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Enyne Metathesis–Oxidation Sequence for the Synthesis of 2-Phosphono Pyrroles: Proof of the "Yne-then-Ene" Pathway

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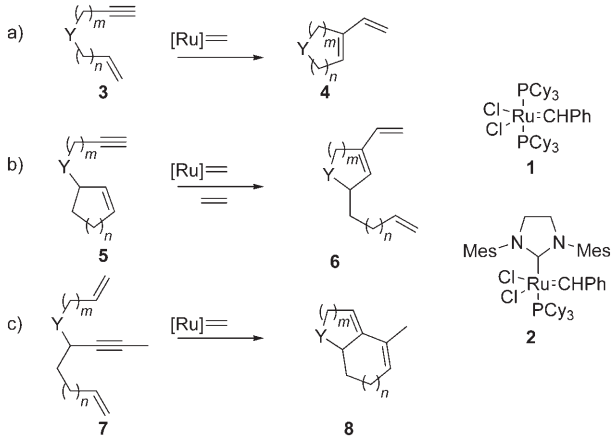
Abstract: A new tandem reaction sequence has been developed for the synthesis of 2-phosphono pyrroles. The sequence consists of ring-closing enyne metathesis of a substituted aminophosphonate, containing a terminal alkyne and an internal alkene, in combination with in situ oxidation of the produced 3-pyrrolines using tetrachloroquinone. By analyzing the formation of the end and certain byproducts, taking into account the difference in reactivity of different substrates and carefully studying spectroscopic data, it was found that the reaction proceeds by means of the "yne-then-ene" pathway. During the initiation phase, a new ruthenium carbene is formed which continues the propagation cycle.

Keywords: amino phosphonates · metathesis · reaction mechanisms · ruthenium carbenes · ruthenium

Introduction

With the discovery of new, well-defined catalysts, like the first- (**1**)[1] and second-generation (**2**)[2] Grubbs catalysts, olefin metathesis has become a very powerful synthetic tool in organic synthesis.[3] Over the years, ring-closing metathesis (RCM) has been applied to the synthesis of a wide variety of ring systems. The very related enyne metathesis, involving reaction between an alkene and an alkyne, has received much less attention.[4] Unlike olefin metathesis, all carbon atoms from the starting material are retained in the end product which contains a synthetically useful 1,3-diene moiety. The intramolecular enyne metathesis is categorized into three reaction patterns as illustrated in Scheme 1.[5] The metathesis of 1,ω-enynes **3** gives cyclic molecules **4** which contain *exo* and *endo* enes (type a). The reaction of alkynylcycloalkenes **5** with ethylene proceeds through the tandem ring-opening, ring-closing metathesis to yield the rearranged products **6** (type b). And finally, the tandem metathesis of the dienynes **7** gives the bicyclic heterocycles **8** (type c). Despite its usefulness, however, little is known about the mechanism of the reaction. Although important mechanistic work has already been carried out by Mori,[6] Kozmin,[7] and Wallace,[8] the question as to whether the reaction proceeds by means of the "yne-then-ene" or the "ene-then-yne" mechanism is still often raised. The yne-then-ene mechanism, a Chauvin-type mechanism,[9] is commonly postulated for the Ru-catalyzed enyne RCM reaction,[10] possibly as a legacy from earlier work with catalysts based on Group VI elements.[11] Recent kinetic studies, however, have brought up evidence for the ene-then-yne pathway in cross-enyne metathesis[12] and enyne metathesis with terminal olefins.[13]



Scheme 1. The three reaction patterns of intramolecular enyne metathesis.

Furthermore, enyne metathesis reactions of acyclic olefins, other than terminal olefins, with terminal alkynes have not been studied systematically.[6,14] A common goal in the

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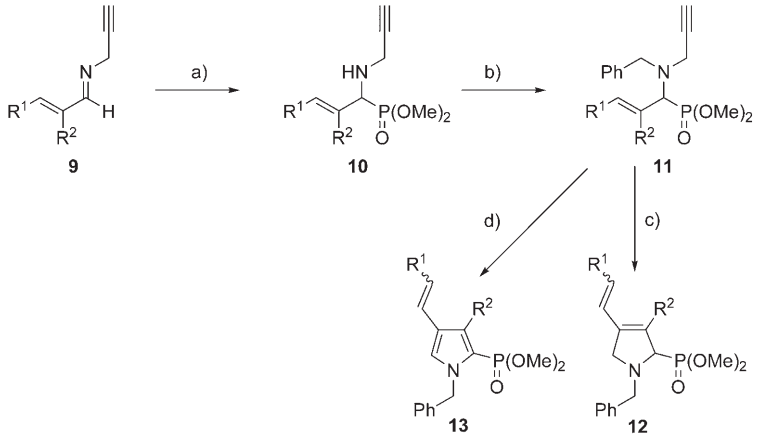
development of new reactions is to achieve multiple chemical transformations in a single synthetic operation.[15] Such sequential reactions have been demonstrated for olefin metathesis,[16] but have hardly been developed for enyne metathesis. So far, only a one-pot combination of enyne metathesis with a Diels–Alder reaction[14,17] or a cyclopropanation[18] have been reported. In this paper, we wish to report on the intramolecular enyne metathesis involving the reaction between a terminal alkyne and an internal olefin leading to 2-phosphono pyrrolines, followed by in situ oxidation to the corresponding 2-phosphono pyrroles.[19] The synthesis of aromatic compounds by RCM has only recently appeared in the literature,[20] but it is emerging as an important area and has very recently been reviewed by Donohoe and co-workers.[21] We also offer evidence pointing to the yne-then-ene pathway in this particular case. The evidence is threefold and is based on 1) the formation of certain end and byproducts, 2) the difference in reactivity of different substrates, and 3) spectroscopic data. With this work, we wish to contribute to a better mechanistic insight in enyne-metathesis and further develop the usefulness of this reaction.

Results and Discussion

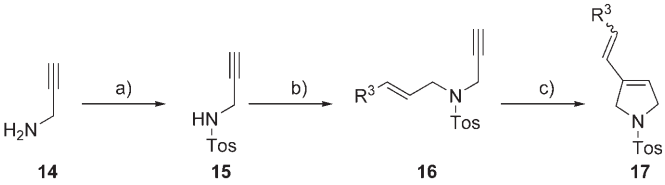
During our ongoing research into the synthesis of phosphonylated azaheterocycles,[22] interest grew in the use of ring-closing enyne metathesis for the synthesis of functionalized phosphono pyrroles. As we have demonstrated before, suitable diallylamines can be converted to the corresponding 3-pyrrolines by treatment with second-generation Grubbs catalyst and in situ oxidation to the pyrrole nucleus by a one-step one-pot protocol with the addition of tetrachloroquinone (TCQ).[23] However, we also observed that the correct choice of oxidizing agent is crucial, as DDQ (DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone) caused decomposition of the metathesis catalyst, illustrating the delicate balance of this one-pot reaction sequence. As enyne metathesis involves different ruthenium-species intermediates, it was hard to predict if TCQ would be able to oxidize the pyrrolines to the corresponding pyrroles while not affecting the metathesis reaction. The compounds thus obtained, 3-(1*H*-pyrrol-3-yl)alk-2-enes, are considered an important class of chemical compounds because of their application in the synthesis of a variety of molecules of biological interest, such as pyrrolobenzodiazepines, analogues of various amino acids, anticancer antibiotics, and analogues of porphobilinogen.[24]

α,β-Unsaturated N-propargyl aldimines **9** were phosphonylated with complete regioselectivity[25] by using dimethyl phosphite (DMP) and α-aminoalkenyl phosphonates **10** were obtained in high purity after a straightforward acid/base extraction (Scheme 2).[26] Subsequent benzylation by using benzyl bromide in acetone with K_2CO_3 as a base and a catalytic amount of NaI provided the substrates **11** for the enyne metathesis.



Scheme 2. a) 2 equiv DMP, MeOH, Δ, 2–3 h; b) 1.5 equiv BnBr, acetone, K_2CO_3, Δ, 16–20 h; c) 5 mol% **2**, benzene, Δ, 1 h; d) 5 mol% **2**, 1 equiv TCQ, benzene, Δ, 1 h.

To evaluate the effect of other substituents, N-tosyl amines **16** were also synthesized in two straightforward steps starting from monopropargylamine **14** (Scheme 3).



Scheme 3. a) 0.95 equiv TosCl, 1.1 equiv pyridine, CH_2Cl_2, RT, 16 h; b) 1.5 equiv electrophile, acetone, K_2CO_3, Δ, 16–20 h; c) 5 mol% **2**, benzene, Δ, 1 h.

Treatment of derivative **11a** with 5% of catalyst **2** in refluxing CH_2Cl_2 under a N_2 atmosphere resulted in a very slow (>12 h) conversion to **12a** as an *E*/*Z* mixture. Adding one equivalent of TCQ to the reaction mixture together with the catalyst resulted in the formation of the corresponding pyrrole **13a** in about the same time. It was found, however, that these transformations occur in less than 30 minutes when switching to refluxing benzene as a solvent (Table 1). In the case of **11b**, only catalytic deprotection of the propargyl amine was observed.[27,28] The detailed mecha-

Table 1. Synthesis of 2-phosphono pyrrolines **12** and 2-phosphono pyrroles **13**.

	R^1	R^2	Yield **10** [%]	Yield **11** [%]	Yield **12** [%] (*E*/*Z*)	Yield **13** [%] (*E*/*Z*)
a	2-furyl	H	69	54	68 (78:22)	78 (75:25)
b	CH_3	Ph	82	68	0	0
c	Ph	CH_3	92	65	88 (100:0)	85 (100:0)
d	propyl	H	95	60	78 (100:0)	48 (79:21)
e	Ph	H	70	64	86 (82:18)	82 (82:18)
f	isopropyl	H	65	46	75 (64:36)	–[a]

[a] The pyrrole could not be obtained in sufficient purity.

