## **Supporting Information**

## Metal- and Oxidant-Free S–P(O) Bond Construction via Direct

### Coupling of P(O)H with Sulfinic Acids

Youngtaek Moon, <sup>a</sup> Yonghoon Moon, <sup>b,a</sup> Hangyeol Choi, <sup>b,a</sup> and Sungwoo Hong\*, <sup>a,b</sup>

<sup>a</sup>Center for Catalytic Hydrocarbon Functionalization Institute for Basic Science (IBS), Daejeon, 305-701,

Korea

<sup>b</sup>Department of Chemistry, Korea Advance Institute of Science and Technology (KAIST), Daejeon 305-701,

Korea

#### I. Optimization Studies

S2

Appendix I

Spectral Copies of <sup>1</sup>H-, <sup>13</sup>C-, and <sup>31</sup>P NMR Data Obtained in this Study

**S**6

## I. Optimization Study

*Table S1.* Optimization study of diphenylphosphine oxide with 4-methylbenzene sulfinic acid.<sup>[a]</sup>

| Ph- | O<br>-P-H<br>Ph   | + SOH                        |         | Ph-P'S                  |
|-----|-------------------|------------------------------|---------|-------------------------|
|     | Entry             | Additive                     | Solvent | Yield(%) <sup>[b]</sup> |
|     | 1[c]              | pyridine                     | PhMe    | 40                      |
|     | 2 <sup>[c]</sup>  | pyridine                     | MeCN    | 28                      |
|     | 3[c]              | pyridine                     | DCE     | 21                      |
|     | 4                 | pyridine                     | PhMe    | 42                      |
|     | 5                 | -                            | PhMe    | 44                      |
|     | 6                 | Cy <sub>3</sub> P            | PhMe    | trace                   |
|     | 7                 | $(C_6F_5)_3P$                | PhMe    | 51                      |
|     | 8                 | (4-MeOPh) <sub>3</sub> P     | PhMe    | 69                      |
|     | 9                 | Ph <sub>3</sub> P            | PhMe    | 72                      |
|     | 10                | (4-FPh) <sub>3</sub> P       | PhMe    | 56                      |
|     | 11                | (2-furyl) <sub>3</sub> P     | PhMe    | 33                      |
|     | 12                | (2-pyridyl)Ph <sub>2</sub> P | PhMe    | N.R.                    |
|     | 13                | (benzyl) <sub>3</sub> P      | PhMe    | N.R.                    |
|     | 14                | Ph <sub>2</sub> CyP          | PhMe    | trace                   |
|     | 15                | (o-tolyl) <sub>3</sub> P     | PhMe    | 53                      |
|     | 16                | $(t-Bu)_3P$                  | PhMe    | 29                      |
|     | 17 <sup>[d]</sup> | Ph <sub>3</sub> P            | PhMe    | 56                      |
|     | 18                | Ph <sub>3</sub> P            | DMF     | trace                   |

| 19                | Ph <sub>3</sub> P      | DMSO                                 | 20    |
|-------------------|------------------------|--------------------------------------|-------|
| 20                | Ph <sub>3</sub> P      | EtOH                                 | 57    |
| 21                | Ph <sub>3</sub> P      | EtOAc                                | 57    |
| 22                | Ph <sub>3</sub> P      | MeCN                                 | 62    |
| 23                | Ph <sub>3</sub> P      | $H_2O$                               | trace |
| 24                | Ph <sub>3</sub> P      | THF                                  | trace |
| 25                | Ph <sub>3</sub> P      | Acetone                              | 12    |
| 26                | Ph <sub>3</sub> P      | iPrOAc                               | 86    |
| 27                | Ph <sub>3</sub> P      | tBuOAc                               | 82    |
| 28 <sup>[e]</sup> | Ph <sub>3</sub> P      | iPrOAc                               | 83    |
| 29 <sup>[f]</sup> | Ph <sub>3</sub> P      | iPrOAc                               | trace |
| 30 <sup>[f]</sup> | Ph <sub>3</sub> P      | <i>i</i> PrOAc/H <sub>2</sub> O(9:1) | N.R.  |
| 31 <sup>[f]</sup> | Ph <sub>3</sub> P      | <i>i</i> PrOAc/TFA(9:1)              | N.R.  |
| 32 <sup>[f]</sup> | Ph <sub>3</sub> P      | <i>i</i> PrOAc/AcOH(9:1)             | N.R.  |
| 33                | Ph <sub>3</sub> P/TFA  | iPrOAc                               | trace |
| 34                | Ph <sub>3</sub> P/AcOH | iPrOAc                               | trace |
|                   |                        |                                      |       |

