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Regioselective Oxyalkylation of Vinylarenes Catalyzed by Diatomite-Supported Manganese Oxide Nanoparticles

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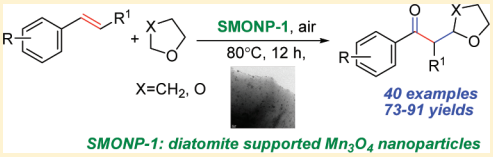
Supporting Information

ABSTRACT: A regioselective oxyalkylation reaction of vinylarenes with cyclic ethers was developed under the catalysis of a new heterogeneous catalyst, the diatomite-supported Mn_3O_4 nanoparticles (SMONP-1). The use of this heterogeneous catalyst provided a novel approach for the synthesis of α-carbonyled β-alkylated aryl derivatives via a sp^3 C−H bond functionalization under mild aerobic conditions.



Transition-metal-catalyzed C−H bond functionalization has attracted considerable attention, providing an efficient approach for the assembly of biologically and industrially useful compounds.[1] Difunctionalization of vinylarenes is an important investigated field of these C−H bond functionalization reactions.[2] Recently, there are many reports for this transition-metal-catalyzed difunctionalization of vinylarenes, including dioxygenation,[3] diamidation,[4] and oxyamidation.[5] The C−C bond formation via the intramolecular oxidative carbofunctionalization of vinylarenes has been broadly studied.[6] However, there are few reports on intermolecular metal-catalyzed oxidative carbofunctionalization of olefins for C−C bond formation,[7] which is still a challenge to the synthetic chemistry. Recently, metal nanoparticles have been widely used in organic reactions. They usually display advantages compared with traditional homogeneous catalysts, such as lower loading, lower toxicity, and good recyclability. Moreover, the characters of the supported metal nanoparticles can be displayed by the characteristics of the supports. To the best of our knowledge, the intermolecular oxidative carbofunctionalization of olefins catalyzed by supported metal nanoparticles has not been reported yet. Our group has been making efforts on nanoparticle-catalyzed organic reactions.[8] Manganese oxide (Mn_3O_4) nanoparticles (NPs) are often used as a catalyst for the oxidation reaction.[9] Herein, we prepared three heterogeneous catalysts by encapsulating Mn_3O_4 NPs on different supports such as diatomite, ZrO_2, and SiO_2. The resulting catalysts were employed in an intermolecular oxyalkylation of vinylarenes. After screening, it was found that Mn_3O_4 NPs immobilized on diatomite could catalyze this reaction to give α-carbonyled β-alkylated aryl derivatives with high regioselectivities and good yields under mild aerobic conditions.

Initially, Mn_3O_4 NPs were encapsulated on different supports, such as diatomite, ZrO_2, and SiO_2 to give the corresponding heterogeneous catalysts SMONP-1, SMONP-2, and SMONP-3, respectively (see the Experimental Section). The as-synthesized three heterogeneous catalysts were characterized by TEM, XRD pattern, and ICP atomic emission (see the Supporting Information). Subsequently, these SMONP-1, SMONP-2, SMONP-3, and other Mn-based species were examined as the potential catalysts in the reaction of styrene with tetrahydrofuran under an air atmosphere. It was found that SMONPs (SMONP-1, 2, 3) could catalyze this oxidation reaction to afford the corresponding oxyalkylation product **2a** with good yields (Table 1, entries 7−9), whereas other manganese oxides gave the corresponding product with lower yields or trace amounts (Table 1, entries 1−4). Manganese salts, such as $MnCl_2{\cdot}4H_2O$ and $Mn(OAc)_2{\cdot}4H_2O$, failed to give the product (Table 1, entries 5−6). In addition, the reaction did not work without the catalyst (Table 1, entry 10).

After screening these SMONPs in detail, the experimental result indicated that SMONP-1 catalysis could give the best result (Table 1, entry 7). Subsequently, the reaction was carried out under different conditions to optimize the reaction conditions. The reaction was carried out under pure oxygen atmosphere to give the product **2a** with an almost the same yield (Table 1, entry 11), while the reaction did not work under nitrogen atmosphere (Table 1, entry 12). It was shown that an oxidant was necessary for this reaction and air was a suitable oxidant for this reaction. Afterward, the reaction solvent was optimized. The other solvents, such as CH_3CN, CH_2Cl_2, $CHCl_3$, toluene, and DMF, were employed in this reaction, and it was found that THF was the best solvent to the reaction (see the Supporting Information). The reaction temperature was also examined, and it was found that 80 °C was the optimal temperature (see the Supporting Information). The formation of C−C bond occurred on the sp^3 C−H bond of C2-position instead of C3-position of tetrahydrofuran. Thus, the optimal conditions were obtained, that is, SMONP-1 as catalyst, THF as solvent, and the reaction being performed at 80 °C for 12 h under air atmosphere.

Under the optimized reaction conditions, the scope of vinylarenes was investigated. As shown in Table 2, a variety of

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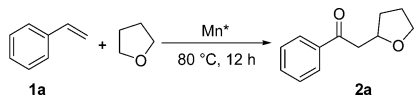
Table 1. Oxyalkylation of Styrene with Different Mn Catalysts[a]

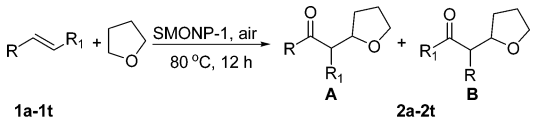


1a 2a

entry	catalyst	yield (%)[b]
1	Mn_3O_4 nanoparticles	45
2[c]	Mn_3O_4	10
3	Mn_2O_3	9
4	MnO_2	7
5	$MnCl_2{\cdot}4H_2O$	
6	$Mn(OAc)_2{\cdot}4H_2O$	
7[d]	SMONP-1	91
8[e]	SMONP-2	59
9[f]	SMONP-3	77
10		
11[g]	SMONP-1	92
12[h]	SMONP-1	

[a]Reaction conditions: styrene (52 mg, 0.5 mmol), 2 mol % Mn catalyst, THF (2 mL), 80 °C, 12 h under air atmosphere. [b]Isolated yield. [c]Commercial Mn_3O_4. [d]2 mol % (7.0 mg) SMONP-1. [e]2 mol % (7.5 mg) SMONP-2. [f]2 mol % (4.0 mg) SMONP-3. [g]Under O_2 atmosphere. [h]Under N_2 atmosphere.

