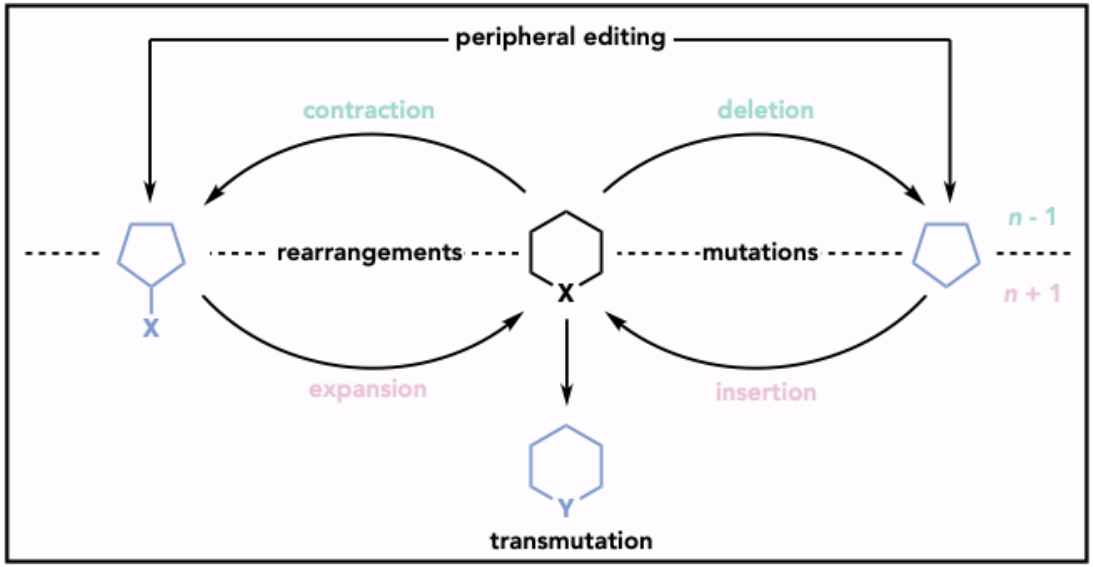
Skeletal Editing & Applications to Total Synthesis

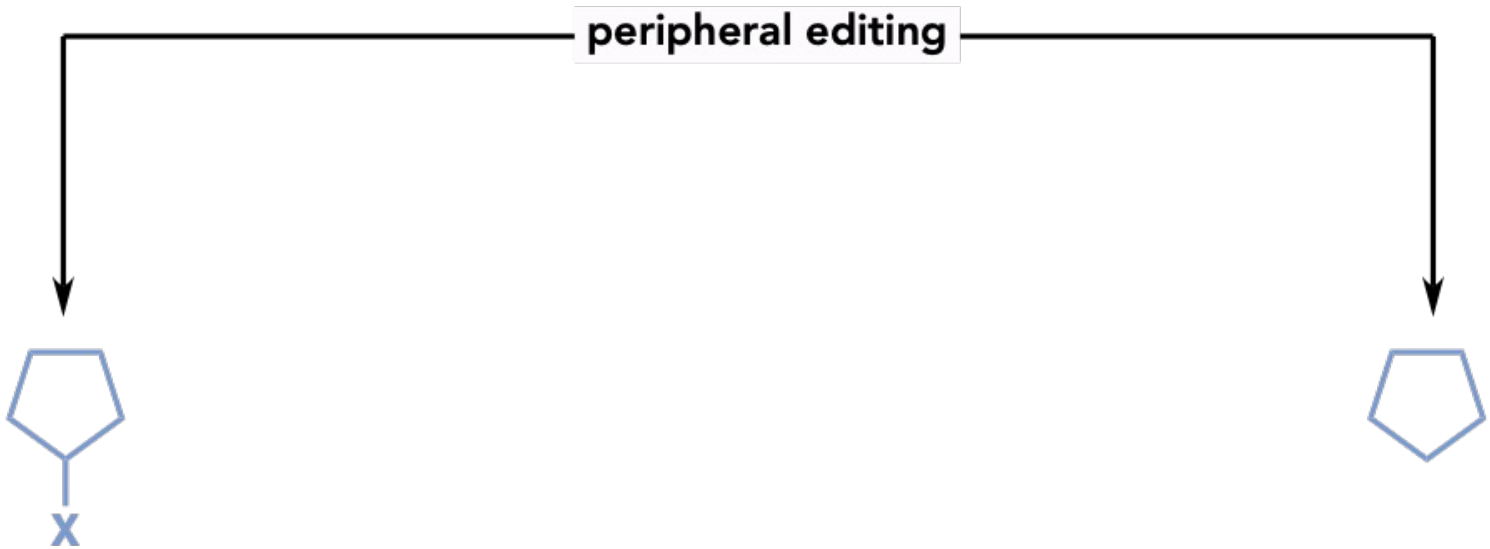


Amy Benedetto

Literature Presentation

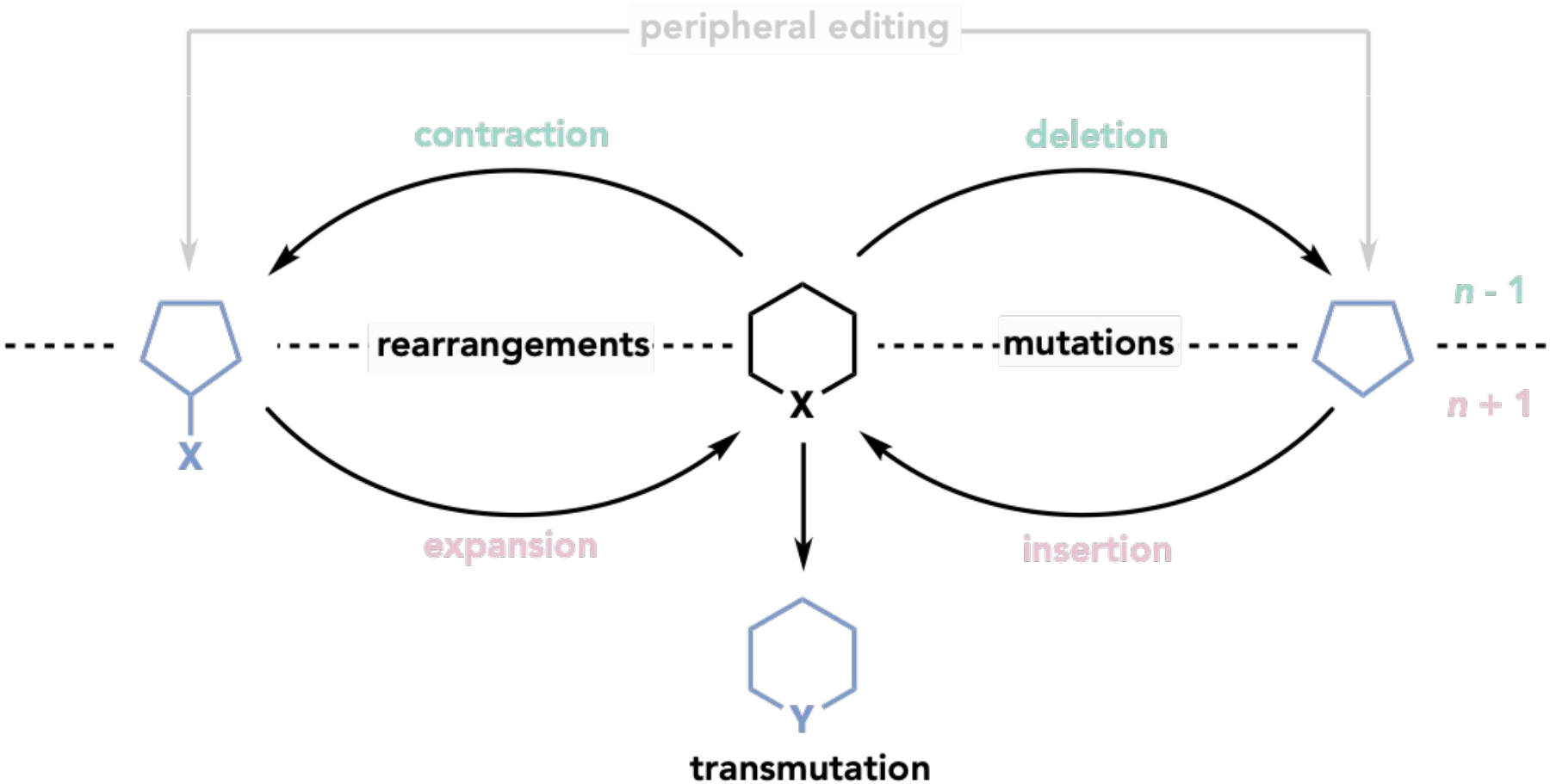
September 25, 2026

Summary of Skeletal Editing



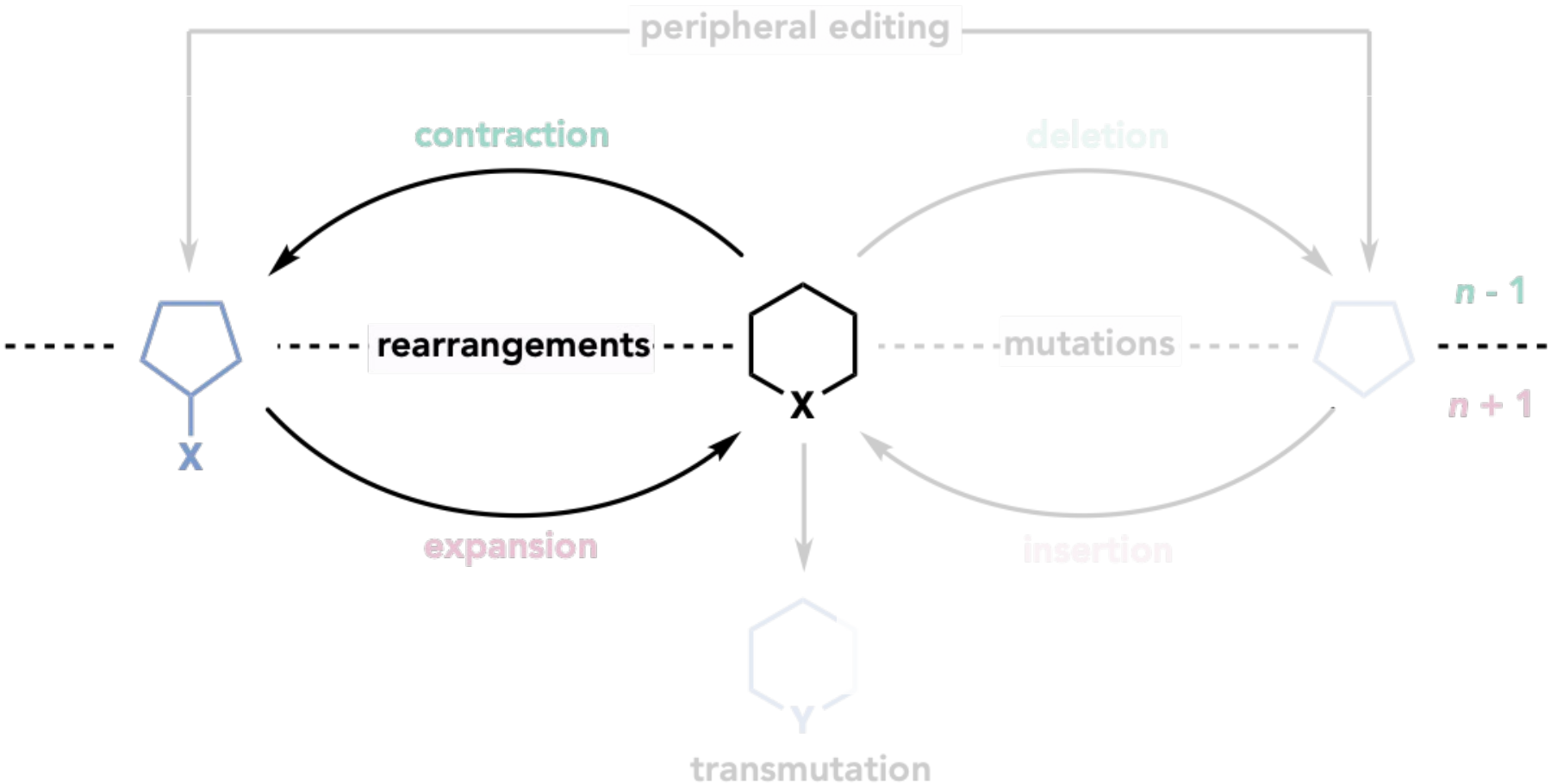
Nature Synthesis **2022**, *1*, 352-364.; *Chem. Eur. J.* ***2026****, 32,* e00014.; *Green Chem.* **2026**, *28*, 4409-4448.; *Synthesis* **2025**, *36*, 3329-3348.; *EurJOC* **2026**, *29*, e202501188.; *Chem. Commun.* **2026**, *62*, 8615-8632.; *Chem. Soc. Rev.* **2025**, *54*, 8145-8169.; *Chem. Rev.* **2026**, *126*, 7004-7028.; *CCS Chem.* **2026**, *8*, 607-692.; *JACS* **2026**, *148*, 21151-21169.; *Chin. JOC* **2024**, *42*, 2656-2667.; *Chem. Eur. J.* **2024**, *30*, e202401993.; *ACIE* e3399600.

Summary of Skeletal Editing



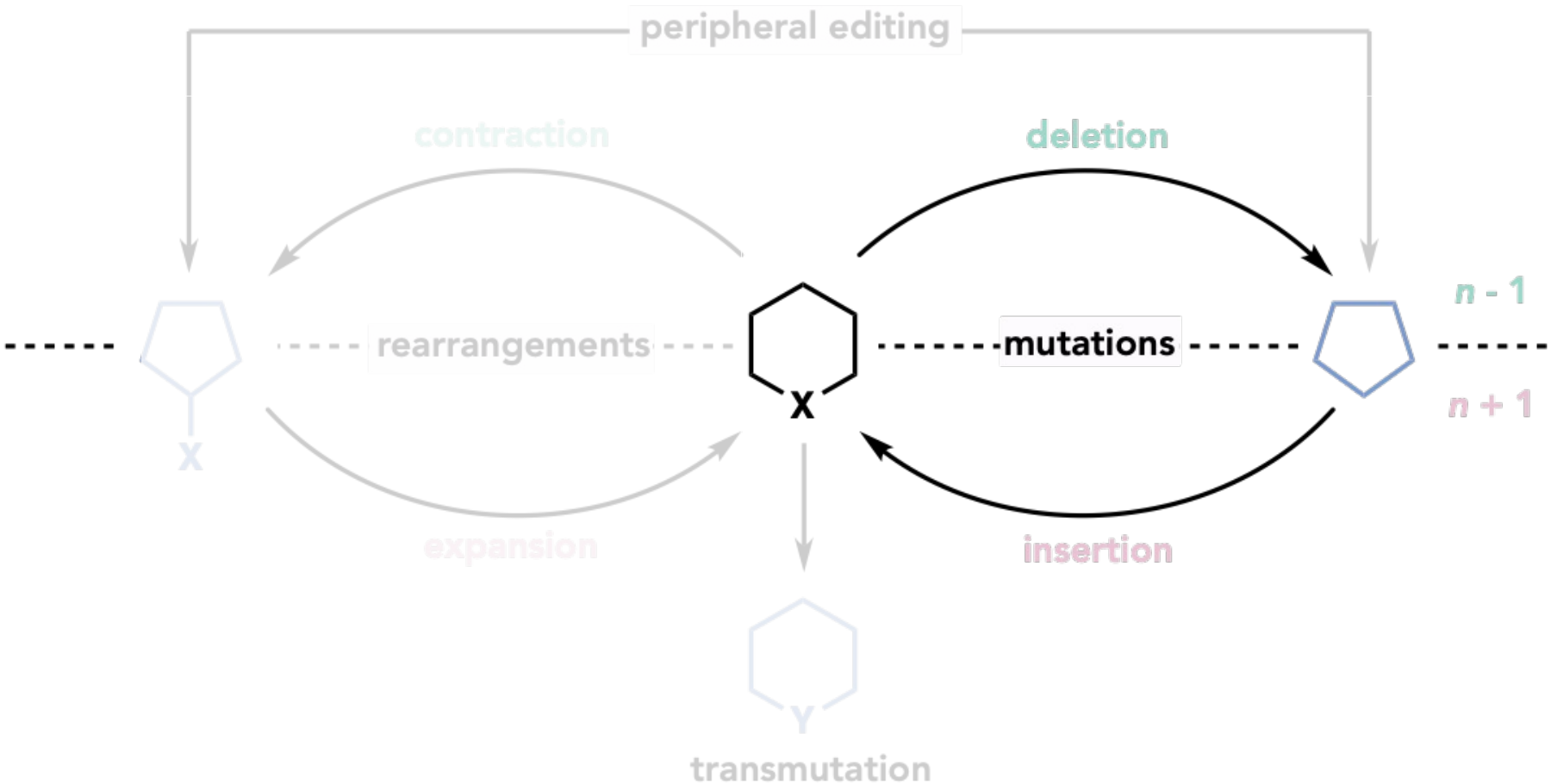
Nature Synthesis **2022**, *1*, 352-364.; *Chem. Eur. J.* ***2026****, 32,* e00014.; *Green Chem.* **2026**, *28*, 4409-4448.; *Synthesis* **2025**, *36*, 3329-3348.; *EurJOC* **2026**, *29*, e202501188.; *Chem. Commun.* **2026**, *62*, 8615-8632.; *Chem. Soc. Rev.* **2025**, *54*, 8145-8169.; *Chem. Rev.* **2026**, *126*, 7004-7028.; *CCS Chem.* **2026**, *8*, 607-692.; *JACS* **2026**, *148*, 21151-21169.; *Chin. JOC* **2024**, *42*, 2656-2667.; *Chem. Eur. J.* **2024**, *30*, e202401993.; *ACIE* e3399600.

Summary of Skeletal Editing



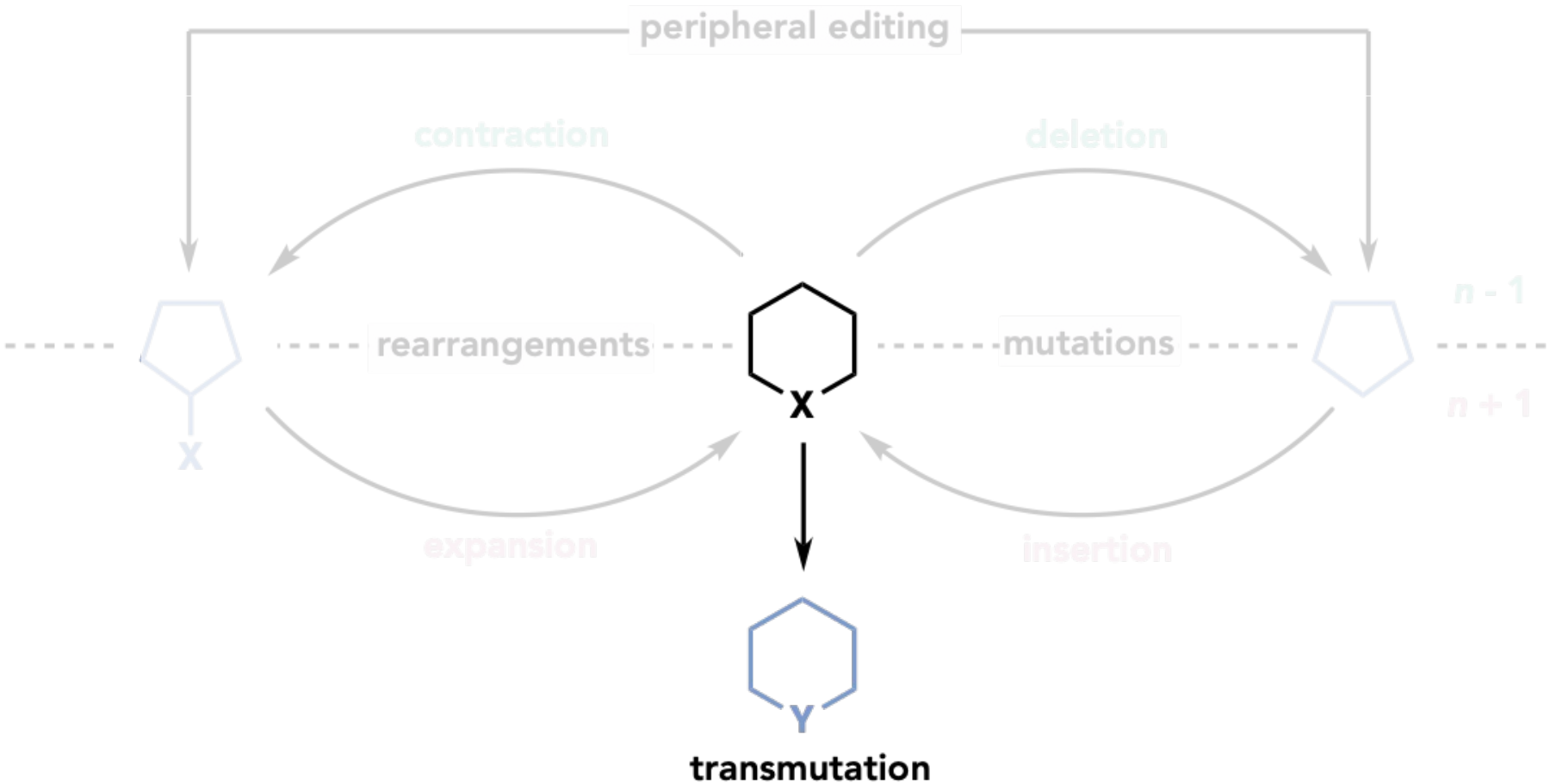
Nature Synthesis **2022**, *1*, 352-364.; *Chem. Eur. J.* ***2026****, 32,* e00014.; *Green Chem.* **2026**, *28*, 4409-4448.; *Synthesis* **2025**, *36*, 3329-3348.; *EurJOC* **2026**, *29*, e202501188.; *Chem. Commun.* **2026**, *62*, 8615-8632.; *Chem. Soc. Rev.* **2025**, *54*, 8145-8169.; *Chem. Rev.* **2026**, *126*, 7004-7028.; *CCS Chem.* **2026**, *8*, 607-692.; *JACS* **2026**, *148*, 21151-21169.; *Chin. JOC* **2024**, *42*, 2656-2667.; *Chem. Eur. J.* **2024**, *30*, e202401993.; *ACIE* e3399600.

Summary of Skeletal Editing



Nature Synthesis **2022**, *1*, 352-364.; *Chem. Eur. J.* ***2026****, 32,* e00014.; *Green Chem.* **2026**, *28*, 4409-4448.; *Synthesis* **2025**, *36*, 3329-3348.; *EurJOC* **2026**, *29*, e202501188.; *Chem. Commun.* **2026**, *62*, 8615-8632.; *Chem. Soc. Rev.* **2025**, *54*, 8145-8169.; *Chem. Rev.* **2026**, *126*, 7004-7028.; *CCS Chem.* **2026**, *8*, 607-692.; *JACS* **2026**, *148*, 21151-21169.; *Chin. JOC* **2024**, *42*, 2656-2667.; *Chem. Eur. J.* **2024**, *30*, e202401993.; *ACIE* e3399600.

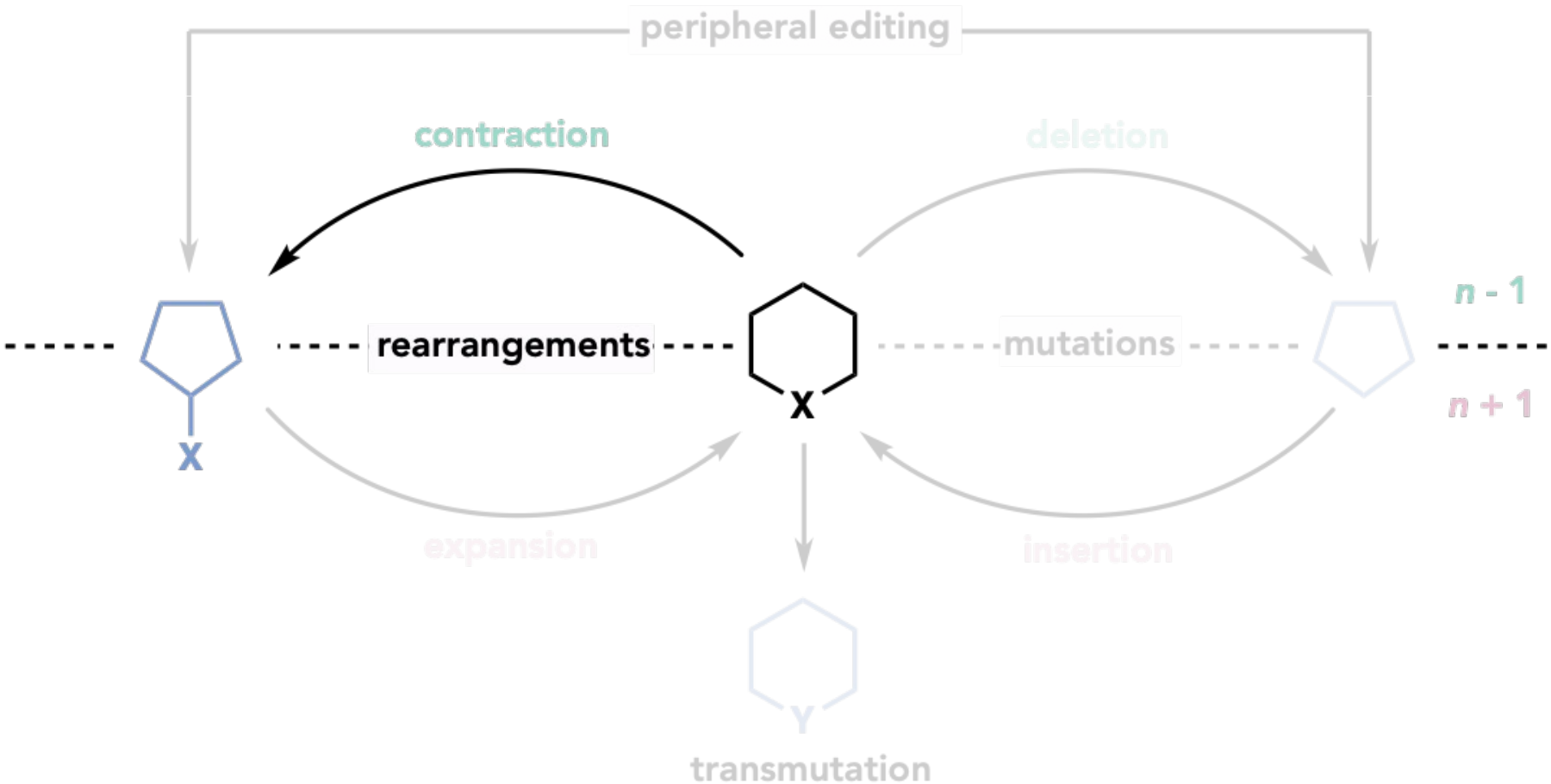
Summary of Skeletal Editing



this presentation excludes transmutations…come back next year!

Nature Synthesis **2022**, *1*, 352-364.; *Chem. Eur. J.* ***2026****, 32,* e00014.; *Green Chem.* **2026**, *28*, 4409-4448.; *Synthesis* **2025**, *36*, 3329-3348.; *EurJOC* **2026**, *29*, e202501188.; *Chem. Commun.* **2026**, *62*, 8615-8632.; *Chem. Soc. Rev.* **2025**, *54*, 8145-8169.; *Chem. Rev.* **2026**, *126*, 7004-7028.; *CCS Chem.* **2026**, *8*, 607-692.; *JACS* **2026**, *148*, 21151-21169.; *Chin. JOC* **2024**, *42*, 2656-2667.; *Chem. Eur. J.* **2024**, *30*, e202401993.; *ACIE* e3399600.

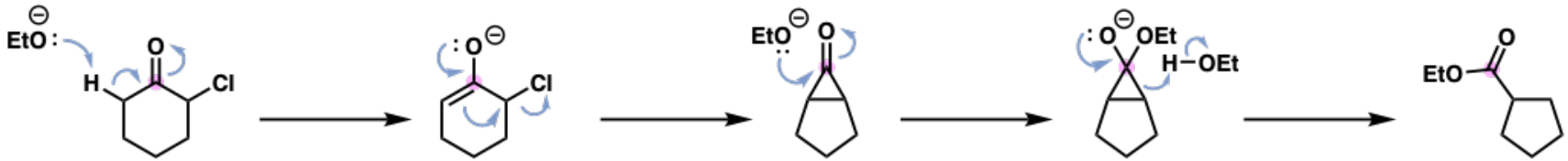
Summary of Skeletal Editing



Nature Synthesis **2022**, *1*, 352-364.; *Chem. Eur. J.* ***2026****, 32,* e00014.; *Green Chem.* **2026**, *28*, 4409-4448.; *Synthesis* **2025**, *36*, 3329-3348.; *EurJOC* **2026**, *29*, e202501188.; *Chem. Commun.* **2026**, *62*, 8615-8632.; *Chem. Soc. Rev.* **2025**, *54*, 8145-8169.; *Chem. Rev.* **2026**, *126*, 7004-7028.; *CCS Chem.* **2026**, *8*, 607-692.; *JACS* **2026**, *148*, 21151-21169.; *Chin. JOC* **2024**, *42*, 2656-2667.; *Chem. Eur. J.* **2024**, *30*, e202401993.; *ACIE* e3399600.

Contractions on Saturated Rings
Carbonyl Removal

Favorskii Rearrangement (1892)

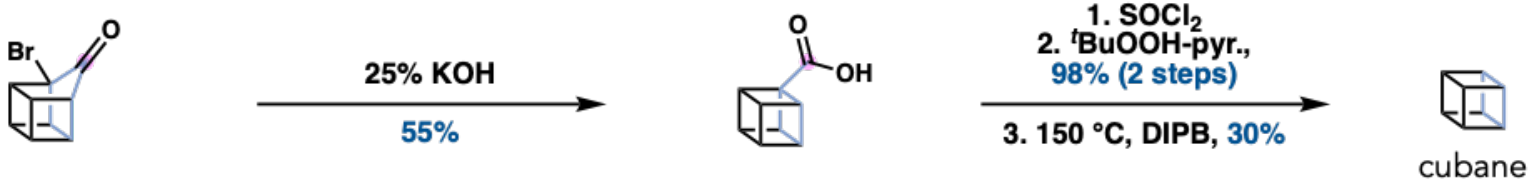


Current Org. Chem. **2005**, *9*, 1713-1735.; *JACS* **1964**, *86*, 3157−3158.; *ACIE* **2017,** *56*, 350-353.; *ChemRxiv*. 02 August 2026. 10.26434/chemrxiv.15006905/v1.; *ACIE* **1975**, *14*, 32-43.; *Helvetica Chimica Acta* **1979**, *62*, 1493-1496.

Contractions on Saturated Rings
Carbonyl Removal

Favorskii Rearrangement (1892)

Cubane Synthesis: Eaton 1964



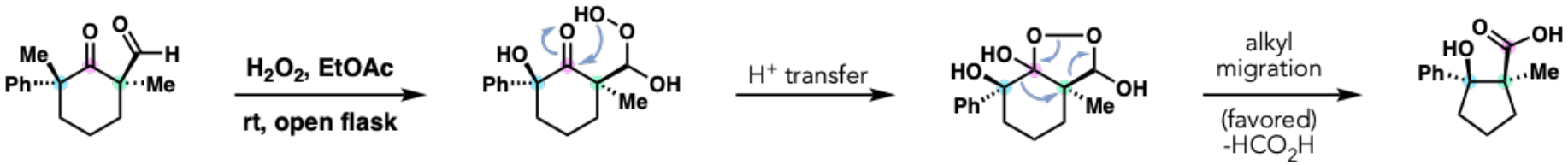
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Contractions on Saturated Rings
Carbonyl Removal

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Cubane Synthesis: Eaton 1964

Oxidative Ring Contraction of α-Formyl Ketones (Zhang & Gao & Xie, 2017)



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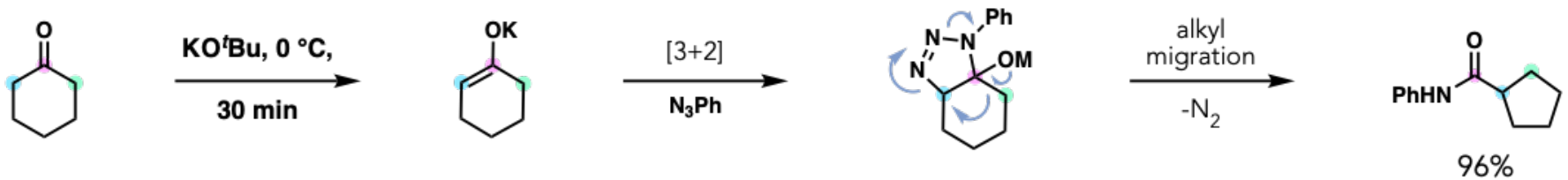
Contractions on Saturated Rings
Carbonyl Removal

Favorskii Rearrangement (1892)

Cubane Synthesis: Eaton 1964

Oxidative Ring Contraction of α-Formyl Ketones (Zhang & Gao & Xie, 2017)

Skeletal Editing of Ketones by Azide-Enolate Cycloaddition-Rearrangement (Furkert, 2026)



Current Org. Chem. **2005**, *9*, 1713-1735.; *JACS* **1964**, *86*, 3157−3158.; *ACIE* **2017,** *56*, 350-353.; *ChemRxiv*. 02 August 2026. 10.26434/chemrxiv.15006905/v1.; *ACIE* **1975**, *14*, 32-43.; *Helvetica Chimica Acta* **1979**, *62*, 1493-1496.

