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Annulation of Diaryl(aryl)phosphenes and Cyclic Imines to Access Benzo-δ-phospholactams

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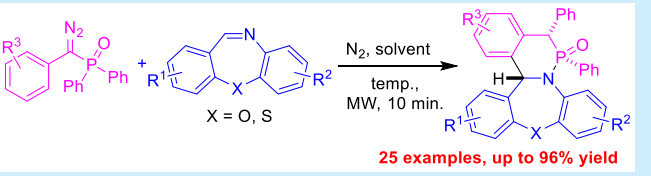
ABSTRACT: Microwave-assisted annulation of cyclic imine dibenzo[*b*,*f*][1,4]oxazepines and diaryl(aryl)phosphenes generated from diazo(aryl)methyl(diaryl)phosphine oxides through the Wolff rearrangement accesses pentacyclic benzo-δ-phospholactams, 4b,16-dihydrodibenzo[*b*,*f*]benzo[4,5][1,2]azaphosphinino[1,6-*d*]-[1,4]oxazepine 15-oxides, in good yields.



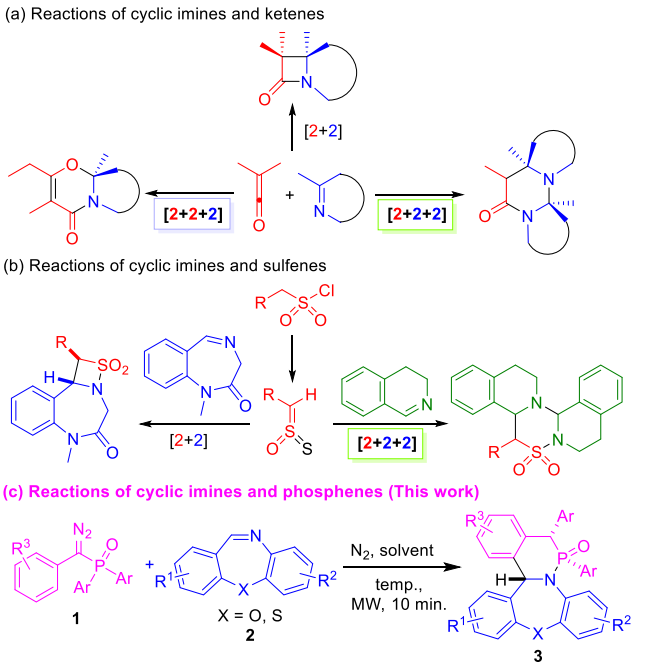
The reaction of ketenes and imines generally gives rise to *β*-lactams whether the ketenes are generated from the organic base elimination of acyl chlorides or the Wolff rearrangement of *α*-diazomethylketones and linear or cyclic imines. The reaction is well-known as the Staudinger cycloaddition.[1] However, in some cases, different six-membered heterocyclic annulated products are generated from two ketenes and one imine or one ketene and two imines, respectively, showing diverse annuloselectivities (Scheme 1a).[2]

For the reaction of sulfenes and imines, sulfenes are generated from alkanesulfonyl chlorides in the presence of weak organic bases and react with various non-*N*-aryl imines and very limited cyclic imines, affording *β*-sultams in most cases[3] but different six-membered thiaheterocyclic annulated products in some cases as well. Similarly, the six-membered thiaheterocycles are generated from two sulfenes and one imine or one sulfene and two imines, showing also various annuloselectivities (Scheme 1b).[4]

To continuously explore the reactivity and annuloselectivity of different ketene analogues and imines, herein, we investigated the annulation of cyclic imine dibenzo[*b*,*f*][1,4]-oxazepines and diaryl(aryl)phosphenes generated from (diazo-(aryl)methyl)diarylphosphine oxides. Obviously different from the reactions of cyclic imines with ketenes and sulfenes, the reaction of diaryl(aryl)phosphenes and cyclic imines generated benzo-δ-phospholactam derivatives, 4-hydrobenzo[*d*][1,2]-azaphosphinine 3-oxide derivatives, in which the aryl groups in diaryl(aryl)phosphenes participated in the annulation (Scheme 1c). Benzo-δ-phospholactam derivatives are important compounds and have mainly been prepared previously through the palladium-catalyzed C−H arylation,[5] the cobalt-catalyzed functionalizations of a phosphinamide sp^2 C−H bond with terminal alkynes or allenes,[6] the cyclization of phenyl phosphite with 2-ethynylanilines,[7] and radical oxidative intramolecular aryl C−H phosphinamidation.[8]

