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Palladium-Catalyzed Direct *mono*-Aroylation of *O*-Arylmethyl and Aryl Substituted Acetoxime Ethers

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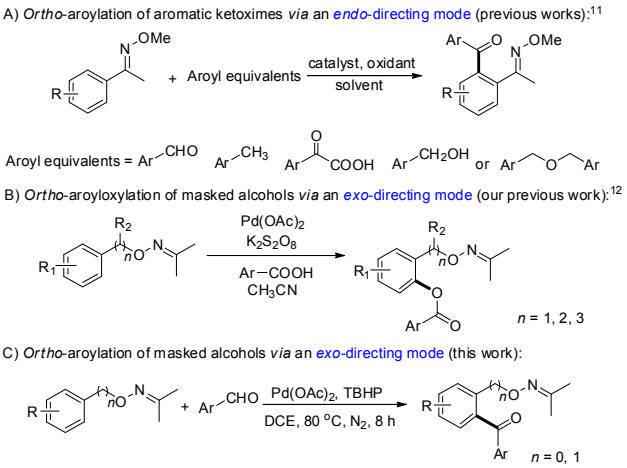
An efficient palladium-catalyzed *ortho*-aroylation of *O*-arylmethyl and aryl substituted acetoxime ethers has been developed in high *mono*-site selectivity without the need for exogenous ligand. Under the direction of the simple *exo*-acetoxime auxiliary, broad scope of masked arylmethyl alcohols and phenols as well as various aromatic aldehydes are compatible with this transformation, which should undertake a mechanistic pathway of six- or five-membered *exo*-cyclopalladated intermediate. The strategy can be expediently adopted to prepare synthetically valuable 1*H*-benzo[*d*][*1,2*]oxazines and benzo[*d*]isoxazoles. The directing group of products can be easily removed to give the functionalized diaryl ketones.

Introduction

Diaryl ketones are crucial structural motifs and precursors for the synthesis of a wide range of natural products, pharmaceuticals, agrochemicals, fragrances, biologically active molecules, and electronic materials.[1] The most classical access to the architechtures is the Friedel–Crafts aroylation[2] of arenes in the presence of a stoichiometric amount of Lewis acid, which extremely limited by poor regioselectivity and narrow functional group tolerance. The Grignard/Barbier reaction is of another tranditional method to prepare diaryl ketones *via* diaryl methanol intermediates followed by an oxidation reaction.[3] However, only specific structures can be adapted to this two-step transformation process.

Therefore, it is deserved to develop more efficient syntheses of diaryl ketones to circumvent the above mentioned existing defects. Over the past decades, the transition-metal-catalyzed direct aromatic C–H aroylation reactions have emerged as atom-economic and environment-friendly tools, avoiding the use of prefunctionalized starting materials and stoichiometric organometallic reagents.[4] Various directing groups such as pyridine,[5] diazo,[6] amide,[7] carboxyl,[8] and others[9] have been employed for *ortho*-C–H bond activation/aroylation.

Given that oxime serves as a common and simple protection group,[10] the pioneering works[11] by Yu and other following works have demonstrated that *O*-methyl oxime moiety holds an excellent directing ability for C–H bond aroylation to construct diaryl ketones *via* a five-membered *endo*-cyclopalladated intermediate (π-bond of the directing group inside the metallocycle, Scheme 1A). Despite these significant advances, the oxime ethers directed C–H bond aroylation of masked aralkyl and aryl alcohols *via* *exo*-cyclopalladated intermediate still remains to be further developed (π-bond of the directing group outside the metallocycle).



Scheme 1 Previous related works and present work.

Recently, the simple acetoxime auxilixary with the exogenous ligand was employed by Zhao group[10c,d] for selective olefination and arylation of masked aromatic alcohols *via* six- or seven-membered *exo*-palladacycle. More recently, without exogenous ligand, we disclosed a site-selective Pd-catalyzed direct Csp^2–H *mono*-aroyloxylation with the *exo*-acetoxime directing group (Scheme 1B).[12] As our continuing interest dealing with direct C–C bond formation, herein a novel

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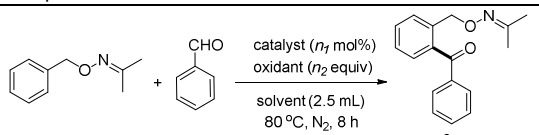
ortho-aroylation of masked *O*-arylmethyl alcohols is carried out by the simple acetoxime auxilixary (Scheme 1C). Notably, the aroylation of masked phenols is firstly achieved *via* a tight five-membered *exo*-palladacycle (Scheme 1C), again revealing a versatile directing ability of acetoxime for C–H functionalization. In this reaction, undecorated catalyst $Pd(OAc)_2$ with the combination of inexpensive oxidant TBHP proved to be highly effective to enable the conversion under mild conditions.

Results and discussion

Initially, we treated model substrates *O*-benzyl acetoxime ether **1a** and benzaldehyde **2a** by using the catalyst $Pd(OAc)_2$ (10 mol%) and different oxidant (2.0 equiv) under N_2 atmosphere at 80 °C for 8 h (Table 1). Disappointingly, the oxidant $K_2S_2O_8$ did not present any aroylation product with almost all starting materials intact (entry **1**). It was found that oxidant plays a critical role for the reaction. For instance, DDQ was ineffective too (entry **2**), and $PhI(OAc)_2$ delivered 15% yield only (entry **3**). To our delight, when organic peroxides as the oxidants, the yields of aroylated product **3a** were obviously increased (entries **4**–**6**). Therein, the oxidants TBPB and DCP handed over inferior yields, while TBHP turned out to be the best one. Afterwords, we surveyed other Pd salt catalysts. $PdCl_2$ was inefficient (entry **7**), while $(\eta^3\text{-}C_3H_5)_2PdCl_2$ and $Pd(PPh_3)_4$ led to lower efficiency (entries **8** and **9**). Albeit a similar outcome with $Pd(TFA)_2$ (entry **10** *versus* **6**), $Pd(OAc)_2$ was still regarded as the suitable catalyst for cost consideration. Furthermore, the screening of solvents uncovered DCE providing the best result (entry **6** *versus* **11**–**14**). In addition, 80 °C was proved to be appropriate reaction temperature with the control experiments, (entries **15** and **16**). When the reaction was carried out in air atmosphere, the yield dropped to 66% (entry **17**), accompanying with a lot of benzoic acid generated. It should be pointed out that, with the amount of 2.0 equiv of **2a**, diaroylated product was not detected. Thus, we established entry **6** as the standard reaction conditions for the functionalization.

Table 1 Optimization of the reaction conditions[a]



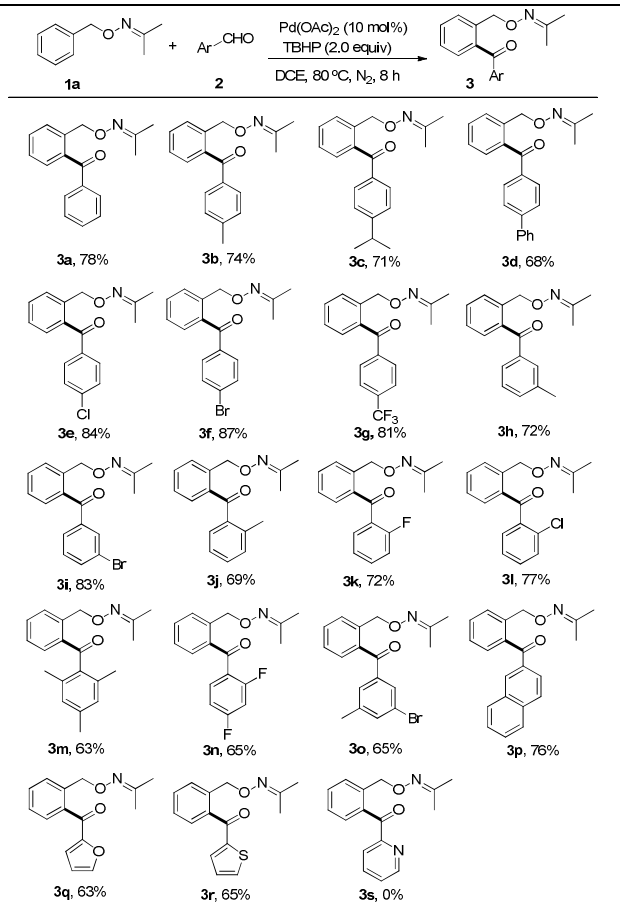
1a 2a 3a

Entry	Catalyst	Oxidant	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	$K_2S_2O_8$	DCE	0
2	$Pd(OAc)_2$	DDQ	DCE	0
3	$Pd(OAc)_2$	$PhI(OAc)_2$	DCE	15
4	$Pd(OAc)_2$	TBPB	DCE	32
5	$Pd(OAc)_2$	DCP	DCE	61
6	**$Pd(OAc)_2$**	**TBHP**	**DCE**	**78**
7	$PdCl_2$	TBHP	DCE	0
8	$(\eta^3\text{-}C_3H_5)_2PdCl_2$	TBHP	DCE	43
9	$Pd(PPh_3)_4$	TBHP	DCE	44
10	$Pd(TFA)_2$	TBHP	DCE	77
11	$Pd(OAc)_2$	TBHP	$PhCH_3$	54
12	$Pd(OAc)_2$	TBHP	*p*-xylene	57
13	$Pd(OAc)_2$	TBHP	CH_3CN	63
14	$Pd(OAc)_2$	TBHP	DCM	65
15[c]	$Pd(OAc)_2$	TBHP	DCE	45
16[d]	$Pd(OAc)_2$	TBHP	DCE	72
17[e]	$Pd(OAc)_2$	TBHP	DCE	66

