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Efficient Suzuki–Miyaura Coupling Reactions between Lithium Alkynyltrimethylborates and Aryl Chlorides

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The Pd-catalysed alkynylation of alkynylboronic esters (generated in situ) with various aryl chlorides in the presence of $Pd_2(dba)_3$, the sterically hindered dihydroimidazolium salt **4** as the precatalyst and CsF is reported. Under these conditions, electron-poor and electron-rich aryl chlorides undergo efficient cross-coupling reactions.

Introduction

Over the last quarter century, Pd-catalysed alkynylation has emerged as an important method for the synthesis of alkynes.[1] The preparation of conjugated aryl alkynes is of great interest in materials science and also because of these compounds' presence in many bioactive natural products.[2] Two strategies have been applied for the synthesis of conjugated acetylenic compounds:[3] Sonogashira alkynylation with terminal alkynes, co-catalysed by Pd[1a] and Cu,[4] and cross-coupling of unsaturated organic halides with preformed alkynylmetals, especially with those containing Zn,[5] Mg,[5a,5b,6] Sn,[5a,5b,7] Al[5b,8] and B.[9] Different aromatic electrophiles can be used in this cross-coupling reaction, with the most routinely employed being the expensive aromatic iodides, bromides and triflates. From an industrial point of view, the chemically more inert but cheap and readily available aryl chlorides are particularly important as starting materials for transition metal-catalysed C–C coupling.[10] In Suzuki–Miyaura-type reactions of nonactivated and deactivated aryl chlorides, the groups of Fu,[11] Buchwald,[12] Guram,[13] Nolan,[14] Nájera,[15] Beller[16] and Herrmann[17] have achieved significant success with palladium catalysts. In general, important improvements in this area have been made possible through the use of catalysts consisting of a Pd^{II} source and sterically hindered, basic ligands such as dialkylarylphosphanes, trialkylphosphanes, *N*-heterocyclic carbenes and palladacycles.

However, such procedures have never been applied to cross coupling reactions with lithium alkynyltrialkoxy borate complexes as nucleophiles. *N*-heterocyclic carbenes have only been reported with B-alkynyl-9-BBN "ate" complexes[9f] and their use represents a lack of atom economy in the shape of the BBN residue.

In this context we have recently reported a new and efficient method for Suzuki–Miyaura couplings between alkynylboronic esters, generated in situ from acetylenic derivatives, and aryl or vinyl bromides to obtain aryl-alkynyl derivatives.[18] Here we report some synthetically useful results of Pd-catalysed alkynylations of activated, nonactivated and deactivated aryl chlorides with alkynylboronic esters with the aid of some of the efficient catalysts described above.

Results and Discussion

Firstly, in order to compare different catalytic systems, we carried out cross-coupling reactions between oct-1-yne and activated aryl chlorides with electron-withdrawing groups such as 1-chloro-4-trifluoromethylbenzene and 4-chlorobenzonitrile (Table 1). Metallation of oct-1-yne with 1 equiv. of BuLi in dimethoxyethane (DME) at –78 °C over 1 h afforded the lithium oct-1-ynyl intermediate, which was treated with 1.5 equiv. of trimethylborate in dimethoxyethane at –78 °C. The Suzuki–Miyaura coupling was then carried out with aryl chlorides in the presence of the catalyst in DME or DME/dioxane at reflux.

Of the best catalytic systems known so far for the Suzuki reaction of aryl chlorides, we chose to examine the water- and air-stable palladacycle **1**, described by Nájera,[15a,15b] and two different alkylphosphane-based systems: Buchwald's[12a] 2-(di-*tert*-butylphosphanyl)biphenyl (**2**) with $Pd(OAc)_2$ and Fu's[11] tri-*tert*-butylphosphane with $Pd_2(dba)_3$. Instead of using $P(tBu)_3$, which is too sensitive to moisture and toward air oxidation, we tested the tri-*tert*-butylphosphonium salt $[(tBu)_3PH]BF_4$ **3**[11c] (Scheme 1), the phosphane being generated in situ by treatment of the phosphonium salt with CsF. Nucleophilic *N*-heterocyclic carbenes were also tested in association with $Pd_2(dba)_3$, in par-

