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An aqueous umpolung addition with hydrazones

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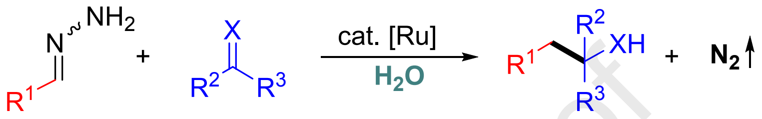

X = O, NR, C-EWG

55 Examples
Yield up to 83%

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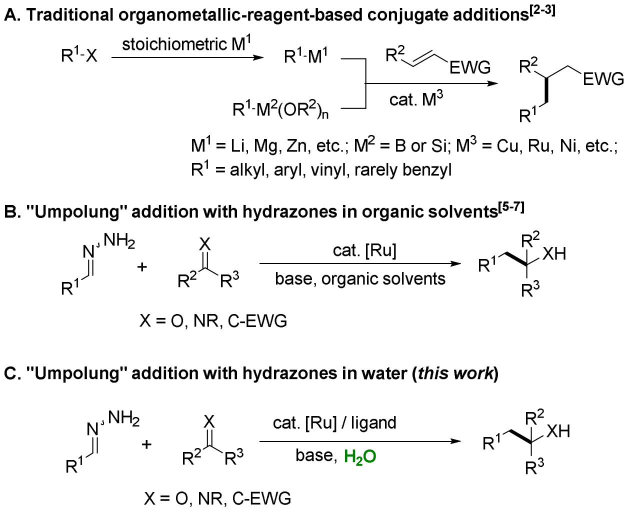
ABSTRACT

The addition of organometallic reagents to unsaturated bonds is one of the most powerful tools for carbon–carbon bond formations. Alkylation through organometallic reagents requires stoichiometric quantity of metal and tedious anhydrous operation in most cases. Here, we report "umpolung" nucleophilic additions of hydrazones to Michael acceptors, carbonyls and imines in water. Under the catalysis of ruthenium(II), the addition reactions could be carried out in pure water to provide various alkylation products in moderate to good yields.

1. Introduction

The nucleophilic addition reaction plays an important role in carbon-carbon bond formations.[1] Grignard reagents and other organometallic reagents serving as nucleophiles have been widely applied in the addition reaction for constructing various molecules.[2-3] Different from enolized or enaminized carbon nucleophiles, organometallic reagents are characterized by polar umpolung transformations of positively charged carbon atoms into negatively charged carbons[3]. Polar transformation can construct a backbone that is difficult to achieve with non-polar transformation methods[4]. Although enormous progress has been made for classical organometallic reactions, there are still obvious shortcomings in view of chemical sustainability. First, the pre-preparation of metal organic reagents as nucleophiles requires the production of equivalent amounts of waste metals. A large amount of scrap metal is both costly to the mining industry and very unfriendly to the environment. In addition, pre-selective preparation of organometallic reagents often requires some halogenated hydrocarbons as feedstock. After the nucleophile is introduced into the reaction, equivalent halogen is discarded as waste. Furthermore, due to the sensitivity of organometallic reagents towards proton, it is often necessary to use a strictly dry organic solvent and tedious anhydrous operation.

Recently, the metal-catalyzed umpolung chemistry through hydrazone intermediates using aldehydes and ketones as carbanion equivalents has attracted much attention in organic synthesis.[5-7] Comparing with organometallic reactions for carbon-carbon bond formations, this strategy exhibited unique advantages such as moisture/air-stable hydrazones as reactants, good functional group compatibility, no waste metal salts or halides and only nitrogen and water as the theoretical byproducts.[8] On the basis of the environmental concern of organic solvents, aqueous organic reactions have made great progress.[9] However, there is no report on transition metal catalyzed reactions of carbonyl compounds masked as "soft" alkyl carbanions *via* hydrazone in aqueous media.[10]



Scheme 1. Carbon nucleophiles used in conjugate additions.

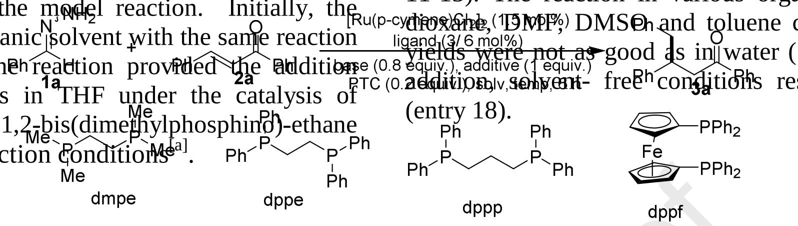
nucleophilic additions of hydrazones to unsaturated bonds in water. The Michael-type addition of hydrazones with chalcones could be carried out in pure water without using a phase transfer catalyst or surfactant. Moreover, the addition of hydrazones to carbonyls and imines in water could also provide the related alkylation products in the presence of catalytic amount of tetrabutylammonium chloride. There are no waste metal salts or halides generation, with nitrogen as the sole byproduct.

2. Results and discussion

The reaction of hydrazone derived from benzaldehyde (**1a**) with chalcone **2a** was chosen as the model reaction. Initially, the reaction was carried out in organic solvent with the same reaction conditions as literature.[6a] The reaction provided the addition product **3a** in 36-40% yields in THF under the catalysis of [Ru(p-cymene)Cl$_2$]$_2$ and 1,2-bis(dimethylphosphino)-ethane

the ligand (Table 1, entries 1-2). When the reaction was carried out in water in the presence of TBAC as a phase transfer catalyst, only very low yield of **3a** was obtained (entry 3). After screening different ligands, triphenylphosphine was found to provide the highest yield (53%) (entries 4-7). Increasing the reaction temperature from 70 °C to 100°C, the yield was improved slightly and the reaction did not require the addition of a phase transfer catalyst (entries 8-9). Furthermore, by removing the additive CsF, the reaction gave **3a** in the optimum yield (71%) (entry 10). When K_3PO_4 was changed to other inorganic or organic bases, the reaction provided relatively lower yields of 52-68% (entries 11-13). The reaction in various organic solvents such as 1,4-dioxane, DMF, DMSO and toluene could generate **3a**, but the yields were not as good as in water (18-62%, entries 14-17). In addition, solvent- free conditions resulted in only 46% yield (entry 18).

Table 1: Optimization of reaction conditions[a].



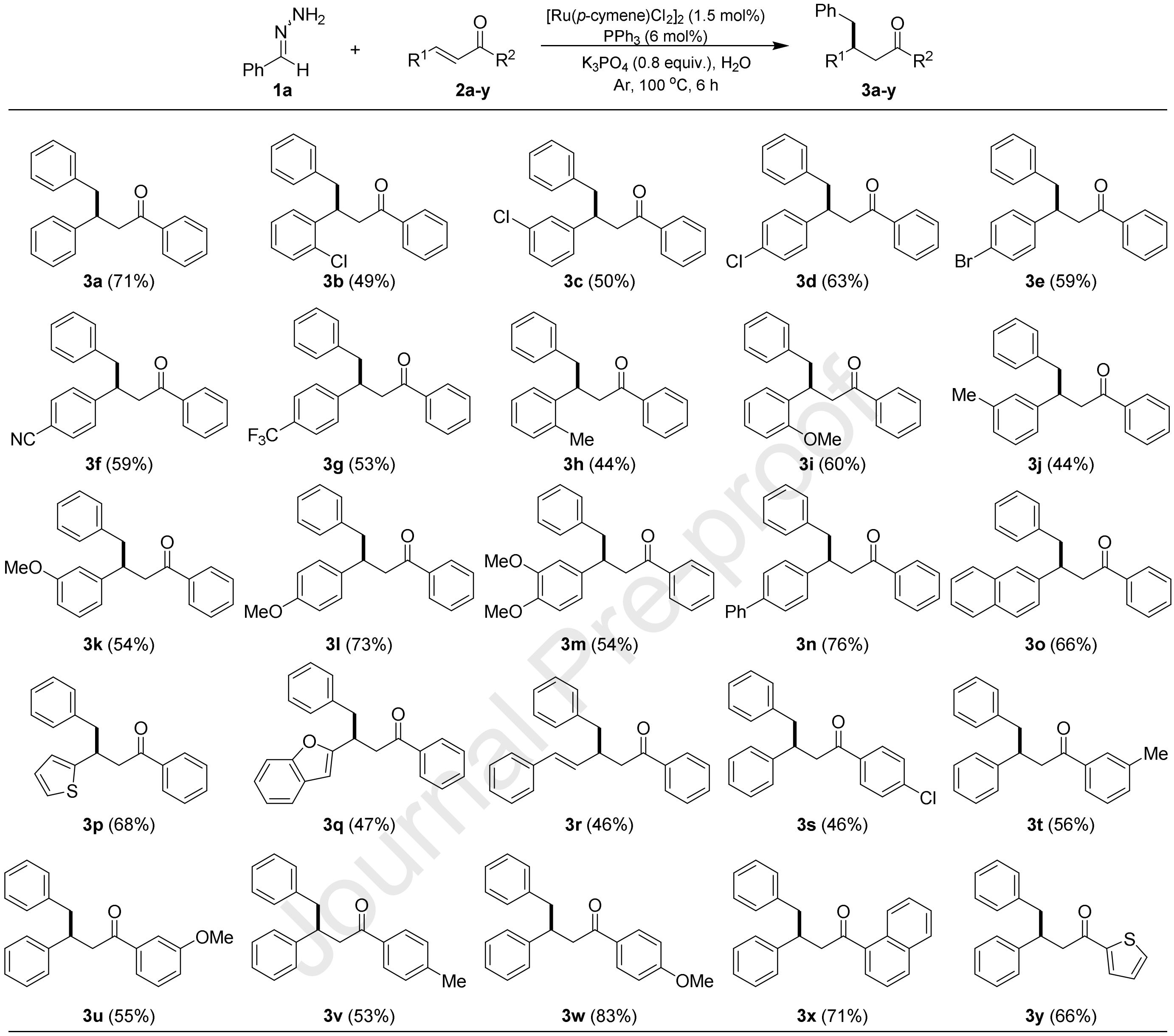
entry	ligand	base	additive	PTC	temp. (°C)	solvent	yield (%)[b]
1[e]	dmpe	K_3PO_4	CsF	-	50	THF	40
2[e]	dppp	K_3PO_4	CsF	-	50	THF	36
3[c]	dmpe	K_3PO_4	CsF	TBAC	70	H_2O	9
4[c]	dppe	K_3PO_4	CsF	TBAC	70	H_2O	37
5[c]	dppp	K_3PO_4	CsF	TBAC	70	H_2O	30
6[c]	dppf	K_3PO_4	CsF	TBAC	70	H_2O	40
7	PPh_3	K_3PO_4	CsF	TBAC	70	H_2O	53
8	PPh_3	K_3PO_4	CsF	TBAC	100	H_2O	56
9	PPh_3	K_3PO_4	CsF	-	100	H_2O	59
10	PPh_3	K_3PO_4	-	-	100	H_2O	71
11	PPh_3	K_2CO_3	-	-	100	H_2O	64
12	PPh_3	NaOH	-	-	100	H_2O	52
13	PPh_3	Et_3N	-	-	100	H_2O	68
14	PPh_3	K_3PO_4	-	-	100	1,4-Dioxane	58
15	PPh_3	K_3PO_4	-	-	100	DMF	49
16	PPh_3	K_3PO_4	-	-	100	DMSO	18
17	PPh_3	K_3PO_4	-	-	100	Toluene	62
18[d]	PPh_3	K_3PO_4	-	-	100	none	46

[a]General reaction conditions: **1a** (0.25 mmol, 2.5 equiv.), **2a** (0.1 mmol, 1.0 equiv.), [Ru(p-cymene)Cl$_2$]$_2$ (1.5 mol %), ligand (6 mol %), base (0.8 equiv.), additive (1.0 equiv.), PTC (0.2 equiv.), solvent (0.5 mL) under Ar atmosphere. [b]Yields were determined by crude ^{1}H NMR using 1,3,5-trimethoxybenzene as an internal standard. [c]Ligand (3 mol %). [d][Ru(p-cymene)Cl$_2$]$_2$ (10 mol %), PPh_3 (40 mol %). [e][Ru(p-cymene)Cl$_2$]$_2$ (0.75 mol %), ligand (3 mol %), base (0.25 equiv.), additive (1.0 equiv.) , THF (0.15 mL) under Ar atmosphere.

