DOI: 10.1002/chem.200800001

A General Synthesis of Diarylketones by Means of a Three-Component Cross-Coupling of Aryl and Heteroaryl Bromides, Carbon Monoxide, and Boronic acids

Helfried Neumann, Anne Brennführer, and Matthias Beller*[a]

Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

Abstract: $Pd(OAc)_2$/di-1-adamantyl-*n*-butylphosphine (cata*CX*ium A) is highly active in the three-component Suzuki carbonylation and represents the most general catalyst system reported up to now. A broad range of aryl/heteroaryl bromides and aryl boronic acids can be coupled to the corresponding diarylketones at low catalyst loadings.

Keywords: carbon monoxide · diarylketones · homogeneous catalysis · palladium · three-component reactions

Introduction

Diarylketones constitute an interesting and versatile structural motif[1] which is frequently present in natural products (e.g. Cotoin, Papaveraldine), in non-steroidal anti-inflammatory drugs (e.g. Suprofen, Ketoprofen), and occurs in UV screens (e.g. Sulisobenzone, Oxybenzone). Typically, diarylketones are prepared by Friedel–Crafts acylation of *ortho*/*para*-directing arenes with acyl halides.[2] Unfortunately, this reaction requires overstoichiometric amounts of Lewis acid and the regioselectivity is often limited to the *para*-position. Other synthetic strategies use cross-coupling reactions of benzoic halides with organotin compounds,[3] palladium-catalyzed coupling of boronic acids with carboxylic anhydride,[4] or nickel-catalyzed coupling reactions of aryl iodides with aromatic aldehydes.[5] An especially versatile approach for the synthesis of diarylketones[6] is the transition-metal-catalyzed three-component cross-coupling of Aryl-X (X = Br, I, OTf, N_2^+) derivatives, carbon monoxide, and arylmetal reagents. However, the coupling reaction of organoaluminium,[7] organosilane,[8] or organotin[9] compounds with electron-poor aryl halides is severely limited due to the formation of biaryl side products. Here, electron-withdrawing groups on the aryl ring accelerate the rate of transmetallation to form the Ar–Pd–Ar intermediate and hinder the insertion of carbon monoxide into the Ar–Pd–X species. In 1993, Suzuki et al. introduced the coupling of aryl boronic acids with aryl iodides in the synthesis of diarylketones (Suzuki carbonylation).[10] In principle, these reactions provide a versatile tool for organic synthesis as boronic acids are generally nontoxic and thermally, air, and moisture stable. However, the selectivity of the coupling reaction drops when aryl bromides are used. Although Suzuki et al. later improved the cross-coupling for aryl triflates and aryl bromides by using $PdCl_2$ and 1,1′-bis(diphenylphosphino)-ferrocene as a catalyst, still three equivalents of NaI or KI were required as an additive.[11]

Until now, relatively few palladium-mediated catalyst systems have been applied to the carbonylative Suzuki reaction, and limitations of the protocols still remain. Castanet et al.[12] introduced a catalyst system ($[PdCl_2(PCy_3)_2]$) which is applicable for carbonylative cross-coupling of pyridyl halides with phenyl boronic acid in the presence of carbon monoxide. Pd/thiourea catalysts with a phosphine-free ligand[13] only promote the Suzuki carbonylation of aryl iodides. More recently, $[Pd(PPh_3)_4]$ has been applied to aryl triflates, but again additional halide salts are needed.[14] To the best of our knowledge, there is no general method for the synthesis of diaryl and aryl heteroaryl ketones by means of a Suzuki-type carbonylative cross-coupling reaction.

Some years ago, we introduced Pd/diadamantylalkylphosphine catalysts for coupling reactions. The most powerful system is based on Pd/diadamantyl-*n*-butylphosphine (cata*CX*ium A), which is active in Heck,[15] Suzuki,[16] and Sonogashira coupling reactions,[17] amination of aryl chlorides,[18] as well as α-arylation of ketones with chloro-

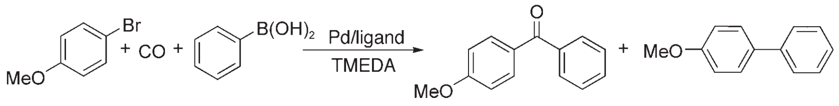
---

[a] Dr. H. Neumann, A. Brennführer, Prof. Dr. M. Beller
Leibniz-Institut für Katalyse an der Universität Rostock e.V.
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)
Fax: (+49) 381-1281-5000
E-mail: matthias.beller@catalysis.de

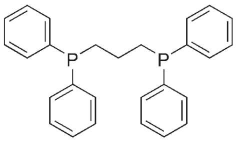
arenes.[19] More recently, we successfully employed this catalyst system in reductive carbonylations[20] and alkoxycarbonylations[21] of aryl and heteroaryl bromides. Encouraged by these results and in order to overcome the limitations of known procedures, we started to look at the palladium-catalyzed Suzuki carbonylation. Herein, we describe our investigations which led to a convenient and general method to synthesize all kinds of symmetrical and unsymmetrical diarylketones.

Results and Discussion

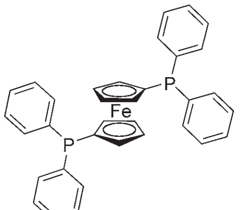
As a starting point the reaction of 4-bromoanisole with phenyl boronic acid (1.5 equiv) in the presence of carbon monoxide was investigated (Scheme 1). The experiments on the model system were carried out in a modified six-fold parallel autoclave (reaction volume 4 mL) under 5 bar CO at 100 °C. Comparably low catalyst loading (0.5 mol% $Pd(OAc)_2$) and a three-fold excess of ligand (P/Pd 3:1) were used. Initially, we tested the activity of 12 different phosphine and carbene ligands. The results of the ligand screening are shown in Table 1.



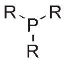
Scheme 1. Carbonylative Suzuki reaction of the model substrate.



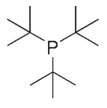
1



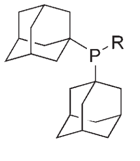
2



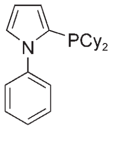
3a: R=Ph
3b: R=*o*Tol
3c: R=Cy



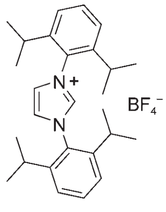
4



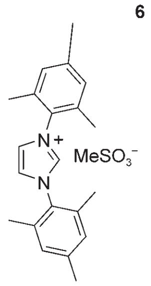
5a: R=*n*Bu
5b: R=Bn
5c: R=H



6



7



8

Table 1. Screening of various ligands for the model reaction.

Entry	Ligand	Ligand [mol%]	Conversion [%][a]	Diaryl ketone [%][a]	Biaryl [%][a]	Selectivity [%][a]
1	**1**	0.75	20	2	0	12
2	**2**	0.75	12	10	0	87
3	**3a**	1.5	6	6	0	92
4	**3b**	1.5	1	0	0	0
5	**3c**	1.5	12	11	0	90
6	**4**	1.5	87	13	1	15
7	**5a**	**1.5**	**99**	**51**	**5**	**54**
8	**5b**	1.5	92	41	13	44
9	**5c**	1.5	21	18	0	86
10	**6**	1.5	26	7	0	27
11	**7**	1.5	1.5	0	0	0
12	**8**	1.5	1.5	0	0	0

Reaction conditions: 4-bromoanisole (2 mmol), $PhB(OH)_2$ (3 mmol), $Pd(OAc)_2$ (0.5 mol%), TMEDA (1 equiv), toluene (2 mL), hexadecane (0.2 equiv), 5 bar CO, 100 °C, 24 h. [a] Determined by gas chromatography.

Chelating ligands 1,3-bis(diphenylphosphino)propane (dppp, **1**) and 1,1′-bis(diphenylphosphino)ferrocene (dppf, **2**), which are used in alkoxycarbonylation of aryl halides,[22] gave only a low conversion (12–20%) and yield (2–10%) of the desired product (Table 1, entries 1–2). Also a number of standard monodentate phosphines (**3a**–**c**) yielded 4-methoxybenzophenone in low amounts (0–11%, Table 1, entries 3–5). In contrast, adamantylphosphines **5a** (cata*CX*ium A), and **5b** afforded the target compound in 41–54% yield and the undesired biaryl side product was obtained in only 5–13% yield, respectively (Table 1, entries 7–8). Interestingly, when we used the sterically and electronically comparable tri-*tert*-butylphosphine **4**, we observed high conversion (87%), but only low selectivity (13% yield) (Table 1, entry 6). Dialkyl heteroaryl phosphines were significantly less active or nearly inactive for the desired reaction (Table 1, entries 10–12).

Based on the promising results, we studied the influence of pressure and base in the model carbonylation in the presence of **5a** more carefully. As shown in Table 2, carbonylative cross-coupling in the presence of solid bases, for example, K_2CO_3, K_3PO_4, or NaOEt, gave low selectivity and yields of the desired product (3–20%, entries 1–3). Applying trialkylamines showed that a proper choice of the CO pressure is crucial for yield and chemoselectivity. Interestingly, $EtN(iPr)_2$ and NEt_3 provided an increased product yield at higher CO pressure than at low pressure (5 bar, 55–88% versus 2.5 bar, 23–66%, Table 2, entries 4–7). In contrast, the unwanted Suzuki coupling product is formed predominantly at low CO pressure (5 bar, 2–7% versus 2.5 bar, 34–35%). This behavior is not surprising as transmetallation of the Ar–Pd–X intermediate is suppressed by a higher CO pressure. Therefore, the yield of the desired diarylketone is increased. In contrast, TMEDA (TMEDA: *N,N,N′,N′*-tetramethylethylenediamine) yielded more product at 2.5 bar CO

(60%) than at 5 bar CO (51%) while the amount of by-product is low (6–7%) in each case (Table 2, entries 8–9).

