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N-methylation of quinolines with CO_2 and H_2 catalyzed by Ru-triphos complexes

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N-methyl-tetrahydroquinolines (MTHQs) are a kind of very useful chemicals, which can be obtained from *N*-methylation of amines. However, the methylation of quinolines which is a kind of highly unsaturated nitrogen-containing heterocyclic aromatic compounds has not been reported. In this work, we report the first work for the synthesis of MTHQs by methylation of quinolines using CO_2 and H_2. It was found that Ru(acac)$_3$-triphos [triphos: 1,1,1-tris(diphenylphosphinomethyl)ethanl] complex was very active and selective for the *N*-methylation reaction of quinolines, and the yield of the desired product could reach 99%.

methylation, hydrogenation, quinoline derivatives, carbon dioxide, homogeneous catalysis

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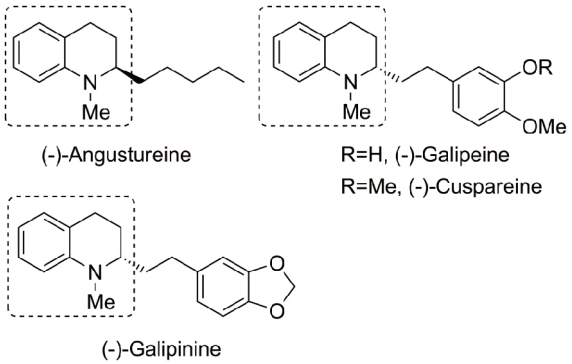
1 Introduction

Quinoline and its derivatives (quinolines), a kind of nitrogen-containing polycyclic aromatic compounds, exist in coal and oil shale and are the by-products of petroleum refining processes [1]. *N*-methyl-1,2,3,4-tetrahydroquinolines (MTHQs) are valuable chemicals in organic synthesis and chemical industry. They are also found in many biologically active natural products and pharmacologically relevant therapeutic agents (Scheme 1) [2,3].

It has been reported that MTHQ (**4a**) can be synthesized from the *N*-methylation of THQ (1,2,3,4-tetrahydro-quinoline, **2a**) that can be produced by selective hydrogenation of quinolines [4]. Different C1 sources have been used in the *N*-methylation reactions, such as CH_3I, HCHO, HCOOH, CO_2 and H_2 or $PhSiH_3$, dimethyl sulfate, MeOTf (OTf=trifluoromethanesulfonate) or diazomethane [5], or the reaction of



Scheme 1 Some antimalarial activity of naturally occurring alkaloids with the structure of *N*-methyl-1,2,3,4-tetrahydroquinoline.

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quinoline with methanol [6] or CH_3I and dihydropyridines [7], as shown in Scheme 2.

CO_2 is a cheap, abundant and safe carbon resource, and its transformation into valuable chemicals and fuel has received much attention [8]. *N*-methylation of amines using CO_2 and reductant such as H_2 and $PhSiH_3$ has been reported [9]. Comparing with $PhSiH_3$, H_2 is a cheaper and desirable reductant, and only water is the by-product in the reaction [10]. Up to now, both heterogeneous catalysts such as $CuAlO_x$ [11], $Pd/CuZrO_x$ [12] and $Pt\text{-}MoO_x/TiO_2$ [13], Au nanoparticles supported on $\gamma\text{-}Al_2O_3$ [14], and homogeneous catalysts such as $Ru(acac)_3$-triphos [15] have been developed for the methylation of amines with CO_2 and H_2. $Ru(acac)_3$-triphos complex has been widely used in organic reactions, such as reduction of secondary and tertiary amides to amines [16], hydrogenation of carboxylic acids or esters to alcohols [17], *N*-alkylation of amines and carboxylic acids [18], CO_2 hydrogenation to methanol [19].