We initially selected the reaction of (diazo(phenyl)methyl)-diphenylphosphine oxide (**1a**) and dibenzo[*b*,*f*][1,4]oxazepine

Scheme 1. Reactivities and Annuloselectivities of Cyclic Imines with Ketenes, Sulfenes, and Phosphenes



(**2a**) as a model reaction for the reaction condition optimization (Table 1). First, a solution of **1a** and **2a** in different representative anhydrous solvents, including DCE, MeCN, toluene, and chlorobenzene, was heated at 130 °C in a

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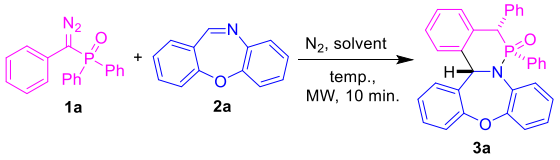
Org. Lett. XXXX, XXX, XXX−XXX

Table 1. Optimization on the Reaction Conditions[a]



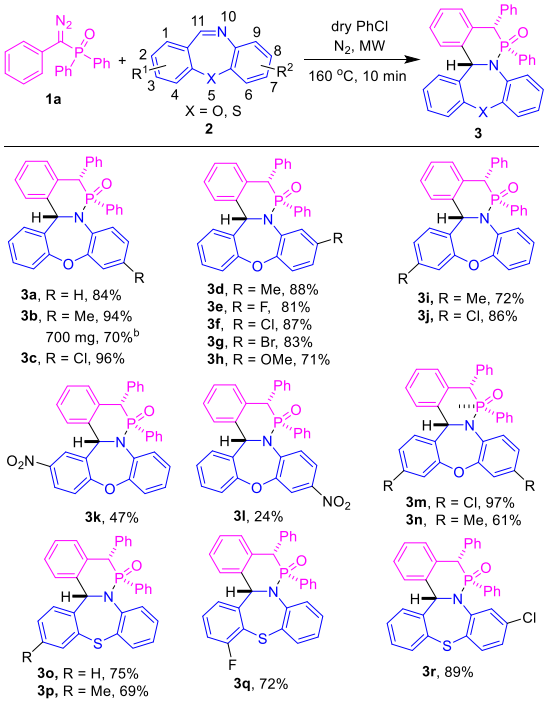
entry	1a (mmol)	2a (mmol)	solvent	temp. (°C)	yield (%)[b]
1	0.20	0.40	DCE	130	45
2	0.20	0.40	MeCN	130	31
3	0.20	0.40	PhMe	130	50
4	0.20	0.40	PhCl	130	54
5	0.20	0.40	PhCl	140	68
6	0.20	0.40	PhCl	150	68
7	**0.20**	**0.40**	**PhCl**	**160**	**73**
8	0.20	0.40	PhCl	170	56
9	**0.40**	**0.20**	**PhCl**	**160**	**86 (84[c])**
10	0.30	0.20	PhCl	160	77 (72[c])
11	0.24	0.20	PhCl	160	74

[a]Reaction conditions: **1** and **2** in 3 mL of anhydrous solvent in a capped microwave reaction tube filled with nitrogen were heated under microwave irradiation for 10 min. [b]Yield based on the ^{1}H NMR analysis with 1,3,5-trimethoxybenzene as an internal standard. [c]Yield of the isolated product in parentheses.

