Electronic Supplementary Information

Restoration of Triphenylphosphine by the "Sulfur Method": Two Valuables from a Waste

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1. Experimental Section

1.1. General Information

Unless otherwise noted, all chemicals were obtained from commercial sources and used without further purification. $Ph_2P(S)Me$ and $PhP(S)Me_2$ was prepared by treating Ph_2PMe and $PhPMe_2$ with S_8 in toluene, respectively. All the reactions were carried out in oven-dried Schlenk tubes, three-neck flasks or 5L reactor under N_2 atmosphere. ^1H, ^{13}C, and ^{31}P NMR spectra of the partial products were acquired on a Bruker AVANCE NEO 600M (600 MHz for ^1H, 151 MHz for^{13}C spectroscopy). Chemical shifts for ^1H NMR are referred to internal Me_4Si (0 ppm) and reported as follows: chemical shift (δ ppm), multiplicity, coupling constant (Hz) and integration. Chemical shifts for ^{31}P NMR were relative to H_3PO_4 (85% solution in D_2O, 0 ppm). ^{31}P NMR and ^1H NMR spectra of Ph_2PMe and $PhPMe_2$ were obtained on a Magritek Spinsolve NMR Ultra 80M (81 MHz for ^1H, 33 MHz for ^{31}P NMR spectroscopy).

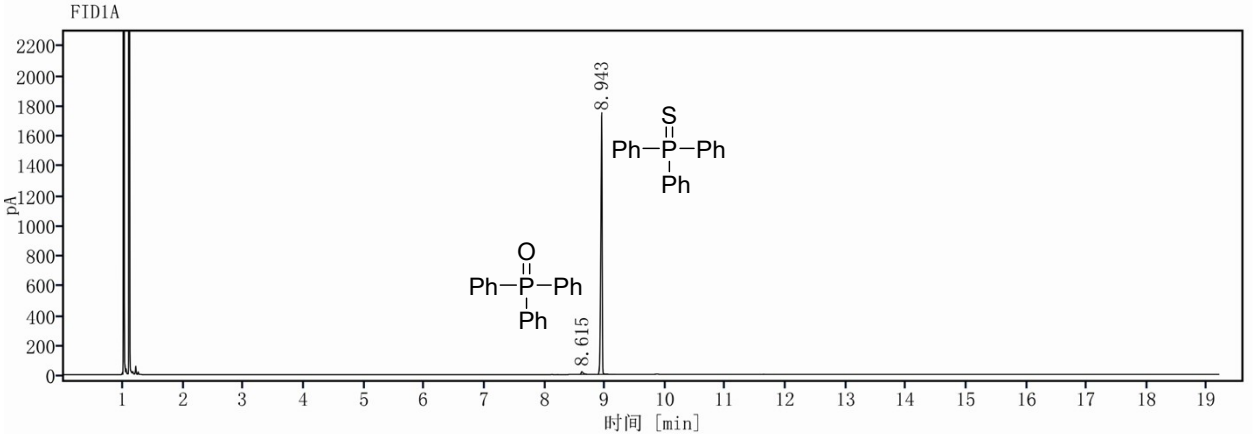
1.2. General procedure for the reactions of Ph_3PS with sodium

Under nitrogen atmosphere, to a 25 mL of Schleck tube was added R_3PS (**1a**) (1.0 mmol), toluene (5.0 mL), and sodium (2.0 mmol). The tube was then sealed and heated 110 ^oC. As the metallic sodium melted, a brown solid was generated, and after heating for 3 h, a pale-yellow toluene solution with dark-brown solids was generated. Under nitrogen, the toluene solution was then transferred to a flask and toluene was removed under vacuum, the corresponding pure phosphine R_3P was obtained (Ph_3P, 91% yield; Ph_2PMe, 96% yield; $PhPMe_2$, 97%yield). And the remained dark-brown solids was washed twice with dry toluene to afford dark-brown solid anhydrous Na_2S.

1.3. Typical procedure for the preparation of anhydrous Na_2S. in three times

Under nitrogen atmosphere, sulfur (0.12 g, 3.8 mmol) was added drop by drop to Ph_3P (1 g, 3.8 mmol) dissolved in dry toluene (10 mL) in a 25 mL of Schleck tube at room temperature. As confirmed by GC, Ph_3P was completely converted to Ph_3PS after 1 h (Fig. 1). Metallic sodium (0.159 g, 6.9 mmol) was then added, and the mixture was heated at 110 ^oC for 3 h. Ph_3P was regenerated from Ph_3PS. The reaction mixture was passed through a filter paper, the toluene

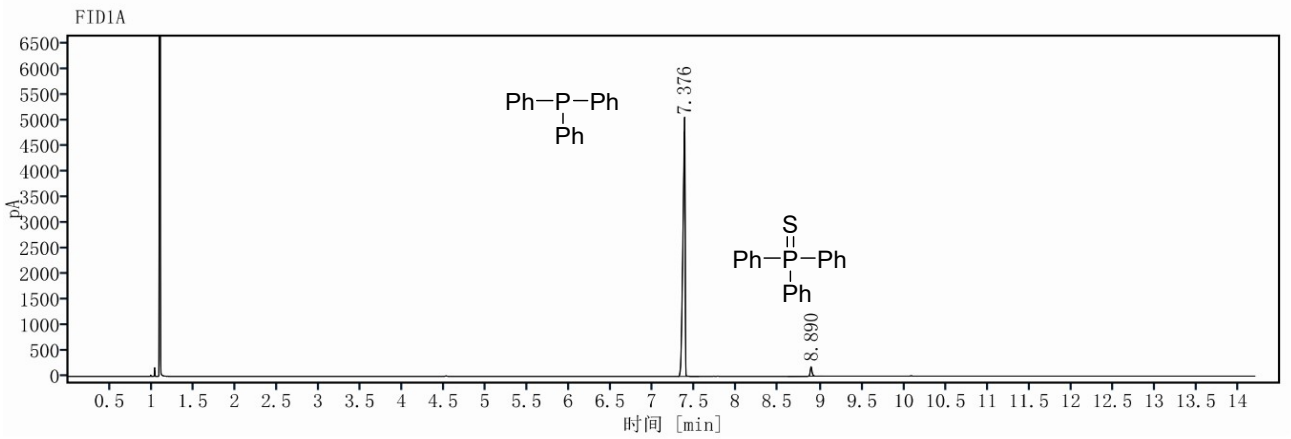
solution (Fig. 2) containing Ph_3P and a little Ph_3PS (ca 2.5%) was then transferred to another glass tube. The remained Na_2S precipitate on the filtration paper was washed by a little toluene, and then it was dried under vacuum, the pure grey Na_2S was obtained. The washed toluene was also combined and transferred to the new glass tube. Again sulfur (0.12 g, 3.8 mmol) was added to the toluene solution and the above processes were repeated. By carrying out three cycles of the above reactions, a total amount of 0.85 g of anhydrous Na_2S was obtained as brown solid (average yield: 96%).



8.615	0.2770	49.2958	18.4753	1.7184
8.943	0.3030	2819.4280	1725.5406	98.2816

(Ph_3PS: 98.3%,T_M = 8.943min; Ph_3PO:1.7%, T_M = 8.615min)

Fig.1 GC spectra of Ph_3PS formed from Ph_3P with S_8

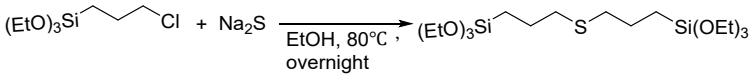


7.376	0.2525	9551.0595	5008.9372	96.9998
8.890	0.4159	295.4116	185.0351	3.0002

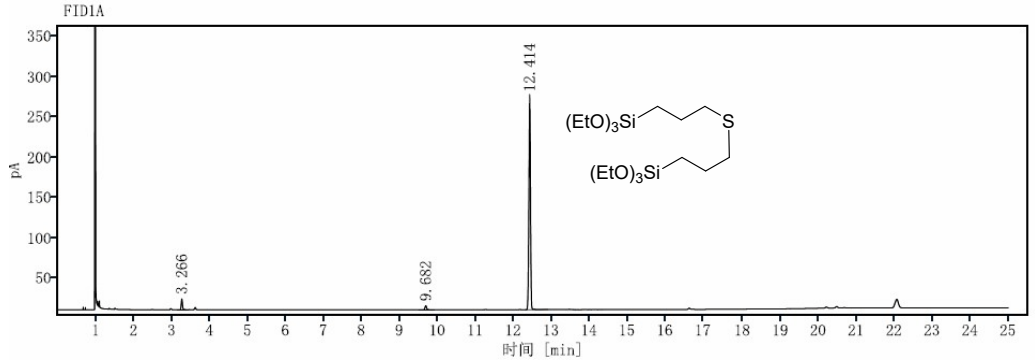
(Ph_3P: 97.0%,T_M = 7.376min; Ph_3PS:3.0%, T_M = 8.890min)

