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RESEARCH ARTICLE

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Tri(1-naphthyl)phosphine as a ligand in palladium-free Sonogashira cross-coupling of arylhalogenides with acetylenes

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Abstract

Tri(1-naphthyl)phosphine (Np_3P) has been easily prepared in 34% yield from red phosphorus and 1-bromonaphthalene in the superbasic system *t*-BuONa/DMSO. The expedient procedures for the synthesis of aryl acetylenes by Sonogashira coupling of aryl iodides with terminal alkynes using Np_3P as a ligand have been developed. For the first time, it is found that the reaction with compounds containing electron-donating substituents preferably affords buta-1,3-diynes.

1 | INTRODUCTION

Owing to their high and unique reactivity, acetylene compounds have found wide application as convenient building blocks in many valuable transformations in organic synthesis, medicinal chemistry, and material science.[1] Meanwhile, the synthetic potential of these compounds is far from to be exhausted. Therefore, it is not surprising that chemistry of alkynes still attracts the attention of wide range of synthetics and biochemists.

Currently, one of the best approaches to the introduction of the triple bond to alkenes, arenes, and hetarenes is based on the Sonogashira reaction, that is, Pd/Cu-catalyzed cross-coupling of haloarenes and haloalkenes with terminal acetylenes.[2,3] However, this method requires the application of expensive palladium compounds. Therefore, over two last decades, the researchers have focused their attention on the development of palladium-free version of the Sonogashira cross-coupling. The first successful results in this area were disclosed by Miura et al[4,5] who showed that triphenylphosphine (Ph_3P) turned out to be the most efficient ligand in the

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CAUTION: Phosphine gas is toxic and explosive. It should be handled with extreme care. All the reactions and handling of phosphine should be carried out under an inert atmosphere in a well-ventilated hood.

Sonogashira reaction, while other phosphorus-containing ligands, $(PhO)_3P$, n-$BuPPh_2$, and $(n\text{-}Bu)_3P$, exerted a significantly lower activity. At the moment, the search for new catalytic systems deprived from costly palladium catalysts with using different ligands keeps being continued.[6-8]

It is known that more sterically hindered tri(1-naphthyl) phosphine (Np_3P) was found to be an excellent ligand for metal complex catalysts inducing many types of transformations (Heck, Suzuki, etc.).[9-24] However, the data on application of Np_3P in the Sonogashira reaction are lacking in the literature.

In continuation of our research on the application of new ligands in the Sonogashira reaction,[25,26] here we report on catalytic activity of Np_3P, synthesized by the Trofimov-Gusarova reaction[27] under the conditions of palladium-free Cu-catalyzed cross-coupling. The synthesis of this ligand described here offers certain advantages over the classic preparation of Ar_3P. For instance, it does not require the application of aggressive corrosive reactants (PCl_3) or flammable expensive organometallic compounds (eg, n-BuLi)[17,18,28] and characterized by easiness of the protocol implementation (vide infra). Previously,[19] Np_3P has been obtained in 10% yield from red phosphorus and 1-bromonaphthalene in the superbasic system KOH/DMSO.

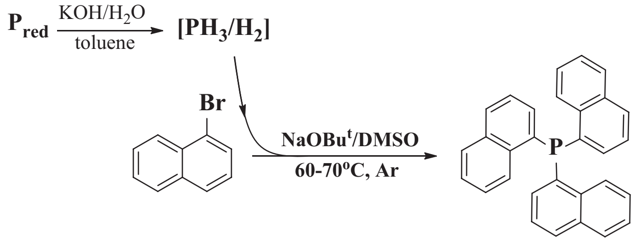
2 | RESULTS AND DISCUSSION

In the present work, we disclose an improved method for the synthesis of tri(1-naphthyl)phosphine from phosphine gas (PH_3) and 1-bromonaphthalene in the superbasic system t-BuONa/DMSO at 60-70°C, which allows the target Np_3P to be obtained in 34% yield (Scheme 1). Phosphine (PH_3) is an industrial tail gas from phosphorus chemical industry[20,21] and can serve as a cheap source of Phosphorus. Therefore its utilization represents an urgent challenge for organic chemistry. Currently, most of yellow phosphorus tail gas is known to be discharged as a burning gas contaminating environment. Here we have tried to convert the toxic PH_3 to commercially important tertiary phosphine ligand. As a phosphine source, its mixture with hydrogen generated from red phosphorus and 60%-70%-aqueous alkali in the separate flask has been used.[22]