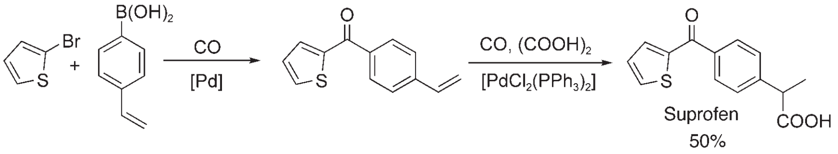
Next, we explored the generality of our catalyst system (Pd/cata*CX*ium A) by reacting different aryl and heteroaryl bromides with aryl boronic acids in the presence of CO. Table 3 shows that both electron-rich and -poor aryl bromides and aryl boronic acids were successfully converted by means of a carbonylative cross-coupling reaction. Notably, for aryl bromides with electron-withdrawing substituents, which are known to support direct coupling to give biaryls, an increased CO pressure of 5 bar often led to better results. As an example, reaction of 4-bromobenzotrifluoride with different boronic acids gave selectively (>99%) the diarylketones as a single product (Table 3, entries 3–5). Experiments using 4-chlorobromobenzene, 3-bromopyridine, and 2- and 4-bromobenzonitrile provided the diarylketone/biaryl in 70/7, 64/4, 60/39, and 89/10% yields, respectively (Table 3, entries 21, 25–27). When electron-rich and electron-neutral aryl bromides were employed, the coupling-reaction proceeded with good yields and in almost every case no biaryl side products were observed (Table 3, entries 1, 2, 6, 9, 22–24, and 28). From a synthetic viewpoint, it is important to note that various combinations of heteroaryl bromides with heteroaryl boronic acids can be coupled efficiently by our catalyst system. Hence, a carbonylative Suzuki reaction of 3-bromobenzothiophene, 3-bromothiophene, and 3-bromopyridine[23] with 3-thiophene boronic acid resulted in diarylketone/biaryl in 81/11, 59/0, and 60/25% yields, respectively (Table 3, entries 13, 17, and 20).

Table 2. Influence of different bases on the yield of 4-methoxybenzophenone.

Entry	Base	p [bar]	Conversion [%][a]	Diaryl ketone [%][a]	Biaryl [%][a]	Selectivity [%][a]
1	K_2CO_3	5.0	52	20	33	38
2	K_3PO_4	5.0	61	19	43	31
3	NaOEt	5.0	94	3	65	4
4	NEt_3	5.0	94	88	2	94
5		2.5	99	66	35	67
6	EtN(*i*Pr)$_2$	5.0	92	55	7	60
7		2.5	69	23	34	33
8	TMEDA	5.0	98	51	6	60
9		2.5	93	60	7	76
10	pyridine	5.0	7	0	0	0
11		2.5	9	1	0	11

Reaction conditions: 4-bromoanisole (2 mmol), $PhB(OH)_2$ (3 mmol), $Pd(OAc)_2$ (0.5 mol%), cata*CX*ium A (1.5 mol%), base (2 equiv), toluene (2 mL), hexadecane (0.2 equiv), 2.5–5.0 bar CO, 100°C, 24 h. [a] Determined by gas chromatography.

When NEt_3 was used as the base, in general the Suzuki carbonylation occurred with lower selectivity with the exception that the symmetrical bis(3-thienyl) ketone was obtained in 67% yield (Table 3, entry 18). Remarkable examples for the high selectivity of the catalyst are the cross-coupling reactions of 4-vinylphenylboronic acid. Despite the possibility of a competitive Heck-, Suzuki-, and carbonylative Heck reaction, these couplings proceeded with excellent selectivity. Thus, 4-bromobenzotrifluoride, 4-bromoanisole, and 2- and 3-bromothiophene reacted with 4-vinylphenylboronic acid in the presence of CO to give exclusively the desired diarylketones in 80, 73, 63, and 65% yields, respectively (Table 3, entries 8–9 and 11–12). The resulting diarylketones are interesting substrates for further refinement towards pharmaceuticals. Hence, 4-vinylphenyl 2-thienyl ketone (Table 3, entry 12) is easily hydroxycarbonylated[24] in one step to Suprofen, a commercial nonsteroidal anti-inflammatory drug (Scheme 2).



Scheme 2. Synthesis of Suprofen.

Conclusion

We have developed a general and efficient synthesis of diaryl-, diheteroaryl-, and aryl heteroaryl ketones by a three-component cross-coupling reaction of aryl/heteroaryl bromides, aryl boronic acids, and carbon monoxide. This reaction offers efficient access to various biologically active compounds as shown by the two-step preparation of Suprofen. Remarkable features of our catalyst are the high selectivity and the improved productivity. Furthermore the system is easily handled (air-stable).

Experimental Section

General information: Toluene was destilled from sodium and benzophenone. All reactions were performed by using standard Schlenk techniques (argon). ^1H and ^{13}C NMR spectra were recorded on a Bruker AV 300/AV 400 spectrometer at 25°C. Chemical shifts (δ) are given in ppm and refer to the residual undeuterated solvent as the internal standard ([D$_6$]DMSO: $\delta = 2.50/39.7$ ppm). Gas chromatography was performed on a Hewlett–Packard HP 6890 chromatograph with a HP5 column. Chemicals were purchased from Fluka, Aldrich, Strem and used as received. The cata*CX*ium A ligand is available from Strem or directly from Evonik Degussa.

General procedure for the 6-fold parallel autoclave: A 50 mL Schlenk flask was charged with $Pd(OAc)_2$ (22.5 mg, 0.5 mol%), cata*CX*ium A (108 mg, 1.5 mol%) and toluene (20 mL). Subsequently, hexadecane (1.17 mL, internal GC standard) and TMEDA (2.25 mL, 15 mmol) were added. This clear-yellow stock solution (2.34 mL) was transferred to six vials (4 mL reaction volume) equipped with a septum, a small cannula, a stirring bar, 2 mmol of the corresponding aryl bromide, and 3 mmol of the corresponding boronic acid. The vials were placed in an alloy plate, which was transferred to a 300 mL autoclave of the 4560 series from Parr Instruments under an argon atmosphere. After flushing the autoclave

Table 3. Scope and limitations of the carbonylative Suzuki reaction.

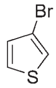
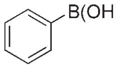
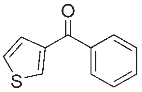
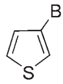
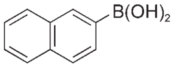
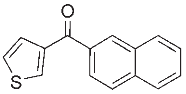
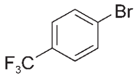
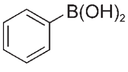
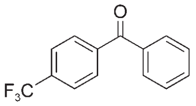
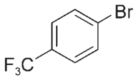
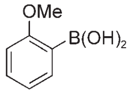
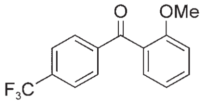
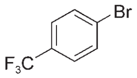
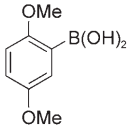
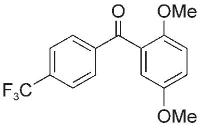
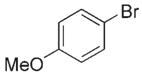
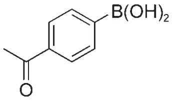
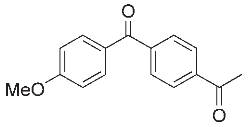
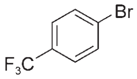
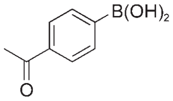
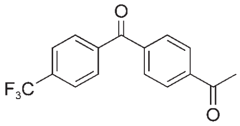
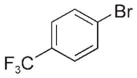
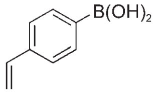
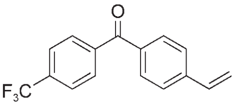
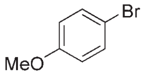
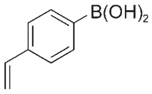
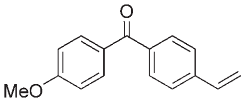
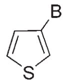
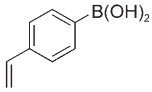
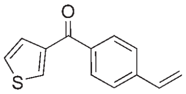
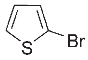
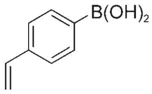
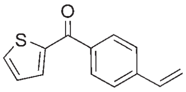
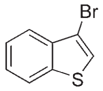
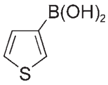
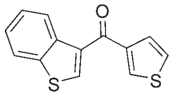
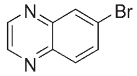
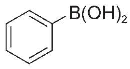
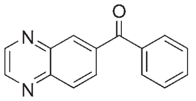
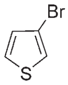
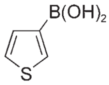
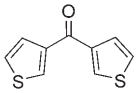
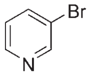
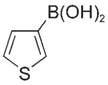
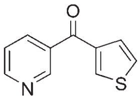
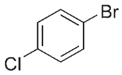
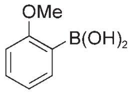
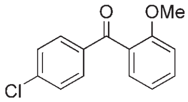
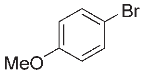
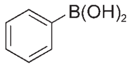
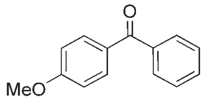
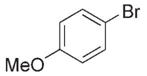
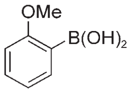
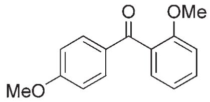
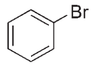
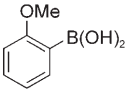
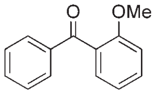
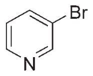
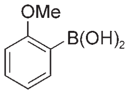
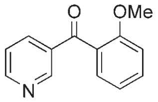
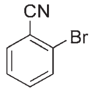
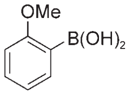
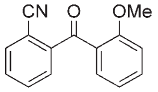
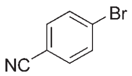
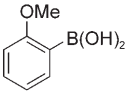
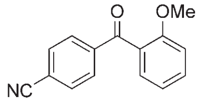
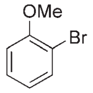
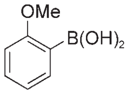
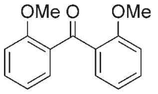
Entry	Aryl bromide	Boronic acid	*T* [°C]	CO [bar]	Ketone	Yield [%]	Biaryl [%]
1			100	5.0		70	0
2			100	5.0		63	0
3			100	5.0		79	0
4			100	5.0		73	0
5			100	5.0		81	0
6[a]			100	2.5		65	0
7[a]			80	2.5		65	3
8[a]			80	2.5		80	0
9[a]			100	2.5		73	0
10[a],[b]			100	5.0		43	35
11[a]			100	2.5		63	0
12[a]			80	2.5		65	0
13[a]			80	2.5		81	11
14[a],[b]			100	5.0		26	84
15[a]			80	2.5		75	10
16[a],[b]			100	5.0		28	62
17[a]			100	2.5		59	0
18[a],[b]			110	5.0		67	0
19[a]			100	5.0		45	30
20[a]			120	10		60	25
21			100	5.0		70	7

