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Practical one-pot preparation of ketones from aryl and alkyl bromides with aldehydes and DIH via Grignard reagents

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ABSTRACT

Various diaryl ketones, alkyl aryl ketones, and dialkyl ketones were efficiently prepared in good yields by the reactions of the Grignard reagents derived from aryl or alkyl bromides, followed by the reactions with aromatic or aliphatic aldehydes and the subsequent treatment with 1,3-diiodo-5,5-dimethylhydantoin and K_2CO_3, in a one-pot method. The same treatment of aromatic bromides bearing electron-withdrawing groups, such as ester, nitrile, ketone, and nitro groups with *i*-PrMgCl·LiCl or PhMgCl instead of Mg, also provided the corresponding diaryl and alkyl aryl ketones in good yields. The above methods are simple and practical transition-metal-free methods for the preparation of various diaryl ketones and alkyl aryl ketones bearing electron-rich aromatic groups and electron-deficient aromatic groups, as well as dialkyl ketones.

1. Introduction

Aromatic and aliphatic ketones are very important and useful building blocks and structural elements for the preparation of pharmaceuticals, agrochemicals, and functional materials.[1] Generally, aromatic and aliphatic ketones are prepared by the oxidation of secondary alcohols.[2] In addition, aromatic ketones, such as diaryl ketones and alkyl aryl ketones, are prepared by the Friedel–Crafts reaction of arenes and acyl halides with Lewis acids,[3,4] the Houben–Hoesch reaction of arenes and nitriles with Lewis acid,[4,5] the Fries rearrangement of aryl esters with Lewis acids,[4,6] the reaction of RCu(CN)M (M=ZnX, MgX, Li) with acyl halides,[7] the reaction of ArZnBr and acyl halides or carboxylic anhydrides with $CoBr_2$,[8] the decarboxylative coupling reaction of α-oxocarboxylates and ArBr with CuBr and $Pd(F_6\text{-acac})_2$,[9] the Ni-catalyzed ($NiCl_2$(DME)/dppp/Zn) coupling reaction of aryl iodides to nitriles,[10] and the direct oxidative reaction of alkylarenes with oxidants, such as *N*-hydroxyphthalimide, *o*-iodylbenzoic acid (IBX), and H_2O_2 with HBr.[11] Recently, the acylation of organometallic reagents, such as organomanganese, organozinc, organocopper, organoiron, and others, has been actively studied.[12] However, a less-toxic and transition-metal-free preparation of aromatic and aliphatic ketones from easily available compounds is still greatly required in view of environmentally benign organic synthesis. In this regard, the synthetic use of the Grignard reagents for the preparation of ketones is very attractive because the Grignard reagents can be easily prepared from aromatic and aliphatic halides with Mg[13] and the practical scale-up preparation with them is easy. Today, as typical and practical transition-metal-free methods for the preparation of ketones with the Grignard reagents and carboxylic acid derivatives, the reaction of RMgX with nitriles[14] and the reaction of RMgX with Weinreb amides[15] are well known. Moreover, recently, it was reported that aromatic and aliphatic ketones were prepared by the reaction of RMgX with acyl halides in the presence of *N*-methylpyrrolidine under transition-metal-free conditions.[16] Although moisture-sensitive acyl halides were used, we are very much interested in this report. Obviously, the synthetic use of aldehydes and RMgX for the preparation of ketones via oxidative reaction is very attractive, as many kinds of aldehydes are easily available. The oxidative reaction of aldehydes with organovanadiums prepared from RMgX and VCl_3 was reported in the past.[17] However, there are still some drawbacks, such as the low yields of ketones depending on the substrates and the use of a transition metal. In order to realize a practical, less toxic, less expensive, and therefore environmentally benign organic synthesis, the emergence of new methods for the preparation of aromatic and aliphatic ketones, such as diaryl ketones, alkyl aryl ketones, and dialkyl ketones, from easily available substrates, i.e., aromatic and aliphatic bromides with aldehydes, without any transition metals under mild conditions is greatly demanded. On the other hand, the synthetic use of molecular iodine and iodine-related reagents, such as 1,3-diiodo-5,5-dimethylhydantoin (DIH), in organic synthesis has become very popular, because they are highly affordable and have very low toxicity.[18] Recently, we reported the preparation of aromatic ketones by the reaction of aromatic bromides with *n*-BuLi, followed

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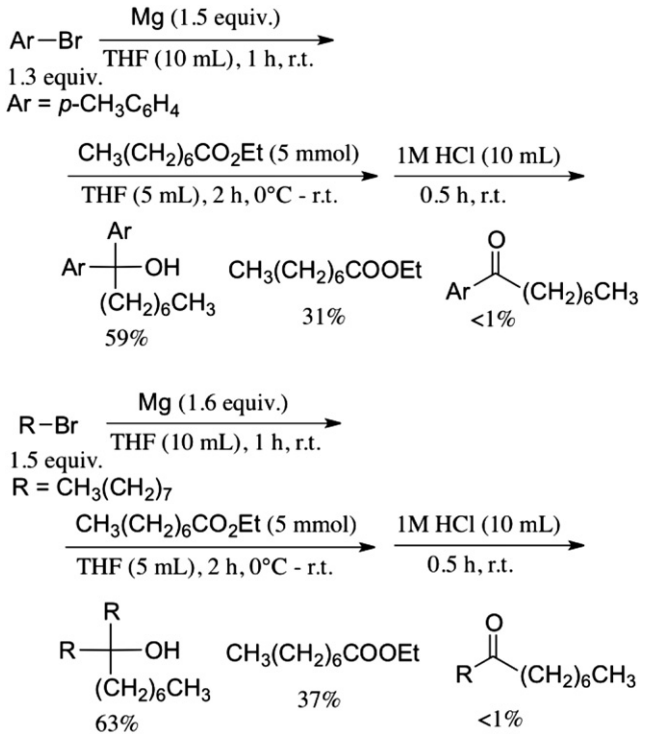
by the reaction with aldehydes and the subsequent oxidation with molecular iodine in the presence of K_2CO_3.[19] We believe this is a simple and useful method for the preparation of aromatic ketones in good yields. However, only aromatic bromides and iodides can be used in this reaction. Therefore, dialkyl ketones cannot be prepared. Moreover, aromatic bromides bearing electron-withdrawing groups, such as ester, nitrile, and nitro groups, cannot be used as the substrate. As part of our ongoing studies on the use of molecular iodine and iodine-related reagents for organic synthesis,[20] we would like to report a simple and practical method for the preparation of various ketones from the reactions of aryl or alkyl bromides with Mg, *i*-PrMgX,[21] or PhMgCl,[22] followed by the reaction with aldehydes and the subsequent oxidation with DIH and K_2CO_3.

