

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Tetrachlorophthalimides as Organocatalytic Acceptors for Electron Donor-Acceptor Complex Photoactivation

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Zhou W., Wu S., Melchiorre P. (2022). Tetrachlorophthalimides as Organocatalytic Acceptors for Electron Donor-Acceptor Complex Photoactivation. JOURNAL OF THE AMERICAN CHEMICAL SOCIETY, 144(20), 8914-8919 [10.1021/jacs.2c03546].

Availability:

This version is available at: <https://hdl.handle.net/11585/897858> since: 2022-11-15

Published:

DOI: <http://doi.org/10.1021/jacs.2c03546>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

Tetrachlorophthalimides as Organocatalytic Acceptors for Electron Donor–Acceptor Complex Photoactivation

Wei Zhou,^{1,2} Shuo Wu,^{1,2} and Paolo Melchiorre^{*,1,3}

¹ICIQ – Institute of Chemical Research of Catalonia, the Barcelona Institute of Science and Technology, Avinguda Països Catalans 16, 43007 Tarragona, Spain

²Department of Analytical Chemistry and Organic Chemistry, University Rovira i Virgili, 43007 Tarragona, Spain

³ICREA – Passeig Lluís Companys 23, 08010 Barcelona, Spain

Supporting Information Placeholder

ABSTRACT: Excitation of photoactive electron donor-acceptor (EDA) complexes is an effective way to generate radicals. Applications in a catalytic regime typically use catalytic donors. Herein, we report that readily available electron-poor tetrachlorophthalimides can act as effective organocatalytic acceptors to trigger the formation of EDA complexes with a variety of radical precursors not amenable to previous catalytic methods. Excitation with visible light generates carbon radicals under mild conditions. The versatility of this EDA complex catalytic platform allowed us to develop mechanistically distinct radical reactions, including in combination with a cobalt-based catalytic system. Quantum yield measurements established that a closed catalytic cycle is operational, which hints at the ability of tetrachlorophthalimides to readily turn over and govern each catalytic cycle.

Visible-light excitation of electron donor-acceptor (EDA) complexes¹ is a useful way to generate radicals under mild conditions. This strategy is attracting growing interest² because of the ease of operation and the possibility of activating colorless substances using light, without exogenous photoredox catalysts. Initial applications focused on the coupling of two stoichiometric donor and acceptor substrates.³ Recently, researchers,⁴ including us,⁵ succeeded in implementing the EDA complex photochemistry within a catalytic regime, thus expanding the strategy's efficiency. These protocols relied on electron-rich catalysts to trigger EDA complex formation upon aggregation with electron-poor substrates adorned with a suitable redox auxiliary (RA in Figure 1a). A photoinduced single-electron transfer (SET) then generated radicals that could engage in a variety of bond-forming processes.

We recently wondered about the feasibility of developing a complementary approach for EDA complex catalysis. Specifically, we thought that the use of catalytic acceptors could allow for the activation of electron-rich substrates

not amenable to previous catalytic protocols (Figure 1b). The crucial step requires the effective turnover of the catalyst via SET oxidation of the catalyst radical anion, arising from the photoactivity of the progenitor EDA complex. A few recent reports used electron-poor catalysts to elicit EDA complex activation,⁶ but these catalysts only proved useful to activate specific radical precursors and were therefore limited to selected transformations.

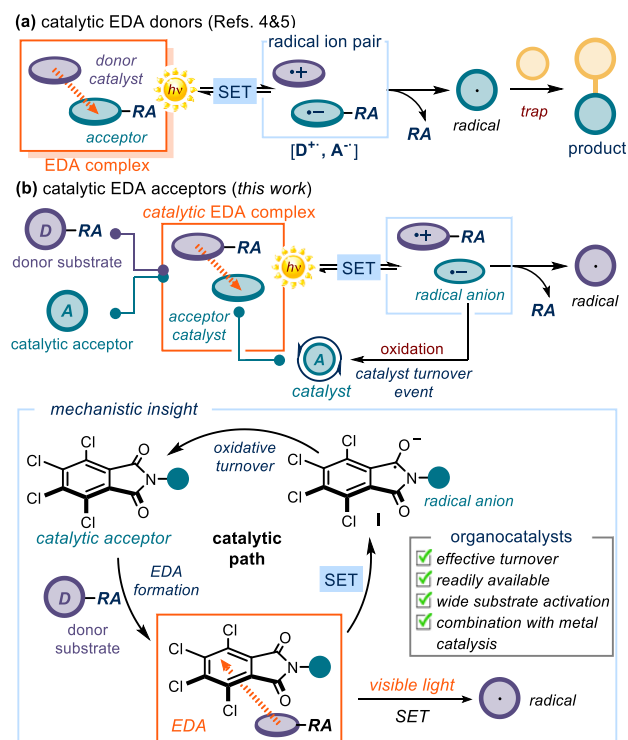


Figure 1. (a) Photochemistry of EDA complexes using catalytic donors. (b) A new general class of acceptor organocatalysts for catalytic EDA complex photochemistry and their use in radical processes; RA: redox auxiliary, which drives EDA complex formation and acts as a fragmenting group.