Fig.2 GC spectra of Ph_3P formed from Ph_3PS and Na

1.4. Procedure for the preparation of bis(triethoxysilylpropyl) sulfide.



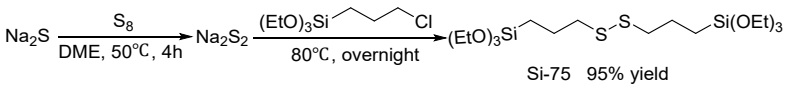
Under nitrogen atmosphere, to a 25 mL Schleck tube was added $(EtO)_3SiCH_2CH_2CH_2Cl$ (1.5 mmol, 361.2g) in dry EtOH (20 mL) and then added Na_2S (1.0 mmol, 78.0 mg), the solution was stirred at 80 °C overnight. Filtration of solid in the reaction solution and removal of the volatiles under vacuum afforded the colorless oil bis(triethoxysilylpropyl) sulfide (398.5g, 90% yield, Fig.3)**.**



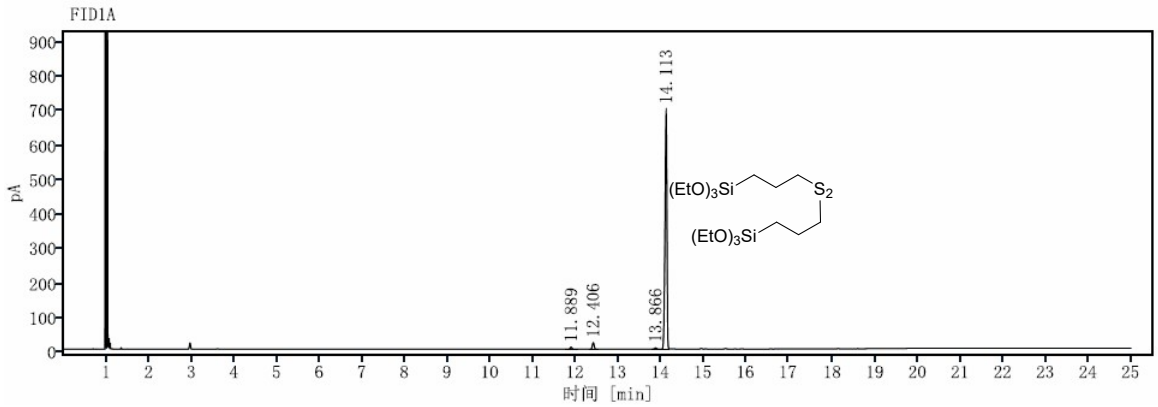
3.266	0.2811	31.6490	13.5148	3.7616
9.682	0.0469	14.9427	4.9932	1.7760
12.414	0.5983	794.7705	264.8639	94.4624

Fig.3 GC spectra of bis(triethoxysilylpropyl) sulfide (94.5% purity)

1.5. Procedure for the preparation of bis(triethoxysilylpropyl) disulfide (Si-75).



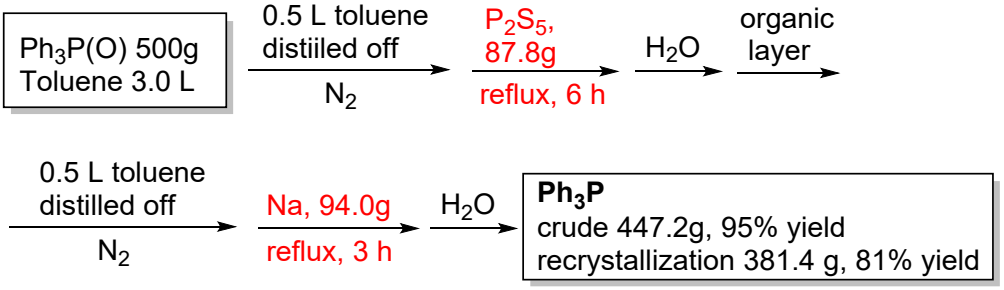
Under nitrogen atmosphere, to a 25 mL Schleck tube was added Na_2S (1.0 mmol), sulfur (1.0 mmol) and DME (2.0 mL), the mixture was stirred at 50 °C for 4 h to generate Na_2S_2. Then, $(EtO)_3SiCH_2CH_2CH_2Cl$ (1.5 mmol) was added. The mixture was stirred at 80 °C overnight to generate Si-75 highly selectively. The solid in the solution was filtered off and the volatiles were removed under a reduced pressure to obtain analytically pure **Si-75** as a pale-yellow oil (451.0 mg, 95% yield, 96% GC purity, Fig. 4).



11.889	0.2517	17.2283	5.6696	0.7354
12.406	0.1819	57.3235	18.9232	2.4470
13.866	0.1900	13.1780	4.0857	0.5625
14.113	0.2195	2254.8675	696.5808	96.2550

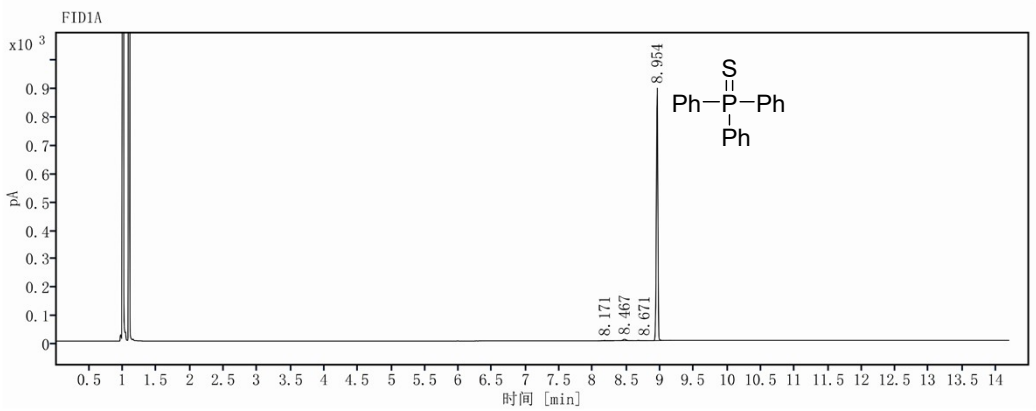
Fig.4 GC spectra of bis(triethoxysilylpropyl) disulfide (96.3% purity)

1.6. Scale-up synthesis of Ph_3P from Ph_3PO (500g)



Under nitrogen atmosphere, triphenylphosphine oxide (500 g, 1.795 mol, 1.0 equiv) and toluene (3.0 L) were added to a 5 L glass reactor. The reactor was heated at 110 °C to distilled off ca. 500 mL toluene for azeotropic water removing. Then solution was cooled down to 70 °C, and P_2S_5 (87.8 g, 0.395 mol, 0.22 equiv) was added. The reactor was then heated again and kept refluxing at 110 °C for 2 h. GC analysis showed Ph_3PS was the only new phosphorus product, and >99% Ph_3PO was converted (Fig.5). Heating was stopped, and at ca. 60 °C, water (500 mL) was added. The organic layer was collected and washed with water twice (250 mL x 2), and was returned to the reactor. The solution was heated under nitrogen again to reflux and distilled off ca. 500 mL toluene for azeotropic water removing. Heating was stopped and sodium lump (94.0 g, 4.08 mol, 2.3 equiv) was added to the solution under nitrogen. The mixture was then heated to reflux again and heating was kept for 3 h. The reaction was monitored by GC to make sure that most of the Ph_3PS was transformed to Ph_3P (Fig.6, 99.1%). Heating was stopped and the

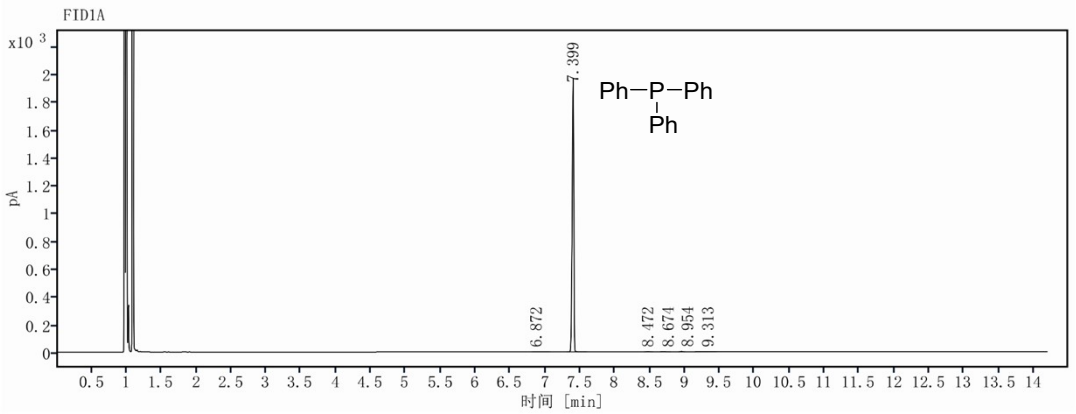
mixture was cooled down to room temperature, and water (500 mL) was added. The organic layer was collected, and volatiles were pumped off to obtained crude Ph_3P as a pale-yellow solid. Recrystallization of the crude Ph_3P using ethanol produced white Ph_3P solid (381.4 g, 81% yield, GC purity =99.6%, Fig. 7).



