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Transition Metal-Based Lewis Acid and Base Ambiphilic Catalysts of Iridium Hydride Complexes: Multicomponent Synthesis of Glutarimides

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General Procedure for $IrH_5(P\text{-}i\text{-}Pr_3)_2$ (1)[1]-Catalyzed Three-Component reaction. A mixture of nitrile (1.0 mmol), olefin (1.1 mmol), H_2O (5.0 mmol), and $IrH_5(P\text{-}i\text{-}Pr_3)_2$ (**1**) (0.1 mmol), and THF (0.25 ml) was placed in a Teflon-cocked sealed tube and stirred at 150 °C for 20 h under argon atmosphere. After removal of the solvent, the mixture was purified by column chromatography (SiO_2, hexane/AcOEt).

3-Methyl-3-phenylpiperidine-2,6-dione (Table 1, Entry 1): mp 106.9 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.59 (s, 3H, C$\underline{H}_3$-), 2.10-2.21 (m, 2H, -COC$\underline{H}_2$-), 2.26-2.64 (m, 2H, -C(Ph)(CH$_3$)C$\underline{H}_2$-), 7.24-7.41 (m, 5H, C$_6\underline{H}_5$-), 8.33 (br, 1H, N$\underline{H}$); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 176.0 (-$\underline{C}$OC(Ph)(CH$_3$)-), 172.6 (-$\underline{C}$OCH$_2$-), 140.4 (ipso $\underline{C}_6$H$_5$-), 129.1 (para $\underline{C}_6$H$_5$-), 127.6 (meta $\underline{C}_6$H$_5$-), 125.5 (ortho $\underline{C}_6$H$_5$-), 47.4 (-CO$\underline{C}$(Ph)(CH$_3$)-), 31.8 (-CO$\underline{C}$H$_2$-), 29.5 (-C(Ph)(CH$_3$)$\underline{C}$H$_2$-), 26.7 ($\underline{C}$H$_3$-); IR (KBr) 3516 (w, NH), 1714 (s, CO), 1711 (s, CO), 1363 (w), 1201 (m), 765 (w), 696 (w); Mass Spectrum, *m*/*z* (CI) 203 (M^+), 202, 175, 160, 158, 118, 117; Anal. Calcd for $C_{12}H_{13}NO_2$: C, 70.92; H, 6.45; N, 6.89. Found: C, 70.79; H, 6.49; N, 6.68.

3-Ethyl-3-phenylpiperidine-2,6-dione (Table 1, Entry 2): mp 82.3 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 0.89 (t, *J* = 7.6 Hz, 3H, C$\underline{H}_3$-), 2.00 (qdd, *J* = 7.6, 13.8, 6.8 Hz, 2H, CH$_3$C$\underline{H}_2$-), 2.17-2.30 (m, 1H, -C(Ph)(Et)C$\underline{H}_2$-), 2.34-2.48 (m, 2H, -COC$\underline{H}_2$-), 2.56-2.64 (m, 1H, -C(Ph)(Et)C$\underline{H}_2$-), 7.28-7.42 (m, 5H, C$_6\underline{H}_5$-), 7.87 (br, 1H, N$\underline{H}$); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 175.1 (-$\underline{C}$OC(Ph)(Et)-), 172.4 (-$\underline{C}$OCH$_2$-), 138.7 (ipso $\underline{C}_6$H$_5$-), 129.0 (meta $\underline{C}_6$H$_5$-), 127.6 (ortho $\underline{C}_6$H$_5$-), 126.0 (para $\underline{C}_6$H$_5$-), 51.1 (-CO$\underline{C}$(Ph)(Et)-), 32.8 (CH$_3\underline{C}$H$_2$-), 29.3 (-CO$\underline{C}$H$_2$-), 27.0 (-C(Ph)(Et)$\underline{C}$H$_2$-), 9.0 ($\underline{C}$H$_3$CH$_2$-); IR (KBr) 3561 (w, NH), 1716 (s, CO), 1691 (s, CO), 1458 (w), 1369 (w), 1273 (w), 1201 (m), 760 (w); Mass Spectrum, *m*/*z* (CI) 218, 217 (M^+), 189, 160, 117, 91; Anal. Calcd for $C_{13}H_{15}NO_2$: C, 71.87; H, 6.96; N, 6.45. Found: C, 71.73; H, 7.07; N, 6.40.

3-Methylpiperidine-2,6-dione (Table 1, Entry 3): mp 95.2 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.31 (d, *J* = 7.5 Hz, 3H, C$\underline{H}_3$-), 1.75 (ddt, *J* = 4.9, 11.4, 13.8 Hz, 1H, -CH(CH$_3$)C$\underline{H}_2$CH$_2$-), 2.07 (ddd, *J* = 4.9, 9.9, 14.6, 1H, -COC$\underline{H}_2$-), 2.47-2.61 (m, 1H, CH$_3$C$\underline{H}$-), 2.52-2.62 (m, 1H, -CH(CH$_3$)C$\underline{H}_2$CH$_2$-), 2.72 (ddd, *J* = 4.9, 4.9, 13.8, 1H, -COC$\underline{H}_2$-), 8.12 (br, 1H, N$\underline{H}$); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 175.3 (-$\underline{C}$OCH(CH$_3$)-), 172.3 (-$\underline{C}$OCH$_2$-), 36.3 (-CH$_2\underline{C}$H(CH$_3$)-), 31.5 (-CO$\underline{C}$H$_2$-), 26.1 (-CH(CH$_3$)$\underline{C}$H$_2$-), 15.2 ($\underline{C}$H$_3$-); IR (KBr) 3208 (m, NH), 1718 (s, CO), 1711 (s, CO), 1361 (s), 1248 (s), 840 (m); Mass Spectrum, *m*/*z* (EI) 127 (M^+), 99, 84, 72, 56, 42; Anal. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.13; N, 11.02. Found: C, 56.42; H, 7.32; N, 10.90.