Table 2. Reaction of Vinylarenes with Tetrahydrofuran Catalyzed by SMONP-1[a]



1a-1t A 2a-2t B

entry	R	R_1	1	A yield (%)[b]	B yield (%)[b]
1	Ph	H	**1a**	91	
2	4-Me-Ph	H	**1b**	92	
3	3-Me-Ph	H	**1c**	85	
4	2-Me-Ph	H	**1d**	83	
5	4-OMe-Ph	H	**1e**	90	
6	2-OMe-Ph	H	**1f**	84	
7	4-Cl-Ph	H	**1g**	82	
8	2-Cl-Ph	H	**1h**	80	
9	2-Br-Ph	H	**1i**	84	
10	4-Br-Ph	H	**1j**	85	
11	1-naphthyl	H	**1k**	79	
12[c]	Ph	H	**1a**	75	
13	Ph	Me	**1m**	80 (100:0)	
14	2-Br-Ph	Me	**1n**	79 (100:0)	
15	4-OMe-Ph	Me	**1o**	83 (100:0)	
16[d]	4-Br-Ph	Me	**1p**	79 (59:41)	
17[d]	Ph	Ph	**1q**	75 (53:47)	
18[e]	4-OMe-Ph	Ph	**1r**	48	34
19[e]	2-OMe-Ph	Ph	**1s**	36	44
20[e]	2-Br-Ph	Ph	**1t**	58	22

[a]Reaction conditions: vinylarenes (0.5 mmol), SMONP-1 (2 mol %, 7.0 mg), THF (2 mL), 80 °C, 12 h under air atmosphere. [b]Isolated yield. [c]THF was replaced with 1,4-dioxane. [d]The diastereselectivity (syn:anti) was determined by ^{1}H NMR. [e]The products were the mixture of the two regioisomers.

vinylarenes can be employed in this reaction to give the products with good yields and regioselectivities via the addition of the α-sp^3 C−H bond adjacent to oxygen to vinylarenes and the subsequent α-position oxidation carbonylation of vinylarenes.

From Table 2, no remarkable electronic effect was obviously observed. Both electron-rich and electron-poor vinylarenes could efficiently afford the products with good yields. Substitutions at the ortho position had slight impact on the yields. For instance, the reaction of *p*-, *m*-, and *o*-metheylvinylbenzene (**1b**−**1d**) afforded **2b**, **2c**, and **2d** with the yields of 92, 85, and 83%, respectively (Table 2, entries 2−4). It was noted that good yields were achieved with Cl or Br-substituted vinylarenes (Table 2, entries 7−10). 2-Vinylnaphthalene also led to the corresponding product in good yield (Table 2, entry 11). Moreover, when tetrahydrofuran was replaced by 1,4-dioxane, the reaction can be also carried out smoothly (Table 2, entry 12). To our delight, the terminal alkenes can be replaced with internal alkenes, and the good reaction yields can be obtained (Table 2, entries 13−20). When R_1 was methyl or phenyl group, the corresponding products (**2m**, **2n**, and **2o**) were obtained with only syn configuration (Table 2, entries 13−15). As for the reaction substrates **1p** and **1q**, the corresponding products **2p** and **2q** were obtained with poor diastereoselectivities (Table 2, entries 16−17). On the other hand, two regioisomers were obtained when **1r**, **1s**, and **1t** were employed respectively as the substrates (Table 2, entries 18−20). This poor regioselectivity can perhaps be ascribed to the similarity of R and R_1 substituents, which resulted in a random attack of the THF to the alkene. When the reaction substrate THF was replaced with 1,3-dioxolane, which possesses two types of C−H bonds adjacent to the oxygen atom, the C−H bond cleavage at C2-position of 1,3-dioxolane preferentially led to yield aryl β-aldehyde protected ketones (Table 3). It was demonstrated that an excellent regioselectivity for 1,3-dioxolane was achieved under the catalysis of SMONP-1.

Various substituted alkenes were also employed as the substrates to react with 1,3-dioxolane, affording C2-oxyalkylation ketones with good yields and excellent regioselectivities to 1,3-dioxolane. In this case, we did not detect the oxidation products at the C4-position under the reaction conditions. When both R and R_1 were aromatic groups, the mixture of regioisomers **A** and **B** were obtained (Table 3, entries 16−19). This can be ascribed to the similar reactivity of the two carbons in the double bond of the alkene.

The recyclability of the catalyst was also investigated with the model reaction of styrene with tetrahydrofuran. The results are listed in Table 4. In the fourth round, the reaction yield was decreased to 83%. The leaching of manganese oxide from the diatomite may account for the sluggishness of the catalysts. A measurable amount of manganese (3.88%) was detected in the mother liquor by ICP atomic emission (see the Supporting Information). After removal of the SMONP-1, the reaction was carried out in this mother liquor, and only 3% yield of the product **2a** was obtained. This indicated that SMONP-1 was the heterogeneous catalyst for this oxyalkylation reaction. The TEM image of the catalyst after the fourth recycle was similar to that of the fresh catalyst, as shown in Figure 1b. The XRD pattern (see the Supporting Information) of SMONP-1 after the fourth round is similar to that of the fresh SMONP-1. These results demonstrated that the structure of SMONP-1 almost remained after the recycling reactions.

To determine the mechanism of the C2-selectivity oxyalkylation of vinylarenes, we carried out several control experiments. The reaction did not work under N_2 atmosphere

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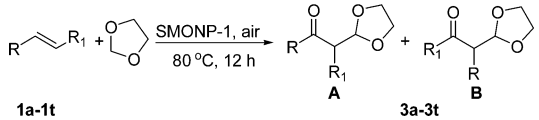
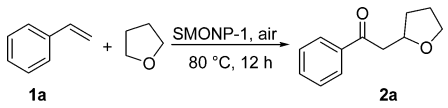
Table 3. Reaction of Vinylarenes with Dioxolane Catalyzed by SMONP-1[a]



entry	R	R_1	1	A yield (%)[b]	B yield (%)[b]
1	Ph	H	**1a**	84	
2	4-Me-Ph	H	**1b**	85	
3	3-Me-Ph	H	**1c**	84	
4	2-Me-Ph	H	**1d**	79	
6	2-OMe-Ph	H	**1f**	79	
7	4-Cl-Ph	H	**1g**	80	
8	2-Cl-Ph	H	**1h**	76	
9	2-Br-Ph	H	**1i**	75	
10	4-Br-Ph	H	**1j**	82	
11	1 -naphthyl	H	**1k**	73	
12	Ph	Me	**1l**	78	
13	4-OMe-Ph	Me	**1m**	75	
14	4-Br-Ph	Me	**1n**	77	
15	Ph	Ph	**1o**	75	
16[c]	4-Br-Ph	Ph	**1p**	37	37
17[c]	4-OMe-Ph	Ph	**1q**	55	24
18[c]	2-OMe-Ph	Ph	**1r**	44	34
19[c]	2-Br-Ph	Ph	**1s**	35	45
20	Ph	Bn	**1t**	76	

[a]Reaction conditions: vinylarenes (0.5 mmol), SMONP-1 (2 mol %, 7.0 mg), 1,3-dioxolane (2 mL), 80 °C, 12 h under air atmosphere. [b]Isolated yield. [c]The products were the mixture of the two regioisomers.

