Exploring Porphyrins, Phthalocyanines and Corroles as Photocatalysts for Organic Transformations

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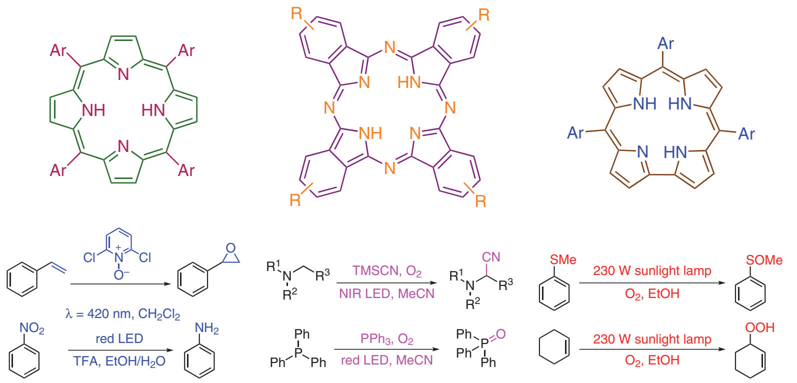

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Abstract In recent years, macrocycles have emerged as efficient and sustainable photosensitizers for the catalysis of organic transformations. This graphical review provides a concise overview of photocatalysis and photoredox catalysis utilizing three common macrocycles: porphyrins, phthalocyanines and corroles. They exhibit strong absorption in the visible region and can be easily oxidized or reduced, making them good candidates for photocatalysis.

Key words photocatalysis, photoredox catalysis, porphyrins, phthalocyanines, corroles

Photocatalysis offers the advantage of using light as an affordable, sustainable and green source of energy to carry out endergonic reactions.[1] It offers the advantage of milder conditions over those of thermal reactions.[2] As visible light is absorbed by sensitizers but not by most organic compounds, it offers an efficient approach to prevent product degradation and side reactions.[3] In photoredox catalysis, the photocatalyst in its excited state differs from that of the ground state by providing a higher electron affinity and a lower ionization potential, thereby making it a better electron donor as well as an acceptor. Versatile applications of photocatalysts are found in CO_2 reduction, H_2O splitting, proton-coupled electron transfer, photovoltaics and in the development of photo-electrochemical solar cells.[4]

The formation of carbon–carbon and carbon–heteroatom bonds has been a challenge in organic chemistry, which has been efficiently tackled by photocatalysis.[5] Traditionally, metal complexes (such as Ru and Ir polypyridyl complexes) and organic dyes (such as eosin Y) have been employed extensively as photocatalysts.[6] However, the high cost and toxic nature of metal complexes, as well as the pH-sensitive nature of organic dyes have prompted researchers to explore macrocycles such as porphyrins, phthalocyanines and corroles for photocatalysis.[7] These macrocycles have been examined for the catalysis of cyclopropanations, hydroxylations, aziridinations, epoxidations, sulfoxidations, etc.[8–10] Typically in photoredox catalysis, under light irradiation, these photocatalysts may undergo oxidation or reduction at different potentials and participate in SET (single-electron transfer) with the substrates. In photooxidation reactions, upon photoexcitation, such catalysts can switch from singlet to triplet excited states via ISC (intersystem crossing), and during this process, they can generate singlet oxygen via the type II pathway. Their ability to participate in SET depends on the reaction conditions, the nature of the substrate and also on the types of meso-substituents (electron-donating or electron-withdrawing) present on the catalyst, which in turn will govern their efficiency.

This graphical review provides an overview of organic transformations photocatalyzed by porphyrins, phthalocyanines and corroles, along with selected substrate scopes, that have been reported over the last five years (2019 to 2023). As photocatalysis by corroles is relatively less explored, all the examples described since 2005 are included. This graphical review describes photooxidations, epoxidations, sulfoxidations, aziridinations and cyanations of aliphatic and/or aromatic compounds by employing these macrocycles. In addition, C–H arylations of heteroarenes and thiocyanations utilizing porphyrins are discussed. Researchers have also explored hydroxylations, cycloadditions, perfluoroalkylations and phosphonylations by employing phthalocyanines as photocatalysts. Examples of brominations mediated by corroles are also provided. However, reactions involving inorganic transformations, polymerization, photodegradation and heterogenous catalysis are excluded.

Biographical Sketches

Ashmita Jain received her M.Sc. in chemistry from Jamia Millia Islamia, India. In 2021, she began her Ph.D. research at the Indian Institute of Technology Gandhinagar, India with Dr. Iti Gupta. Her research is focused on photocatalytic transformations of organic compounds utilizing macrocycles such as corroles and their metal complexes.

Iti Gupta obtained her Ph.D. in chemistry from the Indian Institute of Technology Bombay, India. She received a JSPS Fellowship from Japan and undertook postdoctoral research at Kyushu University, where she worked on expanded porphyrins. Subsequently, she joined the Chemistry Faculty at BITS Pilani, K K Birla Goa Campus (2007–2009), before moving to the Indian Institute of Technology Gandhinagar in July 2009, where she is currently an associate professor. She is a member of the Society of Porphyrins & Phthalocyanines, and is also a life-member of the Chemical Research Society of India. Her current research interests are focused on the applications of porphyrins, corroles and metal dipyrrinato complexes in photocatalysis and the photodynamic therapy of cancer.

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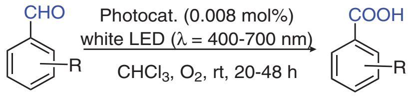
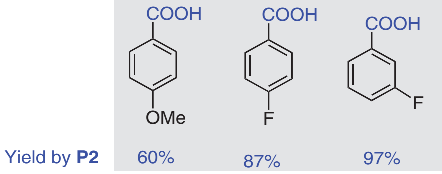
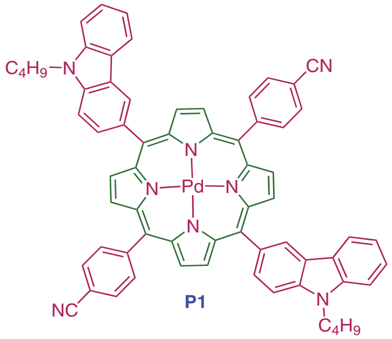
Oxidation of aldehydes to carboxylic acids by photosensitizers[11]

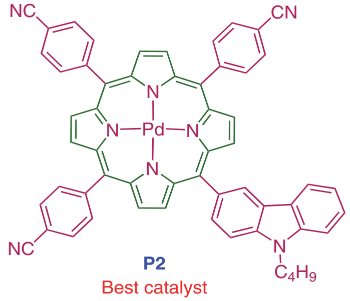


Selected substrate scope



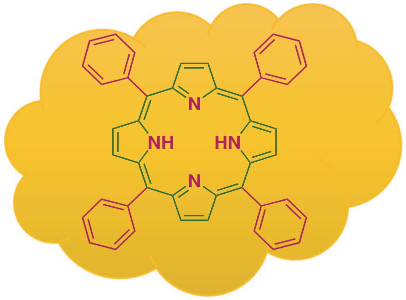


P1



P2
Best catalyst

(11) Gupta, *J. Porphyrins Phthalocyanines* **2021**, *25*, 571-581.



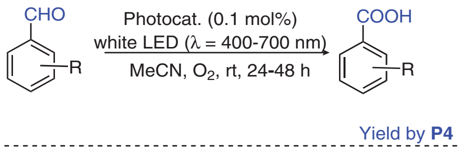
Photophysical properties of porphyrin[12,13]

5,10,15,20-tetraphenylporphyrin in DCM

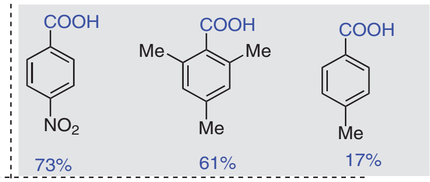
- one Soret and four Q bands in UV-vis spectra
  Soret band- 417 nm
  Q-bands- 514 nm, 549 nm, 592 nm,, 647 nm
- Fluorescence quantum yield (ϕ_f) = 0.11
- Fluorescence lifetime (τ_f) = 9.62 ns

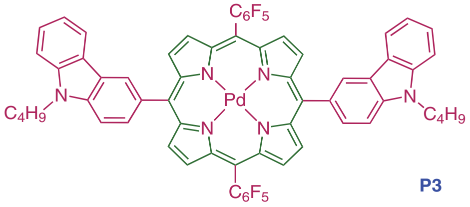
(12) Owens, *Inorganica Chim. Acta.* **1998**, *279*, 226-231.
(13) Ghosh, *J. Phys. Chem. B.* **2003**, *107*, 3613-3623.

