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Note

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Nickel-Catalyzed Suzuki Coupling of Cycloalkyl Silyl Peroxides with Boronic Acids

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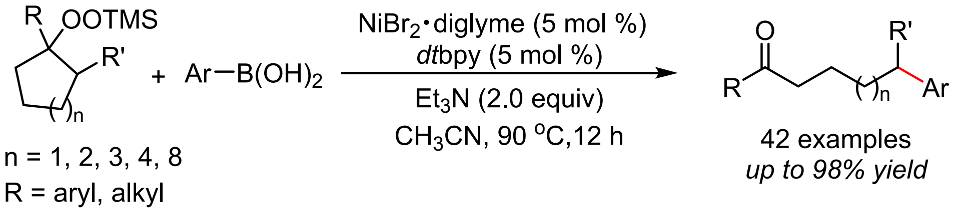


ABSTRACT

A nickel-catalyzed Suzuki alkyl-aryl coupling of cycloalkyl silyl peroxides with boronic acids is reported. The primary and secondary ketoalkyl electrophiles generated through C-C bond cleavage were amenable, providing rapid access to a variety of distal arylated alkyl ketones. A radical pathway is proposed for this reaction.

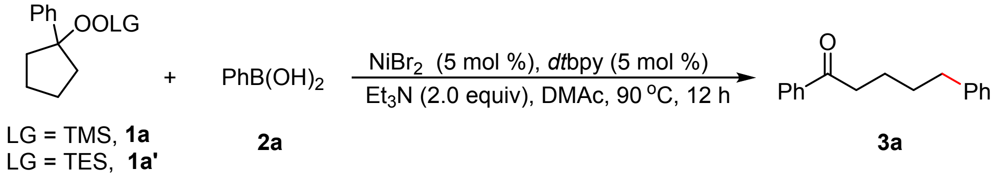
Over past decades, the Suzuki-Miyaura cross-coupling has become a powerful and frequently utilized tool for the C-C bond formations.[1] The reasons for its popularity include the mild conditions, excellent functional group tolerance as well as the ready availability of the boronic acids. Additionally, not only aryl electrophiles but also alkyl electrophiles were viable for this transformation.[2, 3] Since the pioneering work of Suzuki, significant progress has been made in the alkyl-aryl cross couplings. For instance, Fu et al. demonstrated a series of Ni-catalyzed Suzuki couplings of the activated and unactivated alkyl halides with organoboranes.[4] Recently, the group of Baran disclosed the Ni-catalyzed cross-coupling of redox-active esters (RAEs) with boronic acids.[5] Later on, they also presented the Ni-catalyzed decarboxylative cross-coupling to construct the alkyl-aryl bonds. In those reactions, new catalytic systems (including catalysts and ligands) and catalytic cycles (single electron-transfer) have been explored to overcome the β-hydride elimination side reaction. Especially, merging transition-metal catalysis with radical chemistry has become a booming and attractive trend in current organic synthesis, which shows great potential in Csp^3-C bond formations.[6]

In recent years, the oxygen-centered radical triggered C-C bond cleavage has attracted much attention of chemists and has emerged as an efficient strategy to construct the Csp^3-C and Csp^3-X bonds.[7] To access the oxygen-centered radicals, different methods including single electron oxidation,[8] single electron reduction,[9] PCET (proton-coupled electron transfer)[10] and LMCT (ligand-to-metal charge transfer)[11] have been developed. In these transformations, the ketoalkyl radical intermediates generated via C-C bond cleavage could be captured with structurally diverse radical acceptors such as double bonds, aromatic rings and other radicals, delivering the structurally diverse functionalized alkyl ketones. In this field, our group recently disclosed catalytic borylation and decarboxylative olefination of cycloalkyl silyl peroxides relying on alkoxyl radical induced carbon-carbon bond cleavage.[12d, 12e] To fully exploit the potential of the ketoalkyl radicals, we expected to trap them with transition metal species, enabling novel chemical transformations. Herein, we report the Ni-catalyzed Suzuki alkyl-aryl coupling of cycloalkyl silyl peroxides with boronic acids via C-C bond cleavage. A range of primary and secondary ketoalkyl electrophiles reacted well to afford the distal arylated alkyl ketones, which are difficult to obtain via the direct Friedel-Crafts alkylation reactions.[13]

We began our studies with the reaction of cyclopentyl silyl peroxide **1a** and phenylboronic acid **2a** under Ni catalysis (Table 1). Treatment of **1a** with **2a** in the presence of 5 mol % of $NiBr_2$, 5 mol % of 4,4'-di-tert-butyl bipyridine (*dt*bpy) and 2.0 equiv of Et_3N in DMAc at 90 °C led to the desired 1,5-diphenyl-1-pentanone **3a** in 80% yield (entry 1). Screening of ligands including bipyridines, phenanthrolines and others showed that *dt*bpy afforded the best yield (entry 2). The choice of base turned out to be a crucial factor in determining the outcome of this reaction. The organic base Et_3N proved to be most efficient, while K_2CO_3 and ^{t}BuOK were not suitable for this reaction (entries 3 and 4). Other nickel catalysts such as $NiCl_2{\cdot}6H_2O$, $Ni(OAc)_2$ and $NiBr_2{\cdot}$diglyme, all displayed catalytic activity, and $NiBr_2{\cdot}$diglyme gave a slight higher yield than $NiBr_2$ (entries 5 and 6). The palladium catalyst such as $PdCl_2$ was also efficient, while $FeCl_2$ and $CoCl_2$ failed to give any product (entries 7 and 8). With regard to solvents, CH_3CN is superior to DMAc, resulting in 93% yield of **3a** (entry 9). 1,4-Dioxane afforded a comparable yield with DMAc, but toluene was totally ineffective (entry 10). Lowering temperature to 60 ^{o}C or room temperature led to a reduced yield of **3a** (entry 11). Control experiments revealed that the Ni catalyst was essential for this reaction. In the absence of ligand or base, poor yield of **3a** was obtained (entry 12). Finally, changing the leaving group to triethylsilyl group (**1a’**) resulted in a slight lower yield of **3a** (entry 9).

With the optimal conditions in hand, the generality and limitations of boronic acids **2** were evaluated with **1a**. It was found that a variety of arylboronic acids worked well in this reaction (Scheme 1). While using phenylboronic acid pinacol ester and potassium phenyltrifluoroborate

Table 1. Optimization of the Reaction Conditions[a]

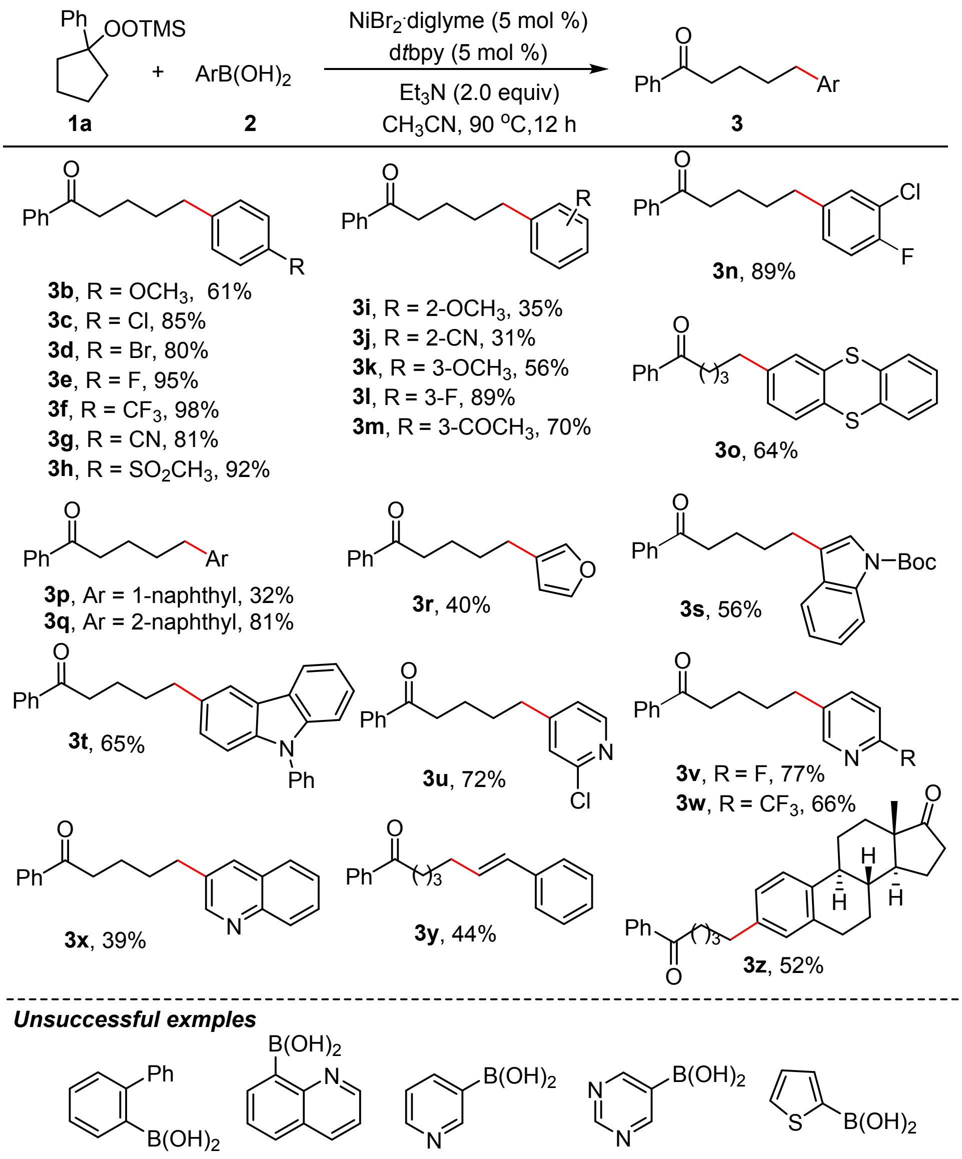


entry	variations from the standard conditions	yield (%)[b]
1	none	80
2	bpy or phenanthroline as the ligand	34, 36
3	DIPEA as the base	61
4	K_2CO_3 or ^{t}BuOK as the base	trace
5	$NiCl_2 \cdot 6H_2O$ or $Ni(OAc)_2$ as the catalyst	47, 24
6	$NiBr_2 \cdot$diglyme as the catalyst	84
7	$FeCl_2$, $CoCl_2$ as the catalyst	trace
8	$PdCl_2$ as the catalyst	26
9	CH_3CN as the solvent	93[b] (81)[c]
10	1,4-dioxane or toluene as the solvent	82[b], trace[b]
11	At 60 °C or room temperature	85[b], 39[b]
12	no Ni, no ligand or no base	0, 20, 30

