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Sonogashira-Hagihara and Buchwald-Hartwig cross-coupling reactions with sydnone and sydnone imine derived catalysts

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Dedicated to Prof. Jan Bergman on the occasion of his 80th birthday

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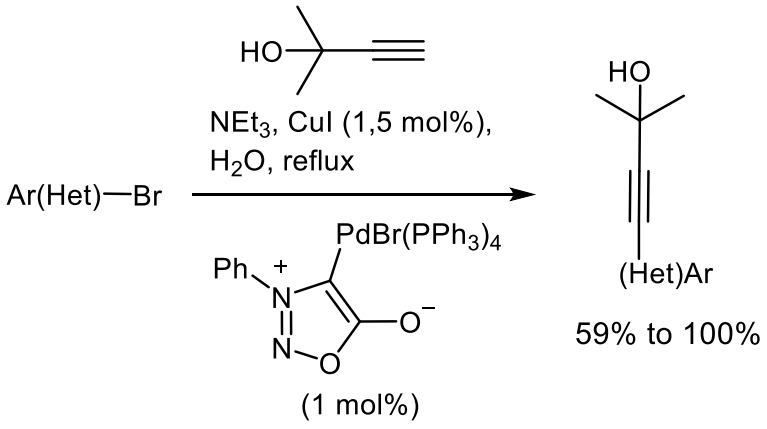
Abstract

Seven different palladium complexes of sydnones and sydnone imines and a co-catalyst system consisting of lithium sydnone-4-carboxylate and $Pd(PPh_3)_4$ catalyzed Sonogashira-Hagihara reactions between (hetero)-aromatic bromides and 2-methylbut-3-yn-2-ol (52 examples, up to 100% yield). The co-catalyst system and a sydnone Pd complex were also tested in Buchwald-Hartwig reactions (9 examples, up to 100% yield).

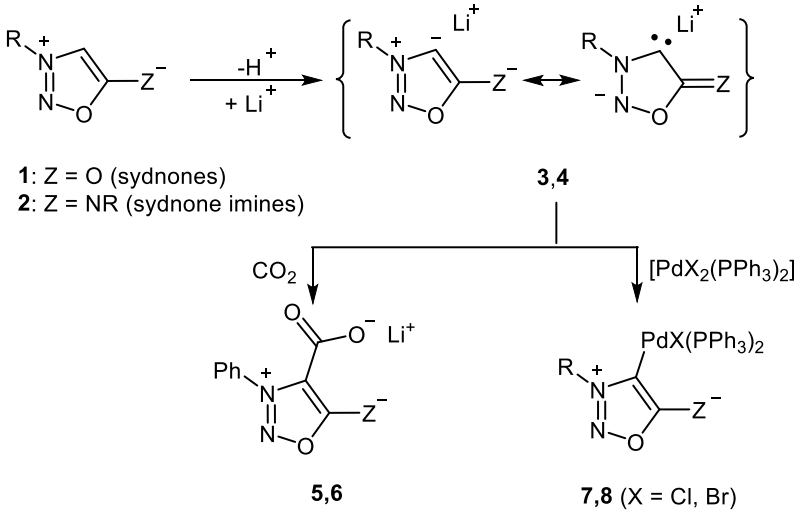


Keywords: Catalysis, Sonogashira-Hagihara cross-couplings, N-heterocyclic carbenes, sydnones, Buchwald-Hartwig reactions

Introduction

The Sonogashira-Hagihara[1-3] and Buchwald-Hartwig[4-6] cross-couplings are widely applied reactions in organic synthesis. Whereas the former mentioned reaction is a method to prepare substituted alkynes by copper-palladium catalysis, the latter leads to C-N and C-O bond formations between aryl halides or pseudo-halides and amines or alcohols. Key features of the Sonogashira-Hagihara reaction include mild conditions in comparison to the Stephens-Castro coupling which can be regarded as its non-catalytic precedent. As catalytic amounts of Cu(I) salts are used, explosive copper acetylides as starting materials can be avoided. A great functional group tolerance is an additional advantage of the Sonogashira-Hagihara cross-coupling.[7] Widely applied catalysts are $Pd(PPh_3)_2Cl_2$ and $Pd(PPh_3)_4$. In parallel to the remarkable carrier of N-heterocyclic carbenes, NHC-palladium catalyzed Sonogashira-Hagihara cross-couplings have been reported.[8] Early reports deal with di(imidazol-1-yl-2-ylidene)methane,[9] 2-(imidazol-1-yl-2-ylidene)methyl)pyridine[10] and bis(1,3-di-*N*-*tert*-butylimidazol-2-ylidene) Pd complexes[11] as catalysts. Since then considerable progress has been made with respect to new and effective NHCs,[12-14] abnormal NHCs,[15] and polymer-supported NHC catalysts in Sonogashira-Hagihara cross-couplings.[16]

