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(54) METHOD FOR CONVERSION OF TERMINAL ALKENES TO ALDEHYDES USING RUTHENIUM(IV) PORPHYRIN CATALYSTS

(76) Inventors: **Chi-Ming Che**, Hong Kong (HK); **Jian Chen**, Shanghai (CN)

Correspondence Address:
COOPER & DUNHAM, LLP
1185 AVENUE OF THE AMERICAS
NEW YORK, NY 10036

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(57) **ABSTRACT**

Aldehydes were obtained in excellent yields from ruthenium-porphyrin-catalyzed oxidation of various terminal alkenes with 2,6-dichloropyridine N-oxide under mild conditions. The aldehydes generated from these ruthenium-catalyzed alkene oxidation reactions can be used in-situ for olefination reactions with ethyl diazoacetate in the presence of PPh_3, leading to one-pot diazoacetate olefination starting from alkenes.

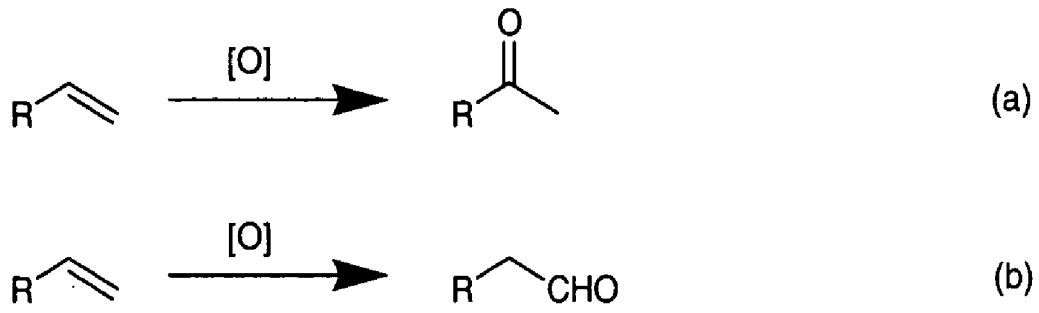
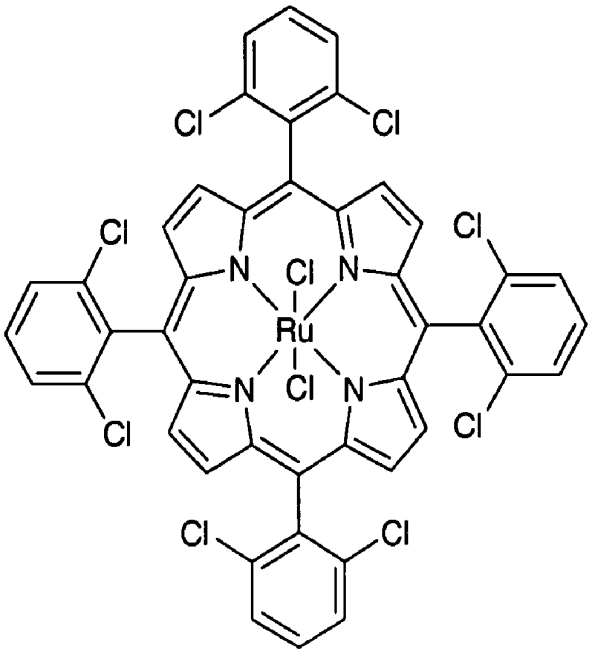
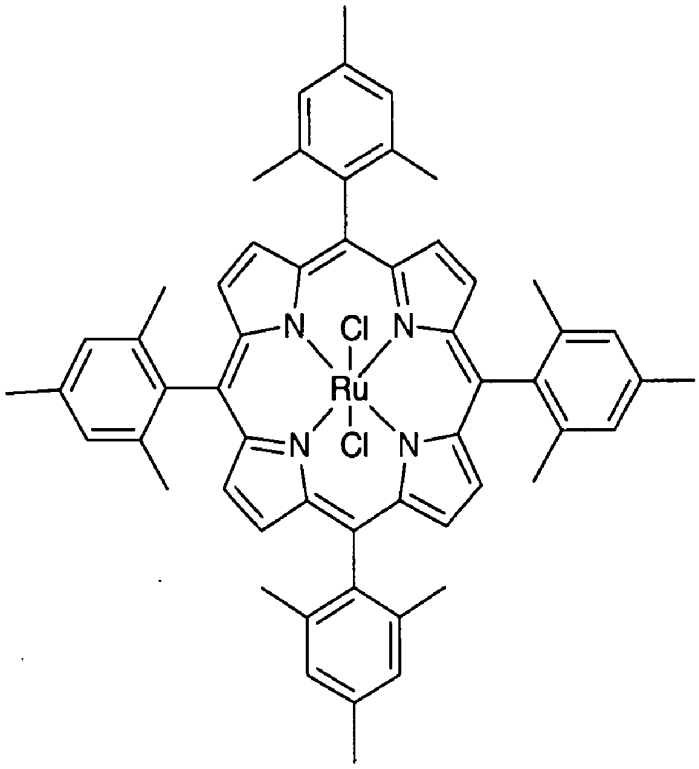


FIG. 1



$[Ru^{IV}(tdcpp)Cl_2]$ (1)



$[Ru^{IV}(tmp)Cl_2]$ (2)

FIG. 2

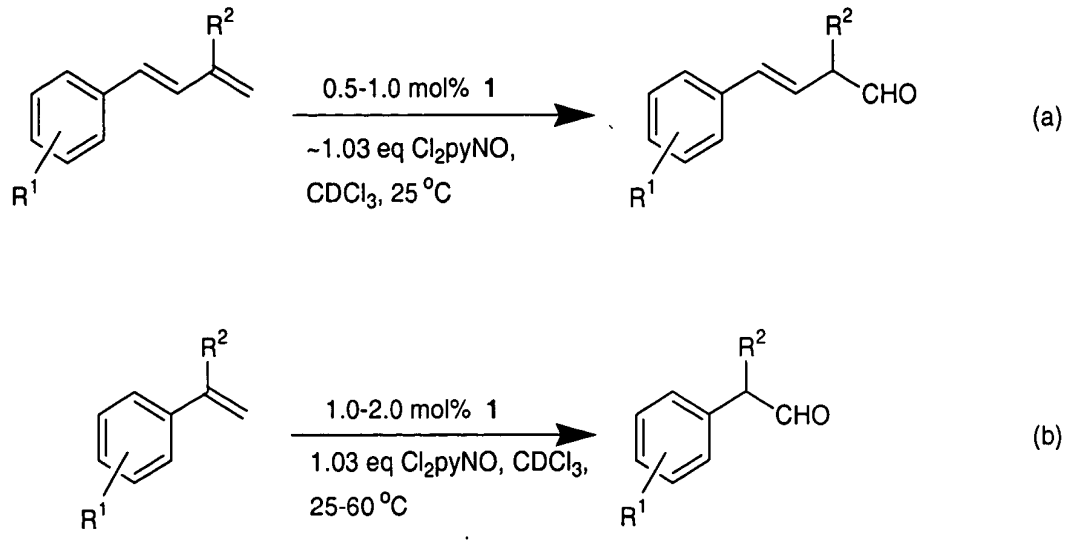
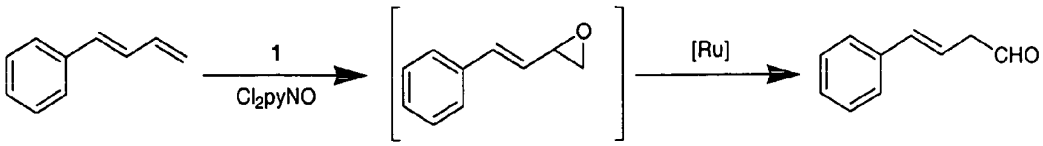

R2
R1
0.5-1.0 mol% 1
~1.03 eq Cl2pyNO,
CDCl3, 25 °C
R2
CHO
R1
(a)
R2
R1
1.0-2.0 mol% 1
1.03 eq Cl2pyNO, CDCl3,
25-60 °C
R2
CHO
R1
(b)

FIG. 3

Oxidation of **3** with various amounts of Cl_2pyNO catalyzed by **1**.