capped microwave reaction tube filled with nitrogen under microwave irradiation for 10 min, affording phospholactam **3a** in a higher yield in chlorobenzene (entries 1−4). The reaction was further optimized in chlorobenzene at different temperatures (entries 4−8). It can be seen that the yield improved along with the increase of temperature from 130 to 160 °C and decreased at 170 °C. A higher yield of 73% was obtained at 160 °C (entry 7). The molar ratio of **1a**:**2a** was further evaluated in chlorobenzene at 160 °C. The target product **3a** was obtained in 84% yield (86% NMR yield) when the diazo compound **1a** and imine **2a** were 0.40 and 0.20 mmol, respectively (entry 9). No *β*-phospholactam was observed in all tests.[9] Therefore, the optimum conditions were determined as follows: a solution of **1a** (0.40 mmol) and **2a** (0.20 mmol) in anhydrous chlorobenzene (3 mL) was heated at 160 °C in a capped microwave reaction tube filled with nitrogen under microwave irradiation for 10 min.

Under the optimal conditions, we first investigated the general scope of cyclic imines **2** (Scheme 2). 7-Methyl- and 7-chlorodibenzo[*b*,*f*][1,4]oxazepines (**2b** and **2c**) yielded the corresponding products **3b** and **3c** in excellent yields (94% and 96%). 8-Substituted dibenzo[*b*,*f*][1,4]oxazepines **2d**−**2h** also gave rise to the corresponding desired products **3d**−**3h** in good yields varied from 71% to 88% whether the substituents were electron-donating or weak withdrawing halo groups. 4-Substituted dibenzo[*b*,*f*][1,4]oxazepines **2i** and **2j** worked as well, affording the desired products **3i** and **3j** in the yields of 72% for Me and 86% for Cl. However, strong electron-withdrawing 2- and 7-nitrodibenzo[*b*,*f*][1,4]oxazepines (**2k** and **2l**) generated their products **3k** and **3l** in low yields of 47% and 24%, respectively. The influence of 7-nitro is stronger than that of the 2-nitro group on the reaction yield. Two 3,7-disubstituted dibenzo[*b*,*f*][1,4]oxazepines **2m** and **2n** were tested, giving the corresponding products **3m** in an excellent yield of 97% for the chloro substituent and **3n** in a satisfactory yield of 61% for the methyl group. Furthermore, we also explored the reactivity of the sulfur analogues of dibenzo[*b*,*f*]-[1,4]oxazepines. Both dibenzo[*b*,*f*][1,4]thiazepine (**3o**) itself

Scheme 2. Scopes of Cyclic Imines 2[a]



[a]Reaction conditions: **1a** (0.4 mmol) and **2** (0.2 mmol) in 3 mL of anhydrous PhCl were heated at 160 °C in a capped microwave reaction tube filled with nitrogen under microwave irradiation for 10 min (200 W), yield of the isolated product. [b]Large-scale preparation.

and its derivatives, 3-methyl, 4-fluoro, and 8-chlorodibenzo-[*b*,*f*][1,4]thiazepines, **2p**−**2r**, produced the desired products **3o**−**3r** in satisfactory to good yields. As a result, imines **2** with electron-donating groups (methyl and methoxy) and weak electron-withdrawing halo groups can give good yields, but for those with strong electron-withdrawing groups (such as nitro), the yields significantly decreased due to the reduced nucleophilicity of the imines.

Because there are only limited protons in the products **3** and ^{31}P−^{13}C spin−spin coupling splitting, resulting in their more complex ^{13}C NMR spectra, to verify the structures of products **3**, pure compound **3c** crystallized from ethyl acetate was further grown as a single crystal from chloroform and determined by XRD single-crystal analysis (Figure 1). The results indicate that two hydrogens and the oxygen of the P═O group in the *δ*-phospholactam ring are *cis* configurations.

The scope of the phosphene precursors, (diazo(aryl)-methyl)diarylphosphine oxides **1**, was evaluated (Scheme 3). The reactions of (diazo(2-fluorophenyl)methyl)diphenylphosphine oxide (**1b**) with imines **2b** and **2c** generated the corresponding desired products **3s** and **3t** in satisfactory to good yields. While the reactions of (diazo(4-methyl/4-chlorophenyl)methyl)diphenylphosphine oxides (**1c** and **1d**) with imine **2b** and (diazo(4-trifluoromethylphenyl)methyl)-diphenylphosphine oxide (**1e**) with imine **2a** gave rise to pairs of *δ*-phospholactam derivatives **3u** and **3u′**, **3v** and **3v′**, and **3w** and **3w′**, respectively, in satisfactory to good yields. However, the reaction of (diazo(4-methoxyphenyl)methyl)-diphenylphosphine oxide (**1f**) and imine **2a** produced a trace amount of *δ*-phospholactam derivatives **3x** and **3x′** possibly because diazo compound **1f**-generated phosphene **Af** with a strong electron-donating 4-methoxyphenyl group showed very