Contractions on Saturated Rings
Carbonyl Removal

Favorskii Rearrangement (1892)

Cubane Synthesis: Eaton 1964

Oxidative Ring Contraction of α-Formyl Ketones (Zhang & Gao & Xie, 2017)

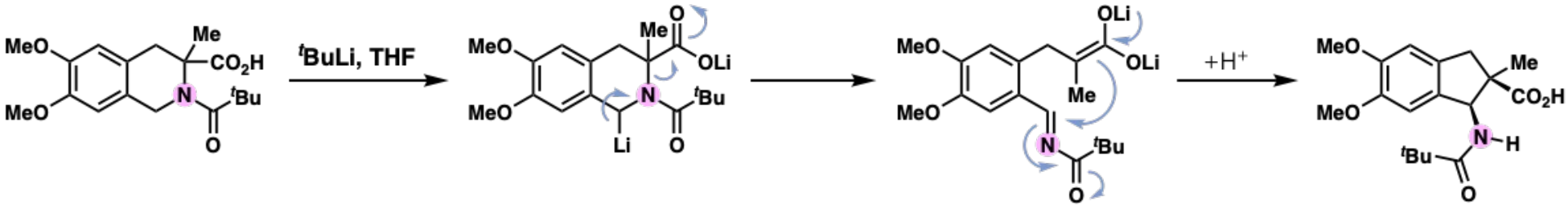
Skeletal Editing of Ketones by Azide-Enolate Cycloaddition-Rearrangement (Furkert, 2026)

Wolff Rearrangement also fits this category
Countless applications to total synthesis including Oppolzer's synthesis of isocomene (1979)

Current Org. Chem. **2005**, *9*, 1713-1735.; *JACS* **1964**, *86*, 3157−3158.; *ACIE* **2017,** *56*, 350-353.; *ChemRxiv*. 02 August 2026. 10.26434/chemrxiv.15006905/v1.; *ACIE* **1975**, *14*, 32-43.; *Helvetica Chimica Acta* **1979**, *62*, 1493-1496.

Contractions on Saturated Rings
Nitrogen Removal

Seebach (1993)



Helvetica Chim. Acta **1993**, *76*, 2640-2653.; *Science* **2021**, *373,* 1004-1012.; *JACS* **2024**, *146*, 5580-5596.*; JACS* **2025**, *147*, 1851-1866.

Contractions on Saturated Rings
Nitrogen Removal

Seebach (1993)

Sarpong (2021)



84% (20:1 dr)

Helvetica Chim. Acta **1993**, *76*, 2640-2653.; *Science* **2021**, *373,* 1004-1012.; *JACS* **2024**, *146*, 5580-5596.*; JACS* **2025**, *147*, 1851-1866.

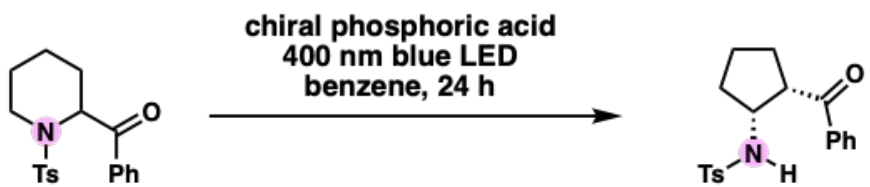
Contractions on Saturated Rings
Nitrogen Removal

Seebach (1993)

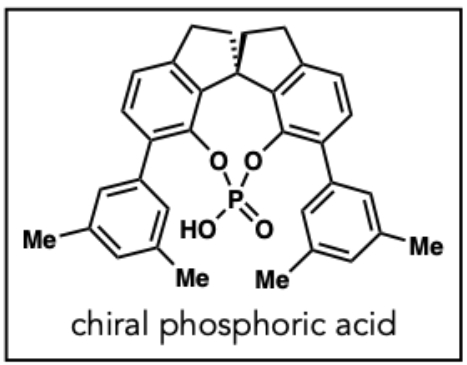
Sarpong (2021)



84% (20:1 dr)



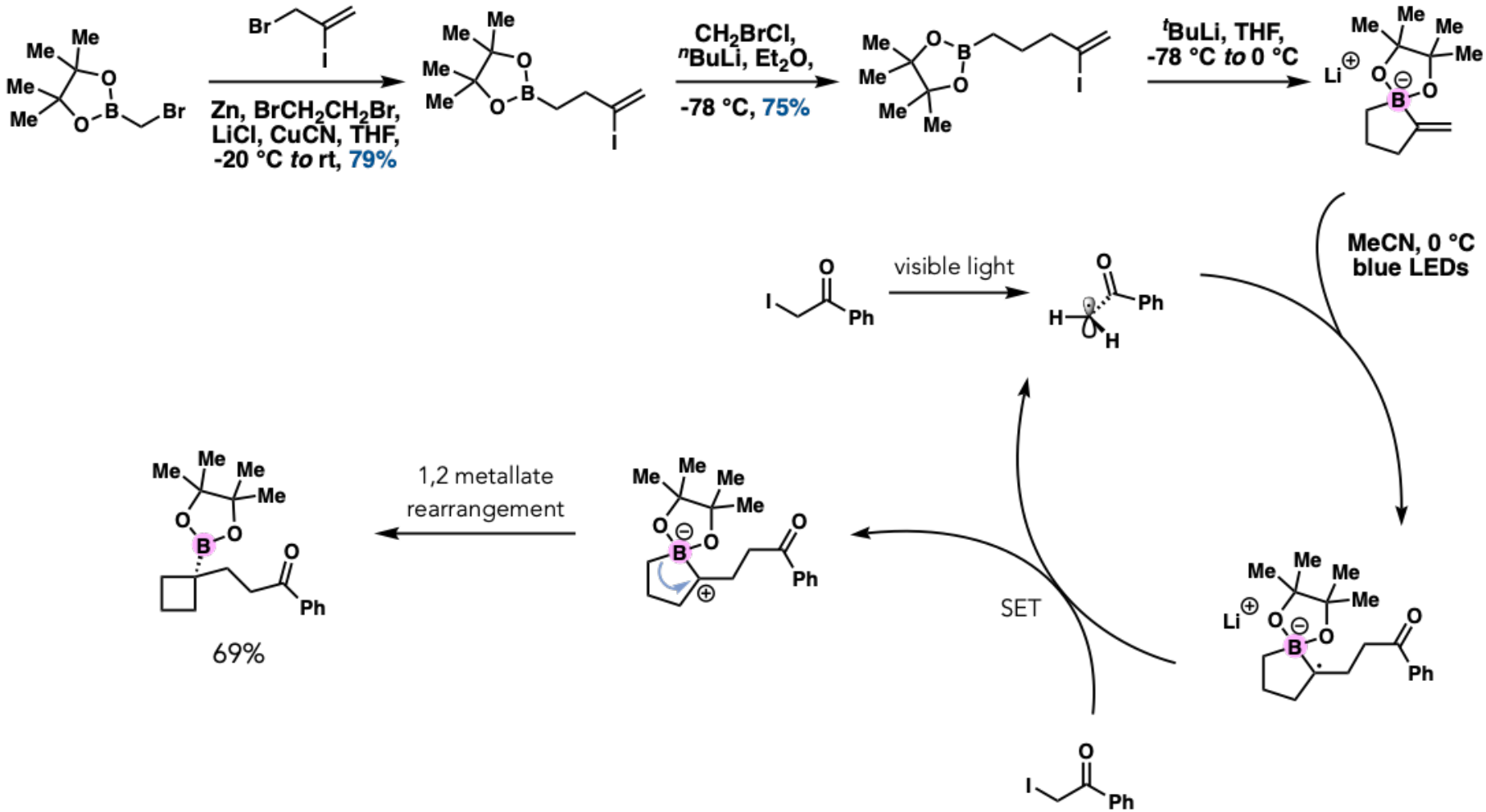
89% (20:1 dr), 95:5 er



Helvetica Chim. Acta **1993**, *76*, 2640-2653.; *Science* **2021**, *373,* 1004-1012.; *JACS* **2024**, *146*, 5580-5596.*; JACS* **2025**, *147*, 1851-1866.

Contractions on Saturated Rings
Boron Removal

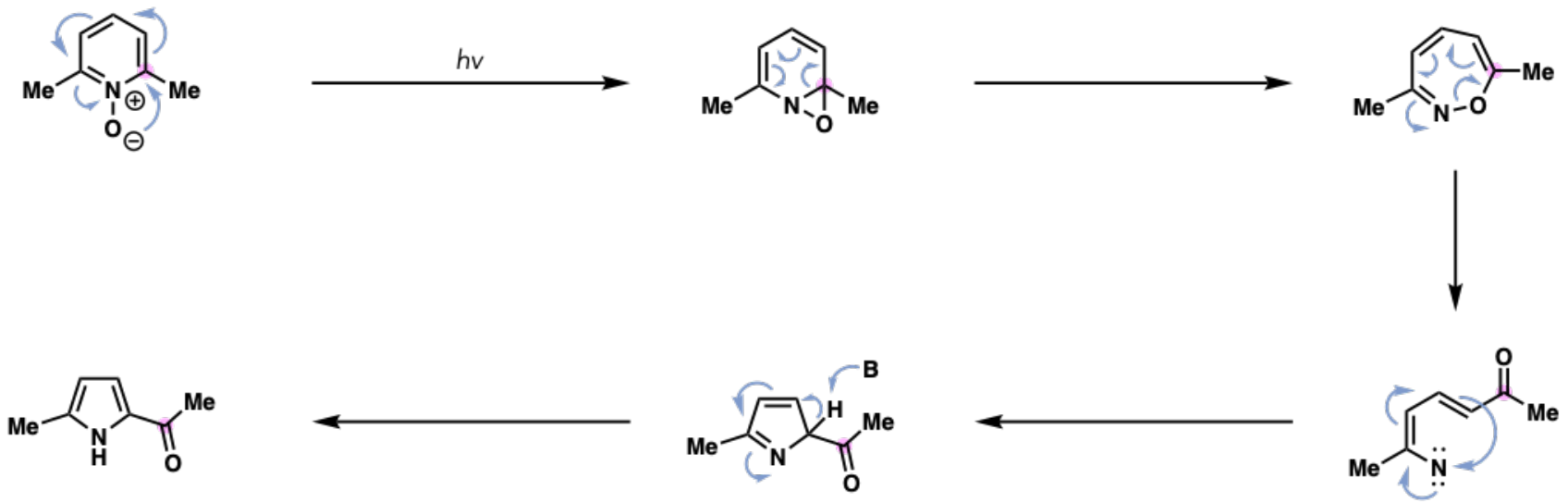
Aggarwal (2020)



ACIE **2020**, *59*, 6525-6528.

Contractions on Aromatic Rings
Carbon Removal

Pyridine *N*-Oxide to Pyrrole (Weber 1988)

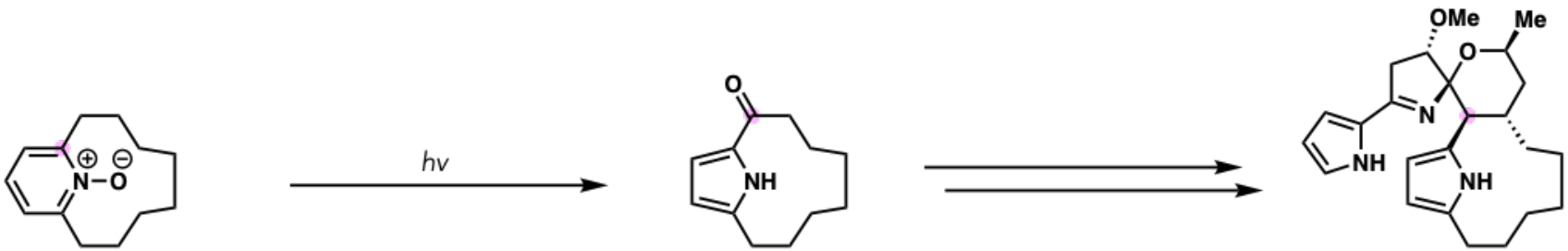


Chemische Berichte ***1989***, *122*, 945-950.; *JACS* **2019**, *141*, 2274-2278.

Contractions on Aromatic Rings
Carbon Removal

Pyridine *N*-Oxide to Pyrrole (Weber 1988)

Harran (2019)

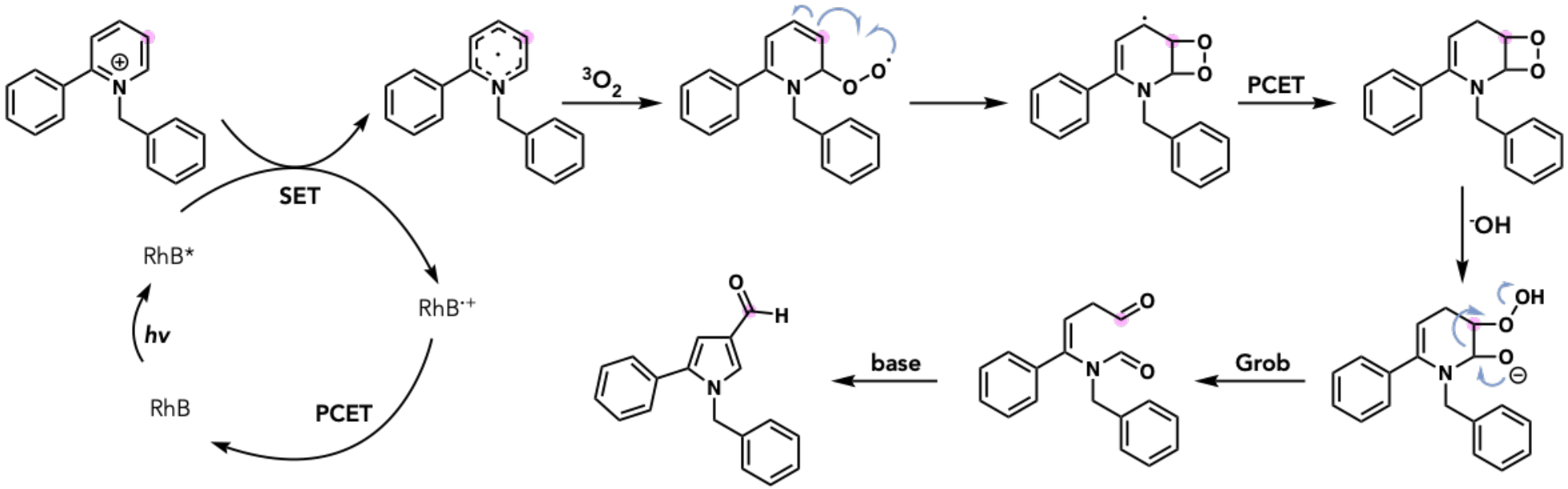


(+)-marineosin A

Chemische Berichte ***1989***, *122*, 945-950.; *JACS* **2019**, *141*, 2274-2278.

Contractions on Aromatic Rings
Carbon Removal

Pyridinium Salts to 3-Formylpyrroles (Wang & Tang & Pan, 2021)

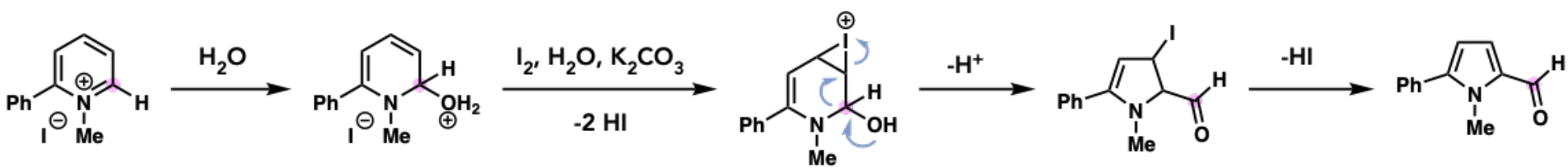


Sci. China Chem. ***2021***, *64*, 753-760.; *Org. Lett.* **2020**, *22*, 6107-6111.

Contractions on Aromatic Rings
Carbon Removal

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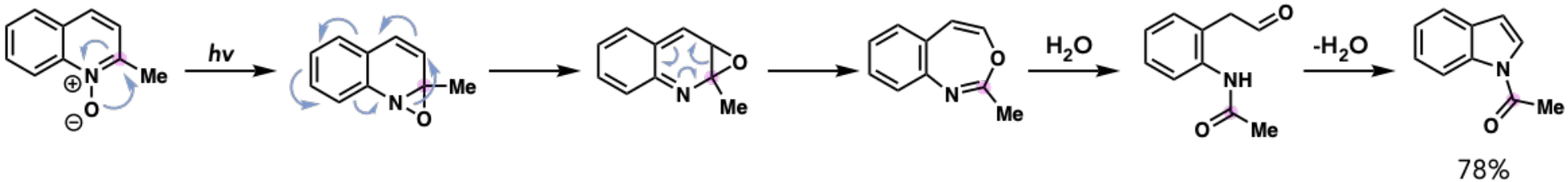
Pyridinium Salts to 2-Formylpyrroles (Fu, 2020)



Sci. China Chem. ***2021***, *64*, 753-760.; *Org. Lett.* **2020**, *22*, 6107-6111.

Contractions on Aromatic Rings
Carbon Removal

Scaffold Hopping: Contraction of Azaarenes (Levin, 2022)



conditions: 390nm LEDs, toluene, rt, 5 h *then* TFA, rt, 5 h

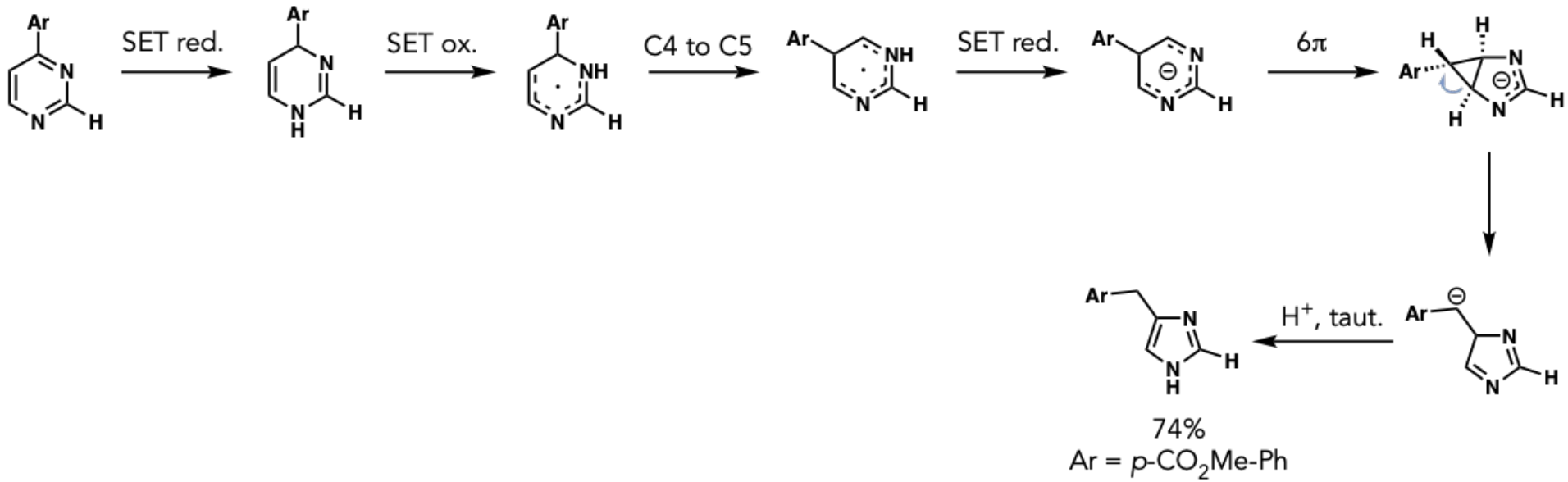
Science ***2022***, *376*, 527-532.; *JACS* **2026**, *148*, 38491-38499.

Contractions on Aromatic Rings
Carbon Removal

Scaffold Hopping: Contraction of Azaarenes (Levin, 2022)

conditions: 390nm LEDs, toluene, rt, 5 h *then* TFA, rt, 5 h

Diazenes to Diazoles (Chiba, 2026)



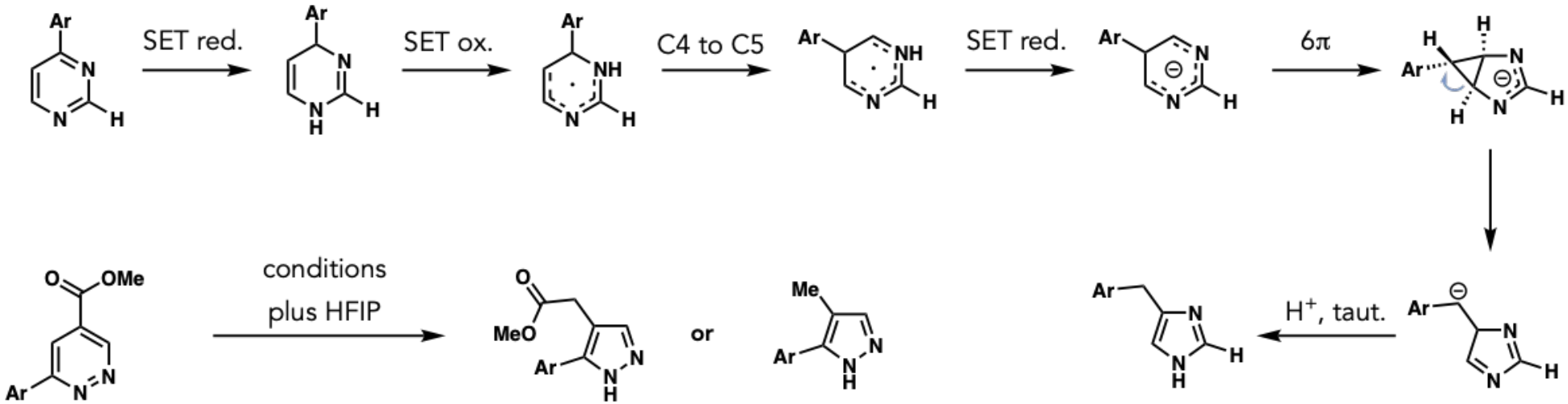
Science ***2022***, *376*, 527-532.; *JACS* **2026**, *148*, 38491-38499.

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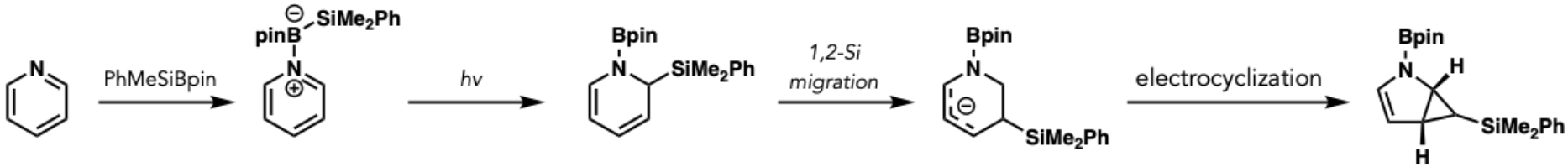


conditions: 3DPAFIPN, HCO_2K, Cs_2CO_3, DMSO, 427nm LEDs, 4 h, 31 °C

Science ***2022***, *376*, 527-532.; *JACS* **2026**, *148*, 38491-38499.

Dearomative Contractions
Carbon Removal

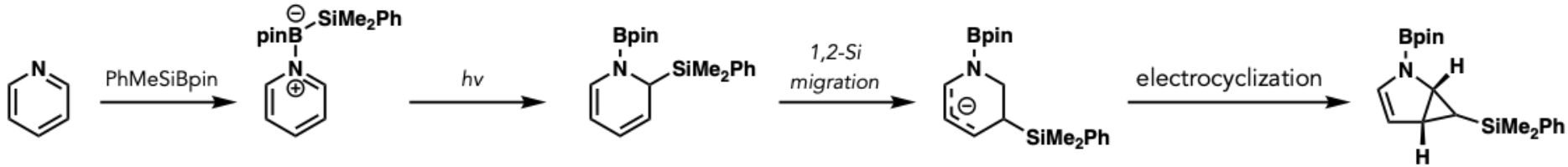
Pyridine to Pyrrolidine (Takaya, 2025)

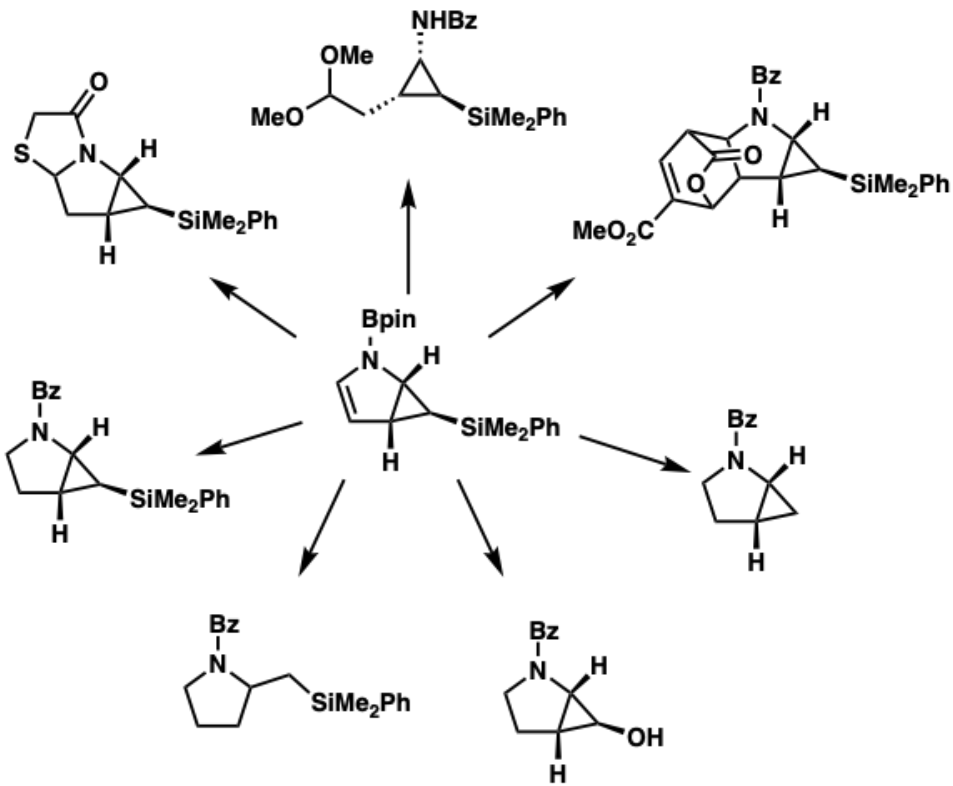


Nature Communications ***2025***, 16, 2426, 1-8.

Dearomative Contractions
Carbon Removal

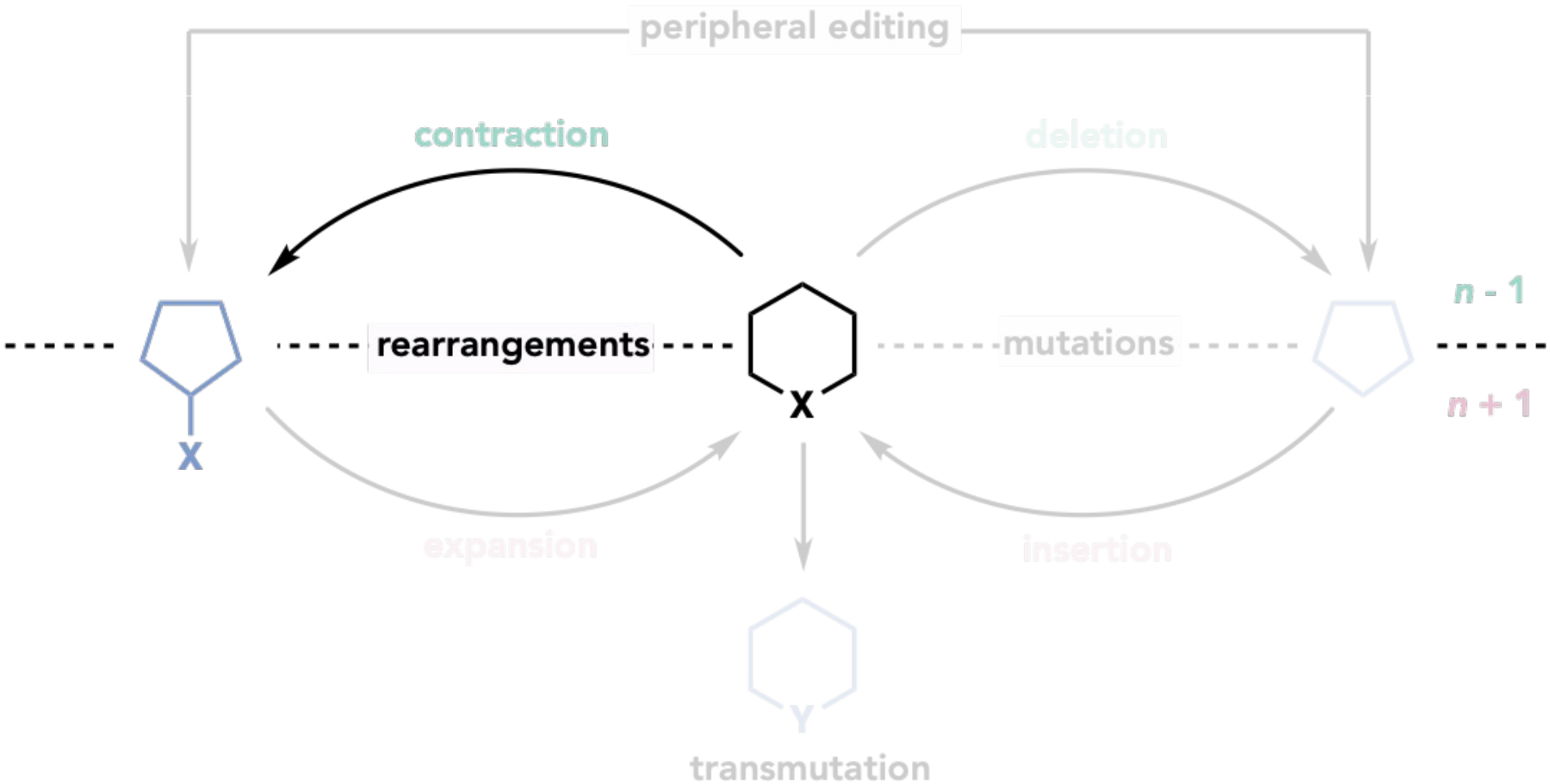
Pyridine to Pyrrolidine (Takaya, 2025)



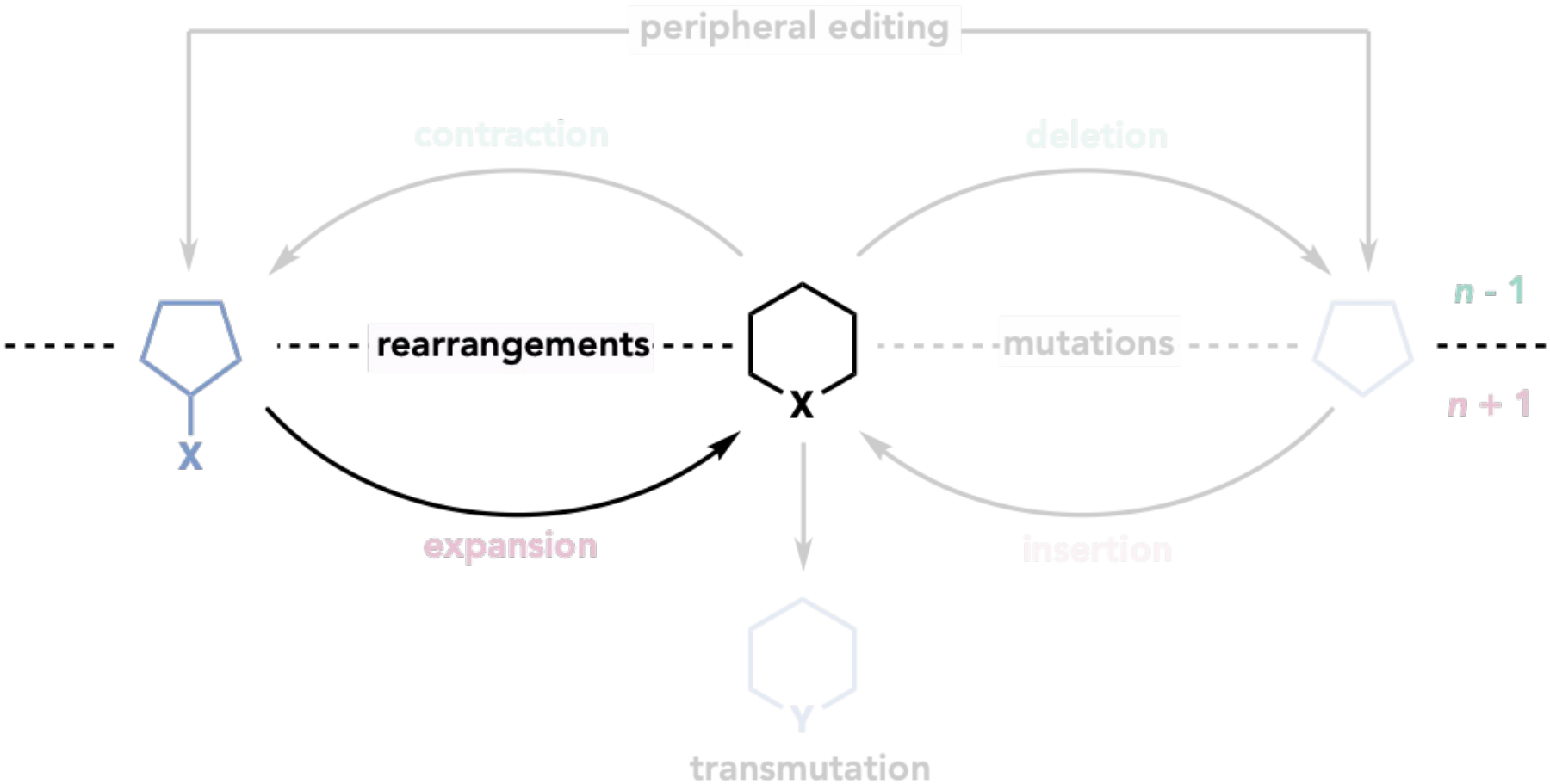


Nature Communications ***2025***, 16, 2426, 1-8.