[a] Reaction conditions: diphenylphosphine oxide (0.17 mmol), 4-methylbenzenesulfinic acid (2.0 equiv), additive (1.0 equiv), and solvent (1.0 mL) at room temperature under N<sub>2</sub> for 24 h. [b] Yields are reported after isolation and purification by flash silica gel chromatography. [c] under O<sub>2</sub>. [d] 4-methylbenzenesulfinic acid (1.5 equiv). [e] 40 °C [f] sodium 4-methylbenzenesulfinate was used. N.R. = no reaction.

Table S2. Optimization study of diethyl phosphite with 4-methylbenzene sulfinic acid.<sup>[a]</sup>



| Entry             | Additive                                 | Solvent        | Temp | Yield(%) <sup>[b]</sup> |
|-------------------|--|----------------|------|-------------------------|
| 1                 | -  | PhMe           | R.T. | N.R.                    |
| 2                 | -  | iPrOAc         | R.T. | N.R.                    |
| 3                 | -  | MeCN           | R.T. | N.R.                    |
| 4                 | -  | <i>t</i> BuOAc | R.T. | N.R.                    |
| 5                 | -  | DMF            | R.T. | N.R.                    |
| 6                 | DBU (1equiv)                             | PhMe           | R.T. | trace                   |
| 7                 | TMG (1equiv)                             | PhMe           | R.T. | trace                   |
| 8                 | TEA (lequiv)                             | PhMe           | R.T. | N.R.                    |
| 9                 | pyridine (1equiv)                        | PhMe           | R.T. | N.R.                    |
| 10                | DBU (1equiv)                             | MeCN           | R.T. | 7                       |
| 11                | DBU (1equiv)                             | DMF            | R.T. | N.R.                    |
| 12                | DBU (1equiv)                             | iPrOAc         | R.T. | N.R.                    |
| 13                | DBU (1equiv)                             | THF            | R.T. | N.R.                    |
| 14                | Na <sub>2</sub> CO <sub>3</sub> (1equiv) | MeCN           | R.T. | N.R.                    |
| 15                | NaHCO <sub>3</sub> (1equiv)              | MeCN           | R.T. | N.R.                    |
| 16                | DIPEA (lequiv)                           | MeCN           | R.T. | trace                   |
| 17                | DABCO (1equiv)                           | MeCN           | R.T. | N.R.                    |
| 18                | DBU (1equiv)                             | MeCN           | 40   | 11                      |
| 19                | DBU (1equiv)                             | MeCN           | 60   | 54                      |
| 20                | DBU (1equiv)                             | MeCN           | 80   | 45                      |
| 21 <sup>[c]</sup> | DBU (1equiv)                             | MeCN           | 60   | 11                      |
| 22                | -  | MeCN           | 60   | 6                       |
|                   |  |                |      |                         |

[a] Reaction conditions: diethylphosphite (0.10 mmol), 4-methylbenzenesulfinic acid (2.0 equiv), triphenylphosphine (1.0 equiv), additive, and solvent (1.0 mL) at room temperature under  $N_2$  for 13 h. [b] Yields are reported after isolation and purification by flash silica gel chromatography. [c] no triphenylphophine. N.R. = no reaction. R.T. = room temperature