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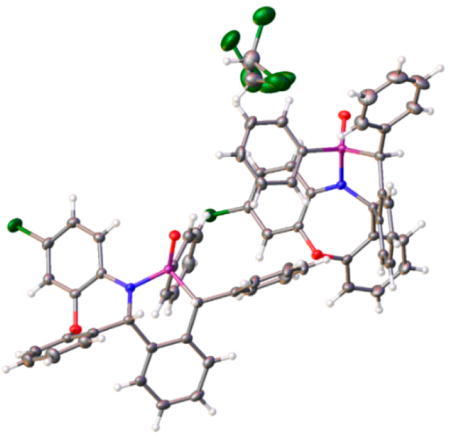


Figure 1. XRD structure of product **3c** (the ellipsoid probability 50%).

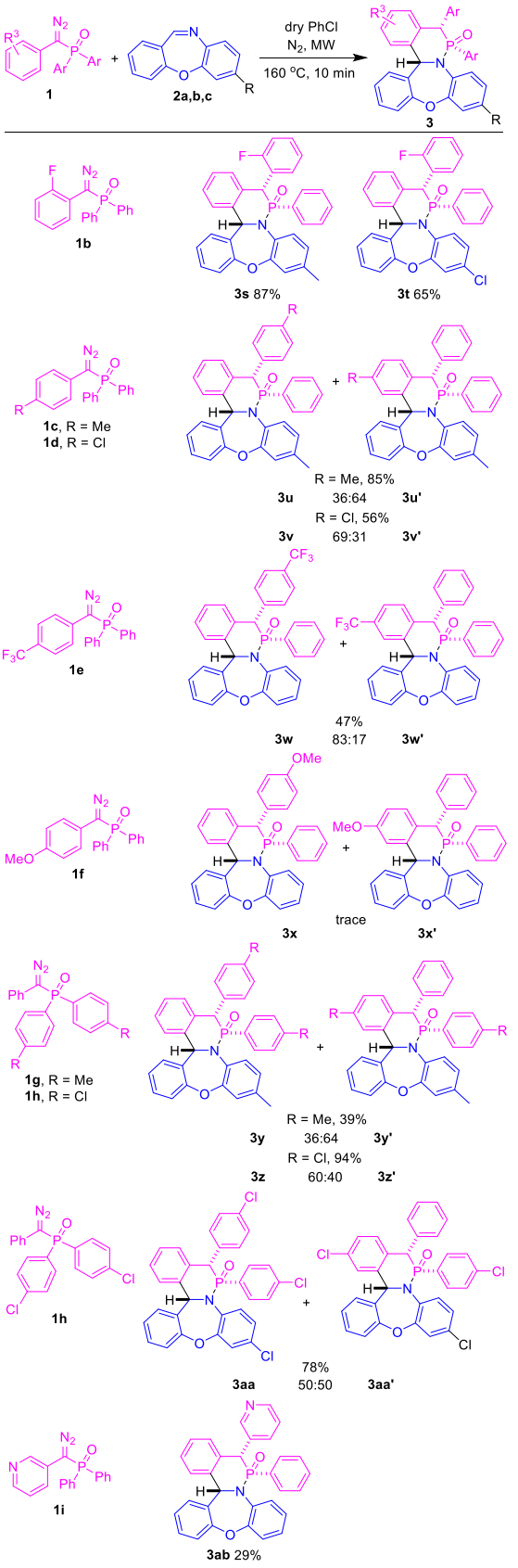
poor electrophilicity, disfavoring the first nucleophilic attack (*vide post*). Similarly, the reactions of (diazo(phenyl)methyl)-di(4-methyl/4-chlorophenyl)phosphine oxides (**1g** and **1h**) with imines **2b** and **2c** produced pairs of *δ*-phospholactam derivatives **3y** and **3y′**, **3z** and **3z′**, and **3aa** and **3aa′**, respectively, in satisfactory to good yields. A heteroaryl diazo compound, (diazo(pyridine-3-yl)methyl)diphenylphosphine oxide (**1i**), was also attempted in the reaction with imine **2a**, giving the desired *δ*-phospholactam **3ab** in a low yield of 29%. The ratios of **3** and **3′** were determined on the basis of their ^{1}H NMR spectra, and the major isomers are the *δ*-phospholactam derivatives involving the electron-rich fused benzo moiety derived from diaryl(aryl)phosphenes (*vide post*).

