An Easy Direct Arylation of 3-Arylsydnones

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Abstract: An easy one-step synthesis of 3,4-diarylsydnones from 3-arylsydnones and arylboronic acids by Pd-catalyzed C–H bond activation is described.

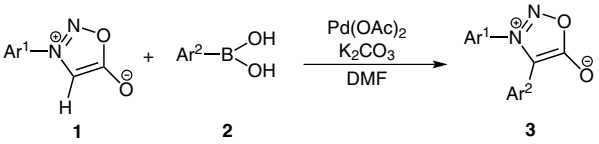
Key words: arylation, sydnones, arylboronic acids, $Pd(OAc)_2$, C–H bond activation

Sydnones are a class of unique, dipolar, mesoionic, five-membered heteroaromatic compounds. These compounds have long attracted considerable interest in the field of chemical synthesis, and thus their chemistry has been widely studied.[1] Over the years, numerous sydnone compounds have been prepared or investigated because of their biological values as antibacterial,[2] antitumor,[3] antimalarial,[4] anti-inflammatory,[5] antihypertensive, analgesic, and antipyretic[6] activities. These compounds can also be used as liquid crystals[7] and electrolytic solvents.[8]

Sydnones can undergo a variety of reactions such as electrophilic aromatic substitutions, 1,3-dipolar cycloadditions, and metalations, which normally occur at the 4-position (if unsubstituted).[9] Among the metalations, lithiation has been the most studied. In lithiation, butyllithium initially deprotonates sydnones at the 4-position, and then the resulting lithiosydnone species react with various electrophiles to generate the corresponding products.[10] Recently, the direct transformation of C–H bond into C–C bond has been found to offer a cleaner and more efficient method of meeting such goals. However, rare examples of such transformations have been described.[11] In particular, the arylation of sydnones by the method of Suzuki coupling reaction often needs preformation of halosydnone,[12] and the direct arylation of sydnones by arylboronic acids has not yet been reported.

In the present study, we report a convenient and catalytic ligand-free synthesis of a series of 3,4-diarylsydnones **3** from 3-arylsydnones **1** and arylboronic acids **2** (Scheme 1). The direct arylation of 3-arylsydnones by Pd-catalyzed C–H bond activation was utilized.

To determine the suitable reaction conditions, 3-(4-methoxyphenyl) sydnone (**1a**) and phenylboronic acid (**2a**) were used as model substrates. A mixture of **1a**, **2a**, $Pd(OAc)_2$, and acetic acid was stirred in the dark under air



1 2 3

Scheme 1 Synthesis of 3,4-diarylsydnones by direct arylation of 3-arylsydnones

(1 atm) in an open tube at 90 °C using an oil bath. After 12 hours, product **3a** was isolated in 16% yield. The effects of different bases and various catalysts in different solvents at various reaction temperatures under different atmosphere on the formation of **3a** were investigated. The optimization of this direct arylation between **1a** and **2a** is summarized in Table 1.

When **1a** was reacted with **2a** in the presence of $Pd(OAc)_2$ as a catalyst and KOAc as a base in acetic acid (90 °C, 12 h), the desired product **3a** was generated smoothly in 62% yield. Changing KOAc and acetic acid to K_2CO_3 and DMF increased the yield to 90% (Table 1, entries 2, 3). Under the above mentioned conditions, several solvents were examined. When the solvent DMF was changed to toluene, xylene, and DMSO, the yields decreased to 43%, 30%, and 65%, respectively (entries 4–6). Changing the base K_2CO_3 to Cs_2CO_3 decreased the yield to 78% (entry 7). When no base was used in the reaction, only traces of **3a** were obtained (entry 8).When Ph_3P as a catalytic ligand was added to the reaction, the yield decreased to 84% (entry 9). Various reaction temperatures were also studied. When the reaction temperatures were 120, 60, and 25 °C, the yields decreased to 48%, 72%, and 21%, respectively (entries 10–12).

