Letter to the Editor

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An efficient $MnCl_2$-catalyzed tandem acylation-cross-coupling reaction of *o*-halobenzoyl chloride with diorganyl magnesium compounds

Fengmin Zhang, Zhuangzhi Shi, Feng Chen and Yu Yuan*

An efficient tandem cross-coupling reaction of *o*-chlorobenzoyl chloride with dialkyl and diaryl magnesium compounds in the presence of manganese (II) chloride was developed, which proceeds in good yield under mild conditions.

Keywords: manganese; magnesium; tandem; coupling reaction; catalysis

Introduction

The cross-coupling reaction of organometallic reagents with organic electrophiles in the presence of a transition-metal catalyst is a classical method of forming C–C bonds.[1,2] Since the discovery of the Kumada coupling reaction,[3] many transition metals, such as nickel, palladium,[4–8] iron[9–13] and copper,[14–17] have been used to catalyze the reaction of organomagnesium compounds with halides. Some examples employ manganese (II) as the catalyst[18–25] and recently Cahiez found that organomanganese reagents could be cross-coupled with *ortho*-acylated aryl chlorides in good yields.[26] Recently we reported the homocoupling reaction of halide compounds in one pot by a combination of metallic magnesium and $MnCl_2$.[27] Herein, we report an efficient tandem cross-coupling reaction of *o*-chlorobenzoyl chloride with dialkyl and diaryl magnesium compounds in the presence of manganese (II) chloride.

Initial studies focused on the cross-coupling reaction of dialkyl magnesium with aryl halides catalyzed by a transition metal. Unfortunately, all attempts to perform this reaction failed (Scheme 1). It was realized that the use of Grignard reagents rather than dialkyl magnesium compounds is of utmost importance in making this kind of cross-coupling reaction proceed. We therefore proposed the tandem cross-coupling reaction of dialkyl magnesium with *o*-halobenzoyl chloride **1**, in which the necessary Grignard reagents would be generated *in situ* from acylation of the dialkyl magnesium **2** with *o*-halobenzoyl chloride (Scheme 1). Cahiez reported the Mn-catalyzed acylation reaction of organomagnesium reagents with acyl chloride,[28] which is similar to this reaction. The resulting Grignard reagent would then react immediately with the aryl halide **4** in the presence of the catalyst. This would provide a one pot synthesis of substituted aryl ketones.

As shown in Table 1, various types of *n*-butylmagnesium reagents **2** were tested (in quantities amounting to 2.6 eq. *n*-butyl group) to optimize the reaction with *o*-chlorobenzoyl chloride **1a** catalyzed by manganese (II) chloride. Alongside the expected product **3a**, some other compounds, **5–8**, were also observed in certain cases due to the reductivity and nucleophilicity of the organomagnesium reagents. Their exact formation can be explained as follows: ketone **5** is the intermediate **4** (in Scheme 1) which has failed to undergo the Kumada type coupling reaction; alcohol **6** is the result of reduction of **5** which occurs by oxygen complexation to an organomagnesium compound followed by β-hydride elimination onto the carbonyl group;[29] **7** and **8** are the products of addition of a second butyl group to **5** followed by elimination. These side reactions led to only moderate yields of the desired product **3a** when Grignard reagent **2a** and tributylmagnesiate complex **2b** were used.[30] The magnesium cyanocuprate **2c** merely underwent acylation in the presence of the catalyst giving no other products. The dibutylmagnesium **2d** reacted well with **1a**, giving only small amounts of the by-products, although all types were detected. The best result for this reaction was obtained using the dibutylmagnesium lithium chloride complex **2e**. Lithium chloride has been shown to enhance the reactivity of Grignard reagents (formed *in situ* in this case) by breaking up RMgCl aggregates and thus forming $RMgCl_2Li$ complexes with magnesiate character.[31–33]

To examine the substrate scope of this tandem cross-coupling reaction, various halogen-substituted benzoyl chlorides were reacted with **2e** under the optimized conditions (Table 2). It was found that iron (III) can also catalyze this type of reaction in good yield, but the result is not better than that using manganese (II). Interestingly, only *ortho*-substituted arenes underwent reaction, with even the equally reactive *para*-substituted compound resisting coupling. This indicates that some kind of intramolecular coordination by the ketone is necessary for activation of metal intermediates or reagents for the coupling reaction to occur. It was also of interest that dichloride **1a** was the best