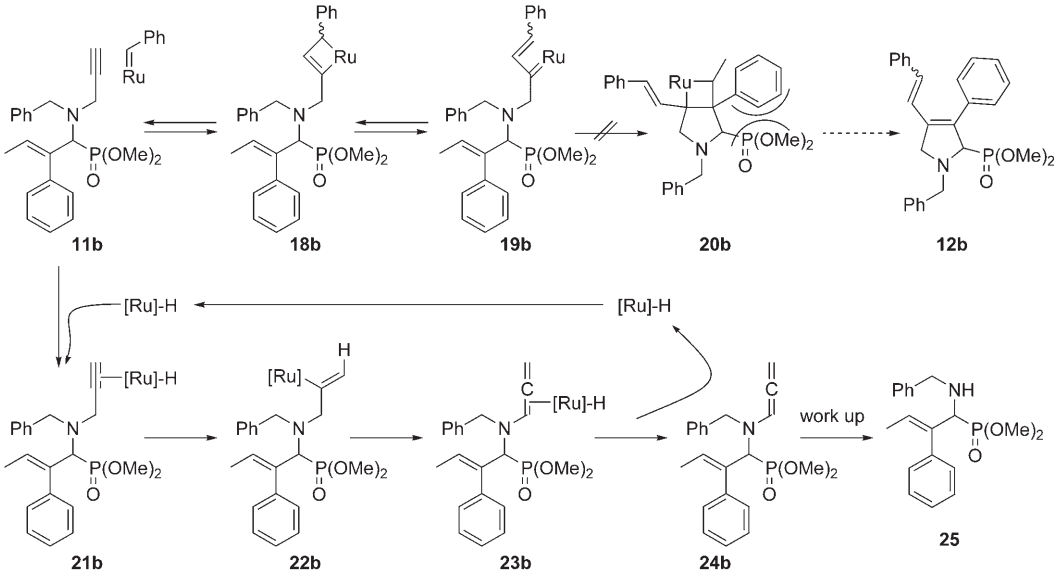
nism for the deprotection of the propargyl amine **11b** is unclear, but the ruthenium-hydride mechanism, which is typically used to explain the deprotection of allyl groups, may also apply in this case (Scheme 4). The conversion of metathesis intermediate **19b** to **20b** does not occur because of the large steric hindrance between the phenyl group and the phosphonate in intermediate **20b**. As all steps are in equilibrium, intermediate **19b** can be converted back to compound **11b**, which can react with a RuH-species, formed by decomposition of the metathesis catalyst, resulting in the production of **25** upon workup.

Derivatives **16** were also cleanly converted to the pyrrolines but could, as we have described before, not be oxidized to the pyrroles because of the electron-withdrawing substituent on nitrogen (Table 2).[29] Looking at the reaction mechanism, two pathways are possible (Scheme 5). In the yne-then-ene pathway enyne **11** reacts with the active catalyst **26**, with the bulky alkylidene group at the least-hindered end of the alkyne, to form metallacyclobutene **18**. Electrocyclic ring opening provides the diene **19**. Subsequent [2+2] cycloaddition and ring opening of the intermediate metallacyclobutane yields diene **12** and regenerates the active catalyst **26**. Alternatively, the ene-then-yne pathway begins with reaction of the alkene and provides the carbenoid **27** and side-product **30**. Carbenoid **27** undergoes an intramolecular cycloaddition to provide bicyclic metallacyclobutene **28**, which collapses to carbenoid **29**. Subsequent cross metathesis with another molecule of **11** generates product **12** and continues the catalytic cycle. Very often, both reaction pathways are reported as possible reaction routes. Recently, Lloyd-Jones and co-workers[13] reported that when working under "Mori's conditions"[30] ethylene gas reacts with carbenoids of type **29** in a second catalytic cycle producing the metathesis products and thus explaining the dramatic effect of ethylene on both the yield and the reaction rate of Ru-catalyzed enyne RCM reactions. As our experiments were performed under an inert nitrogen atmosphere, the fact that complete conversion is observed within 30 minutes tends to rule out the possibility of the ene-then-yne pathway, as this would contradict the low yields of enyne metathesis that predate Mori's observations. Looking at both reaction mechanisms it is clear that although both pathways provide the same end product, the intermediates are very different. The most striking difference is that when *x* mol% of metathesis catalyst is used in case of the yne-then-ene pathway, *x* mol% of the produced pyrrolines **12** should have R = Ph instead of R = R^1. In case of the ene-then-yne pathway, *x* mol% of **30** should be produced.

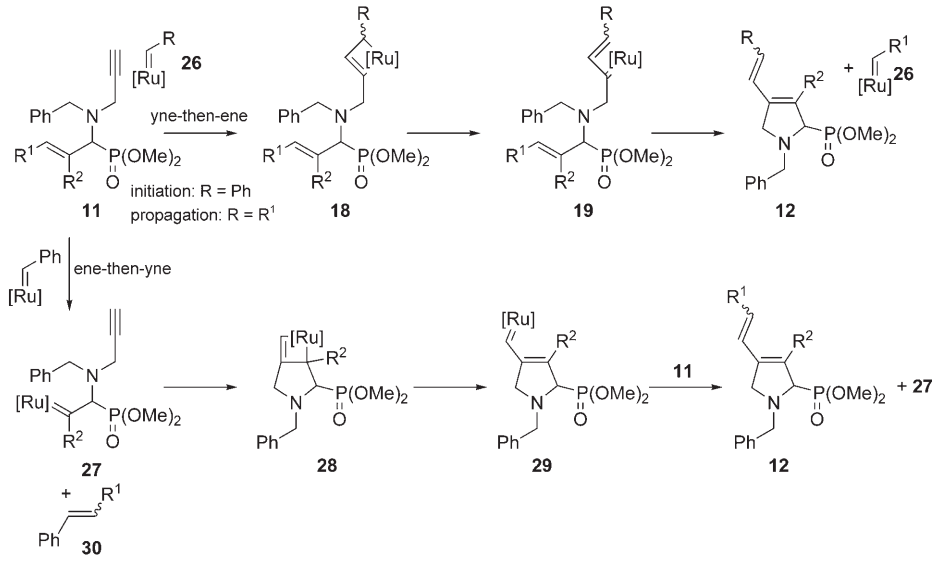
This implies that, for example, derivative **12e** should be produced as a side product during the synthesis of deriva-

Table 2. Synthesis of N-tosyl pyrrolines **17**.

	R^3	Yield **17** [%]	*E*/*Z*
g	CH_2Cl	86	100:0
h	CH_2Br	76	100:0
i	4-chloro-phenoxymethyl	73	63:37
j	Ph	89	100:0

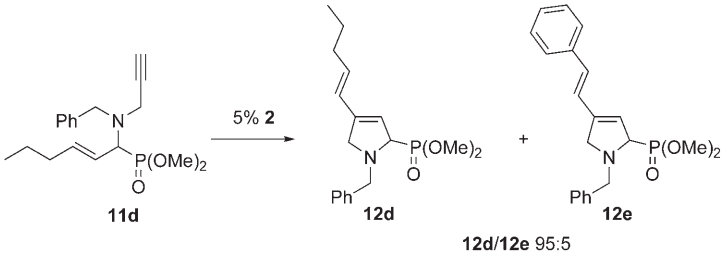


Scheme 4. Proposed mechanism for the catalytic deprotection of amine **11b**.



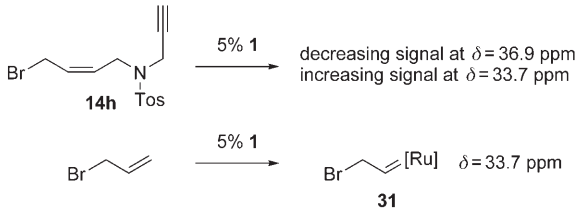
Scheme 5. The yne-then-ene and ene-then-yne pathway.

tives **12a**, **12d**, and **12f**. Indeed, it was found that in the ^{1}H and ^{31}P NMR spectra of the crude reaction mixture of **12d**, about 5% of derivative **12e** was present (Scheme 6). These findings are supported by comparison with a pure sample of **12e** and by LCMS analysis of the reaction mixture. Side products of type **30** were never detected.



Scheme 6. Formation of byproduct **12e** during the synthesis of **12d**.

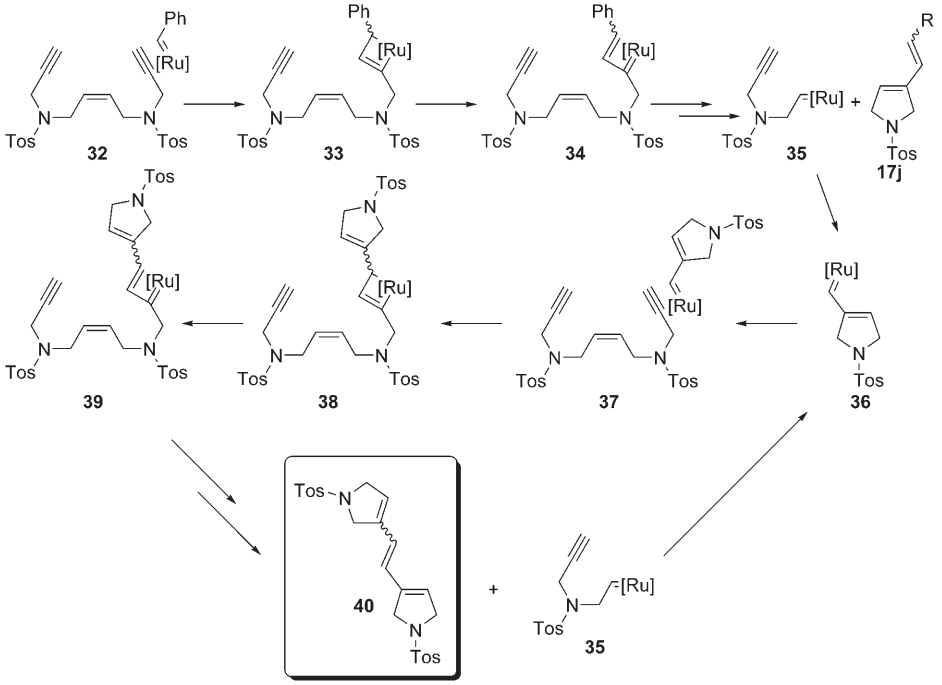
Another striking difference between the two pathways is that, in case of the yne-then-ene pathway, the Grubbs carbene is in situ converted to a new Ru species **26** which continues the catalytic cycle. This carbenoid is not formed in the other pathway. To detect this compound, derivative **14h** was dissolved in C_6D_6 and treated with the first-generation Grubbs catalyst **1** (Scheme 7). The reaction could easily be monitored by using ^{31}P NMR spectroscopy. The intensity of



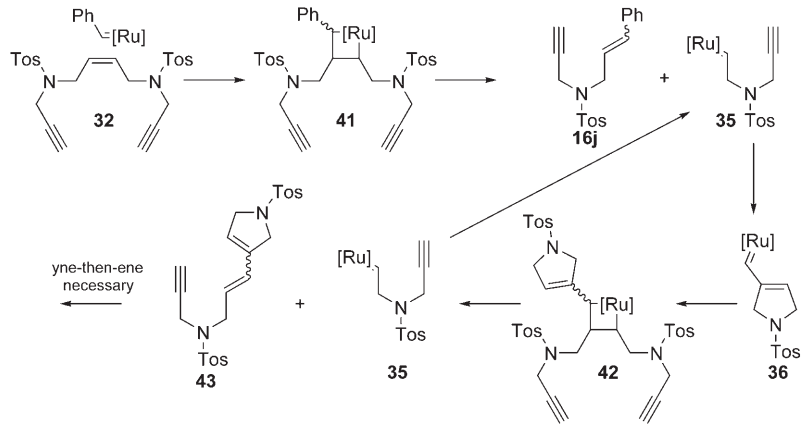
Scheme 7. Spectroscopic evidence for the formation of carbene **31**.

the signal of **1** ($\delta = 36.9$ ppm) slowly decreased and at the same time a new signal appeared at $\delta = 33.7$ ppm. In order to attribute this signal to **31**, allylbromide was treated in a separate experiment with **1**, resulting in the appearance of the same signal. This proves that it was indeed this ruthenium species that was formed during enyne metathesis of **14h**.

