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Facile preparation of aromatic ketones from aromatic bromides and arenes with aldehydes

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ABSTRACT

Aromatic ketones were efficiently prepared in good yields by the reactions of aryl bromides with *n*-BuLi, followed by the reactions with aromatic aldehydes or aliphatic aldehydes and the subsequent treatment with molecular iodine and K_2CO_3, in a one-pot method. The same treatment of arenes, instead of aromatic bromides, also provided the corresponding aromatic ketones in good yields. Using these methods, various diaryl ketones and alkyl aryl ketones bearing electron-rich aromatics and electron-deficient aromatics could be prepared efficiently by a simple, transition-metal-free, and therefore environmentally benign experimental procedure.

1. Introduction

Aromatic ketones are very important and useful building blocks or structural elements for the manufactures of pharmaceuticals and agrochemicals.[1] Generally, aromatic ketones are prepared by the Friedel–Crafts reaction of arenes and acyl halides with Lewis acids,[2,3] the Houben–Hoesch reaction of arenes and nitriles with Lewis acid,[3,4] the Fries rearrangement of aryl esters with Lewis acids,[3,5] the reaction of ArMgX and acyl halides,[6] the oxidative reaction of aldehydes with organovanadiums prepared from RMgX and VCl_3,[7] the reaction of ArZnBr and acyl halides or carboxylic anhydrides with $CoBr_2$,[8] the reaction of methyl esters and vinylmagnesium bromide with CuCN,[9] the reaction of Weinreb amide and Grignard reagents,[10] the decarboxylative coupling reaction of α-oxocarboxylates and ArBr with CuBr and $Pd(F_6\text{-acac})_2$,[11] and the oxidative reaction of alkylarenes with HBr and H_2O_2.[12] However, there are still some drawbacks, such as the low yield depending on the substrate (lack of generality in substrates), the highly acidic condition, and the requirement of transition metals. In order to realize an environmentally benign, less toxic, less expensive, and practical organic synthesis, the preparation of aromatic ketones from easily available substrates, such as aromatic bromides or arenes and aldehydes without any transition metals under mild conditions is required. On the other hand, molecular iodine (I_2) is one of the simplest oxidants currently available. Because it is highly affordable and has very low toxicity, molecular iodine is used in various organic reactions, including the oxidation of alcohols or aldehydes to esters, the oxidation of sulfides to sulfoxides, the introduction of protecting groups, the deprotection of protecting groups, iodocyclization, carbon–carbon bond formation, and the formation of heterocycles.[13] As part of our ongoing studies on the use of molecular iodine for organic synthesis,[14] we would like to report a facile preparation of aromatic ketones from the reactions of aromatic bromides or arenes with *n*-BuLi, followed by the subsequent treatment with aldehydes, molecular iodine, and K_2CO_3.

2. Results and discussion

Treatment of *p*-bromotoluene with *n*-BuLi (1.1 equiv) in THF at −78 °C generated *p*-tolyl carbanion, which was reacted with benzaldehyde to provide the adduct, lithium 1-benzyl-1-(4′-methylbenzyl)methoxide bearing an α-hydrogen atom. After removal of the solvent, treatment of the formed lithium 1-benzyl-1-(4′-methylbenzyl)methoxide with molecular iodine (1.6 equiv) and K_2CO_3 (3.0 equiv) in *t*-BuOH for 3 h at refluxing conditions generated 4-methylbenzophenone in 91% yield, as shown in Table 1 (entry 1). When the last-reaction step was carried out in THF, the oxidation of lithium 1-benzyl-1-(4′-methylbenzyl)methoxide did not proceed efficiently, generating 4-methylbenzophenone in low yield (~20%). Previously, we reported an efficient oxidative conversion of alcohols to esters by molecular iodine and K_2CO_3 in *t*-BuOH, which has no hydrogen atom at the α-position and showed the best reactivity as a protic solvent.[14c] In the present reactions, *t*-BuOH showed the best reactivity again. Using the same procedure and conditions as in entry 1, preparation of aromatic ketones from the reaction of *p*-bromotoluene with *n*-BuLi, followed by the reactions with aldehydes, molecular iodine, and K_2CO_3 was carried out. Thus, *p*-tolyl carbanion was treated with various aromatic

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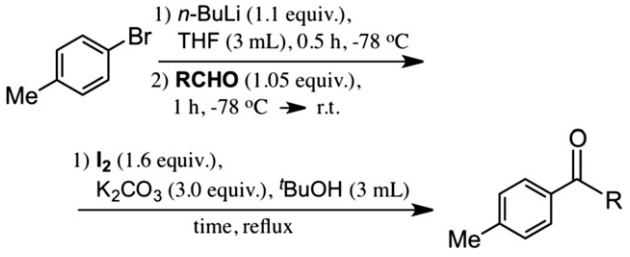
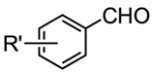
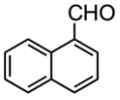
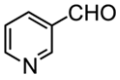
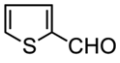
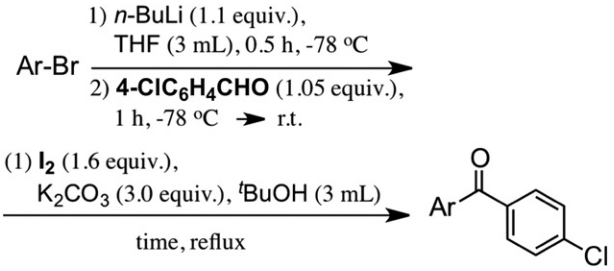
Table 1
Conversion of *p*-bromotoluene into *p*-methylphenyl ketones

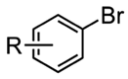
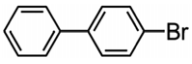
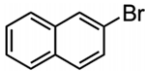
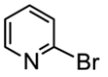
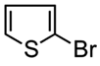


Entry	RCHO	Time[a] (h)	Yield (%)
			
1	R′=H	3	91
2	R′=*p*-F	3	98
3	R′=*p*-Cl	3	90
4	R′=*p*-Br	3	95
5	R′=*p*-CN	3	82
6	R′=*p*-Me	7	>99
7	R′=*p*-OMe	7	92
8	R′=*m*-Cl	3	85
9	R′=*o*-Cl	16	98
10	R′=2,4,6-$(Me)_3$	14	63 (trace)[b]
11		3	81
12		3	80
13		3	88

[a] THF solvent was removed before the second step reaction.
[b] Yield of alcohol.

