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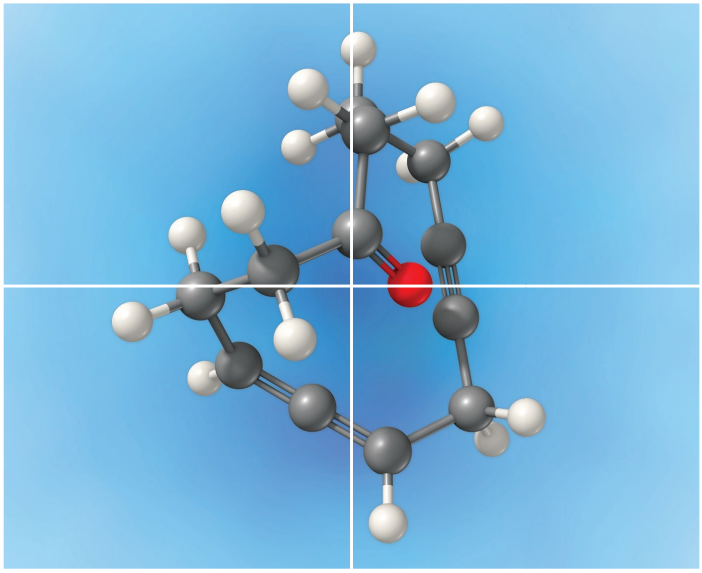

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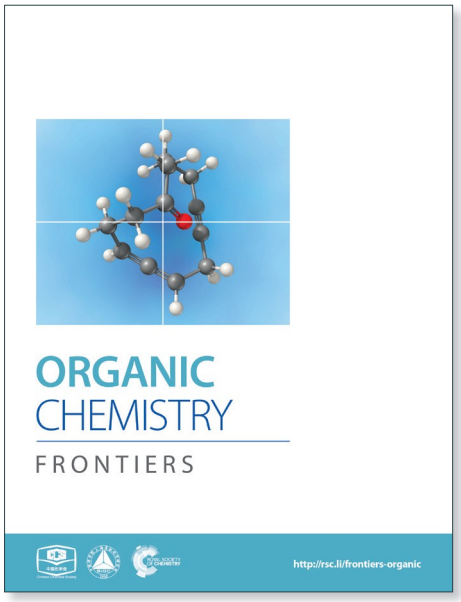

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ARTICLE TYPE

Catalyst-Free Cross-Coupling of *N*-Tosylhydrazones with Chromium(0) Fischer Carbene Complexes: A New Approach to Diarylethanone

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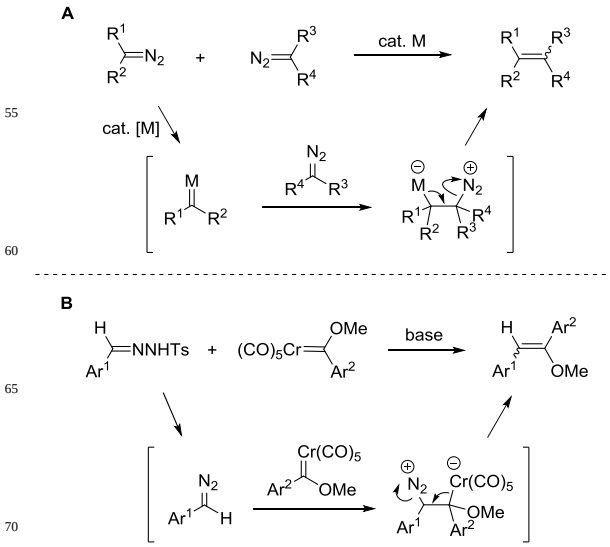
Cross-coupling of *N*-tosylhydrazones with chromium Fischer carbene complexes under catalyst-free conditions has been developed. This protocol is featured by taking advantage of stable carbene complexes and reactive diazo compounds, which are *in situ* generated from *N*-tosylhydrazones. Hydrolysis of the initially formed methyl enolate products, the diarylethnone derivatives could be obtained in moderate to good yields.