To obtain further proof of the yne-then-ene hypothesis, we looked for a compound that, depending on the reaction pathway, would give a different end product. Enediyne **32** was synthesized for this purpose by reacting two equivalents of **15** with one equivalent of (2*Z*)-1,4-dichloro-2-butene. Treatment of **32** with catalyst **2** resulted in complete conversion to **40** upon reflux in benzene. To the best of our knowledge, this is the first example of enyne metathesis for the synthesis of a conjugated triene from an enediyne. Although the steric hindrance of the first step in the yne-then-ene pathway might be lower than the one in the ene-then-yne pathway, the first metallocycle formed in this case is a strained cyclobutene, while in the other case it is a less-strained cyclobutane. Accepting the yne-then-ene pathway cleanly leads to the observed end product with concomitant production of x mol% of **17j** (Scheme 8). If, however, the ene-then-yne pathway is active, the observed end product cannot be obtained without accepting the yne-then-ene pathway at a certain point and the side product produced should be **16j** (Scheme 9). Following this reaction with ^{1}H NMR spectroscopy, a remarkable difference between catalysts **1** and **2** was observed. At room temperature, no conversion at all was observed when using catalyst **2**. Elevating the temperature to 35°C resulted in the immediate production of **40** and only trace amounts of **17j**. ^{1}H NMR spectroscopy revealed, however, that during the entire course of the reaction undissociated catalyst was still present. This is consistent with the fact that **2** shows very slow initiation, but very fast propagation. Thus ruthenium species **36**, continues the catalytic cycle producing **40** without the formation of **17j**. The reaction pattern of **1** is completely different on the other hand. Spectral data showed that running the reaction at 35°C resulted in the production of **17j** as the only reaction product with the simultaneous complete consumption of catalyst **1**. This is consistent with the fact that **1** shows very fast initiation but slower propagation and suggests that ruthenium species **36** with a first-generation ligand (PCy_3) is a rather poor catalyst. Raising the temperature to 60°C resulted in the production of compound **40**. The formation of **16j** as a side product was never observed.

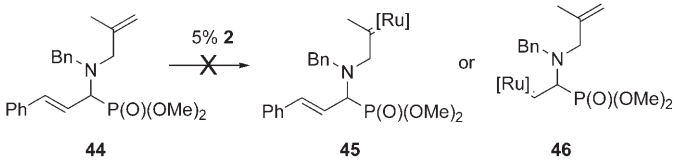


Scheme 8. Conversion of **32** to **40** following the yne-then-ene pathway.



Scheme 9. The "ene-then-yne" pathway does not lead to **40**.

Finally, evaluating **44**[23b] as a substrate showed that no metathesis occurred at all when a 2-methylallyl substituent is introduced at nitrogen (Scheme 10). Initiation at either double bond would result in a ruthenium species **45** or **46** with limited steric hindrance at the other double bound, especially compared to intermediates **19** in Scheme 4. Even switching of solvent to refluxing toluene or chlorobenzene did not result in any metathesis activity. This shows that removing the yne moiety has a very dramatic effect in the reactivity of these compounds.



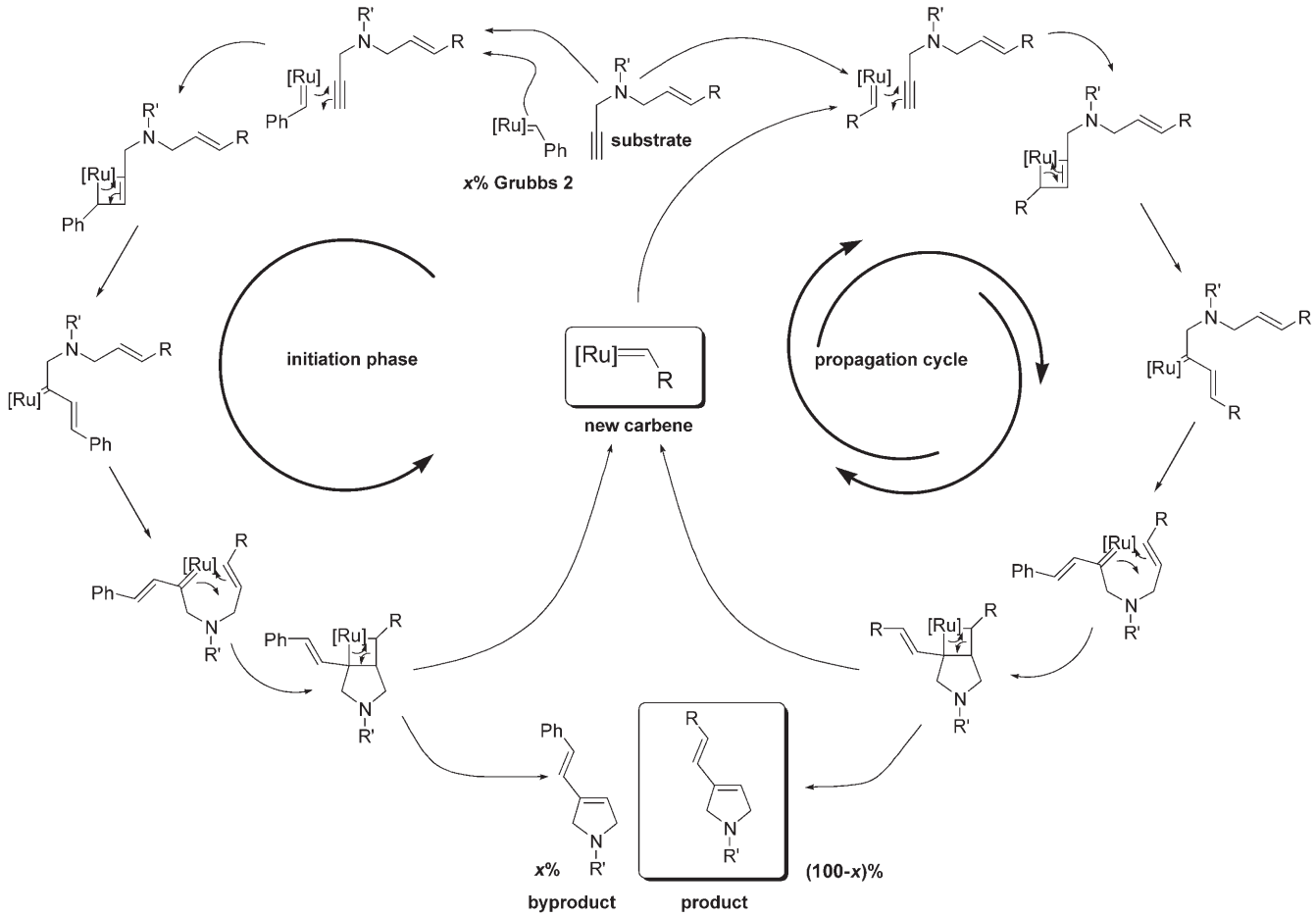
Scheme 10. Removal of the yne moiety blocks metathesis activity.

Besides the aforementioned mechanisms, the oxidative cyclization mechanism[31] and the possibility of a noncarbene complex acting as the catalytic species[32] were also investigated. It was observed however that treating the substrates with $[(p\text{-cymene})RuCl_2]_2$ or $[Cl_2Ru(PPh_3)_3]$ in refluxing toluene did not result in the production of the end products obtained with catalysts **1** or **2**. This observation in combination with the other results seems to rule out this possibility.

Scheme 11 summarizes our findings. In the initiation phase, the substrate reacts with the Grubbs carbene to yield, after a sequence of cycloadditions and cycloreversions, the byproduct and the new carbene. This new carbene can then react further with another molecule of substrate to produce the final product with regeneration of the carbene, after a sequence of cycloadditions and cycloreversions. In the case of complete initiation of the metathesis catalyst, x% of catalyst gives rise to a mixture of x% byproduct and $(100-x)$% of product upon completion of the reaction.

Conclusion

In summary, a new enyne-metathesis approach has been described, leading either to phosphonylated pyrrolines or pyrroles. Combining this enyne metathesis with in situ oxidation using tetrachloroquinone results in the exclusive formation of the 2-phosphono pyrroles. It was proven that, at least in this case, enyne metathesis with terminal alkynes and nonterminal alkenes follows the yne-then-ene pathway. Proof of this reaction mechanism is based on the formation of certain end and side products, spectroscopic data, and finally on the difference in reactivity of different substrates.



Scheme 11. Complete catalytic cycle for the conversion of enynes to pyrrolines.

This work contributes to a better mechanistic insight into enyne metathesis.

Experimental Section

General remarks: High resolution ^{1}H (300 MHz) and ^{13}C NMR (75 MHz) spectra were run on a Jeol JNM-EX 300 NMR spectrometer. Peak assignments were obtained with the aid of DEPT, 2D HSQC, and 2D COSY spectra. The compounds were diluted in deuterated solvents and the solvent used is indicated for each compound. Multiplicities are described by using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. LRMS were recorded on an Agilent 1100 Series VS (ES, 4000 V) mass spectrometer. IR spectra were obtained from a Perkin–Elmer Spectrum One IR spectrometer. For liquid samples, the spectra were collected by preparing a thin film of compound between two sodium chloride plates. The crystalline compounds were mixed with potassium bromide and pressed until a transparent potassium bromide plate was obtained. Melting points of crystalline compounds were measured with a Büchi 540 apparatus and are uncorrected. Elemental analysis was performed on a Perkin–Elmer 2400 Elemental Analyzer. Purification of reaction mixtures was performed by flash chromatography using a glass column with silica gel (Across, particle size: 0.035–0.070 mm, pore diameter: ca. 6 nm).

Synthesis of aldimines 9: A suitable aldehyde was dissolved in dry CH_2Cl_2 (freshly distilled from CaH_2) and 1.1 equivalents of propargylamine and 2 equivalents of $MgSO_4$ were added. The mixture was left to stir at room temperature for 24 h. After filtration of the solids and removal of the volatiles, the obtained aldimines were directly used for the synthesis of α-aminoalkenyl phosphonates **10**.

