Supporting Information

An Easy Direct Arylation of 3-Arylsydnones

Yiwen Yang, a,b Hao Gong a and Chunxiang Kuang *a,c

a Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, China
Fax: +86-21-65983191; E-mail: kuangcx@tongji.edu.cn.
b College of Biological, Chemical Sciences and Engineering, Jiaxing University, Jiaxing 314001, China
c Key Laboratory of Yangtze River Water Environment, Ministry of Education

Experimental procedures

1. General considerations
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. 1H NMR and 13C NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer. Chemical shifts were reported relative to internal tetramethylsilane (δ 0.00 ppm) for 1H and CDCl3 (δ 77.0 ppm) for 13C. 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.1-2

2. General procedure for the synthesis of 3
A mixture of 3-arylsydnones (0.3 mmol), arylboronic acids (0.6 mmol), Pd(OAc)2 (0.03 mmol) and K2CO3 (0.6 mmol) in 2 mL DMF was placed in an open tube. The tube was heated at 90°C for 12 h in dark using an oil bath. After the reaction was completed (as monitored by TLC), the mixture was cooled to room temperature. Then 30 mL water was added to the reaction mixture that was extracted with EtOAc (3×20 mL). The combined organic layers were washed with saturated brine, dried over anhydrous Na2SO4 and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography (petroleum ether/ethyl acetate = 2:1, v/v) to yield 3,4-diarylsydnones (3).

Data of compounds 3

3-(4-methoxyphenyl)-4-phenylsydnone(3a)

Following the General procedure; light yellow solid; yield: 90% (72 mg, 0.27 mmol); mp: 122.2-123.1°C. 1H NMR (400 MHz, CDCl3): δ = 3.91 (s, 3H), 7.05 (d, J = 9.2 Hz, 2H), 7.31-7.33 (m, 5H), 7.41 (d, J = 8.8 Hz, 2H).
3,4-bis(4-methoxyphenyl) sydnone (3b) Following the General procedure; tan solid; yield: 47\% (42 mg, 0.14 mmol); mp: 139.2-140.1 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.81 (s, 3H), 3.92 (s, 3H), 6.85 (d, $J$ = 8.4 Hz, 2H), 7.04 (d, $J$ = 8.8 Hz, 2H), 7.27 (d, $J$ = 10.0 Hz, 2H), 7.41 (d, $J$ = 8.8 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.3, 55.8, 108.0, 114.3 (2C), 115.1 (2C), 117.0, 126.2 (2C), 129.0 (2C), 139.3, 159.8, 162.0, 167.3. IR (KBr): 3033, 2930, 2852, 1733, 1616, 1558, 1507, 1457, 1249, 1177 cm$^{-1}$. HR-MS: m/z calcd for C$_{16}$H$_{14}$N$_2$O$_4$: 298.0982 [M$^+$]; found: 298.0978.

4-(3-methoxyphenyl)-3-(4-methoxyphenyl) sydnone (3c) Following the General procedure; tan solid; yield: 62\% (56 mg, 0.19 mmol); mp: 141.0-141.8 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.73 (s, 3H), 3.92 (s, 3H), 6.84 (d, $J$ = 8.0 Hz, 2H), 6.96 (s, 1H), 7.05 (d, $J$ = 8.8 Hz, 2H), 7.21 (t, $J$ = 8.0 Hz, 1H), 7.43 (d, $J$ = 9.2 Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.2, 55.8, 107.6, 112.5, 114.8, 115.2 (2C), 119.7, 125.8, 126.2 (2C), 129.7, 139.3, 159.7, 162.1, 167.1. IR (KBr): 3037, 2995, 2821, 1717, 1616, 1558, 1507, 1457, 1257, 1152, 1017 cm$^{-1}$. HR-MS: m/z calcd for C$_{16}$H$_{14}$N$_2$O$_4$: 298.0968 [M$^+$]; found: 298.0972.

