Electronic Supplementary Information

Magnetically Recyclable Cu-BTC@Fe$_3$O$_4$

Composite-Catalyzed C$_{\text{aryl}}$-S-P Bonds formation

using aniline, P(O)H Compounds and Sulfur Powder

Liang Wang, Sen Yang, Le Chen, Sheng Yuan, Qun Chen, Ming-Yang He* and Zhi-Hui Zhang*

School of Petrochemical Engineering, Jiangsu Key Laboratory of Advanced Catalytic Materials and Technology, Advanced Catalysis and Green Manufacturing Collaborative Innovation Center, Changzhou University, Changzhou 213164, P. R. China

* Corresponding author. Tel. & Fax: 86-519-86330251, E-mail: zhangzh@cczu.edu.cn (Z.H.Z.), hemingyangjpu@yahoo.com (M.Y.H.)
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1. Experimental procedures

Polyvinylpyrrolidone K-30 (PVP, (C₆H₉NO)ₙ, MW: av. 40,000), Cu(OAc)$_2$·H$_2$O (98%), trimesic acid (H$_3$BTC, 99%), and carboxymethylcellulose (CMC, viscosity > 1900 mPa·s, surface density: 0.35 to 0.60 g·m$^{-1}$), as well as carboxyl functionalized Fe$_3$O$_4$ (about 20 nm). All starting materials are commercially available and used directly without further purification.

Scale-up synthesis

The scale-up experiment was conducted in a two-neck 100 mL flask. The substrate amount was 5 mmol. The amounts of other reagents and the catalyst were increased to 25 times accordingly. The reaction method and purification were the same as the model reaction in Table 1.

Scheme S1 Gram-scale synthesis of 4a.

![Scheme S1](image)

Fig. S1. IR spectra of carboxyl functionalized Fe$_3$O$_4$ (black), Cu-BTC (red) and Cu-BTC@Fe$_3$O$_4$ (blue).
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**Fig. S2.** The EDS element analysis of Cu-BTC@Fe₃O₄, the scale bar is 20 µm.

**Fig. S3.** The TG curves of Cu-BTC@Fe₃O₄ with different ratios of starting materials.
2 Characterization data

\[O,O\text{-diethyl } S\text{-phenyl phosphorothioate (4a). Yellow oil.} \]
\[^1H\text{ NMR (300 MHz, CDCl}_3\text{) } \delta 7.59 - 7.49 \text{ (m, 2H), 7.43 - 7.27 \text{ (m, 3H), 4.28 - 4.06 \text{ (m, 4H), 1.28 \text{ (td, } J = 7.1, 0.6 \text{ Hz, 6H).} \] \]
\[^{13}C\text{ NMR (75 MHz, CDCl}_3\text{) } \delta 134.5 \text{ (d, } J = 5.2 \text{ Hz), 129.3 \text{ (d, } J = 2.3 \text{ Hz), 129.0 \text{ (d, } J = 2.8 \text{ Hz), 126.4 \text{ (d, } J = 7.2 \text{ Hz), 64.0 \text{ (d, } J = 6.2 \text{ Hz), 15.9 \text{ (d, } J = 7.2 \text{ Hz).} \] \]
\[^{31}P\text{ NMR (121 MHz, CDCl}_3\text{): } \delta 22.8.\] MS-ESI: \[m/z = 268.8 \text{ [M + Na]^+}.\]

\[O,O\text{-diethyl } S\text{-}(p\text{-tolyl) phosphorothioate (4b). Yellow oil.} \]
\[^1H\text{ NMR (300 MHz, CDCl}_3\text{) } \delta 7.47 - 7.38 \text{ (m, 2H), 7.14 \text{ (d, } J = 8.4 \text{ Hz, 2H), 4.26 - 4.08 \text{ (m, 4H), 2.33 \text{ (d, } J = 2.0 \text{ Hz, 3H), 1.30 \text{ (td, } J = 7.1, 0.9 \text{ Hz, 6H).} \] \]
\[^{13}C\text{ NMR (75 MHz, CDCl}_3\text{) } \delta 139.2 \text{ (d, } J = 3.2 \text{ Hz), 134.5 \text{ (d, } J = 5.1 \text{ Hz), 130.1 \text{ (d, } J = 2.4 \text{ Hz), 122.7 \text{ (d, } J = 7.3 \text{ Hz), 63.9 \text{ (d, } J = 6.1 \text{ Hz), 21.1 \text{ (d, } J = 0.9 \text{ Hz), 16.0 \text{ (d, } J = 7.2 \text{ Hz).} \] \]
\[^{31}P\text{ NMR (121 MHz, CDCl}_3\text{): } \delta 23.3.\] MS-ESI: \[m/z = 282.9 \text{ [M + Na]^+}.\]

