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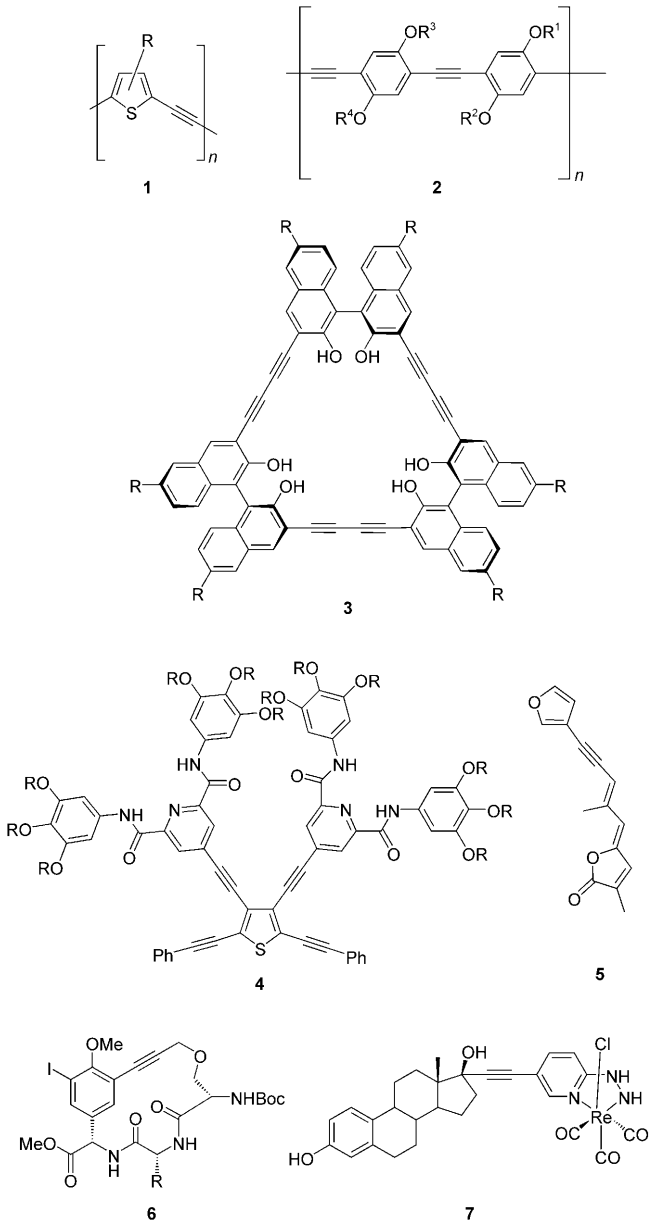
Improved Palladium-Catalyzed Sonogashira Coupling Reactions of Aryl Chlorides

Christian Torborg, Jun Huang, Thomas Schulz, Benjamin Schäffner, Alexander Zapf, Anke Spannenberg, Armin Börner, and Matthias Beller*[a]

The construction of C_{sp}–(aryl)C_{sp^2} bonds is an important transformation in organic chemistry. The resulting aryl alkynes are building blocks often encountered within natural products, pharmaceutical products, and molecular materials.[1] Due to the highly conjugated π system, this structural motif is found in organic semiconductors, and the respective products act as molecular sensors, light-emitting diodes, or polarizers for liquid-crystalline displays.[2] In recent years polyaryleneethynylenes (PAEs) and oligoaryleneethynylenes (OAEs) such as **1** and **2** (Scheme 1) have become an established class of conjugated polymers in addition to poly(*p*-phenylenevinylene)s (PPVs) and polyacetylenes. Moreover, arylene–ethynylene macrocycles (AEMs) (e.g. **3**) and macromolecules such as **4** possess interesting electronic properties and lead to defined nanostructures.[3,4] Apart from material science, the construction of aryl alkynes plays an important role in the synthesis of complex molecules of pharmaceutical and agrochemical interest (e.g. **5**,[5] **6**,[6] **7**[7]), even though the arylene–ethynylene structure itself does not often occur in natural products, which is in marked contrast to the corresponding vinylene–ethynylene motif.[8] However, the alkynylation of aromatic halides and subsequent cyclization is a widely used method for the synthesis of carbo-[9] and heterocycles[10] as well as intermediates of natural products.[11] It is undeniable that the most effective way to form aryl–alkyne bonds is still palladium-catalyzed coupling reactions of aromatic halides with alkynes in the presence of base and copper co-catalysts. Although this reaction was independently discovered by Cassar, Heck, and Sonogashira in 1975,[12] today it is generally known as the Sonogashira reaction, and numerous catalytic systems have been reported for this



Scheme 1. Examples for structures bearing the arylene–ethynylene motif.