The effects of different catalysts on **3a** formation were also remarkable. When no catalyst was used in the reaction, traces of **3a** were obtained (entry 13). Changing $Pd(OAc)_2$ to CuI and $FeCl_3$ decreased the yields to 10% and 5%, respectively (entries 14, 15). When $Cu(OAc)_2$ was used as a catalyst, product **3a** was not obtained (entry 16). Different atmosphere was also examined, when the reaction was under oxygen (1 atm) in a sealed tube, product **3a** could also be obtained in 90% yield (entry 17), but in view of the cheapness and convenience of air, we choose the oxygen of the air as the oxidant of the reaction. Ultimately, the optimum reaction conditions were determined as 2.0 equivalents of K_2CO_3 as base, 0.1 equivalent of $Pd(OAc)_2$ as catalyst, DMF as solvent, 1:2 mol ratio of

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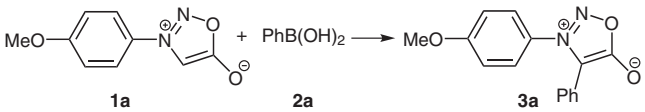
Table 1 Optimization of the Synthesis of **3a**[a]



1a **2a** **3a**

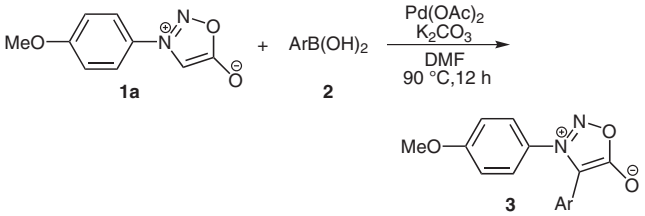
Entry	Base (2 equiv)	Catalyst (0.1 equiv)	Solvent	Temp (°C)	Yield (%)[b]
1	none	$Pd(OAc)_2$	AcOH	90	16
2	KOAc	$Pd(OAc)_2$	AcOH	90	62
3	**K_2CO_3**	**$Pd(OAc)_2$**	**DMF**	**90**	**90**
4	K_2CO_3	$Pd(OAc)_2$	toluene	90	43
5	K_2CO_3	$Pd(OAc)_2$	xylene	90	30
6	K_2CO_3	$Pd(OAc)_2$	DMSO	90	65
7	Cs_2CO_3	$Pd(OAc)_2$	DMF	90	78
8	none	$Pd(OAc)_2$	DMF	90	traces
9[c]	K_2CO_3	$Pd(OAc)_2$	DMF	90	84
10	K_2CO_3	$Pd(OAc)_2$	DMF	120	48
11	K_2CO_3	$Pd(OAc)_2$	DMF	60	72
12	K_2CO_3	$Pd(OAc)_2$	DMF	25	21
13	K_2CO_3	none	DMF	90	traces
14	K_2CO_3	CuI[d]	DMF	90	10
15	K_2CO_3	$FeCl_3$[e]	DMF	90	5
16	K_2CO_3	$Cu(OAc)_2$[f]	DMF	25	0
17[g]	K_2CO_3	$Pd(OAc)_2$	DMF	90	90

[a] Reaction conditions: **1a** (1.0 equiv) and **2a** (2.0 equiv) were stirred in the dark under air (1 atm) in an open tube for 12 h.
[b] Isolated yield.
[c] Ph_3P: 0.2 equiv.
[d] CuI: 0.2 equiv.
[e] $FeCl_3$: 0.3 equiv.
[f] $Cu(OAc)_2$: 0.2 equiv.
[g] Under oxygen (1 atm) in a sealed tube.

1a to **2a**, 90 °C, air atmosphere, and 12 hours in the dark (entry 3).

