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Copper Catalyzed Conjugate Addition of Highly Functionalized Arylmagnesium Compounds to Enones

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Abstract—Highly functionalized arylmagnesium bromides are readily prepared by an iodine–magnesium exchange reaction. In the presence of catalytic amounts of copper(I) salts and chlorotrimethylsilane, they add to various enones leading to the conjugate addition products in 66–89% yield. © 2000 Elsevier Science Ltd. All rights reserved.

The scope of the applications of organometallic reagents to organic synthesis strongly depends on the availability of highly functionalized carbon groups attached to the metal. Numerous functionalized organozinc compounds have been successfully prepared and used in synthesis.[1] Only recently an efficient iodine–magnesium exchange reaction has allowed the preparation of highly functionalized arylmagnesium compounds.[2,3] These reagents led to interesting applications in solution[2–5] and in solid phase synthesis.[2,3] Herein, we wish to report the generation of highly functionalized organomagnesium reagents and their conjugate addition to various enones. The presence of chlorotrimethylsilane proved to be essential for the success of the reaction.[6–10] Thus, the reaction of ethyl 3-iodobenzoate (**1a**, 1.05 equiv.) with *i*-PrMgBr (1.20 equiv.) in THF at −40°C for 1 h produces the expected functionalized arylmagnesium compound **2a** as indicated by gas chromatographical analysis of reaction mixture aliquots quenched with sat. NH_4Cl solution or iodine. To this organometallic, a mixture of cyclohexenone (1.0 equiv.), CuI (0.1 equiv.), LiCl (0.2 equiv.)[11] and Me_3SiCl (1.0 equiv.) was added at −40°C (Method A).[10] After 1 h, the conversion was complete and the desired 1,4-adduct (**3a**) was isolated in 74% yield (see entry 1 of Table 1 and Scheme 1).

Under these conditions, typical cyclic and acyclic enones provide the desired products in satisfactory yields. Alternatively, $CuBr{\cdot}Me_2S$ (5 mol%), Me_3SiCl (2 equiv.) in a THF:HMPA mixture (Method B) gives excellent results as well (see entries 2, 6–9 and 5–6 of Table 1). In summary, the iodine–magnesium exchange reaction allows a low temperature preparation of arylmagnesium derivatives bearing an ester, an amide or a nitrile function. All these organometallics undergo a smooth 1,4-addition to various polyfunctional enones. Extensions of this methodology to more complex organomagnesium reagents is underway.

Experimental

General methods

THF and HMPA were dried over sodium and CaH_2, respectively, and distilled prior to use. Commercially available starting materials were used without further purification.

Typical procedures

Preparation of 3-(3-carbethoxyphenyl)cyclohexanone (3a). *Method A.* A three-necked flash equipped with a septum, a glass stopper and an argon inlet was charged with dry LiCl (dried 1 h at 130°C at 0.1 mmHg; 16.2 mg, 0.384 mmol), CuI (36.6 mg, 0.192 mmol) and THF (6 mL). To the resulting solution, Me_3SiCl (0.25 mL, 1.92 mmol) and 2-cyclohexenone (185 mg, 1.92 mmol) was added. A second three-necked flask equipped with a septum, a thermometer and an argon inlet was charged with ethyl 3-iodobenzoate (**1a**: 566 mg, 2.0 mmol) in THF (1.5 mL) and was cooled to −40°C. *i*-PrMgBr (2.5 mL, 2.3 mmol of a 0.87 M solution in THF) was slowly added and the reaction mixture was stirred for 1 h at this temperature. The solution of the first flask was added and the resulting solution was stirred for 1 h and was quenched with a sat. solution of aq. NH_4Cl. The aqueous phase was extracted several times with ether and the combined organic phase

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Keywords: copper catalysis; conjugate addition; polyfunctional organomagnesium compounds.