[a] C. Torborg, Dr. J. Huang, T. Schulz, B. Schäffner, Dr. A. Zapf, Dr. A. Spannenberg, Prof. Dr. A. Börner, Prof. Dr. M. Beller
Leibniz-Insitut für Katalyse e. V. an der Universität Rostock
Albert-Einstein-Strasse 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-5000
E-mail: matthias.beller@catalysis.de

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transformation.[13] During the last few years important catalyst developments have been described such as the minimization of the catalyst amount,[14] the activation of less-reactive starting materials (aryl chlorides, alkyl halides),[15] the selective transformation of more functionalized substrates,[16] and the application of cost effective and/or sustainable methods.[17] With respect to the latter point, aryl–alkyne coupling methods catalyzed by more cost-effective metals such as iron[18] or copper[19] have become an interesting alternative to Pd-catalyzed procedures regarding the efficient coupling of aryl iodides. However, so far there is no general procedure for the efficient coupling of deactivated aryl bromides and inexpensive aryl chlorides with these metals. A generally accepted mechanism[20] of the Sonogashira reaction consists of two catalytic cycles: a) the 'classic' palladium-based coupling reaction that involves the oxidative addition of an aryl (vinyl) halide (or triflate) R^1–X to a low-coordinate palladium(0) complex, then transmetalation of a copper-acetylide (formed in the second catalytic cycle) to generate a $R^1Pd(-C\equiv CR^2)L_2$ species, which subsequently undergoes a *cis–trans* isomerzation and reductive elimination to give the aryl (vinyl)–alkyne and the regenerated catalyst; and b) the so-called 'copper-cycle', in which the copper–acetylide is generated from the free alkyne in the presence of a base, which is often an amine. This latter cycle is poorly understood: for example, the in situ formation of a copper acetylide is not proven yet, although recently indirect evidence has been found.[21] In fact, most of the amines used are not basic enough to deprotonate the alkyne to provide an anionic species which can further react to the corresponding copper acetylide. Therefore, a π-alkyne–Cu complex, which makes the alkyne proton more acidic, is often proposed as an intermediate. With respect to further catalyst developments the application of copper-free (and also amine-free) protocols is of importance due to the environmental and economical advantages. However, to date, only a few examples of Sonogashira reactions without copper source have been described. Notably, Gelman and Buchwald discovered in 2003 a catalyst system consisting of $[PdCl_2(CH_3CN)_2]$ and the so-called XPhos ligand, which allowed a general coupling of aryl chlorides and aryl tosylates with various terminal alkynes.[15c,22] Although desilylation of trimethylsilylacetylene, an important substrate in the synthesis of larger molecules, was observed during the reaction, an excellent substrate scope was demonstrated. Interestingly from a mechanistic viewpoint, the same authors reported that the presence of copper iodide in the coupling of aryl chlorides with alkynes inhibits coupling reactions. Copper-free Sonogashira reactions were also described in water.[23] More recently, Yi et al. reported in 2006 the application of $[PdCl_2(PCy_3)_2]$ in the coupling of various aryl chlorides with alkynes under copper-free conditions with 3 mol% catalyst at 100–150 °C.[24] Activation of the alkyne without copper is supposed to proceed via formation of a $(\eta^2\text{-}RC\equiv CH)Pd^0L_2$ species.[25,26] However, the term 'copper-free' should be considered carefully, since commercially available palladium salts can contain traces of copper.[27]

For some years we have been interested in the development of palladium catalysts that can be applied for coupling reactions on both laboratory as well as industrial scale. In this respect we have developed palladacycles,[28] adamantylphosphines,[29] carbene ligands,[30] and 2-phosphino-*N*-arylindoles and -pyrroles.[31] More recently, we also reported the synthesis of 2-phosphino-*N*-arylimidazoles and their application in cross-coupling reactions of aryl chlorides and bromides.[32] Importantly, such monodentate *N*-substituted heteroaryl phosphines are conveniently synthesized by selective metalation at the 2-position of the respective *N*-substituted heterocycle (pyrrole, indole, imidazole). Thus, a variety of novel ligands is easily available and can be efficiently prepared in a modular synthesis. This is an important aspect, since the application of palladium-catalyzed coupling reactions in the fine chemical and pharmaceutical industry requires in general a fine-tuning of the catalytic system. Here, we describe for the first time the use of *N*-aryl-heteroarylphosphines in Sonogashira coupling reactions of aryl chlorides without the necessity to add copper salts. Inspired by the work of the Buchwald group on XPhos,[33] we synthesized the novel ligand [*N*-(2,6-diisopropylphenyl)-2-imidazolyl]-di-*tert*-butylphosphine L1 (Figure 1).

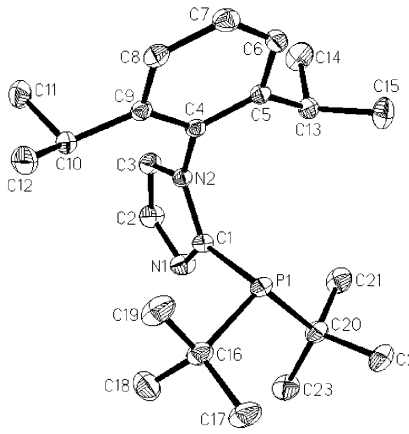
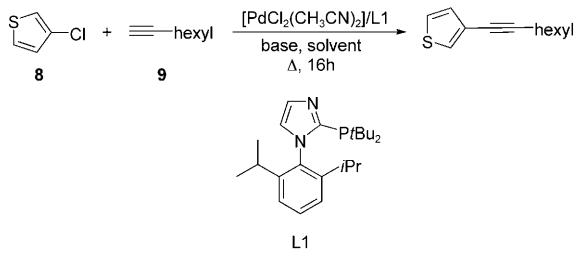


