Supporting Information

Convenient Synthesis of Triphenylphosphine Sulfide from Sulfur and Triphenylphosphine

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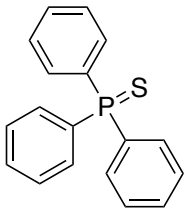
Triphenylphosphine sulfide (2a)



A mixture of triphenylphosphine **1a** (2.62 g, 10 mmol), sulfur (320 mg, 10 mmol) and CH_2Cl_2 (5 mL) was shaken in a 20-mL tube at rt. Sulfur was dissolved completely after 30 second and the reaction mixture became homogeneous and slightly hotter. The reaction mixture was cooled to rt and the precipitated product PPh_3S was filtered, washed with methanol (2 mL × 3) and dried to afford 2.59 g (88%). Concentration of the filtrate provided additional product of acceptable purity (3.2 g, 11%). For larger scale synthesis (40 mmol or 10 g), $CHCl_3$ is used in place of CH_2Cl_2 to avoid vigorous boiling due to low boiling point of CH_2Cl_2. In these cases, the reaction mixtures were concentrated before trituration with methanol. Yields were in general > 90%.

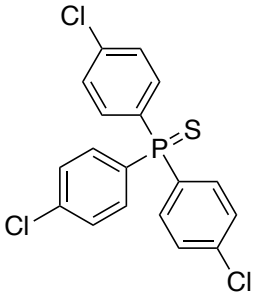
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.73-7.69 (m, 6H), 7.50-7.40 (m, 9H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 133.1 (d, J = 85.4 Hz), 132.4 (d, J = 10.1 Hz), 131.7 (d, J = 2.8 Hz), 128.6 (d, J = 12.8 Hz).

^{31}P NMR ($CDCl_3$, 202 MHz) δ 43.3.

Anal. Calcd for $C_{18}H_{15}PS$: C, 73.45; H, 5.14; S, 10.89. Found: C, 73.32; H, 5.33; S, 10.93.

Tris(4-chlorophenyl)phosphine sulfide (2b)

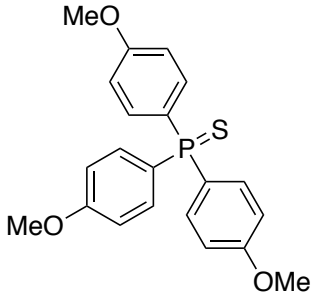


A mixture of tris(4-chlorophenyl)phosphine **1b** (398 mg, 1 mmol), sulfur (34 mg, 1.05 mmol) and $CHCl_3$ (0.2 mL) was stirred in a 7-mL tube at rt. Sulfur was dissolved completely after 5-10 min. Evaporation of the reaction mixture provided the product as a white solid (429 mg, quant).

^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.60 (dd, J = 12.8, 8.4 Hz, 6H), 7.42 (dd, J = 8.4, 2.1 Hz, 6H).

^{31}P NMR ($CDCl_3$, 202 MHz) δ 43.3.

Tris(4-methoxyphenyl)phosphine sulfide (2c)