With the optimized reaction conditions in hand, the scope of Micheal receptor was explored with benzaldehyde-derived hydrazone (**1a**) in H_2O at 100 °C under the catalysis of Ru/PPh_3 with K_3PO_4 as a base (Scheme 2). A wide range of α,β-unsaturated ketones were coupled with hydrazone **1a** to give the corresponding 1,4-addition products in moderate to good yields (Scheme 2). No carbonyl addition product was observed. This reaction demonstrated good functional groups compatibility, including aryl halides (**3b-e**), aryl nitrile (**3f**) and trifluoromethyls (**3g**). Heteroaromatic substituted α,β-unsaturated ketones **3p**, **3q** and **3y** could be also used in this reaction. Steric hindrance affected catalytic reactivity, with lower yields being obtained for the *ortho*-substituted chalcone derivatives **3b** and **3i** compared with the *para*-substituted Michael acceptors **3d** and **3l**. Electronic

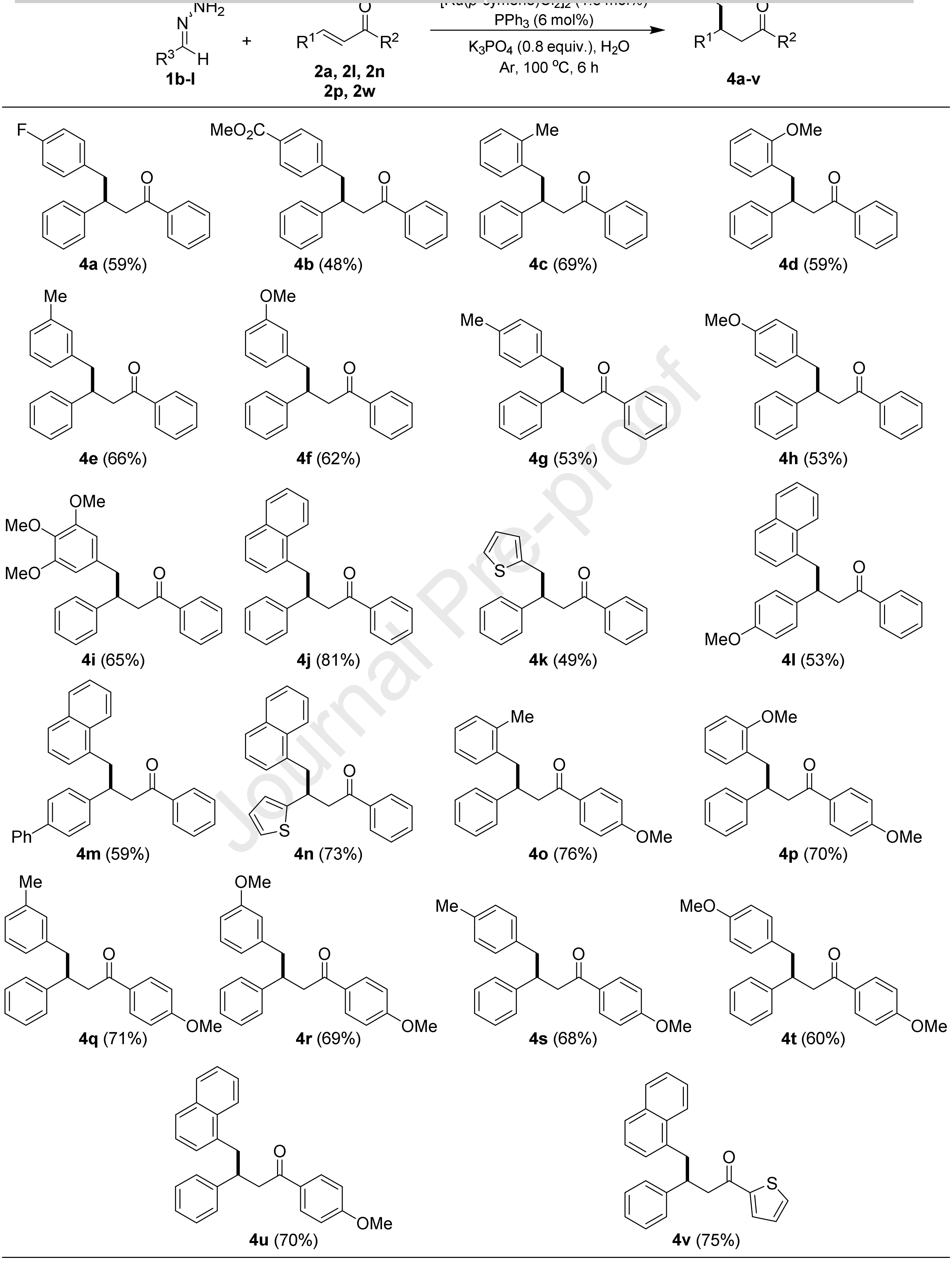
effe
substituted substrates **2**, electron-donating groups such as OMe and Ph on **2** gave higher yields than 4'-CN, 4'-CF$_3$ and 4'-Br substituted substrates (Scheme 2, **3l**, **3n** vs **3d-g**). Conjugated

on
product **3r**.



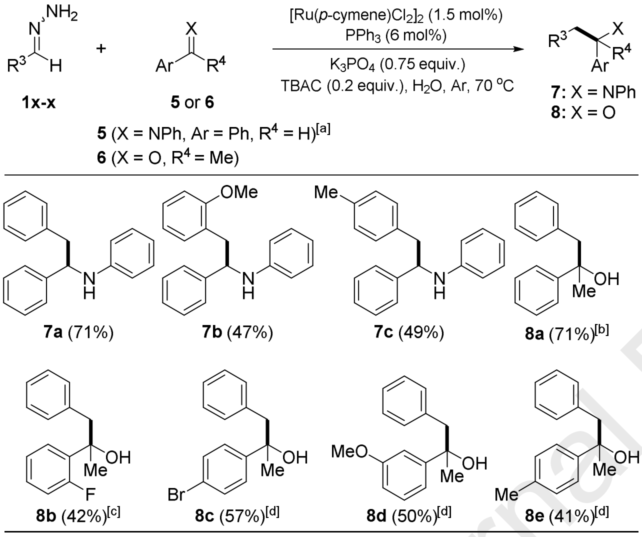
Scheme 2. Scope of Michael receptors **2**.

Having established the scope of various α,β-unsaturated ketones, we turned our attention to nucleophilic partners. A number of substituted benzaldehyde derived hydrazones were used as the substrates. The electronic effect of substituents on **1** did not affect the reaction significantly. Both electron-donating and electron-withdrawing group substituted hydrazones provided the corresponding addition products in 48-66% yields (Scheme 3, **4a-l**). Surprisingly, 2-substituted benzaldehyde derived hydrazones have good reactivities (Scheme 3, **4o-p**). In general, compared to *meta* and *ortho* position, the *para*-substituted aromatic hydrazones gave relatively low yields (**4g** vs **4c** and **4e**; **4h** vs **4d** and **4f**). It may attribute to the competing dimerization of the hydrazones which is faster in the case of the less sterically hindered para-substituted substrates.[6d]



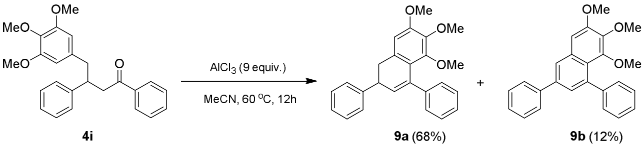
Scheme 3. Scope of hydrazone and conjugate addition products.

N[illegible] carbonyl compounds in water were investigated (Scheme 4). Different from the addition to Michael acceptors, the reaction of hydrazone with benzaldehyde-derived imine **5** and acetophenone **6** required the participation of a phase transfer catalyst in order to get satisfying yields. With the reaction conditions optimized earlier, the reactions of hydrazone **1a** with imine **5** and ketone **6a** in water provided the corresponding products **7a** and **8a** in 33% and 46% yields, respectively (see the Supporting Information for more details). Decreasing the reaction temperature from 100°C to 70°C increased the yield to 43% for **7a** and 59% for **8a** (see the Supporting Information for more details). After the addition of TBAC (0.2 equiv.), both **7a** and **8a** were obtained in 71% yield. Compared with imine, ketone showed lower reactivity in the addition reaction with hydrazone in water, which needed a longer reaction time. 2-, 3- or 4-Substituted acetophenones could gave the corresponding products in moderate yields (Scheme 4, **8b-e**).



Scheme 4. Scope of imine and carbonyl compounds.
[a] 1.5 h. [b] 3 h. [c] 9.5 h. [d] 18 h.

Further transformation of the addition product was demonstrated in Scheme **5**. The alkylation product **4i** of hydrazone with chalcone provided a naphthalene derivative **9a** in 68% yield together with a small amount of aromatized product **9b** via an intramolecular Friedel-Crafts reaction under the promotion of $AlCl_3$.



Scheme 5. Intramolecular Friedel-Crafts reaction of the addition product **4i**.

As shown in Fig. 1, a plausible mechanism is proposed.[6a] The ruthenium complex **A** generated from $[Ru(p\text{-cymene})Cl_2]_2$ with PPh_3 is coordinated by the Michael acceptor **2** to form complex B. Then, after deprotonation in the presence of a base, hydrazones **1** ligates to complex **B** and generates the nucleophilic addition product **3** via a six-membered-ring transition state (complex **C**), by the release of N_2 under the base deprotonation.

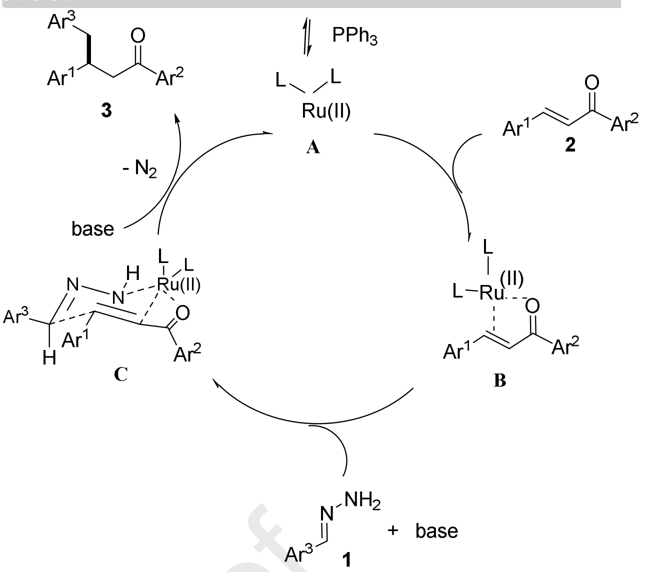


Fig. 1. Proposed mechanism.

