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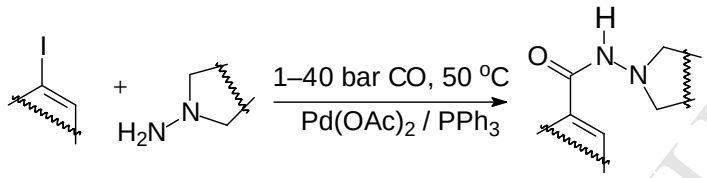
Graphical abstract



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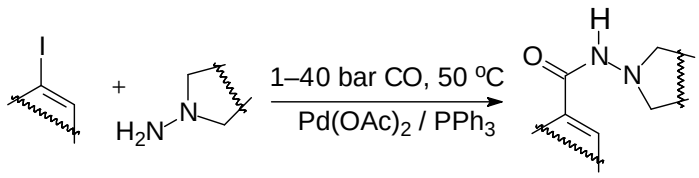

Aminocarbonylation (Hydrazinocarbonylation) of Iodoalkenes and Iodoarenes.

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Abstract: Iodoalkenes such as 1-iodocyclohexene, 4-*tert*-butyl-1-iodocyclohexene, α-iodostyrene and 17-iodoandrost-16-ene were aminocarbonylated in palladium-catalysed reaction using 1,1-disubstituted (cyclic) hydrazines (3-amino-3-azabicyclo[3.3.0]octane and (*S*)-1-amino-2-methoxymethylpyrrolidine (SAMP)/(*R*)-1-amino-2-methoxymethyl-pyrrolidine (RAMP)) as *N*-nucleophiles. The corresponding hydrazides were formed in moderate to high yields. The hydrazinocarbonylation of iodobenzene using the above 1,1-disubstituted hydrazines resulted in a rather complex reaction mixture due to two major types of side-reactions: *i)* the deamination of the 3-amino-3-azabicyclo[3.3.0]octane, and *ii)* the double carbon monoxide insertion. In this way, in addition to the expected benzoylhydrazide derivative, phenylglyoxylhydrazide (double CO insertion product) and benzamide ('deamination' product) were also formed. By the appropriate modification of the reaction conditions, good selectivities towards the target compounds were achieved even in these cases. The formation of the products/side-products were rationalised on the basis of a simplified catalytic cycle.

Key-words: carbonylation**,** palladium**,** hydrazide, hydrazine, carbon monoxide

1. Introduction

The widely used palladium-catalysed amino- and alkoxycarbonylation reactions of aryl halides are based on the seminal work of Heck *et al*. It was discovered that aryl halides, especially aryl bromides and iodides undergo carbonylation reaction in the presence of primary/secondary amines and alcohols used as *N*- and *O*-nucleophiles, respectively.[1] The synthetic importance of these reactions have been illustrated by the variation in structure of both the substrate and nucleophile.[2-6] These carbonylations are among the most important homogeneous catalytic reactions of synthetic importance and have found use in industrial applications.[7,8]

Soon after the discovery of aminocarbonylation of haloaromatics, their synthetic analogues, *i.e.*, iodo- and bromoalkenes as well as the corresponding enol-triflate surrogates have also been synthesized and transferred to the corresponding α,β-unsaturated carboxamides in palladium-catalysed aminocarbonylations.[5,6]

The synthesis of unsubstituted hydrazides is a straightforward methodology for aromatics, however quite difficult for α,β-unsaturated hydrazides which usually undergo undesired Michael-type cyclization.[9] Although the nucleophilic properties of alkyl- and aryl-hydrazine derivatives as well as the importance of their hydrazides are well known,[10] their synthesis via the corresponding ester needs special reaction conditions, for instance, the application of organoaluminium reagents.[11]

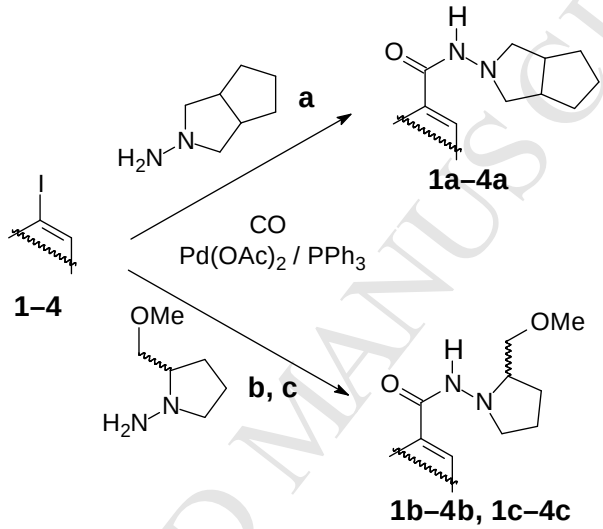
Although transition metal catalysed reactions could provide efficient solutions for the synthesis of carboxylic acid derivatives such as amides, esters, anhydrides, *etc*. from their building blocks, there are only a very few examples for the application of substituted hydrazines as *N*-nucleophiles in palladium-catalysed carbonylations. Steroidal hydrazides were prepared in hydrazinocarbonylation and used for further ring-closure reactions.[12-14] Diiodoaromatics were reacted with hydrazines under a carbon monoxide atmosphere leading to tetrahydrophthalazine derivatives.[15] Sulfonylhydrazides (aminosulfonamides) were synthesised in palladium-catalysed reactions using $(SO_2)_2$•DABCO adduct as sulfur dioxide source and the corresponding 1,1-disusbstituted hydrazines.[16]

As a part of our systematic investigations regarding structure–reactivity and structure–selectivity relationships in palladium-catalysed carbonylation reactions, the above 1,1-disubstituted hydrazines of practical interest[17,18] were used. It is worth noting that the iodoalkene-based aminocarbonylation reaction, described below provided a facile methodology even for the otherwise hardly available α,β-unsaturated hydrazides.

2. Results and discussion

2.1. Aminocarbonylation of iodoalkenes in the presence of 3-amino-3-azabicyclo[3.3.0]octane and SAMP / RAMP as cyclic (1,1-substituted) hydrazines

1-Iodocyclohexene (**1**), 4-*tert*-butyl-1-iodocyclohexene (**2**), α-iodostyrene (**3**) and 17-iodoandrost-16-ene (**4**) were aminocarbonylated in the presence of palladium catalysts formed *in situ* by the reaction of palladium(II) acetate and triphenylphosphine.[19-21] Two 1,1-disubstituted (cyclic) hydrazines, such as 3-amino-3-azabicyclo[3.3.0]octane (**a**) and (*S*)-1-amino-2-methoxymethylpyrrolidine (SAMP, **b**) / (*R*)-1-amino-2-methoxymethylpyrrolidine (RAMP, **c**) (*Scheme 1*) were used as *N*-nucleophiles in DMF.