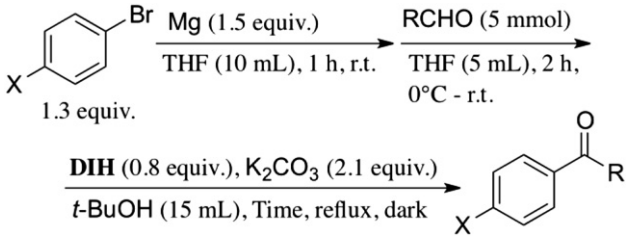
2. Results and discussion

First, treatment of Grignard reagents, such as *p*-tolylmagnesium bromide and *n*-octylmagnesium bromide, with ethyl octanoate generated mainly tertiary alcohols and the starting esters, together with trace amounts of heptyl *p*-tolyl ketone and heptyl octyl ketone, respectively, as shown in Scheme 1. Even if the amounts of the Grignard reagents were reduced or the reaction temperature was lowered, the esters could not be obtained as the main product due to the rapid decomposition of the first addition products to ketones, and subsequent rapid addition of the Grignard reagents to the formed ketones. Therefore, we planned the addition reaction of the Grignard reagents to aldehydes and the subsequent oxidation to ketones in a one-pot procedure, in hopes of obtaining the ketones in good yield. Thus, *p*-bromotoluene (1.3 equiv) was treated with Mg (1.5 equiv) to generate *p*-tolylmagnesium bromide. After 1 h, octanal (5 mmol) was added at 0 °C and the mixture was stirred for 2 h at room temperature. Then, DIH (0.8 equiv), K_2CO_3 (2.1 equiv), and *t*-BuOH were added and the obtained mixture was refluxed for 20 h to provide heptyl *p*-tolyl ketone in 67% yield, as shown in Table 1 (entry 1). When other aldehydes, such as cyclohexanecarboxaldehyde bearing a secondary alkyl group, pivalaldehyde bearing a tertiary alkyl group, *p*-substituted aromatic aldehydes bearing Me,



Scheme 1. Reaction of Grignard reagents and ethyl octanoate.

Table 1
One-pot preparation of aromatic ketones from aryl bromides and aldehydes with DIH via Grignard reagents (**1**)



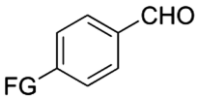
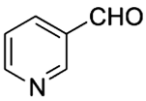
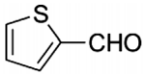
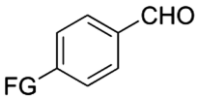
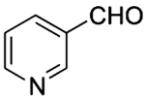
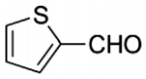
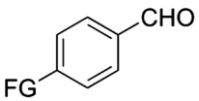
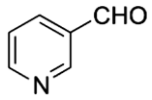
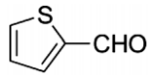
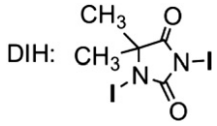
Entry	X	RCHO	Time (h)	Yield (%)
1	CH_3	$CH_3(CH_2)_6CHO$	20	67
2		$CH_3(CH_2)_6CHO$	20	47[a]
3		*c*-$C_6H_{11}CHO$	20	87
4		$(CH_3)_3CCHO$	20	80
				
5		FG=Me	19	76
6		FG=Me	19	61[a]
7		FG=Me	19	89[b]
8		FG=MeO	19	79
9		FG=F	15	74
10		FG=Cl	20	81
11		FG=CF_3	15	80
12			20	81
13			20	76
14	Cl	$CH_3(CH_2)_6CHO$	20	69
15		*c*-$C_6H_{11}CHO$	20	73
16		$(CH_3)_3CCHO$	20	81
				
17		FG=Me	20	93
18		FG=MeO	20	86
19		FG=F	20	82
20		FG=Cl	20	65
21		FG=CF_3	22	77
22			20	73
23			20	84
24	CF_3	$CH_3(CH_2)_6CHO$	20	66
25		*c*-$C_6H_{11}CHO$	20	74
26		$(CH_3)_3CCHO$	20	68
				
27		FG=Me	23	73
28		FG=MeO	23	80
29		FG=F	20	82
30		FG=Cl	20	76
31		FG=CF_3	20	72

Table 1 (*continued*)

Entry	X	RCHO	Time (h)	Yield (%)
32			23	89
33			20	85

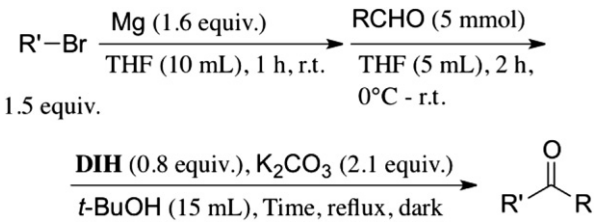
[a] I_2 (2.0 equiv) instead of DIH was used.
[b] Reaction was carried out with 20 mmol of *p*-tolualdehyde.

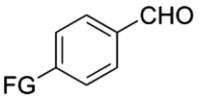
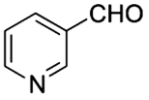
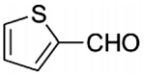
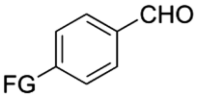


MeO, F, Cl, and CF_3 groups, 3-pyridinecarboxaldehyde, and 2-thiophenecarboxaldehyde, were subjected to the same procedure and conditions, the corresponding aromatic ketones were obtained in good yields, respectively, (entries 3–5, 8–13). The same treatment of *p*-bromochlorobenzene and *p*-bromo(trifluoromethyl) benzene with Mg, followed by the reaction with octanal, cyclohexanecarboxaldehyde, pivalaldehyde, *p*-substituted aromatic aldehydes bearing Me, MeO, F, Cl, and CF_3 groups, 3-pyridinecarboxaldehyde, and 2-thiophenecarboxaldehyde, generated the corresponding aromatic ketones in good yields, respectively, (entries 14–33). Thus, using the present method, various aromatic ketones were obtained in good yields in a one-pot procedure, starting from aromatic bromides, Mg, aldehydes, and DIH. When molecular iodine was used instead of DIH, the yields of ketones were decreased due to the weaker oxidizing ability of molecular iodine (entries 2, 6). This is due to the stronger iodination and oxidation ability of DIH than molecular iodine.[20k,20m,20n,20u] When the reaction was carried out with 20 mmol of *p*-tolualdehyde, the corresponding di(*p*-tolyl) ketone was obtained in good yield (entry 7). Thus, the present method can be used for the large-scale preparation of aromatic ketones. Octyl bromide (1.5 equiv) was treated with Mg (1.6 equiv) to form octylmagnesium bromide. After 1 h, octanal (5 mmol) was added at 0 °C and the mixture was stirred for 2 h at room temperature. Then, DIH (0.8 equiv), K_2CO_3 (2.1 equiv), and *t*-BuOH were added and the obtained mixture was refluxed for 20 h to provide heptyl octyl ketone in 71% yield, as shown in Table 2 (entry 1). Again, DIH was a more efficient oxidant than molecular iodine (entry 2). When other aldehydes, such as cyclohexanecarboxaldehyde, pivalaldehyde, *p*-substituted aromatic aldehydes bearing Me, MeO, F, Cl, and CF_3 groups, 3-pyridinecarboxaldehyde, and 2-thiophenecarboxaldehyde, were subjected to the same procedure and conditions, the corresponding aliphatic and aromatic ketones were obtained in good to moderate yields, respectively, (entries 3–11). The same treatment of cyclohexyl bromide with Mg, followed by the reaction with octanal, cyclohexanecarboxaldehyde, pivalaldehyde, and *p*-substituted aromatic aldehydes bearing Me and CF_3 groups, provided the corresponding aliphatic and aromatic ketones in good to moderate yields, respectively, (entries 12–16). Thus, the present reaction can be used for the preparation of not only aromatic ketones, but also aliphatic ketones. Then, to extend the synthetic utility of the present reaction, ethyl *p*-iodobenzoate and *p*-bromocyanobenzene were used as aromatic halides bearing ester and cyano groups.

