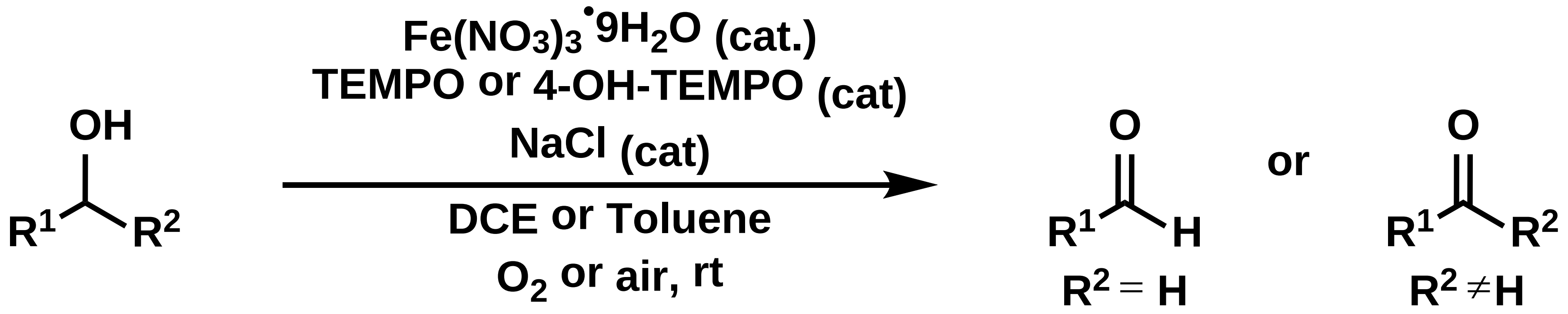
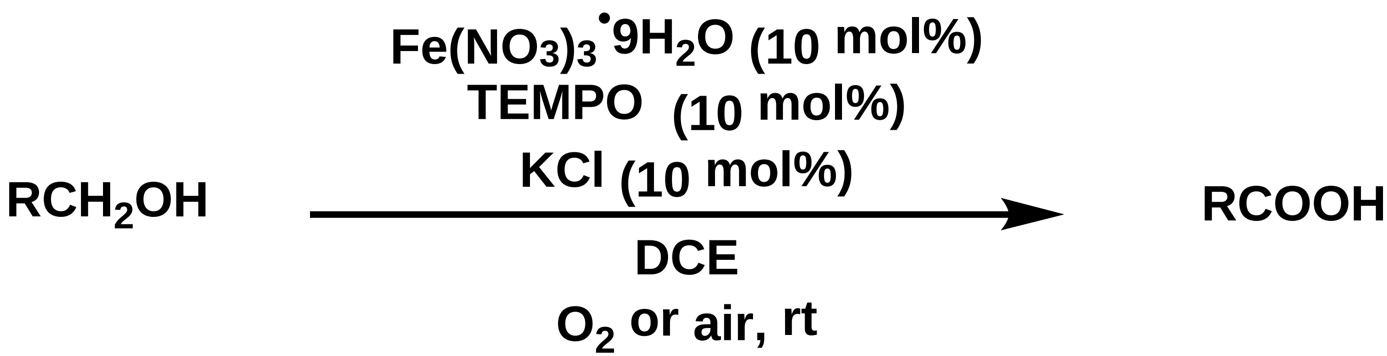
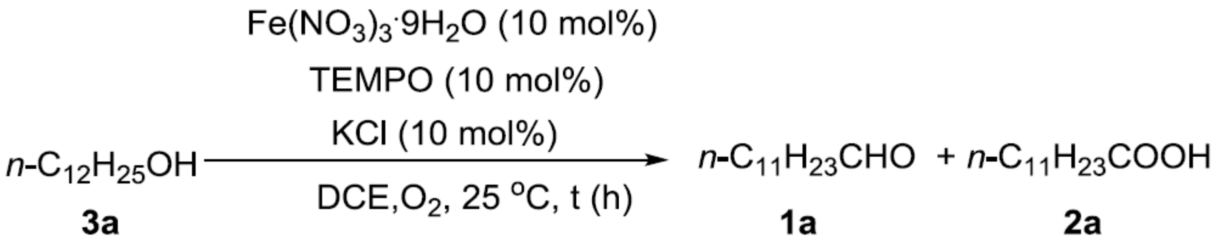
麻生明氧化