White LED induced oxidation of aldehydes by photosensitizers[14]

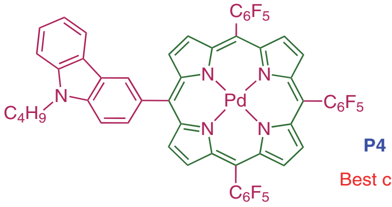


Selected substrate scope

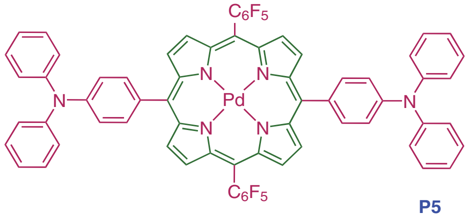




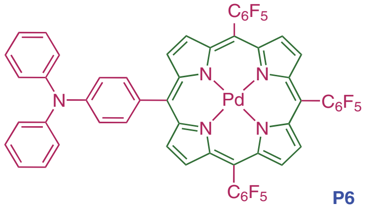
P3



P4
Best catalyst



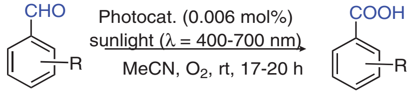
P5



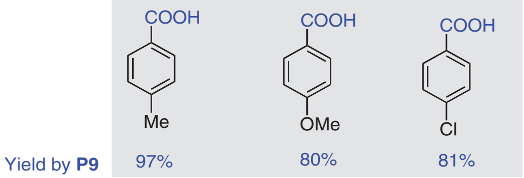
P6

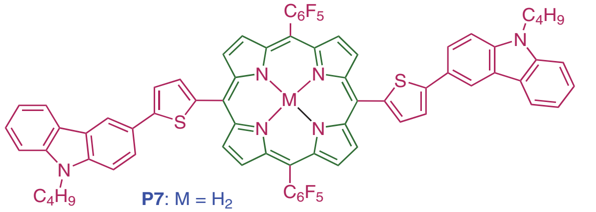
(14) Gupta, *Inorganica Chim. Acta.* **2020**, *502*, 119339-119348.

Oxidation of aldehydes to carboxylic acids under sunlight by photosensitizers[15]

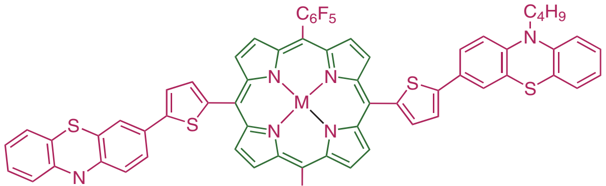


Selected substrate scope





P7: M = H_2
P8: M = Zn(II)
P9: M = Pd(II) - Best catalyst



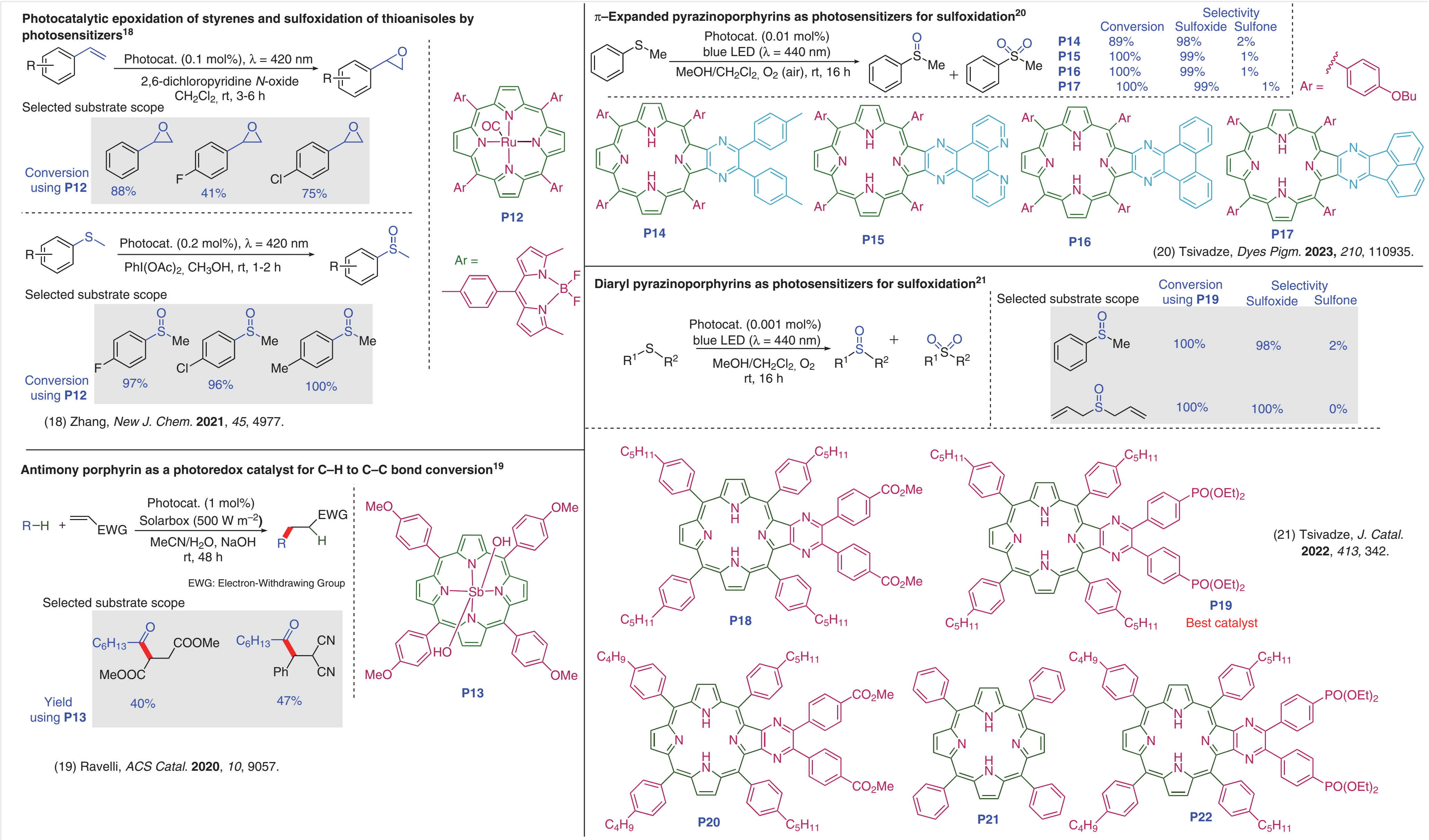
P10: M = H_2
P11: M = Zn(II)

(15) Gupta, *Dyes Pigm.* **2023**, *209*, 110861-110872

- On comparing the yield for oxidation of aldehyde to carboxylic acid, **P9** shows best catalytic activity among **P1-P11**.

Further Reading
(16) Shaabani, *Tetrahedron Lett.* **2010**, *51*, 4061-4065.
(17) Manesh, *J. Porphyrins Phthalocyanines* **2012**, *16*, 93-100.

Figure 1 Photocatalytic oxidation of aldehydes by porphyrins[11–17]



Photocatalytic epoxidation of styrenes and sulfoxidation of thioanisoles by photosensitizers[18]

Photocat. (0.1 mol%), λ = 420 nm
2,6-dichloropyridine *N*-oxide
CH_2Cl_2, rt, 3-6 h

Selected substrate scope

Conversion using **P12**: 88%, 41%, 75%

Photocat. (0.2 mol%), λ = 420 nm
$PhI(OAc)_2$, CH_3OH, rt, 1-2 h

Selected substrate scope

Conversion using **P12**: 97%, 96%, 100%

(18) Zhang, *New J. Chem.* **2021**, *45*, 4977.

P12

Antimony porphyrin as a photoredox catalyst for C–H to C–C bond conversion[19]

Photocat. (1 mol%)
Solarbox (500 W m^{-2})
$MeCN/H_2O$, NaOH
rt, 48 h

EWG: Electron-Withdrawing Group

Selected substrate scope

Yield using **P13**: 40%, 47%

(19) Ravelli, *ACS Catal.* **2020**, *10*, 9057.

P13

π–Expanded pyrazinoporphyrins as photosensitizers for sulfoxidation[20]

Photocat. (0.01 mol%)
blue LED (λ = 440 nm)
$MeOH/CH_2Cl_2$, O_2 (air), rt, 16 h

	Conversion	Selectivity Sulfoxide	Selectivity Sulfone
P14	89%	98%	2%
P15	100%	99%	1%
P16	100%	99%	1%
P17	100%	99%	1%

P14 **P15** **P16** **P17**

(20) Tsivadze, *Dyes Pigm.* **2023**, *210*, 110935.

Diaryl pyrazinoporphyrins as photosensitizers for sulfoxidation[21]

Photocat. (0.001 mol%)
blue LED (λ = 440 nm)
$MeOH/CH_2Cl_2$, O_2
rt, 16 h

Selected substrate scope

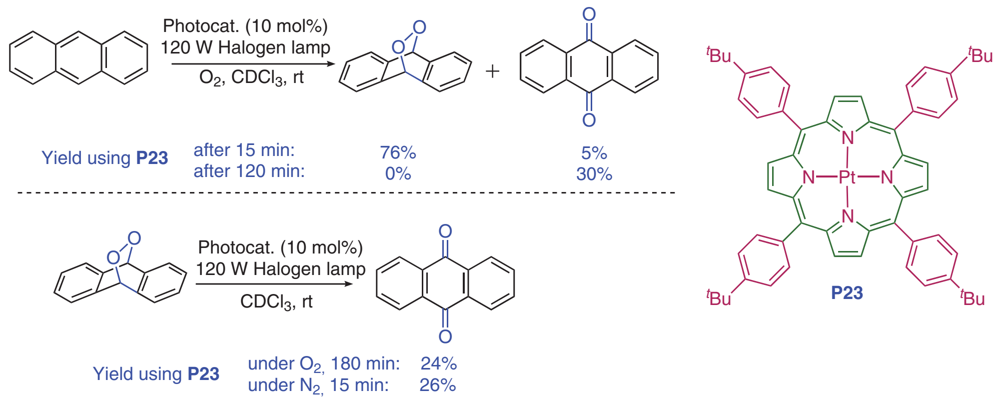
	Conversion using P19	Selectivity Sulfoxide	Selectivity Sulfone
methyl phenyl sulfoxide	100%	98%	2%
diallyl sulfoxide	100%	100%	0%

P18 **P19** Best catalyst **P20** **P21** **P22**

(21) Tsivadze, *J. Catal.* **2022**, *413*, 342.

