Supporting Information

Ultra-Fast Chemistry: Cobalt Carbonyl-Mediated Synthesis of Diaryl Ketones under Microwave Irradiation

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Experimental Section

General: All microwave reactions were conducted in heavy-walled glass tubes (Smith process vials) sealed with aluminum crimp caps fitted with a silicon septum. The microwave heating was performed in a SmithSynthesizer™ single mode cavity, producing continuous irradiation at 2450 MHz. Reaction mixtures were stirred with a magnetic stirring bar during the irradiation. Reaction temperature and pressure were determined using the build-in, on-line IR- and pressure sensors. After completed irradiation, the reaction tube was cooled with high-pressure air until the temperature had fallen below 38 °C. ^{1}H NMR and ^{13}C NMR were recorded with $CDCl_3$ as solvent on a 400 spectrometer. Flash column chromatography was performed on Merck silica gel 60, 0.04-0.063 mm. Thin-layer chromatography was performed using aluminum sheets precoated with silica gel 60 F_{254} (0.2 mm; E. Merck) and visualized with UV light. Mass spectra were recorded on a GC-MS, equipped with a CP-Sil 8 CB-MS (30 m × 0.25 mm) capillary column, utilizing electron impact (EI) at an ionizing energy of 70 eV.

To avoid dangerous over pressurization, sealed reactions should always be performed in dedicated equipment.

General Method for Synthesis of Diaryl Ketones from Aryl Iodides: The aryl iodide (0.60 mmol), $Co_2(CO)_8$ (0.40 mmol, 137 mg), 2,3-dimethylnaphthalene (0.15 mmol, 23 mg) as internal standard and 2.5 mL of dry acetonitrile were mixed in a septum capped tube (a Smith process vial). The microwave synthesizer was set to 250 °C, and the time to 10 s. After 10 s the temperature was ca 130 °C. After cooling the reaction mixture were filtered through celite, concentrated and purified with silica chromatography.

Products **2a**, **2c**, **2e** and **2g** are commercially available. Compounds, **2d**,[1] **2f**,[2,3] **2h**[4] and **2i**[5] are all known compounds (with reported elemental analysis). Spectral data were in agreement with the proposed structures. Although **2b**[6] is a known compound we were unable to find NMR characterizations. For compound **2j**[7,8] we did not find adequate ^{13}C or ^{1}H NMR characterizations. Lacking elementary analysis and spectral data are complemented.

Bis-(4-methoxyphenyl)-methanone (2a) was obtained in 57% yield (41 mg) as white crystals after purification with silica column (eluent: isohexane:dichloromethane, 1:1).

Bis-(2,3,5,6-tetramethylphenyl)-methanone (2b)[6] was obtained in 60% yield (53 mg) as white crystals after purification with silica column (eluent: pure isohexane followed by isohexane:ethylacetate, 10:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.04 (s, 12H), 2.21 (s, 12H), 7.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 16.8, 20.3, 132.4, 133.5, 134.7, 205.0.

Di-*o*-tolylmethanone (2c) was obtained in 91% yield (58 mg) as a yellowish oil after purification with silica column (eluent: isohexane:ethylacetate, 1:1).

Di-thiophen-3-yl-methanone (2d)[1] was obtained in 96% yield (56 mg) as white crystals after purification with silica column (eluent: isohexane:ethylacetate, 10:1).

Benzophenone (2e) was obtained in 78% yield (43 mg) as a yellowish oil after purification with silica column (eluent: isohexane:dichloromethane, 1:1).

Di-naphthalene-1-yl-methanone (2f)[2,3] was obtained in 97% yield (70 mg) as a yellowish oil after purification with silica column (eluent: isohexane:dichloromethane, 1:1).

Bis-(4-chlorophenyl)-methanone (2g) was obtained in 87% yield (66 mg) as white crystals after purification with silica column (eluent: isohexane).

Bis-(4-trifluoromethylphenyl)-methanone (2h)[4] was obtained in 97% yield (102 mg) as white crystals after

purification with silica column (eluent: isohexane: dichloromethane, 3:2).

1-[4-(4-Acetylbenzoyl)-phenyl]-ethanone (2i)[5] was obtained in 91% yield (73 mg) as white crystals after purification with silica column (eluent: isohexane: ethylacetate, 2:1).

4-(4-Cyanobenzoyl)-benzonitrile (2j)[7,8] was obtained in 88% yield (62 mg) as white crystals after purification with silica column (eluent: isohexane:ethylacetate, 5:1). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (AA´ part of AA´XX´, 2H) 7.88 (XX´ part of AA´XX´, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.6, 117.8, 130.4, 132.6, 139.8, 193.6.

Methods for Synthesis of Diaryl Ketones from Aryl Bromides:

Benzophenone (2e): Bromobenzene (0.60 mmol, 94 mg), $Co_2(CO)_8$ (0.50 mmol, 171 mg) and 2.5 mL of dry acetonitrile were mixed in a Smith process vial and irradiated for 30 min at 120 °C. After cooling the reaction mixture was filtered through celite, concentrated and purified with silica chromatography (eluent: isohexane:dichloromethane, 1:1). **2e** was obtained in 64% yield (37.5 mg) as a yellowish oil after purification with silica column (eluent: isohexane:dichloromethane, 1:1).

1-[4-(4-Acetylbenzoyl)-phenyl]-ethanone (2i): 4´-Bromoacetophenone (0.40 mmol, 80 mg), $Co_2(CO)_8$ (0.26 mmol, 90 mg) and 2.5 mL of dry acetonitrile were mixed in a Smith process vial and irradiated for 30 s at 130 °C. After cooling the reaction mixture was filtered through celite, concentrated and purified with silica chromatography (eluent: isohexane:ethylacetate, 2:1). **2i** was obtained in 43% yield (23 mg) as white crystals after purification with silica column (eluent: isohexane: ethylacetate, 2:1).

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