8.171	BV	0.25	6.89	1.06	0.4700
8.467	MM m	0.05	15.54	4.61	1.0603
8.671	MM m	0.05	3.13	0.90	0.2134
8.954	BB	0.26	1440.44	890.31	98.2563
		总和	1466.0063		

(Ph_3PS: 98.3%,T_M = 8.954min; Ph_3PO:0.2%, T_M = 8.671min)

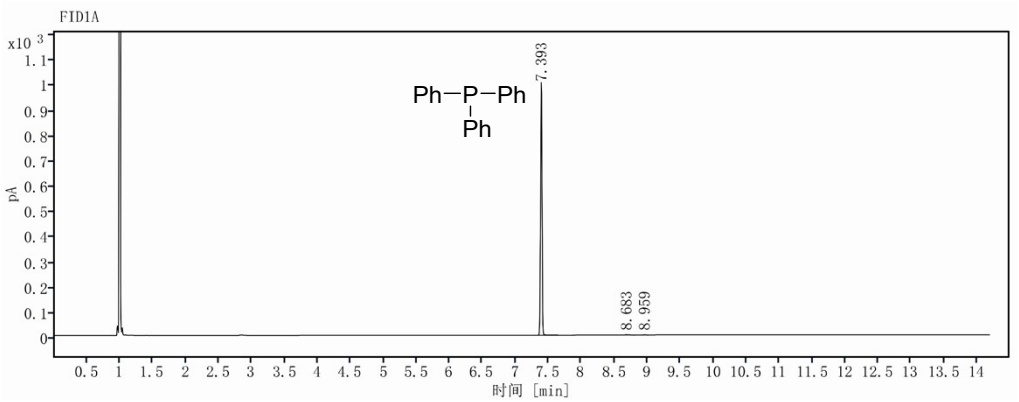
Fig.5 GC spectra of Ph_3PS prepared from Ph_3PO with P_2S_5



6.872	BV	0.26	11.65	1.23	0.3744
7.399	VB	0.29	3081.33	1900.75	99.0563
8.472	MM m	0.05	3.89	1.18	0.1250
8.674	MM m	0.04	5.82	2.03	0.1871
8.954	MM m	0.03	4.39	2.51	0.1412
9.313	BB	0.31	3.61	1.14	0.1160

(**Ph_3P: 99.1%, T_M = 7.399min**; Ph_3PS: 0.14%,T_M = 8.954min; Ph_3PO: 0.19%,T_M = 8.674min)

Fig.6 GC spectra of reaction mixture of Ph_3P prepared from Ph_3PS with Na



7.393	BB	0.47	1507.51	986.85	99.6227
8.683	MM m	0.05	4.19	1.34	0.2772
8.959	MM m	0.03	1.51	0.88	0.1001

(**Ph_3P: 99.6%, T_M = 7.393min**; Ph_3PS: 0.1%,T_M = 8.959min; Ph_3PO: 0.28%,T_M = 8.683min)

Fig.7 GC spectra of purified Ph_3P

2. Cost estimations and economic analysis

2.1 Cost esitimations

A. Cost estimations of producing Ph_3P from Ph_3PS *via* one step

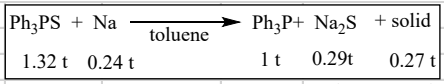
According to the results in Scheme 4 in the manuscript, a cost estimation was conducted.

As shown in the below Table. 1, the material cost of producing a ton of Ph_3P was ca. 5453 RMB, equal to $742.5.

The total cost of producing a ton of Ph_3P was ca. **26143 RMB ($3560)** (including material cost 5453+manufacture cost 20000 + solid waste treatment 690).

And the products (Ph_3P & anhydrous Na_2S) sale price was ca. **84726 RMB ($11661**).

Therefore, by producing a ton of Ph_3P, along with 0.29 tons of anhydrous Na_2S, the profit was up to ca. **58582 RMB ($7977)**, demonstrating our protocol is of great economic benefit.



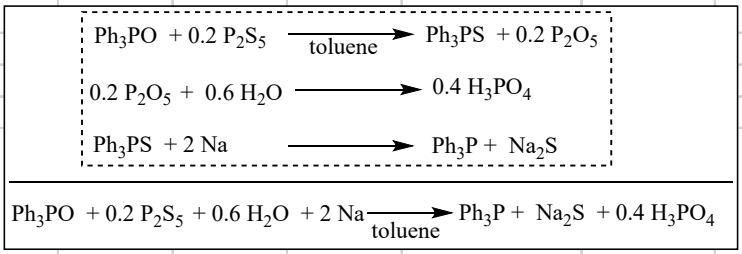
Materials		m.w.	Mass/mg	Molar mass /mmol	Equiv	Unit comsuption /(t/t)	Price /(rmb/t)	Total Price /(rmb/t)	Remarks
Ph_3PS		294.35	294.40	1.00	1.00	1.32	0	0	
Na		23.00	46.00	2.00	2.00	0.24	16000	3840	
Toluene		/	513.43			0.22	7500	1613	2v/w, Recycle 90%
Cost								**5453**	
Manufacture cost							20000	20000	Including devices,electricity,water, and labor, solid waste treatment
Solid waste						0.27	2600	690	
Cost								**20690**	
Products									
Products	Ph_3P	262.28	238.70	0.91	0.91	**1.00**	70000	70000	91% yield
	Na_2S	78.04	70.30	0.90	0.90	0.29	50000	14726	90% yield
Total sales								**84726**	
Total cost = Material cost + manufactur cost								**26143**	
The profit = Products sales - (Material cost + manufactur cost)								**58582**	

Note：Ph_3PS is an industry byproduct and waste, the cost is near to zero.

Table 1. Cost estimations: production of Ph_3P from Ph_3PS via one step

B. Cost estimations of producing Ph_3P from Ph_3PO via two steps

According to the results in Scheme 8 in the manuscript, a cost estimation was conducted. **the material cost (not includes the manufacture cost, etc.) of producing a ton of Ph_3P was ca. 9608 RMB ($1308)**, more than the cost of using Ph_3PS (5453 RMB, **$742.5**), but it is also very economical.



Materials	m.w.	Mass/mg	Molar mass /mmol	Equiv	Unit comsuption /(t/t)	Price /(rmb/t)	Total Price /(rmb/t)	Remarks
Ph_3PO	278.29	**500.00**	1.80	1.00	1.31	0	0	
P_2S_5	222.25	**87.80**	0.40	0.22	0.23	11000	2532	
Toluene	/	**872.00**			0.23	7500	1715	Recycle 90%
H_2O		**1000.00**			2.62	4	10	twice addition
Na	22.99	**94.00**	4.09	2.28	0.25	16000	3943	
EtOH		**789.00**			0.21	6800	1407	Recycle 90%
cost							**9608**	
Products								
Ph_3P	262.28	381.40	1.45	0.81	**1.00**	70000	70000	81% yield
Na_2S(aq.)					/			
H_3PO_4(aq.)					/			

Note：Ph_3PO is an industry byproduct and waste, the cost is near to zero.

Table 2. Cost estimations of production of Ph_3P from Ph_3PO via two steps

2.2 Green metric analysis

Green metrics analysis mainly encourages reducing the use of toxic chemicals/reagents, using energy-efficient equipment, generating minimal waste, etc.

In this work, Ph_3PS and Ph_3PO are the waste from the industry, by applying our strategy, they are converted to high valuable product Ph_3P and Na_2S, and H_3PO_4. The AE and E factor value of the reactions are satisfying.

Below are the 12 principles of Green Chemistry Metrics.

