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Formal reductive addition of acetonitrile to aldehydes and ketones

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† Dedicated to Professor Yuri N. Belokon (Nesmeyanov Institute, Moscow) on the occasion of his 80th birthday.

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Abstract

An efficient and highly productive rhodium-catalyzed method for nitriles synthesis employing aldehydes or ketones, methyl cyanoacetate, water and carbon monoxide as starting materials has been developed. Simple rhodium chloride without any ligands can be used. The fine tuning for the substrate can lead to the activity higher than 5000 TON.

INTRODUCTION

Nitriles are versatile, useful building blocks for organic synthesis[1]. Their utility is amply demonstrated as solvents[1a], initiators of radical chain polymerization[1b], raw materials in the production of fiber-forming polymers[1c] (Nylon) and among other [1d-f]. Nitriles are also frequently encountered structural subunits in numerous bioactive natural products[1g] and pharmaceuticals[1h]. Examples of bioactive agents include Saxagliptin, Odanacatib, Vildagliptine and precursors of Pregabalin[6b] and human renin inhibitors[6b] (Figure 1). In addition, nitriles have occupied a certain niche in organic synthesis[2] being the precursors of amines[2a], carbonyl compounds[2a] and various heterocyclic substances[2b,c,d,e]. The methods which have been devised for the synthesis of alkyl nitriles via C-C bond formation include[3] borrowing-hydrogen approach[3a], radical path[3b], alkylation of active methylene compounds with alkyl halides[3c] and nucleophilic substitution in alkyl halides[3d]. Other recent approaches[4] for the synthesis of aryl and alkyl nitriles are deacylative C-C cleavage[4a], transoximation approach[4b], ammoxidation of methylarenes[4c], transnitrilation[4d] and among other[5]. Arguably, the reductive

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alkylation of active methylene compounds is one of the most direct methods for the synthesis of nitriles. Although different heterogeneous and

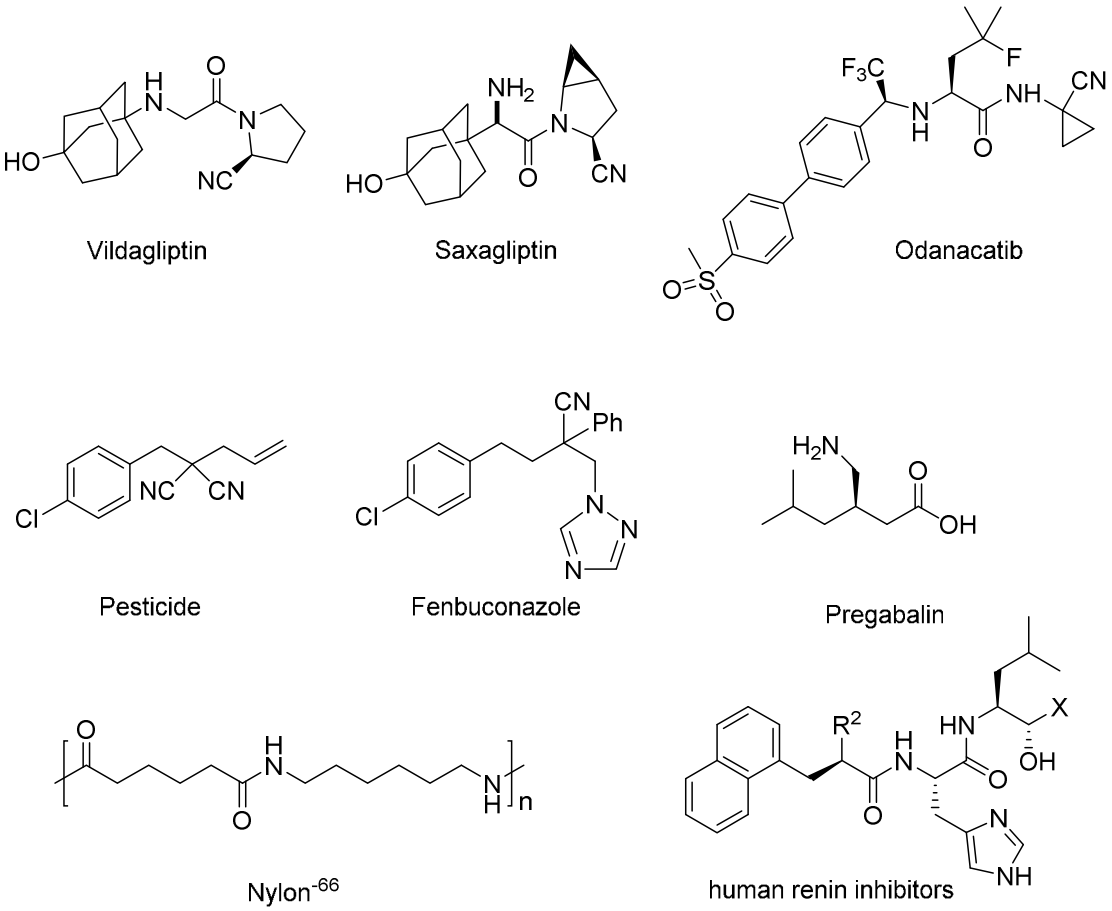

Figure 1. Nitriles used in medicine, in textile industry, agrochemistry.

