Dual-Catalyst Photoinduced Alkenylation of Alkanes and Aldehydes via C–H Activation

Significance: The authors report a site-selective photoinduced alkenylation of various alkanes and aldehydes with aryl and heteroaryl alkenes. This dehydrogenative reaction utilizes two photoactive catalysts (tetra-n-butylammonium decatungstate (TBADT) as HAT agent and Co(dmgH)(dmgH2)Cl2), which eliminates the need for an external oxidant.

Comment: This mild alkenylation was used for the late-stage functionalization of diverse complex molecules, while still ensuring a high level of site-selectivity for the sterically most accessible and most electron-rich C–H bond. Wu and co-workers propose a mechanism that involves cooperation of the tungstate and the cobalt catalysts.
Intramolecular Hydroacylation of Benzaldehyde Derivatives by Cobalt-Catalyzed C–C Bond Cleavage

Significance: Yang and co-workers report an intramolecular cobalt-catalyzed hydroacylation of 2-vinylbenzaldehyde compounds for the synthesis of benzocyclooctadienone and benzocycloheptadienone derivatives in good to excellent yield. Both reactions operate under identical reaction conditions, using an inexpensive cobalt catalyst with zinc as a reducing agent.

Comment: Mechanistic studies were used to support the proposed mechanism for both catalytic cycles. Interestingly, DFT studies indicate that for the reaction of the vinylcyclopropane compounds, C–H oxidative addition is the rate-determining step. When using a disubstituted vinylcyclopropane, the hydroacylation product arises from cleavage of the less substituted C–C bond.
Nickel-Catalyzed Enantioconvergent Coupling of Racemic Partners

**Significance:** Fu and co-workers report a nickel-catalyzed doubly enantioconvergent alkyl–alkyl coupling of racemic partners that proceeds with unprecedented selectivity. The authors employed a chiral nickel catalytic system that generates the product as a single stereoisomer from racemic propargylic halides and racemic β-zincated amides.

**Comment:** The authors propose that the enantioconvergence of the starting materials is facilitated by a radical intermediate arising from both starting materials. The presence of radical intermediates was inferred by the TEMPO adducts formed from both the electrophile and nucleophile partners in the mechanistic study.

---

**Selected derivatizations of products:**

1. BH$_3$ SMe$_2$, THF, reflux (97% yield)
2. Ts$_2$N, H$_2$O, cat. Cul, Et$_3$N, CHCl$_3$, r.t. (96% yield)
3. AZT, cat. CuTc, toluene, 50 °C (96% yield)
4. LiAlH$_4$, THF, reflux (88% yield)
5. 1. Ts$_2$N, DTBMP, CH$_2$Cl$_2$, –78 °C (79% yield)
6. 2. C$_3$MgBr, Ph$_2$CH, –78 °C (71% yield)

**Selected examples:**

- **(C-L2) - 81% yield**
  - 91% ee
  - dr > 99:1
- **(C-L2) - 75% yield**
  - 90% ee
  - dr > 98:2
- **(A-L1) - 93% yield**
  - 90% ee
  - dr > 99:1
Asymmetric Allylation of N-Methyl Anilines by Palladium/Photoredox Cooperative Catalysis

**Significance:** Yu and co-workers report an asymmetric and branch-selective allylation of N-methyl anilines using racemic allylic acetates. Various chiral homoallyl amines are obtained in moderate to good yields and enantioselectivities by dual palladium/photoredox catalysis. Mechanistic studies support the formation of a π-allylpalladium intermediate and indicate that the reaction proceeds through a dynamic kinetic asymmetric transformation.

**Comment:** The authors had previously employed 4-alkyl-1,4-dihydropyridines to generate alkyl radicals in a similar reaction. In contrast, N-methylanilines offer the advantage of being readily available and not requiring prefunctionalization. N-Benzyl anilines were also suitable substrates in this reaction, but, in contrast, delivered the product as a mixture of diastereoisomers.