[a] Reaction conditions: **1a** (49.0 mg, 0.3 mmol), **2a** (63.7 mg, 0.6 mmol), catalyst (10 mol%), oxidant (2.0 equiv), solvent (2.5 mL), N_2 atmosphere, 80 °C, 8 h. [b] Isolated yield. [c] 60 °C. [d] 100 °C. [e] Under air atmosphere. DCE = 1,2-dichloroethane; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone; TBPB = *tert*-butyl peroxybenzoate; DCP = dicumyl peroxide; TBHP = *tert*-butyl hydroperoxide; DCM = dichloromethane.

With the optimized reaction conditions in hand, we turned our attention to evaluating the scope of aromatic aldehydes (Table 2). It was observed that a wide range of functional groups including Me, *i*-Pr, Ph, F, Cl, Br, CF_3, naphthyl, formylofuran, thiophene groups were tolerated. The aromatic coupling partners bearing electron-withdrawing groups showed slightly higher reactivity than those bearing electron-

Table 2 Substrate scope of aromatic aldehydes[a,b]



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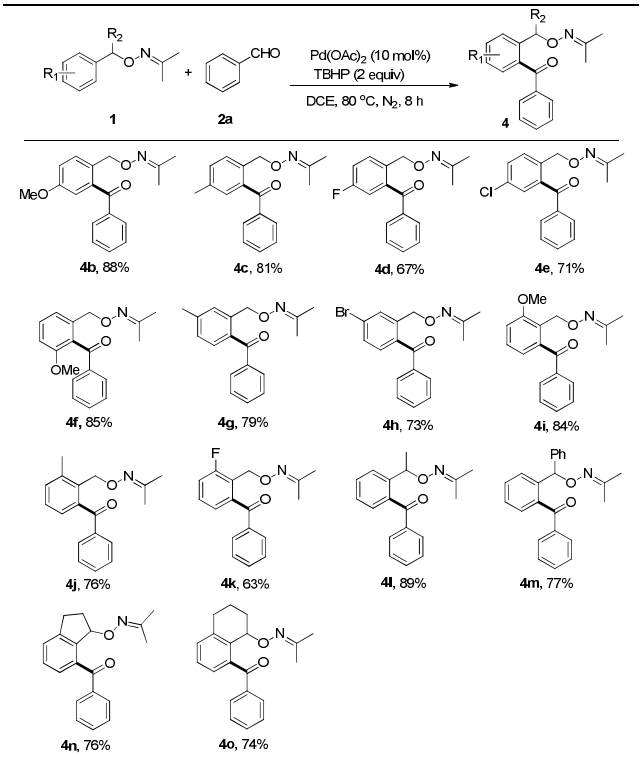
[a] Reaction conditions: **1a** (49.0 mg, 0.3 mmol), **2** (0.6 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), TBHP (54.1 mg, 2.0 equiv), DCE (2.5 mL), N_2 atmosphere, 80 °C, 8 h. [b] Isolated yields.

donating groups (**3e**–**g**, **i**, **k** and **l** *versus* **3b, c, h** and **j**). Nevertheless, 3- or 4-methoxybenzaldehyde failed to deliver any acylation product, with aromatic acid generated.[5a,b] In addition to the electronically and sterically biased *mono*-substututed arylaldehydes (**3a**–**l**) competent for the aroylation, tri- and di-substituted partners could be also applied in the transformation to deliver the aroylated product in moderate yields (**3m**–**o**). Besides, 2-naphthaldehyde was an eligible substrate affording good yield (**3p**). Impressively, 2-formylofuran and 2-thiophenecarboxaldehyde suffered from the protocol offering the products in good yields (**3q** and **r**). Unfortunately, 2-pyridinecarboxaldehyde was unable to give any desired product, possibly due to its strong coordination with Pd, inhibiting the indispensable catalyst turnover (**3s**).

Then, we focused on testing different substituted *O*-arylmethyl acetoxime ethers (Table 3). Similarly, the protocol could tolerate various functional groups, such as Me, MeO, F, Cl, Br and phenyl groups. In particular, the reactive Cl and Br atoms can serve as a synthetic handle for further structural elaboration. The electron-donating group substituted substrates delivered the corresponding products in good to excellent yields of 76–88% (**4b**, **c**, **f**, **g**, **i** and **j**). Whereas, it was observed that the electron-withdrawing group substituted substrates provided relatively lower yields of 63–73%, regardless of their sterical positions (**4d**, **e**, **h** and **k**). On the one hand, as for the *meta*-substituted benzyl moieties, the

Table 3 Substrate scope of *O*-arylmethyl substituted acetoxime ethers.[a,b]



[a] Reaction conditions: **1** (0.3 mmol), **2a** (63.7 mg, 0.6 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), TBHP (54.1 mg, 2.0 equiv), DCE (2.5 mL), N_2 atmosphere, 80 °C, 8 h. [b] Isolated yields.

aroylation reactions tended to happen at less sterically hindered positions (**4g** and **h**). On the other hand, the aroylation particularly took place at the highly crowded *ortho*-position for the *meta*-methoxyl substituted substrate (**4f**), indicating that the coordination of oxygen atom of methoxy group could potentially stabilize the arylpalladium intermediate.[12] *Ortho*-substituted *O*-arylmethyl acetoximes were amenable to the protocol to offer the aroylation products in moderate to good yields, with higher outcomes for the electron-rich substrates (**4i** and **j** *versus* **k**). Substrates derived from secondary benzyl alcohols also worked well under current work conditions (**4l**–**o**).

Interestingly, *O*-aryl acetoximes could be aroylated at the *ortho*-position in good yieids, through a rarer five-membered *exo*-cyclopalladated intermediate (Table 4). It was observed that aromatic aldehydes bearing various substituents were all suitable for the protocol (**6a**–**i**). We noticed that the *ortho*-substituted arylaldehydes here proceeded smoothly to afford the target products in good yields (**6g** and **h**). Furthermore, the different substituted *O*-aryl acetoximes were tested giving good yieids, demonstrating a generality of aroylation of masked phenols under our conditions (**6j**–**l**). To our knowledge, the functionalization of *O*-aryl oximes is firstly achieved *via* a relatively congested five-membered *exo*-activation mode. To further verify the product geometrical configuration, the NMR-based structure of **6h** was determined by X-ray single crystal crystallography (Table 4 and see ESI).

Table 4 *Ortho*-aroylation of *O*-aryl substituted acetoxime ethers.[a,b]

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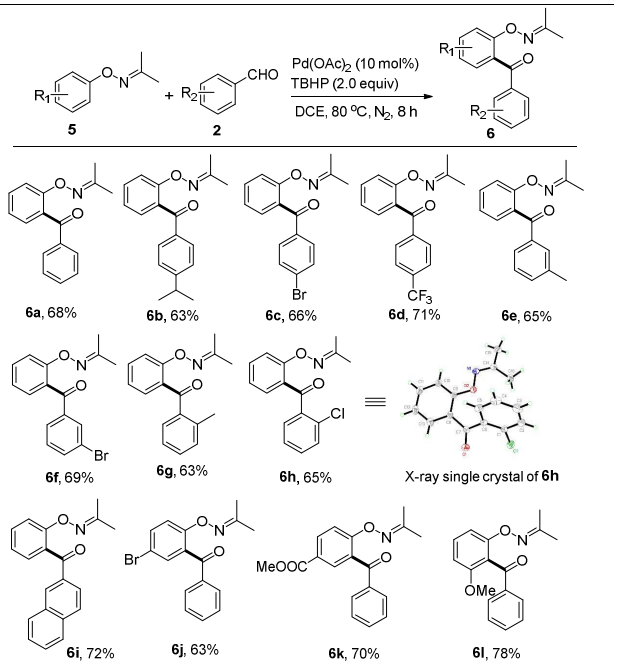
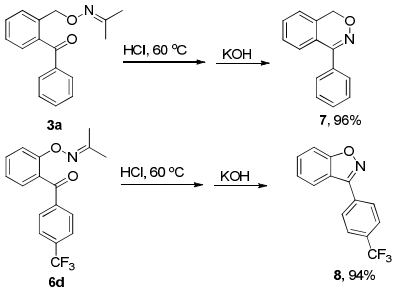


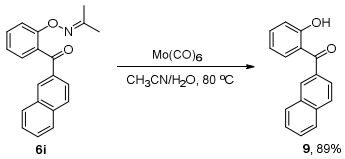
[a] Reaction conditions: **5** (0.3 mmol), **2** (0.6 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), TBHP (54.1 mg, 2.0 equiv), DCE (2.5 mL), N_2 atmosphere, 80 °C, 8 h. [b] Isolated yields.

