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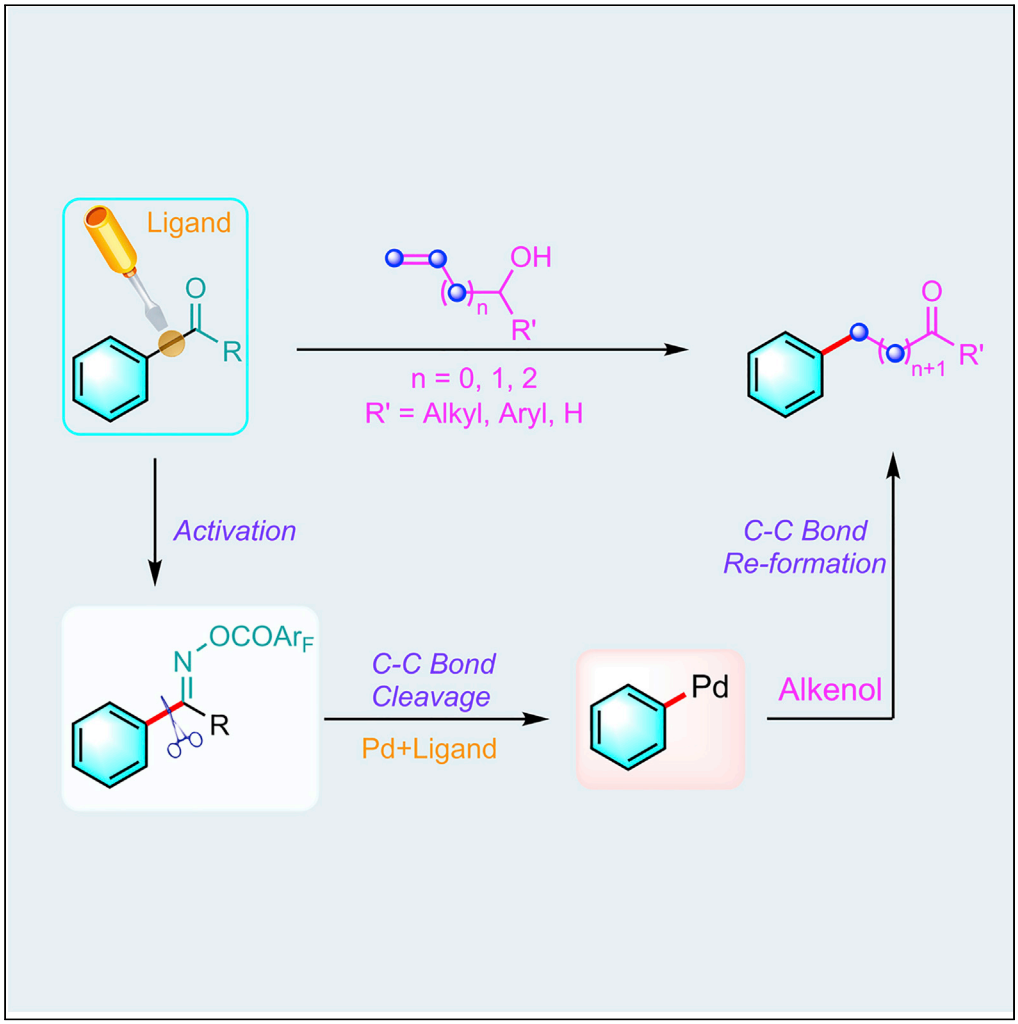

Xing Wang, Ling-Jun Li, Zhen-Yu Wang, Hui Xu, Hui-Xiong Dai

xuhui2018@simm.ac.cn (H.X.)
hxdai@simm.ac.cn (H.-X.D.)

Highlights

Ligand-promoted unstrained Ar–C(O) bond cleavage

Multi-carbon homologation of aryl ketones to long-chain ketones and aldehydes

Late-stage diversification of drug and natural product

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Homologation of aryl ketones to long-chain ketones and aldehydes via C–C bond cleavage

Xing Wang,[1] Ling-Jun Li,[1] Zhen-Yu Wang,[2] Hui Xu,[1,*] and Hui-Xiong Dai[1,2,3,4,*]

SUMMARY

Transition metal-catalyzed C–C bond cleavage is a powerful tool for the reconstruction of a molecular skeleton. We report herein the multi-carbon homologation of aryl ketones to long-chain ketones and aldehydes via ligand-promoted Ar−C(O) bond cleavage and subsequent cross coupling with alkenols. Various (hetero)aryl ketones are compatible in the reaction, affording the corresponding products wtih good to excellent yields with high regioselectivity. Further applications in the late-stage diversification of biologically important molecules demonstrate the synthetic utility of this protocol. Mechanistic studies indicate that the ligand plays an important role in both C–C bond cleavage and the asymmetric migration-insertion process.

INTRODUCTION

Functionalized long-chain ketones and aldehydes are important structural motifs commonly found in bioactive compounds and pharmaceuticals (Figure 1A) (Cao et al., 2005; Ertl and Schuhmann, 2019; Hashimoto et al., 1977; Huang et al., 2016; Itoh et al., 1999; Moser and Bode, 2008; Ngadjui et al., 1991). For example, Prasugrel hydrochloride, developed by Daiichi Sankyo & Co., is a platelet ADP P_2Y_{12} receptor antagonist, used for acute coronary syndrome (Aalla et al., 2012; Baker and White, 2009). Meanwhile, long-chain ketones and aldehyde are often employed as versatile building blocks in organic synthesis via transformations of carbonyl group, such as Grignard reactions, Wittig reactions, adol reaction, etc. (Murray, 2015; Vollhardt and Schore, 2018). Thus, the development of an efficient protocol to synthesize the long-chain ketone and aldehyde has gained much attention. Among various synthetic approaches, the Heck-type reaction of aryl reagent with alkenol is one of the most powerful methods (Beletskaya and Cheprakov, 2000; de Meijere and Meyer, 1994; Dounay and Overman, 2003; Mc Cartney and Guiry, 2011). Aryl halides (Heck and Nolley, 1972; Mizoroki et al., 1971), triflate (Cabri et al., 1992; Race et al., 2019), diazonium salts (Kikukawa and Matsuda, 1977; Patel and Sigman, 2015), boron reagents (Chen et al., 2012, 2016; Liu et al., 2019; Mei et al., 2013, 2014), carboxylic acids (Huang et al., 2013a), sulfonoly-drazide (Huang et al., 2013b), and sulfinic acid salts (Liao et al., 2015) have been developed as the aryl donors in the past few decades (Figure 1B). C−C bonds constitute the main skeleton of organic compounds. Selective C−C bond cleavage and subsequently cross-coupling with alkenol could rapidly generate diversified libraries of long-chain ketones. Recently, Kakiuchi achieved Rh(III)-catalyzed Heck-type cross couplings of styrene derivatives with allylic alcohol via chelation-assisted C−C bond cleavage (Figure 1C) (Onodera et al., 2020).

Aryl ketones are ubiquitous structural motifs found in pharmaceuticals and natural products (Larock, 1999). Homologation of the abundant aryl ketones to long-chain ketones and aldehydes via Ar−C(O) bond cleavage would be highly appealing. One-carbon homologation of aryl ketone via insertion of carbenoids into Ar−C(O) bond has been well known (Candeias et al., 2016; Sebastian et al., 2021). Very recently, Feng and coworkers elegantly achieved asymmetric one-carbon homologation of acyclic and cyclic aryl ketones with α-diazo esters in the presence of a chiral scandium(III)-N,N′-dioxide Lewis acid catalyst (Tan et al., 2021). The low valent metal-catalyzed "Cut and Sew" strategy of Ar−C(O) bond with unsaturated C−C bonds could achieve the two-carbon homologation (Chen et al., 2017; Juliá-Hernández et al., 2015; Kondo et al., 2000; Okumura et al., 2017; Xia et al., 2019; Xu and Dong, 2012). Both strained and unstrained aryl ketones were employed as the substrates, and diverse two-carbon homologated ring structures were obtained via Ar−C(O) bond cleavage and subsequent 1,2- or 2,1-insertion with alkenes and alkynes. An unconventional one-carbon homologation of unstrained aryl ketones was recently reported by Dong and Xia via the Rh-catalyzed intramolecular formal 1,1-insertion process (Huang et al., 2022). However, oxidative

[1]CAS Key Laboratory of Receptor Research, State Key Laboratory of Drug Research, Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shanghai 201203, China

[2]School of Chinese Materia Medica, Nanjing University of Chinese Medicine, Nanjing, Jiangsu 210023, China

[3]School of Pharmaceutical Science and Technology, Hangzhou Institute of Advanced Study, Hangzhou 310024, China

[4]Lead contact

*Correspondence: xuhui2018@simm.ac.cn (H.X.), hxdai@simm.ac.cn (H.-X.D.)

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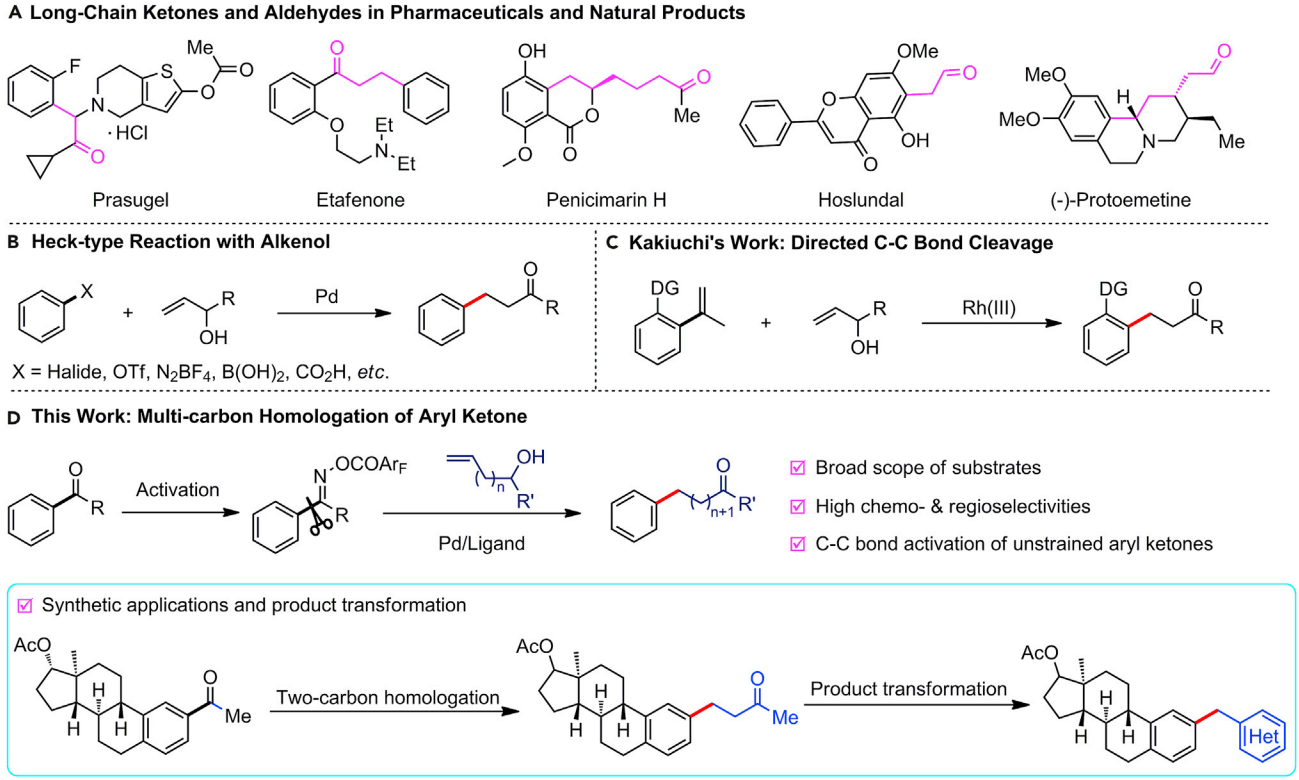


Figure 1. Synthesis of long-chain ketones and aldehydes

(A) Representative natural products and drugs containing long-chain ketones and aldehydes.

(B) Various aryl donors in the Heck-type reaction with alkenol.

(C) Directed C–C bond cleavage.

(D) This work: Multi-carbon homologation of aryl ketones to long-chain ketones and aldehydes.

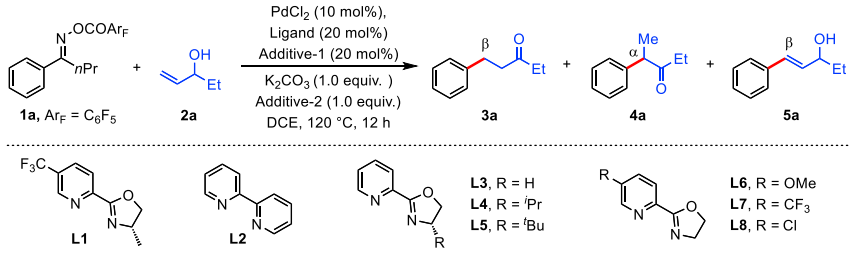
addition of a transition metal into the Ar−C(O) bond is thermodynamically unfavorable and often requires a directing group to enhance the reactivity or utilize the ring-strain release to generate stable cyclic metal species (Dong, 2014; Chen et al., 2014; Deng and Dong, 2020; Jun, 2004; Kim et al., 2017; Marek et al., 2015; Murakami and Ishida, 2016; Rybtchinski and Milstein, 1999; Souillart and Cramer, 2015; Xia and Dong, 2020; Yu et al., 2021). We envisioned that the transition metal-catalyzed Ar−C(O) bond cleavage and subsequently Heck-type coupling with alkenol could homologate aryl ketones to long-chain ketones. Recently, our group achieved the ligand-promoted C–C bond cleavage of unstrained aryl ketone (Guo et al., 2021; Li et al., 2020; Wang et al., 2021; Xu et al., 2021). In this manuscript, we report the multi-carbon homologation of aryl ketone to long-chain ketone and aldehyde via Heck-type cross coupling of alkenol with ketone-derived oxime esters (Figure 1D). By employing appropriate pyridine oxazoline ligand, the transformations were achieved with high chemo- and regioselectivity. To demonstrate the practicality, the two-carbon homologations of biologically important aryl ketones into long-chain ketones were showcased.

RESULTS AND DISCUSSION

Optimization of reaction conditions

Aryl ketones could be conveniently activated to the oxime ester derivatives that could be employed as building blocks in synthesis of various nitrogen-containing heterocycles (Bao et al., 2017; Blake et al., 2004; Faulkner et al., 2015; Huang et al., 2015;Nishimura and Uemura, 2000; Race et al., 2017; Tan and Hartwig, 2010; Tsutsui et al., 1997; Walton, 2014). Thus, we commenced our investigation by treating oxime ester **1a** and 1-penten-3-ol (**2a**) in the presence of 10 mol % $PdCl_2$, 20 mol % ligand **L1**, 2 equiv of K_2CO_3 in DCE at 120°C (Table 1). However, no desired product was observed (Entry 1). Considering that cationic palladium complexes are more electrophilic to coordinate with allyl alcohol, we screened various additives to scavenge the chloride ions (Table S1), including $NaBAr_F$, Ag_2CO_3, AgOAc, AgOTf, and $AgNTf_2$ (Entries

Table 1. Optimization of reaction conditions[a]



Entry	Ligand	Additive-1	Additive-2	Yield (%)[b] 3a/4a/5a
1	L1	w/o	–	–/–/-
2	L1	$NaBAr_F$	–	8/4/-
3	L1	Ag_2CO_3	–	Trace/–/–
4	L1	AgOAc	–	–/–/-
5	L1	AgOTf	–	Trace/–/–
6	L1	$AgNTf_2$	–	44/19/-
7	L2	$AgNTf_2$	–	59/21/-
8	L3	$AgNTf_2$	–	43/7/-
9	L4	$AgNTf_2$	–	52/23/-
10	L5	$AgNTf_2$	–	32/21/-
11	L6	$AgNTf_2$	–	62/15/10
12	L7	$AgNTf_2$	–	44/10/14
13	L8	$AgNTf_2$	–	64/12/10
14	L8	$AgNTf_2$	LiBr	56/12/8
15[c]	L8	$AgNTf_2$	n-Bu_4NBr	–/–/-
16[c]	L8	$AgNTf_2$	TsONa	66/12/4
17[c,d]	L8	$AgNTf_2$	TsONa	72 (68)[e]/12/3

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $PdCl_2$ (10 mol %), ligand (20 mol %), additive-1 (20 mol %), K_2CO_3 (0.2 mmol), additive-2 (0.1 mmol), DCE (2 mL), 120°C, N_2, 12 h
[b]The yield was determined by ^1H NMR analysis of crude reaction mixture using CH_2Br_2 as the internal standard
[c]K_2CO_3 (0.1 mmol)
[d]DCE (3 mL)
[e]isolated yield of **3a**

2–6). To our delight, 1-phenylpentan-3-one **3a** (44%) and 2-phenylpentan-3-one **4a** (19%) could be obtained by employing $AgNTf_2$ as the additive (Entry 6). Base, palladium catalysts, and solvents were also screened; however, no better results were obtained (see Tables S2–S4 in supplemental information for details). To improve the yield and regioselectivity, we examined the different type of ligands (see Schemes S3 and S4 in supplemental information for details). Phosphine ligands were detrimental to the reaction. 2,2′-Bipyridine ligand (**L2**) could effectively improve the yield to 80% with a **3a**/**4a** ratio of 59/21(Entry 7). Pyridine oxazoline (PyrOx) ligands have been widely employed in the enantioselective redox relay Heck reactions (Chen et al., 2016; Liu et al., 2019; Mei et al., 2013, 2014; Patel and Sigman, 2015). After the screening of various pyridine oxazoline ligands, **L3** could significantly improve the regioselectivity of **3a**/**4a** to 43/7, whereas PyrOx ligand with bulky substituent in oxazoline moiety yielded poor results (Entries 8–10). The regioselectivity of the aromatic ring migration onto the deactivated olefin is possibly due to the balance between electronic and steric factors: 1) The subtle electronic differences in alkenyl carbons favor the formation of the linear product **3a**; 2) Migratory insertion of Pd catalyst bearing bulky ligand to the less hindered carbon could relieve steric strain, thus favoring the formation of the branched product **4a** (Cabri et al., 1992; Mei et al., 2014). To further evaluate the electronic effects of the substituents in the ligands, modifications in pyridine moiety were investigated (Entries 11–13). To our delight, ligands containing a chloro group in the five-position of the pyridine moiety (**L8**) gave the desired product **3a** with a 64% yield

(Entry 13). Meanwhile, a 10% yield of alkenol isomer **5a** was obtained as the byproduct, which indicated that part of the PdH species was deactivated during migratory-insertion process. Considering the economic viability of the starting material, oxime ester deriving from cheaper alkanoyl and aroyl chlorides were tested, and perfluoriobenzyl oximes afforded the highest yield at 120°C under an N_2 atmosphere (For details, see Scheme S5, Tables S5 and S6 in supplemental information). To further improve the chemo- and regioselectivity, a series of additives and concentration were investigated (Entries 14–17, also see Tables S7 and S8 in supplemental information for details) (Abelman and Overman, 1988; Abelman et al., 1987; Larock and Gong, 1989; Larock et al., 1988). The addition of TsONa could efficiently inhibit the formation of **5a**. Further screening of the reaction concentration could improve the yield of **3a** to 72% with a 68% isolated yield (Entry17). Aryl ketones (including acetophenone, 1-phenylbutan-1-one, 1-phenylpentan-1-one) with different side chain, including methyl, ethyl, *n*-amyl *i*-propyl, *t*-butyl, cyclohexyl, and phenyl group, were also suitable substrates (**1a-1**–**1a-7**), giving the desired products **3a** with 21–70% isolated yields (for details, see Table S9).

Substrate scope

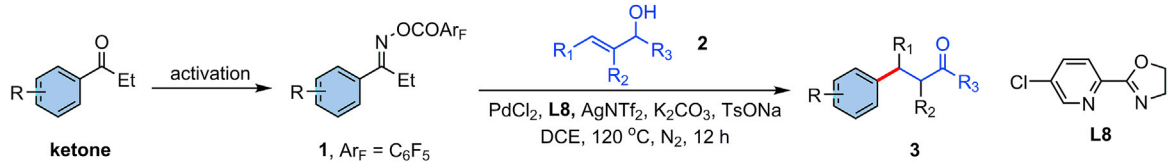
Having established the optimal reaction conditions, the scope of aryl ketones was investigated (Scheme 1). Aryl ketones bearing different substituents at the *ortho*-, *meta*-, and *para*-positions provided the corresponding two-carbon homologated products (**3a**−**3ab**) in moderate to good yields. A variety of electron-donating or electron-withdrawing groups (−Me, −OMe, −NHAc, −Sme, $-OCF_3$, −Ph, −F, −Cl, −CN, $-NO_2$, $-CF_3$, $-SiMe_3$, $-CO_2Et$, $-PO(Oet)_2$, and $-SO_2Me$) could be well accommodated under the optimal reaction conditions. A scale-up experiment with one-pot operation of aryl ketone was carried out by using propiophenone (10 mmol) as the starting material, affording the corresponding product **3a** with a 54% isolated yield. It's worth noting that very sensitive substituent including Bpin and alkenyl could be tolerated, leaving a handle for further transformation. Aryl substrates with disubstituents (**3ac**−**3af, 3ah**−**3ai**), naphthalene (**3aj**−**3al**) are also suitable substrates. This protocol shows high compatibility with various heterocycles, including furan (**3am**), thiophene (**3an**), pyridine (**3ao**−**3aq**), benzofuran (**3ar**), indole (**3as**), benzothiophene (**3at**), quinoline (**3au**, **3av**), diazole (**3aw**), triazole (**3ax**), benzoxazole (**3ay**), and benzothiazole (**3az**), delivering the desirable β-aryl ketone products with 45–81% yields.

