C(sp^2)-C(sp) and C(sp)-C(sp) Coupling Reactions Catalyzed by Oxime-Derived Palladacycles

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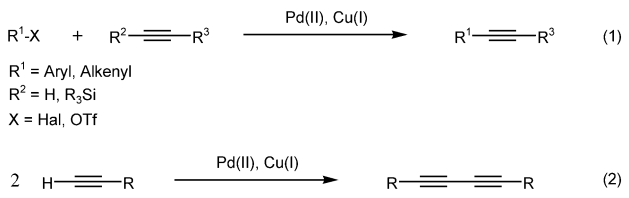
Abstract: Oxime-derived chloro-bridged palladacycle **8a**, derived from 4,4′-dichlorobenzophenone, is an efficient pre-catalyst for the copper- and amine-free Sonogashira coupling between terminal acetylenes and aryl iodides and aryl and vinyl bromides achieving turnover numbers (TON) of up to 72000. Catalyst **8a** has also been shown as a effective promoter for the sila-Sonogashira coupling between 1-(trimethylsilyl)alkynes and aryl iodides and bromides in the presence of CuI or Bu_4NBr as co-catalysts. This complex also catalyzes efficiently the homocoupling reaction (Glaser-type coupling) between 1-alkynes in NMP at room temperature with TONs of up to 1000. All the reactions can be performed under air and employing reagent-grade chemicals under very low loading conditions, which demonstrates the versatility and high activity of oxime-derived palladacycles.

Keywords: alkynes; aryl halides; C–C coupling; homogeneous catalysis; metallacycles; N ligands; palladium

Introduction

Metal-catalyzed acetylenic homo- and cross-coupling processes are currently under intensive study due to the presence of the alkynyl moieties in a wide range of natural and unnatural organic materials.[1] Two of the most useful synthetic transformations of alkynes are the Sonogashira–Hagihara reaction[2] (palladium/copper-catalyzed cross-coupling reactions of sp^2-C to sp-C atoms) or the silane version of the process employing alkynylsilanes (sila-Sonogashira reaction[3]), and the palladium-catalyzed acetylenic oxidative homocoupling reaction between their sp-carbon atoms, called the Glaser-type process.[4]

The Sonogashira coupling of terminal acetylenes with sp^2-C atoms, provides a useful tool for the preparation of alkyl-, aryl-, and diaryl-substituted acetylenes (Eq. 1, $R^2 = H$). The reaction is typically carried out in the presence of copper(I) salts as co-catalysts, and employing amines as solvents. Most frequently, high loadings of palladium (0.1 – 5 mol %) and varying amounts of CuI are required when typical catalysts such as $Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$ or $Pd_2(dba)_3$ are employed. With respect to the methodologies that employ CuI as co-catalyst, Buchwald and Fu,[5] have described $Pd(PhCN)_2Cl_2$/CuI/P(t-Bu)$_3$ as a versatile catalyst system for the Sonogashira reaction of aryl bromides at room temperature (TON up to 200). Using an excess of a bulky and electron-donating ligand such as P(t-Bu)$_3$ (6 mol %) and a high catalyst loading (3 mol % of Pd), these authors could effect the Sonogashira coupling using only an equimolar amount of amine. On the other hand, Mori has carried out the Sonogashira coupling of terminal alkynes with aryl iodides and bromides at room temperature in the presence of $Pd(PPh_3)_2Cl_2$ in THF with aqueous ammonia as base.[6] Very recently, Plenio and colleagues[7] have presented a new and very efficient catalytic system for the Sonogashira coupling of activated and non-activated aryl chlorides with terminal acetylenes, based on the combination Na_2PdCl_4/(1-Ad)$_2$PBn/CuI (1-Ad = 1-adamantyl, Bn = benzyl). On the other hand, *N*-heterocyclic carbene palladium(II) complex **1**,[8] has also been shown to mediate the Sonogashira coupling of aryl bromides with different alkynes at 80 ^{0}C in DMF under inert atmosphere, in the presence of 2 mol % of CuI and 1 mol % of PPh_3. However, and in order to simplify the reaction protocol, copper-free methodologies have lately attracted most attention, as the use of copper(I) salts as co-catalysts usually induces the homocoupling reaction (Glaser-type[4]) of terminal alkynes to diynes in the presence of oxygen as well as the precipitation of catalytically inactive palladium black. Recent advances in this topic have been reported employing amines as solvents



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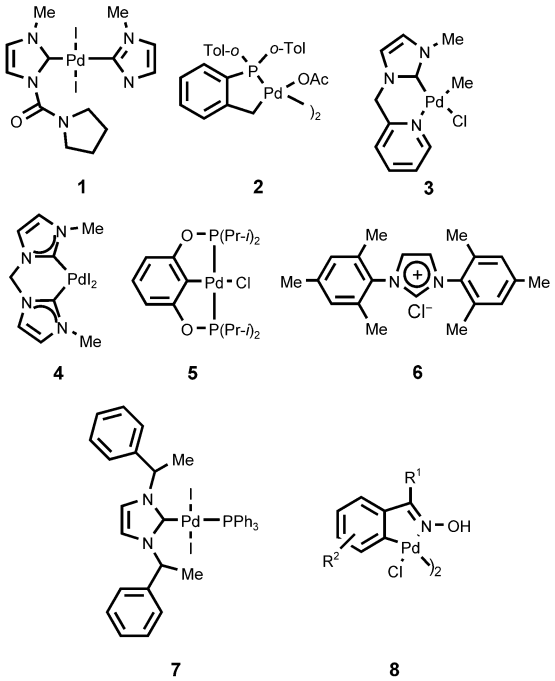


Figure 1.

(piperidine or pyrrolidine) and palladium(0) complexes such as $Pd(PPh_3)_4$ as catalysts.[9] On the other hand, Herrmann and co-workers have recently found that the catalytic system $Pd_2(dba)_3/P(t\text{-}Bu)_3$ promotes the copper-free Sonogashira-type reaction of aryl bromides at room temperature.[10] Likewise, stoichiometric amounts of silver(I) oxide for aryl iodides, and tetrabutylammonium fluoride (Bu_4NF) or tetrabutylammonium hydroxide (Bu_4NOH) for aryl bromides, have also been used as activators in the first described copper- and amine-free procedure,[11] even though when using the ammonium salts as activators, the coupling reaction is rather sluggish and CuI has to be added in a further improved procedure.[12] With respect to the use of palladacycles[13] as pre-catalysts for the copper-free Sonogashira-type reaction, Herrmann's phosphapalladacycle **2**[14] and carbene-derived palladacycles **3**[15] and **4**[16] (Figure 1), have been used in a copper-free protocol employing triethylamine (TEA) as solvent at 90 °C with turnover numbers (TON) of up to 8000 when using catalyst **2**. With regard to the use of aryl chlorides as sp^2 counterparts of the reaction, Eberhard et al.[17] have established the first efficient palladium-based and copper-free catalytic system, which cross-couples efficiently a wide range of activated and non-activated aryl chlorides with phenylacetylene, employing the palladium PCP pincer complex **5** (Figure 1) in the presence of catalytic amounts of $ZnCl_2$.

The use of alkynylsilanes as *sp* components in the palladium-catalyzed cross-coupling reaction (sila-Sonogashira coupling[3]) (Eq. 1, $R^2 = SiR_3$), has become a very important tool in synthetic organic chemistry. This protocol has been used for the synthesis of symmetrically diarylated acetylenes employing either trimethylsilylacetylene (TMSA) or bis(trimethylsilyl)acetylene (BTMSA), which avoids the use of the toxic and tricky to handle acetylene. The sila-Sonogashira reaction is usually carried out in the presence of a palladium catalyst and a fluoride ion source as activator,[18] because trimethylsilylated alkynes are usually inert to the Sonogashira–Hagihara reaction conditions. Lately, silver(I) salts have been shown as very effective co-catalysts for the coupling of aryl iodides or vinyl triflates with alkynylsilanes, employing different Pd(II) or Pd(0) catalysts accompanied by phosphane ligands.[19] Mori and co-workers have also shown that CuCl is a very effective co-catalyst for the palladium-catalyzed reaction of 1-trimethylsilylalkynes with aryl triflates in DMF at 80 °C and under neutral conditions.[20] Yang and Nolan have recently reported a very efficient sila-Sonogashira reaction between aryl bromides and alkynylsilanes catalyzed by the system $Pd(OAc)_2$/imidazolium salt **6** (Figure 1).[21] Finally, Grieco et al. have used the system $PdCl_2(PPh_3)_2$/CuI in the presence of an amidine such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as base, for the one-pot synthesis of symmetrical and unsymmetrical bisarylethynes employing TMSA under aqueous conditions.[22]

Acetylenic homocoupling of terminal alkynes[4] (Glaser reaction), is an atom economic and straightforward method for the synthesis of conjugated diynes, polyynes and acetylenic arrays. These derivatives are finding increasing applications as key structural elements of new materials with unusual electrical and optical properties, and are encountered in numerous natural and biologically active compounds. Since Rossi in 1985 optimized the homocoupling reaction of terminal alkynes as a synthetic method, employing palladium as catalyst in the presence of CuI as co-catalyst and chloroacetone as terminal oxidant,[23] diverse modifications of the procedure have appeared using different oxidants such as DMSO,[24] iodine[25] or (diacetoxy)iodobenzene.[26] Palladium(II) complexes bearing *N*-heterocyclic carbenes modified with phosphines of the type **7** (Figure 1), have also been found to promote the homocoupling of phenylacetylene in the presence of CuI as co-catalyst and TEA as solvent even in the absence of added oxidant.[27] However, there are no reported examples, to the best of our knowledge, about the use of palladacycles as catalysts for the homocoupling reaction of terminal acetylenes.

