Synthesis I. Khan et al. PSP

Dihydroxylation of Olefins with Potassium Permanganate Catalyzed by Imidazolium Salt

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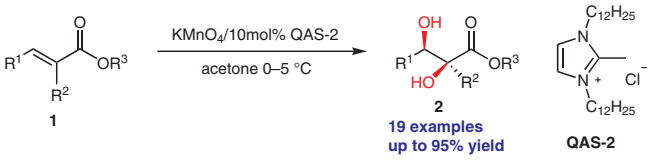

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Abstract The development of an efficient and cost-effective *cis*-dihydroxylation reaction of acrylate derivatives was achieved. The reaction proceeded in acetone with an imidazolium salt as catalyst to furnish the dihydroxylation of olefins at 0–5 °C using $KMnO_4$ as the oxidant. This efficient and non-aqueous protocol was highly suitable for the large-scale preparation of *cis*-dihydroxylated compounds from the corresponding acrylate derivatives in high yields without overoxidation.

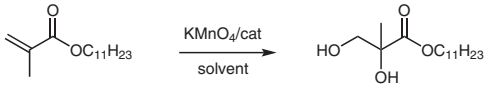
Key words dihydroxylation, diols, acrylates, potassium permanganate, imidazolium salt

Olefin dihydroxylation is among one of the most important methods to prepare vicinal diol compounds, which are indispensable to the pharmaceutical, agrochemical, and food industries.[1] Among the reported methods for olefin *cis*-dihydroxylation, osmium tetroxide/potassium osmate catalyzed protocols are efficient and usually result in high yields, yet a secondary oxidant is required in these methods.[2] Furthermore, the toxicity and high cost of osmium salts restricts its application in industry. Recently, mimicking enzyme catalysis, a series of Mn and Fe complexes were reported to facilitate the dihydroxylation of olefins.[3] The Woodward *cis*-dihydroxylation is promoted by AgOAc, which limits its increased use in industry due to high costs.[4] Using a stoichiometric amount of potassium permanganate as the oxidant under cooled and basic conditions is still the most widely applied method for olefin dihydroxylation in industry owing to the low costs and safe operation conditions.[5] But the reduced yield caused by overoxidation in the aqueous phase makes this strategy unsatisfactory.[5e,6] It takes much effort to improve the efficiency of $KMnO_4$ by converting it into a quaternary ammonium permanganate salt, like tetradecyltrimethylammonium permanganate (TDTAP). This stable reagent was utilized for the dihydroxylation of alkenes in a two phase solvent system at room temperature,[7] yet the yield was still unsatisfactory (21–78%).[7a] The Brown group then reported an asymmetric *cis*-dihydroxylation of olefin using the combination of $KMnO_4$ with a stoichiometric amount of a chiral quaternary ammonium salt.[8] Tan and co-workers further improved this method into a catalytic version using a chiral dicationic bisguanidinium catalyst.[9] However, the reaction is supposed to proceed at very low temperature. Recently our group developed a non-aqueous system for the *cis*-dihydroxylation of acrylate derivatives using an in situ generated quaternary ammonium permanganate from $KMnO_4$and commercially available triethylbenzylammonium chloride (TEBAC) under 0–5 °C, and it gave high yields of the corresponding dihydroxylated products without overoxidation but[10] a stoichiometric amount of TEBAC was required. To improve the reaction conditions and to make it more practical, further investigations have been performed.

As a result, herein we described a new and improved non-aqueous protocol for the *cis*-dihydroxylation of acrylate derivatives using solid potassium permanganate as the oxidant together with only a catalytic amount of quaternary ammonium salt. In the initial investigation, acrylate **1a** was chosen as the model substrate due to the low solubility of product **2a** in water, which simplified the workup procedure. The screening of the catalyst and reaction conditions is summarized in Table 1. When no quaternary ammonium salt was used, the isolated yield of the desired product **2a** was 40% using acetone as solvent (background reaction) (entry 1), with recovery of over 50% of the raw material **1a**, perhaps due to the low solubility of potassium permanganate in organic solvents. When a catalytic amount of TEBAC was used, the yield was slightly improved to 54% (entry 2). A similar result was obtained when benzyltriphenylphosphonium chloride was used as the catalyst (entry 3).