**Selected examples:**

- **Proposed mechanism:**

- **Key words:** photoredox catalysis, dual catalysis, palladium catalysis, asymmetric catalysis, allylation

**Category:** Metals in Synthesis
Nickel-Catalyzed Electrochemical Synthesis of Diarylmethanes

R₁, R₂ = various functional groups

Selected examples:

\[
\begin{align*}
\text{MeO} & \quad \text{MeO} & \quad \text{MeO} \\
\text{76% yield} & \quad \text{60% yield} & \quad \text{70% yield}
\end{align*}
\]

\[
\begin{align*}
\text{MeO} & \quad \text{MeO} & \quad \text{MeO} \\
\text{71% yield} & \quad \text{53% yield} & \quad \text{50% yield}
\end{align*}
\]

Significance: Zhang and Hu describe a convergent paired nickel-catalyzed electrosynthesis of various functionalized diaryl methanes. The use of an electron-rich bipyridine ligand was the key to obtaining the corresponding products in good yields.

Comment: Mechanistically, a benzyl radical is formed via anodic oxidation. Recombination with an Ar-Ni(II) complex and subsequent reductive elimination affords the diaryl methane. The Ar-Ni(II) complex is regenerated via cathodic oxidation followed by oxidative addition to the corresponding aryl bromide.
Stereoselective Palladium-Catalyzed C–F Bond Alkynylation of Tetrasubstituted gem-Difluoroalkenes
Angew. Chem. Int. Ed. 2020, DOI: 10.1002/anie.202002219.

Stereoselective Preparation of Fluoroenynes

Significance: Tsui and co-workers report the highly stereoselective palladium-catalyzed alkyynylation of gem-difluoroalkenes affording the corresponding monofluoroenynes in good to excellent yield. This method affords several structures of interest for pharmaceutical and material applications. The authors proposed a mechanism for the reaction.

Comment: After selective oxidative addition of Pd(0) into the gem-difluoro alkene, assisted by chelation of the ester group to the palladium center, the generated complex undergoes a halide exchange with NaI. The formed intermediate is complexed by the terminal alkyne, which is then deprotonated by Et₃N. Ligand exchange with iodide affords the R-Pd(II)-alkyne complex, which generates the desired products after reductive elimination.

\[
\begin{align*}
R^1 & \text{CO}_2R^2 + \text{Pd(PPh}_3\text{)}_4 (5 \text{ mol%}) \xrightarrow{\text{Et}_3\text{N} (3 \text{ equiv}), \text{NaI} (3 \text{ equiv})} \xrightarrow{\text{PhMe, } 80^\circ\text{C, } 24 \text{ h}} \text{R}^1 \text{CO}_2R^2 \\
& \text{R}^3 \\
\end{align*}
\]

R¹ = (Het)Ar; R² = Alk; R³ = Alk, Ar

E/Z > 99:1
>35 examples, up to 95% yield

Proposed mechanism:

Selected examples:

54% yield
95% yield
**Ruthenium-Catalyzed ortho-C–H Arylation**

**Significance:** Greaney and co-workers report a ruthenium-catalyzed ortho-arylation of arenes using visible light, affording the desired products in good yields. This method delivers C–H arylated products at room temperature, which are typically accessed at elevated temperatures of 100 °C.

**Comment:** The authors proposed a mechanistic pathway in which a precatalyst (A) was formed that, upon irradiation, gave a ruthenium intermediate (B). After decomplexation of the cymene ligand, the bis-cycloruthenated complex (C) was formed. This complex could undergo oxidative addition with an aryl halide, and subsequent reductive elimination affords the desired ortho-arylated arenes.
Synthesis of Enantioenriched Secondary Alcohols by Enantioselective Ru-Catalyzed Coupling of Two Alcohols

\[ \text{R}^1 \text{OH} \quad (3 \text{ mmol}) + \quad \text{HOAr} \quad (1 \text{ mmol}) \xrightarrow{\text{Ru catalyst (1 mol%)}} \quad \text{R}^1 \text{OH} \quad (\text{Ar}) \quad \text{51 examples} \quad \text{up to 85% yield} \quad \text{er up to 99:1} \]

Selected examples:

- 70% yield, er = 67:33 (95:5 er after recrystallization)
- 34% yield, er = 92:8
- 70% yield, er = 95:5
- 72% yield, er = 98:2 (1.2 g; 83% yield, er = 95:5)

Derivatizations:

- 72% yield, er = 90:10
- \[ \text{Pd(OAc)}_2 \quad (3 \text{ mol%}) \quad \text{JohnPhos (3 mol%)} \]
- \[ \text{Cs}_2\text{CO}_3 \quad (1.5 \text{ equiv}) \quad \text{PhMe [0.3 M], 90 °C} \]

Significance: Wang and co-workers report the first asymmetric version of the Guerbet reaction; using ruthenium catalysis to couple racemic secondary alcohols with primary benzylic alcohols to afford enantioenriched chiral secondary alcohols in moderate to good yield with excellent enantioselectivity. The steric bulk of the secondary alcohol was found to influence the enantioselectivity; whereas for the primary alcohol, electronic factors on the aryl ring affected the yield. By using a hydrogen autotransfer process, this reaction negates the need for hydrogen or other reducing agents, leaving water as the only byproduct. The reaction was shown to be scalable, and the utility of the alcohol products was demonstrated through the synthesis of a chiral chroman compound, which is a common core of many biologically active compounds.

Comment: Extensive mechanistic and DFT studies were carried out to support the proposed mechanism, which involves dehydrogenation of both alcohols to yield the respective carbonyl compounds, aldol condensation then reduction by the hydrogen produced during the oxidation. Given that the catalyst is capable of both hydrogenation and dehydrogenation, the authors observed racemization of the products lacking an ortho-methyl group on the secondary alcohol with longer reaction times. Interestingly, this racemization was proposed to occur in the presence of the ketone intermediate as well as base, rather than by the base or catalyst alone.
Bicyclo[1.1.1]pentanes as Electrophiles for Iron-Catalyzed Cross-Coupling

Selected examples:

![Chemical structures](image)

Proposed mechanism:

Significance: Anderson and co-workers have described an iron-catalyzed Kumada cross-coupling of iodo-bicyclo[1.1.1]pentanes (BCPs) with aryl and heteroaryl Grignard reagents under mild conditions to synthesize all-carbon 1,3-disubstituted BCPs in yields ranging from poor to excellent with a wide functional group tolerance.

Comment: The interest in 1,3-disubstituted BCPs as pharmaceutical bioisosteres for 1,4-disubstituted arenes and alkynes prompted the synthesis of BCP analogues of flurbiprofen (anti-inflammatory drug) and brequinar (anti-neoplastic agent) using the methodology. Interestingly, the chemoselectivity of the reaction was demonstrated by a lack of reaction between the Grignard reagent and the pendent ester functionality.
Palladium-Catalyzed Oxidation of \( \beta \)-C–H Bonds of Primary Alkylamines through a Rare Four-Membered Palladacycle Intermediate

**J. Am. Chem. Soc.** 2020, 142, 7912–7919.

**Significance:** Hartwig and co-workers report a challenging palladium-catalyzed oxidation of primary C–H bonds in the \( \beta \)-position of an aliphatic amine via the corresponding imine, leading to a variety of synthetically useful \( \beta \)-hydroxy amines.

**Comment:** Interestingly, the mechanism proceeds via a rare four-membered palladacycle intermediate. A series of mechanistic experiments and DFT calculations revealed that cleavage of the C–H bond is rate-limiting and formation of the strained four-membered intermediate is thermodynamically uphill. However, an intramolecular hydrogen bond between the oxygen of the directing group and hydroxyl group of the ligating acetic acid stabilizes the palladacyclic intermediate.
Dual Photoredox Catalysis for the C–H Arylation/Decarboxylative Vinylation of Cyclic Oxalates

**Significance:** Chu and co-workers have described a domino dual C(sp²)–C(sp³) bond formation via Ni/Ir-catalyzed ipso-C–O and remote C–H functionalization of cyclic oxalates that gives 1,3-vinylarylated products in moderate to good yield. The protocol was extended to include 1,5-vinylarylated products from 4-methylenecyclohexyl oxalate with complete site-selectivity, likely due to steric hindrance.