3-(4-Chlolobenzyl)piperidine-2,6-dione (Table 1, Entry 4): mp 149.4 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 1.66 (dddd, *J* = 1.6, 4.6, 9.1, 17.6 Hz, 1H, -C$\underline{H}_2$CH$_2$CO-), 1.93 (ddd, *J* = 4.6, 9.1, 12.1 Hz, 1H, -C$\underline{H}_2$CH$_2$CO-), 2.47 (ddd, *J* = 6.9, 12.1, 17.6 Hz, 1H, -CH$_2$C$\underline{H}_2$CO-), 2.65-2.70 (m, 1H, -CH$_2$C$\underline{H}_2$CO-), 2.70-2.78 (m, 1H, *p*-ClC$_6$H$_4$CH$_2$C$\underline{H}$-), 2.74 (dd, *J* = 13.7 Hz, 9.1 Hz, 1H, *p*-ClC$_6$H$_4$C$\underline{H}_2$-), 3.38 (dd, *J* = 3.9 Hz, 13.7 Hz, 1H, *p*-ClC$_6$H$_4$C$\underline{H}_2$-), 7.12-7.16 (m, 2H, *p*-ClC$_6\underline{H}_4$CH$_2$-), 7.26-7.30 (m, 2H, *p*-ClC$_6\underline{H}_4$CH$_2$-), 8.19 (br, 1H, N$\underline{H}$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 173.9 (-$\underline{C}$OCH(CH$_2$C$_6$H$_4$-*p*-Cl)-), 172.3 (-$\underline{C}$OCH$_2$-), 136.6 (ipso *p*-Cl$\underline{C}_6$H$_4$), 132.6 (ipso-Cl *p*-Cl$\underline{C}_6$H$_4$), 130.5 (ortho *p*-Cl$\underline{C}_6$H$_4$), 128.8 (ortho-Cl *p*-Cl$\underline{C}_6$H$_4$), 43.0 (-CO$\underline{C}$H(CH$_2$C$_6$H$_4$-*p*-Cl)-), 34.9 (*p*-ClC$_6$H$_4\underline{C}$H$_2$-), 31.3 (-CO$\underline{C}$H$_2$CH$_2$-), 22.7 (-COCH$_2\underline{C}$H$_2$-); IR (KBr) 3036 (m, NH), 1718 (s, CO), 1701 (s, CO), 1491 (m), 1370 (m), 1196 (m), 1089 (w), 868 (w), 715 (w); Mass Spectrum, *m*/*z* (CI) 238, 237 (M^+), 204, 165, 125, 117, 57, 43; Anal. Calcd for $C_{12}H_{12}ClNO_2$: C, 60.64; H, 5.09; N, 5.89. Found: C, 61.04; H, 5.33; N, 5.63.

4-Methylpiperidine-2,6-dione (Table 1, Entries 5 and 6): mp 144.7 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.13 (d, *J* = 6.1 Hz, 3H, C$\underline{H}_3$CH-), 2.19-2.32 (m, 1H, CH$_3$C$\underline{H}$-), 2.25-2.30 (m, 2H, -C$\underline{H}$(H)CH(CH$_3$)C$\underline{H}$(H)-), 2.60-2.74 (m, 2H, -CH(H)CH(CH$_3$)CH(H)-), 8.12 (br, 1H, N$\underline{H}$); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 172.1 ($\underline{C}$O), 39.5 (-$\underline{C}$H$_2$-), 25.5 (CH$_3\underline{C}$H-), 20.2 ($\underline{C}$H$_3$CH-);

IR (KBr) 3180 (m, NH), 1720 (s, CO), 1672 (s), 1460 (m), 1385 (s), 1277 (s), 1142 (s), 866 (s), 584 (s); Mass Spectrum, *m*/*z* (EI) 127 (M^+), 112, 99, 84, 70; Anal. Calcd for $C_6H_9NO_2$: C, 56.68; H, 7.13; N, 11.02. Found: C, 56.71; H, 7.27; N, 10.93.

4-Methyl-4,6,7,8-tetrahydro-1*H*,3*H*-quinoline-2,5-dione (Table 1 Entry 7): mp 185.7 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.02 (d, *J* = 7.2 Hz, 3H, C<u>H</u>$_3$CH-), 1.96-2.13 (m, 2H, -COCH$_2$C<u>H</u>$_2$CH$_2$-), 2.32-2.52 (m, 4H, -COC<u>H</u>$_2$CH$_2$C<u>H</u>$_2$-), 2.42 (dd, *J* = 5.8, 7.2 Hz, 1H, -CH(CH$_3$)C<u>H</u>$_2$-), 2.64 (dd, *J* = 1.8, 7.2 Hz, 1H, -CH(CH$_3$)C<u>H</u>$_2$-), 3.19 (qdd, *J* = 1.8, 5.8, 7.2 Hz, 1H, -C<u>H</u>(CH$_3$)CH$_2$-), 8.51 (s, 1H, N<u>H</u>); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 195.6 (-<u>C</u>OCH$_2$-), 172.1 (-NH<u>C</u>O-), 150.7 (=<u>C</u>NHCO-), 118.2 (-CH$_2$CO<u>C</u>=), 37.9 (-CO<u>C</u>H$_2$CH$_2$CH$_2$-), 36.8 (-CH(CH$_3$)<u>C</u>H$_2$-), 27.3 (-COCH$_2$CH$_2$<u>C</u>H$_2$-), 23.7 (-<u>C</u>H(CH$_3$)CH$_2$-), 21.4 (-COCH$_2$<u>C</u>H$_2$CH$_2$-), 19.0 (-CH(<u>C</u>H$_3$)CH$_2$-); IR (KBr) 3211 (m, NH), 2943 (m), 1701 (s, CO), 1603 (s, CO), 1495 (m), 1385 (m), 1352 (m), 1292 (m), 1244 (m), 1186 (m), 1140 (m), 818 (m); Mass Spectrum, m/e (EI) 179 (M^+), 164, 151, 136, 123, 108, 95, 80; Anal. Calcd for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.06; H, 7.54; N, 7.69.

