HOTf-Catalyzed Alkyl-Heck-type Reaction

HIGHLIGHTS
First acid-catalyzed Heck-type reaction
Aliphatic acids are utilized as the sources of alkyl functionalities
E-alkenes exclusively in most cases
Strong acid effect

First acid catalyzed Heck-type reaction
1°, 2° and 3° alkyl groups
Late stage functionalizations
Mostly only E-selectivity

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HOTf-Catalyzed Alkyl-Heck-type Reaction

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SUMMARY
The Heck reaction, along with other cross-coupling reactions, led to a revolution in organic chemistry. In the last 50 years, metal-catalyzed, photo-induced, or base-mediated Heck and Heck-type reactions have been elegantly developed. Brønsted acid-catalyzed Heck (or Heck-type) reactions are still unknown, however. By introducing alkyl peroxides as the key intermediates, primary, secondary, and tertiary aliphatic carboxylic acids are therefore applied here in a one-pot Brønsted acid-catalyzed Heck-type reaction, to deliver E-alkenes exclusively in most cases. The use of HOTf is vital to the reaction, whose mechanism is supported by both experimental and computational results. This method can be expanded to the direct alkylation of complex natural products.

INTRODUCTION
The Heck reaction, pioneered by Heck and Mizoroki in the late 1960s and the early 1970s (Heck, 1968; Mizoroki et al., 1971; Heck and Nolley, 1972), along with other cross-coupling reactions, led to a revolution in organic chemistry (Johansson Seechurn et al., 2012). In the last 50 years, many types of Heck and Heck-type reactions, including metal-catalyzed (Heck, 1968; Mizoroki et al., 1971; Heck and Nolley, 1972; Littke and Fu, 2001; Farrington et al., 2002; Na et al., 2004; Loska et al., 2008; Delcampo et al., 2013; Nishikata et al., 2013; Standley and Jamison, 2013), photo-induced (Iqbal et al., 2012; Liu et al., 2013; Paria et al., 2014; Yu et al., 2014), or base-mediated (Rueping et al., 2011; Shirakawa et al., 2011; Sun et al., 2011) reactions, have been elegantly developed (Beletskaya and Cheprakov, 2000; Dounay and Overman, 2003; Wu et al., 2010; Le Bras and Muzart, 2011; McCarty and Gurley, 2011; Tang et al., 2013). Notwithstanding these classical reaction modes, there is no precedent of Brønsted acid-catalyzed or Brønsted acid-promoted Heck (or type) reaction being realized. Moreover, compared with aryl Heck reactions, the alkyl-Heck (type) reaction has been developed less. This is due mainly to the potential accompanying side reactions. Significant breakthroughs in alkyl-Heck-type reactions have, however, been made (Ikeda et al., 2002; Liu et al., 2012, 2015; Nishikata et al., 2013; McMahon and Alexanian, 2014; Zou and Zhou, 2014; Kurandina et al., 2018; Wang et al., 2018) (Scheme 1A), and in this article, we report a Brønsted acid-catalyzed alkyl-Heck-type reaction.

As is well known, alkyl halides are one of the most frequently used alkyl functionalities for alkyl-Heck-type reactions (Kambe et al., 2011; Weix, 2015; Tellis et al., 2016; Choi and Fu, 2017). However, their shortcomings, such as limited availability and perceived instability might prevent more extensive applications (Qin et al., 2016). Furthermore, there are still significant challenges remaining for alkyl-Heck-type reactions such as E/Z selectivity, use of metal catalysis, and diversity of alkyl sources (Scheme 1A). Carboxylic acids are inexpensive, stable, non-toxic, and structurally diverse feedstock chemicals that have been widely used in numerous reactions. For example, they have been utilized in cross-coupling with prefunctionalized alkenes such as vinyl halides or their derivatives to generate alkenes (Mai et al., 2013; Noble et al., 2015; Toriyama et al., 2016; Wang et al., 2016; Edwards et al., 2017; Xu et al., 2017; Zhang et al., 2017) (Scheme 1B). However, the decarboxylative cross-couplings of aliphatic acids or their derivatives with alkenes (X = H) are very rare (Wang et al., 2018). As part of our ongoing interest in the application of aliphatic acids as the alkyl source (Li et al., 2016; Ge et al., 2017; Jian et al., 2017; Qian et al., 2017; Ye et al., 2017; Zhu et al., 2017) and our interests in the discovery of different reaction models of alkyl peroxides, we have developed the first Brønsted acid-catalyzed alkyl-Heck-type reaction of alkenes with aliphatic acids via alkyl peroxide intermediates (Scheme 1C).

RESULTS AND DISCUSSION
Optimization Study
We commenced our studies by screening a variety of Brønsted acids for the alkyl-Heck-type reaction of styrene with aliphatic acid. The aliphatic acid was converted into alkyl peresters in the presence of trifluoroacetic anhydride (TFAA) and tert-butyl hydroperoxide (TBHP) and used in situ for the subsequent step.
The best Brønsted acid was found to be HOTf, which offered the desired alkylated alkene exclusively as a single E-isomer in 88% yield, determined by 1H nuclear magnetic resonance (NMR) analysis (Equation 1 and Table 1, entry 1). Studies of acids showed that Tf₂O had a lower efficiency (Table 1, entry 2). Previous studies have shown that decarboxylative vinylic alkylation with aliphatic acid derivatives (Equation 1 and Table 1, entry 1). Studies of acids showed that Tf₂O had a lower efficiency (Table 1, entry 2).

Scheme 1. Intermolecular Alkyl-Heck-Type Reaction of General Alkyl Groups and Decarboxylative Vinylic Alkylation of Aliphatic Acids
(A) Previous alkyl-Heck-type reactions by Oshima, Alexanian, Zhou, Li, Fu, Lei, and Nishikata.
(B) Previous decarboxylative vinylic alkylation with aliphatic acid derivatives.
(C) This work: Brønsted acid-catalyzed alkyl-Heck-type reaction.

(Donchak et al., 2006). The best Brønsted acid was found to be HOTf, which offered the desired alkylated alkene exclusively as a single E-isomer in 88% yield, determined by 1H nuclear magnetic resonance (NMR) analysis (Equation 1 and Table 1, entry 1). Studies of acids showed that Tf₂O had a lower efficiency (Table 1, entry 2). Previous studies have shown that decarboxylative vinylic alkylation with aliphatic acid derivatives (Equation 1 and Table 1, entry 1). Studies of acids showed that Tf₂O had a lower efficiency (Table 1, entry 2).

Table 1. Optimizations of Reaction Condition

| Entry | Variation from the Standard Conditions | Yield(%)<sup>a,b</sup> |
|-------|----------------------------------------|------------------------|
| 1     | None                                    | 88(75<sup>c</sup>)     |
| 2     | Tf₂O instead of HOTf                    | 78                     |
| 3     | TsOH·H₂O instead of HOTf                | Trace                  |
| 4     | CF₃COOH instead of HOTf                 | Trace                  |
| 5     | HOAc instead of HOTf                    | Trace                  |
| 6     | MeSO₃H instead of HOTf                  | Trace                  |
| 7     | Room temperature instead of 50°C        | 70                     |
| 8     | Fresh distilled HOTf                    | 88                     |
| 9     | In dark                                 | 90                     |
| 10    | Without HOTf                            | Trace                  |

<sup>a</sup>Reaction conditions: First, 2-ethylhexanoic acid 1 (1.5 mmol), TBHP (1.5 mmol), and TFAA (1.5 mmol) at 0°C-rt for 4 hr, and then THF (2 mL), styrene 2 (0.5 mmol), and HOTf (0.05 mmol) were added. The mixture was stirred at 50°C for 8 hr.
<sup>b</sup>1H NMR yield.
<sup>c</sup>Yield of the isolated product.
entry 2) and other Brønsted acids such as TsOH, H2O, CF3COOH, HOAc, and MeSO3H were ineffective in this reaction (Table 1, entries 3–6). When performed at room temperature (rt), the reaction afforded the desired product in 70% yield (Table 1, entry 7). To exclude the possibility of interference of trace amount of metal in HOTf, the HOTf was used after redistillation and the product was obtained in the same yield (Table 1, entry 8). The role of light was investigated by conducting the reaction in the dark, but no difference in the yield was observed (Table 1, entry 9). In the absence of HOTf, the alkyl peroxide decomposed completely and the styrene remained unchanged (Table 1, entry 10).

Scope of the Investigation

With the identified conditions in hand, we studied the scope of alkenes for this one-pot process (Figure 1). In most of the cases, the products were obtained as a single E-isomer. Reactions of vinyl arenes containing carbon substituents at the α-, m-, and p-positions afforded the corresponding products (4–10) in good yield (68–84%). Vinyl arenes containing halides reacted with 2-ethylhexanoic acid to give the desired products (11–15) in moderate to good yield (54%–80%). Functional groups, such as dimethylaminomethyl, and even free carboxylic acid and boronic acid were compatible with the reaction conditions (20–23). α-Methylstyrene and α-phenylstyrene participated in the reaction smoothly, providing the products (24, 25) in 82% and 93% yields, respectively. Furthermore, an enyne was a suitable substrate for this reaction, and the corresponding terminal-cross-coupled product (26) was obtained in good yield (71%). 1-Octene, an unactivated alkene, examined under the standard reaction conditions was not reactive to this reaction.
Next, we proceeded to study the scope of the reaction with respect to secondary and tertiary aliphatic carboxylic acids (Figure 2). The desired products (28–43) were obtained in moderate to high yields, using acyclic or cyclic aliphatic acids. The compatibility of various functional groups was good, and many functional groups, such as carbonyl (42), imide (38), amine (43), and ether (36), were tolerated. Most importantly, the E/Z selectivity of this reaction was excellent and only E-alkenes were observed. We then tried to expand this reaction to primary aliphatic acids, but the desired products were obtained in low yields as the methylated vinylic products were observed as by-products (Zhu et al., 2017). To overcome this problem, primary aliphatic acids were converted into alkyl diacyl peroxides and then subjected to the reaction (Figure 3). With the similar reaction conditions (please see Table S4 for details), generic primary aliphatic acids afforded the corresponding products (44–48) in good yields (60–77%). Primary aliphatic acids with functionalities, e.g., the bromide (49), chloride (50), ketones (51 and 52), ester (53), or the alkene (54) were well tolerated in the protocol, delivering the corresponding products in moderate to good yields. In every case, the E-alkene was obtained exclusively.

**Synthetic Applications**

To highlight the synthetic utility of this methodology (Scheme 2), the perester (55), which is readily derived from the corresponding steroidal carboxylic acid, was coupled with styrene in the presence of HOTf. The decarboxylative Heck-type coupling product (56) was obtained in 48% yield as a single isomer. The configuration of the product (56) was reversed, and this was confirmed by X-ray crystallographic analysis (please see Tables S5 and S6 for details). The reaction of 57 afforded the desired product (58) in 65% yield with E-selectivity. Gemfibrozil (59), an oral drug used to lower lipid levels, could also be converted into the vinylated product (60). These examples demonstrated that this reaction is potentially useful for the functionalization of complex molecules in the late stage.
Mechanistic Study

To probe the mechanism of the reaction, a series of control experiments were performed. The reaction of α-phenylstyrene with 2-cyclopropylacetic acid under the standard conditions afforded the ring-opening product (61) in 62% yield (Scheme 3A), supporting the assumption of the involvement of radical species in the reaction. The competitive reaction of styrene and d₈-styrene used in 1:1 ratio in the presence of HOTf and lauroyl peroxide (LPO) offered an identical yield of the corresponding products (Scheme 3B). When the reaction of d₈-styrene with perester 62 was performed in tetrahydrofuran (THF), the desired
product (d\textsubscript{7-3}) was isolated (Scheme 3B). Interestingly, the deuterated side products d\textsubscript{7-3}butanol were detected by gas chromatography-mass spectrometry (GC-MS). To further explore the mechanism, possible intermediates 63 and 64 were synthesized and tested with or without HOTf (Scheme 3C). Compounds 63 and 64 are thermally stable in the absence or presence of one equivalent of C\textsubscript{11}H\textsubscript{23}COOH. Even though compounds 63 and 64 can be converted to the desired alkene products in the presence of 0.2 equivalent of HOTf, it is unlikely that they are competent intermediates because the formation of 63 or 64 was not observed using GC-MS when the corresponding Heck reaction was conducted no matter with or without HOTf (Ge et al., 2017).

**Plausible Reaction Mechanism**

As the result shown in entry 10 of Table 1, no desired product was observed in the absence of HOTf, implying that HOTf must play a vital role in the reaction. Density functional theory (DFT) calculations were carried out to gain further insight into the reaction mechanism. As can be seen from Scheme 4, before the catalytic cycle R* radical l-5 can be formed by homolytic dissociation of the alkyl diacyl peroxide, which is a very slow step with a high barrier of 27.5 kcal/mol. However, this is considered as the trigger to invoke the following catalytic cycle. Attack on the styrene substrate by the active species R* radical to form a benzyl radical (l-6) leads to energies lower by 31.3 kcal/mol with a small barrier of 2.8 kcal/mol, indicating
that such a reaction is both thermodynamically and kinetically favorable. In the beginning of the catalytic cycle, LPO binding a molecule of HOTf forms a complex I-1 with a strong hydrogen bonding of 10.2 kcal/mol. This complex oxidizes benzyl radical (I-6) to yield a benzyl cation species (I-2), a radical (I-3), and an OTf$^-$ anion, which is exothermic by 4.4 kcal/mol. Meanwhile, the generated OTf$^-$ deprotonates I-2 to yield the product and regenerate the acid HOTf with a reaction energy of $-13.4$ kcal/mol. Thus, from the reactions of LPO and I-6 with the product and I-3, a proton-coupled electron transfer process is promoted by HOTf, which serves as the driving force and proton source for the reaction. Thereby, homolytic dissociation of I-3 leads to RCOO• radical (I-4) and RCOOH, which is exothermic by 2.3 kcal/mol without any barrier. Subsequently, C-C cleavage of I-4 is exothermic by 3.8 kcal/mol, which releases the active species R• radical (I-5) and CO$_2$ to close the catalytic cycle. Alternatively, in the absence of HOTf formation of this radical I-4 with carboxylic acid RCOOH requires high energies (>27 kcal/mol, See Scheme S1), indicating that the strong acidity of HOTf plays a significant role in the formation of I-4. A similar mechanism of reaction starting from perester was also calculated and presented in Scheme S2.

**Conclusion**

We have developed a Brønsted acid-catalyzed radical alkyl-Heck-type reaction of alkenes with aliphatic acids. This HOTf-catalyzed process has been shown to be an efficient method to deliver only E-alkenes in most cases. Relatively simple and available starting materials are used, and wide substrate scope and good functional group tolerance are observed. Preliminary mechanistic studies illustrated the vital role of HOTf in the reaction, whose proposed mechanism is supported by both the experimental and computational results.