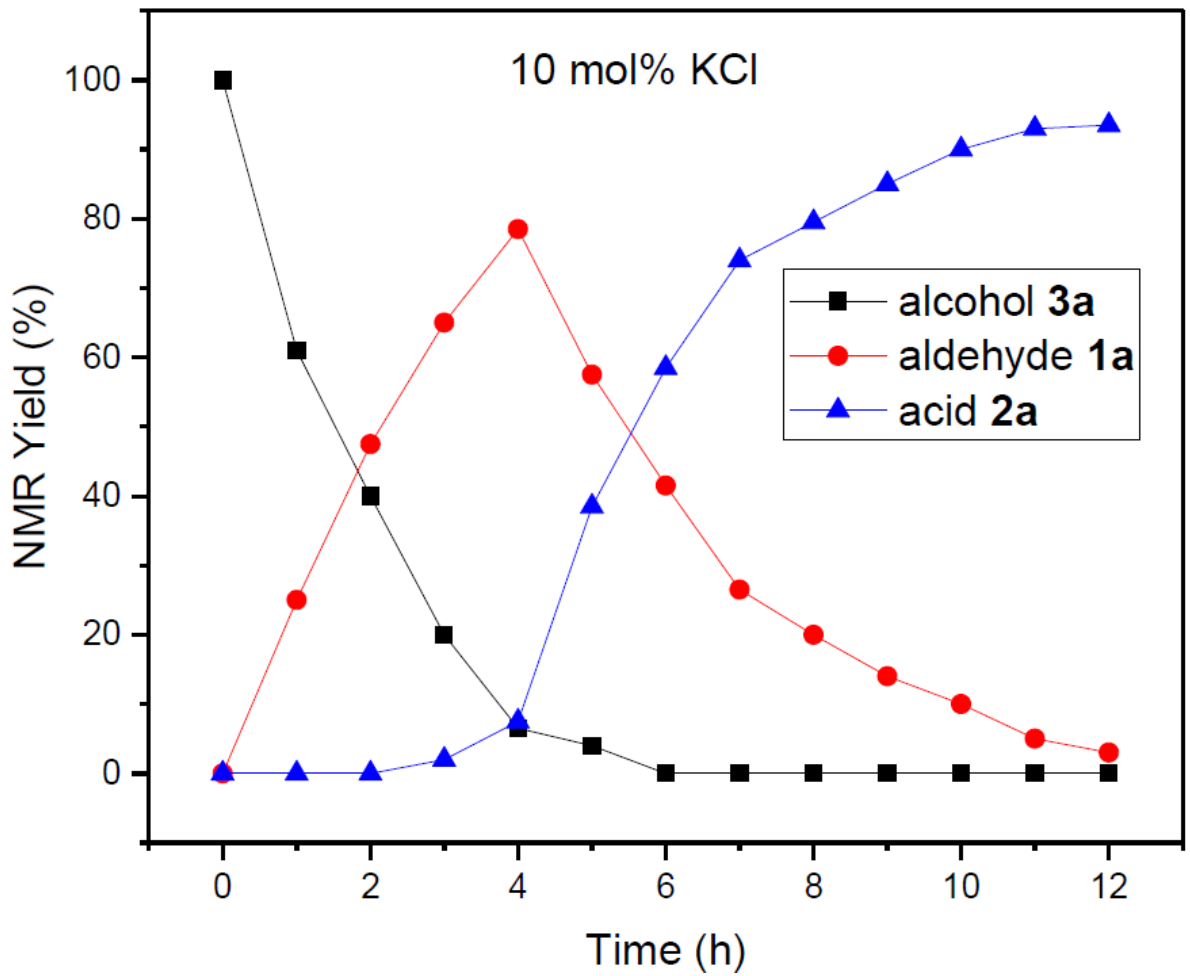
Introduction





Mechanism





Ma S.M. et al. *J. Am. Chem. Soc.* **2016**, 138, 8344−8347.