(3*R, 4*S**)-3-Benzenesulfonyl-4-methylpiperidine-2,6-dione (9a):** A mixture of (benzenesulfonyl)acetonitrile (181 mg, 1.0 mmol), crotononitrile (74 mg, 1.1 mmol), water (90 mg, 5.0 mmol), IrH_5(P-*i*-Pr$_3$)$_2$ (**1**) (52 mg, 0.10 mmol), and THF (0.25 mL) was placed in a Teflon-cocked sealed tube and stirred at 150 °C for 20 h under argon atmosphere. After removal of the solvent, the diastereomer ratio was determined by ^{1}H-NMR analysis ((3*R**, 4*S**)-**9a :** (3*R**, 4*R**)-**10a** = 96:4). The mixture was purified by column chromatography (SiO_2, hexane : AcOEt = 2 : 1) to afford the product (3*R**, 4*S**)-**9a** as a colorless solid in 64% yield (172 mg, 0.64 mmol). The stereochemistry of **9a** was unequivocally determined by x-ray crystallographic analysis. (3*R**, 4*S**)-**9a**: mp 177.3 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 1.21 (d, *J* = 7.1 Hz, 3H, C<u>H</u>$_3$CH-), 2.53 (ddd, *J* = 1.6, 1.6, 17.8 Hz, 1H, -COC<u>H</u>$_2$-), 3.21-3.33 (m, 1H, CH$_3$C<u>H</u>-), 3.39 (ddd, *J* = 1.6, 1.6, 6.9 Hz, 1H, PhSO$_2$C<u>H</u>-), 3.84 (dd, *J* = 1.6, 1.6 Hz, -COC<u>H</u>$_2$-), 7.58-7.66 (m, 2H, C$_6$<u>H</u>$_5$SO$_2$-), 7.72-7.75 (m, 1H, C$_6$<u>H</u>$_5$SO$_2$-), 7.87-7.90 (m, 2H, C$_6$<u>H</u>$_5$SO$_2$-), 8.18 (br, 1H, N<u>H</u>); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 170.3 (-<u>C</u>OCH(SO$_2$Ph)-), 164.0 (-<u>C</u>OCH$_2$-), 137.7 (ipso <u>C</u>$_6$H$_5$-), 134.7 (para <u>C</u>$_6$H$_5$-), 129.3 (meta <u>C</u>$_6$H$_5$-), 129.0 (ortho <u>C</u>$_6$H$_5$-), 71.0 (PhSO$_2$<u>C</u>H-), 35.3 (-CO<u>C</u>H$_2$-), 25.2 (<u>C</u>H$_3$CH-), 20.3 (CH$_3$<u>C</u>H-); IR (KBr) 3107 (m, NH), 1730 (s, CO), 1696 (s, CO), 1448 (w), 1371 (w), 1325 (s, SO_2), 1259 (s, SO_2), 1149 (s, SO_2), 1116 (w), 1082 (w), 860 (w), 725 (m); Mass Spectrum, *m*/*z* (CI) 268, 267 (M^+), 242, 228, 203; Anal. Calcd for $C_{12}H_{13}NO_4S$: C, 53.92; H, 4.90; N, 5.24. Found: C, 54.06; H, 4.91; N, 5.35.

(3*R, 4*R**)-3-Benzenesulfonyl-4-phenylpiperidine-2,6-dione (9b):** A mixture of (benzenesulfonyl)acetonitrile (181 mg, 1.0 mmol), cinnamonitrile (142 mg, 1.1 mmol), water (90 mg, 5.0 mmol), IrH_5(P-*i*-Pr$_3$)$_2$ (**1**) (52 mg, 0.10 mmol), and THF (0.25 mL) was placed in a Teflon-cocked sealed tube and stirred at 150 °C for 20 h under argon atmosphere. The diastereomer (3*R**, 4*S**)-**10b** was not detected in the reaction mixture (^{1}H NMR). After removal of the solvent, the mixture was purified by column chromatography (SiO_2, hexane : AcOEt = 2 : 1) to afford the pure diastereoisomer (3*R**, 4*R**)-**9b** as a colorless solid in 52% yield (171 mg, 0.52 mmol). The stereochemistry of **9b** was unequivocally determined by x-ray crystallographic analysis. mp 190.2 °C; ^{1}H NMR ($CDCl_3$, 270 MHz) δ 3.04 (ddd, *J* = 1.5, 1.5, 18.0 Hz, 1H, -COC<u>H</u>$_2$-), 3.63 (dd, *J* = 6.9, 18.0 Hz, 1H, PhC<u>H</u>-), 4.22 (dd, *J* = 1.5, 1.5 Hz, 1H, -COC<u>H</u>$_2$-), 4.45 (ddd, *J* = 1.5, 1.5, 6.9 Hz, 1H, PhSO$_2$C<u>H</u>-), 7.10-7.16 (m, 2H, C$_6$<u>H</u>$_5$-), 7.24-7.36 (m, 3H, C$_6$<u>H</u>$_5$-), 7.56-7.62 (m, 2H, C$_6$<u>H</u>$_5$SO$_2$-), 7.70-7.76 (m, 1H, C$_6$<u>H</u>$_5$SO$_2$-), 7.90-7.96 (m, 2H, C$_6$<u>H</u>$_5$SO$_2$-), 8.31 (br, 1H, N<u>H</u>); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 170.4 (-<u>C</u>OCH(SO$_2$Ph)-), 164.0 (-<u>C</u>OCH$_2$-), 139.3 (<u>C</u>$_6$H$_5$-), 137.5 (<u>C</u>$_6$H$_5$SO$_2$-), 134.9 (<u>C</u>$_6$H$_5$SO$_2$-), 129.5 (<u>C</u>$_6$H$_5$SO$_2$-), 129.4 (<u>C</u>$_6$H$_5$-), 129.1 (<u>C</u>$_6$H$_5$-), 128.2 (<u>C</u>$_6$H$_5$-), 126.5 (<u>C</u>$_6$H$_5$SO$_2$-), 70.9 (PhSO$_2$<u>C</u>H-), 34.7 (-<u>C</u>H$_2$-), 34.2 (Ph<u>C</u>H-); IR (KBr) 3568 (w, NH), 1736 (s, CO), 1710 (s, CO), 1309 (m), 1257 (m), 1150 (m), 1078 (w), 701 (w); Mass Spectrum, *m*/*z* (CI) 331, 330,

329 (M^+), 313, 265, 264, 200, 188, 131, 117, 91, 43; Anal. Calcd for $C_{17}H_{15}NO_4S$: C, 61.99; H, 4.59; N, 4.25. Found: C, 61.77; H, 4.64; N, 4.09.