Via cation exchange between quaternary ammonium salt and potassium permanganate, permanganate ions were ferried into the organic phase thus accelerating the dihydroxylation. In order to further increase the solubility of the possible intermediate, the quaternary ammonium salt of permanganate, dodecyltrimethylammonium chloride, bearing a long aliphatic chain was used as the catalyst, leading to a significant improvement of the yield (entry 4). This result encouraged us to examine the effects of other catalysts bearing long aliphatic chains on the reaction. Thus the pyridinium salt **QAS-1** and imidazolium salt **QAS-2** (Figure 1) were used as catalysts, affording the desired product **2a** in 75% and 92% yield respectively (entries 5 and 6). Increasing the reaction temperature from 0 °C to room temperature resulted in a lower yield because of side reactions (entry 7). Examination of the solvents showed that acetone was the best choice (entries 6, 8, and 9). Attempts to further reduce the loading of **QAS-2** to 5 mol% and 2 mol% resulted in lower yields (entries 10 and 11), with recovery of the raw material **1a**. No significant improvement of yield was observed by further decreasing the reaction temperature. Thus the optimal reaction conditions were set as: **QAS-2** (10 mol%) and $KMnO_4$ (1.2 equiv), acetone, 0–5 °C. It is important to note that no overoxidation byproduct was observed compared with the oxidation by aqueous potassium permanganate.[5]

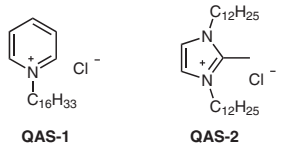
Table 1 Optimization of Reaction Conditions for *cis*-Dihydroxylation[a]



1a **2a**

Entry	Catalyst (equiv)	Temp. (°C)	Solvent	Yield (%)[b]
1	–	0–5	acetone	40
2	TEBAC (0.1)	0–5	acetone	54
3	$BnPPh_3Cl$ (0.1)	0–5	acetone	58
4	$C_{12}H_{25}NMe_3Cl$ (0.1)	0–5	acetone	80
5	**QAS-1** (0.1)	0–5	acetone	75
6	**QAS-2** (0.1)	0–5	acetone	92
7	**QAS-2** (0.1)	25–30	acetone	<40[c]
8	**QAS-2** (0.1)	0–5	CH_2Cl_2	74
9	**QAS-2** (0.1)	0–5	MeCN	65
10	**QAS-2** (0.05)	0–5	acetone	74
11	**QAS-2** (0.02)	0–5	acetone	66

[a] Reaction scale: **1a** (10.0 mmol), $KMnO_4$ (12.0 mmol).
[b] Isolated yield.
[c] Complex reaction product mixture.

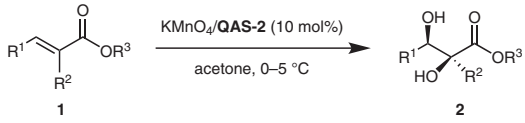


QAS-1 **QAS-2**

Figure Structures of QAS catalysts used

Under the optimized reaction conditions, the *cis*-dihydroxylation of various acrylate derivatives was examined, as shown in Table 2. The acrylate compounds and their derivatives bearing substituents at the 2- and/or 3-position **1a–s** gave high yields of the corresponding products **2a–s** under these conditions, including cinnamate compounds.