**METHODS**

All methods can be found in the accompanying Transparent Methods supplemental file.

**DATA AND SOFTWARE AVAILABILITY**

The data for the X-ray crystallographic structure of 55 and 56 have been deposited in the Cambridge Crystallographic Data Center under accession number CCDC: 1477011 and CCDC: 1476738 (also see Data S2 and Data S3 in Supplemental Information).

**SUPPLEMENTAL INFORMATION**

Supplemental Information includes Transparent Methods, 164 figures, 2 schemes, 6 tables, and 3 data files and can be found with this article online at https://doi.org/10.1016/j.isci.2018.04.020.
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AUTHOR CONTRIBUTIONS

Performed synthetic experiments and analyzed the experimental data: H.Z., L.G., W.J., and Y.L.; theoretical calculations: J.S. and C.L.; performed investigations and prepared the manuscript, H.B.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

HOTf-Catalyzed Alkyl-Heck-type Reaction

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Figure S1. $^1$H NMR spectrum of 4-bromo-2-fluoro-1-vinylbenzene, Related to Figure 1.
**Figure S2.** $^{13}$C NMR spectrum of 4-bromo-2-fluoro-1-vinylbenzene, Related to Figure 1.

**Figure S3.** $^{19}$F NMR spectrum of 4-bromo-2-fluoro-1-vinylbenzene, Related to Figure 1.
Figure S4. $^1$H NMR spectrum of 1-(methylsulfonyl)-4-vinylbenzene, Related to Figure 1.

Figure S5. $^{13}$C NMR spectrum of 1-(methylsulfonyl)-4-vinylbenzene, Related to Figure 1.
**Figure S6.** $^1$H NMR spectrum of 6-vinyl-1,2,3,4-tetrahydronaphthalene, Related to Figure 1.

**Figure S7.** $^{13}$C NMR spectrum of 6-vinyl-1,2,3,4-tetrahydronaphthalene, Related to Figure 1.
Figure S8. $^1$H NMR spectrum of compound 57, related to Scheme 2.

Figure S9. $^{13}$C NMR spectrum of compound 57, related to Scheme 2.
Figure S10. $^1$H NMR spectrum of hexanoic peroxyanhydride, related to Figure 3.

Figure S11. $^{13}$C NMR spectrum of hexanoic peroxyanhydride, related to Figure 3.
Figure S12. $^1$H NMR spectrum of octanoic peroxyanhydride, related to Figure 3.

Figure S13. $^{13}$C NMR spectrum of octanoic peroxyanhydride, related to Figure 3.
Figure S14. $^1$H NMR spectrum of 3-cyclopentylpropanoic peroxyanhydride, related to Figure 3.

Figure S15. $^{13}$C NMR spectrum of 3-cyclopentylpropanoic peroxyanhydride, related to Figure 3.
Figure S16. $^1$H NMR spectrum of 5-chloropentanoic peroxyanhydride, related to Figure 3.

Figure S17. $^{13}$C NMR spectrum of 5-chloropentanoic peroxyanhydride, related to Figure 3.
Figure S18. $^{1}$H NMR spectrum of 2-((3r,5r,7r)-adamantan-1-yl)acetic peroxyanhydride, related to Figure 3.

Figure S19. $^{13}$C NMR spectrum of 2-((3r,5r,7r)-adamantan-1-yl)acetic peroxyanhydride, related to Figure 3.
Figure S20. $^1$H NMR spectrum of 5-oxohexanoic peroxyanhydride, related to Figure 3.

Figure S21. $^{13}$C NMR spectrum of 5-oxohexanoic peroxyanhydride, related to Figure 3.
Figure S22. $^1$H NMR spectrum of 6-methoxy-6-oxohexanoic peroxyanhydride, related to Figure 3.

Figure S23. $^{13}$C NMR spectrum of 6-methoxy-6-oxohexanoic peroxyanhydride, related to Figure 3.
Figure S24. $^1$H NMR spectrum of 5-oxo-5-phenylpentanoic peroxyanhydride, related to Figure 3.

Figure S25. $^{13}$C NMR spectrum of 5-oxo-5-phenylpentanoic peroxyanhydride, related to Figure 3.
Figure S26. $^1$H NMR spectrum of 4-bromobutanoic peroxyanhydride, related to Figure 3.

Figure S27. $^{13}$C NMR spectrum of 4-bromobutanoic peroxyanhydride, related to Figure 3.
Figure S28. $^1$H NMR spectrum of dec-9-enoic peroxyanhydride, related to Figure 3.

Figure S29. $^{13}$C NMR spectrum of dec-9-enoic peroxyanhydride, related to Figure 3.
Figure S30. $^1$H NMR spectrum of tert-butyl(1s,3r,5s,7s)-4-oxoadamantane-1-carboperoxoate, related to Figure 2.

Figure S31. $^{13}$C NMR spectrum of tert-butyl (1s,3r,5s,7s)-4-oxoadamantane-1-carboperoxoate, related to Figure 2.
Figure S32. $^1$H NMR spectrum of tert-butyl 4,4-difluorocyclohexane-1-carboperoxoate, related to Figure 2.

Figure S33. $^{13}$C NMR spectrum of tert-butyl 4,4-difluorocyclohexane-1-carboperoxoate, related to Figure 2.
Figure S34. $^{19}$F NMR spectrum of tert-butyl 4,4-difluorocyclohexane-1-carboperoxoate, related to Figure 2.
**Figure S35.** $^1$H NMR spectrum of tert-butyl tetrahydro-2H-pyran-4-carboperoxoate, related to Figure 2.

**Figure S36.** $^{13}$C NMR spectrum of tert-butyl tetrahydro-2H-pyran-4-carboperoxoate, related to Figure 2.
Figure S37. $^1$H NMR spectrum of tert-butyl 1-tosylpiperidine-3-carboperoxoate, related to Figure 2.

Figure S38. $^{13}$C NMR spectrum of tert-butyl 1-tosylpiperidine-3-carboperoxoate, related to Figure 2.
Figure S39. $^1$H NMR spectrum of tert-butyl 2-(1,3-dioxoisindolin-2-yl)propaneperoxoate, related to Figure 2.

Figure S40. $^{13}$C NMR spectrum of tert-butyl 2-(1,3-dioxoisindolin-2-yl)propaneperoxoate, related to Figure 2.
Figure S41. $^1$H NMR spectrum of compound 55, related to scheme 2.

Figure S42. $^{13}$C NMR spectrum of compound 55, related to scheme 2.
Figure S43. $^1$H NMR spectrum of compound 3, related to Table 1.

Figure S44. $^{13}$C NMR spectrum of compound 3, related to Table 1.
Figure S45. $^1$H NMR spectrum of compound 4, related to Figure 1.

Figure S46. $^{13}$C NMR spectrum of compound 4, related to Figure 1.
Figure S47. $^1$H NMR spectrum of compound 5, related to Figure 1.

Figure S48. $^{13}$C NMR spectrum of compound 5, related to Figure 1.
Figure S49. $^1$H NMR spectrum of compound 6, related to Figure 1.

Figure S50. $^{13}$C NMR spectrum of compound 6, related to Figure 1.
Figure S51. $^1$H NMR spectrum of compound 7, related to Figure 1.

Figure S52. $^{13}$C NMR spectrum of compound 7, related to Figure 1.
Figure S53. $^1$H NMR spectrum of compound 8, related to Figure 1.

Figure S54. $^{13}$C NMR spectrum of compound 8, related to Figure 1.
Figure S55. $^1$H NMR spectrum of compound 9, related to Figure 1.

Figure S56. $^{13}$C NMR spectrum of compound 9, related to Figure 1.
Figure S57. $^1$H NMR spectrum of compound 10, related to Figure 1.

Figure S58. $^{13}$C NMR spectrum of compound 10, related to Figure 1.
Figure S59. $^1$H NMR spectrum of compound 11, related to Figure 1.

Figure S60. $^{13}$C NMR spectrum of compound 11, related to Figure 1.
Figure S61. $^1$H NMR spectrum of compound 12, related to Figure 1.

Figure S62. $^{13}$C NMR spectrum of compound 12, related to Figure 1.
Figure S63. $^1$H NMR spectrum of compound 13, related to Figure 1.

Figure S64. $^{13}$C NMR spectrum of compound 13, related to Figure 1.
Figure S65. $^1$H NMR spectrum of compound 14, related to Figure 1.

Figure S66. $^{13}$C NMR spectrum of compound 14, related to Figure 1.
Figure S67. $^{19}$F NMR spectrum of compound 14, related to Figure 1.
Figure S68. $^1$H NMR spectrum of compound 15, related to Figure 1.

Figure S69. $^{13}$C NMR spectrum of compound 15, related to Figure 1.
Figure S70. $^{19}$F NMR spectrum of compound 15, related to Figure 1.
Figure S71. $^1$H NMR spectrum of compound 16, related to Figure 1.

Figure S72. $^{13}$C NMR spectrum of compound 16, related to Figure 1.

\[ \text{n-Bu} \quad \text{Et} \quad \text{n-Bu} \]

\[ \text{S} \quad \text{O} \]

\[ \text{n-Bu} \quad \text{Et} \quad \text{n-Bu} \]

\[ \text{S} \quad \text{O} \]
Figure S73. $^1$H NMR spectrum of compound 17, related to Figure 1.

Figure S74. $^{13}$C NMR spectrum of compound 17, related to Figure 1.
**Figure S75.** $^1$H NMR spectrum of compound 18, related to Figure 1.

**Figure S76.** $^{13}$C NMR spectrum of compound 18, related to Figure 1.
Figure S77. $^1$H NMR spectrum of compound 19, related to Figure 1.

Figure S78. $^{13}$C NMR spectrum of compound 19, related to Figure 1.
Figure S79. $^1$H NMR spectrum of compound 20, related to Figure 1.

Figure S80. $^{13}$C NMR spectrum of compound 20, related to Figure 1.
Figure S81. $^1$H NMR spectrum of compound 21, related to Figure 1.

Figure S82. $^{13}$C NMR spectrum of compound 21, related to Figure 1.
**Figure S83.** $^1$H NMR spectrum of compound 22, related to Figure 1.

**Figure S84.** $^{13}$C NMR spectrum of compound 22, related to Figure 1.
Figure S85. $^1$H NMR spectrum of compound 23, related to Figure 1.

Figure S86. $^{13}$C NMR spectrum of compound 23, related to Figure 1.
Figure S87. $^1$H NMR spectrum of compound 24, related to Figure 1.

Figure S88. $^{13}$C NMR spectrum of compound 24, related to Figure 1.
Figure S89. NOE spectrum of compound 24, related to Figure 1.
Figure S90. $^1$H NMR spectrum of compound 25, related to Figure 1.

Figure S91. $^{13}$C NMR spectrum of compound 25, related to Figure 1.
Figure S92. $^1$H NMR spectrum of compound 26, related to Figure 1.

Figure S93. $^{13}$C NMR spectrum of compound 26, related to Figure 1.
Figure S94. NOE spectrum of compound 26, related to Figure 1.
Figure S95. $^1$H NMR spectrum of compound 28, related to Figure 2.

Figure S96. $^{13}$C NMR spectrum of compound 28, related to Figure 2.
Figure S97. $^1$H NMR spectrum of compound 29, related to Figure 2.

Figure S98. $^{13}$C NMR spectrum of compound 29, related to Figure 2.
Figure S99. $^1$H NMR spectrum of compound 30, related to Figure 2.

Figure S100. $^{13}$C NMR spectrum of compound 30, related to Figure 2.
**Figure S101.** $^1$H NMR spectrum of compound 31, related to Figure 2.

**Figure S102.** $^{13}$C NMR spectrum of compound 31, related to Figure 2.
Figure S103. $^1$H NMR spectrum of compound 32, related to Figure 2.

Figure S104. $^{13}$C NMR spectrum of compound 32, related to Figure 2.
Figure S105. $^1$H NMR spectrum of compound 33, related to Figure 2.

Figure S106. $^{13}$C NMR spectrum of compound 33, related to Figure 2.
Figure S107. $^1$H NMR spectrum of compound 34, related to Figure 2.

Figure S108. $^{13}$C NMR spectrum of compound 34, related to Figure 2.
Figure S109. $^1$H NMR spectrum of compound 35, related to Figure 2.

Figure S110. $^{13}$C NMR spectrum of compound 35, related to Figure 2.
Figure S11. $^{19}$F NMR spectrum of compound 35, related to Figure 2.
Figure S112. $^1$H NMR spectrum of compound 36, related to Figure 2.

Figure S113. $^{13}$C NMR spectrum of compound 36, related to Figure 2.
Figure S114. $^1$H NMR spectrum of compound 37, related to Figure 2.

Figure S115. $^{13}$C NMR spectrum of compound 37, related to Figure 2.
Figure S116. $^1$H NMR spectrum of compound 38, related to Figure 2.

Figure S117. $^{13}$C NMR spectrum of compound 38, related to Figure 2.
Figure S118. $^1$H NMR spectrum of compound 39, related to Figure 2.

Figure S119. $^{13}$C NMR spectrum of compound 39, related to Figure 2.
Figure S120. $^1$H NMR spectrum of compound 40, related to Figure 2.

Figure S121. $^{13}$C NMR spectrum of compound 40, related to Figure 2.
Figure S122. $^1$H NMR spectrum of compound 41, related to Figure 2.

Figure S123. $^{13}$C NMR spectrum of compound 41, related to Figure 2.
Figure S124. $^1$H NMR spectrum of compound 42, related to Figure 2.

Figure S125. $^{13}$C NMR spectrum of compound 42, related to Figure 2.
Figure S126. $^1$H NMR spectrum of compound 43, related to Figure 2.

Figure S127. $^{13}$C NMR spectrum of compound 43, related to Figure 2.
Figure S128. $^1$H NMR spectrum of compound 44, related to Figure 3.

Figure S129. $^{13}$C NMR spectrum of compound 44, related to Figure 3.
**Figure S130.** $^1$H NMR spectrum of compound 45, related to Figure 3.

**Figure S131.** $^{13}$C NMR spectrum of compound 45, related to Figure 3.
Figure S132. $^1$H NMR spectrum of compound 46, related to Figure 3.

Figure S133. $^{13}$C NMR spectrum of compound 46, related to Figure 3.
Figure S134. $^1$H NMR spectrum of compound 47, related to Figure 3.

Figure S135. $^{13}$C NMR spectrum of compound 47, related to Figure 3.
Figure S136. $^1$H NMR spectrum of compound 48, related to Figure 3.

Figure S137. $^{13}$C NMR spectrum of compound 48, related to Figure 3.
Figure S138. $^1$H NMR spectrum of compound 49, related to Figure 3.

Figure S139. $^{13}$C NMR spectrum of compound 49, related to Figure 3.
**Figure S140.** $^1$H NMR spectrum of compound 50, related to Figure 3.

**Figure S141.** $^{13}$C NMR spectrum of compound 50, related to Figure 3.
Figure S142. $^1$H NMR spectrum of compound 51, related to Figure 3.