Table 2
Conversion of aromatic bromides into aromatic ketones



Entry	Ar–Br	Time[a] (h)	Yield (%)
			
1	R=H	3	97
2	R=4-Me	3	90
3	R=3-Me	3	94
4	R=2-Me	18	99
5	R=4-OMe	3	93
6	R=4-Cl	3	88
7	R=4-Br	3	93
8	R=2,4-$(OMe)_2$	18	83
9	R=2,4,6-$(Me)_3$	18	70
10		3	88
11		3	85
12		3	81
13		3	98

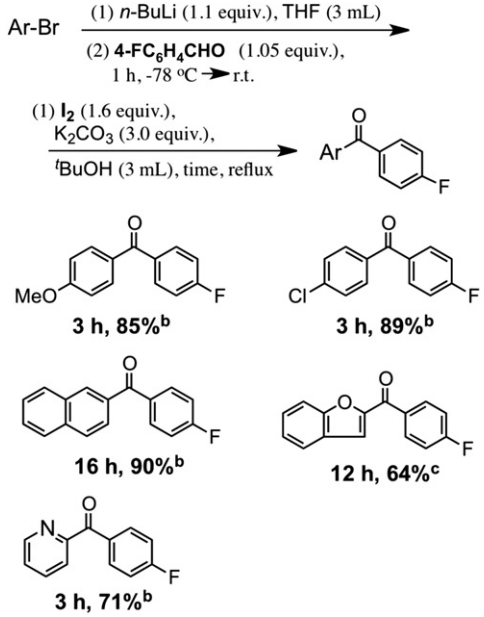
[a] THF solvent was removed before the second step reaction.

aldehydes bearing electron-donating groups and electron-withdrawing groups on the aromatic ring, as well as hetero-aromatic aldehydes, such as 3-pyridinecarboxaldehyde and 1-thiophenecarboxaldehyde, to give the corresponding aromatic ketones in good yields (entries 2–13). Using the same procedure, treatment of various aromatic bromides bearing electron-donating groups and electron-withdrawing groups on the aromatic ring, and heteroaromatic bromides, such as 2-bromopyridine and 2-bromothiophene, with *n*-BuLi at −78 °C, followed by treatments with 4-chlorobenzaldehyde, and molecular iodine and K_2CO_3 generated the corresponding aromatic ketones in good yields, as shown in Table 2. Using this method, electron-deficient aromatic ketones bearing a pyridyl group, a 4-chlorophenyl group, or a 4-bromophenyl group could be obtained efficiently. The same reactions of aromatic bromides with *n*-BuLi, and the subsequent treatment with 4-fluorobenzaldehyde and molecular iodine gave the corresponding 4-fluorobenzophenone derivatives in good yields, as shown in Scheme 1. Today, it is well known that fluoro aromatics are important compounds in the manufacture of pharmaceuticals, agrochemicals, and material science.[15]

The same treatment of 1-bromo-4-methoxybenzene, 1-bromo-4-methylbenzene, 1-bromo-4-chlorobenzene, and 2-bromopyridine with *n*-BuLi, followed by treatments with aliphatic aldehydes, such as propionaldehyde (primary alkyl group), cyclohexanecarboxaldehyde (secondary alkyl group), and pivalaldehyde (tertiary alkyl group), and the subsequent reaction with molecular iodine and K_2CO_3 provided the corresponding alkyl aryl ketones, as shown in Table 3. The corresponding ketones were obtained in good yields with cyclohexanecarboxaldehyde and pivalaldehyde, whereas, the yields with propionaldehyde were moderate due to the abstraction of the α-hydrogen atom of the aldehyde by the formed carbanions. Carbanions derived from arenes, such as anisole, dimethoxybenzenes, trimethoxybenzene, difluorobenzene, tetrafluorobenzene, methoxynaphthalene, *N*-methylimidazole, benzofuran, benzothiophene, and phenylacetylene, after reacting with *n*-BuLi, also reacted with 4-chlorobenzaldehyde, and the formed lithium alkoxides were treated with molecular iodine and K_2CO_3 to generate the corresponding aromatic ketones in good yields in a one-pot method, as shown in Table 4.

3. Conclusion

Various aromatic ketones bearing electron-donating groups and electron-withdrawing groups, including the pyridyl group and the thienyl group, were efficiently prepared by the reactions of aryl bromides with *n*-BuLi, followed by the reactions with aromatic aldehydes or aliphatic aldehydes, and the subsequent treatment with molecular iodine and K_2CO_3 in a one-pot method The same treatment of arenes bearing a methoxy group, a fluoro group, and



[a] THF solvent was removed before the second step reaction.
[b] First step reaction was carried out at -78 °C for 30 min.
[c] First step reaction was carried out at 0 °C for 2 h.

Scheme 1. Reaction with *p*-fluorobenzaldehyde.[a]

heteroaromatics, such as benzofuran and benzothiophene also provided the corresponding aromatic ketones in good yields. Thus, various diaryl ketones and alkyl aryl ketones bearing electron-rich aromatic groups and electron-deficient aromatic groups could be prepared efficiently with a simple experimental procedure. These reactions can be carried out under transition-metal-free conditions and used as an environmentally benign method for the preparation of various aromatic ketones.

