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This graphical review provides a concise overview of the main organic chemical reactions reported in scientific works that used sodium nitrite as a nitrating/nitrosating agent capable of acting on various reactive substrates for the functionalization and synthesis of a wide variety of useful organic molecules.

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Sodium Nitrite ($NaNO_2$): An Expressive and Efficient Nitrating/Nitrosating Reagent in Organic Synthesis.

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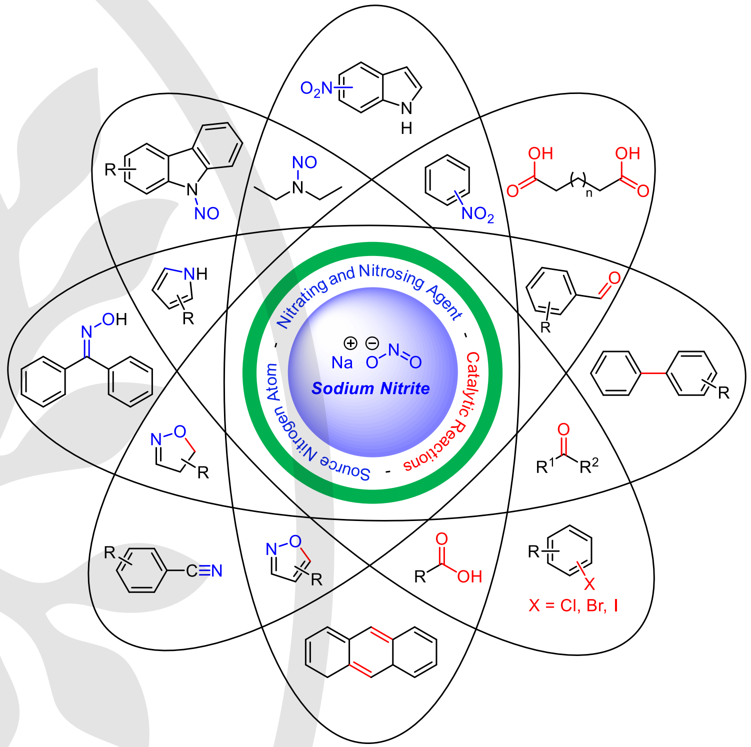

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Abstract This graphical review provides a concise overview of the main organic chemical reactions reported in scientific works that used sodium nitrite as a nitrating/nitrosating agent capable of acting on various reactive substrates for the functionalization and synthesis of a wide variety of useful organic molecules.

Key words sodium nitrite, nitrating, nitrosating, functionalization, synthesis, catalytic reactions

Sodium nitrite ($NaNO_2$) is a hygroscopic and crystalline inorganic salt that slowly oxidizes in air. It is highly soluble in water and slightly soluble in ethyl ether, methanol, and ethanol. Industrially, it is the most important salt produced from nitrous acid. It is obtained on a large scale by the reaction between a mixture of nitrogen oxides and an alkaline solution of sodium hydroxide or carbonate.[1a-b] Sodium nitrite finds extensive use in the chemical and pharmaceutical industries for the production of nitroso and isonitroso compounds, diazotization reactions (especially for dyes), and the synthesis of pharmaceutical products (e.g., caffeine) and agricultural pesticides (e.g., pyramin). In the food industry, it acts as a preservative added to cured meat products due to its ability to enhance flavor, prevent discoloration, and protect against the growth and toxin formation by *C. botulinum*.[1h-k] The applications of sodium nitrite in organic synthesis are widely studied. $NaNO_2$, in mixture with mineral or organic acids, results in the formation of unstable nitrous acid (HNO_2), a reactive species readily available in several reactions. Polyatomic species generated *in situ*, such as nitrosonium (NO^+) and nitronium (NO_2^+) ions, are capable of acting on several organic substrates.[1l] A prominent example is the reaction with primary aromatic amines, forming aryl diazonium salts, widely used in modern organic synthesis. This reaction is represented by classic synthetic routes such as those of Sandmeyer,[1e-g] Gomberg–Bachmann, Balz–Schiemann, as well as more robust methodologies developed by Heck–Matsuda.[1m-n] The objective of this review was to present methodologies that use sodium nitrite in different types of substrates for the synthesis of organic molecules, without involving the formation of aryl diazonium salt intermediates. $NaNO_2$, as a source of nitrite ions, has been used in various reactive sites as a nitrating and nitrosating agent. This includes reactions such as direct nitration of arenes,[2a-aw] nitrosation of secondary amines,[3a-p] synthesis of nitriles[6a-h] and oximes,[7a-n] functionalization and formation of heterocycles,[8a-p] as well as catalytic reactions involving cleavage and formation of C–C bonds.[9-10] Additionally, it plays a role in oxidation and halogenation reactions, acting as a catalyst or co-catalyst in the synthesis of organic compounds, specifically carbonyl and halogenated aromatic compounds.[4-5,11] This work explores pioneering studies and contemporary synthetic methodologies encompassing a variety of synthesized molecules, reaction yields, mechanistic aspects of reactions, and future prospects. All figures are presented in color, highlighting the main reagents, and providing a logical and concise sequence of the key studies discussed.

Biosketches

	**Lamark Carlos I** received his in chemistry from the Federal University of Rio Grande do Norte in 2019. Currently, he is an MSc Pharmaceutical Sciences at the same institution under the supervision of Prof. Dr. A. K. Jordão and Prof. Dr. E. G. Barbosa. His work involves the synthesis and antimalarial evaluation of new 1*H*-1,2,3-triazoles derived from melatonin and tryptamine.
	**Euzebio Guimarães Barbosa** received his PhD in chemistry from Campinas University (UNICAMP) in 2011 under the supervision of Prof. Dr. Marcia Miguel Castro Ferreira. Currently he is a professor at the Federal University of Rio Grande do Norte. His research interests focus on medicinal chemistry and computer-aided drug design.
	**Alessandro Kappel Jordão** received his PhD in chemistry from the Fluminense Federal University (UFF) in 2010 under the supervision of Prof. Vitor Francisco Ferreira and Prof. Anna Claudia. Currently he is a professor at the Federal University of Rio Grande do Norte. His research interests focus on the synthesis of heterocyclic compounds.

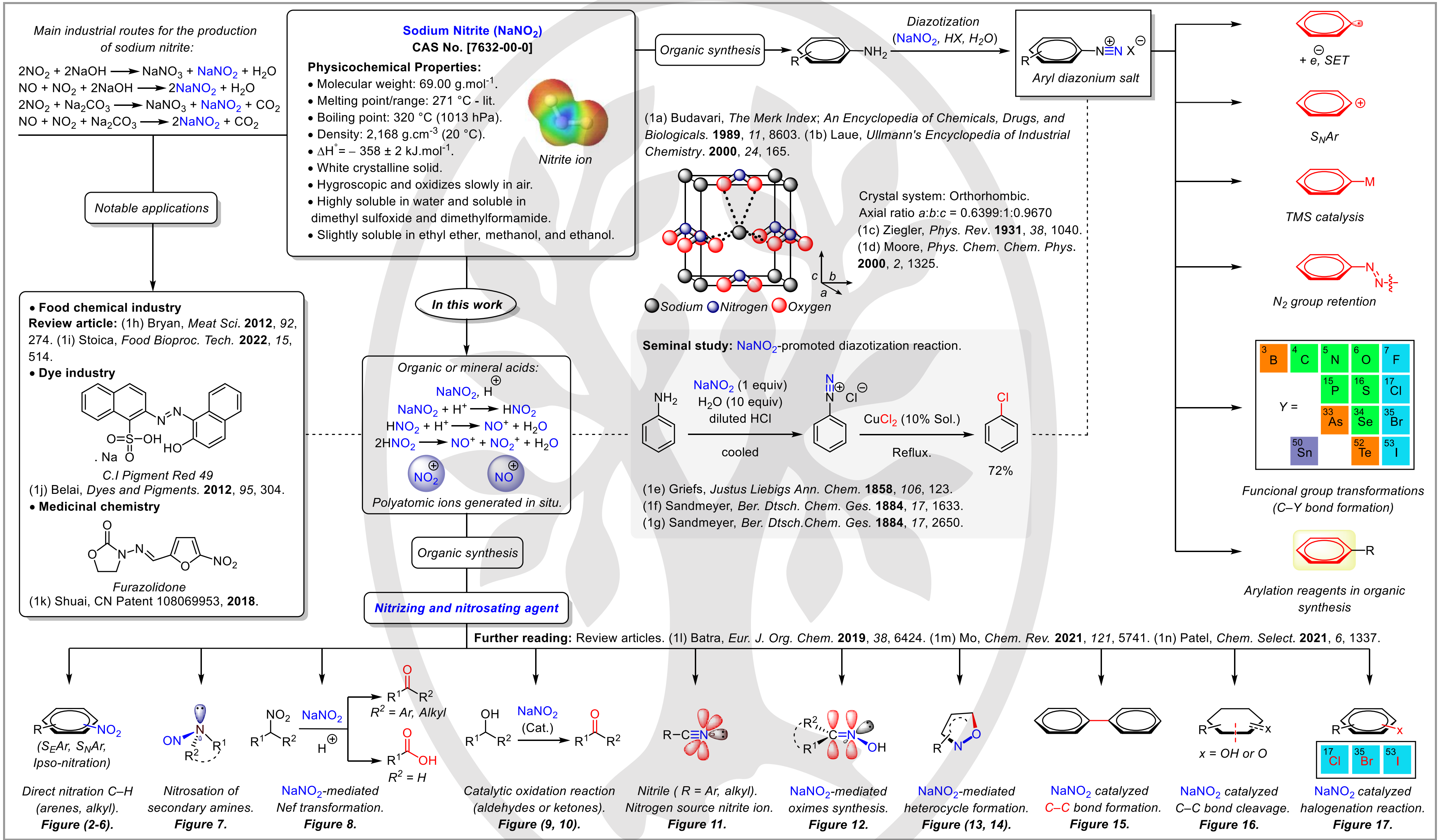
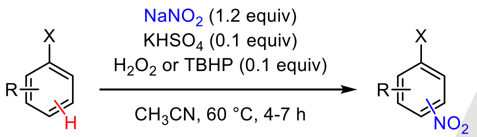


Figure 1: Use of $NaNO_2$ in organic synthesis.[1a–n]

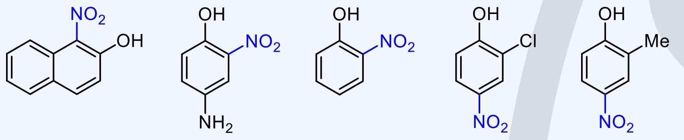
$NaNO_2$-Mediated (C–H) Direct Nitration. Notable Features:

- *In situ* generated nitrating species.
- Nitration via electrophilic and nucleophilic substitution reactions.
- Practical access to nitro compounds under mild reaction conditions.

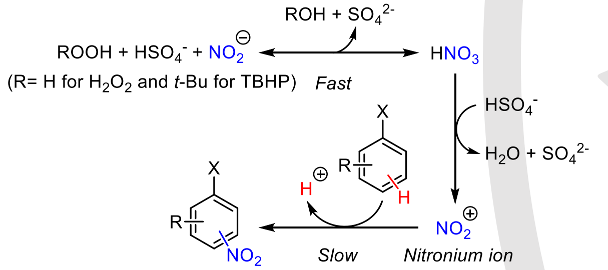
Direct nitration mediated $NaNO_2$/hydroperoxides/$KHSO_4$.



Selected examples



(2a) Kamatala, *Chemical Data Collections*. **2019**, *21*, 1. [a] TBHP (0.1 equiv).



Hydroperoxides triggered mechanism of nitration of aromatic compounds.

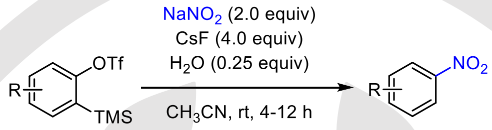
Further reading: $NaNO_2$-mediated synthesis of substituted nitrophenols. **Notable feature:** Distinct methodologies for direct nitration of aromatic compounds.

(2b) Zolfigol, *Molecules*. **2002**, *7*, 734.
(2c) Zolfigol, *Mendeleev Commun*. **2006**, *16*, 41.
(2d) Jereb, *Current Org. Chem*. **2013**, *17*, 1694.
(2e) Rajanna, *Int. J. Chem. Kinet*. **2017**, *49*, 209.
(2f) Rajanna, *Res. Chem. Intermed*. **2018**, *44*, 6023.