(3*R, 4*S**, 5*R**)-3-Benzenesulfonyl-5-phenyl-4-propylpiperidine-2,6-dione (11):** A mixture of (benzenesulfonyl)acetonitrile (362 mg, 2.0 mmol), (*Z*)-2-phenyl-2-hexenenitrile (377 mg, 12.2 mmol), water (180 mg, 10.0 mmol), $IrH_5(P\text{-}i\text{-}Pr_3)_2$ (**1**) (103 mg, 0.20 mmol), and THF (0.5 mL) was placed in a Teflon-cocked sealed tube and stirred at 150 ^oC for 20 h under argon atmosphere. After removal of the solvent, the mixture was purified by column chromatography (SiO_2, hexane : AcOEt = 2 : 1) to afford the pure diastereoisomer **11** as a colorless solid in 30% yield (101 mg, 0.60 mmol). The stereochemistry of **11** was determined by NOE and NOESY experiment. Strong NOE was observed between two protons of 3- and 5-position of **11** (2- and 4-posistions of 2-benzenesulfonyl-4-phenyl-3-propylglutarimide) (10%). Other possible diastereomers were not detected in the reaction mixture by ^1H NMR and HPLC analyses. mp 146.2 ^oC; ^1H NMR ($CDCl_3$, 270 MHz) δ 0.74 (t, *J* = 7.1 Hz, 3H, $C\underline{H}_3CH_2CH_2$-), 1.11-1.79 (m, 4H, $CH_3C\underline{H}_2C\underline{H}_2$-), 3.02-3.18 (m, 1H, $CH_3CH_2CH_2C\underline{H}$-), 4.12 (d, *J* = 1.2 Hz, 1H, $C_6H_5C\underline{H}$-), 4.89 (d, *J* = 4.9 Hz, 1H, $C_6H_5SO_2C\underline{H}$-), 7.56-7.82 (m, 5H, $C_6\underline{H}_5CH$-), 7.84-8.01 (m, 5H, $C_6\underline{H}_5SO_2CH$-), 8.22 (br, 1H, $N\underline{H}$); ^{13}C NMR ($CDCl_3$, 68 MHz) δ 175.1 ($C_6H_5SO_2CH\underline{C}O$-), 170.5 ($C_6H_5CH\underline{C}O$-), 136.7 ($\underline{C}_6H_5$-), 134.8 ($\underline{C}_6H_5SO_2$-), 130.2, 129.5, 128.9, 128.5, 128.1, 127.8, 69.5 ($C_6H_5SO_2\underline{C}H$-), 50.9 ($C_6H_5\underline{C}H$-), 37.7 ($CH_3CH_2\underline{C}H_2$-), 29.9 ($CH_3CH_2CH_2\underline{C}H$-), 19.3 ($CH_3\underline{C}H_2CH_2$-), 13.3 ($\underline{C}H_3CH_2CH_2$-); Mass Spectrum, *m*/*z* (CI) 372, 371 (M^+), 344, 229, 202; Anal. Calcd for $C_{20}H_{21}NO_4S$: C, 64.67; H, 5.70; N, 3.77. Found: C, 64.45; H, 5.79; N, 3.83.

References

1) Clerici, M. G.; Gioacchino, S. D.; Maspero, F.; Perrotti, E.; Zanobi, A. *J. Organomet. Chem.* **1975,** *84,* 379.

Table S1. Summary of Crystallographic Data of **9a**·1/2C_6H_6

Molecular Formula	$C_{12}H_{13}NSO_4$·1/2C_6H_6
Formula Weight	306.36
Crystal Dimensions	0.10 X 0.30 X 0.10 mm
Crystal Color, Habit	colorless, needle
Crystal System	monoclinic
Lattice Type	primitive
Space Group	$P2_1/_C$(#14)
a (Å)	10.4420(6)
b (Å)	6.8961(3)
c (Å)	21.310(1)
β (^{o})	100.194(1)
Cell Volume (Å^3)	1510.3(2)
Z value	4
F (000)	644.00
D_{calc} (g/cm^{-3})	1.347
Temperature	-60.0 ^{o}C
Radiation	graphite monochromated MoKα (λ = 0.71069 Å)
μ (MoKα) (cm^{-1})	2.29
$2\theta_{max}$ (^{o})	55.0
Total Number of Unique Reflections	3421
Unique Observed Reflections with I > 2σ(I)	2888
Number of Variables	191
Reflection / Parameter Ratio	15.12
Final R^a and $R_w{}^b$ (for all data)	0.041, 0.141
Goodness of Fit	1.11
Max Shift / Error	0.00
Method of Phase Determination	direct methods (Shelex-97)

$^aR = \Sigma[\,|Fo| - |Fc|\,] / \Sigma\,|Fo|$. $^bR_w = \{\Sigma(\omega\,|Fo| - |Fc|^2) / \Sigma\omega(|Fo|)^2\}^{1/2}$.