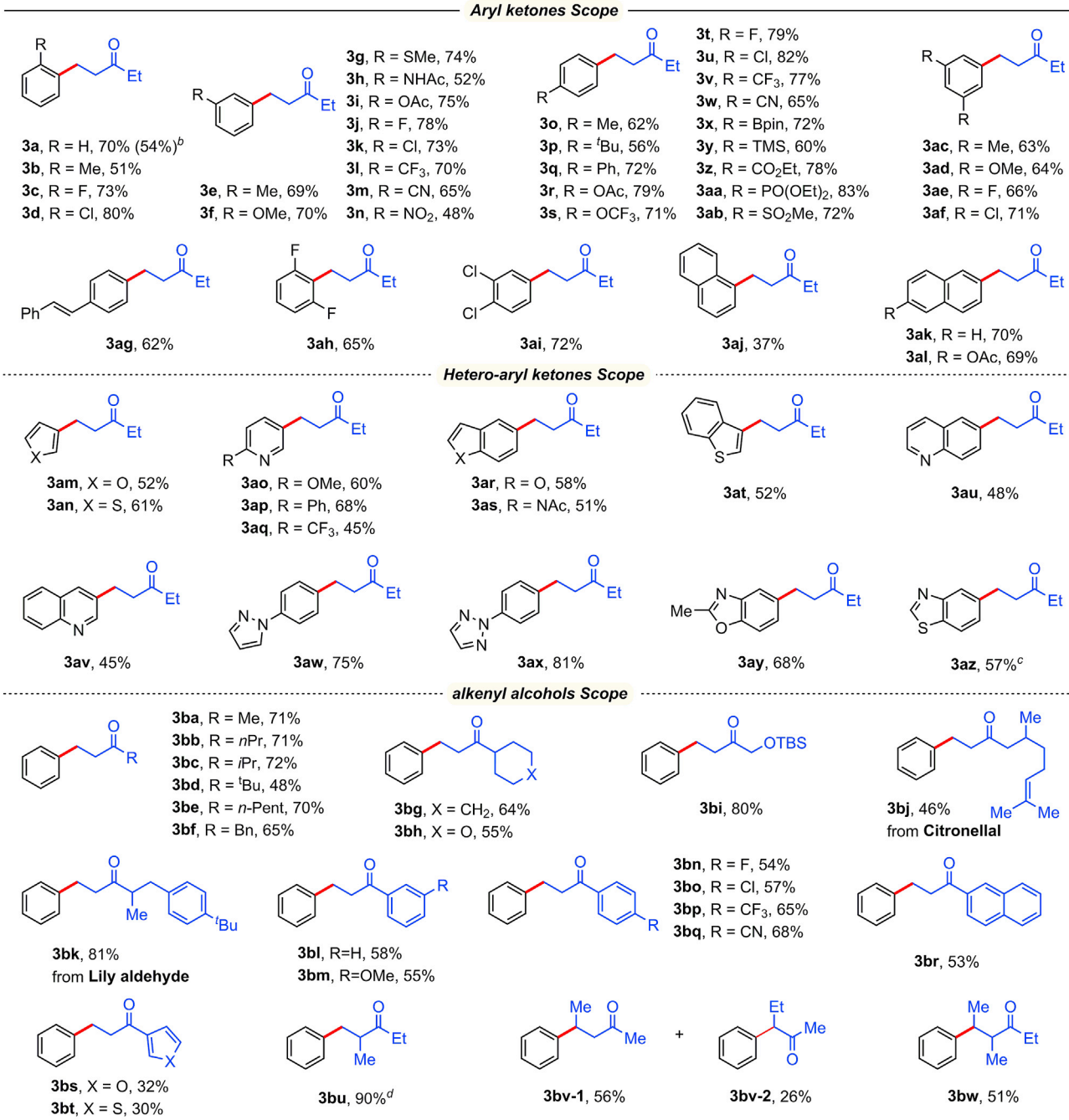
A series of alkyl substituents in alkenol were investigated (including 3-buten-2-ol, 1-hexen-3-ol, 1-octen-3-ol, and other alkenols), providing the corresponding ketone products (**3ba**−**3bg**) in moderate to good yields. Heteroatom-contained alkenols were also compatible in the reaction (**3bh**, **3bi**). In addition, the alkenols derived from the natural products Citronellal and Lily aldehyde could furnish the corresponding products with 46 and 81%, respectively (**3bj**, **3bk**). The aryl substituted alkenols with various electron-donating and electron-withdrawing groups (−OMe, −F, −Cl, $-CF_3$, and −CN) provided the desired products **3bl**−**3bq** with 54–68% yields. Moreover, heteroaryl substrates containing furan (**3bs**) and thiophene (**3bt**) were also tolerated, albeit in lower yields. Significantly, the multi-substituted alkenol substrates showed good compatibility (**3bu**−**3bw**). When 3-penten-2-ol was employed as the coupling partner, both β- and α-regioselective products were obtained with the ratio of 56/26 (**3bv**).

Furthermore, aryl ketone could be homologated to long-chain aldehydes when the primary allylic alcohol substrates **6** were used (Scheme 2).When 3-buten-1-ol was employed, both electron-donating and electron-withdrawing substituents (OMe, OAc, Cl, CF_3, CO_2Et) at the *ortho*-, *meta*-, and *para*-positions of aryl ketones delivered the desirable β-aryl aldehyde products with 54–72% yields. Heteroaryl substrates containing triazole (**7g**), pyridine (**7h**) were also well tolerated. In addition, the multi-substituted alkenol substrates (crotonyl alcohol and 3-methyl-3-buten-1-ol) showed good compatibility (**7i**, **7j**). To further explored the potential applications of this protocol, more challenging homoallyl alcohol substrates were evaluated. After the re-screening of various ligands (Scheme S6), 2,2′-bipyridine (**L2**) was employed instead of **L8**. Aryl and heteroaryl ketone derivatives (**7k-7r**) proceeded smoothly, albeit with lower regioselectivity. Moreover, the alkyl or aryl substituents at three-position of homoallyl alcohols were well tolerated with high reactivity and excellent regioselectivity (**7s**, **7t**). It is worth noting that the δ-aryl aldehyde product (**7u**) could be obtained by using 4-penten-1-ol as the substrate.

Synthetic application

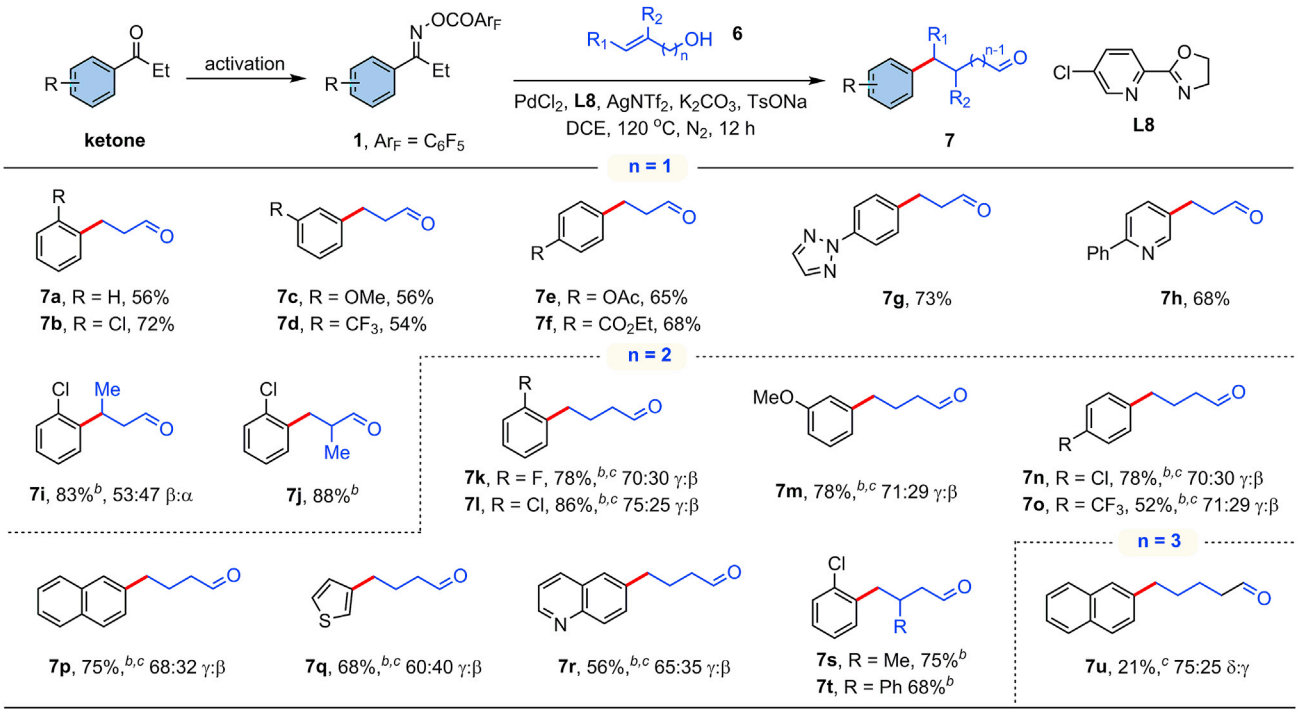
To showcase the potential applications of this protocol, two-carbon homologation of some biologically important molecules was carried out. Vrious aryl ketones derived from medicinal drugs probenecid,





Scheme 1. Homologation of Aryl Ketones to Long-chain Ketones[a]

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $PdCl_2$ (10 mol %), **L8** (20 mol %), $AgNTf_2$ (20 mol %), K_2CO_3 (0.1 mmol), TsONa (0.1 mmol), DCE (3 mL), 120 °C, N_2, 12 h.
[b]10 mmol-scale with one-pot operation of aryl ketone.
[c]*n*-Pr instead of Et in ketone oxime ester **1**.
[d]**L2** instead of **L8**.



Scheme 2. Homologation of Aryl Ketones to Long-chain Aldehydes[a]

[a]Reaction conditions: **1a** (0.1 mmol), **2a** (0.2 mmol), $PdCl_2$ (10 mol %), **L8** (20 mol %), $AgNTf_2$ (20 mol %), K_2CO_3 (0.1 mmol), TsONa (0.1 mmol), DCE (3 mL), 120 °C, N_2, 12 h.

[b]**L2**. instead of **L8**.

[c]18 h.

adapalene, homosalate, and natural products evodiamine, desoxyestrone proceeded smoothly, furnishing the corresponding products (**8a**–**8e**) with good yields (57–81%) (Figure 2A). Furthermore, derivatizations of product **8e** were performed to introduce various functional groups (Figure 2B). α-Bromination of **8e** gave α-bromoketone **9** with a 76% yield, which is a versatile building block in organic synthesis. Moreover, reductive amination of the carbonyl group was readily achieved to afford the aminated product **10** with a 98% yield. It is valuable to introduce heterocycles into drug molecules. Structurally important heterocycles, including indole (**11**), quinoline (**12**), could be efficiently constructed through Fischer indole synthesis and Friedländer annulation reaction. In addition, pyrimidine (**13**) and diazole (**14**) could also be introduced into the target molecule with moderate yields (Nguyen et al., 2020; Zhan et al., 2016).

Mechanistic studies

For a better understanding of the mechanism, some control experiments were carried out (Figure 3). First, the addition of radical scavenger 2, 2, 6, 6-tetra-methylpiperidine-N-oxyl (TEMPO) and butylated hydroxytoluene (BHT) did not inhibit the reaction, indicating that a radical pathway might not be involved in the reaction (Figure 3A). In addition, when oxime ester **1a-8** was employed, the β-aryl ketone product **3a** and nitrile compound **3a-1** were obtained with 69 and 84% yields, indicating the Ar-Pd species were generated via the β-aryl elimination process (Figure 3B). Next, the deuteration experiments were performed (Figure 3C). The coupling of oxime ester **1a-2** with [D]-pent-1-en-3-ol under the standard reaction conditions afforded the [D]-β-aryl ketone product **3a-*d*** with a 71% yield. The deuterium is completely transferred to the α-position of carbonyl group, which indicates that the reaction proceeds via an iterative β-hydride elimination/migratory-insertion sequence (Figure S1). In addition, the intermolecular KIE of 1.1 indicates β-hydride elimination/migratory-insertion might not be involved in the rate-determined step (Figure S2). The moderate enantioselectivity were observed in both β-and α-aryl products when bulkier chiral ligand **L5** was used (Figures S3–S6), indicating that the ligand plays an important role in both C–C bond cleavage and the asymmetric migration-insertion

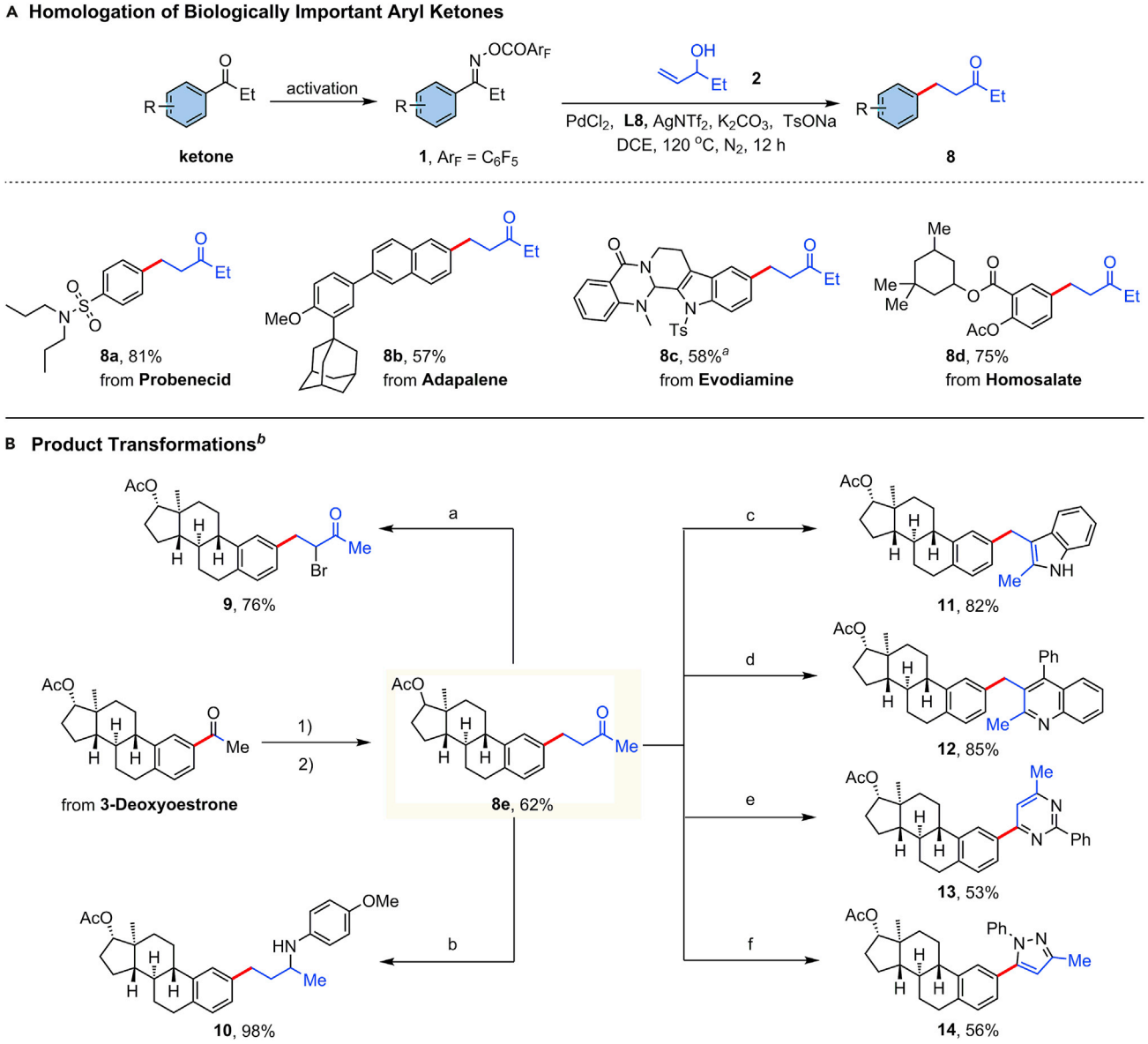


Figure 2. Synthetic application and product transformations

(A) Homologation of biologically important Aryl ketones. [a]Me instead of Et in ketone substrate.

(B) Production transformations[b]. [b]Reaction conditions: For the synthesis of **8e**, see the SI.

[a]**8e** (0.1 mmol), Br_2 (0.1 mmol), DCM (1 mL), r. t, 10 min, air.

[b]**8e** (0.1 mmol), *p*-Anisidine (0.11 mmol), AcOH (0.1 mmol), DCM (1.0 mL), $NaBH(OAc)_3$ (0.15 mmol), r. t, 12 h, N_2.

[c]**8e** (0.1 mmol), Phenylhydrazine hydrochloride (0.1 mmol), AcOH (0.5 mL), 120°C, 1 h, air.

[d]**8e** (0.1 mmol), 2-Aminobenzophenone (0.1 mmol), AcOH (0.5 mL), 120°C, 4 h, air.

[e]**8e** (0.1 mmol), Benzamidine hydrochloride (0.1 mmol), $Cu(OAc)_2$ (10 mol%), 2,2′-bipyridine (10 mol %), 4-HO-TEMPO (0.1 mmol), and NaOAc (0.15 mmol). 1,2-dichlorobenzene (1.0 mL), 140°C, 24 h, air.

[f]**8e** (0.1 mmol), $CuBr_2$ (25 mol %), TEMPO (0.4 mmol), $PhNHNH_2$ (0.4 mmol), acetic acid (0.1 mmol), DMF (1.0 mL), 140°C, 48 h, air.

process (Figure 3D). Based on the previous reports and the control experiments (Nishimura and Uemura, 2000; Patel and Sigman, 2015; Tan and Hartwig, 2010), a possible mechanism was proposed (Figure 3E). The insertion of Pd(0) into the N-O bond of oxime ester **1** generated the intermediate **I′**, which isomerized to intermediate **I.** Ligand-promoted β-aryl elimination of **I** afforded the aryl palladium species **II** and nitrile product. Migratory insertion of Ar-Pd into pent-1-en-3-ol **2a** gave the intermediate **III**, which underwent β-H elimination to form **IV**. The re-insertion of PdH into the **IV** afforded the

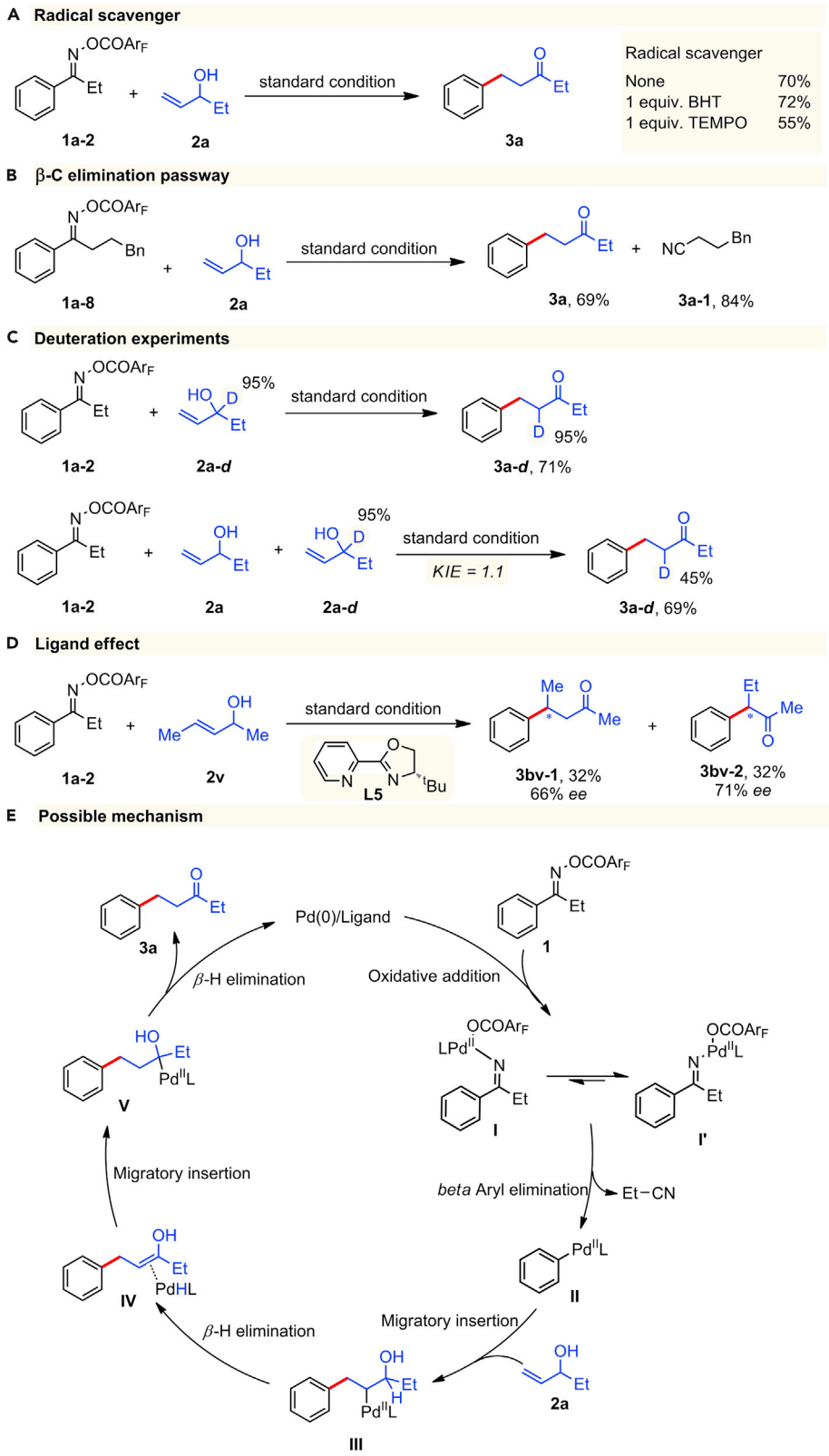


Figure 3. Mechanistic studies

intermediate **V**, which proceeded β-H elimination to generate the homologated product **3a** and regenerate the Pd (0) species.

Conclusions

In summary, we have developed an efficient palladium-catalyzed ligand-promoted redox-relay Heck reaction of aryl ketones with alkenols, affording the homologated long-chain ketones and aldehydes with a good to excellent yield with good regioselectivity. This protocol shows excellent functional-group tolerance and heterocyclic compatibility. Late-stage diversifications of some aryl ketones derived from pharmaceuticals and natural products demonstrate the synthetic practicality of this methodology.

Limitations of the study

Compared with previous well-developed redox-relay Heck work, the reaction afforded moderate site- and enantioselectivity under the optimized reaction conditions. In addition, this reaction is not compatible with unsubstituted pyridine, and the substrate scope limited to ortho-substituted pyridines.

STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

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  - Materials availability
  - Data and code availability
- METHOD DETAILS
  - General information
  - Preparation of ketoxime esters (for ketoxime esters used in this work, see Scheme S1)
  - Preparation of alkenyl alcohols (for alkenyl alcohols used in this work, see Scheme S2)
  - Synthesis of pent-1-en-3-d-3-ol (2a-d) (Vidal et al., 2019)
  - General procedure for the preparation of 3 or 8
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  - 10 mmol scale one-pot synthesis
  - Synthetic application and transformation
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SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.isci.2022.104505.

