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Iminyl-Radical-Promoted C−C Bond Cleavage/Heck-Like Coupling via Dual Cobaloxime and Photoredox Catalysis

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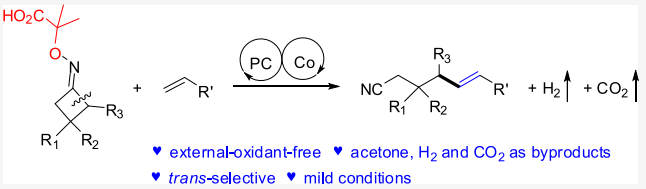
ABSTRACT: We report herein an unprecedented protocol for radical−olefin coupling of α-imino-oxy acids and alkenes for the synthesis of alkene-containing nitriles via synergistic photoredox and cobaloxime catalysis. With visible-light irradiation, the transformation provides a variety of corresponding alkene-containing nitriles under mild reaction conditions. The C−C bond cleavage/Heck-like coupling reaction could generate *E*-selective coupling products with excellent chemo- and stereo-selectivity. This iminyl-radical-mediated reaction is external-oxidant-free, exhibits wide functional-group compatibility, and occurs with the extrusion of acetone, H_2, and CO_2.



INTRODUCTION

The development of methods for C−C bond formation via radical-mediated reactions is a longstanding endeavor in organic synthesis.[1] The Heck-type reaction[2] via cobalt-catalyzed radical−olefin coupling has been acknowledged as a powerful approach for the synthesis of functionalized alkenes which, in general, are achieved via the addition/elimination sequence of organocobalt intermediates.[3−8] A series of alkyl radical precursors, such as alkyl halides,[3,4] carboxylic acids,[5] alkanes,[6] and aldehydes,[7] have been used as effective coupling partners. Of these reports, Oshima and co-workers first described an intermolecular Heck-type coupling of alkyl halides and styrenes via cobalt−phosphine catalysis (Scheme 1a).[3] Furthermore, Carreira et al. developed a cobaloxime-catalyzed intramolecular Heck-type reaction of alkyl iodides with pendant olefins upon visible-light irradiation (Scheme 1a).[4] Carboxylic acids and alkanes have also been employed as efficient alkyl radical precursors, via dual cobalt and photoredox catalysis, providing the olefination[9] and Heck-type products[5,6] (Scheme 1b). Very recently, our group reported a radical cyclization of aldehydes with pendant alkenes via synergistic photoredox, cobaloxime, and amine catalysis (Scheme 1c).[7] Note that powerful photoredox catalysts are essential for the generation of alkyl radicals, and external oxidants were not required in these examples.[5−7] In spite of these significant advances, the development of new cobalt-catalyzed radical−olefin reactions with different alkyl radical precursors to meet various synthetic demands is still of great interest.

With the merge of cobalt catalysis and photoredox organocatalysis, we have recently developed an iminyl-radical-mediated cyclization method for the synthesis of alkene-containing dihydropyrroles.[8c] Note that the photoredox decarboxylation of α-imino-oxy acids via single-electron oxidation could readily give iminyl radicals,[10,11] especially the seminal works from Leonori's group and Studer's lab,[10a−f] thus enabling diverse transformations. On the other hand, Shi[12] and Xiao[13a] developed Cu-catalyzed and photoredox-catalyzed reductive cleavage of cyclobutanone oxime esters and Heck-like coupling with alkenes, respectively. Inspired by these reports,[8c,11−13] we wondered whether the dual catalytic system could be harnessed as a novel radical−olefin coupling strategy to obtain a variety of nitriles with pendant alkenes by an oxidative iminyl-radical formation process. Herein, we describe an iminyl-radical-mediated selective C−C bond cleavage/Heck-like coupling of α-imino-oxy acids and alkenes via synergistic cobaloxime and photoredox catalysis (Scheme 1d).

RESULTS AND DISCUSSION

We commenced our study by exploring the radical−olefin coupling of α-imino-oxy acid **1a** and styrene (**2a**) via synergistic photoredox and cobaloxime catalysis (Table 1). After extensive screening of reaction parameters (see Tables S1, S2 in the Supporting Information for details), we were delighted to find that with 5 mol % Mes−Acr^+ (*N*-methyl-9-mesityl acridinium perchlorate) and 10 mol % Co(dmgH) ($(dmgH_2)Cl_2$ as the synergistic catalyst system, K_3PO_4 (20 mol %) as the base catalyst, and mesitylene (0.1 M) as the solvent, this radical reaction readily furnished the desired product **3a** in 71% yield (*E*/Z > 20:1) upon irradiation by household blue LEDs (22 W) at 35 °C. Notably, the control experiments revealed that the dual photoredox and cobaloxime catalyst system, light, and base were all essential for the success of the reaction.

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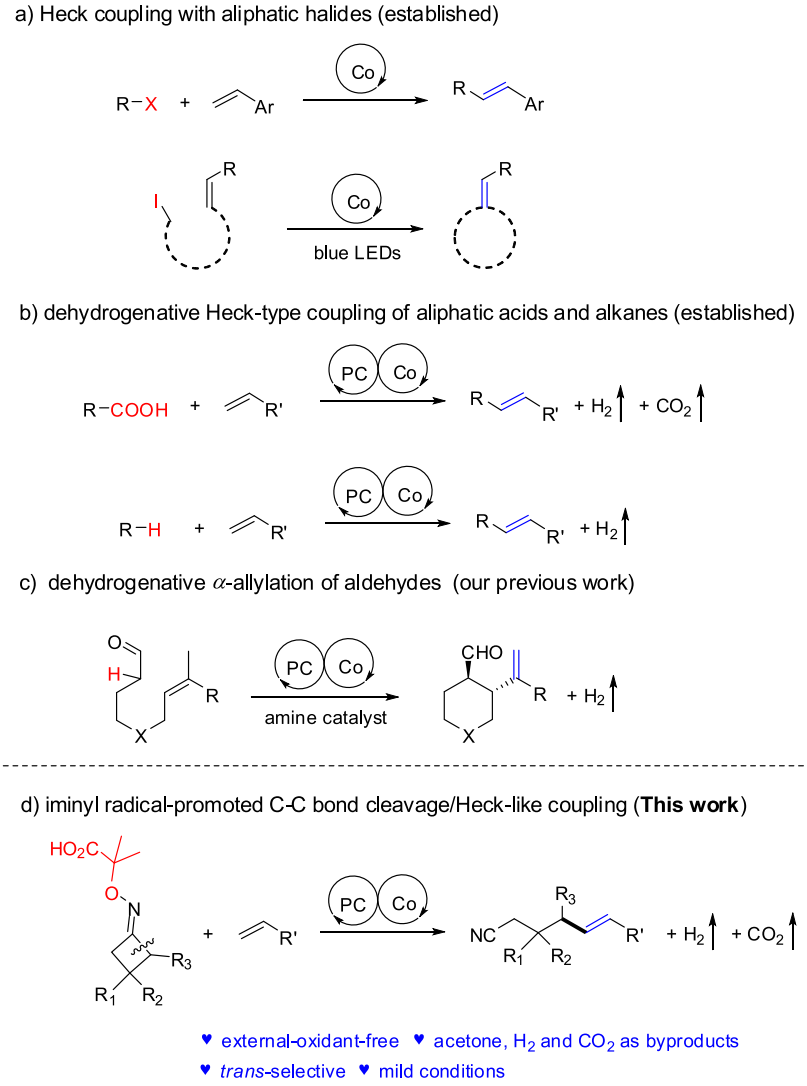
Scheme 1. Co-Catalyzed Radical−Olefin Coupling for C−C Bond Formation



With the optimized reaction conditions in hand, the scope of the reaction was evaluated. Using styrene (**2a**) as the model coupling partner, we first examined the reaction of a variety of α-imino-oxy acids. As shown in Table 2, the substrates with various R_1, R_2, and R_3 groups proved to be suitable for the reaction, affording the expected ring-opening/radical−olefin coupling products in moderate to good yields (**3a−k**). The substrates bearing a range of functional groups such as aromatic substituents, esters, ethers, and amides on the four-membered ring were all accommodated well, furnishing the corresponding alkene-containing nitriles **3a−i** with excellent E/Z selectivity. Note that the reaction could be extended to the coupling of secondary alkyl radicals with an alkene partner, offering **3j** and **3k** with excellent stereoselectivity. To demonstrate the synthetic utility of the reaction, a gram-scale reaction (1 g of **1a**) was conducted. The reaction still proceeded very well, furnishing the desired product **3a** in 62% yield.

Next, we went on to apply this strategy to the coupling of α-imino-oxy acid **1a** with a variety of alkenes. As depicted in Table 3, broad generality and functional-group compatibility were observed. An array of activated alkenes could serve as effective coupling partners in this photocatalytic reaction (**4a−p**). Modulation of the aryl ring with a variety of substituents was well-tolerated, regardless of the electronic nature of the aryl skeleton, furnishing the desired alkenes with excellent E/Z selectivity (**4a−g**). In the examples of **4i** and **4k−l**, sulfur-containing heterocycles and alkynes are compatible with the reaction conditions, and the radical−olefin coupling can be achieved in acceptable yields. Pleasingly, this protocol could enable access to complex molecules with natural-product-like cores (**4n−o**). However, the β-H elimination of organocobalt(III) intermediates is not a regioselective process, and it provided both the internal and terminal alkenes (**4p-a** and **4p-b**). Unfortunately, the reaction of unactivated and internal alkenes failed to give the desired products.

Control experiments were conducted to gain more mechanistic insights into the aforementioned transformation (Scheme 2). In the presence of a radical scavenger, 2,2,6,6-tetramethylpiperidin-1-oxyl (TEMPO), only a trace amount of the corresponding product **3a** was produced under standard reaction conditions. As expected, the TEMPO-adduct **5** was achieved (Scheme 2, eq 1). On the other hand, we observed that compound **1l** can undergo ring-opening/olefination cascade to give compound **6** as the product (eq 2).