Table 4. Recylcing of the Catalyst[a]



run	1	2	3	4	5
yield (%)	91	89	88	85	83

[a]Reaction conditions: styrene (0.5 mmol), SMONP-1 (2 mol %, 7.0 mg), THF (2 mL), 80 °C, 12 h.

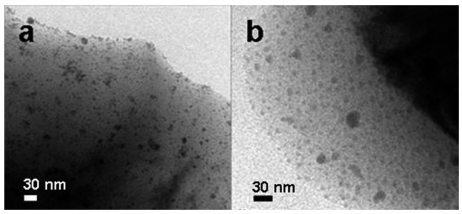
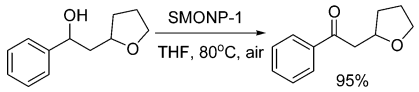


Figure 1. TEM images of (a) fresh SMONP-1 and (b) SMONP-1 after the fourth cycle.

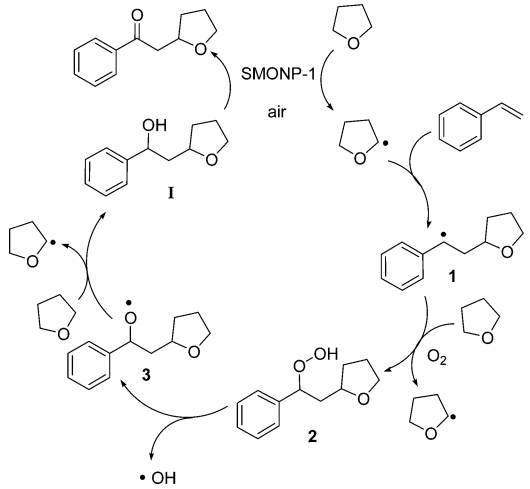
(Table 1, entry 12). Besides, the reaction did not work either when radical inhibitor TEMPO was added to the system. This suggested that a free-radical process might be involved in the reaction. In addition, 1-phenyl-2-(tetrahydrofuran-2-yl)ethanol (**I**) was detected in the reaction process by GC–MS analysis (m/z = 192) (see the Supporting Information), which indicated that **I** was the reaction intermediate. We prepared 1-phenyl-2-(tetrahydrofuran-2-yl)ethanol (**I**), and this compound can be oxidized into the product with a yield of 95%, as shown in Scheme 1.

Scheme 1. Oxidation of I Catalyzed by SMONP-1



On the basis of these experiments, we proposed a mechanism for our oxyalkylation reaction, as depicted in Scheme 2.

Scheme 2. Proposed Mechanism for the Reaction



Reaction of tetrahydrofuran with O_2 catalyzed by SMONP-1 affords tetrahydrofuran free-radical, which reacts with styrene to produce intermediate **1**. Intermediate **1** and O_2 then react to give peroxide **2**. Homolytic cleavage of the O–O bond of **2** generates **3**, which abstracts a hydrogen atom from THF to afford intermediate **I**. Then, **I** is oxidized by SMONP-1 to produce ketone.

In conclusion, a cheap and reusable heterogeneous catalyst SMONP-1 was prepared and applied to the oxyalkylation of vinylarenes. In virtue of this SMONP-1, a new synthesis of α-carbonyl β-alkylated aryl derivatives was developed, and the corresponding products can be obtained with high regioselectivities and good yields. Efforts to apply this heterogeneous catalyst to other organic reactions are in progress in our laboratory.

EXPERIMENTAL SECTION

Preparation of Mn_3O_4 Nanoparticles.[10] $Mn(OAc)_2{\cdot}4H_2O$ (0.50 g) and DMSO (30 mL) were added into a 30 mL Teflon-lined stainless steel autoclave. After $Mn(OAc)_2{\cdot}4H_2O$ was dissolved in DMSO with stirring, the autoclave was sealed. Thermal treatment was carried out at 120 °C for 6 h, and then the autoclave was cooled to room temperature. Water was added into the solution, and the nanoparticles were precipitated after keeping it at room temperature for 2 h under air. The powder was washed with water and anhydrous ethanol for 3 times and dried at 60 °C for 6 h in a vacuum. Manganese oxide nanoparticles were characterized by TEM study (Figure S1, Supporting Information). Typical XRD pattern of the nanoparticles are shown in Figure S5 (Supporting Information). All the strong and shape diffraction peaks are consistent with the reference JCPDS 24–0734, which are indexed to the tetragonal structure of Mn_3O_4.

Preparation of SMONPs. $Mn(OAc)_2{\cdot}4H_2O$ (0.50 g), supports (0.10 g), hexadecyl trimethyl ammonium bromide (CTAB) (30 mg), and DMSO (50 mL) were added into a 50 mL Teflon-lined stainless steel autoclave. After $Mn(OAc)_2{\cdot}4H_2O$ was dissolved in DMSO with stirring, the autoclave was sealed. Thermal treatment was carried out at 120 °C for 6 h, and then the autoclave was cooled to room temperature. Water was added into the solution, and the SMONPs

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were precipitated after keeping it at room temperature for 2 h under air. The powder was washed with water and anhydrous ethanol for 3 times and dried at 60 °C for 6 h in a vacuum. TEM images of SMONPs and the average diameters are shown in Figures S2−S4 (Supporting Information). Typical XRD pattern of these nanoparticles are shown in Figures S6−S12 (Supporting Information).

General Procedure for the Oxyalkylation. SMONP-1 (2 mol %, 7.0 mg) was added into THF solution (2 mL) containing vinylarenes (0.5 mmol). The mixture was carried out at 80 °C for 12 h under air atmosphere. After completion of the reaction, the reaction mixture was centrifuged at ca. 8000 rpm for 6 min. Then, the solution was concentrated under a vacuum. The crude product was purified with column chromatography on silica gel to afford the pure product.

Reuse of the SMONP-1. SMONP-1 (2 mol %, 7.0 mg) was added into THF solution (2 mL) containing styrene (1 mmol). The mixture was carried out at 80 °C for 12 h under air atmosphere. The reaction mixture was centrifuged at ca. 8000 rpm for 6 min. The precipitate was washed with water and ethanol subsequently and then dried at 60 °C in a vacuum. The recovered catalyst was reused for the next round.