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AUTHOR CONTRIBUTIONS

X.W. equally contributed in the discovery and development of these reactions. L.-J., L., Z.-Y. W., and H.X. helped to perform the experiments of substrates scope and synthetic application. H.-X.D. conceived the concept and directed the project. X.W., H.-X.D., and H.X. prepared this manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
Hydroxylammonium chloride	Sinopharm Chemical Reagent Co. LTD	Cas: 5470-11-1
Vinylmagnesium bromide	Energy Chemical	Cas: 1826-67-1
2,3,4,5,6-Pentafluorobenzoylchloride	Sigma-Aldrich	Cas: 2251-50-5
Pyridine	Sinopharm Chemical Reagent Co. LTD	Cas: 110-86-1
$PdCl_2$	J&K Scientific	Cas: 7647-10-1
$AgNTf_2$	J&K Scientific	Cas: 189114-61-2
K_2CO_3	Sinopharm Chemical Reagent Co. LTD	Cas: 584-08-7
TsONa	Sinopharm Chemical Reagent Co. LTD	Cas: 657-84-1
1,2-Dichloroethane	J&K Scientific	Cas: 107-06-2
Acetophenone	Energy Chemical	Cas: 98-86-2
1-Phenylbutan-1-one	Energy Chemical	Cas: 495-40-9
1-Phenylpentan-1-one	bidepharm	Cas: 1009-14-9
3-Buten-2-ol	J&K Scientific	Cas: 598-32-3
1-Penten-3-ol	J&K Scientific	Cas: 616-25-1
1-Hexen-3-ol	bidepharm	Cas: 4798-44-1
1-Octen-3-ol	J&K Scientific	Cas: 3391-86-4
Crotonyl alcohol	Macklin	Cas: 6117-91-5
3-Buten-1-ol	bidepharm	Cas: 627-27-0
3-Methyl-3-buten-1-ol	J&K Scientific	Cas: 763-32-6
$NaBD_4$	Energy Chemical	Cas: 15681-89-7
$CeCl_3 \bullet 7H_2O$	Energy Chemical	Cas: 18618-55-8
BHT	Energy Chemical	Cas: 128-37-0
TEMPO	Energy Chemical	Cas: 2564-83-2
Br_2	Sinopharm Chemical Reagent Co. LTD	Cas: 7726-95-6
$NaBH(OAc)_3$	Energy Chemical	Cas: 56553-60-7
p-Anisidine	Energy Chemical	Cas: 104-94-9
AcOH	Sinopharm Chemical Reagent Co. LTD	Cas: 64-19-7
Phenylhydrazine hydrochloride	Energy Chemical	Cas: 59-88-1
2-Aminobenzophenone	Energy Chemical	Cas: 2835-77-0
Benzamidine hydrochloride	Energy Chemical	Cas: 1670-14-0
$Cu(OAc)_2$	TCI	Cas: 6046-93-1
2,2′-Bipyridine	bidepharm	Cas: 366-18-7
4-OH-TMEPO	Energy Chemical	Cas: 2226-96-2
NaOAc	Sinopharm Chemical Reagent Co. LTD	Cas: 127-09-3
1,2-Dichlorobenzene	Energy Chemical	Cas: 95-50-1
$CuBr_2$	Alfa Aesar	Cas: 7789-45-9
Phenylhydrazine	Sinopharm Chemical Reagent Co. LTD	Cas: 100-63-0

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Hui-Xiong Dai (hxdai@simm.ac.cn).

Materials availability

All materials generated in this study are available within the article and the supplemental information or from the lead contact upon reasonable request.

Data and code availability

- All data reported in this paper will be available from the lead contact upon request.
- This paper does not report original code.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

METHOD DETAILS

General information

All chemicals were used as received without further purification. Solvents were purified prior to use according to conventional procedures. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400, Bruker AVANCE III 500 and Bruker AVANCE III 600 instruments. All chemical shifts (δ) are reported in parts per million (ppm) and coupling constants (J) are reported in Hz. High resolution mass spectra (HRMS) of the substrates, intermediate and products were obtained using UHPLC-QTOF spectrometer and Thermo DFS spectrometer. Melting points were measured by SGWX-4A micro melting point apparatus. All reactions were monitored by thin-layer chromatography (TLC) through GF254 silica gel-coated plates. The aryl ketones were commercially available or readily prepared according to the known method (Xu et al., 2021; Nahm and Weinreb, 1981; Niu et al., 2014; Labeeuw et al., 2004; Nambara et al., 1970; George et al., 2015).

Preparation of ketoxime esters (for ketoxime esters used in this work, see Scheme S1)

To a mixture of hydroxylammonium chloride (278 mg, 4 mmol), NaOAc (640 mg, 8 mmol), EtOH (10 mL) was added aryl ketone (2 mmol), and the mixture was stirred at r.t. for overnight or at 90°C for 2 h. The reaction mixture was cooled down to room temperature, and then EtOH was removed under reduced pressure. The resulting mixture was extracted with EtOAc. The organic layer was then washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum to give oxime (>99% yield), not further purified.

To a mixture of oxime (2 mmol) and CH_2Cl_2 (10 mL) was slowly added 2,3,4,5,6-Pentafluorobenzoylchloride (552 mg, 2.4 mmol), pyridine (221.2 mg, 2.8 mmol) at 0°C. After completion, aq. HCl (1.0 M) was added to the above solution, and the aqueous phase was discarded. The organic portion was washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was isolated by column chromatography (petroleum ether/ethyl acetate 20:1-5:1) or recrystallization to give ketoxime esters **1**.

Preparation of alkenyl alcohols (for alkenyl alcohols used in this work, see Scheme S2)

Procedure (A) (Lafrance et al., 2012): To a stirred solution of aldehyde (5.0 mmol) in dry THF (20 mL) was added vinylmagnesium bromide (1.0 M in THF, 5.5 mL, 5.5 mmol) dropwise through a syringe at 0°C. After stirring for 20 min the reaction mixture could warm to room temperature. The resulting mixture was stirred for additional 4 h and then quenched by saturated NH_4Cl solution (20 mL). The organic phase was extracted with ethyl acetate (30 mL x 3). The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated under vacuum to afford the crude product. It was further purified by flash silica gel column chromatography.

Procedure (B) (Li et al., 2012): To a solution of aldehyde (5.0 mmol, 1.0 equiv) in dry THF (20 mL) was slowly added alkyl magnesium bromide (5.5 mmol, 1.1 equiv) at 0°C. The reaction was stirred at 0°C for 4 h and then quenched with saturated aqueous NH_4Cl. The resultant layers were separated and the aqueous was extracted with diethyl ether. The combined organic fractions were washed with brine, dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by distillation.

Synthesis of pent-1-en-3-d-3-ol (2a-d) (Vidal et al., 2019)

$NaBD_4$ (420 mg, 10 mmol, 1.0 eq.), was added to a mixture of pent-1-en-3-one (840 mg, 10 mmol) and $CeCl_3 \cdot 7H_2O$ (5.0 g, 13 mmol, 1.3 eq.) in MeOH (30 mL, 0.3 M) over a period of 30 min. After 2 h, then

quenched by water (50 mL). The organic phase was extracted with Et_2O (100 mL x 3). The organic phase was washed with brine (100 mL x 3) and dried over Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by distillation to afford **2a-*d*** in 34% yield, 95% D.

General procedure for the preparation of 3 or 8

To a 25 mL sealed tube was added ketoxime esters **1** (0.1 mmol), alkenyl alcohols **2** (0.2 mmol), $PdCl_2$ (10 mol %, 1.8 mg), K_2CO_3 (1.0 eq, 13.8 mg), TsONa (1.0 eq, 19.4 mg), **L8** (20 mol %, 3.6 mg), $AgNTf_2$ (20 mol %, 7.8 mg) and 1,2-dichloroethane (3 mL), then the reaction mixture was stirred at 120°C for 12 h under N_2 atmosphere. After completion, the mixture and then filtered through Celite. The filtrate was evaporated to give the crude product which was then purified by flash column chromatography on silica gel with a gradient eluent of hexane/ethyl acetate to give the product 3 **or** 8.

General procedure for the preparation of 7

To a 25 mL sealed tube was added ketoxime esters **1** (0.1 mmol), alkenyl alcohols **6** (0.2 mmol), $PdCl_2$ (10 mol %, 1.8 mg), K_2CO_3 (1.0 eq, 13.8 mg), TsONa (1.0 eq, 19.4 mg) **L8** or **L1** (20 mol %), $AgNTf_2$ (20 mol %, 7.8 mg) and 1,2-dichloroethane (3 mL), then the reaction mixture was stirred at 120°C for 12–18 h under N_2 atmosphere. After completion, the mixture and then filtered through Celite. The filtrate was evaporated to give the crude product which was then purified by flash column chromatography on silica gel with a gradient eluent of hexane/ethyl acetate to give the product **7**.

10 mmol scale one-pot synthesis

Propiophenone (1.34 g, 10 mmol) was added to the solution of NH_3OCOAr_FOTf (3.9 g, 10.5 mmol) in EtOH (30.0 mL) at r.t. After the mixture stirred for special time (monitored by TLC), K_2CO_3 (1.5 g in 20.0 mL H_2O) was added dropwise. Then EtOH was removed under reduced pressure, and the resulting mixture was extracted with EtOAc. The organic layer was washed with brine and dried over Na_2SO_4. The solvent was removed under vacuum to give the corresponding oxime ester **1a-2** without further purification. Under N_2 atmosphere, a mixture of **1a-2**, $PdCl_2$ (10 mol %, 180 mg), K_2CO_3 (10 mmol, 1.38 g), TsONa (10 mmol, 1.94 g) **L8** (364 mg, 20 mol %), $AgNTf_2$ (20 mol %, 780 mg), DCE (200 mL), and 1-Pentene-3-ol (**2a**) (20 mmol, 2.1 mL) was stirred at 120°C in oil bath for 12 h. After completion, the mixture and then filtered through Celite. The filtrate was evaporated to give the crude product which was then purified by flash column chromatography on silica gel with a gradient eluent of hexane/ethyl acetate (50:1-20:1) to give the product **3a** (886 mg) in 54% yield.

Synthetic application and transformation

Synthesis of product **9**: To a 15 mL sealed tube was added substrates **8e** (36.8 mg, 0.1 mmol), DCM (1 mL), Br_2 (0.1 mL, 1.0 mol/L in DCM) was added to the solution via a syringe. The reaction mixture was stirred at room temperature for 10 min under air. Upon completion, solvent and other volatile components were removed on a rotary evaporator under reduced pressure, and the residue was purified by flash column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (hexane/ethyl acetate 20:1-10:1) to give product **9** in 76% yield.

Synthesis of product 10

To a 15 mL sealed tube was added substrates **8e** (36.8 mg, 0.1 mmol), *p*-Anisidine (13.5 mg, 0.11 mmol), AcOH (6 mg, 0.1 mmol) in DCM (1 mL), then $NaBH(OAc)_3$ (32 mg, 0.15 mmol) was added to the solution. The reaction mixture was stirred at room temperature for 12 h under nitrogen. Upon completion, NH_4Cl solution was added, then the mixture was extracted with EtOAc (10 mL x 3). The organic phase was dried over Na_2SO_4 evaporated then purified by flash column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (hexane/ethyl acetate 20:1-5:1) to give product **10** in 98% yield.

Synthesis of product 11

To a 15 mL sealed tube was added substrates **8e** (36.8 mg, 0.1 mmol), phenylhydrazine hydrochloride (14.5 mg, 0.1 mmol), AcOH (0.5 mL), The reaction mixture was stirred at 120°C for 1 h under air. Upon completion the mixture was cooled to room temperature, cold $NaHCO_3$ solution was added, then the mixture was extracted with EtOAc (10 mL x 3). The organic phase was dried over Na_2SO_4 evaporated then purified by flash column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (hexane/ethyl acetate 20:1-5:1) to give product **11** in 82% yield.

Synthesis of product 12

A 15 mL sealed tube was charged with substrates **8e** (36.8 mg, 0.1 mmol) and 2-Aminobenzophenone (19.8 mg, 0.1 mmol), then AcOH (0.5 mL) was added. The resulting reaction mixture was stirred at 120°C for 4 h. Upon completion the mixture was cooled to room temperature, cold $NaHCO_3$ solution was added, then the mixture was extracted with EtOAc (10 mL x 3). The organic phase was dried over Na_2SO_4 evaporated then purified by flash column chromatography on silica gel with a gradient eluent of hexane and ethyl acetate (hexane/ethyl acetate 10:1-5:1) to give product **12** in 85% yield.

Synthesis of product 13

A 15 mL sealed tube was charged with substrates **8e** (36.8 mg, 0.1 mmol), benzamidine hydrochloride (15.7 mg, 0.1 mmol), $Cu(OAc)_2$ (2.0 mg, 0.01 mmol, 10 mol %), 2,2′-bipyridine (1.6 mg, 0.01 mmol, 10 mol %), 4-HO-TEMPO (17.2 mg, 0.1 mmol), and NaOAc (12.2 mg, 0.15 mmol). Then 1,2-dichlorobenzene (1.0 mL) was added to the tube. The tube was then sealed, and the mixture was stirred at 140°C for 24 h. Upon cooling to room temperature, the reaction mixture was diluted with 10 mL of ethyl acetate, followed by filtration through a pad of silica gel. The filtrate was concentrated under reduced pressure and then purified by flash chromatography on silica gel (gradient eluent of hexane/ethyl acetate: 10/1 to 5/1) to provide product **13** in 53% yield.

Synthesis of product 14

To a 15 mL sealed tube was added substrates **8e** (36.8 mg, 0.1 mmol), $CuBr_2$ (5.6 mg, 25 mol %), TEMPO (63 mg, 0.4 mmol), $PhNHNH_2$ (39 μL, 0.4 mmol) acetic acid (6 μL, 0.1 mmol), and DMF (1.0 mL). The sealed tube was placed into a preheated oil bath (140°C) and vigorously stirred for 48 h. Upon completion, the reaction mixture was cooled to room temperature, quenched with brine (5 mL), then extracted with EtOAc (10 mL x 3). Combined organic phases were dried over Na_2SO_4, filtered, and concentrated. Crude product was purified by flash column chromatography (hexanes/EtOAc, 6:1) to obtain product **14** in 57% yield.

Deuterium labeling study

Deuteriumlabeled experiments

To a 25 mL sealed tube was added substrates **1a** (0.1 mmol), **2a-*d*** (0.2 mmol), $PdCl_2$ (10 mol %, 1.8 mg), K_2CO_3 (1.0 eq, 13.8 mg), TsONa (1.0 eq, 19.4 mg) **L8** (20 mol %, 3.6 mg), $AgNTf_2$ (20 mol %, 7.8 mg) and DCE (3 mL), then the reaction mixture was stirred at 120°C for 12 h Under N_2 atmosphere. After completion, the mixture and then filtered through Celite. The filtrate was evaporated to give the crude product which was then purified by flash column chromatography on silica gel with a gradient eluent of hexane/ethyl acetate (50:1-20:1) to give the product **3a-*d*** in 75 yield.

Intermolecular kinetic isotope effects

To a 25 mL sealed tube was added substrates **1a** (0.1 mmol), **2a** (0.2 mmol), **2a-*d*** (0.2 mmol), $PdCl_2$ (10 mol %, 1.8 mg), K_2CO_3 (1.0 eq, 13.8 mg), TsONa (1.0 eq, 19.4 mg) **L8** (20 mol %, 3.6 mg), $AgNTf_2$ (20 mol %, 7.8 mg) and DCE (3 mL), then the reaction mixture was stirred at 120°C for 12 h Under N_2 atmosphere. After completion, the mixture and then filtered through Celite. The filtrate was evaporated to give the crude product which was then purified by flash column chromatography on silica gel with a gradient eluent of hexane/ethyl acetate (50:1-20:1) to give the product **3a-*d*** in 69% yield.

Analytical data

Characterization data of substrates

ketoxime esters **1a**, **1a-1**-**1a-5**, **1a-7**, **1a-8**, **1az**, **1bc**, **1be** are known product and synthesized according to the literature (Li et al., 2020; Wang et al., 2021; Guo et al., 2021). Alkenyl alcohol **2a′**, **2a-2i**, **2k-2w**, **6a-6g**, are all known products (Liao et al., 2015; Brandt et al., 2012; Deng et al., 2015; Liu et al., 2017; Latham et al., 2019; Shu et al., 2018). These alkenyl alcohols were commercially available or readily prepared according to the general procedure.

(*E*/*Z*)-cyclohexyl(phenyl)methanone *O*-perfluorobenzoyl oxime (**1a-6**).

white solid. Mp = 51–54°C; (*E*/*Z* = 1:1, mixture) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47–7.35 (m, 4H), 7.22–7.14 (m, 1H), 3.30 (tt, *J* = 12.4, 3.4 Hz, 0.5H), 2.78–2.66 (m, 0.5H), 1.98–1.64 (m, 5H), 1.53–1.25 (m, 4H), 1.23–1.11 (m, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 174.0, 173.6, 156.7, 156.6, 146.6–146.0 (m), 144.6–143.6 (m), 142.6–141.8 (m), 139.0–138.3 (m), 136.9–136.2 (m), 133.2, 132.6, 129.6, 129.1, 128.2, 128.1, 128.1, 126.4, 107.4–106.9 (m), 44.8, 40.6, 30.0, 29.4, 25.9, 25.8, 25.6, 25.6; **HRMS-EI** calcd for $C_{20}H_{16}F_5NO_2$ $[M]^+$ 397.1096, found 397.1111.

(*E*)-1-(o-tolyl)propan-1-one *O*-perfluorobenzoyl oxime (**1b**).

colorless colloid; (Major) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33–7.16 (m, 4H), 2.71 (qd, *J* = 7.4, 4.6 Hz, 2H), 1.19 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.6, 156.6, 146.3–146.0 (m), 144.3–144.0 (m), 142.3–142.0 (m), 138.8–138.4 (m), 136.7–136.2 (m), 134.0, 133.3, 130.0, 128.9, 125.5, 125.3, 107.1–106.6 (m), 29.6, 19.1, 10.2; **HRMS-EI** calcd for $C_{17}H_{12}F_5NO_2$ $[M]^+$ 357.0783, found 357.0789.

(*E*)-1-(2-fluorophenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1c**).

white solid. Mp = 40–42°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (td, *J* = 7.5, 1.8 Hz, 1H), 7.49–7.41 (m, 1H), 7.21 (td, *J* = 7.6, 1.1 Hz, 1H), 7.13 (ddd, *J* = 10.8, 8.3, 1.1 Hz, 1H), 2.90 (q, *J* = 7.6 Hz, 2H), 1.15 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.1, 160.5 (d, *J* = 250.9 Hz), 156.5, 146.5–146.4 (m), 144.6–144.4 (m), 142.6–142.4 (m), 139.0–138.7 (m), 137.0–136.6 (m), 132.3 (d, *J* = 8.6 Hz), 130.6 (d, *J* = 3.2 Hz), 124.4 (d, *J* = 3.4 Hz), 121.8 (d, *J* = 13.3 Hz), 116.2 (d, *J* = 21.5 Hz), 107.0–106.7 (m), 24.3 (d, *J* = 4.0 Hz), 10.3; **HRMS-EI** calcd for $C_{16}H_9F_6NO_2$ $[M]^+$ 361.0532, found 361.0550.

(*E*)-1-(2-chlorophenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1d**).

white colloid. Mp = 43–45°C; (Major) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41–7.27 (m, 4H), 2.89 (q, *J* = 7.7 Hz, 2H), 1.06 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.2, 156.2, 146.8–146.1 (m), 144.6–144.2 (m), 142.6–142.0 (m), 138.7–138.4 (m), 136.9–136.4 (m), 132.9, 132.4, 130.8, 130.5, 129.8, 126.7, 107.0–106.6 (m), 24.6, 9.8; **HRMS-EI** calcd for $C_{16}H_9F_5NO_2Cl$ $[M]^+$ 377.0236, found 377.0258.

(*E*)-1-(m-tolyl)propan-1-one *O*-perfluorobenzoyl oxime (**1e**).

white solid. Mp = 81–83°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.60 (d, *J* = 1.8 Hz, 1H), 7.54–7.50 (m, 1H), 7.35–7.27 (m, 2H), 2.90 (q, *J* = 7.6 Hz, 2H), 2.40 (s, 3H), 1.22 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.0, 156.6, 146.6–146.3 (m), 144.6–144.3 (m), 142.6–142.2 (m), 138.9–138.6 (m), 138.5, 136.9–136.5 (m), 132.8, 131.8, 128.6, 127.9, 124.5, 107.3–106.9 (m), 22.3, 21.3, 11.3; **HRMS-EI** calcd for $C_{17}H_{12}F_5NO_2$ $[M]^+$ 357.0783, found 357.0780.

(*E*)-1-(3-methoxyphenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1f**).

white solid. Mp = 76–78°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.35 (t, *J* = 7.8 Hz, 1H), 7.32–7.28 (m, 2H), 7.02 (ddd, *J* = 8.1, 2.5, 1.3 Hz, 1H), 3.85 (s, 3H), 2.89 (q, *J* = 7.6 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.7, 159.8, 156.5, 146.6–146.3 (m), 144.6–144.2 (m), 142.7–142.2 (m), 138.9–138.6 (m), 137.0–136.6 (m), 134.2, 129.8, 119.8, 116.9, 112.6, 107.3–106.9 (m), 77.4–76.6 (m), 55.3, 22.4, 11.3; **HRMS-EI** calcd for $C_{17}H_{12}F_5NO_3$ $[M]^+$ 373.0732, found 373.0740.

(*E*)-1-(3-(methylthio)phenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1g**).

white solid. Mp = 105–107°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.50–7.45 (m, 1H), 7.34 (d, *J* = 5.0 Hz, 2H), 2.88 (q, *J* = 7.6 Hz, 2H), 2.50 (s, 3H), 1.20 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.5, 156.4, 146.6–146.3 (m), 144.6–144.3 (m), 142.6–142.2 (m), 139.6 , 138.9–138.6 (m), 136.9–136.5 (m), 133.5, 129.1, 128.7, 125.0, 123.9, 107.1–106.8 (m), 22.3, 15.6, 11.2; **HRMS-EI** calcd for $C_{17}H_{12}F_5NO_2S$ $[M]^+$ 389.0503, found 389.0478.

