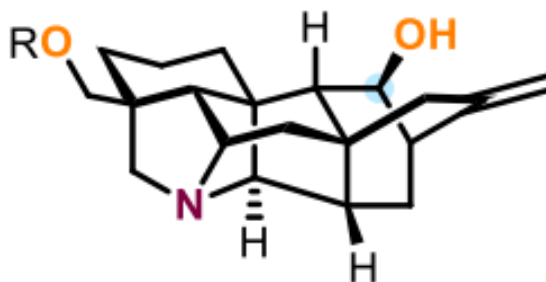


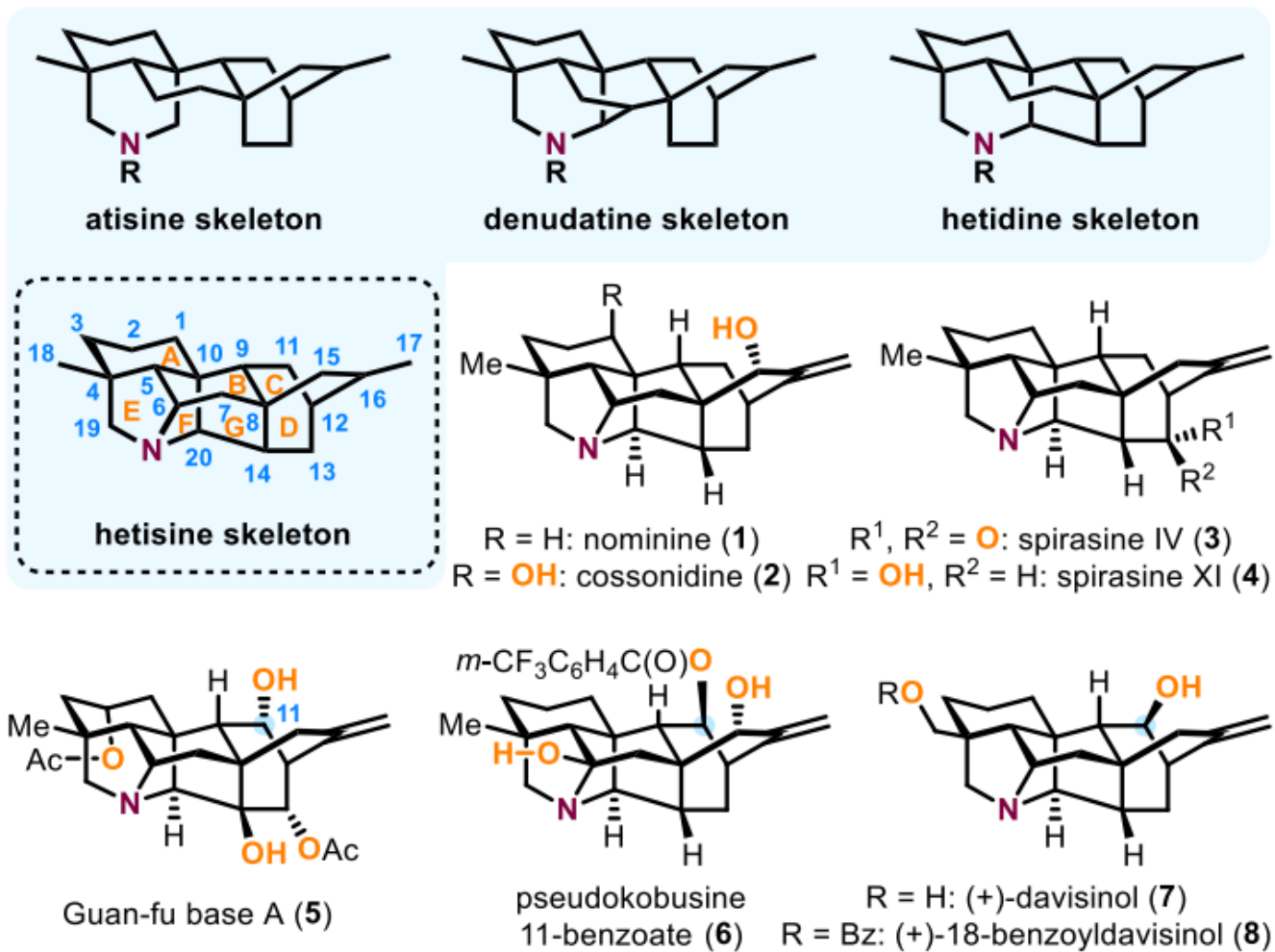
# Asymmetric Total Syntheses of (+)-Davisinol and (+)-18-Benzoyldavisinol: A HAT-Initiated Transannular Redox Radical Approach