Table 2 *cis*-Dihydroxylation of Various Alkenes[a]



1 **2**

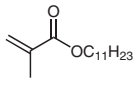
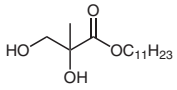
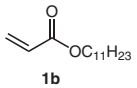
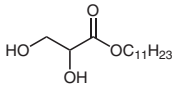
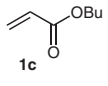
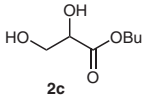
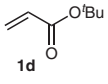
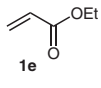
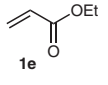
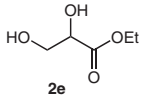
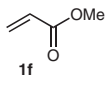
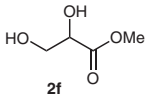
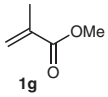
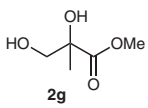
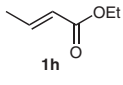
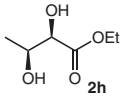
Entry	Alkene	Product	Yield (%)[b]
1	 **1a**	 **2a**	92
2	 **1b**	 **2b**	94
3	 **1c**	 **2c**	95
4	 **1d**	 **1e**	93
5	 **1e**	 **2e**	88
6	 **1f**	 **2f**	91
7	 **1g**	 **2g**	90
8	 **1h**	 **2h**	89

Table 2 (continued)

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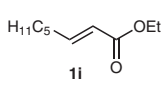
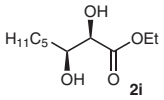
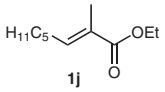
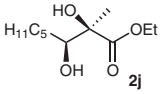
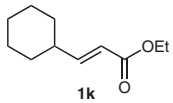
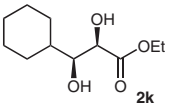
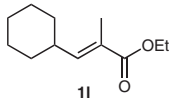
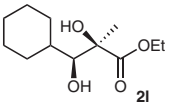
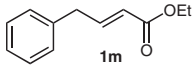
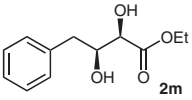
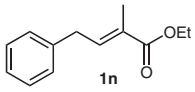
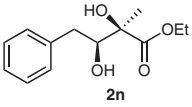
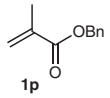
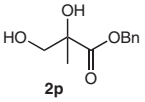
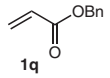
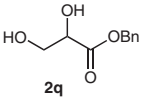
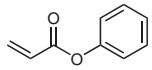
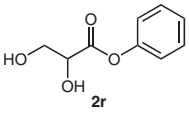
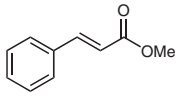
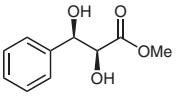
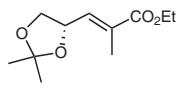
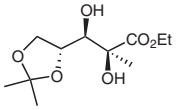
9	 1i	 2i	91
10	 1j	 2j	88
11	 1k	 2k	82
12	 1l	 2l	80
13	 1m	 2m	85
14	 1n	 2n	81
15	 1p	 2p	83
16	 1q	 2q	87
17	 1r	 2r	69
18	 1s	 2s	76
19	 1t	 2t	93[c,d]

[a] Reaction conditions: alkene (5.0 mmol), $KMnO_4$ (6.0 mmol), **QAS-2** (0.5 mmol), acetone (10 mL) 0–5 °C.
[b] Isolated yield.
[c] Yield after recrystallization was 83%.
[d] Diastereoselectivity >98:2 determined by ^1H NMR.

Furthermore, our protocol was efficiently scaled up for the dihydroxylation of **1t**, a key intermediate of Sofubuvir. A three-necked flask was charged with **1t** (54.0 g, 0.25 mol) and acetone (500 mL); **QAS-2** (11.4 g, 25 mmol) was added. The mixture was cooled to 0–5 °C and solid potassium permanganate (47.5 g, 0.3 mol) was added in portions within 10 mins. The mixture was stirred at the same temperature for 2 h. After workup, 57.5 g (93% yield) of **2t** was obtained, recrystallization gave 51.3 g (83% yield).