Introduction

Diazo compounds have been widely employed as carbene sources in transition-metal-catalyzed reactions.[1] Through dediazoniation of the diazo substrates in the presence of transition metals, the metal carbene species could be generated, which undergo various synthetically useful transformations.[2] In this area, the carbene dimerization is a ubiquitous process, which is generally regarded as an annoying side reaction pathway. Nevertheless, the carbene dimerization provides an alternative way for the synthesis of functionalized alkenes. Recently, efforts have been devoted into this reaction, but only a few successful examples have been reported for intermolecular carbene dimerization of two different diazo substrates.[3-5] The apparent problems are the inevitable competition of homo-coupling and the stereoselectivity of the generated double bond. By judiciously adjusting the reactivity of two different diazo substrates, Davies[4c] and Sun[4d] have recently realized selective intermolecular carbene dimerization, affording tri-substituted and tetra-substituted alkenes. Although high selectivity has been achieved in these systems, the diazo substrates are largely restricted to specific structures in order to discriminate their reactivities. In contrast, the intramolecular carbene dimerization of diazo compounds or their surrogates *N*-tosylhydrazones, has been developed into useful methods for the construction of cyclic compounds.[6]

The mechanism of the transition-metal-catalyzed carbene dimerization of diazo compounds is well established.[4c,d] In this process, the transient reactive metal carbene species is firstly formed and subsequently reacts with another diazo substrate (Scheme 1, A). Notably, in the process of metal carbene generation the originally electron-rich carbon to which the diazo group is attached, undergoes reversal of polarity. Thus the electron-deficient carbenic carbon centre of metal carbene can accept the nucleophilic attack by another diazo substrate.

On the other hand, chromium Fischer carbene complexes have been studied extensively over the decades and a number of synthetically useful transformations have been developed.[7] The carbenic centre in chromium Fischer carbene complexes is electron-deficient in nature, which is comparable to the metal carbene intermediates generated in transition-metal-catalyzed reaction of diazo compounds. It is thus conceivable the reaction



Scheme 1 The olefin formation through carbene dimerization.

of nucleophilic diazo compounds with Fischer carbene complexes may generate C=C double bonds. Indeed such transformation has been reported by Casey and co-workers with tungsten carbene complexes.[11a] However, this reaction has not been developed into a synthetically useful transformation due to the limited scope of diazoalkane substrates (only the reactions with diazomethane and diazopropane were reported). Besides, Barluenga and co-workers reported the reaction of chromium Fischer carbene complex with ethyl diazoacetates.[11b]

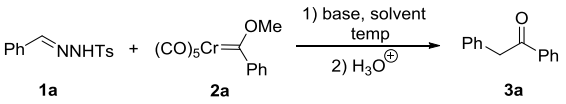
The *N*-tosylhydrazones have been well-established as the precursors for diazo compounds, especially for those without the stabilization of electron-withdrawing substituents.[8] In this context, a series of synthetically useful transformations have been recently developed using *N*-tosylhydrazones as the coupling partners.[9] We report herein the cross-coupling of *N*-tosylhydrazones with chromium Fischer carbene complexes under catalyst-free conditions. The reaction affords olefins, which are further hydrolyzed to diarylethanones.[10] In comparison with the above-mentioned carbene dimerization of two diazo compounds, this

process is featured by employing stable chromium Fischer carbene complexes and reactive diazo compounds, which are *in situ* generated from *N*-tosylhydrazones under basic conditions (Scheme 1, B).

Results and Discussion

We initiated our investigation with *N*-tosylhydrazone **1a** and chromium Fischer carbene complex **2a** as the model substrates. The effects of bases, solvents and temperatures were systematically examined. Among all the bases tested, we found that the best result was obtained with K_3PO_4 (entries 1-3). Then, the effect of solvents was examined. However, the originally used toluene was proved to be the best solvent for the reaction (entries 4-6). Only trace amount of the desired product could be detected with MeCN as the solvent (entry 6). Next, we turned our attention to the reaction temperature, the product **3a** was obtained in 61% and 70% yields at 80 °C and 100 °C, respectively (entries 9, 10). As illustrated in entry 7 and entry 8, increasing the amount of substrate **1a** could improve the yield of the corresponding product. Finally, with K_3PO_4 as the base and toluene as the solvent, the best reaction condition was established (entry 8). Under the optimized reaction conditions, the desired product **3a** was isolated in 78% yield.