3. Conclusion

In summary, we have developed a ruthenium(II)-catalyzed “umpolung” nucleophilic additions of hydrazones to unsaturated bonds in water. Carbon-carbon bonds can be constructed in an environmentally friendly manner by the addition of hydrazones to chalcones, carbonyls and imines in pure water. The related alkylation products were obtained in moderate to good yields. There are no stoichiometric waste metal salts (except the base additive which can be further optimized in future) or halide generation, with dinitrogen as the sole stoichiometric byproduct. Further transformation of the addition product of hydrazone with chalcone provided a naphthalene derivative via an intramolecular Friedel-Crafts reaction.

4. Experimental section

4.1. General exprimental information

The ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 300 (^{1}H, 300 MHz), Bruker Avance 400 (^{1}H, 400 MHz; ^{13}C, 101 MHz) and Bruker Avance III HD 500MHz (^{1}H, 500 MHz; ^{13}C, 126 MHz). All chemical shifts (d) were given in ppm. Data were reported as follows: chemical shift, integration, multiplicity (s = single, d = doublet, t = triplet, q = quartet, m = multiplet) and coupling constants (Hz). Flash column chromatography was performed using H silica gel. For thin-layer chromatography (TLC), silica gel plates (HSGF 254) were used and compounds were visualized by irradiation with UV light. IR spectra were recorded on Nicolet 6700 instrument. High-resolution mass spectra (HRMS) were recorded by a Thermo Fisher Scientific Exactive Orbitrap mass spectrometer.

*4.2. General procedure for the synthesis of compounds **3** and **4***

A Schlenk tube (10 mL) equipped with a magnetic stir bar was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (0.9 mg, 0.0015 mmol, 1.5 mol%), PPh_3 (1.6 mg, 0.006 mmol, 6 mol%), K_3PO_4 (17 mg, 0.08 mmol, 0.8 equiv.), α,β-unsaturated ketone (0.1 mmol, 1.0 equiv.). The reaction system was then protected with an argon atmosphere. After that, THF (50 μL) was added to the reaction system. After stirring for 10 minutes at room temperature, hydrazone (0.25 mmol, 2.5 equiv.) was added to the system.

Th distilled water (0.5 mL) was added to the reaction vessel and heated to 100 °C. The reaction system was stirred at 100 °C for 6 h and then diluted with 3 mL water. After cooling to room temperature, 2 mL HCl solution (3 M) was added to the reaction system, and the mixture was extracted with ethyl acetate (3x5 mL). The combined organic layers was washed with water (5 mL) and then dried over Na_2SO_4. The organic layers were concentrated and the resulting residue was purified by preparative TLC on silica gel to afford the product.

4.2.1. 1,3,4-triphenylbutan-1-one (*3a*)

White solid (21.3 mg, yield 71%); R_f = 0.25 (petroleum ether / acetone = 40/1); mp. 114-115 °C; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.88-7.80 (m, 2H), 7.56-7.48 (m, 1H), 7.44-7.36 (m, 2H), 7.24-7.13 (m, 8H), 7.07 (dd, *J* = 9.9, 3.3 Hz, 2H), 3.74-3.59 (m, 1H), 3.39-3.21 (m, 2H), 3.06-2.88 (m, 2H); ^{13}C NMR (126MHz, $CDCl_3$) δ 199.0, 144.3, 140.0, 137.3, 133.1, 129.4, 128.7, 128.5, 128.3, 128.1, 127.8, 126.5, 126.2, 44.3, 43.2, 43.1; HRMS (APCI, *m/z*), calcd for $C_{22}H_{21}O^+$ $[M+H]^+$, 301.1587; found, 301.1588.

4.2.2. 3-(2-chlorophenyl)-1,4-diphenylbutan-1-one (*3b*)

Yellow solid (16.4 mg, yield 49%); mp. 104-105 °C; R_f = 0.31 (petroleum ether / acetone = 20/1); FT-IR (cm^{-1}) 3359, 2921, 2360, 1685, 1448, 753, 697; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.5 Hz, 2H), 7.52 (s, 1H), 7.42 (d, *J* = 7.8 Hz, 2H), 7.32 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.24-7.05 (m, 8H), 4.29 (s, 1H), 3.34 (dd, *J* = 15.0, 7.0 Hz, 2H), 3.00 (dd, *J* = 21.6, 7.4 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.6, 141.3, 139.5, 137.1, 134.2, 133.1, 130.0, 129.4, 128.7, 128.4, 128.2, 128.1, 127.6, 126.9, 126.4, 42.6, 41.3, 39.1; HRMS (ESI, *m/z*), calcd for $C_{22}H_{18}OCl^-$ $[M-H]^-$, 333.1052; found, 333.1045.

4.2.3. 3-(3-chlorophenyl)-1,4-diphenylbutan-1-one (*3c*)

Colorless solid (16.7 mg, yield 50%); mp. 108-109 °C; R_f = 0.39 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 2922, 2361, 1685, 1079, 695, 613; ^{1}H NMR (300MHz, $CDCl_3$) δ 7.90-7.80 (m, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.5 Hz, 2H), 7.27-7.21 (m, 2H), 7.19 (d, *J* = 4.9 Hz, 3H), 7.14 (dd, *J* = 7.8, 5.4 Hz, 4H), 7.10-6.99 (m, 4H), 3.66 (s, 1H), 3.29 (dd, *J* = 6.9, 3.1 Hz, 2H), 2.96 (dd, *J* = 9.4, 7.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.5, 146.4, 139.5, 137.1, 134.3, 133.2, 129.7, 129.4, 128.7, 128.4, 128.1, 127.8, 126.8, 126.4, 126.3, 44.0, 43.0, 42.8; HRMS (ESI, *m/z*), calcd for $C_{22}H_{18}OCl^-$ $[M-H]^-$, 333.1052; found, 333.1055.

4.2.4. 3-(4-chlorophenyl)-1,4-diphenylbutan-1-one (*3d*)

White solid (21.1 mg, yield 63%); mp. 169-171 °C; R_f = 0.39 (petroleum ether / acetone = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89-7.80 (m, 2H), 7.53 (dd, *J* = 13.2, 5.9 Hz, 1H), 7.41 (dd, *J* = 14.6, 7.0 Hz, 2H), 7.23-7.14 (m, 5H), 7.13-7.07 (m, 2H), 7.04 (dd, *J* = 9.9, 4.3 Hz, 2H), 3.65 (p, *J* = 7.2 Hz, 1H), 3.35-3.23 (m, 2H), 3.03-2.86 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.6, 142.7, 139.5, 137.1, 133.2, 132.1, 129.4, 129.2, 128.7, 128.6, 128.4, 128.1, 126.4, 44.1, 43.1, 42.5; HRMS (ESI, *m/z*), calcd for C22H18OCl$^-$ $[M-H]^-$, 333.1052; found, 333.1049.

4.2.5. 3-(4-bromophenyl)-1,4-diphenylbutan-1-one (*3e*)

White solid (22.3 mg, yield 59%); mp. 174-175 °C; R_f = 0.40 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 3027, 2922, 2361, 1685, 1584, 699; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86-7.81 (m, 2H), 7.53 (dd, *J* = 13.1, 5.7 Hz, 1H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.34 (t, *J* = 6.4 Hz, 2H), 7.24-7.18 (m, 2H), 7.18-7.13 (m, 1H), 3.34-3.23 (m, 2H), 3.03-2.86 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.6, 142.7, 139.5, 137.1, 133.2, 132.1, 129.4, 129.2, 128.7, 128.6, 128.4, 128.1, 126.4, 44.1, 43.1, 42.5; HRMS (ESI, *m/z*), calcd for $C_{22}H_{18}OBr^-$ $[M-H]^-$, 377.0547; found, 377.0541.

4.2.6. 4-(4-oxo-1,4-diphenylbutan-2-yl)benzonitrile (*3f*)

Yellow solid (19.1 mg, yield 59%); mp. 168-169 °C; R_f = 0.15 (petroleum ether / acetone = 10/1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89-7.81 (m, 2H), 7.55-7.50 (m, 2H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.38-7.25 (m, 3H), 7.22 (t, *J* = 7.2 Hz, 2H), 7.20-7.13 (m, 1H), 7.05 (t, *J* = 11.6 Hz, 2H), 3.74 (t, *J* = 6.4 Hz, 1H), 3.41-3.29 (m, 2H), 3.08-2.87 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.1, 149.9, 138.9, 136.9, 133.4, 132.3, 129.3, 128.8, 128.7, 128.5, 128.1, 126.6, 119.1, 110.4, 43.7, 43.2, 42.8; HRMS (ESI, *m/z*), calcd for $C_{23}H_{18}NO^-$ $[M-H]^-$, 324.1394; found, 324.1387.

4.2.7. 3-(4-(trifluoromethyl)phenyl)-1,4-diphenylbutan-1-one (*3g*)

White solid (19.5 mg, yield 53%); mp. 153-154 °C; R_f = 0.25 (petroleum ether / acetone = 40/1); FT-IR (cm^{-1}) 2924, 2358, 1679, 1326, 1129, 690; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89-7.80 (m, 2H), 7.58-7.49 (m, 2H), 7.49-7.37 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.20 (dd, *J* = 7.3, 4.5 Hz, 2H), 7.11-7.01 (m, 2H), 3.82-3.68 (m, 1H), 3.34 (dd, *J* = 6.9, 3.5 Hz, 2H), 2.98 (dd, *J* = 12.6, 7.5 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.4, 148.4, 139.3, 137.1, 133.3, 129.3, 128.8, 128.5, 128.2, 128.1, 126.5, 125.5, 125.4, 43.9, 42.94, 42.90, 1.2; HRMS (APCI, *m/z*), calcd for $C_{23}H_{20}F_3O^+$ $[M+H]^+$, 369.1461; found, 369.1464.

4.2.8. 1,4-diphenyl-3-o-tolylbutan-1-one (*3h*)

Light yellow oil (13.8 mg, yield 44%); R_f = 0.36 (petroleum ether / acetone = 20/1); FT-IR (cm^{-1}) 2921, 2360, 1684, 1492, 1450, 751, 698; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.7 Hz, 2H), 7.51 (d, *J* = 6.9 Hz, 1H), 7.40 (t, *J* = 7.7 Hz, 2H), 7.25 (d, *J* = 4.2 Hz, 1H), 7.17 (t, *J* = 7.9 Hz, 4H), 7.05 (d, *J* = 5.2 Hz, 4H), 4.02-3.86 (m, 1H), 3.33 (dd, *J* = 16.1, 7.0 Hz, 2H), 3.01-2.81 (m, 2H), 2.16 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 142.6, 140.0, 137.3, 136.4, 133.0, 130.4, 129.4, 128.6, 128.3, 128.1, 126.23, 126.19, 126.15, 125.9, 44.2, 43.2, 37.9, 19.7; HRMS (ESI, *m/z*), calcd for $C_{23}H_{21}O^-$ $[M-H]^-$, 313.1598; found, 313.1598.