\[S\text{-}(4\text{-chlorophenyl) O,O-diethyl phosphorothioate (4c). Yellow oil.} \]
\[^1H\text{ NMR (300 MHz, CDCl}_3\text{) } \delta 7.54 - 7.45 \text{ (m, 2H), 7.35 - 7.28 \text{ (m, 2H), 4.29 - 4.07 \text{ (m, 4H), 1.31 \text{ (td, } J = 7.1, 0.8 \text{ Hz).} \]
Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 135.7 (d, $J = 5.2$ Hz), 135.5 (d, $J = 3.5$ Hz), 129.5 (d, $J = 2.3$ Hz), 125.1 (d, $J = 7.2$ Hz), 64.2 (d, $J = 6.4$ Hz), 16.0 (d, $J = 7.1$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ 22.1. MS-ESI: $m/z =$ 302.9 [M + Na]$^+$.  

$S$-(4-fluorophenyl) O,O-diethyl phosphorothioate (4d). Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.55 – 7.50 (m, 2H), 7.03 (t, $J = 8.6$ Hz, 2H), 4.26 – 4.07 (m, 4H), 1.29 (t, $J = 7.1$ Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 163.4 (dd, $J = 250, 3.2$ Hz), 136.8 (dd, $J = 6.3, 3.7$ Hz), 121.6 (dd, $J = 6.8, 2.6$ Hz), 116.5 (dd, $J = 37.3, 22.3$ Hz), 64.1 (d, $J = 6.4$ Hz), 15.9 (d, $J = 7.2$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ 22.6. MS-ESI: $m/z =$ 286.8 [M + Na]$^+$.  

$O,O$-diethyl $S$-(4-nitrophenyl) phosphorothioate (4e). Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.20 (d, $J = 8.4$ Hz, 2H), 7.79 – 7.74 (m, 2H), 4.34 – 4.14 (m, 4H), 1.35 (td, $J = 7.1, 0.9$ Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 147.7, 136.1 (d, $J = 6.6$ Hz), 134.1 (d, $J = 6.0$ Hz), 124.1 (d, $J = 1.5$ Hz), 64.7 (d, $J = 6.4$ Hz), 16.0 (d, $J = 7.0$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ 19.8. MS-ESI: $m/z =$ 314.0 [M + Na]$^+$.  

$S$-(4-cyanophenyl) O,O-diethyl phosphorothioate (4f). Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.69 – 7.66 (m, 2H), 7.61 – 7.58 (m, 2H), 4.29 – 4.09 (m, 4H), 1.30 (td, $J = 7.1, 0.8$ Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 134.2 (d, $J = 6.0$ Hz), 134.0 (d, $J = 6.7$ Hz), 132.6 (d, $J = 1.6$ Hz), 117.9 (d, $J = 1.4$ Hz), 112.4 (d, $J = 2.4$ Hz), 64.5 (d, $J = 6.4$ Hz), 15.9 (d, $J = 7.1$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ 20.3. MS-ESI: $m/z =$ 294.0 [M + Na]$^+$.  

$O,O$-diethyl $S$-(4-(trifluoromethyl)phenyl) phosphorothioate (4g). Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.71 – 7.67 (m, 2H), 7.58 (d, $J = 8.6$ Hz, 2H), 4.30 – 4.10 (m, 4H), 1.31 (td, $J = 7.1, 0.8$ Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 134.2 (d, $J = 5.6$ Hz), 131.8 (d, $J = 6.8$ Hz), 130.8 (dd, $J = 2.5, 32.7$ Hz), 126.0 (dd, $J = 3.7, 1.9$ Hz), 123.6 (q, $J = 270$ Hz), 64.4 (d, $J = 6.3$ Hz), 15.9 (d, $J = 7.1$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ 21.2. MS-ESI: $m/z =$ 337.0 [M + Na]$^+$.  

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S-(4-acetylphenyl) O,O-diethyl phosphorothioate (4h). Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.89 (d, $J = 8.3$ Hz), 7.65 – 7.63 (m, 2H), 4.28 – 4.09 (m, 4H), 2.58 (s, 3H), 1.30 (td, $J = 7.1$, 0.9 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 197.1, 136.9 (d, $J = 2.4$ Hz), 133.8 (d, $J = 5.7$ Hz), 133.1 (d, $J = 6.9$ Hz), 128.9 (d, $J = 1.8$ Hz), 64.3 (d, $J = 6.3$ Hz), 26.6, 15.9 (d, $J = 7.1$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ 21.2. MS-ESI: $m/z = 310.8$ [M + Na]$^+$. 