Ethyl *p*-iodobenzoate (1.1 equiv) and *p*-bromocyanobenzene (1.3 equiv) were treated with *i*-PrMgCl·LiCl (1.2–1.3 equiv)[21] to generate the corresponding arylmagnesium chlorides at -15 °C and 0 °C, respectively. Then, octanal (3 mmol) was added to the mixtures and the mixtures were stirred for 2 h at room temperature, respectively. Then, DIH (0.8 equiv), K_2CO_3 (2.1 equiv), and *t*-BuOH were added and the obtained mixtures were refluxed for 20 h to provide heptyl *p*-(ethoxycarbonyl)phenyl ketone and *p*-cyanophenyl heptyl ketone in 77% yield and 63% yield, respectively, as shown in Table 3 (entries 1, 6). When other aldehydes, such as cyclohexanecarboxaldehyde, pivalaldehyde, and *p*-substituted aromatic aldehydes bearing Me and CF_3 groups, were subjected to the same procedure and conditions, the corresponding aromatic ketones bearing an ester group and a cyano group were obtained in good to moderate yields, respectively, (entries 2–5, 7–9). Then, as a further synthetic application, *o*-iodonitrobenzene was treated with PhMgCl (1.3 equiv)[22] to generate the corresponding arylmagnesium chlorides at −40 °C for 0.5 h. *p*-Nitrobenzaldehyde and *p*-tolualdehyde (3 mmol) were added to the mixtures and the mixtures were stirred for 2 h at room temperature, respectively. As the next step, DIH (2.4 equiv), K_2CO_3 (2.1 equiv), and *t*-BuOH were added and the obtained mixtures were refluxed to provide *o*-nitrophenyl *p*-nitrophenyl ketone and *o*-nitrophenyl *p*-tolyl ketone in 80% yield and 85% yield, respectively, as shown in Scheme 2. The same treatment of 4-benzoyl-2-nitro-1-iodobenzene (1.5 mmol) with PhMgCl (1.1 equiv), followed by the reaction with *p*-tolualdehyde (1.2 equiv) and the subsequent treatment with DIH and K_2CO_3

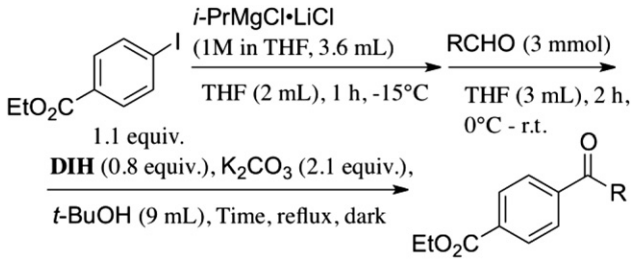
Table 2
One-pot preparation of aromatic and aliphatic ketones from alkyl bromides and aldehydes with DIH via Grignard reagents (**2**)

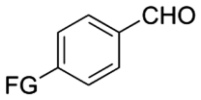


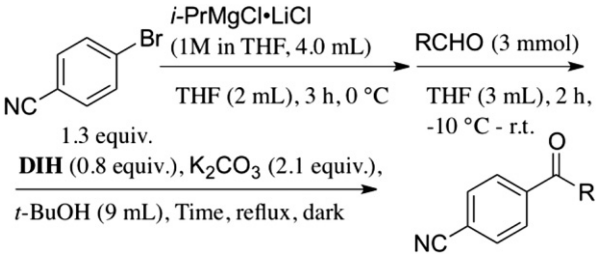
Entry	R′	RCHO	Time (h)	Yield (%)
1	$CH_3(CH_2)_7$	$CH_3(CH_2)_6CHO$	20	71
2		$CH_3(CH_2)_6CHO$	20	37[a]
3		*c*-$C_6H_{11}CHO$	20	74
4		$(CH_3)_3CCHO$	20	75
				
5		FG=Me	20	86
6		FG=MeO	20	80
7		FG=F	21	72
8		FG=Cl	20	67
9		FG=CF_3	20	67
10			20	53
11			20	75
12	*c*-C_6H_{11}	$CH_3(CH_2)_6CHO$	20	60
13		*c*-$C_6H_{11}CHO$	20	60
14		$(CH_3)_3CCHO$	20	64
				
15		FG=Me	23	76
16		FG=CF_3	23	60

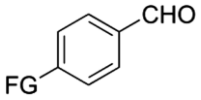
[a] I_2 (2.0 equiv) instead of DIH was used.

Table 3
One-pot preparation of aromatic ketones from aromatic bromides bearing electron-withdrawing group and aldehydes and DIH via Grignard reagents (**2**)



Entry	RCHO	Time (h)	Yield (%)
1	$CH_3(CH_2)_6CHO$	20	77
2	*c*-$C_6H_{11}CHO$	20	79
3	$(CH_3)_3CCHO$	20	68
			
4	FG=Me	19	88
5	FG=CF_3	20	75

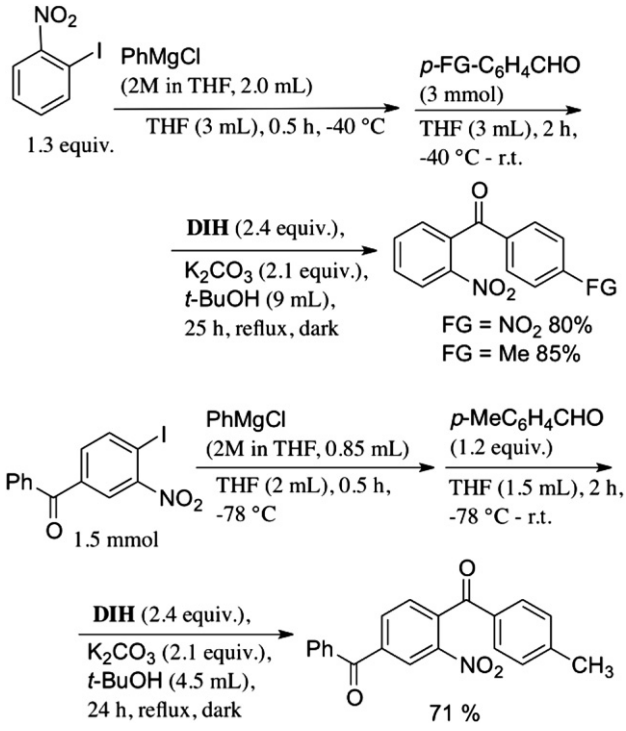


6	$CH_3(CH_2)_6CHO$	20	63
7	*c*-$C_6H_{11}CHO$	20	64
			
8	FG=Me	22	77
9	FG=CF_3	20	52

provided 4-benzoyl-2-nitrophenyl *p*-tolyl ketone in 71% yield. On the other hand, the same treatment of *p*-bromocyanobenzene and *o*-nitroiodobenzene with *n*-BuLi, followed by the reaction with aldehydes and the subsequent oxidation with molecular iodine in the presence of K_2CO_3 did not generate the corresponding ketones, respectively, (the previous method).[19] Thus, the present method involving the reaction of electron-poor aromatic bromides bearing ester, nitrile, ketone, and nitro groups, with *i*-PrMgX or PhMgCl, followed by the reaction with aldehydes and the subsequent oxidation with DIH, can be used for the preparation of diaryl ketones and alkyl aryl ketones bearing electron-deficient aromatic groups.

