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6-Methyl-2,4-pyrimidyl Diesters. A Highly Efficient Acylating Agent for the Synthesis of Unsymmetrical Ketones†

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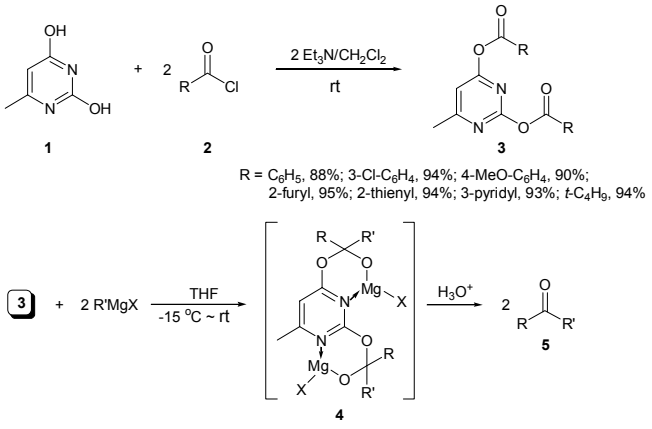
It is well known that the reaction of organometallics with carboxylic acid derivatives is a useful method for the synthesis of ketones.[1] The reaction of acid chlorides with Grignard reagents gives ketones, but yields are low to moderate due to the formation of the corresponding tertiary alcohols.[2] To overcome these drawbacks the reaction of *in situ* formed acyl triphenylphosphonium ions from acid chlorides and Bu_3P with Grignard reagents has been developed, but the separation of Bu_3P is tedious.[3] Alternatively, the coupling of acid chlorides with terminal alkynes[4] or organostannanes[5] in the presence of palladium catalyst and alkynyldimethylaluminum reagents,[6] derived from Et_3N-catalyzed alumination of terminal alkynes, leads to the aromatic ketones or ynones at reflux temperature. Although thiol esters are also coupled with organozinc[7] or organoboron reagents[8] in the presence of $PdCl_2(PPh_3)_2$ to afford ketones including aldehyde, ester, and halide functional groups, these methods are exclusively limited to the synthesis of aliphatic ketones.

The reaction of tertiary amides such as *N*-acylaziridines[9] and morpholine amides[10] with Grignard or organolithium reagents gives ketones upon acidic workup of the tetrahedral intermediates in moderate to high yields. Among tertiary amides, *N*-methoxy-*N*-methylamides[11] developed by Weinreb is most popular, which are converted to ketones with both organolithiums and Grignard reagents through metal-chelated intermediates.[12] However, the high cost of MeONHMe·HCl and low yields in case of less reactive Grignard reagents make Weinreb amides to limit their uses. The most effective acylating agents toward Grignard reagents appear to be the active esters containing 2-pyridyl moiety which enhances the reactivity and prevents the release of carbonyl group by ring nitrogen atom. Thus, the treatment of *S*-(2-pyridyl) thioates[13] and *N*-methyl-*N*-(2-pyridyl) amides[14] with Grignard reagents leads to the 6-membered chelates, which prevent the premature ketones liberation, and are dissociated to afford ketones. The reaction of 2-acyl-3-methylpyrazines[15] and *N*-(acyl-*N*-methylamino)cycloiminium salts[16] with Grignard or organolithium reagents also gives ketones, but 2 equiv of organometallics is required for the high yields formation of ketones.

However, there are no reports of acylating agents that can produce 2 equiv of ketones with ogranometallics except our previous report.[17] In conjunction with the development of new acylating agents we wish to report that 2 equiv of ketones can be efficiently synthesized from 6-methyl-2,4-pyrimidyl diesters and Grignard reagents in high yields. In choosing 6-methyl-2,4-pyrimidyl group as active moiety, we considered that two nitrogen atoms of ring are chelated with magnesium atoms, hence to avoid the formation of the corresponding tertiary alcohol. Furthermore, 6-methyl-2,4-pyrimidyl diesters are the stable crystalline compounds, reactive toward Grignard reagents, and 2,4-dihydroxy-6-methylpyrimidine as a starting material is very cheap.