Herein, we report a general and modular class of electron-acceptor organocatalysts that, although they cannot

absorb visible light themselves, can readily form photoactive EDA complexes with a variety of electron-rich radical precursors. Specifically, we used readily available tetrachlorophthalimide-based catalysts to generate carbon radicals under blue light excitation and to develop mechanistically distinct reactions, including in combination with a metal-based catalytic system.

We started our exploration by using cyclopentyl-1,4-dihydropyridine (DHP **1a**, Figure 2a) as the radical precursor because of its established ability to participate in EDA complex formation acting as a donor.⁷ Initial experiments were conducted with vinylsulfone **2a** at 40 °C in dimethylformamide (DMF) using a blue LED emitting at 456 nm. The choice of suitable acceptor catalysts was informed by the tendency of phthalides and tetrachlorophthalides to serve as suitable electron-poor redox auxiliaries for stoichiometric EDA complex formation.⁸ We surmised that these electron-poor fragments, when embedded within the cata-

lyst structure, could ensure i) effective EDA complex formation, upon ground-state aggregation with electron-rich substrates; and ii) effective turnover, upon SET oxidation of the ensuing radical anion of type **I** (see mechanistic insight in Figure 1b). We first tested the catalytic activity of phthalimide **A** (20 mol%), which failed to provide the target Giese addition product **3a** (entry 1, Figure 2b). In contrast, tetrachlorophthalimides **B** and **C**, which were prepared in a single step from commercial reagents, acted as effective EDA acceptor catalysts, affording **3a** in high yield (entries 2 and 3, respectively). These different catalytic performances can be rationalized by considering the higher electron-acceptor ability of catalysts **B** and **C**, as inferred by their redox properties. Cyclic voltammetry studies, detailed in Figure 2c and Section D3 of the Supporting Information (SI), showed a well-shaped reversible behavior for **B** and **C**. This hints at a certain kinetic stability of the corresponding radical anion of type **I**, which can be crucial for catalyst turnover.