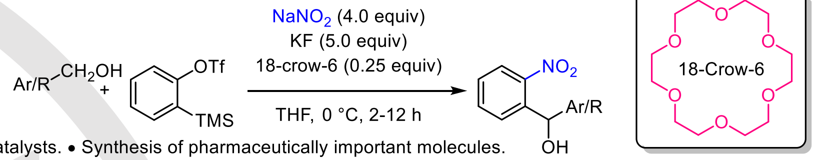
Outher further reading:

(2g) Syvret, *J. Org. Chem*. **2002**, *67*, 4487.
(2h) Rajanna, *Synth. Commun*. **2018**, *48*, 59.
(2i) Terent'ev, *Chem. Eur. J*. **2019**, *25*, 5922.
(2j) Jia, *Org. Lett*. **2019**, *21*, 5030.
(2k) Ranjan, *J. Am. Chem. Soc*. **2023**, *145*, 2745.

Nucleophilic nitration of arynes by $NaNO_2$ and H_2O.

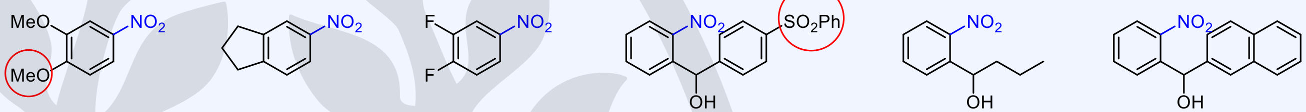


Multicomponent protocol to synthesize substituted (2-nitrophenyl)methanol.



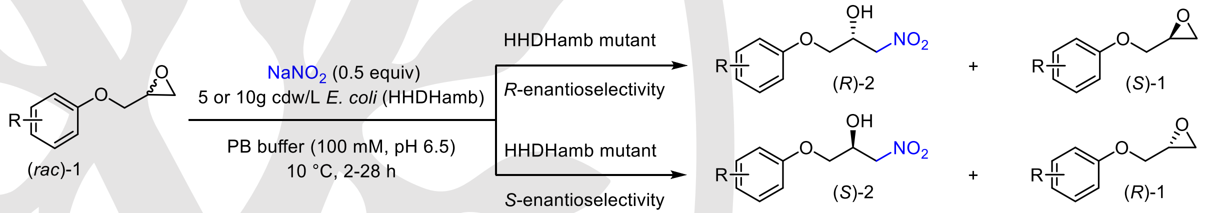
• Mild reaction conditions. • Free from transition metal catalysts. • Synthesis of pharmaceutically important molecules.

Selected examples

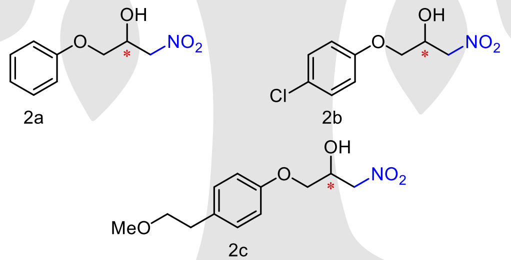


(2l) Mhaske, *Org. Lett*. **2016**, *18*, 3010.

Enantiocomplementary synthesis of β-adrenergic blocker precursors via biocatalytic nitration of phenyl glycidyl ethers.



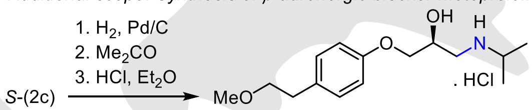
Selected products 2a-c via biocatalytic nitration.

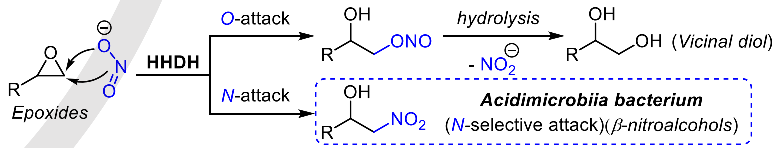


HHDHamb	Substrate	Product	Time (h)	ee 1 (%)[a]	ee 2 (%)[a]	Yield 2 (%)[b]
RM8	1a	R-(2a)	2	97	>99	41
SM7	1a	S-(2a)	21	85	95	42
RM8	1b	R-(2b)	8	96	>99	39
SM7	1b	S-(2b)	20	88	91	42
RM8	1c	R-(2c)	5	>99	99	40
SM7	1c	S-(2c)	28	91	96	41

(2m) Liu, *Bioorg. Chem*. **2023**, *138*, 106640. [a] The *ee* values were determined by chiral HPLC. [b] Isolated yields were obtained by flash chromatography.

Additional scope: Synthesis of β-adrenergic blocker metoprolol.





$NaNO_2$-mediated ring-opening reaction catalyzed by halohydrin dehalogenase (HHDH).

Further reading: (2n) Gao, *Enzyme Microb. Technol*. **2015**, *34*, 73.

Figure 2: Direct nitration (C–H) promoted by $NaNO_2$. (Part 1)[2a–n]

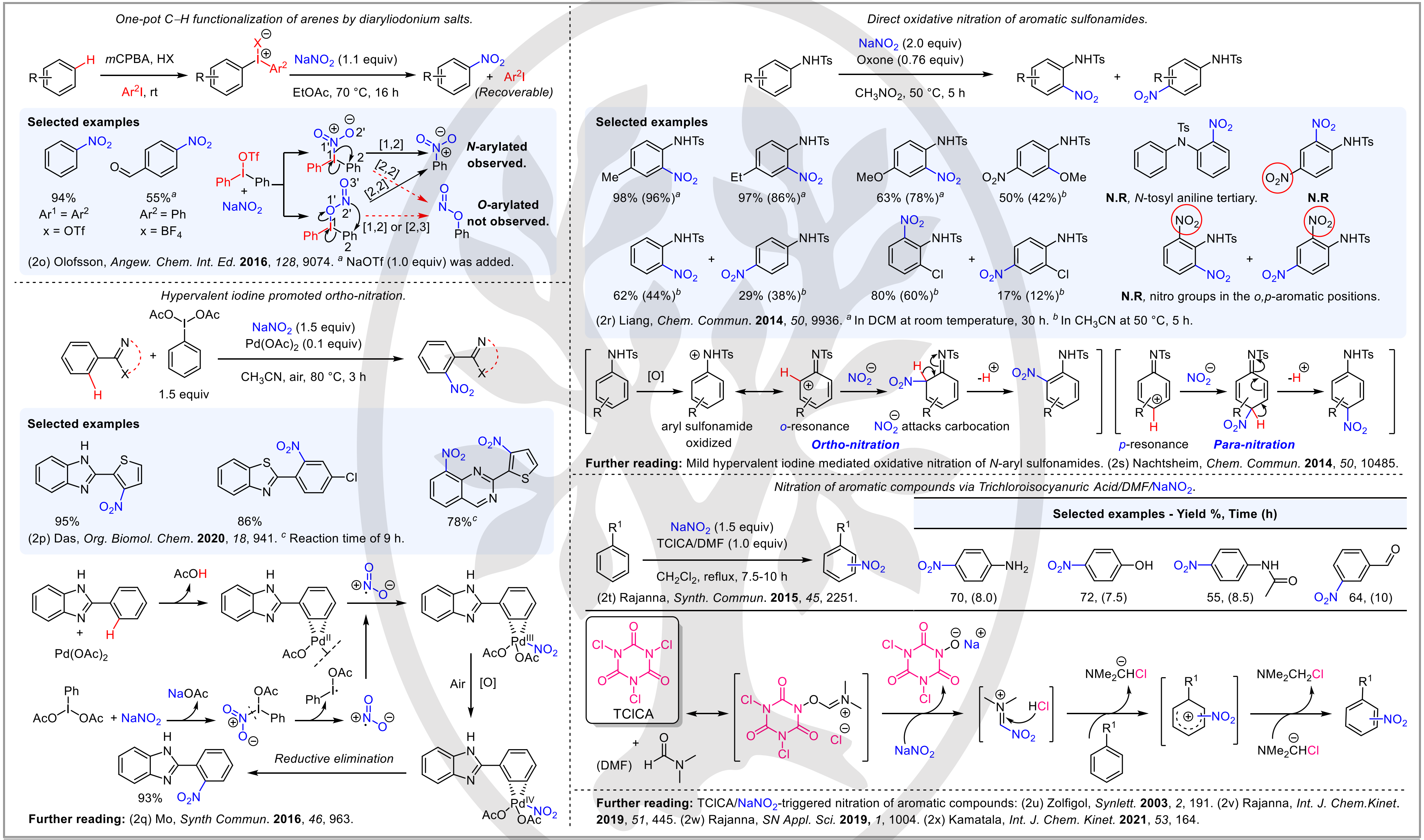


Figure 3: Direct nitration (C–H) promoted by $NaNO_2$. (Part 2)[2o–x]

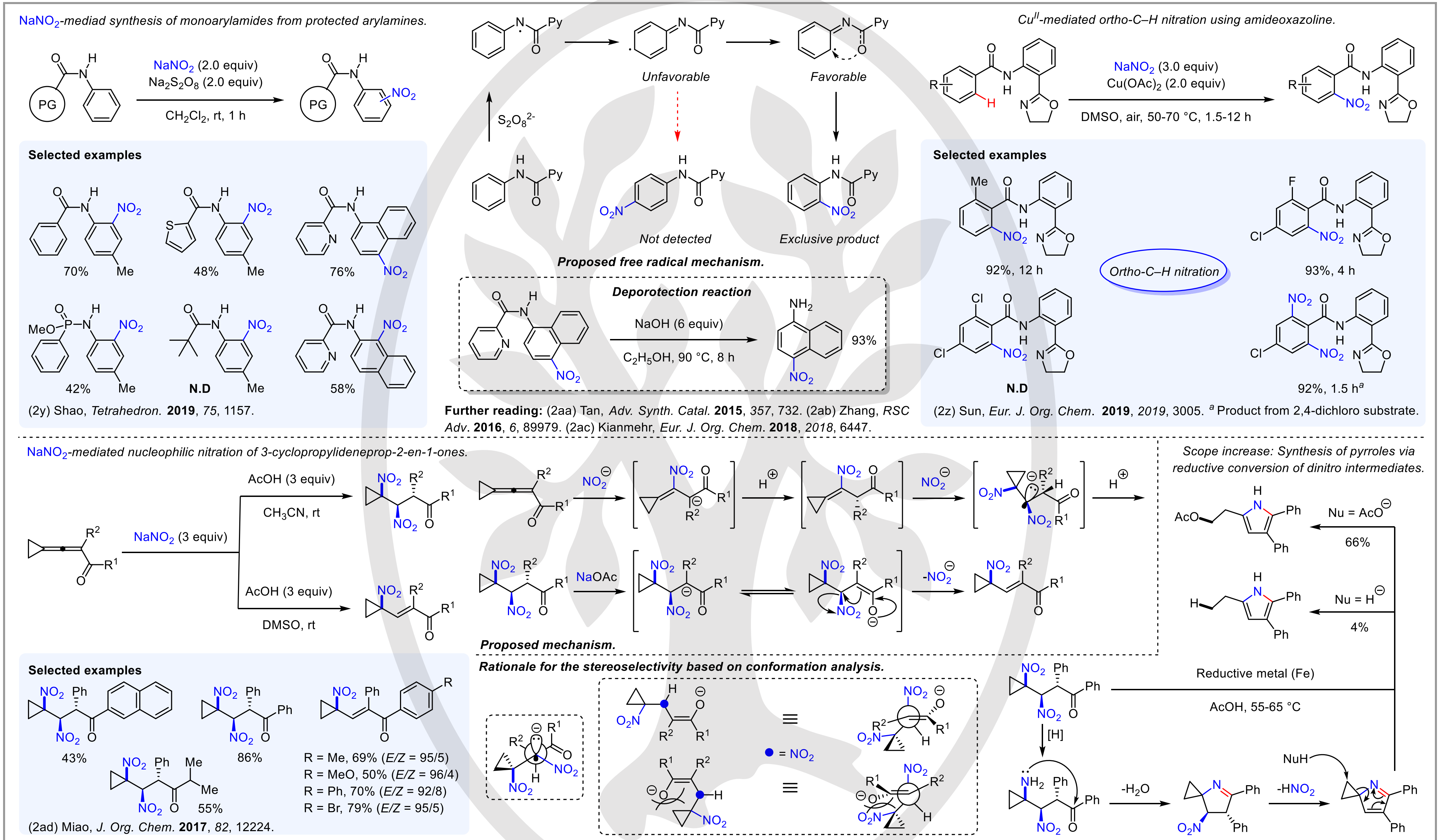
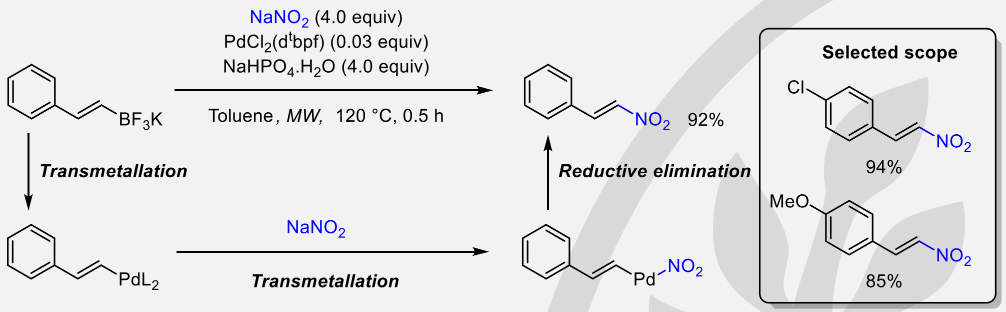


