Supporting information

Reduction of sulfoxides and pyridine-N-oxides over iron powder with water as hydrogen source promoted by carbon dioxide

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1. General procedure for the reduction of sulfoxides

A mixture of sulfoxides (1 mmol), Fe (2 mmol, 0.1117 g), H2O (2 mL) was placed in a 50 mL stainless steel autoclave equipped with an inner glass tube at room temperature. The vessel was sealed and CO2 was subsequently introduced into the autoclave. The system was heated under the predetermined reaction temperature for 25 min to reach the equilibration, then the final pressure was adjusted to the desired pressure by introducing the correct amount of CO2. After the reaction was finished, the vessel was cooled within an ice-bath and the pressure was released slowly to atmospheric pressure. The products were diluted with ethyl acetate and analyzed by GC. The residue was purified by column chromatography on silica gel (200-300 mesh, eluting with n-hexane) to afford the desired product. The isolated products were further identified with NMR spectra and GC-MS, which are consistent with those reported in the literature.

2. General procedure for the reduction of pyridine-N-oxides

A mixture of pyridine-N-oxides (1 mmol), Fe (2 mmol, 0.1117 g), H2O (2 mL) was placed in a 50 mL stainless steel autoclave equipped with an inner glass tube at room temperature. The vessel was sealed and CO2 was subsequently introduced into the autoclave. The system was heated under the predetermined reaction temperature for 25 min to reach the equilibration, then the final pressure was adjusted to the desired pressure by introducing the correct amount of CO2. After the reaction was finished, the vessel was cooled with an ice-bath and the pressure was released slowly to atmospheric pressure. The products were diluted with diethyl ether or acetone and analyzed by GC. The residue was purified by column chromatography on silica gel (200-300 mesh, eluting with n-hexane and ethyl acetate or methanol) to afford the desired product. The isolated products were further identified with NMR spectra and GC-MS, which are consistent with those reported in the literature.

3. Analytic data of the substrate and products

\[ \text{p-Tolyl methyl sulfoxide.} \]

The product was obtained as a yellow liquid. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) (ppm): 7.52 (d, J = 8.0 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 2.69 (s, 3H), 2.40 (s, 3H). \(^1\)C NMR (100.6 MHz, CDCl\(_3\)) \(\delta\) (ppm): 142.44, 141.48, 130.02, 123.52, 43.96, 21.37.
4-Methoxyphenyl methyl sulfoxide. The product was obtained as a pale yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.60 – 7.48 (m, 2H), 6.97 (d, $J = 8.8$ Hz, 2H), 3.79 (s, 3H), 2.64 (s, 3H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 161.96, 136.51, 125.46, 114.85, 55.53, 43.96.

p-Chlorophenyl methyl sulfoxide. The product was obtained as a yellow solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.58 – 7.52 (m, 2H), 7.49 – 7.43 (m, 2H), 2.68 (s, 3H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 144.14, 137.22, 129.64, 124.98, 43.99.

Phenyl vinyl sulfoxide. The product was obtained as a pale yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.67 – 7.40 (m, 5H), 6.58 (dd, $J = 16.5$, 9.6 Hz, 1H), 6.19 (d, $J = 16.5$ Hz, 1H), 5.88 (d, $J = 9.6$ Hz, 1H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 143.17, 142.86, 131.30, 129.48, 124.69, 120.80.

Diphenyl sulfide. The product was obtained as a pale yellow liquid (0.169g, 90.9% yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.39 (d, $J = 7.4$ Hz, 4H), 7.34 (dd, $J = 9.9$, 4.8 Hz, 4H), 7.28 (dd, $J = 7.6$, 5.1 Hz, 2H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 135.86, 131.10, 129.25, 127.10. EI-MS, $m/z$ (%): 186 (100) [M$^+$].