homogeneous-catalyzed variants of this reaction have been suggested in recent years, there is paucity in tandem reductive alkylation protocols of active methylene compounds with reductants other than molecular hydrogen[5b,6]. Reported procedures for one-pot reductive condensation involve most often metal-catalyzed processes (Rh[6a,b], Pd[5b,5j], Pt[5b]). The abovementioned protocols are riddled with some drawbacks. For example, the main drawback of the use of alkyl halides in alkylation of active methylene compounds is their low selectivity causing overalkylation. Also, HCN and cyanide salts that are often used to prepare nitriles[7] are very toxic (KCN: LD_{50} 5–10 mg/kg; malononitrile: LD_{50} 14 mg/kg). Besides, the abovementioned approaches in many cases have low atom-efficiency, low step economy or low selectivity and require special reagents (boronic derivatives and etc.). The classical approach also suffers from narrow

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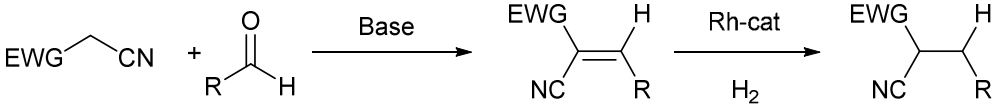
substrate scope, switching reaction from p-methoxybenzaldehyde to p-methylbenzaldehyde decreases the chemical yield (62% to 19%)[8] (Scheme 1).

Scheme 1. Classical approach



Ref. 8 Yield 7-71% (average 35%) 5% Rh-cat

At the same time, approaches involving the use of CO as a reducing agent or CO coupled with water proved to be atom efficient and very selective[6,9]. In particular, Denmark et al. have recently developed method of coupling of active methylene with carbonyl compounds having an indisputable advantage of mild reaction conditions[6c]. Recently, our group developed a direct approach towards nitriles utilizing aldehydes, methyl cyanoacetate, water and CO as starting materials[6a]. Despite good yields, these methods have their own limitations such as relatively high catalytic loading (1-3 mol%). Since the ubiquity of carbonyl compounds is provided by their availability from oil and crude oil products by hydroformylation or Gatterman-Koch methodology, formal reductive addition of acetonitrile to aldehydes and ketones employing the reducing power of carbon monoxide could provide practical, atom- and step-economical method for the nitrile synthesis. Given the importance of nitriles and the paucity of formal reductive addition routes to these intermediates, we sought to develop more general and low catalyst loading method for their synthesis.

RESULTS AND DISCUSSION

Our studies commenced with an experiment in which p-tolylaldehyde **1** and methyl cyanoacetate **2** ($NCCH_2COOMe$: LD_{50} 3062 mg/kg, one of the highest values among cyanide derivatives) were exposed to CO in the presence of a catalytic amount of (1 mol %) $RhCl_3 \cdot 3H_2O$ in MeOH containing two equivalents of water. A facile reaction occurred at 160 ^oC under CO pressure of 50 bar and obtained a mixture **3** & **4** in 1:1 ratio (Table 1, entry 1). Next, we investigated the effect of different solvents (Table 1, entries 2-5) but MeOH along with water remain superior (Table 1, entries 1 & 3) and was chosen for subsequent studies. An increase in the amount of water was advantageous to the formation of the product **4** (Table 1, entries 1, 6 - 7). Furthermore, extending the reaction time to 6

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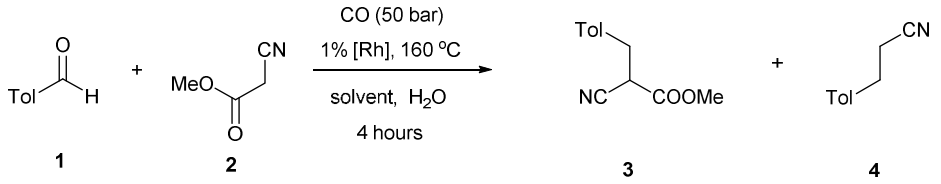
hours furnished product **4** in 77% (Table 1, entry 8). Furthermore, homogeneous catalysts including those have shown excellent results in reductive amination[9i] failed to improve the yield (Table 1, entries 11-13). Though $[(Cod)RhCl]_2$, afforded **4** in 87% yield, however, we refrained from its use due to its rather high cost. Interestingly, when the catalytic loading of $RhCl_3 \cdot 3H_2O$ was reduced to 0.5% or 0.2% the yield of **4** was increased up to 85% (Table 1, entries 14 and 15), which is in the level of the catalytic performance of $[(Cod)RhCl]_2$. With the optimal reaction conditions in hand, we set out to explore the generality of the procedure using both aromatic and aliphatic aldehydes.

Table 1. Optimization of the reaction conditions



1 **2** **3** **4**

#	Catalyst	Solvent	Water, eq	**3**[a], %	**4**[a], %
1	$RhCl_3 \cdot 3H_2O$	MeOH	2	43	43
2	$RhCl_3 \cdot 3H_2O$	THF	2	24	41
3	$RhCl_3 \cdot 3H_2O$	H_2O	50	0	47
4	$RhCl_3 \cdot 3H_2O$	EtOH	2	15 (+48)[b]	22
5	$RhCl_3 \cdot 3H_2O$	iPrOH	2	30 (+38)[c]	16
6	$RhCl_3 \cdot 3H_2O$	MeOH	5	24	68
7	$RhCl_3 \cdot 3H_2O$	MeOH	10	12	71
8[d]	$RhCl_3 \cdot 3H_2O$	MeOH	5	4	77
9	$[(C_4Et_4)Rh(p\text{-xylene})]PF_6$	MeOH	5	63	16
10	$[(Cod)RhCl]_2$	MeOH	5	9	87
11	IndRhCp PF_6	MeOH	5	43	17
12	$Rh_2(tfa)_4$	MeOH	5	4	78
13	$[Cp^*RhCl_2]_2$	MeOH	5	6	66
14[e]	$RhCl_3 \cdot 3H_2O$	MeOH	5	1	82
15[f]	$RhCl_3 \cdot 3H_2O$	MeOH	5	1	85

[a] Yields were determined by NMR with internal standard,[b,c] transesterification product with solvent is observed, [d] 6 hours, [e] 0.5 mol% of the catalyst, 6 hours, [f] 0.2 mol% of the catalyst, 6 hours.