The strategy can be expediently adopted to prepare synthetically valuable 4-aryl-1*H*-benzo[*d*]oxazines and 3-arylbenzo[*d*]isoxazoles (Scheme 2). The treatment of aromatic ketone **3a** or **6d** was hydrolysed by diluted hydrochloric acid, followed by cyclization with 50% potassium hydroxide solution to afford aryl substituted 1*H*-benzo[*d*][*1,2*]oxazine **7** or benzo[*d*]isoxazole **8** in excellent yield without further column chromatographic purification. Benzo[*d*]isoxazole skeletons belong to a privileged heterofused pharmacophore extensively existed bioactive molecules with antipsychotic, antitumor and cholinesterase-inhibiting activities.[13] 1*H*-benzo[*d*][*1,2*]oxazine structures have been disclosed as intermediates for the synthesis of pharmacologically active compounds and as active ingredients of herbicides.[14]



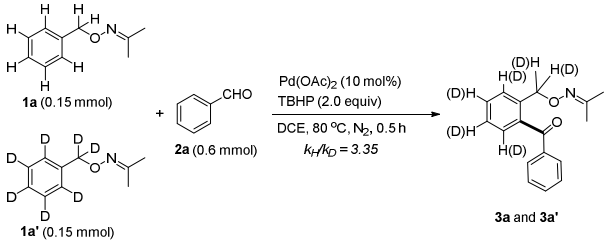
Scheme 2 Convenient access to aryl substituted benzooxazine and benzoisoxazole compounds.

Reasonably, we demonstrated that the acetoxime directing group could be easily removed (Scheme 3). Subjecting **6i** and catalyst $Mo(CO)_6$ to CH_3CN/H_2O (4:1) under N_2 atmosphere, selectively cleaving the N–O bond,[15] furnished the valuable functionalized diaryl ketone **9** in excellent yield.



Scheme 3 Selective removal of the acetoxime directing group.

To gain insight into the reaction mechanism, a deuterium labeling kinetic isotope experiment was conducted to probe the kinetics of Pd^{II}/Pd^{IV}-catalyzed C(sp^2)–H aroylation (Scheme 4). The intermolecular competition reactions between **1a** and **1a'** (**1a**-d_7) with benzaldehyde in one vessel exhibited a notable primary kinetic isotopic effect (k_H/k_D = 3.35; see ESI). The result suggests that the Csp^2–H bond cleavage might be involved in the rate-limiting step.



Scheme 4 Kinetic isotope effect study.

On the basis of the experimental results and previous reports[16], a plausible catalytic cycle is depicted in Scheme 5. The aroylation is probably initiated by oxime-assisted *ortho*-selective *exo*-cyclometalation of the arene by $Pd(OAc)_2$. The *exo*-palladacycle **I** reacts with the aroyl radical, generated *in situ* by a hydrogen atom abstraction, to afford the key Pd^{IV} adduct **II** through an oxidative addition, in which Pd^{II} and the radical conduct a single electron transfer (SET), followed by an oxidation of Pd^{III} into Pd^{IV} with TBHP.[16,17] In the process, TBHP would play the roles of both radical initiator and oxidant.[5c,5f] The highly active hexa-coordinated Pd^{IV} adduct undergoes a following reductive elimination to release the diaryl ketone product and regenerate the Pd^{II} catalyst. It was testified that the employment of radical scavenger TEMPO (2,2,6,6-tetramethylpiperidyl-1-oxyl, 2.5 equiv) in the mode reaction was unable to offer any desired product **3a** while the TEMPO ester **10** was isolated in 69% yield, suggesting the aroyl radical generated in the protocol (see ESI).[18]

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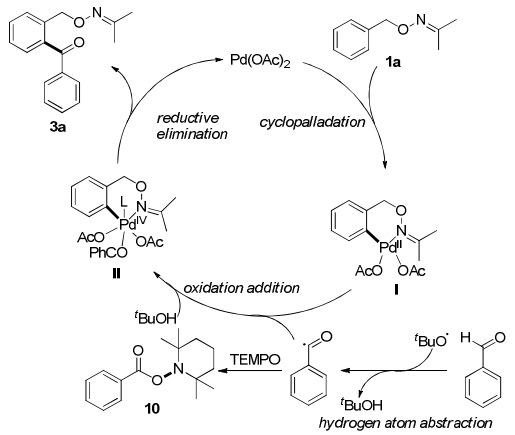

Scheme 5 Plausible reaction mechanism.

Conclusions

In summary, we have developed a Pd-catalyzed *ortho*-aroylation reaction of *O*-arylmethyl and aryl substituted acetoxime ethers *via* direct C–H bond activation with aromatic aldehydes in the presence of TBHP. The protocol exhibits excellent functional group tolerance and broad scope of masked arylmethyl alcohols and phenols. A variety of aromatic aldehydes can be used as aroylation sources to give the diverse diaryl ketones. Particularly, the involved functionalization of *O*-aryl oximes *via* a five-membered *exo*-activation is rather rare in the realm of oxime directing groups. The privileged benzo[*d*]isoxazole and 1*H*-benzo[*d*][*1,2*]oxazine architectures may be expediently accessed from the aroylation products. Besides, facile removal of the directing group can provide valuable functionalized diaryl ketones.

Experimental

General remarks

Unless otherwise indicated, all reagents were obtained from commercial sources and used as received without further purification. All solvents were only dried over 4 Å molecular sieves. TBHP (70 wt% in water) was dried over excess 4 Å molecular sieves.[6a] Reaction products were purified *via* column chromatography on silica gel (300–400 mesh). Melting points were determined using an open capillaries and uncorrected. NMR spectra were determined on Bruker AV400 in $CDCl_3$ with TMS as internal standard for ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz), respectively. HRMS were measured on a QSTAR Pulsar I LC/TOF MS mass spectrometer or Micromass GCTTM gas chromatograph-mass spectrometer.

General procedures for the *ortho*-C–H acylation

A mixture of substrate **1** or **5** (0.3 mmol), **2** (0.6 mmol), $Pd(OAc)_2$ (6.7 mg, 10 mol%), TBHP (54.1 mg, 2.0 equiv) in DCE (2.5 mL) was charged in a glass sealed-tube and stirred under N_2 atmosphere at 80 °C for 8 h. Upon completion of the reaction, saturated brine (15 mL) and DCM (15 mL) were added to the mixture, then the aqueous layer was extracted with DCM (15 mL × 2). The combined organic layer was dried over anhydrous $MgSO_4$. Finally, the solution was concentrated *in vacuo* to provide a crude product, which was further purified *via* a column chromatography on silica gel (eluents: petroleum ether/ethyl acetate = 40:1) to supply the product **3**, **4** or **6**.

Spectral data of compounds

Phenyl(2-(((propan-2-ylideneamino)oxy)methyl)phenyl) methanone (3a): yellow oil, 62.6 mg (78% yield); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.80 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.2 Hz, 1H), 7.50–7.47 (m, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.36–7.34 (m, 2H), 5.16 (s, 2H), 1.71 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.9, 155.3, 138.2, 137.9, 137.5, 133.0, 130.23 (2C), 130.16, 129.0, 128.4, 128.3 (2C), 127.0, 72.9, 21.7, 15.3; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{17}H_{17}NO_2Na$: 290.1157, found: 290.1163.

(2-(((Propan-2-ylideneamino)oxy)methyl)phenyl)(*p*-tolyl)methanone (3b): yellow solid, 62.5 mg (74% yield), m.p. 98–100 °C; ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.70 (d, J = 8.4 Hz, 2H), 7.49 (s, 1H), 7.48−7.44 (m, 1H), 7.35 (d, J = 1.6 Hz, 1H), 7.33 (d, J = 0.8 Hz, 1H), 7.23 (d, J = 8.0 Hz, 2H), 5.16 (s, 2H), 2.42 (s, 3H), 1.72 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.7, 155.4, 143.9, 138.4, 137.7, 135.0, 130.4 (2C), 130.0, 128.98 (2C), 128.95, 128.4, 127.0, 72.9, 21.7 (2C), 15.4; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{18}H_{19}NO_2Na$: 304.1313; found: 304.1301.