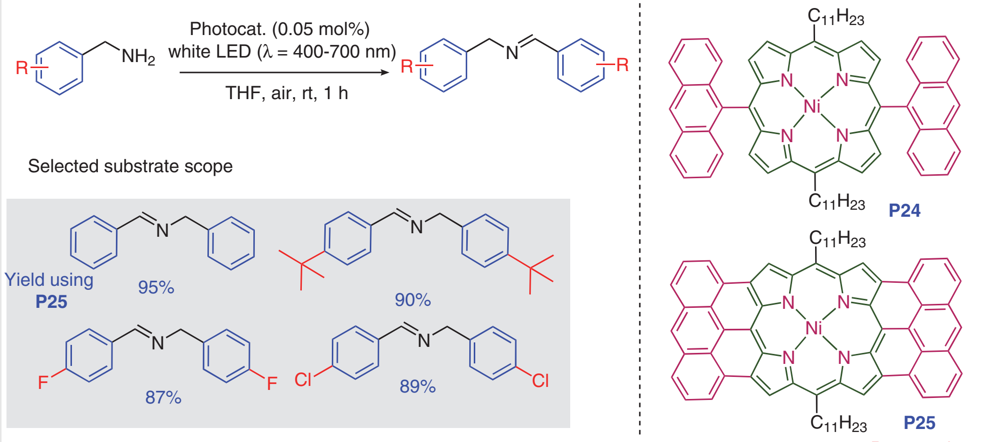
Figure 2 Photocatalytic epoxidation of styrenes, sulfoxidation of thioanisoles and C–H activation of alkenes by porphyrins[18–21]

Photo-oxidation of anthracene using porphyrins as photosensitizers[22]



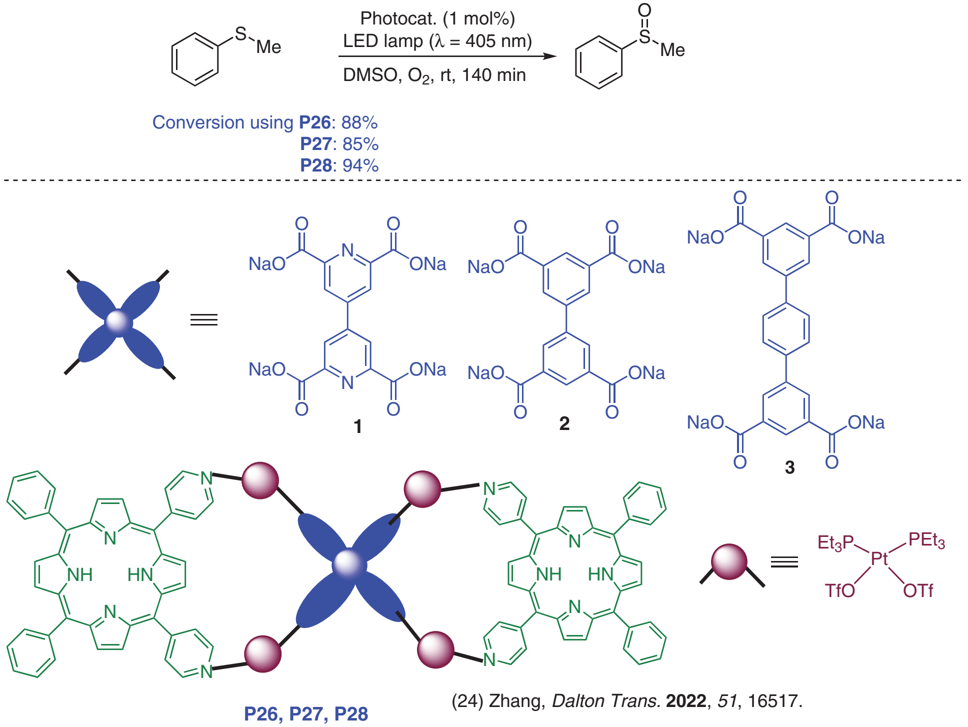
(22) Sugiura, *Tetrahedron Lett.* **2019**, *60*, 151081.

Bis-anthracene-fused porphyrins as photoredox catalysts for oxidative coupling of benzylamines[23]



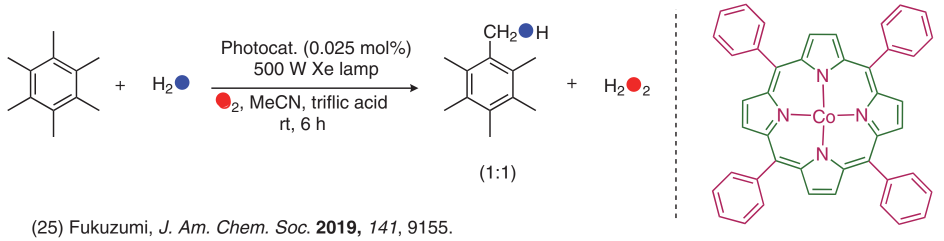
(23) Mai, *Chem. Eur. J.* **2020**, *69*, 16497.

Porphyrin-based bismetallacycles as photosensitizers for photocatalytic sulfoxidation[24]



(24) Zhang, *Dalton Trans.* **2022**, *51*, 16517.

Photocatalytic oxygenation of hexamethylbenzene using water as an oxygen source and O_2 as an oxidant with a photosensitizer[25]



(25) Fukuzumi, *J. Am. Chem. Soc.* **2019**, *141*, 9155.

Figure 3 Photocatalytic oxidation of anthracene, benzyl amine coupling, sulfoxidation of thioanisole and oxygenation of hexamethylbenzene by porphyrins[22–25]

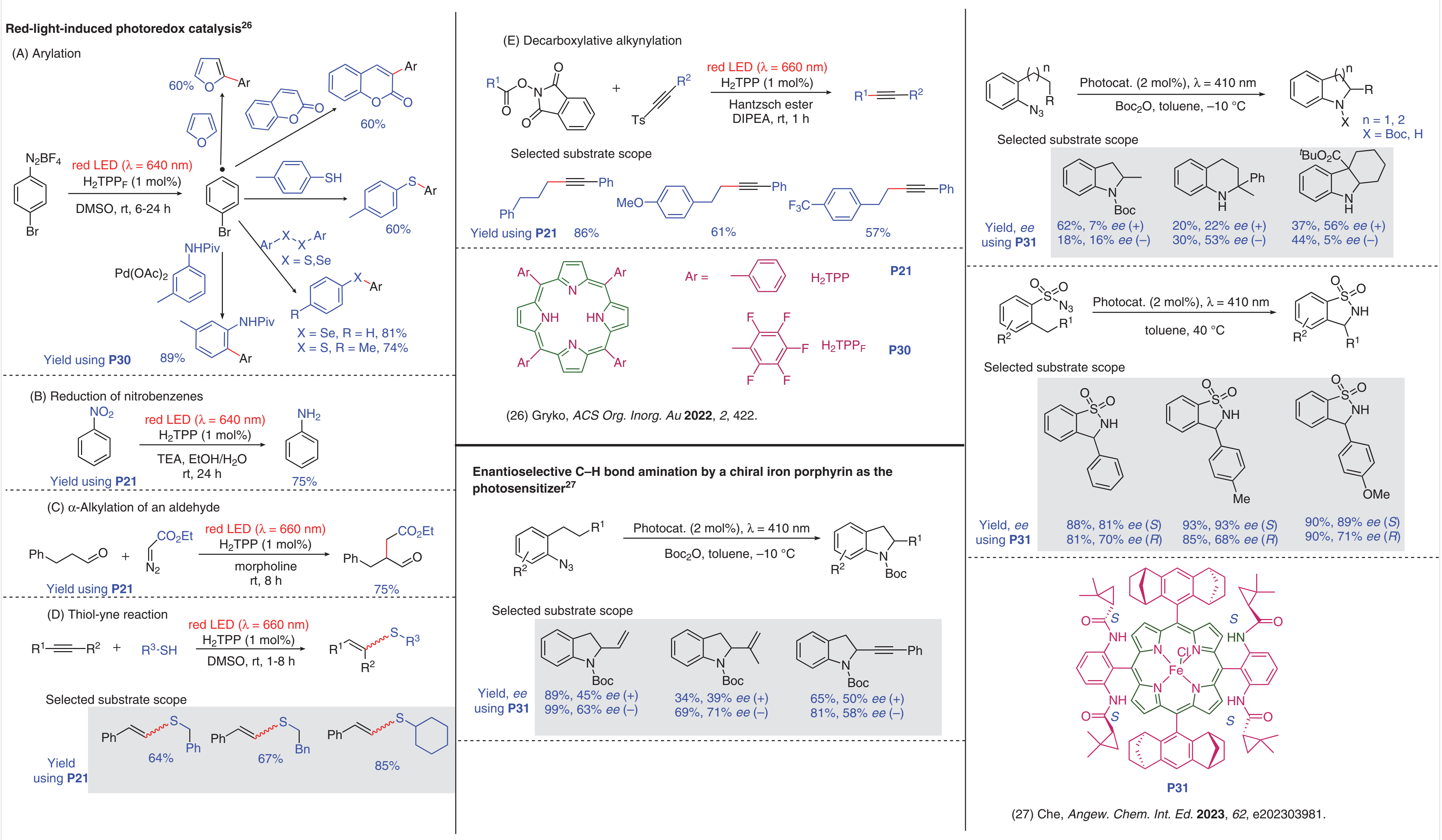
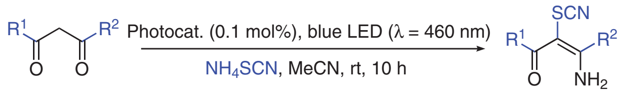
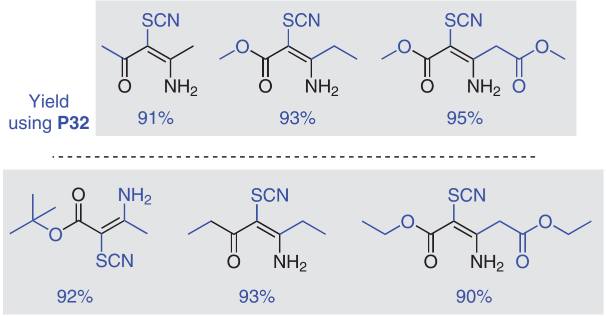


