A highly efficient and recyclable $Pd(PPh_3)_4$/PEG-400 system for Stille cross-coupling reactions of organostannanes with aryl bromides

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$Pd(PPh_3)_4$ in PEG-400 is shown to be a highly efficient catalyst for the Stille cross-coupling reactions of various organotin compounds with aryl bromides. The reaction could be conducted at 80 °C using NaOAc as base, yielding a variety of biaryls, alkynes and alkenes in good to excellent yields. The isolation of the products was readily performed by extraction with petroleum ether and the $Pd(PPh_3)_4$/PEG-400 system could be easily recycled and reused five times without any significant loss of activity.

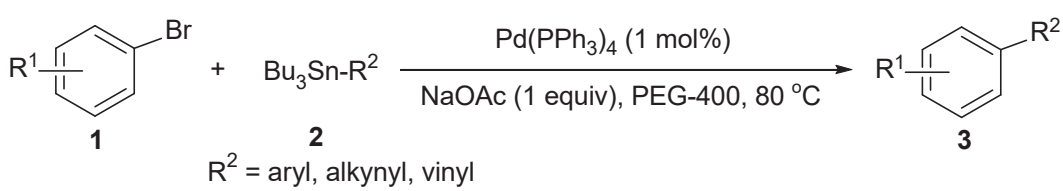
Keywords: palladium, Stille coupling, aryl bromide, PEG-400

The palladium-catalysed cross-coupling of organostannanes with organic halides and triflates, known as the Stille reaction, represents one of the most important transformations in constructing carbon–carbon bonds in organic synthesis.[1–5] The Stille reaction has been widely applied in organic synthesis[6–10] since a wide range of functionality can be tolerated on either coupling partner. The yields of cross-coupled products are often high and the organotin reagents can be readily prepared, purified and stored. However, most of these reactions are performed in organic solvents with a homogeneous palladium complex such as $Pd(PPh_3)_4$, $PdCl_2(PPh_3)_2$ and $PdCl_2(MeCN)_2$ as catalyst or catalyst precursor, which makes the recovery of the metal tedious if not impossible and might result in unacceptable palladium contamination of the product. These problems are of particular environmental and economic concern in industry, especially the pharmaceutical industry. Therefore, from the standpoint of green and sustainable chemistry, the avoidance of any use of hazardous and expensive organic solvents and the development of a recyclable and reusable catalyst system that allows for highly efficient Stille cross-coupling is highly desirable. The issue of potential contamination with toxic organotin remains.

To satisfy both recyclability and environmental concerns, a simple and efficient method is to immobilise the catalyst in a liquid phase by dissolving it into a non-volatile and non-mixing liquid, such as an ionic liquid[11–15] or a polyethylene glycol (PEG).[16–23] Ionic liquids have some disadvantages, such as a complicated method for their preparation. Their environmental safety is still debated since toxicity and environmental burden data are not available for most ionic liquids. By contrast, PEGs are commercially readily available and inexpensive, thermally stable, recoverable, biodegradable and non-toxic compounds, which serve as efficient media for environmentally friendly and safe chemical reactions.[24–26] In recent years, PEGs have been widely utilised as reaction media for a range of palladium-catalysed carbon–carbon bond formation reactions such as the Heck coupling,[16,17] Suzuki-Miyaura coupling,[18,19] the homocoupling and cross-coupling of aryl halides,[20] the direct arylation of 1,2,3-triazoles with aryl bromides[21] and carbonylative Suzuki[22] or Sonogashira[23] cross-couplings with facile recyclability of solvents and palladium catalysts. Recently, J.-X. Wang and co-workers reported a palladium-catalysed atom-efficient Stille cross-coupling reaction of tetraphenylstannane with aryl bromides in PEG-400, but no recyclability of the catalytic system was described.[27,28] To the best of our knowledge, the cross-coupling reactions of alkynylstannanes and vinylstannanes with aryl halides in PEGs have not been reported thus far. We report here the application of the $Pd(PPh_3)_4$/PEG-400 system as a highly efficient and reusable catalytic medium for the Stille cross-coupling reactions of various organotin compounds with aryl bromides leading to a variety of biaryls, alkynes and alkenes in good to excellent yields (Scheme 1).