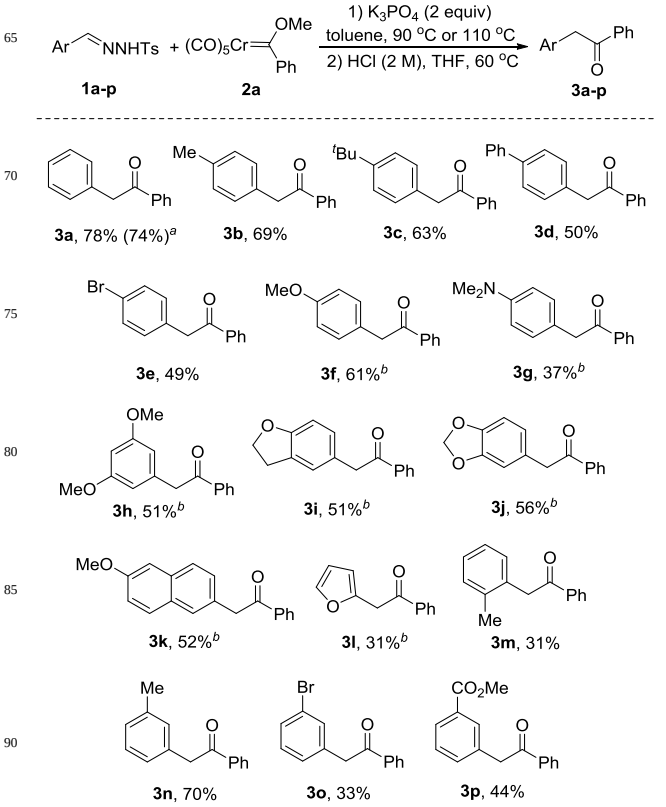
Table 1. Optimization of reaction conditions[a]



entry	solvent	base	*T* (°C)	yield (%)[b]
1	toluene	Cs_2CO_3	90	54
2	toluene	K_2CO_3	90	71
3	toluene	K_3PO_4	90	75
4	dioxane	K_3PO_4	90	53
5	DCE	K_3PO_4	90	65
6	MeCN	K_3PO_4	90	<5
7[c]	toluene	K_3PO_4	90	80(68)[d]
8[e]	toluene	K_3PO_4	90	90(78)[d]
9	toluene	K_3PO_4	80	61
10	toluene	K_3PO_4	100	70

[a]Reaction conditions: **1a** (0.20 mmol), **2a** (0.20 mmol), base (0.30 mmol) in solvent (2 mL) at 90 °C for 1.5 h. The crude product was dissolved in THF (2 mL) and HCl (1 mL, 2 M) at 60 °C for 1 h. [b]Yield determined by ^{1}H NMR analysis using mesitylene as the internal standard. [c]**1a** (0.24 mmol) was used. [d]Isolated yield. [e]**1a** (0.30 mmol), K_3PO_4 (0.40 mmol) and toluene (3 mL) were used.

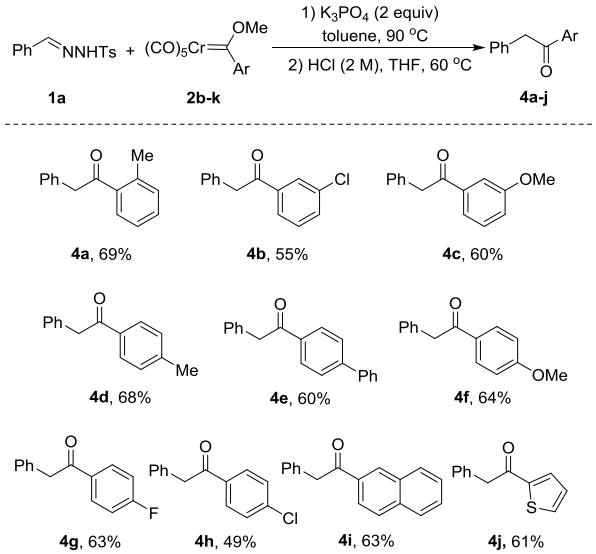
With the optimized reaction conditions established, we then turned our attention to the scope of this reaction. As shown in Scheme 2, a variety of *N*-tosylhydrazones were subjected to the reaction with chromium Fischer carbene complex **2a**. In all the cases, the reaction afforded the corresponding products in moderate to good yields. Similarly, the desired product **3a** was obtained in 74% yield, when pentacarbonyl[(ethoxy)(phenyl)carbene]chromium(0) **2a'** was selected as the reactant. Substituents of different electronic nature in the *para*-position of *N*-tosylhydrazones **1a-g** were all tolerated under the optimized reaction conditions (**3b-g**). It should be noted that elevated temperature was needed for electron-rich substrates (**3f-l**). The reaction with *N*-tosylhydrazones bearing multi-substituted aromatic ring also afforded the desired products (**3h-j**) in moderate yields. Gratifyingly, naphthyl-substituted substrate also worked in this reaction, giving the product **3k** in 52% yield. Hetero-aromatics could equally be accommodated in this protocol, albeit in low yield (**3l**). Additionally, the process was slightly hampered by *ortho* substitution (**3m**). This result indicates that the reaction is influenced by steric hindrance. Our protocol could also be extended to the substrates with *meta*-substituents (**3n-p**). It is noteworthy that *N*-tosylhydrazones bearing electron-withdrawing groups gave the corresponding products in low to moderate yields (**3e**, **3o**, **3p**). The decreased nucleophilicity may account for this phenomenon.[11a]