(*E*)-*N*-(3-(1-(((perfluorobenzoyl)oxy)imino)propyl)phenyl)acetamide (**1h**).

white solid. Mp = 142–144°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.81 (t, *J* = 2.0 Hz, 1H), 7.74 (dt, *J* = 8.0, 1.5 Hz, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 2.86 (q, *J* = 7.7 Hz, 2H), 2.19 (s, 3H), 1.18

(t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.8, 169.2, 156.8, 146.8–146.4 (m), 144.7–144.4 (m), 142.8–142.4 (m), 139.1–138.7 (m), 138.6, 137.1–136.6 (m), 133.3, 129.3, 122.8, 122.5, 118.4, 107.0–106.6 (m), 24.4, 22.3, 11.2; **HRMS-EI** calcd for $C_{18}H_{13}F_5N_2O_3$ $[M]^+$ 400.0841, found 400.0840.

(*E*)-3-(1-(((perfluorobenzoyl)oxy)imino)propyl)phenyl acetate (**1i**).

white solid. Mp = 95–97°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.62 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.53 (t, *J* = 2.0 Hz, 1H), 7.45 (t, *J* = 8.0 Hz, 1H), 7.22 (ddd, *J* = 8.0, 2.3, 1.0 Hz, 1H), 2.88 (q, *J* = 7.7 Hz, 2H), 2.31 (s, 3H), 1.22 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.1, 168.7, 156.4, 150.9, 146.7–146.3 (m), 144.7–144.3 (m), 142.6–142.3 (m), 139.0–138.6 (m), 137.0–136.6 (m), 134.3, 129.7, 124.7, 124.4, 120.6, 107.1–106.7 (m), 77.4–76.4 (m), 22.1, 21.0, 11.2; **HRMS-EI** calcd for $C_{18}H_{12}F_5NO_4$ $[M]^+$ 401.0681, found 401.0682.

(*E*)-1-(3-fluorophenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1j**).

white solid. Mp = 67–69°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (dt, *J* = 7.9, 1.2 Hz, 1H), 7.46 (dt, *J* = 9.8, 2.1 Hz, 1H), 7.44–7.35 (m, 1H), 7.15 (td, *J* = 8.3, 2.0 Hz, 1H), 2.88 (q, *J* = 7.7 Hz, 2H), 1.20 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.6, 162.7 (d, *J* = 247.0 Hz), 156.3, 146.7–146.3 (m), 144.7–144.3 (m), 142.7–142.3 (m), 138.9–138.5 (m), 136.9–136.5 (m), 135.0 (d, *J* = 7.7 Hz), 130.3 (d, *J* = 8.0 Hz), 123.0 (d, *J* = 3.5 Hz), 117.9 (d, *J* = 21.1 Hz), 114.3 (d, *J* = 23.6 Hz), 107.0–106.6 (m), 22.1, 11.0; **HRMS-EI** calcd for $C_{16}H_9F_6NO_2$ $[M]^+$ 361.0532, found 361.0528.

(*E*)-1-(3-chlorophenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1k**).

white solid. Mp = 81–83°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 2.0 Hz, 1H), 7.64 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.46 (ddt, *J* = 8.1, 2.1, 1.0 Hz, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 2.88 (q, *J* = 7.7 Hz, 2H), 1.21 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.7, 156.4, 146.7–146.4 (m), 144.8–144.4 (m), 142.7–142.3 (m), 139.0–138.6 (m), 137.0–136.6 (m), 134.9, 134.7, 131.1, 130.0, 127.5, 125.5, 107.0–106.7 (m), 22.2, 11.2; **HRMS-EI** calcd for $C_{16}H_9F_5NO_2Cl$ $[M]^+$ 377.0236, found 377.0236.

(*E*)-1-(3-(trifluoromethyl)phenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1l**).

white solid. Mp = 82–84°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.00 (d, *J* = 2.0 Hz, 1H), 7.95 (d, *J* = 7.9 Hz, 1H), 7.72 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.9 Hz, 1H), 2.94 (q, *J* = 7.7 Hz, 2H), 1.22 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.6, 156.2, 146.8–146.5 (m), 144.8–144.4 (m), 142.8–142.4 (m), 139.0–138.6 (m), 137.0–136.6 (m), 133.9, 131.3 (q, *J* = 32.8 Hz), 130.6, 129.4, 127.5 (q, *J* = 3.7 Hz), 124.1 (q, *J* = 3.9 Hz), 123.7 (q, *J* = 272.4 Hz), 106.9–106.6 (m), 22.1, 11.0; **HRMS-EI** calcd for $C_{17}H_9F_8NO_2$ $[M]^+$ 411.0500, found 411.0456.

(*E*)-3-(1-(((perfluorobenzoyl)oxy)imino)propyl)benzonitrile (**1m**).

white solid. Mp = 94–96°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.8 Hz, 1H), 8.01 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.76 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.58 (t, *J* = 7.8 Hz, 1H), 2.91 (q, *J* = 7.7 Hz, 2H), 1.22 (td, *J* = 7.7, 1.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.8, 156.1, 146.8–146.5 (m), 144.8–144.4 (m), 142.8–142.4 (m), 139.0–138.6 (m), 137.0–136.6 (m), 134.3, 134.1, 131.4, 130.9, 129.7, 117.9, 113.2, 106.7–106.3 (m), 22.0, 11.0; **HRMS-EI** calcd for $C_{17}H_9F_5N_2O_2$ $[M]^+$ 368.0579, found 368.0573.

(*E*)-1-(3-nitrophenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1n**).

white solid. Mp = 82–84°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 2.0 Hz, 1H), 8.36–8.32 (m, 1H), 8.16 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.66 (t, *J* = 8.0 Hz, 1H), 2.97 (q, *J* = 7.7 Hz, 2H), 1.25 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.8, 156.2, 148.5, 146.8–146.5 (m), 144.8–144.4 (m), 142.8–142.5 (m), 139.1–138.6 (m), 137.0–136.6 (m), 134.7, 133.2, 130.0, 125.6, 122.32, 106.8–106.4 (m), 22.1, 11.1; **HRMS-EI** calcd for $C_{16}H_9F_5N_2O_4$ $[M]^+$ 388.0477, found 388.0449.

(*E*)-1-(p-tolyl)propan-1-one *O*-perfluorobenzoyl oxime (**1o**).

white solid. Mp = 95–97°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 2.89 (q, *J* = 7.7 Hz, 2H), 2.38 (s, 3H), 1.21 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.6, 156.5, 146.60–146.3

(m), 144.5–144.2 (m), 142.5–142.1 (m), 141.4, 138.9–138.5 (m), 136.9–136.5 (m), 129.8, 129.4, 127.2, 107.4–106.9 (m), 22.0, 21.2, 11.2; **HRMS-EI** calcd for $C_{17}H_{12}F_5NO_2$ $[M]^+$ 357.0783, found 357.0779.

(*E*)-1-(4-(tert-butyl)phenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1p**).

white solid. Mp = 86–88°C; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 2.90 (q, *J* = 7.7 Hz, 2H), 1.34 (s, 9H), 1.23 (t, *J* = 7.7 Hz, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 169.6, 156.7, 154.6, 146.6–146.3 (m), 144.6–144.2 (m), 142.5–142.2 (m), 139.0–138.6 (m), 137.0–136.6 (m), 129.9, 127.1, 125.7, 107.4–107.1 (m), 77.6–76.3 (m), 34.8, 31.1, 22.1, 11.4; **HRMS-EI** calcd for $C_{20}H_{18}F_5NO_2$ $[M]^+$ 399.1252, found 399.1270.

(*E*)-1-([1,1′-biphenyl]-4-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1q**).

white solid. Mp = 147–149°C; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 7.63 (d, *J* = 7.0 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 2.95 (q, *J* = 7.7 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 169.3, 156.5, 146.7–146.3 (m), 144.6–144.3 (m), 143.8, 142.6–142.2 (m), 139.9, 139.0–138.6 (m), 137.0–136.5 (m), 131.6, 128.7, 127.9, 127.8, 127.4, 127.0, 107.3–106.9 (m), 22.1, 11.4; **HRMS-EI** calcd for $C_{22}H_{14}F_5NO_2$ $[M]^+$ 419.0939, found 419.0967.

(*E*)-4-(1-(((perfluorobenzoyl)oxy)imino)propyl)phenyl acetate (**1r**).

white solid. Mp = 120–122°C; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.8 Hz, 2H), 7.17 (d, *J* = 8.7 Hz, 2H), 2.89 (q, *J* = 7.7 Hz, 2H), 2.31 (s, 3H), 1.21 (t, *J* = 7.7 Hz, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 168.9, 168.8, 156.5, 152.8, 146.7–146.3 (m), 144.6–144.3 (m), 142.6–142.2 (m), 138.9–138.6 (m), 137.0–136.5 (m), 130.4, 128.6, 122.0, 107.2–106.8 (m), 22.1, 21.0, 11.2; **HRMS-EI** calcd for $C_{18}H_{12}F_5NO_4$ $[M]^+$ 401.0681, found 401.0683.

(*E*)-1-(4-(trifluoromethoxy)phenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1s**).

white solid. Mp = 49–51°C; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 8.15 (d, *J* = 8.8 Hz, 2H), 7.61 (d, *J* = 8.4 Hz, 2H), 3.24 (q, *J* = 7.7 Hz, 2H), 1.56 (t, *J* = 7.7 Hz, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 168.5, 156.4, 151.2, 146.8–146.4 (m), 144.8–144.4 (m), 142.7–142.4 (m), 139.1–138.6 (m), 137.0–136.6 (m), 131.5, 129.1, 120.9, 120.3 (q, *J* = 258.3 Hz), 107.1–106.7 (m), 22.1, 11.1; **HRMS-EI** calcd for $C_{17}H_9F_8NO_3$ $[M]^+$ 427.0449, found 427.0448.

(*E*)-1-(4-fluorophenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1t**).

white solid. Mp = 82–84°C; (Major) ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.80–7.73 (m, 2H), 7.14–7.06 (m, 2H), 2.88 (q, *J* = 7.7 Hz, 2H), 1.20 (t, *J* = 7.7 Hz, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 168.7, 164.5 (d, *J* = 251.9 Hz), 156.4, 146.7–146.4 (m), 144.7–144.3 (m), 142.6–142.2 (m), 139.0–138.6 (m), 137.0–136.5 (m), 129.5 (d, *J* = 8.6 Hz), 128.9 (d, *J* = 3.5 Hz), 115.8 (d, *J* = 21.8 Hz), 107.1–106.8 (m), 22.1, 11.1; **HRMS-EI** calcd for $C_{16}H_9F_6NO_2$ $[M]^+$ 361.0532, found 361.0526.

(*E*)-1-(4-chlorophenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1u**).

white solid. Mp = 82–84°C; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 8.4 Hz, 2H), 2.88 (q, *J* = 7.7 Hz, 2H), 1.20 (t, *J* = 7.7 Hz, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 168.6, 156.4, 146.7–146.4 (m), 144.7–144.3 (m), 142.7–142.3 (m), 139.0–138.6 (m), 137.3, 136.9–136.6 (m), 131.3, 129.0, 128.7, 107.1–106.7 (m), 22.0, 11.2; **HRMS-EI** calcd for $C_{16}H_9F_5NO_2Cl$ $[M]^+$ 377.0236, found 377.0251.

(*E*)-1-(4-(trifluoromethyl)phenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1v**).

white solid. Mp = 63–65°C; ^{1}**H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.1 Hz, 2H), 7.68 (d, *J* = 8.1 Hz, 2H), 2.93 (q, *J* = 7.7 Hz, 2H), 1.22 (t, *J* = 7.7 Hz, 3H); ^{13}**C NMR** (126 MHz, $CDCl_3$) δ 168.6, 156.3, 146.8–146.5 (m), 144.8–144.4 (m), 142.8–142.4 (m), 139.0–138.6 (m), 137.0–136.6 (m), 136.5, 132.7 (q, *J* = 32.8 Hz), 127.8, 125.7 (q, *J* = 3.8 Hz), 123.7 (q, *J* = 272.3 Hz), 107.0–106.5 (m), 22.1, 11.0; **HRMS-EI** calcd for $C_{17}H_9F_8NO_2$ $[M]^+$ 411.0500, found 411.0477.

(*E*)-4-(1-(((perfluorobenzoyl)oxy)imino)propyl)benzonitrile (**1w**).

white solid. Mp = 111–113°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.73 (d, *J* = 8.5 Hz, 2H), 2.91 (q, *J* = 7.7 Hz, 2H), 1.21 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.1, 156.1, 146.8–146.5 (m), 144.8–144.4 (m), 142.8–142.4 (m), 139.0–138.6 (m), 137.2, 137.0–136.6 (m), 132.5, 128.0, 118.0, 114.5, 106.7–106.3 (m), 22.0, 11.0; **HRMS-EI** calcd for $C_{17}H_9F_5N_2O_2$ $[M]^+$ 368.0579, found 368.0544.

(*E*)-1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1x**).

white solid. Mp = 134–136°C; (Major) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.7 Hz, 2H), 7.75 (d, *J* = 7.8 Hz, 2H), 2.91 (q, *J* = 7.6 Hz, 2H), 1.35 (s, 12H), 1.20 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.8, 156.6, 146.6–146.3 (m), 144.6–144.3 (m), 142.6–142.2 (m), 139.0–138.5 (m), 136.9–136.5 (m), 135.2, 135.0, 126.5, 107.2–106.9 (m), 84.1, 24.8, 22.2, 11.2; **HRMS-EI** calcd for $C_{22}H_{21}BF_5NO_4$ $[M]^+$ 469.1478, found 469.1481.

(*E*)-1-(4-(trimethylsilyl)phenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1y**).

white solid. Mp = 94–96°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 7.7 Hz, 2H), 7.60 (d, *J* = 8.0 Hz, 2H), 2.91 (q, *J* = 7.7 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H), 0.30 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.8, 156.6, 146.6–146.3 (m), 144.4, 144.6–144.3 (m), 142.5–142.2 (m), 139.0–138.6 (m), 136.9–136.6 (m), 133.6, 133.1, 126.4, 107.4–107.0 (m), 22.2, 11.3, −1.4; **HRMS-EI** calcd for $C_{19}H_{18}F_5NO_2Si$ $[M]^+$ 415.1022, found 415.1012.

ethyl (*E*)-4-(1-(((perfluorobenzoyl)oxy)imino)propyl)benzoate (**1z**).

white solid. Mp = 94–96°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.4 Hz, 2H), 7.82 (d, *J* = 8.3 Hz, 2H), 4.39 (q, *J* = 7.1 Hz, 2H), 2.92 (q, *J* = 7.7 Hz, 2H), 1.40 (t, *J* = 7.1 Hz, 3H), 1.21 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.0, 166.8, 156.4, 146.7–146.4 (m), 144.7–144.4 (m), 142.7–142.3 (m), 139.0–138.6 (m), 137.0, 136.9–136.6 (m), 132.6, 129.8, 127.3, 107.0–106.6 (m), 61.3, 22.2, 14.2, 11.1; **HRMS-EI** calcd for $C_{19}H_{14}F_5NO_4$ $[M]^+$ 415.0838, found 415.0851.

diethyl (*E*)-(4-(1-(((perfluorobenzoyl)oxy)imino)propyl)phenyl)phosphonate (**1aa**).

white solid. Mp = 65–67°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.88–7.79 (m, 4H), 4.17–4.01 (m, 4H), 2.89 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 6H), 1.18 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 156.2, 146.7–146.3 (m), 144.6–144.3 (m), 142.7–142.2 (m), 138.9–138.5 (m), 136.9–136.6 (m), 136.7 (d, *J* = 3.2 Hz), 132.1 (d, *J* = 10.3 Hz), 131.2 (d, *J* = 187.9 Hz), 127.3 (d, *J* = 15.0 Hz), 106.9–106.5 (m), 62.3 (d, *J* = 5.6 Hz), 22.2, 16.2 (d, *J* = 6.5 Hz), 11.0; **HRMS-EI** calcd for $C_{20}H_{19}F_5NO_5P$ $[M]^+$ 479.0916, found 479.0912.

(*E*)-1-(4-(methylsulfonyl)phenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1ab**).

white solid. Mp = 115–117°C; (Major) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.5 Hz, 2H), 7.96 (d, *J* = 8.5 Hz, 2H), 3.07 (s, 3H), 2.93 (q, *J* = 7.6 Hz, 2H), 1.22 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.2, 156.2, 146.8–146.5 (m), 144.8–144.4 (m), 142.8–142.4 (m), 142.5, 139.0–138.5 (m), 138.3, 137.0–136.6 (m), 128.4, 127.8, 106.7–106.3 (m), 44.3, 22.2, 11.0; **HRMS-EI** calcd for $C_{17}H_{12}F_5NO_4S$ $[M]^+$ 421.0402, found 421.0397.

(*E*)-1-(3,5-dimethylphenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1ac**).

white solid. Mp = 107–109°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 1.5 Hz, 2H), 7.12 (t, *J* = 1.5 Hz, 1H), 2.88 (q, *J* = 7.7 Hz, 2H), 2.36 (s, 6H), 1.21 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.3, 156.6, 146.6–146.4 (m), 144.6–144.3 (m), 142.6–142.2 (m), 138.9–138.6 (m), 138.4, 137.0–136.6 (m), 132.8, 132.7, 125.1, 107.4–107.0 (m), 22.4, 21.2, 11.3; **HRMS-EI** calcd for $C_{18}H_{14}F_5NO_2$ $[M]^+$ 371.0939, found 371.0905.

(*E*)-1-(3,5-dimethoxyphenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1ad**).

white solid. Mp = 109–111°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.86 (d, *J* = 2.3 Hz, 2H), 6.54 (t, *J* = 2.2 Hz, 1H), 3.82 (s, 6H), 2.85 (q, *J* = 7.7 Hz, 2H), 1.20 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.7, 160.9, 156.4, 146.6–146.3 (m), 144.6–144.3 (m), 142.6–142.2 (m), 139.0–138.5 (m), 136.9–136.5 (m), 134.8, 107.3–106.9 (m), 105.4, 102.9, 77.4–76.6 (m), 55.4, 22.4, 11.3; **HRMS-EI** calcd for $C_{18}H_{14}F_5NO_4$ $[M]^+$ 403.0838, found 403.0838.

(*E*)-1-(3,5-difluorophenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1ae**).

white solid. Mp = 59–61°C; (Major) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33–7.27 (m, 2H), 6.92 (tt, *J* = 8.6, 2.4 Hz, 1H), 2.86 (q, *J* = 7.7 Hz, 2H), 1.22 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.7, 163.1 (dd, *J* = 249.8, 12.5 Hz), 156.1, 146.8–146.5 (m), 144.8–144.4 (m), 142.8–142.4 (m), 139.0–138.6 (m), 137.0–136.6 (m), 136.2 (t, *J* = 9.5 Hz), 110.5 (dd, *J* = 20.9, 6.7 Hz), 106.8–106.4 (m), 106.3 (t, *J* = 25.3 Hz), 22.1, 11.0; **HRMS-EI** calcd for $C_{16}H_8F_7NO_2$ $[M]^+$ 379.0438, found 379.0461.

(*E*)-1-(3,5-dichlorophenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1af**).

white solid. Mp = 80–82°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 2.0 Hz, 2H), 7.46 (t, *J* = 1.9 Hz, 1H), 2.86 (q, *J* = 7.7 Hz, 2H), 1.21 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.6, 156.1, 146.8–146.5 (m), 144.9–144.4 (m), 142.8–142.4 (m), 139.1–138.6 (m), 137.0–136.6 (m), 135.9, 135.6, 130.9, 125.8, 106.8–106.4 (m), 22.1, 11.1; **HRMS-EI** calcd for $C_{16}H_8Cl_2F_5NO_2$ $[M]^+$ 410.9847, found 410.9842.

(*E*)-1-(4-((*E*)-styryl)phenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1ag**).

white solid. Mp = 159–161°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.1 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.54 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.40–7.34 (m, 3H), 2.90 (q, *J* = 7.7 Hz, 2H), 1.23 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 156.4, 146.8–146.4 (m), 144.6–144.3 (m), 142.6–142.2 (m), 139.0–138.5 (m), 137.0–136.6 (m), 132.3, 131.8, 131.6, 128.6, 128.4, 127.3, 126.1, 122.7, 107.1–106.7 (m), 91.8, 88.6, 22.0, 11.3; **HRMS-EI** calcd for $C_{24}H_{16}F_5NO_2$ $[M]^+$ 445.1096, found 445.1067.

(*E*)-1-(2,6-difluorophenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1ah**).

white solid. Mp = 65–67°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.40 (tt, *J* = 8.4, 6.3 Hz, 1H), 6.98 (dd, *J* = 8.5, 7.4 Hz, 2H), 2.85 (q, *J* = 7.7 Hz, 2H), 1.11 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 164.0, 160.4 (dd, *J* = 251.7, 6.6 Hz), 156.2, 146.8–146.5 (m), 144.8–144.4 (m), 142.8–142.4 (m), 139.1–138.6 (m), 137.0–136.6 (m), 131.8 (t, *J* = 10.1 Hz), 111.8 (dd, *J* = 20.4, 4.6 Hz), 111.5 (t, *J* = 20.0 Hz), 106.8–106.5 (m), 24.9, 9.7; **HRMS-EI** calcd for $C_{16}H_8F_7NO_2$ $[M]^+$ 379.0438, found 379.0431.

(*E*)-1-(3,4-dichlorophenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1ai**).

white solid. Mp = 102–104°C; (Major) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 2.1 Hz, 1H), 7.61 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 2.87 (q, *J* = 7.7 Hz, 2H), 1.21 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.7, 156.2, 146.8–146.5 (m), 144.8–144.5 (m), 142.8–142.4 (m), 139.0–138.6 (m), 137.0–136.6 (m), 135.5–135.4 (m), 133.3, 132.8, 130.8, 129.2, 126.5, 106.8–106.5 (m), 22.0, 11.1; **HRMS-EI** calcd for $C_{16}H_8Cl_2F_5NO_2$ $[M]^+$ 410.9847, found 410.9820.

(*E*)-1-(naphthalen-1-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1aj**).

white solid. Mp = 89–91°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.96–7.92 (m, 1H), 7.89 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.60–7.51 (m, 2H), 7.52–7.50 (m, 2H), 3.02 (q, *J* = 7.6 Hz, 2H), 1.13 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 172.3, 156.7, 146.7–146.3 (m), 144.6–144.3 (m), 142.6–142.2 (m), 139.0–138.6 (m), 137.0–136.5 (m), 133.6, 131.3, 130.8, 130.2, 128.5, 127.1, 126.6, 126.3, 124.9, 124.8, 107.3–106.9 (m), 26.0, 10.4; **HRMS-EI** calcd for $C_{20}H_{12}F_5NO_2$ $[M]^+$ 393.0783, found 393.0792.