The methodology tolerates a wide range of aldehydes with various electronic nature and substituents. Ortho- (**7**), meta- (**6**) and para-methoxy (**5**) substituted benzaldehydes transformed into nitriles in very good yields (>80%). Electron rich (**5**) and electron deficient benzaldehydes (**8**, **9**) and 1-naphthaldehyde (**13**) gave essentially the same good results. Slightly worse performance was observed for 3-bromo-4-methoxy- (**10**), 3-phenoxy- (**12**) and 4-hydroxy- benzaldehydes (**11**). We were especially intrigued to find that aliphatic aldehydes were competent

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substrates. Among 2-phenyl (**15**) and 3-phenylpropionic (**14**) aldehydes the latter gave better yield. It should be noted that functional group tolerance is one of the key beneficial features of this transformation enabling the synthesis of halogen (Br, Cl) as well as OH-functionalized nitriles (**8**-**11**). Importantly, suitability of ketones for this reaction has been exemplified by using 4-phenyl-2-butanone (**17**) and cyclohexanone (**18**), cyclopentanone (**19**), cyclobutanone (**20**). For ketones, a slightly different optimization condition was chosen (Scheme 2). It should be noted that preparation of nitrile derivatives from ketones is less common than from aldehydes[10]. For the best of our knowledge, there was no examples of one-step formal addition of acetonitrile to ketones.

Scheme 2. Scope of aldehydes and ketones used in the reaction

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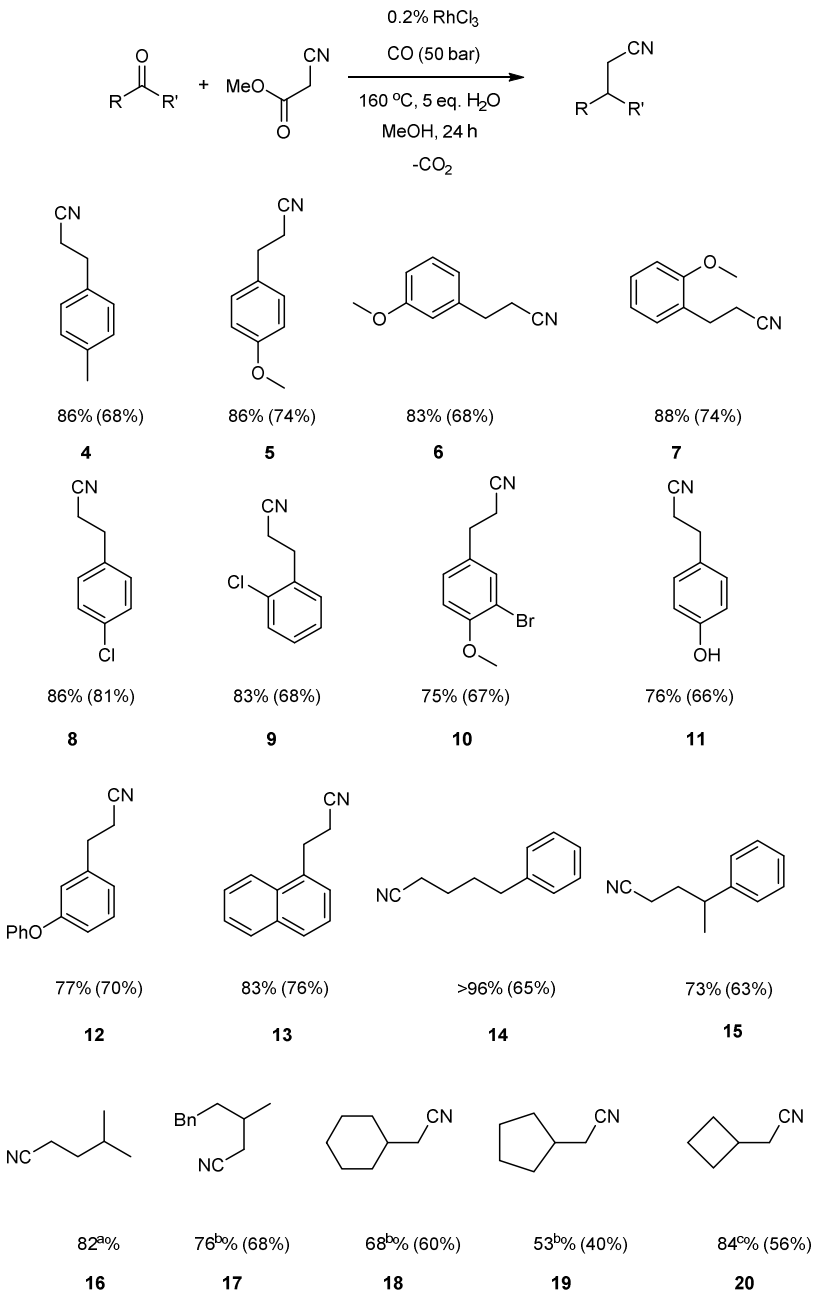

NMR yield, isolated yield in parenthesis.[a]0.02 mol% $RhCl_3$, [b]1.5 eq. of methyl cyanoacetate, 1 eq. of water, 2 mol% $RhCl_3 \cdot 3H_2O$, [c]1.5 eq. of methyl cyanoacetate, 2 eq. of water, 2 mol% $RhCl_3 \cdot 3H_2O$

Further studies have revealed the superiority of our strategy compared to conventional reduction systems ($NaBH_4$, H_2)[11]. Changing the reducing agent to $NaBH_4$ dramatically reduces selectivity of the process, affording no product in the reaction mixture. As far as the reduction with H_2 is concerned, it provides mixture of unidentified products with formation of the desired nitrile in 20% yield (Scheme 3).