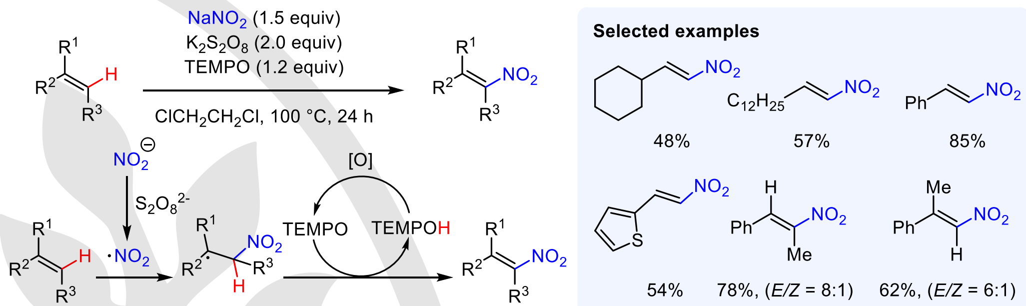
Figure 4: Direct nitration (C–H) promoted by NaNO₂. (Part 3)[2y–2od]

Seminal Study: $NaNO_2$-mediated potassium styryltrifluoroborates nitration via cross-coupling reaction.



(2ae) Saito, *Tetrahedron Lett.* **2005**, *46*, 4715. (2af) Al-Masum, *Tetrahedron Lett.* **2013**, *54*, 1141.

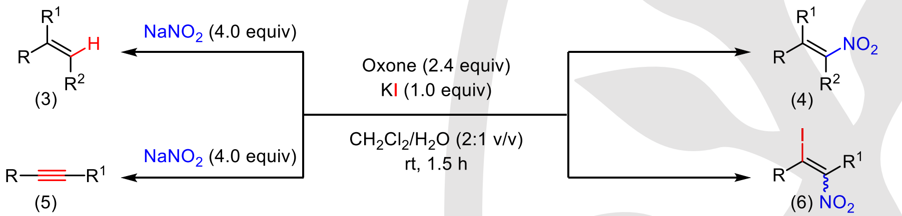
$K_2S_2O_8$-mediated nitration of alkenes with $NaNO_2$ and TEMPO: Stereoselective synthesis of (E)-nitroalkenes.



Proposed mechanism of nitration method.

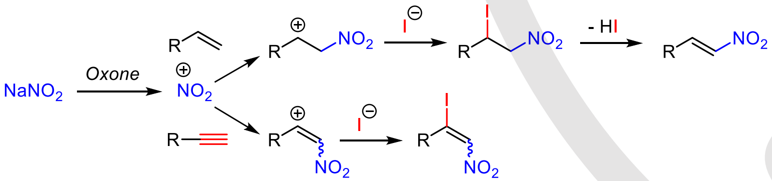
(2ah) Zhao, *Tetrahedron Lett.* **2016**, *57*, 80.

Oxone/KI-mediated nitration of alkenes and alkynes: synthesis of nitro- and β-Iodonitro substituted alkenes.

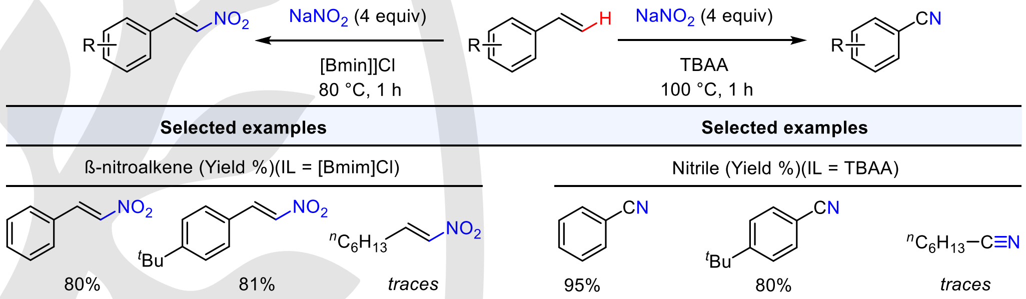


Substrate	R	R^1	R^2	Product	Yield (%)	(E/Z)[b]
3a	4-BrC$_6$H$_4$	H	H	4a	88	-
3b[a]	3-ClC$_6$H$_4$	H	H	4b	87	-
3c[a]	C$_6$H$_5$	H	H	4c	75	-
3d[a]	4-(ClCH$_2$)C$_6$H$_4$	H	H	4d	73	-
5a	C$_6$H$_5$	H	-	6a	62	5.6:1
5b	C$_6$H$_5$	Me	-	6b	53	4.7:1
5c	4-BrC$_6$H$_4$	H	-	6c	63	6.7:1
5d	4-MeC$_6$H$_4$	H	-	6d	70	4.8:1

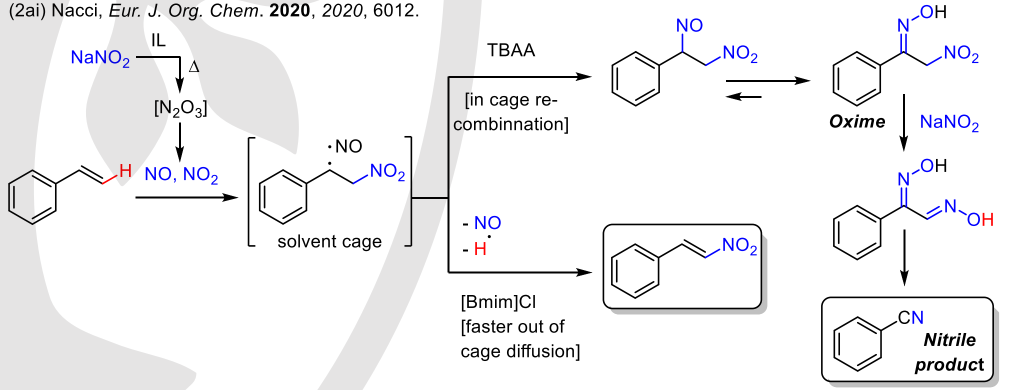
(2ag) Kuhakarn, *Eur. J. Org. Chem.* **2014**, *2014*, 7433. [a] After 1.5 h, aqueous NaOH (10 M, 1 mL) was added, and the mixture was heated at reflux for 1 h. [b] The (E/Z) ratios were determined from by ^1H NMR analysis.



Proposed ionic nitration of alkenes and alkynes.



(2ai) Nacci, *Eur. J. Org. Chem.* **2020**, *2020*, 6012.



Plausible mechanism of nitration of styrenes in ionic liquids.

Beckmann rearrangement

Futher Reading: $NaNO_2$-mediated direct nitration of alkenes and alkynes. (2aj) Bonetti, *J. Org. Chem.* **1967**, *33*, 237. (2ak) Hwu, *J. Chem. Soc., Chem. Commun.* **1994**, *10*, 1425. (2al) Hwu, *Organometallics*. **1996**, *15*, 499. (2am) Buevich, *Tetrahedron Lett.* **2008**, *49*, 2132. (2an) Motornov, *J. Org. Chem.* **2017**, *82*, 5274.

Figure 5: Direct nitration (C–H) promoted by $NaNO_2$. (Part 4)[2ae–an]

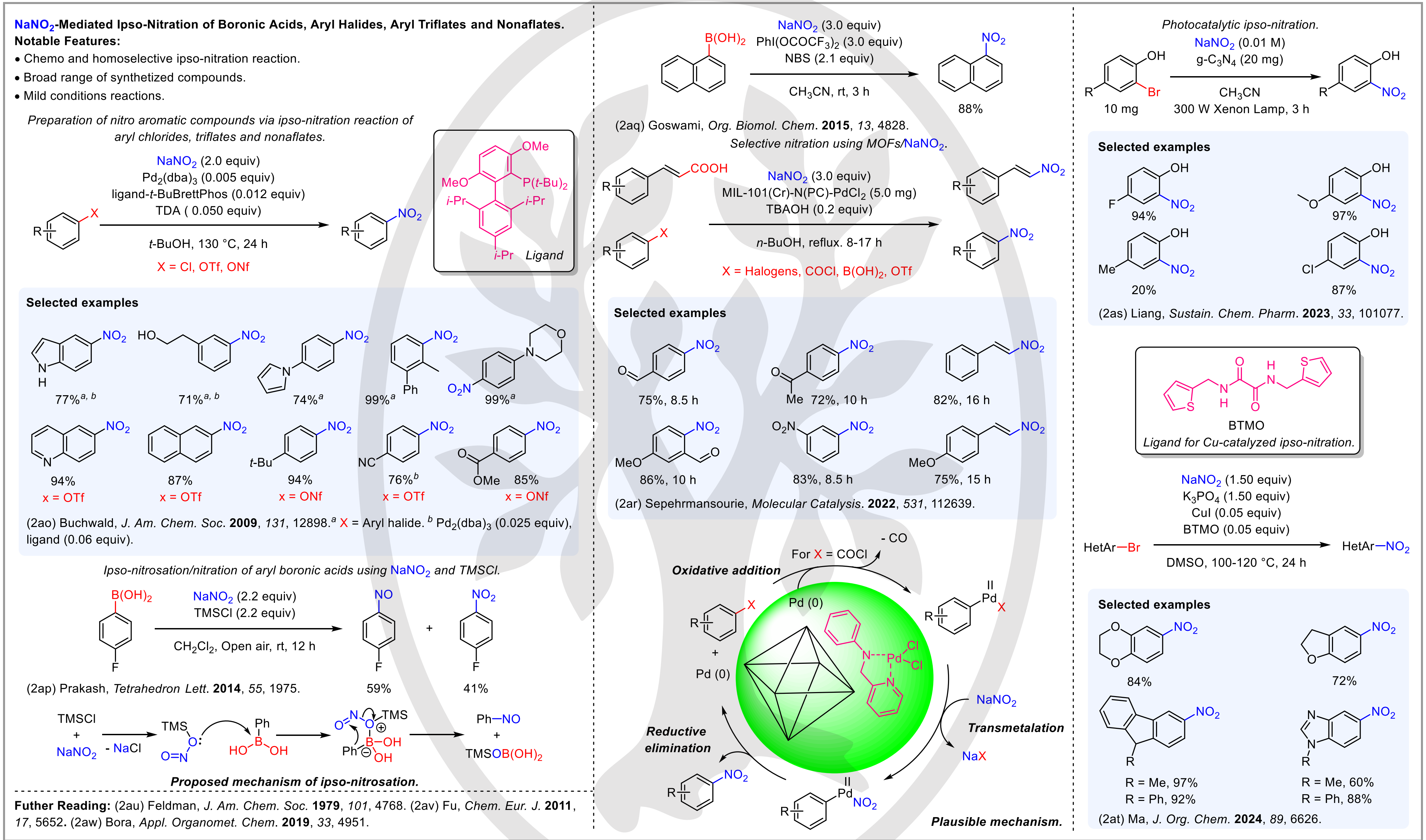
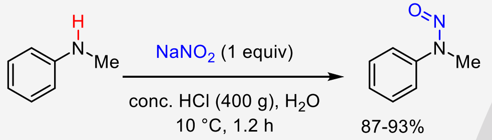


Figure 6: Direct Ipso-nitration (C–H) promoted by $NaNO_2$. (Part 5)[2ao-aw]

Nitrosamines. Notables Features:

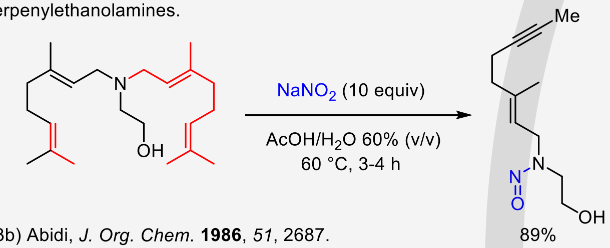
- NaNO$_2$-mediated nitrosation of secondary amines.
- Nitrosonium ions $NO^{\oplus}$ generated *in situ.*

Seminal study: Sodium nitrite-mediated synthesis of *N*-nitrosamines.