4. Experimental

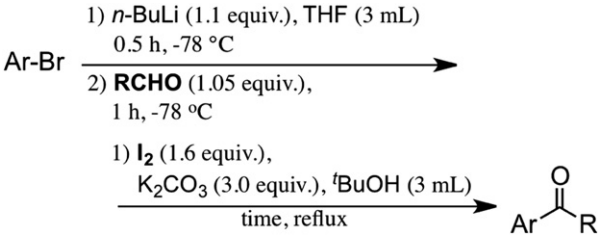
4.1. General

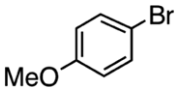
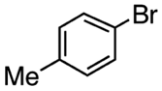
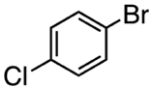
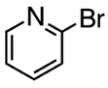
^{1}H NMR and ^{13}C NMR spectra were obtained with JEOL-JNM-ECX400, JEOL-JNM-ECS400, and JEOL-JNM-ECA500 spectrometers. Chemical shifts are expressed in parts per million downfield from TMS in δ units. Mass spectra were recorded on JMS-T100GCV, JMS-HX110, and Thermo LTQ Orbitrap spectrometers. IR spectra were measured with a JASCO FT/IR-4100 spectrometer. Melting points were determined with a Yamato Melting Point Apparatus Model MP-21. Silica gel 60 (Kanto Kagaku Co.) was used for column chromatography and Wakogel B-5F was used for preparative TLC.

4.2. Typical experimental procedure for one-pot conversion of aromatic bromides into ketones

n-Butyllithium (1.67 M solution in hexane, 1.32 mL, 2.2 mmol) was added dropwise to a solution of 1-bromo-4-methylbenzene (342 mg 2.0 mmol) in THF (3 mL) at −78 °C for 30 min. Then, 4-fluorobenzaldehyde (261 mg, 2.1 mmol) was added to the mixture at −78 °C and the obtained mixture was stirred at room temperature for 1 h. Then, after removal of the solvent, I_2 (812 mg, 3.2 mmol), K_2CO_3 (829 mg, 6.0 mmol), and *t*-BuOH (3 mL) were added and the obtained mixture was stirred for 3 h at refluxing conditions. The reaction mixture was quenched with satd aq Na_2SO_3 (5 mL) and was extracted with $CHCl_3$ (3×20 mL). The organic layer was washed with brine and dried over Na_2SO_4 to provide 4-fluoro-4′-methylbenzophenone in 98% yield with high purity. If necessary, the product was purified by a short flash column chromatography (silica gel; hexane/$CHCl_3$=1:3) to give pure 4-fluoro-4′-methylbenzophenone as a colorless solid.

Table 3
Reaction of aromatic bromides with aliphatic aldehydes



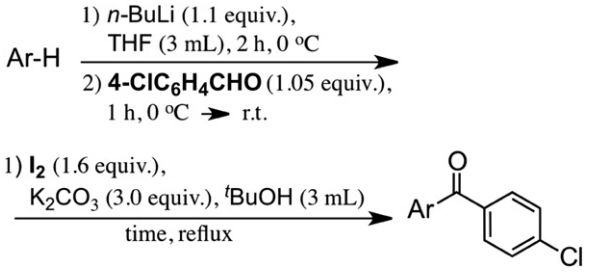
Entry	Ar–Br	–R	Time[a] (h)	Yield (%)
1		CH_3CH_2–	4	57
2			27[b]	83
3		$(CH_3)_3C$–	5	91
4		CH_3CH_2–	3	54
5			3	63
6		$(CH_3)_3C$–	16	86
7		CH_3CH_2–	4	45
8			8[b]	87
9		$(CH_3)_3C$–	5	91
10		CH_3CH_2–	4	32
11			14[b]	80
12		$(CH_3)_3C$–	5	91

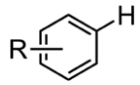
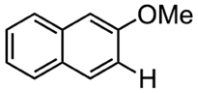
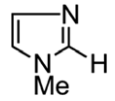
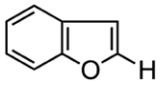
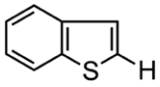
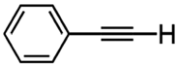
[a] THF solvent was removed before the second step reaction.
[b] Second reaction was carried out at −78 °C for 2 h.

4.2.1. 4-Methylbenzophenone. Mp 56–57 °C (lit.,[16] mp 57–68 °C); IR (Nüjol) 1654 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.44 (s, 3H), 7.23 (d, 2H, *J*=7.9 Hz), 7.44–7.49 (m, 2H), 7.57 (t, 1H, *J*=7.5 Hz), 7.72 (d, 2H, *J*=8.2 Hz), 7.75–7.80 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 128.2, 128.9, 129.9, 130.3, 132.1, 134.8, 137.9, 143.2, 196.5.

4.2.2. 4-Fluoro-4′-methylbenzophenone. Mp 97–98 °C (lit.[17] mp 96–97 °C); IR (Nüjol) 1647 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.11–7.17 (m, 2H), 7.28 (d, 2H, *J*=7.9 Hz), 7.68 (d, 2H,

Table 4
Conversion of arenes into aromatic ketones



Entry	Ar–H	Time[a] (h)	Yield (%)
			
1	R=2-OMe	18	79
2	R=2,6-$(OMe)_2$	18	80
3	R=2,5-$(OMe)_2$	18	79
4	R=2,3-$(OMe)_2$	18	49
5	R=2,4,6-$(OMe)_3$	18	51
6[b]	R=2,6-$(F)_2$	18	99
7[b]	R=2,3,5,6-$(F)_4$	18	97
8		18	88
9		18	62
10		3	87
11		3	90
12		3	83

[a] THF solvent was removed before the second step reaction.
[b] First step reaction was carried out at −78 °C for 1 h.

J=8.2 Hz), 7.79–7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 115.3 (d, J_{C-F}=21.1 Hz), 129.0, 130.0, 132.4 (d, J_{C-F}=8.6 Hz), 134.1 (d, J_{C-F}=2.9 Hz), 134.7, 143.2, 165.2 (d, J_{C-F}=254.8 Hz), 195.0.

4.2.3. 4-Chloro-4′-methylbenzophenone. Mp 128–129 °C (lit.[18] mp 126–127 °C); IR (Nüjol) 1644 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.28 (d, 2H, *J*=7.7 Hz), 7.45 (d, 2H, *J*=8.1 Hz), 7.69 (d, 2H, *J*=8.2 Hz), 7.75 (d, 2H, *J*=8.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 128.5, 129.1, 130.1, 131.3, 134.5, 136.2, 138.6, 143.5, 195.2.

