Published in final edited form as:

*ACS Catal*. 2021 November 05; 11(21): 13714–13720. doi:10.1021/acscatal.1c03969.

# Hydroesterification and difunctionalization of olefins with N-hydroxyphthalimide esters

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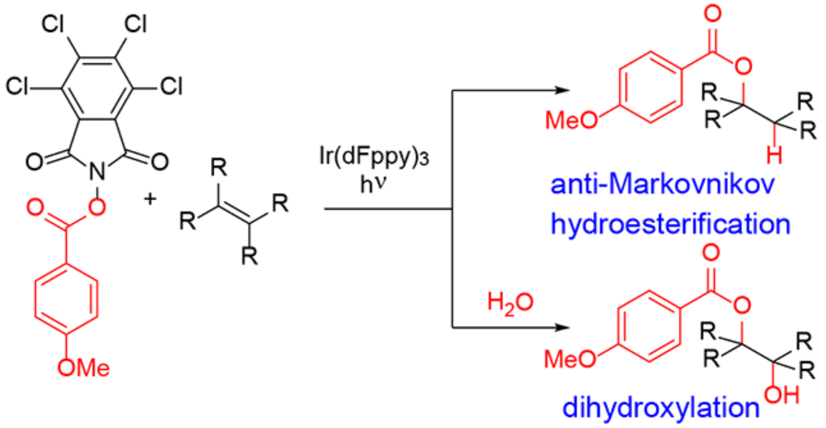
## Abstract

Irradiation of aryl esters of *N*-hydroxyphthalimides in the presence of unactivated olefins promotes a mild and regioselective hydroesterification. Optimal results are obtained with the aid of *fac*-Ir(dFppy)$_3$ in $CH_2Cl_2$. Terminal and 1,1-disubstituted olefins provide primary esters, and trisubstituted olefins provide secondary esters. The anti-Markovnikov selectivity is consistent with alkyl radical intermediates, which are also indicated by the formation of cyclized products from dienes. Mono-acylated diols are formed from tri- and tetrasubstituted olefins in the presence of water.

## Graphical Abstract



## Keywords

photocatalysis; hydroesterification; dihydroxylation; aminohydroxylation; anti-Markovnikov

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No completing financial interests

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Detailed experimental procedures, additional optimization experiments, characterization data (PDF).

X-ray crystal structure of **14b** (cif).

Addition of oxygen nucleophiles to unactivated olefins provides a direct route to alcohols, ethers and esters, which are basic building blocks for organic synthesis. Unfortunately, hydration, hydroetherification and hydroesterification of olefins generally fails (Scheme 1a). Indeed, dehydration of alcohol derivatives to form the corresponding olefin is more common than the reverse addition reactions. The poor performance of direct hydration of olefins has given rise to oxidation/reduction sequences to form the corresponding oxygenated products. Oxymercuration/reduction, hydroboration/oxidation and Wacker oxidation/reduction can provide alcohols and ethers with varying levels of regiocontrol and efficiency.[1] We postulated that *N*-(acyloxy)phthalimides (**1**) might be coaxed into adding to olefins wherein visible light irradiation might provide the driving force to overcome thermodynamic limitations of direct hydration-type reactions.[2]

Alkyl *N*-(acyloxy)phthalimides have traditionally been used as acylating reagents. Pioneering studies from Okada and Odo revealed their propensity to undergo 1-electron reduction followed by N-O bond fragmentation to release alkyl radicals following decarboxylation.[3] This reactivity underpinned the development of decarboxylative additions to olefins, arenes and alkynes, as well as decarboxylative borylation, olefination and cross-coupling.[4, 5, 6] Aryl *N*-(acyloxy)phthalimides have been exploited in decarboxylative borylation reactions,[7] but the decreased stability of aryl radicals relative to alkyl radicals hinders decarboxylative processes. For example, aryl phthalimide esters provided a source of benzoyl esters in a Ni-catalyzed oxidation of aryl zinc reagents.[8] A separate study generated benzoyloxy radicals from the corresponding phthalimide ester, which then underwent intramolecular C-H abstraction followed by alkylation.[9]

To determine if aryl *N*-(acyloxy)phthalimides could effect the hydroesterification of olefins, we exposed phthalimide ester **1a** to cyclohexene in the presence of various photocatalysts. Key results are shown in Table 1. Several organic catalysts provided moderate yields of **4a**, including acridinium-based catalysts **5** and **6** as well as the carbazole-decorated benzene **7** (entries 1-3).[10] Substantial quantities of the corresponding benzoic acid **3** were recovered in these experiments, prompting us to investigate organometallic photoredox catalysts.[11,12] While Ru(bpy)$_3$Cl$_2$ (**8**) proved unsuccessful, three Ir-based catalysts provided ester **4a** in high yield (entries 5-8). The cleanest reaction mixtures were obtained using *fac*-Ir(dFppy)$_3$ (**12**), which provided high yields of ester **4a** and only trace quantities of benzoic acid **3**. The reaction proceeds without external heating or cooling, and does not require acids, bases, oxidants or reductants. Purging the headspace with nitrogen gas provides sufficient protection from oxygen. Control reactions revealed the requirement for irradiation and photocatalyst. Heating alone in the presence of catalyst provided no desired product (entry 10). In the absence of catalyst, irradiation at 427 nM alone provided no desired product (**4a**), and the phthalimide ester was recovered (entry 11). Trace amounts of **4a** (8%) were observed when the reaction mixture was irradiated at 365 nM without catalysts (Table S2 in the SI), but best results were obtained with radiation at 427 nM in the presence of Ir catalyst **12** (427 nM > 440 nM > 390 nM).

