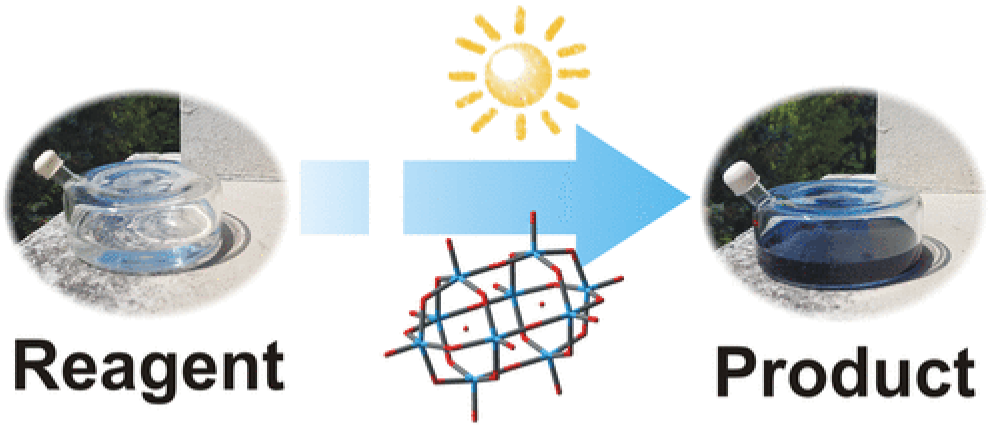
A Brief Introduction of

Tetrabutylammonium decatungstate

(TBADT)



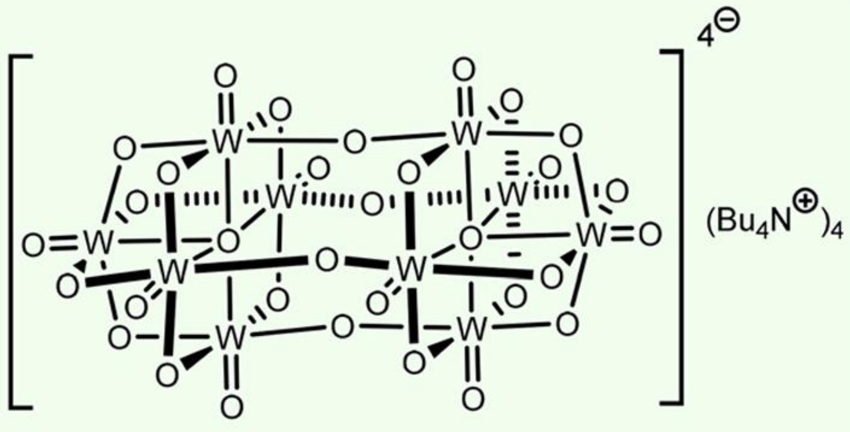
Xiao Liu

2025/11/06

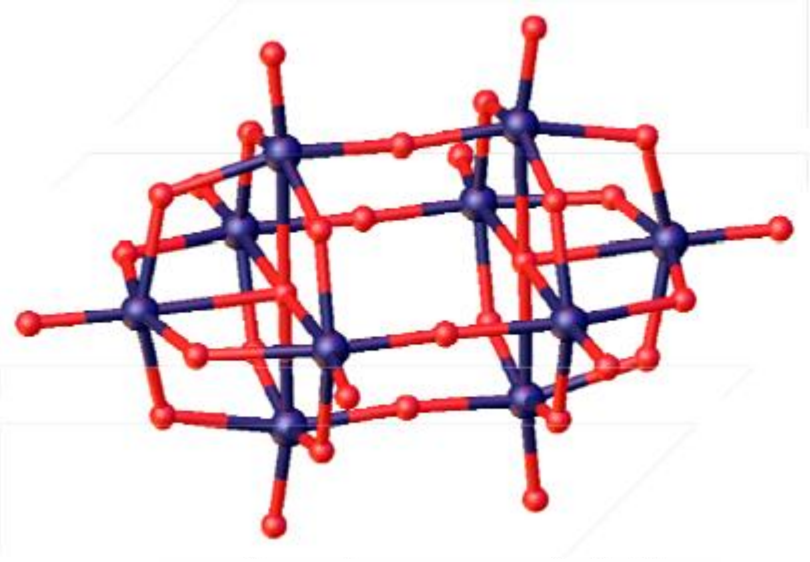
Content

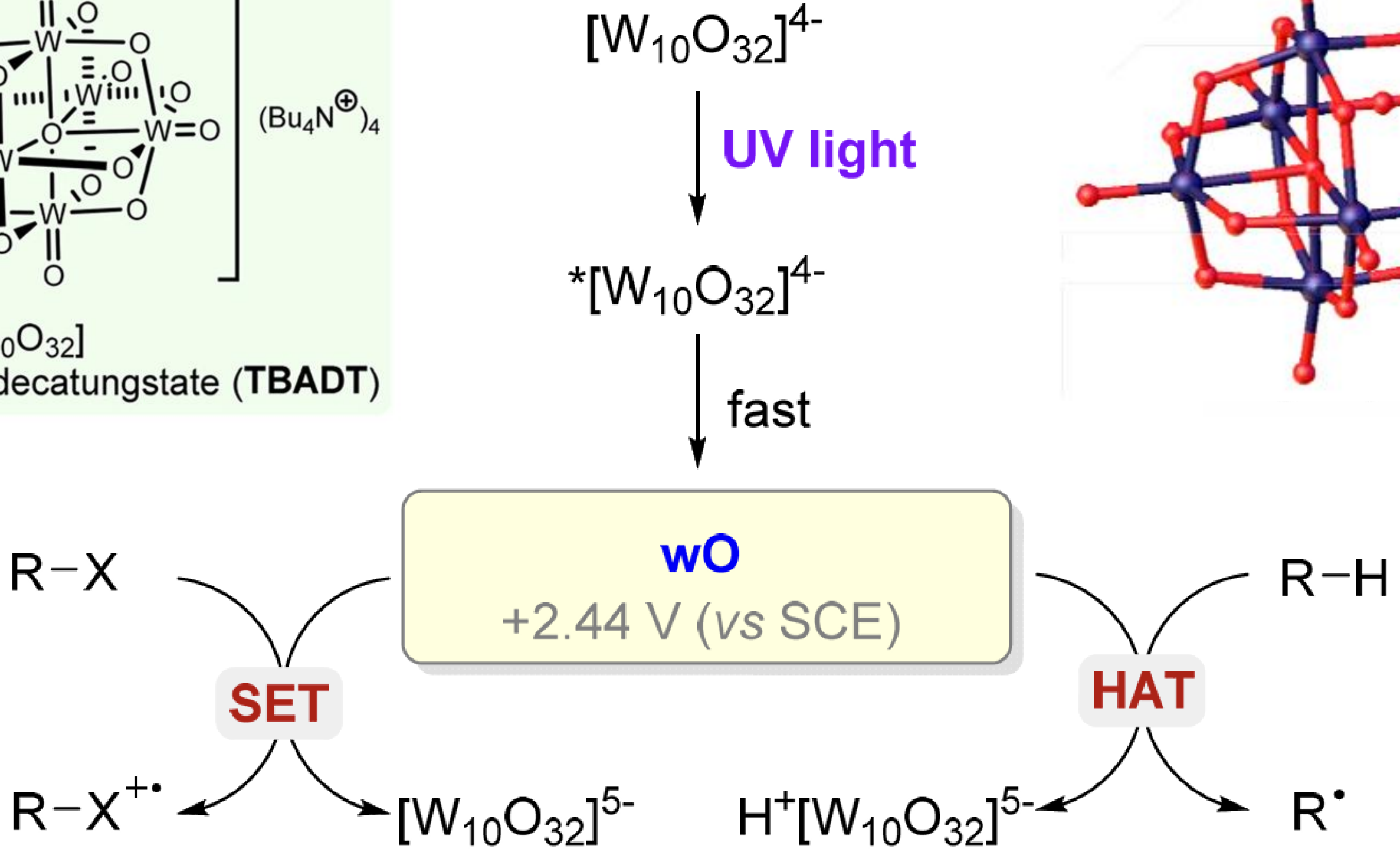
1. ***What is TBADT?***
2. ***Mechanism and Site Selectivity of TBADT Photocatalysis***
3. ***Photochemical Applications of TBADT in Organic Reactions***

TBADT: Tetrabutylammonium Decatungstate $(n\text{-}Bu_4N)_4[W_{10}O_{32}]$



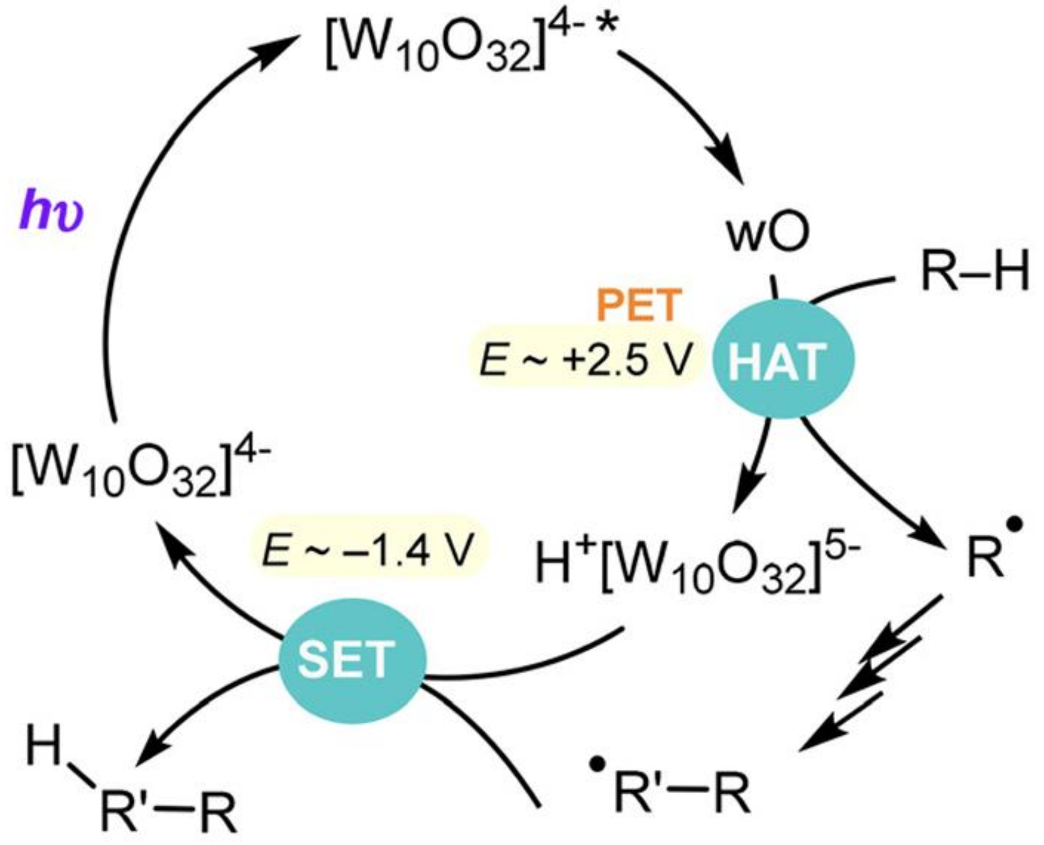
TBADT = $(Bu_4N)_4[W_{10}O_{32}]$
tetrabutylammonium decatungstate (**TBADT**)



