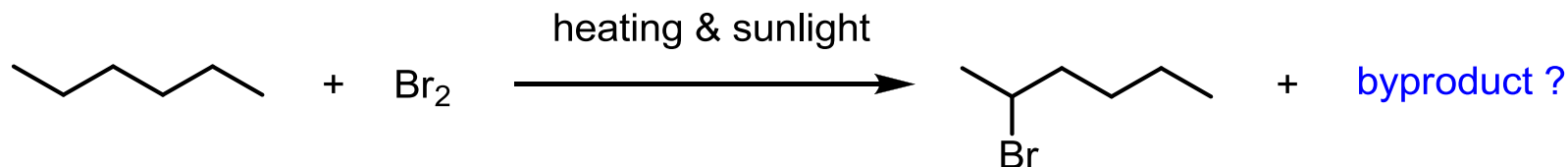


Li_2MnO_3 as Catalyst for Bromination of Alkanes

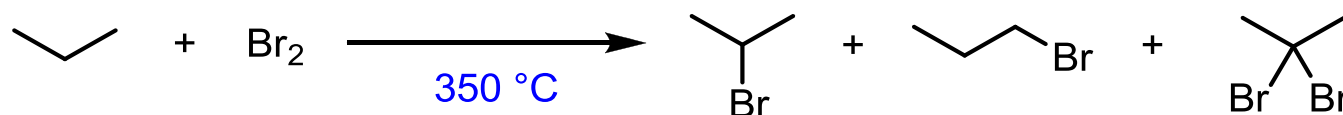
Reported Examples

1) Photoreaction



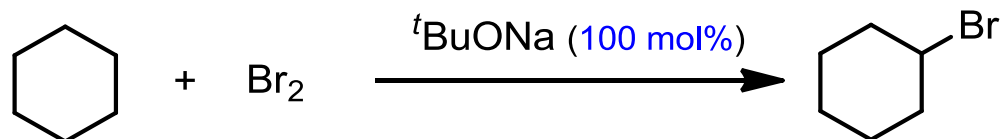
Wanklyn; Erlenmeyer, *J. Chem. Soc.* **1863**, 16, 234.

2) Thermal reaction

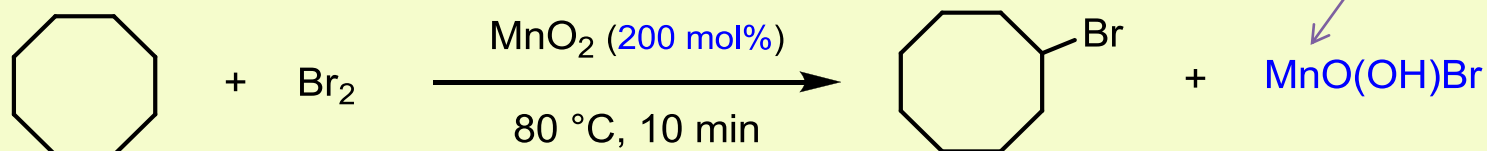


U.S. Pat. Appl. Publ. 2004006246.

3) Base-promoted reaction



Montoro, R; Wirth, T. *Synthesis.* **2005**, 1473.

4) MnO₂-promoted reaction

Jiang, X.; Shen, M.; Tang, Y.; Li, C. *Tetrahedron Lett.* **2005**, 46, 487.