Mechanism

$n\text{-}C_{11}H_{23}CHO$ (**1a**) $\xrightarrow[\text{DCE, r.t., 12 h}]{Fe(NO_3)_3 \cdot 9H_2O \text{ (x mol\%)}, \text{ TEMPO (y mol\%)}, \text{ KCl (z mol\%)}, \; O_2 \text{ balloon}}$ $n\text{-}C_{11}H_{23}COOH$ (**2a**) + $n\text{-}C_{11}H_{23}CO_3H$ (**7a**)

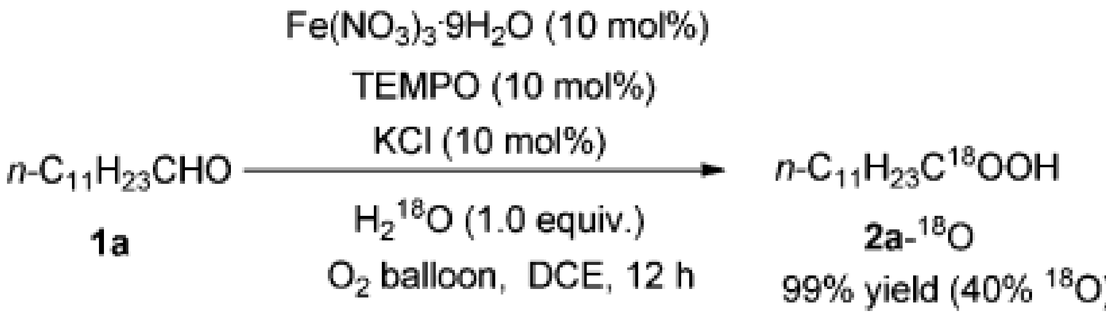
				NMR yield, %		
entry	$Fe(NO_3)_3 \cdot 9H_2O$ (x mol %)	TEMPO (y mol %)	KCl (z mol %)	1a	2a	7a
1	10	10	10	0	95	0
2	–	–	–	98	2	0
3	10	10	–	14	81	0
4	10	–	–	0	78	11
5	10	–	10	15	64	12
6	–	10	10	100	0	0

$n\text{-}C_{11}H_{23}CH_2OH$ (**3a**) $\xrightarrow[\text{DCE, r.t. 12 h}]{Fe(NO_3)_3 \cdot 9H_2O \text{ (10 mol\%)}, \text{ KCl (0 or 10 mol\%)}, \; O_2 \text{ balloon}}$ Recovery of **3a** = 100%

Ma S.M. et al. *J. Am. Chem. Soc.* **2016**, 138, 8344−8347.