3. Conclusion

Various aromatic and aliphatic 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 and alkyl bromides with Mg, respectively, followed by the reactions with aromatic aldehydes or aliphatic aldehydes, and the subsequent treatment with DIH and K_2CO_3 in a one-pot method. The same treatment of aromatic halides bearing ester, cyano, ketone, and nitro groups with *i*-PrMgCl·LiCl or PhMgCl also provided the corresponding aromatic ketones in good to moderate yields. Thus, various diaryl ketones and alkyl aryl ketones bearing electron-rich aromatic groups and electron-deficient aromatic groups, as well as dialkyl ketones, could be prepared efficiently with the simple and practical experimental procedure. The reactions can be carried out under transition-metal-free conditions and used as an environmentally benign method for the preparation of various aromatic and aliphatic ketones.



Scheme 2. One-pot preparation of aromatic ketones from aromatic iodides bearing electron-withdrawing group and aldehydes and DIH via Grignard reagents (**3**).

4. Experimental

4.1. General

^1H NMR, ^{13}C NMR, and ^{19}F 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.

*4.1.1. Typical experimental procedure for one-pot conversion of bromides into ketones (**1**).* [Using Mg turnings]: A solution of *p*-bromotoluene (1112 mg, 6.5 mmol) in dry THF (4 mL) was added dropwise to Mg turnings (182 mg 7.5 mmol) in THF (6 mL) at room temperature and then, the mixture was stirred at room temperature for 1 h. A solution of *p*-chlorobenzaldehyde (703 mg, 5.0 mmol) in THF (5 mL) was added to the mixture at 0 °C and the obtained mixture was stirred at room temperature for 2 h. Then, DIH (1520 mg, 4.0 mmol), K_2CO_3 (1451 mg, 10.5 mmol), and *t*-BuOH (15 mL) were added and the obtained mixture was stirred for 20 h at refluxing conditions. The reaction mixture was quenched with

satd aq Na_2SO_3 (10 mL) and was extracted with $CHCl_3$ (3×25 mL). The organic layer was washed with brine and dried over Na_2SO_4. Purification by short column chromatography (silica gel; hexane/$CHCl_3$=1:1) yielded *p*-chlorophenyl *p*-tolyl ketone (934 mg, 81%).

*4.1.2. Typical experimental procedure for one-pot conversion of bromides into ketones (**2**).* [Using *i*-PrMgCl·LiCl via Br-Exchange]: A solution of *p*-bromobenzonitrile (710 mg, 3.9 mmol) in dry THF (2 mL) was added dropwise to *i*-PrMgCl·LiCl (3.9 mL, ca. 1 M in THF, 3.9 mmol) at 0 °C and then, the mixture was stirred at 0 °C for 3 h. Then, a solution of *p*-tolualdehyde (360 mg, 3.0 mmol) in THF (3 mL) was added to the mixture at −10 °C and the obtained mixture was stirred at −10 °C for 2 h, and then, at 0 °C for 1 h. DIH (912 mg, 2.4 mmol), K_2CO_3 (871 mg, 6.3 mmol), and *t*-BuOH (9 mL) were added to the mixture and the obtained mixture was stirred for 20 h at refluxing conditions. The reaction mixture was quenched with satd aq Na_2SO_3 (10 mL) and was extracted with $CHCl_3$ (3×20 mL). The organic layer was washed with brine and dried over Na_2SO_4. Purification by short column chromatography (silica gel; $CHCl_3$) yielded *p*-cyanophenyl *p*-tolyl ketone (511 mg, 77%).

*4.1.3. Typical experimental procedure for one-pot conversion of bromides into ketones (**3**).* [Using PhMgCl via I-exchange]: A solution of *o*-nitroiodobenzene (896 mg, 3.6 mmol) in dry THF (2 mL) was added dropwise to PhMgCl (2.0 mL, ca. 2 M in THF, 3.9 mmol) at −40 °C and the obtained mixture was stirred at −40 °C for 0.5 h. Then, a solution of *p*-tolualdehyde (360 mg, 3.0 mmol) in THF (3 mL) was added to the mixture at −40 °C and the obtained mixture was stirred at −40 °C for 2 h and then, at 0 °C for 1 h. DIH (2736 mg, 7.0 mmol), K_2CO_3 (871 mg, 6.3 mmol), and *t*-BuOH (9 mL) were added and the obtained mixture was stirred for 20 h at refluxing conditions. The reaction mixture was quenched with satd aq Na_2SO_3 (10 mL) and was extracted with $CHCl_3$ (3×20 mL). The organic layer was washed with brine and dried over Na_2SO_4. Purification by short column chromatography (silica gel; hexane/$CHCl_3$=1:1) yielded *o*-nitrophenyl *p*-tolyl ketone (615 mg, 85%).

4.1.4. Heptyl p-tolyl ketone. Mp 34 °C (lit.[23] colorless solid); IR (nüjol) 1690 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=0.88 (t, *J*=7.2 Hz, 3H), 1.24–1.40 (m, 8H), 1.72 (quint, *J*=7.2 Hz, 2H), 2.41 (s, 3H), 2.93 (t, *J*=7.2 Hz, 2H), 7.25 (d, *J*=8.3 Hz, 2H), 7.86 (d, *J*=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.1, 21.6, 22.6, 24.5, 29.1, 29.4, 31.7, 38.5, 128.2, 129.2, 134.6, 143.5, 200.3.

4.1.5. Cyclohexyl p-tolyl ketone. Mp 65–68 °C (lit.[24] mp 61–63 °C); IR (Nüjol) 1685 cm^{-1}; ^1H 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, *J*=7.9 Hz, 2H), 7.84 (d, *J*=8.2 Hz, 2H); ^{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.

4.1.6. t-Butyl p-tolyl ketone. Colorless oil (lit.[25] oil); IR (neat) 1672 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=1.35 (s, 9H), 2.37 (s, 3H), 7.19 (d, *J*=7.9 Hz, 2H), 7.66 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=21.3, 28.1, 44.0, 128.3, 128.6, 135.3, 141.4, 208.2.

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

4.1.8. p-Anisyl p-tolyl ketone. Mp 89–90 °C (lit.[26] mp 88–89 °C); IR (Nüjol) 1644 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.43 (s, 3H), 3.88 (s, 3H), 6.96 (d, *J*=9.1 Hz, 2H), 7.27 (d, *J*=7.7 Hz, 2H), 7.68 (d, *J*=8.2 Hz, 2H), 7.81 (d, *J*=9.1 Hz, 2H); ^{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.

4.1.9. p-Fluorophenyl p-tolyl ketone. Mp 97–98 °C lit.[26] mp 96–97 °C; IR (Nüjol) 1647 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.44 (s, 3H), 7.11–7.17 (m, 2H), 7.28 (d, *J*=7.9 Hz, 2H), 7.68 (d, *J*=8.2 Hz, 2H), 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; ^{19}F NMR (471 MHZ, $CDCL_3$) δ=106.3.

