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Transition metal control in the reaction of alkyne-substituted phenyl iodides with terminal alkynes: Sonogashira coupling vs cyclic carbopalladation

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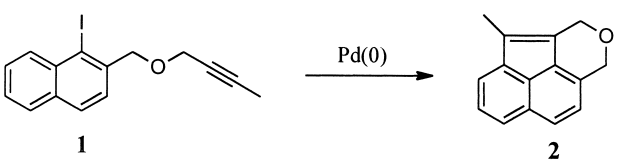
Abstract—Reaction between terminal alkynes and phenyl iodides bearing a tethered alkyne unit can be effectively controlled by the nature of a transition metal catalyst. Whereas the use of Pd(0)/Cu(I) promotes the expected Sonogashira coupling to give phenyl alkynes, the absence of the copper co-catalyst triggers a palladium-mediated cyclisation providing 1,2-dihydroacenaphthylene, 1*H*,3*H*-benzo[*de*]isochromene, (1*Z*)-1-(2-propynylidene)-2,3-dihydro-1*H*-indene and (4*E*)-4-(2-propynylidene)-3,4-dihydro-1*H*-isochromene derivatives. In the latter Pd-catalysed two-component process, the product distribution depends on the structure of alkyne-substituted phenyl iodides, terminal alkynes and secondary amines used as solvents. The proposed reaction mechanism reflects a competitive formation of intermediary σ-(acetylide) vs π-alkyne Pd(II) complexes.

1. Introduction

Transition metal-catalysed cascade reactions belong to the powerful tools of contemporary organic synthesis. They allow a considerable increase in the molecular complexity in a single operation and usually proceed with excellent chemo-, regio- and stereoselectivity.[1,2] Multicyclisations of unsaturated substrates, comprising an alkene/alkyne insertion into the Pd–C bond as a relay step, are central to such effective processes.[2]

Our recent studies on the aryl halide–alkyne coupling,[3] related to the synthesis of molecules with helical chirality,[4] revealed the Pd-catalysed cascade reaction of naphthyl iodide **1** affording the acenaphthylene derivative **2** (Scheme 1).[3a]

In context of our continuing interest in novel syntheses of aromatics, we describe herein the reaction of phenyl iodides **3** with terminal alkynes whose outcome may switch from phenyl alkynes **4** to phenyl enynes **5** and/or acenaphthylene derivatives **6** depending on the nature of a transition metal catalyst used as well as on the structure of reactants and amine solvents (Scheme 2).



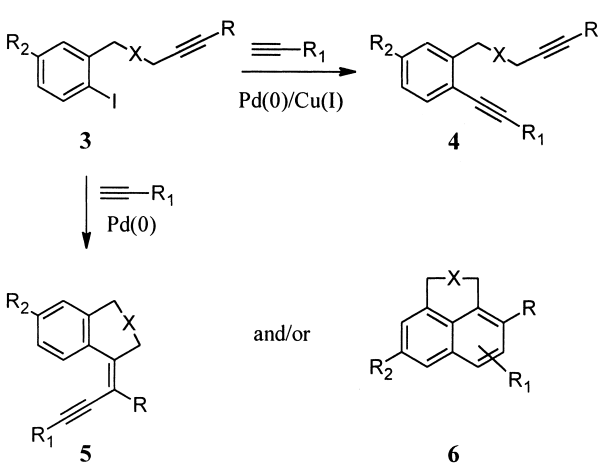
1 **2**

Scheme 1.

2. Results

2.1. Synthesis of model compounds

The model compounds **11**, **12**, **14**–**17** were prepared from the commercially available *o*-iodo benzyl alcohol **7** or from



3 **4** **5** **6**

Scheme 2.

Keywords: alkynes; aryl halides; coupling reactions; cyclisation.

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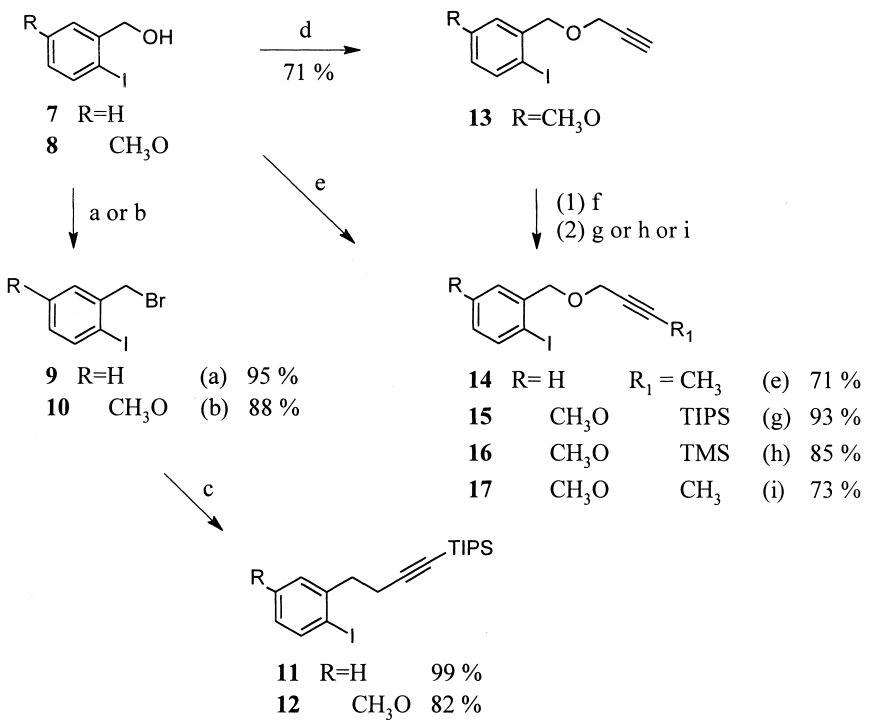
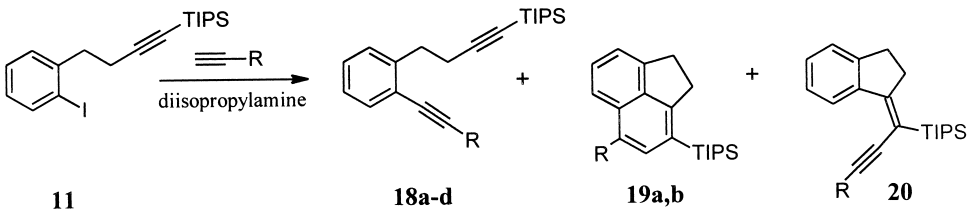


Scheme 3. (a) PBr_3 (1.8 equiv.), THF, 0°C, 30 min; (b) CBr_4 (2.4 equiv.), PPh_3 (2.4 equiv.), CH_3CN, rt, 10 min; (c) $LiCH_2C{\equiv}CTIPS$ (1.1 equiv.), THF, −78°C, 1 h; (d) NaH (1.4 equiv.), DMF, 0°C, 45 min, then $BrCH_2C{\equiv}CH$ (1.5 equiv.), 0°C, 30 min; (e) NaH (1.1 equiv.), THF, 0°C, 1.5 h, then $BrCH_2C{\equiv}CCH_3$ (1.2 equiv.), 0°C to rt, 68 h; (f) LDA (1.0 equiv.), THF, −78°C, 1 h, then an electrophile added; (g) TIPSCl (1.0 equiv.), −78°C to rt overnight; (h) TMSCl (1.0 equiv.), −78°C to rt overnight; (i) CH_3I (1.0 equiv.), −78°C to rt overnight.

its easily accessible methoxy derivative **8**[3a] (Scheme 3). Bromination of **7** and **8** afforded benzyl bromide **9** and **10** that, on reaction with $LiCH_2C{\equiv}CTIPS$ generated in situ from triisopropyl(1-propynyl)silane and *n*-butyllithium, provided smoothly 3-butynylbenzene **11** and **12**, respectively. Benzyl 2-butynyl ether **14** was synthesized directly from **7** by alkylation of a corresponding alkoxide with 1-bromo-2-butyne. Similarly, alkylation of **8** with propargyl bromide gave **13**, allowing the introduction of appropriate substituents at the terminus of the tethered alkyne by quenching a corresponding acetylide with electrophiles. As *n*-butyllithium failed to deprotonate selectively the terminal alkyne in **13** (a halogen/lithium exchange proceeded far more rapidly), LDA cleanly generated acetylide that, on a subsequent reaction with TIPSCl, TMSCl or CH_3I, furnished **15**–**17** with preserved iodine.

Table 1.



Entry	Acetylene (R, equiv.)	$Pd(PPh_3)_4$ (mol%)	CuI (mol%)	Cond. (°C, h)	Products (yield, %)[a]		
					18	**19**	**20**
1	TIPS, 1.0	5	10	rt, 0.3	**18a** (70)		
2	TIPS, 1.0	5	–	80, 22		No rxn[b]	
3	TMS, 1.2	5	10	80, 1	**18b** (92)		
4	TMS, 1.2	5	–	80, 1		**19a** (72)	
5	Ph, 1.0	5	10	rt, 0.1	**18c** (85)		
6	Ph, 1.0	5	–	80, 22		**19b** (30)	**20** (15)
7	^{n}Bu, 1.0	5	10	rt, 0.2	**18d** (85)		
8	^{n}Bu, 1.0	5	–	80, 22	Complex mixture[c]		

[a] Isolated.
[b] A 59% recovery of **11**.
[c] The starting material was consumed and a complex mixture of lipophilic products formed.

2.2. Phenyl–alkynyl coupling vs cyclic carbopalladation

Initially, on treatment of phenyl iodide **11** with TIPS–C≡CH under Pd(0)/Cu(I) catalysis,[5] the expected product of aryl–acetylene coupling **18a** was formed in good yield (Table 1, entry 1). Omitting the copper(I) co-catalyst,[6] no significant conversion took place even after a prolonged reaction period and a substantial part of the educt **11** was recovered (Table 1, entry 2). These results demonstrated the remarkable accelerating effect of the Cu(I) salt on the Pd(0)-promoted aryl–alkynyl coupling.

By contrast, the replacement of the TIPS protecting group by TMS one in a terminal alkyne resulted in a dramatic change of the course of the reaction. Whereas the Pd(0)/Cu(I)-mediated coupling of **11** with TMS–C≡CH proceeded 'ordinarily' to give phenylacetylene **18b** (Table 1, entry 3), the use of Pd(0) alone led unexpectedly to the acenaphthylene derivative **19a** in good yield (Table 1, entry 4). Hence, the exclusive formation of **19a** revealed that a two-component palladium-catalysed cascade process operates in the reaction and that the tethered alkyne can participate easily in it. Similarly, the use of Ph–C≡CH under Pd(0)/Cu(I) catalysis gave clearly rise to the coupled product **18c** (Table 1, entry 5) and the reaction in the absence of Cu(I) tended to afford acenaphthylene **19b** along with the minor partly cyclised phenyl enyne **20** (Table 1, entry 6). For 1-hexyne the Pd(0)/Cu(I)-mediated coupling furnished **18d** (Table 1, entry 7) while catalysis by Pd(0) alone catalysis led to a complex mixture (Table 1, entry 8).