Oxyalkylation Reaction Catalyzed by the Leaking of Manganese from SMONP-1. After removal of the SMONP-1, a measureable amount of manganese (3.88%) was detected in the mother liquor by ICP atomic emission after the four rounds. The reaction was carried out in this mother liquor, and only 3% yield of the product **2a** was obtained.

Characterization Data of All Products. *1-Phenyl-2-(tetrahydrofuran-2-yl)ethanone (**2a**).* Light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.95 (m, 2 H), 7.58−7.54 (m, 1 H), 7.48−7.44 (m, 2 H), 4.43−4.38 (m, 1 H), 3.92−3.87 (m, 1 H), 3.78−3.73 (m, 1 H), 3.40 (q, J = 10.0 Hz, 1 H), 3.06 (q, J = 10.2 Hz, 1 H), 2.24−2.16 (m, 1 H), 1.97−1.89 (m, 1 H), 1.64−1.39 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.6, 137.2, 133.2, 128.7, 128.4, 75.6, 68.0, 44.8, 31.8, 25.8; HRMS calcd for $C_{12}H_{14}O_2$ 190.0994, found 190.0991.

*2-(Tetrahydrofuran-2-yl)-1-p-tolyethanone (**2b**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 10.8 Hz, 2 H), 7.23 (d, J = 14.0 Hz, 2 H), 4.44−4.36 (m, 1 H), 3.90 (q, J = 10.4 Hz, 1 H), 3.75 (q, J = 9.6 Hz, 1 H), 3.38 (q, J = 13.2 Hz, 1 H), 3.03 (q, J = 12.4 Hz, 1 H), 2.41 (s, 3 H), 2.30−2.14 (m, 1 H), 1.96−1.88 (m, 1 H), 1.62−1.56 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 144.1, 134.8, 129.4, 128.5, 75.7, 68.0, 44.7, 31.8, 25.8, 21.8; HRMS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1154.

*2-(Tetrahydrofuran-2-yl)-1-m-tolyethanone (**2c**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.75 (m, 2 H), 7.39−7.32 (m, 2 H), 4.44−4.36 (m, 1 H), 3.92−3.88 (m, 1 H), 3.78−3.72 (m, 1 H), 3.38 (q, J = 10.0 Hz, 1 H), 3.04 (q, J = 9.6 Hz, 1 H), 2.41 (s, 3 H), 2.23−2.15 (m, 1 H), 1.97−1.88 (m, 1 H), 1.61−1.56 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.8, 138.5, 137.3, 134.0, 128.8, 128.6, 126.0, 75.6, 68.0, 44.9, 31.8, 25.8, 21.5; HRMS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1148.

*2-(Tetrahydrofuran-2-yl)-1-o-tolyethanone (**2d**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67−7.65 (m, 1 H), 7.39−7.34 (m, 1 H), 7.27−7.23 (m, 2 H), 4.39−4.33 (m, 1 H), 3.91−3.86 (m, 1 H), 3.75 (q, J = 6.8 Hz, 1 H), 3.28 (q, J = 9.2 Hz, 1 H), 3.00 (q, J = 10.0 Hz, 1 H), 2.51 (s, 3 H), 2.20−2.12 (m, 1 H), 1.96−1.88 (m, 1 H), 1.60−1.51 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.6, 138.4, 138.1, 132.1, 131.5, 128.8, 125.8, 75.7, 68.0, 47.7, 31.7, 25.8, 21.4; HRMS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1151.

*1-(4-Methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethanone (**2e**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.93 (m, 1 H), 7.04−7.02 (m, 1 H), 4.23−4.20 (m, 1 H), 3.84 (s, 3 H), 3.76−3.72 (m, 1 H), 3.60−3.56 (m, 1 H), 3.24 (q, J = 9.6 Hz, 1 H), 3.01 (q, J = 9.6 Hz, 1 H), 2.51−2.49 (m, 1 H), 1.84−1.82 (m, 1 H), 1.52−1.47 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 163.6, 130.9, 130.4, 114.3, 75.7, 67.3, 56.0, 44.2, 31.6, 25.5; HRMS calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1100.

*1-(2-Methoxyphenyl)-2-(tetrahydrofuran-2-yl)ethanone (**2f**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73−7.70 (m, 1 H), 7.48−7.43 (m, 1 H), 7.02−6.95 (m, 1 H), 4.38−4.35 (m, 1 H), 3.90 (s, 3 H), 3.89−3.85 (m, 1 H), 3.73 (q, J = 8.4 Hz, 1 H), 3.39 (q, J = 10.8 Hz, 1 H), 3.14 (q, J = 10.0 Hz, 1 H), 2.17−2.14 (m, 1 H), 1.94−1.87 (m, 1 H), 1.74−1.70 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.5, 158.7, 133.7, 130.6, 120.8, 120.7, 111.7, 75.6, 67.9, 55.7, 50.1, 31.7, 25.8; HRMS calcd for $C_{13}H_{16}O_3$ 220.1099, found 220.1102.

*1-(4-Chlorophenyl)-2-(tetrahydrofuran-2-yl)ethanone (**2g**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.89 (m, 2 H), 7.45−7.42 (m, 2 H), 4.42−4.35 (m, 1 H), 3.91−3.86 (m, 1 H), 3.78−3.72 (m, 1 H), 3.34 (q, J = 10.0 Hz, 1 H), 3.02 (q, J = 10.0 Hz, 1 H), 2.21−2.16 (m, 1 H), 1.97−1.89 (m, 1 H), 1.61−1.52 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.4, 139.7, 135.6, 129.8, 129.1, 75.5, 68.0, 44.8, 31.8, 25.8; HRMS calcd for $C_{12}H_{13}ClO_2$ 224.0624, found 224.0626.

*1-(2-Chlorophenyl)-2-(tetrahydrofuran-2-yl)ethanone (**2h**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53−7.50 (m, 1 H), 7.42−7.30 (m, 3 H), 4.38−4.31 (m, 1 H), 3.87 (q, J = 11.2 Hz, 1 H), 3.74 (q, J = 9.2 Hz, 1 H), 3.29 (q, J = 12.4 Hz, 1 H), 3.12 (q, J = 13.6 Hz, 1 H), 2.20−2.11 (m, 1 H), 1.97−1.87 (m, 1 H), 1.64−1.54 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 139.6, 131.9, 131.0, 130.7, 129.3, 127.1, 75.4, 68.0, 49.1, 31.7, 25.8; HRMS calcd for $C_{12}H_{13}ClO_2$ 224.0624, found 224.0623.

