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Sulfoximinocarbonylation of aryl halides using heterogeneous Pd/C catalyst

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A three component protocol has been developed for the synthesis of *N*-aroyl sulfoximines by the carbonylation of aryl halides followed by nucleophilic attack of *N*H-sulfoximine. This reaction abides a range of aryl iodides and sulfoximines to provide the *N*-aroyl sulfoximine in good to excellent yields. Less reactive aryl bromide also underwent sulfoximinocarbonylation and afforded the products. This methodology is free from phosphine ligands. The heterogeneous Pd/C catalyst was successfully recovered and reused up to five consecutive catalytic cycles.

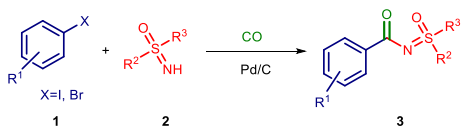
Introduction

Carbonylation reactions exploiting carbon monoxide (CO) as C1-building block is one of the important tools for constructing myriad carbonyl compounds in both academia and industry.[1] In particular, several reports have been advanced on the utility of carbonyl-installing reactions, such as aminocarbonylation, alkoxycarbonylation,[2] thio-carbonylation,[3] oxidative carbonylation,[4] double carbonylation,[5] carbonylative α-arylation,[6] carbonylative Heck,[7] carbonylative Suzuki- Miyaura[8] and carbonylative C-H activation.[9] Though Pd-catalyzed carbonylation reactions have been well travelled over the past decades, these reactions still attract a great deal of attention as CO is inexpensive, readily available, unique reactive and a versatile C1-unit.[10] The quest for carbonylation reaction continues with the objective of increasing the diversity of possible substrates, catalyst-product separation techniques and the recovery of pricy metal catalysts.

In homogeneous Pd catalysis, recycling of the expensive Pd and contamination by residual palladium in the final products are often the major disadvantages. Also, Pd catalyst often needs expensive and easily oxidizable phosphine ligands. The practice of heterogeneous catalyst will overcome these difficulties, especially palladium on carbon (Pd/C) is one of the most common heterogeneous catalyst which has gained a considerable attention in green and sustainable chemistry.[11] Wide commercial availability, recoverability, reusability, relatively low cost and the avoidance of residual metal in the desired product, have crafted Pd/C as an interesting catalytic system.[12] Several literature precedents of Pd/C-catalyzed C-C and C-X (X=N, S or O) bond forming reactions signify its catalytic activity.[13] Recently, Pd/C catalyzed carbonylation reaction has received much attention which includes carbon monoxide and the corresponding surrogates for the synthesis of various carbonyl compounds.[14]

Sulfoximines are isoelectronic with sulfones and they are mono aza analogues of sulfones where S=N unit replaces one of the two S=O units, which deal a versatile chemistry.[15] They serve as pharmacophores and display diverse bioactivities[16a] like, HIV-1 protease inhibitors,[16b] pan-CDK inhibitors (anti-cancer drug),[16c] antiasthmatics,[16d,e] and antiproliferatives.[16f,g] Sulfoximines are also recognized for their application in agricultural chemistry (crop protection),[17] chiral auxiliaries and ligands in asymmetric synthesis.[18] *N*-functionalization of sulfoximine would allow synthetic diversity, specific reactivity and change in chemical as well as physical properties.[15b] *N*-aroyl sulfoximines, a class of sulfoximine have been conventionally achieved from aroyl chlorides and *N*H-sulfoximines.[19] Bolm and other research groups made more advancement in this area, switching acid chlorides to aldehydes or methyl arenes.[20]

Recently, we reported palladium nanoparticle (Pd-BNP) catalyzed sulfoximinocarbonylation of aryl iodide with carbon monoxide which afforded aroylation of *N*H-sulfoximines. Although we have witnessed broad substrate scope and reusability of nanocatalyst, the synthesis of Pd-BNP limits this methodology to be more widely applied.[21] Consequently, herein we report a protocol using commercially available heterogenous Pd/C for the assembly of *N*-aroyl sulfoximine from aryl iodides/bromides, carbon monoxide and *N*H-sulfoximine (Scheme 1).



1 2 3

Scheme 1 Heterogeneous Pd/C catalyzed sulfoximinocarbonylation of aryl halides.

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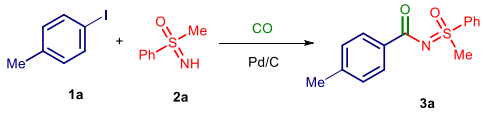
Results and Discussion

At the outset, 4-iodotoluene **1a** and *S*-methyl-*S*-phenyl-sulfoximine **2a** were chosen as the model substrates to optimize the reaction condition. The reaction of **1a** and **2a** with 1 mol% of Pd/C and 1 equiv. of K_2CO_3 under CO balloon in DMF solvent at ambient temperature afforded the product **3a** in 34% yield (Table 1, entry 1). Fortunately, higher yields of **3a** could be obtained by performing the same reaction at 60 °C yielding 91% of the product (entry 2). Further increasing the reaction temperature to 80 °C has no effect on time and yield of **3a** (entry 3). In next exploration steps, solvent effect on this carbonylation was examined and it clearly shows that among various solvents employed in the transformation, none of them gave better yield than DMF (entries 4-10).

Table 1 Optimization of reaction condition for sulfoximino carbonylation[a]