(4-Isopropylphenyl)(2-(((propan-2-ylideneamino)oxy)methyl) phenyl)methanone (3c): yellow oil, 65.9 mg (71% yield); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 8.04 (d, J = 8.4 Hz, 2H), 7.74 (d, J = 8.4 Hz, 2H), 7.50 (s, 1H), 7.35 (s, 1H), 7.34 (s, 1H), 7.32 (s, 1H), 5.17 (s, 2H), 2.98 (q, J = 6.8 Hz, 1H), 1.73 (s , 3H), 1.52 (s , 3H), 1.28 (d, J = 4.4 Hz, 3H), 1.27 (d, J = 4.8 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.7, 171.9, 155.4, 154.7, 138.5, 137.6, 135.3, 130.6 (2C), 129.0, 128.3, 127.0, 126.4 (2C), 72.9, 34.3, 23.7 (2C), 21.7, 15.3; HRMS (EI): *m/z* $[M\text{-}N\text{-}C_3H_6]^+$ calcd. for $C_{17}H_{17}O_2$: 253.1229; found: 253.1228.

[1,1'-Biphenyl]-4-yl(2-(((propan-2-ylideneamino)oxy)methyl) phenyl)methanone (3d): yellow oil, 70.1 mg (68% yield); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.88 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.51 (s, 1H), 7.48 (s, 1H), 7.46 (s, 1H), 7.44 (s, 1H), 7.41 (s, 1H), 7.38 (s, 2H), 5.20 (s, 2H), 1.71 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.5, 155.4, 145.7, 139.9, 138.3, 137.8, 136.3, 130.9 (2C), 130.2, 129.1, 129.0 (2C), 128.4, 128.3, 127.3 (2C), 127.1, 126.9 (2C), 73.0, 21.8, 15.4; HRMS (EI): *m/z* $[M\text{-}N\text{-}C_3H_6]^+$ calcd. for $C_{20}H_{15}O_2$: 287.1072; found: 287.1074.

(4-Chlorophenyl)(2-(((propan-2-ylideneamino)oxy)methyl)phenyl) methanone (3e): yellow oil, 76.0 mg (84% yield); ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.74 (d, J = 8.4 Hz, 2H), 7.50−7.48 (m, 2H), 7.41 (d, J = 8.4 Hz, 2H), 7.36 (td, J_1 = 7.6 Hz, J_2 = 2.4 Hz, 1H), 7.32 (s, 1H), 5.15 (s, 2H), 1.72 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.7, 155.6, 139.5, 137.8, 137.7, 135.9, 131.6 (2C), 130.4, 129.2, 128.6 (2C), 128.3, 127.2, 72.8, 21.7, 15.4; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{17}H_{16}NO_2Na^{35}Cl$: 324.0767; found: 324.0762.

(4-Bromophenyl)(2-(((propan-2-ylideneamino)oxy)methyl)phenyl) methanone (3f): yellow solid, 90.4 mg (87% yield), m.p. 90–92 °C; ^1H NMR (400 MHz, $CDCl_3$, ppm): δ 7.69 (d, J = 6.4 Hz, 1H), 7.67 (d, J = 6.4 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.51 (s, 1H), 7.37 (td, J_1 = 7.6 Hz, J_2 = 2.4 Hz, 1H), 7.33 (s, 1H), 5.16 (s, 2H), 1.74 (s, 3H), 1.56 (s,

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3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.8, 155.4, 137.9, 137.7, 136.3, 132.4, 131.7 (2C), 131.6 (2C), 130.4, 129.2, 128.3, 127.2, 72.8, 21.7, 15.4; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{17}H_{16}NO_2Na^{79}Br$: 368.0262; found: 368.0259.

(2-(((Propan-2-ylideneamino)oxy)methyl)phenyl)(4-(trifluoromethyl)phenyl)methanone (3g): yellow solid, 81.5 mg (81% yield), m.p. 78–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.91 (d, *J* = 8.0 Hz, 2H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 0.8 Hz, 1H), 7.51 (t, *J* = 2.0 Hz, 1H), 7.39–7.35 (m, 1H), 7.34 (s, 1H), 5.17 (s, 2H), 1.71 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.7, 155.5, 140.4, 138.2, 137.3, 134.2 (q, $^2J_{CF}$ = 32.4 Hz), 130.8, 130.4 (2C), 129.2, 128.6, 127.2, 123.6 (q, $^1J_{CF}$ = 271.3 Hz), 125.3 (q, $^3J_{CF}$ = 3.8 Hz, 2C), 72.8, 21.7, 15.3; HRMS (EI): *m/z* $[M\text{-}N\text{-}C_3H_6]^+$ calcd. for $C_{15}H_{10}O_2F_3$: 279.0633; found: 279.0635.

(2-(((Propan-2-ylideneamino)oxy)methyl)phenyl)(*m*-tolyl)methanone (3h): yellow oil, 60.8 mg (72% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.63 (s, 1H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.51 (s, 1H), 7.48 (td, J_1 = 6.0 Hz, J_2 = 2.0 Hz, 1H), 7.40 (d, *J* = 9.6 Hz, 1H), 7.37 (d, *J* = 1.6 Hz, 1H), 7.35 (d, *J* = 1.6 Hz, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 5.18 (s, 2H), 2.38 (s, 3H), 1.75 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 198.2, 155.4, 138.3, 138.1, 137.8, 137.5, 133.8, 130.6, 130.1, 129.0, 128.5, 128.1, 127.7, 127.0, 72.9, 21.7, 21.3, 15.3; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{18}H_{19}NO_2Na$: 304.1313; found: 304.1319.

(3-Bromophenyl)(2-(((propan-2-ylideneamino)oxy)methyl)phenyl)methanone (3i): yellow oil, 86.2 mg (83% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.91 (t, *J* = 1.6 Hz, 1H), 7.73 (dt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.70 (dq, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.51 (d, *J* = 0.8 Hz, 1H), 7.50 (t, *J* = 1.2 Hz, 1H), 7.40–7.36 (m, 1H), 7.34 (d, *J* = 2.0 Hz, 1H), 7.32 (s, 1H), 5.16 (s, 2H), 1.74 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.5, 155.5, 139.4, 138.0, 137.5, 135.8, 133.0, 130.5, 129.9, 129.2, 128.7, 128.4, 127.2, 122.6, 72.8, 21.7, 15.3; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{17}H_{16}NO_2Na^{79}Br$: 368.0262; found: 368.0267.

(2-(((Propan-2-ylideneamino)oxy)methyl)phenyl)(*o*-tolyl)methanone (3j): yellow oil, 58.2 mg (69% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.55 (d, *J* = 7.6 Hz, 1H), 7.49 (td, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 1H), 7.38 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.34 (s, 1H), 7.32 (d, *J* = 1.6 Hz, 2H), 7.29 (d, *J* = 4.8 Hz, 1H), 7.18 (t, *J* = 7.6 Hz, 1H), 5.33 (s, 2H), 2.46 (s, 3H), 1.83 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 200.0, 155.3, 139.3, 138.5, 138.4, 138.3, 131.4, 131.1 (2C), 130.8, 130.3, 128.7, 126.9, 125.2, 73.1, 21.9, 20.8, 15.7; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{18}H_{19}NO_2Na$: 304.1313; found: 304.1307.

(2-Fluorophenyl)(2-(((propan-2-ylideneamino)oxy)methyl)phenyl)methanone (3k): yellow oil, 61.6 mg (72% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.60 (td, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.52 (s, 1H), 7.50 (s, 1H), 7.42 (d, *J* = 7.6 Hz, 1H), 7.35 (t, *J* = 2.4 Hz, 1H), 7.33 (s, 1H), 7.21 (t, *J* = 7.2 Hz, 1H), 7.11 (t, *J* = 8.4 Hz, 1H), 5.30 (s, 2H), 1.80 (s, 3H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 194.7, 161.0 (d, $^1J_{CF}$ = 254.7 Hz), 155.4, 138.8, 137.8, 134.0 (d, $^2J_{CF}$ = 8.6 Hz), 131.6 (d, $^3J_{CF}$ = 2.0 Hz), 131.4, 129.7 (d, $^4J_{CF}$ = 1.7 Hz), 128.6, 127.1, 127.0, 124.1 (d, $^3J_{CF}$ = 3.8 Hz), 116.6 (d, $^2J_{CF}$ = 21.8 Hz), 73.0, 21.8, 15.6; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{17}H_{16}NO_2NaF$: 308.1063; found: 308.1068.