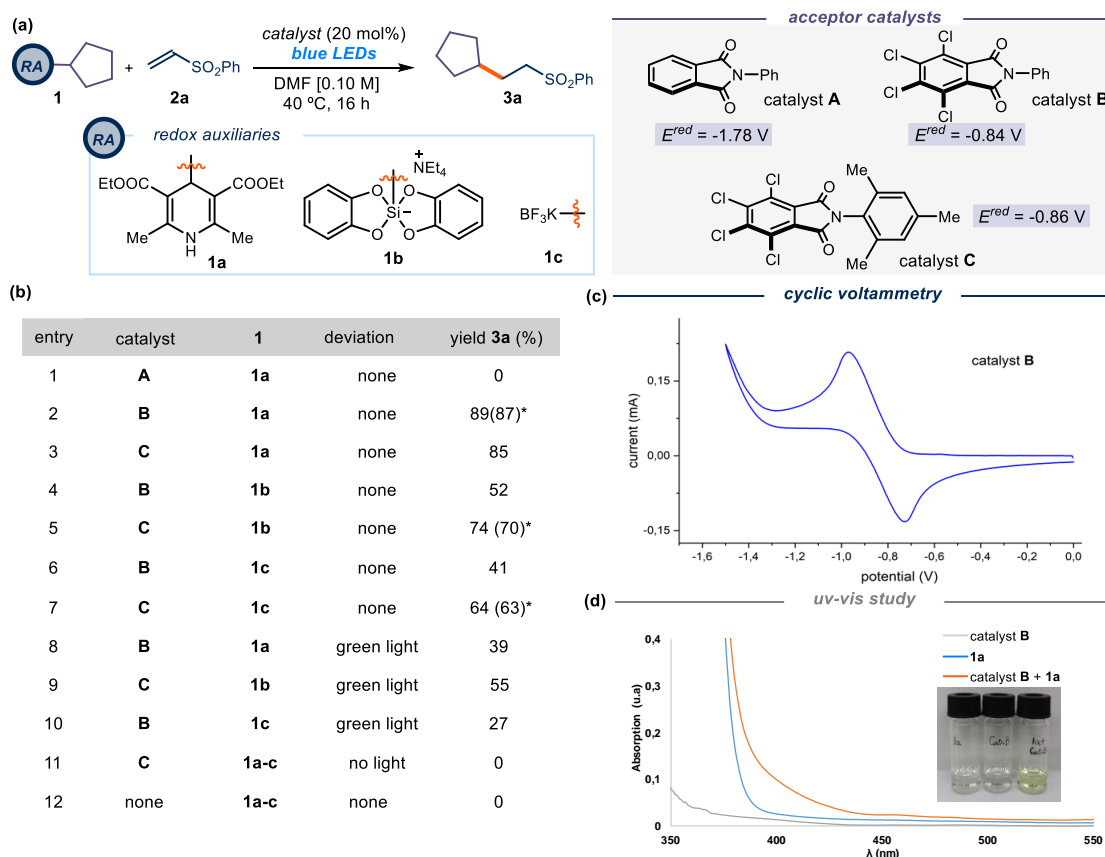


Figure 2. Initial explorations. (a) Model reaction and catalysts tested. (b) Optimization studies: reactions performed on a 0.1 mmol scale at 40 °C for 16 h under illumination by a Kessil lamp ($\lambda_{\text{max}} = 456 \text{ nm}$, 40 W) using 1.5 equiv. of **1**. Yield determined by ^1H NMR analysis. *Yield of the isolated **3a**. (c) Cyclovoltammetric study of catalyst **B** [0.02 M] in DMF vs Ag/AgCl. (d) Optical absorption spectra, recorded in DMF in 1 mm path quartz cuvettes, of the separate reaction components and appearance of the colored EDA complex between catalyst **B** and **1a**. [**1a**] = 0.15 M, [**B**] = 0.02 M.

We then evaluated the ability of our EDA acceptor catalysts to activate electron-rich radical precursors bearing other redox auxiliary groups than DHP. We found that silicate **1b**⁹ and trifluoroborate salt **1c**¹⁰ could also be activated to form a cyclopentyl radical. Catalyst **C** performed better

than **B** in activating **1b** and **1c**, leading to the Giese product **3a** in good yield (entries 5 and 7, respectively). These results highlight how the modular nature of the acceptor catalysts can be leveraged to optimize the activation of electronically different radical precursors.

Investigations were performed to gain mechanistic insights. The formation of an EDA aggregation in the ground state was confirmed through UV/Vis spectroscopic analysis (Figure 2d). After mixing catalyst **B** with **1a**, the solution developed a pale-yellow colour, while its absorption spectrum showed a bathochromic displacement in the visible region. The same behaviour was observed when mixing catalyst **C** and silicate **1b** and trifluoroborate salt **1c** (detail in Figures S9 and S10 in SI). In contrast, no EDA complex formation was observed when mixing substrates **1a-c** and **2a** (see Section D2 in SI for details). We considered also the possibility that other photochemical pathways were operational in the generation of radicals, e.g. the direct excitation of catalysts **B** and **C** followed by SET activation of the substrates or the excitation of DHP **1a**. We therefore conducted the model reaction using substrates **1a**, **1b**, and **1c** under illumination by green light ($\lambda_{\text{max}} = 520 \text{ nm}$), a wavelength which cannot be absorbed by either the catalysts or the substrates (Figure 2d). All of these experiments led to the formation of product **3a**, albeit with moderate yields (entries 8–10). Collectively, these results are congruent with the EDA complex excitation being responsible of radical generation. Further control experiments established that light and the tetrachlorophthalimide-based catalysts were essential for reactivity (entries 11 and 12, respectively).

We then evaluated the scope of the Giese addition protocol using different radical precursors and electron-poor olefins (Figure 3a). In contrast to other methods,¹¹ there is no need for stoichiometric amounts of additional reagents (e.g., bases, reductants, hydrogen-atom donors) or for photoredox catalysts. The tetrachlorophthalimide-based catalyst **B** was used for the EDA complex activation of DHP radical precursors, while the mesitylene catalyst **C** proved more effective for alkylsilicates and organotrifluoroborates. Primary (product **3b**), secondary (**3a** and **3c**), tertiary (**3d**), and α -heteroatom (**3e** and **3f**) radicals were generated efficiently and trapped with vinyl sulfone **2a** in moderate to good yields. Other olefins could be used to intercept the photogenerated radicals, including dimethyl fumarate (products **3g** and **3h**), acrylonitrile (**3i**), cyclopentenone (**3j**), and dibenzoyl ethylene (**3k** and **3l**). The use of bis(phenylsulfonyl)ethene **2b** as the radical trap led to an addition–elimination sequence affording the vinylation products **4a** and **4b** in good yields (Figure 3b). A list of unsuccessful and moderately reactive substrates is reported in Figure S6 of the SI. The process could be readily performed on a synthetically significant scale (5 mmol). For example, the reaction of *tert*-butyl trifluoroborate and **2a** offered product **3d** in 52% yield (0.59 g).

Mechanistically, we propose that the Giese reaction proceeds via a redox-neutral catalytic cycle (Figure 3c). Excitation of the EDA complex formed between the acceptor catalyst **B** or **C** and the electron-rich substrate **1** would generate the alkyl radical **II** along with the catalyst radical anion **I** (path detailed in Figure 1b). Interception of **II** by the electron-poor olefin **2** would lead to the reactive electrophilic radical **III**. SET reduction of **III** by the catalyst radical anion **I** would then afford product **3** while closing the

catalytic cycle. The last SET event, which is crucial for catalyst turnover, is thermodynamically feasible on the basis of the redox properties of the radical anion **I** ($E^{\text{red}} = -0.84$ for catalyst **B**) and radical **III** (e.g. $E^{\text{red}} = -0.54$ vs SCE for the radical generated upon radical trap from fumarate).¹² To corroborate this mechanistic proposal, we measured the quantum yield (Φ) of the reaction of **1a** and **2a** catalyzed by **B**, which was as low as 0.04 ($\lambda = 460 \text{ nm}$, using potassium ferrioxalate as the actinometer, see Section D.4 in SI). This result indicates that a radical-chain process is unlikely, confirming the ability of the EDA catalytic donor to turn over and repeatedly trigger radical formation.