2.3. Scope of cyclic carbopalladation

To understand structural requirements of the Pd(0)-catalysed cyclisation in the absence of the Cu(I) co-catalyst, the reaction between the various alkyne-substituted phenyl iodides **11**, **12**, **14**–**17** and a terminal alkyne or its isoelectronic counterpart was investigated (Table 2). Standard reaction conditions (catalytic amount of $Pd(PPh_3)_4$, diisopropylamine unless noted otherwise, 80°C) were used throughout this study.

On treatment of **11** with trimethylsilyl cyanide, the tethered alkyne did not participate in the reaction at all and instead a partial replacement of iodine by cyanide took place to give **21** in moderate yield (Table 2, entry 1). Hereafter, we paid attention only to the reactions of phenyl iodides with trimethylsilyl acetylene that has been shown to be superior among other terminal alkynes in the cyclisation reaction (see Table 1). The CH_3O-substituted phenyl iodide **12** afforded acenaphthylene **22** as a sole product in good yield, in accord with the outcome of the cascade reaction of the parent unsubstituted derivative **11** (cf. Table 2, entry 2 and Table 1, entry 4). Similarly, compound **15** with a three-atom tether containing oxygen provided benzo[*de*]isochromene **23** in moderate yield together with its minor regioisomer **24** and the partly cyclised phenyl enyne **25** (Table 2, entry 3). Surprisingly, when replacing diisopropylamine by piperidine in the reaction of **15**, a dramatic effect on the product distribution was observed. In this case the partly cyclised phenyl enyne **25** prevailed along with the minor Sonogashira-type phenyacetylene **26** while the cascade reaction product benzo[*de*]isochromene **24** was formed only in a very small amount (cf. Table 2, entry 3 and 4). Furthermore, on going from the bulky TIPS group in **15** to smaller TMS in **16**, the partly cyclised phenyl enyne **27** was exclusively produced in high yield (cf. Table 2, entry 3 and 5). Regardless of what amine had been used as a solvent, the close substrates **17** and **14** both bearing the CH_3-terminated alkyne unit gave the partly cyclised phenyl enyne **28** and **29**, respectively, in moderate yields (Table 2, entry 6 and 7).

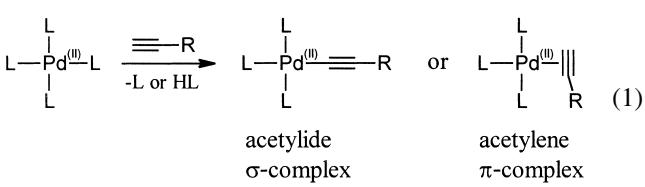
3. Discussion

To rationalise the behaviour of the reaction, we propose the following general mechanism (Scheme 4).[7]

Oxidative addition of a Pd(0) species to phenyl iodide **A** provides the σ-arylpalladium(II) intermediate **B** which represents a common starting point for three pathways. Consecutively, its fate depends on the presence or absence of a Cu(I) salt. Under Pd(0)/Cu(I) catalysis (cycle 1), the fast Cu(I)/amine-assisted coordination of the terminal alkyne **C** to Pd(II) dominates to generate the σ-alkynylpalladium(II) complex **D** that after reductive elimination produces the coupled phenylacetylene **E** leaving a tethered alkyne moiety untouched.

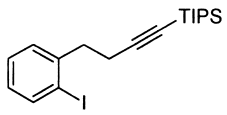
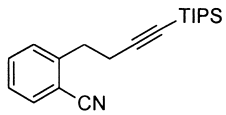
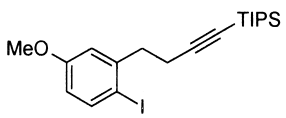
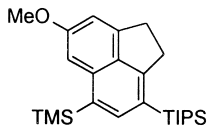
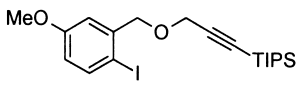
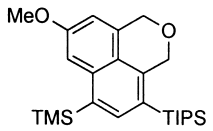
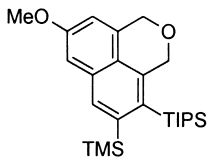
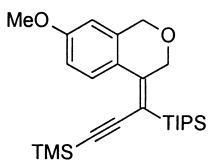
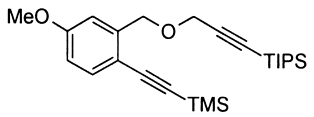
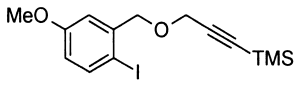
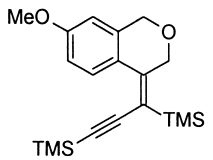
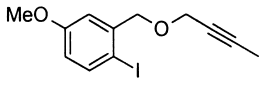
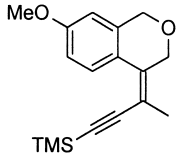
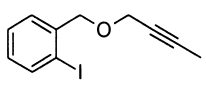
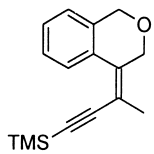
Alternatively, in the absence of the Cu(I) co-catalyst, σ-arylpalladium **B** inserts a tethered alkyne unit to form the σ-vinylpalladium(II) intermediate **F** (5 or 6-*exo* dig cyclisation). Here, the reaction can follow two distinct pathways. Firstly (cycle 2), insertion of the external alkyne **C** provides the new σ-vinylpalladium(II) intermediate **G** that undergoes an intramolecular electrophilic palladation of an aromatic system[8,9] to create the cationic sigma complex **H**. A base-assisted extrusion of HI gives the palladacycle **I** that after a reductive elimination provides the acenaphthylene derivative **J**. Secondly (cycle 3), σ-vinylpalladium **F** may also enter the coupling route that affords, via the palladium(II) acetylide intermediate **K**, enyne **L**.

The mechanistic scheme outlined above (Scheme 4) comprises two key crossings that reflect, under kinetic conditions, a competitive formation of a palladium(II) acetylide σ-complex or a palladium(II) acetylene π-complex from an aryl- or vinylpalladium(II) intermediate and an external or tethered alkyne (Eq. (1)).

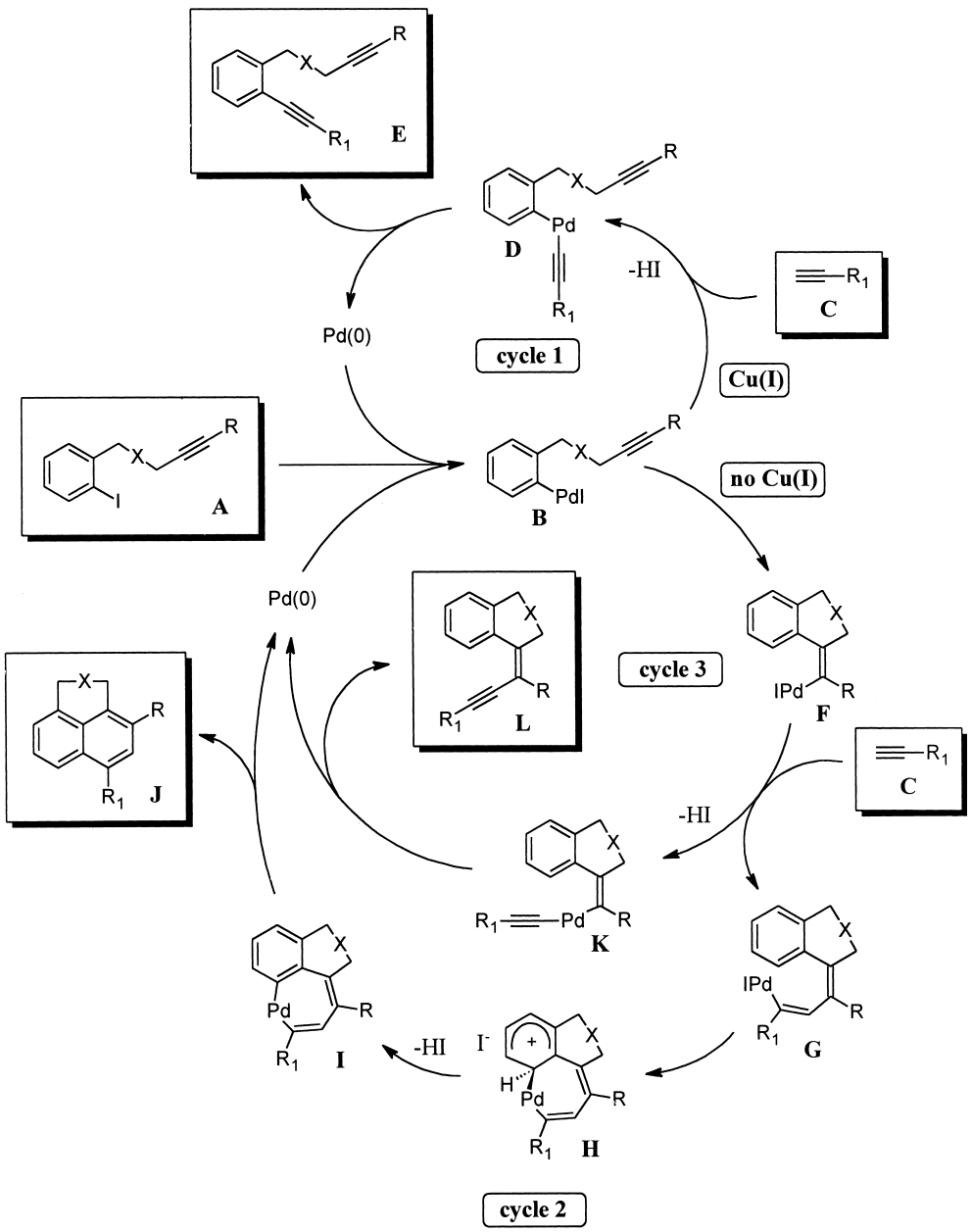


In the presence of a Cu(I) co-catalyst, the formation of the palladium(II) acetylide σ-complex is a considerably faster process that is almost invariant under structural changes of reactants and terminates a cascade reaction (Scheme 4, cycle 1; see also Table 1, entries 1, 3, 5, 7). Under exclusion of the Cu(I) co-catalyst, on the other hand, the generation of the palladium(II) acetylene π-complex may prevail (Scheme 4, cycle 2 and 3; see also Table 1, entries 4, 6 and Table 2, entries 2–7). It is an essential relay step in the

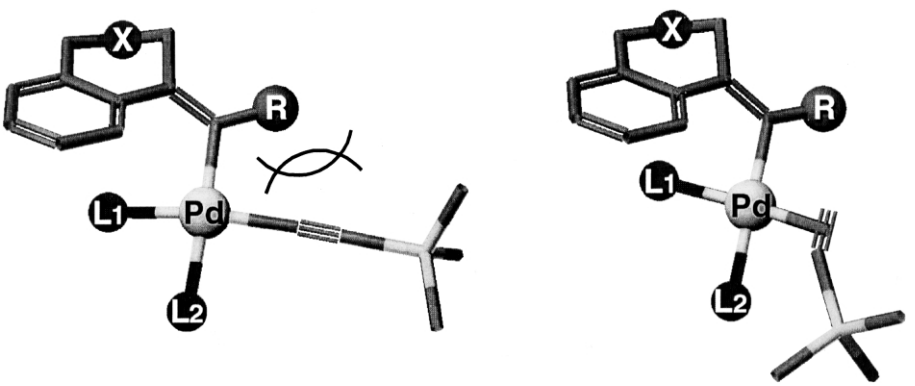
Table 2.