Mechanism

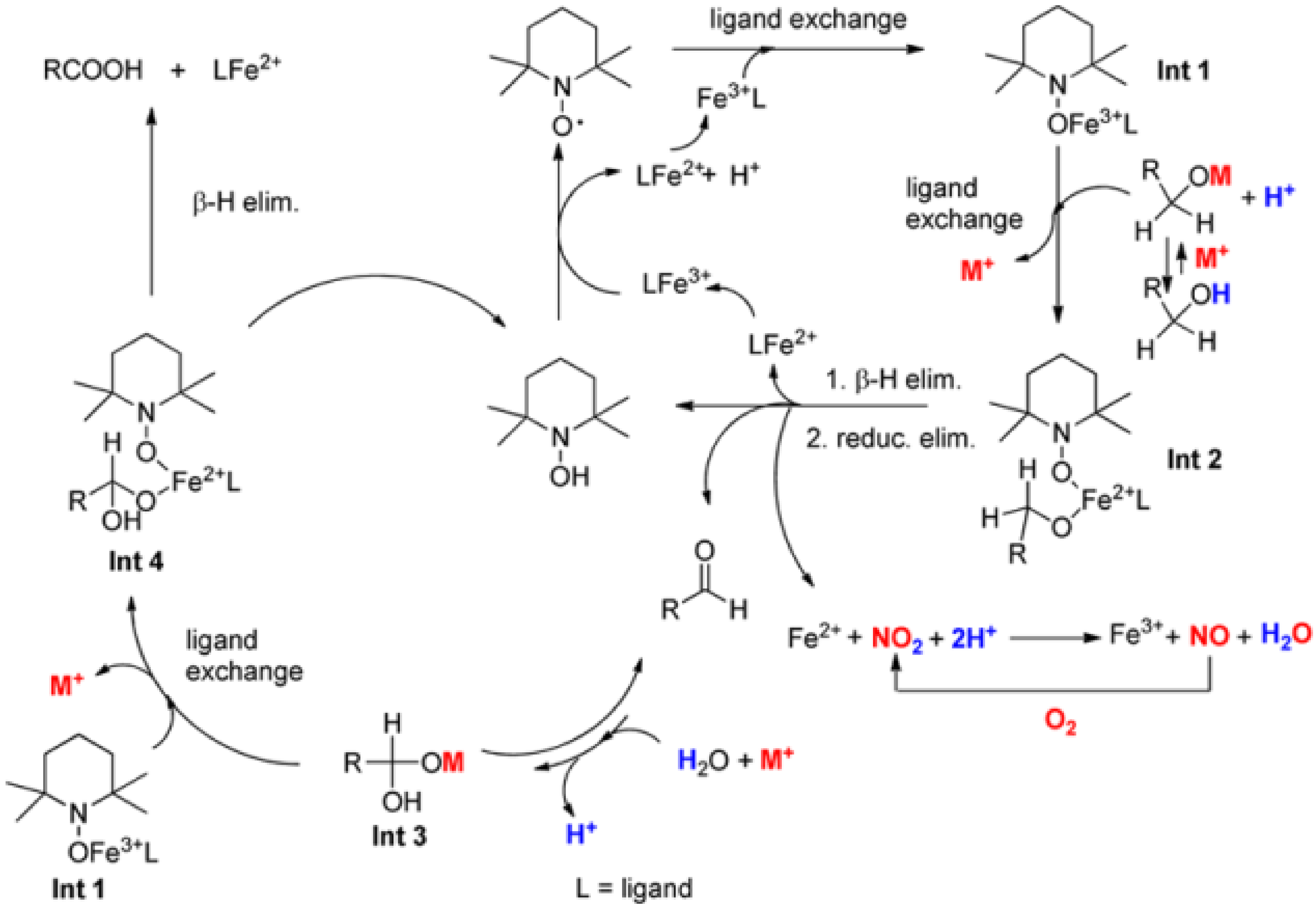
1）



2） Reddish brown gas (NO_2) was observed during the reaction, and NO was detected by GS-MS.

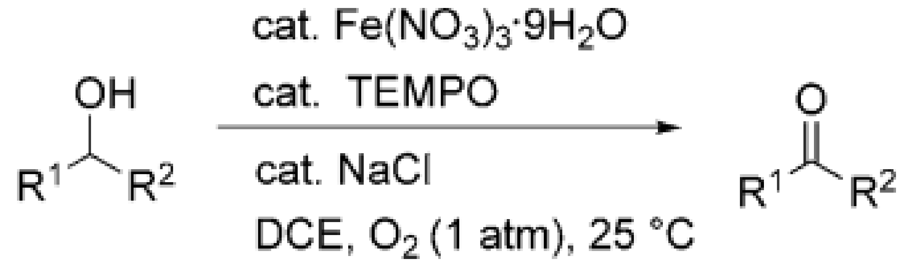
Ma S.M. et al. *J. Am. Chem. Soc.* **2016**, 138, 8344−8347.

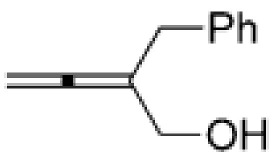
Mechanism



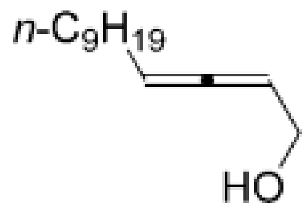
Ma S.M. et al. *J. Am. Chem. Soc.* **2016**, 138, 8344−8347.

Substrate Scope: Aldehydes/Ketones

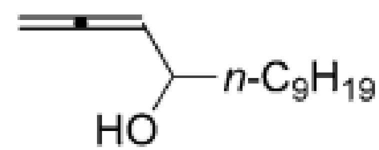




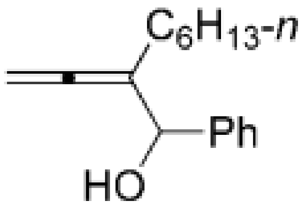
(5 h, 74%, 72%)[a,h]
(10 h, 72%, 71%)[b,h]



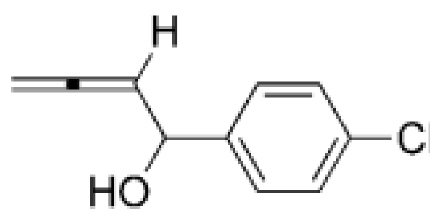
(5 h, 85%, 80%)[a,h]
(9 h, 84%, 82%)[b,h]