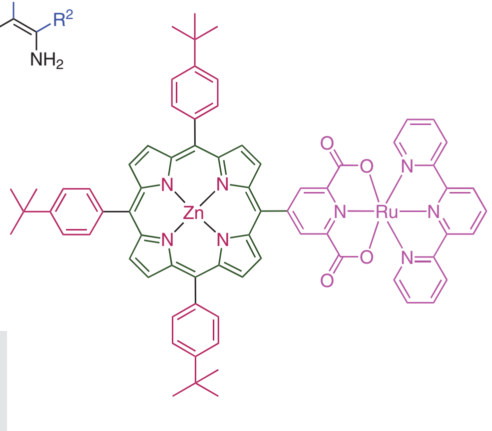
Figure 4 Photoredox catalysis and C–H bond amination by porphyrins[26,27]

Photocatalytic thiocyanation using a ruthenium-porphyrin complex as a photosensitizer[28]

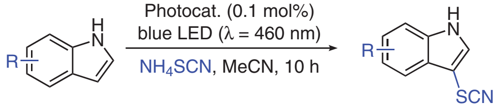


Selected substrate scope





P32



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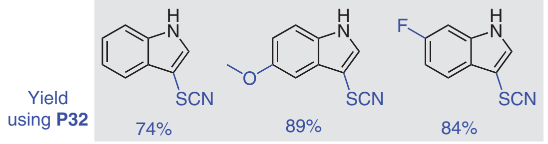
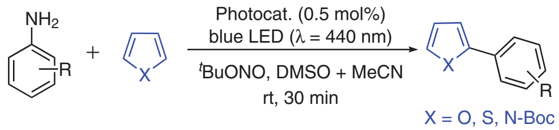


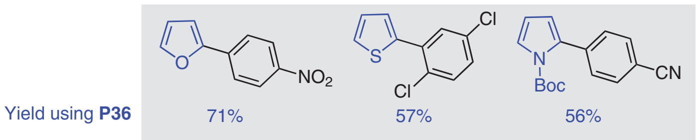
(28) Niu, *J. Mol. Struct.* **2021**, *1237*, 130358-130365

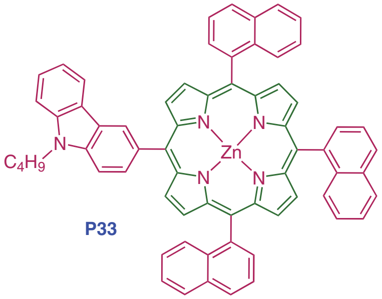
Further Reading
Related articles on photocatalysis by porphyrins:
(29) Gryko, *Eur. J. Org. Chem.* **2017**, *2017*, 2104.
(30) Oliveira, *Molecules.* **2016**, *21*, 310.
(31) Nam, *J. Porphyrins Phthalocyanines* **2016**, *20*, 35.
(32) Gryko, *J. Am. Chem. Soc.* **2016**, *138*, 15451.
(33) Oliveira, *Beilstein J. Org. Chem.* **2020**, *16*, 917.
(34) Oliveira, *J. Org. Chem.* **2018**, *83*, 15077.
(35) Deyhimi, *Green Chem.* **2011**, *13*, 991.
(36) Safari, *J. Porphyrins Phthalocyanines* **2010**, *14*, 639.
(37) Zhang, *Catal. Sci. Technol.* **2023**, *13*, 6132.
(38) Gryko, *J. Porphyrins Phthalocyanines* **2016**, *20*, 76.
(39) Chan, *Organometallics* **2014**, *33*, 7059.

Zinc porphyrins as photoredox catalysts for C–H arylation of heteroarenes[40]

