Supporting Information

Selective oxidation of terminal aryl and aliphatic alkenes to aldehydes catalyzed by iron(III) porphyrins with triflate as counter anion

Guo-Qiang Chen[a], Zhen-Jiang Xu[a], Cong-Ying Zhou[b] and Chi-Ming Che*[a,b]

[a]*Shanghai-Hong Kong Joint Laboratory in Chemical Synthesis, Shanghai Institute of Organic Chemistry,354 Feng Lin Road, Shanghai, China. Fax: (852)2857-1586; Tel: (852) 2859-2154; E-mail:* cmche@hku.hk

[b] *Department of Chemistry, State Key Laboratory of Synthetic Chemistry, and Open Laboratory of Chemical Biology of the Institute of Molecular Technology for Drug Discovery and Synthesis, The University of Hong Kong, Pokfulam Road, Hong Kong, China*

Contents **Page**

General information: Unless otherwise indicated, all reactions were performed under argon atmosphere and all the solvents were dried and freshly distilled. Alkenes were obtained commercially and distilled under reduced pressure before used. ^{1}H NMR spectra were measured on Varian Mercury 300 spectrometer. EI mass were determined on a HP5989A mass spectrometer. IR spectra were measured on Bio-Rad FTS-185 spectrometer. UV-Vis were determined on a CARY100 spectrometer. Elemental analyses were determined by Elemantar Vario EL. GC analyses were performed on a Varian CP-3800, SPB^{TM}-5, FID and *n*-dodecane was used as the internal standard.

Experimental procedures and characterizations:

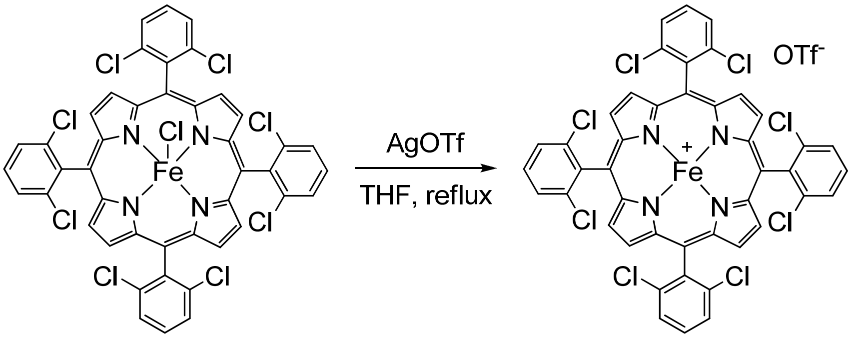
PhIO[1]:

$$\mathrm{PhI(OAc)_2} \xrightarrow[\mathrm{H_2O}]{\mathrm{NaOH}} \mathrm{PhIO}$$

To finely ground $PhI(OAc)_2$ (8.05 g, 25.0 mmol) placed in a 100 mL conical flask was added 45 mL of a 3M NaOH aqueous solution over a period of 10 mins. The resulting yellow heterogeneous mixture was then stirred for 90 mins at rt. The reaction medium was diluted with 40 mL of H_2O and vigorously stirred for 1 h. The yellow solid was collected on a funnel, washed with H_2O (2 × 100 mL) and $CHCl_3$ (100 mL) before being dried under vacuum for 12 h. PhIO was obtained as a yellow powder (4.8 g, 87% yield).

Anal.Calcd.for C_6H_5IO: C, 32.76; H, 2.29. Found: C, 32.91; H, 2.20.

[Fe(2,6-Cl_2TPP)OTf] [2]:



A mixture of [Fe(2,6-Cl_2TPP)Cl] (2.00 g, 2,04 mmol) and AgOTf (524 mg, 2.04 mmol) in THF (200 mL) was refluxed gently for 1 h and then filtered through a coarse frit. Heptane (200 mL) was added gradually with continuous swirling and set aside overnight for crystallization. The product was collected by filtration, washed with heptane and dried under vacuum (1.99 g, 88% yield).

IR (KBr): ν_{max} 1652, 1523, 1488, 1336, 1082, 988, 939, 760 cm^{-1};
UV-Vis (CH_2Cl_2, nm): λ_{max} = 407, 514, 648.