Entry	Educt		Reagent (equiv.)	Cond.[a]	Products (yield, %)[b]		
1		**11**	TMS–CN (1.6)	$^{i}Pr_2NH$ 2.5 h		**21**	(43)[c]
2		**12**	TMS–C≡CH (1.2)	$^{i}Pr_2NH$ 16 h		**22**	(72)
3		**15**	TMS–C≡CH (1.4)	$^{i}Pr_2NH$ 1.5 h		**23**	(55)[d]
						**24**	(10)
						**25**	(9)
4			TMS–C≡CH (2.6)			**25**	(56)
						**26**	(30)
						24	(5)
5		**16**	TMS–C≡CH (1.3)	$^{i}Pr_2NH$ 1.5 h		**27**	(97)
6		**17**	TMS–C≡CH (2.8)	$^{i}Pr_2NH$ 10 h		**28**	(37)
7		**14**	TMS–C≡CH (2.0)	Piperidine 4 h		**29**	(47)

[a] $Pd(PPh_3)_4$ (5 mol%), 80°C.
[b] Isolated.
[c] A 46% recovery of **11**.
[d] A 22% recovery of **15**.



Scheme 4.



acetylide σ-complex **i** acetylene π-complex **ii**

Figure 1.

cascade reaction being highly susceptible to the structural features of reactants. If the R group in the vinylpalladium(II) intermediate **F** is large the cycle 2 dominates and, vice versa, if R is small the cycle 3 is preferred (Scheme 4; cf. Table 2, entries 3, 5–7). In other words, the acetylide σ-complex **i** is formed preferentially unless a sterically less congested acetylene π-complex **ii** is favoured in this specific case (Fig. 1). Finally, the reaction outcome can be influenced also by the terminal alkyne structure as well as by the solvent but these effects remain unclear.

4. Conclusion

In summary, we have observed a striking dichotomy in the reaction of alkyne-substituted phenyl iodides with terminal alkynes depending on the catalyst system used. Under the Pd(0)/Cu(I) catalysis, intermolecular aryl–alkynyl coupling (Sonogashira reaction) has exclusively proceeded regardless of the presence of an tethered alkyne being disposed to participate in it. By contrast, when the Cu(I) co-catalyst is omitted, the adjacent alkyne can take part in the favoured intramolecular 5 or 6-*exo* dig carbopalladation that may be relayed by another alkyne insertion or terminated by alkenyl–alkynyl coupling. Hence, Cu(I) strongly supports the intermolecular coordination of terminal alkyne to an arylpalladium(II) species in an acetylide σ-complex fashion while exclusion of Cu(I) means this process may compete with the intramolecular formation of an acetylene π-complex depending on the structure of reactants and amine solvents.

5. Experimental

5.1. General

Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. ^{1}H NMR spectra were measured at 499.8 or 200.0 MHz, ^{13}C NMR spectra at 125.7 MHz, in $CDCl_3$ with TMS as an internal standard. Chemical shifts are given in δ-scale, coupling constants *J* are given in Hz. HMBC experiments were setup for J_{C-H}= 5 Hz. For correct assignment of both ^{1}H and ^{13}C NMR spectra of key compounds, the HCOSY and HMQC experiments were performed. For all the other compounds, the general semi-empirical equations were applied to the chemical shift assignments. IR spectra were measured in $CHCl_3$. EI MS spectra were determined at an ionizing voltage of 70 eV, *m*/*z* values are given along with their relative intensities (%). HR MS spectra were obtained by the EI technique. GC MS analyses were carried out on a DB-5 column (0.25×30 m×0.25 μm). All reactions were performed under argon unless noted otherwise. Reagent grade materials purchased from Sigma-Aldrich, Fluka, Merck, Acros Chimica (**7**) and Avocado were used as received. The compound **8** was prepared according to the literature procedure.[3a] THF was freshly distilled from sodium/benzophenone under nitrogen; diisopropylamine and piperidine were distilled from calcium hydride under argon and degassed by three freeze–pump–thaw cycles before use; acetonitrile was distilled from calcium hydride under argon and stored over 4 Å molecular sieves; DMF was distilled from calcium hydride under reduced pressure and stored over 4 Å molecular sieves. TLC was performed on Silica gel 60 F_{254}-coated aluminium sheets (Merck) and spots were detected by the solution of $Ce(SO_4)_2{\cdot}4H_2O$ (1%) and $H_3P(Mo_3O_{10})_4$ (2%) in sulfuric acid (10%). Flash chromatography was performed on Silica gel 60 (0.040–0.063 mm or <0.063 mm, Merck). Semipreparative HPLC was carried out on a silica gel column (Partisil M9, Whatman 10/50, 500 mm×10 mm; sample injections on a 10–20 mg scale) using a refractometric detector.

Method A. A Schlenk flask was charged with aryl iodide (1.0 mmol), $Pd(PPh_3)_4$ (5 mol%), CuI (10 mol%) and flushed with argon. Diisopropylamine (10–15 ml) was added and the reaction mixture was briefly heated under stirring to 40–50°C. (Trimethylsilyl)-, (triisopropylsilyl)-, phenyl-, or butylacetylene (1.0–1.2 mmol, 1.0–1.2 equiv.) was added and the reaction mixture was stirred at rt or 80°C for 0.1–1 h until the reaction composition did not change (monitored by TLC). The precipitate was filtered off and washed with petroleum ether (2×2 ml). The combined fractions were evaporated to dryness in vacuo and the residue was chromatographed on silica gel to obtain the product.

Method B. A Schlenk flask was charged with aryl iodide (1.0 mmol), $Pd(PPh_3)_4$ (5 mol%) and flushed with argon. Solvent (diisopropylamine or piperidine, 10–15 ml) was added and the reaction mixture was briefly heated under stirrig to 40–50°C. (Trimethylsilyl)-, (triisopropylsilyl)-, phenyl-or butylacetylene (1.0–2.8 mmol, 1.0–2.8 equiv.) was added and the reaction mixture was stirred at 80°C for 1–22 h until the reaction composition did not change (monitored by TLC). The precipitate was filtered off and washed with petroleum ether (2×2 ml). The combined fractions were evaporated to dryness in vacuo and the residue was chromatographed on silica gel to obtain the product.

5.1.1. 1-(Bromomethyl)-2-iodobenzene 9. Phosphorus tribromide (1.2 ml, 12.63 mmol, 1.8 equiv.) was added at 0°C to benzyl alcohol **7** (5 g, 21.36 mmol) in THF (25 ml) under nitrogen and the mixture was stirred at 0°C for 30 min. The solvent was evaporated in vacuo and the residue was purified by flash chromatography on silica gel (petroleum ether) to get benzyl bromide **9** (6.05 g, 95%) as a white crystalline material, mp 54–55°C (petroleum ether).[10] Caution: lachrymator! ^{1}H NMR (200 MHz): 4.60 (s, 2H, CH_2), 6.99 (dt, 1H, *J*=7.5, 1.7 Hz, 4-H), 7.34 (dt, 1H, *J*=7.5, 1.2 Hz, 5-H), 7.48 (dd, 1H, *J*=7.6, 1.8 Hz, 6-H), 7.86 (dd, 1H, *J*=7.9, 1.2 Hz, 3-H). EI MS: 296 ($M^{+\cdot}$, 18), 217 (100), 90 (38), 63 (9), 39 (5).

5.1.2. 2-(Bromomethyl)-1-iodo-4-methoxybenzene 10. Triphenylphosphine (10.02 g, 38.18 mmol, 2.4 equiv.) in dry acetonitrile (30 ml) was added dropwise at rt to the solution of benzyl alcohol **8** (4.20 g, 15.90 mmol) and tetrabromomethane (12.68 g, 38.22 mmol, 2.4 equiv.) in dry acetonitrile (40 ml) under nitrogen. After stirring at rt for 10 min, the reaction mixture was filtered, the precipitate was washed with petroleum ether–ether (95:5), and the filtrate was evaporated to dryness in vacuo. Flash chromatography on silica gel (petroleum ether–ether 95:5) provided benzyl

bromide **10** (4.58 g, 88%) as a white crystalline solid, mp 106–107°C (petroleum ether–ether 95:5). IR: 3068 vw, 3030 vw, 2964 w, 2940 w, 2909 w, 2838 w, 1593 m, 1567 m, 1474 vs, 1464 m (sh), 1443 w, 1439 m, 1412 m, 1313 s, 1296 m, 1280 s, 1239 vs, 1173 m, 1168 m, 1152 w, 1102 w, 1052 m, 1045 m, 1011 m, 928 w, 875 w, 818 w, 807 w, 647 w, 590 m, 571 m, 528 w, 440 vw. ^{1}H NMR (500 MHz): 3.80 (s, 3H, CH_3), 4.55 (s, 2H, CH_2), 6.60 (dd, 1H, J=8.8, 3.0 Hz, 5-H), 7.03 (d, 1H, J=3.1 Hz, 3-H), 7.70 (d, 1H, J=8.8 Hz, 6-H). ^{13}C NMR: 38.7 (t, CH_2), 55.5 (q, CH_3), 88.3 (s, C-1), 116.2 (d, C-5), 116.4 (d, C-3), 140.5 (d, C-6), 141.0 (s, C-2), 160.2 (s, C-4). EI MS: 326 ($M^{+\cdot}$, 26), 247 (100), 120 (25), 91 (9), 77 (11), 51 (12). HR EI MS: calculated for C_8H_8BrIO 325.8803; found 325.8820.

5.1.3. [4-(2-Iodophenyl)-1-butynyl](triisopropyl)silane 11. *n*-Butyllithium (1.6 M in hexanes, 1.23 ml, 1.97 mmol, 1.1 equiv.) was added at −78°C to 1-(triisopropylsilyl)-1-propyne (0.48 ml, 1.98 mmol, 1.2 equiv.) in dry THF (6 ml). After stirring at −78°C for 2 h, benzyl bromide **9** (510 mg, 1.73 mmol) in dry THF (9 ml) was added and the mixture was stirred at −78°C for 1 h. The reaction mixture was allowed to reach rt and solvents were evaporated in vacuo. Flash chromatography on silica gel (petroleum ether) afforded alkyne **11** (706 mg, 99%) as an oil. IR: 3065 w, 2958 s, 2944 s, 2891 m, 2865 vs, 2171 m, 1588 w, 1563 w, 1466 s, 1453 w (sh), 1436 w, 1429 w (sh), 1383 w, 1367 w, 1338 w, 1322 vw, 1285 vw, 1255 w, 1243 w, 1161 vw, 1112 vw, 1073 w, 1045 w, 1039 w, 1012 m, 996 m, 943 vw, 883 m, 678 m, 661 m, 530 w, 440 w. ^{1}H NMR (500 MHz): 1.03 (m, 21H, 3×(CH_3)$_2$CH), 2.57 (t, 2H, J=7.3 Hz, CH_2C≡C), 2.95 (t, 2H, J=7.3 Hz, CH_2Ar), 6.89 (td, 1H, J=7.6, 1.7 Hz, 4-H), 7.25 (td, 1H, J=7.5, 1.3 Hz, 5-H), 7.31 (dd, 1H, J=7.7, 1.7 Hz, 6-H), 7.80 (dd, 1H, J=7.9, 1.3 Hz, 3-H). ^{13}C NMR: 11.3 (d, 3×(CH_3)$_2$$C$H), 18.6 (q, 3×($CH_3$)$_2$CH), 20.5 (t, CH$_2$C≡C), 40.0 (t, CH_2Ar), 81.4 (s, CH_2C≡C), 100.3 (s, C-2), 107.4 (s, CH_2C≡C), 128.1 (d, C-4), 128.2 (d, C-5), 130.1 (d, C-6), 139.4 (d, C-3), 142.9 (s, C-1). EI MS: 369 ((M−43)$^+$, 100), 341 (9), 327 (13), 299 (8), 243 (16), 209 (34), 199 (20), 171 (13), 153 (97), 139 (14), 125 (34), 111 (31), 97 (53), 83 (64), 59 (25), 43 (17). HR EI MS: calculated for $C_{16}H_{22}ISi$ (M−C_3H_7) 369.0536; found 369.0517.