4.2.4. 4-Bromo-4′-methylbenzophenone. Mp 140–142 °C (lit.[19] mp 139–140 °C); IR (Nüjol) 1644 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.29 (d, 2H, *J*=7.9 Hz), 7.59–7.70 (m, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.6, 127.2, 129.1, 130.2, 131.4, 131.5, 134.4, 136.6, 143.5, 195.3.

4.2.5. 4-Cyano-4′-methylbenzophenone. Mp 160–162 °C (lit.[20] mp 160–160 °C); IR (Nüjol) 1650, 2229 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 7.31 (d, 2H, *J*=7.9 Hz), 7.70 (d, 2H, *J*=8.2 Hz), 7.78 (d, 2H, *J*=8.6 Hz), 7.85 (d, 2H, *J*=8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 115.4, 118.0, 129.3, 130.1, 130.3, 132.1, 133.6, 141.6, 144.4, 194.7.

4.2.6. 4,4′-Dimethylbenzophenone. Mp 92–93 °C (commercial, mp 90–93 °C); IR (Nüjol) 1645 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 6H), 7.27 (d, 4H, *J*=8.4 Hz), 7.70 (d, 4H, *J*=8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 128.9, 130.2, 135.2, 142.9, 196.3.

4.2.7. 4-Methoxy-4′-methylbenzophenone. Mp 89–90 °C (lit.[17] mp 88–89 °C); IR (Nüjol) 1644 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.43 (s, 3H), 3.88 (s, 3H), 6.96 (d, 2H, *J*=9.1 Hz), 7.27 (d, 2H, *J*=7.7 Hz), 7.68 (d, 2H, *J*=8.2 Hz), 7.81 (d, 2H, *J*=9.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 55.4, 113.4, 128.8, 130.0, 130.4, 132.4, 135.5, 142.6, 163.0, 195.3.

4.2.8. 3-Chloro-4′-methylbenzophenone. Mp 97–99 °C (lit.[21] mp 97–98 °C); IR (Nüjol) 1648 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.29 (d, 2H, *J*=8.4 Hz), 7.40 (t, 1H, *J*=7.8 Hz), 7.54 (m, 1H), 7.64 (d, 1H, *J*=7.7 Hz), 7.70 (d, 2H, *J*=8.2 Hz), 7.75 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 127.9, 129.1, 129.5, 129.7, 130.2, 132.0, 134.2, 134.4, 139.6, 143.7, 194.9.

4.2.9. 2-Chloro-4′-methylbenzophenone. Mp 97–98 °C (lit.[22] mp 98.5–99.5 °C); IR (Nüjol) 1660 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.42 (s, 3H), 7.25 (d, 2H, *J*=7.9 Hz), 7.23–7.46 (m, 4H), 7.71 (d, 2H, *J*=8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 126.6, 128.9, 129.3, 129.9, 130.2, 130.9, 131.1, 133.9, 138.8, 144.7, 194.8.

4.2.10. 2,4,6,4′-Tetramethylbenzophenone. Colorless oil (lit.[23] mp 32–33 °C); IR (neat) 1667 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.08 (s, 6H), 2.32 (s, 3H), 2.41 (s, 3H), 6.88 (s, 2H), 7.23 (d, 2H, *J*=7.9 Hz), 7.70 (d, 2H, *J*=7.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 19.3, 21.1, 21.7, 128.2, 129.4, 129.5, 134.1, 134.9, 137.1, 138.3, 144.5, 200.4.

4.2.11. 1-Naphthyl 4′-methylphenyl ketone. Mp 79–81 °C (commercial, mp 83–84 °C); IR (Nüjol) 1644 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.41 (s, 3H), 7.21–7.25 (m, 2H), 7.44–7.58 (m, 4H), 7.76 (d, 2H, *J*=8.3 Hz), 7.90 (d, 1H, *J*=7.7 Hz), 7.98 (d, 1H, *J*=8.3 Hz), 8.04 (d, 1H, *J*=8.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ=21.7, 124.3, 125.7, 126.3, 127.1, 127.3, 128.3, 129.1, 130.5, 130.9, 130.9, 133.6, 135.7, 136.7, 144.5, 197.7.

4.2.12. 3-Pyridyl 4′-methylphenyl ketone. Mp 76–78 °C (lit.[24] mp 76–77 °C); IR (Nüjol) 1650 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.46 (s, 3H), 7.32 (d, 2H, *J*=7.9 Hz), 7.45 (ddd, 1H, J_1=7.9 Hz, J_2=4.9 Hz, J_3=0.9 Hz), 7.74 (d, 2H, *J*=8.4 Hz), 8.10 (dt, 1H, J_1=7.9 Hz, J_2=2.0 Hz), 8.80 (dd, 1H, J_1=4.9 Hz, J_2=2.0 Hz), 8.98 (dd, 1H, J_1=2.0 Hz, J_2=0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.7, 123.3, 129.3, 130.2, 133.5, 134.1, 137.1, 144.2, 150.8, 152.6, 194.5.

4.2.13. 2-Thienyl 4′-methylphenyl ketone. Mp 74–75 °C (lit.[25] mp 75.0–75.6 °C); IR (Nüjol) 1627 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.44 (s, 3H), 7.14–7.17 (m, 1H), 7.30 (d, 2H, *J*=7.9 Hz), 7.64 (dd, 1H, *J*=1.1 Hz, 5.0 Hz), 7.70 (dd, 1H, *J*=1.1 Hz, 6.1 Hz), 7.79 (d, 2H, *J*=8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.6, 127.8, 129.1, 129.4, 133.8, 134.4, 135.4, 143.0, 143.8, 187.9.

4.2.14. 4-Chlorobenzophenone. Mp 74–75 °C (lit.[26] mp 74–76 °C); IR (Nüjol) 1650 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.42–7.51 (m, 4H), 7.59 (t, 1H, *J*=7.4 Hz), 7.72–7.78 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 128.3, 128.6, 129.9, 131.4, 132.6, 135.8, 137.2, 138.8, 195.4.

