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One-pot formation of fluorescent γ-lactams having an α-phosphorus ylide moiety through three-component α(δ′)-Michael reactions of phosphines with an enyne and *N*-tosyl aldimines†

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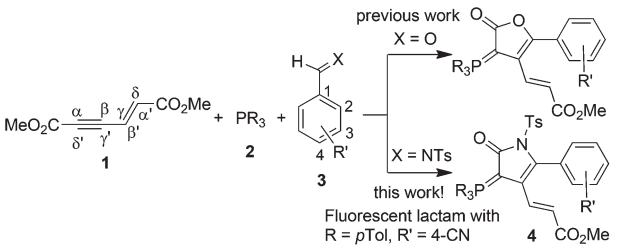
We demonstrate a straightforward synthesis of γ-lactams possessing an α-phosphorus ylide moiety from assembly of phosphines, *N*-tosyl aldimines and an enyne through an initial α(δ′)-attack of phosphines to an enyne in up to 79% yield. The investigated multicomponent reaction tolerates a variety of triarylphosphines and electron-poor aldimines to give γ-lactams in one pot. One of the lactams, with the tri(*p*-tol)phosphine and 4-cyanophenyl moiety, exhibits fluorescence emission at 447 nm with a quantum yield of 0.11.

Introduction

Multicomponent reactions (MCRs) are synthetic reactions showing expediency, molecular diversity and step-economy which are used to construct complex molecular structures from simple reactants in one pot.[1] In this context, the initial reactive intermediates could be generated from nucleophilic attack of amine,[2] phosphine[3] or isocyanide[4] species to electron-deficient acetylenes/allenes followed by subsequent addition to electrophiles. In recent years, versatile reactions using phosphine-catalysis have also been demonstrated for the syntheses of various heterocyclic natural products and bioactive compounds.[5] For example, the highly functionalized coumarins,[6] tetrahydropyridines,[7] 2-pyrones[8] and bicarbocyclic skeletons[9] can be prepared efficiently through the methodology of phosphine-catalysis. Recently, we have developed a three-component reaction (3CR) of phosphines, enynes **1** and aldehydes through an initial region-selective α(δ′)-attack of phosphines to enynes that form γ-lactones possessing an α-phosphorus ylide moiety (Scheme 1).[10] The same methodology can also be used to react with [60]fullerene to give cyclopentenofullerene derivatives in one pot,[11] and is also transferable to substrates such as dimethyl acetylenedicarboxylate (DMAD) in a particular molar ratio of the three reactants.



Scheme 1 Lactones and lactams by three-component reactions.

The assembled products, γ-lactones possessing α-phosphorus ylides, are reactive toward electron-poor aldehydes as Wittig reagents to give substituted α-benzylidine lactones.[12] In addition, primary and secondary amines also undergo α(δ′)-nucleophilic attack to enyne **1**.[13]

Due to our continuing interest in expanding this methodology for practical applications, we subsequently chose to develop the synthesis of the γ-lactam core structure by MCRs since we have noted that the natural products, isatin and its derivatives possessing a γ-lactam moiety, can be used as useful building blocks for the syntheses of other structurally relevant bioactive molecules.[14] We are able to construct isatin derivatives through this developed α(δ′)-Michael addition.[15] Further, the approaches to build up a γ-lactam moiety with multiple functional substituents in one step remain to be developed[16] in addition to other previous examples.[17] Herein, we wish to report the one-pot synthesis and characterization of fluorescent γ-lactams possessing α-phosphorus ylides through an initial α(δ′)-Michael addition of phosphines to an enyne by MCRs (Scheme 1).

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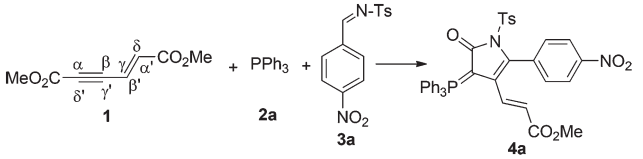
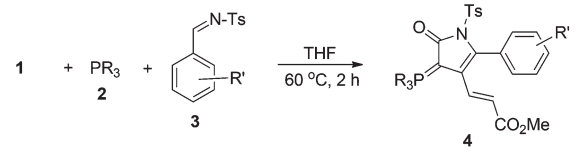
Table 1 Reaction condition optimization[a]



Entry	Solvent	Temp. (°C)	Time (h)	Yield[b] (%)
1	DCM	r.t.	2	21
2	THF	60	2	32
3	Toluene	60	2	25
4	MeCN	60	2	27
5	DCE[e]	60	2	22
6[c]	THF	60	2	44
7[d]	THF	60	2	57
8[d]	THF	60	1	48
9[d]	THF	r.t.	24	48
10[d]	THF	r.t.	48	51

[a] Reaction conditions: a mixture of **1** (0.30 mmol), **2a** (0.30 mmol) and **3a** (0.30 mmol) under nitrogen in anhydrous solvents. [b] Yield is determined by a ^{1}H NMR spectroscopic method using mesitylene as an internal standard. [c] Molar ratio of **1 : 2a : 3a** = 1.5 : 1.5 : 1. [d] Molar ratio of **1 : 2a : 3a** = 2 : 2 : 1. [e] 1,2-Dichloroethane.

Table 2 Reaction scope study[a]



Entry	2; PR_3	3; R′	4	Yield[b] (%)
1	**2a**; PPh_3	**3a**; 4-NO_2	**4a**	57
2	**2b**; $P(p\text{Tol})_3$	**3a**; 4-NO_2	**4b**	49
3	**2c**; $P(4\text{-Cl-}C_6H_4)_3$	**3a**; 4-NO_2	**4c**	57
4	**2d**; $P(4\text{-F-}C_6H_4)_3$	**3a**; 4-NO_2	**4d**	79
5	**2e**; $P(2\text{-thienyl})_3$	**3a**; 4-NO_2	**4e**	56
6[c,d]	**2f**; $P(NMe_2)_3$	**3a**; 4-NO_2	**4f**	53
7	**2a**; PPh_3	**3b**; 3-NO_2	**4g**	59
8	**2b**; $P(p\text{Tol})_3$	**3b**; 3-NO_2	**4h**	54
9	**2g**; $PPh_2(p\text{Tol})$	**3b**; 3-NO_2	**4i**	62
10	**2d**; $P(4\text{-FC}_6H_4)_3$	**3b**; 3-NO_2	**4j**	61
11	**2b**; $P(p\text{Tol})_3$	**3c**; 4-Cl-3-NO_2	**4k**	51
12	**2c**; $P(4\text{-Cl-}C_6H_4)_3$	**3c**; 4-Cl-3-NO_2	**4l**	52
13	**2d**; $P(4\text{-F-}C_6H_4)_3$	**3c**; 4-Cl-3-NO_2	**4m**	56
14	**2b**; $P(p\text{Tol})_3$	**3d**; 4-CN	**4n**	71
15	**2c**; $P(4\text{-Cl-}C_6H_4)_3$	**3d**; 4-CN	**4o**	54
16	**2h**; $P(c\text{Hex})_3$	**3d**; 4-CN	**4p**	22

[a] Reaction conditions: a mixture of **1** (0.30 mmol), **2** (0.30 mmol) and **3** (0.15 mmol) under nitrogen in anhydrous THF. [b] Yields (%) were determined by a ^{1}H NMR spectroscopic method using mesitylene as an internal standard after isolation by flash SiO_2 column chromatography. [c] Room temperature. [d] Molar ratio of **1 : 2 : 3** = 1 : 1 : 1.

