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Bis(pyrazolyl)methane Copper Complexes as Robust and Efficient Catalysts for Sonogashira Couplings

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A series of bis(pyrazolyl)methane copper complexes were found to catalyze a fast palladium-free Sonogashira coupling reaction of several iodoarenes with terminal alkynes such as phenylacetylene, propargyl benzyl ether, and (*tert*-butyldimethyl)silylacetylene. These reactions proceed with $CuCl_2 \cdot 2H_2O$ (10 mol-%) under aerobic conditions and the corresponding chelate ligand (10 mol-%), with its tailored facial coordination mode, is crucial for the success of the reaction. The coupling can also be carried out in water with liquid aryl halides and a phase-transfer catalyst.

Introduction

The Sonogashira reaction[1] has been known since 1975 and allows the coupling of terminal alkynes with alkenyl and aryl halides. The major drawbacks of the Sonogashira reaction are the toxicity, the high cost of palladium salts, and the requirement for inert gas conditions. Owing to the importance of this coupling for the preparation of biologically[2] and synthetically[3] relevant acetylenes, there have been numerous efforts to develop new synthetic protocols for palladium-free Sonogashira cross-couplings. Nickel,[4] cobalt,[5] and copper[6] have been successfully used to perform Sonogashira cross-couplings. Among these, copper-catalyzed couplings have attracted most attention.[6] Some synthetic protocols have been published with the focus on microwave-assisted reactions[7] or on the use of copper nanoparticles[8] as catalysts.[6n] Hwang et al. reported a room temperature blue light (LED) induced coupling of aryl iodides and aryl acetylenes. The copper acetylide is suggested to undergo ligand to metal charge transfer (LMCT), which facilitates nucleophilic attack of electron-rich phenyl halides. The addition of AgOTf (2 mol-%) improves the coupling of aryl bromides.[6l]

For all other homogeneous systems, the addition of a ligand to copper(I) or copper(II) salts is mandatory to enable the coupling. Most of those ligands are commercially available and contain nitrogen, phosphorus, or oxygen donors such as DMEDA,[6o] 1,3-diphenylpropane-1,3-dione,[6e] 1,4-diazabicyclo[2.2.2]octane (DABCO),[6a] Xantphos[6q] or salicylic acid.[6g] The most efficient bases are K_2CO_3, Cs_2CO_3, NaOH, or KOH and it is noticeable that for all thermal protocols, elevated temperatures (80–145 °C) are required. Typical solvents are *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), *N*-methyl-2-pyrrolidinone (NMP), and toluene, which allow high reaction temperatures. A remarkable protocol for the coupling of aryl bromides and chlorides with phenyl acetylenes has been reported by Bhargava et al. using bis(μ-iodo)bis-[(–)-sparteine]dicopper(I) as catalyst.[6r]

Another procedure for carrying out the Sonogashira reaction in water at 100 °C has been developed by Zhou et al.[6i] With the utilization of a water-soluble bisulfonated salen copper(II) catalyst under aerobic conditions, various iodoarenes where coupled with phenylacetylene to afford cross-coupled acetylenes and indoles. To our knowledge, besides Zhou et al.,[6i] only one other report on aerobic Sonogashira cross-coupling has been published.[6d] Li et al. used the catalytic system of copper(II) acetate/1,4-diphenyl-1,4-diazabuta-1,3-diene with three equivalents of tetrabutylammonium fluoride (TBAF) as base for the coupling of iodoarenes with phenylacetylene.[6d]

Results and Discussion

Herein, we report a copper-catalyzed Sonogashira reaction of various iodoarenes with acetylenes under aerobic

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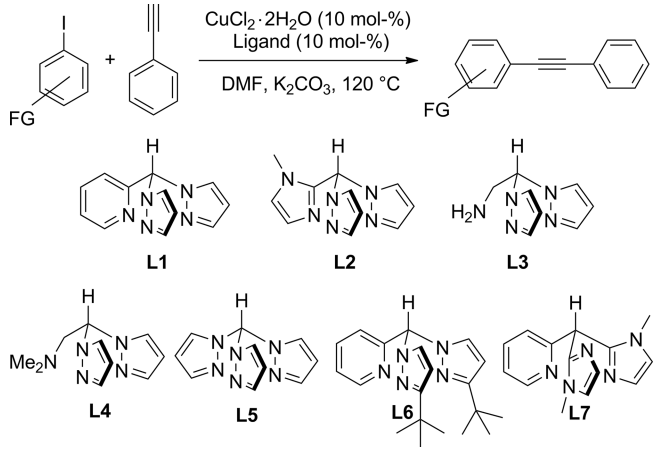
conditions. The reaction is carried out in DMF as solvent and with K_2CO_3 as base. Given that the stabilizing N-donor ligand is crucial for the catalysis, we chose strong facial bis(pyrazolyl)methane ligands for the stabilization of copper complexes. These hetero-scorpionate ligands can be easily electronically and sterically modified and therefore are ideal compounds for ligand design.[9] Similar members of this ligand class, namely (pyridin-2-yl)bis(*tert*-butylpyrazol-1-yl)methane and (1-methylimidazol-2-yl)bis(*tert*-butylpyrazol-1-yl)methane have been utilized in the copper(I)-mediated oxygen activation and catalytic transfer.[10] The unsubstituted ligands are known to form bis- and monofacial complexes with copper(II) salts.[11]

During our investigations, we have used various Cu^{II}/ligand systems (Table 1, ligand **L1**–**7**) to perform the cross-coupling of iodoarenes. Hereby, we have varied the third donor function and the steric encumbrance. Ligands **L1**,[12] **L2**,[12,15] **L3**,[16] **L5**,[17] **L6**,[12] and **L7**[17] are known. Ligands **L1**, **L2**, and **L3** turned out to be the most effective ligands, and these have been tested on two substrates (ethyl 3-iodobenzoate and 4-iodobenzotrifluoride) (Table 1, entries 1–3 and 8–10), giving short reaction times and similar yields. Ligands **L4**–**7** are found to be less efficient in these Sonogashira cross-couplings. This study shows the importance of two factors: firstly, the steric encumbrance of the donor entity should be as small as possible. This can be seen in the catalysis (Table 1, entries 1 and 6) of 3-*tert*-butyl-substituted ligand **L6** compared with that of the nonsubstituted pyrazoles (ligand **L1**). Comparison of the activity of ligands **L3** and **L4**, in which the amine hydrogen atoms are replaced by methyl groups, shows the same behavior (Table 1, entries 3 and 4). Secondly, the donor properties of the non-pyrazolyl donor are essential. Switching the pyridyl substituent with an imidazolyl group led to the fastest coupling (Table 1, entries 1–2 and 8–9), which may be a result of the increased donor strength of the imidazole nitrogen. Nevertheless, the substitution of two pyrazoles with imidazoles does not benefit the catalysis (Table 1, entries 1 and 7).

For the following reactions (1-methylimidazol-2-yl)-bis(pyrazol-1-yl)methane (**L2**)[12] and $CuCl_2{\cdot}2H_2O$ were used. We found that it was not necessary to work under an inert atmosphere. The conversion of the iodoarene proceeds fast and smoothly. Indeed the reaction is one of the fastest reported palladium-free copper-catalyzed Sonogashira reactions, allowing the coupling of iodoarenes with acetylenes in very short reaction times (1.0–2.0 h) at 120 °C. Various iodoarenes bearing electron-withdrawing or electron-donating groups have been used (Table 2, entries 1–12). It is possible to couple a range of acetylenes such as phenylacetylene, propargyl benzyl ether, and (*tert*-butyldimethyl)silylacetylene.