Figure S143. $^{13}$C NMR spectrum of compound 51, related to Figure 3.
Figure S144. $^1$H NMR spectrum of compound 52, related to Figure 3.

Figure S145. $^{13}$C NMR spectrum of compound 52, related to Figure 3.
**Figure S146.** $^1$H NMR spectrum of compound 53, related to Figure 3.

**Figure S147.** $^{13}$C NMR spectrum of compound 53, related to Figure 3.
Figure S148. $^1$H NMR spectrum of compound 54, related to Figure 3.

Figure S149. $^{13}$C NMR spectrum of compound 54, related to Figure 3.
Figure S150. $^1$H NMR spectrum of compound **56**, related to **Scheme 2**.

Figure S151. $^{13}$C NMR spectrum of compound **56**, related to **Scheme 2**.
Figure S152. $^1$H NMR spectrum of compound 58, related to Scheme 2.

Figure S153. $^{13}$C NMR spectrum of compound 58, related to Scheme 2.
Figure S154. $^1$H NMR spectrum of compound 60, related to Scheme 2.

Figure S155. $^{13}$C NMR spectrum of compound 60, related to Scheme 2.
Figure S156. $^1$H NMR spectrum of compound 61, related to Scheme 3A.

Figure S157. $^{13}$C NMR spectrum of compound 61, related to Scheme 3A.
Figure S158. $^1$H NMR spectrum of compounds $d_7$-44 and 44, related to Scheme 3B.

Figure S159. $^1$H NMR spectrum of compound $d_7$-3, related to Scheme 3B.
Figure S160. $^{13}$C NMR spectrum of compound $d_7$-3, related to Scheme 3B.
Figure S161. $^1$H NMR spectrum of compound 62, related to Scheme 3C.

Figure S162. $^{13}$C NMR spectrum of compound 62, related to Scheme 3C.
Figure S163. $^1$H NMR spectrum of compound 63, related to Scheme 3C.

Figure S164. $^{13}$C NMR spectrum of compound 63, related to Scheme 3C.
Supplemental Schemes

Note: R = n-C₈H₁₁ was used for the calculation

Scheme S1. The reaction profiles without HOTf. Related to Scheme 4.

(A) Direct electron transfer from I₆ to peroxide requires a high energy of 17.3 kcal/mol. Protonation of I-2 by RCOOH to form I-3 is endothermic of 12.9 kcal/mol. Without acid direct O-O cleavage to form I-4 is also endothermic of 10.6 kcal/mol. Combined with previous energy requirement of electron transfer the overall reaction energies are more than 27 kcal/mol.

(B) Binding a carboxylic acid RCOOH to peroxide forms a weak hydrogen bond of 3.2 kcal/mol. However, electron transfer process requires high energy of 33.3 kcal/mol. As such, both paths are disfavored compared to the HOTf involved reactions.
Scheme S2. The reaction profile of perester, Related to Scheme 4.

The perester species has a similar mechanism catalyzed by HOTf. Before the catalytic cycle the R• radical J-5 can be formed by homolytic dissociation of the alkyl diacyl peroxide (perester), which is a very slow step with a high barrier of 24.9 kcal/mol. However, this is considered as the trigger to invoke the following catalytic cycle. Attack on the styrene substrate by the active species R• radical J-5 to form a benzyl radical (J-6) leads to energies lower by 23.7 kcal/mol with a small barrier of 6.7 kcal/mol, indicating that such reaction is both thermodynamically and kinetically favourable. In the beginning of the catalytic cycle, LPO binding a molecule of HOTf forms a complex I-1 with a strong hydrogen bonding of 13.7 kcal/mol. This complex oxidizes benzyl radical (J-6) to yield a benzyl cation species (J-2), a radical (J-3) and an OTf- anion, which is exothermic by 2.2 kcal/mol. Meanwhile, the generated OTf deprotonates J-1 to yield the product and regenerate acid HOTf with reaction energy of -13.3 kcal/mol. Thus, from the reactions of LPO and J-6 to the product and J-3 stepwise electron and proton transfers are promoted by HOTf, which serves as the driving force and proton source for the reaction. Thereby hydrogen transfer of J-3 leads to RCOO• radical (J-4) and tBuOH, which is nearly thermal neutral of 1.4 kcal/mol without any barrier. Subsequently, C-C cleavage of J-4 is exothermic by 11.6 kcal/mol in energy which releases the active species R• radical (J-5) and CO₂ to close the catalytic cycle.
### Supplemental Tables

| Acids     | Company          | Acids     | Company          | Acids     | Company          |
|-----------|------------------|-----------|------------------|-----------|------------------|
| n-Bu      | Energy-chemical  | n-Pr      | Energy-chemical  | n-Bu      | Energy-chemical  |
|          |                  |           |                  |           |                  |
|          |                  | COO⁻      | Adamas-beta      |           | Adamas-beta      |
|          |                  |           |                  |           |                  |
|          |                  |           |                  |           |                  |
|          |                  |           |                  |           |                  |
|          |                  |           |                  |           |                  |
|          |                  |           |                  |           |                  |
|          |                  |           |                  |           |                  |
|          |                  |           |                  |           |                  |
|          |                  |           |                  |           |                  |
|          |                  |           |                  |           |                  |
|          |                  |           |                  |           |                  |

**Table S1.** Sources of acids, related to Figure 2 and Figure 3.
| Alkenes | Company            | Alkenes | Company            | Alkenes | Company            |
|---------|--------------------|---------|--------------------|---------|--------------------|
| ![Image] | Energy-chemical    | ![Image] | Energy-chemical    | ![Image] | Adamas-beta        |
| ![Image] | Adamas-beta        | ![Image] | Alfa Aesar         | ![Image] | Energy-chemical    |
| ![Image] | Energy-chemical    | ![Image] | Meryer             | ![Image] | Energy-chemical    |
| ![Image] | Energy-chemical    | ![Image] | Energy-chemical    | ![Image] | Admas              |
| ![Image] | Meryer             | ![Image] | Energy-chemical    | ![Image] | Energy-chemical    |
| ![Image] | Energy-chemical    | ![Image] | Jkchemical         | ![Image] | Energy-chemical    |
| ![Image] | Energy-chemical    | ![Image] | Energy-chemical    | ![Image] | Energy-chemical    |
| ![Image] | Sigma-aldrich      | ![Image] | Energy-chemical    | ![Image] | Energy-chemical    |

**Table S2.** Sources of alkenes, related to Figure 1, Figure 2 and Figure 3.
| Structure | Yield | Structure | Yield |
|-----------|-------|-----------|-------|
| ![Structure](image1) | 90% | ![Structure](image2) | 85% |
| ![Structure](image3) | 84% | ![Structure](image4) | 65% |
| ![Structure](image5) | 84% | ![Structure](image6) | 73% |
| ![Structure](image7) | 71% | ![Structure](image8) | 76% |
| ![Structure](image9) | 55% | ![Structure](image10) | 76% |
| ![Structure](image11) | 75% | ![Structure](image12) | 70% |
| ![Structure](image13) | 78% | ![Structure](image14) | 70% |
| ![Structure](image15) | 64% | ![Structure](image16) | 80% |

*Table S3.* The synthesis of peroxides, related to Figure 3.
| Entry | HOTf (x mol %) | THF (y mL) | Temp. | Yield (%)\(^b\) |
|-------|---------------|------------|-------|-----------------|
| 1     | 5 mol %       | 2 mL       | 90°C  | 5%              |
| 2     | 10 mol %      | 2 mL       | 90°C  | 10%             |
| 3     | 15 mol %      | 2 mL       | 90°C  | 36%             |
| 4     | 20 mol %      | 2 mL       | 90°C  | 65%             |
| 5     | 40 mol %      | 2 mL       | 90°C  | 60%             |
| 6     | 50 mol %      | 2 mL       | 90°C  | 76%\(^c\)       |
| 7     | 20 mol %      | 2 mL       | 100°C | 62%             |
| 8\(^d\) | 20 mol %    | 2 mL       | 80°C  | 43%             |
| 9\(^d\) | 20 mol %    | 2 mL       | 70°C  | 6%              |
| 10    | 20 mol %      | 1 mL       | 90°C  | 76% (73%\(^c\))|
| 11\(^e\) | 20 mol %    | 1 mL       | 90°C  | 67%             |
| 12\(^f\) | 20 mol %    | 1 mL       | 90°C  | 54%             |
| 13\(^g\) | 20 mol %    | 1 mL       | 90°C  | 70%             |
| 14\(^h\) | 20 mol %    | 1 mL       | 90°C  | 40%             |

**Table S4.** Optimizations of reaction conditions with primary aliphatic acid, Related to Figure 3.\(^a\)

\(^a\)2 (0.5 mmol), LPO (1.0 mmol).
\(^b\)Yield detected by GC.
\(^c\)Isolated product.
\(^d\)Reaction with 8 hr.
\(^e\)2 (0.5 mmol), LPO (0.75 mmol).
\(^f\)2 (0.5 mmol), LPO (0.5 mmol).
\(^g\)2 (0.6 mmol), LPO (0.5 mmol).
\(^h\)2 (0.75 mmol), LPO (0.5 mmol).
Single Crystal Data of 55 and 56

Single crystal of 55 and 56 suitable for X-ray diffraction was mounted in Paratone oil onto a glass fiber and frozen under a nitrogen cold stream. The data was collected at 220.0(1) K using an Agilent SuperNova, Dual, Cu at zero, Atlas fitted with Cu Kα radiation (λ = 1.54184 Å). Data collection and unit cell refinement were executed by using CrysAlisPro software. Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with CrysAlisPro. The structure was solved with the SHELXT-2014 and refined with the SHELXL-2014 using Least Squares minimisation. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. CCDC 1477011 and CCDC 1476738 for 55 and 56 contain the supplementary crystallographic data. Crystal data and structure refinements of 55 and 56 are listed in Table S5 and Table S6. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
Identification code | 55  
Empirical formula | C_{24}H_{36}O_{4}  
Formula weight | 388.53  
Temperature | 220.0(1) K  
Wavelength | 1.54184 Å  
Crystal system | Orthorhombic  
Space group | P 21 21 21  
Unit cell dimensions | a = 6.16790(10) Å  
| b = 12.5681(3) Å  
| c = 29.0822(7) Å  
Volume | 2254.42(8) Å³  
Z | 4  
Density (calculated) | 1.145 Mg/m³  
Absorption coefficient | 0.603 mm⁻¹  
F(000) | 848  
Crystal size | 0.220 x 0.200 x 0.170 mm³  
Theta range for data collection | 3.831 to 73.663°.  
Index ranges | -5<=h<=7, -9<=k<=15, -23<=l<=35  
Reflections collected | 7382  
Independent reflections | 3937 [R(int) = 0.0387]  
Completeness to theta = 67.684° | 99.3 %  
Absorption correction | Semi-empirical from equivalents  
Max. and min. transmission | 1.00000 and 0.60854  
Refinement method | Full-matrix least-squares on F²  
Data / restraints / parameters | 3937 / 6 / 258  
Goodness-of-fit on F² | 1.023  
Final R indices [I>2sigma(I)] | R1 = 0.0531, wR2 = 0.1363  
R indices (all data) | R1 = 0.0649, wR2 = 0.1499  
Absolute structure parameter | 0.0(3)  
Extinction coefficient | n/a  
Largest diff. peak and hole | 0.276 and -0.212 e.Å⁻³  

**Table S5.** Crystal data and structure refinement for 55, Related to Scheme 2.
| Property                                      | Value                  |
|-----------------------------------------------|------------------------|
| Identification code                           | 56                     |
| Empirical formula                             | C_{27}H_{34}O           |
| Formula weight                                | 374.54                 |
| Temperature                                   | 100.0(2) K             |
| Wavelength                                    | 1.54184 Å              |
| Crystal system                                | Orthorhombic           |
| Space group                                   | P 21 21 21             |
| Unit cell dimensions                          | a = 6.23490(10) Å      |
|                                               | b = 28.7978(4) Å       |
|                                               | c = 11.7959(2) Å       |
| Volume                                        | 2117.97(6) Å³          |
| Z                                             | 4                      |
| Density (calculated)                          | 1.175 Mg/m³            |
| Absorption coefficient                        | 0.520 mm⁻¹             |
| F(000)                                        | 816                    |
| Crystal size                                  | 0.200 x 0.180 x 0.150 mm³ |
| Theta range for data collection               | 4.050 to 73.331°       |
| Index ranges                                  | -7<=h<=2, -31<=k<=35, -14<=l<=7 |
| Reflections collected                         | 5630                   |
| Independent reflections                       | 3761 [R(int) = 0.0141]  |
| Completeness to theta = 67.684°               | 99.9 %                 |
| Absorption correction                         | Semi-empirical from equivalents |
| Max. and min. transmission                    | 1.00000 and 0.88083    |
| Refinement method                             | Full-matrix least-squares on F² |
| Data / restraints / parameters                 | 3761 / 0 / 256         |
| Goodness-of-fit on F²                          | 1.025                  |
| Final R indices [l>2sigma(l)]                 | R1 = 0.0291, wR2 = 0.0733 |
| R indices (all data)                           | R1 = 0.0302, wR2 = 0.0742 |
| Absolute structure parameter                  | -0.29(15)              |
| Extinction coefficient                         | 0.0041(3)              |
| Largest diff. peak and hole                    | 0.252 and -0.140 e.Å⁻³ |

Table S6. Crystal data and structure refinement for 56, Related to Scheme 2.
Transparent Methods

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring unless otherwise indicated. Commercially obtained reagents were used as received. Solvents were dried by Innovative Technology Solvent Purification System. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. GC-MS data were recorded on Thermo ISQ QD. $^1$H, $^{13}$C and $^{19}$F NMR spectra were recorded on Bruker-BioSpin AVANCE III HD. Data for $^1$H NMR spectra are reported relative to chloroform as an internal standard (7.26 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. Data for $^{13}$C NMR spectra are reported relative to chloroform as an internal standard (77.23 ppm) and are reported in terms of chemical shift (ppm). HRMS data were recorded on Waters Micromass GCT Premier or Thermo Fisher Scientific LTQ FTICR-MS.

Experimental procedures for synthesis of materials

Procedure A for the synthesis of alkenes

General procedure (Haubenreisser et al., 2016): The reaction vessel was charged with phosphonium salt (1.2 equiv) in dry THF. To the stirred mixture, $n$-butyl lithium (1.2 equiv) was added under N$_2$ atmosphere at -78°C. The mixture was stirred at 0°C for 5 mins and then substituted aldehyde (1.0 equiv.) in dry THF was added dropwise in over 15 min. After stirring at rt for 4 hr, the mixture was quenched with saturated NH$_4$Cl, then extracted three times with dichloromethane and water. The combined organic layers were dried over anhydrous sodium sulfate, concentrated and purified by flash column chromatography afford the desired product.

