

Rhodium-Catalyzed Direct Synthesis of Unprotected NH-Sulfoximine from Sulfoxides

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Supporting information

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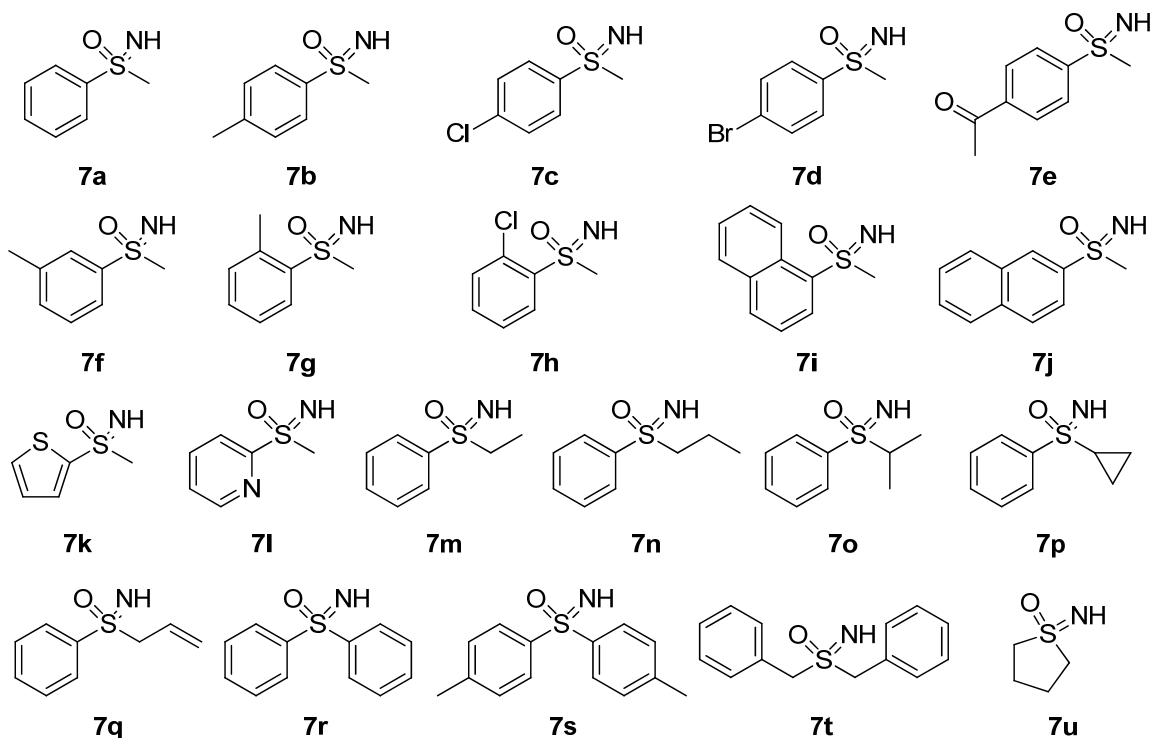
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I. General Information

All the solvents and commercially available reagents were purchased from commercial sources and used directly. For TLC analysis, precoated plates (w/h F254, Dynamic Adsorbents Inc, 0.25 mm thick) were used; for air-flashed column chromatography, Flash Silica Gel (Dynamic Adsorbents Inc, 32-63 μm) was used. The ^1H and ^{13}C NMR spectra were obtained on a Bruker 500 MHz NMR Fourier transform spectrometer. ^1H NMR data was reported as: chemical shift (δ ppm), multiplicity, coupling constant (Hz), and integration. ^{13}C NMR data was reported in terms of chemical shift (δ ppm), multiplicity, and coupling constant (Hz). The infrared spectra were obtained using a Thermo Nicolet IR 330 Spectrometer. Mass (MS) analysis was obtained using Agilent 1100 series LC/MSD system with Electrospray Ionization (ESI). *O*-(2,4-Dinitrophenyl)hydroxylamine (DPH) was purchased from Matrix Sci. and used directly.

II. Experimental Section

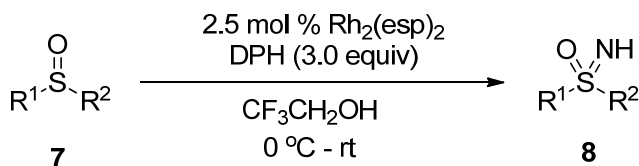
Starting materials:



Sulfoxides **7a**, **7b**, **7p**, **7r**, **7s**, **7t**, and **7u** were purchased from Sigma-Aldrich, TCI, Alfa Aesar, or MP Biomedicals. **7c**, **7d**, **7e**, **7f**, **7g**, **7h**, **7i**, **7j**, **7l**, **7m**, **7n**, **7o** and **7q** were prepared from the

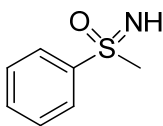
corresponding thiophenols by the addition of alkyl bromides or iodides,¹ followed by the oxidation with *t*-BuOOH according to the reported procedure.² **7k** was prepared by the oxidation of the corresponding sulfide based on the reported protocol.