4.1.10. p-Chlorophenyl p-tolyl ketone. Mp 128–129 °C (lit.[27] mp 126–127 °C); IR (Nüjol) 1644 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.44 (s, 3H), 7.28 (d, *J*=7.7 Hz, 2H), 7.45 (d, *J*=8.1 Hz, 2H), 7.69 (d, *J*=8.2 Hz, 2H), 7.75 (d, *J*=8.8 Hz, 2H); ^{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.

4.1.11. p-Tolyl p-trifluoromethylphenyl ketone. Mp 144–145 °C (lit.[28] mp. 136–137 °C); IR (nüjol) 1647 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=2.46 (s, 3H), 7.31 (d, *J*=8.0 Hz, 2H), 7.70–7.77 (m, 4H), 7.87 (d, *J*=8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=21.7, 123.7 (q, J_{C-F}=272.3 Hz), 125.3 (q, J_{C-F}=3.6 Hz), 129.2, 130.0, 130.3, 133.4 (q, J_{C-F}=32.4 Hz), 134.0, 141.1, 144.1, 195.2; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−62.9.

4.1.12. 3-Pyridyl p-tolyl ketone. Mp 76–78 °C (lit.[29] mp 76–77 °C); IR (Nüjol) 1650 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.46 (s, 3H), 7.32 (d, *J*=7.9 Hz, 2H), 7.45 (ddd, *J*=7.9, 4.9, 0.9 Hz, 1H), 7.74 (d, *J*=8.4 Hz, 2H), 8.10 (dt, *J*=7.9, 2.0 HZ, 1H), 8.80 (dd, *J*=4.9, 2.0 Hz, 1H), 8.98 (dd, *J*=2.0, 0.9 Hz, 1H); ^{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.

4.1.13. 2-Thienyl p-tolyl ketone. Mp 74–75 °C (lit.[30] mp 75.0–75.6 °C); IR (Nüjol) 1627 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.44 (s, 3H), 7.14–7.17 (m, 1H), 7.30 (d, *J*=7.9 Hz, 2H), 7.64 (dd, *J*=5.0, 1.1 Hz, 2H), 7.70 (dd, *J*=6.1, 1.1 Hz, 1H), 7.79 (d, *J*=8.2 Hz, 2H); ^{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.

4.1.14. p-Chlorophenyl heptyl ketone. Mp 59–60 °C; IR (nüjol) 1694 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, *J*=7.0 Hz, 3H), 1.25–1.41 (m, 8H), 1.72 (quint, *J*=7.5 Hz, 2H), 2.93 (t, *J*=7.5 Hz, 2H), 7.42 (d, *J*=8.8 Hz, 2H), 7.90 (d, *J*=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.0, 22.6, 24.2, 29.1, 29.2, 31.7, 38.6, 128.8, 129.4, 135.3, 139.2, 199.2; HRMS (APCI) Calcd for $C_{14}H_{20}OCl$ $[M+H]^+$ 239.1197, Found 239.1195.

4.1.15. p-Chlorophenyl cyclohexyl ketone. Mp 61–62 °C (lit.[31] mp 59–60 °C); IR (Nüjol) 1687 cm^{-1}; ^1H 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, *J*=8.6 Hz, 2H), 7.88 (d, *J*=8.6 Hz, 2H); ^{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.

4.1.16. t-Butyl p-chlorophenyl ketone. Colorless oil (lit.[32] oil); IR (neat) 1676 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=1.34 (s, 9H), 7.38 (d, *J*=8.4 Hz, 2H), 7.67 (d, *J*=8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=28.0, 44.2, 128.3, 129.5, 136.5, 137.2, 207.6.

4.1.17. p-Anisyl p-chlorophenyl ketone. Mp 122–123 °C (lit.[33] mp 119–120 °C); IR (Nüjol) 1638 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=3.89 (s, 3H), 6.97 (d, *J*=8.9 Hz, 2H), 7.45 (d, *J*=8.6 Hz, 2H), 7.71 (d, *J*=8.6 Hz, 2H), 7.80 (d, *J*=8.9 Hz, 2H); ^{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.

4.1.18. p-Chlorophenyl p-fluorophenyl ketone. Mp 116–118 °C (lit.[34] mp 118–119 °C); IR (Nüjol) 1649 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$)

δ=7.17 (t, J=8.6 Hz, 2H), 7.46 (d, J=8.4 Hz, 2H), 7.72 (d, J=8.4 Hz, 2H), 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; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−105.3.

4.1.19. Di(p-chlorophenyl) ketone. Mp 144 °C (commercial, mp. 144–146 °C); IR (nüjol) 1654 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.47 (d, J=8.6 Hz, 4H), 7.72 (d, J=8.6 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=128.7, 131.3, 135.5, 139.1, 194.2.

4.1.20. p-Chlorophenyl p-trifluoromethylphenyl ketone. Mp 120–122 °C (lit.[35] colorless solid); IR (nüjol) 1649 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.49 (d, J=8.6 Hz, 2H), 7.74–7.78 (m, 4H), 7.87 (d, J=8.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=123.6 (q, J_{C-F}=272.3 Hz), 125.5 (q, J_{C-F}=3.6 Hz), 128.9, 130.0, 131.5, 133.9 (q, J_{C-F}=32.4 Hz), 135.0, 139.7, 140.3, 194.3; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−62.9.

4.1.21. p-Chlorophenyl 3-pyridyl ketone. Mp 87–89 °C (lit.[36] mp. 89–90 °C); IR (nüjol) 1644 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.47 (ddd, J=7.9, 4.9, 0.9 Hz, 1H), 7.51 (d, J=8.7 Hz, 2H), 7.78 (d, J=8.7 Hz, 2H), 8.11 (ddd, J=7.9, 2.3, 1.7 Hz, 1H), 8.83 (dd, J=4.9, 1.7 Hz, 1H), 8.98 (dd, J=2.3, 0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=123.5, 129.0, 131.4, 132.8, 134.9, 137.1, 139.8, 150.8, 153.1, 193.6.

4.1.22. p-Chlorophenyl 2-thieyl ketone. Mp 97–101 °C (lit.[24] mp 93–95 °C); IR (Nüjol) 1630 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.17 (dd, J=4.9, 3.7 Hz, 1H), 7.48 (d, J=8.6 Hz, 2H), 7.62 (dd, J=3.7, 1.2 Hz, 1H), 7.74 (dd, J=4.9, 1.2 Hz, 1H), 7.82 (d, J=8.6 Hz, 2H); ^{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.

4.1.23. Heptyl p-trifluoromethylphenyl ketone. Mp 28–31 °C; IR (nüjol) 1698 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.89 (t, J=6.9 Hz, 3H), 1.25–1.42 (m, 8H), 1.75 (quint, J=7.5 Hz, 2H), 2.99 (t, J=7.5 Hz, 2H), 7.73 (d, J=8.3 Hz, 2H), 8.06 (d, J=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.1, 22.6, 24.1, 29.1, 29.2, 31.7, 38.9, 124.7 (q, J_{C-F}=272.3 Hz), 125.6 (q, J_{C-F}=3.6 Hz), 128.3, 134.2 (q, J_{C-F}=32.4 Hz), 139.7, 199.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−63.0; HRMS (APCI) Calcd for $C_{15}H_{20}OF_3$ $[M+H]^+$ 273.1461, Found 273.1465.