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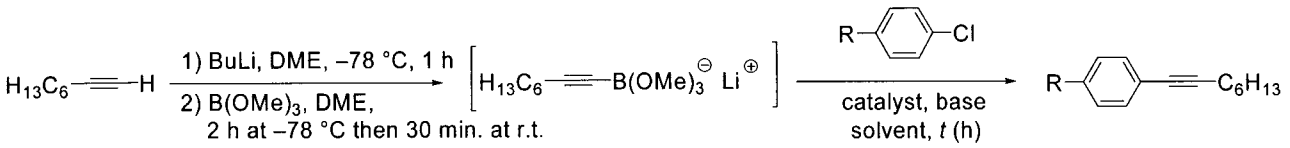
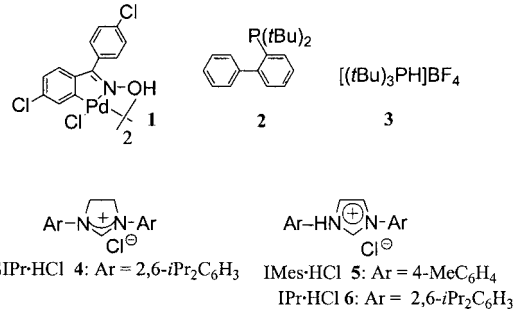
Table 1. Suzuki–Miyaura cross-coupling of activated aryl chlorides and oct-1-yne with different catalytic systems.[a]



Entry	R	Catalyst	Base	Solvent	*t* [h]	Yield [%][b]
1	CF_3	**1**[c]	–	DME	18	30
2	CF_3	**1**[c]	–	DME/dioxane[f]	12	48
3	CF_3	$Pd(OAc)_2$/**2**[d]	–	DME	12	47
4	CF_3	$Pd(OAc)_2$/**2**[d]	–	DME/dioxane[f]	12	59
5	CN	$Pd(OAc)_2$/**2**[d]	–	DME/dioxane[f]	12	68
6	CN	$Pd_2(dba)_3$/**3**[e]	CsF	DME	18	33
7	CF_3	$Pd_2(dba)_3$/**4**[e]	CsF	DME	24	27
8	CF_3	$Pd_2(dba)_3$/**4**[e]	CsF	DME/dioxane[f]	24	75
9	CN	$Pd_2(dba)_3$/**4**[e]	CsF	DME/dioxane[f]	3	94

[a] Reaction conditions: oct-1-yne (1.3 equiv.), aryl chloride (1.0 equiv.), trimethylborate (1.3 equiv.), BuLi (1.3 equiv.), CsF (1 equiv.), solvent (reflux). [b] Isolated yields after flash chromatography. [c] Palladacycle **1** (5 mol-%). [d] $Pd(OAc)_2$ (3 mol-%)/**2** (9 mol-%). [e] $Pd_2(dba)_3$ (3 mol-%)/**3** or **4** (6 mol-%). [f] DME/dioxane = 1:1.

ticular *N*,*N*′-bis(2,6-diisopropylphenyl)dihydroimidazol-2-ylidene (SIPr).[14] These carbenes were obtained in situ by deprotonation of the disubstituted imidazolium salt SIPr·HCl **4** with a base (Scheme 1 and Table 1).[14]



Scheme 1. Catalytic system and ligands tested for C–C coupling reactions of aryl chlorides.

The best results were obtained with the dihydroimidazolium salt **4**, which gave yields of up to 94% in 3 hours with 4-chlorobenzonitrile in a mixture of DME/dioxane (1:1) (Table 1, Entry 9). We have also observed that use of a mixture of DME/dioxane in a ratio of 1:1 as solvent instead of only DME significantly improved the yield (Table 1, Entries 2, 4, 5, 8 and 9).

The use of palladacycle **1** or $[(t\text{Bu})_3\text{PH}]BF_4$ (**3**) with $Pd_2(dba)_3$ afforded the coupling product in modest yields (Table 1, Entries 1, 2 and 6). With the catalytic system **2**/$Pd(OAc)_2$, the reactivity was increased but did not reach those obtained with *N*-heterocyclic carbenes (Table 1, Entries 3, 4 and 5).

The excellent result with carbenes[14a] can be explained in terms of the formation of a zero-valent palladium species by an electron-donating ligand (more effective donors than bulky tertiary phosphanes) and this then undergoing oxidative addition with an aryl halide Ar–X to give a Pd^{II}(Ar)(X) complex. Next, the organometallic species Ar′–M effects a transmetallation to afford the divalent Pd(Ar)(Ar′) intermediate, which undergoes reductive elimination, which is more efficient with bulky ligands such as SIPr·HCl, to couple the two aryl moieties and to regenerate the palladium(0) species. Moreover, electron-donating tertiary phosphanes are subject to P–C degradation in some coupling reactions at elevated temperatures,[19] and in certain catalytic processes this results in deactivation of the catalyst.

