8.3 Hz, CH$_{ar}$), 7.27 (d, 2H, J=7.8 Hz, CH$_{ar}$), 2.40 (s, 3H, CH_3); δ_C (100 MHz, CDCl$_3$): 145.5, 138.7, 136.2, 132.5, 129.8, 127.4, 127.0, 119.0, 110.5, 21.1; ν_{max} (KBr): 3033, 2955, 2919, 2219, 1655, 1600, 1520, 1489, 1447, 1308, 1261, 1178, 1108, 1032, 852, 810, 732, 639 cm^{-1}.

4.2.16. *2-Cyanobiphenyl*[16c] (**6a**)

The crude product was purified on SiO$_2$ by column chromatography (1% ethyl acetate in petroleum ether) to give **6a** as a pale yellow liquid; R_f (10% ethyl acetate in petroleum ether) 0.43; δ_H (400 MHz, CDCl$_3$): 7.74–7.76 (m, 1H, CH$_{ar}$), 7.61–7.64 (m, 1H, CH$_{ar}$), 7.40–7.56 (m, 7H, CH$_{ar}$); δ_C (100 MHz, CDCl$_3$): 145.5, 138.1, 133.7, 132.8, 130.1, 128.7, 127.5, 118.7, 111.3; ν_{max} (liquid film): 3062, 3031, 2925, 2223, 1595, 1562, 1476, 1450, 1433, 1267, 1075, 1048, 1008, 777, 758, 734, 699 cm^{-1}.

4.2.17. *4-Trifluoromethylbiphenyl*[17a,g] (**7a**)

The crude product was purified on SiO$_2$ by column chromatography (petroleum ether) to give **7a** as a white solid; Mp 67–68 °C (lit. 70–70.5 °C); R_f (10% ethyl acetate in petroleum ether) 0.75; δ_H (400 MHz, CDCl$_3$): 7.68 (s, 4H, CH$_{ar}$), 7.57–7.60 (m, 2H, CH$_{ar}$), 7.44–7.48 (m, 2H, CH$_{ar}$), 7.37–7.41 (m, 1H, CH$_{ar}$); δ_C (100 MHz, CDCl$_3$): 144.7, 139.7, 129.0, 128.2, 127.4, 127.2, 125.7, 125.7, 122.9; ν_{max} (KBr): 3081, 2930, 1685, 1612, 1568, 1488, 1453, 1402, 1335, 1279, 1166, 1120, 1076, 1009, 844, 767, 728, 690, 638, 600 cm^{-1}.

4.2.18. *4-Methoxy-4′-trifluoromethylbiphenyl*[17b] (**7b**)

The crude product was purified on SiO$_2$ by column chromatography (0.5% ethyl acetate in petroleum ether) to give **7b** as a white solid; Mp 119–120 °C (lit. 124.1–124.5 °C); R_f (10% ethyl acetate in petroleum ether) 0.50; δ_H (400 MHz, CDCl$_3$): 7.64 (s, 4H, CH$_{ar}$), 7.53 (d, 2H, J=8.8 Hz, CH$_{ar}$), 7.00 (d, 2H, J=8.8 Hz, CH$_{ar}$), 3.85 (s, 3H, OCH_3); δ_C (100 MHz, CDCl$_3$): 159.8, 144.2, 132.1, 128.3, 126.8, 125.7, 125.6, 123.0, 114.4, 55.3; ν_{max} (KBr): 2923, 2845, 1686, 1605, 1530, 1501, 1461, 1401, 1335, 1297, 1277, 1258, 1203, 1169, 1073, 1034, 1010, 829, 815, 702 cm^{-1}.