Scheme 2 Reaction scope of *N*-tosylhydrazones. Unless otherwise noted, reaction conditions: **1a-p** (0.30 mmol), **2a** (0.20 mmol), K_3PO_4 (0.40 mmol), toluene (3 mL), 90 °C under N_2 for 1.5 h. The crude product was dissolved in THF (2 mL), HCl (1 mL, 2 M), 60 °C, 1 h. All the yields refer to isolated yields after silica gel column chromatography. [a]Pentacarbonyl[(ethoxy)(phenyl)carbene]chromium(0) (**2a'**) was used as substrate. [b]The reaction was carried out at 110 °C.

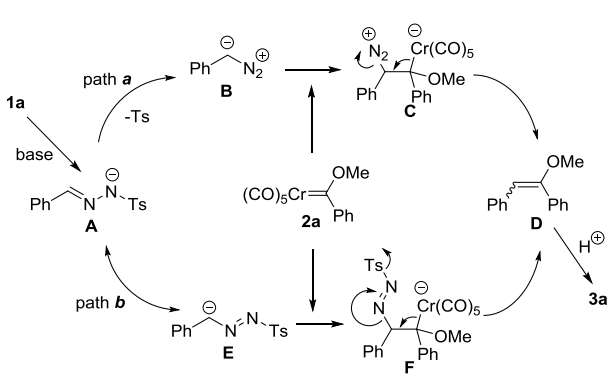
Encouraged by the results with various *N*-tosylhydrazones, we next turned our attention to explore the scope of chromium Fischer carbene complexes. Gratifyingly, the substrate **2b** with an *ortho*-substituted group was also reactive in this protocol, affording the product **4a** in 69% yield. The reaction proceeded smoothly in the presence of electron-withdrawing or electron-donating substituents at the *meta*-position of chromium Fischer carbene complexes (**4b**, **4c**). As clearly depicted in **4d-h**, the electronic nature of substituents has no significant impact on the outcome. It is notable that polycyclic aromatic and heteroaryl substrates **2j** and **2k** were reacted smoothly to deliver the

corresponding products **4i** and **4j** in 63% and 61% yields, respectively.



Scheme 3. Reaction scope of chromium carbene complexes. Unless otherwise noted, reaction conditions: **1a** (0.30 mmol), **2b**-**k** (0.20 mmol), K_3PO_4 (0.40 mmol), toluene (3 mL), 90 °C under N_2 for 1.5 h. The crude product was dissolved in THF (2 mL), HCl (1 mL, 2 M), 60 °C, 1 h. All the yields refer to isolated yields.

According to our understanding of diazo chemistry and the literature precedents,[11] a plausible mechanism was proposed as shown in Scheme 4. Initially, the intermediate **A** is generated through deprotonation from *N*-tosylhydrazone. In principle, two reaction pathways are possible from intermediate **A** leading to the final product. For path *a*, the diazo compound intermediate **B** is formed. Subsequently, the reaction proceeds with nucleophilic attack of diazo carbon atom to electron deficient carbenic carbon center. Then, the olefin **D** is formed with the release of N_2 and elimination of chromium carbonyl fragment. In path *b*, from the anion **E**, which is the resonance structure of the intermediate **A**, a similar nucleophilic attack occurs to form **F**. The release of Ts group and N_2 triggers the elimination of $Cr(CO)_5$ fragment to afford product **D**. Since **D** is labile in silica gel chromatography, it is converted into arylketone **3a** through hydrolysis of the crude product with acid.