6-Methyl-2,4-pyrimidyl diesters **3** were newly prepared by the addition of 2 equiv of acid chlorides **2** to a mixture solution of 2,4-dihydroxy-6-methylpyrimidine **1** and 2 equiv of triethylamine in dichloromethane at room temperature (Scheme 1). The nucleophilic acyl substitution of **2** with **1** was completed in 3 ~ 12 h at room temperature because **1** was slightly soluble in dichloromethane. After evaporation of dichloromethane, the mixture was dissolved in THF, followed by filtering off triethylamine hydrochloride and was separated by usual workup. The active esters **3** were obtained in 88 ~ 95% yields after recrystallization from 15 ~ 20% EtOAc/*n*-hexane and are thermally stable, thus their melting points were measured without any decomposition.

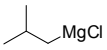
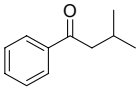
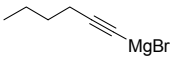
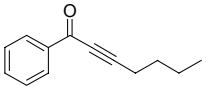
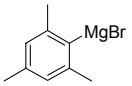
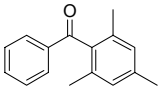
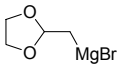
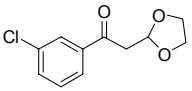
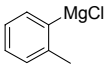
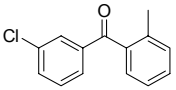
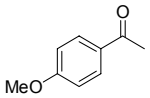
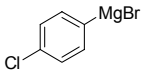
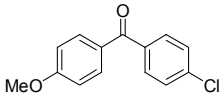
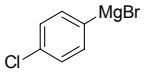
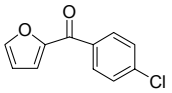
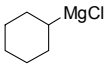
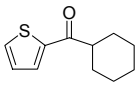
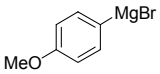
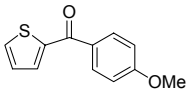
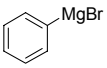
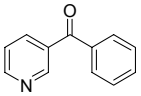
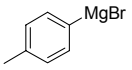
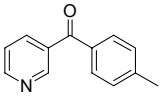
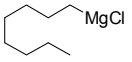
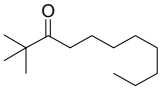
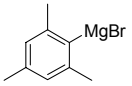
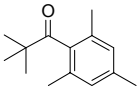
The successful synthesis of ketones **5** using **3** was carried out by the slow addition of 2 equiv of Grignard reagents to a solution of **3** in THF at −15 °C. For example, 2 equiv of 2,4,6-trimethylphenylmagnesium bromide was added to a solution of 1 equiv of 6-methyl-2,4-pyrimidyl dibenzoate in THF over 5 min at −15 °C and stirred for 3 h between −15 °C and room



Scheme 1

†This paper is dedicated to Professor Sunggak Kim on the occasion of his honorable retirement.

Table 1. Preparation of unsymmetrical ketones from 6-methyl-2,4-pyrimidyl diesters and Grignard reagents

entry **5**	R	R'MgX	reaction conditions temp (°C) ; time (h)	ketones	isolated yield (%)
a	C_6H_5		−15 ; 0.5		85
b			−15 → rt ; 2		73
c			−15 → rt ; 3		95
d	3-Cl-C_6H_4		rt ; 7		84
e			−15 → 0 ; 3		91
f	4-MeO-C_6H_4	CH_3MgBr	−15 → 0 ; 1		78
g			−15 → 0 ; 1		94
h	2-Furyl		−15 → rt ; 1		87
i	2-Thienyl		−15 → rt ; 0.5		81
j			−15 → rt ; 1.5		82
k	3-Pyridyl		−15 → rt ; 1		90
l			−15 → rt ; 1		87
m	$(CH_3)_3C$		−15 → 0 ; 1		81
n			0 → rt ; 6		78

temperature. The mixture was hydrolyzed with saturated NH_4Cl solution to give 2,4,6-trimethylbenzophenone in 95% yield without the formation of the corresponding tertiary alcohol. The success of ketone synthesis may be ascribed to the formation of 6-membered chelate **4** between magnesium atoms of Grignard reagent and carbonyl oxygen/ring nitrogen atoms of **3**, which would react very sluggishly with Grignard reagent and is dissociated to give **5** after acidic hydrolysis.