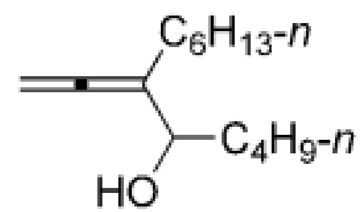
(3 h, 93%, 87%)[a,h]
(5 h, 94%, 88%)[b,h]



(24 h, 58%, 54%)[c,h]



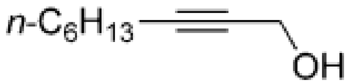
(4 h, 84%)[a,h]
(8.5 h, 83%)[b,h]
(5.5 h, 84%, 78%)[d,h]



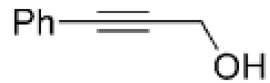
(4 h, 75%, 75%)[c,h]
(24 h, 73%, 65%)[d,i]

Ma S.M. et al. *Adv. Synth. Catal.* **2011**, 353, 1005 – 1017.

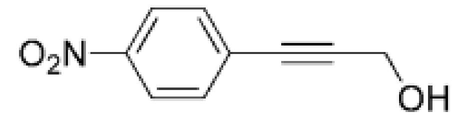
Substrate Scope: Aldehydes/Ketones



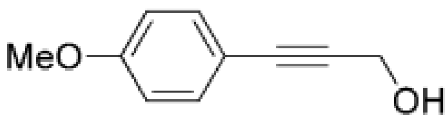
(5 h, 86%, 86%)[e,h]



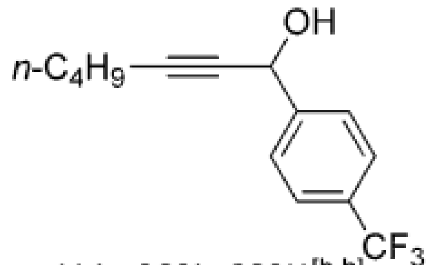
(4 h, 91%, 86%)[b,h]
(2.5 h, 82%, 79%)[e,i]



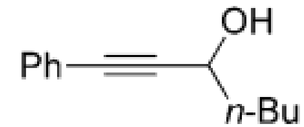
(6.5 h, 84%, 76%)[e,h]



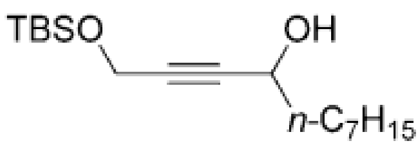
(3.5 h, 67%, 69%)[a,h]
(4 h, 75%, 78%)[d,h]



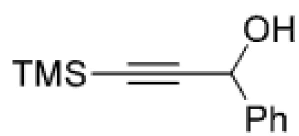
(4 h, 98%, 89%)[b,h]
(5.5 h, 88%, 78%)[e,h]



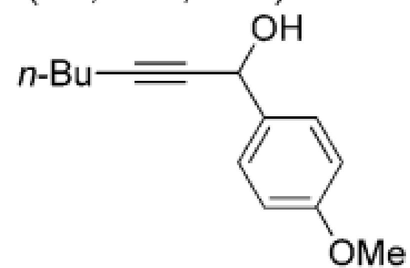
(8 h, 91%, 91%)[b,h]
(4 h, 97%, 93%)[e,i]



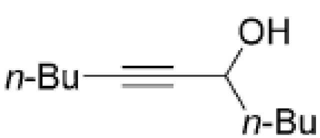
(4 h, 95%, 92%)[b,h]
(8.5 h, 89%, 89%)[e,h]



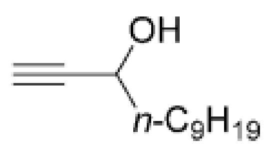
(2 h, 97%, 92%)[b,h]
(4 h, 96%, 93%)[e,h]



(3.5 h, 87%, 84%)[b,h]
(5.5 h, 83%, 85%)[e,h]