Under the optimized conditions, a series of arylboronic acid substrates **2** were examined. Table 2 shows that all desired 4-aryl-3-(4-methoxyphenyl)sydnones **3** were generated smoothly in moderate to good yields. The phenyl of arylboronic acids **2** carrying either an electron-donating group such as methoxyl (**2b**, **2c** and **2d**), or an electron-withdrawing substituent including fluorine (**2e** and **2f**) and nitryl (**2g**) proceeded smoothly. Higher yields were obtained when the phenyl of arylboronic acids **2** carried an electron-withdrawing group. The presence of a strong electron-withdrawing group in the phenyl of arylboronic acids **2e** and **2g** significantly increased the reaction yield (Table 2, entries 5, 7). On the other hand, the presence of an electron-donating substituent on the phenyl of arylboronic acids **2b** and **2c** provided relatively low yields of sydnones **3**. Lower yields were obtained when the substrates had an electron-donating substituent at the *para*-position than that at the *meta*-position because an electron-donating group at the *para*-position exerts a stronger electron-donating inductive effect than a group at the *meta*-position (entries 2, 3). Lower yields were also obtained when the substrates had a substituent at the *ortho*-position than that at the *para*-position, the result may be caused by the effect of steric hindrance of the substituent at the *ortho*-position (cf. **3b** and **3e** with **3d** and **3f)**. Naphthalen-1-yl-1-boronic acid produced a lower yield of sydnones **3** than that of phenylboronic acid because of steric hindrance (entries 1 and 8).

Table 2 Synthesis of 4-Aryl-3-(4-methoxyphenyl)sydnones **3**



1a **2** **3**

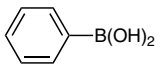
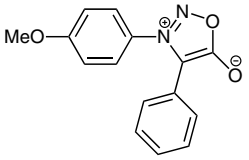
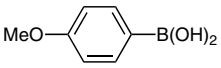
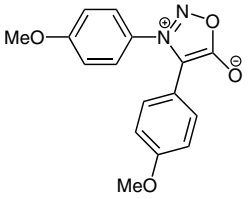
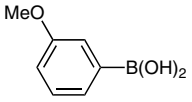
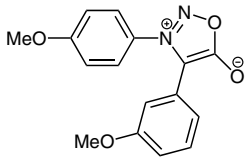
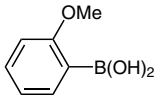
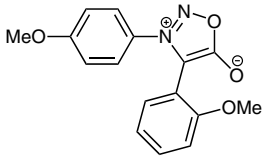
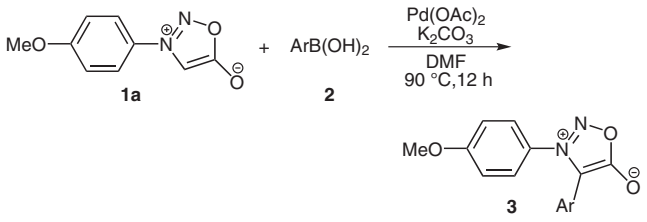
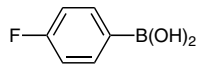
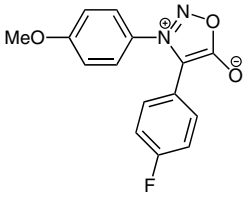
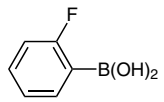
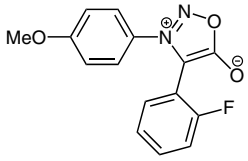
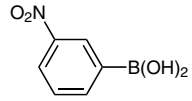
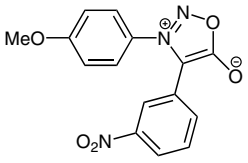
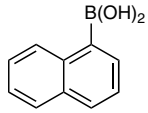
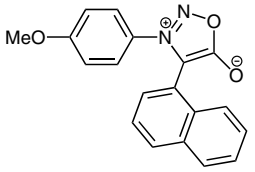
Entry	$ArB(OH)_2$ **2**	Sydnone **3**	Yield (%)[a]
1	 **2a**	 **3a**	90
2	 **2b**	 **3b**	47
3	 **2c**	 **3c**	62
4	 **2d**	 **3d**	21

Table 2 Synthesis of 4-Aryl-3-(4-methoxyphenyl)sydnones **3** (continued)