[a] Reaction conditions: catalyst (5 mol %), 4,4'-di-tert-butyl bipyridine (*dt*bpy) (5 mol %), **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), base (0.4 mmol, 2.0 equiv) in solvent (2.0 mL) at 90 °C for 12 h under N_2. Isolated yield. [b] $NiBr_2 \cdot$diglyme was used as the catalyst. [c] **1a'** was used.

instead of phenylboronic acid **2a** led to no formation of **3a**. The reactions of electron-deficient arylboronic acids performed better than the electron-rich substrates. For example, a set of *para*-substituted arylboronic acids with electron-withdrawing groups gave the corresponding products **3c-h** in 80%-98% yields. While the arylboronic acid **2b** with electron-donating group only afforded 61% yield. The *ortho*-substituted boronic acids **2i** and **2j** furnished poor yields and 2-phenyl substrate didn't give any anticipated product. These results indicated that the reaction is significantly hampered by the steric hindrance, which is different with Maruoka's Cu catalytic system. The *meta*-substituted arylboronic acids with electron-donating or -withdrawing groups all provided moderate to good yields (**3k-3m**). The 3,4-disubstituted substrate **2n** also gave the desired product **3n** in 89% yield.

Scheme 1 Scope of Boronic Acids



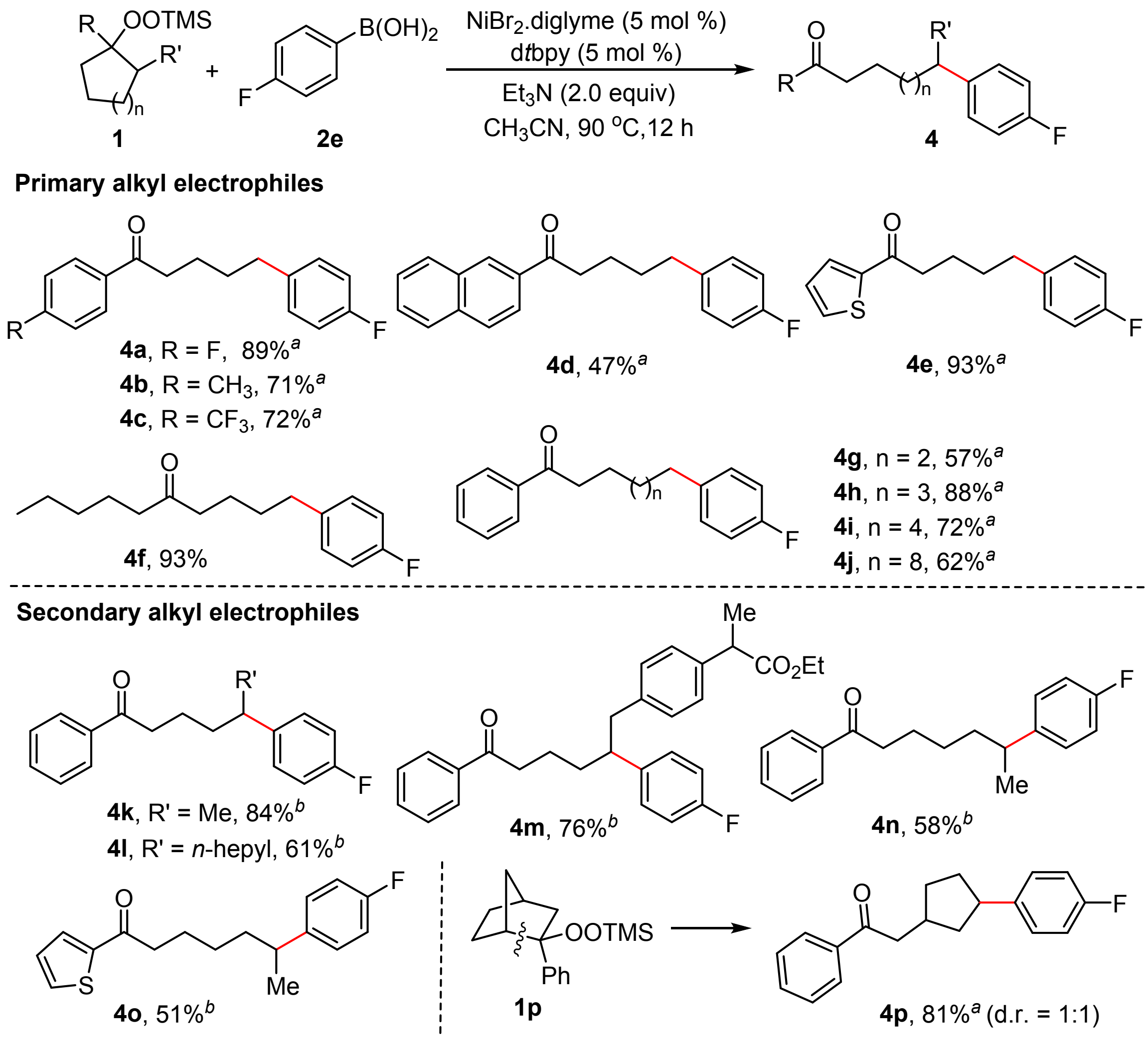
[a]Reaction conditions: catalyst (5 mol %), *dt*bpy (5 mol %), **1a** (0.2 mmol, 1.0 equiv), **2** (0.3 mmol, 1.5 equiv), Et_3N (0.4 mmol, 2.0 equiv) in MeCN (2.0 mL) at 90 °C for 12 h under N_2. [b]1,4-dioxane was used as the solvent.

However, the 3,5-bis(trifluoromethyl)phenylboronic acid failed to participate in this transformation (not shown). A wide variety of functional groups such as halogens (**3c-e**, **3l**), nitrile (**3g**, **3j**), sulfone (**3h**), and ketone (**3m**) were tolerated well under the standard conditions. As expected, 2-naphthylboronic acid delivered much better yield than the 1-naphthylboronic acid (**3p** vs. **3q**). Satisfactorily, a series of heteroarylboronic acids **2r-2x** could deliver the corresponding products in good yields. The existence of electron-withdrawing substituent is beneficial for the reaction (**3u-3w)**. Vinylic boronic acid **2y** also underwent coupling smoothly to afford the product **3y** in moderate yield. Notably, the estrone-derived arylboronic acid reacted successfully to provide the desired product **3z** in 52% yield, which highlights its potential application for late-stage functionalization of complex molecules. However, when quinolyl or pyrimidinyl and others boronic acid using as substrate, no corresponding products were obtained, neither protodeboronation nor homocoupling of the boronic acids were detected in these cases (Scheme 1). Unfortunately, the alkyl boronic acids such as cyclopentyl boronic acid didn’t give the desired product, along with the ring-opened/hydrogenation byproduct observed (not shown).

Subsequently, the scope of cycloalkyl silyl peroxides **1** was investigated using **2e** as the coupling partner (Scheme 2). The 1-aryl cyclopentylsilyl peroxides underwent the C-C bond cleavage/coupling efficiently to afford the desired products **4a-d** in moderate to good yields. The thienyl-substituted peroxide survived well and gave the product **4e** in 93% yield. The 1-alkyl cyclopentylsilyl peroxide also reacted smoothly to form the desired product **4f** in 93% yield. Satisfactorily, peroxides with larger-ring systems including six-, seven-, eight- and even twelve-membered rings were also amenable, delivering the desired coupling products **4g-j** in 57-88% yields. The size of the ring systems didn’t largely affect the reaction. A vareity of secondary alkyl electrophiles were also applicable to the Suzuki cross-couplings. By changing the solvent to 1,4-dioxane, the reactions proceeded efficiently to give the corresponding products **4k-4o** in good yields. In Maruoka's work, only one example was investigated. Peroxide **1p** was also suitable, generating the desired product **4p** in 81% yield with excellent regioselectivity. Unfortunately, the ter-tiary alkyl electrophiles were unavailable at present.