Figure 1. Molecular structure of L1. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

Advantageously, this ligand is formed straightforwardly from easily available substrates (2,6-diisopropylamine, glyoxal, formaldehyde,[34] and chloro-di-*tert*-butylphosphine) in two steps. For our catalytic studies we chose the reaction of 3-chlorothiophene (**8**) and 1-octyne (**9**), which is a more challenging coupling reaction. Propylene carbonate (PC) was first chosen as solvent for the reaction. Its usage in coupling reactions offers several advantages including the possibility of catalyst recycling a) via extraction of the nonpolar product with nonpolar solvents from the reaction mixture[35] or b) as PC can form part of temperature-dependent multicomponent solvent systems (TMS systems).[36] To our delight the reaction proceeded with 1 mol% $[PdCl_2(CH_3CN)_2]$ and 8 mol% of phosphine ligand L1 in 76% yield at 90 °C (Table 1, entry 1).[37] Unfortunately, decreasing the Pd/ligand

Table 1. Sonogashira coupling of 3-chlorothiophene and 1-octyne without copper.[a]



Entry	Pd [mol%]	L [mol%]	Solvent	Base	Conv. [%]	Yield [%][b]
1	1	8	PC	Cs_2CO_3	8	76
2	1	3	PC	Cs_2CO_3	3	25
3	2	6	PC	Cs_2CO_3	4	30
4	1	8	toluene	Na_2CO_3	80	71
5	1	3	toluene	Na_2CO_3	73	68
6	1	2	toluene	Na_2CO_3	18	18
7	1	1	toluene	Na_2CO_3	10	10
8[c]	1	3	toluene	Na_2CO_3	90	87
9[d]	1	3	toluene	Na_2CO_3	45	45
10[e]	1	3	toluene	Na_2CO_3	18	2
11[f]	1	1	toluene	Na_2CO_3	60	40
12[g]	1	3	toluene	Na_2CO_3	90	86

[a] Reaction conditions: 3-chlorothiophene (1 equiv), 1-octyne (1.3 equiv), base (2.6 equiv), solvent (0.5 M), 16 h (reaction times not optimized). [b] GC yields (internal standard: hexadecane). [c] 2 equiv of 1-octyne and 4 equiv of base. [d] $Pd(OAc)_2$. [e] 1 mol% of CuI. [f] 2 equiv of 1-octyne and 4 equiv of base, 1 mol% of complex **10**. [g] 2 equiv of 1-octyne and 4 equiv of base, 1 mol% of complex **10**, 2 mol% L1.

ratio from 1:8 to 1:3 lowered the product yield (Table 1, entries 2 and 3) significantly. Apparently, the reaction in propylene carbonate needs an excess of ligand, which may be explained by partial displacement of the ligand by solvent molecules.[38] In contrast to the reaction in propylene carbonate, the Sonogashira coupling in toluene with sodium carbonate as base yielded the desired 3-octinylthiophene in good yield at lower ligand concentration (Table 1, entries 4 and 5). However, an excess of ligand is obviously needed (Table 1, entries 6 and 7). The best yield is obtained by addition of two equivalents of the alkyne (Table 1, entry 9, 87% yield); most likely because the Pd^{II} species is reduced to the catalytically active Pd^0 species by the alkyne in the first place. After a standard procedure,[39] complex **10** was prepared from one equivalent of $[PdCl_2(CH_3CN)_2]$ and one equivalent of L1. Remarkably, X-ray analysis showed a η^2-P,N chelation of L1 to the metal center (Figure 2).[40] Time-dependent ^{31}P NMR experiments showed that this complex is also formed from a mixture of one equivalent of $[PdCl_2(CH_3CN)_2]$ and three equivalents of L1 in propylene carbonate as well as in toluene. Therefore it is most likely that it is also present in the reaction mixture and should act as a precursor for a monoligated Pd^0 species. Monoligated Pd^0 species are supposed to be the catalyst in coupling reactions, if bulky biarylphosphines like L1 are applied.[41] With the phosphine already attached to the metal center, the creation of the catalytically active species is considered to be easier from **10** than from a mixture of $[PdCl_2(CH_3CN)_2]$ and L1.