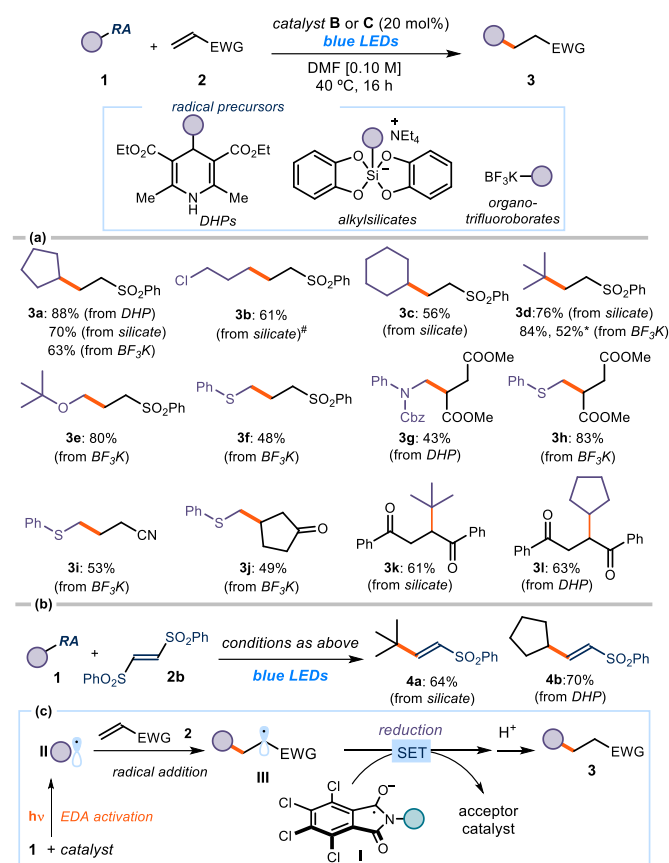


Figure 3. (a) Substrate scope for the Giese reaction catalyzed by EDA acceptors. Reactions performed on a 0.2 mmol scale using 1.5 equiv. of **1**; catalyst **B** was used for DHP substrates, **C** for silicates and trifluoroborates. Yields refer to isolated products **3** (average of two runs per substrate); *using K⁺ as cation of the silicate; *5 mmol scale reaction. (b) Formal radical vinylation. (c) Proposed mechanism.

One of our goals was to identify a general acceptor catalyst suitable for the design of mechanistically distinct radical processes. Specifically, we sought to integrate our EDA complex catalytic platform with a cobalt-based catalytic process. The literature contains a few reports on the use of EDA complexes to generate radicals and feed a metal-based catalytic cycle.¹³ However, to the best of our knowledge, the synergy of EDA catalysis and metal catalysis has not been realized. This idea was successfully implemented by combining the action of the EDA acceptor cat-

alyst **C** and cobaloxime **7**¹⁴ to perform the Heck-type coupling of radical precursors **1** with styrene derivatives **5** (Figure 4a).¹⁵