Table S2. Summary of Crystallographic Data of **9b**

Molecular Formula	$C_{17}H_{15}NSO_4$
Formula Weight	329.37
Crystal Dimensions	0.20 X 0.20 X 0.1 mm
Crystal Color, Habit	colorless, block
Crystal System	monoclinic
Lattice Type	primitive
Space Group	$P2_1/_C$(#14)
a (Å)	10.1526(6)
b (Å)	12.6895(7)
c (Å)	12.0965(6)
β (^{o})	96.420(2)
Cell Volume (Å^3)	1548.6(1)
Z value	4
F (000)	688.00
D_{calc} (g/cm^{-3})	1.413
Temperature	-63.0 ^{o}C
Radiation (Å)	graphite monochromated MoKα (λ = 0.71069 Å)
μ (MoKα) (cm^{-1})	2.29
$2\theta_{max}$ (^{o})	55.0
Total Number of Unique Reflections	3489
Unique Observed Reflections with I > 2σ(I)	2815
Number of Variables	209
Reflection / Parameter Ratio	13.47
Final R^a and $R_w{}^b$ (for all data)	0.045, 0.144
Goodness of Fit	1.07
Max Shift / Error	0.00
Method of Phase Determination	direct methods (Shelex-97)

$^aR = \Sigma[\,|Fo| - |Fc|\,] / \Sigma\,|Fo|$. $^bRw = \{\Sigma(\omega\,|Fo| - |Fc|^2) / \Sigma\omega(|Fo|)^2\}^{1/2}$.

Table S3. Atomic Coordinates and B_{iso}/B_{eq} of **9a**

atom	x	y	z	Beq
S(1)	0.20654(4)	0.04266(6)	0.14401(2)	2.86(1)
O(1)	0.2195(1)	-0.0660(2)	0.08831(6)	4.20(3)
O(2)	0.2554(1)	0.2382(2)	0.15007(7)	4.13(3)
O(3)	0.0281(1)	0.1978(1)	0.24892(5)	2.97(2)
O(4)	-0.0627(2)	0.6035(2)	0.08274(6)	4.59(3)
N(1)	-0.0220(1)	0.3907(2)	0.16354(5)	2.66(2)
C(1)	-0.0279(2)	0.2747(2)	0.05367(6)	2.79(3)
C(2)	-0.0491(2)	0.0736(2)	0.08024(6)	2.48(2)
C(3)	0.0336(1)	0.0514(2)	0.14724(6)	2.12(2)
C(4)	0.0136(1)	0.2160(2)	0.19135(6)	2.25(2)
C(6)	0.2804(1)	-0.0907(3)	0.21199(8)	3.04(3)
C(7)	0.3018(2)	-0.2874(3)	0.2058(1)	4.04(3)
C(8)	0.3671(2)	-0.3889(3)	0.2582(1)	5.04(5)
C(9)	0.4070(2)	-0.2958(4)	0.3154(1)	5.32(5)
C(10)	0.3837(2)	-0.1021(4)	0.3218(1)	5.28(5)
C(11)	0.3185(2)	0.0046(3)	0.26975(9)	4.08(3)
C(12)	-0.0404(2)	0.4365(2)	0.09885(7)	2.88(3)
C(13)	-0.1927(2)	0.0384(2)	0.08213(8)	3.39(3)
C(14)	0.5921(3)	-0.1296(5)	0.4903(1)	6.27(6)
C(15)	0.6010(2)	0.0565(5)	0.4728(1)	6.30(7)
C(16)	0.5089(3)	0.1862(3)	0.4819(1)	6.29(6)
H(1)	-0.0356	0.4924	0.1916	3.1725
H(2)	0.2724	-0.3512	0.1666	4.8985
H(3)	0.3842	-0.5228	0.2543	6.1089
H(4)	0.4511	-0.3675	0.3505	6.2889
H(5)	0.4114	-0.0417	0.3617	6.2952
H(6)	0.3013	0.1395	0.2736	4.9253
H(7)	0.6725	0.0980	0.4545	7.3825
H(8)	-0.0213	-0.0203	0.0530	2.9443
H(9)	0.0100	-0.0664	0.1654	2.5724
H(10)	0.0570	0.2784	0.0436	3.3486
H(11)	-0.0905	0.2936	0.0162	3.3486
H(12)	-0.2221	0.1315	0.1091	4.0584
H(13)	-0.2418	0.0486	0.0404	4.0584
H(14)	-0.2028	-0.0882	0.0984	4.0584
H(16)	0.6576	-0.2192	0.4841	7.5238
H(18)	0.5159	0.3176	0.4692	7.6620

$B_{eg} = 3/8\pi^2[(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$

Table S4. Anisotropic Displacement Parameters for **9a**·1/2C_6H_6

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0399(2)	0.0392(3)	0.0326(2)	0.0007(1)	0.0143(2)	-0.0002(1)
O(1)	0.0576(7)	0.0697(9)	0.0360(7)	0.0166(6)	0.0192(6)	-0.0071(6)
O(2)	0.0502(7)	0.0456(7)	0.0643(8)	-0.0126(5)	0.0190(6)	0.0096(6)
O(3)	0.0658(7)	0.0280(5)	0.0218(5)	0.0036(5)	0.0147(5)	0.0026(4)
O(4)	0.116(1)	0.0256(6)	0.0361(6)	0.0089(6)	0.0218(7)	0.0071(5)
N(1)	0.0610(8)	0.0199(5)	0.0224(6)	0.0018(5)	0.0138(5)	-0.0014(4)
C(1)	0.0586(9)	0.0276(7)	0.0212(6)	0.0004(6)	0.0109(6)	0.0003(5)
C(2)	0.0464(8)	0.0233(6)	0.0250(7)	0.0002(5)	0.0080(6)	-0.0042(5)
C(3)	0.0377(7)	0.0196(6)	0.0249(6)	-0.0004(5)	0.0104(5)	-0.0012(5)
C(4)	0.0416(7)	0.0216(6)	0.0242(6)	-0.0012(5)	0.0112(5)	0.0000(5)
C(6)	0.0334(7)	0.0443(8)	0.0390(8)	-0.0003(6)	0.0094(6)	0.0022(6)
C(7)	0.0492(9)	0.0483(10)	0.058(1)	0.0079(8)	0.0146(8)	0.0048(8)
C(8)	0.056(1)	0.060(1)	0.079(2)	0.0158(9)	0.021(1)	0.024(1)
C(9)	0.0437(10)	0.093(2)	0.066(1)	0.011(1)	0.0109(9)	0.034(1)
C(10)	0.049(1)	0.106(2)	0.043(1)	-0.012(1)	-0.0010(8)	0.006(1)
C(11)	0.0498(9)	0.061(1)	0.0422(10)	-0.0104(8)	0.0037(7)	-0.0017(8)
C(12)	0.0611(10)	0.0251(7)	0.0257(7)	0.0011(6)	0.0139(6)	0.0030(5)
C(13)	0.0470(9)	0.0350(8)	0.0451(9)	-0.0009(6)	0.0030(7)	-0.0017(6)
C(14)	0.078(2)	0.094(2)	0.061(1)	0.033(1)	0.000(1)	-0.008(1)
C(15)	0.056(1)	0.128(3)	0.053(1)	-0.029(1)	0.0038(10)	0.013(1)
C(16)	0.111(2)	0.048(1)	0.068(1)	-0.017(1)	-0.017(1)	0.009(1)