Scheme 1. Hydrazinocarbonylation of iodoalkenes (**1**-**4**) in the presence of 3-amino-3-azabicyclo[3.3.0]octane (**a**) and SAMP (**b**) or RAMP (**c**) as *N*-nucleophile

The aminocarbonylation of iodoalkenes (**1**-**4**) with **a** resulted in the high-yielding formation of the α,β-unsaturated hydrazide products (**1a-4a**) in all cases (*Table 1*). The reaction is highly chemoselective, no further products could be detected. The increase in carbon monoxide pressure had no influence on the selectivity, that is, no double carbon monoxide insertion leading to 2-ketocarboxamides took place (*entries 3 and 5*). Practically complete conversion was obtained in all cases in 4 h enabling facile isolation of the target products. The high reactivity of iodoalkenes (**1a-4a**) towards nucleophile **a** can be illustrated by the hydrazinocarbonylation of **1** providing conversion of 2%, 10%, 51% and 98% in 0.5 h, 1 h, 2 h and 4h, respectively.

All products were isolated in high analytical purity (>98%) from reaction mixtures when the substrates were practically fully converted (*Table 1).* Good to excellent yields were obtained and the target compounds were fully characterised (See *Experimental*).

Table 1. Palladium-catalysed hydrazinocarbonylation of iodoalkenes (**1**–**4**) in the presence of 3-amino-3-azabicyclo[3.3.0]octane (**a**) [a)]

entry	Substrate	p(CO) [bar]	Isolated yield [%] (compound)
1	**1**	1	83 (**1a**)
2	**2**	1	69 (**2a**)
3	**2**	40	79 (**2a**)
4	**3**	1	54 (**3a**)
5	**3**	40	64 (**3a**)
6	**4**	1	53 (**4a**)

a) Reaction conditions (unless otherwise stated): 1 mmol of substrate (**1**–**4**); 1.2 mmol of **a**; 0.025 mmol of $Pd(OAc)_2$; 0.05 mmol of PPh_3; 0.5 mL of triethylamine; 10 mL of DMF, 50 ^oC; 4 h.

Similarly, carboxamides **1b**–**4b** or **1c**–**4c** were obtained exclusively when the above iodoalkene substrates, **1**–**4** were reacted with **b** (or **c**) under atmospheric carbon monoxide pressure (*Table 2*). As above, the reaction was practically complete in 4 h resulting in good to excellent isolated yields. As for the substrates, the only exception was **3**. In spite of the full conversion and good chemoselectivity, the isolation in high yields was unsuccessful.

When SAMP (or RAMP), *i.e.*, the enantiomerically pure hydrazine derivative was used, a 1/1 mixture of two diastereoisomers was formed in the hydrazinocarbonylation of the chiral substrate **2** applied always as a racemic mixture. On the other hand, the diastereoselectivity of the hydrazinocarbonylation was investigated using (*R/S*)-1-amino-2-methoxymethylpyrrolidine as racemate (**b**/**c**=1/1). No diastereoselection was observed, that is, *ca*. a 1/1 mixture of the two diastereoisomers (**4a**/**4b**) were obtained in the presence of 2.2 equivalents of racemic 1-amino-2-methoxymethylpyrrolidine and **4** as a substrate (*Table 2*).

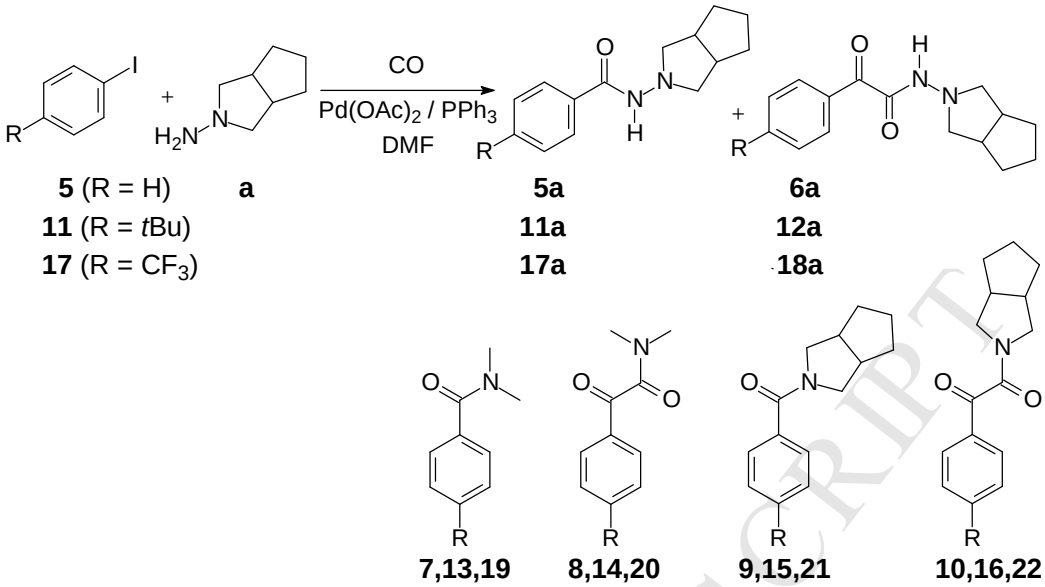
Table 2. Hydrazinocarbonylation of iodoalkenes (**1**–**4**) in the presence of (*S*)-1-amino-2-methoxymethylpyrroplidine (SAMP, **b**) / (*R*)-1-amino-2-methoxymethylpyrrolidine (RAMP, **c**) [a)]

entry	substrate	nucleophile	Isolated yield [%] (compound)
1	**1**	**c**	88 (**1c**)
2	**1**	**b**	80 (**1b**)
3	**2**	**c**	98 (**2c**)
4	**2**	**b**	88 (**2b**)
5	**3**	**c**	40 (**3c**)
6	**3**	**b**	39 (**3b**)
7	**4**	**c**	99 (**4c**)
8	**4**	**b**	84 (**4b**)
9 [b)]	**4**	**b/c**	88 (**4b**/**4c**)[c)]

a) Reaction conditions: 1 mmol of substrate (**1**–**4**); 0.025 mmol of $Pd(OAc)_2$; 0.05 mmol of PPh_3; 1.2 mmol of *N*-nucleophile (**b** or **c**); 0.5 mL of triethylamine; 10 mL of DMF, 50 °C; p(CO)=1 bar, 4 h.
b) 2.2 mmol of racemic **b/c** was used.
c) The two epimers were obtained in a ratio of *ca*. 1/1.

2.2 Hydrazinocarbonylation of iodobenzene in the presence of 3-amino-3-azabicyclo[3.3.0]octane as cyclic (1,1-disubstituted) hydrazine

As a comparison to iodoalkenes, the aminocarbonylation of iodobenzene (**5**) was carried out under similar conditions (*Scheme 2*). The detailed analysis of the reaction mixtures revealed that **5** is much less reactive than **1**–**4** in palladium-catalysed hydrazinocarbonylation and in general, rather complex mixtures can be obtained. In addition to the expected products, benzoic hydrazide (**5a**) and phenylglyoxylic hydrazide (**6a**) formed via mono and double carbon monoxide insertion, respectively, further types of side-products were identified. First, due to the relatively low reactivity of the substrate and the long reaction times, the *N*,*N*-dimethylbenzamide (**7**) and *N*,*N*-dimethylphenylglyoxylamide (**8**) were formed. Second, deamination of nucleophile **a** yielded the formation of two additional carboxamide and 2-ketocarboxamide-type products (**9** and **10**, respectively) containing the 3-azabicyclo[3.3.0]octane moiety only.