Additional optimization data is provided in the supporting information, but some observations warrant discussion. The non-chlorinated version of **1a** was nearly as effective as **1a** (81% yield), as was the 2,4-dimethoxy congener (77% yield). However, alternative aryl esters were much less effective (see Figure S2 in the SI). For example, the parent benzoyloxy phthalimide and heteroaromatic phthalimide esters all provided complex reaction mixtures, as did the 2-methoxy and 3-methoxy analogs of **1a**. Several common additives for photoredox reactions decreased yields, including amines, Hantzsch ester, silanes, thiols, and copper salts (Table S3). The reaction proceeded to varying degrees in different solvents. Dichloromethane, dichloroethane, acetone and acetonitrile were similarly effective (Table S4). Modest amounts of **4a** (10-60%) were observed in chloroform, ethyl acetate, toluene, THF and methanol, while no product was observed in polar solvents such as trifluoroethanol, DMSO or DMF.

With optimal conditions identified, we determined the generality of the reaction (Scheme 2). A wide range of terminal olefins underwent hydroesterification in good yields and moderate-good regioselectivity. For example, linear alkenes reacted with regioselectivities around 3:1 (**4b**, **4c**). Steric bulk near the olefin markedly increased regioselectivity, with a cyclohexyl group adjacent or even one carbon away from the olefin steering addition to the terminal carbon (**4d**, **4e**). *tert*-Butyl ethylene was a poor substrate (**4f**), and in general, substrates lacking allylic C-H's did not perform well. Aryl groups (**4g**, **4h**), olefins (**4i**, **4j**) and halides (**4k**, **4l**) were accommodated. Existing oxygenation did not compromise reactivity, as demonstrated by a protected alcohol (**4m**), epoxide (**4n**), ketone (**4o**) and esters **4p**, **4q**. 1,1-Disubstituted olefins reacted in similar yields as terminal olefins but with complete regioselectivity favoring oxygenation of the terminal carbon. Internal olefins generally provided higher yields than terminal and 1,1-disubstituted olefins. Linear (**4w**, **4x**) and cyclic (**4z** – **4ee**) disubstituted alkenes performed well. Trisubstituted (**4ff**) and even tetrasubstituted olefins (**4y**) were competent reaction partners. Complete regioselectivity was observed for cyclic ethers (**4gg**, **4hh**) using the non-chlorinated phthalimide **1b**. *para*-Methoxy benzoic acid accounted for the remaining mass balance in most cases along with tetrachlorophthalimide, and the reaction performed similarly on a 0.1 and 1 mmol scale.

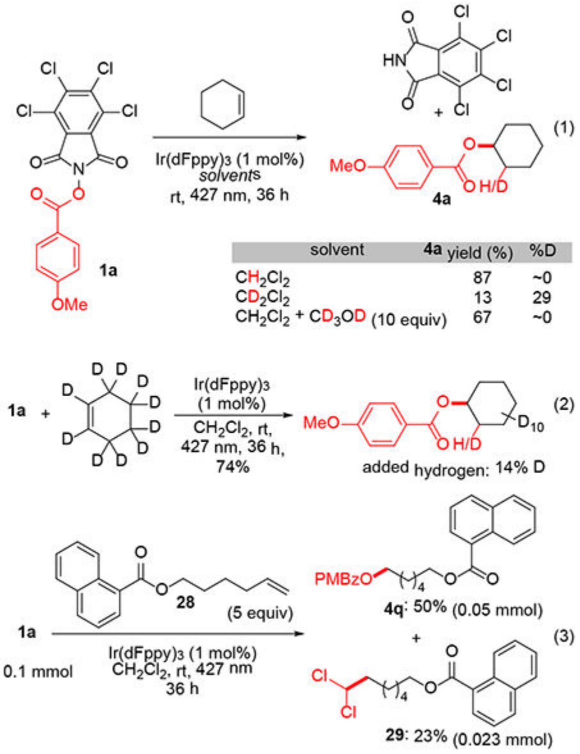
Under the standard conditions, but in the presence of added water, we observed difunctionalization of 1,1-disubstituted, tetrasubstituted and activated disubstituted olefins (Scheme 3). Monobenzoyl-protected diols (**13**) were obtained in moderate yield and complete regioselectivity. Under these modified conditions, terminal olefins and internal disubstituted olefins continued to generate the hydroesterification products (**4**) with trace amounts of the diol being observed. This difference likely arises from the relative ease of accessing tertiary carbocations *vs*. secondary carbocations (see below).

Some electron-rich olefins gave unexpected oxidation products (Scheme 4). For example, three olefins provided aminohydroxylation products in which both the benzoate and phthalimide moieties of **1a** were transferred to the olefin.[13] 2,3-Dimethoxy-1,3-butadiene reacted with complete regiocontrol (**14a**) while dihydrofuran and *trans*-stilbene generated single stereoisomers (**14b**, **14c**).[14] 1,1-Diphenylethylene, styrene and a silyl enol ether were oxidized under the standard conditions, but in slightly different ways. Enol ester **15** was obtained from diphenylethylene whereas the bis-benzoate **16** was formed in low yield from styrene. The only substrate we have observed to undergo allylic oxidation was a silyl enol ether, which yielded allylic benzoate **17**.[15]

## Mechanistic considerations.

Radical intermediates in the reaction were implicated by several cyclizations and fragmentations (Scheme 5). For example, dienes **18**, **20** and **22** underwent addition/cyclization consistent with intramolecular radical addition to the pendent olefins. Cyclopropyl-containing substrate **24** generated naphthalene **25** in a process that likely involves cyclopropyl ring-opening followed by cyclization onto the arene and aerobic oxidation. Finally, α-pinene was converted to cyclohexene **27**, suggestive of radical fragmentation of the cyclobutyl ring.

We attempted to identify the source of the hydrogen that is added to the olefin along with the benzoate group. Remarkably, the reaction was substantially suppressed in $CD_2Cl_2$ (eq 1). The recovered product showed partial deuteration at the newly introduced H/D. Control experiments with mixed solvents ($CH_2Cl_2$ + $CD_2Cl_2$) confirmed that there were no catalyst poisons in the $CD_2Cl_2$ (79% yield of **4a**). Similar results were obtained with other substrates and with $CD_3CN$. Additionally, no deuterium incorporation was observed when $CD_3OD$ was included in the reaction mixture. This evidence suggested that $CH_2Cl_2$ could be the source of the added hydrogen, and that a kinetic isotope effect could be operative in a hydrogen atom transfer step. A reciprocal experiment with cyclohexene-$d_{10}$ provided consistent results (eq 2). The newly introduced hydrogen was predominantly $^1$H, but partial $^2$H incorporation suggested some C-D abstraction from the allylic position of the starting material.



| solvent | **4a** yield (%) | %D |
|---|---|---|
| $CH_2Cl_2$ | 87 | ~0 |
| $CD_2Cl_2$ | 13 | 29 |
| $CH_2Cl_2$ + $CD_3OD$ (10 equiv) | 67 | ~0 |

The overall reaction is redox neutral with regard to the olefin, but the *N*-hydroxyphthalimide ester undergoes net $2e^-$ reduction. To better understand the redox profile of the reaction, we subjected non-volatile substrate **28** to the hydroesterification (eq 3) to search for any oxidized products. In addition to the expected product **4q**, we observed the dichloromethyl adduct **29**.[16] While this observation provides evidence for formation of the dichloromethyl radical through H-atom transfer, it does not resolve the overall redox balance for the transformation because **1a** + $CH_2Cl_2$ **29** is also redox neutral. We did not observe any oxidized products (*e.g.* diene, allylic alcohol derivative, dimer) derived from **28**, which was recovered from the reaction unreacted. Our current interpretation is that dichloromethane provides the H atom for the hydroesterification, but the ultimate fate of the dichloromethyl radical is not clear.

Steady-state Stern-Volmer quenching experiments demonstrated that benzoyloxy phthalimide **1a** effectively quenched the fluorescence of *fac*-Ir(dFppy)$_3$ (**12**) whereas cyclohexene had no effect (Figure S3, S4). We considered electron transfer and energy transfer as possible mechanisms to activate the phthalimide ester. The excited state of *fac*-Ir(dFppy)$_3$ is less reducing (−1.28V vs SCE) than would be required to reduce benzoyloxy phthalimide ($E_{1/2} = -1.4$V).[7] Moreover several catalysts that provide reasonable yields are much less reducing in the excited state (4-CzIPN, −1.18V; Ir(ppy)$_2$(dtbbpy)PF$_6$, −0.96V).[10,12,17] Even more striking, two acridinium catalysts (**5**, **6**, see Table 1) catalyzed the reaction with 5-9 turnovers. These catalysts are unlikely to act as excited state reductants, as SET would form dicationic intermediates. Overall, we consider it more likely that the reaction proceeds through energy transfer from the excited state of **12** to the phthalimide ester,[18,19] although there is not a clear correlation between catalyst triplet energy levels and reaction efficiency.[20] In this regard, it is possible that different catalysts operate through slightly different mechanisms.

A potential mechanism for the hydroesterification is outlined in Scheme 6. Energy transfer between the photoactivated [Ir]* species and hydroxyphthalimide ester **1a** could generate the excited reagent **1a***. Homolysis of the N-O bond could yield *para*-methoxybenzoyl radical (PMBzO·) and the phthalimide radical. Addition of the former to the olefin followed by C-H abstraction, possibly from solvent, could generate the observed product. However, several observations are difficult to reconcile with homolysis of **1a***. First, terminal olefins react more slowly than internal olefins, even though both substrates would form similar secondary radicals. Second, in reactions involving slower-reacting substrates, such as terminal olefins, the hydroxyphthalimide ester **1a** can be recovered. Homolysis of the N-O bond is unlikely to be reversible, suggesting that the olefin could be intimately involved in consumption of **1a***. Third, we have observed no evidence of allylic C-H abstraction or oxidation other than a single example (product **17**). By contrast, Li and coworkers showed allylic C-H oxidation of cyclohexene with benzoyloxy radicals.[15,21] Fourth, we observed no evidence of decarboxylation, which has also been reported for benzoyloxy radicals.[22,23,24] Finally, the modest regioselectivity observed with terminal olefins contrasts with the high selectivity observed in reported additions of O-centered radicals to olefins.[13,25] Alternatively, olefin could react directly with triplet **1a*** to yield the phthalimide radical and the alkyl radical **30**. In this scenario, relaxation of **1a*** in the presence of less-reactive substrates could explain why we recover **1a**. The absence of products associated with the benzoyl radical could likewise indicate that the benzoyl radical is not an intermediate. Difunctionalization products (see Schemes 3 and 4) could arise from oxidation of the alkyl radical to the tertiary cation **31** followed by trapping with water under non-anhydrous conditions.

In summary, we have described a mild, regioselective hydroesterification of unfunctionalized olefins. While the current protocol requires an excess of olefin, it offers a single-step route to alkyl esters.

## Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

## ACKNOWLEDGMENT

Funding support from the Welch Foundation (I-1612) and the NIH (RM1 GM142002).

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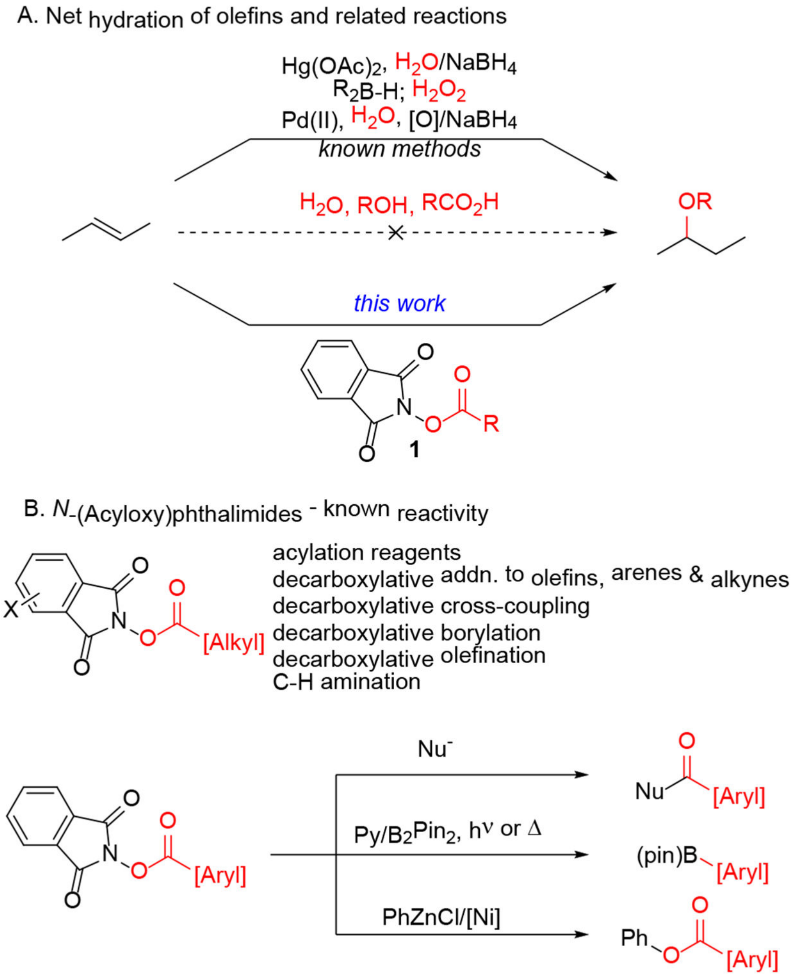
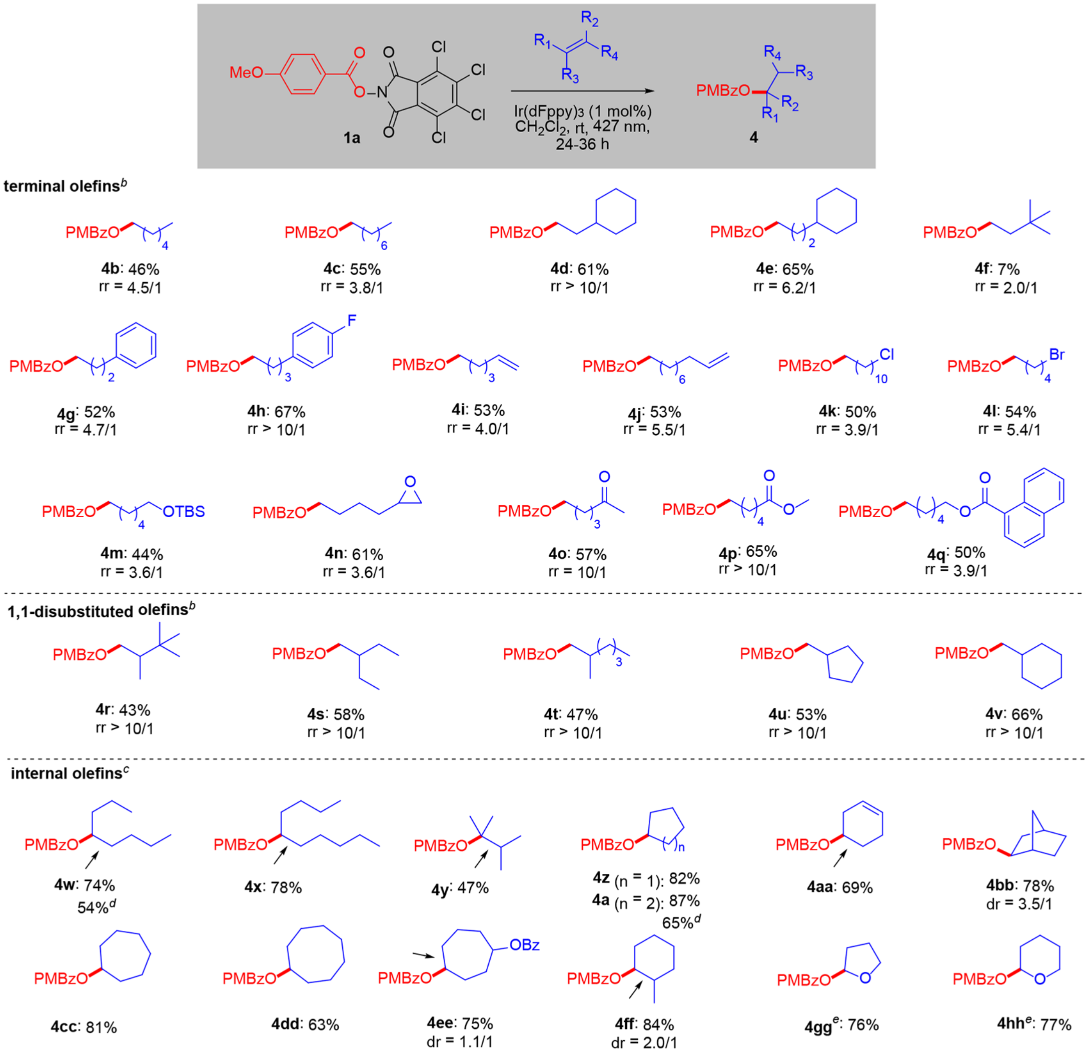


**Scheme 1.**

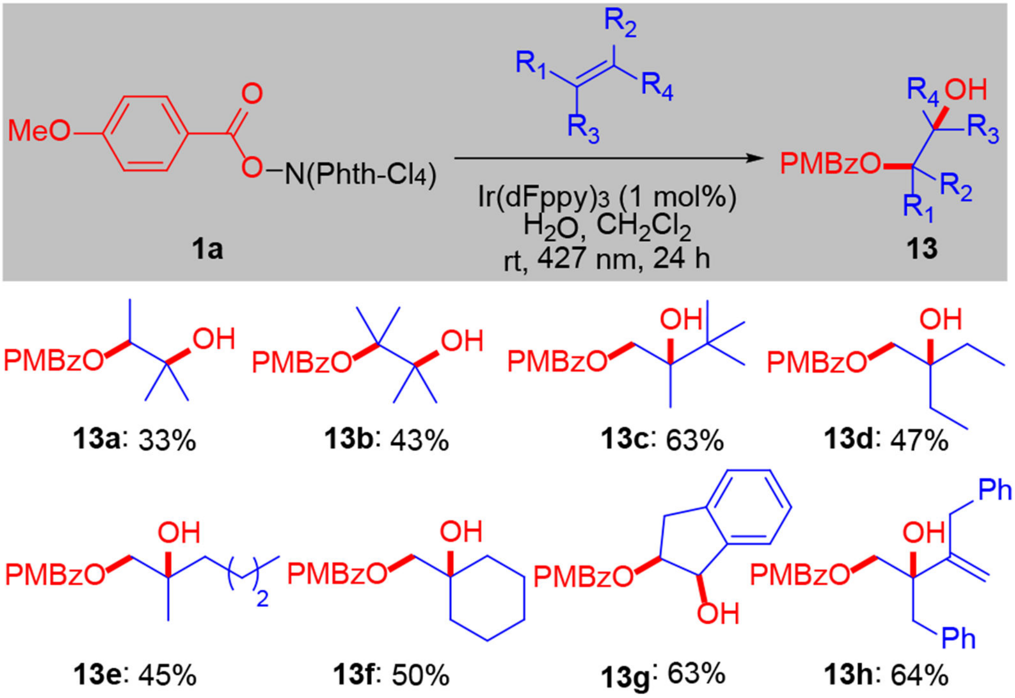
Background



**Scheme 2.**

Scope of the hydroesterification[a]

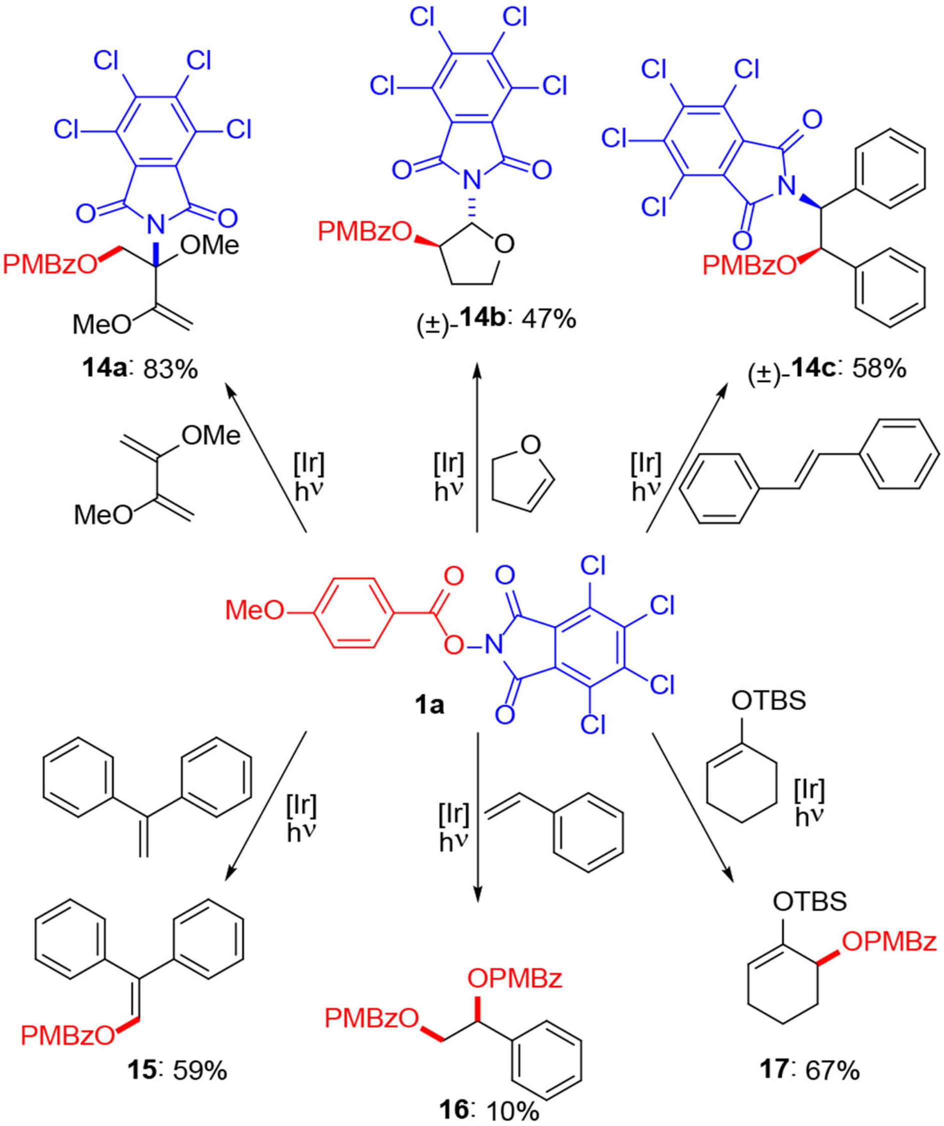
[a]rr: regioisomer ratio. Isolated yields. Reaction conditions: **1a** (0.1 mmol), olefin (0.5 mmol), Ir(dFppy)$_3$ (1 mol%). Irradiation with Kessil PR160L-427 nm LED. Arrow indicates position of olefin in starting material. [b]36 h reaction time. [c]24 h reaction time. [d]1 mmol **1a**. [e]Non-chlorinated phthalimide **1b** (1,3-dioxoisoindolin-2-yl 4-methoxybenzoate) was used.



**Scheme 3.**

Difunctionalization of olefins[a]

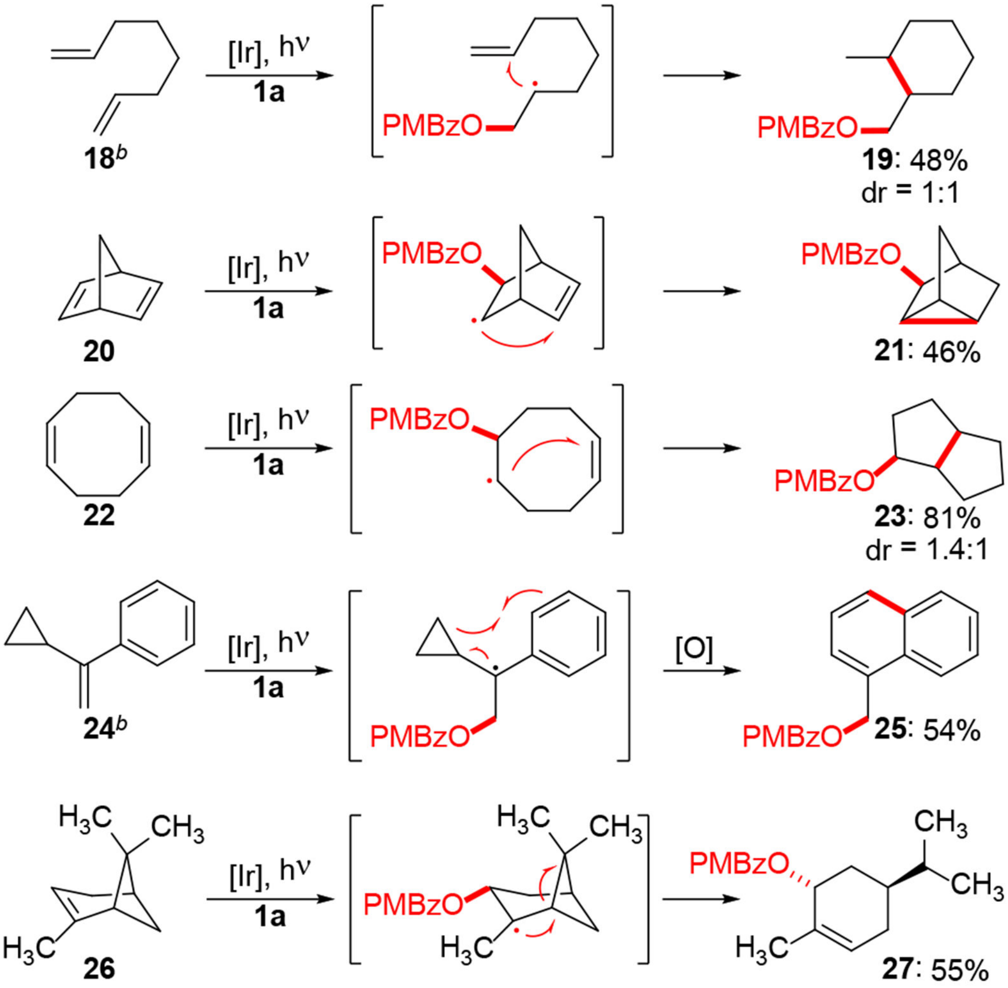
[a]Reaction conditions: **1a** (0.1 mmol), olefin (0.5 mmol), Ir(dFppy)$_3$ (1 mol%), $H_2O$ (10 equiv), 20 mM in $CH_2Cl_2$. Irradiation for 24 h with Kessil PR160L-427 nm LED.



**Scheme 4.**

Unexpected oxidations with 1a[a]

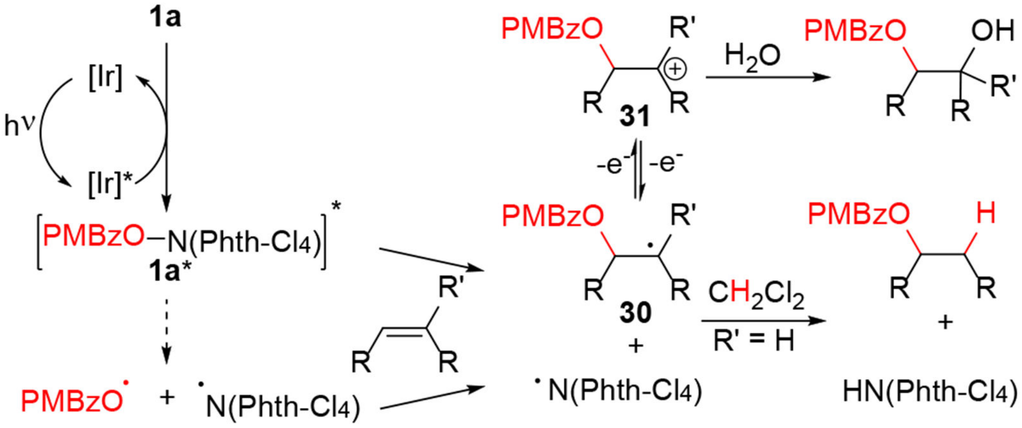
[a]Reaction conditions: **1a** (0.1 mmol), olefin (0.5 mmol), Ir(dFppy)$_3$ (1 mol%), 20 mM in CH$_2$Cl$_2$. Irradiation for 24 h with Kessil PR160L-427 nm LED.



**Scheme 5.**

Evidence for radical intermediates[a]

[a] Reaction conditions: 4,5,6,7-tetrachloro-1,3-dioxoisoindolin-2-yl 4-methoxybenzoate (**1a**, 0.1 mmol), olefin (0.5 mmol), Ir(dFppy)$_3$ (1 mol%), 20 mM in $CH_2Cl_2$. Irradiation for 24 h with Kessil PR160L-427 nm LED. [b] Irradiation for 36 h.

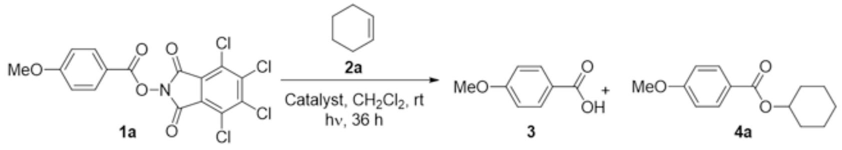


**Scheme 6.**

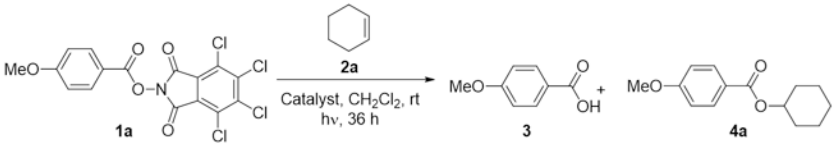
Potential mechanism

## Table 1.

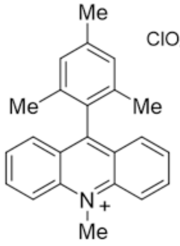
Identification of photocatalyst[a]

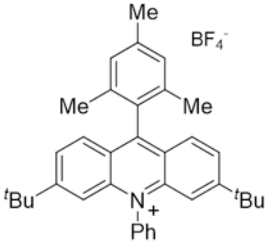


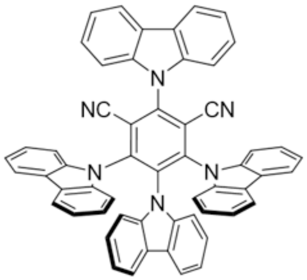
| entry | catalysts | $E_T$ (kcal/mol) | $E_{1/2}$ (M*/M+, V) | light source | yield 3 (%) | yield 4a (%) |
|---|---|---|---|---|---|---|
| 1[b] | 9-Mes-10-Me-Acr·$ClO_4$ (**5**) | 44.7[c] | - | Kessil H150-BLUE | 45 | 38 |
| 2[b] | Acridinium·$BF_4$ (**6**) | | | Kessil H150-BLUE | 28 | 25 |
| 3[b] | 4-CzIPN (**7**) | 58.8[d] | −1.18[e] | Kessil PR160L (440 nm) | 22 | 62 |
| 4[b] | $Ru(bpy)_3Cl_2$ (**8**) | 46.5[f,g] | −0.81[f,g] | Kessil H150-BLUE | 0[h] | 0 |
| 5 | $Ir(ppy)_2(dtbbpy)PF_6$ (**9**) | 49.2[f] | −0.96[f] | Kessil PR160L (440 nm) | 18 | 73 |
| 6 | *fac*-$Ir(ppy)_3$ (**10**) | 55.2[f] | −1.73[f] | Kessil PR160L (440 nm) | 11 | 81 |
| 7 | $Ir(dF(CF_3)ppy)_2(dtbbpy)PF_6$ (**11**) | 60.1[f] | −0.89[f] | Kessil PR160L (440 nm) | 40 | 10 |
| 8 | *fac*-$Ir(dFppy)_3$ (**12**) | 60.1[f] | −1.28[f] | Kessil PR160L (440 nm) | <5 | 87 |
| 9 | *fac*-$Ir(dFppy)_3$ (**12**) | | | Kessil PR160L (427 nm) | <5 | 91 |
| 10 | *fac*-$Ir(dFppy)_3$ (**12**) | | | None (40 °C) | 0[h] | 0 |
| 11 | None | | | Kessil PR160L (427 nm) | 0[h] | 0 |

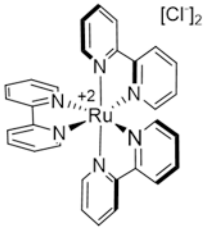


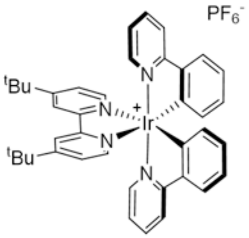
| entry | catalysts | $E_T$ (kcal/mol) | $E_{1/2}$ (M*/M+, V) | light source | yield 3 (%) | yield 4a (%) |
|---|---|---|---|---|---|---|

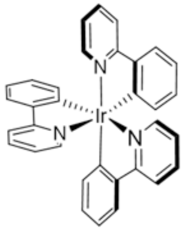

9-Mes-10-Me-Acr·$ClO_4$ (**5**)

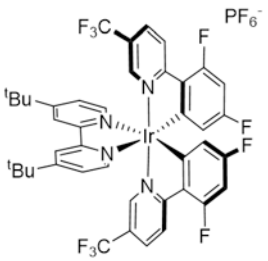

Acridinium·$BF_4$ (**6**)

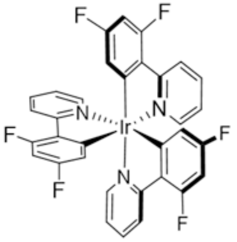

4-CzIPN (**7**)


$Ru(bpy)_3Cl_2$ (**8**)


$[Ir(ppy)_2(dtbbpy)]PF_6$ (**9**)


*fac*-$Ir(ppy)_3$ (**10**)


$[Ir(dF(CF_3)ppy)_2(dtbbpy)]PF_6$ (**11**)


*fac*-$Ir(dFppy)_3$ (**12**)

[a] Unless described otherwise, the reactions were conducted with substrate **1a** (44.0 mg, 0.1 mmol, 1.0 equiv), $CH_2Cl_2$ (5.0 mL), catalyst (1 mol%), cyclohexene (5.0 equiv), without heating or cooling (actual reaction solution temperature: 40 - 45 °C) under a nitrogen atmosphere. 8 mL glass vials were irradiated with LED as indicated for 36 h. Yields were obtained by $^1H$ NMR integrations by using 1,3,5-trimethoxybenzene as internal standard.

[b] 5 mol% catalyst.

[c] Ref 10.

[d] Ref 20.

[e] Ref 17.

[f] Ref 12.

[g] Values for Ru(bpy)$_3$(PF$_6$)$_2$.

[h] Substrate **1a** recovered.