

Feature Article

Piperidine-appended imidazolium ionic liquid as task-specific basic-IL for Suzuki and Heck reactions and for tandem Wittig-Suzuki, Wittig-Heck, Horner-Emmons-Suzuki, and Horner-Emmons-Heck protocols

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ABSTRACT

Facile, high yielding, one-pot methods for the synthesis of a library of diversely substituted bi-aryls, diarylethenes, and aryl-enoates, via Suzuki and Heck reactions, and by sequential Wittig-Suzuki, Wittig-Heck, Horner-Emmons-Suzuki, and Horner-Emmons-Heck reactions are reported. The reactions employ piperidine-appended imidazolium ionic liquid [PAIM][NTf₂] as a task-specific basic-IL, butyl-methyl-imidazolium ionic liquid [BMIM][X] (X = PF₆, BF₄) as solvent, and catalytic amounts of Pd(OAc)₂, with no other additives. Wittig and Horner-Emmons reactions are effected by reacting substituted benzaldehydes with 4-bromobenzyl-PPh₃ (or bromomethyl-PPh₃) phosphonium salts, or diethylphosphonate with bromobenzaldehydes respectively, to form the corresponding ethenes. Subsequent cross-coupling reactions are accomplished by addition of aryl-boronic acid or phenyl-ethenes along with Pd(OAc)₂ to bring about the aforementioned hyphenated transformations. The feasibility to perform double-olefination via Wittig and Horner-Emmons reactions with dialdehydes to form highly conjugated bis-styryl and bis-enoate compounds is also shown. The [BMIM][X] solvent is recycled and reused.

1. Introduction

The Suzuki-Miyaura and Mizoroki-Heck reactions are two of the most important C–C bond forming protocols that have had a tremendous impact on the practice of synthetic/preparative chemistry, not only in academia but also in industry [1–4]. Their wide application stems from broad scope, flexibility and tolerance toward functional groups, and availability of the coupling components.

The essential ingredients of the Suzuki coupling reaction are Pd (or Ni) catalyst, along with a base, and ligand (depending on the substrates), and solvents such as THF, DMF and dioxane. The Heck reaction uses a Pd catalyst, with or without phosphine ligand, along with a base, and requires high temperature. In some cases, bases such as Et₃N also serve as solvent, but otherwise high boiling solvents such as DMF and THF are employed [3,4].

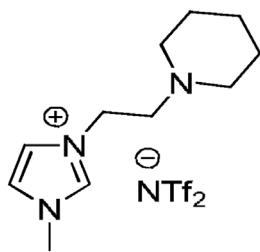
Ionic liquids (ILs) offer numerous advantages in Pd-catalyzed cross-coupling reactions, namely by lowering the energy of the polar transition state or intermediates in the catalytic cycle, by increasing the reactivity of the reactants, and by virtue of their ability to solubilize the Pd catalyst. They replace hazardous organic solvents and also offer good prospects for recycling and reuse. Various classes of ILs and Pd

catalysts have been employed in the Suzuki and Heck reactions. Task-specific ILs (TSILs) that are base-appended, and/or ligand tethered, and supported-ILs with immobilized-Pd catalysts, have opened up new vistas in cross-coupling reactions. Progress in the Pd-catalyzed cross-coupling reactions in ILs is summarized in a comprehensive recent survey [5].

In continuation of our previous studies on the utility of ILs and TSILs as solvent and catalyst in metal-mediated transformations [6–8], and their utility in the Sonogashira coupling [9], we report here on high yielding one-pot methods for the synthesis of a library of diversely substituted biaryls, diarylethenes, and aryl-enoates via Suzuki and Heck reactions, and by sequential Wittig-Suzuki, Wittig-Heck, Horner-Emmons-Suzuki, and Horner-Emmons-Heck transformations, employing the piperidine-appended imidazolium-IL [PAIM][NTf₂] (Fig. 1) as a task-specific basic-IL, [BMIM][X] (X = PF₆, BF₄) as solvent and catalytic amounts of Pd(OAc)₂, with no other additives. Wittig and Horner-Emmons reactions were effected in [PAIM][NTf₂]/[BMIM][X] by using phosphonium salts or phosphonates respectively. Subsequent addition of the Pd-catalyst along with boronic acids or styrenes brings about the indicated hyphenated transformations, leading to a host of high value small molecules. The [BMIM][X] is used as solvent and is recycled and reused.

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Fig. 1. [PAIM][NTf₂].

2. Experimental

2.1. General

The reagents employed were of high purity commercial samples which were used as received (Fischer, Merck and Sigma-Aldrich). Butyl methyl imidazolium ILs [BMIM][X] were synthesized by using established literature procedures [10], similarly the basic IL [PAIM][NTf₂] was synthesized in two steps by using previously reported procedures [9,11]. Column chromatography was performed on silica gel (200–400 mesh) and TLC was performed on silica gel 60F₂₅₄ (Fischer) TLC plates visualized under UV light (254 nm) or by iodine vapors. Melting points were determined in open capillaries on a Buchi apparatus and are uncorrected. ¹H NMR and ¹³C NMR spectra were recorded using Bruker AC-300F (300 MHz) and AC-400F (400 MHz) instruments, using CDCl₃ or DMSO-*d*₆ as solvent, with TMS as internal standard. GC analyses were performed on Nucon 5700 series gas chromatograph. GC–MS analyses were performed on a Shimadzu 2010 series mass selective detector instrument. Elemental analysis was carried out by using Heraeus CHN rapid analyzer. Boiling points were determined by Thiele tube apparatus and are uncorrected. All compounds gave C, H and N analysis within ± 0.4% of the theoretical values.

2.2. General procedure for the Suzuki and Heck coupling reactions (Tables 1 and 2)

An oven-dried reaction tube equipped with a magnetic stirrer bar was charged with the aryl-boronic acid (Table 1) or the substituted alkene (Table 2) (1.3 mmol), aryl (or benzyl) bromide (1.1 mmol), Pd (OAc)₂ (5–6 mol%), [PAIM][NTf₂] (4 mmol), and [BMIM][PF₆] (7 mL). The reaction mixture was stirred under a nitrogen atmosphere at 60–70 °C, and the progress of the reaction was monitored by TLC. After completion (2–3 h in the Suzuki reaction and 4–7 h for the Heck reaction) the reaction mixture was extracted 3 times with hexane/ethyl acetate (80:20) and the products were purified by flash column chromatography using hexane/ethyl acetate (80:20) or DCM/MeOH (95:5).

2-Phenylfuran (1.1): [12,13] White solid. mp 160–162 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.21–6.33 (m, 2H, ArH), 7.15–7.28 (m, 6H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 118.9, 120.6, 125.30, 126.8, 129.1, 130.3, 134.2 and 145.6. GC–MS: *m/z* 144 M⁺; Anal. Calc. For C₁₀H₈O: C, 83.31; H, 5.59%. Found: C, 83.30; H, 5.60%.

2-(Naphthalen-2-yl)furan (1.2): [14] White solid. mp 77–79 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.39–6.40 (m, 2H, ArH), 7.35–7.44 (m, 3H, ArH), 7.54–7.68 (m, 4H, ArH), 7.83 (s, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 103.7, 108.5, 122.6, 123.8, 124.8, 125.7, 126.1, 126.9, 128.0, 128.7, 134.2, 135.3, 153.1 and 155.2. GC–MS: *m/z* 194 M⁺. Anal. Calc. For C₁₄H₁₀O: C, 86.57; H, 5.19%. Found: C, 86.58; H, 5.20%.

2-(Furan-2-yl)pyridine (1.3): Colorless liquid bp 228–230 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.49–6.61 (m, 2H, ArH), 6.95–7.06 (m, 4H, ArH), 8.16 (d, *J* = 7.2 Hz, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 107.8, 107.9, 121.2, 122.2, 132.5, 140.9, 146.8, 149.9 and 153.3. GC–MS: *m/z* 145 M⁺. Anal. Calc. For C₉H₇NO: C, 74.47; H, 4.86; N, 9.65%. Found: C, 74.46; H, 4.85; N, 9.64%.

Diphenylmethane (1.4): [15] Colorless liquid. bp 260–262 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.92 (s, 2H, CH₂), 7.31 (m, 4H, ArH), 7.40–7.58 (m, 6H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 40.8, 120.5, 121.3, 122.3, 125.0, 123.6 and 142.0. GC–MS: *m/z* 168 M⁺. Anal. Calc. For C₁₃H₁₂: C, 92.81; H, 7.19%. Found: C, 92.82; H, 7.20%.

2-Phenylnaphthalene (1.5): [16] White solid. mp 104–106 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.28 (t, *J* = 7.8, 6.8 Hz, 1H, ArH), 7.32–7.41 (m, 4H, ArH), 7.42–7.57 (m, 4H, ArH), 7.61 (d, *J* = 8 Hz, 1H, ArH), 7.70 (d, *J* = 7.6 Hz, 1H, ArH), 7.89 (s, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 120.9, 121.5, 122.2, 123.0, 124.1, 124.3, 125.2, 126.3, 127.1, 128.4, 128.6, 129.5, 133.5, 137.0, 137.9 and 139.4. GC–MS: *m/z* 204 M⁺. Anal. Calc. For C₁₆H₁₂: C, 94.08; H, 5.92%. Found: C, 94.09; H, 5.92%.