4.2.9. 3-(2-methoxyphenyl)-1,4-diphenylbutan-1-one (*3i*)

Light yellow solid (19.8 mg, yield 60%); mp. 119-120 °C; R_f = 0.47 (petroleum ether / acetone = 20/1); FT-IR (cm^{-1}) 2919, 2359, 1683, 1492, 1241, 1110, 749, 614; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.5 Hz, 2H), 7.50 (s, 1H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.3 Hz, 2H), 7.12 (dd, *J* = 10.7, 4.6 Hz, 5H), 6.88-6.77 (m, 2H), 4.02 (s, 1H), 3.74 (s, 3H), 3.32 (dd, *J* = 18.1, 7.0 Hz, 2H), 3.10-2.91 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 157.4, 140.6, 137.4, 132.8, 132.1, 129.4, 128.5, 128.4, 128.17, 128.15, 127.5, 126.0, 120.6, 110.9, 55.4, 42.8, 41.0, 37.7; HRMS (ESI, *m/z*), calcd for $C_{23}H_{21}O_2^-$ $[M-H]^-$, 329.1547; found, 329.1548.

4.2.10. 1,4-diphenyl-3-m-tolylbutan-1-one (*3j*)

Light yellow oil (13.7 mg, yield 44%); R_f = 0.47 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 2921, 2361, 1684, 1449, 1076, 700, 612; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90-7.78 (m, 2H), 7.51 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.18 (dd, *J* = 13.5, 7.1 Hz, 3H), 7.11-7.05 (m, 3H), 6.97 (d, *J* = 9.9 Hz, 3H), 3.63 (s, 1H), 3.40-3.17 (m, 2H), 2.96 (d, *J* = 7.4 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 144.3, 140.1, 138.0, 137.4, 133.0, 130.8, 130.7, 129.4, 128.6, 128.3, 128.2, 127.3, 126.2, 124

$C_{23}H_{21}O^-$ [M-H]$^-$, 313.1598; found, 313.1600.

*4.2.11. 3-(3-methoxyphenyl)-1,4-diphenylbutan-1-one (**3k**)*

Light yellow oil (17.8 mg, yield 54%); R_f = 0.31 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 2922, 1684, 1599, 1451, 1260, 699; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.89-7.80 (m, 2H), 7.52 (s, 1H), 7.42 (d, *J* = 7.7 Hz, 2H), 7.22-7.13 (m, 4H), 7.11-7.05 (m, 2H), 6.78 (d, *J* = 7.7 Hz, 1H), 6.70 (d, *J* = 6.5 Hz, 2H), 3.73 (s, 2H), 3.65 (s, 1H), 3.29 (dd, *J* = 10.2, 7.0 Hz, 2H), 3.03-2.91 (m, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 199.0, 159.6, 146.0, 139.9, 137.3, 133.1, 130.8, 129.4, 128.7, 128.3, 128.1, 126.2, 120.1, 113.8, 111.7, 55.3, 44.2, 43.2, 43.0; HRMS (ESI, *m/z*), calcd for $C_{23}H_{21}O_2^-$ [M-H]$^-$, 329.1547; found, 329.1551.

*4.2.12. 3-(4-methoxyphenyl)-1,4-diphenylbutan-1-one (**3l**)*

Colorless solid (24.1 mg, yield 73%); mp. 146-147 °C; R_f = 0.47 (petroleum ether / ethyl acetate = 5/1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.83 (d, *J* = 7.3 Hz, 2H), 7.51 (t, *J* = 7.3 Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.23-7.14 (m, 3H), 7.07 (dd, *J* = 7.4, 5.4 Hz, 4H), 6.77 (d, *J* = 8.6 Hz, 2H), 3.74 (s, 3H), 3.61 (p, *J* = 7.2 Hz, 1H), 3.35-3.17 (m, 2H), 3.03-2.85 (m, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 199.2, 158.2, 140.1, 137.3, 136.3, 133.0, 129.4, 128.7, 128.6, 128.3, 128.1, 126.2, 113.9, 55.3, 44.5, 43.3, 42.4; HRMS (ESI, *m/z*), calcd for $C_{23}H_{21}O_2^-$ [M-H]$^-$, 329.1547; found, 329.1540.

*4.2.13. 3-(3,4-dimethoxyphenyl)-1,4-diphenylbutan-1-one (**3m**)*

Yellow solid (19.4 mg, yield 54%); mp. 86-88 °C; R_f = 0.25 (petroleum ether / acetone = 5/1); FT-IR (cm^{-1}) 3360, 2923, 1683, 1516, 1450, 1261, 1028, 698; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.91-7.78 (m, 2H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.41 (t, *J* = 7.5 Hz, 2H), 7.18 (dd, *J* = 12.6, 7.1 Hz, 3H), 7.10-7.04 (m, 2H), 6.73 (d, *J* = 2.6 Hz, 2H), 6.61 (s, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 3.61 (s, 1H), 3.29 (t, *J* = 7.3 Hz, 2H), 2.95 (dd, *J* = 12.5, 7.4 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 199.2, 148.7, 147.6, 140.0, 137.4, 136.8, 133.1, 129.5, 128.7, 128.3, 128.1, 126.2, 119.3, 111.5, 111.2, 55.9, 44.4, 43.3, 42.9; HRMS (ESI, *m/z*), calcd for $C_{24}H_{25}O_3^+$ [M+H]$^+$, 361.1798; found, 361.1797.

*4.2.14. 3-(4-phenyl)-1,4-diphenylbutan-1-one (**3n**)*

White solid (28.5 mg, yield 76%); mp. 160-162 °C; R_f = 0.28 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 3027, 2922, 2360, 1683, 1488, 1261, 1022, 697; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.90-7.80 (m, 2H), 7.54 (t, *J* = 6.5 Hz, 3H), 7.48 (d, *J* = 8.3 Hz, 3H), 7.41 (t, *J* = 7.9 Hz, 5H), 7.32 (d, *J* = 7.3 Hz, 1H), 7.19 (d, *J* = 6.4 Hz, 2H), 7.11 (d, *J* = 6.7 Hz, 3H), 3.79-3.65 (m, 1H), 3.34 (dd, *J* = 9.0, 7.0 Hz, 2H), 3.01 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 199.0, 143.4, 141.1, 139.9, 139.3, 137.3, 133.1, 129.5, 128.8, 128.7, 128.4, 128.19, 128.15, 127.2, 127.1, 126.3, 44.2, 43.1, 42.8; HRMS (APCI, *m/z*), calcd for $C_{28}H_{23}O^-$ [M-H]$^-$, 375.1754; found, 375.1747.

*4.2.15. 3-(naphthalen-2-yl)-1,4-diphenylbutan-1-one (**3o**)*

Yellow solid (23.1 mg, yield 66%); mp. 200-202 °C; R_f = 0.32 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 3734, 3057, 2360, 1683, 744, 698; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.90-7.81 (m, 2H), 7.79-7.69 (m, 3H), 7.59 (s, 1H), 7.51 (t, *J* = 7.4 Hz, 1H), 7.40 (qd, *J* = 8.9, 3.4 Hz, 5H), 7.19 (t, *J* = 7.2 Hz, 2H), 7.14 (d, *J* = 7.1 Hz, 1H), 7.09 (d, *J* = 7.0 Hz, 2H), 3.85 (p, *J* = 7.2 Hz, 1H), 3.40 (ddd, *J* = 23.3, 16.8, 6.9 Hz, 2H), 3.13-3.01 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 198.9, 141.8, 139.9, 137.3, 133.6, 133.1, 132.5, 129.4, 128.7, 128.4, 128.2, 128.1, 127.8, 127.7, 126.30, 126.29, 126.27, 126.0, 125.5, 44.3, 43.2, 43.0;

43;

found, 351.1741.

*4.2.16. 1,4-diphenyl-3-(thiophen-2-yl)butan-1-one (**3p**)*

Yellow oil (20.8 mg, yield 68%); R_f = 0.41 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 2922, 2360, 1684, 1448, 1216, 746, 695; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.93-7.82 (m, 2H), 7.53 (dd, *J* = 10.5, 4.3 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 7.25-7.21 (m, 2H), 7.17 (dq, *J* = 9.5, 4.8 Hz, 1H), 7.12 (d, *J* = 7.2 Hz, 2H), 7.09 (dd, *J* = 5.1, 0.9 Hz, 1H), 6.84 (dt, *J* = 7.1, 3.5 Hz, 1H), 6.73 (t, *J* = 6.0 Hz, 1H), 4.03 (p, *J* = 7.2 Hz, 1H), 3.32 (ddd, *J* = 23.2, 16.9, 6.8 Hz, 2H), 3.09-2.97 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 198.5, 148.1, 139.5, 137.2, 133.2, 129.4, 128.7, 128.4, 128.2, 126.7, 126.4, 124.3, 123.2, 45.2, 43.9, 38.4; HRMS (ESI, *m/z*), calcd for $C_{20}H_{17}OS^-$ [M-H]$^-$, 305.1006; found, 305.0999.

*4.2.17. 3-(benzofuran-2-yl)-1,4-diphenylbutan-1-one (**3q**)*

Yellow solid (15.9 mg, yield 47%); mp. 106-108 °C; R_f = 0.34 (petroleum ether / acetone = 20/1); FT-IR (cm^{-1}) 3358, 2922, 2360, 1685, 1453, 1253, 747, 697; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.89 (s, 2H), 7.52 (d, *J* = 7.4 Hz, 1H), 7.42 (dd, *J* = 5.1, 3.6 Hz, 4H), 7.19 (dd, *J* = 8.8, 4.5 Hz, 4H), 7.13 (d, *J* = 1.6 Hz, 3H), 6.32 (s, 1H), 3.95 (s, 1H), 3.38 (dd, *J* = 37.3, 6.8 Hz, 2H), 3.13 (dd, *J* = 18.3, 7.2 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 198.2, 159.9, 154.7, 139.2, 137.0, 133.3, 129.3, 128.7, 128.5, 128.2, 126.5, 123.5, 122.6, 120.7, 111.0, 103.1, 41.5, 39.9, 36.9; HRMS (ESI, *m/z*), calcd for $C_{24}H_{19}O_2^-$ [M-H]$^-$, 339.1391; found, 339.1382.

*4.2.18. 3-benzyl-1,5-diphenylpent-4-en-1-one (**3r**)*

White solid (14.8 mg, yield 46%); mp. 169-171 °C; R_f = 0.49 (petroleum ether / acetone = 10/1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.87 (d, *J* = 7.1 Hz, 2H), 7.53 (s, 1H), 7.42 (s, 2H), 7.25 (s, 10H), 6.33 (d, *J* = 16.0 Hz, 1H), 6.16 (dd, *J* = 15.9, 7.9 Hz, 1H), 3.27 (dq, *J* = 14.2, 7.1 Hz, 1H), 3.14-2.99 (m, 2H), 2.84 (t, *J* = 8.1 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 199.3, 139.7, 137.5, 137.4, 133.1, 132.8, 130.4, 129.6, 128.7, 128.6, 128.5, 128.2, 127.2, 126.34, 126.28, 43.0, 41.5, 40.5; HRMS (ESI, *m/z*), calcd for $C_{24}H_{21}O^-$ [M-H]$^-$, 325.1598; found, 325.1593.