4.2.15. 4-Chloro-3′-methylbenzophenone. Mp 103–105 °C (lit.[27] mp 101–102 °C); IR (Nüjol) 1650 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$):

δ 2.42 (s, 3H), 7.34–7.42 (m, 2H), 7.46 (d, 2H, *J*=8.9 Hz), 7.54 (d, 1H, *J*=7.5 Hz), 7.59 (s, 1H), 7.75 (d, 2H, *J*=8.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.3, 127.2, 128.2, 128.6, 130.3, 131.4, 133.4, 136.0, 137.3, 138.3, 138.8, 195.7.

4.2.16. 4-Chloro-2′-methylbenzophenone. Yellow oil. (lit.[27] yellow oil); IR (neat) 1667 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.32 (s, 3H), 7.22–7.31 (m, 3H), 7.37–7.44 (m, 3H), 7.73 (d, 2H, *J*=8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.9, 125.2, 128.4, 128.7, 130.4, 131.1, 131.4, 136.0, 136.7, 138.0, 139.6, 197.2.

4.2.17. 4-Chloro-4′-methoxylbenzophenone. Mp 122–123 °C (lit.[28] mp 119–120 °C); IR (Nüjol) 1638 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.89 (s, 3H), 6.97 (d, 2H, *J*=8.9 Hz), 7.45 (d, 2H, *J*=8.6 Hz), 7.71 (d, 2H, *J*=8.6 Hz), 7.80 (d, 2H, *J*=8.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 113.7, 128.5, 129.8, 131.1, 132.4, 136.5, 138.3, 163.4, 194.2.

4.2.18. 4,4′-Dichlorlbenzophenone. Mp 144 °C (commercial, mp 144–146 °C); IR (Nüjol) 1654 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, 4H, *J*=8.9 Hz), 7.72 (d, 4H, *J*=8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 128.7, 131.3, 135.5, 139.1, 194.2.

4.2.19. 4-Bromo-4′-chlorobenzophenone. Mp 145–146 °C (lit.[19] mp 146–148 °C); IR (Nüjol) 1644 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.47 (d, 2H, *J*=8.6 Hz), 7.62–7.66 (m, 4H), 7.72 (d, 2H, *J*=8.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 127.7, 128.7, 131.2, 131.3, 131.7, 135.4, 135.9, 139.1, 194.3.

4.2.20. 4-Chloro-2′,4′-dimethoxybenzophenone. Mp 95–97 °C (lit.[29] mp 99 °C); IR (Nüjol) 1655 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.69 (s, 3H), 3.87 (s, 3H), 6.50 (s, 1H), 6.56 (d, 1H, *J*=8.3 Hz), 7.35–7.43 (m, 3H), 7.70 (d, 2H, *J*=8.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.4, 55.5, 98.7, 104.8, 121.0, 128.3, 131.0, 132.2, 137.3, 138.5, 159.5, 163.6, 194.2.

4.2.21. 4-Chloro-2′,4′,6′-trimethylbenzophenone. Mp 67–69 °C (lit.[30] mp 68–69.5 °C); IR (Nüjol) 1663 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 2.07 (s, 6H), 2.33 (s, 3H), 6.90 (s, 2H), 7.41 (d, 2H, *J*=8.9 Hz), 7.74 (d, 2H, *J*=8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 19.3, 21.1, 128.4, 129.1, 130.8, 134.1, 135.7, 136.3, 138.8, 140.1, 199.4.

4.2.22. 4-Chlorophenyl 4′-biphenyl ketone. Mp 169–170 °C (lit.[31] mp 169.5–170.5 °C); IR (Nüjol) 1642 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.38–7.42 (m, 1H), 7.44–7.49 (m, 4H), 7.63 (d, 2H, *J*=8.6 Hz), 7.69 (d, 2H, *J*=8.6 Hz), 7.77 (d, 2H, *J*=8.6 Hz), 7.85 (d, 2H, *J*=8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 127.0, 127.2, 128.2, 128.6, 128.9, 130.5, 131.3, 135.8, 136.0, 138.8, 139.8, 145.4, 194.9.

4.2.23. 4-Chlorophenyl 2′-naphthyl ketone. Mp 125–126 °C (lit.[32] mp 125.6–126 °C); IR (Nüjol) 1655 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.48 (d, 2H, *J*=8.6 Hz), 7.53–7.63 (m, 2H), 7.80 (d, 2H, *J*=8.9 Hz), 7.89–7.95 (m, 4H), 8.22 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 125.6, 125.8, 126.9, 127.8, 128.4, 128.7, 129.4, 131.5, 131.7, 132.2, 134.5, 135.3, 136.2, 138.8, 195.5.

4.2.24. 4-Chlorophenyl 2′-pyridyl ketone. Mp 64–67 °C (lit.[33] mp 66–69 °C); IR (Nüjol) 1659 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.44–7.52 (m, 3H), 7.91 (td, 1H, J_1=7.7 Hz, J_2=1.4 Hz), 8.05–8.08 (m, 3H), 8.72 (d, 1H, *J*=4.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 124.7, 126.4, 128.4, 132.5, 134.6, 137.2, 139.4, 148.5, 154.7, 192.4.

4.2.25. 4-Chlorophenyl 2′-thienyl ketone. Mp 97–101 °C (lit.[26] mp 93–95 °C); IR (Nüjol) 1630 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.17 (dd, 1H, J_1=4.9 Hz, J_2=3.7 Hz), 7.48 (d, 2H, *J*=8.6 Hz), 7.62 (dd, 1H, J_1=3.7 Hz, J_2=1.2 Hz), 7.74 (dd, 1H, J_1=4.9 Hz, J_2=1.2 Hz), 7.82 (d, 2H, *J*=8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 128.0, 128.7, 130.6, 134.5, 134.7, 136.4, 138.7, 143.2, 186.9.

