Alkoxyl Radical Generation

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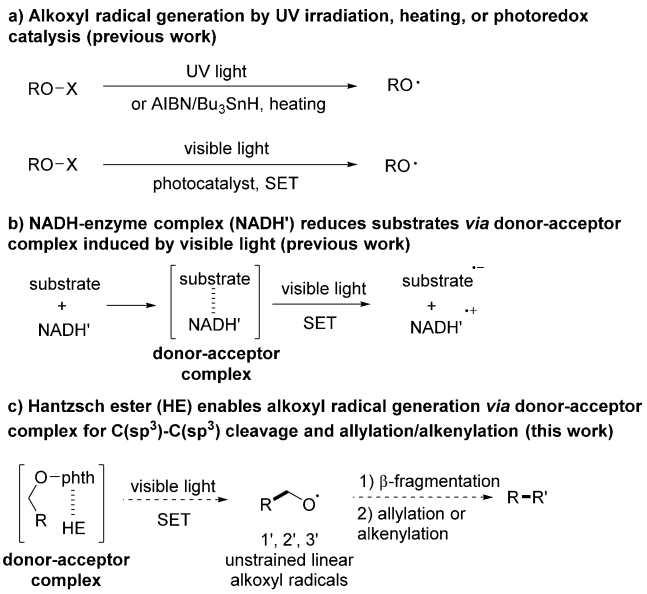
Donor–Acceptor Complex Enables Alkoxyl Radical Generation for Metal-Free C(sp^3)–C(sp^3) Cleavage and Allylation/Alkenylation

*Jing Zhang, Yang Li, Ruoyu Xu, and Yiyun Chen**

Abstract: *The alkoxyl radical is an essential and prevalent reactive intermediate for chemical and biological studies. Here we report the first donor–acceptor complex-enabled alkoxyl radical generation under metal-free reaction conditions induced by visible light. Hantzsch ester forms the key donor–acceptor complex with N-alkoxyl derivatives, which is elucidated by a series of spectrometry and mechanistic experiments. Selective C(sp^3)-C(sp^3) bond cleavage and allylation/alkenylation is demonstrated for the first time using this photocatalyst-free approach with linear primary, secondary, and tertiary alkoxyl radicals.*

The alkoxyl radical is a prevalent reactive intermediate for chemical and biological studies, however its generation under mild reaction conditions has been challenging.[1] Traditionally, alkoxyl radicals are generated under relatively harsh reaction conditions such as heating or UV light irradiation, which limit their synthetic scope and functional group compatibilities (Scheme 1 a).[2] Recently, the development of photoredox catalysis methods enables alkoxyl radical generation under mild reaction conditions, however these photoredox catalysis methods require expensive heavy-metal photocatalysts.[3,4] We envision a new alkoxyl radical generation method that under mild and metal-free conditions will be beneficial for synthetic, material, and biological applications of alkoxyl radicals.[5]

Donor–acceptor complexes are molecular complexes resulting from the association of an electron donor molecule (D) with an electron acceptor molecule (A), which generally demonstrate partial or total electron transfer from D to A upon irradiation (Scheme 1 b).[6] However, its application in organic synthesis is limited and the donor–acceptor complex for alkoxyl radical generation is unknown.[7,8] The NADH (the reduced form of nicotinamide adenine dinucleotide) is known to form the donor–acceptor complex when bound to the enzyme,[9] however its synthetic analog Hantzsch ester (HE) has not been reported for donor–acceptor complex formation.[10,11] We hypothesize that the donor–acceptor complex formation between alkoxyl radical precursors and HE will enable the alkoxyl radical generation without photocatalysts (Scheme 1 c).



Scheme 1. Donor–acceptor complex enables alkoxyl radical generation for metal-free C(sp^3)-C(sp^3) bond cleavage and functionalization (SET = single electron transfer).