The application of N-heterocyclic carbenes in Buchwald-Hartwig cross-couplings is well-established.[17] First reports of NHC/palladium systems to couple aryl chlorides with amines describe 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene and its 4,5-dihydro derivative. These NHCs were formed *in situ* in the presence of $Pd(dba)_2$ and alcoholates.[18,19] Nowadays, well-defined NHC complexes are employed in Buchwald-Hartwig reactions rather than *in situ* generated catalysts. *N,N*-Dimethyl-[1,1'-biphenyl]-2-amine and 4-hydroxypent-3-en-2-one based palladacycles are examples of defined catalysts applied.[17] Similarly, Pd complexes of 3-chloropyridine and *N*-methylimidazole with NHC ligands have been described, respectively.[17] They proved to be very efficient and tolerant toward steric hindrance as well as functional groups, and they work at mild reaction temperatures.[20] As part of an ongoing project dealing with the intersection of the substance classes of mesomeric betaines and N-heterocyclic carbenes (NHC)[21-24] we became interested in mesoionic compounds as potential catalysts. Sydnones **1**[25,26] and sydnone imines **2**[27] can be deprotonated to form lithium adducts of sydnone anions which can be formulated as anionic, π-electron rich NHCs **3**[28] and **4**.[29] The sydnone **1** can be brominated at C4 and subsequently treated with $Pd(PPh_3)_4$ to form Pd complexes.[28,30]

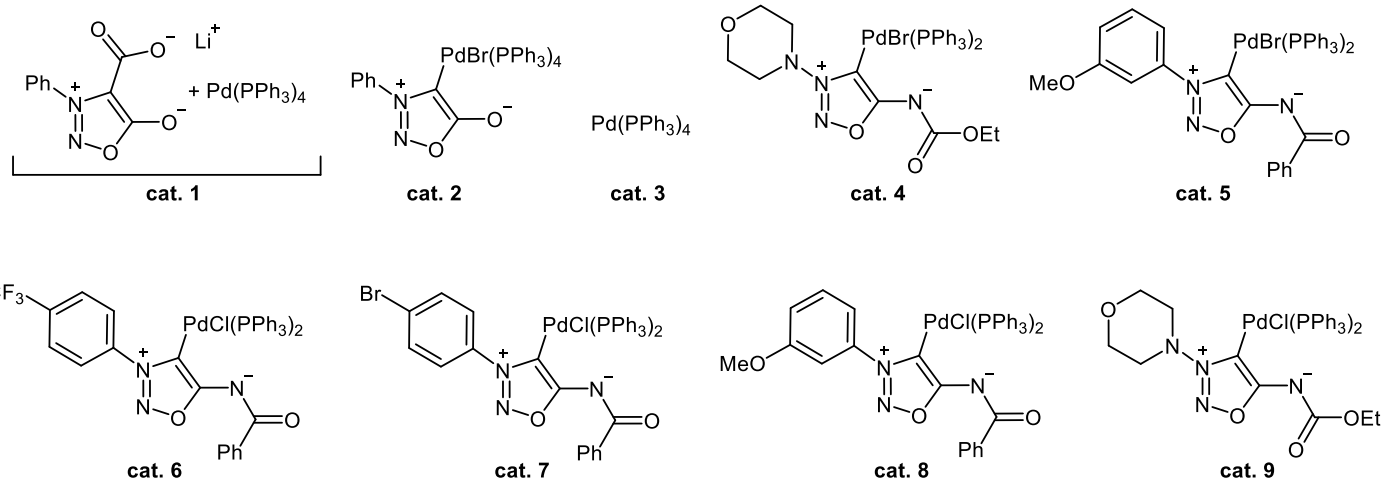


Scheme 1. Sydnones, sydnone imines, their corresponding anionic sydnone carbenes, carbon dioxide adducts, and palladium complexes.