Procedure B for the synthesis of alkenes

General procedure (Huang and Doyle, 2012): A flask was flame dried and charged with phenol (1.0 equiv), dichloromethane, and Et$_3$N (2.0 equiv). The mixture was cooled in a 0°C ice-water bath, and Tf$_2$O (1.1 equiv) was added dropwise. The mixture was allowed to warm up to room temperature and stirred at room temperature under argon for 5 hr. The resulting brown mixture was diluted with dichloromethane, washed with sat. NH$_4$Cl, and the aqueous layer was
extracted with dichloromethane. The combined organic layers were dried over MgSO₄, and the filtrate was concentrated. The crude was purified with column chromatography to afford triflate. A threaded tube was charged with triflate (1.0 equiv), potassium vinyltrifluoroborate (1.2 equiv), PdCl₂ (2 mol %), PPh₃ (6 mol %), Cs₂CO₃ (3.0 equiv) were added, then THF and water were added under N₂ atmosphere. The mixture was stirred at 85°C for overnight. The resulting dark brown mixture was allowed to cool to room temperature, diluted with dichloromethane, and washed with water. The aqueous layer was extracted with dichloromethane. The combined organic layers were dried over MgSO₄, and the filtrate was concentrated. The crude was purified with column chromatography to afford the desired product.

Procedure C for the synthesis of diacyl peroxides

\[
\text{R-OH} \xrightarrow{\text{DCC, DMAP}} \text{R-O-R}
\]

General procedure (Jian et al., 2017): A solution of DMAP (10 mol %), 30% hydrogen peroxide (1.2 equiv), and acid in CH₂Cl₂ was cooled to -5°C for about 10 min. Then DCC (1.2 equiv) was added. Then the mixture was stirred at -5°C to room temperature for 1.5 ~4 hr. The solution was concentrated on a rotary evaporator under vacuum at 10~15°C and the residue was chromatographed on silica gel to give the diacyl peroxide.

Procedure D for the synthesis of peresters

\[
\text{R²R³-OH} \xrightarrow{\text{DCC, DMAP, TBHP}} \text{R²R³-O-R³}
\]

General procedure (Zhu et al., 2017): A solution of DMAP (10 mol %), TBHP (aqueous solution, 1.2 equiv), and acid in CH₂Cl₂ was cooled to -5°C for about 10 min. Then DCC (1.2 equiv) was added. Then the mixture was stirred at -5°C to room temperature for 4 hr. The solution was concentrated on a rotary evaporator under vacuum at 20~25°C and the residue was chromatographed on silica gel to give the perester.
General procedure for the alkyl-Heck-type reaction

Procedure E for the alkyl-Heck-type reaction of alkenes

\[
\text{R} = + \text{Et} \xrightarrow{1.\text{TBHP, TFAA, } 0^\circ\text{C} \to r.t, 4\text{ hr}} \xrightarrow{2.\text{THF, HOTf, } 50^\circ\text{C, 8 hr}} \text{Et} \quad \text{n-Bu}
\]

To a flame-dried Schlenk tube were added 2-ethylhexanoic acid (1.5 mmol, 3.0 equiv), TBHP (1.5 mmol, 3.0 equiv, in decane) and TFAA (2.0 mmol, 4.0 equiv) at 0°C under the atmosphere of nitrogen. The mixture was then stirred at rt for 4 hours. After completion, THF (2 mL), alkene (0.5 mmol, 1.0 equiv) and HOTf (0.05 mmol, 10 mol %) were added into the Schlenk tube under the atmosphere of nitrogen. The mixture was then stirred at 50°C for 8 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product.

Procedure F for the alkyl-Heck-type reaction of secondary and tertiary aliphatic acids

\[
\begin{align*}
\text{R} & = \text{R}^1 \text{R}^2 \quad \text{R}^1 \text{R}^2 \quad \text{R}^1 \text{R}^2 \\
\text{1.\text{TBHP, TFAA, } 0^\circ\text{C} \to r.t, 3-5\text{ hr}} & \quad \text{2.\text{THF, HOTf, } 50^\circ\text{C, 8 hr}}
\end{align*}
\]

General procedure: To a flame-dried Schlenk tube were added acid (1.5 mmol, 3.0 equiv), TBHP (1.5 mmol, 3.0 equiv, in decane) and TFAA (2.0 mmol, 4.0 equiv) at 0°C under the atmosphere of nitrogen. The mixture was then stirred at rt for 3-5 hours. After completion, THF (2 mL), 4-tert-butylstyrene (0.5 mmol, 1.0 equiv) and HOTf (0.05 mmol, 10 mol %) were added into the Schlenk tube under the atmosphere of nitrogen. The mixture was then stirred at 50°C for 8 hours. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product.

Procedure G for the alkyl-Heck-type reaction with peresters

\[
\text{R} = \text{R}^1 \text{R}^2 \quad \text{R}^1 \text{R}^2 \quad \text{R}^1 \text{R}^2 \\
\text{THF, HOTf, } 80^\circ\text{C, 6 hr}
\]

To a flame-dried Schlenk tube were added THF (2 mL), 4-tert-butylstyrene (0.5 mmol, 1.0 equiv), perester (1.25 mmol, 2.5 equiv) and HOTf (0.1 mmol, 20 mol %) under the atmosphere of nitrogen. The mixture was then stirred at 80°C for 6 hours. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product.

Procedure H for the alkyl-Heck-type reaction with diacyl peroxides

\[
\text{R} = \text{R}^1 \text{R}^2 \quad \text{R}^1 \text{R}^2 \quad \text{R}^1 \text{R}^2 \\
\text{HOTf, THF, } 90^\circ\text{C, 6 hr}
\]

To a flame-dried Schlenk tube were added THF (2 mL), 4-tert-butylstyrene (0.5 mmol, 1.0 equiv), perester (1.25 mmol, 2.5 equiv) and HOTf (0.1 mmol, 20 mol %) under the atmosphere of nitrogen. The mixture was then stirred at 80°C for 6 hours. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product.
To a flame-dried Schlenk tube were added THF (1 mL), styrene (0.5 mmol, 1.0 equiv) diacyl peroxides (1.0 mmol, 2.0 equiv) and HOTf (0.1 mmol, 20 mol %) under the atmosphere of nitrogen. The mixture was then stirred at 90°C for 6 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product.
Experimental procedures for synthetic applications

(i)

To a flame-dried Schlenk tube were added THF (2 mL), styrene 2 (0.5 mmol, 1.0 equiv) perester 55 (1.25 mmol, 2.5 equiv) and HOTf (0.1 mmol, 20 mol %) under the atmosphere of nitrogen. The mixture was then stirred at 80°C for 8 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product 56.

(ii)

To a flame-dried Schlenk tube were added acid 1 (1.5 mmol, 3.0 equiv), TBHP (1.5 mmol, 3.0 equiv) and TFAA (2.0 mmol, 4.0 equiv) at 0°C under the atmosphere of nitrogen. The mixture was then stirred at rt for 5 hr. After completion, THF (2 mL), alkene 57 (0.5 mmol, 1.0 equiv) and HOTf (0.05 mmol, 10 mol %) were added into the Schlenk tube under the atmosphere of nitrogen. The mixture was then stirred at 50°C for 8 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product 58.

(iii)

To a flame-dried Schlenk tube were added acid 59 (1.5 mmol, 3.0 equiv), TBHP (1.5 mmol, 3.0 equiv) and TFAA (2.0 mmol, 4.0 equiv) at 0°C under the atmosphere of nitrogen. The mixture was then stirred at rt for 5 hr. After completion THF (2 mL), 4-tert-butylstyrene 27 (0.5 mmol, 1.0 equiv) and HOTf (0.05 mmol, 10 mol %) were added into the Schlenk tube under the atmosphere of nitrogen. The mixture was then stirred at 50°C for 8 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product 60.
Experimental procedures for preliminary mechanistic studies

Radical clock experiment

To a flame-dried Schlenk tube were added acid (1.5 mmol, 3.0 equiv), TBHP (1.5 mmol, 3.0 equiv) and TFAA (2.0 mmol, 4.0 equiv) at 0°C under the atmosphere of nitrogen. The mixture was then stirred at rt for 5 hr. After completion, THF (2 mL), styrene (0.5 mmol, 1.0 equiv) and HOTf (0.05 mmol, 10 mol %) were added into the Schlenk tube under the atmosphere of nitrogen. The mixture was then stirred at 50°C for 8 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product 61.

Deuterium labeling experiment

To a flame-dried Schlenk tube were added THF (1 mL), 2 (1.0 mmol, 1.0 equiv), d8-2 (1.0 mmol, 1.0 equiv), LPO (0.5 mmol, 0.5 equiv) and HOTf (0.1 mmol, 20 mol %) under the atmosphere of nitrogen. The mixture was then stirred at 90°C for 6 hr. After completion detected by TLC, the solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired product 44 and d7-44.

To a flame-dried Schlenk tube were added THF (2 mL), d8-2 (0.50 mmol, 1.0 equiv), 62 (1.25 mmol, 2.5 equiv) and HOTf (0.1 mmol, 20 mol %) under the atmosphere of nitrogen. The mixture was then stirred at 80°C. The reaction mixture was tested by GC-MS after 5 minutes and 30 minutes. The deuterated side-products d(OD)-butanol was detected by GC-MS. The mixture was then stirred at 80°C for 6 hr. After the reaction mixture was cooled to ambient temperature. The solvent was removed by rotary evaporation under vacuum, and the residue was chromatographed on silica gel to give the desired d7-3.
Exclusion of possible intermediates

\[
\begin{align*}
\text{OOC}_{11}H_{23} & \quad \xrightarrow{\text{THF, 90°C, 6 hr}} \quad \text{PhC}_{11}H_{23} \\
\text{63} & \quad \text{0%, 63 was recovered in 92% yield} \\
\text{63} & \quad \text{0%, C}_{11}H_{23}\text{COOH (1 equiv), 63 was recovered in 93% yield} \\
& \quad \text{91%, HOTf (20 mol %).}
\end{align*}
\]

Ester 63 (Ge et al., 2017): (0.2 mmol) was charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6 hr. No reaction was observed and the ester 63 was recovered in 92% yield.

Ester 63 (0.2 mmol) and C\text{11}H\text{23}COOH (1 equiv) were charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6 hr. No reaction was observed and the ester 63 was recovered in 93% yield.

Ester 63 (0.2 mmol) and HOTf (20 mol %) were charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6 hr. The reaction mixture was diluted with DCM (30 mL) and washed with saturated aq. NaHCO₃. The organic layer was dried (anhydrous Na₂SO₄), filtered, and concentrated in vacuo. The residue was chromatographed on silica gel affording product 44 in 91% yield.

\[
\begin{align*}
\text{C}_{11}H_{23}OH & \quad \xrightarrow{\text{THF, 90°C, 6 hr}} \quad \text{PhC}_{11}H_{23} \\
\text{64} & \quad \text{0%, 64 was recovered in 93% yield} \\
& \quad \text{0%, C}_{11}H_{23}\text{COOH (1 equiv), 64 was recovered in 93% yield} \\
& \quad \text{87%, HOTf (20 mol %, 6 hr).}
\end{align*}
\]

Benzyl alcohol 64 (Jian et al., 2017) (0.2 mmol) was charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6 hr. No reaction was observed and the alcohol 64 was recovered in 93% yield.

Benzyl alcohol 64 (0.2 mmol) and C\text{11}H\text{23}COOH (1 equiv) were charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6 hr. No reaction was observed and the alcohol 64 was recovered in 93% yield.

Benzyl alcohol 64 (0.2 mmol) and HOTf (20 mol %) were charged in anhydrous THF (0.5 mL) at 90°C and then stirred for 6 hr. The reaction mixture was diluted with DCM (30 mL) and washed with saturated aq. NaHCO₃. The organic layer was dried (anhydrous Na₂SO₄), filtered, and concentrated in vacuo. The residue was chromatographed on silica gel affording product 44 in 87% yield.
Characterization of all compounds

Following procedure A for the synthesis of alkenes, 4-bromo-2-fluoro-1-vinylbenzene (related to Figure 1) was obtained as a clear liquid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.34 (t, $J = 8.3$ Hz, 1H), 7.26 – 7.19 (m, 2H), 6.79 (dd, $J = 17.7, 11.2$ Hz, 1H), 5.81 (d, $J = 17.7$ Hz, 1H), 5.40 (d, $J = 11.2$ Hz, 1H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 159.92 (d, $J = 254.0$ Hz), 128.45 (d, $J = 3.6$ Hz), 128.11 (d, $J = 4.4$ Hz) 127.43 (d, $J = 3.7$ Hz), 124.49 (d, $J = 12.4$ Hz), 121.34 (d, $J = 9.7$ Hz), 119.34 (d, $J = 25.5$ Hz), 117.10 (d, $J = 4.7$ Hz). $^{19}$F NMR (376 MHz, Chloroform-$d$) $\delta$ -115.94.

Following procedure A for synthesis of alkenes, 1-(methylsulfonyl)-4-vinylbenzene (related to Figure 1) was obtained as a white solid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.90 (d, $J = 8.4$ Hz, 2H), 7.58 (d, $J = 8.3$ Hz, 2H), 6.77 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.91 (d, $J = 17.6$ Hz, 1H), 5.47 (d, $J = 10.9$ Hz, 1H), 3.05 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 142.88, 139.34, 135.21, 127.74, 126.95, 118.02, 44.57.

Following procedure B for synthesis of alkenes, 6-vinyl-1,2,3,4-tetrahydronaphthalene (related to Figure 1) was obtained as a clear liquid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.14 (d, $J = 7.8$ Hz, 1H), 7.09 (s, 1H), 7.01 (d, $J = 7.9$ Hz, 1H), 6.65 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.67 (d, $J = 17.6$ Hz, 1H), 5.15 (d, $J = 10.9$ Hz, 1H), 2.79 – 2.70 (m, 4H), 1.84 – 1.74 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 137.19, 137.03, 136.91, 134.91, 129.32, 127.05, 123.27, 112.64, 29.46, 29.28, 23.26.

Following procedure B for synthesis of alkenes, (8R,9S,13S,14S)-13-Methyl-3-vinyl-6,7,8,9,11,12,13,14,15,16-decahydro-17$^H$-cyclopenta[a]phenanthren-17-one (compound 57, related to scheme 2) was obtained as a white solid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.28 – 7.20 (m, 2H), 7.14 (s, 1H), 6.66 (dd, $J = 17.6, 10.9$ Hz, 1H), 5.70 (dd, $J = 17.6, 1.0$ Hz, 1H), 5.19 (dd, $J = 10.9, 0.9$ Hz, 1H), 2.91 (dd, $J = 9.0, 4.2$ Hz, 2H), 2.50 (dd, $J = 18.8, 8.7$ Hz, 1H), 2.45 – 2.39 (m, 1H), 2.34 – 2.25 (m, 1H), 2.19 – 1.93 (m, 4H), 1.66 – 1.41 (m, 6H), 0.91 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 220.89, 139.55, 136.59, 135.22, 126.89, 125.56, 123.62, 113.20, 50.52, 48.00, 44.46, 38.18, 35.88, 31.61, 29.40, 26.52, 25.74, 21.61, 13.87. The spectrum data matches previously reported values.
Following procedure C for synthesis of diacyl peroxides, hexanoic peroxyanhydride (related to Figure 3) was obtained as a clear liquid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 2.42 (t, $J = 7.5$ Hz, 4H), 1.78 – 1.66 (m, 4H), 1.41 – 1.29 (m, 8H), 0.91 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 169.25, 31.03, 29.95, 24.49, 22.15, 13.78.