On the basis of our observations and previous reports,[3−8] a proposed mechanism is depicted in Scheme 3. The initial step

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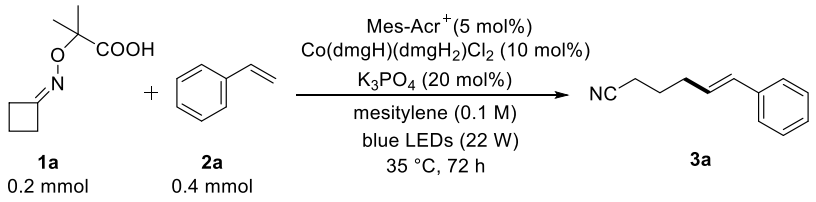
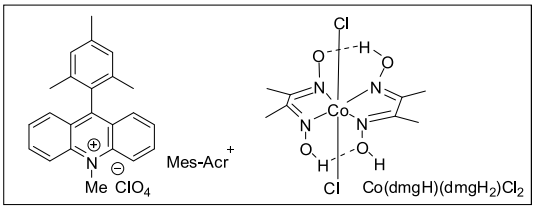
Table 1. Optimization of Reaction Conditions[a]



entry	variation	yield (%)[b]
1	No	71
2	K_2CO_3, Li_3PO_4, or Na_3PO_4 instead of K_3PO_4	<5
3	K_3PO_4 (10 mol %) as base	51
4	K_3PO_4 (50 mol %) as base	48
5	$Ir(ppy)_3$, $Ru(bpy)_3Cl_2 \cdot 6H_2O$, or 4CzIPN instead of Mes−Acr^+	<5
6	$Co(dmgH)_2PyCl$ instead of $Co(dmgH)(dmgH_2)Cl_2$	63
7	$Co(dmgH)_2$(4-CN-Py)Cl instead of $Co(dmgH)(dmgH_2)Cl_2$	43
8	$Co(dmgH)_2$(4-OMe-Py)Cl instead of $Co(dmgH)(dmgH_2)Cl_2$	53
9	$Co(dmgH)_2$(4-CF_3-Py)Cl instead of $Co(dmgH)(dmgH_2)Cl_2$	52
10	without K_3PO_4	<5
11	without photocatalyst, Co catalyst, or light	0

entry	variation	yield (%)[b]
1	no	71
2	K_2CO_3, Li_3PO_4, or Na_3PO_4 instead of K_3PO_4	< 5
3	K_3PO_4 (10 mol%) as base	51
4	K_3PO_4 (50 mol%) as base	48
5	$Ir(ppy)_3$, $Ru(bpy)_3Cl_2 \bullet 6H_2O$, or 4CzIPN instead of $Mes\text{-}Acr^+$	< 5
6	$Co(dmgH)_2PyCl$ instead of $Co(dmgH)(dmgH_2)Cl_2$	63
7	$Co(dmgH)_2$(4-CN-Py)Cl instead of $Co(dmgH)(dmgH_2)Cl_2$	43
8	$Co(dmgH)_2$(4-OMe-Py)Cl instead of $Co(dmgH)(dmgH_2)Cl_2$	53
9	$Co(dmgH)_2$(4-CF_3-Py)Cl instead of $Co(dmgH)(dmgH_2)Cl_2$	52
10	without K_3PO_4	< 5
11	without photocatalyst, or Co catalyst, or light	0



[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.40 mmol), Mes−Acr^+ (5 mol %), $Co(dmgH)(dmgH_2)Cl_2$ (10 mol %), and K_3PO_4 (20 mol %) in mesitylene (2 mL, used without dehydration), 35 °C, household blue LEDs (22 W), 72 h. [b]Isolated yield.

involves single oxidation of the carboxylate derived from *α*-imino-oxy acid **1** and base by Mes−Acr^+*, generating a carboxyl radical **A1**, and subsequently, giving an iminyl radical **A2** with loss of CO_2 and acetone, followed by ring-opening to deliver an alkyl radical **B**. The reduced photocatalyst Mes−$Acr^\bullet$ is single-electron-oxidized by a Co^{III} complex to close the photoredox catalytic cycle, as well as to generate a Co^{II} complex. Meanwhile, the radical addition of alkyl radical **B** to alkene **2** occurs to give the alkyl radical **C**, which can be captured by the Co^{II} complex to form an organocobalt (III) complex **D**. The critical *β*-H elimination step readily occurs to furnish the alkene-containing nitriles **3** or **4** and a Co^{III}−H intermediate. The reaction of the Co^{III}−H complex with a proton leads to H_2 extrusion and completion of the cobalt catalytic cycle.

CONCLUSIONS

In summary, we have developed an iminyl-radical-mediated ring-opening/radical−olefin coupling method for the synthesis of alkene-containing nitriles via an oxidative decarboxylation process. With the merge of cobalt catalysis and photoredox organocatalysis, the reaction is external-oxidant-free and occurs under mild conditions with extrusion of acetone, H_2, and CO_2. This method exhibits wide functional-group compatibility and enables the synthesis of a range of desired products with excellent *E*/*Z* selectivity.

EXPERIMENTAL SECTION

General Information. ^1H NMR spectra were recorded on a 400 or 600 MHz (100 or 150 MHz for ^{13}C NMR) Agilent NMR spectrometer with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. Chemical shifts were reported in parts per million (ppm, *δ*

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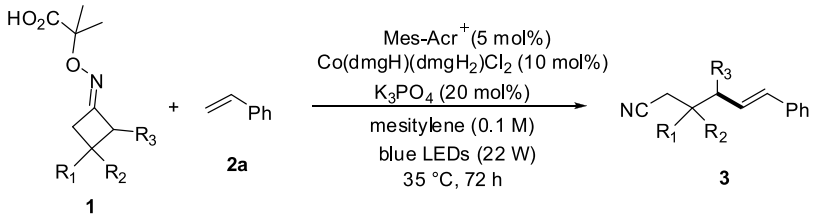
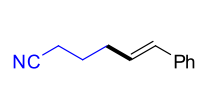
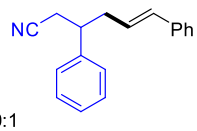
Table 2. Substrate Scope of α-Imino-oxy Acids[a,b]

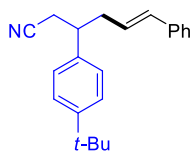




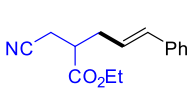
3a, 71% (62%[b]), *E*/*Z* > 20:1



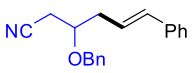
3b, 62%, *E*/*Z* > 20:1



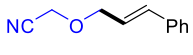
3c, 54%, *E*/*Z* > 20:1



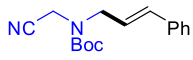
3d, 76%, *E*/*Z* > 20:1



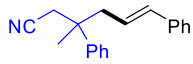
3e, 55%, *E*/*Z* = 9:1



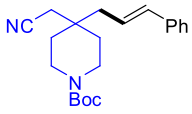
3f, 72%, *E*/*Z* > 20:1



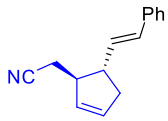
3g, 63%, *E*/*Z* > 20:1



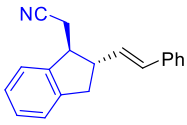
3h, 56%, *E*/*Z* > 20:1



3i, 66%, *E*/*Z* > 20:1



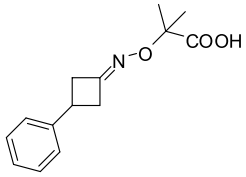
3j, 46%, *E*/*Z* > 20:1 and d.r. > 20:1



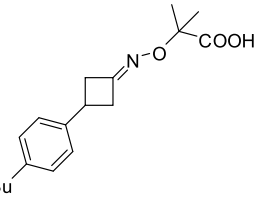
3k, 39%, *E*/*Z* > 20:1 and d.r. > 20:1

[a]Reaction conditions: **1** (0.20 mmol), **2a** (0.40 mmol), Mes−Acr$^+$ (5 mol %), Co(dmgH) (dmgH$_2$)Cl$_2$ (10 mol %), and K$_3$PO$_4$ (20 mol %) in mesitylene (2 mL, used without dehydration), 35 °C, household blue LEDs (22 W), 72 h. Isolated yield; *E*/Z and diastereoselectivity (d.r.) ratios, as determined by crude ^{1}H NMR spectroscopy. [b]**1a** (1 g, 5.84 mmol).

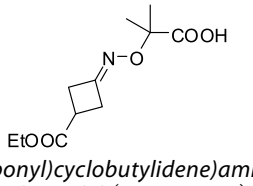
scale) downfield from TMS at 0.00 ppm and referenced to CDCl$_3$ at 7.26 ppm (for ^{1}H NMR) or 77.16 ppm (for ^{13}C NMR). High-resolution mass spectroscopy (HRMS) data of products were collected using an Agilent 6540 Q-TOF (ESI) mass spectrometer. Fourier-transform infrared (FT-IR) spectra were recorded on a Varian 1000 FT-IR, ν_{max} in cm^{-1}. Melting points were measured using SGW X-4B and values are uncorrected. For details on the light source and the material of the irradiation vessel, see the Supporting Information. All commercially available reagents and solvents were used as received unless otherwise specified. Starting materials α-imino-oxy acids **1** were prepared according to the literature procedures.[10d,f,14,15] The photocatalyst Mes−Acr$^+$ClO$_4^-$ was purchased. All cobalt catalysts were prepared according to the literature procedures.[5,8b,16]



*2-Methyl-2-(((3-phenylcyclobutylidene)amino)oxy)propanoic Acid (**1b**).* White solid (870 mg, 88%); m.p. 90−93 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38−7.31 (m, 2H), 7.29−7.26 (m, 2H), 7.25−7.22 (m, 1H), 3.69−3.57 (m, 1H), 3.51−3.34 (m, 2H), 3.13−3.00 (m, 2H), 1.54 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 177.9, 158.3, 143.8, 128.6, 126.7, 126.4, 81.0, 39.7, 38.9, 32.9, 24.21, 24.18; FT-IR (thin film, KBr): ν (cm^{-1}): 2958, 1708, 1495, 1402, 1162, 967, 615; HRMS (ESI) *m*/*z*: [M + Na]$^+$ calcd for C$_{14}$H$_{17}$N O$_3$Na, 270.1101; found, 270.1105.