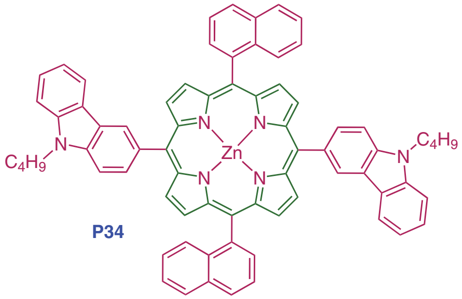


Selected substrate scope

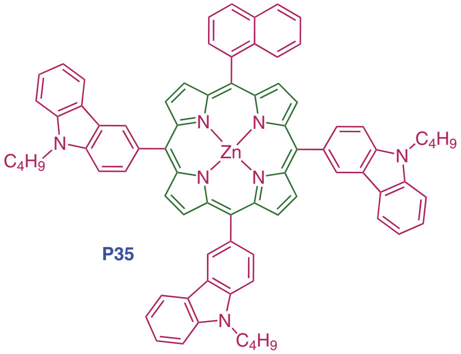




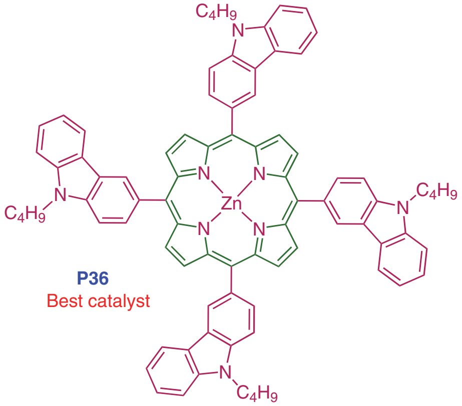
P33



P34



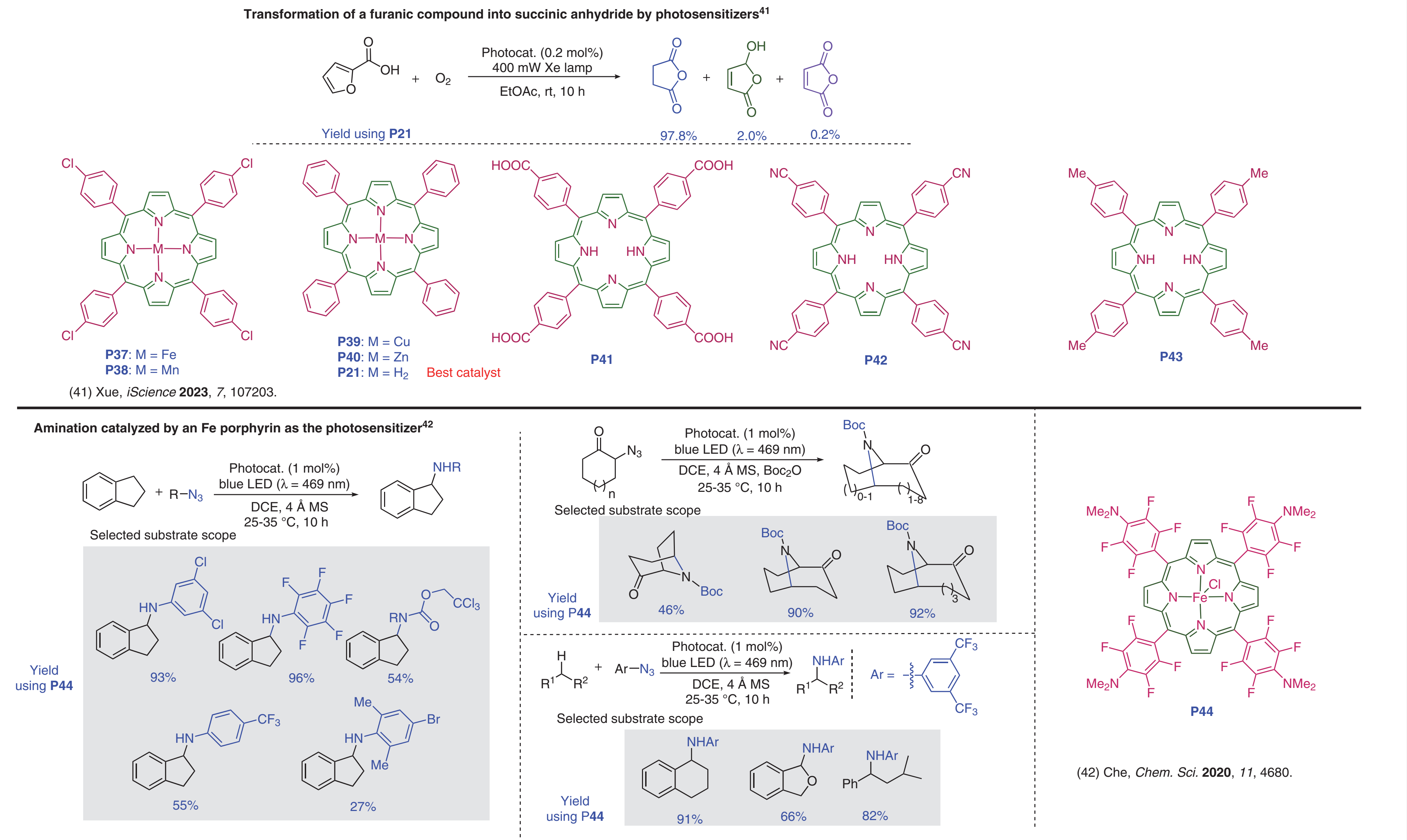
P35



P36
Best catalyst

(40) Gupta, *J. Org. Chem.* **2023**, *88*, 9424.

Figure 5 Photocatalytic thiocyanation of diketones and indoles and C–H arylation of heteroarenes by porphyrins[28–40]



Transformation of a furanic compound into succinic anhydride by photosensitizers[41]

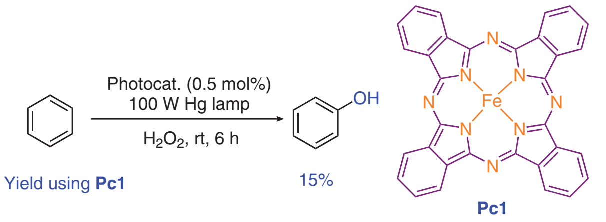
(41) Xue, *iScience* **2023**, *7*, 107203.

Amination catalyzed by an Fe porphyrin as the photosensitizer[42]

(42) Che, *Chem. Sci.* **2020**, *11*, 4680.

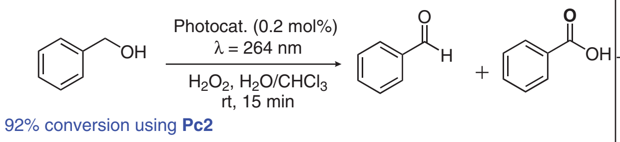
Figure 6 Photocatalytic oxygenation of a furanic compound, amination and aziridination of alkenes by porphyrins[41,42]

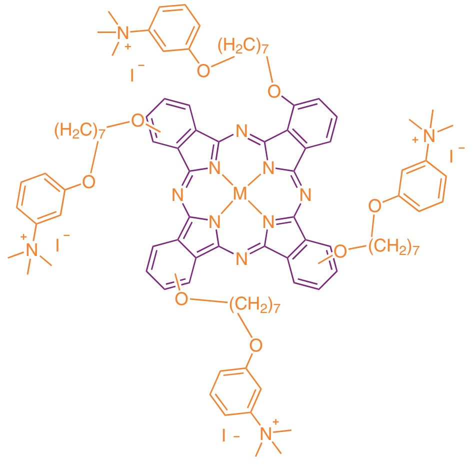
Photoredox hydroxylation of benzene to phenol[43]



(43) Ghiaci, *J. Photochem. Photobiol. A* **2020**, *392*, 112412.

Photo-oxidation of benzylic alcohol by water soluble metallophthalocyanines as photosensitizers[44]

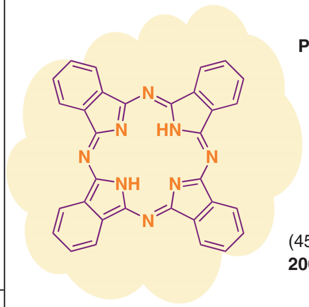




Pc2: M = Co Best catalyst
Pc3: M = Cu

(44) Biyiklioglu, *Inorg. Chem. Commun.* **2023,** *158*, 111647.

Photophysical properties of phthalocyanine[45]

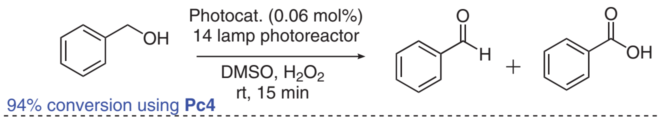


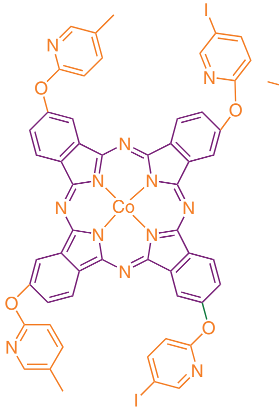
Phthalocyanine in DMF

- λ_{abs}= 695 nm, 667 nm, 705 nm
- Fluorescence quantum yield (ϕ_f) = 0.60
- Fluorescence lifetime (τ_f) = 5.25 ns

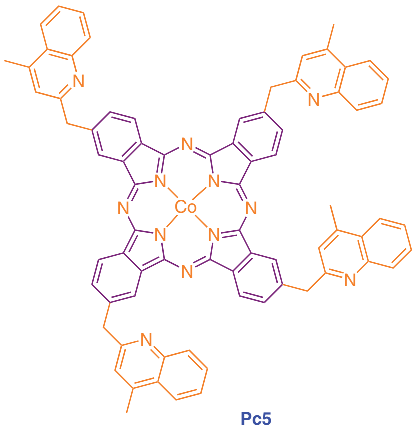
(45) Sahoo, *J. Porphyrin Phthalocyanines* **2003**, *7*, 548-550.

Photooxidation of benzyl alcohol by photosensitizers[46]





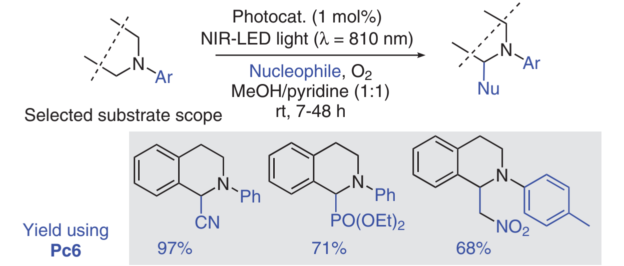
Pc4
Best catalyst

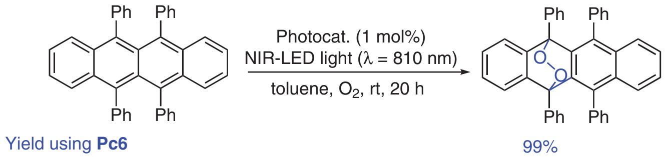


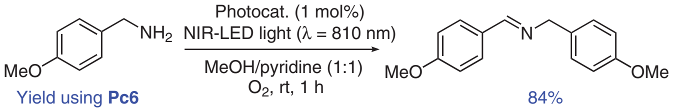
Pc5

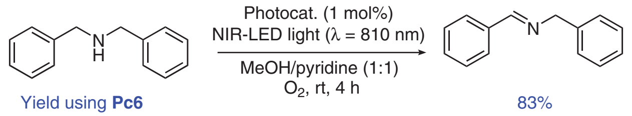
(46) Kantekin, *Appl. Organomet. Chem.* **2023**, *37*, e6975.

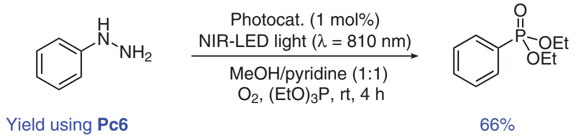
NIR-light-mediated cross-dehydrogenative coupling (CDC) using zinc phthalocyanine as the photosensitizer[47]

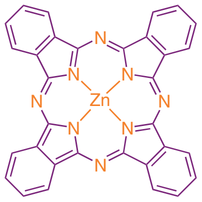












Pc6

(47) Furuyama, *Chem. Eur. J.* **2023**, *28*, e202103223.