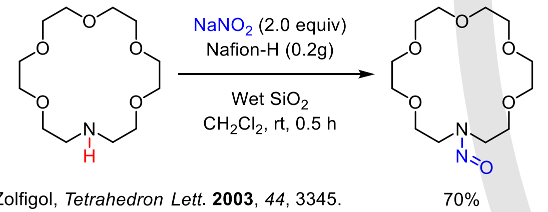
(3a) Hartman, *Org. Synth.***1933**,*13*, 8.

Seminal study: Sodium nitrite-mediated nitrosative dealkylation of tertiary terpenylethanolamines.

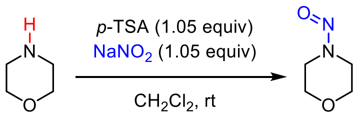


(3b) Abidi, *J. Org. Chem.* **1986**, *51*, 2687.

Further reading: NaNO$_2$-mediated Abidi transformation (Review article).
(3c) Zard, *Chem. Commun.* **2002**, *15*, 1555.

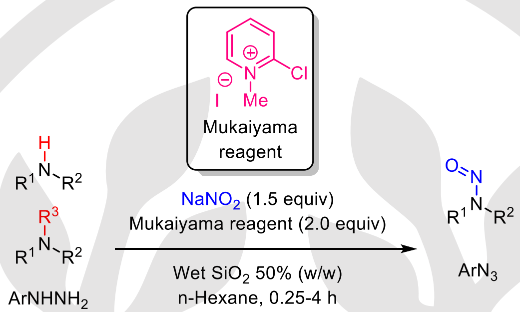


(3d) Zolfigol, *Tetrahedron Lett.* **2003**, *44*, 3345.

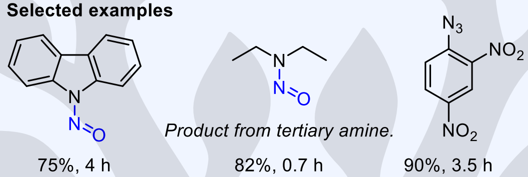


(3e) Borikar, *Synth. Commun.* **2010**, *40*, 654.

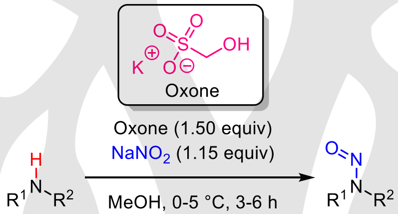
Futher Reading:
(3l) Smith, *J. Am. Chem. Soc.* **1967**, *89*, 1147.
(3m) Hecht, *J. Org. Chem.* **1978**, *43*, 72.
(3n) Nakajima, *Tetrahedron Lett.* **1984**, *25*, 2619.
(3o) Giumanini, *Tetrahedron.* **1990**, *46*, 4303.
(3p) Chehardoli, *J. Chem. Sci.* **2009**, *121*, 441.



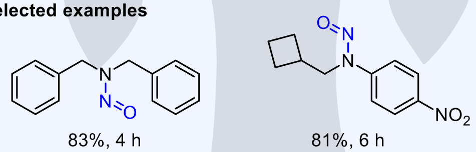
Selected examples



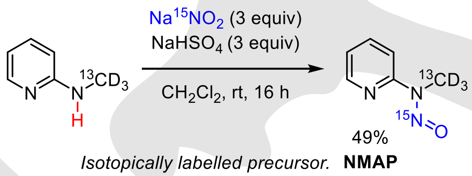
(3f) Azadi, *Tetrahedron Lett.* **2015**, *56*, 5613.



Selected examples

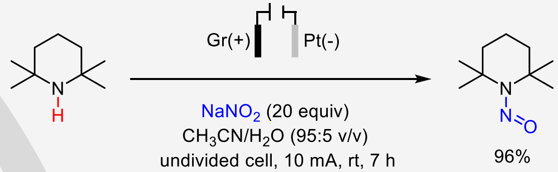


(3g) Banerjee, *Synth. Commun.* **2019**, *49*, 2270.

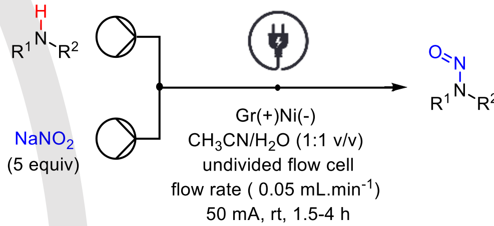


(3h) Derdau, *Labelled. Comp. Radiopharm.* **2023**, *66*, 41.

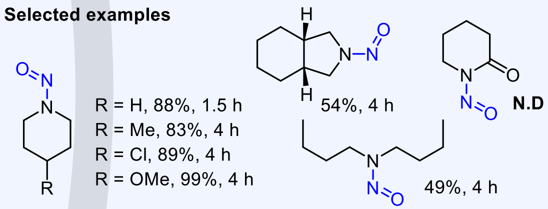
Seminal study: Electrochemical flow method mediated by sodium nitrite.



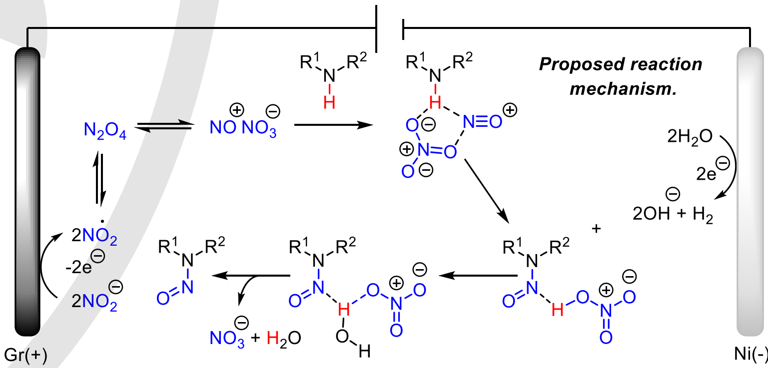
(3i) Masui, *Chem. Pharm. Bull.* **1988**, *36*, 459.



Selected examples



(3j) Ali, *Chem. Eur. J.* **2023**, *29*, e202300957.

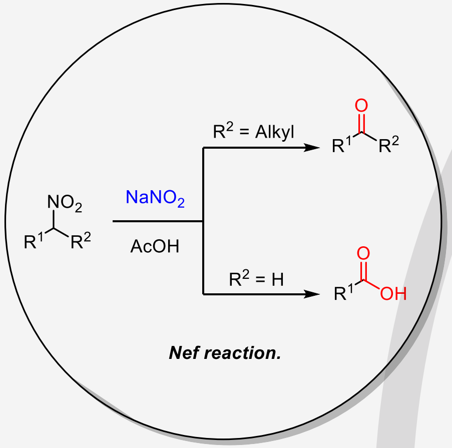


Futher Reading: Review article using electrochemical methods.
(3k) Ali, *Chemistry-Methods.* **2024**, *4*. e20230005.

Figure 7: NaNO$_2$-mediated nitrosation of secondary amines.[3a–p]

$NaNO_2$-Mediated Nef Transformations.

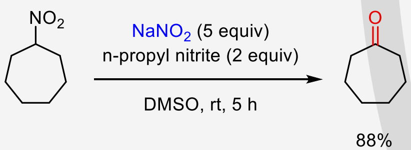
Seminal study: Acid hydrolysis of primary and secondary nitroalkane salts into aldehyde or ketone.



(4a) Nef, *Justus Liebigs Ann. Chem.* **1894**, *280*, 263.

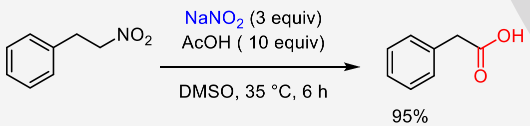
Use of sodium nitrite in the nef reaction:

Seminal study: Synthesis of ketones and carboxylic acids from nitro compounds mediated by $NaNO_2$/alkyl nitrite.

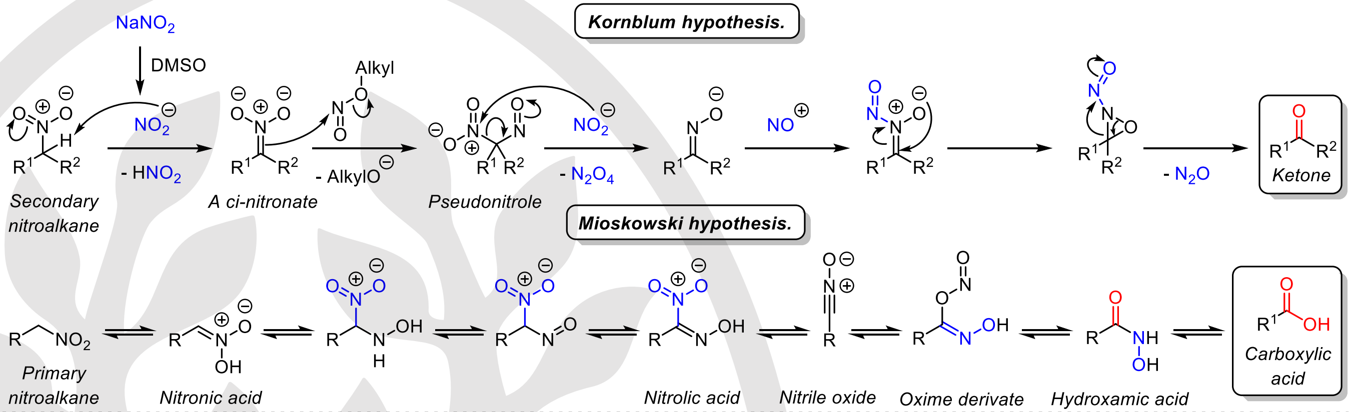


(4b) Kornblum, *J. Am. Chem. Soc.* **1956**, *78*, 1501. (4c) Kornblum, *J. Org. Chem.* **1973**, *38*, 1418.

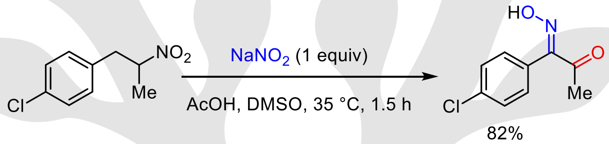
Seminal study: Conversion of primary nitro compounds into carboxylic acids in the presence of $NaNO_2$/AcOH.



(4d) Mioskowski, *J. Org. Chem.* **1997**, *62*, 234.

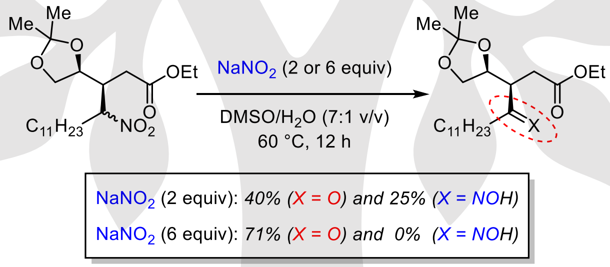


Oxidation of secondary nitro-compounds.



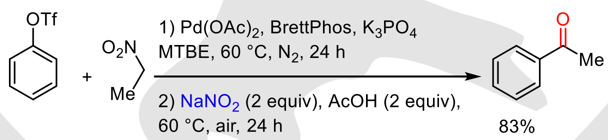
(4e) Ran, *Tetrahedron. Lett.* **2003**, *44*, 8061.

Effect of the sodium nitrite concentration on product distribution.



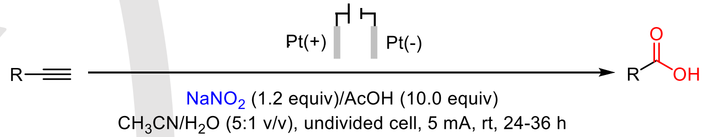
(4f) Patrocinio Pereira, *Tetrahedron Lett.* **2009**, *50*, 6389.