Scheme 4. Proposed reaction mechanism

Conclusions

In conclusion, we have developed a catalyst-free strategy to the synthesis of diarylethanones from *N*-tosylhydrazones and chromium Fischer carbene complexes. In contrast to previous carbene dimerization of two diazo substrates, this reaction utilizes a stable chromium Fischer carbene complexes as reaction partners; while the highly reactive diazo substrates are generated *in situ* from *N*-tosylhydrazones under basic conditions.[8] This protocol is featured by simple reaction conditions and wide substrate tolerance. Further exploration of chromium Fischer carbene complexes in the development of novel synthetic methods are currently underway in our laboratory and the results will be reported in due course.

Experimental Section

General. All reactions were performed under a nitrogen atmosphere in a Schlenk reaction flask. All solvents were distilled under a nitrogen atmosphere prior to use. 1,4-Dioxane and toluene were dried over Na with benzophenone-ketyl intermediate as indicator. MeCN and DCE were dried over CaH_2. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^1H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz with Brucker ARX 400 spectrometer. Chemical shifts were reported in ppm using tetramethylsilane as internal standard when $CDCl_3$ was used as the solvent. IR spectra were recorded with a Thermo Electron Corporation Nicolet AVATAR 330 FT-IR spectrometer. HRMS data were obtained on a VG ZAB-HS mass spectrometer, Brucker Apex IV FTMS spectrometer. The chromium(0) Fischer carbene complexes were prepared according to the literature procedure: **2a**,[12a] **2b**,[12a] **2c**,[12b] **2d**,[12a] **2e**,[12b] **2g**,[12b] **2h**,[12b], **2i**,[12b] **2j**,[12c] **2k**.[12d]

*Pentacarbonyl[(4-biphenyl)(methoxy)carbene]chromium(0) (**2f**).* IR (film): 667, 741, 1218, 1916, 2058 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.40 (m, 9H), 4.79 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 348.35, 224.00, 216.31, 152.04, 143.57, 139.64, 128.92, 128.12, 127.12, 126.67, 124.90, 67.24. Anal. Calcd for $C_{19}H_{12}CrO_6$: C, 58.77; H, 3.11; Found: C, 58.79; H, 3.31.

Typical procedure for catalyst-free cross-coupling of *N*-tosylhydrazones with chromium(0) Fischer carbene complexes. *N*-Tosylhydrazones **1a** (82.2 mg, 0.30 mmol), chromium carbene complex **2a** (62.4mg, 0.20 mmol) and potassium phosphate (K_3PO_4, 85mg, 0.40 mmol) were successively added to a 25 mL Schlenk reaction flask. The reaction flask was then degassed for two times with nitrogen and toluene (3 mL) was added using a syringe. The resulting solution was stirred at indicated temperatures for 1.5 h. The mixture was then cooled to room temperature and filtered through a short plug of silica gel (washed with petroleum ether : EtOAc = 10 : 1). Solvent was removed to provide a crude mixture. Then, the mixture was transferred to a 25 mL round-bottom flask. After the solvent was removed, 2.0 mL of tetrahydrofuran (THF) and 1.0 mL of aqueous HCl (2M) were added to the reaction mixture under stirring. The reaction was further stirred for 1 h at 60 °C and then was cooled to room temperature again. Next, the resulting mixture was extracted with diethyl ether (Et_2O) for three times. After being washed by saturated $NaHCO_3$ and NaCl, combined organic layers were dried over Na_2SO_4 and filtered. Solvent was then removed in *vacuo* to leave a crude mixture, which was purified by silica gel column chromatography to afford the pure product.

1,2-Diphenylethanone (3a).[13] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (30.7 mg, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.00 (m, 2H), 7.58-7.53 (m, 1H), 7.48-7.44 (m, 2H), 7.35-7.31 (m, 2H), 7.28-7.23 (m, 3H), 4.29 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.59, 136.54, 134.49, 133.14, 129.43, 128.64, 128.61, 128.58, 126.86, 45.47.

1-Phenyl-2-(*p*-tolyl)ethanone (3b).[13] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (29.0 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (m, 2H), 7.56-7.52 (m, 1H), 7.46-7.42 (m, 2H), 7.16-7.11 (m, 4H), 4.24 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.77, 136.60, 136.43, 133.04, 131.39, 129.36, 129.26, 128.57, 45.10, 21.03.

2-(4-(*tert*-Butyl)phenyl)-1-phenylethanone (3c).[13] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a yellow oil (31.6 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-8.01 (m, 2H), 7.57-7.53 (m, 1H), 7.47-7.43 (m, 2H), 7.34 (d, J_{AB} = 8.3 Hz, 2H), 7.2 (d, J_{AB} = 8.3 Hz, 2H), 4.25 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.77, 149.66, 136.70, 133.07, 131.38, 129.08, 128.61, 128.59, 125.60, 44.91, 34.41, 31.31.