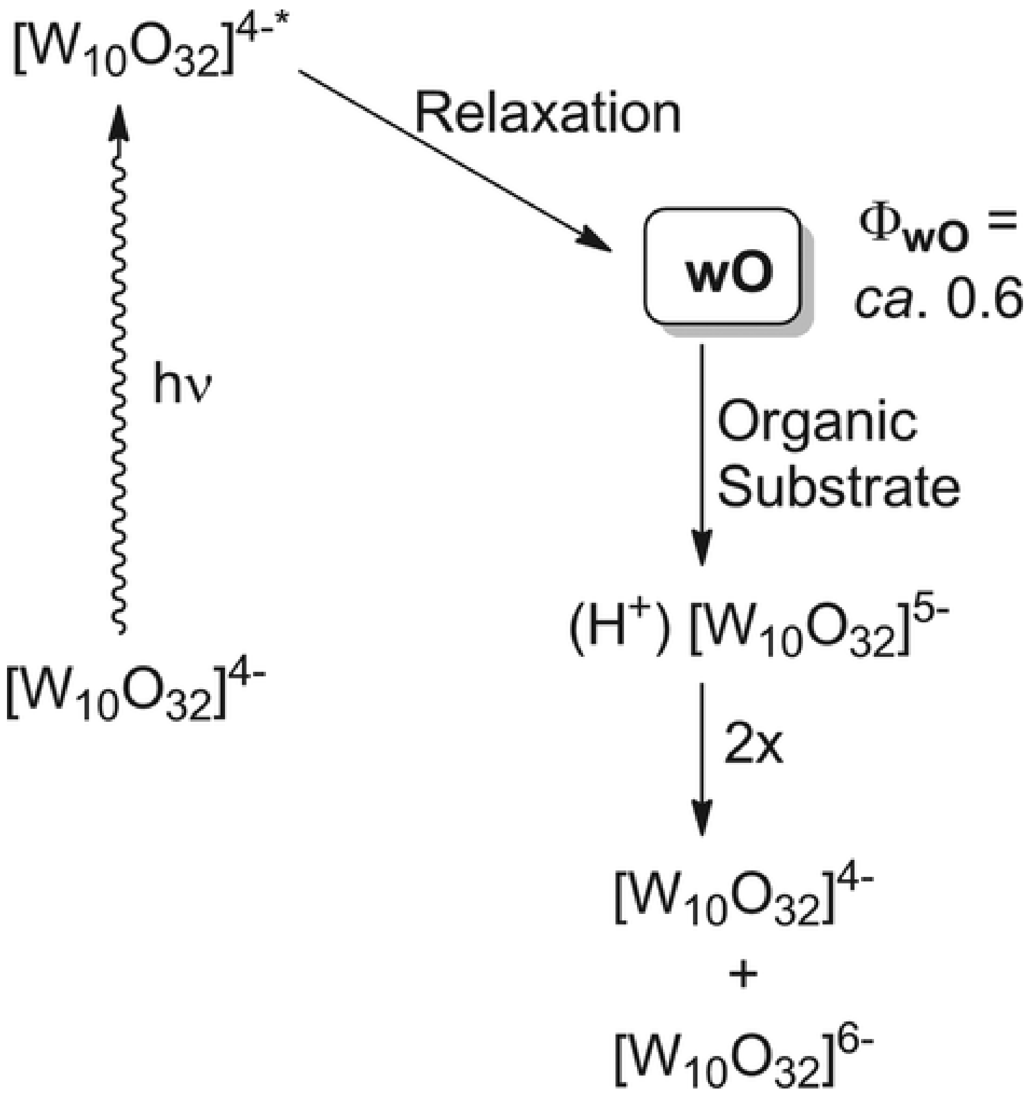


Org. Biomol. Chem., **2024**, *22*, 3799–3842.
Chin. J. Org. Chem. **2020**, *40*, 3620–3632.
Polyhedron, **1986**, *5*, 1267–1271.

Mechanism


[W10O32]4- *
hυ
wO
R–H
PET
E ~ +2.5 V
HAT
[W10O32]4-
E ~ –1.4 V
H+[W10O32]5-
R•
SET
H
R'–R
•R'–R

Mechanism



Acc. Chem. Res., **2016**, *49*, 2232–2242.

Photocatalytic Oxidation and Mechanism

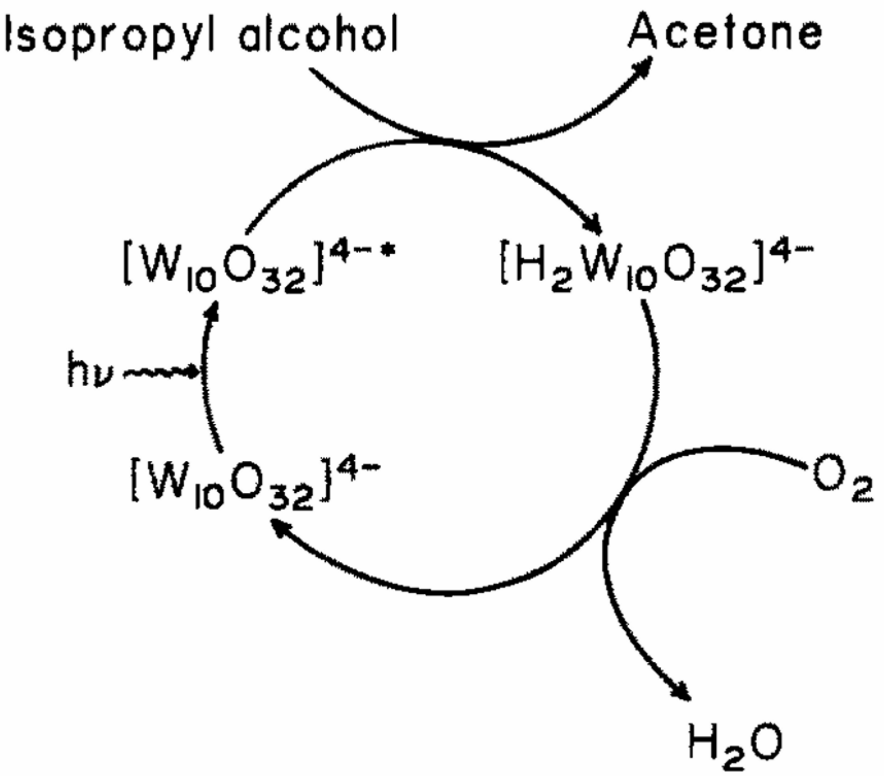


Fig. 5. Schematic diagram of photo-oxidation of isopropyl alcohol by decatungstate.

Polyhedron, **1986**, *5*, 1267–1271.

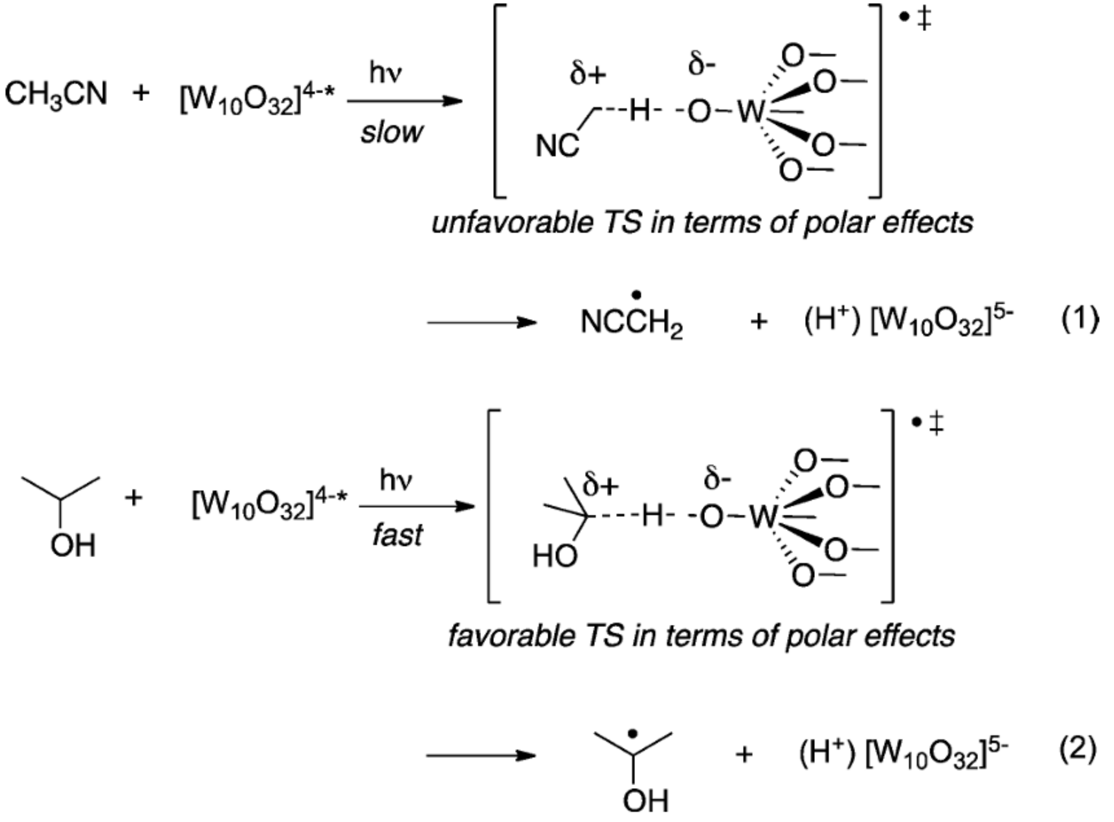
Site-selectivity: Synergistic Control by Polar and Steric Effects

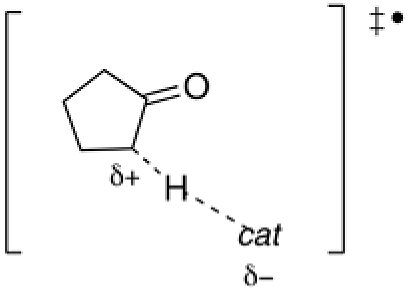
Table 1. Selected Rate Constants ($k_{R\text{-}H}$) for Hydrogen Abstraction from Various Hydrogen Donors by Excited Decatungstate Anion[a]

hydrogen donor	$k_{R\text{-}H}$ ($M^{-1}\cdot s^{-1}$)	references
CH_3CN	6.5×10^4	24a
$CHCl_3$	2.5×10^6	24d
cyclopentane	2.4×10^7	24b
cyclohexane	4×10^7	28
cycloheptane	5.6×10^7	24b
$(CH_3)_2CHOH$	1.0×10^8	28
$PhCH_2OH$	2.8×10^8	29

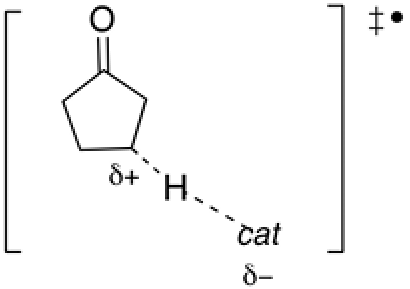
[a]Measured in acetonitrile as solvent. Temperatures of the experiment were not reported with the exception of cyclohexane (298 K).