As shown in Table 1, various unsymmetrical ketones were efficiently prepared in high yields (73 ~ 95%) by this method. The reaction worked well with both aliphatic and aromatic Grignard reagents regardless of the kind of electron donating (**5e**, **5j**, **5l**) and electron withdrawing group (**5g**, **5h**) in the substituted phenylmagnesium bromide. Also the kind of electron withdrawing (**5d**, **5e**) and electron donating group (**5f**, **5g**) in the substituted 6-methyl-2,4-pyrimidyl dibenzoate didn't in-

fluence on the substitution of 6-methyl-2,4-pyrimidyl group by Grignard reagents. The reaction proceeded equally well with 6-methyl-2,4-pyrimidyl diesters containing heteroaromatic groups (**5h-5l**) to give the corresponding ketones in high yields (81 ~ 90%) within 1.5 h between −15 °C and room temperature. Although the reaction of **3** with 1-hexynylmagnesium bromide (**5b**) and highly hindered 2,4,6-trimethylphenylmagnesium bromide (**5c**, **5n**) proceeded slowly between −15 °C and room temperature, the corresponding ketones were obtained in 73%, 95%, and 78% yield, respectively. Especially, it was worth while to note that the reaction of 6-methyl-2,4-pyrimidyl di(3-chlorobenzoate) with (1,3-dioxolan-2-ylmethyl)magnesium bromide afforded α-(1,3-dioxolan-2-yl) 3'-chloroacetophenone **5d** in 84% yield in 7 h at room temperature. The corresponding reaction using *N*-methoxy-*N*-methyl 3-chlorobenzamide didn't proceed to give **5d** even after 24 h at room temperature and the starting material was recovered in 98% yield.

In summary, 6-methyl-2,4-pyrimidyl diesters are newly developed by the reaction of 2 equiv of acid chlorides and cheap 2,4-dihydroxy-6-methylpyrimidine, are stable for long periods of time, and react efficiently with Grignard reagents to give 2 equiv of ketones in high yields under mild conditions, and thus may be utilized in many ketone syntheses.

Experimental Section

Preparation of 6-methyl-2,4-pyrimidyl dibenzoate (General procedure). To a suspension of 2,4-dihydroxy-6-methylpyrimidine (883 mg, 7.0 mmol) in dichloromethane (50 mL) was added triethylamine (1.97 mL, 14.1 mmol) and benzoyl chloride (1.97 g, 14.0 mmol) at room temperature. After being stirred overnight, dichloromethane was evaporated in vacuo. The mixture was dissolved in THF, followed by filtering off triethylamine hydrochloride. After evaporation of THF, the mixture was poured into saturated $NaHCO_3$ solution (40 mL), extracted with dichloromethane (3 × 30 mL), and washed with brine (40 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was recrystallized from 15% EtOAc/*n*-hexane to give 6-methyl-2,4-pyrimidyl dibenzoate (2.06 g, 88%). mp 82 ~ 83 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19-8.24 (m, 4H), 7.62-7.70 (m, 2H), 7.48-7.54 (m, 4H), 7.25 (s, 1H), 2.66 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 173.6, 167.0, 164.0, 163.1, 161.0, 134.6, 134.2, 130.6 (overlapped), 128.8, 128.6, 128.4, 128.0, 110.6, 24.3; FT-IR (KBr) 3068, 1748 (C=O), 1595, 1450, 1259, 997, 699 cm^{-1}; Ms *m/z* (%) 334 (M^+, 1), 306 (22), 278 (16), 229 (21), 105 ($C_6H_5C{\equiv}O^+$, 100), 77 (92).