General procedure for the imination of sulfoxides

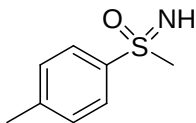


An oven-dried schlenk flask was charged with Rh₂(esp)₂ (11.4 mg, 0.015 mmol) and DPH (0.9 mmol), and then a solution of sulfoxide (**7**, 0.3 mmol) in CF₃CH₂OH was added under nitrogen flow. The reaction mixture was stirred at 0 °C for 2 h under nitrogen, and then warmed to room temperature and stirred for another 20 h. The reaction mixture was diluted with EtOAc, filtered through a pad of Celite, and the filtrate was concentrated in vacuo. The residue was purified by flash chromatography on silica gel (Hexane/EtOAc 4:1~1:2, v/v) to yield the desired product **8**.

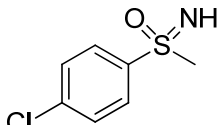
Data of products



Compound **8a**. Yellow oil, yield: 78%. ¹H NMR (500 MHz, CDCl₃) δ: 2.69 (br s, 1 H), 3.08 (s, 3 H), 7.51-7.56 (m, 2 H), 7.57-7.62 (m, 1 H), 7.97-8.01 (m, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ: 46.5, 127.9, 129.5, 133.3, 143.9. Ms (ESI): m/z = 156.1, [M + H⁺].

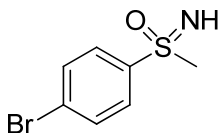


Compound **8b**. Yellow oil, yield: 84%. ¹H NMR (500 MHz, CDCl₃) δ: 2.42 (s, 3 H), 2.50 (br s, 1 H), 3.06 (s, 3 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.86 (d, *J* = 8.0 Hz, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ: 21.8, 46.6, 128.0, 130.1, 140.9, 144.2. IR (neat) ν 3271, 3060, 3025, 2926, 1539, 1455, 1409, 1224, 1097, 1004, 1027, 799, 750, 625, 525 cm⁻¹; Ms (ESI): m/z = 170.1 [M + H⁺].

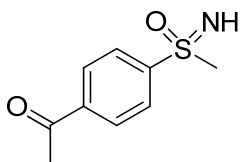


Compound **8c**. Yellow oil, yield: 90%. ¹H NMR (500 MHz, CDCl₃) δ: 2.72 (br s, 1 H), 3.09 (s, 3 H), 7.51 (d, *J* = 8.5 Hz, 2 H), 7.94 (d, *J* = 8.5 Hz, 2 H). ¹³C NMR (125 MHz,

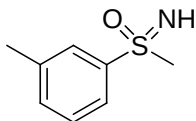
CDCl_3) δ : 46.6, 129.6, 129.9, 140.1, 142.5. IR (neat) ν 3269, 3086, 3019, 2926, 1580, 1470, 1409, 1393, 1321, 1225, 1085, 1002, 829, 762, 731, 557, 519 cm^{-1} ; Ms (ESI): m/z = 190.0, $[\text{M} + \text{H}^+]$.



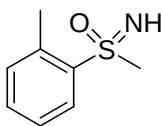
Compound **8d**. Yellow oil, yield: 86%. ^1H NMR (500 MHz, CDCl_3) δ : 2.71 (br s, 1 H), 3.07 (s, 3 H), 7.67 (d, J = 8.5 Hz, 2 H), 7.85 (d, J = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 46.5, 128.5, 129.6, 132.8, 142.9. IR (neat) ν 3268, 3084, 3015, 2926, 2853, 1572, 1472, 1387, 1321, 1225, 1093, 1066, 999, 823, 760, 717 cm^{-1} ; Ms (ESI): m/z = 234.0, 236.0, $[\text{M} + \text{H}^+]$.



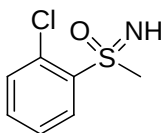
Compound **8e**. Yellow solid, yield: 58%. ^1H NMR (500 MHz, CDCl_3) δ : 2.63 (s, 3 H), 2.74 (s, 3 H), 7.72 (d, J = 8.5 Hz, 2 H), 8.08 (d, J = 8.5 Hz, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 27.1, 44.1, 124.0, 129.4, 139.4, 151.3, 197.3. IR (neat) ν 3084, 2990, 2912, 2851, 1675, 1425, 1396, 1362, 1295, 1269, 1092, 1047, 959, 828, 596 cm^{-1} ; Ms (ESI): m/z = 198.1, $[\text{M} + \text{H}^+]$.