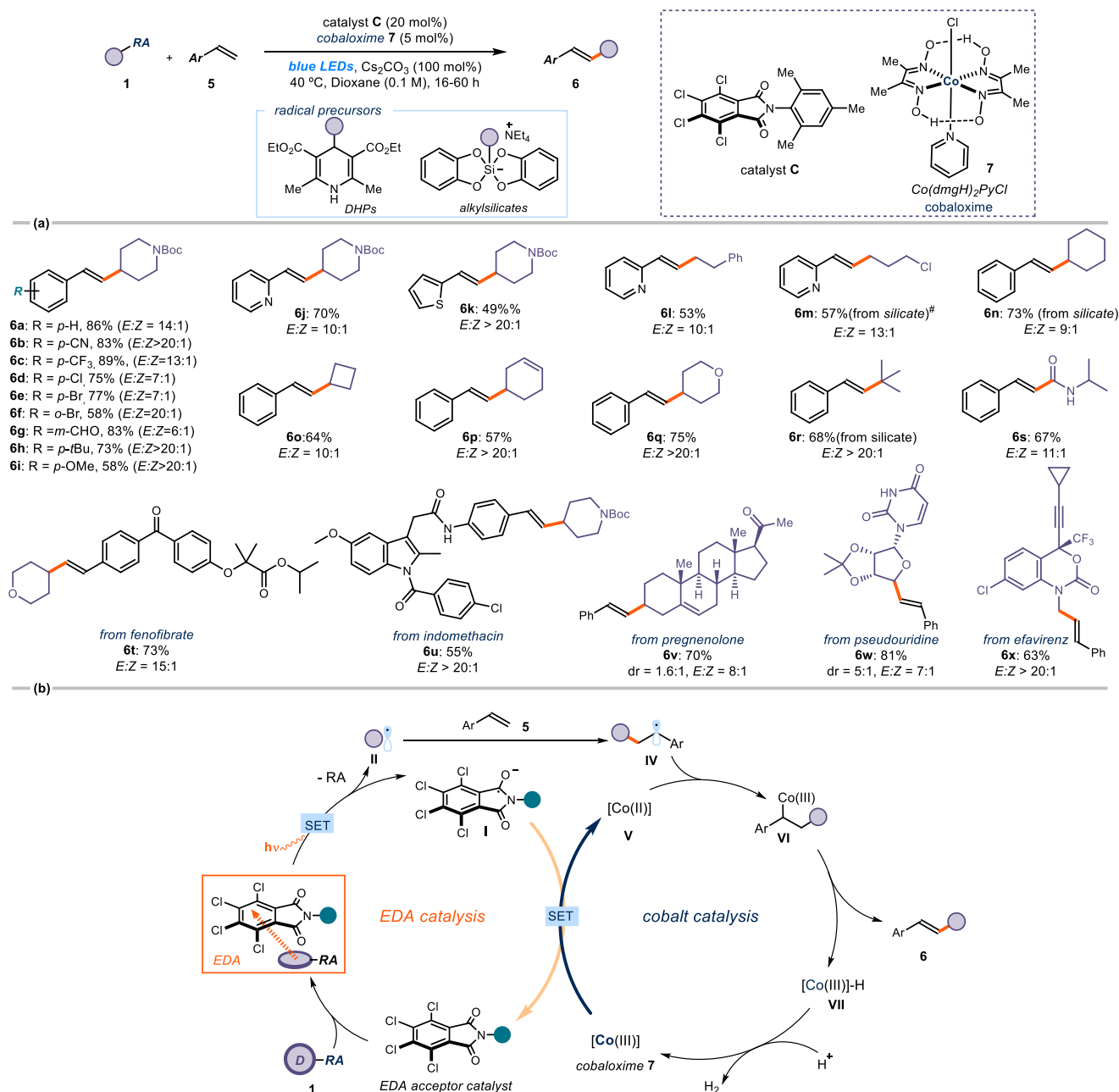


Figure 4. Dual photochemical EDA complex-cobalt catalytic system for the Heck-type reaction. (a) Scope of the Heck-type process; reactions performed on a 0.2 mmol scale using 5 equiv. of **5** and 1 equiv. of **1**. Yields refer to isolated products **6** after purification (average of two runs); *E*/*Z* ratio determined by ¹H NMR analysis of the crude mixture; [#]using K⁺ as cation of the silicate. (b) Proposed mechanism, with the cobalt and EDA catalytic cycles intertwined.

The generality of this dual catalytic protocol, which afforded products **6**, was first investigated with respect to the styrene component. Electron-poor (products **6b–g**) and electron-rich (adducts **6h** and **6i**) styrenes bearing ortho-, meta-, or para-substituents on the aryl ring all reacted smoothly to provide the corresponding disubstituted al-

kene products in moderate to good yields. Vinyl heteroarenes, bearing a pyridine (**6j**) or a thiophene (**6k**) scaffold, were competent substrates. While a large variety of DHP radical precursors were amenable to this Heck-type process, alkyl silicates could also be used. Primary (**6l** and **6m**), secondary (**6n–q**), and tertiary (**6r**) carbon-centered radicals were effectively generated and coupled with vinyl-

pyridine or styrene. A carbamoyl radical could also be used effectively (product **6s**). We also demonstrated that this method is suitable for the direct functionalization of bio-relevant compounds, since we installed the *fenofibrate* (**6t**), *indomethacin* (**6u**), *pregnenolone* (**6v**), *pseudouridine* (**6w**), and *efavirenz* (**6x**) scaffold within the Heck-type products.

The proposed mechanism is depicted in Figure 4b. The photoactivity of the catalytic EDA complex, formed by association of the acceptor catalyst **C** with the electron-rich radical precursor **1**, would lead to the alkyl radical **II** and the catalyst radical anion **I**. Subsequent addition of **II** to styrene would furnish a stable benzylic radical intermediate **IV**. At this juncture, the EDA catalytic cycle would intersect the cobaloxime cycle: the catalyst radical anion **I** would undergo SET oxidation from the Co(III) catalyst **7** ($E^{\text{red}} [\text{Co}^{\text{III}}/\text{Co}^{\text{II}}] = -0.67 \text{ V}$ versus the saturated calomel electrode (SCE) in MeCN)¹⁶ to afford the Co(II) species **V** while turning over the EDA acceptor catalyst. The cobalt-based catalytic cycle would continue with the Co(II) intermediate **V** intercepting the benzylic radical **IV** to form the Co(III) intermediate **VI**, which is known to undergo facile β -hydride eliminations.¹⁷ This step would deliver the alkene product **6** and the Co(III)–H intermediate **VII**, which, upon reaction with either protic sources (e.g. protonated pyridine arising from DHPs) or another molecule of **VII**, would release H_2 ¹⁶ and regenerate the Co(III) catalyst **7**. The quantum yield of the Heck-type reaction leading to product **6a** was as low as 0.01 ($\lambda = 460 \text{ nm}$, details in SI), which is congruent with the proposed dual catalytic cycle.