Results and discussion

Initially, the Stille cross-coupling of 4-bromobenzonitrile with $PhSnBu_3$ in PEG-400 was chosen as a model reaction to determine the optimum conditions and the results are summarised in Table 1. Firstly, the effect of base on the model reaction was examined by using $Pd(PPh_3)_4$ as the catalyst at 80 ºC (Table 1, entries 1–6). Of the bases tested, K_3PO_4, KF, $NaHCO_3$ and NaOAc afforded good yields of product with NaOAc giving the best result, whilst K_2CO_3 and Na_2CO_3 were substantially less effective. We next turned our attention to the effect of catalyst on the model reaction. When other palladium catalysts such as $PdCl_2(PPh_3)_2$, $PdCl_2(PhCN)_2$ and $Pd(OAc)_2/2PPh_3$ were used, the desired 4-cyanonbiphenyl was obtained in lower yields (Table 1, entries 7–9), so $Pd(PPh_3)_4$ was the best choice. For the temperatures evaluated (60, 80 and 100 °C), 80 °C was found to be the most efficient (Table 1, entries 6, 10 and 11). Finally, the amount of catalyst was also screened. Reducing the quantity of the catalyst resulted in a



Scheme 1

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Table 1 Optimisation of the Stille cross-coupling of 4-bromobenzonitrile with $PhSnBu_3$[a]

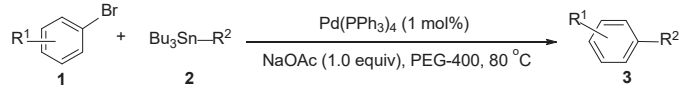
Entry	Catalyst	Base	Temp. (ºC)	Time (h)	Yield (%)[b]
1	$Pd(PPh_3)_4$	K_2CO_3	80	6	49
2	$Pd(PPh_3)_4$	Na_2CO_3	80	6	37
3	$Pd(PPh_3)_4$	K_3PO_4	80	5	78
4	$Pd(PPh_3)_4$	KF	80	5	74
5	$Pd(PPh_3)_4$	$NaHCO_3$	80	5	62
6	$Pd(PPh_3)_4$	NaOAc	80	3	91
7	$PdCl_2(PPh_3)_2$	NaOAc	80	3	83
8	$PdCl_2(PhCN)_2$	NaOAc	80	6	65
9	$Pd(OAc)_2/2PPh_3$	NaOAc	80	6	61
10	$Pd(PPh_3)_4$	NaOAc	60	8	69
11	$Pd(PPh_3)_4$	NaOAc	100	2	88
12[c]	$Pd(PPh_3)_4$	NaOAc	80	8	76
13[d]	$Pd(PPh_3)_4$	NaOAc	80	2	90

[a]Reaction conditions: 4-bromobenzonitrile (0.5 mmol), $PhSnBu_3$ (0.6 mmol), catalyst (1 mol%), base (0.5 mmol) in PEG-400 (2 mL) under Ar.
[b]Isolated yield.
[c]0.5 mol% catalyst was used.
[d]2 mol% catalyst was used.

decreased yield and a longer reaction time (Table 1, entry 12). Increasing the amount of the catalyst could shorten the reaction time, but did not improve the yield (Table 1, entry 13). Taken together, excellent results were obtained when the coupling reaction was carried out under Ar for 3 h with 1 mol% of $Pd(PPh_3)_4$ as the catalyst and NaOAc (1.0 equiv.) as the base in PEG-400 at 80 °C (Table 1, entry 6).