Phenyl methyl sulfide. The product was obtained as a pale yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.32 – 7.20 (m, 4H), 7.17 – 7.07 (m, 1H), 2.47 (s, 3H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 138.40, 128.80, 126.61, 125.00, 15.83. EI-MS, $m/z$ (%): 124 (100) [M$^+$].

p-Tolyl methyl sulfide. The product was obtained as a yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.24 – 7.16 (m, 2H), 7.12 (d, $J = 8.0$ Hz, 2H), 2.48 (s, 3H), 2.33 (s, 3H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 135.03, 134.68, 129.59, 127.27, 20.91, 16.51. EI-MS, $m/z$ (%): 138 (100) [M$^+$].
4-Methoxyphenyl methyl sulfide. The product was obtained as a yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.23 (d, $J = 8.6$ Hz, 2H), 6.81 (d, $J = 8.6$ Hz, 2H), 3.75 (s, 3H), 2.40 (s, 3H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 158.21, 130.21, 128.78, 114.62, 55.37, 18.09. EI-MS, m/z (%): 154 (93) [M$^+$].

p-Chlorophenyl methyl sulfide. The product was obtained as a yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.24 (d, $J = 8.5$ Hz, 2H), 7.20 – 7.12 (m, 2H), 2.46 (s, 3H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 136.99, 130.89, 128.90, 127.90, 16.09. EI-MS, m/z (%): 158 (100) [M$^+$].

Phenyl vinyl sulfide. The product was obtained as a yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.50 (d, $J = 7.5$ Hz, 1H), 7.39 (d, $J = 7.3$ Hz, 2H), 7.36 – 7.30 (m, 3H), 6.55 (dd, $J = 16.6$, 9.6 Hz, 1H), 5.36 (dd, $J = 13.1$, 5.7 Hz, 2H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 134.26, 131.89, 130.52, 129.13, 127.52, 127.16, 127.13, 115.49. EI-MS, m/z ( %): 136 (77) [M$^+$].

4,4’-Dimethyldiphenylsulfide. The product was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.23 (d, $J = 8.1$ Hz, 4H), 7.10 (d, $J = 8.0$ Hz, 4H), 2.32 (s, 6H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 136.91, 132.66, 131.06, 129.91, 21.07. EI-MS, m/z (%): 214 (100) [M$^+$].

4-CHLOROPHENYL SULFIDE. The product was obtained as a white solid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 7.36 – 7.13 (m, 8H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 133.93, 133.46, 132.30, 129.48. EI-MS, m/z 255 (14) [M$^+$].

Di-N-butyl sulfide. The product was obtained as a pale yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 2.56 – 2.44 (m, 4H), 1.56 (ddd, $J = 12.5$, 8.8, 7.2 Hz, 4H), 1.40 (dq, $J = 14.3$, 7.2 Hz, 4H), 0.91 (t, $J = 7.3$ Hz, 6H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$
Tetrahydrothiophene. The product was obtained as a pale yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 2.95–2.64 (m, 4H), 2.03–1.78 (m, 4H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ (ppm): 31.80, 31.08. EI-MS, m/z (%): 88 (74) [M$^+$].

Pyridine. The product was obtained as a pale yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.67–8.55 (m, 2H), 7.66 (dd, $J = 10.7, 4.6$ Hz, 1H), 7.34–7.22 (m, 2H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ (ppm): 149.86, 135.93, 123.72. EI-MS, m/z (%): 88 (74) [M$^+$].

2-Methylpyridine. The product was obtained as a yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.47 (d, $J = 4.4$ Hz, 1H), 7.54 (t, $J = 7.6$ Hz, 1H), 7.12 (d, $J = 7.8$ Hz, 1H), 7.09–6.99 (m, 1H), 2.53 (s, 3H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ (ppm): 158.39, 149.14, 136.24, 123.25, 120.68, 24.48. EI-MS, m/z (%): 93 (100) [M$^+$].