*2-(((3-(4-(tert-Butyl)phenyl)cyclobutylidene)amino)oxy)-2-methylpropanoic Acid (**1c**).* White solid (1.21 g, 74%); m.p. 175−177 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.22 (d, *J* = 8.3 Hz, 2H), 3.65−3.55 (m, 1H), 3.51−3.30 (m, 2H), 3.06 (ddt, *J* = 16.4, 6.8, 3.5 Hz, 2H), 1.55 (s, 6H), 1.33 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$): δ 179.2, 158.0, 149.6, 140.9, 126.2, 125.5, 80.8, 39.8, 39.0, 34.5, 32.5, 31.4, 24.22, 24.17; FT-IR (thin film, KBr): ν (cm^{-1}): 2915, 1721, 1384, 1208, 951, 772; HRMS (ESI) *m*/*z*: [M + Na]$^+$ calcd for C$_{18}$H$_{25}$N O$_3$Na, 326.1727; found, 326.1718.



*2-(((3-(Ethoxycarbonyl)cyclobutylidene)amino)oxy)-2-methylpropanoic Acid (**1d**).* White solid (948 mg, 78%); m.p. 88−90 °C; ^{1}H NMR (600 MHz, CDCl$_3$): δ 4.18 (q, *J* = 7.1 Hz, 2H), 3.28−3.11 (m, 5H), 1.51 (s, 3H), 1.50 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C{^{1}H}NMR (100 MHz, CDCl$_3$): δ 178.2, 173.8, 156.0, 81.0, 61.1, 35.6, 35.1, 31.4, 24.2, 24.0, 14.1; FT-IR (thin film, KBr): ν (cm^{-1}): 2990, 1712, 1445, 1178, 1006, 9316, 878,728; HRMS (ESI) *m*/*z*: [M + Na]$^+$ calcd for C$_{11}$H$_{17}$N O$_5$Na, 266.0999; found, 266.0996.

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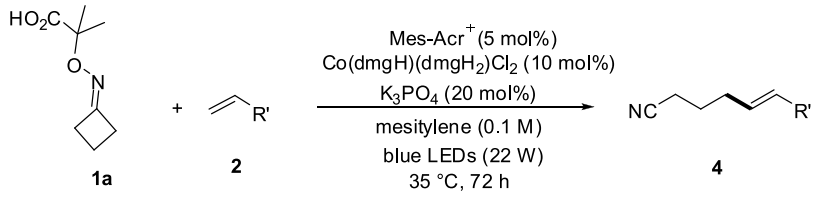
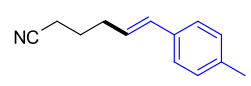
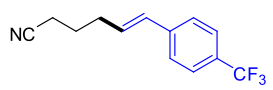
Table 3. Substrate Scope of Alkenes[a,b]

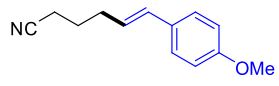




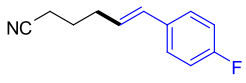
4a, 58%, *E*/*Z* > 20:1



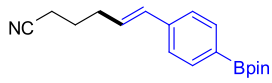
4b, 69%, *E*/*Z* > 20:1



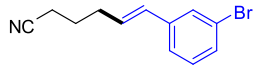
4c, 65%, *E*/*Z* > 20:1



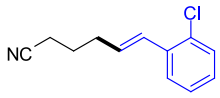
4d, 66%, *E*/*Z* > 20:1



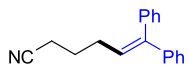
4e, 54%,, *E*/*Z* > 20:1



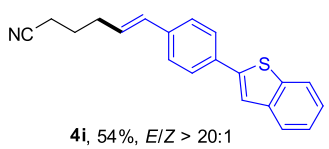
4f, 65%, *E*/*Z* > 20:1



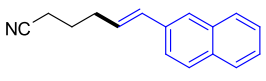
4g, 49%, *E*/*Z* > 20:1



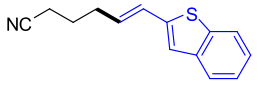
4h, 55%



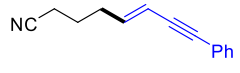
4i, 54%, *E*/*Z* > 20:1



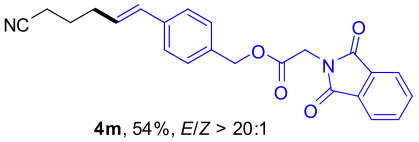
4j, 68%, *E*/*Z* > 20:1



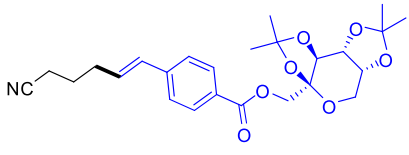
4k, 72%, *E*/*Z* > 20:1



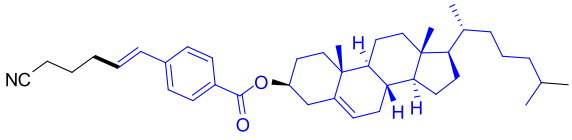
4l, 42%, *E*/*Z* = 2:1



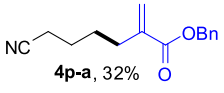
4m, 54%, *E*/*Z* > 20:1



4n, 57%, *E*/*Z* > 20:1
from *Diacetonefructose*

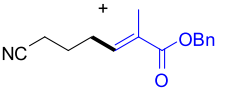


4o, 58%, *E*/*Z* > 20:1
from *Cholesterol*

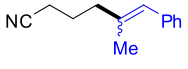


4p-a, 32%

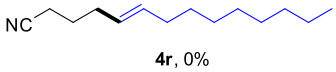
+



4p-b, 43%, *E*/*Z* > 20:1

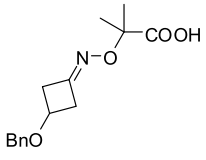


4q, trace[b]



4r, 0%

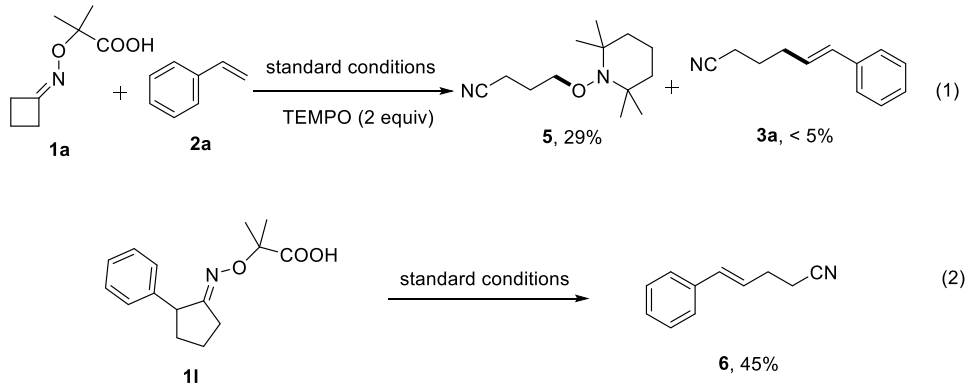
[a]Reaction conditions: **1** (0.20 mmol), **2** (0.40 mmol), Mes−Acr$^+$ (5 mol %), Co(dmgH) (dmgH$_2$)Cl$_2$ (10 mol %), and K_3PO_4 (20 mol %) in mesitylene (2 mL, used without dehydration), 35 °C, household blue LEDs (22 W), 72 h. Isolated yield; *E*/Z and diastereoselectivity (d.r.) ratios determined by crude ^{1}H NMR spectroscopy. [b]Detected by crude ^{1}H NMR spectroscopy and HRMS.



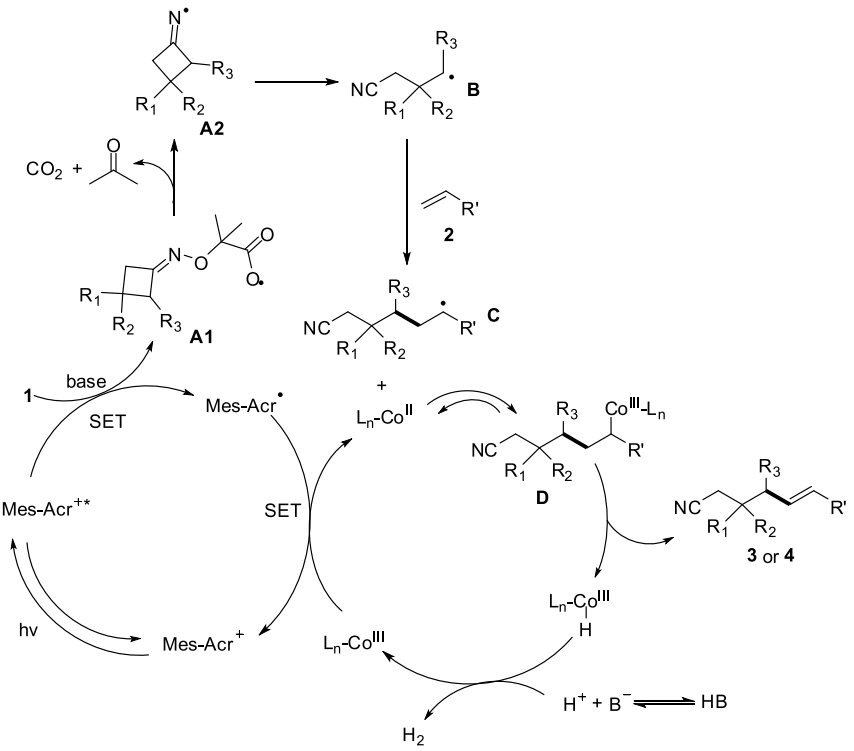
*2-(((3-(Benzyloxy)cyclobutylidene)amino)oxy)-2-methylpropanoic Acid (**1e**).* White solid (1.3 g, 95%); m.p. 97−98 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44−7.29 (m, 5H), 4.48 (s, 2H), 4.30−4.15 (m, 1H), 3.34−3.06 (m, 2H), 3.05−2.84 (m, 2H), 1.50 (s, 3H), 1.49 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 178.3, 154.9, 137.4, 128.6, 128.0, 127.9, 80.9, 71.0, 67.2, 40.2, 39.6, 24.2, 24.1; FT-IR (thin film, KBr): ν (cm^{-1}): 2990, 1728, 1392, 1354, 1260, 1163, 1002, 914; HRMS (ESI) *m*/*z*: $[M + Na]^+$ calcd for $C_{15}H_{19}N\,O_4Na$, 300.1206; found, 300.1204.