Synthesis of α-aminoalkenyl phosphonates 10: Aldimine **9** (10 mmol) was dissolved in MeOH (20 mL) in a round-bottomed flask. Then, dimethyl phosphite (DMP, 20 mmol) was added and the mixture was refluxed for 3–4 h. After removing the solvent under vacuum, the resulting oil was dissolved in diethyl ether (20 mL) and added to a separating funnel containing aq HCl (1 M, 20 mL). Both phases were vigorously mixed and the organic phase was removed from the funnel. The aqueous phase was washed twice with diethyl ether (10 mL), added to dichloromethane (20 mL), and then neutralized by using aq NaOH (3 M) until slightly alkaline. Both phases were vigorously mixed and the organic phase was then collected. The aqueous phase was extracted twice more with dichloromethane (10 mL) and the combined organic phases were dried by using $MgSO_4$. The α-aminoalkenyl phosphonates **10** were obtained in pure form after filtration and evaporation of the solvent.

Dimethyl (2*E*)-3-(2-furyl)-1-(prop-2-ynylamino)prop-2-enylphosphonate (10a): Yield: 69%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.88$ (br s, 1H; NH), 2.26 (t, $^{4}J(H,H) = 2.3$ Hz, 1H; CH_{alkyne}), 3.40 (br d, $^{2}J = 16.8$ Hz, 1H; NCH_AH_B), 3.57 (br d, $^{2}J(H,H) = 16.8$ Hz, $J = 2.0$ Hz, 1H; NCH_AH_B), 3.79–3.84 (m, 6H; $2 \times OCH_3$), 3.99 (dd, $^{2}J(H,P) = 17.3$ Hz, $^{3}J(H,H) = 8.9$ Hz, 1H; CHP), 5.98 (ddd, $^{3}J(H,H) = 15.7$ Hz, $^{3}J(H,H) = 8.9$ Hz, $^{3}J(H,P) = 6.5$ Hz, 1H; PCHC*H*), 6.29 (br s, 1H; CH_{furyl}), 6.38 (br s, 1H; CH_{furyl}), 6.55 (dd, $^{3}J(H,H) = 15.7$ Hz, $^{4}J(H,P) = 4.5$ Hz, 1H; C*H*), 7.36 ppm (br s, 1H; OCH_{furyl}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 36.1$ (d, $^{3}J(C,P) = 18.5$ Hz; NCH_2), 53.6 (d, $^{2}J(C,P) = 7.5$ Hz; OCH_3), 53.7 (d, $^{2}J(C,P) = 7.5$ Hz; OCH_3), 56.5 (d, $^{1}J(C,P) = 156.9$ Hz; CHP), 72.5 (*C*CH), 80.9 (*C*CH),

109.0 (d, ^5J(C,P) = 2.3 Hz; C*C*H$_{furyl}$), 111.5 (CH*C*H$_{furyl}$), 121.0 (d, ^2J = 10.4 Hz; *C*HCHP), 123.7 (d, ^3J(C,P) = 15.0 Hz; CH), 142.5 (O*C*H$_{furyl}$), 151.9 ppm (d, ^4J(C,P) = 3.5 Hz; C$_{quat,furyl}$); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 26.2 ppm; IR (film): $\tilde{\nu}$ = 1243 (P=O), 2105 cm^{-1} (alkyne); MS: *m*/*z* (%): 270.7 [*M*+H]$^+$ (52), 160.8 [*M*−P(O)(OMe)$_2$+H]$^+$ (100); elemental analysis (%) calcd for $C_{12}H_{16}NO_4P$: C 53.53, H 5.99, N 5.20; found: C 53.84, H 6.18, N 5.26.

The aldehyde used for the synthesis of aldimine **9b** was an *E*/*Z* mixture. As a consequence, derivative **10b** was also obtained as a mixture. The two forms could be separated. Total yield: 82%.

Dimethyl (2*E*)-2-phenyl-1-(prop-2-ynylamino)but-2-enylphosphonate (10b): ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67 (dd, ^5J(H,P) = 5.5 Hz, ^3J(H,H) = 6.9 Hz, 3H; CH_3), 1.95 (brs, 1H; NH), 2.34 (t, ^4J(H,H) = 2.3 Hz, 1H; CH), 3.51 (dd, ^4J(H,H) = 2.3 Hz, ^2J(H,H) = 16.9 Hz, 1H; NC*H*$_A$H$_B$), 3.59 (dt, ^4J(H,H) = 2.3 Hz, ^2J(H,H) = 16.9 Hz, 1H; NCH$_A$*H*$_B$), 3.60 (d, ^3J(H,P) = 10.4 Hz, 3H; OCH_3), 3.68 (d, ^3J(H,P) = 10.4 Hz, 3H; OCH_3), 4.09 (d, ^2J(H,H) = 20.6 Hz, 1H; CHP), 6.00 (dq, ^3J(H,H) = 6.9 Hz, ^4J(H,P) = 5.0 Hz, 1H; CHPh), 7.24–7.38 ppm (m, 5H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.0 (CH_3), 35.9 (d, ^3J(C,P) = 17.3 Hz; NCH_2), 53.3 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 53.4 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 60.2 (d, ^1J(C,P) = 155.8 Hz; CHP), 72.40 (CH), 81.3 (C), 127.1 (CH_{arom}), 128.0 (d, ^3J(C,P) = 10.4 Hz, C*C*H), 128.2 (2×CH_{arom}), 129.4 (2×CH_{arom}), 134.6 (d, ^2J(C,P) = 4.6 Hz; *C*CH), 139.0 ppm (d, ^3J(C,P) = 2.3 Hz; C_{arom}); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 26.6 ppm; IR (film): $\tilde{\nu}$ = 3293 (NH), 1246 (P=O), 1055, 1030 cm^{-1}; MS: *m*/*z* (%): 184.2 [*M*−P(O)(OMe)]$^+$ (100), 294.2 [*M*+H]$^+$ (23); elemental analysis (%) calcd for $C_{15}H_{20}NO_3P$: C 61.43, H 6.87, N 4.78; found: C 61.61, H 6.99, N 4.80.

Dimethyl (2*Z*)-2-phenyl-1-(prop-2-ynylamino)but-2-enylphosphonate (10b): M.p. 81–82 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.89 (brs, 1H; NH), 1.94 (dd, ^5J(H,P) = 4.5 Hz, ^3J(H,H) = 7.0 Hz, 3H; CH_3), 2.41 (t, ^4J(H,H) = 2.0 Hz, 1H; CH), 3.25 (dd, ^4J(H,H) = 2.0 Hz, ^2J(H,H) = 16.8 Hz, 1H; NC*H*$_A$H$_B$), 3.39 (dt, ^4J(H,H) = 2.0 Hz, ^2J(H,H) = 16.8 Hz, 1H; NCH$_A$*H*$_B$), 3.72 (d, ^3J(H,P) = 8.8 Hz, 3H; OCH_3), 3.75 (d, ^3J(H,P) = 9.1 Hz, 3H; OCH_3), 4.60 (d, ^2J(H,P) = 24.5 Hz, 1H; CHP), 6.02 (dq, ^3J(H,H) = 7.0 Hz, ^4J(H,P) = 4.3 Hz, 1H; CHPh), 7.23–7.35 (m, 3H; 3×CH_{arom}), 7.57–7.60 ppm (m, 2H; 2×CH_{arom}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.5 (CH_3), 36.3 (d, ^3J(C,P) = 19.6 Hz; NCH_2), 53.4 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 53.7 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 54.4 (d, ^1J(C,P) = 156.9 Hz, 1H; CHP), 72.2 (CH), 81.3 (C), 127.2 (CH_{arom}), 128.3 (2×CH_{arom}), 128.3 (2×CH_{arom}), 131.7 (d, ^3J(C,P) = 11.5 Hz; C*C*H), 135.4 (d, ^2J(C,P) = 3.5 Hz; *C*CH), 140.9 ppm (C_{arom}); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 27.02; IR (KBr): $\tilde{\nu}$ = 3239 (NH), 1235 (P=O), 1060, 1027 cm^{-1}; MS: *m*/*z* (%): 184.2 [*M*−P(O)(OMe)]$^+$ (100), 294.2 [*M*+H]$^+$ (65); elemental analysis (%) calcd for $C_{15}H_{20}NO_3P$: C 61.43, H 6.87, N 4.78; found: C 61.28, H 7.06, N 4.86.

Dimethyl (2*E*)-2-methyl-3-phenyl-1-(prop-2-ynylamino)prop-2-enylphosphonate (10c): Yield: 92%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98 (brs, 1H; NH), 2.01 (dd, ^4J(H,P) = 3.3 Hz, ^4J(H,H) = 1.4 Hz, 3H; CH_3), 2.48 (t, ^4J(H,H) = 2.3 Hz, 1H; CH), 3.34 (dd, ^4J(H,H) = 2.3 Hz, ^2J(H,H) = 16.1 Hz, 1H; NC*H*$_A$H$_B$), 3.52 (dt, ^4J(H,H) = 2.3 Hz, ^2J(H,H) = 16.1 Hz, 1H; NCH$_A$*H*$_B$), 3.81 (d, ^3J(H,P) = 10.7 Hz, 3H; OCH_3), 3.83 (d, ^3J(H,P) = 10.5 Hz, 3H; OCH_3), 3.96 (d, ^2J(H,P) = 19.5 Hz, 1H; CHP), 6.65 (brd, ^4J(H,P) = 4.7 Hz, 1H; CHPh), 7.22–7.38 ppm (m, 5H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.8 (CH_3), 36.0 (d, ^3J(C,P) = 19.6 Hz; NCH_2), 53.6 (d, ^2J(C,P) = 6.9 Hz, 2×OCH_3), 62.1 (d, ^1J(C,P) = 153.4 Hz; CHP), 72.4 (CH), 81.0 (C), 126.9 (CH_{arom}), 128.3 (2×CH_{arom}), 129.1 (CH_{arom}), 129.1 (CH_{arom}), 131.0 (d, ^3J(C,P) = 12.7 Hz, C*C*H), 131.5 (d, ^2J(C,P) = 6.9 Hz; *C*CH), 137.2 ppm (d, ^4J(C,P) = 2.3 Hz; C_{arom}); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 26.67 ppm; IR (film): $\tilde{\nu}$ = 3293 (NH), 1246 (P=O), 1053, 1030 cm^{-1}; MS: *m*/*z* (%): 294.2 [*M*+H]$^+$ (100); elemental analysis (%) calcd for $C_{15}H_{20}NO_3P$: C 61.43, H 6.87, N 4.78; found: C 61.37, H 6.65, N 4.89.

