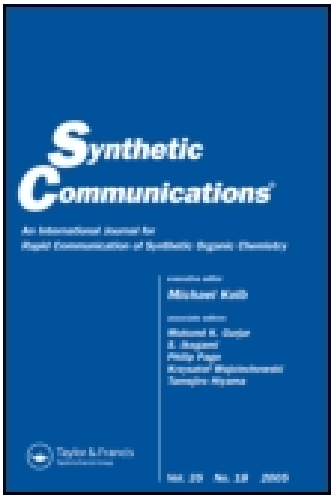

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A Practical Synthesis of Biaryls and Aromatic Acetylenes by Stille Coupling in Room-Temperature Ionic Liquids

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A PRACTICAL SYNTHESIS OF BIARYLS AND AROMATIC ACETYLENES BY STILLE COUPLING IN ROOM-TEMPERATURE IONIC LIQUIDS

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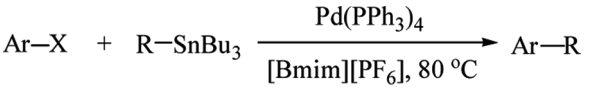
GRAPHICAL ABSTRACT



X = I, Br
R = aryl, alkynyl

Abstract *The Stille cross-coupling reactions of aryl halides with aryl or alkynylstannanes have been achieved under mild conditions in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), affording the corresponding biaryls and aromatic acetylenes in good yields. Use of this solvent allows for facile recycling of the solvent and catalyst system, which can be used at least five times without loss of activity.*

Keywords Alkynylstannane; aromatic acetylene; biaryl; ionic liquid; Stille coupling

INTRODUCTION

The palladium-catalyzed cross-coupling of organostannanes with organic halides and triflates, known as the Stille reaction, is one of the most important, powerful, and versatile tools for the formation of carbon–carbon bonds.[1] This coupling reaction has been widely applied in organic synthesis[2] because a variety of functionality can be tolerated on either partner. The yields of coupled products are often excellent, and the organotin reagents can be readily synthesized, purified, and stored. However, the reaction generally proceeds in the presence of a homogeneous palladium catalyst such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$, and $PdCl_2(MeCN)_2$, which makes the recovery of the expensive metal tedious, if not impossible, and might result in unacceptable palladium contamination of the product. Ideally, one would be able to recover and recycle the entire catalyst system but avoid the challenges presented by either mounting the catalyst on a solid support or by preparing designer ligands for use in aqueous or fluorous biphasic systems.

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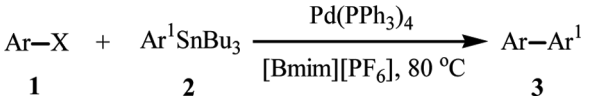
Recently, a new alternative solution for catalyst recycling has been reported. This involves the use of room-temperature ionic liquids (RTILs), in essence salts that are liquid at or below room temperature.[3] RTILs, especially those based upon the 1,3-dialkylimidazolium cation, have attracted growing interest in recent years.[4] They offer an alternative and ecologically sound medium compared to conventional organic solvents, as they are nonvolatile, recyclable, thermally robust, and excellent solvents for a wide range of organic and inorganic materials. Furthermore, their good compatibility with transition-metal catalysts and limited miscibility with common solvents enables easy product and catalyst separation with the retention of the stabilized catalyst in the ionic phase.[5] These and related ionic liquids have been successfully applied to hydrogenations,[6] alkene dimerizations,[7] Friedel–Crafts reactions,[8] Diels–Alder reactions,[9] Heck reactions,[10] Bechmann condensations,[11] Suzuki reactions,[12] Baylis–Hillman reactions,[13] and Sonogashira reactions.[14] Handy and Zhang reported that the Stille coupling reaction of aryl and vinyl iodides with vinyl- or arylstannanes could be performed in 1-butyl-3-methylimi-dazolium tetrafluoroborate ([bmim][BF_4]): however, the use of CuI as cocatalyst and highly toxic Ph_3As was required.[15] Chiappe et al. reported ligandless Stille cross-coupling of aryl iodides with vinyl and alkylstannanes in ionic liquids.[16] However, to the best of our knowledge, there have been no reports on the Stille coupling reaction of aryl halides with alkynylstannanes in ionic liquids to date. In this article, we report a new palladium catalytic system made from 1-butyl-3-methylimidazolium hexafluoro phosphate ([bmim][PF_6]) and $Pd(PPh_3)_4$ for the Stille coupling of aryl halides with aryl or alkynylstannanes to give a variety of biaryls and aromatic acetylenes in good yields without the use of Ph_3As and CuI.