4.2.26. 4-Fluoro-4′-methoxybenzophenone. Mp 92–94 °C (lit.[26] mp 89–91 °C); IR (Nüjol) 1639 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.88 (s, 3H), 6.97 (d, 2H, *J*=8.8 Hz), 7.14 (t, 2H, *J*=8.7 Hz), 7.76–7.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 113.6, 115.3 (d, J_{C-F}=22.0 Hz) 123.0, 132.3 (d, J_{C-F}=9.6 Hz), 132.3, 134.4 (d, J_{C-F}=2.9 Hz), 163.2, 165.0 (d, J_{C-F}=253.9 Hz), 194.0.

4.2.27. 4-Chloro-4′-fluorobenzophenone. Mp 116–118 °C (lit.[34] mp 118–119 °C); IR (Nüjol) 1649 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.17 (t, 2H, *J*=8.6 Hz), 7.46 (d, 2H, *J*=8.4 Hz), 7.72 (d, 2H, *J*=8.4 Hz), 7.78–7.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.6 (d, J_{C-F}=22.1 Hz), 128.6, 131.2, 132.5 (d, J_{C-F}=8.6 Hz), 133.4 (d, J_{C-F}=2.9 Hz), 135.7, 138.9, 165.4 (d, J_{C-F}=253.2 Hz), 193.9.

4.2.28. 4-Fluorophenyl 2′-naphthyl ketone. Mp 109–110 °C (lit.[35] mp 110–110.8 °C); IR (Nüjol) 1651 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, 2H, *J*=8.7 Hz), 7.53–7.64 (m, 2H), 7.87–7.96 (m, 6H), 8.23 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.5 (d, J_{C-F}=21.1 Hz), 123.6, 126.9, 127.8, 128.4, 129.3, 131.6, 132.2, 132.7 (d, J_{C-F}=9.6 Hz), 132.7, 134.1 (d, J_{C-F}=3.8 Hz), 134.7, 135.2, 165.4 (d, J_{C-F}=254.8 Hz), 195.3.

4.2.29. 2-Benzofuryl 4′-fluorophenyl ketone. Mp 133–135 °C; IR (Nüjol) 1648 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (t, 2H, *J*=8.6 Hz), 7.33 (t, 1H, *J*=7.5 Hz), 7.49 (t, 1H, *J*=8.4 Hz), 7.54 (s, 1H), 7.62 (d, 1H, *J*=8.4 Hz), 7.72 (d, 1H, *J*=7.7 Hz), 8.08–8.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 112.4, 115.7 (d, J_{C-F}=22.0 Hz), 116.2, 123.2, 124.0, 126.8, 128.4, 132.1 (d, J_{C-F}=8.6 Hz), 133.3 (d, J_{C-F}=2.9 Hz), 152.1, 155.9, 165.6 (d, J_{C-F}=255.8 Hz), 182.6; HRMS(APCI)[M+H]$^+$, calcd for $C_{15}H_{10}FO_2$=241.0659, observed=241.0656.

4.2.30. 4-Fluorophenyl 2′-pyridyl ketone. Mp 82–83 °C (lit.[36] mp 68–69 °C); IR (Nüjol) 1654 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (t, 2H, *J*=8.7 Hz), 7.50 (ddd, 1H, J_1=7.7 Hz, J_2=4.8 Hz, J_3=1.1 Hz), 7.91 (td, 1H, J_1=7.7 Hz, J_2=1.8 Hz), 8.06 (dt, 1H, J_1=7.7 Hz, J_2=1.1 Hz), 8.14–8.19 (m, 2H), 8.72 (ddd, 1H, J_1=4.8 Hz, J_2=1.8 Hz, J_3=0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.3 (d, J_{C-F}=22.0 Hz), 124.6, 126.3, 132.5 (d, J_{C-F}=2.9 Hz), 133.8 (d, J_{C-F}=9.6 Hz), 137.1, 148.4, 154.9, 165.7 (d, J_{C-F}=255.8 Hz), 192.0; HRMS (ESI) [M]$^+$, calcd for $C_{12}H_8FNO$=201.0590, observed=201.0593.

4.2.31. Ethyl 4-methoxyphenyl ketone. Colorless oil (commercial, mp 25–27 °C); IR (neat) 1681 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.21 (t, 3H, *J*=7.2 Hz), 2.95 (q, 2H, *J*=7.2 Hz), 3.87 (s, 3H), 6.94 (d, 2H, *J*=8.8 Hz), 7.95 (d, 2H, *J*=8.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.4, 31.4, 55.4, 113.6, 130.0, 130.2, 163.3, 199.4.

4.2.32. Cyclohexyl 4-methoxyphenyl ketone. Mp 63–65 °C (lit.[37] mp 62–64 °C); IR (Nüjol) 1682 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22–1.31 (m, 1H), 1.34–1.44 (m, 2H), 1.46–1.54 (m, 2H), 1.70–1.76 (m, 1H), 1.81–1.90 (m, 4H), 3.18–3.26 (m, 1H), 3.86 (s, 3H), 6.93 (d, 2H, *J*=9.2 Hz), 7.94 (d, 2H, *J*=8.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.9, 26.0, 29.5, 45.3, 55.4, 113.7, 129.3, 130.5, 163.2, 202.4.

4.2.33. tert-Butyl 4-methoxypheny ketone. Colorless oil (lit.[38] oil); IR (neat) 1666 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (s, 9H), 3.85 (s, 3H), 6.90 (d, 2H, *J*=9.0 Hz), 7.85 (d, 2H, *J*=9.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.3, 43.8, 55.3, 113.2, 130.0, 130.9, 161.9, 206.2.

4.2.34. Ethyl 4-methylphenyl ketone. Colorless oil (commercial, oil); IR (neat) 1685 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21 (t, 3H, *J*=7.3 Hz), 2.39 (s, 3H), 2.95 (q, 2H, *J*=7.2 Hz), 7.23 (d, 2H, *J*=8.6 Hz),

7.85 (d, 2H, J=8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 8.2, 21.4, 31.5, 128.0, 129.1, 134.3, 143.4, 200.3.