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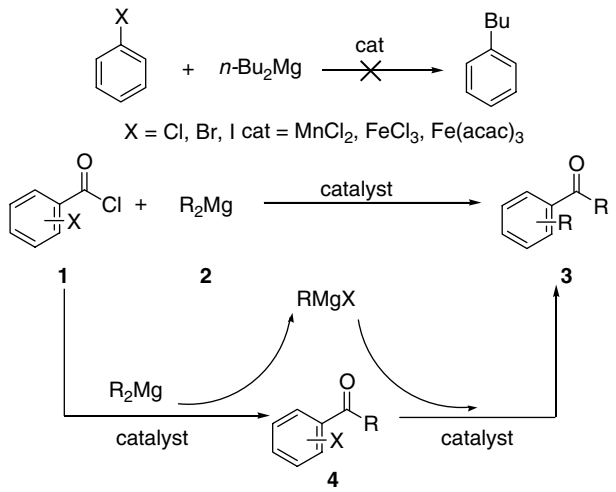
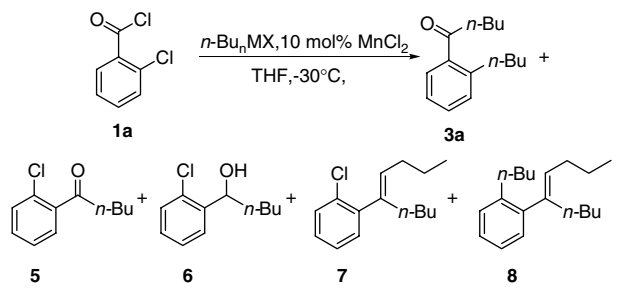


Scheme 1. Possible reaction path of the aryl halides with dialkyl magnesium.

Table 1. Mn(II)-catalyzed cross-coupling reaction between *o*-chlorobenzoyl chloride and different organometallic reagents[a]



Entry	*n*-Bu$_n$MX	Conversion (%)[b] 3a	5	6	7	8
1	*n*-BuMgBr (2.6 equiv.) **2a**	51	10	23	9	4
2	*n*-Bu$_3$MgLi (0.87 equiv.) **2b**	59	32	9	0	0
3	*n*-BuCu(CN)MgBr (2.6 equiv.) **2c**	0	99	0	0	0
4	*n*-Bu$_2$Mg (1.3 equiv.) **2d**	83	7	2	5	2
5	*n*-Bu$_2$Mg•LiCl (1.3 equiv.) **2e**	94	1	1	0	0

[a] Reactions were carried out with *n*-Bu$_n$MX (2.6 equiv. of *n*-Bu) and $MnCl_2$ (0.1 equiv.) in THF at −30 °C for 0.5 h by pump.
[b] Conversions were determined by GC.

reagent for the tandem cross-coupling reaction with heavier halogen-substituted benzoyl chlorides giving progressively lower yields – only a modest yield was obtained using iodo-substituted **1c** in the reaction, which is unusual in normal cross-coupling reactions.

With these pleasing results in hand, the tandem cross-coupling reaction of **1a** with various dialkylmagnesium-lithium chloride complexes **2** was investigated in the presence of 10 mol% $MnCl_2$ in THF at −30 °C. (Table 3) The reactions of all dialkylmagnesium compounds with **1a**, shown in Table 3, took place smoothly to afford the corresponding products in good yields. It was found that the reactions using higher dialkylmagnesium compounds (**2i, 2k, 2l**) as substrates were better than that using using diethylmagnesium, **2f**, which demonstrates that the reductivity and nucleophilicity of **2f** is stronger than those of higher dialkylmagnesiates, as noted previously in the literature,[34] and lead more quickly to by-products. The best results were obtained with the long-chain dialkylmagnesium compounds **2i** and **2k**. More sterically hindered dicyclopentylmagnesium **2j** gave a lower yield (79%) than the open chain analog **2i** (91%).

Finally, we investigated the scope of diarylmagnesium–LiCl complexes (prepared according to the literature[35]) compatible with the $MnCl_2$-catalyzed tandem cross-coupling reaction of various *o*-halobenzoyl chlorides. (Table 4). In contrast with the dialkylmagnesium compounds, the best yield, using diphenylmagnesium **2m**, was obtained using iodo-arene **1c**. Because of the instability of **1c**, the almost equally reactive bromo-arene **1b** was chosen as the substrate for testing the remaining diarylmagnesium compounds in the reaction. All revealed high reactivity in giving products containing a biphenyl core – a structure found widely in ligands and drugs.

