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Palladium NNC Pincer Complex as an Efficient Catalyst for the Cycloisomerization of Alkynoic Acids

Nerea Conde,[a] Raul SanMartin,[a,*] María Teresa Herrero,[a] and Esther Domínguez[a,*]

[a] Department of Organic Chemistry II, Faculty of Science and Technology, University of the Basque Country (UPV/EHU), Sarriena auzoa z/g, 48940 Leioa, Spain
Fax: (+34)-94-601-2748; e-mail: raul.sanmartin@ehu.es or esther.dominguez@ehu.es

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Abstract: A two-step (nucleophilic substitution/palladation by oxidative addition) sequence provides a high-yielding access to a non-symmetrical palladium NNC pincer complex. A number of terminal and internal alkynoic acids with different substitution patterns at the α- and β-positions are regio- and diastereoselectively cycloisomerized to the corresponding exocyclic enol lactones in the presence of exceedingly low amounts of the latter palladium complex, so that unprecedented turnover numbers and frequencies ranging from 1,000,000 to 700,000 and from 41,667 to 9722 h^{-1}, respectively, are achieved. The optimized protocol, based on the use of a catalytic amount of triethylamine as base, allows an easy real-time monitoring of the reaction by NMR spectroscopy. Several pieces of evidence in favor of the direct participation of the above pincer complex as the catalyst of the reaction have been gathered from kinetic and poisoning experiments

Keywords: alkynoic acids; cycloisomerization; lactones; palladium; pincer complexes

The enol lactone motif is present in several naturally occurring products, such as cyanobacterin,[1] freelingyne,[2] or eremofargurein A[3] and in a number of biologically active compounds.[4] In addition, the preparation of enol lactones continues to be actively pursued due to the broad use of such heterocyclic structures as synthetic intermediates,[5] and therefore several routes[6] towards γ- or δ-alkylidenelactones, classified into three main strategies (coupling reactions with already formed lactones,[7] condensation reactions,[8] and electrophilic lactonizations, such as halolactonization and cycloisomerization[9]) have been developed over the years.

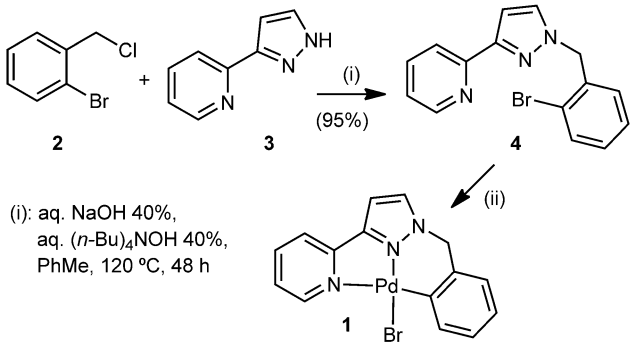
The cycloisomerization reaction of γ-alkynoic acids is an extremely valuable transformation that provides an easy and atom-economical entry to enol-lactones. In recent years, a number of well-designed protocols based on transition metals such as Rh,[10] Hg,[11] Ru,[12] Ag,[13] Au,[14] Cu,[15] and Pd[16] have been developed for the preparation of the γ-alkylidenelactone motif. However, most of these procedures require relatively high catalyst loadings (10–0.01 mol%), prolonged reaction times and/or elevated temperatures. The use of more elaborated catalysts from specially designed ligands or complexes,[17,18] and heterogeneous scaffolds[19] has overcome the above limitations to some extent. In this regard, it is worth mentioning the high activity shown by pincer-type complexes in spite of the few examples described to date.[18b–e]

Herein, we report the synthesis and characterization of a new non-symmetrical palladium pincer NNC that resulted to be an exceedingly efficient catalyst for the intramolecular addition of carboxylic acids to alkynes. In addition to the exceptionally low catalyst loadings achieved, a number of experiments have shed light on the role of the above palladacycle in this advantageous route to diversely structured alkylidenelactones.

As displayed in Table 1, complex **1** was synthesized from commercially available *o*-bromobenzyl chloride **2** and pyrazolylpyridine **3**. For the synthesis of the intermediate ligand **4**, a modification of the procedure for the alkylation of pyrazoles reported independently by the groups of Mukherjee and Bu[20] was tested, thus prolonging the heating of both substrates and a phase-transfer catalyst [(*n*-Bu)$_4$NOH] in a biphasic system (H_2O/PhMe) for 48 h to provide regioselectively the intermediate bromo-derivative **4** in an excellent yield (95%).

The insertion of palladium was carried out by an oxidative addition process. In the first assays $Pd_2(dba)_3$ was used as the palladium source, in tolu-

Table 1. Synthesis of palladium pincer complex **1**. Optimization of the oxidative addition step.



Entry	Conditions (ii)	**1** [%][a]
1	$Pd_2(dba)_3$, PhMe, 60 °C, 48 h	–
2	$Pd_2(dba)_3$, PhMe, r.t., 48 h	–
3	$Pd(dba)_2$, THF, 120 °C, 8 h	88
4	$Pd(dba)_2$, THF, r.t., 48 h	42
5	$Pd(dba)_2$, THF, 80 °C, 8 h	65
6	$Pd(dba)_2$, THF, r.t., 5 days	82

[a] Isolated yields.

ene at room temperature and at 60 °C during 48 h. In none of the trials was the desired product obtained (Table 1, entries 1 and 2). Therefore, we decided to change both the source of Pd(0) and the solvent, thus reacting *ortho*-bromo derivative **4** with $Pd(dba)_2$ in tetrahydrofuran in a similar way as described by Xia and co-workers for the formation of iminophosphinite palladium complexes.[21]

Process optimization by adjusting temperature and reaction times led to the isolation of target palladacycle **1** in a good yield (entry 3), and although longer reaction times were necessary to obtain similar yields, oxidative addition/coordination was also attained at room temperature (entry 6). Thus, metal complex **1** was prepared in just two steps with an overall yield of 83%.