Scheme 3. Comparison of selectivity of different reducing agents

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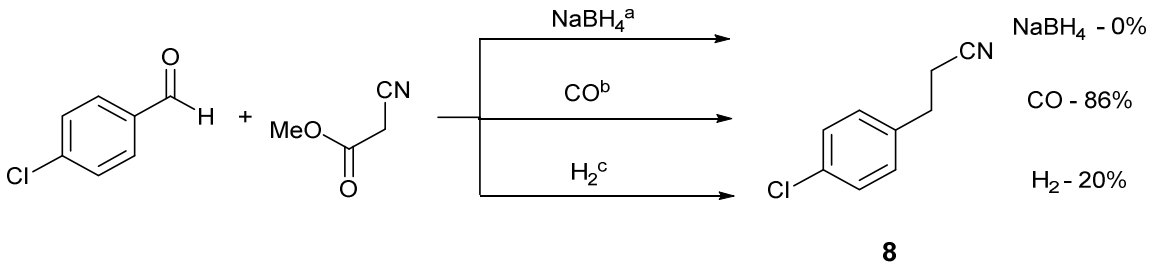
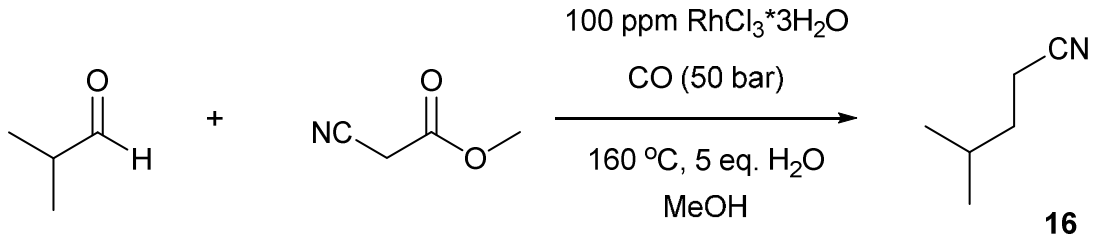


8

Conditions: [a] 0.2 mol% $RhCl_3 \cdot 3H_2O$, 417 mol% $NaBH_4$, 24h, 65°C, [b] 0.2 mol% $RhCl_3 \cdot 3H_2O$, 24h, 160 °C, 50 bar CO, [c] 0.2 mol% $RhCl_3 \cdot 3H_2O$, 24h, 160 °C, 50 bar H_2

The efficiency of this rather low catalyst loading reductive addition was further demonstrated in the case of isobutyraldehyde. It was found that catalytic system consisting of $RhCl_3 \cdot 3H_2O$ is quite stable and very low catalyst loadings (100 ppm) could be achieved producing the corresponding nitrile **16** with a TON of 5600 (the average of two experiments) (Scheme 4).

Scheme 4. Testing the catalytic activity



16

TON=5600 average of two experiments

The FT-IR experiments show two absorption bands at 2001 and 2076 cm^{-1} (see SI) which corresponds to the rhodium carbonyl intermediate. These results also correlate with our previous experiments[13], where we monitored formation rhodium carbonyl complex and subsequent formation of rhodium hydride (cf. D, scheme 5). On the basis of experiments discussed in this article and our previous reports[6a,b], a plausible process of the tandem catalytic reductive addition is depicted in Scheme 5. The addition of methyl cyanoacetate to the carbonyl compound provides the alcohol **A**. The alcohol **A** could deliver alkene **G** but we found that preformed alkene **G** reacts much slower under the reaction conditions (see SI). Alternatively, $RhCl_3$ catalysed deoxygenation of the alcohol **A** followed by the reduction affords ester **E**. The hydrolysis of the ester **E** (see SI) and a late stage decarboxylation resultant carboxylic acid **F** delivers the alkyl nitrile (scheme 5).

Scheme 5. Tandem catalytic process

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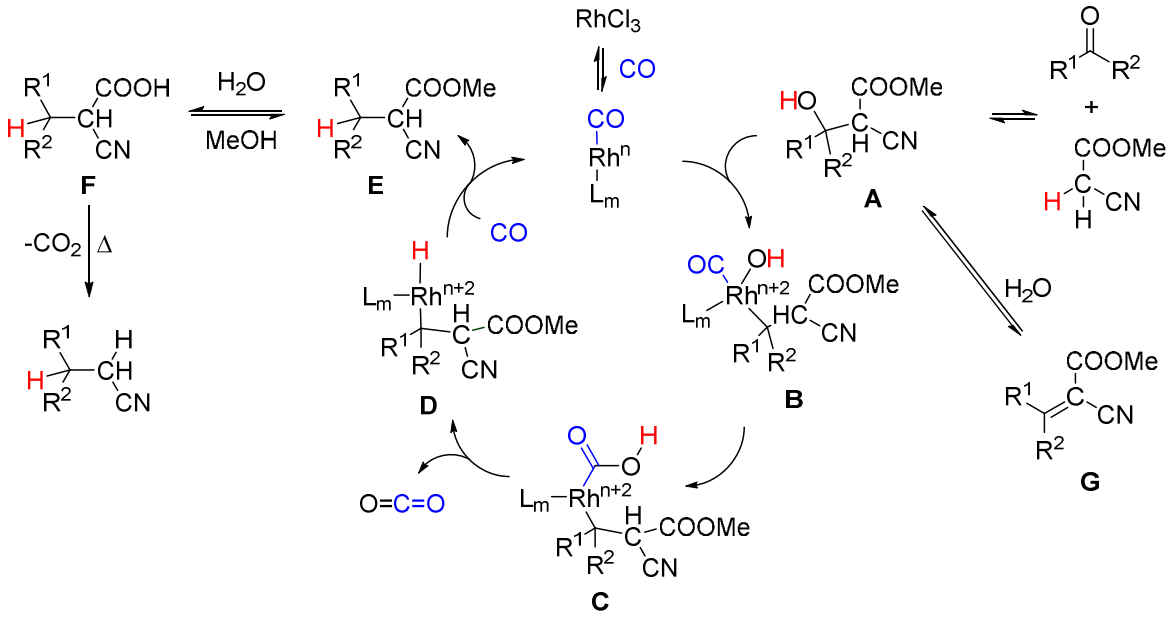