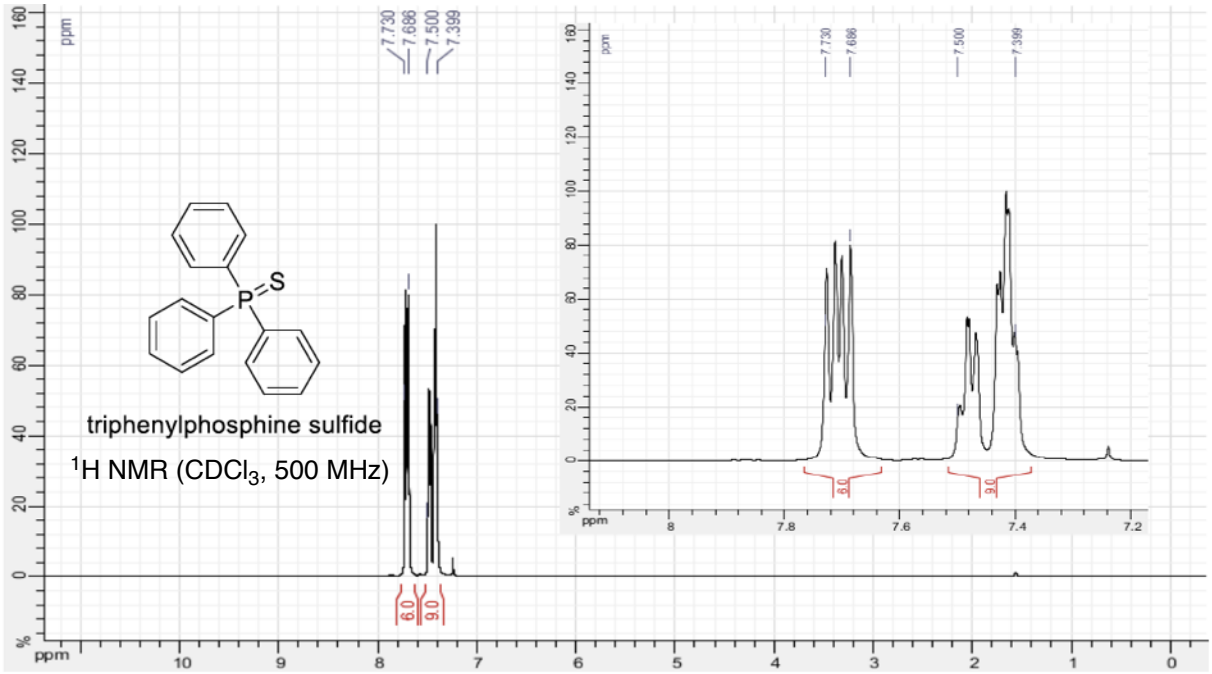


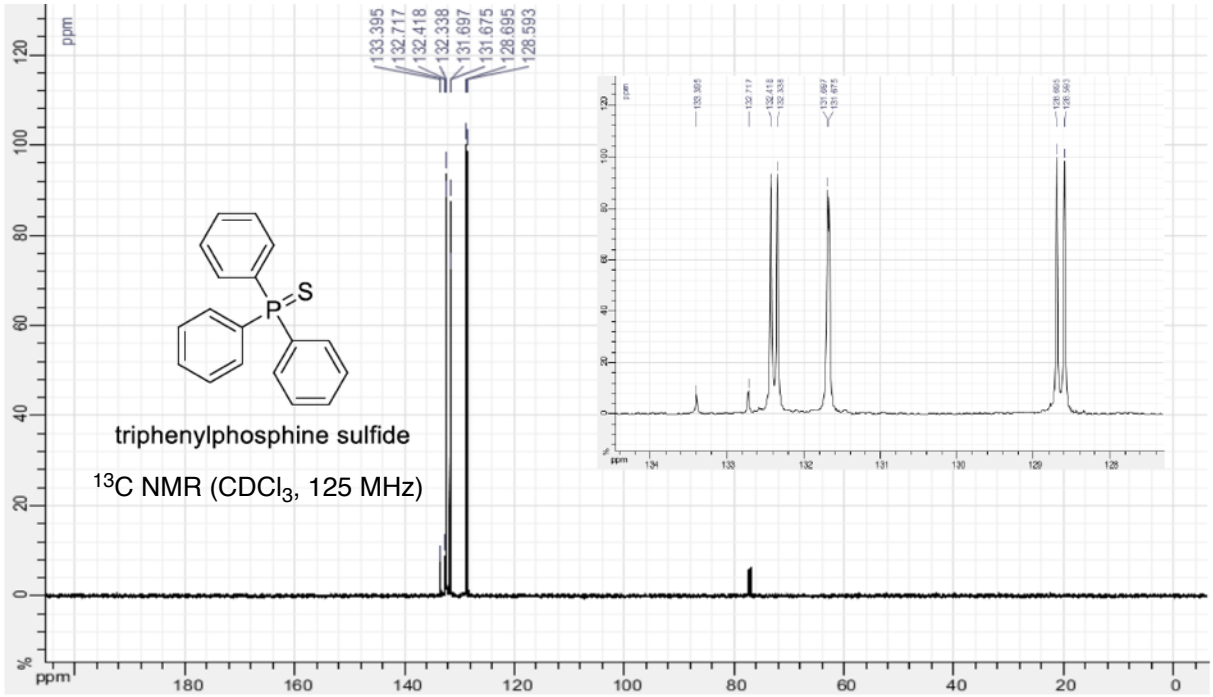
A mixture of tris(4-methoxyphenyl)phosphine **1c** (384 mg, 1 mmol), sulfur (34 mg, 1.05 mmol) and $CHCl_3$ (0.2 mL) was stirred in a 7-mL tube at rt. Sulfur was dissolved completely after 5-10 min. Evaporation of the reaction mixture provided the product as a white solid (417 mg, quant).