Scheme 2. Hydrazinocarbonylation of iodobenzene (**5**), 4-*tert*-butyliodobenzene (**11**) and 4-(trifluoromethyl)-iodobenzene (**17**) in the presence of 3-amino-3-azabicyclo[3.3.0]octane (**a**) as *N*-nucleophile

The formation of *N,N*-dimethylcarboxamide (**7**) and *N,N*-dimethylglyoxylamide (**8**) derivative in the presence of DMF is known in carbonylations. That is, the solvent (DMF) served also as a source of amino or carbamoyl moieties. A similar side-reaction has been observed recently using supported palladium catalysts in the carbonylation of iodobenzene.[22] Furthermore, the various roles of DMF as a reagent, among them as a source of CO, NMe_2, $CONMe_2$ have also been reviewed.[23]

However, the loss of the amino group in hydrazinocarbonylations, to the best of our knowledge, is unprecedented. In these cases **a** served as a precursor of a pyrrolidine type nucleophile whose application might result in carboxamide compounds (**9**, **15**, **21**) and 2-ketocarboxamide compounds (**10**, **16**, **22**) in mono- and double carbon monoxide insertion, respectively.

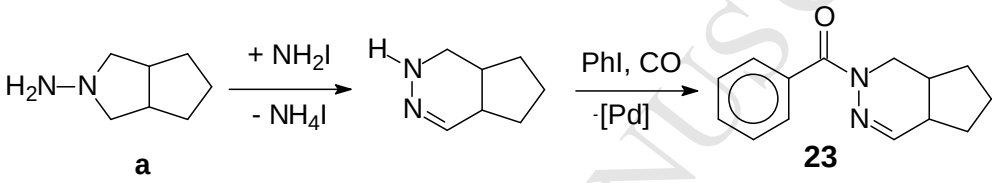
The use of Pd/PPh_3 'in situ' catalyst resulted in a complex reaction mixture (*Table 3, entry 1*). The benzoyl hydrazide (**5a**) can be obtained as major product at higher temperature (*entry 2*). Similar yields of **5a** and higher reactivity was observed using *xantphos* as ligand (*entry 4*). The deamination of **a** and the acylation of the N-nucleophile formed took place in high extent in toluene (*Table 3, entry 3*).

Two further iodobenzenes containing electron releasing (4-*tert*-butyliodobenzene, **11**) and electron-withdrawing groups (4-(trifluoromethyl)iodobenzene, **17**) were also tested as a substrate (*Table 3, entry 5 and 6*). Using **17** as a substrate the carboxamide side-products (**19**, **21**) were obtained in small amount and the corresponding hydrazide **17a** was isolated as a target compound. (Products **18a**, **20** and **22**, whose analogues were obtained as minor products with substrate **5**, were not formed even in traces.) However, **11** showed low reactivity and the product composition was also rather different: carboxamides (**13**, **15**) were obtained in large

amount while the target hydrazide (**11a**) was formed in 29% only, regarding the converted substrate. (Products **12a** and **16**, whose analogues were obtained with substrate **5**, were not formed even in traces.)

The carbonylation reactions carried out under 40 bar CO pressure resulted in the preferred formation of phenylglyoxylhydrazide (**6a**) formed via double carbonylation (*enries 7-9*) while hydrazide **5a** is also present in the reaction mixtures. Higher amount of the target hydrazide (**5a**) and ketohydrazide (**6a**) were obtained at higher temperatures (*entry 8*). Surprisingly, the decarbonylation of **6a** to **5a** was observed in elevated reaction times (*entry 9*).

It is worth noting that the formation of a tetrahydropyridazine derivative (**23**) (*Scheme 3*) possessing the 3,4-diazabicyclo[4.3,0]non-2-ene framework[24] was also observed under 40 bar of CO (*entry 6*). The formation of the diaza-nucleophile can be explained by the oxidation of **a** with the iodoamine formed *in situ* (See *Scheme 4*, cycle-C).



Scheme 3. Formation of the ring expansion product (tetrahydropyridazine derivative) used as nucleophile

The formation of the above products can be rationalized by simplified catalytic cycles (*Scheme 4*). The oxidative addition of the iodoaromatic substrate (**5**) onto palladium(0) complex, the activation of carbon monoxide and its insertion into the Pd-aryl bond resulted in the formation of the acyl complex (**C**). The coordination of the hydrazine derivative and the consecutive loss of hydrogen iodide gave the palladium(II)-amido-acyl complex (**E**) which undergoes reductive elimination leading to palladium(0) complex and **5a** (cycle-A).