5.1.4. [4-(2-Iodo-5-methoxyphenyl)-1-butynyl](triisopropyl)silane 12. The same procedure as described for **11**, starting from *n*-butyllithium (1.6 M in hexanes, 3.4 ml, 5.44 mmol, 1.2 equiv.), 1-(triisopropylsilyl)-1-propyne (1.3 ml, 5.43 mmol, 1.2 equiv.), THF (20 ml), −78°C, 2 h, then benzyl bromide **10** (1.55 g, 4.74 mmol), THF (15 ml), −78°C, 1 h. Flash chromatography on silica gel (petroleum ether–ether 95:5) furnished alkyne **12** (1.73 g, 82%) as an oil. IR: 3077 vw, 3065 vw, 2960 vs, 2944 vs, 2922 s, 2892 s, 2866 vs, 2840 m (sh), 2171 s, 1591 m, 1568 s, 1467 vs, 1429 m, 1412 m, 1383 m, 1366 w, 1336 w, 1302 s, 1293 s, 1277 s, 1238 vs, 1173 m (sh), 1162 m, 1112 w, 1072 m, 1056 s, 1043 s, 996 m, 953 w, 884 s, 678 s, 661 s, 593 m. ^{1}H NMR (500 MHz): 1.03 (m, 21H, 3×(CH_3)$_2$CH), 2.56 (t, 2H, J=7.3 Hz, CH_2C≡C), 2.90 (t, 2H, J=7.3 Hz, CH_2Ar), 3.77 (s, 3H, CH_3O), 6.51 (dd, 1H, J=8.7, 3.0 Hz, 4-H), 6.87 (d, 1H, J=3.0 Hz, 6-H), 7.66 (d, 1H, J=8.7 Hz, 3-H). ^{13}C NMR: 11.3 (d, 3×(CH_3)$_2$$C$H), 18.6 (q, 3×($CH_3$)$_2$CH), 20.4 (t, CH$_2$C≡C), 40.1 (t, CH_2Ar), 55.3 (q, CH_3O), 81.3 (s, CH_2C≡C), 88.7 (s, C-2), 107.4 (s, CH_2C≡C), 113.9 (d, C-6), 116.3 (d, C-4), 139.8 (d, C-3), 143.9 (s, C-1), 159.9 (s, C-5). EI MS: 442 ($M^{+\cdot}$, 10), 399 (100), 371 (9), 351 (15), 329 (9), 273 (29), 247 (9), 229 (30), 215 (9), 201 (18), 172 (11), 121 (14), 89 (7), 73 (8), 59 (18), 43 (11). HR EI MS: calculated for $C_{20}H_{31}IOSi$ 442.1189; found 442.1191.

5.1.5. 1-Iodo-4-methoxy-2-[(2-propynyloxy)methyl]benzene 13. Alcohol **8** (555 mg, 2.24 mmol) in dry DMF (2 ml) was added dropwise to sodium hydride (80% suspension in mineral oil, 91 mg, 3.03 mmol, 1.4 equiv.) in dry DMF (1 ml) at 0°C. After stirring at 0°C for 45 min, propargyl bromide (300 μl, 3.37 mmol, 1.5 equiv.) was added and the mixture was stirred at 0°C for 30 min. The reaction mixture was diluted with water and extracted with diethyl ether (2×). The ethereal fractions were combined, washed with water (1×) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo and the crude product was purified by flash chromatography on silica gel (hexane–diethyl ether 100:0 to 90:10) to obtain alkyne **13** (476 mg, 71%) as a white amorphous solid. IR: 3307 s, 3075 w, 2841 m, 2120 w, 1590 s, 1570 s, 1469 vs, 1442 s, 1416 m, 1405 m, 1386 m, 1356 m, 1297 vs, 1275 s, 1257 s, 1237 vs, 1165 s, 1119 s, 1095 vs, 1086 vs (sh), 1056 s, 1009 s, 859 m, 816 m, 678 m, 635 s, 590 m, 548 w. ^{1}H NMR (500 MHz): 2.50 (t, 1H, J=2.4 Hz, HC≡C), 3.80 (s, 3H, CH_3), 4.27 (d, 2H, J=2.4 Hz, HC≡CCH_2), 4.56 (brs, 2H, CH_2Ar), 6.60 (dd, 1H, J=8.6, 3.1 Hz, 5-H), 7.04 (dt, 1H, J=3.1, 0.6 Hz, 3-H), 7.67 (d, 1H, J=8.7 Hz, 6-H). ^{13}C NMR: 55.4 (q, CH_3), 57.9 (t, HC≡CCH$_2$), 75.0 (t, CH_2Ar), 75.3 (d, HC≡C), 79.4 (s, HC≡C), 85.9 (s, C-1), 114.6 (d, C-3), 115.6 (d, C-5), 139.6 (d, C-6), 140.8 (s, C-2), 160.1 (s, C-4). EI MS: 302 ($M^{+\cdot}$, 84), 261 (9), 248 (28), 233 (4), 175 (18), 145 (90), 121 (100), 102 (18), 91 (32), 77 (26), 63 (28), 51 (18), 39 (27). HR EI MS: calculated for $C_{11}H_{11}IO_2$ 301.9804; found 301.9799.

5.1.6. 1-[(2-Butynyloxy)methyl]-2-iodobenzene 14. Alcohol **7** (500 mg, 2.14 mmol) in dry THF (6 ml) was added dropwise over 5 min to sodium hydride (80% suspension in mineral oil, 70 mg, 2.32 mmol, 1.1 equiv.) in dry THF (4 ml) at 0°C. After stirring at 0°C for 1.5 h, 1-bromo-2-butyne (350 mg, ca. 230 μl, 2.63 mmol, 1.2 equiv.) was added and the mixture was stirred at 0°C to rt for 68 h. The precipitate was filtered off, washed with dichloromethane and the filtrate was evaporated in vacuo to drynes. Flash chromatography on silica gel (petroleum ether–acetone 95:5) gave alkyne **14** (436 mg, 71%) as an oil. IR: 3061 w, 2954 m, 2924 s, 2856 s, 2245 w, 2233 w (sh), 1588 w, 1566 m, 1466 m, 1439 s, 1386 m, 1273 m, 1156 m, 1114 m, 1085 vs, 1075 vs, 1045 s, 1014 vs, 949 m, 650 w, 530 w, 429 w. ^{1}H NMR (200 MHz): 1.89 (t, 3H, J=2.2 Hz, CH_3), 4.22 (q, 2H, J=2.2 Hz, CH_2C≡C), 4.57 (s, 2H, CH_2Ar), 6.98 (td, 1H, J=7.6, 1.5 Hz, 4-H), 7.34 (td, 1H, J=7.6, 1.5 Hz, 5-H), 7.45 (dd, 1H, J=7.6, 1.5 Hz, 6-H), 7.82 (dd, 1H, J=7.6, 1.5 Hz, 3-H). ^{13}C NMR: 3.6 (q, CH_3), 58.4 (t, CH$_2$C≡C), 74.9 (s, CH_2C≡C), 75.3 (t, CH_2Ar), 83.0 (s, CH_2C≡C), 98.0 (s, C-2), 128.2 (d, C-5), 129.0 (d, C-6), 129.3 (d, C-4), 132.2 (d, C-3), 140.1 (s, C-1). EI MS: 286 ($M^{+\cdot}$, 16), 271 (7), 256 (6), 231 (100), 217 (53), 203 (9), 129 (79), 115 (7), 104 (25), 91 (49), 90 (49), 78 (45), 63 (16), 53 (49), 39 (30). HR EI MS: calculated for $C_{11}H_{11}IO$ 285.9855; found 285.9868.

5.1.7. {3-[(2-Iodo-5-methoxybenzyl)oxy]-1-propynyl}-(triisopropyl)silane 15. Lithium diisopropylamide (2 M solution in THF–heptane–ethylbenzene, 535 μl, 1.07 mmol, 1.0 equiv.) was added dropwise to terminal alkyne **13** (323 mg, 1.07 mmol) in dry THF (3 ml) at −78°C. After stirring at 78°C for 1 h, triisopropylsilyl chloride (230 μl, 1.08 mmol, 1.0 equiv.) was added and the mixture was stirred at −78°C to rt overnight. The solvents were removed in vacuo. Flash chromatography on silica gel (petroleum ether–ether 100:0 to 90:10) afforded silylated alkyne **15** (455 mg, 93%) as an oil. IR: 2959 s, 2944 vs, 2891 s, 2866 vs, 1590 m, 1570 m, 1466 vs, 1443 m, 1416 w, 1405 w, 1383 m, 1367 w, 1352 m, 1297 s, 1275 m, 1255 m, 1237 s, 1193 w, 1165 m, 1118 m, 1088 s, 1056 m, 1029 m, 996 m (sh), 883 s, 816 w, 679 s, 670 s, 589 m, 453 w. ^{1}H NMR (500 MHz): 1.08–1.10 (m, 21H, 3×(CH_3)$_2$CH), 3.79 (s, 3H, CH_3), 4.32 (s, 2H, C≡CCH_2), 4.59 (t, 2H, J=0.7 Hz, CH_2Ar), 6.59 (ddt, 1H, J=8.7, 3.1, 0.6 Hz, 4-H), 7.05 (dt, 1H, J=3.1, 0.8 Hz, 6-H), 7.66 (d, 1H, J=8.7 Hz, 3-H). ^{13}C NMR: 11.2 (d, 3×(CH_3)$_2$$C$H), 18.6 (q, 3×($CH_3$)$_2$CH), 55.4 (q, CH_3), 58.6 (t, C≡CCH$_2$), 74.9 (t, CH_2Ar), 85.8 (s, C-2), 88.4 (s, SiC≡C), 102.9 (s, SiC≡C), 114.4 (d, C-6), 115.9 (d, C-4), 141.2 (s, C-1), 160.1 (s, C-5). EI MS: 458 ($M^{+\cdot}$, 14), 415 (100), 373 (6), 301 (9), 289 (10), 247 (39), 210 (16), 179 (18), 121 (10), 91 (28), 83 (9), 59 (9), 41 (8). HR EI MS: calculated for $C_{20}H_{31}IO_2Si$ 458.1138; found 458.1111.