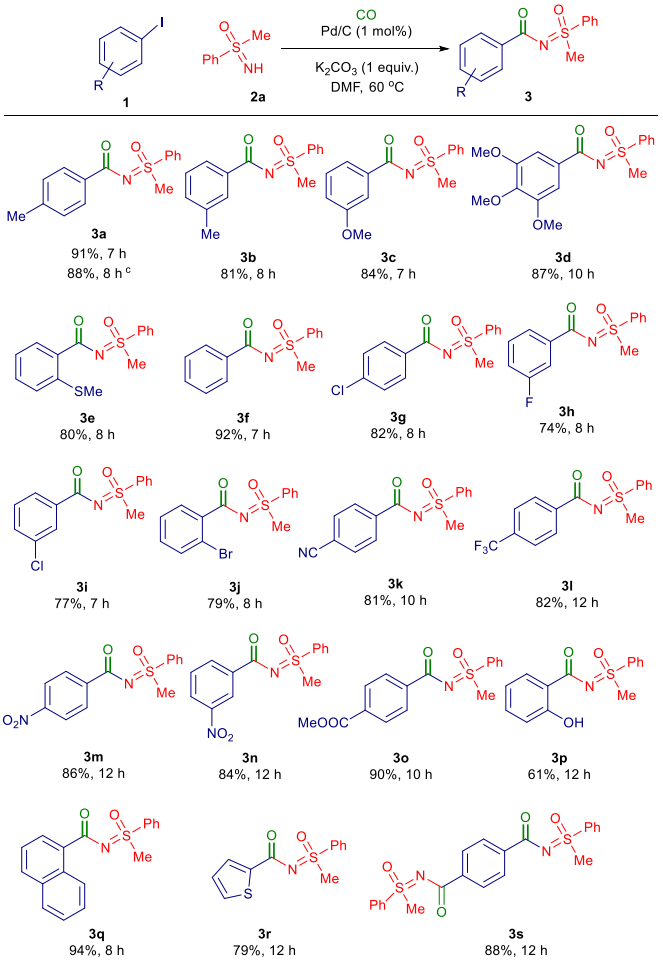
Entry	Solvent	Base (equiv)	Time (h)	Yield[b] (%)
1	DMF	K_2CO_3 (1)	24	34[c]
2	**DMF**	**K_2CO_3 (1)**	**7**	**91**
3	DMF	K_2CO_3 (1)	7	90[c]
4	Toluene	K_2CO_3 (1)	12	68
5	DCE	K_2CO_3 (1)	12	31
6	THF	K_2CO_3 (1)	10	71
7	MeCN	K_2CO_3 (1)	8	53
8	2-Me THF	K_2CO_3 (1)	12	76
9	Water	K_2CO_3 (1)	10	49
10	PEG-600	K_2CO_3 (1)	7	73
11	DMF	Cs_2CO_3 (1)	10	74
12	DMF	Na_2CO_3 (1)	10	76
13	DMF	NaOEt (1)	9	67
14	DMF	KO^{t}Bu (1)	12	84
15	DMF	K_3PO_4 (1)	10	80
16	DMF	Et_3N (1)	12	41
17	DMF	DABCO (1)	12	52
18	DMF	K_2CO_3 (0.5)	20	56
19	DMF	K_2CO_3 (1.5)	7	88
20	DMF	--	30	31[d]
21	DMF	K_2CO_3 (1)	24	--[e]
22	DMF	K_2CO_3 (1)	16	67[f]
23	DMF	K_2CO_3 (1)	6	89[g]

[a] Reaction conditions: 0.5 mmol of **1a**, 0.75 mmol of **2a**, CO balloon and 1 mol% of 10 wt% Pd/C (5.3 mg) in 1 mL of solvent at 60 °C. [b] Isolated yield. [c] Reaction at rt for entry 1 and at 80 °C for entry 3. [d] Reaction without base. [e] Reaction without Pd/C. [f] 0.5 mol% of Pd/C was used. [g] 2 mol% of Pd/C was used.

To further improve the yield, various bases were screened. Cs_2CO_3 and Na_2CO_3 gave lower yields than K_2CO_3 (entries 11 and 12). Strong bases like NaOEt and KO^{t}Bu were also failed to improve the yield (entries 13 and 14). Organic bases such as Et_3N and DABCO provided diminished yield 41% and 52% of the product respectively (entries 16 and 17). Changing the base equivalents from 1 to 0.5 and 2 equivalents were also not fruitful (entries 18 and 19). Increase in the amount of catalyst loading from 1 mol% to 2 mol% of Pd/C had no significant effect on the yield. While decrease in the catalyst loading to 0.5 mol%, the yield of the product was decreased to 67% (entry 22). It is important to note that the reaction in the absence of base afforded 31% of **3a** and no product formation was observed in the absence of Pd/C (entries 20 and 21).

Having suitable optimized conditions in hand (Table 1, entry 2), the scope of the sulfoximinocarbonylation with regard to aryl iodide was next studied (Table 2). The generality of this method is proven by the reaction of **2a** with different substrates, which afforded the desired products (**3a-s**) in good to excellent yields. Aryl iodides bearing electron-donating substituents (Me, OMe and SMe) (**3a-e**) as well as electron-withdrawing substituents (CN, CF_3 and COOMe) (**3k-o**) resulted into good yield of *N*-aroyl sulfoximines. The carbonylation reaction of *para, meta* and *ortho*-substituted iodoarenes took place readily and delivered the products in good yields. Sulfoximinocarbonylation of iodobenzene and 1-iodonapthalene also afforded the desired products **3f**, **3q** in 92% and 94% yields respectively.

Table 2 Synthesis of *N*-aroyl sulfoximines with different aryl iodides[a,b]



[a] Reaction conditions: 0.5 mmol of **1**, 0.75 mmol of **2a**, CO balloon, 1 mL of DMF. [b] Isolated yield. [c] 4.6 mmol of **1a**, 6.9 mmol of **2a** in 10 mL of DMF.

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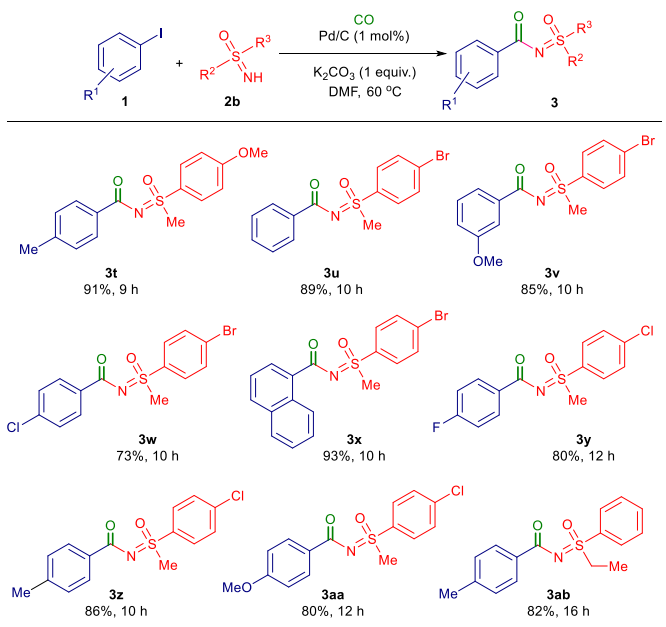
Iodoarenes having other halogen substitution like bromo, chloro and fluoro groups were observed to give only the mono *N*-aroylated products in very good yield (**3g-j**). *o*-Iodophenol underwent this carbonylation and afforded the product in moderate yield of 61%. Heteroaryl substrate like 2-iodothiophene was also efficiently transformed in this optimized condition furnished the product **3r** in 79% yield. Delightfully, the double carbonylation of 1,4-diiodobenzene proceeded smoothly and afforded desired *N*-aroyl sulfoximine **3s** in 88% yield. However, the carbonylation reaction of heteroaryl iodies like 2-iodopyridine, 3-iodopyridine and 3-iodo-1-methyl-1*H*-indole failed to provide the desired product.