Conclusion

In summary, we have developed a one-pot synthesis of (ortho-organyl)aryl organyl ketones, in which the organyl groups are the same, which proceeds in good yield under mild conditions. This Mn(II)-catalyzed reaction of diorganyllmagnesium lithium chloride complexes with *o*-halobenzoyl chlorides involves acylation followed by cross-coupling reaction of the resulting Grignard reagent and is thus more atom-economic and less time consuming than the equivalent two step procedure using Grignard reagents. Current work in our laboratory is concerned with the use of hetero-diorganylmagnesium compounds to put different substituents on the arene and the ketone in one pot.

Experimental Section

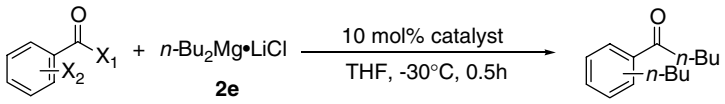
General

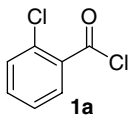
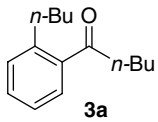
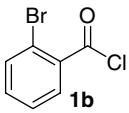
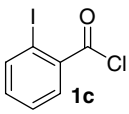
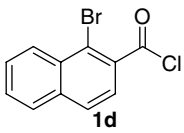
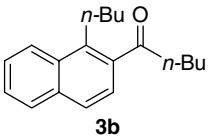
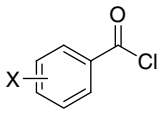
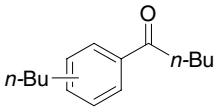
Melting points were recorded on an electrothermal digital melting point apparatus and uncorrected. ^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker Avance 600 spectrometer in $CDCl_3$ with TMS as an internal standard. Infrared spectra were recorded with a Bruker Tensor 27 FT-IR spectrophotometer using KBr pellets. GC-MS was performed on a Finnigan Trace DSQ chromatograph. The analytical data for the known compounds was found to match the literature data.

Materials

All reactions were carried out under a argon atmosphere in dried Schlenk-flask. THF and 1,4-dioxane were continously refluxed and freshly distilled from sodium benzophenone ketyl under nitrogen. LiCl (anhydrous, 99%), *n*-Bu$_2$Mg (1.0 M in THF), *i*-PrMgCl (1.0 M in THF), *n*-BuLi (2.5 M in hexane), 2-chlorobenzoyl chloride, 3-chlorobenzoyl chloride, 4-chlorobenzoyl chloride, 2-bromobenzoyl chloride, 3-bromobenzoyl chloride, 4-bromobenzoyl chloride, 2-iodobenzoyl chloride, 1-bromo-4-methylbenzene and 1-bromo-4-methoxybenzene were purchased

Table 2. Tandem cross-coupling reaction of *o*-halobenzoyl chloride with dibutylmagnesium[a]



Entry	Substrate	Catalyst	Product	Yield (%)[b]
1	 **1a**	$MnCl_2$	 **3a**	93
2	**1a**	$FeCl_3$	**3a**	80
3	**1a**	$Fe(acac)_3$	**3a**	83
4	 **1b**	$MnCl_2$	**3a**	76
5	 **1c**	$MnCl_2$	**3a**	41
6	 **1d**	$MnCl_2$	 **3b**	84
7	 X=*m*-Cl, *p*-Cl, *m*-Br, *p*-Br **1e**	$MnCl_2$		0

[a] Reactions were carried out with *n*-Bu_2Mg·LiCl(1.3 equiv.) and catalyst (0.1 equiv.) in THF at −30 °C for 0.5 h by pump.
[b] Yield after column.

from Alfa Aesar. $MnCl_2·4H_2O$ (purum p.a.) and LiCl (anhydrous, 99%) were dried in a vacuum oven at 200 °C under reduced pressure (0.1 torr) for 24 h. Organometallic reagents [*n*-BuCu(CN)MgBr,[36] *n*-Bu_3MgLi[30]] in Table 1 were prepared according to the literature.