5.1.8. {3-[(2-Iodo-5-methoxybenzyl)oxy]-1-propynyl}-(trimethyl)silane 16. Lithium diisopropylamide (2 M solution in THF–heptane–ethylbenzene, 265 μl, 0.530 mmol, 1.0 equiv.) was added dropwise to terminal alkyne **13** (160 mg, 0.530 mmol) in dry THF (3 ml) at −78°C. After stirring at −78°C for 1 h, trimethylsilyl chloride (68 μl, 0.536 mmol, 1.0 equiv.) was added and the mixture was stirred at −78°C to rt overnight. The solvents were removed in vacuo. Flash chromatography on silica gel (petroleum ether–ether 100:0 to 98:2) afforded silylated alkyne **16** (160 mg, 85%) as an oil. IR: 3074 vw, 2900 m, 2841 m, 2175 w, 1590 m, 1570 m, 1568 s, 1441 m, 1416 m, 1406 m, 1385 m, 1352 m, 1297 s, 1275 s, 1252 vs, 1237 s, 1193 w, 1165 s, 1118 m, 1088 s, 1056 s, 1030 s, 847 vs, 817 m, 701 w, 690 w, 639 w, 440 w. ^{1}H NMR (500 MHz): 0.20 (s, 9H, (CH_3)$_3$Si), 3.80 (s, 3H, CH_3), 4.26 (s, 2H, C≡CCH_2), 4.56 (t, 2H, J=0.7 Hz, CH_2Ar), 6.60 (ddt, 1H, J=8.6, 3.1, 0.6 Hz, 4-H), 7.05 (dt, 1H, J=3.1, 0.8 Hz, 6-H), 7.67 (d, 1H, J=8.6 Hz, 3-H). ^{13}C NMR: −0.2 (q, (CH_3)$_3$Si), 55.4 (q, CH_3), 58.6 (t, C≡CCH$_2$), 75.2 (t, CH_2Ar), 86.0 (s, C-2), 92.5 (s, SiC≡C), 103.2 (s, SiC≡C), 114.6 (d, C-6), 115.6 (d, C-4), 139.6 (d, C-3), 141.0 (s, C-1), 160.1 (s, C-5). EI MS: 374 ($M^{+\cdot}$, 20), 247 (16), 217 (100), 202 (13), 121 (39), 91 (7), 83 (8), 73 (25), 59 (13), 43 (5). HR EI MS: calculated for $C_{14}H_{19}IO_2Si$ 374.0199; found 374.0207.

5.1.9. 2-[(2-Butynyloxy)methyl]-1-iodo-4-methoxybenzene 17. Lithium diisopropylamide (2 M solution in THF–heptane–ethylbenzene, 250 μl, 0.500 mmol, 1.0 equiv.) was added dropwise to terminal alkyne **13** (151 mg, 0.500 mmol) in dry THF (3 ml) at −78°C. After stirring at −78°C for 1 h, methyl iodide (32 μl, 0.514 mmol, 1.0 equiv.) was added and the mixture was stirred at −78°C to rt overnight. The solvents were removed in vacuo. Flash chromatography on silica gel (petroleum ether–ether 100:0 to 98:2) afforded the crude product which was purified by preparative HPLC (petroleum ether–acetone 99:1) to obtain the methylated alkyne **17** (115 mg, 73%) as an oil. IR: 2230 w, 1590 s, 1571 s, 1468 vs, 1443 s, 1416 s, 1405 m, 1296 vs, 1276 s, 1258 s, 1237 vs, 1193 m, 1165 s, 1117 s, 1088 vs, 1055 s, 1045 s (sh), 816 m, 590 m, 443 w. ^{1}H NMR (500 MHz): 1.89 (t, 3H, J=2.4 Hz, CH_3C≡C), 3.80 (s, 3H, CH_3), 4.23 (q, 2H, J=2.4 Hz, C≡CCH_2), 4.53 (t, 2H, J=0.7 Hz, CH_2Ar), 6.59 (ddt, 1H, J=8.7, 3.1, 0.6 Hz, 5-H), 7.05 (dt, 1H, J=3.1, 0.7 Hz, 3-H), 7.66 (d, 1H, J=8.7 Hz, 6-H). ^{13}C NMR: 3.7 (q, CH$_3$C≡C), 55.4 (q, CH_3), 58.5 (t, C≡CCH$_2$), 74.8 (s, CH_3C≡C), 75.2 (t, CH_2Ar), 83.1 (s, CH_3C≡C), 85.9 (s, C-1), 114.5 (d, C-3), 115.5 (d, C-5), 139.5 (d, C-6), 141.2 (s, C-2), 160.1 (s, C-4). EI MS: 316 ($M^{+\cdot}$, 13), 261 (5), 247 (9), 159 (100), 135 (6), 121 (49), 91 (16), 77 (17), 63 (13), 53 (26), 39 (16). HR EI MS: calculated for $C_{12}H_{13}IO_2$ 315.9960; found 315.9973.

5.1.10. Triisopropyl(4-{2-[(triisopropylsilyl)ethynyl]-phenyl}-1-butynyl)silane 18a. Method A: **11** (92 mg, 0.220 mmol), $Pd(PPh_3)_4$ (13 mg, 0.011 mmol, 5 mol%), CuI (4 mg, 0.022 mmol, 10 mol%), (triisopropylsilyl)-acetylene (50 μl, 0.220 mmol, 1.0 equiv.), diisopropylamine (2 ml), rt, 20 min. Flash chromatography on silica gel (petroleum ether) afforded **18a** (73 mg, 70%) as an oil. IR: 3095 vw, 3069 vw, 2959 s, 2944 s, 2891 m, 2866 vs, 2170 w, 2153 w, 1482 w, 1463 m, 1383 w, 1367 w, 1099 w, 1072 w, 1018 w, 996 m, 883 m, 859 w, 835 w, 678 s, 662 s, 640 m, 460 w. ^{1}H NMR (500 MHz): 1.04 (m, 42H, 6×(CH_3)$_2$CH), 2.60 (t, 2H, J=7.7 Hz, CH_2C≡C), 3.04 (t, 2H, J=7.7 Hz, CH_2Ar), 7.15 (td, 1H, J=7.5, 1.5 Hz, 4-H), 7.22 (td, 1H, J=7.6, 1.4 Hz, 5-H), 7.26 (ddd, 1H, J=7.7, 1.5, 0.5 Hz, 6-H), 7.46 (ddd, 1H, J=7.6, 1.4, 0.5 Hz, 3-H). ^{13}C NMR: 11.3 (d, ((CH_3)$_2$$C$H)$_3$SiC≡$CCH_2$), 11.4 (d, (($CH_3$)$_2$$C$H)$_3$-SiC≡CAr), 18.6 (q, (($CH_3$)$_2$CH)$_3$-SiC≡$CCH_2$), 18.7 (q, (($CH_3$)$_2$CH)$_3$SiC≡CAr), 21.0 (t, CH$_2$C≡C), 34.4 (t, CH_2Ar), 80.7 (s, C≡CH$_2$), 94.6 (s, C≡CAr), 105.1 (s, C≡CAr), 108.1 (s, C≡CCH$_2$), 122.8 (s, C-2), 126.1 (d, C-4), 128.3 (d, C-5), 129.2 (d, C-6), 132.8 (d, C-3), 142.8 (s, C-1). EI MS: 446 ($M^{+\cdot}$, 18), 423 (91), 381 (38), 339 (11), 308 (7), 265 (6), 190 (11), 157 (100), 134 (13), 115 (43), 101 (8), 87 (29), 73 (40), 59 (55). HR EI MS: calculated for $C_{30}H_{50}Si_2$ 466.3451; found 466.3440.

5.1.11. Triisopropyl(4-{2-[(trimethylsilyl)ethynyl]phenyl}-1-butynyl)silane 18b. Method A: **11** (110 mg, 0.26 mmol), $Pd(PPh_3)_4$ (16 mg, 0.014 mmol, 5 mol%), CuI (5 mg, 0.025 mmol, 10 mol%), (trimethylsilyl)acetylene (45 μl, 0.320 mmol, 1.2 equiv.), diisopropylamine (5 ml), 80°C, 1 h. Flash chromatography on silica gel (petroleum ether) afforded **18b** (93 mg, 92%) as an oil. IR: 3095 w, 3069 w, 2961 vs, 2944 vs, 2920 vs (sh), 2893 s, 2866 vs, 2170 s, 2155 s, 1599 w, 1581 vw, 1482 s, 1464 s, 1451 s, 1429 w, 1408 w, 1383 m, 1366 w, 1339 w, 1262 m, 1251 vs, 1160 w, 1074 m, 1018 m, 996 s, 947 w, 883 vs, 867 vs, 844 vs, 678 s, 661 s, 646 s, 604 m, 583 w, 457 m. ^{1}H NMR (500 MHz): 0.26 (s, 9H, (CH_3)$_3$Si), 1.04 (m, 21H, 3×(CH_3)$_2$CH), 2.60 (t, 2H, J=7.7 Hz, CH_2C≡C), 3.01 (t, 2H, J=7.7 Hz, CH_2Ar), 7.14 (ddd, 1H, J=7.6, 7.1, 1.9 Hz, 4-H), 7.22 (ddd, 1H, J=7.7, 7.1, 1.5 Hz, 5-H), 7.25 (ddd, 1H, J=7.7, 1.9, 0.7 Hz, 6-H), 7.42 (ddd, 1H, J=7.6, 1.5, 0.7 Hz, 3-H). ^{13}C NMR: 0.0 (q, (CH_3)$_3$Si), 11.3 (d, 3×(CH_3)$_2$$C$H), 18.6 (q, 3×($CH_3$)$_2$CH), 20.6 (t, CH$_2$C≡C), 34.4 (t, CH_2Ar), 80.7

(s, $CH_2C{\equiv}C$), 98.5 (s, $ArC{\equiv}C$), 103.5 (s, $ArC{\equiv}C$), 108.2 (s, $CH_2C{\equiv}C$), 122.4 (s, C-2), 126.2 (d, C-4), 128.5 (d, C-5), 129.1 (d, C-6), 132.2 (d, C-3), 143.0 (s, C-1). EI MS: 382 ($M^{+\cdot}$, 16), 367 (3), 339 (75), 297 (16), 265 (5), 255 (16), 237 (6), 223 (10), 195 (41), 183 (9), 157 (11), 134 (16), 129 (14), 101 (25), 73 (100), 59 (95), 43 (33). HR EI MS: calculated for $C_{24}H_{38}Si_2$ 382.2512; found 382.2501.