Table 3. (Continued)

Entry	Aryl bromide	Boronic acid	T [°C]	CO [bar]	Ketone	Yield [%]	Biaryl [%]
22[a]			100	2.5		60	0
23			100	5.0		74	0
24			100	5.0		73	0
25			100	5.0		64	4
26[a]			100	5.0		60	39
27[a]			100	5.0		89	10
28[a]			100	5.0		64	0

Reaction conditions: aryl bromide (2 mmol), aryl boronic acid (3 mmol), Pd(OAc)$_2$ (0.5 mol%), cata*CX*ium A (1.5 mol%), TMEDA (1 equiv), toluene (2 mL), hexadecane (0.2 equiv), 2.5–5.0 bar CO, 80°C–120°C, 24 h. [a] Yield determined by gas chromatography. [b] NEt$_3$ (2 equiv) is used as the base.

three times with carbon monoxide a pressure of 2.5 to 5 bar, the carbon monoxide was adjusted at ambient temperature and the reaction was performed for 24 h at 80–100°C. Before and after the reaction, an aliquot of the reaction mixture was subjected to GC analysis for determination of yield and conversion.

Phenyl thiophen-3-yl methanone: Colorless oil; yield 70%; $R_f = 0.11$ (EtOAc/heptane 0.25:10); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta = 8.22$ (dd, $J = 2.8$, 1.3 Hz, 1H), 7.82–7.79 (m, 2H), 7.72 (dd, $J = 4.9$, 2.8 Hz, 1H), 7.70–7.64 (m, 1H), 7.59–7.52 ppm (m, 3H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 189.3$ (C=O), 140.6, 138.3, 135.5 (CH), 132.6 (CH), 129.2 (CH), 128.8 (CH), 128.2 (CH), 127.8 ppm (CH); IR (KBr): $\tilde{\nu} = 3106$ (m), 2927 (w), 1650 (vs, C=O), 1598 (s), 1577 (m), 1510 (vs), 1446 (s), 1410 (vs), 1388 (s), 1307 (m), 1277 (vs), 1178 (m), 1138 (m), 1075 (m), 1028 (w), 1001 (w), 969 (m), 859 (vs), 821 (s), 781 (s), 718 (vs), 672 cm^{-1} (s); MS (70 eV): m/z (%): 188 (100) [M^+], 160 (6), 111 (93), 105 (31), 83 (14), 77 (40), 51 (21); elemental analysis calcd (%) for $C_{11}H_8OS$: C 70.18, H 4.28, S 17.03; found: C 70.20, H 4.39, S 16.87.

Naphthalen-2-yl thiophen-3-yl methanone: Yield 63%; m.p. 109–110°C; $R_f = 0.14$ (EtOAc/heptane 1:20); ^{1}H NMR (400 MHz; [D$_6$]DMSO): $\delta = 8.44$ (brs, 1H), 8.33 (dd, $J = 2.7$, 1.2 Hz, 1H), 8.14 (d, $J = 8.1$ Hz, 1H), 8.08 (d, $J = 8.5$ Hz, 1H), 8.03 (d, $J = 8.3$ Hz, 1H), 7.88 (dd, $J = 8.5$, 1.9 Hz, 1H), 7.75 (dd, $J = 5.0$, 2.7 Hz, 1H), 7.70–7.62 (m, 2H), 7.60 ppm (dd, $J = 5.0$, 1.2 Hz, 1H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 189.3$ (C=O), 140.7, 135.6 (CH), 135.5, 134.9, 132.1, 130.8 (CH), 129.7 (CH), 128.6 (CH), 128.5 (CH), 128.3 (CH), 127.8 (CH), 127.8 (CH), 127.1 (CH), 125.2 ppm (CH); IR (KBr): $\tilde{\nu} = 3120$ (s), 3103 (s), 3090 (s), 3058 (m), 1636 (vs, C=O), 1574 (m), 1510 (vs), 1467 (s), 1411 (vs), 1391 (vs), 1349 (m), 1283 (vs), 1271 (vs), 1237 (vs), 1206 (m), 1184 (vs), 1139 (vs), 1114 (s), 1073 (s), 1019 (w), 980 (m), 960 (m), 918 (s), 887 (vs), 872 (vs), 836 (vs), 830 (vs), 812 (s), 792 (vs), 771 (vs), 732 (vs), 718 (s), 629 (m), 597 (s), 488 cm^{-1} (vs); MS (70 eV): m/z (%): 238 (100) [M^+], 210 (9), 155 (49), 127 (54), 111 (57), 83 (11), 77 (9); HRMS (EI): m/z: calcd for $C_{15}H_{10}OS$: 238.04469; found: 238.04424 [M^+].

4-Trifluoromethylbenzophenone: Yield 79%; m.p. 109°C; $R_f = 0.25$ (EtOAc/heptane 0.25:10); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta = 7.96$–7.90 (brs, 4H), 7.79–7.76 (m, 2H), 7.75–7.70 (m, 1H), 7.61–7.56 ppm (m, 2H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 195.1$ (C=O), 140.9, 136.4, 133.5 (CH), 132.1 (q, ^2J(C,F) = 32 Hz), 130.4 (CH), 130.0 (CH), 128.9 (CH), 125.7 (q, ^3J(C,F) = 3.9 Hz, CH), 124.0 ppm (q, ^1J(C,F) = 272 Hz); IR (KBr): $\tilde{\nu} = 3063$ (w), 1652 (vs, C=O), 1598 (m), 1577 (m), 1508 (m), 1448 (m), 1409 (s), 1330 (vs), 1282 (vs), 1169 (vs), 1122 (vs), 1066 (vs), 1017 (s), 943 (s), 925 (s), 858 (vs), 797 (m), 751 (s), 716 (s), 699 (vs), 656 (m), 468 cm^{-1} (m); MS (70 eV): m/z (%): 250 (67) [M^+], 231 (12), 181 (9), 173 (42), 145 (54), 125 (9), 105 (100), 95 (11), 77 (50), 51 (21); HRMS (EI): m/z: calcd for $C_{14}H_9F_3O$: 250.06000; found: 250.05946 [M^+].

2-Methoxyphenyl 4-trifluoromethylphenyl methanone: Yield 73%; m.p. 78°C; $R_f = 0.15$ (EtOAc/heptane 0.5:10); ^{1}H NMR (400 MHz; [D$_6$]DMSO): $\delta = 7.90$–7.85 (m, 4H), 7.59 (quasitd, $J = 7.9$, 1.3 Hz, 1H), 7.41 (dd, $J = 7.5$, 1.3 Hz, 1H), 7.22 (d, $J = 8.3$ Hz, 1H), 7.12 (t, $J = 7.5$ Hz, 1H), 3.66 ppm (s, 3H; OCH_3); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 195.1$ (C=O), 157.1, 140.7, 133.1 (CH), 132.6 (q, ^2J(C,F) = 31 Hz), 129.9 (CH), 129.5 (CH), 127.6, 125.8 (q, ^3J(C,F) = 3.7 Hz, CH), 124.0 (q, ^1J(C,F) = 274 Hz), 121.0 (CH), 112.4 (CH), 55.8 ppm (OCH$_3$); IR (KBr): $\tilde{\nu} = 3069$ (m), 3013 (w), 2941 (w), 2840 (m), 1677 (vs, C=O), 1601 (vs), 1585 (s), 1510 (m), 1488 (vs), 1468 (vs), 1433 (vs), 1411 (vs), 1327 (vs), 1315 (vs), 1295 (vs), 1265 (vs), 1248 (vs), 1161 (vs), 1139 (vs), 1111 (vs), 1065 (vs), 1048 (s), 1018 (s), 943 (vs), 926 (vs), 864 (vs), 773 (s), 756 (vs), 703 (s), 648 cm^{-1} (s); MS (70 eV): m/z (%): 280 (40) [M^+], 263 (22), 211 (12), 173 (17), 145 (39), 135 (100), 121 (10), 92 (16), 77 (27); elemental analysis calcd (%) for $C_{15}H_{11}F_3O_2$: C 64.29, H 3.96; found: C 64.34, H 3.72.