To further extend the scopes of imines and diazomethylphosphine oxide compounds, 11-methyl and 11-phenyl dibenzo[*b*,*f*][1,4]oxazepines (**2s** and **2t**), (diazomethyl)-diphenylphosphine oxide (**1j**), and ethyl (diazo(phenyl)-methyl)phenylphosphinate (**1k**) were prepared and attempted for the reaction. However, no desired reaction was observed. The reactions of (diazo(phenyl)methyl)diphenylphosphine oxide (**1a**) with linear imines, PhCH = NMe, 4-MeC_6H_4CH = NBn, and PhCH = NC_6H_4OMe-4, were tested as well, and no desired reaction occurred, either. The results indicate that the steric hindrance of imines is very sensitive to bulky diphenyl(phenyl)phosphenes. Only (*Z*)-cyclic imines **2** without substituents on the imine C═N bond can give rise to the desired products **3** (Scheme 4).

A large-scale preparation was performed in 70% yield with 700 mg of the product **3b** (Scheme 2). A further application of product **3g** was conducted in the Suzuki coupling with phenylboronic acid, affording the desired product **4** in 59% yield (Scheme 5).

The reaction mechanism is assumed on the basis of the XRD structure of product **3c** and the product ratios involving phosphenes with different aryl groups (Scheme 3). (Diazo)-(phenyl)methyl(diphenyl)phosphine oxide (**1a**) first undergoes a Wolff rearrangement under microwave-irradiated heating to generate diphenylmethylidene(phenyl)phosphine oxide (phosphene **A**).[11] Cyclic imine dibenzo[*b*,*f*][1,4]-oxazepine (**2a**) nucleophilically attacks the phosphene **A** to give rise to zwitterionic intermediate **B**. It can resonate into another zwitterionic intermediate **C**. The electron-rich phenyl group in the benzylcarbanion in **C** nucleophilically attacks the iminium moiety (intramolecular Friedel−Craft alkylation)

Scheme 3. Scopes of Diazo Compounds 1[a]



[a]Reaction conditions: The same as those in Scheme 2.

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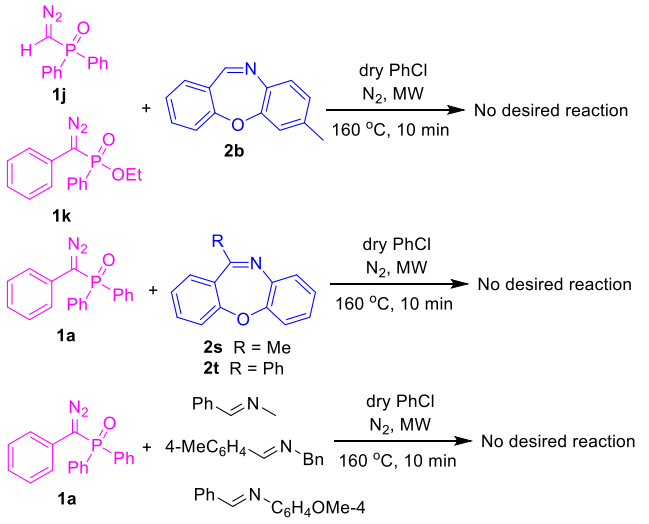
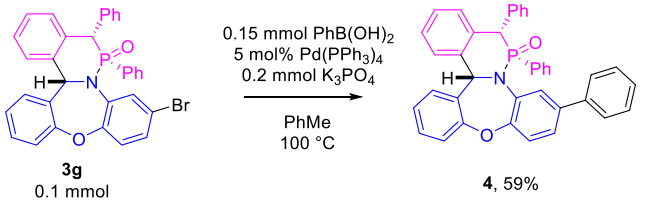
Scheme 4. Further Attempts