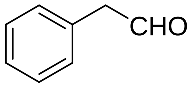
Typical procedure for [Fe(2,6-Cl_2TPP)OTf]-catalyzed aryl alkenes to aldehydes:

To a solution of [Fe(2,6-Cl_2TPP)OTf] (4.4 mg, 0.004 mmol), styrene (62.4 mg, 0.6 mmol) and DCM (2 mL) was added PhIO (44.0 mg, 0.2 mmol). The resulting heterogeneous mixture was stirred at room temperature for 6 h and then filtered through a short column of silica (2-3 cm), washed with DCM. The yield was determined by ^{1}H NMR with PhTMS as a internal standard.

Typical procedure for [Fe(2,6-Cl_2TPP)OTf]-catalyzed aliphatic alkenes to aldehydes:

To a solution of [Fe(2,6-Cl_2TPP)OTf] (6.6 mg, 0.006 mmol), dodec-1-ene (33.7 mg, 0.2 mmol) in DCM (1 mL) was added PhIO (52.8 mg, 0.24 mmol). The resulting heterogeneous mixture was stirred at room temperature for 1 h. Then dioxane (3 mL) was added and the reaction mixture was stirred at 80 °C for 3 h. After cooling to room temperature, the mixture was filtered through a short column of silica (2-3 cm), washed with DCM. The yield was determined by ^{1}H NMR with PhTMS as the internal standard.

2-phenylacetaldehyde [3]

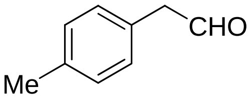


2a

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.75 (t, *J* = 2.4 Hz, 1H), 7.41-7.21 (m, 5H), 3.69 (d, *J* = 2.4 Hz, 2H);

EI-MS m/z(relative intensity): 120(M^+, 70), 91(100), 44(54), 107(40), 77(39), 79(31), 105(31), 45(25).

2-p-tolylacetaldehyde [3]

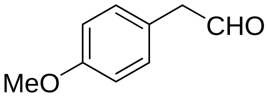


2b

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.73 (t, *J* = 2.1 Hz, 1H), 7.18 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.8 Hz, 2H), 3.65 (d, *J* = 2.1 Hz, 2H), 2.35 (s, 3H);

EI-MS m/z(relative intensity): 134(M^+, 32), 105(100), 119(93), 84(91), 91(88), 86(57), 120(55), 77(45).

2-(4-methoxyphenyl)acetaldehyde [3]

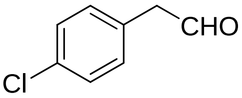


2c

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.72 (t, *J* = 2.4 Hz, 1H), 7.13 (d, *J* = 8.7 Hz, 2H), 6.90 (d, *J* = 8.7 Hz, 2H), 3.80 (s, 3H), 3.63 (d, *J* = 2.1 Hz, 2H);

EI-MS m/z(relative intensity): 150(M^+, 6), 135(100), 136(63), 77(30), 121(30), 92(14), 107(13), 91(10).

2-(4-chlorophenyl)acetaldehyde [4]

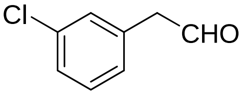


2d

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.71 (t, *J* = 2.1 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 2H), 7.32 (d, *J* = 8.7 Hz, 2H), 3.88 (d, *J* = 2.1 Hz, 2H);

EI-MS m/z(relative intensity): 154(M^+, 18), 84(100), 139(93), 140(65), 86(61), 77(53), 125(50), 111(43).

2-(3-chlorophenyl)acetaldehyde [5]

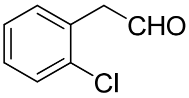


2e

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.75 (t, *J* = 1.8 Hz, 1H), 7.34-7.28 (m, 2H), 7.23 (s, 1H), 7.12-7.10 (m, 1H), 3.69 (d, *J* = 1.8 Hz, 2H);

EI-MS m/z(relative intensity): 154(M^+, 40), 84(100), 139(86), 125(82), 86(68), 140(67), 91(60), 77(53).