We have recently reported that phosphane-free oxime-based palladacycles **8** (Figure 1), are air- and water-stable pre-catalysts for a wide range of cross-coupling processes such as Heck, Suzuki, Stille, Sonogashira and Ullmann-type reactions in organic[28] and aqueous solvents.[29] In a preliminary communication,[28d] we have shown complexes **8** as very efficient and versatile catalysts for amine- and copper-free Sonogashira-type reactions of aryl iodides and aryl

bromides with a variety of terminal acetylenes in air and using reagent-grade chemicals with turnover numbers of up to 72000. Herein, we report the full account of oxime-derived complexes as efficient pre-catalysts not only for the palladium-catalyzed Sonogashira-type coupling, but also for the sila-Sonogashira and homocoupling reactions of acetylenes under air atmosphere. We describe first the copper- and amine-free Sonogashira-type coupling of aryl iodides and vinyl and aryl bromides with different terminal acetylenes in *N*-methylpyrrolidinone (NMP) as solvent and tetrabutylammonium acetate (Bu_4NOAc) as base. Secondly, the synthesis of symmetrical diarylethynes from the palladium cross-coupling reaction of TMSA or BTMSA with aryl iodides and bromides in the presence of CuI as co-catalyst is studied, as well as the synthesis of monoarylated trimethylsilylalkynes from the palladium cross-coupling reaction of TMSA or BTMSA with aryl iodides and bromides in the presence of tetrabutylammonium bromide (Bu_4NBr) as co-catalyst. Finally, the palladium-catalyzed homocoupling reaction of terminal alkynes at room temperature in NMP as solvent and pyrrolidine as base to afford symmetrical conjugated diynes will be considered.

Results and Discussion

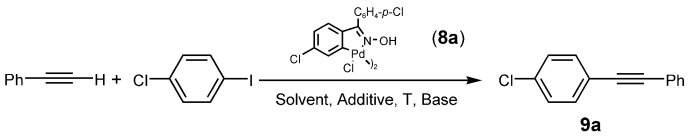
Sonogashira-type Coupling of Aryl and Vinyl Halides with Terminal Alkynes

The alkynylation reaction of aryl halides was evaluated with an oxime catalyst derived from 4,4′-dichlorobenzophenone **8a**. Other palladacycles under study in our group, derived from benzophenone, acetophenone, pinacolone and 4,4′-dimethoxybenzophenone oximes, all gave in general similar or inferior results. In order to determine the optimum reaction conditions, we chose the coupling between 1-chloro-4-iodobenzene and phenylacetylene in the presence of catalyst **8a** (0.1–0.5 mol % of Pd) as a model reaction (Scheme 1, Table 1). As we have previously reported,[28d] the coupling reaction, provided a good yield of the arylated acetylene **9a** after 1 h (84%) when pyrrolidine was used as solvent in the presence of CuI as co-catalyst (5 mol %) at 90 °C under air using 0.5 mol % of Pd (Table 1, entry 1). Unexpectedly, when using NMP as solvent and only 2 equiv. of pyrrolidine as base in the absence of CuI at 110 °C (Table 1, entry 2), an excellent 96% yield of product was obtained. As a consequence of this result, we carried out a base study, which showed that inorganic bases such as NaOAc or NH_4OAc (150 mol %), only led to poor reaction yields (Table 1, entries 3 and 4). Other bases such as tetrabutylammonium fluoride (Bu_4NF) (150 mol %), gave an acceptable 86% yield after 3 h. Aqueous tetrabutylammonium hydroxide (Bu_4NOH) did not promote the reaction coupling at all (Table 1, entry 6). However, tetrabutylammonium acetate (Bu_4NOAc, 150 mol %) showed the best activity even when the catalyst loading was reduced to 0.1 mol % of Pd (Table 1, entry 7) and also in the presence of small amounts of water (Table 1, entry 8). The reaction could be carried out at lower temperature (80 ^{0}C) and using 1.1 equiv. of Bu_4NOAc as well (Table 1, entry 9). Changing the solvent from NMP to THF under reflux, resulted in a lower yield and longer reaction times (Table 1, en-

Table 1. Sonogashira coupling: reaction conditions study.

Entry	Solvent	Additive [mol %]	T[a] [^{0}C]	**8a** [mol % Pd]	t [h]	Yield[b] [%]	TON[c]
1	Pyrrolidine	CuI (5)	90	0.5	1	84	168
2	NMP	Pyrrolidine[d]	110	0.5	1	96	192
3	NMP	NaOAc[e]	110	0.5	1	36[f]	72
4	NMP	NH_4OAc[e]	110	0.5	3.5	29[f]	58
5	NMP	Bu_4NF (150)	110	0.5	3	86[f]	172
6	NMP	Bu_4NOH (150)	110	0.1	3	0	–
7	NMP	Bu_4NOAc (150)	110	0.1	2	> 99	990
8	NMP/H_2O, 95/5	Bu_4NOAc (110)	110	0.1	1	> 99	990
9	NMP	Bu_4NOAc (110)	80	0.1	4	> 99	990
10	THF	Bu_4NOAc (110)	-[g]	0.1	5	89	890
11	NMP	Bu_4NOAc (110)	110	10^{-2}	24	97	9700
12	NMP	Bu_4NOAc (110)	110	10^{-3}	24	72	72000

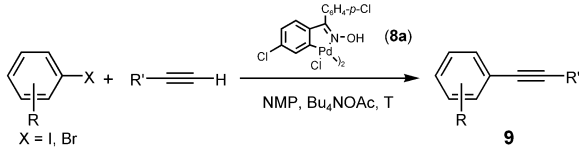
[a] Bath temperature.
[b] Conversion determined by GLC using decane as internal standard and based on starting 1-chloro-4-iodobenzene.
[c] TON = turnover number (mol product mol Pd^{-1}).
[d] 2 equiv. were used.
[e] 1.5 equiv. were used.
[f] Several non-identified enyne by-products were also obtained in variable yields as a result of the addition of the terminal alkyne to the reaction product.
[g] Under THF reflux.



Scheme 1.

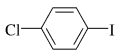
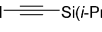
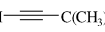
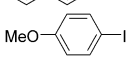
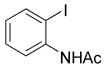
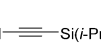
try 10). Higher TONs, 9700 and 72000, accompanied with very good yields could be obtained at 110 °C, when the catalyst loading was reduced to 10^{-2} and 10^{-3} mol % of Pd, respectively (Table 1, entries 11 and 12).

Using NMP as solvent and Bu_4NOAc as base, complex **8a** catalyzed the Sonogashira coupling of a wide variety of aryl iodides with terminal acetylenes to afford the corresponding arylated alkynes **9** (Scheme 2, X = I, Table 2). Reaction conversions (determined by GLC using decane as internal standard), were generally high after short reaction times for all type of substrates, and the chromatographic purification of the compounds were carried out using either silica gel or florisil. Activated substrates such as 1-chloro-4-iodobenzene reacted with an array of aromatic and aliphatic alkynes in good to excellent yields (Table 2, entries 1–5). (Triisopropylsilyl)acetylene had to be used for the preparation of silylated alkynes (Table 2, entries 2 and 8), as trimethylsilylacetylene (TMSA), always gave variable amounts of the sila-Sonogashira products. In the case of employing 2-propyn-1-ol as the *sp*-counterpart (Table 2, entry 5), a 60% isolated yield of the corresponding alcohol **9e** was obtained together with a 10% yield of the acetylated compound **9e'**. As illustrated in entries 7 and 8, the less reactive, electron-rich 4-iodoanisole also coupled with similar good efficiency. Steric effects as in 2-iodotoluene (Table 2, entry 9), did not influence the yield of the reaction. *N*-Acetyl-*o*-iodoaniline, gave the alkylynated product **9j** in 65% isolated yield. These types of substrates have been used in indole synthesis,[30] though in our case, no traces of cyclization product were observed (Table 2, entry 10). We also found that an excess of 1-octyne reacted with



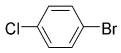
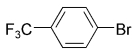
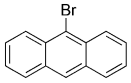
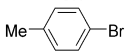
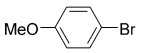
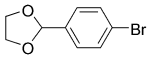
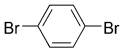
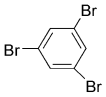
Scheme 2.

Table 2. Sonogashira-type coupling of aryl iodides catalyzed by **8a**.

Entry	Aryl iodide	Alkyne	**8a** [mol % Pd]	T[a] [^{0}C]	t [h]	Product	
						No.	Yield[b, c] [%]
1			0.1	110	1	**9a**	>99 (73)
2			0.5	110	1	**9b**	>99
3			0.5	110	1	**9c**	100 [76]
4			0.1	110	5	**9d**	85 (60)
5			0.1	110	1	**9e**	99 (60)[d]
6			0.1	110	1	**9f**	>99 [88]
7			0.1	110	1	**9 g**	89 [80]
8			0.1	110	1	**9 h**	90
9			0.1	110	1	**9i**	92 (80)
10			0.1	110	2	**9j**	100 (65)
11			0.1	110	4	**9k**	80[e, f]

[a] Bath temperature.
[b] Determined by GLC, based on ArI using decane as internal standard. In parenthesis isolated yield after flash chromatography. In brackets isolated yield after florisil chromatography.
[c] Reaction conditions: ArI (0.5 mmol), alkyne (0.6 mmol), Bu_4NOAc (0.55 mmol), **8a**, NMP (2 mL).
[d] 10% of acetylated alcohol, **9e'**, was also obtained
[e] Reaction conditions: ArI (0.5 mmol), alkyne (1.2 mmol), Bu_4NOAc (1.1 mmol), **8a**, NMP (2 mL).
[f] 14% of monoalkynylated compound, **9k'**, was also obtained.