To find the most effective imidazolium salt, two different 1,3-disubstituted imidazolium salts with different electronic and steric properties were tested in cross-coupling reactions between oct-1-yne and 4-chlorobenzonitrile (Table 2).

Screening with the imidazolium salts **5** or **6** in the presence of Pd_2dba_3 and CsF did not produce the same excellent yields as had been obtained with the dihydroimidazolium salt **4** (Table 2, Entries 4 and 5). An investigation of the activity of the catalyst system revealed that the Pd_2dba_3/SIPr·HCl system displayed the best catalytic behaviour in comparison with $Pd(OAc)_2$/SIPr·HCl (Table 2, Entries 1 and 2).

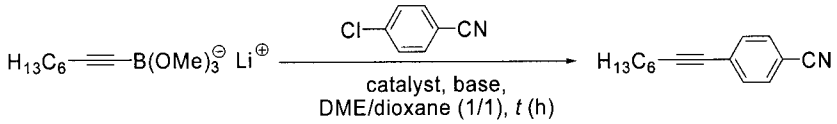
Surprisingly, CsF revealed a better activity to generate the carbene than Cs_2CO_3 (Table 2, Entries 1 and 3).[14b]

We next studied Suzuki coupling reactions between oct-1-yne and several aryl chlorides under these optimized reaction conditions ($Pd_2(dba)_3$/SIPr·HCl **4**, CsF in DME/dioxane: 1:1; Table 3).

As described above, cross-coupling with activated aryl chlorides such as 2-chloropyridine, 4-chlorobenzonitrile and 1-chloro-4-(trifluoromethyl)benzene gave good to excellent yields (Table 3, Entries 1, 2 and 3).

Good yields were also obtained in the case of chlorobenzene, a nonactivated aryl chloride (Table 3, Entries 4 and 5). When the amount of catalyst was decreased [$Pd_2(dba)_3$ (1 mol-%)/SIPr·HCl **4** (2 mol-%)] the coupling product was obtained in similar yield but required longer reaction times.

Table 2. Suzuki–Miyaura cross-coupling between 4-chlorobenzonitrile and oct-1-yne in the presence of different imidazolium salts.[a]



Entry	Catalyst	Base	*t* [h]	Yield [%][b]
1	$Pd_2(dba)_3$/**4**[c]	CsF	3	94
2	$Pd(OAc)_2$/**4**[d]	CsF	18	66
3	$Pd_2(dba)_3$/**4**[c]	Cs_2CO_3	3	85
4	$Pd_2(dba)_3$/**5**[c]	CsF	18	60
5	$Pd_2(dba)_3$/**6**[c]	CsF	3	85

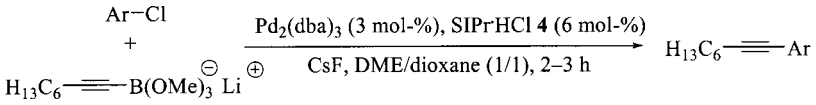
[a] Reaction conditions: lithium oct-1-ynyltrimethylborate (1.3 equiv.), 4-chlorobenzonitrile (1.0 equiv.), base (1.0 equiv.), solvent (reflux). [b] Isolated yields after flash chromatography. [c] $Pd_2(dba)_3$ (3 mol-%)/**L** (6 mol-%). [d] $Pd(OAc)_2$ (3 mol-%)/**4** (6 mol-%).

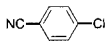
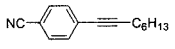
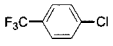
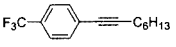
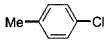
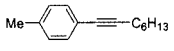
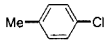
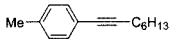
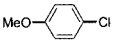
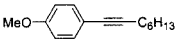
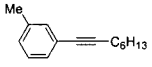
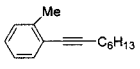
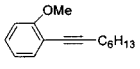
With deactivated aryl chlorides such as 4-chloroanisole and 4-chloro- and 3-chlorotoluene the yields were satisfactory (Table 3, Entries 6, 7, 8 and 9). With 4-chlorotoluene the use of a mixture of dimethoxyethane/toluene instead of dimethoxyethane/dioxane did not result in a significant increase in the yield (Table 3, Entries 6 and 7).