With the optimised conditions established, we investigated the scope of this palladium(0)-catalysed Stille cross-coupling reaction. The results are listed in Table 2. Firstly, the Stille cross-coupling reactions of aryl bromides with tributyl(phenyl) stannane were investigated under the optimised conditions. As shown in Table 2, both electron-deficient and electron-rich aryl bromides were good substrates and gave the desired biphenyls **3a–d** in excellent yields (Table 2, entries 1–4). The developed methodology was also applicable for the Stille cross-coupling reactions of alkynylstannanes and alkenylstannanes with aryl bromides. The Stille coupling reactions of tributyl(phenylethynyl)stannane with aryl bromides also proceeded smoothly at 80 ºC in PEG-400 with NaOAc as base to give the corresponding diaryl alkynes **3e–i** in good to excellent yields (Table 2, entries 5–9). The reactivity of aryl bromides with an electron-withdrawing group was higher than that of aryl bromides with an electron-donating group. In addition, aliphatic alkynylstannanes such as tributyl(hex-1-ynyl)stannane, tributyl(3-methoxyprop-1-ynyl)stannane and 1-tributylstannyl-2-trimethylsilylethyne were also good coupling partners and coupled effectively with a variety of aryl bromides to afford the desired alkyl- and aryl-substituted alkynes **3j–m** and trimethylsilyl- and aryl-substituted alkynes **3n** and **3o** in high yields (Table 2, entries 10–15), the trimethylsilyl group remaining intact. The reactions of tributyl(vinyl)stannane with aryl bromides gave the substituted styrenes **3p–r** in good yields (Table 2, entries 16–18). To our delight, the Stille cross-coupling reactions of a variety of aryl bromides with (*E*)- or (*Z*)-alkenylstannanes also proceeded smoothly at 80 ºC in PEG-400 to afford the corresponding cross-coupled products in high yields with retention of configuration (Table 2, entries 19–26). The reactivity of the electron-deficient aryl bromides was higher than that of the electron-rich aryl bromides. The optimised catalyst system was quite general and compatible

Table 2 Stille cross-coupling reactions of organostannanes with aryl bromides[a]



Entry	R^1	R^2	Time (h)	Product	Yield (%)[b]
1	H	Ph	3	**3a**	91
2	4-Me	Ph	3	**3b**	93
3	4-NC	Ph	3	**3c**	91
4	4-MeCO	Ph	3	**3d**	92
5	H	PhC≡C	4	**3e**	89
6	$4\text{-}O_2N$	PhC≡C	3	**3f**	93
7	4-MeOCO	PhC≡C	3	**3g**	92
8	4-MeO	PhC≡C	5	**3h**	82
9	4-Me	PhC≡C	4	**3i**	85
10	4-Cl	$n\text{-}C_4H_9C{\equiv}C$	4	**3j**	87
11	3-NC	$n\text{-}C_4H_9C{\equiv}C$	4	**3k**	88
12	3-Me	$n\text{-}C_4H_9C{\equiv}C$	5	**3l**	82
13	H	$MeOCH_2C{\equiv}C$	4	**3m**	88
14	4-Cl	$Me_3SiC{\equiv}C$	4	**3n**	85
15	4-MeO	$Me_3SiC{\equiv}C$	5	**3o**	81
16	4-NC	$CH_2{=}CH$	3	**3p**	89
17	$4\text{-}O_2N$	$CH_2{=}CH$	3	**3q**	83
18	4-MeCO	$CH_2{=}CH$	3	**3r**	86
19	4-MeO	(*E*)-BuCH=CH	5	**3s**	81
20	4-Cl	(*E*)-BuCH=CH	4	**3t**	87
21	4-MeO	(*E*)-PhCH=CH	5	**3u**	85
22	4-Me	(*E*)-PhCH=CH	4	**3v**	90
23	3-NC	(*Z*)-BuCH=CH	3	**3w**	86
24	$4\text{-}O_2N$	(*Z*)-BuCH=CH	3	**3x**	89
25	4-Me	(*Z*)-PhCH=CH	4	**3y**	83
26	$4\text{-}O_2N$	(*Z*)-PhCH=CH	3	**3z**	87

[a]Reaction conditions: aryl bromide (0.5 mmol), organotin reagent (0.6 mmol), $Pd(PPh_3)_4$ (1 mol%), NaOAc (0.5 mmol) in PEG-400 (2 mL) at 80 ºC under Ar.
[b]Isolated yield.

with a wide range of functional groups such as nitro, cyano, chloro, methoxy, carbonyl and silyl on either coupling partner.

To examine the reusability of $Pd(PPh_3)_4$ and PEG-400, the cross-coupling reaction of methyl 4-bromobenzoate (0.5 mmol) with tributyl(phenylethynyl)stannane (0.6 mmol) was evaluated in the presence of $Pd(PPh_3)_4$ (1.0 mol%) and NaOAc (0.5 mmol) in PEG-400 (2.0 mL) at 80 ºC for 3 h. As demonstrated in Fig. 1, we were pleased to observe that the $Pd(PPh_3)_4$/PEG-400 system could be recycled and reused five times without observing any significant loss of catalytic activity. After the first experiment, the reaction mixture was extracted three times with light petroleum ether (30–60 °C) and the $Pd(PPh_3)_4$/PEG-400 system was then subjected to a second run of the reaction by charging with the same substrates [methyl 4-bromobenzoate, tributyl(phenylethynyl)stannane and NaOAc] without the addition of $Pd(PPh_3)_4$. The results of six runs showed that they were almost consistent in yields within an average reaction time of 4 h (92, 91, 90, 91, 89 and 89% respectively). We also determined the amount of palladium in the product **3g** isolated after the first cycle by inductively coupled plasma atom emission spectrometry (ICP-AES) analysis. It was found that only 0.3 ppm of palladium was detected in the isolated product **3g**.