Table 3. Sonogashira coupling of aryl and vinyl bromides catalyzed by **8a**.

Entry	ArBr	Alkyne	**8a** [mol % Pd]	T[a] [^{0}C]	t [h]	Product	
						No.	Yield[b, c] [%]
1		H—≡—Ph	0.5	110	7.5	**9a**	93 (90)[d]
2		H—≡—*n*-Hex	0.1	110	2	**9b**	78
3		H—≡—Ph	0.1	110	7	**9 l**	66 (40)
4		H—≡—*n*-Hex	0.1[e]	110	1	**9 m**	96 (75)
5		H—≡—Ph	0.1	110	1	**9n**	81
6		H—≡—Si(*i*-Pr)$_3$	0.1	110	3.5	**9o**	79
7		H—≡—Ph	0.1	110	1	**9p**	96
8		H—≡—Si(*i*-Pr)$_3$	0.25	130	4	**9q**	81
9		H—≡—Si(*i*-Pr)$_3$	0.25	130	1	**9 h**	85
10		H—≡—*n*-Hex	0.1	110	3	**9r**	45 [30]
11		H—≡—*n*-Hex	0.1	130	23	**9 s**	89 (39) [52][f, g]
12		H—≡—Ph	0.1	110	7.5	**9 t**	73 (58)[f, h]
13		H—≡—*n*-Hex	0.1	110	3	**9k**	75 [60][f, i]
14		H—≡—*n*-Hex	0.1	110	29	**9u**	86 [73][j, k]
15		H—≡—*n*-Hex	0.1	110	3	**9v**	85 (40) [62]
16		H—≡—Si(*i*-Pr)$_3$	0.1	110	1	**10**	63 (36)

[a] Bath temperature.
[b] Determined by GLC, based on ArBr using decane as internal standard. In parenthesis isolated yield after flash chromatography. In brackets isolated yield after florisil chromatography.
[c] Reaction conditions: ArBr (0.5 mmol), alkyne (0.6 mmol), Bu_4NOAc (0.55 mmol), **8a**, NMP (2 mL).
[d] In parenthesis crude yield after work-up (pure by ^1H and ^{13}C NMR).
[e] 2.5 equiv. of 1-octyne were used.
[f] Reaction conditions: ArBr (0.5 mmol), alkyne (1.5 mmol), Bu_4NOAc (1.2 mmol), **8a**, NMP (2 mL).
[g] 11% of pure monoalkynylated compound, **9 s'**, was also obtained.
[h] 17% of pure monoalkynylated compound, **9 t'**, was also obtained.
[i] 25% of pure monoalkynylated compound, **9k'**, was also obtained.
[j] Reaction conditions: ArBr (0.5 mmol), alkyne (2.5 mmol), Bu_4NOAc (2.5 mmol), **8a**, NMP (2 mL).
[k] 14% and 2% of pure di- and monoalkynylated compounds, **9u'** and **9u''** were also obtained, respectively

fairly good yield with 1,2-diiodobenzene to afford the *bis*-Sonogashira coupling product **9k** (Table 2, entry 11).

In order to evaluate the scope of this methodology, we also examined the Sonogashira-type coupling of diverse aryl bromides with alkyl- and aryl-substituted alkynes (Scheme 2, X = Br, Table 3). Activated substrates such as 1-chloro-4-bromobenzene, 1-bromo-4-(trifluoromethyl)benzene and 1-bromonaphthalene reacted with phenylacetylene and 1-octyne in good yields (Table 3, entries 1–4). 9-Bromoanthracene, reacted with phenylacetylene and (triisopropylsilyl)acetylene to afford, in high yields (Table 3, entries 5 and 6), the corresponding 9-alkynylanthracenes **9n** and **9o** with no observable formation of aceanthrylenes.[31] Sterically hindered 2-bromobenzonitrile also coupled with fairly good efficiency with phenylacetylene at 110 °C (Table 3, entry 7). However, in the case of less reactive electron-rich aryl bromides such as 4-bromotoluene and 4-bromoanisole, 0.25 mol % of Pd and 130 °C were used to achieve fast conversions (Table 3, entries 8 and 9). 4-Bromobenzal-

dehyde ethylene glycol acetal, gave the corresponding coupling product **9r** after reaction with 1-octyne in a moderate 30% isolated yield, with no observable deprotection product (Table 3, entry 10). Polybromobenzenes, such as 1,2-dibromobenzene, 1,4-dibromobenzene and 1,3,5-tribromobenzene, reacted with an excess of the corresponding alkyne (3 or 5 equiv.), affording the resultant products in satisfactory yields (Table 3, entries 11 – 14). The yield of the corresponding peralkynylated product could not be improved when the amount of alkyne was considerably increased. Heterocyclic 2-bromothiophene was likewise converted efficiently to the corresponding cross-coupling product **9v** (Table 3, entry 15). In the case of the vinyl bromide *trans*-β-bromostyrene, the coupling with (triisopropylsilyl)acetylene, afforded the corresponding *trans*-enyne **10** after 1 h at 110 °C in a moderate 36% isolated yield (Table 3, entry 16). As described above, moderate to good yields were generally obtained, and these were usually higher when fluorisil was used instead of silica gel in the chromatographic purification of the crude products (see Table 3, entries 11 and 15).

The efficiency as catalyst in the Sonogashira-type reaction of oxime-derived palladacycle **8a**, is apparent when compared with Herrmann's phosphapalladacycle **2**,[14] which only works efficiently when phenylacetylene is used as *sp* counterpart, even employing triethylamine as solvent.

Sila-Sonogashira Coupling of Aryl Halides with Silylated Alkynes

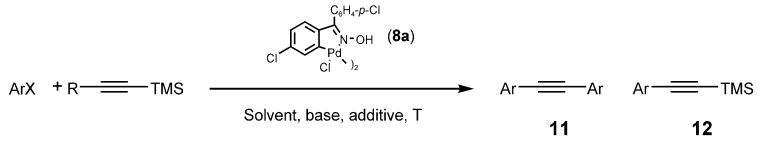
During the course of our studies about the Sonogashira–Hagihara coupling of trimethylsilylacetylene (TMSA) with different aryl halides, and contrary to the case of the triisopropylsilyl moiety which remained stable under the reaction conditions (see Tables 2 and 3), we observed the formation, in variable and small amounts, of the corresponding sila-Sonogashira coupling products. We then decided to carry out an investigation of the catalytic activity of complex **8a** in the cross-coupling reaction between aryl halides and silylated alkynes (Scheme 3, Table 4). In initial experiments, a catalytic system consisting of **8a** (0.5 mol % of Pd) and CuI (5 mol %) in pyrrolidine as solvent at 90 ^{0}C (Method A), was used to achieve with rather good yields the coupling of 1-chloro-4-iodobenzene, 1-naphthalene and 4-iodoanisole with both TMSA (1.2 equiv.) and BTMSA (0.75 equiv.) as synthetic equivalents of acetylene, to afford the corresponding diarylated ethynes **11** (Table 4, entries 1, 2, 6, 7 and 11). The reaction coupling with BTMSA could be carried out with similar levels of efficiency employing NMP as solvent and 3 equiv. of pyrrolidine as base, by just increasing the temperature to 110 °C (Method B) (Table 4, entries 3, 8 and 12).

When Bu_4NBr, (20 mol %), was used as co-catalyst instead of CuI (Method C), the monosilylated alkynes **12**, were isolated as the major products both in the case of using TMSA (Table 4, entries 4, 9 and 13), and BTMSA (Table 4, entries 5, 10 and 14).

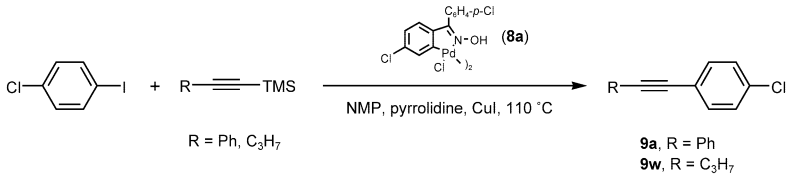
As depicted in Table 4, entries 15 – 19, aryl bromides reacted sluggishly with TMSA and BTMSA. Again when using CuI as co-catalyst (Method B, Table 4, entries 16 and 17) diarylated acetylenes **11** were the main reaction products. On the contrary, in the presence of TBAB (Method C) the major products were the monoarylated silylalkynes **12** (Table 4, entries 15, 18 and 19). Consequently, TMSA and BTMSA behaved as acetylene equivalents when the coupling reaction was carried out in the presence of CuI. However, in the absence of CuI, TMSA gave only the Sonogashira coupling products and BTMSA the monosila-Sonogashira products.

The catalytic system was also competent for the sila-Sonogashira coupling of 1-chloro-4-iodobenzene with other silylated alkynes such as 1-phenyl-2-(trimethylsilyl)acetylene and 1-trimethylsilyl-1-pentyne, which gave after 7 h the asymmetrical substituted alkynes **9a** and **9w** in 76 and 50% yield, respectively, under the conditions of Method B (Scheme 4).