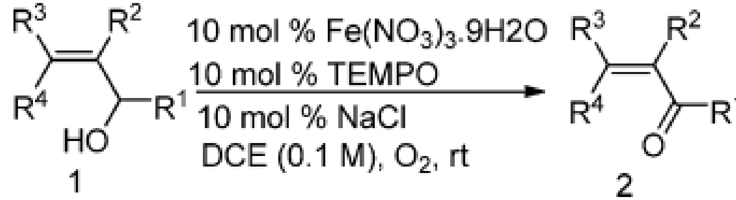
(4 h, 94%, 92%)[b,h]
(5.5 h, 97%, 92%)[e,h]

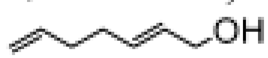
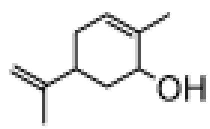
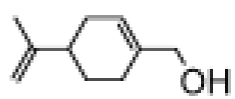


(5 h, 95%, 93%)[b,h]
(12.5 h, 98%, 91%)[e,h]

Ma S.M. et al. *Adv. Synth. Catal.* **2011**, 353, 1005 – 1017.

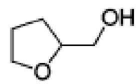
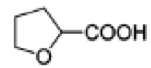
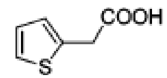
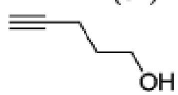
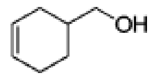
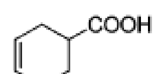
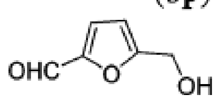
Substrate Scope: Aldehydes/Ketones



entry	R^1; R^2; R^3; R^4	t (h)	yield of **2** (E/Z)(%)
1	H;H;$Me_2C{=}CH(CH_2)_3$; CH_3 (**1a**)[a]	3	91 (97:3) (**2a**)
2	H;H;n-C_4H_9;H (**1b**)	5	83 (>99/1) (**2b**)
3	H; H; n-C_8H_{17}; H (**1c**)	2	98 (>99/1) (**2c**)
4	H; H; p-$NO_2C_6H_4$; H (**1d**)	2	99 (>99/1) (**2d**)
5	CH_3; H; n-C_4H_9; H (**1e**)	2	92 (>99/1) (**2e**)
6	C_2H_5; CH_3; C_2H_5; H (**1f**)	3	60 (>99/1) (**2f**)
7	Cy; H; CH_3; H (**1g**)[b]	9	75 (97:3) (**2g**)
8	Ph; CH_3; H; H (**1h**)	6	75 (**2h**)
9[c]	n-C_5H_{11}; H; H; H (**1i**)	13	76 (**2i**)
10[c]	n-C_6H_{13}; H; H; H (**1j**)	12.5	86 (**2j**)
11	 (2E,6E-**1k**/2Z,6E-**1k** = 90/10)	47	66 (2E,6E-**2k**/2Z,6E-**2k** = 89/11)
12	 (E-**1l**, E/Z = 87/13)	9	72 (E-**2l**, E/Z = 88/12)
13	 (2E,4E-**1m**/2E,4Z-**1m** = 94/6)	4	70 (2E,4E-**2m**/2E,4Z-**2m** = 95/5)
14	 (**1n**)	12	67 (**2n**)
15	 (**1o**)	9	90 (**2o**)

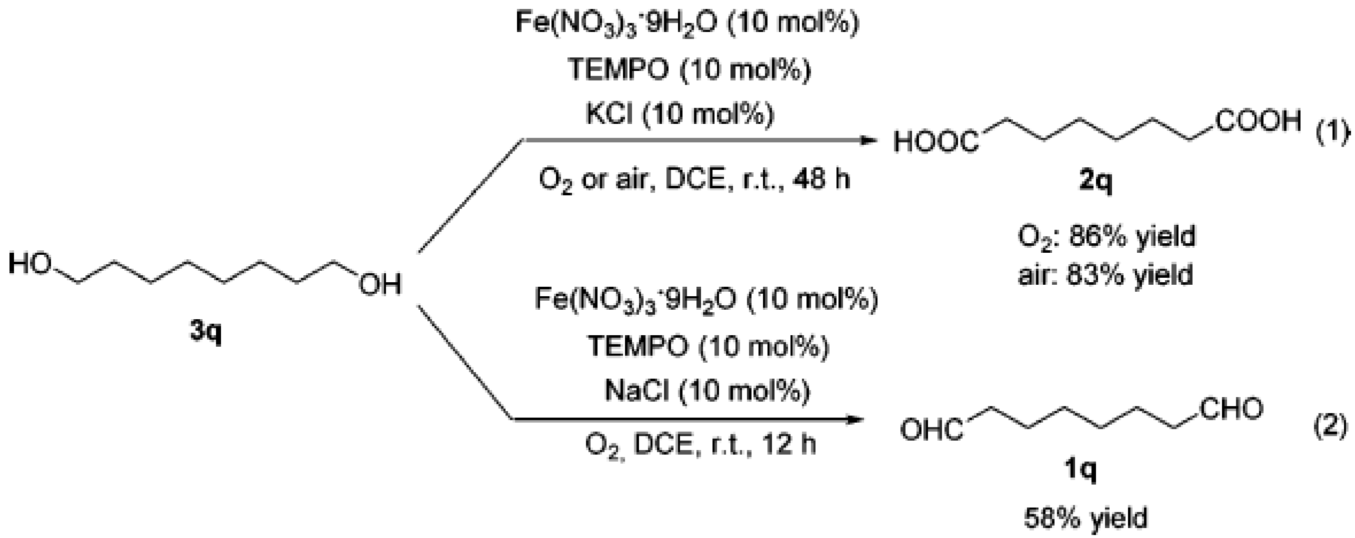
Ma S.M. et al. *Org. Lett.* **2013**,15, 5150 – 5153.