Access to ketones through Pd-catalyzed cross-coupling of phenol derivatives with nitroalkanes.

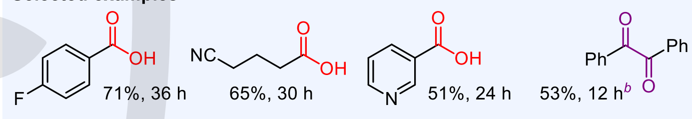


(4g) Yu, *Eur. J. Org. Chem.* **2022**, *2022*, e202200731.

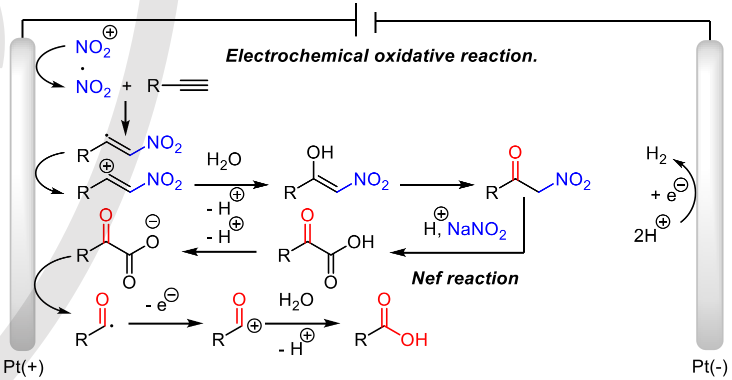
Electrochemical oxidative cleavage of alkynes to carboxylic acids.



Selected examples



(4h) Huang, *Org. Lett.* **2023**, *25*, 293. [b] Product from internal alkyne.



Further reading: Review article on new perspectives on the Nef reaction and $NaNO_2$-mediated methodologies. (4i) Petrini, *Adv. Synth. Catal.* **2015**, *357*, 2371.

Figure 8: $NaNO_2$-mediated Nef reaction.[4a–i]

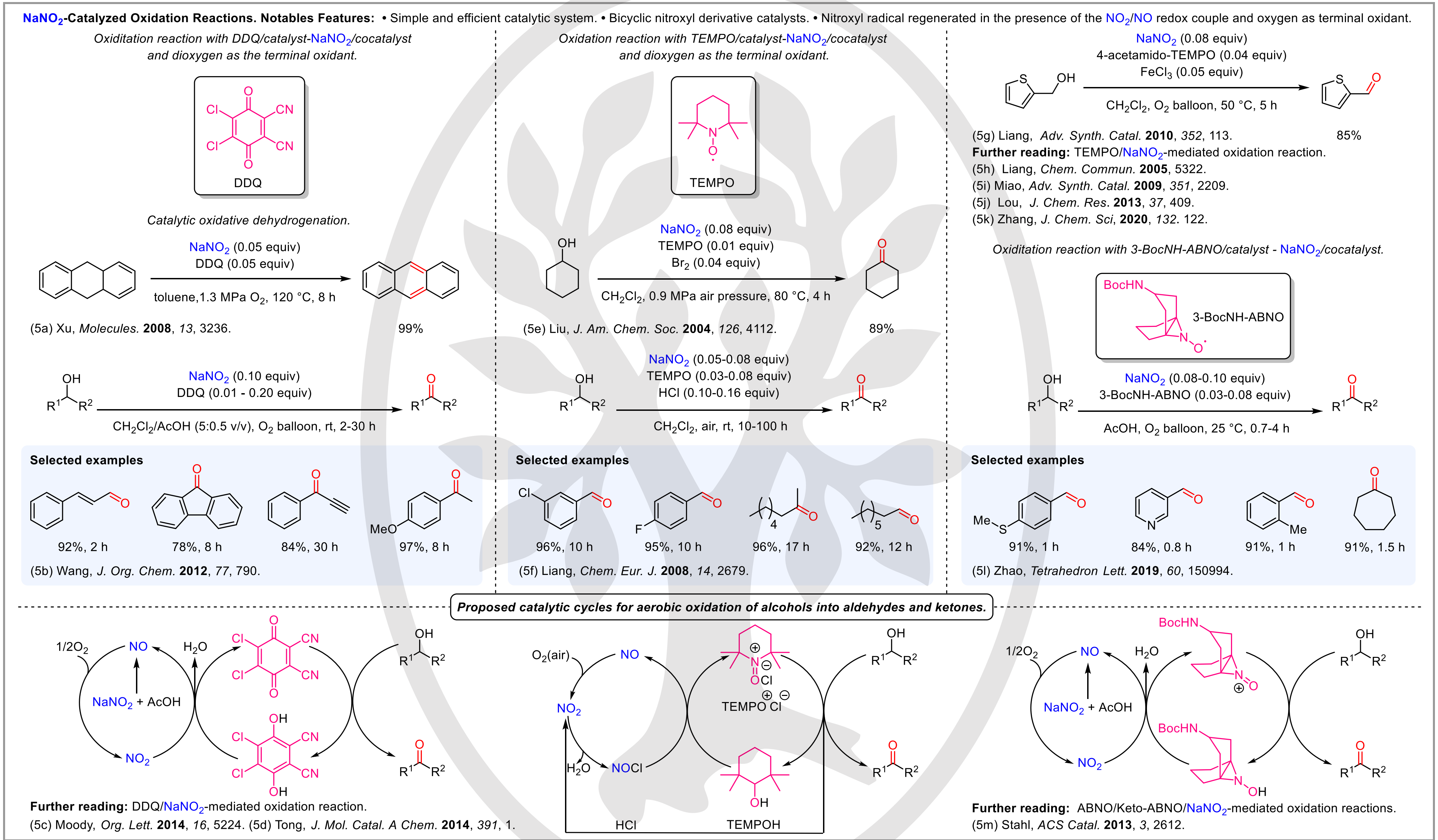
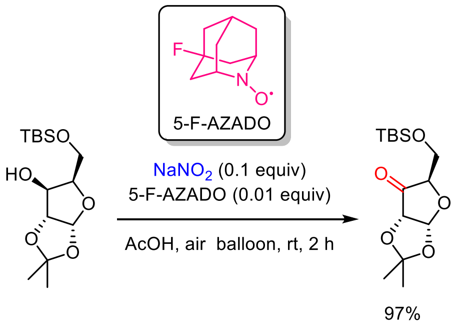
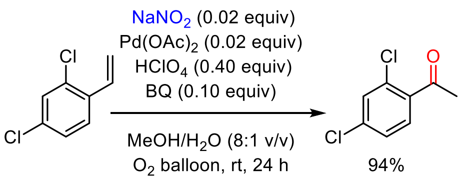


Figure 9: $NaNO_2$-mediated oxidation reactions. (Part 1)[5a–m]

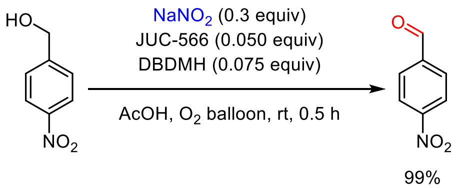


(5n) Iwabuchi, *J. Am. Chem. Soc.* **2011**, *133*, 6497.
Further reading: Mechanistic studies.
(5o) Iwabuchi, *J. Org. Chem.* **2014**, *79*, 10256.
Chemoselective oxidation of α-hydroxy acids to α-keto acids catalyzed by AZADO/NaNO$_2$:
(5p) Shibuya, *Org. Lett.* **2016**, *18*, 4230.

Wacker oxidation of styrene derivatives into ketones.

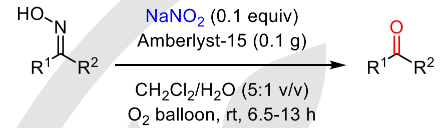


(5q) Ding, *Org. Biomol. Chem.* **2013**, *11*, 2947.
Further reading: Wacker oxidation.
(5r) Grubbs, *J. Am. Chem. Soc.* **2014**, *136*, 890.
(5s) Wan, *Org. Biomol. Chem.* **2022**, *20*, 7814.

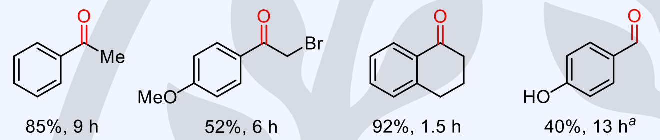


(5t) Chen, *Angew. Chem. Int. Ed.* **2021**, *60*, 22230.
Other further reading:
(5u) Bosch, *J. Org. Chem.* **1994**, *59*, 2529.
(5v) Liang, *Angew. Chem. Int. Ed.* **2005**, *44*, 5520.
(5w) Xu, *Adv. Synth. Catal.* **2009**, *351*, 558.
(5x) Liu, *Org. Lett.* **2021**, *23*, 4057.

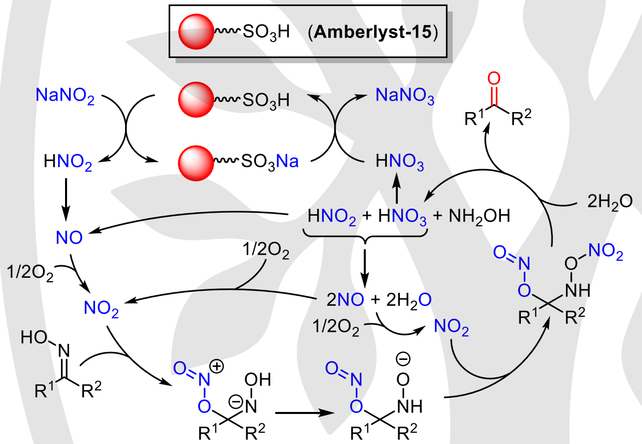
NaNO$_2$ catalyzed aerobic oxidative deoximation.



Selected examples

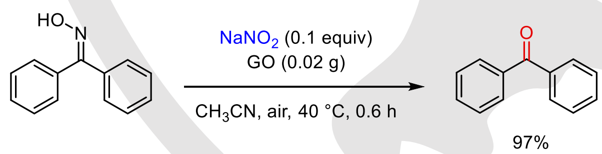


(5y) Ding, *J. Org. Chem.* **2011**, *76*, 4665. [a] Incomplete conversion.

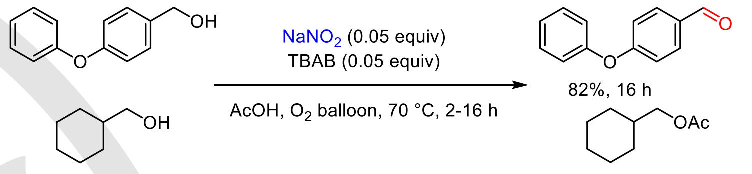


Plausible mechanism for aerobic oxidative deoximation catalyzed by NaNO$_2$.

Deoximation method for deprotection of ketones and aldhydes using a Graphene-Oxide/Sodium Nitrite-based catalystic system.



(5z) Tong, *Adv. Synth. Catal.* **2019**, *361*, 3137.

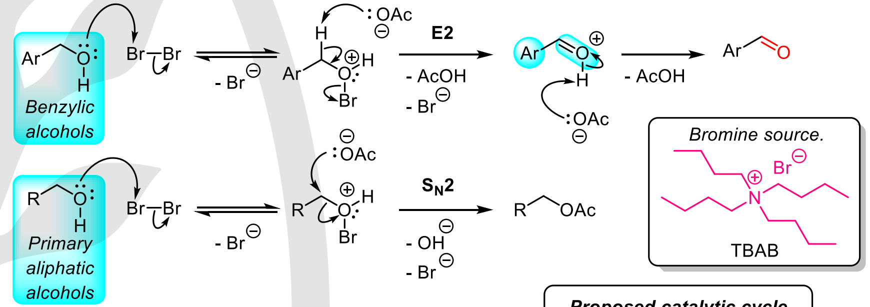


(5aa) Sheykhan, *RSC Adv.* **2016**, *6*, 51347.

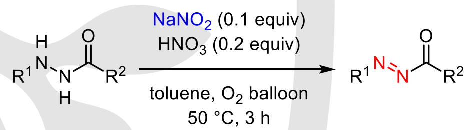
72%, 4 h

(1) $NO_2^{\ominus}$ + 2AcOH → $NO^{\oplus}$ + H_2O + $2AcO^{\ominus}$ (2) $NO^{\oplus}$ + O_2 + H_2O → $NO_2^{\oplus}$ + H_2O_2

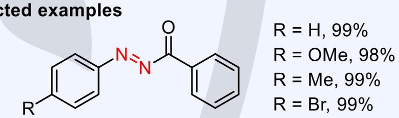
(3) $NO_2^{\oplus}$ + $2Br^{\ominus}$ → $NO_2^{\ominus}$ + Br_2 *Re-cycle into step* (1).