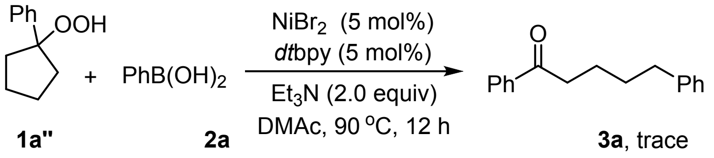
To gain insight into the reaction, some control experiments were conducted. Firstly, using the alkyl hydroperoxide **1a''** instead of **1a** led to only trace amount of **3a**, and the **1a''** was decomposed to the corresponding alcohol (eq 1). In addition, TEMPO and BHT, well known radical scavengers, were subjected into the reaction, respectively (eqs 2 and 3). In the presence of 2.0 equiv of TEMPO, the TEMPO-adduct **5a** was obtained in 80% yield and

Scheme 2 Scope of Cycloalkyl Silyl Peroxides

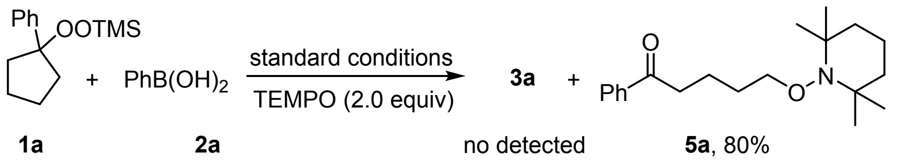


[a] Reaction conditions: catalyst (5 mol %), *dt*bpy (5 mol %), **1** (0.2 mmol, 1.0 equiv), **2e** (0.3 mmol, 1.5 equiv), Et_3N (0.4 mmol, 2.0 equiv) in MeCN (2.0 mL) at 90 °C for 12 h under N_2. [b] 1,4-dioxane was used as the solvent.

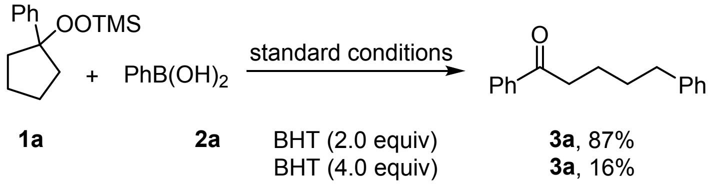
no product **3a** was detected. The addition of BHT could also inhibit the reaction. These results implied that the reaction probably proceed through a radical pathway. A proposed mechanism has been described in the Supporting Information (for details, see SI).[14] Satisfactorily, the reaction of **1a** with **2a** could also be scaled up to 2.0 mmol, and the product **3a** was obtained in 83% yield (eq 4)



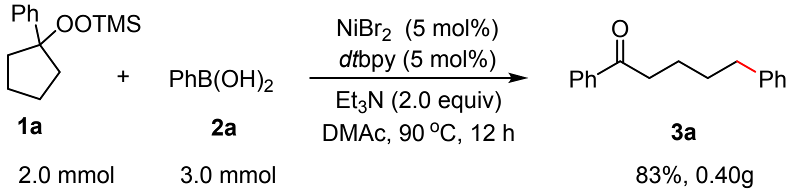
(1)



(2)



(3)



(4)

In conclusion, a Ni-catalyzed Suzuki alkyl-aryl coupling via alkoxyl radical induced C-C bond cleavage has been developed. A wide range of cycloalkyl silyl peroxides and boronic acids reacted efficiently to afford the distal arylated alkyl ketones in moderate to good yields. The electronic and steric effects of arylboronic acids displayed obvious influence on the reaction efficiency. Mechanistic studies suggest that the reaction proceeds via a radical pathway.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Advance III-400 and Bruker Advance III-600 in solvents as indicated. Chemical shift are reported in ppm from TMS with the solvent resonance as internal standard ($CDCl_3$: ^1H NMR: δ = 7.26; ^{13}C NMR: δ = 77.0). Coupling constants are reported in Hz with multiplicities denoted as s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet). IR spectra were recorded on a Bruker Tensor 27 spectrometer and only major peaks are reported in cm-1. HRMS were obtained on WATERS I-Class VION IMS QTof. TGA was obtained on METTLER TOLEDO TGA2. All catalytic reactions were conducted in oven-dried Schlenk-tube under an atmosphere of nitrogen. Oil bath is used for reactions that require heating. Reactions were monitored by thin layer chromatography (aluminum backed plates pre-coated (0.25 mm) with Merck Silica Gel 60F-254.) and visualized using UV light. Column chromatography purifications were carried out using 200-300 mesh silica gel. Unless otherwise stated, all reagents were purchased from commercial sources and used without further purification.

Starting Materials

All of cycloalkylsilyl peroxides were prepared from the corresponding cycloalkyl alcohols according to the literature.[12] All of the NMR spectra of known compounds were in full accordance with the data in the literatures. Note: The alkyl trimethylsilyl peroxides should be stored at -20°C. The primary studies indicated that thermal degradation of **1a** occurred at 105.1 °C (measured by TGA, for details, see the SI). The hydrolytic stability of **1a** is nice, even stirring it in CH_3CN/H_2O (v/v=10/1) for 12h at room temperature.

Triethyl((1-phenylcyclopentyl)peroxy)silane (1a'): The compound was synthesized from (1-hydroperoxycyclopentyl)benzene on a 2 mmol scale, colorless oil, 0.22 g, 38% yield; ^1H NMR (400 MHz, $CDCl_3$) δ = 7.48 (d, J = 7.6 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.28 (s, 1H), 2.40– 2.30 (m, 2H), 1.97 – 1.85 (m, 4H), 1.83 – 1.74 (m, 2H), 0.96 – 0.92 (m, 9H), 0.62 (q, J = 8.0 Hz, 6H).

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 144.3, 127.6, 126.7, 126.6, 94.9, 36.6, 24.3, 6.7, 3.7. ppm. IR (neat): υ_{max} 3031, 2956, 2880, 1456, 1329, 1249, 1090, 1015, 972, 850, 805, 736, 548, cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{28}NaO_2Si$ $[M+Na]^+$ 315.1751, found 315.1751.

Representative Procedure for the Ni-Catalyzed Suzuki Coupling of Cycloalkyl Silyl Peroxides 1 with Boronic Acids 2

An oven-dried 10 mL Schlenk-tube equipped with a magnetic stir bar was charged with boron acid **2** (0.3 mmol, 1.5 equiv), $NiBr_2$ • diglyme (5 mol %) and *dt*bpy (5 mol %). Then, the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of cycloalkyl silyl peroxide **1** (0.2 mmol, 1.0 equiv) in CH_3CN (1 mL) followed by a solution of Et_3N (0.4 mmol, 2.0 equiv) in CH_3CN (1 mL) were injected into the tube by syringe under nitrogen atmosphere. The mixture was stirred at the specified temperature for the indicated reaction time. After the reaction completed, the mixture was directly concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (petroleum ether/ethyl acetate: 100:1) affords the product **3** or **4** in yields listed in Scheme 1 and 2.

Note: For 2-substituted cycloalkyl silyl peroxides, 1,4-dioxane was used as the solvent.

Larger Scale for the Ni-Catalyzed Suzuki Coupling of 1a with 2a

An oven-dried 50 mL Schlenk-tube equipped with a magnetic stir bar was charged with boron acid **2a** (3 mmol, 1.5 equiv), $NiBr_2$ • diglyme (5 mol %) and *dt*bpy (5 mol %). Then, the tube was evacuated and backfilled with nitrogen (three times). Subsequently, a solution of cycloalkyl silyl peroxide **1a** (2 mmol, 1.0 equiv) in CH_3CN (10 mL) followed by a solution of Et_3N (4 mmol, 2.0 equiv) in CH_3CN (10 mL) were injected into the tube by syringe under nitrogen atmosphere. The mixture was stirred at the 90 ^oC for the 12 h. After the reaction completed, the mixture was directly concentrated in vacuo. Purification of the crude product by flash chromatography on silica gel (petroleum ether/ethyl acetate: 100:1) affords the product **3a** (396.5mg, 83%).

Characterization of Products 3 and 4

1,5-Diphenylpentan-1-one (3a) (known compound) Colorless oil (93%, 44.3 mg); R_f 0.40 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 7.3 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.35 – 7.29 (m, 2H)., 7.23 – 7.19 (m, 3H)., 3.01 (t, *J* = 7.1 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 1.86 – 1.71 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.0, 142.0, 136.7, 132.7, 128.3, 128.2, 128.1, 127.8, 125.5, 38.1, 35.6, 30.9, 23.7 ppm. Spectral data match those previously reported.[15a]

5-(4-Methoxyphenyl)-1-phenylpentan-1-one (3b): (known compound) Colorless oil (61%, 32.6 mg); R_f 0.35 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.99 – 7.96 (m, 2H), 7.60 – 7.56 (m, 1H), 7.50 – 7.46 (m, 2H), 7.15 – 7.11 (m, 2H), 6.87 – 6.83 (m, 2H), 3.81 (s, 3H), 3.01 (t, *J* = 7.2 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 1.85 – 1.67 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.3, 157.7, 137.0, 134.3, 132.9, 129.2, 128.5, 128.0, 113.7, 55.2, 38.4, 34.8, 31.3, 23.9 ppm. IR (neat): υ_{max} 2935, 2856, 1683, 1608, 1511, 1453, 1362, 1291, 1245, 1181, 1035, 821, 747 cm^{-1}. Spectral data match those previously reported.[15b]

5-(4-Chlorophenyl)-1-phenylpentan-1-one (3c): Colorless oil (85%, 43.1 mg); R_f 0.31 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.85 (d, *J* = 7.8 Hz, 2H), 7.47 (t, *J* = 7.2 Hz, 1H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.15 (d, *J* = 7.3 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 2H), 2.90 (t, *J* = 7.0 Hz, 2H), 2.55 (t, *J* = 7.4 Hz, 2H), 1.73 – 1.66 (m, 2H), 1.64 – 1.56(m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.0, 140.6, 137.0, 132.9, 131.4, 129.7, 128.5, 128.3, 128.0, 38.2, 35.1, 30.9, 23.8 ppm. IR (neat): υ_{max} 3050, 2932, 2859, 2306, 1964, 1904, 1674, 1587, 1492, 1454, 1405, 1372, 1308, 1249, 1197, 1089, 1017, 940, 900, 809, 741 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{18}ClO$ $[M+H]^+$ 273.1041, found 273.1039.