As would be expected, *ortho*-substituted, deactivated aryl chlorides such as 2-methyl- and 2-methoxy-substituted chlorobenzene, which are more sterically hindered, gave the coupling products in slightly lower yields (60 and 65%, respectively; Table 3, Entries 10 and 11).

The use of *N*-heterocyclic carbene (NHC) ligands in Sonogashira reactions has been reported, but to our knowledge Batey[20] demonstrated the effectiveness of carbamoyl-substituted NHC complexes for palladium in cross-coupling reactions with electron-rich aryl iodides and bromides and

Table 3. Suzuki–Miyaura cross-couplings between oct-1-yne and aryl chlorides.[a]



Entry	Ar–Cl	Product	Yield (%)[b]
1			94
2			75
3			70
4			75
5			65[c]
6			70
7			72[d]
8			73
9			68
10			60
11			65

[a] Reaction conditions: lithium oct-1-ynyltrimethylborate (1.3 equiv.), aryl chloride (1 equiv.), CsF (1 equiv.), solvent (reflux). [b] Isolated yields after flash chromatography. [c] $Pd_2(dba)_3$ (1 mol-%)/**4** (2 mol-%). [d] DME/toluene 1:1.

Nolan has shown that in combination with $Pd(OAc)_2$, the IMes·HCl species **5** promoted cross-coupling with deactivated aryl bromides and chlorobenzene but not with deactivated aryl chlorides.

Conclusion

In summary, a combination of $Pd_2(dba)_3$ with the *N*,*N*′-bis(2,6-diisopropylphenyl)dihydroimidazolium salt **4** appears to be the most efficient catalyst system for palladium-catalysed Suzuki cross-coupling between aryl chlorides and alkynylboronic esters generated in situ from terminal acetylenes, giving good to excellent yields with activated, nonactivated and deactivated chloroarenes.

Experimental Section

General Remarks: All reactions were carried out under Ar. 1,2-Dimethoxyethane and dioxane were dried under argon over sodium-benzophenone, whilst toluene was dried under argon over sodium. All reagents were purchased from commercial sources and were used without further purification, unless indicated otherwise. Trimethylborate was purchased by Aldrich and was dried under argon over sodium. Cesium carbonate and cesium fluoride were flamed-dried at <1 Torr. All reactions were monitored by gas chromatography. GLC analyses were performed on a Hewlett Packard 6890 Series Gas Chromatograph with an HP-5 capillary column (5% phenyl methyl siloxane, 30 m × 320 μm). Flash column chromatography was carried out on Merck silica (Si 60, 40–63 μm). Eluting solvents are indicated in the text. The NMR spectra were recorded with a Bruker Avance 300 spectrometer with working frequencies of 300 MHz for ^1H and 75.43 MHz for ^{13}C spectroscopy. The different ligands were either purchased from commercial sources, such as the 2-(di-*tert*-butylphosphanyl)biphenyl (**2**) and $[(t\text{Bu})_3PH]BF_4$ (**3**) from STREM, or were obtained by preparation, as in the cases of the palladacycle **1**[15a] and the different imidazolium salts **4**, **5** and **6**.[21]

General Procedure for Suzuki–Miyaura Cross-Coupling: *n*-BuLi (2.23 mmol, 1,6 M solution in hexanes) was added at –78 °C to a solution of oct-1-yne (0.19 mL, 2.15 mmol) in dry dimethoxyethane (3 mL) in a dried two-necked flask. One hour later, trimethylborate (0.15 mL, 2.15 mmol) was added at –78 °C and stirring was continued for 2 h at –78 °C, after which it was warmed to room temperature for 30 min. In a second dried two-necked flask, $Pd_2(dba)_3$ (3 mol-%), ligand (6 mol-%), base (1.65 mmol) and aryl chloride (1.65 mmol) were added to dry dioxane (3 mL). After this system had been stirred for 10 minutes at room temperature, the solution of lithium oct-1-ynyltrimethylborate in dimethoxyethane was added and the resulting mixture was heated at reflux for 2–3 hours. The reaction was monitored by gas chromatography. The reaction mixture was cooled to room temperature and quenched by addition of water (10 mL). The aqueous layer was extracted with ethyl acetate (total 40 mL) and the combined organic layer were dried with $MgSO_4$, filtered and concentrated under vacuum. The residue was purified by flash chromatography (SiO_2).