In summary, we found that tetrachlorophthalimide-based catalysts can act as effective and general acceptors for EDA complex activation. These organocatalysts can activate a variety of radical precursors bearing different redox auxiliaries, including DHPs, silicates, and trifluoroborates, which could not be activated by previous EDA catalytic protocols. Excitation with visible light granted access to alkyl radicals under mild conditions. Importantly, this EDA complex catalytic platform proved flexible enough to promote mechanistically different radical processes, including the first combination with a metal-based catalytic cycle.

ASSOCIATED CONTENT

Supporting Information

Details of experimental procedures and full characterization data and copies of NMR spectra (PDF). The Supporting Information is available free of charge on the ACS Publications website.

AUTHOR INFORMATION

Corresponding Author

*pmelchiorre@iciq.es

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENT

Financial support was provided by Agencia Estatal de Investigación (PID2019-106278GB-I00) and the MCIN/AEI/10.13039/501100011033 (CEX2019-000925-S). W.Z. and S.W. thank the China Scholarship Council for predoctoral fellowships (CSC201908310093 and CSC202006920025).

REFERENCES

- (1) (a) Foster, R. Electron Donor-Acceptor Complexes. *J. Phys. Chem.* **1980**, *84*, 2135–2141. (b) Rosokha, S. V.; Kochi, J. K. Fresh Look at Electron-Transfer Mechanisms via the Donor/Acceptor Bindings in the Critical Encounter Complex. *Acc. Chem. Res.* **2008**, *41*, 641–653.
- (2) Crisenza, G. E. M.; Mazzarella, D.; Melchiorre, P. Synthetic Methods Driven by the Photoactivity of Electron Donor–Acceptor Complexes. *J. Am. Chem. Soc.* **2020**, *142*, 5461–5476.
- (3) Selected applications of stoichiometric EDA complexes: (a) Sankararaman, S.; Haney, W. A.; Kochi, J. K. Annihilation of Aromatic Cation Radicals by Ion-Pair and Radical-Pair Collapse. Unusual Solvent and Salt Effects in the Competition for Aromatic Substitution. *J. Am. Chem. Soc.* **1987**, *109*, 7824–7838. (b) Russell, G. A.; Wang, K. Homolytic Alkylation of Enamines by Electrophilic Radicals. *J. Org. Chem.* **1991**, *56*, 3475–3479. (c) Tobisu, M.; Furukawa, T.; Chatani, N. Visible Light-mediated Direct Arylation of Arenes and Heteroarenes Using Diaryliodonium Salts in the Presence and Absence of a Photocatalyst. *Chem. Lett.* **2013**, *42*, 1203–1205. (d) Kandukuri, S. R.; Bahamonde, A.; Chatterjee, I.; Jurberg, I. D.; Escudero-Adán, E. C.; Melchiorre, P. X-Ray Characterization of an Electron Donor–Acceptor Complex Drives the Photochemical Alkylation of Indoles. *Angew. Chem., Int. Ed.* **2015**, *54*, 1485–1489. (e) Liu, B.; Lim, C.-H.; Miyake, G. M. Visible-Light-Promoted C–S Cross-Coupling via Intermolecular Charge Transfer. *J. Am. Chem. Soc.* **2017**, *139*, 13616–13619. (f) Lubbessmeyer, M.; Mackay, E. G.; Raycroft, M. A. R.; Elfert, J.; Pratt, D. A.; Studer, A. Base-Promoted C–C Bond Activation Enables Radical Allylation with Homoallylic Alcohols. *J. Am. Chem. Soc.* **2020**, *142*, 2609–2616.
- (4) (a) Fu, M.-C.; Shang, R.; Zhao, B.; Wang, B.; Fu, Y. Photocatalytic decarboxylative alkylations mediated by triphenylphosphine and sodium iodide. *Science* **2019**, *363*, 1429–1434. (b) Bosque, I.; Bach, T. 3-Acetoxyquinuclidine as Catalyst in Electron Donor–Acceptor Complex-Mediated Reactions Triggered by Visible Light. *ACS Catal.* **2019**, *9*, 9103–9109. (c) McClain, E. J.; Monos, T. M.; Mori, M.; Beatty, J. W.; Stephenson, C. R. J. Design and Implementation of a Catalytic Electron Donor–Acceptor Complex Platform for Radical Trifluoromethylation and Alkylation. *ACS Catal.* **2020**, *10*, 12636–12641. (d) Fu, M.-C.; Wang, J. X.; Shang, R. Triphenylphosphine-Catalyzed Alkylative Iododecarboxylation with Lithium Iodide under Visible Light. *Org. Lett.* **2020**, *22*, 8572–8577. For photochemical enzymatic processes that use co-factors as catalytic donors in EDA complexes, see: (e) Emmanuel, M. A.; Greenberg, N. R.; Oblinsky, D. G.; Hyster, T. K., Accessing non-natural reactivity by irradiating nicotinamide-dependent enzymes with light. *Nature* **2016**, *540*, 414–417. (f) Page, C. G.; Cooper, S. J.; DeHovitz, J. S.; Oblinsky, D. G.; Biegasiewicz, K. F.; Antropow, A. H.; Armbrust, K. W.; Ellis, J. M.; Hamann, L. G.; Horn, E. J.; Oberg, K. M.; Scholes, G. D.; Hyster, T. K., Quaternary Charge-Transfer Complex Enables Photoenzymatic Intermolecular Hydroalkylation of Olefins. *J. Am. Chem. Soc.* **2021**, *143*, 97–102. (g) Liu, C.; Shen, N.; Shang, R., Photocatalytic decarboxylative

