Note

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Base-Catalyzed Hydrophosphination of Azobenzenes with Diarylphosphine Oxides: A Precise Construction of N-N-P Unit

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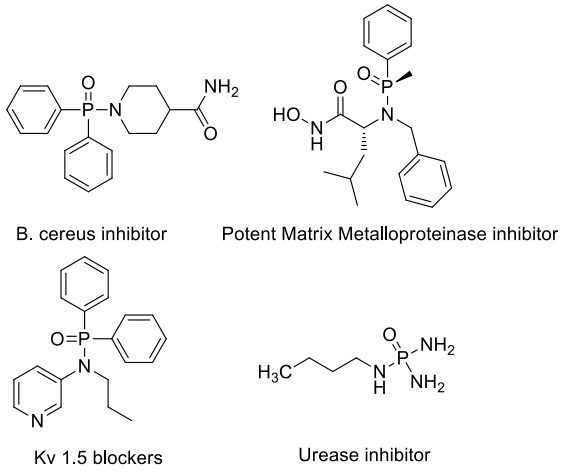
ABSTRACT: Addition of diarylphosphine oxides to the N=N double bond of azobenzenes leads to the formation of the P-substituted hydrazines in up to 98% yield for 24 examples and the formation of diphenylphosphinic amides was observed in 3 substrates. This strategy features tolerance of a wide range of functional groups, simple operation, and mild reaction conditions. Specially, this method can be also applied to the gram-scale synthesis of the product. A polar reaction mechanism is also proposed based on control experiments.

Recently, significant attention has been paid to organophosphorous compounds for their wide application in organic synthesis, asymmetric catalysis, and medicinal chemistry.[1] Some pharmaceutical compounds containing P(=O)-N bond are depicted in Scheme 1. Thus,

various methods have been developed to prepare organophosphorous compounds including the construction of C-P bond,[2] S-P bond,[3] and N-P bond,[4] among which the formation of N-P bond usually suffered from anaerobic reagents, the use of toxic and moisture sensitive halides $(RO)_2P(O)Cl$, and inert conditions. Thus, it is always valuable to achieve N-P bond formation under milder conditions to update the existing methods.

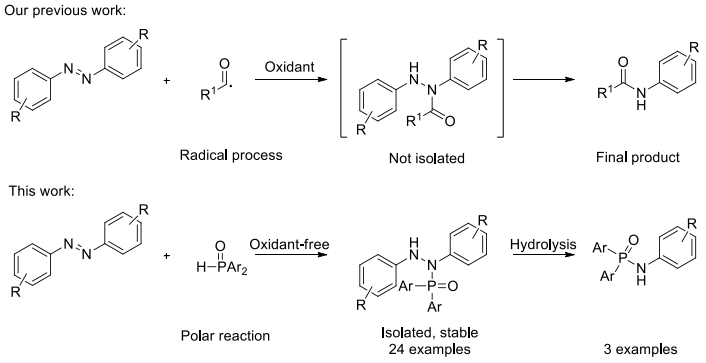
Scheme 1. Structure of Pharmaceutical Compounds with Phosphinic Amide Unit



Azobenzenes are important scaffolds and have been widely applied in such fields as organic dyes, protein probes, chemosensors, and molecular machines due to their unique properties.[5] Thus, the preparation of these compounds is well developed considering the broad utility of azobenzenes.[6] In 2014, our group realized the *ortho*-C-H phosphonation of azobenzenes using N=N double bond as directing group,[2b] which further expanded the scope of steric azo compounds. Meanwhile, the cleavage of the N=N bond is valuable in understanding the mechanism of dinitrogen fixation as well as developing new transformations using azo compounds as synthon. In 2014, Xi group utilized the cleavage N=N bond of azobenzenes to synthesize benzimidazole derivatives.[7] In 2015, the same

group reported a new method for the synthesis of quinolones from azobenzenes and allyl bromides *via* N=N bond cleavage.[8] Recently, our group realized direct synthesis of amide compounds from azobenzenes and aroyl surrogates *via* radical process (Scheme 2).[9] However, it is still highly desirable to further explore the utilities of azobenzenes. Herein, we report a highly efficient method for the construction of N-N-P unit by reaction of azobenzenes with diarylphosphine oxides. To the best of our knowledge, only a few cases for the synthesis of P-substituted hydrazines were reported.[10]

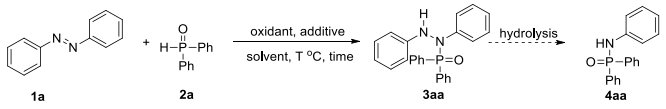
Scheme 2. Different Approaches for the Cleavage of N=N Double Bond



At the outset, based on our previous work,[9] we envisaged that P-centered radical, generated from diphenylphosphine oxide,[11] could attack the N=N double bond. Subsequently, the hydrolysis of the intermediate **3aa** could afford the final product **4aa** (Table 1). Our initial efforts focused on the model reaction of azobenzene (**1a**) with diphenylphosphine oxide (**2a**) to optimize the reaction condition. Unexpectedly, screening on the oxidant showed the use of DTBP (*tert*-butyl peroxide) afforded **3aa** in 76% yield, however our expected product **4aa** was not observed (Table 1, entries 1-5). Encouraged by this result, we further optimized the reaction conditions through adding base as additive and found that the use of base did

increase the yield of **3aa**, and Cs_2CO_3 enhanced the product **3aa** yield up to 88% for 6 h (Table 1, entries 6-8). Surprisingly, this reaction could proceed well even without oxidant, affording **3aa** in up to 96% yield (Table 1, entry 9). What's more, 95% yield was obtained when shortening the reaction time to only 30 minutes (Table 1, entry 10). Solvent screening including DCE, DMSO, PhCl, and DMF revealed that these tested solvents were all inferior in terms of the reaction yields (Table1, entries 11-14). Gratifyingly, the yield was increased to 98% when the temperature was decreased to 100 ^oC (Table 1, entries 15 and 16). Also, decreasing the amount of Cs_2CO_3 to 0.2 equiv led to 16% yield of the product (Table 1. entry 17). The reaction did not proceed in the absence of Cs_2CO_3 (Table 1, entry 18). It should be noted that the assumed product **4aa** was not observed during the whole screening process.