3 **5** **4**

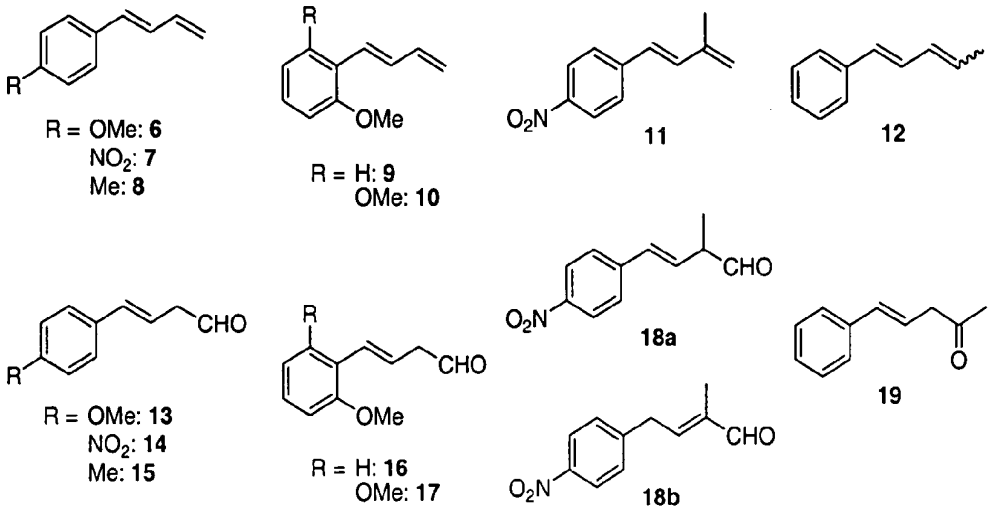
Entry[a]	Cl_2pyNO	Conversion of **3** (%)	Yield (%)[b]	
			5	**4**
1	2.0	100	49	51
2	1.03	100	0	99
3	0.9	90	0	>99

[a]Reaction conditions: **3**: 0.1 mmol, **1**: 0.5 mol%, $CDCl_3$: 0.5 mL; 25 °C, open to air.

[b]Determined by ^1H NMR (based on consumed substrate).

FIG. 4

Oxidation of 1,3-dienes **6**–**12** with Cl_2pyNO catalyzed by **1**

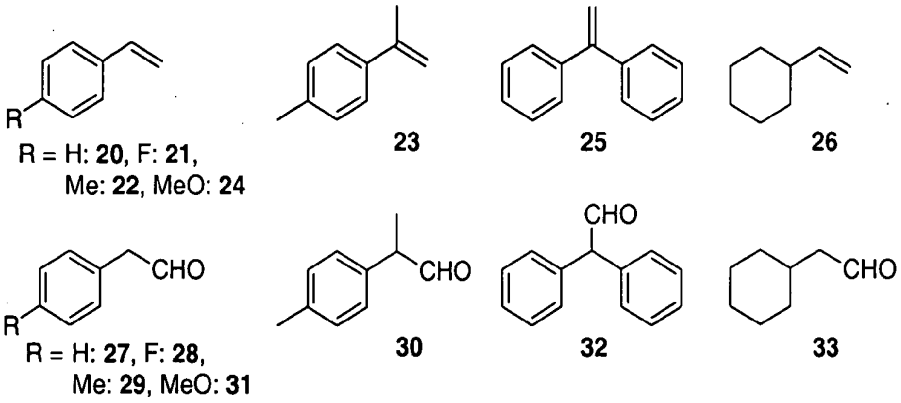


Entry[a]	Substrate	Temperature (°C)	Time (h)	Product	Yield[b] (%)
1	**6**	25	0.5	**13**	83
2	**7**	25	1	**14**	99
3	**8**	25	0.5	**15**	88
4	**9**	25	0.5	**16**	81
5[c]	**10**	25	0.5	**17**	91[d]
6	**11**	25	0.5	**18a**	90
7	**12**	60	6	**19**	99

[a]Reaction conditions: diene: 0.1 mmol, Cl_2pyNO: 1.03 equiv, **1**: 0.5–1.0 mol%, $CDCl_3$: 0.5–1.0 mL; open to air. [b]Determined by GC or ^1H NMR. [c]Reaction conditions: diene: 0.65 mmol, Cl_2pyNO: 1.03 equiv, **1**: 1.0 mol%, $CHCl_3$: 10 mL; open to air. [d]Isolated yield.

FIG. 5

Oxidation of terminal alkenes **20–26** with Cl_2pyNO catalyzed by **1**



Entry[a]	Substrate	Temperature (°C)	Time (h)	Product	Yield[b] (%)
1	**20**	60	12	**27**	99
2	**21**	60	12	**28**	99
3	**22**	60	2	**29**	96
3	**22**	25	60	**29**	99
4	**23**	25	0.5	**30**	91
5	**24**	25	0.5	**31**	99
6	**25**	25	0.5	**32**	92
7	**26**	60	24	**33**	0[c]

[a]Reaction conditions: alkene: 0.1 mmol, Cl_2pyNO: 1.03 equiv, **1**: 1.0–2.0 mol%, $CDCl_3$: 0.5–2.0 mL; open to air. [b]Determined by GC or ^1H NMR. [c]The corresponding epoxide was produced in 99% yield (determined by ^1H NMR).

FIG. 6

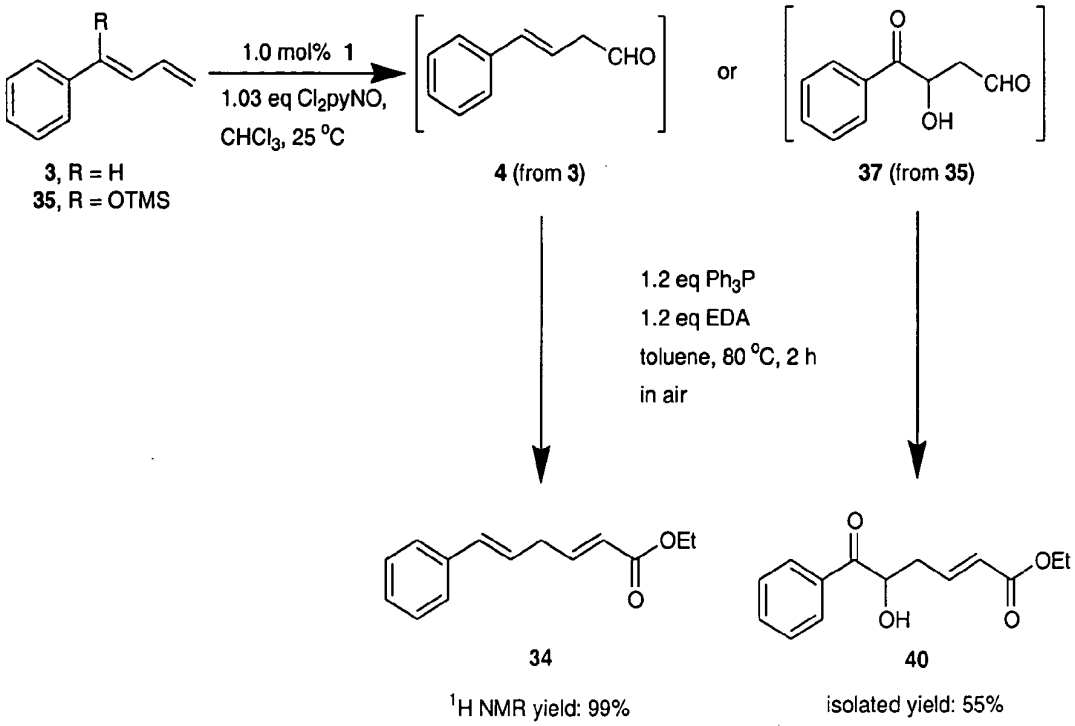

R
1.0 mol% 1
1.03 eq Cl2pyNO,
CHCl3, 25 °C
CHO
or
O
CHO
OH
3, R = H
35, R = OTMS
4 (from 3)
37 (from 35)
1.2 eq Ph3P
1.2 eq EDA
toluene, 80 °C, 2 h
in air
OEt
O
34
1H NMR yield: 99%
O
OH
OEt
O
40
isolated yield: 55%