With respect to the reaction mechanism, we observed the fast formation of a 1:1 mixture of phenylacetylene

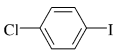
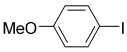
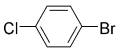
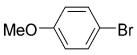


Scheme 3.



Scheme 4.

Table 4. Sila-Sonogashira coupling of aryl halides catalyzed by **8a**.

Entry	ArX	R	**8a**[a] [mol % Pd]	Method[b]	t [h]	Products No. [Yield[c] %]
1		TMS	0.5	A	3	**11a**/**12a**: 61/0
2		H	1	A	7	**11a**/**12a**: 84/6
3		TMS	0.25	B	6	**11a**/**12a**: 88/0
4		H	0.5	C	2	**11a**/**12a**: 11/77
5		TMS	0.5	C	8	**11a**/**12a**: 11/53
6		H	0.5	A	6	**11b**/**12b**: 90/0
7		TMS	0.5	A	8	**11b**/**12b**: 99/0
8		TMS	0.25	B	6	**11b**/**12b**: 78/11
9		H	0.5	C	5	**11b**/**12b**: 15/61
10		TMS	0.5	C	21	**11b**/**12b**: 11/74
11		TMS	0.5	A	24	**11c**/**12c**: 75/0
12		TMS	0.25	B	6	**11c**/**12c**: 35/10
13		H	0.5	C	5	**11c**/**12c**: 5/45
14		TMS	0.5	C	8	**11c** / **12c**: 0/54
15		TMS	0.5	C	5	**11a**/**12a**: 8/53
16		H	0.25	B	24	**11b** / **12b**: 25/0
17		TMS	0.25	B	8	**11b**/**12b**: 28/6
18		TMS	0.25	C[d]	22	**11b**/**12b**: 22/64
19		TMS	0.5	C	8	**11c**/**12c**: 6/59

[a] Mol % of Pd with respect to the aryl halide.
[b] Method A: ArX (1 mmol), TMSA (1.2 mmol) or BTMSA (0.75 mmol), pyrrolidine (3 mL), CuI (5 mol %), 90 °C. Method B: ArX (1 mmol), TMSA (0.75 mmol) or BTMSA (0.6 mmol), pyrrolidine (3 mmol), CuI (5 mol %), NMP (2 mL), 110 °C. Method C: ArX (1 mmol), alkyne (1.2 mmol), pyrrolidine (1 mmol), TBAB (20 mol %), NMP (2 mL), 110 °C.
[c] Determined by GLC, based on ArX using decane as internal standard.
[d] The reaction was carried out at 130 °C.

and the corresponding diyne (80% conversion after 30 min.), when 1-phenyl-2-(trimethylsilyl)acetylene was heated in NMP at 110 ^{0}C under Method B conditions. However, in the absence of the palladium and copper catalysts, a 36% conversion to phenylacetylene was observed as well after 1 h. This result seems to indicate that the reaction could proceed merely *via* protodesilylation and coupling of the *in situ* formed terminal alkyne, though the fact that the desilylation is much faster in the presence of the catalysts (Method B), does not rule out the possibility a simultaneous direct coupling of the silyl alkynes through a transmetallation process.

In conclusion, oxime-derived palladacycle **8a**, has been shown, to the best of our knowledge, to be the only catalyst of this type that is active in sila-Sonogashira couplings.

Homocoupling Reactions of Terminal Alkynes

During the course of our initial studies about the palladium-catalyzed Sonogashira cross-coupling reaction between phenylacetylene and iodobenzene, employing other bases than pyrrolidine as solvent, such as TEA and Hünig's base, in the presence of CuI as co-catalyst,[28a] we found that significant amounts of 1,4-diphenylbuta-1,3-diyne were always obtained. Consequently, we also decided to investigate and optimize the ability of catalyst **8a** to promote the oxidative homocoupling reaction of different terminal alkynes (Scheme 5, Table 5).

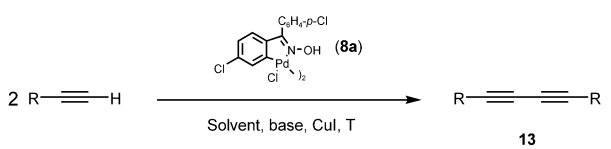
As illustrated in Table 5, good isolated yields of conjugated diynes **13** could be obtained by dimerization of 1-alkynes in the presence of oxime-derived catalyst **8a** (Scheme 5). We found that complex **8a** can effectively promote the coupling of 1-octyne in the presence of CuI (5 mol %) as co-catalyst, using TEA as solvent and pyrrolidine as base (1.1 equiv.) (Table 5, entry 1). As mentioned above for the sila-Sonogashira reaction, catalyst **8a** avoids the use of the amine as solvent, and the homocoupling reaction showed even higher levels of effectiveness when the solvent was changed to NMP at 110 °C still employing pyrrolidine as base and under

Table 5. Homocoupling reactions of terminal alkynes catalyzed by **8a**.

Entry	R	**8a**[a] [mol % Pd]	Solvent	Base	T[b] [^{0}C]	t [h]	Product No.	Product Yield[c],[d] [%]
1	C_6H_{13}	0.5	TEA	Pyrrolidine	90	8	**13a**	99 (70)
2	C_6H_{13}	0.05	NMP	Pyrrolidine	110	3	**13a**	99 (60)
3	C_7H_{15}	0.05	NMP	Pyrrolidine	110	2	**13b**	99 (50)
4	Ph	0.05	NMP	Pyrrolidine	110	2	**13c**	99 (82)
5	*i*-Pr_3Si	0.05	NMP	Pyrrolidine	110	2.5	**13d**	90 (75)
6	C_6H_{13}	0.1	NMP	Bu_4NOAc	110	9	**13a**	73
7	$Me_2(OH)C$	0.05	NMP	Pyrrolidine	110	23	**13e**	25
8	Ph	0.5	NMP	Pyrrolidine	rt	2	**13c**	99
9	Ph	0.05	NMP	Pyrrolidine	rt	6	**13c**	92 (80)
10	Ph	0.05	NMP[e]	Pyrrolidine	rt	6	**13c**	58
11	Ph	0.5	*i*-Pr_2NH[f]	–	rt	2	**13c**	87
12	Ph	0.5	NMP	TEA[g]	rt	21	**13c**	11

[a] Mol% of Pd with respect to the starting alkyne.
[b] Bath temperature.
[c] Determined by GLC, based on alkyne using decane as internal standard. In parenthesis isolated yield after flash chromatography.
[d] Reaction conditions: alkyne (1 mmol), CuI (5 mol %), base (pyrrolidine, Bu_4NOAc or TEA 1.1 mmol.), solvent (2 mL).
[e] The reaction was carried out under Ar atmosphere employing degassed NMP.
[f] The reaction was carried out in the presence of 0.5 equiv. of I_2.
[g] The reaction was carried out in the presence of 1 equiv. of chloroacetone.

lower catalyst loadings (0.05 mol % of Pd, TON = 1000) (Table 5, entry 2). Under these conditions, 1-nonyne, phenylacetylene and (triisopropylsilyl)acetylene also gave good yields of the corresponding dialkylated and diarylated diynes **13b**, **13c** and **13d**, respectively (Table 5, entries 3–5). Other bases such as Bu_4NOAc lengthened the reaction time and gave lower conversions (Table 5, entry 6). The homocoupling of 2-methyl-3-butyn-2-ol (Table 5, entry 7), gave a poor 25% yield of the corresponding homocoupled diol **13e**. It is worthy to note that the homocoupling process worked very efficiently (99% yield after 2 h, 0.5 mol % of Pd) at room temperature (Table 5, entry 8). At this temperature, reducing the catalyst loading to 0.05 mol % of Pd (Table 5, entry 9), longer reaction times were necessary to completion. It was found that under these conditions the reaction proceeded sluggishly in the absence of oxygen (compare entries 9 and 10). However, the presence of external oxidants such as iodine[25] did not result in any significant improvement in rate or yield (compare entries 8 and 11). Other oxidants such as chloroacetone[23] seriously inhibited the reaction (Table 5, entry 12). Therefore, oxime-derived palladacycle **8a** is a competent promoter of the palladium-catalyzed homocoupling reaction of terminal alkynes at room temperature achieving turnover numbers of up to 1000.



Scheme 5.

Conclusion

In summary, we have shown that the phosphane-free oxime-derived palladacycle **8a**, is an efficient and versatile pre-catalyst for the amine- and copper-free Sonogashira-type reaction of aryl iodides and aryl- and vinyl bromides with a variety of terminal acetylenes. The catalytic system has also been successfully applied to the cross-coupling of aryl iodides with alkynylsilanes. Tuning the reaction conditions, it is possible to control the reaction outcome to obtain either the diarylated alkynes (Methods A and B) or the silylated monoarylated alkynes (Method C). Complex **8a** also catalyzes very efficiently, even at room temperature, the synthesis of conjugated diynes through the homocoupling of terminal alkynes using copper iodide as co-catalyst. Consequently, we have demonstrated that oxime-derived palladacycles are extremely active pre-catalysts for C(sp^2)-C(sp) and C(sp)-C(sp) reaction couplings under air and very low loading conditions employing reagent-grade chemicals. Further studies on the applicability of these systems in other organic transformations are currently under investigation in our group.