Characterization of the Different Products

4-Oct-1-ynylbenzonitrile: (Table 3, Entry 1): Previously described.[18] Yellow oil. R_f (hexane/CH_2Cl_2, 85:15) = 0.1. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 6.9 Hz, 3 H, CH_3), 1.28–1.65 (m, 8 H, 4×CH_2), 2.42 (t, J = 6.9 Hz, 2 H, CH_2), 7.50 (A_2B_2, J_{AB} = 8.6 Hz, $\Delta\nu$ = 32.2 Hz, 4 H, 4×CH arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.5 (CH_2), 20.6 (CH_2), 28.4 (CH_2), 28.6 (CH_2), 31.3 (CH_2), 79.4 (*C*≡C–CH_2), 94.7 (C≡*C*–CH_2), 110.8 (*C*–CN), 118.6 (*C*N), 129.2 (*C*–C≡C), 131.5 (2×CH arom.), 132.1 (2×CH arom.) ppm.

1-Oct-1-ynyl-4-trifluoromethylbenzene: (Table 3, Entry 2): Yellow oil. R_f (hexane) = 0.5. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.5 Hz, 3 H, CH_3), 1.32–1.62 (m, 8 H, 4×CH_2), 2.42 (t, J = 6.9 Hz, 2 H, CH_2), 7.52 (A_2B_2, J_{AB} = 8.7 Hz, $\Delta\nu$ = 9.4 Hz, 4 H, 4×CH arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.3 (CH_2), 22.6 (CH_2), 28.4 (CH_2), 28.7 (CH_2), 31.5 (CH_2), 79.5 (*C*≡C–CH_2), 93.3 (C≡*C*–CH_2), 124.2 (q, J = 270 Hz, *C*F_3), 125.8 (2×CH arom.), 128.0 (*C*–C≡C), 128.6 (q, J = 129 Hz, *C*–CF_3), 131.4 (2×CH arom.) ppm. $C_{15}H_{17}F_3$ (254.77): C 70.85, H 6.74, F 22.41; found C 71.33, H 7.12, F 21.55.

2-Oct-1-ynylpyridine: (Table 3, Entry 3): Previously described.[23] Orange oil. R_f (hexane/AcOEt, 70:30) = 0.3. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.84 (t, J = 6.4 Hz, 3 H, CH_3), 1.23–1.62 (m, 8 H, 4×CH_2), 2.38 (t, J = 7.1 Hz, 2 H, CH_2), 7.1 (t, J = 6.0 Hz, 1 H, CH arom.), 7.3 (d, J = 7.0 Hz, 1 H, CH arom.), 7.5 (t, J = 7.1 Hz, 1 H, CH arom.), 8.4 (d, J = 6.0 Hz, 1 H, CH arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9 (CH_3), 19.1 (CH_2), 22.3 (CH_2), 28.1 (CH_2), 28.4 (CH_2), 31.1 (CH_2), 80.2 (*C*≡C–CH_2), 90.9 (C≡*C*–CH_2), 122.0 (CH arom.), 126.6 (CH arom.), 135.7 (*C*–C≡C), 143.8 (CH arom.), 149.6 (CH arom.) ppm.

Oct-1-ynylbenzene: (Table 3, Entry 4): Previously described.[22] Orange oil. R_f (hexane) = 0.4. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, J = 6.4 Hz, 3 H, CH_3), 1.29–1.66 (m, 8 H, 4×CH_2), 2.41 (t, J = 7.0 Hz, 2 H, CH_2), 7.26–7.43 (m, 5 H, 5×CH arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.4 (CH_2), 22.6 (CH_2), 28.6 (CH_2), 28.7 (CH_2), 31.4 (CH_2), 80.6 (*C*≡C–CH_2), 90.5 (C≡*C*–CH_2), 124.1 (CH arom.), 127.4, (2×CH arom.), 128.2 (CH arom.), 131.5 (CH arom.) ppm.

4-Oct-1-ynyltoluene: (Table 3, Entry 6): Previously described.[22] Yellow oil. R_f (hexane) = 0.5. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 6 Hz, 3 H, CH_3), 1.22–1.61 (m, 8 H, 4×CH_2), 2.34 (s, 3 H, CH_3), 2.40 (t, J = 7.0 Hz, 2 H, CH_2), 7.19 (A_2B_2, J_{AB} = 8.1 Hz, $\Delta\nu$ = 41.0 Hz, 4 H, 4×CH arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.4 (CH_2), 20.7 (CH_3), 21.3 (CH_2), 28.6 (CH_2), 28.8 (CH_2), 31.4 (CH_2), 80.6 (*C*≡C–CH_2), 89.6 (C≡*C*–CH_2), 121.1 (*C*–C≡C), 128.8 (2×CH arom.), 131.3 (2×CH arom.), 137.3 (*C*–CH_3) ppm.