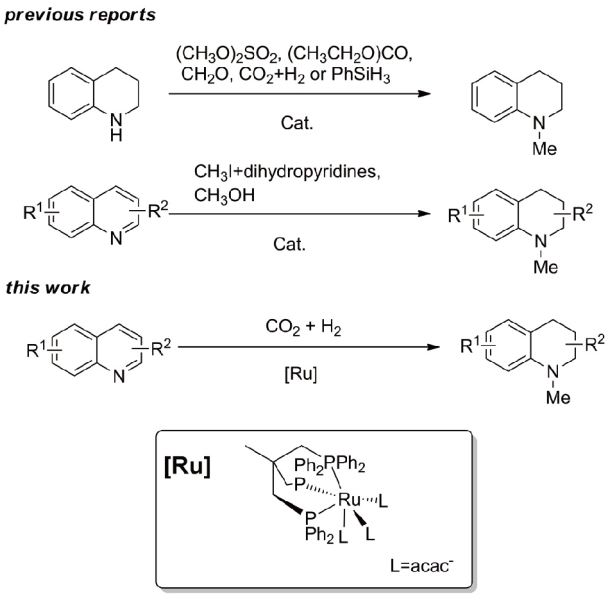
In this work, we found that $Ru(acac)_3$-triphos complex was very active and selective homogeneous catalyst for *N*-methylation of quinolines with CO_2 and H_2, and 99% yield of MTHQs could be obtained. This route is compared with reported methods in Scheme 2. As far as we known, this is the first work for the *N*-methylation of quinolines with CO_2 and H_2.

2 Experimental

2.1 General

All the chemicals were purchased from commercial sources and used without further purification. $Ru(acac)_3$ (Ru>24%), $RuBr_3$ (Ru>25%), RuI_3 (Ru>20.5%), methanesulfonic acid (98%) and paraformaldehyde (97.0%) were from Alfa Aesar (USA). $RuCl_3$ (99.99%), tricyclohexanylphosphine (97%), 1,2-bis(diphenylphosphino)benzene (98%), 1,3-bis(diphenylphosphino)propane (98%), 1,5-bis(diphenylphosphino)pentane (98%), bis(2-diphenylphosphinoethyl)phenylphosphine (97%), quinoline (99%), 6-methoxyquinoline (98%), 7-methylquinoline (98%), 6-methylquinoline (98%), 6-chloroquinoline (97%), 3-methylquinoline (98%), 4-methylquinoline (99%) and tetrahydrofuran (THF, 99.85%) were from J&K Chemicals (China). $Ru_3(CO)_{12}$ (>98%) was from Adamas Reagent Co., Ltd. (China). 1,1,1-Tris(diphenylphosphinomethyl)ethanl (97%) was from Strem Chemicals (USA). Dimethylbisdiphenylphosphinoxanthene (98%) was from Energy Chemical (China). HCOOH (98.0%) was from Sinopharm Chemical Reagent Co., Ltd. (China). CO_2 (99.99%) and H_2 (99.99%) were provided by Beijing Analytical Instrument Company (China).

Gas chromatograph (GC) analysis was carried out on an Agilent Technologies 7890B system equipped with an HP-5 column. GC-MS characterization was conducted on an Agilent 7892B/MSD 5975C system equipped with a HP-5MS column. ^1H and ^{13}C NMR spectra were recorded on a Bruker Avance III HD 400 MHz NMR spectrometer (Germany) (400 MHz for ^1H and 101 MHz for ^{13}C) at ambient temperature in $CDCl_3$.



Scheme 2 Synthesis of *N*-methyl-1,2,3,4-tetrahydroquinolines.