4.2.19. *4-Methyl-4′-trifluoromethylbiphenyl*[17b,h] (**7c**)

The crude product was purified on SiO$_2$ by column chromatography (petroleum ether) to give **7c** as a white solid; Mp 123–124 °C (lit. 121.2–121.3 °C); R_f (10% ethyl acetate in petroleum ether) 0.73; δ_H (400 MHz, CDCl$_3$): 7.67 (s, 4H, CH$_{ar}$), 7.49 (d, 2H, J=8.3 Hz, CH$_{ar}$), 7.27 (d, 2H, J=7.8 Hz, CH$_{ar}$), 2.40 (s, 3H, CH_3); δ_C (100 MHz, CDCl$_3$): 144.6, 138.1, 136.8, 129.7, 129.7, 127.2, 127.1, 127.0, 125.7, 123.0, 21.1; ν_{max} (KBr): 3033, 2923, 2862, 1656, 1612, 1564, 1538, 1500, 1398, 1328, 1274, 1172, 1130, 1072, 1008, 851, 811, 738, 702 cm^{-1}.

4.2.20. *4-Benzoylbiphenyl*[17c] (**8a**)

The crude product was purified on SiO$_2$ by column chromatography (1% ethyl acetate in petroleum ether) to give **8a** as a white solid; Mp 101–102 °C (lit. 103.2–106.2 °C); R_f (10% ethyl acetate in petroleum ether) 0.37; δ_H (400 MHz, CDCl$_3$): 7.90 (d, 2H, J=8.3 Hz, CH$_{ar}$), 7.83 (d, 2H, J=8.1 Hz, CH$_{ar}$), 7.70 (d, 2H, J=8.3 Hz, CH$_{ar}$), 7.65 (d, 2H, J=7.1 Hz, CH$_{ar}$), 7.57–7.61 (m, 1H, CH$_{ar}$), 7.45–7.51 (m, 4H, CH$_{ar}$), 7.37–7.41 (m, 1H, CH$_{ar}$); δ_C (100 MHz, CDCl$_3$): 196.3, 145.2, 139.9, 137.7, 136.2, 132.3, 130.7, 130.0, 128.9, 128.3, 128.2, 127.3, 126.9; ν_{max} (KBr): 3053, 2923, 2854, 1643, 1599, 1482, 1445, 1400, 1317, 1291, 1151, 1073, 968, 939, 851, 799, 759, 729, 693 cm^{-1}.

4.2.21. 4-Benzoyl-4′-methylbiphenyl[17d] (***8b***)

The crude product was purified on SiO_2 by column chromatography (1% ethyl acetate in petroleum ether) to give **8b** as a white solid; Mp 121–122 °C (lit. 128–129 °C);[17e] R_f (10% ethyl acetate in petroleum ether) 0.45; δ_H (400 MHz, $CDCl_3$): 7.78–7.85 (m, 4H, CH_{ar}), 7.64–7.66 (m, 2H, CH_{ar}), 7.46–7.56 (m, 5H, CH_{ar}), 7.24–7.26 (m, 2H, CH_{ar}), 2.38 (s, 3H, CH_{ar}); δ_C (100 MHz, $CDCl_3$): 196.4, 145.1, 138.1, 137.7, 137.0, 135.9, 132.3, 130.7, 129.9, 129.7, 128.2, 127.1, 126.7, 21.1; ν_{max} (KBr): 3023, 2912, 1644, 1598, 1527, 1489, 1443, 1397, 1289, 1143, 1073, 999, 938, 853, 819, 787, 734, 692 cm^{-1}.

4.2.22. 4-Carboethoxybiphenyl[17a] (***9a***)

The crude product was purified on SiO_2 by column chromatography (0.5% ethyl acetate in petroleum ether) to give **9a** as a pale yellow solid; Mp 48–49 °C (lit. 48–49 °C);[17f] R_f (10% ethyl acetate in petroleum ether) 0.43; δ_H (400 MHz, $CDCl_3$): 8.10 (d, 2H, J=8.3 Hz, CH_{ar}), 7.65 (d, 2H, J=8.5 Hz, CH_{ar}), 7.61 (d, 2H, J=7.1 Hz, CH_{ar}), 7.45 (t, 2H, J=7.4 Hz, CH_{ar}), 7.38 (t, 1H, J=7.3 Hz, CH_{ar}), 4.39 (q, 2H, J=7.2 Hz, OCH_2CH_3), 1.40 (t, 3H, J=7.1 Hz, OCH_2CH_3); δ_C (100 MHz, $CDCl_3$): 166.5, 145.5, 140.0, 130.0, 129.2, 128.9, 128.1, 127.2, 127.0, 60.9, 14.3; ν_{max} (KBr): 3069, 3028, 2986, 2930, 1704, 1604, 1478, 1450, 1401, 1373, 1280, 1192, 1110, 1019, 863, 751, 696 cm^{-1}.