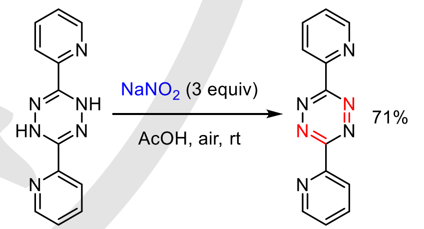
Proposed catalytic cycle for the aerobic oxidation.



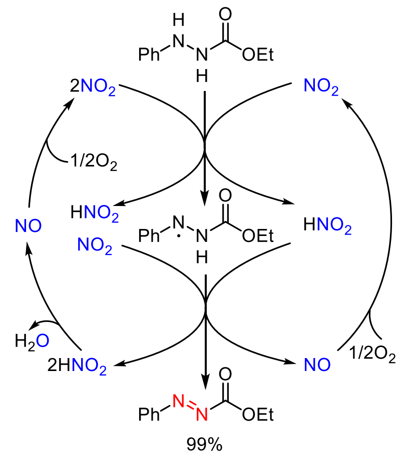
Selected examples



(5ab) Kim, *J. Org. Chem. Frontiers.* **2020**, *7*, 834.



(5ac) Méndez, *Angew. Chem. Int. Ed.* **2023**, *62*, 11186.



Synthesis of azo compounds catalyzed by NaNO$_2$.

Figure 10: NaNO$_2$-mediated oxidation reactions. (Part 2)[5m–ac]

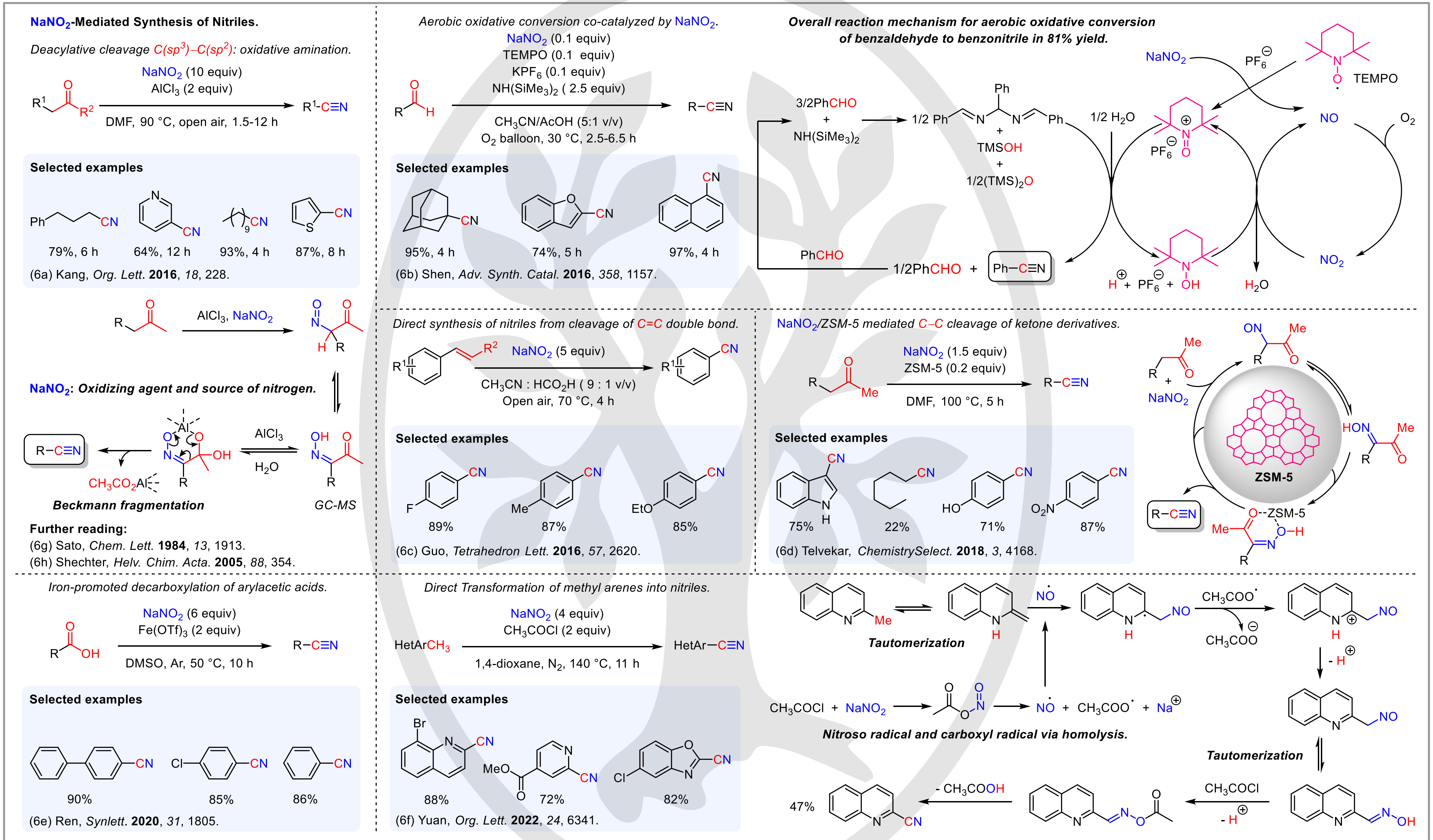


Figure 11: NaNO2-mediated synthesis of nitriles.[6a–h]

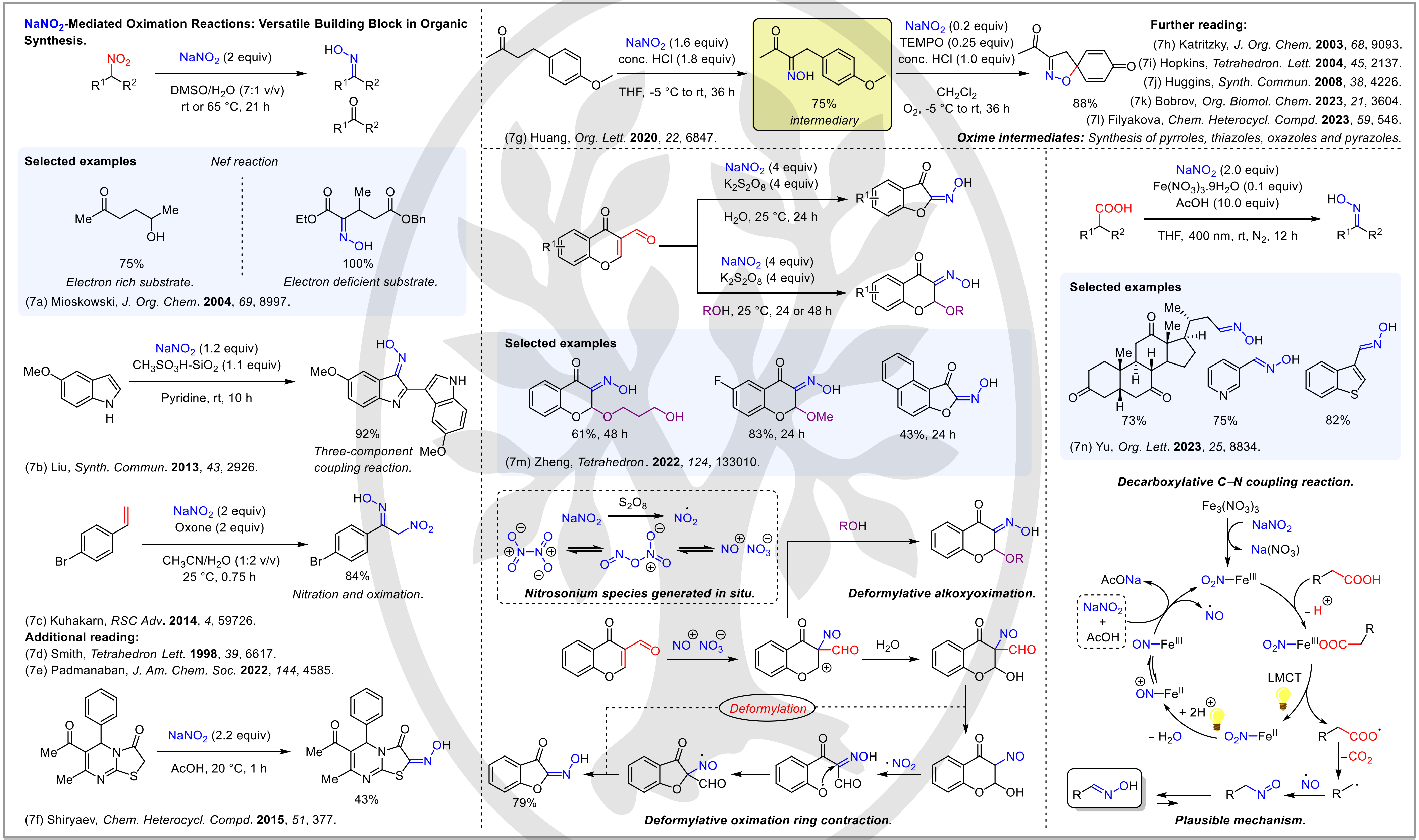


Figure 12: NaNO$_2$-mediated oximation reaction.[7a–n]