2-(2-chlorophenyl)acetaldehyde [6]

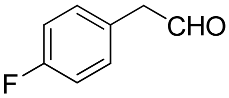


2f

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.76 (t, *J* = 1.5 Hz, 1H), 7.45-7.42 (m, 1H), 7.29-7.22 (m, 3H), 3.85 (s, 2H);

EI-MS m/z(relative intensity): 154(M^+, 6), 84(100), 86(64), 47(17), 49(14), 125(14), 88(10), 139(9).

2-(4-fluorophenyl)acetaldehyde [3]

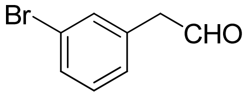


2g

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.75 (t, *J* = 1.5 Hz, 1H), 7.21-7.16 (m, 2H), 7.09-7.04 (m, 2H), 3.69 (d, *J* = 1.5 Hz, 2H);

EI-MS m/z(relative intensity): 138(M^+, 9), 109(100), 123(38), 95(20), 83(14), 125(13), 97(10), 75(8).

2-(3-bromophenyl)acetaldehyde [7]

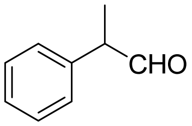


2h

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.78 (t, *J* = 2.1 Hz, 1H), 7.48 (d, *J* = 8.1 Hz, 1H), 7.42 (s, 1H), 7.26-7.23 (m, 1H), 7.18 (d, *J* = 7.8 Hz, 1H), 3.71 (d, *J* = 2.1 Hz, 2H);

EI-MS m/z(relative intensity): 198(M^+, 6), 84(100), 86(64), 184(43), 77(40), 183(33), 185(33), 186(24).

2-phenylpropanal [8]

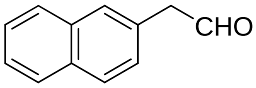


2i

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.69 (s, 1H), 7.42-7.21 (m, 5H), 3.64 (q, *J* = 7.2 Hz, 1H), 1.45 (d, *J* = 7.2 Hz, 3H);

EI-MS m/z(relative intensity): 134(M^+, 3), 43(30), 105(28), 77(10), 58(10), 121(8), 117(8), 118(7).

2-(naphthalen-2-yl)acetaldehyde [8]

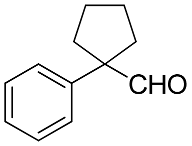


2j

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.75 (t, *J* = 2.1 Hz, 1H), 7.86-7.79 (m, 3H), 7.69 (s, 1H), 7.50-7.47 (m, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 3.76 (d, *J* = 2.1 Hz, 2H);

EI-MS m/z(relative intensity): 170(M^+, 18), 154(100), 153(60), 152(37), 155(23), 141(18), 127(14), 151(12).

1-phenylcyclopentanecarbaldehyde [9]

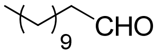


2k

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.36 (s, 1H), 7.28-7.24 (m, 2H), 7.19-7.15 (m, 3H), 2.54-2.48 (m, 2H), 1.90-1.84 (m, 2H), 1.75-1.71 (m, 2H), 1.67-1.61 (m, 2H);

EI-MS m/z(relative intensity): 174(M^+, 27), 105(100), 77(85), 115(38), 51(35), 173(33), 133(30), 120(28).

n-dodecanal [10]

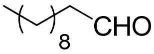


4a

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.77 (t, *J* = 1.5 Hz, 1H), 2.42 (td, *J* = 7.2, 1.5 Hz, 2H), 1.66-1.58 (m, 2H), 1.31-1.26 (m, 16H), 0.88 (t, *J* = 6.6 Hz, 3H);

EI-MS m/z(relative intensity): 184(M^+, 1), 43(100), 57(81), 41(80), 71(58), 55(58), 82(53), 69(40).

n-undecanal [11]

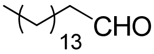


4b

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.77 (s, 1H), 2.42 (td, *J* = 7.2, 1.5 Hz, 2H), 1.65-1.60 (m, 2H), 1.31-1.26 (m, 14H), 0.88 (t, *J* = 6.6 Hz, 3H);

EI-MS m/z(relative intensity): 170(M^+, 1), 57(100), 82(93), 43(87), 55(75), 41(72), 68(61), 71(60).

n-palmitaldehyde [12]

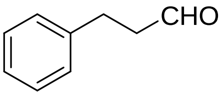


4c

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.76 (t, *J* = 2.1 Hz, 1H), 2.44-2.39 (m, 2H), 1.64-1.58 (m, 2H), 1.31-1.26 (m, 24H), 0.89 (t, *J* = 6.6 Hz, 3H);

EI-MS m/z(relative intensity): 240(M^+, 2), 43(25), 188(10), 58(8), 57(6), 242(6), 173(5), 160(5).