Experimental Section

General

The reagents and solvents were obtained from commercial sources and were generally used without further purification. Palladacycle **8a** can be purchased from MEDALCHEMY S. L. Gas chromatographic analyses were performed on an HP-5890 instrument equipped with a WCOT HP-1 fused silica capillary column using decane as internal standard. ^{1}H NMR spectra were recorded on a Bruker AC-300 MHz spectrometer. Chemical shifts are reported in ppm using tetramethylsilane (TMS, 0.00 ppm) as internal standard. ^{13}C NMR spectra were recorded at 75 MHz with $CDCl_3$ as the internal reference. The catalysts were weighed out in an electronic microscale (Sartorius, XM1000P) with a precision of 1 μg. IR data were collected on a Nicolet Impact 400D of FT. Solid products were recrystallized in hexane/EtOAc unless otherwise stated, and melting points were not corrected. When mentioned, the reactions were set up with the aid of carousel reaction equipment equipped with gas-tight threaded caps with a valve, cooling reflux head system, and digital temperature controller.

Compound **9b**, reported in Table 2 (entry 2), has been previously reported[32] and was characterized by comparison of the GLC/MS and ^{1}H NMR spectra; the purity was confirmed by GLC analysis. Compounds **9n**,[31a] **9o**[31a] and **9p**[33] (Table 3, entries 5, 6 and 7, respectively) and compounds **12a**,[34] **11c**[35] and **12c**[34] (Table 4), have been previously reported and were characterized by comparison of their GLC/MS and ^{1}H NMR spectra; their purities were confirmed by GLC analyses.

Typical Procedure for Sonogashira-type Coupling of Aryl Iodides and Bromides with 1-Alkynes

A reaction tube of the carousel reaction equipment, was charged with 2-iodotoluene (65 μL, 0.5 mmol), decane (97 μL, 0.5 mmol), phenylacetylene (67 μL, 0.6 mmol), tetrabutylammonium acetate (171 mg, 0.55 mmol), **8a** (0.204 mg, 0.00025 mmol, 0.1 mol % Pd) and NMP (2 mL). The mixture was stirred at 110 °C in air and the reaction progress was analyzed by GLC. The crude reaction mixture was extracted with water and EtOAc (3 × 15 mL). The organic phases were dried, evaporated (15 mm Hg) and the resulting crude material was purified by flash chromatography (hexane) affording pure *1-(2-methylphenyl)-2-phenylacetylene* (**9i**);[5] yield: 76.3 mg (80%); R_f: 0.44 (hexane); oil; IR (film): ν = 3059, 3021, 2215 cm^{-1}; ^{1}H NMR: δ = 2.51 (s, 3H, CH_3), 7.12 – 7.23 (m, 3H, ArH), 7.31 – 7.34 (m, 3H, ArH), 7.48 – 7.55 (m, 3H, ArH); ^{13}C NMR: δ = 20.7, 88.3, 93.3, 123.0, 123.5, 125.6, 128.1, 128.3, 129.4, 131.5, 131.8, 140.1; MS: *m/z* (rel. int.) = 193 ($M^+ + 1$, 15), 192 (M^+, 100), 191 ($M^+ - 1$, 92), 190 (18), 189 (34), 165 (28), 115 (13).

1-(4-Chlorophenyl)-2-phenylacetylene (9a):[10] mp 81 °C; IR (KBr): ν = 3048 cm^{-1}; ^{1}H NMR: δ = 7.32 – 7.37 (m, 5H, ArH), 7.45 – 7.55 (m, 4H, ArH); ^{13}C NMR: δ = 88.3, 90.3, 121.8, 123.0, 128.4, 128.5, 128.7, 131.6, 132.8, 134.3; MS: *m/z* (rel. int.) = 214 ($M^+ + 2$, 32), 213 ($M^+ + 1$, 16), 212 (M^+, 100), 176 (41), 151 (15), 150 (11), 106 (10), 88 (11).

2-(4-Chlorophenyl)-1-(triisopropylsilyl)acetylene (9c): R_f: 0.65 (hexane); oil; IR (film): ν = 2157 cm^{-1}; ^{1}H NMR: δ = 1.12 [m, 21H, 3 × $CH(CH_3)_2$], 7.26, 7.39 (2d, 4H, J = 8.52 Hz, ArH); ^{13}C NMR: δ = 11.3, 18.6, 91.8, 105.8, 122.0, 128.5, 133.2, 134.3; MS: *m/z* (rel. int.) = 294 ($M^+ + 2$, 3), 292 (M^+, 8), 251 (31), 249 ($M^+ - 43$, 78), 223 (9), 221 (27), 209 (14), 207 (38), 195 (25), 193 (69), 181 (36), 179 (100), 165 (21), 163 (27), 139 (14), 97 (18), 63 (17); HRMS: calcd. for $C_{17}H_{25}ClSi$: 292.1414; found: 292.1429.

3-(4-Chlorophenyl)-1,1-dimethylprop-2-yn-1-ol (9d):[36] R_f: 0.12 (hexane/EtOAc, 9/1); mp 55 – 57 °C (toluene); IR (KBr): ν = 3725 – 3026 cm^{-1} (OH); ^{1}H NMR: δ = 1.61 (s, 6H, 2 × CH_3), 2.35 (s, 1H, OH), 7.25 – 7.35 (m, 4H, ArH); ^{13}C NMR: δ = 31.3, 65.5, 81.0, 94.7, 121.2, 128.5, 132.8, 134.2; MS: *m/z* (rel. int.) = 196 ($M^+ + 2$, 7), 194 (M^+, 21), 181 (31), 179 ($M^+ - 15$, 100), 159 (12), 136 (28), 116 (13), 115 (24), 101 (12), 75 (12).

3-(4-Chlorophenyl)prop-2-yn-1-ol (9e):[37] mp 76 – 78 °C (Lit. 78.5 – 79 °C); IR (KBr): ν = 3617 – 2979, 2241 cm^{-1}; ^{1}H NMR: δ = 1.82 (s, 1H, OH), 4.49 (s, 2H, CH_2), 7.28, 7.36 (2d, 4H, J = 8.64 Hz, ArH); ^{13}C NMR: δ = 51.6, 84.6, 88.1, 121.0, 128.7, 132.9, 134.6; MS: *m/z* (rel. int.) = 168 ($M^+ + 2$, 17), 167 ($M^+ + 1$, 14), 166 (M^+, 51), 165 (27), 149 (20), 138 (16), 137 (18), 136 (12), 132 (10), 131 (100), 114 (13), 113 (10), 103 (74), 102 (38), 101 (40), 77 (23), 75 (26), 74 (14), 63 (14), 51 (24).

3-(4-Chlorophenyl)prop-2-ynyl acetate (9e'): R_f: 0.22 (hexane/EtOAc, 9/1); oil; IR (CH_2Cl_2): ν = 3086, 2237, 1748, 1223 cm^{-1}; ^{1}H NMR: δ = 2.13 (s, 3H, CH_3), 4.89 (s, 2H, CH_2), 7.29, 7.38 (2d, 4H, J = 8.51 Hz, ArH); ^{13}C NMR: δ = 20.8, 52.7, 83.9, 85.3, 120.6, 128.7, 133.1, 134.9, 170.3; MS: *m/z* (rel. int.) = 208 (M^+, 10), 193 (19), 151 (17), 150 (36), 149 (53), 148 (100), 145 (13), 137 (17), 131 (35), 114 (21), 113 (45), 102 (11), 101 (15), 75 (11), 63 (12); HRMS: calcd. for $C_{11}H_9ClO_2$: 208.0291; found: 208.0273.

1-(1-Naphthyl)-2-phenylacetylene (9f):[19] R_f: 0.22 (hexane); oil; IR (film): ν = 3057, 2211 cm^{-1}; ^{1}H NMR: δ = 7.37 – 7.77 (m, 11H, ArH), 8.44 (d, 1H, J = 8.22 Hz, ArH); ^{13}C NMR: δ = 87.5, 94.3, 120.9, 123.4, 125.3, 126.2, 126.4, 126.8, 128.3, 128.36, 128.42, 128.7, 130.3, 131.6, 133.2, 133.3; MS: *m/z* (rel. int.) = 229 ($M^+ + 1$, 20), 228 (M^+, 100), 227 ($M^+ - 1$, 18), 226 ($M^+ - 2$, 40), 114 (16), 113 (18).

1-(4-Methoxyphenyl)-2-phenylacetylene (9 g):[5] R_f: 0.15 (hexane); mp 51 – 53 °C (Lit. 52 – 54 °C); IR (KBr): ν = 3053, 2216, 1246, 1028 cm^{-1}; ^{1}H NMR: δ = 3.81 (s, 3H, CH_3), 6.87 (d, 2H, J = 8.52 Hz, ArH), 7.32 (m, 3H, ArH), 7.45 – 7.52 (m, 4H, ArH); ^{13}C NMR: δ = 55.3, 88.0, 89.3, 114.0, 115.3, 123.6, 127.9, 128.3, 131.4, 133.0, 159.6; MS: *m/z* (rel. int.) = 209 ($M^+ + 1$, 16), 208 (M^+, 100), 193 (53), 165 (53), 164 (19), 163 (15), 139 (16).

1-(4-Methoxyphenyl)-2-(triisopropylsilyl)acetylene (9 h):[38] R_f: 0.18 (hexane); oil; IR (film): ν = 3038, 3001, 2154, 1249, 1036 cm^{-1}; ^{1}H NMR: δ = 1.12 [s, 21H, 3 × $CH(CH_3)_2$], 3.80 (s, 3H, OCH_3), 6.81, 7.41 (2d, 4H, J = 8.45 Hz, ArH); ^{13}C NMR: δ = 11.4, 18.7, 55.3, 88.6, 107.1, 113.8, 115.8, 133.5, 159.6; MS: *m/z* (rel. int.) = 288 (M^+, 23), 246 (22), 245 (100), 217 (24), 203 (47), 189 (53), 176 (13), 175 (79), 161 (11), 159 (14), 135 (10), 94 (19).