(*E*)-1-(naphthalen-2-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1ak**).

white solid. Mp = 164–166°C; (Major) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.21 (s, 1H), 7.95 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.93–7.90 (m, 1H), 7.90–7.85 (m, 2H), 7.59–7.52 (m, 2H), 3.03 (q, *J* = 7.7 Hz, 2H), 1.29 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.6, 156.6, 146.7–146.4 (m), 144.7–144.3 (m), 142.6–142.2 (m), 139.0–138.6 (m), 137.0–136.6 (m), 134.5, 132.9, 130.2, 128.8, 128.6, 128.0, 127.7, 127.6, 126.7, 123.9, 107.2–106.9 (m), 22.1, 11.5; **HRMS-EI** calcd for $C_{20}H_{12}F_5NO_2$ $[M]^+$ 393.0783, found 393.0792.

(*E*)-6-(1-(((perfluorobenzoyl)oxy)imino)propyl)naphthalen-2-yl acetate (**1al**).

white solid. Mp = 167–169°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.20 (d, *J* = 1.8 Hz, 1H), 7.95 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.92 (d, *J* = 8.9 Hz, 1H), 7.84 (d, *J* = 8.7 Hz, 1H), 7.59 (d, *J* = 2.3 Hz, 1H), 7.29 (dd, *J* = 8.8, 2.3 Hz, 1H),

3.01 (q, *J* = 7.7 Hz, 2H), 2.36 (s, 3H), 1.27 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.4, 169.3, 156.5, 149.6, 146.7–146.4 (m), 144.7–144.4 (m), 142.6–142.3 (m), 139.0–138.6 (m), 137.0–136.6 (m), 134.9, 130.8, 130.3, 130.1, 128.3, 127.7, 124.6, 122.0, 118.5, 107.2–106.8 (m), 22.0, 21.1, 11.4; **HRMS-EI** calcd for $C_{22}H_{14}F_5NO_4$ $[M]^+$ 451.0838, found 451.0839.

(*E*)-1-(furan-3-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1am**).

white solid. Mp = 81–83°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 3.0, 1.3 Hz, 1H), 7.56 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.37 (dd, *J* = 5.1, 2.9 Hz, 1H), 2.85 (q, *J* = 7.7 Hz, 2H), 1.24 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.2, 156.4, 146.6–146.3 (m), 144.6–144.2 (m), 142.5–142.2 (m), 138.9–138.5 (m), 137.0–136.5 (m), 134.6, 127.6, 126.7, 125.8, 107.2–106.9 (m), 22.6, 11.5; **HRMS-EI** calcd for $C_{14}H_8F_5NO_3$ $[M]^+$ 333.0419, found 333.0394.

(*E*)-1-(thiophen-3-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1an**).

white solid. Mp = 104–106°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (t, *J* = 1.1 Hz, 1H), 7.46 (t, *J* = 1.7 Hz, 1H), 6.82 (dd, *J* = 1.9, 0.8 Hz, 1H), 2.72 (q, *J* = 7.7 Hz, 2H), 1.23 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 163.7, 156.4, 146.7–146.4 (m), 144.7–144.4 (m), 144.4, 144.1, 142.6–142.2 (m), 138.9–138.6 (m), 136.9–136.6 (m), 120.7, 108.0, 107.2–106.8 (m), 22.8, 11.6; **HRMS-EI** calcd for $C_{14}H_8F_5NO_2S$ $[M]^+$ 349.0190, found 349.0195.

(*E*)-1-(6-methoxypyridin-3-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1ao**).

white solid. Mp = 64–66°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.48 (dd, *J* = 2.5, 0.7 Hz, 1H), 8.05 (dd, *J* = 8.7, 2.5 Hz, 1H), 6.77 (dd, *J* = 8.8, 0.7 Hz, 1H), 3.95 (s, 3H), 2.86 (q, *J* = 7.7 Hz, 2H), 1.20 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.3, 165.9, 156.4, 146.7–146.5 (m), 146.5, 144.6–144.4 (m), 142.7–142.3 (m), 139.0–138.6 (m), 137.3, 137.0–136.6 (m), 122.0, 111.3, 107.1–106.8 (m), 53.8, 21.7, 11.3; **HRMS-EI** calcd for $C_{16}H_{11}F_5N_2O_3$ $[M]^+$ 374.0684, found 374.0689.

(*E*)-1-(6-phenylpyridin-3-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1ap**).

white solid. Mp = 146–148°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.00 (d, *J* = 2.3 Hz, 1H), 8.18 (dd, *J* = 8.4, 2.4 Hz, 1H), 8.03 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.79 (d, *J* = 8.4 Hz, 1H), 7.50–7.41 (m, 3H), 2.93 (q, *J* = 7.7 Hz, 2H), 1.25 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.3, 159.2, 156.2, 148.1, 146.7–146.4 (m), 144.7–144.3 (m), 142.6–142.3 (m), 138.9–138.5 (m), 138.0, 136.9–136.5 (m), 135.5, 129.7, 128.8, 127.0, 126.9, 120.0, 106.9–106.5 (m), 21.7, 11.1; **HRMS-EI** calcd for $C_{21}H_{13}F_5N_2O_2$ $[M]^+$ 420.0892, found 420.0893.

(*E*)-1-(6-(trifluoromethyl)pyridin-3-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1aq**).

white solid. Mp = 47–49°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.02 (d, *J* = 2.1 Hz, 1H), 8.28 (dd, *J* = 8.2, 2.2 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 2.95 (q, *J* = 7.7 Hz, 2H), 1.22 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.5, 156.0, 149.7 (q, *J* = 35.3 Hz), 148.4, 146.9–146.5 (m), 144.9–144.5 (m), 142.9–142.5 (m), 139.0–138.6 (m), 137.0–136.6 (m), 136.3, 131.8, 121.1 (q, *J* = 274.0 Hz), 120.4 (d, *J* = 3.1 Hz), 106.5–106.1 (m), 22.0, 10.8; **HRMS-EI** calcd for $C_{16}H_8F_8N_2O_2$ $[M]^+$ 412.0453, found 412.0469.

(*E*)-1-(benzofuran-5-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1ar**).

white solid. Mp = 130–132°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.74 (d, *J* = 8.7 Hz, 1H), 7.66 (d, *J* = 2.3 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 6.81 (s, 1H), 2.96 (q, *J* = 7.7 Hz, 2H), 1.24 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.9, 156.5, 156.3, 146.6–146.3 (m), 146.1, 144.6–144.3 (m), 142.5–142.1 (m), 138.9–138.5 (m), 136.9–136.5 (m), 127.8, 127.7, 123.6, 120.9, 111.7, 107.3–106.9 (m), 106.8, 22.5, 11.3; **HRMS-EI** calcd for $C_{18}H_{10}F_5NO_3$ $[M]^+$ 383.0575, found 383.0582.

(*E*)-1-(5-(1-(((perfluorobenzoyl)oxy)imino)propyl)-1H-indol-1-yl)ethan-1-one (**1as**).

white solid. Mp = 177–179°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 8.7 Hz, 1H), 8.02 (d, *J* = 1.8 Hz, 1H), 7.75 (dd, *J* = 8.7, 1.8 Hz, 1H), 7.48 (d, *J* = 3.8 Hz, 1H), 6.70 (d, *J* = 3.7 Hz, 1H), 2.97 (q, *J* = 7.7 Hz, 2H), 2.66 (s, 3H), 1.25 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.0, 168.6, 156.7, 146.7–146.4 (m), 144.6–144.2

(m), 142.6–142.3 (m), 139.0–138.6 (m), 137.0, 137.0–136.6 (m), 130.7, 128.3, 126.4, 124.3, 120.4, 116.8, 109.4, 107.4–107.1 (m), 23.9, 22.5, 11.5; **HRMS-EI** calcd for $C_{20}H_{13}F_5N_2O_3$ $[M]^+$ 424.0841, found 424.0865.

(*E*)-1-(benzo[b]thiophen-3-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1at**).

light yellow solid. Mp = 169–171°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 8.2 Hz, 1H), 7.91 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.51 (ddd, *J* = 8.2, 7.1, 1.2 Hz, 1H), 7.43 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 2.99 (q, *J* = 7.7 Hz, 2H), 1.32 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.8, 156.5, 146.8–146.5 (m), 144.8–144.4 (m), 142.7–142.3 (m), 140.2, 139.0–138.7 (m), 137.0–136.6 (m), 136.0, 131.3, 129.3, 126.5, 125.7, 125.4, 122.4, 107.3–106.9 (m), 23.1, 11.9; **HRMS-EI** calcd for $C_{18}H_{10}F_5NO_2S$ $[M]^+$ 399.0347, found 399.0360.

(*E*)-1-(quinolin-6-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1au**).

white solid. Mp = 138–140°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.92 (dd, *J* = 4.3, 1.7 Hz, 1H), 8.20–8.16 (m, 2H), 8.11 (d, *J* = 1.7 Hz, 2H), 7.41 (dd, *J* = 8.3, 4.3 Hz, 1H), 2.99 (q, *J* = 7.7 Hz, 2H), 1.24 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.9, 156.3, 151.7, 149.1, 146.7–146.4 (m), 144.7–144.3 (m), 142.6–142.3 (m), 138.9–138.5 (m), 136.9–136.5 (m), 136.6, 130.9, 130.1, 127.7, 127.7, 127.4, 121.8, 107.0–106.6 (m), 22.1, 11.3; **HRMS-EI** calcd for $C_{19}H_{11}F_5N_2O_2$ $[M]^+$ 394.0735, found 394.0716.

(*E*)-1-(quinolin-3-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1av**).

white solid. Mp = 151–153°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.29 (d, *J* = 2.3 Hz, 1H), 8.49 (d, *J* = 2.3 Hz, 1H), 8.12 (d, *J* = 8.4 Hz, 1H), 7.87 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.77 (ddd, *J* = 8.4, 6.8, 1.4 Hz, 1H), 7.59 (t, *J* = 7.5 Hz, 1H), 3.02 (q, *J* = 7.7 Hz, 2H), 1.28 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.7, 156.4, 148.9, 148.3, 146.8–146.4 (m), 144.8–144.4 (m), 142.8–142.3 (m), 139.0–138.6 (m), 137.0–136.6 (m), 135.3, 131.0, 129.3, 128.5, 127.4, 127.1, 125.8, 106.9–106.6 (m), 22.0, 11.2; **HRMS-EI** calcd for $C_{19}H_{11}F_5N_2O_2$ $[M]^+$ 394.0735, found 394.0733.

(*E*)-1-(4-(1H-pyrazol-1-yl)phenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1aw**).

white solid. Mp = 140–142°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (d, *J* = 2.5 Hz, 1H), 7.90–7.85 (m, 2H), 7.80–7.76 (m, 2H), 7.74 (d, *J* = 1.7 Hz, 1H), 6.49 (t, *J* = 2.2 Hz, 1H), 2.91 (q, *J* = 7.7 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.7, 156.5, 146.7–146.4 (m), 144.7–144.3 (m), 142.6–142.3 (m), 141.9, 141.7, 138.9–138.6 (m), 136.9–136.6 (m), 130.5, 128.7, 126.7, 118.8, 108.3, 107.2–106.7 (m), 22.0, 11.3; **HRMS-EI** calcd for $C_{19}H_{12}F_5N_3O_2$ $[M]^+$ 409.0844, found 409.0829.

(*E*)-1-(4-(2H-1,2,3-triazol-2-yl)phenyl)propan-1-one *O*-perfluorobenzoyl oxime (**1ax**).

white solid. Mp = 171–173°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.17 (d, *J* = 8.8 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.85 (s, 2H), 2.94 (q, *J* = 7.7 Hz, 2H), 1.25 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.7, 156.5, 146.8–146.4 (m), 144.7–144.4 (m), 142.7–142.3 (m), 141.5, 139.0–138.6 (m), 137.0–136.6 (m), 136.1, 131.8, 128.6, 119.0, 107.1–106.8 (m), 22.1, 11.3; **HRMS-EI** calcd for $C_{18}H_{11}F_5N_4O_2$ $[M]^+$ 410.0797, found 410.0780.

(*E*)-1-(2-methylbenzo[d]oxazol-5-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1ay**).

white solid. Mp = 94–96°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 1.6 Hz, 1H), 7.71 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 2.94 (q, *J* = 7.7 Hz, 2H), 2.66 (s, 3H), 1.23 (t, *J* = 7.6 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.4, 165.9, 156.5, 151.1, 146.7–146.4 (m), 144.7–144.4 (m), 144.0, 142.6–142.3 (m), 139.0–138.6 (m), 136.9–136.6 (m), 129.4, 123.7, 119.5, 109.5, 107.1–106.8 (m), 22.5, 14.6, 11.4; **HRMS-EI** calcd for $C_{18}H_{11}F_5N_2O_3$ $[M]^+$ 398.0684, found 398.0651.

(*E*)-4-(1-(((perfluorobenzoyl)oxy)imino)propyl)-N,N-dipropylbenzenesulfona-mide (**1ba**).

white solid. Mp = 89–91°C; (Major) **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.87 (d, *J* = 8.5 Hz, 2H), 7.84 (d, *J* = 8.7 Hz, 2H), 3.06 (td, *J* = 7.4, 1.6 Hz, 4H), 2.91 (q, *J* = 7.7 Hz, 2H), 1.52 (h, *J* = 7.4 Hz, 4H), 1.20 (t, *J* = 7.6 Hz, 3H), 0.84 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.5, 156.2, 146.7–146.4 (m), 144.8–144.4 (m), 142.7–142.4 (m),

142.4, 139.0–138.6 (m), 136.9–136.5 (m), 136.6, 128.0, 127.3, 106.8–106.4 (m), 49.9, 22.2, 21.8, 11.0; **HRMS-EI** calcd for $C_{22}H_{23}F_5N_2O_4S$ $[M]^+$ 506.1293, found 506.1265.

(*E*)-1-(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)propan-1-one *O*-perfluorobenzoyl oxime (**1bb**).

white solid. Mp = 196–198°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.22 (d, *J* = 1.6 Hz, 1H), 8.01 (d, *J* = 1.7 Hz, 1H), 7.98–7.92 (m, 3H), 7.80 (dd, *J* = 8.5, 1.8 Hz, 1H), 7.61 (d, *J* = 2.4 Hz, 1H), 7.55 (dd, *J* = 8.3, 2.3 Hz, 1H), 7.00 (d, *J* = 8.5 Hz, 1H), 3.91 (s, 3H), 3.04 (q, *J* = 7.7 Hz, 2H), 2.20 (d, *J* = 2.9 Hz, 6H), 2.15–2.09 (m, 3H), 1.84–1.79 (m, 6H), 1.31 (t, *J* = 7.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 168.5, 156.2, 146.7–146.4 (m), 144.8–144.4 (m), 142.7–142.4 (m), 142.4, 139.0–138.6 (m), 136.9–136.5 (m), 136.6, 128.0, 127.3, 106.8–106.4 (m), 49.9, 22.2, 21.8, 11.0; **HRMS-EI** calcd for $C_{37}H_{32}F_5NO_3$ $[M]^+$ 633.2297, found 633.2292.

3,3,5-trimethylcyclohexyl (E)-2-acetoxy-5-(1-(((perfluorobenzoyl)oxy)imino) propyl)benzoate (**1bd**).

white solid. Mp = 89–91°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.29 (d, *J* = 2.3 Hz, 1H), 7.97 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.16 (d, *J* = 8.4 Hz, 1H), 5.11 (tt, *J* = 11.6, 4.4 Hz, 1H), 2.90 (q, *J* = 7.7 Hz, 2H), 2.35 (s, 3H), 2.12–2.04 (m, 1H), 1.81–1.70 (m, 2H), 1.39–1.33 (m, 1H), 1.25–1.19 (m, 4H), 1.00–0.94 (m, 7H), 0.92 (d, *J* = 6.5 Hz, 3H), 0.82 (t, *J* = 12.7 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 169.0, 168.2, 163.4, 156.4, 152.3, 146.7–146.4 (m), 144.6–144.3 (m), 142.6–142.3 (m), 138.9–138.5 (m), 136.9–136.5 (m), 132.2, 130.8, 130.7, 124.6, 124.4, 107.0–106.6 (m), 72.5, 47.4, 43.8, 40.2, 32.9, 32.3, 27.1, 25.4, 22.2, 21.0, 11.1; **HRMS (ESI-TOF)** calcd for $C_{28}H_{32}F_5N_2O_6$ $[M + NH_4]^+$ 587.2175, found 587.2174.

pent-1-en-3-*d*-3-ol (**2a-*d***).

colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$): δ 5.85 (ddt, *J* = 17.2, 10.4, 0.9 Hz, 1H), 5.21 (dd, *J* = 17.2, 1.6 Hz, 1H), 5.11 (dd, *J* = 10.4, 1.6 Hz, 1H), 4.02 (qt, *J* = 6.3, 1.3 Hz, 0.05H). 1.59–1.51 (m, 2H), 0.92 (t, *J* = 7.5 Hz, 3H). **^{2}H NMR** (500 MHz, $CHCl_3$): δ 4.02 (q, *J* = 1.0 Hz, 1H).

(*5S*)-5,9-dimethyldeca-1,8-dien-3-ol (**1j**).

colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.91–5.78 (m, 1H), 5.21 (dq, *J* = 17.2, 1.6 Hz, 1H), 5.11–5.04 (m, 2H), 4.21–4.14 (m, 1H), 2.05–1.88 (m, 2H), 1.69–1.62 (m, 4H), 1.59 (d, *J* = 1.4 Hz, 3H), 1.57–1.51 (m, 1H), 1.48–1.29 (m, 2H), 1.28–1.11 (m, 2H), 0.91 (t, *J* = 6.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 141.8, 141.4, 131.2, 124.7, 114.7, 114.1, 71.6, 71.0, 44.4, 44.3, 37.5, 36.9, 29.0, 28.7, 25.7, 25.4, 25.3, 19.9, 19.2, 17.6; **HRMS-EI** calcd for $C_{12}H_{22}O$ $[M]^+$ 182.1665, found 182.1687.

Characterization data of products

1-phenylpentan-3-one (**3a**) (Zhang et al., 2013).

11.3 mg, 70% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31–7.25 (m), 7.22–7.15 (m), 2.90 (t, *J* = 7.7 Hz), 2.73 (t, *J* = 7.7 Hz), 2.41 (q, *J* = 7.3 Hz), 1.05 (t, *J* = 7.3 Hz).

1-(*o*-tolyl)pentan-3-one (**3b**) (Zhang et al., 2013).

8.9 mg, 51% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17–7.09 (m, 4H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.69 (t, *J* = 7.7 Hz, 2H), 2.43 (q, *J* = 7.3 Hz, 2H), 2.31 (s, 3H), 1.06 (t, *J* = 7.3 Hz, 3H).

1-(2-fluorophenyl)pentan-3-one (**3c**).

13.1 mg, 71% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.23–7.13 (m, 2H), 7.04 (td, *J* = 7.5, 1.3 Hz, 1H), 7.04–6.96 (m, 1H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.3, 161.1 (d, *J* = 245.0 Hz), 130.8 (d, *J* = 5.0 Hz), 127.9 (d, *J* = 15.3 Hz), 127.8 (d, *J* = 7.8 Hz), 124.0 (d, *J* = 4.1 Hz), 115.2 (d, *J* = 22.2 Hz), 42.3, 36.0, 23.5, 7.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ −118.6–118.7 (m). **HRMS-EI** calcd for $C_{11}H_{13}FO$ $[M]^+$ 180.0945, found 180.0931.

1-(2-chlorophenyl)pentan-3-one (**3d**).

15.7 mg, 80% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.23 (dd, *J* = 7.3, 2.0 Hz, 1H), 7.19–7.12 (m, 2H), 3.00 (t, *J* = 7.7 Hz, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.3, 138.7, 133.8, 130.6, 129.5, 127.6, 126.9, 41.8, 36.0, 27.9, 7.7; **HRMS-EI** calcd for $C_{11}H_{13}ClO$ $[M]^+$ 196.0649, found 196.0649.

1-(*m*-tolyl)pentan-3-one (**3e**) (Zhang et al., 2013).

12.1 mg, 69% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.9 Hz, 1H), 6.99 (q, *J* = 7.4 Hz, 3H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 2.33 (s, 3H), 1.05 (t, *J* = 7.3 Hz, 3H).

1-(3-methoxyphenyl)pentan-3-one (**3f**) (Molander and Petrillo, 2008).

13.4 mg, 70% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19 (td, *J* = 7.5, 1.8 Hz, 1H), 6.77 (d, *J* = 7.6 Hz, 1H), 6.75–6.71 (m, 2H), 3.79 (s, 3H), 2.88 (t, *J* = 7.7 Hz, 2H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

1-(3-(methylthio)phenyl)pentan-3-one (**3g**).

15.4 mg, 74% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21–7.17 (m, 1H), 7.10–7.06 (m, 2H), 6.95 (d, *J* = 7.5 Hz, 1H), 2.86 (t, *J* = 7.7 Hz, 2H), 2.72 (t, *J* = 7.7 Hz, 2H), 2.47 (s, 3H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.4, 141.9, 138.5, 128.9, 126.4, 125.1, 124.2, 43.7, 36.1, 29.7, 15.7, 7.7; **HRMS-EI** calcd for $C_{12}H_{16}OS$ $[M]^+$ 208.0916, found 208.0915.

N-(3-(3-oxopentyl)phenyl)acetamide (**3h**).

11.5 mg, 52% yield; white solid. Mp = 64–66°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (brs, 1H), 7.36 (s, 1H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.5 Hz, 1H), 2.85 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.39 (q, *J* = 7.3 Hz, 2H), 2.15 (s, 3H), 1.03 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.7, 168.5, 142.1, 138.1, 129.0, 124.2, 119.7, 117.6, 43.6, 36.1, 29.7, 24.5, 7.7; **HRMS-EI** calcd for $C_{13}H_{17}NO_2$ $[M]^+$ 219.1254, found 219.1248.

3-(3-oxopentyl)phenyl acetate (**3i**).

16.6 mg, 75% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30–7.26 (m, 1H), 7.05 (d, *J* = 7.8 Hz, 1H), 6.93–6.89 (m, 2H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 2.28 (s, 3H), 1.04 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.3, 169.5, 150.7, 142.9, 129.4, 125.9, 121.4, 119.2, 43.5, 36.1, 29.5, 21.1, 7.7; **HRMS-EI** calcd for $C_{13}H_{16}O_3$ $[M]^+$ 220.1094, found 220.1096.

1-(3-fluorophenyl)pentan-3-one (**3j**) (Kumar et al., 2018).

14.0 mg, 78% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25–7.19 (m, 1H), 6.95 (d, *J* = 7.6 Hz, 1H), 6.92–6.84 (m, 2H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

1-(3-chlorophenyl)pentan-3-one (**3k**).