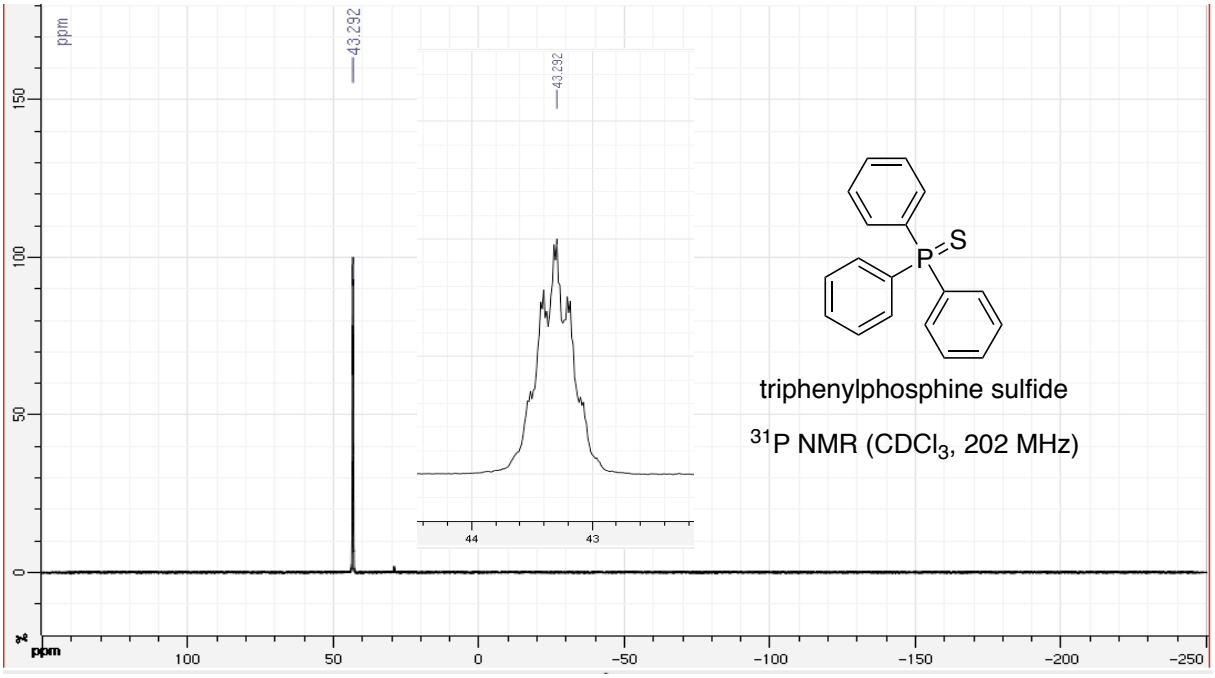
^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.60 (dd, J = 12.6, 8.8 Hz, 6H), 6.91 (dd, J = 8.4, 2.1 Hz, 6H), 3.80 (s, 9H).

^{31}P NMR ($CDCl_3$, 202 MHz) δ 40.9.

Triphenylphosphine sulfide (2a)