(2-Chlorophenyl)(2-(((propan-2-ylideneamino)oxy)methyl)phenyl)methanone (3l): yellow sold, 69.7 mg (77% yield), m.p. 84–86 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.60 (d, *J* = 7.2 Hz, 1H), 7.53 (td, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 7.43 (t, *J* = 0.8 Hz, 1H), 7.43–7.42 (m, 1H), 7.40 (t, *J* = 1.6 Hz, 1H), 7.37 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.34 (dd, J_1 = 6.0 Hz, J_2 = 2.4 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 5.47 (s, 2H), 1.92 (s, 3H), 1.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.6, 155.3, 140.9, 138.9, 135.7, 132.3, 132.1, 131.62, 131.56, 130.4, 130.2, 128.2, 126.8, 126.6, 73.2, 21.9, 15.9; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{17}H_{16}NO_2Na^{35}Cl$: 324.0767; found: 324.0774.

Mesityl(2-(((propan-2-ylideneamino)oxy)methyl)phenyl)methanone (3m): yellow solid, 58.5 mg (63% yield), m.p. 92–94 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.66 (d, *J* = 8.0 Hz, 1H), 7.53 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 1H), 6.88 (s, 2H), 5.66 (s, 2H), 2.32 (s, 3H), 2.09 (s, 6H), 2.00 (s, 3H), 1.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 202.3, 155.2, 141.7, 138.5, 138.0, 135.2, 134.5 (2C), 132.7, 132.2, 128.4 (2C), 127.6, 126.9, 73.5, 22.0, 21.2, 19.5 (2C), 15.9; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{20}H_{23}NO_2Na$: 332.1626; found: 332.1622.

(2,4-Difluorophenyl)(2-(((propan-2-ylideneamino)oxy)methyl)phenyl)methanone (3n): yellow oil, 59.1 mg (65% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.66 (dd, J_1 = 15.2 Hz, J_2 = 8.4 Hz, 1H), 7.51 (d, *J* = 1.2 Hz, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.39 (d, *J* = 7.2 Hz, 1H), 7.34 (td, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 1H), 6.95 (td, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 6.85 (td, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 5.25 (s, 2H), 1.79 (s, 3H), 1.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 193.4 (d, $^3J_{CF}$ = 1.0 Hz), 165.5 (dd, $^1J_{CF}$ = 254.6 Hz, $^3J_{CF}$ = 11.7 Hz), 162.0 (dd, $^1J_{CF}$ = 258.3 Hz, $^3J_{CF}$ = 12.4 Hz), 155.4, 138.4, 138.0, 133.5 (dd, $^3J_{CF}$ = 10.5 Hz, $^3J_{CF}$ = 3.4 Hz), 131.3, 129.2 (d, $^4J_{CF}$ = 1.7 Hz), 128.8, 127.3, 123.5 (dd, $^2J_{CF}$ = 11.3 Hz, $^4J_{CF}$ = 3.6 Hz), 111.7 (dd, $^2J_{CF}$ = 21.3 Hz, $^4J_{CF}$ = 3.7 Hz), 104.9 (t, $^2J_{CF}$ = 25.3 Hz), 72.9, 21.8, 15.6; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{17}H_{15}NO_2F_2Na$: 326.0969; found: 326.0963.

(3-Bromo-5-methylphenyl)(2-(((propan-2-ylideneamino)oxy)methyl)phenyl)methanone (3o): yellow oil, 70.2 mg (65% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.60 (d, *J* = 8.0 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 1H), 7.47 (s, 1H), 7.36 (d, *J* = 6.4 Hz, 1H), 7.28 (dd, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 2H), 7.16 (d, *J* = 7.6 Hz, 1H), 5.46 (s, 2H), 2.39 (s, 3H), 1.92 (s, 3H), 1.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.2, 155.2, 142.5, 140.8, 137.8, 135.8, 134.1, 132.1, 131.6, 130.5, 128.1, 127.8, 126.8, 120.4, 73.1, 21.9, 21.1, 15.9; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{18}H_{18}NO_2BrNa$: 382.0419; found: 382.0418.

Naphthalen-2-yl(2-(((propan-2-ylideneamino)oxy)methyl)phenyl)methanone (3p): yellow solid, 72.4 mg (76% yield), m.p. 88–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.16 (s, 1H), 8.02 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 7.92 (s, 1H), 7.89 (d, *J* = 6.4 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.61 (td, J_1 = 6.8 Hz, J_2 = 1.2 Hz, 1H), 7.56 (d, *J* = 7.6 Hz, 1H), 7.53 (d, *J* = 8.4 Hz, 1H), 7.50 (d, *J* = 1.6 Hz, 1H), 7.41 (t, *J* = 5.2 Hz, 2H), 5.22 (s, 2H), 1.67 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 198.0, 171.1, 155.5, 138.4, 137.9, 135.6, 134.9, 132.9, 132.3, 130.2, 129.6, 129.1, 128.5, 128.3, 127.8, 127.2, 126.8, 125.1, 73.0, 21.7, 15.3; HRMS (ESI): *m/z* $[M+Na]^+$ calcd. for $C_{21}H_{19}NO_2Na$: 340.1313; found: 340.1309.

Furan-2-yl(2-(((propan-2-ylideneamino)oxy)methyl)phenyl)methanone (3q): yellow oil, 48.6 mg (63% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.65 (t, *J* = 0.8 Hz, 1H), 7.49 (d, *J* = 7.6 Hz, 1H), 7.47 (d, *J* = 0.8 Hz, 1H), 7.46 (d, *J* = 3.2 Hz, 1H), 7.36–7.31 (m, 1H), 6.97 (dd, J_1 = 3.2 Hz, J_2 = 0.4 Hz, 1H), 6.52 (dd, J_1 = 3.6 Hz, J_2 = 1.6 Hz, 1H), 5.21 (s, 2H), 1.72 (s, 3H), 1.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$,

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ppm): δ 184.5, 155.4, 152.6, 147.4, 138.0, 136.9, 130.7, 128.9, 128.3, 127.0, 121.1, 112.3, 72.6, 21.7, 15.3; HRMS (EI): *m/z* [M-N-C_3H_6]$^+$ calcd. for $C_{12}H_9O_3$: 201.0552; found: 201.0551.

(2-(((Propan-2-ylideneamino)oxy)methyl)phenyl)(thiophen-2-yl) methanone (3r): yellow oil, 53.3 mg (65% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.70 (dd, J_1 = 5.2 Hz, J_2 = 1.2 Hz, 1H), 7.49 (s, 2H), 7.48−7.45 (m, 1H), 7.41 (dd, J_1 = 3.6 Hz, J_2 = 1.6 Hz, 1H), 7.37 (td, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 1H), 7.09 (dd, J_1 = 4.8 Hz, J_2 = 4.0 Hz, 1H), 5.20 (s, 2H), 1.73 (s, 3H), 1.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 188.8, 154.4, 143.8, 136.9, 136.5, 134.4, 133.6, 129.3, 128.1, 127.0, 126.9, 126.0, 71.7, 20.7, 14.1; HRMS (EI): *m/z* [M-N-C_3H_6]$^+$ calcd. for $C_{12}H_9O_2S$: 217.0323; found: 217.0324.

(5-Methoxy-2-(((propan-2-ylideneamino)oxy)methyl)phenyl) (phenyl)methanone (4b): yellow oil, 78.5 mg (88% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.11 (d, J = 6.8 Hz, 1H), 7.82 (d, J = 7.2 Hz, 1H), 7.63−7.53 (m, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.42−7.39 (m, 1H), 6.99 (dd, J_1 = 8.4 Hz, J_2 = 2.8 Hz, 1H), 6.87 (d, J = 2.8 Hz, 1H), 5.06 (s, 2H), 3.79 (s, 3H), 1.69 (s, 3H), 1.48 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.7, 158.6, 155.3, 139.8, 137.2, 133.7, 133.2, 130.9, 130.3 (2C), 128.3 (2C), 115.3, 113.9, 72.5, 55.5, 21.7, 15.3; HRMS (EI): *m/z* [M]$^+$ calcd. for $C_{18}H_{19}NO_3$: 297.1365; found: 297.1360.