In conclusion, a highly efficient $Pd(PPh_3)_4$/PEG-400 system for the Stille cross-coupling reaction of various organotin compounds with aryl bromides has been developed. In the presence of $Pd(PPh_3)_4$ (1 mol%), the reactions of a variety of aryl bromides with various organotin compounds proceeded smoothly and efficiently at 80 °C using NaOAc (1.0 equiv.) as base in PEG-400 to furnish the corresponding cross-coupled products in good to excellent yields. The $Pd(PPh_3)_4$/PEG-

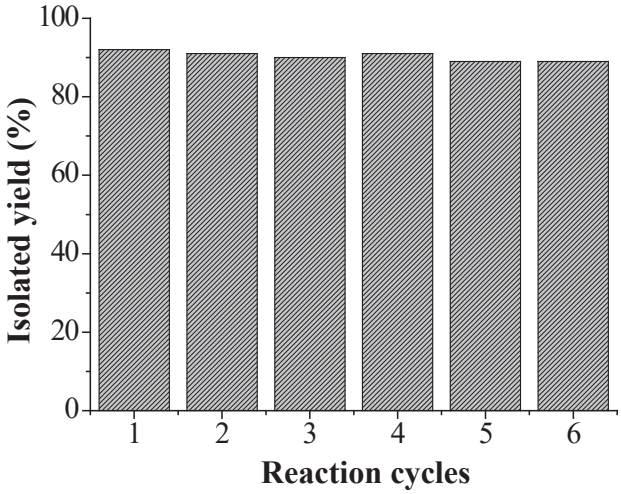


Fig. 1 Recycling of the catalytic system.

400 system could be recycled and reused five times without observing any significant loss of catalytic activity. This protocol will serve as an efficient and practical method for the synthesis of a variety of biaryls, alkynes and alkenes although the use of toxic organotin reagents, in excess, has to be acknowledged. Currently, further efforts to extend the application of this system to other palladium-catalysed transformations are underway in our laboratory.

Experimental

All reagents were used as received without further purification. Both tributyl(phenyl) stannane and tributyl(vinyl)stannane were purchased from Sigma-Aldrich Co. Alkynylstannanes,[29] (*Z*)-vinylstannanes[30] and (*E*)-vinylstannanes[31] were prepared according to literature methods. All reactions were carried out under an atmosphere of Ar in oven-dried glassware with magnetic stirring. FTIR spectra were obtained on a Nicolet MAGNA-IR 750 spectrometer. ^{1}H NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400 Mhz with TMS as an internal standard using $CDCl_3$ as the solvent. ^{13}C NMR spectra were recorded on the Bruker Avance 400 spectrometer at 100 Mhz using $CDCl_3$ as the solvent. Palladium content in the product was determined with ICP-AES. Microanalyses were obtained using a PerkinElmer 240 elemental analyser.

Stille cross-coupling reaction of organotin reagents with aryl bromides in PEG-400; general procedure

A mixture of aryl bromide **1** (0.5 mmol), organotin reagent **2** (0.6 mmol), NaOAc (0.5 mmol) and $Pd(PPh_3)_4$ (0.005 mmol) in PEG-400 (2 mL) was stirred at 80 °C under an argon atmosphere for 3–5 h until complete consumption of the aryl bromide was observed as judged by TLC. After being cooled to room temperature, the mixture was extracted three times with light petroleum ether (30–60 °C) (3 × 10 mL). The combined organic phases were concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel [light petroleum ether (30–60 °C)/ethyl acetate] to afford the desired product **3**.

The mixture of $Pd(PPh_3)_4$ and PEG-400 was then subjected to a second run of the reaction by charging with the same substrates (aryl bromide **1**, organotin reagent **2** and NaOAc) under the same conditions without further addition of $Pd(PPh_3)_4$.