Results and discussion

First of all, we briefly delineate the condition optimization of the synthesis of γ-lactams by three-component assembly of enyne **1**, triphenylphosphine (**2a**), and aldimine **3a**. We find that the reaction with a molar ratio of **1 : 2a : 3a** = 1 : 1 : 1 gives a relatively better yield (32%) in the aprotic etherate solvent tetrahydrofuran (THF) at 60 °C for 2 h (Table 1, entries 1–5). When we increase the molar ratio of both **1** and **2a** (1.5 equiv.) for generating relatively greater amounts of reactive 1,3-dipolar species, we observe an increase of reaction yield to 44% (entry 6). Further increment of the relative molar ratio of **1 : 2a : 3a** to 2 : 2 : 1 gives the highest yield of 57% (entry 7). Other adjustments of the conditions such as time-shortening to 1 h (entry 8) or carrying out the reaction under milder conditions at r.t. (entries 9 and 10) do not improve the yields of the reaction notably.

We investigate the scope of currently developed three-component reactions with other triarylphosphines and electron-poor aldimines. As shown in Table 2, γ-lactams can be assembled with isolated yields ranging from 49 to 79%, with variously substituted triarylphosphines **2a–f** and 4-nitrobenzaldimine (**3a**) (entries 1–6); among these phosphines, tris(4-chlorophenyl)phosphine (**2c**) performs the best to give 79% yield (entry 4) and the reaction with a non-aryl hexamethylphosphorus triamide (**2f**, HMPT) produces **4f** in a comparable yield of 53% (entry 6) as those with phosphines **2a–f**. We next evaluate the performance with other substituted aldimines **3b–d** and find that the reactions proceed to give yields spanning from 22 to 71%. It is worthy to note that the present assembly reaction proceeds with phosphines such as the more nucleophilic $P(c\text{Hex})_3$ (**2h**) and the less nucleophilic $P(NMe_2)_3$ (**2f**), but these two phosphines did not work well in the syntheses of the corresponding γ-lactones with aldehydes as substrates.[9] The reaction with a more nucleophilic tricyclohexylphosphine (**2h**) gives a relatively poor yield (entry 16, 22%), likely due to the presence of a $P(c\text{Hex})_3$ moiety that makes the corresponding product (**4p**) unstable. This notion is further evidenced from the fact that reaction products are not isolable when we use trialkylphosphines such as PMe_3, PEt_3, $P(n\text{-Pr})_3$ and $P(n\text{-Bu})_3$; with these trialkylphosphines, only a trace amount of products resulting from $P(n\text{-Bu})_3$ is observed.

We characterized these γ-lactams **4a–p** by using infrared (IR) and ^{1}H, ^{31}P and ^{13}C nuclear magnetic resonance (NMR) spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and X-ray crystallography. All MS data corresponded to the expected formulae of the isolated γ-lactams. In their IR spectra, the C=O group, next to the ylidic carbanion, shows stretching bands at *ca.* 1629–1658 cm^{-1}, lower than that of a normal C=O stretching frequency due to electronic resonance. It is interesting to note that the C=O stretching frequency of the lactam **4f** with a HMPT moiety appears at 1658 cm^{-1} and that of lactam **4p** with $P(c\text{Hex})_3$ appears at 1629 cm^{-1}. This indicated that $P(c\text{Hex})_3$ behaves as a strong electron-donating group and HMPT as a strong electron-pulling group—such an effect renders strong and weak delocalizations of the ylide carbanion through resonance to the lactam carbonyl moiety, respectively. For the characterization of an example of compound **4a** by NMR, we observe a signal at 12.7 ppm in its ^{31}P NMR spectrum, corresponding to a typical

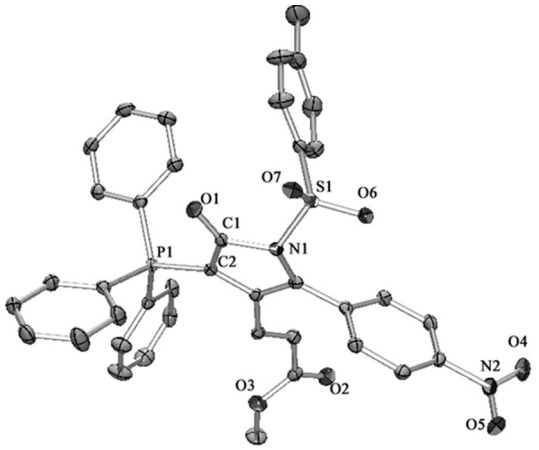


Fig. 1 X-ray crystal structure of compound **4a**.

α-ylidic γ-lactam. Its ^{1}H NMR spectrum displays simple singlets at 2.46 and 3.38 ppm, corresponding to methyl and methoxy groups, respectively. Two signals at 165.7 and 167.0 ($^{2}J_{PC}$ = 15.8 Hz) ppm correspond to the carbonyl resonances of ester and lactam in the ^{13}C NMR spectrum. The ylidic carbon (C2, Fig. 1) appears at 61.3 ppm with one bond coupling to phosphorus P1 ($^{1}J_{PC}$ = 129.2 Hz).

Further, we find that these isolated ylide compounds tend to crystallize by slow evaporation of their dichloromethane or chloroform solution. We obtain the crystal structure of compounds **4a**[18] (Fig. 1) and **4l**[19] (Fig. 2) by X-ray diffraction analysis. The phosphorus atom P1 is clearly covalently bonded to C2 and C22 with a bond length of 1.7319(18) and 1.7360(4) Å for **4a** and **4l**, respectively. Due to the delocalization of negative charge from ylidic carbon C2 and C22 to the lactam carbonyl π bond (C1–O1 and C19–O1), the C1–C2 and C19–C22 bond lengths 1.4170(2) and 1.4280(7) Å for **4a** and **4l**, respectively, are shorter than a normal carbon to carbon single bond. The bond lengths of C1–O1 and C19–O1, 1.2350(2) and 1.2120(6) Å for **4a** and **4l**, respectively, are longer than a normal carbon to

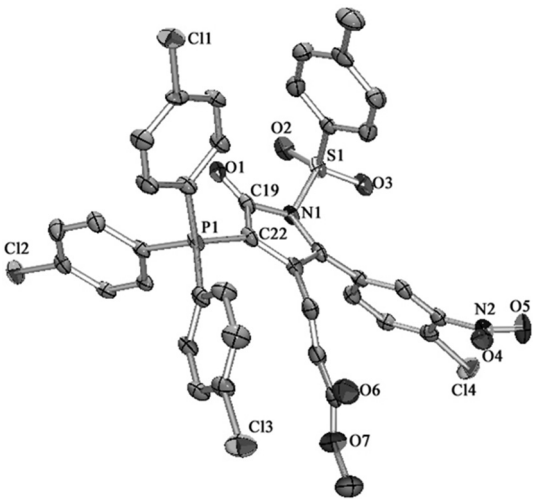
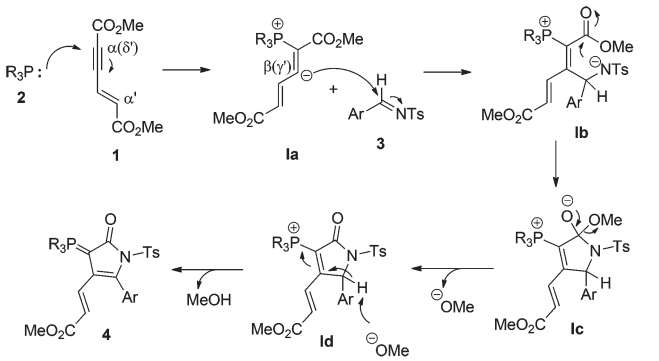


Fig. 2 X-ray crystal structure of compound **4l**.