Ethyl 4-((diethoxyphosphoryl)thio)benzoate (4i). Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.98 (d, $J = 8.2$ Hz, 2H), 7.64 – 7.60 (m, 2H), 4.35 (q, $J = 7.1$ Hz, 2H), 4.25 – 4.10 (m, 4H), 1.36 (t, $J = 7.1$ Hz, 3H), 1.29 (td, $J = 7.1$, 0.8 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 165.8, 133.6 (d, $J = 5.7$ Hz), 132.7 (d, $J = 6.9$ Hz), 130.7 (d, $J = 2.5$ Hz), 130.2 (d, $J = 1.8$ Hz), 64.3 (d, $J = 6.3$ Hz), 61.2, 15.9 (d, $J = 7.2$ Hz), 14.2. $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ 21.4. MS-ESI: $m/z = 341.0$ [M + Na]$^+$. 

O,O-diethyl S-(o-tolyl) phosphorothioate (4j). Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.65 – 7.57 (m, 1H), 7.30 – 7.23 (m, 2H), 7.22 – 7.13 (m, 1H), 4.22 – 4.07 (m, 4H), 2.52 (d, $J = 1.4$ Hz, 3H), 1.29 (td, $J = 7.1$, 0.8 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 142.2 (d, $J = 5.6$ Hz), 136.1 (d, $J = 4.2$ Hz), 130.8 (d, $J = 2.6$ Hz), 129.4 (d, $J = 3.1$ Hz), 126.7 (d, $J = 2.7$ Hz), 125.7 (d, $J = 7.4$ Hz), 64.1 (d, $J = 6.7$ Hz), 21.4, 16.0 (d, $J = 7.1$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ 23.0. MS-ESI: $m/z = 283.0$ [M + Na]$^+$. 

S-(2-chlorophenyl) O,O-diethyl phosphorothioate (4k). Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.78 – 7.75 (m, 1H), 7.48 – 7.45 (m, 1H), 7.34 – 7.23 (m, 2H), 4.33 – 4.14 (m, 4H), 1.33 (td, $J = 7.1$, 0.9 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 137.9 (d, $J = 6.9$ Hz), 136.8 (d, $J = 4.1$ Hz), 130.3 (d, $J = 6.7$ Hz), 127.5 (d, $J = 2.4$ Hz), 64.4 (d, $J = 6.2$ Hz), 16.0 (d, $J = 7.3$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ 21.2. MS-ESI: $m/z = 302.9$ [M + Na]$^+$. 
**O,O-diethyl S-(2-nitrophenyl) phosphorothioate (4l).** Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.01–7.89 (m, 2H), 7.60–7.45 (m, 2H), 4.32–4.09 (m, 4H), 1.31 (td, $J$ = 7.1, 0.8 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 151.6 (d, $J$ = 7.8 Hz), 136.1 (d, $J$ = 4.9 Hz), 132.8 (d, $J$ = 1.7 Hz), 129.2 (d, $J$ = 2.0 Hz), 125.2 (d, $J$ = 1.6 Hz), 123.0 (d, $J$ = 6.3 Hz), 64.8 (d, $J$ = 6.7 Hz), 15.9 (d, $J$ = 7.0 Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): δ 19.9. MS-ESI: $m/z$ = 314.0 [M + Na]$^+$.  

**O,O-diethyl S-(m-tolyl) phosphorothioate (4m).** Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.40–7.33 (m, 2H), 7.27–7.15 (m, 2H), 4.29–4.10 (m, 4H), 2.35 (s, 3H), 1.31 (td, $J$ = 7.1, 0.9 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 139.1 (d, $J$ = 2.3 Hz), 135.1 (d, $J$ = 5.2 Hz), 131.5 (d, $J$ = 5.2 Hz), 129.8 (d, $J$ = 2.9 Hz), 129.1 (d, $J$ = 2.3 Hz), 126.0 (d, $J$ = 7.2 Hz), 63.9 (d, $J$ = 6.2 Hz), 21.2 (s), 15.9 (d, $J$ = 7.3 Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): δ 23.1. MS-ESI: $m/z$ = 282.9 [M + Na]$^+$.  

**O,O-diethyl S-(3-nitrophenyl) phosphorothioate (4n).** Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.41 (dd, $J$ = 3.9, 1.9 Hz, 1H), 8.20 (ddd, $J$ = 8.3, 2.8, 2.1 Hz, 1H), 7.90 (ddd, $J$ = 7.8, 2.8, 1.8 Hz, 1H), 7.54 (t, $J$ = 8.0 Hz, 1H), 4.31–4.12 (m, 4H), 1.32 (td, $J$ = 7.1, 0.9 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 148.3, 140.4 (d, $J$ = 5.4 Hz), 130.4, 129.5 (dd, $J$ = 13.5, 9.8 Hz), 129.0 (dd, $J$ = 15.2, 5.3 Hz), 123.9, 64.5 (d, $J$ = 6.5 Hz), 15.9 (d, $J$ = 7.1 Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): δ 20.9. MS-ESI: $m/z$ = 314.0 [M + Na]$^+$.  