alkylation of silyl enol ether and enamide with N-(acyloxy)phthalimide using ammonium iodide. *Org. Chem. Front.* **2021**, *8*, 4166–4170. (h) Wang, G.-Z.; Fu, M.-C.; Zhao, B.; Shang, R., Photocatalytic decarboxylative alkylations of C(sp³)-H and C(sp²)-H bonds enabled by ammonium iodide in amide solvent. *Sci. China: Chem.* **2021**, *64*, 439–444. (i) Fuse, H.; Irie, Y.; Fukui, M.; Kobori, Y.; Kato, K.; Yamakata, A.; Higashi, M.; Mitsunuma, H.; Kanai, M., Identification of a Self-Photosensitizing Hydrogen Atom Transfer Organocatalyst System. *J. Am. Chem. Soc.* **2022**, *144*, 6566–6574.

(5) (a) de Pedro Beato, E.; Spinnato, D.; Zhou, W.; Melchiorre, P. A General Organocatalytic System for Electron Donor–Acceptor Complex Photoactivation and Its Use in Radical Processes. *J. Am. Chem. Soc.* **2021**, *143*, 12304–12314. (b) Arceo, E.; Jurberg, I. D.; Álvarez-Fernández, A.; Melchiorre, P. Photochemical activity of a key donor–acceptor complex can drive stereoselective catalytic α -alkylation of aldehydes. *Nat. Chem.* **2013**, *5*, 750–756. (c) Woźniak, Ł.; Murphy, J. J.; Melchiorre, P. Photo-organocatalytic Enantioselective Perfluoroalkylation of β -Ketoesters. *J. Am. Chem. Soc.* **2015**, *137*, 5678–5681. (d) Bahamonde, A.; Melchiorre, P. Mechanism of the Stereoselective α -Alkylation of Aldehydes Driven by the Photochemical Activity of Enamines. *J. Am. Chem. Soc.* **2016**, *138*, 8019–8030.

(6) (a) Morack, T.; Mück-Lichtenfeld, C.; Gilmour, R. Bioinspired Radical Stetter Reaction: Radical Umpolung Enabled by Ion-Pair Photocatalysis. *Angew. Chem., Int. Ed.* **2019**, *58*, 1208–1212. (b) Aramaki, Y.; Imaizumi, N.; Hotta, M.; Kumagai, J.; Ooi, T., Exploiting single-electron transfer in Lewis pairs for catalytic bond-forming reactions. *Chem. Sci.* **2020**, *11*, 4305–4311. (c) Runemark, A.; Sundén, S. Aerobic Oxidative EDA Catalysis: Synthesis of Tetrahydroquinolines Using an Organocatalytic EDA Active Acceptor. *J. Org. Chem.* **2022**, *87*, 1457–1469.

(7) (a) Li, Y.; Xu, R.; Chen, Y., Donor–Acceptor Complex Enables Alkoxy Radical Generation for Metal-Free C(sp³)–C(sp³) Cleavage and Allylation/Alkenylation. *Angew. Chem., Int. Ed.* **2017**, *56*, 12619–12623. (b) Marcaurrelle, L. A.; Molander, G. A., Photoredox-mediated hydroalkylation and hydroarylation of functionalized olefins for DNA-encoded library synthesis. *Chem. Sci.* **2021**, *12*, 12036–12045. (c) Elkhaila, M.; Elbaum, M. B.; Chenoweth, D. M.; Molander, G. A., Solid-Phase Photochemical Decarboxylative Hydroalkylation of Peptides. *Org. Lett.* **2021**, *23*, 8219–8223.