Table S3. Optimization study of triethyl phosphite with 4-methylbenzene sulfinic acid.<sup>[a]</sup>



| Entry | Additive | Solvent | Tem<br>p | Yield(%) <sup>[b]</sup> |
|-------|----------|---------|----------|-------------------------|
| 1     | -        | MeCN    | R.T.     | 17                      |
| 2     | -        | PhMe    | R.T.     | 15                      |
| 3     | -        | DMF     | R.T.     | 13                      |
| 4     | -        | THF     | R.T.     | 10                      |
| 5     | -        | iPrOAc  | R.T.     | 14                      |
| 6     | -        | DMF     | 60       | 20                      |
| 7     | -        | DMF     | 80       | 50                      |
| 8     | -        | DMF     | 100      | 33                      |
| 9     | -        | DMF     | 120      | 19                      |
| 10    | -        | PhMe    | 80       | 28                      |
| 11    | -        | DME     | 80       | N.R.                    |
| 12    | -        | Dioxane | 80       | 22                      |
| 13    | -        | MeCN    | 80       | 41                      |
| 14    | -        | iPrOAc  | 80       | 20                      |
| 15    | -        | EtOH    | 80       | trace                   |

| 16                | -                 | DMSO   | 80 | 61   |
|-------------------|-------------------|--------|----|------|
| 17                | aectic acid (10%) | DMSO   | 80 | 24   |
| 18                | Water (3equiv)    | DMSO   | 80 | 26   |
| 19                | DMSO (10%)        | MeCN   | 80 | 42   |
| 20                | DMSO (10%)        | DME    | 80 | N.R. |
| 21                | DMSO (10%)        | iPrOAc | 80 | 29   |
| 22                | DMSO (10%)        | THF    | 80 | 40   |
| 23                | DMSO (10%)        | PhMe   | 80 | 55   |
| 24 <sup>[c]</sup> | -                 | DMSO   | 80 | 33   |

[a] Reaction conditions: triethyl phosphite (0.10 mmol), 4-methylbenzenesulfinic acid (2.0 equiv), triphenylphosphine (1.0 equiv), additive, and solvent (1.0 mL) at room temperature under  $N_2$  for 13 h. [b] Yields are reported after isolation and purification by flash silica gel chromatography. [c] no triphenylphosphine. N.R. = no reaction. R.T. = room temperature.

## Appendix I

# Spectral Copies of <sup>1</sup>H, <sup>13</sup>C, and <sup>31</sup>P NMR Data

**Obtained in this Study** 







190 170 150 130 110 90 70 50 30 10 - -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 162 MHz, <sup>31</sup>P NMR in CDCl<sub>3</sub>

#### S-o-tolyl diphenylphosphinothioate (3b)



-2.32

400 MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>





S-phenyl diphenylphosphinothioate (3c) 2012



400 MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>



\_190 170 150 130 110 90 70 50 30 10 \_ -10 -30 -50 -70 -90 -110 -130 -150 -170 -190

#### 162 MHz, <sup>31</sup>P NMR in CDCl<sub>3</sub>



S-(4-(tert-butyl)phenyl) diphenylphosphinothioate (3d)

190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190





S-(4-fluorophenyl) diphenylphosphinothioate (3e)





190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190







S-(4-chlorophenyl) diphenylphosphinothioate (3f)

1717 38 1718 38 171





190 170 150 130 110 90 70 50 30 10 <u>-</u> -10 -30 -50 -70 -90 -110 -130 -150 -170 -190



Ph. Ph. S. CI

S-(4-bromophenyl) diphenylphosphinothioate (3g)









Ph.p.S Ph.D.Br

#### S-(4-iodophenyl) diphenylphosphinothioate (3h)







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S5.47
S5.47
S77.32
T7.32
T7.32
T7.00
S76.68

138.10 136.73 137.73 136.73 137.74 137.74 147.74 17.74 1

162 MHz, <sup>31</sup>P NMR in CDCl<sub>3</sub>

S-(4-(trifluoromethyl)phenyl) diphenylphosphinothioate (3i)



400 MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>

. 190 170 150 130 110 90 70 50 30 10 - 10 -30 -50 -70 -90 -110 -130 -150 -170 -190