5.1.12. Triisopropyl{4-[2-(phenylethynyl)phenyl]-1-butynyl}silane 18c. Method A: **11** (110 mg, 0.260 mmol), $Pd(PPh_3)_4$ (16 mg, 0.014 mmol, 5 mol%), CuI (5 mg, 0.027 mmol, 10 mol%), phenylacetylene (30 μl, 0.260 mmol, 1.0 equiv.), diisopropylamine (6 ml), rt, 5 min. Flash chromatography on silica gel (petroleum ether) afforded **18c** (90 mg, 85%) as an oil. IR: 3098 vw, 3084 w, 3064 w, 2958 s, 2944 vs, 2920 s (sh), 2891 m, 2865 vs, 2215 vw, 2170 s, 1601 w, 1572 vw, 1495 m, 1464 m, 1452 m, 1443 w, 1429 w, 1383 w, 1366 w, 1338 w, 1309 vw, 1243 w, 1160 vw, 1070 w, 1027 w, 1018 w, 996 m, 946 w, 917 w, 884 m, 862 w, 844 vw, 690 s, 678 m, 661 m, 622 w, 600 w, 588 w, 460 w. ^{1}H NMR (500 MHz): 1.04 (m, 21H, 3×(CH_3)$_2$CH), 2.68 (t, 2H, J=7.6 Hz, $CH_2C{\equiv}C$), 3.10 (t, 2H, J=7.6 Hz, CH_2Ar), 7.20 (td, 1H, J=7.4, 1.5 Hz, 4-H (−Ar−)), 7.25 (td, 1H, J=7.5, 1.6 Hz, 5-H (−Ar−)), 7.30 (bdd, 1H, J=7.6, 1.4 Hz, 6-H (−Ar−)), 7.32–7.38 (m, 3H, 3, 4, 5-H (Ph)), 7.50 (bdd, 1H, J=7.4, 1.5 Hz, 3-H (−Ar−)), 7.53–7.55 (m, 2H, 2, 6-H (Ph)). ^{13}C NMR: 11.3 (d, 3×(CH_3)$_2$$C$H), 18.6 (q, 3×($CH_3$)$_2$CH), 20.9 (t, $CH_2C{\equiv}C$), 34.4 (t, CH_2Ar), 80.9 (s, $CH_2C{\equiv}C$), 87.8 (s, $ArC{\equiv}C$Ph), 93.5 (s, $ArC{\equiv}C$Ph), 108.2 (s, $CH_2C{\equiv}C$), 122.6 (s, C-2 (−Ar−)), 123.4 (s, C-1 (Ph)), 126.3 (d, C-4 (−Ar−)), 128.2 (d, C-5 (−Ar−)), 128.3 (d, C-4 (Ph)), 128.4 (d, C-3, 5 (Ph)), 129.2 (d, C-6 (−Ar−)), 131.5 (d, C-2, 6 (Ph)), 132.0 (d, C-3 (−Ar−)), 142.5 (s, C-1 (−Ar−)). EI MS: 386 ($M^{+\cdot}$, 100), 343 (41), 301 (40), 273 (24), 259 (86), 245 (28), 241 (13), 229 (30), 215 (21), 202 (16), 189 (29), 165 (20), 144 (26), 135 (43), 121 (35), 105 (9), 73 (13), 59 (62), 43 (14). HR EI MS: calculated for $C_{27}H_{34}Si$ 386.2430; found 386.2439.

5.1.13. {4-[2-(1-Hexynyl)phenyl]-1-butynyl}(triisopropyl)-silane 18d. Method A: **11** (97 mg, 0.235 mmol), $Pd(PPh_3)_4$ (14 mg, 0.0121 mmol, 5 mol%), CuI (5 mg, 0.0263 mmol, 10 mol%), 1-hexyne (28 μl, 0.244 mmol, 1.0 equiv.), diisopropylamine (2 ml), rt, 10 min. Flash chromatography on silica gel (petroleum ether) afforded **18d** (74 mg, 85%) as an oil. IR: 3096 vw, 3069 w, 2960 vs, 2943 vs, 2892 s, 2865 vs, 2227 w, 2170 s, 1599 w, 1485 m, 1464 s, 1452 m, 1430 w, 1382 w, 1366 w, 1339 w, 1328 w, 1160 vw, 1104 w, 1073 w, 1018 w, 996 m, 946 w, 884 s, 678 s, 661 s, 599 w, 587 w, 523 w, 498 w, 418 w. ^{1}H NMR (500 MHz): 0.95 (t, 3H, J=7.4 Hz, $CH_3CH_2CH_2CH_2$), 0.98–1.06 (m, 21H, 3×(CH_3)$_2$CH), 1.46–1.53 (m, 2H, $CH_3CH_2CH_2CH_2$), 1.58–1.64 (m, 2H, $CH_3CH_2CH_2CH_2$), 2.44 (t, 2H, J=7.0 Hz, $CH_3CH_2CH_2CH_2$), 2.55 (t, 2H, J=7.5 Hz, $CH_2C{\equiv}C$), 2.99 (t, 2H, J=7.5 Hz, CH_2Ar), 7.12 (td, 1H, J=7.5 Hz, 1.6, 5-H), 7.17 (td, 1H, J=7.5, 1.5 Hz, 4-H), 7.24 (bdd, 1H, J=7.5, 1.5 Hz, 6-H), 7.36 (dd, 1H, J=7.5 Hz, 1.6, 3-H). ^{13}C NMR: 11.28 (d, 3×(CH_3)$_2$$C$H), 13.58 (q, $CH_3CH_2CH_2CH_2$), 18.60 (q, 3×(CH_3)$_2$CH), 19.19 (t, $CH_3CH_2CH_2CH_2$), 20.77 (t, $CH_2C{\equiv}C$), 22.01 (t, $CH_3CH_2CH_2CH_2$), 30.88 (t, $CH_3CH_2CH_2CH_2$), 34.26 (t, CH_2Ar), 78.83 (s, $ArC{\equiv}C$), 80.61 (s, TIPS$C{\equiv}C$), 94.38 (s, $ArC{\equiv}C$), 108.41 (s, TIPS$C{\equiv}C$), 123.35 (s, C-2), 126.10 (d, C-4), 127.47 (d, C-5), 129.07 (d, C-6), 132.04 (d, C-3), 142.25 (s, C-1). EI MS: 366 ($M^{+\cdot}$, 100), 323 (11), 281 (49), 253 (13), 239 (40), 225 (25), 211 (28), 197 (63), 183 (45), 165 (20), 119 (17), 85 (14), 73 (30), 59 (99). HR EI MS: calculated for $C_{25}H_{38}Si$ 366.22743; found 366.2758.

5.1.14. Triisopropyl[5-(trimethylsilyl)-1,2-dihydro-3-acenaphthylenyl]silane 19a. Method B: **11** (100 mg, 0.24 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol, 5 mol%), (trimethylsilyl)acetylene (40 μl, 0.280 mmol, 1.2 equiv.), diisopropylamine (5 ml), 80°C, 1 h. Flash chromatography on silica gel (petroleum ether) afforded **19a** (65 mg, 72%) as an oil. IR: 3066 w, 2947 vs, 2925 s, 2891 m, 2866 s, 1607 w, 1585 w, 1558 w, 1464 m, 1447 w, 1407 w, 1389 w, 1383 w, 1367 w, 1251 s, 1073 w, 995 w, 883 s, 858 s, 838 vs, 690 w, 677 m, 660 m, 649 m, 627 w, 601 w. ^{1}H NMR (500 MHz): 0.43 (s, 9H, $(CH_3)_3Si$), 1.12 (d, 18H, J=7.5 Hz, 3×(CH_3)$_2$CH), 1.56 (septet, 3H, J=7.5 Hz, 3×(CH_3)$_2$CH), 3.34–3.38 (m, 2H, 2-H), 3.42–3.46 (m, 2H, 1-H), 7.30 (dtd, 1H, J=6.8, 1.4, 0.8 Hz, 8-H), 7.47 (dd, 1H, J=8.3, 6.9 Hz, 7-H), 7.75 (s, 1H, 4-H), 7.77 (dq, 1H, J=8.3, 0.9 Hz, 6-H). ^{13}C NMR: 0.1 (q, $(CH_3)_3Si$), 11.9 (d, 3×(CH_3)$_2$$C$H), 18.8 (q, 3×($CH_3$)$_2$CH), 30.1 (t, C-1), 32.5 (t, C-2), 118.9 (d, C-8), 122.9 (d, C-7), 125.0 (s, C-8b), 127.7 (d, C-6), 130.5 (s, C-8a), 135.5 (s, C-3), 138.3 (s, C-5), 141.8 (d, C-4), 146.8 (s, C-5a), 155.9 (s, C-2a). EI MS: 382 ($M^{+\cdot}$, 57), 367 (9), 339 (69), 310 (6), 297 (53), 286 (12), 269 (24), 255 (32), 243 (61), 223 (37), 209 (34), 201 (28), 195 (21), 183 (14), 171 (20), 157 (20), 134 (23), 127 (31), 115 (14), 97 (10), 85 (17), 73 (100), 59 (55), 41 (40). HR EI MS: calculated for $C_{24}H_{38}Si_2$ 382.2512; found 382.2501.

5.2. Reaction of 11 with phenylacetylene in diisopropylamine to get 19b and 20

Method B: **11** (85 mg, 0.210 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol, 5 mol%), phenylacetylene (23 μl, 0.210 mmol, 1.0 equiv.), diisopropylamine (4 ml), 80°C, 22 h. Flash chromatography on silica gel (petroleum ether) afforded acenaphthylene **19b** (20 mg, 30%) and more polar indene **20** (10 mg, 15%) as oils.

5.2.1. Triisopropyl(5-phenyl-1,2-dihydro-3-acenaphthylenyl)silane 19b. IR: 3082 w (sh), 3063 m, 3035 m, 2945 vs, 2927 vs, 2891 s, 2866 vs, 2170 w, 1714 m, 1608 m, 1601 m, 1576 m, 1561 m, 1502 m, 1463 s, 1456 m, 1446 s, 1425 m, 1417 m, 1389 m, 1383 m, 1367 m, 1342 m, 1327 m, 1286 m, 1254 m, 1178 w, 1164 w, 1092 m, 1073 m, 1032 m, 1016 s, 1008 s, 883 vs, 846 m, 703 vs, 679 s, 663 m, 622 m, 595 m, 526 s, 420 w. ^{1}H NMR (500 MHz): 1.14 (d, 18H, J=7.5 Hz, 3×(CH_3)$_2$CH), 1.59 (septet, 3H, J=7.5 Hz, 3×(CH_3)$_2$CH), 3.42–3.44 (m, 2H, 2-H), 3.49–3.51 (m, 2H, 1-H), 7.31 (bd, 1H, J=6.8 Hz, 6-H), 7.38–7.42 (m, 1H, 4-H (Ph)), 7.43 (dd, 1H, J=8.2, 6.8 Hz, 7-H), 7.47–7.51 (m, 2H, 3, 5-H (Ph)), 7.51 (s, 1H, 4-H), 7.55 (dd, 1H, J=8.2, 1.7 Hz, 8-H), 7.69 (dd, 2H, J=8.2, 0.8 Hz, 6-H (Ph)). ^{13}C NMR: 11.9 (d, 3×(CH_3)$_2$$C$H), 18.8 (q, 3×($CH_3$)$_2$CH), 30.4 (t, C-1), 32.5 (t, C-2), 119.2 (d, C-6), 120.6 (d, C-7), 125.8 (s, C-8a), 126.8 (d, C-4 (Ph)), 128.2 (d, C-8), 128.3 (d, C-2, 6 (Ph)), 129.9 (d, C-3, 5 (Ph)), 130.1 (s, C-8b), 134.3 (s, C-5a), 135.3 (d, C-4), 139.1 (s, C-5), 140.9 (s, C-1 (Ph)), 146.1 (s, C-2a), 153.7 (s, C-3). EI MS: 386 ($M^{+\cdot}$, 22), 343 (17), 301 (20), 273 (8), 259 (15), 243 (20), 202 (100), 173 (7), 144 (6), 101

(8), 69 (12), 43 (13). HR EI MS: calculated for $C_{27}H_{34}Si$ 386.2430; found 386.2435.