2-Phenylethynyl-*N*-acetylaniline (9j):[39] mp 120 – 122 °C (Lit. 119 – 121 °C); IR (KBr): ν = 3305, 1661, 1532 cm^{-1}; ^{1}H NMR: δ = 2.24 (s, 3H, CH_3), 7.07 (t, 1H, J = 7.55 Hz, ArH), 7.32 – 7.40 (m, 4H, ArH), 7.48 – 7.55 (m, 3H, ArH), 7.97 (s, 1H, NH), 8.41 (d, 1H, J = 8.22 Hz, ArH); ^{13}C NMR: δ = 24.9, 84.3, 96.4, 111.8, 119.3, 122.3, 123.4, 128.6, 128.9, 129.7, 131.5, 131.6, 138.9, 168.1; MS: *m/z* (rel. int.) = 235 (M^+, 40), 194 (16), 193 (100), 192 (16), 165 (34), 90 (13), 89 (11).

1,2-Bis(1-octynyl)benzene (9k):[40] R_f: 0.17 (hexane); oil; IR (film): ν = 2228 cm^{-1}; ^{1}H NMR: δ = 0.93 (t, 6H, J = 6.87 Hz, 2 × CH_3), 1.35 – 1.71 (m, 16H, 8 × CH_2), 2.49 (t, 4H, J =

7.00 Hz, 2 × CCH_2), 7.18 – 7.21 (m, 2H, ArH), 7.38 – 7.41 (m, 2H, ArH); ^{13}C NMR: δ = 14.1, 19.7, 22.6, 28.6, 28.8, 31.4, 79.5, 94.1, 126.3, 127.1, 131.8; MS: *m/z* (rel. int.) = 294 (M^+, 29), 195 (17), 182 (13), 181 (68), 179 (21), 178 (23), 169 (28), 168 (18), 167 (90), 166 (35), 165 (70), 156 (12), 155 (55), 154 (25), 153 (48), 152 (62), 151 (20), 142 (24), 141 (100), 139 (13), 129 (30), 128 (29), 115 (18), 97 (11), 55 (48).

1-Bromo-2-(oct-1-ynyl)benzene (9k'): R_f: 0.40 (hexane); oil; IR (film): ν = 2232 cm^{-1}; ^{1}H NMR: δ = 0.91 (t, 3H, *J* = 6.53 Hz, CH_3), 1.24 – 1.68 (m, 8H, 4 × CH_2), 2.46 (t, 2H, *J* = 6.86 Hz, CCH_2), 7.10 (dt, 1H, *J* = 7.82, 1.65 Hz, ArH), 7.22 (dt, 1H, *J* = 7.55, 0.96 Hz, ArH), 7.42 (dd, 1H, *J* = 7.68, 1.65 Hz, ArH), 7.55 (dd, 1H, *J* = 7.96, 0.96 Hz, ArH); ^{13}C NMR: δ = 14.1, 19.6, 22.57, 28.3, 28.5, 31.3, 79.3, 95.6, 125.4, 126.1, 126.8, 128.6, 132.2, 133.2; MS: *m/z* (rel. int.) = 266 (M^+ + 2, 14), 264 (M^+, 12), 223 (19), 221 (18), 195 (27), 193 (20), 182 (20), 180 (15), 171 (22), 169 (22), 156 (40), 155 (11), 143 (26), 142 (87), 141 (45), 130 (16), 129 (81), 128 (64), 127 (23), 126 (10), 117 (16), 116 (100), 115 (77), 114 (63), 113 (25), 102 (12), 101 (12), 95 (40), 91 (12), 88 (20), 87 (10), 82 (10), 77 (10), 75 (13), 67 (15), 63 (16), 55 (11); HRMS: calcd. for $C_{14}H_{17}Br$: 264.0514; found: 264.0513.

1-Phenyl-2-(trifluoromethylphenyl)acetylene (9 l):[41] mp 103 ^{0}C; IR (KBr): ν = 2218 cm^{-1}; ^{1}H NMR: δ = 7.34 – 7.36 (m, 3H, ArH), 7.53 – 7.60 (m, 6H, ArH); ^{13}C NMR: δ = 88.0, 91.8, 122.5, 123.9 (*J* = 270.5 Hz), 125.3 (*J* = 14.6 Hz), 127.1, 128.4, 128.8, 129.9 (*J* = 31.5 Hz), 131.7, 131.8; MS: *m/z* (rel. int.) = 247 (M^+ + 1, 20), 246 (M^+, 100), 196 (12), 176 (14), 98 (31), 85 (12), 75 (13).

1-(Oct-1-ynyl)naphthalene (9 m): R_f: 0.38 (hexane); oil; IR (film): ν = 3058, 2955, 2930, 2857, 2224 cm^{-1}; ^{1}H NMR: δ = 0.92 (t, 1H, *J* = 6.87 Hz, CH_3), 1.34 – 1.74 (m, 8H, 4 × CH_2), 2.55 (t, 2H, *J* = 7.07 Hz, ≡CCH_2), 7.38 (t, 1H, *J* = 7.38 Hz, ArH), 7.45 – 7.57 (m, 2H, ArH), 7.61 (d, 1H, *J* = 6.3 Hz, ArH), 7.75 (d, 1H, *J* = 8.22 Hz, ArH), 7.81 (d, 1H, *J* = 7.53 Hz, ArH), 8.25 (d, 1H, *J* = 8.04 Hz, ArH); ^{13}C NMR: δ = 14.1, 19.7, 22.6, 28.7, 28.9, 31.4, 78.6, 95.6, 121.8, 125.2, 126.2, 126.3, 126.4, 127.8, 128.2, 129.9, 133.2, 133.5; MS: *m/z* (rel. int.) = 236 (M^+, 35), 207 (12), 193 (22), 179 (28), 178 (28), 167 (60), 166 (24), 165 (100), 164 (25), 163 (21), 153 (13), 152 (27), 141 (10); HRMS: calcd. for $C_{18}H_{20}$: 236.1565; found: 236.1550.

1-(4-Methylphenyl)-2-(triisopropylsilyl)acetylene (9q): R_f: 0.28 (hexane); oil; IR (film): ν = 3081, 3049, 3028, 2155 cm^{-1}; ^{1}H NMR: δ = 1.12 [m, 21H, 3 × $CH(CH_3)_2$], 2.33 (s, 3H, $ArCH_3$), 7.09, 7.37 (2d, 4H, *J* = 7.92 Hz, ArH); ^{13}C NMR: δ = 11.3, 18.7, 21.5, 89.5, 107.3, 120.5, 128.9, 131.9, 138.4; MS: *m/z* (rel. int.) = 272 (M^+, 7), 230 (16), 229 (70), 201 (22), 187 (41), 174 (11), 173 (60), 160 (16), 159 (100), 145 (16), 143 (29), 119 (19), 86 (20); HRMS: calcd. for $C_{18}H_{28}Si$: 272.1960; found: 272.1966.

2-[4-(Oct-1-ynyl)phenyl]-1,3-dioxolane (9r): R_f: 0.31 (hexane/EtOAc, 9/1); oil; IR (film): ν = 2226 cm^{-1}; ^{1}H NMR: δ = 0.90 (m, 3H, CH_3), 1.26 – 1.65 (m, 8H, 4 × CH_2), 2.40 (t, 2H, *J* = 7.07 Hz, CCH_2), 4.00 – 4.14 (m, 4H, OCH_2CH_2O), 5.79 (s, 1H, OCHO), 7.38, 7.51 (2d, 4H, *J* = 8.37 Hz, ArH); ^{13}C NMR: δ = 14.0, 19.4, 22.5, 28.6, 28.7, 31.3, 65.3, 80.3, 91.1, 103.4, 125.0, 126.3, 131.5, 137.0; MS: *m/z* (rel. int.) = 258 (M^+, 53), 257 (M^+ – 1, 92), 213 (18), 187 (21), 157 (18), 144 (25), 143 (62), 142 (14), 141 (18), 131 (13), 130 (23), 129 (53), 128 (52), 127 (19), 117 (42), 116 (25), 115 (100), 104 (15), 102 (12), 91 (20), 73 (94); HRMS: calcd. for $C_{17}H_{22}O_2$: 258.1620; found: 258.1587.

1,4-Di(oct-1-ynyl)benzene (9 s):[42] R_f: 0.36 (hexane); oil; IR (film): ν = 2228 cm^{-1}; ^{1}H NMR: δ = 0.90 (t, 6H, *J* = 6.86 Hz, 2 × CH_3), 1.29 – 1.64 (m, 16H, 8 × CH_2), 2.40 (t, 4H, *J* = 7.07 Hz, 2 × CCH_2), 7.29 (s, 4H, ArH); ^{13}C NMR: δ = 14.0, 19.5, 22.6, 28.6, 28.7, 31.4, 80.4, 91.9, 123.2, 131.3; MS: *m/z* (rel. int.) = 295 (M^+ + 1, 15), 294 (M^+, 65), 251 (22), 225 (31), 223 (22), 183 (11), 181 (19), 179 (20), 178 (21), 169 (24), 168 (12), 167 (45), 166 (30), 165 (72), 157 (11), 156 (13), 155 (68), 154 (20), 153 (51), 152 (82), 151 (22), 143 (23), 142 (21), 141 (100), 139 (47), 130 (11), 129 (80), 128 (34), 127 (11), 126 (11), 115 (33), 109 (16), 91 (11), 79 (12), 67 (24), 55 (36).