RESULTS AND DISCUSSION

Biaryls are important building blocks of numerous agrochemicals, pharmaceuticals, natural products, conducting materials, and asymmetric catalysts.[17] Because of their widespread applications, the development of straightforward and environmentally friendly methods for the preparation of biaryls has aroused attentions.[18] The Stille cross-coupling of aryl halides with arylstannanes is one of the effective methods. Our choice of solvent was the readily prepared 1-butyl-3-methylimidazolium hexa fluorophosphate ([bmim][PF_6]). The Stille coupling of a variety of aryl halides with arylstannanes in [bmim][PF_6] was investigated (Scheme 1), and the experimental results are summarized in Table 1. As shown in Table 1, the Stille coupling reactions of a variety of aryl iodides with different arylstannanes proceeded smoothly in [bmim][PF_6] at 80 °C, giving a variety of unsymmetrical biaryls in good yields (entries 1–12). The reactions of sterically hindered 2-iodoanisole and bulky 1-iodonaphthalene with phenylstannane also provided good yields of the desired



Scheme 1. Synthesis of unsymmetrical biaryls.

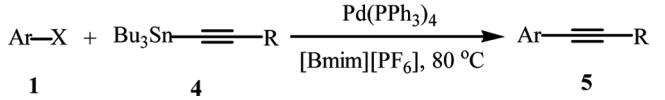
Table 1. Stille cross-coupling reactions of arylstannanes with aryl halides[a]

Entry	Ar	X	Ar′	Time (h)	Product	Yield[b] (%)
1	Ph	I	Ph	18	**3a**	88
2	4-$O_2NC_6H_4$	I	Ph	16	**3b**	91
3	4-$MeOC_6H_4$	I	Ph	21	**3c**	85
4	4-NCC_6H_4	I	Ph	17	**3d**	89
5	2-$MeOC_6H_4$	I	Ph	21	**3e**	82
6	1-Naphthyl	I	Ph	20	**3f**	84
7	2-Thienyl	I	Ph	18	**3g**	86
8	2-Pyridinyl	I	Ph	18	**3h**	85
9	4-$MeCOC_6H_4$	I	4-$MeOC_6H_4$	17	**3i**	90
10	4-$O_2NC_6H_4$	I	4-$MeOC_6H_4$	16	**3j**	88
11	4-$MeOC_6H_4$	I	4-ClC_6H_4	21	**3k**	87
12	4-$MeOCOC_6H_4$	I	4-ClC_6H_4	17	**3l**	89
13	4-$O_2NC_6H_4$	Br	4-$MeOC_6H_4$	20	**3j**	83
14	4-$MeOC_6H_4$	Br	4-ClC_6H_4	24	**3k**	79
15	Ph	Br	4-MeC_6H_4	20	**3m**	84
16	2-Thienyl	Br	4-MeC_6H_4	20	**3n**	81

[a]All reactions were performed using 1.0 mmol of aryl halide, 1.2 mmol of arylstannane, and 0.05 mmol of $Pd(PPh_3)_4$ in [Bmim][PF_6] (1.5 mL) at 80 °C under Ar.
[b]Isolated yield based on aryl halide used.

biaryls **3e** and **3f** under mild reaction conditions, respectively (entries 5 and 6). The Stille coupling reactions of heteroaryl iodides such as 2-iodothiophene and 2-iodopyridine with phenylstannane gave the corresponding coupled products **3g** and **3h** in 86% and 85% yields, respectively (entries 7 and 8). A range of functional groups such as $–CH_3$, $–OCH_3$, –Cl, –CN, $–NO_2$, $–COCH_3$, and $–CO_2CH_3$ on either coupling partner can be tolerated. The Stille coupling reactions of a variety of aryl bromides with arylstannanes also proceeded smoothly in [bmim][PF_6] at 80 °C giving the corresponding unsymmetrical biaryls in good yields within longer reaction times (entries 13–16).