Terminal aryl acetylenes and aryl iodides bearing both electron-withdrawing and electron-donating groups were used as substrates (Scheme 2). It is a common knowledge that rate of the Sonogashira coupling increases when passing from electron-donating to electron-withdrawing substituents. In other words, the higher CH-acidity of alkynes-1 (pK), the higher the reaction rate.[23]

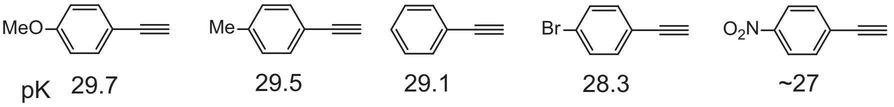
We have compared the efficiency of the most popular Ph_3P with that of a novel ligand, Np_3P, under the conditions of Sonogashira cross-coupling between aryl iodides and terminal acetylenes in the presence of both Ph_3P-CuI-K_2CO_3 (**A**)[5] and Np_3P-CuI-K_2CO_3 (**B**) systems (Table 1).

When both iodine and acetylenic reactants contain the electron-withdrawing groups (eg NO_2, Ac), the cross-coupling in system **B** affords the target tolane **3a, 3b** (94%-100%) according to GC-MS data (Table 1, entry 1, 3). It should be underlined that in the recently published paper,[7] the cross-coupling (Ph_3P-CuI-K_2CO_3-TMEDA) of electron-withdrawing alkynes-1 does not result in the target acetylenes at all due to the side processes, that is, formation of the Michael adducts and further transformations. However, in the case of the system **A** the reaction is finished for 4 hours (entry 2). Unsubstituted iodobenzene reacts with 4-bromo- and 4-acetylphenylacetylenes much more slowly to give exclusively a Sonogashira's product (entry 4, 5). The reaction of iodide **1a** with less reactive phenylacetylene **2d** gives other composition and ratio of the products in system **B**. According to GC-MS data (entry 6), in 7 hours, in the reaction mixture, iodide **1a** (14%), alkyne-1 **2d** (5%), tolane **3e** (62%), and buta-1,3-diyne **4a** (18%) are detected. Noteworthy, earlier in various palladium-free Cu(I)-catalyzed Sonogashira cross-couplings, the formation of buta-1,3-diyne was not observed.[4,5,7] For the comparison purpose, we have implemented a similar reaction with the Ph_3P (system **A**).[5] For the same time (7 hours), the reaction mixture contains the same products, but buta-1,3-diyne **4a** is formed in minor amounts (~ 3%, entry 7). It was found that the presence of the acetyl or carboxy groups in phenylacetylene as well as in iodarene (see entries 5 and 8) leads to dramatic drop of the reaction products content probably due to the formation of more stable copper complex with the carbonyl group, which deactivates system **B**.