2,5-Dimethoxyphenyl 4-trifluoromethylphenyl methanone: Yield 81%; m.p. 85–86°C; $R_f = 0.08$ (EtOAc/heptane 0.5:10); ^{1}H NMR (400 MHz;

[D$_6$]DMSO): δ=7.88 (brs, 4H), 7.15 (brs, 2H), 6.98 (brs, 1H), 3.75 (s, 3H, OCH_3), 3.59 ppm (s, 3H, OCH_3); ^{13}C NMR (75 MHz; [D$_6$]DMSO): δ=194.7 (C=O), 153.4, 151.1, 140.6, 132.3 (q, ^2J(C,F)=33 Hz), 130.0 (CH), 128.2, 125.8 (q, ^3J(C,F)=4.0 Hz, CH), 123.9 (q, ^1J(C,F)=276 Hz), 118.1 (CH), 114.2 (CH), 113.8 (CH), 56.2 (OCH$_3$), 55.8 ppm (OCH$_3$); IR (KBr): $\tilde{\nu}$=3067 (w), 2963 (w), 2836 (m), 1954 (w), 1677 (vs, C=O), 1588 (m), 1495 (vs), 1473 (s), 1445 (s), 1425 (vs), 1410 (s), 1325 (vs), 1313 (vs), 1290 (vs), 1263 (s), 1236 (vs), 1219 (vs), 1171 (vs), 1139 (vs), 1112 (s), 1064 (vs), 1048 (vs), 1023 (vs), 967 (vs), 867 (vs), 850 (s), 810 (vs), 777 (s), 726 (s), 705 cm^{-1} (s); MS (70 eV): *m/z* (%): 310 (100) [M^+], 293 (23), 252 (17), 173 (25), 165 (57), 151 (34), 145 (55), 122 (8), 107 (13), 95 (8), 77 (10); elemental analysis calcd (%) for $C_{16}H_{13}F_3O_3$: C 61.94, H 4.22; found: C 61.99, H 4.02.

1-[4-(4-Methoxybenzoyl)phenyl]-ethanone: Yield 57%; m.p. 105–106°C; R_f=0.17 (EtOAc/heptane 1:5); ^{1}H NMR (400 MHz; [D$_6$]DMSO): δ=8.09 (quasi d, J=8.5 Hz, 2H), 7.78 (quasi d, J=8.5 Hz, 2H), 7.76 (quasi d, J=9.0 Hz, 2H), 7.10 (quasi d, J=9.0 Hz, 2H), 3.87 (s, 3H; OCH_3), 2.65 ppm (s, 3H; COCH_3); ^{13}C NMR (75 MHz; [D$_6$]DMSO): δ=197.7 (C=O), 193.9 (C=O), 163.3, 141.5, 138.9, 132.3 (CH), 129.3 (CH), 128.9, 128.2 (CH), 114.0 (CH), 55.6 (OCH$_3$), 27.0 ppm (COCH$_3$); IR (KBr): $\tilde{\nu}$=2967 (m), 2938 (m), 2843 (m), 1685 (vs, C=O), 1642 (vs, C=O), 1603 (vs), 1576 (m), 1509 (m), 1497 (m), 1417 (m), 1403 (m), 1358 (m), 1307 (vs), 1291 (vs), 1258 (vs), 1175 (s), 1149 (s), 1119 (m), 1028 (s), 963 (w), 932 (s), 862 (s), 850 (s), 837 (s), 766 (vs), 684 (s), 652 cm^{-1} (m); MS (70 eV): *m/z* (%): 254 (58) [M^+], 239 (28), 211 (8), 147 (6), 136 (9), 135 (100), 107 (6), 92 (16), 77 (16); elemental analysis calcd (%) for $C_{16}H_{14}O_3$: C 75.57, H 5.55; found: C 75.35, H 5.31.

1-{4-[4-(trifluoromethyl)benzoyl]phenyl}-ethanone: Yield 56%; m.p. 124–125°C; R_f=0.16 (EtOAc/heptane 1:7); ^{1}H NMR (400 MHz; [D$_6$]DMSO): δ=8.12 (quasi d, J=8.6 Hz, 2H), 7.95 (brs, 4H), 7.88 (quasi d, J=8.6 Hz, 2H), 2.66 ppm (s, 3H; COCH_3); ^{13}C NMR (75 MHz; [D$_6$]DMSO): δ=197.9 (C=O), 194.8 (C=O), 140.3, 139.9, 139.9, 132.5 (q, ^2J(C,F)=32 Hz), 130.6 (CH), 130.2 (CH), 128.6 (CH), 125.9 (q, ^3J(C,F)=3.7 Hz; CH), 124.0 (q, ^1J(C,F)=274 Hz), 27.3 ppm (COCH$_3$); IR (KBr): $\tilde{\nu}$=2925 (w), 2850 (w), 1687 (vs, C=O), 1650 (vs, C=O), 1406 (s), 1362 (m), 1330 (vs), 1313 (vs), 1283 (s), 1266 (s), 1173 (s), 1135 (vs), 1068 (vs), 1017 (s), 964 (w), 932 (s), 865 (s), 837 (m), 771 (s), 754 (m), 697 (m), 679 (s), 617 (w), 604 (w), 590 cm^{-1} (m); MS (70 eV): *m/z* (%): 292 (16) [M^+], 277 (100), 201 (10), 180 (6), 173 (24), 145 (26), 76 (7); elemental analysis calcd (%) for $C_{16}H_{11}F_3O_2$: C 65.76, H 3.79; found: C 65.86, H 3.75.

4-Trifluoromethylphenyl 4-vinylphenyl methanone: Yield 30%; m.p. 132–133°C; R_f=0.47 (EtOAc/heptane 1:10); ^{1}H NMR (400 MHz; [D$_6$]DMSO): δ=7.95–7.90 (m, 4H), 7.76 (d, J=8.4 Hz, 2H), 7.67 (d, J=8.4 Hz, 2H), 6.86 (dd, J=17.7, 10.9 Hz, 1H), 6.04 (d, J=17.7 Hz, 1H), 5.47 ppm (d, J=10.9 Hz, 1H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): δ=194.6 (C=O), 142.0, 141.1, 135.9 (CH), 135.5, 132.1 (q, ^2J(C,F)=32 Hz), 130.6 (CH), 130.3 (CH), 126.6 (CH), 125.7 (q, ^3J(C,F)=3.7 Hz, CH), 124.0 (q, ^1J(C,F)=273 Hz), 117.9 ppm (CH_2); IR (KBr): $\tilde{\nu}$=3069 (w), 2855 (w), 1940 (w), 1650 (vs, C=O), 1603 (vs), 1579 (w), 1554 (w), 1509 (w), 1408 (vs), 1329 (vs), 1314 (vs), 1287 (vs), 1171 (vs), 1130 (vs), 1110 (vs), 1068 (vs), 1017 (vs), 991 (s), 974 (w), 933 (vs), 865 (vs), 847 (s), 779 (vs), 772 (m), 704 (s), 688 (vs), 600 cm^{-1} (w); MS (70 eV): *m/z* (%): 276 (70) [M^+], 257 (8), 173 (15), 145 (32), 131 (100), 103 (20), 95 (7), 77 (25); elemental analysis calcd (%) for $C_{16}H_{11}F_3O$: C 69.56, H 4.01; found: C 69.34, H 4.30.

4-Methoxyphenyl 4-vinylphenyl methanone: Yield 53%; m.p. 90–91°C; R_f=0.35 (EtOAc/heptane 1:10); ^{1}H NMR (400 MHz; [D$_6$]DMSO): δ=7.75 (quasi d, J=9.0 Hz, 2H), 7.68 (quasi d, J=8.6 Hz, 2H), 7.64 (quasi d, J=8.6 Hz, 2H), 7.09 (quasi d, J=9.0 Hz, 2H), 6.84 (dd, J=17.8, 11.0 Hz, 1H), 6.01 (d, J=17.8 Hz, 1H), 5.43 (d, J=11.0 Hz, 1H), 3.86 ppm (s, 3H; OCH_3); ^{13}C NMR (75 MHz; [D$_6$]DMSO): δ=193.9 (C=O), 162.9, 140.7, 136.9, 135.9 (CH), 132.1 (CH), 129.8 (CH), 129.5, 126.1 (CH), 117.0 (CH_2), 113.9 (CH), 55.6 ppm (OCH$_3$); IR (KBr): $\tilde{\nu}$=3003 (w), 2964 (m), 2839 (m), 1642 (vs, C=O), 1604 (vs), 1577 (s), 1554 (m), 1504 (s), 1465 (w), 1442 (w), 1416 (m), 1401 (m), 1308 (vs), 1292 (vs), 1251 (vs), 1175 (vs), 1148 (s), 1120 (m), 1032 (s), 996 (m), 968 (w), 932 (s), 859 (vs), 839 (vs), 776 (vs), 739 (m), 693 cm^{-1} (vs); MS (70 eV): *m/z* (%): 238 (91) [M^+], 207 (11), 195 (6), 165 (6), 135 (100), 103 (12), 92 (16), 77 (30), 63 (7); elemental analysis calcd (%) for $C_{16}H_{14}O_2$: C 80.65, H 5.92; found: C 80.66, H 5.80.