Scheme 3. Postulated S_H2 TSs Exerted by Polar Effects with Decatungstate Anion



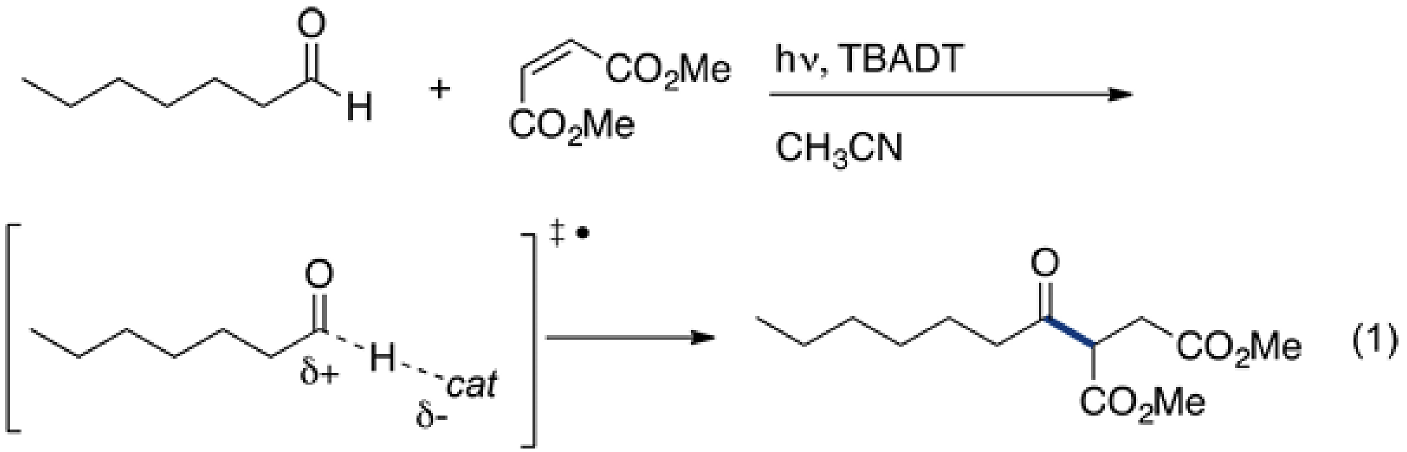


polarity-mismatched TS

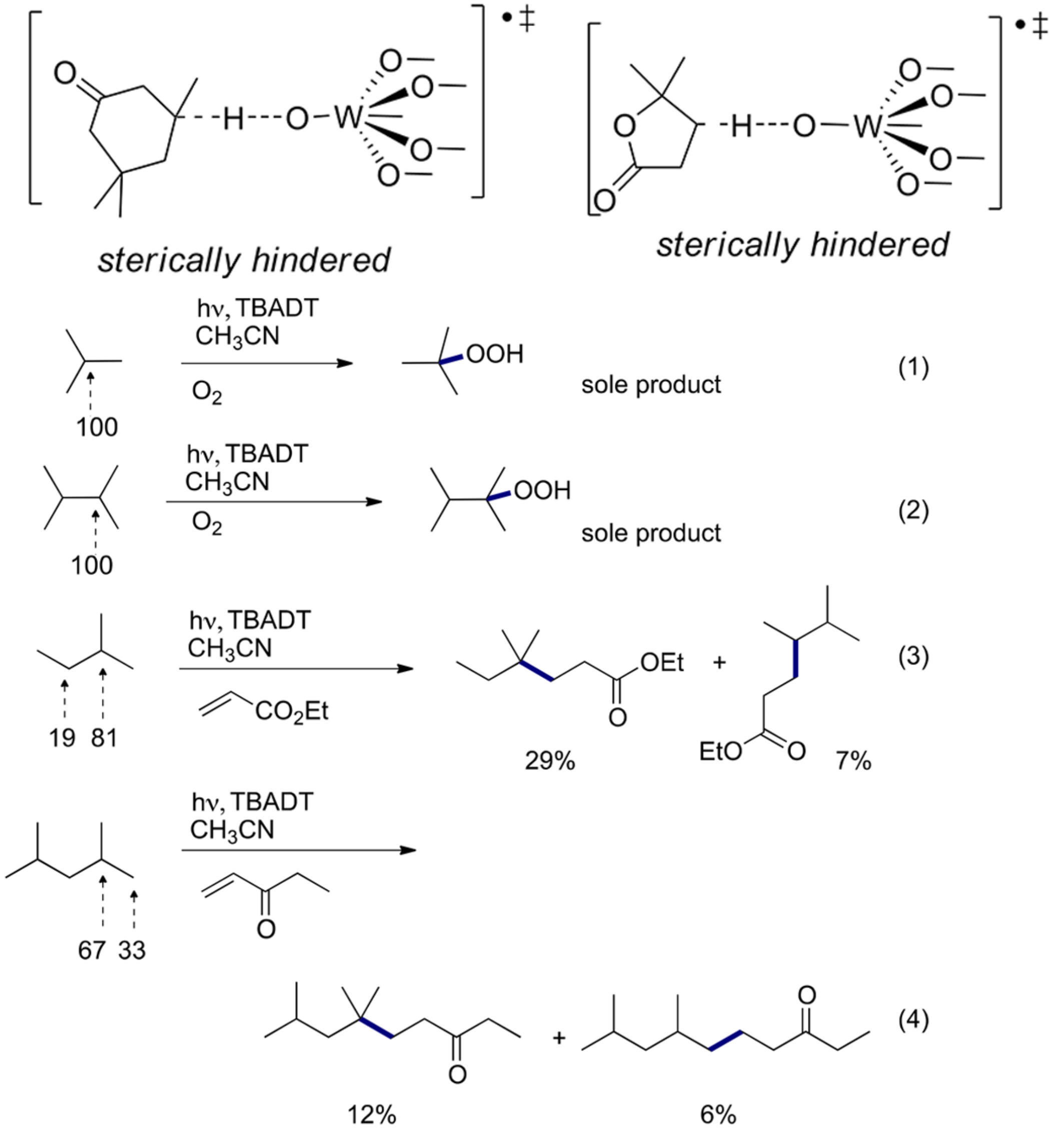


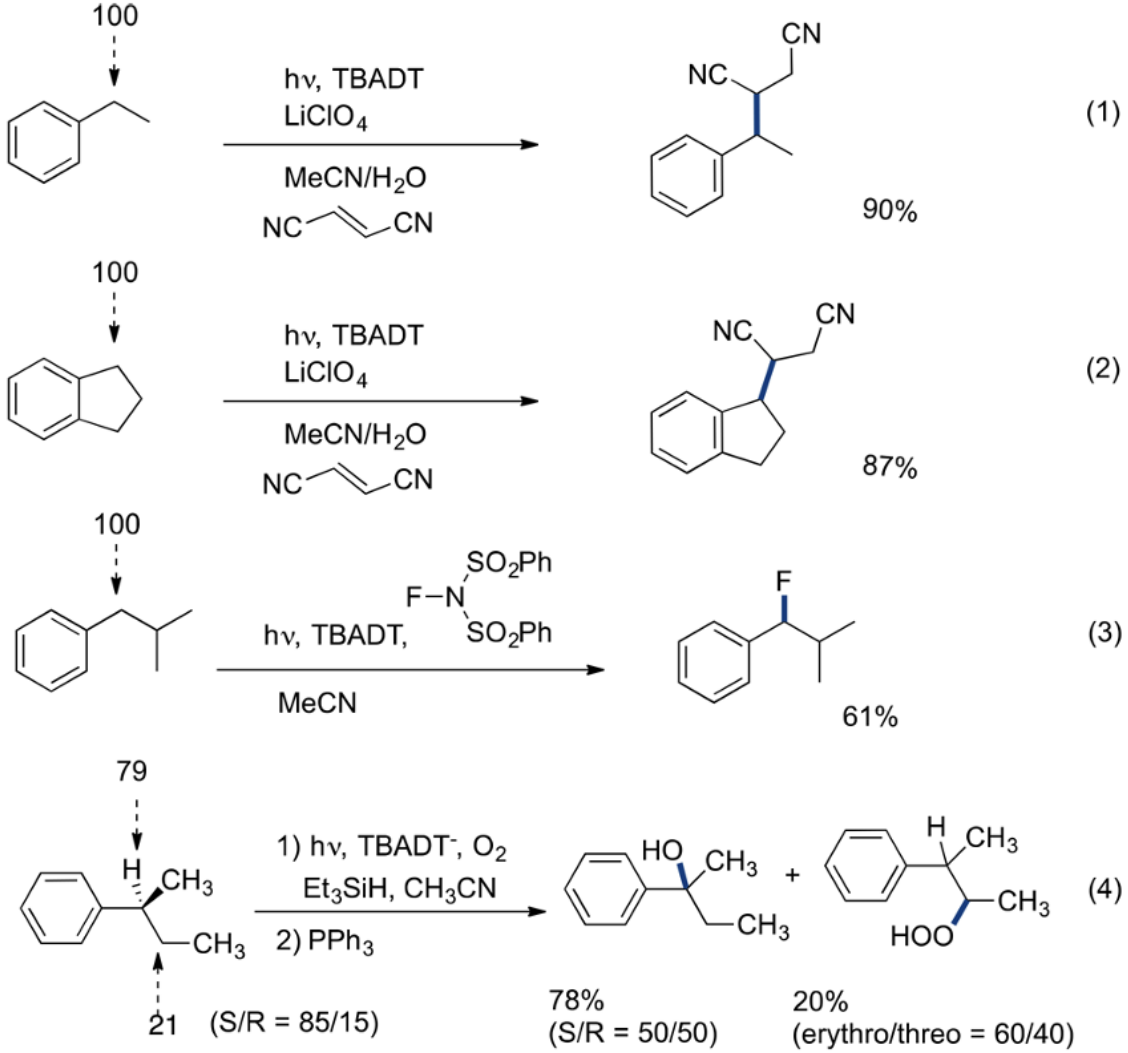
polarity-matched TS

Site-selectivity: Synergistic Control by Polar and Steric Effects

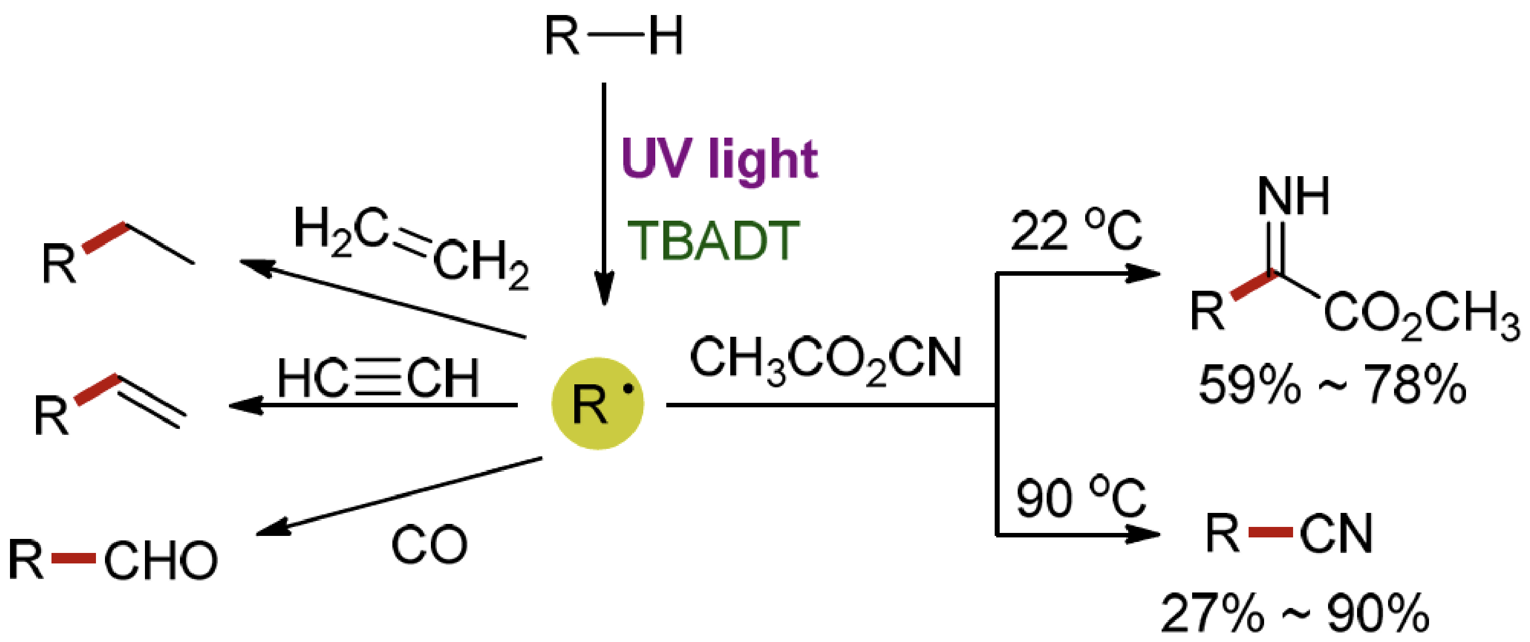


Site-selectivity: Synergistic Control by Polar and Steric Effects



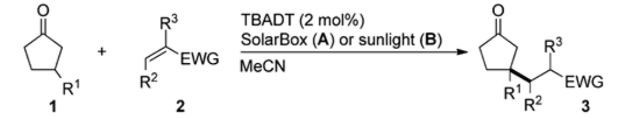


Applications in Organic Reactions

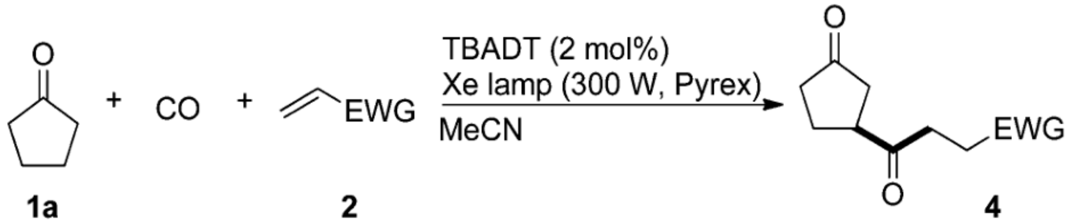


J. Am. Chem. Soc. **1993**, *115*, 12212.
Synlett **1995**, 127.
J. Am. Chem. Soc. **1995**, *117*, 4704.
Chem. Commun. **1998**, 2467.