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Table 1. Conjugate addition products **3a–p** obtained by the copper(I) catalyzed addition of polyfunctional organomagnesium compounds to enones in the presence of TMSCl

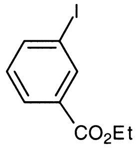
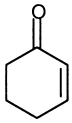
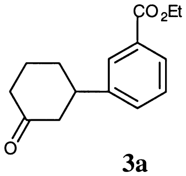
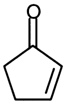
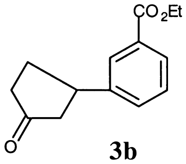
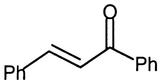
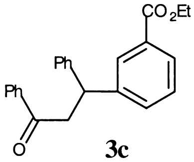
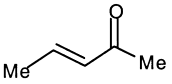
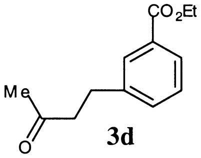
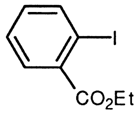
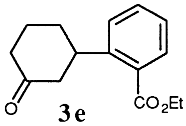
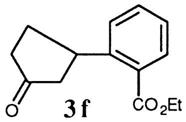
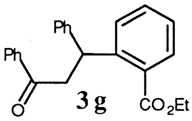
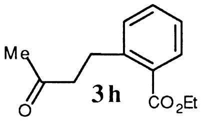
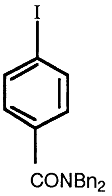
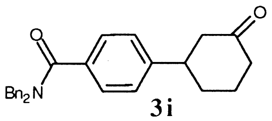
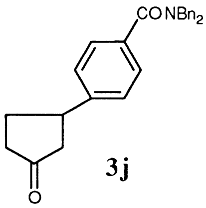
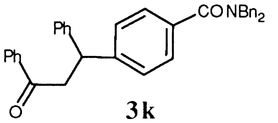
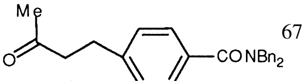
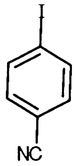
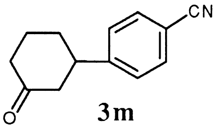
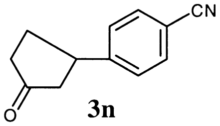
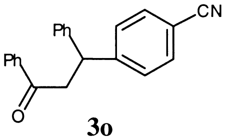
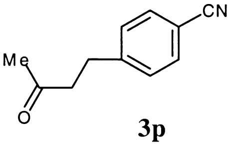
Entry	Substrate of type **1**	Method	Enone **2**	Product of type **3**	Yield[a] (%)
1	 **1a**	Method A		 **3a**	74
2	**1a**	Method B			72
3	**1a**	Method A		 **3b**	74
4	**1a**	Method A		 **3c**	80
5	**1a**	Method A		 **3d**	68
6	 **1b**	Method B		 **3e**	73
7	**1b**	Method B		 **3f**	75
8	**1b**	Method B		 **3g**	69
9	**1b**	Method B		 **3h**	74
10	 **1c**	Method A		 **3i**	89
11	**1c**	Method A		 **3j**	73

Table 1 (*continued*)

Entry	Substrate of type **1**	Method	Enone **2**	Product of type **3**	Yield[a] (%)
12	**1c**	Method A		 **3k**	69
13	**1a**	Method A		 **3l**	67
14	 **1d**	Method A		 **3m**	72
15	**1d**	Method B		 **3n**	66
16	**1d**	Method B		 **3o**	68
17	**1d**	Method A		 **3p**	70

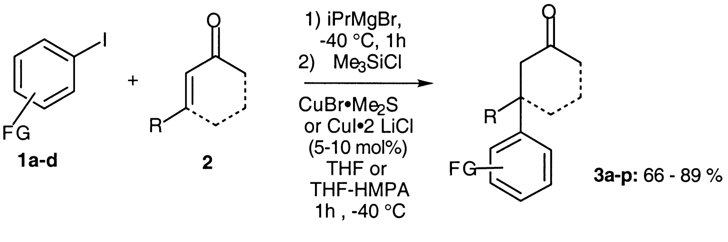
[a] Isolated yield of analytically pure product.

was dried ($MgSO_4$) and the solvent was evaporated. The crude residue was purified by flash-chromatography (ether: pentane 1:5) affording the desired ketone **3a** (349 mg, 74% yield) as a yellowish oil.