In summary, we presented a non-aqueous system **QAS-2**/$KMnO_4$ for efficient *cis*-dihydroxylation of acrylate derivatives with high yields under mild conditions. No overoxidation byproducts were found, probably because the Mn–O bond in the Mn–dioxygenated 5-membered-ring complex intermediate served as a protective group, and free hydroxyl group was not released until quenched with aqueous $NaHSO_3$. All the reagents were cheap and readily available. The workup procedure was simple and suitable for large-scale production. Further catalyst type screening, substrate scope extension, and asymmetric version of this protocol are under investigation.

Unless otherwise stated, all reagents and solvents were obtained from commercial sources and used without further purification. Silica gel (200–300 mesh) was used for column chromatography. Analytical TLC was carried out using GF254 commercial silica gel plates. All ^1H NMR spectra were recorded on a Bruker 400 MHz spectrometer.

Alkyl 2,3-Dihydroxyalkanoates 2; General Procedure

Imidazolium chloride **QAS-2** (0.5 mmol) and alkene (5.0 mmol) were mixed in acetone (10 mL) and the mixture was stirred at r.t. for 10 mins. Then the mixture was cooled to 0 °C and $KMnO_4$ (6.0 mmol) was added in portions. The resulting mixture was stirred for further 2 h at 0–5 °C. TLC indicated complete consumption of the alkene. Aq $NaHSO_3$ (10 mL) was added in one portion to quench the reaction. The mixture was filtered on Celite, washed thoroughly with acetone. The combined filtrate was concentrated under reduced pressure and the residue was extracted with EtOAc (3 × 10 mL). The organic phase was dried (Na_2SO_4), filtered, and evaporated to dryness. The crude product was purified by column chromatography (silica gel).

Undecyl 2,3-Dihydroxy-2-methylpropanoate (2a)

Colorless oil; yield: 2.52 g (92%).

IR: 3444 (br, s), 2926 (s), 1736 cm^{-1} (s).

^1H NMR (400 MHz, $CDCl_3$): δ = 4.22 (td, *J* = 4.0, 8.0 Hz, 2 H), 3.80 (t, *J* = 8.0 Hz, 2 H), 2.73 (br, 2 H), 1.68, (m, 2 H), 1.37 (s, 3 H), 1.35–1.28 (m, 16 H), 0.89 (t, *J* = 4.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 175.7 (CO), 75.5 (CO), 68.4 (CO), 66.4 (OCH_2CH_3), 29.6 (CH_2), 29.5 (CH_2), 29.4 (CH_2), 29.3 (CH_2), 29.1 (CH_2), 28.5 (CH_2), 25.7 (CH_2), 22.7 (CH_2), 22.0 (CH_2),14.1 (CH_2CH_3).

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{15}H_{31}O_4$: 275.2222; found: 275.2219.

Undecyl 2,3-Dihydroxypropanoate (2b)[11]

Colorless oil; yield: 2.44 g (94%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.3–3.7 (m, 5 H), 2.36 (br, 2 H), 1.68 (m, 2 H), 1.34–1.28 (m, 16 H), 0.90 (t, *J* = 8.0 Hz, 3 H).

Butyl 2,3-Dihydroxypropanoate (2c)[8]

Colorless oil; yield: 1.54 g (95%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.22–4.28 (m, 3 H), 3.83 (m, 2 H), 3.39 (br, 2 H), 1.65 (m, 2 H), 1.39 (m, 2 H), 0.94 (t, *J* = 8.0 Hz, 3 H).

***tert*-Butyl 2,3-Dihydroxypropanoate (2d)**[8]

Colorless oil; yield: 1.50 g (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.15 (t, *J* = 4.0 Hz, 1 H), 3.83 (dd, *J* = 12.0, 12.0 Hz, 2 H), 2.82 (br, 2 H), 1.51 (s, 9 H).

Ethyl 2,3-Dihydroxypropanoate (2e)[8]

Colorless oil; yield: 1.18 g (88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.28 (m, 3 H), 3.88 (m, 2 H), 3.17 (br, 2 H), 1.30 (m, 3 H).