Summary of Skeletal Editing

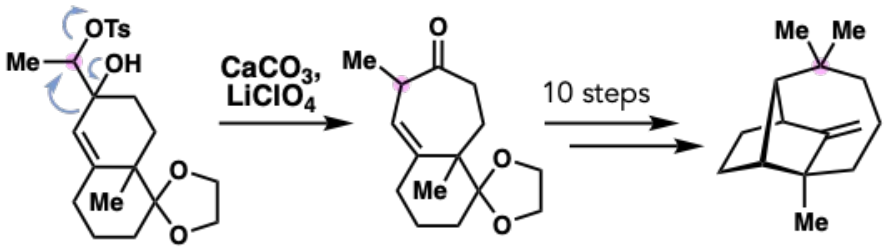


Summary of Skeletal Editing



Expansions of Saturated Rings
Carbon Addition

Semi-Pinacol Rearrangement



longifolene

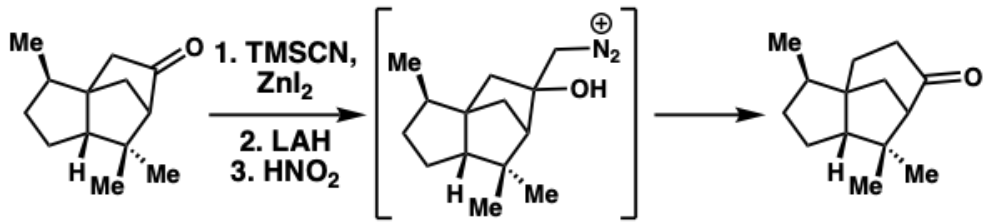
JACS **1961**, *83*, 1251-1253.; *Can. J. Chem.* **1976**, *54*, 1991-1993.; *Org. Lett.* **2014**, *16*, 3376-3379.; *Chem. Sci.* **2023**, *14*, 6930-6935.

Expansions of Saturated Rings
Carbon Addition

Semi-Pinacol Rearrangement

longifolene

Tiffeneau-Demjanov Rearrangement



cedrone

JACS **1961**, *83*, 1251-1253.; *Can. J. Chem.* **1976**, *54*, 1991-1993.; *Org. Lett.* **2014**, *16*, 3376-3379.; *Chem. Sci.* **2023**, *14*, 6930-6935.

Expansions of Saturated Rings
Carbon Addition

Semi-Pinacol Rearrangement

Tiffeneau-Demjanov Rearrangement

Dowd-Beckwith Ring Expansion



JACS **1961**, *83*, 1251-1253.; *Can. J. Chem.* **1976**, *54*, 1991-1993.; *Org. Lett.* **2014**, *16*, 3376-3379.; *Chem. Sci.* **2023**, *14*, 6930-6935.

Expansions of Saturated Rings
Carbon Addition

Semi-Pinacol Rearrangement

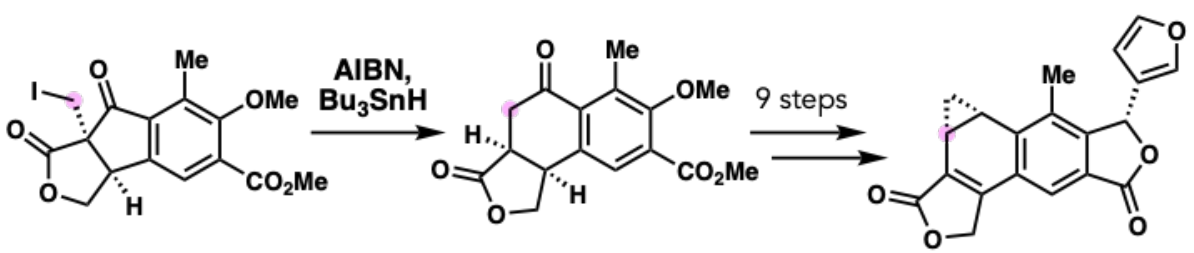
longifolene

Tiffeneau-Demjanov Rearrangement

cedrone

Dowd-Beckwith Ring Expansion





JACS **1961**, *83*, 1251-1253.; *Can. J. Chem.* **1976**, *54*, 1991-1993.; *Org. Lett.* **2014**, *16*, 3376-3379.; *Chem. Sci.* **2023**, *14*, 6930-6935.

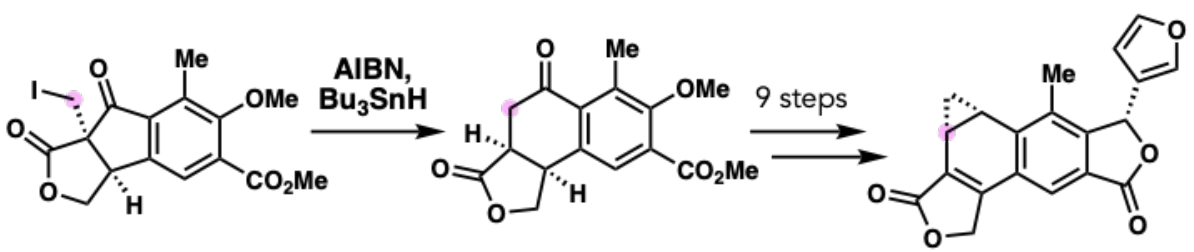
Expansions of Saturated Rings
Carbon Addition

Semi-Pinacol Rearrangement

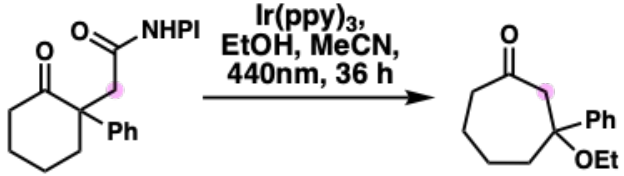
Tiffeneau-Demjanov Rearrangement

Dowd-Beckwith Ring Expansion





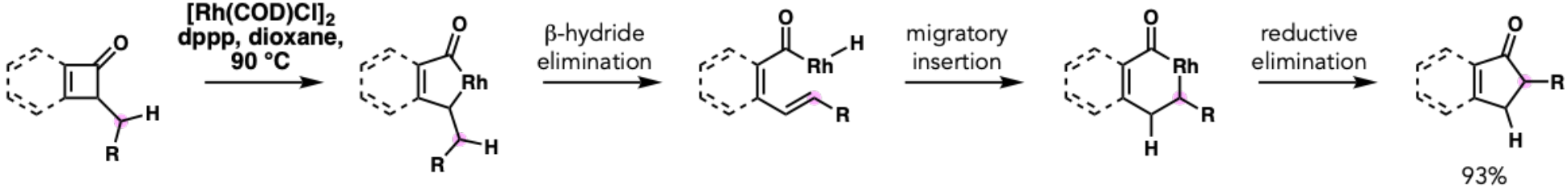
Photocatalytic (Hari, 2023)



JACS **1961**, *83*, 1251-1253.; *Can. J. Chem.* **1976**, *54*, 1991-1993.; *Org. Lett.* **2014**, *16*, 3376-3379.; *Chem. Sci.* **2023**, *14*, 6930-6935.

Expansions of Saturated Rings
Carbon Addition

Dong Ring Expansion (2015)

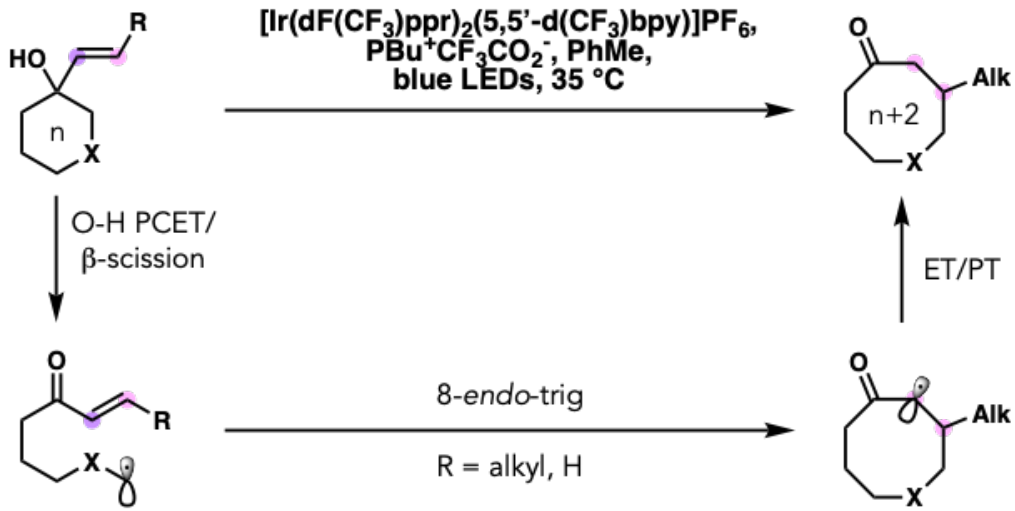


Chem. Sci. **2015**, *6*, 5440-5445.; *JACS* **2019**, *141*, 8752-8757.; Dihydropyridine to Azepine (Au cat): *Adv. Synth. & Cat.* **2019**, *361*, 4065-4074.

Expansions of Saturated Rings
Carbon Addition

Dong Ring Expansion (2015)

Cyclic Alcohol Ring Expansions (Knowles, 2019)

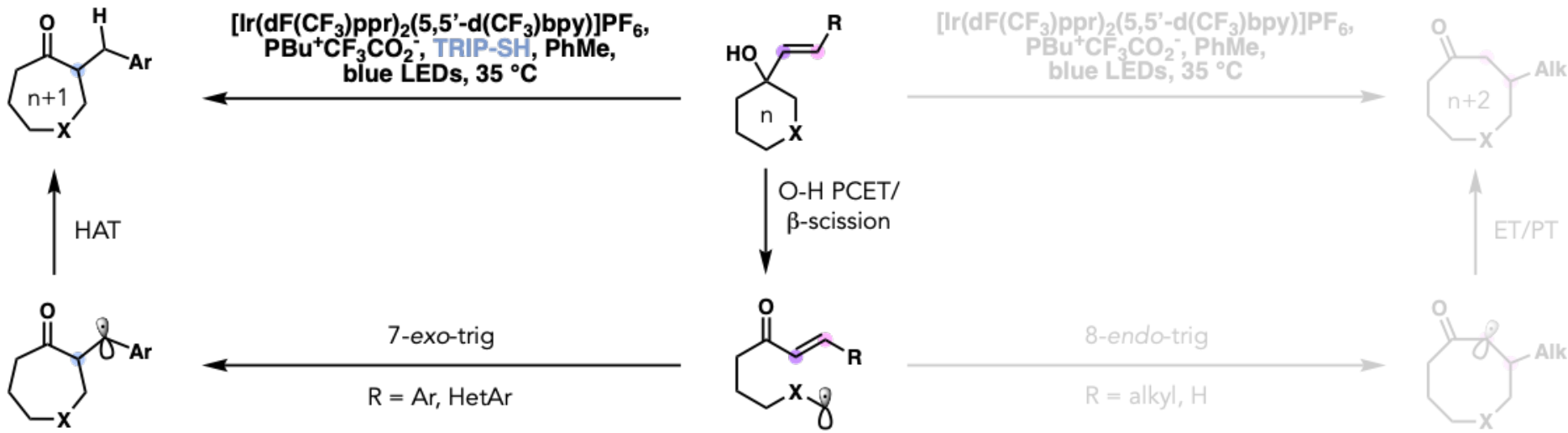


Chem. Sci. **2015**, *6*, 5440-5445.; *JACS* **2019**, *141*, 8752-8757.; Dihydropyridine to Azepine (Au cat): *Adv. Synth. & Cat.* **2019**, *361*, 4065-4074.

Expansions of Saturated Rings
Carbon Addition

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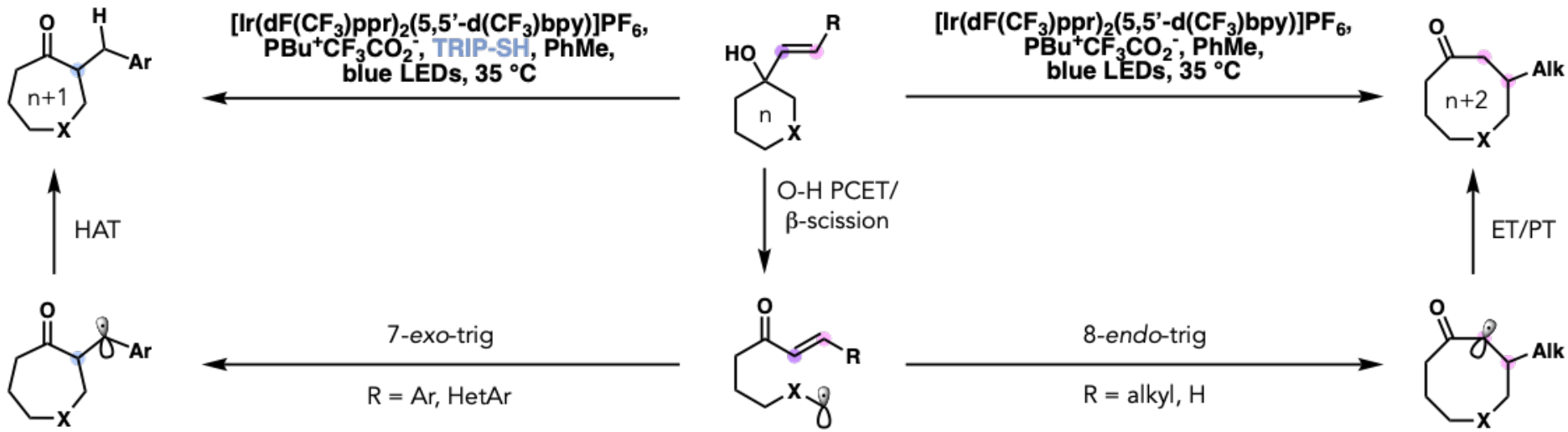


Chem. Sci. **2015**, *6*, 5440-5445.; *JACS* **2019**, *141*, 8752-8757.; Dihydropyridine to Azepine (Au cat): *Adv. Synth. & Cat.* **2019**, *361*, 4065-4074.

Expansions of Saturated Rings
Carbon Addition

Dong Ring Expansion (2015)

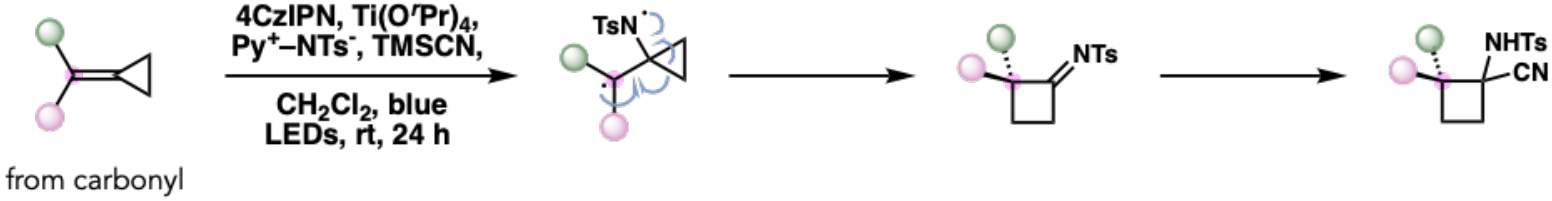
Cyclic Alcohol Ring Expansions (Knowles, 2019)



Chem. Sci. **2015**, *6*, 5440-5445.; *JACS* **2019**, *141*, 8752-8757.; Dihydropyridine to Azepine (Au cat): *Adv. Synth. & Cat.* **2019**, *361*, 4065-4074.

Expansions of Saturated Rings
Carbon Addition

Hindered Cyclobutane Synthesis (Zhang, 2026)



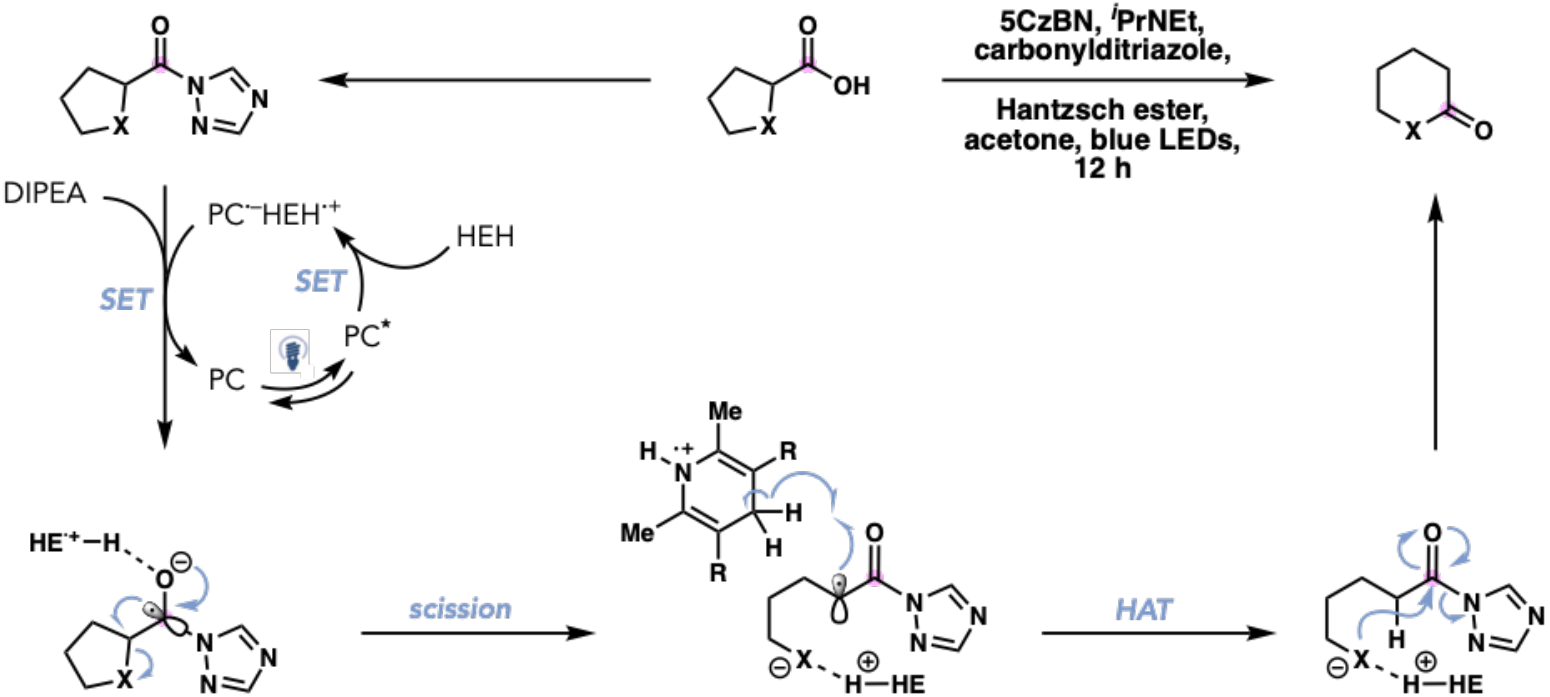
from carbonyl

Nature Chem. **2026**, *18*, 1422-1430.; *JACS* **2025**, *147*, 45884-45892.

Expansions of Saturated Rings
Carbon Addition

Hindered Cyclobutane Synthesis (Zhang, 2026)

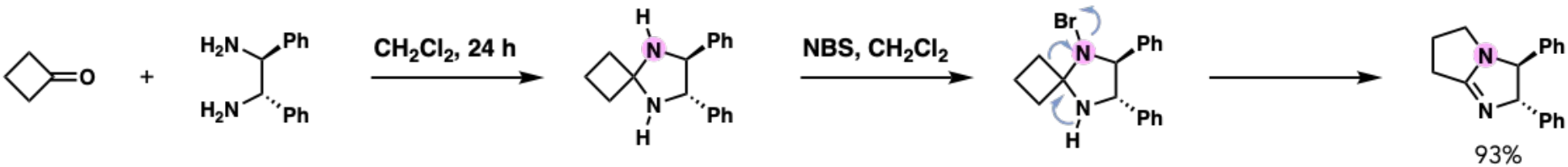
Carbonylative Ring Expansion of Cyclic Carboxylic Acids (Nagao & Ohmiya, 2025)



Nature Chem. **2026**, *18*, 1422-1430.; *JACS* **2025**, *147*, 45884-45892.

Expansions of Saturated Rings
Nitrogen Addition

Spiro Cyclobutane Cyclic Aminals to Bicyclic Amidines (Fujioka, 2012)

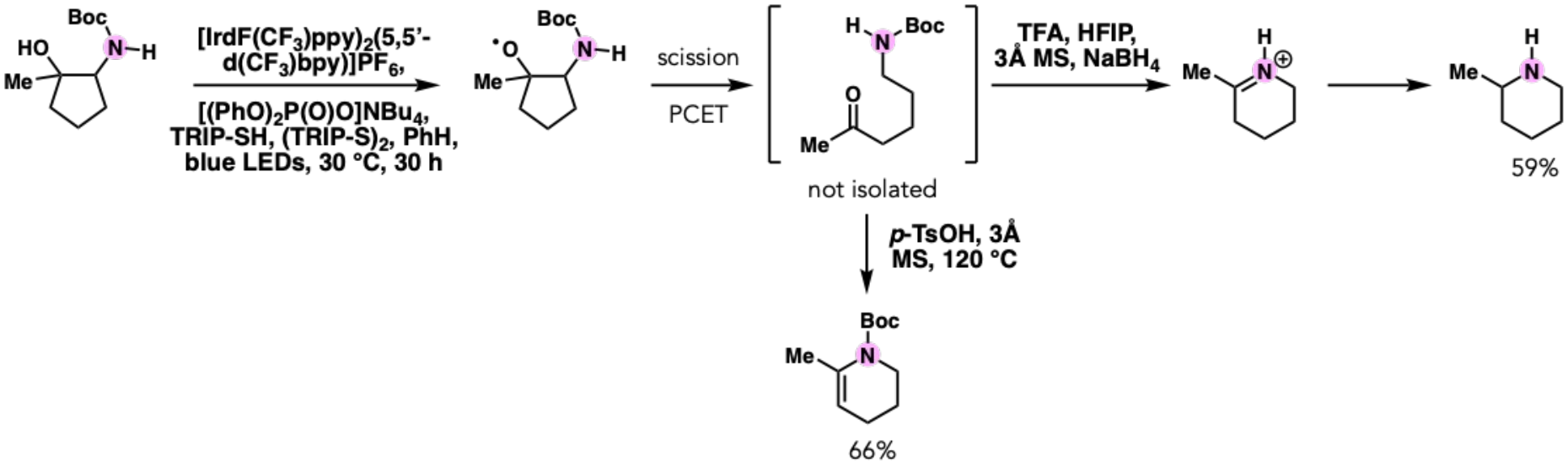


Org. Lett. **2012**, *14*, 772-775.; *JACS* **2025**, *147*, 21818-21823.

Expansions of Saturated Rings
Nitrogen Addition

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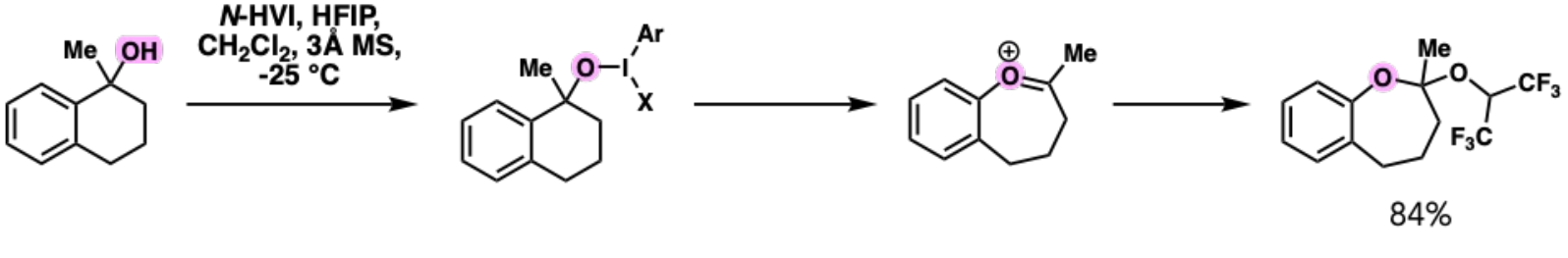
1,2-Amino Alcohols to Amine Heterocycles (Knowles, 2025)

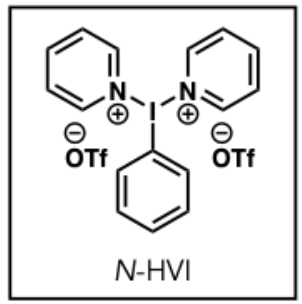


Org. Lett. **2012**, *14*, 772-775.; *JACS* **2025**, *147*, 21818-21823.

Expansions of Saturated Rings
Oxygen Addition

Oxidative Rearrangement of Tertiary Alcohols (Wengryniuk, 2016)



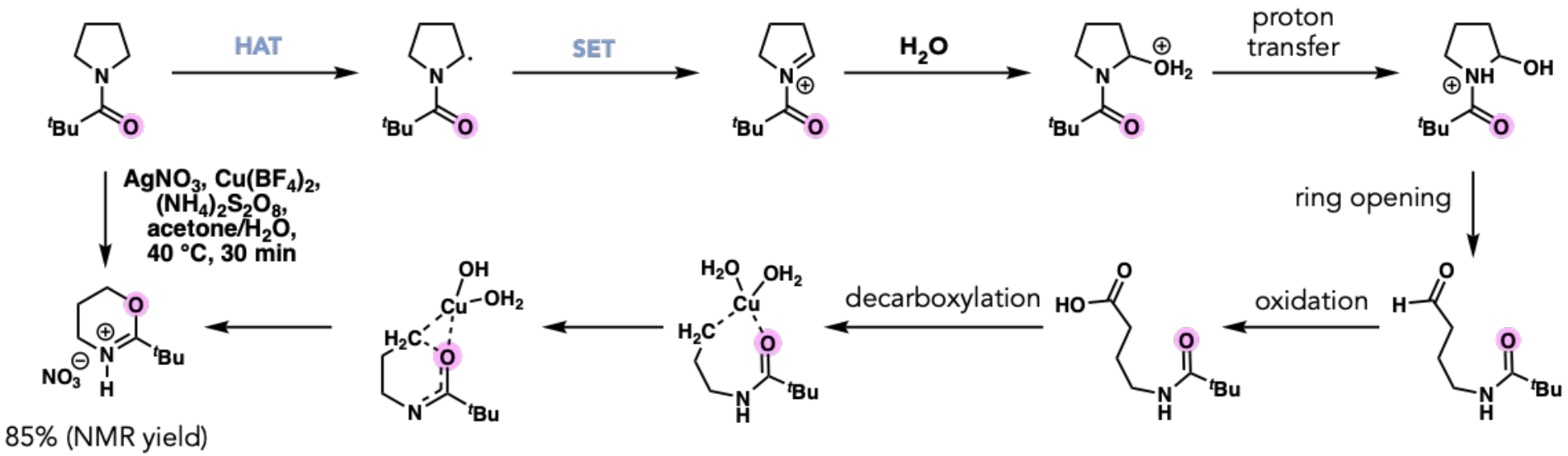


Org. Lett. **2016**, *18*, 1896-1899.; *JACS.* **2023**, *145*, 11245-11257.; *Nature Synthesis* **2026**, *5*, 349-356.

Expansions of Saturated Rings
Oxygen Addition

Oxidative Rearrangement of Tertiary Alcohols (Wengryniuk, 2016)

Expansion of Pyrrolidines to Oxazines (Sarpong, 2023)



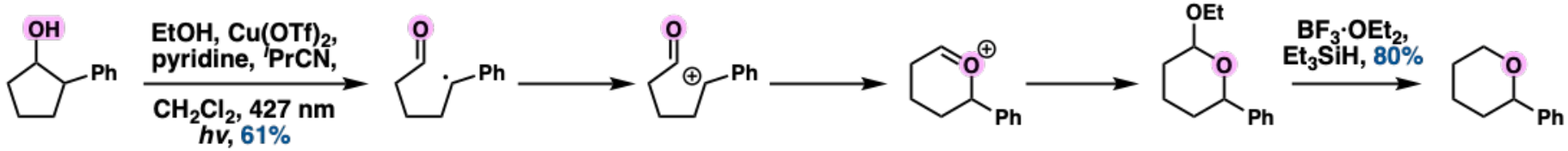
Org. Lett. **2016**, *18*, 1896-1899.; *JACS.* **2023**, *145*, 11245-11257.; *Nature Synthesis* **2026**, *5*, 349-356.

Expansions of Saturated Rings
Oxygen Addition

Oxidative Rearrangement of Tertiary Alcohols (Wengryniuk, 2016)

Expansion of Pyrrolidines to Oxazines (Sarpong, 2023)

Oxygen Migration into C–C Single Bonds (Yoon, 2026)



Org. Lett. **2016**, *18*, 1896-1899.; *JACS.* **2023**, *145*, 11245-11257.; *Nature Synthesis* **2026**, *5*, 349-356.

Dearomative Expansions

Carbon: Synthesis of Azepines (Beeler, 2021 & Yoo, 2021)



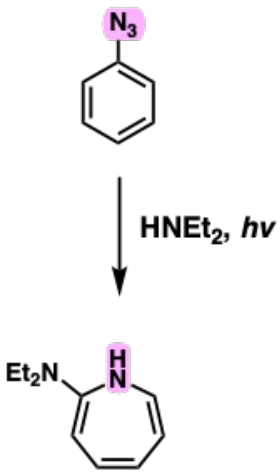
91%

Org. Lett. **2021**, *23*, 525-529.; *Org. Lett.* **2021** *23*, 4256-4260.; *JACS.* ***1972***, *94*, 513-520.; *Nature Chemistry* **2024**, *16*, 771-779.; *Tetrahedron* **2018**, *74*, 5351-5357.

Dearomative Expansions

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Aryl Azide to Azepine
(Brenner, 1971):



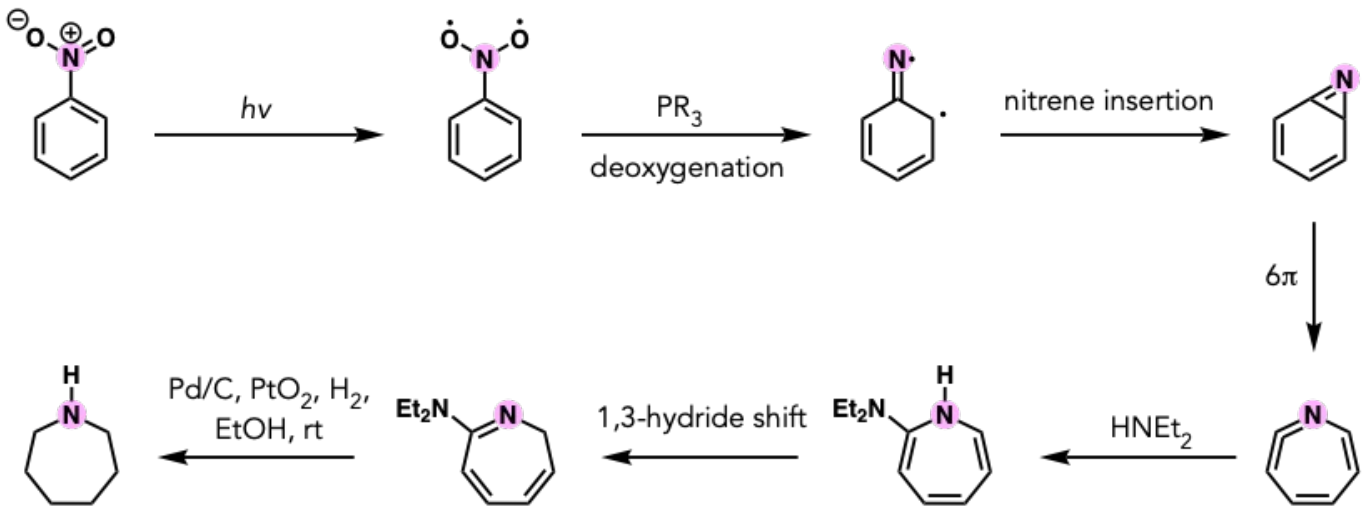
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Dearomative Expansions

Carbon: Synthesis of Azepines (Beeler, 2021 & Yoo, 2021)

Aryl Azide to Azepine (Brenner, 1971):

Nitrogen: Nitro Azide to Azepine or Azepane (Ruffoni & Leonori, 2024)



Org. Lett. **2021**, *23*, 525-529.; *Org. Lett.* **2021** *23*, 4256-4260.; *JACS.* ***1972***, *94*, 513-520.; *Nature Chemistry* **2024**, *16*, 771-779.; *Tetrahedron* **2018**, *74*, 5351-5357.