^{1}H NMR signals, slightly shifted downfield compared to ligand **4**, and the absence of C_{arom}–Br in ^{13}C NMR were indicative of the formation of complex **1**. The structure of palladacycle **1**, determined by single crystal X-ray diffractometry (Figure 1), showed a distortion from square planar geometry, probably due to the uncommon combination of 5- and 6-membered rings in the metal coordination sphere.[22a]

Whereas the 5-membered ring containing pyridine and pyrazole heterocyclic moieties and Pd(II) core is almost flat, the planarity of the adjacent 6-membered ring is far from ideal, as the meaningful N-3–N-2–Pd–C-15 and C-9–C-10–C-15–Pd (6.4 and 9.2°, respectively) torsion angles clearly reflect. Such a distortion can be also visualized by observation of bond angles C-15–Pd–N-1 and N-2–Pd–Br, which instead of 180°, are 164.9 and 169.9°, respectively.[22b]

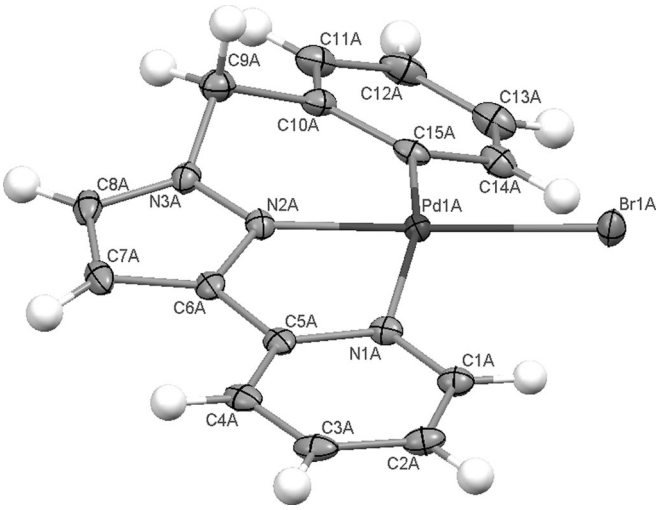


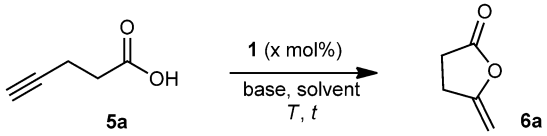
Figure 1. Molecular structure of palladium pincer complex **1** with the atomic numbering scheme. Thermal ellipsoids are given at the 50% probability level.

The cycloisomerization of 4-pentynoic acid **5a** into 5-methylenedihydrofuran-2(3*H*)-one **6a** was then explored in the presence of palladacycle **1**. In order to facilitate the observation of target **6a** in the reaction medium by ^{1}H NMR, deuterated solvents were chosen, and the initial catalyst loading and reaction concentration were set at 10^{-2} mol% and 0.1 M, respectively.

The first experiments were assayed at room temperature, in the absence and in the presence of substoichiometric amounts of base (5 mol%) (Table 2, entries 1–6). Only the use of Et_3N in $CDCl_3$ provided enol lactone **6a** with 27% yield (entry 4), so the latter base and solvent were chosen for further studies. Temperature and reaction time were increased (entries 7 and 8), and the product was obtained with excellent yields in both cases. The required loading of Et_3N was also investigated, and it was found that an increase from 5 to 10 mol% caused a decline in the yield from 99% to 70%, thus indicating that relatively high base concentrations had an inhibitory effect on the reaction, while 2 mol% of Et_3N was enough to get quantitative yields (entries 7, 8 and 10–12). Encouraged by this excellent result we decided to reduce the catalyst loading (Table 2, entries 13–16). Even when employing 10^{-4} mol% or 10^{-5} mol% of complex **1** the desired lactone was obtained in quantitative yield, although at the cost of longer reaction times or higher temperatures, respectively (entries 14 and 16 *vs.* entry 12). On account of a balance between the above factors (catalyst amount, temperature and reaction time), the conditions displayed in Table 2, entry 14 were determined as optimal. The same result was obtained when using $CHCl_3$ as solvent.

It should be mentioned that the cycloisomerization neither occurred in the absence of the pincer complex

Table 2. Cycloisomerization of 4-pentynoic acid **5a** in the presence of complex **1**.[a]