-77.32

135,19 135,15 135,15 132,265 132,265 132,265 131,50 131,50 131,50 131,50 131,50 131,50 131,50 131,50 131,50 131,50 131,50 132,53 152,73 125,75 125,73 125,755 125,755 125,755 125,755 125,7555 125,75555 125,755555555555555555555

#### S-(4-(trifluoromethoxy)phenyl) diphenylphosphinothioate (3j)





400 MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>

. 190 170 150 130 110 90 70 50 30 10 - -10 -30 -50 -70 -90 -110 -130 -150 -170 -190



#### S-(4-methoxyphenyl) diphenylphosphinothioate (3k)





. 190 170 150 130 110 90 70 50 30 10 - 10 -30 -50 -70 -90 -110 -130 -150 -170 -190



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#### S-(naphthalen-2-yl) diphenylphosphinothioate (3l)



400 MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>



190 170 150 130 110 90 70 50 30 10 - -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 162 MHz, <sup>31</sup>P NMR in CDCl<sub>3</sub>

135.29 133.24 133.24 133.33 133.33 133.33 133.33 133.33 133.33 133.33 133.33 133.34 133.24 133.24 133.24 133.41 133.41 133.41 133.41 133.41 133.41 133.41 133.41 133.41 133.41 133.41 133.41 133.41 133.41 133.41 133.43 133.41 133.43 133.44 143.44 144.44 144.44 144.44 144.44 144.44 144.44 144.44 144.44 144.44 144.44 144.44 144.44 144.44 14 77.32 76.68

#### S-isopropyl diphenylphosphinothioate (3m)





. 190 170 150 130 110 90 70 50 30 10 - 10 -30 -50 -70 -90 -110 -130 -150 -170 -190



#### S-benzyl diphenylphosphinothioate (3n)





. 190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190



C11.32

33.15 33.13 33.13

136.72 135.72 132.24 132.24 132.25 132.55 152.55 155.55 155.55 155.55 155.55 155.55 155.55 155.55 15 S-phenethyl diphenylphosphinothioate (30)



Ph\_p\_S\_ Ph

400 MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>
. 190 170 150 130 110 90 70 50 30 10 - 10 -30 -50 -70 -90 -110 -130 -150 -170 -190



### S-cyclopropyl diphenylphosphinothioate (3p)

7,28 1 11.135 11

> Ph ⊕ S Ph ♥





. 190 170 150 130 110 90 70 50 30 10 - 10 -30 -50 -70 -90 -110 -130 -150 -170 -190



717.22 848 722 848 731.17 738.61 7

## S-(thiophen-2-yl) diphenylphosphinothioate (3q)





. 190 170 150 130 110 90 70 50 30 10 - -10 -30 -50 -70 -90 -110 -130 -150 -170 -190



-77.32

## S-(2,3-dihydrobenzofuran-5-yl) diphenylphosphinothioate (3r)







. 190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190



# O-ethyl S-(p-tolyl) phenylphosphonothioate (4a)

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|---|-----|------|
|   | V   | SV/  |



<sup>400</sup> MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>



190 170 150 130 110 90 70 50 30 10 - -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 162 MHz, <sup>31</sup>P NMR in CDCl<sub>3</sub>





600 MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 243 MHz, <sup>31</sup>P NMR in CDCl<sub>3</sub>





600 MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>



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77.21 77.00 76.79 63.89 63.89

<|33.22 |33.19 <|34.54 <|34.54 <|34.54 <|34.54 <|34.54 <|34.54 <|34.54</pre>

190 180 170 160 150 140 130 120 110 100 90 80 - 70 60 50 40 30 20 10 0 -10 -20 -30 -40 243 MHz, <sup>31</sup>P NMR in CDCl<sub>3</sub>



# O,O-diisopropyl S-p-tolyl phosphorothioate (4d)



# O,O-dibutyl S-p-tolyl phosphorothioate (4e)



<sup>400</sup> MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>

. 190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190

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|---|---------|---------|--------|-------|-------|---|---|---------------------|
| 150 MHz, <sup>13</sup> C NMR in CDCl <sub>3</sub>   | 140 130 | 120 110 | 100 90 | 80 70 | 60 50 | 40 30   | 20 1                                      | 0                   |
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 $\begin{pmatrix} 77.21\\76.79\\76.79\\67.66\end{pmatrix}$ 