2-Phenylpyridine (1.6): [16] Colorless liquid. bp 265–267 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.04–7.13 (m, 2H, ArH), 7.15–7.30 (m, 5H, ArH), 7.33 (d, 1H, *J* = 7.2 Hz, ArH), 8.05 (d, 1H, *J* = 7.6 Hz, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 122.2, 124.0, 125.0, 126.3, 127.1, 127.9, 129.1, 134.0, 138.1, 150.9 and 154.7. GC–MS: *m/z* 155 M⁺. Anal. Calc. For C₁₁H₉N: C, 85.13; H, 5.85; N, 9.03%. Found: C, 85.14; H, 5.86; N, 9.05%.

2-Benzylfuran (1.7): Colorless liquid. bp 220–222 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.90 (s, 2H, CH₂), 6.36–6.94 (m, 2H, ArH), 7.0–7.13 (m, 5H, ArH), 7.63 (d, 1H, *J* = 7.2 Hz, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 40.8, 119.4, 123.4, 126.5, 129.5, 130.0, 132.1, 137.4 and 143.5. GC–MS: *m/z* 159 M⁺. Anal. Calc. For C₁₁H₁₀O: C, 83.51; H, 6.37%. Found: C, 83.52; H, 6.36%.

2-(6-Methoxynaphthalen-2-yl)furan (1.8): Colorless liquid. bp 360–362 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.83 (s, 3H, OCH₃), 6.41 (d, *J* = 7.6 Hz, 1H, ArH), 6.52 (t, *J* = 7.2, 6.8 Hz, 1H, ArH), 7.22 (s, 1H, ArH), 7.25–7.36 (m, 5H, ArH), 7.44 (s, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 57.1, 112.8, 118.0, 118.3, 120.0, 125.7, 128.5, 128.9, 129.2, 129.8, 132.8, 138.9, 147.2, 152.9, and 154.7. GC–MS: *m/z* 224 M⁺. Anal. Calc. For C₁₅H₁₂O₂: C, 80.34; H, 5.39%. Found: C, 80.35; H, 5.40%.

2-Methoxy-6-phenylnaphthalene (1.9): [15] Yellow solid. mp 158–160 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.92 (s, 3H, OCH₃), 6.30 (s, 1H, ArH), 7.06 (d, *J* = 8 Hz, 1H, ArH), 7.41–7.55 (m, 5H, ArH), 7.59–7.69 (m, 3H, ArH), 7.81 (s, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 55.2, 102.4, 116.1, 121.2, 121.4, 123.9, 124.1, 125.8, 127.0, 128.5, 130.0, 131.1, 132.5, 133.0, 136.5, 138.1 and 155.9. GC–MS: *m/z* 236 M⁺. Anal. Calc. For C₁₇H₁₄O: C, 87.15; H, 6.02%. Found: C, 87.16; H, 6.04%.

Biphenyl (1.10): [15–17] White solid. mp 64–66 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.33 (t, 2H, *J* = 7.6 Hz, ArH), 7.40 (t, *J* = 7.6 Hz, 4H, ArH), 7.61 (d, 4H, *J* = 7.8 Hz, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 123.9, 124.8, 127.1, 128.4, 129.0, and 134.8. GC–MS: *m/z* 154 M⁺. Anal. Calc. For C₁₂H₁₀: C, 93.46; H, 6.54%. Found: C, 93.47; H, 6.55%.

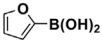
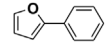
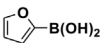
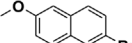
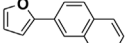
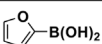
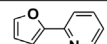
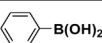
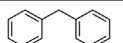
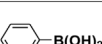
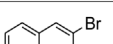
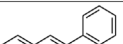
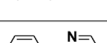
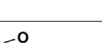
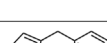
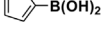
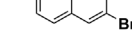
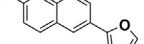
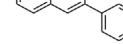
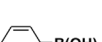
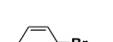
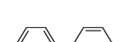
4-Methylbiphenyl (1.11): [17,18] White solid. mp 48–50 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.07 (s, 3H, CH₃), 7.22 (d, *J* = 7.6 Hz, 2H, ArH), 7.31 (d, *J* = 7.8 Hz, 2H, ArH), 7.25 (d, *J* = 7.6 Hz, 2H, ArH), 7.70–7.77 (m, 3H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 22.9, 121.3, 122.5, 123.2, 124.2, 124.9, 126.3, 127.0, 128.2, 129.9 and 133.1. GC–MS: *m/z* 168 M⁺. Anal. Calc. For C₁₃H₁₂: C, 92.81; H, 7.19%. Found: C, 92.82; H, 7.20%.

4-Methoxybiphenyl (1.12): [15,17] White solid. mp 90–92 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.91 (s, 3H, OCH₃), 7.12 (d, *J* = 7.6 Hz, 2H, ArH), 7.42 (d, *J* = 7.8 Hz, 2H, ArH), 7.45–7.52 (m, 5H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 59.8, 119.5, 122.4, 124.0, 126.4, 127.0, 129.5, 130.5, 134.5 and 156.1. GC–MS: *m/z* 184 M⁺. Anal. Calc. For C₁₃H₁₂O: C, 84.75; H, 6.57%. Found: C, 84.76; H, 6.58%.

2-(4-Methoxyphenyl)furan (1.13): [19] White solid. mp 49–52 °C. ¹H NMR (400 MHz, CDCl₃-*d*₆): δ 3.85 (s, 3H, OCH₃), 6.36–6.43 (m, 2H, ArH), 6.93 (d, *J* = 7.6, 2H, ArH), 7.29–7.40 (m, 3H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 57.9, 104.2, 107.2, 115.9, 125.7, 130.2, 140.1, 152.2 and 163.3. GC–MS: *m/z* 174 M⁺. Anal. Calc. For C₁₁H₁₀O₂: C, 75.84; H, 5.79%. Found: C, 75.85; H, 5.80%.

Table 1

Suzuki coupling reaction with [PAIM][NTf₂]/[BMIM][X].

Entry No.	ArB(OH) ₂	Ar-Br	Product ^a	IL	Time [h] ^b	Yield [%]
1				[BMIM][PF ₆]	3	84 ^c
2				[BMIM][PF ₆]	3	82 ^c
3				[BMIM][PF ₆]	3	80 ^d
4				[BMIM][BF ₄]	2	82 ^d
5				[BMIM][BF ₄]	3	80 ^d
6				[BMIM][BF ₄]	2	87 ^c
7				[BMIM][BF ₄]	2	86 ^c
8				[BMIM][BF ₄]	3	78 ^c
9				[BMIM][BF ₄]	3	76 ^c
10				[BMIM][PF ₆]	2	92 ^c
11				[BMIM][PF ₆]	2	90 ^c
12				[BMIM][PF ₆]	2	89 ^d
13				[BMIM][PF ₆]	3	84 ^e

^aReaction conditions: ArB(OH)₂ (1.1 mmol), Ar-Br (1.3 mmol), basic-IL (4 mmol), [BMIM][X] (7 mL), and Pd(OAc)₂ (5 mol%); ^bOil bath temperature 60 °C; ^cYield employing fresh IL;^dYield using recycled IL (2nd cycle); ^eYield using recycled IL (3rd cycle).

(E)-2-Styrylthiophene (2.1): [20] Yellow solid. mp 111–113 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.73 (d, *J* = 16.3 Hz, 1H, *trans*-olefinic H), 6.97 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.01–7.1 (m, 3H, ArH), 7.31–7.40 (m, 5H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 121.0, 121.3, 123.3, 124.1, 125.8, 127.9, 129.5, 133.3, 136.2, 138.2, 139.0 and 140.3. GC-MS: *m/z* 186 M⁺. Anal. Calc. For C₁₂H₁₀S: C, 77.37; H, 5.41%. Found: C, 77.38; H, 5.40%.

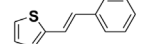
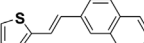
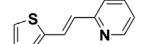
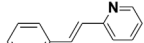
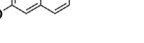
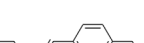
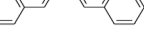
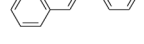
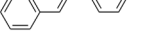
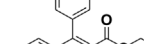
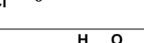
(E)-2-(2-(Naphthalen-2-yl)vinyl)thiophene (2.2): Yellow solid. mp 208–210 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.78 (d, *J* = 16.5 Hz, 1H, *trans*-olefinic H), 6.91 (d, *J* = 16.6 Hz, 1H, *trans*-olefinic H), 7.09–7.18 (m, 3H, ArH), 7.30–7.42 (m, 3H, ArH), 7.43–7.45 (m, 4H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ = 111.8, 119.3, 120.5, 121.7, 123.0, 124.3, 125.1, 126.3, 127.4, 128.3, 132.5, 133.0, 134.5, 135.2, 136.8 and 138.0. GC-MS: *m/z* 236 M⁺. Anal. Calc. For C₁₆H₁₂S: C, 81.31; H, 5.12%. Found: C, 81.32; H, 5.13%.