5a **6a**

Entry	Solvent	**1** [mol%]	Base	*T* [°C]	*t* [h]	Conversion [%][b]
1	$CDCl_3$	10^{-2}	–	r.t.	2	–
2	CD_3COCD3	10^{-2}	–	r.t.	2	–
3	$CDCl_3$	10^{-2}	K_2CO_3 (5 mol%)	r.t.	2	–
4	$CDCl_3$	10^{-2}	Et_3N (5 mol%)	r.t.	2	27
5	CD_3COCD_3	10^{-2}	Et_3N (5 mol%)	r.t.	2	–
6	$CDCl_3$	10^{-2}	KO-*t*-Bu (5 mol%)	r.t.	2	–
7	$CDCl_3$	10^{-2}	Et_3N (5 mol%)	90	12	99
8	$CDCl_3$	10^{-2}	Et_3N (5 mol%)	50	12	99
9	CH_2Cl_2	10^{-2}	Et_3N (5 mol%)	50	12	11
10	$CDCl_3$	10^{-2}	Et_3N (2 mol%)	90	12	99
11	$CDCl_3$	10^{-2}	Et3N (10 mol%)	90	12	70
12	$CDCl_3$	10^{-2}	Et_3N (2 mol%)	50	12	99
13	$CDCl_3$	10^{-3}	Et_3N (2 mol%)	50	24	99
14	$CDCl_3$	10^{-4}	Et_3N (2 mol%)	50	24	99
15	$CDCl_3$	10^{-5}	Et_3N (2 mol%)	50	24	83
16	$CDCl_3$	10^{-5}	Et_3N (2 mol%)	90	12	99
17	$CDCl_3$	10^{-4}	Et_3N (2 mol%)	50	12	72
18	$CDCl_3$	–	Et_3N (2 mol%)	50	24	–
19[c]	$CDCl_3$	10^{-4}	Et_3N (2 mol%)	50	24	–

[a] *Reaction conditions:* 4-pentynoic acid **5a** (0.2 mmol), solvent (0.1 M).
[b] Conversion rate determined by ^1H NMR spectroscopy.
[c] $Pd(OAc)_2$

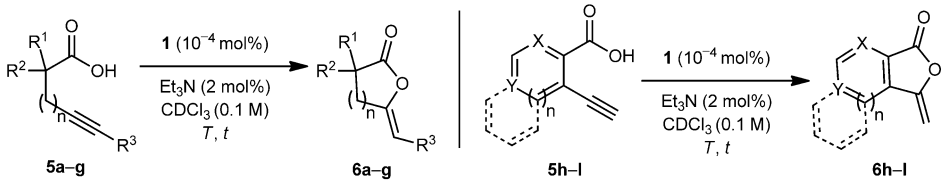
1 nor in the presence of such small amounts of commercially available palladium sources like $Pd(OAc)_2$ (Table 2, entries 17 and 18). Moreover, the reaction could be carried out in an air atmosphere without the requirement of inert conditions.

Subsequently the scope of the reaction was examined by submitting a series of commercial or readily available acetylenic acids **5**[23] to the optimized reaction conditions. As shown in Table 3, the reaction proved to be highly regioselective for 4-alkynoic acids **5a–e** and **5h–l** assayed, affording the corresponding 5-*exo*-dig lactones.

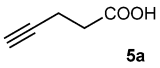
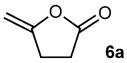
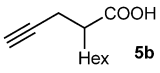
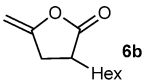
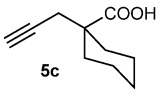
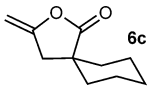
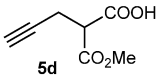
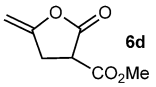
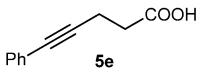
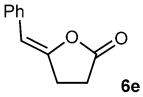
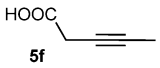
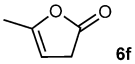
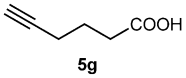
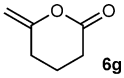
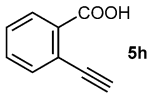
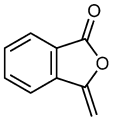
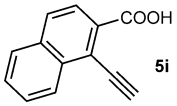
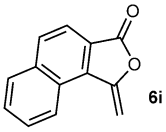
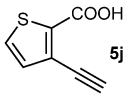
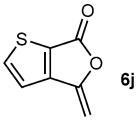
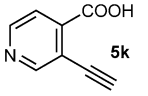
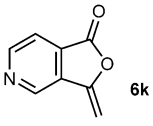
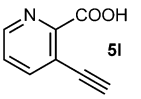
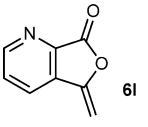
Our protocol tolerated the presence of different substituents at the α-position to the carboxy group (Table 3, entries 2–4), although higher temperatures were required when a long *n*-hexyl chain was attached at that position (entry 2). A complete regiocontrol was also achieved from intrinsically challenging substrates such as internal alkynes, 3-alkynoic and 5-alkynoic acids (Table 3, entries 5–7). For lactones **6f–6g** an increase of the temperature was required (90 °C) to get full conversion to 5-*endo*-dig and 6-*exo*-dig products, respectively. We should also mention the complete diastereoselectivity in the transformation of 5-phenylpent-4-ynoic acid **5e** into (*Z*)-benzylidenedihydrofuranone **6e**. A set of rigid aromatic and heteroaromatic 4-alkynoic acids **5h–l** was also submitted to the optimized reaction conditions to provide the corresponding benzo-, naphtho-, thieno- and pyridofuranone derivatives **6h–l** in good to excellent yields (entries 8–12). TON and TOF values ranged from 1,000,000 to 700,000 and from 41,667 to 9722 h^{-1}, respectively, the highest achieved so far for any metal catalyst.