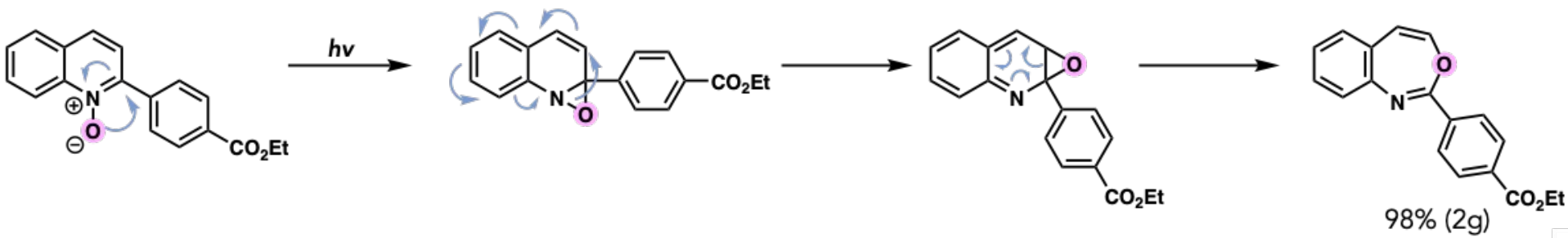
Dearomative Expansions

Carbon: Synthesis of Azepines (Beeler, 2021 & Yoo, 2021)

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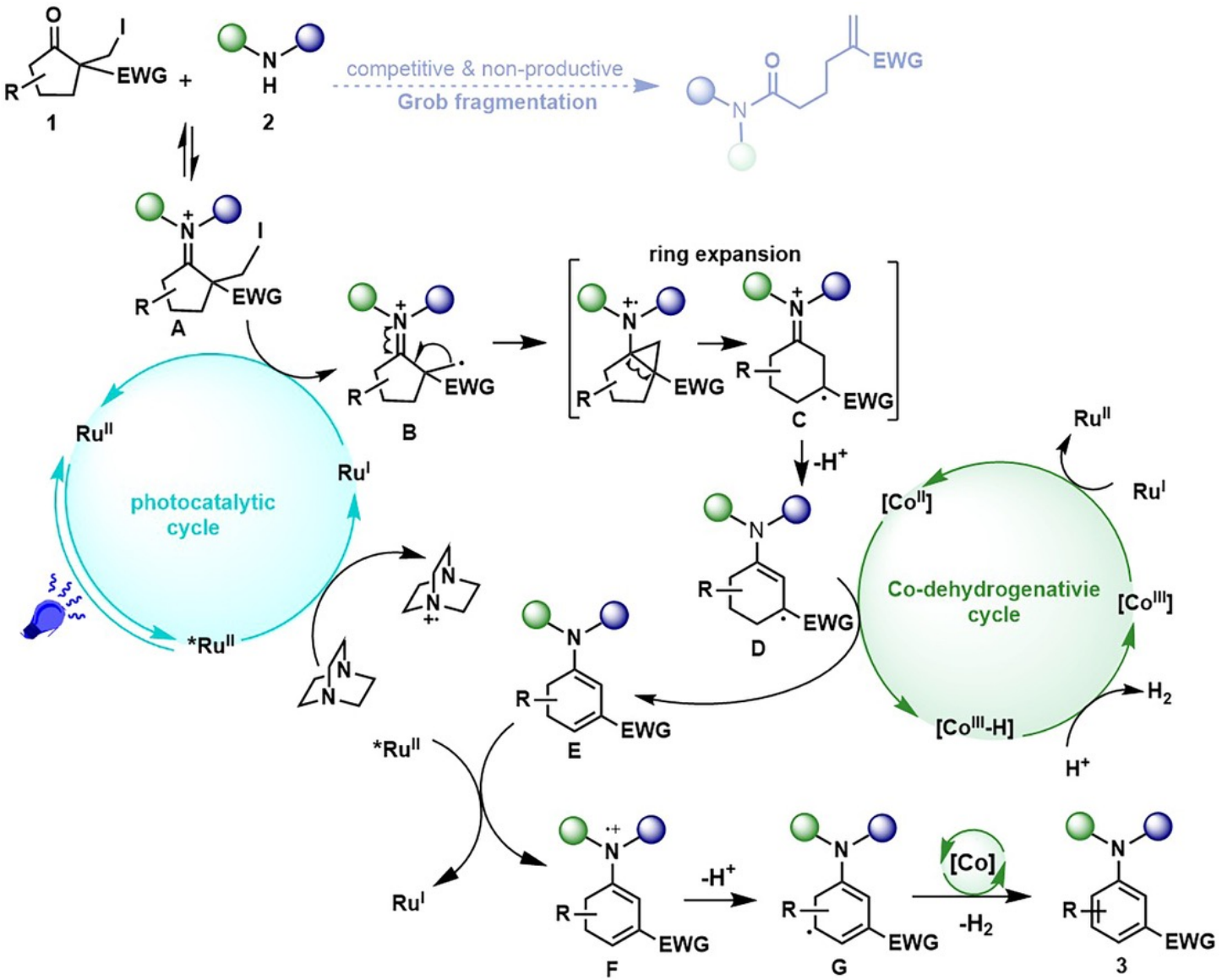
Oxygen: Synthesis of benzo[1,3]oxazepines (Smith, 2018)



Org. Lett. **2021**, *23*, 525-529.; *Org. Lett.* **2021** *23*, 4256-4260.; *JACS.* ***1972***, *94*, 513-520.; *Nature Chemistry* **2024**, *16*, 771-779.; *Tetrahedron* **2018**, *74*, 5351-5357.

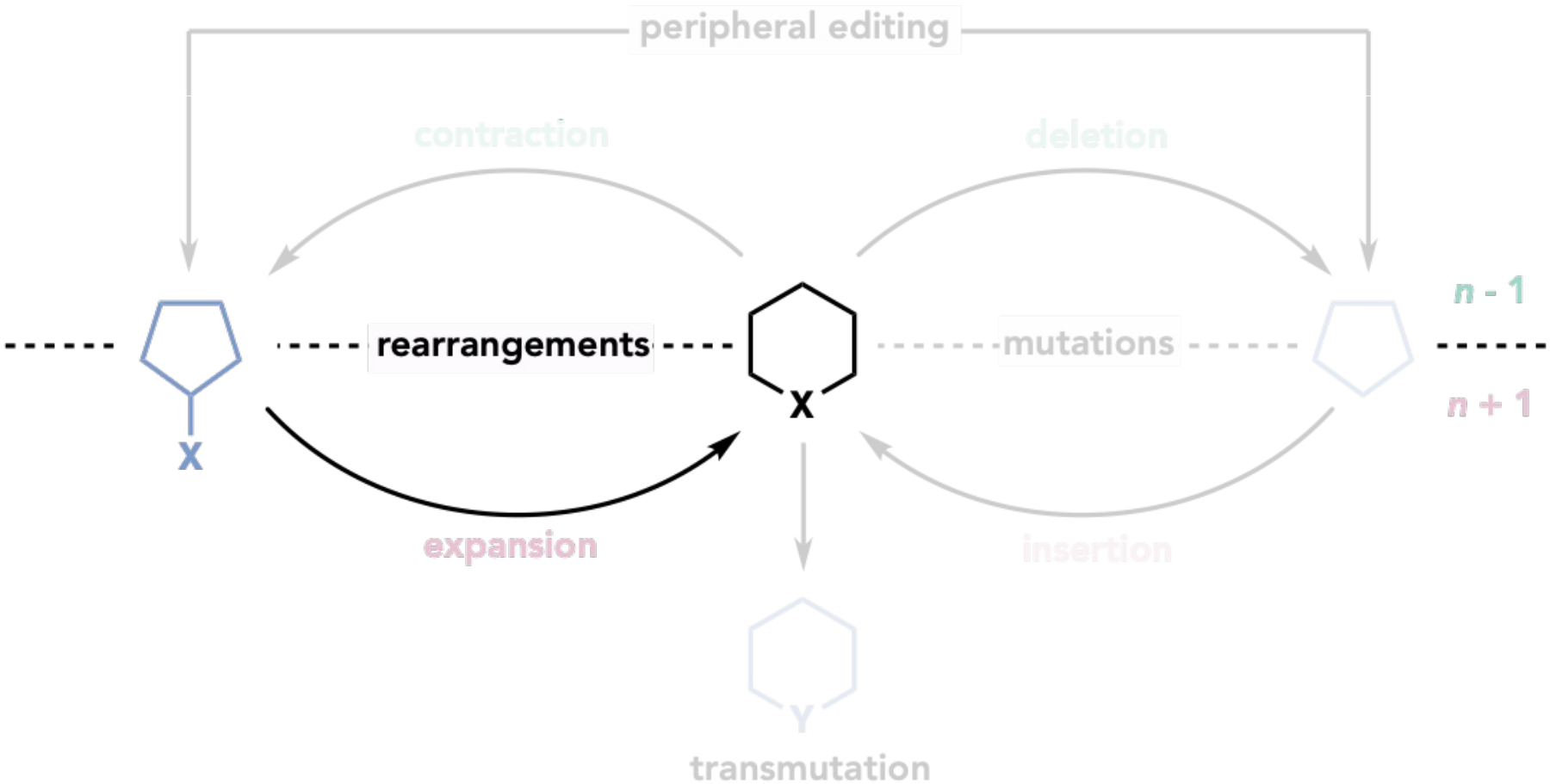
Aromative Expansions

Adding Carbon: Dehydrogenative Aromatization Strategy

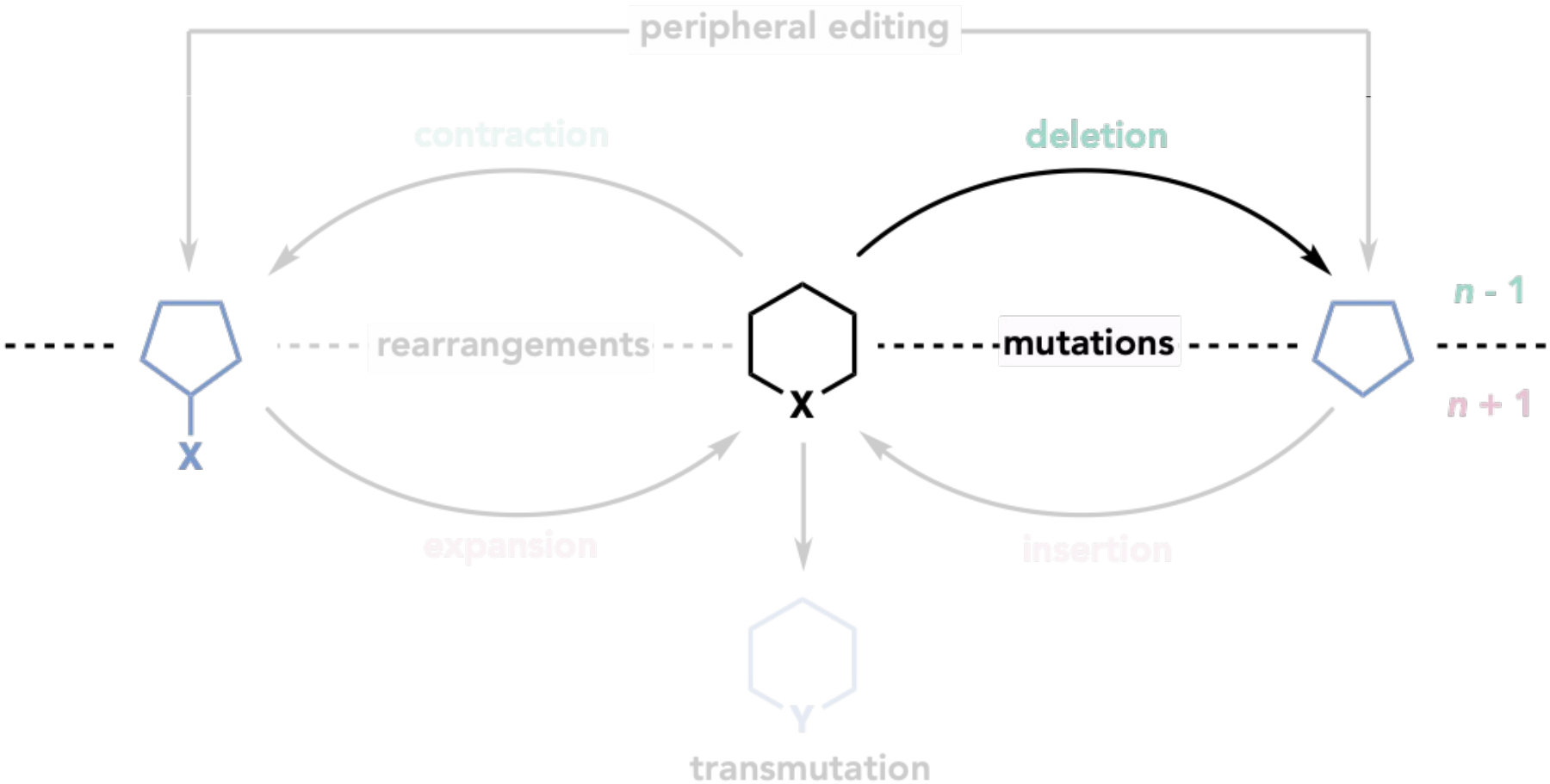


Chem. Cat. **2024**, *4*, 1100873.

Summary of Skeletal Editing

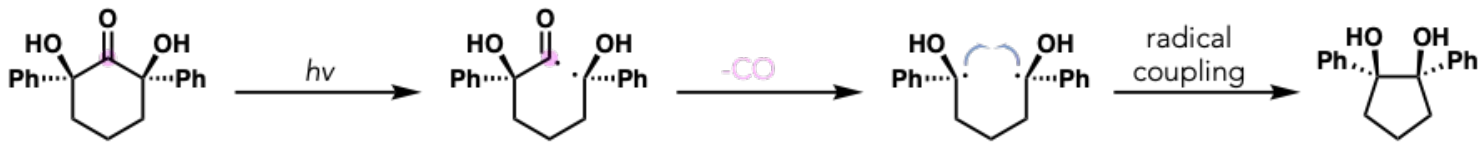


Summary of Skeletal Editing



Deletions of Saturated Rings
Carbonyl Deletion

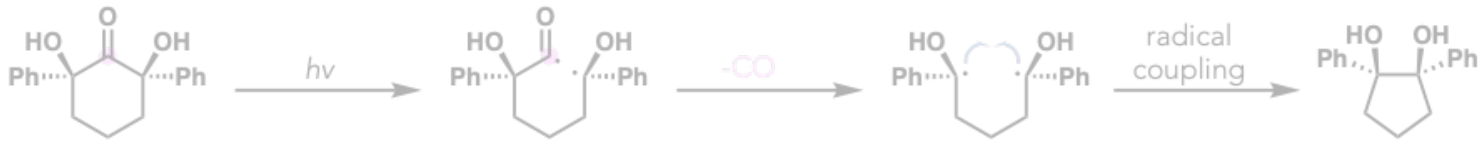
Photoinduced Decarbonylation on Crystalline Ketones (Garcia-Garibay, 1995)



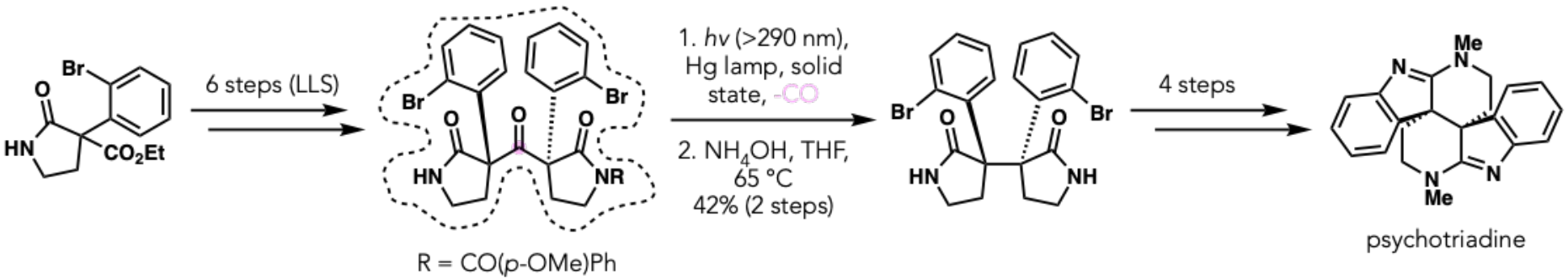
JACS **1995**, *117*, 12893-12894.; *JACS* **2020**, *142*, 11685-11690; *JACS* **2021**, *143*, 4043-4054.; *JACS* **2004**, *126*, 613-627.

Deletions of Saturated Rings
Carbonyl Deletion

Photoinduced Decarbonylation on Crystalline Ketones (Garcia-Garibay, 1995)



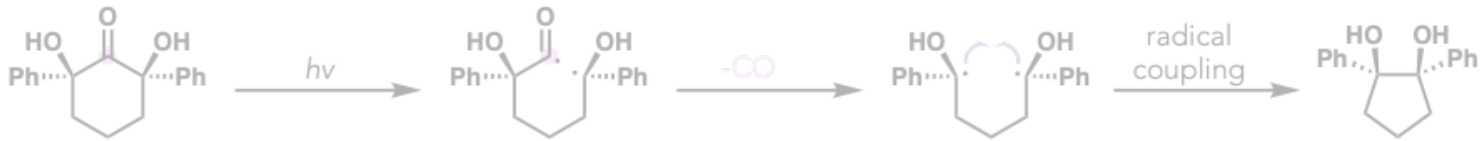
Synthesis of Psychotriadine (Garcia-Garibay & Garg & Houk, 2020 & 2021)



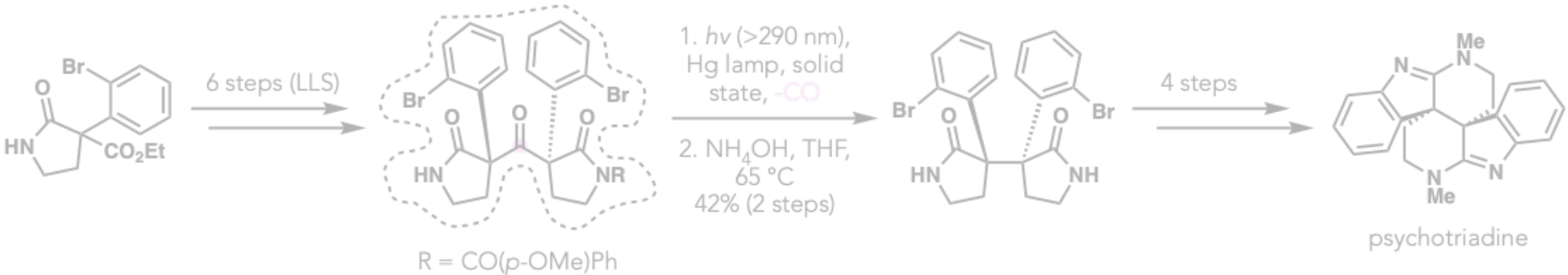
JACS **1995**, *117*, 12893-12894.; *JACS* **2020**, *142*, 11685-11690; *JACS* **2021**, *143*, 4043-4054.; *JACS* **2004**, *126*, 613-627.

Deletions of Saturated Rings
Carbonyl Deletion

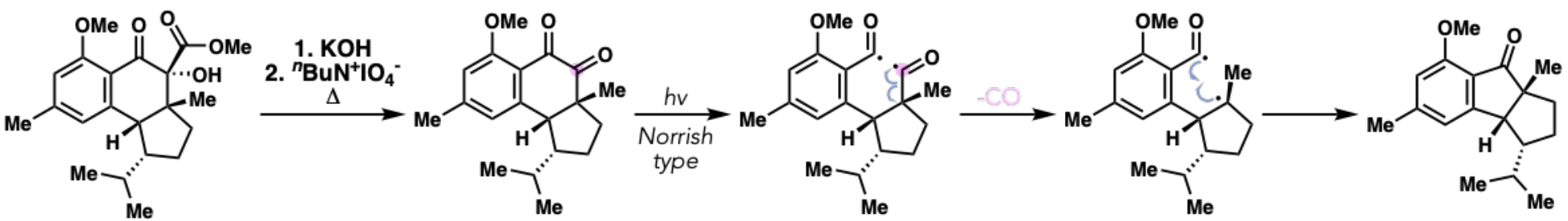
Photoinduced Decarbonylation on Crystalline Ketones (Garcia-Garibay, 1995)



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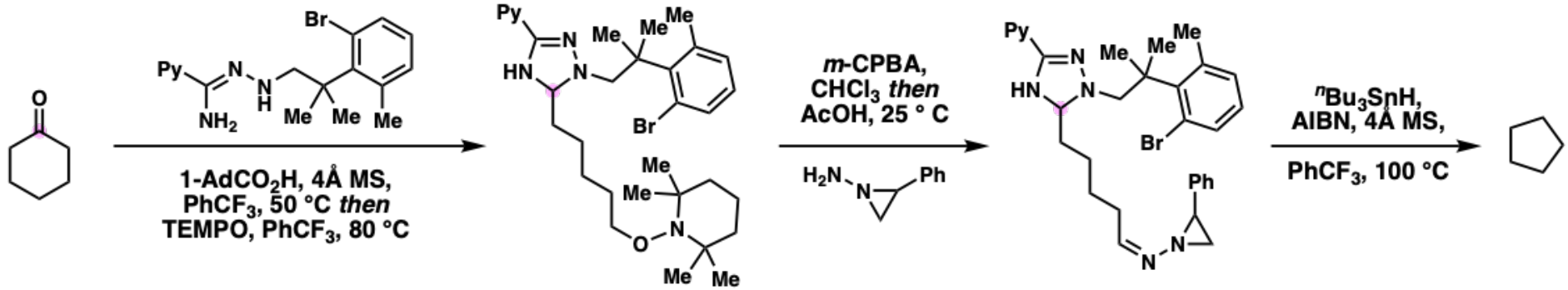
Unexpected Byproduct During Synthesis of Hamigerans (Nicolaou, 2004)



JACS **1995**, *117*, 12893-12894.; *JACS* **2020**, *142*, 11685-11690; *JACS* **2021**, *143*, 4043-4054.; *JACS* **2004**, *126*, 613-627.

Deletions of Saturated Rings
Carbonyl Deletion

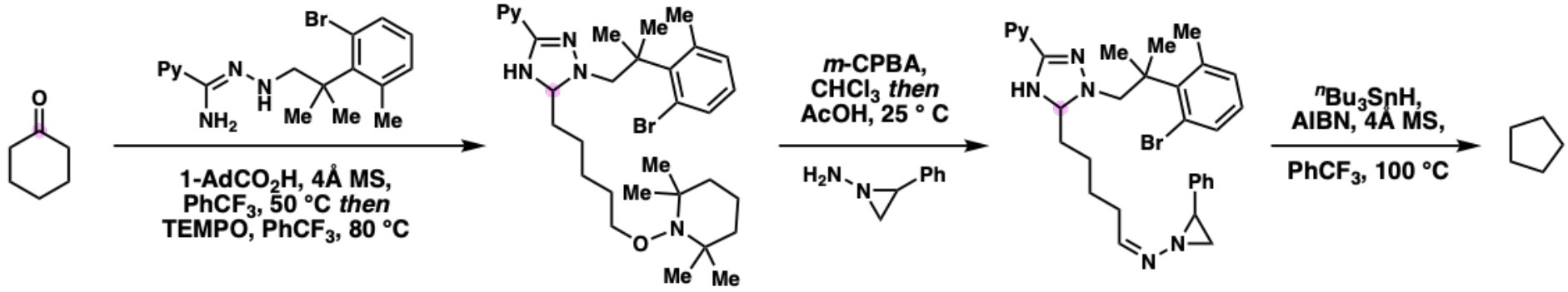
Carbonyl Removal via Sequential Double Carbon–Carbon Bond Cleavage (Dong, 2026)

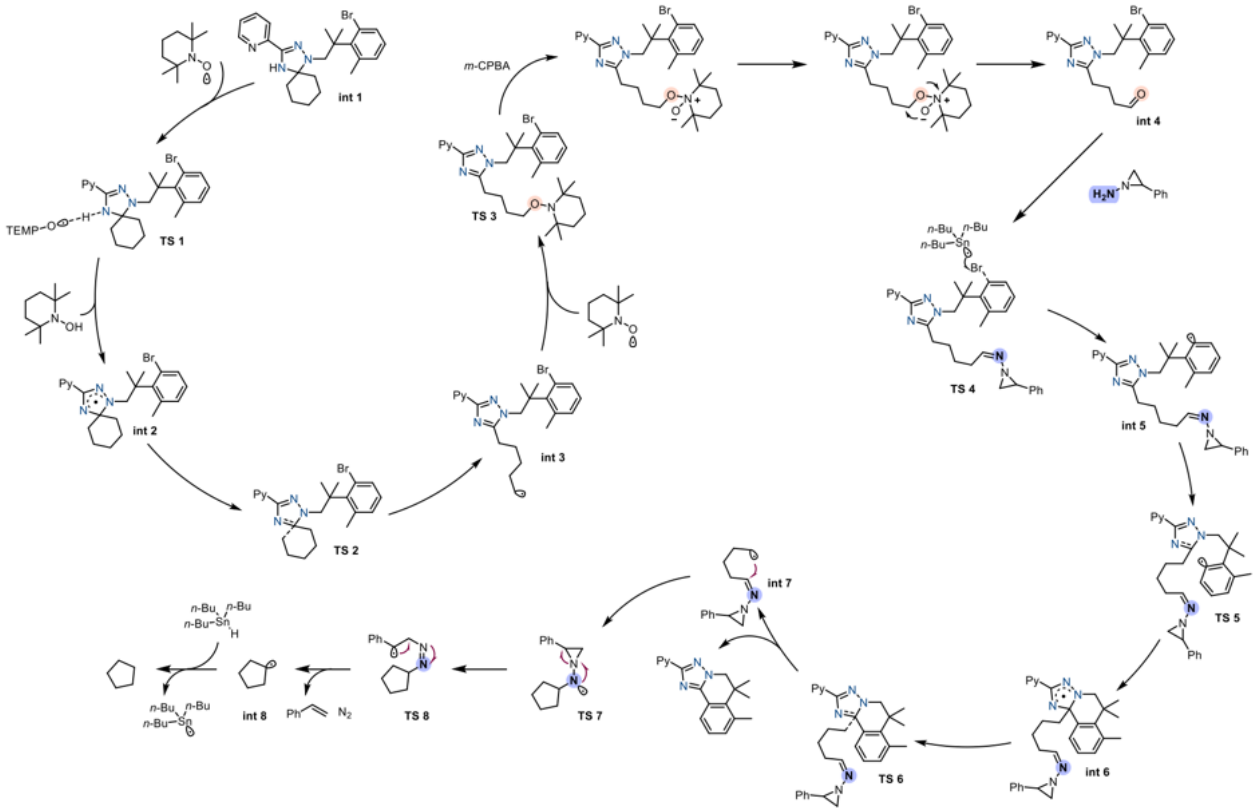


JACS, **2026**, *148*, 28061-28067.

Deletions of Saturated Rings
Carbonyl Deletion

Carbonyl Removal via Sequential Double Carbon–Carbon Bond Cleavage (Dong, 2026)





JACS, **2026**, *148*, 28061-28067.

Deletions of Saturated Rings
Carbon Deletion

Piperidine to Pyrrolidine (Sarpong, 2018)

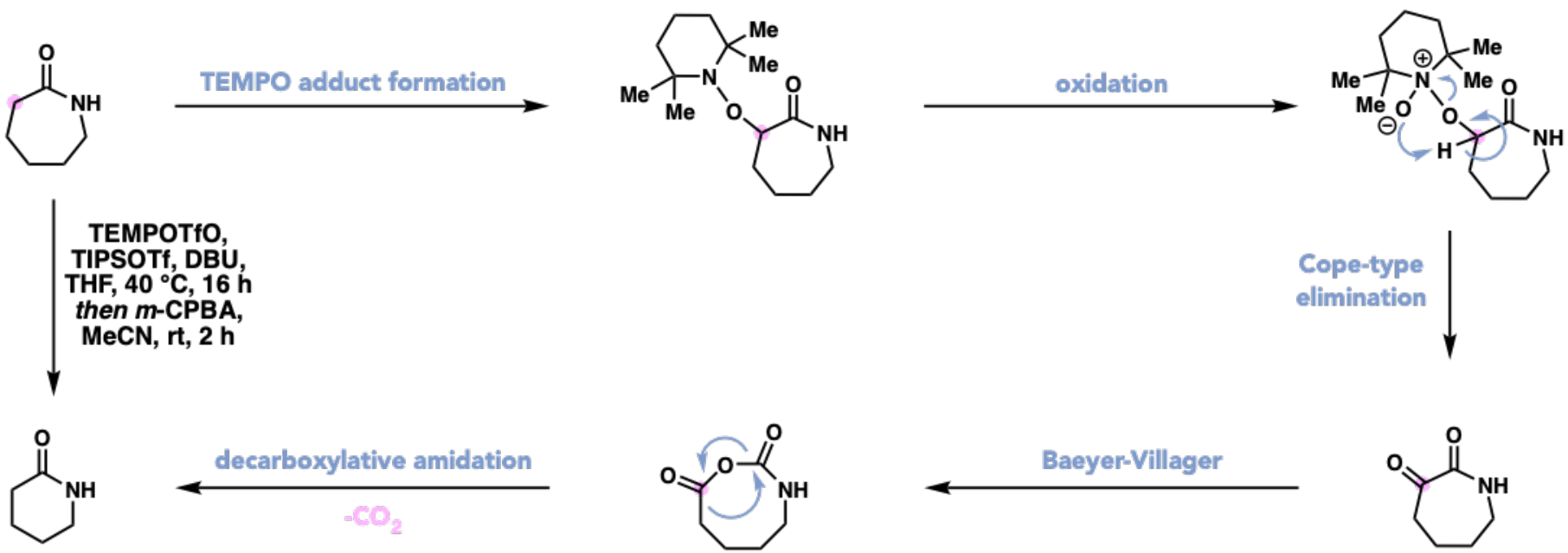


Nature **2018**, *564*, 244-248.; *JACS* **2026**, *148*, 282930-28301.

Deletions of Saturated Rings
Carbon Deletion

Piperidine to Pyrrolidine (Sarpong, 2018)

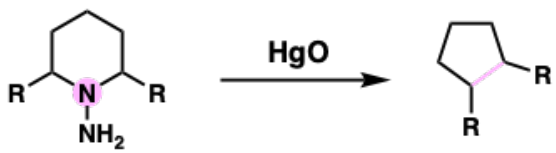
Methylene Deletion in Lactams (Dixon, 2026)



Nature **2018**, *564*, 244-248.; *JACS* **2026**, *148*, 282930-28301.

Deletions of Saturated Rings
Nitrogen Deletion

Original Harsh Report (Overberger, 1957)

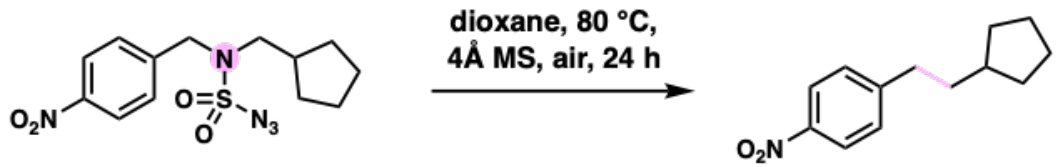


JACS **1957**, *79*, 6430-6435.; *JOC* **2017**, *82*, 4677-4688.; *Nature* **2021**, *2021*, 223-227.; *JACS* **2024**, *146*, 17719-17727.; *JACS* **2025**, *147*, 28179-28188.

Deletions of Saturated Rings
Nitrogen Deletion

Original Harsh Report (Overberger, 1957)

Thermal Rearrangement of Sulfamoyl Azides (Lu, 2017)



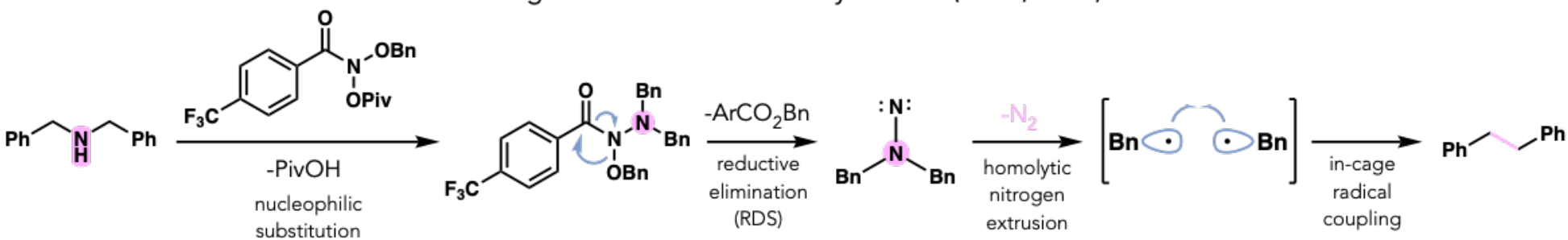
JACS **1957**, *79*, 6430-6435.; *JOC* **2017**, *82*, 4677-4688.; *Nature* **2021**, *2021*, 223-227.; *JACS* **2024**, *146*, 17719-17727.; *JACS* **2025**, *147*, 28179-28188.