4.2.35. Cyclohexyl 4-methylphenyl ketone. Mp 65–68 °C (lit.[26] mp 61–63 °C); IR (Nüjol) 1685 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19–1.31 (m, 1H), 1.32–1.50 (m, 4H), 1.70–1.78 (m, 1H), 1.79–1.94 (m, 4H), 2.39 (s, 3H), 3.19–3.28 (m, 1H), 7.24 (d, 2H, J=7.9 Hz), 7.84 (d, 2H, J=8.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.5, 25.8, 25.9, 29.4, 43.4, 128.3, 129.1, 133.7, 143.3, 203.4.

4.2.36. tert-Butyl 4-methylphenyl ketone. Colorless oil (lit.[39] oil); IR (neat) 1672 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35 (s, 9H), 2.37 (s, 3H), 7.19 (d, 2H, J=7.9 Hz), 7.66 (d, 2H, J=8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.3, 28.1, 44.0, 128.3, 128.6, 135.3, 141.4, 208.2.

4.2.37. Ethyl 4-chlorophenyl ketone. Mp 34–36 °C (commercial, mp 34–35 °C); IR (Nüjol) 1697 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.22 (t, 3H, J=7.2 Hz), 2.97 (q, 2H, J=7.2 Hz), 7.43 (d, 2H, J=8.6 Hz), 7.90 (d, 2H, J=8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 8.1, 31.8, 128.9, 129.4, 135.2, 139.3, 199.5.

4.2.38. Cyclohexyl 4-chlorophenyl ketone. Mp 61–62 °C (lit.[40] mp 59–60 °C); IR (Nüjol) 1687 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.21–1.32 (m, 1H), 1.32–1.55 (m, 4H), 1.70–1.78 (m, 1H), 1.81–1.90 (m, 4H), 3.16–3.24 (m, 1H), 7.43 (d, 2H, J=8.6 Hz), 7.88 (d, 2H, J=8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 25.8, 25.9, 29.3, 45.6, 128.9, 129.7, 134.6, 139.1, 202.6.

4.2.39. tert-Butyl 4-chlorophenyl ketone. Colorless oil (lit.,[41] oil); IR (neat) 1676 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.34 (s, 9H), 7.38 (d, 2H, J=8.4 Hz), 7.67 (d, 2H, J=8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 28.0, 44.2, 128.3, 129.5, 136.5, 137.2, 207.6.

4.2.40. Ethyl 2-pyridyl ketone. Colorless oil (lit.[42] oil); IR (neat) 1699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.22 (t, 3H, J=7.2 Hz), 3.25 (q, 2H, J=7.2 Hz), 7.46 (ddd, 1H, J_1=7.7 Hz, J_2=4.7 Hz, J_3=1.2 Hz), 7.83 (td, 1H, J_1=7.7 Hz, J_2=1.7 Hz), 8.04 (dt, 1H, J_1=7.7 Hz, J_2=1.2 Hz), 8.68 (ddd, 1H, J_1=4.7 Hz, J_2=1.7 Hz, J_3=0.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 7.87, 31.0, 121.6, 126.9, 136.8, 148.8, 153.4, 202.5.

4.2.41. Cyclohexyl 2-pyridyl ketone. Colorless oil (lit.[43] bp 138–140 °C/10 Torr); IR (neat) 1693 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 1.19–1.31 (m, 1H), 1.38–1.51 (m, 4H), 1.69–1.77 (m, 1H), 1.77–1.98 (m, 4H), 3.80–3.91 (m, 1H), 7.45 (ddd, 1H, J_1=7.7 Hz, J_2=4.7 Hz, J_3=1.2 Hz), 7.83 (td, 1H, J_1=7.7 Hz, J_2=1.7 Hz), 8.02 (dt, 1H, J_1=7.7 Hz, J_2=1.2 Hz), 8.69 (ddd, 1H, J_1=4.7 Hz, J_2=1.7 Hz, J_3=0.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 25.7, 26.0, 28.8, 43.9, 122.4, 126.7, 136.8, 148.8, 153.0, 204.9.

4.2.42. tert-Butyl 2-pyridyl ketone. Colorless oil (lit.[44] bp 96 °C/10 Torr); IR (neat) 1686 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.45 (s, 9H), 7.36 (ddd, 1H, J_1=7.7 Hz, J_2=4.7 Hz, J_3=1.2 Hz), 7.79 (td, 1H, J_1=7.7 Hz, J_2=1.7 Hz), 7.87 (dt, 1H, J_1=7.7 Hz, J_2=1.2 Hz), 8.61 (ddd, 1H, J_1=4.7 Hz, J_2=1.7 Hz, J_3=0.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.4, 44.0, 123.4, 125.6, 136.5, 147.6, 154.7, 206.7.

4.2.43. 4-Chloro-2′-methoxybenzophenone. Mp 81–82 °C (lit.[45] mp 80.9–83.2 °C); IR (Nüjol) 1660 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.71 (s, 3H), 6.99 (d, 1H, J=8.3 Hz), 7.05 (t, 1H, J=7.5 Hz), 7.35–7.43 (m, 3H), 7.48 (t, 1H, J=7.5 Hz), 7.74 (d, 2H, J=8.3 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.5, 111.4, 120.6, 128.3, 128.5, 129.6, 131.1, 132.2, 136.2, 139.2, 157.3, 195.2.

4.2.44. 4-Chloro-2′,6′-dimethoxybenzophenone. Mp 125–128 °C; IR (Nüjol) 1671 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.69 (s, 6H), 6.61 (d, 2H, J=8.6 Hz), 7.31–7.40 (m, 3H), 7.77 (d, 2H, J=8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.8, 104.0, 117.3, 128.7, 130.7, 131.0, 136.0, 139.5, 157.5, 194.0; HRMS(ESI)[M+Na]$^+$, calcd for $C_{15}H_{13}ClO_3Na$=299.0445, observed=299.0443.