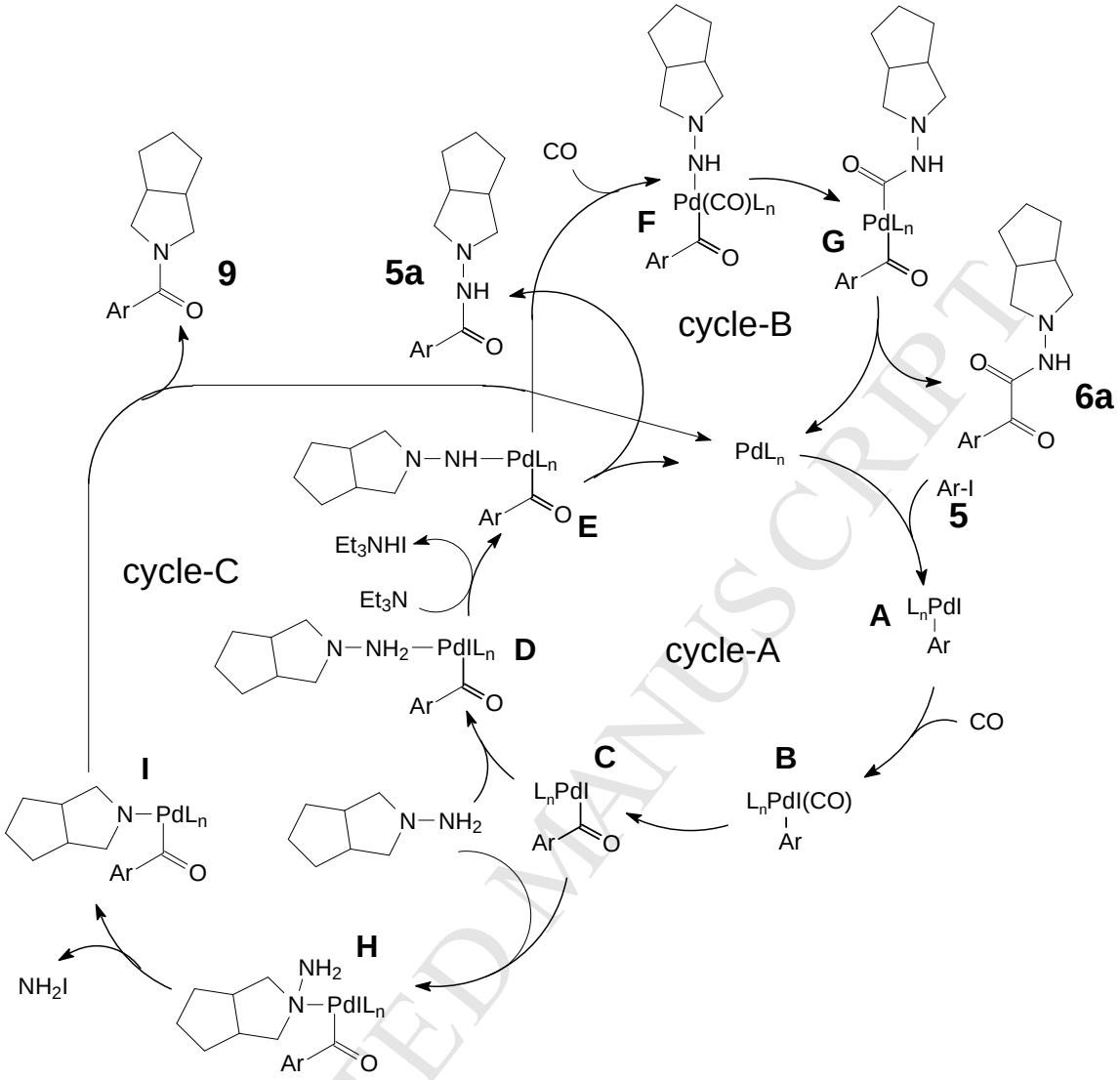
The amido-acyl complex is apt to coordinate a 'second' carbon monoxide, which is inserted into the palladium(II)-amide bond resulting in the acyl-carbamoyl-palladium(II) species (**G**). The reductive elimination provided the double carbonylation product (**6a**) (cycle-B).

It can be supposed that the acyl-iodo complex (**C**) is able to coordinate the hydrazine (**a**) via more nucleophilic (however, sterically more hindered) 'ring-nitrogen' donor yielding complex **H**. The loss of the amino group takes place probably in this step forming amido-acyl-complex (**I**) which provides **9** via reductive elimination (cycle-C). (A further cycle rationalizing the formation of **10** is omitted for clarity. As above, carbon monoxide insertion into palladium(II)-N bond of complex **I** leads to the corresponding carbamoyl complex which might be responsible for the formation of the phenylglyoxyloyl hydrazide **10**.)

Table 3. Palladium-catalysed hydrazinocarbonylation of iodobenzenes (**5, 11, 17**) in the presence of 3-amino-3-azabicyclo[3.3.0]octane (**a**) [a)]

entry	Substr.	p(CO) [bar]	Temp. [°C]	Conv. [%]	Ratio of the reaction products[b)] [%]					
					5a	**6a**	**7**	**8**	**9**	**10**
1	**5**	1	50	45	18	3	16	0	59	4
2	**5**	1	70	76	67	0	16	5	12	0
3[c)]	**5**	1	70	>98	7	0	0	0	93	0
4[d)]	**5**	1	50	>98	65	0	11	13	11	0
5	**11**	1	70	49	29 (**11a**)	0 (**12a**)	41 (**13**)	7 (**14**)	23 (**15**)	0 (**16**)
6	**17**	1	70	92	83 (**17a**)	0 (**18a**)	9 (**19**)	0 (**20**)	8 (**21**)	0 (**22**)
7[e)]	**5**	40	50	88	14	31	9	9	10	10
8	**5**	40	70	>98	48	45	3	0	4	0
9[f)]	**5**	40	70	>98	75	17	0	0	8	0

a) Reaction conditions (unless otherwise stated): 1 mmol of substrate (**5** or **11** or **17**); 1.2 mol of **a**; 0.025 mmol of $Pd(OAc)_2$; 0.05 mmol of PPh_3; 0.5 mL of triethylamine; solvent: 10 mL of DMF; reaction time: 24 h. (The selective formation of a given product obtained by the modification of the reaction conditions is indicated by underlined numbers.)
b) Determined by GC-MS. (In case of substrates **11** and **17** the corresponding products (**11a**–**16** and **17a**–**22**, respectively) are indicated in the table.)
c) 10 mL of toluene as solvent.
d) Pd/xantphos catalyst
e) 17% of tetrahydropyridazine side product (**23**) was formed.
f) Reaction time: 48 h.



Scheme 4. Simplified catalytic cycles leading to products formed in hydrazinocarbonylation of iodobenzene (**5**) in the presence of 3-amino-3-azabicyclo[3.3.0]octane

Conclusions

Iodoalkenes underwent palladium-catalysed hydrazinocarbonylation using 1,1-disubstituted (cyclic) hydrazines (3-amino-3-azabicyclo[3.3.0]octane and (*S*)-1-amino-2-methoxymethylpyrrolidine (SAMP)/(*R*)-1-amino-2-methoxymethyl-pyrrolidine (RAMP) as *N*-nucleophiles. The reaction proved to be completely chemoselective and the unsaturated hydrazides were isolated in moderate to high yields. However, when iodobenzene was used as substrate, the hydrazinocarbonylation was accompanied by side reactions such as deamination of the nucleophile followed by aminocarbonylation with the pyperidine derivative, and aminocarbonylation with DMF as amine source.

3. Experimental

3.1. General procedures

^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ on a Bruker Avance III 500 spectrometer at 500 and 125.7 MHz, respectively. Chemical shifts δ are reported in ppm relative to $CHCl_3$ (7.26 and 77.00 ppm for ^{1}H and ^{13}C, respectively). Elemental analyses were measured on a 1108 Carlo Erba apparatus. Samples of the catalytic reactions were analysed with a Hewlett Packard 5830A gas chromatograph fitted with a capillary column coated with OV-1 (internal standard: naphthalene; injector temp. 250 °C; oven: starting temp. 50 °C (hold-time 1 min), heating rate 15 °C·min^{-1}, final temp. 320 °C (hold-time 11 min); detector temp. 280 °C; carrier gas: helium (rate: 1 mL·min^{-1})). Samples of the catalytic reactions were analysed with an MS (Agilent LC/MSD Trap XCT Plus) (electrospray ionizer, eluent: methanol (0.2 v/v% acetic acid)). The FT-IR spectra were taken in KBr pellets using an IMPACT 400 spectrometer (Nicolet) applying a DTGS detector in the region of 400–4000 cm^{-1}, the resolution was 4 cm^{-1}. The amount of the samples was *ca*. 0.5 mg.