Following procedure C for synthesis of diacyl peroxides, octanoic peroxyanhydride (related to Figure 3) was obtained as a clear liquid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 2.42 (t, $J = 7.5$ Hz, 4H), 1.71 (p, $J = 7.4$ Hz, 4H), 1.42 – 1.22 (m, 16H), 0.87 (t, 6H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 169.25, 31.54, 30.00, 28.87, 28.75, 24.81, 22.55, 14.00.

Following procedure C for synthesis of diacyl peroxides, 3-cyclopentylpropanoic peroxyanhydride (related to Figure 3) was obtained as a clear liquid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 2.44 (t, $J = 7.8$ Hz, 4H), 1.86 – 1.69 (m, 10H), 1.68 – 1.49 (m, 8H), 1.17 – 1.03 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 169.39, 39.46, 32.29, 30.94, 29.35, 25.10.

Following procedure C for synthesis of diacyl peroxides, 5-chloropentanoic peroxyanhydride (related to Figure 3) was obtained as a clear liquid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 3.61 – 3.54 (m, 4H), 2.53 – 2.45 (m, 4H), 1.97 – 1.82 (m, 8H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 168.70, 44.17, 31.36, 29.14, 22.09.

Following procedure C for synthesis of diacyl peroxides, 2-((3r,5r,7r)-adamantan-1-yl)acetic peroxyanhydride (related to Figure 3) was obtained as a white solid. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 2.19 (s, 4H), 2.00 (s, 6H), 1.74 – 1.62 (m, 24H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 166.72, 44.46, 42.11, 36.53, 32.99, 28.55.
Following procedure C for synthesis of diacyl peroxides, 5-oxohexanoic peroxyanhydride (related to Figure 3) was obtained as a white solid. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 2.60 (t, $J = 7.0$ Hz, 4H), 2.49 (t, $J = 7.1$ Hz, 4H), 2.16 (s, 6H), 1.97 (p, $J = 6.9$ Hz, 4H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 207.42, 168.74, 41.59, 29.94, 28.88, 18.63.

Following procedure C for synthesis of diacyl peroxides, 6-methoxy-6-oxohexanoic peroxyanhydride (related to Figure 3) was obtained as a white solid. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 3.67 (s, 6H), 2.46 (t, $J = 7.0$ Hz, 4H), 2.35 (t, $J = 6.9$ Hz, 4H), 1.81 – 1.68 (m, 8H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 173.46, 168.75, 51.59, 33.42, 29.65, 24.21, 24.09.

Following procedure C for synthesis of diacyl peroxides, 5-oxo-5-phenylpentanoic peroxyanhydride (related to Figure 3) was obtained as a white solid. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 8.00 – 7.93 (m, 4H), 7.63 – 7.54 (m, 2H), 7.53 – 7.42 (m, 4H), 3.14 (t, $J = 7.0$ Hz, 4H), 2.60 (t, $J = 7.0$ Hz, 4H), 2.18 (p, $J = 7.0$ Hz, 4H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 198.85, 168.92, 136.68, 133.21, 128.64, 128.03, 36.85, 29.23, 19.20.

Following procedure C for synthesis of diacyl peroxides, 4-bromobutanoic peroxyanhydride (related to Figure 3) was obtained as a clear liquid. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 3.55 – 3.40 (m, 4H), 2.69 – 2.56 (m, 4H), 2.31 – 2.14 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 168.19, 31.77, 28.39, 27.60.
Following procedure C for synthesis of diacyl peroxides, dec-9-enoic peroxyanhydride (related to Figure 3) was obtained as a clear liquid. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 5.88 – 5.72 (m, 2H), 5.17 – 4.77 (m, 4H), 2.42 (t, $J = 7.4$ Hz, 4H), 2.11 – 1.94 (m, 4H), 1.80 – 1.64 (m, 4H), 1.52 – 1.16 (m, 16H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 169.20, 138.99, 114.23, 33.71, 29.97, 28.92, 28.84, 28.80, 28.78, 24.78.

Following procedure D for synthesis of peresters, tert-butyl (1s,3r,5s,7s)-4-oxoadamantane-1-carboperoxoate (related to Figure 2) was obtained as a clear liquid. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 2.62 (t, $J = 3.0$ Hz, 2H), 2.27 (d, $J = 2.9$ Hz, 4H), 2.22 (q, $J = 3.1$ Hz, 1H), 2.19 (d, $J = 3.2$ Hz, 2H), 2.11 – 1.99 (m, 4H), 1.32 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 215.64, 172.31, 83.74, 45.66, 40.59, 39.99, 38.12, 37.81, 27.15, 26.07.

Following procedure D for synthesis of peresters, tert-butyl 4,4-difluorocyclohexane-1-carboperoxoate (related to Figure 2) was obtained as a white solid. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 2.54 – 2.44 (m, 1H), 2.21 – 2.08 (m, 2H), 2.06 – 1.71 (m, 6H), 1.33 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 171.35, 122.25 (t, $J = 241.2$ Hz), 83.65, 38.63, 32.45 (t, $J = 24.7$ Hz), 26.11, 25.22 (dd, $J = 7.8$ Hz, $J = 2.5$ Hz). $^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -94.22 (d, $J = 238.5$ Hz), -99.94 (d, $J = 237.9$ Hz).

Following procedure D for synthesis of peresters, tert-butyl tetrahydro-2H-pyran-4-carboperoxoate (related to Figure 2) was obtained as a clear liquid. $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 4.00 (t, $J = 3.6$ Hz, 1H), 3.97 (t, $J = 3.6$ Hz, 1H), 3.48 – 3.41 (m, 2H), 2.68 – 2.59 (m, 1H), 1.93 – 1.82 (m, 4H), 1.33 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 171.51, 83.58, 66.87, 38.30, 28.58, 26.11.
Following procedure D for synthesis of peresters, tert-butyl 2-(1,3-dioxoisooindolin-2-yl)propaneperoxoate (related to Figure 2) was obtained as a clear liquid. \(^{1}\)H NMR (400 MHz, Chloroform-\(d_2\)) \(\delta\) 7.83 – 7.78 (m, 2H), 7.71 – 7.66 (m, 2H), 5.00 (q, \(J = 7.3\) Hz, 1H), 1.68 (d, \(J = 7.3\) Hz, 3H), 1.21 (s, 9H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d_2\)) \(\delta\) 167.08, 166.96, 134.35, 131.73, 123.59, 84.49, 46.38, 26.04, 15.28.

Following procedure D for synthesis of peresters, tert-butyl 1-tosylpiperidine-3-carboperoxoate (related to Figure 2) was obtained as a white solid. \(^{1}\)H NMR (400 MHz, Chloroform-\(d_2\)) \(\delta\) 7.64 (d, \(J = 8.1\) Hz, 2H), 7.33 (d, \(J = 8.0\) Hz, 2H), 3.80 (dd, \(J = 11.6, 3.7\) Hz, 1H), 3.66 – 3.56 (m, 1H), 2.77 – 2.65 (m, 1H), 2.56 (t, \(J = 10.9\) Hz, 1H), 2.44 (s, 3H), 2.40 – 2.29 (m, 1H), 2.03 – 1.88 (m, 1H), 1.83 – 1.76 (m, 1H), 1.73 – 1.61 (m, 1H), 1.56 – 1.42 (m, 1H), 1.33 (s, 9H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d_2\)) \(\delta\) 170.12, 143.81, 132.89, 129.78, 127.66, 83.94, 47.55, 46.19, 39.23, 26.67, 26.12, 23.84, 21.54.

Following procedure D for synthesis of peresters, tert-butyl(8\(S\),9\(S\),10\(R\),13\(S\),14\(S\),17\(S\))-10,13-dimethyl-3-oxo-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1\(H\)-cyclopenta[a]phenanthrene-17-carboperoxoate (compound 55, related to scheme 2) was obtained as a white solid. \(^{1}\)H NMR (400 MHz, Chloroform-\(d_2\)) \(\delta\) 5.74 (s, 1H), 2.50 – 2.25 (m, 5H), 2.24 – 2.13 (m, 1H), 2.09 – 2.00 (m, 2H), 1.95 – 1.82 (m, 2H), 1.80 – 1.66 (m, 3H), 1.64 – 1.56 (m, 3H), 1.51 – 1.39 (m, 1H), 1.33 (s, 9H), 1.19 (s, 3H), 1.15 – 1.04 (m, 2H), 1.02 – 0.92 (m, 1H), 0.80 (s, 3H). \(^{13}\)C NMR (100 MHz, Chloroform-\(d_2\)) \(\delta\) 199.42, 170.94, 170.84, 123.96, 82.94, 55.30, 53.66, 52.67, 44.14, 38.59, 37.89, 35.72, 35.67, 33.95, 32.76, 31.88, 26.32, 24.45, 23.88, 20.90, 17.38, 13.46.
Following the procedure E, product 3 (related to Figure 1) was obtained as a clear liquid (75.8 mg, 75% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.36 (d, $J = 7.5$ Hz, 2H), 7.29 (t, $J = 7.5$ Hz, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 6.32 (d, $J = 15.8$ Hz, 1H), 5.95 (dd, $J = 15.8, 9.0$ Hz, 1H), 2.05 – 1.95 (m, 1H), 1.52 – 1.40 (m, 2H), 1.34 – 1.22 (m, 6H), 0.88 (t, $J = 7.5$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 138.09, 135.64, 129.78, 128.55, 126.82, 126.08, 45.30, 35.02, 29.78, 28.36, 23.02, 14.24, 11.98. The spectrum data matches previously reported values (Xu et al., 2017).

Following the procedure E, product 4 (related to Figure 1) was obtained as a clear liquid (87.5 mg, 81% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.25 (d, $J = 7.8$ Hz, 2H), 7.09 (d, $J = 7.7$ Hz, 2H), 6.29 (d, $J = 15.8$ Hz, 1H), 5.89 (dd, $J = 15.8, 9.0$ Hz, 1H), 2.32 (s, 3H), 2.03 – 1.94 (m, 1H), 1.52 – 1.39 (m, 2H), 1.37 – 1.20 (m, 6H), 0.87 (t, $J = 7.2$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 136.41, 135.24, 134.61, 129.44, 129.17, 125.87, 45.19, 34.97, 29.69, 28.31, 22.93, 21.16, 14.17, 11.91. HRMS (El+) calcd for [C$_{16}$H$_{24}$]+ ([M]+): 216.1878, found: 216.1887.

Following the procedure E, product 5 (related to Figure 1) was obtained as a clear liquid (78.8 mg, 73% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.21 – 7.13 (m, 3H), 7.00 (d, $J = 7.2$ Hz, 1H), 6.29 (d, $J = 15.8$ Hz, 1H), 5.94 (dd, $J = 15.8, 9.0$ Hz, 1H), 2.33 (s, 3H), 2.05 – 1.95 (m, 1H), 1.52 – 1.41 (m, 2H), 1.35 – 1.24 (m, 6H), 0.88 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 138.01, 135.40, 129.81, 128.45, 127.59, 126.74, 123.24, 45.31, 35.03, 29.76, 28.37, 22.99, 21.49, 14.21, 11.96. HRMS (El+) calcd for [C$_{16}$H$_{24}$]+ ([M]+): 216.1878, found: 216.1880.

Following the procedure E, product 6 (related to Figure 1) was obtained as a clear liquid (79.9 mg, 74% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.41 (d, $J = 7.0$ Hz, 1H), 7.16 – 7.08 (m, 3H), 6.50 (d, $J = 15.6$ Hz, 1H), 5.79 (dd, $J = 15.6, 9.0$ Hz, 1H), 2.33 (s, 3H), 2.07 – 1.98 (m, 1H), 1.52 – 1.45 (m, 2H), 1.36 – 1.27 (m, 6H), 0.90 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 137.33, 137.09, 134.90, 130.12, 127.66, 126.72, 126.00, 125.61, 45.45, 34.91,
Following the procedure E, product 7 (related to Figure 1) was obtained as a clear liquid (90.7 mg, 79% yield). \( ^1 \)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.24 (s, 1H), 7.01 (d, \( J = 7.7 \) Hz, 1H), 6.93 (dd, \( J = 7.8, 1.9 \) Hz, 1H), 6.48 (d, \( J = 15.6 \) Hz, 1H), 5.77 (dd, \( J = 15.7, 9.1 \) Hz, 1H), 2.31 (s, 3H), 2.29 (s, 3H), 2.07 – 1.98 (m, 1H), 1.54 – 1.42 (m, 2H), 1.37 – 1.25 (m, 6H), 0.93 – 0.86 (m, 6H). \( ^{13} \)C NMR (100 MHz, Chloroform-d) \( \delta \) 137.01, 136.75, 135.32, 131.84, 130.07, 127.70, 127.48, 126.16, 45.48, 34.95, 29.70, 28.32, 22.88, 21.07, 19.43, 14.17, 11.94. HRMS (EI+) calcd for \([C_{16}H_{24}]^+ \) ([M]+): 216.1878, found: 216.1883.

Following the procedure E, product 8 (related to Figure 1) was obtained as a clear liquid (108 mg, 84% yield). \( ^1 \)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.43 – 7.26 (m, 4H), 6.30 (d, \( J = 15.8 \) Hz, 1H), 5.91 (dd, \( J = 15.8, 9.0 \) Hz, 1H), 2.06 – 1.95 (m, 1H), 1.53 – 1.41 (m, 2H), 1.35 – 1.24 (m, 15H), 0.87 (t, \( J = 7.3 \) Hz, 6H). \( ^{13} \)C NMR (100 MHz, Chloroform-d) \( \delta \) 149.75, 135.25, 134.86, 129.36, 125.68, 125.42, 45.27, 35.02, 34.52, 31.38, 29.71, 28.37, 22.92, 14.18, 11.93. HRMS (EI+) calcd for \([C_{19}H_{26}]^+ \) ([M]+): 258.2348, found: 258.2343.