**S-(3,5-dichlorophenyl) O,O-diethyl phosphorothioate (4o).** Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.46 (t, $J$ = 1.9 Hz, 2H), 7.35 (q, $J$ = 1.8 Hz, 1H), 4.30–4.11 (m, 4H), 1.34 (td, $J$ = 7.1, 0.9 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 135.3 (d, $J$ = 2.4 Hz), 132.3 (d, $J$ = 5.4 Hz), 129.9 (d, $J$ = 7.1 Hz), 129.2 (d, $J$ = 2.7 Hz), 64.5 (d, $J$ = 6.4 Hz), 15.9 (d, $J$ = 7.1 Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): δ 21.5. MS-ESI: $m/z$ = 336.9 [M + Na]$^+$. 

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**O,O-diethyl S-(naphthalen-1-yl) phosphorothioate (4p).** Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 8.53 (d, $J = 8.4$ Hz, 1H), 7.92 – 7.84 (m, 3H), 7.63 – 7.43 (m, 3H), 4.22 – 4.02 (m, 4H), 1.18 (td, $J = 7.1$, 0.6 Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 135.2 (d, $J = 5.6$ Hz), 134.6 (d, $J = 4.1$ Hz), 134.2 (d, $J = 2.3$ Hz), 130.2 (d, $J = 3.5$ Hz), 128.5, 127.0, 126.4, 125.7 (dd, $J = 17.5$, 2.1 Hz), 123.6 (d, $J = 8.1$ Hz), 64.2 (d, $J = 6.5$ Hz), 15.9 (d, $J = 7.2$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): δ 22.6. MS-ESI: m/z = 319.0 [M + Na]$^+$.

**O,O-dimethyl S-phenyl phosphorothioate (4q).** Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.56 – 7.52 (m, 2H), 7.37 – 7.31 (m, 3H), 3.82 (s, 3H), 3.77 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 134.5 (d, $J = 5.2$ Hz), 129.4 (d, $J = 2.3$ Hz), 129.1 (d, $J = 2.9$ Hz), 125.9 (d, $J = 7.3$ Hz), 54.2 (d, $J = 6.1$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): δ 26.2. MS-ESI: m/z = 240.8 [M + Na]$^+$.

**S-phenyl diisopropylphosphinothioate (4r).** Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.60 – 7.56 (m, 2H), 7.34 – 7.29 (m, 3H), 4.80 – 4.69 (m, 2H), 1.31 (d, $J = 6.2$ Hz, 6H), 1.24 (d, $J = 6.2$ Hz, 6H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 134.5 (d, $J = 5.5$ Hz), 129.3 (d, $J = 5.2$ Hz), 128.7 (d, $J = 1.8$ Hz), 127.3 (d, $J = 5.2$ Hz), 73.3 (d, $J = 5.5$ Hz), 23.8 (d, $J = 4.1$ Hz), 23.5 (d, $J = 6.0$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): δ 20.4. MS-ESI: m/z = 297.0 [M + Na]$^+$.

**O,O-dibenzyl S-phenyl phosphorothioate (4s).** Yellow oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.50 – 7.46 (m, 2H), 7.33 – 7.24 (m, 13H), 5.17 – 5.05 (m, 4H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 135.3 (d, $J = 7.6$ Hz), 134.7 (d, $J = 5.3$ Hz), 129.3 (d, $J = 2.4$ Hz), 129.0 (d, $J = 3.0$ Hz), 128.5, 128.4, 128.0, 125.8 (d, $J = 7.3$ Hz), 69.3 (d, $J = 6.3$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): δ 23.9. MS-ESI: m/z = 370.9 [M + H]$^+$.

**S-phenyl diphenylphosphinothioate (4u).** White solid. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.88 – 7.81 (m, 4H), 7.50 – 7.39 (m, 8H), 7.24 – 7.15 (m, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 135.3 (d, $J = 3.9$ Hz), 133.2, 132.2 (d, $J = 3.0$ Hz), 131.5 (d, $J = 10.2$ Hz), 129.0 (d, $J = 1.7$ Hz), 128.9 (d, $J = 2.2$ Hz),
128.5 (d, $J = 13.2$ Hz), 126.1 (d, $J = 5.2$ Hz). $^{31}$P NMR (121 MHz, CDCl$_3$): $\delta$ 41.4. MS-ESI: $m/z = 333.1$ [M + Na]$^+$. 
3 Copies of $^1$H NMR and $^{13}$C NMR spectra
\[ \text{Cl} \quad \text{S} \quad \text{P} \quad \text{O} \quad \text{Et} \quad \text{OEt} \]

\[ \text{S} \quad \text{P} \quad \text{O} \quad \text{Et} \quad \text{OEt} \]

\[ \text{Cl} \quad \text{S} \quad \text{P} \quad \text{O} \quad \text{Et} \quad \text{OEt} \]