1-Iodocyclohexene[25] (**1**), 4-*tert*-butylcyclohexene[25] (**2**), 1´-iodostyrene[26] (**3**) and 17-iodoandrost-16-ene[27] (**4**) were synthesised by the modified Barton-procedure.[28,29] Iodobenzene and the amine nucleophiles were purchased from Sigma-Aldrich and were used without further purification.

The synthesis of compounds **7**,[30,31] **8**,[32] **13**,[30,31] **14**[32] and **19**[30] have already been described. The analytical data obtained in our laboratory correspond well with those published. For the minor products (**10**, **15**, **21**) MS data are given only, since the isolation in analytically pure form was unsuccessful.

*3.2. Hydrazinocarbonylation (aminocarbonylation) of iodobenzene (**5**) in the presence of 3-amino-3-azabicyclo[3.3.0]octane (**a**) under high carbon monoxide pressure*

In a typical experiment $Pd(OAc)_2$ (5.6 mg, 0.025 mmol), triphenylphosphine (13.2 mg, 0.05 mmol), iodoalkene (**1**–**4**) (1 mmol), 1,1-disubstituted hydrazine (**a, b** or **c**) (1.2 mmol) and triethylamine (0.5 ml) were dissolved in DMF (10 mL) under argon in a 100 mL autoclave. The autoclave was pressurized to the given pressure by carbon monoxide. (Caution: High pressure carbon monoxide should only be used with adequate ventillation (hood) using CO sensors as well.) The reaction was conducted for the given reaction time upon stirring at 50 °C and analyzed by GC and GC-MS. The mixture was then concentrated and evaporated to dryness. The residue was dissolved in chloroform (20 ml) and washed with water (3x20 mL). The organic phase was dried over Na_2SO_4, filtered and evaporated to a crystalline material or to a waxy residue. All compounds were subjected to column chromatography (Silicagel 60 (Merck), 0.063–0.200 mm), MeOH/EtOAc/$CHCl_3$ (the exact ratios are specified in *Characterization* (*3.4.*) for each compound).

*3.3. Hydrazinocarbonylation (aminocarbonylation) of iodoalkenes (**1**–**4**) in the presence of 3-amino-3-azabicyclo[3.3.0]octane (**a**) under atmospheric carbon monoxide pressure*

In a typical experiment $Pd(OAc)_2$, triphenylphosphine, iodoalkene, hydrazine nucleophile and triethylamine were dissolved in DMF (for the quantity of the reagents *See Section 3.2*) under argon in a 100 mL three-necked flask equipped with a gas inlet, reflux condenser with a balloon (filled with argon) at the top. The atmosphere was changed to carbon monoxide. The reaction was conducted for 4 h upon stirring at 50 ^{o}C and analysed by GC and GC-MS. The mixture was then concentrated and evaporated to dryness and worked-up as described in *Section 3.2*.

3.4. Characterization of the products

N-(3-azabicyclo[3.3.0]octane-3-yl)cyclohex-1-enecarboxamide ***(1a)***. Yield: 193.9 mg (83%), pale yellow needles, sublimation point 116–117 °C; [Found: C, 71.55; H, 9.51; N, 11.69; $C_{14}H_{22}N_2O$ requires C, 71.76; H, 9.46; N, 11.95%]; R_f (3% MeOH, 97% $CHCl_3$) 0.62; δ_H (500 MHz, $CDCl_3$) 6.54 (1H, br s, =CH), 6.25 (1H, br s, NH), 3.29 (2H, br s, NC$H_{eq}H_{ax}$), 2.67 (2H, br s, CH(Cp)), 2.36 (2H, br s, NC$H_{ax}H_{eq}$), 2.24 (2H, br s, CH_2), 2.13–2.17 (2H, m, CH_2), 1.56–1.70 (8H, m, 4xCH_2), 1.49 (2H, br s, CH_2); δ_C (125.7 MHz, $CDCl_3$) 167.0, 133.1, 132.8, 62.6, 40.5, 32.2, 25.5, 25.3, 24.4, 22.1, 21.6. IR (KBr ν (cm^{-1})) 3223 (NH), 1657 (CON); MS m/z (rel int.): 234 (8, M^+), 190 (6), 125 (17), 110 (100), 81 (26), 79 (29).

4-(tert-butyl)-N-(3-azabicyclo[3.3.0]octane-3-yl)cyclohex-1-enecarboxamide ***(2a)***. Yield: 229.1 mg (79%), yellow solid, sublimation point 121–122 °C; [Found: C, 74.35; H, 10.21; N, 9.49; $C_{18}H_{30}N_2O$ requires C, 74.44; H, 10.41; N, 9.64%]; R_f (10% EtOAc, 90% $CHCl_3$) 0.34; δ_H (500 MHz, $CDCl_3$) 6.56 (1H, br s, =CH), 6.29 (1H, br s, NH), 3.29 (2H, br s, NC$H_{eq}H_{ax}$), 2.67 (2H, br s, CH), 2.34–2.46 (3H, m, NC$H_{ax}H_{eq}$ and 3-C$H_{eq}H_{ax}$), 2.12–2.23 (2H, m, 3-C$H_{ax}H_{eq}$ and 6-C$H_{eq}H_{ax}$), 1.86–1.94 (2H, m, 5-C$H_{eq}H_{ax}$ and 6-C$H_{ax}H_{eq}$), 1.45–1.96 (6H, m, CH_2), 1.27 (1H, m, 4-CH), 1.16 (1H, qd, 12.2, 4.9 Hz, 5-C$H_{ax}H_{eq}$); δ_C (125.7 MHz, $CDCl_3$) 166.8, 133.7, 132.6, 62.6, 43.4, 40.5, 32.2, 32.1, 27.1, 27.0, 25.9, 25.5, 23.6. IR (KBr ν (cm^{-1})) 3220 (N-H), 1658 (CON); MS m/z (rel int.): 290 (<1; M^+), 275 (2), 246 (6), 165 (3), 125 (23), 110 (100), 81 (27), 57 (17).

N-(3-azabicyclo[3.3.0]octane-3-yl)atropic carboxamide ***(3a)***. Yield: 163.8 mg (64%), orange solid, mp 94–95 °C; [Found: C, 74.74; H, 7.71; N, 10.69; $C_{16}H_{20}N_2O$ requires C, 74.97; H, 7.86; N, 10.93%]; R_f (20% EtOAc, 80% $CHCl_3$) 0.45; δ_H (500 MHz, $CDCl_3$) 7.40 (br s, 5H, CH(Ph)), 6.27 (1H, s, NHCO), 6.09 (1H, d, 0.9 Hz, =CH), 5.65 (1H, d, 0.9 Hz, =CH), 3.28 (2H, t, 8.2 Hz, NC$H_{eq}H_{ax}$), 2.68 (2H, br s, CH), 2.36 (2H, dd, 8.2, 6.1 Hz, NC$H_{ax}H_{eq}$), 1.45-1.67 (6H, m, CH_2); δ_C (125.7 MHz, $CDCl_3$) 165.6, 143.9, 136.7, 128.7, 128.6, 127.9, 121.9, 62.4, 40.5, 32.2, 25.5. IR (KBr ν (cm^{-1})) 3233 (N-H), 1654 (CON); MS m/z (rel int.): 256 (2), 240 (7), 211 (16), 183 (6), 146 (23), 125 (47), 110 (63), 103 (100), 81 (47), 77 (43), 67 (10), 53 (11), 51 (9).