FIG. 7

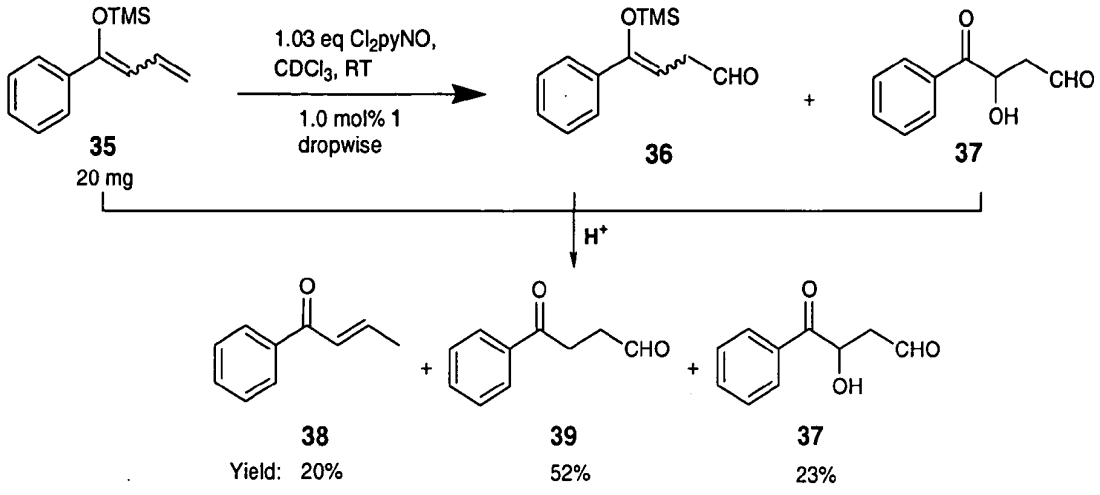

OTMS
1.03 eq Cl2pyNO,
CDCl3, RT
1.0 mol% 1
dropwise
35
20 mg
OTMS
CHO
36
O
CHO
OH
37
H+
O
38
Yield: 20%
O
CHO
39
52%
O
CHO
OH
37
23%

FIG. 8

METHOD FOR CONVERSION OF TERMINAL ALKENES TO ALDEHYDES USING RUTHENIUM(IV) PORPHYRIN CATALYSTS

BACKGROUND OF THE INVENTION

[0001] Wacker-type alkene oxidation to carbonyl compounds is one of the most important oxidation reactions in synthetic chemistry and pharmaceutical industry (Smidt et al. *Angew. Chem.* (1959), 71, 176; Smidt et al. *Angew. Chem. Int. Ed. Engl.* (1962), 1, 80; Tsuji, *Synthesis* (1984), 369; Tsuji, (1998) *Palladium Reagents and Catalysts Innovation in Organic Synthesis*; John Wiley & Sons, New York). Conversion of alkenes RCH═CH_2 to acetaldehyde (R═H) or methyl ketones (R≠H) through Wacker process (**FIG. 1***a*) has been well documented by Smidt and Tsuji; however, highly selective formation of aldehydes from catalytic oxidation of RCH═CH_2 (R≠H) without C═C bond cleavage (**FIG. 1***b*) remains a challenge. Previous work by Feringa (Feringa, *Chem. Commun.* (1986), page 909), Murahashi (Murahashi et al., *Chem. Commun.*, (1991), page 1559), and Wenzel (Wenzel et al. *Chem. Commun.* (1993), page 862) showed that oxidation of aliphatic alkenes (such as oct-1-ene and dec-1-ene), N-allyl amides/lactams, and allyl esters with O_2 or air in the presence of certain palladium or palladium/copper catalysts affords a mixture of aldehyde and methyl ketone products. Recently, Ho and co-workers reported palladium/copper-catalyzed oxidation of a few 1,5-aliphatic dienes with O_2 to form aldehydes in 60-99% yields (Ho et al. *Tetrahedron Lett.* (2003), Vol. 44, page 6955).

[0002] In efforts to develop new oxidation technology based on ruthenium porphyrin catalysts, we found that the oxidation of a wide variety of terminal alkenes with 2,6-dichloropyridine N-oxide (Cl_2pyNO) in the presence of dichlororuthenium(IV) porphyrin catalysts [Ru^{IV}(por)Cl_2] (port=dcpp 1, tmp 2, where H_2tdcpp=meso-tetrkis(2,6-dichlorophenyl)porphyrin and H_2tmp=meso-tetramesitylporphyrin) produced aldehydes in up to 99% yields with 100% substrate conversion without C═C bond cleavage. The present invention describes the first ruthenium-catalyzed "Wacker-type oxidation" of terminal alkenes (Hirobe et al., *Heterocycles* (1995), Vol. 40, page 867; Groves et al., *J. Am. Chem. Soc.* (1996), Vol. 118, page 8961; Berkessel et al., *J. Chem. Soc. Perkin Trans.* 1 (1997), page 2265; Che et al., *Chem. Commun.* (1998), page 1583; Che et al., *J. Org. Chem.* (1998), Vol. 63, page 7364; Gross et al. *Org. Lett.* (1999), Vol. 1, page 2077; Gross et al., *Inorg. Chem.* (1999), Vol. 38, page 1446; Che et al., *J. Am. Chem. Soc.* (2000), Vol. 122, page 5337; Che et al., J. Org. Chem. (2001), Vol. 66, page 8145; Che et al., Chem. Eur. J. (2002), Vol. 8, page 1554; Che et al., *Org. Lett.* (2002), Vol. 4, page 1911; Che et al., *Chem. Commun.* (2002), page 2906; Berkessel et al., *Chem. Eur. J.* (2003), Vol. 9, page 4746; Simonneaux et al., *J. Mol. Catal. A* (2003), Vol. 206, page 95; Gray et al., *Inorg. Chim. Acta* (1998), Vol. 270, page 433), which apparently proceeded by a different mechanism from those proposed for the palladium- or palladium/copper-catalyzed reactions reported by the respective groups of Feringa, Murahashi, Wenzel and Ho. The realization of a one-pot diazoacetate olefination directly from aldehyde substrates generated in-situ from this ruthenium-porphyrin-catalyzed alkene oxidation reaction is also reported herein.

SUMMARY OF THE INVENTION

[0003] The invention provides a mild and practical protocol using [Ru^{IV}(tdcpp)Cl_2] as a catalyst for highly regioselective formation of aldehydes from terminal alkenes without C═C bond cleavage. This protocol is a supplement to the Wacker process for oxidation of terminal alkenes to ketones or aldehydes. The catalytic reactions reported herein can be conducted in air at room temperature, affording a series of isolable β-γ-unsaturated aldehydes in good-to-excellent yields. The present work provides a new, practical, and convenient method for preparing multi functional compounds.