Scheme 2 Proposed reaction mechanism.

oxygen double bond. The relatively shorter C19–O1 in **4l** may be inferred from the slightly larger electron-pulling ability of the tris(4-chlorophenyl)phosphine than a triphenylphosphine moiety, making the α-carbanion show lesser extent of resonance toward the carbonyl group.

We account for the formation of lactam ylide **4** by an initial nucleophilic attack of phosphine PR_3 (**2**) at α(δ′)-position of the enyne **1** (Scheme 2), generating a reactive zwitterionic species **Ia** bearing a carbenoid moiety at β(γ′)-carbon. Nucleophilic addition of **Ia** to the aldiminyl carbon of aldimines **3** generates **Ib**. Intramolecular cyclization of **Ib** gives **Ic** followed by release of a methoxide molecule. Finally, deprotonation on **Id** by the methoxide takes place to form the product **4**.

These isolated lactam compounds **4a–4p** exhibit remarkable visible colors from light yellow to orange. As a result, we measure the UV-vis absorption of compounds **4a–p**, and these absorption data are shown in the ESI (Fig. S33 to S36†). In Fig. S33,† we find that benzaldimines equipped with the 4-NO_2 group display absorptions spanning from 330 to 600 nm. Among these compounds (**4a–f**), their maximum absorptions in the visible region are blue-shifted for phosphines with more electron-releasing groups—compound **4b** with P(*p*Tol)$_3$ shows absorption maxima at 458 nm and those of compounds **4a** (with PPh_3), **4f** (with $P(NMe_2)_3$), **4e** (with P(2-thienyl)$_3$), **4d** (with P(4-F-C_6H_4)$_3$) and **4c** (with P(4-Cl-C_6H_4)$_3$) appear at 452, 452, 444, 441 and 436 nm, respectively (Fig. S33†). However, the switch of 4-nitro to 3-nitro substitution (compounds **4g–j**) causes an apparent blue shift of the absorption maxima spanning from 376 to 400 nm, with compound **4j** showing the most blue-shift (Fig. S33–S34†). Further, lactams with 3-chloro-4-nitro and 4-cyano substitutions (**4k–4p**) exhibit a pale-yellow solution in $CHCl_3$ and do not show intense absorptions (Fig. S34†).

Interestingly, we note that lactams **4a–p** were fluorescent and measure their fluorescent emission spectra with a solution concentration of 5.0×10^{-5} M. As shown in Fig. 3, while compounds **4a–m** and **4o** show extremely poor fluorescent emission with quantum yields less than 0.01, compounds **4n** and **4p** exhibit relatively observable blue fluorescence. Their fluorescence quantum yields, determined by using anthracene as a reference standard (Φ = 0.27 in EtOH), are 0.112 and 0.038

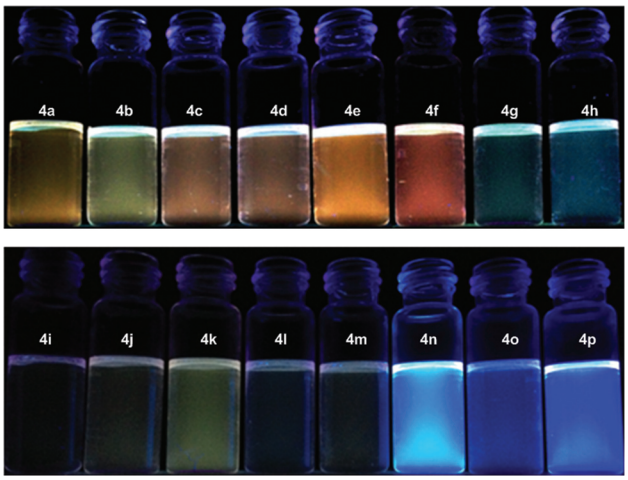


Fig. 3 Fluorescent image of lactams **4a–p**.

with maximum emission wavelengths of 447 and 445 nm when excited at 363 nm, respectively (Fig. 4). Further, we note that the fluorescence of compound **4n** is concentration-dependent in $CHCl_3$—the fluorescence emission is bathochromic-shifted while the concentration of solutions increases (Fig. 5).

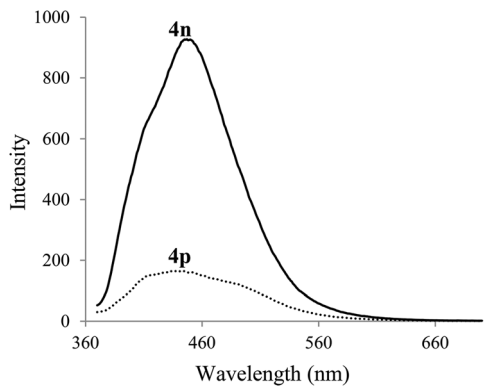


Fig. 4 Fluorescence emission spectra of **4n** and **4p** (excitation wavelength at 363 nm).

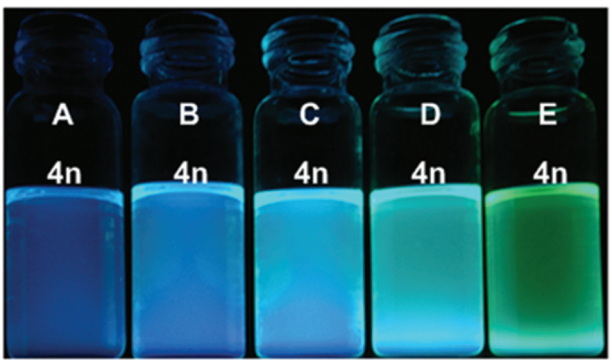


Fig. 5 Concentration-dependent emission phenomenon of compound **4n** at concentrations of 5.0×10^{-5} (A), 7.5×10^{-5} (B), 1.0×10^{-4} (C), 2.0×10^{-4} (D), and 4.0×10^{-4} (E), respectively.