*N-(3-azabicyclo[3.3.0]octane-3-yl)androst-16-en-17-carboxamide (**4a**).* Yield: 218.6 mg (53%), white crystal, mp 93–94 °C; [Found: C, 78.79; H, 10.15; N, 6.59; $C_{27}H_{42}N_2O$ requires C, 78.97; H, 10.31; N, 6.82%]; R_f (2% MeOH, 98% $CHCl_3$) 0.55; δ_H (500 MHz, $CDCl_3$) 6.28 (1H, br s, =CH), 6.20 (1H, s, NHCO), 3.22 (2H, br s, NC$H_{eq}H_{ax}$), 2.65 (2H, br s, CH), 2.44 (2H, br s, NC$H_{ax}H_{eq}$), 2.19 (1H, ddd, 16.2, 5.8, 2.8 Hz, 15- C$H_{eq}H_{ax}$), 0.75-2.00 (27H, m, androstane skeleton protons and 3xCH_2), 0.99 (3H, s, 18-CH_3), 0.83 (3H, s, 19-CH_3); δ_C (125.7 MHz, $CDCl_3$) 164.4, 149.8, 135.4, 62.5, 56.8, 55.2, 47.3, 46.8, 40.5, 38.5, 36.5, 35.0, 33.9, 32.4, 32.0, 31.7, 29.1, 28.9, 26.8, 25.7, 22.2, 20.7, 16.6, 12.2. IR (KBr ν (cm^{-1})) 3279 (N-H), 1646 (CON). MS m/z: 411 (MH^+), 433 (MNa^+), 449 (MK^+); MS^2 (tandem MS) of MH^+ (m/z (rel. int.): 257 (67), 153 (100).

*(R)-N-(2-(methoxymethyl)pyrrolidin-1-yl)cyclohex-1-ene carboxamide (**1c**).* Yield: 210.2 mg (88%); pale yellow needle crystal, mp 92–93 °C; [Found: C, 65.33; H, 9.55; N, 11.52; $C_{13}H_{22}N_2O_2$ requires C, 65.52; H, 9.30; N, 11.75%]; R_f (3% MeOH, 97% $CHCl_3$) 0.53; δ_H (500 MHz, $CDCl_3$) 6.77 (1H, br s, NH), 6.57 (1H, br s, =CH), 3.48 (1H, dd, 9.5, 5.2 Hz, OC$H_a$$H_b$), 3.43 (1H, dd, 9.5, 5.2 Hz, OC$H_a$$H_b$), 3.35 (3H, s, OCH_3), 3.32 (1H, dt, 8.5, 5.5 Hz, NC$H_{eq}H_{ax}$), 3.15 (1H, tt, 7.8, 5.2 Hz, NCH), 2.91 (1H, q, 8.5 Hz, NC$H_{ax}H_{eq}$), 2.24 (2H, br s, CH_2), 2.14–2.18 (2H, m, CH_2), 2.04 (1H, dq, 12.7, 7.8 Hz, 3-C$H_{eq}H_{ax}$), 1.84–1.90 (2H, m, 4-CH_2), 1.59–1.71 (5H, m, 2xCH_2 and 3-C$H_{ax}H_{eq}$); δ_C (125.7 MHz, $CDCl_3$) 167.6, 133.2, 132.9, 75.3, 64.0, 59.2, 55.2, 26.6, 25.3, 24.3, 22.1, 21.5, 21.4. IR (KBr ν (cm^{-1})) 3217 (NH), 1658 (CON); MS m/z (rel int.): 238 (1>, M^+), 206 (5), 193 (100), 129 (5), 114 (47), 109 (23), 97 (29), 85 (15), 81 (19).

*4-(tert-butyl)-N-((R)-2-(methoxymethyl)pyrrolidin-1-yl)cyclohex-1-ene carboxamide (**2c**)* (isolated as a *ca.* 50/50 mixture of two rotamers). Yield: 288.7 mg (98%), yellow viscous oil; [Found: C, 69.47; H, 10.43; N, 9.30; $C_{17}H_{30}N_2O_2$ requires C, 69.35; H, 10.27; N, 9.51%]; R_f (3% MeOH, 97% $CHCl_3$) 0.52; δ_H (500 MHz, $CDCl_3$) 6.78 (1H, br s, NH), 6.59 (1H, dd, 5.2, 2.4 Hz, =CH), 3.48 (1H, dd, 9.5, 5.3 Hz, OC$H_a$$H_b$), 3.43 (1H, dd, 9.5, 5.3 Hz, OC$H_a$$H_b$), 3.36 (3H, s, OCH_3), 3.32 (1H, dq, 8.2, 5.8 Hz, NC$H_{eq}H_{ax}$), 3.16 (1H, tt, 7.6, 5.3 Hz, NCH), 2.92 (1H, qi, 8.2 Hz, NC$H_{ax}H_{eq}$), 2.43 (1H, m, C$H_{eq}H_{ax}$), 2.13–2.25 (2H, m, CH_2), 2.04 (1H, dq, 12.8, 7.6 Hz, C$H_{eq}H_{ax}$), 1.82–1.95 (4H, m, 2xCH_2), 1.66 (1H, dq, 12.8, 7.6 Hz, C$H_{ax}H_{eq}$), 1.28 (1H, tdd, 11.8, 4.6, 1.8 Hz, CH), 1.17 (1H, qd, 12.2, 4.9 Hz, C$H_{ax}H_{eq}$), 0.90 (9H, s, CH_3); δ_C (125.7 MHz, $CDCl_3$) 167.4, 133.8/133.7 (rotamers), 132.6/132.5 (rotamers), 75.3, 64.0/63.9 (rotamers), 59.2, 55.2/55.1 (rotamers), 43.4, 32.1, 27.1, 27.0, 26.6/26.5 (rotamers), 25.8, 23.6, 21.5. IR (KBr ν (cm^{-1})) 3236 (N-H), 1663 (CON); MS m/z (rel int.): 294 (1>, M^+), 279 (4), 263 (4), 249 (100), 182 (7), 165 (5), 129 (13), 114 (56), 57 (12).