Structure change of MnO_2



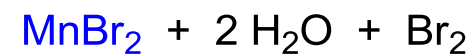
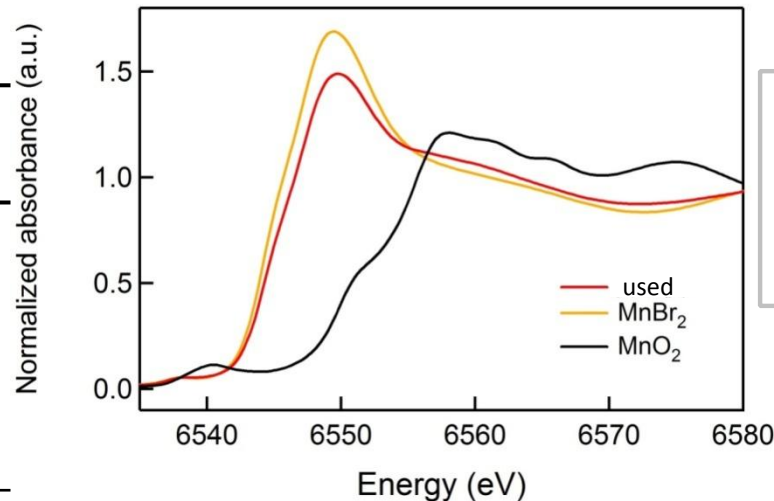
Fresh (black)



Used (gray, hydroscopic)