Thiophen-3-yl 4-vinylphenyl methanone: Yield 63%; m.p. 45–46°C; R_f=0.26 (EtOAc/heptane 1:20); ^{1}H NMR (400 MHz; [D$_6$]DMSO): δ=8.24 (dd, J=2.8, 1.4 Hz, 1H), 7.79 (quasi d, J=8.3 Hz, 2H), 7.72 (dd, J=5.1, 2.8 Hz, 1H), 7.65 (quasi d, J=8.3 Hz, 2H), 7.53 (dd, J=5.1, 1.4 Hz, 1H), 6.85 (dd, J=17.7, 10.9 Hz, 1H), 6.02 (d, J=17.7 Hz, 1H), 5.44 ppm (d, J=10.9 Hz, 1H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): δ=188.7 (C=O), 141.2, 140.6, 137.4, 136.0 (CH), 135.2 (CH), 129.8 (CH), 128.2 (CH), 127.8 (CH), 126.4 (CH), 117.3 ppm (CH_2); IR (KBr): $\tilde{\nu}$=3102 (m), 3082 (s), 2925 (w), 1635 (vs, C=O), 1603 (vs), 1558 (m), 1511 (s), 1411 (vs), 1387 (s), 1308 (m), 1281 (vs), 1232 (m), 1202 (w), 1180 (m), 1138 (s), 1118 (m), 1077 (w), 995 (s), 972 (s), 914 (s), 880 (m), 864 (vs), 855 (vs), 813 (s), 766 (vs), 717 (vs), 701 cm^{-1} (vs); MS (70 eV): *m/z* (%): 214 (100) [M^+], 186 (9), 152 (3); elemental analysis calcd (%) for $C_{13}H_{10}OS$: C 72.87, H 4.70, S 14.96; found: C 72.52, H 4.96, S 14.56.

Thiophen-2-yl 4-vinylphenyl methanone: Yield 60%; m.p. 47–48°C; R_f=0.22 (EtOAc/heptane 1:20); ^{1}H NMR (400 MHz; [D$_6$]DMSO): δ=8.12 (dd, J=4.9, 1.1 Hz, 1H), 7.83 (quasi d, J=8.3 Hz, 2H), 7.74 (dd, J=3.8, 1.1 Hz, 1H), 7.67 (quasi d, J=8.3 Hz, 2H), 7.29 (dd, J=4.9, 3.8 Hz, 1H), 6.85 (dd, J=17.7, 10.9 Hz, 1H), 6.02 (d, J=17.7 Hz, 1H), 5.45 ppm (d, J=10.9 Hz, 1H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): δ=186.7 (C=O), 142.8, 141.0, 136.6, 135.8 (CH), 135.6 (CH), 135.3 (CH), 129.4 (CH), 128.8 (CH), 126.3 (CH), 117.2 ppm (CH_2); IR (KBr): $\tilde{\nu}$=3084 (m), 1623 (vs, C=O), 1602 (s), 1510 (m), 1411 (s), 1355 (s), 1294 (s), 1233 (w), 1183 (w), 1056 (w), 1003 (w), 928 (m), 884 (m), 860 (s), 780 (m), 740 (s), 714 cm^{-1} (s); MS (70 eV): *m/z* (%): 214 (100) [M^+], 197 (9) 187 (11), 152 (2); elemental analysis calcd (%) for $C_{13}H_{10}OS$: C 72.87, H 4.70, S 14.96; found: C 73.06, H 4.63, S 14.61.

Benzo[*b*]thiophen-3-yl thiophen-3-yl methanone: Yield 40%; m.p. 86–87°C; R_f=0.21 (EtOAc/heptane 1:20); ^{1}H NMR (300 MHz; [D$_6$]DMSO): δ=8.62 (brs, 1H), 8.41–8.40 (m, 1H), 8.36 (dd, J=2.8, 1.4 Hz, 1H), 8.14–8.11 (m, 1H), 7.74 (dd, J=5.1, 2.8 Hz, 1H), 7.60 (dd, J=5.1, 1.4 Hz, 1H), 7.56–7.46 ppm (m, 2H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): δ=183.7 (C=O), 142.0, 139.8, 139.1 (CH), 137.1, 134.6 (CH), 134.4, 128.0 (CH), 127.8 (CH), 125.7 (CH), 124.4 (CH), 123.1 ppm (CH); IR (KBr): $\tilde{\nu}$=3104 (s), 2925 (w), 1635 (vs, C=O), 1591 (s), 1557 (m), 1507 (vs), 1494 (vs), 1459 (vs), 1425 (vs), 1351 (s), 1261 (vs), 1243 (vs), 1202 (s), 1180 (vs), 1152 (m), 1134 (m), 1090 (s), 1051 (s), 1019 (m), 938 (w), 864 (s), 834 (vs), 789 (vs), 767 (vs), 737 (vs), 719 (vs), 706 (vs), 636 (m), 568 cm^{-1} (m); MS (70 eV): *m/z* (%): 244 (100) [M^+], 227 (7), 211 (29), 171 (13), 161 (43); HRMS (EI): calcd for $C_{13}H_8OS_2$: 244.00111; found: 244.00110 [M^+].

3-Thiophen-3-yl-benzo[*b*]thiophene: Colorless oil: yield 45%; R_f=0.25 (EtOAc/heptane 0.5:10); ^{1}H NMR (300 MHz; [D$_6$]DMSO): δ=8.07–8.03 (m, 2H), 7.88 (brs, 1H), 7.86 (dd, J=2.9, 1.3 Hz, 1H), 7.72 (dd, J=4.9, 2.9 Hz, 1H), 7.50 (dd, J=4.9, 1.3 Hz, 1H), 7.47–7.40 ppm (m, 2H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): δ=140.1, 137.3, 135.7, 132.0, 128.1 (CH), 126.9 (CH), 124.9 (CH), 124.8 (CH), 124.4 (CH), 123.4 (CH), 122.9 (CH), 122.5 ppm (CH); IR (KBr): $\tilde{\nu}$=3100 (m), 3064 (w), 1559 (m), 1457 (m), 1428 (vs), 1404 (m), 1322 (w), 1259 (m), 1216 (m), 1178 (m), 1082 (s), 1060 (vs), 1022 (m), 883 (w), 837 (s), 791 (s), 773 (vs), 759 (vs), 732 (vs), 648 (vs), 617 cm^{-1} (w); MS (70 eV): *m/z* (%): 216 (100) [M^+], 184 (8), 171 (30); elemental analysis calcd (%) for $C_{12}H_8S_2$: C 66.63, H 3.73, S 29.65; found: C 66.85, H 3.61, S 30.00.

Phenyl-quinoxalin-6-yl methanone: Yield 65%; m.p. 117°C; R_f=0.11 (EtOAc/heptane 1:5); ^{1}H NMR (300 MHz; [D$_6$]DMSO): δ=9.07 (dd, J=4.7, 1.9 Hz, 2H), 8.32 (d, J=1.9 Hz, 1H), 8.26 (d, J=8.5 Hz, 1H), 8.17 (dd, J=8.5, 1.9 Hz, 1H), 7.86–7.83 (m, 2H), 7.77–7.71 (m, 1H), 7.63–7.58 ppm (m, 2H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): δ=195.2 (C=O), 147.8 (CH), 147.2 (CH), 144.0, 141.5, 138.2, 136.7, 133.4 (CH), 131.7 (CH), 130.1 (CH), 130.0 (CH), 129.7 (CH), 128.9 ppm (CH); IR (KBr): $\tilde{\nu}$=3061 (m), 1654 (vs, C=O), 1609 (m), 1597 (s), 1576 (m), 1444 (s), 1421 (m), 1370 (s), 1352 (vs), 1298 (vs), 1279 (vs), 1247 (s), 1207 (w), 1176 (s), 1133 (s), 1113 (vs), 1024 (s), 964 (s), 931 (m), 910 (s), 872 (vs), 843 (m), 784 (m), 729 (vs), 703 (vs), 685 (m), 619 cm^{-1} (s); MS (70 eV): *m/z* (%): 234 (61) [M^+], 205 (45), 157 (66), 129 (36), 105 (100), 102 (31), 77 (77), 51 (29); HRMS (EI): *m/z*: calcd for $C_{15}H_{10}N_2O$: 234.07876; found: 234.07815 [M^+].

6-Phenyl-quinoxaline: Yield 26%; m.p. 89–91 °C; $R_f = 0.19$ (EtOAc/heptane 1:5); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta = 8.96$ (dd, $J = 10.6$, 1.9 Hz, 2H), 8.34 (d, $J = 1.9$ Hz, 1H), 8.21 (quasi dd, $J = 8.7$, 1.9 Hz, 1H), 8.17 (quasi dd, $J = 8.7$, 0.8 Hz, 1H), 7.91–7.87 (m, 2H), 7.58–7.52 (m, 2H), 7.49–7.44 ppm (m, 1H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 146.4$ (CH), 145.8 (CH), 142.7, 141.9, 141.8, 138.8, 129.9 (CH), 129.6 (CH), 129.4 (CH), 128.6 (CH), 127.5 (CH), 126.3 ppm (CH); IR (KBr): $\tilde{\nu} = 3066$ (w), 3024 (w), 2924 (s), 2853 (m), 1935 (w), 1616 (s), 1578 (m), 1484 (vs), 1454 (s), 1431 (s), 1370 (s), 1348 (m), 1317 (w), 1305 (m), 1245 (w), 1168 (m), 1134 (s), 1078 (m), 1023 (vs), 1013 (vs), 951 (vs), 897 (vs), 885 (m), 866 (vs), 839 (s), 775 (vs), 766 (vs), 698 (vs), 665 (m), 608 (w), 560 (w), 496 (m), 409 cm^{-1} (s); MS (70 eV): *m/z* (%): 206 (100) [M^+], 179 (4), 152 (34), 102 (28), 76 (10), 63 (5); HRMS (EI): *m/z*: calcd for $C_{14}H_{10}N_2$: 206.08385; found: 206.08402 [M^+].