*(R)-N-(2-(methoxymethyl)pyrrolidin-1-yl)atropic carboxamide (**3c**).* Yield: 57.2 mg (22%), yellow viscous oil; [Found: C, 69.33; H, 7.80; N, 10.58; $C_{15}H_{20}N_2O_2$ requires C, 69.20; H, 7.74; N, 10.76%]; R_f (5%

MeOH, 95% $CHCl_3$) 0.65; δ_H (500 MHz, $CDCl_3$) 7.44–7.36 (5H, m, Ph), 6.84 (1H, s, NHCO), 6.09 (1H, d, 1.2 Hz, =CH), 5.64 (1H, d, 1.2 Hz, =CH), 3.49 (1H, dd, 9.6, 5.6 Hz, OCH_aH$_b$), 3.43 (1H, dd, 9.6, 4.6 Hz, OCH$_a$H$_b$), 3.32 (1H, m, NCH_{eq}H$_{ax}$), 3.31 (3H, s, OCH_3), 3.16 (1H, m, NCH), 2.91 (1H, q, 8.4 Hz, NCH_{ax}H$_{eq}$), 2.01 (1H, m, CH_{eq}H$_{ax}$), 1.87 (2H, m, CH_2), 1.65 (1H, m, CH_{ax}H$_{eq}$); δ_C (125.7 MHz, $CDCl_3$) 166.1, 144.0, 136.7, 128.6, 128.5, 127.9, 121.7, 75.3, 63.8, 59.1, 55.1, 26.4, 21.4. IR (KBr ν (cm^{-1})) 3236 (N-H), 1670 (CON); MS m/z (rel int.): 260 (1, M^+), 215 (100), 187 (13), 158 (3), 129 (10), 120 (5), 114 (6), 103 (48), 97 (13), 77 (25).

*N-((R)-2-(methoxymethyl)pyrrolidin-1-yl)androst-16-en-17-carboxamide (**4c**)*. Yield: 408.7 mg (99%), light yellow solid, mp 78–79 °C; [Found: C, 75.45; H, 10.34; N, 6.50; $C_{26}H_{42}N_2O_2$ requires C, 75.32; H, 10.21; N, 6.76%]; R_f (5% MeOH, 95% $CHCl_3$) 0.69; δ_H (500 MHz, $CDCl_3$) 6.74 (1H, br s, NH), 6.33 (1H, br s, =CH), 3.48 (1H, dd, 9.6, 5.3 Hz, OCH_aH$_b$), 3.44 (1H, dd, 9.6, 5.3 Hz, OCH$_a$$H_b$), 3.36 (3H, s, OCH_3), 3.32 (1H, dt, 8.4, 5.6 Hz, 24-CH_{eq}H$_{ax}$), 3.20 (1H, tt, 7.6, 5.3 Hz, 21-CH), 2.96 (1H, q, 8.3 Hz, 24-CH_{ax}H$_{eq}$), 2.20 (1H, ddd, 16.3, 6.6, 3.1 Hz, 15-CH_{eq}H$_{ax}$), 0.76–2.14 (25H, m, androstane skeleton protons and 2xCH_2), 1.00 (3H, s, 18-CH_3), 0.84 (3H, s, 19-CH_3); δ_C (125.7 MHz, $CDCl_3$) 165.0, 149.8, 135.7, 75.4, 63.6, 59.2, 56.9, 55.2, 55.1, 47.3, 46.7, 38.5, 36.5, 35.0, 33.9, 32.0, 31.6, 29.0, 28.9, 26.8, 26.6, 22.1, 21.5, 20.7, 16.5, 12.2. IR (KBr ν (cm^{-1})) 3257 (NH), 1654 (CON); MS m/z (rel int.): 414 (1, M^+), 399 (3), 383 (2), 369 (100), 302 (4), 285 (3), 257 (2), 207 (8), 129 (8), 114 (35).

*N-((S)-2-(methoxymethyl)pyrrolidin-1-yl)androst-16-en-17-carboxamide (**4b**)*. Yield: 348.5 mg (84%), yellow solid, mp 118–119 °C; [Found: C, 75.54; H, 10.38; N, 6.52; $C_{26}H_{42}N_2O_2$ requires C, 75.32; H, 10.21; N, 6.76%];R_f (5% MeOH, 95% $CHCl_3$) 0.69; δ_H (500 MHz, $CDCl_3$) 6.75 (1H, br s, NH), 6.32 (1H, br s, =CH), 3.48 (1H, dd, 9.5, 5.5 Hz, OCH_aH$_b$), 3.42 (1H, dd, 9.5, 5.5 Hz, OCH$_a$$H_b$), 3.36 (3H, s, OCH_3), 3.30 (1H, dt, 8.5, 5.5 Hz, 24-CH_{eq}H$_{ax}$), 3.22 (1H, tt, 7.6, 5.5 Hz, 21-CH), 2.97 (1H, q, 8.5 Hz, 24-CH_{ax}H$_{eq}$), 2.20 (1H, ddd, 16.3, 6.4, 3.2 Hz, 15-CH_{eq}H$_{ax}$), 0.75–2.13 (25H, m, androstane skeleton protons and 2xCH_2), 1.00 (3H, s, 18-CH_3), 0.83 (3H, s, 19-CH_3); δ_C (125.7 MHz, $CDCl_3$) 165.1, 149.8, 135.7, 75.3, 63.6, 59.1, 56.8, 55.2, 55.0, 47.3, 46.8, 38.5, 36.5, 35.0, 33.8, 32.0, 31.6, 29.0, 28.9, 26.8, 26.6, 22.1, 21.6, 20.7, 16.6, 12.2. IR (KBr ν (cm^{-1})) 3245 (N-H), 1649 (br s, CON); MS m/z (rel int.): 414 (1, M^+), 399 (4), 369 (100), 281 (6), 207 (7), 129 (7), 114 (47).

*N-(3-azabicyclo[3.3.0]octane-3-yl)benzamide (**5a**)*. Yield: 65.6 mg (28%), colorless needles, sublimation point 118–119 °C; [Found: C, 73.18; H, 7.97; N, 12.01; $C_{14}H_{18}N_2O$ requires C, 73.01; H, 7.88; N, 12.16%]; R_f (10% EtOAc, 90% $CHCl_3$) 0.28; δ_H (500 MHz, $CDCl_3$) 7.75 (2H, d, 7.6 Hz, H_{ortho}(Ph)), 7.51 (1H, t, 7.3 Hz,

H_{para}(Ph)), 7.43 (2H, t, 7.6 Hz, H_{meta}(Ph)), 6.72 (1H, br s, NH), 3.38 (2H, t, 7.8 Hz, NC$H_{eq}H_{ax}$), 2.73 (2H, br s, CH), 2.49 (2H, dd, 7.8, 6.1 Hz, NC$H_{ax}H_{eq}$), 1.50–1.74 (6H, m, CH_2); δ_C (125.7 MHz, $CDCl_3$) 166.0, 133.9, 131.5, 128.6, 127.0, 62.7, 40.5, 32.2, 25.6. IR (KBr ν (cm^{-1})) 3212 (NH), 1643 (CON); MS m/z (rel int.): 230 (<1, M^+), 125 (40), 110 (100), 105 (42), 81 (50), 77 (58), 51 (20).