Methyl 2,3-Dihydroxypropanoate (2f)[8]

Colorless oil; yield: 1.09 g (91%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.30 (t, *J* = 4.0 Hz, 1 H), 3.88 (m, 5 H), 3.01 (br, 2 H).

Methyl 2,3-Dihydroxy-2-methylpropanoate (2g)[8]

Colorless oil; yield: 1.20 g (90%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.80 (m, 4 H), 3.57 (m, 1 H), 3.29 (br, 2 H), 1.35 (s, 3 H).

Ethyl 2,3-Dihydroxybutanoate (2h)[8]

Colorless oil; yield: 1.31 g (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.27 (q, *J* = 8.0 Hz, 2 H), 4.08 (m, 1 H), 4.00 (d, *J* = 4.0 Hz, 1 H), 1.30 (m, 6 H).

Ethyl 2,3-Dihydroxyoctanoate (2i)[8]

White solid; yield: 1.85 g (91%); mp 41–42 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.31 (q, *J* = 8.0 Hz, 2 H), 4.10 (d, *J* = 2.0 Hz, 1 H), 3.90 (m, 1 H), 2.79 (br, 2 H), 1.70–1.57 (m, 2 H), 1.56–1.20 (m, 9 H), 0.91 (t, *J* = 8.0 Hz, 3 H).

Ethyl 2,3-Dihydroxy-2-methyloctanoate (2j)[8]

White solid; yield: 1.92 g (88%); mp 45–46 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.27 (m, 2 H), 3.72 (d, *J* = 12.0 Hz, 1 H), 1.64-1.26 (m, 16 H), 0.90 (t, *J* = 8.0 Hz, 3 H).

Ethyl 3-Cyclohexyl-2,3-dihydroxypropanoate (2k)[8]

White solid; yield: 1.77 g (82%), mp 50–51 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.30 (m, 3 H), 3.57 (d, *J* = 8.0 Hz, 1 H), 2.77 (br, 2 H), 2.07 (m, 1 H), 0.97–1.48 (m, 13 H).

Ethyl 3-Cyclohexyl-2,3-dihydroxy-2-methylpropanoate (2l)[8]

Colorless oil; yield: 1.84 g (80%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.27 (m, 2 H), 4.0–4.5 (br, 2 H), 3.62 (d, *J* = 4.0 Hz, 1 H), 1.08–1.92 (m, 17 H).

Ethyl 2,3-Dihydroxy-4-phenylbutanoate (2m)[8]

White solid; yield: 1.90 g (85%); mp 60–61 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (m, 5 H), 4.27 (m, 2 H), 4.18 (m, 1 H), 4.08 (d, *J* = 2.0 Hz, 1 H), 2.98 (m, 2 H), 2.76 (br, 2 H), 1.31 (t, *J* = 8.0 Hz, 3 H).

Ethyl 2,3-Dihydroxy-2-methyl-4-phenylbutanoate (2n)[8]

White solid; yield: 1.93 g (81%), mp 65–67 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.31 (m, 5 H), 4.27 (m, 2 H), 4.01 (dd, *J* = 2.0, 8.0 Hz, 1 H), 3.03 (dd, *J* = 2.0, 12.0 Hz, 1 H), 2.75 (m, 1 H), 1.47 (s, 3 H), 1.32 (t, *J* = 8.0 Hz, 3 H).

Benzyl 2,3-Dihydroxy-2-methylpropanoate (2p)[8]

White solid; yield: 1.74 g (83%); mp 45–46 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.37 (m, 5 H), 5.24 (q, *J* = 12.0 Hz, 2 H), 3.85 (d, *J* = 12.0 Hz, 1 H), 3.61 (d, *J* = 12.0 Hz, 1 H), 3.52 (br, 2 H), 1.37 (s, 3 H).