**Comment:** Although a cyclopentyl substrate reacted to give the expected product under these conditions, the importance of conformation for the intramolecular 1,5-hydrogen atom transfer was shown by a lack of reactivity for cyclic oxalates of smaller or larger ring sizes, as well as bicyclic or linear oxalates. The authors demonstrated the utility of their products through a series of derivatization reactions.
E. SEMINA, P. TUZINA, F. BIENEWALD, A. S. K. HASHMI, T. SCHAUB* (CATALYSIS RESEARCH LABORATORY (CARLA), HEIDELBERG AND BASF SE, LUDWIGSHAFEN, GERMANY)

Ruthenium-Catalyzed Synthesis of Vinylamides at Low Acetylene Pressure
Chem. Commun. 2020, 56, 5977–5980.

Ruthenium-Catalyzed Synthesis of Vinylamides

**Significance:** The authors report a ruthenium-catalyzed reaction of cyclic amides with acetylene under low pressure, leading to a variety of N-vinylated amides of high industrial interest in good yields. This mild method was used to functionalize a range of N-nucleophiles, which are not compatible with the harsh conditions of standard Reppe chemistry.

**Comment:** By using this method a wide range of vinylamides were prepared such as (azabicyclic) lactams, oxazolidinones, benzoisoxazolones, isoindolinones, quinoxalinones, oxazinanones, cyclic urea derivatives, nucleobases (thymine), amino acid anhydrides and thiazolidinones, showing the synthetic utility.

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Rhodium-Catalyzed Hydroaminative Cyclizations

S. Takano, R. Shiomi, Y. Morimoto, T. Kochi, F. Kakiuchi* (Keio University, Yokohama, Japan)

Carbon–Carbon Bond Formation via Catalytically Generated Aminocarbene Complexes: Rhodium-Catalyzed Hydroaminative Cyclization of Enynes with Secondary Amines

Angew. Chem. Int. Ed. 2020, DOI: 10.1002/anie.202002710.

Significance: The authors report a hydroaminative cyclization of enynes with secondary amines using phosphine-quinolinolato rhodium catalysts. By using this method a variety of 2-aminoindenes were prepared in good yields.

Comment: Interestingly, the hydroaminative cyclization proceeds via [2+2] cycloaddition of the formed aminocarbene complex with the intramolecular alkene moiety, followed by β-hydride elimination and reductive elimination.

Selected examples:

- 71% yield (30% isolated) 
  A/B = 48(25):23(5)

- 64% yield (40% isolated) 
  A/B = 40(29):24(11)

- 61% yield (38% isolated) 
  A/B = 39(24):22(14)

- 54% yield (37% isolated) 
  A/B = 42(33):12(4)

- 69% yield (52% isolated) 
  A/B = 39(33):30(19)
Enantioselective Annulation of N-Methoxybenzamides with Quinones by Rhodium-Catalyzed C–H Activation

Proposed mechanism:

Selected examples:

Significance: Gou, Wang, and co-workers report an asymmetric rhodium-catalyzed C–H activation reaction of N-methoxybenzamides with quinones. Chiral dihydrophenanthridinones were obtained in moderate to excellent yield and stereoselectivity.

Comment: The developed methodology provides direct access to the tricyclic core of amaryllidaceae alkaloids. Interestingly, benzoquinone not only acts as a reaction partner, but also as an oxidant to form the catalytically active rhodium(III) species.
**New Ru(II)-NHC-Diamine Precatalysts for Asymmetric Hydrogenation**

**Significance:** The authors report the preparation and applications of novel Ru(II)-NHC diamine precatalysts for asymmetric hydrogenation. The isolated precatalysts are air- and moisture-stable and display excellent enantioselectivity and yield for asymmetric hydrogenations of isocoumarins, benzothiophenes, 1,1-dioxides and ketones.

**Comment:** The ruthenium monochloride precatalyst displays unusual tridentate binding to the diamine ligand, via cyclometallation to the 2-position of the phenyl ring. Notably, even in the presence of this carbon-metal bond, the precatalyst is stable in the solid state to both air and moisture.