(E)-2-(2-(Thiophen-2-yl)vinyl)pyridine (2.3): [21] White solid. mp 82–84 °C. ¹H NMR (400 MHz, CDCl₃): δ = 6.85–6.91 (m, 2H, ArH), 7.18 (d, *J* = 16 Hz, 1H, *trans*-olefinic H) 7.30–7.45 (m, 4H, ArH), 7.55 (d, *J* = 16.6 Hz, 1H, *trans*-olefinic H), 8.01 (d, *J* = 7.6 Hz, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 124.1, 125.3, 127.2, 129.3, 133.2, 133.9, 135.0, 136.4, 138.2, 145.1 and 146.9. GC-MS: 187 *m/z* M⁺. Anal. Calc. For C₁₁H₉NS: C, 70.55; H, 4.84; N, 7.48%. Found: C, 70.56; H, 4.85; N, 7.49%.

(E)-2-Styrylpyridine (2.4): [20,22] White solid. mp 150–152 °C. ¹H NMR (400 MHz, CDCl₃): δ 7.06–7.15 (m, 2H, ArH), 7.21 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H), 7.31–7.42 (m, 6H, ArH), 7.49 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 8.01 (d, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 121.5, 123.3, 124.0, 126.3, 127.1, 127.8, 128.2, 130.0, 131.2, 133.9, 138.5, 149.1 and 153.5. GC-MS: 181 *m/z* M⁺. Anal. Calc. For C₁₃H₁₁N: C, 86.15; H, 6.12; N, 7.73%. Found: C, 86.16; H, 6.11; N, 7.75%.

Table 2

Heck coupling reaction with [PAIM][NTf₂]/[BMIM][X].

Entry No.	Substrate 1	Substrate 2	Product ^a	IL	Time [h] ^b	Yield [%]
1				[BMIM][PF ₆]	5	78 ^c
2				[BMIM][PF ₆]	6	83 ^c
3				[BMIM][PF ₆]	6	79 ^c
4				[BMIM][BF ₄]	6	80 ^c
5				[BMIM][BF ₄]	6	74 ^d
6				[BMIM][BF ₄]	6	75 ^d
7				[BMIM][PF ₆]	5	89 ^d
8				[BMIM][PF ₆]	4	91 ^c
9				[BMIM][PF ₆]	4	90 ^c
10				[BMIM][BF ₄]	7	77 ^d
11				[BMIM][BF ₄]	6	80 ^c
12				[BMIM][PF ₆]	7	74 ^c
13				[BMIM][PF ₆]	6	76 ^c
14				[BMIM][BF ₄]	6	78 ^c

^aReaction conditions: substrate 1 (1.0 mmol), substrate 2 (1.2 mmol), basic-IL (4 mmol), [BMIM][X] (7 mL) and Pd(OAc)₂ (6 mol%); ^bOil bath temperature 70 °C; ^cYield employing fresh IL; ^dYield using recycled IL (2nd cycle); ^eYield using recycled IL (3rd cycle).

(E)-2-(2-(6-Methoxynaphthalen-2-yl)vinyl)thiophene(2.5): Yellow solid. mp 198–200 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.55 (s, 3H, OCH₃), 6.81 (s, 1H, ArH), 6.89 (d, *J* = 16.3 Hz, *trans*-olefinic H), 6.99 (d, *J* = 16.5 Hz, *trans*-olefinic H), 7.10–7.11 (m, 3H, ArH), 7.41 (d, *J* = 7.8 Hz, 1H, ArH), 7.51–7.58 (m, 3H, ArH), 7.73 (d, *J* = 7.2 Hz, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 56.4, 119.4, 121.0, 122.5, 123.0, 125.1, 126.9, 128.1, 129.0, 130.9, 131.1, 132.0, 134.5, 135.3, 136.4,

138.2 and 151.9. GC–MS: *m/z* 266 M⁺. Anal. Calc. For C₁₇H₁₄OS: C, 76.66; H, 5.30%. Found: C, 76.67; H, 5.32%.

(E)-2-Methoxy-6-styryl-naphthalene (2.6): [23] White solid. mp 175–177 °C. ¹H NMR (400 MHz, CDCl₃): δ 3.82 (s, 3H, OCH₃), 6.85 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.02 (s, 1H, ArH), 7.10 (d, *J* = 16 Hz, *trans*-olefinic H), 7.12–7.23 (m, 5H, ArH), 7.42–7.53 (m, 4H, ArH), 7.82 (s, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 56.5, 107.8, 111.2, 119.7,

121.0, 121.5, 123.1, 123.4, 123.8, 125.1, 125.7, 126.0, 127.1, 128.5, 130.0, 132.0, 136.3, 139.1 and 154.5. GC–MS: m/z 260 M^+ . Anal. Calc. For $C_{19}H_{16}O$: C, 87.66; H, 6.19%. Found: C, 87.67; H, 6.18%.

(E)-2-Styryl-naphthalene (2.7): [16,24,25] White crystalline solid. mp 70–71 °C. 1H NMR (400 MHz, $CDCl_3$): δ 6.96 (d, J = 16 Hz, 1H, *trans*-olefinic H), 7.07 (d, J = 16 Hz, 1H, *trans*-olefinic H), 7.31–7.40 (m, 5H, ArH), 7.45–7.55 (m, 6H, ArH), 7.77 (s, 1H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 120.0, 121.1, 121.9, 122.1, 122.7, 124.8, 125.3, 126.3, 127.0, 128.1, 128.6, 129.1, 130.8, 131.0, 132.1, 135.9, 136.9 and 139.4. GC–MS: m/z 230 M^+ . Anal. Calc. For $C_{18}H_{14}$: C, 93.87; H, 6.13%. Found: C, 93.88; H, 6.15%.

(E)-1,2-Diphenylethene (2.8): [6,16,8,24,26,27][6b,16,8,24,26,27] White crystalline solid. mp 122–124 °C. 1H NMR (400 MHz, $CDCl_3$): δ 7.01 (s, 2H), 7.12–7.27 (m, 6H, ArH), 7.50 (m, 4H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.0, 127.9, 128.3, 129.3 and 134.4. GC–MS: m/z 180 M^+ . Anal. Calc. For $C_{14}H_{12}$: C, 93.29; H, 6.71%. Found: C, 93.31; H, 6.72%.

(E)-1-Methyl-4-styryl-benzene (2.9): [26,28][6b,16,26,28] White crystalline solid. mp 119–122 °C. 1H NMR (400 MHz, $CDCl_3$): δ 2.49 (s, 3H, CH_3), 6.98 (d, J = 16.4 Hz, 1H, *trans*-olefinic H), 7.10 (d, J = 16.5 Hz, 1H, *trans*-olefinic H), 7.16–7.27 (m, 5H, ArH), 7.30 (d, J = 7.8 Hz, 2H, ArH), 7.39 (d, J = 7.6 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 28.2, 121.5, 122.8, 123.9, 124.2, 125.5, 126.3, 127.7, 128.2, 129.3, 134.9, 137.2 and 138.6. GC–MS: m/z 194 M^+ . Anal. Calc. For $C_{15}H_{14}$: C, 92.74; H, 7.26%. Found: C, 92.73; H, 7.27%.

(E)-Ethyl 3-(4-chlorophenyl)-3-phenyl-acrylate (2.10): [6b,29] Brown liquid. 1H NMR (400 MHz, $CDCl_3$): δ 1.58 (t, 3H), 4.80–4.92 (q, 2H), 6.55 (s, 1H), 7.19–7.29 (m, 5H, ArH), 7.45 (d, J = 8 Hz, 2H, ArH), 7.53 (d, J = 8.6 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 53.1, 117.9, 126.0, 127.5, 128.6, 129.0, 129.8, 133.2, 137.0, 138.4, 152.8 and 168.7. GC–MS: m/z 286 M^+ . Anal. Calc. For $C_{17}H_{15}ClO_2$: C, 71.20; H, 5.27%. Found: C, 71.21; H, 5.25%.

(E)-Methyl 3-(4-methoxyphenyl)-2-methyl-acrylate (2.11): [6b,28] Colorless liquid. bp 290–292 °C. 1H NMR (400 MHz, $CDCl_3$): δ

2.11 (s, 3H), 3.65 (s, 3H), 3.91 (s, 3H), 7.08 (d, J = 8 Hz, 2H, ArH), 7.15 (d, J = 7.6 Hz, 2H, ArH), 7.35 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.0, 53.3, 54.8, 117.9, 127.92, 128.5, 130.9, 138.2, 155.5 and 163.1. GC–MS: m/z 206 M^+ . Anal. Calc. For $C_{12}H_{14}O_3$: C, 69.88; H, 6.84%. Found: C, 69.89; H, 6.85%.

(E)-Ethyl 3-(4-methoxyphenyl)-3-phenyl-acrylate (2.12): [6b,29] Colorless liquid. bp 380–382 °C. 1H NMR (400 MHz, $CDCl_3$): δ 1.82 (t, J = 7.2 Hz, 3H), 3.40 (s, 3H), 4.05 (q, 2H), 6.45 (s, 1H), 6.77 (d, J = 8 Hz, 2H, ArH), 7.18–7.21 (m, 5H, ArH), 7.40 (d, J = 7.6 Hz, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ 15.1, 56.9, 59.0, 119.1, 120.1, 127.0, 128.0, 129.8, 130.9, 136.7, 139.5, 140.9, 153.9 and 164.5. GC–MS: m/z 282 M^+ . Anal. Calc. For $C_{18}H_{18}O_3$: C, 76.57; H, 6.43%. Found: C, 76.58; H, 6.42%.