1-Bromo-4-(oct-1-ynyl)benzene (9 s'): R_f: 0.18 (hexane); oil; IR (CH_2Cl_2): ν = 2204 cm^{-1}; ^{1}H NMR: δ = 0.89 (m, 3H, CH_3), 1.30 – 1.68 (m, 8H, 4 × CH_2), 2.38 (t, 2H, *J* = 7.07 Hz, CCH_2), 7.24, 7.40 (2d, 4H, *J* = 8.51 Hz, ArH); MS: *m/z* (rel. int.) = 266 (M^+ + 2, 17), 264 (M^+, 17), 223 (15), 221 (15), 197 (13), 195 (40), 193 (27), 182 (16), 180 (10), 171 (14), 169 (15), 156 (31), 143 (29), 142 (86), 141 (38), 130 (11), 129 (66), 128 (55), 127 (21), 117 (14), 116 (100), 115 (56), 114 (48), 113 (23), 102 (10), 101 (11), 95 (10), 88 (17), 63 (15); HRMS: calcd. for $C_{14}H_{17}Br$: 264.0514; found: 264.0535.

1,4-Bis(2-phenyl-1-ethynyl)benzene (9 t):[43] R_f: 0.20 (hexane); mp 177 – 179 ^{0}C (Lit. 178 – 180 ^{0}C); IR (KBr): ν = 3048, 1595, 1516 cm^{-1}; ^{1}H NMR: δ = 7.34 – 7.36 (m, 6H, ArH), 7.51 – 7.55 (m, 8H, ArH); ^{13}C NMR: δ = 89.1, 91.2, 123.0, 123.1, 128.38, 128.45, 131.5, 131.6; MS: *m/z* (rel. int.) = 279 (M^+ + 1, 26), 278 (M^+, 100), 276 (17), 139 (19).

1,3,5-Tri(oct-1-ynyl)benzene (9u): R_f: 0.29 (hexane); oil; IR (film): ν = 2229, 2200 cm^{-1}; ^{1}H NMR: δ = 0.902 (t, 9H, *J* = 6.66 Hz, 3 × CH_3), 1.31 – 1.62 (m, 24H, 12 × CH_2), 2.37 (t, 6H, *J* = 6.93 Hz, 3 × CCH_2), 7.30 (s, 3H, ArH); ^{13}C NMR: δ = 14.1, 19.3, 22.6, 28.56, 28.61, 31.4, 79.4, 91.2, 124.3, 133.5; MS: *m/z* (rel. int.) = 403 (M^+ + 1, 11), 402 (M^+, 32), 359 (13), 333 (22), 219 (11), 216 (11), 215 (13), 209 (16), 208 (18), 207 (100), 205 (22), 203 (21), 202 (23), 193 (23), 191 (29), 190 (15), 189 (25), 179 (38), 178 (22), n167 (19), 165 (30), 153 (11), 152 (12), 133 (11), 109 (23), 96 (21), 95 (20), 81 (12), 79 (15), 73 (10), 69 (12), 67 (33), 55 (45); HRMS: calcd. for $C_{30}H_{42}$: 402.3287; found: 402.3278.

1-Bromo-3,5-di(oct-1-ynyl)benzene (9u'): oil; MS: *m/z* (rel. int.) = 374 (M^+ + 2, 22), 372 (M^+, 21), 331 (12), 224 (20), 209 (21), 208 (28), 207 (99), 195 (19), 194 (17), 193 (22), 192 (13), 191 (18), 183 (10), 182 (33), 181 (34), 180 (27), 179 (49), 178 (49), 177 (12), 169 (15), 168 (22), 167 (62), 166 (45), 165 (100), 164 (19), 163 (21), 156 (16), 155 (54), 154 (22), 153 (52), 152 (60), 151 (34), 150 (30), 142 (20), 141 (48), 139 (23), 133 (12), 129 (16), 128 (27), 115 (14), 109 (14), 96 (19), 95 (48), 93 (16), 91 (11), 81 (13), 79 (26), 69 (14), 37 (30), 55 (39); HRMS: calcd. for $C_{22}H_{29}Br$: 372.1453; found: 372.1458.

1,3-Dibromo-5-(oct-1-ynyl)benzene (9u''): oil; IR (CH_2Cl_2): ν = 2227 cm^{-1}; ^{1}H NMR: δ = 0.91 (t, 3H, *J* = 6.86 Hz, CH_3), 1.24 – 1.61 (m, 8H, 4 × CH_2), 2.39 (t, 2H, *J* = 6.99 Hz, CH_2), 7.46 (d, 2H, *J* = 1.77 Hz, ArH), 7.56 (d, 2H, *J* = 1.77 Hz, ArH); MS: *m/z* (rel. int.) = 346 (M^+ + 4, 10), 344 (M^+ + 2, 20), 342 (M^+, 10), 331 (15), 275 (10), 273 (18), 260 (15), 249 (10), 236 (14), 234 (13), 222 (20), 221 (10), 220 (17), 196 (18), 195 (15), 194 (28), 193 (15), 155 (24), 142 (26), 141 (50), 129 (16), 128 (100), 127 (25), 126 (23), 115 (32), 114 (23), 113 (53), 95 (33), 87 (13), 82 (13), 69 (29), 67 (24), 55 (15); HRMS calcd. for $C_{14}H_{16}Br_2$: 341.9619; found: 341.9660.

2-(Oct-1-ynyl)thiophene (9v):[44] R_f: 0.48 (hexane); oil; IR (film): ν = 2225 cm^{-1}; ^{1}H NMR: δ = 0.90 (t, 3H, *J* = 6.80 Hz, CH_3), 1.29 – 1.62 (m, 8H, 4 × CH_2), 2.41 (t, 3H, *J* = 7.07 Hz, ≡CCH_2), 6.93 (dd, 1H, *J* = 5.07, 3.69 Hz, ArH), 7.11 (d, 1H, *J* =

3.45 Hz, ArH), 7.16 (d, 1H, $J = 5.22$ Hz, ArH); ^{13}C NMR: $\delta =$ 14.0, 19.7, 22.5, 28.5, 28.6, 31.3, 73.6, 94.6, 124.3, 125.8, 126.7, 130.8; MS: *m/z* (rel. int.) = 192 (M^+, 32), 163 (22), 150 (18), 149 (36), 136 (25), 135 (42), 134 (21), 124 (13), 123 (100), 122 (14), 121 (83), 116 (10), 115 (34), 110 (15), 108 (19), 97 (28), 91 (13), 79 (13), 77 (28), 69 (11), 63 (11).

Triisopropyl[(*E*)-4-phenyl-3-buten-1-ynyl]silane (10):[45] oil; IR (film): $\nu = 3081$, 3061, 3029, 2165, 2118 cm^{-1}; ^{1}H NMR: $\delta = 1.11$ [m, 21H, $3 \times CH(CH_3)_2$], 6.21 and 6.99 (2d, 2H, $J = 16.47$ Hz, CH=CH), 7.25 – 7.39 (m, 5H, ArH); ^{13}C NMR: $\delta = 11.3$, 18.6, 93.3, 106.2, 108.4, 126.2, 128.6, 128.7, 136.2, 142.0; MS: *m/z* (rel. int.) = 284 (M^+, 19), 242 (24), 241 ($M^+ - 43$, 100), 213 (18), 199 (30), 186 (11), 185 (61), 183 (26), 172 (16), 171 (88), 169 (19), 167 (11), 157 (19), 155 (34), 145 (31), 131 (14), 129 (24), 105 (10), 92 (29), 59 (36).

Typical Procedure for Sila-Sonogashira Coupling of Aryl Iodides and Bromides to Afford Diarylated Alkynes

Method A: A 25-mL round-bottom flask was charged with 1-iodonaphthalene (295 μL, 2 mmol), decane (194 μL, 1 mmol), bis(trimethylsilyl)acetylene (345 μL, 1.5 mmol) or trimethylsilylacetylene (340 μL, 2.4 mmol), CuI (19.4 mg, 0.1 mmol), **8a** (4.079 mg, 0.005 mmol, 0.5 mol % Pd) and pyrrolidine (6 mL). The mixture was stirred at 90 ^{0}C in air and the reaction progress was analyzed by GLC. The crude reaction mixture was extracted with water and EtOAc (3×15 mL). The organic phases were dried, evaporated (15 mm Hg) and the resulting crude was purified by flash chromatography (hexane/EtOAc) affording the corresponding *1,2-di(1-naphthyl)acetylene* (**11b**);[46] yield: 756.3 mg (54%); R_f: 0.23 (hexane/EtOAc, 99/1); mp 125 ^{0}C (Lit. 127 – 129 ^{0}C); IR (KBr): $\nu = 3052$, 3044 cm^{-1}; ^{1}H NMR: $\delta = 7.48 - 7.67$ (m, 6H, ArH), 7.87 – 7.91 (m, 6H, ArH), 8.57 (d, 2H, $J = 8.3$ Hz, ArH); ^{13}C NMR: $\delta =$ 92.4, 121.1, 125.3, 126.3, 126.5, 126.9, 128.4, 128.9, 130.6, 133.3; MS: *m/z* (rel. int.) = 279 ($M^+ + 1$, 24), 278 (M^+, 100), 277 ($M^+ -$ 1, 23), 276 (M^+-2, 47), 139 (30), 138 (50), 137 (26), 125 (20).