*4.2.19. 1-(4-chlorophenyl)-3,4-diphenylbutan-1-one (**3s**)*

Yellow solid (15.4 mg, yield 46%); mp. 158-160 °C; R_f = 0.44 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 3027, 2923, 2360, 1685, 699; ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.6 Hz, 2H), 7.36 (d, *J* = 8.6 Hz, 2H), 7.27-7.19 (m, 4H), 7.19-7.12 (m, 4H), 7.06 (t, *J* = 7.2 Hz, 2H), 3.64 (p, *J* = 7.3 Hz, 1H), 3.26 (qd, *J* = 16.7, 6.9 Hz, 2H), 3.02-2.92 (m, 2H); ^{13}C NMR (126MHz, CDCl$_3$) δ 197.8, 144.0, 139.8, 139.5, 135.6, 129.6, 129.4, 129.0, 128.6, 128.4, 127.7, 126.7, 126.3, 44.2, 43.3, 43.1; HRMS (ESI, *m/z*), calcd for $C_{22}H_{18}OCl^-$ [M-H]$^-$, 335.1052; found, 333.1050.

*4.2.20. 3,4-diphenyl-1-m-tolylbutan-1-one (**3t**)*

Yellow solid (17.5 mg, yield 56%); mp. 103-105 °C; R_f = 0.34 (petroleum ether / acetone = 20/1); FT-IR (cm^{-1}) 3027, 2360, 1683, 1102, 615; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.64 (d, *J* = 5.3 Hz, 2H), 7.37-7.27 (m, 2H), 7.28-7.23 (m, 2H), 7.21 (dd, *J* = 4.0, 2.3 Hz, 2H), 7.19-7.11 (m, 4H), 7.11-7.04 (m, 2H), 3.74-3.58 (m, 1H), 3.29 (dd, *J* = 6.9, 3.5 Hz, 2H), 2.98 (t, *J* = 6.9 Hz, 2H), 2.36 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 199.2, 144.3, 140.0, 138.4, 137.3, 133.8, 129.4, 128.7, 128.51, 128.47, 128.3, 127.8, 126.5, 126.2, 125.3, 44.4, 43.2, 43.1, 21.5; HRMS (ESI, *m/z*), calcd for $C_{23}H_{21}O^-$ [M-H]$^-$, 313.1598; found, 313.1591.

4. *one (**3u**)*

Colorless oil (18.1 mg, yield 55%); R_f = 0.23 (petroleum ether / acetone = 20/1); FT-IR (cm^{-1}) 3027, 2360, 1683, 1453, 1256, 699; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.42 (d, *J* = 7.7 Hz, 1H), 7.37 (d, *J* = 2.3 Hz, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.24-7.20 (m, 3H), 7.19-7.15 (m, 5H), 7.09-7.03 (m, 3H), 3.81 (s, 3H), 3.65 (d, *J* = 7.2 Hz, 1H), 3.41-3.18 (m, 2H), 3.07-2.90 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 198.9, 159.9, 144.2, 140.0, 138.7, 129.6, 129.4, 128.5, 128.3, 127.8, 126.6, 126.2, 120.8, 119.6, 112.3, 55.6, 44.4, 43.2, 43.1; HRMS (ESI, *m/z*), calcd for $C_{23}H_{21}O_2^-$ [M-H]$^-$, 329.1547; found, 329.1539.

*4.2.22. 3,4-diphenyl-1-p-tolylbutan-1-one (**3v**)*

White solid (16.6 mg, yield 53%); mp. 176-178 °C; R_f = 0.41 (petroleum ether / acetone = 10/1); ^{1}H NMR (500 MHz, CDCl$_3$) δ 7.75 (d, *J* = 8.2 Hz, 2H), 7.26-7.11 (m, 10H), 7.09-7.04 (m, 2H), 3.66 (p, *J* = 7.2 Hz, 1H), 3.28 (qd, *J* = 16.6, 7.0 Hz, 2H), 2.97 (ddd, *J* = 31.4, 13.5, 7.4 Hz, 2H), 2.38 (s, 3H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 198.7, 144.3, 143.8, 140.0, 134.9, 129.4, 129.3, 128.5, 128.28, 128.27, 127.8, 126.5, 126.2, 44.2, 43.2, 43.1, 21.7; HRMS (ESI, *m/z*), calcd for $C_{23}H_{23}O^+$ [M+H]$^+$, 315.1743; found, 315.1740.

*4.2.23. 1-(4-methoxyphenyl)-3,4-diphenylbutan-1-one (**3w**)*

Orange solid (27.4 mg, yield 83%); mp. 158-159 °C; R_f = 0.53 (petroleum ether / ethyl acetate = 5/1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.83 (d, *J* = 8.9 Hz, 2H), 7.24-7.10 (m, 8H), 7.10-7.02 (m, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.84 (s, 3H), 3.72-3.58 (m, 1H), 3.35-3.16 (m, 2H), 3.06-2.88 (m, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 197.6, 163.5, 144.4, 140.0, 130.43, 130.41, 129.4, 128.5, 128.3, 127.8, 126.5, 126.2, 113.8, 55.6, 43.9, 43.3, 43.1; HRMS (ESI, *m/z*), calcd for $C_{23}H_{21}O_2^-$ [M-H]$^-$, 329.1547; found, 329.1540.

*4.2.24. 1-(naphthalen-1-yl)-3,4-diphenylbutan-1-one (**3x**)*

Yellow oil (24.8 mg, yield 71%); R_f = 0.25 (petroleum ether / acetone = 20/1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 8.21-8.11 (m, 1H), 7.92 (d, *J* = 8.2 Hz, 1H), 7.87-7.76 (m, 1H), 7.60 (dd, *J* = 7.2, 1.0 Hz, 1H), 7.53-7.32 (m, 3H), 7.29-7.11 (m, 8H), 7.11-7.03 (m, 2H), 3.70 (p, *J* = 7.3 Hz, 1H), 3.47-3.28 (m, 2H), 3.01 (d, *J* = 7.5 Hz, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 203.7, 144.0, 139.9, 136.8, 134.0, 132.4, 130.1, 129.4, 128.5, 128.4, 127.9, 127.8, 127.0, 126.6, 126.5, 126.3, 125.8, 124.4, 48.0, 43.8, 43.2; HRMS (APCI, *m/z*), calcd for $C_{26}H_{23}O^+$ [M+H]$^+$, 351.1743; found, 351.1746.

*4.2.25. 3,4-diphenyl-1-(thiophen-2-yl)butan-1-one (**3y**)*

Yellow solid (20.2 mg, yield 66%); mp. 142-144 °C; R_f = 0.25 (petroleum ether / acetone = 20/1); FT-IR (cm^{-1}) 3026, 2359, 1655, 1451, 1068, 613; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.57 (dd, *J* = 7.0, 2.1 Hz, 2H), 7.27-7.11 (m, 8H), 7.10-7.02 (m, 3H), 3.64 (dd, *J* = 14.5, 7.2 Hz, 1H), 3.32-3.14 (m, 2H), 3.07-2.89 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 191.9, 144.7, 143.9, 139.8, 133.6, 131.9, 129.4, 128.5, 128.3, 128.1, 127.8, 126.6, 126.3, 45.1, 43.5, 42.9; HRMS (APCI, *m/z*), calcd for $C_{20}H_{19}OS^+$ [M+H]$^+$, 307.1151; found, 307.1151.

*4.2.26. 4-(4-fluorophenyl)-1,3-diphenylbutan-1-one (**4a**)*

Colorless solid (18.7 mg, yield 59%); mp. 122-124 °C; R_f = 0.47 (petroleum ether / acetone = 5/1); FT-IR (cm^{-1}) 3358, 2923, 1684, 1508, 1220, 747, 698; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.94-7.84 (m, 2H), 7.56 (dd, *J* = 10.4, 4.2 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 2H), 7.27 (dd, *J* = 9.2, 4.9 Hz, 2H), 7.22-7.13 (m, 3H), 7.01

.73-3.58 (m, 1H), 3.34 (dd, *J* = 6.9, 4.8 Hz, 2H), 2.98 (ddd, *J* = 21.7, 13.4, 7.3 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 198.9, 162.7, 160.3, 143.9, 137.3, 135.6, 133.2, 130.8, 130.7, 128.7, 128.5, 128.1, 127.8, 126.6, 115.1, 44.3, 43.3, 42.2; HRMS (ESI, *m/z*), calcd for $C_{22}H_{18}FO^-$ [M-H]$^-$, 317.1347; found, 317.1344.

*4.2.27. methyl 4-(4-oxo-2,4-diphenylbutyl)benzoate (**4b**)*

Yellow solid (17.1 mg, yield 48%); mp. 210-211 °C; R_f = 0.20 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 2922, 2358, 1717, 1508, 1104, 615; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.94-7.78 (m, 4H), 7.52 (dd, *J* = 4.9, 3.7 Hz, 1H), 7.42 (dd, *J* = 10.4, 4.6 Hz, 2H), 7.25-7.19 (m, 2H), 7.19-7.05 (m, 5H), 3.87 (s, 3H), 3.74-3.63 (m, 1H), 3.33 (t, *J* = 6.6 Hz, 2H), 3.03 (ddd, *J* = 21.9, 13.3, 7.4 Hz, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 198.7, 167.3, 145.5, 143.6, 137.2, 133.2, 129.6, 129.4, 128.7, 128.6, 128.2, 128.1, 127.8, 126.7, 52.1, 44.4, 43.0, 42.9; HRMS (ESI, *m/z*), calcd for $C_{24}H_{23}O_3^+$ [M+H]$^+$, 359.1642; found, 359.1638.

*4.2.28. 1,3-diphenyl-4-o-tolylbutan-1-one (**4c**)*

White solid (21.6 mg, yield 69%); mp. 164-166 °C; R_f = 0.40 (petroleum ether / acetone = 20/1); FT-IR (cm^{-1}) 3357, 2923, 2360, 1682, 1451, 1261, 750, 698; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.83 (s, 2H), 7.51 (d, *J* = 7.4 Hz, 1H), 7.40 (s, 2H), 7.21 (s, 2H), 7.18 (s, 3H), 7.13-6.91 (m, 4H), 3.70-3.55 (m, 1H), 3.35 (t, *J* = 6.5 Hz, 2H), 2.96 (ddd, *J* = 34.1, 13.6, 7.5 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 199.0, 144.5, 138.2, 137.3, 136.6, 133.0, 130.4, 130.3, 128.6, 128.5, 128.1, 127.7, 126.6, 126.4, 125.7, 44.3, 42.0, 40.7, 19.6; HRMS (ESI, *m/z*), calcd for $C_{23}H_{23}O^+$ [M+H]$^+$, 315.1743; found, 315.1737.

