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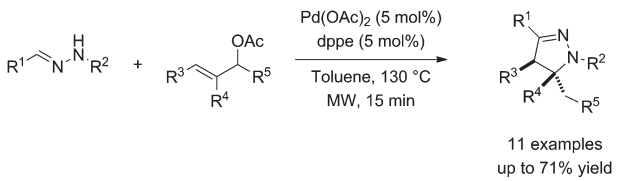

Selective Tsuji–Trost type *C*-allylation of hydrazones: a straightforward entry into 4,5-dihydropyrazoles

El Hachemia El Mamouni, Martin Cattoen, Marie Cordier, Janine Cossy, Stellios Arseniyadis, Hocine Ilitki* and Laurent El Kaïm*

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Selective Tsuji–Trost type *C*-allylation of hydrazones: a straightforward entry into 4,5-dihydropyrazoles†

Cite this: DOI: 10.1039/c6cc08171a

Received 10th October 2016,
Accepted 18th November 2016

DOI: 10.1039/c6cc08171a

www.rsc.org/chemcomm

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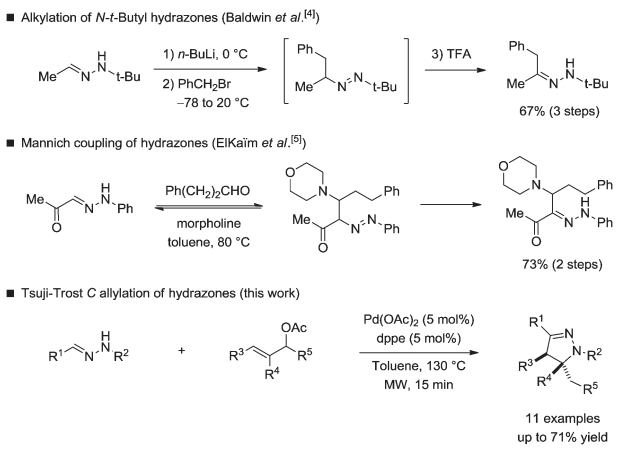
The 4,5-dihydropyrazole motif has drawn considerable attention over the years as it was shown to exhibit a plethora of biological and pharmacological properties, including anticancer, antibacterial, antifungal, antiviral, and anti-inflammatory properties. As such, it has been the target of a number of methods and drug discovery programs. We report here a straightforward and highly selective approach featuring a key palladium-catalysed Tsuji–Trost type *C*-allylation and subsequent intramolecular 1,4-addition of hydrazones.

The chemistry of hydrazones goes back to the 19th century and the early developments of organic synthesis.[1] Indeed, due to their ease of formation starting from carbonyl derivatives, they have been associated with many fundamental syntheses of nitrogen-containing heterocycles such as the Fischer indole[2] and the Knorr pyrazole[3] syntheses. One of the most interesting features of hydrazones is linked to their ability to react with both nucleophiles and electrophiles at the same carbon atom. While the reaction with nucleophiles, leading to the corresponding hydrazone derivatives, is rather classical for iminyl-type compounds, the reaction with electrophiles is associated with the azaenamine nature of the hydrazone moiety. In the case of N–H hydrazones, for example, deprotonation leads to ambident nucleophiles that usually react with electrophiles at the nitrogen atom. However, the selectivity may be reversed by using either sterically hindered hydrazones, such as *N-tert*-butyl derivatives,[4] or by selecting electrophiles that can add onto the nitrogen atom in a reversible fashion as previously observed when using hydrazones in the context of a Mannich reaction[5] (Scheme 1).



Scheme 1 *C*-Alkylation strategies for NH hydrazones.

Indeed, following our previous reports on the use of α-keto hydrazones in such reactions,[6] we envisioned that the anion derived from these hydrazones could be sufficiently stabilized to allow a palladium-catalysed *C*-allylation process to occur. Herein, we wish to report our efforts in this direction, culminating in the development of a new pyrazole synthesis *via* an unprecedented Tsuji–Trost type *C*-allylation of NH hydrazones.[7]

Our journey began when trying to promote a *C*-allylation when subjecting hydrazone **1a** to allyl methyl carbonate in the presence of a catalytic amount of $Pd(PPh_3)_4$. Unfortunately, under these conditions, we were unable to isolate the desired product, but instead obtained the *N*-allylated product in a moderate 64% yield (Scheme 2). Heating the latter in the presence of various palladium catalysts [$Pd(PPh_3)_4$, $Pd(OAc)_2$/dppe] at temperatures reaching as high as 140 °C under both conventional heating or microwave irradiation, failed to trigger a transfer of the allyl residue from the nitrogen to the carbon atom.