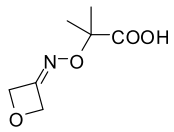
https://dx.doi.org/10.1021/acs.joc.0c02834
J. Org. Chem. 2021, 86, 2929−2940

Scheme 2. Control Experiments

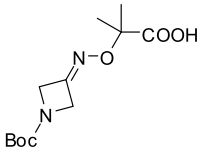


Scheme 3. Proposed Mechanism

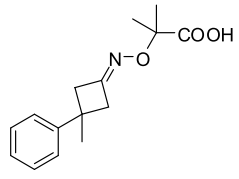




*2-Methyl-2-((oxetan-3-ylideneamino)oxy)propanoic Acid (**1f**).* White solid (369 mg, 72%); m.p. 86–89 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 5.34–5.27 (m, 4H), 1.52 (s, 6H); $^{13}C\{^1H\}$NMR (150 MHz, $CDCl_3$): δ 178.7, 154.0, 81.4, 79.0, 78.9, 23.9; FT-IR (thin film, KBr): ν (cm^{-1}): 2991, 1696, 1475, 1364, 977, 739; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_7H_{11}NO_4Na$, 196.0580; found, 196.0578.



*2-(((1-(tert-Butoxycarbonyl)azetidin-3-ylidene)amino)oxy)-2-methylpropanoic Acid (**1g**).* White solid (479 mg, 63%); m.p. 145–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 4.67–4.59 (m, 4H), 1.51 (s, 6H), 1.46 (s, 9H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 178.6, 156.3, 149.0, 81.5, 80.8, 58.3, 28.3, 23.9; FT-IR (thin film, KBr): ν (cm^{-1}): 2977, 1694, 1460, 1166, 1125, 943, 766; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{12}H_{20}N_2O_5Na$, 295.1264; found, 295.1268.



*2-Methyl-2-(((3-methyl-3-phenylcyclobutylidene)amino)oxy)-propanoic Acid (**1h**).* White solid (814 mg, 78%); m.p. 112–114 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 9.94 (s, 1H), 7.35 (t, J = 7.4 Hz, 2H), 7.26–7.20 (m, 3H), 3.37–3.21 (m, 2H), 3.14–3.07 (m, 1H), 2.99 (d, J = 16.0 Hz, 1H), 1.55 (s, 3H), 1.54 (s, 3H), 1.53 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 179.7, 156.5, 148.7, 128.5, 126.1, 125.2, 80.7, 44.9, 44.3, 38.0, 30.9, 24.2, 24.1; FT-IR (thin film, KBr): ν (cm^{-1}): 2986, 1716, 1593, 1488, 1168, 971; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{19}NO_3Na$, 284.1257; found, 284.1261.

https://dx.doi.org/10.1021/acs.joc.0c02834
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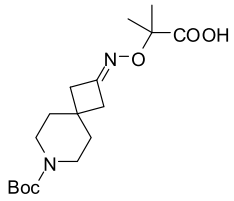
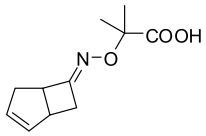
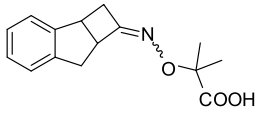


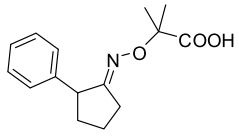
*2-(((7-(tert-Butoxycarbonyl)-7-azaspiro[3.5]nonan-2-ylidene)amino)oxy)-2-methylpropanoic Acid (**1i**).* White solid (1.36 g, 95%); m.p. 92−93 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.47−3.24 (m, 4H), 2.70−2.64 (m, 4H), 1.60 (t, J = 5.5 Hz, 4H), 1.50 (s, 6H), 1.45 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 177.8, 156.9, 154.8, 80.8, 79.6, 41.8, 41.2, 36.4, 33.3, 28.4, 24.1; FT-IR (thin film, KBr): ν (cm^{-1}): 2980, 1684, 1417, 1363, 1236, 1165, 973, 867; HRMS (ESI) m/z: $[M + H]^+$ calcd for $C_{17}H_{29}N_2O_5$, 341.2071; found, 341.2066.



*(E)-2-((Bicyclo[3.2.0]hept-3-en-6-ylideneamino)oxy)-2-methylpropanoic Acid (**1j**).* White solid (962 mg, 92%); m.p. 86−87 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.86−5.71 (m, 2H), 3.81−3.71 (m, 1H), 3.45−3.36 (m, 1H), 3.09 (dd, J = 17.5, 8.3 Hz, 1H), 2.72−2.60 (m, 3H), 1.48 (s, 6H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 179.8, 166.1, 132.5, 132.0, 81.0, 46.8, 41.1, 38.5, 37.8, 24.3, 24.0; FT-IR (thin film, KBr): ν (cm^{-1}): 2918, 1705, 1468, 1180, 1021, 965, 714; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_{15}N\,O_3Na$, 232.0944; found, 232.0930.

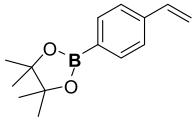


*2-((Bicyclo[4.2.0]octan-7-ylideneamino)oxy)-2-methylpropanoic Acid (**1k**).* White solid (983 mg, 76%); m.p. 130−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 10.09 (s, 1H), 7.21−7.09 (m, 4H), 4.02−3.71 (m, 2H), 3.42 (d, J = 17.1 Hz, 0.43H), 3.29 (ddd, J = 17.5, 11.4, 9.0 Hz, 1H), 3.21−3.08 (m, 1.57 H), 2.78−2.53 (m, 1H), 1.45/1.37 (s, 3H), 1.42/1.36 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 179.5, 163.4/161.9, 144.9/144.9, 143.5/143.4, 127.3, 127.2, 127.1, 125.2/125.0, 125.0/124.8, 80.8/80.8, 47.6/47.4, 40.8/39.6, 39.8/39.6, 37.2/35.0, 24.4/24.3, 24.1/23.8; FT-IR (thin film, KBr): ν (cm^{-1}):2918, 1708, 1403, 1364, 1162, 1174, 970, 827; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{17}N\,O_3Na$, 282.1101; found, 282.1106.

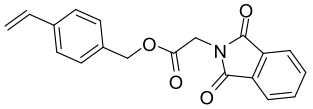


*(E)-2-Methyl-2-(((2-phenylcyclopentylidene)amino)oxy)-propanoic Acid (**1l**).* White solid (1.0 g, 62%); m.p. 147−149 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (t, J = 7.4 Hz, 2H), 7.25−7.17 (m, 3H), 3.83−3.74 (m, 1H), 2.79−2.69 (m, 1H), 2.66−2.51 (m, 1H), 2.34−2.24 (m, 1H), 2.05−1.73 (m, 3H), 1.48 (s, 3H), 1.45 (s, 3H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 176.8, 170.7, 140.9, 128.5, 127.8, 126.8, 81.2, 49.5, 34.9, 28.7, 24.4, 24.3, 22.7; FT-IR (thin film, KBr): ν (cm^{-1}): 2917, 1717, 1615, 1520, 1305, 1174, 970, 827; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{19}N\,O_3Na$, 284.1257; found, 284.1260.

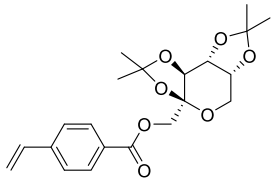
Procedures for the Preparation of Alkenes.



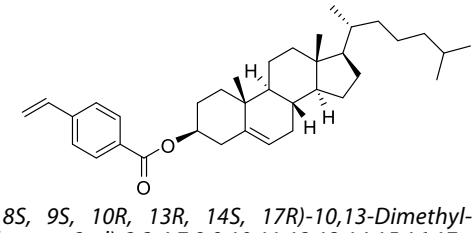
*4,4,5,5-Tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (**2e**).*[5] 4-Vinylphenyl boronic acid (10 mmol) was added to a mixture of 2,3-dimethylbutane-2,3-diol (20 mmol) and anhydrous $MgSO_4$ (10 mmol) in Et_2O (0.2 M) at room temperature and stirred for 12 h. Next, the reaction mixture was filtered and concentrated on a rotary evaporator. The residue was purified by flash column chromatography on silica gel (petroleum/ethyl acetate = 20:1) to give the product as a white solid (1.98 g, 86%); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87 (d, J = 8.1 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 6.78 (dd, J = 17.6, 10.9 Hz, 1H), 5.86 (dd, J = 17.6, 0.8 Hz, 1H), 5.34 (dd, J = 10.9, 0.8 Hz, 1H), 1.39 (s, 12H); $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ 140.3, 136.9, 135.1, 125.6, 114.9, 83.7, 24.9; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.90 (s).



*4-(3-(5-Phenyl-3,4-dihydro-2H-pyrrol-2-yl)prop-1-en-1-yl) Benzyl 2-(1,3-dioxoisoindolin-2-yl)acetate (**2m**).* In a dry round-bottomed flask, 2-(1,3-dioxoisoindolin-2-yl) acetic acid (1.25 g, 5 mmol) was weighed and DMF (25 mL) was added. K_2CO_3 (1.04 g, 6.5 mmol) and KI (1.25 g, 6.5 mmol) were then added and stirred. To this stirring suspension, 4-vinylbenzyl chloride (839 mg, 5.5 mmol) was added and stirred for 12 h at room temperature. After the reaction was complete, EtOAc (50 mL) and water (30 mL) were added to the mixture and extracted and washed three times with water. The organic layer was collected and dried. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1). White solid (75%, 1.94 g); m.p. 105−106 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94−7.80 (m, 2H), 7.80−7.65 (m, 2H), 7.39 (d, J = 8.1 Hz, 2H), 7.29 (d, J = 8.1 Hz, 2H), 6.70 (dd, J = 17.6, 10.9 Hz, 1H), 5.75 (d, J = 17.6 Hz, 1H), 5.26 (d, J = 10.9 Hz, 1H), 5.18 (s, 2H), 4.48 (s, 2H); $^{13}C\{^1H\}$NMR (100 MHz, $CDCl_3$): δ 167.4, 167.2, 137.9, 136.3, 134.5, 134.3, 132.0, 128.6, 126.5, 123.6, 114.5, 67.3, 39.0; FT-IR (thin film, KBr): ν (cm^{-1}): 2923, 1849, 1544, 1344, 905; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{19}H_{15}NO_4Na$, 344.0893; found, 344.0891.