The general temperature factor expression: $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$

Table S5. Selected Bond Lengths of **9a**·1/2C_6H_6 (Å)

atom	atom	distance	atom	atom	distance
S(1)	O(1)	1.430(1)	C(2)	C(13)	1.527(2)
S(1)	O(2)	1.439(1)	C(3)	C(4)	1.512(2)
S(1)	C(3)	1.820(2)	C(6)	C(7)	1.385(3)
S(1)	C(6)	1.773(2)	C(6)	C(11)	1.390(3)
O(3)	C(4)	1.216(2)	C(7)	C(8)	1.390(3)
O(4)	C(12)	1.212(2)	C(8)	C(9)	1.376(3)
N(1)	C(4)	1.365(2)	C(9)	C(10)	1.369(4)
N(1)	C(12)	1.394(2)	C(10)	C(11)	1.402(3)
C(1)	C(2)	1.528(2)	C(14)	C(15)	1.344(5)
C(1)	C(12)	1.495(2)	C(14)	C(16)	1.356(5)
C(2)	C(3)	1.540(2)	C(15)	C(16)	1.352(4)

Table S6. Selected Bond Angles of **9a**·1/2C_6H_6 (°)

atom	atom	atom	angle	atom	atom	atom	angle
O(1)	S(1)	O(2)	118.75(9)	N(1)	C(4)	C(3)	116.7(1)
O(1)	S(1)	C(3)	106.80(7)	S(1)	C(6)	C(7)	119.0(1)
O(1)	S(1)	C(6)	108.36(8)	S(1)	C(6)	C(11)	119.6(1)
O(2)	S(1)	C(3)	107.70(7)	C(7)	C(6)	C(11)	121.5(2)
O(2)	S(1)	C(6)	108.46(8)	C(6)	C(7)	C(8)	118.8(2)
C(3)	S(1)	C(6)	106.10(7)	C(7)	C(8)	C(9)	120.4(2)
C(4)	N(1)	C(12)	127.5(1)	C(8)	C(9)	C(10)	120.8(2)
C(2)	C(1)	C(12)	113.8(1)	C(9)	C(10)	C(11)	120.2(2)
C(1)	C(2)	C(3)	109.8(1)	C(6)	C(11)	C(10)	118.4(2)
C(1)	C(2)	C(13)	111.2(1)	O(4)	C(12)	N(1)	118.8(1)
C(3)	C(2)	C(13)	110.6(1)	O(4)	C(12)	C(1)	124.1(1)
S(1)	C(3)	C(2)	111.4(1)	N(1)	C(12)	C(1)	117.1(1)
S(1)	C(3)	C(4)	107.20(9)	C(15)	C(14)	C(16)	119.5(3)
C(2)	C(3)	C(4)	112.6(1)	C(14)	C(15)	C(16)	120.5(3)
O(3)	C(4)	N(1)	120.4(1)	C(14)	C(16)	C(15)	120.0(3)
O(3)	C(4)	C(3)	122.9(1)				

Table S7. Atomic Coordinates and B_{iso}/B_{eq} for **9b**

atom	x	y	z	Beq
S(1)	0.23420(4)	0.19233(3)	0.77996(4)	2.47(1)
O(1)	0.5170(1)	-0.06675(9)	0.6215(1)	2.91(3)
O(2)	0.4248(1)	0.2793(1)	0.5948(1)	2.94(3)
O(3)	0.2128(1)	0.1309(1)	0.8760(1)	3.25(3)
O(4)	0.1771(1)	0.1570(1)	0.6722(1)	3.73(3)
N(1)	0.4773(2)	0.1070(1)	0.6138(1)	2.56(3)
C(1)	0.8256(2)	0.1336(3)	1.0194(2)	5.17(6)
C(2)	0.6992(2)	0.1040(2)	0.9767(2)	4.12(5)
C(3)	0.6333(2)	0.1550(1)	0.8839(2)	2.57(3)
C(4)	0.6999(2)	0.2327(2)	0.8326(2)	3.47(4)
C(5)	0.8277(2)	0.2627(2)	0.8760(2)	4.42(5)
C(6)	0.8893(2)	0.2143(2)	0.9702(2)	4.69(5)
C(7)	0.4904(2)	0.1227(1)	0.8486(1)	2.22(3)
C(8)	0.4137(2)	0.2047(1)	0.7756(1)	2.08(3)
C(9)	0.4760(2)	0.0142(1)	0.7923(1)	2.40(3)
C(10)	0.4384(2)	0.2026(1)	0.6544(2)	2.22(3)
C(11)	0.4936(2)	0.0138(1)	0.6709(1)	2.23(3)
C(12)	0.1109(3)	0.5261(2)	0.8391(3)	4.63(5)
C(13)	0.1480(2)	0.4615(2)	0.9286(2)	4.05(4)
C(14)	0.1839(2)	0.3577(2)	0.9092(2)	3.14(3)
C(15)	0.1834(2)	0.3224(1)	0.8012(2)	2.57(3)
C(16)	0.1489(2)	0.3882(2)	0.7107(2)	3.53(4)
C(17)	0.1116(3)	0.4911(2)	0.7310(2)	4.56(5)
H(1)	0.8673	0.3145	0.8362	3.9186
H(2)	0.9778	0.2327	0.9977	3.9186
H(3)	0.8725	0.0967	1.0778	3.9186
H(4)	0.6612	0.2723	0.7693	3.9186
H(5)	0.6545	0.0318	1.0054	3.9186
H(6)	0.1433	0.3549	0.6414	3.9186
H(7)	0.0887	0.5439	0.6690	3.9186
H(8)	0.0929	0.6064	0.8583	3.9186
H(9)	0.1606	0.4871	1.0081	3.9186
H(10)	0.2091	0.3062	0.9769	3.9186
H(11)	0.4324	0.2731	0.8031	3.9186
H(12)	0.4574	0.1164	0.9167	3.9186
H(13)	0.5371	-0.0415	0.8319	3.9186
H(14)	0.3908	-0.0180	0.7979	3.9186
H(15)	0.4799	0.1048	0.5515	3.9186