14.3 mg, 73% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22–7.14 (m, 3H), 7.06 (dt, *J* = 7.2, 1.6 Hz, 1H), 2.87 (t, *J* = 7.6 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.1, 143.2, 134.1, 129.7, 128.4, 126.6, 126.2, 43.4, 36.1, 29.3, 7.7; **HRMS-EI** calcd for $C_{11}H_{13}ClO$ $[M]^+$ 196.0649, found 196.0657.

1-(3-(trifluoromethyl)phenyl)pentan-3-one (**3l**).

16.0 mg, 70% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.41–7.36 (m, 2H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.9, 142.1, 131.8, 130.8 (q, *J* = 31.9 Hz), 128.9, 125.0 (q, *J* = 3.9 Hz), 124.2 (q, *J* = 272.3 Hz), 123.0 (q, *J* = 3.6 Hz), 43.4, 36.1, 29.4, 7.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ −62.6; **HRMS-EI** calcd for $C_{12}H_{13}F_3O$ $[M]^+$ 230.0913, found 230.0911.

3-(3-oxopentyl)benzonitrile (**3m**) (Molander and Petrillo, 2008).

12.1 mg, 65% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.49–7.45 (m, 2H), 7.43 (dt, *J* = 7.8, 1.6 Hz, 1H), 7.37 (t, *J* = 7.9 Hz, 1H), 2.92 (t, *J* = 7.4 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H).

1-(3-nitrophenyl)pentan-3-one (**3n**) (Shen et al., 2011).

9.9 mg, 48% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.13–8.03 (m, 2H), 7.57 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.47 (dd, *J* = 8.8, 7.6 Hz, 1H), 3.04 (t, *J* = 7.4 Hz, 2H), 2.83 (t, *J* = 7.4 Hz, 2H), 2.46 (q, *J* = 7.3 Hz, 2H), 1.08 (t, *J* = 7.3 Hz, 3H).

1-(*p*-tolyl)pentan-3-one (**3o**) (Zhang et al., 2013).

10.9 mg, 62% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12–7.04 (m, 4H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 2.31 (s, 3H), 1.04 (t, *J* = 7.3 Hz, 3H).

1-(4-(tert-butyl)phenyl)pentan-3-one (**3p**) (Zhang et al., 2013).

12.2 mg, 56% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 2.87 (t, *J* = 7.7 Hz, 2H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.30 (s, 9H), 1.05 (t, *J* = 7.3 Hz, 3H).

1-([1,1′-biphenyl]-4-yl)pentan-3-one (**3q**) (Jana and Tunge., 2009).

17.1 mg, 72% yield; white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (dd, *J* = 8.3, 1.1 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 2H), 2.96 (t, *J* = 7.7 Hz, 2H), 2.78 (t, *J* = 7.7 Hz, 2H), 2.44 (q, *J* = 7.3 Hz, 2H), 1.07 (t, *J* = 7.3 Hz, 3H).

4-(3-oxopentyl)phenyl acetate (**3r**) (Schlosser and Michel, 1996).

17.4 mg, 79% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.20–7.15 (m, 2H), 7.01–6.96 (m, 2H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.71 (t, *J* = 7.6 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 2.28 (s, 3H), 1.04 (t, *J* = 7.3 Hz, 3H).

1-(4-(trifluoromethoxy)phenyl)pentan-3-one (**3s**) (Zhang et al., 2013).

17.4 mg, 71% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.22–7.17 (m, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H).

1-(4-fluorophenyl)pentan-3-one (**3t**) (Clifton et al., 1982).

14.2 mg, 79% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.19–7.13 (m, 2H), 7.01–6.95 (m, 2H), 2.90 (t, *J* = 7.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.43 (q, *J* = 7.3 Hz, 2H), 1.07 (t, *J* = 7.3 Hz, 3H).

1-(4-chlorophenyl)pentan-3-one (**3u**) (Zhang et al., 2013).

16.1 mg, 82% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.25–7.21 (m, 2H), 7.12–7.09 (m, 2H), 2.86 (t, *J* = 7.5 Hz, 2H), 2.70 (t, *J* = 7.5 Hz, 2H), 2.39 (q, *J* = 7.3 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H).

1-(4-(trifluoromethyl)phenyl)pentan-3-one (**3v**) (Zhang et al., 2013).

17.7 mg, 77% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.96 (t, *J* = 7.5 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

4-(3-oxopentyl)benzonitrile (**3w**) (Shen et al., 2011).

12.2 mg, 65% yield; white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 2.95 (t, *J* = 7.4 Hz, 2H), 2.74 (t, *J* = 7.4 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H).

1-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pentan-3-one (**3x**).

20.7 mg, 72% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.19 (d, *J* = 7.7 Hz, 2H), 2.91 (t, *J* = 7.7 Hz, 2H), 2.72 (t, *J* = 7.6 Hz, 2H), 2.39 (q, *J* = 7.3 Hz, 2H), 1.33 (s, 12H), 1.03 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.5, 144.5, 135.0, 127.7, 83.7, 43.6, 36.1, 30.0, 24.8, 7.7; **HRMS-EI** calcd for $C_{17}H_{25}BO_3$ $[M]^+$ 288.1891, found 288.1910.

1-(4-(trimethylsilyl)phenyl)pentan-3-one (**3y**).

14.0 mg, 60% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.9 Hz, 2H), 7.18 (d, *J* = 7.8 Hz, 2H), 2.89 (t, *J* = 7.7 Hz, 2H), 2.74 (t, *J* = 7.7 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H), 0.25 (s, 9H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.6, 141.8, 137.8, 133.5, 127.7, 43.7, 36.0, 29.7, 7.8, −1.1; **HRMS-EI** calcd for $C_{14}H_{22}OSi$ $[M]^+$ 234.1434, found 234.1419.

ethyl 4-(3-oxopentyl)benzoate (**3z**) (Shen et al., 2011).

18.3 mg, 71% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97–7.93 (m, 2H), 7.26–7.22 (m, 2H), 4.36 (q, *J* = 7.2 Hz, 2H), 2.95 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H), 1.04 (t, *J* = 7.3 Hz, 3H).

diethyl (4-(3-oxopentyl)phenyl)phosphonate (**3aa**).

24.8 mg, 83% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.1 Hz, 1H), 7.69 (d, *J* = 8.0 Hz, 1H), 7.27 (d, *J* = 8.1 Hz, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 4.17–4.06 (m, 2H), 4.09–4.00 (m, 2H), 2.93 (t, *J* = 7.5 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 1.30 (t, *J* = 7.0 Hz, 6H), 1.03 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.0, 146.1 (d, *J* = 3.6 Hz), 132.0 (d, *J* = 10.4 Hz), 128.5 (d, *J* = 15.7 Hz), 125.8 (d, *J* = 190.0 Hz), 62.0 (d, *J* = 5.6 Hz), 43.2, 36.1, 29.6, 16.3 (d, *J* = 6.6 Hz), 7.7; **^{31}P NMR** (202 MHz, $CDCl_3$) δ 19.2; **HRMS-EI** calcd for $C_{15}H_{23}O_4P$ $[M]^+$ 299.1328, found 298.1348.

1-(4-(methylsulfonyl)phenyl)pentan-3-one (**3ab**).

17.3 mg, 72% yield; light yellow solid. Mp = 69–71°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.4 Hz, 2H), 3.03 (s, 3H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.6, 147.9, 138.3, 129.4, 127.6, 44.5, 43.0, 36.1, 29.4, 7.7; **HRMS-EI** calcd for $C_{12}H_{16}O_3S$ $[M]^+$ 240.0815, found 240.0807.

1-(3,5-dimethylphenyl)pentan-3-one (**3ac**).

12.0 mg, 63% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.84 (s, 1H), 6.81 (s, 2H), 2.83 (t, *J* = 7.7 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 2.29 (s, 6H), 1.06 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.8, 141.0, 137.9, 127.7, 126.1, 44.0, 36.0, 29.7, 21.2, 7.8; **HRMS-EI** calcd for $C_{13}H_{18}O$ $[M]^+$ 190.1352, found 190.1358.

1-(3,5-dimethoxyphenyl)pentan-3-one (**3ad**) (Krishnamurty and Prasad, 1975).

14.2 mg, 64% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.33 (d, *J* = 2.3 Hz, 2H), 6.30 (t, *J* = 2.3 Hz, 1H), 3.77 (s, 6H), 2.84 (t, *J* = 7.7 Hz, 2H), 2.71 (t, *J* = 7.7 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

1-(3,5-difluorophenyl)pentan-3-one (**3ae**).

13.1 mg, 66% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.74–6.65 (m, 2H), 6.62 (tt, *J* = 9.0, 2.4 Hz, 1H), 2.88 (t, *J* = 7.5 Hz, 2H), 2.72 (t, *J* = 7.5 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.7, 163.0 (dd, *J* = 248.0, 13.2 Hz), 145.1 (t, *J* = 9.0 Hz), 111.1 (dd, *J* = 19.4, 5.8 Hz), 101.6 (t, *J* = 25.3 Hz), 42.9, 36.1, 29.3, 7.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ −110.4 (t, *J* = 7.6 Hz); **HRMS-EI** calcd for $C_{11}H_{12}F_2O$ $[M]^+$ 198.0851, found 198.0856.

1-(3,5-dichlorophenyl)pentan-3-one (**3af**).

16.3 mg, 71% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.18 (t, *J* = 1.9 Hz, 1H), 7.06 (d, *J* = 1.9 Hz, 2H), 2.85 (t, *J* = 7.3 Hz, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.5, 144.6, 134.8, 126.9, 126.3, 43.0, 36.1, 29.0, 7.7; **HRMS-EI** calcd for $C_{11}H_{12}Cl_2O$ $[M]^+$ 230.0260, found 230.0257.

(*E*)-1-(4-styrylphenyl)pentan-3-one (**3ag**).

16.4 mg, 62% yield; white solid. Mp = 99–101°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 (dd, *J* = 8.2, 1.3 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.36 (t, *J* = 7.7 Hz, 2H), 7.30–7.22 (m, 1H), 7.18 (d, *J* = 8.2 Hz, 2H), 7.08 (d, *J* = 1.0 Hz, 2H), 2.92 (t, *J* = 7.6 Hz, 2H), 2.74 (t, *J* = 7.6 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.6, 140.7, 137.4, 135.2, 128.6, 128.4, 128.1, 127.5, 126.6, 126.4, 43.7, 36.1, 29.6, 7.7; **HRMS-EI** calcd for $C_{19}H_{21}O$ $[M]^+$ 265.1587, found 265.1560.

1-(2,6-difluorophenyl)pentan-3-one (**3ah**).

12.9 mg, 65% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.13 (tt, *J* = 8.5, 6.5 Hz, 1H), 6.83 (p, *J* = 6.8, 6.2 Hz, 2H), 2.94 (t, *J* = 7.8 Hz, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.43 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.9, 161.5 (dd, *J* = 246.9, 8.6 Hz), 127.6 (t, *J* = 10.4 Hz), 116.4 (t, *J* = 19.9 Hz), 111.1 (dd, *J* = 20.1, 5.9 Hz), 41.4, 35.8, 16.7, 7.7; **^{19}F NMR** (471 MHz, $CDCl_3$) δ −110.4 (t, *J* = 7.2 Hz); **HRMS-EI** calcd for $C_{11}H_{12}F_2O$ $[M]^+$ 198.0851, found 198.0856.

1-(3,4-dichlorophenyl)pentan-3-one (**3ai**).

16.6 mg, 72% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.2 Hz, 1H), 7.27 (d, *J* = 2.1 Hz, 1H), 7.02 (dd, *J* = 8.2, 2.1 Hz, 1H), 2.85 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.8, 141.5, 132.2, 130.3, 130.3, 130.0, 127.9, 43.2, 36.1, 28.7, 7.7; **HRMS-EI** calcd for $C_{11}H_{12}Cl_2O$ $[M]^+$ 230.0260, found 230.0266.

1-(naphthalen-1-yl)pentan-3-one (**3aj**) (Zhang et al., 2013).

7.8 mg, 37% yield; Colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.5, 1.2 Hz, 1H), 7.87 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.73 (d, *J* = 8.1 Hz, 1H), 7.55–7.47 (m, 2H), 7.43–7.36 (m, 1H), 7.34 (dd, *J* = 7.0, 1.2 Hz, 1H), 3.38 (t, *J* = 7.6 Hz, 2H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.07 (t, *J* = 7.3 Hz, 3H).

1-(naphthalen-2-yl)pentan-3-one (**3ak**) (Watanabe et al., 2013).

14.8 mg, 70% yield; white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 1.6 Hz, 1H), 7.48–7.41 (m, 2H), 7.33 (dd, *J* = 8.4, 1.7 Hz, 1H), 3.07 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.7 Hz, 2H), 2.43 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H).

6-(3-oxopentyl)naphthalen-2-yl acetate (**3al**).

18.6 mg, 69% yield; white solid. Mp = 77–79°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.8 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.62 (s, 1H), 7.51 (d, *J* = 2.3 Hz, 1H), 7.33 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.20 (dd, *J* = 8.8, 2.3 Hz, 1H), 3.05 (t, *J* = 7.6 Hz, 2H), 2.80 (t, *J* = 7.6 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 2.35 (s, 3H), 1.04 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.5, 169.7, 147.9, 138.6, 132.3, 131.6, 128.9, 127.8, 127.8, 126.3, 121.2, 118.3, 43.7, 36.2, 29.9, 21.2, 7.7; **HRMS-EI** calcd for $C_{17}H_{18}O_3$ $[M]^+$ 270.1250, found 270.1256.

1-(furan-3-yl)pentan-3-one (**3am**).

7.9 mg, 52% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 1.7 Hz, 1H), 7.21 (t, *J* = 1.2 Hz, 1H), 6.27–6.23 (m, 1H), 2.71 (dd, *J* = 8.1, 4.8 Hz, 2H), 2.68–2.63 (m, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.6, 142.8, 139.0, 123.9, 110.9, 42.6, 36.1, 19.0, 7.7; **HRMS-EI** calcd for $C_9H_{12}O_2$ $[M]^+$ 152.0832, found 152.0820.

1-(thiophen-3-yl)pentan-3-one (**3an**) (Tamaru et al., 1979).

10.2 mg, 61% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26–7.23 (m, 1H), 6.96–6.91 (m, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.73 (t, *J* = 7.5 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H).

1-(6-methoxypyridin-3-yl)pentan-3-one (**3ao**).

11.6 mg, 60% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 2.3 Hz, 1H), 7.40 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.66 (d, *J* = 8.5 Hz, 1H), 3.90 (s, 3H), 2.82 (t, *J* = 7.4 Hz, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.2, 162.8, 146.0, 139.0, 129.1, 110.5, 53.3, 43.6, 36.1, 25.9, 7.7; **HRMS-EI** calcd for $C_{11}H_{15}NO_2$ $[M]^+$ 193.1097, found 193.1108.

1-(6-phenylpyridin-3-yl)pentan-3-one (**3ap**).

16.2 mg, 68% yield; white solid. Mp = 36–38°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (d, *J* = 2.3 Hz, 1H), 7.98–7.93 (m, 2H), 7.64 (dd, *J* = 8.1, 0.9 Hz, 1H), 7.58 (dd, *J* = 8.1, 2.3 Hz, 1H), 7.49–7.42 (m, 2H), 7.42–7.37 (m, 1H), 2.94 (t, *J* = 7.4 Hz, 2H), 2.77 (t, *J* = 7.4 Hz, 2H), 2.43 (q, *J* = 7.3 Hz, 2H), 1.06 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.9, 155.4, 149.5, 139.1, 136.8, 135.0, 128.7, 128.7, 126.7, 120.2, 43.2, 36.1, 26.5, 7.7; **HRMS-EI** calcd for $C_{16}H_{17}NO$ $[M]^+$ 239.1305, found 239.1297.

1-(6-(trifluoromethyl)pyridin-3-yl)pentan-3-one (**3aq**).

10.4 mg, 45% yield; white solid. Mp = 41–43°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (d, *J* = 2.1 Hz, 1H), 7.70 (dd, *J* = 7.9, 2.0 Hz, 1H), 7.57 (d, *J* = 8.0, 1H), 2.97 (t, *J* = 7.3 Hz, 2H), 2.77 (t, *J* = 7.3 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.1, 150.1, 146.1 (q, *J* = 34.7 Hz), 140.1, 137.2, 121.6 (q, *J* = 274.0 Hz), 120.1 (q, *J* = 2.5 Hz), 42.6, 36.0, 26.5, 7.6; **^{19}F NMR** (376 MHz, $CDCl_3$) δ −67.8; **HRMS-EI** calcd for $C_{11}H_{12}F_3NO$ $[M]^+$ 231.0866, found 231.0852.

1-(benzofuran-5-yl)pentan-3-one (**3ar**).

11.7 mg, 58% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.59 (d, *J* = 2.3 Hz, 1H), 7.42–7.39 (m, 2H), 7.11 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.71 (d, *J* = 2.1 Hz, 1H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.6 Hz, 2H), 2.40 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.8, 153.6, 145.2, 135.6, 127.6, 124.7, 120.4, 111.2, 106.4, 44.5, 36.2, 29.7, 7.7; **HRMS-EI** calcd for $C_{13}H_{14}O_2$ $[M]^+$ 202.0988, found 202.0984.

1-(1-acetyl-1H-indol-5-yl)pentan-3-one (**3as**).

12.4 mg, 51% yield; white solid. Mp = 86–88°C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.32 (d, *J* = 6.7 Hz, 1H), 7.43–7.33 (m, 2H), 7.17 (dd, *J* = 8.4, 1.7 Hz, 1H), 6.58 (d, *J* = 3.8 Hz, 1H), 2.99 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.7 Hz, 2H), 2.62 (s, 3H), 2.40 (q, *J* = 7.3 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 210.8, 168.5, 136.6, 134.1, 130.7, 125.6, 125.4, 120.3, 116.4, 109.0, 44.3, 36.2, 29.8, 23.9, 7.7; **HRMS-EI** calcd for $C_{15}H_{17}NO_2$ $[M]^+$ 243.1254, found 243.1251.

1-(benzo[b]thiophen-3-yl)pentan-3-one (**3at**).

11.3 mg, 52% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.9 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.43–7.32 (m, 2H), 7.10 (s, 1H), 3.14 (t, *J* = 7.6 Hz, 2H), 2.86 (t, *J* = 7.6 Hz, 2H), 2.44 (q, *J* = 7.4 Hz, 2H), 1.07 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.5, 140.4, 138.6, 135.4, 124.2, 123.9, 122.9, 121.5, 121.5, 41.6, 36.1, 22.4, 7.8; **HRMS-EI** calcd for $C_{13}H_{14}OS$ $[M]^+$ 218.0760, found 218.0760.

1-(quinolin-6-yl)pentan-3-one (**3au**).

10.2 mg, 48% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.84 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.07 (dd, *J* = 8.4, 1.6 Hz, 1H), 8.01 (d, *J* = 8.6 Hz, 1H), 7.59 (s, 1H), 7.54 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.36 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.08 (t, *J* = 7.5 Hz, 2H), 2.82 (t, *J* = 7.5 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.2, 149.8, 147.0, 139.6, 135.6, 130.6, 129.4, 128.2, 126.3, 121.1, 43.4, 36.1, 29.6, 7.7; **HRMS-EI** calcd for $C_{14}H_{15}NO$ $[M]^+$ 213.1148, found 213.1148.

1-(quinolin-3-yl)pentan-3-one (**3av**).

9.6 mg, 45% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.78 (d, *J* = 2.1 Hz, 1H), 8.06 (d, *J* = 8.4 Hz, 1H), 7.94 (s, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 3.09 (t, *J* = 7.4 Hz, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.8, 151.7, 146.8, 134.5, 133.8, 129.1, 128.8, 128.0, 127.3, 126.7, 43.2, 36.1, 26.9, 7.7; **HRMS-EI** calcd for $C_{14}H_{15}NO$ $[M]^+$ 213.1148, found 213.1148.

1-(4-(1H-pyrazol-1-yl)phenyl)pentan-3-one (**3aw**).

17.1 mg, 75% yield; white solid. Mp = 63–65°C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 7.89 (d, *J* = 2.4 Hz, 1H), 7.71 (d, *J* = 1.8 Hz, 1H), 7.61–7.57 (m, 2H), 7.28–7.24 (m, 2H), 6.45 (t, *J* = 2.1 Hz, 1H), 2.93 (t, *J* = 7.6 Hz, 2H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 210.4, 140.9, 139.5, 138.5, 129.3, 126.7, 119.3, 107.4, 43.7, 36.2, 29.2, 7.7; **HRMS-EI** calcd for $C_{14}H_{16}N_2O$ $[M]^+$ 228.1257, found 228.1252.

1-(4-(2H-1,2,3-triazol-2-yl)phenyl)pentan-3-one (**3ax**).

18.5 mg, 81% yield; white solid. Mp = 44–46°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.79 (s, 2H), 7.29 (d, *J* = 8.5 Hz, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.41 (q, *J* = 7.3 Hz, 2H), 1.04 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.3, 140.7, 138.2, 135.3, 129.2, 119.0, 43.6, 36.2, 29.2, 7.7; **HRMS-EI** calcd for $C_{13}H_{15}N_3O$ $[M]^+$ 229.1210, found 229.1210.

1-(2-methylbenzo[d]oxazol-5-yl)pentan-3-one (**3ay**).

14.8 mg, 68% yield; yellowish oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 1H), 7.28 (s, 1H), 7.11 (d, *J* = 8.1 Hz, 1H), 3.00 (t, *J* = 7.5 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.60 (s, 3H), 2.39 (q, *J* = 7.3 Hz, 2H), 1.03 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.3, 163.6, 151.2, 139.8, 138.1, 124.5, 119.0, 109.9, 44.1, 36.2, 29.9, 14.5, 7.7; **HRMS-EI** calcd for $C_{13}H_{25}NO_2$ $[M]^+$ 217.1097, found 217.1087.

1-(benzo[d]thiazol-5-yl)pentan-3-one (**3az**).

12.5 mg, 57% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.97 (s, 1H), 7.94 (d, *J* = 0.9 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.30 (dd, *J* = 8.2, 1.6 Hz, 1H), 3.08 (t, *J* = 7.6 Hz, 2H), 2.82 (t, *J* = 7.6 Hz, 2H), 2.43 (q, *J* = 7.3 Hz, 2H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.2, 154.2, 153.7, 139.8, 131.4, 126.6, 122.8, 121.7, 43.9, 36.2, 29.6, 7.8; **HRMS-EI** calcd for $C_{12}H_{13}NOS$ $[M]^+$ 219.0712, found 219.0710.

4-phenylbutan-2-one (**3ba**) (Jana and Tunge, 2009).

10.5 mg, 71% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31–7.26 (m, 2H), 7.22–7.17 (m, 3H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.76 (t, *J* = 7.6 Hz, 2H), 2.14 (s, 3H).