*((3aS, 5aR, 8aR, 8bS)-2,2,7,7-Tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4′,5′-d]pyran-**3a**-yl)methyl 4-Vinylbenzoate (**2n**).* 4-Vinylbenzoic acid (20 mmol) was added to a mixture of diacetonefructose (20 mmol) and DMAP (20 mmol) in CH_2Cl_2 (0.2 M) at room temperature. *N*,*N*′-Diisopropylcarbodiimide (22 mmol) was then added and stirred overnight. The residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1). White solid (89%, 6.9 g); m.p. 111−112 °C; ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.01 (d, J = 8.4 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 6.73 (dd, J = 17.6, 10.9 Hz, 1H), 5.84 (d, J = 17.6 Hz, 1H), 5.37 (d, J = 11.0 Hz, 1H), 4.67 (d, J = 11.8 Hz, 1H), 4.63 (dd, J = 7.9, 2.6 Hz, 1H), 4.46 (d, J = 2.6 Hz, 1H), 4.31 (d, J = 11.8 Hz, 1H), 4.24 (dd, J = 7.9, 1.1 Hz, 1H), 3.94 (dd, J = 13.0, 1.8 Hz, 1H), 3.78 (d, J = 12.9 Hz, 1H), 1.53 (s, 3H), 1.45 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 165.6, 142.1, 135.9, 130.0, 129.0, 126.1, 116.6, 109.1, 108.8, 101.7, 265, 25.9, 25.5, 24.0; FT-IR (thin film, KBr): ν (cm^{-1}):2924, 1721, 1605, 1461, 1376, 1070, 860; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{21}H_{26}\,O_7Na$, 413.1571; found, 413.1576.



*(3R, 8S, 9S, 10R, 13R, 14S, 17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-Vinylbenzoate (**2o**).* 4-Vinylbenzoic acid (20 mmol) was added to a mixture of cholesterol (20 mmol), DMAP (20 mmol), and *N*,*N*′-dicyclohexylcarbodiimide (20 mmol) in CH_2Cl_2 (0.2 M) at room temperature and then stirred

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overnight. Next, the reaction mixture was filtered, concentrated on a rotary evaporator, and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1) to give a white solid (88%, 5.66 g). m.p. 172−173 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.99 (d, J = 8.3 Hz, 2H), 7.45 (d, J = 8.3 Hz, 2H), 6.75 (dd, J = 17.6, 10.9 Hz, 1H), 5.86 (d, J = 17.6 Hz, 1H), 5.42 (d, J = 4.0 Hz, 1H), 5.37 (d, J = 10.9 Hz, 1H), 4.99−4.76 (m, 1H), 2.46 (d, J = 7.7 Hz, 2H), 2.09−1.95 (m, 3H), 1.94−1.66 (m, 3H), 1.65−1.43 (m, 8H), 1.35 (ddd, J = 19.9, 15.5, 8.0 Hz, 4H), 1.26−1.12 (m, 5H), 1.07 (s, 3H), 0.99 (dd, J = 10.5, 5.8 Hz, 3H), 0.92 (d, J = 6.5 Hz, 3H), 0.87 (dd, J = 6.6, 1.6 Hz, 6H), 0.69 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 165.7, 141.7, 139.6, 136.1, 130.0, 129.8, 126.0, 122.7, 116.3, 74.5, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.9, 31.9, 28.2, 28.0, 27.9, 24.3, 23.8, 22.8, 22.5, 21.0, 19.4, 18.7, 11.8; FT-IR (thin film, KBr): ν (cm^{-1}):2879, 1710, 1615, 1468, 1274, 1120, 856; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{36}H_{52}O_2Na$, 539.3860; found, 539.3857.

General Procedure for the Synthesis of Alkene-Containing Nitriles. To a 10 mL oven-dried round-bottomed Schlenk bottle equipped with a magnetic stir bar, the corresponding oxime acid (0.2 mmol, 1.0 equiv.), olefin (0.24 mmol, 1.2 equiv., if solid), Mes−Acr$^+$$ClO_4^-$ (4.2 mg, 0.01 mmol, 5 mol %), Co(dmgH) (dmgH$_2$)Cl$_2$ (7.2 mg, 0.02 mmol, 10 mol %), and K_3PO_4 (8.4 mg, 0.04 mmol, 20 mol %) were added. The corresponding olefin (0.4 mmol, 2.0 equiv., if liquid) and mesitylene (2 mL) were then added under an argon atmosphere. The resulting mixture was sealed and then subjected to the freeze−pump−thaw cycle three times. After that, the reaction mixture was placed under a 22 W blue LED and irradiated for 72 h. The temperature was maintained at 35 °C when the LED light was on. After the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel.

Gram-Scale Synthesis of Compound 3a. To a 100 mL oven-dried round-bottomed Schlenk bottle equipped with a magnetic stir bar, **1a** (1 g, 5.84 mmol, 1.0 equiv.), Mes−Acr$^+$$ClO_4^-$ (122 mg, 0.29 mmol, 5 mol %), Co(dmgH) (dmgH$_2$)Cl$_2$ (209 mg, 0.58 mmol, 10 mol %), and K_3PO_4 (246 mg, 1.16 mmol, 20 mol %) were added. Styrene (11.6 mmol, 2.0 equiv.) and mesitylene (40 mL) were then added under an argon atmosphere. The resulting mixture was sealed and then subjected to the freeze−pump−thaw cycle three times. After that, the reaction was placed under a 22 W blue LED and irradiated for 96 h. The temperature was maintained at 35 °C when the LED light was on. After the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure, and the residue was purified by flash column chromatography on silica to give the desired product **3a** in 62% yield (0.62 g).

*(E)-6-Phenylhex-5-enenitrile (**3a**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and styrene (42 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 24 mg of the title compound (yellow oil; 71% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.23 (t, J = 7.2 Hz, 1H), 6.47 (d, J = 15.8 Hz, 1H), 6.14 (dt, J = 15.7, 7.1 Hz, 1H), 2.43−2.34 (m, 4H), 1.85 (p, J = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 137.1, 132.0, 128.6, 127.6, 127.3, 126.0, 119.5, 31.6, 25.0, 16.4; FT-IR (thin film, KBr): ν (cm^{-1}): 2918, 1652, 1541, 1308, 1457, 743; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{12}H_{14}N$, 172.1121; found, 172.1122.

*(E)-3,6-Diphenylhex-5-enenitrile (**3b**).* Following the general procedure with 2-methyl-2-(((3-phenylcyclobutylidene)amino)oxy)-propanoic acid (49 mg, 0.2 mmol) and styrene (42 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 31 mg of the title compound (yellow oil; 62% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (t, J = 7.6 Hz, 2H), 7.32−7.28 (m, 6H), 7.27−7.25 (m, 1H), 7.24−7.18 (m, 1H), 6.48 (d, J = 15.8 Hz, 1H), 6.11−6.01 (m, 1H), 3.13 (p, J = 7.1 Hz, 1H), 2.75−2.65 (m, 4H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 141.2, 136.9, 133.2, 128.9, 128.5, 127.5, 127.4, 127.1, 126.1, 126.0, 118.4, 42.1, 38.4, 23.9; FT-IR (thin film, KBr): ν (cm^{-1}):2929, 1598, 1575, 1455, 752; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{18}H_{17}NNa$, 270.1253; found, 270.1249.

*(E)-3-(4-(tert-Butyl)phenyl)-6-phenylhex-5-enenitrile (**3c**).* Following the general procedure with 2-(((3-(4-(*tert*-butyl)phenyl)-cyclobutylidene)amino)oxy)-2-methyl propanoic acid (65 mg, 0.2 mmol) and styrene (42 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 33 mg of the title compound (yellow oil; 54% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, J = 8.2 Hz, 2H), 7.33−7.27 (m, 4H), 7.24−7.17 (m, 3H), 6.49 (d, J = 15.8 Hz, 1H), 6.15−6.02 (m, 1H), 3.11 (p, J = 6.9 Hz, 1H), 2.73−2.60 (m, 4H), 1.33 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 150.3, 138.2, 137.0, 133.1, 128.5, 127.4, 126.7, 126.3, 126.1, 125.8, 118.6, 41.5, 38.4, 34.5, 31.3, 23.9; FT-IR (thin film, KBr): ν (cm^{-1}): 2932, 1605, 1578, 1455, 753; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{22}H_{25}NNa$, 326.1879; found, 326.1872.

*Ethyl (E)-2-(cyanomethyl)-5-phenylpent-4-enoate (**3d**).* Following the general procedure with 2-(((3-(ethoxycarbonyl)cyclobutylidene)-amino)oxy)-2-methyl propanoic acid (53 mg, 0.2 mmol) and styrene (42 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 37 mg of the title compound (yellow oil; 76% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36−7.29 (m, 4H), 7.24 (t, J = 7.1 Hz, 1H), 6.52 (d, J = 15.7 Hz, 1H), 6.11−6.03 (m, 1H), 4.26−4.17 (m, 2H), 2.89 (p, J = 6.6 Hz, 1H), 2.74−2.59 (m, 4H), 1.32−1.26 (m, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 171.9, 136.6, 134.2, 128.6, 127.7, 126.2, 124.0, 117.7, 61.5, 41.4, 34.4, 18.6, 14.2; FT-IR (thin film, KBr): ν (cm^{-1}): 2921, 1729, 1493, 1364, 1183, 967, 742; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{15}H_{17}NO_2Na$, 266.1151; found, 266.1144.