(5-Methyl-2-(((propan-2-ylideneamino)oxy)methyl)phenyl)(phenyl) methanone (4c): yellow solid, 68.4 mg (81% yield), m.p. 67–69 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.82 (d, J = 0.8 Hz, 1H), 7.80 (d, J = 1.2 Hz, 1H), 7.56 (t, J = 7.2 Hz, 1H), 7.50−7.45 (m, 1H), 7.42 (d, J = 7.6 Hz, 1H), 7.38 (d, J = 7.6 Hz, 1H), 7.29 (d, J = 0.8 Hz, 1H), 7.15 (s, 1H), 5.11 (s, 2H), 2.36 (s, 3H), 1.72 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 198.2, 155.3, 138.4, 137.6, 137.0, 134.6, 133.0, 130.8, 130.2 (2C), 129.2, 128.9, 128.3 (2C), 72.8, 21.7, 21.1, 15.3; HRMS (EI): *m/z* [M-N-C_3H_6]$^+$ calcd. for $C_{15}H_{13}O_2$: 225.0916; found: 225.0917.

(5-Fluoro-2-(((propan-2-ylideneamino)oxy)methyl)phenyl)(phenyl) methanone (4d): yellow solid, 57.3 mg (67% yield), m.p. 99–101 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.12 (d, J = 7.2 Hz, 1H), 7.80 (d, J = 7.2 Hz, 1H), 7.65−7.56 (m, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.47 (s, 1H), 7.44 (d, J = 7.6 Hz, 1H), 7.17 (td, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 7.05 (dd, J_1 = 8.4 Hz, J_2 = 2.4 Hz, 1H), 5.10 (s, 2H), 1.71 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.4 (d, $^4J_{CF}$ = 1.7 Hz), 171.8, 161.4 (d, $^1J_{CF}$ = 246.7 Hz), 155.7, 136.8, 133.7, 133.4, 131.2 (d, $^3J_{CF}$ = 7.8 Hz), 130.2 (2C), 128.4 (2C), 116.8 (d, $^2J_{CF}$ = 20.9 Hz), 115.4 (d, $^2J_{CF}$ = 22.8 Hz), 72.2, 21.7, 15.3; HRMS (EI): *m/z* [M-N-C_3H_6]$^+$ calcd. for $C_{14}H_{10}O_2F$: 229.0665; found: 229.0666.

(5-Chloro-2-(((propan-2-ylideneamino)oxy)methyl)phenyl)(phenyl) methanone (4e): yellow oil, 64.3 mg (71% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.12 (d, J = 6.8 Hz, 1H), 7.80 (d, J = 6.8 Hz, 1H), 7.64−7.57 (m, 1H), 7.49 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 1.2 Hz, 2H), 7.32 (s, 1H), 5.10 (s, 2H), 1.70 (s, 3H), 1.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.4, 155.8, 139.8, 136.8, 136.4, 133.7, 133.4, 133.1, 130.6, 130.2 (2C), 128.4 (2C), 128.2, 72.2, 21.7, 15.3; HRMS (EI): *m/z* [M-N-C_3H_6]$^+$ calcd. for $C_{14}H_{10}O_2{}^{35}Cl$: 245.0369; found: 245.0370.

(2-Methoxy-6-(((propan-2-ylideneamino)oxy)methyl)phenyl) (phenyl)methanone (4f): white solid, 75.8 mg (85% yield), m.p. 78–80 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.78 (s, 1H), 7.76 (d, J = 1.6 Hz, 1H), 7.55 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.2 Hz, 2H), 7.38 (d, J = 8.8 Hz, 1H), 7.10 (d, J = 2.4 Hz, 1H), 6.82 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 5.29 (s, 2H), 3.88 (s, 3H), 1.80 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.2, 161.5, 155.5, 141.9, 138.5, 132.5, 132.1, 130.1 (2C), 129.7, 128.2 (2C), 114.4, 111.3, 73.0, 55.4, 21.8, 15.6; HRMS (EI): *m/z* [M-N-C_3H_6]$^+$ calcd. for $C_{15}H_{13}O_3$: 241.0865; found: 241.0866.

(4-Methyl-2-(((propan-2-ylideneamino)oxy)methyl)phenyl)(phenyl) methanone (4g): yellow oil, 66.7 mg (79% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.79 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.42 (t, J = 7.2 Hz, 2H), 7.32 (s, 1H), 7.25 (d, J = 6.8 Hz, 1H), 7.16 (t, J = 7.2 Hz, 1H), 5.17 (s, 2H), 2.42 (s, 3H), 1.72 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 198.0, 155.3, 140.6, 138.1, 137.9, 135.3, 132.8, 130.2 (2C), 129.8, 129.0, 128.2 (2C), 127.6, 73.0, 21.8, 21.6, 15.4; HRMS (EI): *m/z* [M+Na]$^+$ calcd. for $C_{18}H_{19}NO_2Na$: 304.1313; found: 304.1297.

(4-Bromo-2-(((propan-2-ylideneamino)oxy)methyl)phenyl)(phenyl) methanone (4h): yellow oil, 75.8 mg (73% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.79 (s, 1H), 7.77 (d, J = 1.2 Hz, 1H), 7.66 (d, J = 1.6 Hz, 1H), 7.61−7.55 (m, 1H), 7.49 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.44 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 8.0 Hz, 1H), 5.13 (s, 2H), 1.72 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.9, 155.9, 140.6, 137.2, 136.7, 133.3, 131.9, 130.2 (2C), 130.1, 130.0, 128.4 (2C), 124.7, 72.2, 21.7, 15.4; HRMS (EI): *m/z* [M-N-C_3H_6]$^+$ calcd. for $C_{14}H_{10}O_2{}^{79}Br$: 288.9864; found: 288.9865.

(3-Methoxy-2-(((propan-2-ylideneamino)oxy)methyl)phenyl) (phenyl)methanone (4i): yellow oil, 74.9 mg (84% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.82 (s, 1H), 7.80 (d, J = 1.2 Hz, 1H), 7.52 (tt, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 8.0 Hz, 1H), 7.00 (d, J = 8.0 Hz, 1H), 6.88 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 5.21 (s, 2H), 3.86 (s, 3H), 1.60 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.7, 157.5, 155.1, 140.9, 137.3, 133.0, 130.2 (2C), 128.4, 128.1 (2C), 125.1, 119.9, 112.1, 66.0, 55.9, 21.6, 15.1; HRMS (EI): *m/z* [M-N-C_3H_6]$^+$ calcd. for $C_{15}H_{13}O_3$: 241.0865; found: 241.0863.

(3-Methyl-2-(((propan-2-ylideneamino)oxy)methyl)phenyl)(phenyl) methanone (4j): yellow oil, 64.1 mg (76% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.82 (d, J = 7.6 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.30 (t, J = 7.2 Hz, 1H), 7.25 (d, J = 6.8 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 5.11 (s, 2H), 2.47 (s, 3H), 1.65 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 198.5, 155.1, 140.3, 138.2, 137.6, 134.2, 133.0, 131.8, 130.4 (2C), 128.1 (2C), 127.2, 125.4, 69.2, 21.7, 19.8, 15.2; HRMS (EI): *m/z* [M+Na]$^+$ calcd. for $C_{18}H_{19}NO_2Na$: 304.1313; found: 304.1317.

(3-Fluoro-2-(((propan-2-ylideneamino)oxy)methyl)phenyl)(phenyl) methanone (4k): yellow solid, 53.9 mg (63% yield), m.p. 87–89 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.74 (d, J = 7.2 Hz, 2H), 7.50 (t, J = 7.2 Hz, 1H), 7.36 (t, J = 8.0 Hz, 2H), 7.31−7.25 (m, 1H), 7.12 (t, J = 8.4 Hz, 1H), 7.03 (d, J = 7.6 Hz, 1H), 5.12 (s, 2H), 1.53 (s, 3H), 1.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 195.5, 159.9 (d, $^1J_{CF}$ = 247.6 Hz), 154.5, 140.5 (d, $^4J_{CF}$ = 3.0 Hz), 135.9, 132.2, 129.3 (2C), 127.8 (d, $^3J_{CF}$ = 8.7 Hz), 127.2 (2C), 123.5 (d, $^2J_{CF}$ = 15.4 Hz), 122.5 (d, $^3J_{CF}$ = 3.5 Hz), 116.0 (d, $^2J_{CF}$ = 22.9 Hz), 63.9 (d, $^3J_{CF}$ = 4.9 Hz), 20.6, 14.0; H RMS (EI): *m/z* [M+Na]$^+$ calcd. for $C_{17}H_{16}NO_2NaF$: 308.1063; found: 308.1049.