$B_{eg} = 3/8\pi^2[(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha)$

Table S8. Anisotropic Displacement Parameters for **9b**

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1)	0.0297(3)	0.0309(3)	0.0335(3)	-0.0048(2)	0.0051(2)	-0.0023(2)
O(1)	0.0561(8)	0.0249(6)	0.0302(7)	0.0069(6)	0.0077(6)	-0.0020(5)
O(2)	0.0513(8)	0.0253(6)	0.0362(7)	0.0020(6)	0.0089(6)	0.0061(5)
O(3)	0.0383(7)	0.0374(7)	0.0497(8)	-0.0023(6)	0.0144(6)	0.0092(6)
O(4)	0.0410(8)	0.0572(9)	0.0427(8)	-0.0153(7)	0.0003(6)	-0.0154(7)
N(1)	0.0491(9)	0.0243(7)	0.0254(7)	0.0024(6)	0.0100(6)	0.0012(6)
C(1)	0.043(1)	0.109(2)	0.042(1)	-0.004(1)	-0.0060(10)	0.011(1)
C(2)	0.040(1)	0.079(2)	0.036(1)	-0.007(1)	0.0002(9)	0.011(1)
C(3)	0.0332(9)	0.0342(9)	0.0304(9)	0.0002(7)	0.0044(7)	-0.0049(7)
C(4)	0.0375(10)	0.037(1)	0.056(1)	-0.0026(8)	0.0008(9)	0.0061(9)
C(5)	0.039(1)	0.044(1)	0.084(2)	-0.0074(9)	0.003(1)	0.002(1)
C(6)	0.036(1)	0.079(2)	0.062(2)	-0.006(1)	-0.003(1)	-0.012(1)
C(7)	0.0337(9)	0.0274(8)	0.0237(8)	-0.0003(6)	0.0051(6)	-0.0004(6)
C(8)	0.0287(8)	0.0221(8)	0.0288(8)	-0.0018(6)	0.0061(7)	-0.0043(6)
C(9)	0.0408(10)	0.0237(8)	0.0271(8)	-0.0004(7)	0.0060(7)	0.0009(6)
C(10)	0.0318(8)	0.0217(8)	0.0311(9)	-0.0018(6)	0.0046(7)	-0.0007(6)
C(11)	0.0333(8)	0.0238(8)	0.0275(8)	0.0005(6)	0.0041(6)	0.0001(6)
C(12)	0.052(1)	0.044(1)	0.082(2)	0.015(1)	0.015(1)	0.000(1)
C(13)	0.048(1)	0.048(1)	0.059(1)	0.0094(10)	0.012(1)	-0.008(1)
C(14)	0.0347(9)	0.044(1)	0.041(1)	0.0065(8)	0.0065(8)	-0.0028(9)
C(15)	0.0257(8)	0.0354(9)	0.0369(10)	0.0020(7)	0.0042(7)	0.0015(7)
C(16)	0.042(1)	0.049(1)	0.042(1)	0.0043(9)	0.0010(9)	0.0082(9)
C(17)	0.055(1)	0.047(1)	0.071(2)	0.013(1)	0.004(1)	0.022(1)

The general temperature factor expression: $\exp[-2\pi^2(a^{*2}U_{11}h^2 + b^{*2}U_{22}k^2 + c^{*2}U_{33}l^2 + 2a^*b^*U_{12}hk + 2a^*c^*U_{13}hl + 2b^*c^*U_{23}kl)]$

Table S9. Selected Bond Lengths of **9b** (Å)

atom	atom	distance	atom	atom	distance
S(1)	O(3)	1.436(2)	C(4)	C(5)	1.398(3)
S(1)	O(4)	1.437(2)	C(5)	C(6)	1.380(4)
S(1)	C(8)	1.836(2)	C(7)	C(8)	1.522(2)
S(1)	C(15)	1.757(2)	C(7)	C(9)	1.535(2)
O(1)	C(11)	1.221(2)	C(8)	C(10)	1.515(3)
O(2)	C(10)	1.211(2)	C(9)	C(11)	1.499(2)
N(1)	C(10)	1.382(2)	C(12)	C(13)	1.377(4)
N(1)	C(11)	1.370(2)	C(12)	C(17)	1.383(4)
C(1)	C(2)	1.381(3)	C(13)	C(14)	1.393(3)
C(1)	C(6)	1.380(4)	C(14)	C(15)	1.381(3)
C(2)	C(3)	1.400(3)	C(15)	C(16)	1.390(3)
C(3)	C(4)	1.381(3)	C(16)	C(17)	1.389(3)
C(3)	C(7)	1.522(2)			