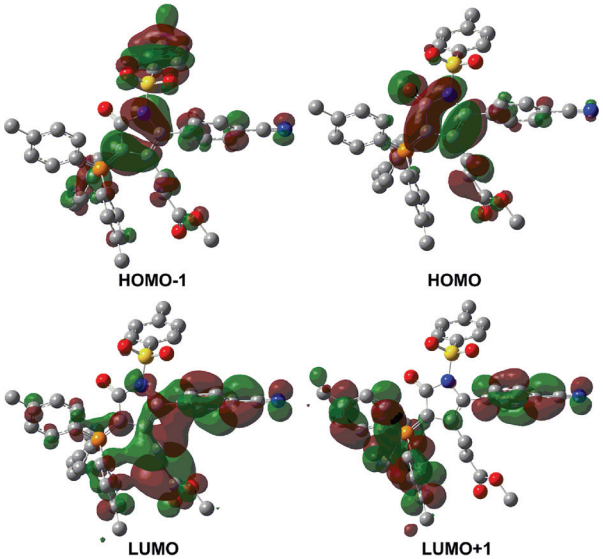


Fig. 6 HOMO−1 (−0.35227 eV), HOMO (−0.29164 eV), LUMO (−0.21441 eV) and LUMO+1 (−0.20384 eV) energy levels of **4n** calculated by a semiempirical AM1 method.

The emission wavelength maxima for solutions A to E of **4n** are 447, 486, 491, 490 and 494 nm, respectively. However, this concentration-dependent notion is minute when **4n** is dissolved in THF or dichloromethane. This typical change is attributed to more ordered packing of **4n** in $CHCl_3$ than in THF or dichloromethane—consistent with the notion that **4n** shows higher propensity for crystallization in $CHCl_3$.

It is noteworthy that the assembled γ-lactam **4n** with multiple functional groups exhibits fluorescent properties. We perform semiempirical calculations to retrieve the HOMO−1, HOMO, LUMO and LUMO+1 molecular orbitals of **4n**. As shown in Fig. 6, the HOMO−1 and HOMO orbitals are primarily located at the lactam moiety while the LUMO and LUMO+1 orbitals are distributed over the 4-cyanophenyl and ester moiety. The electronic excitation may be contributed by the electron excited from the lactam core to the outer moiety to facilitate the subsequent fluorescent emission.

Conclusions

We have demonstrated a one-pot multicomponent reaction for the synthesis of γ-lactams possessing an α-phosphorus ylide moiety from assembly of phosphines, *N*-tosyl aldimines and an enyne through an initial α(δ′)-Michael addition of phosphines to an enyne in up to 79% yield. The investigated MCRs tolerate a variety of phosphines such as triarylphosphines, tricyclohexylphosphine and hexamethylphosphorus triamide with electron-deficient aldimines, providing γ-lactams having α-phosphorus ylides in a one-pot procedure. One of these compounds, with the tri(*p*-tol)phosphine and 4-cyanophenyl moiety, exhibits blue fluorescence with a quantum yield of 0.112.

Experimental section

General methods

All reactions were performed under argon. Anhydrous benzene and THF were distilled from sodium/benzophenone under argon. The chemical shifts of ^{31}P NMR were taken with reference to 85% H_3PO_4 in D_2O and that of ^{1}H and ^{13}C with reference to TMS or $CHCl_3$.

Typical procedure for the synthesis of 4a–p

A benzene solution containing **1** (0.30 mmol) and aldimines **3** (0.15 mmol) was distilled three times to remove water using a Dean–Stark apparatus. Then, 8 mL of THF was added to the resulting mixture followed by phosphines **2** (0.30 mmol). The mixture was heated at 60 °C and monitored by thin layer chromatography (TLC). Upon completion of the reaction, THF was removed under reduced pressure and subjected to flash chromatography. Elution first with DCM–EA (3/1) gave products **4**.

Measurement of fluorescence spectroscopy

The quantum yield was calculated according to the following equation: $\Phi_S/\Phi_R = (A_S/A_R) \times (Abs_R/Abs_S) \times (\eta_S^2/\eta_R^2)$, where Φ_S and Φ_R are the fluorescence quantum yields of the sample and the reference, respectively; A_S and A_R are the emission areas of the sample and the reference; Abs_S and Abs_R are the corresponding absorbances of the sample and the reference solution at the wavelength of excitation; η_S and η_R are the refractive indices of the sample and the reference.[20]

(*E*)-Methyl 3-(2-(4-nitrophenyl)-5-oxo-1-tosyl-4-(triphenylphosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (4a)

Red solid. M.p. 174–175 °C. R_f = 0.27 (DCM–EA, 3 : 1). Isolated yield 57% (0.0600 g). ^{1}H NMR (600 MHz, $CDCl_3$, 25 °C): δ = 2.46 (3H, s, Me), 3.38 (3H, s, CO_2Me), 5.01 (1H, d, J = 16.1 Hz, CH), 6.35 (1H, d, J = 16.0 Hz, CH), 7.25 (2H, d, J = 8.8 Hz, Ph), 7.38–7.42 (6H, m, Ph), 7.45 (6H, t, J = 7.8 Hz, Ph), 7.50 (2H, d, J = 8.5 Hz, Ph), 7.56, (3H, t, J = 7.1 Hz, Ph), 7.67 (2H, d, J = 8.1 Hz, Ph), 8.13 (2H, d, J = 8.6 Hz, Ph) ppm. ^{13}C NMR (150 MHz, $CDCl_3$, 25 °C): δ = 21.6, 51.0, 61.3 (d, $^{1}J_{PC}$ = 129.2 Hz), 121.9, 122.6 (d, $^{1}J_{PC}$ = 92.3 Hz), 122.7, 122.8, 124.0 (d, $^{3}J_{PC}$ = 11.9 Hz), 128.0, 129.0, 129.1 (d, $^{3}J_{PC}$ = 12.8 Hz), 130.8, 133.1 (d, $^{4}J_{PC}$ = 2.7 Hz), 133.8 (d, $^{2}J_{PC}$ = 10.5 Hz), 135.7, 136.3, 140.0, 143.8, 146.1, 165.7, 167.0 (d, $^{2}J_{PC}$ = 15.8 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ = 12.7 ppm. FTIR (KBr): $\tilde{\nu}$ = 1640, 1716 cm^{-1}. $\lambda_{max}(CHCl_3)$: 452 nm. HRMS (ESI^+): calcd for $C_{39}H_{31}N_2O_7PS$ [M^+] 702.1590; found 702.1585.

(*E*)-Methyl 3-(2-(4-nitrophenyl)-5-oxo-1-tosyl-4-(tri-*p*-tolylphosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (4b)

Red solid. M.p. 72–76 °C. R_f = 0.33 (DCM–EA, 3 : 1). Isolated yield 49% (0.0547 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.40 (9H, s, Me), 2.51 (3H, s, Me), 3.45 (3H, s, CO_2Me), 5.00 (1H, d, J = 16.0 Hz, CH), 6.39 (1H, d, J = 15.5 Hz, CH), 7.21 (6H, dd, J = 3.0, 8.0 Hz, Ph), 7.28 (2H, d, J = 5.0 Hz, Ph), 7.33 (6H, dd, J = 8.5, 12.5 Hz, Ph), 7.51 (2H, d, J = 8.5 Hz, Ph), 7.73 (2H, d, J = 8.5 Hz, Ph), 8.17 (2H, d, J = 8.5 Hz, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 21.56, 21.62, 51.1, 62.2 (d, $^{1}J_{PC}$ = 129.3 Hz), 119.6 (d, $^{1}J_{PC}$ = 95.4 Hz), 121.7, 122.7, 122.8, 124.5 (d, $^{3}J_{PC}$ = 12.2 Hz), 128.1, 129.0, 129.9 (d, $^{3}J_{PC}$ = 13.3 Hz), 130.9, 133.8 (d, $^{2}J_{PC}$ = 11.1 Hz), 135.9, 136.7, 140.2, 143.7, 144.0, 146.1, 166.0, 167.0 (d, $^{2}J_{PC}$ = 15.5 Hz), ppm. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ = 11.8 ppm. $\lambda_{max}(CHCl_3)$: 458 nm. FTIR (KBr): $\tilde{\nu}$ = 1646, 1717 cm^{-1}. HRMS (ESI^+): calcd for $C_{42}H_{37}N_2O_7PS$ [M^+] 744.2059; found 744.2058.