Phenyl(2-(1-((propan-2-ylideneamino)oxy)ethyl)phenyl)

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methanone (4l): yellow solid, 75.1 mg (89% yield), m.p. 81–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.82 (d, J = 7.2 Hz, 2H), 7.56 (t, J = 7.6 Hz, 1H), 7.53 (d, J = 8.0 Hz, 1H), 7.48 (td, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.42 (t, J = 8.0 Hz, 2H), 7.30 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.24 (d, J = 1.2 Hz, 1H), 5.39−5.32 (m, 1H), 1.67 (s, 3H), 1.59 (s, 3H), 1.57 (d, J = 6.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 198.2, 154.7, 143.4, 137.7, 137.5, 133.1, 130.5 (2C), 130.0, 128.2 (2C), 127.9, 126.8, 126.3, 76.8, 22.2, 21.8, 15.4; H RMS (EI): *m/z* $[M+Na]^+$ calcd. for $C_{18}H_{19}NO_2Na$: 304.1313; found: 304.1313.

Phenyl(2-(phenyl((propan-2-ylideneamino)oxy)methyl)phenyl) methanone (4m): yellow oil, 79.3 mg (77% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.78 (d, J = 8.4 Hz, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.45−7.41 (m, 1H), 7.40 (s, 1H), 7.37 (d, J = 7.6 Hz, 1H), 7.34 (s, 1H), 7.33−7.32 (m, 3H), 7.30 (d, J = 1.2 Hz, 2H), 7.28 (s, 1H), 7.22 (t, J = 6.8 Hz, 1H), 6.45 (s, 1H), 1.67 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.9, 155.3, 141.1, 141.0, 138.7, 137.6, 133.0, 130.4 (2C), 129.9, 128.3, 128.2 (2C), 128.1 (2C), 128.0, 127.7 (2C), 127.4, 126.7, 82.4, 21.8, 15.7; HRMS (EI): *m/z* $[M\text{-}N\text{-}C_3H_6]^+$ calcd. for $C_{20}H_{15}O_2$: 287.1072; found: 287.1073.

Phenyl(3-((propan-2-ylideneamino)oxy)-2,3-dihydro-1*H*-inden-4-yl) methanone (4n): yellow oil, 66.9 mg (76% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.82 (d, J = 7.2 Hz, 2H), 7.55 (t, J = 7.2 Hz, 1H), 7.43 (t, J = 7.6 Hz, 3H), 7.34 (t, J = 7.2 Hz, 1H), 7.26 (t, J = 2.8 Hz, 1H), 5.77 (dd, J_1 = 6.8 Hz, J_2 = 3.6 Hz, 1H), 3.18−3.09 (m, 1H), 2.97−2.88 (m, 1H), 2.51−2.42 (m, 1H), 2.27−2.18 (m, 1H), 1.53 (s, 3H), 1.45 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.5, 154.5, 145.8, 141.3, 137.6, 137.0, 132.7, 130.1 (2C), 128.2 (2C), 128.1, 127.1, 126.4, 83.8, 31.8, 30.5, 21.6, 15.2; HRMS (EI): *m/z* $[M+Na]^+$ calcd. for $C_{19}H_{19}NO_2Na$: 316.1313; found: 316.1316.

Phenyl(8-((propan-2-ylideneamino)oxy)-5,6,7,8-tetrahydro naphthalen-1-yl)methanone (4o): yellow oil, 68.2 mg (74% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.82 (s, 1H), 7.80 (d, J = 1.2 Hz, 1H), 7.52 (tt, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 7.48 (t, J = 7.2 Hz, 1H), 7.39 (t, J = 7.6 Hz, 2H), 7.25−7.21 (m, 1H), 7.12 (dd, J_1 = 6.8 Hz, J_2 = 2.0 Hz, 1H), 5.40 (t, J = 5.6 Hz, 1H), 2.94−2.86 (m, 1H), 2.83−2.75 (m, 1H), 2.02 (q, J = 5.6 Hz, 2H), 1.93−1.84 (m, 1H), 1.80−1.71 (m, 1H), 1.61 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 198.0, 154.4, 139.2, 137.5, 134.1, 132.8, 130.5, 130.2 (2C), 128.5, 128.0 (2C), 126.7, 125.4, 74.5, 30.2, 29.0, 21.7, 18.9, 15.0; HRMS (EI): *m/z* $[M\text{-}N\text{-}C_3H_6]^+$ calcd. for $C_{17}H_{15}O_2$: 251.1072; found: 251.1073.

Phenyl(2-((propan-2-ylideneamino)oxy)phenyl)methanone (6a): yellow oil, 51.7 mg (68% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.80 (d, J = 7.2 Hz, 2H), 7.55−7.51 (m, 1H), 7.50 (s, 2H), 7.48 (d, J = 2.8 Hz, 1H), 7.41 (t, J = 7.6 Hz, 2H), 7.13−7.09 (m, 1H), 1.85 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.3, 159.5, 157.3, 138.6, 132.5, 132.4, 129.8, 129.6 (2C), 128.2 (2C), 126.8, 122.0, 115.3, 21.5, 15.7; HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{16}H_{15}NO_2$: 253.1103; found: 253.1098.

(4-Isopropylphenyl)(2-((propan-2-ylideneamino)oxy)phenyl) methanone (6b): yellow oil, 55.8 mg (63% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.73 (d, J = 8.0 Hz, 2H), 7.49 (d, J = 8.8 Hz, 1H), 7.47 (d, J = 7.2 Hz, 2H), 7.25 (d, J = 8.4 Hz, 2H), 7.09 (t, J = 7.2 Hz, 1H), 2.98−2.91 (m, 1H), 1.84 (s, 3H), 1.36 (s, 3H), 1.26 (s, 3H), 1.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 195.8, 159.4, 157.2, 154.1, 136.5, 132.1, 129.9 (2C), 129.7, 127.1, 126.2 (2C), 121.9, 115.3, 34.3, 23.8 (2C), 21.5, 15.7; HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{19}H_{21}NO_2$: 295.1572; found: 295.1573.

(4-Bromophenyl)(2-((propan-2-ylideneamino)oxy)phenyl) methanone (6c): yellow oil, 65.8 mg (66% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.66 (dt, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 2H), 7.55 (dt, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 2H), 7.48 (d, J = 3.6 Hz, 2H), 7.46 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 7.13−7.08 (m, 1H), 1.86 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 194.0, 158.6, 156.2, 136.3, 131.6, 130.4 (2C), 130.0 (2C), 128.7, 126.5, 125.2, 121.0, 114.4, 20.5, 14.7; HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{16}H_{14}NO_2{}^{79}Br$: 331.0208; found: 331.0211.

(2-((Propan-2-ylideneamino)oxy)phenyl)(4-(trifluoromethyl) phenyl)methanone (6d): white solid, 68.4 mg (71% yield), m.p. 89–90 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.88 (d, J = 8.4 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.53 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 2H), 7.51 (d, J = 1.2 Hz, 1H), 7.13 (td, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 1H), 1.84 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 194.9, 159.6, 157.5, 141.7, 133.7 (q, $^2J_{CF}$ = 32.4 Hz), 133.1, 130.0, 129.7 (2C), 123.7 (q, $^1J_{CF}$ = 271.0 Hz), 125.9, 125.1 (q, $^3J_{CF}$ = 3.7 Hz, 2C), 122.2, 115.6, 21.4, 15.5; H RMS (EI): *m/z* $[M]^+$ calcd. for $C_{17}H_{14}NO_2F_3$: 321.0977; found: 321.0976.

(2-((Propan-2-ylideneamino)oxy)phenyl)(*m*-tolyl)methanone (6e): yellow oil, 52.1 mg (65% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.59 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 2.4 Hz, 1H), 7.47 (dd, J_1 = 6.4 Hz, J_2 = 2.0 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 7.29 (t, J = 7.6 Hz, 1H), 7.22 (t, J = 7.6 Hz, 1H), 7.10 (td, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 1H), 6.92−6.83 (m, 1H), 2.37 (s, 3H), 1.86 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.6, 159.6, 157.3, 138.5, 137.9, 133.4, 132.3, 130.0, 129.8, 129.6, 128.1, 127.0, 121.9, 115.5, 21.5, 21.2, 15.7; HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{17}H_{17}NO_2$: 267.1258; found: 267.1259.

(3-Bromophenyl)(2-((propan-2-ylideneamino)oxy)phenyl) methanone (6f): yellow oil, 68.8 mg (69% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.93 (t, J = 1.6 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 3.2 Hz, 1H), 7.48 (d, J = 5.2 Hz, 2H), 7.29 (t, J = 8.0 Hz, 1H), 7.12 (td, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 1.87 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 194.5, 159.6, 157.4, 140.5, 135.2, 132.8, 132.3, 129.9, 129.7, 128.1, 126.1, 122.3, 122.2, 115.8, 21.5, 15.8; H RMS (EI): *m/z* $[M]^+$ calcd. for $C_{16}H_{14}NO_2{}^{79}Br$: 331.0208; found: 331.0209.