Table S10. Selected Bond Angles of **9b** (^{o})

atom	atom	atom	angle	atom	atom	atom	angle
O(3)	S(1)	O(4)	118.84(9)	S(1)	C(8)	C(7)	111.7(1)
O(3)	S(1)	C(8)	108.07(8)	S(1)	C(8)	C(10)	107.4(1)
O(3)	S(1)	C(15)	108.55(9)	C(7)	C(8)	C(10)	114.8(1)
O(4)	S(1)	C(8)	107.55(8)	C(7)	C(9)	C(11)	114.9(1)
O(4)	S(1)	C(15)	109.31(9)	O(2)	C(10)	N(1)	120.8(2)
C(8)	S(1)	C(15)	103.42(8)	O(2)	C(10)	C(8)	122.8(2)
C(10)	N(1)	C(11)	127.0(2)	N(1)	C(10)	C(8)	116.4(1)
C(2)	C(1)	C(6)	120.1(2)	O(1)	C(11)	N(1)	119.7(2)
C(1)	C(2)	C(3)	120.9(2)	O(1)	C(11)	C(9)	122.2(2)
C(2)	C(3)	C(4)	118.5(2)	N(1)	C(11)	C(9)	118.0(1)
C(2)	C(3)	C(7)	117.1(2)	C(13)	C(12)	C(17)	121.5(2)
C(4)	C(3)	C(7)	124.4(2)	C(12)	C(13)	C(14)	118.9(2)
C(3)	C(4)	C(5)	120.4(2)	C(13)	C(14)	C(15)	119.5(2)
C(4)	C(5)	C(6)	120.3(2)	S(1)	C(15)	C(14)	118.3(1)
C(1)	C(6)	C(5)	119.7(2)	S(1)	C(15)	C(16)	120.1(2)
C(3)	C(7)	C(8)	112.9(1)	C(14)	C(15)	C(16)	121.7(2)
C(3)	C(7)	C(9)	114.0(1)	C(15)	C(16)	C(17)	118.3(2)
C(8)	C(7)	C(9)	109.8(1)	C(12)	C(17)	C(16)	120.0(2)

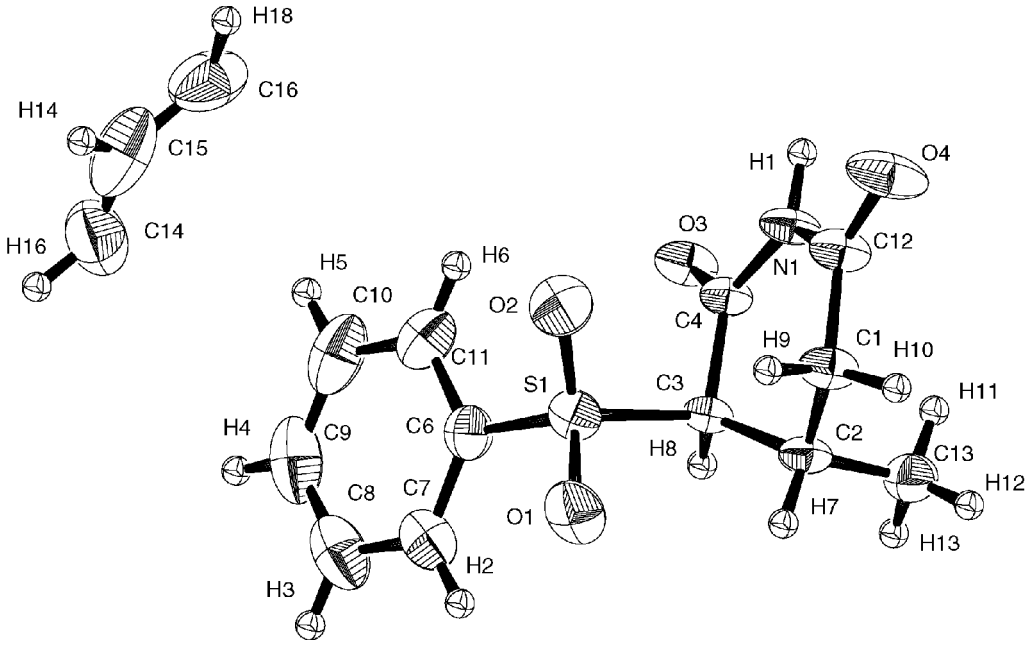

Figure S1. ORTEP Drawing of **9a**·1/2C_6H_6

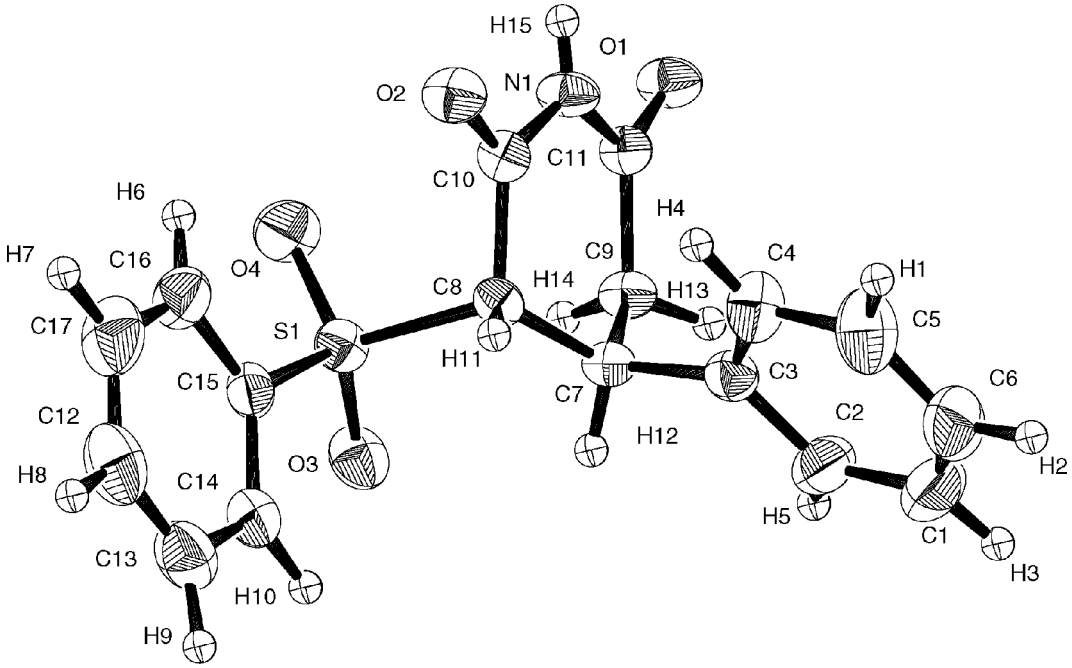

Figure S2. ORTEP Drawing of **9b**