Alternatively, the anionic NHC **3** reacts with $[PdX_2(PPh_3)_2]$ to give the complexes **7** and **8**. Trapping of the anionic NHC **3** with carbon dioxide results in the formation of the lithium salt of sydnone-4-carboxylic acid **5** which regenerates the carbene on heating.[31] Sydnone derived catalyst systems proved to be very efficient. Recently we reported on Suzuki-Miyaura reactions under basic conditions as well as in acid employing sydnones as co-catalysts.[32-34] We report here on sydnones as catalysts or co-catalysts of Sonogashira-Hagihara and of Buchwald-Hartwig cross-coupling reactions.

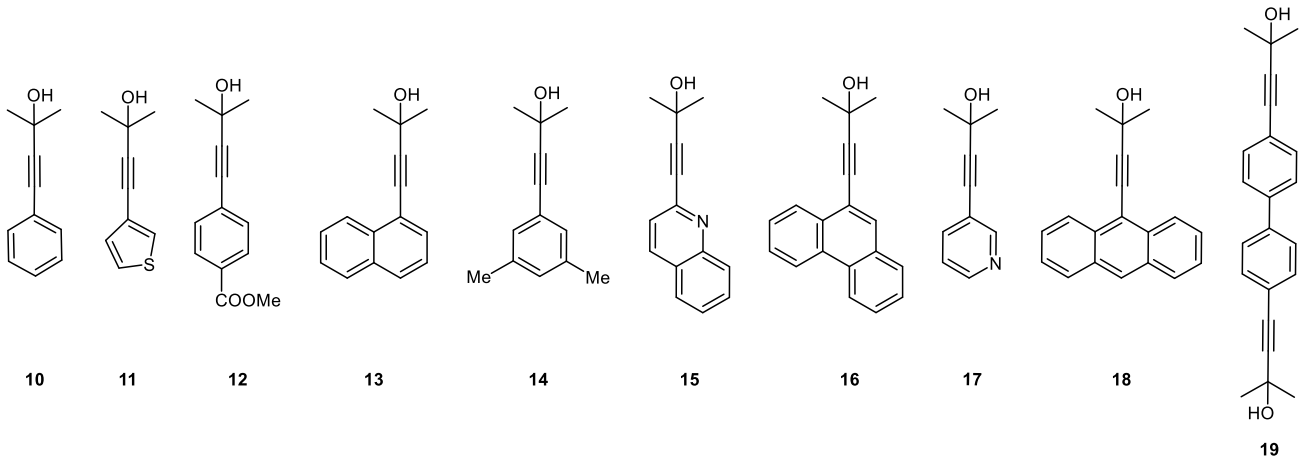
Results and Discussion

We studied the catalysts and catalyst systems shown in Scheme 2 for Sonogashira-Hagihara and Buchwald-Hartwig cross-coupling reactions. The lithium salt of sydnone-4-carboxylic acid **5** and $Pd(PPh_3)_4$ which proved to be very efficient to catalyze Suzuki-Miyaura reactions in acid, is catalyst system **1** (cat. **1**). We also tested the Pd complex of the anionic sydnone carbene **3** (R = Ph) (cat. **2**) and, as comparison, $Pd(PPh_3)_4$ (cat. **3**) without any sydnone as additive. The catalysts cat. **4** – cat. **9** are sydnone imine derived Pd complexes.[29]



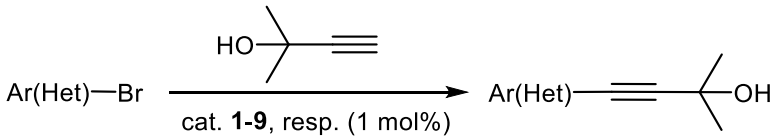
Scheme 2. Catalysts and catalyst systems used in this study.

Results of Sonogashira-Hagihara cross-couplings of (hetero)aromatic bromides **9** and 2-methylbut-3-yn-2-ol to form the acetylenes **10** – **19** (Scheme 3) are summarized in Table 1. With few exceptions, we chose fixed reaction times (5 h, 48 h, 72 h, respectively) to compare the relative reactivities of the catalysts; therefore, the yields of the conversions described here are not always optimized. Entries 1 - 9 show that 2-methyl-4-phenylbut-3-yn-2-ol **10** was obtained in good to very good yields in all cases. The sydnone-imine Pd complexes (entries 4 - 9) required much longer reaction times to achieve similar yields than the sydnone-derived catalysts (entries 1 and 2).