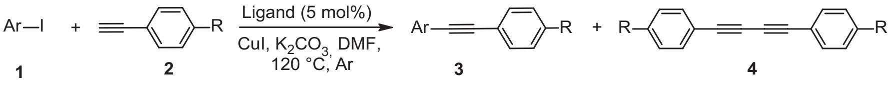
Np_3P, 34%

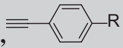
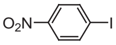
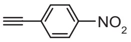
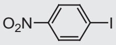
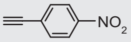
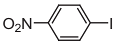
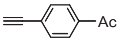
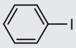
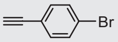
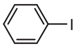
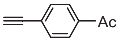
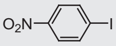
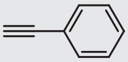
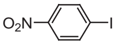
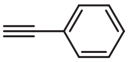
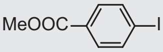
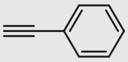
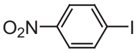
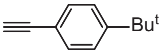
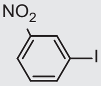
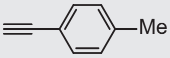
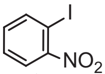
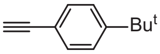
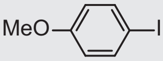
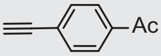
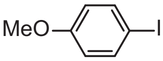
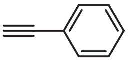
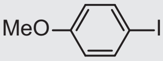
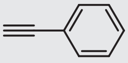
SCHEME 1 Synthesis of tri(1-naphthyl)phosphine



SCHEME 2 pK values for the alkynes

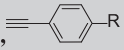
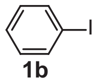
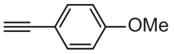
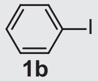
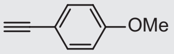
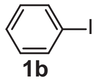
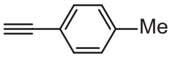
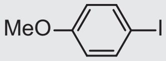
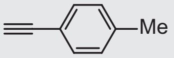
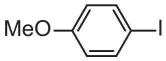
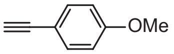
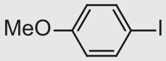
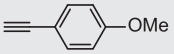
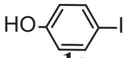
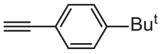
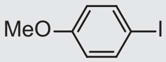
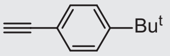
TABLE 1 Comparative study of effectiveness of ligands in cross-coupling of **1** with **2**[a]



					The composition of the reaction mixture according to GC-MS data, (%)			
Entry	**Iodarene, ArI**	**Alkyne,** 	**Ligand**	***t*, hour**	1	2	3	4
1	 **1a**	 **2a**	Np_3P	5	**1a** (6)	**2a** (-)	**3a** (94)	(-)
2	 **1a**	 **2a**	Ph_3P	4	**1a** (4)	(-)	**3a** (95)	(-)
3	 **1a**	 **2b**	Np_3P	5	**1a** (-)	**2b** (-)	**3b** (100)	(-)
4	 **1b**	 **2c**	Np_3P	14.5	**1b** (18)	(-)	**3c** (82%)	(-)
5	 **1b**	 **2b**	Np_3P	14.5	**1b** (67)	**2b** (22)	**3d** (11)	(-)
6	 **1a**	 **2d**	Np_3P	7	**1a** (14)	**2d** (5)	**3e** (62)	**4a** (18)
7	 **1a**	 **2d**	Ph_3P	7	**1a** (5)	**2d** (4)	**3e** (86)	**4a** (3)
8	 **1c**	 **2d**	Np_3P	10	**1c** (52)	**2d** (21)	**3f** (23)	**4a** (1)
9	 **1a**	 **2e**	Np_3P	17.5	**1a** (18)	**2e** (5)	**3g** (77)	(-)
10	 **1d**	 **2f**	Np_3P	10	**1d** (4)	**2f** (2)	**3h** (94)	**4b** (1)
11	 **1e**	 **2e**	Np_3P	18	(-)	**2e** (36)	**3i** (52)	**4c** (12)
12	 **1f**	 **2b**	Np_3P	16	**1f** (52)	**2b** (32)	**3j** (16)	(-)
13	 **1f**	 **2d**	Ph_3P	6	**1f** (6)	**2d** (5)	**3k** (80)	**4a** (4)
14	 **1f**	 **2d**	Np_3P	10	**1f** (38)	**2d** (2)	**3k** (2)	**4a** (58)

(Continues)

TABLE 1 (Continued)