The developed methodology was also applicable for the Stille coupling reactions of alkynylstannanes with aryl halides. The Stille coupling of aryl halides with a variety of alkynylstannanes in [bmim][PF_6] was investigated (Scheme 2), and the experimental results are summarized in Table 2. As shown in Table 2, the Stille cross-coupling reaction of a variety of aryl iodides with different alkynylstannanes proceeded smoothly in [bmim][PF_6] at 80 °C to afford the corresponding coupled products in good yields after 10–13 h of reaction times (entries 1–9). The reactions of sterically hindered 2-iodoanisole with alkynylstannanes also gave the desired coupled products **5b** and **5e** in good yields (entries 2 and 5). The coupling reaction of alkynylstannanes with aryl iodides was faster than that of arylstannanes with aryl



Scheme 2. Synthesis of aromatic acetylenes.

Table 2. Stille cross-coupling reactions of alkynylstannanes with aryl halides[a]

Entry	Ar	X	R	Time (h)	Product	Yield[b] (%)
1	4-$MeOC_6H_4$	I	*n*-C_4H_9	11	**5a**	88
2	2-$MeOC_6H_4$	I	*n*-C_4H_9	13	**5b**	84
3	4-$MeOCOC_6H_4$	I	*n*-C_4H_9	11	**5c**	91
4	4-ClC_6H_4	I	*n*-C_4H_9	10	**5d**	89
5	2-$MeOC_6H_4$	I	Ph	12	**5e**	85
6	4-$MeOC_6H_4$	I	Ph	12	**5f**	87
7	4-$O_2NC_6H_4$	I	Ph	10	**5g**	90
8	3-$O_2NC_6H_4$	I	Ph	11	**5h**	88
9	Ph	I	$MeOCH_2$	12	**5i**	89
10	3-NCC_6H_4	Br	*n*-C_4H_9	11	**5j**	83
11	3-MeC_6H_4	Br	*n*-C_4H_9	12	**5k**	85
12	4-MeC_6H_4	Br	Ph	13	**5l**	82
13	3-MeC_6H_4	Br	Ph	12	**5m**	85
14	2-MeC_6H_4	Br	Ph	15	**3n**	78

[a]All reactions were performed using 1.0 mmol of aryl halide, 1.2 mmol of alkynylstannane, and 0.05 mmol of $Pd(PPh_3)_4$ in [Bmim][PF_6] (1.5 mL) at 80 °C under Ar.
[b]Isolated yield based on aryl halide used.

iodides. Aryl bromides could also couple with alkynylstannanes under the same conditions, giving good yields of the corresponding coupled products (entries 10–14). The catalyst system was quite general and compatible with a wide range of functional groups such as $–NO_2$, –CN, –Cl, $–OCH_3$, and $–CO_2CH_3$ on aryl halides. A favorable effect of electron-withdrawing substituents is normally observed in palladium-catalyzed organic reactions. With our catalyst system, however, electron-withdrawing groups in aryl halides have relatively little effect on the coupling reaction.

Isolation of the coupled products from the [bmim][PF_6] reaction mixtures can be conveniently achieved by extraction with diethyl ether three times. To evaluate the possibility of recycling the ionic liquid and palladium catalyst used in the reaction, 4-nitroiodobenzene and phenylstannane were allowed to react in [bmim][PF_6] at 80 °C for 16 h and then the product was extracted with diethyl ether three times, affording the cleaned, ionic liquid catalytic solution. After the recovered ionic liquid containing palladium catalyst was concentrated in vacuo (5.0 torr/rt for 1 h), a second amount of reactants was added and the process was repeated up to five times. It seems that there is no effect on the rate and yield of the reaction during 1–5 cycles, and 4-nitrodiphenyl was formed in 91, 90, 91, 89, and 89% yields, respectively. Mathews et al. reported that $Pd(PPh_3)_4$ can be reused four times without loss of activity in the Suzuki coupling reaction of 4-bromoanisole with phenylboronic acid in [bmim][BF_4], and no decomposition of the catalyst was observed.[12a] Handy and Zhang reported that $PdCl_2(PhCN)_2$ can be recycled at least five times with essentially no loss in activity in the Stille coupling of 4-methyliodobenzene with phenylstannane in [bmim][BF_4].[15] The good recyclability of the palladium catalysts in these reactions may be due to the retention of the stabilized catalyst in the ionic phase. When 2 mol% of $Pd(PPh_3)_4$ was used, the Stille coupling reaction of 4-nitroiodobenzene with phenylstannane could also proceed smoothly to give the desired coupled

product in 90% yield, but a longer reaction time (36 h) was required. Additionally, this ionic liquid layer could be stored for several weeks with no special precautions to exclude air or moisture and still afford comparable results to the fresh ionic liquid/catalyst system. The result is important from a practical point of view.

