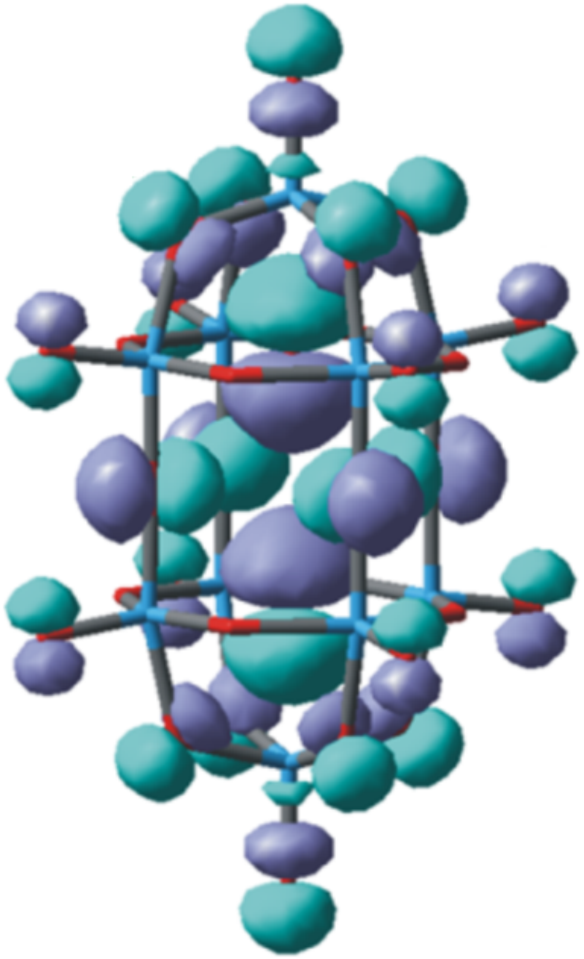
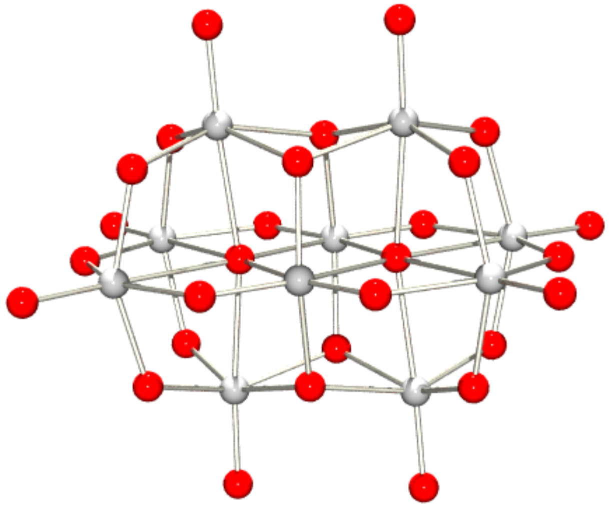
Polyoxometalate Photocatalysis



Thomas Brewer
MacMillan Group Meeting
December 13, 2017

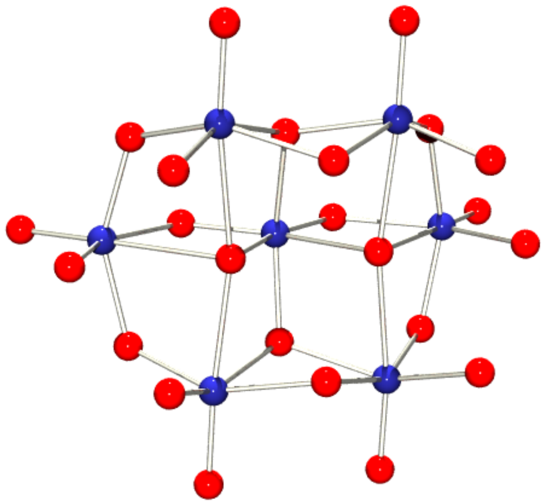
What are polyoxometalates (POMs)?

Type I
monooxo terminal groups



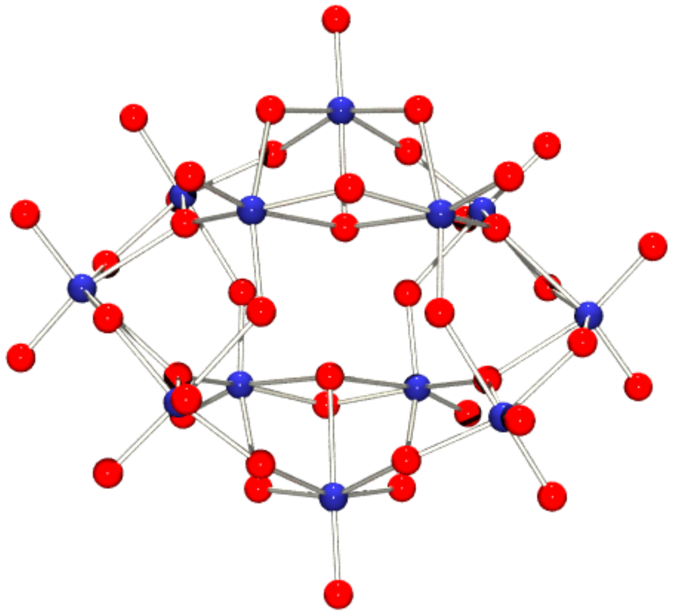
Ex: $[M_{10}O_{28}]^{6-}$ (M = Nb, Ta, V)

Type II
cis-*dioxo terminal groups*



Ex: $[W_7O_{24}]^{6-}$

Type III
monooxo and cis-*dioxo terminal groups*



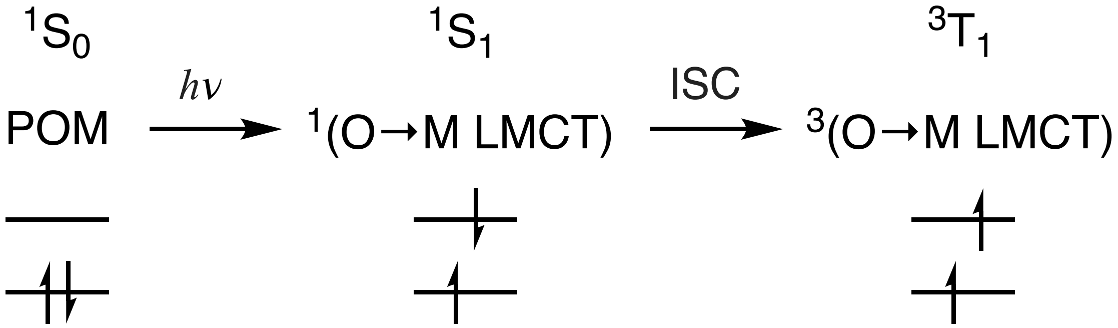
Ex: $[H_2W_{12}O_{42}]^{10-}$

- ≥ 3 transition metal oxyanions linked by shared oxygen atoms
- closed, 3-dimensional frameworks
- typically group 6 (Mo, W) and group 5 (V, Nb, Ta)
- type I & III POMs shown to be reversibly reduced to “heteropoly blues”

Pope, M. T. *Inorg. Chem.*, **1972**, *11*, 1973
structures from http://verahill.blogspot.com/search/label/molecules

Outline

Polyoxometalate Fundamentals



$^1S_0$ POM $\xrightarrow{h\nu}$ $^1S_1$ $^1(O\rightarrow M\ LMCT)$ $\xrightarrow{ISC}$ $^3T_1$ $^3(O\rightarrow M\ LMCT)$

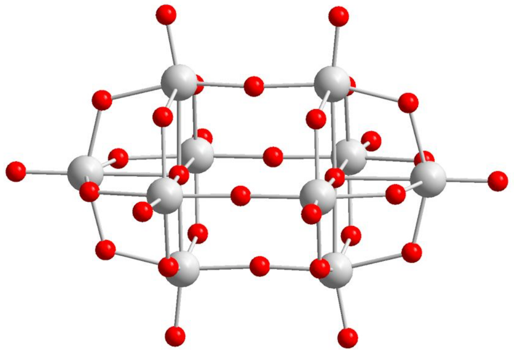
C–H Oxygenation/Fluorination Reactions

C–C Bond-Forming Reactions

POM synthesis

$$[MO_4]^{n-} \xrightarrow[H_2O]{[H^+]} [M_mO_r]^{t-}$$

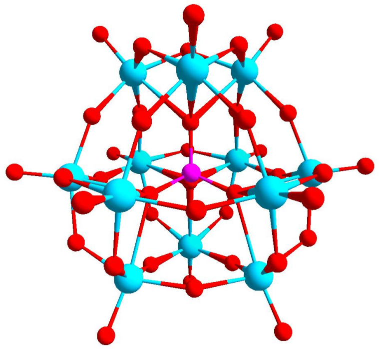
isopolyoxometalates
only TM and oxide ions



Ex: $[W_{10}O_{32}]^{4-}$

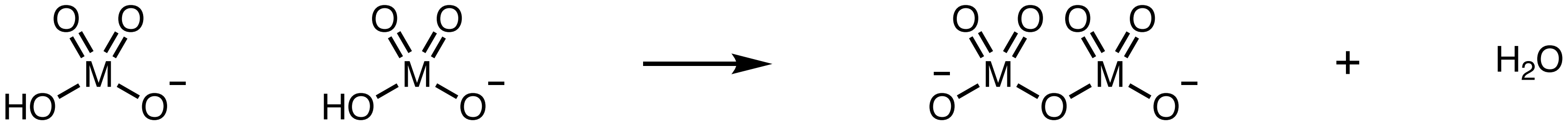
$$[MO_4]^{n-} \quad [XO_pH_h]^{q-} \xrightarrow[H_2O]{[H^+]} [X_xM_mO_r]^{t-}$$

heteropolyoxometalates
contain ≧1 ‘heteroatom’



Ex: $[PMo_{12}O_{40}]^{3-}$
(fun fact: discovered in 1826!)

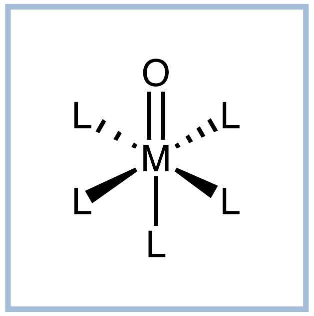
via olation:



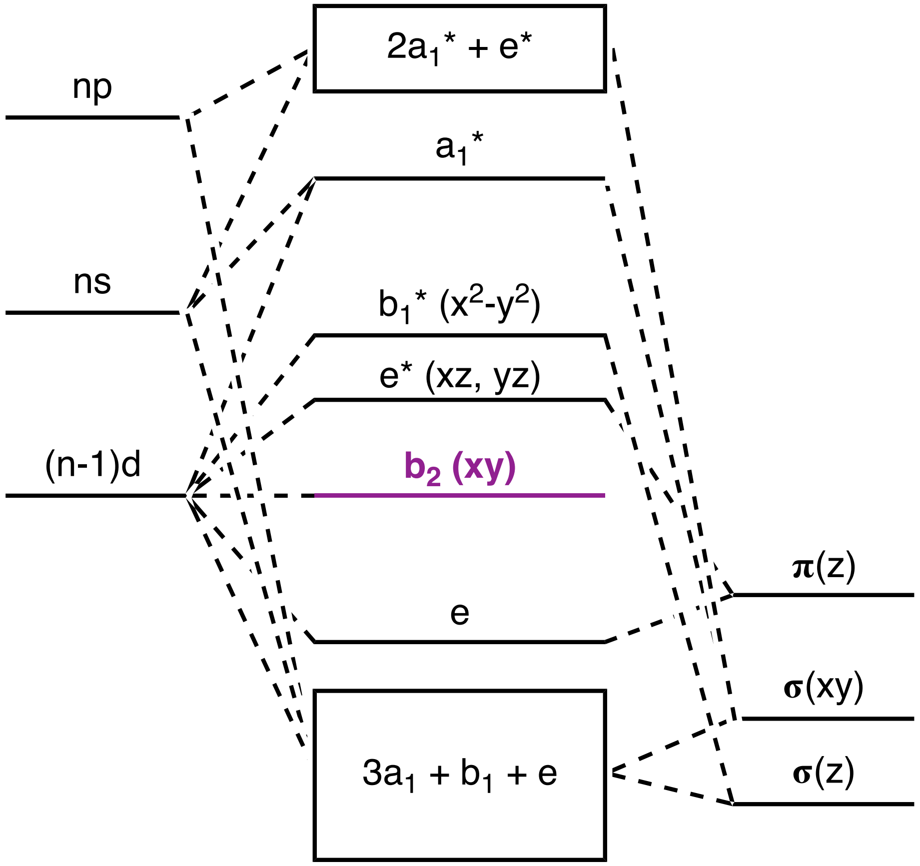
- can include heteroatoms “X” to form hetero-POMs
- frequently involve equilibria between several POMs
- controlled by pH, counterion identity, temperature, cosolvent, M/X ratio

Berzelius, J. J. *Pogg. Ann.* **1826**, *6*, 380
Weinstock, I. A. *Chem. Rev.* **1998**, *98*, 113
Hill, C. L.; McCartha-Prosser, C. M. *Catal. Met. Complexes*

Type I POMs have rich redox chemistry



idealized local symmetry

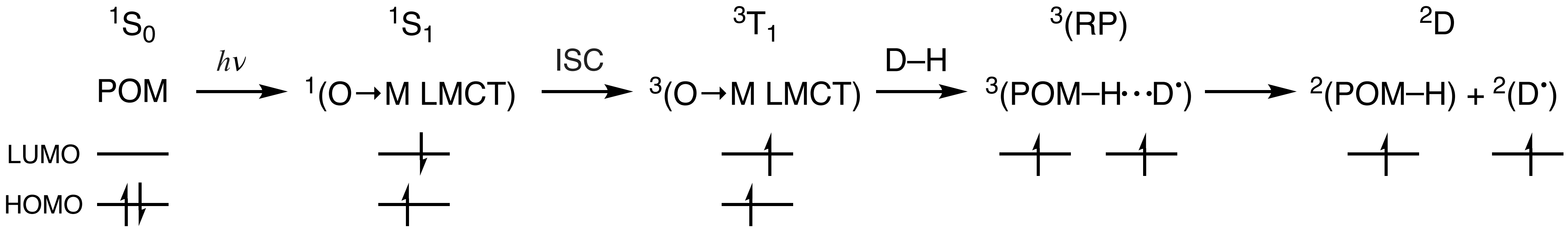


MOL_5 MO diagram (C_{4v}, no xy π-bonding)

- TM atoms in highest (d^0) oxidation state ⇒ POMs act as oxidants
- Type I POMs have formally nonbonding LUMO (b_2)
- In type II POMs, former d_{xy} orbital is π^*

Polyoxometalate Molecular Science; Almenar-Borras, J. J., Coronado, E., Muller, A., Pope, M., Eds.; Springer: Dordrecht, 2003

POM photoredox reactivity



	$[W_{10}O_{32}]^{4-}$	$[PW_{12}O_{40}]^{3-}$	$[PMo_{12}O_{40}]^{3-}$	$[V_{10}O_{28}]^{6-}$	$[V_{13}O_{34}]^{3-}$
λ_{max}	324 nm	263 nm	220 nm	240 nm	202 nm
0,0 transition	450 nm	415 nm	415 nm	490 nm	560 nm
ground state reduction[a]	-0.97 V	-0.37 V	+0.14 V	-0.24 V[b]	+0.63 V
excited state reduction[a]	2.44 V	2.63 V	2.67 V	2.01 V	2.84 V

- Potentials are very approximate[c]
- V, Mo POMs strong oxidants, but difficult to re-oxidize to d^0
- V, Mo POMs can be sufficiently oxidizing in ground state to react with oxidizable intermediates
- POMs typically show long (100s of nm), tailing absorbance