					The composition of the reaction mixture according to GC-MS data, (%)			
Entry	**Iodarene, ArI**	**Alkyne,** 	**Ligand**	***t*, hour**	1	2	3	4
15	 **1b**	 **2g**	Ph_3P	4	**1b** (12)	**2g** (22)	**3k** (53)	**4d** (10)
16	 **1b**	 **2g**	Np_3P	7	**1b** (1)	**2g** (6)	**3k** (3)	**4d** (85)
17	 **1b**	 **2f**	Np_3P	12	**1b** (40)	**2f** (50)	**3l** (2)	**4b** (8)
18	 **1f**	 **2f**	Np_3P	18.5	**1f** (59)	**2f** (17)	**3m** (4)	**4b** (20)
19	 **1f**	 **2g**	Np_3P	16	**1f** (19)	**2g** (4)	**3n** (6)	**4d** (70)
20	 **1f**	 **2g**	-[b]	26	**1f** (68)	**2g** (10)	**3n** (4)	**4d** (17)
21[c]	 **1g**	 **2e**	Np_3P	16	**1g** (4)	**2e** (11)	(-)	**4c** (80)
22	 **1f**	 **2e**	Np_3P	17.5	**1f** (47)	**2e** (31)	**3o** (11)	**4c** (11)

[a] Reaction conditions: Ligand (0.05 mmol), CuI (0.025 mmol), K_2CO_3 (0.75 mmol), DMF (4 mL), 120°C.

[b] Without ligand.

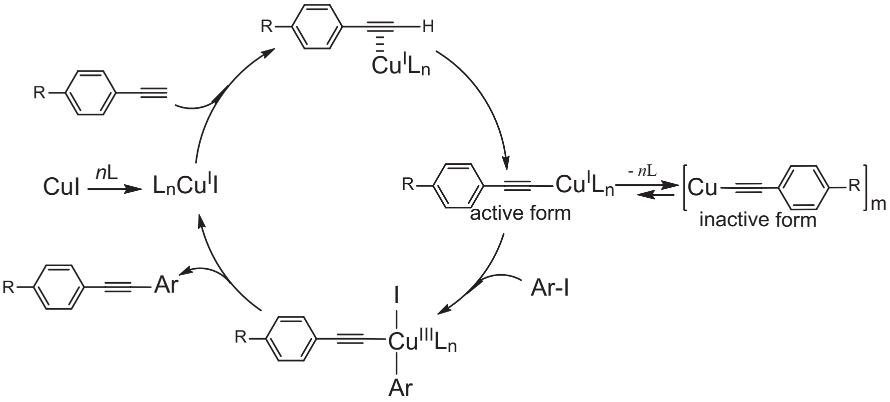
[c] As side-product phenol was obtained.

Cross-coupling of iodobenzenes (**1d**, **1e**), containing the NO_2 group in ortho- or meta-position, occurs in the case of para-iodonitrobenzene **1a** (entries 6, 7) affording Sonogashira products (entries 9-11). However, the presence of electron-donating (CH_3, ^{t}Bu) moieties in the phenylacetylene leads to significant increase of the reaction time (10 hours for Me, and ~18 hours for ^{t}Bu, entries 9-11).

Deactivated or unsubstituted both phenylacetylenes and iodoarenes give mainly buta-1,3-diynes (entries 14, 16, 19, 21). In runs 5, 8, 12, 17, 18, and 22, conversion of the starting reagents is incomplete.

The replacement of electron-withdrawing nitro group by the electron-donating (OCH_3) moiety in the aryl iodide insignificantly alters a ratio of the reaction products (system **A**, 6 hours, entry 13). A reaction mixture contains the starting iodide **1f** (6%), alkyne-1 **2d** (5%), tolane **3k** (80%), and buta-1,3-diyne **4d** (4%). The system **B** turns out to be more sensitive toward introduction of less reactive iodoarene **1f** into the reaction. Even if duration of the process increases up to 10 hours, the reaction mixture contains 38% of unreacted iodide **1f** and 2% of the terminal acetylene **2d** (entry 14). At the same time, the yield of the target product **3k** sharply drops (2%), and the content of buta-1,3-diynes **4a** augments to 58%. The presence of the electron-donating methoxy group in acetylene substrate leads to unexpected results of the cross-coupling. For example, when iodobenzene and 4-methoxyphenylacetylene reacts in the system **A** (4 hours), the products are formed at the following ratio: 12% of iodide **1b**, 22% of alkyne **2 g**, 53% of tolane **3k,** and 10% of 1,4-bis(4-methoxyphenyl)buta-1,3-diyne **4d** (entry 15). If Np_3P (system **B**, 7 hours) is employed in the reaction, the predominant formation of diyne **4d** (85%) is observed (entry 16). Similar results were also obtained in entries 19 and 21.