4-Methoxypyridine. The product was obtained as a yellow liquid. $^1$H NMR (400 MHz, CDCl$_3$) δ (ppm): 8.40 (d, $J = 5.2$ Hz, 2H), 6.79 (d, $J = 6.2$ Hz, 2H), 3.82 (s, 3H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) δ (ppm): 165.59, 151.02, 109.87, 55.06. EI-MS, m/z (%): 109 (100) [M$^+$].

2-Hydroxypyridine. The product was obtained as a brown solid. $^1$H NMR (400 MHz, MeOD) δ (ppm): 7.74–7.26 (m, 2H), 6.71–6.22 (m, 2H). $^{13}$C NMR (100.6 MHz, MeOD) δ (ppm): 165.84, 143.80, 136.05, 120.85, 108.59. EI-MS, m/z (%): 95 (100) [M$^+$].

2-Chloropyridine. The product was obtained as a pale yellow liquid. $^1$H NMR (400 MHz, MeOD) δ (ppm): 8.48 (dd, $J = 6.4, 1.4$ Hz, 1H), 7.80 (dd, $J = 8.1, 1.9$ Hz, 1H),
7.57 (td, J = 7.9, 1.5 Hz, 1H), 7.53–7.46 (m, 1H). $^{13}$C NMR (100.6 MHz, MeOD) $\delta$ (ppm): 142.13, 140.39, 130.95, 129.22, 126.32. EI-MS, m/z (%): 113 (61) [M$^+$].

**Isoquinoline.**$^{13}$ The product was obtained as a yellow liquid.$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 9.25 (s, 1H), 8.52 (d, J = 5.8 Hz, 1H), 7.96 (d, J = 8.2 Hz, 1H), 7.81 (d, J = 8.2 Hz, 1H), 7.73–7.52 (m, 3H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 152.51, 142.96, 135.79, 130.37, 128.68, 127.64, 127.26, 126.47, 120.48. EI-MS, m/z (%): 129 (100) [M$^+$].

![Isoquinoline structure](image)

**4-Phenylpyridine.**$^{11}$ The product was obtained as a white solid.$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 8.67 (d, J = 5.3 Hz, 2H), 7.65 (d, J = 7.2 Hz, 2H), 7.59–7.40 (m, 5H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 150.19, 148.47, 138.11, 129.13, 127.01, 121.67. EI-MS, m/z (%): 155 (100) [M$^+$].

![4-Phenylpyridine structure](image)

**4-methyl morpholine.**$^{14}$ The product was obtained as a pale yellow liquid.$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ (ppm): 3.90–3.59 (m, 4H), 2.39 (s, 4H), 2.28 (s, 3H). $^{13}$C NMR (100.6 MHz, CDCl$_3$) $\delta$ (ppm): 66.95, 55.46, 46.47. EI-MS, m/z (%): 101 (100) [M$^+$].
4. NMR and GC-MS spectra of the substrate and products

4.1 $^1$H NMR and $^{13}$C NMR spectra of the substrate and products

![1H NMR spectrum](image)

![13C NMR spectrum](image)
Electronic Supplementary Material (ESI) for Green Chemistry

1H NMR(400 MHz, CDCl3)

13C NMR(100.6 MHz, CDCl3)
1H NMR (400 MHz, CDC3)

13C NMR (100.6 MHz, CDC3)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C NMR (100.6 MHz, CDCl$_3$)
Electronic Supplementary Material (ESI) for Green Chemistry

1H NMR (400 MHz, CDCl3)

13C NMR (100 MHz, CDCl3)
1H NMR (400 MHz, CDCl3)

13C NMR (100.6 MHz, CDCl3)
Electronic Supplementary Material (ESI) for Green Chemistry

1H NMR (400 MHz, CD3OD)

13C NMR (100.6 MHz, CD3OD)
Electronic Supplementary Material (ESI) for Green Chemistry

1H NMR (400 MHz, CDCl3)

13C NMR (100.6 MHz, CDCl3)
4.2 GC-MS Spectral of the Products.
Electronic Supplementary Material (ESI) for Green Chemistry
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2.2 GC-MS Spectral Data of the Pyridines
5. References