Under the aerobic conditions, the homo-coupling of the acetylene[13,14] was found to be a controllable side-reaction. However, to avoid a reduction in yield, it was necessary to add 1.5 equiv. of the alkyne. Under these conditions, full conversion was rapidly reached and only small amounts of homocoupled acetylenic byproducts were obtained (diacetylenes). When the substrates were changed from iodoarenes to bromoarenes, a large amount of homocoupling was observed. Only 4-nitrobromobenzene gave 50% yield under an air atmosphere within 3 h. When the reaction was performed under an inert gas atmosphere, the conversion stopped at 48% after 24 h, probably due to deactivation of the catalyst.

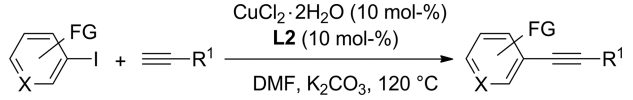
Table 1. Efficiency of bis(pyrazolyl)methane ligands in the cross-coupling of phenylacetylene and 4-iodobenzotrifluoride.



Entry[a]	FG[b]	Ligand	Time [h]	Yield [%][c]
1	4-CF_3	**L1**	1.5	79
2	4-CF_3	**L2**	1.0	77
3	4-CF_3	**L3**	1.0	74
4	4-CF_3	**L4**	2.5	77
5	4-CF_3	**L5**	2.5	8
6	4-CF_3	**L6**	2.0	trace
7	4-CF_3	**L7**	2.5	39
8	3-CO_2Et	**L1**	2.5	70
9	3-CO_2Et	**L2**	1.0	71
10	3-CO_2Et	**L3**	1.5	70

[a] See standard procedure for the preparation. [b] FG: functional group. [c] Isolated yield.

Table 2. Coupling reactions of iodoarenes and acetylenes.



Entry[a]	FG[b]	R^1	Time [h]	Yield [%][c]
1[d]	3-CO_2Et	Ph	1.5	70
2[d]	4-CF_3	Ph	1.0	74
3[d]	4-OMe	Ph	1.0	87
4[e]	–	Ph	2.0	84
5[d]	3-CO_2Et	CH_2OBn	1.0	74
6[d]	4-OMe	CH_2OBn	1.0	68
7[d]	4-CF_3	CH_2OBn	1.0	75
8[e]	–	CH_2OBn	2.0	66
9[d]	3-CO_2Et	Si(*t*Bu)$(Me)_2$	1.0	74
10[d]	4-OMe	Si(*t*Bu)$(Me)_2$	1.0	62
11[d]	4-CF_3	Si(*t*Bu)$(Me)_2$	1.0	62
12[e]	–	Si(*t*Bu)$(Me)_2$	1.0	61

[a] See standard procedure for the preparation. [b] FG: functional group. [c] Isolated yield. [d] X = C. [e] X = N.

It is remarkable that the use of copper(I) halides did not give any cross-coupling product under an inert gas atmosphere. However, performing the reaction under aerobic conditions led to full conversion of the electrophile, affording the cross-coupling product. Using copper(II) chloride under an inert gas atmosphere indeed enabled the cross-coupling reaction, albeit at slightly reduced rate and with lower conversion. We observe that initially the green DMF solution of the catalyst $CuCl_2 \cdot 2H_2O$/**L2** turns orange after the addition of K_2CO_3 and phenylacetylene. This is due to an oxidative homocoupling,[13,14] which consequently gives copper(I) and a diphenyldiacetylene. EPR spectroscopic analysis verified the absence of copper(II) (EPR silence) after the addition of K_2CO_3 and phenylacetylene.

We interpret this data as follows: bis(pyrazolyl)methane ligands with unsubstituted heteroarenes are known to form easily both bisfacial and monofacial complexes with copper(II) halides.[11] Thus, adding ligands **L1**–**5** to the copper(II) halides may lead to a catalytically inactive bisfacial complex. We provide two molecular structures of bis(pyrazolyl)methane catalysts obtained from single-crystal X-ray diffraction, which show monofacial ligand-coordination behavior (Figure 1). The reductive reaction medium for the copper(II) complex may lead to an activated monofacial copper(I) chloride complex. We assume that this copper(I) complex is not a simple complex of type [Cu^{I}**L**Cl], because the independently prepared copper(I) complex does not show any activity. Moreover, we propose that this activated species is an intermediate [Cu^{I}**L**(DMF)] complex, which is formed during the first homocoupling step and possesses superior reactivity.

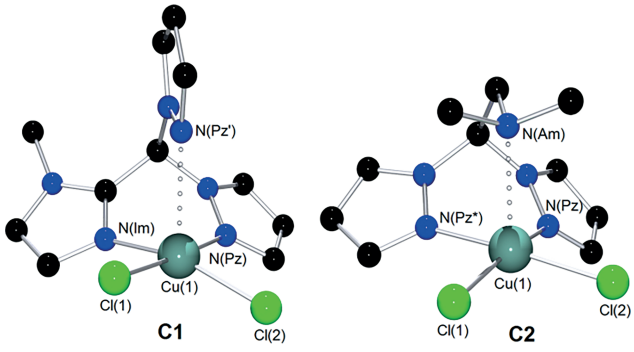


Figure 1. Molecular structures of [Cu(**L2**)Cl_2] (**C1**) and [Cu(**L4**)Cl_2] (**C2**).

Selected bond lengths and angles of [Cu(**L2**)Cl_2] (**C1**) and [Cu(**L4**)Cl_2] (**C2**) are given in Table 3, with crystallographic details presented in Table 4. Another complex, [Cu(**L1**)Cl_2]·MeOH (**C3**), has been reported previously.[11] These three complexes have the bispyrazolyl moiety in common and can be compared regarding the third donor. All complexes **C1**–**3** adopt pyramidal square-planar geometries (τ_5 = 0.05–0.24).[11] Exclusively in **C1**, the non-pyrazolyl donor (imidazolyl) lies in the square-planar plane. Concerning the smallest equatorial N–Cu bond length, **C1** possesses a shorter bond [Cu(1)–N(Im) 2.002(3) Å] compared with **C3** [Cu(1)–N(Pz) 2.032(2) Å] and an equal bond length by comparison to **C2** [Cu(1)–N(Pz) 2.006(2) Å], which indicates that imidazolyl and pyrazolyl donors are stronger donating than the pyridinyl or amine groups. Additionally, the axial N–Cu bond varies from 2.500(3) (**C1**), 2.387(2) (**C2**), to 2.243(2) Å (**C3**) and plays an auxiliary role in the stabilization of the copper(II) complex, which is crucial for efficient catalysis.

Table 3. Selected bond length [Å] and angles [°] of **C1** and **C2**.