Scheme 3. Coupling products obtained by Sonogashira-Hagihara reaction.

Table 1. Yields of Sonogashira-Hagihara cross-couplings to yield the acetylenes **10** - **19** in dependence on the catalyst system used

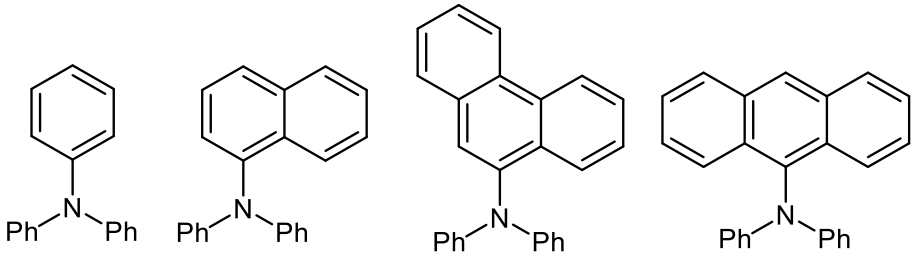


Entry	Pr.	Catalyst	Yield[a]	Entry	Pr.	Catalyst	Yield[a]	Entry	Pr.	Catalyst	Yield[a]
1	**10**	**cat. 1**	85%[b]	19	**13**	**cat. 1**	42%[b]	37	**16**	**cat. 1**	35%[b]
2		**cat. 2**	100%[c]	20		**cat. 2**	83%[b]	38		**cat. 2**	80%[b]
3		**cat. 3**	82%[b]	21		**cat. 3**	61%[d]	39		**cat. 5**	45%[e]
4		**cat. 4**	88%[d]	22		**cat. 4**	76%[d]	40		**cat. 8**	61%[e]
5		**cat. 5**	86%[d]	23		**cat. 5**	85%[d]	41		**cat. 9**	56%[e]
6		**cat. 6**	75%[d]	24		**cat. 6**	63%[d]	44	**17**	**cat. 1**	25%[b]
7		**cat. 7**	71%[d]	25		**cat. 7**	51%[d]	45		**cat. 2**	59%[b]
8		**cat. 8**	87%[d]	26		**cat. 8**	60%[d]	46		**cat. 3**	48%[d]
9		**cat. 9**	82%[b]	27		**cat. 9**	63%[d]	47		**cat. 9**	46%[d]
10	**11**	**cat. 1**	75%[b]	28	**14**	**cat. 1**	75%[b]	48	**18**	**cat. 1**	15%[b]
11		**cat. 2**	95%[b]	29		**cat. 2**	95%[b]	49		**cat. 2**	65%[b]
12		**cat. 4**	64%[d]	30		**cat. 4**	64%[d]	50		**cat. 8**	58%[e]
13		**cat. 5**	72%[d]	31		**cat. 5**	72%[d]	51		**cat. 9**	56%[e]
14		**cat. 8**	69%[d]	32		**cat. 8**	69%[d]	52	**19**	**cat. 1**	23%[b]
15		**cat. 9**	78%[d]	33		**cat. 9**	78%[d]	53		**cat. 2**	95%[b]
16	**12**	**cat. 1**	91%[b]	34	**15**	**cat. 1**	85%[b]	54		**cat. 3**	34%[d]
17		**cat. 2**	97%[b]	35		**cat. 2**	97%[b]				
18		**cat. 10**[f]	95%[b]	36		**cat. 3**	95%[b]				

[a]Isolated yields after chromatography. [b]Reaction time: 5 h. [c] Reaction time 7 h.
[d]Reaction time: 48 h. [e]Reaction time: 72 h. [f] $PdCl_2(PPh_3)_2$