4.2.45. 4-Chloro-2′,5′-dimethoxybenzophenone. Mp 70–73 °C; IR (Nüjol) 1663 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.66 (s, 3H), 3.79 (s, 3H), 6.90–6.94 (m, 2H), 6.99–7.04 (m, 1H), 7.40 (d, 2H, J=8.6 Hz), 7.75 (d, 2H, J=8.8 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.8, 56.2, 113.0, 114.4, 117.7, 128.5, 128.9, 131.1, 136.1, 139.3, 151.4, 153.5, 195.0; HRMS(ESI)[M+Na]$^+$, calcd for $C_{15}H_{13}ClO_3Na$=299.0445, observed=299.0445.

4.2.46. 4-Chloro-2′,3′-dimethoxybenzophenone. Colorless oil (lit.[46] bp 130–132 °C/3 Torr); IR (neat) 1671 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.70 (s, 3H), 3.90 (s, 3H), 6.90 (d, 1H J=8.3 Hz), 7.04–7.15 (m, 2H), 7.40 (d, 2H, J=8.3 Hz), 7.76 (d, 2H, J=8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.8, 61.5, 114.5, 120.3, 124.1, 128.5, 131.1, 133.6, 135.8, 139.4, 146.7, 152.6, 194.9.

4.2.47. 4-Chloro-2′,4′,6′-trimethoxybenzophenone. Mp 170–173 °C (lit.[29] mp 176.5 °C); IR (Nüjol) 1659 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.68 (s, 6H), 3.86 (s, 3H), 6.17 (s, 2H), 7.37 (d, 2H, J=8.6 Hz), 7.77 (d, 2H, J=8.9 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.4, 55.7, 90.6, 110.3, 128.5, 130.8, 136.7, 139.2, 158.7, 162.6, 193.6.

4.2.48. 4-Chloro-2′,6′-difluorobenzophenone. Mp 73–74 °C; IR (Nüjol) 1670 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.99–7.04 (m, 2H), 7.42–7.51 (m, 3H), 7.81 (d, 2H, J=10.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 112.0 (dd, J_{C-F}=20.4 Hz, J_{C-F}=4.8 Hz), 116.5 (t, J_{C-F}=21.6 Hz), 129.1, 130.9, 132.2 (t, J_{C-F}=9.6 Hz), 135.2, 140.8, 159.8 (dd, J_{C-F}=251.0, J_{C-F}=8.4 Hz), 187.6; HRMS(FD)[M]$^+$, calcd for $C_{13}H_7ClF_2O$=252.0153, observed=252.0137.

4.2.49. 4-Chlorophenyl-2′,3′,5′,6′-tetrafluorobenzophenone. Mp 64–68 °C; IR (Nüjol) 1678 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.20–7.27 (m, 1H), 7.50 (d, 2H, J=8.6 Hz), 7.81 (d, 2H, J=8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 108.0 (t, J_{C-F}=22.8 Hz), 119.2 (t, J_{C-F}=20.4 Hz), 129.4, 130.9, 134.2, 141.6, 143.1 (ddt, J_{C-F}=249.8 Hz, J_{C-F}=15.0 Hz, J_{C-F}=4.8 Hz), 145.9 (ddt J_{C-F}=250.4 Hz, J_{C-F}=11.4 Hz, J_{C-F}=4.8 Hz), 184.9; HRMS(FD)[M]$^+$, calcd for $C_{13}H_5ClF_4O$=287.9965, observed=287.9983.

4.2.50. 4-Chlorophenyl 3′-methoxynaphth-2′-yl ketone. Mp 118–120 °C; IR (Nüjol) 1651 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 3.79 (s, 3H), 7.21 (s, 1H), 7.36–7.42 (m, 3H), 7.52 (t, 1H, J=7.7 Hz), 7.75–7.81 (m, 4H), 7.83 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 55.6, 106.2, 124.5, 126.6, 127.9, 128.0, 128.4, 128.6, 129.8, 130.4, 131.2, 135.5, 136.2, 139.4, 154.9, 194.8; HRMS(ESI)[M+H]$^+$, calcd for $C_{18}H_{14}ClO_2$=297.0677, observed=297.0675.

4.2.51. 4-Chlorophenyl 1′-methylimidazo-2′-yl ketone. Mp 62–65 °C (lit.[47] mp 54–56 °C); IR (nüjol) 1632 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.08 (s, 3H), 7.12 (d, 1H, J=0.9 Hz), 7.23 (d, 1H, J=0.9 Hz), 7.45 (d, 2H, J=8.6 Hz), 8.28 (d, 2H, J=8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 36.5, 127.0, 128.3, 129.4, 132.2, 135.6, 139.1, 142.9, 182.6.

4.2.52. 2-Benzofuryl 4′-chlorophenyl ketone. Mp 150–152 °C (lit.[48] mp 152 °C); IR (Nüjol) 1650 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.34 (t, 1H, J=7.6 Hz), 7.48–7.56 (m, 4H), 7.64 (d, 1H, J=8.3 Hz), 7.74 (d, 1H, J=8.0 Hz), 8.03 (d, 2H, J=8.6 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 112.5, 116.4, 123.3, 124.1, 126.9, 128.5, 128.9, 130.9, 135.4, 139.4, 152.1, 156.0, 182.9.

4.2.53. 2-Benzothienyl 4′-chlorophenyl ketone. Mp 139–142 °C; IR (Nüjol) 1626 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.39–7.55 (m, 4H), 7.81–7.94 (m, 5H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 123.0, 125.1,

126.1, 127.6, 128.9, 130.7, 132.1, 136.1, 138.9, 138.9, 142.6, 142.7, 188.3; HRMS(APCI)$[M+H]^+$, calcd for $C_{15}H_{10}ClOS$=273.0135, observed=273.0133.

4.2.54. 4-Chlorophenyl phenylethynyl ketone. Mp 102–103 °C (lit.[49] mp 105–106 °C); IR (Nüjol) 1651, 2199 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.39–7.44 (m, 2H), 7.46–7.51 (m, 3H), 7.68 (d, 2H, J=8.3 Hz), 8.15 (d, 2H, J=8.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ 86.5, 93.6, 119.8, 128.7, 128.9, 130.8, 130.9, 133.1, 135.2, 140.6, 176.6.

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