	Twelve Green Chemistry Principle	Evaluation Result of our work
1	Waste prevention not remediation	The product Ph_3P, Na_2S, and H_3PO_4 are useful chemicals, and the solvent PhMe & ErOH are recycled, with less waste. E factor of two reactions are around 0.1.
2	Atom efficiency	The AE of two reactions are over 90%.
3	Less hazardous/toxic materials	Ph_3PS and Ph_3PO are stable and less toxic starting material
4	. Safer products by design	Ph_3P and Na_2S, and H_3PO_4 are safe products.
5	Innocuous solvents and auxiliaries	Toluene, water and EtOH are green solvents and auxiliaries
6	Energy efficient by design	The reactions were conducted in normal temperature and pressure.
7	Renewable rather than depleting raw material	The Ph_3P is restored efficiently by our strategy.
8	Shorter synthesis (avoid derivatization)	Only one/two-step reaction and facial post-processing procedures
9	Catalytic rather than stoichiometric reagents	/
10	Design products for degradation	/
11	Analytical methods for pollution prevention	/
12	Inherently safer processes	Under N_2, the reaction proceeded safely. The 5L-scale reaction in Scheme 8 proceeded smoothly and safely.

Table 3. Green metric analysis

2.2.1 The AE and E factor value of the reaction of Ph_3PS with Na: producing Ph_3P and Na_2S

Reaction stoichiometry

$$Ph_3PS + 2\,Na \xrightarrow[\text{toluene}]{} Ph_3P + Na_2S$$

294.35	46.00		262.28	78.04
			91%	90%

Theoretical Atom Economy = mass of products/the total mass = 100%

Experimental Atom economy = mass of products/the total mass

= (262.28*91%+78.04*90%)/(262.28+78.04) = **ca. 90.8%**

Mass of Waste = 294.35+46+513.43-(238.70+70.30+462.09) = 82.74 mg

E factor = mass of the waste/ mass of the products= 82.74/(238.70+70.30+462.09+82.74) = **ca. 0.097**

2.2.2 The AE and E factor value of the reaction of Ph_3PO with P_2S_5 and then with Na: producing Ph_3P, Na_2S and H_3PO_4

$$Ph_3PO + 1/5\,P_2S_5 \xrightarrow[\text{toluene}]{} Ph_3PS + 1/5\,P_2O_5 \quad (1)$$

278.29 222.25 294.35 141.94*0.2

$$1/5\,P_2O_5 + 3/5\,H_2O \longrightarrow 2/5\,H_3PO_4 \quad (2)$$

141.94*0.2 18*0.6 97.99*0.4

$$Ph_3PS + 2\,Na \xrightarrow[\text{toluene}]{} Ph_3P + Na_2S \quad (3)$$

294.35 46 262.28 78.04

Reaction Stoichiometry:

$$Ph_3PO + 1/5\,P_2S_5 + 3/5\,H_2O + 2\,Na \longrightarrow Ph_3P + Na_2S + 2/5\,H_3PO_4$$

278.29	222.25*0.2	18*0.6	46	262.28	78.04	97.99*0.4
				81%	a%	b%

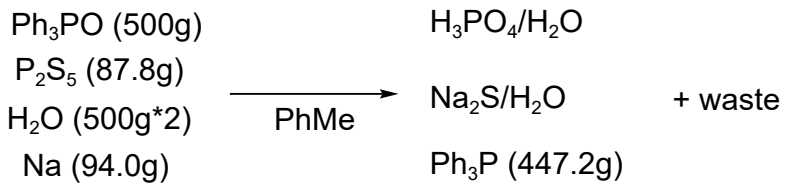
Theoretical Atom Economy = mass of products/the total mass = 100%

Experimental Atom Economy = mass of products/the total mass

= (262.28*81%+78.04*a%+97.99*0.4*b%)/(262.28+78.04+97.99*0.4) ≤ ca.**86.9%**

Note: yield of Na_2S = a%, yield of H_3PO_4 = b% (a%, b% ≤100%)

Materials	m.w.	Mass/g	Molar mass /mol	Equiv	Remark
Ph_3PO	278.29	**500.00**	1.80	1.00	
P_2S_5	222.25	**87.80**	0.40	0.22	
Toluene	/	**872.00**			
H_2O		**1000.00**			
Na	22.99	**94.00**	4.09	2.28	
EtOH		**789.00**			
Products					
H_3PO_4(aq.)	98.00	**535.22**	0.36	0.20	
Na_2S (aq.)	78.04	**640.21**	1.80	1.00	
Ph_3P	262.28	**381.40**	1.45	0.81	
Toluene		**784.80**			Recycle 90%
EtOH		**710.10**			Recycle 90%
waste		**291.07**			



Waste (g) = mass of starting materials mass- mass of products

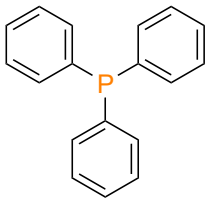
= (500+87.8+872+500*2+94.0+789)-(535.22+640.21+381.40+784.80+710.10) = 291.07

(If a%, b% =100%)

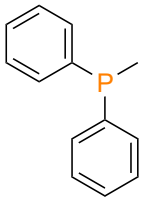
E factor = mass of the waste / mass of the products

= 291.07/(535.22+64.021+381.40+784.80+710.10+291.07) = **ca. 0.105**

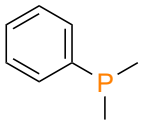
3. Characterization of products



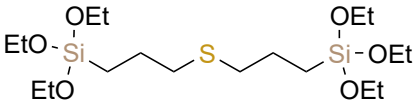
Triphenylphosphine. Prepared by procedure 1.2. White solid, 238.7mg, 91% yield. ^{1}H NMR (81 MHz, $CDCl_3$): δ 7.49-7.43 (m, 15H); ^{31}P NMR (33 MHz, $CDCl_3$): δ -5.29. This compound was known.[1]



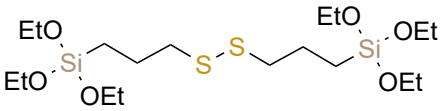
Diphenylmethylphosphine. Prepared by procedure 1.2. Colorless oil, 192.2mg, 96% yield. ^{1}H NMR (81 MHz, $CDCl_3$): δ 7.47-7.17 (m, 10H), δ 1.56 (d, 3H, $J_{P\text{-}H}$ = 3.56 Hz); ^{31}P NMR (33 MHz, $CDCl_3$): δ -26.98. This compound was known.[2]



Dimethylphenylphosphine. Prepared by procedure 1.2. Colorless oil, 134.1mg, 97% yield.. ^{1}H NMR (81 MHz, $CDCl_3$): δ 7.61-7.30 (m, 5H), 1.36 (d, 6H, $J_{P\text{-}H}$ = 2.67 Hz); ^{31}P NMR (33 MHz, $CDCl_3$): δ -45.64. This compound was known.[3]



Bis(triethoxysilylpropyl) sulfide. Prepared by procedure 1.4. Pail-yellow oil, 398.5mg 90% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.83–3.79 (q, 12H, J = 7.2 Hz), 2.53–2.51 (m, 4H), 1.72–1.67 (m, 4H), 1.22 (t, 18H, J = 7.2 Hz), 0.74–0.72 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 58.34, 35.01, 23.27, 18.27, 9.93. This compound was known.[4]



Bis[3-(triethoxysilyl)propyl] disulfide (Si-75). Prepared by procedure 1.5. Pail-yellow oil, 451.1mg, 95% yield. ^{1}H NMR (600 MHz, $CDCl_3$): δ 3.84–3.80 (q, 12H, J = 7.2 Hz), 2.72–2.69 (m, 4H), 1.83–1.78(m, 4H), 1.23 (t, 18H, J = 7.2 Hz), 0.75–0.72 (m, 4H). ^{13}C NMR (151 MHz, $CDCl_3$): δ 58.38, 41.88, 22.62, 18.28, 9.45. This compound was known.[5]

References:

1) C. Petit, et al., *ACS Catal*., 2013, **3**, 1431-1438.

2) M. Mehta, et al., *Organometallics*, 2016, **35**, 1030-1035.

3) L.T. Mika, et al. *Organometallics*, 2009, **28**, 1593-1596.

4) C. Hu, et al. Syntheses of Organofunctional Chlorosilanes Catalyzed by A Sulfur-Containing PolysilaxamePlatinum Coinplex. *Kexue Tongbao*, 1988, **33**, 843-847.

5) M. Khiterer, et al., *Chem. Mater.*, 2006, **18**, 3665-3673.