Table 1. Hydrophosphination of Azobenzene 1a with Diphenylphosphine Oxide 2a under Various Conditions[a]



Entry	Oxidant (equiv)	Additive (equiv)	Solvent	T (^oC)	Time (h)	Yield of **3aa**[b]
1	$K_2S_2O_8$ (3)	/	CH_3CN	110	20	0
2	TBHP (3)	/	CH_3CN	110	20	21%
3	AgOAc (3)	/	CH_3CN	110	20	0
4	$Mn(OAc)_3$ (3)	/	CH_3CN	110	20	0
5	DTBP (3)	/	CH_3CN	110	20	76%
6	DTBP (3)	K_2CO_3 (1.1)	CH_3CN	110	6	84%
7	DTBP (3)	Cs_2CO_3 (1.1)	CH_3CN	110	6	88%
8	DTBP (3)	Na_2CO_3 (1.1)	CH_3CN	110	6	78%
9	/	Cs_2CO_3 (1.1)	CH_3CN	110	6	96%
10	/	Cs_2CO_3 (1.1)	CH_3CN	110	0.5	95%

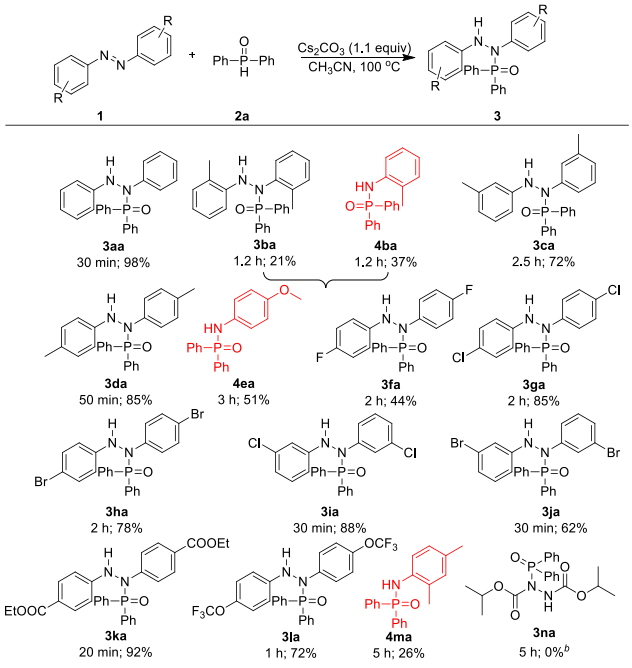
11	/	Cs_2CO_3 (1.1)	DCE	110	0.5	92%
12	/	Cs_2CO_3 (1.1)	DMSO	110	0.5	27%
13	/	Cs_2CO_3 (1.1)	PhCl	110	0.5	48%
14	/	Cs_2CO_3 (1.1)	DMF	110	0.5	66%
15	/	Cs_2CO_3 (1.1)	CH_3CN	100	0.5	98%
16	/	Cs_2CO_3 (1.1)	CH_3CN	80	0.5	86%
17	/	Cs_2CO_3 (0.2)	CH_3CN	100	0.5	16%
18	/	/	CH_3CN	100	0.5	0

[a]Reaction conditions: **1a** (0.25 mmol), **2a** (0.5 mmol), oxidant (equiv), additive (equiv), solvent (2 mL), time, air. [b]Isolated yield.

Having found the optimal reaction conditions, the scope of this interesting reaction was explored using various azobenzenes **1** with diphenylphosphine oxide (**2a**). Gratifyingly, the reaction was tolerant toward a variety of substituted azobenzenes and showed good compatibility with a wide range of functional groups (Scheme 3). Unexpectedly, when azobenzene **1b** having 2-methyl group on the phenyl ring reacted with **2a**, the desired product **3ba** was isolated in 21% yield. Meanwhile, diphenylphosphinic amide **4ba** was obtained in 37% yield, which may be attributed to the hydrolysis of **3ba**. 3- and 4-methyl-substituted azobenzenes were well transformed to the corresponding products in 72% and 85% yields, respectively (**3ca**, **3da**). As for 4-methoxy azobenzene **1ea**, only **4ea** was afforded in 51% yield, and no desired product **3ea** was observed. Azobenzenes possessing halogen moieties on the *para* and *meta* positions furnished the hydrophosphinated products in 44-88% yields (**3fa**, **3ga**, **3ha**, **3ia**, **3ja**). Substrates with electron-withdrawing groups such as $–OCF_3$, -COOEt on the aromatic ring underwent hydrophosphination to give the corresponding products in good yields (**3ka**, **3la**).

Surprisingly, 2,4-disubstituted azobenzene **1ma** only furnished diphenylphosphinic amide **4ma** in 26% yield for 5 h. Overall, azobenzenes with electron-donating and electron-withdrawing groups worked well with diphenylphosphine oxide. When nonaromatic azo compound reacted with diphenylphosphine oxide, no desired product was formed (**3na**).

Scheme 3. Hydrophosphination of Substituted Azoarenes with Diphenylphosphine Oxide[a]

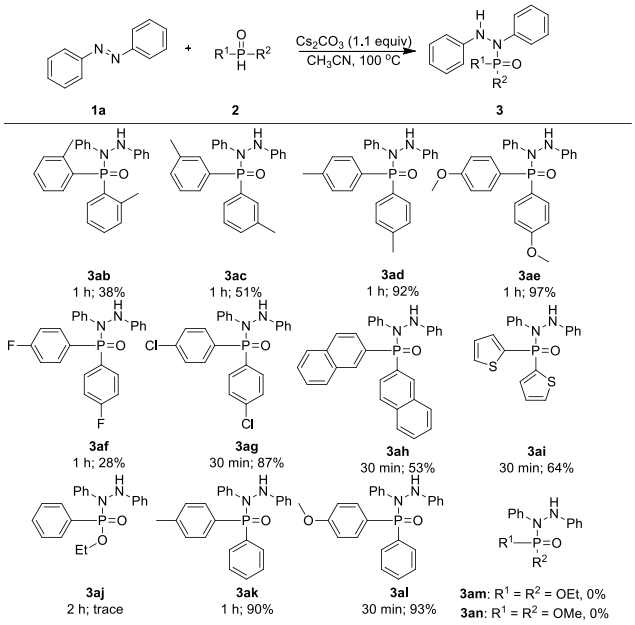


[a]Reaction conditions: **1** (0.25 mmol), **2a** (0.5 mmol), Cs_2CO_3 (1.1 equiv) and CH_3CN (2 mL) at 100 °C for indicated time; Isolated yields. [b]Diisopropyl diazene-1,2-dicarboxylate was tested instead of azoarenes; Run twice at 40 °C and 60 °C, respectively.

Next, the reactions of variously substituted phenylphosphine oxides with **1a** were examined and the results are listed in Scheme 4. Both electron-donating and electron-withdrawing

substituents on the aryl groups were well tolerated in this reaction (**3ab**-**3ag**). Among them, the *o*-methyl substituted substrate **2b** afforded a relatively lower yield of 38% probably due to steric hindrance (**3ab**). Delightedly, di-2-naphthylphosphine oxide could also deliver the corresponding product **3ah** with a good yield of 53%. Moreover, heterocyclic phosphine oxide compound was also well tolerated, affording the desired product **3ai** in 64% yield. Subsequently, phosphine oxides with two different substituents were employed. The unsymmetric phosphine oxides, such as phenyl(*p*-tolyl)phosphine oxide, (4-methoxyphenyl)(phenyl)phosphine oxide worked well to deliver the corresponding products in excellent yields (**3ak**, **3al**). Unfortunately, ethyl phenylphosphinate was less effective in the reaction (**3aj**). When dialkyl phosphites like diethyl phosphonate and dimethyl phosphonate were tested, no desired product was obtained (**3am**, **3an**). Notably, no diphenylphosphinic amides were observed when broadening the scope of substituted phenylphosphine oxides.