EXPERIMENTAL

Infrared (IR) spectra were determined on a Perkin-Elmer 683 instrument. ^{1}H NMR spectra were recorded on a Bruker AC-P400 (400-MHz) spectrometer with tetramethylsilane (TMS) as an internal standard in $CDCl_3$ as solvent. ^{13}C NMR spectra were recorded on a Bruker AC-P400 (100-MHz) spectrometer in $CDCl_3$ as solvent. Microanalyses were measured using a Yanaco MT-3 CHN microelemental analyzer. Melting points are uncorrected.

General Procedure for the Stille Cross-Coupling Reactions of Aryl Halides with Organostannanes in [Bmim][PF_6]

$Pd(PPh_3)_4$(0.05 mmol), aryl halide (1.0 mmol), organostannane (1.2 mmol), and [bmim][PF_6] (1.5 mL) were placed into a two-necked flask equipped with a magnetic stirring bar under an argon atmosphere. The mixture was stirred at 80 °C for 10–24 h, then cooled to 25 °C and extracted with diethyl ether (3 × 10 mL). The recovered ionic liquid containing palladium catalyst was concentrated in vacuo (5.0 torr/rt for 1 h) and reused in the next run. Combined ether solution was treated with 20% aqueous KF (10 mL) for 30 min before being dried and concentrated. The solvent was removed under vacuum, and the residue was purified by flash chromatography on silica gel to give the desired product.

Data

Diphenyl (3a). White solid. Mp 70 °C (lit.[19] mp 70 °C). IR (KBr): ν (cm^{-1}) 3033, 1569, 1478, 730, 690; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, J = 7.6 Hz, 4H), 7.44 (t, J = 7.8 Hz, 4H), 7.35 (t, J = 7.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.25, 128.77, 127.27, 127.19.

4-Nitrodiphenyl (3b). Yellow solid. Mp 113 °C (lit.[19] mp 113 °C). IR (KBr): ν (cm^{-1}) 1596, 1576, 1514, 1346, 853, 739; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.30 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.8 Hz, 2H), 7.64–7.43 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.65, 147.08, 138.78, 129.18, 128.94, 127.82, 127.41, 124.14.

4-Methoxydiphenyl (3c). White solid. Mp 88–90 °C (lit.[19] mp 90–91 °C). IR (KBr): ν (cm^{-1}) 1606, 1486, 1253, 1038, 759, 689; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56–7.51 (m, 4H), 7.42 (t, J = 7.6 Hz, 2H), 7.32–7.28 (m, 1H), 6.98 (d, J = 8.4 Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.14, 140.81, 133.78, 128.74, 128.17, 126.76, 126.67, 114.20, 55.36.

4-Cyanodiphenyl (3d). White solid. Mp 85–87 °C (lit.[19] mp 86–87 °C). IR (KBr): ν (cm^{-1}) 2226, 1605, 1483, 848, 770, 697; ^{1}H NMR (400 MHz, $CDCl_3$): δ

7.73–7.66 (m, 4H), 7.60–7.57 (m, 2H), 7.50–7.40 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.68, 139.18, 132.62, 129.14, 128.68, 127.75, 127.25, 118.98, 110.92.

2-Methoxydiphenyl (3e). Oil. IR (neat): ν (cm^{-1}) 1597, 1501, 1489, 1251, 1032, 743, 688; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.51 (m, 2H), 7.39 (t, $J = 7.8$ Hz, Hz, 2H), 7.33–7.28 (m, 3H), 7.03–6.96 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.45, 138.53, 130.90, 130.71, 129.55, 128.61, 127.98, 126.92, 120.82, 111.21, 55.56. Anal. calcd. for $C_{13}H_{12}O$: C, 84.78; H, 6.52. Found: C, 84.51; H, 6.33.

1-Phenylnaphthalene (3f). Oil.[20] IR (neat): ν (cm^{-1}) 3057, 1591, 1507, 1493, 1395, 761, 703; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89–7.82 (m, 3H), 7.53–7.40 (m, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.81, 140.31, 133.84, 131.67, 130.12, 128.29, 127.67, 127.27, 127.21, 126.96, 126.07, 126.05, 125.80, 125.41.