β-Alkylation and Acylation of Cyclopentanones



Entry	1	Alkene 2	Method[a]	Product 3	Yield[b] (%)
1	1a	2a	A	3a	61
2[c]	1a	2b	A	3b	41
3	1a	2b	B	3b	58
4	1a	2c	A	3c	46
5[d]	1a	2d	A	3d	51
6	1a	2e	A	3e	61 (d.r. 1.1/1)[e]
7	1a	2f	B	3f	70
8	1a	2g	B	3g	73 (d.r. 1/1)[f]



Entry	Alkene 2	Product 4	Yield[b] (%)
1	2a	4a	58
2	2b	4b	50
3	2f	4c	61

Chem. Sci., **2014**, *5*, 2893–2898.

hydro-carbamoylation,-acylation,-alkylation, and-silylation of styrenes

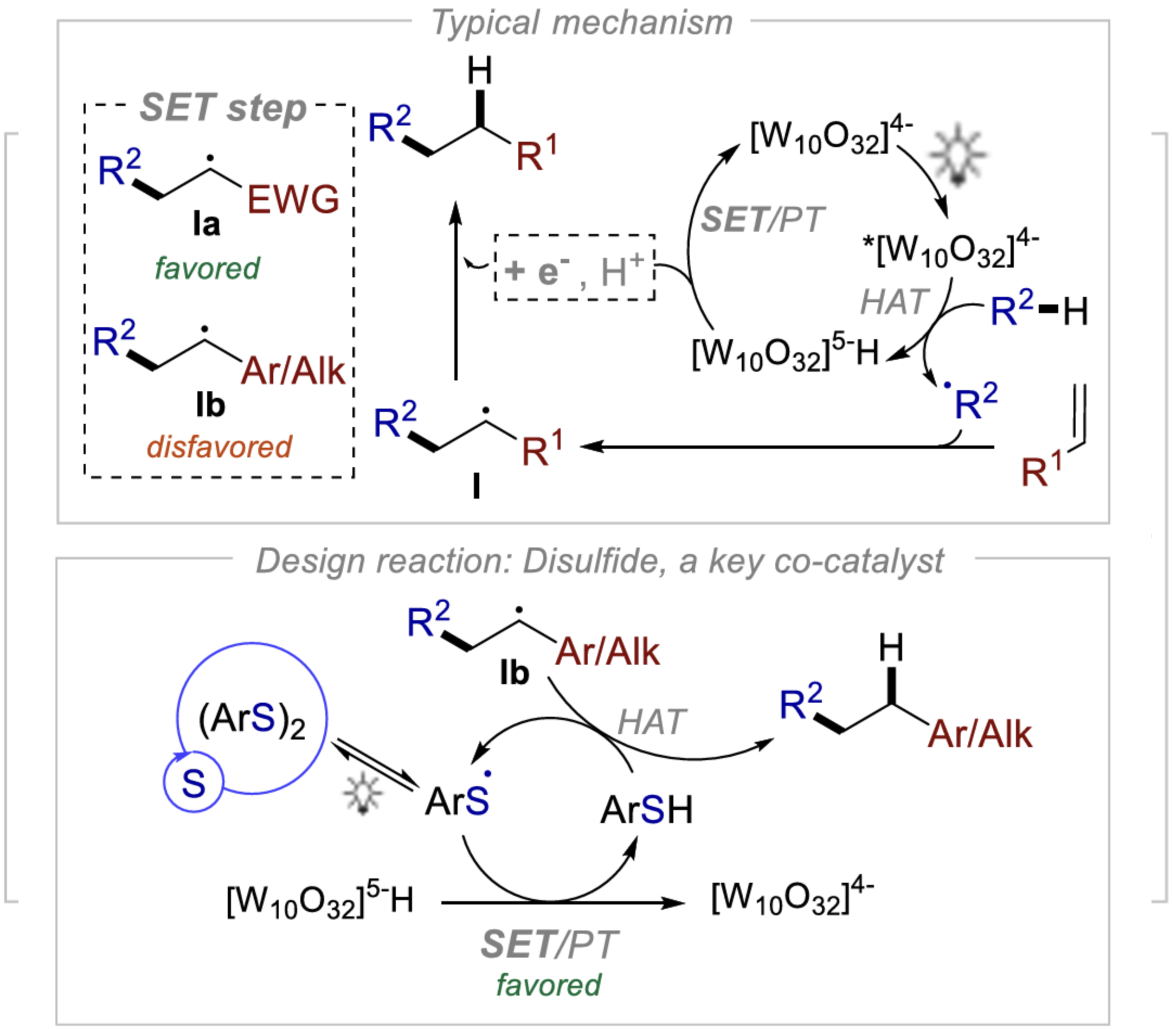
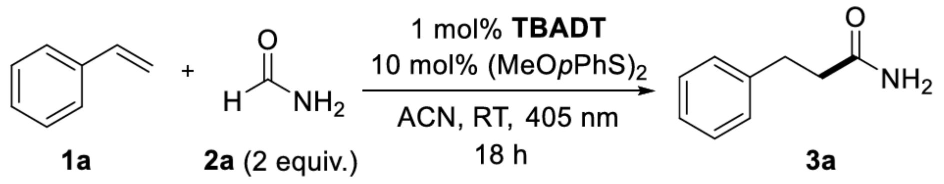


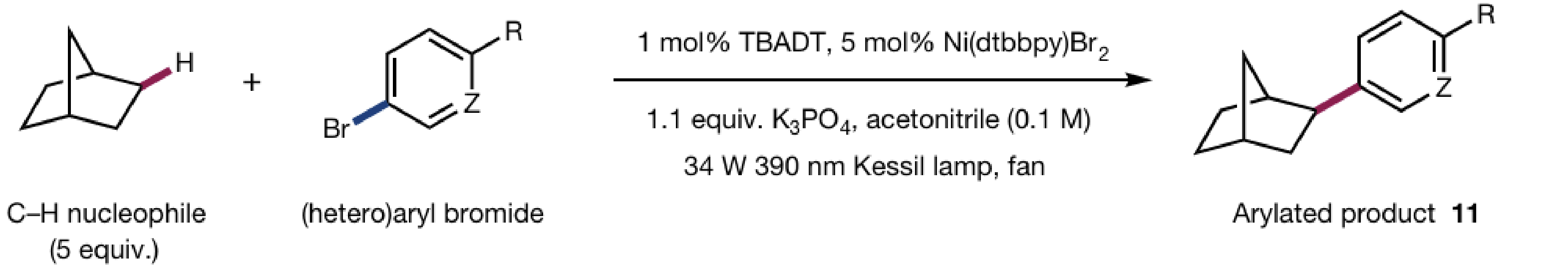
Table 1. Optimization of the Hydrocarbamoylation Reaction[a]



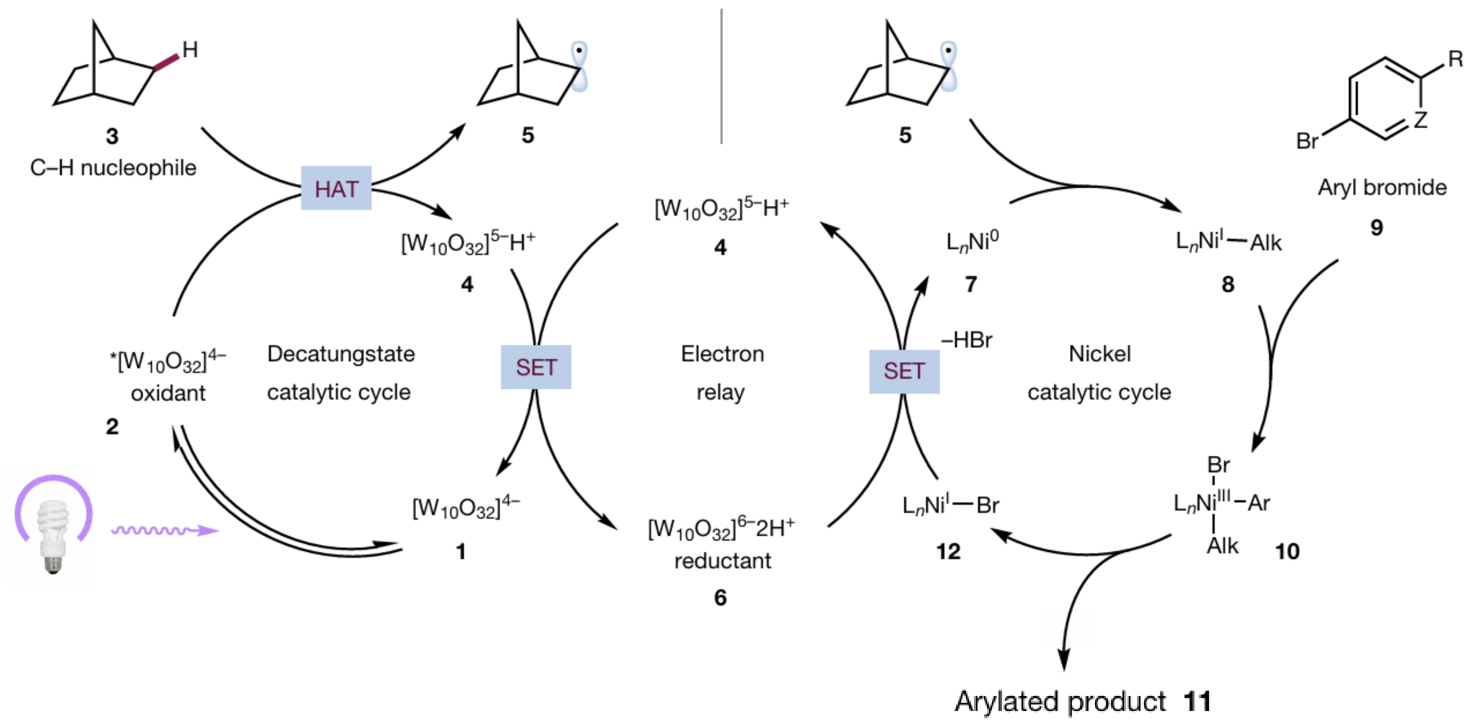
Entry	Deviation from standard conditions	Yield **3a** (%)[b]
1	w/o $(MeOpPhS)_2$	N.R.
2	$(PhS)_2$ instead of $(MeOpPhS)_2$	57
3	PhSH[c] instead of $(MeOpPhS)_2$	42[d]
4	none	75 (59)[e]
5	w/o light	N.R.
6	w/o TBADT	N.R.
7	365 nm instead of 405 nm	70
8	3 mol % TBADT	70
9	**1a** (2 equiv), **2a** (1 equiv)	49

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.6 mmol) in ACN (0.6 mL). [b]Yields were determined by ^{1}H NMR using trichloroethylene as an internal standard. [c]20 mol %. [d]Around 10% thiol−ene product was detected. [e]Isolated yield. TBADT = Tetra-*n*-butylammonium decatungstate. N.R. = no reaction, the starting materials were fully recovered.