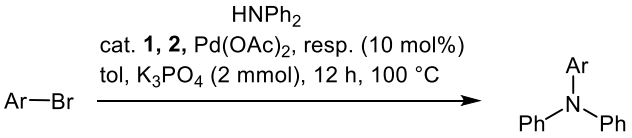
Employing catalyst system **cat. 2**, a quantitative yield was obtained after a reaction time of 7 h. The method described here gives the same yield as a system described in the literature, consisting of $Pd(PhCN)_2Cl_2$, CuI, P(*t*-Bu)$_3$, and HN(*i*Pr)$_2$ in dioxane, which needed reaction times up to 15 h. It has, however, the advantage that the coupling can be performed at room temperature.[35] A systematic study under variation of the palladium and copper source, the phosphorus ligand, the amine added, and the reaction time has been carried out and described in the literature.[36] It has been found that an almost quantitative yield of **10** was obtained when $Pd(OAc)_2$, CuI, PPh_3, *n*-butylamine was reacted for 24 h at 78 °C. A comparison with other literature procedures to prepare acetylene **10** revealed that reaction times between 6 h[37] and 36 h[38] are required when $Pd(OAc)_2$ is used as palladium source. In all reactions tested here, the catalyst system **cat. 2** gives better yields than the reference $Pd(PPh_3)_4$ (**cat. 3**) under analogous reaction conditions, and, with one exception, it proved to be the best catalyst to prepare the acetylenes shown in Scheme 3. The exception is the sydnone imine derived catalyst **cat. 5** which gave best yields to prepare naphthalene **13** (entry 23). The study shows that especially **cat. 2** is at least on par with other literature-known catalysts with respect to the yield (compounds **10**,[37] **14** [39]) after analogous reaction times and temperatures. The preparation of **11**, however, is much faster than reported (24 h at 60 °C;[40] 20 h at 80 °C [41]). Reaction times to prepare **12** differ between 40 min (88 °C[42]) and 48 h.[38] It gives higher yields to prepare *e.g*. quinoline **15**[43] which was prepared before using $PdCl_2(PPh_3)_2$ and CuI in 60% yield. Yields for the 1,1'-biphenyl derivate **19** are higher than those reported in the literature, where yields of 88% were documented.[44] It is worth mentioning that the synthesis of thiophene **11**[29] was accomplished with a mesoionic bis(pyridine-1,2,3-triazol-5-ylidene) palladium(II) complex which was applied for 1 h at 100 °C to give 87% yield.[45]

We next tested Buchwald-Hartwig cross-couplings and prepared the amines **20**–**23** as model compounds (Scheme 4, Table 2). The major drawback of palladium-NHC-catalyzed aryl aminations is that they usually require the application of strong bases which can induce undesired side reactions.[17] We therefore chose the mild base potassium phosphate for our reactions. Triphenylamine was prepared in almost quantitative yields, when **cat. 2** was applied. It is as effective as an expanded-ring NHC for the synthesis of **20** [46] and imidazol-ylidene Pd complexes for the synthesis of **20** [47] and **21**.[46] Compound **22** was prepared in better yields when $Pd(OAc)_2$, NaOtBu, $tBuP_3$ in *o*-xylene was used.[48] The synthesis of **23** failed under the conditions applied here.



Scheme 4. Coupling products obtained by Buchwald-Hartwig reaction.

Table 2. Yields of Buchwald-Hartwig cross-couplings to yield the amines **20** - **23** in dependence on the catalyst system used



9 **20 - 23**

Entry	Pr.	Catalyst	yield[a]	Entry	Pr.	Catalyst	yield[a]
1	**20**	**cat. 1**	45%	7	**22**	**cat. 1**	31%
2		**cat. 2**	98%	8		**cat. 2**	70%
3		$Pd(OAc)_2$	88%	9		$Pd(OAc)_2$	62%
4	**21**	**cat. 1**	48%	10	**23**	**cat. 1**	0%
5		**cat. 2**	95%	11		**cat. 2**	0%
6		$Pd(OAc)_2$	82%	12		$Pd(OAc)_2$	0%

[a] Isolated yields after chromatography.

Conclusions

In summary, we demonstrated that the catalysts derived from sydnones and sydnone imines can efficiently be applied in Sonogashira-Hagihara cross-couplings. Best results were achieved with the complex [sydnon-4-yl-$PdBr(PPh_3)_2$] (**cat. 2**) which gave yields between 59% and 100%. The same holds true for Buchwald-Hartwig reactions which we performed with a co-catalyst system consisting of lithium sydnone-4-carboxylate / $Pd(PPh_3)_4$ (**cat. 1**) and with the aforementioned sydnone palladium complex (**cat. 2**). The coupling of 9-bromo-anthracene and diphenylamine, however, failed under the conditions applied here.

Experimental Section

General. A Bruker Avance 400 MHz was used to measure the nuclear magnetic resonance (NMR) spectra. The ^1H NMR spectra were recorded at 400 MHz, and the ^{13}C NMR spectra were recorded at 100 MHz. The solvent peaks or tetramethylsilane were used as internal references. Multiplicities are described using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet.