XANES analysis

sample	oxidation state
MnO_2 (fresh)	4
MnO_2 (used)	2
MnBr_2	2

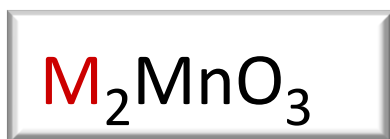


low durability to HBr

Mn oxide with high durability to HBr

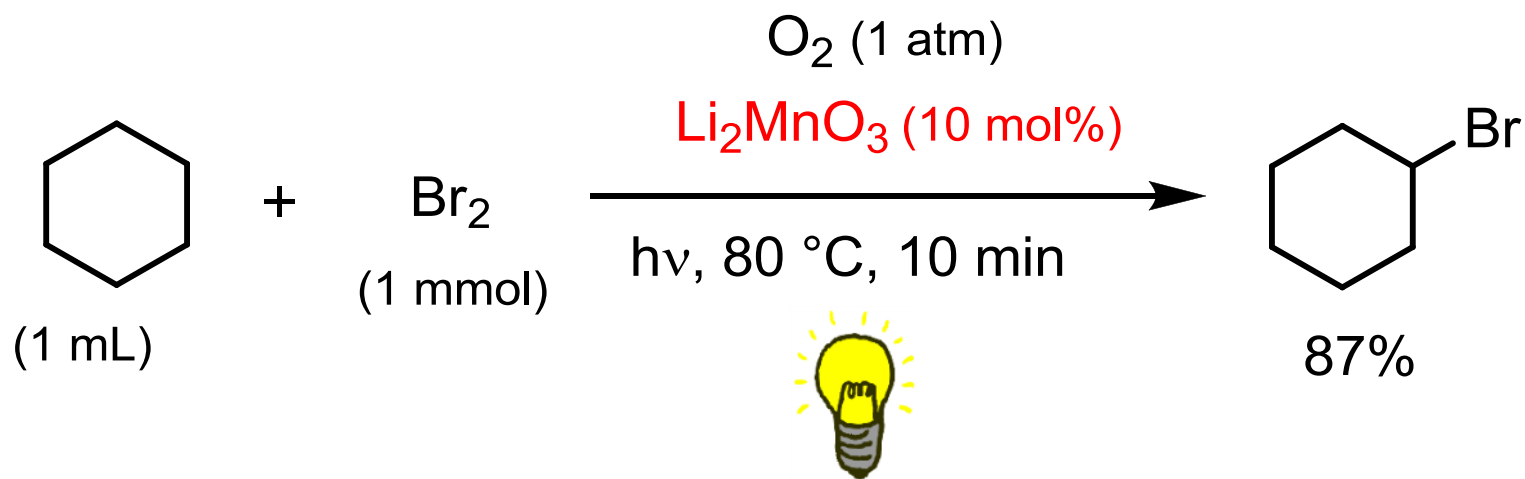


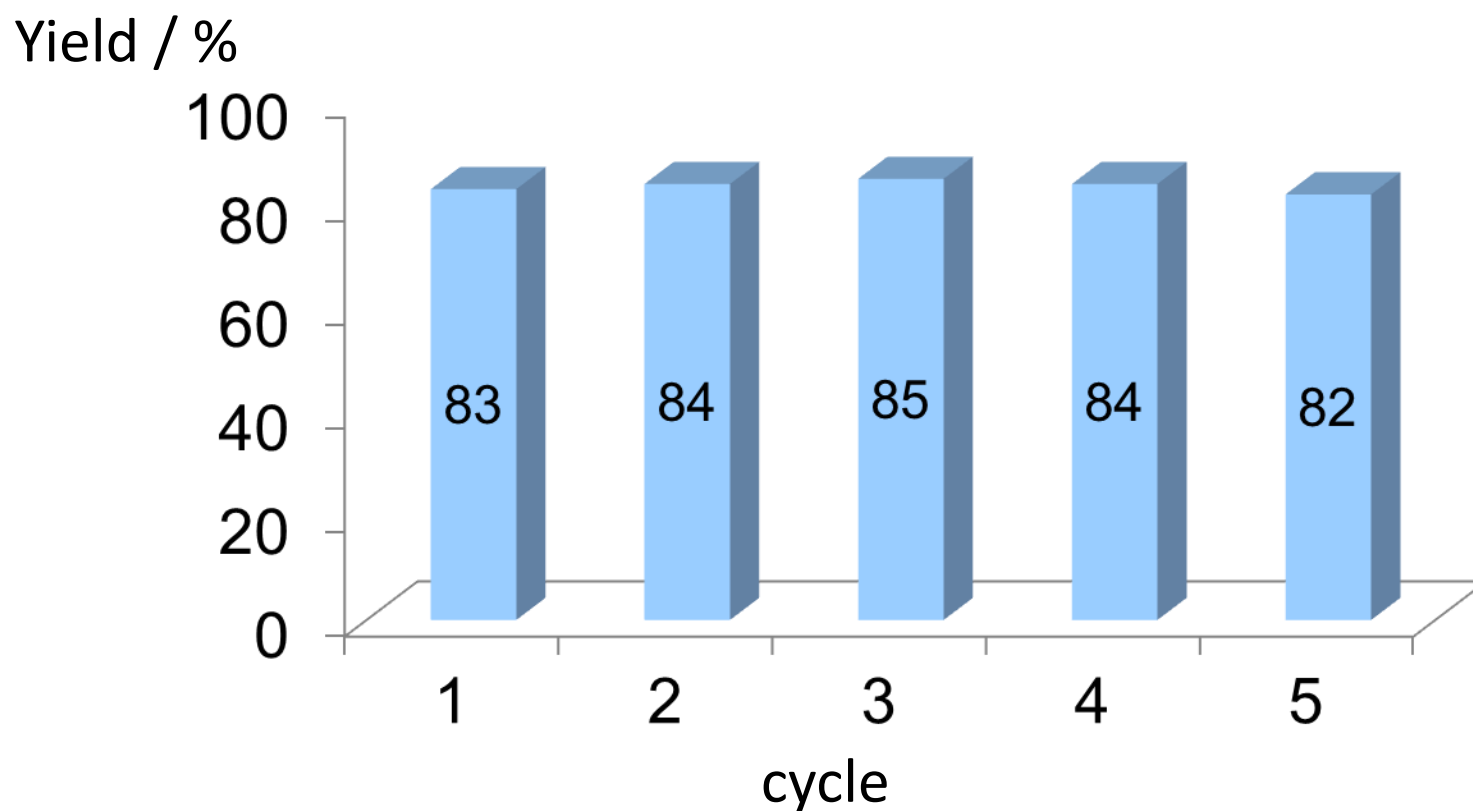
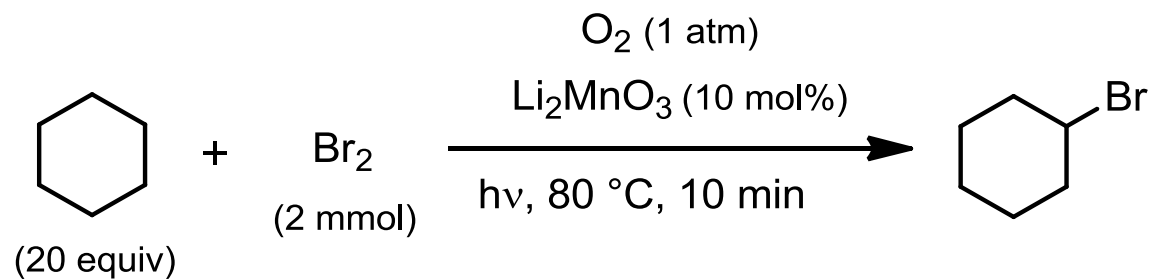
Composite Mn oxide