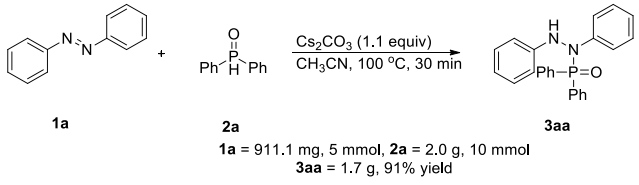
Scheme 4. Reaction of P(O)-H Compounds with Azobenzene[a]



[a]Reaction conditions: **1** (0.25 mmol), **2a** (0.5 mmol), Cs_2CO_3 (1.1 equiv) and CH_3CN (2 mL) at 100 °C for indicated time; Isolated yields.

To test whether the reaction was amenable to scale-up (Scheme 5), we attempted a reaction using 5 mmol of azobenzene (**1a**) and 10 mmol of diphenylphosphine oxide (**2a**). Gratifyingly, **1a** was converted into corresponding product **3aa** in 91% yield.

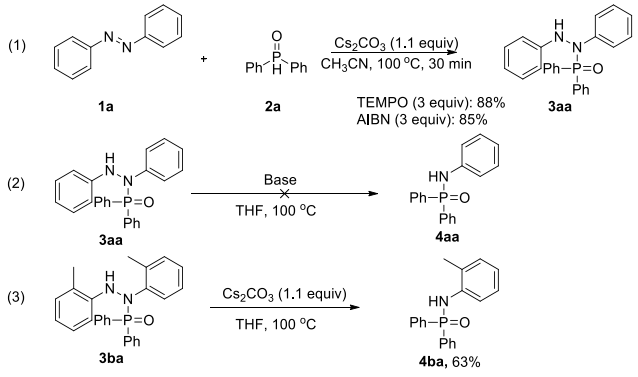
Scheme 5. Synthesis of 3aa on Gram Scale



To establish a possible mechanism of the Cs_2CO_3-promoted hydrophosphination reaction, some control experiments were carried out. First of all, to confirm whether the reaction process was performed *via* a radical way, **1a** and **2a** were subjected to the standard conditions using TEMPO and AIBN as radical scavenger, respectively (Scheme 6, eq 1). To

our surprise, the yield of **3aa** was not largely affected by the addition of these radical-trapping reagents. These results indicate that this transformation *via* radical process is excluded. Then the hydrophosphinated products **3aa** was found to be intact under strong base conditions using Cs_2CO_3, KOH, ^tBuOK respectively (Scheme 6, eq 2), however **3ba** was converted into diphenylphosphinic amide **4ba** in 63% yield under base condition (Scheme 6, eq 3).[12] These results confirm that the formation of diphenylphosphinic amides in some substrates was through the corresponding hydrophosphinated products as the intermediates, and it depends on the stability of the hydrophosphinated products under base condition.

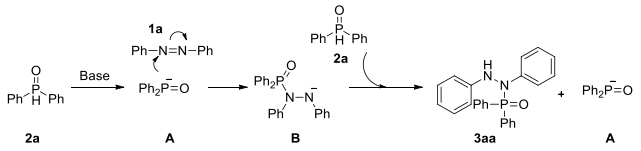
Scheme 6. Investigation of the Reaction Mechanism



Based on the above results and literature reports,[10,13] it is reasonable to propose that the hydrophosphination of aromatic azo compounds with diarylphosphine oxides proceeds *via* a polar reaction mechanism as shown in Scheme 7. First, diphenylphosphine oxide can be deprotonated to generate **A** under basic condition, then the N=N double bond is attacked by **A** to form intermediate **B**. Finally this intermediate **B** abstracts H^+ from **2a** leading to the final product **3aa** and regenerating **A**. It should be noted that some diphenylphosphinic

amides were obtained *via* the hydrolysis process of hydrophosphinated products observed in some substrates.

Scheme 7. Plausible Mechanism



In summary, we have disclosed a convenient and practical method for the construction of N-N-P unit. This newly developed protocol features short reaction time, good functional group tolerance, and a plausible mechanism is proposed. Considering the valuable structure of the products, this concise method to construct N-P bond may have potential applications in the synthesis of related natural compounds and pharmaceuticals.

EXPERIMENTAL SECTION

General Information. ^{1}H NMR , ^{13}C NMR, ^{19}F NMR and ^{31}P NMR spectra were recorded at 400 MHz , 100 MHz, 376 MHz and 162 MHz respectively using tetramethylsilane as an internal reference. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively. Melting points were uncorrected. High-resolution mass spectrometry (HRMS) was performed on an ESI-TOF spectrometer. Chemicals were commercially available and used without purification. Aromatic azo compound substrates were prepared according to the literature procedure.[14] Substituted phenylphosphine oxides were synthesized according to the reported procedure.[15] Chromatography: Column chromatography was performed with silica gel (200-300 mesh ASTM).

General Experimental Procedures and Characterizations.

Azobenzene (0.25 mmol), diphenylphosphine oxide (0.5 mmol, 2 equiv), Cs_2CO_3 (1.1 equiv), dry CH_3CN (2 mL) and a stir bar were added to a sealed tube. After being stirred at 100 ^oC for indicated time, the mixture was evaporated under vacuum. The corresponding products were isolated by silica gel column chromatography with a dichloromethane/ethyl acetate mixture (100:4) as eluent.

N,N',P,P-tetraphenylphosphinic hydrazide (3aa). White solid. mp: 217-219 ^oC. Yield: 98% (94 mg). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.82 (dd, J_1 = 7.6 Hz, J_2 = 12.0 Hz, 4H), 7.48-7.34 (m, 8H), 7.16 (t, J = 7.6 Hz, 2H), 7.07 (t, J = 7.6 Hz, 2H), 6.98 (t, J = 7.6 Hz, 1H), 6.73 (d, J = 8.4 Hz, 2H), 5.92 (s, 1H), 5.30 (s, 1H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 147.1 (d, $J_{C\text{-}P}$ = 1.2 Hz), 143.8 (d, $J_{C\text{-}P}$ = 12.0 Hz), 133.4 (d, $J_{C\text{-}P}$ = 117.7 Hz), 131.9 (d, $J_{C\text{-}P}$ = 8.5 Hz), 128.5 (d, $J_{C\text{-}P}$ = 11.6 Hz), 123.3, 120.9 (d, $J_{C\text{-}P}$ = 2.5 Hz)， 119.0, 113.0. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.87. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{22}N_2OP$ 385.1470; Found 385.1465.