5-(4-Bromophenyl)-1-phenylpentan-1-one (3d): Colorless oil (80%, 50.7 mg); R_f 0.31 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 7.4 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 8.3 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 2.98 (t, *J* = 7.1 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.72 – 1.65 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.0, 141.1, 136.9, 132.9, 131.3, 130.1, 128.5, 128.0, 119.4, 38.2, 35.2, 30.8, 23.8 ppm. IR (neat): υ_{max} 3057, 2935, 2861, 2312, 1683, 1591, 1487, 1450, 1405, 1362, 1218, 1072, 1008, 969, 805, 746cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{18}BrO$ [M+H]$^+$ 317.0536, found 317.0529.

5-(4-Fluorophenyl)-1-phenylpentan-1-one (3e): (Known compound) Colorless oil (95%, 48.6 mg); R$_f$ 0.44 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.96 – 7.94 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.15 – 7.12 (m, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 2.99 (t, *J* = 7.1 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 1.82 – 1.75 (m, 2H), 1.73 – 1.65 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 200.1, 161.2 (d, *J* = 243.1 Hz), 137.8 (d, *J* = 3.2 Hz), 136.9, 132.9, 129.6 (d, *J* = 7.7 Hz), 128.5, 128.0, 115.0 (d, *J* = 21.0 Hz), 38.3, 34.9, 31.2, 23.8 ppm. IR (neat): υ_{max} 3055, 2934, 2861, 1684, 1596, 1508, 1450, 1409, 1363, 1221, 1165, 1093, 1007, 827, 750 cm^{-1}. Spectral data match those previously reported.[15c]

1-Phenyl-5-(4-(trifluoromethyl)phenyl)pentan-1-one (3f): Colorless oil (98%, 50.0 mg); R$_f$ 0.40 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.95 (d, *J* = 7.7 Hz, 2H), 7.58-7.51 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.30 (d, *J* = 7.9 Hz, 2H), 3.00 (t, *J* = 6.9 Hz, 2H), 2.73 (t, *J* = 7.3 Hz, 2H), 1.84 – 1.70 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 200.0, 146.3, 136.9, 133.0, 128.7, 128.6, 128.0, 125.2 (q, *J* = 3.8 Hz), 124.4 (q, *J* = 270.6 Hz), 38.2, 35.6, 30.7, 23.8 ppm. IR (neat): υ_{max} 3059, 2939, 2863, 1917, 1684, 1611, 1451, 1415, 1325, 1258, 1221, 1164, 1118, 1068, 1017, 810, 745 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{17}F_3NaO$ [M+Na]$^+$ 329.1124, found 329.1121.

4-(5-Oxo-5-phenylpentyl)benzonitrile (3g): Colorless oil (81%, 42.7 mg); R$_f$ 0.22 (EtOAc/petroleum ether = 1:8). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.94 (d, *J* = 7.5 Hz, 2H), 7.57 – 7.55 (m, 3H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 3.00 (t, *J* = 6.9 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 1.83 – 1.68 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 199.9, 147.9, 136.9, 133.0, 132.2, 129.2, 128.6, 128.0, 119.1, 109.6, 38.1, 36.0, 30.5, 23.7 ppm. IR (neat): υ_{max} 3055, 2932, 2858, 2310, 2220, 1739, 1675, 1603, 1505, 1452, 1406, 1311, 1250, 1194, 1087, 1019, 973, 809, 742 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{18}NO$ [M+H]$^+$ 264.1383, found 264.1382.

5-(4-(Methylsulfonyl)phenyl)-1-phenylpentan-1-one (3h): Colorless oil (92%, 58.1 mg); R$_f$ 0.35 (EtOAc/petroleum ether = 1:3). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.95 – 7.93 (m, 2H), 7.84 (d, *J* = 8.3 Hz, 2H), 7.58 – 7.54 (m, 1H), 7.47 – 7.44 (m, 2H), 7.38 (d, *J* = 8.3 Hz, 2H), 3.03 (s, 3H), 3.00 (t, *J* = 6.9 Hz, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 1.83 – 1.69 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)

δ = 199.9, 148.8, 137.9, 136.8, 133.0, 129.3, 128.6, 127.9, 127.4, 44.6, 38.1, 35.7, 30.6, 23.6 ppm. IR (neat): υ_{max} 3019, 2933, 2863, 2312, 1682, 1593, 1451, 1408, 1364, 1306, 1220, 1148, 1091, 1018, 961, 802, 759 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{21}O_3S$ [M+H]$^+$ 317.1206, found 317.1201.

5-(2-Methoxyphenyl)-1-phenylpentan-1-one (3i): Colorless oil (35%, 18.8 mg); R$_f$ 0.36 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.64 (dd, *J* = 7.7, 1.8 Hz, 1H), 7.46 – 7.42 (m, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.25 (s, 1H), 7.19 – 7.15 (m, 3H), 7.01 – 6.94 (m, 2H), 3.87 (s, 3H), 2.99 (t, *J* = 7.1 Hz, 2H), 2.64 (t, *J* = 7.3 Hz, 2H), 1.78 – 1.64 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 203.0, 158.3, 142.5, 133.1, 130.1, 128.7, 128.4, 128.2, 125.6, 120.6, 111.4, 55.4, 43.6, 35.8, 31.2, 24.1 ppm. IR (neat): υ_{max} 2944, 2870, 2384, 2307, 1675, 1596, 1483, 1250, 1094, 1015, 802, 755, 706 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{20}NaO_2$ [M+Na]$^+$ 291.1356, found 291.1351.

2-(5-Oxo-5-phenylpentyl)benzonitrile (3j): Colorless oil (31%, 16.3 mg); R$_f$ 0.34 (EtOAc/petroleum ether = 1:10). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.96 – 7.94 (m, 2H), 7.62 – 7.60 (m, 1H), 7.57 – 7.54 (m, 1H), 7.52 – 7.49 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.8 Hz, 1H), 7.30 – 7.27 (m, 1H), 3.04 (t, *J* = 7.0 Hz, 2H), 2.91 (t, *J* = 7.5 Hz, 2H), 1.86 – 1.76 (m, 4H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 199.9, 146.2, 136.9, 133.0, 132.8, 132.8, 129.6, 128.6, 128.0, 126.5, 118.2, 112.3, 38.1, 34.4, 30.4, 23.6 ppm. IR (neat): υ_{max} 3061, 2927, 2859. 2386, 2302, 2220, 1680, 1590, 1449, 1362, 1258, 1215, 1092, 1009, 802, 757 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{17}NNaO$ [M+Na]$^+$ 286.1202, found 286.1209.

5-(3-Methoxyphenyl)-1-phenylpentan-1-one (3k): Colorless oil (56%, 29.8 mg); R$_f$ 0.36 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 – 7.93 (m, 2H), 7.58 – 7.53 (m, 1H), 7.47 – 7.44 (m, 2H), 7.21 – 7.18 (m, 1H), 6.79 (d, *J* = 7.6 Hz, 1H), 6.74 – 6.72 (m, 2H), 3.80 (s, 3H), 2.99 (t, *J* = 7.1 Hz, 2H), 2.65 (t, *J* = 7.5 Hz, 2H), 1.84 – 1.68 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.2, 159.6, 143.9, 137.0, 132.9, 129.2, 128.5, 128.0, 120.8, 114.1, 111.0, 55.1, 38.4, 35.8, 31.0, 24.0 ppm. IR (neat): υ_{max} 2936, 2862, 2311, 1683, 1594, 1484, 1451, 1362, 1259, 1158, 1045, 969, 867, 744 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{21}O_2$ [M+H]$^+$ 269.1536, found 269.1531.

5-(3-Fluorophenyl)-1-phenylpentan-1-one (3l): Colorless oil (89%, 45.4 mg); R$_f$ 0.42 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.96 – 7.94 (m, 2H), 7.58 – 7.54 (m, 1H), 7.48 – 7.44 (m, 2H), 7.25 – 7.20 (m, 1H), 6.96 (d, *J* = 7.6 Hz, 1H), 6.91 – 6.84 (m, 2H), 2.99 (t, *J* = 7.1 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.84 – 1.67 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.1, 162.9 (d, *J* = 245.2 Hz), 144.8 (d, *J* = 7.0 Hz), 137.0, 133.0, 129.7 (d, *J* = 8.3 Hz), 128.6, 128.0, 124.0 (d, *J* = 2.7 Hz), 115.1 (d, *J* = 20.7 Hz), 112.6 (d, *J* = 21.0 Hz), 38.3, 35.5, 30.8, 23.8 ppm. IR (neat): υ_{max} 3062, 2935, 2862, 2312, 1684, 1588, 1486, 1449, 1363, 1253, 1139, 1081, 1016, 930, 872, 790, 745 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{18}FO$ $[M+H]^+$ 257.1336, found 257.1332.