Kuan Yu,<sup>#</sup> Fengjie Yao,<sup>#</sup> Qingrui Zeng, Hujun Xie, and Hanfeng Ding\*

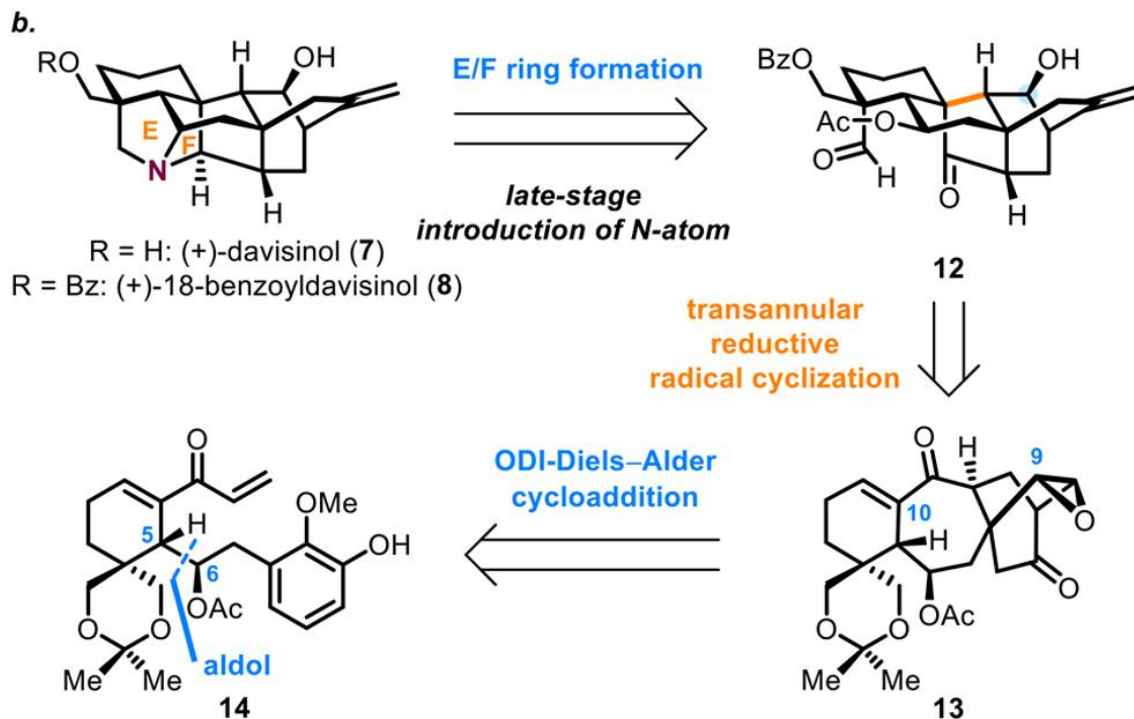
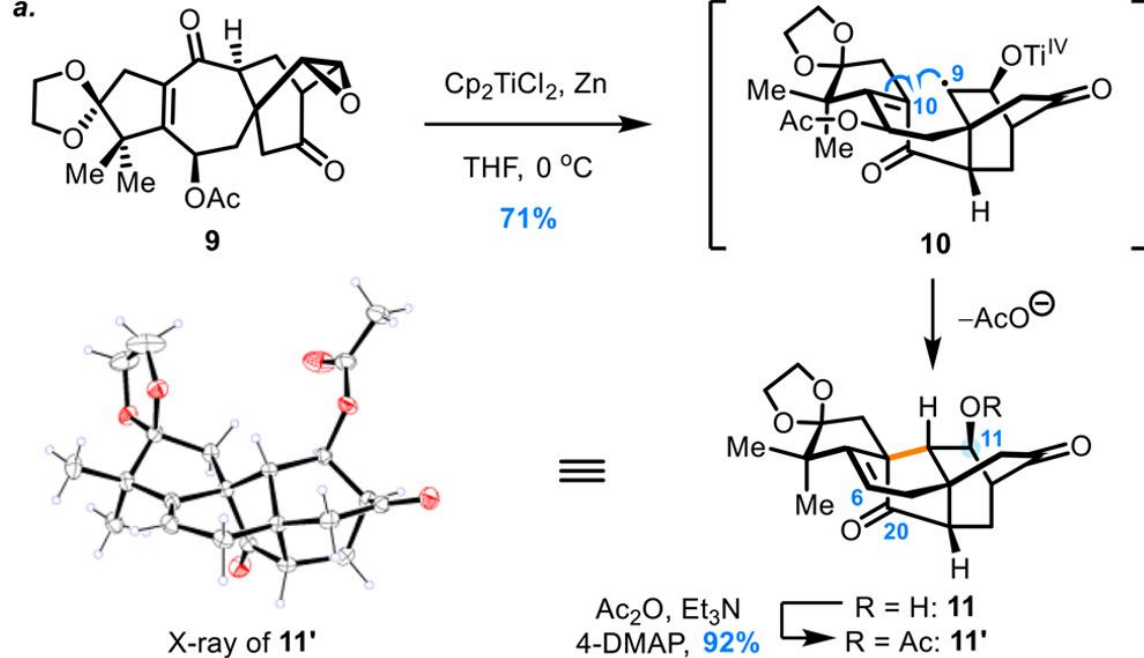