The presence of the electron-donating (MeO, ^{t}Bu, Me) groups in both reagents expectedly decreases activity of these compounds in the Sonogashira reaction (entries 18-22). Even after 18.5 hours (entry 18), the cross-coupling is incomplete: the reaction mixture contains the iodide **1f** (59%), alkyne-1 **2f** (17%), tolane **3m** (4%) and buta-1,3-diyne **4b** (20%) according to GC-MS data.



SCHEME 3 Mechanism of cross-coupling

The reaction of the same pair of source reagents (**1f-2g**) in the absence of ligand is significantly slower (entry 20). After 26 hours of heating, the main component of the reaction mixture is iodide **1f** (68%).

Thus, an efficient catalysis of palladium-free Sonogashira-type reaction for aryl iodides or terminal alkynes activated by electron-withdrawing groups (NO_2) using Np_3P/CuI pair has been implemented. In this case, the highest yields of disubstituted acetylenes (62%-94%) are consistent with the increased CH-acidity of these alkynes-1. The presence of electron-donating methoxy group both in halo- and in ethynyl derivatives decreases the yields of disubstituted alkynes (1.5%-6%) and leads to predominant formation of 1,4-disubstituted buta-1,3-diynes (58%-85%).

The mechanism of Sonogashira cross-coupling is a complex phenomenon even for its palladium-free Cu-catalyzed version. Beletskaya et al[7] have proposed a mechanism for the formation of the target internal alkynes involving Cu(III) complex.[24,29] It is assumed that the reaction involves formation of the intermediate copper acetylide, which may be in “active” and “inactive” forms (Scheme 3). We believe that in our case such a mechanism is also realized.

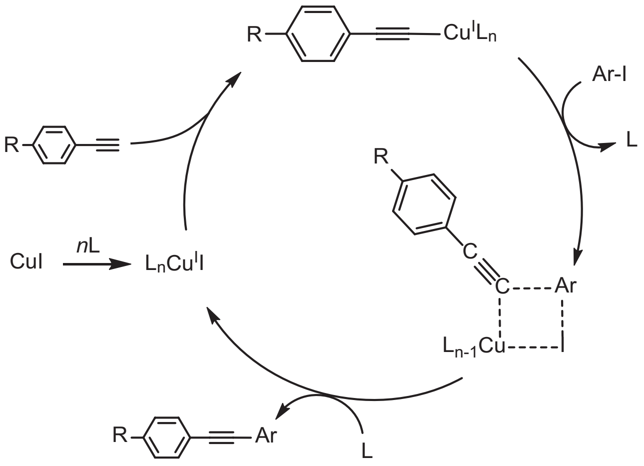
Since the Cu-catalyzed version of the Sonogashira reaction proceeds via the intermediate copper acetylides, we cannot exclude an alternative mechanism this reaction. The formation of disubstituted acetylenes can occur through a concerted mechanism with the participation of four-centered transition state (Scheme 4).[30]

The mechanism of 1,4-disubstituted-buta-1,3-diynes formation by copper-catalyzed Sonogashira reaction in the presence of tri(1-naphthyl)phosphine will be established elsewhere.