5.2.2. [(1*E*)-1-(2,3-Dihydro-1*H*-inden-1-ylidene)-3-phenyl-2-propynyl](triisopropyl)silane 20. IR: 2946 vs, 2926 s, 2891 m, 2866 vs, 2175 w, 1596 w, 1547 w, 1488 m, 1464 m, 1442 w, 1383 w, 1367 w, 1327 w, 1279 vw, 1175 vw, 1094 w, 1070 w, 1036 w (sh), 1020 m, 997 w, 942 vw, 913 w,(sh), 883 m, 690 m, 645 m, 613 w, 590 w, 492 w. ^{1}H NMR (500 MHz): 1.21 (d, 18H, J=7.4 Hz, 3×(CH_3)$_2$CH), 1.55 (septet, 3H, J=7.4 Hz, 3×(CH$_3$)$_2$*C*H), 2.94–3.02 (m, 4H, 2, 3-H), 7.25–7.36 and 7.43–7.46 (m, 9H, 4,5,6,7-H (indene) and 2,3,4,5,6-H (Ph)). ^{13}C NMR: 12.9 (d, 3× (CH$_3$)$_2$*C*H), 19.0 (q, 3×(*C*H$_3$)$_2$CH), 30.4 (t, C-2), 34.1 (t, C-3), 94.0 (s, Ph*C*≡C), 97.5 (s, PhC≡*C*), 109.8 (s, C═*C*–Si), 125.0 (d, C-7), 125.2 (s, C-1 (Ph)), 126.0 (d, C-6), 126.2 (d, C-5), 127.3 (d, C-4), 128.4 (d, C-3,5 (Ph)), 129.0 (d, C-4 (Ph)), 130.8 (d, C-2,6 (Ph)), 142.4 (s, C-3a), 148.1 (s, C-7a), 162.4 (s, C-1). EI MS: 386 (M$^{+\cdot}$, 70), 343 (100), 301 (20), 273 (9), 259 (18), 229 (29), 199 (15), 185 (15), 171 (15), 157 (16), 145 (24), 129 (14), 115 (18), 87 (10), 73 (21), 59 (51), 43 (15). HR EI MS: calculated for $C_{27}H_{34}Si$ 386.2430; found 386.2419.

5.2.3. 2-[4-(Triisopropylsilyl)-3-butynyl]benzonitrile 21. A Schlenk flask was charged with iodide **11** (60 mg, 0.145 mmol) and Pd(PPh$_3$)$_4$ (8 mg, 0.007 mmol, 5 mol%). Diisopropylamine (1.5 ml) was added and the mixture was briefly heated under stirring at 40–50°C. Trimethylsilyl cyanide (29 μl, 0.232 mmol, 1.6 equiv.) was added and the reaction mixture was stirred at 80°C for 2.5 h. The precipitate was filtered off and the filtrate was evaporated to dryness. Flash chromatography on silica gel (petroleum ether–ether 100:0 to 96:4) afforded **11** (28 mg, 46% recovery) and the more polar cyanide **21** (19 mg, 43%) as an oil. IR: 3074 w, 3060 w, 3027 w, 2892 s, 2866 vs, 2226 s, 2172 s, 1601 m, 1575 w, 1487 m, 1463 s, 1452 s, 1435 s, 1383 m, 1367 w, 1338 w, 1330 w, 1120 m, 1097 m, 1072 m, 1028 m, 996 s, 953 w, 884 s, 861 w, 696 s, 679 s, 661 s, 602 m, 557 m, 480 m. ^{1}H NMR (200 MHz): 1.00 (brs, 18H, 3×(CH_3)$_2$CH), 1.01 (s, 3H, 3×(CH$_3$)$_2$C*H*), 2.68 (t, 2H, J=7.0 Hz, C≡CCH$_2$), 3.07 (t, 2H, J=7.0 Hz, CH$_2$Ar), 7.30–7.68 (m, 4H, arom.). EI MS: 268 ((M−C$_3$H$_7$)$^+$, 100), 240 (6), 226 (8), 198 (8), 182 (7), 59 (7). HR EI MS: calculated for $C_{17}H_{22}NSi$ (M−C$_3$H$_7$) 268.1522; found 268.1520.

5.2.4. Triisopropyl[7-methoxy-5-(trimethylsilyl)-1,2-dihydro-3-acenaphthylenyl]silane 22. Method B: **12** (85 mg, 0.190 mmol), Pd(PPh$_3$)$_4$ (11 mg, 0.00952 mmol, 5 mol%), (trimethylsilyl)acetylene (30 μl, 0.230 mmol, 1.2 equiv.), diisopropylamine (3 ml), 80°C, 16 h. Flash chromatography on silica gel (petroleum ether–ether 99:1) afforded **22** (60 mg, 72%) as an oil. IR: 3052 w, 3006 w, 2891 m, 2866 vs, 1616 s, 1588 w, 1556 w, 1464 s, 1445 w, 1389 w, 1383 w, 1367 w, 1333 w, 1300 w, 1251 s, 1073 w, 1029 m, 995 w, 883 s, 841 vs, 677 m, 662 m, 645 m. ^{1}H NMR (500 MHz): 0.43 (s, 9H, (CH$_3$)$_3$Si), 1.11 (d, 18H, J=7.5 Hz, 3×(CH_3)$_2$CH), 1.53 (septet, 3H, J=7.5 Hz, 3×(CH$_3$)$_2$C*H*), 3.29–3.33 (m, 2H, 1-H), 3.41–3.43 (m, 2H, 2-H), 3.92 (s, 3H, CH$_3$O), 6.96 (dt, 1H, J=2.1, 1.5 Hz, 8-H), 7.11 (dt, 1H, J=2.1, 0.8 Hz, 6-H), 7.70 (s, 1H, 4-H). ^{13}C NMR: 0.0 (q, (CH$_3$)$_3$Si), 11.9 (d, 3×(CH$_3$)$_2$*C*H), 18.8 (q, 3×(*C*H$_3$)$_2$CH), 29.8 (t, C-1), 32.8 (t, C-2), 55.5 (q, CH$_3$O), 102.6 (d, C-8), 111.0 (d, C-6), 122.4 (s, C-5), 129.1 (s, C-3), 134.0 (s, C-8b), 136.2 (s, C-8a), 142.6 (d, C-4), 148.6 (s, C-5a), 155.4 (s, C-2a), 160.1 (s, C-7). EI MS: 412 (M$^{+\cdot}$, 85), 397 (10), 369 (86), 354 (7), 327 (75), 313 (12), 299 (18), 285 (47), 253 (28), 239 (17), 225 (10), 209 (6), 157 (12), 149 (43), 142 (50), 73 (100), 59 (26), 41 (22). HR EI MS: calculated for $C_{25}H_{40}OSi_2$ 412.2618; found 412.2608.

5.3. Reaction of 15 with (trimethylsilyl)acetylene in diisopropylamine to give 23–25

Method B: **15** (101 mg, 0.220 mmol), Pd(PPh$_3$)$_4$ (12 mg, 0.010 mmol, 5 mol%), (trimethylsilyl)acetylene (45 μl, 0.318 mmol, 1.4 equiv.), diisopropylamine (2 ml), 80°C, 1.5 h. Flash chromatography on silica gel (petroleum ether–ether 100:0 to 99:1) afforded the most lipophilic **15** (22 mg, 22% recovery), then **24** (9 mg, 10%), **25** (8 mg, 9%), and the most polar **23** (52 mg, 55%).

5.3.1. Triisopropyl[8-methoxy-6-(trimethylsilyl)-1*H*,3*H*-benzo[de]isochromen-4-yl]silane 23. IR: 3009 m, 2868 s, 2840 m, 1629 w, 1602 m, 1561 w, 1505 w, 1441 m, 1316 m, 1262 m, 1251 s, 1192 w, 1071 s, 1046 s, 1027 m, 882 s, 854 vs, 637 m. ^{1}H NMR (500 MHz): 0.28 (s, 9H, (CH$_3$)$_3$Si), 1.16 (d, 18H, J=7.4 Hz, 3×(CH_3)$_2$CH), 1.43 (m, 3H, 3× (CH$_3$)$_2$C*H*), 3.84 (s, 3H, CH$_3$O), 4.70 (t, 2H, J=0.8 Hz, 1-H), 4.87 (d, 2H, J=0.7 Hz, 3-H), 6.51 (dt, 1H, J=2.0, 0.8 Hz, 9-H), 6.77 (t, 1H, J=0.8 Hz, 5-H), 6.92 (dt, 1H, J=2.0, 0.7 Hz, 7-H). ^{13}C NMR: −0.1 (q, (CH$_3$)$_3$Si), 12.9 (d, 3×(CH$_3$)$_2$*C*H), 19.1 (q, 3×(*C*H$_3$)$_2$CH), 56.0 (q, CH$_3$O), 66.8 (t, C-1), 67.0 (t, C-3), 102.4 (d, C-9), 103.3 (s, C-6), 105.9 (d, C-7), 124.1 (s, C-9b), 137.3 (s, C-4), 140.4 (s, C-9a), 143.4 (s, C-6a), 144.7 (d, C-5), 147.5 (s, C-3a), 160.8 (s, C-8). EI MS: 428 (M$^{+\cdot}$, 24), 413 (5), 385 (50), 355 (10), 343 (6), 269 (18), 256 (5), 241 (17), 227 (5), 157 (7), 133 (10), 115 (17), 107 (15), 87 (18), 73 (100), 59 (62), 45 (18). HR EI MS: calculated for $C_{25}H_{40}O_2Si_2$ 428.2567; found 428.2543.

5.3.2. Triisopropyl[8-methoxy-5-(trimethylsilyl)-1*H*,3*H*-benzo[de]isochromen-4-yl]silane 24. IR: 3031 w, 3010 m, 2868 s, 1558 w, 1465 s, 1384 m, 1368 m, 1308 m, 1251 s, 1178 m, 1075 s, 1036 s, 998 m, 883 s, 844 vs, 691 w, 661 m, 640 m, 609 w. ^{1}H NMR (500 MHz): 0.45 (s, 9H, (CH$_3$)$_3$Si), 1.13 (d, 18H, J=7.5 Hz, 3×(CH_3)$_2$CH), 1.49 (m, 3H, 3× (CH$_3$)$_2$C*H*), 3.91 (s, 3H, CH$_3$O), 5.01 (dd, 2H, J=1.1, 0.7 Hz, 1-H), 5.09 (s, 2H, 3-H), 6.83 (dt, 1H, J=2.5, 1.1 Hz, 9-H), 7.27 (dt, 1H, J=2.6, 0.7 Hz, 7-H), 7.77 (s, 1H, 6-H). ^{13}C NMR: 0.1 (q, (CH$_3$)$_3$Si), 12.7 (d, 3×(CH$_3$)$_2$*C*H), 19.1 (q, 3×(*C*H$_3$)$_2$CH), 55.2 (q, CH$_3$O), 69.8 (t, C-1), 70.8 (t, C-3), 105.6 (d, C-7), 111.8 (d, C-9), 122.3 (s, C-9b), 123.4 (s, C-6a), 132.8 (s, C-9a), 135.5 (s, C-4), 138.4 (s, C-5), 140.7 (d, C-6), 141.7 (s, C-3a), 157.1 (s, C-8). EI MS: 428 (M$^{+\cdot}$, 32), 385 (93), 343 (13), 313 (7), 205 (12), 165 (8), 149 (50), 135 (11), 111 (13), 97 (21), 85 (27), 73 (100), 57 (89), 43 (93). HR EI MS: calculated for $C_{25}H_{40}O_2Si_2$ 428.2567; found 428.2549.