Method B. A three-necked flask equipped with a septum, a glass stopper and an argon inlet was charged with $CuBr{\cdot}Me_2S$ (10.3 mg, 0.05 mmol), Me_3SiCl (0.26 mL, 2 mmol) and 2-cyclohexenone (96 mg, 1 mmol) in HMPA (0.35 mL, 2 mmol). This solution was added at −40°C to a three-necked flask containing 3-carbethoxyphenylmagnesium bromide prepared from ethyl 3-iodobenzoate (**1a**; 389 mg, 1.4 mmol) and *i*-PrMgBr (1.66 mL, 1.61 mmol of a 0.97 M solution in THF) prepared according to method A. After 1 h reaction time, the reaction mixture was worked up as described above and the crude residue was purified by flash-chromatography (ether:pentane 1:5) affording the desired product **3a** (177 mg, 72% yield) as a yellowish oil.

Analytical data of compounds (3a–p) of Table 1

3-(3-Carbethoxyphenyl)cyclohexanone (3a). ^1H NMR (300 MHz, $CDCl_3$): δ 1.42 (3H, t, J=7.1 Hz, CH_3), 1.64–1.89 (2H, m, CH_2), 2.02–2.11 (2H, m, CH_2), 2.30–2.48 (2H, m, CH_2), 2.49–2.62 (2H, m, CH_2), 2.98–3.14 (1H, m, CH), 4.35 (2H, q, J=7.1 Hz, CH_2). 7.36–7.45 (2H, m, ArH), 7.88–7.97 (2H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 14.1 (CH_3), 25.2 (CH_2), 32.3 (CH_2), 40.7 (CH_2), 44.2



Scheme 1.

(CH), 48.4 (CH_2), 60.7 (OCH_2), 127.4, 127.6, 128.4 (ArCH), 130.9 (ArC), 130.9 (ArCH), 144.5 (ArC), 166.1 (COOEt), 209.7 (CO). MS (EI): 246 (M^+), 200 (M^+-EtO), 131, 103. IR: ($CHCl_3$): 3514–2252 (ArCH),1720 (CO, COOEt); (cm^{-1}). Anal. Calcd For $C_{15}H_{18}O_3$: C 73.15, H 7.37. Found: C 73.20, H 7.32

3(3-Carbethoxyphenyl)cyclopentanone (3b). ^1H NMR (300 MHz, $CDCl_3$): δ 1.40 (3H, t, J=7.2 Hz, CH_3), 1.93–2.31 (1H, m, CH_2), 2.24–2.54 (4H, m, CH_2), 2.62–2.76 (1H, m, CH_2), 3.40–3.55 (1H, m, CH_2), 4.38 (2H, q, J=7.1 Hz, CH_2). 7.36–7.45 (2H, m, ArH), 7.88–7.97 (2H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 14.2 (CH_3), 31.0 (CH_2), 38.7 (CH), 41.9 (CH_2), 45.5 (CH_2), 60.9 (OCH_2), 127.7, 127.8, 127.9 (ArCH), 130.8 (ArC), 131.1 (ArCH), 143.3 (ArC), 166.3 (COOEt), 217.4 (CO). MS (EI): 232 (M^+), 186 (M^+-EtO), 131, 103. IR: ($CHCl_3$): 3522–2263 (ArCH),1725 (CO, COOEt); (cm^{-1}). Anal. Calcd For $C_{14}H_{16}O_3$: C 72.39, H 6.07. Found: C 72.12, H 6.34