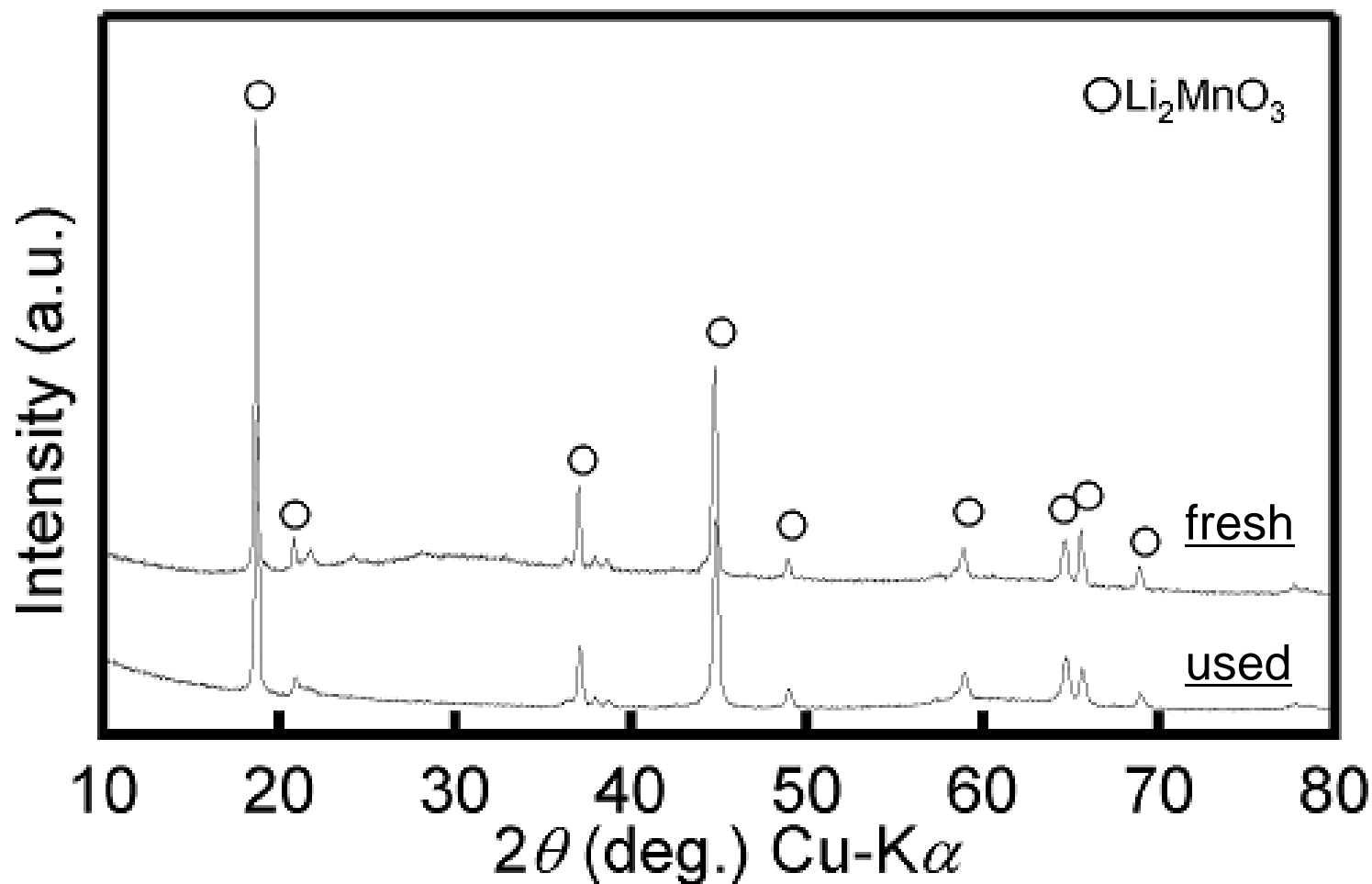
- chemically stable (even in H_2SO_4)
- oxidation state of Mn is 4 (same as MnO_2)