(E)-Methyl 2-methyl-3-*p*-tolyl-acrylate (2.13): [6b,24] Colorless liquid. bp 260–262 °C. 1H NMR (400 MHz, $CDCl_3$): δ 1.85 (s, 3H), 2.11 (s, 3H), 3.80 (s, 3H), 7.29 (d, J = 7.6 Hz, 2H, ArH), 7.40 (d, J = 8 Hz, 2H, ArH), 7.45 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 16.3, 55.3, 65.4, 122.9, 124.2, 128.9, 131.1, 134.2, 138.7 and 160.7. GC–MS: m/z 190 M^+ . Anal. Calc. For $C_{12}H_{14}O_2$: C, 75.76; H, 7.42%. Found: C, 75.75; H, 7.40%.

(E)-Methyl 2-methyl-3-phenylacrylate (2.14): [6b,32] Colorless liquid. bp 250–252 °C. 1H NMR (400 MHz, $CDCl_3$): δ 1.69 (s, 3H), 3.80 (s, 3H), 7.10–7.20 (m, 3H, ArH), 7.35 (d, J = 8 Hz, 2H, ArH), 7.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 14.5, 55.8, 122.8, 124.1, 125.2, 125.8, 127.9, 130.1, 135.2, 138.2 and 161.1. GC–MS: m/z 176 M^+ . Anal. Calc. For $C_{11}H_{12}O_2$: C, 74.98; H, 6.86%. Found: C, 74.96; H, 6.87%.

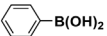
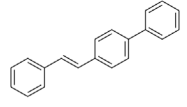
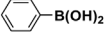
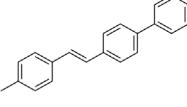
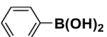
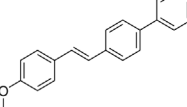
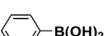
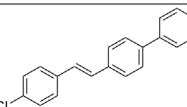
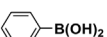
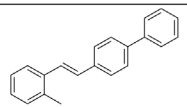
2.3. General procedure for the Wittig-Suzuki (Tables 3a and 3b) and Wittig-Heck (Table 4) tandem reactions

2.3.1. Wittig-Suzuki

An oven-dried reaction tube equipped with a magnetic stirrer bar was charged with the selected aldehyde (1.3 mmol), 4-bromobenzyl-PPh₃ bromide or bromomethyl-PPh₃ bromide salts (1.1 mmol), [PAIM][NTf₂] (4 mmol), and [BMIM][X] (5–6 mL). The reaction mixture was

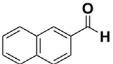
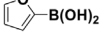
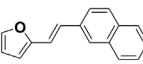
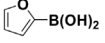
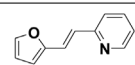
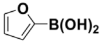
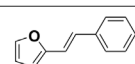
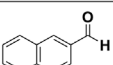
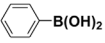
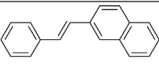
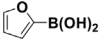
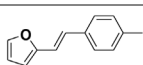
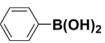
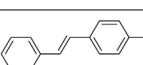
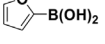
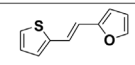
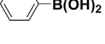
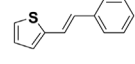
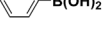
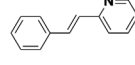
Table 3a

Tandem Wittig-Suzuki reaction with [4-bromobenzyl-PPh₃][Br], [PAIM][NTf₂]/[BMIM][X].

Entry No.	Substrate 1	Substrate 2	Product ^a	IL	Total Time [h] ^b	Yield [%]
1				[BMIM][PF ₆]	8	75 ^c
2				[BMIM][PF ₆]	8	70 ^d
3				[BMIM][BF ₄]	8	68 ^c
4				[BMIM][BF ₄]	8	65 ^d
5				[BMIM][PF ₆]	8	80 ^c

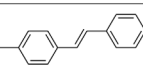
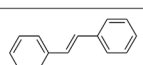
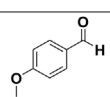
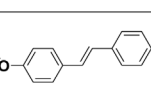
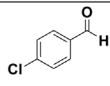
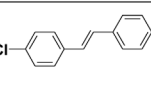
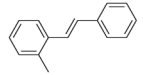
^aReaction conditions: substrate 1 (1.3 mmol), substrate 2 (1.4 mmol), basic-IL (4 mmol), phosphonium salt (1.1 mmol), [BMIM][X] (6 mL), and Pd(OAc)₂ (10 mol%); ^bOil bath temperature 60–65 °C; ^cYield employing fresh IL; ^dYield using recycled IL (2nd cycle).

Table 3bTandem Wittig-Suzuki reaction with [bromomethyl-PPh₃][Br], [PAIM][NTf₂]/[BMIM][X].

Entry No.	Substrate 1	Substrate 2	Product ^a	IL	Total Time [h] ^b	Yield [%]
1				Bmim-PF ₆	7	68 ^c
2				Bmim-PF ₆	6	70 ^c
3				Bmim-BF ₄	6	71 ^c
4				Bmim-BF ₄	7	80 ^c
5				Bmim-PF ₆	5	74 ^d
6				Bmim-PF ₆	5	82 ^c
7				Bmim-BF ₄	7	79 ^c
8				Bmim-BF ₄	7	78 ^c
9				Bmim-PF ₆	7	74 ^d

^aReaction conditions: substrate 1 (1.0 mmol), substrate 2 (1.2 mmol), phosphonium salt (1.1 mmol), basic-IL (4 mmol), [BMIM][X] (5 mL) and Pd(OAc)₂ (10 mol%); ^bOil bath temperature 60–65 °C; ^cYield employing fresh IL; ^dYield using recycled IL (2nd cycle); ^eYield using recycled IL (3rd cycle).

Table 4Tandem Wittig-Heck reaction with [methyl-PPh₃][I], [PAIM][NTf₂]/[BMIM][X].

Entry No.	Substrate 1	Substrate 2	Product ^a	IL	Total Time [h] ^b	Yield [%]
1				[BMIM][BF ₄]	7	65 ^d
2				[BMIM][BF ₄]	8	78 ^c
3				[BMIM][PF ₆]	8	74 ^d
4				[BMIM][PF ₆]	8	70 ^c
5				[BMIM][PF ₆]	8	76 ^c

^aReaction conditions: substrate 1 (1.3 mmol), substrate 2 (1.0 mmol), phosphonium salt (1.2 mmol), basic-IL (3 mmol); [BMIM][X] (6–7 mL); Pd(OAc)₂ (10 mol%); ^bOil bath temperature 65 °C; ^cYield employing fresh IL; ^dYield using recycled IL (2nd cycle); ^eYield using recycled IL (3rd cycle).

stirred and heated at 60–65 °C under a nitrogen atmosphere for 30 min. Then the aryl boronic acid (1.3 mmol) was introduced along with Pd(OAc)₂ (10 mol%) and heating was resumed for an additional 5–8 h while monitoring by TLC. Upon completion, the reaction mixture was extracted 4 times with hexane/ethyl acetate (80:20), dried over anhydrous magnesium sulfate, the solvent was removed under vacuum, and the crude products were purified by flash chromatography hexane/ethyl acetate (80:20) or DCM/MeOH (95:5).

2.3.2. Wittig-Heck

The same procedure as in 2.3.1 was followed except that methyl-Ph₃P iodide salt was used for the Wittig reaction with selected aldehydes and PhI was used instead of boronic acids

4-Styryl-1,1'-biphenyl(3a.1): [27,30] White solid. mp 215–217 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.97 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.13 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.33 (d, *J* = 7.6 Hz, 2H, ArH), 7.35–7.41 (m, 6H, ArH), 7.45–7.52 (m, 6H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 125.5, 126.0, 126.2, 127.0, 127.5, 127.8, 128.3, 128.9, 129.1, 130.3, 130.7, 131.1, 131.8 and 132.4. GC–MS: *m/z* 270 M⁺. Anal. Calc. For C₂₀H₁₆: C, 93.71; H, 6.29%. Found: C, 93.72; H, 6.28%.

4-(4-Methylstyryl)-1, 1'-biphenyl (3a.2): [30] White solid, mp 224–226 °C; ¹H NMR (400 MHz, CDCl₃): δ 2.15 (s, 3H, CH₃), 7.03 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.10 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.14–7.23 (m, 5H, ArH), 7.42 (d, *J* = 7.8 Hz, 2H, ArH), 7.53–7.65 (m, 6H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 25.8, 122.0, 123.4, 125.2, 126.4, 127.0, 128.7, 129.5, 130.4, 132.4, 133.2, 134.9, 135.5, 136.1, 137.0, 137.6 and 138.4. GC–MS: *m/z* 270 M⁺. Anal. Calc. For C₂₁H₁₈: C, 93.29; H, 6.71%. Found: C, 93.28; H, 6.72%.

4-(4-Methoxystyryl)-1, 1'-biphenyl (3a.3): [30] White solid, mp 199–201 °C; ¹H NMR (400 MHz, CDCl₃): δ 3.68 (s, 3H, OCH₃), 6.91 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.06 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.37 (d, *J* = 7.6 Hz, 2H, ArH), 7.42 (d, *J* = 7.6 Hz, 2H, ArH), 7.55–7.62 (m, 3H, ArH), 7.73–7.83 (m, 6H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 59.5, 121.4, 122.7, 123.9, 124.5, 125.0, 126.7, 127.0, 127.6, 128.7, 129.9, 130.5, 131.6, 132.4, 134.2, 134.9 and 155.6. GC–MS: *m/z* 286 M⁺. Anal. Calc. For C₂₁H₁₈O: C, 88.08; H, 6.34%. Found: C, 88.09; H, 6.35%.