Entry	$ArB(OH)_2$ **2**	Sydnone **3**	Yield (%)[a]
5	 **2e**	 **3e**	68
6	 **2f**	 **3f**	38
7	 **2g**	 **3g**	80
8	 **2h**	 **3h**	63

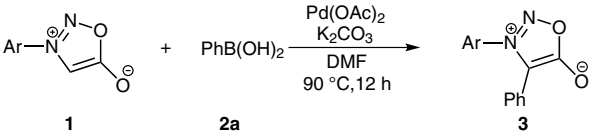
[a] Isolated yield.

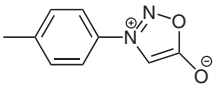
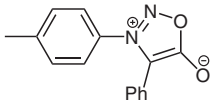
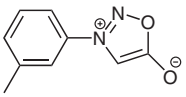
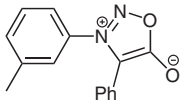
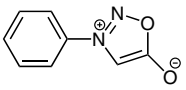
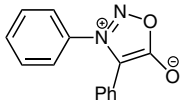
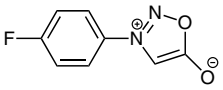
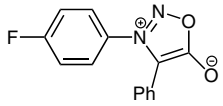
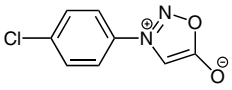
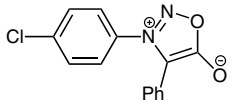
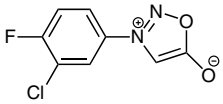
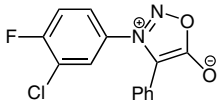
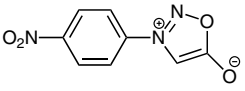
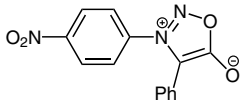
The scope of 3-arylsydnone substrates **1** was also explored. Table 3 shows that in most cases, the desired sydnones **3** were generated smoothly in good yields. The reaction of phenyl of 3-arylsydnones **1** carrying either an electron-donating substituent such as methyl (**1b** and **1c**) or an electron-withdrawing group including halogens (**1e**, **1f**, and **1g**) and nitryl (**1h**) proceeded smoothly in moderate to good yields.

Compared to **1d**, higher yields were obtained when the phenyl of 3-arylsydnones **1** carried an electron-donating group. The presence of an electron-donating group in the phenyl of 3-arylsydnones **1b** and **1c** remarkably increased the reaction yield (Table 3, entries 1, 2). Higher yields were obtained when the substrates had an electron-donating substituent at the *para*-position than that at the *meta*-position because an electron-donating group at the *para*-position exerts a stronger electron-donating inductive effect than a group at the *meta*-position (Table 3, entries 1, 2). On the other hand, the presence of an electron-withdrawing substituent on the phenyl of 3-arylsydnones **1e**–**h** provided relatively low yields of products **3** (Table 3, entries 4–7).

A plausible mechanism for the synthesis of 3,4-diarylsydnones **3** has been previously proposed (Scheme 2).[11b] At first, species **A** is formed by the electrophilic addition of palladium acetate with 3-arylsydnones. Then, the resulting species **A** reacted with arylboronic acid to generate the

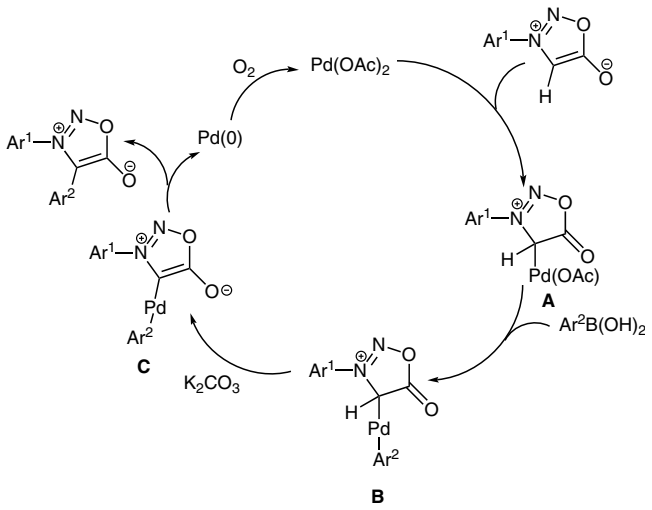
Table 3 Synthesis of 3-Aryl-4-phenylsydnones **3**