Preparation of 1-phenyl-2-heptyn-1-one 5b (General procedure). To a solution of 1-hexyne (345 μL, 3.0 mmol) in THF (5 mL) was slowly added methylmagnesium bromide (0.5 M in THF, 6.0 mL, 3.0 mmol) at 0 °C. After being stirred for 0.5 h, the resulting solution was added to a solution of 6-methyl-2,4-pyrimidyl dibenzoate (501 mg, 1.5 mmol) in THF (15 mL) over 5 min at −15 °C. After being stirred for 2 h between −15 °C and room temperature, the mixture was quenched with saturated NH_4Cl solution (3 mL) and THF was evaporated in vacuo. The mixture was poured into saturated NH_4Cl solution (30 mL), extracted with dichloromethane (3 × 20 mL), and washed with saturated $NaHCO_3$ solution (30 mL). The combined organic phases were dried over $MgSO_4$, filtered, and concentrated in vacuo. The residue was purified by vacuum distillation using Kugelrohr apparatus to give **5b** (408 mg, 73%). bp 95 ~ 100 °C/1.0 mmHg; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.14 (d, J = 8.4 Hz, 2H), 7.57-7.62 (m, 1H), 7.45-7.50 (m, 2H), 2.51 (t, J = 7.0 Hz, 2H), 1.62-1.69 (m, 2H), 1.47-1.55 (m, 2H), 0.97 (t, J = 7.3 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 178.3, 136.9, 133.9, 129.6, 128.5, 96.9, 79.7, 29.9, 22.1, 18.9, 13.5; FT-IR (film) 3060, 2959, 2200 (C≡C), 1644 (C=O), 1597, 1449, 1265, 701 cm^{-1}; Ms *m/z* (%) 186 (M^+, 10), 185 (23), 157 (44), 144 ([C_6H_5-CO-C≡C-CH_3]$^+$, 100), 115 (55), 105 (74), 77 (46).

3-Methylbutyrophenone (5a): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 8.3 Hz, 2H), 7.52-7.55 (m, 1H), 7.43-7.48 (m, 2H), 2.83 (d, J = 6.9 Hz, 2H), 2.25-2.34 (m, 1H), 1.00 (d, J = 6.7 Hz, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 200.3, 137.4, 132.9, 128.5, 128.1, 47.5, 25.2, 22.8; FT-IR (film) 3062, 2958, 2871, 1686 (C=O), 1598, 1449, 1366, 1213, 752, 691 cm^{-1}; Ms *m/z* (%) 162 (M^+, 29), 120 (40), 107 (37), 105 (100), 77 (53).

2,4,6-Trimethylbenzophenone (5c): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 8.5 Hz, 2H), 7.54-7.59 (m, 1H), 7.40-7.46 (m, 2H), 6.89 (s, 2H), 2.33 (s, 3H), 2.08 (s, 6H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 200.8, 138.5, 137.3, 136.9, 134.2, 133.6, 129.4, 128.8, 128.3, 21.2, 19.4; FT-IR (film) 3061, 2920, 1671 (C=O), 1611, 1596, 1448, 1379, 1268, 1170, 910, 711 cm^{-1}; Ms *m/z* (%) 224 (M^+, 83), 223 (100), 209 (43), 147 (51), 119 (27), 105 (16), 77 (28).

***α*-(1,3-Dioxolan-2-yl) 3'-chloroacetophenone (5d):** ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (t, J = 1.7 Hz, 1H), 7.94 (dt, J_1 = 7.8 Hz, J_2 = 1.3 Hz, 1H), 7.52 (dt, J_1 = 7.8 Hz, J_2 = 1.1 Hz, 1H), 7.38 (dd, J_1 = 7.9 Hz, J_2 = 7.9 Hz, 1H), 6.52 (dd, J_1 = 14.3 Hz, J_2 = 6.8 Hz, 1H), 4.54-4.58 (m, 2H), 4.24 (dd, J_1 = 14.3 Hz, J_2 = 2.3 Hz, 1H), 4.08 (dd, J_1 = 6.8 Hz, J_2 = 2.3 Hz, 1H), 4.00-4.04 (m, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 165.3, 151.4, 134.5, 133.1, 131.6, 129.7, 127.9, 87.2, 65.7, 63.5; FT-IR (film) 2925, 1722 (C=O), 1621, 1427, 1257, 819, 748 cm^{-1}; Ms *m/z* (%) 226 (M^+, 1), 185 (33), 183 (94), 141 (36), 139 (100), 111 (58).