**Selected examples:**
- 83% yield, enantiomeric ratio (er) up to 98.5:1.5
- 99% yield, er up to 99:1
- 86% yield, er up to 96.5:3.5
- 99% yield, er up to 93:7
- 99% yield, er up to 91:9
Cobalt-Catalyzed Synthesis of Eight-Membered Rings

Significance: The authors report a cobalt-catalyzed synthesis of eight-membered rings. The reaction enables the formation of various substitution patterns. Various monobenzocyclooctadienes and dibenzocyclooctadienes were obtained in good to excellent yields. The formation of six-membered rings is not observed. A first attempt towards enantioselective products was made using a [Co(porphyrin)] catalyst, which delivered a moderate enantiomeric excess of 18%.

Comment: A plausible reaction mechanism based on mechanistic and DFT studies is proposed. The carbene precursor is formed by reaction of an aldehyde with p-toluenesulfonyl hydrazide in a one-pot procedure. The catalytic cycle proceeds via a radical carbene complex. The formation of the final product might occur via two different pathways. The monobenzocyclooctadienes are likely formed via a radical-rebound step.
Photocatalyzed Difunctionalization of Carbonyls

**Significance:** The authors report a difunctionalization of carbonyl groups using a photocatalyzed Wolff–Kishner reaction. For sulfur-centered radicals, the formed carbanions have been functionalized with various electrophiles, such as CO$_2$ or aldehydes. In the case of CF$_3$ radical addition, a wide range of gem-difluoroalkenes have been obtained through β-fluoride elimination.

**Comment:** König and co-workers propose a plausible mechanism, based on various mechanistic investigations (radical inhibition, deuterium labeling, fluorescence quenching and cyclic voltammetry). The experiments indicate the formation of a radical via SET to the photocatalyst followed by addition to the N-sulfonylhydrazone.
Photoredox-Catalyzed Diastereoselective C–H Arylation/Epimerization of Piperidines

**Significance:** The authors report an iridium(III) photoredox-catalyzed cascade reaction system to achieve α-amino C–H arylation of highly functionalized piperidines with excellent diastereoselectivity. The reaction accommodated piperidine derivatives of varying substitution patterns with pre-existing stereogenic centers.

**Comment:** The authors note that the α-amino C–H arylation is rapid and unselective, and the selectivity observed in the products originates from the slower epimerization process that follows the arylation step. Based on DFT calculations, the diastereomeric distribution follows the thermodynamic ratio of isomers.
Iron-Catalyzed Photoinduced C–H Bond Amination Using Organic Azides

**Significance:** The authors report an iron-catalyzed photoinduced nitrene addition to C–H bonds. The reaction uses an iron(III) porphyrin catalyst and organic azides as nitrogen source. The intermediate iron-nitrene reacts readily in sp³-C–H aminations and alkene aziridinations.

**Comment:** Given the high chemo- and regioselectivity, combined with the mild reaction conditions, this method enables an effective late-stage functionalization of natural and bioactive compounds. Based on mechanistic studies, Che and co-workers revealed a dual role of the iron catalyst as a photosensitizer and for the reactive iron-nitrene intermediate.
Significance: The authors report a photoredox cobalt dual catalyzed hydrofunctionalization. A ruthenium complex is used as a photoredox catalyst. A mechanism guided approach towards the design of the dual catalytic system was taken. Detailed mechanistic studies were conducted to establish the viability of the used cobalt and ruthenium catalysts. These included cyclic voltammetry as well as kinetic studies and Stern–Volmer quenching studies.

Comment: Whereas the reaction with oxygen nucleophiles used 1-hydroxy-3-oxobenziodoxole as two-electron oxidant, nitrogen nucleophiles required the use of N-fluorotrimethylpyridinium triflate. Otherwise the iodo species, which itself is able to act as an excellent nucleophile, might compete with the nitrogen containing nucleophiles. The procedure results in the Markovnikov products and enables the addition of phenols.
Chemo- and Enantioselective Reduction of β-Keto-Enamides by Transfer Hydrogenation

Significance: The authors report an asymmetric transfer hydrogenation of β-hydroxy-γ-acetal enamides. A tethered rhodium(III)-DPEN catalyst provided the secondary alcohols in excellent yields and enantioselectivities.

Comment: The authors had previously developed an asymmetric hydrogenation of identical substrates using a rhodium(I) catalyst. In sharp contrast, the present work shows full selectivity for the C=O bond over the C=C bond. A gram-scale experiment at low catalyst loading highlights the practical utility of this method.
Electrosynthetic Reductive Pyridylation of Alkenes in an Undivided Cell

**Significance:** The authors report an electrochemical protocol for the reductive 4-pyridylation of alkenes. This reaction is particularly difficult because the reduction potentials of the alkene and the pyridine precursor are similar, which can cause homocouplings. Screening showed that the reaction proceeds even without the nickel additive but the yields drop by about a third. Ni(acac)_2 is thought to complex the 4-cyanopyridine and thereby alter its reductive potential.

**Comment:** A plausible reaction mechanism is proposed that is mostly based on the results of cyclic voltammetry (CV) studies. Two different pathways are given for the addition of the pyridine. The CV experiments also showed the effect of the Ni(acac)_2 on the reductive potential of the 4-cyanopyridine. The potential increased upon addition of the nickel salt; therefore, the 4-cyanopyridine is harder to reduce and the gap between the alkene is broadened.
**Iridium-Catalyzed Ring-Expansion Proceeding via Hydrogen Borrowing**

**Significance:** The authors report an iridium-catalyzed ring expansion starting from cyclopropyl alcohols and pentamethylphenyl (Ph*) methyl ketone, resulting in the Ph* cyclopentane ketones in good yields and excellent diastereomeric ratios. The applicability of the procedure is shown by subsequently transforming the Ph* group into the corresponding esters, amides or thioesters in excellent yields through a one-pot procedure. Furthermore, the approach enables the construction of complex bicyclic scaffolds.

**Comment:** A plausible reaction mechanism based on detailed mechanistic studies is proposed. During a hydrogen-borrowing phase the cyclopropyl alcohol is oxidized towards the ketone, which undergoes condensation, subsequent SET initiates a rearrangement process forming the five-membered ring. The radical is transferred to the condensation product about to enter the rearrangement phase. The Ir hydride finally reduces the α,β-unsaturated ketone. cataCXium is a bulky ligand that retards the hydrogen-returning reduction.

**Selected examples:**

- **69% yield**
  - dr > 95:5
- **78% yield**
  - dr > 95:5
- **74% yield**
  - dr > 95:5
- **54% yield**
  - dr 95:5
Enantioselective Copper-Catalyzed Cycloaddition: Preparation of Pyrrole-Fused Bridged [2.2.1] Scaffolds

**Significance:** Ye and co-workers report a Cu-catalyzed tandem cyclization/[3+2] cycloaddition reaction that proceeds via a Cu-containing all-carbon 1,3-dipole species. The reaction affords access to complex and synthetically useful chiral pyrrole-fused bridged [2.2.1] cores in excellent enantio- and diastereoselectivity.

**Comment:** Under the standard reaction conditions, in the absence of styrene, the all-carbon 1,3-dipole intermediate undergoes protodemetalation and tautomerization to form a pyrrole-fused cyclopentene product. Reaction of this adduct with styrene under the standard conditions did not yield the desired bridged product.
A. C. S. Reddy, K. Ramachandran, P. M. Reddy, P. Anbarasan* (Indian Institute of Technology Madras, India)  
Rhodium-Catalyzed Sommelet-Hauser Type Rearrangement of α-Diazoimines: Synthesis of Functionalized Enamides  
Chem. Commun. 2020, 56, 5649–5652.

Synthesis of Functionalized Enamides via Rhodium-Catalyzed Cleavage of Triazoles

Significance: Anbarasan and co-workers have demonstrated the utility of α-diazoimines generated in situ from the ring-chain isomerization of triazoles via reaction with α-thioesters under rhodium catalysis. A variety of aryl α-thio esters and triazoles could participate in the reaction to generate functionalized enamides in good to excellent yield. Although nitro- and cyano-substituted phenylsulfides did not form the product, alkyl α-thio esters were successfully reacted.

Comment: The practicality of this methodology was shown by subsequent transformation of the product under oxidative and reductive conditions. Additionally, a one-pot transformation was developed by combining the current methodology with copper-catalyzed azide-alkyne cycloaddition for the stereo- and regioselective functionalization of terminal alkynes. The final step of the proposed mechanism involves an aza-[2,3]-sigmatropic rearrangement from the in situ generated sulfur ylide.

Proposed mechanism:

Selected examples:

- 65% yield
- 74% yield
- 73% yield
- 27% yield, E/Z = 3:2
- 56% yield
Enantioselective Synthesis of Tetrahydrobenzofurans by Gold/Cobalt Dual Catalysis

**Significance:** Dong, Feng, and co-workers report a tandem cycloisomerization/Diels–Alder reaction of enynones and electron-deficient alkenes. Tetrahydrobenzofuran derivatives bearing four contiguous stereocenters were obtained in high yield and stereoselectivity through the action of a gold/cobalt dual catalytic system.

**Comment:** The reaction relies on the formation in situ of a reactive furan-based ortho-quinodimethane intermediate by base-promoted H-transfer. The authors propose that the TFA⁻ counteranion mediates this process. In addition to cobalt, magnesium salts also proved able to catalyze this process, but the product was obtained with slightly lower enantioselectivity.
**Photoinduced Copper-Catalyzed Alkynylation of Redox-Active Esters**

**Significance:** The authors report a photoinduced copper-catalyzed decarboxylative alkynylation of redox-active N–O phthalimide esters. The reaction utilizes the cooperation of a copper(I) and a copper(II) catalyst \([\text{CuCl and Cu(acac)}_2]\), leading to various functionalized double substituted alkynes in good yields.

**Comment:** The method can be extended to aliphatic alkenes and alkynyl silanes by adding catalytic amounts of preformed copper-phenylacetylide (conditions B). Based on DFT calculations, the authors propose a plausible mechanism, revealing the importance of the acetylacetonate ligand.

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**DOI:** 10.1055/s-0040-1707851; **Reg-No.:** P07520SF
**Dual Light-Driven Palladium-Catalyzed Carbonylation**

Significance: The authors report palladium-catalyzed carbonylations under ambient conditions with aryl or alkyl halides as well as with difficult nucleophiles leading to valuable carbonyl derivatives such as acid chlorides, esters, amides and ketones in high yields.

Comment: Remarkably, mechanistic studies suggest that concurrent excitation of palladium(0) and palladium(II) intermediates is responsible for the high activity. This versatile method allows access to various useful classes of products from carbon monoxide. The synthetic utility was shown in the preparation of the cholesterol-lowering drug fenofibrate.

**Selected examples:**

- **aryl bromide or iodide substrates**
  - 99% yield (14-W light)
  - 94% yield
  - 72% yield

- **alkyl iodide substrates**
  - 90% yield (no nucleophile added)
  - 80% yield
  - 85% yield

- **alkyl bromide substrates**
  - 88% yield (no nucleophile added)
  - 86% yield
  - 93% yield
Miyaura Borylation Reaction

**Significance:** Miyaura and co-workers reported a direct catalytic approach for the preparation of arylboronic esters from aryl halides that proceeded in excellent yields and selectivity. This palladium-catalyzed reaction proved to have a broader functional group tolerance (e.g. to ketones, esters, nitriles) than prior syntheses of these useful synthetic linchpins via reactions with organometallic reagents.

**Comment:** The authors noted that the use of the KOAc as a base was critical to the formation of the desired aryl boronic esters in high yields and selectivities. They proposed that the base accelerates the transmetalation process, preventing the biaryl byproducts from being formed (see Review below).

**Review:** E. C. Neeve, S. J. Geier, I. A. I. Mkhald, S. A. Westcott, T. B. Marder Chem. Rev. 2016, 116, 9091–9161.