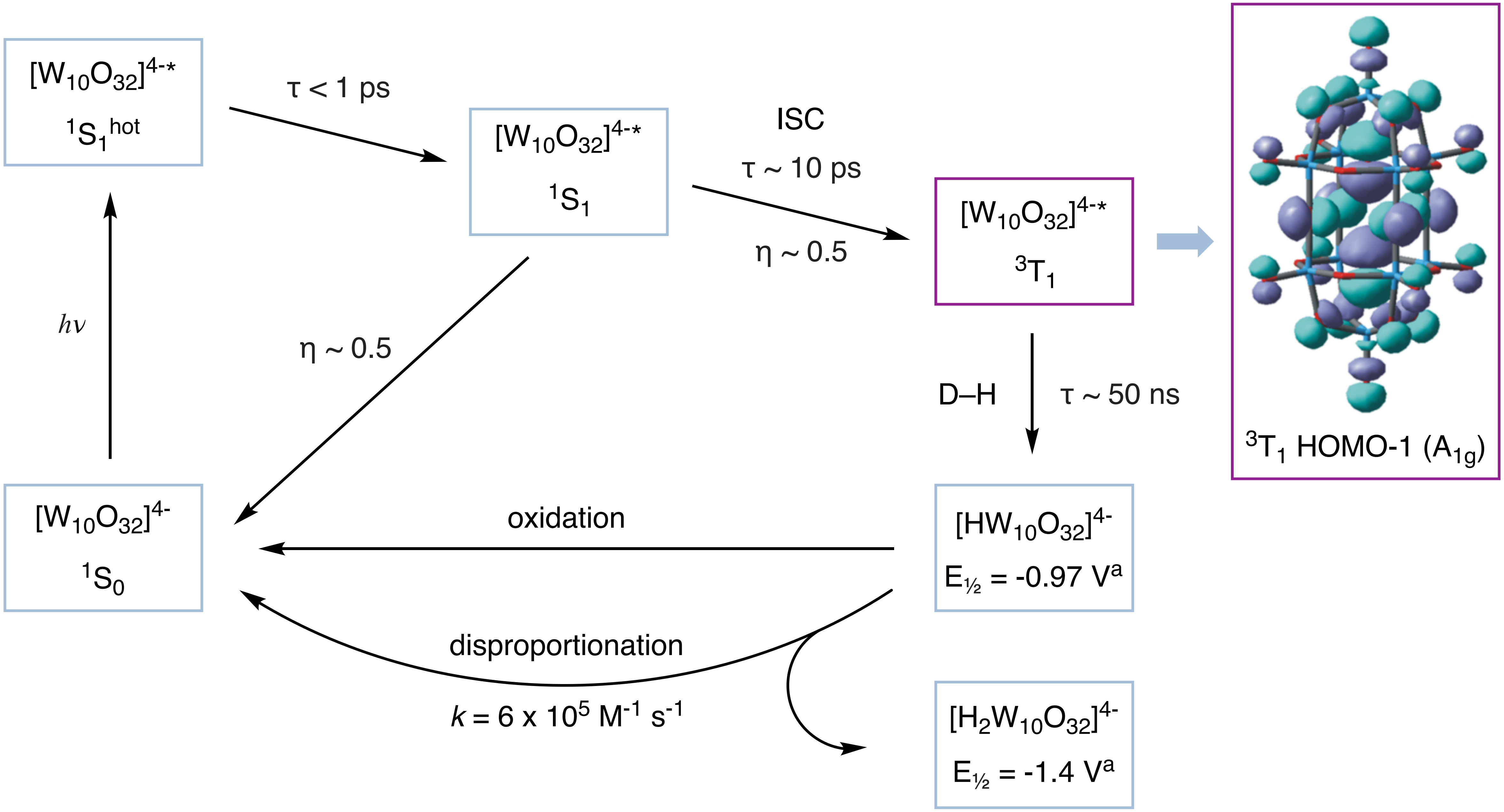
[a]potential vs. NHE | [b]irreversible reduction | [c]various reference electrodes and experimental conditions; literature not in agreement

De Waele, V., Poizat, O., Fagnoni, M., Bagno, A., Ravelli, D. *ACS Catal.*, **2016**, *6*, 7174

Hou, D., Hagen, K. S., Hill, C. L., *J. Am. Chem. Soc.*, **1992**, *114*, 5864

Polyoxometalate Molecular Science; Almenar-Borras, J. J., Coronado, E., Muller, A., Pope, M., Eds.; Springer: Dordrecht, 2003

A closer look at decatungstate photochemistry



$[W_{10}O_{32}]^{4-*}$ $^1S_1{}^{hot}$

$\tau < 1$ ps

$[W_{10}O_{32}]^{4-*}$ $^1S_1$

ISC

$\tau \sim 10$ ps

$\eta \sim 0.5$

$[W_{10}O_{32}]^{4-*}$ $^3T_1$

$h\nu$

$\eta \sim 0.5$

D–H

$\tau \sim 50$ ns

$^3T_1$ HOMO-1 (A_{1g})

$[W_{10}O_{32}]^{4-}$ $^1S_0$

oxidation

$[HW_{10}O_{32}]^{4-}$

$E_{½} = -0.97$ V[a]

disproportionation

$k = 6 \times 10^5$ M^{-1} s^{-1}

$[H_2W_{10}O_{32}]^{4-}$

$E_{½} = -1.4$ V[a]

- after excitation, fast ($\tau \sim 10$ ps) ISC yields the reactive $^3T_1$ state
- $^3T_1$ HOMO-1 has highest (accessible) density on apical oxo ligands
- Singly-reduced $[HW_{10}O_{32}]^{4-}$ can disproportionate to $[W_{10}O_{32}]^{4-}$ and $[H_2W_{10}O_{32}]^{4-}$

[a] potential vs. SCE

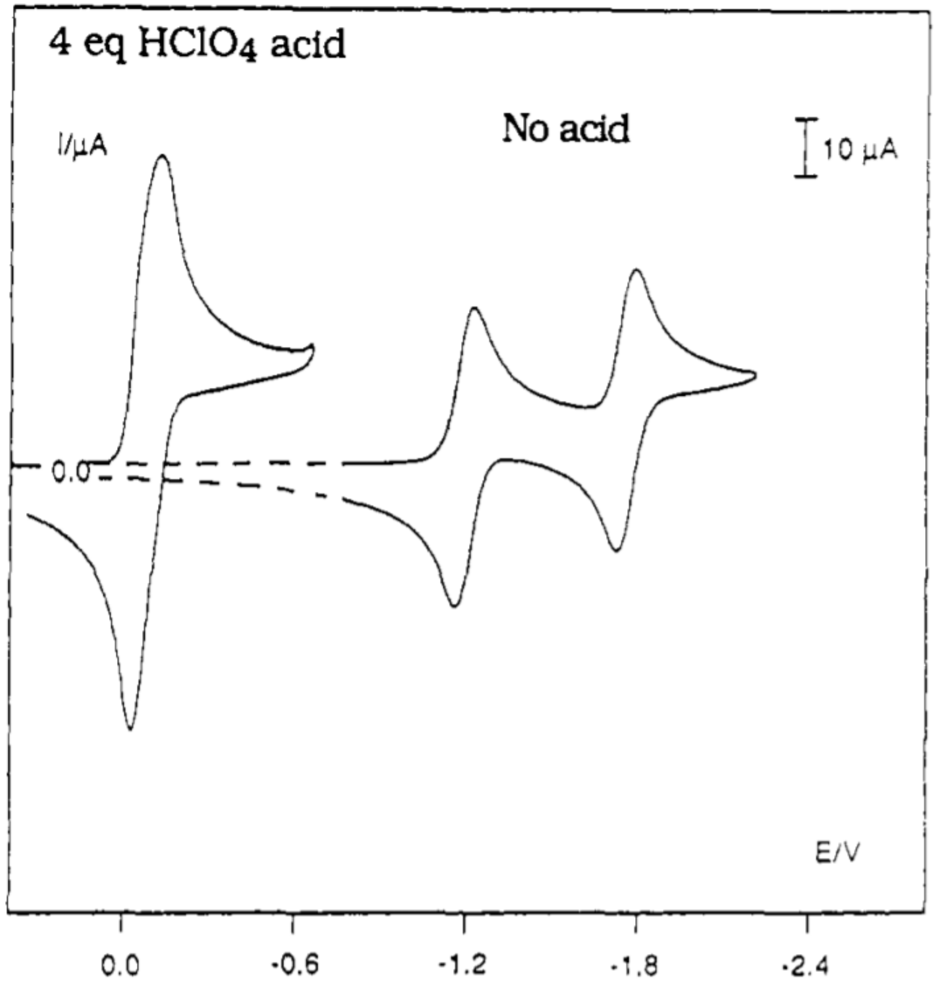
De Waele, V., Poizat, O., Fagnoni, M., Bagno, A., Ravelli, D. *ACS Catal.* **2016**, *6*, 7174

Yamase, T., Takabayashi, N., Kaji, M. *J. Chem. Soc. Dalton Trans.* **1984**, 793

Decatungstate redox potentials vary widely

$$[W_{10}O_{32}]^{4-} \xrightleftharpoons[E_{½}(1)]{e^-} [W_{10}O_{32}]^{5-} \xrightleftharpoons[E_{½}(2)]{e^-} [W_{10}O_{32}]^{6-}$$

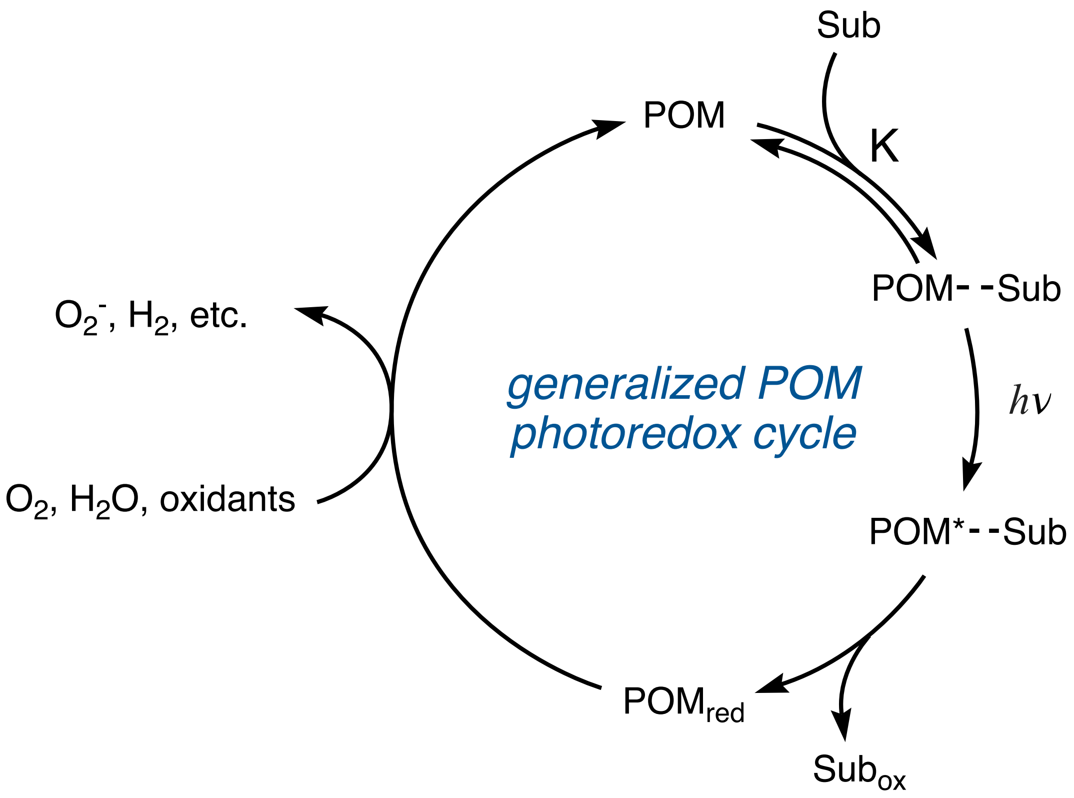
MeCN : H_2O	$E_{½}(1)$[a]	$E_{½}(2)$[a]
10 : 0	-0.94	-1.37
9 : 1	-0.72	-0.96
8 : 2	-0.62	-0.81
7 : 3	-0.59	-0.74



- strongly dependent on solvent
- strongly dependent on protonation state

[a] potential vs. Ag/AgCl **I** protonation-dependent CV potentials vs. $Ag/AgNO_3$
Renneke, R. F., Kadkhodayan, M., Pasquali, M., Hill, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 8357
Yamase, T., Takabayashi, N., Kaji, M. *J. Chem. Soc. Dalton Trans.* **1984,** *0*, 793

POM photoredox catalysis



generalized POM photoredox cycle

Sub

K

POM

POM- -Sub

$h\nu$

POM*- -Sub

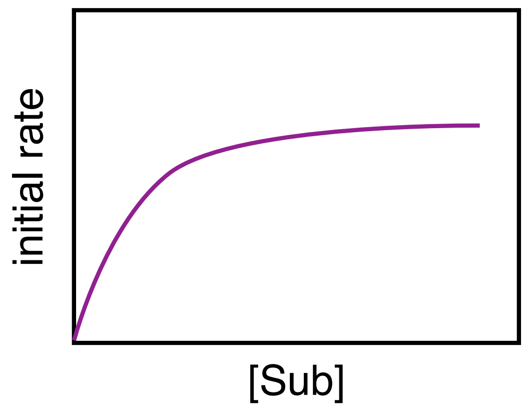
$\mathrm{POM_{red}}$

$\mathrm{Sub_{ox}}$

$\mathrm{O_2}$, $\mathrm{H_2O}$, oxidants

$\mathrm{O_2^-}$, $\mathrm{H_2}$, etc.

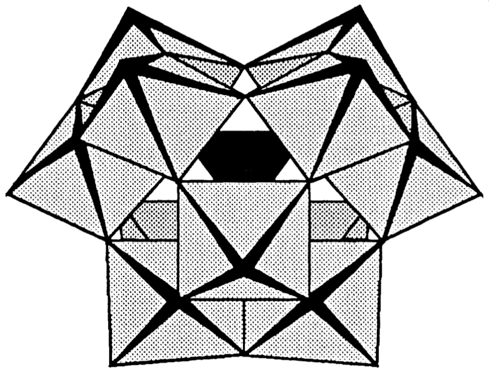
Kinetics of POM photoredox



$$R = \frac{k\mathrm{K[Sub]}}{1 + \mathrm{K[Sub]}}$$

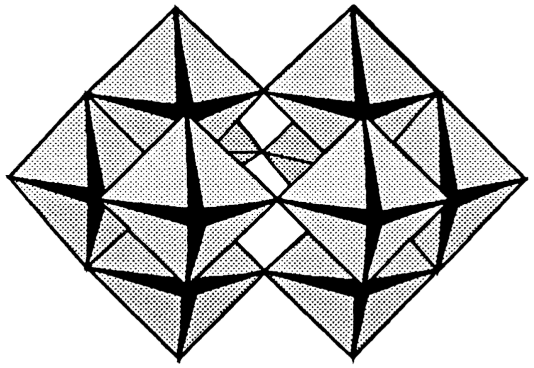
- $k \sim 10^{12}\ \mathrm{M^{-1}s^{-1}} \Rightarrow$ preassociation
- shows similar dependence on [POM]

