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# Nickel catalysed electrosynthesis of ketones from organic halides and iron pentacarbonyl. Part 2: Unsymmetrical ketones

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**Abstract**—Unsymmetrical aryl–benzyl or aryl–alkyl ketones are obtained by electrolysing in an undivided cell a DMF solution containing two organic halides, iron pentacarbonyl and a catalytic amount of a nickel-2,2′-bipyridine complex. © 2001 Elsevier Science Ltd. All rights reserved.

## 1. Introduction

The carbonylation of organic halides (RX) into ketones can be achieved by coupling between RX and CO itself or, often more efficiently from transition metal carbonyl complexes.[1]

The balance of the reaction involves necessarily a two-electron reduction as expressed by Eq. (1).

$$R^1X + R^2X + \text{'CO'} + 2e \rightarrow R^1\text{–CO–}R^2 + 2X^- \qquad (1)$$

Several ways can be considered to achieve this reduction. One method consists in a preliminary conversion of one of the organic halides into an organometallic compound (organolithium, Grignard reagent,…). Conversely a transition metal carbonyl complex can be initially reduced into a nucleophilic compound. This second way has been widely explored since Collman, two decades ago, showed the versatility of the reagent $Fe(CO)_4^{2-}$.[2] This super nucleophile reacts with various organic halides to give alkyl metal carbonyl complexes that evolve into acyl metal carbonyl complexes in a key-step for the obtaining of carbonylated products.[1] A third way which has not been much explored consists in performing the reduction step by an electrochemical method. Some work has been devoted to the electrochemistry of metal carbonyl complexes and especially iron pentacarbonyl which undergoes a cathodic reduction at $-2$ V vs. SCE[3]. It has been reported that electrolysis of mixtures of an alkyl- or benzyl-halide and iron pentacarbonyl leads to aldehydes[4] or symmetrical ketones[4b,5] with moderate yields.

Some years ago, we have envisaged a new approach by the conjoined use of electrochemistry and homogeneous catalysis based on nickel–2,2′-bipyridine complexes. Thus, we have shown that the electroreduction of $Nibpy^{2+}$ allows the formation of a symmetrical ketone from DMF solutions of an organic halide maintained under a carbon monoxide atmosphere.[6] Electroanalytical investigations led us to propose that the catalytic cycle is induced by the electrogeneration of an unsaturated transient zerovalent complex NibpyCO which reacts with the organic halide.[7]

This method, using CO gas in mild conditions, provides good yields of symmetrical ketones derived from benzylic or aliphatic halides. However, aromatic halides were much less reactive. In addition, attempts to obtain unsymmetrical ketones from solutions containing two halides were not successful since the selectivity was low. Another limitation was the necessity to adjust accurately the experimental conditions in order to avoid a lack or an excess of carbon monoxide. Indeed, a lack of CO results in a competition between the obtaining of the ketone and the $Ni^{(0)}$bpy catalysed formation of the dimer R–R whereas an excess of CO leads to the stable saturated complex $Nibpy(CO)_2$ inactive towards RX.

This difficulty was overcome by the use of a metal carbonyl complex like $Fe(CO)_5$, $Fe_3(CO)_{12}$, $W(CO)_6$, $Cr(CO)_6$, $Mo(CO)_5$ or $Co_2(CO)_8$ instead of gaseous CO[8] that offers the advantage of having in the solution an adjustable source of CO. In these new conditions the electrosynthesis of symmetrical benzyl or alkyl ketones is easily achieved with moderate to excellent yields.

In this paper we wish to present our results related to

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*Keywords*: metal carbonyl; ketone electrosynthesis; nickel catalysis; organic halides electroreduction.