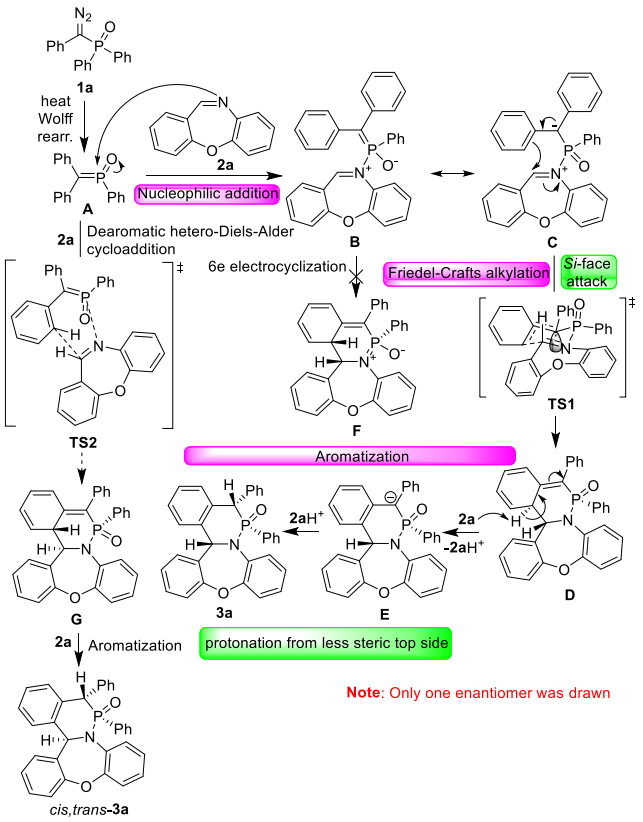
Scheme 5. Application



through a chairlike six-membered ring transition state **TS1**, in which two phenyl groups locate on the equatorial bond, to generate cyclized intermediate **D**. Intermediate **D** further aromatizes into final product **3a** in the presence of imine **2a** as a base. In the last protonation step, the acid iminium **2a**H$^+$ accesses the carbanion from the less steric top side, resulting in the formation of product **3a** with the indicated stereostructure (Scheme 6). The cyclic imines with electron-donating and weak electron-withdrawing halo substituents give rise to the corresponding products in obviously higher yields than those with a strong electron-withdrawing nitro group, indicating that the imine nucleophilic attack step is the possible rate-limiting step. According to the proposed mechanism, the major products are assigned as the products with the electron-rich benzo-fused δ-phospholactams because the electron-rich phenyl groups predominately nucleophilically attack the iminium moiety in the cyclization step.

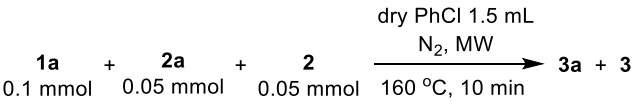
There are two other possibilities to generate products **3**. One is that the intermediate **B** undergoes a disrotatary 6e electrocyclization to yield intermediate **F**. However, the disrotation is very hard due to the existence of the rigid benzene and dibenzo[*b*,*f*][1,4]oxazepine rings in the 6e conjugated system. Dearomatic hetero-Diels–Alder cycloaddition of the phosphene **A** and imine **2a** is another possible pathway through transition state **TS2**. However, the cycloaddition would give intermediate **G**, which would aromatize into *cis*,*trans*-**3a** rather than product **3a** (Scheme 5). Arylmethylphosphonochloridate-generated arylphosphenes also underwent a stepwise annulation with α,β-unsaturated ketones rather than cycloaddition,[10] supporting our assumed stepwise nucleophilic addition, intramolecular Friedel–Craft alkylation, and aromatization pathway.