3-Chloro-2'-methylbenzophenone (5e): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 (d, J = 1.8 Hz, 1H), 7.66 (d, J = 7.8 Hz, 1H), 7.52 (d, J = 7.5 Hz, 1H), 7.38-7.42 (m, 2H), 7.25-7.31 (m, 3H), 2.34 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 197.1, 139.4, 137.8, 137.0, 134.8, 133.0, 131.2, 130.7, 129.9, 129.8, 128.6, 128.3, 125.5, 20.0; FT-IR (film) 3020, 1666 (C=O), 1570, 1422, 1260, 738, 675 cm^{-1}; Ms *m/z* (%) 232 (M^++2, 16), 230 (M^+, 48), 195 (100), 119 (73), 91 (80).

4-Methoxyacetophenone (5f): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.94 (d, J = 6.9 Hz, 2H), 6.93 (d, J = 6.9 Hz, 2H), 3.87 (s, 3H), 2.56 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 196.8, 163.5, 130.6, 130.3, 113.7, 55.5, 26.4; FT-IR (film) 3010, 2965, 1673 (C=O), 1602, 1359, 1258, 833 cm^{-1}; Ms *m/z* (%) 150 (M^+, 56), 135 (100), 107 (21), 92 (23), 77 (39).

4-Chloro-4'-methoxybenzophenone (5g): mp 126 ~ 127 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80 (d, J = 6.9 Hz, 2H), 7.71 (d, J = 6.7 Hz, 2H), 7.45 (d, J = 6.7 Hz, 2H), 6.97 (d, J = 6.9 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 194.3, 163.4, 138.3, 136.5, 132.5, 131.2, 129.8, 128.5, 113.7, 55.5; FT-IR (KBr) 3025, 2924, 1640 (C=O), 1601, 1493, 1452, 1371, 1029, 853, 759 cm^{-1}; Ms *m/z* (%) 248 (M^++2, 16), 246 (M^+, 47), 141

(4), 139 (14), 135 (100), 111 (11).

4-Chlorophenyl (2'-furyl) methanone (5h): mp 58 ~ 59 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, J = 8.4 Hz, 2H), 7.71 (s, 1H), 7.47 (d, J = 8.4 Hz, 2H), 7.26 (d, J = 3.7 Hz, 1H), 6.61 (dd, J_1 = 3.5 Hz, J_2 = 1.6 Hz, 1H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 181.1, 152.2, 147.2, 139.1, 135.4, 130.8, 128.8, 120.6, 112.4; FT-IR (KBr) 3128, 1651 (C=O), 1586, 1461, 1308, 1089, 961, 837, 754 cm^{-1}; Ms *m*/*z* (%) 208 (M^++2, 11), 206 (M^+, 32), 141 (13), 139 (39), 111 (18), 95 (100).

Cyclohexyl (2-thienyl) methanone (5i): ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 (dd, J_1 = 3.8 Hz, J_2 = 1.1 Hz, 1H), 7.61 (dd, J_1 = 5.0 Hz, J_2 = 1.1 Hz, 1H), 7.13 (dd, J_1 = 5.0 Hz, J_2 = 3.8 Hz, 1H), 3.05-3.15 (m, 1H), 1.83-1.94 (m, 4H), 1.72-1.76 (m, 1H), 1.48-1.61 (m, 2H), 1.20-1.45 (m, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 196.8, 143.9, 133.4, 131.4, 128.0, 47.5, 29.6, 25.8 (overlapped); FT-IR (film) 2930, 2853, 1651 (C=O), 1519, 1415, 1252, 719 cm^{-1}; Ms *m*/*z* (%) 196 (M^++2, 3), 194 (M^+, 74), 139 (34), 126 (40), 113 (13), 111 (100).