3. Copies of ^{1}H, ^{31}P NMR spectra of the products

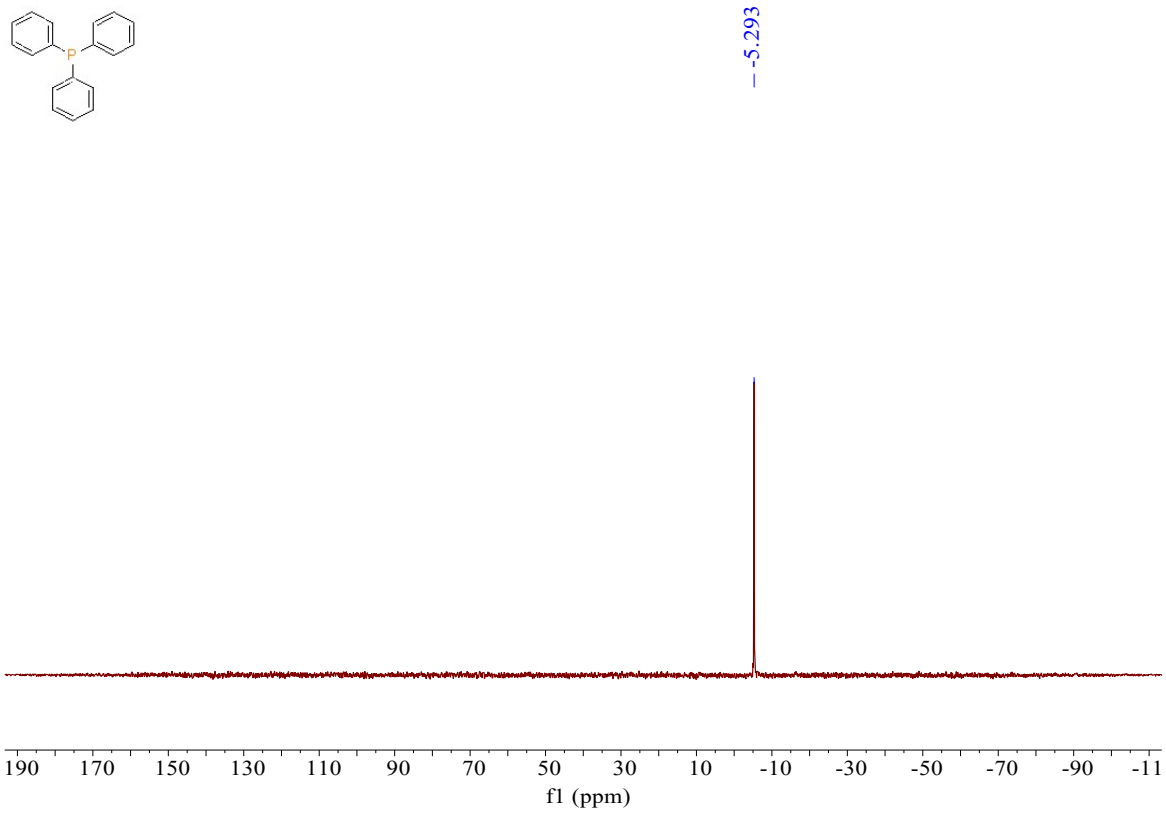


Fig.8 ^{31}P NMR spectra of Ph_3P ($CDCl_3$, 33MHz)

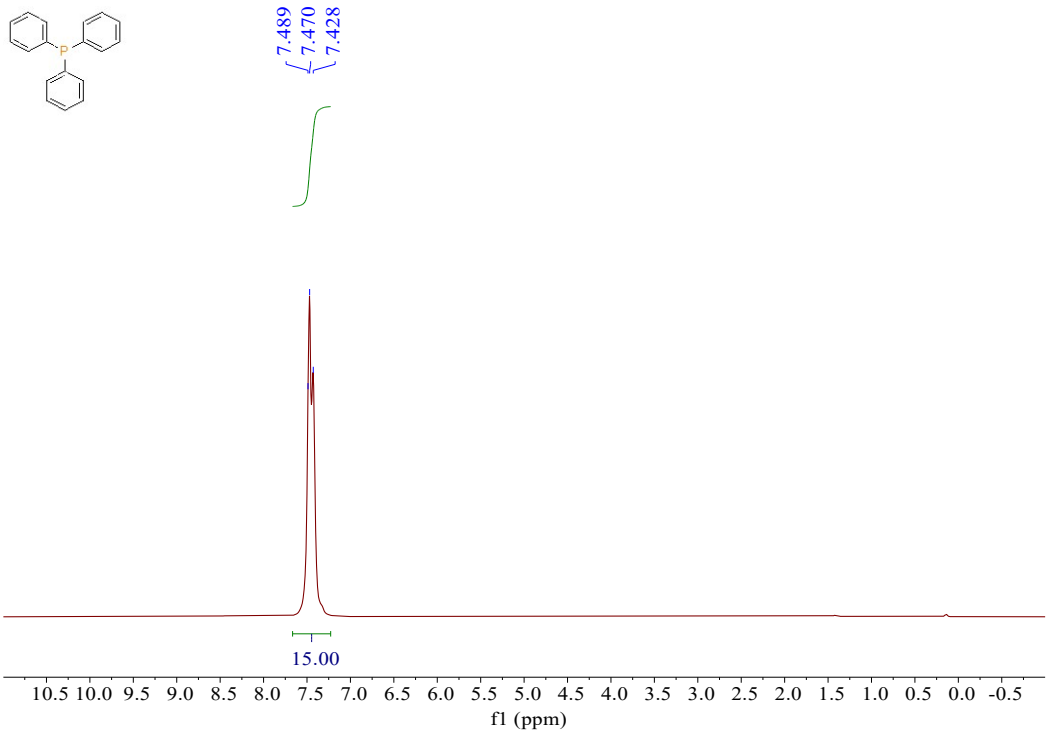


Fig.9 ^{1}H NMR spectra of Ph_3P ($CDCl_3$, 81MHz)

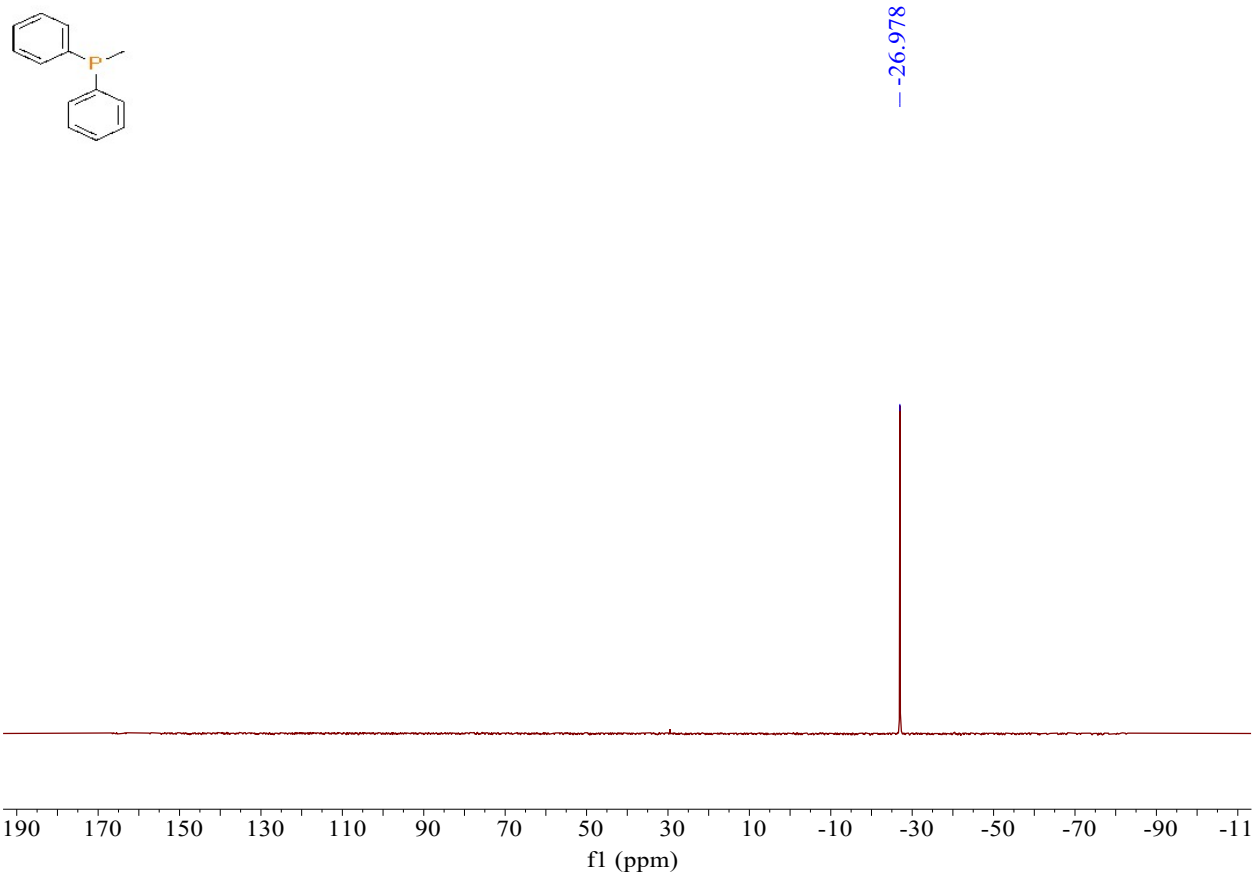


Fig.10 ^{31}P NMR spectra of $Ph_2PMe(CDCl_3$, 33MHz)