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**Table 1.** Ni-bpy catalysed electrosyntheses of aryl–alkyl ketones from organic halides and iron pentacarbonyl (general conditions: DMF (50 mL), $Bu_4NBF_4$ 1.5 mmol, RX 10 mmol, ArX′ 20 mmol, $Fe(CO)_5$ 3 mmol, $NiBr_2bpy$ 3 mmol, stainless steel anode ($Fe_{64}/Ni_{36}$), nickel grid cathode, $I$=0.3–0.5 Å)

| Entry | RX | ArX′ | Ar–CO–R | | Isolated yield (%) |
|---|---|---|---|---|---|
| 1 | $Ph-CH_2Cl$ | PhI | $Ph-CO-CH_2-Ph$ | *1* | 82 |
| 2 | $Ph-CH_2Cl$ | PhBr | $Ph-CO-CH_2-Ph$ | | 42 |
| 3 | $Ph-CH_2Cl$ | PhCl | $Ph-CO-CH_2-Ph$ | | Traces |
| 4 | $Ph-CH_2Cl$ | $2\text{-}MeO-C_6H_4I$ | $2\text{-}MeO-C_6H_4-CO-CH_2-Ph$ | *2* | 54 |
| 5 | $Ph-CH_2Cl$ | $3\text{-}MeO-C_6H_4I$ | $3\text{-}MeO-C_6H_4-CO-CH_2-Ph$ | *3* | 70 |
| 6 | $Ph-CH_2Cl$ | $4\text{-}MeO-C_6H_4I$ | $4\text{-}MeO-C_6H_4-CO-CH_2-Ph$ | *4* | 88 |
| 7 | $Ph-CH_2Cl$ | $4\text{-}MeO-C_6H_4Br$ | $4\text{-}MeO-C_6H_4-CO-CH_2-Ph$ | | 49 |
| 8 | $Ph-CH_2Cl$ | $2\text{-}HO-C_6H_4I$ | $2\text{-}HO-C_6H_4-CO-CH_2-Ph$ | *5* | 80 |
| 9 | $Ph-CH_2Cl$ | $3\text{-}HO-C_6H_4I$ | $3\text{-}HO-C_6H_4-CO-CH_2-Ph$ | *6* | 57 |
| 10 | $Ph-CH_2Cl$ | $4\text{-}HO-C_6H_4I$ | $4\text{-}HO-C_6H_4-CO-CH_2-Ph$ | *7* | 84 |
| 11 | $Ph-CH_2Cl$ | $2\text{-}H_2N\text{-}C_6H_4I$ | $2\text{-}H_2N\text{-}C_6H_4-CO-CH_2-Ph$ | *8* | 76 |
| 12 | $Ph-CH_2Cl$ | $3\text{-}H_2N\text{-}C_6H_4I$ | $3\text{-}H_2N\text{-}C_6H_4-CO-CH_2-Ph$ | *9* | 43 |
| 13 | $Ph-CH_2Cl$ | $4\text{-}H_2N\text{-}C_6H_4I$ | $4\text{-}H_2N\text{-}C_6H_4-CO-CH_2-Ph$ | *10* | 63 |
| 14 | $Ph-CH_2Cl$ | $4\text{-}H_2N\text{-}C_6H_4Br$ | $4\text{-}H_2N\text{-}C_6H_4-CO-CH_2-Ph$ | | Traces |
| 15 | $Ph-CH_2Cl$ | $4\text{-}Me_2N\text{-}C_6H_4Br$ | $4\text{-}Me_2N\text{-}C_6H_4-CO-CH_2-Ph$ | *11* | 60 |
| 16 | $Ph-CH_2Cl$ | $4\text{-}CN\text{-}C_6H_4Br$ | $4\text{-}CN\text{-}C_6H_4-CO-CH_2-Ph$ | *12* | Traces |
| 17 | $Ph-CH_2Cl$ | $3\text{-}Et-CO-C_6H_4Br$ | $3\text{-}Et-CO-C_6H_4-CO-CH_2-Ph$ | *13* | 39 |
| 18 | $Ph-CH_2Cl$ | $4\text{-}Et-CO-C_6H_4Br$ | $4\text{-}Et-CO-C_6H_4-CO-CH_2-Ph$ | *14* | 32 |
| 19 | $2\text{-}Cl-C_6H_4-CH_2Cl$ | $4\text{-}MeO-C_6H_4I$ | $4\text{-}MeO-C_6H_4-CO-CH_2\text{-}(2\text{-}Cl-C_6H_4)$ | *15* | 71 |
| 20 | $3\text{-}Cl-C_6H_4-CH_2Cl$ | $4\text{-}MeO-C_6H_4I$ | $4\text{-}MeO-C_6H_4-CO-CH_2\text{-}(3\text{-}Cl-C_6H_4)$ | *16* | 72 |
| 21 | $4\text{-}Cl-C_6H_4-CH_2Cl$ | $4\text{-}MeO-C_6H_4I$ | $4\text{-}MeO-C_6H_4-CO-CH_2\text{-}(4\text{-}Cl-C_6H_4)$ | *17* | 73 |
| 22 | $n\text{-}C_8H_{17}I$ | PhI | $Ph-CO-C_8H_{17}$ | *18* | 42 |
| 23 | $n\text{-}C_8H_{17}I$ | $4\text{-}MeO-C_6H_4I$ | $4\text{-}MeO-C_6H_4-CO-C_8H_{17}$ | *19* | 35 |
| 24 | $Ph-CH_2Cl$ | $Ph-CH{=}CHBr$ (E) | $Ph-CH{=}CH-CO-CH_2-Ph$ | *20* | 52 |