BRIEF DESCRIPTION OF THE FIGURES

[0004] **FIG. 1**. illustrates the conversion of alkenes RCH═CH_2 to acetaldehyde (R═HH) or methyl ketones (R≠H) through oxidation process.

[0005] **FIG. 2**. provides examples of metalloporphyrin catalysts capable of catalyzing the highly selective conversion of terminal alkenes to aldehydes via a subsequent epoxidation/isomerization route.

[0006] **FIG. 3**. illustrates the described method which involves the highly selective conversion of terminal alkenes to aldehydes via a subsequent epoxidation/isomerization route using metalloporphyrins as general and efficient catalysts.

[0007] **FIG. 4**. provides representative examples of oxidation of 1-phenyl-1,3-butadiene (3) with various amounts of Cl_2pyNO catalyzed by a dichlororuthenium(IV) porphyrin to give the corresponding aldehyde (4) or epoxide (5) in good to excellent yields and excellent regioselectivity.

[0008] **FIG. 5**. provides representative examples of conversion of terminal 1,3-dienes using a dichlororuthenium(IV) porphyrin catalyst to give the corresponding aldehydes in good to excellent yields and excellent regioselectivity.

[0009] **FIG. 6**. provides representative examples of conversion of variously substituted alkenes using a dichlororuthenium(IV) porphyrin catalyst to give the corresponding aldehydes in good to excellent yields.

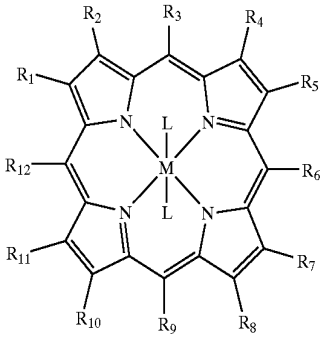
[0010] **FIG. 7**. provides representative examples of conversion of alkenes using a dichlororuthenium(IV) porphyrin catalyst and subsequent in-situ olefination of the aldehyde products obtained with ethyl diazoacetate in the presence of PPh_3, leading to one-pot diazoacetate olefination starting from alkenes in good to excellent yields over two steps.

[0011] **FIG. 8**. illustrates the utility of the metalloporphyrin catalyzed oxidation reaction for organic synthesis through the preparation of representative examples of synthetically useful compounds afforded from dichlororuthenium(IV) porphyrin catalyzed oxidative epoxidation/isomerization reaction of silyl enol ethers.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The present invention provides a practical and mild process for highly selective conversion of terminal alkenes to aldehydes via a subsequent epoxidation/isomerization

route using using non-chiral metalloporphyrin catalysts represented by structural formula:



wherein

[0013] each R_1-R_{12} is independently H, optionally substituted hydroxyl, optionally substituted amino, halogen, —CN, —NO_2, optionally substituted C_{1-20} alkyl, optionally substituted phenyl; optionally substituted naphthyl; optionally substituted anthracenyl, —SR^{13}, —SO_2R^{13}, —CO_2R^{13}, and optionally substituted heteroatom-containing aromatic ring, in which the optional substitutents are independently selected from the foregoing alkyl, phenyl, naphthyl, anthracenyl and heteroatom-containing aromatic groups; R^{13} is independently selected from the same groups as R^1 other than —SR^{13} and —SO_2R^{13}; and L is a halogen molecule, solvent molecule, CO or R^1. The various R groups may be optically pure or can be stereo and regio isomers.

[0014] In an embodiment of this invention, the metalloporphyrin is a transition metal porphyrin, such as ruthenium, manganese, iron, osmium, copper or cobalt porphyrin. In an embodiment of this invention, the porphyrin ligand is a tetraphenylporphyrin and the phenyl rings are attached at the mesopositions of the porphyrin. In an embodiment of the present invention, the catalysts are capable of exhibiting regioselectivity. Two of the preferred catalysts are shown in **FIG. 2**. In an embodiment of the present invention, the catalysts are capable of selectively catalyzing oxidation of C═C bonds without C—C bond cleavage. In an embodiment of this invention, the regioselectivity is the oxidation of terminal C═C bonds.

[0015] Additionally, the present invention provides a method for the preparation of carbonyl compounds with the catalysts from alkenes as starting materials. Further, the present invention provides a method for producing primary aldehydes with the catalyst. The present invention also provides a method for producing regioselective carbonyl compounds with the catalyst. Preferably, the method involves the use of an oxidant which selectively alters the oxidation state of the substrate, preferably in the presence of a solvent. The solvent can be CH_3OH, CH_3CN, N,N-dimethylformaldehyde (DMF), $C_4H_4Cl_2$, CH_2Cl_2 and benzene. A typical oxidant is Cl_2pyNO. In an embodiment of this invention, the substrate is an alkene derivative, or a hydrocarbon containing a C═C functional group. As shown in the figures, carbon to which the alkene moiety is attached can be a part of a cyclic or non-cyclic moiety, which in turn can be substituted with a functional group such as $^-CO_2Me$ or by an aromatic or cycloaliphatic group.

[0016] As used herein, the term "regioselective" refers to selection of terminal C═C bonds over internal C═C bond that undergo reaction. The term "conversion" refers to the relative number of molecules of substrate that is consumed under the applied reaction conditions.

EXAMPLES

Example 1

Regioselective Conversion of Terminal Alkenes to Aldehydes Via a Subsequent Epoxidation/Isomerization Route Catalyzed by Either Dichlororuthenium(IV) Porphyrins 1 or 2

[0017] The invention relates to a practical and mild method for the synthesis of aldehydes using either dichlororuthenium(IV) porphyrins 1 or 2 (prepared according to Leung et al. *J. Chem. Soc. Dalton Trans* (1997), 237) as general and effective catalysts for the oxidation of terminal alkenes.

[0018] Typical conditions employ 0.1 mmol of alkene substrate, Cl_2pyNO (1.03 equiv), and 1 (0.5-2.0 mol %) dissolved in $CDCl_3$ (0.5-1.0 mL) in a NMR tube at room temperature or 60° C. The progress of the reaction was monitored by ^1H NMR. After determination of the product yield by ^1H NMR spectroscopy, the reaction mixture was separated by flash chromatography on silica gel. For the large-scale reaction, 0.65 mmol of alkene substrate, Cl_2pyNO (1.03 equiv), and 1.0 mol % of 1 in 10 mL of $CHCl_3$ were used and reaction was carried out at room temperature for 30 min.

[0019] With 0.5 mol % catalyst loading, a solution of 1-phenyl-1,3-butadiene (3) and 1.03 equiv Cl_2pyNO, in $CDCl_3$ was stirred for 30 min at room temperature, affording the β-γ-unsaturated aldehyde 4-phenyl-but-3-enal (4, styrylacetaldehyde) in 99% yield (**FIG. 4**). No ketone products were detected in the reaction mixture. The reaction gave similar results with $CHCl_3$ and CH_2Cl_2 as solvents. Other solvents, such as benzene, toluene, acetone, ether, and methanol, were inferior to $CHCl_3$ and CH_2Cl_2 for this catalytic process.

[0020] The 1,3-diene 3 was first oxidized by Cl_2pyNO to form epoxide 5 in the presence of catalyst 1. The same catalyst, or its derivative, induced subsequent isomerization of the epoxide to β-γ-unsaturated aldehyde (Alper et al. *J. Org. Chem.* (1976), Vol. 41, page 3611; Sankararaman et al. *J. Org. Chem.* (1996), Vol. 61, page 1877; Kulawiec et al. *J. Org. Chem.* (1997), Vol. 62, page 6547; Ranu et al. *J. Org. Chem.* (1998), Vol. 63, page 8212; Suda et al. *Tetrahedron Lett.* (1999), Vol. 40, page 7243; Llama et al. *J. Chem. Soc. Perkin Trans.* 1 (2000), page 1749). We abbreviate the epoxidation of terminal alkenes followed by isomerization of the epoxide products as E-I reactions.