CONCLUSION

In conclusion, we have developed an easy one-step procedure for the formal reductive addition of acetonitrile to aldehydes with a TON 365-5600 and ketones. To the best of our knowledge, this TON exceeds any other existing protocols for this type of reaction. Furthermore, remarkable chemoselectivity was achieved in the reductive addition of aldehydes containing chlorine, bromine or hydroxy groups. Given the ready availability of rhodium chloride precatalyst, aldehydes or ketones and cyanoacetates, we anticipate further applications of this methodology.

EXPERIMENTAL SECTION

General methods and materials

Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification. Rhodium complexes $[(C_4Et_4)Rh(p\text{-xylene})]PF_6$[9i], $IndRhCpPF_6$[12a] were synthesized according to published procedures. For all reactions, distilled water was used. Carbon monoxide of >98% purity was obtained from NII KM (Moscow, Russia). Isolation of products was performed by column chromatography (Acros Organics, silica gel 0.06-0.200 mm). The ^1H and ^{13}C NMR spectroscopic data were recorded with Bruker AV-300, AV400, and AV-600 spectrometers at ambient temperature. Chemical shifts are reported in parts per million relative to $CHCl_3$ (7.26

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and 77.16 ppm for ^{1}H and ^{13}C respectively). Chemical shifts δ are reported in ppm relative to the solvent resonance signal as an internal standard. The following abbreviations were used to designate chemical shift multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, sept = septet, m = multiplet, br = broad; coupling constants are given in Hertz (Hz). GC detection was performed on GC Chromatec Crystall 5000.2.

General procedure for synthesis of nitriles

10 mL stainless-steel autoclave was charged with the catalyst (0.02–2 mol%), methanol, methyl cyanoacetate, water and the carbonyl compound. Catalyst should be weigh better in a solid form than be added as an aliquot to obtain about 5-10% more product according to NMR yield. The autoclave was sealed, flushed 3 times with 10 bar of CO, and then charged with 50 bar CO. The reactor was placed into a preheated to 160 °C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were combined and then concentrated on a rotary evaporator, extracted with dichloromethane from water, solvent was removed under reduced pressure and the residue was analyzed by NMR. The residue was purified by column chromatography on silica gel.

Reaction of 4-chlorobenzaldehyde with $NaBH_4$

To a stirred solution of $RhCl_3 \cdot 3H_2O$ (2.16 mg; 8.2 μmol; 0.2 mol%), 4-chlorobenzaldehyde (576 mg; 4.10 mmol; 100 mol%), methyl cyanoacetate (362.9 μl; 407.5 mg; 4.11 mmol; 100 mol%), methanol (2 ml) and water (367.2 μl; 367.2 mg; 20.40 mmol; 497 mol%) in 25 ml flask with reflux condenser was added $NaBH_4$ (647.4 mg; 17.11 mmol; 417 mol%) and stirred for 24h at 65^0C. The reaction mixture was filtered, the flask was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were combined and then concentrated on a rotary evaporator, extracted with dichloromethane from water, solvent was removed under reduced pressure and the residue was analyzed by NMR (no product was observed).

Reaction of 4-chlorobenzaldehyde with H_2

A 10 ml stainless steel autoclave was charged with $RhCl_3 \cdot 3H_2O$ (0.2 mg; 0.76 μmol; 0.2 mol%), 4-chlorobenzaldehyde (50 mg; 0.36 mmol; 100 mol%), methanol (356 μl), methyl cyanoacetate (31 μl; 0.35 mmol; 97 mol%) and water (32 μl; 1.78 mmol; 494

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mol%). The autoclave was sealed, flushed 3 times with 10 bar of H_2, and then charged with 50 bar H_2. The reactor was placed into a preheated to 160 °C oil bath. After 24 h, the reactor was cooled to room temperature and depressurized. The reaction mixture was transferred to a flask, and the autoclave was washed with dichloromethane (2 × 1 mL). The reaction mixture and the dichloromethane rinsings were combined and then concentrated on a rotary evaporator, extracted with dichloromethane from water, solvent was removed under reduced pressure and the residue was analyzed by NMR (20% of the product).

3-(p-tolyl)propanenitrile (4)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.56 mg; 2.1 μmol; 0.2 mol%), 4-methylbenzaldehyde (125 μl; 127.4 mg; 1.06 mmol; 100 mol%), methanol (475 μl), methyl cyanoacetate (94.1 μl; 105.7 mg; 1.07 mmol; 101 mol%) and water (95.2 μl; 95.2 mg; 5.28 mmol; 498 mol%). 86% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 30/1 (R_f = 0.18). Isolated as colourless oil - 68% (105 mg). The obtained NMR data was in agreement with the literature report[12b].