Common POM photoredox catalysts



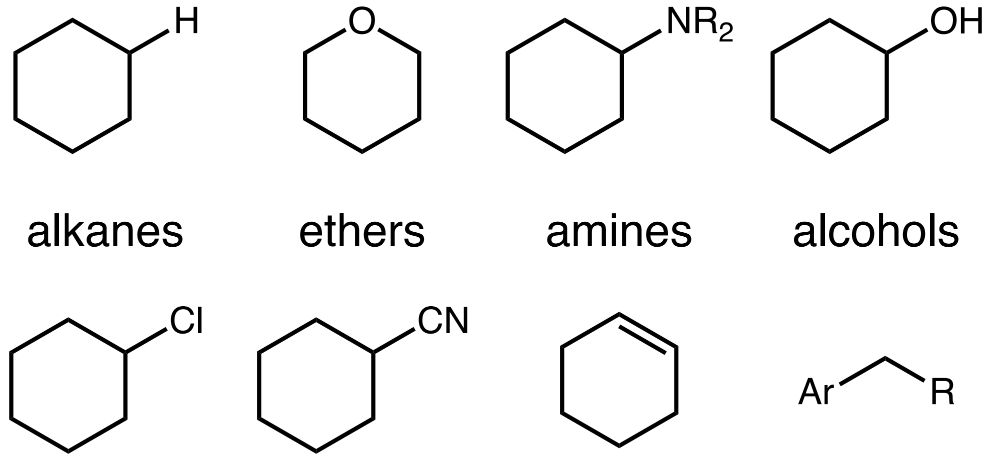
$[\mathrm{XM_{12}O_{40}}]^{n-}$

X = P, Si, Fe, $\mathrm{H_2}$, etc.
M = W, Mo



$[\mathrm{W_{10}O_{32}}]^{4-}$

Selected substrate classes

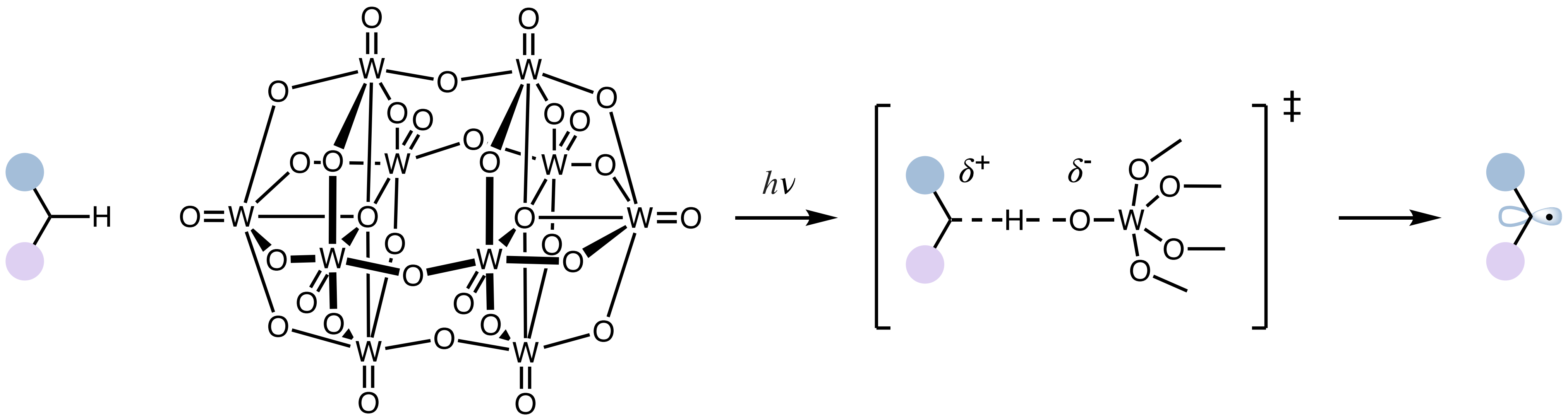


alkanes ethers amines alcohols

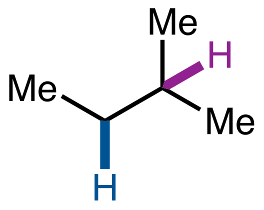
alkyl-Cl nitriles alkenes benzylic

Fox, M. A., Cardona, R., Gaillard, E. *J. Am. Chem. Soc.* **1987**, *109*, 6347
Papaconstantinou, E. *Chem. Soc. Rev.* **1989**, *18*, 1
Polyoxometalate Molecular Science; Almenar-Borras, J. J., Coronado, E., Muller, A., Pope, M., Eds.; Springer: Dordrecht, 2003

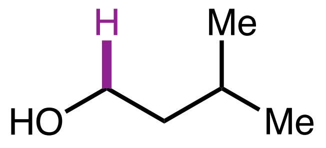
Site selectivity in decatungstate-mediated C–H abstraction



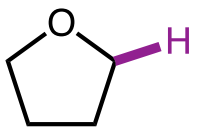
Polar effects



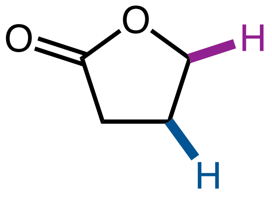
19% / 81%[a]



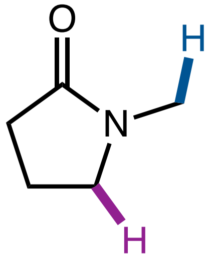
100%[a]



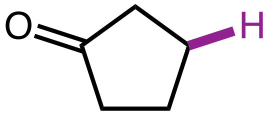
100%[a]



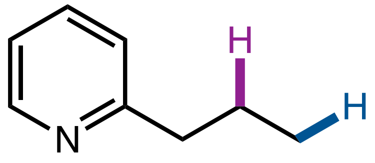
15% / 85%[a]



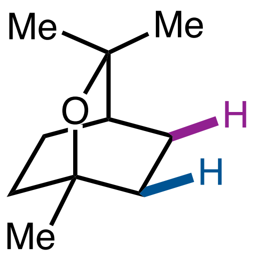
7% / 93%[a]



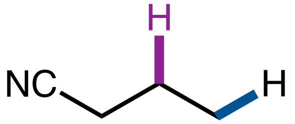
100%[a]



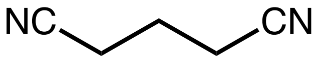
14% / 86%[a]



29% / 71%[b]



9% / 91%[a]

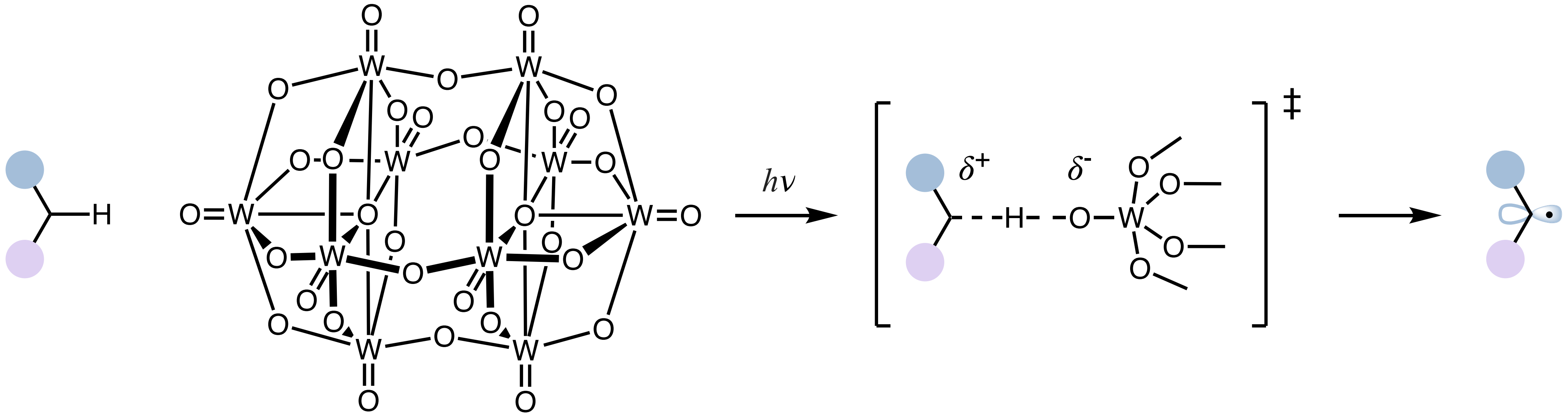


n.r.[a]

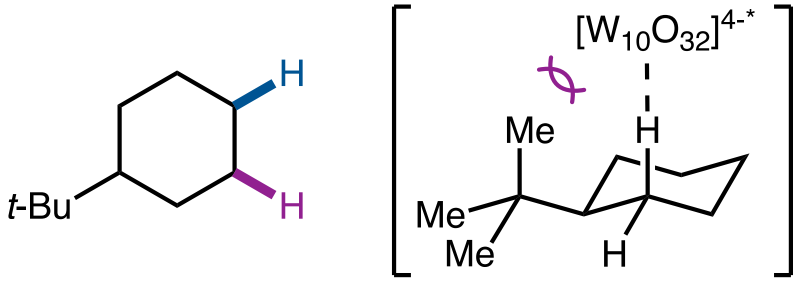
[a] Michael addition **I** [b] oxygenation **I** decatungstate chemdraw provided by Ian Perry

Ravelli, D., Fagnoni, M., Fukuyama, T., Nishikawa, T., Ryu, I. *ACS Catal.* **2017**, *just accepted*

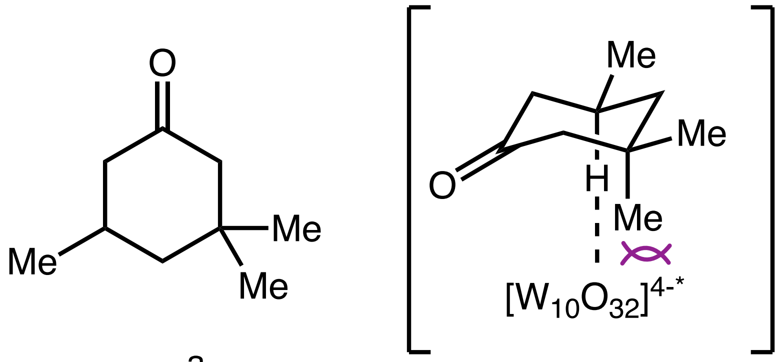
Site selectivity in decatungstate-mediated C–H abstraction



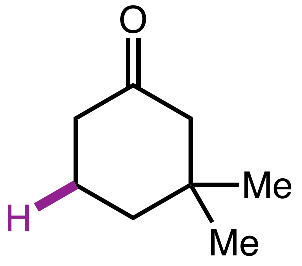
Steric effects



30% / 70%[a]

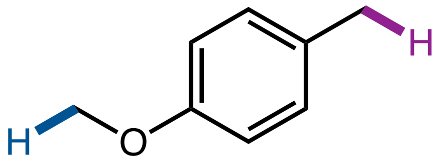


n.r.[a]

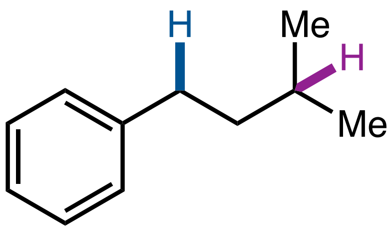


100%[a]

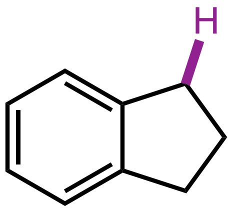
weak C–H bonds



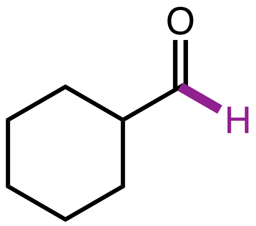
20% / 80%[a]



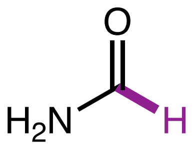
48% / 52%[a]



100%[a]



100%[a]



100%[a]

[a]Michael addition **I** decatungstate chemdraw provided by Ian Perry

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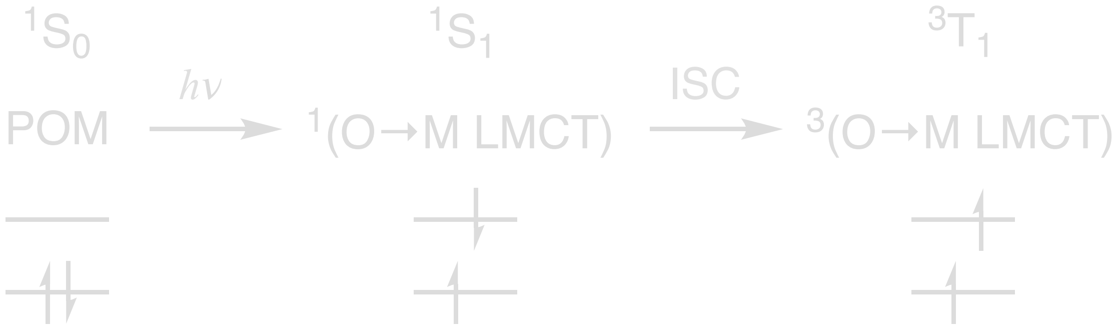
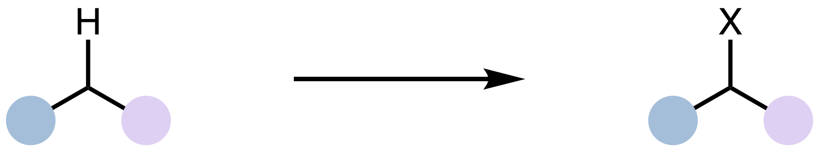


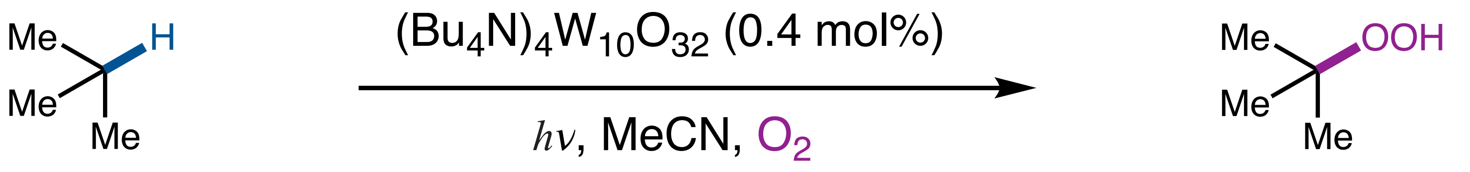
$^1S_0$ POM $\xrightarrow{h\nu}$ $^1S_1$ ^{1}(O→M LMCT) $\xrightarrow{\text{ISC}}$ $^3T_1$ ^{3}(O→M LMCT)