the Ni-bpy catalysed one-step electrosynthesis of unsymmetrical ketones from the mixture of two organic halides and a metal carbonyl complex, especially iron pentacarbonyl, as the source of CO.

We were particularly interested in the preparation of aryl–alkyl-ketones, which are important synthetic intermediates. The overall reaction accords with Eq. (2):

$$RX + ArX' \xrightarrow[\text{NiBr}_2\text{bpy, e}]{\text{Fe(CO)}_5} Ar\text{–}CO\text{–}R \qquad (2)$$

## 2. Results and discussion

The experimental conditions were similar to those employed for the synthesis of symmetrical ketones.[8] To DMF was added a supporting electrolyte ($Bu_4NBF_4$), iron pentacarbonyl, the catalytic precursor $NiBr_2bpy$ and the two organic halides. The undivided cell was fitted with a sacrificial stainless steel rod as the anode surrounded by a cylindrical nickel grid as the cathode ($40\ cm^2$). A calomel reference electrode was set near the nickel grid allowing us to measure the potential of the cathode during the electrolysis which were carried out at room temperature and at constant current intensity until the full consumption of the benzyl (or alkyl) halide. The faradaïc yields stand in the range of 50–70%.

Our first experiments were conducted with $PhCH_2Cl$ and PhI as model reagents. Starting from equal amounts of both halides, only 50–60% of the unsymmetrical ketone was obtained, the formation of dibenzyl ketone being a non negligible side reaction. Then we used a two-fold excess of the aromatic halide. Concerning the amount of $Fe(CO)_5$, we have shown, as for the synthesis of symmetrical ketones,[8] that, when $Fe(CO)_5$ is in default, more than 4 mol of CO per mole of $Fe(CO)_5$ are available for the formation of ketones. Presumably, $Fe(CO)_5$ loose one CO group and forms dimers and trimers (e.g. $Fe_2(CO)_9$ and $Fe_3(CO)_{12}$) which subsequently function as CO source. A moderate excess of $Fe(CO)_5$ (3 mmol of $Fe(CO)_5$ vs. 10 mmol of RX) is then sufficient to prevent the formation of uncarbonylated side-products like R–R, Ar–Ar or Ar–R. This avoids also, at the end of the electrolysis, the presence in the solution of large amounts of hazardous metal carbonyl species that would complicate the further workup.

Results given in Table 1 show that an aryl iodide is effective as a partner of benzylic chlorides. Yields become moderate to poor for aryl bromides (Table 1, entries 2, 7, 14, 16–18) and still lower from chlorobenzene (Table 1, entry 3), the formation of dibenzylketone being then largely competitive.

Various substituted aryl iodides are compatible but yields depend on the position of the substitutent. When the aromatic halide is iodophenol (Table 1, entries 8–10) or iodoaniline (Table 1, entries 11–13) yields decrease in the order *ortho*≈*para*>*meta* while the *ortho* position of the OMe group is the less favourable for iodoanisoles (Table 1, entries 4–6). The presence of an electron-withdrawing group on the aryl halide (Table 1, entries 16–18) give yields lower than in the presence of an electron-donating group. No clear interpretation of the effect of the substitutent was possible. Substitution on the aromatic group of benzyl chloride has no effect on the reaction (Table 1, entries 19–21).