	C1	**C2**
Cu(1)–N(Im/Pz*)	2.002(3)	2.006(2)
Cu(1)–N(Pz)	2.021(4)	2.036(2)
Cu(1)–N(Pz′/Am)	2.500(3)	2.387(2)
Cu(1)–Cl(1,2)	2.260(1), 2.254 (1)	2.263(1), 2.263(1)
N(Im/Pz*)–Cu(1)–Cl(1)	90.7 (1)	90.2(1)
N(Pz)–Cu(1)–Cl(1)	176.3 (1)	173.3(1)
N(Pz′/Am)–Cu(1)–Cl(1)	98.0(1)	102.6(1)
N(Im/Pz*)–Cu(1)–Cl(2)	161.9(1)	166.6(1)
N(Pz)–Cu(1)–Cl(2)	90.3(1)	90.4(1)
N(Pz′/Am)–Cu(1)–Cl(2)	113.5(1)	103.9(1)
N(Im/Pz*)–Cu(1)–N(Pz)	85.9(1)	85.0(1)
N(Pz′/Am)–Cu(1)–N(Pz)	80.4(1)	82.1(1)
N(Pz′/Am)–Cu(1)–N(Im/Pz*)	83.3(1)	88.0(1)
Cl(1)–Cu(1)–Cl(2)	93.3(1)	93.2(1)
τ_5[a]	0.24	0.11

[a] $\tau_5 = \frac{\alpha - \beta}{60°}$.[18]

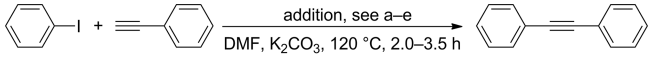
Table 4. Crystallographic data and parameters of **C1** and **C2**.

	C1	**C2**
Empirical formula	$C_{11}H_{12}Cl_2CuN_6$	$C_{10}H_{15}Cl_2CuN_5$
Formula mass [g mol^{-1}]	362.71	339.71
Crystal size [mm]	0.16 × 0.05 × 0.03	0.12 × 0.10 × 0.08
T [K]	100	100
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/n$
a [Å]	9.3266(4)	9.8783(4)
b [Å]	14.1665(6)	13.4853(5)
c [Å]	10.8849(5)	9.9701(4)
α [°]	90	90
β [°]	97.8080(10)	92.4780(10)
γ [°]	90	90
V [Å^3]	1424.84(11)	1326.89(9)
Z	4	4
$\rho_{calcd.}$ [g cm^{-3}]	1.691	1.701
μ [mm^{-1}]	1.906	2.037
λ [Å]	0.71073	0.71073
F(000)	732	692
hkl range	±11, ±17, ±13	±12, ±16, ±12
Reflections collected	24194	22422
Independent reflections	2914	2708
$R_{int.}$	0.0564	0.0279
Reflections observed	2914	2708
Number of parameters	158	165
R_1 [$I \geq 2\sigma[I]$]	0.0467	0.0260
wR_2 (all data)	0.1142	0.0602
Goodness-of-fit	1.072	1.122
Largest diff. peak, hole [e Å^{-3}]	1.770, –0.908	0.335, –0.273

A comparative study between the imidazolyl and pyrazolyl nitrogen donors in copper(II)-bis(*tert*-butylpyrazol-1-yl)methanes has been performed by Herres-Pawlis et al.[10b] They reasoned from NBO charges and charge-transfer energies that the imidazolyl nitrogen lone-pair displays

a slightly larger donor ability. As a result, a tremendous increase in the catalytic oxygen transfer rate for the hydroxylation of phenols occurs, which could be deduced from the increased donor strength of the imidazolyl nitrogen.

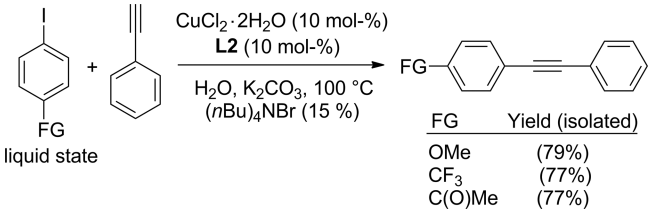
To verify the necessity of the ligand/$CuCl_2{\cdot}2H_2O$ combination for the catalysis, control experiments were carried out (Scheme 1, reactions a and b), indicating both ligand and the degree of copper(II) oxidation to be pivotal for the catalysis. Furthermore, the use of only the heterocyclic fragments, 1-methylpyrazole and pyridine, instead of the tridentate ligand **L1**, resulted in no cross-coupling product (Scheme 1, reaction c). Thus, the facial coordination of ligand **L1** is crucial for the success of the cross-coupling. To establish the role of the copper complex with respect to the catalyst activity, a reaction with $CuCl_2{\cdot}2H_2O$/**L1** and $Cu(NO_3)_2{\cdot}2.5H_2O$/**L1** (Scheme 1, reaction d and e) was performed. No difference of activity could be identified, indicating that the halide substituent does not play an important role in the catalysis.



a: $CuCl_2 \cdot 2H_2O$ (10 mol-%), no ligand	yield (GC):	0%
b: no $CuCl_2 \cdot 2H_2O$, ligand **L1** (10 mol-%)		0%
c: $CuCl_2 \cdot 2H_2O$ (10 mol-%), 1-MePz (6.7 mol-%), Py (3.3 mol-%)		0%
d: $CuCl_2 \cdot 2H_2O$ (10 mol-%), ligand **L1** (10 mol-%)		76%
e: $Cu(NO_3)_2 \cdot 2.5H_2O$ (10 mol-%), ligand **L1** (10 mol-%)		76%

Scheme 1. Systematic variation of the catalyst composition.

For liquid (or solubilized under the reaction conditions) aryl halides, it is possible to conduct the coupling in water under an air atmosphere (Scheme 2). The addition of a phase-transfer agent such as $(n\text{Bu})_4\text{NBr}$ is mandatory. In this biphasic mixture, we assume the reaction to occur in the organic substrate phase. The use of solid substrates does not lead to any cross-coupling product. Besides the system of Zhou et al.[6i] also Guan et al.,[6p] Wan et al.[7b] and Hu et al.[6k] reported copper-catalyzed Sonogashira reactions in water. Except for the group of Guan et al.,[6p] every system required a phase-transfer catalyst. They used a simple CuI/PPh_3 catalyst under N_2 with KOH as base in water. Wan et al.[7b] reported a similar system but with K_2CO_3 as base, microwave radiation, and TBAB as additive. Hu et al.[6k] used phenanthroline/CuI and TBAB at 120 °C under N_2 for the cross-coupling in water. We present the only system beside Zhou et al.,[6i] which provides cross-coupling under aerobic conditions *and* in water.



Scheme 2. Coupling of liquid iodoarenes with phenylacetylene in water.

Palladium is known to catalyze Sonogashira couplings at the ppm level.[19] Thus, it is important to check for trace impurities in copper salts or alkali carbonates. Based on the highly selective complexation[20] of palladium with the ligand *N′*-benzoyl-*N*,*N*-di-*n*-hexylthiourea (BDHT),[21] a dry sample of a typical reaction mixture (1 mmol haloarene) was examined for traces of palladium (see the Supporting Information for the calculation and procedure). Palladium separation and enrichment was performed by cloud point extraction followed by electrothermal atomic absorption spectrometry (ET-AAS). Traces of palladium (0.912 ± 0.244 ppm; μmol Pd/mol haloarene) have been found in the dry mass of a typical reaction mixture (error is in the standard derivation of three independent measurements, $N = 3$). This small amount of palladium is not critical for the reported series of reactions, considering that no coupling takes place in the absence of ligand (Scheme 1, reaction a).

Conclusions

We have shown that bis(pyrazolyl)methane copper(II) complexes are valuable new catalysts in the palladium-free copper-catalyzed and aerobic Sonogashira reaction. A large array of iodoarenes and terminal alkynes can be converted into the desired cross-coupling products under air. Most remarkable is the excellent reaction rate, resulting from the use of the bis(pyrazolyl)methane copper catalysts. The possibility to perform the coupling in aqueous media with liquid substrates offers a viable alternative to the use of solvent DMF. Further investigations will focus on the activation of bromo- and chloroarenes and on mechanistic studies.