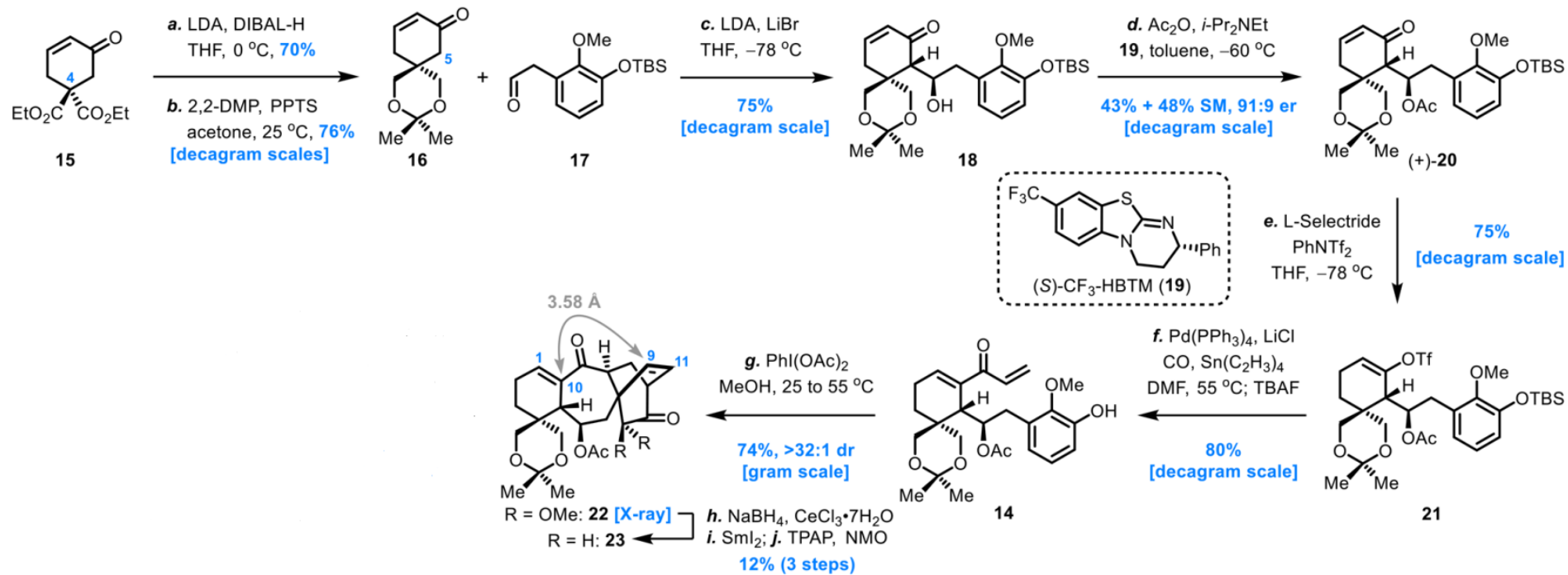
R = H: (+)-davisinol (**7**)