The cleavage of unactivated C(sp^3)-C(sp^3) bond to engage in new C–C bond formation is a desirable organic transformation, however it is challenging to achieve the excellent regioselectivity and chemoselectivity.[12] The alkoxyl radical is known for β-fragmentation reactivity to selectively cleave the adjacent C–C bond, however its synthetic application for intermolecular C–C bond formation is limited to alkoxyl radicals derived from strained cycloalkanols.[13] For unstrained linear alkoxyl radicals, the resulting C(sp^3) radical from β-fragmentation is usually trapped by reductive hydrogenation or oxidation, and the intermolecular trapping of the C(sp^3) radical for C–C bond formation is challenging.[4b,14] Herein we report the first donor–acceptor complex formation between Hantzsch ester and *N*-alkoxyl derivatives to generate alkoxyl radicals upon visible light irradiation (Scheme 1 c). Selective C(sp^3)-C(sp^3) bond cleavage and intermolecular allylation/alkenylation are enabled via linear primary, secondary, and tertiary alkoxyl radicals.

We started our investigation with the unstrained linear alkoxyl radical precursor *N*-alkoxyphthalimides, which was bench-stable and could be easily prepared from readily available alcohols.[4a,d,15] While the *N*-alkoxyphthalimide was unknown for donor–acceptor complex formation, we

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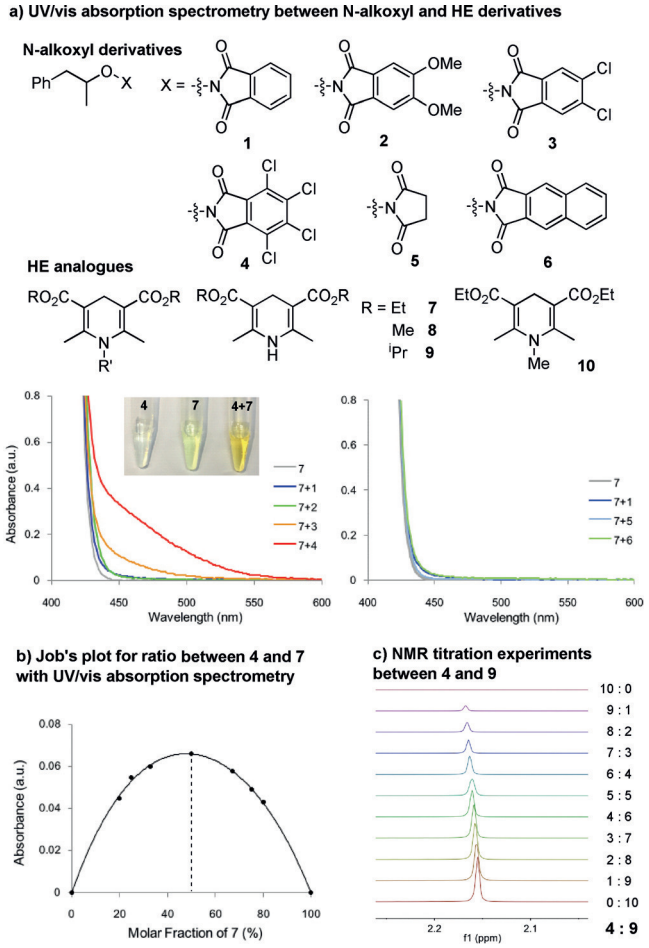
hypothesized that its conjugated π system and electron-deficient character would enable the donor–acceptor complex formation with suitable electron donors. We then synthesized a panel of *N*-alkoxyphthalimide analogs **1**–**4** with different substituents, as well as *N*-alkoxysuccinimide **5** and *N*-alkoxylnaphthalimide **6** (Scheme 2a). When mixed with HE **7**, the



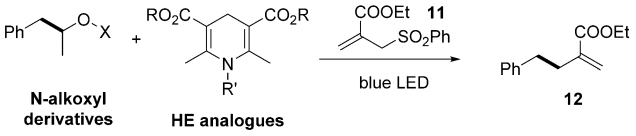
Scheme 2. Interactions between *N*-alkoxyl and Hantzsch ester derivatives.