Benzyl 2,3-Dihydroxypropanoate (2q)[12]

Colorless oil; yield: 1.70 g (87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (m, 5 H), 5.27 (m, 2 H), 4.33 (t, *J* = 4.0 Hz, 1 H), 3.91 (m, 2 H), 2.83 (br, 2 H).

Phenyl 2,3-Dihydroxypropanoate (2r)[13]

White solid; yield: 1.25 g (69%); mp 85–86 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.43 (m, 2 H), 7.30 (m, 1 H), 7.15 (m, 2 H), 4.56 (t, *J* = 4.0 Hz, 1 H), 4.09 (m, 2 H), 2.51 (br, 2 H).

Methyl 2,3-Dihydroxy-3-phenylpropanoate (2s)[14]

Colorless oil; yield: 1.49 g (76%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.42–7.28 (m, 5 H), 5.06 (d, *J* = 4.0 Hz, 1 H), 4.41 (d, *J* = 4.0 Hz, 1 H), 3.84 (s, 3 H).

Ethyl (2*S*,3*R*)-3-[(*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-2,3-dihydroxy-2-methylpropanoate (2t);[8] Scaled Up Synthesis

To a 1000-mL three-necked flask was charged **1t** (54.0 g, 0.25 mol) and acetone (500 mL); **QAS-2** (11.4 g, 25.0 mmol) was added. The mixture was cooled to 0–5 °C. Solid $KMnO_4$ (47.5 g, 0.3 mol) was added in 10 portions within 10 min. The mixture was stirred at the same temperature for 2 h, and TLC indicated complete consumption of **1t**. A solution of $NaHSO_3$ (25.0 g) in water (50 mL) was added in one portion to quench the reaction. The mixture was stirred for 15 min and then filtered on Celite, which was washed thoroughly with acetone (3 × 100 mL). The combined filtrates were concentrated to remove acetone under reduced pressure and the residue was extracted with EtOAc (3 × 150 mL). The combined organic phases were washed with sat. brine (3 × 50 mL), dried (Na_2SO_4), filtered, and evaporated to dryness to afford a colorless oil (57.5 g, 93%), which was recrystallized (petroleum ether, 200 mL) to afford the product as a white solid; yield: 51.3 g (83%); mp 75–76 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.20–4.31 (m, 3 H), 4.09 (m, 2 H), 3.93 (d, *J* = 8.0 Hz, 1 H), 2.52 (br, 2 H), 1.31–1.49 (m, 12 H).

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Supporting Information

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References

(1) (a) Bolm, C.; Hildebrand, J. P.; Muñiz, K. In *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, **2000**, 399. (b) Kolb, H. C.; Van Nieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, *94*, 2483. (c) Schröder, M. *Chem. Rev.* **1980**, *80*, 187.

(2) (a) Johnson, R. A.; Sharpless, K. B. *Catalytic Asymmetric Synthesis*, 2nd ed.; Ojima, I., Ed.; Wiley-VCH: New York, **2000**, 357. (b) Gao, Y.; Cheun, Y. *Osmium Tetroxide–N-Methylmorpholine N-Oxide*, In *e-EROS Encyclopedia of Reagents for Organic Synthesis*; Wiley: Hoboken, **2013**, ; DOI: 10.1002/047084289X.ro009.pub2. (c) Chughtai, M. J.; Donohoe, T. J.; Gao, Y.; Harris, R. M.; Kim, S.-M.; Oh, J. S.; Song, C.-E.; Yang, J. W. *Handbook of Reagents for Organic Synthesis: Catalytic Oxidation Reagents*; Fuchs, P. L., Ed.; Wiley: Chichester, **2013**, 433.