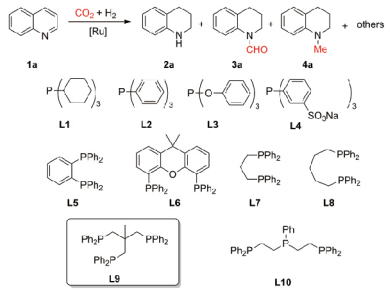
2.2 *N*-methylation of quinolines with CO_2 and H_2

Typical procedures (Table 1, entry 1) were carried out as follows: quinoline (0.129 g, 1.0 mmol), $Ru(acac)_3$ (2.0 mg, 0.005 mmol), triphos (6 mg, 0.010 mmol), methanesulfonic acid (MSA, 5 mg, 0.05 mmol) and dry THF (2.0 mL) were added into a 16 mL autoclave with a Teflon inner container. Then the reactor was sealed and purged with CO_2 to remove the air (5×8 bar). After that, 2 MPa of CO_2 and 8 MPa of H_2 were charged into the reactor and the mixture was stirred at 160 °C for 16 h. Afterwards, the reaction was quenched by transferring it into ice-water. After it was cooled to 0 °C, the reactor was vented slowly. The reaction mixture was analyzed by gas chromatograph-mass spectrometer (GC-MS) and GC with decane as an internal standard, or purified by flash column chromatography on silica gel to afford the desired product was characterized by ^1H and ^{13}C NMR.

2.3 NMR spectra of products

N-methyl-1,2,3,4-tetrahydroquinoline (**4a**): ^1H NMR (400 MHz, $CDCl_3$) δ 7.06 (t, J=7.8 Hz, 1H), 6.94 (d, J=7.13, 1H), 6.60 (t, J=6.7 Hz, 2H), 3.21 (t, J=5.7 Hz, 2H), 2.87 (s, 3H), 2.76 (t, J=6.32 Hz, 2H), 1.97 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.8, 128.8, 127.1, 122.9, 116.2, 111.0, 51.3, 39.1, 27.8, 22.5.

Table 1 One-pot hydrogenation and *N*-methylation of quinoline and CO_2 with H_2 over various catalysts [a)]



Entry	Cat.	L	Conv. (%)	Yield (%) [b)]			
				2a	**3a**	**4a**	Others [c)]
1	$Ru(acac)_3$	**L9**	100	0	0	99	1
2	$RuCl_3$	**L9**	60	44	0	3	14
3	$RuBr_3$	**L9**	82	46	32	3	1
4	RuI_3	**L9**	94	73	16	4	2
5	$Ru_3(CO)_{12}$	**L9**	98	86	12	0	0
6	$Pd(OAc)_2$	**L9**	100	84	15	0	1
7	$PdCl_2$	**L9**	100	99	0	0	1
8	H_2PtCl_6	**L9**	99	98	0	0	0
9	$Ru(acac)_3$	**L1**	96	95	0	0	1
10	$Ru(acac)_3$	**L2**	95	95	0	0	0
11	$Ru(acac)_3$	**L3**	93	89	0	0	4
12 [d)]	$Ru(acac)_3$	**L4**	93	91	0	0	2
13	$Ru(acac)_3$	**L5**	100	86	0	0	14
14	$Ru(acac)_3$	**L6**	58	58	0	0	0
15	$Ru(acac)_3$	**L7**	100	73	19	3	6
16	$Ru(acac)_3$	**L8**	96	74	14	5	3
17	$Ru(acac)_3$	**L10**	97	63	9	22	3
18 [e) f)]	$Ru(acac)_3$	**L9**	78	78	0	0	0
19 [e)]	$Ru(acac)_3$	**L9**	99	99	0	0	0
20 [f)]	$Ru(acac)_3$	**L9**	83	83	0	0	0
21 [f) g)]	$Ru(acac)_3$	**L9**	0	–	0	0	0

a) Reaction conditions: quinoline 1.0 mmol, $Ru(acac)_3$ 0.5 mol%, triphos 1.0%, MSA 10 mol%, THF 2 mL, 160 °C, 16 h, CO_2 2 MPa, H_2 8 MPa; b) GC yield; c) others contained mainly decahydroquinoline and 5,6,7,8-tetrahydroquinoline etc; d) water (2 mL) as solvent; e) without CO_2; f) without MSA; g) 1.0 mmol of **2a** was the substrate.