General Procedure for the preparation of compounds 10-19

Under an inert atmosphere (N_2) the haloaromatic was dissolved in 15 mL of triethylamine at rt. Then 10 mol-% of the corresponding catalyst and 0.010 g (0.05 mmol) of Cu(I)I as co-catalyst was added. After the acetylene was carefully added, the mixture was stirred at reflux temperature over a period of 5 h - 72 h. After cooling to rt, the mixture was treated with 15 mL of distilled water and subsequently extracted with $CHCl_3$ or CH_2Cl_2. The organic phase was dried over $MgSO_4$, and then the solvent was removed under reduced pressure. The resulting crude product was finally purified by column chromatography.

2-Methyl-4-phenylbut-3-yn-2-ol (**10**)**.**[37,38] Samples of 0.400 g (2.55 mmol) of bromobenzene and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with petroleum ether :

ethyl acetate = 2 : 1. Brownish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.43-7.40 (m, 2 H), 7.32-7.29 (m, 3 H), 1.99 (br s, 1 H), 1.62 (s, 6 H) ppm.

2-Methyl-4-(thiophen-3-yl)but-3-yn-2-ol (**11**)**.**[40] Samples of 0.400 g (2.46 mmol) of 1-bromothiophene and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with petroleum ether : ethyl acetate = 2 : 1. Yellowish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.33 (d, $J_{H,H}$ 7.8 Hz, 1 H), 7.18-7.15 (m, 1 H), 7.01 (d, $J_{H,H}$ 7.8 Hz, 1 H), 2.19 (br s, 1 H), 1.53 (s, 6 H), ppm.

Methyl 4-(3-hydroxy-3-methylbut-1-yn-1-yl)benzoate (**12**)**.**[37] Samples of 1.00 g (4.65 mmol) of methyl-4-bromobenzoate and 1.2 mL (12.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with petroleum ether : ethyl acetate = 2:1. Yellowish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.01-7.97 (m, 2 H), 7.50-7.46 (m, 2 H), 3.91 (s, 3 H), 2.29 (s, 1 H), 1.63 (s, 6 H) ppm.

2-Methyl-4-(naphth-1-yl)but-3-yn-2-ol (**13**)**.**[37] Samples of 0.500 g (2.41 mmol) of 1-bromonaphthalene and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with petroleum ether : ethyl acetate = 2 : 1. Brownish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.28 (d, $J_{H,H}$ 7.8 Hz, 1 H)), 7.80-7.74 (m, 2 H), 7.60 (d, $J_{H,H}$ 7.8 Hz, 1 H), 7.55-7.52 (m, 1 H), 7.48-7.44 (m, 1 H), 7.36-7.33 (m, 1 H), 2.72 (br s, 1 H), 1.71 (s, 6 H) ppm.

4-(3,5-Dimethylphenyl)-2-methylbut-3-yn-2-ol (**14**)**.**[39] Samples of 0.500 g (2.70 mmol) of 1-bromo-3,5-dimethylbenzene and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with petroleum ether : ethyl acetate = 4 : 1. Brownish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.04 (s, 2 H), 6.93 (s, 1 H), 2.27 (s, 6 H), 2.27 (br s, 1 H),1.60 (s, 6 H) ppm.

2-Methyl-4-(quinolin-2-yl)but-3-yn-2-ol (**15**).[44] Samples of 0.500 g (2.40 mmol) of 2-bromoquinoline and 0.6 mL (6.0 mmol) of 2--methyl-but-3-yn-2-ol were used. Column chromatography was performed with petroleum ether : ethyl acetate = 2 : 1. Brownish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 9.07-9.06 (m, 1 H), 8.15-8.10 (m, 2 H), 7.72-7.66 (m, 2 H), 7.54-7.50 (m, 1 H), 5.58 (br. s, 1 H), 1.69 (s, 6 H) ppm.

2-Methyl-4-(phenanthren-9-yl)but-3-yn-2-ol (**16**).[49] Samples of 0.500 g (1.95 mmol) of 9-bromophenanthrene and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with petroleum ether : ethyl acetate = 2 : 1. Brownish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.70-8.64 (m, 3 H) 8.40-8.38 (m, 1 H), 7.98 (s, 1 H), 7.85-7.83 (m, 2 H), 7.70-7.66 (m, 1 H), 7.65-7.60 (m, 1 H), 2.00 (br s, 1 H), 1.76 (s, 6 H) ppm.