UV/Vis absorption spectrometry showed no signal change from *N*-alkoxysuccinimide **5**, however there were clear red-shifts from *N*-alkoxyl derivatives **1**–**4** and **6**. The *N*-alkoxyphthalimides **3** and **4** bearing electron-withdrawing chlorides showed stronger red-shifts compared to *N*-alkoxyphthalimides **2** bearing electron-rich methoxy groups, which was consistent with the *N*-alkoxyphthalimides as the electron acceptor. In particular, a charge-transfer orange-yellowish color appeared when tetrachloro-substituted *N*-alkoxyphthalimides **4** was mixed with HE **7** (Scheme 2a). We also prepared substituted HE **8**–**10** (methyl and isopropyl ester HE as well as *N*-methyl-substituted HE) and observed red-shifts when mixed with *N*-alkoxyphthalimide **1** (see Figure S2 in the Supporting information).

The donor–acceptor complex between *N*-alkoxyphthalimides and Hantzsch esters was further investigated by the Job's plot with UV/Vis absorption experiments.[16] The maximal absorption at 50% molar fraction of HE **7** suggested a 1:1 ratio between **4** and **7** (Scheme 2b). The dissociation constant K_{EDA} between **4** and **7** was calculated to be 8.4 M^{-1} in dichloromethane with Benesi–Hildebrand methodology.[17] We also did NMR titration experiments and found the ^{1}H NMR signal of isopropyl HE **9** shifted downfield with the addition of tetrachloro-substituted *N*-alkoxyphthalimide **4** (Scheme 2c, see Figures S6–S12 for the UV/Vis absorption spectrometry, K_{EDA}, and NMR titration experiments of other derivatives). Taken together, the donor–acceptor complex is formed between *N*-alkoxyphthalimides and Hantzsch esters.[8b,c]

We next subjected *N*-alkoxyphthalimide **1** and HE **7** to the radical acceptor allyl sulfone **11**.[18] Under blue LED irradiation in dichloromethane, we observed **12** in 31% yield, which indicated that the alkoxyl radical was generated without photocatalysts and the resulting alkyl radical successfully underwent allyl addition (entry 1 in Table 1). The solvent

Table 1: Reactions between *N*-alkoxyl and Hantzsch ester derivatives under visible light irradiation.



Entry	Conditions[a]	Conversion[b]	Yield[b]
1	**1** + HE **7**, CH_2Cl_2	49%	31%
2	**1** + HE **7**, MeOH	>95%	64%(60%)
3	**1** + HE **7**, dioxane	>95%	72%(67%)
4	**2** + HE **7**, dioxane	70%	64%
5	**3** + HE **7**, dioxane	>95%	66%
6	**4** + HE **7**, dioxane	44%	37%
7	**5** + HE **7**, dioxane	<5%	<5%
8	**6** + HE **7**, dioxane	>95%	77%(73%)
9	**1** + CO_2Me-HE **8**, dioxane	79%	67%
10	**1** + CO_2^iPr-HE **9**, dioxane	38%	21%
11	**1** + *N*-Me-HE **10**, dioxane	<5%	<5%
12	**6** + HE **7**, MeOH, 12 h	>95%	70%(65%)
13	entry 12, band-pass 450 nm	>95%	70%
14	entry 12, band-pass 475 nm	44%	37%

[a] Reaction conditions: *N*-alkoxyl derivatives (0.10 mmol, 1.0 equiv), **11** (0.30 mmol, 3.0 equiv), and Hantzsch ester derivatives (0.50 mmol, 5.0 equiv) in 1.0 mL solvent under nitrogen with 8 W blue LED irradiation at ambient temperature for 36 h, unless otherwise noted. Conversion and yields were determined by ^{1}H NMR analysis and isolated yields were in parentheses.

screening indicated that 1,4-dioxane was optimal to give **12** in 72% yield (67% isolated yield, entries 2–3).[19] The use of *N*-alkoxyl derivatives **2, 3** and **6** gave **12** in similar 64–77% yields (entries 4, 5 and 8). The tetrachloro-substituted *N*-alkoxyphthalimides **4** gave slow conversion due to the product inhibition from tetrachloro-phthalimides (entry 6).[20] The formation of the donor–acceptor complex was necessary as *N*-alkoxysuccinimide **5** did not lead to any conversion (entry 7). Among the substituted HE **8**–**10**, the methyl HE **8** gave similar 67% yield, the isopropyl HE **9** gave lower 21%