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 – 7.10 (m, 4H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.60 (t, *J* = 7.4 Hz, 2H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 136.9, 135.1, 129.6, 128.2, 119.3, 31.2, 21.1, 19.5

3-(4-methoxyphenyl)propanenitrile (5)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.56 mg; 2.1 μmol; 0.21 mol%), 4-methoxybenzaldehyde (136 μl; 152.2 mg; 1.12 mmol; 100 mol%), methanol (475 μl), methyl cyanoacetate (94.1 μl; 105.6 mg; 1.07 mmol; 96 mol%) and water (95.2 μl; 95.2 mg; 5.28 mmol; 472 mol%). 86% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 10/1 (R_f = 0.18). Isolated as pale-yellow oil - 74% (127 mg). The obtained NMR data was in agreement with the literature report[6b].

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, *J* = 8.5 Hz, 2H), 6.87 (d, *J* = 8.5 Hz, 2H), 3.79 (s, 3H), 2.89 (t, *J* = 7.3 Hz, 2H), 2.57 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 158.7, 130.2, 129.4, 119.4, 114.2, 55.3, 30.7, 19.7

3-(3-methoxyphenyl)propanenitrile (6)

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Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.25 mg 0.95 µmol; 0.2 mol%), 3-methoxybenzaldehyde (58 µl; 64.8 mg; 0.48 mmol; 100 mol%), methanol (238 µl), methyl cyanoacetate (42 µl; 47.1 mg; 0.48 mmol; 100 mol%) and water (42.5 µl; 42.5 mg; 2.36 mmol; 491 mol%). 83% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 10/1 (R_f = 0.17). Isolated as pale-yellow oil - 68% (53 mg). The obtained NMR data was in agreement with the literature report[12c].

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.32 (dd appears as t, *J* = 7.8 Hz, 1H), 6.93 – 6.81 (m, 3H), 3.87 (s, 3H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.67 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 159.9, 139.7, 130.0, 120.6, 119.3, 114.1, 112.5, 55.3, 31.6, 19.3

3-(2-methoxyphenyl)propanenitrile (7)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.56 mg 2.1 µmol; 0.2 mol%), 3-methoxybenzaldehyde (144.5 mg; 1.06 mmol; 100 mol%), methanol (475 µl), methyl cyanoacetate (92.4 µl; 103.8 mg; 1.05 mmol; 99 mol%) and water (93.5 µl; 93.5 mg; 5.19 mmol; 490 mol%). 88% NMR yield. Purification: gradient column chromatography, eluent hexane/ethyl acetate from 30/1 (R_f = 0.14) to 15/1 (R_f = 0.21). Isolated as pale-yellow oil - 74% (125 mg). The obtained NMR data was in agreement with the literature report[12d].

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.33 (dd appears as t, *J* = 7.8 Hz, 1H), 7.25 (d, *J* = 7.4 Hz, 1H), 7.06 – 6.89 (m, 2H), 3.90 (s, 3H), 3.02 (t, *J* = 7.4 Hz, 2H), 2.69 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3, 130.3, 128.7, 126.4, 120.7, 119.8, 110.4, 55.2, 27.1, 17.5

3-(4-chlorophenyl)propanenitrile (8)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.2 mg 0.76 µmol; 0.2 mol%), 4-chlorobenzaldehyde (50 mg; 0.36 mmol; 100 mol%), methanol (260 µl), methyl cyanoacetate (31 µl; 34.8 mg; 0.35 mmol; 97 mol%) and water (32 µl; 32 mg; 1.80 mmol; 500 mol%). 86% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 20/1 (R_f = 0.13). Isolated as colourless oil - 81% (47.1 mg). The obtained NMR data was in agreement with the literature report[12d].

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^{1}H NMR (300 MHz, $CDCl_3$) δ 7.31 (d, *J* = 8.3 Hz, 2H), 7.17 (d, *J* = 8.3 Hz, 2H), 2.92 (t, *J* = 7.3 Hz, 2H), 2.60 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 136.5, 133.2, 129.8, 129.1, 119.0, 30.9, 19.4

3-(2-chlorophenyl)propanenitrile (9)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.22 mg 0.83 μmol; 0.23 mol%), 2-chlorobenzaldehyde (40 μl, 50 mg; 0.36 mmol; 100 mol%), methanol (250 μl), methyl cyanoacetate (31 μl; 34.8 mg; 0.35 mmol; 97 mol%) and water (32 μl; 32 mg; 1.80 mmol; 500 mol%). 83% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 20/1 (R_f = 0.21). Isolated as colourless oil - 68% (39.3 mg). The obtained NMR data was in agreement with the literature report[6a].

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.30 (m, 1H), 7.30 – 7.15 (m, 3H), 3.05 (t, *J* = 7.3 Hz, 2H), 2.64 (t, *J* = 7.3 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 135.6, 133.8, 130.9, 129.9, 129.0, 127.4, 119.0, 29.7, 17.5

3-(3-bromo-4-methoxyphenyl)propanenitrile (10)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.17 mg 0.65 μmol; 0.2 mol%), 3-bromo-4-methoxybenzaldehyde (70 mg; 0.326 mmol; 100 mol%), methanol (250 μl), methyl cyanoacetate (28.7 μl; 32.2 mg; 0.33 mmol; 100 mol%) and water (29 μl; 29 mg; 1.61 mmol; 494 mol%). 75% NMR yield. Purification: gradient column chromatography, eluent hexane/ethyl acetate from 25/1 (R_f = 0.05) to 10/1. Isolated as pale-yellow oil - 67% (52.2 mg). The obtained NMR data was in agreement with the literature report[6a].