(3) (a) Chen, K.; Que, L. Jr. *Angew. Chem. Int. Ed.* **1999**, *38*, 2227. (b) Chen, K.; Costas, M.; Kim, J.; Tipton, A. K.; Que, L. Jr. *J. Am. Chem. Soc.* **2002**, *124*, 3026. (c) Chen, K.; Costas, M.; Que, L. Jr. *J. Chem. Soc., Dalton Trans.* **2002**, 672. (d) Fujita, M.; Costas, M.; Que, L. Jr. *J. Am. Chem. Soc.* **2003**, *125*, 9912. (e) Klopstra, M.; Roelfes, G.; Hage, R.; Kellogg, R. M.; Feringa, B. L. *Eur. J. Inorg. Chem.* **2004**, 846. (f) Rotthaus, O.; Le Roy, S.; Tomas, A.; Barkigia, K. M.; Artaud, I. *Inorg. Chim. Acta* **2004**, *357*, 2211. (g) De Vos, D. E.; de Wildeman, S.; Sels, B. F.; Grobet, P. J.; Jacobs, P. A. *Angew. Chem. Int. Ed.* **1999**, *38*, 980. (h) de Boer, J. W.; Brinksma, J.; Browne, W. R.; Meetsma, A.; Alsters, P. L.; Hage, R.; Feringa, B. L. *J. Am. Chem. Soc.* **2005**, *127*, 7990. (i) Codola, Z.; Lloret-Fillol, J.; Costas, M. *Prog. Inorg. Chem.* **2014**, *59*, 447. (j) Oloo, W. N.; Que, L. Jr. *Acc. Chem. Res.* **2015**, *48*, 2612.

(4) Mergott, D. J. *Name Reactions for Functional Group Transformations*; Li, J. J.; Corey, E. J., Eds.; Wiley-Interscience: Hoboken, **2007**, 327.

(5) (a) Stewart, R. *Oxidation Mechanisms: Applications to Organic Chemistry*; Benjamin: New York, **1964**, 58. (b) Wiberg, K. B.; Saebarth, K. A. *J. Am. Chem. Soc.* **1957**, *79*, 2822. (c) Lee, D. G.; Brownridge, J. R. *J. Am. Chem. Soc.* **1973**, *95*, 3033. (d) Wiberg, K. B.; Deutsch, C. J. *J. Am. Chem. Soc.* **1973**, *95*, 3034. (e) Fatiadi, A. J. *Synthesis* **1987**, 85. (f) Zimmer, R.; Collas, M.; Czerwonka, R.; Hain, U.; Reissig, H. *Synthesis* **2008**, 237.

(6) (a) Foglia, T. A.; Barr, P. A.; Malloy, A. J. *J. Am. Oil Chem. Soc.* **1977**, *54*, 858. (b) Watber, W. P.; Shepherd, J. P. *Tetrahedron Lett.* **1972**, *13*, 4907. (c) Taylor, J. E.; Williams, D.; Edwards, K.; Otonnaa, D.; Samanich, D. *Can. J. Chem.* **1984**, *62*, 11.

(7) (a) Hazra, B. G.; Pore, V. S.; Chordia, M. D.; Bahule, B. B.; Basu, S. *J. Chem. Res.* **2001**, 500. (b) Hazra, B. G.; Pore, V. S. *J. Indian Chem. Soc.* **2003**, *80*, 1065.

(8) Bhunnoo, R. A.; Hu, Y.; Laine, D. I.; Brown, R. C. D. *Angew. Chem. Int. Ed.* **2002**, *41*, 3479.

(9) Wang, C.; Zong, L.; Tan, C.-H. *J. Am. Chem. Soc.* **2015**, *137*, 10677.

(10) Luo, Z. B.; Zhao, C.; Xie, J. M.; Lu, H. F. *Synthesis* **2016**, *48*, 3696.

(11) Wang, J.; Xia, Q. *Drug Delivery* **2014**, *21*, 328.

(12) Chow, W.-S.; Liu, Y.; Che, C.-M. *Chem. Commun.* **2011**, *47*, 11204.

(13) Gupta, S. K. US 20060110415, **2006**.

(14) Borrell, M.; Costas, M. *J. Am. Chem. Soc.* **2017**, *139*, 12821.