N-(3-azabicyclo[3.3.0]octane-3-yl)phenylglyoxylamide ***(6a)***. Yield: 32.7 mg (13%), white crystal, sublimation point 125–126 °C; R_f 0.53 (20% EtOAc, 80% $CHCl_3$); (ca. 1/2 mixture of two C(O)N rotamers) δ_H (500 MHz, $CDCl_3$) 8.33/7.95 (minor/major) (2H, d, 7.3 Hz, H_{ortho}(Ph)), 7.64 (1H, t, 7.3 Hz, H_{para}(Ph)), 7.53/7.49 (major/minor) (2H, t, 7.9/7.6 Hz, H_{meta}(Ph)), 7.34 (1H, br s, NH), 3.28/2.73 (minor/major) (2H, t, 8.1 Hz, NC$H_{eq}H_{ax}$), 2.73/2.35 (minor/major) (2H, br s, CH), 2.58/2.53 (major/minor) (2H, d/dd, 8.2/8.5, 5.5 Hz, NC$H_{ax}H_{eq}$), 1.50–1.74 (minor) (6H, m, CH_2), 1.50–1.61 (major) (2H, m, CH_2), 1.19–1.35 (major) (2H, m, CH_2), 0.90 (major) (2H, br s, CH_2); δ_C (125.7 MHz, $CDCl_3$) 191.5/188.2 (major/minor), 169.5/159.7 (major/minor), 134.5/133.9 (minor/major), 133.3, 131.1/128.7 (minor/major), 128.6/128.5 (major/minor), 62.5/62.4 (major/minor), 40.5/40.2 (minor/major), 33.5/32.3 (major/minor), 26.2/25.7 (major/minor). IR (KBr ν (cm^{-1})) 3248 (NH), 1695 (CO), 1686 (CO), 1677 (CON), 1656 (CON); MS m/z (rel int.): 258 (<2, M^+), 185 (11), 125 (100), 110 (89), 105 (83), 81 (76), 77 (95), 67 (17), 51 (35).

N-(3-azabicyclo[3.3.0]octane-3-yl)-4-(tert-butyl)benzamide ***(11a)***. Yield: 56.1 mg (20%), yellow viscous oil; [Found: C, 75.55; H, 9.02; N, 9.60; $C_{18}H_{26}N_2O$ requires C, 75.48; H, 9.15; N, 9.78%]; R_f (10% EtOAc, 90% $CHCl_3$) 0.39; δ_H (500 MHz, $CDCl_3$) 7.69 (2H, d, 8.2 Hz, H_{ortho}(Ph)), 7.44 (2H, d, 8.2 Hz, H_{meta}(Ph)), 6.80 (1H, br s, NH), 3.35 (2H, t, 7.6 Hz, NC$H_{eq}H_{ax}$), 2.71 (2H, br s, CH), 2.49 (2H, t, 7.6 Hz, NC$H_{ax}H_{eq}$), 1.48–1.74 (6H, m, CH_2), 1.34 (9H, s, CH_3); δ_C (125.7 MHz, $CDCl_3$) 165.9, 155.0, 131.0, 126.8, 125.5, 62.6, 40.5, 34.9, 32.2, 31.2, 25.6. IR (KBr ν (cm^{-1})) 3249 (NH), 1651 (CON); MS m/z (rel int.): 286 (<1, M^+), 242 (7), 162 (30), 161 (30), 125 (22), 110 (100), 81 (22).

N-(3-azabicyclo[3.3.0]octane-3-yl)-4-(trifluoromethyl)benzamide ***(17a)***. Yield: 175.4 mg (59%), colorless needles, sublimation point 121–122 °C; [Found: C, 60.25; H, 5.90; N, 9.22; $C_{15}H_{17}N_2O_2F_3$ requires C, 60.40; H, 5.74; N, 9.39%]; R_f (2% MeOH, 98% $CHCl_3$) 0.50; δ_H (500 MHz, $CDCl_3$) 7.86 (2H, d, 7.9 Hz, H_{ortho}(Ph)), 7.70 (2H, d, 7.9 Hz, H_{meta}(Ph)), 6.70 (1H, br s, NH), 3.37 (2H, t, 7.6 Hz, NC$H_{eq}H_{ax}$), 2.74 (2H, br s, CH), 2.52 (2H, br s, NC$H_{ax}H_{eq}$), 1.50–1.74 (6H, m, CH_2); δ_C (125.7 MHz, $CDCl_3$) 164.8, 137.3, 133.1 (q, 32.7Hz, 4-C(Ph)), 127.6, 125.5, 123.7 (q, 272.5Hz, CF_3), 62.4, 40.5, 32.2, 25.5. δ_F (470.4 MHz, $CDCl_3$) -63.0 (s, CF_3). IR (KBr ν (cm^{-1})) 3209 (NH), 1650 (CON), 1330 (ν_{as}, CF_3), 1127 (ν_s, CF_3); MS m/z (rel int.): 298 (2, M^+), 279 (2), 190 (5), 173 (35), 145 (54), 125 (100), 110 (96), 81 (88), 69 (23).

*3-benzoyl-3-azabicyclo[3.3.0]octane (**9**).* Yield: 49.3 mg (23%), yellow viscous oil; R_f (20% EtOAc, 80% $CHCl_3$) 0.38; δ_H (500 MHz, $CDCl_3$) 7.38–7.49 (5H, m, Ph, 3.87 (1H, t, 8.9 Hz, NCH_{eq}H$_{ax}$), 3.62 (1H, t, 8.9 Hz, NCH_{eq}H$_{ax}$), 3.52 (1H, d, 8.5 Hz, NCH_{ax}H$_{eq}$), 3.21 (1H, d, 8.5 Hz, NCH_{ax}H$_{eq}$), 2.72 (1H, br s, CH), 2.65 (1H, br s, CH), 1.36–1.90 (6H, m, CH_2); δ_C (125.7 MHz, $CDCl_3$) 169.5, 137.3, 129.6, 128.2, 127.1, 55.3, 51.8, 43.8, 42.0, 32.3, 31.7, 25.6. MS m/z (rel int.): 215 (51, M^+), 186 (15), 110 (5), 105 (100), 77 (62), 67 (12), 51 (13).

*3-phenylglyoxyloyl-3-azabicyclo[3.3.0]octane (**10**).* MS m/z (rel int.): 243 (<2, M^+), 138 (93), 110 (30), 105 (77), 95 (82), 77 (100), 67 (32), 51 (29).

*3-(4'-tert-butylbenzoyl)-3-azabicyclo[3.3.0]octane (**15**).* MS m/z (rel int.): 217 (60, M^+),.242 (11), 161 (100), 146 (18), 118 (21), 91 (11).

*3-(4'-trifluoromethylbenzoyl)-3-azabicyclo[3.3.0]octane (**21**).* MS m/z (rel int.): 283 (52, M^+), 264 (8), 254 (16), 173 (100), 145 (55), 126 (7), 110 (6), 95 (8).

*4-benzoyl-3,4-diazabicyclo[4.3.0]non-2-ene (**23**).* MS m/z (rel int.): 228 (11, M^+), 123 (11), 105 (100), 77 (63), 51 (14).

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