Deletions of Saturated Rings
Nitrogen Deletion

Original Harsh Report (Overberger, 1957)

Thermal Rearrangement of Sulfamoyl Azides (Lu, 2017)

Nitrogen Deletion of Secondary Amines (Levin, 2021)



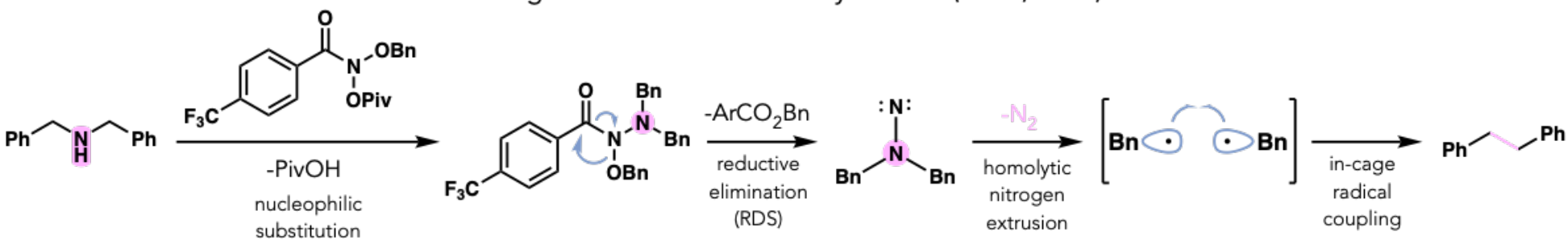
JACS **1957**, *79*, 6430-6435.; *JOC* **2017**, *82*, 4677-4688.; *Nature* **2021**, *2021*, 223-227.; *JACS* **2024**, *146*, 17719-17727.; *JACS* **2025**, *147*, 28179-28188.

Deletions of Saturated Rings
Nitrogen Deletion

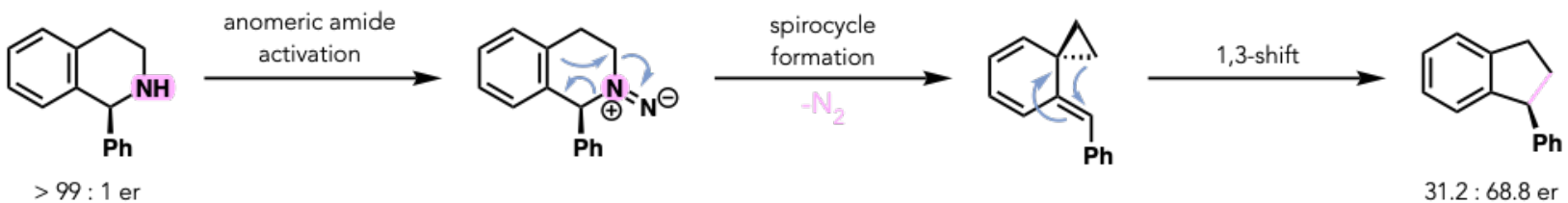
Original Harsh Report (Overberger, 1957)

Thermal Rearrangement of Sulfamoyl Azides (Lu, 2017)

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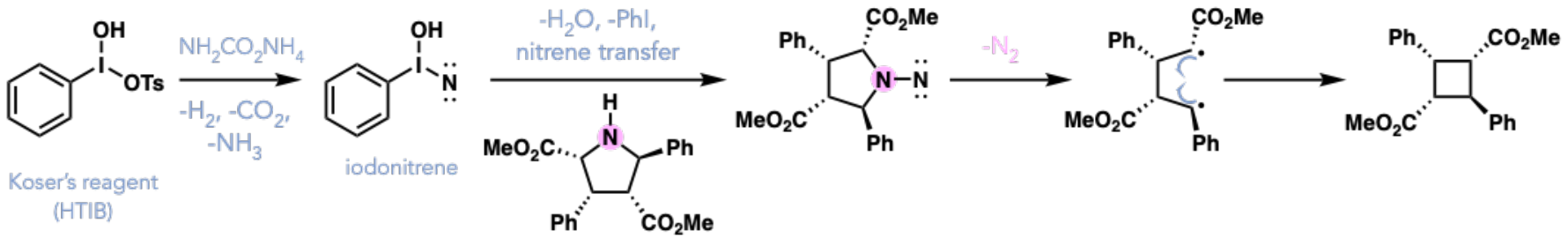
Evidence for Spriocyclization in Tetrahydroisoquinolines (Levin, 2024)



JACS **1957**, *79*, 6430-6435.; *JOC* **2017**, *82*, 4677-4688.; *Nature* **2021**, *2021*, 223-227.; *JACS* **2024**, *146*, 17719-17727.; *JACS* **2025**, *147*, 28179-28188.

Deletions of Saturated Rings
Nitrogen Deletion

Pyrrolidines to Cyclobutanes (Antonchick, 2021)

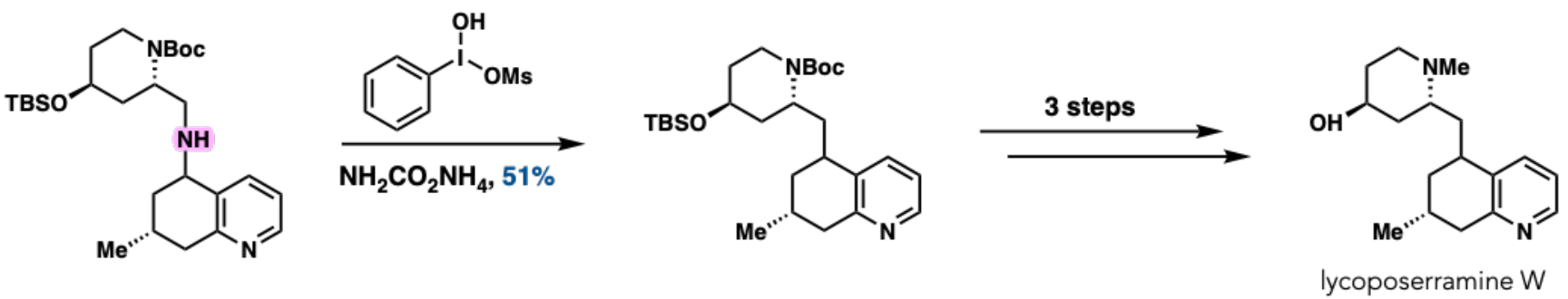


JACS **2021**, *143*, 18864-18870.; *Nature Commun*. **2025**, *16*, 1659.

Deletions of Saturated Rings
Nitrogen Deletion

Pyrrolidines to Cyclobutanes (Antonchick, 2021)

Total Synthesis of Lycoposerramine W (Renata, 2025)

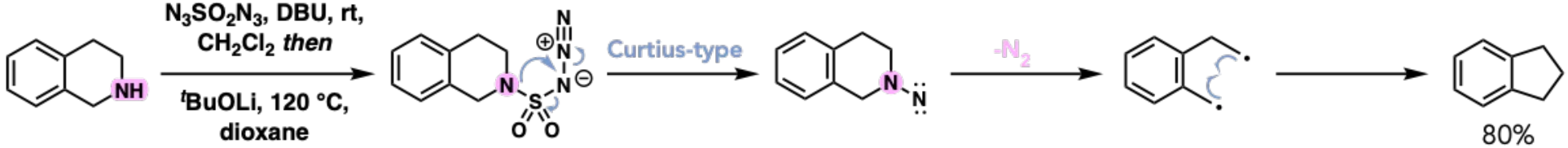


lycoposerramine W

JACS **2021**, *143*, 18864-18870.; *Nature Commun*. **2025**, *16*, 1659.

Deletions of Saturated Rings
Nitrogen Deletion

Thermal Rearrangement of Sulfamoyl Azides (Lu, 2021)

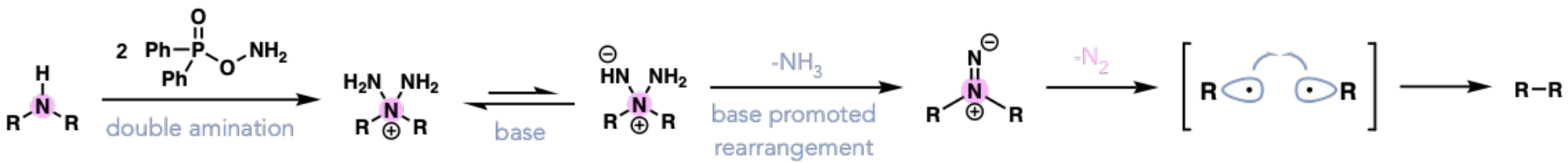


ACIE **2021**, *60*, 20678-20683.; *Nature Synthesis* **2024**, *3*, 913-921.; *JACS* **2023**, *145*, 10960-10966.; *ACS Catal.* **2025**, *15*, 5825-5834.; *Nature Chemistry* **2025**, *17*, 393-402.; *JACS* **2017**, *139*, 6546-6549.

Deletions of Saturated Rings
Nitrogen Deletion

Thermal Rearrangement of Sulfamoyl Azides (Lu, 2021)

Use of *O*-diphenylphosphinylhydroxylamine (Lu, 2024)



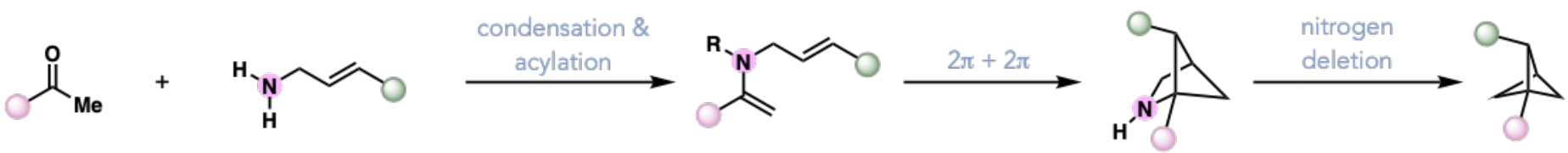
ACIE **2021**, *60*, 20678-20683.; *Nature Synthesis* **2024**, *3*, 913-921.; *JACS* **2023**, *145*, 10960-10966.; *ACS Catal.* **2025**, *15*, 5825-5834.; *Nature Chemistry* **2025**, *17*, 393-402.; *JACS* **2017**, *139*, 6546-6549.

Deletions of Saturated Rings
Nitrogen Deletion

Thermal Rearrangement of Sulfamoyl Azides (Lu, 2021)

Use of *O*-diphenylphosphinylhydroxylamine (Lu, 2024)

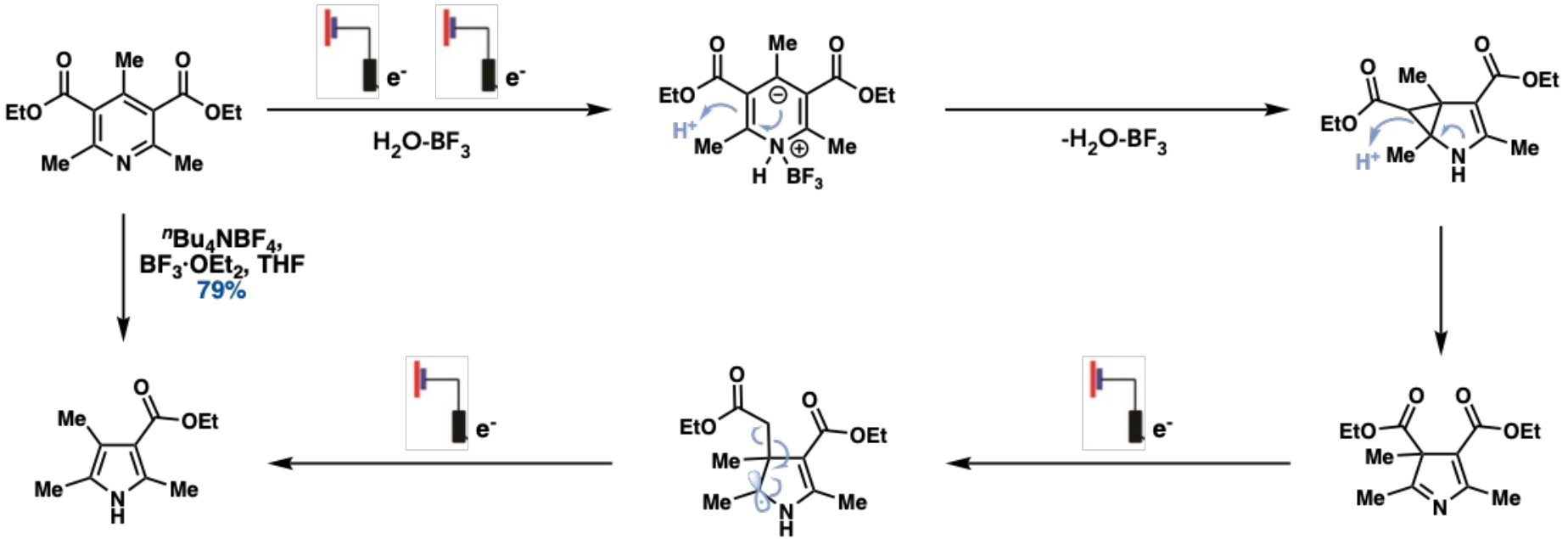
Synthesis of Bicyclopentanes (Sarpong & Lu & Ding & Tan, 2023 & 2025)



ACIE **2021**, *60*, 20678-20683.; *Nature Synthesis* **2024**, *3*, 913-921.; *JACS* **2023**, *145*, 10960-10966.; *ACS Catal.* **2025**, *15*, 5825-5834.; *Nature Chemistry* **2025**, *17*, 393-402.; *JACS* **2017**, *139*, 6546-6549.

Deletions of Aromatic Rings
Carbon Deletion

Electrochemical Carbon Deletion in Hantzsch Esters (Cheng, 2021)

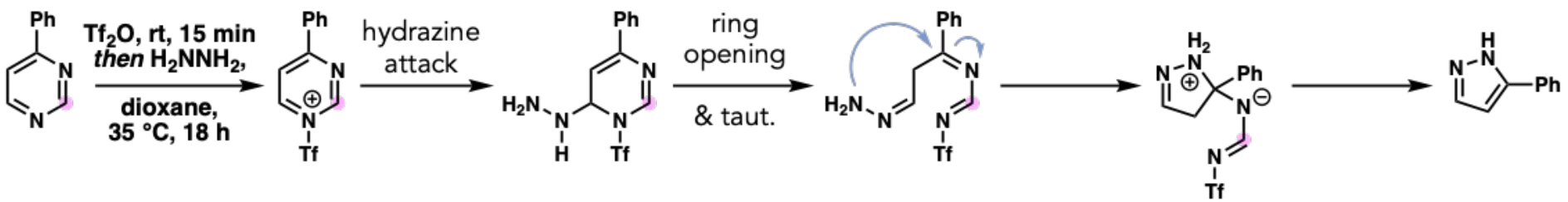


Green Chem. **2021**, *23*, 3468-3473.; *JACS* **2022**, *144*, 22309-22315.

Deletions of Aromatic Rings
Carbon Deletion

Electrochemical Carbon Deletion in Hantzsch Esters (Cheng, 2021)

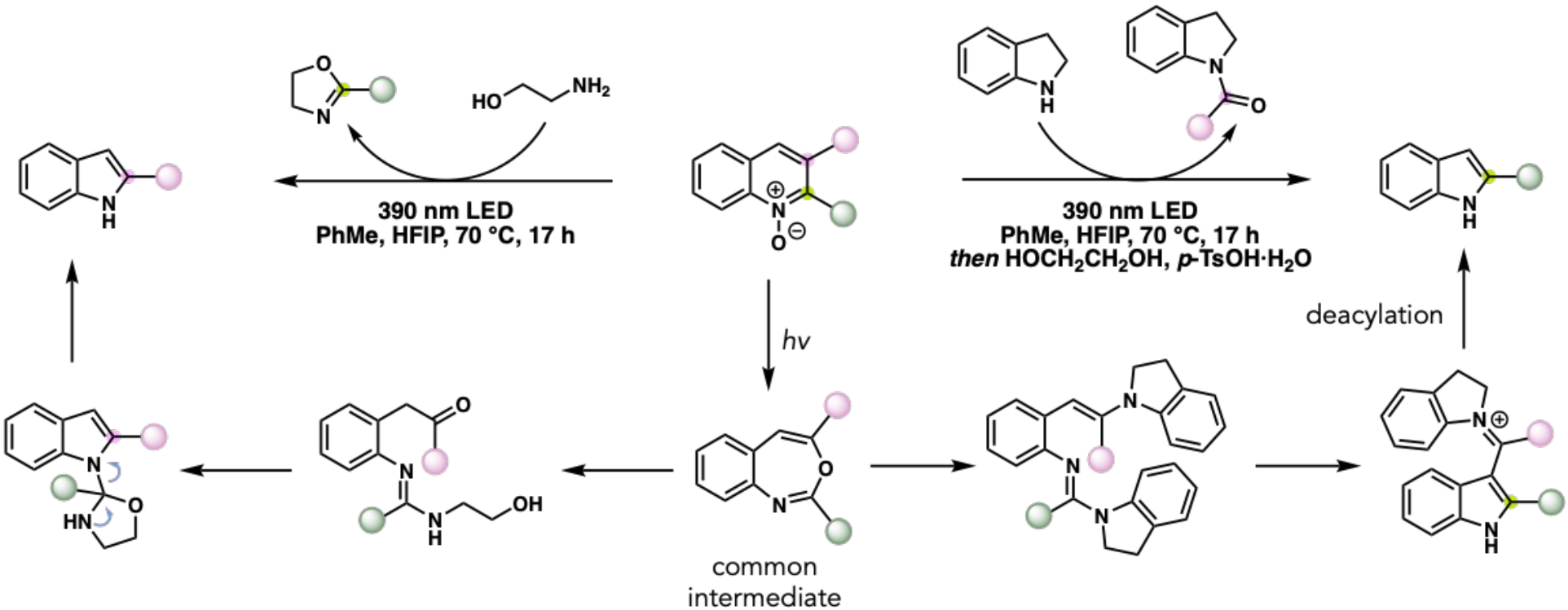
Pyrimidines to Pyrazoles by Formal Carbon Deletion (Sarpong, 2022)



Green Chem. **2021**, *23*, 3468-3473.; *JACS* **2022**, *144*, 22309-22315.

Deletions of Aromatic Rings
Carbon Deletion

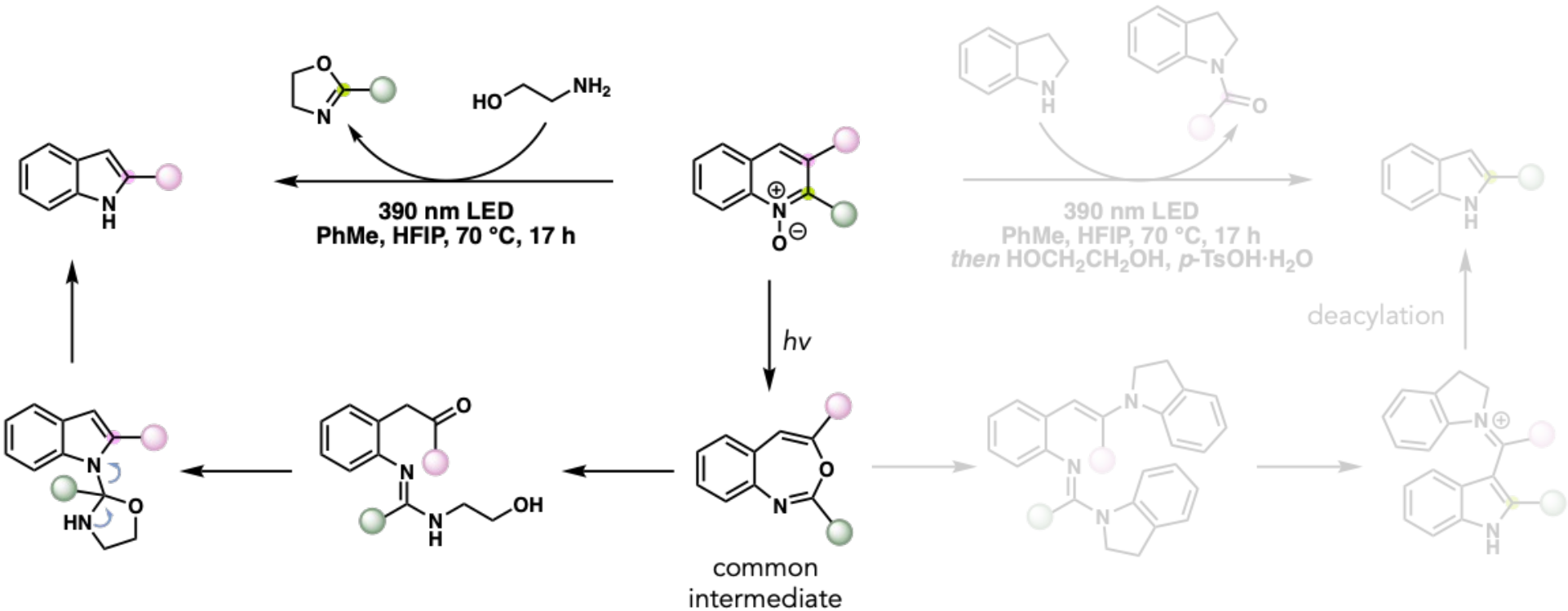
Selective Carbon Deletion of Azarenes (Levin, 2025)



JACS **2025**, *147*, 20120-20131.; *JACS* **2024**, *146*, 31348-31355.

Deletions of Aromatic Rings
Carbon Deletion

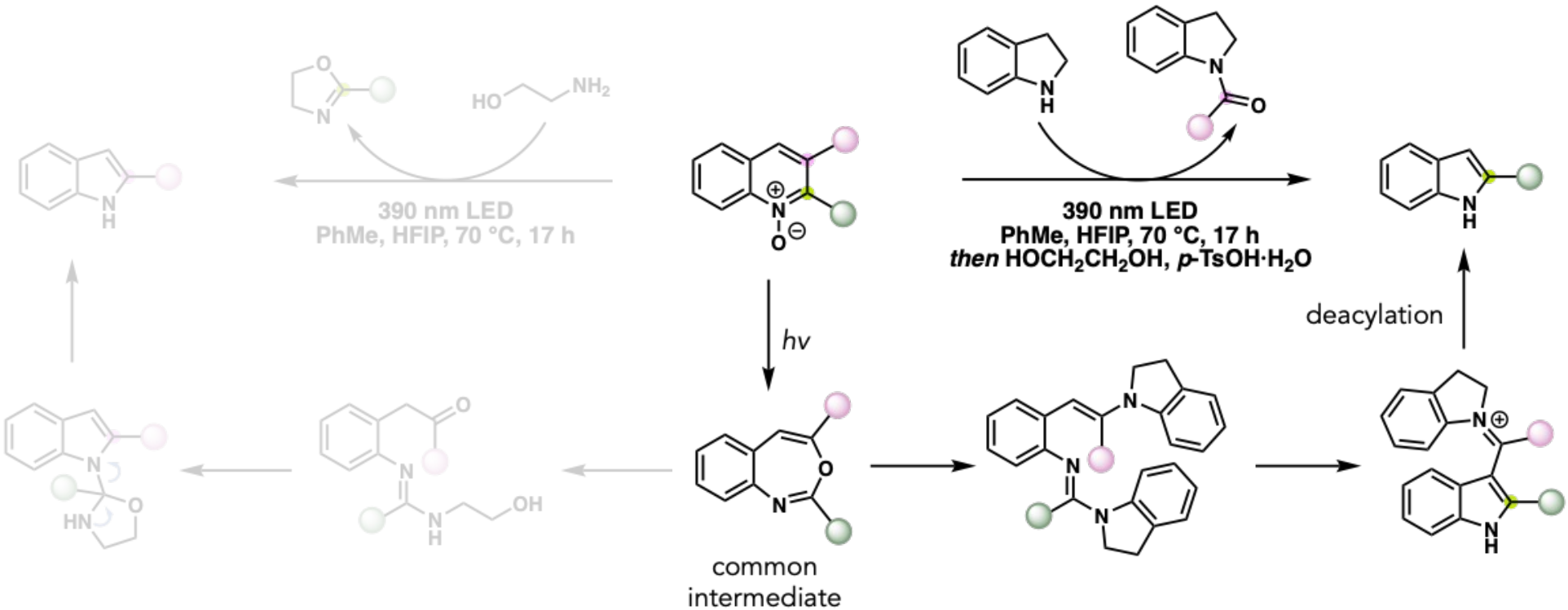
Selective Carbon Deletion of Azarenes (Levin, 2025)



JACS **2025**, *147*, 20120-20131.; *JACS* **2024**, *146*, 31348-31355.

Deletions of Aromatic Rings
Carbon Deletion

Selective Carbon Deletion of Azarenes (Levin, 2025)

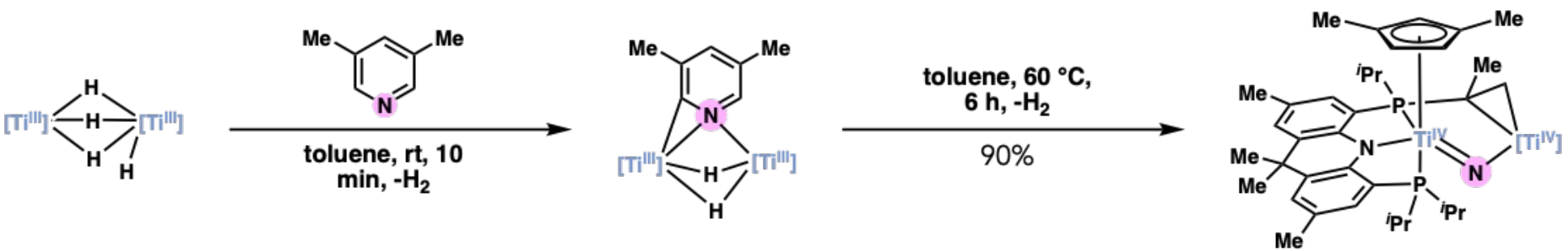


JACS **2025**, *147*, 20120-20131.; *JACS* **2024**, *146*, 31348-31355.

Deletions of Aromatic Rings
Carbon Deletion

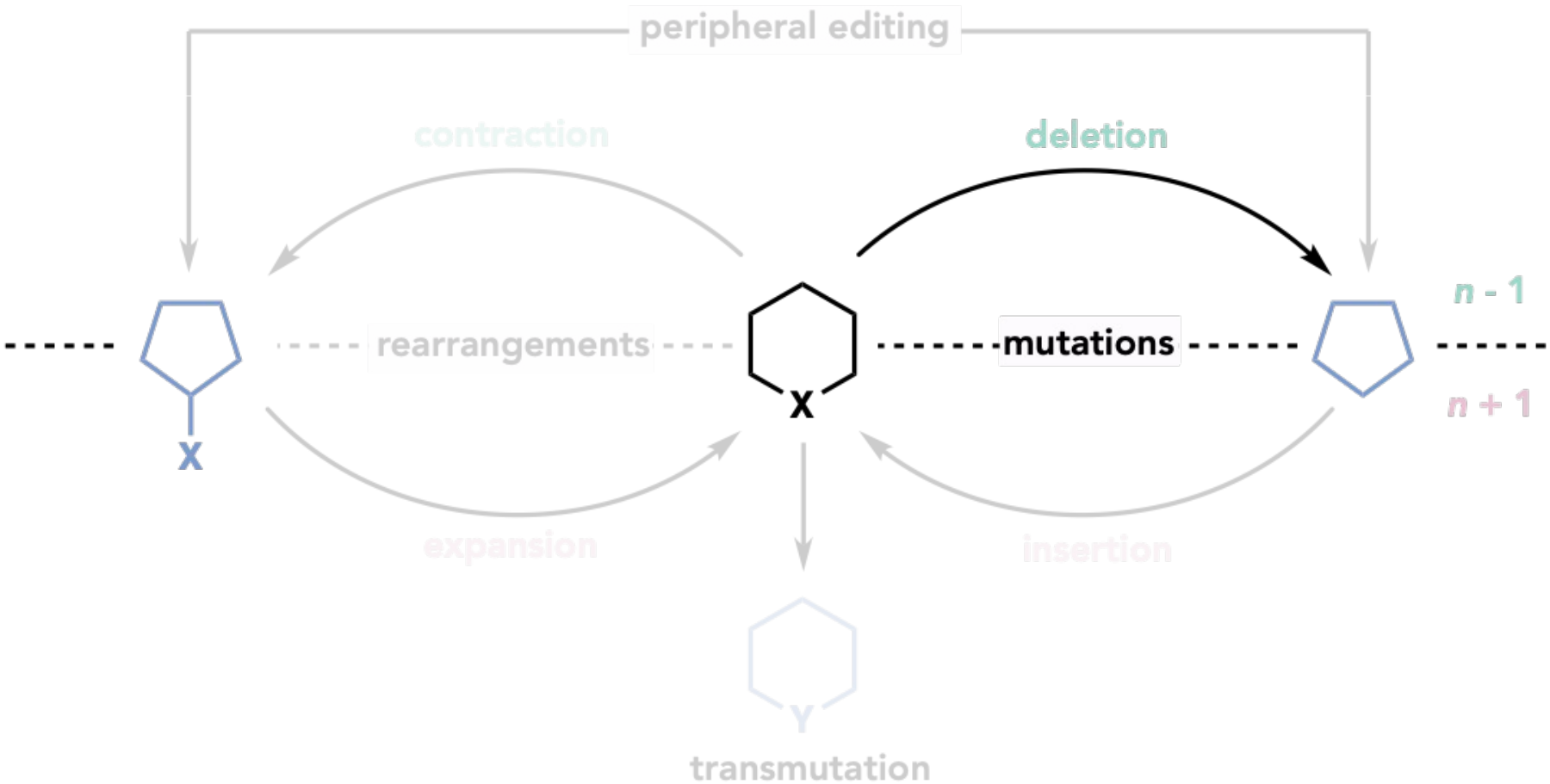
Selective Carbon Deletion of Azarenes (Levin, 2025)

Nitrogen Deletion Remains Elusive (Shima & Kang & Hou, 2024)

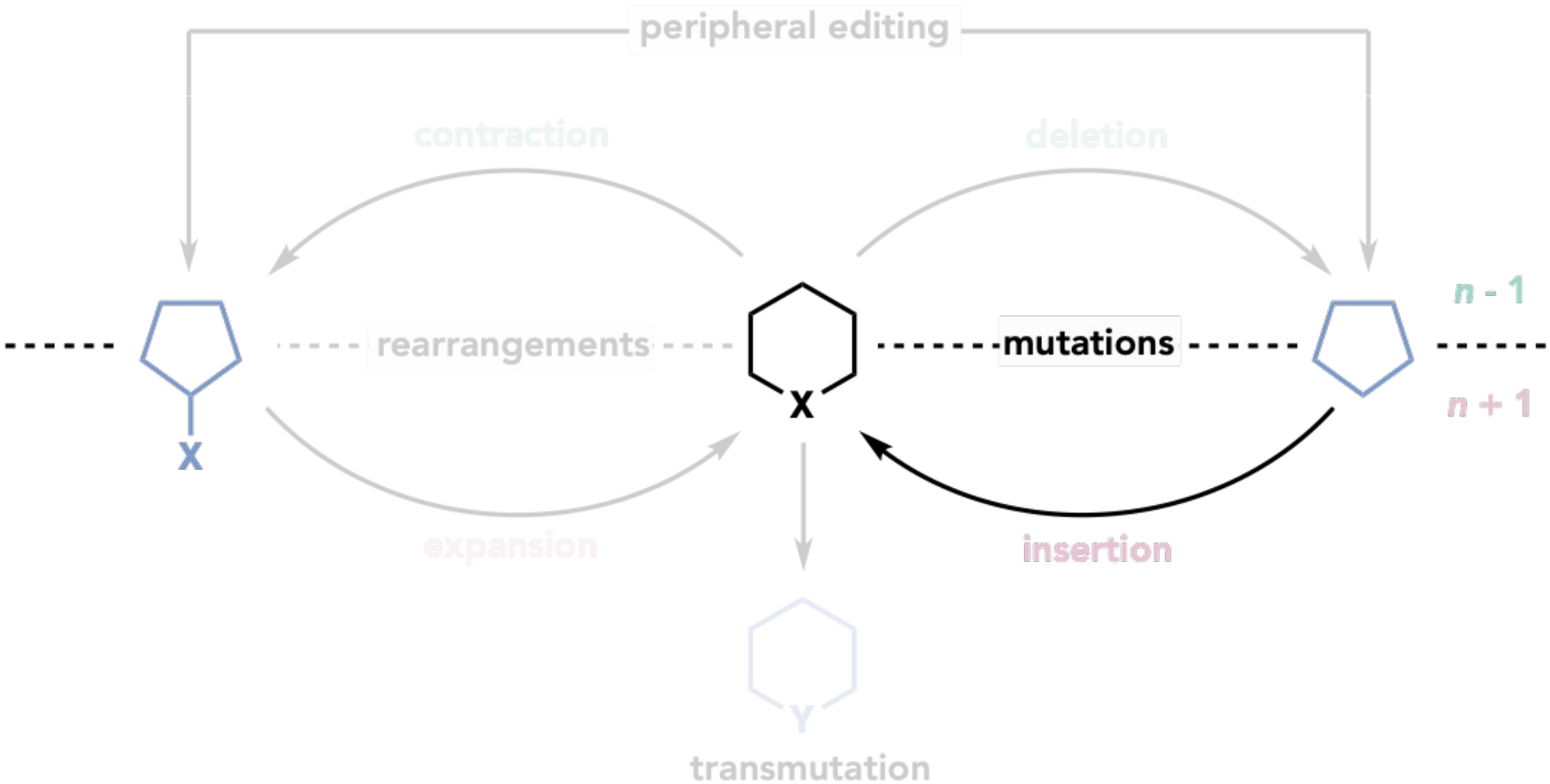


JACS **2025**, *147*, 20120-20131.; *JACS* **2024**, *146*, 31348-31355.