4-(2-methoxyphenyl)-3-(4-methoxyphenyl) sydnone (3d) Following the General procedure; tan solid; yield: 21\% (19 mg, 0.06 mmol); mp: 128.3-129.5 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.42 (s, 3H), 3.85 (s, 3H), 6.79 (d, $J$ = 8.4 Hz, 1H), 6.93 (d, $J$ = 9.2 Hz, 2H), 7.05 (t, $J$ = 7.6 Hz, 1H), 7.34(d, $J$ = 8.8 Hz, 2H), 7.36-7.42 (m, 1H), 7.46 (dd, $J$ = 1.6, 1.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 54.9, 55.7, 105.3, 111.2, 113.6, 114.5 (2C), 121.2, 124.4 (2C), 128.9, 131.4 (2C), 156.6, 161.5, 167.9. IR (KBr): 3026, 2942, 2845, 1750, 1628, 1560, 1455, 1329, 1238, 1170, 1011, 948, 849, 713 cm$^{-1}$. HR-MS: m/z calcd for C$_{16}$H$_{14}$N$_2$O$_4$: 298.0982 [M$^+$]; found: 298.0980.
4-(4-fluorophenyl)-3-(4-methoxyphenyl) sydnone (3e) Following the General procedure; tan oil; yield: 68% (58 mg, 0.20 mmol). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.93 (s, 3H), 7.01 (d, $J = 8.8$ Hz, 2H), 7.06 (d, $J = 8.8$ Hz, 2H), 7.31-7.34 (m, 2H), 7.41 (d, $J = 9.2$ Hz, 2H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.8, 107.0, 115.3 (2C), 116.0 (d, $J = 21.9$ Hz, 2C), 120.8 (d, $J = 3.6$ Hz, 1C), 126.2 (2C), 127.1, 129.4 (d, $J = 8.3$ Hz, 2C), 162.2, 162.5 (d, $J = 249.0$ Hz, 1C), 167.1. IR (KBr): 2927, 2854, 1717, 1558, 1507, 1457, 1253, 1163 cm$^{-1}$. HR-MS: m/z calcd for C$_{15}$H$_{11}$FN$_2$O$_3$: 286.0812 [M$^+$]; found: 286.0816.

4-(2-fluorophenyl)-3-(4-methoxyphenyl) sydnone (3f) Following the General procedure; tan oil; yield: 38% (33 mg, 0.11 mmol). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.88 (s, 3H), 6.97 (d, $J = 9.2$ Hz, 2H), 7.02 (t, $J = 9.6$ Hz, 1H), 7.25 (t, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 8.8$ Hz, 2H), 7.38-7.45 (m, 1H), 7.50 (ddd, $J = 1.6$, 1.6, 1.6 Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.7, 102.9, 113.0 (d, $J = 14.5$ Hz, 1C), 114.9 (2C), 115.1 (d, $J = 2.1$ Hz, 1C), 116.2 (d, $J = 20.9$ Hz, 1C), 124.9 (2C), 127.8, 131.2, 131.7 (d, $J = 8.2$ Hz, 1C), 159.4 (d, $J = 249.9$ Hz, 1C), 162.0, 167.2. IR (KBr): 2942, 2866, 1717, 1629, 1569, 1448, 1367, 1276, 1143, 913, 747 cm$^{-1}$. HR-MS: m/z calcd for C$_{15}$H$_{11}$FN$_2$O$_3$: 286.0812 [M$^+$]; found: 286.0806.

3-(4-methoxyphenyl)-4-(3-nitrophenyl) sydnone (3g) Following the General procedure; yellow solid; yield: 80% (75 mg, 0.24 mmol); mp: 182.1-182.9 °C. $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 3.95 (s, 3H), 7.12 (d, $J = 8.8$ Hz, 2H), 7.45 (d, $J = 9.2$ Hz, 2H), 7.54 (t, $J = 8.2$ Hz, 1H), 7.84 (d, $J = 7.6$ Hz, 1H), 8.06 (s, 1H), 8.13 (d, $J = 8.0$ Hz, 1H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 55.9, 105.5, 114.1, 115.7 (2C), 121.3, 122.8, 126.1 (2C), 129.9, 132.3, 139.3, 148.3, 162.7, 166.6. IR (KBr): 3048, 2951, 2829, 1717, 1616, 1558, 1540, 1507, 1457, 1191, 1011 cm$^{-1}$. HR-MS: m/z calcd for C$_{15}$H$_{11}$N$_2$O$_5$: 313.0692 [M$^+$]; found: 313.0687.
3-(4-methoxyphenyl)-4-(naphthalen-1-yl)sydnone (3h) Following the General procedure; tan solid; yield: 63% (60 mg, 0.19 mmol); mp: 193.3-194.0 °C. 1H NMR (400 MHz, CDCl3): δ = 3.79 (s, 3H), 6.83 (d, J = 8.8 Hz, 2H), 7.25-7.28 (m, 2H), 7.28-7.29 (m, 1H), 7.37-7.44 (m, 1H), 7.53-7.56 (m, 2H), 7.80-7.83 (m, 1H), 7.89-7.93 (m, 2H). 13C NMR (100 MHz, CDCl3): δ = 55.6, 106.9, 114.1, 114.8 (2C), 121.8, 124.8, 125.3 (2C), 126.7, 127.4, 128.7, 130.2, 130.5, 131.8, 133.9, 139.3, 161.8, 167.6. IR (KBr): 3004, 2950, 2834, 1734, 1699, 1635, 1558, 1540, 1507, 1457, 1188 cm⁻¹. HR-MS: m/z calcd for C19H14N2O3: 318.1022 [M]+; found: 318.1027.