Compound **8f**. Yellow oil, yield: 88%. ^1H NMR (500 MHz, CDCl_3) δ : 2.23-2.67 (m, 4 H), 3.08 (s, 3 H), 7.38-7.44 (m, 2 H), 7.76-7.82 (m, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 21.6, 46.5, 125.1, 128.3, 129.4, 134.1, 139.8, 143.7. IR (neat) ν 3271, 3061, 3021, 2925, 1599, 1477, 1411, 1321, 1226, 1094, 1019, 993, 792, 750, 687 cm^{-1} ; Ms (ESI): m/z = 170.1, $[\text{M} + \text{H}^+]$.

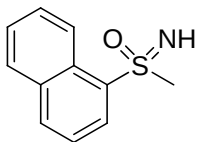


Compound **8g**. Yellow oil, yield: 36%. ^1H NMR (500 MHz, CDCl_3) δ : 2.71-2.77 (m, 4 H), 3.13 (s, 3 H), 7.28-7.37 (m, 2 H), 7.44-7.50 (m, 1 H), 8.09 (d, J = 7.5 Hz, 1 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 21.1, 44.9, 127.0, 129.7, 133.2, 133.3, 137.8, 142.0. IR (neat) ν 3272, 3059, 3015, 2928, 2854, 1470, 1456, 1410, 1319, 1274, 1222, 1195, 1069, 1003, 768, 747 cm^{-1} ; Ms (ESI): m/z = 170.1, $[\text{M} + \text{H}^+]$.

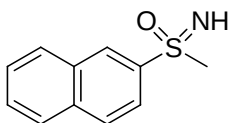


Compound **8h**. Yellow oil, yield: 32%. ^1H NMR (500 MHz, CDCl_3) δ : 2.91 (br s, 1 H), 3.30 (s, 3 H), 7.42-7.47 (m, 1 H), 7.49-7.55 (m, 2 H), 8.17 (d, J = 7.5 Hz, 1 H). ^{13}C NMR

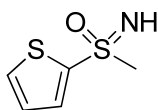
(125 MHz, CDCl₃) δ : 43.8, 127.7, 131.0, 132.4, 132.7, 134.3, 141.3. IR (neat) ν 3273, 3084, 3008, 2928, 2853, 1576, 1450, 1431, 1319, 1231, 1118, 1050, 1003, 959, 755 cm⁻¹; Ms (ESI): m/z = 190.0, [M + H⁺].



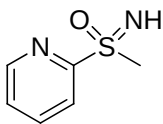
Compound **8i**. Yellow solid, yield: 38%. ¹H NMR (500 MHz, CDCl₃) δ : 2.98 (br s, 1 H), 3.28 (s, 3 H), 7.56-7.64 (m, 2 H), 7.67-7.72 (m, 1 H), 7.97 (d, J = 8.0 Hz, 1 H), 8.09 (d, J = 8.0 Hz, 1 H), 8.38 (dd, J = 1.0, 8.0 Hz, 1 H), 8.99 (d, J = 8.5 Hz, 1 H). ¹³C NMR (125 MHz, CDCl₃) δ : 45.3, 124.8, 125.0, 127.2, 128.7, 129.3, 129.6, 130.0, 134.8, 134.9, 139.0. IR (neat) ν 3272, 3059, 3010, 2927, 2854, 1592, 1506, 1225, 1019, 952, 807, 772, 750 cm⁻¹; Ms (ESI): m/z = 206.1, [M + H⁺].



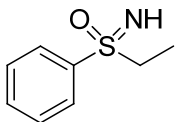
Compound **8j**. Yellow solid, yield: 70%. ¹H NMR (500 MHz, CDCl₃) δ : 2.79 (br s, 1 H), 3.16 (s, 3 H), 7.58-7.67 (m, 2 H), 7.92 (d, J = 8.5 Hz, 1 H), 7.94-8.00 (m, 3 H), 8.56 (s, 1 H). ¹³C NMR (125 MHz, CDCl₃) δ : 46.5, 123.2, 127.9, 128.2, 129.3 (2), 129.6, 129.9, 132.6, 135.3, 140.7. IR (neat) ν 3264, 3050, 3034, 3014, 2931, 1584, 1407, 1343, 1324, 1222, 1123, 1076, 1004, 948, 823, 760, 631 cm⁻¹; Ms (ESI): m/z = 206.1, [M + H⁺].