6-Methoxy-1-methyl-1,2,3,4-tetrahydroquinoline (**4b**): ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.58 (dd, J=2.76 Hz, 1 H), 6.49 (m, 2H), 3.64 (s, 3H), 3.03 (t, J=5.65 Hz, 2H), 2.74 (s, 3H), 2.67 (t, J=6.6 Hz, 2H), 1.89 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ=150.35, 140.59, 123.59, 114.08, 111.43, 111.24, 76.36, 76.04, 75.72, 54.74, 50.62, 38.86, 26.95, 21.68.

1,6-Dimethyl-1,2,3,4-tetrahydroquinoline (**4c**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, J=8.06 Hz, 1H), 6.80 (s, 1H), 6.55 (d, J=8.22 Hz, 1H), 3.17 (t, J=5.6, 2H), 2.8 (s, 3H), 2.75 (t, J=6.6 Hz, 2H), 2.23 (s, 3H),1.99 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ=144.77, 129.62, 127.40, 125.54, 123.09, 111.43, 51.51, 39.45, 27.73, 22.68, 20.22.

1,7-Dimethyl-1,2,3,4-tetrahydroquinoline (**4d**): ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.83 (d, J=7.21 Hz, 1H), 6.42 (d, J=8.42, 2H), 3.17 (t, J=5.76 Hz, 2H), 2.9 (s, 3H), 2.71 (t, J=6.6 Hz, 2H), 2.3 (s,3H), 1.96 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ=146.70, 136.61, 128.77, 120.03, 117.08, 111.84, 51.45, 39.21, 27.93, 27.53, 22.73, 21.66.

1,4-Dimethyl-1,2,3,4-tetrahydroquinoline (**4f**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (m, 2H), 6.6 (m, 2H), 3.3–3.15 (m, 3H), 2.88 (s, 3H), 2.01 (m, 1H), 1.67 (m, 2H), 1.27 (d, J=6.8 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 128.03, 127.79, 127.07, 127.03, 116.19, 110.97, 48.30, 39.18, 31.03, 30.85, 30.06, 22.69.

6-Chloro-1-methyl-1,2,3,4-tetrahydroquinoline (**4g**): ^{1}H NMR (400 MHz, $CDCl_3$) δ=6.99 (dd, J=2.57, 8.8 Hz, 1H), 6.89 (s, 2H), 6.47 (d, J=8.6 Hz, 1H), 3.19 (t, J=5.6 Hz, 2H), 2.85 (s, 3H), 2.71 (t, J=6.5 Hz, 3H), 1.95 (m, 2H). ^{13}C

NMR (101 MHz, $CDCl_3$) δ=145.31, 128.35, 126.65, 124.45, 120.66, 111.90, 51.12, 39.15, 27.72, 22.23.

Angustureine (**4h**): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.0–7.1 (t, 1H), 6.90–7.10 (d, 1H), 6.55–6.65 (t, 1H), 6.45–6.55 (d, 1H), 3.2 (m, 1H), 2.9 (s, 3H), 2.7–2.85 (m, 1H), 2.6–2.7 (m, 1H), 1.9 (m, 2H), 1.5–1.6 (m, 21H), 1.2–1.4 (m, 8H), 0.8–0.9 (t, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.4, 128.8, 127.1, 121.9, 115.2, 110.4, 59.0, 38.0, 32.1, 31.3, 25.8, 24.5, 23.6, 22.7, 14.1.