C–H Oxygenation/Fluorination Reactions

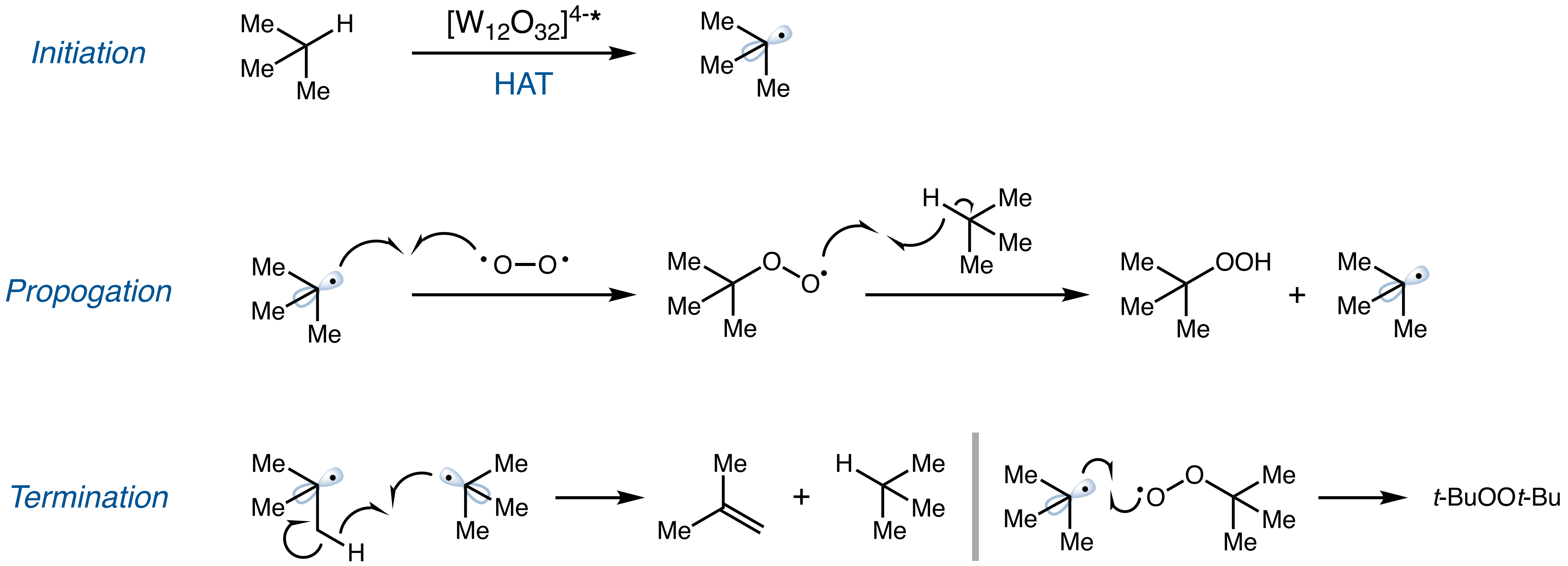


C–C Bond-Forming Reactions

Early work in decatungstate-catalyzed C–H oxygenation



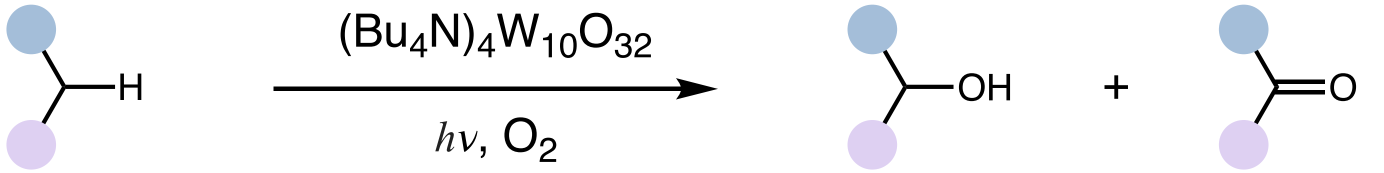
55%, sole product



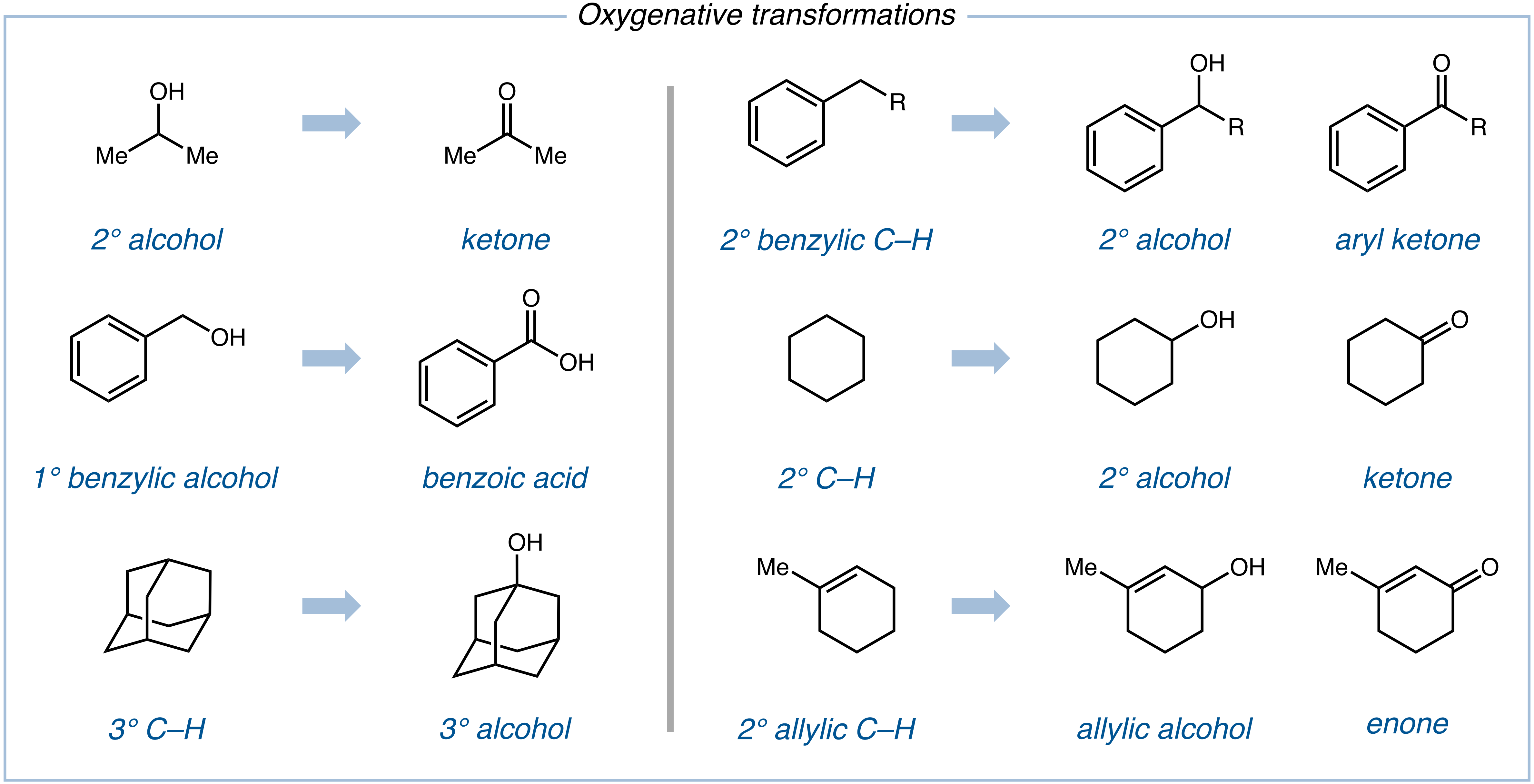
- $[HW_{10}O_{32}]^{4-}$ turned over by O_2
- Alternative to organic radical intitiators

Chambers, R. C., Hill, C. L. *Inorg. Chem.* **1989**, *28*, 2509

Further studies on decatungstate-catalyzed C–H oxygenation



Oxygenative transformations



2° alcohol → *ketone*

1° benzylic alcohol → *benzoic acid*

3° C–H → *3° alcohol*

2° benzylic C–H → *2° alcohol*, *aryl ketone*

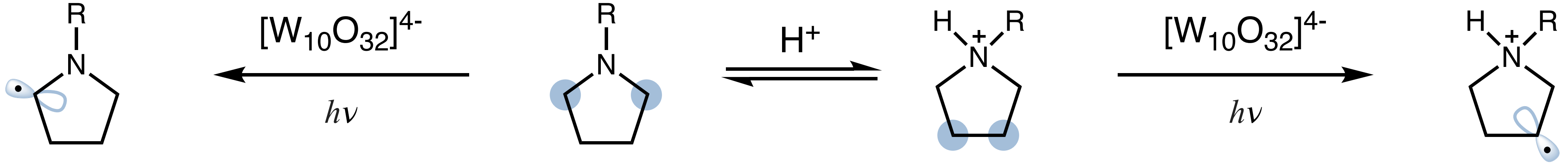
2° C–H → *2° alcohol*, *ketone*

2° allylic C–H → *allylic alcohol*, *enone*

Tzirakis, M. D., Lykakis, I. N., Orfanopoulos, M. *Chem. Soc. Rev.*, **2009**, *38*, 2609

Oxyfunctionalization of remote C–H bonds of aliphatic amines

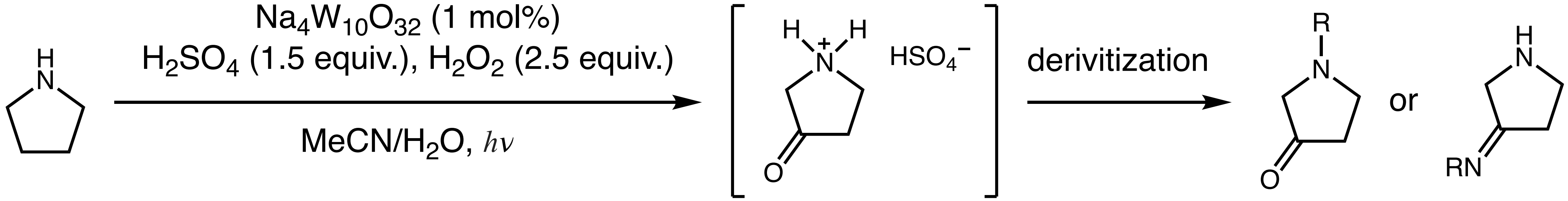
α-amino C–H polarity inversion



● most hydridic C–H

- Protonation inverts polarity of α-amino C–H bonds ⇒ distal C–H abstraction possible

Distal C–H oxygenation



$Na_4W_{10}O_{32}$ (1 mol%)
H_2SO_4 (1.5 equiv.), H_2O_2 (2.5 equiv.)
$MeCN/H_2O$, hν

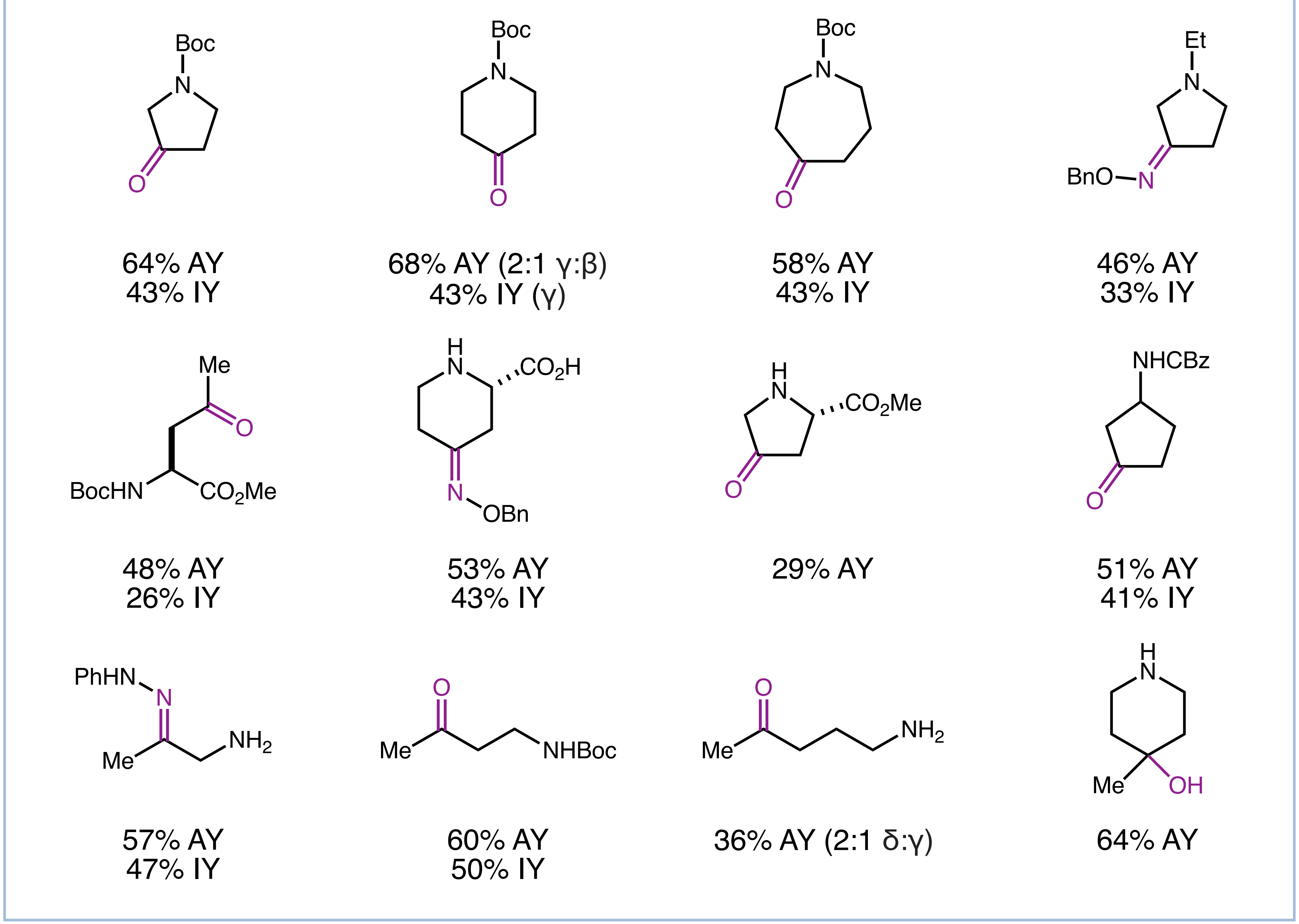
derivitization

- Uses desirable unprotected aliphatic amines
- keto-amine substitution pattern common motif in biologically-relevant molecules
- amenable to flow (0.7 M, 5 g scale, 5.0 bar O_2 as oxidant)

Schultz, D. M., Davies, I. W., *et al. Angew. Chem. Int. Ed.* **2017,** *56*, 15274

Oxyfunctionalization of remote C–H bonds of aliphatic amines

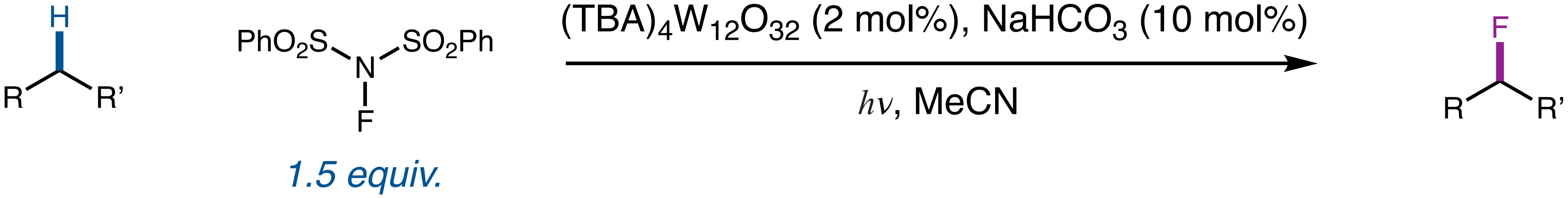
Substrate scope[a]



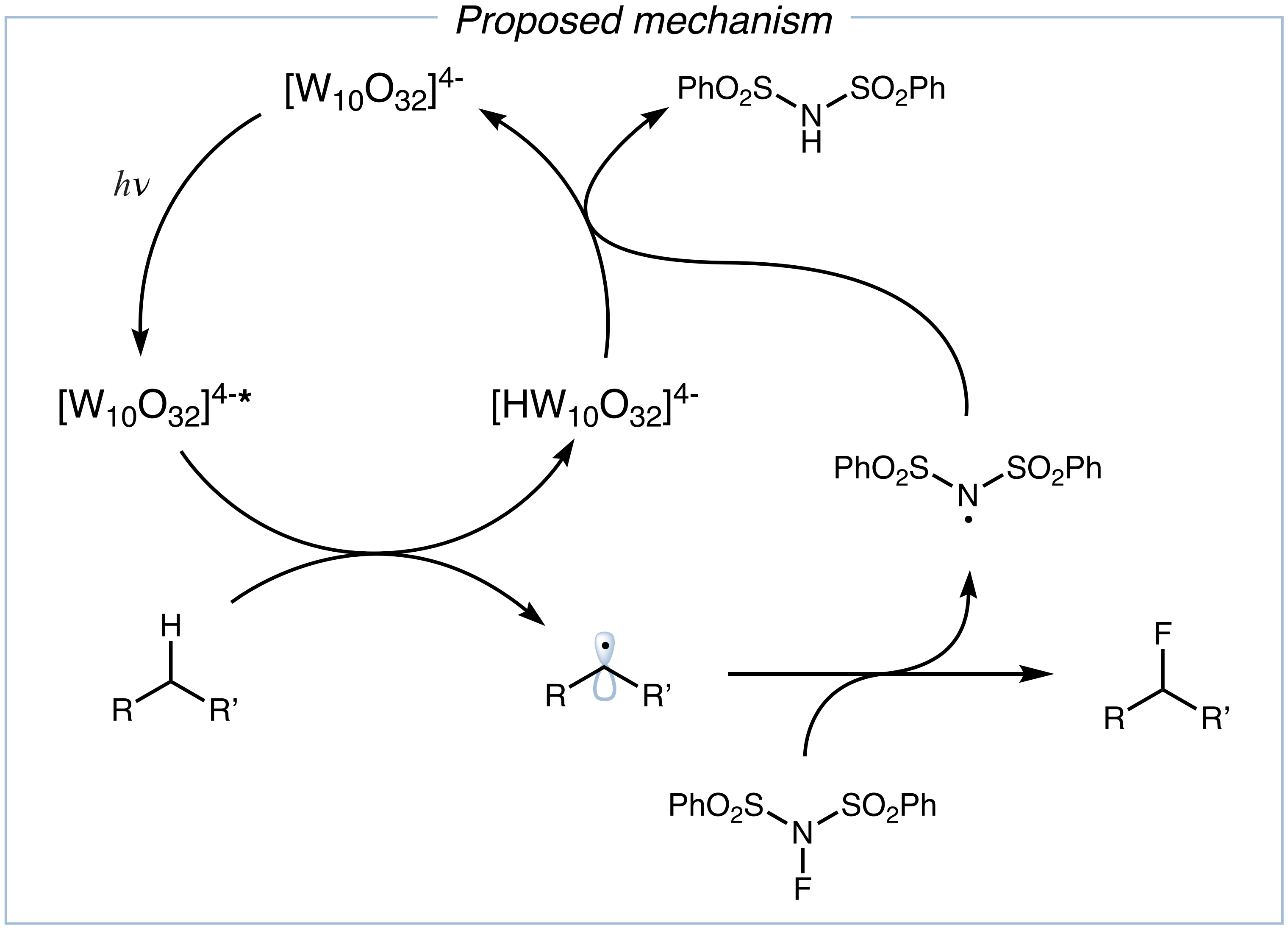
[a] AY = assay yield before derivitization; IY = isolated yield after derivitization