4-Oct-1-ynylanisole: (Table 3, Entry 8): Previously described.[22] Yellow oil. R_f (cyclohexane) = 0.4. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, J = 6.9 Hz, 3 H, CH_3), 1.23–1.65 (m, 8 H, 4×CH_2), 2.39 (t, J = 7.0 Hz, 2 H, CH_2), 3.71 (s, 3 H, CH_3), 7.0 (A_2B_2, J_{AB} = 8.85 Hz, $\Delta\nu$ = 45.0 Hz, 4 H, 4×CH arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.4 (CH_2), 24.2 (CH_2), 28.6 (CH_2), 28.9 (CH_2), 31.4 (CH_2), 55.2 (OCH_3), 80.2 (*C*≡C–CH_2), 88.8 (C≡*C*–CH_2), 113.8 (*C*–C≡C), 116.3 (2×CH arom.), 132.8 (2×CH arom.), 159.0 (*C*–OCH_3) ppm.

3-Oct-1-ynyltoluene: (Table 3, Entry 9): Yellow oil. R_f (cyclohexane) = 0.5. ^1H NMR (300 MHz, $CDCl_3$): δ = 0.92 (t, J = 6.8 Hz, 3 H, CH_3), 1.28–1.71 (m, 8 H, 4×CH_2), 2.32 (s, 3 H, CH_3), 2.41 (t, J = 7.0 Hz, 2 H, CH_2), 7.07–7.23 (m, 4 H, 4×CH arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.2 (CH_2), 21.2 (CH_3), 22.6 (CH_2), 28.3 (CH_2), 28.5 (CH_2), 31.4 (CH_2), 80.7 (*C*≡C–CH_2), 90.0 (C≡*C*–CH_2), 123.9 (*C*–C≡C), 128.0 (CH arom.), 128.3 (CH arom.), 128.6 (CH arom.), 132.2 (CH arom.), 137.8 (*C*–CH_3) ppm. $C_{15}H_{20}$ (200.32): C 89.94, H 10.06; found C 89.77, H 10.23.

2-Oct-1-ynyltoluene: (Table 3, Entry 10): Previously described.[22] Yellow oil. R_f (hexane) = 0.5. ^1H NMR (300 MHz, $CDCl_3$): δ =

0.92 (t, J = 6.5 Hz, 3 H, CH_3), 1.29–1.70 (m, 8 H, 4×CH_2), 2.42 (s, 3 H, CH_3), 2.46 (t, J = 6.7 Hz, 2 H, CH_2), 7.08–7.19 (m, 3 H, 3×CH arom.), 7.37 (dd, J = 6.4 Hz and 1.6 Hz, 1 H, H arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.5 (CH_2), 20.7 (CH_3), 22.6 (CH_2), 28.4 (CH_2), 28.7 (CH_2), 31.3 (CH_2), 79.4 (C≡C–CH_2), 94.4 (C≡C–CH_2), 123.8 (C–C≡C), 125.4 (CH arom.), 127.3 (CH arom.), 129.2 (CH arom.), 131.8 (CH arom.), 139.9 (C–CH_3) ppm.

2-Oct-1-ynylanisole: (Table 3, Entry 11): Previously described.[22] Yellow oil. R_f (cyclohexane) = 0.4. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, J = 6.7 Hz, 3 H, CH_3), 1.22–1.65 (m, 8 H, 4×CH_2), 2.47 (t, J = 7.0 Hz, 2 H, CH_2), 3.88 (s, 3 H, CH_3) 6.75–7.30 (m, 4 H, 4×CH arom.) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.0 (CH_3), 19.9 (CH_2), 20.7 (CH_2), 22.4 (CH_2), 28.8 (CH_2), 31.2 (CH_2), 55.8 (OCH_3), 73.4 (C≡C–CH_2), 89.1 (C≡C–CH_2), 105.6 (C–C≡C), 114.5 (CH arom.), 123.5 (CH arom.), 128.7 (CH arom.), 132.9 (CH arom.), 159.9 (C–OCH_3) ppm.

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