Procedure to Prepare some Organometallic Reagents in Table 1

Entry l

A 10 ml Schlenk-flask, equipped with a magnetic stirring bar, was charged with the $MnCl_2$ (0.05 mmol), THF (2 ml) and *o*-chlorobenzoyl chloride (0.5 mmol) were added and the solution cooled to −30 °C. Subsequently, organometallic reagent [*n*-BuMgBr (1.3 ml, 1.0 M in THF, 1.3 mmol)/*n*-BuCu(CN)MgBr (1.3 ml, 1.0 M in THF, 1.3 mmol)/(1.8 ml, 0.25 M in THF, 0.45 mmol)/*n*-Bu_2 Mg (0.65 ml, 1.0 M in THF, 0.65 mmol)/*n*-Bu_2 Mg·LiCl (1.30 ml, 0.50 M in THF, 0.65 mmol)] was added by pump in 10 min and then reaction mixture was stirred at this temperature for another 20 min. The mixture was quenched with HCl (5 ml, 1 M) and extracted with Et_2O (3 × 10 ml). The organic fractions were washed with brine, dried over $MgSO_4$, filtered and the solvent evaporated *in vacuo*. Yields were determined by GC-MS.

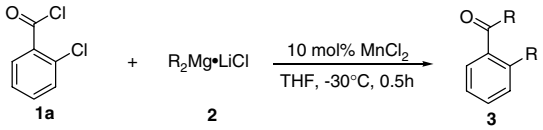
Typical Procedure for Tandem Reaction of *o*-Halogenbenzoyl Chloride with Dialkylmagnesium

Magnesium turnings (44 mmol) were placed in an Ar-flushed flask and THF (10 ml) was added. A solution of *n*-BuBr (40 mmol) in THF (15 ml) was slowly added at room temperature (r.t.). The reaction started within a few minutes. After addition, the reaction mixture was stirred for 12 h at r.t. The gray solution of *n*-BuMgBr was cannulated to another flask under argon and removed in this way from the excess of magnesium. A yield of *ca* 95–98% of *n*-BuMgBr (25 ml, 1.6 M in THF, 40 mmol) was obtained.

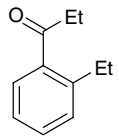
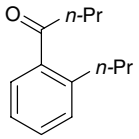
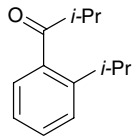
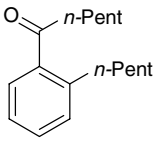
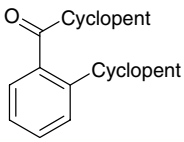
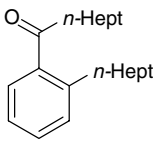
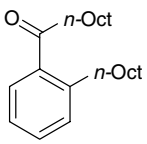
Anhydrous LiCl (20 mmol) was placed in an Ar-flushed Schlenk-flask and THF (10 ml) was added. A solution of *n*-BuMgBr (25 ml, 1.6 M in THF, 40 mmol) was added. After 5 min dry 1,4-dioxane (4 ml, ∼10 vol%, ∼1.1 equiv. referring to $MgCl_2$) was added. The reaction was slightly exothermic and a white precipitate was formed. After 2 h of stirring at room temperature, the white precipitate was filtrated off under Ar. The concentration of the resulting clear solution *n*-Bu_2Mg·LiCl was about 0.5 M.

A 10 ml Schlenk-flask, equipped with a magnetic stirring bar, was charged with the $MnCl_2$ (0.05 mmol), THF (2 ml) and *o*-chlorobenzoyl chloride (0.5 mmol) were added and the solution cooled to −30 °C. Subsequently, *n*-Bu_2Mg·LiCl (1.3 ml, 0.5 M, 0.65 mmol) was added by pump in 10 min and then the reaction

Table 3. Tandem cross-coupling reaction of *o*-chlorobenzoyl chloride with dialkylmagnesium[a]



1a **2** **3**

Entry	Alkyl$_2$Mg	Product		Yield (%)[b]
1	$Et_2Mg \cdot LiCl$ **2f**		**3c**	70
2	$n\text{-}Pr_2Mg \cdot LiCl$ **2g**		**3d**	76
3	$i\text{-}Pr_2Mg \cdot LiCl$ **2h**		**3e**	81
4	$n\text{-}Pent_2Mg \cdot LiCl$ **2i**		**3f**	91
5	$Cyclopent_2Mg \cdot LiCl$ **2j**		**3g**	79
6	$n\text{-}Hept_2Mg \cdot LiCl$ **2k**		**3h**	90
7	$n\text{-}Oct_2Mg \cdot LiCl$ **2l**		**3i**	85