Ethyl 3-(1,3-diphenyl-3-oxopropyl)benzoate (3c). ^1H NMR (300 MHz, $CDCl_3$): δ 1.34 (3H, t, J=7.1 Hz, CH_3), 3.76 (2H, d, J=5.5 Hz CH_2), 4.3 (2H, q, J=7.1 Hz, CH_2), 4.88 (1H, t, J=5.6 Hz, CH), 7.12–7.49 (10H, m, ArH), 7.90–7.98 (4H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 14.5 (CH_3), 44.7 (CH_2), 46.0 (CH), 61.1 (OCH_2), 126.8, 127.8, 128.0, 128.2, 128.8, 128.8, 128.9, 129.8 (ArCH), 131.0 (ArC), 132.8, 133.3 (ArCH), 137.2, 143.9, 144.7 (ArC), 166.7 (COOEt), 197.8 (CO). MS (EI): 358 (M^+), 312(M^+-EtO), 207 (312-COPh), 165, 105. IR: ($CHCl_3$): 2890–3010 (ArCH), 1790 (CO_2Et), 1705 (CO); (cm^{-1}). Anal. Calcd For $C_{24}H_{22}O_3$: C 80.42, H 6.19. Found: C 80.63, H 5.98

Ethyl 3-(3-oxobutyl)benzoate (3d). ^1H NMR (300 MHz, $CDCl_3$): δ 1.39 (3H, t, J=7.2 Hz, CH_3), 2.14 (3H, s, CH_3), 2.79 (2H, t, J=7.4 Hz, CH_2), 4.36 (2H, q, J=7.1 Hz, CH_2), 7.31–7.41 (2H, m, ArH), 7.80–7.90 (2H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 14.2 (CH_3), 29.3 (CH_3), 29.8 (CH_2), 44.6 (CH_2), 60.8 (CH_2), 127.2, 128.3, 129.1, 132.8 (ArCH), 130.6, 141.2 (ArC), 166.4 (COOEt), 207.1 (CO). MS (EI): 220 (M^+), 174 (M^+-EtO), 147 (M^+-CO_2Et), 131, 91. IR: ($CHCl_3$): 2890–3007 (ArCH), 1750 (CO_2Et, CO); (cm^{-1}). Anal. Calcd For $C_{13}H_{16}O_3$: C 70.88, H 7.32. Found: C 70.63, H 7.58.

Ethyl 2-(3-oxocycloheyl)benzoate (3e). ^1H NMR (300 MHz, $CDCl_3$): δ 1.30 (3H, t, J=7.1 Hz, CH_3), 1.74–1.79 (2H, m, CH_2), 2.00–2.10 (2H, m, CH_2), 2.37–2.51 (4H, m,CH_2), 3.77–3.81 (1H, m, CH), 4.27 (2H, q, J=7.1 Hz, CH_2), 7.20–7.42 (3H, m, ArH), 7.73 (1H, dd, J=8.7 and 1.4 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 14.2 (CH_3), 25.4 (CH_2), 32.7 (CH_2), 40.1 (CH), 41.1 (CH_2), 48.4 (CH_2), 61.0 (CH), 126.2, 126.4 (ArCH), 130.1 (ArC), 130.3, 131.8 (ArCH), 144.8 (ArC), 167.7 (COOEt), 210.6 (CO). MS (EI): 246 (M^+), 200 (M^+-EtO), 172 (200-CO), 144. IR: ($CHCl_3$): 2895–3000 (ArCH),1730 (CO, CO_2Et); (cm^{-1}). Anal. Calcd For $C_{15}H_{18}O_3$: C 73.15, H 7.37. Found: C 73.25, H 7.27.

Ethyl 2-(3-oxocyclopentyl)benzoate (3f). ^1H NMR (300 MHz, $CDCl_3$): δ 1.39 (3H, t, J=7.0 Hz, CH_3), 1.99–2.32 (1H, m, CH_2), 2.33–2.41 (4H, m, CH_2), 2.66–2.73 (1H, m, CH_2), 4.24–4.31 (1H, m, CH), 4.37 (2H, q, J=7.1 Hz, CH_2), 7.28–7.46 (3H, m, ArH), 7.85 (1H, dd, J=7.8 and 1.4 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 14.1 (CH_3), 30.8 (CH_2), 38.3 (CH), 38.5 (CH_2), 45.7 (CH), 60.9 (OCH_2), 126.0, 126.2, 130.3 (ArCH), 130.5 (ArC), 131.9 (ArCH), 143.7 (ArC), 167.6 (COOEt), 218.0 (CO). MS (EI): 232 (M^+), 186 (M^+-EtO), 133, 105. IR: ($CHCl_3$): 3530–2270 (ArCH),1715 (CO, COOEt); (cm^{-1}). Anal. Calcd For $C_{14}H_{16}O_3$: C 72.39, H 6.07. Found: C 72.54, H 5.92.