Promising catalyst





Recyclable for 5 cycles.

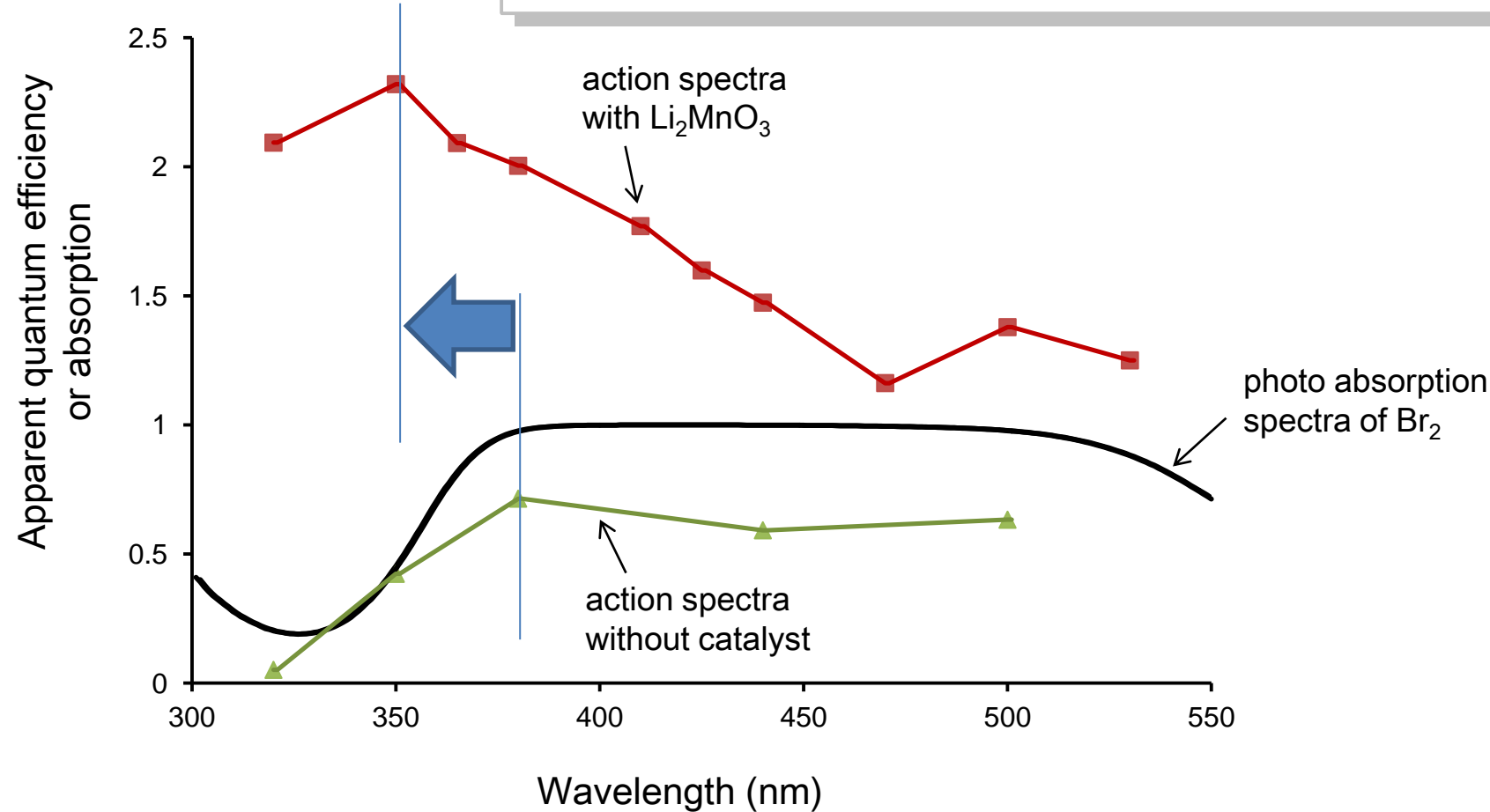
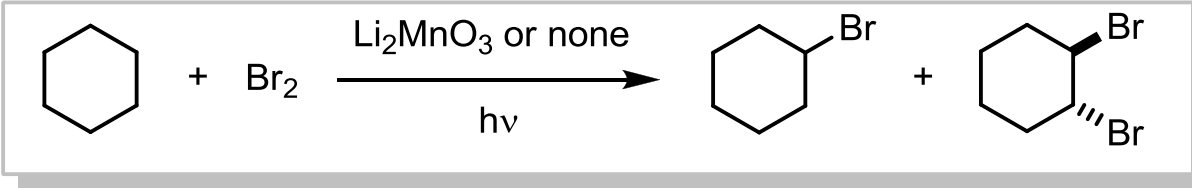