P,P-diphenyl-N,N'-di-o-tolylphosphinic hydrazide (3ba). Colorless oil. Yield: 21% (22 mg). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.88-7.82 (m, 4H), 7.47 (t, J = 7.6 Hz, 2H), 7.41-7.35 (m, 4H), 7.29 (d, J = 7.6 Hz, 2H), 7.09-7.04 (m, 2H), 7.00 (t, J = 4.8 Hz, 2H), 6.88 (d, J = 7.2 Hz, 1H), 6.68 (t, J = 7.2 Hz, 1H), 5.90 (s, 1H), 2,47 (s, 3H), 1.93 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 143.8 (d, $J_{C\text{-}P}$ = 5.3 Hz), 141.1 (d, $J_{C\text{-}P}$ = 5.9 Hz), 135.4 (d, $J_{C\text{-}P}$ = 3.6 Hz), 132.3 (d, $J_{C\text{-}P}$ = 9.3 Hz), 131.9 (d, $J_{C\text{-}P}$ = 2.7 Hz), 130.5 (d, $J_{C\text{-}P}$ = 121.5 Hz), 128.5, 128.2 (d, $J_{C\text{-}P}$ = 12.7 Hz), 127.0, 126.8 (d, $J_{C\text{-}P}$ = 2.1 Hz), 126.4, 126.3, 122.2, 120.2, 114.0, 19.3, 16.9. ^{31}P

NMR ($CDCl_3$, 162 MHz): δ 30.43. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}N_2OP$ 413.1783; Found 413.1790.

P,P-diphenyl-N-(o-tolyl)phosphinic amide (4ba).[16] Pale white solid. mp: 130-132 ^oC. Yield: 37% (29 mg). ^1H NMR (DMSO-d_6, 400 MHz): δ 7.85 (dd, J_1 = 6.8 Hz, J_2 = 11.6 Hz, 4H), 7.55-7.44 (m, 6H), 7.42 (s, 1H), 7.18 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 7.2 Hz, 1H), 6.89 (t, J = 7.2 Hz, 1H), 6.81 (t, J = 7.2 Hz, 1H), 2.39 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 139.4, 133.3 (d, J_{C-P} = 127.3 Hz), 131.7 (d, J_{C-P} = 9.4 Hz), 131.6 (d, J_{C-P} = 2.4 Hz), 130.4, 129.6 (d, J_{C-P} = 8.5 Hz), 128.5 (d, J_{C-P} = 12.2 Hz), 126.0, 122.4, 121.4 (d, J_{C-P} = 4.8 Hz), 18.1. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 16.18. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}NOP$ 308.1204; Found 308.1201.

P,P-diphenyl-N,N'-di-m-tolylphosphinic hydrazide (3ca). White solid. mp: 210-212 ^oC. Yield: 72% (74 mg). ^1H NMR ($CDCl_3$, 400 MHz): δ 7.82 (dd, J_1 = 7.6 Hz, J_2 = 12.4 Hz, 4H), 7.45 (t, J = 6.8 Hz, 2H), 7.39-7.33 (m, 4H), 7.22 (s, 1H), 7.13 (d, J = 8.0 Hz, 1H), 7.02 (t, J = 7.6 Hz, 1H), 6.95 (t, J = 8.0 Hz, 1H), 6.78 (d, J = 7.6 Hz, 1H), 6.56 (t, J = 7.6 Hz, 2H), 6.49 (s, 1H), 5.95 (s, 1H), 2.19 (s, 3H), 2.16 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 146.2 (d, J_{C-P} = 3.4 Hz), 143.9 (d, J_{C-P} = 9.2 Hz), 138.6 (d, J_{C-P} = 8.1 Hz), 132.2 (d, J_{C-P} = 9.6 Hz), 131.9 (d, J_{C-P} = 2.7 Hz), 130.9 (d, J_{C-P} = 128.4 Hz), 128.6 (d, J_{C-P} = 15.4 Hz), 128.3 (d, J_{C-P} = 12.7 Hz), 125.1, 122.2 (d, J_{C-P} = 2.5 Hz), 121.4, 118.5 (d, J_{C-P} = 2.7 Hz), 114.2, 110.8, 21.5, 21.4. ^{31}P NMR ($CDCl_3$, 162 MHz): δ 30.68. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{26}H_{25}N_2NaOP$ 435.1602; Found 435.1625.

P,P-diphenyl-N,N'-di-p-tolylphosphinic hydrazide (3da). White solid. mp: 219-221 ^oC.

Yield: 85% (88 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.25 (d, J = 4.0 Hz, 1H), 7.82 (dd, J_1 = 7.2 Hz, J_2 = 12.0 Hz, 4H), 7.49-7.40 (m, 6H), 7.33-7.27 (m, 2H), 6.91 (d, J = 8.4 Hz, 2H), 6.82 (d, J = 8.0 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 2.10 (s, 3H), 2.07 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 Hz): δ 142.7, 132.9, 132.1, 129.7 (d, J_{C-P} = 23.0 Hz), 128.7 (d, J_{C-P} = 2.0 Hz), 124.9 (d, J_{C-P} = 83.2 Hz), 120.7 (d, J_{C-P} = 5.3 Hz), 116.7, 20.7, 20.6. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 17.76. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{26}N_2OP$ 413.1783; Found 413.1785.

N-(4-methoxyphenyl)-P,P-diphenylphosphinic amide (4ea).[16] White solid. mp: 146-148 ^{o}C. Yield: 51% (41 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.99 (d, J = 11.2 Hz, 1H), 7.82-7.76 (m, 4H), 7.58-7.47 (m, 6H), 7.01 (d, J = 9.2 Hz, 2H), 6.71 (d, J = 9.2 Hz, 2H), 3.62 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 153.7, 134.3 (d, J_{C-P} = 112.3 Hz), 132.5, 131.6 (d, J_{C-P} = 9.9 Hz), 128.5 (d, J_{C-P} = 12.4 Hz), 119.8 (d, J_{C-P} = 6.7 Hz), 114.1, 55.0. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 16.27. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{19}H_{19}NO_2P$ 324.1153; Found 324.1160.

N,N'-bis(4-fluorophenyl)-P,P-diphenylphosphinic hydrazide (3fa). Yellow solid. mp: 199-201 ^{o}C. Yield: 44% (46 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.43 (d, J = 3.2 Hz, 1H), 7.84 (dd, J_1 = 7.2 Hz, J_2 = 12.0 Hz, 4H), 7.54-7.42 (m, 8H), 7.01 (t, J = 8.8 Hz, 2H), 6.88-6.83 (m, 4H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 158.6 (d, J_{C-F} = 257.5 Hz), 156.2 (d, J_{C-F} = 250.9 Hz), 143.2 (d, J_{C-P} = 1.8 Hz), 139.6 (dd, J_{C-F} = 11.2 Hz, J_{C-P} = 2.5 Hz), 131.9 (d, J_{C-P} = 8.7 Hz), 131.3 (d, J_{C-P} = 124.7 Hz), 131.1 (d, J_{C-P} = 9.5 Hz), 128.7 (d, J_{C-P} = 12.4 Hz), 128.4 (m), 124.1 (dd, J_{C-F} = 8.0 Hz, J_{C-P} = 2.1 Hz), 115.2 (dd, J_{C-F} = 22.6 Hz, J_{C-P} = 9.5 Hz),

114.6 (d, J_{C-P} = 7.3 Hz). ^{31}P NMR (DMSO-d_6, 162 MHz): δ 28.14. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -118.74, -125.31. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}F_2N_2OP$ 421.1281; Found 421.1275.