Di[3]thienyl ketone: Yield 43%; m.p. 71 °C; $R_f = 0.22$ (EtOAc/heptane 1:10); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta = 8.36$ (quasi dd, $J = 2.4$, 1.2 Hz, 2H), 7.71 (quasi dd, $J = 4.9$, 2.4 Hz, 2H), 7.55 ppm (quasi dd, $J = 4.9$, 1.2 Hz, 2H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 182.6$ (C=O), 141.3, 134.3 (CH), 128.0 (CH), 127.7 ppm (CH); IR (KBr): $\tilde{\nu} = 3106$ (s), 1629 (vs, C=O), 1513 (vs), 1427 (vs), 1394 (w), 1271 (s), 1219 (w), 1178 (w), 1136 (vs), 1078 (m), 984 (w), 916 (w), 883 (s), 850 (vs), 826 (vs), 776 (s), 741 (vs), 697 (vs), 624 cm^{-1} (w); MS (70 eV): *m/z* (%): 194 (78) [M^+], 166 (6), 111 (100), 83 (18), 57 (7); HRMS (EI): *m/z*: calcd for $C_9H_6OS_2$: 193.98546; found: 193.98529 [M^+].

Pyridin-3-ylthiophen-3-yl methanone: Yield 45%; m.p. 68 °C; $R_f = 0.16$ (EtOAc/heptane 1:2); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta = 8.94$ (d, $J = 1.4$ Hz, 1H), 8.83 (dd, $J = 4.9$, 1.4 Hz, 1H), 8.34 (dd, $J = 2.8$, 1.4 Hz, 1H), 8.17 (dt, $J = 7.9$, 2.0 Hz, 1H), 7.75 (dd, $J = 4.9$, 2.8 Hz, 1H), 7.62–7.59 (m, 1H), 7.57 ppm (dd, $J = 4.9$, 1.4 Hz, 1H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 187.9$ (C=O), 152.9 (CH), 149.6 (CH), 140.3, 136.7 (CH), 136.6 (CH), 134.0, 128.2 (CH), 127.9 (CH), 123.9 ppm (CH); IR (KBr): $\tilde{\nu} = 3062$ (s), 1650 (vs, C=O), 1586 (vs), 1512 (s), 1478 (m), 1419 (vs), 1389 (s), 1336 (w), 1284 (vs), 1197 (m), 1155 (m), 1025 (m), 977 (w), 967 (w), 885 (w), 859 (s), 845 (s), 825 (m), 746 (s), 713 (vs), 694 (s), 623 cm^{-1} (w); MS (70 eV): *m/z* (%): 189 (97) [M^+], 161 (10), 111 (100), 106 (7), 83 (18), 78 (21), 51 (25); HRMS (EI): *m/z*: calcd for $C_{10}H_7NOS$: 189.02429; found: 189.02382 [M^+].

3-Thiophen-3-yl-pyridine: Yield 30%; m.p. 70–71 °C; $R_f = 0.24$ (EtOAc/heptane 1:2); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta = 8.98$ (d, $J = 1.5$ Hz, 1H), 8.49 (dd, $J = 4.9$, 1.2 Hz, 1H), 8.11 (quasi dt, $J = 8.0$, 1.2 Hz, 1H), 8.04 (dd, $J = 2.9$, 1.5 Hz, 1H), 7.70 (quasi dd, $J = 4.9$, 2.9 Hz, 1H), 7.65 (dd, $J = 4.9$, 1.5 Hz, 1H), 7.43 ppm (quasi dd, $J = 8.0$, 4.9 Hz, 1H); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 148.2$ (CH), 147.4 (CH), 138.4, 133.4 (CH), 130.9, 127.8 (CH), 126.2 (CH), 124.1 (CH), 122.4 ppm (CH); IR (KBr): $\tilde{\nu} = 3100$ (s), 3077 (s), 3030 (s), 2924 (s), 1574 (s), 1527 (w), 1473 (s), 1431 (s), 1366 (m), 1322 (s), 1260 (m), 1223 (s), 1207 (m), 1182 (s), 1128 (w), 1080 (w), 1020 (s), 983 (w), 949 (m), 895 (m), 862 (vs), 822 (m), 797 (vs), 706 (vs), 641 cm^{-1} (s); MS (70 eV): *m/z* (%): 161 (100) [M^+], 134 (12), 117 (31), 108 (9), 89 (13), 63 (12); HRMS (EI): *m/z*: calcd for C_9H_7NS: 161.02937; found: 161.02929 [M^+].

4-Chlorophenyl 2-methoxyphenyl methanone: Yield 70%; m.p. 78 °C; $R_f = 0.2$ (EtOAc/heptane 1:10); ^{1}H NMR (400 MHz; [D$_6$]DMSO): $\delta = 7.70$–7.67 (m, 2H), 7.59–7.54 (m, 3H), 7.35 (dd, $J = 7.5$, 1.8 Hz, 1H), 7.19 (d, $J = 8.2$ Hz, 1H), 7.09 (td, $J = 7.5$, 1.0 Hz, 1H), 3.67 ppm (s, 3H; OC*H$_3$*); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 194.6$ (C=O), 156.7, 138.1, 135.8, 132.3 (CH), 131.0 (CH), 128.9 (CH), 128.8 (CH), 127.8, 120.7 (CH), 112.0 (CH), 55.5 ppm (O*C*H$_3$); IR (KBr): $\tilde{\nu} = 3310$ (w), 3086 (w), 3056 (m), 3018 (w), 2939 (m), 2838 (m), 1662 (vs, C=O), 1601 (vs), 1585 (vs), 1489 (vs), 1466 (vs), 1453 (s), 1432 (vs), 1399 (s), 1365 (w), 1304 (vs), 1296 (vs), 1266 (vs), 1244 (vs), 1178 (m), 1152 (s), 1111 (s), 1086 (vs), 1047 (s), 1024 (vs), 1013 (s), 972 (w), 941 (vs), 924 (vs), 848 (vs), 767 (s), 753 (vs), 742 (vs), 684 (m), 655 (s), 562 (m), 536 (m), 506 (s), 486 cm^{-1} (m); MS (70 eV): *m/z* (%): 246 (100) [M^+], 229 (60), 211 (75), 201 (17), 193 (23), 181 (17), 168 (27), 152 (19); HRMS (EI): *m/z*: calcd for $C_{14}H_{11}ClO_2$: 246.04421; found: 246.04437 [M^+]; elemental analysis calcd (%) for $C_{14}H_{11}ClO_2$: C 68.16, H 4.49; found: C 68.32, H 4.70.

4′-Chloro-2-methoxybiphenyl: Pale-yellow oil; yield 31%; $R_f = 0.46$ (EtOAc/heptane 0.5:20); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta = 7.51$–7.43 (m, 4H), 7.39–7.33 (m, 1H), 7.29 (dd, $J = 7.5$, 1.7 Hz, 1H), 7.12 (d, $J = 8.3$ Hz, 1H), 7.03 (td, $J = 7.5$, 1.2 Hz, 1H), 3.76 ppm (s, 3H; OC*H$_3$*); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 156.2$, 137.1, 131.8, 131.2 (CH), 130.4 (CH), 129.5 (CH), 128.6, 128.2 (CH), 121.0 (CH), 112.0 (CH), 55.7 ppm (O*C*H$_3$); IR (KBr): $\tilde{\nu} = 3067$ (w), 2936 (m), 2835 (m), 1502 (m), 1479 (vs), 1463 (s), 1436 (s), 1397 (m), 1256 (s), 1236 (s), 1180 (m), 1162 (m), 1123 (s), 1090 (vs), 1056 (m), 1028 (s), 1004 (s), 829 (m), 801 (w), 747 cm^{-1} (vs); MS (70 eV): *m/z* (%): 218 (89) [M^+], 203 (11), 183 (7), 168 (100), 152 (9), 149 (9), 139 (39); elemental analysis calcd (%) for $C_{13}H_{11}ClO$: C 71.40, H 5.07, Cl 16.21; found: C 71.55, H 4.82, Cl 15.9.

4-Methoxybenzophenone: Yield 75%; m.p. 52 °C; $R_f = 0.2$ (EtOAc/heptane 1:10); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta = 7.76$ (quasi d, $J = 9.0$ Hz, 2H), 7.70–7.62 (m, 3H), 7.57–7.52 (m, 2H), 7.09 (quasi d, $J = 9.0$ Hz, 2H), 3.86 ppm (s, 3H; OC*H$_3$*); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 194.5$ (C=O), 163.0, 137.8, 132.2 (CH), 132.1 (CH), 129.4, 129.3 (CH), 128.5 (CH), 113.9 (CH), 55.6 ppm (O*C*H$_3$); IR (KBr): $\tilde{\nu} = 3060$ (w), 2934 (m), 2840 (m) 1653 (vs, C=O), 1600 (vs), 1577 (vs), 1508 (vs), 1446 (vs), 1420 (s), 1318 (vs), 1282 (vs), 1258 (vs), 1172 (vs), 1149 (m), 1112 (m), 1074 (w), 1029 (vs), 938 (s), 923 (vs), 844 (s), 793 (m), 740 (s), 702 (s), 678 (m), 600 cm^{-1} (s); MS (70 eV): *m/z* (%): 212 (42) [M^+], 135 (100), 105 (8), 92 (10), 77 (21); elemental analysis calcd (%) for $C_{14}H_{12}O_2$: C 79.22, H 5.70; found: C 78.92, H 5.77.