4-phenyl-3-p-tolylsydnone (3i) Following the General procedure; yellow solid; yield: 78% (59 mg, 0.23 mmol); mp: 148.5-149.3 °C. 1H NMR (400 MHz, CDCl3): δ = 2.50 (s, 3H), 7.30-7.34 (m, 5H), 7.35-7.40 (m, 4H). 13C NMR (100 MHz, CDCl3): δ = 21.5, 107.7, 114.1, 124.6 (2C), 127.4 (2C), 128.7 (2C), 130.7 (2C), 132.3, 139.3, 142.8, 167.2. IR (KBr): 3094, 2928, 2858, 1717, 1635, 1558, 1540, 1507, 1457, 1395 cm⁻¹. HR-MS: m/z calcd for C15H12N2O2: 252.0916 [M]+; found: 252.0912.

4-phenyl-3-m-tolylsydnone (3j) Following the General procedure; tan solid; yield: 70% (53 mg, 0.21 mmol); mp: 132.6-133.5 °C. 1H NMR (400 MHz, CDCl3): δ = 2.46 (s, 3H), 7.25-7.28 (m, 1H), 7.29-7.35 (m, 6H), 7.43-7.49 (m, 2H). 13C NMR (100 MHz, CDCl3): δ = 21.3, 107.8, 122.0, 124.6, 125.2, 127.3 (2C), 128.6, 128.7 (2C), 129.9, 132.8, 134.7, 140.8, 167.1. IR (KBr): 3081, 2939, 2836, 1734, 1635, 1558, 1540, 1507, 1457, 1395 cm⁻¹. HR-MS: m/z calcd for C15H12N2O2: 252.0876 [M]+; found: 252.0882.

3,4-diphenylsydnone (3k) Following the General procedure; light yellow solid; yield: 67% (48 mg, 0.20 mmol); mp: 179.8-181.0 °C. 1H NMR (400 MHz, CDCl3): δ = 7.30-7.32 (m, 5H), 7.51 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.8 Hz, 2H), 7.69 (t, J = 7.4 Hz, 1H).

3-(4-fluorophenyl)-4-phenylsydnone (3l) Following the General procedure; tan solid; yield: 55%
(42 mg, 0.17 mmol); mp: 180.9-181.6 °C. 1H NMR (400 MHz, CDCl3): δ = 7.27-7.35 (m, 7H), 7.51-7.55 (m, 2H). 13C NMR (100 MHz, CDCl3): δ = 108.0, 114.1, 117.4 (d, J = 23.5 Hz, 2C), 124.2, 127.0 (d, J = 9.2 Hz, 2C), 127.5 (2C), 128.9 (2C), 130.7 (d, J = 2.9 Hz, 1C), 164.3 (d, J = 253.3 Hz, 1C), 167.0. IR (KBr): 3023, 1734, 1636, 1558, 1540, 1507, 1457, 1374 cm⁻¹. HR-MS: m/z calcd for C14H9FN2O2: 256.0623 [M]+; found: 256.0630.

3-(4-chlorophenyl)-4-phenylsydnone (3m) Following the General procedure; tan solid; yield: 60% (49 mg, 0.18 mmol); mp: 134.0-135.2 °C. 1H NMR (400 MHz, CDCl3): δ = 7.30-7.40 (m, 5H), 7.47 (d, J = 8.8 Hz, 2H), 7.58 (d, J = 8.8 Hz, 2H). 13C NMR (100 MHz, CDCl3): δ = 108.0, 114.1, 125.1, 126.1(2C), 127.3, 127.5 (2C), 128.9(2C), 130.5 (2C), 138.5, 167.0. IR (KBr): 3084, 1717, 1636, 1558, 1540, 1507, 1457, 748 cm⁻¹. HR-MS: m/z calcd for C14H9ClN2O2: 272.0389 [M]+; found: 272.0380.