N,N'-bis(4-chlorophenyl)-P,P-diphenylphosphinic hydrazide (3ga). White solid. mp: 204-206 ^{o}C. Yield: 85% (96 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.67 (d, J = 2.4 Hz, 1H), 7.85-7.75 (m, 4H), 7.56-7.78 (m, 8H), 7.23 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 150.9, 147.9 (d, J_{C-P} = 12.0 Hz), 137.1 (d, J_{C-P} = 11.7 Hz), 133.7 (d, J_{C-P} = 4.6 Hz), 132.8 (d, J_{C-P} = 113.1 Hz), 127.8, 127.3 (d, J_{C-P} = 1.8 Hz), 119.6. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 34.03. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}Cl_2N_2OP$ 453.0690; Found 453.0689.

N,N'-bis(4-bromophenyl)-P,P-diphenylphosphinic hydrazide (3ha). White solid. mp: 203-205 ^{o}C. Yield: 78% (106 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.67 (d, J = 2.8 Hz, 1H), 7.79 (br, 4H), 7.61-7.42 (m, 6H), 7.39 (d, J = 9.2 Hz, 2H), 7.23 (d, J = 8.8 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 6.75 (d, J = 8.8 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 145.7 (d, J_{C-P} = 1.1 Hz), 142.6, 131.9 (d, J_{C-P} = 3.4 Hz), 131.8, 131.7 (d, J_{C-P} = 7.8 Hz), 131.3 (d, J_{C-P} = 9.9 Hz), 128.5 (d, J_{C-P} = 4.5 Hz), 127.8 (d, J_{C-P} = 112.4 Hz), 122.4 (d, J_{C-P} = 26.2 Hz), 122.1 (d, J_{C-P} = 2.4 Hz), 117.6, 114.6 (d, J_{C-P} = 43.9 Hz). ^{31}P NMR (DMSO-d_6, 162 MHz): δ 29.31. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}Br_2N_2OP$ 540.9680; Found 540.9675.

N,N'-bis(3-chlorophenyl)-P,P-diphenylphosphinic hydrazide (3ia). White solid. mp: 219-221 ^{o}C. Yield: 88% (99 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.79 (d, J = 2.4 Hz,

1H), 7.86-7.75 (m, 4H), 7.61-7.42 (m, 6H), 7.41 (d, J = 6.4 Hz, 2H), 7.34 (d, J = 9.2 Hz, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.07-6.98 (m, 2H), 6.73-6.64 (m, 2H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 148.3, 145.3 (d, $J_{C\text{-}P}$ = 12.1 Hz), 133.2 (d, $J_{C\text{-}P}$ = 24.3 Hz), 132.1 (d, $J_{C\text{-}P}$ = 25.4 Hz), 131.9, 131.1 (d, $J_{C\text{-}P}$ = 154.5 Hz), 128.9 (d, $J_{C\text{-}P}$ = 12.4 Hz), 128.1 (d, $J_{C\text{-}P}$ = 12.1 Hz), 123.1, 119.4 (d, $J_{C\text{-}P}$ = 2.5 Hz), 118.9, 118.5 (d, $J_{C\text{-}P}$ = 2.1 Hz), 112.0, 111.3. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 29.89. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}Cl_2N_2OP$ 453.0690; Found 453.0692.

N,N'-bis(3-bromophenyl)-P,P-diphenylphosphinic hydrazide (3ja). White solid. mp: 220-222 ^{o}C. Yield: 62% (84 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.76 (d, J = 1.6 Hz, 1H), 7.85-7.74 (m, 4H), 7.63-7.35 (m, 8H), 7.17-7.11 (m, 2H), 6.98 (t, J = 8.0 Hz, 1H), 6.85 (s, 1H), 6.78 (d, J = 8.0 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 148.4, 145.4 (d, $J_{C\text{-}P}$ = 12.1 Hz), 132.2 (d, $J_{C\text{-}P}$ = 26.5 Hz), 131.8 (d, $J_{C\text{-}P}$ = 3.3 Hz), 131.7 (d, $J_{C\text{-}P}$ = 2.6 Hz), 130.7, 129.7 (d, $J_{C\text{-}P}$ = 166.6 Hz), 128.8, 128.1 (d, $J_{C\text{-}P}$ = 12.7 Hz), 126.0, 122.3 (d, $J_{C\text{-}P}$ = 2.3 Hz), 121.9, 121.6 (d, $J_{C\text{-}P}$ = 15.6 Hz), 118.9 (d, $J_{C\text{-}P}$ = 2.0 Hz), 114.9, 111.6. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 29.85. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}Br_2N_2OP$ 540.9680; Found 540.9680.

Diethyl 4,4'-(1-(diphenylphosphoryl)hydrazine-1,2-diyl)dibenzoate (3ka). White solid. mp: 234-236 ^{o}C. Yield: 92% (122 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 9.29 (s, 1H), 7.87 (dd, J_1 = 8.4 Hz, J_2 = 12.4 Hz, 2H), 7.80-7.70 (m, 6H), 7.65-7.59 (m, 4H), 7.46 (d, J = 9.2 Hz, 2H), 7.41-7.33 (m, 2H), 6.71 (d, J = 8.8 Hz, 2H), 4.24-4.15 (m, 4H), 1.23 (t, J = 6.8 Hz, 6H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 165.2 (d, $J_{C\text{-}P}$ = 28.1 Hz), 150.9, 148.6 (d, $J_{C\text{-}P}$ = 12.2 Hz),

132.4 (d, J_{C-P} = 2.9 Hz), 131.9 (d, J_{C-P} = 10.1 Hz), 131.8, 131.7 (d, J_{C-P} = 6.5 Hz), 130.6, 130.3, 130.1 (d, J_{C-P} = 5.2 Hz), 129.0 (d, J_{C-P} = 5.0 Hz), 128.8 (d, J_{C-P} = 5.2 Hz), 128.0 (d, J_{C-P} = 13.0 Hz), 127.1 (d, J_{C-P} = 162.5 Hz), 117.8 (d, J_{C-P} = 1.9 Hz), 111.2, 60.3, 59.9, 14.2, 14.1. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 31.06. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{30}H_{29}N_2NaO_5P$ 551.1712; Found 551.1707.

P,P-diphenyl-N,N'-bis(4-(trifluoromethoxy)phenyl)phosphinic hydrazide (3la). Yellow solid. mp: 174-176 ^{o}C. Yield: 72% (99 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.79 (d, J = 2.0 Hz, 1H), 7.87-7.75 (m, 4H), 7.59-7.48 (m, 6H), 7.47-7.37 (m, 2H), 7.22 (d, J = 8.8 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 6.78 (d, J = 9.2 Hz, 2H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 145.9, 143.8 (d, J_{C-P} = 1.6 Hz), 142.8 (d, J_{C-P} = 12.1 Hz), 140.7 (d, J_{C-P} = 1.4 Hz), 131.8 (d, J_{C-P} = 9.7 Hz), 131.6 (d, J_{C-P} = 116.2 Hz), 128.7 (d, J_{C-P} = 14.2 Hz), 128.0 (d, J_{C-F} = 11.4 Hz), 124.9, 120.3 (q, J_{C-F} = 253.0 Hz), 120.1 (q, J_{C-F} = 254.2 Hz), 118.7 (d, J_{C-P} = 16.9 Hz) 113.4. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 29.61. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -57.08, -57.29. HRMS (ESI-TOF) m/z: $[M - H]^-$ Calcd for $C_{26}H_{18}F_6N_2O_3P$ 551.0959; Found 551.0953.