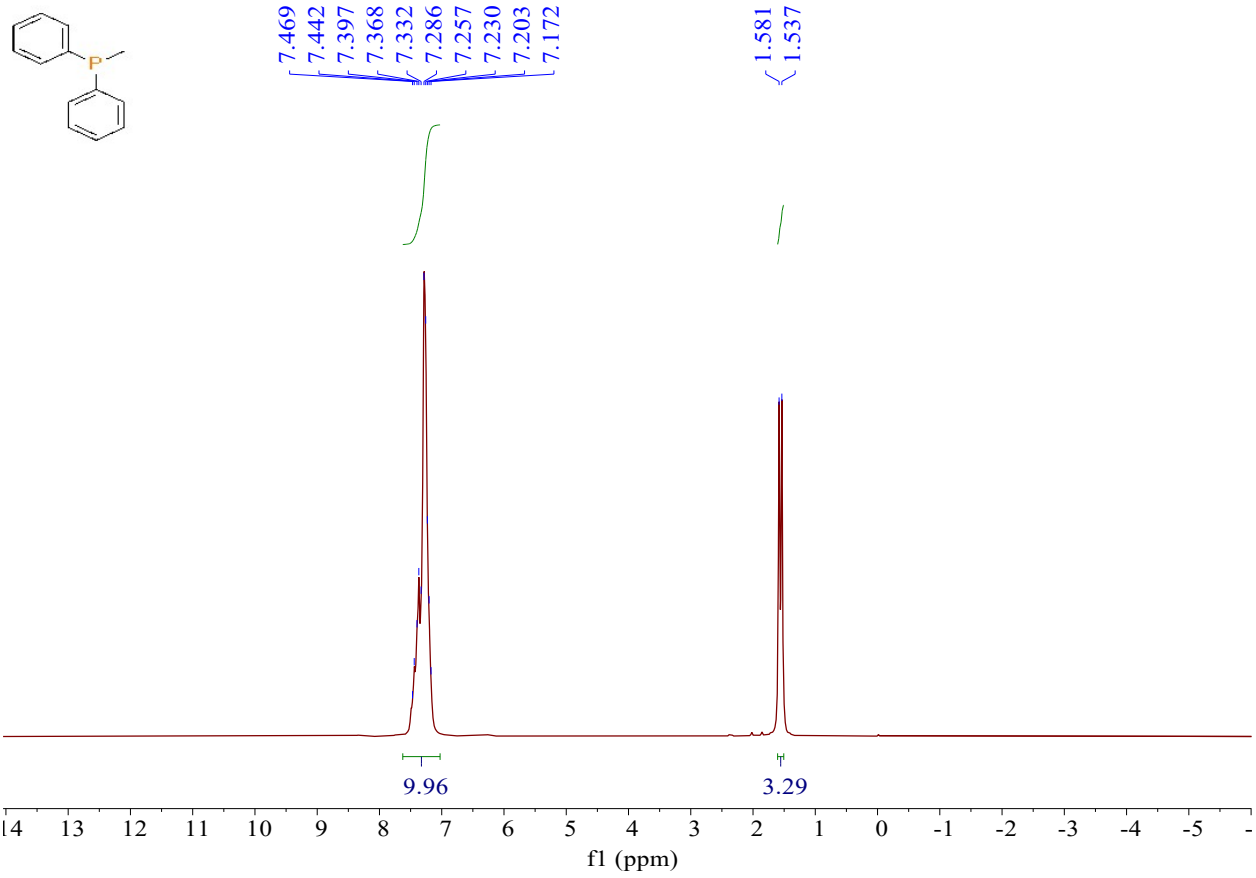


Fig.11 ^{1}H NMR spectra of $Ph_2PMe(CDCl_3$, 81MHz)

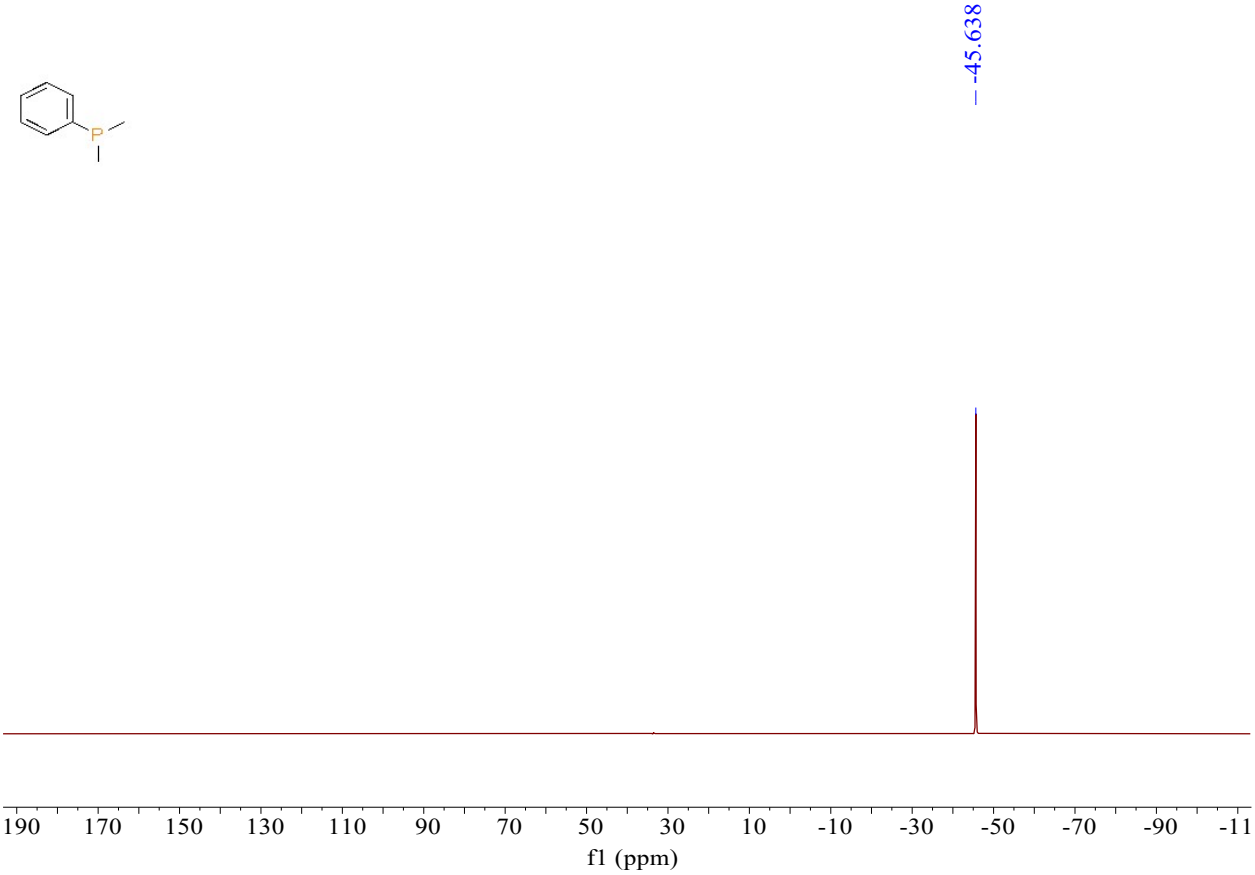


Fig.12 ^{31}P NMR spectra of $PhPMe_2$ ($CDCl_3$, 33MHz)