Dimethyl (2*E*)-1-(prop-2-ynylamino)hex-2-enylphosphonate (10d): Yield: 95%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.91 (t, 3H, ^3J(H,H) = 7.2 Hz; CH_3), 1.44 (sextet, ^3J(H,H) = 7.2 Hz, 3H; CH_3CH_2), 1.82 (brs, 1H; NH), 2.09 (dt, ^3J(H,H) = 10.7 Hz, ^3J = 7.2 Hz, 2H; CH_2CH), 2.23 (t, ^4J(H,H) = 2.2 Hz, 1H; CH_{alkyne}), 3.35 (dd, ^2J(H,H) = 17.1 Hz, ^4J(H,H) = 2.2 Hz, 1H; NC*H*$_A$H$_B$), 3.52 (dt, ^2J(H,H) = 17.1 Hz, ^4J(H,H) = 2.2 Hz, 1H; NC*H*$_A$H$_B$), 3.78–3.85 (m, 7H; CHP + 2×OCH_3), 5.25–5.35 (m, 1H; CH), 5.78–5.89 ppm (m, 1H; CH_2CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.6 (CH_3), 22.2 (CH_3CH_2), 34.6 (*C*H$_2$CH), 35.7 (d, ^3J(C,P) = 18.4 Hz; NCH_2), 53.5 (d, ^2J(C,P) = 13.8 Hz; OCH_3), 53.5 (d, ^2J(C,P) = 13.8 Hz; OCH_3), 56.5 (d, ^1J(C,P) = 157.2 Hz; CHP), 72.2 (C*C*H), 81.1 (*C*CH), 122.8 (d, ^2J(C,P) = 9.2 Hz; CH), 138.3 ppm (d, ^3J(C,P) = 13.8 Hz; CH); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 27.4 ppm; IR (film): $\tilde{\nu}$ = 1245 (P=O), 2104 cm^{-1} (alkyne); MS: *m*/*z* (%): 246.7 [*M*+H]$^+$ (100); elemental analysis (%) calcd for $C_{11}H_{20}NO_3P$: C 53.87, H 8.22, N 5.71; found: C 53.69, H 8.19, N 5.71.

Dimethyl (2*E*)-3-phenyl-1-(prop-2-ynylamino)prop-2-enylphosphonate (10e): Yield: 70%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.89 (brs, 1H; NH), 2.27 (t, ^4J(H,H) = 2.0 Hz, 1H; CH_{alkyne}), 3.40 (dd, ^2J(H,H) = 17.2 Hz, ^4J(H,H) = 2.0 Hz, 1H; NC*H*$_A$H$_B$), 3.57 (dt, ^2J(H,H) = 17.2 Hz, ^4J(H,H) = 2.0 Hz, 1H; NCH$_A$*H*$_B$), 3.81 (d, ^3J(H,P) = 10.7 Hz, 3H; OCH_3), 3.82 (d, ^3J(H,P) = 10.7 Hz, 3H; OCH_3), 4.03 (dd, ^2J(H,P) = 16.9 Hz, ^3J(H,H) = 8.8 Hz, 1H; CHP), 6.07 (ddd, ^3J(H,H) = 16.0 Hz, ^3J(H,H) = 8.8 Hz, ^3J(H,P) = 6.1 Hz, 1H; PCHC*H*), 6.73 (dd, ^3J(H,H) = 16.0 Hz, ^4J(H,P) = 6.7 Hz, 1H; C*H*Ph), 7.24–7.43 ppm (m, 5H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 36.1 (d, ^3J(C,P) = 17.2 Hz; NCH_2), 53.6 (d, ^2J(C,P) = 7.5 Hz; OCH_3), 53.7 (d, ^2J(C,P) = 7.5 Hz; OCH_3), 56.8 (d, ^1J(C,P) = 156.0 Hz; CHP), 72.5 (C*C*H), 81.0 (*C*CH), 122.6 (d, ^2J (C,P) = 9.2 Hz; *C*HCHP), 126.8 (2×CH_{arom}), 128.2 (CH_{arom}), 128.7 (2×CH_{arom}), 135.8 (d, ^3J(C,P) = 13.8 Hz, CH), 136.2 ppm (C_{arom}); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 26.5; IR (film): $\tilde{\nu}$ = 1243 (P=O), 2106 cm^{-1} (alkyne); MS: *m*/*z* (%): 280.7 [*M*+H]$^+$ (50), 170.8 [*M*−P(O)(OMe)$_2$+H]$^+$ (100); elemental analysis (%) calcd for $C_{14}H_{18}NO_3P$: C 60.21, H 6.50, N 5.02; found: C 60.38, H 6.53, N 5.22.

Dimethyl (2*E*)-4-methyl-1-(prop-2-ynylamino)pent-2-enylphosphonate (10f): Yield: 65%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.02 (d, ^3J(H,H) = 6.9 Hz, 6H; CH_3), 1.74 (brs, 1H; NH), 2.22 (t, ^4J(H,H) = 2.2 Hz, 1H; CH_{alkyne}), 2.30–2.43 (m, 1H; CH), 3.34 (dd, ^2J(H,H) = 16.9 Hz, ^4J(H,H) = 2.2 Hz, 1H; NC*H*$_A$H$_B$), 3.52 (ddd, ^2J(H,H) = 16.9 Hz, ^4J(H,H) = 2.2 Hz, ^4J(H,P) = 2.0 Hz, 1H; NCH$_A$*H*$_B$), 3.77 (dd, ^2J(H,P) = 19.3 Hz, ^3J(H,H) = 10.2 Hz, 1H; CHP), 3.79 (d, ^3J(H,P) = 10.5 Hz, 3H; OCH_3), 3.80 (d, ^3J(H,P) = 10.5 Hz, 3H; OCH_3), 5.22–5.32 (m, 1H; =C*H*CHP), 5.82 ppm (ddd, ^3J(H,H) = 14.5 Hz, ^3J(H,H) = 6.6 Hz, ^4J(H,P) = 4.3 Hz, 1H; =CH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.14 (2×CH_3), 31.1 (CH), 35.6 (d, ^3J(C,P) = 18.5 Hz; NCH_2), 53.4 (d, ^2J(C,P) = 8.1 Hz; OCH_3), 53.5 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 56.4 (d, ^1J(C,P) = 158.1 Hz; CHP), 72.1 (C*C*H), 81.1 (*C*CH), 119.8 (d, ^2J(C,P) = 8.1 Hz; =*C*HCHP), 145.0 ppm (d, ^3J(C,P) = 12.7 Hz; =CH); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 27.32 ppm; IR (film): $\tilde{\nu}$ = 2104 (C=C), 1243 (P=O), 1035 cm^{-1} (br, P−O); MS: *m*/*z* (%): 246 [*M*+H]$^+$ (62), 136 [*M*+H−PO(OMe)$_2$]$^+$ (100); elemental analysis (%) calcd for $C_{11}H_{20}NO_3P$: C 53.87, H 8.22, N 5.71; found: C 53.97, H 8.23, N 5.72.

Synthesis of *N*-benzyl α-aminoalkenyl phosphonates 11: α-Aminoalkenyl phosphonate **10** (5 mmol), K_2CO_3 (20 mmol), NaI (0.5 mmol), and acetone (10 mL) were added to a round-bottomed flask. Then, benzyl bromide (10 mmol) was added and the mixture was refluxed for 24 h. The course of the reaction was conveniently monitored by means of ^{31}P NMR spectroscopic analysis of samples taken directly from the reaction mixture. After complete conversion of the starting material, the solids were removed by filtration and the solvent was removed by evaporation under reduced pressure. The corresponding *N*-benzyl α-aminoalkenyl phosphonate **11** can be obtained in pure form as a pale yellow oil after column chromatography over silica gel by using a hexane/ethyl acetate mixture as a mobile phase.

Dimethyl (2*E*)-1-[benzyl(prop-2-ynyl)amino]-3-(2-furyl)prop-2-enylphosphonate (11a): Yield: 54%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.25 (t, ^4J(H,H) = 2.2 Hz, 1H; CH_{alkyne}), 3.43 (dd, ^2J(H,H) = 17.2 Hz, ^4J(H,H) = 2.2 Hz, 1H; NC*H*$_A$H$_B$C), 3.63 (brd, ^2J(H,H) = 17.2 Hz, ^4J(H,H) = 2.2 Hz, 1H; NCH$_A$*H*$_B$C), 3.67 (d, ^2J(H,H) = 13.8 Hz, 1H; NC*H*$_A$H$_B$Ph), 3.74 (d, ^3J(H,P) = 10.8 Hz, 3H; OCH_3), 3.86 (d, ^3J(H,P) = 10.2 Hz, 3H; OCH_3), 3.97 (dd, ^2J(H,P) = 22.4 Hz, ^3J(H,H) = 9.5 Hz, 1H; CHP), 4.23 (d, ^2J(H,H) = 13.8 Hz, 1H; NCH$_A$*H*$_B$Ph), 6.20–6.40 (m, 3H; PCHC*H* + CC*HCH*$_{furyl}$), 6.51 (dd, ^3J(H,H) = 15.7 Hz, ^4J(H,P) = 3.0 Hz, 1H; C*H*), 7.06–7.39 ppm (m, 6H; Ph + OCH_{furyl}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.7 (d, ^3J(C,P) = 8.1 Hz; N*C*H$_2$C), 53.1 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 53.8

(d, ^2J(C,P) = 6.9 Hz; OCH_3), 55.4 (d, ^3J(C,P) = 6.9 Hz; NCH_2Ph), 60.5 (d, ^1J(C,P) = 161.5 Hz; CHP), 73.0 (*C*CH), 80.6 (*C*CH), 109.0 (d, ^5J(C,P) = 2.3 Hz; CCH_{furyl}), 111.5 (CCHCH_{furyl}), 118.4 (*C*HCHP), 125.0 (d, ^3J(C,P) = 15.0 Hz; CH), 127.4 (CH_{arom}), 128.5 (2×CH_{arom}), 129.1 (2×CH_{arom}), 138.5 (C_{arom}), 142.6 (OCH), 152.0 ppm (OC); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 25.9 ppm; IR (film): $\tilde{\nu}$ = 1245 cm^{-1} (P=O); MS: *m*/*z* (%): 360.8 $[M+H]^+$ (100); chromatography (hexane/EtOAc 4:6): R_f = 0.28; elemental analysis (%) calcd for $C_{19}H_{22}NO_4P$: C 63.50, H 6.17, N 3.90; found: C 63.85, H 6.36, N 3.79.

For the synthesis of derivative **11b**, the (2*E*)-form of **10b** was used.