5.3.3. Triisopropyl[(1*Z*)-1-(7-methoxy-1*H*-isochromen-4(3*H*)-ylidene)-3-(trimethylsilyl)-2-propynyl]silane 25. IR: 3031 w, 3010 m, 2867 vs, 2107 w, 1608 s, 1573 w, 1492 s, 1466 s, 1437 w (sh), 1384 w, 1368 w, 1324 m, 1269 s, 1250 s, 1177 w, 1162 w, 1034 m, 998 m, 883 s, 845 s, 696

w, 681 w, 645 w. ^{1}H NMR (500 MHz): 0.19 (s, 9H, $(CH_3)_3Si$), 1.15 (d, 18H, J=7.4 Hz, 3×$(CH_3)_2CH$), 1.44 (m, 3H, 3×$(CH_3)_2CH$), 3.82 (s, 3H, CH_3O), 4.38 (s, 1H, 3-H), 4.81 (dd, 1H, J=1.0, 0.8 Hz, 1-H), 6.53 (dt, 1H, J=2.7 Hz, 1.0, 8-H), 6.75 (ddt, 1H, J=9.0, 2.7, 0.8 Hz, 6-H), 8.96 (d, 1H, J=9.0 Hz, 5-H). ^{13}C NMR: −0.3 (q, $(CH_3)_3Si$), 13.3 (d, 3×$(CH_3)_2CH$), 18.9 (q, 3×$(CH_3)_2CH$), 55.3 (q, CH_3O), 68.9 (t, C-1), 70.3 (t, C-3), 103.8 (s, SiC≡C), 108.3 (d, C-8), 109.3 (s, SiC≡C), 111.6 (d, C-6), 112.9 (s, SiC═C), 127.0 (s, C-4a), 130.2 (d, C-5), 137.7 (s, C-8a), 150.5 (s, SiC═C), 159.6 (s, C-7). EI MS: 428 ($M^{+\cdot}$, 51), 385 (26), 355 (66), 257 (6), 241 (7), 225 (7), 183 (5), 165 (5), 142 (10), 133 (18), 115 (11), 91 (22), 73 (100), 59 (75), 45 (19). HR EI MS: calculated for $C_{25}H_{40}O_2Si_2$ 428.2567; found 428.2565.

5.4. Reaction of 15 with (trimethylsilyl)acetylene in piperidine to get 24–26

Method B: **15** (21 mg, 0.046 mmol), $Pd(PPh_3)_4$ (2.7 mg, 0.002 mmol, 5 mol%), (trimethylsilyl)acetylene (17 μl, 0.120 mmol, 1.6 equiv.), piperidine (2 ml), 80°C, 1.5 h. Flash chromatography on silica gel (petroleum ether–ether 100:0 to 99:1) afforded the most lipophilic **26** (6 mg, 30%), then **24** (1 mg, 5%), and the most polar **25** (11 mg, 56%) as oils. Compounds **24** and **25**: for spectral data, see above.

5.4.1. {[4-Methoxy-2-({[3-(triisopropylsilyl)-2-propynyl]-oxy}methyl)phenyl]ethynyl}(trimethyl)silane 26. IR: 3080 w, 3061 w, 3010 m, 2867 vs, 2172 w (sh), 2150 s, 1606 s, 1568 m, 1494 s, 1466 s, 1438 s, 1408 w, 1384 m, 1367 m, 1351 m, 1300 s, 1280 s, 1251 vs, 1192 w, 1164 s, 1120 s, 1079 s, 1029 s, 999 s, 947 w, 883 s, 862 vs, 845 vs, 695 m, 680 s, 663 m, 636 m. ^{1}H NMR (500 MHz): 0.24 (s, 9H, $(CH_3)_3Si$), 1.07–1.11 (m, 21H, 3×$(CH_3)_2CH$), 3.81 (s, 3H, CH_3O), 4.31 (s, 2H, CH_2C≡C), 4.75 (t, 2H, J=0.7 Hz, CH_2Ar), 6.74 (ddt, 1H, J=8.5, 2.7, 0.6 Hz, 5-H), 7.02 (dt, 1H, J=2.7, 0.8 Hz, 3-H), 7.37 (d, 1H, J=8.5 Hz, 6-H). ^{13}C NMR: 0.1 (q, $(CH_3)_3Si$), 11.1 (d, 3×$(CH_3)_2CH$), 18.6 (q, 3×$(CH_3)_2CH$), 55.3 (q, CH_3O), 58.9 (t, CH_2C≡C), 69.6 (t, CH_2Ar), 87.8 (s, TIPSC≡C), 97.5 (s, TMSC≡C), 102.6 (s, TIPSC≡C), 103.3 (s, TMSC≡C), 112.3 (d, C-3), 113.2 (d, C-5), 113.5 (s, C-1), 133.8 (d, C-6), 142.1 (s, C-2), 160.0 (s, C-4). EI MS: 428 ($M^{+\cdot}$, 7), 385 (3), 355 (8), 243 (15), 217 (6), 178 (13), 161 (8), 149 (78), 128 (23), 105 (11), 97 (21), 83 (30), 73 (73), 57 (95), 43 (100). HR EI MS: calculated for $C_{25}H_{40}O_2Si_2$ 428.2567; found 428.2562.

5.4.2. [(1*Z*)-1-(7-Methoxy-1*H*-isochromen-4(3*H*)-ylidene)-3-(trimethylsilyl)-2-propynyl](trimethyl)silane 27. Method B: **16** (94 mg, 0.264 mmol), $Pd(PPh_3)_4$ (15 mg, 0.013 mmol, 5 mol%), (trimethylsilyl)acetylene (50 μl, 0.354 mmol, 1.3 equiv.), diisopropylamine (2 ml), 80°C, 1.5 h. Flash chromatography on silica gel (petroleum ether–ether 100:0 to 98:2) afforded **27** (84 mg, 97%) as an oil. IR: 3088 vw, 2900 w, 2840 w, 2106 w, 1608 s, 1574 m, 1493 s, 1466 m, 1456 m, 1444 w, 1435 w, 1408 w, 1296 m, 1272 s, 1252 s, 1236 s, 1193 w, 1164 m, 1117 m, 1065 s, 1033 s, 847 vs, 696 w, 636 w, 543 w. ^{1}H NMR (500 MHz): 0.22 (s, 9H, $(CH_3)_3SiC$≡C), 0.30 (s, 9H, $(CH_3)_3SiC$═C), 3.82 (s, 3H, CH_3O), 4.52 (s, 2H, 3-H), 4.74 (dd, 2H, J=1.0, 0.6 Hz, 1-H), 6.54 (dt, 1H, J=2.7, 1.0 Hz, 8-H), 6.76 (ddt, 1H, J=8.9, 2.7, 0.6 Hz, 6-H), 9.01 (d, 1H, J=8.9 Hz, 5-H). ^{13}C NMR: −0.1 (q, $(CH_3)_3SiC$≡C), 0.5 (q, $(CH_3)_3SiC$═C), 55.3 (q, CH_3O), 69.0 (t, C-1), 70.2 (t, C-3), 105.5 (s, $(CH_3)_3SiC$≡C), 108.0 (s, $(CH_3)_3SiC$≡C), 108.8 (d, C-1), 111.9 (d, C-6), 115.1 (s, $(CH_3)_3SiC$═C), 126.0 (s, C-4a), 129.8 (d, C-5), 137.8 (s, C-8a), 148.7 (s, C-4), 159.6 (s, C-7). EI MS: 344 ($M^{+\cdot}$, 26), 329 (5), 271 (9), 241 (5), 147 (71), 134 (24), 73 (100), 59 (7), 45 (14). HR EI MS: calculated for $C_{19}H_{28}O_2Si_2$ 344.1628; found 344.1621.

5.4.3. [(3*E*)-3-(7-Methoxy-1*H*-isochromen-4(3*H*)-ylidene)-1-butynyl](trimethyl)silane 28. Method B: **17** (24 mg, 0.076 mmol), $Pd(PPh_3)_4$ (4 mg, 0.003 mmol, 5 mol%), (trimethylsilyl)acetylene (30 μl, 0.212 mmol, 2.8 equiv.), diisopropylamine (2 ml), 80°C, 10 h. Flash chromatography on silica gel (petroleum ether–ether 100:0 to 99:1) afforded **28** (8 mg, 37%) as an oil. IR: 2839 w, 2131 w, 1610 m, 1588 w, 1570 w, 1495 m, 1436 w, 1409 w, 1307 m, 1249 s, 1192 w, 1164 w, 1116 m, 1061 m, 1033 w, 933 w, 888 m, 866 m, 845 vs, 698 w. ^{1}H NMR (200 MHz): 0.23 (s, 9H, $(CH_3)_3SiC$≡C), 1.93 (s, 3H, CH_3C═C), 3.82 (s, 3H, CH_3O), 4.52 (d, 2H, J=1.2 Hz, 3-H), 4.59 (s, 2H, 1-H), 6.60 (d, 1H, J=2.8 Hz, 8-H), 6.78 (dd, 1H, J=8.9, 2.8 Hz, 6-H), 8.68 (d, 1H, J=8.9 Hz, 5-H). EI MS: 286 ($M^{+\cdot}$, 70), 271 (15), 243 (8), 213 (9), 185 (11), 173 (6), 159 (8), 134 (16), 122 (25), 97 (11), 83 (39), 73 (1000, 57 (15), 43 (15). HR EI MS: calculated for $C_{17}H_{22}O_2Si$ 286.1389; found 286.1394.

5.4.4. [(3*E*)-3-(1*H*-Isochromen-4(3*H*)-ylidene)-1-butynyl](trimethyl)silane 29. Method B: **14** (100 mg, 0.350 mmol), $Pd(PPh_3)_4$ (20 mg, 0.0173 mmol, 5 mol%), (trimethylsilyl)acetylene (100 μl, 0.708 mmol, 2.0 equiv.), piperidine (2 ml), 80°C, 4 h. Flash chromatography on silica gel (petroleum ether–acetone 98:2) afforded **29** (42 mg, 47%) as an oil. IR: 3066 w, 3029 m, 3012 m, 2900 m, 2134 w, 1604 w, 1484 w, 1453 m, 1408 m, 1252 vs, 1163 m, 846 vs, 699 w, 637 w, 429 w. ^{1}H NMR (200 MHz): 0.22 (s, 9H, $(CH_3)_3Si$), 1.95 (s, 3H, CH_3), 4.54 (d, 2H, J=0.9 Hz, 1-H), 4.61 (s, 2H, 3-H), 7.05–7.10 (m, 1H, H-arom.), 7.21–7.25 (m, 2H, H-arom.), 8.66–8.71 (m, 1H, H-arom.). EI MS: 256 ($M^{+\cdot}$, 20), 241 (8), 187 (10), 167 (8), 152 (5), 147 (10), 135 (10), 125 (22), 118 (8), 105 (20), 97 (19), 90 (9), 83 (16), 73 (100), 67 (5), 59 (13), 43 (23). HR EI MS: calculated for $C_{16}H_{20}OSi$ 256.1283; found 256.1274.

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