*(E)-3-(Benzyloxy)-6-phenylhex-5-enenitrile (**3e**).* Following the general procedure with 2-(((3-(ethoxycarbonyl)cyclobutylidene)-amino)oxy)-2-methylpropanoic acid (60 mg, 0.2 mmol) and styrene (42 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 30 mg of the title compound (yellow oil; 55% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40−7.29 (m, 9H), 7.26−7.22 (m, 1H), 6.52 (d, J = 15.8 Hz, 1H), 6.18−6.11 (m, 1H), 4.66 (s, 2H), 3.87−3.80 (m, 1H), 2.67−2.54 (m, 4H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 137.4, 136.9, 134.0, 128.6, 128.5, 128.0, 127.8, 127.5, 126.2, 123.8, 117.4, 74.2, 71.8, 37.3, 22.7; FT-IR (thin film, KBr): ν (cm^{-1}): 2926, 1596, 1501, 1454, 1260, 753; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{19}H_{19}NONa$, 300.1359; found, 300.1350.

*2-(Cinnamyloxy)acetonitrile (**3f**).* Following the general procedure with 2-methyl-2-((oxetan-3-ylideneamino)oxy)propanoic acid (40 mg, 0.2 mmol) and styrene (42 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 25 mg of the title compound (yellow oil; 72% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.41 (d, J = 7.5 Hz, 2H), 7.35 (t, J = 7.6 Hz, 2H), 7.29 (t, J = 7.3 Hz, 1H), 6.70 (d, J = 15.9 Hz, 1H), 6.23 (dt, J = 15.9, 6.4 Hz, 1H), 4.31 (dd, J = 6.4, 0.9 Hz, 2H), 4.29 (s, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 135.9, 135.3, 128.7, 128.3, 126.7, 123.0, 116.0, 71.7, 54.6; FT-IR (thin film, KBr): ν (cm^{-1}): 2934, 1696, 1475, 1364, 1224, 1047, 977, 739; HRMS (ESI) m/z: [M + H]$^+$ calcd for $C_{11}H_{12}NO$, 174.0913; found, 174.0910.

*tert-Butyl cinnamyl(cyanomethyl)carbamate (**3g**).* Following the general procedure with 2-methyl-2-((oxetan-3-ylideneamino)oxy)-propanoic acid (54 mg, 0.2 mmol) and styrene (42 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 34 mg of the title compound (yellow oil; 63% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.37 (d, J = 7.5 Hz, 2H), 7.32 (t, J = 7.5 Hz, 2H), 7.25 (t, J = 7.2 Hz, 1H), 6.56 (d, J = 15.4 Hz, 1H), 6.16−6.04 (m, 1H), 4.22−4.03 (m, 4H), 1.50 (s, 9H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 156.0, 136.0, 128.6, 128.1, 126.5, 123.2, 115.9, 81.0, 49.2, 34.4, 28.2; FT-IR (thin film, KBr): ν (cm^{-1}): 2977, 1698, 1398, 1366, 1244, 1158, 966, 745; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{16}H_{20}N_2O_2Na$, 295.1417; found, 295.1421.

*(E)-3-Methyl-3,6-diphenylhex-5-enenitrile (**3h**).* Following the general procedure with 2-methyl-2-(((3-methyl-3-phenylcyclobutylidene)amino)oxy)propanoic acid (57 mg, 0.2 mmol) and styrene (42 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 29 mg of the title compound (yellow oil; 56% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40−7.32 (m, 5H), 7.32−7.27 (m, 3H), 7.24−7.19 (m, 2H), 6.46 (d, J = 15.7 Hz, 1H), 5.85 (dt, J = 15.2, 7.4 Hz, 1H), 2.76−2.71 (m, 1H),

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2.70 (s, 2H), 2.68−2.63 (m, 1H), 1.55 (s, 3H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 144.0, 137.0, 134.0, 128.7, 128.5, 127.4, 127.0, 126.1, 125.6, 124.7, 118.1, 49.4, 45.1, 30.2, 25.7; FT-IR (thin film, KBr): ν (cm^{-1}): 2924, 1494, 1443, 968, 746, 695; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{19}H_{20}N$, 262.1590; found, 262.1599.

*tert-Butyl 4-Cinnamyl-4-(cyanomethyl)piperidine-1-carboxylate (**3i**).* Following the general procedure with 2-(((7-(*tert*-butoxycarbonyl)-7-azaspiro[3.5]nonan-2-ylidene)amino)oxy)-2-methylpropanoic acid (68 mg, 0.2 mmol) and styrene (42 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 45 mg of the title compound (yellow oil; 66% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.1 Hz, 1H), 6.54 (d, *J* = 15.7 Hz, 1H), 6.13 (dt, *J* = 15.6, 7.7 Hz, 1H), 3.51−3.39 (m, 4H), 2.43 (d, *J* = 7.7 Hz, 2H), 2.38 (s, 2H), 1.62 (d, *J* = 8.1 Hz, 2H), 1.57 (dd, *J* = 7.6, 4.2 Hz, 2H), 1.46 (s, 9H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 154.7, 136.7, 134.9, 128.6, 127.6, 126.2, 123.1, 117.5, 79.8, 40.0, 35.9, 35.2, 34.1, 28.4, 26.0; FT-IR (thin film, KBr): ν (cm^{-1}): 2927, 1681, 1417, 1363, 1248, 1151, 963, 751; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{21}H_{28}N_2O_2Na$, 363.2043; found, 363.2033.

*(E)-2-(5-Styrylcyclopent-2-en-1-yl)acetonitrile (**3j**).* Following the general procedure with (*E*)-2-((bicyclo[3.2.0]hept-3-en-6-ylideneamino)oxy)-2-methylpropanoic acid (42 mg, 0.2 mmol) and styrene (42 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 19 mg of the title compound (yellow oil; 46% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.36 (d, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 6.46 (d, *J* = 15.7 Hz, 1H), 6.22 (dd, *J* = 15.7, 8.0 Hz, 1H), 5.95−5.90 (m, 1H), 5.75−5.70 (m, 1H), 2.90−2.83 (m, 1H), 2.77−2.68 (m, 2H), 2.57 (dd, *J* = 16.8, 5.2 Hz, 1H), 2.40 (dd, *J* = 16.8, 7.0 Hz, 1H), 2.38−2.31 (m, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 136.9, 132.7, 131.9, 130.8, 130.7, 128.6, 127.4, 126.1, 118.6, 48.6, 48.3, 39.4, 21.7; FT-IR (thin film, KBr): ν (cm^{-1}): 2921, 1599, 1491, 1447, 966, 746; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{15}H_{15}NNa$, 232.1097; found, 232.1089.

*(E)-2-(2-Styryl-2,3-dihydro-1H-inden-1-yl)acetonitrile (**3k**).* Following the general procedure with (*E*)-2-((bicyclo[3.2.0]hept-3-en-6-ylideneamino)oxy)-2-methylpropanoic acid (56.4 mg, 0.2 mmol) and styrene (42 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 20 mg of the title compound (yellow oil; 39% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.40−7.37 (m, 2H), 7.36−7.34 (m, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.26−7.22 (m, 4H), 6.57 (d, *J* = 15.8 Hz, 1H), 6.29 (dd, *J* = 15.7, 8.7 Hz, 1H), 3.28 (dd, *J* = 14.0, 6.2 Hz, 1H), 3.19 (dd, *J* = 15.1, 7.3 Hz, 1H), 3.00−2.94 (m, 1H), 2.91 (dd, *J* = 15.2, 9.1 Hz, 1H), 2.84 (dd, *J* = 17.0, 5.0 Hz, 1H), 2.68 (dd, *J* = 17.0, 6.6 Hz, 1H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 142.3, 142.1, 136.7, 132.0, 130.8, 128.6, 127.8, 127.6, 127.0, 126.2, 124.7, 123.2, 118.4, 50.7, 46.9, 38.3, 20.1; FT-IR (thin film, KBr): ν (cm^{-1}): 2918, 1508, 1403, 1364, 1174, 958, 847; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{19}H_{17}NNa$, 282.1253; found, 282.1247.

*(E)-6-(p-Tolyl)hex-5-enenitrile (**4a**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and 1-methyl-4-vinylbenzene (47 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 22 mg of the title compound (yellow oil; 58% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.35 (d, *J* = 7.6 Hz, 2H), 7.22 (d, *J* = 7.9 Hz, 2H), 6.53 (d, *J* = 15.8 Hz, 1H), 6.25−6.14 (m, 1H), 2.49−2.45 (m, 4H), 2.44 (s, 3H), 1.94 (p, *J* = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 137.1, 134.3, 131.9, 129.3, 126.5, 126.0, 119.6, 31.6, 25.1, 21.1, 16.4; FT-IR (thin film, KBr): ν (cm^{-1}): 2919, 1512, 1208, 971, 774; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{15}NNa$, 208.1097; found, 208.1092.

*(E)-6-(4-(Trifluoromethyl)phenyl)hex-5-enenitrile (**4b**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and 1-(trifluoromethyl)-4-vinylbenzene (69 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 33 mg of the title compound (yellow oil; 69% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 2H), 6.50 (d, *J* = 15.8 Hz, 1H), 6.35−6.14 (m, 1H), 2.47−2.37 (m, 4H), 1.87 (p, *J* = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 140.5, 130.8, 130.4, 129.1 (C−F, $2J_{C-F}$ = 32.4 Hz), 126.2, 125.5, 124.2 (C−F, $1J_{C-F}$ = 271.7 Hz), 119.3, 31.7, 24.8, 16.5; ^{19}F NMR (377 MHz, $CDCl_3$): δ −62.50 (s, 3F); FT-IR (thin film, KBr): ν (cm^{-1}):2925, 1614, 1332, 1162, 1065, 968; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{12}F_3NNa$, 262.0814; found, 262.0810.

*(E)-6-(4-Methoxyphenyl)hex-5-enenitrile (**4c**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and 1-methoxy-4-vinylbenzene (54 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 26 mg of the title compound (yellow oil; 65% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.33−7.25 (m, 2H), 6.85 (d, *J* = 8.6 Hz, 2H), 6.40 (d, *J* = 15.8 Hz, 1H), 5.98 (dt, *J* = 15.7, 7.0 Hz, 1H), 3.81 (s, 3H), 2.42−2.28 (m, 4H), 1.83 (p, *J* = 7.1 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 159.0, 131.4, 129.9, 127.2, 125.3, 119.6, 114.0, 55.3, 31.6, 25.1, 16.4; FT-IR (thin film, KBr): ν (cm^{-1}): 2927, 1704, 1647, 1273, 1018, 970, 734; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{13}H_{15}NONa$, 224.1046; found, 224.1044.