The merits of this electrochemical method lie in the access to unsymmetrical ketones which would not be accessible by

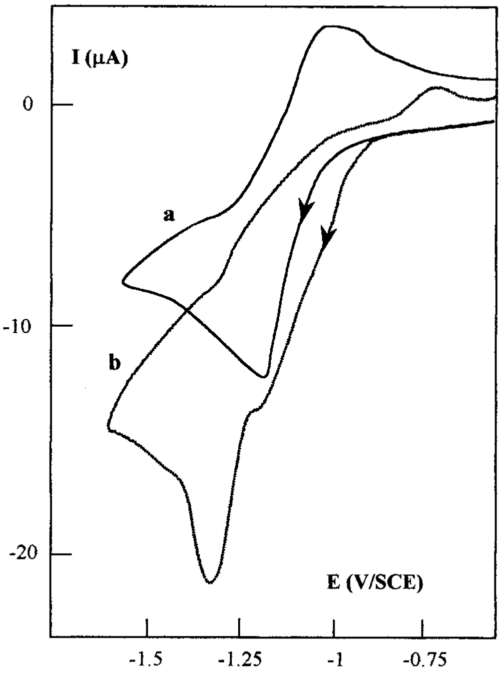

**Figure 1.** Cylic voltametry in DMF+$Bu_4NBF_4$ 0.1 mol $L^{-1}$ at a gold disk electrode (1 mm diameter); scan rate of 0.1 $Vs^{-1}$ at room temperature. Curve **a**: $Nibpy^{2+}$ 0.02 mol $L^{-1}$, curve **b**: after addition of $Fe(CO)_5$ 0.02 mol $L^{-1}$.

a Friedel–Crafts coupling between an arene and an arylacetyl chloride. Indeed, no Friedel–Crafts coupling product at the *meta* position will be obtained between phenol, aniline or anisole and phenylacetyl chloride. Furthermore, from phenol or aniline, *O*- or *N*-acylation will compete with *C*-acylation.

The carbonylating coupling between an aliphatic iodide and an aromatic iodide is also possible but yields are moderate (Table 1, entries 22, 23). Some other experiments involving a heteroaromatic halide instead of the aromatic halide have not been very successful since benzyl chloride and 2-bromopyridine or 3-bromothiophene leads only to 10–20% (GC yields) of the corresponding unsymmetrical ketone. On the other hand, moderate yields are obtained when starting from benzyl chloride and β-bromostyrene (Table 1, entry 24).

With regard to the mechanism of the reaction, our electroanalytical work is not sufficient to propose a well argued pathway and we can only give partial data. During the electrolysis achieved under controlled-current conditions, we monitored the potential of the cathode which was about $-1.1$–$-1.3$ V vs SCE. This indicates that direct electroreductions of benzyl chlorides[10] or $Fe(CO)_5$[3] are not involved since they both require a potential lower than $-2$ V.

As shown on Fig. 1, the cathodic potential agrees with the electrochemical reduction at $-1.2$ V vs. SCE of the catalytic precursor $Nibpy^{2+}$.[9] In the presence of $Fe(CO)_5$ (or other metal carbonyl complexes), cyclic voltammetry at potential scan rates of 0.1–5 $Vs^{-1}$ indicates the total lack of reversibility of the bielectronic $Nibpy^{2+}/Ni^0bpy$ transition. As previously reported when CO itself was the source of CO,[7] we suppose that the reduction of $Nibpy^{2+}$ is followed by a fast capture of CO to yield a mixed zerovalent complex $Ni^0bpyCO$ or $Ni^0bpy(CO)_2$. However, we think that the role of $Fe(CO)_5$ does not consist only in being a donor of CO and several arguments can be put forward.

First, cyclic voltammograms of solutions containing $Nibpy^{2+}$ and $Fe(CO)_5$ (see Fig. 1) show that the reduction step of $Nibpy^{2+}$ is followed by another signal at $-1.3$ V vs. SCE which was not observed for the electroreduction of $Nibpy^{2+}$ in the presence of CO.[7] We then suppose that this new unidentified signal might be related to a transient iron carbonyl species resulting from the rapid loss of CO from $Fe(CO)_5$ to $Ni^0bpy$. Besides, the presence of $Fe(CO)_5$ allows the efficient formation of unsymmetrical ketones, while the yields are poor when CO gas itself is the source of CO.[6] Moreover we have found, on the model reaction involving $PhCH_2Cl$ and PhI, that the yield in $PhCH_2COPh$ is very dependent on the nature of the metal carbonyl complex. The use of $W(CO)_6$ or $Mo(CO)_6$ leads only to 35 and 45% (GC yields), respectively, of the mixed ketone instead of 90% from $Fe(CO)_5$, while no difference between the three metal carbonyls was observed for the synthesis of symmetrical ketones.[8] Obviously, further experiments are necessary for a better understanding of the very role of $Fe(CO)_5$.