Summary of Skeletal Editing



Summary of Skeletal Editing



Insertions of Saturated Rings
Boron Insertion

Boron Insertion into Alkyl Ether Bonds (Dong, 2021)

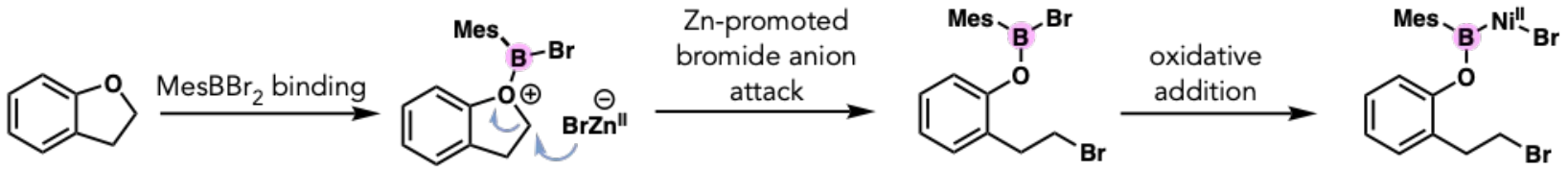


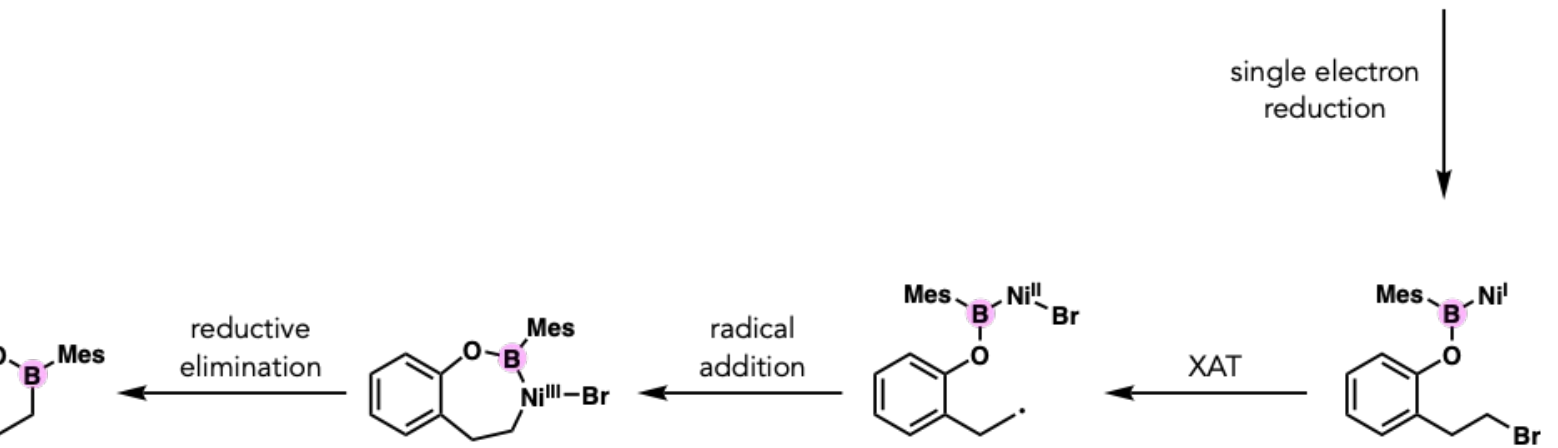
Science **2021**, *372*, 175-182.

Insertions of Saturated Rings
Boron Insertion

Boron Insertion into Alkyl Ether Bonds (Dong, 2021)





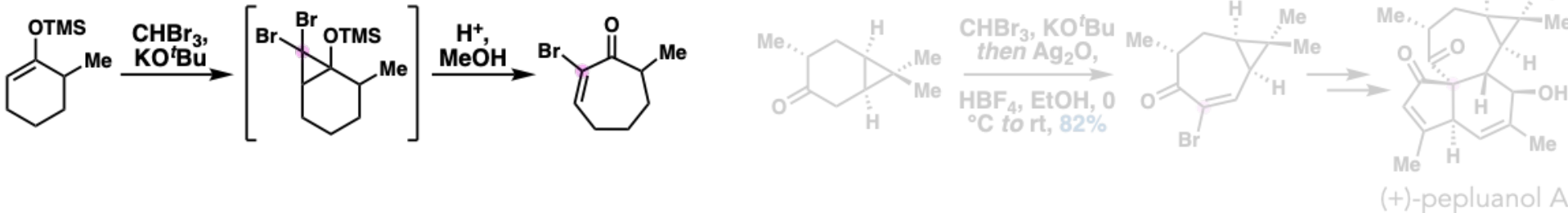


Note: also applied to *O*-to-*N* transmutation

Science **2021**, *372*, 175-182.

Insertions of Saturated Rings
Carbon Insertion

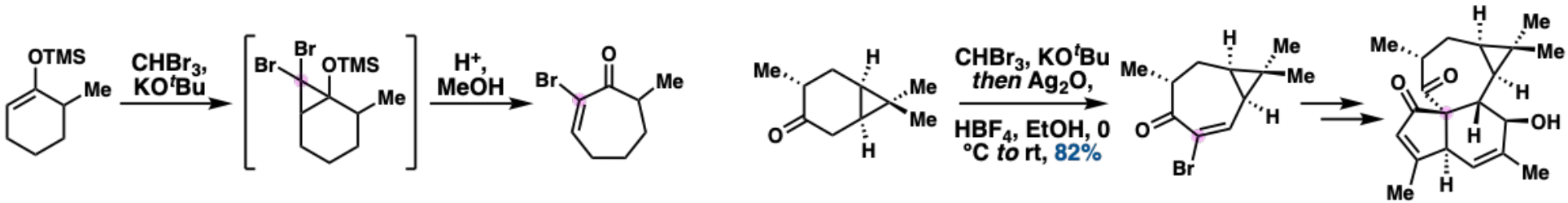
Halocarbene Cyclopropanation (Conia, 1976 & Gaich, 2021)



Synthesis **1976**, *3*, 196-197.; *JACS* **2021**, *143*, 11934-11938.; *Adv. Synth. Catal.* **2009**, *351*, 308-312.; *Chem. Sci.* **2019**, *10*, 10129-10134.; *JACS*, **2021**, *143*, 12968-12973.; *JACS*, **2025**, *147*, 33879-33887.; *JACS*, **2022**, *144*, 4739-4745.; *ACIE* **2024**, *63*, e202318072.

Insertions of Saturated Rings
Carbon Insertion

Halocarbene Cyclopropanation (Conia, 1976 & Gaich, 2021)



(+)-pepluanol A

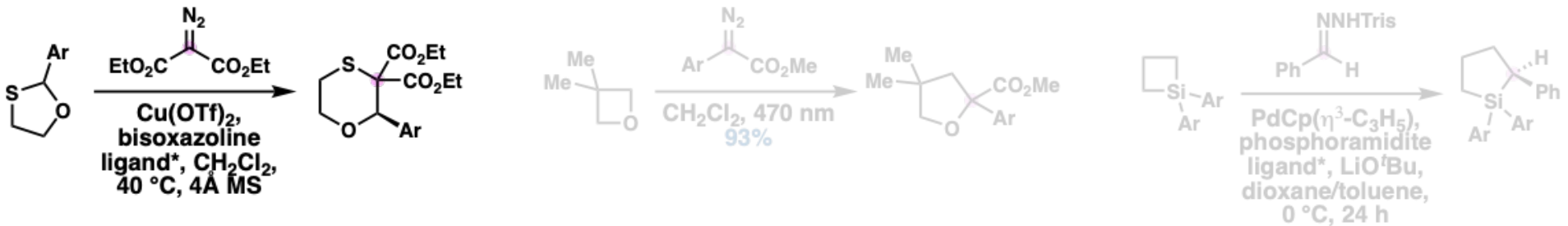
Synthesis **1976**, *3*, 196-197.; *JACS* **2021**, *143*, 11934-11938.; *Adv. Synth. Catal.* **2009**, *351*, 308-312.; *Chem. Sci.* **2019**, *10*, 10129-10134.; *JACS*, **2021**, *143*, 12968-12973.; *JACS*, **2025**, *147*, 33879-33887.; *JACS*, **2022**, *144*, 4739-4745.; *ACIE* **2024**, *63*, e202318072.

Insertions of Saturated Rings
Carbon Insertion

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(+)-pepluanol A

Carbene Insertion into Sulfur Ylides (Tang, 2008); Oxetanes (Xu & Koenigs, 2019); C–Si Bonds (Lan & Wang, 2021)



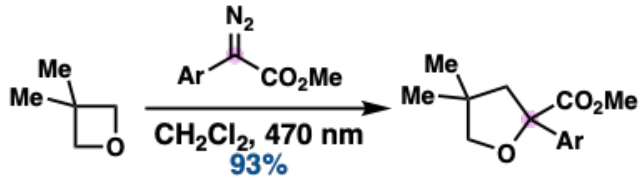
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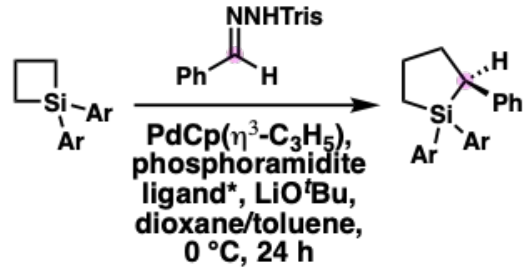
Synthesis **1976**, *3*, 196-197.; *JACS* **2021**, *143*, 11934-11938.; *Adv. Synth. Catal.* **2009**, *351*, 308-312.; *Chem. Sci.* **2019**, *10*, 10129-10134.; *JACS*, **2021**, *143*, 12968-12973.; *JACS*, **2025**, *147*, 33879-33887.; *JACS*, **2022**, *144*, 4739-4745.; *ACIE* **2024**, *63*, e202318072.

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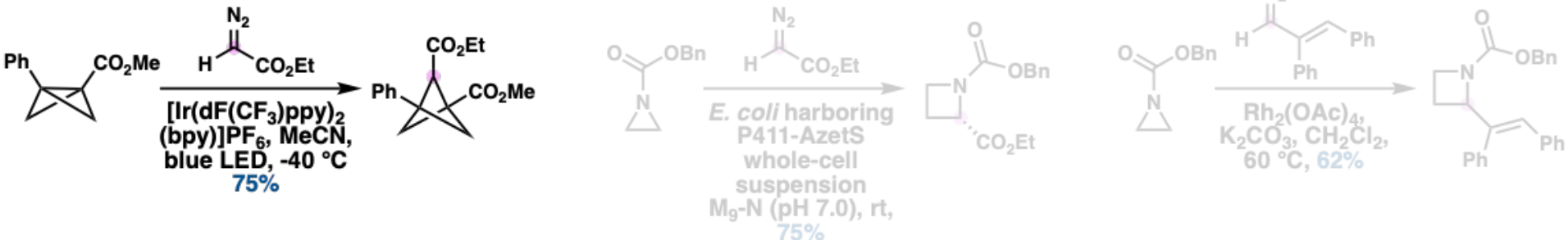
Insertions of Saturated Rings
Carbon Insertion

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Synthesis **1976**, *3*, 196-197.; *JACS* **2021**, *143*, 11934-11938.; *Adv. Synth. Catal.* **2009**, *351*, 308-312.; *Chem. Sci.* **2019**, *10*, 10129-10134.; *JACS*, **2021**, *143*, 12968-12973.; *JACS*, **2025**, *147*, 33879-33887.; *JACS*, **2022**, *144*, 4739-4745.; *ACIE* **2024**, *63*, e202318072.

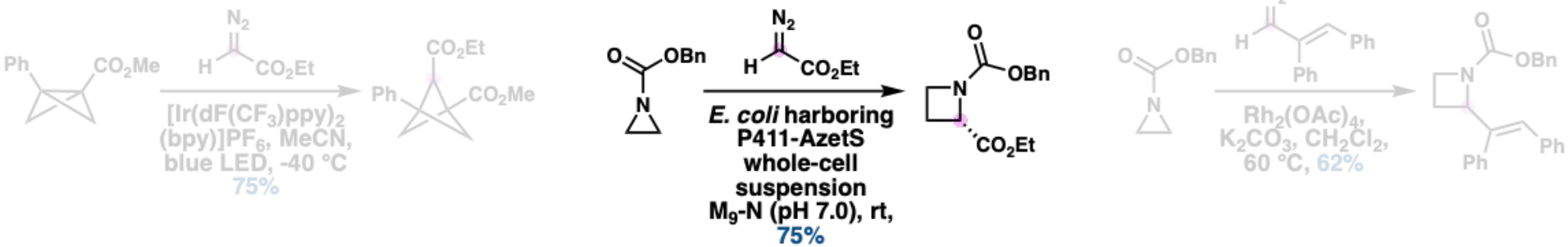
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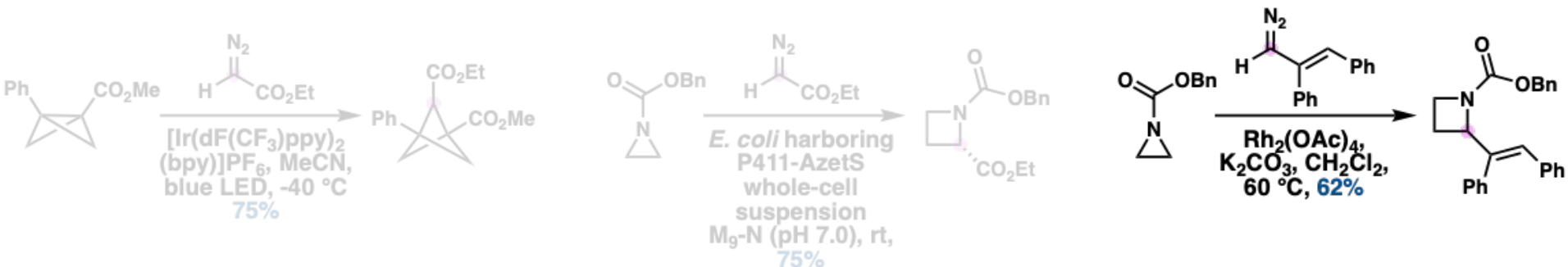
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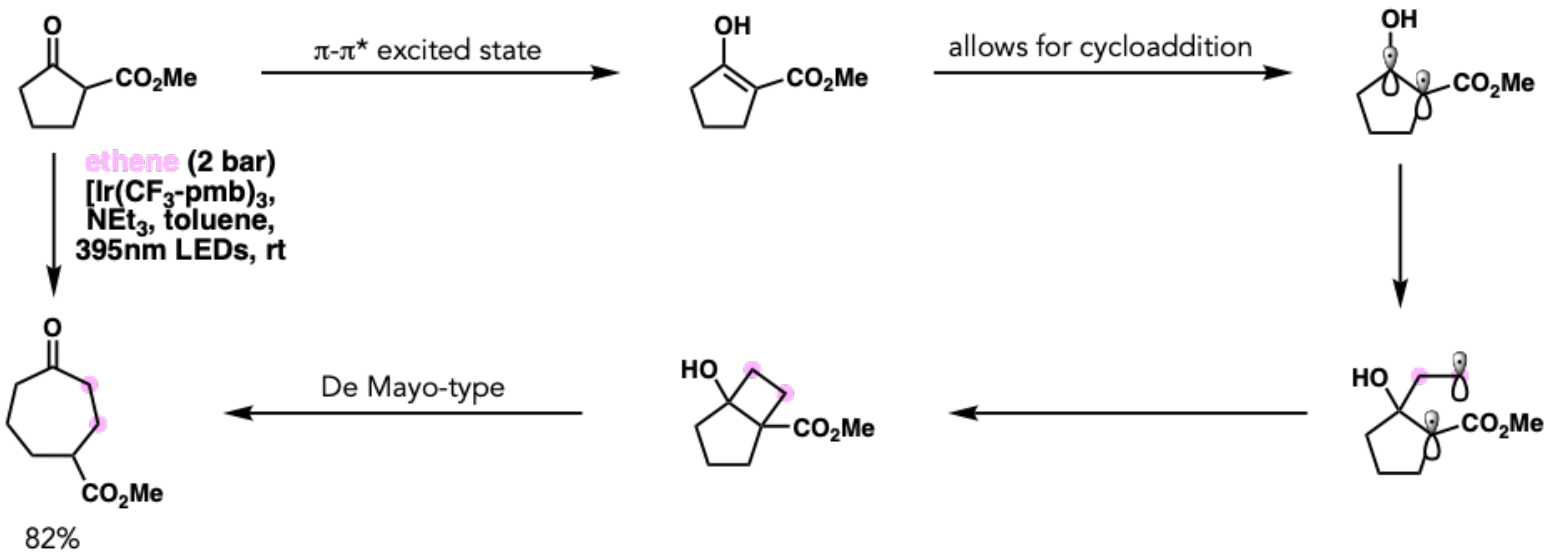
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Insertions of Saturated Rings
Carbon Insertion

De Mayo-Type Two-Carbon Insertion (Glorius, 2021)

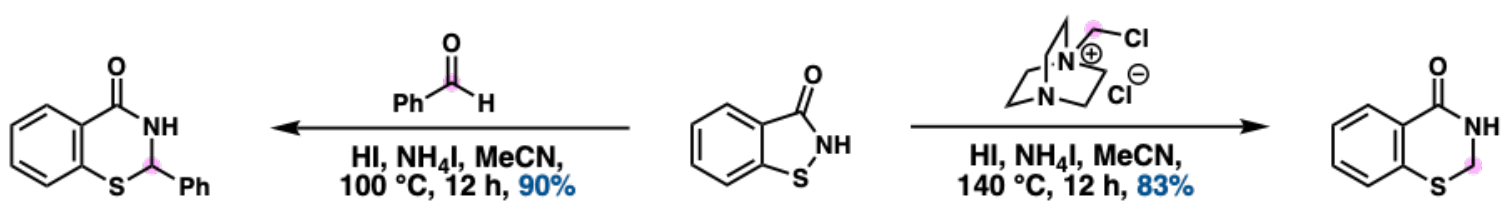


ACIE, **2022**, *61*, e202112695.; *Org. Chem. Front.* **2025**, *12*, 478-484.

Insertions of Saturated Rings
Carbon Insertion

De Mayo-Type Two-Carbon Insertion (Glorius, 2021)

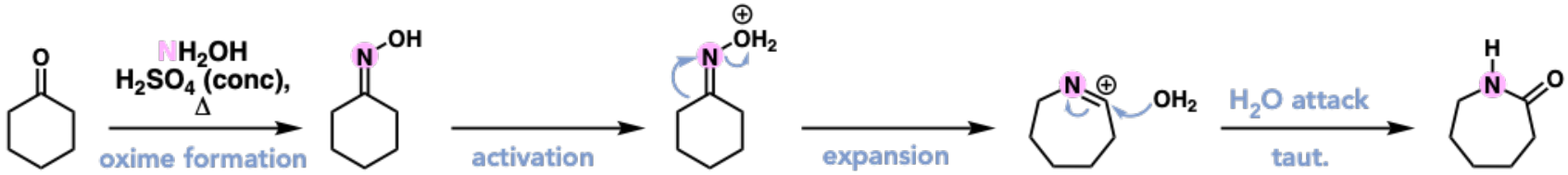
Transition Metal Free Single Carbon Insertion (Yang & Li, 2025)



ACIE, **2022**, *61*, e202112695.; *Org. Chem. Front.* **2025**, *12*, 478-484.

Insertions of Saturated Rings
Nitrogen Insertion

The Beckmann Rearrangement (Beckmann, 1886)

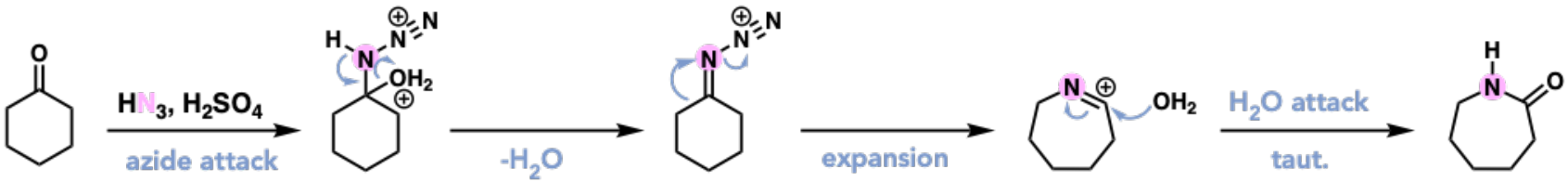


Chem. Rev. **1933**, *12*, 215-260.; *New J. Chem.* **2020**, *44*, 18530-18572.; *Angew. Chem.* **1923**, *36*, 511.; *JACS*, **1957**, *79*, 5558-5564.; *Science* **2019**, *367*, 281-285.

Insertions of Saturated Rings
Nitrogen Insertion

The Beckmann Rearrangement (Beckmann, 1886)

The Schmidt Reaction (Schmidt, 1924)



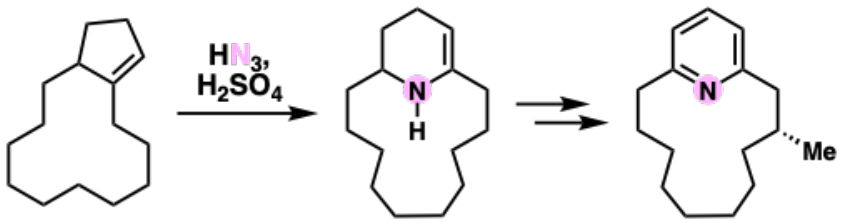
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Insertions of Saturated Rings
Nitrogen Insertion

The Beckmann Rearrangement (Beckmann, 1886)

The Schmidt Reaction (Schmidt, 1924)

Synthesis Application (Büchi, 1957)



(+)-muscopyridine

Chem. Rev. **1933**, *12*, 215-260.; *New J. Chem.* **2020**, *44*, 18530-18572.; *Angew. Chem.* **1923**, *36*, 511.; *JACS*, **1957**, *79*, 5558-5564.; *Science* **2019**, *367*, 281-285.

Insertions of Saturated Rings
Nitrogen Insertion

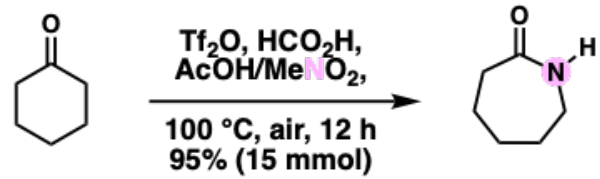
The Beckmann Rearrangement (Beckmann, 1886)

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Synthesis Application (Büchi, 1957)

(+)-muscopyridine

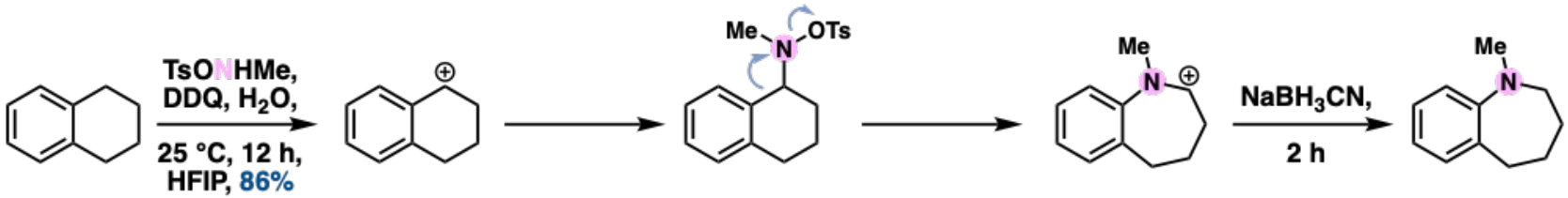
$MeNO_2$ for Mild Schmidt (Jiao, 2019)



Chem. Rev. **1933**, *12*, 215-260.; *New J. Chem.* **2020**, *44*, 18530-18572.; *Angew. Chem.* **1923**, *36*, 511.; *JACS*, **1957**, *79*, 5558-5564.; *Science* **2019**, *367*, 281-285.

Insertions of Saturated Rings
Nitrogen Insertion

N-Insertion into Aryl Alkanes (Jiao & Zhang, 2024)

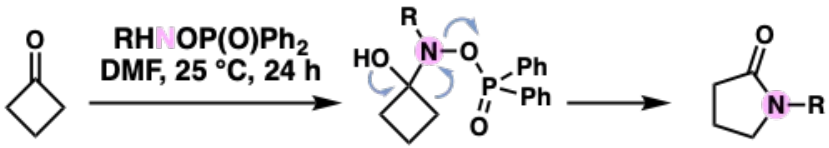


Nature Communications **2024**, *15*, 6106.; *Org. Lett.* **2022**, *24*, 6171-6175.; *ACIE* **2025**, *64*, e202420485.; *JACS* **2024**, *146*, 21129-21136.; *JOC*, **2024**, *89*, 17655-17663.; *Science* **2025**, *389*, 275-281.

Insertions of Saturated Rings
Nitrogen Insertion

N-Insertion into Aryl Alkanes (Jiao & Zhang, 2024)

Aza-Baeyer-Villager Rearrangement (Wahl, 2022)



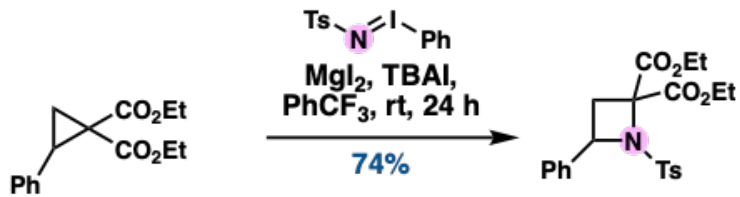
Nature Communications **2024**, *15*, 6106.; *Org. Lett.* **2022**, *24*, 6171-6175.; *ACIE* **2025**, *64*, e202420485.; *JACS* **2024**, *146*, 21129-21136.; *JOC*, **2024**, *89*, 17655-17663.; *Science* **2025**, *389*, 275-281.

Insertions of Saturated Rings
Nitrogen Insertion

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Nature Communications **2024**, *15*, 6106.; *Org. Lett.* **2022**, *24*, 6171-6175.; *ACIE* **2025**, *64*, e202420485.; *JACS* **2024**, *146*, 21129-21136.; *JOC*, **2024**, *89*, 17655-17663.; *Science* **2025**, *389*, 275-281.

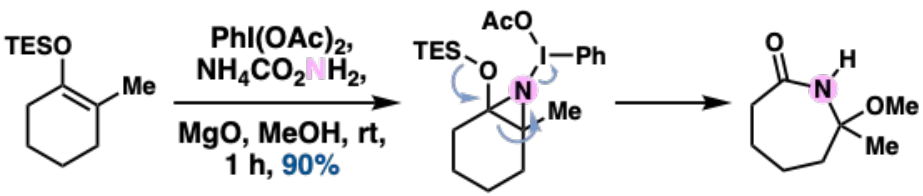
Insertions of Saturated Rings
Nitrogen Insertion

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N-Insertion into Silyl Enol Ethers (Ball & Kürti, 2024)



Nature Communications **2024**, *15*, 6106.; *Org. Lett.* **2022**, *24*, 6171-6175.; *ACIE* **2025**, *64*, e202420485.; *JACS* **2024**, *146*, 21129-21136.; *JOC*, **2024**, *89*, 17655-17663.; *Science* **2025**, *389*, 275-281.

Insertions of Saturated Rings
Nitrogen Insertion

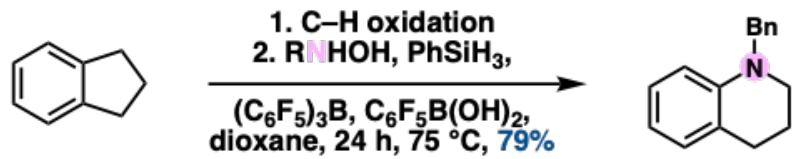
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Formal *N*-Insertion (Sarpong, 2024)



Nature Communications **2024**, *15*, 6106.; *Org. Lett.* **2022**, *24*, 6171-6175.; *ACIE* **2025**, *64*, e202420485.; *JACS* **2024**, *146*, 21129-21136.; *JOC*, **2024**, *89*, 17655-17663.; *Science* **2025**, *389*, 275-281.

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N-Insertion into Aryl Alkanes (Jiao & Zhang, 2024)

Aza-Baeyer-Villager Rearrangement (Wahl, 2022)

Azetidine Formation (Parasram, 2025)

N-Insertion into Silyl Enol Ethers (Ball & Kürti, 2024)

Formal *N*-Insertion (Sarpong, 2024)

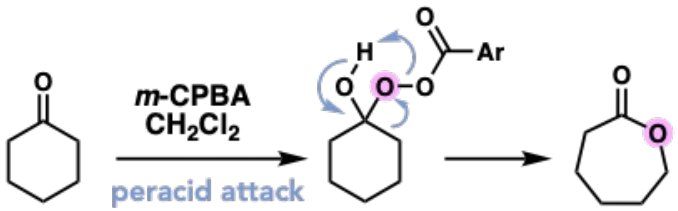
N-Insertion into Pyrrolidines (Jiao & Zhang, 2024)



Nature Communications **2024**, *15*, 6106.; *Org. Lett.* **2022**, *24*, 6171-6175.; *ACIE* **2025**, *64*, e202420485.; *JACS* **2024**, *146*, 21129-21136.; *JOC*, **2024**, *89*, 17655-17663.; *Science* **2025**, *389*, 275-281.

Insertions of Saturated Rings
Oxygen Insertion

Baeyer-Villager Oxidation (1899)

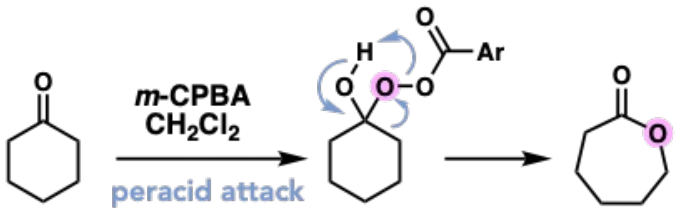


regiochemistry dictated by migratory aptitude

Chem. Rev. **2004**, *104*, 4105-4124.; *JACS* **1988**, *110*, 649-651.; *JACS*, **2022**, *144*, 20207-20213.; *Org. Chem. Front.* **2023**, *10*, 3307-3312.

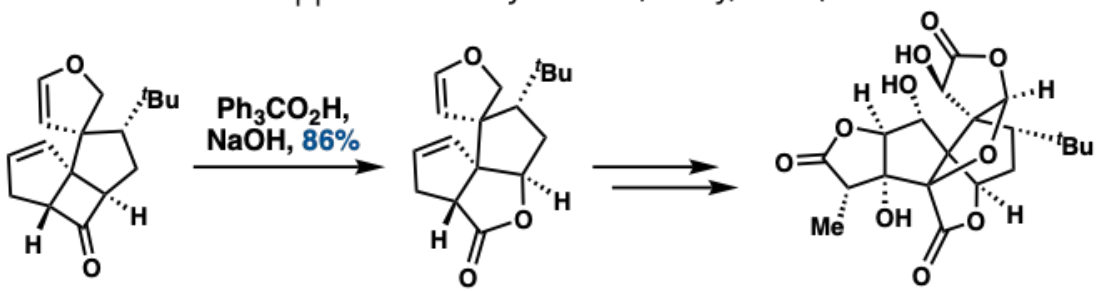
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regiochemistry dictated by migratory aptitude

Application to Synthesis (Corey, 1988)



ginkgolide B

Chem. Rev. **2004**, *104*, 4105-4124.; *JACS* **1988**, *110*, 649-651.; *JACS*, **2022**, *144*, 20207-20213.; *Org. Chem. Front.* **2023**, *10*, 3307-3312.