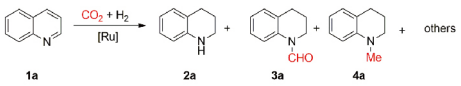
3 Results and discussion

The complexes with different ligands (**L1**–**L10**) and metals were tested for the reaction and the results are shown in Table 1. $Ru(acac)_3$ with the tridentate ligand **L9** was very active and selective for the reaction and 99% yield of **4a** could be obtained (entry 1). However, the other metal species with **L9** showed very low selectivity to **4a** (entries 2–8). In addition, $Ru(acac)_3$ was not effective for the reaction when combined with other ligands. Most of the products were **2a** for the monophosphine ligands such as **L1**–**L4** (entries 9–12), indicating that the monophosphine ligands checked with $Ru(acac)_3$ were inactive for the methylation of **2a** with CO_2 and H_2. The bisphosphine ligand **L5** was active but afforded low selectivity for the formation of **4a**. Only hydrogenated product **2a** was detected with 86% yield. In addition to **2a**, 14% yield of the over-hydrogenated products was obtained (entry 13). The **L6** gave only the product of **2a** with the yield of 58%, indicating that it was less active for the selective hydrogenation and inactive for the methylation (entry 14). Both **3a** and **4a** were detected by using $Ru(acac)_3$ with **L7** and **L8** as catalyst. However, the yield of **4a** was only 3% and 5%, respectively (entries 15 and 16). Ligand **L10** gave **4a** with the yield of 22% (entry 17), which was much lower than that of **L9**. Thus, $Ru(acac)_3$ with **L9** catalyst had highest activity and selectivity among the catalysts that we checked, which was possible due to their specific configurations in Scheme 1.

The above reactions were all performed in the presence of MSA. To check its influence on the reaction, several control experiments were carried out. 78% yield of **2a** was obtained in the absence of MSA and CO_2, which was increased to 99% when MSA was used, indicating that the acid could promote the hydrogenation (Table 1, entries 18 and 19). No methylated product (**4a**) was detected in the absence of MSA for the *N*-methylation of **1a** and **2a** (entries 20 and 21), demonstrating that the MSA is crucial for the *N*-methylation, which was similar to that of previous report [15]. The results show that MSA simultaneously promotes the selective hydrogenation of **1a** and *N*-methylation of **2a**.

The reaction conditions of direct *N*-methylation of **1a** with CO_2 and H_2 catalyzed by Ru-triphos were optimized, and the results are given in Table 2. The conversions of **1a** were all above 95% at the reaction temperature from 120 to 180 °C in the presence of H_2. However, the yield of **4a** depended strongly on temperature. Increasing temperature from 120 to 160 °C led to an increase in yield of **4a** from 57% to 99% (Table 2, entry 1 vs. Table 1, entry 1). However, further increased the temperature resulted in a lower yield of **4a**, which was probably due to the higher temperature was not favorable

Table 2 Optimization of reaction conditions on the coupling of selective hydrogenation and *N*-methylation of quinolone [a)]



1a 2a 3a 4a

Entry	*T* (°C)	P_{CO_2} / P_{H_2}(MPa)	Sol.	Conv. (%)	Yield (%) [b)]			
					2a	**3a**	**4a**	Others [c)]
1	120	2/8	THF	96	39	0	57	0
2	140	2/8	THF	97	31	0	65	0
3	180	2/8	THF	98	48	0	50	0
4	160	0/8	THF	91	92	0	0	0
5	160	0.5/8	THF	90	28	0	62	1
6	160	1/8	THF	100	11	1	89	0
7	160	2/0	THF	0	0	0	0	0
8	160	2/4	THF	99	19	5	74	0
9	160	2/6	THF	99	7	1	91	0
10	160	2/8	cy	98	42	0	56	0
11	160	2/8	Tol [d)]	96	43	1	53	0
12	160	2/8	1,4-dioxane	90	79	0	11	0
13	160	2/8	TMB [e)]	97	22	1	75	0

a) Reaction conditions: quinoline 1.0 mmol, $Ru(acac)_3$ 0.5 mol%, triphos 1.0%, MSA 10 mol%, 16 h; b) GC yield; c) others contained mainly decahydroquinoline and 5,6,7,8-tetrahydroquinoline etc.; d) toluene; e) 1,2,4-trimethylbenzene.

to the stability of the catalyst. The effect of CO_2 and H_2 pressure on the catalytic performances was also studied. No methylated product was detected in the absence of CO_2 (Table 2, entry 4), indicating that CO_2 was the source of methyl group. When the pressure of CO_2 was 0.5 MPa, 62% yield of **4a** was obtained, which was increased to 89% under 1.0 MPa of CO_2 (Table 2, entries 5 vs. 6), indicating that the higher CO_2 pressure was beneficial for the reaction. Neither **2a** nor **4a** was detected in the absence of H_2 (Table 2, entry 7), indicating that in this reaction, the hydrogenation of **1a** firstly occurred to produce **2a** which was then methylated with CO_2 and H_2 to **4a**. The properties of the solvent also have an effect on the reaction (Table 2, entries 10–13). Cyclohexane, toluene, 1,4-dioxane and 1,2,4-trimethyltoulene gave low yields to **4a**.