To investigate the versatility of this methodology, a gram scale reaction of **1a** (1g) was performed with **2a** under optimized condition, and it afforded *N*-(4-methylbenzoyl)-*S*-methyl-*S*-phenyl sulfoximine (**3a**) in 88% yield (Table 2) proving its efficiency and practical utility.

Having established a good scope with aryl iodides, the optimized reaction condition was then applied to *N*H-sulfoximines having substituents at the aryl ring. The substituents such as methoxy, bromo and chloro, were applicable for this carbonylation reaction and afforded the product in good to excellent yields (Table 3, **3t-z** and **3aa**). *S*-ethyl-*S*-phenyl-*N*H-sulfoximine also provided the corresponding *N*-aroyl sulfoximine **3ab** in good yield.

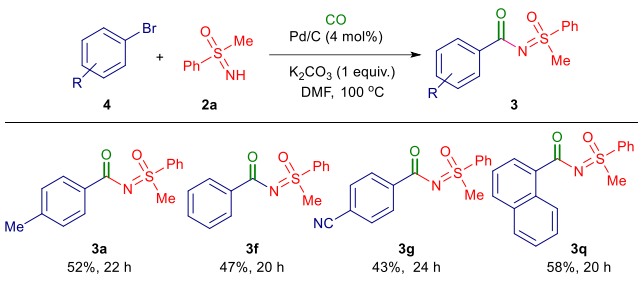
Table 3 Synthesis of *N*-aroyl sulfoximines with different *N*H-sulfoximines[a,b]



[a] Reaction conditions: 0.5 mmol of **1**, 0.75 mmol of **2b**, CO balloon, 1 mL of DMF. [b] Isolated yield.

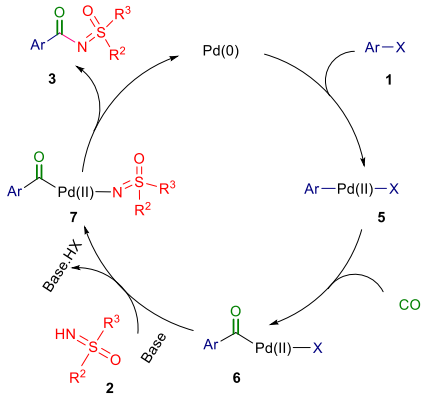
These results prompted to expand the scope of the sulfoximinocarbonylation with less reactive aryl bromides. Initial attempts to apply the above optimized reaction conditions to aryl bromide was unsuccessful. However, increasing the reaction temperature to 100 °C and higher catalyst loading helped to acquire the desired product. Next, few more bromoarenes were investigated under the optimized conditions and the results are given in Table 4. The sulfoximinocarbonylation of heteroaryl bromides like 2-bromopyridine, 3-bromopyridine and 5-bromoindole failed to occur.

Table 4 Synthesis of *N*-aroyl sulfoximines with different aryl bromides[a,b]



[a] Reaction conditions: 0.5 mmol of **1**, 0.75 mmol of **2a**, CO balloon, in 1 mL of DMF. [b] Isolated yield.

A plausible mechanism for the sulfoximinocarbonylation reaction of aryl iodide is depicted in Scheme 2.[22] Initially Pd(0) undergoes oxidative addition with aryl iodide to afford **5** which upon CO insertion furnish the acylpalladium complex **6**. Presumably nucleophilic attack of sulfoximine to **6** forms intermediate **7**. Finally, reductive elimination expelled the *N*-aroyl sulfoximine and regenerated the active Pd(0) catalyst.



Scheme 2 Plausible mechanism for Pd/C-catalyzed sulfoximinocarbonylation of aryl halide.

The reusability of Pd/C would make this process economically and environmentally benign. Thus we next tested the recyclability of the catalyst for carbonylation reaction of 4-iodotoluene **1a** and *S*-methyl-*S*-phenyl-sulfoximine **2a** under standard reaction condition. Pd/C has been easily recovered by centrifugation of reaction mixture and washed with nanopure water, methanol and dried under vacuum. The recovered catalyst shows good catalytic activity up to five reaction cycles (Table 5).

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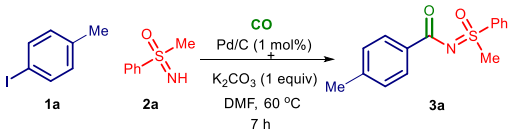
Table 5 Recycling of Pd/C catalyst



Run	1	2	3	4	5
Yield (%)[a]	91	89	90	88	85

[a] Isolated yield.

The reaction mixture after fifth cycle was examined by ICP-OES analysis. ICP analysis revealed that no detectable amount of palladium (0.02 ppm) was present in the reaction mixture which shows no significant leaching of palladium and it was further confirmed by hot filtration test and mercury poisoning test.[23]

Conclusion

In conclusion, the present study demonstrates Pd/C as an efficient heterogenous catalyst for the suloximino carbonylation of aryl halides. The developed procedure allows wide range of electron rich and poor substrates and furnished the *N*-aroylated sulfoximines in moderate to excellent yields. Further developement of this statergy with slight modified condition on aryl bromides afforded the product in moderate yield. The recyclability of Pd/C up to five reaction cycles without significant loss in its catalytic activity makes this methodology valuable for environmental and economic concerns.

Experimental Section

General Procedure for the synthesis of *N*-aroyl sulfoximine 3

Aryl iodide **1** (0.5 mmol), *N*H-sulfoximine **2** (0.75 mmol), Pd/C (5.3 mg) (1 mol%) and K_2CO_3 (0.5 mmol) were taken in a reaction tube with magnetic pellet and covered using septum. It was first evacuated (10 min) and DMF (1 mL) was added, again it was evacuated (10 min). CO balloon was introduced and stirred at 60 °C until the completion of the reaction (TLC). After completion, the reaction mixture was first extracted with ethyl acetate (3 X 5 mL), followed by brine solution. Then the organic layer was dried over Na_2SO_4 and concentrated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (hexanes:ethyl acetate) to get *N*-aroyl sulfoximine **3**.

***N*-(4-Methylbenzoyl)-*S*-methyl-*S*-phenyl sulfoximine (3a):**[21] Yield 91%; 124 mg; white solid; mp 161-163 °C [lit.168-169 °C];[21] R_f 0.40 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 3.45 (s, 3H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.56-7.62 (m, 2H), 7.63-7.70 (m, 1H), 8.00-8.08 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 44.4, 127.2, 128.8, 129.6, 129.7, 133.0, 133.8, 139.2, 142.8, 174.3; FTIR (KBr) 757, 840, 983, 1138, 1220, 1446, 1573, 1628, 2925, 3021 cm^{-1}; MS (*m*/*z*): [M]$^+$: 273.00.