2,4′-Dimethoxybenzophenone: Colorless oil; yield 4%; $R_f = 0.17$ (EtOAc/heptane 1:5); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta = 7.66$ (quasi d, $J = 9.0$ Hz, 2H), 7.54–7.48 (m, 1H), 7.26 (dd, $J = 7.4$, 1.9 Hz, 1H), 7.17 (d, $J = 8.1$ Hz, 1H), 7.07 (dd, $J = 7.4$, 0.9 Hz, 1H), 7.03 (quasi d, $J = 9.0$ Hz, 2H), 3.83 (s, 3H; OC*H$_3$*), 3.68 ppm (s, 3H; OC*H$_3$*); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 194.3$ (C=O), 163.5, 156.5, 131.9 (CH), 131.7 (CH), 130.1, 129.1, 128.6 (CH), 120.7 (CH), 114.1 (CH), 112.0 (CH), 55.7 (O*C*H$_3$), 55.7 ppm (O*C*H$_3$); IR (KBr): $\tilde{\nu} = 3006$ (m), 2964 (m), 2938 (m), 2845 (m), 2055 (w), 1918 (w), 1727 (m), 1654 (vs, C=O), 1600 (vs), 1576 (vs), 1509 (vs), 1486 (vs), 1465 (vs), 1450 (vs), 1422 (vs), 1306 (vs), 1296 (vs), 1257 (vs), 1195 (s), 1180 (vs), 1148 (vs), 1109 (s), 1046 (s), 1032 (vs), 942 (s), 925 (vs), 851 (vs), 789 (m), 771 (s), 756 (vs), 698 (m), 635 (m), 610 (vs), 586 (m), 561 (m), 513 cm^{-1} (m); MS (70 eV): *m/z* (%): 242 (40) [M^+], 225 (43), 211 (19), 197 (10), 135 (100), 121 (25), 107 (11), 92 (28), 77 (36), 64 (11); elemental analysis calcd (%) for $C_{15}H_{14}O_3$: C 74.36, H 5.82; found: C 74.38, H 5.82.

2-Methoxybenzophenone: Pale-yellow oil; yield 73%; $R_f = 0.16$ (EtOAc/heptane 1:10); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta = 7.71$–7.61 (m, 3H), 7.57–7.48 (m, 3H), 7.32 (dd, $J = 7.5$, 1.9 Hz, 1H), 7.19 (d, $J = 7.9$ Hz, 1H), 7.08 (td, $J = 7.5$, 0.9 Hz, 1H), 3.67 ppm (s, 3H; OC*H$_3$*); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 195.9$ (C=O), 156.8, 137.3, 133.5 (CH), 132.2 (CH), 129.4 (CH), 128.9 (CH), 128.8 (CH), 128.6, 120.8 (CH), 112.2 (CH), 55.7 ppm (O*C*H$_3$); IR (KBr): $\tilde{\nu} = 3061$ (m), 2942 (m), 2838 (m), 1667 (vs, C=O), 1599 (vs), 1581 (s), 1487 (vs), 1463 (vs), 1449 (vs), 1436 (vs), 1316 (vs), 1295 (vs), 1245 (vs), 1181 (m), 1163 (m), 1151 (m), 1110 (m), 1073 (w), 1048 (s), 1024 (s), 926 (vs), 807 (m), 756 (s), 703 (s), 636 cm^{-1} (s); MS (70 eV): *m/z* (%): 212 (48) [M^+], 195 (26), 181 (7), 167 (9), 152 (7), 135 (100), 121 (20), 105 (33), 92 (21), 77 (72), 63 (8), 51 (19); elemental analysis calcd (%) for $C_{14}H_{12}O_2$: C 79.22, H 5.70; found: C 79.11, H 5.37.

3-(2-Methoxybenzoyl)pyridine: Yellow oil; yield 64%; $R_f = 0.1$ (EtOAc/heptane 1:3); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta = 8.79$–8.77 (m, 2H), 8.03 (quasi dt, $J = 3.4$, 1.7 Hz, 1H), 7.63–7.53 (m, 2H), 7.42 (dd, $J = 7.5$, 1.7 Hz, 1H), 7.21 (d, $J = 8.2$ Hz, 1H), 7.12 (td, $J = 7.5$, 0.9 Hz, 1H), 3.67 ppm (s, 3H, OC*H$_3$*); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta = 194.9$ (C=O), 157.1, 153.5 (CH), 150.2 (CH), 136.6 (CH), 133.2 (CH), 132.9, 129.6 (CH), 127.4, 124.0 (CH), 121.0 (CH), 112.4 (CH), 55.8 ppm (O*C*H$_3$); IR (KBr): $\tilde{\nu} = 3048$ (m), 2964 (m), 2944 (m), 2839 (m), 1666 (vs, C=O), 1599 (vs), 1585 (vs), 1487 (vs), 1464 (s), 1437 (s), 1418 (s), 1329 (m), 1302 (vs), 1263 (vs), 1247 (vs), 1195 (w), 1182 (w), 1163 (m), 1112 (m), 1049 (m), 1024 (s), 928 (vs), 757 (vs), 714 (s), 648 cm^{-1} (s); MS (70 eV): *m/z* (%): 213 (32) [M^+], 196 (16), 184 (10), 168 (6), 135 (100), 106 (8), 92 (22), 77 (33), 63 (8), 51 (18); HRMS (EI): *m/z*: calcd for $C_{13}H_{11}NO_2$: 213.07843; found: 213.07781 [M^+].

3-(2-Methoxyphenyl)pyridine: Pale-yellow oil; yield 4%; $R_f = 0.18$ (EtOAc/heptane 1:3); ^{1}H NMR (300 MHz; CDCl$_3$): $\delta = 8.78$ (brs, 1H), 8.56 (d, $J=3.8$ Hz, 1H), 7.87 (dt, $J=3.4$, 1.8 Hz, 1H), 7.41–7.31 (m, 3H), 7.07 (td, $J=7.5$, 1.0 Hz, 1H), 7.02 (quasi d, $J=8.2$ Hz, 1H), 3.83 ppm (s, 3H; OCH_3); ^{13}C NMR (75 MHz; CDCl$_3$): $\delta=156.7$, 150.5 (CH), 148.1 (CH), 137.0 (CH), 134.4, 130.8 (CH), 129.7 (CH), 127.2, 123.1 (CH), 121.2 (CH), 111.4 (CH), 55.7 ppm (OCH_3); IR (KBr): $\tilde{\nu}=2937$ (w), 2836 (w), 1731 (w), 1599 (m), 1583 (w), 1497 (s), 1463 (s), 1436 (s), 1406 (vs), 1266 (vs), 1237 (vs), 1180 (s), 1122 (vs), 1060 (m), 1049 (m), 1025 (vs), 999 (s), 801 (s), 752 (vs), 711 cm^{-1} (vs); MS (70 eV): m/z (%): 185 (100) [M^+], 170 (58), 141 (6), 115 (30), 89 (8), 63 (8); HRMS (EI): calcd for $C_{12}H_{11}NO$: 185.08352; found: 185.08319 [M^+].

2-(2-Methoxybenzoyl)benzonitrile: Yield 66%; m.p. 89–90°C; $R_f=0.07$ (EtOAc/heptane 1:5); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta=8.03$–8.00 (m, 1H), 7.78 (quasi dd, $J=5.4$, 3.6 Hz, 2H), 7.66–7.60 (m, 1H), 7.58–7.55 (m, 1H), 7.52 (dd, $J=7.6$, 1.7 Hz, 1H), 7.19 (d, $J=8.3$ Hz, 1H), 7.13 (td, $J=7.6$, 1.0 Hz, 1H), 3.60 ppm (s, 3H; OCH_3); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta=193.8$ (C=O), 158.1, 141.5, 134.8 (CH), 134.4 (CH), 133.2 (CH), 132.6 (CH), 130.6 (CH), 130.4 (CH), 126.7, 121.1 (CH), 117.7, 112.7 (CH), 109.7, 55.9 ppm (OCH_3); IR (KBr): $\tilde{\nu}=3076$ (w), 2959 (m), 2929 (m), 2837 (m), 2227 (s, CN), 1729 (m), 1661 (vs, C=O), 1601 (vs), 1571 (s), 1487 (vs), 1473 (s), 1456 (s), 1437 (s), 1381 (w), 1305 (vs), 1259 (vs), 1190 (m), 1161 (m), 1120 (s), 1098 (w), 1073 (w), 1023 (s), 947 (m), 931 (vs), 811 (m), 774 (vs), 751 (vs), 691 (m), 642 (vs), 558 (w), 493 cm^{-1} (w); MS (70 eV): m/z (%): 237 (72) [M^+], 220 (22), 208 (16), 181 (37), 135 (100), 130 (17), 102 (31), 92 (31), 77 (45), 63 (13), 51 (12); elemental analysis calcd (%) for $C_{15}H_{11}NO_2$: C 75.94, H 4.67, N 5.90; found: C 76.02, H 4.46, N 5.73.