*1-(2-Bromophenyl)-2-(tetrahydrofuran-2-yl)ethanone (**2i**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61−7.58 (m, 1 H), 7.45−7.43 (m, 1 H), 7.39−7.36 (m, 1 H), 7.30−7.27 (m, 1 H), 4.37−4.31 (m, 1 H), 3.90−3.84 (m, 1 H), 3.76−3.71 (m, 1 H), 3.25 (q, J = 9.2 Hz, 1 H), 3.10 (q, J = 10.0 Hz, 1 H), 2.20−2.12 (m, 1 H), 1.94−1.89 (m, 1 H), 1.66−1.57 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 141.8, 133.7, 131.7, 128.9, 127.6, 118.7, 75.3, 68.0, 48.8, 32.3, 25.7; HRMS calcd for $C_{12}H_{13}BrO_2$ 268.0099, found 268.0101.

*1-(4-Bromophenyl)-2-(tetrahydrofuran-2-yl)ethanone (**2j**).* Light yellow solid (mp 43−45 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.81 (m, 2 H), 7.61−7.58 (m, 2 H), 4.41−4.34 (m, 1 H), 3.91−3.86 (m, 1 H), 3.77−3.72 (m, 1 H), 3.33 (q, J = 10.0 Hz, 1 H), 3.01 (q, J = 9.6 Hz, 1 H), 2.23−2.15 (m, 1 H), 1.96−1.88 (m, 1 H), 1.59−1.52 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 135.9, 131.2, 129.9, 128.4, 75.4, 68.0, 44.7, 31.8, 25.7; HRMS calcd for $C_{12}H_{13}BrO_2$ 268.0099, found 268.0098.

*1-(Naphthalen-2-yl)-2-(tetrahydrofuran-2-yl)ethanone (**2k**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 1 H), 8.05−8.03 (m, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 7.91−7.87 (m, 2 H), 7.62−7.53 (m, 2 H), 4.49−4.45 (m, 1 H), 3.95−3.90 (m, 1 H), 3.78 (q, J = 6.8 Hz, 1 H), 3.54 (q, J = 10.0 Hz, 1 H), 3.19 (q, J = 9.2 Hz, 1 H), 2.24−2.21 (m, 1 H), 1.99−1.93 (m, 1 H), 1.66−1.54 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.5, 135.8, 134.6, 132.7, 130.2, 129.8, 128.6, 128.5, 127.9, 126.9, 124.0, 75.7, 68.0, 44.9, 31.8, 25.8; HRMS calcd for $C_{16}H_{16}O_2$ 240.1150, found 240.1151.

*2-(1,4-Dioxan-2-yl)-1-phenylethanone (**2l**).* Light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.94 (m, 2 H), 7.59−7.54 (m, 1 H), 7.50−7.45 (m, 2 H), 4.28−4.21 (m, 1 H), 3.93−3.89 (m, 1 H), 3.80−3.71 (m 3 H), 3.70−3.60 (m, 1 H), 3.38 (q, J = 10.0 Hz, 1 H), 3.24 (q, J = 9.2 Hz, 1 H), 2.89 (q, J = 10.4 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 136.9, 133.3, 128.9, 128.2, 71.8, 71.0, 66.9, 40.7; HRMS calcd for $C_{12}H_{14}O_3$ 206.0693, found 206.0690.

*1-Phenyl-2-(tetrahydrofuran-2-yl)propan-1-one (**2m**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.97 (m, 2 H), 7.57−7.52 (m, 1 H), 7.48−7.44 (m, 2 H), 4.21−4.15 (m, 1 H), 3.88−3.81 (m, 1 H), 3.75−3.69 (m, 1 H), 3.65−3.58 (m, 1 H), 2.09−2.00 (m, 1 H), 1.95−1.87 (m, 2 H), 1.69−1.60 (m, 1 H), 1.17 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 203.2, 137.3, 133.0, 128.7, 128.6, 81.0, 68.3, 46.0, 29.3, 25.8, 14.0; HRMS calcd for $C_{13}H_{16}O_2$ 204.1150, found 204.1152.

*1-(2-Bromophenyl)-2-(tetrahydrofuran-2-yl)propan-1-one (**2n**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57−7.55 (m, 1 H), 7.36−7.32 (m, 1 H), 7.28−7.24 (m, 1 H), 7.21−7.18 (m, 1 H), 3.85−3.81 (m, 2 H), 3.66−3.60 (m, 1 H), 3.37−3.31 (m, 1 H), 2.38−2.30 (m, 2 H), 1.95 (d, J = 4.8 Hz, 3 H), 1.69−1.62 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 149.8, 133.0, 130.5, 128.7, 127.1, 119.7, 67.1, 66.4, 32.5, 28.5, 26.4, 11.0; HRMS calcd for $C_{13}H_{15}BrO_2$ 282.0255, found 282.0254.

*1-(4-Methoxyphenyl)-2-(tetrahydrofuran-2-yl)propan-1-one (**2o**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.96 (m, 2 H),

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6.95−6.92 (m, 2 H), 4.19−4.13 (m, 1 H), 3.87 (s, 3 H), 3.85−3.81 (m, 2 H), 3.74−3.69 (m, 1 H), 3.59−3.55 (m, 1 H), 2.04−2.00 (m, 1 H), 1.94−1.88 (m, 2 H), 1.68−1.61 (m, 1 H), 1.15 (d, J = 7.2 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 163.6, 130.9, 130.3, 113.9, 81.1, 68.3, 55.6, 45.5, 29.8, 25.8, 14.0; HRMS calcd for $C_{14}H_{18}O_3$ 234.1256, found 234.1257.

1-(4-Bromophenyl)-2-(tetrahydrofuran-2-yl)propan-1-one (**2p**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86−7.82 (m, 2 H), 7.63−7.58 (m, 2 H), 4.15−4.07 (m, 1 H), 3.85−3.79 (m, 1 H), 3.77−3.68 (m, 2 H), 3.58−3.49 (m, 1 H), 2.09−1.97 (m, 2 H), 1.95−1.88 (m, 2 H), 1.87−1.79 (m, 2 H), 1.67−1.61 (m, 2 H), 1.58−1.49 (m, 1 H), 1.29 (d, J = 6.8 Hz, 3 H), 1.15 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 202.2, 136.1, 135.9, 132.1, 131.9, 130.2, 130.1, 128.4, 128.2, 81.2, 81.1, 68.3, 68.1, 16.1, 45.9, 29.6, 29.5, 25.9, 25.7, 15.4, 14.0; HRMS calcd for $C_{13}H_{15}BrO_2$ 282.0255, found 282.0257.