3-(3-chloro-4-fluorophenyl)-4-phenylsydnone (3n) Following the General procedure; brown solid; yield: 59% (52 mg, 0.18 mmol); mp: 123.8-124.4 °C. 1H NMR (400 MHz, CDCl3): δ = 7.30-7.34 (m, 2H), 7.35-7.40 (m, 5H), 7.67-7.70 (m, 1H). 13C NMR (100 MHz, CDCl3): δ = 115.7, 123.6, 125.6 (2C), 126.2 (2C), 127.7 (2C), 129.2 (2C), 129.5, 139.0, 149.7, 166.7. IR (KBr): 3036, 1734, 1636, 1558, 1540, 1507, 1457, 1395, 766 cm⁻¹. HR-MS: m/z calcd for C14H8ClFN2O2: 290.0276 [M]+; found: 290.0270.

3-(4-nitrophenyl)-4-phenylsydnone (3o) Following the General procedure; tan solid; yield: 30% (25 mg, 0.09 mmol); mp: 140.0-141.1 °C. 1H NMR (400 MHz, CDCl3): δ = 7.29-7.34 (m, 2H), 7.35-7.39 (m, 3H), 7.76 (d, J = 8.8 Hz, 2H), 8.47 (d, J = 8.8 Hz, 2H). 13C NMR (100 MHz, CDCl3): δ = 115.7, 123.6, 125.6 (2C), 126.2 (2C), 127.7 (2C), 129.2 (2C), 129.5, 139.0, 149.7, 166.7. IR (KBr): 3030, 1734, 1636, 1558, 1540, 1507, 1457 cm⁻¹. HR-MS: m/z calcd for C14H9N3O4: 283.0612 [M]+; found: 283.0618.
References


\(^1\)H NMR: 3-(4-methoxyphenyl)-4-phenylsydnone (3a)

\(^1\)H NMR: 3,4-bis(4-methoxyphenyl) sydnone (3b)
$^{13}$C NMR: 3,4-bis(4-methoxyphenyl) sydnone(3b)

$^1$H NMR: 4-(3-methoxyphenyl)-3-(4-methoxyphenyl) sydnone(3c):
$^{13}$C NMR: 4-(3-methoxyphenyl)-3-(4-methoxyphenyl) sydnone (3c):

$^1$H NMR: 4-(2-methoxyphenyl)-3-(4-methoxyphenyl) sydnone (3d):
$^{13}$C NMR: 4-(2-methoxyphenyl)-3-(4-methoxyphenyl) sydnone(3d):

$^1$HNMR: 4-(4-fluorophenyl)-3-(4-methoxyphenyl) sydnone(3e)
$^{13}$C NMR: 4-(4-fluorophenyl)-3-(4-methoxyphenyl) sydnone (3e)

$^1$H NMR: 4-(2-fluorophenyl)-3-(4-methoxyphenyl) sydnone (3f)
$^{13}$C NMR: 4-(2-fluorophenyl)-3-(4-methoxyphenyl) sydnone(3f)

$^1$H NMR: 3-(4-methoxyphenyl)-4-(3-nitrophenyl) sydnone(3g)
$^{13}$C NMR: 3-(4-methoxyphenyl)-4-(3-nitrophenyl) sydnone (3g)

$^1$H NMR: 3-(4-methoxyphenyl)-4-(naphthalen-1-yl)sydnone (3h)
$^{13}$C NMR: 3-(4-methoxyphenyl)-4-(naphthalen-1-yl)sydnone(3h)

$^1$HNMR: 4-phenyl-3-$p$-tolysydnone(3i)
$^{13}$C NMR: 4-phenyl-3-<i>p</i>-tolylsydnone (3i)

$^1$H NMR: 4-phenyl-3-<i>m</i>-tolylsydnone (3j)
$^{13}$C NMR: 4-phenyl-3-$m$-tolysydnone(3j)

$^1$HNMR: 3,4-diphenysydnone(3k)
$^1$H NMR: 3-(4-fluorophenyl)-4-phenylsydnone(3l)

$^{13}$C NMR: 3-(4-fluorophenyl)-4-phenylsydnone(3l)
$\text{HNMR: } 3\text{-}(4\text{-chlorophenyl})\text{-}4\text{-phenylsydnone(3m)}$

![HNMR spectrum diagram]

$\text{C NMR: } 3\text{-}(4\text{-chlorophenyl})\text{-}4\text{-phenylsydnone(3m)}$

![C NMR spectrum diagram]
$^1$HNMR: 3-(3-chloro-4-fluorophenyl)-4-phenylsydnone(3n)

$^{13}$C NMR: 3-(3-chloro-4-fluorophenyl)-4-phenylsydnone(3n)
$^1$HNMR: 3-(4-nitrophenyl)-4-phenylsydnone(3o)

$^{13}$C NMR: 3-(4-nitrophenyl)-4-phenylsydnone(3o)