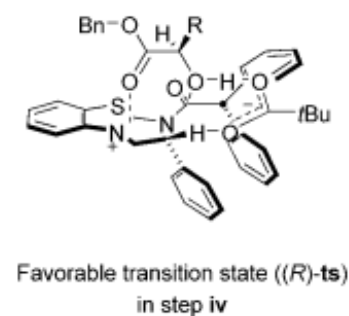
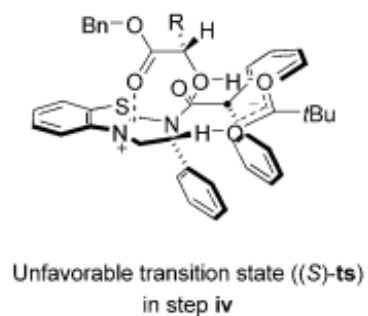
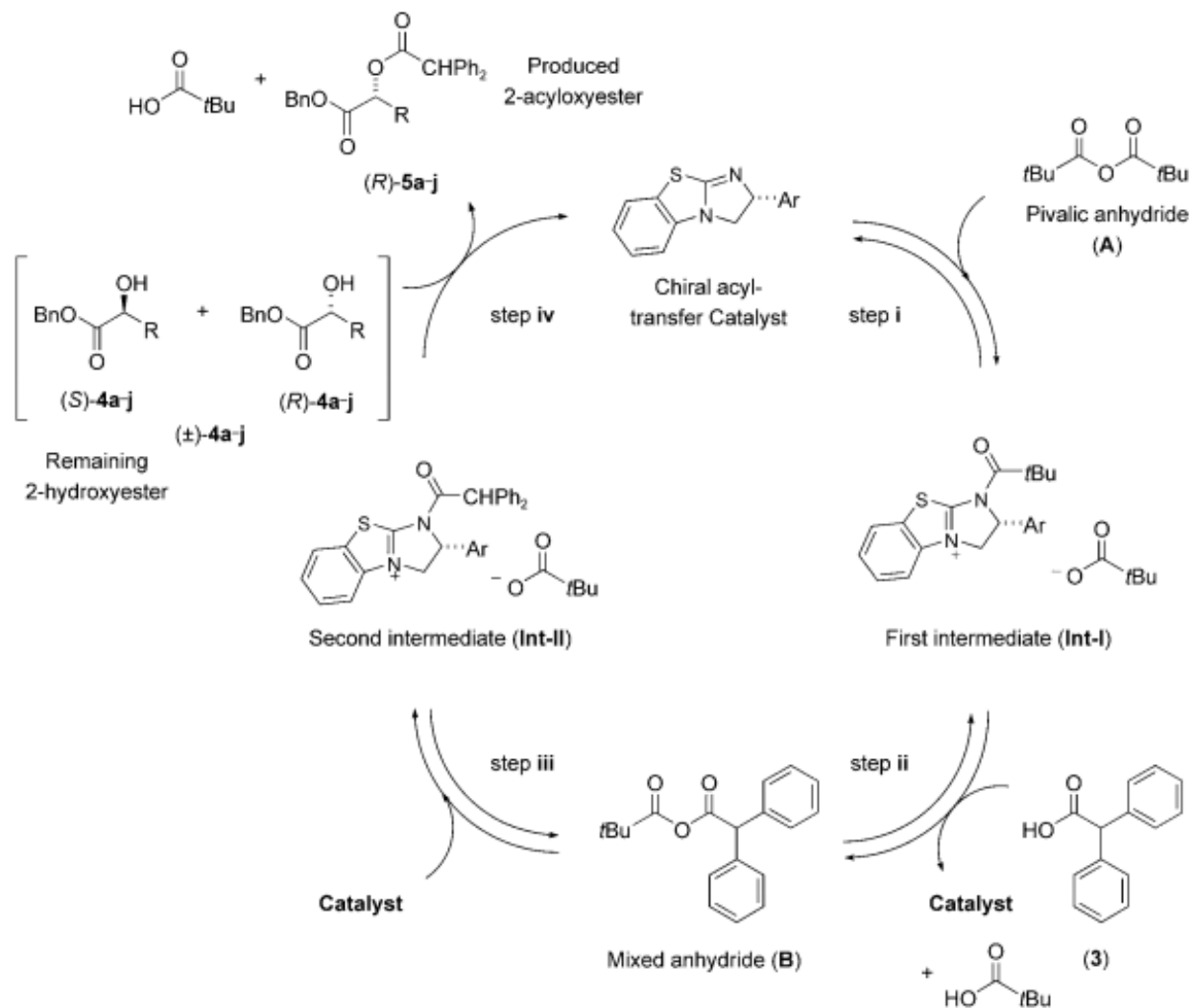
R = Bz: (+)-18-benzoyldavisinol (**8**)