[0021] To provide support for the above mechanism, we examined the effect of Cl_2pyNO on the catalysis (**FIG. 4**). With Cl_2pyNO in excess, the yield of aldehyde 4 significantly decreased from 99% to 51%, and epoxide 5 was obtained in 49% yield. This could be rationalized by the coordination of epoxide to the active ruthenium porphyrin species for the isomerization reactions. Excess Cl_2pyNO would compete with the epoxide for coordination to ruthenium, thus decreasing the aldehyde yield. We found that the use of 1.01-1.03 equiv Cl_2pyNO could give the best results in terms of reaction completion time (30 min) and aldehyde yield (99%). Changing the temperature from room temperature to 10° C. or 40° C. did not appreciably affect the reaction.

[0022] The E-I reaction of 3 with Cl_2pyNO could be equally efficiently catalyzed by 2 but less efficiently catalyzed by [Ru^{VI}(tdcpp)O_2]. Oxidation of 3 with Cl_2pyNO catalyzed by [Ru^{VI}(tdcpp)O_2] under similar conditions to those for catalyst 1 (1.03 equiv Cl_2pyNO, 1.7 mol % catalyst loading) afforded 4 in 41% yield within 5 h. However, complex [Ru^{II}(tdcpp)(CO)] was a relatively inactive catalyst toward the E-I reaction.

[0023] A series of other 1,3-dienes were treated with 1.01-1.03 equiv Cl_2pyNO and 0.5-1.0 mol % 1 at room temperature (**FIG. 5**). For dienes 6-10, the corresponding β-γ-unsaturated aldehydes 13-17 were obtained in 81-99% yields and were stable enough to be purified by flash chromatography on silica gel. However, the aldehyde product 18a (formed in 90% yield) in the oxidation of diene 11 was converted to 18b upon flash chromatography on silica gel. Non-terminal alkene 12 was oxidized more slowly, affording the β-γ-unsaturated ketone 19 in 99% yield after the reaction proceeded at 60° C. for 6 h.

[0024] When styrene (20) was treated with 1.03 equiv Cl_2pyNO and 1.0 mol % 1 in refluxing CH_2Cl_2 for 5 h, a mixture of styrene oxide and phenylacetaldehyde (27) was obtained in 90% and 10% yield, respectively (Collman et al. *J. Am. Chem. Soc.* (1986), Vol. 108, page 2588; Burrows et al. *J. Am. Chem. Soc.* (1988), Vol. 110, page 6124; Minisci et al. *J. Am. Chem. Soc.* (1995), Vol. 117, page 226; Gross et al. *Angew. Chem. Int. Ed.* (2000), Vol. 39, page 4045; Gray et al. *Angew. Chem. Int. Ed.* (2001), Vol. 40, page 2132). To our surprise, adding more catalyst 1 and allowing the reaction to proceed for a longer time resulted in complete conversion of styrene oxide to aldehyde 27. For example, reaction of styrene with 1.03 equiv Cl_2pyNO in the presence of 2.0 mol % 1 in $CHCl_3$ at 60° C. for 12 h afforded 27 in 99% yield; no benzaldehyde was observed (Gray et al. *Inorg. Chim. Acta* (1998), Vol. 270, page 433). Other styrene derivatives 21-25 could also be converted to the corresponding arylacetaldehydes 28-32 in excellent yields (**FIG. 6**). However, for the non-aromatic alkene 26, only the epoxide product was obtained.

[0025] All the target aldehydes were characterized by ^1H, ^{13}C NMR and IR spectroscopy, and LRMS, HRMS spectrometry. The spectral data of 5 (*Org. Synth., Coll. Vol.* 4, (1963), page. 424), 13 (Frejd et al. *J. Org. Chem.* (1998), Vol. 63, page 3595), 19 (Brookhart et al. *J. Am. Chem. Soc.* (1994), Vol. 116, page 1869) and 27-33 (Palecek et al. *Collect. Czech. Chem. Commun.* (1988), Vol. 53, page 822; Paris et al. *Synth. Commun.* (1991), Vol. 21, page 819; Chikashita et al. *Synth. Commun.* (1987), Vol. 17, page 677; Kulawiec et al. *J. Org. Chem.* (1997), Vol. 62, page 6547; Stratakis et al. *J. Org. Chem.* (2002), Vol. 67, page 8758) are identical with those reported in the literature. 4 ^1H NMR (300 MHz, $CDCl_3$): δ9.76 (t, 1H, J=1.8 Hz), 7.23-7.40 (m, 5H), 6.54 (d, 1H, J=16.2 Hz), 6.29 (dt, 1H, J=16.2, 6.9 Hz), 3.36 (ddd, 2H, J=6.9, 1.8, 1.2 Hz); ^{13}C NMR(75 MHz, $CDCl_3$): 6199.4, 136.5, 134.9, 128.5, 127.7, 126.2, 119.2, 47.3; IR: 1724, 1599, 1496, 967, 748, 694 cm^{-1}; MS (EI) m/z (rel intensity) 146 (31) $[M]^+$; HRMS: calcd for $C_{10}H_{10}O$ 146.0732, found 146.0731. 14 ^1H NMR (300 MHz, $CDCl_3$): δ9.57 (d, 1 H, J=7.8 Hz), 8.22 (d, 2H, J=9.0 Hz), 7.38 (d, 2H, J=9.0 Hz), 6.95 (dt, 1H, J=15.3, 6.9 Hz), 6.13 (ddt, 1H, J=15.3, 7.8, 1.5 Hz), 3.78 (d, 2H, J=6.9 Hz), IR: 1689, 1598, 1517, 1347, 980, 856, 736 cm^{-1}; MS (EI): m/z 191 (8) $[M]^+$. 15 ^1H NMR (300 MHz, $CDCl_3$): δ9.77(t, 1H, J=1.8 Hz), 7.30(d, 2H, J=8.1 Hz), 7.15(d, 2H, J=8.4 Hz), 6.53(d, 1H, J=15.6 Hz), 6.25(dt, 1H, J=7.2, 16.5 Hz), 3.34-3.37(m, 2H); 2.36 (s, 3H); ^{13}C NMR(75 MHz, $CDCl_3$): δ199.8, 137.7, 135.1, 133.9, 129.3, 126.2, 118.1, 47.6, 21.3; IR: 1721, 1513, 974, 799, 505 cm^{-1}; MS (EI): m/z 160 (27) $[M]^+$; HRMS: calcd for $C_{11}H_{12}O$+H 161.0966, found 161.0959. 16 ^1H NMR (300 MHz, $CDCl_3$): δ9.75(t, 1H, J=2.1 Hz), 7.43 (dd, 1H, J=7.5, 1.5 Hz), 7.23 (td, 1H, J=7.5, 2.1 Hz), 6.83-6.95 (m, 3H), 6.28 (dt, 1H, J=16.2, 7.2 Hz), 3.84 (s, 3H), 3.35 (dt, 2H, J=7.2, 1.5, 2.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ199.7, 156.6, 130.1, 128.8, 126.9, 125.8, 120.7, 119.8, 110.9, 55.5, 48.0; IR: 1721, 1598, 1490, 1245, 1028, 975, 752 cm^{-1}; MS (EI): m/z (rel intensity) 176 (6) $[M]^+$; HRMS: calcd for $C_{11}H_2O_2$ 176.0837, found 176.0829. 17 ^1H NMR (300 MHz, $CDCl_3$): δ9.68 (t, 1H, J=1.8 Hz), 7.22 (t, 1H, J=8.4 Hz), 6.56 (d, 2H, J=8.4 Hz), 6.50 (d, 1H, J=11.1 Hz), 6.02 (dt, 1H, J=11.1, 7.5 Hz), 3.77 (s, 6H), 3.04 (ddd, 2H, J=7.5, 1.5, 1.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ201.1, 157.6, 129.0, 125.2, 123.5, 113.6, 103.7, 55.6, 44.9; IR: 1724, 1593, 1585, 1471, 1253, 1113, 748 cm^{-1}; MS (EI) m/z (rel intensity); 206 (51) $[M]^+$; HRMS: calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0960.18b ^1H NMR (300 MHz, $CDCl_3$): δ9.47 (s, 1H), 8.20 (d, 2H, J=8.7 Hz), 7.38 (d, 2H, J=9.0 Hz), 6.61 (t, 1H, J=7.2 Hz), 3.82 (d, 2H, J=7.2 Hz), 1.89 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$): δ194.6, 149.2, 146.9, 145.8, 140.8, 129.4, 124.1, 34.8, 29.7; IR: 1681, 1145, 1606, 1594, 1511, 851, 750, 700 cm^{-1}; MS (EI) m/z (rel intensity) 205 (42) $[M]^+$; HRMS: calcd for $C_{11}H_{11}NO_3$+H 206.0817, found 206.0802.