4.1.24. Cyclohexyl p-trifluoromethylphenyl ketone. Colorless oil (lit.[37] oil); IR (nüjol) 1692 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.22–1.33 (m, 1H), 1.34–1.56 (m, 4H), 1.71–1.79 (m, 1H), 1.82–1.93 (m, 4H), 3.25 (tt, J=11.1, 3.2 Hz, 1H), 7.73 (d, J=8.2 Hz, 2H), 8.03 (d, J=8.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=25.7, 25.8, 29.2, 45.9, 123.6 (q, J_{C-F}=272.3 Hz), 125.6 (q, J_{C-F}=3.6 Hz), 128.5, 134.0 (q, J_{C-F}=32.4 Hz), 139.1, 202.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−63.0.

4.1.25. t-Butyl p-trifluoromethylphenyl ketone. Colorless oil (lit.[38] oil); IR (neat) 1685 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.34 (s, 9H), 7.67 (d, J=8.3 Hz, 2H), 7.73 (d, J=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=27.6, 44.4, 123.7 (q, J_{C-F}=272.3 Hz), 125.1 (q, J_{C-F}=3.6 Hz), 127.8, 132.2 (q, J_{C-F}=32.4 Hz), 142.1, 208.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−62.9.

4.1.26. p-Anisyl p-trifluoromethylphenyl ketone. Mp 120–124 °C (lit.[39] mp. 118.9–119.4 °C); IR (nüjol) 1644 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=3.90 (s, 3H), 6.98 (d, J=8.9 Hz, 2H), 7.74 (d, J=8.3 Hz, 2H), 7.80–7.86 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=55.5, 113.8, 123.7 (q, J_{C-F}=272.3 Hz), 125.2 (q, J_{C-F}=3.6 Hz), 129.3, 129.8, 132.6, 133.2 (q, J_{C-F}=33.6 Hz), 141.5, 163.7, 194.2; ^{19}F NMR (471 MHz, $CDCL_3$) δ = −62.9.

4.1.27. p-Fluorophenyl p-trifluoromethylphenyl ketone. Mp 99–100 °C (lit.[40] mp. 100–101 °C); IR (nüjol) 1651 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.19 (t, J=8.6 Hz, 2H), 7.76 (d, J=8.0 Hz, 2H), 7.83–7.88 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=115.8 (d, J_{C-F}=22.8 Hz), 123.6 (q, J_{C-F}=272.3 Hz), 125.4 (q, J_{C-F}=3.6 Hz), 129.9, 132.8 (d, J_{C-F}=9.6 Hz), 133.0 (d, J_{C-F}=3.6 Hz), 133.8 (q, J_{C-F}=33.6 Hz), 140.6, 165.7 (d, J_{C-F}=255.5 Hz), 194.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−104.4, −62.9.

4.1.28. Di(p-trifluoromethylphenyl) ketone. Mp 108–110 °C (lit.[41] mp. 107–108 °C); IR (nüjol) 1655 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.79 (d, J=8.0 Hz, 4H), 7.91 (d, J=8.0 Hz, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=123.5 (q, J_{C-F}=272.6 Hz), 125.6 (q, J_{C-F}=3.9 Hz), 130.2, 134.3 (q, J_{C-F}=32.7 Hz), 139.7, 194.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−63.0.

4.1.29. 3-Pyridyl p-trifluoromethylphenyl ketone. Mp 53–54 °C; IR (nüjol) 1654 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.49 (ddd, J=7.9, 4.9, 0.8 Hz, 1H), 7.80 (d, J=8.6 Hz, 2H), 7.93 (d, J=8.6 Hz, 2H), 8.14 (ddd, J=7.9, 2.2, 1.8 Hz, 1H), 8.86 (dd, J=4.9, 1.8 Hz, 1H), 9.00 (dd, J=2.2, 0.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=123.48 (q, J_{C-F}=272.9 Hz), 123.54, 125.7 (q, J_{C-F}=3.7 Hz), 130.1, 132.3, 134.4 (q, J_{C-F}=32.8 Hz), 137.2, 139.6, 151.0, 153.4, 193.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ=63.0; HRMS (APCI) Calcd for $C_{13}H_9ONF_3$ $[M+H]^+$ 252.0631, Found 252.0623.

4.1.30. 2-Thieyl p-trifluoromethylphenyl ketone. Mp 103–104 °C (lit.[39] not shown); IR (nüjol) 1629 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=7.19 (dd, J=4.9, 3.9 Hz, 1H), 7.63 (dd, J=3.9, 1.1 Hz, 1H), 7.75–7.80 (m, 3H), 7.96 (d, J=7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=123.6 (q, J_{C-F}=272.8 Hz), 125.5 (q, J_{C-F}=3.8 Hz), 128.2, 129.3, 133.6 (q, J_{C-F}=32.7 Hz), 135.1, 135.3, 141.2, 143.0, 187.0; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−62.9.

4.1.31. Heptyl octyl ketone. Mp 36–37 °C; IR (nüjol) 1719 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.85–0.90 (m, 6H), 1.20–1.34 (m, 18H), 1.50–1.61 (m, 4H), 2.35–2.41 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.05, 14.07, 22.59, 22.63, 23.9 (2C), 29.07, 29.13, 29.22, 29.26, 29.4, 31.7, 31.8, 42.8 (2C), 211.8; HRMS (APCI) Calcd for $C_{16}H_{33}O$ $[M+H]^+$ 241.2526, Found 241.2525.

4.1.32. Octyl cyclohexyl ketone. Colorless oil (lit.[42] oil); IR (neat) 1709 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.89 (t, J=6.9 Hz, 3H), 1.14–1.38 (m, 15H), 1.54 (quint, J=7.5 Hz, 2H), 1.64–1.69 (m, 1H), 1.75–1.85 (m, 4H), 2.29–2.36 (tt, J=11.2, 3.4 Hz, 1H), 2.41 (t, J=7.5 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.0, 22.6, 23.7, 25.7, 25.8, 28.5, 29.1, 29.3, 29.4, 31.8, 40.6, 50.8, 214.4; HRMS (APCI) Calcd for $C_{15}H_{29}O$ $[M+H]^+$ 225.2213, Found 225.2209.

4.1.33. t-Butyl octyl ketone. Colorless oil (lit.[43] oil); IR (neat) 1708 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, J=7.0 Hz, 3H), 1.13 (s, 9H), 1.21–1.32 (m, 10H), 1.54 (quint, J=7.3 Hz, 2H), 2.47 (t, J=7.3 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.1, 22.6, 23.9, 26.4, 29.2, 29.3, 29.5, 31.8, 36.4, 44.1, 216.2.

4.1.34. Octyl p-tolyl ketone. Mp 36–37 °C (lit.[44] mp. 37 °C); IR (nüjol) 1689 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, J=7.0 Hz, 3H), 1.23–1.41 (m, 10H), 1.72 (quint, J=7.3 Hz, 2H), 2.41 (s, 3H), 2.93 (t, J=7.3 Hz, 2H), 7.25 (d, J=7.9 Hz, 2H), 7.86 (d, J=7.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.1, 21.6, 22.6, 24.5, 29.2, 29.39, 29.43, 31.8, 38.5, 128.2, 129.2, 134.6, 134.5, 200.3.