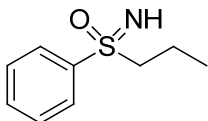
Compound **8k**. Yellow oil, yield: 75%. ¹H NMR (500 MHz, CDCl₃) δ : 3.10 (br s, 1 H), 3.23 (s, 3 H), 7.08-7.12 (m, 1 H), 7.63-7.67 (m, 2 H). ¹³C NMR (125 MHz, CDCl₃) δ : 47.9, 128.2, 133.5, 133.8, 146.3. IR (neat) ν 3267, 3091, 3021, 2926, 1506, 1404, 1342, 1321, 1225, 1096, 1024, 994, 854, 731, 568 cm⁻¹; Ms (ESI): m/z = 162.0, [M + H⁺].



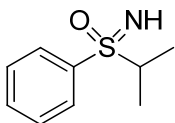
Compound **8l**. Yellow oil, yield: 56%. ¹H NMR (500 MHz, CDCl₃) δ : 2.84 (br s, 1H), 3.26 (s, 3 H), 7.48-7.53 (m, 1 H), 7.91-7.97 (m, 1 H), 8.13 (d, J = 8.0 Hz, 1 H), 8.73 (d, J = 4.5 Hz, 1 H). ¹³C NMR (125 MHz, CDCl₃) δ : 42.7, 121.4, 127.0, 138.6, 150.4, 161.0. IR (neat) ν 3262, 3013, 2925, 2853, 1655, 1578, 1454, 1426, 1317, 1223, 1136, 1068, 1014, 991, 783, 756, 511 cm⁻¹; Ms (ESI): m/z = 157.0, [M + H⁺].



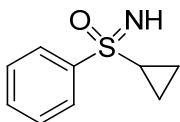
Compound **8m**. Yellow oil, yield: 90%. ^1H NMR (500 MHz, CDCl_3) δ : 1.21-1.26 (m, 3 H), 2.61 (br s, 1 H), 3.15 (q, $J = 7.5$ Hz, 2 H), 7.50-7.56 (m, 2 H), 7.57-7.63 (m, 1 H), 7.95 (d, $J = 8.0$ Hz, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 7.1, 51.1, 127.8, 128.4, 132.3, 140.7. IR (neat) ν 3269, 3063, 2976, 2937, 2877, 1647, 1583, 1477, 1446, 1409, 1380, 1231, 1201, 1098, 973, 761, 721, 691, 674, 568, 510 cm^{-1} ; Ms (ESI): $m/z = 170.1$, $[\text{M} + \text{H}^+]$.



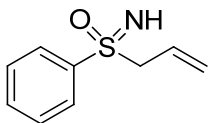
Compound **8n**. Yellow solid, yield: 94%. ^1H NMR (500 MHz, CDCl_3) δ : 0.94 (t, $J = 7.5$ Hz, 3 H), 1.59-1.80 (m, 2H), 2.58 (br s, 1 H), 3.03-3.15 (m, 2 H), 7.49-7.54 (m, 2 H), 7.56-7.61 (m, 1 H), 7.94 (d, $J = 7.5$ Hz, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 13.1, 17.2, 59.5, 128.7, 129.4, 133.3, 142.4. IR (neat) ν 3268, 3063, 2969, 2935, 2877, 1701, 1446, 1406, 1224, 1100, 985, 754, 690, 572, 544, 510 cm^{-1} ; Ms (ESI): $m/z = 184.1$, $[\text{M} + \text{H}^+]$.



Compound **8o**. Yellow solid, yield: 92%. ^1H NMR (500 MHz, CDCl_3) δ : 1.21-1.34 (m, 6 H), 2.41 (br s, 1 H), 3.19-3.29 (m, 1 H), 7.50-7.56 (m, 2 H), 7.58-7.63 (m, 1 H), 7.94 (d, $J = 7.5$ Hz, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 16.3, 16.7, 56.8, 129.3, 129.7, 133.3, 140.2. IR (neat) ν 3270, 3063, 2975, 2929, 2872, 1666, 1467, 1445, 1385, 1366, 1261, 1214, 1105, 978, 759, 716, 692, 650, 565, 548 cm^{-1} ; Ms (ESI): $m/z = 184.1$, $[\text{M} + \text{H}^+]$.