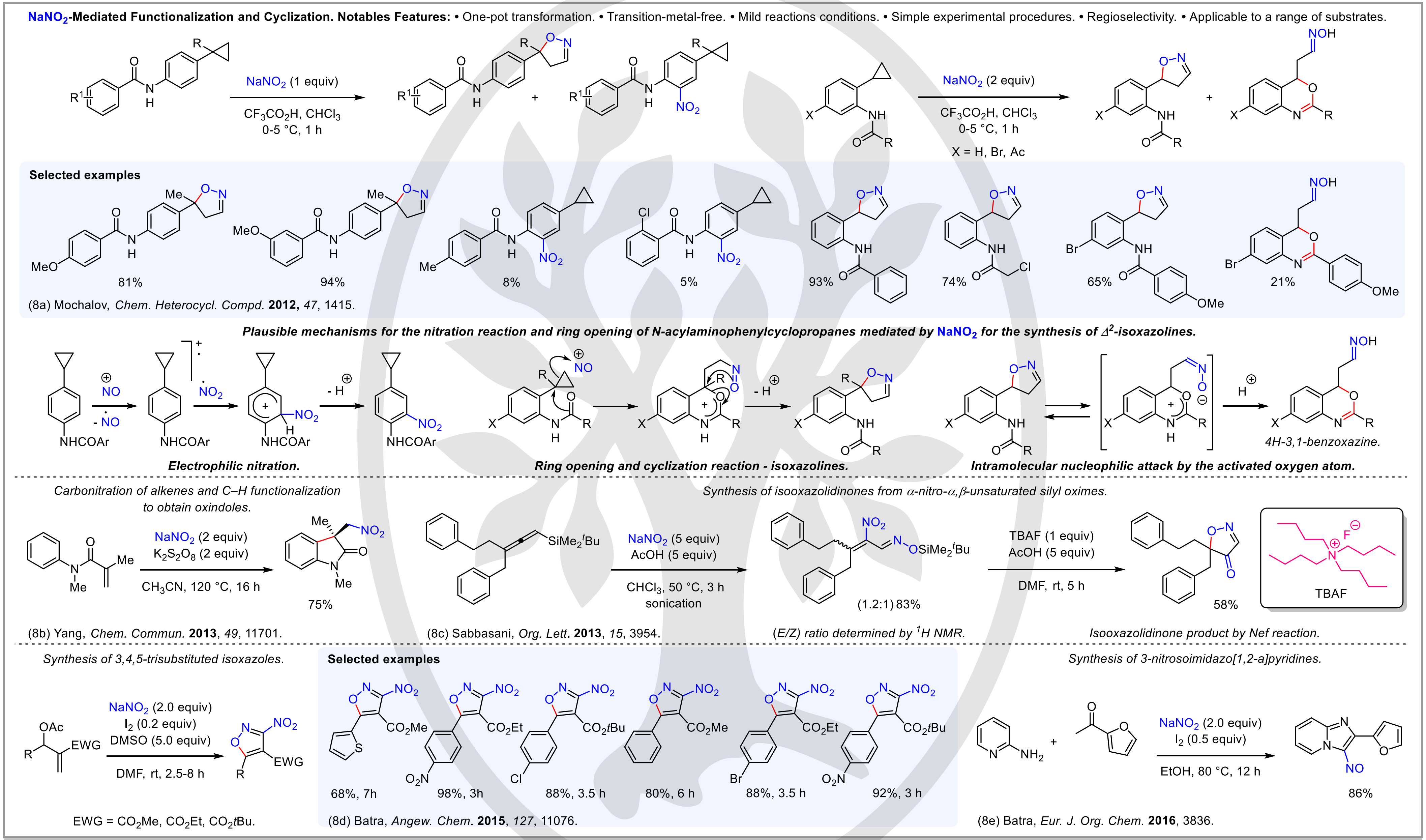
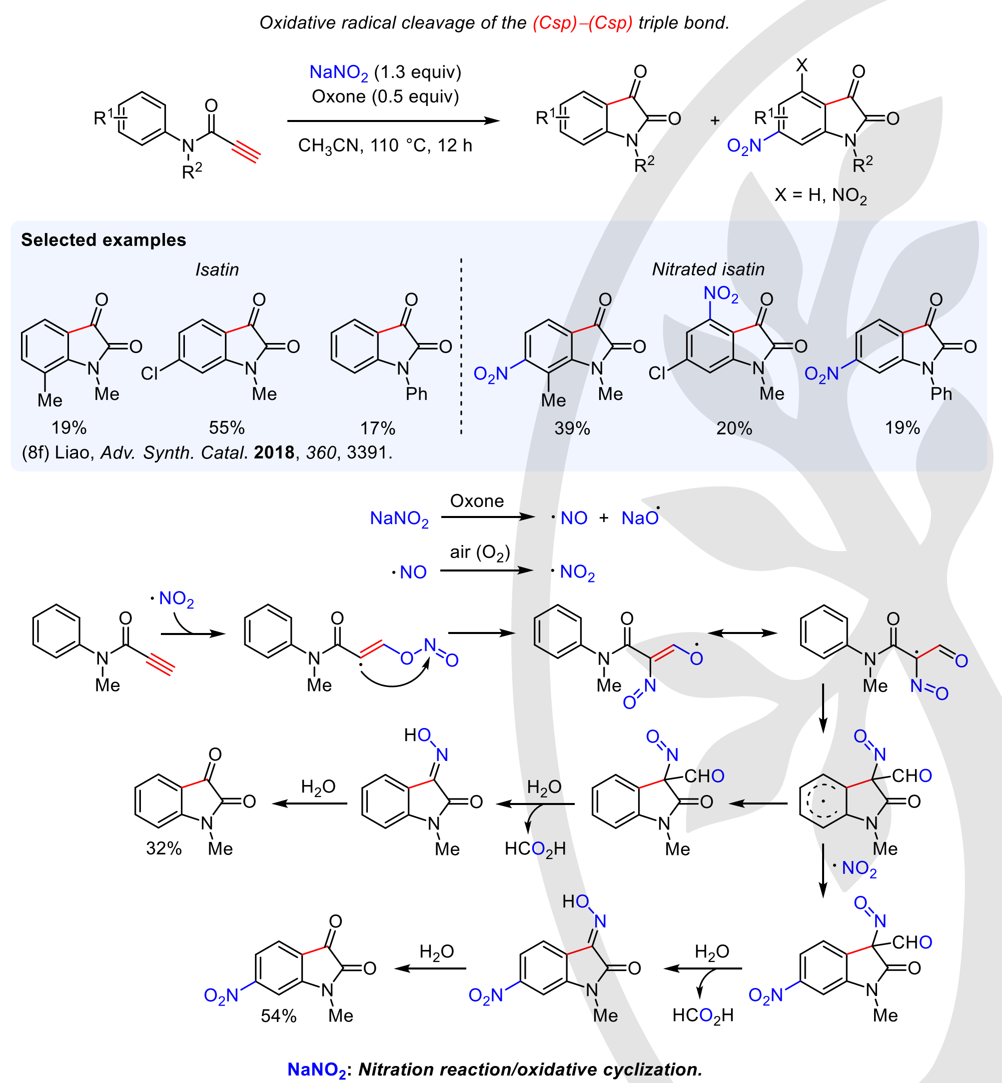
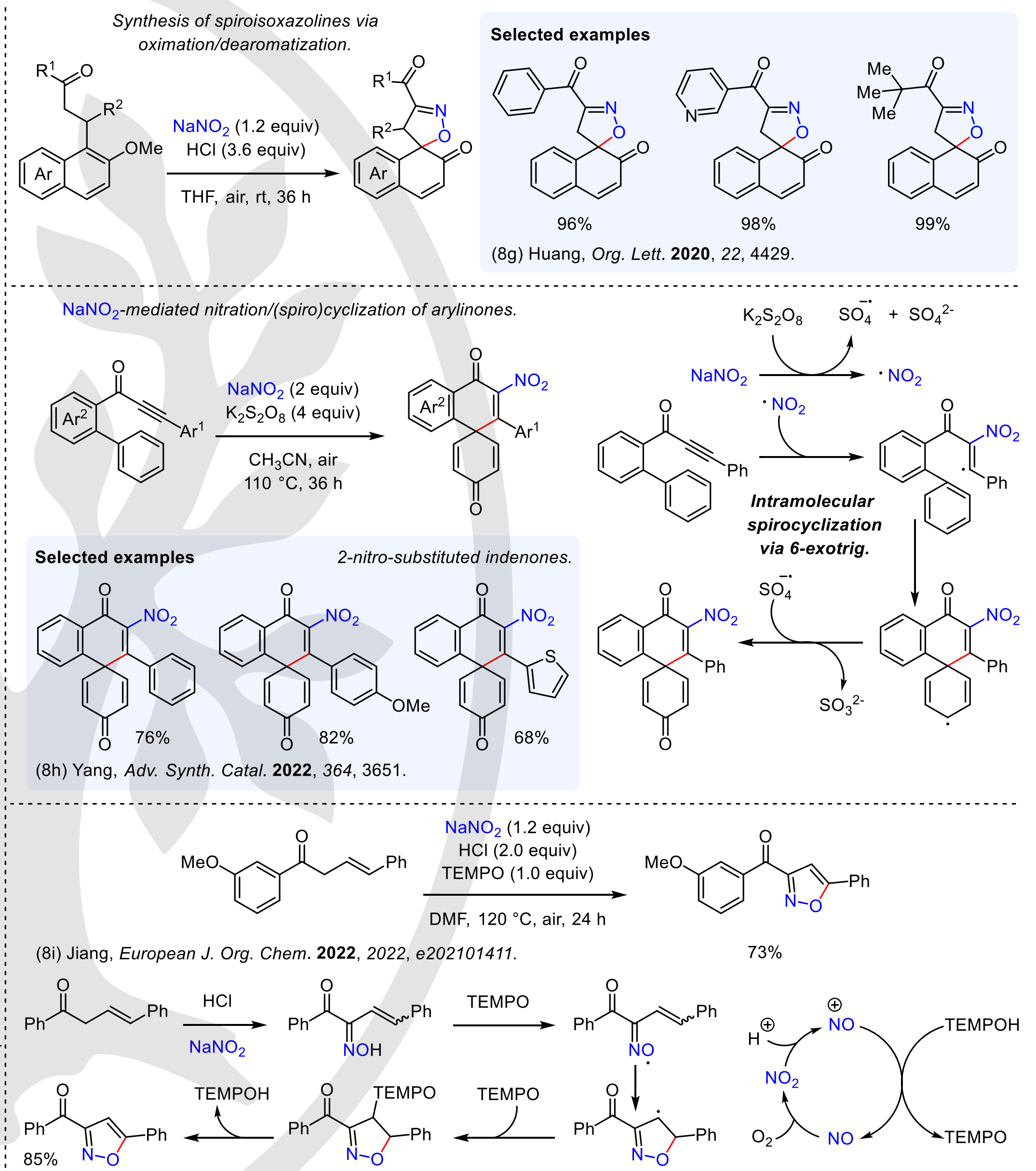


Figure 13: $NaNO_2$-mediated heterocycle formation. (Part 1)[8a–e]





Further reading:

(8j) Tan, *Tetrahedron Lett*. **2008**, *49*, 4424.
(8k) Robina, *Org. Lett.* **2009**, *11*, 4778.
(8l) Saikia, *Asian J. Org. Chem.* **2016**, *5*, 528.
(8m) Ila, *J. Org. Chem.* **2016**, *81*, 5606.
(8n) Patil, *Org. Lett.* **2022**, *24*, 5840.

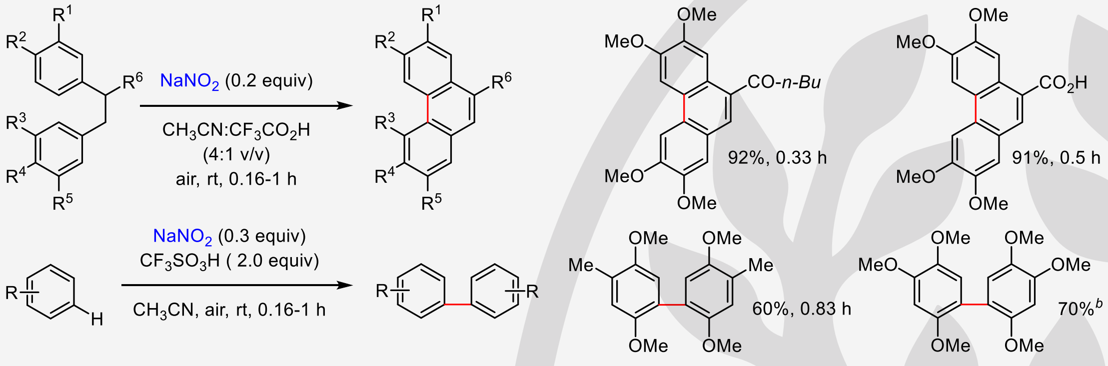
Copper-mediated nitrosation: 2-Nitrosophenolato complexes and their use in the synthesis of heterocycles:

(8o) McKillop, *J. Org. Chem.* **1976**, *41*, 1079.
(8p) Baxendale, *Molecules*. **2019**, *24*, 4154.

Figure 14: $NaNO_2$-mediated heterocycle formation. (Part 2)[8f–p]

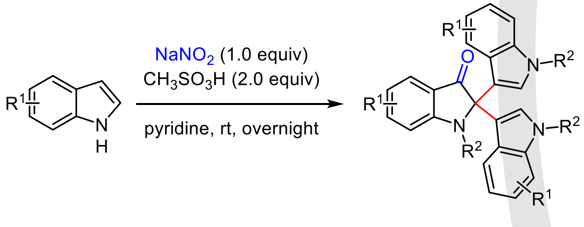
Coupling Reaction and C–C Bond Formation Catalyzed/Mediated by $NaNO_2$.

Seminal Study: $NaNO_2$-catalyzed oxidative coupling reaction for construction of the phenanthrene ring using O_2 as terminal oxidant.



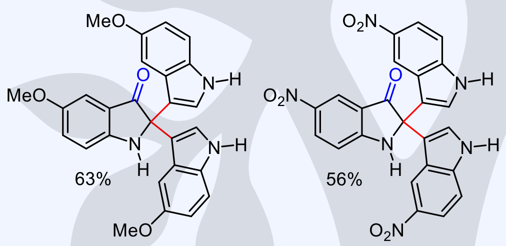
(9a) Wang, *Adv. Synth. Catal.* **2012**, *354*, 383. [b] $CF_3CO_2H:CH_3CN$ (1:9 v/v), 0.16 h. *Synthesis of methoxybiaryls.*

Oxidative trimerization of indoles using $NaNO_2$ to construct quaternary carbon centers.