Following the procedure E, product 9 (related to Figure 1) was obtained as a white solid (94.5 mg, 68% yield). \( ^1 \)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.59 – 7.55 (m, 2H), 7.54 – 7.50 (m, 2H), 7.43 – 7.38 (m, 4H), 7.33 – 7.26 (m, 1H), 6.36 (d, \( J = 15.8 \) Hz, 1H), 6.00 (dd, \( J = 15.8, 9.0 \) Hz, 1H), 2.08 – 1.97 (m, 1H), 1.55 – 1.44 (m, 2H), 1.37 – 1.24 (m, 6H), 0.92 – 0.85 (m, 6H). \( ^{13} \)C NMR (100 MHz, Chloroform-d) \( \delta \) 141.01, 139.61, 137.12, 135.90, 129.26, 128.82, 127.26, 127.19, 126.98, 126.45, 45.34, 34.99, 29.76, 28.34, 22.99, 14.23, 11.98. HRMS (EI+) calcd for \([C_{21}H_{26}]^+ \) ([M]+): 278.2035, found: 278.2040.

Following the procedure E, product 10 (related to Figure 1) was obtained as a clear liquid (87.6 mg, 70% yield). \( ^1 \)H NMR (400 MHz, Chloroform-d) \( \delta \) 7.36 – 7.28 (m, 4H), 6.32 (d, \( J = 15.8 \) Hz, 1H), 5.97 (dd, \( J = 15.8, 9.0 \) Hz, 1H), 4.57 (s, 2H), 2.07 – 1.96 (m, 1H), 1.53 – 1.41 (m, 2H), 1.35 – 1.23 (m, 6H), 0.87 (t, \( J = 7.3 \) Hz, 6H). \( ^{13} \)C NMR (100 MHz, Chloroform-d) \( \delta \) 138.25,
Following the procedure E, product 11 (related to Figure 1) was obtained as a clear liquid (105.4 mg, 75% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.40 (d, $J = 8.5$ Hz, 2H), 7.21 (d, $J = 8.5$ Hz, 2H), 6.26 (d, $J = 15.8$ Hz, 1H), 5.94 (dd, $J = 15.8$, 9.0 Hz, 1H), 2.05 – 1.95 (m, 1H), 1.51 – 1.42 (m, 2H), 1.35 – 1.22 (m, 6H), 0.87 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 136.89, 136.53, 131.49, 128.46, 127.51, 120.30, 45.17, 34.74, 29.64, 28.10, 22.87, 14.12, 11.86. HRMS (EI+) calcd for [C$_{16}$H$_{24}$Cl]+ ([M]+): 250.1488, found: 250.1485.

Following the procedure E, product 12 (related to Figure 1) was obtained as a clear liquid (93.9 mg, 80% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.29 – 7.22 (m, 4H), 6.27 (d, $J = 15.8$ Hz, 1H), 5.93 (dd, $J = 15.8$, 9.0 Hz, 1H), 2.06 – 1.95 (m, 1H), 1.54 – 1.41 (m, 2H), 1.35 – 1.24 (m, 6H), 0.87 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 136.48, 136.39, 132.25, 128.57, 128.44, 127.17, 45.16, 34.78, 29.65, 28.13, 22.88, 14.12, 11.85. The spectrum data matches previously reported values (Mai et al., 2016)

Following the procedure E, product 13 (related to Figure 1) was obtained as a clear liquid (81.3 mg, 69% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.51 (dd, $J = 7.8$, 1.8 Hz, 1H), 7.32 (d, $J = 7.9$ Hz, 1H), 7.19 (t, $J = 7.4$ Hz, 1H), 7.15 – 7.09 (m, 1H), 6.70 (d, $J = 15.8$ Hz, 1H), 5.93 (dd, $J = 15.8$, 9.0 Hz, 1H), 2.13 – 2.04 (m, 1H), 1.52 – 1.43 (m, 2H), 1.35 – 1.27 (m, 6H), 0.90 (t, $J = 7.8$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 138.53, 136.11, 132.55, 129.57, 127.74, 126.68, 125.97, 45.21, 34.70, 29.59, 28.09, 22.86, 14.12, 11.84. HRMS (EI+) calcd for [C$_{15}$H$_{21}$Cl]+ ([M]+): 236.1332, found: 236.1329.

Following the procedure E, product 14 (related to Figure 1) was obtained as a clear liquid (76.8 mg, 70% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.30 (dd, $J = 8.6$, 5.4 Hz, 2H), 6.97 (t, $J = 8.6$ Hz, 2H), 6.28 (d, $J = 15.8$ Hz, 1H), 5.86 (dd, $J = 15.8$, 9.0 Hz, 1H), 2.04 – 1.94 (m, 1H), 1.52 – 1.41 (m, 2H), 1.35 – 1.22 (m, 6H), 0.88 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 161.85 (d, $J = 245.4$ Hz), 135.34 (d, $J = 2.2$ Hz), 134.13 (d, $J = 3.3$ Hz), 128.43, 127.33 (d, $J = 7.7$ Hz), 115.26 (d, $J = 21.5$ Hz), 45.13, 34.85, 29.66, 28.20, 22.89, 14.12, 11.86. $^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -115.97. HRMS (EI+) calcd for [C$_{15}$H$_{21}$F]+ ([M]+): 225.0896, found: 225.0893.
Following the procedure E, product 15 (related to Figure 1) was obtained as a clear liquid (80.5 mg, 54% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.31 (t, $J$ = 8.3 Hz, 1H), 7.23 – 7.17 (m, 2H), 6.40 (d, $J$ = 16.0 Hz, 1H), 6.03 (dd, $J$ = 16.0, 9.0 Hz, 1H), 2.09 – 1.99 (m, 1H), 1.53 – 1.42 (m, 2H), 1.36 – 1.25 (m, 6H), 0.88 (t, $J$ = 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 159.57 (d, $J$ = 252.6 Hz), 139.09 (d, $J$ = 4.3 Hz), 128.01 (d, $J$ = 4.8 Hz), 127.26 (d, $J$ = 3.6 Hz), 124.87 (d, $J$ = 12.5 Hz), 120.99 (d, $J$ = 3.3 Hz), 119.90 (d, $J$ = 9.7 Hz), 119.19 (d, $J$ = 25.7 Hz), 45.57, 34.63, 29.60, 28.00, 22.84, 14.09, 11.81. $^{19}$F NMR (376 MHz, Chloroform-d) $\delta$ -116.27. HRMS (EI+) calcd for [C$_{15}$H$_{20}$BrF]$^+$ ([M]$^+$): 298.0732, found: 298.0739.

Following the procedure E, product 16 (related to Figure 1) was obtained as a white solid (33.6 mg, 24% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.78 (d, $J$ = 8.4 Hz, 2H), 7.44 (d, $J$ = 8.4 Hz, 2H), 6.31 (d, $J$ = 15.8 Hz, 1H), 6.08 (dd, $J$ = 15.8, 9.0 Hz, 1H), 2.96 (s, 3H), 2.05 – 1.93 (m, 1H), 1.50 – 1.36 (m, 2H), 1.29 – 1.18 (m, 6H), 0.81 (t, $J$ = 7.5 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 143.44, 140.29, 138.16, 128.11, 126.59, 45.32, 44.64, 34.57, 29.62, 27.96, 22.82, 14.08, 11.83. HRMS (EI+) calcd for [C$_{16}$H$_{24}$O$_2$S]$^+$ ([M]$^+$): 280.1497, found: 280.1501.

Following the procedure E, product 17 (related to Figure 2) was obtained as a clear liquid (91.9 mg, 73% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.84-7.78 (m, 3H), 7.72 (s, 1H), 7.63 (dd, $J$ = 8.6, 1.8 Hz, 1H), 7.50 – 7.41 (m, 2H), 6.53 (d, $J$ = 15.8 Hz, 1H), 6.13 (dd, $J$ = 15.8, 9.0 Hz, 1H), 2.16 – 2.06 (m, 2H), 1.60 – 1.52 (m, 2H), 1.43 – 1.30 (m, 6H), 0.97 – 0.91 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 136.16, 135.44, 133.75, 132.64, 129.72, 128.00, 127.79, 127.62, 126.11, 125.39, 125.27, 123.68, 45.30, 34.91, 29.69, 28.26, 22.91, 14.14, 11.92. HRMS (EI+) calcd for [C$_{19}$H$_{24}$]+ ([M]$^+$): 252.1878, found: 252.1873.

Following the procedure E, product 18 (related to Figure 1) was obtained as a clear liquid (79.8 mg, 63% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.10 (dd, $J$ = 7.9, 1.4 Hz, 1H), 7.05 (s, 1H), 6.98 (d, $J$ = 7.9 Hz, 1H), 6.25 (d, $J$ = 15.8 Hz, 1H), 5.87 (dd, $J$ = 15.8, 9.0 Hz, 1H), 2.74

220.1627, found: 220.1621.
(d, J = 6.1 Hz, 4H), 2.04 – 1.93 (m, 1H), 1.82 – 1.74 (m, 4H), 1.52 – 1.40 (m, 2H), 1.33 – 1.23 (m, 6H), 0.87 (t, J = 7.4 Hz, 6H). 13C NMR (100 MHz, Chloroform-d) δ 137.11, 135.86, 135.31, 134.47, 129.59, 129.27, 126.62, 123.16, 45.22, 35.00, 29.69, 29.49, 29.21, 28.35, 23.34, 23.32, 22.91, 14.16, 11.90. HRMS (EI+) calcd for [C19H28]⁺ ([M⁺]): 256.2191, found: 256.2197.

Following the procedure E, product 19 (related to Figure 1) was obtained as a clear liquid (89.3 mg, 82% yield). ¹H NMR (400 MHz, Chloroform-d) δ 7.24 (d, J = 8.7 Hz, 2H), 6.76 (d, J = 8.5 Hz, 2H), 6.25 (d, J = 15.8 Hz, 1H), 5.79 (dd, J = 15.8, 9.0 Hz, 1H), 4.88 (s, 1H), 2.02 – 1.94 (m, 1H), 1.52 – 1.38 (m, 2H), 1.32 – 1.25 (m, 6H), 0.87 (t, J = 7.4 Hz, 6H). 13C NMR (100 MHz, Chloroform-d) δ 154.48, 133.55, 131.06, 128.82, 127.21, 115.33, 45.08, 34.94, 29.64, 28.28, 22.89, 14.12, 11.86. HRMS (EI+) calcd for [C15H22O]⁺ ([M⁺]): 218.1671, found: 218.1673.

Following the procedure E, product 20 (related to Figure 1) was obtained as a light yellow oil (43.9 mg, 36% yield). ¹H NMR (400 MHz, Chloroform-d) δ 8.17 (d, J = 7.8 Hz, 2H), 7.50 (d, J = 7.9 Hz, 2H), 6.43 (d, J = 15.8 Hz, 1H), 6.15 (dd, J = 15.8, 8.9 Hz, 1H), 2.10 (m, 1H), 1.61 – 1.47 (m, 2H), 1.44 – 1.30 (m, 6H), 0.96 – 0.90 (m, 6H). ¹³C NMR (100 MHz, Chloroform-d) δ 142.23, 137.77, 136.14, 129.90, 125.73, 45.50, 34.99, 29.88, 28.35, 23.11, 14.34, 12.11. HRMS (DART-) calcd for [C₁₅H₂₂O₂B]⁻ ([M-H]⁻): 244.1755, found: 244.1757.

Following the procedure E, product 21 (related to Figure 1) was obtained as a clear liquid (64 mg, 52% yield). ¹H NMR (400 MHz, Chloroform-d) δ 8.04 (d, J = 8.3 Hz, 2H), 7.44 (d, J = 8.3 Hz, 2H), 6.38 (d, J = 15.8 Hz, 1H), 6.13 (dd, J = 15.8, 9.0 Hz, 1H), 2.13 – 2.00 (m, 1H), 1.56 – 1.44 (m, 2H), 1.32 – 1.25 (m, 6H), 0.91 – 0.86 (m, 6H). ¹³C NMR (100 MHz, Chloroform-d) δ 171.83, 143.37, 139.21, 130.55, 128.87, 127.33, 125.91, 45.32, 34.67, 29.63, 28.04, 22.85, 14.09, 11.85. HRMS (EI+) calcd for [C₁₆H₂₉O₂⁺]⁺ ([M⁺]): 246.1620, found: 246.1621.

Following the procedure E, product 22 (related to Figure 1) was obtained as a clear liquid (65 mg, 50% yield). ¹H NMR (400 MHz, Chloroform-d) δ 7.32 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 7.9 Hz, 2H), 6.32 (d, J = 15.8 Hz, 1H), 5.95 (dd, J = 15.8, 9.0 Hz, 1H), 3.40 (s, 2H), 2.24 (s, 6H), 2.07 – 1.95 (m, 1H), 1.54 – 1.43 (m, 2H), 1.31 – 1.26 (m, 6H), 0.92 – 0.85 (m, 6H). ¹³C NMR (100 MHz, Chloroform-d) δ 137.27, 136.89, 135.33, 129.33, 129.28, 125.84, 64.11, 45.31, 45.16, 34.88, 29.64, 28.23, 22.88, 14.12, 11.87. HRMS (EI+) calcd for [C₁₈H₂₉N⁺]⁺ ([M⁺]):
Following the procedure E, product 23 (related to Figure 1) was obtained as a clear liquid (66.3 mg, 51% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.88 (d, $J = 8.4$ Hz, 2H), 7.32 (d, $J = 8.4$ Hz, 2H), 6.28 (d, $J = 15.8$ Hz, 1H), 6.02 (dd, $J = 15.8$, 9.0 Hz, 1H), 3.82 (s, 3H), 2.01 – 1.92 (m, 1H), 1.50 – 1.33 (m, 2H), 1.32 – 1.14 (m, 6H), 0.81 (t, $J = 7.5$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 167.00, 142.49, 138.63, 129.87, 128.90, 128.19, 125.79, 51.97, 45.29, 34.68, 29.63, 28.05, 22.85, 14.09, 11.84. HRMS (EI+) calcd for [C$_{17}$H$_{24}$O$_2$]$^+$ ([M$^+$]): 260.1776, found: 260.1778.

Following the procedure E, product 24 (related to Figure 1) was obtained as a clear liquid (88.5 mg, 82% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.42 – 7.36 (m, 2H), 7.30 (t, $J = 7.7$ Hz, 2H), 7.23 – 7.19 (m, 1H), 5.48 (d, $J = 9.9$ Hz, 1H), 2.36 – 2.27 (m, 1H), 2.03 (d, $J = 1.4$ Hz, 3H), 1.54 – 1.44 (m, 2H), 1.33 – 1.22 (m, 6H), 0.88 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 144.52, 134.52, 134.42, 128.32, 126.60, 125.90, 40.63, 35.78, 29.98, 29.08, 23.21, 16.57, 14.37, 12.16. HRMS (EI+) calcd for [C$_{16}$H$_{24}$]$^+$ ([M$^+$]): 216.1878, found: 216.1875.