## 3. Conclusions

We have shown that the $Nibpy^{2+}$ electroreduction into a zerovalent nickel complex provides a good catalytic system to achieve the synthesis of unsymmetrical ketones especially from benzylic chlorides and aromatic iodides using iron pentacarbonyl as the source of CO. This method, as well as the electrochemical device, are very simple and the experimental conditions are mild.

## 4. Experimental

CAUTION: $Fe(CO)_5$ is toxic and easily flammable. It must be handled with care.

Electrolysis was conducted according to the conditions described above. The progress of the reaction was monitored by GC analysis of samples. The electrolytic solution were poured in HCl 6 mol $L^{-1}$ (1/1 v/v) during at least 2 h in order to destroy residual metal complexes. The resulting mixtures were extracted with a suitable organic solvent (generally diethyl ether) and evaporated. The ketones were recovered by chromatography on a silica gel column (elution by a mixture pentane–diethyl ether) and characterized by GC–MS by EI (Finnigan Ion Trap Detector 800), $^1H$ NMR ($CDCl_3$/TMS, 200 MHz), $^{13}C$ NMR ($CDCl_3$/TMS, 50 MHz), and IR plus elementary analysis for unregistered products. The analytical data given below are satisfactory.

### 4.1. 1,2-Diphenylethanone RN [451-40-1]

IR $\nu_{CO}$: 1685 $cm^{-1}$; Mass., *m*/*z* (rel. intensity): 197(6), 105(100), 89(10), 77(57), 65(29), 51(46); $^1H$ NMR ($\delta$

ppm) 7.97–7.2 (10H, m), 4.2 (2H, s); $^{13}$C NMR ($\delta$ ppm): 197.4 (1C, C=O), 136.4–126.9 (12C, Ar), 45.3 (1C, CH$_2$).

### 4.2. 1-(2-Methoxyphenyl)-2-phenylethanone RN [33470-10-9]

IR: $\nu_{CO}$: 1680 cm$^{-1}$; Mass., *m/z* (rel. intensity): 227(4), 135(100), 91(8), 77(8), 63(7), 51(4); $^1$H NMR ($\delta$ ppm): 7.57–6.80 (9H, m), 4.2 (2H, s), 3.8 (3H, s); $^{13}$C NMR ($\delta$ ppm): 200.0 (1C, C=O), 158.4 (1C, C–O), 135.3–120.6 (11C, Ar), 55.4 (1C, O–CH$_3$), 50.1 (1C, CH$_2$).

### 4.3. 1-(3-Methoxyphenyl)-2-phenylethanone RN [62381-24-2]

IR: $\nu_{CO}$ 1680 cm$^{-1}$; Mass., *m/z* (rel. intensity): 227(5), 135(100), 91(30), 77(20), 63(20), 51(7); $^1$H NMR ($\delta$ ppm): 7.56–7.0 (9H, m), 4.2 (2H, s), 3.8 (3H, s); $^{13}$C NMR ($\delta$ ppm): 197. 2 (1C, C=O), 159. 6 (1C, C–O), 137.7–112.6 (11C, Ar), 55.1 (1C, O–CH$_3$), 45.3 (1C, CH$_2$).

### 4.4. 1-(4-Methoxyphenyl)-2-phenylethanone RN [1023-17-2]

IR: $\nu_{CO}$ 1680 cm$^{-1}$; Mass., *m/z* (rel. intensity): 227(3), 135(100), 91(9), 77(8), 63(10); $^1$H NMR ($\delta$ ppm): 7.93 (2H, d, *J*=6.9 Hz), 7.29–7.13 (5H, m), 6.86 (2H, d, *J*=6.9 Hz), 4.2 (2H, s), 3.8 (3H, s); $^{13}$C NMR ($\delta$ ppm): 196.5 (1C, C=O), 163.5 (1C, O–C), 135.0–113.8 (11C, Ar), 55.4 (O–CH$_3$), 45.2 (1C, CH$_2$).