Entry	Sydnone **1**	Sydnone **3**	Yield (%)[a]
1	 **1b**	 **3i**	78
2	 **1c**	 **3j**	70
3	 **1d**	 **3k**	67
4	 **1e**	 **3l**	55
5	 **1f**	 **3m**	60
6	 **1g**	 **3n**	59
7	 **1h**	 **3o**	30

[a] Isolated yield.

corresponding intermediate **B**. This step is followed by deprotonation, rearomatization, and reductive elimination to provide the product and generate Pd(0). Finally, Pd(II) was regenerated by the oxidation of Pd(0).



Scheme 2 Proposed mechanism for the synthesis of **3**

In summary, we have synthesized a series of 3,4-diarylsydnones in moderate to good yields by the reaction between 3-arylsydnones and arylboronic acids in the presence of $Pd(OAc)_2$ catalyst. The direct arylation of 3-arylsydnones was convenient and free of a catalytic ligand. These 3,4-diarylsydnones are important heterocyclic compounds used in medicinal and biological research.

All commercially available reagents and solvent were obtained from the commercial providers and used without further purification. Melting points were recorded using a WRS-2A melting point apparatus and were uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer. Chemical shifts were reported relative to internal TMS (δ = 0.00 ppm) for ^{1}H and $CDCl_3$ (δ = 77.0 ppm) for ^{13}C. IR spectra were obtained on a Nexus FT-IR spectrophotometer. High-resolution mass spectra were determined using a Finnigan-NAT GC/MS/DS 8430 spectrometer. Flash column chromatography was performed on 300–400 mesh silica gel. 3-Arylsydnones were prepared according to literature procedures.[13,14]

3,4-Diarylsydones 3; General Procedure

A mixture of 3-arylsydnone **1** (0.3 mmol), arylboronic acid **2** (0.6 mmol), $Pd(OAc)_2$ (0.03 mmol), and K_2CO_3 (0.6 mmol) in DMF (2 mL) was placed in an open tube. The tube was heated at 90 °C for 12 h in the dark using an oil bath. After completion of the reaction (as monitored by TLC), the mixture was cooled to r.t. Then, H_2O (30 mL) was added and the mixture extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with brine (60 mL), dried (Na_2SO_4), and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography [petroleum ether (bp 30–60 °C)–EtOAc, 2:1, v/v] to yield the 3,4-diarylsydnone **3**.

3-(4-Methoxyphenyl)-4-phenylsydnone (3a)[15]

Yield: 72 mg (90%, 0.27 mmol); light yellow solid; mp 122.2–123.1 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.91 (s, 3 H), 7.05 (d, *J* = 9.2 Hz, 2 H), 7.31–7.33 (m, 5 H), 7.41 (d, *J* = 8.8 Hz, 2 H).

3,4-Bis(4-methoxyphenyl)sydnone (3b)

Yield: 42 mg (47%, 0.14 mmol); tan solid; mp 139.2–140.1 °C.

IR (KBr): 3033, 2930, 2852, 1733, 1616, 1558, 1507, 1457, 1249, 1177 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.81 (s, 3 H), 3.92 (s, 3 H), 6.85 (d, *J* = 8.4 Hz, 2 H), 7.04 (d, *J* = 8.8 Hz, 2 H), 7.27 (d, *J* = 10.0 Hz, 2 H), 7.41 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.3, 55.8, 108.0, 114.3 (2 C), 115.1 (2 C), 117.0, 126.2 (2 C), 129.0 (2 C), 139.3, 159.8, 162.0, 167.3.