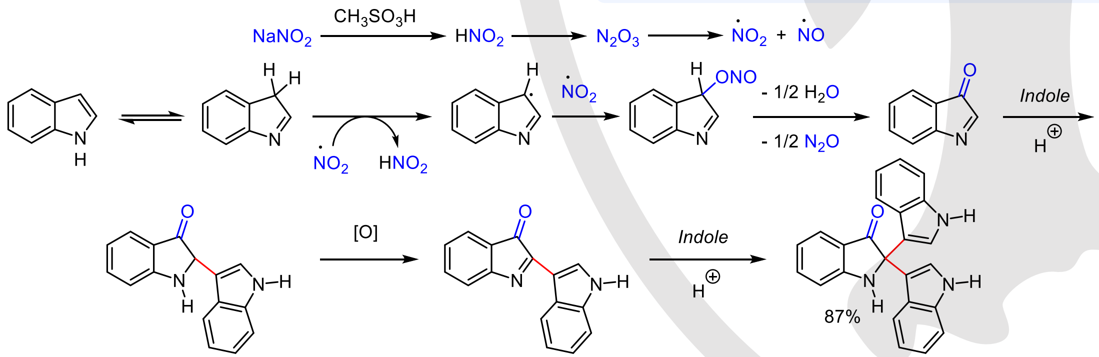


Synthesis of 2-(1H-Indol-3-yl)-2,3'-biindolin-3-ones.

Selected examples

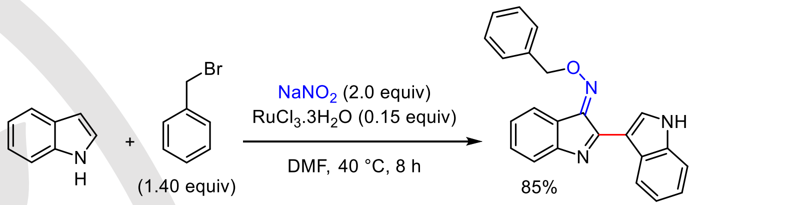


(9b) Liu, *Syn. Commun.* **2014**, *44*, 2215.



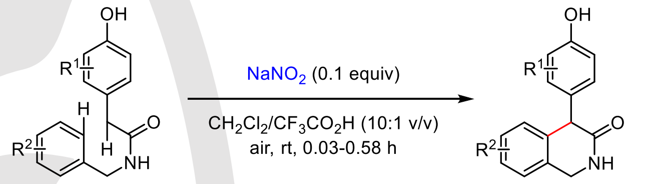
Plausible mechanism for $NaNO_2$-promoted oxidative trimerization of indoles.

Additional study: $NaNO_2$/*ruthenium-catalyzed synthesis of (E)-2,30-bi(3H-indol)-3-one O-alkyl oximes.*

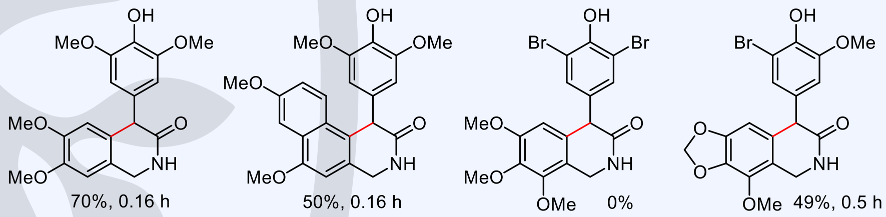


(9c) Qu, *Synth. Commun.* **2015**, *45*, 993. *C–C, C=N, and C–O bonds formed in one pot.*

Construction of the 4-aryldihydroisoquinolinone moiety via direct oxidative Csp^2–Csp^3 coupling.

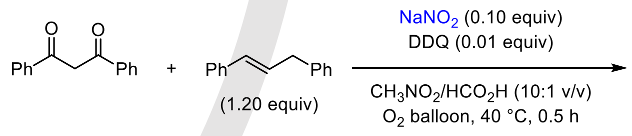


Selected examples

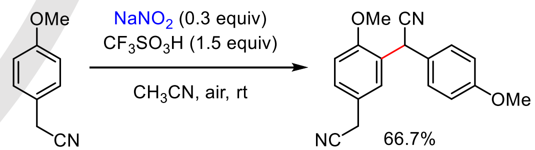


(9d) Wang, *Adv. Synth. Catal.* **2014**, *356*, 977.

$NaNO_2$-*catalyzed aerobic oxidative coupling of benzylic compounds.*



(9e) Yan, *Tetrahedron Lett.* **2015**, *56*, 1641.



(9f) Wang, *Curr. Org. Synth.* **2018**, *15*, 989. **Further reading:** (9g) Basavaiah, *RSC Adv.* **2014**, *4*, 23966.

Figure 15: $NaNO_2$- catalyzed/mediated C–C bond formation reaction. [9a–g]

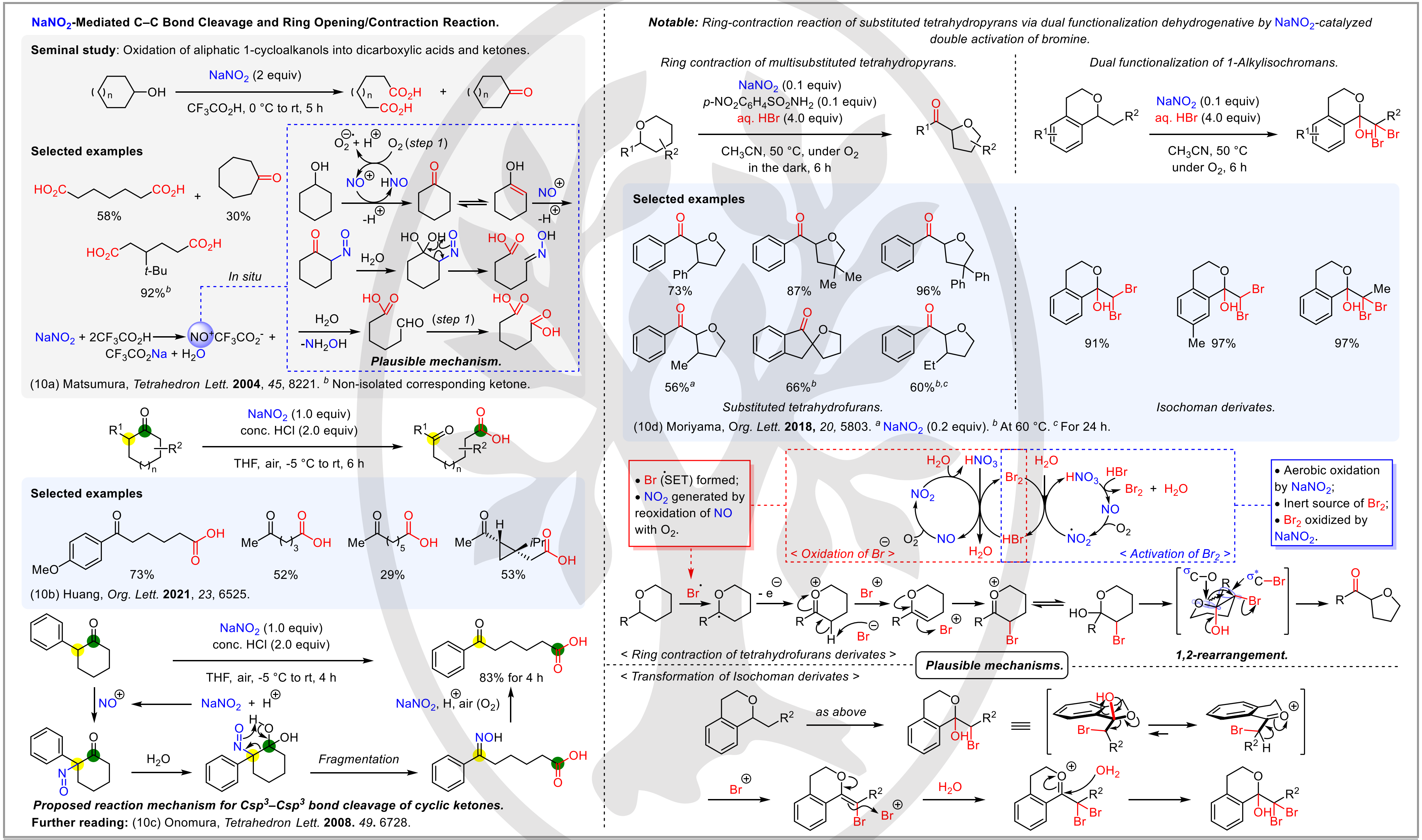
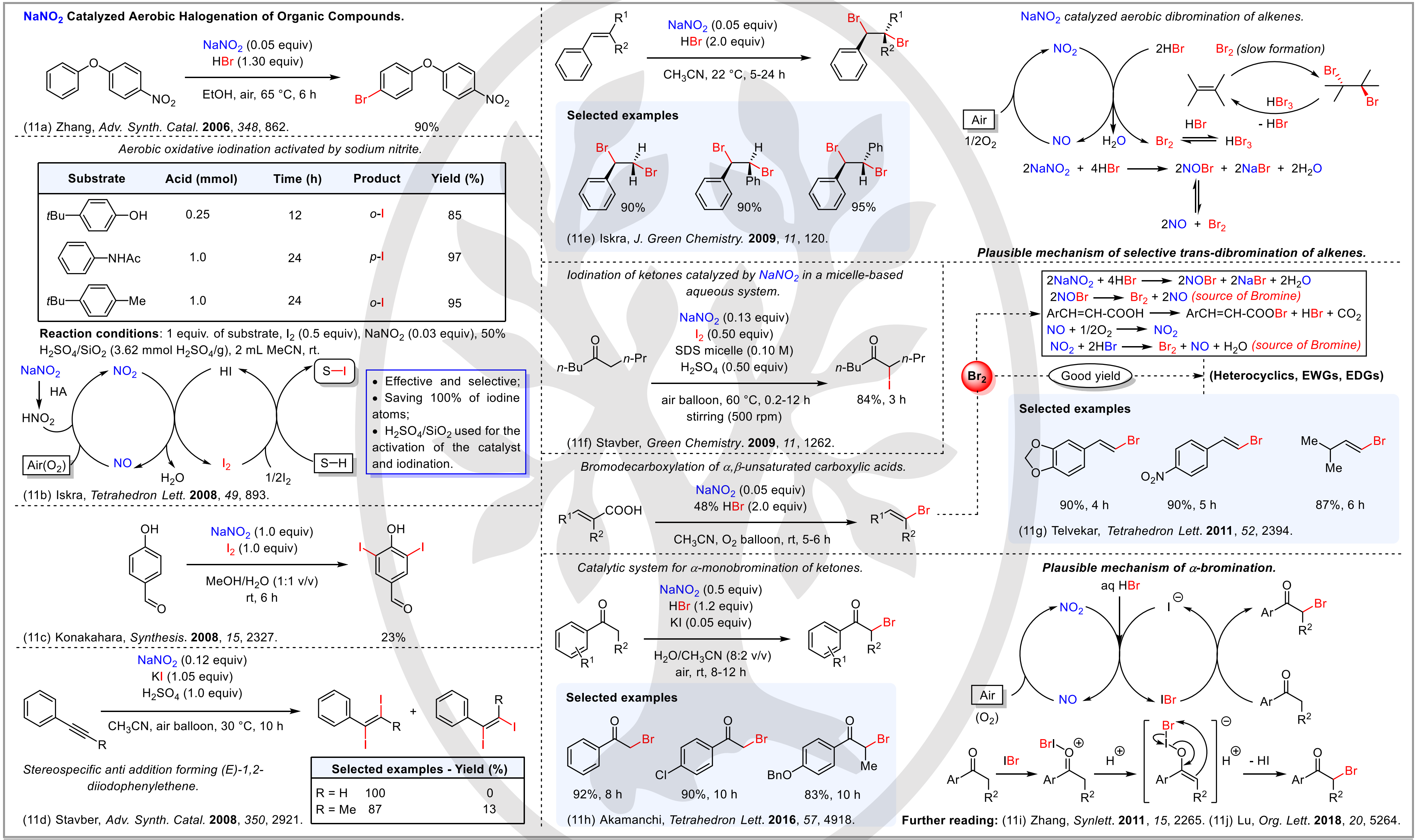


Figure 16: NaNO$_2$-mediated ring opening/contraction reaction. [10a–d]



Substrate	Acid (mmol)	Time (h)	Product	Yield (%)
tBu–C6H4–OH	0.25	12	o-I	85
C6H5–NHAc	1.0	24	p-I	97
tBu–C6H4–Me	1.0	24	o-I	95

Selected examples - Yield (%)		
R = H	100	0
R = Me	87	13

Figure 17: $NaNO_2$-mediated halogenation reactions. [11a–j]

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Acknowledgment

To the postgraduate program in pharmaceutical sciences at the Federal University of Rio Grande do Norte and collaborating members of the pharmaceutical chemistry laboratory of the pharmacy department.

Conflict of Interest

The authors declare no conflict of interest.

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