2-([1,1'-Biphenyl]-4-yl)-1-phenylethanone (3d).[14] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (27.2 mg, 50%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.5 Hz, 2H), 7.57-7.54 (m, 5H), 7.48-7.39 (m, 4H), 7.34-7.30 (m, 3H), 4.32 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.51, 140.77, 139.81, 136.58, 133.52, 133.18, 129.87, 128.70, 128.64, 128.58, 127.37, 127.18, 127.01, 45.06.

2-(4-Bromophenyl)-1-phenylethanone (3e).[15] The title compound was prepared via the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (26.8 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H), 7.59-7.55 (m, 1H), 7.48-7.43 (m, 4H), 7.13 (d, J = 8.3 Hz, 2H), 4.24 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 196.94, 136.34, 133.41, 133.33, 131.69, 131.23, 128.69, 128.46, 120.92, 44.70.

2-(4-Methoxyphenyl)-1-phenylethanone (3f).[14] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (27.4 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (m, 2H), 7.56-7.52 (m, 1H), 7.46-7.43 (m, 2H), 7.18 (d, J = 8.6 Hz, 2H), 6.86 (d, J = 8.7 Hz, 2H), 4.22 (s, 2H), 3.77 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.88, 158.50, 136.58, 133.04, 130.41, 128.57, 128.54, 126.46, 114.10, 55.19, 44.57.

2-(4-(Dimethylamino)phenyl)-1-phenylethanone (3g).[16] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a pale yellow solid (17.8 mg, 37%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (m, 2H), 7.54-7.50 (m, 1H), 7.44-7.41 (m, 2H), 7.13 (d, J = 8.7 Hz, 2H), 6.69 (d, J = 8.7 Hz, 2H), 4.17 (s, 2H), 2.90 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 198.25, 149.51, 136.72, 132.85, 129.98, 128.62, 128.50, 122.22, 112.96, 44.62, 40.63.

2-(3,5-Dimethoxyphenyl)-1-phenylethanone (3h).[15] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a colorless oil (26.0 mg, 51%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.99 (m, 2H), 7.56-7.52 (m, 1H), 7.46-7.42 (m, 2H), 6.43-6.42 (m, 2H), 6.35-6.34 (m, 1H), 4.20 (s, 2H), 3.75 (s, 6H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.36, 160.90, 136.65, 136.51, 133.12, 128.59, 128.58, 107.46, 98.89, 55.23, 45.77.

2-(2,3-Dihydrobenzofuran-5-yl)-1-phenylethanone (3i). The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (24.1 mg, 51%). mp: 104-105 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-7.99 (m, 2H), 7.56-7.52 (m, 1H), 7.47-7.43 (m, 2H), 7.09 (s, 1H), 6.98 (d, J = 8.1 Hz, 1H), 6.73 (d, J = 8.1 Hz, 1H), 4.53 (t, J = 8.7 Hz, 2H), 4.20 (s, 2H), 3.17 (t, J = 8.7 Hz, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 198.06, 159.09, 136.61, 133.03, 129.00, 128.57, 128.55, 127.48, 126.20, 125.91, 109.27, 71.21, 44.81, 29.68. HRMS (ESI, *m*/*z*): calcd for $C_{16}H_{15}O_2$ $[M+H]^+$ 239.1067, found 239.1070; LRMS (EI, *m*/*z*): 238 (M^+, 20), 133 (100), 105 (26), 77 (30), 51 (12); IR (film): 693, 758, 1492, 1689, 2924 cm^{-1}.

2-(Benzo[*d*][1,3]dioxol-5-yl)-1-phenylethanone (3j).[17] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a colorless oil (26.7 mg, 56%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00-7.98 (m, 2H), 7.57-7.53 (m, 1H), 7.47-7.43 (m, 2H), 6.77-6.75 (m, 2H), 6.71-6.69 (m, 1H), 5.91 (s, 2H), 4.18 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.60, 147.81, 146.52, 136.48, 133.12, 128.60, 128.52, 128.01, 122.50, 109.86, 108.38, 100.95, 45.04.