1-phenylhexan-3-one (**3bb**) (Liao et al., 2015).

12.5 mg, 71% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.21–7.16 (m, 3H), 2.90 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.37 (t, *J* = 7.3 Hz, 2H), 1.59 (h, *J* = 7.4 Hz, 2H), 0.89 (t, *J* = 7.4 Hz, 3H).

4-methyl-1-phenylpentan-3-one (**3bc**) (Kotani et al., 2011).

12.7 mg, 72% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31–7.26 (m, 2H), 7.22–7.17 (m, 3H), 2.89 (t, *J* = 7.6 Hz, 2H), 2.77 (t, *J* = 7.5 Hz, 2H), 2.57 (hept, *J* = 6.9 Hz, 1H), 1.07 (d, *J* = 7.0 Hz, 6H).

4,4-dimethyl-1-phenylpentan-3-one (**3bd**) (Kotani et al., 2011)

9.1 mg, 48% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.22–7.17 (m, 3H), 2.91–2.84 (m, 2H), 2.84–2.76 (m, 2H), 1.11 (s, 9H).

1-phenyloctan-3-one (**3be**) (Liao et al., 2015).

14.3 mg, 70% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32–7.25 (m, 2H), 7.22–7.16 (m, 3H), 2.90 (t, *J* = 7.7 Hz, 2H), 2.73 (t, *J* = 7.7 Hz, 2H), 2.38 (t, *J* = 7.5 Hz, 2H), 1.56 (p, *J* = 7.5 Hz, 2H), 1.35–1.18 (m, 4H), 0.88 (t, *J* = 7.1 Hz, 3H).

1,4-diphenylbutan-2-one (**3bf**) (Bay et al., 2020).

14.6 mg, 65% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.32 (t, *J* = 7.3 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 3H), 7.21–7.16 (m, 3H), 7.13 (d, *J* = 7.0 Hz, 2H), 3.67 (s, 1H), 2.87 (t, *J* = 7.2 Hz, 1H), 2.78 (t, *J* = 7.2 Hz, 1H).

1-cyclohexyl-3-phenylpropan-1-one (**3bg**) (Amani and Molander, 2017).

13.8 mg, 64% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30–7.26 (m, 2H), 7.21–7.16 (m, 3H), 2.88 (t, *J* = 7.6 Hz, 2H), 2.78–2.73 (m, 2H), 2.31 (tt, *J* = 11.3, 3.4 Hz, 1H), 1.84–1.73 (m, 4H), 1.68–1.61 (m, 1H), 1.37–1.16 (m, 5H).

3-phenyl-1-(tetrahydro-2H-pyran-4-yl)propan-1-one (**3bh**) (Amani and Molander, 2017).

12.0 mg, 55% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31–7.28 (m, 2H), 7.23–7.17 (m, 3H), 3.99 (ddd, *J* = 11.4, 4.1, 2.7 Hz, 2H), 3.41 (td, *J* = 11.4, 2.9 Hz, 2H), 2.92 (t, *J* = 7.5 Hz, 2H), 2.82–2.76 (m, 2H), 2.52 (tt, *J* = 10.9, 4.3 Hz, 1H), 1.76–1.64 (m, 4H).

1-((tert-butyldimethylsilyl)oxy)-5-phenylpentan-3-one (**3bi**) (Hon et al., 2007).

23.4 mg, 80% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.31–7.27 (m, 2H), 7.22–7.18 (m, 3H), 4.15 (s, 2H), 2.94–2.90 (m, 2H), 2.86–2.81 (m, 2H), 0.91 (s, 9H), 0.07 (s, 6H).

(*S*)-5,9-dimethyl-1-phenyldec-8-en-3-one (**3bj**).

11.9 mg, 46% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33–7.29 (m, 2H), 7.25–7.20 (m, 3H), 5.13–5.07 (m, 1H), 2.92 (t, *J* = 7.7 Hz, 2H), 2.74 (td, *J* = 7.8, 7.3, 2.8 Hz, 2H), 2.41 (dd, *J* = 15.8, 5.6 Hz, 1H), 2.23 (dd, *J* = 15.7, 8.2 Hz, 1H), 1.99 (ddt, *J* = 29.7, 14.4, 7.1 Hz, 3H), 1.71 (q, *J* = 1.4 Hz, 3H), 1.62 (d, *J* = 1.3 Hz, 3H), 1.35–1.27 (m, 1H), 1.25–1.16 (m, 1H), 0.90 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.0, 141.2, 131.5, 128.4, 128.3, 126.0, 124.3, 50.4, 44.8, 36.9, 29.7, 28.9, 25.7, 25.4, 19.7, 17.6; **HRMS-EI** calcd for $C_{18}H_{26}O$ $[M]^+$ 258.1978, found 258.1982.

1-(4-(tert-butyl)phenyl)-2-methyl-5-phenylpentan-3-one (**3bk**) (Liao et al., 2015).

24.9 mg, 81% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (d, *J* = 8.3 Hz, 2H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.4 Hz, 1H), 7.11 (d, *J* = 6.9 Hz, 2H), 7.06 (d, *J* = 8.0 Hz, 2H), 2.92 (dd, *J* = 13.4, 7.3 Hz, 1H), 2.86–2.78 (m, 3H), 2.76–2.68 (m, 1H), 2.59–2.51 (m, 2H), 1.32 (s, 9H), 1.08 (d, *J* = 6.9 Hz, 3H).

1,3-diphenylpropan-1-one (**3bl**) (Liao et al., 2015).

12.2 mg, 58% yield; white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.97 (dd, *J* = 8.3, 1.4 Hz, 2H), 7.58–7.54 (m, 1H), 7.48–7.44 (m, 2H), 7.33–7.28 (m, 2H), 7.28–7.25 (m, 2H), 7.24–7.19 (m, 1H), 3.33–3.29 (m, 2H), 3.11–3.05 (m, 2H).

1-(3-methoxyphenyl)-3-phenylpropan-1-one (**3bm**) (Zhang et al., 2017).

13.2 mg, 55% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.54 (dt, *J* = 7.7, 1.2 Hz, 1H), 7.50 (dd, *J* = 2.7, 1.6 Hz, 1H), 7.36 (t, *J* = 7.9 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.26 (d, *J* = 6.6 Hz, 2H), 7.24–7.19 (m, 1H), 7.11 (ddd, *J* = 8.2, 2.7, 0.9 Hz, 1H), 3.85 (s, 3H), 3.32–3.27 (m, 2H), 3.07 (t, *J* = 7.7 Hz, 2H).

1-(4-fluorophenyl)-3-phenylpropan-1-one (**3bn**) (Zhang et al., 2017).

12.3 mg, 54% yield; white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.01–7.96 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.27–7.24 (m, 2H), 7.22 (td, *J* = 7.0, 1.5 Hz, 1H), 7.12 (t, *J* = 8.6 Hz, 2H), 3.31–3.24 (m, 2H), 3.07 (t, *J* = 7.7 Hz, 2H).

1-(4-chlorophenyl)-3-phenylpropan-1-one (**3bo**) (Zhang et al., 2017).

13.9 mg, 57% yield; white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.27 (d, *J* = 7.0 Hz, 2H), 7.25–7.21 (m, 1H), 3.31–3.26 (m, 2H), 3.09 (t, *J* = 7.7 Hz, 2H).

3-phenyl-1-(4-(trifluoromethyl)phenyl)propan-1-one (**3bp**) (Zhang et al., 2017).

18.1 mg, 65% yield; white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.1 Hz, 2H), 7.72 (d, *J* = 8.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.26 (d, *J* = 6.8 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 3.34 (t, *J* = 7.6 Hz, 2H), 3.09 (t, *J* = 7.6 Hz, 2H).

4-(3-phenylpropanoyl)benzonitrile (**3bq**) (Das et al., 2019).

16.0 mg, 68% yield; white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.02 (d, *J* = 8.5 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.25–7.20 (m, 3H), 3.31 (t, *J* = 7.6 Hz, 2H), 3.08 (t, *J* = 7.6 Hz, 2H).

1-(naphthalen-2-yl)-3-phenylpropan-1-one (**3br**) (Zhang et al., 2017).

13.8 mg, 53% yield; white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 1.7 Hz, 1H), 8.05 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.89 (t, *J* = 8.8 Hz, 2H), 7.60 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.55 (ddd, *J* = 8.2, 6.8, 1.3 Hz, 1H), 7.34–7.31 (m, 3H), 7.25–7.21 (m, 1H), 3.45 (t, *J* = 7.5 Hz, 2H), 3.14 (t, *J* = 7.5 Hz, 2H).

1-(furan-3-yl)-3-phenylpropan-1-one (**3bs**).

6.4 mg, 32% yield; white solid. Mp = 60–62°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.99 (t, *J* = 1.0 Hz, 1H), 7.43 (t, *J* = 1.7 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.25–7.19 (m, 3H), 6.77 (d, *J* = 1.8 Hz, 1H), 3.10–3.06 (m, 2H), 3.05–3.01 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 194.0, 147.1, 144.2, 141.0, 128.5, 128.4, 127.6, 126.2, 108.5, 42.1, 30.0; **HRMS-EI** calcd for $C_{11}H_{11}N_3O$ $[M]^+$ 200.0832, found 200.0823.

3-phenyl-1-(thiophen-3-yl)propan-1-one (**3bt**) (Nicholson et al., 2021).

6.5 mg, 30% yield; white solid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.03 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.56 (dd, *J* = 5.1, 1.3 Hz, 1H), 7.33–7.29 (m, 3H), 7.27–7.24 (m, 2H), 7.24–7.19 (m, 1H), 3.22 (t, *J* = 7.7 Hz, 2H), 3.06 (t, *J* = 7.7 Hz, 2H).

2-methyl-1-phenylpentan-3-one (**3bu**) (Kaku et al., 2013).

15.8 mg, 90% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29–7.25 (m, 2H), 7.21–7.17 (m, 1H), 7.16–7.12 (m, 2H), 2.97 (dd, *J* = 13.4, 7.2 Hz, 1H), 2.84 (h, *J* = 7.0 Hz, 1H), 2.57 (dd, *J* = 13.4, 7.4 Hz, 1H), 2.43 (dq, *J* = 17.9, 7.2 Hz, 1H), 2.26 (dq, *J* = 17.9, 7.2 Hz, 1H), 1.08 (d, *J* = 7.0 Hz, 3H), 0.97 (t, *J* = 7.3 Hz, 3H).

4-phenylpentan-2-one (**3bv-1**) (Funabiki et al., 2009).

9.1 mg, 56% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.30 (t, *J* = 7.6 Hz, 2H), 7.24–7.17 (m, 3H), 3.31 (h, *J* = 7.0 Hz, 1H), 2.76 (dd, *J* = 16.3, 6.5 Hz, 1H), 2.66 (dd, *J* = 16.3, 7.9 Hz, 1H), 2.07 (s, 3H), 1.27 (d, *J* = 6.9 Hz, 3H).

3-phenylpentan-2-one (**3bv-2**) (Méndez-Sánchez et al., 2016).

4.2 mg, 26% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 (t, *J* = 7.5 Hz, 2H), 7.28–7.24 (m, 1H), 7.21 (d, *J* = 7.7 Hz, 2H), 3.51 (t, *J* = 7.4 Hz, 1H), 2.11–2.02 (m, 4H), 1.71 (dp, *J* = 14.9, 7.5 Hz, 1H), 0.83 (t, *J* = 7.4 Hz, 3H).

4-methyl-5-phenylhexan-3-one (**3bw**) (Oi et al., 2002).

9.7 mg, 51% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.26 (t, *J* = 7.6 Hz, 2H), 7.19–7.14 (m, 3H), 2.99 (dq, *J* = 9.0, 7.0 Hz, 1H), 2.76 (dq, *J* = 9.0, 6.9 Hz, 1H), 2.23 (dq, *J* = 17.9, 7.2 Hz, 1H), 1.95 (dq, *J* = 17.9, 7.3 Hz, 1H), 1.25 (d, *J* = 7.0 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H), 0.79 (t, *J* = 7.2 Hz, 3H).

3-phenylpropanal (**7a**) (Huang et al., 2017).

7.5 mg, 56% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.83 (t, *J* = 1.5 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.24–7.18 (m, 3H), 2.97 (t, *J* = 7.6 Hz, 2H), 2.79 (td, *J* = 7.6, 1.4 Hz, 2H).

3-(2-chlorophenyl)propanal (**7b**) (Huang et al., 2017).

12.1 mg, 72% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.83 (t, *J* = 1.3 Hz, 1H), 7.35 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.25 (dd, *J* = 7.3, 2.1 Hz, 1H), 7.22–7.14 (m, 2H), 3.06 (t, *J* = 7.5 Hz, 2H), 2.81 (td, *J* = 7.6, 1.3 Hz, 2H).

3-(3-methoxyphenyl)propanal (**7c**) (Huang et al., 2017).

9.2 mg, 56% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.82 (t, *J* = 1.4 Hz, 1H), 7.21 (t, *J* = 7.7 Hz, 1H), 6.80–6.73 (m, 3H), 3.80 (s, 3H), 2.94 (t, *J* = 7.6 Hz, 2H), 2.78 (td, *J* = 7.3, 1.2 Hz, 2H).

3-(3-(trifluoromethyl)phenyl)propanal (**7d**) (Airoldi et al., 2020).

10.9 mg, 54% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.83 (t, *J* = 1.2 Hz, 1H), 7.49–7.44 (m, 2H), 7.43–7.37 (m, 2H), 3.02 (t, *J* = 7.5 Hz, 2H), 2.83 (td, *J* = 7.5, 1.1 Hz, 2H).

4-(3-oxopropyl)phenyl acetate (**7e**) (Christensen et al., 2015).

12.5 mg, 65% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.82 (s, 1H), 7.20 (d, *J* = 8.3 Hz, 2H), 7.00 (d, *J* = 8.3 Hz, 2H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.78 (t, *J* = 7.5 Hz, 2H), 2.29 (s, 3H).

ethyl 4-(3-oxopropyl)benzoate (**7f**) (Soni et al., 2015).

14.0 mg, 68% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.82 (t, *J* = 1.3 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.1 Hz, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.81 (td, *J* = 7.6, 1.2 Hz, 2H), 1.38 (t, *J* = 7.1 Hz, 3H).

3-(4-(2H-1,2,3-triazol-2-yl)phenyl)propanal (**7g**).

14.7 mg, 73% yield; yellowish colloid; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.84 (t, *J* = 1.4 Hz, 1H), 7.99 (d, *J* = 8.4 Hz, 2H), 7.79 (s, 2H), 7.31 (d, *J* = 8.2 Hz, 2H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.82 (td, *J* = 7.5, 1.3 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 201.1, 139.9, 138.3, 135.4, 129.2, 119.2, 45.1, 27.5; **HRMS-EI** calcd for $C_{11}H_{11}N_3O$ $[M]^+$ 201.0897, found 201.0898.

3-(6-phenylpyridin-3-yl)propanal (**7h**).

14.3 mg, 68% yield; white solid; Mp = 61–63°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.85 (s, 1H), 8.56 (d, *J* = 2.3 Hz, 1H), 7.95 (d, *J* = 7.3 Hz, 2H), 7.66 (d, *J* = 8.1 Hz, 1H), 7.61 (dd, *J* = 8.2, 2.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.43–7.38 (m, 1H), 3.00 (t, *J* = 7.4 Hz, 2H), 2.85 (t, *J* = 7.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 200.6, 155.7, 149.5, 139.0, 136.8, 134.3, 128.8, 128.7, 126.8, 120.4, 44.8, 24.9; **HRMS-EI** calcd for $C_{14}H_{13}NO$ $[M]^+$ 211.0992, found 211.0994.

3-(2-chlorophenyl)butanal (**7i-1** or **7l-2**) (Larionov et al., 2014).

8.0 mg, 44% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.73 (t, *J* = 2.1 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.25 (d, *J* = 4.2 Hz, 2H), 7.16 (dt, *J* = 8.0, 4.4 Hz, 1H), 3.89 (dq, *J* = 13.7, 6.9 Hz, 1H), 2.78 (ddd, *J* = 16.7, 6.0, 1.8 Hz, 1H), 2.64 (ddd, *J* = 16.7, 8.3, 2.4 Hz, 1H), 1.32 (d, *J* = 6.9 Hz, 3H).

2-(2-chlorophenyl)butanal (**7i-2**).

7.1 mg, 39% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.71 (d, *J* = 0.9 Hz, 1H), 7.45 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.31–7.23 (m, 2H), 7.13 (dd, *J* = 7.5, 1.9 Hz, 1H), 4.06–3.99 (m, 1H), 2.22–2.12 (m, 1H), 1.82–1.72 (m, 1H),

0.92 (t, J = 7.4 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 200.2, 134.9, 134.5, 130.0, 129.7, 128.7, 127.3, 56.7, 22.4, 11.6; **HRMS-EI** calcd for $C_{10}H_{11}ClO$ $[M]^+$ 182.0493, found 182.0482.

3-(2-chlorophenyl)-2-methylpropanal (**7j**).

16.0 mg, 88% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.73 (d, J = 1.4 Hz, 1H), 7.38–7.34 (m, 1H), 7.23–7.15 (m, 3H), 3.24 (dd, J = 13.7, 6.3 Hz, 1H), 2.85–2.76 (m, 1H), 2.69 (dd, J = 13.7, 8.1 Hz, 1H), 1.12 (d, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 203.9, 136.7, 134.1, 131.4, 129.7, 128.0, 126.8, 46.3, 34.3, 13.3; **HRMS-EI** calcd for $C_{10}H_{11}ClO$ $[M]^+$ 182.0493, found 182.0493.

4-(2-fluorophenyl)butanal (**7k-1**).

9.1 mg, 55% yield; colorless liquid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.77 (t, J = 1.6 Hz, 1H), 7.22–7.15 (m, 2H), 7.07 (td, J = 7.5, 1.3 Hz, 1H), 7.04–6.99 (m, 1H), 2.70 (t, J = 7.5 Hz, 2H), 2.47 (td, J = 7.3, 1.6 Hz, 2H), 1.96 (p, J = 7.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.1, 161.1 (d, J = 245.0 Hz), 130.7 (d, J = 4.7 Hz), 128.0 (d, J = 15.4 Hz), 127.9 (d, J = 8.2 Hz), 124.0 (d, J = 3.9 Hz), 115.3 (d, J = 22.0 Hz), 43.1, 28.2, 22.4; **^{19}F NMR** (471 MHz, $CDCl_3$) δ −118.8; **HRMS-EI** calcd for $C_{10}H_{11}FO$ $[M]^+$ 166.0788, found 166.0782.

3-(2-fluorophenyl)butanal (**7k-2**) (Bräuer et al., 2017).

3.8 mg, 23% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.73 (t, J = 2.0 Hz, 1H), 7.24–7.17 (m, 2H), 7.10 (td, J = 7.5, 1.3 Hz, 1H), 7.02 (ddd, J = 10.7, 8.1, 1.3 Hz, 1H), 3.66 (h, J = 7.1 Hz, 1H), 2.80 (ddd, J = 16.9, 6.6, 1.8 Hz, 1H), 2.70 (ddd, J = 16.9, 7.8, 1.9 Hz, 1H), 1.33 (d, J = 6.9 Hz, 3H).

4-(2-chlorophenyl)butanal (**7l-1**) (Stockwell and Welsch, 2017).

11.8 mg, 65% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.78 (t, J = 1.6 Hz, 1H), 7.34 (dd, J = 7.5, 1.3 Hz, 1H), 7.22–7.13 (m, 3H), 2.81–2.74 (m, 2H), 2.49 (td, J = 7.3, 1.6 Hz, 2H), 1.98 (tt, J = 9.2, 6.8 Hz, 2H).

4-(3-methoxyphenyl)butanal (**7m-1**).

9.8 mg, 55% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.76 (t, J = 1.6 Hz, 1H), 7.21 (t, J = 7.8 Hz, 1H), 6.80–6.71 (m, 3H), 3.80 (s, 3H), 2.64 (t, J = 7.6 Hz, 2H), 2.46 (td, J = 7.3, 1.6 Hz, 2H), 1.96 (p, J = 7.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.3, 159.7, 142.8, 129.4, 120.8, 114.2, 111.3, 55.1, 43.1, 35.0, 23.5; **HRMS-EI** calcd for $C_{11}H_{14}O_2$ $[M]^+$ 178.0988, found 178.0986.

3-(3-methoxyphenyl)butanal (**7m-2**) (Itooka et al., 2003).

4.1 mg, 23% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.71 (t, J = 2.0 Hz, 1H), 7.23 (td, J = 7.6, 0.9 Hz, 1H), 6.82 (dt, J = 7.4, 1.3 Hz, 1H), 6.78–6.74 (m, 2H), 3.80 (s, 3H), 3.33 (h, J = 7.0 Hz, 1H), 2.75 (ddd, J = 16.6, 6.9, 1.8 Hz, 1H), 2.65 (ddd, J = 16.7, 7.7, 2.2 Hz, 1H), 1.31 (d, J = 7.0 Hz, 3H).

4-(4-chlorophenyl)butanal (**7n-1**) (Sakaguchi et al., 2019).

10.0 mg, 55% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.76 (t, J = 1.5 Hz, 1H), 7.25 (d, J = 7.9 Hz, 2H), 7.10 (d, J = 8.4 Hz, 2H), 2.62 (t, J = 7.3 Hz, 2H), 2.45 (td, J = 7.3, 1.5 Hz, 2H), 1.93 (p, J = 7.4 Hz, 2H).

3-(4-chlorophenyl)butanal (**7n-2**) (Ren et al., 2016).

4.2 mg, 23% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.70 (t, J = 1.9 Hz, 1H), 7.27 (d, J = 8.5 Hz, 2H), 7.15 (d, J = 8.5 Hz, 2H), 3.35 (h, J = 7.0 Hz, 1H), 2.73 (ddd, J = 16.9, 7.0, 1.8 Hz, 1H), 2.66 (ddd, J = 16.9, 7.5, 2.0 Hz, 1H), 1.29 (d, J = 7.0 Hz, 3H).

4-(4-(trifluoromethyl)phenyl)butanal (**7o-1**) (Lu and Guo, 2019).

7.8 mg, 36% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.78 (t, J = 1.5 Hz, 1H), 7.54 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 2.71 (t, J = 7.7 Hz, 2H), 2.48 (td, J = 7.2, 1.4 Hz, 2H), 1.97 (p, J = 7.3 Hz, 2H).

3-(4-(trifluoromethyl)phenyl)butanal (**7o-2**) (You et al., 2018).