(2-((Propan-2-ylideneamino)oxy)phenyl)(*o*-tolyl)methanone (6g): yellow oil, 50.5 mg (63% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.59 (d, J = 7.2 Hz, 1H), 7.48 (d, J = 0.8 Hz, 1H), 7.47 (t, J = 1.6 Hz, 1H), 7.37 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.32 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.23 (d, J = 7.6 Hz, 1H), 7.16 (t, J = 7.6 Hz, 1H), 7.11−7.06 (m, 1H), 2.47 (s, 3H), 1.86 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 197.7, 159.5, 157.9, 139.8, 137.6, 133.2, 131.1, 130.7, 130.5, 130.0, 127.5, 125.4, 121.8, 115.4, 21.6, 20.6, 15.6; HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{17}H_{17}NO_2$: 267.1259; found: 267.1258.

(2-Chlorophenyl)(2-((propan-2-ylideneamino)oxy)phenyl) methanone (6h): yellow solid, 56.1 mg (65% yield), m.p. 81–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.70 (d, J = 7.2 Hz, 1H), 7.50 (d, J = 3.6 Hz, 2H), 7.46 (d, J = 7.2 Hz, 1H), 7.39 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.30 (d, J = 7.2 Hz, 1H), 7.11−7.06 (m, 1H), 1.88 (s, 3H), 1.39 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 194.0, 159.7, 158.7, 140.4, 134.2, 131.8, 131.2, 130.9, 130.2, 130.0, 126.6, 125.9,

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121.8, 115.5, 21.6, 15.7; H RMS (EI): *m/z* $[M]^+$ calcd. for $C_{16}H_{14}NO_2{}^{35}Cl$: 287.0713; found: 287.0714.

Naphthalen-2-yl(2-((propan-2-ylideneamino)oxy)phenyl) methanone (6i): yellow oil, 65.5 mg (72% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.25 (s, 1H), 7.97 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 7.88 (s, 1H), 7.86 (s, 2H), 7.58 (d, *J* = 6.8 Hz, 1H), 7.55 (s, 1H), 7.53 (d, *J* = 1.2 Hz, 1H), 7.53 (d, *J* = 4.0 Hz, 1H), 7.49 (d, *J* = 6.4 Hz, 1H), 7.15 (td, J_1 = 7.2 Hz, J_2 = 2.4 Hz, 1H), 1.77 (s, 3H), 1.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 196.1, 159.5, 157.3, 135.8, 135.4, 132.5, 132.3, 131.7, 129.8, 129.6, 128.2, 128.0, 127.7, 127.1, 126.6, 125.1, 122.0, 115.6, 21.4, 15.7; HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{20}H_{17}NO_2$: 303.1259; found: 303.1260.

(5-Bromo-2-((propan-2-ylideneamino)oxy)phenyl)(phenyl methanone (6j): yellow oil, 62.8 mg (63% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.78 (d, *J* = 7.2 Hz, 2H), 7.57 (s, 1H), 7.55 (d, *J* = 2.4 Hz, 1H), 7.53 (d, *J* = 7.2 Hz, 1H), 7.43 (d, *J* = 7.6 Hz, 2H), 7.41−7.38 (m, 1H), 1.84 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 194.5, 160.0, 156.3, 138.0, 134.9, 132.9, 132.1, 129.5 (2C), 128.33, 128.28 (2C), 117.1, 114.2, 21.4, 15.7; HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{16}H_{14}NO_2{}^{79}Br$: 331.0208; found: 331.0209.

Methyl 3-benzoyl-4-((propan-2-ylideneamino)oxy)benzoate (6k): yellow solid, 65.4 mg (70% yield), m.p. 86–88 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.18–8.14 (m, 2H), 7.78 (d, *J* = 8.4 Hz, 2H), 7.59 (d, *J* = 9.2 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 8.0 Hz, 2H), 3.90 (s, 3H), 1.88 (s, 3H), 1.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 195.1, 166.2, 160.8, 160.5, 138.1, 133.8, 132.9, 131.7, 129.5 (2C), 128.3 (2C), 126.3, 123.6, 114.5, 52.1, 21.5, 15.9; HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{18}H_{17}NO_4$: 311.1158; found: 311.1159.

(2-Methoxy-6-((propan-2-ylideneamino)oxy)phenyl)(phenyl) methanone (6l): yellow oil, 66.3 mg (78% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.75 (d, *J* = 6.8 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 1H), 7.48 (dt, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.08 (d, *J* = 2.4 Hz, 1H), 6.63 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 3.88 (s, 3H), 1.87 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 195.4, 163.7, 159.7, 159.4, 139.7, 132.1, 132.0, 129.4 (2C), 128.0 (2C), 119.2, 108.0, 100.4, 55.6, 21.5, 15.7; HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{17}H_{17}NO_3$: 283.1208; found: 283.1209.

General procedures for the product 7 or 8

A mixture of substrate **3a** or **6d** (0.2 mmol) and diluted hydrochloric acid (2.5 mL) was heated to 60 °C for 1 h. Upon completion of the reaction, 50 % potassium hydroxide solution (5.0 mL) were added to the mixture, then the aqueous layer was extracted with dichloromethane (15 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$. Finally, the solution was concentrated *in vacuo* to provide the product **7** or **8**.

Spectral data of the compounds 7 and 8

4-Phenyl-1*H*-benzo[*d*][1,2]oxazine (7): yellow solid, 40.2 mg (96% yield), m.p. 75–77 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.65 (d, *J* = 2.0 Hz, 1H), 7.64 (t *J* = 2.0 Hz, 1H), 7.52 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.50−7.46 (m, 2H), 7.46 (s, 1H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.25 (d, *J* = 3.6 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 1H), 5.03 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 161.0, 133.1, 132.9, 132.1, 129.9, 129.0 (2C), 128.6 (2C), 128.4, 126.1, 124.4, 122.7, 67.2; HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{14}H_{11}NO$: 209.0841; found: 209.0843.

3-(4-(Trifluoromethyl)phenyl)benzo[*d*]isoxazole (8): yellow oil, 49.5 mg (94% yield), m.p. 105–107 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 8.10 (d, *J* = 8.0 Hz, 2H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.63 (t, *J* = 7.2 Hz, 1H), 7.42 (t, *J* = 7.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 163.1, 155.1, 131.5, 131.1 (q, $^2J_{CF}$ = 32.6 Hz), 129.1, 127.4 (2C), 122.8 (q, $^1J_{CF}$ = 270.7 Hz), 125.1 (q, $^3J_{CF}$ = 3.8 Hz, 2C), 123.3, 120.8, 119.0, 109.4; HRMS (EI): *m/z* $[M]^+$ calcd. for $C_{14}H_8NO\ F_3$: 263.0558; found: 263.0557.

General procedures for the product 9

To the compound **6i** (60.7mg, 0.2 mmol) in acetonitrile (2.0 mL) containing water (0.5 mL), was added molybdenum hexacarbony (52.8 mg, 0.2 mmol). The flask was evacuated and backfilled with N_2 three times and then heated at reflux for 4 h. Upon completion of the reaction, silica gel (0.2 g) was added to the cooled mixture. After removal of the solvent *in vacuo,* the dry residue was purified by flash column chramatography on silica gel (eluents: petroleum ether/ethyl acetate 20:1) to give the product **9**.

Spectral data of the compound 9

(2-Hydroxyphenyl)(naphthalen-2-yl)methanone (9): brown oil, 44.2 mg (89% yield); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 12.07 (s, 1H), 8.19 (s, 1H), 7.95 (q, *J* = 8.0 Hz, 3H), 7.78 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.68 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.63 (t, *J* = 6.8 Hz, 1H), 7.59 (t, *J* = 6.8 Hz, 1H), 7.54 (t, *J* = 6.8 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ 201.5, 163.3, 136.4, 135.1, 134.9, 133.7, 132.2, 130.5, 129.2, 128.4, 128.3, 127.9, 127.0, 125.4, 119.4, 118.8, 118.4; HRMS (EI): *m/z* $[M+H]^+$ calcd. for $C_{17}H_{13}O_2$: 249.0916; found: 249.0918.

Conflicts of interest

There are no conflicts to declare.

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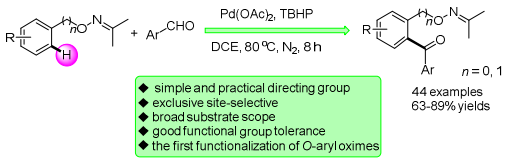

Palladium-Catalyzed Direct *mono*-Aroylation of *O*-Arylmethyl and Aryl Substituted Acetoxime Ethers

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A palladium-catalyzed *ortho*-aroylation of *O*-arylmethyl and aryl substituted acetoxime ethers *via* direct C–H bond activation has been developed.