Experimental Section

General Methods: Some manipulations were carried out under nitrogen atmosphere. Nitrogen was dried by passage through P_2O_5. NMR spectra were recorded with a JEOL EX-400-NMR spectrometer or a Varian NMR-system 300 MHz. ^{1}H and ^{13}C NMR spectra data are given relative to deuterated solvent ($CDCl_3$, 25 °C) as an internal standard. Mass spectra data were measured with a Thermo Finnigan MAT 95 and a Jeol MStation Sektorfeld spectrometer. IR spectra were recorded with a Perkin–Elmer Spectrum BX II FTIR Spectrometer with ATR technique. EPR measurements were performed with a Magnettech MiniScope MS400 in DMF samples at 10 mM. Gas chromatographic measurements were obtained with a Hewlett-Packard 7890A Series (HP 5 capillary column; 5% phenylmethylpolysiloxane, length: 15 m, diameter: 0.25 mm, film thickness: 0.25 μm, flame ionization detector). Melting points were measured with a Büchi B-540 apparatus and are uncorrected. All chemicals were purchased from ABCR, Bayer, Riedel-de Haën, Sigma–Aldrich or TCI. Benzyl propargyl ether[22] and 1-methylpyrazole[23] have been synthesized according to reported procedures. The solvents used were dried by standard procedures.[24]

Determination of relative response factors for the gas chromatographic analysis:

The relative response factors (f_P)[25] were calculated as

$$f_P = \frac{Ap{\cdot}[IS]}{A_{IS}{\cdot}[P]}$$

allowing the concentration of the product to be calculated as

$$[P] = \frac{Ap \cdot [IS]}{A_{IS} \cdot f_P}$$

where A_P is the area of the product signal, A_{IS} is the area of the internal standard signal, [*IS*] is the concentration of the internal standard, and [*P*] is the concentration of the product.

For a typical procedure, three mixtures of the product and the internal standard were analyzed by GC to give area ratios. Each mixture was run three times. The value for the response factors was obtained as average over all runs. For the product 4-trifluoromethyl-1-(2-phenylethynyl)benzene, a response factor of 2.08 was estimated.

For some samples, the GC-conversion of the electrophile is given. These were obtained by comparison with an internal standard by using the area ratios of the electrophile and the internal standard at the start of the reaction (t = 0 s) and at a given time.

Standard Procedure: A tube was charged with $CuCl_2 \cdot 2H_2O$ (17.1 mg, 0.1 mmol, 0.1 equiv.) and the ligand (0.1 mmol, 0.1 equiv.) under an air atmosphere and sealed with a rubber septum. DMF (2 mL) was then added and the resulting suspension was stirred for 15 min at room temperature. K_2CO_3 (0.40 g, 2.0 mmol, 2.0 equiv.), the haloarene (1.0 mmol, 1.0 equiv.), and 1,3-dimethoxybenzene (100 μL, internal standard) were added and the reaction mixture was heated to 120 °C. After stirring for 3 min at 120 °C, the acetylene (1.5 mmol, 1.5 equiv.) was added. Complete conversion of the haloarene was indicated by GC analysis. The reaction mixture was cooled to room temperature and filtered. NH_3 solution (aq., 25%, 15 mL) was added and the mixture was extracted with ethyl acetate (3 × 10 mL). Evaporation of the solvent gave the crude product, which was purified by column chromatography (SiO_2).

For coupling with water as solvent, $(n\text{Bu})_4\text{NBr}$ (48.4 mg, 0.15 mmol, 0.15 equiv.) was added in the same step as the catalyst and DMF was replaced with water.

Crystallographic Data and Parameters of C1 and C2: The crystal data for **C1** and **C2** are presented in Table 4. The data was collected with a D8 Venture diffractometer with graphite monochromated Mo-K_α radiation (λ = 0.71073 Å). Data reduction and absorption correction was performed with SAINT and SADABS.[26] The structure was solved by direct and conventional Fourier methods and all non-hydrogen atoms were refined anisotropically with full-matrix least-squares based on F^2 (XPREP,[27] SHELXS[28] and ShelXle[29]). Hydrogen atoms were derived from difference Fourier maps and placed at idealized positions, riding on their parent C atoms, with isotropic displacement parameters $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}$(C methyl). All methyl groups were allowed to rotate but not to tip.

Full crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary no. CCDC-1045301 (for **C1**) and -1045302 (for **C2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Determination of Palladium Content

Chemicals and Instrumentation: All purchased chemicals were of analytical grade or better. Moreover, all solvents and chemicals were tested for Pd contamination by control blank measurements with ET-AAS. Ethanol, 36 wt.-% hydrochloric acid, 30 wt.-% hydrogen peroxide, and 65 wt.-% nitric acid were purchased from Merck (Darmstadt, Germany). TritonX-114 was purchased from AppliChem (Darmstadt, Germany). Palladium stock solution [$Pd(NO_3)_2$ in 0.5 M HNO_3, 1000 mg L^{-1}, Merck] was used for palladium serial dilution for AAS calibration. Ultrapure water (UPW) was provided by a DirectQ 3 Ultrapure Water System (Millipore, Billerica, MA, USA), the conductivity was always above 17.5 MΩ cm^{-1}. *N*′-Benzoyl-*N*,*N*-di-*n*-hexylthiourea (BDHT) was synthesized according to a reported procedure[30] and recrystallized from ethanol.

A Perkin–Elmer 4100 ZL atomic absorption spectrometer equipped with Zeeman-effect background correction, a transversally heated graphite atomizer (THGA), and an AS-70 furnace autosampler was used for ET-AAS measurement. High purity argon (99.996%) served as inert gas for THGA operation. A Photron hollow-cathode lamp (Photron, Victoria, Australia) was employed as primary source, the wavelength was set at 247.6 nm; the lamp current to 30 mA; the slit width (low) to 0.7 nm. The time-temperature program for graphite furnace operation is given in Table 5.

Table 5. THGA time-temperature program.

Temp. [°C]	Ramp [s]	Hold [s]	Argon flow [mL min^{-1}]	Step
80	1	15	250	drying 1
130	15	15	250	drying 2
1650	30	30	250	pyrolysis
2380	0	5	0	measurement
2600	1	6	250	clean out

Sample Preparation and Calibration Procedure: A constant-weight dried sample of the catalytic mixture was homogenized by using a mortar and three aliquots of 500 mg were taken. These aliquots were digested in a mixture of nitric acid (65 wt.-%, 2 mL), hydrochloric acid (36 wt.-%, 3 mL) and hydrogen peroxide (30 wt.-%, 1 mL) for 24 h at 60 °C. After 10 h additional hydrogen peroxide (30 wt.-%, 1 mL) was added. The digestion solution was then filtered through a syringe filter (polystyrene, 0.45 μm). The filter was rinsed with UPW, and the rinsing solution was added to the filtrate, which was then filled up with UPW to a weight of 40.00 g. Calibration was performed by means of the standard addition method. For selective Pd enrichment, the sample and calibration solutions were treated with 500 μL 10 wt.-% TritonX-114 (in UPW) and 100 μL of a solution containing BDHT (1.0 g L^{-1}) dissolved in methanol as highly selective complexing agent.[20] The solutions were homogenized by a vortex mixer and incubated for 2 h at 62 °C in a water bath. Phase separation was accelerated by centrifugation at 3210 rcf for 20 min and the phase separated solution was then cooled in ice water for 2 to 3 min to increase the viscosity of the surfactant-rich phase. The aqueous supernatant was then removed by decanting. The remaining surfactant droplet, containing Pd as $Pd(BDHT)_2$ complex was dissolved in a mixture of ethanol (100 μL) and HCl (36 wt.-%, 100 μL) and then forwarded to ET-AAS measurement. The correlation coefficient (R^2) of the calibration was 0.9987 and the limit of detection, calculated from the confidence interval of the linear regression,[31] was 0.5 ng Pd g^{-1}. The arithmetic mean of the Pd content of the measured samples was 0.164 μg g^{-1} and the standard derivation was ± 0.044 μg g^{-1} (N = 3).