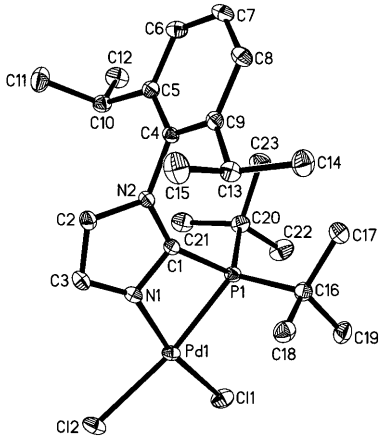
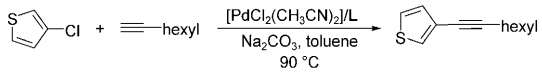
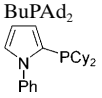
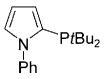
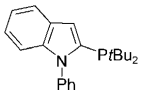
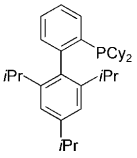
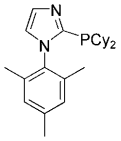
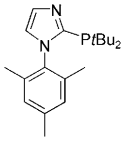
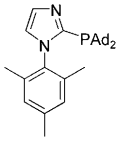
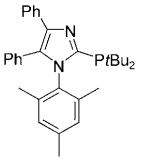
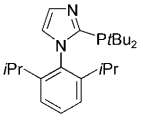
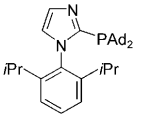


Figure 2. Molecular structure of **10**. Hydrogen atoms are omitted for clarity. The thermal ellipsoids correspond to 30% probability.

For the same reasons, an excess of ligand is not necessary any more. Hence, complex **10** was directly applied in the reaction (Table 1, entry 11). However, the reaction yielded only 40% of the coupling product under optimized conditions; with an additional 2 mol% of L1, the same activity of the catalyst was observed as with 1 mol% of $[PdCl_2(CH_3CN)_2]$ and 3 mol% of L1 (Table 1, entry 12). In agreement with the observation by Buchwald et al., inhibition of the reaction is observed when CuI was applied as co-catalyst (Table 1, entry 10). Next, a series of commercially available phosphines and novel dialkyl-2-(*N*-arylimidazolyl)phosphines were compared in the model reaction. Selected results of this ligand screening are shown in Table 2. Not surprisingly, triphenylphosphine (Table 2, entry 1), but also sterically hindered, basic ligands such as tri-*tert*-butylphosphine (employed as the HBF_4 salt; Table 2, entry 2) and cataCXium A (Table 2, entry 3) showed no reactivity without any copper co-catalyst, too. Similarly, *N*-aryl-2-phosphinopyrroles and *N*-aryl-2-phosphinoindoles (Table 2, entries 4–6) gave no conversion. Unexpectedly, even XPhos (Table 2, entry 7) showed only low reactivity under these conditions. However, significant amounts of the desired coupling product are obtained in the presence of the tested imidazole-based phosphine ligands. Among this class of ligands the following trends can be observed: within the applied *N*-mesityl-substituted ligands the di-1-adamantyl derivative gave the best result (Table 2, entry 10, 55% yield), while the yield drops significantly going over the corresponding 2-(di-*tert*- butylphosphino)imidazole ligand (Table 2, entry 9) to the sterically less demanding 2-(dicyclohexylphosphino)imidazole (Table 2, entry 8). Evidently, the more sterically hindered ligands gave favorable catalytic results probably because they accelerate the reductive elimination. Comparing entries 9 and 11 in Table 2, the ligand substituted with two phenyl rings in the backbone gave a better yield and selectivity (47% yield; 58% conversion). However, ligand L1 (Table 2, entry 12) showed the best performance compared to all other ligands tested. Interestingly, the corresponding 2-(di-1-adamantyl)phosphine (Table 2, entry 13) gave only

Table 2. Reaction of 3-chlorothiophene and 1-octyne using different phosphine ligands.[a]

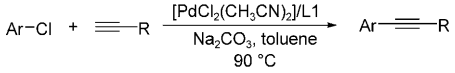


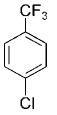
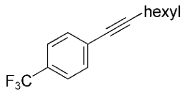
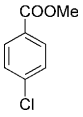
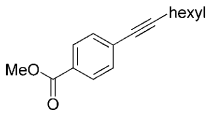
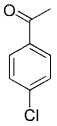
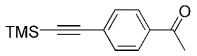
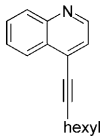
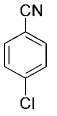
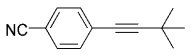
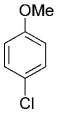
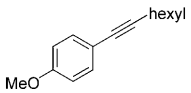
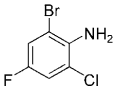
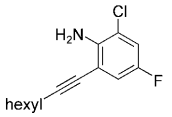
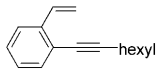
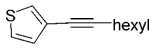
Entry	Ligand	Conversion [%]	Yield [%][b]
1	PPh_3	0	0
2	$P(tBu)_3$*HBF_4	3	0
3	$BuPAd_2$	0	0
4		2	0
5		3	0
6		7	0
7		34	6
8		19	1
9		76	21
10		63	55
11		58	47
12		73	68
13		31	25

[a] Reaction conditions: 3-chlorothiophene (1 equiv), 1-octyne (1.3 equiv), Na_2CO_3 (2.6 equiv), $[PdCl_2(CH_3CN)_2]$ (1 mol%), ligand (3 mol%), toluene (0.5 M), 90 °C, 16 h (reaction times not optimized). [b] GC yields (internal standard: hexadecane).