Dimethyl (2*E*)-1[benzyl(prop-2-ynyl)amino]-2-phenylbut-2-enylphosphonate (11b): Yield: 68%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.71 (dd, 3H, ^5J(H,P) = 1.9 Hz, ^3J(H,H) = 6.9 Hz; CH_3), 2.48 (t, ^4J(H,H) = 2.3 Hz, 1H; CH), 3.43 (dd, ^4J(H,H) = 2.3 Hz, ^2J(H,H) = 17.0 Hz, 1H; NC*H*$_A$H$_B$), 3.59 (d, ^2J(H,H) = 13.2 Hz, 1H; NC*H*$_A$H$_B$Ph), 3.68 (dt, ^4J(H,H) = 2.3 Hz, ^2J(H,H) = 17.0 Hz, 1H; NCH$_A$*H*$_B$), 3.71 (d, ^3J(H,P) = 10.5 Hz, 3H; OCH_3), 3.79 (d, ^3J(H,P) = 10.5 Hz, 3H; OCH_3), 4.05 (dd, ^4J(H,P) = 1.6 Hz, ^2J(H,H) = 13.2 Hz, 1H; NCH$_A$*H*$_B$Ph), 4.10 (d, ^2J(H,P) = 22.8 Hz, 1H; CHP), 6.44 (dq, ^3J(H,H) = 6.9 Hz, ^4J(H,P) = 2.5 Hz, 1H; C*H*CH_3), 7.05–7.38 ppm (m, 10H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 15.3 (CH_3), 40.5 (d, ^3J(C,P) = 5.8 Hz; NCH_2), 53.0 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 53.6 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 55.7 (d, ^3J(C,P) = 9.2 Hz; NCH_2Ph), 62.4 (d, ^1J(C,P) = 156.9 Hz; CHP), 72.6 (CH), 80.8 (C), 127.0 (CH_{arom}), 127.2 (CH_{arom}), 128.2 (2×CH_{arom}), 128.2 (2×CH_{arom}), 129.1 (2×CH_{arom}), 129.2 (2×CH_{arom}), 129.9 (d, ^3J(C,P) = 5.8 Hz, *C*CH), 133.7 (d, ^2J(C,P) = 4.6 Hz, *C*CH), 138.6 (C_{arom}), 141.1 ppm (d, ^3J(C,P) = 10.4 Hz, *C*Ph); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 26.38 ppm; IR (film): $\tilde{\nu}$ = 1243 (P=O), 1058, 1030 cm^{-1}; MS: *m*/*z* (%): 384.2 $[M-P(O)(OMe)]^+$ (100), 294.2 $[M+H]^+$ (23); chromatography (hexane/EtOAc 4:6): R_f = 0.43; elemental analysis (%) calcd for $C_{22}H_{26}NO_3P$: C 68.92, H 6.83, N 3.65; found: C 68.80, H 6.82, N 3.64.

Dimethyl (2*E*)-[benzyl(prop-2-ynyl)amino]-2-methyl-3-phenylprop-2-enyl phosphonate (11c): Yield: 65%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.11 (t, ^4J(H,H) = 1.4 Hz, 3H; CH_3), 2.28 (t, ^4J(H,H) = 2.1 Hz, 1H; CH), 3.39 (dd, ^4J(H,H) = 2.1 Hz, ^2J(H,H) = 17.5 Hz, 1H; NC*H*$_A$H$_B$), 3.56 (dt, ^4J(H,H) = 2.1 Hz, ^2J(H,H) = 17.5 Hz, 1H; NCH$_A$*H*$_B$), 3.78 (d, ^3J(H,P) = 10.7 Hz, 3H; OCH_3), 3.84 (d, ^3J(H,P) = 10.7 Hz, 3H; OCH_3), 3.91 (d, ^2J(H,P) = 17.6 Hz, 1H; CHP), 3.93 (d, ^2J(H,H) = 13.3 Hz, 1H; NC*H*$_A$H$_B$Ph), 4.01 (d, ^2J(H,P) = 13.3 Hz, 1H; NCH$_A$*H*$_B$Ph), 6.77 (brs, 1H; CHPh), 7.22–7.42 ppm (m, 10H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 17.6 (d, ^3J(C,P) = 4.6 Hz; CH_3), 40.1 (d, ^3J(C,P) = 9.2 Hz; NCH_2), 53.0 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 53.5 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 55.3 (d, ^3J(C,P) = 8.1 Hz; NCH_2Ph), 67.1 (d, ^1J(C,P) = 154.6 Hz; CHP), 73.6 (CH), 79.2 (C), 127.0 (CH_{arom}), 127.3 (CH_{arom}), 128.3 (2×CH_{arom}), 128.4 (CH_{arom}), 128.4 (2×CH_{arom}), 128.9 (CH_{arom}), 129.1 (2×CH_{arom}), 132.4 (d, ^3J(C,P) = 11.5 Hz; *C*CH), 132.4 (d, ^2J(C,P) = 3.5 Hz; *C*CH), 137.3 (C_{arom}), 138.7 ppm (C_{arom}); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 26.7; IR (film): $\tilde{\nu}$ = 1600, 1248 (P=O), 1031 cm^{-1}; MS: *m*/*z* (%): 384.2 $[M+H]^+$ (100); chromatography (hexane/EtOAc 4:6): R_f = 0.20; elemental analysis (%) calcd for $C_{22}H_{26}NO_3P$: C 68.92, H 6.83, N 3.65; found: C 68.76, H 7.03, N 3.45.

Dimethyl (2*E*)-1-[benzyl(prop-2-ynyl)amino]hex-2-enylphosphonate (11d): Yield: 60%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, ^3J(H,H) = 6.9 Hz, 3H; CH_3), 1.46 (sextet, ^3J(H,H) = 6.9 Hz, 2H; C$H_2$$CH_3$), 2.04 (dq, ^3J(H,H) = 6.9 Hz, ^3J(H,H) = 2.5 Hz, 2H; CHCH_2), 2.21 (t, ^4J(H,H) = 2.1 Hz, 1H; CH), 3.35 (dd, ^4J(H,H) = 2.1 Hz, ^2J(H,H) = 17.6 Hz, 1H; NC*H*$_A$H$_B$), 3.56 (d, ^2J(H,H) = 13.3 Hz, 1H; NC*H*$_A$H$_B$Ph), 3.60 (dt, ^4J(H,H) = 2.1 Hz, ^2J(H,H) = 17.6 Hz, 1H; NCH$_A$*H*$_B$), 3.72 (d, ^3J(H,P) = 10.5 Hz, 3H; OCH_3), 3.82 (dd, ^3J(H,H) = 9.2 Hz, ^3J(H,P) = 27.4 Hz, 1H; CHP), 3.84 (d, ^2J(H,P) = 10.4 Hz, 3H; OCH_3), 4.18 (d, ^2J(H,H) = 13.3 Hz, 1H; NCH$_A$*H*$_B$Ph), 5.62 (ddd, ^3J(H,H) = 15.2 Hz, ^3J(H,H) = 9.2 Hz, ^3J(H,P) = 6.0 Hz, 1H; *C*HCH), 5.79 (ddt, ^3J(H,H) = 15.2 Hz, ^3J(H,H) = 6.9 Hz, ^4J(H,P) = 2.9 Hz, 1H; C*H*CH_2), 7.23–7.38 ppm (m, 5H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.7 (CH_3), 22.2 (CH_2CH_3), 34.8 (CH*C*H$_2$), 40.6 (d, ^3J(C,P) = 9.2 Hz; NCH_2), 52.9 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 53.7 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 55.3 (d, ^3J(C,P) = 8.1 Hz; NCH_2Ph), 60.5 (d, ^1J(C,P) = 161.5 Hz; CHP), 72.7 (CH), 80.8 (C), 119.7 (NCH*C*H), 127.3 (CH_{arom}), 128.4 (2×CH_{arom}), 129.1 (2×CH_{arom}), 138.7 (C_{arom}), 139.8 ppm (d, ^3J(C,P) = 15.0 Hz; *C*HCH$_2$); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 26.98 ppm; IR (film): $\tilde{\nu}$ = 1244 (P=O), 1034 cm^{-1}; MS: *m*/*z* (%): 336.7 $[M+H]^+$ (100); chromatography (hexane/EtOAc 4:6): R_f = 0.27; elemental analysis (%) calcd for $C_{18}H_{26}NO_3P$: C 64.46, H 7.81, N 4.18; found: C 64.27, H 7.79, N 4.29.

Dimethyl (2*E*)-1-[benzyl(prop-2-ynyl)amino]-3-phenylprop-2-enylphosphonate (11e): ^{1}H NMR (300 MHz, $CDCl_3$): δ: 2.26 (t, ^4J(H,H) = 2.5 Hz, 1H; CH_{alkyne}), 3.54 (dd, ^2J(H,H) = 17.1 Hz, ^4J(H,H) = 2.5 Hz, 1H; NC*H*$_A$H$_B$C), 3.65 (dd, ^2J(H,H) = 17.1 Hz, ^4J(H,H) = 2.5 Hz, 1H; NCH$_A$*H*$_B$C), 3.69 (d, ^2J(H,H) = 13.5 Hz, 1H; NC*H*$_A$H$_B$Ph), 3.73 (d, ^3J(H,P) = 10.5 Hz, 3H; OCH_3), 3.87 (d, ^3J(H,P) = 10.5 Hz, 3H; OCH_3), 3.99 (dd, ^2J(H,P) = 22.3 Hz, ^3J(H,H) = 9.5 Hz, 1H; CHP), 4.22 (d, ^2J(H,H) = 13.5 Hz, 1H; NCH$_A$*H*$_B$Ph), 6.42 (ddd, ^3J(H,H) = 15.8 Hz, ^3J(H,H) = 9.5 Hz, ^3J(H,P) = 6.9 Hz, 1H; PCHC*H*), 6.66 (dd, ^3J(H,H) = 15.8 Hz, ^4J(H,P) = 3.0 Hz, 1H; C*H*Ph), 7.26–7.45 ppm (m, 10H; Ph); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 40.7 (d, ^4J(C,P) = 8.1 Hz; NCH_2C), 53.1 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 53.9 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 55.5 (d, ^3J(C,P) = 8.1 Hz; NCH_2Ph), 61.0 (d, ^1J(C,P) = 161.5 Hz, CHP), 73.1 (*C*CH), 80.8 (*C*CH), 119.9 (*C*HCHP), 126.8 (2×CH_{arom}), 127.4 (CH_{arom}), 128.3 (CH_{arom}), 128.5 (2×CH_{arom}), 128.8 (2×CH_{arom}), 129.1 (2×CH_{arom}), 136.3 (C_{arom}), 137.2 (d, ^3J(C,P) = 15.0 Hz, CH), 138.5 ppm (C_{arom}); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 26.1 ppm; IR (film): $\tilde{\nu}$ = 1246 cm^{-1} (P=O); MS: *m*/*z* (%): 370.8 $[M+H]^+$ (100); chromatography (hexane/EtOAc 4:6): R_f = 0.42; elemental analysis (%) calcd for $C_{21}H_{24}NO_3P$: C 68.28, H 6.55, N 3.79; found: C 68.42, H 6.56, N 3.78. Yield: 64%.