### 4.5. 1-(2-Hydroxyphenyl)-2-phenylethanone RN [2491-31-8]

IR: $\nu_{CO}$ 1680 cm$^{-1}$; Mass., *m/z* (rel. intensity): 212(6), 122(7), 121(100), 93(12), 91(12), 65(40), 63(10); $^1$H NMR ($\delta$ ppm): 12.1 (1H, s), 7.73–6.7 (9H, m), 4.2 (2H, s); $^{13}$C NMR ($\delta$ ppm): 203.7 (1C, C=O), 162.7 (1C, C–O), 136.3–118.4 (11C, Ar), 44.9 (1C, CH$_2$).

### 4.6. 1-(3-Hydroxyphenyl)-2-phenylethanone

Calcd for $C_{14}H_{12}O_2$: C, 79.2; H, 5.7. Found: C, 78.6; H, 5.8; IR $\nu_{CO}$ 1680 cm$^{-1}$; Mass., *m/z* (rel. intensity): 213(3), 122(7), 121(100), 93(25), 65(44), 51(6); $^1$H NMR ($\delta$ ppm): 9.77 (1H, s), 7.47–6.91 (9H, m), 4.14 (2H, s); $^{13}$C NMR ($\delta$ ppm): 199.5 (1C, C=O), 156.6 (1C, C–O), 137.7–115.3 (11C, Ar), 45.6 (1C, CH$_2$).

### 4.7. 1-(4-Hydroxyphenyl)-2-phenylethanone RN [2491-32-9]

IR $\nu_{CO}$ 1680 cm$^{-1}$; Mass., *m/z* (rel. intensity): 213(1), 121(100), 93(13), 91(11), 77(1), 65(30); $^1$H NMR ($\delta$ ppm): 9.2 (1H, s), 7.97 (2H, d, *J*=8.5 Hz), 7.3–7.2 (5H, m), 6.93 (2H, d, *J*=8.5 Hz), 4.3 (2H, s); $^{13}$C NMR ($\delta$ ppm): 196.1 (1C, C=O), 162.6 (1C, C–O), 131.9–116.0 (11C, Ar), 45.3 (1C, CH$_2$).

### 4.8. 1-(2-Aminophenyl)-2-phenylethanone RN [835-38-1]

IR $\nu_{CO}$ 1676 cm$^{-1}$; Mass., *m/z* (rel. intensity): 333(100), 212(29), 121(28), 120(77), 92(18), 65(30); $^1$H NMR ($\delta$ ppm): 7.76–6.53 (9H, m), 6.22 (2H, s, NH$_2$), 4.19 (2H, s, CH$_2$). $^{13}$C NMR ($\delta$ ppm): 199.7 (1C, C=O), 150.7 (1C, C–N), 135.2–115.5 (11C, Ar), 45.9 (1C, CH$_2$).

### 4.9. 1-(3-Aminophenyl)-2-phenylethanone RN [55221-36-0]

IR $\nu_{CO}$ 1680 cm$^{-1}$; Mass., *m/z* (rel. intensity): 212(24), 211(48), 121(56), 120(100), 92(57), 65(58); $^1$H NMR ($\delta$ ppm): 7.34–7.11 (8H, m), 6.80–6.74 (1H, m), 4.16 (2H, s, CH$_2$), 3.71 (2H, s, NH$_2$); $^{13}$C NMR ($\delta$ ppm): 197.7 (1C, C=O), 146.7 (1C, C–N), 137.5–114.1 (11C, Ar), 45.3 (1C, CH$_2$).

### 4.10. 1-(4-Aminophenyl)-2-phenylethanone RN [72433-45-5]

IR $\nu_{CO}$ 1680 cm$^{-1}$; Mass., *m/z* (rel. intensity) 212(6), 121(100), 120(85), 92(27), 77(1), 65(42); $^1$H NMR ($\delta$ ppm): 7.70 (2H, d, *J*=8.6 Hz), 7.16–7.02 (5H, m), 6.55 (2H,d, *J*=8.6 Hz), 5.4 (2H, s, NH$_2$), 4.0 (2H, s, CH$_2$); $^{13}$C NMR ($\delta$ ppm): 195.6 (1C, C=O), 150.9 (1C, C–N), 135.2–126.3 (11C, Ar), 44.7 (1C, CH$_2$).

### 4.11. 1-[4-(Dimethylamino)phenyl]-2-phenylethanone RN [97606-39-8]

IR $\nu_{CO}$ 1680 cm$^{-1}$; Mass., *m/z* (rel. intensity): 239(8), 148(100), 120(6), 104(7), 91(17), 77(12), 65(8), 51(6); $^1$H NMR ($\delta$ ppm): 7.86 (2H, d, *J*=7.2 Hz), 7.23–7.13 (5H, m), 6.56 (2H,d, *J*=7.2 Hz), 4.1 (2H, s), 3.0 (6H, s); $^{13}$C NMR ($\delta$ ppm): 195.5 (1C, C=O), 153.2 (1C, C–N), 135.6–126.3 (11C, Ar), 44.7 (1C, CH$_2$), 39.7 (2C, CH$_3$).

### 4.12. 1-[3-(1-Oxo-propyl)-phenyl]-2-phenylethanone

Calcd for $C_{17}H_{16}O_2$: C, 80.7; H, 6.4. Found: C, 80.4; H, 6.6; IR: $\nu_{CO}$ 1685 and 1681 cm$^{-1}$; Mass., *m/z* (rel. intensity): 253(19), 162(100),133(6), 105(25), 91(21), 77(15), 65(14), 51(10); $^1$H NMR ($\delta$ ppm): 8.5 (1H, s), 8.14–8.05 (2H, m), 7.53–7.15 (6H, m), 4.3 (2H, s), 2.96 (2H, q, *J*=7.3 Hz), 1.17 (3H, t, *J*=7.3 Hz); $^{13}$C NMR ($\delta$ ppm): 199.8 (1C, C=O), 196.7 (1C, C=O), 137.1–127.0 (12C, Ar), 45.6 (1C, *C*H$_2$–Ph), 31.9 (1C, *C*H$_2$–CH$_3$), 8.0 (1C, CH$_2$–*C*H$_3$).

### 4.13. 1-[4-(1-Oxo-propyl)-phenyl]-2-phenylethanone

Calcd for $C_{17}H_{16}O_2$: C, 80.7; H, 6.4. Found: C, 80.4; H, 6.6; IR: $\nu_{CO}$ 1684 and 1680 cm$^{-1}$; Mass., *m/z* (rel. intensity): 253(23), 162(100), 133(25), 104(37), 91(29), 76(14), 65(18), 51(10); $^1$H NMR ($\delta$ ppm): 8.02–7.91 (4H, m), 7.30–7.14 (5H, m), 4.2 (2H, s), 2.94 (2H, q, *J*=7.3 Hz), 1.16 (3H, t, *J*=7.3 Hz); $^{13}$C NMR ($\delta$ ppm): 200.1 (1C, C=O), 197.1 (1C, C=O), 140.1 -127.1 (12C, Ar), 45.8 (1C, *C*H$_2$–Ph), 32.2 ((1C, *C*H$_2$–CH$_3$), 8.1 (1C, CH$_2$–*C*H$_3$).

### 4.14. 2-(2-Chlorophenyl)-1-(4-methoxyphenyl)ethanone RN [41840-95-3]

IR: $\nu_{CO}$ 1680 cm$^{-1}$; Mass., *m/z* (rel. intensity): 261(1), 152(1), 135(100), 125(6), 107(9), 92(14), 77(26), 63(16); $^1$H NMR ($\delta$ ppm): 7.94 (2H, d, *J*= 6.9 Hz), 7.34–7.28 (1H, m), 7.17–7.10 (3H, m), 6.86 (2H, d, *J*=6.9 Hz), 4.3

(2H, s), 3.8 (3H, s); $^{13}$C NMR ($\delta$ ppm): 194.7 (1C, C=O), 163.5 (1C, O–C), 134.2–113.7 (11C, Ar), 55.3 (1C, O–$CH_3$), 42.7 (1C, $CH_2$).