Example 2

Regioselective Conversion of Terminal Alkenes to Aldehydes Via a Subsequent Epoxidation/Isomerization Route Catalyzed by Either Dichlororuthenium(IV) Porphyrins 1 and In-Situ Olefination with Ethyl Diazoacetate in the Presence of PPh_3, Leading to One-Pot Diazoacetate Olefination Starting from Alkenes

[0026] Recently, Woo (Woo et al. *J. Am. Chem. Soc.* (2002), Vol. 124, pagr 176), Aggarwal (Aggarwal et al. *J. Am. Chem. Soc.* (2003), Vol. 125, page 6034), and Zhang (Zhang et al. *J. Org. Chem.* (2003), Vol. 68, page 3714) reported that iron or ruthenium mesotetraaryl porphyrins [Fe^{II}(ttp)], [Fe^{III}(tpp)Cl], or [Ru^{II}(tpp)(CO)] can catalyze the olefination of certain classes of aldehydes with ethyl diazoacetate (EDA) in the presence of PPh_3.

[0027] We observed that both 1 and [Ru^{II}(tdcpp)(CO)] could also catalyze such olefination reactions. Recognizing that the aldehyde products in the 1-catalyzed E-I reactions could be in-situ used as the substrates for olefination reactions, we were interested in developing a practical one-pot E-I-olefination reaction, i.e. one-pot diazoacetate olefination directly starting from alkenes rather than from aldehydes.

[0028] Typical conditions involve using the "1+Cl_2pyNO" protocol, 0.1 mmol 3 was converted to aldehyde 4 in $CHCl_3$ within 30 min (the reaction conditions are exactly the same as that stated for EXAMPLE 1). Removal of the solvent, followed by addition of 1.2 equiv Ph_3P, 1 mL toluene, and 1.2 equiv EDA, the olefination product 34 was obtained in 99% yield after the reaction mixture was heated at 80° C. for 2 h, cooled to room temperature and separated by flash chromatography on silica gel with petroleum ether/ethyl acetate (3:1) as eluent. Similarly, through a one-pot E-I-olefination reaction of 35, we isolated the olefination product 40 in 55% yield (**FIG. 7**).

[0029] The target olefination products were characterized by ^1H, ^{13}C NMR and IR spectroscopy, and LRMS, HRMS spectrometry. 34 ^1H NMR (300 MHz, $CDCl_3$): δ7.22-7.37 (m, 5H), 7.04 (dt, 1H, J=15.3, 6.3 Hz), 6.45 (d, 1H, J=16.2 Hz), 6.19 (dt, 1H, J=15.9, 6.9 Hz), 5.90 (td, 1H, J=1.5, 15.3 Hz), 4.20 (q, 2H, J=6.9 Hz), 3.08-3.13 (m, 2H), 1.29 (t, 3H, J=6.9 Hz); IR: 1720, 1653, 1267, 1160, 1043, 967, 745, 693 cm^{-1}; MS (EI) m/z (rel intensity) 216 (67) $[M]^+$. 40 ^1H

NMR (300 MHz, $CDCl_3$): δ7.91 (d, 2H, J=7.8 Hz), 7.66 (t, 1H, J=7.5 Hz), 7.53 (t, 2H, J=7.5 Hz), 6.94 (dt, 1H, J=7.8, 15.9 Hz), 5.83 (d, 1H, J=15.9 Hz), 5.19-5.15 (m, 1H), 4.18 (q, 2H, J=6.9 Hz), 3.84 (d, 1H, J=6.6 Hz), 2.76-2.84 (m, 1H), 2.41-2.51 (m, 1H), 1.28 (t, 3H, J=6.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ200.5, 165.9, 142.6, 134.4, 133.2, 129.1, 128.6, 124.6, 71.9, 60.4, 38.5, 14.3; IR: 3467, 1716, 1684, 1657, 1598, 1581, 1450, 1271, 1167, 979, 695 cm^{-1}; MS (EI) m/z (rel intensity) 248 (0.1) $[M]^+$; HRMS ($[M+Na]^+$): calcd for $C_{14}H_{16}O_4Na$ 271.0941, found 271.0919.

Example 3

Preparation of Synthetically Organic Compounds by Application of the Dichlororuthenium(IV) Porphyrin Catalyzed Oxidation of Silyl Enol Ethers

[0030] 4-Oxoarylbutanal derivatives are useful compounds for organic synthesis. For example, the preparation and application of 4-oxo-4-phenylbutanal (39) have been extensively studied in the literature. (Kruse et al. *Heterocycles* (1987), Vol. 26, page 3141; Molander et al. *Tetrahedron Lett.* 1989, Vol. 30, page 2351; Molander et al. *J. Org. Chem.* (1991), Vol. 56, page 2617; Molander et al. *J. Am. Chem. Soc.* 1993, Vol. 115, page 830; Savoia et al. *Tetrahedron Lett.* (1994), Vol. 35, page 2775; Utimoto et al. *Tetrahedron Lett.* (1995), Vol. 36, page 8067). In this work, we found that 39 could be prepared in 52% NMR yield (isolated yield: 41%) from the E-I reaction of silyl enol ether 35 (**FIG. 8**). The same reaction also afforded hydroxyl ketoaldehyde 37 in 23% yield. When 2.06 equiv Cl_2pyNO were used, 37 could be obtained in 88% yield (determined by ^1H NMR).

[0031] Typical conditions involve dropwise addition of a solution of 1 (0.02 mmol) in $CHCl_3$ (50 mL) over 30 min to a well-stirred solution of 35 (2.0 mmol) and Cl_2pyNO (2.2 mmol) in $CHCl_3$ (100 mL) in a 25-mL flask. A drop of 12 N HCl was then added. The resulting mixture was stirred for 5 min. The product was purified by flash chromatography on silica gel.

[0032] The spectral data of 38 (Chong et al. *Tetrahedron* 1999, Vol. 55, page 14233) and 39 (Molander et al. *J. Am. Chem. Soc.* 1993, Vol. 115, page 830) are identical with those reported in the literature.

1. A method for producing an aldehyde from an unsaturated compound having one or more C═C functional groups, which comprises catalyzing the reaction of an oxidant with the compound with a catalytic amount of metalloporphyrin, thereby producing the aldehyde.