Biphenyl (**3a**): White solid; m.p. 68–70 ºC (lit.[32] 69–70 ºC); IR (KBr): 3033, 1569, 1478, 730, 690 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.63–7.53 (m, 4H), 7.43 (t, *J* = 7.6 Hz, 4H), 7.34 (t, *J* = 7.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.1, 128.9, 127.3, 127.2.

4-Methylbiphenyl (**3b**): White solid; m.p. 45–46 ºC (lit.[32] 46–47 ºC); IR (KBr): 3053, 1486, 823, 757, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 2H), 7.48 (d, *J* = 7.6 Hz, 2H), 7.43–7.38 (m, 2H), 7.33–7.28 (m, 1H), 7.23 (d, *J* = 7.6 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.2, 138.4, 137.0, 129.5, 128.7, 127.3, 127.2, 127.0, 21.1.

4-Cyanobiphenyl (**3c**): White solid; m.p. 85–86 ºC (lit.[32] 86–87 ºC); IR (KBr): 2226, 1605, 1483, 848, 770, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 7.6 Hz, 2H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 145.7, 139.2, 132.6, 129.1, 128.7, 127.8, 127.2, 119.0, 110.9.

4-Acetylbiphenyl (**3d**): White solid; m.p. 119–121 ºC (lit.[32] 120–122 ºC); IR (KBr): 2999, 1681, 1602, 1264, 961, 766 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.02 (d, *J* = 7.6 Hz, 2H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.62 (d, *J* = 7.6 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.42–7.38 (m, 1H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.7, 145.7, 139.9, 135.9, 129.0, 128.9, 128.2, 127.3, 127.2, 26.6.

1,2-Diphenylacetylene (**3e**): White solid; m.p. 60–61 °C (lit.[33] 59–60 ºC); IR (KBr): 3063, 1599, 1492, 756, 689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55–7.52 (m, 4H), 7.37–7.32 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 131.6, 128.4, 128.3, 123.3, 89.4.

1-(4-Nitrophenyl)-2-phenylacetylene (**3f**): Yellow solid; m.p. 120–121 °C (lit.[33] 121–122 ºC); IR (KBr): 3082, 2217, 1592, 1511, 1495, 858, 765, 690 cm^{-1}; ^{1}H 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 146.9, 132.3, 131.8, 130.3, 129.3, 128.5, 123.7, 122.1, 94.7, 87.5.

Methyl 4-phenylethynylbenzoate (**3g**): White solid; m.p. 120 °C (lit.[33] 119–120 ºC); IR (KBr): 2948, 2218, 1717, 1605, 1438, 1109, 770 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.04–8.02 (m, 2H), 7.61–7.58 (m, 2H), 7.56–7.54 (m, 2H), 7.38–7.36 (m, 3H), 3.93 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 131.8, 131.5, 129.5, 129.4, 128.8, 128.5, 128.0, 122.7, 92.4, 88.6, 52.3.

1-(4-Methoxyphenyl)-2-phenylacetylene (**3h**): White solid; m.p. 58–59 °C (lit.[33] 59–60 ºC); IR (KBr): 3024, 2212, 1602, 1498, 1185, 835, 750, 690 cm^{-1}; ^{1}H 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 159.5, 133.0, 131.4, 128.3, 127.9, 123.4, 115.5, 113.9, 89.4, 88.1, 55.2.

1-(4-Methylphenyl)-2-phenylacetylene (**3i**): White solid; m.p. 73–74 °C (lit.[33] 75–76 ºC); IR (KBr): 3029, 2968, 2859, 2215, 1594, 1509, 818, 690 cm^{-1}; ^{1}H 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 138.4, 131.6, 131.5, 129.1, 128.3, 128.1, 123.5, 120.2, 89.6, 88.7, 21.5.

1-(4-Chlorophenyl)hex-1-yne (**3j**): Colourless liquid; IR (neat): 2959, 2932, 2232, 1489, 1466, 827, 753 cm^{-1}; ^{1}H 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. Anal. calcd for $C_{12}H_{13}Cl$: C, 74.78; H, 6.80; found: C, 74.52; H, 6.91%.