(*E*)-Methyl 3-(2-(4-nitrophenyl)-5-oxo-1-tosyl-4-(tris(4-chlorophenyl)phosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)-acrylate (4c)

Red solid. M.p. 174–175 °C. R_f = 0.30 (hexanes–EA, 1.5 : 1). Isolated yield 79% (0.0953 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.52 (3H, s, Me), 3.51 (3H, s, CO_2Me), 5.02 (1H, d, J = 16.2 Hz, CH), 6.36 (1H, d, J = 15.9 Hz, CH), 7.30 (2H, d, J = 8.1 Hz, Ph), 7.35–7.45 (12H, m, Ph), 7.51 (2H, d, J = 9.0 Hz, Ph), 7.73 (2H, d, J = 8.1 Hz, Ph), 8.18 (2H, d, J = 8.7 Hz, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.7, 51.5, 60.3 (d, $^{1}J_{PC}$ = 130.9 Hz), 120.5 (d, $^{1}J_{PC}$ = 95.2 Hz), 122.1, 122.6 (d, $^{2}J_{PC}$ = 12.1 Hz), 122.8, 123.6 (d, $^{3}J_{PC}$ = 12.6 Hz), 128.2, 129.1, 129.8 (d, $^{3}J_{PC}$ = 13.7 Hz), 131.0, 134.9 (d, $^{2}J_{PC}$ = 11.8 Hz), 135.6, 136.0, 139.6, 140.7 (d, $^{4}J_{PC}$ = 3.8 Hz), 144.2, 146.4, 165.6, 166.9 (d, $^{2}J_{PC}$ = 15.9 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ = 12.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 1640, 1717 cm^{-1}. $\lambda_{max}(CHCl_3)$: 436 nm. HRMS (ESI^+): calcd for $C_{39}H_{28}Cl_3N_2O_7PS$ [M^+] 804.0420; found 804.0428.

(*E*)-Methyl 3-(2-(4-nitrophenyl)-5-oxo-1-tosyl-4-(tris(4-fluorophenyl)phosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)-acrylate (4d)

Red solid. M.p. 122–124 °C. R_f = 0.30 (hexanes–EA, 1.25 : 1). Isolated yield 57% (0.0646 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.47 (3H, s, Me), 3.44 (3H, s, CO_2Me), 5.00 (1H, d, J = 16.0 Hz, CH), 6.28 (1H, d, J = 16.0 Hz, CH), 7.12 (6H, td, J = 2.5, 9.0 Hz, Ph), 7.26 (2H, d, J = 7.5 Hz, Ph), 7.44–7.48 (8H, m, Ph), 7.69 (2H, d, J = 8.5 Hz, Ph), 8.13 (2H, d, J = 8.5 Hz, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 21.6, 51.3, 61.3 (d, $^{1}J_{PC}$ = 132.1 Hz), 117.0 (dd, $^{3}J_{PC}$ = 14.3, $^{2}J_{FC}$ = 21.0 Hz), 118.2 (d, $^{1}J_{PC}$ = 97.7 Hz), 122.0, 122.8, 123.3 (d, $^{3}J_{PC}$ = 12.2 Hz), 126.2, 128.1, 129.1, 131.0, 135.7, 136.0, 136.3, (dd, $^{2}J_{PC}$ = 12.2, $^{3}J_{FC}$ = 21.0 Hz), 139.7, 144.1, 146.4, 165.7, 165.8 (dd, $^{4}J_{PC}$ = 3.3, $^{1}J_{FC}$ = 258.6 Hz), 166.8 (d, $^{2}J_{PC}$ = 15.6 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ = 11.4 ppm. FTIR (KBr): $\tilde{\nu}$ = 1640, 1721 cm^{-1}. $\lambda_{max}(CHCl_3)$: 441 nm. HRMS (ESI^+): calcd for $C_{39}H_{28}F_3N_2O_7PS$ [M^+] 756.1307; found 756.1298.

(*E*)-Methyl 3-(2-(4-nitrophenyl)-5-oxo-1-tosyl-4-(tri(thiophen-2-yl)phosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (4e)

Red solid. M.p. 165–168 °C. R_f = 0.28 (hexanes–EA, 1 : 3). Isolated yield 56% (0.0604 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.47 (3H, s, Me), 3.48 (3H, s, CO_2Me), 5.14 (1H, d, J = 16.2 Hz, CH), 6.57 (1H, d, J = 16.2 Hz, CH), 7.19 (3H, ddd, J =

2.1, 3.6, 4.7 Hz, Ph), 7.28 (2H, d, J = 7.2 Hz, Ph), 7.51–7.56 (5H, m, Ph), 7.74 (2H, d, J = 8.4 Hz, Ph), 7.86 (3H, td, J = 0.9, 4.8 Hz, Ph), 8.20 (2H, d, J = 8.7 Hz, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.7, 51.3, 63.2 (d, $^1J_{PC}$ = 142.6 Hz), 121.3, 122.6 (d, $^2J_{PC}$ = 13.6 Hz), 122.9, 123.9 (d, $^3J_{PC}$ = 13.3 Hz), 124.6 (d, $^1J_{PC}$ = 117.9 Hz), 128.1, 129.1 (d, $^3J_{PC}$ = 15.9 Hz), 129.2, 131.0, 135.7, 135.8, 137.0 (d, $^2J_{PC}$ = 6.0 Hz), 139.8, 140.0 (d, $^3J_{PC}$ = 12.1 Hz), 143.9, 146.5, 166.6, 166.7 (d, $^2J_{PC}$ = 18.9 Hz) ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = −10.6 ppm. FTIR (KBr): $\tilde{\nu}$ = 1645, 1716 cm^{-1}. λ_{max}($CHCl_3$): 444 nm. HRMS (ESI$^+$): calcd for $C_{33}H_{25}N_2O_7PS_4$ [M$^+$] 720.0282; found 720.0278.