Following the procedure E, product 25 (related to Figure 1) was obtained as a clear liquid (129.7 mg, 93% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.37 – 7.32 (m, 2H), 7.30 – 7.21 (m, 5H), 7.21 – 7.13 (m, 3H), 5.82 (d, $J = 10.5$ Hz, 1H), 2.15 – 2.03 (m, 1H), 1.47 – 1.23 (m, 5H), 1.22 – 1.11 (m, 3H), 0.87 – 0.81 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 142.81, 141.37, 140.77, 135.25, 130.01, 128.08, 128.05, 127.01, 126.72, 126.63, 40.56, 35.47, 29.67, 28.82, 22.97, 14.11, 12.00. HRMS (EI+) calcd for [C$_{21}$H$_{26}$]$^+$ ([M$^+$]): 278.2035, found: 278.2038.

Following the procedure E, product 26 (related to Figure 1) was obtained as a clear liquid (68.2 mg, 71% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 5.27 (dd, $J = 9.8$, 1.6 Hz, 1H), 2.49 – 2.39 (m, 1H), 2.33 (q, $J = 7.5$ Hz, 2H), 1.82 (d, $J = 1.4$ Hz, 2H), 1.43 – 1.21 (m, 8H), 1.20 – 1.14 (m, 4H), 0.90 – 0.83 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 141.60, 117.98, 93.82, 79.91, 41.97, 34.89, 29.49, 28.32, 23.54, 22.90, 14.22, 14.13, 13.17, 11.77. HRMS (EI+) calcd for [C$_{14}$H$_{24}$]$^+$ ([M$^+$]): 192.1878, found: 192.1887.
Following the procedure F, product **28** (related to Figure 2) was obtained as a clear liquid (97.2 mg, 90% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.34 – 7.27 (m, 4H), 6.32 (d, $J =$ 15.8 Hz, 1H), 6.05 (dd, $J =$ 15.8, 7.9 Hz, 1H), 2.24 – 2.14 (m, 1H), 1.45 – 1.35 (m, 2H), 1.31 (s, 9H), 1.06 (d, $J =$ 6.7 Hz, 3H), 0.89 (t, $J =$ 7.4 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 149.76, 136.04, 135.22, 127.83, 125.65, 125.39, 38.96, 34.50, 31.35, 29.88, 20.33, 11.85. HRMS (EI+) calcd for [C$_{18}$H$_{24}$]$^+$ ([M]$^+$): 216.1878, found: 216.1877.

Following the procedure F, product **29** (related to Figure 2) was obtained as a clear liquid (93.4 mg, 81% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.36 – 7.27 (m, 4H), 6.31 (d, $J =$ 15.8 Hz, 1H), 5.91 (dd, $J =$ 15.8, 8.9 Hz, 1H), 1.97 – 1.87 (m, 1H), 1.52 – 1.44 (m, 2H), 1.33 – 1.28 (m, 11H), 0.87 (t, $J =$ 7.4 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 149.75, 135.23, 134.52, 129.54, 125.66, 125.38, 46.94, 34.50, 31.35, 27.91, 11.88. HRMS (EI+) calcd for [C$_{17}$H$_{26}$]$^+$ ([M]$^+$): 230.2035, found: 230.2030.

Following the procedure F, product **30** (related to Figure 2) was obtained as a clear liquid (105.8 mg, 82% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.35 – 7.27 (m, 4H), 6.29 (d, $J =$ 15.8 Hz, 1H), 5.90 (dd, $J =$ 15.8, 9.1 Hz, 1H), 2.18 – 2.08 (m, 1H), 1.37 – 1.25 (m, 17H), 0.87 (t, $J =$ 6.9 Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 149.72, 135.18, 135.06, 129.06, 125.61, 125.38, 42.91, 37.84, 34.48, 31.33, 20.46, 14.19. HRMS (EI+) calcd for [C$_{19}$H$_{30}$]$^+$ ([M]$^+$): 258.2348, found: 258.2350.

Following the procedure F, product **31** (related to Figure 2) was obtained as a clear liquid (90.9 mg, 79% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.33 – 7.26 (m, 4H), 6.31 (d, $J =$ 15.8 Hz, 1H), 6.04 (dd, $J =$ 15.8, 8.0 Hz, 1H), 2.33 – 2.23 (m, 1H), 1.36 – 1.31 (m, 4H), 1.30 (s, 9H), 1.05 (d, $J =$ 6.7 Hz, 3H), 0.91 – 0.87 (m, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 149.76, 136.32, 135.22, 127.64, 125.65, 125.39, 39.43, 37.05, 34.50, 31.36, 20.79, 20.52, 14.21. HRMS (EI+) calcd for [C$_{17}$H$_{26}$]$^+$ ([M]$^+$): 230.2035, found: 230.2038.
Following the procedure F, product 32 (related to Figure 2) was obtained as a clear liquid (115.0 mg, 95% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.33 – 7.25 (m, 4H), 6.32 (d, $J = 16.0$ Hz, 1H), 6.13 (dd, $J = 15.9, 7.0$ Hz, 1H), 2.17 – 2.06 (m, 1H), 1.91 – 1.62 (m, 6H), 1.30 (s, 9H), 1.27 – 1.13 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 149.74, 136.16, 135.30, 126.89, 125.61, 125.37, 41.18, 34.48, 33.04, 31.34, 26.21, 26.08. The spectrum data matches previously reported values (Zhu and Wei, 2014)

Following the procedure F, product 33 (related to Figure 2) was obtained as a clear liquid (80.1 mg, 75% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.33 – 7.27 (m, 4H), 6.31 – 6.26 (m, 2H), 3.14 – 3.03 (m, 1H), 2.21 – 2.13 (m, 2H), 2.00 – 1.78 (m, 4H), 1.31 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 149.82, 135.03, 134.58, 127.28, 125.67, 125.39, 38.79, 34.50, 31.34, 28.84, 18.59. HRMS (EI+) calcd for [C$_{16}$H$_{22}$]+ ([M]+): 214.1722, found: 214.1725.

Following the procedure F, product 34 (related to Figure 2) was obtained as a clear liquid (117.8 mg, 92% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.34 – 7.27 (m, 4H), 6.31 (d, $J = 15.9$ Hz, 1H), 6.19 (dd, $J = 15.9, 7.5$ Hz, 1H), 2.38 – 2.26 (m, 1H), 1.87 – 1.78 (m, 2H), 1.74 – 1.67 (m, 2H), 1.66 – 1.61 (m, 1H), 1.58 – 1.51 (m, 4H), 1.50 – 1.38 (m, 3H), 1.32 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 148.88, 136.21, 134.57, 125.52, 124.82, 124.58, 42.46, 34.02, 33.68, 30.54, 27.62, 25.49. HRMS (EI+) calcd for [C$_{19}$H$_{28}$]+ ([M]+): 256.2191, found: 256.2190.

Following the procedure G for the reaction with perester, product 35 (related to Figure 2) was obtained as a white solid (73.7 mg, 53% yield). $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.35 – 7.26 (m, 4H), 6.39 (d, $J = 16.0$ Hz, 1H), 6.10 (dd, $J = 16.0, 7.0$ Hz, 1H), 2.29 – 2.19 (m, 1H), 2.18 – 2.07 (m, 2H), 1.92 – 1.70 (m, 4H), 1.63 – 1.54 (m, 2H), 1.31 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-$d$) $\delta$ 150.29, 134.62, 132.88 (d, $J = 2.5$ Hz), 128.64, 125.74, 125.48, 122.14 (d, $J = 240.2$ Hz), 39.04, 34.54, 33.25 (dd, $J = 25.2, 22.9$ Hz), 31.32, 28.93 (d, $J = 9.2$ Hz). $^{19}$F NMR
Following the procedure G for the reaction with perester, product 36 (related to Figure 2) was obtained as a white solid (90.3 mg, 74% yield). $^1$H NMR (400 MHz, Chloroform- $d$) $\delta$ 7.34 – 7.27 (m, 4H), 6.36 (d, $J$ = 16.0 Hz, 1H), 6.11 (dd, $J$ = 15.9, 6.8 Hz, 1H), 4.02 – 3.96 (m, 2H), 3.48 – 3.37 (m, 2H), 2.40 – 2.30 (m, 1H), 1.71 – 1.65 (m, 2H), 1.61 – 1.49 (m, 2H), 1.30 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform- $d$) $\delta$ 150.30, 134.92, 134.02, 128.13, 125.90, 125.60, 67.90, 38.53, 34.67, 32.87, 31.48. HRMS (EI+) calcd for [C$_{18}$H$_{24}$F$_2$]+ ([M]+): 278.1846, found: 278.1848.

[Chemical structure image]

Following the procedure F, product 37 (related to Figure 2) was obtained as a clear liquid (104.5 mg, 70% yield, dr = 1:1). $^1$H NMR (400 MHz, Chloroform- $d$) $\delta$ 7.33 – 7.26 (m, 4H), 6.38 – 6.29 (m, 1H), 6.25 (dd, $J$ = 16.0, 6.4 Hz, 0.56H), 6.12 (dd, $J$ = 15.9, 7.0 Hz, 0.41H), 2.39 – 2.32 (m, 0.54H), 2.09 – 1.99 (m, 0.49H), 1.85 – 1.76 (m, 2H), 1.63 – 1.54 (m, 3H), 1.42 – 1.32 (m, 3H), 1.31 – 1.30 (m, 9H), 1.27 – 1.14 (m, 7H), 0.89 (t, $J$ = 6.9 Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform- $d$) $\delta$ 149.74, 136.12, 135.34, 135.29, 134.87, 127.80, 126.91, 125.60, 125.38, 125.37, 41.49, 37.31, 37.17, 34.48, 33.00, 31.34, 29.62, 29.41, 29.23, 29.05, 23.04, 23.01, 14.19. HRMS (EI+) calcd for [C$_{22}$H$_{34}$]+ ([M]+): 298.2661, found: 298.2668.

[Chemical structure image]

Following the procedure G for the reaction with perester, product 38 (related to Figure 2) was obtained as a clear liquid (95 mg, 57% yield). $^1$H NMR (400 MHz, Chloroform- $d$) $\delta$ 7.82 (dd, $J$ = 5.4, 3.1 Hz, 2H), 7.69 (dd, $J$ = 5.5, 3.0 Hz, 2H), 7.33 – 7.30 (m, 4H), 6.64 – 6.55 (m, 2H), 5.13 – 5.04 (m, 1H), 1.66 (d, $J$ = 7.1 Hz, 3H), 1.29 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform- $d$) $\delta$ 167.99, 150.97, 133.86, 133.61, 132.11, 131.80, 127.36, 126.29, 125.47, 123.13, 49.09, 34.58, 31.27, 19.06. HRMS (EI+) calcd for [C$_{22}$H$_{23}$NO$_2$]+ ([M]+): 333.1729, found: 333.1725.

[Chemical structure image]
Following the procedure F, product 39 (related to Figure 2) was obtained as clear liquid (82.1 mg, 76 % yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.36 – 7.26 (m, 4H), 6.28 (d, $J = 16.2$ Hz, 1H), 6.21 (d, $J = 16.2$, 1H), 1.31 (s, 9H), 1.11 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 149.76, 141.17, 135.27, 125.68, 125.39, 124.21, 34.49, 33.30, 31.35, 29.66. The spectrum data matches previously reported values (Aydin et al., 2009).

Following the procedure F, product 40 (related to Figure 2) was obtained as a clear liquid (102.4 mg, 80% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.35 – 7.28 (m, 4H), 6.30 (d, $J = 16.4$ Hz, 1H), 6.17 (d, $J = 16.4$ Hz, 1H), 1.64 – 1.56 (m, 2H), 1.52 – 1.46 (m, 4H), 1.42 – 1.32 (m, 4H), 1.31 (s, 9H), 1.05 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 149.74, 140.28, 135.49, 125.61, 125.40, 38.06, 36.17, 34.49, 31.36, 27.84, 26.37, 22.51. HRMS (EI+) calcd for [C$_{19}$H$_{28}$]+ ([M]+): 256.2191, found: 256.2189.

Following the procedure F, product 41 (related to Figure 2) was obtained as a white solid (128 mg, 87% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.34 – 7.27 (m, 4H), 6.22 (d, $J = 16.2$ Hz, 1H), 6.06 (d, $J = 16.3$, 1H), 2.05 – 1.99 (m, 3H), 1.77 – 1.67 (m, 12H), 1.32 – 1.29 (m, 9H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 149.71, 141.45, 135.43, 125.64, 125.37, 124.14, 42.31, 36.93, 35.11, 34.48, 31.34, 28.53. HRMS (EI+) calcd for [C$_{22}$H$_{30}$]+ ([M]+): 294.2348, found: 294.2352.

Following the procedure G for the reaction with perester, product 42 (related to Figure 2) was obtained as a white solid (127 mg, 82% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.28 – 7.20 (m, 4H), 6.21 (d, $J = 16.2$ Hz, 1H), 6.01 (d, $J = 16.3$, 1H), 2.56 – 2.52 (m, 2H), 2.17 – 2.11 (m, 1H), 1.98 – 1.84 (m, 1H), 1.23 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 217.99, 150.34, 137.54, 134.61, 125.95, 125.78, 125.49, 46.42, 43.44, 41.17, 38.66, 35.01, 34.54, 31.32, 27.78. HRMS (EI+) calcd for [C$_{22}$H$_{28}$O]+ ([M]+): 308.2140, found: 308.2134.
Following the procedure G for the reaction with perester, product 43 (related to Figure 2) was obtained as white solid (79 mg, 40% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.65 (d, $J = 8.3$ Hz, 2H), 7.34 – 7.29 (m, 4H), 7.26 (d, $J = 5.2$ Hz, 2H), 6.41 (d, $J = 16.0$ Hz, 1H), 5.96 (dd, $J = 16.0, 7.2$ Hz, 1H), 3.79 – 3.57 (m, 2H), 2.54 – 2.46 (m, 1H), 2.43 (s, 3H), 2.30 – 2.23 (m, 1H), 2.11 (t, $J = 10.9$ Hz, 1H), 1.86 – 1.65 (m, 3H), 1.30 (s, 3H), 1.13 (m, 1H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 150.53, 143.43, 134.30, 133.24, 130.25, 130.05, 129.64, 127.71, 125.82, 125.49, 51.38, 46.44, 39.08, 34.56, 31.32, 29.99, 24.43, 21.56. HRMS (EI+) calcd for [C_{24}H_{31}NO_{2}S]+ ([M]+): 397.2075, found: 397.2079.

Following the procedure H for the reaction with diacyl peroxide, product 44 (related to Figure 3) was obtained as a clear liquid (94 mg, 73% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.34 (d, $J = 7.7$ Hz, 2H), 7.28 (t, $J = 7.5$ Hz, 2H), 7.18 (t, $J = 7.2$ Hz, 1H), 6.37 (d, $J = 15.8$ Hz, 1H), 6.27 – 6.18 (m, 1H), 2.24 – 2.16 (m, 2H), 1.49 – 1.40 (m, 2H), 1.34 – 1.22 (m, 1H), 0.88 (t, $J = 6.6$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 137.97, 131.28, 129.67, 128.46, 126.73, 125.90, 33.09, 31.96, 29.71, 29.68, 29.66, 29.57, 29.42, 29.39, 29.28, 22.73, 14.15. The spectrum data matches previously reported values (Habrant et al., 2007).