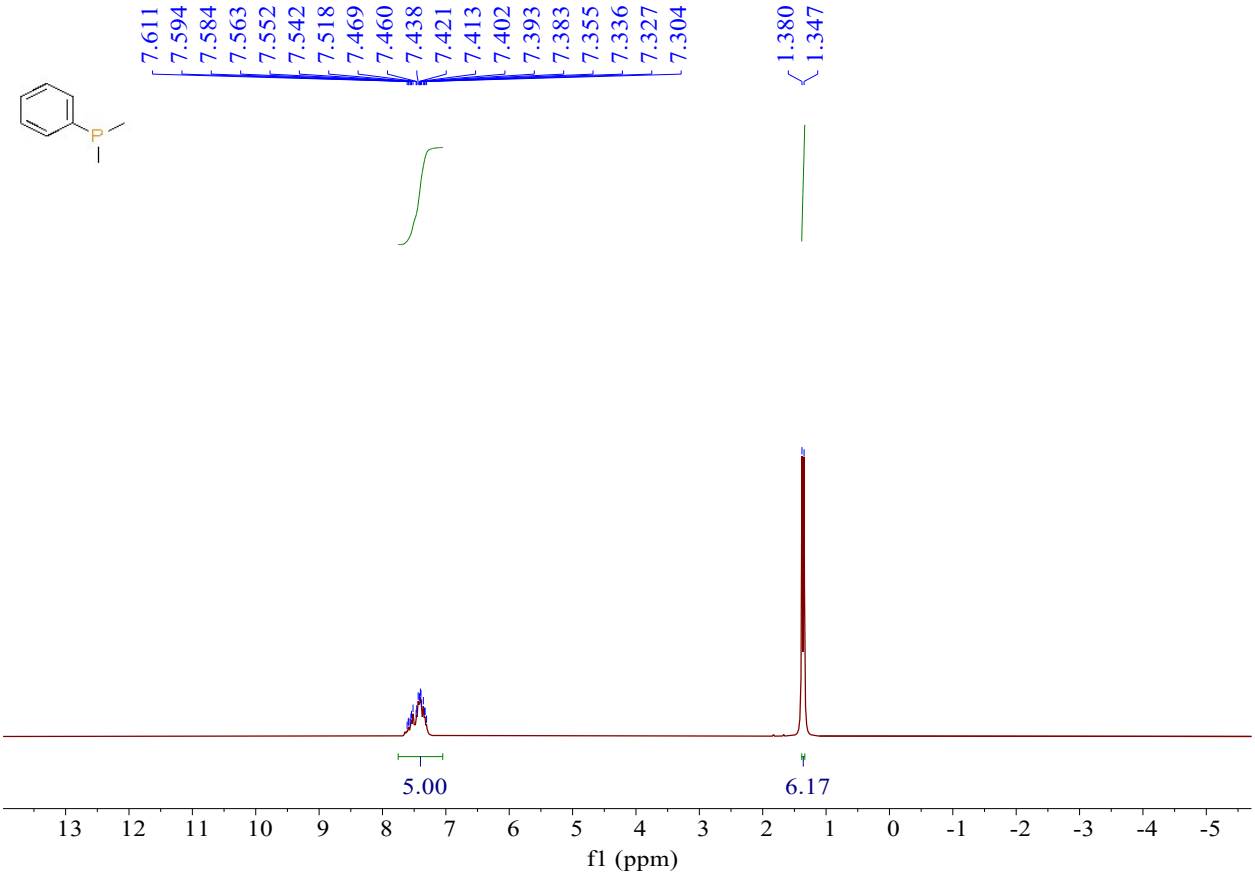


Fig.13 ^{1}H NMR spectra of $PhPMe_2$ ($CDCl_3$, 81MHz)

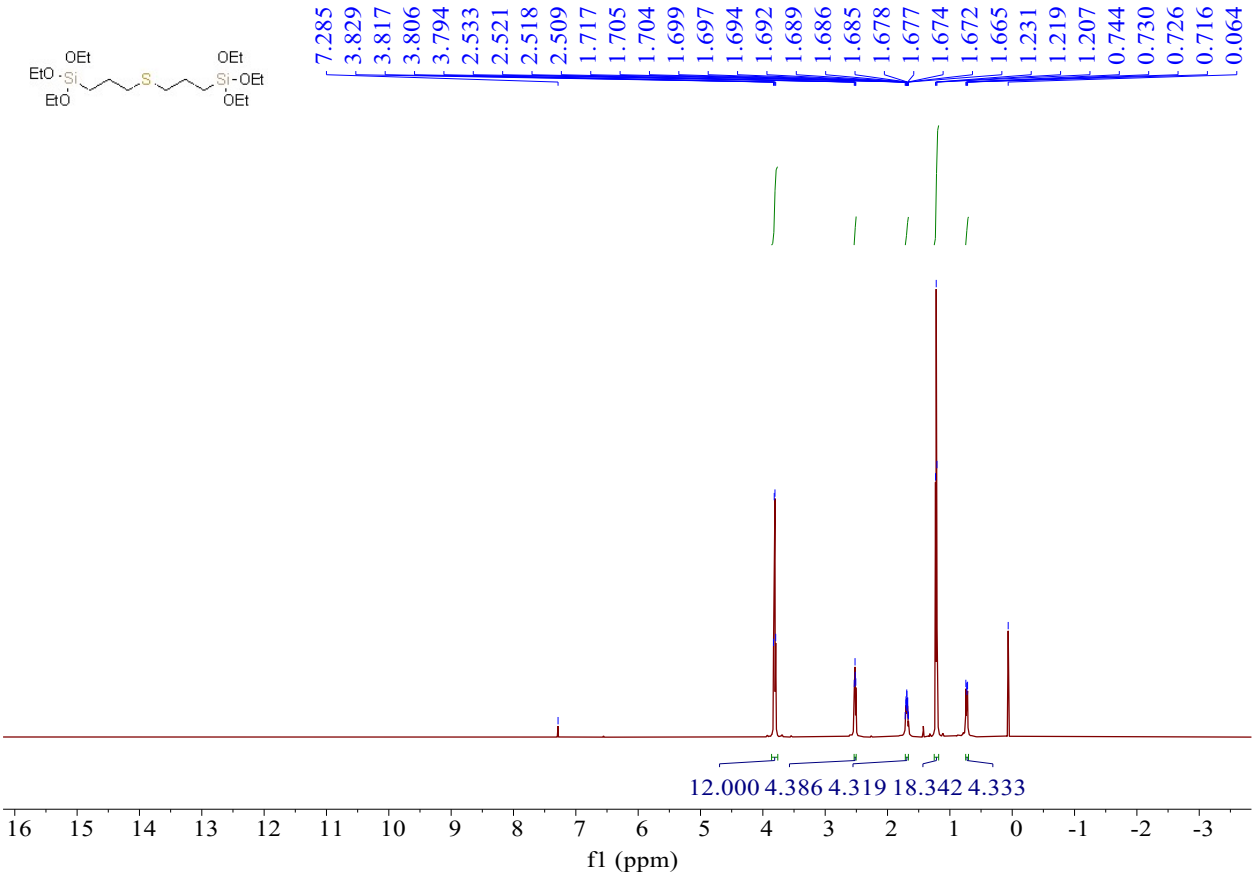


Fig.14 ^{1}H NMR spectra of $(EtO)_3Si(CH_2)_3S(CH_2)_3Si(EtO)_3$ ($CDCl_3$, 600MHz)

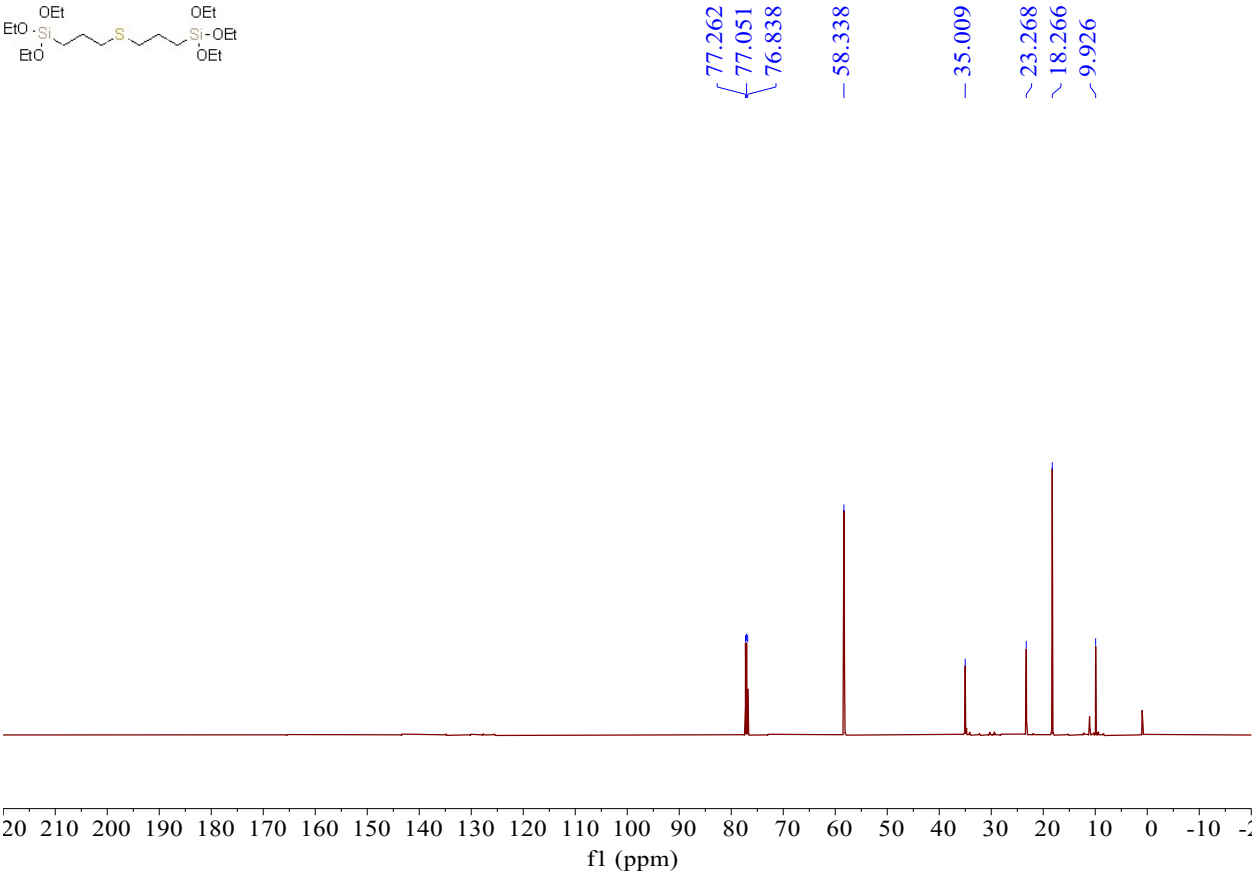


Fig.15 ^{13}C NMR spectra of $(EtO)_3Si(CH_2)_3S(CH_2)_3Si(EtO)_3$ ($CDCl_3$, 151MHz)