Ethyl 2-(1,3-diphenyl-3-oxopropyl)benzoate (3g). ^1H NMR (300 MHz, $CDCl_3$): δ 1.37 (3H, t, J=7.1 Hz, CH_3), 3.73 (2H, d, J=5.6 Hz CH_2), 4.35 (2H, q, J=7.1 Hz, CH_2), 4.91 (1H, t, J=5.6 Hz CH), 7.16–7.52 (10H, m, ArH), 7.87–7.99 (4H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 14.2 (CH_3), 41.1 (CH), 44.8 (CH_2), 61.1 (OCH_2), 126.0, 126.2, 127.6, 127.8, 128.0, 128.3, 128.5, 128.6, (ArCH), 130.1 (ArC), 131.5, 132.9 (ArCH), 136.9, 143.5, 144.8 (ArC), 167.9 (COOEt), 197.5 (CO). MS (EI): 358 (M^+), 312(M^+-EtO),225, 207 (312-COPh), 197. IR: ($CHCl_3$): 2895–3000 (ArCH), 1730 (CO_2Et), 1700 (CO); (cm^{-1}). Anal. Calcd For $C_{24}H_{22}O_3$: C 80.42, H 6.19. Found: C 80.63, H 5.98

Ethyl 2-(3-oxobutyl)benzoate (3h). ^1H NMR (300 MHz, $CDCl_3$): δ 1.29 (3H, t, J=7.1 Hz, CH_3), 2.05 (3H, s, CH_3), 2.68 (2H, t, J=5.0 Hz, CH_2), 5.01 (2H, t, J=7.1 Hz, CH_2), 4.26 (2H, q, J=7.1 Hz, CH_2), 7.14–7.19 (2H, m, ArH), 7.30–7.35 (1H, m, ArH), 7.81 (1H, dd, J=7.3 and 1.5 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 14.2 (CH_3), 27.2 (CH_3), 28.8 (CH_2), 29.7 (CH_2), 45.3 (CH), 60.8 (CH_2), 126.5, 130.7, 131.1, 132.0 (ArCH), 134.0, 142.8 (ArC), 167.3 (COOEt), 207.8 (CO). MS (EI): 220 (M^+), 174 (M^+-EtO), 147 (M^+-CO_2Et), 131, 91. IR: ($CHCl_3$): 2895–3010 (ArCH), 1735 (CO_2Et, CO); (cm^{-1}). Anal. Calcd For $C_{13}H_{16}O_3$: C 70.88, H 7.32. Found: C 70.97, H 7.23.

***N*,*N*-Dibenzyl 4-(3-oxocyclohexyl)benzamide (3i).** ^1H NMR (300 MHz, $CDCl_3$): δ 1.59–1.65 (2H, m, CH_2), 1.86–1.93 (2H, m, CH_2), 2.22–2.26 (2H, m,CH_2), 2.33–2.39 (2H, m,CH_2), 2.75–2.97 (1H, m, CH), 4.29 (2H, s,CH_2Ph), 4.56 (2H, s,CH_2Ph), 6.89–7.88 (12H, m, ArH), 7.35 (2H, d, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 24.8 (CH_2), 32.0 (CH_2), 40.5 (CH_2), 43.9 (CH), 46.4 (CH_2Ph), 48.0 (CH_2), 51.1 (CH_2Ph), 126.3, 126.4, 126.7 (ArCH), 127.0, 127.8, 128.2 (ArCH), 134.0, 135.9, 136.4, 145.5 (ArC), 171.4 ($CON(CH_2Ph)_2$), 209.7 (CO). MS (EI): 397 (M^+), 306 (M^+-91), 231 (M^+-NBn_2), 91. IR: ($CHCl_3$): 2890–2990 (ArCH), 1720 ($CONBn_2$), 1640 (CO); (cm^{-1}). Anal. Calcd For $C_{27}H_{27}NO_2$: C 81.58, H 6.85. Found: C 81.71, H 6.72.