5-(3-Acetylphenyl)-1-phenylpentan-1-one (3m): Colorless oil (70%, 39.5 mg); R_f 0.32 (EtOAc/petroleum ether = 1:3). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.96 – 7.93 (m, 2H), 7.79 – 7.76 (m, 2H), 7.58 – 7.53 (m, 1H), 7.47 – 7.44 (m, 2H), 7.41 – 7.35 (m, 2H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.73 (t, *J* = 7.4 Hz, 2H), 2.60 (s, 3H), 1.84 – 1.70 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.1, 198.4, 142.7, 137.2, 136.9, 133.3, 133.0, 128.6, 128.5, 128.1, 128.0, 126.0, 38.3, 35.6, 30.9, 26.7, 23.8 ppm. IR (neat): υ_{max} 2940, 2383, 2312, 1721, 1682, 1519, 1447, 1361, 1276, 967, 744, 695, 592, 514, 427 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{20}NaO_2$ $[M+Na]^+$ 303.1356, found 303.1350.

5-(3-Chloro-4-fluorophenyl)-1-phenylpentan-1-one (3n): Colorless oil (89%, 51.1 mg); R_f 0.29 (EtOAc/petroleum ether = 1:15). ^1H NMR (400 MHz, $CDCl_3$) δ = 7.94 (d, *J* = 8.0 Hz, 2H), 7.56 (t, *J* = 7.0 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.20 (d, *J* = 7.0 Hz, 1H), 7.02 (d, *J* = 6.8 Hz, 2H), 2.99 (t, *J* = 7.0 Hz, 2H), 2.62 (t, *J* = 7.5 Hz, 2H), 1.81 – 1.74 (m, 2H), 1.72 – 1.65 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.0, 156.4 (d, *J* = 246.2 Hz), 139.14 (d, *J* = 3.9 Hz), 136.9, 133.0, 130.2, 128.6, 128.0, 127.9, 120.4 (d, *J* = 17.6 Hz), 116.2 (d, *J* = 20.7 Hz), 38.2, 34.8, 30.9, 23.7 ppm. IR (neat): υ_{max} 3059, 2937, 2863, 1684, 1592, 1499, 1451, 1406, 1363, 1251, 1061, 1009, 885, 816, 742cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{17}ClFO$ $[M+H]^+$ 291.0946, found 291.0947.

5-(5a, 9a-Dihydrothianthren-2-yl)-1-phenylpentan-1-one (3o): Colorless oil (64%, 47.8 mg); R_f 0.41 (EtOAc/petroleum ether = 1:15). ^1H NMR (600 MHz, $CDCl_3$) δ = 7.96 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.50 – 7.45 (m, 4H), 7.38 – 7.35 (m, 1H), 7.25 – 7.22 (m, 2H), 7.15 – 7.14 (m, 2H), 3.04 (t, *J* = 7.3 Hz, 2H), 2.93 (t, *J* = 7.7 Hz, 2H), 1.90 – 1.85 (m, 2H), 1.77 – 1.72 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 200.2, 141.8, 137.0, 136.5, 135.6, 135.5, 135.1, 132.9, 129.0, 128.6, 128.5, 128.4, 128.0, 127.8, 127.6, 127.3, 126.9, 38.3, 34.6, 30.3, 24.0 ppm. IR (neat): υ_{max} 3055, 2932, 2860, 2382, 2313, 1682, 1565, 1446, 1409, 1362, 1259, 1185, 1105, 1018, 908, 791, 744 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{22}KOS_2$ $[M+H]^+$ 417.0744, found 417.0730.

5-(Naphthalen-1-yl)-1-phenylpentan-1-one (3p): Colorless oil (32%, 18.3 mg); R_f 0.45

(EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.04 (d, *J* = 8.2 Hz, 1H), 7.97 – 7.94 (m, 2H), 7.87 – 7.84 (m, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.58 – 7.44 (m, 5H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 6.4 Hz, 1H), 3.14 (t, *J* = 7.3 Hz, 2H), 3.02 (t, *J* = 7.0 Hz, 2H), 1.95 – 1.81 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 200.3, 138.3, 137.0, 133.8, 132.9, 131.8, 128.7, 128.6, 128.0, 126.6, 125.9, 125.7, 125.5, 125.4, 123.8, 38.4, 33.0, 30.4, 24.4 ppm. IR (neat): υ_{max} 3054, 2936, 2864, 2384, 2312, 1725, 1682, 1592, 1515, 1451, 1403, 1364, 1263, 1095, 1013, 788, 736 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}NaO$ [M+Na]$^+$ 311.1406, found 311.1402.

5-(Naphthalen-2-yl)-1-phenylpentan-1-one (3q): Colorless oil (81%, 46.9 mg); R$_f$ 0.31 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.84 (d, *J* = 7.3 Hz, 2H), 7.71 – 7.66 (m, 3H), 7.53 (s, 1H), 7.44 (t, *J* = 7.4 Hz, 1H), 7.37 – 7.30 (m, 4H), 7.26 – 7.23 (m, 1H), 2.90 (t, *J* = 6.8 Hz, 2H), 2.74 (t, *J* = 7.0 Hz, 2H), 1.79 – 1.67 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 200.2, 139.7, 137.0, 133.6, 132.9, 132.0, 128.5, 128.0, 127.8, 127.6, 127.4, 127.3, 126.3, 125.8, 125.0, 38.4, 35.9, 30.9, 24.0 ppm. IR (neat): υ_{max} 3051, 2936, 2862, 2383, 2311, 1680, 1592, 1508, 1450, 1363, 1227, 1009, 966, 894, 855, 815, 745 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}NaO$ [M+Na]$^+$ 311.1406, found 311.1401.

5-(Furan-3-yl)-1-phenylpentan-1-one (3r): Colorless oil (40%, 18.3 mg); R$_f$ 0.30 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 7.95 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 2H), 7.34 (s, 1H), 7.22 (s, 1H), 6.27 (s, 1H), 3.00 (t, *J* = 7.2 Hz, 2H), 2.48 (t, *J* = 7.5 Hz, 2H), 1.83 – 1.76 (m, 2H), 1.69 – 1.61 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 200.2, 142.7, 138.8, 137.0, 133.0, 128.6, 128.0, 124.8, 110.9, 38.3, 29.6, 24.6, 23.9 ppm. IR (neat): υ_{max} 2962, 2384, 2312, 1685, 1518, 1450, 1404, 1260, 1088, 1023, 869, 801 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{16}NaO_2$ [M+Na]$^+$ 251.1043, found 251.1048.

***Tert*-butyl 3-(5-oxo-5-phenylpentyl)-1H-indole-1-carboxylate (3s)**: Colorless oil (56%, 42.1 mg); R$_f$ 0.28 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.12 – 8.11 (m, 1H), 7.96 – 7.94 (m, 2H), 7.58 – 7.52 (m, 2H), 7.48 – 7.44 (m, 2H), 7.40 – 7.35 (m, 1H), 7.33 – 7.29 (m, 1H), 7.25 – 7.21 (m, 1H), 3.03 (t, *J* = 7.0 Hz, 2H), 2.75 (t, *J* = 6.9 Hz, 2H), 1.91 – 1.77 (m, 4H), 1.67 (s, 9H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 200.2, 136.9, 132.9, 128.5, 128.0, 124.2, 122.3, 122.2, 120.8, 118.9, 115.2, 38.3, 28.8, 28.2, 24.8, 24.1 ppm. IR (neat): υ_{max} 2934, 2312, 1729, 1684, 1597, 1452, 1375, 1311, 1258, 1161, 1089, 1019, 854, 804, 753 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{27}NNaO_3$ [M+Na]$^+$ 400.1883, found 400.1894.

1-Phenyl-5-(9-phenyl-9H-carbazol-3-yl)pentan-1-one (3t): Colorless oil (65%, 41.6 mg); R$_f$ 0.34 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.13 (d, *J* = 7.9 Hz, 1H), 7.97 – 7.95 (m, 3H), 7.62 – 7.53 (m, 6H), 7.45 (t, *J* = 7.6 Hz, 3H), 7.41 – 7.37 (m, 2H), 7.34 (d, *J* = 8.4 Hz, 1H), 7.29 – 7.27 (m, 1H), 3.03 (t, *J* = 6.8 Hz, 2H), 2.88 (t, *J* = 7.0 Hz, 2H), 1.91 – 1.79 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 200.4, 141.0, 139.4, 137.8, 137.0, 133.9, 132.9, 129.8, 128.5, 128.0, 127.2, 127.0, 126.6, 125.7, 123.4, 123.2, 120.2, 119.7, 119.6, 109.7, 109.5, 38.5, 35.8, 31.9, 24.0 ppm. IR (neat): υ_{max} 3055, 2932, 2858, 2383, 2313, 1724, 1682, 1595, 1495, 1452, 1361, 1327, 1230, 1081, 1016, 910, 805, 744 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{25}NNaO$ [M+Na]$^+$ 426.1828, found 426.1837.

5-(2-Chloropyridin-4-yl)-1-phenylpentan-1-one (3u): Colorless oil (72%, 54.6 mg); R$_f$ 0.12 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.26 (d, *J* = 5.1 Hz, 1H), 7.94 (d, *J* = 7.6 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.16 (s, 1H), 7.05 (d, *J* = 5.0 Hz, 1H), 3.01 (t, *J* = 6.9 Hz, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.83 – 1.69 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 199.7, 154.5, 151.6, 149.5, 136.9, 133.1, 128.6, 128.0, 124.1, 122.6, 38.0, 34.9, 29.6, 23.6 ppm. IR (neat): υ_{max} 3058, 2930, 2860, 1732, 1683, 1591, 1545, 1456, 1382, 1220, 1125, 1084, 997, 882, 834, 743 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{17}ClNO$ [M+H]$^+$ 274.0993, found 274.0993.