Scheme 6. Proposed Reaction Mechanism



To verify the proposed mechanism, we conducted the competitive experiments (Table 2). When equivalent amounts

Table 2. Competitive Experiments



entry	2	relative rate (k)[a] ^{1}H NMR	relative rate (k)[a] ^{31}P NMR	relative rate (k)[a] Average	σ[b]
1	**2b**	–[c]	35.1	35.1	−0.17
2	**2a**	1.00	1.00	1.00	0
3	**2c**	1.11	1.10	1.10	0.23
4	**2l**	0.54	0.52	0.53	0.78
5	**2i**	–[a]	1.41	1.41	−0.17
6	**2j**	0.76	0.75	0.75	0.23
7	**2k**	0.63	0.62	0.62	0.71

[a]Relative rate is calculated by the ratio of **3**/**3a**. [b]Hammett constant. [c]Yield of the isolated product in parentheses. [d]Inseparable.

of two different cyclic imines were reacted with diazo phosphine oxide **1a**, the electron-rich imines generally produced the corresponding products in higher yields than the electron-deficient ones. Hammett plot analyses indicate that both plots show negative reaction constant ρ values (Figure 2), supporting that the imine nucleophilic attack step is the rate-limiting step. Although one Hammett plot shows a low correlation coefficient, its tendency is clear with a negative reaction constant ρ value.

In conclusion, the microwave-assisted reaction of dibenzo[*b*,*f*][1,4]oxazepines and diazo(aryl)methyl(diaryl)phosphine oxides efficiently gives rise to 4b,16-dihydrodibenzo[*b*,*f*]-

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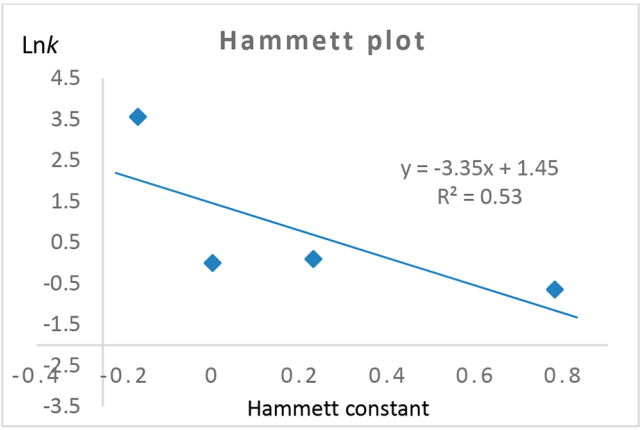
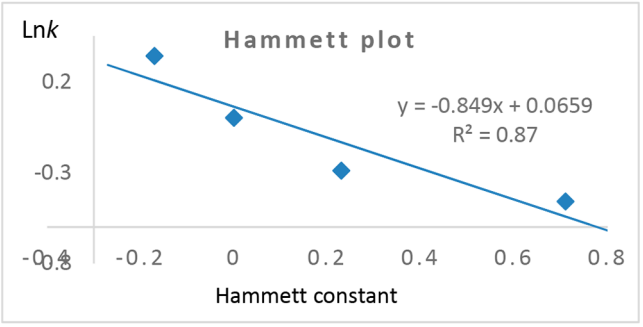


(a) Hammett plot for different imine *N*-aryl groups



(b) Hammett plot for different imine *C*-aryl groups

Figure 2. Hammett plots.

benzo[4,5][1,2]azaphosphinino[1,6-*d*][1,4]oxazepine 15-oxide derivatives, pentacyclic fused *δ*-phospholactams, in good yields. The reaction follows a sequence of cyclic imines nucleophilic attack on diaryl(aryl)phosphenes which generated from diazo(aryl)methyl(diaryl)phosphine oxides through the Wolff rearrangement, intramolecular Friedel−Craft alkylation, and aromatization. It is a metal-free and efficient method for the synthesis of polycyclic benzo-*δ*-phospholactam derivatives.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c02346.

Experimental details, compound characterization, and spectra (PDF)

Accession Codes

CCDC 2015827 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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