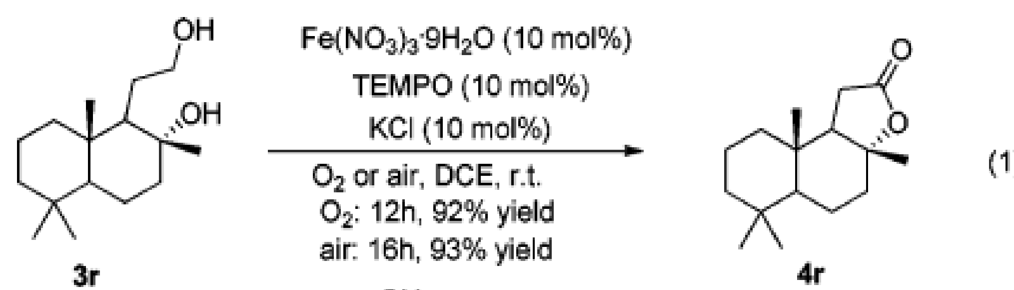
Substrate Scope: Carboxylic Acids

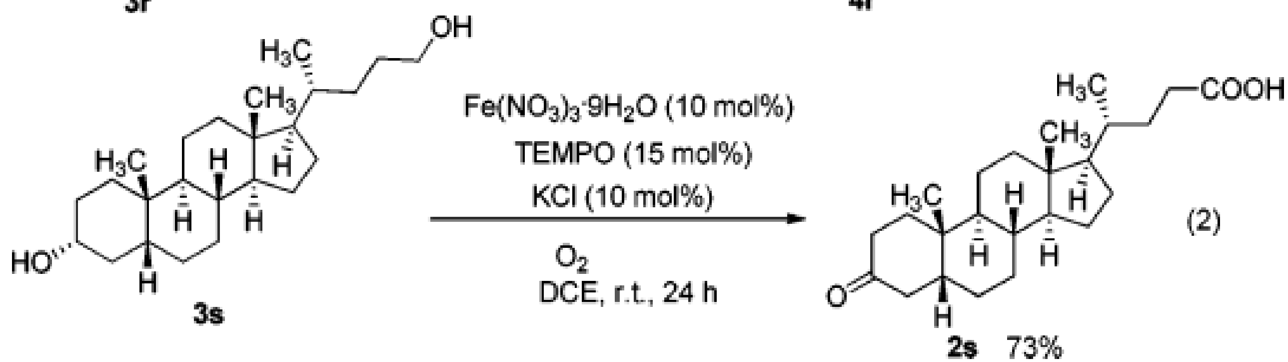
Entry	Alcohol	Product	Yield of **2** (%)[b]	
			O_2	Air
1	*n*-$C_{12}H_{25}OH$ (**3a**)	*n*-$C_{11}H_{23}CO_2H$ (**2a**)	100	95
2	*n*-$C_8H_{17}OH$ (**3c**)	*n*-$C_7H_{15}CO_2H$ (**2c**)	85	89
3	$Ph(CH_2)_3OH$ (**3d**)	$Ph(CH_2)_2CO_2H$ (**2d**)	98	99
4	*n*-$C_{16}H_{33}OH$ (**3e**)	*n*-$C_{15}H_{31}CO_2H$ (**2e**)	99	98
5	$MeO_2C(CH_2)_5OH$ (**3f**)	$MeO_2C(CH_2)_4CO_2H$(**2f**)	94	86
6	$AcO(CH_2)_8OH$ (**3g**)	$AcO(CH_2)_7CO_2H$ (**2g**)	93	93
7	 (**3h**)	 (**2h**)	70	73
8	 (**3i**)	 (**2i**)	85	81
9	$Br(CH_2)_9OH$ (**3j**)	$Br(CH_2)_8CO_2H$ (**2j**)	98	98
10	*n*-$C_6H_{13}O(CH_2)_2OH$ (**3k**)	*n*-$C_6H_{13}OCH_2CO_2H$ (**2k**)	92	84
11	 (**3l**)	 (**2l**)	80	80
12	 (**3m**)	 (**2m**)	60	68
13	 (**3n**)	 (**2n**)	95	90
14	 (**3o**)	 (**2o**)	66[c]	65[d]
15	 (**3p**)	 (**2p**)	81[d,e]	70[d,e]
16			55[d,e,f]	-
17	*p*-nitrobenzyl alcohol	4-nitrobenzoic acid	76[d]	-