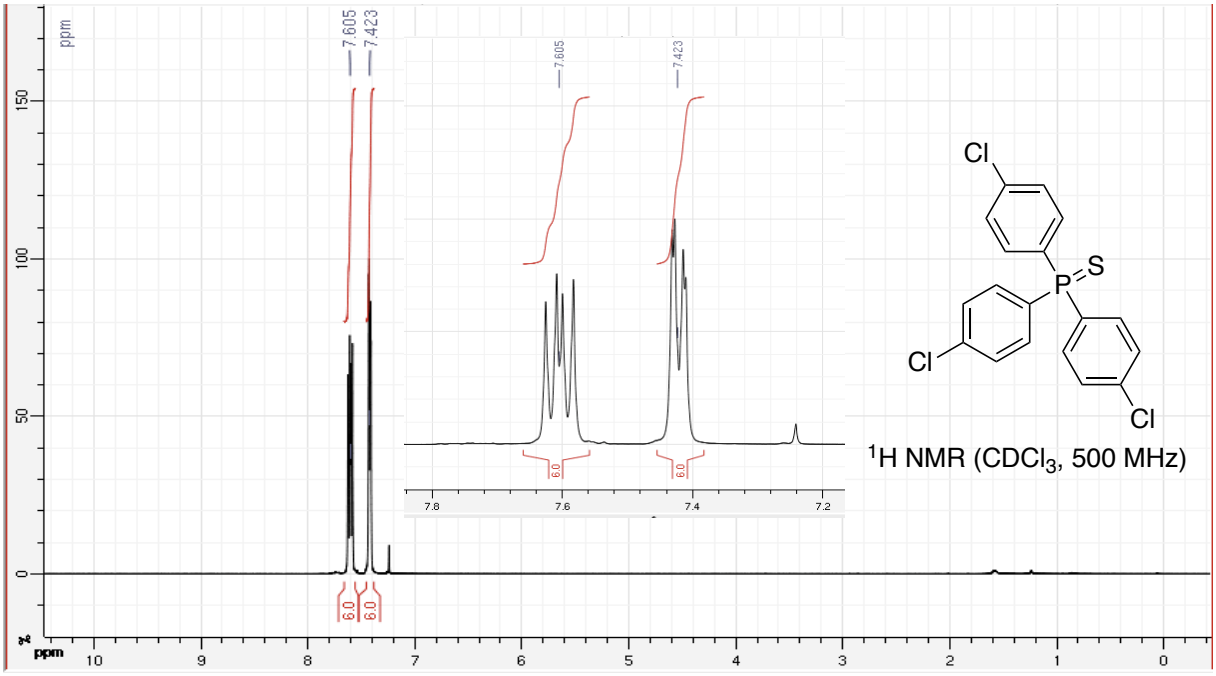


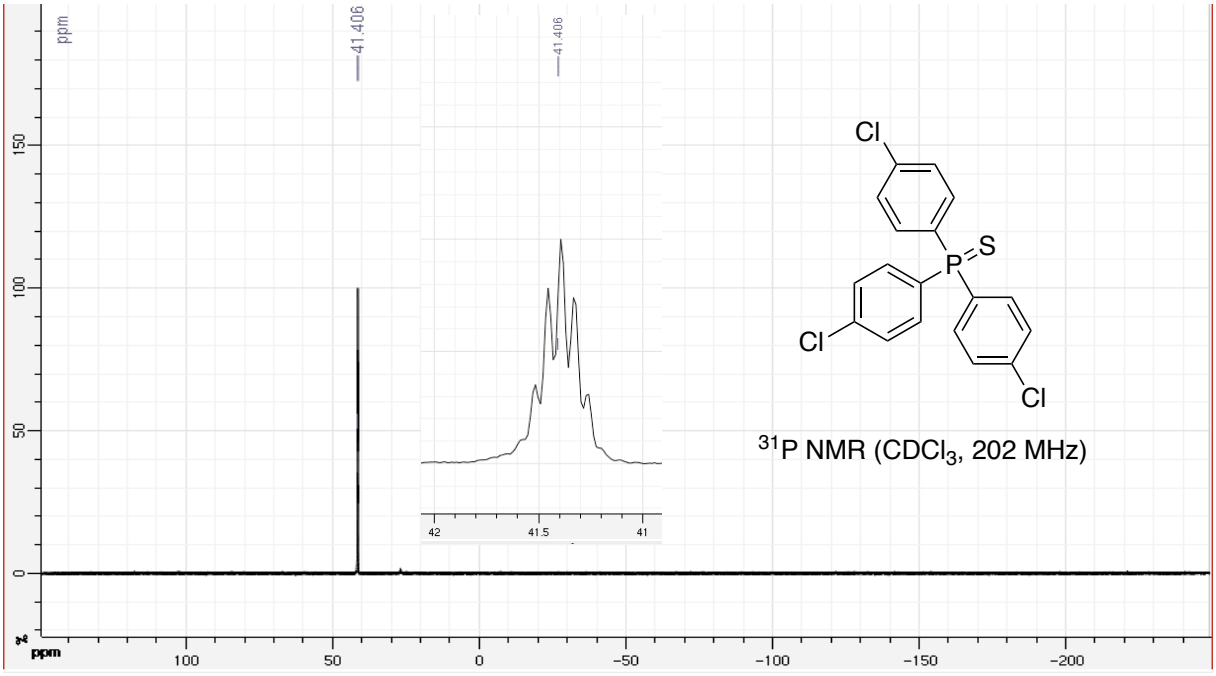


triphenylphosphine sulfide

^{31}P NMR ($CDCl_3$, 202 MHz)

tris(4-chlorophenyl)phosphine sulfide (2b)





tris(4-methoxyphenyl)phosphine sulfide (2c)