Dimethyl (2*E*)-1-[benzyl(prop-2-ynyl)amino]-4-methylpent-2-enylphosphonate (11f): Yield: 46%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (d, ^3J(H,H) = 6.6 Hz, 3H; CH_3), 1.05 (d, ^3J(H,H) = 6.1 Hz, 3H; CH_3), 2.22 (t, ^4J(H,H) = 2.2 Hz, 1H; CH_{alkyne}), 2.34–2.45 (m, 1H; CH), 3.38 (dd, ^2J(H,H) = 16.9 Hz, ^4J(H,P) = 2.1 Hz, 1H; NC*H*$_A$H$_B$), 3.57 (d, ^2J(H,H) = 13.2 Hz, 1H; NC*H*$_A$H$_B$Ph), 3.59 (brd, ^2J(H,H) = 16.8 Hz, 1H; NCH$_A$*H*$_B$), 3.71 (d, ^3J(H,P) = 10.5 Hz, 3H; OCH_3), 3.78 (dd, ^2J(H,P) = 22.0 Hz, ^3J(H,H) = 9.6 Hz, 1H; CHP), 3.83 (d, ^3J(H,P) = 10.5 Hz, 3H; OCH_3), 4.17 (d, ^2J(H,H) = 13.5 Hz, 1H; NCH$_A$*H*$_B$Ph), 5.59 (ddd, ^3J(H,H) = 15.4 Hz, ^3J(H,H) = 9.4 Hz, ^3J(H,P) = 6.6 Hz, 1H; =C*H*CHP), 5.77 (ddd, ^3J(H,H) = 15.4 Hz, ^3J(H,H) = 6.3 Hz, ^4J(H,P) = 2.8 Hz, 1H; =CH), 7.22–7.37 (m, 5H; CH_{arom}); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.2 (CH_3), 22.2 (CH_3), 31.4 (CH), 40.5 (d, ^3J(C,P) = 9.2 Hz; NCH_2), 53.0 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 53.6 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 55.1 (d, ^3J(C,P) = 8.1 Hz; NCH_2Ph), 60.5 (d, ^1J(C,P) = 161.5 Hz; CHP), 72.7 (C*C*H), 80.7 (*C*CH), 116.5 (=*C*HCHP), 127.2 (2×CH_{arom}), 128.3 (2×CH_{arom}), 129.1 (CH_{arom}), 138.6 ($C_{q,arom}$), 146.6 ppm (d, ^3J(C,P) = 15.0 Hz; =CH); ^{31}P NMR (121 MHz, $CDCl_3$): δ = 26.86 ppm; IR (film): $\tilde{\nu}$ = 2238 (alkyne), 1244 (P=O), 1034 cm^{-1} (br, P–O); MS: *m*/*z* (%): 336 $[M+H]^+$ (100), 226 $[M+H-PO(OMe)_2]^+$ (27); chromatography (hexane/EtOAc 3:2): R_f = 0.22; elemental analysis (%) calcd for $C_{18}H_{26}NO_3P$: C 64.46, H 7.81, N 4.18; found: C 64.67, H 7.94, N 4.28.

Synthesis of 2-phosphono 3-pyrrolines 12: Aminoalkenyl phosphonate **11** (0.39 mmol) and benzene (10 mL) were added to an oven-dried round-bottomed flask. The solution was refluxed under a nitrogen atmosphere and Grubbs second-generation catalyst **2** (0.02 mmol, 5 mol%) was added to the boiling solution. The reaction mixture was then further refluxed for 16 h. The course of the reaction was conveniently monitored by means of ^{31}P NMR spectroscopic analyses of samples taken directly from the reaction mixture. The product was coated on silica gel by removal of the solvent in vacuo and purified by flash chromatograhy. The 2-phosphono 3-pyrrolines **12** could also be obtained by an acid–base extraction, but the yield was significantly lower in this fashion.

Dimethyl 1-benzyl-4-[(*E*)-2-(2-furyl)vinyl]-2,5-dihydro-1*H*-pyrrol-2-ylphosphonate (12a): Yield: 68%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.43–3.56 (m, 1H; NC*H*$_A$H$_B$C), 3.69 (d, ^2J(H,H) = 13.0 Hz, 1H; NC*H*$_A$H$_B$Ph), 3.77–3.87 (m, 7H; 2×OCH_3 + NCH$_A$*H*$_B$C), 4.20–4.26 (m, 1H; CHP), 4.36 (d, ^2J(H,H) = 13.0 Hz, 1H; NCH$_A$*H*$_B$Ph), 5.81 (brs, 1H; NCHC*H*), 6.09 (d, 1H, ^2J(H,H) = 16.5 Hz; NCH_2CCHC*H*), 6.23 (d, ^3J(H,H) = 3.3 Hz, 1H; OCCH), 6.35–6.38 (m, 1H; OCHC*H*), 6.79 (d, ^3J(H,H) = 16.5 Hz, 1H; NCH_2CC*H*), 7.14–7.44 ppm (m, 6H; Ph+OCH); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 53.2 (d, ^2J(C,P) = 8.1 Hz; OCH_3), 53.9 (d, ^2J(C,P) = 6.9 Hz; OCH_3), 59.2 (d, ^3J(C,P) = 9.2 Hz, NCH_2C), 60.3 (d, ^3J(C,P) = 4.6 Hz, NCH_2Ph), 69.0 (d, ^1J(C,P) = 174.2 Hz, CHP), 109.4 (OCCH),

111.8 (OCH*C*H), 119.2 (d, J=4.6 Hz; NCH$_2$CCH*C*H), 120.7 (d, ^4J(C,P)= 5.8 Hz; NCH$_2$C*C*H), 122.6 (d, ^2J(C,P)=8.1 Hz; NCH*C*H), 128.4 (CH$_{arom}$), 128.5 (2×CH$_{arom}$), 128.7 (2×CH$_{arom}$), 139.3 (C$_{arom}$), 142.6 (OCH), 152.7 ppm (OC); ^{31}P NMR (121 MHz, CDCl$_3$): δ=24.28 ppm; IR (film): $\tilde{\nu}$=1240 (P=O), 1056, 1033 cm^{-1}; MS: m/z (%): 360.8 [M+H]$^+$ (100); chromatography (hexane/EtOAc 4:6): R_f=0.12; elemental analysis (%) calcd for $C_{19}H_{22}NO_4P$: C 63.50, H 6.17, N 3.90; found: C 63.31, H 6.07, N 3.91.

As described before, treatment of **11b** with catalyst **2** resulted in catalytic deprotection of the propargyl group after 72 h in refluxing benzene.

Dimethyl (2*E*)-1[benzylamino]-2-phenylbut-2-enylphosphonate (25): Yield: 42%; ^{1}H NMR (300 MHz, CDCl$_3$): δ=1.69 (dd, ^5J(H,P)=5.2 Hz, ^3J(H,H)=6.9 Hz, 3H; CH$_3$), 2.58 (brs, 1H; NH), 3.63 (d, ^3J(H,P)= 10.5 Hz, 3H; OCH$_3$), 3.66 (d, ^3J(H,H)=10.5 Hz, 3H; OCH$_3$), 3.76 (d, ^2J(H,P)=22.8 Hz, 1H; CHP), 3.76 (d, ^2J(H,H)=13.1 Hz, 1H; NCH_AH$_B$Ph), 3.98 (d, ^2J(H,H)=13.1 Hz, 1H; NCH$_A$$H_B$Ph), 5.97 (dq, ^3J(H,H)=6.9 Hz, ^4J(H,P)=5.0 Hz, 1H; C*H*CH$_3$), 7.20–7.36 ppm (m, 10H; Ph); ^{13}C NMR (75 MHz, CDCl$_3$): δ=15.1 (CH$_3$), 51.3 (d, ^3J(C,P)= 17.3 Hz; NCH$_2$Ph), 53.1 (d, ^2J(C,P)=6.9 Hz; OCH$_3$), 53.7 (d, ^2J(C,P)= 6.9 Hz, OCH$_3$), 61.1 (d, ^1J(C,P)=155.8 Hz; CHP), 127.1 (CH$_{arom}$), 127.2 (CH$_{arom}$), 127.6 (d, ^3J(C,P)=5.8 Hz, C*C*H), 128.2 (2×CH$_{arom}$), 128.4 (2× CH$_{arom}$), 128.5 (2×CH$_{arom}$), 129.2 (2×CH$_{arom}$), 135.9 (d, ^2J(C,P)=2.3 Hz, *C*CH), 139.0 (d, ^3J(C,P)=10.4 Hz, C$_{arom}$), 139.5 ppm (C$_{arom}$); ^{31}P NMR (121 MHz, CDCl$_3$): δ=26.38; IR (film): $\tilde{\nu}$=1248 (P=O), 1057, 1031 cm^{-1}; MS: m/z (%): 346.3 [M+H]$^+$ (100); chromatography (hexane/EtOAc 4:6): R_f=0.28; elemental analysis (%) calcd for $C_{19}H_{24}NO_3P$: C 66.07, H 7.00, N 4.06; found: C 66.26, H 7.31, N 4.07.