2′-Methoxybiphenyl-2-carbonitrile: Colorless oil; yield 33%; $R_f=0.27$ (EtOAc/heptane 1:5); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta=7.88$ (dd, $J=7.7$, 1.0 Hz, 1H), 7.75 (td, $J=7.7$, 1.3 Hz, 1H), 7.55 (dd, $J=7.7$, 1.0 Hz, 1H), 7.52–7.43 (m, 2H), 7.26 (dd, $J=7.5$, 1.7 Hz, 1H), 7.18 (d, $J=8.2$ Hz, 1H), 7.08 (td, $J=7.5$, 1.0 Hz, 1H), 3.77 ppm (s, 3H, OCH_3); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta=156.1$, 141.9, 133.0 (CH), 132.7 (CH), 130.9 (CH), 130.6 (CH), 130.4 (CH), 127.9 (CH), 126.8, 120.6 (CH), 118.4, 112.4, 111.7 (CH), 55.4 ppm (OCH_3); IR (KBr): $\tilde{\nu}=3066$ (w), 2935 (m), 2837 (m, OCH$_3$), 2227 (s, CN), 1602 (s), 1583 (m), 1500 (vs), 1479 (vs), 1463 (vs), 1433 (vs), 1281 (vs), 1255 (vs), 1237 (vs), 1181 (m), 1163 (m), 1126 (s), 1100 (m), 1054 (s), 1026 (vs), 1004 (m), 808 (w), 755 (vs), 621 (w), 550 cm^{-1} (m); MS (70 eV): m/z (%): 209 (100) [M^+], 194 (11), 181 (51), 166 (18), 152 (10), 140 (35), 113 (7), 63 (7); elemental analysis calcd (%) for $C_{14}H_{11}NO$: C 80.40, H 5.30, N 6.69; found: C 77.16, H 5.23, N 6.17.

2,2′-Dimethoxybenzophenone: Yield 52%; m.p. 90–91°C; $R_f=0.15$ (EtOAc/heptane 1:5); ^{1}H NMR (300 MHz; [D$_6$]DMSO): $\delta=7.53$–7.47 (m, 2H), 7.39 (dd, $J=7.5$, 1.9 Hz, 2H), 7.08 (d, $J=8.3$ Hz, 2H), 7.01 (td, $J=7.5$, 0.8 Hz, 2H), 3.58 ppm (s, 6H; 2OCH_3); ^{13}C NMR (75 MHz; [D$_6$]DMSO): $\delta=194.5$ (C=O), 158.0, 133.1 (CH), 129.9, 129.7 (CH), 120.4 (CH), 112.2 (CH), 55.8 ppm (OCH_3); IR (KBr): $\tilde{\nu}=3103$ (m), 3074 (m), 2969 (s), 2944 (s), 2842 (m), 1728 (w), 1629 (vs), 1596 (vs), 1486 (vs), 1461 (vs), 1435 (vs), 1313 (vs), 1282 (vs), 1249 (vs), 1180 (vs), 1161 (vs), 1115 (s), 1049 (s), 1018 (vs), 945 (m), 930 (vs), 793 (m), 759 (vs), 690 (m), 635 (vs), 532 (m), 419 cm^{-1} (s); MS (70 eV): m/z (%): 242 (27) [M^+], 225 (15), 211 (17), 181 (11), 135 (100), 121 (23), 92 (26), 77 (37), 63 (11), 51 (8); elemental analysis calcd (%) for $C_{15}H_{14}O_3$: C 74.36, H 5.82; found: C 74.39, H 5.86.

Acknowledgements

The authors thank S. Giertz for excellent technical and analytical assistance, as well as Dr. R. Jackstell and Dr. T. Schareina (all at the Leibniz Institute for Catalysis) for providing ligands and complexes. Generous financial support from Mecklenburg-Vorpommern, the Fonds der Chemischen Industrie, the Bundesministerium für Bildung und Forschung (BMBF), and the DFG (Leibniz-Price) is gratefully acknowledged.

---

[1] S. Budavari, *The Merck Index*, 11th ed., Merck, Rahway, USA, **1989**.

[2] G. A. Olah, *Friedel–Crafts Chemistry*, Wiley, New York, **1973**.

[3] a) G. F. Silbestri, R. Bogel-Masson, M. T. Lockhart, A. B. Chopa, *J. Organomet. Chem.* **2006**, *691*, 1520–1524; b) W. P. Neumann, H. Hillgärtner, K. M. Baines, R. Dicke, K. Vorspohl, U. Kowe, U. Nussbeutel, *Tetrahedron* **1989**, *45*, 951–960; c) J. W. Labadie, J. K. Stille, *J. Am. Chem. Soc.* **1983**, *105*, 6129–6137.

[4] L. J. Gooßen, K. Ghosh, *Angew. Chem.* **2001**, *113*, 3566–3568; *Angew. Chem. Int. Ed.* **2001**, *40*, 3458–3460.

[5] Y. C. Huang, K. K. Majumdar, C.-H. Cheng, *J. Org. Chem.* **2002**, *67*, 1682–1684.

[6] See review: *Synthesis of Diarylketones through Carbonylative Coupling*, J.-J. Brunet, R. Chauvin, *Chem. Soc. Rev.* **1995**, 24, 89–95.

[7] N. A. Bumagin, A. B. Ponomaryov, I. P. Beletskaya, *Tetrahedron Lett.* **1985**, *26*, 4819–4822.

[8] a) Y. Hatanaka, S. Fukushima, T. Hiyama, *Tetrahedron* **1992**, *48*, 2113–2126; b) Y. Hatanaka, T. Hiyama, *Synlett* **1991**, 845–853; c) Y. Hatanaka, T. Hiyama, *Chem. Lett.* **1989**, 2049–2052.

[9] a) A. M. Echavarren, J. K. Stille, *J. Am. Chem. Soc.* **1988**, *110*, 1557–1565; b) K. Kikukawa, T. Idemoto, A. Katayama, K. Kono, F. Wada, T. Matsuda, *J. Chem. Soc. Perkin Trans. 1* **1987**, 1511–1514; c) J. K. Stille, *Angew. Chem.* **1986**, *98*, 504–519; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 508–524; d) K. Kikukawa, K. Kono, F. Wada, T. Matsuda, *Chem. Lett.* **1982**, 35–36; e) N. A. Bumagin, I. G. Bumagina, A. N. Kashin, I. P. Beletskaya, *Dokl. Akad. Nauk SSSR* **1981**, *261*, 1141–1144; f) M. Tanaka, *Tetrahedron Lett.* **1979**, *20*, 2601–2602.

[10] T. Ishiyama, H. Kizaki, N. Miyaura, A. Suzuki, *Tetrahedron Lett.* **1993**, *34*, 7595–7598.

[11] T. Ishiyama, H. Kizaki, T. Hayashi, A. Suzuki, N. Miyaura, *J. Org. Chem.* **1998**, *63*, 4726–4731.

[12] a) S. Couve-Bonnaire, J.-F. Carpentier, A. Mortreux, Y. Castanet, *Tetrahedron* **2003**, *59*, 2793–2799; b) E. Maerten, F. Hassouna, S. Couve-Bonnaire, A. Mortreaux, J.-F. Carpentier, Y. Castanet, *Synlett* **2003**, 1874–1876.

[13] D. Mingji, B. Liang, C. Wang, Z. You, J. Xiang, G. Dong, J. Chen, Z. Yang, *Adv. Synth. Catal.* **2004**, *346*, 1669–1673.

[14] O. Rahman, T. Kihlberg, B Långström, *Eur. J. Org. Chem.* **2004**, 474–478.

[15] A. Ehrentraut, A. Zapf, M. Beller, *Synlett* **2000**, 1589–1592.

[16] A. Zapf, A. Ehrentraut, M. Beller, *Angew. Chem.* **2000**, *112*, 4315–4317; *Angew. Chem. Int. Ed.* **2000**, *39*, 4153–4155.

[17] A. Köllhofer, T. Pullmann, H. Plenio, *Angew. Chem.* **2003**, *115*, 1086–1088; *Angew. Chem. Int. Ed.* **2003**, *42*, 1056–1058.

[18] a) A. Tewari, M. Hein, A. Zapf, M. Beller, *Tetrahedron* **2005**, *61*, 9705–9709; b) A. Ehrentraut, A. Zapf, M. Beller, *J. Mol. Catal. A* **2002**, *182*, 515–523.

[19] A. Ehrentraut, A. Zapf, M. Beller, *Adv. Synth. Catal.* **2002**, *344*, 209–217.

[20] S. Klaus, H. Neumann, A. Zapf, D. Strübing, S. Hübner, J. Almena, T. Riermeier, P. Groß, M. Sarich, W.-R. Krahnert, K. Rossen, M. Beller, *Angew. Chem.* **2006**, *118*, 161–165; *Angew. Chem. Int. Ed.* **2006**, *45*, 154–158.

[21] H. Neumann, A. Brennführer, P. Groß, T. Riermeier, J. Almena, M. Beller, *Adv. Synth. Catal.* **2006**, *348*, 1255–1261.

[22] See for example: a) M. Beller, W. Mägerlein, A. F. Indolese, C. Fischer, *Synthesis* **2001**, 1098–1109 and cited references therein. b) H.-U. Blaser, M. Diggelmann, H. Meier, F. Naud, E. Scheppach, A. Schnyder, M. Studer, *J. Org. Chem.* **2003**, *68*, 3725–3728.

[23] In this single case, a higher temperature and pressure (120°C/10 bar CO) are needed.

[24] I. del Río, N. Ruiz, C. Claver, L. A. van der Veen, P. W. N. M. van Leeuwen, *J. Mol. Catal. B* **2000**, *161*, 39–48.

Received: January 2, 2007