4.1.35. p-Anisyl octyl ketone. Mp 43–44 °C; IR (nüjol) 1685 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.88 (t, J=7.1 Hz, 3H), 1.23–1.40 (m, 10H), 1.71 (quint, J=7.5 Hz, 2H), 2.90 (t, J=7.5 Hz, 2H), 3.87 (s, 3H), 6.93 (d, J=8.9 Hz, 2H), 7.94 (d, J=8.9 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.1, 22.6, 24.6, 29.2, 29.42, 29.44, 31.8, 38.3, 55.4, 113.6, 130.1, 130.3, 163.2, 199.3; HRMS (APCI) Calcd for $C_{16}H_{25}O_2$ $[M+H]^+$ 249.1849, Found 249.1844.

4.1.36. p-Fluorophenyl octyl ketone. Mp 34 °C (lit.[45] oil); IR (nüjol) 1692 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.88 (t, J=7.2 Hz, 3H),

1.21–1.41 (m, 10H), 1.72 (quint, J=7.5 Hz, 2H), 2.93 (t, J=7.5 Hz, 2H), 7.12 (t, J=8.6 Hz, 2H), 7.99 (dd, J=8.6, 5.4 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.1, 22.6, 24.3, 29.1, 29.3, 29.4, 31.8, 38.5, 115.6 (d, J_{C-F}=21.6 Hz), 130.6 (d, J_{C-F}=8.4 Hz), 133.5 (d, J_{C-F}=2.4 Hz), 165.6 (d, J_{C-F}=254.3 Hz), 198.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−105.7.

4.1.37. p-Chlorophenyl octyl ketone. Mp 58–59 °C (lit.[46] colorless solid); IR (nüjol) 1694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, J=7.2 Hz, 3H), 1.22–1.41 (m, 10H), 1.72 (quint, J=7.5 Hz, 2H), 2.92 (t, J=7.5 Hz, 2H), 7.43 (d, J=8.6 Hz, 2H), 7.90 (d, J=8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.1, 22.6, 24.3, 29.1, 29.3, 29.4, 31.8, 38.6, 128.9, 129.5, 135.4, 139.2, 199.3.

4.1.38. Octyl p-trifluoromethylphenyl ketone. Mp 35–37 °C; IR (nüjol) 1699 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.88 (t, J=7.2 Hz, 3H), 1.23–1.42 (m, 10H), 1.74 (quint, J=7.5 Hz, 2H), 2.98 (t, J=7.5 Hz, 2H), 7.73 (d, J=8.0 Hz, 2H), 8.06 (d, J=8.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.1, 22.6, 24.1, 29.1, 29.3, 29.4, 31.8, 38.9, 123.6 (q, J_{C-F}=272.3 Hz), 125.6 (q, J_{C-F}=3.6 Hz), 128.3, 134.2 (q, J_{C-F}=32.4 Hz), 139.7, 199.5; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−63.0; HRMS (APCI) Calcd for $C_{16}H_{22}F_3O$ $[M+H]^+$ 287.1617, Found 287.1617.

4.1.39. Octyl 3-pyridyl ketone. Colorless oil; IR (neat) 1691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, J=7.0 Hz, 3H), 1.22–1.44 (m, 10H), 1.75 (quint, J=7.3 Hz, 2H), 2.99 (t, J=7.3 Hz, 2H), 7.43 (ddd, J=7.9, 4.8, 0.9 Hz, 1H), 8.24 (ddd, J=7.9, 2.3, 1.8 Hz, 1H), 8.78 (dd, J=4.8, 1.8 Hz, 1H), 9.17 (dd, J=2.3, 0.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.1, 22.6, 24.0, 29.1, 29.2, 29.4, 31.8, 38.9, 123.6, 132.2, 135.4, 149.6, 153.3, 199.3; HRMS (APCI) Calcd for $C_{14}H_{22}ON$ $[M+H]^+$ 220.1696, Found 220.1693.

4.1.40. Octyl 2-thieyl ketone. Colorless oil; IR (neat) 1663 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=0.88 (t, J=7.0 Hz, 3H), 1.22–1.42 (m, 10H), 1.74 (quint, J=7.5 Hz, 2H), 2.89 (t, J=7.5 Hz, 2H), 7.12 (dd, J=4.9, 3.6 Hz, 1H), 7.62 (dd, J=4.9, 1.1 Hz, 1H), 7.71 (dd, J=3.6, 1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.1, 22.6, 24.8, 29.1, 29.3, 29.4, 31.8, 39.4, 128.0, 131.6, 133.3, 144.5, 193.6; HRMS (APCI) Calcd for $C_{13}H_{21}OS$ $[M+H]^+$ 225.1308, Found 225.1303.

4.1.41. Heptyl cyclohexyl ketone. Colorless oil (lit.[42] oil); IR (neat) 1709 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.88 (t, J=7.2 Hz, 3H), 1.14–1.37 (m, 13H), 1.54 (quint, J=7.2 Hz, 2H), 1.63–1.69 (m, 1H), 1.75–1.85 (m, 4H), 2.33 (tt, J=11.2, 3.4 Hz, 1H), 2.42 (t, J=7.2 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.1, 22.6, 23.7, 25.7, 25.8, 28.5, 29.1, 29.3, 31.7, 40.6, 50.8, 214.5; HRMS (APCI) Calcd for $C_{14}H_{27}O$ $[M+H]^+$ 211.2056, Found 211.2056.

4.1.42. Dicyclohexyl ketone. Colorless oil (commercial, oil); IR (neat) 1704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.12–1.38 (m, 10H), 1.62–1.69 (m, 2H), 1.71–1.83 (m, 8H), 2.48 (tt, J=11.1, 2.9 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=25.6, 25.8, 28.5, 49.1, 217.0.

4.1.43. t-Butyl cyclohexyl ketone. Colorless oil. (lit.[47] oil); IR (neat) 1701 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.14 (s, 9H), 1.21–1.46 (m, 5H), 1.58–1.70 (m, 3H), 1.73–1.80 (m, 2H), 2.84 (tt, J=11.5, 3.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=25.7, 25.8, 26.0, 29.9, 44.6, 44.9, 218.9.

4.1.44. Ethyl p-octanoylbenzoate. Mp 56–57 °C; IR (nüjol) 1682, 1728 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.89 (t, J=7.2 Hz, 3H), 1.25–1.45 (m, 11H), 1.74 (quint, J=7.2 Hz, 2H), 2.99 (t, J=7.2 Hz, 2H), 4.41 (q, J=7.2 Hz, 2H), 8.00 (d, J=8.3 Hz, 2H), 8.12 (d, J=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.1, 14.3, 22.6, 24.1, 29.1, 29.2, 31.7, 39.0, 61.4, 127.9, 129.7, 134.0, 140.1, 165.8, 200.1; HRMS (APCI) Calcd for $C_{17}H_{25}O_3$ $[M+H]^+$ 277.1798, Found 277.1794.

4.1.45. Ethyl p-(cyclohexanecarbonyl)benzoate. Mp 46–48 °C; IR (neat) 1685, 1720 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.21–1.33 (m, 1H), 1.34–1.55 (m, 7H), 1.71–1.79 (m, 1H), 1.82–1.94 (m, 4H), 3.26 (tt, J=11.1, 3.2 Hz, 1H), 4.41 (q, J=7.3 Hz, 2H), 7.98 (d, J=8.8 Hz, 2H), 8.12 (d, J=8.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.2, 25.7, 25.9, 29.2, 45.9, 61.3, 128.1, 129.7, 133.8, 139.6, 165.8, 203.4; HRMS (APCI) Calcd for $C_{16}H_{21}O_3$ $[M+H]^+$ 261.1485, Found 261.1480.