5-(6-Fluoropyridin-3-yl)-1-phenylpentan-1-one (3v): Colorless oil (77%,39.5 mg); R$_f$ 0.15 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.02 (s, 1H), 7.94 (d, *J* = 7.9 Hz, 2H), 7.62 – 7.54 (m, 2H), 7.46 (t, *J* = 7.6 Hz, 2H), 6.84 (dd, *J* = 8.3, 2.8 Hz, 1H), 3.00 (t, *J* = 7.0 Hz, 2H), 2.66 (t, *J* = 7.5 Hz, 2H), 1.83 – 1.76 (m, 2H), 1.73 – 1.66 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 199.85, 162.3 (d, *J* = 236.9 Hz), 146.92 (d, *J* = 14.2 Hz), 140.9 (d, *J* = 7.7 Hz), 136.9, 134.9 (d, *J* = 4.5 Hz), 133.0, 128.6, 128.0, 109.0 (d, *J* = 37.4 Hz), 38.1, 31.9, 30.8, 23.6 ppm. IR (neat): υ_{max} 2927, 2859, 2312, 1681, 1591, 1479, 1391, 1244, 967, 831, 745 cm^{-1}; HRMS (ESI) calcd for $C_{16}H_{17}FNO$ [M+H]$^+$ 258.1289, found 258.1288.

1-Phenyl-5-(6-(trifluoromethyl)pyridin-3-yl)pentan-1-one (3w): Colorless oil (66%, 40.4 mg); R$_f$ 0.18 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, CDCl$_3$) δ = 8.56 (s, 1H), 7.94 (d, *J* = 7.7 Hz, 2H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 3.02 (t, *J* = 6.7 Hz, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 1.86 – 1.71 (m, 4H). ^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$) δ = 198.7, 149.1,145.0 (q, *J* = 34.7 Hz), 139.8, 135.9, 135.9, 132.1, 127.6, 127.0, 120.7 (q, *J* = 272.0

Hz), 119.1 (q, *J* = 2.7 Hz), 37.0, 31.8, 29.4, 22.6 ppm. IR (neat): υ_{max} 2940, 2866, 1684, 1590, 1451, 1403, 1339, 1256, 1176, 1135, 1087, 1025, 802, 748 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{17}F_3NO$ [M+H]$^+$ 308.1257, found 308.1257.

1-Phenyl-5-(quinolin-3-yl)pentan-1-one (3x): Colorless oil (39%, 22.5 mg); R_f 0.23 (EtOAc/petroleum ether = 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.79 (s, 1H), 8.08 (t, *J* = 8.6 Hz, 1H), 7.95 (d, *J* = 8.1 Hz, 3H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.66 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.50 (m, 2H), 7.45 (t, *J* = 7.5 Hz, 2H), 3.03 (t, *J* = 6.5 Hz, 2H), 2.87 (t, *J* = 6.9 Hz, 2H), 1.92 – 1.78 (m, 4H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.0, 152.0, 146.8, 136.9, 134.7, 134.2, 133.0, 129.1, 128.6, 128.1, 128.0, 127.3, 126.6, 38.2, 33.1, 30.7, 23.8 ppm. IR (neat): υ_{max} 2943, 2383, 2311, 1684, 1629, 1519, 1451, 1404, 1239, 1052, 1008, 794, 750 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{20}NO$ [M+H]$^+$ 290.1539, found 290.1537.

(*E*)-1,7-Diphenylhept-6-en-1-one (3y): Known Compound Colorless oil (44%, 23.0 mg); R_f 0.40 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.98 – 7.96 (m, 2H), 7.57 – 7.54 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.34 (d, *J* = 7.3 Hz, 2H), 7.29 (t, *J* = 7.7 Hz, 2H), 7.20 (t, *J* = 7.3 Hz, 1H), 6.41 (d, *J* = 15.8 Hz, 1H), 6.26 – 6.21 (m, 1H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.30 – 2.26 (m, 2H), 1.85 – 1.80 (m, 2H), 1.61 – 1.57 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 200.3, 137.7, 137.0, 132.9, 130.4, 130.1, 128.5, 128.4, 128.0, 126.8, 125.9, 38.4, 32.8, 29.0, 23.9 ppm. IR (neat): υ_{max} 3025, 2932, 2312, 1684, 1592, 1493, 1448, 1362, 1278, 1222, 1073, 968, 744 cm^{-1}. Spectral data match those previously reported.[12e]

(8*R*,9*S*,13*S*,14*S*)-13-Methyl-3-(5-oxo-5-phenylpentyl)-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (3z): Colorless oil (52%, 43.0 mg); R_f 0.34 (EtOAc/petroleum ether = 1:8). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.95 (d, *J* = 7.3 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.93 (s, 1H), 2.99 (t, *J* = 7.2 Hz, 2H), 2.90 – 2.87 (m, 2H), 2.61 (t, *J* = 7.5 Hz, 2H), 2.54 – 2.47 (m, 1H), 2.44 – 2.39 (m, 1H), 2.31 – 2.25 (m, 1H), 2.19 – 2.12 (m, 1H), 2.10 – 2.05 (m, 1H), 2.04 – 1.92 (m, 2H), 1.84 – 1.77 (m, 2H), 1.74 – 1.68 (m, 2H), 1.63 – 1.44 (m, 6H), 0.90 (s, 3H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$): δ = 221.0, 200.3, 139.7, 137.1, 137.0, 136.3, 132.9, 129.0, 128.5, 128.0, 125.8, 125.3, 50.5, 48.0, 44.3, 38.4, 38.2, 35.9, 35.2, 31.6, 31.1, 29.4, 26.6, 25.7, 24.0, 21.6, 13.8 ppm. IR (neat): υ_{max} 2929, 2863, 2383, 2313, 2250, 1736, 1684, 1594, 1501, 1451, 1407, 1367, 1261, 1221, 1086, 1016, 910, 805, 737cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{34}NaO_2$ [M+Na]$^+$ 437.2451, found

437.2447.

1,5-*Bis*(4-fluorophenyl)pentan-1-one (4a): Known Compound Colorless oil (89%, 48.2 mg); R_f 0.40 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 – 7.93 (m, 2H), 7.15 – 7.09 (m, 4H), 6.97 – 6.93 (m, 2H), 2.95 (t, *J* = 7.1 Hz, 2H), 2.64 (t, *J* = 7.4 Hz, 2H), 1.81 – 1.74 (m, 2H), 1.72 – 1.64 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 198.4, 165.6 (d, *J* = 254.5 Hz), 161.1 (d, *J* = 243.2 Hz), 137.7 (d, *J* = 3.1 Hz), 133.4 (d, *J* = 3.0 Hz), 130.6 (d, *J* = 9.2 Hz), 129.6 (d, *J* = 7.7 Hz), 115.6 (d, *J* = 21.8 Hz), 115.0 (d, *J* = 21.0 Hz), 38.2, 34.9, 31.1, 23.7 ppm. IR (neat): υ_{max} 3068, 2936, 2862, 1892, 1685, 1598, 1508, 1453, 1410, 1362, 1226, 1156, 1097, 1009, 833, 757, 702 cm^{-1}. Spectral data match those previously reported.[15d]

5-(4-Fluorophenyl)-1-(*p*-tolyl)pentan-1-one (4b): Colorless oil (71%, 38.6 mg); R_f 0.40 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.87 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.4 Hz, 2H), 7.17 – 7.14 (m, 2H), 7.00 – 6.96 (m, 2H), 2.98 (t, *J* = 7.1 Hz, 2H), 2.66 (t, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.83 – 1.76 (m, 2H), 1.74 – 1.67 (m, 2H). ^{13}C{^{1}H} NMR (100MHz, $CDCl_3$) δ = 199.8, 161.2 (d, *J* = 243.1 Hz), 143.7, 137.8 (d, *J* = 3.1 Hz), 134.5, 129.7 (d, *J* = 7.7 Hz), 129.2, 128.1, 115.0 (d, *J* = 21.0 Hz), 38.2, 35.0, 31.2, 23.9, 21.6 ppm. IR (neat): υ_{max} 2925, 2859, 2384, 2312, 1725, 1682, 1608, 1556, 1453, 1406, 1366, 1262, 1180, 1098, 814, 733 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{20}FO$ $[M+H]^+$ 271.1493, found 271.1489.

5-(4-Fluorophenyl)-1-(4-(trifluoromethyl)phenyl)pentan-1-one (4c): Colorless oil (72%, 46.5 mg); R_f 0.39 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.04 (d, *J* = 7.7 Hz, 2H), 7.72 (d, *J* = 7.7 Hz, 2H), 7.13 (t, *J* = 5.7 Hz, 2H), 6.96 (t, *J* = 8.1 Hz, 2H), 3.01 (t, *J* = 6.7 Hz, 2H), 2.65 (t, *J* = 7.0 Hz, 2H), 1.81 – 1.77 (m, 2H), 1.71 – 1.68 (m, 2H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 199.0, 161.2 (d, *J* = 243.3 Hz), 139.6, 137.6 (d, *J* = 3.2 Hz), 134.3 (q, *J* = 32.7 Hz), 129.6 (d, *J* = 7.7 Hz), 128.3, 125.6 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 270.0 Hz),115.0 (d, *J* = 21.1 Hz), 38.6, 34.9, 31.0, 23.5 ppm. IR (neat): υ_{max} 2935, 2863, 2312, 1692, 1599, 1510, 1454, 1409, 1324, 1223, 1169, 1129, 1067, 1010, 833, 756 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{17}F_4O$ $[M+H]^+$ 325.1210, found 325.1207.