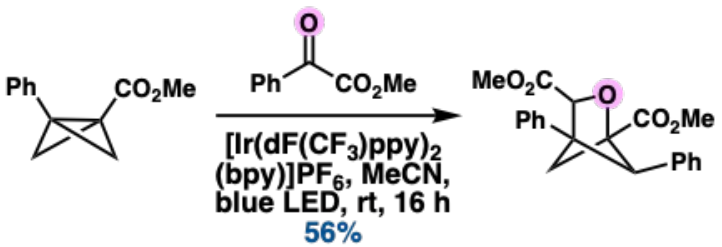
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Oxygen Insertion

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2-Oxa-BCHs (Glorius, 2022)



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Insertions of Saturated Rings
Oxygen Insertion

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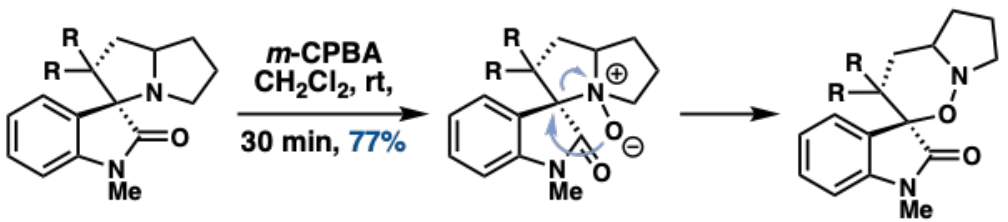
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ginkgolide B

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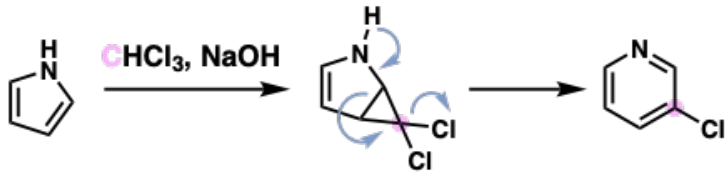
Unexpected *O*-Insertion (Liu, 2023)



Chem. Rev. **2004**, *104*, 4105-4124.; *JACS* **1988**, *110*, 649-651.; *JACS*, **2022**, *144*, 20207-20213.; *Org. Chem. Front.* **2023**, *10*, 3307-3312.

Insertions of Aromatic Rings
Carbon Insertion

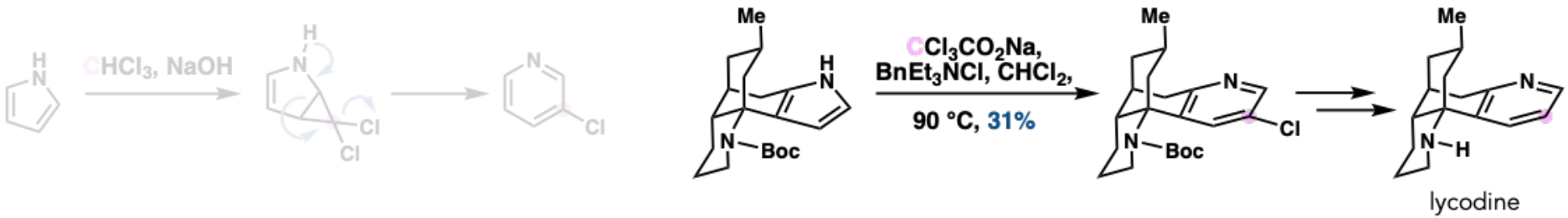
Ciamician-Dennstedt Rearrangement (1881); Application in Synthesis (Dai, 2021)



Ber. **1881**, *14*, 1153-1163.; *JACS* **2021**, *143*, 16383-16387.; *JACS* **2021**, *143*, 11337-11344.; *JACS* **2022**, *144*, 19258-19264.; *ACIE* **2023**, *62*, e202305081.; *Beilstein JOC* **2015**, *11*, 1944-1949.; *ACS Catal*. **2024**, *14*, 13343-13351.; *ACIE* **2025**, *64*, e202501966.; *Nature Commun*. **2024**, *15*, 9998.; *ACIE* **2024**, *63*, e202317104.; *Chin. JOC* **2024**, *42*, 1128-1132.; *JACS*, **2025**, *147*, 13824-13832.; *JACS* **2026**, *148*, 3672-3680.; *Chem* **2026**, *12*, 102968.

Insertions of Aromatic Rings
Carbon Insertion

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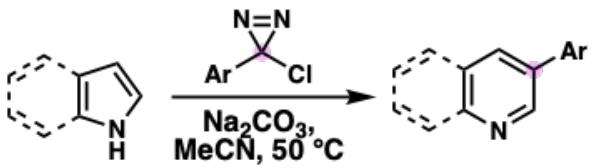
lycodine

Ber. **1881**, *14*, 1153-1163.; *JACS* **2021**, *143*, 16383-16387.; *JACS* **2021**, *143*, 11337-11344.; *JACS* **2022**, *144*, 19258-19264.; *ACIE* **2023**, *62*, e202305081.; *Beilstein JOC* **2015**, *11*, 1944-1949.; *ACS Catal*. **2024**, *14*, 13343-13351.; *ACIE* **2025**, *64*, e202501966.; *Nature Commun*. **2024**, *15*, 9998.; *ACIE* **2024**, *63*, e202317104.; *Chin. JOC* **2024**, *42*, 1128-1132.; *JACS*, **2025**, *147*, 13824-13832.; *JACS* **2026**, *148*, 3672-3680.; *Chem* **2026**, *12*, 102968.

Insertions of Aromatic Rings
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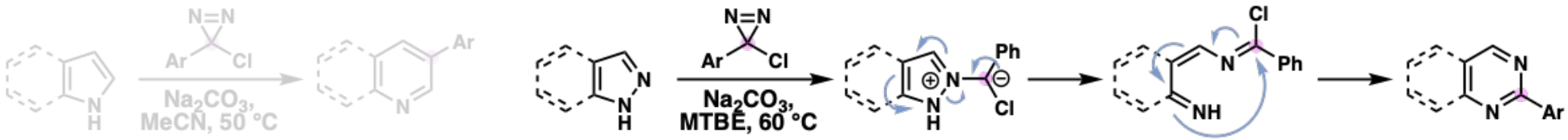


Ber. **1881**, *14*, 1153-1163.; *JACS* **2021**, *143*, 16383-16387.; *JACS* **2021**, *143*, 11337-11344.; *JACS* **2022**, *144*, 19258-19264.; *ACIE* **2023**, *62*, e202305081.; *Beilstein JOC* **2015**, *11*, 1944-1949.; *ACS Catal*. **2024**, *14*, 13343-13351.; *ACIE* **2025**, *64*, e202501966.; *Nature Commun*. **2024**, *15*, 9998.; *ACIE* **2024**, *63*, e202317104.; *Chin. JOC* **2024**, *42*, 1128-1132.; *JACS*, **2025**, *147*, 13824-13832.; *JACS* **2026**, *148*, 3672-3680.; *Chem* **2026**, *12*, 102968.

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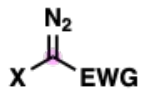
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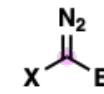
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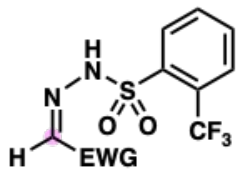
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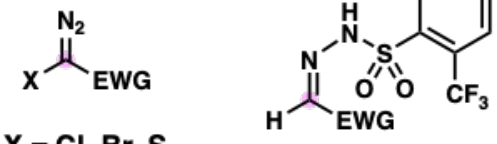
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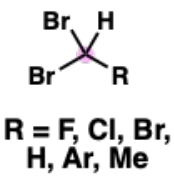
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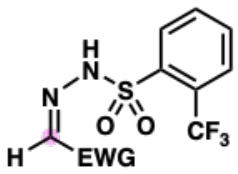
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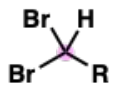


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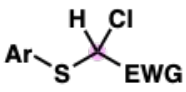


Anderson & Bi (2024)



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Xu (2023), Song (2024)



Sharma (2025)

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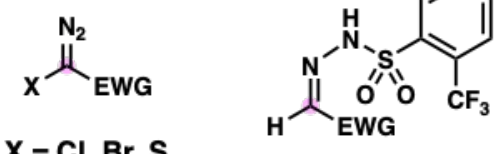
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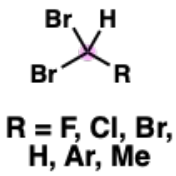
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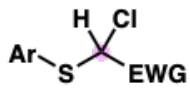


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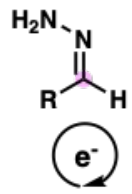
Anderson & Bi (2024)



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Sharma (2025)



Ji & Huang & Pang (2026)

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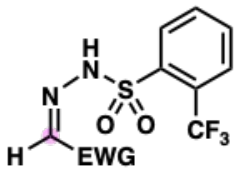
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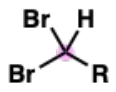


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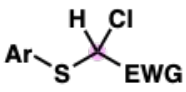


Anderson & Bi (2024)

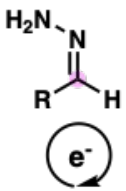


R = F, Cl, Br, H, Ar, Me

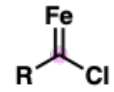
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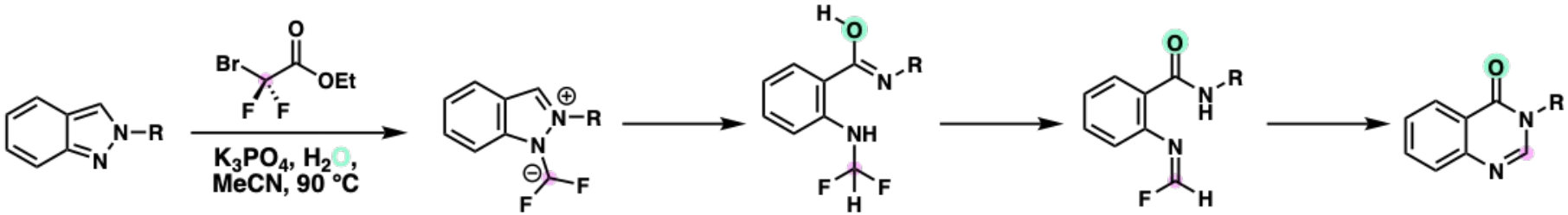
R = H, Ar, EWG

Levin & Nagib (2026)

Ber. **1881**, *14*, 1153-1163.; *JACS* **2021**, *143*, 16383-16387.; *JACS* **2021**, *143*, 11337-11344.; *JACS* **2022**, *144*, 19258-19264.; *ACIE* **2023**, *62*, e202305081.; *Beilstein JOC* **2015**, *11*, 1944-1949.; *ACS Catal*. **2024**, *14*, 13343-13351.; *ACIE* **2025**, *64*, e202501966.; *Nature Commun*. **2024**, *15*, 9998.; *ACIE* **2024**, *63*, e202317104.; *Chin. JOC* **2024**, *42*, 1128-1132.; *JACS*, **2025**, *147*, 13824-13832.; *JACS* **2026**, *148*, 3672-3680.; *Chem* **2026**, *12*, 102968.

Insertions of Aromatic Rings
Carbon Insertion

Difluorocarbene Editing of 2H-indazoles (Song, 2023)

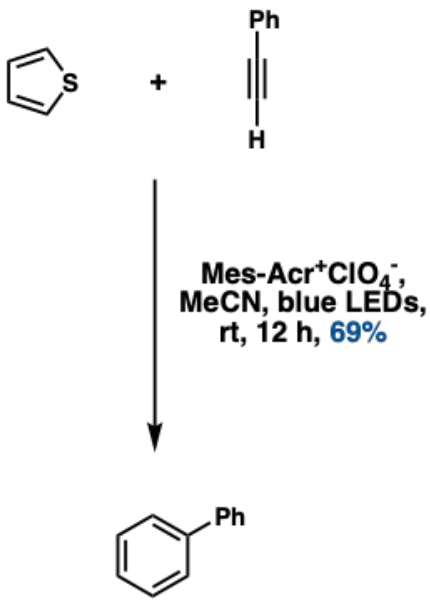


Sci. China Chem. **2023**, *66*, 1965-1981.; *ACIE* **2019**, *58*, 12206-12210.

Insertions of Aromatic Rings
Carbon Insertion

Difluorocarbene Editing of 2H-indazoles (Song, 2023)

Thiophenes to Benzenes via [4+2] Annulation (Chiang & Lei, 2019)

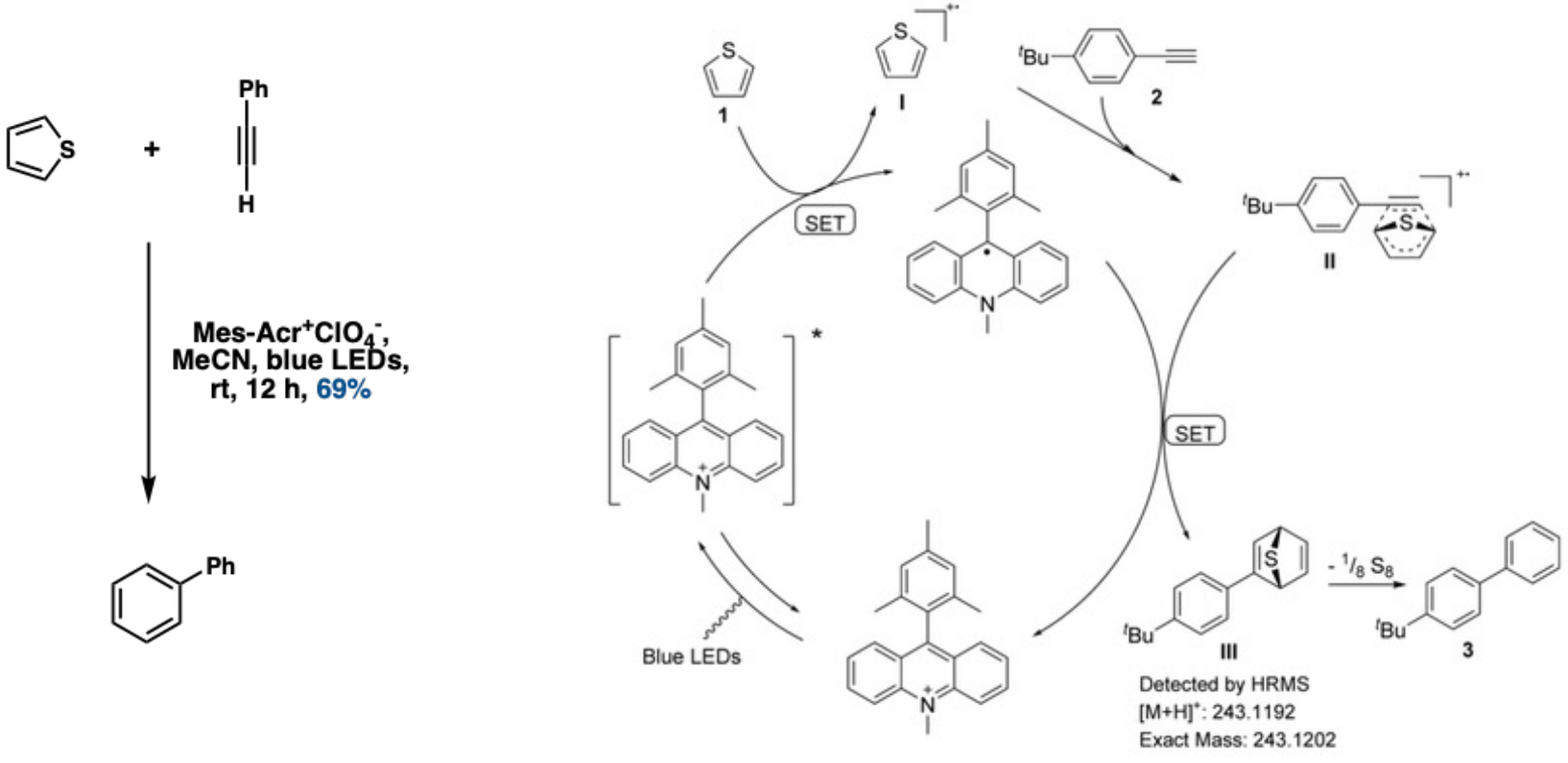


Sci. China Chem. **2023**, *66*, 1965-1981.; *ACIE* **2019**, *58*, 12206-12210.

Insertions of Aromatic Rings
Carbon Insertion

Difluorocarbene Editing of 2H-indazoles (Song, 2023)

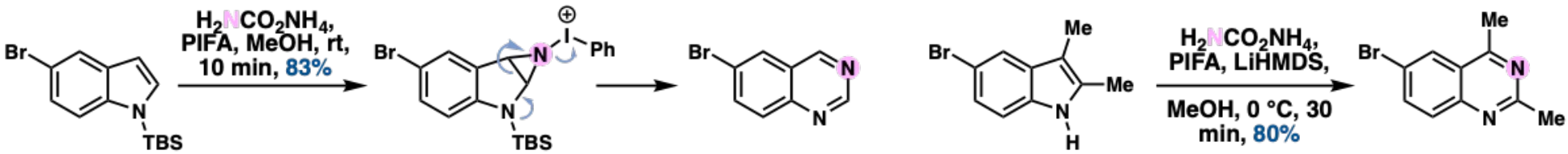
Thiophenes to Benzenes via [4+2] Annulation (Chiang & Lei, 2019)



Sci. China Chem. **2023**, *66*, 1965-1981.; *ACIE* **2019**, *58*, 12206-12210.

Insertions of Aromatic Rings
Nitrogen Insertion

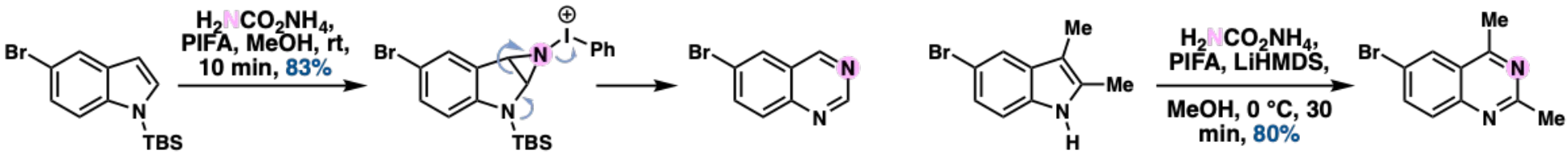
Iodonitrene *N*-Insertion into Indoles (Morandi, 2022, 2023)



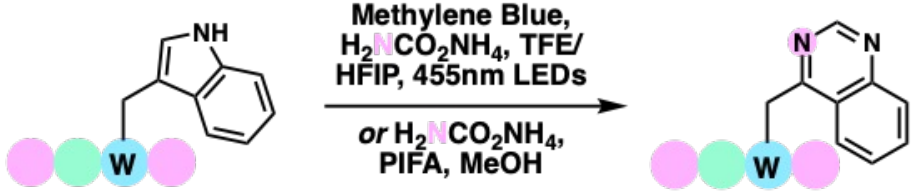
Science **2022**, *377*, 1104-1109.; *Org. Lett.* **2023**, *25*, 8419-8423.; *JACS* **2025**, *147*, 35211-35218.; *JACS* **2026**, *148*, 55-60.; *Science* **2025**, *387*, 102-107.; *ACIE* **2024**, *63*, e202407384.; *Chem* **2026**, *12*, 102753.

Insertions of Aromatic Rings
Nitrogen Insertion

Iodonitrene *N*-Insertion into Indoles (Morandi, 2022, 2023)



applied to late stage diversification of
Tryptophan-containing peptides
(Liu, Li, 2025 & Morandi, 2026)



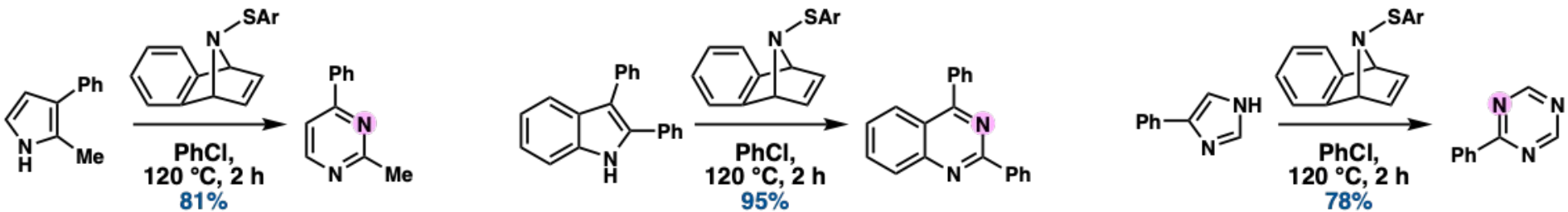
Science **2022**, *377*, 1104-1109.; *Org. Lett.* **2023**, *25*, 8419-8423.; *JACS* **2025**, *147*, 35211-35218.; *JACS* **2026**, *148*, 55-60.; *Science* **2025**, *387*, 102-107.; *ACIE* **2024**, *63*, e202407384.; *Chem* **2026**, *12*, 102753.

Insertions of Aromatic Rings
Nitrogen Insertion

Iodonitrene *N*-Insertion into Indoles (Morandi, 2022, 2023)

applied to late stage diversification of Tryptophan-containing peptides (Liu, Li, 2025 & Morandi, 2026)

Sulfenylnitrene *N*-Insertion into Pyrroles, Indoles, Imidazoles (Sharma, 2025)



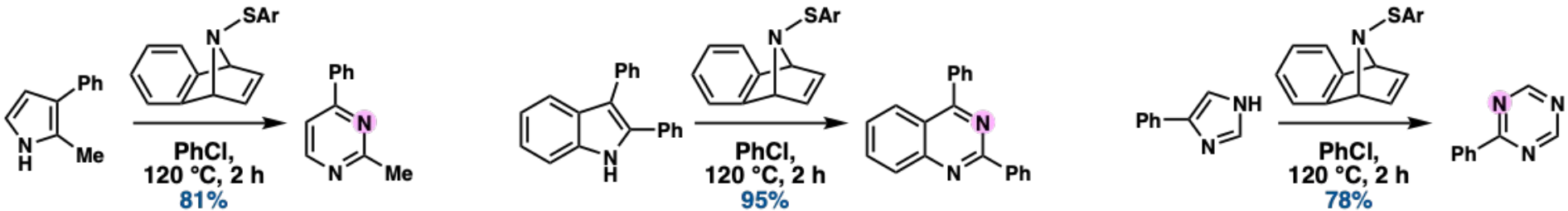
Science **2022**, *377*, 1104-1109.; *Org. Lett.* **2023**, *25*, 8419-8423.; *JACS* **2025**, *147*, 35211-35218.; *JACS* **2026**, *148*, 55-60.; *Science* **2025**, *387*, 102-107.; *ACIE* **2024**, *63*, e202407384.; *Chem* **2026**, *12*, 102753.

Insertions of Aromatic Rings
Nitrogen Insertion

Iodonitrene *N*-Insertion into Indoles (Morandi, 2022, 2023)

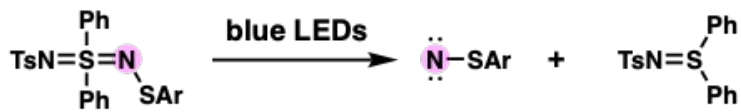
applied to late stage diversification of Tryptophan-containing peptides (Liu, Li, 2025 & Morandi, 2026)

Sulfenylnitrene *N*-Insertion into Pyrroles, Indoles, Imidazoles (Sharma, 2025)



Also generated via electrochemical activation of ammonium carbamate (Ackermann, 2024)

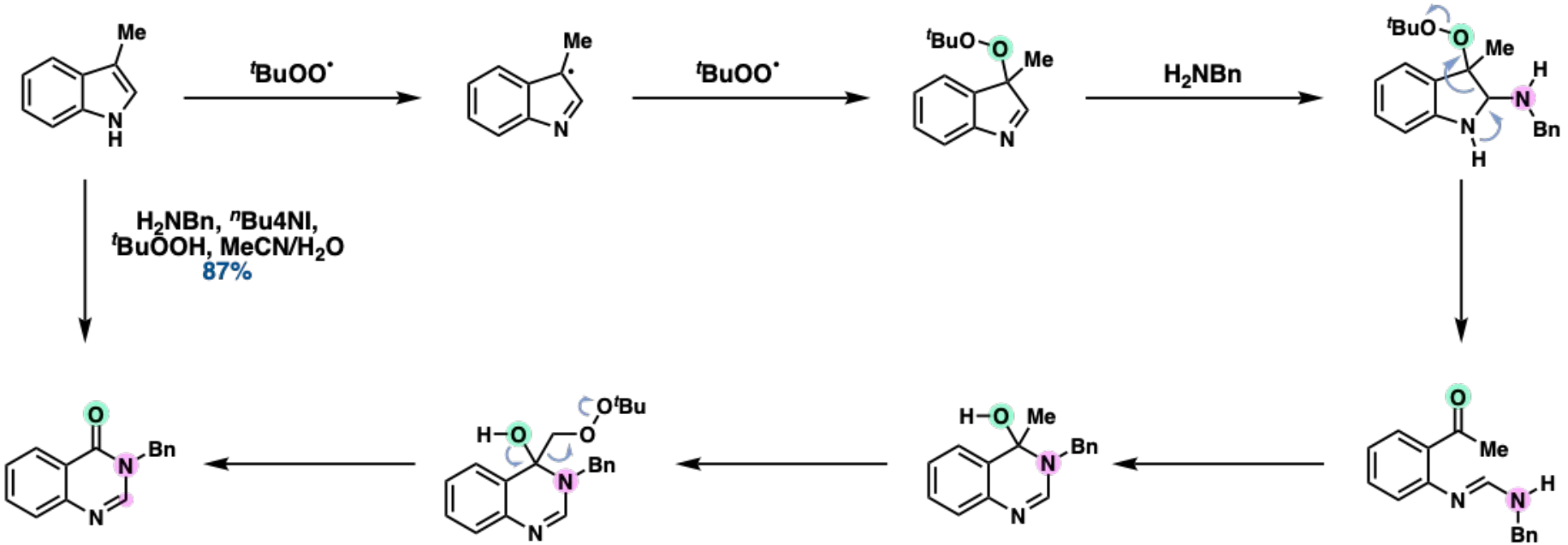
Also generated with chemoselective photolysis of N=S bond (Sharma, 2026):



Science **2022**, *377*, 1104-1109.; *Org. Lett.* **2023**, *25*, 8419-8423.; *JACS* **2025**, *147*, 35211-35218.; *JACS* **2026**, *148*, 55-60.; *Science* **2025**, *387*, 102-107.; *ACIE* **2024**, *63*, e202407384.; *Chem* **2026**, *12*, 102753.

Insertions of Aromatic Rings
Nitrogen Insertion

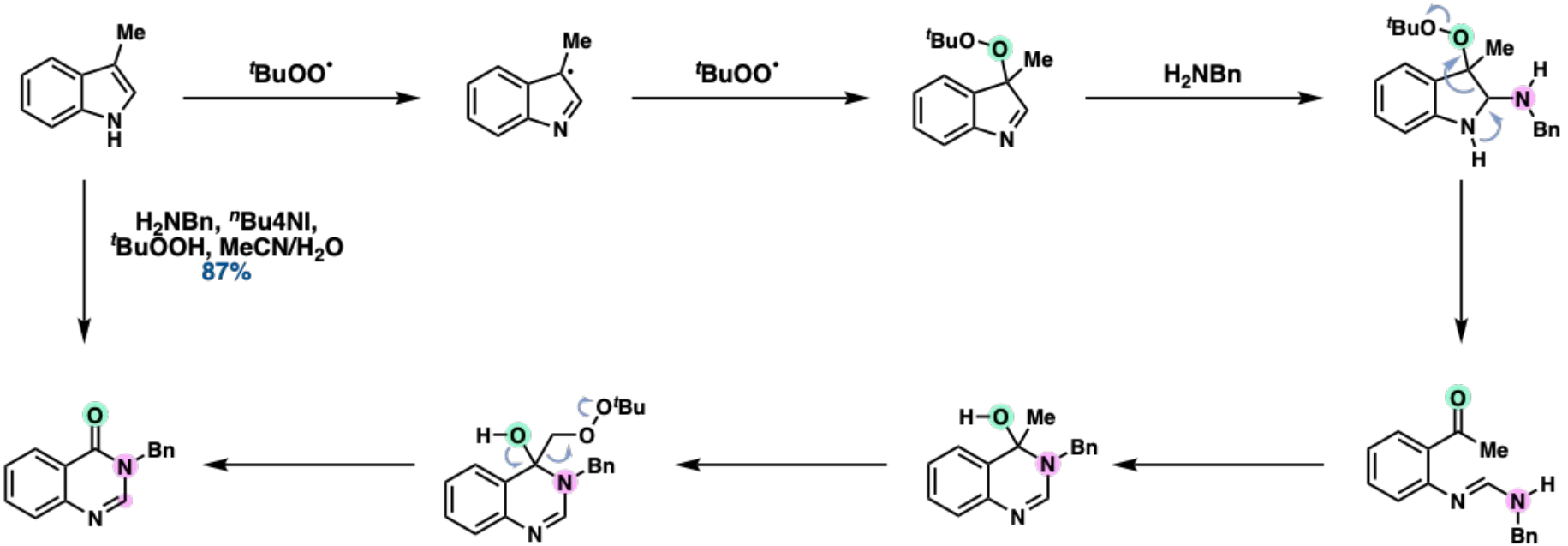
3-Methylindoles to Quinazolinones (Zhou, 2020)



Org. Lett. **2022**, *22*, 2522-2526.; *RSC Adv.* **2024**, *14*, 15597-15603.; *Nature Synthesis* **2026**, *5*, 1269-1277.

Insertions of Aromatic Rings
Nitrogen Insertion

3-Methylindoles to Quinazolinones (Zhou, 2020)



also accomplished with I_2-mediated oxidation (Le & Ha & Truong, 2024)

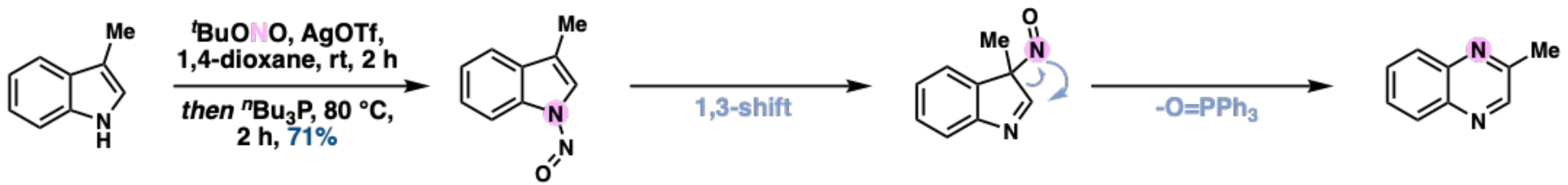
Org. Lett. **2022**, *22*, 2522-2526.; *RSC Adv.* **2024**, *14*, 15597-15603.; *Nature Synthesis* **2026**, *5*, 1269-1277.

Insertions of Aromatic Rings
Nitrogen Insertion

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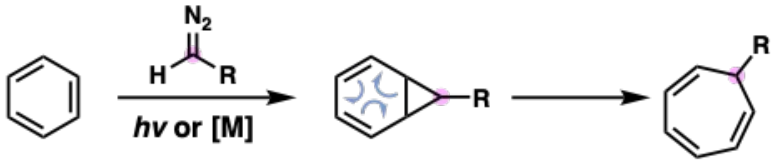
N-Insertion into Indoles via NO Translocation (Chung, 2026)



Org. Lett. **2022**, *22*, 2522-2526.; *RSC Adv.* **2024**, *14*, 15597-15603.; *Nature Synthesis* **2026**, *5*, 1269-1277.

Dearomative Insertions
Carbon Insertion

Büchner Reaction (1885)

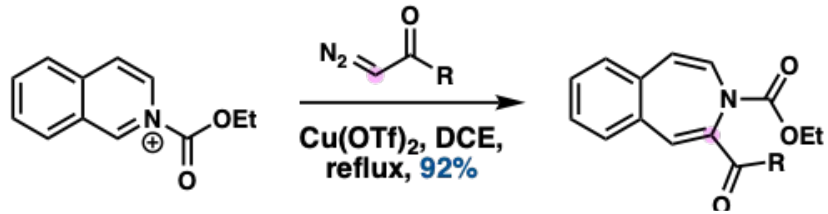


Org. Biomol. Chem. **2023**, *21*, 5150-5157.; *Chem. Commun.* **2004**, *40*, 2124-2125.; *Synthesis* **2010**, *24*, 4221-4227.; *JACS*, **2024**, *146*, 1813-1818.; *Tetrahedron* **2008**, *64*, 6901-6908.; *Adv. Sci.* **2024**, *11*, 2307563.; *ACIE* **2023**, *63*, e202313807.; *Nature Chem.* **2024**, *16*, 988-997.; *Nature Chem.* **2025**, *17*, 215-225.