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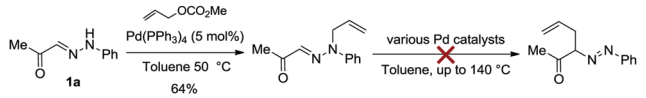
† Electronic supplementary information (ESI) available: Details of experimental procedures, ^{1}H NMR and ^{13}C NMR spectra for all unknown compounds. CCDC 1495182–1495184. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c6cc08171a



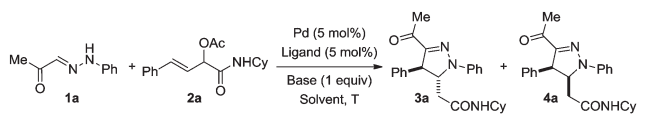
Scheme 2 Allylation of hydrazone **1a** with methylallyl carbonate.

Despite these disappointing results, we were encouraged by our recent use of Passerini adducts as a valuable allylic Tsuji–Trost partner for 1,3-bis-nucleophiles,[8] and thus decided to subject these allyl acetate derivatives to our hydrazone. Interestingly, when **1a** was heated in toluene under microwave irradiation at 130 °C for 15 min in the presence of $Pd(OAc)_2$ (5 mol%), PPh_3 (10 mol%), Cs_2CO_3 (1 equiv.) and the Passerini adduct **2a**, prepared in one step from cyclohexyl isocyanide, cinnamaldehyde and acetic acid, we were pleased to observe the formation of two diastereoisomeric pyrazoles, **3a** and **4a**, in a 7 : 3 ratio (Table 1, entry 1). The relative stereochemistry of the major isomer, **3a**, which was isolated from the reaction mixture in 60% yield after column chromatography over silica gel, was confirmed as *trans* by NMR analysis (see ESI† for details).

With this result in hand, we decided to fine-tune the reaction conditions in order to optimize the method (Table 1). As a general trend, the reaction proceeds with various catalytic systems such as $Pd(OAc)_2/PPh_3$, $Pd(OAc)_2$/dppf or $Pd(OAc)_2$/dppe, with yields ranging from 45% to 72% (Table 1, entries 1–3). The use of organic bases such as DBU or DIPEA did not improve the yield (Table 1, entries 4 and 5), nor did the use of other solvents such as THF and DMF (Table 1, entries 6 and 7). Interestingly, the reaction could also be run at a lower temperature (60 °C) under conventional heating, albeit with an extended reaction time (Table 1, entries 8 and 9). Overall, running the reaction in the presence of $Pd(OAc)_2$/dppe and Cs_2CO_3 in toluene at 130 °C under microwave irradiation for 15 min afforded a good compromise in terms of selectivity, yield, and reaction time (Table 1, entry 3).

To evaluate the scope of this new pyrazoline synthesis, various Passerini adducts **2a–h** were prepared under solvent-free conditions and reacted with a set of hydrazones **1a–c** under the aforementioned conditions. The results are summarized in Table 2. In general, both aryl- and alkyl-substituted α,β-unsaturated derivatives could be converted to the corresponding 4,5-dihydro-pyrazole, with the aromatic derivatives affording slightly higher yields than the aliphatic ones (Table 2, entries 1–4). Changing the amide moiety did not affect the outcome of the reaction as both the *tert*-butyl- and the *para*-chloro benzyl amide afforded roughly the same yields as the cyclohexyl amide (Table 2, entries 5 to 7 *vs.* entries 1 to 2). Interestingly, trisubstituted olefins could also be used (Table 2, entry 8), affording the corresponding pyrazoline bearing a quaternary stereogenic center in 53% yield. Finally, switching from α-acetyl hydrazone **1a** to hydrazones **1b** and **1c** did not hamper the reaction as the corresponding 4,5-dihydropyrazoles were obtained in descent yields ranging from 50% to 70% (Table 2, entries 9–11). All 4,5-dihydropyrazoles obtained showed similar NMR coupling patterns in agreement with a *trans* stereochemistry, which was further confirmed by the single crystal X-ray analysis of compounds **3e** and **3h** (Fig. 1).[9]

Table 1 Conditions screening[a]