4.2.23. 4-Carboethoxy-4′-methylbiphenyl[17a] (***9b***)

The crude product was purified on SiO_2 by column chromatography (0.5% ethyl acetate in petroleum ether) to give **9b** as a white solid; Mp 75–76 °C (lit. 80–80.5 °C);[18a] R_f (10% ethyl acetate in petroleum ether) 0.44; δ_H (400 MHz, $CDCl_3$): 8.08 (d, 2H, J=8.6 Hz, CH_{ar}), 7.62 (d, 2H, J=8.6 Hz, CH_{ar}), 7.51 (d, 2H, J=8.3 Hz, CH_{ar}), 7.25 (d, 2H, J=8.1 Hz, CH_{ar}), 4.38 (q, 2H, J=7.2 Hz, OCH_2CH_3), 2.40 (s, 3H, CH_3), 1.40 (t, 3H, J=7.2 Hz, OCH_2CH_3); δ_C (100 MHz, $CDCl_3$): 166.5, 145.4, 138.0, 137.1, 130.0, 129.6, 128.9, 127.1, 126.7, 60.9, 21.1, 14.3; ν_{max} (KBr): 2955, 1704, 1605, 1528, 1491, 1446, 1397, 1366, 1272, 1221, 1199, 1175, 1110, 1020, 861, 818, 768, 697 cm^{-1}.

4.2.24. 4-Methoxy-4′-methylbiphenyl[18b] (***10a***)

The crude product was purified on SiO_2 by column chromatography (0.25% ethyl acetate in petroleum ether) to give **10a** as a white solid; Mp 104–106 °C (lit. 105–107 °C);[18c] R_f (10% ethyl acetate in petroleum ether) 0.62; δ_H (400 MHz, $CDCl_3$): 7.51 (d, 2H, J=8.8 Hz, CH_{ar}), 7.45 (d, 2H, J=7.8 Hz, CH_{ar}), 7.23 (d, 2H, J=8.3 Hz, CH_{ar}), 6.96 (d, 2H, J=8.6 Hz, CH_{ar}), 3.84 (s, 3H, OCH_3), 2.38 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$): 158.9, 137.9, 136.3, 133.7, 129.4, 127.9, 126.5, 114.1, 55.3, 21.0; ν_{max} (KBr): 2956, 2918, 2855, 1607, 1531, 1499, 1443, 1400, 1321, 1288, 1251, 1219, 1182, 1136, 1038, 1015, 840, 808 cm^{-1}.

4.2.25. 4-Methoxy-3′-methylbiphenyl[17c,18b] (***11a***)

The crude product was purified on SiO_2 by column chromatography (0.25% ethyl acetate in petroleum ether) to give **11a** as a white solid; Mp 48–49 °C (lit. 48.1–49.5 °C); R_f (10% ethyl acetate in petroleum ether) 0.60; δ_H (400 MHz, $CDCl_3$): 7.53 (d, 2H, J=8.8 Hz, CH_{ar}), 7.30–7.38 (m, 3H, CH_{ar}), 7.13 (d, 1H, J=7.3 Hz, CH_{ar}), 6.97 (d, 2H, J=8.8 Hz, CH_{ar}), 3.85 (s, 3H, OCH_3), 2.42 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$): 159.0, 140.8, 138.2, 133.8, 128.6, 128.1, 127.5, 127.4, 123.8, 114.1, 55.3, 21.5; ν_{max} (KBr): 3029, 2945, 2910, 2846, 1659, 1601, 1514, 1480, 1283, 1253, 1184, 1120, 1026, 896, 835, 784, 690 cm^{-1}.