25% yield, even though it is considered to be more bulky. Finally, the Sonogashira reaction without added copper co-catalyst in the presence of ligand L1 was studied in more detail. Table 3 demonstrates that good to excellent results can be obtained under mild conditions in the case of activated aryl and heteroaryl chlorides using 1 mol% catalyst

Table 3. Sonogashira coupling of various aryl and heteroaryl chlorides with different alkynes.[a]



Entry	Aryl chloride	Alkyne	Product	Yield [%][b]
1				97
2				93
3				75
4				97
5[c]				42
6				87
7				64
8				31
9				87
10				73
11				77
12[c]				83
13[c]				45

[a] Reaction conditions: 3-chlorothiophene (1 equiv), 1-octyne (2 equiv), Na_2CO_3 (4 equiv), $[PdCl_2(CH_3CN)_2]$ (1 mol%), L1 (3 mol%), toluene (0.5 M), 90 °C, 16 h (reaction times not optimized). [b] Yield of isolated product. [c] 0.5 mol% $[PdCl_2(CH_3CN)_2]$, 1.5 mol% L1. [d] 2 equiv aryl halide, 1 equiv alkyne.

(Table 3, entries 1–4; 75–97% yield). Moreover, electron-rich aryl chlorides such as 4-chloroanisole react readily with 1-octyne in 87% yield (Table 3, entry 6). Notably, amino groups are tolerated under these conditions as shown by the reaction of 2-bromo-6-chloro-4-fluoroaniline, which is converted into the corresponding 2-subsituted product (Table 3, entry 7). The reaction of 2-chlorostyrene with 1-octyne gave an interesting highly conjugated coupling product (Table 3, entry 8). This reaction also shows that the catalyst system is chemoselective for the coupling of the alkyne, as no stilbene or stilbene oligomers are observed. Finally, 3-chlorothiophene was allowed to react with various alkynes. In addition to the reaction of 1-octyne (87%; Table 3, entry 9) also reactions with cyclopentyl-, triethylsilyl-, and phenylacetylene proceeded smoothly (73–83%; Table 3, entries 10–12).

In summary, palladium-catalyzed Sonogashira couplings have been performed in the presence of *N*-substituted heteroaryl phosphines without copper co-catalysts for the first time. In general, good to excellent coupling results of a variety of aryl and heteroaryl chlorides—including challenging substrates—have been obtained in the presence of [*N*-(2,6-diisopropylphenyl)-2-imidazolyl]-di-*tert*-butylphosphine L1 at low catalyst loading. Various functional groups including amino, silyl, and vinyl groups are tolerated under these conditions, in contrast to previously reported copper-free procedures. The novel procedure is cost effective and benign with respect to solvent, base, and avoiding the addition of copper salts.

Experimental Section

General: All reactions were performed under an argon atmosphere using standard Schlenk techniques. All starting materials and reactants were used as received from commercial suppliers, except toluene, which was distilled from sodium and stored under argon before use. Phosphine ligands and complexes were stored in Schlenk flasks but weighed under air. NMR spectra were recorded on an ARX300 (Bruker) spectrometer; chemical shifts are given in ppm and are referenced to the residual solvent peak. Mass spectra were recorded on an AMD 402 double-focusing, magnetic sector spectrometer (AMD Intectra). GC-MS spectra were recorded on a HP 5989A (Hewlett Packard) chromatograph equipped with a quadropole analyzer. Gas chromatography analyses were realized on a HP 6890 (Hewlett Packard) chromatograph using a HP 5 column. Melting points were measured on a SMP3 (Stuart) and are not corrected.

X-ray structure determinations: Data were collected with a STOE-IPDS diffractometer using graphite-monochromated $Mo_{K\alpha}$ radiation. The structures were solved by direct methods [SHELXS-97: G. M. Sheldrick, University of Göttingen, Germany, **1997**] and refined by full-matrix least-squares techniques against F^2 [SHELXL-97: G. M. Sheldrick, University of Göttingen, Germany, **1997**]. XP (Bruker AXS) was used for graphical representations.

CCDC-712744 (L1) and CCDC-712745 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Sonogashira reaction of aryl chlorides: A 25 mL Schlenk tube was evacuated and backfilled with argon. It was charged with $[PdCl_2(CH_3CN)_2]$ (2.59 mg, 0.01 mmol), L1 (11.2 mg, 0.03 mmol), and Na_2CO_3 (424 mg, 4 mmol). If it was a solid, the (hetero)aryl chloride was also added at that point. Then, toluene (2 mL), the corresponding (hetero)aryl chloride (if liquid) (1 mmol), and the alkyne (2 mmol) were added successively under argon atmosphere. The reaction mixture was heated up to 90°C for 16 h (reaction times not optimized) while it was stirred vigorously. After cooling to room temperature, the mixture was then quenched with water (3 mL), and the aqueous phase was extracted with diethyl ether (3×4 mL). The organic phases were combined, concentrated, and the desired product was isolated by column chromatography (cyclohexane or cyclohexane/ethyl acetate mixtures). Alternatively, the reaction mixture was quenched with water (3 mL) and diluted with diethyl ether (8 mL). Hexadecane was then added as an internal standard and quantitative analysis was performed by gas chromatography.