2-Methyl-4-(pyridin-3-yl)but-3-yn-2-ol (**17**)**.**[37] Samples of 0.500 g (3.16 mmol) of 3-bromopyridine and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with petroleum ether : ethyl acetate = 5 : 1. Brownish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.76-8.73 (m, 1 H), 8.52-8.49 (m, 1 H), 7.75-7.70 (m, 1 H), 7.26-7.21 (m, 1 H), 3.92 (br. s, 1 H), 1.61 (s, 6 H) ppm.

4-(Anthracen-9-yl)-2-methylbut-3-yn-2-ol (**18**)**.**[50] Samples of 0.500 g (1.95 mmol) of 9-bromoanthracene and 0.6 mL (6.0 mmol) of 2-methyl-but-3-yn-2-ol were used. Column chromatography was performed with petroleum ether : ethyl acetate = 2 : 1. Yellowish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.48 (d, $J_{H,H}$ 8.6 Hz, 2 H), 8.41 (s, 1 H), 7.98 (d, $J_{H,H}$ 8.6 Hz, 2 H), 7.58-7.55 (m, 2 H), 7.51-7.47 (m, 2H), 2.30 (br s, 1H), 1.85 (s, 6 H), ppm.

4,4'-([1,1'-Biphenyl]-4,4'-diyl)bis-(2-methylbut-3-yn-2-ol) (**19**)**.**[44] Samples of 0.200 g (0.64 mmol) of 4,4'-dibromo-1,1'-biphenyl and 0.3 mL (3.0 mmol) of 2--methyl-but-3-yn-2-ol were used. Column chromatography was performed with petroleum ether : ethyl acetate = 8 : 1. Brownish solid. ^{1}H-NMR (400 MHz, DMSO-d_6): δ 7.70 (d, $J_{H,H}$ 8.4 Hz, 4 H), 7.48 (d, $J_{H,H}$ 8.4 Hz, 4 H), 5.51 (bs, 2 H), 1.49 (s, 12 H), ppm.

General Procedure for the preparation of compounds 20-23.

Under an inert atmosphere (N_2) the halogen compound was dissolved in 20 ml of dry toluene and 10 mol-% of the corresponding catalyst was added. After stirring the mixture for 10 min at rt 0.075 g (0.4 mmol) diphenylamine and 0.424 g (2.0 mmol) potassium phosphate (K_3PO_4) were added. Then the mixture was

stirred at 100 °C for 12 h. After cooling the mixture to room temperature, the solvent was removed under reduced pressure. The resulting crude product was finally purified by column chromatography which was performed with petroleum ether : dichloromethane = 1 : 1.

***N,N,N*-Triphenylamine** (**20**).[46] Sample of 0.150 g (0.96 mmol) of bromobenzene was used. The product was isolated as brownish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 7.47 (d, $J_{H,H}$ = 8.5 Hz, 6 H), 7.29-7.20 (m, 9 H) ppm.

***N,N*-Diphenylnaphthalen-1-amine** (**21**).[46] Sample of 0.150 g (0.72 mmol) of 1-bromonaphthalene was used. The product was isolated as brownish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.20 (d, $J_{H,H}$ 8.5 Hz, 2 H), 7.78-7.72 (m, 5 H), 7.56-7.52 (m, 2 H), 7.50-7.45 (m, 2 H), 7.26-7.20 (m, 3 H), 7.01 (d, $J_{H,H}$ 8.5 Hz, 2 H), 6.88 (t, $J_{H,H}$ 8.5 Hz, 1 H) ppm.

***N,N*-Diphenylphenanthren-9-amine** (**22**).[48] Sample of 0.150 g (0.58 mmol) 9-bromophenanthrene was used. Brownish solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ 8.62-8.56 (m, 4 H), 8.30-8.28 (m, 2 H), 8.03 (s, 2 H), 7.71 (d, J_H 8.5 Hz, 2 H), 7.65-7.53 (m, 7 H), 7.51 (t, $J_{H,H}$ 8.5 Hz, 2 H) ppm.

Acknowledgements

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Supplementary Material

The Experimental Section and the ^{1}H-NMR spectra for all compounds can be found using the link "Supplementary Material" on the Publisher's web site.

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