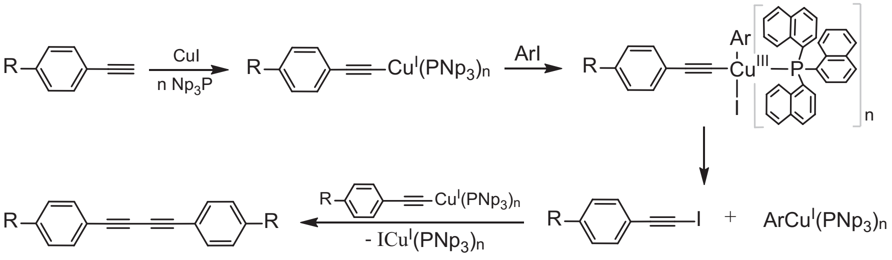
Predominant formation of buta-1,3-diynes, even in spite of the careful maintenance of an inert atmosphere, can be rationalized as follows. First, a complex Cu(III) is formed through the oxidative addition of iodoarene to copper acetylenide as described in (Schemes 3 and 5).[7] Further decomposition of this complex can occur via an alternative route, that is, reductive elimination of metal arene and iodoethynylarene likely due to the bulky ligand. The interaction of (iodoethynyl)arene with copper acetylides furnishes buta-1,3-diynes by Cadiot-Chodkiewicz type reaction (Scheme 5).

2.1 | X-ray crystallography of tri(1-naphthyl)phosphine

We have attempted to grow a crystal of Np_3P in hot DMSO. The X-ray study of the product reveals that a cocrystallization of Np_3P and its oxide takes place in the crystal in 3:1 ratio. Crystal structure of the compound is formed by one crystallographically independent molecule $Np_3PO_{0.24}$ (Figure 1) taking a special position in the unit cell: P and O atoms of the molecule are placed on a threefold axis. The crystal also contains a solvent molecule (DMSO, Figure 1). Naphthyl bicycles in $Np_3PO_{0.24}$ molecule are almost flat, the maximum deviation of atom out of the bicycle plane being 0.02 Å (C(10) atom). Dihedral angles between the bicycles planes are 108°. Phosphorus atom possesses the distorted tetrahedral coordination and deviates from the plane of the three bound carbon atoms by 0.77 Å in the direction of O(1) atom. Angles at the phosphorus atom differ from the tetrahedral angle 109.5°: O(1)-P-C(1) angles are 114.78(3)°, C(1)-P-C(1) angles are 103.68(4)°. P-C and P=O distances in the molecule are 1.832(1) and 1.379(6) Å, respectively. P-C bonds lengths correspond to the average value in similar Ph_3P, whereas P=O bond length is much less than the typical P=O length, 1.49(1) Å. This difference can be explained by a cocrystallization of three molecules—Np_3P and one Np_3PO, and the corresponding averaging the distances.



SCHEME 4 Alternative mechanism of cross-coupling



SCHEME 5 A plausible mechanism for the formation of buta-1,3-diynes

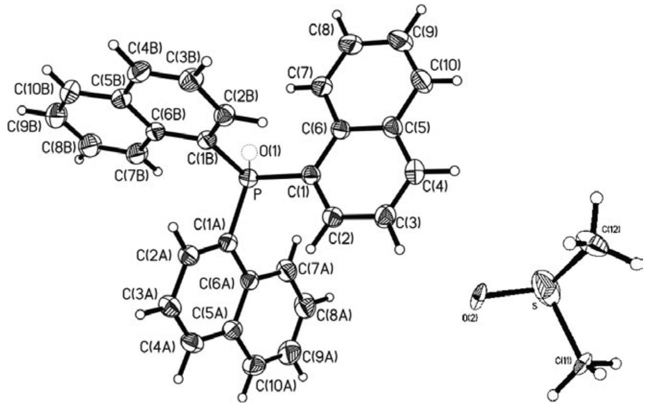


FIGURE 1 X-ray structure of tri(1-naphthyl)phosphine

3 | CONCLUSION

The study of new ligand, tri(1-naphthyl)phosphine, in palladium-free Sonogashira cross-coupling has revealed two peculiarities. In summary, the expedient procedures for the synthesis of arylacetylenes by the Sonogashira coupling of aryl iodides with terminal alkynes using Np_3P as ligand have been developed. Firstly, activity of Np_3P in the cross-coupling of aryl iodides and alkyne-1 containing electron-withdrawing groups is comparable with that of Ph_3P. Secondly, for the first time it is found that the reaction with substrates containing electron-donating substituents preferably affords buta-1,3-diynes. Such course of the reaction is unexpected for the palladium-free Cu(I)-catalyzed Sonogashira version. Tri(1-naphthyl)phosphine has been easily prepared in 34% yield from red phosphorus and 1-bromonaphthalene in the superbasic system t-BuONa/DMSO.