Entry	Catalyst	Base	Solvent	Temperature (°C)/time (min)	Yield **3a**[b] (%)	**3a**/**4a**[c]
1	$Pd(OAc)_2/PPh_3$[d]	Cs_2CO_3	Toluene	130/15	60	7 : 3
2	$Pd(OAc)_2$/dppf	Cs_2CO_3	Toluene	130/15	45	8 : 2
3	**$Pd(OAc)_2$/dppe**	**Cs_2CO_3**	**Toluene**	**130/15**	**72**	**8 : 2**
4	$Pd(OAC)_2$/dppe	DBU	Toluene	130/15	45	8.5 : 1.5
5	$Pd(OAC)_2$/dppe	DIPEA	Toluene	130/15	42	8 : 2
6	$Pd(OAC)_2$/dppe	Cs_2CO_3	THF	130/15	54	9.5 : 0.5
7	$Pd(OAC)_2$/dppe	Cs_2CO_3	DMF	130/15	61	10 : 0
8	$Pd(OAC)_2$/dppe	Cs_2CO_3	Toluene	60/60	60	9 : 1
9	$Pd(PPh_3)_4$	Cs_2CO_3	Toluene	60/60	70	8 : 2

[a] All reactions were run on a 0.5 mmol scale. [b] Isolated yield. [c] Determined by NMR on the crude reaction mixture. [d] 10 mol% of PPh_3 were used.

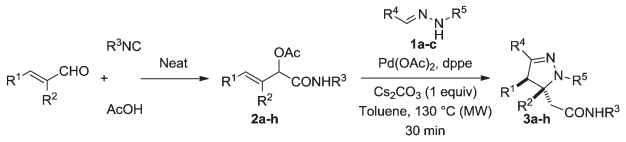
To widen the scope of the reaction, we envisioned the use of an alternative allyl acetate partner, which could undergo a similar Tsuji–Trost/cyclization cascade. Phosphonate **5** was therefore chosen.[10] The latter was easily prepared in 80% yield under solvent-free conditions by simply adding diethylphosphite to cinnamaldehyde in the presence of acetic anhydride and potassium carbonate.[11]

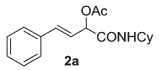
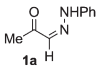
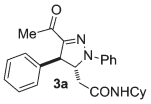
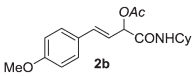
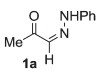
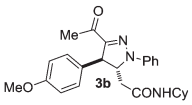
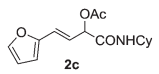
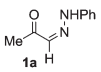
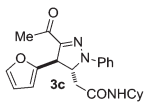
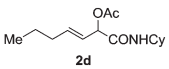
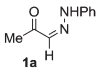
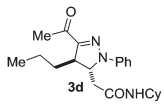
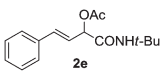
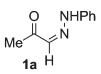
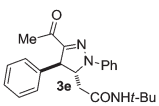
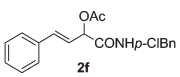
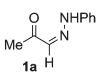
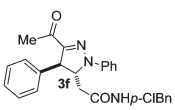
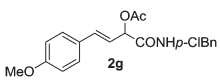
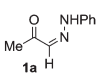
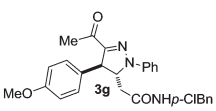
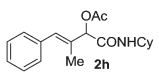
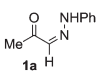
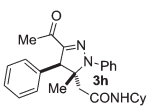
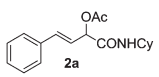
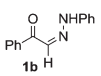
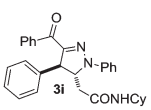
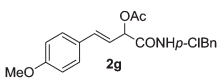
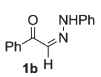
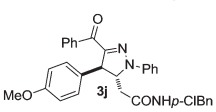
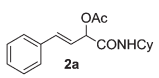
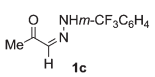
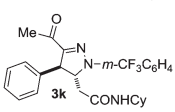
When **5** was subjected to the reaction conditions settled for the Passerini adducts **2a–h** [$Pd(OAc)_2$/dppe, Cs_2CO_3, Toluene, 130 °C (MW), 15 min], we were delighted to observe the formation of the new phosphonopyrazole **6a** in 76% isolated yield. The latter could be increased to 87% by simply replacing $Pd(OAc)_2$/dppe with $Pd(PPh_3)_4$ and switching to conventional heating (1 h at 50 °C instead of 15 min at 130 °C under microwave irradiation, see ESI† for details). Interestingly, under these conditions, the phosphonopyrazole was formed as a single *trans* isomer. Hence, these conditions [$Pd(PPh_3)_4$ (5 mol%), Cs_2CO_3 (1 equiv.) in toluene at 50 °C for 1 h] were selected to evaluate the scope of the reaction (see Table 3).