*4.2.29. 4-(2-methoxyphenyl)-1,3-diphenylbutan-1-one (**4d**)*

White solid (19.5 mg, yield 59%); mp. 145-147 °C; R_f = 0.27 (petroleum ether / acetone = 20/1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.81 (d, *J* = 7.3 Hz, 2H), 7.50 (t, *J* = 7.3 Hz, 1H), 7.39 (s, 2H), 7.22 (d, *J* = 6.6 Hz, 4H), 7.18-7.08 (m, 2H), 7.00-6.91 (m, 1H), 6.84-6.71 (m, 2H), 3.72 (d, *J* = 14.0 Hz, 4H), 3.29 (dd, *J* = 10.6, 7.1 Hz, 2H), 3.06-2.91 (m, 2H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 199.2, 157.8, 144.9, 137.4, 132.8, 131.2, 128.5, 128.3, 128.3, 128.1, 127.7, 127.6, 126.3, 120.3, 110.4, 55.3, 44.1, 41.6, 37.5; HRMS (ESI, *m/z*), calcd for $C_{23}H_{23}O_2^+$ [M+H]$^+$, 331.1693; found, 331.1690.

4.2.30. *1,3-diphenyl-4-m-tolylbutan-1-one (**4e**)*

Colorless oil (20.7 mg, yield 66%); R_f = 0.39 (petroleum ether / acetone = 20/1); FT-IR (cm^{-1}) 3359, 2921, 1684, 1449, 748, 697; ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.83 (d, *J* = 7.5 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.6 Hz, 2H), 7.28-7.14 (m, 5H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.01-6.81 (m, 3H), 3.65 (d, *J* = 7.2 Hz, 1H), 3.29 (t, *J* = 6.4 Hz, 2H), 2.94 (d, *J* = 7.4 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, CDCl$_3$) δ 199.1, 144.4, 139.9, 137.9, 137.4, 133.0, 130.2, 128.6, 128.5, 128.2, 128.1, 127.8, 127.0, 126.5, 126.4, 44.2, 43.1, 43.1, 21.5; HRMS (APCI, *m/z*), calcd for $C_{23}H_{23}O^+$ [M+H]$^+$, 315.1743; found, 315.1746.

*4.2.31. 4-(3-methoxyphenyl)-1,3-diphenylbutan-1-one (**4f**)*

Yellow solid (20.4 mg, yield 62%); mp. 137-139 °C; R_f = 0.24 (petroleum ether / acetone = 20/1); ^{1}H NMR (300 MHz, CDCl$_3$) δ 7.91-7.78 (m, 2H), 7.56-7.46 (m, 1H), 7.45-7.34 (m, 3H), 7.30-7.08 (m, 6H), 6.75-6.63 (m, 2H), 6.58 (d, *J* = 1.8 Hz, 1H), 3.75-3.58 (m, 4H), 3.40-3.20 (m, 2H), 3.05-2.87 (m, 2H); ^{13}C NMR (126 MHz, CDCl$_3$) δ 199.0, 159.6, 144.3, 141.5, 137.3, 133.1, 129.3, 128.7, 128.5, 128.1, 127.8, 126.6, 121.9, 114.9, 111.9, 55.2, 44.2, 43.2, 43.0; HRMS (APCI, *m/z*), calcd for $C_{23}H_{23}O_2^+$ [M+H]$^+$, 331.1693; found, 331.1695.

4.2

Light yellow solid (16.6 mg, yield 53%); mp. 145-146 °C; R_f = 0.38 (petroleum ether / acetone = 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.88-7.77 (m, 2H), 7.51 (s, 1H), 7.41 (d, *J* = 7.7 Hz, 2H), 7.27-7.14 (m, 5H), 6.99 (q, *J* = 8.0 Hz, 4H), 3.65 (s, 1H), 3.29 (t, *J* = 6.8 Hz, 2H), 2.94 (d, *J* = 7.4 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.1, 144.4, 137.3, 136.8, 135.7, 133.0, 129.3, 129.0, 128.6, 128.5, 128.1, 127.8, 126.5, 44.2, 43.2, 42.7, 21.2; HRMS (ESI, *m/z*), calcd for $C_{23}H_{21}O^-$ [M-H]$^-$, 313.1598; found, 313.1591.

*4.2.33. 4-(4-methoxyphenyl)-1,3-diphenylbutan-1-one (**4h**)*

White solid (17.4 mg, yield 53%); mp. 135-136 °C; R_f = 0.23 (petroleum ether / acetone = 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.8 Hz, 2H), 7.50 (d, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.5 Hz, 2H), 7.29-7.12 (m, 5H), 6.97 (d, *J* = 8.5 Hz, 2H), 6.74 (d, *J* = 8.5 Hz, 2H), 3.75 (s, 3H), 3.62 (s, 1H), 3.29 (dd, *J* = 6.9, 3.8 Hz, 2H), 2.92 (dd, *J* = 7.2, 2.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 158.1, 144.4, 137.3, 133.0, 132.0, 130.3, 128.6, 128.5, 128.1, 127.8, 126.5, 113.7, 55.3, 44.2, 43.3, 42.2; HRMS (ESI, *m/z*), calcd for $C_{23}H_{21}O_2^-$ [M-H]$^-$, 329.1547; found, 329.1551.

*4.2.34. 4-(3,4,5-trimethoxyphenyl)-1,3-diphenylbutan-1-one (**4i**)*

Orange solid (25.3 mg, yield 65%); mp. 138-140 °C; R_f = 0.45 (petroleum ether / acetone = 2/1); FT-IR (cm^{-1}) 2934, 2356, 1683, 1589, 1454, 1239, 1125, 750, 614; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 5.2, 3.3 Hz, 2H), 7.58-7.49 (m, 1H), 7.42 (dd, *J* = 10.3, 4.6 Hz, 2H), 7.26 (dd, *J* = 9.1, 5.4 Hz, 2H), 7.22-7.11 (m, 3H), 6.18 (s, 2H), 3.78 (d, *J* = 3.8 Hz, 3H), 3.72-3.58 (m, 6H), 3.33 (d, *J* = 6.9 Hz, 2H), 3.01-2.82 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.0, 152.9, 144.2, 137.3, 136.4, 135.4, 133.1, 128.7, 128.5, 128.1, 127.9, 126.6, 106.4, 61.0, 56.0, 44.0, 43.4, 43.0; HRMS (ESI, *m/z*), calcd for $C_{25}H_{27}O_4^+$ [M+H]$^+$, 391.1904; found, 391.1903.

*4.2.35. 4-(naphthalen-1-yl)-1,3-diphenylbutan-1-one (**4j**)*

Colorless solid (28.4 mg, yield 81%); mp. 127-129 °C; R_f = 0.23 (petroleum ether / acetone = 20/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, *J* = 8.4 Hz, 1H), 7.89-7.77 (m, 3H), 7.65 (s, 1H), 7.58-7.43 (m, 3H), 7.39 (d, *J* = 7.7 Hz, 2H), 7.27-7.19 (m, 3H), 7.16 (d, *J* = 7.2 Hz, 3H), 7.05 (s, 1H), 3.86 (s, 1H), 3.61-3.21 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 144.5, 137.3, 136.0, 134.0, 133.1, 132.3, 128.8, 128.6, 128.5, 128.1, 127.7, 127.1, 126.6, 126.1, 125.6, 125.2, 124.3, 44.8, 42.1, 40.6; HRMS (APCI, *m/z*), calcd for $C_{26}H_{23}O^+$ [M+H]$^+$, 351.1743; found, 351.1746.

*4.2.36. 1,3-diphenyl-4-(thiophen-2-yl)butan-1-one (**4k**)*

Yellow solidl (14.9 mg, yield 49%); mp. 93-95 °C; R_f = 0.33 (petroleum ether / acetone = 20/1); FT-IR (cm^{-1}) 3359, 2921, 1684, 1449, 1215, 696; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.92-7.81 (m, 2H), 7.52 (s, 2H), 7.42 (d, *J* = 7.5 Hz, 2H), 7.31-7.16 (m, 5H), 7.07 (dd, *J* = 5.1, 1.0 Hz, 1H), 6.84 (s, 1H), 6.68 (d, *J* = 3.3 Hz, 1H), 3.68 (d, *J* = 7.2 Hz, 1H), 3.34 (dd, *J* = 6.9, 1.0 Hz, 2H), 3.31-3.12 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.7, 143.8, 142.3, 137.2, 133.1, 128.8, 128.7, 128.6, 128.1, 127.8, 126.8, 125.8, 123.8, 44.3, 43.3, 36.8; HRMS (ESI, *m/z*), calcd for $C_{20}H_{17}OS^-$ [M-H]$^-$, 305.1006 ; found, 305.1008.

*4.2.37. 3-(4-methoxyphenyl)-4-(naphthalen-1-yl)-1-phenylbutan-1-one (**4l**)*

Yellow oil (20.1 mg, yield 53%); R_f = 0.19 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 3359, 2924, 1673, 1600, 1259,

H), 7.83 (d, *J* = 8.8 Hz, 3H), 7.65 (s, 1H), 7.53 (s, 3H), 7.24-7.09 (m, 5H), 7.06-6.99 (m, 1H), 6.86 (d, *J* = 8.9 Hz, 2H), 3.87 (d, *J* = 15.7 Hz, 4H), 3.64-3.19 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 163.5, 144.6, 136.1, 134.0, 132.3, 130.41, 130.36, 128.8, 128.5, 127.68, 127.65, 127.0, 126.5, 126.1, 125.6, 125.2, 124.3, 113.8, 55.6, 44.4, 42.3, 40.5; HRMS (ESI, *m/z*), calcd for $C_{27}H_{25}O_2^+$ [M+H]$^+$, 381.1849; found, 381.1846.

*4.2.38. 3-(4-phenyl)-4-(naphthalen-1-yl)-1-phenylbutan-1-one (**4m**)*

Yellow oil (25.1 mg, yield 59%); R_f = 0.25 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 3359, 2922, 1680, 1508, 1099, 777, 612; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.29-8.10 (m, 2H), 7.96-7.89 (m, 1H), 7.84 (s, 2H), 7.73-7.64 (m, 1H), 7.57 (s, 1H), 7.48 (dd, *J* = 6.6, 3.0 Hz, 5H), 7.38-7.31 (m, 1H), 7.25 (s, 7H), 7.10-7.02 (m, 1H), 3.96-3.83 (m, 1H), 3.47 (d, *J* = 1.5 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.7, 144.2, 136.6, 135.9, 134.04, 133.99, 132.4, 132.2, 130.1, 128.9, 128.6, 128.4, 127.82, 127.75, 127.69, 127.2, 127.1, 126.7, 126.5, 126.1, 125.8, 125.6, 125.3, 124.4, 124.2, 48.5, 42.8, 40.6; HRMS (APCI, *m/z*), calcd for $C_{32}H_{27}O^+$ [M+H]$^+$, 427.2056; found, 427.2053.

*4.2.39. 4-(naphthalen-1-yl)-1-phenyl-3-(thiophen-2-yl)butan-1-one (**4n**)*

Yellow oil (26.1 mg, yield 73%); R_f = 0.23 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 2924, 1659, 1415, 1235, 727; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.27-8.16 (m, 1H), 7.88-7.77 (m, 1H), 7.72-7.61 (m, 1H), 7.58 (d, *J* = 4.4 Hz, 4H), 7.29-7.18 (m, 4H), 7.17 (s, 2H), 7.04 (s, 2H), 3.92-3.76 (m, 1H), 3.33 (d, *J* = 6.8 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.9, 144.6, 144.2, 135.9, 134.0, 133.6, 132.2, 131.9, 128.8, 128.5, 128.1, 127.7, 127.1, 126.7, 126.2, 125.6, 125.2, 124.2, 45.5, 42.4, 40.4; HRMS (ESI, *m/z*), calcd for $C_{24}H_{21}OS^+$ [M+H]$^+$, 357.1308; found, 357.1304.