4.2.26. 4-Methoxy-2′-methylbiphenyl[17b] (***12a***)

The crude product was purified on SiO_2 by column chromatography (0.25% ethyl acetate in petroleum ether) to give **12a** as a colorless liquid; R_f (10% ethyl acetate in petroleum ether) 0.63; δ_H (400 MHz, $CDCl_3$): 7.20–7.26 (m, 6H, CH_{ar}), 6.95 (d, 2H, J=8.8 Hz, CH_{ar}), 3.85 (s, 3H, OCH_3), 2.27 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$): 158.5, 141.5, 135.5, 134.3, 130.2, 129.9, 126.9, 125.7, 113.5, 55.3, 20.5; ν_{max} (liquid film): 3059, 3016, 2952, 2933, 2834, 1612, 1578, 1515, 1483, 1462, 1441, 1409, 1379, 1293, 1267, 1243, 1176, 1119, 1106, 1038, 1017, 834, 786, 761, 731 cm^{-1}.

4.2.27. 4-Chlorobiphenyl[17a] (***13a***)

The crude product was purified on SiO_2 by column chromatography (petroleum ether) to give **13a** as a white solid; Mp 75–76 °C (lit. 77–78.5 °C); R_f (10% ethyl acetate in petroleum ether) 0.75; δ_H (400 MHz, $CDCl_3$): 7.47–7.55 (m, 4H, CH_{ar}), 7.32–7.44 (m, 5H, CH_{ar}); δ_C (100 MHz, $CDCl_3$): 139.9, 139.6, 133.3, 128.9, 128.3, 127.5, 126.9; ν_{max} (KBr): 3065, 2922, 1656, 1586, 1473, 1393, 1095, 1002, 831, 756, 686, 618 cm^{-1}.

4.2.28. 4-Chloro-4′-methoxybiphenyl[17b] (***13b***)

The crude product was purified on SiO_2 by column chromatography (0.5% ethyl acetate in petroleum ether) to give **13b** as a white solid; Mp 112–113 °C (lit. 111.1–111.3 °C); R_f (10% ethyl acetate in petroleum ether) 0.45; δ_H (400 MHz, $CDCl_3$): 7.44–7.50 (m, 4H, CH_{ar}), 7.36 (d, 2H, J=8.6 Hz, CH_{ar}), 6.95 (d, 2H, J=8.8 Hz, CH_{ar}), 3.84 (s, 3H, OCH_3); δ_C (100 MHz, $CDCl_3$): 159.3, 139.2, 132.6, 132.5, 128.8, 128.0, 127.9, 114.3, 55.3; ν_{max} (KBr): 3009, 2962, 2935, 2838, 1654, 1603, 1522, 1483, 1394, 1287, 1257, 1197, 1130, 1097, 1036, 1008, 814, 731 cm^{-1}.

4.2.29. 4-Chloro-4′-methylbiphenyl[18d] (***13c***)

The crude product was purified on SiO_2 by column chromatography (petroleum ether) to give **13c** as a white solid; Mp 116–118 °C; R_f (10% ethyl acetate in petroleum ether) 0.75; δ_H (400 MHz, $CDCl_3$): 7.47 (d, 2H, J=8.8 Hz, CH_{ar}), 7.43 (d, 2H, J=8.1 Hz, CH_{ar}), 7.36 (d, 2H, J=8.6 Hz, CH_{ar}), 7.23 (d, 2H, J=7.8 Hz, CH_{ar}), 2.38 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$): 139.5, 137.4, 137.0, 133.0, 129.6, 128.8, 128.1, 126.8, 21.1; ν_{max} (KBr): 3023, 2917, 2853, 1516, 1478, 1391, 1184, 1089, 1000, 844, 807, 727, 601 cm^{-1}.

4.2.30. 3-Cyanobiphenyl[18e] (***14a***)

The crude product was purified on SiO_2 by column chromatography (1% ethyl acetate in petroleum ether) to give **14a** as a colorless liquid; R_f (10% ethyl acetate in petroleum ether) 0.40; δ_H (400 MHz, $CDCl_3$): 7.79–7.84 (m, 2H, CH_{ar}), 7.38–7.62 (m, 7H, CH_{ar}); δ_C (100 MHz, $CDCl_3$): 142.3, 138.8, 131.4, 130.6, 129.5, 129.1, 128.3, 127.0, 118.8, 112.9; ν_{max} (liquid film): 3063, 3032, 2229, 1597, 1580, 1500, 1476, 1450, 1264, 1173, 1097, 1076, 1048, 1022, 895, 843, 802, 757, 695 cm^{-1}.