As a general trend, the reaction proceeded smoothly independently of the hydrazone used, affording the corresponding pyrazole in yields ranging from 51% to 90%. As observed for the related Passerini adduct **2a–h**, the successful coupling of carbomethoxy hydrazone **1d** with **5** is in agreement with a higher reactivity of the phosphonate compared to the analogous amide. This was further emphasized by the ability of simple *N*-nitroarylhydrazones such as **1f** and **1g**, prepared from aromatic and heteroaromatic aldehydes, to afford the corresponding pyrazoles **6f** and **6g** (Table 3, entries 6 and 7), which structures were secured by NMR analysis and single crystal X-ray analysis in the case of **6f** (see ESI† for details).[9] Interestingly, electron-rich hydrazone **1e** failed to provide the corresponding pyrazole **6e** (Table 3, entry 5) but led to the formation of the α,β-unsaturated hydrazone **7** instead (Scheme 3).

This result gave a clear indication of the mechanism. Indeed, as hydrazones bearing an α-carbonyl group or a nitro substituent on the *N*-aryl moiety are rather acidic, this does not only facilitate the deprotonation of the substrate but also favours the azo-hydrazone isomerisation of the *C*-allylated product **C** (Scheme 3). This last point is actually crucial in

Table 2 Scope of the pyrazoline synthesis[a]



Entry	Passerini adduct	Yield[b] (%)	Hydrazone	Pyrazole	Yield[b] (%)
1		80			72
2		75			54
3		80			51
4		70			35
5		75			71[c]
6		74			50
7		76			70
8		79			53[c]
9		80			70
10		76			50
11		80			60

[a] All reactions were run a 0.5 mmol scale. [b] Isolated yield. [c] X-ray structures in Fig. 1.

pulling the equilibrium towards the formation of the desired product, since poorly acidic azo intermediates are not able to rearrange into the corresponding hydrazones as also shown by Baldwin and co-workers.[4] With this in mind, we propose the mechanism depicted in Scheme 3, where the formation of the π-allyl intermediate **A** is followed by a nucleophilic attack of the deprotonated hydrazone, leading to the reversible formation of **B** and **C**.[12] Alternatively, the palladium may also complex the hydrazone at the initial NH position leading to intermediate **F**, which can selectively be converted to **C**. The latter can then rearrange according to two pathways depending on the acidity of the hydrazone. Hence, more acidic hydrazones undergo fast azo-hydrazono tautomerism to afford intermediate **D**, which will eventually cyclize to the corresponding 4,5-dihydropyrazole **3** or **6**. In contrast, less acidic hydrazones such as **1e**, where the benzylic position becomes more acidic, are prone to isomerise into **E**, which in turn can undergo an azo-hydrazone rearrangement to afford **7** that can no longer cyclize.

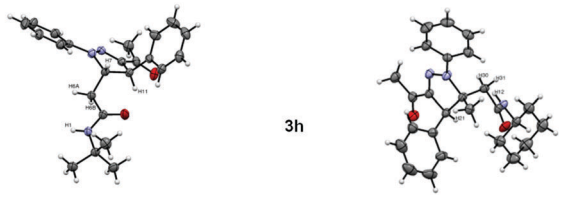
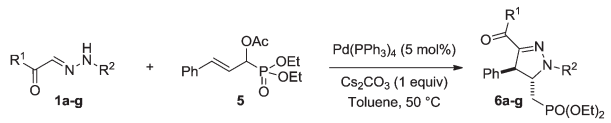
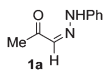
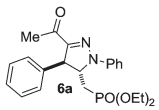
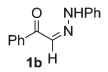
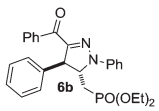
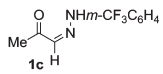
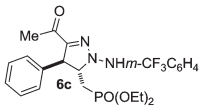
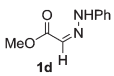
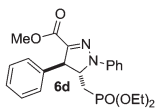
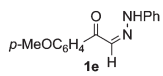
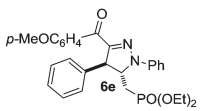
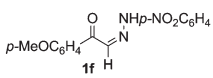
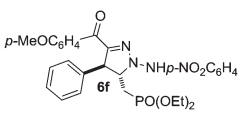
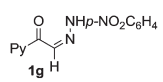
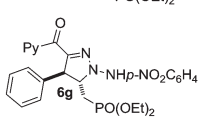


Fig. 1 X-ray structure of **3e** and **3h**.