(*E*)-Methyl 3-(2-(4-nitrophenyl)-5-oxo-1-tosyl-4-(tris-(dimethylamino)phosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (4f)

Red solid. M.p. 100–102 °C. R_f = 0.21 (EA). Isolated yield 53% (0.0480 g). Recrystallization from hexanes–EA gave pure products. ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.37 (3H, s, Me), 2.58 (18H, d, J = 9.7 Hz, NMe_2), 3.68 (3H, s, CO_2Me), 5.84 (1H, d, J = 16.2 Hz, CH), 7.21 (2H, d, J = 8.2 Hz, Ph), 7.25 (1H, d, J = 16.2 Hz, CH), 7.56 (2H, d, J = 8.0 Hz, Ph), 7.70 (2H, d, J = 8.0 Hz, Ph), 8.26 (2H, d, J = 7.9 Hz, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.5, 35.9 (d, $^2J_{PC}$ = 5.2 Hz), 51.5, 65.1 (d, $^1J_{PC}$ = 190.0 Hz), 116.8, 122.8, 123.3 (d, $^3J_{PC}$ = 10.6 Hz), 127.6, 127.9 (d, $^3J_{PC}$ = 14.2 Hz), 128.8, 131.1, 135.9, 136.7, 139.5, 143.9, 146.6, 166.8 (d, $^2J_{PC}$ = 21.5 Hz), 167.7 ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 50.8 ppm. FTIR (KBr): $\tilde{\nu}$ = 1658, 1723 cm^{-1}. λ_{max}($CHCl_3$): 452 nm. HRMS (ESI$^+$): calcd for $C_{27}H_{34}N_5O_7PS$ [M$^+$] 603.1917; found 603.1916.

(*E*)-Methyl 3-(2-(3-nitrophenyl)-5-oxo-1-tosyl-4-(triphenylphosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)-acrylate (4g)

Orange solid. M.p. 96–99 °C. R_f = 0.13 (hexanes–EA, 2 : 1). Isolated yield 59% (0.0621 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.48 (3H, s, Me), 3.38 (3H, s, CO_2Me), 5.01 (1H, d, J = 16.1 Hz, CH), 6.34 (1H, d, J = 16.1 Hz, CH), 7.29 (2H, d, J = 8.2 Hz, Ph), 7.41–7.77 (19H, m, Ph), 8.12 (1H, dd, J = 1.3, 8.2 Hz, Ph), 8.19 (1H, t, J = 1.8 Hz, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.6, 50.9, 60.0 (d, $^1J_{PC}$ = 129.8 Hz), 120.9, 122.4 (d, $^2J_{PC}$ = 11.3 Hz), 122.7 (d, $^3J_{PC}$ = 12.1 Hz), 122.8 (d, $^1J_{PC}$ = 92.8 Hz), 125.2, 127.9, 128.3, 129.0 (d, $^3J_{PC}$ = 12.8 Hz), 129.1, 131.9, 133.0 (d, $^4J_{PC}$ = 3.0 Hz), 133.8 (d, $^2J_{PC}$ = 10.6 Hz), 134.8, 135.9, 136.3, 137.0, 143.8, 147.4, 165.9, 166.4 (d, $^2J_{PC}$ = 15.9 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ = 12.8 ppm. FTIR (KBr): $\tilde{\nu}$ = 1639, 1722 cm^{-1}. λ_{max}($CHCl_3$): 385 nm. HRMS (ESI$^+$): calcd for $C_{39}H_{31}N_2O_7PS$ [M$^+$] 702.1590; found 702.1581.

(*E*)-Methyl 3-(2-(3-nitrophenyl)-5-oxo-1-tosyl-4-(tri-*p*-tolylphosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (4h)

Orange solid. M.p. 116–119 °C. R_f = 0.32 (hexanes–EA, 1.25 : 1). Isolated yield 54% (0.0603 g). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 2.36 (9H, s, Me), 2.45 (3H, s, Me), 3.37 (3H, s, CO_2Me), 4.96 (1H, d, J = 16.0 Hz, CH), 6.33 (1H, d, J = 16.0 Hz, CH), 7.19 (6H, dd, J = 2.0, 8.5 Hz, Ph), 7.25 (2H, d, J = 7.0 Hz, Ph), 7.34 (6H, dd, J = 8.0, 13.0 Hz, Ph), 7.44 (1H, t, J = 8.0 Hz, Ph), 7.69 (1H, d, J = 7.5 Hz, Ph), 7.71 (2H, d, J = 8.5 Hz, Ph), 8.07 (1H, dt, J = 1.5, 8.0 Hz, Ph), 8.13 (1H, s, Ph) ppm. ^{13}C NMR (125 MHz, $CDCl_3$, 25 °C): δ = 21.5, 21.6, 51.0, 61.0 (d, $^1J_{PC}$ = 129.8 Hz), 119.7 (d $^1J_{PC}$ = 95.8 Hz), 120.8, 121.9, 122.4 (d, $^2J_{PC}$ = 12.2 Hz), 122.9 (d, $^3J_{PC}$ = 11.1 Hz), 125.1, 127.9, 128.2, 129.0, 129.7 (d, $^3J_{PC}$ = 13.3 Hz), 133.7 (d, $^2J_{PC}$ = 11.2 Hz), 135.0, 136.1, 136.5, 137.0, 143.6, 143.8 (d, $^4J_{PC}$ = 2.3 Hz), 147.4, 165.9, 166.4 (d, $^2J_{PC}$ = 16.5 Hz) ppm. ^{31}P NMR (202 MHz, $CDCl_3$, 25 °C): δ = 11.90 ppm. FTIR (KBr): $\tilde{\nu}$ = 1637, 1723 cm^{-1}. λ_{max}($CHCl_3$): 400 nm. HRMS (ESI$^+$): calcd for $C_{42}H_{37}N_2O_7PS$ [M$^+$] 744.2059; found 744.2052.

(*E*)-Methyl 3-(4-(diphenyl(*p*-tolyl)phosphoranylidene)-2-(3-nitrophenyl)-5-oxo-1-tosyl-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (4i)

Orange solid. M.p. 96–98 °C. R_f = 0.25 (hexanes–EA, 1 : 2). Isolated yield 62% (0.0666 g). ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 2.41 (3H, s, Me), 2.49 (3H, s, Me), 3.40 (3H, s, CO_2Me), 4.98 (1H, d, J = 16.0 Hz, CH), 6.33 (1H, d, J = 16.0 Hz, CH), 7.23–7.26 (2H, m, Ph), 7.36–7.46 (7H, m, Ph), 7.49–7.57 (8H, m, Ph), 7.72–7.77 (3H, m, Ph), 8.10–8.15 (2H, m, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.6 (d, $^5J_{PC}$ = 1.6 Hz), 21.6, 51.0, 60.3 (d, $^1J_{PC}$ = 129.8 Hz), 119.1 (d, $^1J_{PC}$ = 95.1 Hz), 121.5 (d, $^1J_{PC}$ = 92.1 Hz), 122.5, 122.65, 122.70 (d, $^3J_{PC}$ = 12.1 Hz), 123.7, 125.2, 128.0, 128.3, 129.0 (d, $^3J_{PC}$ = 12.8 Hz), 129.1, 129.9 (d, $^3J_{PC}$ = 12.8 Hz), 133.0 (d, $^4J_{PC}$ = 3.0 Hz), 133.7 (d, $^2J_{PC}$ = 10.6 Hz), 133.8 (d, $^2J_{PC}$ = 10.6 Hz), 134.9, 136.0, 136.4, 137.0, 143.8, 144.1 (d, $^4J_{PC}$ = 3.1 Hz), 147.4, 165.9, 166.5 (d, $^2J_{PC}$ = 16.0 Hz) ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 11.7 ppm. FTIR (KBr): $\tilde{\nu}$ = 1632, 1726 cm^{-1}. λ_{max}($CHCl_3$): 385 nm. HRMS (ESI$^+$): calcd for $C_{40}H_{33}N_2O_7PS$ [M$^+$] 716.1746; found 716.1732.