[a] Reactions were carried out with dialkylmagnesium (1.3 equiv.) and $MnCl_2$ (0.1 equiv.) in THF at −30 °C for 0.5 h by pump.
[b] Yield after column.

mixture was stirred at this temperature for another 20 min. The mixture was quenched with HCl (5 ml, 1 M) and was extracted with Et_2O (3 × 10 ml). The organic fractions were washed with brine, dried over $MgSO_4$, filtered and the solvent was evaporated *in vacuo*. The residue was purified by chromatography on silica gel to give pure products.

Typical Procedure for the Reaction of *o*-Halogenbenzoyl Chloride with Diarylmagnesium

Magnesium turnings (110 mmol) and anhydrous LiCl (100 mmol) were placed in an Ar-flushed flask and THF (50 ml) was added. A solution of *i*-PrBr (100 mmol) in THF (50 ml) was slowly added at r.t. The reaction started within a few minutes. After addition, the reaction mixture was stirred for 12 h at r.t. The gray solution of *i*-PrMgBr·LiCl was cannulated to another flask under Ar and removed in this way from the excess of magnesium. A yield of *ca* 95–98% of *i*-PrMgBr·LiCl (1.05 M in THF) was obtained.

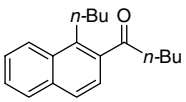
A dry and argon-flushed 50 ml Schlenk-flask, equipped with a magnetic stirrer and a septum, was charged with *i*-PrMgBr·LiCl (25 ml, 1.0 M in THF, 25 mmol) and neat 1-bromo-4-methoxybenzene (25 mmol). Dioxane (2.5 ml) was added in one portion to the reaction mixture at 25 °C. The reaction mixture was stirred at 25 °C and the completion of the Br/Mg exchange was checked by GC-analysis using tetradecane as internal standard. The Br/Mg-exchange was completed after 24 h at r.t.

A 10 ml Schlenk-flask, equipped with a magnetic stirring bar, was charged with the $MnCl_2$ (0.05 mmol), THF (2 ml) and *o*-bromobenzoyl chloride (0.5 mmol) were added and the solution cooled to −30 °C. Subsequently, (4-methoxyphenyl)$_2$Mg·LiCl (3.1 ml, 0.4 M, 1.2 mmol) was added and then reaction mixture was stirred at this temperature for 1 h. The mixture was quenched with HCl (5 ml, 1 M) and was extracted with Et_2O (3 × 10 ml). The organic fractions were washed with brine, dried over $MgSO_4$, filtered and the solvent evaporated *in vacuo*. The residue was purified by chromatography on silica gel to give pure products.

*1-(2-butylphenyl)pentan-1-one (**3a**)*[26]

A colorless liquid. The spectra data is identical to the literature.

*1-(1-butyl-2-naphthyl)pentan-1-one (**3b**)*



A viscous slightly yellow liquid. IR:(KBr) ν_{max} 2956, 2928, 2867, 1691, 1461, 1377, 812, 751 cm^{-1}; ^{1}H NMR: (600 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4 Hz, 1H, CH arom), 7.85 (d, J = 7.8 Hz, 1H, CH arom), 7.73 (d, J = 8.4 Hz, 1H, CH arom), 7.58–7.48 (m, 3H, CH arom), 3.11 (t, J = 7.8 Hz, 2H, CH_2 to C=O), 2.92 (t, J = 7.2 Hz, 2H, PhCH_2), 1.75–1.68 (m, 4H, 2CH_2), 1.55–1.50 (m, 4H, 2CH_2), 1.00–0.94 (m, 6H, 2CH_3); ^{13}C NMR: (150 MHz, $CDCl_3$) δ 207.30 (C=O), 138.08 (C arom), 137.26 (C arom), 134.38 (C arom), 132.26 (C arom), 128.73 (C arom), 126.75 (C arom), 126.63 (C arom), 126.40 (C arom), 125.26 (C arom), 123.69 (C arom), 43.19 (CH_2 to C=O), 34.11 (PhCH_2), 29.35 (CH_2), 26.60 (CH_2), 23.40 (CH_2), 22.56 (CH_2), 14.03 (CH_3), 14.01 (CH_3); HRMS calcd for $C_{19}H_{24}O$ 268.1827; found: 268.1830.