Schultz, D. M., Davies, I. W., *et al. Angew. Chem. Int. Ed.* **2017,** *56*, 15274

TBADT-catalyzed fluorination of unactivated C–H bonds



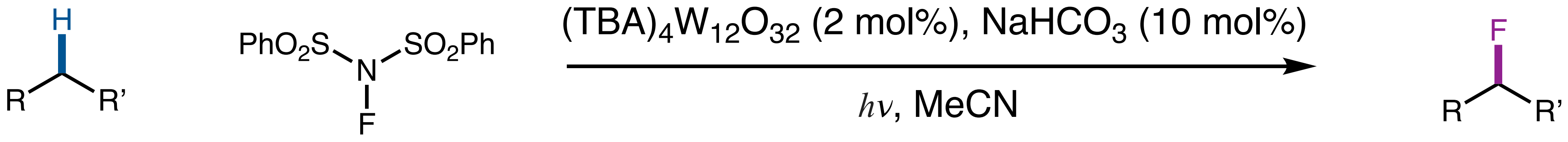
Proposed mechanism



- synergistic H atom transfer/F atom transfer
- fluorinates C–H bonds potentially prone to oxidative metabolism

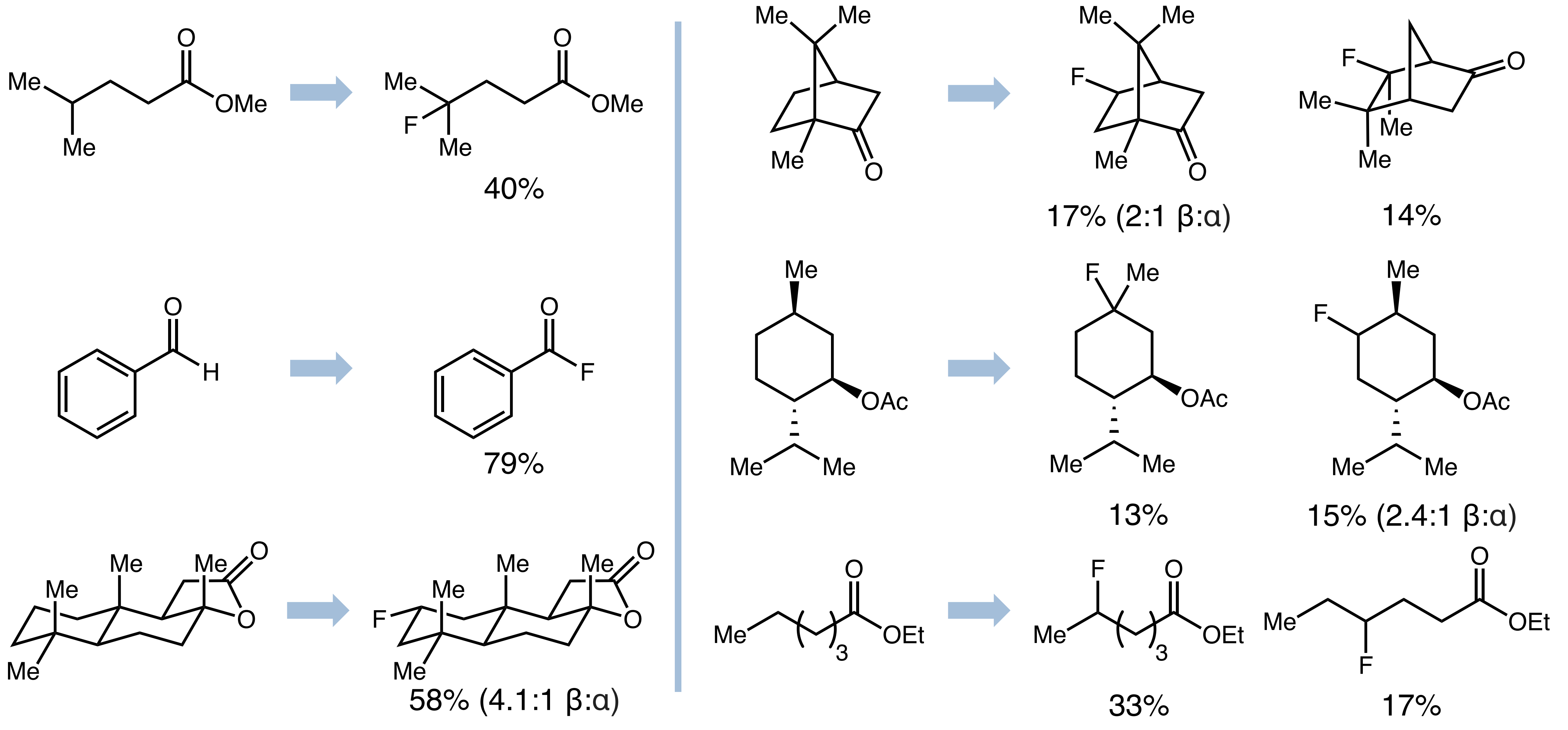
Halperin, S. D., Fan, H., Chang, S., Martin, R. E., Britton, R. *Angew. Chem. Int. Ed.* **2014**, *53*, 4690

TBADT-catalyzed fluorination of unactivated C–H bonds



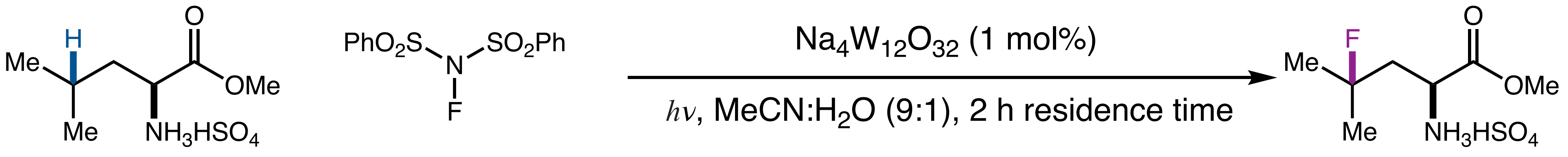
1.5 equiv.

C–H substrate scope



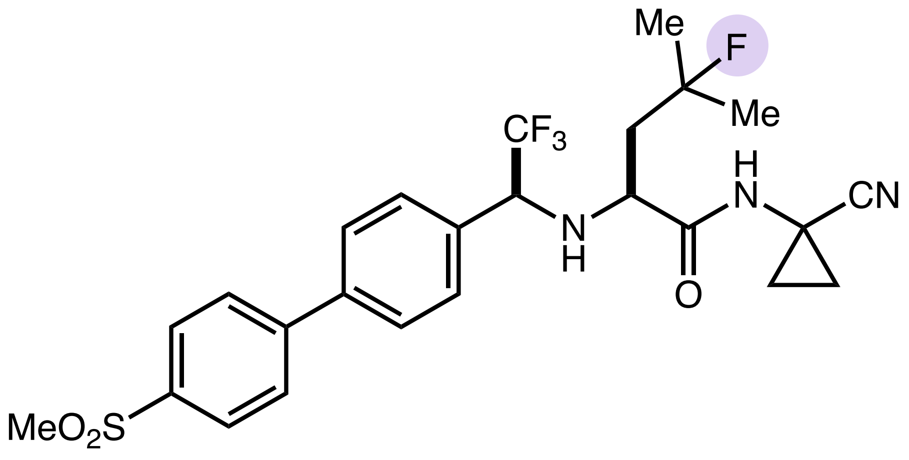
Halperin, S. D., Fan, H., Chang, S., Martin, R. E., Britton, R. *Angew. Chem. Int. Ed.* **2014**, *53*, 4690

TBADT-catalyzed fluorination of leucine on large scale



1.5 equiv.

90% isolated yield
44.7 g



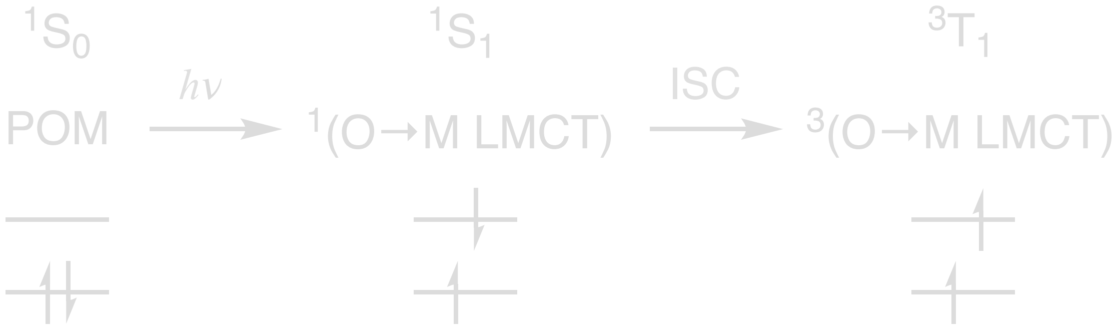
odanacatib
potent and selective inhibitor of cathpesin K

- large scale for the synthesis of odanacatib (development now discontinued)
- previously processes required 2-6 steps (F introduced by alkene or epoxide hydrofluorination)

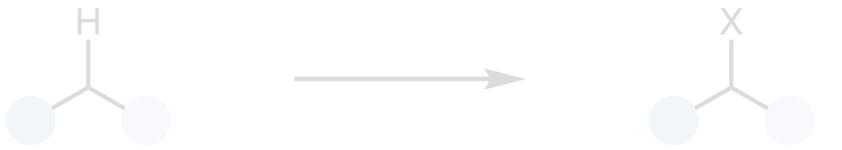
Halperin, S. D., Kwon, D., Holmes, M., Regalado, E. L., Campeau, L.-C., DiRocco, D. A., Britton, R. *Org. Lett.* **2015**, *17*, 5200