1-(3-Cyanophenyl)hex-1-yne (**3k**): Colourless liquid; IR (neat): 3069, 2958, 2873, 2232, 2227, 1597, 1478, 896, 798, 683 cm^{-1}; ^{1}H 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 135.7, 135.0, 130.7, 129.1, 125.7, 118.3, 112.6, 93.4, 78.5, 30.5, 22.0, 19.1, 13.7. Anal. calcd for $C_{13}H_{13}N$: C, 85.21; H, 7.15; N, 7.64; found: C, 85.02; H, 6.91; N, 7.41%.

1-(3-Methylphenyl)hex-1-yne (**3l**): Colourless oil; IR (neat): 3037, 2959, 2932, 2228, 1603, 1580, 783 cm^{-1}; ^{1}H 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 137.8, 132.2, 128.6, 128.4, 128.1, 123.9, 90.0, 80.7, 30.9, 22.1, 21.2, 19.1, 13.7. Anal. calcd for $C_{13}H_{16}$: C, 90.64; H, 9.36; found: C, 90.48; H, 9.23%.

1-Phenyl-3-methoxyprop-1-yne (**3m**): Colourless liquid; IR (neat): 2930, 2237, 1599, 1490, 1099, 757, 691 cm^{-1}; ^{1}H 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 131.8, 128.4, 128.3, 122.7, 86.4, 84.9,

60.4, 57.7. Anal. calcd for $C_{10}H_{10}O$: C, 82.16; H, 6.84; found: C, 81.93; H, 6.61%.

1-(4-Chlorophenyl)-2-trimethylsilylacetylene (**3n**):[34] Colourless liquid; IR (neat): 3030, 2159, 1590, 1488, 1250, 844, 759, 685 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.4 Hz, 2H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 134.6, 133.2, 128.6, 121.7, 103.9, 95.4, –0.1.

1-(4-Methoxyphenyl)-2-trimethylsilylacetylene (**3o**):[34] Colourless liquid; IR (neat): 2156, 1606, 1508, 1249, 834, 756, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41 (d, *J* = 8.8 Hz, 2H), 6.81 (d, *J* = 8.8 Hz, 2H), 3.81 (s, 3H), 0.24 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.7, 133.5, 115.3, 113.8, 105.2, 92.5, 55.3, 0.1.

4-Vinylbenzonitrile (**3p**):[35] Colourless liquid; IR (neat): 3068, 2227, 1629, 1606, 1508, 1405, 846 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.49 (d, *J* = 8.4 Hz, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.88 (d, *J* = 17.6 Hz, 1H), 5.45 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.9, 135.3, 132.4, 126.7, 118.9, 117.7, 111.1.

1-Nitro-4-vinylbenzene (**3q**):[35] Colourless liquid; IR (neat): 3014, 1633, 1531, 1485, 1348, 1314, 921, 852 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 6.78 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.94 (d, *J* = 17.6 Hz, 1H), 5.51 (d, *J* = 10.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.1, 143.8, 134.9, 126.8, 123.9, 118.6.

1-Acetyl-4-vinylbenzene (**3r**): White solid; m.p. 33–34 °C (lit.[35] 35–36 ºC); IR (KBr): 3054, 2987, 1681, 1605, 1265, 739, 705 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 6.75 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.87 (d, *J* = 17.6 Hz, 1H), 5.40 (d, *J* = 10.9 Hz, 1H), 2.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.5, 142.1, 136.3, 135.9, 128.7, 126.3, 116.7, 26.6.

(E)-1-(4-Methoxyphenyl)hex-1-ene (**3s**): Colourless oil; IR (neat): 2957, 1608, 1577, 1464, 1174, 1038, 965, 804 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.27 (d, *J* = 8.4 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 6.32 (d, *J* = 16.0 Hz, 1H), 6.09 (dt, *J* = 16.0, 7.2 Hz, 1H), 3.80 (s, 3H), 2.22–2.16 (m, 2H), 1.47–1.34 (m, 4H), 0.93 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 158.6, 130.9, 129.1, 129.0, 127.0, 113.9, 55.3, 32.7, 31.7, 22.3, 14.0. Anal. calcd for $C_{13}H_{18}O$: C, 82.06; H, 9.54; found: C, 82.25; H, 9.71%.