***N*-(3-Methylbenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3b):**[21] Yield 81%; 110 mg; pale white solid; mp 75-77 °C [lit.78-80 °C];[21] R_f 0.42 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.39 (s, 3H), 3.46 (s, 3H), 7.27-7.35 (m, 2H), 7.57-7.65 (m, 2H), 7.67-7.72 (m, 1H), 7.93-8.01 (m, 2H), 8.03-8.08 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.3, 44.3, 126.6, 127.2, 128.0, 129.7, 130.0, 133.0, 133.8, 135.6, 137.7, 139.1, 174.5; FTIR (KBr) 749, 979, 1125, 1213, 1447, 1583, 1627, 2926, 3023 cm^{-1}; MS (*m*/*z*): [M]$^+$ 273.00.

***N*-(3-Methoxybenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3c):**[21] Yield 84%; 121 mg; pale white solid; mp 90-92 °C [lit.92-94 °C];[21] R_f 0.45 (40% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45 (s, 3H), 3.83 (s, 3H), 7.01-7.10 (m, 1H), 7.31 (t, *J* =8.0 Hz, 1H), 7.56-7.64 (m, 2H), 7.65-7.71 (m, 2H), 7.79 (d, *J*= 7.6 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.4, 55.5, 113.9, 118.8, 122.1, 127.2, 129.1, 129.8, 133.9, 137.1, 139.0, 159.5, 174.1; FTIR (KBr) 759, 982, 1119, 1222, 1285, 1580, 1627, 2931, 3012 cm^{-1}; MS (*m*/*z*): [M]$^+$ 289.00.

***N*-(3,4,5-Trimethoxybenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3d):**[21] Yield 87%; 152 mg; white solid, mp 136-138 °C [lit. 140-142 °C];[21] R_f 0.27 (40% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45 (s, 3H), 3.89 (s, 9H), 7.44 (s, 2H), 7.58-7.64 (m, 2H), 7.65-7.71 (m, 1H), 8.00-8.06 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.4, 56.3, 61.0, 106.7, 127.2, 129.8, 130.9, 133.9, 141.7, 152.7, 173.8; FTIR (KBr) 762, 998, 1127, 1224, 1335, 1580, 1624, 2935, 3006 cm^{-1}; HRMS (*m*/*z*): [M+Na]$^+$ calcd. for $C_{17}H_{19}NO_5SNa$: 372.0882; found: 372.0875.

***N*-((2-Methylthio)benzoyl)-*S*-methyl-*S*-phenylsulfoximine (3e):**[21] Yield 80%; 122 mg; colourless viscous liquid; R_f 0.30 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 2.37 (s, 3H), 3.44 (s, 3H), 7.10 (t, *J* = 7.6 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 7.35-7.41 (m, 1H), 7.55 (t, *J* = 8.4 Hz, 2H), 7.59-7.65 (m, 1H), 8.03 (d, *J*= 7.6 Hz, 2H), 8.17 (dd, *J*= 8.0, 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.8, 44.3, 123.2, 124.1, 127.2, 129.6, 131.6, 131.7, 132.5, 133.8, 138.7, 142.2, 174.6; FTIR (Neat) 713, 978, 1136, 1220, 1447, 1577, 1627, 2925, 3062 cm^{-1}; MS (*m*/*z*): [M]$^+$ 305.00.

***N*-Benzoyl-*S*-methyl-*S*-phenylsulfoximine (3f):**[21] Yield 92%; 119 mg; white solid, mp 114-116 °C [lit.120-122 °C];[21] R_f 0.36 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.42 (s, 3H), 7.35-7.41 (m, 2H), 7.48 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.54-7.60 (m, 2H), 7.64 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.99-8.06 (m, 2H), 8.13-8.19 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.3, 127.1, 128.0, 129.4, 129.7, 132.2, 133.8, 135.5, 138.8, 174.2; FTIR (KBr) 713, 978, 1136, 1220, 1447, 1577, 1627, 2925, 3062 cm^{-1}; MS (*m*/*z*): [M]$^+$ 258.75.

***N*-(4-Chlorobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3g):**[21] Yield 82%; 120 mg; white solid; mp 111-113 °C [lit. 114-116 °C];[21] R_f 0.42 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.47 (s, 3H), 7.38 (d, *J*= 8.4 Hz, 2H), 7.59-7.66 (m, 2H), 7.40 (tt, *J*= 7.2, 1.2 Hz, 1H), 8.01-8.06 (m, 2H), 8.10 (d, *J*= 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.5, 127.2, 128.4, 129.9, 131.0, 134.0, 134.2, 138.6, 138.9, 173.3; FTIR (KBr) 763, 836, 978, 1136, 1281, 1588, 1627, 2926, 3065 cm^{-1}; MS (*m*/*z*): [M]$^+$ 292.70.

***N*-(3-Fluorobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3h):**[21] Yield 74%; 102 mg; white solid; mp 79-81 °C [lit. 86-88 °C];[21] R_f 0.39 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45 (s, 3H), 7.18 (tdd, *J* = 8.4, 2.8, 0.8 Hz, 1H), 7.32-7.41 (m, 1H), 7.56-7.64 (m, 2H), 7.67 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.79-7.85 (m, 1H), 7.93 (dt, *J* = 8.0, 1.2 Hz, 1H), 7.99-8.05 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.4, 116.2 (d, J_{C-F} = 22.0 Hz), 119.1 (d, J_{C-F} = 21.0 Hz), 125.1 (d, J_{C-F} = 3.0 Hz), 127.2, 129.6, 129.8, 134.0, 138.0 (d, J_{C-F} = 7.0 Hz), 138.7, 162.6, (d, J_{C-F} = 245 Hz), 173.0 (d, J_{C-F} = 2.0 Hz); ^{19}F NMR ($CDCl_3$, 470 MHz) δ -116.5; FTIR (KBr) 760, 813, 982, 1110, 1220, 1291, 1587, 1629, 2930, 3020 cm^{-1}; MS (*m*/*z*): $[M]^+$ 277.05.