Figure 7 Photocatalytic hydroxylation of benzene, oxidation of benzylic alcohol and cross-dehydrogenative couplings by phthalocyanines[43–47]

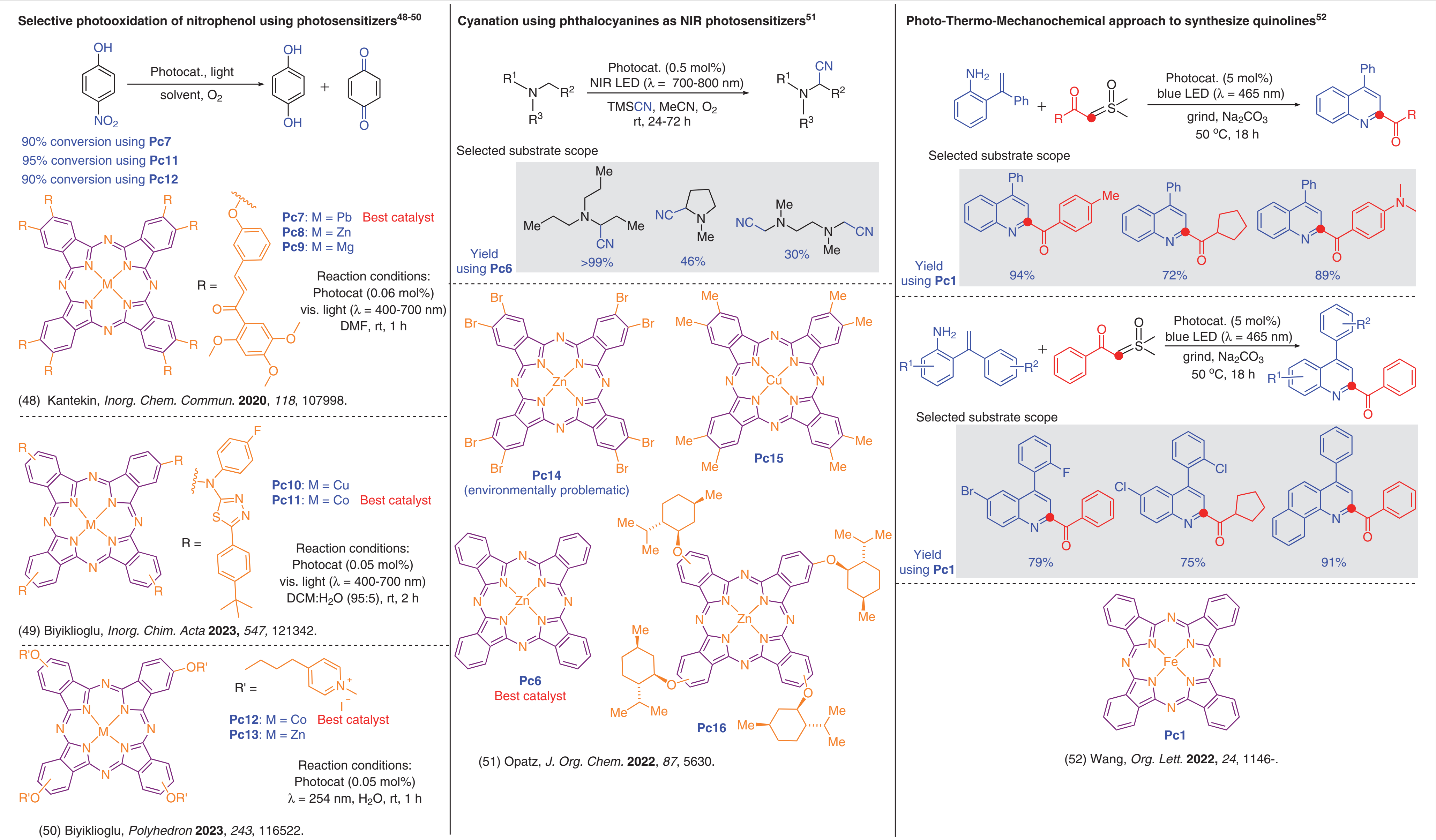
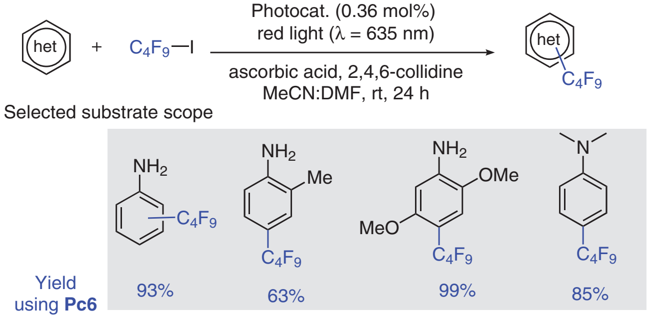
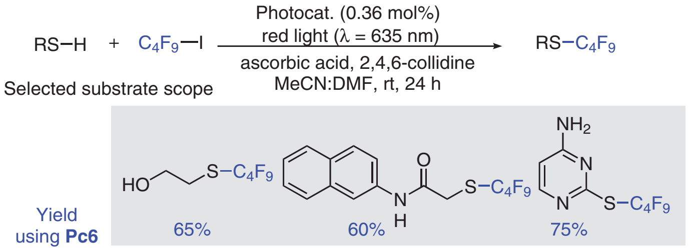
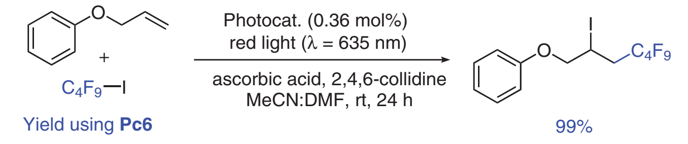


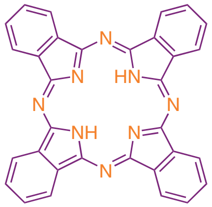
Figure 8 Photocatalytic oxidation of nitrophenol, cyanation of amines and cyclization to quinolones by phthalocyanines[48–52]

Perfluoroalkylation of (hetero)aromatics and sulfides under red-light photocatalysis by photoredox catalyst[53]

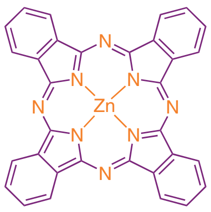




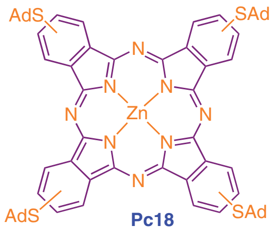




Pc17



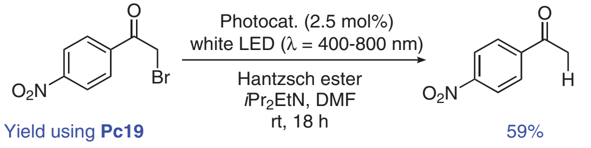
Pc6
Best catalyst

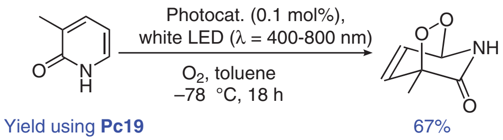


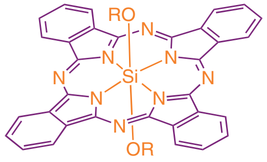
Pc18

(53) Postigo, *Org. Biomol. Chem.* **2019**, *17*, 3741.

[2+4] Cycloaddition and dehalogenation by silicon phthalocyanine as a photoredox catalyst[54]





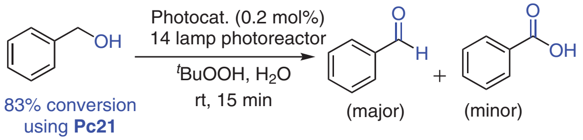


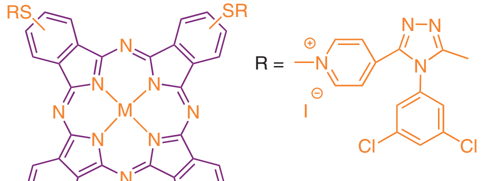
Pc19 R = —Si((CH$_2$)$_5$Me)$_3$ Best catalyst

Pc20 R = —(CH$_2$)$_4$Me

(54) Wiskur, *J. Photochem. Photobiol. A* **2022**, *422*, 113547.

Photocatalytic oxidation of benzyl alcohol by photosensitizers[55]

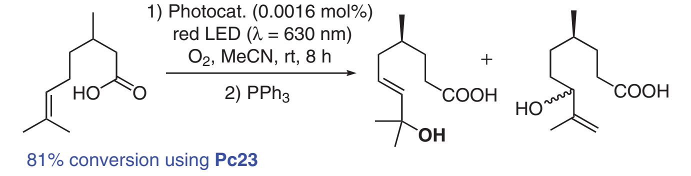


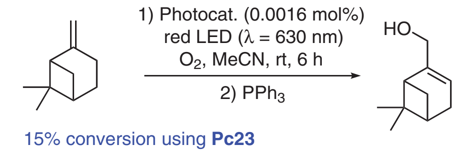


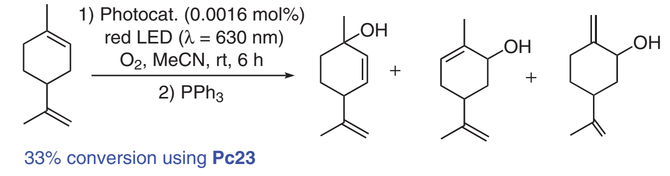
Pc21: M = Cu Best catalyst
Pc22: M = MnCl

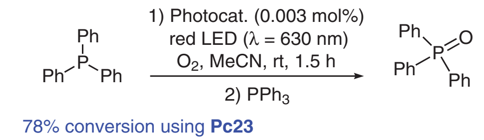
(55) Bekircan, *J. Organomet. Chem.* **2023**, *983*, 122553.