(4-Acetylphenylethynyl)trimethylsilane: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75–7.71 (m, 2H, 2×H_{arom}), 7.41–7.35 (m, 2H, 2×H_{arom}), 2.43 (s, 3H, CH_3(C=O)), 0.11 ppm (s, 9H, Si(CH_3)$_3$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 197.5 (CH_3(*C*=O)), 136.5 (C_{arom}), 132.2 (C_{arom}), 128.3 (C_{arom}), 128.1 (C_{arom}), 104.2 (C_{acetyl}–C_{arom}), 98.3 (*C*-Si(CH_3)), 26.8 (CH_3(C=O)), 0.00 ppm (Si(CH_3)$_3$); MS (70 eV): *m/z* (%): 216 (18) [M^+], 201 (100), 158 (9), 143 (7); HRMS: calcd for $C_{13}H_{16}OSi$: 216.09649; found: 216.09620.

3-(Phenylethynyl)thiophene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.49–7.39 (m, 3H, 3×H_{arom}), 7.33–7.19 (m, 4H, 4×H_{arom}), 7.16–7.09 ppm (m, 1H, 2×H_{arom}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 131.6 (C_{arom}), 129.9 (C_{arom}), 128.6 (C_{arom}), 128.4 (C_{arom}), 128.3 (C_{arom}), 125.4 (C_{arom}), 123.2 (C_{arom}), 122.3 (C_{arom}), 88.9 (C_{acetyl}), 84.5 ppm (C_{acetyl}); MS (70 eV): *m/z* (%): 184 (100) [M^+], 152 (11), 139 (24); HRMS: calcd for $C_{12}H_8S$: 184.03412; found: 184.03381.

3-(Cyclopentylethynyl)thiophene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.28 (m, 1H, H_{arom}), 7.23–7.16 (m, 1H, H_{arom}), 7.08–7.01 (m, 1H, H_{arom}), 2.78 (quin, *J* = 8.0 Hz, 1H, CH), 2.07–1.85 (m, 2H), 1.84–1.43 ppm (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.1 (C_{arom}), 127.4 (C_{arom}), 124.9 (C_{arom}), 123.1 (C_{arom}), 94.1 (C_{acetyl}), 75.1 (C_{acetyl}), 33.9 (CH-*C*H_2), 30.8 (CH), 25.1 ppm (CH(CH_2)*C*H_2);. MS (70 eV): *m/z* (%): 176 (87) [M^+], 161 (13), 147 (100), 134 (30) 128 (18), 121 (18), 115 (18), 108 (23), 97 (10), 91 (11), 77 (9), 69 (8), 63 (11), 45 (10); HRMS: calcd for $C_{11}H_{12}S$: 176.06542; found: 176.06560.

3-(1-Octynyl)thiophene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.29 (m, 1H, H_{arom}), 7.23–7.16 (m, 1H, H_{arom}), 7.07–7.01 (m, 1H, H_{arom}), 2.36 (t, *J* = 7.0 Hz, 2H, C_{acetyl}-*C*H_2), 1.65–1.19 (m, 8H, (*C*H_2)$_4$$CH_3$), 0.89 ppm (t, *J* = 7.0 Hz, 3H, (CH_2)$_4$*C*H_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 130.1 (C_{arom}), 127.5 (C_{arom}), 125.0 (C_{arom}), 123.1 (C_{arom}), 90.0 (C_{acetyl}-C_{arom}), 75.6 (C_{acetyl}-CH_2), 31.4, 28.8, 28.7, 22.6, 19.4 (C_{acetyl}-*C*H_2), 14.1 ppm ((CH_2)$_4$*C*H_3); MS (70 eV): *m/z* (%): 192 (54) [M^+], 163 (22), 149 (45), 135 (61), 123 (100), 115 (52), 108 (22), 97 (32), 91 (17), 77 (26), 63 (13), 45 (17); HRMS: calcd for $C_{12}H_{16}S$: 192.09644; found: 192.09672.

2-Methyl-4-(3-thiophenyl)-3-butyn-2-ol: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.36–7.32 (m, 1H, H_{arom}), 7.20–7.14 (m, 1H, H_{arom}), 7.04–6.99 (m, 1H, H_{arom}), 2.19 (br s, 1H, OH), 1.53 ppm (s, 6H, 2× CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 129.9 (C_{arom}), 128.7 (C_{arom}), 125.3 (C_{arom}), 121.8 (C_{arom}), 93.4 (C_{acetyl}-C(CH_3)$_2$OH), 77.3 (C_{acetyl}-C_{arom}), 65.7 (*C*-(CH_3)$_2$OH), 31.5 ppm ((CH_3)$_2$); MS (70 eV): *m/z* (%): 166 (33) [M^+], 151 (100), 135 (7), 123 (10), 108 (13), 89 (6), 75 (6), 69 (6), 63 (11) 43 (59); HRMS: calcd for $C_9H_{10}OS$: 166.04469; found: 166.04494.