***N*-(3-Chlorobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3i):**[21] Yield 77%; 113 mg; white solid; mp 101-103 °C [lit. 106-108 °C];[21] R_f 0.40 (30% ethylacetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.46 (s, 3H), 7.34 (t, *J* = 8.0 Hz, 1H), 7.44-7.50 (m, 1H), 7.62 (t, *J* = 7.6 Hz, 2H), 7.66-7.72 (m, 1H), 8.00-8.06 (m, 3H), 8.14 (t, *J* = 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.4, 127.2, 127.6, 129.4, 129.6, 129.8, 132.1, 134.0, 134.2, 137.5, 138.7, 172.9; FTIR (KBr) 748, 980, 1146, 1221, 1565, 1627, 2927, 3022 cm^{-1}; MS (*m*/*z*): $[M]^+$ 292.85.

***N*-(2-Bromobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3j):**[21] Yield 79%; 113 mg; white solid; mp 89-91 °C [lit. 89-91 °C];[21] R_f 0.30 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.49 (s, 3H), 7.24 (td, *J* = 7.6, 1.6 Hz, 1H), 7.33 (td, *J* = 7.6, 1.6 Hz, 1H), 7.58-7.66 (m, 3H), 7.67-7.73 (m, 1H), 7.80 (dd, *J* = 7.6, 1.6 Hz, 1H), 8.08-8.14 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.3, 120.4, 127.2, 127.4, 129.8, 130.7, 131.3, 133.8, 134.1, 138.5, 175.1; FTIR (KBr) 743, 981, 1146, 1220, 1447, 1584, 1633, 2924, 3061 cm^{-1}.

***N*-(4-Cyanobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3k):**[21] Yield 81%; 115 mg; white solid; mp 81-83 °C [lit. 78-80 °C];[21] R_f 0.22 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.48 (s, 3H), 7.60-7.66 (m, 2H), 7.67-7.74 (m, 3H), 8.01-8.06 (m, 2H), 8.24 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.3, 115.3, 118.5, 127.1, 129.8, 129.9, 131.9, 134.2, 138.3, 139.5, 172.3; FTIR (KBr) 739, 839, 983, 1136, 1283, 1447, 1561, 1629, 2926, 3019 cm^{-1}; MS (*m*/*z*): $[M]^+$ 284.15.

***N*-(4-Trifluorobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3l):**[21] Yield 82%; 134 mg; white solid; mp 105-107 °C [lit. 102-104 °C];[21] R_f 0.40 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.47 (s, 3H), 7.58-7.67 (m, 4H), 7.69 (tt, *J* = 7.2, 1.6 Hz, 1H), 8.00-8.07 (m, 2H), 8.26 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.4, 124.0 (q, *J* = 271.0 Hz), 125.1(q, J_{C-F} = 3.0 Hz), 127.2, 129.8, 133.6 (q, J_{C-F} = 32.0 Hz), 134.2, 138.6, 138.8, 173.0; ^{19}F NMR ($CDCl_3$, 470 MHz) δ -66.0; FTIR (KBr) 737, 863, 979, 1174, 1283, 1320, 1449, 1580, 1629, 2923, 3058 cm^{-1}; MS (*m*/*z*): 327.05.

***N*-(4-Nitrobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3m):**[21] Yield 87%; 132 mg; pale yellow solid; mp 128-130 °C [lit. 126-128 °C];[21] R_f 0.48 (40% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.50 (s, 3H), 7.61-7.67 (m, 2H), 7.72 (tt, *J*= 7.2, 1.2 Hz, 1H), 8.02-8.07 (m, 2H), 8.21-8.26 (m, 2H), 8.28-8.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.5, 123.3, 127.2, 130.0, 130.5, 134.4, 138.4, 141.1, 150.1, 172.2; FTIR (KBr) 720, 830, 978, 1275, 1347, 1521, 1599, 1632, 2855, 2925 cm^{-1}; MS (*m*/*z*): $[M]^+$ 304.05.

***N*-(3-Nitrobenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3n):**[21] Yield 84%; 127 mg; pale yellow solid; mp 102-104 °C [lit. 103-105 °C];[21] R_f 0.44 (40% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ δ 3.48 (s, 3H), 7.56 (d, *J*= 8.0 Hz, 1H), 7.59-7.66 (m, 2H), 7.67-7.72 (m, 1H), 7.99-8.06 (m, 2H), 8.31 (ddd, *J*= 8.4, 6.4, 1.2 Hz, 1H), 8.42 (dt, *J*= 7.6, 1.2 Hz, 1H), 8.94 (t, *J*= 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.4, 124.4, 126.6, 127.1, 129.2, 129.9, 134.2, 135.1, 137.4, 138.2, 148.1, 171.8; FTIR(KBr) 720, 981, 1152, 1291, 1528, 1631, 2921, 3050 cm^{-1}; HRMS (*m*/*z*): $[M+Na]^+$ calcd. for $C_{14}H_{12}N_2O_4SNa$: 327.0415; found: 327.0406.

***N*-(4-Methylcarbonylesterbenzoyl)-*S*-methyl-*S*-phenyl sulfoximine (3o):**[21] Yield 90%; 142 mg; white solid; mp 122-124 °C [lit. 121-123 °C];[21] R_f 0.48 (40% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.47 (s, 3H), 3.91 (s, 3H), 7.57-7.65 (m, 2H), 7.66-7.72 (m, 1H), 8.00-8.09 (m, 4H), 8.19 (d, *J*= 7.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.4, 52.4, 127.2, 129.3, 129.4, 129.8, 133.1, 134.1, 138.7, 139.5, 166.7, 173.4; FTIR (KBr) 732, 820, 983, 1139, 1221, 1278, 1447, 1572, 1630, 1719, 2929, 3019 cm^{-1}; MS (*m*/*z*): $[M]^+$ 317.00.

***N*-(2-Hydroxybenzoyl)-*S*-methyl-*S*-phenylsulfoximine (3p):**[21] Yield 61%; 83 mg; brown viscous liquid; R_f 0.41 (40% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.47 (s, 3H), 6.82-6.89 (m, 1H), 6.92 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.36-7.44 (m, 1H), 7.60-7.68 (m, 2H), 7.72 (tt, *J* = 7.6, 1.6 Hz, 1H), 8.01-8.07 (m, 2H), 8.09 (dd, *J* = 8.0, 1.6 Hz, 1H), 11.84 (br s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.9, 117.5, 117.6, 118.7, 127.2, 130.0, 131.2, 134.3, 135.1, 138.5, 162.2, 178.3; FTIR (Neat) 759, 982, 1159, 1223, 1340, 1482, 1590, 1627, 2928, 3020, 3449 cm^{-1}; MS (*m*/*z*): $[M]^+$ 275.00.