fresh



used

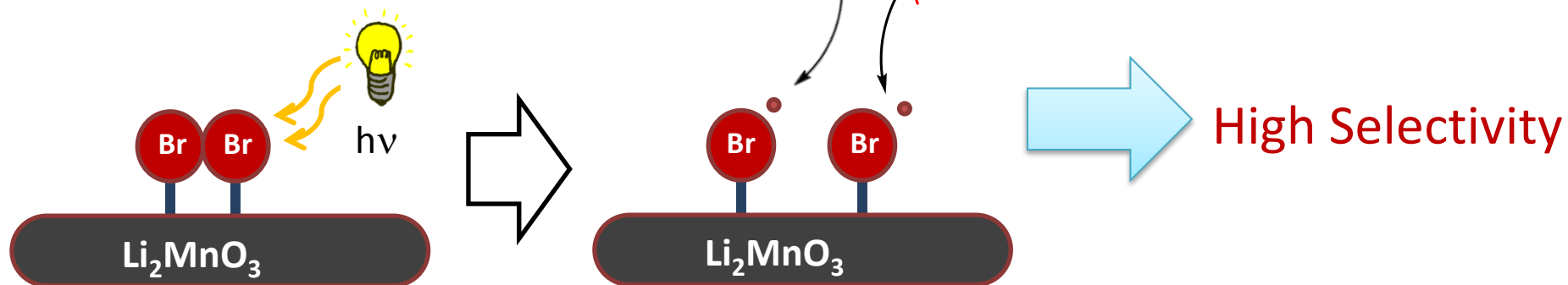
Crystal structure did not change before and after the reaction



Shorter wavelength shift

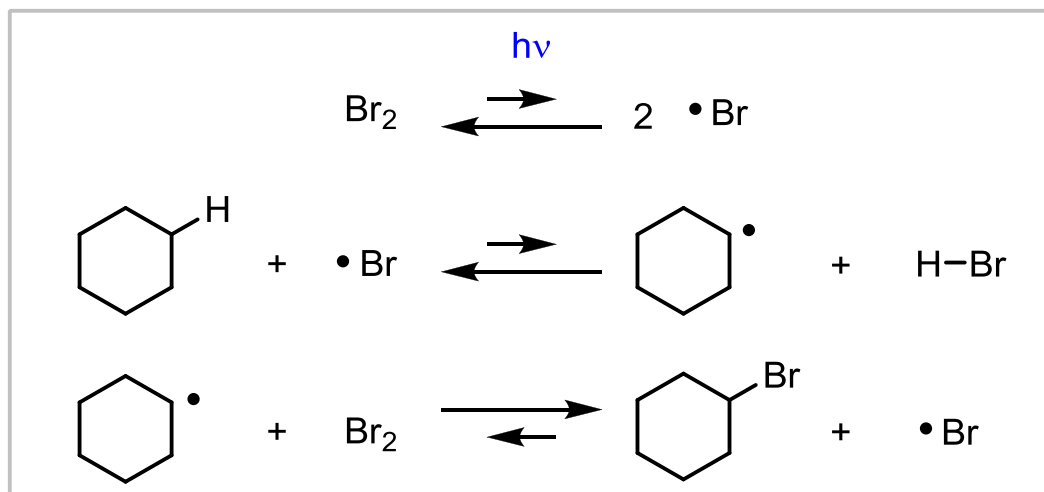
The adsorbed Br_2 absorbed light.

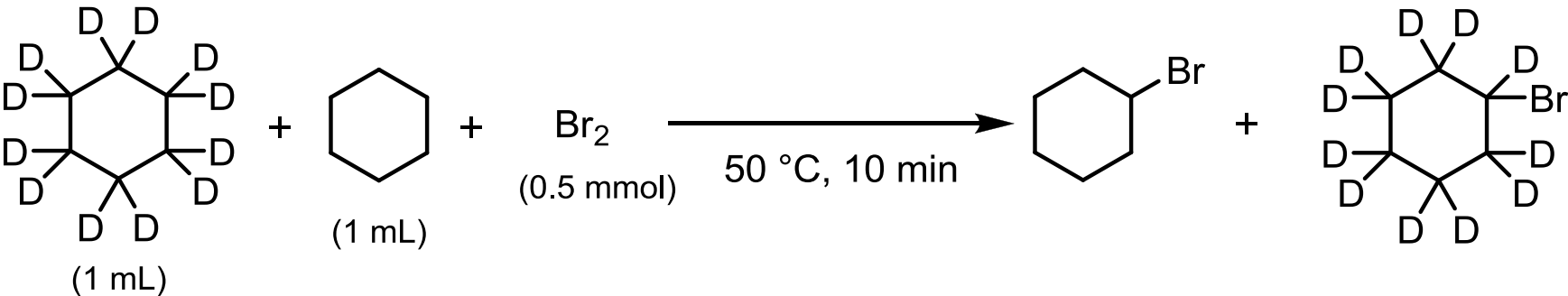
Ref. *J. Am. Chem. Soc.* **2003**, 125, 12907.



Quantum efficiency exceeded "1"

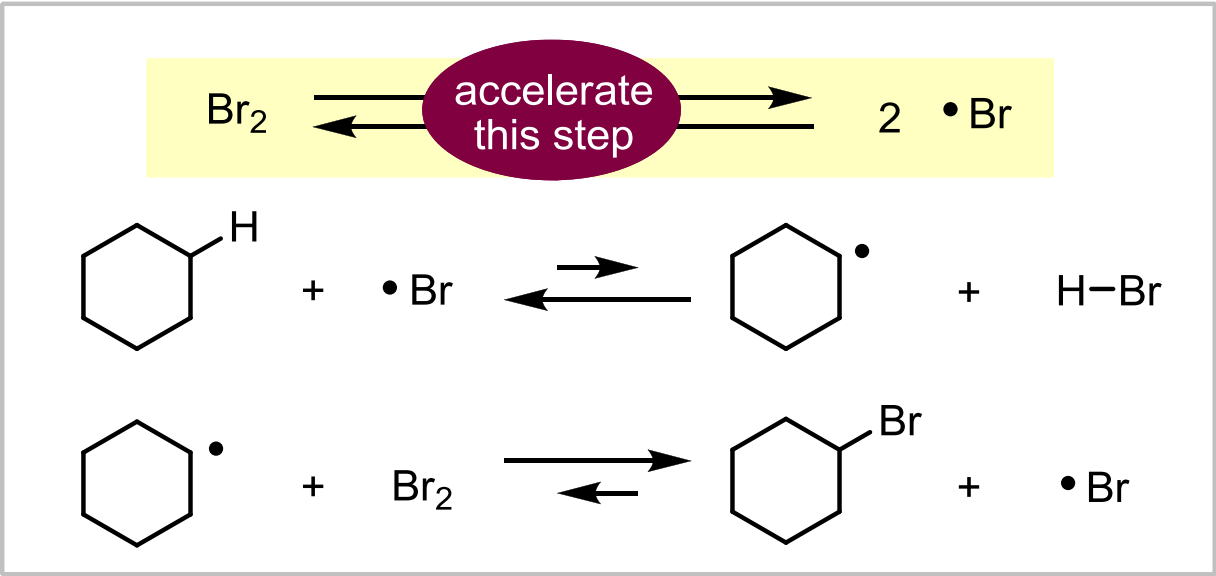
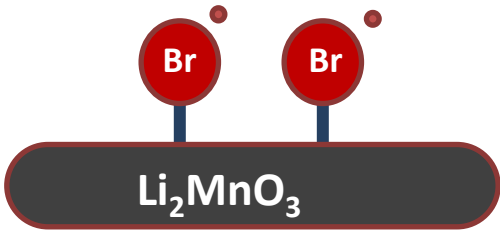
Radical mediated reaction.

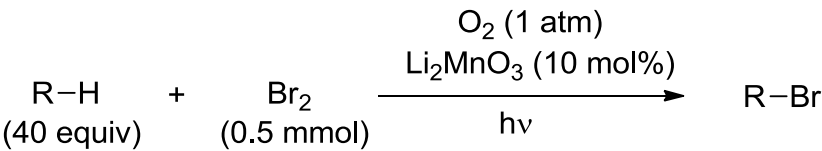


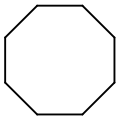
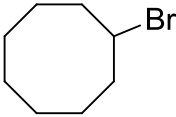

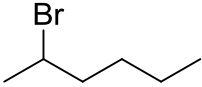
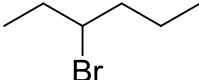
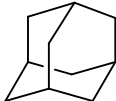
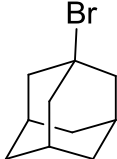
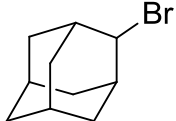
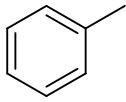
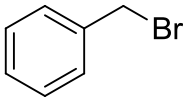
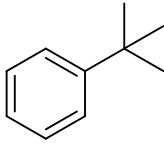
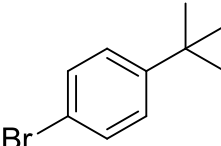


no catalyst with light 12% KIE = 3.03

Li₂MnO₃ (10 mol%) in dark 42% KIE = 3.05





entry ^[a]	R-H	temp / °C	time / h	product yield
1	 1d	25	0.2	 2d quant
2 ^[b]	 1e	40	0.5	 2e 59%  2e' 23%
3 ^[c]	 1f	100	24	 2f 42%  2f' 5%
4	 1b	25	0.2	 2b 93%
5	 1g	80	3	 2g 86%