Dearomative Insertions
Carbon Insertion

Büchner Reaction (1885)

Activated Isoquinolines to Novel Benzoazepines (Yadav, 2004)



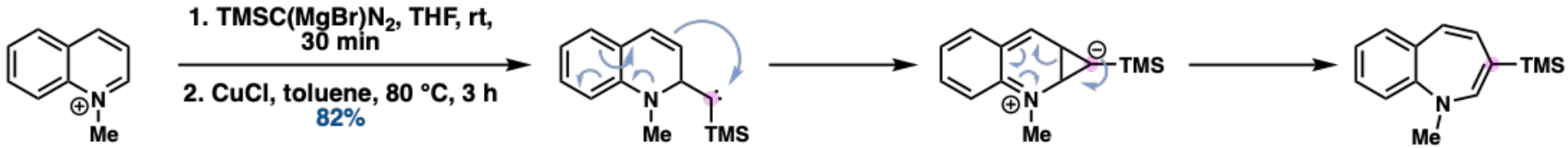
Org. Biomol. Chem. **2023**, *21*, 5150-5157.; *Chem. Commun.* **2004**, *40*, 2124-2125.; *Synthesis* **2010**, *24*, 4221-4227.; *JACS*, **2024**, *146*, 1813-1818.; *Tetrahedron* **2008**, *64*, 6901-6908.; *Adv. Sci.* **2024**, *11*, 2307563.; *ACIE* **2023**, *63*, e202313807.; *Nature Chem.* **2024**, *16*, 988-997.; *Nature Chem.* **2025**, *17*, 215-225.

Dearomative Insertions
Carbon Insertion

Büchner Reaction (1885)

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Activated Quinolines to Novel Benzoazepines: Nucleophilic Addition (Hari, 2010)



Org. Biomol. Chem. **2023**, *21*, 5150-5157.; *Chem. Commun.* **2004**, *40*, 2124-2125.; *Synthesis* **2010**, *24*, 4221-4227.; *JACS*, **2024**, *146*, 1813-1818.; *Tetrahedron* **2008**, *64*, 6901-6908.; *Adv. Sci.* **2024**, *11*, 2307563.; *ACIE* **2023**, *63*, e202313807.; *Nature Chem.* **2024**, *16*, 988-997.; *Nature Chem.* **2025**, *17*, 215-225.

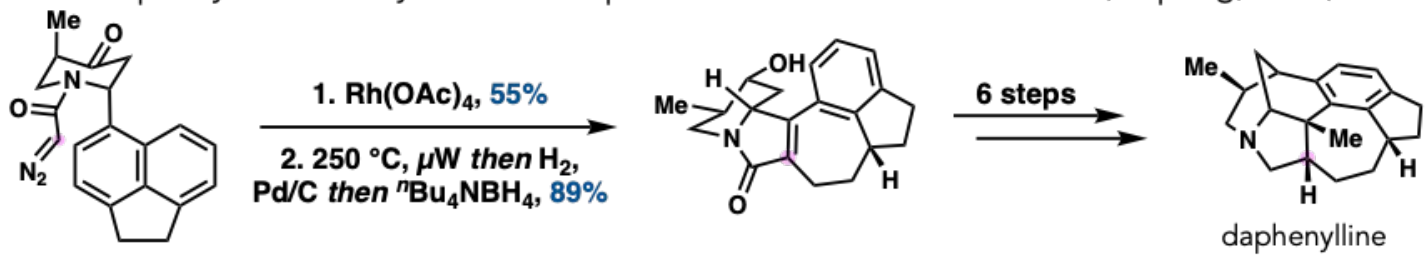
Dearomative Insertions
Carbon Insertion

Büchner Reaction (1885)

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Activated Quinolines to Novel Benzoazepines: Nucleophilic Addition (Hari, 2010)

Daphenylline Total Synthesis Example of Büchner Carbene Insertion (Sarpong, 2024)



daphenylline

Org. Biomol. Chem. **2023**, *21*, 5150-5157.; *Chem. Commun.* **2004**, *40*, 2124-2125.; *Synthesis* **2010**, *24*, 4221-4227.; *JACS*, **2024**, *146*, 1813-1818.; *Tetrahedron* **2008**, *64*, 6901-6908.; *Adv. Sci.* **2024**, *11*, 2307563.; *ACIE* **2023**, *63*, e202313807.; *Nature Chem.* **2024**, *16*, 988-997.; *Nature Chem.* **2025**, *17*, 215-225.

Dearomative Insertions
Carbon Insertion

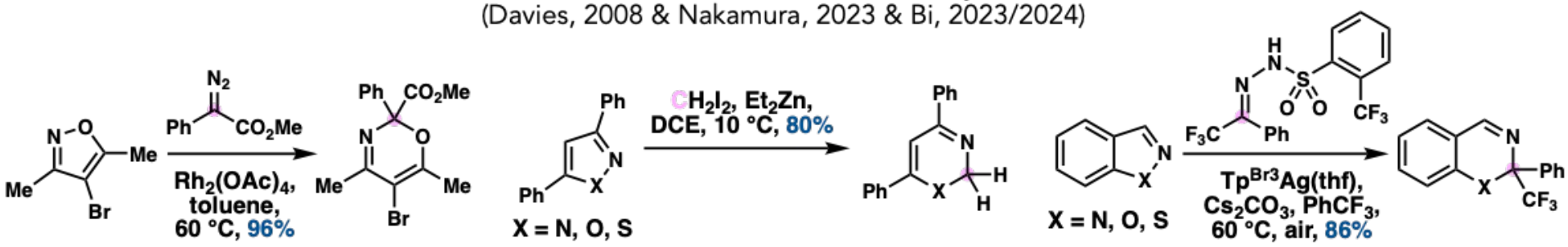
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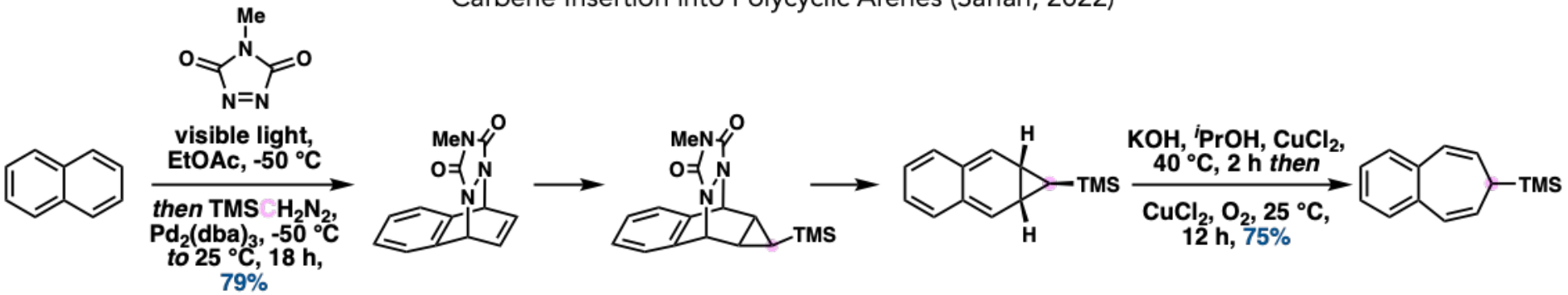
Rhodium or Zinc or Silver Carbene Insertion into Isoxazoles, Pyrazoles, Indazoles, Isothiazoles
(Davies, 2008 & Nakamura, 2023 & Bi, 2023/2024)



Org. Biomol. Chem. **2023**, *21*, 5150-5157.; *Chem. Commun.* **2004**, *40*, 2124-2125.; *Synthesis* **2010**, *24*, 4221-4227.; *JACS*, **2024**, *146*, 1813-1818.; *Tetrahedron* **2008**, *64*, 6901-6908.; *Adv. Sci.* **2024**, *11*, 2307563.; *ACIE* **2023**, *63*, e202313807.; *Nature Chem.* **2024**, *16*, 988-997.; *Nature Chem.* **2025**, *17*, 215-225.

Dearomative Insertions
Carbon Insertion

Carbene Insertion into Polycyclic Arenes (Sarlah, 2022)

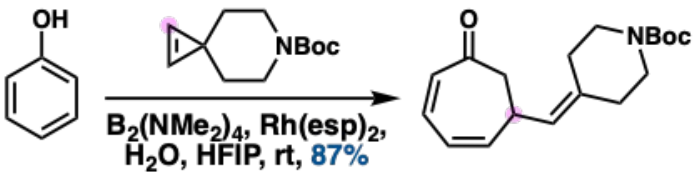


ACIE **2022**, *61*, e202208014.; *ACIE*, **2025**, *64*, e202416468.; *JACS* **2025**, *147*, 44699-44707.; *Science* **2023**, *381*, 75-81.

Dearomative Insertions
Carbon Insertion

Carbene Insertion into Polycyclic Arenes (Sarlah, 2022)

Phenols to Cycloheptadienones (Jiang, 2025)



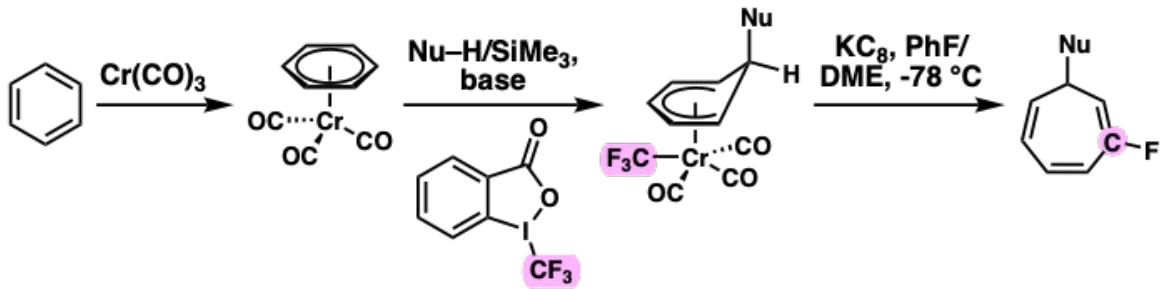
ACIE **2022**, *61*, e202208014.; *ACIE*, **2025**, *64*, e202416468.; *JACS* **2025**, *147*, 44699-44707.; *Science* **2023**, *381*, 75-81.

Dearomative Insertions
Carbon Insertion

Carbene Insertion into Polycyclic Arenes (Sarlah, 2022)

Phenols to Cycloheptadienones (Jiang, 2025)

Fluorocarbyne Insertion into Benzenes (Hong & Li, 2025)



ACIE **2022**, *61*, e202208014.; *ACIE*, **2025**, *64*, e202416468.; *JACS* **2025**, *147*, 44699-44707.; *Science* **2023**, *381*, 75-81.

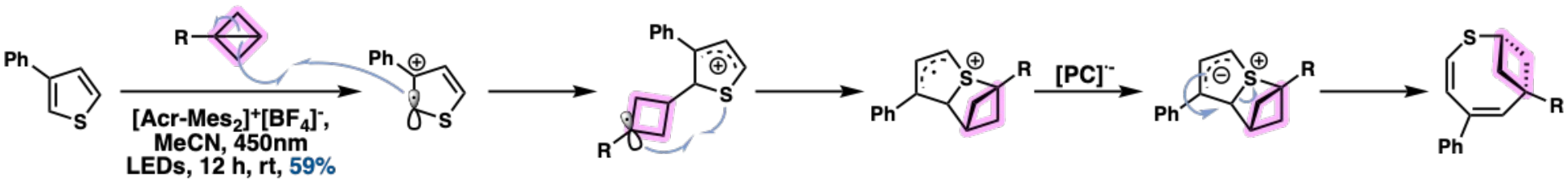
Dearomative Insertions
Carbon Insertion

Carbene Insertion into Polycyclic Arenes (Sarlah, 2022)

Phenols to Cycloheptadienones (Jiang, 2025)

Fluorocarbyne Insertion into Benzenes (Hong & Li, 2025)

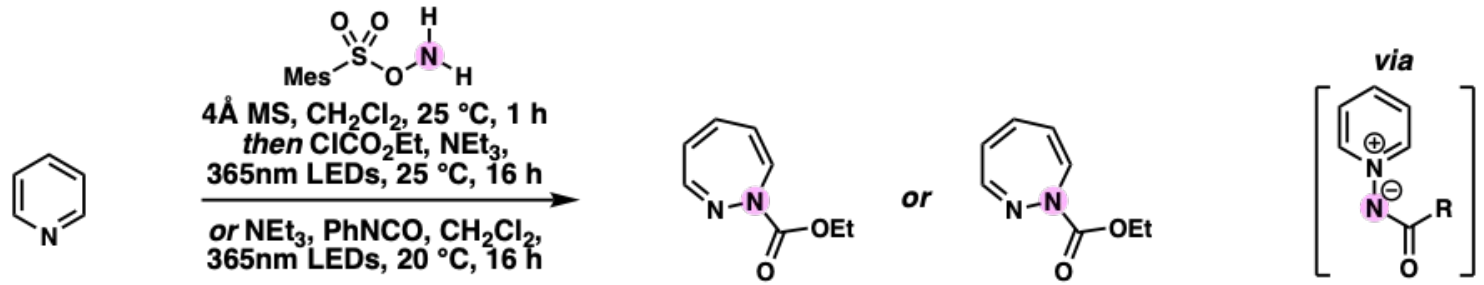
Bicyclobutane Insertion into Thiophenes (Glorius & Houk, 2023)



ACIE **2022**, *61*, e202208014.; *ACIE*, **2025**, *64*, e202416468.; *JACS* **2025**, *147*, 44699-44707.; *Science* **2023**, *381*, 75-81.

Dearomative Insertions
Nitrogen Insertion

Carbene Insertion into Polycyclic Arenes (Ghiazza & Moreau, 2024)

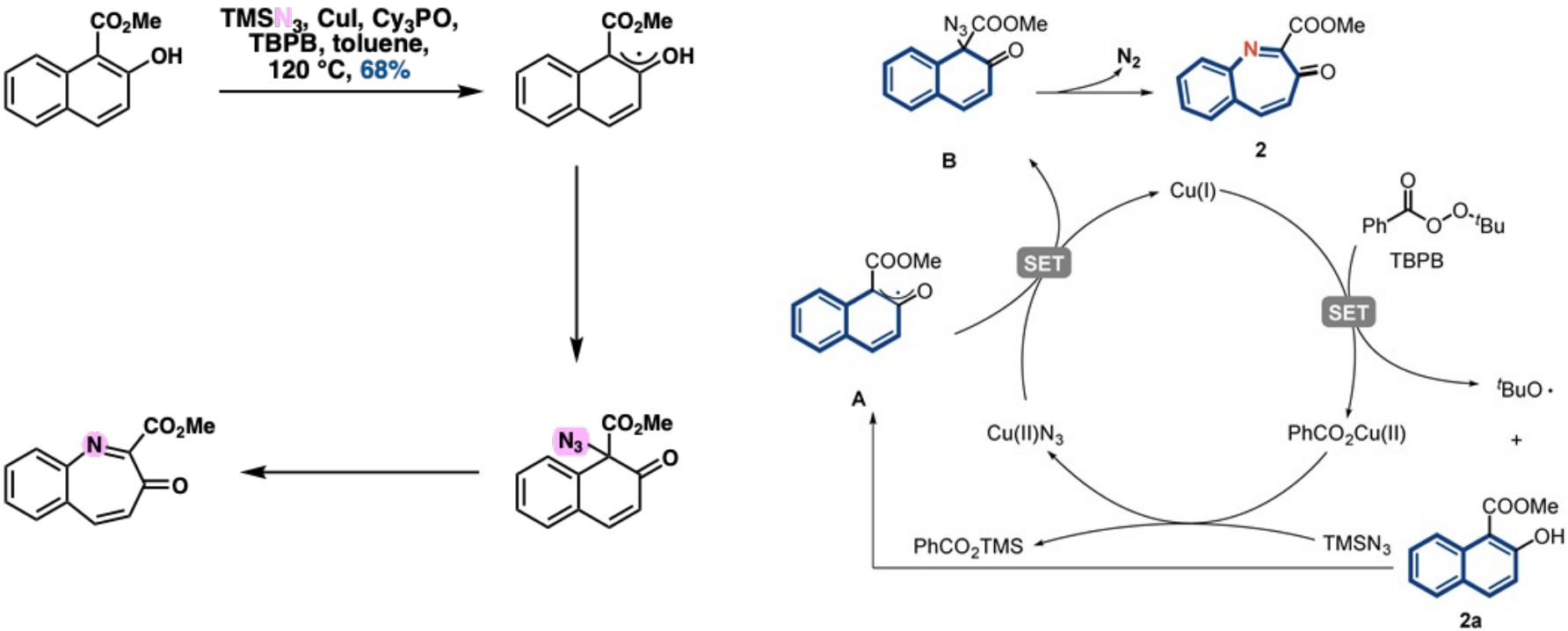


JACS **2024**, *146*, 2845-2854.; *Adv. Synth. & Cat.* **2025**, *367*, e20241201.; *Chem. Sci.* **2024**, *15*, 2612-2617.

Dearomative Insertions
Nitrogen Insertion

Carbene Insertion into Polycyclic Arenes (Ghiazza & Moreau, 2024)

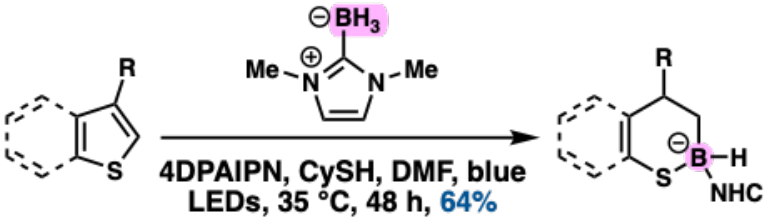
Arenols to Benzazepines (Wei, 2024)



JACS **2024**, *146*, 2845-2854.; *Adv. Synth. & Cat.* **2025**, *367*, e20241201.; *Chem. Sci.* **2024**, *15*, 2612-2617.

Dearomative Insertions
Heteroatom Insertion

Boryl Radical Insertion into Thiaarenes (Ye, 2025)

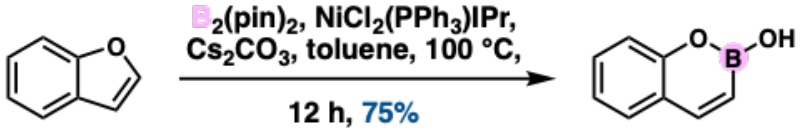


ACIE, **2025**, *64*, e202508379.; *JACS*, **2016**, *138*, 15315-15318.; *Org. Lett.* **2017**, *19*, 5557-5560.; *JACS* **2026**, *148*, 12486-12494.; *JACS* **2020**, *142*, 10125-10131.

Dearomative Insertions
Heteroatom Insertion

Boryl Radical Insertion into Thiaarenes (Ye, 2025)

Ni-Cat Boron Insertion into Benzofurans (Yorimitsu, 2016)



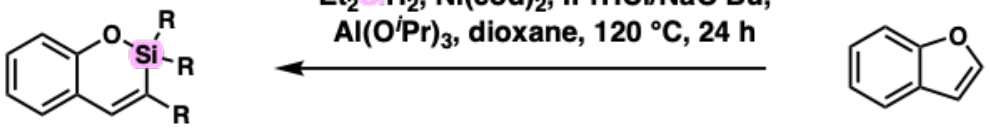
ACIE, **2025**, *64*, e202508379.; *JACS*, **2016**, *138*, 15315-15318.; *Org. Lett.* **2017**, *19*, 5557-5560.; *JACS* **2026**, *148*, 12486-12494.; *JACS* **2020**, *142*, 10125-10131.

Dearomative Insertions
Heteroatom Insertion

Boryl Radical Insertion into Thiaarenes (Ye, 2025)

Ni-Cat Boron Insertion into Benzofurans (Yorimitsu, 2016)

Silicon Insertion into Benzofurans (Lu & Wei, 2026)



ACIE, **2025**, *64*, e202508379.; *JACS*, **2016**, *138*, 15315-15318.; *Org. Lett.* **2017**, *19*, 5557-5560.; *JACS* **2026**, *148*, 12486-12494.; *JACS* **2020**, *142*, 10125-10131.

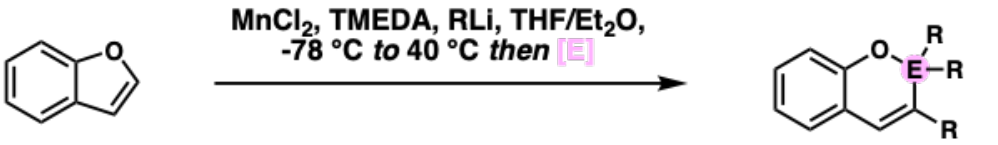
Dearomative Insertions
Heteroatom Insertion

Boryl Radical Insertion into Thiaarenes (Ye, 2025)

Ni-Cat Boron Insertion into Benzofurans (Yorimitsu, 2016)

Silicon Insertion into Benzofurans (Lu & Wei, 2026)

Mn-Cat Heteroatom Insertion into Benzofurans (Yorimitsu, 2017)



E = Si, B, P, Ge, Ti

ACIE, **2025**, *64*, e202508379.; *JACS*, **2016**, *138*, 15315-15318.; *Org. Lett.* **2017**, *19*, 5557-5560.; *JACS* **2026**, *148*, 12486-12494.; *JACS* **2020**, *142*, 10125-10131.

Dearomative Insertions
Heteroatom Insertion

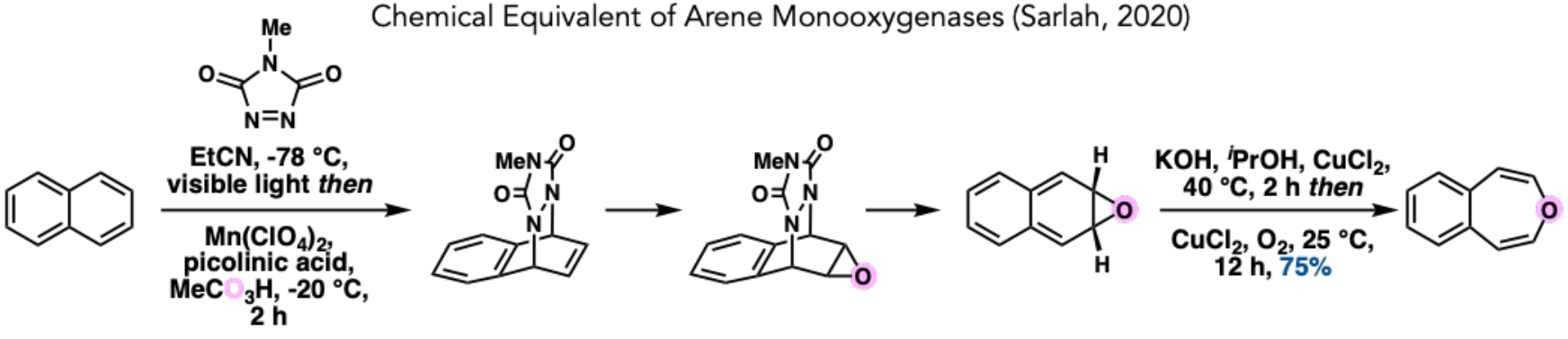
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Ni-Cat Boron Insertion into Benzofurans (Yorimitsu, 2016)

Silicon Insertion into Benzofurans (Lu & Wei, 2026)

Mn-Cat Heteroatom Insertion into Benzofurans (Yorimitsu, 2017)

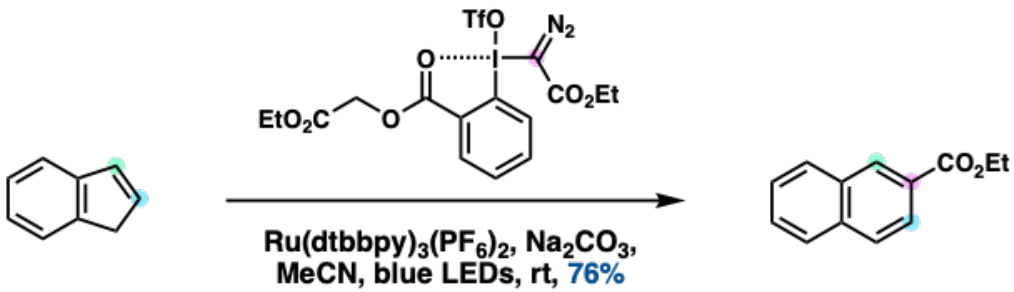
Chemical Equivalent of Arene Monooxygenases (Sarlah, 2020)



ACIE, **2025**, *64*, e202508379.; *JACS*, **2016**, *138*, 15315-15318.; *Org. Lett.* **2017**, *19*, 5557-5560.; *JACS* **2026**, *148*, 12486-12494.; *JACS* **2020**, *142*, 10125-10131.

Aromative Insertions

Carbon Insertion: Indene to Naphthalene (Gutierrez & Glorius, 2024)

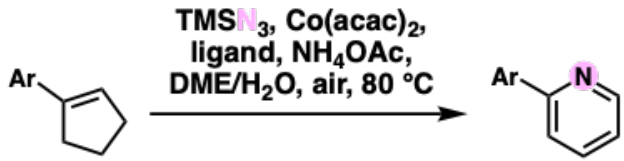


Nature Catal. **2024**, *7*, 242-251.; *JACS* **2022**, *144*, 22433-22439.; *ACIE* **2024**, *63*, e202408230.

Aromative Insertions

Carbon Insertion: Indene to Naphthalene (Gutierrez & Glorius, 2024)

Alkenes to Pyridines via Azide Radicals (Wei, 2022)

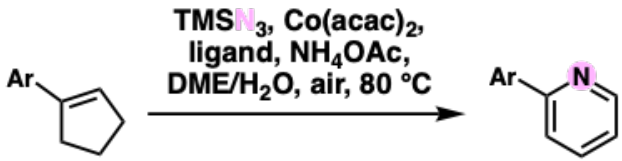


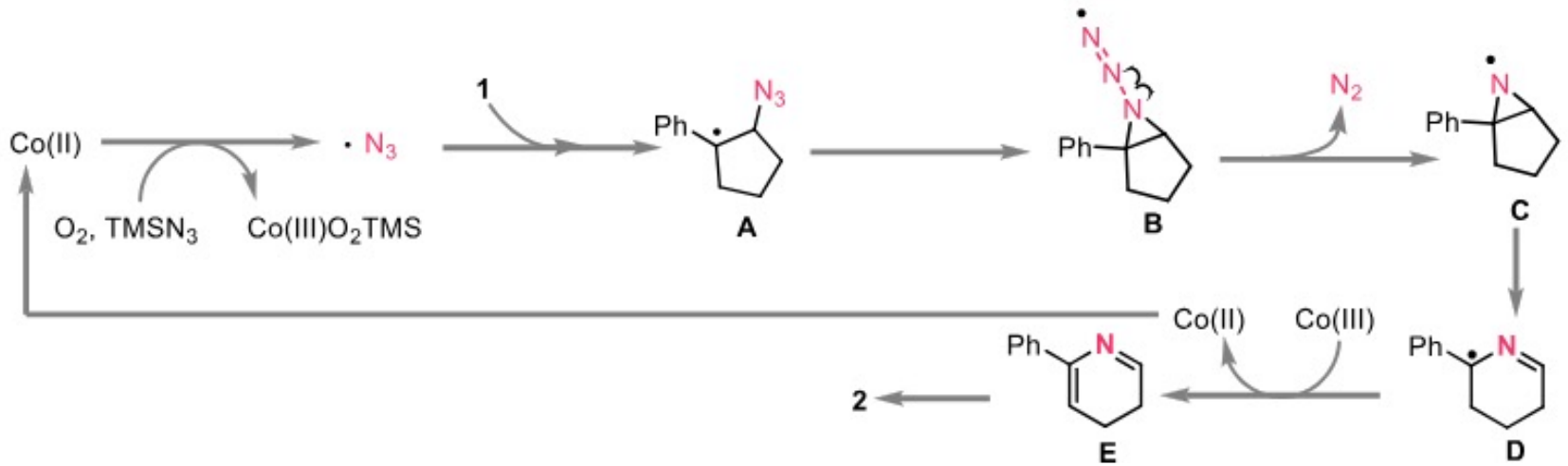
Nature Catal. **2024**, *7*, 242-251.; *JACS* **2022**, *144*, 22433-22439.; *ACIE* **2024**, *63*, e202408230.

Aromative Insertions

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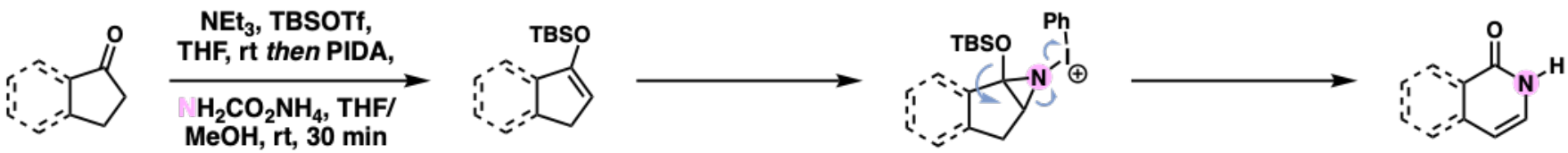
Nature Catal. **2024**, *7*, 242-251.; *JACS* **2022**, *144*, 22433-22439.; *ACIE* **2024**, *63*, e202408230.

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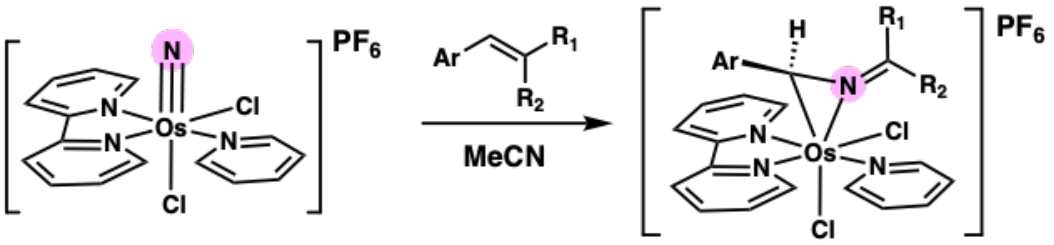
Nitrogen Insertion: Cyclopentenones to Pyridones (Morandi, 2024)



Nature Catal. **2024**, *7*, 242-251.; *JACS* **2022**, *144*, 22433-22439.; *ACIE* **2024**, *63*, e202408230.

Aromative Insertions
Nitrogen Insertion: Indene to Isoquinoline

Metal Nitride Insertion into C=C (Brown, 1999)

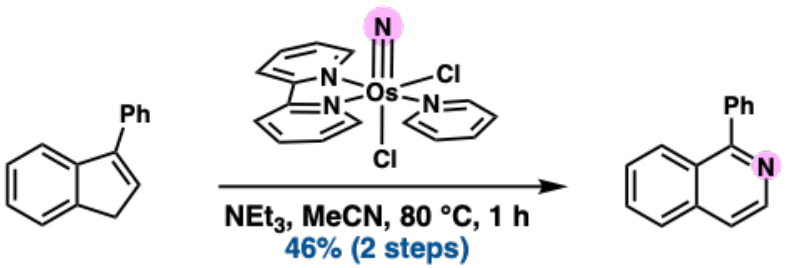


JACS **1999**, *121*, 9752-9753.; *ACIE* **2022**, *61*, e202213041.; *Nature Commun.* **2022**, *13*, 425.; *Chem. Sci.* **2023**, *14*, 2954-2959.; *ACIE* **2024**, *63*, e202403826.

Aromative Insertions
Nitrogen Insertion: Indene to Isoquinoline

Metal Nitride Insertion into C=C (Brown, 1999)

Levin (2022)



Nitride Regeneration:
1. $NH_4O_2CNH_2$, $PhI(OAc)_2$, MeOH, 25 °C, 12 h *then* NH_4PF_6, 74%
2. $HOTs{\cdot}H_2O$, $PhI(OAc)_2$), MeCN, 25 °C, 10 min *then* Bu_4NCl
3. LiCl, MeOH, 50 °C, 15 min *then* NH_4PF_6, 48% (2 steps)

JACS **1999**, *121*, 9752-9753.; *ACIE* **2022**, *61*, e202213041.; *Nature Commun.* **2022**, *13*, 425.; *Chem. Sci.* **2023**, *14*, 2954-2959.; *ACIE* **2024**, *63*, e202403826.

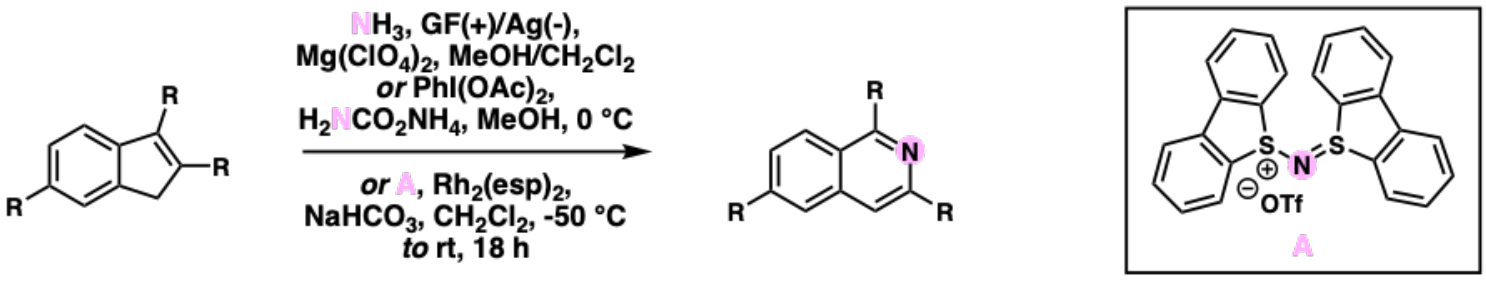
Aromative Insertions
Nitrogen Insertion: Indene to Isoquinoline

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Cheng (2022), Morandi (2023), Alcarazo (2024)



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Summary of Skeletal Editing