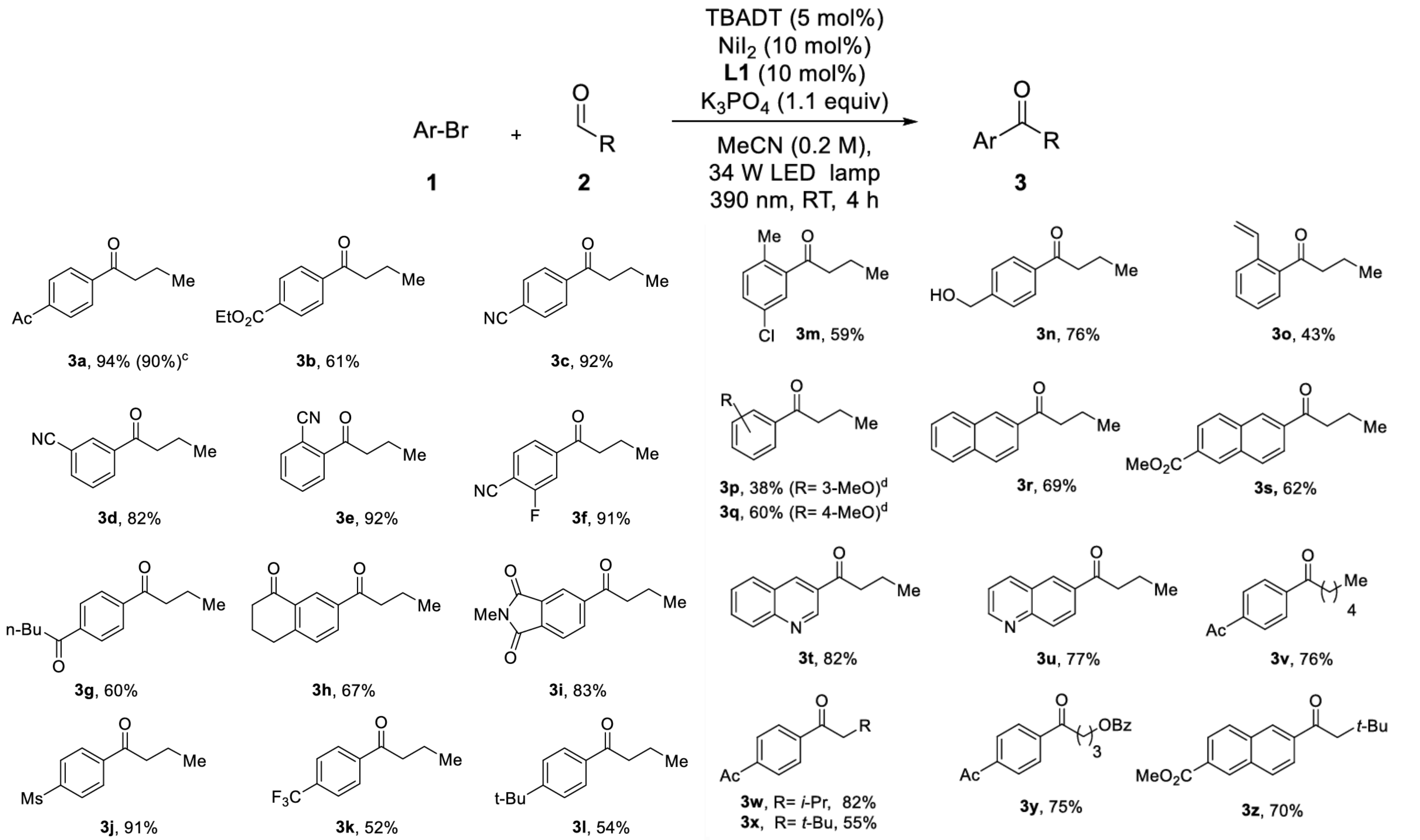
Direct Arylation of Strong Aliphatic C–H Bonds



- Light-enabled
- Mild conditions
- Broad scope

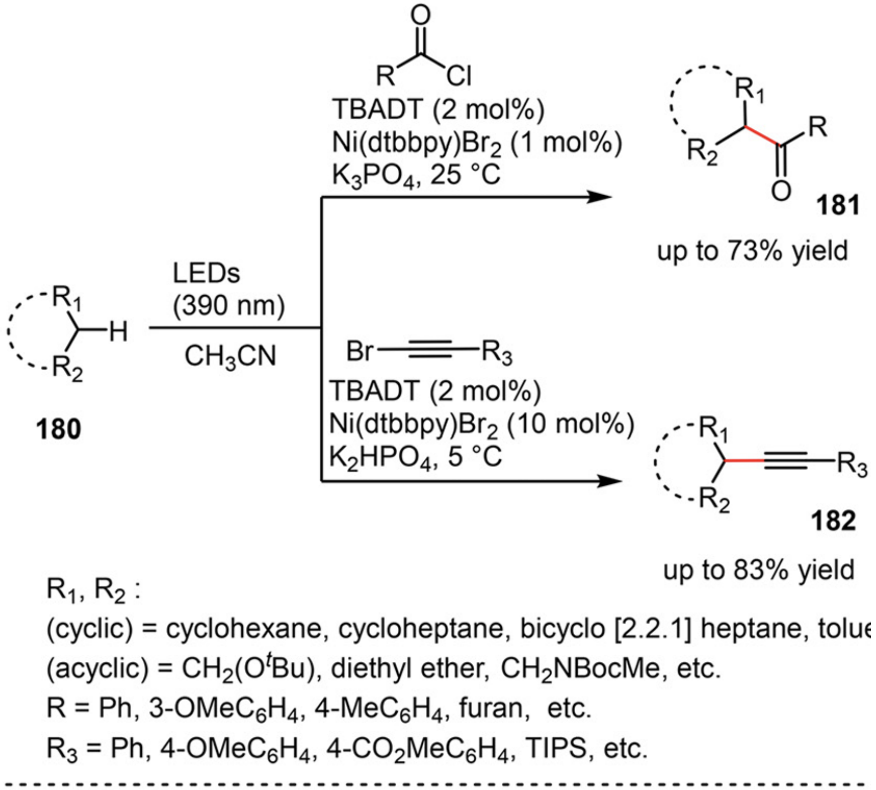


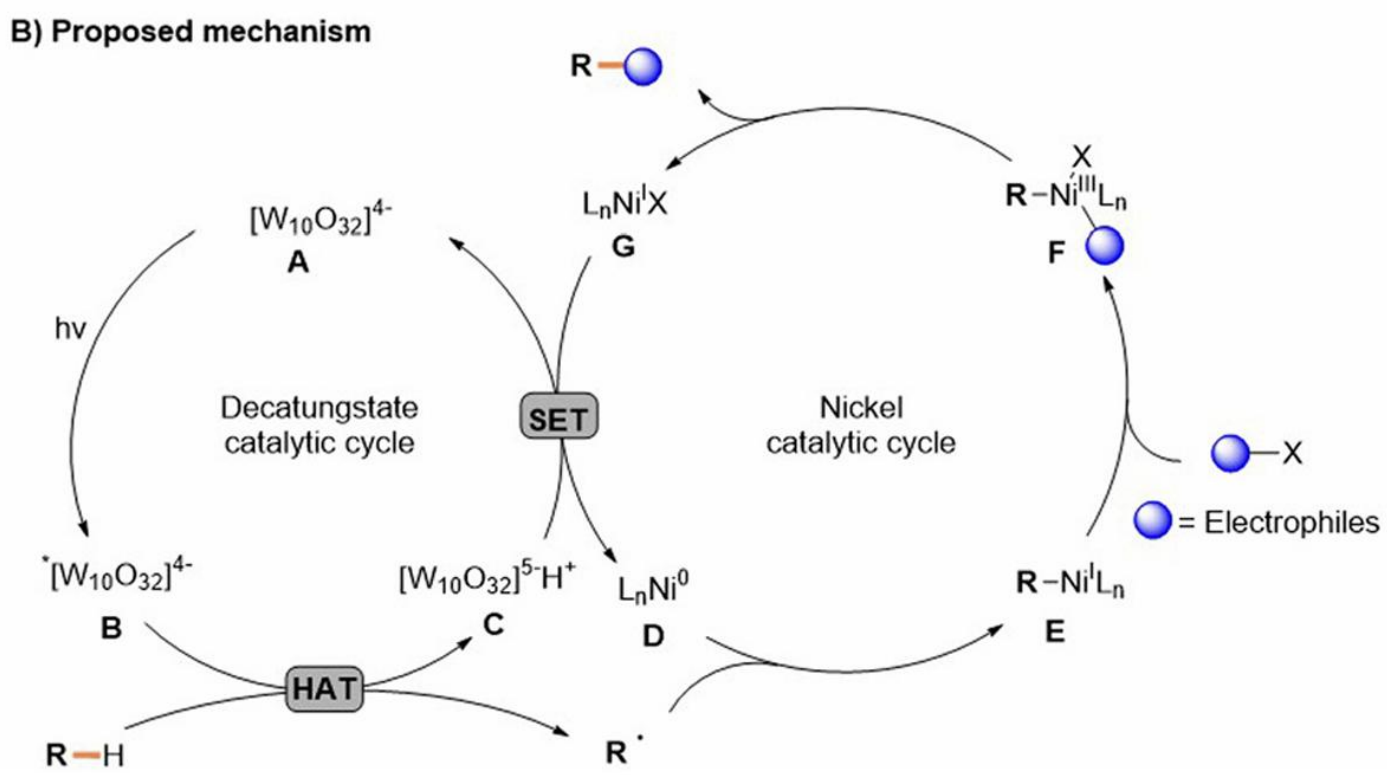
Acylation of Aryl Halides and α-Bromo Acetates