4-(4-Chlorostyryl)-1, 1'-biphenyl (3a.4): [30] White solid. mp 245–247 °C; ¹H NMR (400 MHz, CDCl₃): δ 6.90 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.01 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.31 (d, *J* = 8 Hz, 2H, ArH), 7.38–7.46 (m, 5H, ArH), 7.49–7.67 (m, 6H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 123.1, 123.5, 125.3, 125.9, 126.4, 127.3, 128.0, 128.3, 130.0, 130.5, 131.6, 132.1, 132.9, 135.2, 135.8 and 154.2. GC–MS: *m/z* 290 M⁺. Anal. Calc. For C₂₀H₁₅Cl: C, 82.61; H, 5.20%. Found: C, 82.63; H, 5.21%.

4-(2-Methylstyryl)-1,1'-biphenyl(3a.5): White solid. mp 201–203 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.01 (s, 3H, CH₃), 6.91 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.03 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.12–7.21 (m, 2H, ArH), 7.32 (d, *J* = 7.6 Hz, 1H, ArH), 7.35–7.41 (m, 4H, ArH), 7.49–7.58 (m, 6H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 20.4, 122.9, 123.8, 124.1, 125.4, 126.0, 127.2, 128.1, 128.9, 129.5, 130.5, 131.3, 132.0, 133.1, 133.6, 135.6, 136.2, 136.5 and 137.3. GC–MS: *m/z* 270 M⁺. Anal. Calc. For C₂₁H₁₈: C, 93.29; H, 6.71%. Found: C, 93.27; H, 6.72%.

(E)-2-(2-(Naphthalen-2-yl)vinyl)furan (3b.1): [33] Colorless liquid. bp 280–282 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.62–6.70 (m, 2H, ArH), 6.83 (d, *J* = 16.6 Hz, 1H, *trans*-olefinic H), 7.10 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H), 7.45–7.56 (m, 4H, ArH), 7.77–7.82 (m, 4H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 110.0, 112.5, 119.6, 120.0, 122.1, 122.9, 124.3, 128.7, 129.1, 129.5, 131.5, 134.1, 137.9, 139.2, 147.9 and 152.5. GC–MS: *m/z* 220 M⁺. Anal. Calc. For C₁₆H₁₂O: C, 87.25; H, 5.49%. Found: C, 87.24; H, 5.48%.

(E)-2-(2-(Furan-2-yl)vinyl)pyridine (3b.2): Colorless liquid. bp 260–262 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.33–6.41 (m, 2H, ArH), 7.05 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H), 7.28 (d, *J* = 16.6 Hz, 1H,

trans-olefinic H), 7.52–7.68 (m, 4H, ArH), 8.09 (d, *J* = 7.2 Hz, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 114.7, 116.9, 124.6, 128.2, 129.8, 136.8, 138.1, 142.3, 150.0, 152.9 and 154.1. GC–MS: *m/z* 171 M⁺. Anal. Calc. For C₁₁H₉NO: C, 77.17; H, 5.30; N, 8.18%. Found: C, 77.18; H, 5.32; N, 8.19%.

(E)-2-styryl-furan (3b.3): [25] White solid; mp 50–52 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.55–6.73 (m, 2H, ArH), 6.87 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H), 6.99 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 7.33 (t, *J* = 7.4, 6.8 Hz, 1H, ArH), 7.41–7.50 (m, 2H, ArH), 7.51–7.62 (m, 3H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 118.2, 121.2, 122.0, 124.3, 125.1, 128.9, 130.5, 131.2, 134.0, 134.5, 149.5 and 152.9. GC–MS: *m/z* 170 M⁺. Anal. Calc. For C₁₂H₁₀O: C, 84.68; H, 5.92%. Found: C, 84.67; H, 5.93%.

(E)-2-(4-methylphenyl)vinyl)furan (3b.5): Colorless liquid; bp 268–270 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.55 (s, 3H, CH₃), 7.71–7.83 (m, 4H, ArH), 7.02 (d, *J* = 16.4 Hz, 1H, *trans*-olefinic H), 7.18 (d, *J* = 16.5 Hz, 1H, *trans*-olefinic H), 7.51 (d, *J* = 7.6 Hz, 2H, ArH), 7.58 (d, *J* = 7.6 Hz, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ = 29.9, 117.4, 119.2, 123.1, 123.8, 126.1, 134.4, 135.0, 139.2, 147.9 and 153.2. GC–MS: *m/z* 184 M⁺. Anal. Calc. For C₁₃H₁₂O: C, 84.75; H, 6.57%. Found: C, 84.77; H, 6.58%.

(E)-2-(2-(Thiophen-2-yl)vinyl)furan(3b.7): White solid. mp 80–82 °C; ¹H NMR (400 MHz, CDCl₃): δ 6.31–6.39 (m, 2H, ArH), 6.85 (d, *J* = 16 Hz, 1H, *trans*-olefinic H), 6.98 (d, *J* = 16.6 Hz, 1H, *trans*-olefinic H), 7.00–7.09 (m, 2H, ArH), 7.30 (d, *J* = 7.6 Hz, 1H, ArH), 7.45 (d, *J* = 7.2 Hz, 1H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 114.7, 119.2, 122.8, 127.2, 127.8, 131.9, 134.1, 138.1, 143.0 and 152.2. GC–MS: *m/z* 176 M⁺. Anal. Calc. For C₁₀H₈OS: C, 68.15; H, 4.58%. Found: C, 68.14; H, 4.57%.

(E)-1-4-(4-chlorostyryl)benzene (4.4): [6b,24,26] Colorless solid. mp 125–126 °C. ¹H NMR (400 MHz, CDCl₃): δ 6.81 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H), 7.02 (d, *J* = 16.4 Hz, 1H, *trans*-olefinic H), 7.28–7.36 (m, 5H, ArH), 7.65 (d, *J* = 7.6 Hz, 2H, ArH), 7.82 (d, *J* = 7.6 Hz, 2H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 124.0, 125.2, 127.1, 127.4, 128.4, 129.2, 129.4, 130.7, 131.4, 132.8, 134.4 and 152.4. GC–MS: *m/z* 270 M⁺. Anal. Calc. For C₁₄H₁₁Cl: C, 78.32; H, 5.16%. Found: C, 78.33; H, 5.14%.

(E)-1-methyl-2-styryl-benzene (4.5): [16,26] Colorless oil. bp 285–287 °C. ¹H NMR (400 MHz, CDCl₃): δ 2.58 (s, 3H, CH₃), 6.95 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H), 6.98 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H), 7.04–7.12 (m, 4H, ArH), 7.17 (m, 5H, ArH). ¹³C NMR (100 MHz, CDCl₃): δ 20.7, 121.5, 121.7, 122.8, 123.1, 123.8, 124.5, 125.1, 125.4, 127.6, 127.9, 129.1, 130.8, 131.5 and 134.1. GC–MS: *m/z* 194 M⁺. Anal. Calc. For C₁₅H₁₄: C, 92.74; H, 7.26%. Found: C, 92.72; H, 7.25%.

2.4. General procedure for the Horner-Emmons-Suzuki and Horner-Emmons-Heck reactions (Tables 5 and 6)

2.4.1. Horner-Emmons-Suzuki

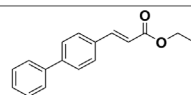
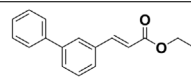
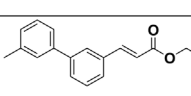
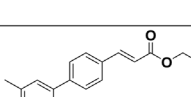
An oven-dried reaction tube equipped with a magnetic stirrer bar was charged with a mixture of 4-bromobenzaldehyde (1.3 mmol), ethyl 2-(diethylphosphoryl)acetate (1.1 mmol), [PAIM][NTf₂] (4 mmol) and [BMIM][PF₆] (7 mL). The reaction mixture was stirred and heated at 60–70 °C under a nitrogen atmosphere for 4–5 h. Upon completion of the Horner-Emmons transformation (TLC monitoring), aryl boronic acid (1.5 mmol) was introduced along with Pd(OAc)₂ (10 mol%) and heating was resumed. Upon completion (TLC monitoring), the crude reaction mixture was extracted in dry ether (3-times), dried over anhydrous magnesium sulfate, and the solvent was removed under vacuum to furnish the crude product which was purified by flash column chromatography using hexane/ethyl acetate (70:30) or DCM/MeOH (90:10).

2.4.2. Horner-Emmons-Heck

A similar procedure as in 2.4.1 was followed. Upon completion of

Table 5

Tandem Horner-Emmons-Suzuki sequence in [PAIM][NTf₂]/[BMIM][X].

Entry No.	Substrate 1	Substrate 2	Product ^a	IL	Total Time [h] ^b	Yield [%]
1				[BMIM][PF ₆]	6	78 ^c
2				[BMIM][PF ₆]	6	72 ^d
3				[BMIM][PF ₆]	7	70 ^e
4				[BMIM][BF ₄]	6	70 ^e

^aReaction conditions: substrate 1 (1.3 mmol), substrate 2 (1.5 mmol), phosphonate ester (1.1 mmol), basic-IL (4 mmol), [BMIM][X] (8 mL), and Pd(OAc)₂ (10 mol%); ^bOil bath temperature 65 °C; ^cYield employing fresh IL; ^dYield using recycled IL (2nd cycle); ^eYield using recycled IL (3rd cycle).

the Horner-Emmons reaction TLC analysis), the selected aryl-ethene was introduced (1.2 mmol) and heating was resumed. The progress of the reaction was monitored by TLC and after completion, the crude product was twice extracted in dry ether, dried (magnesium sulfate), and the solvent was removed to furnish the crude product which was purified by flash column chromatography using hexane/ethyl acetate (70:30) or DCM/MeOH (90:10).