1,2-Diphenyl-2-(tetrahydrofuran-2-yl)ethanone (**2q**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00−7.94 (m, 2 H), 7.51−7.47 (m, 1 H), 7.47−7.38 (m, 4 H), 7.33−7.28 (m, 2 H), 7.25−7.20 (m, 1 H), 4.75−4.53 (m, 2 H), 3.88−3.67 (m, 2 H), 2.28−2.12 (m, 1 H), 1.93−1.80 (m, 2 H), 1.78−1.68 (m, 1 H), 1.61−1.51 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.1, 198.9, 137.5, 137.2, 136.9, 136.3, 133.2, 133.0, 129.1, 129.0, 138.9, 128.8, 128.8, 128.7, 128.6, 127.7, 127.5, 81.5, 80.8, 68.5, 68.1, 59.3, 59.1, 31.0, 29.8, 25.8, 25.6; HRMS calcd for $C_{18}H_{18}O_2$ 266.1307, found 266.1305.

1-(4-Methoxyphenyl)-2-phenyl-2-(tetrahydrofuran-2-yl)-ethanone and 2-(4-Methoxyphenyl)-1-phenyl-2-(tetrahydrofuran-2-yl)ethanone (**2r**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.93 (m, 2 H), 7.52−7.45 (m, 1 H), 7.41−7.36 (m, 2 H), 7.32−7.27 (m, 2 H), 6.90−6.82 (m, 2 H), 4.71−4.48 (m, 2 H), 3.86−3.67 (m, 2 H), 3.82 (s, 3 H), 3.79 (s, 3H), 3.74 (s, 3 H), 2.31−2.18 (m, 1 H), 1.95−1.68 (m, 2 H), 1.62−1.48 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.3, 199.2, 197.5, 163.5, 159.0, 158.9, 137.8, 137.1, 136.8, 133.0, 132.8, 131.0, 129.8, 129.7, 129.6, 129.4, 128.8, 128.7, 128.6, 128.4, 127.6, 114.4. 114.3, 113.8, 81.5, 81.4, 80.6, 68.4, 68.0, 58.9, 58.4, 58.0, 55.5, 55.2, 55.1, 30.9, 30.8, 29.7, 25.7, 25.5; HRMS calcd for $C_{19}H_{20}O_3$ 296.1412, found 296.1411.

1-(2-Methoxyphenyl)-2-phenyl-2-(tetrahydrofuran-2-yl)-ethanone and 2-(2-Methoxyphenyl)-1-phenyl-2-(tetrahydrofuran-2-yl)ethanone (**2s**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06−7.99 (m, 2 H), 7.47−7.43 (m, 1 H), 7.39−7.32 (m, 4 H), 7.23−7.20 (m, 2 H), 7.08−7.02 (m, 2 H), 6.92−6.84 (m, 2 H), 5.24−5.18 (m, 1 H), 4.70−4.61 (m, 2 H), 3.95 (s, 3 H), 3.92 (s, 3 H), 3.82 (s, 3 H), 3.91−3.69 (m, 2 H), 2.22−2.17 (m, 1 H), 1.91−1.84 (m, 2 H), 1.61−1.53 (m, 1 H), ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.3, 201.5, 199.7, 199.1, 156.7, 156.3, 137.4, 136.9, 136.8, 136.5, 133.3, 133.1, 132.8, 132.7, 130.9, 129.2, 128.8, 128.7, 128.6, 128.5, 128.4, 128.3, 127.2, 127.0, 121.2, 121.1, 120.7, 120.6, 111.4, 111.3, 111.0, 110.8, 81.5, 81.2, 80.8, 80.7, 68.7, 68.5, 68.3, 67.9, 55.8, 55.6, 55.3, 55.2, 50.2, 49.5, 30.8, 30.6, 29.7, 28.8, 25.7, 25.6, 25.5, 25.4; HRMS calcd for $C_{19}H_{20}O_3$ 296.1412, found 296.1411.

1-(2-Bromophenyl)-2-phenyl-2-(tetrahydrofuran-2-yl)ethanone and 2-(2-Bromophenyl)-1-phenyl-2-(tetrahydrofuran-2-yl)-ethanone (**2t**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10−8.07 (m, 1 H), 8.01−7.98 (m, 1 H), 7.61−7.59 (m, 1 H), 7.52−7.48 (m, 1 H), 7.42−7.39 (m, 3 H), 7.25−7.20 (m, 1 H), 7.09−7.05 (m, 1 H), 5.44−5.42 (m, 1 H), 5.25−5.17 (m, 1 H), 4.78−4.52 (m, 2 H), 3.91−3.85 (m, 4 H), 2.29−2.18 (m, 2 H), 1.94−1.82 (m, 6 H), 1.74−1.64 (m, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 202.4, 198.9, 198.5, 141.9, 136.9, 136.6, 135.8, 135.6, 135.1, 133.6, 133.5, 133.4, 133.2, 133.1, 131.3, 131.2, 129.7, 129.3, 129.2, 129.0, 128.8, 128.8, 128.7, 128.6, 128.5, 128.0, 127.9, 125.8, 125.1, 81.5, 81.4, 80.7, 68.6, 68.4, 68.1, 67.0, 63.0, 62.9, 56.9, 55.8, 32.3, 31.1, 30.5, 25.8, 25.6, 25.4; HRMS calcd for $C_{18}H_{17}BrO_2$ 344.0412, found 344.0410.

2-(1,3-Dioxolan-2-yl)-1-phenylethanone (**3a**). Light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.96 (m, 2 H), 7.60−7.55 (m, 1 H), 7.49−7.45 (m, 2 H), 5.45 (t, J = 5.2 Hz, 1 H). 4.03−3.99 (m, 2 H), 3.93−3.89 (m, 2 H), 3.35 (d, J = 5.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.7, 137.1, 133.5, 129.0, 128.8, 128.5, 101.5, 65.2, 43.5; HRMS calcd for $C_{11}H_{12}O_3$ 192.0786, found 192.0785.

2-(1,3-Dioxolan-2-yl)-1-p-tolylethanone (**3b**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (d, J = 8.4 Hz, 2 H), 7.26 (d, J = 8.0 Hz, 2 H), 5.44 (t, J = 5.2 Hz, 1 H), 4.02−3.96 (m, 2 H), 3.95−3.89 (m, 2 H), 3.32 (d, J = 5.2 Hz, 2 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.3, 144.3, 134.7, 129.5, 128.6, 101.6, 65.2, 43.5, 21.8; HRMS calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0944.

2-(1,3-Dioxolan-2-yl)-1-m-tolylethanone (**3c**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.75 (m, 2 H), 7.40−7.33 (m, 2 H), 5.44 (t, J = 5.2 Hz, 1 H), 4.03−3.97 (m, 2 H), 3.95−3.89 (m, 2 H), 3.33 (d, J = 5.2 Hz, 2 H), 2.41 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.9, 138.6, 137.1, 134.3, 128.9, 128.6, 125.7, 101.6, 65.1, 43.6, 43.6, 21.5; HRMS calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0942.