2. The method according to claim 1, wherein the compound comprises a terminal alkene.

3. The method according to claim 1, wherein the oxidant comprises 2,6-dichloropyridine N-oxide (Cl_2pyNO).

4. The method according to claim 1, wherein the reaction is carried out using $CDCl_3$, $CHCl_3$, CH_2Cl_2, diethyl ether, acetone, CH_3OH, toluene or benzene as a solvent.

5. The method according to claim 1, wherein the metalloporphyrin is a transition metal metalloporphyrin.

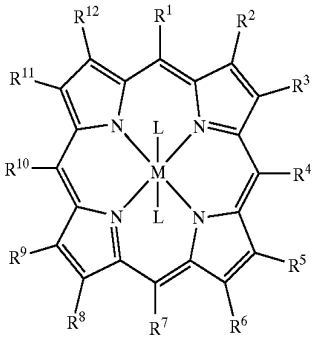
6. The method according to claim 5, wherein the transition metal metalloporphyrin is ruthenium, manganese, iron, cobalt, copper or osmium metalloporphyrin.

7. The method according to claim 6, wherein the metalloporphyrin is ruthenium porphyrin.

8. The method of claim 3, wherein the metalloporphyrin is a transition metal metalloporphyrin, and the method is carried out using $CDCl_3$, $CHCl_3$, CH_2Cl_2, diethyl ether, acetone, CH_3OH, toluene or benzene as a solvent.

9. The method of claim 8, wherein the metalloporphyrin exhibits regioselectivity and provides yields of at least 52 percent.

10. The method according to claim 1, wherein the metalloporphyrin has the structure:



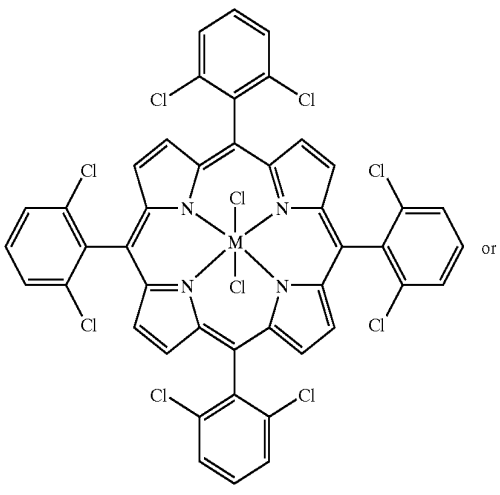
wherein M is a transition metal;

wherein each R_1-R_{12} is independently H, optionally substituted hydroxyl, optionally substituted amino, halogen, —CN, —NO_2, optionally substituted C_{1-20} alkyl, optionally substituted phenyl; optionally substituted naphthyl; optionally substituted anthracenyl, —SR^{13}, —SO_2R^{13}, —CO_2R^{13}, and optionally substituted heteroatom-containing aromatic ring, in which the optional substitutents are independently selected from the foregoing alkyl, phenyl, naphthyl, anthracenyl and heteroatom-containing aromatic groups; R^{13} is independently selected from the same groups as R^1 other than —SR^{13} and —SO_2R^{13}; and

wherein L is a halogen molecule, solvent molecule, CO or R^1.

11. The method according to claim 10, wherein the metalloporphyrin has the structure A or B:

A



or

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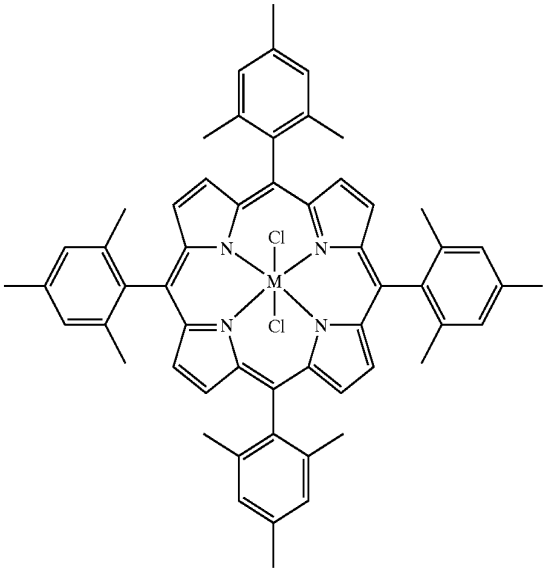
B

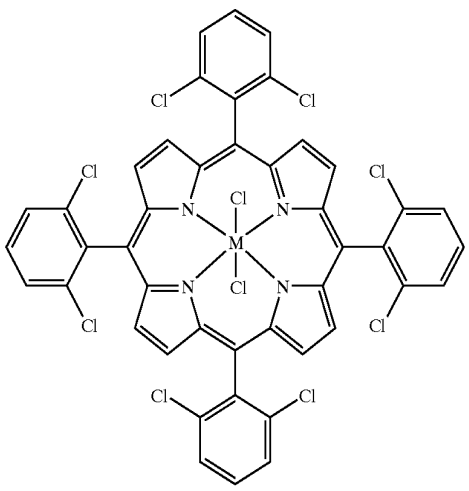


wherein M represents a metal.

12. The method according to claim 11, wherein M is a transition metal.

13. The method according to claim 12, wherein the metalloporphyrin has structure A or B:

A



or

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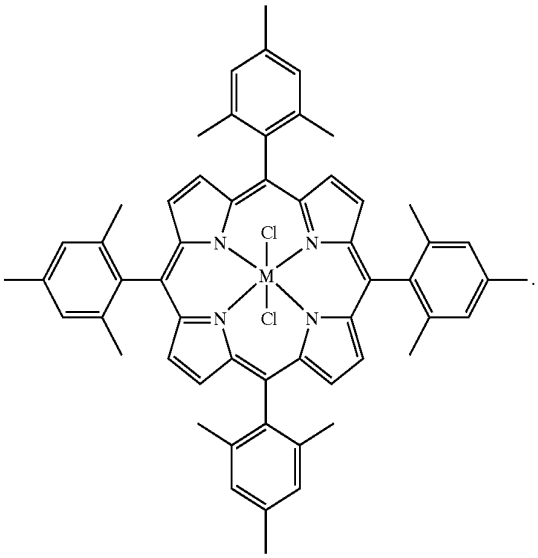
B



14. A method for producing diazoacetate olefination from an unsaturated compound having one or more C═C functional groups, which comprises catalyzing the reaction of an oxidant with the unsaturated compound in the presence of a catalytic amount of metalloporphyrin and adding a Lewis base and a diazo compound to the reaction, thereby producing an α, β-unsaturated ester of the diazoacetate olefination.

15. The method according to claim 14, wherein the compound comprises a terminal alkene.

16. The method according to claim 14, wherein the oxidant comprises 2,6-dichloropyridine N-oxide (Cl_2pyNO).

17. The method according to claim 14, wherein the Lewis base comprises PPh_3.

18. The method according to claim 14, wherein the diazo compound comprises ethyl diazoacetate (EDA).

19. The method according to claim 14, wherein the reaction in carried out with $CDCl_3$, $CHCl_3$, CH_2Cl_2, diethyl ether, acetone, CH_3OH, toluene or benzene as a solvent.

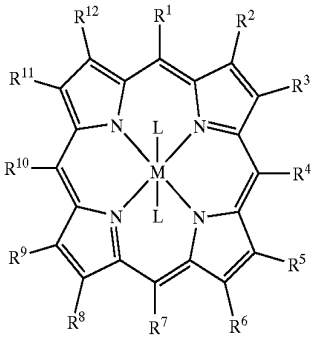
20. The method according to claim 14, wherein the metalloporphyrin is a transition metal metalloporphyrin.

21. The method according to claim 20, wherein the transition metal metalloporphyrin is ruthenium, manganese, iron, cobalt, copper or osmium metalloporphyrin.