*1-(2-ethylphenyl)propan-1-one (**3c**)*[37]

A colorless liquid. The spectra data is identical to the literature.

*1-(2-propylphenyl)butan-1-one (**3d**)*[38]

A colorless liquid. The spectra data is identical to the literature.

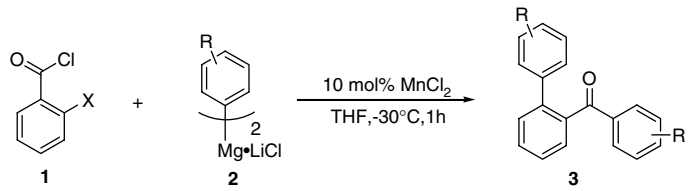
*1-(2-isopropylphenyl)-2-methylpropan-1-one (**3e**)*[39]

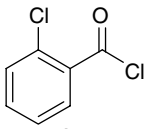
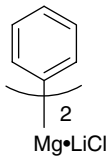
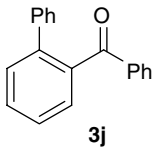
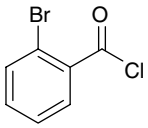
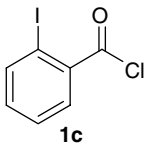
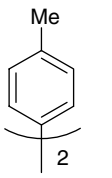
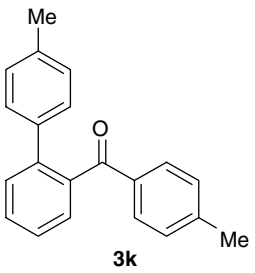
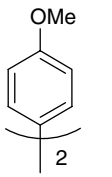
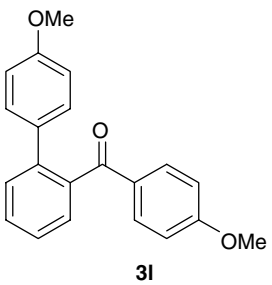
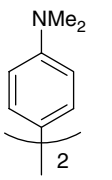
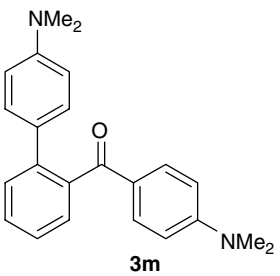
A colorless liquid. The spectra data is identical to the literature.

*1-(2-pentylphenyl)hexan-1-one (**3f**)*[40]

A colorless liquid. The spectra data is identical to the literature.

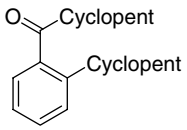
Table 4. Tandem cross-coupling reaction of *o*-chlorobenzoyl chloride with diarylmagnesium[a]



Entry		$Aryl_2Mg$	Product	Yield (%)[b]
1	 **1a**	 **2m**	 **3j**	53
2	 **1b**	**2m**	**3j**	90
3	 **1c**	**2m**	**3j**	92
4	**1b**	 **2n**	 **3k**	96
5	**1b**	 **2o**	 **3l**	88
6	**1b**	 **2p**	 **3m**	75

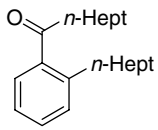
[a] Reactions were carried out with diarylmagnesium (2.0–3.0 equiv.) and $MnCl_2$ (0.1 equiv.) in THF at −30 °C for 1.0 h.
[b] Yield after column.

*Cyclopentyl(2-cyclopentylphenyl)methanone (**3g**)*



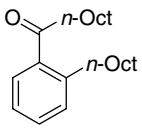
A colorless liquid. IR:(KBr) ν_{max} 2953, 2867, 1807, 1765, 1687, 1464, 1371, 1119, 1071, 758 cm^{-1}; ^1H NMR: (600 MHz, $CDCl_3$) δ 7.39–7.35 (m, 3H, CH arom), 7.21–7.19 (m, 1H, CH arom), 3.47 (tt, J = 15.6 Hz, 7.8 Hz, 1H, C*H* to C═O), 3.20 (tt, J = 17.4 Hz, 8.4 Hz, 1H, PhC*H*), 1.86–1.62 (m, 8H, 4CH_2), 1.58–1.25 (m, 8H, 4CH_2); ^{13}C NMR: (150 MHz, $CDCl_3$) δ 208.83 (C═O), 144.11 (C arom), 140.02 (C arom), 129.34 (C arom), 126.05 (C arom), 125.53 (C arom), 124.30 (C arom), 50.12 (*C*H to C═O), 40.91 (PhCH), 34.71 (CH_2), 28.81 (CH_2), 26.52 (CH_2), 25.20 (CH_2), 25.08 (CH_2); HRMS calcd for $C_{17}H_{22}O$ 242.1671; found: 242.1678.