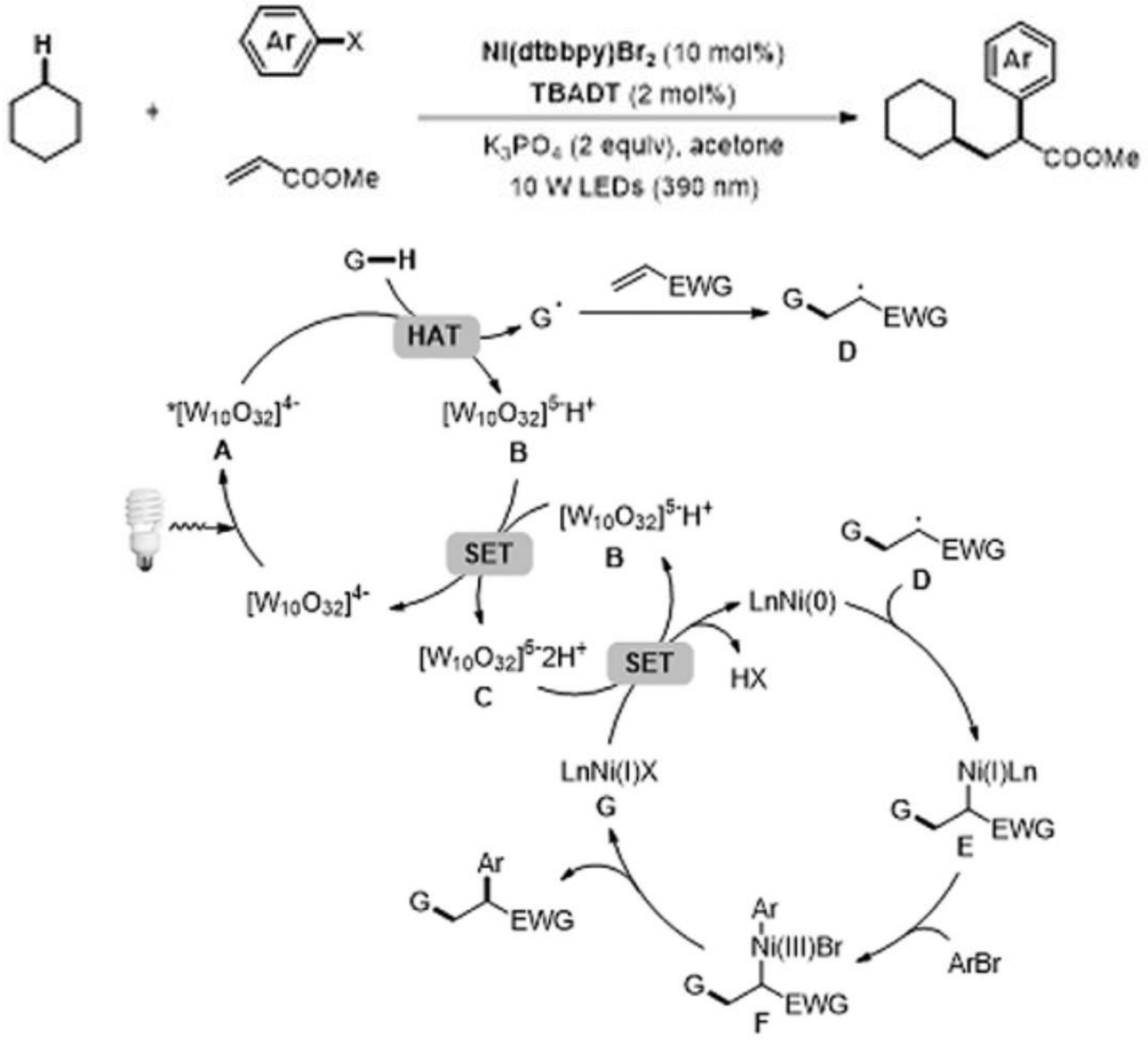
Org. Lett., **2020**, *22*, 3875–3878.

Direct acylation and alkynylation

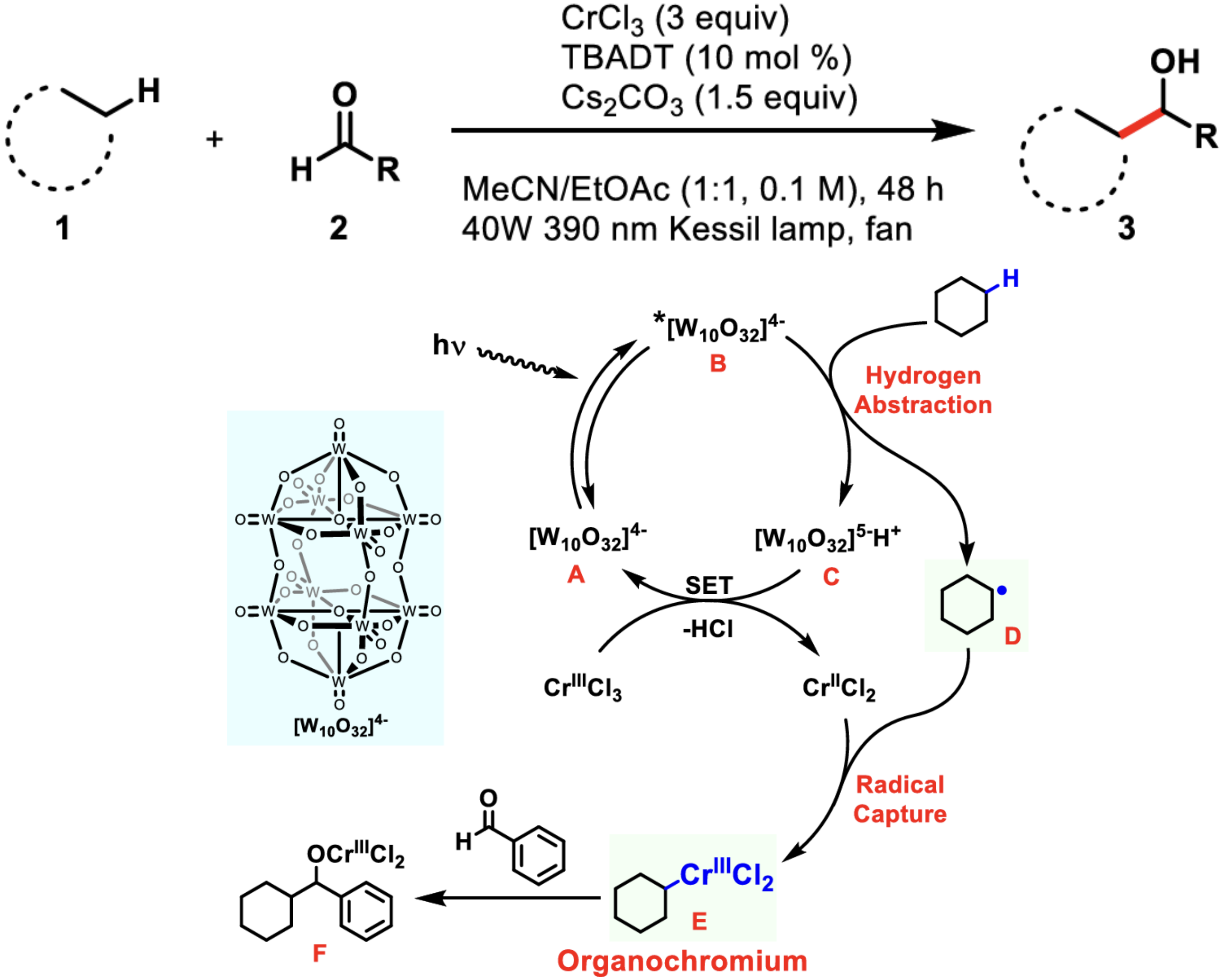




Three-Component Alkene Difunctionalization

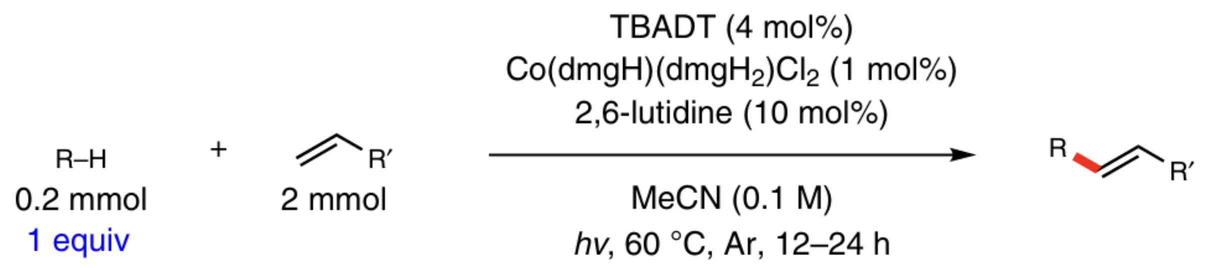


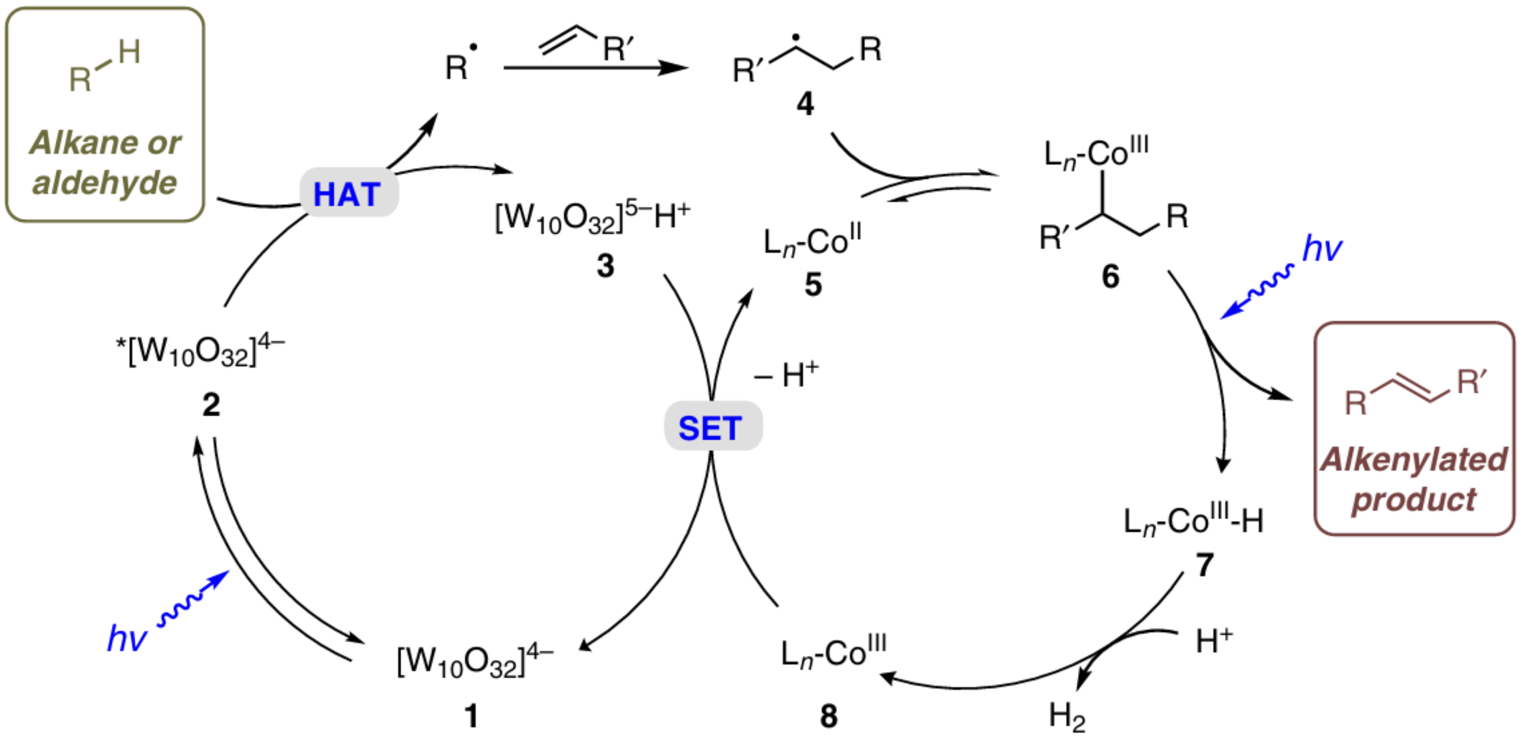
Coupling Reaction between Aldehydes and Non-Activated Hydrocarbons