Outline

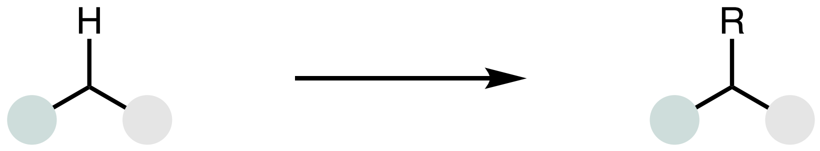
Polyoxometalate Fundamentals



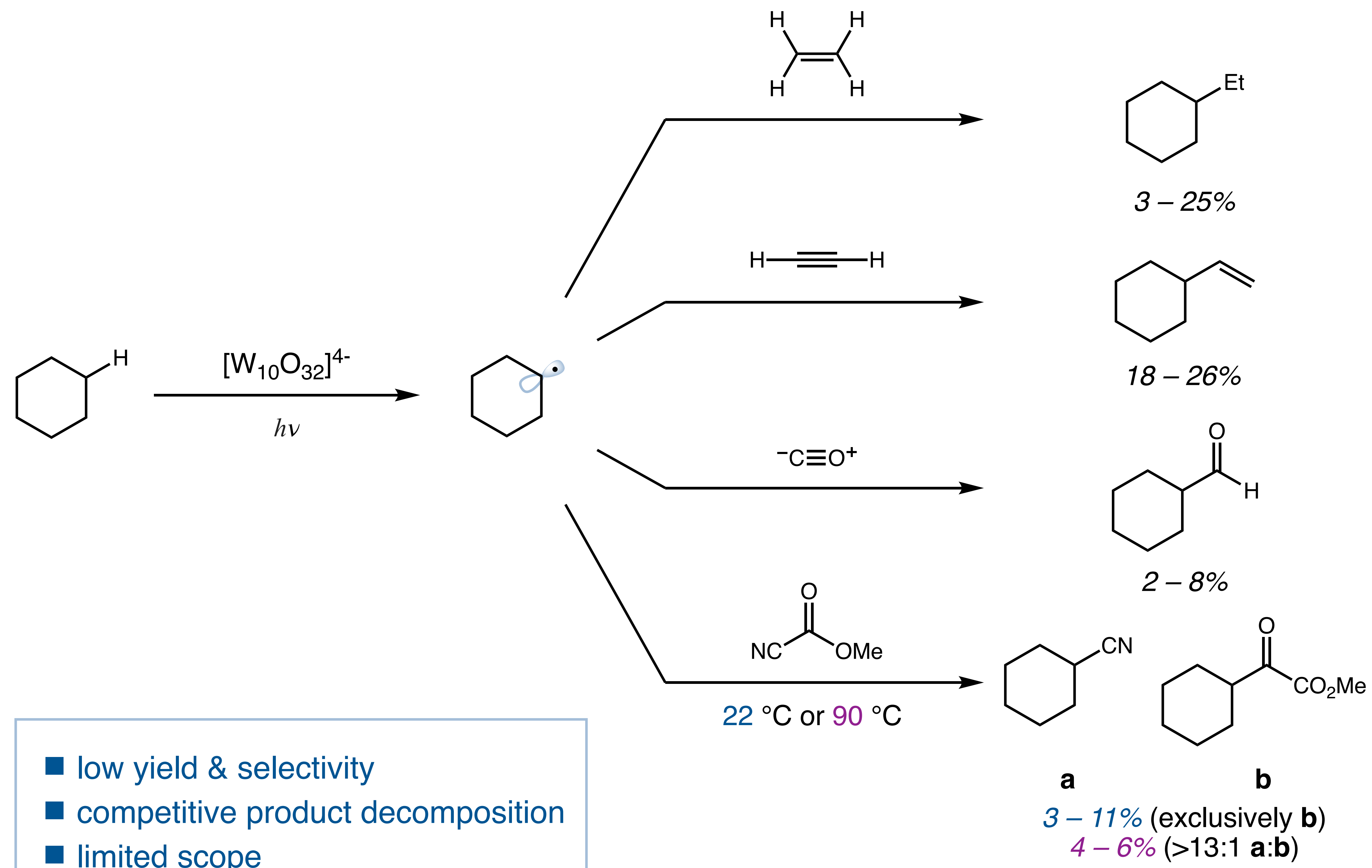
C–H Oxygenation/Fluorination Reactions



C–C Bond-Forming Reactions



Early work in TBADT-catalyzed C–C bond-forming reactions



3 – 25%

18 – 26%

2 – 8%

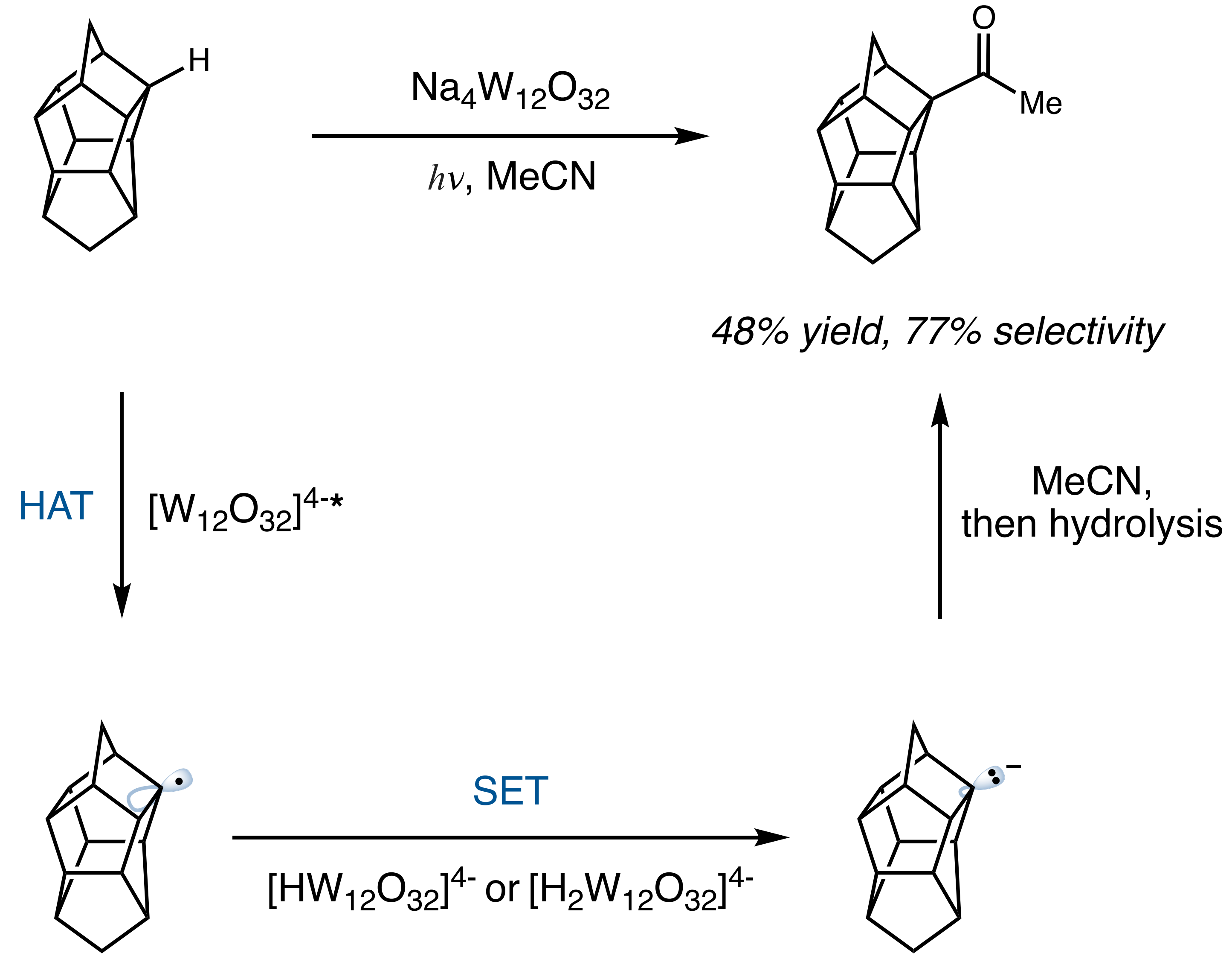
a **b**

3 – 11% (exclusively **b**)
4 – 6% (>13:1 **a**:**b**)

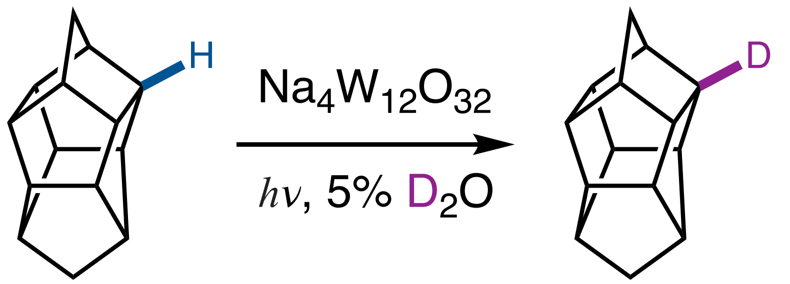
- low yield & selectivity
- competitive product decomposition
- limited scope

Jaynes, B. S., Hill, C. L. *J. Am. Chem. Soc.*, **1993**, *115*, 12212
Jaynes, B. S., Hill, C. L. *J. Am. Chem. Soc.*, **1995**, *117*, 4704
Zheng, Z., Hill, C. L. *Chem. Commun.*, **1998**, 2467
Hill, C. L. *Synlett*, **1995**, *1995*, 127

TBADT-catalyzed acetylation



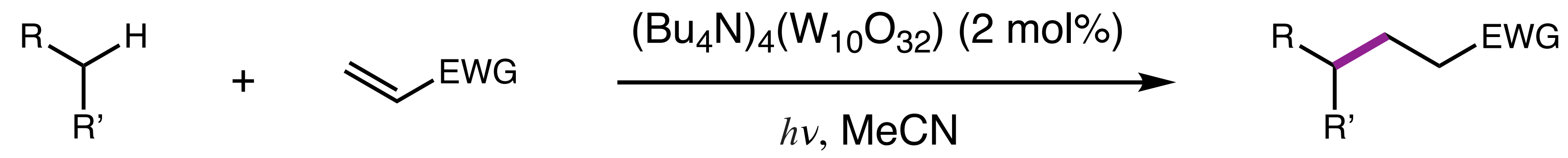
Mechanistic evidence



- rare example of a carbanion intermediate in POM photoredox
- product deactivated toward further functionalization

Prosser-McCartha, C. M., Hill, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 3671

TBADT-catalyzed alkylation of electrophilic alkenes

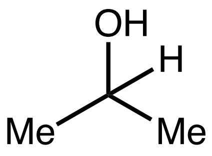
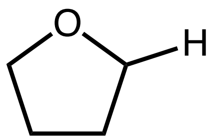
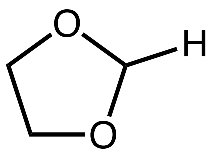
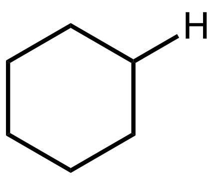
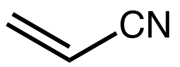
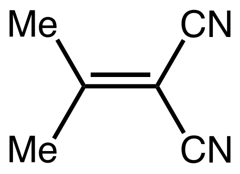


$(Bu_4N)_4(W_{10}O_{32})$ (2 mol%)

$h\nu$, MeCN

5 equiv. *1 equiv.*

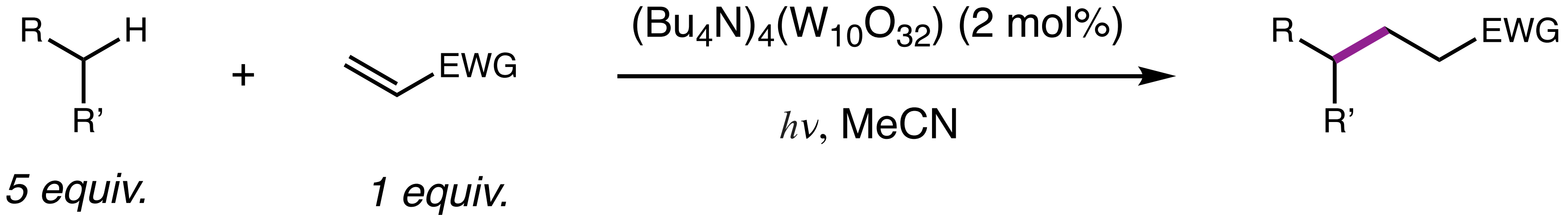
Reaction scope

				
	72%	78%	76%	63%
	50%	75%	50%	65%

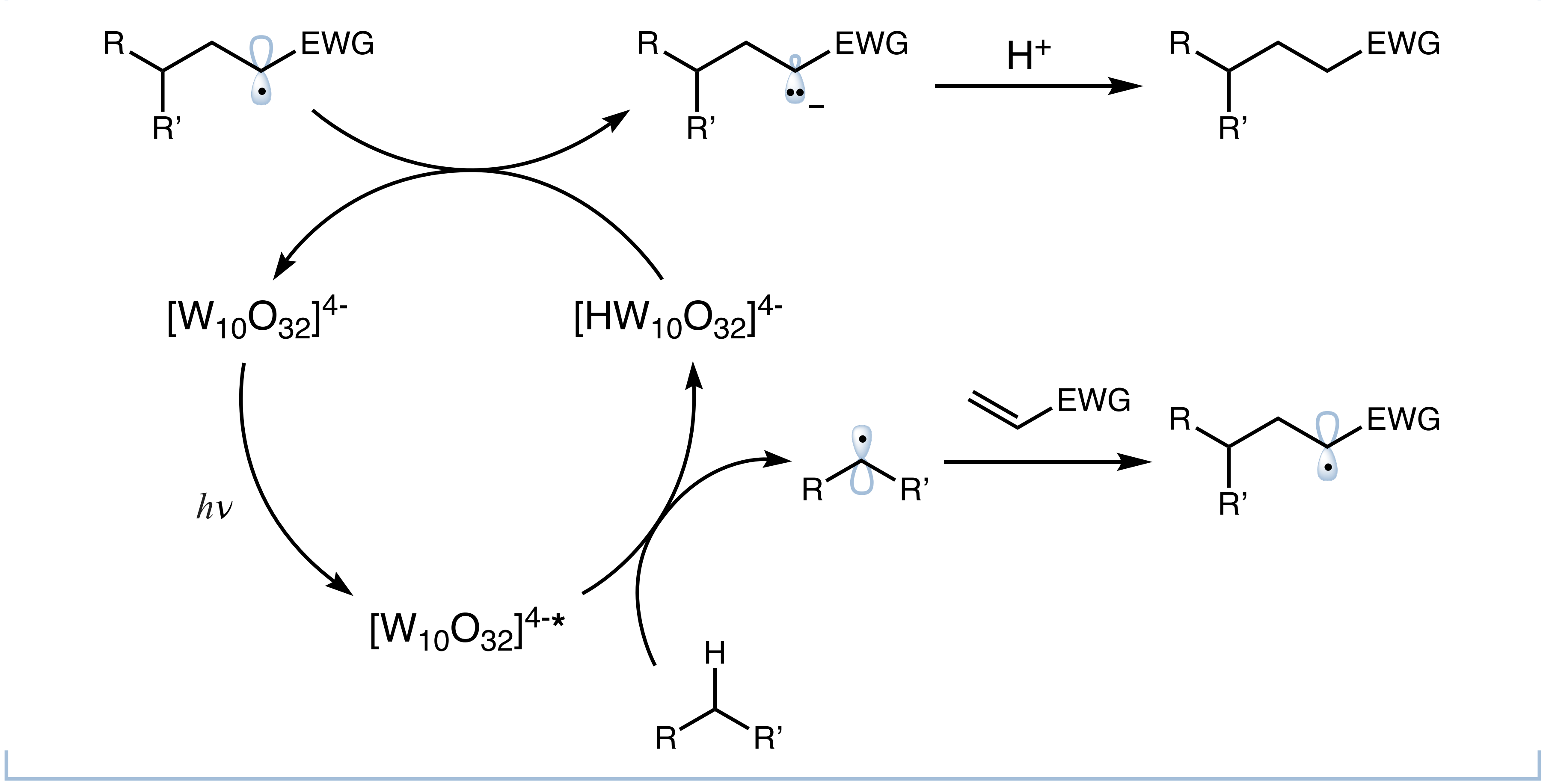
- nucleophilic alkyl radicals trapped efficiently by electrophilic alkenes
- complete conversion
- *Φ* ranges from 0.06–0.58 depending on alkyl radical nucleophilicity

Dondi, D., Fagnoni, M., Molinari, A., Maldotti, A., Albini, A. *Chem. Eur. J.* **2004**, *10*, 142
Dondi, D., Fagnoni, M., Albini, A. *Chem. Eur. J.* **2006**, *12*, 4153

TBADT-catalyzed alkylation of electrophilic alkenes



Proposed mechanism

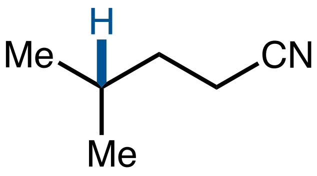


- electrophilic radical turns over $[HW_{10}O_{32}]^{4-}$ by SET

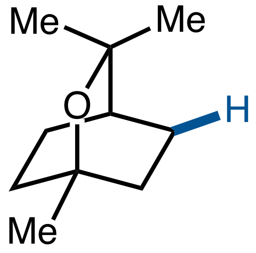
Dondi, D., Fagnoni, M., Molinari, A., Maldotti, A., Albini, A. *Chem. Eur. J.* **2004**, *10*, 142
Dondi, D., Fagnoni, M., Albini, A. *Chem. Eur. J.* **2006**, *12*, 4153