*1-(2-Heptylphenyl)octan-1-one (**3h**)*



A colorless liquid. IR:(KBr) ν_{max} 2924, 2858, 1689, 1457, 1372, 1220, 653 cm^{-1}; ^1H NMR: (600 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 1H, CH arom), 7.37–7.35 (m, 1H, CH arom), 7.26–7.22 (m, 2H, CH arom), 2.86 (t, J = 7.8 Hz, 2H, CH_2 to C═O), 2.76 (t, J = 7.8 Hz, 2H, PhCH_2), 1.72–1.67 (m, 2H, CH_2), 1.61–1.53 (m, 2H, CH_2), 1.35–1.26 (m, 16H, 8CH_2), 0.89–0.86 (m, 6H, 2CH_3); ^{13}C NMR: (150 MHz, $CDCl_3$) δ 205.73 (C═O), 142.29 (C arom), 139.10 (C arom), 130.94 (C arom), 130.73 (C arom), 127.90 (C arom), 125.58 (C arom), 42.38 (*C*H$_2$ to C═O), 33.84 (PhCH$_2$), 32.07 (CH_2), 31.93 (CH_2), 31.81 (CH_2), 29.78 (CH_2), 29.40 (CH_2), 29.28 (CH_2), 29.23 (CH_2), 24.51 (CH_2), 22.75 (CH_2), 22. 71 (CH_2), 14.18 (CH_3), 14.15 (CH_3); HRMS calcd for $C_{21}H_{34}O$ 302.2610; found: 302.2606.

*1-(2-Octylphenyl)nonan-1-one (**3i**)*

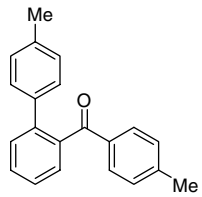


A colorless liquid. IR:(KBr) ν_{max} 2953, 2929, 2857, 1690, 1467, 1366, 752 cm^{-1}; ^1H NMR: (600 MHz, $CDCl_3$) δ 7.52 (d, J = 7.8 Hz, 1H, CH arom), 7.37–7.35 (m, 1H, CH arom), 7.26–7.22 (m, 2H, CH arom), 2.86 (t, J = 7.2 Hz, 2H, CH_2 to C═O), 2.76 (t, J = 7.8 Hz, 2H, PhCH_2), 1.71–1.68 (m, 2H,CH_2), 1.56–1.54 (m, 2H,CH_2), 1.34–1.22 (m, 20H, 10CH_2), 0.88 (m, 6H, 2CH_3); ^{13}C NMR: (150 MHz, $CDCl_3$) δ 205.59 (C═O), 142.28 (C arom), 139.11 (C arom), 130.92 (C arom), 130.69 (C arom), 127.88 (C arom), 125.55 (C arom), 42.35 (*C*H$_2$ to C═O), 33.83 (PhCH$_2$), 32.04 (CH_2), 31.97 (CH_2), 31.92 (CH_2), 29.82 (CH_2), 29.56 (CH_2), 29.52 (CH_2), 29.43 (CH_2), 29.35 (CH_2), 29.25 (CH_2), 24.50 (CH_2), 22.74 (CH_2), 22.72 (CH_2), 14.18 (CH_3), 14.14 (CH_3); HRMS calcd for $C_{23}H_{38}O$ 330.2923; found: 330.2917.

*Biphenyl-2-yl-phenyl-methanone (**3j**)*[41]

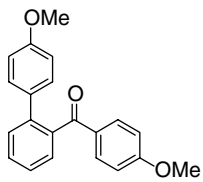
A white solid. The spectra data is identical to the literature.