***N*,*N*-Dibenzyl 4(3-oxocyclopentyl)benzamide (3j).** ^1H NMR (300 MHz, $CDCl_3$): δ 2.17–2.33 (1H, m, CH_2), 2.49–2.78 (4H, m, CH_2), 2.87–2.99 (1H, m,CH_2), 3.61–3.78 (1H, m, CH), 4.71 (2H, s, CH_2Ph), 4.99 (2H, s,CH_2Ph), 7.40–7.68 (12H, m, ArH), 7.79 (2H, d, J=8.05 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 30.8 (CH_2), 38.5 (CH_2), 41.8 (CH), 45.3 (CH_2), 46.8 (CH_2Ph), 51.4 (CH_2Ph), 126.8, 127.0, 127.4, 127.8, 127.9, 128.2, 128.6 (ArCH), 134.4, 136.3, 136.7, 144.7 (ArC), 171.8

(CON($CH_2Ph)_2$), 217.4 (CO). MS (EI): 383 (M^+), 292 (M^+-91), 187 (M^+-NBn_2), 91. IR: ($CHCl_3$): 2895–3000 (ArCH), 1715 ($CONBn_2$), 1670 (CO); (cm^{-1}). Anal. Calcd For $C_{26}H_{25}NO_2$: C 81.43, H 6.57. Found: C 81.61, H 6.39.

***N*,*N*-Dibenzyl 4-(1,3-diphenyl-3-oxopropyl)benzamide (3k).** ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.71 (2H, d, *J*=7.4 Hz, CH_2), 4.39 (2H, s,CH_2Ph), 4.65 (2H, s,CH_2Ph), 4.85 (1H, t, *J*=6.4 Hz, CH), 7.05–7.55 (12H, m, ArH), 7.81 (2H, d, *J*=8.1 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 44.3 (CH_2), 45.6 (CH), 46.8 (CH_2Ph), 51.5 (CH_2Ph), 126.5, 126.6, 126.8, 126.9, 127.1, 127.3, 127.4, 127.7, 127.9, 128.0 (ArCH), 129.6 (ArC), 133.1 (ArCH), 133.9, 136.3, 143.4, 145.9 (ArC), 171.9 (CON($CH_2Ph)_2$), 197.5 (CO). MS (EI): 509 (M^+), 418 (M^+-91), 313 (M^+-NBn_2), 298, 91. IR: ($CHCl_3$): 2890–3000 (ArCH), 1722 ($CONBn_2$), 1674 (CO); (cm^{-1}). Anal. Calcd For $C_{26}H_{25}NO_2$: C 84.84, H 6.13. Found: C 84.79, H 6.18.

***N*,*N*-Dibenzyl 4-(3-oxobutyl)benzamide (3l).** ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.12 (3H, s, CH_3), 2.75 (2H, dd, *J*=10 and 3 Hz, $2CH_2$), 2.87 (2H, dd, *J*=10 Hz, *J*=3 Hz, $2CH_2$), 4.45 (2H, s, CH_2Ph), 4.70 (2H, s, CH_2Ph), 7.05–7.62 (14H, m, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 29.2(CH_2), 29.5 (CH_3), 44.6 (CH_2), 47.0 (CH_2Ph), 51.4 (CH_2Ph), 126.9, 127.4, 127.8, 128.0, 128.3 (ArCH) 129.1, 133.7, 142.8 (ArC), 172.1 (CON(CH_2Ph)2), 207.3 (CO). MS (EI): 371 (M^+), 280 (M^+-91), 175 (M^+-NBz2), 91. IR: ($CHCl_3$): 2880–2990 (ArCH), 1721 ($CONBn_2$), 1669 (CO); (cm^{-1}). Anal. Calcd For $C_{25}H_{25}NO_2$: C 80.83, H 6.78. Found: C 80.91, H 6.70.