### 4.15. 2-(3-Chlorophenyl)-1-(4-methoxyphenyl)ethanone RN [68968-13-8]

IR: $\nu_{CO}$ 1683 cm$^{-1}$; Mass., *m/z* (rel. intensity): 261(3), 152(1), 136(100), 125(5), 107(6), 92(13), 77(15), 64(8); $^{1}$H NMR ($\delta$ ppm):7.91 (2H, d, *J*=6.9 Hz), 7.19–7.03 (4H, m), 6.86 (2H, d, *J*=6.9 Hz), 4.1 (2H, s), 3.8 (3H, s); $^{13}$C NMR ($\delta$ ppm): 195.1 (1C, C=O), 163.5 (1C, O–C), 136.6–113.7 (11C, Ar), 55.2 (1C, O–$CH_3$), 44.3 (1C, $CH_2$).

### 4.16. 2-(4-Chlorophenyl)-1-(4-methoxyphenyl)ethanone RN [52578-11-7]

IR: $\nu_{CO}$ 1682 cm$^{-1}$; Mass., *m/z* (rel. intensity): 261(2), 152(1), 135(100), 125(5), 107(8), 92(16), 77(24), 63(17); $^{1}$H NMR ($\delta$ ppm): 7.91 (2H, d, *J*= 6.9 Hz), 7.2–7.1 (4H, m), 6.86 (2H, d, *J*=6.9 Hz), 4.1 (2H, s), 3.8 (3H, s); $^{13}$C NMR ($\delta$ ppm): 195.7 (1C, C=O), 163.7 (1C, O–C), 133.4–113.9 (11C, Ar), 55.6 (1C, O–$CH_3$), 44.4 (1C, $CH_2$).

### 4.17. 1-Phenylnonan-1-one RN [6008-36-2]

IR $\nu_{CO}$ 1685 cm$^{-1}$; Mass., *m/z* (rel. intensity): 219(38), 120(35), 105(100), 77(58), 51(21); $^{1}$H NMR ($\delta$ ppm): 7.88–7.82 (2H, m), 7.42–7.27 (3H, m), 2.8 (2H, t; *J*=7.4 Hz), 1.2 (12H, m), 0.8 (3H, t, *J*=6.5 Hz); $^{13}$C NMR ($\delta$ ppm): 200.1 (1C, C=O), 136.9–128.1 (6C, Ar), 38.3 (1C, $CH_2$), 32.0–22.5 (6C, Aliph), 13.9 (1C, $CH_3$).

### 4.18. 1-(4-Methoxyphenyl)-nonan-1-one RN [52754-68-4]

IR $\nu_{CO}$ 1683 cm$^{-1}$; Mass., *m/z* (rel. intensity): 249(42), 150(68), 135(100), 92(10), 77(11); $^{1}$H NMR ($\delta$ ppm): 7.87 (2H, d, *J*=8.5 Hz), 6.87 (2H, d, *J*=8.5 Hz), 3.8 (3H, s), 2.85 (2H, t, *J*=7.5 Hz), 1.25–1.14 (12H, m), 0.84–0.78 (3H, t, *J*=7.0 Hz); $^{13}$C NMR ($\delta$ ppm): 199.6 (1C, C=O), 163.1 (1C, C–O), 130.1 (2C, Ar), 113.4 (2C, Ar), 55.2 (1C, O–$CH_3$), 38.1(1C, $CH_2$), 31.6–18.3 (6C, Aliph.), 13.9 (1C, $CH_2$–$CH_3$).

### 4.19. 1,4-Diphenylbut-3-en-2-one (*E*) RN [5409-59-6]

IR $\nu_{CO}$ 1690 cm$^{-1}$; Mass., *m/z* (rel. intensity): 223(14), 131(100), 103(45), 91(35), 77(37), 65(16), 51(23); $^{1}$H NMR ($\delta$ ppm): 7.54 (1H, d, *J*=16 Hz), 7.48–7.07 (10H, m), 6.70 (1H, d, *J*=16 Hz), 3.9 (2H, s); $^{13}$C NMR ($\delta$ ppm): 197.4 (1C, C=O), 143.4–125.5 (14C, Ar+C=C), 48.4 (1C, $CH_2$).

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