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.15 (d, *J* = 8.4 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 3.87 (s, 3H), 2.86 (t, *J* = 7.2 Hz, 2H), 2.58 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 155.1, 133.1, 131.6, 128.5, 119.0, 112.2, 111.8, 56.3, 30.3, 19.6

3-(4-hydroxyphenyl)propanenitrile (11)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.28 mg 1.06 μmol; 0.2 mol%), 4-hydroxybenzaldehyde (65 mg; 0.53 mmol; 100 mol%), methanol (280 μl), methyl cyanoacetate (47 μl; 52.8 mg; 0.53 μmol; 100 mol%) and water (48 μl; 48 mg; 2.66 mmol; 501 mol%). 76% NMR yield. Purification: gradient column chromatography, eluent hexane/ethyl acetate from 10/1 to 5/1 (R_f = 0.09).

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Isolated as pale-yellow oil - 66% (51.4 mg). The obtained NMR data was in agreement with the literature report[12e].

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.08 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.4 Hz, 2H), 6.4 – 6.05 (br s, 1H), 2.86 (t, *J* = 7.1 Hz, 2H), 2.59 (t, *J* = 7.1 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.1, 129.8, 129.5, 119.5, 115.8, 30.6, 19.7

3-(3-phenoxyphenyl)propanenitrile (12)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.58 mg 2.2 μmol; 0.2 mol%), 3-phenoxybenzaldehyde (190 μl; 217.9 mg; 1.10 mmol; 100 mol%), methanol (475 μl), methyl cyanoacetate (97.5 μl; 109.5 mg; 1.10 mmol; 100 mol%) and water (98.6 μl; 98.6 mg; 5.48 mmol; 498 mol%). 77% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 10/1 (R_f = 0.22). Isolated as colourless oil - 70% (171.8 mg). The obtained NMR data was in agreement with the literature report[12f].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.28 (m, 3H), 7.14 (t, *J* = 7.4 Hz, 1H), 7.06 – 6.88 (m, 5H), 2.93 (t, *J* = 7.4 Hz, 2H), 2.61 (t, *J* = 7.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 156.9, 140.0, 130.3, 129.9, 123.6, 123.1, 119.1, 119.0, 118.6, 117.5, 31.4, 19.2

3-(naphthalen-1-yl)propanenitrile (13)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.52 mg; 2 μmol; 0.2 mol%), 1-naphthaldehyde (134 μl; 154.1 mg; 0.99 mmol; 100 mol%), methanol (475 μl), methyl cyanoacetate (87.4 μl; 98.1 mg; 0.99 mmol; 100 mol%) and water (88.5 μl; 88.5 mg; 4.91 mmol; 497 mol%). 83% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 12/1 (R_f = 0.26). Isolated as pale-yellow oil - 76% (137 mg). The obtained NMR data was in agreement with the literature report[6a].

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.88 (m, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.66 – 7.50 (m, 2H), 7.49 – 7.38 (m, 2H), 3.43 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 134.0, 133.9, 131.1, 129.2, 128.2, 126.6, 126.0, 125.7, 122.7, 119.3, 28.8, 18.5

5-phenylpentanenitrile (14)

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Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.6 mg 2.3 µmol; 0.2 mol%), 3-phenylpropionaldehyde (142 µl; 143.4 mg; 1.07 mmol; 100 mol%), methanol (475 µl), methyl cyanoacetate (100.8 µl; 113.2 mg; 1.14 mmol; 106 mol%) and water (102 µl; 102 mg; 5.67 mmol; 530 mol%). >96% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 10/1 (R_f = 0.28). Isolated as colourless oil - 65% (110 mg). The obtained NMR data was in agreement with the literature report[12g].

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.36 (dd appears as t, *J* = 7.6 Hz, 2H), 7.27 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.6 Hz, 2H), 2.70 (t, *J* = 7.6 Hz, 2H), 2.35 (t, *J* = 7.2 Hz, 2H), 1.86 – 1.79 (m, 2H), 1.75 – 1.68 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.2, 128.3, 128.2, 125.9, 119.6, 34.8, 30.1, 24.7, 16.9

4-phenylpentanenitrile (15)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (0.55 mg 2.1 µmol; 0.2 mol%), 2-phenylpropionaldehyde (132 µl; 132.2 mg; 0.99 mmol; 100 mol%), methanol (475 µl), methyl cyanoacetate (92.4 µl; 103.7 mg; 1.05 mmol; 106 mol%) and water (93.5 µl; 93.5 mg; 5.19 mmol; 524 mol%). 73% NMR yield. Purification: column chromatography, eluent hexane/ethyl acetate 10/1 (R_f = 0.31). Isolated as colourless oil - 63% (99 mg). The obtained NMR data was in agreement with the literature report[12h].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd appears as t, *J* = 7.3 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 7.23 (d, *J* = 7.3 Hz, 2H), 2.97 – 2.86 (m, 1H), 2.36 – 1.86 (m, 4H), 1.35 (d, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.6, 128.8, 126.9, 126.8, 119.7, 38.9, 33.5, 21.9, 15.4

Experiment with two consecutive reaction cycles

A 20 ml stainless steel autoclave was charged with $RhCl_3 \cdot 3H_2O$ (0.22 mg; 8.3 µmol; 0.02 mol%), isobutyraldehyde (378.4 µl; 298.9 mg; 4.15 mmol; 100 mol%), methanol (2080 µl), methyl cyanoacetate (368.4 µl; 413.7 mg; 4.18 mmol; 101 mol%) and water (372.8 µl; 372.8 mg; 20.70 mmol; 499 mol%). The autoclave was sealed and charged with 50 bar CO. The reactor was placed into a preheated to 160 °C oil bath. After 24 h, the reactor was cooled to liquid nitrogen temperature and depressurized. Then 90 µl of mesitylene was added in to the reaction mixture and 30 µl of solution was taken from