(8) Selected applications of tetrachlorophthalides as redox auxiliaries for EDA complex formation: (a) Candish, L.; Teders, M.; Glorius, F., Transition-Metal-Free, Visible-Light-Enabled Decarboxylative Borylation of Aryl N-Hydroxyphthalimide Esters. *J. Am. Chem. Soc.* **2017**, *139*, 7440–7443. (b) Li, Y.; Zhang, J.; Li, D.; Chen, Y., Metal-Free C(sp³)-H Allylation via Aryl Carboxyl Radicals Enabled by Donor–Acceptor Complex. *Org. Lett.* **2018**, *20*, 3296–3299. (c) Le Saux, E.; Zanini, M.; Melchiorre, P. Photochemical Organocatalytic Benzoylation of Allylic C–H Bonds. *J. Am. Chem. Soc.* **2022**, *144*, 1113–1118. See also Ref. 4a.

(9) Corcé, V.; Chamoreau, L.-M.; Derat, E.; Goddard, J.-P.; Ollivier, C.; Fensterbank, L., Silicates as Latent Alkyl Radical Precursors: Visible-Light Photocatalytic Oxidation of Hypervalent Bis-Catecholato Silicon Compounds. *Angew. Chem., Int. Ed.* **2015**, *54*, 11414–11418.

(10) (a) Duan, K.; Yan, X.; Liu, Y.; Li, Z., Recent Progress in the Radical Chemistry of Alkylborates and Alkylboronates. *Adv. Synth. Catal.* **2018**, *360*, 2781–2795. (b) Corcé, V.; Ollivier, C.; Fensterbank, L., Boron, silicon, nitrogen and sulfur-based contemporary precursors for the generation of alkyl radicals by single electron transfer and their synthetic utilization. *Chem. Soc. Rev.* **2022**, *51*, 1470–1510.

(11) Gant Kanegusuku, A. L.; Roizen, J. L., Recent Advances in Photoredox-Mediated Radical Conjugate Addition Reactions: An Expanding Toolkit for the Giese Reaction. *Angew. Chem., Int. Ed.* **2021**, *60*, 21116–21149.

(12) van Leeuwen, T.; Buzzetti, L.; Perego, L. A.; Melchiorre, P., A Redox-Active Nickel Complex that Acts as an Electron Mediator in Photochemical Giese Reactions. *Angew. Chem., Int. Ed.* **2019**, *58*, 4953–4957.

(13) (a) Kammer, L. M.; Badir, S. O.; Hu, R.-M.; Molander, G. A., Photoactive electron donor–acceptor complex platform for Ni-mediated C(sp³)–C(sp²) bond formation. *Chem. Sci.* **2021**, *12*, 5450–5457. (b) Li, R.-H.; Zhao, Y.-L.; Shang, Q.-K.; Geng, Y.; Wang, X.-L.; Su, Z.-M.; Li, G.-F.; Guan, W., Photocatalytic C(sp³)-O/N Cross-Couplings by NiI–PPh₃/CuBr Cooperative Catalysis: Computational Design and Experimental Verification. *ACS Catal.* **2021**, *11*, 6633–6642.

(14) For selected applications of cobaloxime catalysis, see: (a) Sun, X.; Chen, J.; Ritter, T., Catalytic dehydrogenative decarboxyolefination of carboxylic acids. *Nat. Chem.* **2018**, *10*, 1229–1233. (b) U. Dighe, S.; Juliá, F.; Luridiana, A.; Douglas, J. J.; Leonori, D., A photochemical dehydrogenative strategy for aniline synthesis. *Nature* **2020**, *584*, 75–81. (c) Zhao, H.; McMillan, A. J.; Constantin, T.; Mykura, R. C.; Juliá, F.; Leonori, D., Merging Halogen-Atom Transfer (XAT) and Cobalt Catalysis to Override E₂-Selectivity in the Elimination of Alkyl Halides: A Mild Route toward contra-Thermodynamic Olefins. *J. Am. Chem. Soc.* **2021**, *143*, 14806–14813. (d) Zhou, M.-J.; Zhang, L.; Liu, G.; Xu, C.; Huang, Z., Site-Selective Acceptorless Dehydrogenation of Aliphatics Enabled by Organophotoredox/Cobalt Dual Catalysis. *J. Am. Chem. Soc.* **2021**, *143*, 16470–16485.

(15) A similar Heck-type process was realized by combining a photoredox catalyst and cobaloxime chemistry: Cao, H.; Jiang, H.; Feng, H.; Kwan, J. M. C.; Liu, X.; Wu, J., Photo-induced Decarboxylative Heck-Type Coupling of Unactivated Aliphatic Acids and Terminal Alkenes in the Absence of Sacrificial Hydrogen Acceptors. *J. Am. Chem. Soc.* **2018**, *140*, 16360–16367.

(16) Dempsey, J. L.; Brunschwig, B. S.; Winkler, J. R.; Gray, H. B., Hydrogen Evolution Catalyzed by Cobaloximes. *Acc. Chem. Res.* **2009**, *42*, 1995–2004.

(17) Gridnev, A. A.; Ittel, S. D. Catalytic chain transfer in free-radical polymerizations. *Chem. Rev.* **2001**, *101*, 3611–3660.

Proposed graphical abstract:

