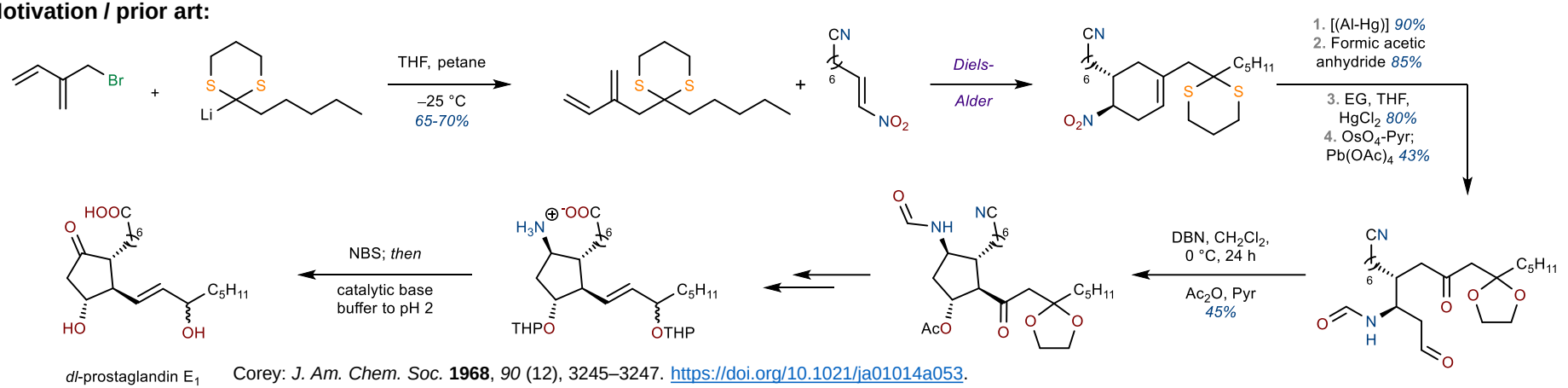
Biomimetic Oxidation of Amines to Carbonyls

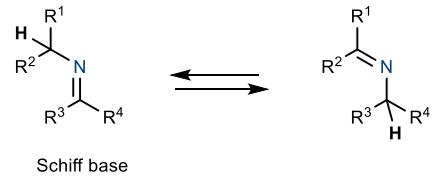
Motivation / prior art:



dl-prostaglandin E_1

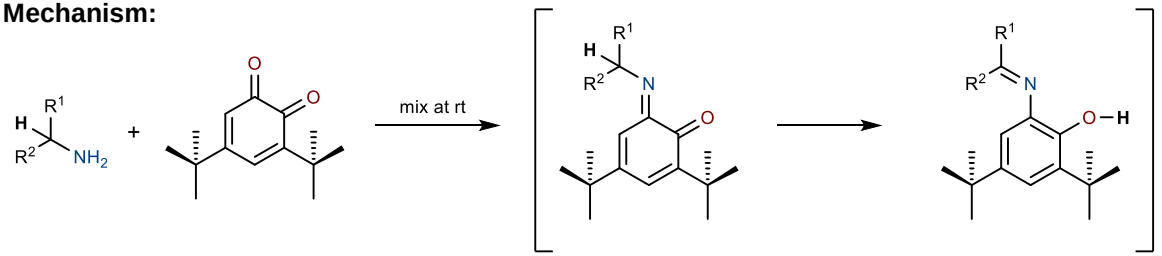
Corey: *J. Am. Chem. Soc.* **1968**, *90* (12), 3245–3247. https://doi.org/10.1021/ja01014a053.

Biomemetic inspiration:

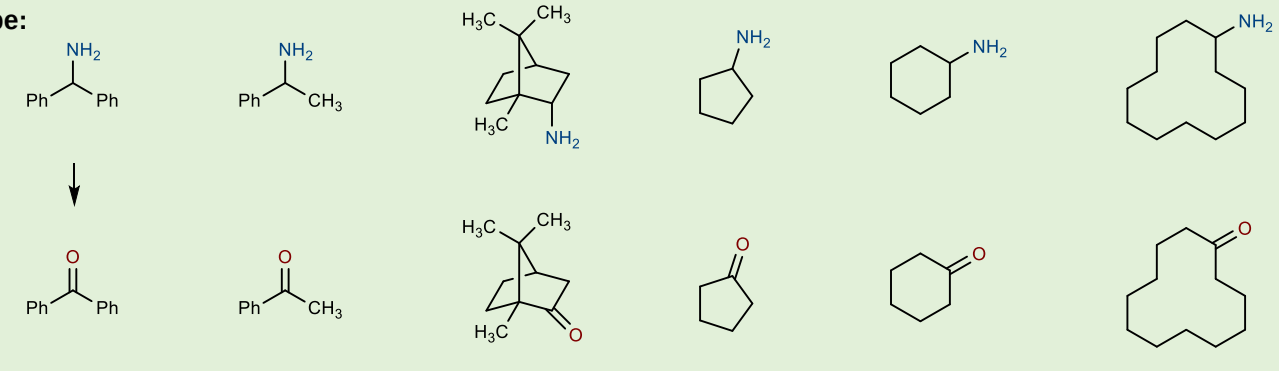


Schiff base

Mechanism:



Scope:



Corey: *J. Am. Chem. Soc.***1969**, *91*, 1429.
https://pubs.acs.org/doi/10.1021/ja01034a027

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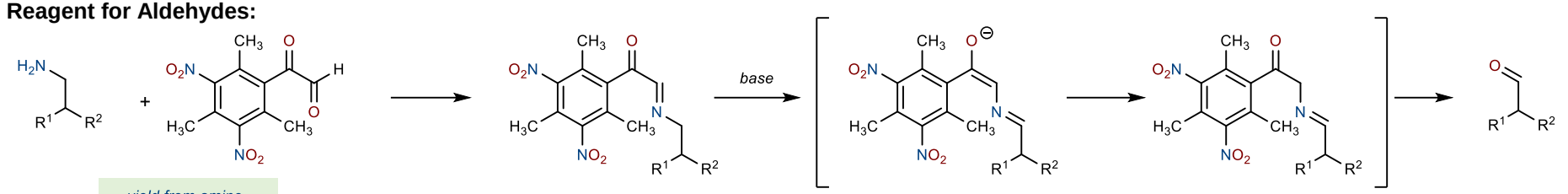
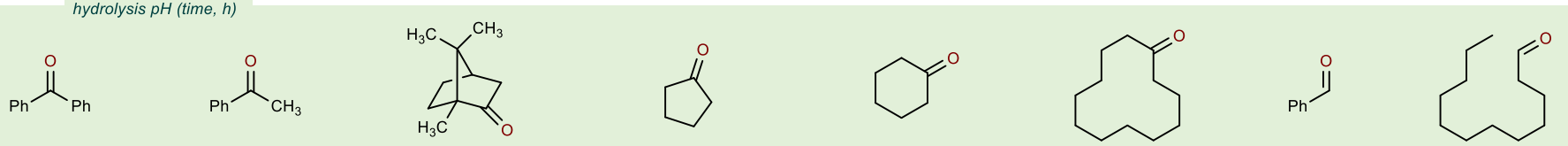
Reagent for Aldehydes:



Corey: *J. Am. Chem. Soc.* **1969**, *91*, 1429. https://pubs.acs.org/doi/10.1021/ja01034a027

yield from amine
eq of base (time, h)
hydrolysis pH (time, h)



91%
0.1 Et_3N (0.33)
2 (2)

80%
0.1 Et_3N (0.5)
3 (2)

92%
1.0 Et_3N (19)
1 (25)

75%
0.1 NaOMe (0.33)
3 (1)

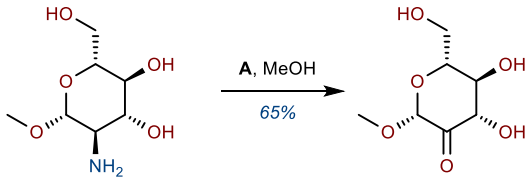
62%
0.1 KOtBu (0.33)
3 (1)

80%
0.1 KOtBu (0.5)
3 (1)

78%
none
3 (2)

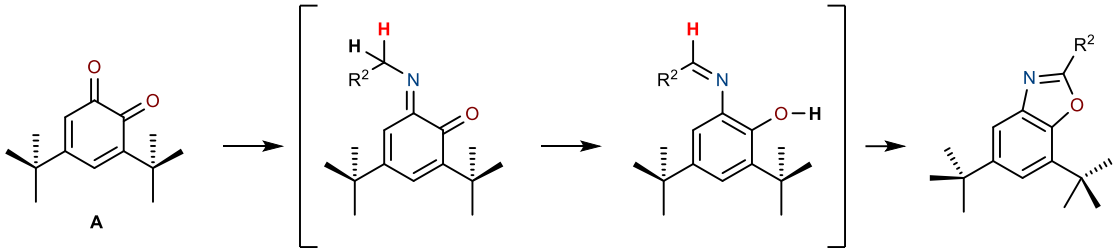
91%
0.1 NaOMe (0.5)
3 (1)

Applications:

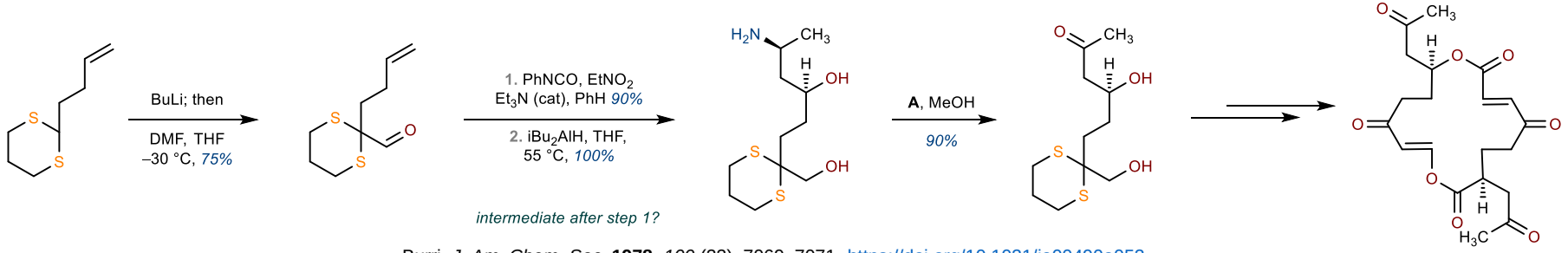


Lengstad & Lönngren *Carbohydrate Research* **1979**, *72*, 312–314. https://doi.org/10.1016/S0008-6215(00)83957-9.

Aldehyde Limitation:



Corey: *J. Am. Chem. Soc.* **1969**, *91*, 1429. https://pubs.acs.org/doi/10.1021/ja01034a027



Burri. *J. Am. Chem. Soc.* **1978**, *100* (22), 7069–7071. https://doi.org/10.1021/ja00490a052.

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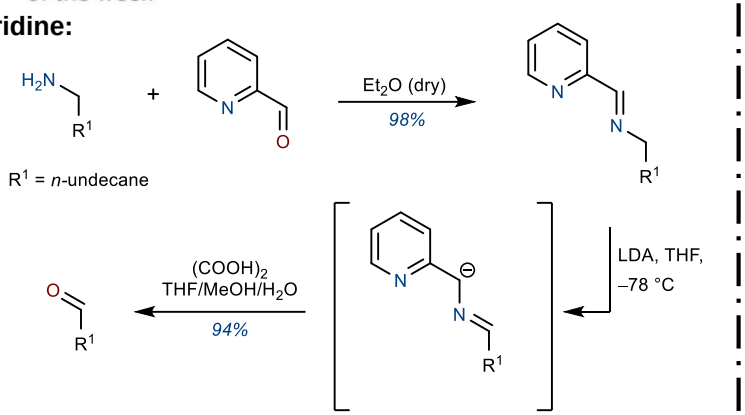
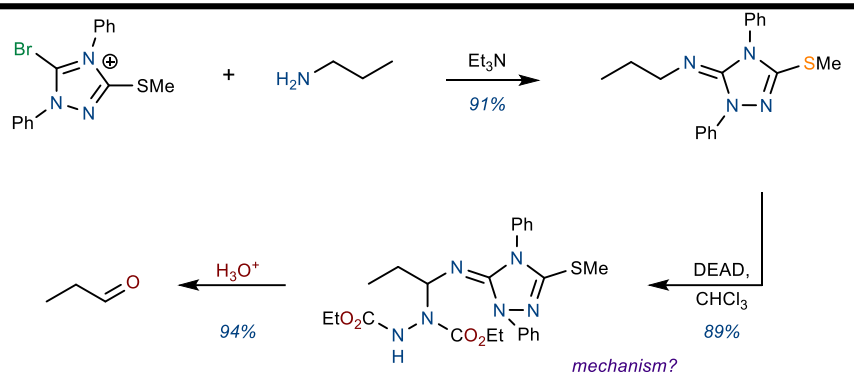
Pyridine:



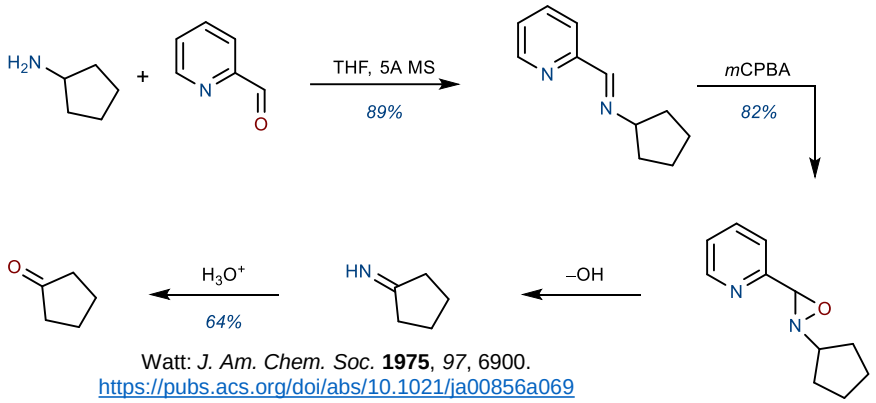
Babler: *J. Org. Chem.* **1981**, *46*, 1937.
https://pubs.acs.org/doi/abs/10.1021/jo00322a046

Triazolium:



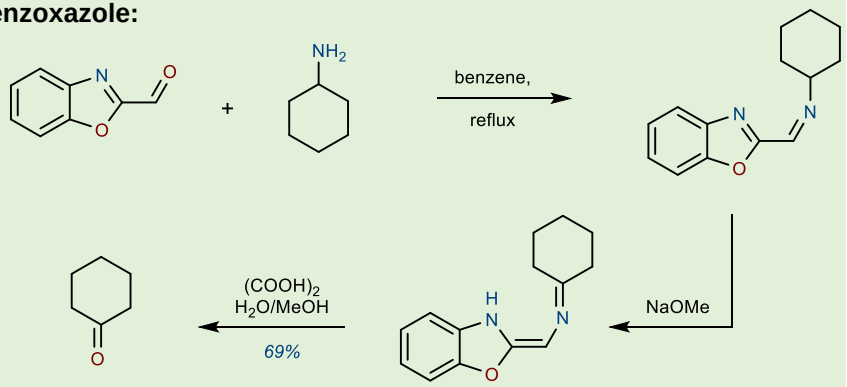
Doleschall: *Tetrahedron Letters* **1978**, *19* (24), 2131–2132.
https://doi.org/10.1016/S0040-4039(01)94769-0.

Oxaziridine:



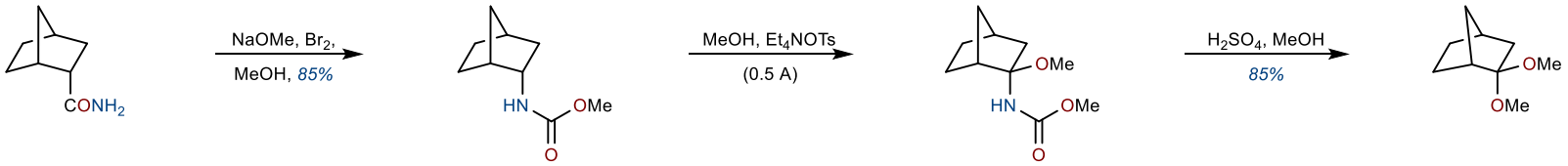
Watt: *J. Am. Chem. Soc.* **1975**, *97*, 6900.
https://pubs.acs.org/doi/abs/10.1021/ja00856a069

Benzoxazole:



Caló: *J. Chem. Soc., Perkin Trans. 1* **1972**, No. 0, 1652–1653. https://doi.org/10.1039/P19720001652.

Shono oxidation:



Shono: *J. Org. Chem.* **1983**, *48*, 3338. https://pubs.acs.org/doi/abs/10.1021/jo00167a039

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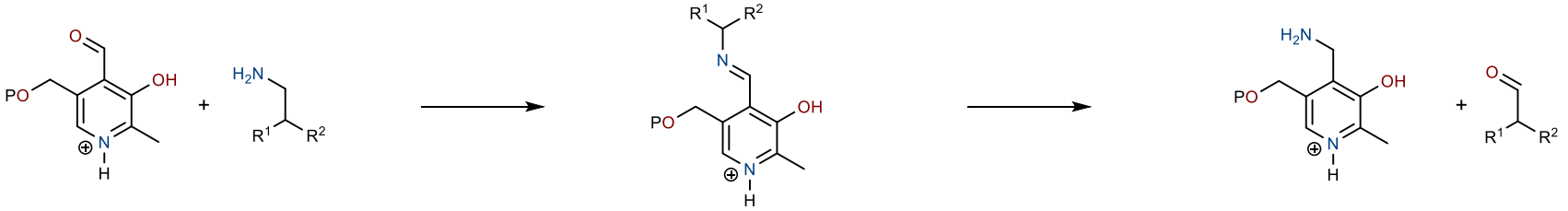
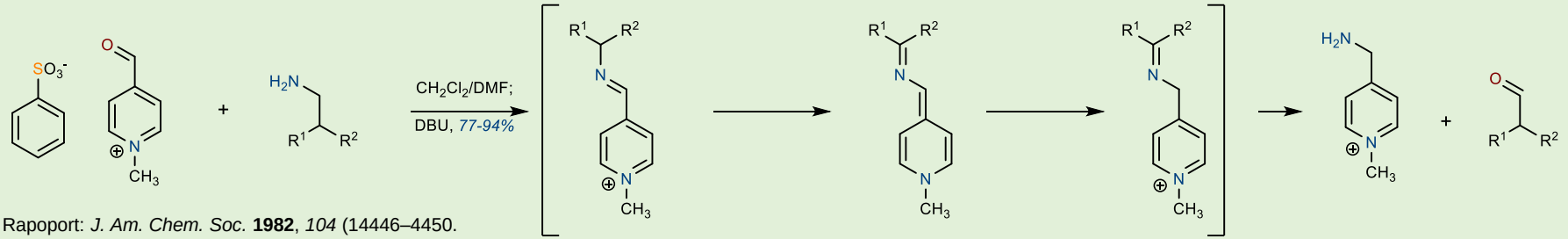
Biosynthesis:

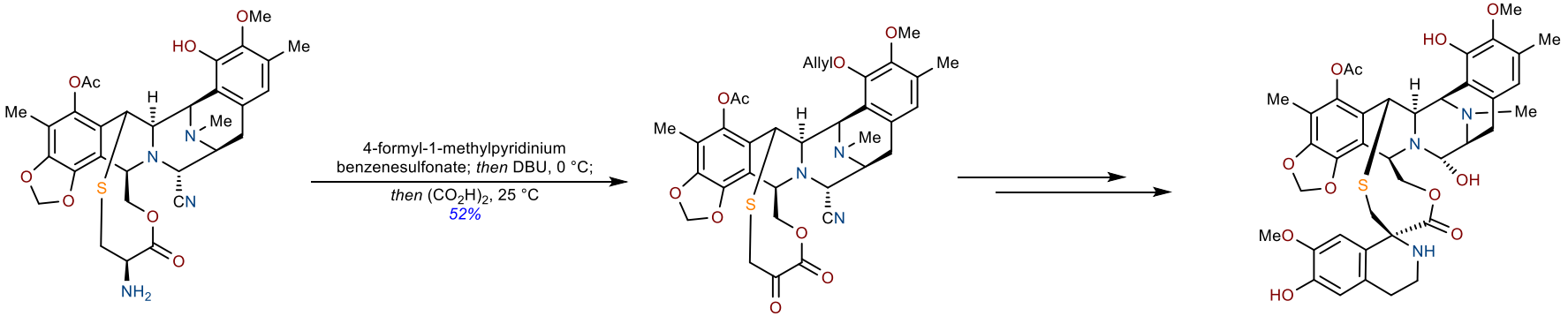


Rapoport:



Rapoport: *J. Am. Chem. Soc.* **1982**, *104* (14446–4450. https://doi.org/10.1021/ja00380a019.

Application:



Angew. Chem. Int. Ed. **2019**, *58* (12), 3972–3975. https://doi.org/10.1002/anie.201900035.

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