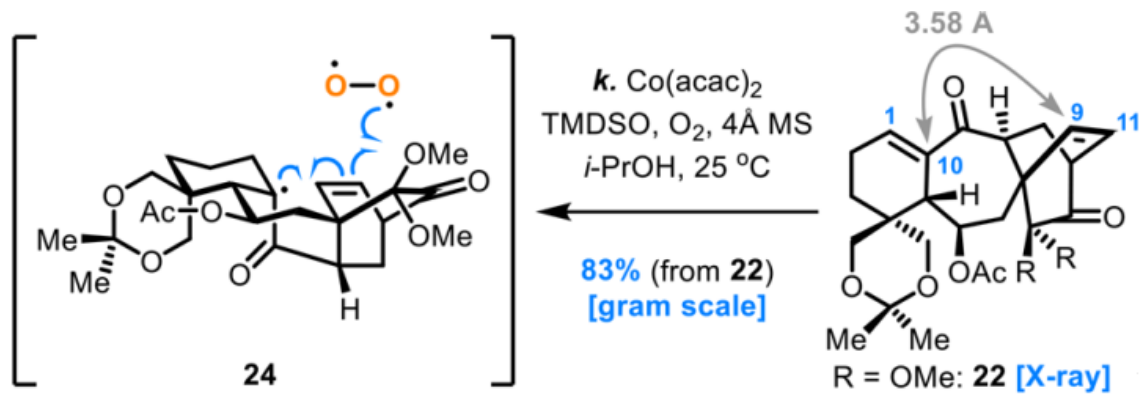


**Figure 1.** Main skeleton types of C<sub>20</sub>-diterpenoid alkaloids and representative members of the hetisine subfamily.