***N*-(1-Naphthoyl)-*S*-methyl-*S*-phenylsulfoximine (3q):**[21] Yield 94%; 145 mg; colourless viscous liquid; R_f 0.34 (30% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.44 (s, 3H), 7.45-7.59 (m, 5H), 7.63 (tt, *J* = 7.2, 1.2 Hz, 1H), 7.81-7.86 (m, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 8.03-8.08 (m, 2H), 8.36 (dd, *J* = 7.2, 1.2 Hz, 1H), 9.01 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.4, 124.5, 125.9, 126.4, 127.1, 127.2, 128.3, 129.7, 129.8, 131.3, 132.3, 132.8, 133.8, 133.9, 138.7, 176.5; FTIR (KBr) 731, 973, 1146, 1297, 1509, 1586, 1625, 2930, 3055 cm^{-1}.

***N*-(Thiophene-2-carbonyl)-*S*-methyl-*S*-phenylsulfoximine (3r):** Yield 79%; 104 mg; white solid; mp 116-118 °C; R_f 0.45 (40% ethyl acetate in hexanes); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 3.45 (s, 3H), 7.06 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.48 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.57-7.64 (m, 2H), 7.68 (tt, *J* = 7.2, 1.6 Hz, 1H), 7.79 (dd, *J* = 3.6, 1.2 Hz, 1H), 8.01-8.07 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.5, 127.3, 127.8, 129.8, 131.7, 132.2, 134.0, 141.2, 169.0; FTIR (KBr) 735, 975, 1119, 1219, 1273, 1518, 1609, 2919, 3079 cm^{-1}; HRMS (*m*/*z*): $[M+H]^+$ calcd. for $C_{12}H_{12}NO_2S_2$: 266.0309; found: 266.0291.

***N,N*-(Terephthaloyl)bis(*S*-methyl-*S*-phenylsulfoximine) (3s):** Yield 88%; 194 mg; white solid; mp 190-192 °C; R_f 0.31 (60% ethyl acetate in hexanes); ^{1}H NMR (DMSO-d_6, 400 MHz) δ 3.65 (s, 6H), 7.68-7.74 (m, 4H), 7.75-7.85 (m, 3H), 8.03-8.10 (m, 7H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ 41.4, 125.3, 126.9, 127.8, 132.0, 136.7, 136.8, 170.3; FTIR (KBr) 733, 969, 1132, 1211,

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1267, 1446, 1601, 2920, 3020 cm^{-1}; HRMS (*m/z*): $[M+H]^+$ calcd. for $C_{22}H_{21}N_2O_4S_2$: 441.0943; found: 441.0971.

***N*-(4-Methylbenzoyl)-*S*-methyl-*S*-(4-methoxyphenyl) sulfoximine (3t):**[21] Yield 91%; 138 mg; white solid; mp 106-108 °C [lit. 111-113 °C];[21] R_f 0.42 (40% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ δ 2.38 (s, 3H), 3.43 (s, 3H), 3.86 (s, 3H), 7.04-7.07 (m, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.93-8.00 (m, 2H), 8.05 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 44.8, 55.8, 115.0, 128.8, 129.4, 129.5, 130.2, 133.2, 142.6, 163.9, 174.3; FTIR (KBr) 831, 982, 1139, 1282, 1593, 1624, 2929, 3019 cm^{-1}.

***N*-Benzoyl-*S*-methyl-*S*-(4-bromophenyl)sulfoximine (3u):** Yield 89%; 150 mg; white solid; mp 102-104 °C; R_f 0.54 (30% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) 3.45 (s, 3H), 7.38-7.44 (m, 2H), 7.52 (tt, *J* = 7.6, 1.6 Hz, 1H), 7.75 (d, *J* = 8.4 2H), 7.91 (d, *J* = 8.4 Hz, 2H), 8.11-8.16 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.5, 128.2, 128.9, 129.3, 129.6, 132.5, 133.1, 135.4, 138.2, 174.3; FTIR (KBr) 712, 821, 981, 1135, 1281, 1571, 1628, 2925, 3020 cm^{-1}; MS (*m/z*): $[M]^+$ 336.75, $[M+2]^+$ 338.75.

***N*-(3-Methoxybenzoyl)-*S*-methyl-*S*-(4-bromophenyl) sulfoximine (3v):** Yield 85%; 156 mg; white solid; mp 98-100 °C; R_f 0.45 (30% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.43 (s, 3H), 3.83 (s, 3H), 7.06 (d, *J* = 8.0 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.66 (s, 1H), 7.73-7.78 (m, 3H), 7.89 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.4, 55.5, 113.8, 118.9, 122.1, 128.8, 129.1, 129.2, 133.1, 126.8, 138.1, 159.5, 174.0; FTIR (KBr) 759, 803, 983, 1118, 1222, 1286, 1579, 1627, 2927, 3014 cm^{-1}.

***N*-(4-Chlorobenzoyl)-*S*-methyl-*S*-(4-bromophenyl)sulfoximine (3w):** Yield 73%; 136 mg; white solid; mp 116-118 °C; R_f 0.57 (30% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.44 (s, 3H), 7.37 (d, *J* = 8.4 Hz, 2H), 7.75 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 8.4 Hz, 2H), 8.07 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.5, 128.5, 128.8, 129.5, 131.0, 133.2, 133.9, 138.0, 138.8, 173.3; FTIR (KBr) 819, 978, 1136, 1215, 1281, 1567, 1622, 2922, 3010 cm^{-1}; MS (*m/z*): $[M]^+$ 370.35, $[M+2]^+$ 372.20.

***N*-(1-Naphthoyl)-*S*-methyl-*S*-(4-bromophenyl)sulfoximine (3x):** Yield 93%; 180 mg; colourless viscous liquid; R_f 0.54 (30% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.43 (s, 3H), 7.44-7.57 (m, 3H), 7.71 (d, *J* = 8.8 Hz, 2H), 7.83-7.87 (m, 1H), 7.90 (d, *J* = 8.8 Hz, 2H), 7.96 (d, *J* = 8.4 Hz, 1H), 8.34 (dd, *J* = 7.2, 1.6 Hz, 1H), 8.96-9.02 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.4, 124.5, 126.0, 126.4, 127.4, 128.4, 128.8, 129.2, 130.1, 131.4, 132.5, 132.6, 133.1, 133.9, 138.0, 176.4; FTIR (Neat) 782, 820, 973, 1147, 1220, 1246, 1571, 1630, 2927, 3054 cm^{-1}; MS (*m/z*): $[M]^+$ 386.70, $[M+2]^+$ 388.95.