With the purpose of gaining new insight into the catalytic profile observed for pincer complex **1**, a number of poisoning assays and kinetic studies were carried out. The procedures reported by Finke and Widegren serve to make a distinction between homogeneous and heterogenous catalysis.[24,25] Indeed, heterogeneous catalysts expose only a fraction of the active metal atoms in their surface, so the addition of certain additives in substoichiometric amounts is enough to poison (partially or totally) the catalyst. In contrast, homogeneous catalysts are unaffected by such amounts.[24] In this context, it is also known that mercury metal has an ability to poison metal(0) particles, both by amalgamating the metal or adsorbing on the metal surface.[25] As shown in Table 4 (entry 1), when a drop of mercury was added to the reaction mixture, the desired product **6a** was still obtained in excellent yield (negative mercury drop test). With

Table 3. Cycloisomerization of alkynoic acids **5** in the presence of palladium complex **1**.[a]

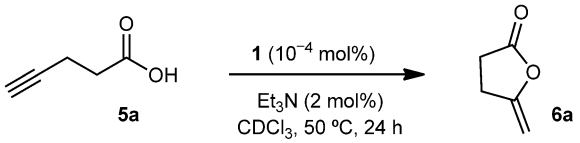


5a–g **6a–g** **5h–l** **6h–l**

Entry	Substrate **5**	Product **6**	T [°C]	t [h]	Yield [%][b]
1	 **5a**	 **6a**	50	24	94 (97)[c]
2	 **5b**	 **6b**	70	24	88
3	 **5c**	 **6c**	50	24	97
4	 **5d**	 **6d**	50	24	85
5	 **5e**	 **6e**	50	72	70
6	 **5f**	 **6f**	90	24	93 (96)[c]
7	 **5g**	 **6g**	90	24	95 (98)[c]
8	 **5h**	 **6h**	50	4	94
9	 **5i**	 **6i**	50	24	76
10	 **5j**	 **6j**	90	24	98
11	 **5k**	 **6k**	50	24	95
12	 **5l**	 **6l**	50	24	96

[a] *Reaction conditions:* alkynoic acid **5** (0.2 mmol),palladium complex **1** (10^{-4} mol%), Et_3N (2 mol%), $CDCl_3$ (2 mL).
[b] Isolated yields.
[c] Determined by ^1H NMR spectroscopy. 3,4,5-Trichloropyridine was used as internal standard.

Table 4. Summary of poisoning experiments.



Entry	Poisoning additive	**6a** [%][a]
1	Hg (one drop)	99
2	CS_2 (0.5 equiv. per metal atom)	99
3	CS_2 (2.0 equiv. per metal atom)	97
4	PPh_3 (0.03 equiv. per metal atom)	99
5	PPh_3 (0. 3 equiv. per metal atom)	99
6	PPh_3 (4.0 equiv. per metal atom)	98
7[b]	Py (150 equiv. per metal atom)	99
8[c]	PVPy (300 equiv. per metal atom)	99

[a] Determined by ^{1}H NMR. 3,4,5-Trichloropyridine was used as internal standard.
[b] Py = pyridine.
[c] PVPy = polyvinylpyridine.

regard to the addition of other poisoning additives in sub- and overstoichiometric amounts, the yields for the cycloisomerization in the presence of CS_2 and PPh_3 were unchanged regardless of the amount of additive added, as displayed in Table 4, entries 2–6.

These results provide evidence for the participation of homogeneous catalytic species, a proposal supported by the behavior observed in the presence of pyridine and polyvinylpyridine (PVPy). Once again no changes were observed in the reaction after adding overstoichiometric amounts of these additives (entries 7 and 8), known for their application to detect participation of Pd(0) colloids and soluble Pd species prone to temporarily coordinate with pyridine and therefore to get trapped in the insoluble anchored PVPy.[26]

On account of the extremely low amount of the catalyst employed, a convenient NMR monitoring of the reaction was also possible by recording ^{1}H NMR spectra at regular intervals for 24 h (represented as a stacked plot, Figure 2). The transformation of 4-pentynoic acid **5a** into 5-methylenedihydrofuran-2(3*H*)-one **6a** can be easily monitored by observing the decrease of the signal corresponding to the acetylenic proton and the rise of the signals belonging to the alkene moiety. No intermediates or other species were detected, and as shown in Figure 2, the reaction was almost finished in 6 h.

Furthermore, integration of the above ^{1}H NMR signals at different reaction times allowed a very easy conversion rate *vs.* time plot (Figure 3). According to the latter data, the reported cycloisomerization is a first-order reaction in pentynoic acid, with a rate constant $k = 9.3 \times 10^{-3}\ s^{-1}$.

The shape of the observed kinetic curve, with no induction period,[27] also indicated the participation of homogeneous catalytic species other than colloidal palladium clusters or nanoparticles formed by decomposition of the organometallic complex.

Finally, the reaction was carried out with a high catalyst loading (1 mol%) in order to verify that the catalyst **1** did not disintegrate or undergo degradation during the cycloisomerization process. After 3 h the reaction was stopped and the crude mixture was evaporated under vacuum. The residue was analyzed by ^{1}H NMR, showing that the pincer complex **1** remained intact. This fact, in addition to providing more proof of the role of **1** as a true catalyst, opens further possibilities for a potential recycling protocol.

To sum up, an extremely efficient procedure for the cycloisomerization of acetylenic acids to the corresponding enol lactones under relatively mild reaction conditions has been developed, using infinitesimal amounts of a new non-symmetrical palladium pincer complex as the catalyst and a catalytic loading of triethylamine as base. This method tolerates the presence of different substitution patterns on both α- and β-positions of the alkynoic acid. Furthermore, the reactions were found to be highly regioselective, resulting in selective formation of the *exo*-dig products and, for internal γ-alkynes, the *Z*-alkene was steroselectively obtained. The direct participation of the readily available NNC palladium complex as the catalyst is evidenced by several kinetic and poisoning experiments and NMR monitoring techniques.