4.1.46. Ethyl p-pivaloylbenzoate. Colorless oil (lit.[48] oil); IR (neat) 1682, 1719 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.33 (s, 9H), 1.41 (t, J=7.2 Hz, 3H), 4.40 (q, J=7.2 Hz, 2H), 7.66 (d, J=8.6 Hz, 2H), 8.07 (d, J=8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.3, 27.7, 44.3, 61.3, 127.3, 129.2, 132.0, 142.8, 165.8, 209.5.

4.1.47. Ethyl p-(methylbenzoyl)benzoate. Mp 73–74 °C; IR (nüjol) 1650, 1711 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ=1.43 (t, J=7.3 Hz, 3H), 2.45 (s, 3H), 4.43 (q, J=7.3 Hz, 2H), 7.30 (d, J=8.2 Hz, 2H), 7.72 (d, J=8.2 Hz, 2H), 7.82 (d, J=8.6 Hz, 2H), 8.15 (d, J=8.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=14.3, 21.7, 61.4, 129.1, 129.4, 129.6, 130.3, 133.3, 134.3, 141.6, 143.9, 165.9, 195.8; HRMS (APCI) Calcd for $C_{17}H_{17}O_3$ $[M+H]^+$ 269.1172, Found 269.1167.

4.1.48. Ethyl p-(trifluoromethylbenzoyl)benzoate. Mp 81–82 °C; IR (nüjol) 1651, 1718 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.44 (t, J=7.2 Hz, 3H), 4.44 (q, J=7.2 Hz, 2H), 7.78 (t, J=8.3 Hz, 2H), 7.85 (d, J=8.3 Hz, 2H), 7.91 (d, J=8.3 Hz, 2H), 8.02 (d, J=8.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.2, 61.5, 123.5 (q, J_{C-F}=272.6 Hz), 125.5 (q, J_{C-F}=3.6 Hz), 129.6, 129.8, 130.2, 134.11 (q, J_{C-F}=32.7 Hz), 134.14, 140.0, 140.1, 165.6, 194.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−62.9; HRMS (APCI) Calcd for $C_{17}H_{14}O_3F_3$ $[M+H]^+$ 323.0890, Found 323.0887.

4.1.49. p-Cyanophenyl hepyl ketone. Mp 38–39 °C; IR (nüjol) 1698, 2233 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=0.89 (t, J=6.9 Hz, 3H), 1.25–1.41 (m, 8H), 1.74 (quint, J=7.5 Hz, 2H), 2.98 (t, J=7.5 Hz, 2H), 7.77 (d, J=8.6 Hz, 2H), 8.04 (d, J=8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=14.1, 22.6, 24.0, 29.1, 29.2, 31.6, 38.9, 116.1, 118.0, 128.4, 132.5, 139.9, 199.1; HRMS (APPI) Calcd for $C_{15}H_{19}ON$ $[M]^+$ 229.1461, Found 229.1462.

4.1.50. p-Cyanophenyl cyclohexyl ketone. Mp 59–60 °C (lit.[37] oil); IR (nüjol) 1685, 2227 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=1.23–1.32 (m, 1H), 1.35–1.54 (m, 4H), 1.72–1.79 (m, 1H), 1.83–1.91 (m, 4H), 3.23 (tt, J=11.2, 3.2 Hz, 1H), 7.77 (d, J=8.6 Hz, 2H), 8.12 (d, J=8.6 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=25.7, 25.8, 29.1, 45.9, 115.9, 118.0, 128.6, 132.5, 139.4, 202.4.

4.1.51. p-Cyanophenyl p-tolyl ketone. Mp 160–162 °C (lit.[49] 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, J=7.9 Hz, 2H), 7.70 (d, J=8.2 Hz, 2H), 7.78 (d, J=8.6 Hz, 2H), 7.85 (d, J=8.6 Hz, 2H); ^{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.

4.1.52. p-Cyanophenyl p-trifluoromethylphenyl ketone. Mp 85–86 °C; IR (nüjol) 1655, 2239 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=7.80 (d, J=8.3 Hz, 2H), 7.83 (d, J=8.6 Hz, 2H), 7.88–7.92 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=116.3, 117.8, 124.5 (q, J_{C-F}=272 Hz), 125.7 (q, J_{C-F}=3.6 Hz), 130.2, 130.3, 132.4, 134.5 (q, J_{C-F}=32.4 Hz), 139.3, 140.1, 193.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ=−63.0; HRMS (APCI) Calcd for $C_{15}H_8ONF_3$ $[M]^-$ 275.0563, Found 275.0567.

4.1.53. o-Nitrophenyl p-tolyl ketone. Mp 152–154 °C; IR (nüjol) 1351, 1523, 1668 cm^{-1}; ^{1}H NMR (500 MHz, $CDCl_3$) δ=2.41 (s, 3H), 7.25 (d, J=8.3 Hz, 2H), 7.48 (dd, J=7.5, 1.4 Hz, 1H), 7.63–7.69 (m, 3H), 7.77 (dt, J=7.5, 1.4 Hz, 1H), 8.22 (dd, J=7.5, 1.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=21.7, 124.4, 128.9, 129.4, 129.5, 130.4, 133.4,

134.1, 136.3, 144.9, 146.6, 193.1; HRMS (APCI) Calcd for $C_{14}H_{12}O_3N$ $[M+H]^+$ 242.0812, Found 242.0810.

4.1.54. o-Nitrophenyl p-nitrophenyl ketone. Mp 198–200 °C; IR (nüjol) 1687, 1520, 1351 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ=7.54 (dd, J=7.5, 1.4 Hz, 1H), 7.78 (dt, J=7.5, 1.4 Hz, 1H), 7.87 (dt, J=7.5, 1.4 Hz, 1H), 7.91 (d, J=9.2 Hz, 2H), 8.29–8.33 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ=124.0, 124.7, 128.8, 129.9, 131.3, 134.7, 135.0, 140.5, 146.5, 150.6, 191.7; HRMS (APCI) Calcd for $C_{13}H_8O_5N_2$ $[M]^-$ 272.0439, Found 272.0440.

4.1.55. 2-Nitro-4-benzoylphenyl p-tolyl ketone. Mp 141–142 °C; IR (nüjol) 1352, 1534, 1662 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ=2.43 (s, 3H), 7.28 (d, J=8.6 Hz, 2H), 7.57 (t, J=7.9 Hz, 2H), 7.61 (d, J=7.7 Hz, 1H), 7.66–7.72 (m, 3H), 7.85 (dd, J=7.9, 1.4 Hz, 2H), 8.18 (dd, J=7.7, 1.1 Hz, 1H), 8.61 (d, J=1.1 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ=21.8, 125.6, 128.9, 129.2, 129.5, 129.6, 130.0, 133.0, 133.6, 134.8, 135.9, 139.3, 139.7, 145.4, 146.6, 192.3, 193.5; HRMS (APCI) Calcd for $C_{21}H_{16}O_4N$ $[M+H]^+$ 346.1074, Found 346.1065.

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