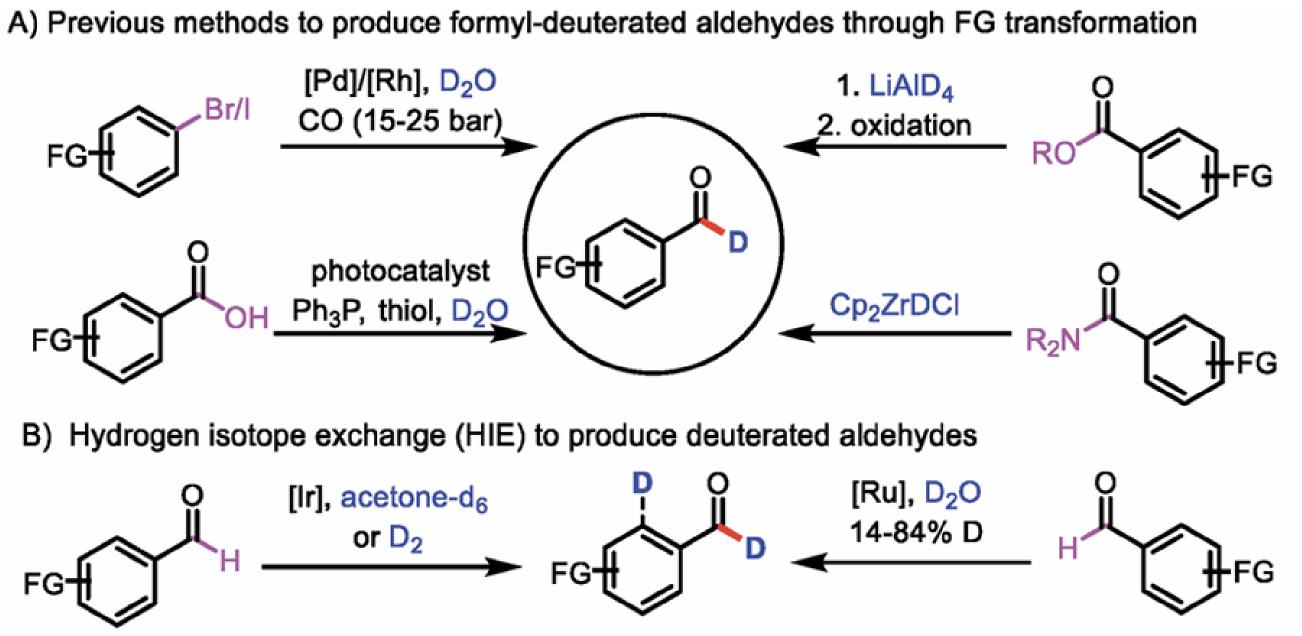
Org. Lett., **2020**, *22*, 1199–1203.

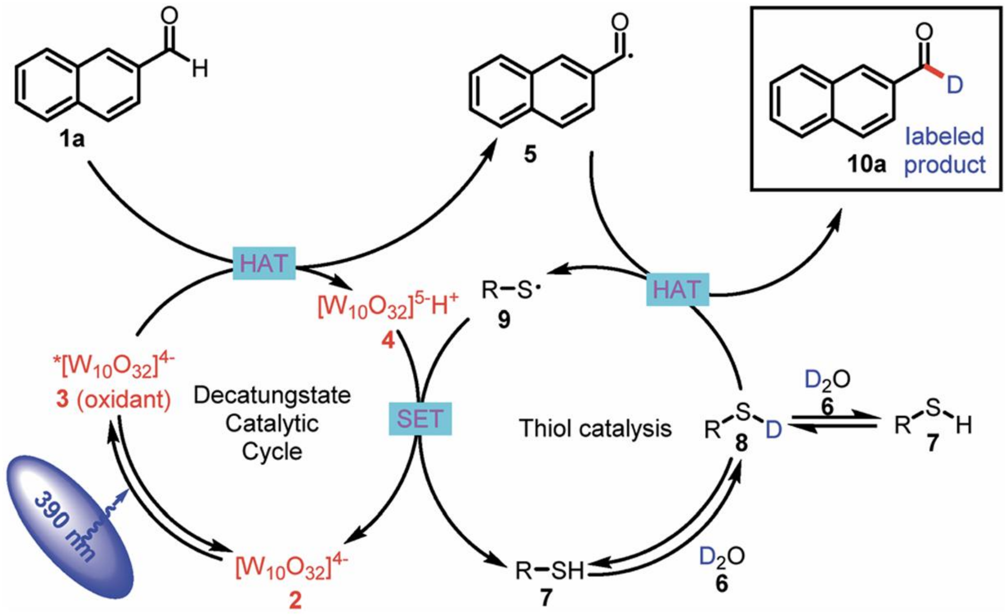
site-selective alkenylation of alkanes and aldehydes



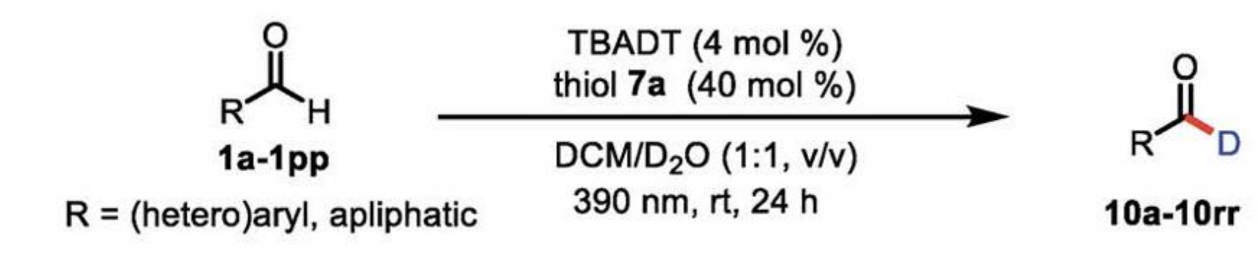


direct hydrogen isotope exchange



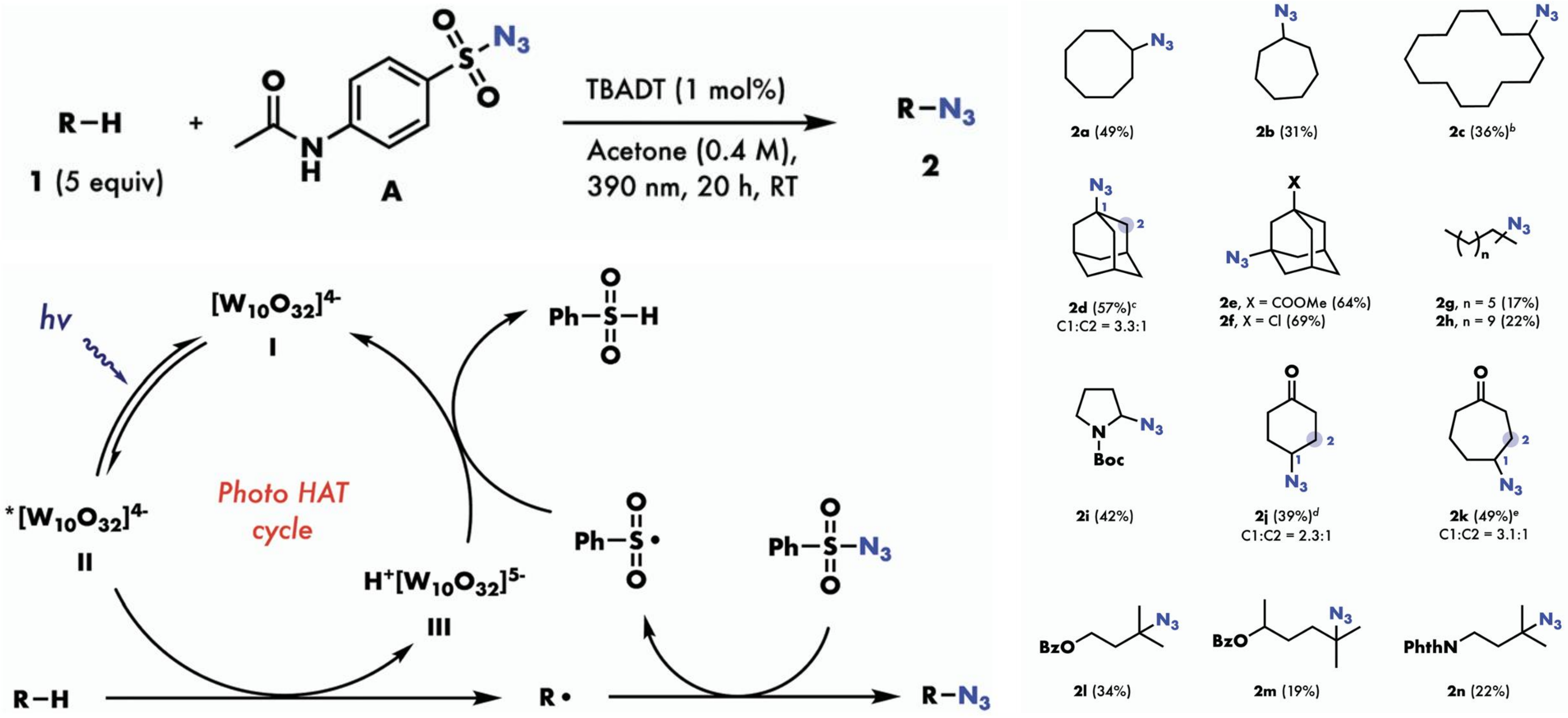


Scheme 2 Proposed mechanism.