The palladium content of a typical reaction mixture (1 mmol haloarene) for phenylacetylene and iodobenzene with the catalyst **L1**/$CuCl_2 \cdot 2H_2O$ for a full conversion was determined as follows:

The dry mass of such a mixture contains diphenylacetylene (0.178 g, 1.00 mmol), K_2CO_3 (0.207 g, 1.50 mmol), KI (0.166 g,

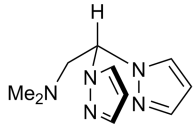
1.00 mmol), $CuCl_2$ (13.4 mg, 0.10 mmol), and **L1** (22.5 mg, 0.10 mmol) resulting in a dry mass of 0.59 g ($KHCO_3$ decomposes to K_2CO_3 during the drying procedure).

The palladium content of the measured samples was 0.164 ± 0.044 µg g^{-1}, thus resulting in $91.2 \pm 24.4 \times 10^{-11}$ mol palladium for a reaction mixture of 1 mmol iodobenzene. Division by the amount of iodobenzene gives 0.912 ± 0.244 ppm (µmol Pd/mol iodobenzene) palladium.

Synthesis of Ligands and Complexes

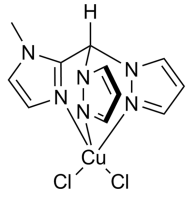
Synthesis of Ligands L1–L7: Ligands **L1**,[12] **L2**,[12,15] **L3**,[16] **L5**,[17] **L6**,[12] and **L7**[17] were synthesized according to reported procedures.

Synthesis of N,N′-Dimethyl-2,2-dipyrazol-1-yl-ethanamine (L4)



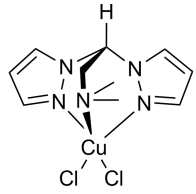
2,2-Dipyrazol-1-yl-ethanamine (1.51 g, 8.34 mmol, 1.0 equiv.) was dissolved in formalin (37%, 8 mL, 0.26 mol, 30 equiv.) and formic acid (99%, 1 mL, 26.5 mmol, 3.2 equiv.). The solution was heated to reflux for 24 h and cooled to room temperature. The volatiles where removed under high vacuum and the residue was taken up in water (10 mL). The reaction mixture was brought to pH 9 with K_2CO_3 and extracted with CH_2Cl_2 (3 × 10 mL). Subsequent washing with brine (2 × 10 mL), drying over Na_2SO_4, and evaporation of the solvent afforded the product (1.78 g, 8.53 mmol, 98%) as a slightly yellow solid. ^{1}H NMR (400 MHz): δ = 7.65 [d, $^3J_{H,H}$ = 2.4 Hz, 2 H, 5-H_{Pz}], 7.54 ppm [d, $^3J_{H,H}$ = 1.7 Hz, 2 H, 3-H_{pz}], 6.51 [t, $^3J_{H,H}$ = 7.2 Hz, CH], 6.27 [d, $^3J_{H,H}$ = 2.4 Hz, 2 H, 4-H_{Pz}], 3.43 [d, $^3J_{H,H}$ = 7.2 Hz, 2 H, CH_2], 2.28 (s, 6 H, CH_3) ppm. ^{13}C NMR (101 MHz): δ = 140.3 (2 C; 3-C_{Pz}), 128.9 (2 C; 5-C_{Pz}), 106.7 (2 C; 4-C_{Pz}), 73.9 (1 C; CH), 61.2 (1 C; CH_2), 45.8 (2 C; CH_3) ppm. IR (ATIR, neat): $\tilde{\nu}$ = 3113 (w), 2950 (w), 2869 (vw), 2830 (w), 2774 (w), 1731 (vw), 1513 (w), 1464 (w), 1437 (w), 1391 (m), 1344 (w), 1325 (m), 1293 (m), 1249 (w), 1204 (m), 1151 (w), 1090 (m), 1050 (m), 1034 (vs), 967 (w), 916 (w), 867 (m), 796 (s), 761 (v), 721 (m) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 204 (5) [M – H]$^+$, 147 (34) [$C_7H_7N_7$]$^+$. HRMS (70 eV, EI): *m*/*z* calcd. for $C_{10}H_{14}N_5$ [M – H] 204.1248; found 204.1237.

Synthesis of [$CuCl_2${HC(Pz)$_2$(MeIm)}] (C1)



$CuCl_2 \cdot 2H_2O$ (85 mg, 0.5 mmol, 1.0 equiv.) was dissolved in MeOH (5 mL) and added to a solution of {HC(Pz)$_2$(MeIm)} (**L2**) (114 mg, 0.5 mmol, 1.0 equiv.) in CH_2Cl_2 (6 mL). After 2 h, blue plates, crystals suitable for X-ray diffraction were obtained (0.11 g, 0.3 mmol, 62%). IR (ATIR, neat): $\tilde{\nu}$ = 3113 (w), 2950 (w), 2869 (vw), 2830 (w), 2774 (w), 1731 (vw), 1513 (w), 1464 (w), 1437 (w), 1391 (m), 1344 (w), 1325 (m), 1293 (m), 1249 (w), 1204 (m), 1151 (w), 1090 (m), 1050 (m), 1034 (vs), 967 (w), 916 (w), 867 (m), 796 (s), 761 (v), 721 (m) cm^{-1}. MS (FAB+): *m*/*z* (%) = 330 (11) [$C_{11}H_{12}{}^{37}Cl^{65}CuN_6$]$^+$, 328 (61) [$C_{11}H_{12}{}^{37}Cl^{63}CuN_6$, $C_{11}H_{12}{}^{35}Cl^{65}CuN_6$]$^+$, 326 (72) [$C_{11}H_{12}{}^{35}Cl^{63}CuN_6$]$^+$, 291 (100) [$C_{11}H_{12}{}^{63}CuN_6$]$^+$; elemental analysis calcd. (%) for $C_{11}H_{12}Cl_2CuN_6$: C 36.43, N 23.17, H 3.33; found C 36.34, N 23.17, H 3.33.