5-(4-Fluorophenyl)-1-(naphthalen-2-yl)pentan-1-one (4d): Colorless oil (47%, 29.0 mg); R_f 0.37 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.45 (s, 1H), 8.04 – 8.01 (m, 1H), 7.97 – 7.95 (m, 1H), 7.91 – 7.87 (m, 2H), 7.62 – 7.58 (m, 1H), 7.58 – 7.54 (m, 1H), 7.17 – 7.12 (m, 2H), 6.99 – 6.93 (m, 2H), 3.12 (t, *J* = 7.2 Hz, 2H), 2.67 (t, *J* = 7.5 Hz, 2H), 1.88 – 1.81

(m, 2H), 1.77 – 1.69 (m, 2H). $^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ = 200.1, 161.2 (d, *J* = 243.1 Hz), 137.8 (d, *J* = 3.2 Hz), 135.5, 134.3, 132.5, 129.7 (d, *J* = 7.2 Hz), 129.6, 129.5, 128.4, 127.8, 126.7, 123.9, 115.0 (d, *J* = 21.0 Hz), 38.4, 35.0, 31.2, 24.0 ppm. IR (neat): υ_{max} 3056, 2933, 2860, 2312, 1680, 1598, 1508, 1462, 1364, 1265, 1222, 1170, 1092, 1022, 816, 751 cm^{-1}; HRMS (ESI) calcd for $C_{21}H_{20}FO$ $[M+H]^+$ 307.1493, found 307.1489.

5-(4-Fluorophenyl)-1-(thiophen-2-yl)pentan-1-one (4e): Colorless oil (93%, 48.7 mg); R_f 0.20 (EtOAc/petroleum ether = 1:15). ^1H NMR (600 MHz, $CDCl_3$) δ = 7.69 – 7.68 (m, 1H), 7.62 – 7.61 (m, 1H), 7.14 – 7.11 (m, 3H), 6.97 – 6.94 (m, 2H), 2.91 (t, *J* = 7.3 Hz, 2H), 2.63 (t, *J* = 7.6 Hz, 2H), 1.81 – 1.76 (m, 2H), 1.71 – 1.66 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 193.1, 161.2 (d, *J* = 243.1 Hz), 144.4, 137.7 (d, *J* = 3.0 Hz), 133.4, 131.7, 129.6 (d, *J* = 7.7 Hz), 128.0, 115.0 (d, *J* = 21.1 Hz), 39.1, 34.9, 31.1, 24.2 ppm. IR (neat): υ_{max} 2937, 2864, 2383, 2312, 1662, 1603, 1511, 1451, 1414, 1361, 1224, 1160, 1052, 923, 827, 726 cm^{-1}; HRMS (ESI) calcd for $C_{15}H_{16}FOS$ $[M+H]^+$ 263.0900, found 263.0896.

1-(4-Fluorophenyl)decan-5-one (4f): Colorless oil (93%, 46.5 mg); R_f 0.39 (EtOAc/petroleum ether = 1:15). ^1H NMR (600 MHz, $CDCl_3$) δ = 7.12 – 7.10 (m, 2H), 6.95 (t, *J* = 8.7 Hz, 2H), 2.58 (t, *J* = 7.0 Hz, 2H), 2.41 (t, *J* = 6.7 Hz, 2H), 2.36 (t, *J* = 7.5 Hz, 2H), 1.59 – 1.53 (m, 6H), 1.33 – 1.29 (m, 2H), 1.27 – 1.22 (m, 2H), 0.88 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 211.3, 161.2 (d, *J* = 243.2 Hz), 137.8 (d, *J* = 3.2 Hz), 129.6 (d, *J* = 7.7 Hz), 115.0 (d, *J* = 21.1 Hz). 42.8, 42.5, 34.9, 31.4, 31.1, 23.5, 23.3, 22.4, 13.9 ppm. IR (neat): υ_{max} 2941, 2866, 2384, 2312, 1712, 1602, 1510, 1458, 1408, 1369, 1261, 1222, 1089, 1023, 807, 756 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{19}FNaO$ $[M+Na]^+$ 293.1312, found 293.1307.

6-(4-Fluorophenyl)-1-phenylhexan-1-one (4g): Colorless oil (57%, 33.0 mg); R_f 0.42 (EtOAc/petroleum ether = 1:15). ^1H NMR (600 MHz, $CDCl_3$) δ = 7.96 – 7.94 (m, 2H), 7.57 – 7.54 (m, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.13 – 7.10 (m, 2H), 6.97 – 6.93 (m, 2H), 2.96 (t, *J* = 7.4 Hz, 2H), 2.60 (t, *J* = 7.7 Hz, 2H), 1.80 – 1.75 (m, 2H), 1.68 – 1.62 (m, 2H), 1.44 – 1.39 (m, 2H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 200.4, 161.2 (d, *J* = 243.2 Hz), 138.1 (d, *J* = 2.8 Hz), 137.0, 132.9, 129.6 (d, *J* = 7.7 Hz), 128.6, 128.0, 114.9 (d, *J* = 21.0 Hz), 38.5, 34.9, 31.4, 28.8, 24.1 ppm. IR (neat): υ_{max} 3055, 2928, 2870, 2383, 2312, 1682, 1518, 1455, 1408, 1262, 1084, 842, 808, 734 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{19}FNaO$ $[M+Na]^+$ 293.1312, found 293.1309.

7-(4-Fluorophenyl)-1-phenylheptan-1-one (4h): Colorless oil (88%, 50.1 mg); R_f 0.44

(EtOAc/petroleum ether = 1:15). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.96 (d, J = 7.3 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.11 (dd, J = 8.4, 5.6 Hz, 2H), 6.95 (t, J = 8.7 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 2.58 (t, J = 7.6 Hz, 2H),, 1.77 – 1.72 (m, 2H), 1.63 – 1.58 (m, 2H), 1.44 – 1.35 (m, 4H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 200.4, 161.1 (d, J = 243.2 Hz), 138.2 (d, J = 3.2 Hz), 137.0, 132.9, 129.6 (d, J = 7.7 Hz), 128.5, 128.0, 114.9 (d, J = 21.0 Hz), 38.5, 35.0, 31.4, 29.1, 28.9, 24.2 ppm. IR (neat): υ_{max} 2932, 2860, 2384, 2312, 1685, 1597, 1539, 1510, 1451, 1365, 1220, 1072, 970, 830, 751 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{22}FO$ $[M+H]^+$ 285.1649, found 285.1648.

8-(4-Fluorophenyl)-1-phenyloctan-1-one (4i): Colorless oil (72%, 42.9 mg); R_f 0.29 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.96 – 7.95 (m, 2H), 7.57 – 7.54 (m, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.12 – 7.10 (m, 2H), 6.96 – 6.93 (m, 2H), 2.96 (t, J = 7.4 Hz, 2H), 2.57 (t, J = 7.8 Hz, 2H), 1.76 – 1.71 (m, 2H), 1.61 – 1.56 (m, 2H), 1.41 – 1.32 (m, 6H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 200.5, 161.1 (d, J = 242.9 Hz), 138.3 (d, J = 3.2 Hz), 137.0, 132.9, 129.6 (d, J = 7.7 Hz), 128.5, 128.0, 114.9 (d, J = 20.9 Hz), 38.6, 35.1, 31.5, 29.3, 29.2, 29.0, 24.3 ppm. IR (neat): υ_{max} 3054, 2923, 2856, 2383, 2312, 1682, 1516, 1455, 1408, 1223, 1085, 1009, 900, 805, 736 cm^{-1}; HRMS (ESI) calcd for $C_{20}H_{24}FO$ $[M+H]^+$ 299.1806, found 299.1801.

12-(4-Fluorophenyl)-1-phenyldodecan-1-one (4j): Colorless oil (62%, 44.1 mg); R_f 0.52 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.96 (d, J = 8.0 Hz, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.7 Hz, 2H), 7.13 – 7.10 (m, 2H), 6.95 (t, J = 8.7 Hz, 2H), 2.96 (t, J = 7.4 Hz, 2H), 2.56 (t, J = 7.6 Hz, 2H), 1.76 – 1.71 (m, 2H), 1.40 – 1.26 (m, 16H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 200.6, 161.1 (d, J = 243.0 Hz), 138.5 (d, J = 3.2 Hz), 137.1, 132.8, 129.6 (d, J = 7.7 Hz), 128.5, 128.0, 114.9 (d, J = 21.0 Hz), 38.6, 35.1, 31.6, 29.6, 29.5, 29.5, 29.4, 29.3, 29.2, 24.4 ppm. IR (neat): υ_{max} 2983, 2918, 2853, 2384, 2312, 1683, 1518, 1461, 1405, 1283, 1239, 1083, 933, 821, 733 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{32}FO$ $[M+H]^+$ 355.2432, found 355.2425.