2-(6-Methoxynaphthalen-2-yl)-1-phenylethanone (3k). The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (28.9 mg, 52%). mp: 147-148 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.3 Hz, 2H), 7.70-7.63 (m, 3H), 7.54-7.51 (m, 1H), 7.45-7.41 (m, 2H), 7.34 (dd, J = 8.4 Hz, 1.4 Hz, 1H), 7.13-7.09 (m, 2H), 4.38 (s, 2H), 3.88 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.78, 157.54, 136.59, 133.45, 133.09, 129.69, 129.07, 129.03, 128.60, 128.02, 127.87, 127.13, 118.88, 105.60, 55.23, 45.47. HRMS (ESI, *m*/*z*): calcd for $C_{19}H_{17}O_2$ $[M+H]^+$ 277.1223, found 277.1226; LRMS (EI, *m*/*z*): 276 (M^+, 35), 171 (100), 128 (33), 105 (34), 77 (24); IR (film): 689, 748, 1209, 1687, 2926 cm^{-1}.

2-(Furan-2-yl)-1-phenylethanone (3l).[18] The title compound was prepared via the general procedure. After purification by silica gel column chromatography, the product was isolated as a yellow oil (11.6 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 2H), 7.37 (d, J = 1.1 Hz, 1H), 6.35-6.33 (m, 1H), 6.24-6.23 (m, 1H), 4.31 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 195.01, 148.25, 142.04, 136.21, 133.35, 128.64, 128.56, 110.64, 108.27, 38.40.

1-Phenyl-2-(*o*-tolyl)ethanone (3m).[14] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a colorless oil (13.0 mg, 31%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J = 7.4 Hz, 2H), 7.59-7.56 (m, 1H), 7.49-7.46 (m, 2H), 7.21-7.11 (m, 4H), 4.30 (s, 2H), 2.26 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.45, 136.88, 136.86, 133.43, 133.12, 130.33, 130.26, 128.64, 128.31, 127.20, 126.08, 43.46, 19.76.

1-Phenyl-2-(*m*-tolyl)ethanone (3n).[13] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a colorless oil (29.2 mg, 70%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.56-7.52 (m, 1H), 7.46-7.43 (m, 2H), 7.21 (t, J = 7.6 Hz, 1H), 7.08-7.05 (m, 3H), 4.24 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.71, 138.27, 136.61, 134.39, 133.08, 130.12, 128.59, 128.52, 127.63, 126.44, 45.42, 21.35.

2-(3-Bromophenyl)-1-phenylethanone (3o).[13] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a pale yellow oil (18.0 mg, 33%). ^{1}H NMR (400

MHz, $CDCl_3$) δ 8.01-7.98 (m, 2H), 7.60-7.56 (m, 1H), 7.49-7.45 (m, 2H), 7.42 (s, 1H), 7.40-7.38 (m, 1H), 7.20-7.19 (m, 2H), 4.25 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 196.75, 136.66, 136.34, 133.38, 132.53, 130.09, 130.05, 128.72, 128.49, 128.21, 122.60, 44.80.

Methyl 3-(2-oxo-2-phenylethyl)benzoate (3p). The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (22.1 mg, 44%). mp: 74-76 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02-8.00 (m, 2H), 7.95-7.93 (m, 2H), 7.59-7.55 (m, 1H), 7.49-7.45 (m, 3H), 7.43-7.39 (m, 1H), 4.34 (s, 2H), 3.90 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 196.94, 166.87, 136.40, 134.82, 134.12, 133.32, 130.70, 130.49, 128.69, 128.63, 128.46, 128.17, 52.07, 44.99. HRMS (ESI, *m*/*z*): calcd for $C_{16}H_{15}O_3$ $[M+H]^+$ 255.1016, found 255.1019; LRMS (EI, *m*/*z*): 223 (M^+-31, 8), 207 (6), 105 (100), 90 (9), 77 (34); IR (film): 691, 1214, 1285, 1689, 1720 cm^{-1}.

2-Phenyl-1-(*o*-tolyl)ethanone (4a).[14] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a colorless oil (29.0 mg, 69%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7 Hz, 1H), 7.37-7.29 (m, 3H), 7.26-7.21 (m, 5H), 4.20 (s, 2H), 2.43 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 201.46, 138.55, 137.66, 134.49, 131.99, 131.34, 129.55, 128.64, 126.89, 125.63, 48.46, 21.28.

1-(3-Chlorophenyl)-2-phenylethanone (4b).[19] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (25.3 mg, 55%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (t, *J* = 1.6 Hz, 1H), 7.87 (d, *J* = 7.8 Hz, 1H), 7.53-7.50 (m, 1H), 7.38 (t, *J* = 7.9 Hz, 1H), 7.35-7.31 (m, 2H), 7.28-7.24 (m, 3H), 4.25 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 196.26, 138.10, 134.97, 133.93, 133.05, 129.94, 129.40, 128.74, 128.63, 127.05, 126.66, 45.54.