Method B: A reaction tube of the carousel reaction equipment was charged with 1-iodonaphthalene (148 μL, 1 mmol), decane (194 μL, 1 mmol), bis(trimethylsilyl)acetylene (136 μL, 0.6 mmol), pyrrolidine (253 μL, 3 mmol), CuI (9.7 mg, 0.05 mmol), **8a** (1.020 mg, 0.00125 mmol, 0.25 mol % Pd) and NMP (2 mL). The mixture was stirred at 110 ^{0}C in air and the reaction progress was analyzed by GLC. The crude reaction mixture was extracted with water and EtOAc ($3 \times$ 15 mL). The organic phases were dried, evaporated (15 mm Hg) and the resulting crude was purified by flash chromatography (hexane/EtOAc) affording the corresponding *1,2-di(1-naphthyl)acetylene* (**11b**).

1,2-Bis(4-chlorophenyl)acetylene (11a):[41] R_f: 0.52 (hexane/EtOAc, 99/1); mp 176 ^{0}C (Lit. 174 – 176 ^{0}C); IR (KBr): $\nu =$ 3078, 831 cm^{-1}; ^{1}H NMR: $\delta = 7.32$ (d, 4H, $J = 8.3$ Hz, ArH), 7.45 (d, 4H, $J = 8.3$ Hz, ArH); ^{13}C NMR: $\delta = 89.2$, 121.4, 128.7, 132.8, 134.5; MS: *m/z* (rel. int.) = 248 ($M^+ + 2$, 50), 246 (M^+, 100), 176 (47), 123 (22), 99 (10), 88 (19), 75 (17).

1-Chloro-4-(pent-1-ynyl)benzene (9w): R_f: 0.52 (hexane); oil; IR (film): $\nu = 3054$, 3035, 2237 cm^{-1}; ^{1}H NMR: $\delta = 1.04$ (t, 3H, $J = 7.41$ Hz, CH_3), 1.51 – 1.68 (m, 2H, CH_3CH_2), 2.37 (t, 2H, $J = 6.99$ Hz, $\equiv CCH_2$), 7.24, 7.32 (2d, 4H, $J = 8.39$ Hz, ArH); ^{13}C NMR: $\delta = 13.5$, 21.4, 22.1, 79.6, 91.3, 122.6, 128.4, 132.7, 133.4; MS: *m/z* (rel. int.) = 180 ($M^+ + 2$, 22), 178 (M^+, 54), 163 (10), 151 (36), 150 (12), 149 (100), 143 (39), 142 (18), 141 (14), 136 (14), 128 (72), 127 (32), 115 (25), 114 (26), 113 (21), 99 (18), 98 (12), 75 (11), 63 (16); HRMS: calcd. for $C_{11}H_{11}Cl$: 178.0549; found: 178.0539.

Typical Procedure for Sila-Sonogashira Coupling of Aryl Iodides and Bromides to Afford Silylated Alkynes

Method C: A reaction tube of the carousel reaction equipment was charged with 1-iodonaphthalene (295 μL, 2 mmol), decane (390 μL, 2 mmol), bis(trimethylsilyl) acetylene (542 μL, 2.4 mmol) or trimethylsilylacetylene (340 μL, 2.4 mmol), tetrabutylammonium bromide (129 mg, 0.4 mmol), pyrrolidine (177 μL, 2.1 mmol), catalyst **8a** (4.079 mg, 0.005 mmol, 0.5 mol % Pd) and NMP (4 mL). The mixture was stirred at 110 ^{0}C in air and the reaction progress was analyzed by GLC. The crude reaction mixture was extracted with water and EtOAc (3×15 mL). The organic phases were dried, evaporated (15 mm Hg) and the resulting crude was purified by flash chromatography (hexane/EtOAc) affording the corresponding *trimethyl[2-(1-naphthyl)-1-ethynyl]silane* (**12b**);[47] oil; IR (film): $\nu = 2147$ cm^{-1}; ^{1}H NMR: $\delta = 0.34$ (s, 9H, $3 \times CH_3$), 7.37 – 7.84 (m, 6H, ArH), 8.34 (d, 1H, $J = 7.89$ Hz, ArH); ^{13}C NMR: $\delta = 99.4$, 103.1, 120.7, 125.1, 126.2, 126.3, 126.8, 128.2, 129.0, 130.8, 133.1; MS: *m/z* (rel. int.) = 224 (M^+, 36), 210 (20), 209 (100), 179 (10), 165 (23), 104 (11).

Typical Procedure for the Homocoupling Reaction of Terminal Alkynes

A reaction tube of the carousel reaction equipment was charged with 1-octyne (152 μL, 1 mmol), decane (97 μL, 0.5 mmol), pyrrolidine (93 μL, 1.1 mmol), CuI (9.7 mg, 0.05 mmol), **8a** (0.204 mg, 0.00025 mmol, 0.05 mol % Pd) and NMP (2 mL). The mixture was stirred at the temperature indicated in Table 5 (110 ^{0}C or rt) in air and the reaction progress was analyzed by GLC. The crude reaction mixture was extracted with water and EtOAc (3×15 mL). The organic phases were dried, evaporated (15 mm Hg) and the resulting crude was purified by flash chromatography (hexane/EtOAc) affording the corresponding *7,9-hexadecadiyne* (**13a**);[19] yield: 65 mg (60%); oil; IR (film): $\nu = 2956$, 2931, 2871, 2859, 2233 cm^{-1}; ^{1}H NMR: $\delta = 0.89$ (t, 6H, $J = 6.8$ Hz, $2 \times CH_3$), 1.22 – 1.56 (2 m, 16H, $8 \times CH_2$), 2.24 (t, 4H, $J = 7.0$ Hz, $2 \times \equiv CCH_2$); ^{13}C NMR: $\delta = 14.0$, 19.2, 22.5, 28.3, 28.5, 31.3, 65.3, 77.3; MS: *m/z* (rel. int.) = 189 ($M^+ - 29$, 3), 147 (5), 133 (9), 119 (16), 105 (29), 91 (58), 79 (41), 77 (25), 67 (47), 55 (40), 44 (34), 41 (100).

8,10-Octadecadiyne (13b):[48] R_f: 0.58 (hexane); oil; IR (film): $\nu = 2234$ cm^{-1}; ^{1}H NMR: $\delta = 0.87$ (t, 6H, $J = 6.72$ Hz, $2 \times CH_3$), 1.27 – 1.53 (m, 20H, $10 \times CH_2$), 2.23 (t, 4H, $J =$ 6.71 Hz, $2 \times CCH_2$); ^{13}C NMR: $\delta = 14.0$, 19.2, 22.6, 28.3, 28.75, 28.78, 31.7, 65.2, 77.5; MS: *m/z* (rel. int.) = 246 (M^+, 0.1), 161 (12), 147 (20), 135 (14), 133 (36), 122 (11), 121 (30), 120 (13), 119 (51), 117 (18), 115 (12), 109 (19), 107 (38), 106 (13), 105 (60), 103 (12), 95 (28), 94 (15), 93 (48), 92 (21), 91 (100), 81 (51), 80 (14), 79 (60), 78 (28), 77 (33), 69 (16), 67 (56), 65 (16), 57 (10), 55 (49), 51 (11).

1,4-Diphenyl-1,3-butadiyne (13c):[19] R_f: 0.33 (hexane/EtOAc, 99/1); mp 87 ^{0}C (Lit. 87 ^{0}C); IR (KBr): $\nu = 3047$ cm^{-1}; ^{1}H NMR: $\delta = 7.33-7.36$ (m, 6H, ArH), 7.52–7.55 (m, 4H, ArH); ^{13}C NMR: $\delta = 73.9$, 81.6, 124.8, 128.4, 129.2, 132.5; MS: *m/z* (rel. int.) = 202 (M^+, 100), 200 ($M^+ - 2$, 25), 101 (15), 88 (9).

1,4-Bis(triisopropylsilyl)-1,3-butadiyne (13d):[49] mp 108–110 ^{0}C; IR (KBr): $\nu = 2061$ cm^{-1}; ^{1}H NMR: $\delta = 1.09$ [s, 42H, $6 \times CH(CH_3)_2$]; ^{13}C NMR: $\delta = 11.3$, 18.6, 81.5, 90.2; MS: *m/z* (rel. int.) = 362 (M^+, 13), 321 (11), 320 (31), 319 (M^+-43, 100), 291 (18), 277 (17), 263 (14), 249 (24), 137 (12), 82 (27), 73 (12), 59 (13).

2,7-Dimethyl-3,5-octadiyne-2,7-diol (13e):[42] R_f: 0.83 (hexane/EtOAc, 3/2); mp 131–133 ^{0}C (Lit. 133 ^{0}C); IR (KBr): $\nu =$ 3664–2663, 2144 cm^{-1}; ^{1}H NMR: $\delta = 1.53$ (s, 12H, $4 \times CH_3$), 1.89 (s, 2H, CH_2); ^{13}C NMR: $\delta = 31.0$, 65.6, 66.3, 84.0; MS: *m/z* (rel. int.) = 166 (M^+, 4), 152 (11), 151 (100), 134 (13), 133 (85), 123 (52), 109 (24), 108 (15), 107 (15), 106 (19), 105 (80), 93 (35), 91 (33), 81 (10), 79 (30), 77 (47), 75 (11), 74 (11), 69 (33), 68 (12), 67 (19), 65 (27), 63 (26), 62 (11), 55 (27), 53 (22), 51 (24).

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References and Notes

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