4.2.31. 3-Cyano-4′-methoxybiphenyl[16c] (***14b***)

The crude product was purified on SiO_2 by column chromatography (2% ethyl acetate in petroleum ether) to give **14b** as a white solid; Mp 63–65 °C; R_f (10% ethyl acetate in petroleum ether) 0.25; δ_H (400 MHz, $CDCl_3$): 7.74–7.80 (m, 2H, CH_{ar}), 7.47–7.57 (m, 4H, CH_{ar}), 6.97–7.00 (m, 2H, CH_{ar}), 3.84 (s, 3H, OCH_3); δ_C (100 MHz, $CDCl_3$): 159.9, 141.9, 131.2, 130.9, 130.1, 130.0, 129.5, 128.1, 118.9, 114.5, 112.8, 55.3; ν_{max} (KBr): 3055, 2977, 2934, 2840, 2225, 1605, 1576, 1512, 1470, 1398, 1293, 1247, 1177, 1113, 1047, 1021, 836, 803, 690 cm^{-1}.

4.2.32. 3-Cyano-4′-methylbiphenyl[19a] (***14c***)

The crude product was purified on SiO_2 by column chromatography (1% ethyl acetate in petroleum ether) to give **14c** as a white solid; Mp 66–68 °C; R_f (10% ethyl acetate in petroleum ether) 0.43; δ_H (400 MHz, $CDCl_3$): 7.83 (s, 1H, CH_{ar}), 7.77 (d, 1H, J=7.8 Hz, CH_{ar}), 7.58 (d, 1H, J=7.6 Hz, CH_{ar}), 7.44–7.52 (m, 3H, CH_{ar}), 7.27 (d, 2H, J=8.0 Hz, CH_{ar}), 2.39 (s, 3H, CH_3); δ_C ($CDCl_3$, 100 MHz):

142.3, 138.4, 135.9, 131.2, 130.4, 129.8, 129.5, 126.8, 118.9, 112.8, 21.1; ν_{max} (KBr): 3033, 2917, 2860, 2225, 1666, 1603, 1570, 1472, 1388, 1320, 1263, 1170, 1040, 891, 826, 795, 686 cm^{-1}; HRMS(ES^+) for (M+H) $C_{14}H_{12}N$, calcd 194.0970; found 194.0971.

4.2.33. *4-Methoxybiphenyl*[17a] (***15a***)

The crude product was purified on SiO_2 by column chromatography (0.5% ethyl acetate in petroleum ether) to give **15a** as a white solid; Mp 84–86 °C (lit. 86 °C);[18f] R_f (10% ethyl acetate in petroleum ether) 0.45; δ_H (400 MHz, $CDCl_3$): 7.52–7.56 (m, 4H, CH_{ar}), 7.41 (t, 2H, J=7.6 Hz, CH_{ar}), 7.30–7.31 (m, 1H, CH_{ar}), 6.96–6.99 (m, 2H, CH_{ar}), 3.85 (s, 3H, OCH_3); δ_C (100 MHz, $CDCl_3$): 159.1, 140.8, 133.7, 128.7, 128.1, 126.7, 126.6, 114.2, 55.3; ν_{max} (KBr): 3034, 3000, 2960, 2930, 2836, 1604, 1521, 1484, 1280,1248, 1196, 1036, 834, 759, 687 cm^{-1}.