Ethyl (2E)-3-(biphenyl-4-yl)prop-2-enoate (5.1): White solid. mp. 92–94 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.49 (s, 3H, CH₃), 4.33 (q, 2H, CH₂), 7.11 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H), 7.33–7.42 (m, 3H, Ar-H), 7.43–7.51 (m, 2H, Ar-H), 7.53–7.64 (m, 4H, Ar-H), 7.68 (d, *J* = 16.4 Hz, 1H, *trans*-olefinic H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 15.7, 68.1, 119.5, 126.8, 127.9, 128.8, 129.0, 129.5, 131.1, 131.8,

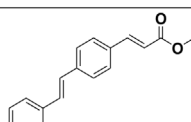
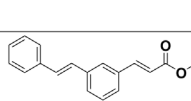
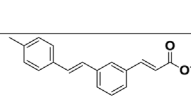
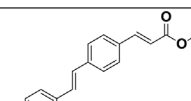
139.0 and 166.4. Anal. Calc. For C₁₇H₁₆O₂: C, 80.93; H, 6.39%. Found: C, 80.94; H, 6.41%.

Ethyl (2E)-3-(biphenyl-3-yl)prop-2-enoate (5.2): Pale yellow solid. mp. 64–66 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.56 (t, 3H, CH₃), 4.12 (q, 2H, CH₂), 7.01 (d, *J* = 16.0 Hz, 1H, *trans*-olefinic H), 7.26 (s, 1H, ArH), 7.28–7.35 (m, 5H, ArH), 7.39–7.50 (m, 3H, ArH), 7.54 (d, *J* = 16.4 Hz, 1H, *trans*-olefinic H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 15.9, 60.9, 121.4, 125.5, 126.0, 127.0, 127.5, 128.5, 129.0, 129.5, 130.1, 131.3, 132.9, 139.8, and 167.4. Anal. Calc. For C₁₇H₁₆O₂: C, 80.93; H, 6.39%. Found: C, 80.91; H, 6.40%.

Ethyl (2E)-3-(3'-methylbiphenyl-3-yl)prop-2-enoate (5.3): Light brown solid. mp. 96–98 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.48 (t, 3H, CH₃), 2.37 (s, 3H, CH₃), 4.25 (q, 2H, CH₂), 6.82 (d, *J* = 16.2 Hz,

Table 6

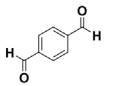
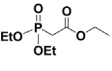
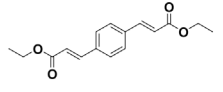
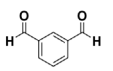
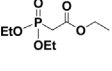
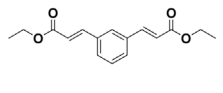
Tandem Horner-Emmons-Heck sequence in [PAIM][NTf₂]/[BMIM][X].

Entry No.	Substrate 1	Substrate 2	Product ^a	IL	Total Time [h] ^b	Yield [%]
1				[BMIM][BF ₄]	6	70 ^c
2				[BMIM][BF ₄]	7	66 ^d
3				[BMIM][BF ₄]	7	61 ^e
4				[BMIM][PF ₆]		70 ^c

^aReaction conditions: substrate 1 (1.0 mmol), substrate 2 (1.2 mmol), phosphonate ester (1.1 mmol), basic-IL (4 mmol), [BMIM][X] (8 mL) and Pd(OAc)₂ (10 mol%); ^bOil bath temperature 65 °C; ^cYield employing fresh IL; ^dYield using recycled IL (2nd cycle); ^eYield using recycled IL (3rd cycle).

Table 7a

Bis-olefination via double Horner-Emmons reaction in [PAIM][NTf₂]/[BMIM][X].

Entry No.	Substrate 1	Substrate 2	Product ^a	IL	Time [h] ^b	Yield [%] ^c
1				[BMIM][PF ₆]	7	68
2				[BMIM][PF ₆]	6	71

^aReaction conditions: substrate 1 (1.0 mmol), substrate 2 (2.1 mmol), basic-IL (4 mmol), [BMIM][X] (8 mL), and Pd(OAc)₂ (10 mol%); ^bOil bath temperature 70 °C; ^cYield employing fresh IL.

1H, *trans*-olefinic H), 7.20 (s, 1H, ArH), 7.33 (s, 1H, ArH), 7.49–7.58 (m, 6H, ArH), 7.75 (d, *J* = 16.0 Hz, 1H, *trans*-olefinic H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 16.8, 20.9, 65.0, 118.1, 125.1, 125.4, 126.4, 126.8, 128.7, 128.7, 129.0, 132.0, 132.5, 134.2, 136.9, 138.7, 149.3 and 166.0. Anal. Calc. For C₁₈H₁₈O₂: C, 81.17; H, 6.81%. Found: C, 81.16; H, 6.80%.

Ethyl (2*E*)-3-(3'-methylbiphenyl-4-yl)prop-2-enoate (5.4): Yellow solid. mp. 109–111 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.48 (t, 3H, CH₃), 2.32 (s, 3H, Me), 4.24 (q, 2H, CH₂), 7.01 (d, *J* = 16.4 Hz, 1H, *trans*-olefinic H), 7.21–7.33 (m, 3H, ArH), 7.34 (s, 1H, ArH), 7.37–7.50 (m, 4H, ArH), 7.68 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 13.9, 21.2, 65.2, 117.8, 126.5, 127.3, 128.4, 129.5, 129.8, 132.8, 134.1, 134.7, 136.3, 138.1, 147.5 and 166.7. Anal. Calc. For C₁₈H₁₈O₂: C, 81.17; H, 6.81%. Found: C, 81.15; H, 6.82%.

Ethyl (2*E*)-3-{4-[(*E*)-2-phenylethenyl]phenyl}prop-2-enoate (6.1): [34] White solid. mp 137–139 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.63 (t, 3H, CH₃), 4.33 (q, 2H, CH₂), 6.84 (d, *J* = 16.0 Hz, 1H, *trans*-olefinic H), 7.11 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H), 7.13–7.24 (m, 3H, ArH), 7.32 (d, *J* = 8.4 Hz, 2H, ArH), 7.5 (d, *J* = 8.0 Hz, 2H, ArH), 7.65 (d, *J* = 8.6 Hz, 2H, ArH), 7.75 (d, *J* = 16.4 Hz, 1H, *trans*-olefinic H), 7.81 (d, *J* = 16.4 Hz, 1H, *trans*-olefinic H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 17.6, 63.5, 116.3, 125.3, 125.8, 126.2, 127.3, 127.5, 128.4, 128.7, 129.1, 129.8, 131.3, 132.5, 133.0, 144.0 and 165.1. Anal. Calc. For C₁₉H₁₈O₂: C, 81.99; H, 6.52%. Found: C, 81.97; H, 6.53%.

Ethyl (2*E*)-3-{3-[(*E*)-2-phenylethenyl]phenyl}prop-2-enoate (6.2): [31] Brown solid. mp. 129–131 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.52 (t, 3H, CH₃), 4.31 (q, 2H, CH₂), 6.79 (d, *J* = 16.8 Hz, 1H, *trans*-olefinic H), 7.08 (d, *J* = 16.2 Hz, 1H, olefinic H), 7.15–7.25 (m, 5H, ArH), 7.37 (s, 1H, ArH), 7.59 (d, *J* = 7.8 Hz, 2H, ArH), 7.61 (d, *J* = 8.0 Hz, 1H, ArH), 7.81 (d, *J* = 16.0 Hz, 1H, *trans*-olefinic H), 7.87

(d, *J* = 16.4 Hz, 1H, *trans*-olefinic H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 18.1, 65.4, 112.6, 124.3, 124.8, 125.3, 125.7, 126.4, 127.0, 127.5, 128.0, 128.7, 129.1, 129.5, 135.4, 137.0, 138.8, 143.8 and 163.0. Anal. Calc. For C₁₉H₁₈O₂: C, 81.99; H, 6.52%. Found: C, 82.00; H, 6.50%.

Ethyl (2*E*)-3-{3-[(*E*)-2-(4-methylphenyl)ethenyl]phenyl}prop-2-enoate (6.3): Brown solid. mp. 138–140 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.55 (t, 3H, CH₃), 2.25 (s, 3H, Me), 4.20 (q, 2H, CH₂), 6.77 (d, *J* = 16.4 Hz, 1H, *trans*-olefinic H), 6.79 (d, *J* = 16.8 Hz, 1H, *trans*-olefinic H), 7.15–7.25 (m, 7H, ArH), 7.35 (s, 1H, ArH), 7.50 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H), 7.67 (d, *J* = 16.02 Hz, 1H, *trans*-olefinic H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 19.3, 27.4, 117.1, 126.0, 126.1, 126.9, 127.5, 127.8, 128.5, 129.2, 130.1, 133.7, 135.5, 136.0, 139.2, 149.2 and 164.7. Anal. Calc. For C₂₀H₂₀O₂: C, 82.16; H, 6.89%. Found: C, 82.17; H, 6.87%.