N-(2,4-dimethylphenyl)-P,P-diphenylphosphinic amide (4ma). Orange solid. mp: 144-146 ^{o}C. Yield: 26% (21 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 7.84 (dd, J_1 = 6.4 Hz, J_2 = 11.6 Hz, 4H), 7.51-7.44 (m, 6H), 7.34 (d, J = 8.8 Hz, 1H), 7.09 (d, J = 8.0 Hz, 1H), 6.93 (s, 1H), 6.69 (d, J = 8.0 Hz, 1H) 2.35 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 136.6, 133.4 (d, J_{C-P} = 127.4 Hz), 131.8 (d, J_{C-P} = 9.3 Hz), 131.5 (d, J_{C-P} = 2.5 Hz), 131.3, 131.0, 129.8 (d, J_{C-P} = 8.4 Hz), 128.5 (d, J_{C-P} = 12.2 Hz), 126.4, 121.7 (d, J_{C-P} = 4.5 Hz), 20.2, 18.0.

^{31}P NMR (DMSO-d_6, 162 MHz): δ 16.06. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{20}H_{20}NNaOP$ 344.1180; Found 344.1177.

N,N'-diphenyl-P,P-di-o-tolylphosphinic hydrazide (3ab). White solid. mp: 195-197 ^{o}C. Yield: 38% (39 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.39 (s, 1H), 7.70-7.43 (m, 6H), 7.29 (br, 3H), 7.19 (t, J = 7.6 Hz, 2H), 7.07-6.93 (m, 4H), 6.66 (d, J = 8.0 Hz, 2H), 6.56 (t, J = 7.2 Hz, 1H), 2.37 (s, 3H), 2.23 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 146.7 (d, $J_{C\text{-}P}$ = 1.3 Hz), 144.8 (d, $J_{C\text{-}P}$ = 11.8 Hz), 141.9, 132.5 (d, $J_{C\text{-}P}$ = 139.2 Hz), 131.1 (d, $J_{C\text{-}P}$ = 11.7 Hz), 128.4 (d, $J_{C\text{-}P}$ = 18.4 Hz), 125.4 (d, $J_{C\text{-}P}$ = 16.8 Hz), 124.7, 122.5, 119.2 (d, $J_{C\text{-}P}$ = 1.6 Hz), 118.8, 112.5, 21.4, 20.9. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 34.84. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{26}H_{26}N_2OP$ 413.1783; Found 413.1789.

N,N'-diphenyl-P,P-di-m-tolylphosphinic hydrazide (3ac). White solid. mp: 205-207 ^{o}C. Yield: 51% (53 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.44 (d, J = 3.6 Hz, 1H), 7.71-7.56 (m, 4H), 7.40 (d, J = 8.8 Hz, 2H), 7.30 (br, 4H), 7.14 (t, J = 7.6 Hz, 2H), 7.01 (t, J = 8.8 Hz, 2H), 6.88 (t, J = 7.6 Hz, 1H), 6.78 (d, J = 8.8 Hz, 2H), 6.60 (t, J = 7.6 Hz, 1H), 2.27 (s, 6H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 147.1 (d, $J_{C\text{-}P}$ = 0.9 Hz), 143.9 (d, $J_{C\text{-}P}$ = 11.9 Hz), 137.3, 132.2 (d, $J_{C\text{-}P}$ = 4.9 Hz), 131.2 (d, $J_{C\text{-}P}$ = 120.9 Hz), 129.0 (d, $J_{C\text{-}P}$ = 9.3 Hz), 128.4 (d, $J_{C\text{-}P}$ = 8.6 Hz), 123.1, 120.7 (d, $J_{C\text{-}P}$ = 2.5 Hz), 118.9, 112.9, 20.9. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 28.78. HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{26}H_{25}N_2NaOP$ 435.1602; Found 435.1595.

N,N'-diphenyl-P,P-di-p-tolylphosphinic hydrazide (3ad). White solid. mp: 215-217 ^{o}C. Yield: 92% (94 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.43 (d, J = 3.6 Hz, 1H), 7.68 (t, J =

8.0 Hz, 4H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.23 (br, 4H), 7.12 (t, *J* = 7.6 Hz, 2H), 7.01 (t, *J* = 7.6 Hz, 2H), 6.88 (t, *J* = 7.6 Hz, 1H), 6.80 (d, *J* = 7.6 Hz, 2H), 6.60 (t, *J* = 7.2 Hz, 1H), 2.28 (s, 6H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 147.2 (d, $J_{C\text{-}P}$ = 1.1 Hz), 143.9 (d, $J_{C\text{-}P}$ = 11.8 Hz), 131.8 (d, $J_{C\text{-}P}$ = 9.1 Hz), 128.5 (d, $J_{C\text{-}P}$ =17.0 Hz), 123.1, 121.9 (d, $J_{C\text{-}P}$ = 127.4 Hz), 120.8, 118.8, 112.9, 20.9. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 29.01. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{26}H_{26}N_2OP$ 413.1783; Found 413.1783.

P,P-bis(4-methoxyphenyl)-N,N'-diphenylphosphinic hydrazide (3ae). White solid. mp: 202-204 ^{o}C. Yield: 97% (107 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.41 (d, *J* = 2.8 Hz, 1H), 7.70 (t, *J* = 8.8 Hz, 4H), 7.38 (d, *J* = 8.4 Hz, 2H), 7.12 (t, *J* = 7.6 Hz, 2H), 7.03-6.96 (m, 6H), 6.87 (t, *J* = 7.2 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 2H), 6.59 (t, *J* = 7.6 Hz, 1H), 3.75 (s, 6H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 161.7 (d, $J_{C\text{-}P}$ = 1.7 Hz), 147.3 (d, $J_{C\text{-}P}$ = 1.0 Hz), 144.1 (d, $J_{C\text{-}P}$ = 11.9 Hz), 133.7 (d, $J_{C\text{-}P}$ =10.7 Hz), 128.4 (d, $J_{C\text{-}P}$ = 20.2 Hz), 123.9 (d, $J_{C\text{-}P}$ = 2.1 Hz), 123.2 (d, $J_{C\text{-}P}$ = 132.2 Hz), 122.6, 120.6 (d, $J_{C\text{-}P}$ = 2.5 Hz), 118.7, 113.4 (d, $J_{C\text{-}P}$ = 34.0 Hz), 112.8, 55.2. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 28.92. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{26}H_{26}N_2O_3P$ 445.1681; Found 445.1686.