22. The method according to claim 21, wherein the metalloporphyrin is ruthenium porphyrin.

23. The method of claim 16, wherein the metalloporphyrin is a transition metal metalloporphyrin, the Lewis base is PPh_3, the diazo compound is ethyl diazoacetate, and the reaction is carried out using $CDCl_3$, $CHCl_3$, CH_2Cl_2, diethyl ether, acetone, CH_3OH, toluene or benzene as a solvent.

24. The method according to claim 14, wherein the metalloporphyrin has the structure:



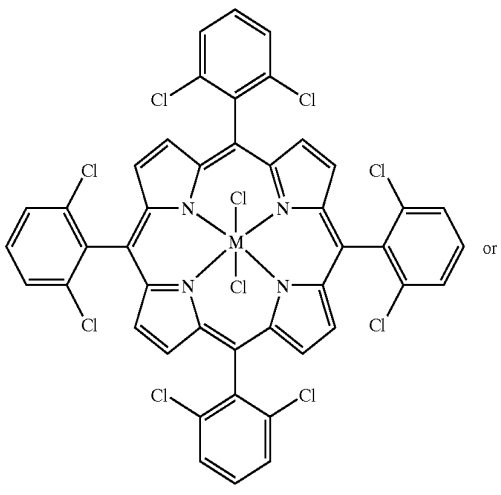
wherein M is a transition metal;

wherein each R_1-R_{12} is independently H, optionally substituted hydroxyl, optionally substituted amino, halogen, —CN, —NO_2, optionally substituted C_{1-20} alkyl, optionally substituted phenyl; optionally substituted naphthyl; optionally substituted anthracenyl, —SR^{13}, —SO_2R^{13}, —CO_2R^{13}, and optionally substituted heteroatom-containing aromatic ring, in which the optional substitutents are independently selected from the foregoing alkyl, phenyl, naphthyl, anthracenyl and heteroatom-containing aromatic groups; R^{13} is independently selected from the same groups as R^1 other than —SR^{13} and —SO_2R^{13}; and

wherein L is a halogen molecule, solvent molecule, CO or R^1.

25. The method according to claim 24, wherein the metalloporphyrin has the structure A or B:

A



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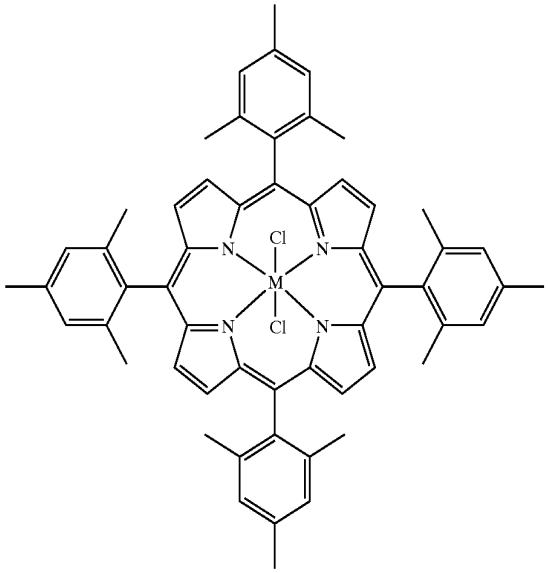
B

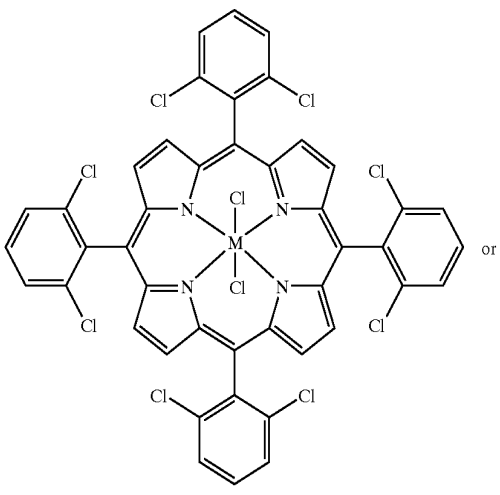


wherein M represents a metal.

26. The method according to claim 25, wherein M is a transition metal.

27. The method according to claim 26, wherein the catalyst is a compound having the structure A or B:

A



or

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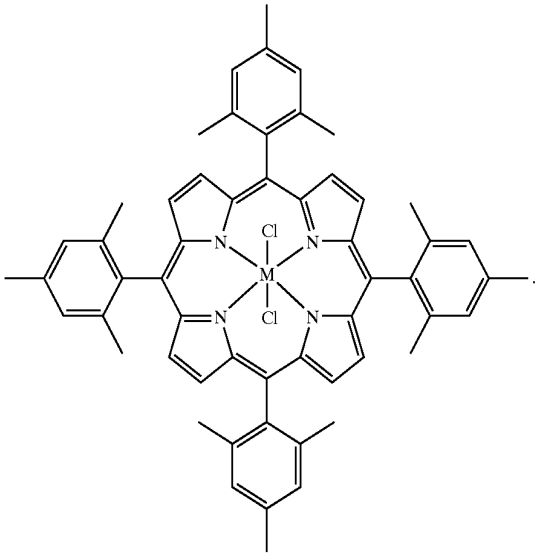
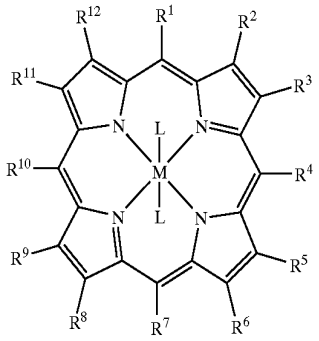
B



28. The method of claim 23 wherein the metalloporphyrin exhibits regioselectivity.

29. The method of claim 28, wherein the catalyst exhibits trans-selectivity and yields a trans-α,β-unsaturated ester.

30. A compound having the structure:



wherein M is a transition metal;

wherein each R_1-R_{12} is independently H, optionally substituted hydroxyl, optionally substituted amino, halogen, —CN, —NO_2, optionally substituted C_{1-20} alkyl, optionally substituted phenyl; optionally substituted naphthyl; optionally substituted anthracenyl, —SR^{13}, —SO_2R^{13}, —CO_2R^{13}, and optionally substituted heteroatom-containing aromatic ring, in which the optional substitutents are independently selected from the foregoing alkyl, phenyl, naphthyl, anthracenyl and heteroatom-containing aromatic groups; R^{13} is independently selected from the same groups as R^1 other than —SR^{13} and —SO_2R^{13}; and

wherein L is a halogen molecule, solvent molecule, CO or R^1.

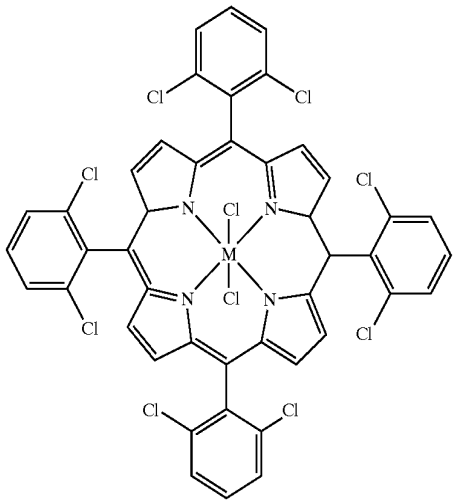
31. (canceled)

32. The compound of claim 35, wherein M comprises a transition metal.

33. The compound of claim 35, wherein the transition metal is ruthenium, manganese, cobalt, iron, copper or osmium.

34. The compound of claim 33, wherein the transition metal is ruthenium.

35. The compound of claim 30 having the following structure



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