2-(1,3-Dioxolan-2-yl)-1-o-tolylethanone (**3d**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68−7.66 (m, 1 H), 7.40−7.36 (m, 1 H), 7.28−7.23 (m, 2 H), 5.40 (t, J = 4.8 Hz, 1 H), 4.01−3.95 (m, 2 H), 3.94−3.88 (m, 2 H), 3.28 (d, J = 4.8 Hz, 2 H), 2.52 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.3, 138.8, 137.7, 132.2, 131.8, 129.1, 125.8, 101.7, 65.1, 46.2, 21.5; HRMS calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0946.

2-(1,3-Dioxolan-2-yl)-1-(4-methoxyphenyl)ethanone (**3e**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96−7.94 (m, 2 H), 6.96−6.93 (m, 2 H), 5.43 (t, J = 5.2 Hz, 1 H), 4.02−3.96 (m, 2 H), 3.95 (s, 3 H), 3.92−3.87 (m, 2 H), 3.30 (d, J = 4.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.2, 163.9, 130.8, 130.3, 113.9, 101.7, 65.1, 55.6, 43.2; HRMS calcd for $C_{12}H_{14}O_4$ 222.0892, found 222.0890.

2-(1,3-Dioxolan-2-yl)-1-(2-methoxyphenyl)ethanone (**3f**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.75 (m, 1 H), 7.49−7.45 (m, 1 H), 7.02−6.95 (m, 2 H), 5.43 (t, J = 4.8 Hz, 1 H), 4.00−3.96 (m, 2 H), 3.91 (s, 3 H), 3.90−3.88 (m, 2 H), 3.41 (d, J = 5.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 198.2, 158.9, 134.0, 130.8, 128.0, 120.9, 111.7, 101.5, 65.1, 55.6, 48.8; HRMS calcd for $C_{12}H_{14}O_4$ 222.0892, found 222.0891.

1-(4-Chlorophenyl)-2-(1,3-dioxolan-2-yl)ethanone (**3g**). Light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92−7.89 (m, 2 H), 7.46−7.43 (m, 2 H), 5.42 (t, J = 4.8 Hz, 1 H), 4.02−3.96 (m, 2 H), 3.95−3.89 (m, 2 H), 3.31 (d, J = 5.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.5, 140.0, 135.5, 129.9, 129.1, 101.4, 65.2, 43.6; HRMS calcd for $C_{11}H_{11}ClO_3$ 226.0397, found 226.0396.

1-(2-Chlorophenyl)-2-(1,3-dioxolan-2-yl)ethanone (**3h**). Orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55−7.53 (m, 1 H), 7.42−7.40 (m, 2 H), 7.36−7.31 (m, 1 H), 5.39 (t, J = 4.8 Hz, 1 H), 3.99−3.96 (m, 2 H), 3.93−3.86 (m, 2 H), 3.36 (d, J = 5.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.4, 139.2, 132.2, 131.3, 130.7, 129.6, 127.1, 101.4, 65.2, 47.8; HRMS calcd for $C_{11}H_{11}ClO_3$ 226.0397, found 226.0395.

1-(2-Bromophenyl)-2-(1,3-dioxolan-2-yl)ethanone (**3i**). Orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62−7.59 (m, 1 H), 7.48−7.46 (m, 1 H), 7.39−7.35 (m, 1 H), 7.32−7.28 (m, 1 H), 5.38 (t, J = 5.2 Hz, 1 H), 3.99−3.93 (m, 2 H), 3.92−3.86 (m, 2 H), 3.34 (d, J = 4.8 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 141.4, 133.8, 132.0, 129.2, 127.6, 118.9, 101.3, 65.1, 47.4; HRMS calcd for $C_{11}H_{11}BrO_3$ 269.9892, found 269.9890.

1-(4-Bromophenyl)-2-(1,3-dioxolan-2-yl)ethanone (**3j**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84−7.81 (m, 2 H), 7.62−7.59 (m, 2 H), 5.41 (t, J = 4.8 Hz, 1 H), 4.02−3.96 (m, 2 H), 3.94−3.88 (m, 2 H), 3.30 (d, J = 5.2 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 195.7, 135.8, 132.1, 130.0, 128.7, 101.4, 65.2, 43.5; HRMS calcd for $C_{11}H_{11}BrO_3$ 269.9892, found 269.9895.

2-(1,3-Dioxolan-2-yl)-1-(naphthalen-2-yl)ethanone (**3k**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (s, 1 H), 8.04 (q, J = 6.8 Hz, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 7.89 (t, J = 8.4 Hz, 2 H), 7.63−7.54 (m, 2 H), 5.51 (t, J = 4.8 Hz, 1 H), 4.05−3.99 (m, 2 H), 3.97−3.91 (m, 2 H), 3.48 (d, J = 5.2 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6, 135.9, 134.5, 132.6, 130.5, 129.8, 128.8, 128.7, 127.9, 127.0, 124.0, 101.7, 65.2, 43.6; HRMS calcd for $C_{15}H_{14}O_3$ 242.0943, found 242.0941.

2-(1,3-Dioxolan-2-yl)-1-phenylpropan-1-one (**3l**). Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.96 (m, 2 H), 7.59−7.55 (m, 1 H), 7.49−7.45 (m, 2 H), 5.16 (d, J = 5.6 Hz, 1 H), 3.98−3.92 (m, 2 H), 3.90−3.83 (m, 2 H), 3.71 (q, J = 13.2 Hz, 1 H), 1.31 (d, J = 6.8 Hz, 3 H);

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^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 137.0, 133.3, 128.7, 128.6, 128.5, 105.5, 65.3, 65.1, 45.5, 13.2; HRMS calcd for $C_{12}H_{14}O_3$ 206.0943, found 206.0946.

*2-(1,3-Dioxolan-2-yl)-1-(4-methoxyphenyl)propan-1-one (**3m**).* Orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99−7.95 (m, 2 H), 6.96−6.92 (m, 2 H), 5.14 (d, J = 9.6 Hz, 1 H), 3.98−3.92 (m, 2 H), 3.90 (s, 3 H), 3.89−3.83 (m, 1 H), 3.65 (q, J = 13.2 Hz, 1 H), 1.29 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 163.7, 131.0, 129.9, 113.9, 105.7, 65.3, 65.0, 55.6, 45.0, 13.3; HRMS calcd for $C_{13}H_{16}O_4$ 236.1049, found 236.1050.

*1-(4-Bromophenyl)-2-(1,3-dioxolan-2-yl)propan-1-one (**3n**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85−7.82 (m, 2 H), 7.62−7.59 (m, 2 H), 5.11 (d, J = 6.0 Hz, 1 H), 3.96−3.89 (m, 2 H), 3.88−3.82 (m, 2 H), 3.68−3.63 (m, 1 H), 1.29 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.2, 135.7, 132.0, 130.2, 128.5, 105.4, 65.3, 65.1, 45.5, 13.1; HRMS calcd for $C_{12}H_{13}BrO_3$ 284.0048, found 284.0050.