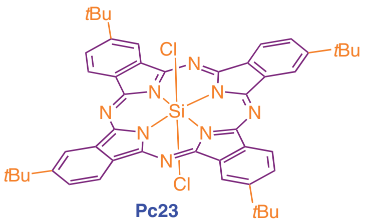
Photooxidation on multigram scale mediated by red light and photosensitizers[56]









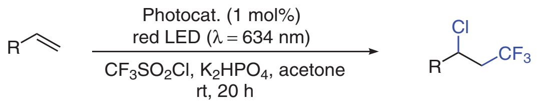


Pc23

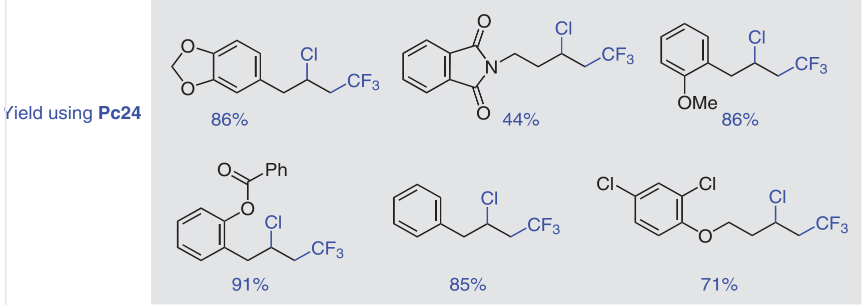
(56) Amara, *ACS Sustainable Chem. Eng.* **2023**, *11*, 15674.

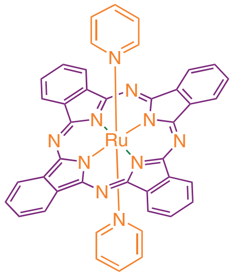
Figure 9 Photocatalytic perfluoroalkylation of aromatics, sulfides and alkenes, cycloaddition and dehalogenation, and oxidation by phthalocyanines[53–56]

Red-light-mediated chlorotrifluoromethylation of alkenes using a ruthenium phthalocyanine as a photoredox catalyst[57]



Selected substrate scope

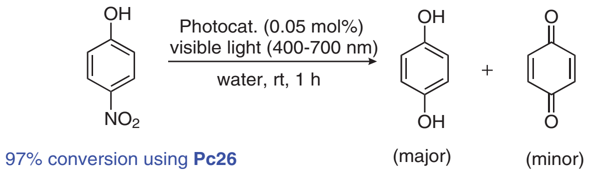


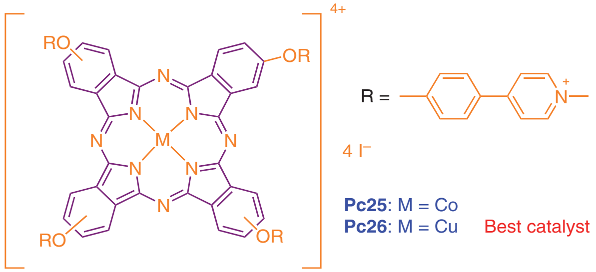


Pc24

(57) Furuyama, *Chem. Commun.* **2021**, *57*, 13594.

Photooxidation of 4-nitrophenol in aqueous medium by photosensitizers[58]





Pc25: M = Co
Pc26: M = Cu Best catalyst

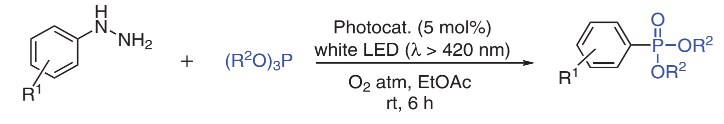
(58) Tekintas, *J. Mol. Struct.* **2020**, *1215*, 128189.

Further reading

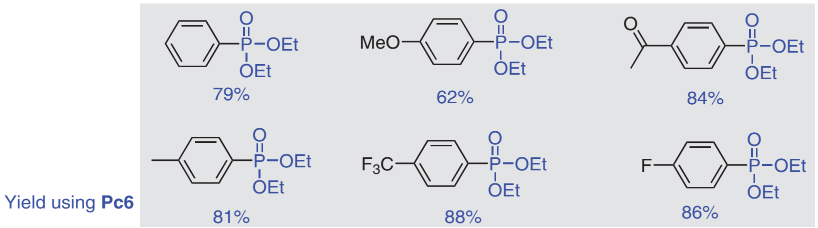
Related articles on photocatalysis by phthalocyanines:

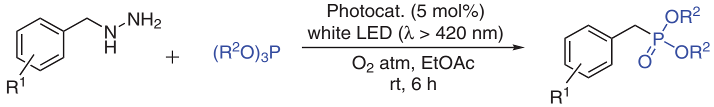
(59) Liang, *Curr. Org. Chem.* **2018**, *22*, 485.
(60) Vorozhtsov, *J. Porphyrin Phthalocyanines* **1999**, *3*, 592.
(61) Lever, *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 27.
(62) Doorslaer, *Dalton Trans.* **2014**, *43*, 14942.
(63) Nyokong, *J. Mol. Catal. A: Chem.* **2007**, *261*, 36.
(64) Bilyarska, *J. Mol. Catal. A: Chem.* **1999**, *137*, 15.
(65) Nyokong, *J. Mol. Struct.* **2010**, *973*, 96.
(66) Nyokong, *J. Mol. Catal. A: Chem.* **2007**, *273*, 149.

Photocatalytic phosphonylation mediated by zinc phthalocyanine as a photosensitizer[67]

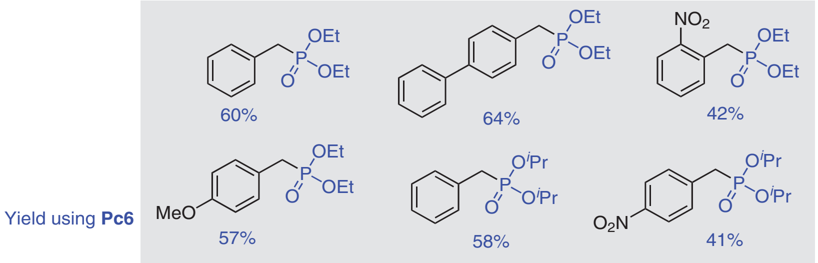


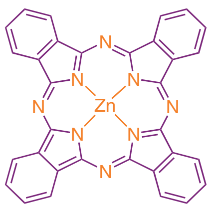
Selected substrate scope





Selected substrate scope





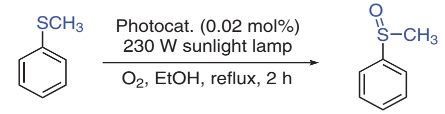
Pc6

(67) Sarvari, *Org. Biomol. Chem.* **2021**, *19*, 5905.

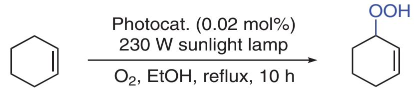
Figure 10 Photocatalytic chlorotrifluoromethylation of alkenes, oxidation of nitrophenol and phosphonylation of hydrazines by phthalocyanines[57–67]

Georg Thieme Verlag KG, Rüdigerstraße 14, 70469 Stuttgart, Germany

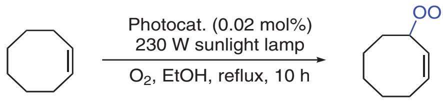
Photocatalytic aerobic oxygenation reactions catalyzed by antimony corroles as photosensitizers[8c]



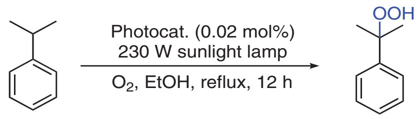
100% conversion using **C1**



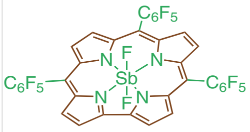
78% conversion using **C1**



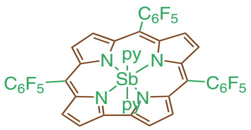
67% conversion using **C1**



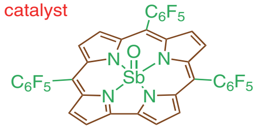
60% conversion using **C1**



C1
Best catalyst

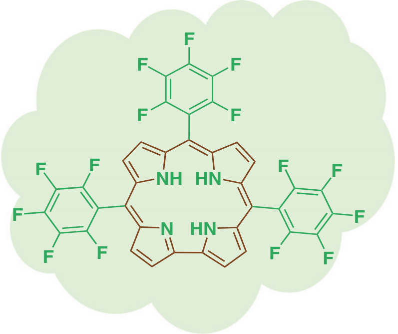


C2



C3

(8c) Gross, *Inorg. Chem.* **2006**, *45*, 386-394.



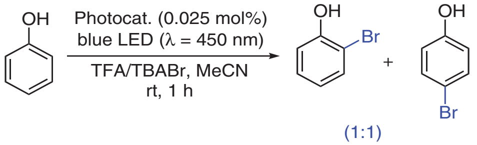
Photophysical properties of corrole[68]

5,10,15-trispentafluorophenylcorrole in DCM

- one Soret and four Q bands in UV-vis spectra
  Soret band: 407 nm
  Q-bands: 523 nm, 561 nm, 604 nm, 632 nm
- absorption exhibits a high solvent-dependent shift
- Fluorescence quantum yield (ϕ_f) = 0.14
- Fluorescence lifetime (τ_f) = 3.7 ns

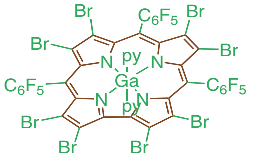
(68) Ziegler, *J. Phys. Chem. A* **2005**, *109*, 7411.