*4.2.40. 1-(4-methoxyphenyl)-3-phenyl-4-o-tolylbutan-1-one (**4o**)*

Yellow solid (26.2 mg, yield 76%); mp. 121-123 °C; R_f = 0.39 (petroleum ether / acetone = 5/1); FT-IR (cm^{-1}) 2932, 1675, 1600, 1259, 1170, 1029, 834, 700; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.9 Hz, 2H), 7.22 (d, *J* = 7.0 Hz, 2H), 7.16 (d, *J* = 7.1 Hz, 3H), 7.11-6.92 (m, 4H), 6.88 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 3.62 (s, 1H), 3.41-3.20 (m, 2H), 2.95 (dd, *J* = 25.1, 7.5 Hz, 2H), 2.24 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 163.5, 144.6, 138.2, 136.6, 130.40, 130.35, 130.27, 128.5, 127.7, 126.5, 126.3, 125.7, 113.8, 55.6, 43.9, 42.2, 40.6, 19.5; HRMS (ESI, *m/z*), calcd for $C_{24}H_{25}O_2^+$ [M+H]$^+$, 345.1849; found, 345.1842.

*4.2.41. 4-(2-methoxyphenyl)-1-(4-methoxyphenyl)-3-phenylbutan-1-one (**4p**)*

Colorless solid (25.1 mg, yield 70%); mp. 138-139 °C; R_f = 0.31 (petroleum ether / acetone = 5/1); FT-IR (cm^{-1}) 2922, 1675, 1600, 1493, 1245, 1171, 1029, 754, 700; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.9 Hz, 2H), 7.25-7.07 (m, 6H), 6.95 (s, 1H), 6.86 (d, *J* = 8.9 Hz, 2H), 6.79 (dd, *J* = 7.4, 2.6 Hz, 2H), 3.84 (s, 3H), 3.70 (m, 4H), 3.24 (dd, *J* = 12.1, 7.1 Hz, 2H), 2.98 (d, *J* = 7.3 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.8, 163.3, 157.8, 145.0, 131.1, 130.5, 130.4, 128.4, 128.3, 127.7, 127.5, 126.2, 120.3, 113.6, 110.3, 55.5, 55.3, 43.8, 41.8, 37.4; HRMS (ESI, *m/z*), calcd for $C_{24}H_{25}O_3^+$ [M+H]$^+$, 361.1798; found, 361.1790.

*4.2.42. 1-(4-methoxyphenyl)-3-phenyl-4-m-tolylbutan-1-one (**4q**)*

Yellow solid (24.4 mg, yield 71%); mp. 134-136 °C; R_f = 0.36 (petroleum ether / acetone = 5/1); FT-IR (cm^{-1}) 3360, 2921, 1675, 1601, 1259, 1170, 700, 612; ^{1}H NMR (300 MHz, $CDCl_3$) δ

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(dd, J = 10.8, 3.9 Hz, 5H), 3.85 (s, 3H), 3.64 (s, 1H), 3.24 (d, J = 1.2 Hz, 2H), 2.93 (d, J = 7.4 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 163.4, 144.5, 139.9, 137.8, 130.5, 130.4, 130.2, 128.4, 128.1, 127.8, 126.9, 126.4, 113.7, 55.6, 43.8, 43.3, 43.1, 21.5; HRMS (ESI, *m/z*), calcd for $C_{24}H_{25}O_2^+$ $[M+H]^+$, 345.1849; found, 345.1840.

*4.2.43. 4-(3-methoxyphenyl)-1-(4-methoxyphenyl)-3-phenylbutan-1-one (**4r**)*

Yellow solid (24.8 mg, yield 69%); mp. 129-131 °C; R_f = 0.28 (petroleum ether / acetone = 5/1); FT-IR (cm^{-1}) 2934, 1674, 1600, 1259, 1169, 1031, 833, 699; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 8.9 Hz, 2H), 7.20 (d, J = 7.9 Hz, 6H), 6.88 (d, J = 8.9 Hz, 2H), 6.73-6.64 (m, 2H), 6.61-6.54 (m, 1H), 3.85 (s, 3H), 3.70 (m, 4H), 3.25 (s, 2H), 3.04-2.86 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.5, 163.5, 159.5, 144.4, 141.6, 130.4, 129.2, 128.5, 127.8, 126.5, 121.8, 114.9, 113.8, 111.9, 55.6, 55.2, 43.9, 43.2, 43.1; HRMS (ESI, *m/z*), calcd for $C_{24}H_{25}O_3^+$ $[M+H]^+$, 361.1798; found, 361.1791.

*4.2.44. 1-(4-methoxyphenyl)-3-phenyl-4-p-tolylbutan-1-one (**4s**)*

Yellow solid (23.4 mg, yield 68%); mp. 145-147 °C; R_f = 0.35 (petroleum ether / acetone = 5/1); FT-IR (cm^{-1}) 2922, 1675, 1600, 1259, 1170, 1028, 700; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.83 (d, J = 8.9 Hz, 2H), 7.22 (d, J = 21.7 Hz, 6H), 6.98 (d, J = 9.0 Hz, 3H), 6.89 (s, 2H), 3.85 (s, 3H), 3.63 (s, 1H), 3.23 (s, 2H), 2.93 (d, J = 6.7 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.6, 163.4, 144.5, 136.9, 135.6, 130.5, 130.4, 129.3, 129.0, 128.4, 127.8, 126.4, 113.7, 55.6, 43.9, 43.3, 42.7, 21.1; HRMS (ESI, *m/z*), calcd for $C_{24}H_{25}O^+$ $[M+H]^+$, 345.1849; found, 345.1841.

*4.2.45. 1,4-bis(4-methoxyphenyl)-3-phenylbutan-1-one (**4t**)*

Yellow solid (21.5 mg, yield 60%); mp. 174-176 °C; R_f = 0.28 (petroleum ether / acetone = 5/1); FT-IR (cm^{-1}) 2930, 1674, 1602, 1510, 1250, 1170, 1031, 613; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.84 (d, J = 8.9 Hz, 2H), 7.19 (dd, J = 18.6, 7.2 Hz, 4H), 6.96 (d, J = 8.5 Hz, 3H), 6.88 (d, J = 8.8 Hz, 2H), 6.74 (d, J = 8.6 Hz, 2H), 3.86 (s, 3H), 3.75 (s, 3H), 3.67-3.54 (m, 1H), 3.34-3.14 (m, 2H), 3.00-2.81 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.7, 163.5, 161.2, 158.0, 144.5, 130.4, 130.3, 128.4, 127.8, 126.4, 114.4, 113.74, 113.66, 55.6, 55.3, 43.8, 43.5, 42.2; HRMS (ESI, *m/z*), calcd for $C_{24}H_{25}O_3^+$ $[M+H]^+$, 361.1798; found, 361.1791.

*4.2.46. 1-(4-methoxyphenyl)-4-(naphthalen-1-yl)-3-phenylbutan-1-one (**4u**)*

Yellow oil (26.5 mg, yield 70%); R_f = 0.18 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 2930, 2360, 1682, 1511, 1248, 778; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.28-8.14 (m, 1H), 7.86-7.77 (m, 3H), 7.66 (s, 1H), 7.50 (dd, J = 11.6, 7.7 Hz, 3H), 7.40 (d, J = 7.7 Hz, 2H), 7.25 (s, 2H), 7.07 (d, J = 8.8 Hz, 2H), 6.76 (d, J = 8.7 Hz, 2H), 3.80 (d, J = 33.2 Hz, 4H), 3.36 (d, J = 6.7 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.3, 158.2, 137.3, 136.6, 136.1, 134.0, 133.0, 132.3, 130.4, 128.8, 128.7, 128.61, 128.55, 128.1, 127.7, 127.0, 126.1, 125.6, 125.3, 124.3, 113.9, 55.3, 45.0, 41.4, 40.7; HRMS (ESI, *m/z*), calcd for $C_{27}H_{23}O_2^-$ $[M-H]^-$, 379.1704; found, 379.1703.

*4.2.47. 4-(naphthalen-1-yl)-3-phenyl-1-(thiophen-2-yl)butan-1-one (**4v**)*

Yellow oil (26.6 mg, yield 75%); R_f = 0.33 (petroleum ether / acetone = 10/1); FT-IR (cm^{-1}) 2923, 1683, 1213, 1077, 778, 614; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 (d, J = 8.4 Hz, 1H), 7.85 (dd, J = 7.1, 5.7 Hz, 3H), 7.70 (d, J = 8.2 Hz, 1H), 7.52 (dd, J =

7.11

(dd, J = 12.2, 7.9 Hz, 2H), 6.82 (dd, J = 5.0, 3.5 Hz, 1H), 6.67 (d, J = 3.0 Hz, 1H), 4.31-4.12 (m, 1H), 3.42 (dd, J = 10.2, 6.8 Hz, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.6, 148.1, 137.1, 135.6, 134.0, 133.2, 132.2, 128.9, 128.7, 128.2, 127.7, 127.3, 126.7, 126.3, 125.7, 125.3, 124.4, 124.1, 123.2, 45.8, 41.4, 37.6; HRMS (ESI, *m/z*), calcd for $C_{24}H_{19}OS^-$ $[M-H]^-$, 355.1162; found, 355.1162.

*4.3. General procedure for the synthesis of compounds **7***

A Schlenk tube (10 mL) equipped with a magnetic stir bar was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (1.8 mg, 0.003 mmol, 1.5 mol%), PPh_3 (3.1 mg, 0.012 mmol, 6 mol%), K_3PO_4 (31.8 mg, 0.15 mmol, 0.75 equiv.), TBAC (11.1 mg, 0.04 mmol, 0.2 equiv.) and N-benzylideneaniline (0.2 mmol, 1.0 equiv.). The reaction system was then protected with an argon atmosphere. After that, THF (50 μL) was added and the reaction system was placed at room temperature. After stirring for 10 min, hydrazone (0.3 mmol, 1.5 equiv.) was added to the system. THF was removed *in vacuo* and argon was filled into the reaction system. Then, distilled water (0.2 mL) was added to the reaction system and heated to 70 °C. After stirring at 70 °C for 1.5 h, 3 mL water was added. After cooling to room temperature, 2 mL HCl solution (3 M) was added to the reaction system. The mixture was extracted with ethyl acetate (3x5 mL). The combined organic layers was washed with water (5 mL) and then dried over Na_2SO_4. The organic layers were concentrated and the resulting residue was purified by preparative TLC on silica gel to afford the product.