4.2.34. *3-Acetylbiphenyl*[17c,i] (***16a***)

The crude product was purified on SiO_2 by column chromatography (2% ethyl acetate in petroleum ether) to give **16a** as a colorless liquid; R_f (10% ethyl acetate in petroleum ether) 0.37; δ_H (400 MHz, $CDCl_3$): 8.17–8.18 (m, 1H, CH_{ar}), 7.90–7.93 (m, 1H, CH_{ar}), 7.76–7.79 (m, 1H, CH_{ar}), 7.59–7.62 (m, 2H, CH_{ar}), 7.43–7.54 (m, 3H, CH_{ar}), 7.35–7.39 (m, 1H, CH_{ar}), 2.64 (s, 3H, $COCH_3$); δ_C (100 MHz, $CDCl_3$): 198.1, 141.6, 140.1, 137.5, 131.7, 129.0, 128.9, 127.8, 127.1, 126.9, 26.7; ν_{max} (liquid film): 3060, 3032, 2923, 1684, 1595, 1478, 1451, 1419, 1356, 1297, 1235, 1079, 1020, 960, 906, 803, 758, 697 cm^{-1}.

4.2.35. *3-Acetyl-4′-methoxybiphenyl* (***16b***)

The crude product was purified on SiO_2 by column chromatography (3% ethyl acetate in petroleum ether) to give **16b** as a white solid; Mp 54–56 °C; R_f (10% ethyl acetate in petroleum ether) 0.23; δ_H (400 MHz, $CDCl_3$): 8.12 (t, 1H, J=1.7 Hz, CH_{ar}), 7.86 (d, 1H, J=7.8 Hz, CH_{ar}), 7.73 (d, 1H, J=7.6 Hz, CH_{ar}), 7.54 (d, 2H, J=8.8 Hz, CH_{ar}), 7.49 (t, 1H, J=7.8 Hz, CH_{ar}), 6.98 (d, 2H, J=8.8 Hz, CH_{ar}), 3.84 (s, 3H, OCH_3), 2.63 (s, 3H, $COCH_3$); δ_C (100 MHz, $CDCl_3$): 198.2, 159.5, 141.2, 137.5, 132.6, 131.3, 128.9, 128.2, 126.6, 126.4, 114.3, 55.3, 26.8; ν_{max} (KBr): 3001, 2959, 2933, 2837, 1684, 1608, 1516, 1478, 1434, 1356, 1297, 1247, 1180, 1139, 1045, 1025, 960, 909, 835, 796, 692 cm^{-1}; HRMS(ES^+) for (M+H) $C_{15}H_{15}O_2$, calcd 227.1072; found 227.1077.

4.2.36. *3-Acetyl-4′-methylbiphenyl* (***16c***)

The crude product was purified on SiO_2 by column chromatography (2% ethyl acetate in petroleum ether) to give **16c** as a white solid; Mp 41–43 °C; R_f (10% ethyl acetate in petroleum ether) 0.40; δ_H (400 MHz, $CDCl_3$): 8.09–8.10 (m, 1H, CH_{ar}), 7.82–7.85 (m, 1H, CH_{ar}), 7.69–7.71 (m, 1H, CH_{ar}), 7.43–7.47 (m, 3H, CH_{ar}), 7.18–7.25 (m, 2H, CH_{ar}), 2.58 (s, 3H, $COCH_3$), 2.33 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$): 198.2, 141.6, 137.7, 137.5, 137.2, 131.5, 129.6, 129.0, 127.0, 126.9, 126.7, 26.8, 21.1; ν_{max} (KBr): 3025, 2923, 2856, 1694, 1578, 1513, 1480, 1356, 1298, 1234, 1020, 823, 797, 695 cm^{-1}; HRMS(ES^+) for (M+H) $C_{15}H_{15}O$, calcd 211.1123; found 211.1124.

4.2.37. *4-Fluoro-4′-methoxybiphenyl*[17b] (***17a***)

The crude product was purified on SiO_2 by column chromatography (0.5% ethyl acetate in petroleum ether) to give **17a** as a white solid; Mp 82–84 °C (lit. 87.3–87.8 °C); R_f (10% ethyl acetate in petroleum ether) 0.45; δ_H (400 MHz, $CDCl_3$): 7.45–7.50 (m, 4H, CH_{ar}), 7.09 (t, 2H, J=8.8 Hz, CH_{ar}), 6.96 (d, 2H, J=8.8 Hz, CH_{ar}), 3.84 (s, 3H, OCH_3); δ_C (100 MHz, $CDCl_3$): 162.0 (d, J=243.6 Hz), 159.1, 136.9, 132.8, 128.2 (d, J=8.2 Hz), 128.0, 115.5 (d, J=21.4 Hz), 114.2, 55.3; ν_{max} (KBr): 3067, 3014, 2924, 2849, 1601, 1494, 1326, 1289, 1234, 1182, 1157, 1127, 1036, 1013, 826, 789 cm^{-1}.