2-Phenylthiophene (3g). White solid. Mp 36–37 °C (lit.[21] mp 37–38 °C). IR (KBr): ν (cm^{-1}) 3073, 1600, 1531, 1488, 1446, 1256, 850, 755; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.59–7.57 (m, 2H), 7.34–7.18 (m, 5H), 7.03–7.01 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.56, 134.54, 129.04, 128.16, 127.60, 126.09, 124.94, 123.23.

2-Phenylpyridine (3h). Oil.[21] IR (neat): ν (cm^{-1}) 3062, 1586, 1564, 1468, 1449, 746, 693; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, $J = 4.8$ Hz, 1H), 7.99–7.97 (m, 2H), 7.68–7.66 (m, 2H), 7.47–7.37 (m, 3H), 7.18–7.14 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.45, 149.51, 139.40, 136.80, 129.00, 128.79, 126.95, 122.14, 120.60.

4-Acetyl-4′-methoxydiphenyl (3i). White solid. Mp 152 °C (lit.[22] mp 151–152 °C). IR (KBr): ν (cm^{-1}) 2957, 1675, 1601, 1581, 1497, 1033, 818; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.01 (d, $J = 8.4$ Hz, 2H), 7.65 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 8.8$ Hz, 2H), 7.01 (d, $J = 8.8$ Hz, 2H), 3.87 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.81, 159.93, 145.44, 135.31, 132.34, 129.04, 128.42, 126.61, 114.42, 55.43, 26.72.

4-Methoxy-4′-nitrodiphenyl (3j). Yellow solid. Mp 99–100 °C (lit.[22] mp 100–102 °C). IR (KBr): ν (cm^{-1}) 2956, 1601, 1594, 1510, 1344, 1187, 1108; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.27 (d, $J = 8.8$ Hz, 2H), 7.70 (d, $J = 8.8$ Hz, 2H), 7.58 (d, $J = 8.8$ Hz, 2H), 7.02 (d, $J = 8.8$ Hz, 2H), 3.88 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.51, 147.23, 146.62, 131.14, 128.63, 127.11, 124.24, 114.61, 55.43.

4-Chloro-4′-methoxydiphenyl (3k). White solid. Mp 122–123 °C (lit.[22] mp 122–124 °C). IR (KBr): ν (cm^{-1}) 2963, 1606, 1484, 1290, 1263, 1199, 822, 812; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.46 (m, 4H), 7.37 (d, $J = 8.4$ Hz, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.33, 139.26, 132.67, 132.48, 128.86, 128.05, 127.96, 114.30, 55.39.

4-Chloro-4′-methoxycarbonyldiphenyl (3l). White solid. Mp 94–95 °C (lit.[22] Mp 95-96 °C). IR (KBr): ν (cm^{-1}) 2959, 1725, 1435, 1292, 1105, 828, 770; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.11 (d, $J = 8.4$ Hz, 2H), 7.63 (d, $J = 8.4$ Hz, 2H), 7.56 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.87, 144.32, 138.40, 134.32, 130.94, 130.19, 129.14, 128.52, 126.89, 52.23.

4-Methyldiphenyl (3m). White solid. Mp 47 °C (lit.[19] mp 47.5 °C). IR (KBr): ν (cm^{-1}) 3030, 2916, 1599, 1487, 823, 757, 689; ^1H NMR (400 MHz, $CDCl_3$): δ 7.58–7.56 (m, 2H), 7.49 (d, $J = 8.0$ Hz, 2H), 7.43–7.39 (m, 2H), 7.33–7.29 (m, 1H), 7.24 (d, $J = 8.0$ Hz, 2H), 2.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.20, 138.40, 137.06, 129.53, 128.76, 127.04, 127.02, 126.86, 21.15.

2-(4-Methylphenyl)thiophene (3n). White solid. Mp 63–64 °C (lit.[21] Mp.60–62 °C). IR (KBr): ν (cm^{-1}) 3075, 2912, 1533, 1501, 1431, 1124, 851, 809, 686; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, $J = 8.0$ Hz, 2H), 7.25–7.19 (m, 2H), 7.16 (d, $J = 7.6$ Hz, 2H), 7.05–7.03 (m, 1H), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.61, 137.35, 131.66, 129.58, 127.96, 125.92, 124.30, 122.63, 21.21.