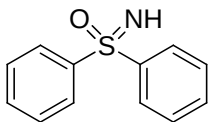


Compound **8p**. Yellow oil, yield: 80%. ^1H NMR (500 MHz, CDCl_3) δ : 0.85-0.94 (m, 1 H), 0.99-1.07 (m, 1 H), 1.13-1.21 (m, 1 H), 1.33-1.41 (m, 1 H), 2.32-2.62 (m, 2 H), 7.49-7.55 (m, 2 H), 7.56-7.61 (m, 1 H), 7.95 (d, $J = 7.5$ Hz, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 5.9, 6.3, 34.5, 128.1, 129.4, 133.0, 143.5. IR (neat) ν 3267, 3060, 3015, 2924, 2853, 1477, 1445, 1418, 1305, 1224, 1188, 1096, 984, 884, 827, 758, 718, 690, 562, 525 cm^{-1} ; Ms (ESI): $m/z = 182.1$, $[\text{M} + \text{H}^+]$.

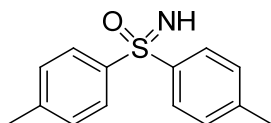


Compound **8q**. Yellow oil, yield: 76%. ^1H NMR (500 MHz, CDCl_3) δ : 2.84 (br s, 1 H), 3.78-3.90 (m, 2 H), 5.13 (d, $J = 17.0$ Hz, 1 H), 5.33 (d, $J = 1.0$ Hz, 1 H), 5.78-5.88 (m, 1

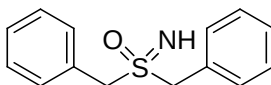
H), 7.51-7.56 (m, 2 H), 7.59-7.64 (m, 1 H), 7.95 (m, 2 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 62.8, 124.7, 125.7, 129.1, 129.3, 133.5, 141.2. Ms (ESI): m/z = 182.1, $[\text{M} + \text{H}^+]$.



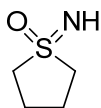
Compound **8r**. Yellow solid, yield: 90%. ^1H NMR (500 MHz, CDCl_3) δ : 3.07 (br s, 1 H), 7.42-7.52 (m, 6 H), 8.03 (d, J = 7.5 Hz, 4 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 128.1, 129.4, 132.8, 143.6. IR (neat) ν 3269, 3062, 3003, 2923, 1583, 1476, 1447, 1230, 1129, 1094, 1069, 980, 760, 721, 688, 569, 542 cm^{-1} ; Ms (ESI): m/z = 218.1, $[\text{M} + \text{H}^+]$.



Compound **8s**. Yellow solid, yield: 84%. ^1H NMR (500 MHz, CDCl_3) δ : 2.37 (s, 6 H), 2.97 (br s, 1 H), 7.26 (d, J = 8.0 Hz, 4 H), 7.91 (d, J = 8.0 Hz, 4 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 21.8, 128.2, 130.1, 141.1, 143.6. IR (neat) ν 3272, 3060, 3027, 2956, 2923, 2855, 720, 1596, 1491, 1450, 1401, 1380, 1228, 1130, 1095, 1019, 977, 818, 662, 623, 541 cm^{-1} ; Ms (ESI): m/z = 246.1, $[\text{M} + \text{H}^+]$.



Compound **8t**. Yellow solid, yield: 74%. ^1H NMR (500 MHz, CDCl_3) δ : 4.17 (d, J = 8.0 Hz, 2 H), 4.28 (d, J = 8.0 Hz, 2 H), 7.39-7.42 (m, 5 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 60.8, 128.2, 129.2, 129.3, 131.4. IR (neat) ν 3250, 3086, 3064, 3030, 2976, 2919, 1493, 1455, 1417, 1259, 1246, 1156, 1150, 1073, 1039, 776, 697, 586 cm^{-1} ; Ms (ESI): m/z = 246.1, $[\text{M} + \text{H}^+]$.



Compound **8u**. Yellow oil, yield: 70%. ^1H NMR (500 MHz, CDCl_3) δ : 2.19-2.29 (m, 4 H), 2.75 (br s, 1 H), 3.06-3.16 (m, 4 H). ^{13}C NMR (125 MHz, CDCl_3) δ : 24.3, 55.7. IR (neat) ν 3386, 3262, 2951, 2926, 2876, 2854, 1654, 1603, 1448, 1416, 1110, 1138, 1078, 1009, 895, 796, 720 cm^{-1} ; Ms (ESI): m/z = 120.0, $[\text{M} + \text{H}^+]$.

III. References and notes:

- (1) M. Hughes, T. Boulwood, G. Zeppetelli and J. A. Bull, *J. Org. Chem.*, 2013, **78**, 844.
- (2) R. Das and D. Chakraborty, *Synthesis*, 2011, 277.

CN(S(=O)(=O)c1ccccc1)C