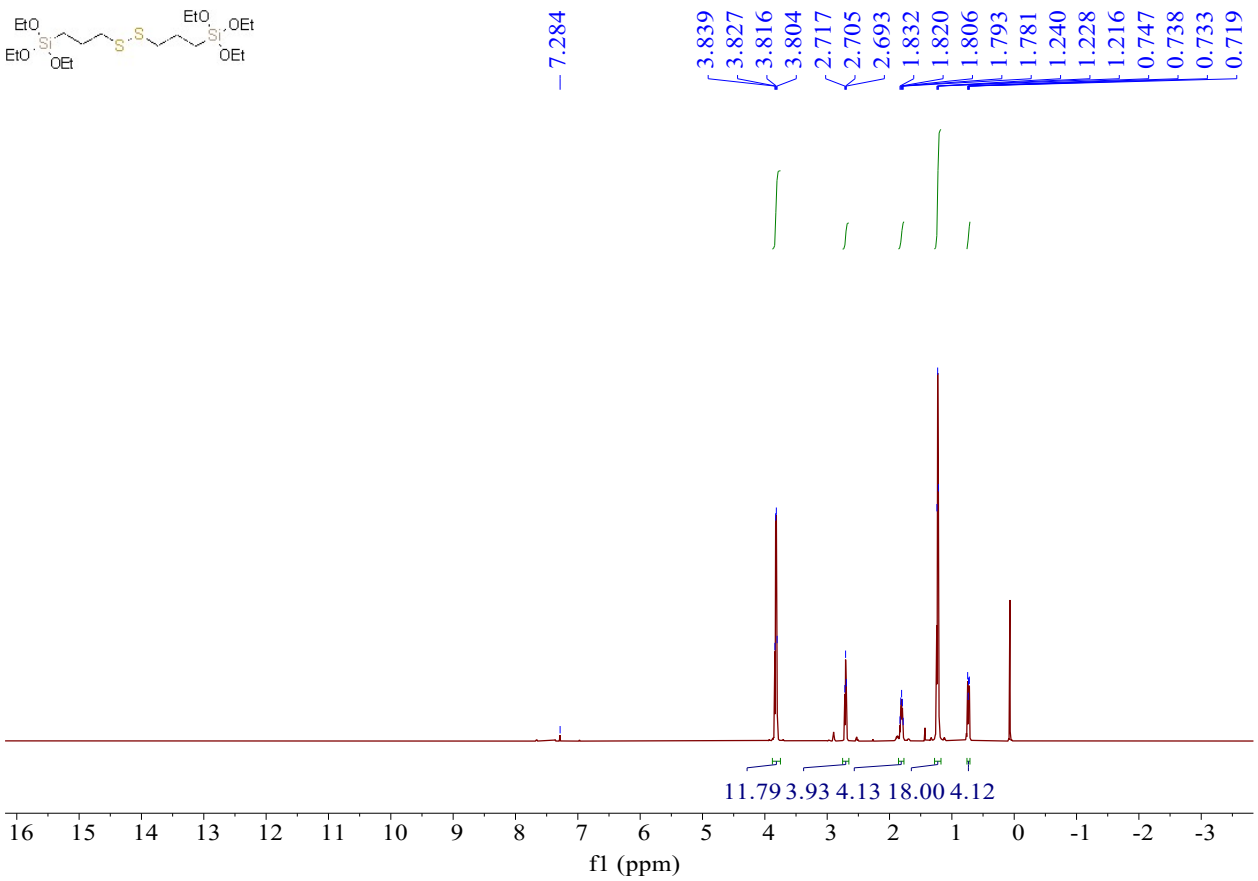


Fig.16 ^{1}H NMR spectra of $(EtO)_3Si(CH_2)_3SS(CH_2)_3Si(EtO)_3$ ($CDCl_3$, 600MHz)

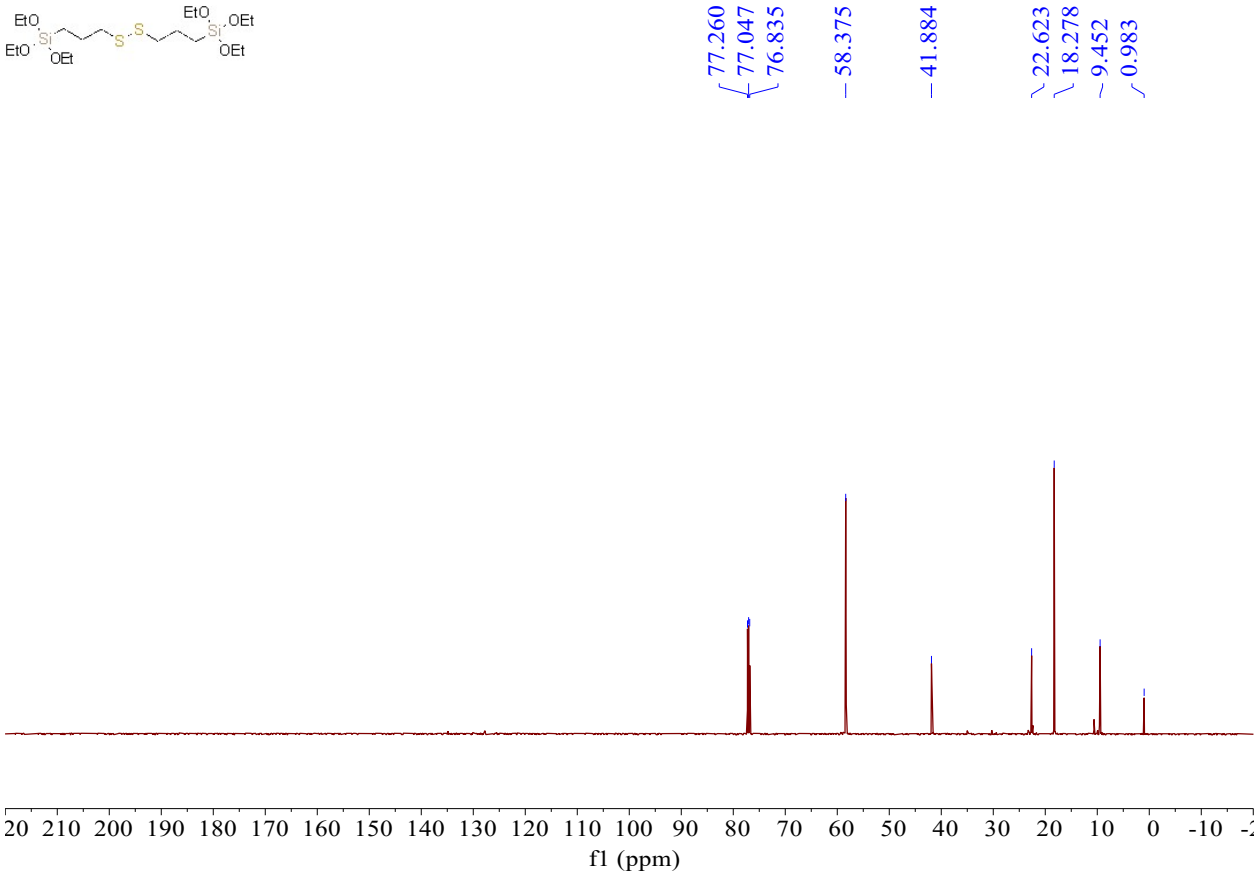


Fig.17 ^{13}C NMR spectra of $(EtO)_3Si(CH_2)_3SS(CH_2)_3Si(EtO)_3$ ($CDCl_3$, 151MHz)