4 | EXPERIMENTAL

Analytical TLC was performed using Merck silica gel 60 F_{254} plates. GC-MS analyses were performed on a Hewlett-Packard instrument, which included a gas chromatograph HP 5890 series II and mass-selective detector HP 5971 (70 eV). Melting points were established using a Kofler micro hot stage. The CH microanalyses were performed on a Flash EA 1112 CHNS-O/MAS analyzer.

All reagents and solvents apart from acetylenes 2a, 2g are commercially available reactants. All the organic solvents were of analytical quality. All steps of the experiments were carried out in anhydrous inert atmosphere (argon).

1-Ethynyl-4-nitrobenzene **2a**,[31] 1-ethynyl-4-methoxybenzene **2g**[32] were synthesized as previously described. DMSO was dried over activated Al_2O_3 for 2-3 days, then distilled in vacuum over KOH and stored over molecular sieves (4Å). Instead of pure phosphine (PH_3), a phosphine-hydrogen mixture generated from red phosphorus ("KSAN SIA", Riga, UK) suspensions in toluene in argon atmosphere under the action of aq. KOH was used.[22] The phosphine stream was additionally dried by passing it through calcined $CaCl_2$ and KOH.

4.1 | Synthesis of tri(1-naphthyl)phosphine

A solution of *t*-BuONa (5.60 g, 58.3 mmol) and DMSO (70 mL) was blown through with argon and saturated with PH_3. To this suspension, a solution of 1-bromonaphthalene (8.00 g, 38.6 mmol) in DMSO (10 mL) was added dropwise for 2.5 hours at 60°C under stirring and continuous bubbling of the good phosphine stream. After 3 hours, the phosphine feeding was stopped, the mixture was blown through with argon to remove the dissolved PH_3, then new portion of *t*-BuONa (1.40 g, 14.5 mmol) and solution of 1-bromonaphthalene (2.01 g, 9.7 mmol) in DMSO (5 mL) was added. The reaction mixture was heated (70°C) and stirred for 2 hours, then MBr (M = Li, Na) was added to saturation and the mixture was allowed to cool overnight to room temperature. The precipitate of Np_3P with MBr was filtered off, washed with water many times to remove DMSO and MBr, and dried under vacuum to give 2.26 g (34%) of tri(1-naphthyl)phosphine, mp 265°C, lit.[19] 280°C. ^1H NMR (400.13 MHz, $CDCl_3$), $\delta = 8.55$ (dd, 1H, C^8-H, $^3J_{H\text{-}H} = 8.2$ Hz, $^4J_{P\text{-}H} = 4.5$ Hz), 7.91 (d, 1H, C^5-H, $^3J_{H\text{-}H} = 7.5$ Hz), 7.86 (d, 1H, C^4-H, $^3J_{H\text{-}H} = 8.3$ Hz), 7.52 (dd, 1H, C^6-H, $^3J_{H\text{-}H} = 7.7$ Hz, $^3J_{H\text{-}H} = 7.5$ Hz), 7.44 (dd, 1H, C^7-H, $^3J_{H\text{-}H} = 8.2$ Hz, $^3J_{H\text{-}H} = 7.5$ Hz), 7.25 (dd, 1H, C^3-H, $^3J_{H\text{-}H} = 8.3$ Hz, $^3J_{H\text{-}H} = 7.5$ Hz), 6.97 (dd, 1H, C^2-H, $^3J_{H\text{-}H} = 7.5$ Hz, $^3J_{H\text{-}P} = 5.9$ Hz). ^{13}C NMR (100.61 MHz, $CDCl_3$), $\delta = 135.7$ (d, C1, $^1J_{P\text{-}C} = 24$ Hz), 133.5 (d, C2, $^2J_{P\text{-}C} = 4.8$ Hz), 133.4 (C9), 132.8 (d, C10, $^3J_{P\text{-}C} = 11.2$ Hz), 129.6 (C4), 128.6 (C5), 126.6 (d, C8, $^3J_{P\text{-}C} = 4.9$ Hz), 126.6 (C7), 126.01 (C6), 125.8 (C3). $^{31}P\{^1H\}$ NMR (121.49 MHz, $CDCl_3$, r.t.): δ -32.43 ppm. FT-IR (KBr, cm^{-1}): 405 (w), 440 (m), 521 (m), 552 (w), 625 (w), 660 (m), 733 (m), 772 (vs), 795 (vs), 860 (w), 919 (w), 953 (w), 976 (w), 1018 (m), 1057 (w), 1138 (s), 1207 (s), 1254 (s), 1327 (s), 1377 (s), 1454 (m), 1497 (s), 1585 (w), 1620 (w), 1643 (w), 1708 (w), 1829 (w), 1890 (w), 1948 (w), 3005 (s), 3047 (s). Anal. Calcd. for $C_{30}H_{21}P$: C, 87.36; H, 5.13%. Found: C, 87.19; H, 5.08%.