1-(4-Methoxyphenyl)-1-hexyne (5a). Oil.[23] IR (neat): ν (cm^{-1}) 1607, 1510, 1246, 1173, 831; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.31 (m, 2H), 6.81–6.78 (m, 2H), 3.79 (s, 3H), 2.39 (t, $J = 7.0$ Hz, 2H), 1.60–1.54 (m, 2H), 1.50–1.44 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.97, 132.85, 116.28, 113.84, 88.75, 80.22, 55.24, 30.98, 22.04, 19.11, 13.67.

1-(2-Methoxyphenyl)-1-hexyne (5b). Oil.[23] IR (neat): ν (cm^{-1}) 1603, 1514, 1247, 1175; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39–7.36 (m, 1H), 7.26–7.21 (m, 1H), 6.89–6.84 (m, 2H), 3.87 (s, 3H), 2.47 (t, $J = 7.2$ Hz, 2H), 1.64–1.56 (m, 2H), 1.52–1.47 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.80, 133.66, 128.84, 120.38, 113.17, 110.53, 94.68, 76.59, 55.79, 30.95, 22.05, 19.49, 13.68.

1-(4-Methoxycarbonylphenyl)-1-hexyne (5c). Oil.[23] IR (neat): ν (cm^{-1}) 2230, 1725, 1606, 1274, 1175, 1107, 857; ^1H NMR (400 MHz, $CDCl_3$): δ 7.95 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 3.90 (s, 3H), 2.43 (t, $J = 7.2$ Hz, 2H), 1.60–1.55 (m, 2H), 1.49–1.43 (m, 2H), 0.93 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.66, 131.45, 129.38, 128.96, 128.78, 93.95, 80.09, 52.13, 30.65, 22.02, 19.19, 13.62.

1-(4-Chlorophenyl)-1-hexyne (5d). Oil.[23] IR (neat): ν (cm^{-1}) 2932, 2232, 1489, 1466, 827, 753; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (d, $J = 8.4$ Hz, 2H), 7.24 (d, $J = 8.4$ Hz, 2H), 2.40 (t, $J = 7.2$ Hz, 2H), 1.60-1.55 (m, 2H), 1.50–1.44 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 133.4, 132.8, 128.5, 122.6, 91.5, 79.5, 30.7, 22.0, 19.1, 13.7.

1-(2-Methoxyphenyl)-2-phenylethyne (5e). Oil. IR (neat): ν (cm^{-1}) 2217, 1593, 1276, 1246, 753; ^1H NMR (400 MHz, $CDCl_3$): δ 7.57–7.47 (m, 3H), 7.36–7.24 (m, 4H), 6.95–6.89 (m, 2H), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.95, 133.60, 131.69, 129.78, 128.25, 128.12, 123.59, 120.51, 112.48, 110.73, 93.45, 85.74, 55.86. Anal. calcd. for $C_{15}H_{12}O$: C, 86.54; H, 5.77. Found: C, 85.25; H, 5.49.

1-(4-Methoxyphenyl)-2-phenylethyne (5f). White solid. Mp 58–59 °C (lit.[23] mp 57–58 °C). IR (KBr): ν (cm^{-1}) 3024, 2212, 1602, 1498, 1185, 835, 750, 690; ^1H NMR (400 MHz, $CDCl_3$): δ 7.52–7.43 (m, 4H), 7.32–7.29 (m, 3H), 6.86–6.83 (m, 2H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.54, 133.03, 131.41, 128.32, 127.93, 123.41, 115.52, 113.90, 89.40, 88.13, 55.24.

1-(4-Nitrophenyl)-2-phenylethyne (5g). Yellow solid. Mp 120–121 °C (lit.[23] mp 118–119 °C). IR (KBr): ν (cm^{-1}) 2217, 1592, 1511, 1495, 858, 765, 690; ^1H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, $J = 8.8$ Hz, 2H), 7.67 (d, $J = 8.8$ Hz, 2H), 7.58–7.55 (m, 2H), 7.41–7.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.93, 132.32, 131.84, 130.34, 129.31, 128.53, 123.71, 122.12, 94.71, 87.50.