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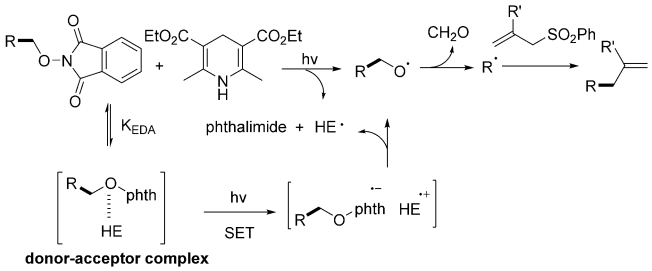
yield due to the steric hindrance, and no conversion was observed with *N*-methyl HE **10** (entries 9–11).

We further investigated whether the HE was directly photoexcited by the shorter wavelength irradiation without donor–acceptor complex formation.[11] Using the irradiation with band-pass at 450 nm, in which HE has minimal absorption, the reaction went uncompromised with 70% yield (entries 12,13). Using band-pass at 475 nm without emission at below 460 nm (see Figures S15,16), 37% yield of **12** could be obtained (entry 14). Taken together, the donor–acceptor complex formation is essential for the reaction at longer wavelength.[21] The light irradiation and HE were found both critical for the reaction (see Table S3).

Based on mechanistic investigations above, we propose that the reaction is initiated by the formation of the donor–acceptor complex between Hantzsch esters and *N*-alkoxyphthalimides (Scheme 3). After visible-light-induced electron

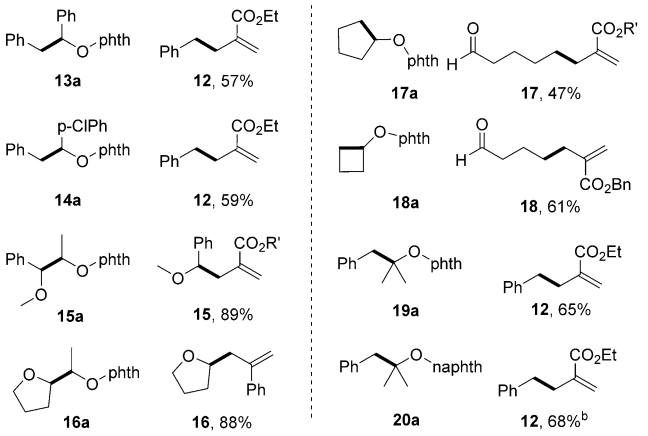


Scheme 3. Mechanistic proposal of the reaction.

transfer,[22] the *N*-alkoxyphthalimide radical anion is formed and eliminates phthalimides to generate the alkoxyl radical. The resulting alkoxyl radical undergoes β-fragmentation to yield the alkyl radical and is trapped by allyl sulfones for radical allylation reaction.

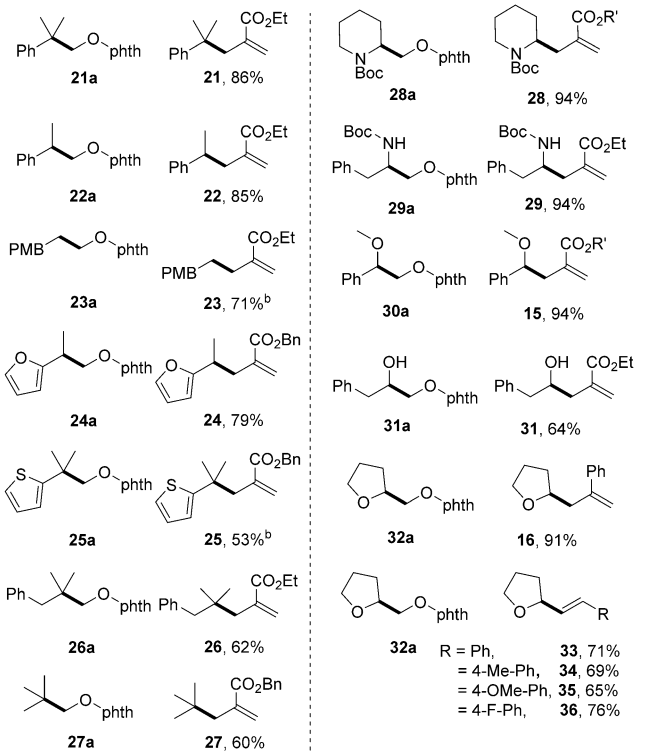
With this metal-free donor–acceptor complex approach, we then tested various linear secondary and tertiary *N*-alkoxyphthalimides for $C(sp^3)$-$C(sp^3)$ bond cleavage and allylation reaction (Scheme 4, conditions in entry 3 of Table 1). Both acetaldehydes and benzaldehydes could be eliminated smoothly from *N*-alkoxyphthalimides **13a**–**16a**, and the allylation went smoothly to yield **12**, **15** and **16** in 57–89% yields. The cyclopentanol- and cyclobutanol-derived *N*-alkoxyphthalimides underwent $C(sp^3)$-$C(sp^3)$ bond cleavage and allylation to give alkenyl aldehydes **17** and **18** in 47–61% yields. The linear tertiary alkoxyl radical was generated with *N*-alkoxyphthalimide **19a** and *N*-alkoxylnaphthalimide **20a**, which both afforded **12** in 65–68% yields after acetone elimination.