(E)-1-(4-Chlorophenyl)hex-1-ene (**3t**): Colourless oil; IR (neat): 2957, 1593, 1490, 1469, 966, 809 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.30 (d, *J* = 16.0 Hz, 1H), 6.20 (dt, *J* = 16.0, 7.2 Hz, 1H), 2.21–2.18 (m, 2H), 1.47–1.32 (m, 4H), 0.92 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.7, 134.2, 132.0, 130.5, 128.6, 127.1, 32.7, 31.5, 22.3, 14.0. Anal. calcd for $C_{12}H_{15}Cl$: C, 74.01; H, 7.76; found: C, 73.79; H, 7.57%.

(E)-1-(4-Methoxyphenyl)-2-phenylethene (**3u**): White solid; m.p. 134–135 °C (lit.[36] 135–136 ºC); IR (KBr): 2963, 1602, 1513, 1112, 967, 813 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.6 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.25–7.23 (m, 1H), 7.07 (d, *J* = 16.4 Hz, 1H), 6.97 (d, *J* = 16.4 Hz, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.3, 137.7, 130.2, 128.6, 128.2, 127.7, 127.2, 126.7, 126.3, 114.2, 55.3.

(E)-1-(4-Methylphenyl)-2-phenylethene (**3v**): White solid; m.p. 117–118 °C (lit.[36] 118–119 ºC); IR (KBr): 3023, 1643, 1594, 1511, 970, 809, 690 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, *J* = 7.6 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.26–7.22 (m, 1H), 7.16 (d, *J* = 8.0 Hz, 2H), 7.07 (s, 2H), 2.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.6, 137.5, 134.6, 129.4, 128.7, 128.6, 127.7, 127.4, 126.5, 126.4, 21.3.

(Z)-1-(3-Cyanophenyl)hex-1-ene (**3w**): Colourless oil; IR (neat): 3065, 2958, 2927, 2230, 1643, 1597, 1575, 1465, 806, 687 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.54 (s, 1H), 7.51–7.40 (m, 3H), 6.36 (d, *J* = 11.6 Hz, 1H), 5.78 (dt, *J* = 11.6, 7.2 Hz, 1H), 2.31–2.25 (m, 2H), 1.48–1.32 (m, 4H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.9, 135.8, 133.1, 132.1, 129.9, 129.0, 126.6, 119.0, 112.3, 31.9, 28.3, 22.4, 13.9. Anal. calcd for $C_{13}H_{15}N$: C, 84.28; H, 8.16; N, 7.56; found: C, 84.05; H, 7.97; N, 7.38%.

(Z)-1-(4-Nitrophenyl)hex-1-ene (**3x**): Yellow oil; IR (neat): 2958, 2929, 1640, 1596, 1516, 1343, 856 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 6.44 (d, *J* = 11.6 Hz, 1H), 5.87 (dt, *J* = 11.6, 7.2 Hz, 1H), 2.34–2.30 (m, 2H), 1.48–1.44 (m, 2H), 1.38–1.32 (m, 2H), 0.90 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.2, 144.6, 137.2, 129.3, 127.0, 123.5, 31.8, 28.5, 22.4, 13.9. Anal. calcd for $C_{12}H_{15}NO_2$: C, 70.22; H, 7.37; N, 6.82; found: C, 70.42; H, 7.51; N, 6.59%.

(Z)-1-(4-Methylphenyl)-2-phenylethene (**3y**): Colourless oil; IR (neat): 3012, 1629, 1599, 1492, 821, 772 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.28–7.19 (m, 5H), 7.15 (d, *J* = 8.0 Hz, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 6.56 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 137.4, 136.9, 134.3, 130.2, 129.6, 128.9, 128.8, 128.7, 128.2, 127.0, 21.3. Anal. calcd for $C_{15}H_{14}$: C, 92.74; H, 7.26; found: C, 92.50; H, 7.31%.

(Z)-1-(4-Nitrophenyl)-2-phenylethene (**3z**): Yellow solid; m.p. 60–61 °C; IR (KBr): 1627, 1592, 1505, 1342, 856, 778, 696 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H), 7.26–7.19 (m, 5H), 6.82 (d, *J* = 12.4 Hz, 1H), 6.62 (d, *J* = 12.4 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 146.6, 144.2, 136.1, 134.0, 129.7, 128.8, 128.6, 128.0, 127.9, 123.6. Anal. calcd for $C_{14}H_{11}NO_2$: C, 74.65; H, 4.92; N, 6.22; found: C, 74.38; H, 4.71; N, 6.04%.

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