3-phenylpropanal [13]

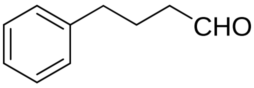


4d

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.83 (d, *J* = 0.9 Hz, 1H), 7.33-7.19 (m, 5H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.79 (t, *J* = 7.5 Hz, 2H);

EI-MS m/z(relative intensity): 134(M^+, 1), 43(100), 58(45), 42(9), 91(7), 92(7), 44(3), 41(3).

4-phenylbutanal [13]

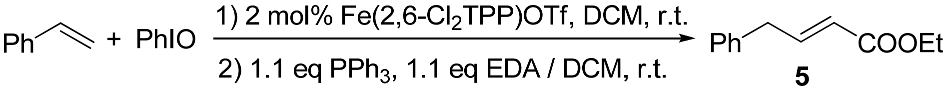


4e

^{1}H NMR (300 MHz, $CDCl_3$): δ 9.74 (s, 1H), 7.31-7.27 (m, 2H), 7.23-7.16 (m, 3H), 2.65 (t, *J* = 7.2 Hz, 2H), 2.44 (t, *J* = 7.2 Hz, 2H), 1.95 (quintet, *J* = 7.2 Hz, 2H);

EI-MS m/z(relative intensity): 148(M^+, 4), 104(24), 91(19), 43(13), 105(8), 130(6), 92(6), 51(6).

ethyl 4-phenylbut-2-enoate (5) [14]



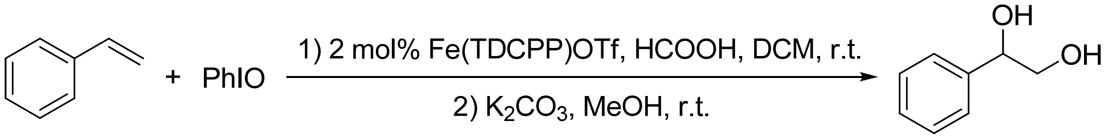
To a solution of [Fe(2,6-Cl_2TPP)OTf] (4.4 mg, 0.004 mmol), styrene (62.4 mg, 0.6 mmol) and DCM (2 mL) was added PhIO (44.0 mg, 0.2 mmol). The resulting heterogeneous mixture was stirred at room temperature for 6 h and then the solvent and excess styrene were removed under reduced pressure. PPh_3 (57.6 mg, 0.22 mmol) and DCM (1 mL) were added to the mixture. To the mixture the solution of ethyl diazoacetate (25.1 mg, 0.22 mmol) in 1 mL DCM was added for 1 h and stirred at room temperature for additonal 1 h. The crude product was purified by silica gel flash column chromatography (PE:EtOAc = 50:1) to give the product as a colorless oil (32.1 mg, 84% yield).

^1H NMR (300 MHz, $CDCl_3$): δ 7.36-7.15 (m, 5H), 7.10 (dt, *J* = 15.8, 7.2 Hz, 1H), 5.81 (d, *J* = 15.8 Hz, 1H), 4.17 (q, *J* = 7.2 Hz, 2H), 3.52 (d, *J* = 7.2 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H);

EI-MS m/z(relative intensity): 190(M^+, 56), 117(100), 115(70), 145(40), 116(34), 144(26), 91(25), 127(17);

IR (film): ν_{max} 3028, 2981, 1719, 1652, 1496, 1270, 1163, 1042, 984, 699 cm^{-1}.