Ethyl (2*E*)-3-{4-[(*E*)-2-(4-methylphenyl)ethenyl]phenyl}prop-2-enoate (6.4): Brown solid. mp 124–126 °C. ¹H NMR (400 MHz, DMSO-*d*₆): δ 1.70 (t, 3H, CH₃), 2.71 (s, 3H, Me), 4.22 (q, 2H, CH₂), 6.70 (d, *J* = 16.0 Hz, 1H, *trans*-olefinic H), 6.75 (d, *J* = 16.2 Hz, 1H, *trans*-olefinic H), 7.07 (m, 4H, ArH), 7.25 (d, *J* = 7.8 Hz, 1H, *trans*-olefinic H), 7.33 (d, *J* = 8.0 Hz, 2H, ArH), 7.49 (d, *J* = 16.4 Hz, 2H, ArH), 7.79 (d, *J* = 16.8 Hz, 1H, *trans*-olefinic H). ¹³C NMR (100 MHz, DMSO-*d*₆): δ 19.9, 24.9, 65.2, 113.4, 127.0, 127.4, 127.9, 128.5, 128.6, 129.0, 132.0, 132.5, 136.2, 137.5, 149.2 and 162.5. Anal. Calc. For C₂₀H₂₀O₂: C, 82.16; H, 6.89%. Found: C, 82.17; H, 6.87%.

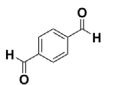
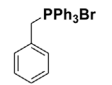
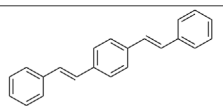
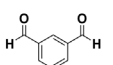
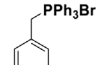
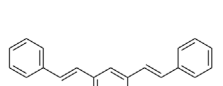
2.5. General procedure for the double olefination via Horner-Emmons and Wittig Transformations (Tables 7a and 7b)

2.5.1. Double Horner-Emmons

In an oven dry nitrogen-flushed reaction tube was placed a mixture

Table 7b

Bis-olefination via double Wittig reaction in [PAIM][NTf₂]/[BMIM][X].

Entry No.	Substrate 1	Substrate 2	Product ^a	IL	Time [h] ^b	Yield [%] ^c
1				[BMIM][PF ₆]	7	65
2				[BMIM][PF ₆]	8	67

^aReaction conditions: substrate 1 (1.0 mmol), substrate 2 (2.1 mmol), basic-IL (4 mmol), [BMIM][X] (7 mL), and Pd(OAc)₂ (10 mol%); ^bOil bath temperature 70 °C; ^cYield employing fresh IL.

of dialdehyde (1.0 mmol), ethyl 2-(diethylphosphoryl)acetate (2.1 mmol), [PAIM][NTf₂] (4 mmol), and [BMIM][PF₆] (8 mL), and the reaction was heated to 65–70 °C for 6–7 h. After completion (TLC monitoring) the crude reaction mixture was extracted 3 times with hexane/EtOAc (80:20), dried (magnesium sulfate), and the solvent was removed under vacuum to furnish the crude product which was then purified by flash column chromatography with hexane/ethyl acetate (80:20).

2.5.2. Double Wittig

An oven-dried reaction tube equipped with a magnetic stirrer bar was charged with a mixture of dialdehyde (1.3 mmol), benzyl-triphenylphosphonium bromide (2.2 mmol), [PAIM][NTf₂] (4 mmol) and [BMIM][PF₆] (7 mL). The reaction mixture was stirred and heated at 60–70 °C under a nitrogen atmosphere for 7–8 h. After completion (TLC monitoring) the crude reaction mixture was extracted 3 times with hexane/EtOAc (80:20), dried (magnesium sulfate), and the solvent was removed under vacuum to furnish the crude product which was then purified by flash column chromatography with hexane/ethyl acetate (80:20).

Diethyl (2E,2'E)-3,3'-benzene-1,4-diyl-bis-prop-2-enoate (7a.1): White solid. mp 90–92 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 1.67 (t, 6H, CH₃), 4.33 (q, 4H, CH₂), 6.99 (d, *J* = 16.2 Hz, 2H, *trans*-olefinic Hs), 7.04 (d, *J* = 16.0 Hz, 2H, *trans*-olefinic Hs), 7.25–7.37 (m, 4H, ArH). ¹³C NMR (100 MHz, DMSO-d₆): δ 20.1, 65.0, 117.0, 127.4, 137.5, 148.8 and 164.2. Anal. Calc. For C₁₆H₁₈O₄: C, 70.06; H, 6.61%. Found: C, 70.08; H, 6.63%.

Diethyl (2E,2'E)-3,3'-benzene-1,3-diyl-bis-prop-2-enoate (7a.2): [28] White solid. mp 56–58 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 1.35 (t, 6H, CH₃), 4.18 (q, 4H, CH₂), 7.03 (d, *J* = 16.0 Hz, 2H, *trans*-olefinic Hs), 7.07 (d, *J* = 16.4 Hz, 2H, *trans*-olefinic Hs), 7.20–7.32 (m, 3H, ArH), 7.34 (s, 1H, ArH). ¹³C NMR (100 MHz, DMSO-d₆): δ 18.1, 65.1, 114.8, 126.2, 127.5, 128.4, 134.8, 145.0 and 167.7. Anal. Calc. For C₁₆H₁₈O₄: C, 70.06; H, 6.61%. Found: C, 70.04; H, 6.62%.

1,4-bis[(E)-2-phenylethenyl] benzene (7b.1): [18] Pale yellow solid. mp 260–262 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 7.07 (d, *J* = 16.0 Hz, 2H, *trans*-olefinic Hs), 7.13 (d, *J* = 16.0 Hz, 2H, *trans*-olefinic Hs), 7.39–7.50 (m, 6H, ArH), 7.50–7.63 (m, 8H, ArH). ¹³C NMR (100 MHz, DMSO-d₆): δ 124.9, 125.5, 126.2, 126.7, 127.2, 127.6, 128.3, 129.0, 131.1 and 132.3. Anal. Calc. For C₂₂H₁₈: C, 93.57; H, 6.43%. Found: C, 93.56; H, 6.42%.

1,3-bis[(E)-2-phenylethenyl] benzene (7b.2): [18] Yellow solid. mp 178–180 °C. ¹H NMR (400 MHz, DMSO-d₆): δ 6.89 (d, *J* = 16.2 Hz, 2H, *trans*-olefinic Hs), 7.00 (d, *J* = 16.4 Hz, 2H, *trans*-olefinic Hs), 7.29 (t, 1H, ArH), 7.37–7.49 (m, 10H, ArH), 7.52 (d, *J* = 8.2 Hz, 2H, ArH), 7.66 (s, 1H, ArH). ¹³C NMR (100 MHz, DMSO-d₆): δ = 124.2, 124.8, 125.6, 126.0, 126.3, 126.7, 127.8, 129.5, 130.1, 132.0 and 133.0. Anal. Calc. For C₂₂H₁₈: C, 93.57; H, 6.43%. Found: C, 93.58; H, 6.42%.

2.6. Recycling and reuse of the IL solvents

The recovered brown-colored [BMIM][X] (also containing [PAIM][NTf₂] and its conjugate acid) was dried overnight under vacuum at 60 °C and reused directly in the next cycle(s), after which it was collected and set aside for recovery and recycling as follows: the combined brown-colored IL recovered from several runs were dissolved in dry MeCN and filtered through Celite to remove insoluble dark (brown/black) particles. After removal of solvent from the filtrate under vacuum, the recycled IL was dried overnight under vacuum at 60 °C and reused in subsequent runs. Control experiment showed that addition of fresh [PAIM][NTf₂] to recycled IL was necessary in order to reach the reported yields.

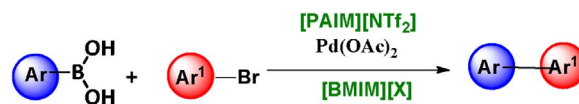


Fig. 2. Suzuki cross-coupling in ILs.

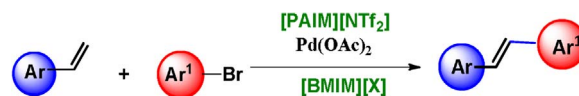


Fig. 3. Heck cross-coupling in ILs.

3. Results and discussion

3.1. Suzuki and Heck cross-coupling reactions (Tables 1 and 2)

The utility of [PAIM][NTf₂]/Pd(OAc)₂/[BMIM][X] system to effectively promote the Suzuki and Heck cross-coupling reactions without using any other additives was examined by reacting various aryl(heteroaryl)bromides with aryl(heteroaryl)-boronic acids or with various substituted ethenes and enoates (Figs. 2 and 3), and the results are summarized in Tables 1 and 2. Isolated yields for the Suzuki reaction were in the 92% to 76% range under relatively mild conditions and with short reaction times. Slightly lower conversions were observed in cases where recycled ILs had been used. For the Heck reactions isolated yields were in 91% to 74% range, with lower conversions observed in recycled ILs. Longer reactions times and slightly higher temperatures were employed in the Heck reaction in order to achieve optimal conversions. Formation of purely *trans*-alkenes in all cases was evident based on magnitude of the H/H coupling. Although isolated yields obtained in [BMIM][PF₆] versus [BMIM][BF₄] were typically comparable, recycled [BMIM][PF₆] appeared to perform better (see the recycling and reuse section).