5-(4-Fluorophenyl)-1-phenylhexan-1-one (4k): Colorless oil (84%, 48.4 mg); R_f 0.42 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.92 – 7.90 (m, 2H), 7.55 (t, J = 7.4 Hz, 1H), 7.44 (t, J = 7.7 Hz, 2H), 7.16 – 7.13 (m, 2H), 6.99 – 6.95 (m, 2H), 2.97 – 2.88 (m, 2H), 2.76 – 2.70 (m, 1H), 1.74 – 1.64 (m, 2H), 1.63 – 1.56 (m, 2H), 1.25 (d, J = 6.9 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 200.2, 161.2 (d, J = 243.2 Hz), 142.8 (d, J = 3.0 Hz), 136.9, 132.9, 128.2 (d, J = 7.7 Hz), 128.2, 128.0, 115.0 (d, J = 20.9 Hz), 39.2, 38.4, 38.0, 22.5, 22.4 ppm.

IR (neat): υ_{max} 2961, 2383, 2312, 1685, 1598, 1514, 1450, 1405, 1283, 1222, 1053, 833, 748 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{19}FNaO$ [M+Na]$^+$ 293.1312, found 293.1307.

5-(4-Fluorophenyl)-1-phenyldodecan-1-one (4l): Colorless oil (61%, 43.1 mg); R_f 0.39 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.91 – 7.89 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.11 – 7.08 (m, 2H), 6.98 – 6.95 (m, 2H), 2.98 – 2.83 (m, 2H), 2.55 – 2.50 (m, 1H), 1.74 – 1.68 (m, 1H), 1.59 – 1.47 (m, 3H), 1.26 – 1.08 (m, 12H), 0.86 (t, *J* = 7.2 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 200.2, 161.2 (d, *J* = 243.2 Hz), 141.3 (d, *J* = 3.0 Hz), 136.9, 132.9, 128.8 (d, *J* = 7.7 Hz), 128.5, 128.0, 115.0 (d, *J* = 20.9 Hz). 45.3, 38.5, 37.0, 36.5, 31.8, 29.6, 29.2, 27.5, 22.6, 22.4, 14.1 ppm. IR (neat): υ_{max} 2983, 2891, 2384, 2312, 1696, 1519, 1403, 1283, 1238, 1052, 889 cm^{-1}; HRMS (ESI) calcd for $C_{24}H_{31}FNaO$ [M+Na]$^+$ 377.2251, found 377.2252.

Ethyl 2-(4-(1-(4-fluorophenyl)-5-oxo-5-phenylpentyl)phenyl)propanoate (4m): Colorless oil (76%, 65.7 mg); R_f 0.22 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.88 – 7.87 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.14 – 7.12 (m, 2H), 7.06 – 7.04 (m, 2H), 6.95 – 6.91 (m, 4H), 4.15 – 4.06 (m, 2H), 3.64 (q, *J* = 7.1 Hz, 1H), 2.93 – 2.78 (m, 5H), 1.79 – 1.74 (m, 1H), 1.70 – 1.66 (m, 1H), 1.61 – 1.56 (m, 2H), 1.46 (d, *J* = 7.2 Hz, 3H), 1.19 (td, *J* = 7.1, 2.0 Hz, 3H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 200.1, 174.6 , 161.3 (d, *J* = 243.6 Hz) , 140.1 (d, *J* = 2.8 Hz), 139.0, 138.1, 136.9, 132.9, 129.2, 129.0 (d, *J* = 7.7 Hz), 128.5, 127.9, 127.1, 115.0 (d, *J* = 21.0 Hz), 60.6, 47.2, 47.2, 45.1, 45.1, 43.5, 38.4, 35.1, 22.2, 18.5, 18.4, 14.1 ppm. IR (neat): υ_{max} 2978, 2932, 2312, 1730, 1685, 1598, 1509, 1452, 1369, 1325, 1218, 1168, 1087, 1020, 833, 746 cm^{-1}; HRMS (ESI) calcd for $C_{29}H_{31}FNaO_3$ [M+Na]$^+$ 469.2149, found 469.2152.

6-(4-Fluorophenyl)-1-phenylheptan-1-one (4n): Colorless oil (58%, 33.1 mg); R_f 0.45 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.93 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.13 – 7.11 (m, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 2.91 (t, *J* = 7.4 Hz, 2H), 2.72 – 2.66 (m, 1H), 1.77 – 1.66 (m, 2H), 1.61 – 1.57 (m, 2H), 1.26 – 1.19 (m, 5H). $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ = 199.4, 160.1 (d, *J* = 243.1 Hz), 142.1 (d, *J* = 2.9 Hz), 136.0, 131.9, 127.5, 127.2 (d, *J* = 7.7 Hz), 127.0, 114.0 (d, *J* = 21.0 Hz), 38.1, 37.5, 37.3, 26.4, 23.2, 21.5 ppm. IR (neat): υ_{max} 3055, 2957, 2862, 2312, 1727, 1684, 1597, 1508, 1453, 1409, 1367, 1262, 1223, 1154, 1093, 1020, 803, 745 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{22}FO$ [M+H]$^+$ 285.1649, found 285.1645.

6-(4-Fluorophenyl)-1-(thiophen-2-yl)heptan-1-one (4o): Colorless oil (51%, 29.4 mg); R_f 0.36 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.67 (d, *J* = 3.7 Hz, 1H), 7.61 (d, *J* = 4.9 Hz, 1H), 7.13 – 7.10 (m, 3H), 6.96 (t, *J* = 8.6 Hz, 2H), 2.84 (t, *J* = 7.4 Hz, 2H), 2.72 – 2.63 (m, 1H), 1.79 – 1.64 (m, 2H), 1.61 – 1.55 (m, 2H), 1.31 – 1.20 (m, 5H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 193.3, 161.1 (d, *J* = 243.6 Hz), 144.4, 143.1 (d, *J* = 3.2 Hz), 133.4, 131.6, 128.2 (d, *J* = 7.7 Hz), 128.0, 115.0 (d, *J* = 20.9 Hz), 39.3, 39.1, 38.2, 27.3, 24.6, 22.5 ppm. IR (neat): υ_{max} 3094, 2957, 2863, 2312, 1663, 1602, 1510, 1454, 1414, 1364, 1260, 1226, 1156, 1191, 1024, 803, 726 cm^{-1}; HRMS (ESI) calcd for $C_{17}H_{19}FNaOS$ $[M+Na]^+$ 313.1033, found 313.1043.

2-(3-(4-Fluorophenyl)cyclopentyl)-1-phenylethan-1-one (4p): Colorless oil (81%, 45.5 mg); R_f 0.42 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.98 (d, *J* = 7.6 Hz, 2H), 7.57 (t, *J* = 7.3 Hz, 1H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.20 – 7.17 (m, 2H), 6.96 (t, *J* = 8.7 Hz, 2H), 3.20 – 3.03 (m, 3H), 2.80 – 2.69 (m, 0.5H), 2.66 – 2.56 (m, 0.5H), 2.36 – 2.30 (m, 0.5H), 2.17 – 2.04 (m, 2H), 2.00 – 1.93 (m, 0.5H), 1.83 – 1.76 (m, 0.5H), 1.73 – 1.58 (m, 1H), 1.54 – 1.44 (m, 0.5H), 1.42 – 1.25 (m, 1H). ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$) δ = 199.9, 161.10 (d, *J* = 244.2 Hz), 141.9 (d, *J* = 3.2 Hz), 141.4, 137.1, 132.9, 128.6, 128.3, 128.0, 114.9 (d, *J* = 21.0 Hz), 45.3, 45.0, 44.8, 43.6, 42.2, 40.4, 35.8, 35.1, 34.9, 33.3, 33.2, 31.8 ppm. IR (neat): υ_{max} 3055, 2948, 2868, 2312, 1683, 1596, 1509, 1451, 1406, 1369, 1332, 1272, 1220, 1164, 1090, 1011, 828, 753 cm^{-1}; HRMS (ESI) calcd for $C_{19}H_{20}FO$ $[M+H]^+$ 283.1493, found 283.1490.

Investigation of the Reaction Mechanism

When 2.0 equiv of TEMPO was added to the reaction of **1a** with **2a** under the standard conditions, no product **3a** was detected. Meanwhile, the TEMPO-adduct **5a** was isolated in 80% yield. These results indicate that radical intermediate was probably involved in this transformation.

1-phenyl-5-((2,2,6,6-tetramethylpiperidin-1-yl)oxy)pentan-1-one (5a) Known Compound[12]. Colorless oil (80%, 51.0 mg); R_f 0.39 (EtOAc/petroleum ether = 1:15). ^{1}H NMR (600 MHz, $CDCl_3$) δ = 7.97 (d, *J* = 7.5 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 3.78 (t, *J* = 6.4 Hz, 2H), 3.02 (t, *J* = 7.4 Hz, 2H), 1.87 – 1.82 (m, 2H), 1.65 – 1.60 (m, 3H), 1.47 – 1.43 (m, 4H), 1.32 – 1.30 (m, 1H), 1.15 (s, 2H), 1.08 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ = 200.4, 137.0, 132.9, 128.5, 128.0, 59.6, 39.6, 38.6, 33.1, 28.4, 21.5, 20.1, 17.1 ppm.

When 2.0 equiv of BHT was added to the reaction of **1a** with **2a** under the standard conditions, the yield of **3a** just reduced a little bit. Increasing it to 4.0 equiv led to a largely reduced yield. These results indicate that the reaction probably proceed via a radical pathway.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc. XXXXX

^{1}H and ^{13}C spectra of all new compounds; the primary mechanistic studies of the reactions.

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