1-phenylethane-1,2-diol (6) [15]



6

4.4 mg Fe(TDCPP)OTf (0.004 mmol), 62.4 mg styrene (0.6 mmol), 22 μL formic acid (0.6 mmol) were disolved in 1 mL dichloromethane, followed by 44.0 mg PhIO (0.2 mmol) and additional 1 mL dichloromethane. The reaction mixture were stirred at room temperature for 10 h, after which the volatile were evaporated and 41.4 mg potassium carbonate (0.3 mmol) together with 6 mL methanol was added. After strring at room temperature for 6 h, the reaction mixture was subjected to flash chromatography (ethyl acetate: petrol ether = 2:3) to afford the desired diol as a white solid (20.2 mg, 73%).

^1H NMR (300 MHz, $CDCl_3$): δ 7.39-7.27 (m, 5H), 4.83-4.79 (m, 1H), 3.76-3.61 (m, 2H), 3.12 (brs, 1H), 2.70 (brs, 1H);

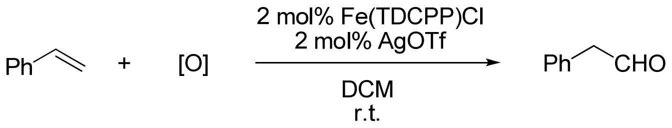
EI-MS m/z(relative intensity): 138(M^+, 11), 107(100), 79(56), 77(35), 108(8), 51(7), 78(6), 105(6);

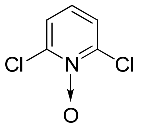
IR (KBr): ν_{max} 3208, 3061, 2963, 2933, 1494, 1448, 1343, 1101, 1053, 887, 832, 699 cm^{-1}.

References

1. Dauban, P.; Sanière, L.; Tarrade, A.; Dodd, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 7707.
2. Suda, K.; Baba, K.; Nakajima, S.; Takanami, T. *Tetrahedron Lett.* **1999**, *40*, 7243.
3. Chen, J.; Che, C. M. *Angew. Chem., Int. Ed.* **2004**, *43*, 4950.
4. Sheng, S. R.; Wang, Q. Y.; Huang, Y. X.; Xin, Q.; Liu, X. L. *Synth. Commun.* **2006**, *36*, 429.
5. Okada, H.; Noma, T.; Katsuyama, Y.; Hashimoto, H. *Bull. Chem. Soc. Jpn.* **1968**, *41*, 1395.
6. Zhang, Z.; Pan, Y.; Hu, H.; Kao, T. *Synthesis* **1991**, *7*, 539.
7. Davies, J. R.; Kane, P. D.; Moody, C. J. *J. Org. Chem.* **2005**, *70*, 7305.
8. Jiang, G.; Chen, J.; Thu, H. Y.; Huang, J. S.; Zhu, N.; Che, C. M. *Angew. Chem., Int. Ed.* **2008**, *47*, 6638.
9. Ertürk, E.; Göllii, M.; Demir, A. S. *Tetrahedron* **2010**, *66*, 2373.
10. Kantam, M. L.; Arundhathi, R.; Likhar, P. R.; Damodara, D. *Adv. Synth. Catal.* **2009**, *351*, 2633.
11. Makado, G.; Morimoto, T.; Sugimoto, Y.; Tsutsumi, K.; Kagawa, N.; Kakiuchi, K. *Adv. Synth. Catal.* **2010**, *352*, 299.
12. Miao, C. X.; He, L. N.; Wang, J. Q.; Wang, J. L. *Adv. Synth. Catal.* **2009**, *351*, 2209.
13. Suda, K.; Baba, K.; Nakajima, S.; Takanami, T. *Tetrahedron Lett.* **1999**, *40*, 7243.
14. Aggarwal, V.; Fulton, J. R.; Sheldon, C. G.; Vicente, J. De *J. Am. Chem. Soc.* **2003**, *125*, 6034.
15. Hu, W-X.; Li, P.-R.; Jiang, G.; Che, C.-M.; Chen, J. *Adv. Synth. Catal.* **2010**, *352*, 3190;

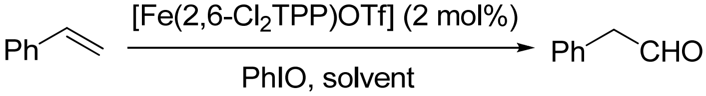
Table SI Effect of different oxidants on [Fe(2,6-Cl_2TPP)OTf] catalyzed E-I reaction of styrene to phenylacetaldehyde:



Entry[a]	Oxidant	Yield (%)[b]
1	PhIO	45
2		0
3	TBHP	0
4	urea peroxide	1
5	*m*-CPBA	0
6	H_2O_2 (30% aq.)	0
7	NaClO (aq.)	0
8	oxone	6

[a] 0.3 mmol styrene, 0.2 mmol oxidant in 2 mL CH_2Cl_2 were stirred for 8 h; [b] yield based on GC with *n*-dodecane as the internal standard.