Experimental Section

General Information

Commercially available reagents were used throughout without purification unless otherwise stated. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 instrument (300 MHz for ^{1}H and 75.4 MHz for ^{13}C) at 20 °C.

Chemical shifts (δ) are given in ppm downfield from Me_4Si and are referenced as internal standard to the residual solvent (unless indicated) $CDCl_3$ ($\delta = 7.26$ for ^{1}H and $\delta = 77.00$ for ^{13}C). Coupling constants, *J*, are reported in hertz (Hz). Melting points were determined in a capillary tube and are uncorrected. TLC was carried out on SiO_2 (silica gel 60 F254, Merck), and the spots were located with UV light. Flash chromatography was carried out on SiO_2 (silica gel 60, Merck, 230–400 mesh ASTM). IR spectra were recorded on Perkin–Elmer 1600 FT and JASCO FTIR-4100 infrared spectrophotometers as thin films, and only noteworthy absorptions are reported in cm^{-1}. Drying of organic extracts during work-up of reactions was performed over anhydrous Na_2SO_4. Evaporation of solvents was accomplished with a Büchi rotatory evaporator. Mass spectra were recorded on an Agilent 5975 mass spectrometer under electronic impact (EI) conditions. HR-mass spectra were recorded using a Waters GCT mass spectrometer. Intensity data were col-

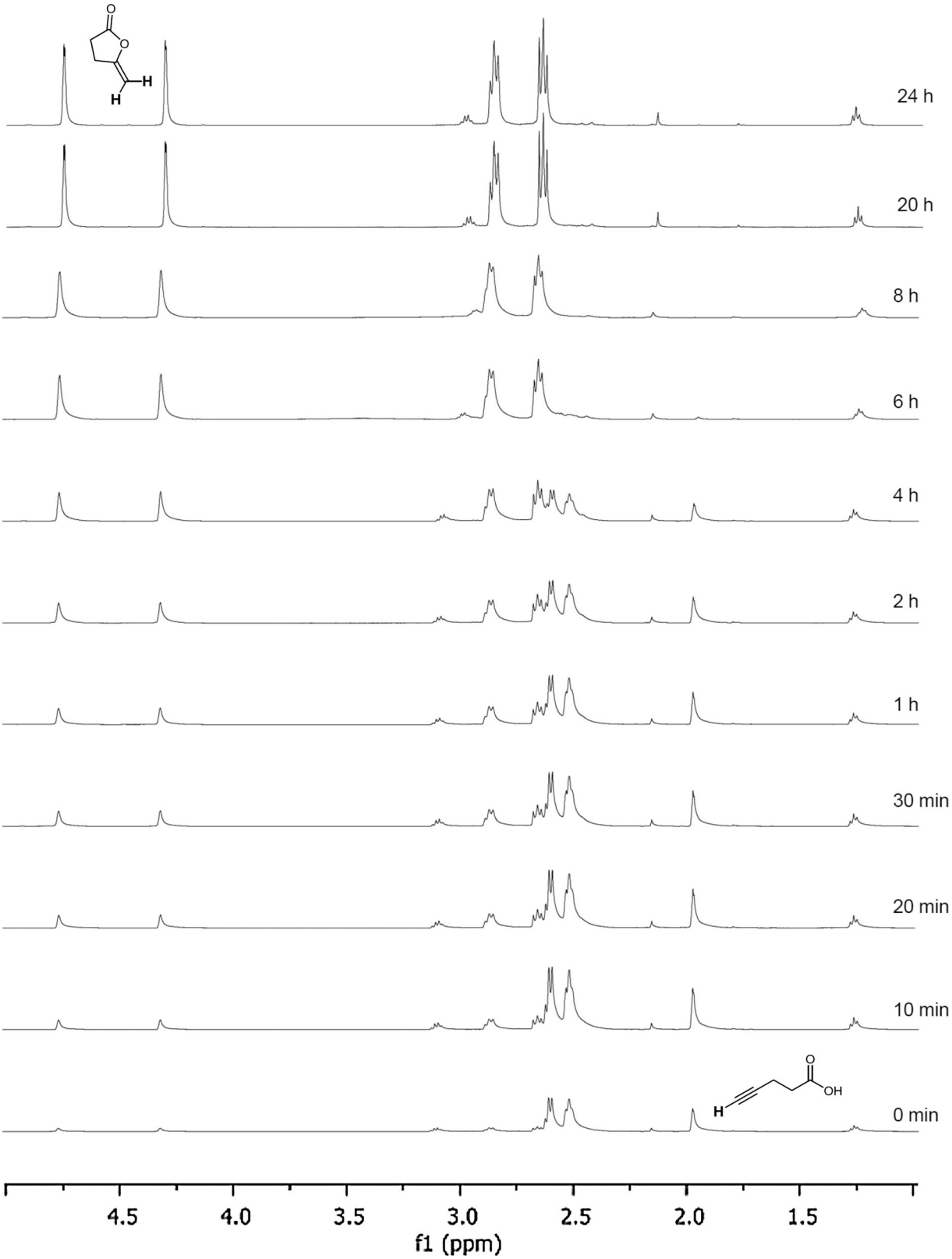


Figure 2. Stacked plot of the time-dependent ^{1}H NMR spectra for the cycloisomerization of 4-pentynoic acid **5a** in the presence of non-symmetrical pincer complex **1**.