P,P-bis(4-fluorophenyl)-N,N'-diphenylphosphinic hydrazide (3af). White solid. mp: 203-205 ^{o}C. Yield: 28% (30 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.51 (d, *J* = 3.2 Hz, 1H), 7.88 (br, 4H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.30 (br, 4H), 7.16 (t, *J* = 7.6 Hz, 2H), 7.03 (t, *J* = 8.0 Hz, 2H), 6.92 (t, *J* = 7.2 Hz, 1H), 6.79 (d, *J* = 7.6 Hz, 2H), 6.62 (t, *J* = 7.2 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 164.2 (d, $J_{C\text{-}F}$ = 254.6 Hz), 162.9, 146.9 (d, $J_{C\text{-}P}$ = 1.3 Hz), 143.4 (d, $J_{C\text{-}P}$ = 12.1 Hz), 134.8 (d, $J_{C\text{-}P}$ = 9.5 Hz), 134.7, 128.6 (d, $J_{C\text{-}P}$ = 7.9 Hz), 123.5,

120.9, 120.1 (d, J_{C-P} = 184.5 Hz), 115.6 (m), 112.9. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 26.65. ^{19}F NMR (DMSO-d_6, 376 MHz): δ -107.29, -107.64. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{20}F_2N_2OP$ 421.1281; Found 421.1277.

P,P-bis(4-chlorophenyl)-N,N'-diphenylphosphinic hydrazide (3ag). White solid. mp: 202-204 ^{o}C. Yield: 87% (98 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.48 (d, J = 3.6 Hz, 1H), 7.85-7.79 (m, 4H), 7.53-7.39 (m, 6H), 7.13 (t, J = 7.6 Hz, 2H), 7.01 (t, J = 8.0 Hz, 2H), 6.89 (t, J = 7.6 Hz, 1H), 6.79 (d, J = 8.0 Hz, 2H), 6.60 (t, J = 7.2 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 147.1 (d, J_{C-P} = 1.3 Hz), 143.7 (d, J_{C-P} = 12.0 Hz), 133.4, 132.6 (d, J_{C-P} = 139.4 Hz), 131.8, 131.2 (d, J_{C-P} =9.9 Hz), 128.7 (d, J_{C-P} = 36.0 Hz), 123.2, 120.9 (d, J_{C-P} = 2.6 Hz), 118.9, 112.9. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 28.34. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{24}H_{20}Cl_2N_2OP$ 453.0690; Found 453.0686.

P,P-di(naphthalen-2-yl)-N,N'-diphenylphosphinic hydrazide (3ah). White solid. mp: 211-213 ^{o}C. Yield: 53% (64 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.64 (d, J = 3.6 Hz, 1H), 8.56 (br, 2H), 8.02 (d, J = 7.6 Hz, 2H), 7.91 (d, J = 8.0 Hz, 6H), 7.63-7.56 (m, 4H), 7.50 (d, J = 8.4 Hz, 2H), 7.13 (t, J = 7.6 Hz, 2H), 7.01 (t, J = 8.4 Hz, 2H), 6.90-6.85 (m, 3H), 6.59 (t, J = 7.2 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 147.1, 143.7 (d, J_{C-P} = 11.9 Hz), 134.0 (d, J_{C-P} = 3.9 Hz), 128.8, 128.6 (d, J_{C-P} = 8.6 Hz), 127.5 (d, J_{C-P} = 137.3 Hz), 126.9, 123.4, 121.0, 119.0, 113.1. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 28.03. HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{32}H_{26}N_2OP$ 485.1783; Found 485.1780.

N,N'-diphenyl-P,P-di(thiophen-2-yl)phosphinic hydrazide (3ai). White solid. mp: 185-187 ^{o}C. Yield: 64% (63 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.45 (d, J = 0.8 Hz, 1H), 7.98

(br, 2H), 7.66 (q, J = 4.0 Hz, 2H), 7.48 (d, J = 8.4 Hz, 2H), 7.21 (t, J = 7.6 Hz, 4H), 7.07-6.98 (m, 3H), 6.80 (d, J = 8.6 Hz, 2H), 6.65 (t, J = 7.2 Hz, 1H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 146.8 (d, $J_{C\text{-}P}$ = 3.8 Hz), 142.8 (d, $J_{C\text{-}P}$ = 12.5 Hz), 128.6 (d, $J_{C\text{-}P}$ = 7.7 Hz), 123.9, 121.3, 119.4 (d, $J_{C\text{-}P}$ = 180.4 Hz), 113.4. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 15.00. HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{17}N_2NaOPS_2$ 419.0418; Found 419.0415.

N,N',P-triphenyl-P-(p-tolyl)phosphinic hydrazide (3ak). White solid. mp: 200-202 ^{o}C. Yield: 90% (89 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.46 (d, J = 3.6 Hz, 1H), 7.79 (t, J = 8.0 Hz, 2H), 7.71 (t, J = 8.0 Hz, 2H), 7.46-7.38 (m, 5H), 7.25 (br, 2H), 7.13 (t, J = 7.6 Hz, 2H), 7.01 (t, J = 8.4 Hz, 2H), 6.88 (t, J = 7.2 Hz, 1H), 6.79 (d, J = 8.0 Hz, 2H), 6.60 (t, J = 7.2 Hz, 1H), 2.29 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 147.2 (d, $J_{C\text{-}P}$ = 1.1 Hz), 143.8 (d, $J_{C\text{-}P}$ = 11.9 Hz), 131.8 (m), 128.5 (d, $J_{C\text{-}P}$ = 14.3 Hz), 123.1, 120.8, 118.9, 112.9, 21.00. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 28.75. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}N_2OP$ 399.1626; Found 399.1634.

P-(4-methoxyphenyl)-N,N',P-triphenylphosphinic hydrazide (3al). White solid. mp: 176-178 ^{o}C. Yield: 93% (96 mg). ^{1}H NMR (DMSO-d_6, 400 MHz): δ 8.45 (d, J = 3.2 Hz, 1H), 7.81-7.71 (m, 5H), 7.39 (d, J = 8.4 Hz, 4H), 7.16-7.10 (m, 2H), 7.01 (t, J = 8.4 Hz, 4H), 6.88 (t, J = 7.2 Hz, 1H), 6.79 (d, J = 7.6 Hz, 2H), 6.60 (t, J = 7.2 Hz, 1H), 3.75 (s, 3H). ^{13}C NMR (DMSO-d_6, 100 Hz): δ 162.3, 147.2 (d, $J_{C\text{-}P}$ = 0.9 Hz), 133.8 (d, $J_{C\text{-}P}$ = 29.8 Hz), 131.5 (d, $J_{C\text{-}P}$ = 50.0 Hz), 128.4 (d, $J_{C\text{-}P}$ = 15.9 Hz), 123.1, 121.9 (d, $J_{C\text{-}P}$ = 129.5 Hz), 120.7, 118.8, 114.6, 112.9, 55.2. ^{31}P NMR (DMSO-d_6, 162 MHz): δ 29.51. HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{24}N_2O_2P$ 415.1575; Found 415.1565.

Supporting Information

This Supporting Information is available free of charge on the ACS Publications websites at http://pubs.acs.org. Copies of ^{1}H, ^{13}C, ^{31}P, and ^{19}F NMR spectra for products (PDF).

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Notes

The authors declare no competing financial interest.

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References

(1) (a) Murphy, P. J. *Organophosphorus Reagents*; Ed.; Oxford University Press: Oxford, U.K., **2004.** (b) Tang, W.; Zhang, X. *Chem. Rev.* **2003**, *103*, 3029. (c) Baumgartner, T.; Réau, R. *Chem. Rev*. **2006**, *106*, 4681.