The dependence of the reaction time on the catalytic performances was also studied, and the results are given in Figure 1. When the reaction time was 4 h, **2a** was produced with 80% yield, but only 6% of **4a** was detected. A prolonged reaction time led to a decrease in **2a** yield but an increase in **4a**. When the reaction time was prolonged to 8 and 12 h, the yield of **2a** was decreased to 59% and 42%, while **4a** was increased to 32% and 52%, respectively. The results indicated that **2a** could be transferred into **3a** which was further reduced into **4a**. This hints that the *N*-methylation of **1a** with CO_2 and H_2 was achieved via three steps, i.e., the selective hydrogenation of **1a** to **2a**, the *N*-formylation of **2a** to **3a**, and followed by the reduction of **3a** to **4a**. In the reaction, the catalyst played at least three roles. At beginning, it catalyzed the selective hydrogenation of **1a** to **2a**, which is highly important for the whole reaction. Because the pyridine-N cannot be directly methylated, the selective hydrogenation of pyridine unit to piperidine is prerequisite for the formation of **4a**. Then, the catalyst catalyzed the formation of formamide, which is recognized as the intermediate for the *N*-methylation of amine with CO_2 [12,15]. The above results suggest that this is the rate determining step for the whole reaction.

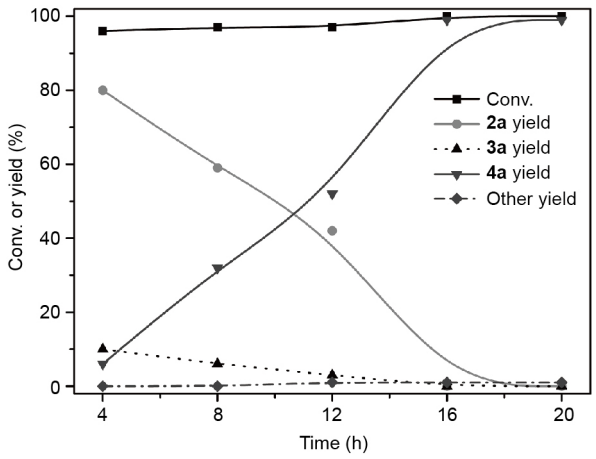


Figure 1 Dependence of reaction time on the catalytic performances of *N*-methylation of quinoline and CO_2 with H_2. Reaction conditions were similar to that of Table 1, entry 1, except for the reaction time.

Generally, CO_2 can be reduced to HCOOH, CO or HCHO etc., depending upon the catalyst used and reaction conditions operated. In this work, we also investigated other C1 sources to find out their performances in methylation of **1a**, and the results are given in Table 3. Among the C1 sources, formic acid gave the highest yield of **4a**, indicating that CO_2 may initially be transferred into HCOOH, which was then reacted with **2a** to **3a**. Furthermore, the Ru catalyst can reduce the formylamine to methylamine. The low yields of **4a** obtained from $(HCHO)_n$ and CH_3OH indicated that they could also be transferred under the given conditions but via other routes.