***N*-(4-Fluorobenzoyl)-*S*-methyl-*S*-(4-chlorophenyl)sulfoximine (3y):** Yield 80%; 124 mg; white solid; mp 86-88 °C; R_f 0.52 (30% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.44 (s, 3H), 7.02-7.11 (m, 2H), 7.58 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 8.10-8.18 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.5, 115.2 (d, J_{C-F} = 21.0 Hz), 128.8, 130.2, 131.7 (d, J_{C-F} = 3.0 Hz), 132.0 (d, J_{C-F} = 9.0 Hz), 137.5, 140.8, 165.6 (d, J_{C-F} = 251.0 Hz), 173.2; ^{19}F NMR ($CDCl_3$, 470 MHz) δ -110.4; FTIR (KBr) 766, 830, 980, 1143, 1282, 1502, 1629, 2935, 3020 cm^{-1}; MS (*m/z*): $[M]^+$ 311.05.

***N*-(4-Methylbenzoyl)-*S*-methyl-*S*-(4-chlorophenyl)sulfoximine (3z):** [21] Yield 86%; 132 mg; white solid; mp 118-120 °C [lit. 122-124 °C];[21] R_f 0.41 (30% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 2.40 (s, 3H), 3.44 (s, 3H), 7.21 (d, *J* = 8.0 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 8.03 (d, *J* = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.7, 44.5, 128.8, 128.9, 129.6, 130.1, 132.8, 137.7, 140.7, 143.0, 174.3; FTIR (KBr) 829, 984, 1136, 1222, 1573, 1625, 2925, 3022 cm^{-1}; MS (*m/z*): $[M]^+$ 306.85.

***N*-(4-Methoxybenzoyl)-*S*-methyl-*S*-(4-chlorophenyl) sulfoximine (3aa):** Yield 80%; 129 mg; pale white solid; mp 106-108 °C; R_f 0.36 (40% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 3.43 (s, 3H), 3.85 (s, 3H), 6.89 (d, *J* = 8.8 Hz, 2H), 7.57 (d, *J* = 8.8 Hz, 2H), 7.97 (d, *J* = 8.8 Hz, 2H), 8.10 (d, *J* = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.6, 55.5, 113.4, 128.1, 128.8, 130.1, 131.6, 137.9, 140.6, 163.1, 173.8; FTIR (KBr) 814, 973, 1131, 1252, 1467, 1610, 2959, 3016 cm^{-1}; MS (*m/z*): $[M]^+$ 322.95.

***N*-(4-Methylbenzoyl)-*S*-ethyl-*S*-phenylsulfoximine (3ab):**[21] Yield 81%; 116 mg; pale yellow solid, mp 122-124 °C [lit. 127-129 °C];[21] R_f 0.40 (30% ethyl acetate in hexanes); ^1H NMR ($CDCl_3$, 400 MHz) δ 1.29 (t, *J* = 7.2 Hz, 3H), 2.39 (s, 3H), 3.59 (q, *J* = 7.2 Hz, 2H), 7.21 (d, *J* = 7.6 Hz, 2H), 7.56-7.61 (m, 2H); 7.66 (tt, *J* = 7.6, 1.2 Hz, 1H), 7.96-8.01 (m, 2H); 8.07 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 7.4, 21.7, 50.7, 128.1, 128.8, 129.6, 129.7, 133.2, 133.8, 136.8, 142.7, 174.3; FTIR (KBr) 755, 836, 929, 1173, 1283, 1446, 1571, 1625, 2977, 3060 cm^{-1}; MS (*m/z*): $[M]^+$ 286.65.

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Notes and references

1 (a) H. M. Colquhoun, D. J. Thompson and M. V. Twigg, *Carbonylation: Direct Synthesis of Carbonyl Compounds*; Plenum Press: New York, 1991; (b) S. T. Gadge and B. M. Bhanage, *RSC Adv.*, 2014, **4**, 10367-10389; (c) C. F. J. Barnard, *Organometallics*, 2008, **27**, 5402-5422.

2 (a) J. R. Martinelli, D. A. Watson, D. M. M. Freckmann, T. E. Barder and S. L. Buchwald, *J. Org. Chem.*, 2008, **73**, 7102-7107; (b) J. A. Marshall and M. Wolf, *J. Org. Chem.*, 1996, **61**, 3238-3239.

3 H. Cao, L. McNamee and H. Alper, *J. Org. Chem.*, 2008, **73**, 3530-3534.

4 (a) X.-F. Wu, H. Neumann and M. Beller, *ChemSusChem*, 2013, **6**, 229-241; (b) E. Amadio, Z. Freixa, P. W. N. M. van Leeuwen and L. Toniolo, *Catal. Sci. Technol.*, 2015, **5**, 2856-2864; (c) F. Ji, X. Li, W. Wu and H. Jiang, *J. Org. Chem.*, 2014, **79**, 11246-11253.

5 (a) H. Cao, W.-J. Xiao and H. Alper, *Adv. Synth. Catal.*, 2006, **348**, 1807-1812; (b) Y. Uozumi, T. Arii and T. Watanabe, *J. Org. Chem.*, 2001, **66**, 5272-5274.