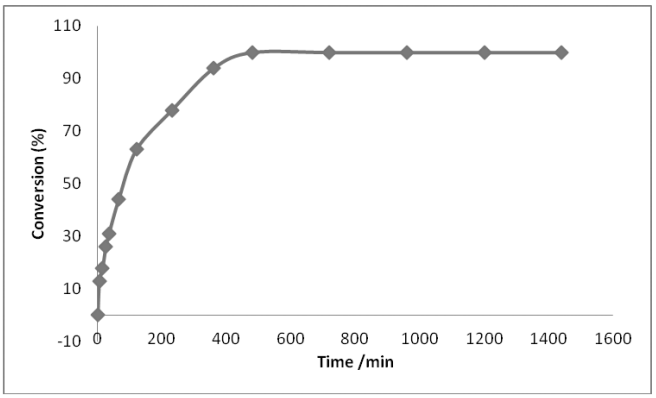


Figure 3. Conversion rate (%) of 4-pentynoic acid **5a** *vs.* time.

lected on an Agilent Technologies Super-Nova diffractometer, which was equipped with monochromatic Cu kα radiation ($\lambda = 1.54184$ Å) and Atlas CCD detector. Measurement was carried out at 100(2) K with the help of an Oxford Cryostream 700 PLUS temperature device. Data frames were processed (united cell determination, analytical absorption correction with face indexing, intensity data integration and correction for Lorentz and polarization effects) using the Crysalis software package. The structure was solved using Olex22 and refined by full-matrix least-squares with SHELXL-97.3 Final geometrical calculations were carried out with Mercury4. and PLATON5 as integrated in WinGX.

Synthesis of the Palladium Pincer NNC

2-[1-(2-Bromobenzyl)-1*H*-pyrazol-3-yl]pyridine (4): In a round-bottom flask 2-bromobenzyl chloride **2** (0.29 mL, 2.28 mmol), 2-(1*H*-pyrazol-3-yl)pyridine **3** (333 mg, 2.23 mmol), 3.5 mL of a 40% aqueous solution of NaOH, and 165 μL of a 40% aqueous solution of $(n\text{-Bu})_4\text{OH}$ were dissolved in toluene (27 mL) at room temperature under an argon atmosphere. The mixture was heated to 120 °C for 48 h. After cooling the reaction mixture was washed with H_2O (3×5 mL) and the aqueous layer was extracted with diethyl ether (3×5 mL). The organic layers were combined and dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude oil was purified by flash column chromatography using hexanes:EtOAc (6:4) as eluent to afford pure product **4** as a yellow powder; yield: 682 mg (95%); mp 62–65 °C (hexanes/EtOAc). ^{1}H NMR ($CDCl_3$): $\delta = 8.61$ (d, $J = 4.7$ Hz, 1H), 7.93 (d, $J = 7.9$ Hz, 1H), 7.66 (td, $J = 7.8$, 1.7 Hz, 1H), 7.55 (d, $J = 7.8$ Hz, 1H), 7.47 (d, $J = 2.3$ Hz, 1H, H-8), 7.28–7.06 (m, 3H), 6.93 (d, $J = 2.4$ Hz, 2H), 5.46 (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta = 151.9$, 151.8, 149.2, 136.3, 135.8, 132.5, 131.3, 129.2, 129.0, 127.6, 122.4, 122.0, 119.8, 104.6, 55.7; HR-MS (*m/z*): *m/z* = 313.0209 $[M]^+$, calcd. for $C_{15}H_{12}N_3Br$: 131.0215.

(2-{1-[(Phenyl-κC2)-methyl]-1*H*-pyrazol-3-yl-κN2]-pyridine-κN-palladium(II) bromide (1): In a round-bottom flask pyrazole **1** (200 mg, 0.63 mmol) was dissolved in 15 mL of THF under an argon atmosphere and then added to previously dried $Pd(dba)_2$ (400 mg, 0.69 mmol). The reaction mixture was heated to 120 °C for 8 h. After cooling it was filtered through a plug of celite. The filtrate was evaporated under reduced pressure and the crude was purified by flash chromatography with a gradient starting at hexanes:EtOAc (1:1) and ending at 100% EtOAc. Complex **1** was obtained as an orange powder; yield: 191 mg (88%); mp 142–144 °C (hexanes:EtOAc). ^{1}H NMR ($CDCl_3$): $\delta = 9.1$ (d, $J = 5.3$ Hz, 1H), 8.41 (d, $J = 2.8$ Hz, 1H), 7.83 (td, $J = 9.3$, 1.6 Hz, 1H), 7.65 (d, $J = 5.1$ Hz, 2H), 7.32 (m, 1H), 7.00–6.89 (m, 3H), 6.71 (d, $J = 5.3$ Hz, 1H), 5.31 (s, 2H); ^{13}C NMR ($CDCl_3$): $\delta =$ 151.2, 150.8, 149.2, 143.1, 138.9, 135.6, 132.4, 131.5, 127.3, 127.0, 124.6, 124.5, 120.4, 104.9, 60.6; HR-MS: *m/z* = 340.00613 $[M]^+$, calcd. for $C_{15}H_{12}N_3Pd$: 340.00665.