3.2 mg, 15% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.72 (t, *J* = 1.8 Hz, 1H), 7.56 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 3.44 (h, *J* = 7.1 Hz, 1H), 2.78 (ddd, *J* = 17.1, 6.9, 1.6 Hz, 1H), 2.71 (ddd, *J* = 17.1, 7.5, 1.8 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 3H).

4-(naphthalen-2-yl)butanal (**7p-1**) (Grissom and Klingberg, 1993).

10.1 mg, 51% yield; colorless oil; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 9.78 (t, *J* = 1.6 Hz, 1H), 7.83–7.77 (m, 3H), 7.62 (s, 1H), 7.48–7.42 (m, 2H), 7.33 (dd, *J* = 8.4, 1.8 Hz, 1H), 2.83 (t, *J* = 7.5 Hz, 2H), 2.49 (td, *J* = 7.3, 1.6 Hz, 2H), 2.06 (p, *J* = 7.4 Hz, 2H).

3-(naphthalen-2-yl)butanal (**7p-2**) (You et al., 2018).

4.8 mg, 24% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.75 (t, *J* = 2.0 Hz, 1H), 7.84–7.78 (m, 3H), 7.66 (d, *J* = 1.7 Hz, 1H), 7.50–7.43 (m, 2H), 7.38 (dd, *J* = 8.5, 1.8 Hz, 1H), 3.54 (h, *J* = 7.0 Hz, 1H), 2.86 (ddd, *J* = 16.7, 6.9, 1.8 Hz, 1H), 2.75 (ddd, *J* = 16.7, 7.6, 2.2 Hz, 1H), 1.41 (d, *J* = 6.9 Hz, 3H).

4-(thiophen-3-yl)butanal (**7q-1**).

6.3 mg, 41% yield; yellowish oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.76 (t, *J* = 1.6 Hz, 1H), 7.28–7.25 (m, 1H), 6.97–6.91 (m, 2H), 2.69 (t, *J* = 7.5 Hz, 2H), 2.47 (td, *J* = 7.3, 1.6 Hz, 2H), 1.97 (p, *J* = 7.4 Hz, 2H). **^{13}C NMR** (151 MHz, $CDCl_3$) δ 202.2, 141.5, 128.0, 125.6, 120.6, 43.2, 29.4, 22.8; **HRMS-EI** calcd for $C_8H_{10}OS$ $[M]^+$ 154.0447, found 154.0434.

3-(thiophen-3-yl)butanal (**7q-2**) (Schlosser and Michel, 1996).

4.2 mg, 27% yield; yellowish oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.73 (t, *J* = 2.0 Hz, 1H), 7.30–7.27 (m, 1H), 7.00–6.97 (m, 2H), 3.49 (h, *J* = 7.0 Hz, 1H), 2.75 (ddd, *J* = 16.6, 6.7, 1.9 Hz, 1H), 2.63 (ddd, *J* = 16.7, 7.5, 2.1 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 3H).

4-(quinolin-6-yl)butanal (**7r-1**).

7.2 mg, 36% yield; yellowish colloid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.77 (t, *J* = 1.6 Hz, 1H), 8.86 (dd, *J* = 4.3, 1.8 Hz, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.6 Hz, 1H), 7.58 (d, *J* = 1.9 Hz, 1H), 7.55 (dd, *J* = 8.6, 2.0 Hz, 1H), 7.37 (dd, *J* = 8.3, 4.2 Hz, 1H), 2.83 (t, *J* = 7.7 Hz, 2H), 2.49 (td, *J* = 7.2, 1.5 Hz, 2H), 2.05 (p, *J* = 7.3 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.0, 149.7, 147.0, 139.7, 135.7, 130.8, 129.3, 128.3, 126.3, 121.2, 43.0, 34.8, 23.3; **HRMS-EI** calcd for $C_{13}H_{13}NO$ $[M]^+$ 199.0992, found 199.0975.

3-(quinolin-6-yl)butanal (**7r-2**).

4.0 mg, 20% yield; yellowish colloid; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.74 (s, 1H), 8.89 (s, 1H), 8.12 (d, *J* = 8.3 Hz, 1H), 8.08 (d, *J* = 8.6 Hz, 1H), 7.66–7.58 (m, 2H), 7.39 (dd, *J* = 8.3, 4.2 Hz, 1H), 3.57 (h, *J* = 7.1 Hz, 1H), 2.87 (dd, *J* = 17.1, 6.8 Hz, 1H), 2.77 (ddd, *J* = 17.0, 7.5, 2.0 Hz, 1H), 1.41 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.2, 150.0, 147.2, 143.8, 135.9, 129.8, 129.0, 128.3, 124.9, 121.3, 51.5, 34.1, 22.0; **HRMS-EI** calcd for $C_{13}H_{13}NO$ $[M]^+$ 199.0992, found 199.0982.

4-(2-chlorophenyl)-3-methylbutanal (**7s**).

14.7 mg, 75% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.71 (t, *J* = 2.2 Hz, 1H), 7.35 (dt, *J* = 7.4, 1.2 Hz, 1H), 7.20–7.14 (m, 3H), 2.71 (qd, *J* = 13.4, 7.2 Hz, 2H), 2.53–2.41 (m, 2H), 2.30 (ddd, *J* = 16.2, 8.0, 2.5 Hz, 1H), 1.01 (d, *J* = 6.6 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 202.5, 137.7, 134.2, 131.4, 129.6, 127.7, 126.6, 50.2, 40.5, 28.8, 19.9; **HRMS-EI** calcd for $C_{11}H_{13}ClO$ $[M]^+$ 196.0649, found 196.0650.

4-(2-chlorophenyl)-3-phenylbutanal (**7t**).

17.5 mg, 68% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.59 (t, *J* = 2.1 Hz, 1H), 7.35 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.23–7.17 (m, 3H), 7.14 (td, *J* = 7.6, 1.8 Hz, 1H), 7.08 (td, *J* = 7.4, 1.4 Hz, 1H), 6.96

(dd, *J* = 7.5, 1.8 Hz, 1H), 3.63 (dtd, *J* = 8.8, 7.6, 6.0 Hz, 1H), 3.10–2.99 (m, 2H), 2.84 (ddd, *J* = 16.7, 8.9, 2.3 Hz, 1H), 2.74 (ddd, *J* = 16.7, 6.0, 1.9 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.6, 142.9, 136.9, 134.2, 131.5, 129.6, 128.6, 127.9, 127.4, 126.8, 126.6, 48.6, 41.0, 40.1; **HRMS-EI** calcd for $C_{16}H_{15}ClO$ $[M]^+$ 258.0806, found 258.0800.

5-(naphthalen-2-yl)pentanal (**7u**) (Nicolaou et al., 2009).

4.5 mg, 21% yield; yellowish oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.76 (t, *J* = 1.9 Hz, 1H), 7.82–7.75 (m, 3H), 7.61 (s, 1H), 7.47–7.40 (m, 2H), 7.32 (dd, *J* = 8.4, 1.6 Hz, 1H), 2.81 (t, *J* = 7.2 Hz, 2H), 2.47 (td, *J* = 7.1, 1.7 Hz, 2H), 1.80–1.67 (m, 4H).

4-(3-oxopentyl)-*N*,*N*-dipropylbenzenesulfonamide (**8a**).

(26.3 mg, 81% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 3.06–3.01 (m, 4H), 2.94 (t, *J* = 7.5 Hz, 2H), 2.74 (t, *J* = 7.5 Hz, 2H), 2.39 (q, *J* = 7.3 Hz, 2H), 1.53 (h, *J* = 7.4 Hz, 4H), 1.02 (t, *J* = 7.3 Hz, 3H), 0.85 (t, *J* = 7.4 Hz, 6H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 209.8, 146.0, 137.8, 128.9, 127.2, 50.0, 43.1, 36.1, 29.4, 22.0, 11.1, 7.7; **HRMS-EI** calcd for $C_{17}H_{27}NO_3S$ $[M]^+$ 325.1706, found 325.1699.

1-(6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)naphthalen-2-yl)pentan-3-one (**8b**).

25.8 mg, 57% yield; white solid. Mp = 151–153°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 1.7 Hz, 1H), 7.82 (d, *J* = 8.4 Hz, 2H), 7.72 (dd, *J* = 8.5, 1.9 Hz, 1H), 7.63 (d, *J* = 1.6 Hz, 1H), 7.59 (d, *J* = 2.4 Hz, 1H), 7.53 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.34 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.99 (d, *J* = 8.4 Hz, 1H), 3.90 (s, 3H), 3.08 (t, *J* = 7.6 Hz, 2H), 2.84 (t, *J* = 7.6 Hz, 2H), 2.44 (q, *J* = 7.3 Hz, 2H), 2.20 (d, *J* = 2.9 Hz, 6H), 2.15–2.08 (m, 4H), 1.82 (d, *J* = 3.7 Hz, 6H), 1.07 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.7, 158.4, 138.8, 138.4, 138.3, 133.1, 132.3, 128.2, 127.8, 127.4, 126.1, 125.8, 125.8, 125.5, 124.7, 112.0, 55.1, 43.8, 40.6, 37.1, 37.1, 36.2, 30.0, 29.1, 7.8; **HRMS-EI** calcd for $C_{32}H_{36}O_2$ $[M]^+$ 452.2710, found 452.2709.

14-methyl-10-(3-oxopentyl)-13-tosyl-8,13,13b,14-tetrahydroindolo[2′,3′:3,4]pyrido[2,1-b]quinazolin-5(7H)-one (**8c**).

31.4 mg, 58% yield; white solid. Mp = 137–139°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.6 Hz, 1H), 8.09 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.83 (d, *J* = 8.5 Hz, 2H), 7.48 (ddd, *J* = 8.0, 7.3, 1.6 Hz, 1H), 7.32 (d, *J* = 1.7 Hz, 1H), 7.27 (t, *J* = 8.6 Hz, 3H), 7.16 (td, *J* = 7.6, 1.1 Hz, 1H), 7.05 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.31 (d, *J* = 1.5 Hz, 1H), 4.85 (ddd, *J* = 12.7, 5.1, 1.6 Hz, 1H), 3.13–3.03 (m, 1H), 3.01 (t, *J* = 7.5 Hz, 2H), 2.93–2.88 (m, 1H), 2.79 (t, *J* = 7.5 Hz, 2H), 2.77–2.71 (m, 1H), 2.42 (q, *J* = 7.4 Hz, 2H), 2.39 (s, 3H), 2.16 (s, 3H), 1.05 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.4, 164.4, 150.7, 145.0, 137.1, 136.0, 135.8, 133.1, 129.4, 129.2, 129.0, 128.2, 127.0, 126.6, 123.6, 123.0, 122.9, 120.4, 118.6, 115.2, 67.8, 44.0, 38.3, 36.1, 35.2, 29.5, 21.6, 20.8, 7.7; **HRMS-EI** calcd for $C_{31}H_{31}N_3O_4S$ $[M]^+$ 541.2030, found 541.2052.

3,3,5-trimethylcyclohexyl 2-acetoxy-5-(3-oxopentyl)benzoate (**8d**).

29.1 mg, 75% yield; colorless oil; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 2.3 Hz, 1H), 7.35 (dd, *J* = 8.2, 2.3 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 5.09 (tt, *J* = 11.6, 4.4 Hz, 1H), 2.91 (t, *J* = 7.6 Hz, 2H), 2.73 (t, *J* = 7.6 Hz, 2H), 2.42 (q, *J* = 7.3 Hz, 2H), 2.33 (s, 3H), 2.11–2.05 (m, 1H), 1.81–1.72 (m, 2H), 1.40–1.34 (m, 1H), 1.22 (t, *J* = 12.2 Hz, 1H), 1.05 (t, *J* = 7.3 Hz, 3H), 0.97 (d, *J* = 2.2 Hz, 7H), 0.92 (d, *J* = 6.4 Hz, 3H), 0.82 (t, *J* = 12.7 Hz, 1H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 210.0, 169.7, 164.1, 148.6, 139.1, 133.6, 131.3, 123.8, 123.6, 72.0, 47.5, 44.0, 43.5, 40.4, 36.1, 33.0, 32.3, 28.9, 27.1, 25.5, 22.3, 21.1, 7.7; **HRMS-EI** calcd for $C_{23}H_{32}O_5$ $[M]^+$ 388.2244, found 388.2242.

(*8R,9S,13S,14S,17S*)-13-methyl-2-(3-oxobutyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl acetate (**8e**).

22.8 mg, 62% yield; white solid. Mp = 99–101°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 (s, 1H), 7.00 (d, *J* = 7.7 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 4.69 (dd, *J* = 9.2, 7.8 Hz, 1H), 2.88–2.82 (m, 4H), 2.78–2.71 (m, 2H), 2.37–2.28 (m, 1H), 2.27–2.19 (m, 2H), 2.15 (s, 3H), 2.07 (s, 3H), 1.94–1.85 (m, 2H), 1.79–1.72 (m, 1H), 1.59–1.25 (m, 7H), 0.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 208.1, 171.2, 140.2, 138.1, 134.3, 129.1, 125.5, 125.3, 82.6, 49.8, 45.4,

44.2, 42.8, 38.3, 36.8, 30.0, 29.6, 29.1, 27.5, 27.1, 25.9, 23.2, 21.2, 12.0; **HRMS-EI** calcd for $C_{24}H_{32}O_3$ $[M]^+$ 368.2346, found 368.2350.

(*8R,9S,13S,14S,17S*)-2-(2-bromo-3-oxobutyl)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl acetate (**9**).

33.8 mg, 76%; white solid; Mp = 126–128°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.11 (s, 1H), 7.01 (d, *J* = 7.8 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 4.72–4.67 (m, 1H), 4.44 (td, *J* = 7.5, 1.3 Hz, 1H), 3.39 (dd, *J* = 14.4, 7.5 Hz, 1H), 3.12 (ddd, *J* = 14.3, 7.4, 3.9 Hz, 1H), 2.83 (dd, *J* = 9.1, 4.2 Hz, 2H), 2.33 (d, *J* = 1.0 Hz, 3H), 2.32–2.29 (m, 1H), 2.27–2.18 (m, 2H), 2.06 (s, 3H), 1.94–1.85 (m, 2H), 1.80–1.70 (m, 1H), 1.59–1.51 (m, 1H), 1.50–1.31 (m, 5H), 1.31–1.22 (m, 1H), 0.83 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 201.4, 171.2, 140.5, 135.5, 134.1, 129.2 (d, *J* = 4.3 Hz), 126.3 (d, *J* = 7.7 Hz), 126.2, 82.6, 53.5 (d, *J* = 9.2 Hz), 49.9, 44.2, 42.8, 39.5 (d, *J* = 8.1 Hz), 38.2, 36.8, 29.1, 27.5, 27.1, 26.9 (d, *J* = 7.8 Hz), 26.0 (d, *J* = 4.0 Hz), 23.2, 21.2, 12.0; **HRMS (ESI-TOF)** calcd for $C_{24}H_{35}NO_3Br$ $[M + NH_4]^+$ 464.1795, found 464.1800.

(*8R,9S,13S,14S,17S*)-2-(3-((4-methoxyphenyl)amino)butyl)-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl acetate (**10**).

46.5 mg, 98%; yellow sticky foam; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.12 (d, *J* = 2.3 Hz, 1H), 7.02 (d, *J* = 7.8 Hz, 1H), 6.96 (dd, *J* = 7.8, 1.7 Hz, 1H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.55 (dd, *J* = 8.9, 1.4 Hz, 2H), 4.72 (t, *J* = 8.4 Hz, 1H), 3.77 (s, 3H), 3.42 (h, *J* = 6.3 Hz, 1H), 2.90–2.83 (m, 2H), 2.70 (t, *J* = 7.8 Hz, 2H), 2.33–2.20 (m, 3H), 2.09 (d, *J* = 1.7 Hz, 3H), 1.95–1.84 (m, 3H), 1.81–1.70 (m, 2H), 1.63–1.52 (m, 1H), 1.53–1.35 (m, 5H), 1.33–1.26 (m, 1H), 1.21 (d, *J* = 6.2 Hz, 3H), 0.86 (d, *J* = 4.9 Hz, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.1, 151.8, 141.7, 140.0 (d, *J* = 3.7 Hz), 139.1, 133.9, 129.0, 125.6 (d, *J* = 4.6 Hz), 125.4, 114.8, 114.7, 82.6, 55.7, 49.8, 48.9 (d, *J* = 11.2 Hz), 44.3 (d, *J* = 5.4 Hz), 42.8, 39.0 (d, *J* = 5.2 Hz), 38.3, 36.9, 32.3, 29.1, 27.5, 27.2, 25.9 (d, *J* = 9.2 Hz), 23.2, 21.1, 20.8, 12.0; **HRMS (ESI-TOF)** m/z Calcd for $C_{31}H_{42}NO_3$ $[M + H]^+$ 476.3159, found 476.3158.

(*8R,9S,13S,14S,17S*)-13-methyl-2-((2-methyl-1H-indol-3-yl)methyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl acetate (**11**).

36.2 mg, 82%; yellowish solid; m.p. 113–115°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.83 (s, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 8.3 Hz, 1H), 7.23 (s, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.95 (s, 2H), 4.70 (t, *J* = 8.5 Hz, 1H), 4.04 (s, 2H), 2.85–2.79 (m, 2H), 2.40 (s, 3H), 2.30–2.20 (m, 3H), 2.08 (s, 3H), 1.92–1.85 (m, 2H), 1.78–1.72 (m, 1H), 1.60–1.53 (m, 1H), 1.50–1.43 (m, 2H), 1.41–1.34 (m, 2H), 1.32–1.24 (m, 2H), 0.84 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.2, 139.8, 138.8, 135.2, 133.8, 131.4, 128.9, 128.9, 125.4, 125.2, 120.8, 119.1, 118.3, 110.7, 110.0, 82.7, 49.8, 44.3, 42.8, 38.3, 36.9, 29.9, 29.1, 27.5, 27.2, 25.9, 23.2, 21.2, 12.0, 11.8; **HRMS-EI** calcd for $C_{30}H_{35}NO_2$ $[M]^+$ 441.2662, found 441.2657.

(*8R,9S,13S,14S,17S*)-13-methyl-2-((2-methyl-4-phenylquinolin-3-yl)methyl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl acetate (**12**).

45.2 mg, 85%; white solid; Mp = 123–125°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.65 (ddd, *J* = 8.3, 5.8, 2.2 Hz, 1H), 7.43 (d, *J* = 6.4 Hz, 3H), 7.36 (d, *J* = 6.0 Hz, 2H), 7.27–7.20 (m, 2H), 6.92–6.88 (m, 2H), 6.67 (d, *J* = 7.8 Hz, 1H), 4.67 (t, *J* = 8.5 Hz, 1H), 3.98 (s, 2H), 2.84–2.77 (m, 2H), 2.63 (s, 3H), 2.26–2.09 (m, 3H), 2.05 (s, 3H), 1.90–1.80 (m, 2H), 1.78–1.68 (m, 1H), 1.59–1.48 (m, 1H), 1.47–1.37 (m, 2H), 1.38–1.32 (m, 2H), 1.32–1.19 (m, 2H), 0.82 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.1, 159.5, 147.6, 146.4, 140.0, 137.1, 136.7, 134.1, 129.6, 129.3, 128.9, 128.6, 128.4, 128.3, 128.3, 127.8, 126.9, 126.4, 125.6, 125.1, 125.0, 82.6, 49.8, 44.2, 42.8, 38.2, 36.8, 35.9, 29.0, 27.5, 27.1, 25.9, 24.4, 23.2, 21.1, 12.0; **HRMS (ESI-TOF)** m/z Calcd for $C_{37}H_{40}NO_2$ $[M + H]^+$ 530.3054, found 530.3064.

(*8R,9S,13S,14S,17S*)-13-methyl-2-(6-methyl-2-phenylpyrimidin-4-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl acetate (**13**).

24.5 mg, 53%; white solid; Mp = . 147–149°C; **^{1}H NMR** (600 MHz, $CDCl_3$) δ 8.57 (d, *J* = 7.1 Hz, 2H), 8.17 (s, 1H), 7.94 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.54–7.47 (m, 3H), 7.44 (s, 1H), 7.22 (d, *J* = 7.9 Hz, 1H), 4.73 (t, *J* = 8.4 Hz, 1H), 2.98–2.91 (m, 2H), 2.64 (s, 3H), 2.55–2.48 (m, 1H), 2.40–2.32 (m, 1H), 2.28–2.19 (m, 1H), 2.08 (s, 3H), 2.00–1.92 (m, 2H), 1.82–1.74 (m, 1H), 1.67–1.60 (m, 1H), 1.59–1.53 (m, 1H), 1.51–1.41 (m, 3H), 1.37–1.29 (m, 2H), 0.87

(s, 3H); **^{13}C NMR** (151 MHz, $CDCl_3$) δ 171.2, 167.4, 164.1, 164.0, 140.8, 139.8, 138.2, 134.6, 130.4, 129.5, 128.4, 128.3, 124.4, 124.2, 113.7, 82.6, 49.9, 44.3, 42.9, 38.3, 36.9, 29.5, 27.5, 27.0, 26.0, 24.6, 23.2, 21.2, 12.1; **HRMS (ESI-TOF)** m/z Calcd for $C_{31}H_{35}N_2O_2$ $[M + H]^+$ 467.2693, found 467.2694.

(*8R,9S,13S,14S,17S*)-13-methyl-2-(3-methyl-1-phenyl-1H-pyrazol-5-yl)-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-17-yl acetate (**14**).

26.1 mg, 57%; white solid; Mp = 86–88°C; **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.34–7.26 (m, 5H), 7.10 (s, 1H), 6.99–6.94 (m, 2H), 6.29 (s, 1H), 4.67 (t, *J* = 8.4 Hz, 1H), 2.84 (dd, *J* = 8.9, 4.2 Hz, 2H), 2.37 (s, 3H), 2.25–2.11 (m, 2H), 2.06 (s, 3H), 1.98–1.92 (m, 1H), 1.91–1.85 (m, 1H), 1.84–1.76 (m, 1H), 1.78–1.69 (m, 1H), 1.60–1.49 (m, 1H), 1.45–1.38 (m, 2H), 1.37–1.30 (m, 2H), 1.30–1.22 (m, 2H), 0.80 (s, 3H); **^{13}C NMR** (126 MHz, $CDCl_3$) δ 171.2, 149.3, 144.1, 140.4, 140.2, 136.7, 128.9, 128.8, 127.8, 127.0, 125.8, 125.7, 125.4, 107.1, 82.6, 49.9, 44.0, 42.8, 38.2, 36.8, 29.2, 27.5, 27.0, 25.6, 23.2, 21.2, 13.6, 12.0; **HRMS (ESI-TOF)** m/z Calcd for $C_{30}H_{35}N_2O_2$ $[M + H]^+$ 455.2693, found 455.2697.