1-(3-Nitrophenyl)-2-phenylethyne (5h). Yellow solid. Mp 69–70 °C (lit.[23] mp 71–72 °C). IR (KBr): ν (cm^{-1}) 2210, 1597, 1517, 1347, 810, 759, 692; ^1H NMR (400 MHz, $CDCl_3$): δ 8.38 (s, 1H), 8.19–8.16 (m, 1H), 7.82 (d, $J = 7.6$ Hz, 1H), 7.57–7.51 (m, 3H), 7.40–7.37 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 148.24, 137.20, 131.81, 129.44, 129.13, 128.50, 126.41, 125.24, 122.90, 122.21, 92.03, 86.92.

3-Methoxy-1-phenylpropyne (5i). Oil.[22] IR (neat): ν (cm^{-1}) 2930, 2237, 1599, 1490, 1099, 757, 691; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46–7.44 (m, 2H), 7.32–7.30 (m, 3H), 4.32 (s, 2H), 3.46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.82, 128.44, 128.31, 122.73, 86.40, 84.91, 60.42, 57.73.

1-(3-Cyanophenyl)-1-hexyne (5j). Oil.[23] IR (neat): ν (cm^{-1}) 2232, 2227, 1597, 1478, 896, 798, 683; ^1H NMR (400 MHz, $CDCl_3$): δ 7.66 (s, 1H), 7.60–7.53 (m, 2H), 7.39 (t, $J = 7.6$ Hz, 1H), 2.42 (t, $J = 7.2$ Hz, 2H), 1.61–1.56 (m, 2H), 1.50–1.45 (m, 2H), 0.96 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 135.71, 135.03, 130.73, 129.11, 125.73, 118.34, 112.61, 93.42, 78.53, 30.50, 22.04, 19.12, 13.71.

1-(3-Methylphenyl)-1-hexyne (5k). Oil.[23] IR (neat): ν (cm^{-1}) 2228, 1603, 1580, 783; ^1H NMR (400 MHz, $CDCl_3$): δ 7.22–7.13 (m, 3H), 7.06 (d, $J = 7.2$ Hz, 1H), 2.40 (t, $J = 7.2$ Hz, 2H), 2.30 (s, 3H), 1.60–1.54 (m, 2H), 1.51–1.39 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.83, 132.21, 128.61, 128.43, 128.12, 123.90, 90.04, 80.72, 30.91, 22.13, 21.24, 19.13, 13.71.

1-(4-Methylphenyl)-2-phenylethyne (5l). White solid. Mp 73–74 °C (lit.[23] mp 75–76 °C). IR (KBr): ν (cm^{-1}) 3029, 2968, 2859, 2215, 1594, 1509, 818, 690; ^1H NMR (400 MHz, $CDCl_3$): δ 7.53–7.51 (m, 2H), 7.42 (d, $J = 8.0$ Hz, 2H), 7.36–7.27 (m, 3H), 7.14 (d, $J = 8.0$ Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.42, 131.61, 131.53, 129.14, 128.31, 128.10, 123.52, 120.21, 89.60, 88.71, 21.53.

1-(3-Methylphenyl)-2-phenylethyne (5m). Oil.[23] IR (neat): ν (cm^{-1}) 2207, 1602, 1580, 1494, 783, 755, 689; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54–7.51 (m, 2H), 7.37–7.32 (m, 5H), 7.26–7.21 (m, 1H), 7.16–7.13 (m, 1H), 2.35 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.04, 132.21, 131.63, 129.21, 128.70, 128.44, 128.32, 128.21, 123.43, 123.14, 89.61, 89.03, 21.33.

1-(2-Methylphenyl)-2-phenylethyne (5n). Oil. IR (neat): ν (cm^{-1}) 2214, 1601, 1494, 755, 690; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55–7.49 (m, 3H), 7.35–7.32 (m, 3H), 7.25–7.15 (m, 3H), 2.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.20, 131.84, 131.52, 129.47, 128.36, 128.31, 128.17, 125.58, 123.57, 123.04, 93.34, 88.34, 20.75. Anal. calcd. for $C_{15}H_{12}$: C, 93.75; H, 6.25. Found: C, 93.44; H, 6.31.

CONCLUSION

In summary, we have demonstrated that Stille cross-coupling reactions of aryl halides with aryl or alkynylstannanes can be successfully conducted in 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), affording the corresponding biaryls and aromatic acetylenes in good yields. Easy product isolation and recycling of the ionic liquid and catalyst are important advantages of our methodology.

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