Ma S.M. et al. *J. Am. Chem. Soc.* **2016**, 138, 8344−8347.

Synthetic Applications

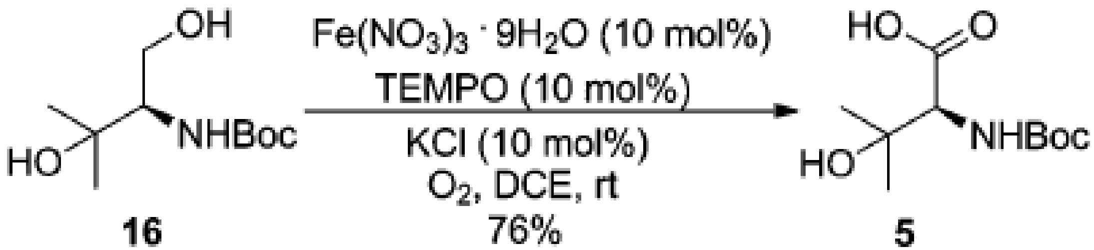




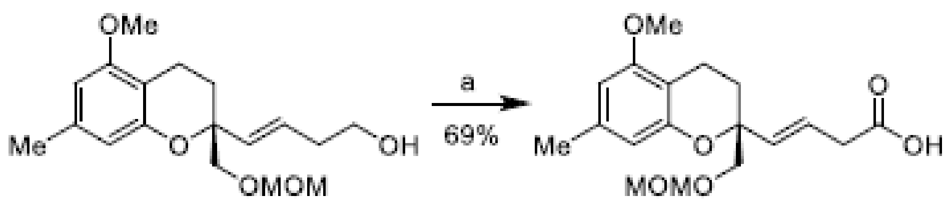


Ma S.M. et al. *J. Am. Chem. Soc.* **2016**, 138, 8344−8347.

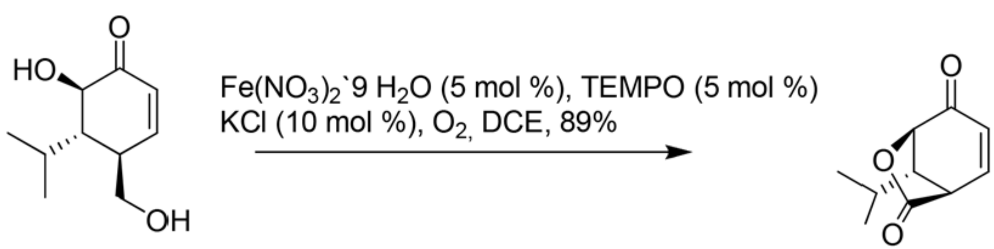
Synthetic Applications



Liu B. et al. *Chem. Commun.*, **2017**, 53, 5549—5552.



Wang P.S. et al. *Chem. Lett.* **2017**,



Plietker B. et al. *Org. Lett.* **2018**, 20, 4328−4331.