6 (a) J. Schranck, M. Burhardt, C. Bornschein, H. Neumann, T. Skrydstrup and M. Beller, *Chem. - Eur. J.*, 2014, **20**, 9534-9538; (b) M. T. Jensen, M. Juhl, D. U. Nielsen, M. F. Jacobsen, A. T. Lindhardt and T. Skrydstrup, *J. Org. Chem.*, 2016, **81**, 1358-1366.
7 (a) J. Schranck, X.-F. Wu, H. Neumann and M. Beller, *Chem. - Eur. J.*, 2012, **18**, 4827-4831; (b) T. M. Goegsig, D. U. Nielsen, A. T. Lindhardt and T. Skrydstrup, *Org. Lett.*, 2012, **14**, 2536-2539.
8 M. V. Khedkar, P. J. Tambade, Z. S. Qureshi and B. M. Bhanage, *Eur. J. Org. Chem.*, 2010, 6981-6986.
9 (a) X.-F. Wu, P. Anbarasan, H. Neumann and M. Beller, *Angew. Chem., Int. Ed.*, 2010, **49**, 7316-7319; (b) Z. Lian, S. D. Friis and T. Skrydstrup, *Chem. Commun.,* 2015, **51**, 1870-1873.
10 X.-F. Wu, H. Neumann and M. Beller, *Chem. Rev.,* 2013, **113**, 1-35.
11 (a) J. Mitra, X. Zhou and T. Rauchfuss, *Green Chem.*, 2015, **17**, 307-313; (b) S. N. Jadhav, A. S. Kumbhar, C. V. Rode and R. S. Salunkhe, *Green Chem.*, 2016, **18**, 1898-1911.
12 (a) C. Liu, X. Rao, Y. Zhang, X. Li, J. Qiu and Z. Jin, *Eur. J. Org. Chem.*, 2013, **2013**, 4345-4350; (b) T. Maegawa, Y. Kitamura, S. Sako, T. Udzu, A. Sakurai, A. Tanaka, Y. Kobayashi, K. Endo, U. Bora, T. Kurita, A. Kozaki, Y. Monguchi and H. Sajiki, *Chem. - Eur. J.*, 2007, **13**, 5937-5943; (c) V. Subramanian, V. R. Batchu, D. Barange and M. Pal, *J. Org. Chem.*, 2005, **70**, 4778-4783.
13 (a) H. Yu, R. N. Richey, W. D. Miller, J. Xu and S. A. May, *J. Org. Chem.*, 2011, **76**, 665-668; (b) H. Hagiwara, Y. Shimizu, T. Hoshi, T. Suzuki, M. Ando, K. Ohkubo and C. Yokoyama, *Tetrahedron Lett.*, 2001, **42**, 4349-4351; (c) Y. Cheng, Q. Peng, W. Fan and P. Li, *J. Org. Chem.*, 2014, **79**, 5812-5819; (d) F.-X. Felpin, *J. Org. Chem.*, 2005, **70**, 8575-8578; (e) R. S. Mane and B. M. Bhanage, *J. Org. Chem.*, 2016, **81**, 1223-1228.
14 (a) S. P. Chavan and B. M. Bhanage, *Tetrahedron Lett.*, 2014, **55**, 1199-1202; (b) S. T. Gadge, M. V. Khedkar, S. R. Lanke and B. M. Bhanage, *Adv. Synth. Catal.*, 2012, **354**, 2049-2056; (c) S. T. Gadge and B. M. Bhanage, *J. Org. Chem.*, 2013, **78**, 6793-6797; R. S. Mane and B. M. Bhanage, *RSC Adv.*, 2015, **5**, 76122-76127.
15 (a) C. R. Johnson, *Accounts Chem. Res.*, 1973, **6**, 341-347; (b) M. Reggelin and C. Zur, *Synthesis*, 2000, 1-64; (c) V. Bizet, R. Kowalczyk and C. Bolm, *Chem. Soc. Rev.*, 2014, **43**, 2426-2438.
16 (a) U. Luecking, *Angew. Chem., Int. Ed.,* 2013, **52**, 9399-9408; (b) D. Lu, Y. Y. Sham and R. Vince, *Bioorg. Med. Chem.,* 2010, **18**, 2037-2048; (c) U. Luecking, R. Jautelat, M. Krueger, T. Brumby, P. Lienau, M. Schaefer, H. Briem, J. Schulze, A. Hillisch, A. Reichel, A. M. Wengner and G. Siemeister, *ChemMedChem,* 2013, **8**, 1067-1085; (d) P. Miller and G. W. L. James, *Arch. Int. Pharmacodyn. Ther.,* 1978, **231**, 328-339; e) A. C. Barnes, P. W. Hairsine, S. S. Matharu, P. J. Ramm and J. B. Taylor, *J. Med. Chem.,* 1979, **22**, 418-424; (f) S. J. Park, H. Baars, S. Mersmann, H. Buschmann, J. M. Baron, P. M. Amann, K. Czaja, H. Hollert, K. Bluhm, R. Redelstein and C. Bolm, *ChemMedChem,* 2013, **8**, 217-220; (g) X. Y. Chen, H. Buschmann and C. Bolm, *Synlett,* 2012, **23**, 2808-2810.
17 Y.-M. Zhu, M. R. Loso, G. B. Watson, T. C. Sparks, R. B. Rogers, J. X. Huang, B. C. Gerwick, J. M. Babcock, D. Kelley, V. B. Hegde, B. M. Nugent, J. M. Renga, I. Denholm, K. Gorman, G. J. DeBoer, J. Hasler, T. Meade and J. D. Thomas, *J. Agric. Food Chem.,* 2011, **59**, 2950-2957.
18 (a) M. Frings, D. Goedert and C. Bolm, *Chem. Commun.,* 2010, **46**, 5497-5499; b) M. Frings, I. Thome and C. Bolm, *Beilstein J. Org. Chem.,* 2012, **8**, 1443-1451.
19 (a) C. Bolm, C. P. R. Hackenberger, O. Simic, M. Verrucci, D. Muller and F. Bienewald, *Synthesis*, 2002, 879-887; (b) C. P. R. Hackenberger, G. Raabe and C. Bolm, *Chem. - Eur. J.*, 2004, **10**, 2942-2952.
20 (a) L. Wang, D. L. Priebbenow, L.-H. Zou and C. Bolm, *Adv. Synth. Catal.,* 2013, **355**, 1490-1494; (b) W.-J. Qin, Y. Li, X. Yu and W.-P. Deng, *Tetrahedron,* 2015, **71**, 1182-1186; (c) Z. Zhao, T. Wang, L. Yuan, X. Jia and J. Zhao, *RSC Adv.,* 2015, **5**, 75386-75389; (d) Y. Zou, J. Xiao, Z. Peng, W. Dong and D. An, *Chem. Commun.,* 2015, **51**, 14889-14892; (e) M. Muneeswara, S. S. Kotha and G. Sekar, *Synthesis,* 2016, **48**, 1541-1549; (f) A. Porey, S. Santra and J. Guin, *Asian J. Org. Chem.,* 2016, **5**, 870-873.
21 N. Sharma and G. Sekar, *RSC Adv.,* 2016, **6**, 37226- 37235.
22 B. Liegault, J.-L. Renaud and C. Bruneau, *Chem. Soc. Rev.*, 2008, **37**, 290-299.
23 See the supporting information for detailed procedure.

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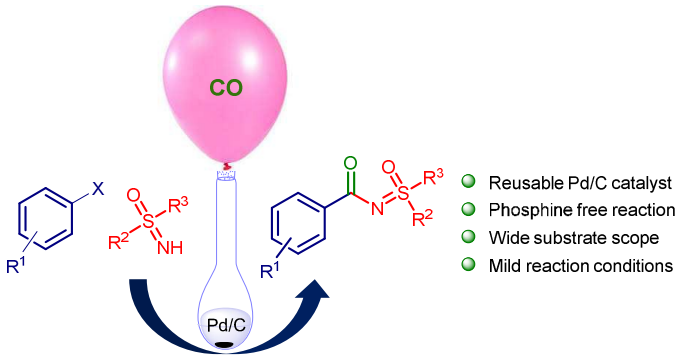

Heterogeneous Pd/C catalyzed three component protocol is developed for the sulfoximinocarbonylation of aryl halides.