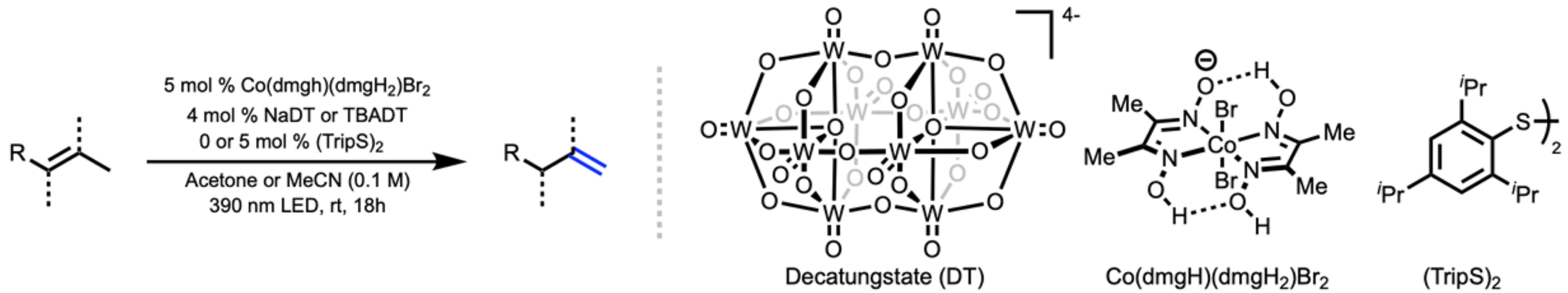


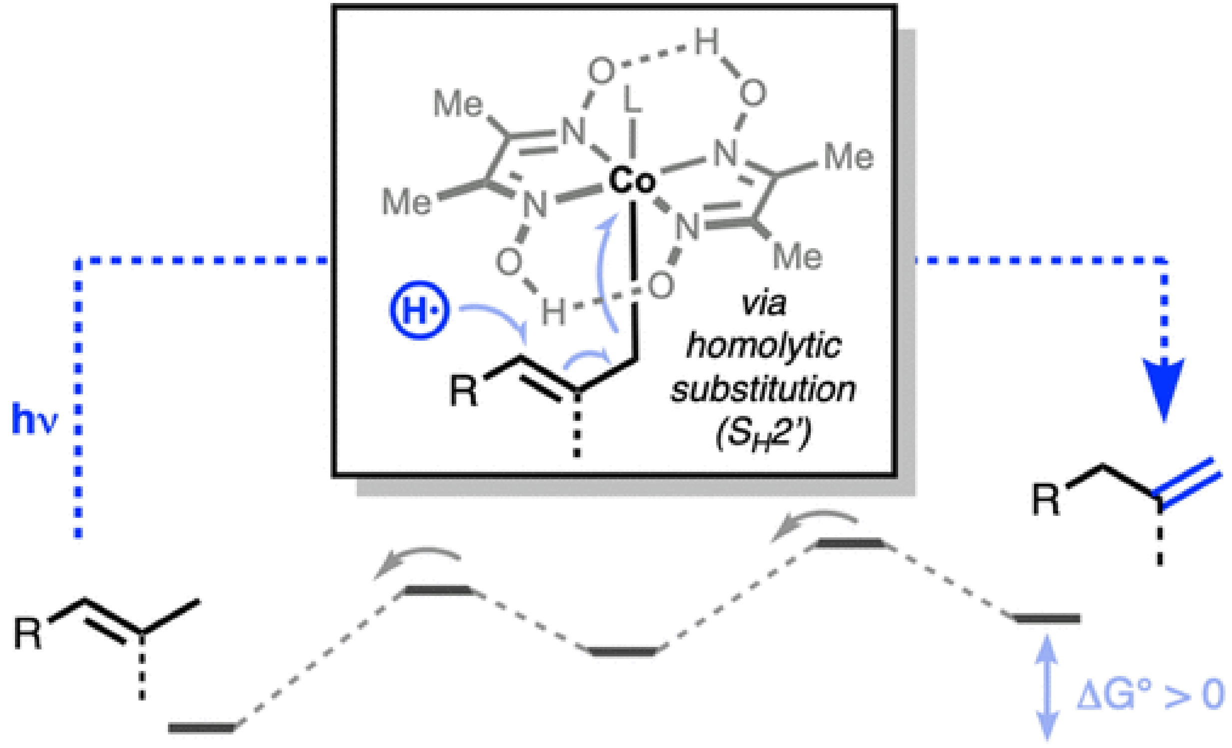
Chem. Sci. **2020**, *11*, 1026.

C(sp³)–H azidation

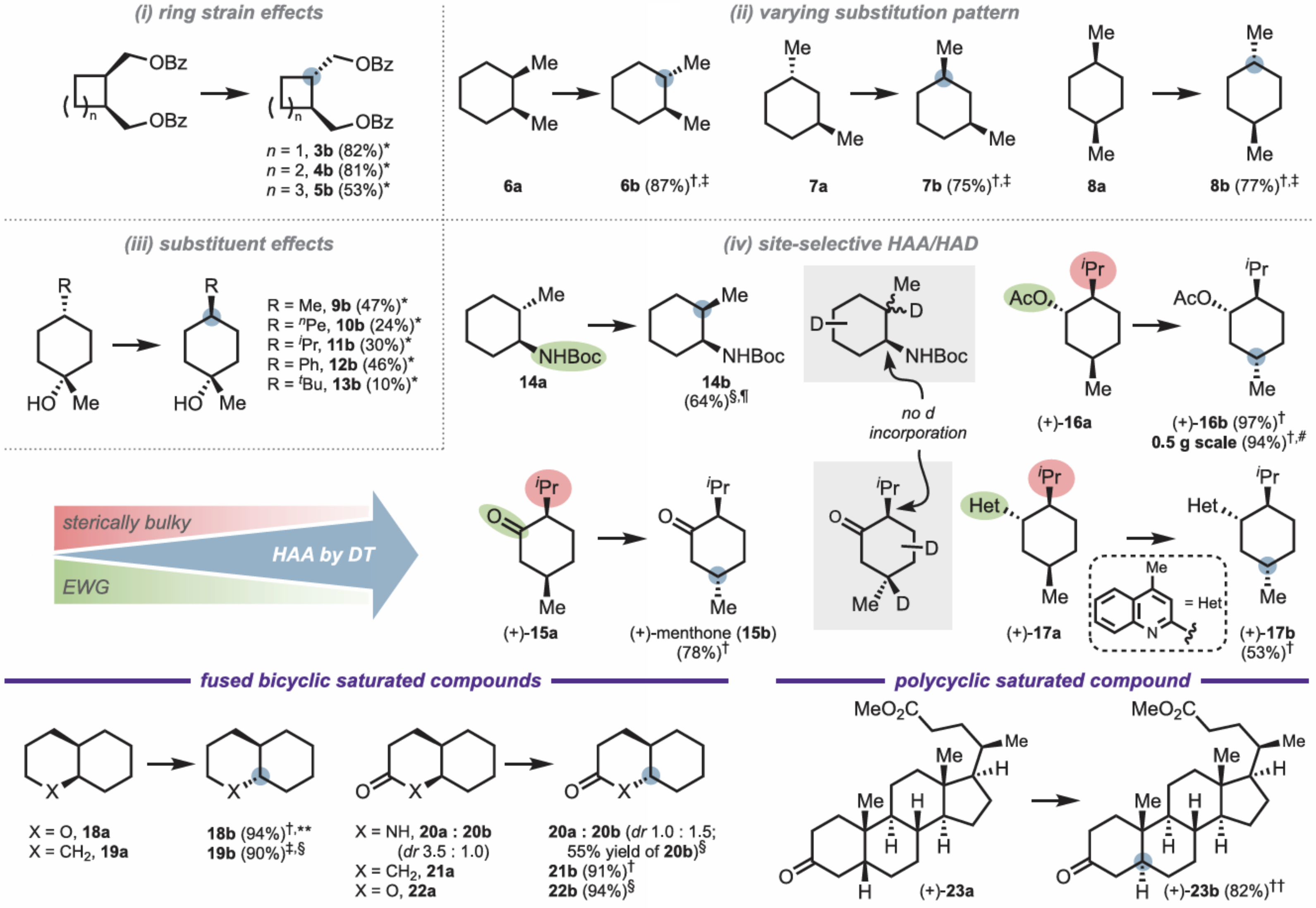


Positional Alkene Isomerization

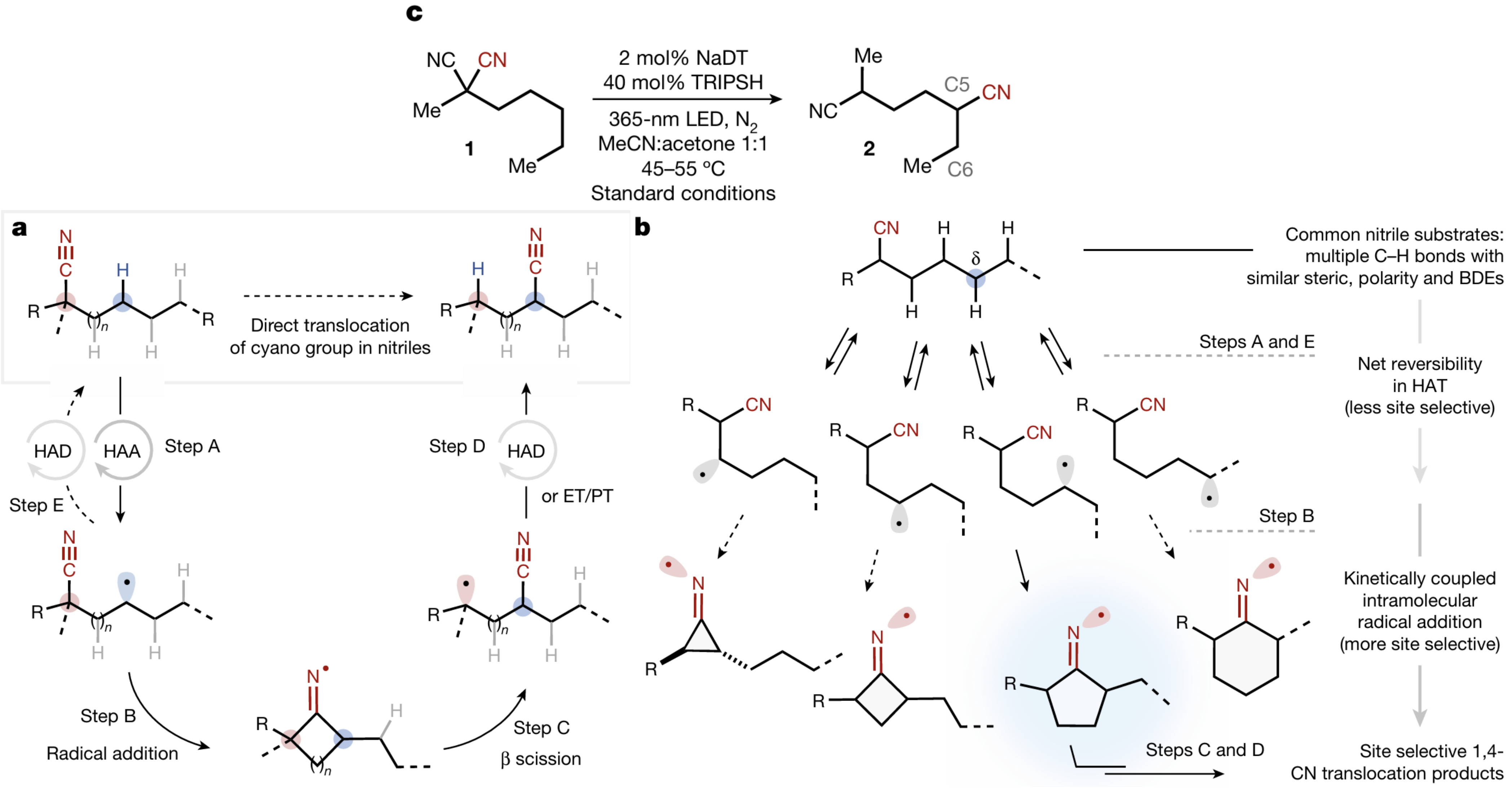




Isomerization of Stereocenters

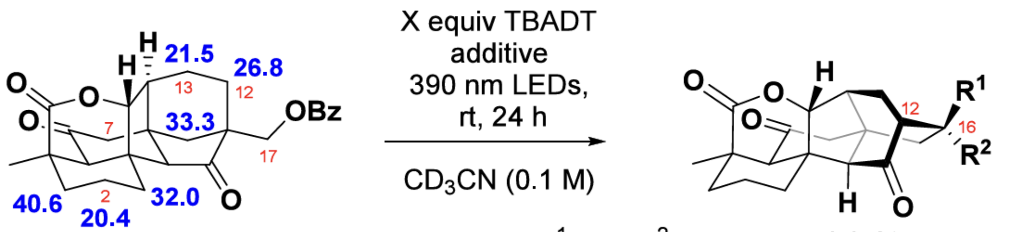


Functional-group translocation of cyano groups



Nature, **2023**, *620*, 1007–1012.

Application in total synthesis



(+)-15
δ (13C NMR)

R^1 = H, R^2 = CH_2OBz: **(+)-12a** (X-ray)
R^1 = CH_2OBz, R^2 = H: **(+)-12b** (X-ray)

entry	X	additive	conversion (%)[a]	yield (%)[b] 12a	yield (%)[b] 12b
1	0.05	–	61	13	0
2	0.2	–	58	24	0
3	0.5	–	70	27	0
4	0.2	0.4 equiv TFA	28	<10	0
5	0.2	0.4 equiv **T1**	73	30	16
6	0.2	0.4 equiv **T1**[c]	66	32	12
7	0.2	0.4 equiv **T1**[d]	63	30	8
8	0.2	0.4 equiv **T1**[e]	88	23	10
9	0.2	0.4 equiv **T1**[f]	89	39	38

[a]Irradiation was performed with a 12 W, 390 nm LED lamp. [b]NMR yield using 1,3,5-trimethoxybenzene as the internal standard; [**15**] = 0.1 M (0.011 mmol). [c]The reaction was performed at 60 C. [d]CD_3CN/acetone = 1:1. [e]NaDT instead of TBADT was used. [f]100 W LED was used.

J. Am. Chem. Soc. **2025**, *147*, 8132−8137.