*4.3.1. 1,2-diphenylethyl)benzenamine (**7a**)*

Colorless solid (38.7 mg, yield 71%); mp. 58-60 °C; R_f = 0.54 (petroleum ether / dichloromethane = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35-7.26 (m, 5H), 7.25-7.19 (m, 3H), 7.12 (d, J = 6.4 Hz, 2H), 7.03 (d, J = 8.4 Hz, 2H), 6.66-6.56 (m, 1H), 6.45 (d, J = 7.7 Hz, 2H), 4.65-4.50 (m, 1H), 4.24-3.99 (m, 1H), 3.13 (dd, J = 14.0, 5.7 Hz, 1H), 3.00 (dd, J = 14.0, 8.2 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.4, 143.6, 137.8, 129.4, 129.2, 128.71, 128.68, 127.2, 126.9, 126.6, 117.6, 113.8, 59.4, 45.3; HRMS (ESI, *m/z*), calcd for $C_{20}H_{20}N^+$ $[M+H]^+$, 274.1590; found, 274.1587.

*4.3.2. N-(2-(2-methoxyphenyl)-1-phenylethyl)benzenamine (**7b**)*

Colorless solid (28.4 mg, yield 47%); mp. 133-136 °C; R_f = 0.45 (petroleum ether / dichloromethane = 1/1); FT-IR (cm^{-1}) 3405, 2921, 2361, 1601, 1494, 1242, 749, 697; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.38 (d, J = 7.2 Hz, 2H), 7.30 (t, J = 7.3 Hz, 2H), 7.24 (s, 2H), 7.01 (t, J = 7.8 Hz, 3H), 6.92-6.80 (m, 2H), 6.57 (t, J = 7.3 Hz, 1H), 6.40 (d, J = 7.7 Hz, 2H), 4.71 (s, 1H), 4.54 (dd, J = 8.7, 4.9 Hz, 1H), 3.88 (s, 3H), 3.10 (dd, J = 13.7, 8.8 Hz, 1H), 3.01 (dd, J = 13.8, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.7, 147.9, 144.4, 131.2, 129.1, 128.6, 128.1, 127.04, 126.99, 126.5, 120.9, 116.9, 113.4, 110.6, 59.6, 55.5, 40.1; HRMS (ESI, *m/z*), calcd for $C_{21}H_{22}NO^+$ $[M+H]^+$, 304.1696; found, 304.1702.

*4.3.3. N-(1-phenyl-2-p-tolylethyl)benzenamine (**7c**)*

Colorless oil (28.1 mg, yield 49%); R_f = 0.53 (petroleum ether / dichloromethane = 2/1); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41-7.16 (m, 5H), 7.13-6.92 (m, 6H), 6.61 (t, J = 7.3 Hz, 1H), 6.44 (d, J = 7.5 Hz, 2H), 4.65-4.44 (m, 1H), 4.10 (s, 1H), 3.09 (dd, J = 14.0, 5.5 Hz, 1H), 2.94 (dd, J = 14.0, 8.3 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.5, 143.7, 136.4, 134.7, 129.4, 129.2, 129.1, 128.7, 127.7, 126.6, 117.5, 113.8, 59.3, 44.9, 21.2; HRMS (ESI, *m/z*), calcd for $C_{21}H_{22}N^+$ $[M+H]^+$, 288.1747; found, 288.1747.

4.4.

A Schlenk tube (10 mL) equipped with a magnetic stir bar was charged with $[Ru(p\text{-cymene})Cl_2]_2$ (1.8 mg, 0.003 mmol, 1.5 mol%), PPh_3 (3.1 mg, 0.012 mmol, 6 mol%), K_3PO_4 (31.8 mg, 0.15 mmol, 0.75 equiv.), TBAC (11.1 mg, 0.04 mmol, 0.2 equiv.) and ketones (0.2 mmol, 1.0 equiv.). The reaction system was then protected with an argon atmosphere. After that, THF (50 μL) was added and the reaction system was placed at room temperature. After stirring for 10 min, hydrazone (0.3 mmol, 1.5 equiv.) was added. THF was removed *in vacuo* and argon was filled into the reaction system. Then, distilled water (0.2 mL) was added to the reaction mixture and heated to 70 ^oC. The reaction progress was followed by TLC and the reaction time was determined (3-18 hours). The reaction mixture was diluted with 3 mL of water. After cooling to room temperature, 2 mL HCl solution (3 M) was added. The reaction mixture was extracted with ethyl acetate (3x5 mL). The combined organic layers were washed with water (5 mL) and then dried over Na_2SO_4. The organic layers were concentrated and the resulting residue was purified by preparative TLC on silica gel to afford the product.

*4.4.1. 1,2-diphenylpropan-2-ol (**8a**)*

Colorless oil (30.1 mg, yield 71%); $R_f = 0.32$ (petroleum ether / acetone = 10/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.40 (dd, J = 5.4, 3.4 Hz, 2H), 7.37-7.29 (m, 2H), 7.29-7.15 (m, 5H), 7.06-6.91 (m, 2H), 3.13 (d, *J* = 13.3 Hz, 1H), 3.02 (d, *J* = 13.3 Hz, 1H), 1.85 (s, 1H), 1.56 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 136.9, 130.7, 128.2, 126.78, 126.77, 125.1, 74.6, 50.6, 29.5; HRMS (APCI, *m/z*), calcd for $C_{15}H_{15}O^+$ $[M\text{-}H]^+$, 211.1117; found, 211.1116.

*4.4.2. 2-(2-fluorophenyl)-1-phenylpropan-2-ol (**8b**)*

Yellow oil (19.3 mg, yield 42%); $R_f = 0.46$ (petroleum ether / acetone = 10/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.32 (ddd, J = 8.2, 6.4, 1.7 Hz, 1H), 7.28-7.11 (m, 4H), 7.11-6.92 (m, 4H), 3.33 (d, *J* = 13.4 Hz, 1H), 3.11 (d, *J* = 13.4 Hz, 1H), 2.11 (t, *J* = 5.2 Hz, 1H), 1.64 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.6, 158.7, 136.7, 134.1, 134.0, 130.6, 128.9, 128.8, 128.3, 127.6, 127.5, 126.9, 124.13, 124.11, 116.1, 115.9, 73.71, 73.68, 48.14, 48.10, 28.38, 28.35; HRMS (APCI, *m/z*), calcd for $C_{15}H_{14}F^+$ $[M\text{-}O\text{-}H]^+$, 213.1074; found, 213.1076.

*4.4.3. 2-(4-bromophenyl)-1-phenylpropan-2-ol (**8c**)*

Orange oil (33.1 mg, yield 57%); $R_f = 0.34$ (petroleum ether / acetone = 10/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.48-7.38 (m, 2H), 7.30-7.16 (m, 5H), 7.04-6.93 (m, 2H), 3.09 (d, *J* = 13.3 Hz, 1H), 2.99 (d, *J* = 13.3 Hz, 1H), 1.84 (s, 1H), 1.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.8, 136.4, 131.2, 130.7, 128.3, 127.1, 127.0, 120.7, 74.4, 50.5, 29.6; HRMS (APCI, *m/z*), calcd for $C_{15}H_{14}BrO^-$ $[M\text{-}H]^-$, 289.0234; found, 289.0240.

*4.4.4. 2-(3-methoxyphenyl)-1-phenylpropan-2-ol (**8d**)*

Orange oil (24.1 mg, yield 50%); $R_f = 0.29$ (petroleum ether / acetone = 10/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.26-7.17 (m, 4H), 7.06-6.93 (m, 4H), 6.78 (ddd, J = 8.2, 2.4, 0.9 Hz, 1H), 3.78 (s, 3H), 3.12 (d, *J* = 13.3 Hz, 1H), 3.00 (d, *J* = 13.3 Hz, 1H), 1.86 (s, 1H), 1.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.6, 149.6, 136.8, 130.7, 129.2, 128.2, 126.8, 117.6, 112.0, 111.2, 74.5, 55.4, 50.5, 29.6; HRMS (EI, *m/z*), calcd for $C_{16}H_{18}O_2^+$ $[M]^+$, 242.1307; found, 242.1306.

*4.4.5. 1-phenyl-2-p-tolylpropan-2-ol (**8e**)*

Orange oil (18.5 mg, yield 41%); $R_f = 0.38$ (petroleum ether / acetone = 10/1); ^1H NMR (300 MHz, $CDCl_3$) δ 7.27 (t, J = 6.2 Hz, 2H), 7.25-7.18 (m, 3H), 7.14 (t, J = 8.4 Hz, 2H), 7.04-6.95), 2.34 (s, 3H), 1.81 (s, 1H), 1.54 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 144.8, 137.0, 136.3, 130.8, 128.9, 128.2, 126.7, 125.0, 74.5, 50.6, 29.6, 21.1; HRMS (APCI, *m/z*), calcd for $C_{16}H_{17}^+$ $[M\text{-}O\text{-}H]^+$, 209.1325; found, 209.1328.

*4.5. General procedure for the synthesis of compounds **9***

A Schlenk tube (10 mL) equipped with a magnetic stir bar was charged with 4-(3,4,5-trimethoxyphenyl)-1,3-diphenylbutan-1-one (**4i**) (39 mg, 0.1 mmol), $AlCl_3$ (120 mg, 0.9 mmol, 9 equiv.). After that, acetonitrile (2 mL) was added and heated to 60 ^oC. The reaction system was stirred at 60 ^oC for 12 hours. After cooling to room temperature, the reaction mixture was diluted with 3 mL of water. 2 mL HCl solution (3 M) was added and the reaction mixture was extracted with ethyl acetate (3x5 mL). The combined organic layers were washed with water (5 mL) and then dried over Na_2SO_4. The organic layers were concentrated and the resulting residue was purified by preparative TLC on silica gel to afford the product.

*4.5.1. 1,2-dihydro-5,6,7-trimethoxy-2,4-diphenylnaphthalene (**9a**)*

Colorless solid (25.3 mg, 68%); mp. 74-76 ^oC; $R_f = 0.22$ (petroleum ether / dichloromethane = 1:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.18 (m, 10H), 6.57 (s, 1H), 6.02 (d, *J* = 3.5 Hz, 1H), 3.87 (s, 3H), 3.80 (s, 3H), 3.69 (ddd, *J* = 12.3, 6.1, 3.6 Hz, 1H), 3.28 (s, 3H), 3.03-2.85 (m, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.73, 151.23, 144.61, 143.11, 141.46, 138.50, 133.60, 132.92, 128.64, 127.80, 127.69, 127.12, 126.66, 126.41, 121.25, 107.26, 61.08, 60.81, 56.13, 41.63, 39.20; HRMS (APCI, *m/z*), calcd for $C_{25}H_{25}O_3^+$ $[M+H]^+$, 373.1798; found, 373.1795.

*4.5.2. 1,2,3-trimethoxy-6,8-diphenylnaphthalene (**9b**)*

Light yellow solid (4.4 mg, 12%); mp. 67-69 ^oC; $R_f = 0.26$ (petroleum ether / dichloromethane = 1:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 1.7 Hz, 1H), 7.71 (d, *J* = 7.3 Hz, 2H), 7.51-7.29 (m, 9H), 7.10 (s, 1H), 4.02 (s, 3H), 3.91 (s, 3H), 3.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.26, 149.78, 144.53, 142.53, 140.75, 139.00, 137.38, 132.45, 129.12, 128.95, 127.52, 127.42, 127.30, 127.00, 126.23, 124.49, 121.77, 103.63, 61.27, 60.73, 55.98; HRMS (APCI, *m/z*), calcd for $C_{25}H_{23}O_3^+$ $[M+H]^+$, 371.1642; found, 371.1639.

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