*4-Methyl-biphenyl-2-yl)-(4-methyl-phenyl)-methanone (**3k**)*



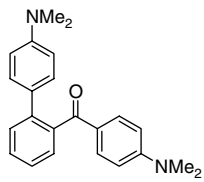
A white solid. M.p. = 152–153 °C IR:(KBr) ν_{max} 3030, 2963, 1659, 1600, 1512, 1474, 1379, 1253, 1150, 1044, 923, 823, 775 cm^{-1}; ^1H NMR: (600 MHz, $CDCl_3$) δ 7.60 (d, J = 7.8 Hz, 2H, CH arom), 7.53 (t, J = 7.8 Hz, 2H, CH arom), 7.47–7.40 (m, 3H, CH arom), 7.16 (d, J = 7.8 Hz, 1H, CH arom), 7.10 (d, J = 7.8 Hz, 2H, CH arom), 7.02 (d, J = 7.8 Hz, 2H, CH arom), 2.34 (s, 3H, CH_3), 2.25 (s, 3H, CH_3); ^{13}C NMR: (150 MHz, $CDCl_3$) δ 198.51 (C═O), 143.82 (C arom), 141.02 (C arom), 139.12 (C arom), 137.37 (C arom), 137.03 (C arom), 134.88 (C arom), 130.27 (C arom), 130.17 (C arom), 130.12 (C arom), 129.07 (C arom), 128.94 (C arom), 128.81 (C arom), 128.56 (C arom), 126.69 (C arom), 22.25 (CH_3), 21.72 (CH_3); HRMS calcd for $C_{21}H_{18}O$ 286.1358; found: 286.1366.

*4-Methoxy-biphenyl-2-yl)-(4-methoxy-phenyl)-methanone (**3l**)*



A white solid. M.p. = 101–102 °C IR:(KBr) ν_{max} 2933, 2839, 1644, 1601, 1511, 1450, 1301, 1251, 1144, 1023, 926, 841, 765 cm^{-1}; ^1H NMR: (600 MHz, $CDCl_3$) δ 7.60 (d, J = 8.4 Hz, 2H, CH arom), 7.53 (t, J = 7.2 Hz, 2H, CH arom), 7.46–7.39 (m, 3H, CH arom), 7.24 (d, J = 8.4 Hz, 1H, CH arom), 6.76 (t, J = 8.4 Hz, 4H, CH arom), 3.80 (s, 3H, OCH_3), 3.73 (s, 3H, OCH_3); ^{13}C NMR: (150 MHz, $CDCl_3$) δ 197.66 (C═O), 163.38 (C arom), 158.92 (C arom), 140.33 (C arom), 139.18 (C arom), 132.76 (C arom), 132.39 (C arom), 130.34 (C arom), 130.05 (C arom), 129.99 (C arom), 129.95 (C arom), 128.42 (C arom), 126.62 (C arom), 113.79 (C arom), 113.45 (C arom), 55.44 (OCH$_3$), 55.20 (OCH$_3$); HRMS calcd for $C_{21}H_{18}O_3$ 318.1256; found: 318.1259.

*4-Dimethylamino-biphenyl-2-yl)-(4-dimethylamino-phenyl)-methanone (**3m**)*



A green solid. M.p. = 171–173 °C IR:(KBr) ν_{max} 3898, 1593, 1531, 1478, 1441, 1370, 1291, 1190, 1142, 1062, 934, 817, 762 cm^{-1}; ^1H NMR: (600 MHz, $CDCl_3$) δ 7.68 (d, J = 9.0 Hz, 2H, CH arom), 7.50–7.46 (m, 3H), 7.39–7.33 (m, 2H, CH arom), 7.25 (d, J = 8.4 Hz, 1H, CH arom), 6.62 (d, J = 9.0 Hz, 2H, CH arom), 6.54 (d, J = 9.0 Hz, 2H, CH arom), 3.02 [s, 6H, N(CH_3)$_2$], 2.90 [s, 6H, N(CH_3)$_2$]; ^{13}C NMR: (150 MHz, $CDCl_3$) δ 197.32 (C═O), 153.28 (C arom), 149.61 (C arom), 140.53 (C arom), 139.68 (C arom), 132.52 (C arom), 129.75 (C arom),

129.60 (C arom), 129.28 (C arom), 128.60 (C arom), 128.19 (C arom), 125.75 (C arom), 125.34 (C arom), 112.35 (C arom), 110.42 (C arom), 40.47 ($2CH_3$), 40.01 ($2CH_3$); HRMS calcd for $C_{23}H_{24}N_2O$ 344.1889; found: 344.1895.

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