Photocatalytic bromination by a gallium corrole photosensitizer[69]

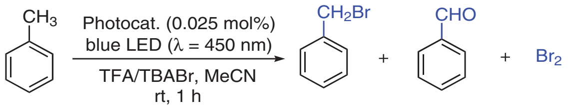


(1:1)

TON using **C4**: 296



C4

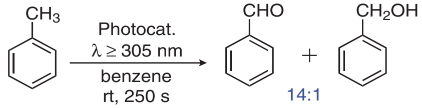


TON using **C4**: 50 129 200

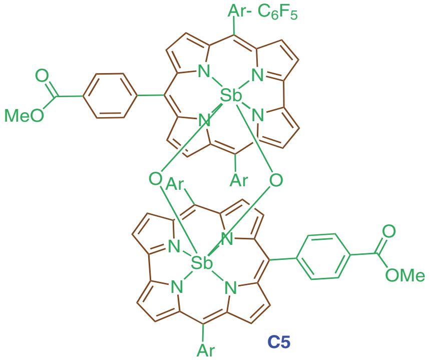
(69) Gross, *Angew. Chem. Int. Ed.* **2015**, *54*, 12547.

Further reading
Related articles on photocatalysis by corroles:
(70) Gross, *Chem. Eur. J.* **2009**, *15*, 8382.
(71) Gross, *Chem. Commun.* **2007**, *20*, 1987.
(72) Lemon, *Pure Appl. Chem.* **2020**, *92*, 1901.
(73) Gryko, *Eur. J. Org. Chem.* **2002**, *2002*, 1735.
(74) Paolesse, *Chem. Soc. Rev.* **2022**, *51*, 1277.
(75) Gryko, *Chem. Rev.* **2017**, *117*, 3102.

C-H photoactivation by Sb(V) oxo corrole as photosensitizers[76]



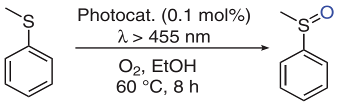
14:1



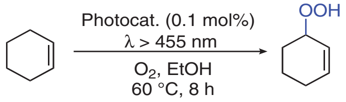
C5

(76) Nocera, *Chem. Commun.* **2020**, *56*, 5247.

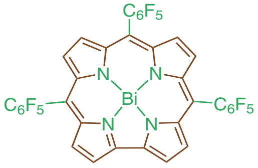
Oxidation of thioanisole and cyclohexene photocatalyzed by a bismuth corrole as a photosensitizer[77]



Full conversion using **C6**



Partial conversion using **C6**

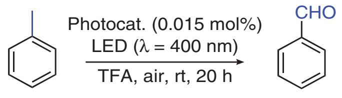


C6

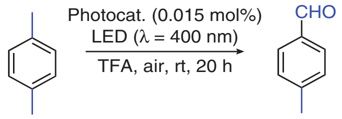
(77) Schoefberger, *Inorg. Chem.* **2011**, *50*, 6788.

Figure 11 Photocatalytic oxygenation of thioanisole and alkenes, bromination of phenol and toluene, and oxidation of toluene, thioanisole and cyclohexene by corroles[8c,68–77]

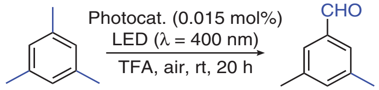
Photooxygenation of toluene, *p*-xylene and mesitylene by transition-metal- and main-group-metallated corroles as photosensitizers[78]



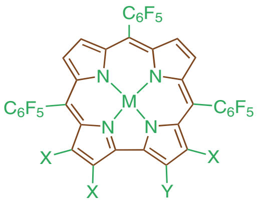
Yield using **C15** 3.9%



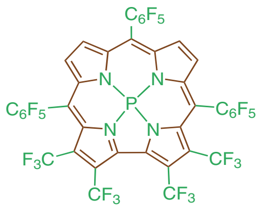
Yield using **C15** 8.2%



Yield using **C15** 17.2%



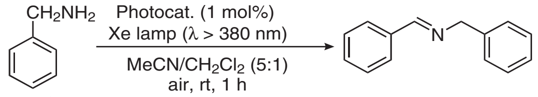
C7: M = Ga, X = CF_3, Y = H
C8: M = Al, X = CF_3, Y = H
C9: M = Au, X = CF_3, Y = H
C10: M = P, X = CF_3, Y = H
C11: M = Co, X = CF_3, Y = H
C12: M = Ga, X = Y = CF_3
C13: M = Al, X = Y = CF_3
C14: M = Au, X = Y = CF_3
C15: M = P, X = Y = CF_3 Best catalyst



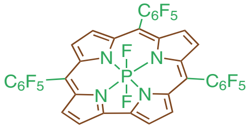
C15

(78) Gross, *Photochem. Photobiol. Sci.* **2020**, *19*, 996.

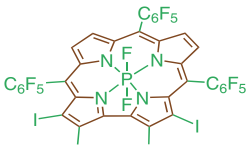
Aza-Henry coupling of benzylamine mediated by phosphorus corroles as photosensitizers[80]



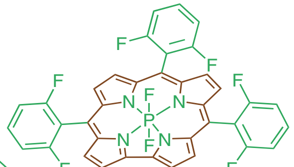
Conversion using **C22**: 100%



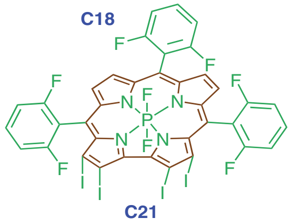
C18



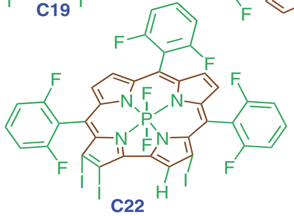
C19



C20
Best catalyst



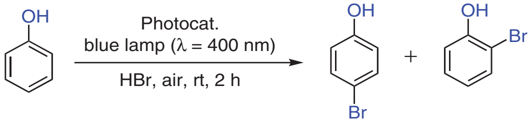
C21



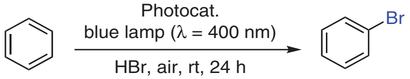
C22

(80) Gross, *Chem. Sci.* **2019**, *10*, 7091.

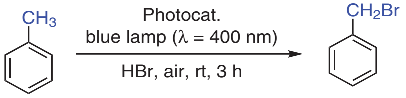
Photocatalytic bromination by phosphorus corroles as photosensitizers[79]



TON using **C16**: 1840

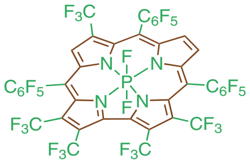


TON using **C16**: 106

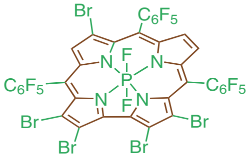


TON using **C16**: 320

(79) Gross, *Inorg. Chem.* **2019**, *58*, 6184.

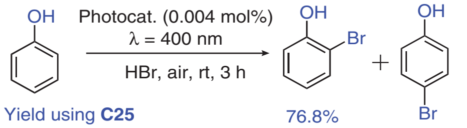


C16 Best catalyst

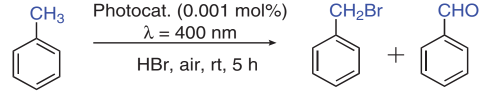


C17

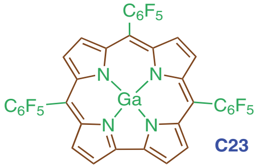
Metallocorrole-photocatalyzed bromination of phenol and toluene by photosensitizers[81]



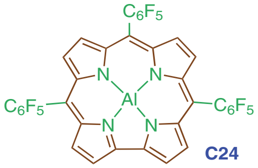
Yield using **C25** 76.8%



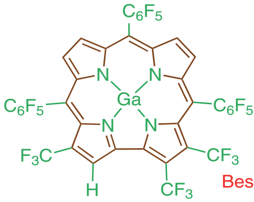
Yield using **C25** 22.5% 10.9%



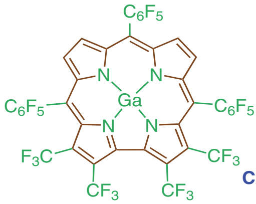
C23



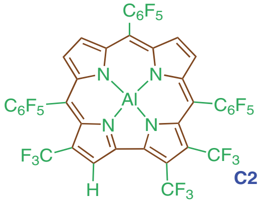
C24



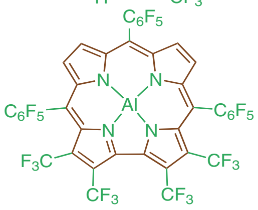
C25
Best catalyst



C26



C27



C28

(81) Gross, *Dalton Trans.* **2019**, *48*, 12279.

Figure 12 Photocatalytic oxygenation of aromatics, benzylamine coupling and bromination of benzene, phenol and toluene by corroles[78–81]

Conflict of Interest

The authors declare no conflict of interest.

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