Further studies on TBADT-catalyzed alkylation of electrophilic alkenes

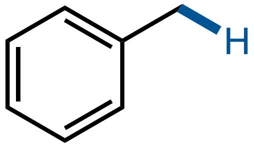
C–H nucleophiles



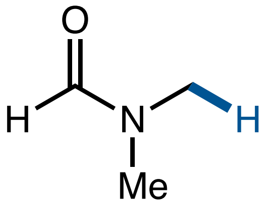
3° C–H



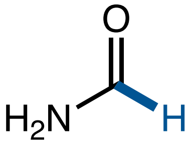
bridged bicyclic C–H



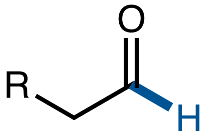
benzylic C–H



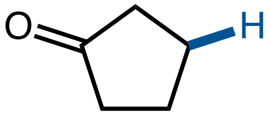
α-amino C–H



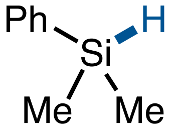
formamide C–H



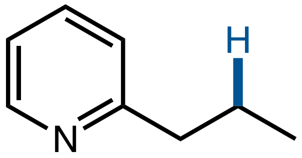
aldehyde C–H



β-keto C–H

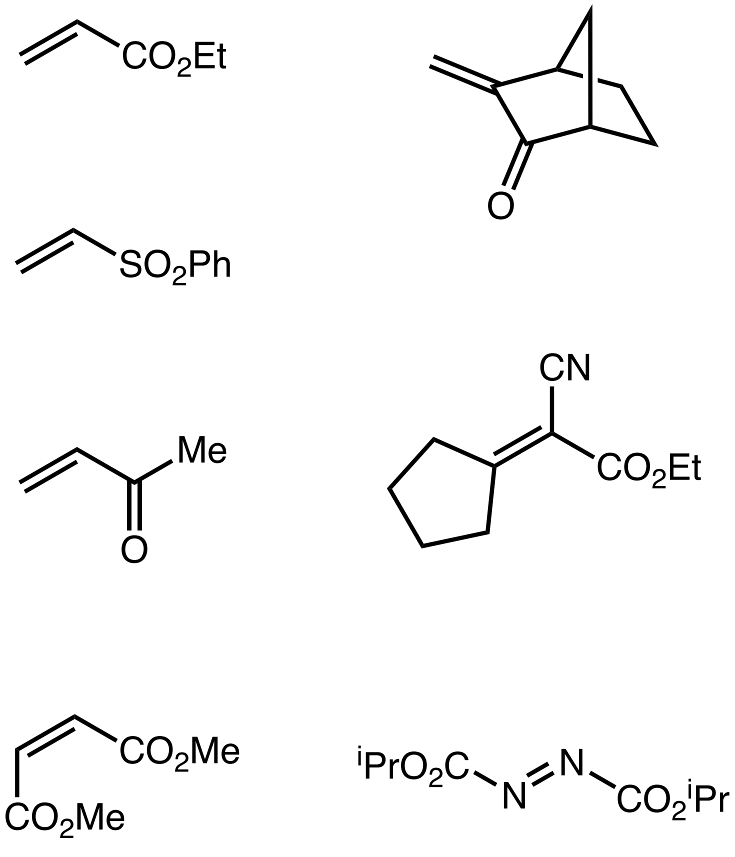


silane Si–H



β-pyridyl C–H

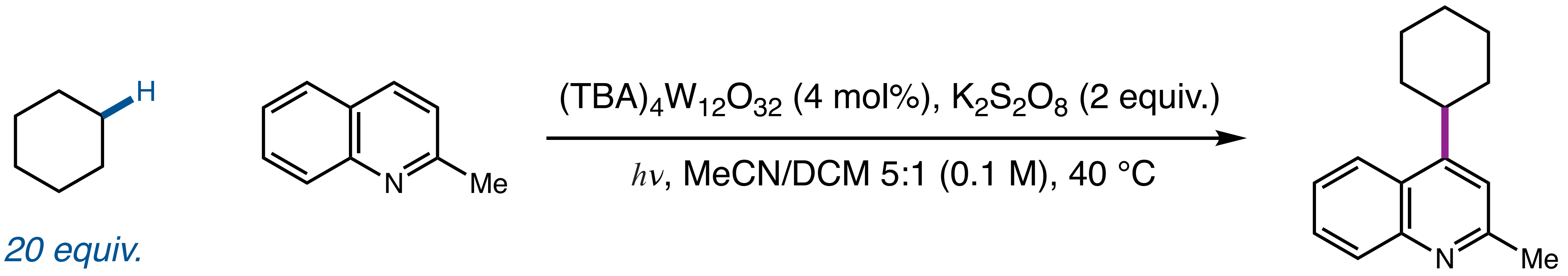
Michael acceptors

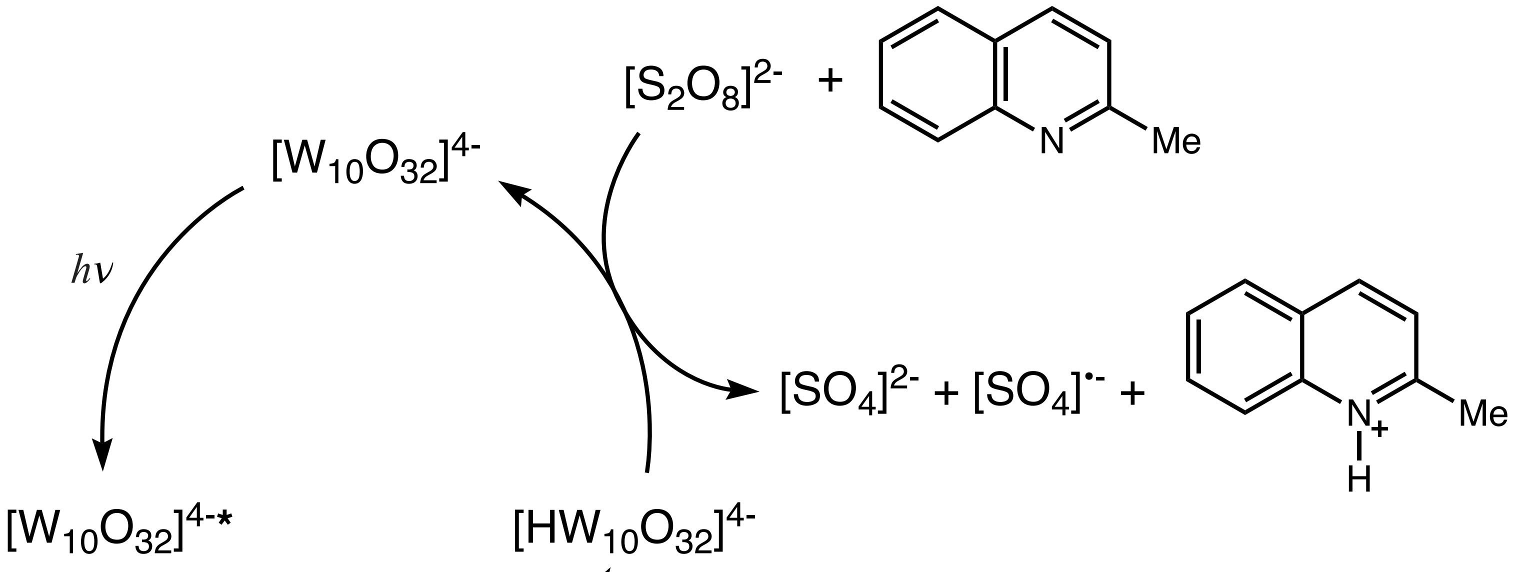


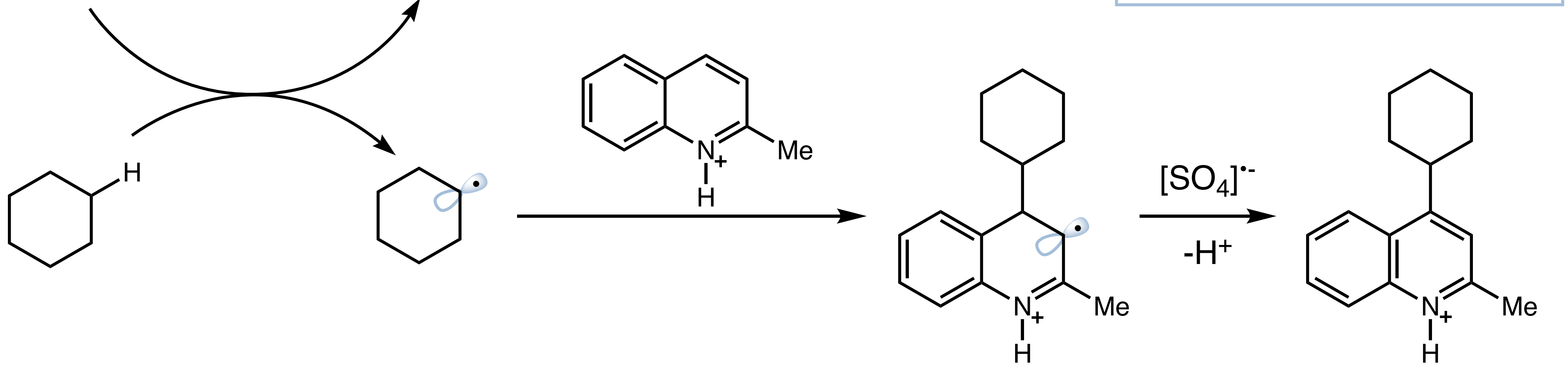
- Scope has been extended to many classes of C–H nucelophile
- Site selectivity is governed by a combination of steric and polar effects

Ravelli, D., Protti, S., Fagnoni, M.. *Acc. Chem. Res.* **2016**, *49*, 2232
Ravelli, D., Fagnoni, M., Fukuyama, T., Nishikawa, T., Ryu, I. *ACS Catal.* **2017**, *just accepted*

TBADT-catalyzed cross-dehydrogenative coupling



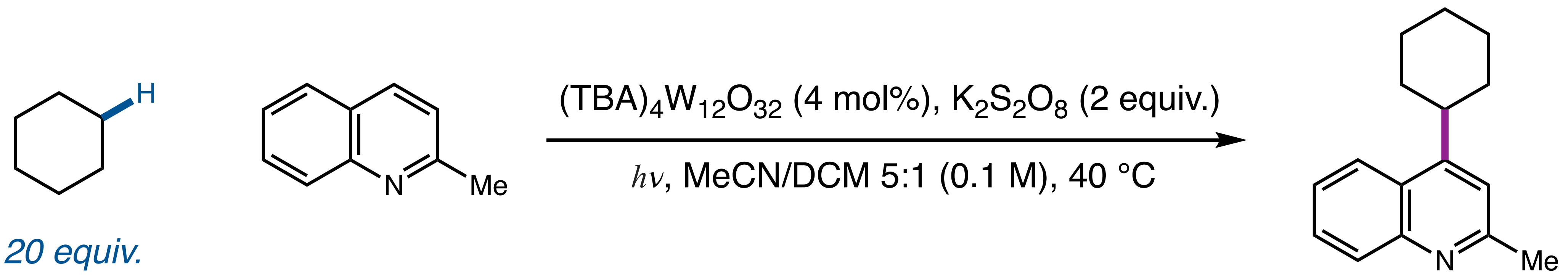




- Minisci-type reaction
- requires 20 equiv. C–H nucleophile
- 15 examples
- 40-81% yield

Quattrini, M. C., Fujii, S., Yamada, K., Fukuyama, T., Ravelli, D., Fagnoni, M., Ryu, I. *Chem. Commun.* **2017**, *53*, 2335

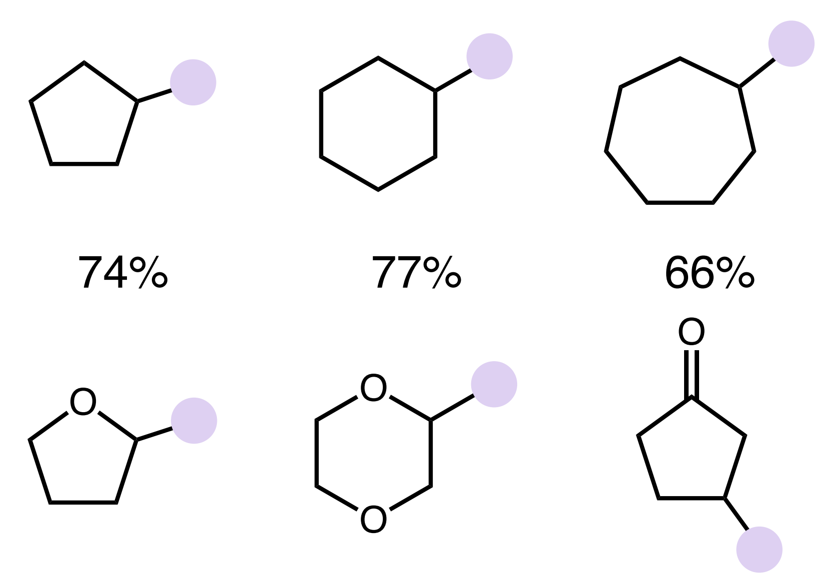
TBADT-catalyzed cross-dehydrogenative coupling



$(TBA)_4W_{12}O_{32}$ (4 mol%), $K_2S_2O_8$ (2 equiv.)

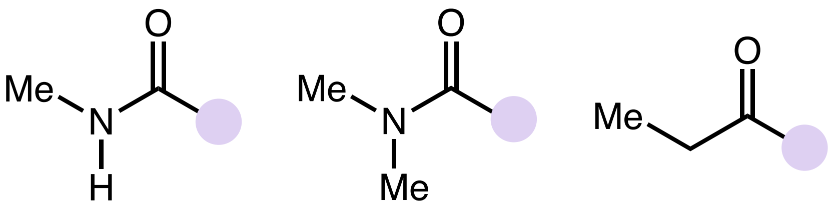
hν, MeCN/DCM 5:1 (0.1 M), 40 °C

C–H nucleophile scope



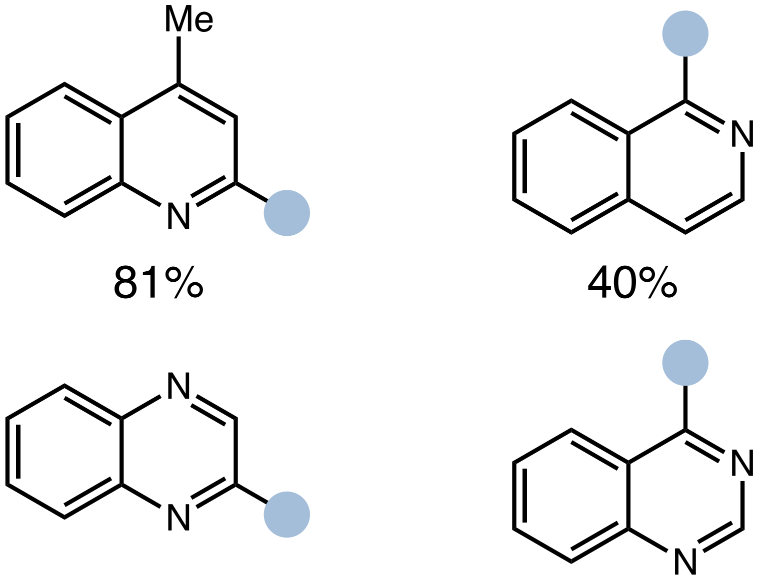
74% 77% 66%

53% 73% 69%



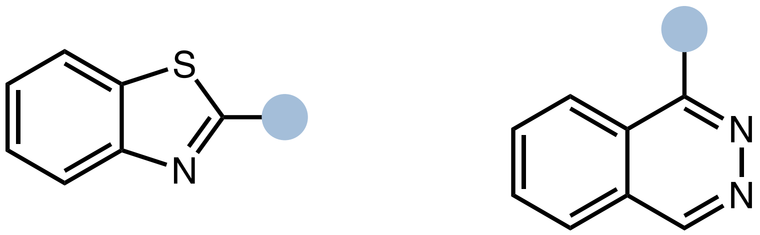
47% 73% 67%

Heteroarene scope



81% 40%

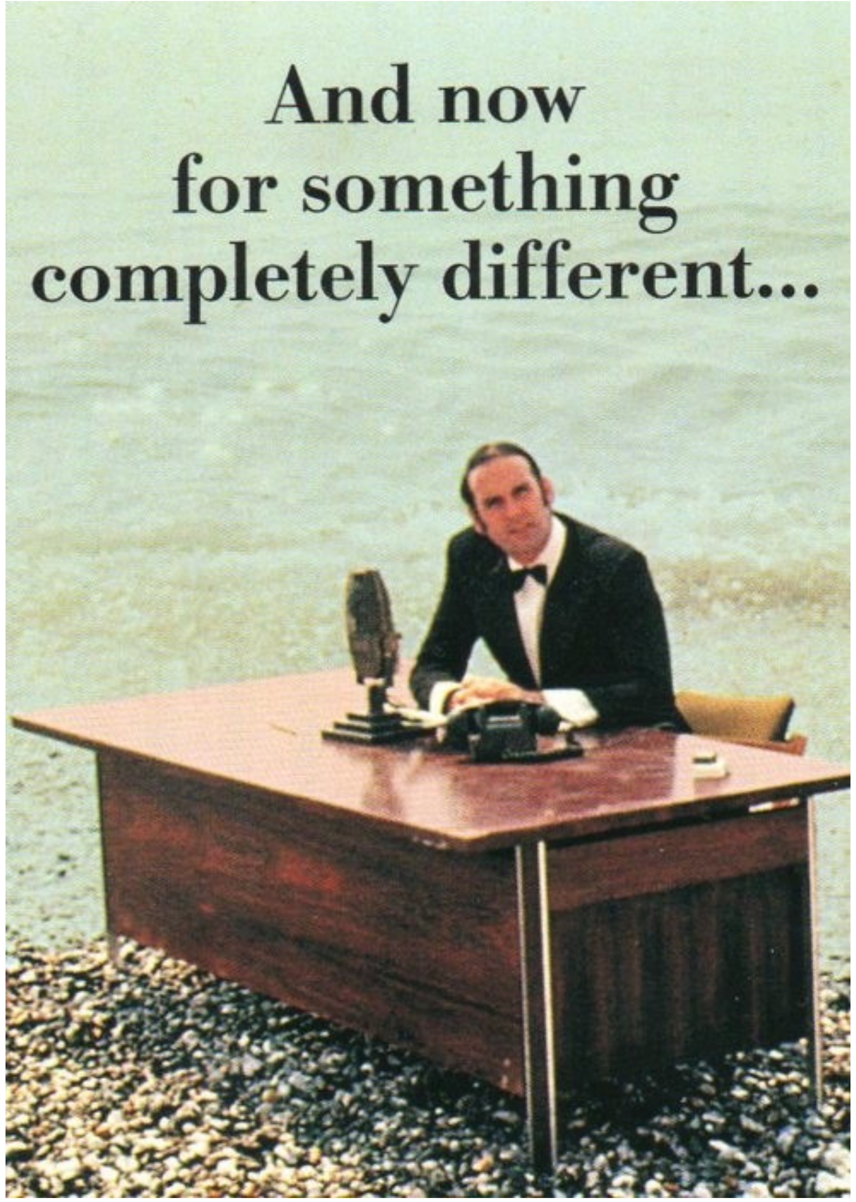
60% (24% bis-Cy) 43% (14% bis-Cy)