(2) For selected examples of C-P bond formation, see: (a) Zheng, H. L.; Gu, Z. X.; Li, Z. Y.; Pan, C. D.; Li, W. P.; Hu, H. W.; Zhu, C. J. *J. Org. Chem.* **2016**, *81*, 2122. (b) Hong, G.; Mao, D.; Wu, S. Y.; Wang, L. M. *J. Org. Chem.* **2014**, *79*, 10629. (c) Yang, J.; Xiao, J.; Chen, T. Q.; Han, L. B. *J. Org. Chem.***2016**, *81*, 3911. (d) Zhou, Y.; Rao, C. Q.; Mai, S. Y.; Song, Q.

L. *J. Org. Chem.* **2016**, *81*, 2027. (e) Hu, G.; Chen, W.; Ma, D.; Zhang, Y.; Xu, P.; Gao, Y.; Zhao, Y. *J. Org. Chem.* **2016**, *81*, 1704. (f) Peng, P.; Peng, L.; Wang, G. Y.; Wang, F. Y.; Luo, Y.; Lei. A. W. *Org. Chem. Front.* **2016**, *3*, 749.

(3) (a) Zhu, Y. Y.; Chen, T. Q.; Li, S.; Shimada. S.; Han, L. B. *J. Am. Chem. Soc*. **2016**, *138*, 5825. (b) Xu, J.; Zhang, L.; Li, X.; Gao, Y.; Tang, G.; Zhao, Y. *Org. Lett.* **2016**, *18*, 1266. (c) Bi, X.; Li, J.; Meng, F.; Wang, H.; Xiao, J. *Tetrahedron* **2016**, *72*, 706. (d) Wang, J.; Huang, X.; Ni, Z.; Wang, S.; Wu, J.; Pan, Y. *Green Chem*. **2015**, *17*, 314.

(4) (a) Zhu, R.; Pan, C.; Gu, Z. *Org. Lett.* **2015**, *17*, 5862. (b) Kiss, N. Z.; Keglevich, G. *Curr. Org. Chem*. **2014**, *18*, 2673. (c) Popovici, C.; Ona-Burgos, P.; Fernandez, I.; Roces, L.; Garcia-Granda, S.; Iglesias, M. J.; Ortiz, F. L. *Org. Lett.* **2010**, *12*, 428. (d) Vishwanatha, B. T. M.; Panguluri, N. R.; Sureshbabu, V. V. *Synthesis* **2013**, *45*, 1569. (e) Jablonkai, E.; Henyecz, R.; Milen, M.; Koti, J.; Keglevich, G. *Tetrahedron* **2014**, *70*, 8280.

(5) (a) Bafana, A.; Devi, S. S.; Chakrabarti, T. *Environ. Rev.* **2011**, *19*, 350. (b) Gainsford, G. J.; Bhuiyan, M. D. H.; Asselberghs, I.; Clays, K. *Dyes Pigm.* **2012**, *95*, 455. (c) Harvey, A. J.; Abell, A. D. *Tetrahedron* **2000**, *56*, 9763. (d) Banghart, M. R.; Mourot, A.; Fortin, D. L.; Yao, J. Z.; Kramer,R. H.; Trauner, D. *Angew. Chem., Int. Ed.* **2009**, *48*, 9097. (e) Puntoriero, F.; Ceroni, P.; Balzani, V.; Bergamini, G.; Voegtle, F. *J. Am. Chem. Soc.* **2007**, *129*, 10714.

(6) Selected examples: (a) Nguyen, T. H. L.; Gigant, N.; Delarue-Cochin S.; Joseph, D. *J. Org. Chem.* **2016**, *81*, 1850. (b) Jeong, T.; Han, S. H.; Han, S.; Sharma, S.; Park, J.; Lee, J. S.; Kwak, J. H.; Jung, W. H.; Kim, I. S. *Org. Lett*. **2016**, *18*, 232. (c) Xia, C.; Wei, Z.; Shen,

C.; Xu, J.; Yang, Y.; Su, W.; Zhang, P. *RSC Adv*. **2015**, *5*, 52588. (d) Khatun, N.; Modi, A.; Ali, W.; Patel, B. K. *J. Org. Chem.* **2015**, *80*, 9662.

(7) Yan, X.; Yi, X.; Xi, C. *Org. Chem. Front*. **2014**, *1*, 657.

(8) Yi, X.; Xi, C. *Org. Lett*. **2015**, *17*, 5836.

(9) (a) Hong, G.; Mao, D.; Zhu, X.; Wu, S.; Wang, L. *Org. Chem. Front.* **2015**, *2*, 985. (b) Hong, G.; Wu, S.; Zhu, X.; Mao, D.; Wang, L. *Tetrahedron* **2016**, *72*,436. (c) Hong, G.; Aruma, A. N.; Zhu, X.; Wu, S.; Wang, L. *Synthesis* **2016**, *48*, 1147.

(10) (a) Linke, K. H.; Brandt, W. *Z. anorg. allg. Chem.***1977**, *433*, 119. (b) Chong, C. C.; Hirao, H.; Kinjo, R. *Angew. Chem. Int. Ed.* **2014**, *53*, 3342.

(11) (a) Li, Y.-M.; Sun, M.; Wang, H.-L.; Tian, Q.-P.; Yang, S. D. *Angew. Chem., Int. Ed.* **2013**, *52*, 3972. (b) Zhang, B.; Daniliuc, C. G.; Studer, A. *Org. Lett.* **2014**, *16*, 250. (c) Yoo, W.-J.; Kobayashi, S. *Green Chem.* **2013**, *15*, 1844. (d) Xuan, J.; Zeng, T.-T.; Chen, J.-R.; Lu, L.-Q.; Xiao, W.-J. *Chem. Eur. J.* **2015**, *21*, 4962. (e) Xiang, C.; Bian, Y.; Mao, X.; Huang, Z. *J. Org. Chem.* **2012**, *77*, 7706. (f) Zhang, G.-Y.; Li, C.-K.; Li, D.-P.; Zeng, R.-S.; Shoberu, A.; Zou, J.-P. *Tetrahedron* **2016**, *72*, 2972.

(12) The hydrophosphinated products can well dissolve in THF, so THF was used as solvent in these two control experiments instead of CH_3CN.

(13) (a) Camp, D.; Healy, P. C.; Jenkins, I. D.; Skelton, B. W.; White, A. H. *J. Chem. Soc., Perkin Trans. 1*, **1991**, 1323. (b) Morrison, D. C. *J. Org. Chem.* **1958**, *23*, 1072.

(14) Zhang, C.; Jiao, N. *Angew. Chem.* **2010**, *122*, 6310; *Angew. Chem. Int. Ed.* **2010**, *49*, 6174.

(15) Ke, J.; Tang, Y.; Yi, H.; Li, Y.; Cheng, Y.; Liu, C.; Lei, A. *Angew. Chem. Int. Ed.* **2015**, *54*, 6604.

(16) Li, J.; Zhang, S. L.; Tao, C. Z.; Fu, Y.; Guo, Q. X. *Chin. Chem. Lett.* **2007**, *18*, 1033.

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