Having developed this reliable method for the catalytic synthesis of **4a**, we further studied the *N*-methylation of substituted quinolines with CO_2 and H_2 to corresponding products. The substituted quinolines with electron-donating and electron-withdrawing groups were studied and the results are given in Table 4. The electron-donating groups, such as CH_3O– and CH_3– group in the 6- and 7-positions of quinoline, gave **4b**, **4c**, and **4d** with the yields of 90%, 89%, and 92%, respectively (Table 4, entries 1–3). However, longer reaction times were required to produce **4e** and **4f** with the yields of 88% and 89% respectively for the CH_3– in the 3- and 4- positions of quinoline (**1e** and **1f**, Table 4, entries 4 and 5), suggesting that their activities were lower than that of **1a**. The main reason may be that the methyl group on the pyridine unit (3- or 4-position of quinoline) hindered the reaction. Meanwhile, 6-chloroquinoline (**1g**), with an electron-withdrawing group on quinoline, gave 85% yield of **4g** after 36 h (Table 4, entry 6). The preliminary results demonstrated that the present method has a good tolerance in the selective hydrogenation and *N*-methylation of quinolines. To our delight, (±) angustureine (**4h**), one of the important alkaloids mentioned above, could be synthesized by this method with a high yield of 86% (Table 4, entry 7).

4 Conclusions

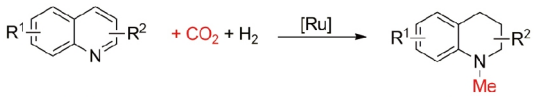
It has been found that $Ru(acac)_3$-triphos complex is an very efficient catalyst for the synthesis of MTHQs from quinolines,

Table 3 Direct *N*-methylation of quinoline with diverse C1 sources catalyzed by Ru catalyst [a)]

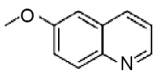
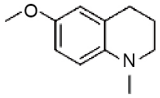
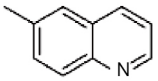
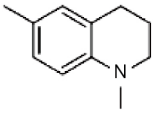
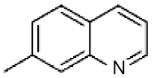
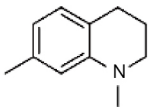
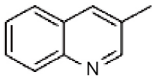
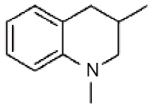
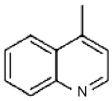
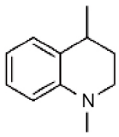
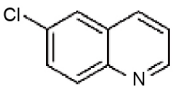
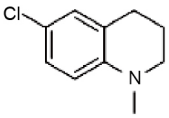
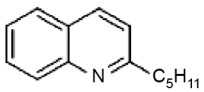
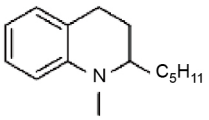
Entry	C1	Conv. (%)	Yield (%) [b)]			
			2a	**3a**	**4a**	Others [c)]
1	CO [d)]	63	63	0	0	0
2	$(HCHO)_n$	95	78	0	17	0
3	HCOOH	99	10	0	80	9
4	CH_3OH	99	89	0	10	0

a) Reaction conditions were same that entry 1 in Table 1, except for the addition of $(HCHO)_n$, HCOOH and CH_3OH as C1 sources (3 eq.); b) GC yield; c) others contained mainly decahydroquinoline and 5,6,7,8-tetrahydroquinoline, etc.; d) 2 MPa of CO was added.

Table 4 Ru-triphos catalyzed direct *N*-methylation of quinolines and CO_2 with H_2 [a]



1a-1h 4a-4h

Entry	Substrate		Product		Yield (%) [b]
1		**1b**		**4b**	90
2		**1c**		**4c**	89
3		**1d**		**4d**	92
4 [c]		**1e**		**4e**	88
5 [c]		**1f**		**4f**	89
6 [c]		**1g**		**4g**	85
7 [d]		**1h**		**4h**	86

a) Reaction conditions are similar to that of entry 1 in Table 1; b) isolated yield; c) the reaction time was 36 h; d) $Ru(acac)_3$ 1.5 mol%, triphos 3.0 mol%.

CO_2 and H_2, and satisfactory yield of desired products could be obtained from the quinolines with methyl, methoxy and chloride groups. This route has some obvious advantages, such as using quinolines, CO_2 and H_2 as the reactants. We believe that this simple, efficient, and greener method has potential of application.

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Conflict of interest The authors declare that they have no conflict of interest.

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