*2-(1,3-Dioxolan-2-yl)-1,2-diphenylethanone (**3o**).* Light yellow solid (mp 57−59 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98−7.95 (m, 2 H), 7.51−7.43 (m, 1 H), 7.42−7.40 (m, 4 H), 7.37−7.29 (m, 2 H), 7.25−7.22 (m, 1 H), 5.63 (d, J = 6.8 Hz, 1 H), 4.73 (d, J = 6.8 Hz, 1 H), 3.96−3.88 (m, 3 H), 3.86−3.81 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.5, 136.7, 134.6, 133.3, 129.1, 129.0, 128.9, 128.7, 127.9, 105.4, 65.4, 65.2, 58.2; HRMS calcd for $C_{17}H_{16}O_3$ 266.1099, found 266.1097.

*1-(4-Bromophenyl)-2-(1,3-dioxolan-2-yl)-2-phenylethanone and 2-(4-Bromophenyl)-2-(1,3-dioxolan-2-yl)-1-phenylethanone (**3p**).* Light yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95−7.92 (m, 1 H), 7.82−7.80 (m, 1 H), 7.54−7.48 (m, 2 H), 7.47−7.38 (m, 3 H), 7.35−7.26 (m, 2H), 5.60 (d, J = 6.8 Hz, 1 H), 5.57 (d, J = 6.8 Hz, 1 H), 4.71 (d, J = 6.8 Hz, 1 H), 4.65 (d, J = 7.2 Hz, 1 H), 3.95−3.81 (m, (m, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.1, 196.5, 136.5, 135.4, 134.2, 133.6, 133.5, 132.2, 132.0, 130.8, 130.4, 129.2, 129.1, 128.9, 128.8, 128.6, 122.2, 105.2, 105.1, 65.4, 65.3, 65.2, 58.3, 57.5; HRMS calcd for $C_{17}H_{15}BrO_3$ 346.0205, found 346.0206.

*2-(1,3-Dioxolan-2-yl)-1-(4-methoxyphenyl)-2-phenylethanone and 2-(1,3-Dioxolan-2-yl)-2-(4-methoxyphenyl)-1-phenylethanone (**3q**).* Orange oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97−7.94 (m, 2 H), 7.49−7.37 (m, 2 H), 7.35−7.30 (m, 2 H), 7.27−7.23 (m, 1 H), 6.88−6.85 (m, 2 H), 5.62 (d, J = 7.2 Hz, 1 H), 5.58 (d, J = 6.8 Hz, 1 H), 4.68 (d, J = 2.0 Hz, 1 H), 4.66 (d, J = 2.0 Hz, 1 H), 3.95−3.88 (m, 3 H), 3.86−3.82 (m, 1 H), 3.81 (s, 3 H), 3.75 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.7, 195.9, 163.7, 159.4, 136.7, 135.0, 133.2, 131.3, 130.1, 129.0, 128.9, 128.7, 127.8, 114.6, 113.9, 105.5, 105.4, 65.4, 65.3, 65.2, 57.9, 57.4, 55.6, 55.3; HRMS calcd for $C_{18}H_{18}O_4$ 298.1205, found 298.1206.

*2-(1,3-Dioxolan-2-yl)-1-(2-methoxyphenyl)-2-phenylethanone and 2-(1,3-Dioxolan-2-yl)-2-(2-methoxyphenyl)-1-phenylethanone (**3r**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−8.01 (m, 2 H), 7.72−7.69 (m, 1H), 7.49−7.45 (m, 1 H), 7.39−7.36 (m, 6 H), 7.24−7.20 (m, 4 H), 6.93−6.89 (m, 4 H), 5.70 (d, J = 7.2 Hz, 1 H), 5.59 (d, J = 6.8 Hz, 1 H), 5.34 (d, J = 6.8 Hz, 1 H), 4.88 (d, J = 6.8 Hz, 1 H), 3.98−3.86 (m, 8 H), 3.92 (s, 3 H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 199.6, 198.0, 158.3, 156.7, 136.6, 134.8, 133.7, 133.0, 131.1, 129.5, 128.9, 128.7, 128.4, 128.3, 127.3, 126.5, 123.5, 121.1, 120.7, 111.5, 105.6, 65.2, 65.1, 65.0, 55.9, 55.3, 49.2; HRMS calcd for $C_{18}H_{18}O_4$ 298.1205, found 298.1207.

*1-(2-Bromophenyl)-2-(1,3-dioxolan-2-yl)-2-phenylethanone and 2-(2-Bromophenyl)-2-(1,3-dioxolan-2-yl)-1-phenylethanone (**3s**).* Yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04−8.01 (m, 2 H), 7.64−7.62 (m, 1 H), 7.53−7.48 (m, 2 H), 7.47−7.39 (m, 4 H), 7.26−7.22 (m, 1H), 7.13−7.10 (m, 8 H), 5.71 (d, J = 6.8 Hz, 1 H), 5.62 (d, J = 8 Hz, 1 H), 5.37 (d, J = 6.8 Hz, 1 H), 5.34 (d, J = 4.4 Hz, 1 H), 4.03−3.85 (m, (m, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.3, 141.0, 136.9, 136.4, 134.2, 133.5, 133.4, 132.6, 129.6, 129.5, 128.9, 128.8, 128.6, 128.0, 127.8, 127.3, 127.0, 125.7, 105.7, 65.4, 65.3, 65.2, 64.8, 55.9, 54.6; HRMS calcd for $C_{17}H_{15}BrO_3$ 346.0205, found 346.0203.

*2-(1,3-Dioxolan-2-yl)-1,3-diphenylpropan-1-one (**3t**).* Light yellow solid (mp 69−71 °C): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77−7.74 (m, 2 H), 7.48−7.44 (m, 1 H), 7.36−7.31 (m, 2 H), 7.17−7.13 (m, 4 H), 7.11−7.08 (m, 1 H), 5.15 (d, J = 6.0 Hz, 1 H) 4.13−3.70 (m, 5 H), 3.26−3.20 (m, 1 H), 3.14−3.10 (m, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 200.6, 139.1, 138.2, 133.0, 129.2, 128.5, 128.4, 128.4, 126.4, 105.0, 65.3, 65.1, 53.1, 34.6; HRMS calcd for $C_{18}H_{18}O_3$ 288.1256, found 288.1257.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and characterization data, ^{1}H NMR and ^{13}C NMR spectra for all the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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