1-(3-Methoxyphenyl)-2-phenylethanone (4c).[14] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a colorless oil (27.0 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.53-7.52 (m, 1H), 7.37-7.30 (m, 3H), 7.27-7.22 (m, 3H), 7.09 (dd, *J* = 8.2 Hz, 2.5 Hz, 1H), 4.26 (s, 2H), 3.82 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.40, 159.80, 137.92, 134.52, 129.56, 129.39, 128.63, 126.84, 121.24, 119.60, 112.80, 55.36, 45.58.

2-Phenyl-1-(*p*-tolyl)ethanone (4d).[13] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (28.5 mg, 68%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 8.2 Hz, 2H), 7.33-7.21 (m, 7H), 4.24 (s, 2H), 2.39 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.24, 143.92, 134.74, 134.07, 129.39, 129.27, 128.71, 128.59, 126.75, 45.37, 21.58.

1-([1,1'-Biphenyl]-4-yl)-2-phenylethanone (4e).[14] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (32.7 mg, 60%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.3 Hz, 2H), 7.66 (d, *J* = 8.3 Hz, 2H), 7.61-7.59 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 2H), 7.40-7.23 (m, 6H), 4.30 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.15, 145.77, 139.76, 135.23, 134.57, 129.42, 129.19, 128.91, 128.66, 128.21, 127.23, 127.21, 126.86, 45.53.

1-(4-Methoxyphenyl)-2-phenylethanone (4f).[13] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (29.1 mg, 64%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01-7.97 (m, 2H), 7.33-7.21 (m, 5H), 6.93-6.90 (m, 2H), 4.22 (s, 2H), 3.84 (s, 3H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 196.17, 163.47, 134.94, 130.90, 129.60, 129.34, 128.58, 126.72, 113.74, 55.41, 45.22.

1-(4-Fluorophenyl)-2-phenylethanone (4g).[20] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (27.1 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05-8.00 (m, 2H), 7.34-7.31 (m, 2H), 7.26-7.24 (m, 3H), 7.14-7.08 (m, 2H), 4.25 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 196.00, 165.71 (d, J_{CF} = 255.2 Hz), 134.31, 132.95 (d, J_{CF} = 2.9 Hz), 131.23 (d, J_{CF} = 9.4 Hz), 129.34, 128.71, 126.96, 115.71 (d, J_{CF} = 21.9 Hz), 45.46.

1-(4-Chlorophenyl)-2-phenylethanone (4h).[20] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (22.5 mg, 49%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.92 (m, 2H), 7.43-7.40 (m, 2H), 7.34-7.30 (m, 2H), 7.27-7.23 (m, 3H), 4.24 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 196.36, 139.58, 134.83, 134.15, 130.00, 129.34, 128.93, 128.73, 127.00, 45.51.

1-(Naphthalen-2-yl)-2-phenylethanone (4i).[21] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a white solid (31.1 mg, 63%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.05 (d, *J* = 8.6 Hz, 1H), 7.94 (d, *J* = 8.0 Hz, 1H), 7.85 (t, *J* = 8.4 Hz, 2H), 7.60-7.51 (m, 2H), 7.35-7.30 (m, 4H), 7.26-7.23 (m, 1H), 4.40 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 197.53, 135.53, 134.63, 133.90, 132.44, 130.34, 129.56, 129.45, 128.65, 128.49, 128.46, 127.71, 126.85, 126.73, 124.21, 45.49.

2-Phenyl-1-(thiophen-2-yl)ethanone (4j).[22] The title compound was prepared *via* the general procedure. After purification by silica gel column chromatography, the product was isolated as a pale yellow oil (24.6 mg, 61%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (dd, *J* = 3.8 Hz, 1.0 Hz, 1H), 7.62 (dd, *J* = 4.9 Hz, 0.8 Hz, 1H), 7.34-7.28 (m, 4H), 7.27-7.23 (m, 1H), 7.12-7.10 (m, 1H), 4.18 (s, 2H). ^{13}C NMR (400 MHz, $CDCl_3$) δ 190.39, 143.84, 134.29, 133.98, 132.60, 129.35, 128.65, 128.13, 127.00, 46.33.

Notes and references

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