~ 32.17 32.12 --11.6 --13.65 --13.55

<|3317 <|3315 <|33454 <|33454 <|3306 <|30.08 <|30.08 <|30.08</pre>

## O,O-diphenyl S-p-tolyl phosphorothioate (4f)





190 180 170 160 150 140 130 120 110 100 90 80 - 70 60 50 40 30 20 10 0 -10 -20 -30 -40 243 MHz, <sup>31</sup>P NMR in CDCl<sub>3</sub>





<sup>600</sup> MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>



190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 243 MHz, <sup>31</sup>P NMR in CDCl<sub>3</sub>

## 6-(p-tolylthio)dibenzo[c,e][1,2]oxaphosphinine 6-oxide (4h)



<217 216

. 190 170 150 130 110 90 70 50 30 10 - 10 -30 -50 -70 -90 -110 -130 -150 -170 -190



# S-(p-tolyl) di-tert-butylphosphinothioate (4i)



. 190 170 150 130 110 90 70 50 30 10 - 10 -30 -50 -70 -90 -110 -130 -150 -170 -190



### S-(p-tolyl) isopropyl(phenyl)phosphinothioate (4j)

Landard Control (1998)
Landard Control



. 190 170 150 130 110 90 70 50 30 10 - 10 -30 -50 -70 -90 -110 -130 -150 -170 -190



138.87 138.887 138.525 138.525 131.91 131.93 131.64 131.64 131.64 131.64 131.64 131.64 131.64 131.64 131.64 131.64 131.64 121.90 121.90 121.90

## S-(p-tolyl) di-p-tolylphosphinothioate (4k)





~234 ~222 ~221

. 190 170 150 130 110 90 70 50 30 10 <u>-</u> -10 -30 -50 -70 -90 -110 -130 -150 -170 -190



# S-(p-tolyl) bis(4-fluorophenyl)phosphinothioate (4l)





. 190 170 150 130 110 90 70 50 30 10 - 10 -30 -50 -70 -90 -110 -130 -150 -170 -190



C 168.02 169. ₹77.32 76.68

# S-(p-tolyl) bis(4-methoxyphenyl)phosphinothioate (4m)



. 190 170 150 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190



Control 10 - 2010
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## S-(p-tolyl) bis(4-(trifluoromethyl)phenyl)phosphinothioate (4n)

7,298 7,298 7,298 7,299 7,209 7,209 7,200



<226 225

. 190 170 150 130 110 90 70 50 30 10 <u>-</u> -10 -30 -50 -70 -90 -110 -130 -150 -170 -190



S-(p-tolyl) bis(4-chlorophenyl)phosphinothioate (40)




# S-(p-tolyl) bis(4-(dimethylamino)phenyl)phosphinothioate (4p)



<sup>400</sup> MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>



# S-(p-tolyl) bis(3,5-dimethylphenyl)phosphinothioate (4q)



400 MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>



### S-(p-tolyl) di(naphthalen-2-yl)phosphinothioate (4r)



-217

400 MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>



















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#### <151.98 <151.95 |35.05 |35.05 |35.05 |34.16 |33.16 |32.08 |32.12 |32.09 |32.09 |132.09 |132.09 |132.09 |132.09

# -112.12 -122.12 -12





<sup>400</sup> MHz, <sup>1</sup>H NMR in CDCl<sub>3</sub>







. 190 170 150 130 110 90 70 50 30 10 - -10 -30 -50 -70 -90 -110 -130 -150 -170 -190

#### 162 MHz, <sup>31</sup>P NMR in CDCl<sub>3</sub>

(1R,2S,5R)-2-isopropyl-5-methylcyclohexyl phenylphosphinate (1c)



O-((1R,2S,5R)-2-isopropyl-5-methylcyclohexyl) S-p-tolyl phenylphosphonothioate (6a)