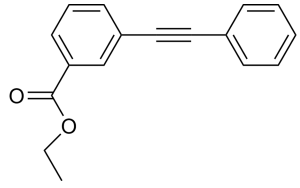
Synthesis of [$CuCl_2${HC(Pz)$_2$(CH$_2$N(Me)$_2$)}] (C2)



$CuCl_2 \cdot 2H_2O$ (43.3 mg, 0.3 mmol, 1.0 equiv.) was dissolved in MeOH (3 mL) and added to a solution of {HC(Pz)$_2$(CH$_2$N(Me)$_2$)} (**L4**) (61.6 mg, 0.3 mmol, 1.0 equiv.) in CH_2Cl_2 (3 mL). After 2 h, blue-green plates, crystals suitable for X-ray diffraction were obtained (65.2 mg, 0.2 mmol, 64%). IR (ATIR, neat): $\tilde{\nu}$ = 3104 (w), 2952 (vw), 1639 (vw), 1515 (m), 1438 (w), 1402 (m), 1284 (m), 1238 (w), 1210 (w), 1186 (w), 1159 (vw), 1086 (m), 1086 (m), 1071 (m), 1046 (m), 988 (w), 960 (m), 860 (m), 817 (m), 801 (s), 767 (s), 752 (vs), 693 (m), 670 (m), 658 (m) cm^{-1}. MS (FAB+): *m*/*z* (%) = 307 (5) [$C_{10}H_{15}{}^{37}Cl^{65}CuN_5$]$^+$, 305 (30) [$C_{10}H_{15}{}^{37}Cl^{63}CuN_5$, $C_{10}H_{15}{}^{35}Cl^{65}CuN_5$]$^+$, 303 (35) [$C_{10}H_{15}{}^{35}Cl^{63}CuN_5$]$^+$, 268 (5) [$C_{10}H_{15}{}^{63}CuN_5$]$^+$, 206 (40) [$C_{10}H_{15}N_5$] $^+$. HRMS (FAB+): *m*/*z* calcd. for $C_{10}H_{13}N_5{}^{35}Cl^{63}Cu$ 303.0312; found 303.0287.

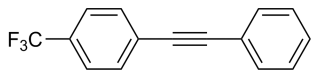
Analytical Data of the Cross-Coupled Compounds

Ethyl 3-(2-Phenylethynyl)benzoate



R_f = 0.3 (isohexane/Et_2O, 19:1); m.p. 20 °C. ^{1}H NMR (300 MHz): δ = 8.22–8.20 (m, 1 H, Ph-H), 8.03–7.99 (m, 1 H, Ph-H), 7.72–7.68 (m, 1 H, Ph-H), 7.57–7.51 (m, 2 H, Ph-H), 7.46–7.40 (m, 1 H, Ph-H), 7.39–7.33 (m, 3 H, Ph-H), 7.40 [q, $^3J_{H,H}$ = 7.1 Hz, 2 H, C(O)OCH_2], 1.41 [t, $^3J_{H,H}$ = 7.1 Hz, 3 H, C(O)OCH_2CH_3] ppm. ^{13}C NMR (75 MHz): δ = 165.9, 135.6, 132.7, 131.7, 130.8, 129.2, 128.5, 128.5, 128.4, 123.7, 122.9, 90.2, 88.4, 61.2, 14.3 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 3064 (vw), 3036 (vw), 2981 (w), 2935 (w), 2905 (vw), 2213 (vw), 1717 (s), 1602 (w), 1578 (w), 1493 (m), 1443 (w), 1428 (w), 1392 (w), 1367 (m), 1317 (m), 1280 (m), 1303 (m), 1280 (m), 1250 (vs), 1146 (m), 1100 (m), 1080 (m), 1025 (m), 914 (m), 750 (vs), 686 (s) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 250 (100) [M]$^+$, 205 (80) [$C_{15}H_9O_1$]$^+$, 176 (45) [$C_{14}H_8$]$^+$, 151 (25) [$C_{12}H_7$]$^+$. HRMS (70 eV, EI): *m*/*z* calcd. for $C_{17}H_{14}O_2$ 250.0994; found 250.0991.

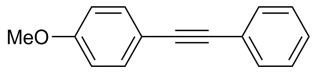
4-Trifluoromethyl-1-(2-phenylethynyl)benzene



R_f = 0.6 (isohexane →isohexane/Et_2O, 19:1); m.p. 100.6 °C. ^{1}H NMR (300 MHz): δ = 7.67–7.51 (m, 6 H, Ph-H), 7.41–7.33 ppm (m, 3 H, Ph-H) ppm. ^{13}C NMR (75 MHz): δ = 132.0, 131.9, 130.1 [q, $J_{C,F}$ = 32.7 Hz], 129.0, 128.6, 127.3 [q, $J_{C,F}$ = 1.0 Hz], 125.4 [q, $J_{C,F}$ = 3.8 Hz], 124.3 [q, $J_{C,F}$ = 272.2 Hz], 122.7, 91.2, 88.1 ppm. ^{19}F NMR (282 MHz): δ = –62.8 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 3036 (vw), 2925 (vw), 2200 (w), 1608 (m), 1572 (w), 1486 (w), 1442 (w), 1405 (w), 1322 (m), 1154 (m), 1129 (m), 1104 (vs), 1065 (s), 1018 (m), 920 (w), 842 (s), 757 (s), 689 (s), 596 (m) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 246 (100) [M]$^+$, 202 (40) [$C_{13}H_8F_2$]$^+$, 149 (17)

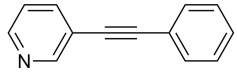
$[C_9H_3F_2]^+$. HRMS (70 eV, EI): *m*/*z* calcd. for $C_{15}H_9F_3$ 246.0657; found 246.0659.

3-(2-Phenylethynyl)anisole



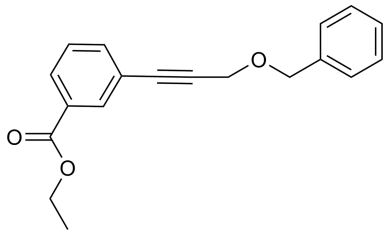
R_f = 0.15 (isohexane→CH_2Cl_2); m.p. 57.2 °C. ^{1}H NMR (300 MHz): δ = 7.51–7.45 (m, 4 H, Ar-H), 7.34–7.29 (m, 3 H, Ar-H), 6.86 [d, $J_{H,H}$ = 8.8 Hz, 2 H, Ar-H], 3.81 (s, 3 H, OCH_3) ppm. ^{13}C NMR (75 MHz): δ = 159.8, 133.3, 131.7, 128.5, 128.1, 123.8, 115.6, 114.2, 89.6, 88.3, 55.5 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 3061 (vw), 2993 (vw), 2960 (vw), 2835 (vw), 2216 (w), 1604 (w), 1593 (m), 1569 (w), 1508 (m), 1464 (w), 1454 (w), 1439 (w), 1288 (w), 1245 (s), 1179 (m), 1139 (w), 1108 (m), 1070 (w), 1027 (m), 917 (w), 840 (vs), 813 (m), 779 (w), 752 (s), 691 (s) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 208 (100) $[M]^+$, 193 (42) $[C_{14}H_9O]^+$, 165 (32) $[C_{13}H_9]^+$. HRMS (70 eV, EI): *m*/*z* calcd. for $C_{15}H_{12}O$ 208.0886; found 208.0877.

3-(Phenylethynyl)pyridine



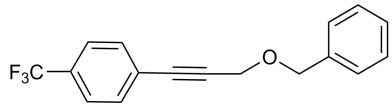
R_f = 0.15 (isohexane/Et_2O, 9:1→isohexane/Et_2O, 6:4); yellow solid; m.p. 51.2 °C. ^{1}H NMR (300 MHz): δ = 8.78 [dd, $J_{H,H}$ = 2.1, 0.9 Hz, 1 H, 2-py], 8.56 [dd, $J_{H,H}$ = 5.0, 1.8 Hz, 1 H, 6-py], 7.84 [dt, $J_{H,H}$ = 8.0, 1.9 Hz, 1 H, 4-py], 7.59–7.54 (m, 2 H, Ph-H), 7.41–7.36 (m, 3 H, Ph-H), 7.31 [ddd, $J_{H,H}$ = 8.0, 5.0, 1.0 Hz, 1 H, 5-py] ppm. ^{13}C NMR (75 MHz): δ = 152.1, 148.3, 138.6, 131.7, 128.8, 128.5, 123.1, 122.5, 120.6, 92.8, 85.8 ppm. ^{19}F NMR (282 MHz): δ = –118.0 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 3005 (vw), 1558 (w), 1489 (m), 1470 (m), 1442 (m), 1414 (m), 1189 (w), 1176 (w), 1145 (w), 1123 (w), 1071 (w), 1020 (m), 920 (w), 814 (m), 756 (s), 709 (s), 690 (vs) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 179 (100) $[M]^+$, 151 (10) $[C_{12}H_8]^+$, 126 (18) $[C_{10}H_6]^+$. HRMS (70 eV, EI): *m*/*z* calcd. for $C_{13}H_9N$ 170.0604; found 179.0729.