HRMS: *m*/*z* calcd for $C_{16}H_{14}N_2O_4$: 298.0982 [M]$^+$; found: 298.0978.

4-(3-Methoxyphenyl)-3-(4-methoxyphenyl)sydnone (3c)

Yield: 56 mg (62%, 0.19 mmol); tan solid; mp 141.0–141.8 °C.

IR (KBr): 3037, 2995, 2821, 1717, 1616, 1558, 1507, 1457, 1257, 1152, 1017 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.73 (s, 3 H), 3.92 (s, 3 H), 6.84 (d, *J* = 8.0 Hz, 2 H), 6.96 (s, 1 H), 7.05 (d, *J* = 8.8 Hz, 2 H), 7.21 (t, *J* = 8.0 Hz, 1 H), 7.43 (d, *J* = 9.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.2, 55.8, 107.6, 112.5, 114.8, 115.2 (2 C), 119.7, 125.8, 126.2 (2C), 129.7, 139.3, 159.7, 162.1, 167.1.

HRMS: *m*/*z* calcd for $C_{16}H_{14}N_2O_4$: 298.0968 [M]$^+$; found: 298.0972.

4-(2-Methoxyphenyl)-3-(4-methoxyphenyl)sydnone (3d)

Yield: 19 mg (21%, 0.06 mmol); tan solid; mp 128.3–129.5 °C.

IR (KBr): 3026, 2942, 2845, 1750, 1628, 1560, 1455, 1329, 1238, 1170, 1011, 948, 849, 713 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.42 (s, 3 H), 3.85 (s, 3 H), 6.79 (d, *J* = 8.4 Hz, 1 H), 6.93 (d, *J* = 9.2 Hz, 2 H), 7.05 (t, *J* = 7.6 Hz, 1 H), 7.34 (d, *J* = 8.8 Hz, 2 H), 7.36–7.42 (m, 1 H), 7.46 (dd, *J* = 1.6, 1.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 54.9, 55.7, 105.3, 111.2, 113.6, 114.5 (2 C), 121.2, 124.4 (2 C), 128.9, 131.4 (2 C), 156.6, 161.5, 167.9.

HRMS: *m*/*z* calcd for $C_{16}H_{14}N_2O_4$: 298.0982 [M]$^+$; found: 298.0980.

4-(4-Fluorophenyl)-3-(4-methoxyphenyl)sydnone (3e)[16]

Yield: 58 mg (68%, 0.20 mmol); tan oil.

IR (neat): 2927, 2854, 1717, 1617, 1558, 1507, 1457, 1253, 1163 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.93 (s, 3 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 7.06 (d, *J* = 8.8 Hz, 2 H), 7.31–7.34 (m, 2 H), 7.41 (d, *J* = 9.2 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.8, 107.0, 115.3 (2 C), 116.0 (d, *J* = 21.9 Hz, 2 C), 120.8 (d, *J* = 3.6 Hz, 1 C), 126.2 (2 C), 127.1, 129.4 (d, *J* = 8.3 Hz, 2 C), 162.2, 162.5 (d, *J* = 249.0 Hz, 1 C), 167.1.

HRMS: *m*/*z* calcd for $C_{15}H_{11}FN_2O_3$: 286.0812 [M]$^+$; found: 286.0816.

4-(2-Fluorophenyl)-3-(4-methoxyphenyl)sydnone (3f)

Yield: 33 mg (38%, 0.11 mmol); tan oil.