General Procedure for the Cycloisomerization of Alkynoic Acids 5 in the Presence of Complex 1

The alkynoic acid **5** (0.2 mmol), triethylamine (25 μL of a 0.16 M solution in $CHCl_3$, 4×10^{-3} mmol), palladacycle **1** (50 μL of a 4×10^{-6} M solution in $CHCl_3$, 2×10^{-7} mmol) and $CDCl_3$ (2 mL) were placed in a screw-capped tube and heated in an oil bath at the indicated temperature for an appropriate time. The reaction mixture was subsequently filtered through a short plug of silica gel to remove triethylamine, thus providing pure lactone **6**, or alternatively, purified by flash column chromatography using hexanes:EtOAc (7:3) in the referred cases. The progress of the reaction was monitored by ^{1}H NMR.

5-Methylenedihydrofuran-2(3*H*)-one (6a):[19a] The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 50 °C for 24 h. Due to the volatility of the product, initial NMR yields (using 3,4,5-trichloropyridine was as internal standard) were determined from the crude. Special care was taken for the vacuum evaporation of the solvent. Compound **6a** was obtained as a colorless oil; yield: 19.1 mg (94%). ^{1}H NMR ($CDCl_3$): $\delta = 4.75$ (dd, $J = 4.2$, 2.0 Hz, 1H), 4.31 (dd, $J = 4.2$, 2.0 Hz, 1H), 2.93–2.83 (m, 2H), 2.72–2.63 (m, 2H); ^{13}C NMR ($CDCl_3$): $\delta =$ 175.0, 155.6, 88.7, 28.0, 25.1.

4-Hexyl-5-methylenedihydrofuran-2(3*H*)-one (6b):[19a] The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 70 °C for 24 h. Compound **6b** was obtained as a colorless oil; yield: 32.1 mg (88%). ^{1}H NMR ($CDCl_3$): $\delta = 4.71$ (dd, $J = 3.9$, 2.0 Hz, 1H), 4.30 (dd, $J = 3.9$, 2.0 Hz, 1H), 2.99 (dd, $J = 15.9$, 9.6 Hz, 1H), 2.74 (ddd, $J = 14.1$, 8.7, 4.9 Hz, 1H), 2.54 (ddt, $J = 15.9$, 7.7, 2.1 Hz, 1H), 1.94–1.77 (m, 1H), 1.59–1.44 (m, 1H), 1.43–1.21 (m, 8H), 0.88 (t, $J = 6.6$ Hz, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 177.2$, 154.5, 88.6, 39.9, 31.6, 31.5, 30.9, 28.9, 26.9, 22.5, 14.0.

3-Methylene-2-oxaspiro[4.5]decan-1-one (6c):[28] The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 50 °C for 24 h. Compound **6c** was obtained as a colorless oil; yield: 32.4 mg (97%). ^{1}H NMR ($CDCl_3$): $\delta = 4.72$ (dd, $J = 4.1$, 2.0 Hz, 1H), 4.31 (dd, $J = 4.1$, 2.0 Hz, 1H), 2.73 (t, $J = 1.7$ Hz, 2H), 1.83–1.68 (m, 4H), 1.68–1.50 (m, 3H), 1.43–1.20 (m, 3H); ^{13}C NMR ($CDCl_3$): $\delta = 179.7$, 153.8, 88.9, 44.7, 37.2, 32.8, 25.1, 22.0.

Methyl 5-methylene-2-oxotetrahydrofuran-3-carboxylate (6d):[19a] The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 50 °C for 24 h. Compound **6d** was obtained as a colorless oil; yield: 26.0 mg (85%). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 4.82$ (dd,

J=4.5, 2.3 Hz, 1H), 4.41 (dd, J=4.4, 1.8 Hz), 3.83 (s, 3H), 3.76 (dd, J=10.4, 7.6 Hz, 1H), 3.31 (ddt, J=16.6, 7.6, 2.1 Hz, 1H), 3.09 (ddt, J=16.6, 10.4, 1.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=169.5, 167.3, 153.1, 89.9, 53.4, 46.2, 29.3.

(*Z*)-5-Benzylidenedihydrofuran-2(3*H*)-one (6e):[19a] The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 50 °C for 72 h. Compound **6e** was obtained as a white powder after purification by flash chromatography; yield: 24.4 mg (70%); mp 88–91 °C ($CHCl_3$)(Lit.[29] 91–93 °C). ^{1}H NMR ($CDCl_3$): δ=7.55 (d, J=7.4 Hz, 2H), 7.33 (t, J=7.5 Hz, 2H), 7.21 (t, J=7.3 Hz, 1H), 5.55 (s, 1H), 3.12–2.93 (m, 2H), 2.81–2.62 (m, 2H); ^{13}C NMR ($CDCl_3$): δ=174.9, 148.1, 133.9, 128.5, 128.3, 126.7, 104.9, 27.0, 26.3;.

5-Methylfuran-2(3*H*)-one (6f):[18b] The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 90 °C for 24 h. Due to the volatility of the product, initial NMR yields (using 3,4,5-trichloropyridine was as internal standard) were determined from the crude. Special care was taken for the vacuum evaporation of the solvent. Compound **6f** was obtained as a colorless oil; yield: 19.3 mg (93%). ^{1}H NMR ($CDCl_3$): δ=5.11 (td, J=3.3, 2.0 Hz, 1H,), 3.20–3.09 (m, 2H,), 1.99 (d, J=2.0, 3H); ^{13}C NMR ($CDCl_3$): δ=176.9, 153.3, 99.0, 34.1, 14.0.