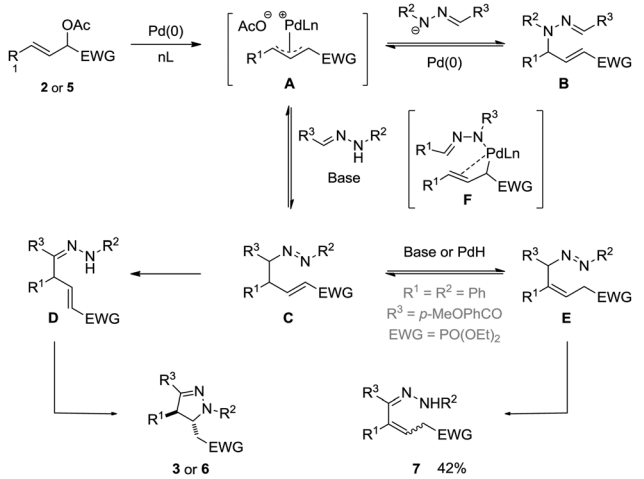
Table 3 Reaction of phosphonate **5** with hydrazones[a]



Entry	Hydrazone	Product	Yield[b] (%)
1			87
2			70
3			51
4			63
5			0
6			90
7			60

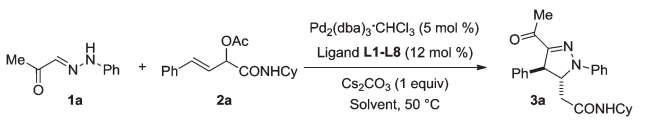
[a] All reactions were run on a 0.5 mmol scale. [b] Isolated yield.

Inspired by the pioneering work of Stoltz,[13] Trost[14] and Tunge[15] and following our previous experience in the field of palladium-catalysed allylic alkylation,[16–18] we then set out to develop an enantioselective method. A set of reactions were therefore run using hydrazone **1a** and amide **2a** as the model substrates, and a catalytic system consisting of $Pd_2(dba)_3{\cdot}CHCl_3$ (5 mol%) and various chiral ligands (**L1–L6**, 10 mol%). As a general trend all the reactions afforded the desired product **3a** in moderate to good yields and ees ranging from 8% to 61%. The best selectivity was obtained with the axially dissymmetric C_2-chiral diphosphine (*S*)-BINAPHANE (**L6**) (Table 4, entries 11 and 12), however (*S*)-BINAP (**L3**), and the mixed P/N ligands



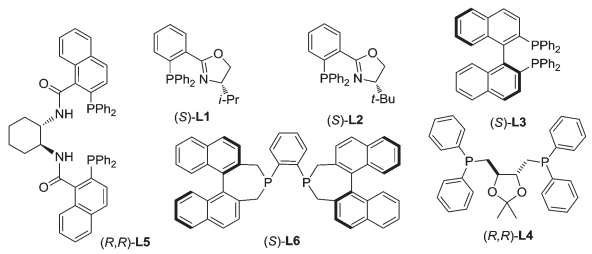
Scheme 3 Plausible mechanism.

Table 4 Asymmetric formation of pyrazole **3a**[a]



Entry	Solvent	Ligand	Yield[b] (%)	ee[c] (%)
1	Toluene	(*S*)-**L1**	75	42
2	THF	(*S*)-**L1**	52	40
3	Toluene	(*S*)-**L2**	78	57
4	THF	(*S*)-**L2**	45	52
5	Toluene	(*S*)-**L3**	55	32
6	THF	(*S*)-**L3**	45	52
7	Toluene	(*R*,*R*)-**L4**	85	12
8	THF	(*R*,*R*)-**L4**	60	8
9	Toluene	(*R*,*R*)-**L5**	77	51
10	THF	(*R*,*R*)-**L5**	26	34
11	Toluene	(*S*)-**6**	67	61
12	THF	(*S*)-**6**	60	36

[a] All reactions were run on a 0.5 mmol scale. [b] Isolated yield. [c] Determined by Supercritical Fluid Chromato-graphy (SFC) analysis. The relative configuration of **3a** was randomly attributed.



such as phosphine oxazoline **L2** also gave some promising selectivities (Table 4, entries 3 and 4).

In conclusion, we have disclosed a particularly straightforward synthesis of 4,5-dihydropyrazoles starting from readily available hydrazones and three-component adducts derived from cinnamaldehyde. Besides the potential of these heterocycles in both

medicinal and agrochemical applications,[19] the reaction settles an unprecedented and highly regioselective Tsuji–Trost *C*-alkylation of NH hydrazones. In agreement with the organometallic nature of the process, the use of chiral phosphine ligands has allowed the formation of the desired heterocycles with moderate, albeit promising, levels of enantioselectivity. Catalytic systems involving other metals such as iridium are currently under evaluation.

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