IR (neat): 2942, 2866, 1717, 1629, 1569, 1448, 1367, 1276, 1143, 913, 747 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.88 (s, 3 H), 6.97 (d, *J* = 9.2 Hz, 2 H), 7.02 (t, *J* = 9.6 Hz, 1 H), 7.25 (t, *J* = 7.6 Hz, 1 H), 7.36 (d, *J* = 8.8 Hz, 2 H), 7.38–7.45 (m, 1 H), 7.50 (ddd, *J* = 1.6, 1.6, 1.6 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.7, 102.9, 113.0 (d, *J* = 14.5 Hz, 1 C), 114.9 (2 C), 115.1 (d, *J* = 2.1 Hz, 1 C), 116.2 (d, *J* = 20.9 Hz, 1 C), 124.9 (2 C), 127.8, 131.2, 131.7 (d, *J* = 8.2 Hz, 1 C), 159.4 (d, *J* = 249.9 Hz, 1 C), 162.0, 167.2.

HRMS: *m*/*z* calcd for $C_{15}H_{11}FN_2O_3$: 286.0812 $[M]^+$; found: 286.0806.

3-(4-Methoxyphenyl)-4-(3-nitrophenyl)sydnone (3g)
Yield: 75 mg (80%, 0.24 mmol); yellow solid; mp 182.1–182.9 °C.

IR (KBr): 3048, 2951, 2829, 1717, 1616, 1558, 1540, 1507, 1457, 1191, 1011 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.95 (s, 3 H), 7.12 (d, *J* = 8.8 Hz, 2 H), 7.45 (d, *J* = 9.2 Hz, 2 H), 7.54 (t, *J* = 8.2 Hz, 1 H), 7.84 (d, *J* = 7.6 Hz, 1 H), 8.06 (s, 1 H), 8.13 (d, *J* = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.9, 105.5, 114.1, 115.7 (2 C), 121.3, 122.8, 126.1 (2 C), 129.9, 132.3, 139.3, 148.3, 162.7, 166.6.

HRMS: *m*/*z* calcd for $C_{15}H_{11}N_3O_5$: 313.0692 $[M]^+$; found: 313.0687.

3-(4-Methoxyphenyl)-4-(naphthalen-1-yl)sydnone (3h)
Yield: 60 mg (63%, 0.19 mmol); tan solid; mp 193.3–194.0 °C.

IR (KBr): 3004, 2950, 2834, 1734, 1699, 1635, 1558, 1540, 1507, 1457, 1188 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.79 (s, 3 H), 6.83 (d, *J* = 8.8 Hz, 2 H), 7.25–7.28 (m, 2 H), 7.28–7.29 (m, 1 H), 7.37–7.44 (m, 1 H), 7.53–7.56 (m, 2 H), 7.80–7.83 (m, 1 H), 7.89–7.93 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 55.6, 106.9, 114.1, 114.8 (2 C), 121.8, 124.8, 125.3 (2 C), 126.7, 127.4, 128.7, 130.2, 130.5, 131.8, 133.9, 139.3, 161.8, 167.6.

HRMS: *m*/*z* calcd for $C_{19}H_{14}N_2O_3$: 318.1022 $[M]^+$; found: 318.1027.

4-Phenyl-3-*p*-tolylsydnone (3i)[16]
Yield: 59 mg (78%, 0.23 mmol); yellow solid; mp 148.5–149.3 °C.

IR (KBr): 3094, 2928, 2858, 1717, 1635, 1558, 1540, 1507, 1457, 1395 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.50 (s, 3 H), 7.30–7.34 (m, 5 H), 7.35–7.40 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.5, 107.7, 114.1, 124.6 (2 C), 127.4 (2 C), 128.7 (2 C), 130.7 (2 C), 132.3, 139.3, 142.8, 167.2.

HRMS: *m*/*z* calcd for $C_{15}H_{12}N_2O_2$: 252.0916 $[M]^+$; found: 252.0912.

4-Phenyl-3-*m*-tolylsydnone (3j)
Yield: 53 mg (70%, 0.21 mmol); tan solid; mp 132.6–133.5 °C.

IR (KBr): 3081, 2939, 2836, 1734, 1635, 1558, 1540, 1507, 1457, 1395 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.46 (s, 3 H), 7.25–7.28 (m, 1 H), 7.29–7.35 (m, 6 H), 7.43–7.49 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 21.3, 107.8, 122.0, 124.6, 125.2, 127.3 (2 C), 128.6, 128.7 (2 C), 129.9, 132.8, 134.7, 140.8, 167.1.