3.2. Tandem Wittig-Suzuki Transformations (Tables 3a and 3b)

The [PAIM][NTf₂]/[BMIM][X] system proved efficient in promoting the Wittig reaction under mild conditions, with substituted benzaldehydes and 4-bromobenzyl-PhP₃ or bromomethyl-PhP₃ bromide salts respectively (Fig. 4). Subsequent addition of aryl(heteroaryl) boronic acids along with catalytic amounts of Pd(OAc)₂ induced the Suzuki reaction which led to the isolation of a small library of high value *trans*-alkenes in isolated yields ranging from 80 to 65%. The lower conversions were typically those obtained in the recycled ILs (Tables 3a and 3b).

3.3. Tandem Wittig- Heck Transformations (Table 4)

The [PAIM][NTf₂]/[BMIM][X] system also proved efficient in promoting the Wittig-Heck tandem reactions. When benzaldehydes were allowed to react with [Me-PPh₃][I] salt, the Wittig olefination products were formed, and subsequent introduction of PhI along with the Pd-catalyst induced the Heck cross-coupling (Fig. 5), leading to the isolation of substituted *trans*-diphenyl-ethenes in yields ranging from 78% to 65% (Table 4).

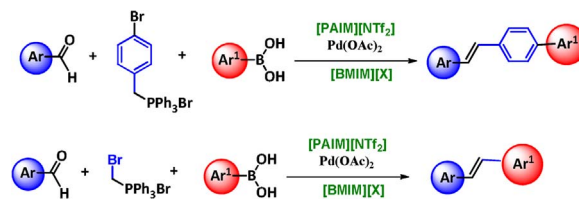


Fig. 4. Wittig-Suzuki tandem reactions.

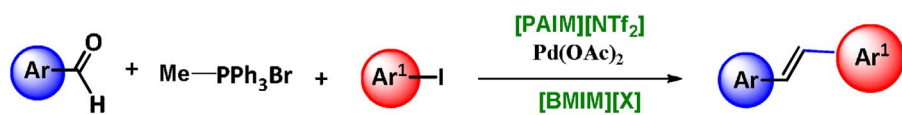


Fig. 5. Wittig-Heck tandem reactions.

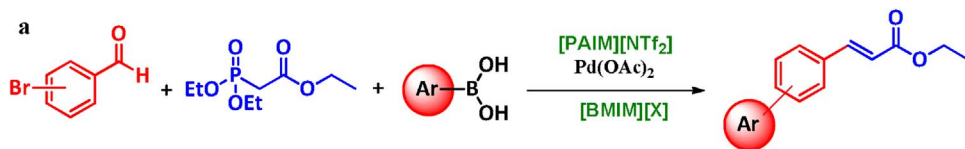


Fig. 6. (a) Horner-Emmons-Suzuki tandem reactions. (b) Horner-Emmons-Heck tandem reactions.

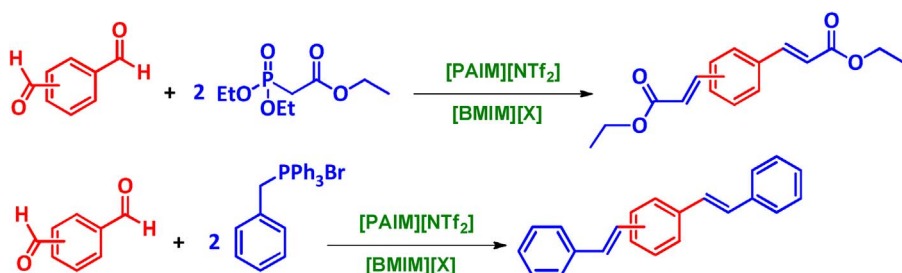
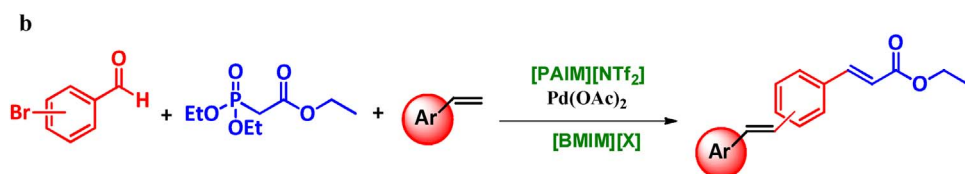


Fig. 7. Bis-olefination feasibility study.

3.4. Horner-Emmons-Suzuki and Horner-Emmons-Heck reactions (Tables 5 and 6)

Horner-Emmons (HE) olefinations were effected in [PAIM][NTf₂]/[BMIM][X] by reacting isomeric bromobenzaldehyde with diethylphosphonate under moderate heating. Subsequent addition of the boronic acid and the Pd-catalyst induced the Suzuki reaction (Fig. 6a). The resulting biaryl-enoates were isolated in 78% to 70% yield, with lower yields obtained in recycled IL. Following a similar protocol the HE-Heck sequence were performed (Fig. 5b) by addition of substituted styrenes in place of the boronic acids in 60–70% isolated yields (Tables 5 and 6).

3.5. Double olefination via Horner-Emmons and Wittig reactions (Tables 7a and 7b)

The feasibility to perform bis-olefination in [PAIM][NTf₂]/[BMIM][X] was explored by reacting isomeric phthalaldehydes with diethylphosphonate and with benzyl-PPh₃ bromide (Fig. 7). In representative cases, the bis-propenoates and the bis-styryl-derivatives were isolated in acceptable yields (Tables 7a and 7b).

4. Recycling and reuse of the IL solvent

The yield data summarized in Tables along with table footnotes give an overall sense of the feasibility to employ recycled/reused [BMIM][X] in the described transformations. But to get a better sense of how far this could go, one entry out of each table was selected and the reaction was repeated four additional times in the same IL to compare isolated yields. The outcomes are summarized in Chart 1. It can be seen that there is a sharp decrease in yields beyond the 3rd cycle which is likely due to accumulation of tar and impurities, suggesting that beyond the 3rd cycle either fresh IL must be employed or the used ILs should be put

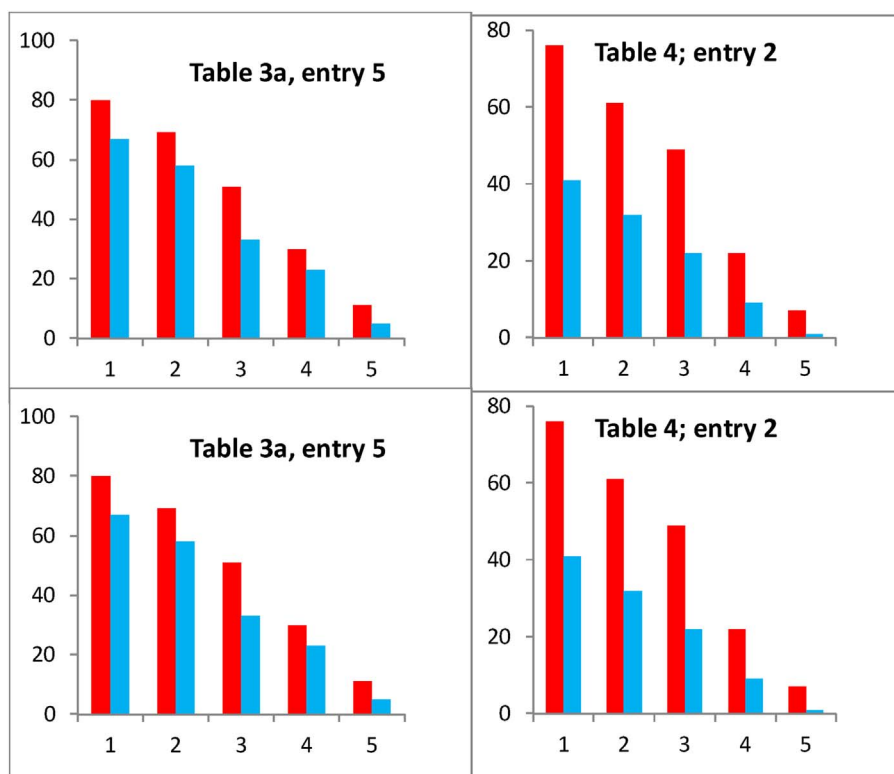
through a clean-up/regeneration process (see experimental). Similar observations were made previously in Pd-catalyzed Heck and Sonogashira reactions in ILs [6b,9]. Data in Chart 1 shows that whereas initially the conversions in [BMIM][PF₆] and [BMIM][BF₄] are comparable (slightly better in the former), [BMIM][PF₆] appears to be “more pliable” and performs better when re-used.

5. Conclusion

The efficacy of [PAIM][NTf₂]/[BMIM][X]/Pd-catalyst system in the Suzuki and Heck cross-coupling reactions without the need for any other additives is demonstrated. The [PAIM][NTf₂]/[BMIM] system also proved effective for the Wittig and Horner-Emmons olefinations employing readily available phosphonium salts. These findings led to the development of simple to perform one-pot Wittig-Suzuki, Wittig-Heck, Horner-Emmons-Suzuki, and Horner-Emmons-Heck hyphenated transformations, and the study the scope of these transformations which resulted in the synthesis of a diverse pool of biaryls, diarylethenes, and aryl-enoates. The feasibility to recycle and re-use the IL solvent was also investigated.

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**Chart 1.** Recycling and reuse of [BMIM][X].

Footnotes. X axis: number of cycles; Y axis: isolated yields; red: [BMIM][PF₆]; blue: [BMIM][BF₄].

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