4-(3-Oxocyclohexyl)benzonitrile (3m). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.65–1.89 (2H, m, CH_2), 1.98–2.20 (2H, m, CH_2), 2.29–2.61 (4H, m,CH_2), 2.95–3.15 (1H, m, CH), 7.30 (2H, d, *J*=7.5 Hz, ArH), 7.60 (2H, d, *J*=7.5 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 25.1 (CH_2), 32.1 (CH_2), 40.8 (CH_2), 44.4 (CH), 48.0 (CH_2), 110.4 (CN), 118.1 (ArC), 127.3, 132.4 (ArCH), 149.4 (ArC), 209.5 (CO). MS (EI): 199 (M^+), 170(M^+-29), 103, 89. IR: ($CHCl_3$): 2890–2990 (ArCH), 2220 (CN), 1715 (CO); (cm^{-1}). Anal. Calcd For $C_{13}H_{13}NO$: C 78.36, H 6.58. Found: C 78.45, H 6.41

4-(3-Oxocyclopentyl)benzonitrile (3n). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.81–2.05 (1H, m, CH_2), 2.18–2.73 (5H, m, CH_2), 3.31–3.52 (1H, m, CH), 7.35 (2H, d, *J*=7.2 Hz, ArH), 7.61 (2H, d, *J*=7.2 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 30.7 (CH_2), 38.5 (CH_2), 42.1 (CH), 45.1 (CH_2), 110.4 (CN), 118.6 (ArC), 127.5, 132.4 (ArCH), 148.4 (ArC), 216.8 (CO). MS (EI): 185 (M^+), 156 (M^+-29), 129, 103. IR: ($CHCl_3$): 2890–2990 (ArCH), 2215 (CN), 1722 (CO); (cm^{-1}). Anal. Calcd For $C_{13}H_{13}NO$: C 77.81, H 5.99. Found: C 77.96, H 5.84.

4-(1,3-Diphenyl-3-oxopropyl)benzonitrile (3o). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.67 (2H, d, *J*=7.5 Hz, CH_2), 4.90 (1H, t, *J*=7.2 Hz, CH), 7.05–7.55 (12H, m, ArH),7.63 (2H, d, *J*=7.8 Hz, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 44.4 (CH_2), 45.6 (CH), 109.9 (CN), 118.2 (ArC), 127.4, 132.7 (ArCH), 148.5 (ArC), 198.7 (CO). MS (EI): 311 (M^+), 282 (M^+-29), 220(M^+-91), 103, 89. IR: ($CHCl_3$): 2890–2990 (ArCH), 2218 (CN), 1689 (CO); (cm^{-1}). Anal. Calcd For $C_{22}H_{17}NO$: C 84.86, H 5.50. Found: C 84.74, H 5.62.

4-(3-Oxobutyl)benzonitrile (3p). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.12 (3H, s, CH_3), 2.75 (2H, dd, *J*=9.7 and 2.6 Hz, CH_2), 2.87 (2H, dd, *J*=9.7 and 2.6 Hz, CH_2), 7.25 (2H, d, ArH), 7.50 (2H, d, ArH). ^{13}C NMR (75 MHz, $CDCl_3$): 29.3 (CH_2), 29.8 (CH_3), 43.9 (CH_2), 109.6 (CN), 118.7 (ArC), 129.0, 132.0 (ArCH), 146.6 (ArC), 206.6 (CO). MS (EI): 173 (M^+), 158 (M^+-15), 130(M^+-COMe), 103. IR: ($CHCl_3$): 2890–2990 (ArCH), 2215 (CN), 1720 (CO); (cm^{-1}). Anal. Calcd For $C_{11}H_{11}NO$: C 76.28, H 6.40. Found: C 76.34, H 6.34.

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