HRMS: *m*/*z* calcd for $C_{15}H_{12}N_2O_2$: 252.0876 $[M]^+$; found: 252.0882.

3,4-Diphenylsydnone (3k)[11b]
Yield: 48 mg (67%, 0.20 mmol); light yellow solid; mp 179.8–181.0 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.32 (m, 5 H), 7.51 (d, *J* = 7.6 Hz, 2 H), 7.60 (t, *J* = 7.8 Hz, 2 H), 7.69 (t, *J* = 7.4 Hz, 1 H).

3-(4-Fluorophenyl)-4-phenylsydnone (3l)[16]
Yield: 42 mg (55%, 0.17 mmol); tan solid; mp 180.9–181.6 °C.

IR (KBr): 3023, 1734, 1636, 1558, 1540, 1507, 1457, 1374 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.27–7.35 (m, 7 H), 7.51–7.55 (m, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.0, 114.1, 117.4 (d, *J* = 23.5 Hz, 2 C), 124.2, 127.0 (d, *J* = 9.2 Hz, 2 C), 127.5 (2 C), 128.9 (2 C), 130.7 (d, *J* = 2.9 Hz, 1 C), 164.3 (d, *J* = 253.3 Hz, 1 C), 167.0.

HRMS: *m*/*z* calcd for $C_{14}H_9FN_2O_2$: 256.0623 $[M]^+$; found: 256.0630.

3-(4-Chlorophenyl)-4-phenylsydnone (3m)
Yield: 49 mg (60%, 0.18 mmol); tan solid; mp 134.0–135.2 °C.

IR (KBr): 3084, 1717, 1636, 1558, 1540, 1507, 1457, 748 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.40 (m, 5 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 7.58 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.0, 114.1, 125.1, 126.1 (2 C), 127.3, 127.5 (2 C), 128.9 (2 C), 130.5 (2 C), 138.5, 167.0.

HRMS: *m*/*z* calcd for $C_{14}H_9{}^{35}ClN_2O_2$: 272.0389 $[M]^+$; found: 272.0380.

3-(3-Chloro-4-fluorophenyl)-4-phenylsydnone (3n)
Yield: 52 mg (59%, 0.18 mmol); brown solid; mp 123.8–124.4 °C.

IR (KBr): 3036, 1734, 1636, 1558, 1540, 1507, 1457, 1395, 766 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.30–7.34 (m, 2 H), 7.35–7.40 (m, 5 H), 7.67–7.70 (m, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 108.2, 118.2 (d, *J* = 22.9 Hz, 1 C), 119.8, 123.9, 124.0 (d, *J* = 74.5 Hz, 1 C), 125.0 (d, *J* = 8.2 Hz, 1 C), 127.5 (2 C), 129.1 (2 C), 129.2, 130.4, 160.0 (d, *J* = 255.6 Hz, 1 C), 166.8.

HRMS: *m*/*z* calcd for $C_{14}H_8{}^{35}ClFN_2O_2$: 290.0276 $[M]^+$; found: 290.0270.

3-(4-Nitrophenyl)-4-phenylsydnone (3o)
Yield: 25 mg (30%, 0.09 mmol); tan solid; mp 140.0–141.1 °C.

IR (KBr): 3030, 1734, 1636, 1558, 1540, 1507, 1457 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29–7.34 (m, 2 H), 7.35–7.39 (m, 3 H), 7.76 (d, *J* = 8.8 Hz, 2 H), 8.47 (d, *J* = 8.8 Hz, 2 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 115.7, 123.6, 125.6 (2 C), 126.2 (2 C), 127.7 (2 C), 129.2 (2 C), 129.5, 139.0, 149.7, 166.7.

HRMS: *m*/*z* calcd for $C_{14}H_9N_3O_4$: 283.0612 $[M]^+$; found: 283.0618.

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