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reactor and analyzed by NMR. 82% NMR yield. Then autoclave was charged with isobutyraldehyde (378.4 µl; 298.9 mg; 4.15 mmol; 100 mol%), methyl cyanoacetate (368.4 µl; 413.7 mg; 4.18 mmol; 101 mol%) and water (74.5 µl; 74.5 mg; 4.14 mmol; 100 mol%), sealed and charged with 50 bar CO. The reactor was placed into a preheated to 160 °C oil bath. After 24 h, the reactor was cooled to liquid nitrogen temperature and depressurized. Then 41.5 mg of 4-dinitrobenzene was added into the reaction mixture and 30 µl of solution was taken from reactor and analyzed by NMR. The total TON = 5700. The obtained NMR data for **16** was in agreement with the literature report[12i].

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.31 (t, *J* = 7.4 Hz, 2H), 1.77 – 1.61 (m, 1H), 1.51 (dt appears as q, *J* = 7.4 Hz, 2H), 0.90 (d, *J* = 6.6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 120.0, 33.9, 27.2, 21.7, 15.1

3-methyl-5-phenylpentanenitrile (17)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (2 mg; 7.6 µmol; 2 mol%), 4-phenylbutan-2-one (56.9 µl; 56.3 mg; 0.38 mmol; 100 mol%), methanol (200 µl), methyl cyanoacetate (50.3 µl; 56.4 mg; 0.57 mmol; 150 mol%) and water (6.8 µl; 6.8 mg; 0.38 mmol; 100 mol%). No extraction from water was needed. 76% NMR yield. Purification: column chromatography, eluent hexane/DCM 2/1 (R_f = 0.4). Isolated as colourless oil - 68% (45 mg). The obtained NMR data was in agreement with the literature report[12b].

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 2H), 7.24 – 7.16 (m, 3H), 2.80 – 2.55 (m, 2H), 2.41 – 2.21 (m, 2H), 1.96 – 1.85 (m, 1H), 1.84 – 1.72 (m, 1H), 1.70 – 1.62 (m, 1H), 1.13 (d, *J* = 6.7 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.5, 128.6, 128.4, 126.2, 118.8, 37.6, 33.2, 30.0, 24.6, 19.5

2-cyclohexylacetonitrile (18)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (2 mg; 7.6 µmol; 2 mol%), cyclohexanone (39.3 µl; 37.3 mg; 0.38 mmol; 100 mol%), methanol (200 µl), methyl cyanoacetate (50.3 µl; 56.4 mg; 0.57 mmol; 150 mol%) and water (6.8 µl; 6.8 mg; 0.38 mmol; 100 mol%). No extraction from water was needed. 68% NMR yield. Purification: column chromatography, eluent hexane/DCM 1/1. Detection with GC-FID. Isolated as colourless oil - 60% (28 mg). The obtained NMR data was in agreement with the literature report[12j].

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^{1}H NMR (300 MHz, $CDCl_3$) δ 2.23 (d, *J* = 5.3 Hz, 2H), 1.94 – 1.56 (m, 6H), 1.38 – 0.94 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 119.1, 34.9, 32.5, 25.8, 25.8, 24.9

2-cyclopentylacetonitrile (19)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (7.9 mg; 30 μmol; 2 mol%), cyclopentanone (132.5 μl; 126.0 mg; 1.5 mmol; 100 mol%), methanol (800 μl), methyl cyanoacetate (198.7 μl; 222.8 mg; 2.25 mmol; 150 mol%) and water (27 μl; 27 mg; 1.5 mmol; 100 mol%). No extraction from water was needed. 53% GC yield. Purification: column chromatography, eluent pentane/DCM 2/1. Detection with GC-FID. Isolated as colourless oil - 40% (65.4 mg). The obtained NMR data was in agreement with the literature report[12j].

^{1}H NMR (600 MHz, $CDCl_3$) δ 2.35 (d, J = 6.8 Hz, 2H), 2.22 – 2.13 (m, 1H), 1.94 – 1.83 (m, 2H), 1.73 – 1.64 (m, 2H), 1.64 – 1.55 (m, 2H), 1.35 – 1.25 (m, 2H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 119.6, 36.4, 32.2, 25.1, 22.9.

2-cyclobutylacetonitrile (20)

Synthesis was accomplished according to the general procedure using $RhCl_3 \cdot 3H_2O$ (8.0 mg; 30.4 μmol; 2 mol%), cyclopentanone (113.5 μl; 106.5 mg; 1.5 mmol; 100 mol%), methanol (800 μl), methyl cyanoacetate (201.1 μl; 225.8 mg; 2.28 mmol; 150 mol%) and water (54 μl; 54 mg; 3 mmol; 200 mol%). No extraction from water was needed. 84% GC yield. Purification: column chromatography, eluent pentane/DCM 2/1. Detection with GC-FID. Isolated as colourless oil - 56% (81 mg). The obtained NMR data was in agreement with the literature report[12k]. The product is volatile and can be lost during the evaporation.

^{1}H NMR (400 MHz, $CDCl_3$) δ 2.67 – 2.56 (m, 1H), 2.40 (d, J = 6.7 Hz, 2H), 2.23 – 2.10 (m, 2H), 1.96 – 1.77 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 118.9, 31.6, 27.4, 23.7, 17.9.

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ASSOCIATED CONTENT

Supporting Information

^{1}H-, ^{13}C- NMR spectra of all compounds and mechanistic details.

NOTES

The authors declare no competing financial interest.

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