4.2.38. *2-Phenylnaphthalene*[19b] (***18a***)

The crude product was purified on SiO_2 by column chromatography (petroleum ether) to give **18a** as a white solid; Mp 103–104 °C (lit. 94–97 °C); R_f (10% ethyl acetate in petroleum ether) 0.70; δ_H (400 MHz, $CDCl_3$): 8.05 (s, 1H, CH_{ar}), 7.86–7.93 (m, 3H, CH_{ar}), 7.72–7.77 (m, 3H, CH_{ar}), 7.47–7.53 (m, 4H, CH_{ar}), 7.37–7.40 (m, 1H, CH_{ar}); δ_C (100 MHz, $CDCl_3$): 141.1, 138.5, 133.6, 132.6, 128.8, 128.4, 128.2, 127.6, 127.4, 127.3, 126.3, 125.9, 125.8, 125.6; ν_{max} (KBr): 3053, 1624, 1594, 1491, 1451, 1358, 1272, 1204, 1162, 1127, 1074, 1015, 947, 891, 858, 820, 756, 687 cm^{-1}.

4.2.39. *2-(4-Methoxyphenyl)naphthalene*[19b] (***18b***)

The crude product was purified on SiO_2 by column chromatography (0.5% ethyl acetate in petroleum ether) to give **18b** as a white solid; Mp 130–132 °C (lit. 135–137 °C); R_f (10% ethyl acetate in petroleum ether) 0.50; δ_H (400 MHz, $CDCl_3$): 7.98 (s, 1H, CH_{ar}), 7.83–7.89 (m, 3H, CH_{ar}), 7.71 (dd, 1H, J=8.6, 1.7 Hz, CH_{ar}), 7.66 (d, 2H, J=8.8 Hz, CH_{ar}), 7.43–7.50 (m, 2H, CH_{ar}), 7.02 (d, 2H, J=8.6 Hz, CH_{ar}), 3.86 (s, 3H, OCH_3); δ_C (100 MHz, $CDCl_3$): 159.2, 138.1, 133.7, 133.6, 132.2, 128.4, 128.3, 128.0, 127.6, 126.2, 125.6, 125.4, 125.0, 114.3, 55.3; ν_{max} (KBr): 3050, 2954, 2837, 1606, 1521, 1467, 1439, 1282, 1253, 1201, 1183, 1038, 967, 949, 894, 865, 830,790 cm^{-1}.

4.2.40. *2-(4-Methylphenyl)naphthalene*[19b] (***18c***)

The crude product was purified on SiO_2 by column chromatography (petroleum ether) to give **18c** as a white solid; Mp 85–86 °C (lit. 75–78 °C); R_f (10% ethyl acetate in petroleum ether) 0.70; δ_H (400 MHz, $CDCl_3$): 8.03 (s, 1H, CH_{ar}), 7.85–7.91 (m, 3H, CH_{ar}), 7.73–7.75 (m, 1H, CH_{ar}), 7.63 (d, 2H, J=8.0 Hz, CH_{ar}), 7.45–7.51 (m, 2H, CH_{ar}), 7.30 (d, 2H, J=8.0 Hz, CH_{ar}), 2.43 (s, 3H, CH_3); δ_C (100 MHz, $CDCl_3$): 138.4, 138.2, 137.1, 133.7, 132.4, 129.6, 128.3, 128.1, 127.6, 127.2, 126.2, 125.7, 125.5, 125.4, 21.1; ν_{max} (KBr): 3052, 3020, 2919, 2855, 2371, 2339, 1598, 1497, 1429, 1344, 1269, 1213, 1111, 1016, 947, 893, 857, 811, 746 cm^{-1}.

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