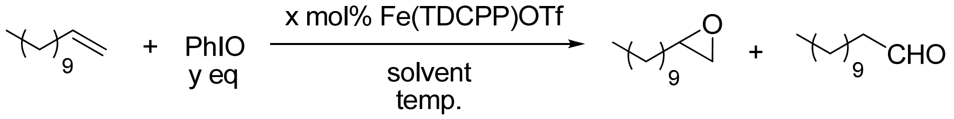
Table SII Optimization of [Fe(2,6-Cl_2TPP)OTf] catalyzed E-I reaction of styrene to phenylacetaldehyde



Entry[a]	Solvent	Temp.	Styrene:PhIO	Conversion(%)[b]	Yield(%)[c]
1	DCM	rt	1:1.5	100	59
2	DCE	rt	1:1.5	100	45
3	dioxane	rt	1:1.5	56	57
4	Toluene	rt	1:1.5	59	49
5	EtOAc	rt	1:1.5	97	39
6	MeCN	rt	1:1.5	100	4
7	THF	rt	1:1.5	15	13
8	DCM	40	1:1.5	100	53
9	DCM	0	1:1.5	100	49
10	DCM	-20	1:1.5	100	35
11	DCM	rt	1:1.1	75	60
12	DCM	rt	1.5:1	-	45[d]
13	DCM	rt	3:1	-	83[d]

[a] 0.2 mmol styrene; 0.3 mmol PhIO; 2 mL solvent; [b] determined by GC with *n*-dodecane as internal standard. [c] base on conversion. [d] based on oxidant.

Table SIII Optimization of [Fe(2,6-Cl$_2$TPP)OTf] catalyzed E-I reaction of aliphatic alkene



Entry[a]	X	Y	Solvent	Temp.	Conversion[b]	Epoxide	Aldehyde
1	2	1.5	2 mL DCE	r.t.-80	93	12	38
2	2	1.5	2 mL DCE	80	83	14	25
3	4	2	2 mL DCE	r.t.-80	>99	trace	40
4	2	1.5	2 mL DCM	r.t.-40	>99	51	17
5[c]	4	2	1 mL DCE 1 mL dioxane	r.t. 80	>99	Not detected	47
6[c]	2	1.5	1 mL DCM 2 mL dioxane	r.t. 80	>99	22	36
7[c]	4	1.5	1 mL DCE 2 mL dioxane	r.t. 80	>99	Not detected	68
8[c]	3	1.5	1 mL DCE 2 mL dioxane	r.t. 80	>99	Not detected	63
9[c]	3	1.5	1 mL DCE 1 mL dioxane	r.t. 80	>99	Not detected	47
10[c]	4	1.5	1 mL DCM 2 mL dioxane	r.t. 80	>99	Not detected	60
11[c]	2	1.5	1 mL DCE 3 mL dioxane	r.t. 80	>99	trace	63
12[c]	4	1.5	1 mL DCE 3 mL dioxane	r.t. 80	>99	Not detected	70
13[c]	3	1.5	1 mL DCE 3 mL dioxane	r.t. 80	>99	Not detected	72
14[c]	**3**	**1.2**	**1 mL DCE** **3 mL dioxane**	**r.t.** **80**	**>99**	**Not detected**	**70**

[a] 0.2 mmol alkene were used; [b] Conversion and yield based on ^{1}H NMR with PhTMS as internal standard. [c] The alkene was treated with corresponding amount of catalyst and oxidant in 1 mL DCM or DCE at room temperature, after the oxidation was complete, additional dioxane were added and the reaction was run at 80°C till completion.