(*E*)-Methyl 3-(2-(3-nitrophenyl)-5-oxo-1-tosyl-4-(tris(4-fluorophenyl)phosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)-acrylate (4j)

Yellow solid. M.p. 104–107 °C. R_f = 0.28 (hexanes–EA, 1 : 1). Isolated yield 61% (0.0692 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.50 (3H, s, Me), 3.45 (3H, s, CO_2Me), 4.99 (1H, d, J = 16.1 Hz, CH), 6.26 (1H, d, J = 16.1 Hz, CH), 7.17 (6H, td, J = 2.2, 8.7 Hz, Ph), 7.30 (2H, d, J = 8.3 Hz, Ph), 7.47–7.57 (7H, m, Ph), 7.71–7.77 (3H, m, Ph), 8.14–8.17 (2H, m, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 22.1, 51.7, 60.6 (d, $^1J_{PC}$ = 132.2 Hz), 117.5 (dd, $^3J_{PC}$ = 14.3 Hz, $^2J_{FC}$ = 21.9 Hz), 118.9 (dd, $^4J_{FC}$ = 3.5 Hz, $^1J_{PC}$ = 97.4 Hz), 121.7, 121.9 (d, $^2J_{PC}$ = 12.2 Hz), 123.0, 123.8 (d, $^3J_{PC}$ = 12.5 Hz), 125.7, 128.6, 129.0, 129.7, 135.0, 136.4, 136.5, 136.9 (dd, $^3J_{FC}$ = 9.2 Hz, $^2J_{PC}$ = 12.4 Hz), 137.6, 144.6, 148.0, 166.3 (dd, $^4J_{PC}$ = 3.3 Hz, $^1J_{FC}$ = 257.9 Hz), 166.3, 166.8 (d, $^2J_{PC}$ = 16.2 Hz) ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 10.77 ppm. FTIR (KBr): $\tilde{\nu}$ = 1640, 1722 cm^{-1}. λ_{max}($CHCl_3$): 376 nm. HRMS (ESI$^+$): calcd for $C_{39}H_{28}F_3N_2O_7PS$ [M$^+$] 756.1307; found 756.1312.

(*E*)-Methyl 3-(2-(4-chloro-3-nitrophenyl)-5-oxo-1-tosyl-4-(tri-*p*-tolylphosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (4k)

Orange solid. M.p. 102–104 °C. R_f = 0.15 (hexanes–EA, 1 : 1). Isolated yield 51% (0.0595 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.39 (9H, s, Me), 2.49 (3H, s, Me), 3.44 (3H, s, CO_2Me), 5.03 (1H, d, J = 16.2 Hz, CH), 6.34 (1H, d, J = 15.9 Hz, CH), 7.20–7.38 (14H, m, Ph), 7.45 (1H, d, J = 8.4 Hz, Ph), 7.53 (1H, dd, J = 8.0, 1.8 Hz, Ph), 7.74 (2H, d, J = 8.1 Hz, Ph), 7.82 (1H, d, J = 1.5 Hz, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.55 (d, $^5J_{PC}$ = 1.1 Hz), 21.64, 51.1, 61.5 (d, $^1J_{PC}$ = 129.0 Hz), 119.6 (d, $^1J_{PC}$ = 94.9 Hz), 120.9 (d, $^2J_{PC}$ = 11.8 Hz), 121.4, 123.9 (d, $^3J_{PC}$ = 11.7 Hz), 125.2, 127.2, 128.0, 129.1, 129.8 (d, $^3J_{PC}$ = 12.9 Hz), 130.8, 133.4, 133.7 (d, $^2J_{PC}$ = 10.6 Hz), 135.4, 135.9, 136.4, 143.8, 143.9 (d, $^4J_{PC}$ = 2.6 Hz), 146.7, 165.8, 166.5 (d, $^2J_{PC}$ = 15.9 Hz) ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 11.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 1643, 1723 cm^{-1}. λ_{max}($CHCl_3$): 398 nm. HRMS (ESI^+): calcd for $C_{42}H_{36}ClN_2O_7PS$ [M^+] 778.1669; found 778.1670.

(*E*)-Methyl 3-(2-(4-chloro-3-nitrophenyl)-5-oxo-1-tosyl-4-(tris(4-chlorophenyl)phosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)-acrylate (4l)

Yellow solid. M.p. 182–185 °C. R_f = 0.30 (hexanes–EA, 2 : 1). Isolated yield 56% (0.0704 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.51 (3H, s, Me), 3.51 (3H, s, CO_2Me), 5.04 (1H, d, J = 15.9 Hz, CH), 6.32 (1H, d, J = 16.2 Hz, CH), 7.30 (2H, d, J = 8.1 Hz, Ph), 7.37–7.45 (12H, m, Ph), 7.51–7.52 (2H, m, Ph), 7.74 (2H, d, J = 8.1 Hz, Ph), 7.81 (1H, d, J = 1.5 Hz, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, 25 °C): δ = 21.7, 51.6, 59.7 (d, $^1J_{PC}$ = 130.9 Hz), 120.6 (d, $^1J_{PC}$ = 95.2 Hz), 121.9, 122.1, 122.2 (d, $^3J_{PC}$ = 12.6 Hz), 126.1, 127.3, 128.2, 129.3, 129.9 (d, $^3J_{PC}$ = 13.3 Hz), 131.1, 132.8, 135.0 (d, $^2J_{PC}$ = 11.8 Hz), 135.5, 135.8, 135.9, 140.7 (d, $^4J_{PC}$ = 3.4 Hz), 144.3, 146.8, 165.6, 166.5 (d, $^2J_{PC}$ = 16.3 Hz) ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 11.4 ppm. FTIR (KBr): $\tilde{\nu}$ = 1640, 1721 m^{-1}. λ_{max}($CHCl_3$): 380 nm. HRMS (ESI^+): calcd for $C_{39}H_{27}Cl_4N_2O_7PS$ [M^+] 838.0031; found 838.0030.