4.2 | General procedure for cross-coupling of alkynes 2 with iodoarenes 1

4.2.1 | Method A and B

A mixture of alkyne **2** (0.5 mmol), 1-iodoarene **1** (0.5 mmol), CuI (4.75 mg, 0.025 mmol), K_2CO_3 (103.5 mg, 0.75 mmol), and Ph_3P or Np_3P (0.05 mmol) in DMF (4 mL) was stirred under an argon atmosphere at 120°C. The reaction mixture was cooled and diluted with EtOAc and washed with solution of NH_4Cl, and dried over Na_2SO_4. The solvents were evaporated under reduced pressure. After working-up the reaction mixture samples were analyzed by GC-MS.

4.2.2 | X-ray crystallographic data for $Np_3PO_{0.24}$·DMSO

$C_{32}H_{27}O_{1.24}PS$, $M = 494.38$, trigonal, space group $R\ \bar{3}$, $a = b = 12.774(2)$ Å, $c = 28.713(4)$, $\alpha = \beta = 90°$, $\gamma = 120°$, $V = 4057.5(11)$ Å^3, $Z = 6$, $d_{calc} = 1.21$ g/cm^3, $\mu = 0.202$ mm^{-1}, $(2\theta)_{max} = 54.94°$, a total number of reflections was 2191, the number of independent reflections was 2020, the number of refined parameters was 199, $R = 0.031$ for 1550 reflections with $F_0 > 4\sigma(F_0)$. X-ray diffraction study was carried out at room temperature using an *Enraf-Nonius CAD-4* diffractometer ($\omega/2\theta$-scanning, *Mo-K*α radiation, graphite monochromator). The crystal structure was solved by direct methods and subsequent Fourier synthesis using the SHELXS-97[33] software package. The structure was refined by full-matrix least-squares procedures using an anisotropic approximation for all non-H atoms with the SHELXL-97[33] program. Hydrogen atoms partly were found experimentally and partly fixed in ideal geometry positions. The O(1) atom population was found to be 0.24, what corresponds to the compound formula $C_{30}H_{21}PO_{0.24}$·C_2H_6SO. DMSO molecule was found to be statistically disordered over six (two independent) positions with populations equal to 0.17 (independent – 0.5). Atomic coordinates, bond lengths, bond angles, and thermal parameters of the compound have been deposited at the Cambridge Crystallographic Data Centre (CCDC). These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336 033; or deposit@ccdc.cam.ac.uk). Any request to the CCDC for data should quote the full literature citation and CCDC reference number 720574.

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