60% 28% (20% bis-Cy)

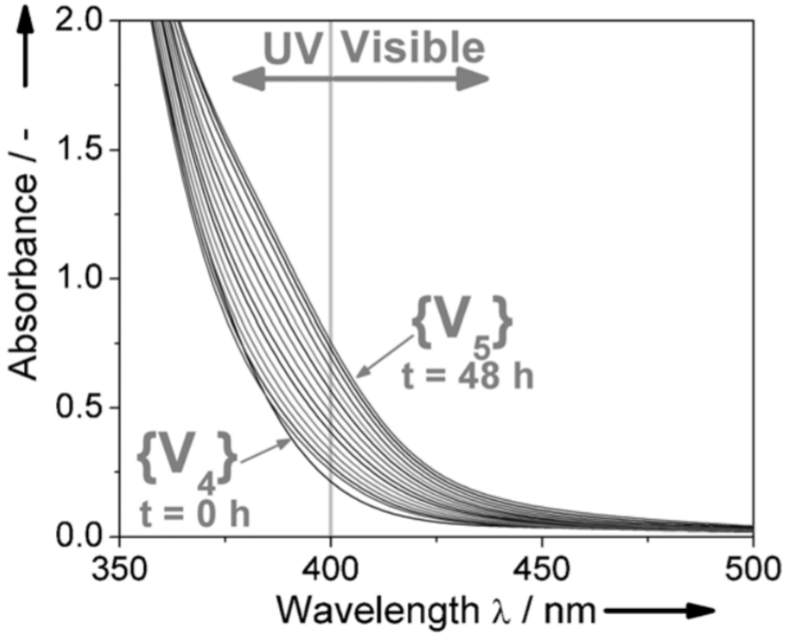
Quattrini, M. C., Fujii, S., Yamada, K., Fukuyama, T., Ravelli, D., Fagnoni, M., Ryu, I. *Chem. Commun.* **2017**, *53*, 2335

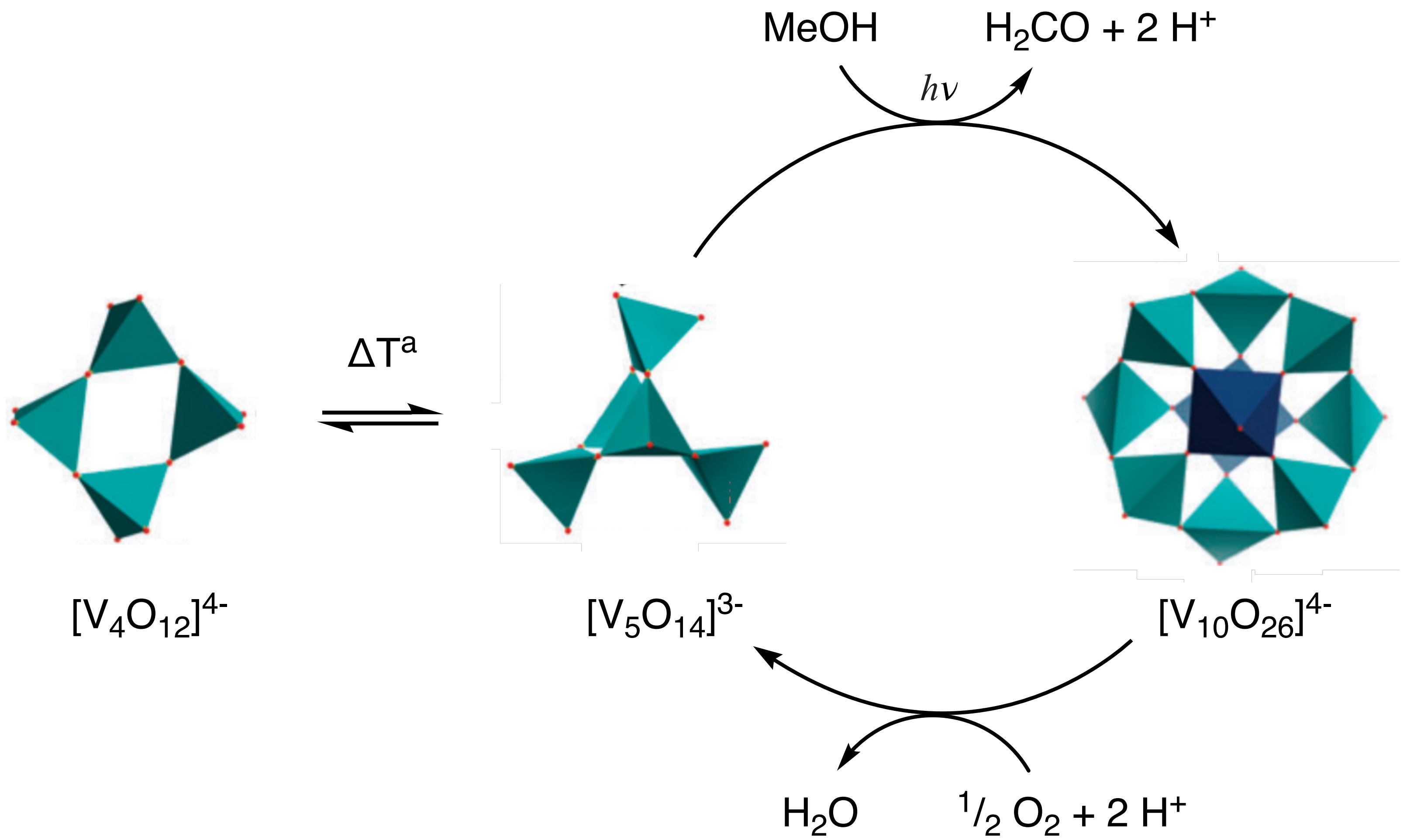
A final comment on visible light-excitable POMs



Visible light photocatalysis with polyoxovanadates

UV/vis spectra of $[V_4] \rightleftharpoons [V_5]$





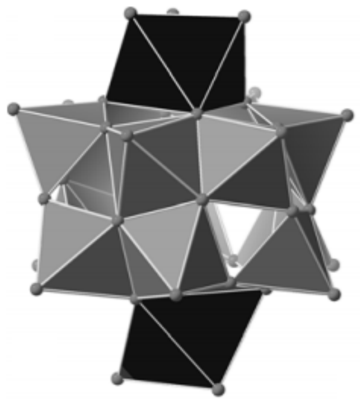
- *in situ* thermal conversion of $\{V_4\}$ to $\{V_5\}$ allows visible light photoredox catalysis
- turnover by O_2 is quite slow (weeks), but turnover by H_2O_2 is fast (seconds)

[a] 80 °C

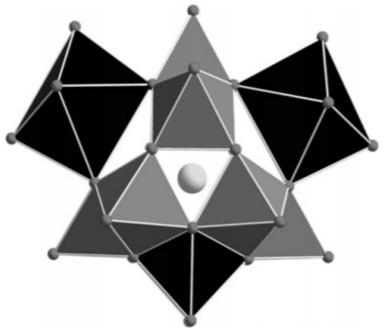
Forster, J., Rösner, B., Khusniyarov, M. M., Streb, C. *Chem. Commun.* **2011**, *47*, 3114

Visible light photoredox catalysis with heteropolyoxovanadates

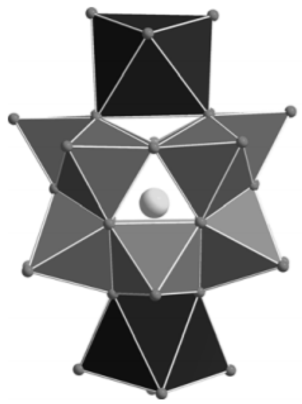
Cerium vanadate oxide clusters



$[(Ce(dmso)_3)_2V_{12}O_{33}Cl]^{2-}$
(**1**)

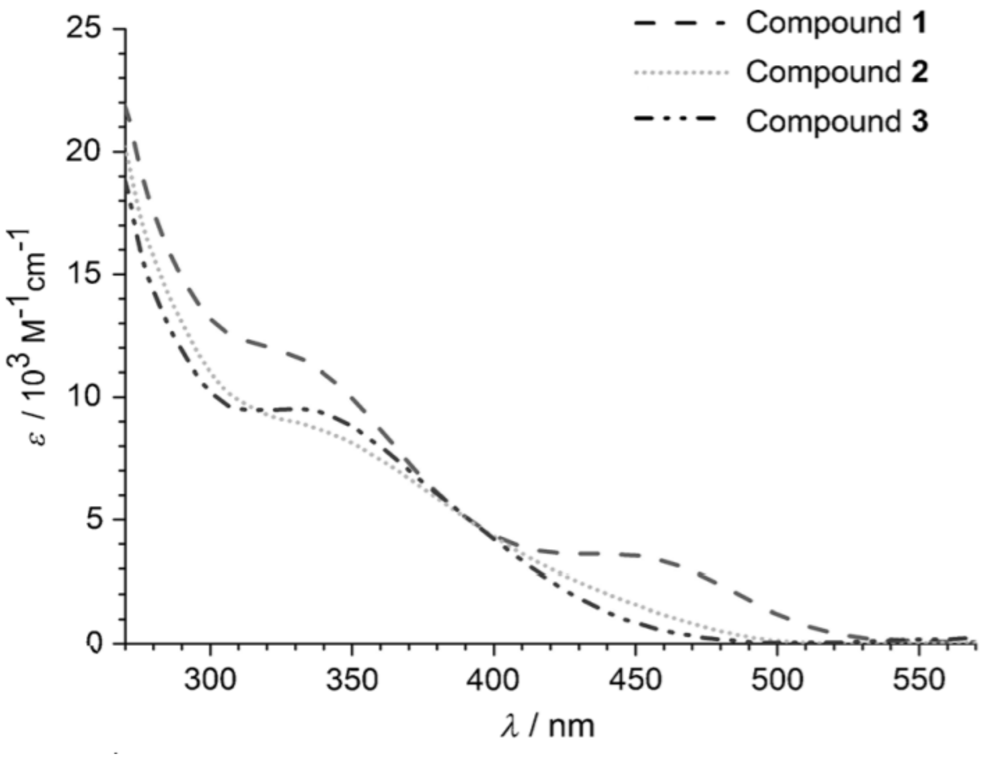


$[(Ce(dmso)_4)_2V_{11}O_{30}Cl]$
(**2**)

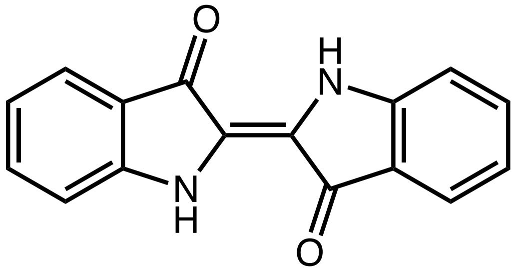


$[(Ce(nmp)_4)_2V_{12}O_{32}Cl]$
(**3**)

UV/vis spectra



- explored for oxidation of pollutants



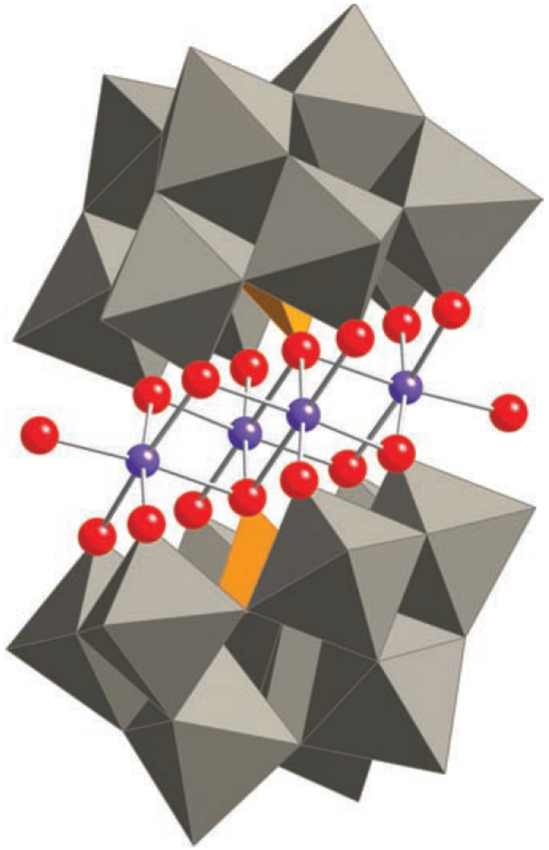
indigo (model pollutant)

- $\Phi \sim 2\%$ for photooxidation of indigo at $\lambda_{ex} = 450$ nm

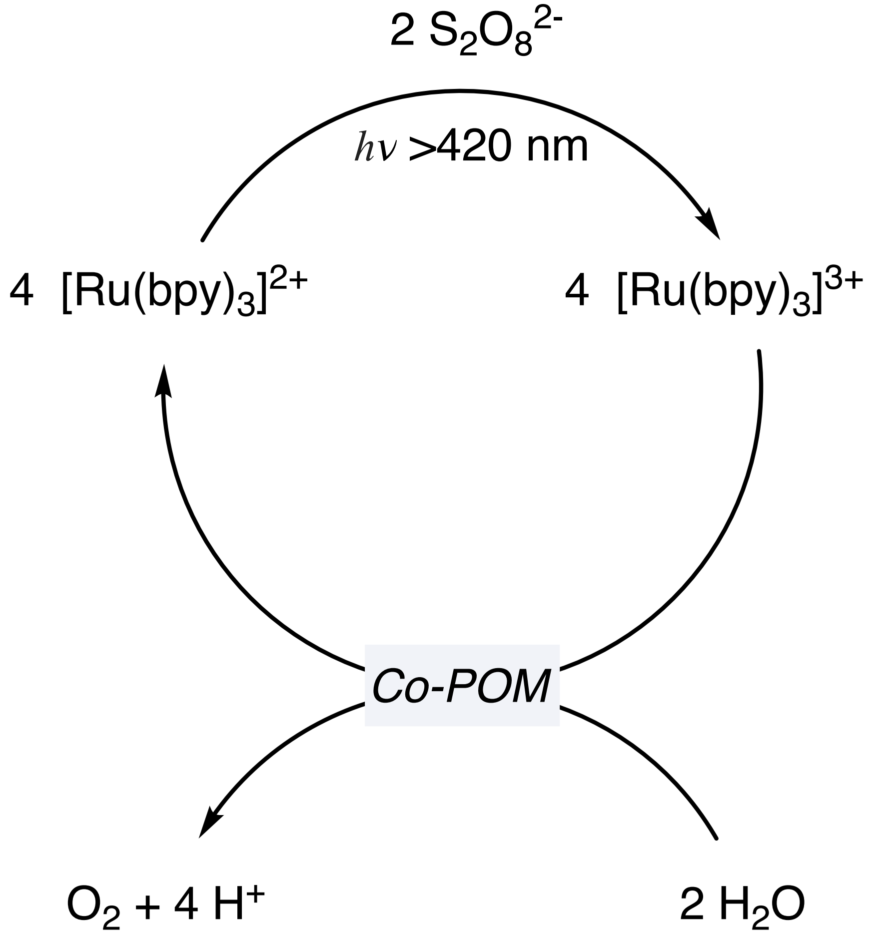
Seliverstov, A., Streb, C. *Chem. Eur. J.* **2014**, *20*, 9733

POM–photosensitizer co-catalyzed water oxidation

Water oxidation catalyst



$[Co_4(H_2O)_2(PW_9O_{34})_2]^{10-}$
key: Co, O, PO_4, WO_6
Co-POM



$2\ S_2O_8^{2-}$

$h\nu$ >420 nm

$4\ [Ru(bpy)_3]^{2+}$

$4\ [Ru(bpy)_3]^{3+}$

Co-POM

$O_2 + 4\ H^+$

$2\ H_2O$

- POM catalysis can be coupled to external photoredox processes
- $[Ru(bpy)_3]^{2+}$ acts as electron shuttle between Co-POM and stoichiometric oxidant

Yin, Q., Hill, C. L., *et al. Science* **2010**, *328*, 342
Huang, Z., Hill, C. L., Lian, T., *et al. J. Am. Chem. Soc.* **2011**, *133*, 2068