Following the procedure H for the reaction with diacyl peroxide, product 45 (related to Figure 3) was obtained as a clear liquid (61 mg, 60% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.33 (d, $J = 7.6$ Hz, 2H), 7.27 (t, $J = 7.5$ Hz, 2H), 7.17 (t, $J = 7.2$ Hz, 1H), 6.37 (d, $J = 15.8$ Hz, 1H), 6.27 – 6.15 (m, 1H), 2.25 – 2.14 (m, 2H), 1.52 – 1.41 (m, 2H), 1.36 – 1.25 (m, 8H), 0.88 (t, $J = 6.5$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 137.99, 131.27, 129.71, 128.48, 126.76, 125.93, 33.11, 31.91, 29.45, 29.27, 22.73, 14.16. The spectrum data matches previously reported values (Thiot et al., 2007).

Following the procedure H for the reaction with diacyl peroxide, product 46 (related to Figure 3) was obtained as a clear liquid (59 mg, 68% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.34 (d, $J = 7.1$ Hz, 2H), 7.28 (t, $J = 7.5$ Hz, 2H), 7.22 – 7.15 (m, 1H), 6.37 (d, $J = 15.8$ Hz, 1H), 6.27 – 6.18 (m, 1H), 2.24 – 2.17 (m, 2H), 1.50 – 1.43 (m, 2H), 1.37 – 1.29 (m, 4H), 0.90 (t, $J = 6.7$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 137.97, 131.27, 129.68, 128.47, 126.74, 125.90, 33.05, 31.47, 29.09, 22.60, 14.10. The spectrum data matches previously reported values (Denmark and Wehrli, 2000).

Following the procedure H for the reaction with diacyl peroxide, product 47 (related to Figure 3) was obtained as a clear liquid (77 mg, 77% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.33 (d,
Following the procedure H for the reaction with diacyl peroxide, product 48 (related to Figure 3) was obtained as clear liquid (83 mg, 66% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.37 – 7.33 (m, 2H), 7.32 – 7.26 (m, 2H), 7.21 – 7.15 (m, 1H), 6.33 (d, $J = 15.9$ Hz, 1H), 6.29 – 6.22 (m, 1H), 1.98 – 1.93 (m, 5H), 1.73 – 1.67 (m, 3H), 1.66 – 1.59 (m, 3H), 1.55 – 1.52 (m, 6H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 137.96, 131.88, 128.48, 128.47, 127.14, 126.02, 33.19, 32.21, 31.30. The spectrum data matches previously reported values (Tanaka et al., 1987).

Following the procedure H for the reaction with diacyl peroxide, product 49 (related to Figure 3) was obtained as a clear liquid (62 mg, 55% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.36 – 7.32 (m, 2H), 7.32 – 7.27 (m, 2H), 7.23 – 7.18 (m, 1H), 6.44 (d, $J = 15.8$ Hz, 1H), 6.21 – 6.10 (m, 1H), 3.45 (t, $J = 6.7$ Hz, 2H), 2.42 – 2.34 (m, 2H), 2.07 – 1.99 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 137.43, 131.31, 128.54, 128.47, 127.09, 126.76, 125.98, 48.12, 42.61, 37.14, 33.52, 28.81. The spectrum data matches previously reported values (Matsubara and Jamison, 2010).

Following the procedure H for the reaction with diacyl peroxide, product 50 (related to Figure 3) was obtained as a clear liquid (53 mg, 55% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.38 – 7.26 (m, 4H), 7.23 – 7.17 (m, 1H), 6.40 (d, $J = 15.8$ Hz, 1H), 6.26 – 6.15 (m, 1H), 3.56 (t, $J = 6.7$ Hz, 2H), 2.29 – 2.22 (m, 2H), 2.19 – 2.17 (m, 2H), 1.90 – 1.77 (m, 2H), 1.69 – 1.57 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 137.63, 130.43, 130.06, 128.52, 126.98, 125.96, 44.98, 32.23, 32.0, 26.56. The spectrum data matches previously reported values (Hu et al., 1999).

Following the procedure H for the reaction with diacyl peroxide, product 51 (related to Figure 3) was obtained as a white solid (50.7 mg, 54% yield). $^1$H NMR (400 MHz, Chloroform-$d$) δ 7.36 – 7.26 (m, 4H), 7.24 – 7.17 (m, 1H), 6.39 (d, $J = 15.7$ Hz, 1H), 6.21 – 6.12 (m, 1H), 2.48 (t, $J = 7.4$ Hz, 2H), 2.26 – 2.19 (m, 1H), 2.14 (s, 3H), 1.82 – 1.72 (m, 1H). $^{13}$C NMR (100 MHz, Chloroform-$d$) δ 208.85, 137.57, 130.68, 129.83, 128.52, 127.01, 125.97, 42.88, 32.30, 30.02, 23.25. The spectrum data matches previously reported values (Musacchio et al., 2014).
Following the procedure H for the reaction with diacyl peroxide, product 52 (related to Figure 3) was obtained as a white solid (70 mg, 56% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.98 – 7.93 (m, 2H), 7.58 – 7.53 (m, 1H), 7.48 – 7.42 (m, 2H), 7.36 – 7.27 (m, 4H), 7.23 – 7.17 (m, 1H), 6.41 (d, $J = 15.9$ Hz, 1H), 6.27 – 6.18 (m, 1H), 3.03 (t, $J = 7.3$ Hz, 2H), 2.36 – 2.29 (m, 2H), 1.99 – 1.91 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 200.22, 137.62, 137.02, 132.96, 130.73, 129.94, 128.58, 128.51, 128.05, 126.98, 125.99, 37.75, 32.47, 31.37, 23.80. The spectrum data matches previously reported values (Hilt et al., 2016).

Following the procedure H for the reaction with diacyl peroxide, product 53 (related to Figure 3) was obtained as a white solid (61 mg, 56% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.35 – 7.25 (m, 4H), 7.21 – 7.15 (m, 1H), 6.38 (d, $J = 15.9$ Hz, 1H), 6.23 – 6.15 (m, 1H), 3.66 (s, 3H), 2.34 (t, $J = 7.5$ Hz, 2H), 2.26 – 2.19 (m, 2H), 1.74 – 1.65 (m, 2H), 1.55 – 1.46 (m, 2H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 174.11, 137.74, 130.32, 130.21, 128.49, 126.88, 125.95, 51.51, 33.96, 32.64, 28.84, 24.52. The spectrum data matches previously reported values (Ramón-Azcón et al., 2006).

Following the procedure H for the reaction with diacyl peroxide, product 54 (related to Figure 3) was obtained as a clear liquid (70 mg, 61% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.36 – 7.32 (m, 2H), 7.30 – 7.25 (m, 2H), 7.21 – 7.15 (m, 1H), 6.27 – 6.17 (m, 1H), 5.91 – 5.74 (m, 1H), 5.04 – 4.90 (m, 2H), 2.25 – 2.16 (m, 2H), 2.09 – 2.00 (m, 2H), 1.50 – 1.42 (m, 2H), 1.40 – 1.28 (m, 8H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 139.22, 137.96, 131.21, 129.73, 128.48, 126.76, 125.92, 114.17, 33.84, 33.07, 29.40, 29.21, 29.13, 28.96. The spectrum data matches previously reported values (Kulasegaram and Kulawiec, 1997).

Following the procedure G, product 56 (related to Scheme 2) was obtained as a white solid (89.8 mg, 48% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.35 – 7.32 (m, 2H), 7.31 – 7.25 (m, 2H), 7.20 – 7.15 (m, 1H), 6.26 (d, $J = 15.7$ Hz, 1H), 6.13 (dd, $J = 15.7$, 9.3 Hz, 1H), 5.73 (s, 1H), 2.46 – 2.33 (m, 4H), 2.31-2.15 (m, 1H), 2.18 – 2.09 (m, 1H), 2.03 – 1.97 (m, 1H), 1.94 – 1.88 (m, 1H), 1.85 – 1.78 (m, 1H), 1.75 – 1.62 (m, 2H), 1.55 – 1.50 (m, 3H), 1.46 – 1.37 (m, 1H), 1.36 – 1.23 (m, 3H), 1.18 (s, 2H), 1.14 – 1.04 (m, 1H), 0.97 – 0.91 (m, 1H), 0.88 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 199.61, 171.46, 137.80, 133.85, 128.88, 128.50, 126.82,
Following the procedure E, product 58 (related to Scheme 2) was obtained as a white solid (123 mg, 65% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.23 (d, $J = 8.1$ Hz, 1H), 7.16 (d, $J = 8.3$ Hz, 1H), 7.10 (s, 1H), 6.27 (d, $J = 15.8$ Hz, 1H), 5.90 (dd, $J = 15.8$, 9.0 Hz, 1H), 2.91 (dd, $J = 8.8$, 4.0 Hz, 2H), 2.50 (dd, $J = 18.7$, 8.6 Hz, 1H), 2.45 – 2.39 (m, 1H), 2.33 – 2.26 (m, 1H), 2.19 – 1.93 (m, 5H), 1.65 – 1.58 (m, 2H), 1.55 – 1.39 (m, 6H), 1.33 – 1.24 (m, 6H), 0.90 (s, 3H), 0.87 (t, $J = 7.4$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 221.13, 138.58, 136.68, 135.81, 135.24, 129.44, 126.71, 126.68, 125.70, 123.65, 123.62, 50.69, 48.20, 45.39, 44.61, 38.44, 36.06, 35.13, 31.80, 29.84, 29.62, 28.48, 26.74, 25.97, 23.05, 21.79, 14.32, 14.04, 12.06. HRMS (EI+) calcd for [C$_{27}$H$_{34}$O]$^+$ ([M]$^+$): 374.2610, found: 374.2613.

Following the procedure E, product 60 (related to Scheme 2) was obtained as a clear liquid (76 mg, 42% yield). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.34 – 7.28 (m, 4H), 6.99 (d, $J = 7.4$ Hz, 1H), 6.64 (d, $J = 8.1$ Hz, 1H), 6.60 (s, 1H), 6.29 (d, $J = 16.2$ Hz, 1H), 6.16 (d, $J = 16.2$ Hz, 1H), 3.90 (t, $J = 6.4$ Hz, 2H), 2.28 (s, 3H), 2.18 (s, 3H), 1.80 – 1.71 (m, 2H), 1.59 – 1.52 (m, 2H), 1.31 (s, 9H), 1.13 (s, 6H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 157.11, 149.90, 139.54, 136.45, 135.17, 130.28, 125.81, 125.74, 125.44, 123.62, 120.59, 112.01, 68.43, 39.44, 36.08, 34.52, 31.37, 27.37, 25.03, 21.44, 15.86. HRMS (EI+) calcd for [C$_{26}$H$_{36}$O]$^+$ ([M]$^+$): 364.2766, found: 364.2761.

Following the procedure E, product 61 (related to Scheme 3A) was obtained as a clear liquid (72.3 mg, 62%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.38 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 7.27 – 7.24 (m, 1H), 7.24 – 7.19 (m, 4H), 7.19 – 7.16 (m, 2H), 6.10 – 6.05 (m, 1H), 5.86 – 5.73 (m, 1H), 5.08 – 4.80 (m, 2H), 2.25 – 2.17 (m, 4H). $^{13}$C NMR (100 MHz, Chloroform-d) $\delta$ 142.79, 141.95, 140.19, 138.13, 129.92, 129.20, 128.16, 128.08, 127.26, 126.91, 126.86, 114.94, 34.06, 29.15. The spectrum data matches previously reported values (Jiménez-Aquino et al., 2011).
Following the procedure H, product \textit{44} and \textit{d7-44} (related to \textbf{Scheme 3B}) were obtained as a clear liquid (60\% total yield). $^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.37 – 7.31 (m, 2H), 7.31 – 7.26 (m, 2H), 7.21 – 7.15 (m, 1H), 6.37 (d, $J = 15.9$ Hz, 1H), 6.27 – 6.17 (m, 1H), 2.23 – 2.16 (m, 4H), 1.50 – 1.41 (m, 4H), 1.34 – 1.24 (m, 32H), 0.88 (t, $J = 6.8$ Hz, 6H).

Following the procedure G, product \textit{d7-3} (related to \textbf{Scheme 3B}) was obtained as a clear liquid (62.2 mg, 60\% yield). $^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 2.05 – 1.97 (m, 1H), 1.54 – 1.41 (m, 2H), 1.35 – 1.24 (m, 6H), 0.88 (t, $J = 7.5$ Hz, 6H). $^{13}$C NMR (101 MHz, Chloroform-\textit{d}) $\delta$ 137.80, 135.14 (t, $J = 22.4$ Hz), 129.14 (t, $J = 22.9$ Hz), 127.97 (t, $J = 24.00$ Hz), 126.20 (t, $J = 23.8$ Hz), 125.54 (t, $J = 23.7$ Hz), 45.02, 34.88, 29.68, 28.23, 22.92, 14.15, 11.89.

Compound \textit{63} (related to \textbf{Scheme 3C}): $^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.35-7.30 (m, 4H), 7.29-7.26 (m, 1H), 5.72 (dd, $J = 7.8$, 6.1 Hz, 1H), 2.34-2.28 (m, 2H), 1.94-1.83 (m, 1H), 1.80-1.69 (m, 1H), 1.65-1.58 (m, 2H), 1.31-1.21 (m, 36H), 0.88 (t, $J = 6.7$ Hz, 6H). $^{13}$C NMR (100 MHz, Chloroform-\textit{d}) $\delta$ 173.23, 141.10, 128.37, 127.72, 126.49, 75.86, 36.42, 34.65, 31.94, 29.68, 29.66, 29.63, 29.58, 29.50, 29.38, 29.36, 29.30, 29.14, 25.55, 25.05, 22.72, 14.15. Synthesized according to reported method (Ge et al., 2017).

Compound \textit{64} (related to \textbf{Scheme 3C}): $^1$H NMR (400 MHz, Chloroform-\textit{d}) $\delta$ 7.36 – 7.30 (m, 4H), 7.29 – 7.22 (m, 1H), 4.63 (dd, $J = 7.5$, 5.9 Hz, 1H), 2.06 (s, 1H), 1.83 – 1.73 (m, 1H), 1.72 – 1.62 (m, 1H), 1.45 – 1.35 (m, 1H), 1.31 – 1.18 (m, 19H), 0.88 (t, $J = 6.9$ Hz, 3H). $^{13}$C NMR (100 MHz, Chloroform-\textit{d}) $\delta$ 144.96, 128.43, 127.47, 125.92, 74.72, 39.14, 31.97, 29.71, 29.69, 29.64, 29.60, 29.58, 29.41, 25.88, 22.74, 14.18. Synthesized according to reported method (Jian et al., 2017).
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