Ethyl 3-[(3-Benzyloxy)prop-1-ynyl]benzoate



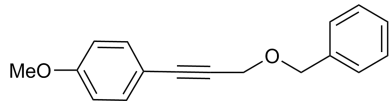
R_f = 0.24 (isohexane/Et_2O, 19:1); light-yellow oil. ^{1}H NMR (300 MHz): δ = 8.15 [td, $J_{H,H}$ = 2.2, 0.5 Hz, 1 H, Ph-H], 8.01 [ddd, $J_{H,H}$ = 7.9, 1.6, 1.3 Hz, 1 H, Ph-H], 7.63 [td, $J_{H,H}$ = 8.7, 1.5 Hz, 1 H, Ph-H], 7.44–7.28 (m, 7 H, Ph-H), 4.60 (s, 2 H, CH_2), 4.42 (s, 2 H, CH_2), 4.39 [q, $J_{H,H}$ = 7.1 Hz, 2 H, $C(O)OCH_2$], 1.41 [t, $J_{H,H}$ = 7.1 Hz, 3 H, $C(O)OCH_2CH_3$] ppm;^{13}C NMR (75 MHz): δ = 165.8, 137.4, 135.8, 132.8, 130.8, 129.4, 128.5, 128.4, 128.1, 127.9, 123.0, 86.1, 85.5, 71.8, 61.2, 57.8, 14.3 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 3066 (vw), 3032 (vw), 2982 (w), 2938 (vw), 2853 (w), 1717 (vs), 1602 (w), 1580 (w), 1478 (w), 1454 (w), 1431 (w), 1367 (m), 1353 (m), 1289 (s), 1224 (vs), 1168 (w), 1103 (s), 1073 (vs), 1026 (s), 913 (m), 817 (w), 751 (vs), 736 (s), 697 (s), 683 (s) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 265 (54) $[C_{18}H_{17}O_2]^+$, 191 (23) $[C_{15}H_{11}]^+$, 143 (65) $[C_{10}H_7O_1]^+$, 91 (100) $[C_7H_7]^+$; HRMS (70 eV, EI): *m*/*z* calcd. for $C_{19}H_{18}O_3$ 294.1257; found 294.1254.

1-[(3-Benzyloxy)prop-1-ynyl]-4-(trifluoromethyl)benzene



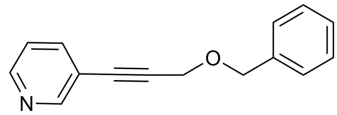
R_f = 0.56 (isohexane/Et_2O, 19:1); yellow liquid. ^{1}H NMR (300 MHz): δ = 7.61–7.53 (m, 4 H), 7.43–7.39 (m, 4 H), 7.37–7.31 (m, 1 H), 4.70 (s, 2 H), 4.43 (s, 2 H) ppm. ^{13}C NMR (75 MHz): δ = 137.4, 132.1, 130.3 [q, $^2J_{C,F}$ = 32 Hz], 128.6, 128.2, 128.1, 126.6 [q, $^4J_{C,F}$ = 1.4 Hz], 125.4 [q, $^3J_{C,F}$ = 3.8 Hz], 124.0 [q, $^1J_{C,F}$ = 270 Hz], 87.8, 85.2 [q, $^4J_{C,F}$ = 1.4 Hz], 71.9, 57.9 ppm. ^{19}F NMR (282 MHz): δ = –118.0 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 3071 (vw), 3036 (vw), 2925 (vw), 2855 (vw), 1888 (vw), 1586 (w), 1498 (s), 1443 (m), 1229 (m), 1187 (m), 1111 (m), 918 (w), 893 (m), 826 (s), 752 (vs), 687 (s) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 210 (100) $[M]^+$, 183 (10) $[C_{13}H_8F_1]^+$. HRMS (70 eV, EI): *m*/*z* calcd. for $C_{15}H_{11}F$ 210.0843; found 210.0837.

4-[(3-Benzyloxy)prop-1-ynyl]anisole



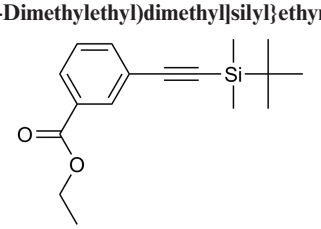
R_f = 0.18 (isohexane/EtOAc, 99:1); yellow liquid. ^{1}H NMR (300 MHz): δ = 7.46–7.29 (m, 7 H, Ph-H), 6.89–6.84 (m, 2 H, Ph-H), 4.70 (s, 2 H, OCH_2), 4.41 (s, 2 H, OCH_2), 3.82 (s, 3 H, OCH_2) ppm. ^{13}C NMR (75 MHz): δ = 159.8, 137.6, 133.3, 128.5, 128.1, 127.8, 114.8, 114.0, 86.4, 83.7, 71.6, 58.0, 55.3 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 3064 (vw), 3032 (vw), 2934 (w), 2838 (w), 2236 (w), 1606 (m), 1568 (w), 1508 (vs), 1454 (m), 1353 (m), 1291 (m), 1246 (vs), 1172 (m), 1070 (s), 964 (w), 830 (vs), 799 (m), 736 (s), 697 (s), 604 (m) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 252 (15) $[M]^+$, 146 (100) $[C_{10}H_{10}O_1]^+$, 131 (45) $[C_9H_7O]^+$. HRMS (70 eV, EI): *m*/*z* calcd. for $C_{17}H_{16}O_2$ 252.1153; found 252.1144.

3-[(3-Benzyloxy)prop-1-ynyl]pyridine



R_f = 0.47 (isohexane/Et_2O, 5:5); yellow oil. ^{1}H NMR (300 MHz): δ = 8.70 [d, $J_{H,H}$ = 1.3 Hz, 1 H, 2-py], 8.56 [dd, $J_{H,H}$ = 4.9, 1.6 Hz, 1 H, 6-py], 7.76 [dt, $J_{H,H}$ = 7.9, 3.9 Hz, 1 H, 4-py], 7.43–7.26 (m, 6 H, Ph-H, 5-py), 4.69 (s, 2 H, OCH_2), 4.43 (s, 2 H, OCH_2) ppm. ^{13}C NMR (75 MHz): δ = 152.3, 148.7, 138.8, 137.2, 128.5, 128.1, 128.0, 123.0, 120.0, 88.7, 83.0, 77.3, 77.2, 77.0, 76.7 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 3030 (vw), 2852 (vw), 1584 (vw), 1561 (vw), 1496 (w), 1475 (m), 1453 (vw), 1407 (m), 1353 (m), 1261 (vw), 1206 (vw), 1187 (w), 1071 (s), 1023 (m), 961 (w), 804 (m), 737 (s), 696 (vs) cm^{-1}. MS (70 eV, EI): *m*/*z* (%) = 222 (36) $[C_{15}H_{13}NO]^+$, 117 (63) $[C_8H_7N]^+$, 91 (100) $[C_7H_7]^+$. HRMS (70 eV, EI): *m*/*z* calcd. for $C_{15}H_{13}N$ 222.0900; found 222.0914.

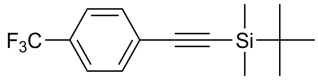
Ethyl 3-(2-{[(1,1-Dimethylethyl)dimethylsilyl}ethynyl)benzoate



R_f = 0.42 (isohexane/Et_2O, 99:1); light-yellow liquid. ^{1}H NMR (300 MHz): δ = 8.12 [td, $J_{H,H}$ = 1.7, 0.5 Hz, 1 H, Ph-H], 7.97 [ddd,

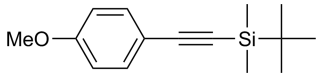
$J_{H,H}$ = 7.9, 1.7, 1.3 Hz, 1 H, Ph-H], 7.63 [ddd, $J_{H,H}$ = 7.7, 1.6, 1.3 Hz, 1 H, Ph-H], 7.37 [td, $J_{H,H}$ = 7.0, 0.8 Hz, 1 H, Ph-H], 4.38 [q, $J_{H,H}$ = 7.1 Hz, 2 H, $C(O)OCH_2$], 3.35 [t, $J_{H,H}$ = 7.1 Hz, 3 H, $C(O)OCH_2CH_3$], 1.00 [s, 9 H, $SiC(CH_3)_3$], 0.19 [s, 6 H, $Si(Me)_2$] ppm. ^{13}C NMR (75 MHz): δ = 165.9, 136.0, 133.0, 130.6, 129.4, 128.3, 123.6, 104.6, 93.6, 61.2, 26.1, 16.7, 14.3, –4.7 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 3069 (vw), 2954 (w), 2930 (m), 2886 (w), 2857 (w), 2162 (w), 1722 (s), 1600 (w), 1579 (w), 1471 (w), 1464 (w), 1428 (w), 1368 (w), 1281 (s), 1249 (m), 1204 (s), 1103 (m), 1079 (m), 1023 (m), 920 (m), 828 (vs), 810 (m), 774 (s), 752 (vs), 684 (s), 672 (m), 620 (m) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 288 (7) $[M]^+$, 231 (100) $[C_{13}H_{15}O_2Si]^+$, 203 (15) $[C_{11}H_{11}O_2Si]^+$. HRMS (70 eV, EI): *m/z* calcd. for $C_{17}H_{24}O_2{}^{28}Si$ 288.1543; found 288.1541.

1-(2-{[(1,1-Dimethylethyl)dimethyl]silyl}ethynyl)-4-(trifluoromethyl)benzene



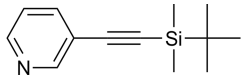
R_f = 0.72 (isohexane/Et_2O, 99:1); yellow liquid. ^1H NMR (300 MHz): δ = 7.56 (s, 4 H), 1.01 (s, 9 H), 0.21 (s, 6 H) ppm. ^{13}C NMR (75 MHz): δ = 132.4, 130.3 [q, $^2J_{C,F}$ = 34 Hz], 127.2 [q, $^4J_{C,F}$ = 1.4 Hz], 125.3 [q, $^3J_{C,F}$ = 3.8 Hz], 124.1 [q, $^1J_{C,F}$ = 271 Hz], 104.3 [q, $^4J_{C,F}$ = 1.4 Hz], 95.8, 26.3, 16.9, –4.6 ppm. ^{19}F NMR (282 MHz): δ = –62.9 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 2954 (w), 2930 (w), 2888 (vw), 2859 (w), 2162 (w), 1614 (m), 1471 (w), 1463 (w), 1404 (w), 1363 (vw), 1320 (vs), 1250 (m), 1221 (w), 1167 (s), 1127 (vs), 1104 (vs), 1066 (vs), 1017 (m), 1007 (vw), 939 (vw), 836 (vs), 821 (vs), 807 (vs), 774 (vs), 682 (vs) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 284 (3) $[M]^+$, 227 (100) $[C_{11}H_{10}F_3Si]^+$, 197 (5) $[C_9H_4F_3Si]^+$. HRMS (70 eV, EI): *m/z* calcd. for $C_{15}H_{11}F$ 210.0843; found 210.0837.

4-(2-{[(1,1-Dimethylethyl)dimethyl]silyl}ethynyl)anisole



R_f = 0.68 (isohexane/Et_2O, 99:1); yellow liquid. ^1H NMR (300 MHz): δ = 7.42–7.39 (m, 2 H, Ph-H), 6.83–6.80 (m, 2 H, Ph-H), 3.81 (s, 3 H, OCH_3), 0.99 [s, 9 H, $SiC(CH_3)_3$], 0.18 [s, 6 H, $Si(Me)_2$] ppm. ^{13}C NMR (75 MHz): δ = 159.7, 133.5, 115.4, 113.8, 105.8, 90.7, 55.3, 26.2, 16.7, –4.5 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 2954 (m), 2929 (m), 2896 (w), 2856 (m), 2154 (m), 1606 (m), 1571 (w), 1507 (s), 1463 (m), 1292 (m), 1246 (vs), 1171 (m), 1106 (w), 1034 (m), 1007 (w), 851 (s), 824 (vs), 807 (vs), 773 (vs), 754 (s), 676 (m), 589 (w) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 246 (18) $[M]^+$, 189 (100) $[C_{11}H_{13}OSi]^+$, 174 (7) $[C_{10}H_{10}OSi]^+$. HRMS (70 eV, EI): *m/z* calcd. for $C_{15}H_{22}O^{28}Si$ 246.1440; found 261.1435.

3-(2-{[(1,1-Dimethylethyl)dimethyl]silyl}ethynyl)pyridine



R_f = 0.31 (isohexane/Et_2O, 9:1); yellow oil. ^1H NMR (300 MHz): δ = 8.70 [d, $J_{H,H}$ = 1.3 Hz, 2-py], 8.53 [dd, $J_{H,H}$ = 4.8, 1.5 Hz, 1 H, 6-py], 7.77 [dt, $J_{H,H}$ = 7.7, 1.9 Hz, 1 H, 4-py], 7.26 [ddd, $J_{H,H}$ = 8.0, 4.8, 1.0 Hz, 1 H, 5-py], 1.00 [s, 9 H, $SiC(CH_3)_3$], 0.20 [s, 6 H, $Si(Me)_2$] ppm. ^{13}C NMR (75 MHz): δ = 152.3, 148.3, 139.2, 123.0, 120.6, 101.9, 97.0, 77.3, 77.2, 77.0, 76.7, 26.1 ppm. IR (ATIR, neat): $\tilde{\nu}$ = 2953 (w), 2929 (m), 2885 (vw), 2857 (w), 2161 (w), 1559 (vw), 1473 (m), 1463 (m), 1406 (m), 1362 (w), 1249 (m), 1236 (w), 1183 (w), 1022 (w), 1007 (w), 833 (vs), 802 (vs), 774 (vs), 703 (s), 683 (s) cm^{-1}. MS (70 eV, EI): *m/z* (%) = 217 (12) $[M]^+$, 160 (100) $[C_9H_{10}NSi]^+$, 130 (8) $[C_7H_4NSi]^+$. HRMS (70 eV, EI): *m/z* calcd. for $C_{13}H_{19}N^{28}Si$ 217.1299; found 217.1286.

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