*(E)-6-(4-Fluorophenyl)hex-5-enenitrile (**4d**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and 1-fluoro-4-vinylbenzene (48.8 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 25 mg of the title compound (yellow oil; 66% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.30 (dd, *J* = 8.3, 5.6 Hz, 2H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.42 (d, *J* = 15.9 Hz, 1H), 6.10−5.97 (m, 1H), 2.42−2.34 (m, 4H), 1.84 (p, *J* = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 162.1 (C−F, $1J_{C-F}$ = 246.5 Hz), 133.2, 130.8, 127.5 (C−F, $3J_{C-F}$ = 7.9 Hz), 127.3, 119.5, 115.4 (C−F, $2J_{C-F}$ = 21.6 Hz), 31.6, 25.0, 16.4; ^{19}F NMR (377 MHz, $CDCl_3$): δ −114.85−−114.97 (m, 1F); FT-IR (thin film, KBr): ν (cm^{-1}): 2928, 1721, 1501, 1259, 967, 799; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{12}H_{12}FNNa$, 212.0846; found, 212.0840.

*(E)-6-(4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)-hex-5-enenitrile (**4e**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and 4,4,5,5-tetramethyl-2-(4-vinylphenyl)-1,3,2-dioxaborolane (92 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 32 mg of the title compound (yellow oil; 54% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.34 (d, *J* = 8.0 Hz, 2H), 6.47 (d, *J* = 15.8 Hz, 1H), 6.20 (dt, *J* = 15.7, 7.1 Hz, 1H), 2.42−2.36 (m, 4H), 1.85 (p, *J* = 7.2 Hz, 2H), 1.34 (s, 12H); $^{13}C\{^1H\}$NMR (150 MHz, $CDCl_3$): δ 139.7, 135.1, 132.1, 128.7, 125.4, 119.5, 115.4, 83.7, 31.7, 24.9, 24.8, 16.5; ^{11}B NMR (128 MHz, $CDCl_3$): δ 30.7 (br, 1B); FT-IR (thin film, KBr): ν (cm^{-1}): 2927, 1608, 1515, 1360, 1144, 859; HRMS (ESI) *m/z*: $[M + H]^+$ calcd for $C_{18}H_{25}BO_2N$, 298.1973; found, 298.1967.

*(E)-6-(3-Bromophenyl)hex-5-enenitrile (**4f**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and 1-bromo-3-vinylbenzene (73 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 32 mg of the title compound (yellow oil; 65% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.49 (s, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 6.39 (d, *J* = 15.8 Hz, 1H), 6.20−6.07 (m, 1H), 2.42−2.35 (m, 4H), 1.84 (p, *J* = 7.2 Hz, 2H); $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$): δ 139.2, 130.6, 130.2, 130.1, 129.3, 128.9, 124.8, 122.7, 119.4, 31.6, 24.8, 16.5; FT-IR (thin film, KBr): ν (cm^{-1}): 2933, 1590, 1561, 1473, 1422, 1070, 964, 775; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{12}H_{12}{}^{79}BrNNa$, 272.0045; found, 272.0043.

*(E)-6-(2-Chlorophenyl)hex-5-enenitrile (**4g**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and 1-chloro-2-vinylbenzene (55 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 20 mg of the title compound (yellow oil; 49% yield); ^1H NMR (600 MHz, $CDCl_3$): δ 7.49 (d, *J* = 7.7 Hz, 1H), 7.34 (d, *J* = 7.9 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 6.83 (d, *J* = 15.8 Hz, 1H), 6.19−6.08 (m, 1H), 2.48−2.38 (m, 4H), 1.88 (p, *J* = 7.2 Hz, 2H); $^{13}C\{^1H\}$NMR (150 MHz, $CDCl_3$): δ 135.2, 132.7, 130.6, 129.6, 128.34, 128.27, 126.8, 126.7, 119.4, 31.8, 24.9, 16.5; FT-IR (thin film, KBr): ν (cm^{-1}): 2933, 1590, 2562, 1473, 1422, 1010, 994, 775; HRMS (ESI) *m/z*: $[M + Na]^+$ calcd for $C_{12}H_{12}{}^{35}ClNNa$, 228.0550; found, 228.0544.

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*6,6-Diphenylhex-5-enenitrile (**4h**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and ethene-1,1-diyldibenzene (72 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 27 mg of the title compound (yellow oil; 55% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.43−7.36 (m, 2H), 7.36−7.31 (m, 1H), 7.30−7.26 (m, 2H), 7.25−7.21 (m, 3H), 7.16 (d, J = 7.2 Hz, 2H), 6.02 (t, J = 7.4 Hz, 1H), 2.43−2.17 (m, 4H), 1.81 (p, J = 7.3 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 143.8, 142.1, 139.6, 129.7, 128.4, 128.2, 127.23, 127.21, 127.1, 126.6, 119.5, 28.7, 25.7, 16.7; FT-IR (thin film, KBr): ν (cm^{-1}): 2923, 1523, 1423, 1058, 965, 833; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{18}H_{17}NNa$, 270.1253; found, 270.1256.

*(E)-6-(4-(Benzo[b]thiophen-2-yl)phenyl)hex-5-enenitrile (**4i**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and 2-(4-vinylphenyl)benzo[b]thiophene (57 mg, 0.24 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 33 mg of the title compound (yellow solid; m.p. 134−135 °C; 54% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.96−7.90 (m, 2H), 7.55 (d, J = 8.0 Hz, 2H), 7.47 (d, J = 8.0 Hz, 2H), 7.44−7.38 (m, 3H), 6.54 (d, J = 15.8 Hz, 1H), 6.28−6.11 (m, 1H), 2.47−2.39 (m, 4H), 1.88 (p, J = 7.1 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 140.7, 137.8, 137.7, 136.4, 135.0, 131.6, 128.9, 128.0, 126.4, 124.4, 124.3, 123.3, 122.94, 122.87, 119.5, 31.7, 25.01, 16.5; FT-IR (thin film, KBr): ν (cm^{-1}): 2923, 1523, 1423, 1058, 965, 833, 731; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{20}H_{17}NNaS$, 326.0974; found, 326.0980.

*(E)-6-(Naphthalen-2-yl)hex-5-enenitrile (**4j**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and 2-vinylnaphthalene (37 mg, 0.24 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 30 mg of the title compound (yellow solid; m.p. 72−73 °C; 68% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.82−7.76 (m, 3H), 7.69 (s, 1H), 7.57 (dd, J = 8.5, 1.5 Hz, 1H), 7.50−7.41 (m, 2H), 6.63 (d, J = 15.8 Hz, 1H), 6.26 (dt, J = 15.7, 7.0 Hz, 1H), 2.49−2.40 (m, 4H), 1.89 (p, J = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 134.6, 133.7, 132.9, 132.2, 128.2, 128.0, 127.9, 127.7, 126.3, 125.82, 125.78, 123.4, 119.5, 31.8, 25.1, 16.5; FT-IR (thin film, KBr): ν (cm^{-1}): 2920, 1735, 1455, 1125, 1016, 974, 751; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{16}H_{15}NNa$, 244.1097; found, 244.1096.

*(E)-6-(Benzo[b]thiophen-2-yl)hex-5-enenitrile (**4k**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and 2-vinylbenzo[b]thiophene (38 mg, 0.24 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 33 mg of the title compound (yellow solid; m.p. 64−65 °C; 72% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.77−7.72 (m, 1H), 7.67 (d, J = 7.3 Hz, 1H), 7.33−7.26 (m, 2H), 7.09 (s, 1H), 6.69 (d, J = 15.6 Hz, 1H), 6.10−6.01 (m, 1H), 2.48−2.36 (m, 4H), 1.86 (p, J = 7.2 Hz, 2H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 142.2, 140.0, 138.6, 130.2, 125.9, 124.6, 124.4, 123.4, 122.1, 122.0, 119.4, 31.5, 24.8, 16.5; FT-IR (thin film, KBr): ν (cm^{-1}): 2926, 1514, 1457, 1220, 954, 758; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{14}H_{13}NNaS$, 250.0661; found, 250.0659.

*(E/Z)-8-Phenyloct-5-en-7-ynenitrile (**4l**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and but-3-en-1-yn-1-ylbenzene (51 mg, 0.4 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 16 mg of the title compound (yellow oil; 42% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.49−7.38 (m, 2H), 7.36−7.27 (m, 3H), 6.15 (dt, J = 14.6, 7.2 Hz, 0.33H), 5.92 (dt, J = 10.7, 7.5 Hz, 0.66H), 5.84−5.75 (m, 1H), 2.56 (q, J = 7.3 Hz, 1H), 2.47−2.30 (m, 3H), 1.89−1.78 (m, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 141.3/140.3, 131.4, 128.33, 128.29, 128.2/128.1, 119.5/119.2, 111.9/111.6, 94.5/88.9, 87.5/85.5, 31.7/29.1, 24.8/24.5, 16.6/16.4; FT-IR (thin film, KBr): ν (cm^{-1}): 2927, 1681, 1418, 1362, 1249, 1096, 961, 733; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{14}H_{13}NNa$, 218.0940; found, 218.0934.

*(E)-4-(5-Cyanopent-1-en-1-yl)benzyl 2-(1,3-Dioxoisoindolin-2-yl)acetate (**4m**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and 4-vinylbenzyl 2-(1,3-dioxoisoindolin-2-yl)acetate (77 mg, 0.24 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 42 mg of the title compound (yellow solid; m.p. 102−104 °C; 54% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.89 (dd, J = 5.1, 3.0 Hz, 2H), 7.75 (dd, J = 5.2, 3.0 Hz, 2H), 7.34 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.1 Hz, 2H), 6.45 (d, J = 15.8 Hz, 1H), 6.20−6.10 (m, 1H), 5.17 (s, 2H), 4.48 (s, 2H), 2.46−2.36 (m, 4H), 1.85 (p, J = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 167.4, 167.2, 137.4, 134.2, 133.9, 132.0, 131.4, 128.7, 128.4, 126.3, 123.6, 119.4, 67.3, 38.9, 31.6, 24.9, 16.4; FT-IR (thin film, KBr): ν (cm^{-1}): 2927, 1714, 1466, 1412, 1275, 1110, 926, 713; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{23}H_{20}N_2O_4Na$, 411.1315; found, 411.1306.