1-Methoxy-4-(oct-1-ynyl)benzene: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.35–7.27 (m, 2H, 2×H_{arom}), 6.83–6.75 (m, 2H, 2×H_{arom}), 3.78 (s, 3H, OCH_3), 2.36 (t, *J* = 6.9 Hz, 2H, CH_2(C_5H_{11})), 1.63–1.18 (m, 8H, CH_2(C_4H_8)CH_3), 0.88 ppm (t, *J* = 6.9 Hz, 3H, CH_2(C_4H_8)*C*H_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.0, 132.9, 116.3, 113.8, 88.9, 80.2, 55.3, 31.4, 28.9, 28.7, 22.6, 19.5, 14.1 ppm; MS (70 eV): *m/z* (%): 216 (51) [M^+], 187 (19), 173 (38), 159 (38), 145 (100), 130 (15), 115 (29), 102 (28); HRMS: calcd for $C_{15}H_{20}O$: 216.15087; found: 216.15080.

Methyl-4-(oct-1-ynyl)benzoate: ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.95–7.87 (m, 2H, 2×H_{arom}), 7.44–7.37 m, 2H, 2×H_{arom}), 3.86 (s, 3H, *C*H_3(C=O)), 2.38 (t, *J* = 7.0 Hz, 2H, *C*H_2(C_5H_{11})), 1.64–1.20 (m, 8H, CH_2-(C_4H_8)CH_3), 0.87 ppm (t, *J* = 7.0 Hz, 3H, CH_2(C_4H_8)*C*H_3); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 166.6 (CH_3O(*C*=O)), 131.5 (C_{arom}), 129.4 (C_{arom}), 129.0 (C_{arom}), 128.8 (C_{arom}), 94.0 (C_{acetyl}-CH_2), 80.1 (C_{acetyl}-C_{arom}), 52.1 (*C*H_3O(C=O)), 31.4, 28.6, 28.6, 22.6, 19.5 (C_{acetyl}-*C*H_2), 14.1 ppm ((CH_2)$_4$*C*H_3); MS (70 eV): *m/z* (%): 244 (36) [M^+], 213 (29), 201 (45),

173 (35), 143 (52), 129 (100), 115 (43); HRMS: calcd for $C_{16}H_{20}O_2$: 244.14578; found: 244.14578.

3-Chloro-5-fluoro-2-(oct-1-ynyl)aniline: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 6.98–6.86 (m, 2H, 2×H_{arom}), 4.60–4.00 (br s, 2H, 2×NH_2), 2.48 (t, $J =$ 7.0 Hz, 2H, $CH_2(C_5H_{11})$), 1.66–1.25 (m, 8H, $CH_2(C_4H_8)CH_3$), 0.88 ppm (t, $J =$7.0 Hz, 3H, $CH_2(C_4H_8)CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$ 155.6, 152.4, 141.1 (d, $J =$2.4 Hz), 118.6 (d, $J =$11.5 Hz), 116.6 (dd, $J =$ 39.4 Hz, 24.5 Hz), 110.3 (d, $J =$10.1), 97.8, 75.9 (d, $J =$3.6), 31.4, 28.7, 28.7, 22.6, 19.6, 14.1 ppm; IR (ATR): $\tilde{\nu} =$3484, 3385, 3082, 2955, 2928, 2857, 2223, 1589, 1572, 1469, 1301, 1201, 1157, 1069, 850, 793, 728 cm^{-1}; MS (70 eV): *m/z* (%): 253 (87) [M^+], 224 (20), 210 (18), 196 (26), 182 (100), 175 (19), 158 (29), 149 (44), 126 (23); HRMS: calcd for $C_{14}H_{17}ClFN$: 253.10281; found: 253.10287.

4-(3,3-Dimethylbut-1-ynyl)benzonitrile: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.56–7.49 (m, 2H, 2×H_{arom}), 7.55–7.38 (m, 2H, 2×H_{arom}), 1.29 ppm (s, 9H, $C(CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$132.1, 131.9, 129.2, 118.7, 110.7, 103.5, 78.0, 30.8, 28.2. MS (70 eV): *m/z* (%): 183 (20) [M^+], 168 (100), 153 (31), 140 (13); HRMS: calcd for $C_{13}H_{13}N$: 183.10425; found: 183.10477.

1-(Oct-1-ynyl)-2-vinylbenzene: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$7.58–7.52 (m, 1H, 1×H_{arom}), 7.43–7.35 (m, 1H, 1×H_{arom}), 7.30–7.12 (m, 3H, 2×H_{arom}, 1×H_{vinyl}), 5.78 (dd, $J =$17.7 Hz, 1.2 Hz, 1H, 1×H_{vinyl}), 5.32 (dd, $J =$11.0 Hz, 1.2 Hz, 1H, 1×H_{vinyl}), 2.46 (t, $J =$6.9 Hz, 2H, $CH_2(C_5H_{11})$), 1.70–1.20 (m, 8H, $CH_2(C_4H_8)CH_3$), 0.91 ppm (t, $J =$6.9 Hz, 3H, $CH_2(C_4H_8)CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$138.8, 135.2, 132.5, 127.7, 127.4, 124.5, 122.9, 115.0, 95.4, 78.9, 31.4, 28.8, 28.7, 22.6, 19.6, 14.1 ppm; MS (70 eV): *m/z* (%): 212 (1) [M^+], 169 (16), 155 (59), 141 (100), 128 (44), 115 (67); HRMS: calcd for $C_{16}H_{20}$: 212.15595; found: 212.15596.