(*E*)-Methyl 3-(2-(4-chloro-3-nitrophenyl)-5-oxo-1-tosyl-4-(tris(4-fluorophenyl)phosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)-acrylate (4m)

Yellow solid. M.p. 124–126 °C. R_f = 0.33 (hexanes–EA, 1 : 1). Isolated yield 52% (0.0616 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.50 (3H, s, Me), 3.49 (3H, s, CO_2Me), 5.06 (1H, d, J = 16.1 Hz, CH), 6.27 (1H, d, J = 16.1 Hz, CH), 7.16 (6H, td, J = 2.2, 7.2 Hz, Ph), 7.30 (2H, d, J = 8.1 Hz, Ph), 7.32–7.29 (8H, m, Ph), 7.74 (2H, d, J = 8.3 Hz, Ph), 7.82 (1H, d, J = 1.7 Hz, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.6, 51.3, 60.7 (d, $^1J_{PC}$ = 132.1 Hz), 117.0 (dd, $^3J_{PC}$ = 14.3, $^2J_{FC}$ = 21.9 Hz), 118.2 (dd, $^4J_{FC}$ = 3.4, $^1J_{PC}$ = 97.6 Hz), 121.7, 121.8 (d, $^2J_{PC}$ = 12.5 Hz), 122.3 (d, $^3J_{PC}$ = 12.1 Hz), 125.9, 127.3, 128.0, 129.2, 131.1, 132.8, 132.9, 135.5, 135.8, 136.4 (dd, $^3J_{FC}$ = 9.2, $^2J_{PC}$ = 12.3 Hz), 144.2, 146.8, 165.7, 165.8 (dd, $^4J_{PC}$ = 3.3, $^1J_{FC}$ = 257.9 Hz), 166.4 (d, $^2J_{PC}$ = 16.2 Hz) ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 10.6 ppm. FTIR (KBr): $\tilde{\nu}$ = 1640, 1720 cm^{-1}. λ_{max}($CHCl_3$): 363 nm. HRMS (ESI^+): calcd for $C_{39}H_{27}ClF_3N_2O_7PS$ [M^+] 790.0917; found 790.0904.

(*E*)-Methyl 3-(2-(4-cyanophenyl)-5-oxo-1-tosyl-4-(tri-*p*-tolylphosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)acrylate (4n)

Yellow solid. M.p. 130–132 °C. R_f = 0.16 (hexanes–EA, 1 : 1). Isolated yield 71% (0.0771 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.39 (9H, s, Me), 2.49 (3H, s, Me), 3.44 (3H, s, CO_2Me), 5.00 (1H, d, J = 16.1 Hz, CH), 6.40 (1H, d, J = 16.1 Hz, CH), 7.20–7.36 (14H, m, Ph), 7.48 (2H, d, J = 8.2 Hz, Ph), 7.57 (2H, d, J = 7.8 Hz, Ph), 7.72 (2H, d, J = 7.8 Hz, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.4, 21.5, 50.9, 61.5 (d, $^1J_{PC}$ = 128.7 Hz), 109.7, 119.0, 119.4 (d, $^1J_{PC}$ = 95.2 Hz), 121.1, 122.9 (d, $^2J_{PC}$ = 12.1 Hz), 123.8 (d, $^3J_{PC}$ = 10.1 Hz), 127.8, 128.8, 129.6 (d, $^3J_{PC}$ = 13.2 Hz), 130.8, 130.9, 133.5 (d, $^2J_{PC}$ = 10.9 Hz), 135.5, 136.5, 138.0, 143.5, 143.7 (d, $^4J_{PC}$ = 2.9 Hz), 165.8, 166.7 (d, $^2J_{PC}$ = 16.0 Hz) ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 10.8 ppm. FTIR (KBr): $\tilde{\nu}$ = 1648, 1717 cm^{-1}. λ_{max}($CHCl_3$): 363 nm. HRMS (ESI^+): calcd for $C_{43}H_{37}N_2O_5PS$ [M^+] 724.2160; found 724.2291.

(*E*)-Methyl 3-(2-(4-cyanophenyl)-5-oxo-1-tosyl-4-(tris(4-chlorophenyl)phosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)-acrylate (4o)

Yellow solid. M.p. 134–136 °C. R_f = 0.44 (hexanes–EA, 1 : 1). Isolated yield 54% (0.0635 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.51 (3H, s, Me), 3.50 (3H, s, CO_2Me), 4.98 (1H, d, J = 16.0 Hz, CH), 6.35 (1H, d, J = 16.0 Hz, CH), 7.29 (2H, d, J = 9.1 Hz, Ph), 7.34–7.47 (14H, m, Ph), 7.61 (2H, d, J = 8.1 Hz, Ph), 7.72 (2H, d, J = 8.1 Hz, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.7, 51.5, 59.7 (d, $^1J_{PC}$ = 132.0 Hz), 110.7, 118.9, 120.6 (d, $^1J_{PC}$ = 95.6 Hz), 121.7, 121.9, 124.3 (d, $^3J_{PC}$ = 12.5 Hz), 128.1, 129.1, 129.8 (d, $^3J_{PC}$ = 13.7 Hz), 131.0, 131.3, 134.9 (d, $^2J_{PC}$ = 11.7 Hz), 135.7, 136.0, 137.5, 140.6 (d, $^4J_{PC}$ = 3.5 Hz), 144.1, 165.8, 166.8 (d, $^2J_{PC}$ = 16.1 Hz) ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 11.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 1640, 1716 cm^{-1}. λ_{max}($CHCl_3$): 359 nm. HRMS (ESI^+): calcd for $C_{40}H_{28}Cl_3N_2O_5PS$ [M^+] 784.0522; found 784.0474.

(*E*)-Methyl 3-(2-(4-cyanophenyl)-5-oxo-1-tosyl-4-(tricyclohexylphosphoranylidene)-4,5-dihydro-1*H*-pyrrol-3-yl)-acrylate (4p)

Yellow solid. M.p. 115–117 °C. R_f = 0.08 (hexanes–EA, 1 : 1). Isolated yield 22% (0.0231 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.11–1.35 (18H, br, CH_2), 1.62–1.67 (12H, br, CH_2), 2.37 (3H, s, Me), 2.72–2.76 (3H, br, CH), 3.67 (3H, s, CO_2Me), 5.49 (1H, d, J = 15.9 Hz, CH), 7.22–7.25 (3H, m, Ph), 7.50 (2H, d, J = 8.4 Hz, Ph), 7.59 (2H, d, J = 8.1 Hz, Ph), 7.70 (2H, d, J = 8.1 Hz, Ph) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 21.5, 25.7, 26.9 (d, $^3J_{PC}$ = 15.8 Hz), 27.0 (d, $^2J_{PC}$ = 5.3 Hz), 30.8 (d, $^1J_{PC}$ = 46.8 Hz), 51.6, 57.5 (d, $^1J_{PC}$ = 105.7 Hz), 109.8, 113.8, 119.2, 120.1 (d, $^2J_{PC}$ = 10.4 Hz), 123.0, 123.8 (d, $^3J_{PC}$ = 9.4 Hz), 127.8, 128.7, 131.0, 131.2, 135.7, 138.1, 143.5, 166.6, 166.9

(d, $^2J_{PC}$ = 15.1 Hz) ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 27.6 ppm. FTIR (KBr): $\tilde{\nu}$ = 1629, 1720 cm^{-1}. $\lambda_{max}(CHCl_3)$: 413 nm. HRMS (ESI^+): calcd for $C_{40}H_{49}N_2O_5PS$ [M^+] 700.3099; found 700.3090.

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19 X-ray crystallographic data for compound **4l**: orange-red blocks; crystal size: 0.15 × 0.12 × 0.05 mm^3; formula: $C_{40}H_{28}Cl_7N_2O_7PS$; crystal system: triclinic; space group $P\bar{1}$; d = 1.539 mg m^{-3}, V = 2070.7(6) $Å^3$; a = 10.2628(16) Å; b = 14.1040(2) Å; c = 15.1470(2) Å; α = 85.999(3)°, β = 73.595(3)°, γ = 79.998(3)°; R_1 = 0.0726; R_w = 0.1825. CCDC-912012 contains the supplementary crystallographic data for this paper.

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