6-Methylenetetrahydro-2*H*-pyran-2-one (6g):[19a] The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 90 °C for 24 h. Due to the volatility of the product, initial NMR yields (using 3,4,5-trichloropyridine was as internal standard) were determined from the crude. Special care was taken for the vacuum evaporation of the solvent. Compound **6g** was obtained as a colorless oil; yield: 23.9 mg (95%). ^{1}H NMR ($CDCl_3$): δ=4.64 (s, 1H), 4.29 (s, 1H), 2.63 (t, J=6.8 Hz, 2H), 2.48 (t, J=6.5 Hz, 2H), 1.93–1.81 (m, 2H); ^{13}C NMR ($CDCl_3$): δ=168.1, 155.3, 93.7, 30.3, 26.7, 18.6.

3-Methyleneisobenzofuran-1(3*H*)-one (6h):[18b] The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 50 °C for 24 h. Compound **6h** was obtained as a white powder; yield: 30 mg (94%); mp 50–53 °C ($CHCl_3$)(Lit.[30] 55–57 °C). ^{1}H NMR (CD_3OD): δ=7.90 (t, J=7.5 Hz, 1H), 7.85 (t, J=7.5 Hz, 1H), 7.79 (td, J=7.5, 1.1 Hz, 1H), 7.64 (td, J=7.4, 1.0 Hz, 1H), 5.40 (d, J=3.0 Hz, 1H), 5.22 (d, J=3.0 Hz, 1H); ^{13}C NMR (CD_3OD): δ=166.9, 152.0, 138.9, 134.6, 130.4, 124.6, 124.5, 120.7, 90.4.

1-Methylenenaphtho[1,2-*c*]furan-3(1*H*)-one (6i): The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 50 °C for 24 h. Compound **6i** was obtained as a white powder after purification by flash chromatography; yield: 29.8 mg (76%); mp 90–93 °C ($CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=8.37–8.25 (m, 1H), 8.06–7.94 (m, 2H), 7.84 (d, J=8.4 Hz, 1H), 7.78–7.65 (m, 2H), 5.71 (d, J=3.3 Hz, 1H), 5.57 (d, J=3.3 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=167.1, 152.5, 136.6, 136.0, 132.2, 129.9, 128.9, 128.8, 126.9, 124.7, 124.1, 120.0, 96.7; IR (ATR): ν_{max}=3619, 2965, 2926, 2857, 1759, 1289, 1063, 991, 962, 754 cm^{-1}; HR-MS: m/z=197.0596 $[M+H]^+$, calcd. for $C_{13}H_9O_2$: 197.0603.

4-Methylenethieno[2,3-*c*]furan-6(4*H*)-one (6j): The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 90 °C for 24 h. Compound **6j** was obtained as an orange powder; yield: 30 mg (98%); m.p. 85–88 °C ($CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=7.48 (d, J=4.9 Hz, 1H), 7.25 (d, J=4.9 Hz, 1H), 5.17 (d, J=3.1 Hz, 1H), 5.00 (d, J=3.1 Hz, 1H); ^{13}C NMR ($CDCl_3$): δ=161.2, 153.2, 149.1, 140.6, 130.2, 118.9, 92.60; IR (ATR): ν_{max}=3091, 2951, 2922, 2915, 1763, 1662, 1289, 991, 941, 776 cm^{-1}; HR-MS: m/z=153.0004 $[M+H]^+$, calcd. for $C_7H_5O_2S$: 153.0010.

3-Methylenefuro[3,4-*c*]pyridin-1(3*H*)-o (6k): The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 50 °C for 24 h. Compound **6k** was obtained as a white powder; yield: 27.9 mg (95%); mp 99–102 °C ($CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=9.17 (s, 1H), 8.89 (d, J=5.0 Hz, 1H), 7.80 (d, J=5.0 Hz, 1H), 5.41 (s, 2H); ^{13}C NMR ($CDCl_3$): δ=165.2, 150.7, 149.8, 143.8, 133.2, 130.0, 118.2, 93.9; IR (ATR): ν_{max}=3105, 3001, 2930, 2847, 1788, 1432, 1285, 1001, 951, 682 cm^{-1}; HR-MS: m/z=148.0389 $[M+H]^+$, calcd. for $C_8H_6NO_2$: 148.0399.

5-Methylenefuro[3,4-*b*]pyridin-7(5*H*)-one (6l): The general procedure for cycloisomerization was followed, and the reaction mixture was heated at 50 °C for 24 h. Compound **6l** was obtained as a white powder; 27.4 mg (93%); mp 129–132 °C ($CHCl_3$). ^{1}H NMR ($CDCl_3$): δ=8.93 (dd, J=4.7, 1.3 Hz, 1H), 8.09 (dd, J=8.0, 1.3 Hz, 1H), 7.63 (dd, J=8.0, 4.7 Hz, 1H), 5.44–5.36 (m, 1H), 5.36–5.27 (m, 1H); ^{13}C NMR ($CDCl_3$): δ=164.3, 153.5, 149.2, 143.7, 133.5, 129.0, 127.7, 94.2; IR (ATR): ν_{max}=2962, 2919, 2875, 2851, 1784, 1257, 1095, 1009, 811, 689 cm^{-1}; HR-MS: m/z=148.0391 $[M+H]^+$, calcd. for $C_8H_6NO_2$: 148.0396.

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