1-(Oct-1-ynyl)-4-(trifluoromethyl)benzene: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$7.54–7.42 (m, 4H, 4×H_{arom}), 2.40 (t, $J =$7.1 Hz, 2H, 2×C_{acetyl}-CH_2), 1.67–1.21 (m, 8H, $(CH_2)_4CH_3$), 0.89 ppm (t, $J =$4.6 Hz, 3H, $(CH_2)_4CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$131.8, 129.2 (q, $J =$23.6 Hz), 128.0, 125.2 (q, $J =$3.8 Hz), 124.1 (q, $J =$272.1 Hz), 93.4, 79.5, 31.4, 28.6, 28.5, 22.6, 19.5, 14.1 ppm; MS (70 eV): *m/z* (%): 254 (44) [M^+], 235 (26), 225 (81), 211 (98), 197 (45), 183 (100), 170 (37), 159 (62), 129 (78) 115 (40); HRMS: calcd for $C_{15}H_{17}F_3$: 254.12769; found: 254.12722.

Triethyl(thiophen-3-ylethynyl)silane: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$ 7.46 (dd, $J =$3.0 Hz, 1.1 Hz, 1H, 1×H_{arom}), 7.22 (dd, $J =$5.0 Hz, 3.0 Hz, 1H, 1×H_{arom}), 7.11 (dd, $J =$5.0 Hz, 1.2 Hz, 1H, 1×H_{arom}), 1.03 (t, $J =$ 7.9 Hz, 9H, $Si(CH_2CH_3)_3$), 0.66 ppm (t, $J =$4.9 Hz, 6H, $Si(CH_2CH_3)_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$130.3, 129.5, 125.1, 122.6, 101.1, 91.4, 7.5, 4.5 ppm; IR (ATR): $\tilde{\nu} =$3109, 2953, 2934, 2910, 2873, 2151, 1005, 945, 869, 779, 722, 680 cm^{-1}; MS (70 eV): *m/z* (%): 222 (13) [M^+], 193 (99), 165 (100), 137 (83), 111 (16); HRMS: calcd for $C_{12}H_{18}SSi$: 222.08930; found: 222.08877.

4-(Oct-1-ynyl)quinoline: ^{1}H NMR (300 MHz, $CDCl_3$): $\delta =$8.79 (d, $J =$ 4.5 Hz, 1H, 1×H_{arom}), 8.29–8.01 (m, 2H, 2×H_{arom}), 7.75–7.48 (m, 2H, 2×H_{arom}), 7.39 (d, $J =$4.5 Hz, 1H, 1×H_{arom}), 2.53 (t, $J =$7.1 Hz, 2H, C_{acetyl}-CH_2), 1.74–1.23 (m, 8H, $(CH_2)_4CH_3$), 0.95–0.79 ppm (m, 3H, $(CH_2)_4CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta =$149.8, 148.1, 130.8, 129.8, 129.7, 128.2, 126.9, 126.1, 123.6, 101.1, 31.4, 28.7, 28.5, 22.6, 19.8, 14.1 ppm; MS (70 eV): *m/z* (%): 237 (100) [M^+], 208 (34), 194 (52), 180 (59), 166 (71), 153 (45), 139 (36); HRMS: calcd for $C_{17}H_{19}N$: 237.15120; found: 237.15135.

Complex 10: m.p. >245 °C (decomp); ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta =$ 7.57 (dd, $J =$2.6 Hz, 1.5 Hz, 1H, H_{imid}), 7.49 (t, $J =$7.8 Hz, 1H, 4-H_{arom}), 7.27 (d, $J =$7.8 Hz, 2H, 3-H_{arom}, 5-H_{arom}), 7.02 (dd, $J =$1.5 Hz, 0.6 Hz, 1H, H_{imid}), 2.29 (sep, $J =$6.8 Hz, 2H, 2×$CH(CH_3)_2$), 1.42 (s, 9H, $C(CH_3)_3$), 1.37 (s, 9H, $C(CH_3)_3$), 1.23 (d, $J =$6.9 Hz, 6H, $CH(CH_3)_2$), 0.97 ppm (d, $J =$6.9 Hz, 6H, $CH(CH_3)_2$); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta =$146.6, 132.5, 131.9, 128.2, 128.1, 127.7, 125.0, 38.9 (d, $J =$9.6 Hz), 30.0 (d, $J =$3.8 Hz), 29.4, 27.6, 21.3 ppm; ^{31}P NMR (120 MHz, CD_2Cl_2): $\delta =$53.7; IR (ATR): $\tilde{\nu} =$3162, 3140, 2962, 2923, 2866, 1457, 1444, 1173, 1132, 813, 805, 787, 770, 763 cm^{-1}; HRMS (ESI, [M^+ Na^+]): calcd for $C_{23}H_{37}Cl_2N_2NaPPd$: 573.10026; found: 573.09955.

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