4-Methoxyphenyl (2'-thienyl) methanone (5j): mp 73 ~ 74 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 (d, J = 8.9 Hz, 2H), 7.68 (dd, J_1 = 5.0 Hz, J_2 = 1.1 Hz, 1H), 7.64 (dd, J_1 = 3.8 Hz, J_2 = 1.1 Hz, 1H), 7.15 (dd, J_1 = 4.9 Hz, J_2 = 3.8 Hz, 1H), 6.98 (d, J = 8.9 Hz, 2H), 3.89 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 186.9, 163.1, 143.8, 134.0, 133.4, 131.6, 130.7, 127.8, 113.7, 55.5; FT-IR (KBr) 3110, 3009, 2969, 1630 (C=O), 1505, 1417, 1253, 1023, 835, 740 cm^{-1}; Ms *m*/*z* (%) 220 (M^++2, 3), 218 (M^+, 80), 135 (100), 111 (37), 92 (13), 77 (15).

Pheny (3-pyridyl) methanone (5k): ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.00 (d, J = 1.5 Hz, 1H), 8.81 (dd, J_1 = 4.8 Hz, J_2 = 1.7 Hz, 1H), 8.12 (ddd, J_1 = 7.9 Hz, J_2 = 2.0 Hz, J_3 = 2.0 Hz, 1H), 7.80-7.84 (m, 2H), 7.61-7.64 (m, 1H), 7.43-7.54 (m, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 194.9, 152.8, 150.9, 137.2, 136.7, 133.2, 130.0, 128.6, 128.1, 123.4; FT-IR (film) 3058, 1662 (C=O), 1585, 1416, 1284, 923, 713 cm^{-1}; Ms *m*/*z* (%) 183 (M^+, 100), 182 (53), 106 (22), 105 (91), 77 (59).

4-Methylphenyl (3'-pyridyl) methanone (5l): mp 76 ~ 77 °C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.97-8.99 (m, 1H), 8.80 (dd, J_1 = 4.8 Hz, J_2 = 1.7 Hz, 1H), 8.10 (ddd, J_1 = 7.9 Hz, J_2 = 2.0 Hz, J_3 = 2.0 Hz, 1H), 7.74 (d, J = 8.0 Hz, 2H), 7.44 (ddd, J_1 = 7.9 Hz, J_2 = 4.9 Hz, J_3 = 0.8 Hz, 1H), 7.32 (d, J = 8.0 Hz, 2H), 2.46 (s, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 194.5, 152.6, 150.8, 144.2, 137.1, 134.1, 133.5, 130.3, 129.3, 123.3, 21.7; FT-IR (KBr) 3030, 1651 (C=O), 1606, 1420, 1288, 1024, 825, 741 cm^{-1}; Ms *m*/*z* (%) 197 (M^+, 98), 182 (52), 119 (100), 106 (18), 91 (59).

2,2-Dimethyl-3-undecanone (5m): ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.47 (t, J = 7.3 Hz, 2H), 1.52-1.59 (m, 2H), 1.25-1.32 (m, 10H), 1.13 (s, 9H), 0.88 (t, J = 6.7 Hz, 3H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 216.1, 44.1, 36.4, 31.9, 29.5, 29.4, 29.2, 26.4, 24.0, 22.7, 14.1; FT-IR (film) 2926, 2852, 1708 (C=O), 1452, 1365, 1070 cm^{-1}; Ms *m*/*z* (%) 198 (M^+, 4), 142 (10), 141 (100), 85 (10), 71 (41).

2',4',6'-Trimethyl-2,2-dimethylpropiophenone (5n): ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.82 (s, 2H), 2.26 (s, 3H), 2.17 (s, 6H), 1.23 (s, 9H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 219.5, 139.6, 137.3, 132.0, 128.4, 44.8, 28.1, 20.9, 20.3; FT-IR (film) 2968, 2871, 1688 (C=O), 1611, 1477, 1379, 1365, 1147, 930, 851 cm^{-1}; Ms *m*/*z* (%) 204 (M^+, 1), 148 (30), 147 (100), 119 (56), 91 (23).

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