*((3aS, 5aR, 8aR, 8bS)-2,2,7,7-Tetramethyltetrahydro-3aH-bis([1,3]dioxolo)[4,5-b:4′,5′-d]pyran-**3a**-yl)methyl 4-((E)-5-cyanopent-1-en-1-yl)benzoate (**4n**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and ((3a*S*, 5a*R*, 8a*R*, 8b*S*)-2,2,7,7-tetramethyl tetrahydro-3a*H*-bis([1,3]dioxolo)[4,5-b:4′,5′-d]pyran-3**a**-yl)methyl 4-vinylbenzoate (94 mg, 0.24 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 52 mg of the title compound (yellow solid; m.p. 123−124 °C; 57% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 (d, J = 8.2 Hz, 2H), 7.39 (d, J = 8.2 Hz, 2H), 6.49 (d, J = 15.9 Hz, 1H), 6.33−6.21 (m, 1H), 4.68 (d, J = 11.8 Hz, 1H), 4.64 (dd, J = 7.9, 2.4 Hz, 1H), 4.46 (d, J = 2.4 Hz, 1H), 4.31 (d, J = 11.8 Hz, 1H), 4.26 (d, J = 7.9 Hz, 1H), 3.99−3.91 (m, 1H), 3.80 (d, J = 13.0 Hz, 1H), 2.47−2.38 (m, 3H), 1.86 (p, J = 7.2 Hz, 2H), 1.54 (s, 3H), 1.46 (s, 3H), 1.36 (s, 3H), 1.34 (s, 3H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 165.7, 141.7, 131.2, 130.7, 130.1, 129.8, 128.5, 125.9, 119.3, 109.2, 108.8, 101.7, 70.8, 70.5, 70.1, 65.2, 61.3, 31.7, 26.5, 25.9, 25.5, 24.8, 24.0, 16.5; FT-IR (thin film, KBr): ν (cm^{-1}): 2936, 1719, 1606, 1376, 1251, 1201, 976, 731; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{25}H_{31}NO_7Na$, 480.1993; found, 480.1990.

*(2R, 8S, 9S, 10R, 13R, 14S, 17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-2-yl 4-((E)-5-cyanopent-1-en-1-yl)benzoate (**4o**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and (2*R*, 8*S*, 9*S*, 10*R*, 13*R*, 14*S*, 17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradeca hydro-1*H*-cyclopenta[*a*]phenanthren-2-yl 4-vinylbenzoate (124 mg, 0.24 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 68 mg of the title compound (yellow solid; m.p. 164−165 °C; 58% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.97 (d, J = 8.3 Hz, 2H), 7.38 (d, J = 8.3 Hz, 2H), 6.49 (d, J = 15.8 Hz, 1H), 6.34−6.16 (m, 1H), 5.41 (d, J = 4.0 Hz, 1H), 4.93−4.79 (m, 1H), 2.46 (d, J = 7.8 Hz, 2H), 2.43−2.38 (m, 4H), 2.05−1.96 (m, 3H), 1.94−1.89 (m, 1H), 1.88−1.84 (m, 2H), 1.83 (d, J = 7.8 Hz, 1H), 1.77−1.69 (m, 1H), 1.57 (dd, J = 6.2, 4.0 Hz, 2H), 1.55−1.50 (m, 3H), 1.46 (dd, J = 10.1, 4.6 Hz, 2H), 1.38 (s, 1H), 1.35 (d, J = 4.3 Hz, 2H), 1.29 (s, 1H), 1.22−1.18 (m, 2H), 1.15 (d, J = 3.0 Hz, 2H), 1.13−1.10 (m, 2H), 1.06 (s, 3H), 1.03−0.98 (m, 3H), 0.92 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 6.6, 3H), 0.86 (d, J = 6.6, 3H), 0.69 (s, 3H); ^{13}C {^{1}H} NMR (150 MHz, $CDCl_3$): δ 165.7, 141.3, 139.6, 131.3, 130.3, 129.9, 129.5, 125.8, 122.7, 119.3, 74.5, 56.7, 56.1, 50.0, 42.3, 39.7, 39.5, 38.2, 37.0, 36.6, 36.2, 35.8, 31.91, 31.86, 31.7, 28.2, 28.0, 27.9, 24.8, 24.3, 23.8, 22.8, 22.6, 21.0, 19.4, 18.7, 16.5, 11.9; FT-IR (thin film, KBr): ν (cm^{-1}): 2930, 1704, 1606, 1466, 1274, 1109, 970, 760; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{40}H_{57}NO_2Na$, 606.4282; found, 606.4278.

*Benzyl 6-Cyano-2-methylenehexanoate (**4p-a**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and benzyl methacrylate (53 mg, 0.3 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 16 mg of the title compound (yellow oil; 32% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40−7.35 (m, 4H), 7.35−7.31 (m, 1H), 6.24 (s, 1H), 5.59 (s, 1H), 5.20 (d, J = 3.8 Hz, 2H), 2.40−2.32 (m, 4H), 1.71−1.62 (m, 4H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 166.7, 139.6, 135.9, 128.6, 128.2, 128.1, 125.7, 119.5, 66.5, 31.0, 27.5, 24.9, 17.0; FT-IR (thin film, KBr): ν (cm^{-1}): 2918, 1720, 1621, 1364, 1162, 1174, 970, 827; HRMS (ESI) m/z: [M + Na]$^+$ calcd for $C_{15}H_{17}NO_2Na$, 266.1151; found, 266.1144.

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*Benzyl (E)-6-cyano-2-methylhex-2-enoate (**4p-b**).* Following the general procedure with 2-((cyclobutylideneamino)oxy)-2-methylpropanoic acid (34 mg, 0.2 mmol) and benzyl methacrylate (53 mg, 0.3 mmol) and purified using flash chromatography (petroleum ether/EtOAc = 20:1) gave 21 mg of the title compound (yellow oil; 43% yield); ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.40−7.35 (m, 4H), 7.35−7.31 (m, 1H), 6.72 (t, J = 7.4 Hz, 1H), 5.19 (s, 2H), 2.41−2.33 (m, 4H), 1.90 (s, 3H), 1.82 (p, J = 7.2 Hz, 2H); ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$): δ 167.5, 139.3, 136.1, 129.7, 128.5, 128.1, 128.0, 119.1, 66.4, 27.3, 24.35, 16.7, 12.6; FT-IR (thin film, KBr): ν (cm^{-1}): 2918, 1718, 1580, 1364, 1165, 1174, 970, 827; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{15}H_{17}NO_2Na$, 266.1151; found, 266.1156.

*4-((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)butanenitrile (**5**).* Colorless oil; 29% yield (13 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.85 (t, J = 5.8 Hz, 2H), 2.49 (t, J = 7.2 Hz, 2H), 1.94−1.83 (m, 2H), 1.50−1.29 (m, 6H), 1.16 (s, 6H), 1.10 (s, 6H); ^{13}C{^{1}H}NMR (150 MHz, $CDCl_3$): δ 119.7, 73.6, 59.8, 39.6, 33.1, 25.1, 20.1, 14.5; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{13}H_{24}N_2ONa$, 247.1781; found, 247.1775.

*(E)-5-Phenylpent-4-enenitrile (**6**).* Yellow oil; 45% yield (14 mg). ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38−7.35 (m, 2H), 7.34−7.30 (m, 2H), 7.27−7.23 (m, 1H), 6.52 (d, J = 15.8 Hz, 1H), 6.18 (dt, J = 15.8, 6.8 Hz, 1H), 2.57−2.52 (m, 2H), 2.50−2.46 (m, 2H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$): δ 136.7, 133.0, 128.7, 127.8, 126.3, 125.6, 119.2, 28.8, 17.6; FT-IR (thin film, KBr): ν (cm^{-1}): 2933, 1590, 1561, 1473, 1422, 1070, 994, 775; HRMS (ESI) m/z: $[M + Na]^+$ calcd for $C_{11}H_{11}NNa$, 180.0784; found, 180.0786.

Control Experiment 1 (Scheme 2, eq 1). To a 10 mL oven-dried round-bottomed Schlenk bottle equipped with a magnetic stir bar, **1a** (34 mg, 0.2 mmol), **2a** (42 mg, 0.4 mmol), Mes−Acr$^+$$ClO_4^-$ (4.2 mg, 0.01 mmol, 5 mol %), Co(dmgH) ($dmgH_2$)Cl_2 (7.2 mg, 0.02 mmol, 10 mol %), and K_3PO_4 (8.4 mg, 0.04 mmol) were added and dissolved in mesitylene (2 mL). Then, TEMPO (62 mg, 0.4 mmol) was added to the reaction system. The resulting mixture was sealed and then subjected to the freeze−pump−thaw cycle three times. After that, the reaction system was placed under a 22 W blue LED and irradiated for 72 h. The temperature was maintained at 35 °C when the LED light was on. After the reaction was complete (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 30:1) to give the desired product **5** as an oil in 29% yield (13 mg).

Control Experiment 2 (Scheme 2, eq 2). To a 10 mL oven-dried round-bottomed Schlenk bottle equipped with a magnetic stir bar, (*E*)-2-methyl-2-(((2-phenylcyclopentylidene)amino)oxy)propanoic acid (52 mg, 0.2 mmol), Mes−Acr$^+$$ClO_4^-$ (4.2 mg, 0.01 mmol, 5 mol %), Co(dmgH) ($dmgH_2$)Cl_2 (7.2 mg, 0.02 mmol, 10 mol %), and potassium phosphate (8.4 mg, 0.04 mmol, 20 mol %) were added. Mesitylene (2 mL) was then added under an argon atmosphere. The resulting mixture was sealed and then subjected to the freeze−pump−thaw cycle three times. After that, the reaction mixture was placed under a 22 W blue LED and irradiated for 72 h. The temperature was maintained at 35 °C when the LED light was on. After the reaction finished (monitored by TLC), the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel. The crude product was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate, 30:1) to give the desired product **6** as an oil in 45% yield (14 mg).

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c02834.

Experimental details, including photochemical reaction setup, optimization of reaction conditions, and determination of hydrogen gas with GC, and copies of ^{1}H and ^{13}C NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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