Finally, we challenged the reactivity of primary alkoxyl radicals, which has not been realized by previous methods for $C(sp^3)$-$C(sp^3)$ bond cleavage/functionalization due to the facile side reactions (Scheme 5).[4b,c,e] With linear *N*-alkoxyphthalimides **21a**–**23a**, the primary alkoxyl radicals were generated and yielded allylation adducts **21**–**23** in 71–86% yields. The heterocycles furan and thiophene were well tolerated to give **24** and **25** in 53–79% yields. The alkoxyl



Reaction condition is in entry 3 in Table 1, reaction condition b uses MeOH, and isolated yields are reported. R' = 1-Naph-CH_2-.

Scheme 4. $C(sp^3)$-$C(sp^3)$ bond cleavage/functionalization with linear secondary and tertiary alkoxyl radicals.



Reaction condition is in entry 3 in Table 1, reaction condition b uses MeOH, and isolated yields are reported. R' = 1-Naph-CH_2-.

Scheme 5. $C(sp^3)$-$C(sp^3)$ bond cleavage/functionalization with linear primary alkoxyl radicals.

radical fragmentation also afforded tertiary alkyl radicals to yield **26**–**27** in 60–62% yields. The heteroatoms facilitated the β-fragmentation of alkoxyl radicals that **28a**–**30a** reacted smoothly to give excellent 94% yields.

With the diol-derived *N*-alkoxyphthalimide **31a**, the alkoxyl radical was selectively generated without interfering the free hydroxyl group to yield homoallylic alcohol **31** in

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64% yield. The reaction was not limited to electron-withdrawing allyl sulfones that styrene **16** could be obtained in 91% yield. In addition, the vinyl sulfones acted as radical acceptors effectively to give the $C(sp^3)$-$C(sp^3)$ bond cleavage and alkenylation adducts **33**–**36** in 65–76% yields.[23]

In conclusion, we have developed the first donor–acceptor complex method for alkoxyl radical generation under mild and metal-free conditions. Selective $C(sp^3)$-$C(sp^3)$ bond cleavage and allylation/alkenylation is achieved via linear primary, secondary and tertiary alkoxyl radicals. We envision this donor–acceptor complex method will be instrumental for new visible-light-induced reaction design and the further investigation is undergoing in our laboratory.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: alkoxyl radicals · donor–acceptor complexes · Hantzsch ester · photocatalysis · radical reactions

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[21] The redox potentials of *N*-alkoxyl derivatives were irrelevant to their reactivity, which further suggested the direct photoexcitation of HE to reduce the *N*-alkoxyl derivatives was unlikely: $E_p(\mathbf{1}) = -1.40$ V, $E_p((\mathbf{2}) = -1.50$ V, $E_p((\mathbf{3}) = -1.19$ V, $E_p((\mathbf{4}) = -0.98$ V, $E_p((\mathbf{5}) = -0.77$ V, and $E_p((\mathbf{6}) = -1.40$ V vs. SCE in MeCN.
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