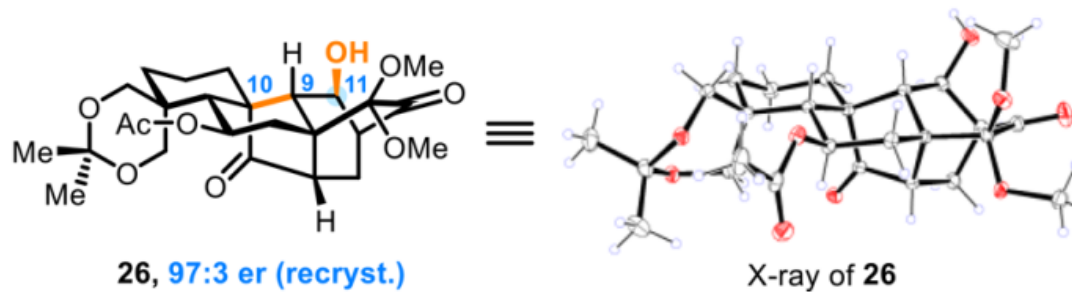


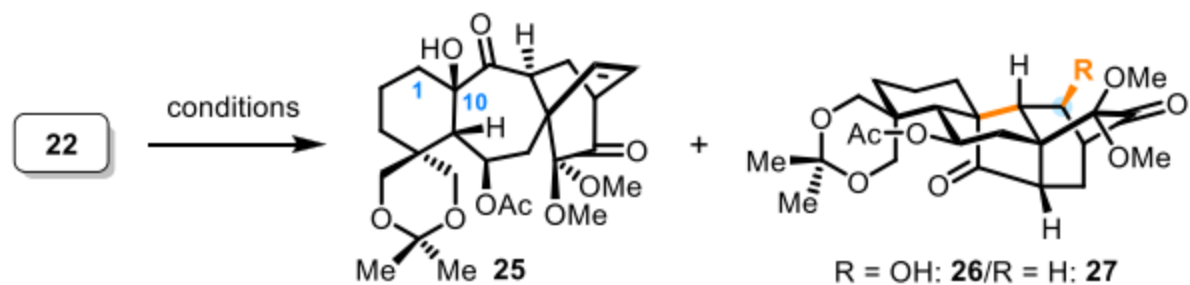




**HAT-initiated  
 redox radical  
 cyclization**

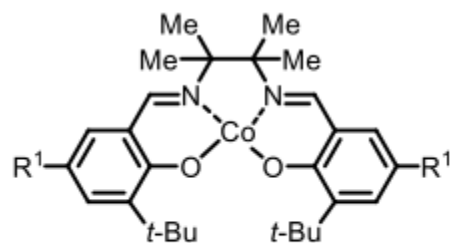
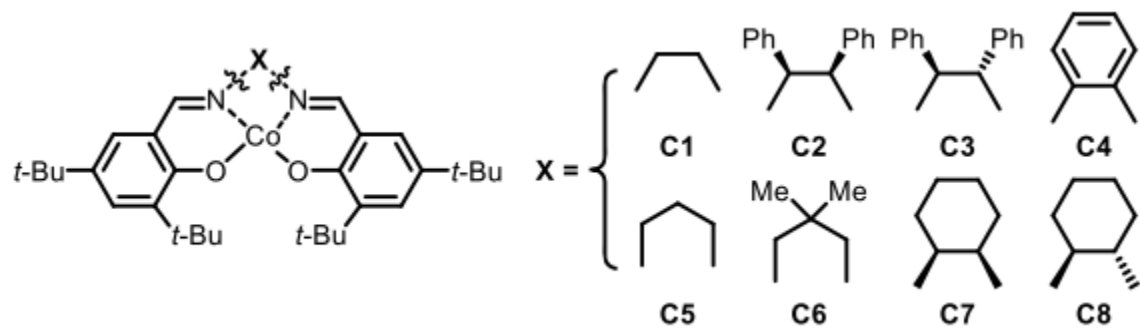
see Table 1  
 for optimization



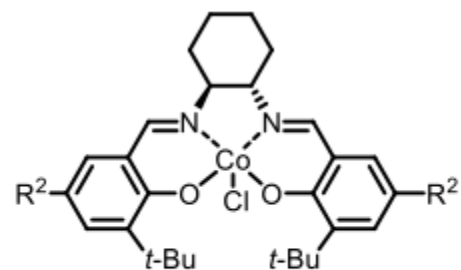


entry	conditions	yield (%) <sup>b</sup>		
		25	26	27
1	Fe( <i>Pc</i> ), NaBH <sub>4</sub> , O <sub>2</sub> , EtOH	0	0	0
2 <sup>c</sup>	Fe(acac) <sub>3</sub> , PhSiH <sub>3</sub> or Ph( <i>i</i> -PrO)SiH <sub>2</sub> , O <sub>2</sub> , EtOH/(CH <sub>2</sub> OH) <sub>2</sub> (5:1 v/v)	0	0	0
3	Mn(acac) <sub>2</sub> , PhSiH <sub>3</sub> , Ph <sub>3</sub> P, O <sub>2</sub> , EtOH	89	0	0
4	Co(acac) <sub>2</sub> , PhSiH <sub>3</sub> , O <sub>2</sub> , <i>i</i> -PrOH	<5	75	12
5	<b>C1-16</b> , PhSiH <sub>3</sub> , O <sub>2</sub> , <i>i</i> -PrOH or EtOH	<5	12-69	<5
6 <sup>d,e</sup>	Co(acac) <sub>2</sub> , TMDSO, O <sub>2</sub> , <i>i</i> -PrOH	<5	83	<5
7 <sup>d</sup>	Co(acac) <sub>2</sub> , TMDSO O <sub>2</sub> /Ar (1:10 v/v, 1 atm), <i>i</i> -PrOH	40	15	0
8 <sup>d,f</sup>	<b>C15</b> , TMDSO, TBHP, <i>i</i> -PrOH	0	0	65

<sup>a</sup>Reaction conditions are as follows: **22** (0.05 mmol), [M] (20 mol %), [B]/[Si] (2.0 equiv), O<sub>2</sub> (2.2 equiv), and solvent (4 mL) at 25 °C. <sup>b</sup>Isolated yields. <sup>c</sup>Performed at 60 °C. <sup>d</sup>Added 4 Å MS (0.10 g). <sup>e</sup>Gram scale. <sup>f</sup>TBHP (2.0 equiv).



$\text{R}^1 = t\text{-Bu}$ : **C9**;  $\text{R}^1 = \text{H}$ : **C10**  
 $\text{R}^1 = \text{OMe}$ : **C11**;  $\text{R}^1 = \text{CF}_3$ : **C12**



$\text{R}^2 = t\text{-Bu}$ : **C13**;  $\text{R}^2 = \text{H}$ : **C14**  
 $\text{R}^2 = \text{OMe}$ : **C15**;  $\text{R}^2 = \text{NO}_2$ : **C16**