Dimethyl 1-benzyl-3-methyl-4-[(*E*)-2-phenylvinyl]-2,5-dihydropyrrol-2-ylphosphonate (12c): Yield: 88%; ^{1}H NMR (300 MHz, CDCl$_3$): δ=2.00 (d, ^4J(H,P)=1.9 Hz, 3H; CH$_3$), 3.56 (d, ^2J(H,H)=12.0 Hz, 1H; NCH_AH$_B$C), 3.67 (d, ^2J(H,H)=13.2 Hz, 1H; NCH_AH$_B$Ph), 3.82 (d, ^3J(H,P)=10.2 Hz, 6H; 2×OCH$_3$), 4.00 (dd, ^2J(H,H)=12.0 Hz, ^4J(H,H)=5.8 Hz, 1H; NCH$_A$$H_B$C), 4.05–4.14 (m, 1H; CHP), 4.32 (d, ^2J(H,H)=13.2 Hz, 1H; NCH$_A$$H_B$Ph), 6.25 (dd, ^3J(H,H)=16.2 Hz, ^4J(H,H)=1.5 Hz, 1H; CHPh), 6.95 (d, ^3J(H,H)=16.2 Hz, 1H; C*H*CHPh), 7.12–7.45 ppm (m, 10H; 2× Ph); ^{13}C NMR (75 MHz, CDCl$_3$): δ=12.4 (CH$_3$), 53.4 (d, ^3J(C,P)= 8.1 Hz; NCH$_2$C), 53.1 (d, ^2J(C,P)=6.9 Hz; OCH$_3$), 53.6 (d, ^2J(C,P)= 6.9 Hz; OCH$_3$), 60.2 (d, ^3J(C,P)=6.9 Hz; NCH_2C), 60.9 (d, ^3J(C,P)= 5.8 Hz, NCH$_2$Ph), 73.1 (d, ^1J(C,P)=171.9 Hz; CHP), 120.5 (d, ^4J(C,P)= 4.6 Hz; *C*HCHPh), 126.4 (2×CH$_{arom}$), 127.2 (CH$_{arom}$), 127.7 (CH$_{arom}$), 128.5 (2×CH$_{arom}$), 128.7 (4×CH$_{arom}$), 130.0 (d, ^5J(C,P)=3.5 Hz; *C*HPh), 130.9 (d, ^2J(C,P)=6.9 Hz; *C*CH$_3$), 134.0 (d, ^3J(C,P)=12.7 Hz; *C*CH), 137.4 (C$_{arom}$), 139.5 ppm (NCH$_2$*C*$_{arom}$); ^{31}P NMR (121 MHz, CDCl$_3$): δ= 24.8 ppm; IR (film): $\tilde{\nu}$=1255 (P=O), 1056, 1030 cm^{-1}; MS: m/z (%): 384.2 [M+H]$^+$ (100); chromatography (hexane/EtOAc 2:8) R_f=0.26; elemental analysis (%) calcd for $C_{22}H_{26}NO_3P$: C 68.92, H 6.83, N 3.65; found: C 68.75, H 6.85, N 3.70.

Dimethyl 1-benzyl-4-[(1*E*)-pent-1-enyl]-2,5-dihydro-1*H*-pyrrol-2-ylphosphonate (12d): Yield: 78%; ^{1}H NMR (300 MHz, CDCl$_3$): δ=0.87 (t, ^3J(H,H)=7.3 Hz, 3H; CH$_3$), 1.37 (sextet, ^3J(H,H)=7.3 Hz, 2H; CH_2CH$_3$), 2.04 (q, ^3J(H,H)=7.3 Hz, 2H; CHCH_2), 3.34–3.46 (m, 1H; NCH_AH$_B$), 3.66 (d, ^2J(H,H)=13.2 Hz, 1H; NCH_AH$_B$Ph), 3.78–3.88 (m, 1H; NCH$_A$$H_B$), 3.80 (d, ^3J(H,P)=10.5 Hz, 3H; OCH$_3$), 3.83 (d, ^3J(H,P)= 10.2 Hz, 3H; OCH$_3$), 4.13–4.19 (m, 1H; CHP), 4.33 (d, ^2J(H,H)= 13.2 Hz, 1H; NCH$_A$$H_B$Ph), 5.46 (dt, ^3J(H,H)=15.8 Hz, ^3J(H,H)=7.3 Hz, 1H; C*H*CH$_2$), 5.56 (s, 1H; NCHC*H*), 6.16 (d, ^3J(H,H)=15.8 Hz, 1H; C*H*CH), 7.23–7.45 ppm (m, 5H; Ph); ^{13}C NMR (75 MHz, CDCl$_3$): δ= 13.8 (CH$_3$), 22.4 (*C*H$_2$CH$_3$), 35.0 (CHCH_2), 53.2 (d, ^2J(C,P)=8.1 Hz; OCH$_3$), 53.8 (d, ^2J(C,P)=6.9 Hz; OCH$_3$), 59.7 (d, ^3J(C,P)=8.1 Hz; NCH$_2$), 60.4 (d, ^3J(C,P)=3.5 Hz; NCH_2Ph), 68.8 (d, ^1J(C,P)=174.2 Hz; CHP), 119.2 (d, ^2J(C,P)=6.9 Hz; NCH*C*H), 124.1 (d, ^4J(C,P)=4.6 Hz; *C*HCH), 127.1 (CH$_{arom}$), 128.4 (2×CH$_{arom}$), 128.7 (2×CH$_{arom}$), 134.4 (d, ^5J(C,P)=3.5 Hz, *C*HCH$_2$), 139.5 (C$_{arom}$), 141.6 ppm (d, ^4J(C,P)=12.7 Hz; C$_q$); ^{31}P NMR (121 MHz, CDCl$_3$): δ=24.80 ppm; IR (film): $\tilde{\nu}$=1241 (P= O), 1058, 1033 cm^{-1}; MS: m/z (%): 336.7 [M+H]$^+$ (100); chromatography (hexane/EtOAc 0:1): R_f=0.4; elemental analysis (%) calcd for $C_{18}H_{26}NO_3P$: C 64.46, H 7.81, N 4.18; found: C 64.67, H 7.80, N 4.21.

Dimethyl 1-benzyl-4-[(*E*)-2-phenylvinyl]-2,5-dihydro-1*H*-pyrrol-2-ylphosphonate (12e): Yield: 86%; *trans*/*cis* 82:18; ^{1}H NMR (300 MHz, CDCl$_3$): δ=3.57 (d, ^2J(H,H)=12.9 Hz, 1H; NCH_AH$_B$C), 3.71 (d, ^2J(H,H)=13.5 Hz, 1H; NCH_AH$_B$Ph), 3.76 (d, 3H, ^3J(H,P)=10.5 Hz; OCH$_3$), 3.79 (d, ^3J(H,P)=10.2 Hz, 3H; OCH$_3$), 3.81 (d, ^3J(H,P)= 10.5 Hz, 3H; OCH$_3$), 3.85 (d, ^3J(H,P)=10.2 Hz, 3H; OCH$_3$), 4.00 (dt, ^2J(H,H)=12.9 Hz, ^4J(H,H)=7.0 Hz, 1H; NCH$_A$$H_B$C), 4.20–4.28 (m, 1H; CHP), 4.37 (d, ^2J(H,H)=13.5 Hz, 1H; NCH$_A$$H_B$Ph), 5.73 (brs, 1H; CCH), 5.83 (brs, 1H; CCH), 6.20 (d, ^3J(H,H)=12.0 Hz, 1H; CHC*H*Ph), 6.29 (d, ^2J(H,H)=16.0 Hz, 1H; CHC*H*Ph), 6.56 (d, ^2J(H,H)=12.0 Hz, 1H; C*H*CHPh), 6.88 (d, ^2J(H,H)=16.0 Hz, 1H; C*H*CHPh), 7.15–7.44 ppm (m, 10H; 2×Ph); ^{13}C NMR (75 MHz, CDCl$_3$): δ=53.2 (d, ^2J(C,P)=6.9 Hz; OCH$_3$), 53.9 (d, ^2J(C,P)=8.1 Hz; OCH$_3$), 59.4 (d, ^3J(C,P)=8.1 Hz; NCH_2C), 60.0 (d, ^3J(C,P)=5.8 Hz; NCH_2C), 60.4 (d, ^3J(C,P)=4.6 Hz; NCH$_2$Ph), 61.3 (d, ^3J(C,P)=6.9 Hz; NCH$_2$Ph), 67.7 (d, ^1J(C,P)=174.2 Hz; NCHP), 69.0 (d, ^1J(C,P)=175.4 Hz; NCHP), 122.3 (d, ^4J(C,P)=4.6 Hz; *C*HCHPh), 122.6 (d, ^2J(C,P)=8.1 Hz; NCH*C*H), 122.3 (d, ^3J(C,P)=17.3 Hz; NCH*C*H), 122.6 (*C*HCHPh), 126.0 (CH$_{arom}$), 126.6 (2×CH$_{arom}$), 127.0 (CH$_{arom}$), 127.2 (CH$_{arom}$), 127.3 (2×CH$_{arom}$), 127.9 (2× CH$_{arom}$), 128.0 (CH$_{arom}$), 128.3 (2×CH$_{arom}$), 128.5 (2×CH$_{arom}$), 128.7 (2× CH$_{arom}$), 128.8 (2×CH$_{arom}$), 128.9 (2×CH$_{arom}$), 131.5 (d, ^5J(C,P)=3.5 Hz; *C*HPh), 132.1 (d, ^5J(C,P)=3.5 Hz; *C*HPh), 136.8 (NCH$_2$*C*), 137.6 (NCH$_2$*C*), 138.8 (C$_{arom}$), 139.3 (C$_{arom}$), 140.7 (d, ^6J(C,P)=13.8 Hz; C$_{arom}$), 141.6 ppm (d, ^6J(C,P)=12.7 Hz; C$_{arom}$); ^{31}P NMR (121 MHz, CDCl$_3$): δ= 24.57, 24.36 ppm; IR (film): $\tilde{\nu}$=1602, 1241 (P=O), 1057, 1032 cm^{-1}; MS: m/z (%): 370.8 [M+H]$^+$ (100); chromatography (hexane/EtOAc 2:8): R_f=0.35; elemental analysis (%) calcd for $C_{21}H_{24}NO_3P$: C 68.28, H 6.55, N 3.79; found: C 68.12, H 6.67, N 3.95.

Dimethyl 1-benzyl-4-(3-methyl-but-1-enyl)-2,5-dihydro-1*H*-pyrrol-2-ylphosphonate (12f): Yield: 75%; *trans*/*cis* 64:36; ^{1}H NMR (300 MHz, CDCl$_3$): δ=0.92 (d, ^3J(H,H)=6.6 Hz, 3H; CH$_3$), 0.94 (d, ^3J(H,H)= 6.6 Hz, 3H; CH$_3$), 0.96 (d, ^3J(H,H)=6.9 Hz, 6H; CH$_3$), 2.25–2.40 (m, 1H; CH), 2.48–2.61 (m, 1H; CH), 3.34–3.45 (m, 1H; CH_AH$_B$), 3.46–3.59 (m, 1H; CH_AH$_B$), 3.66 (d, ^2J(H,H)=13.5 Hz, 1H; CH_AH$_B$Ph), 3.70 (d, ^2J(H,H)=13.5 Hz, 1H; CH_AH$_B$Ph), 3.80 (d, ^3J(H,P)=10.2 Hz, 6H; OCH$_3$), 3.83 (d, ^3J(H,P)=10.2 Hz, 3H; OCH$_3$), 3.84 (d, ^3J(H,P)= 10.2 Hz, 3H; OCH$_3$), 3.83–3.89 (m, 1H; CH$_A$$H_B$), 3.90–3.98 (m, 1H; CH$_A$$H_B$), 4.08–4.19 (m, 2×1H; CHP, *trans*+*cis*), 4.30 (d, ^2J(H,H)= 13.5 Hz, 1H; CH$_A$$H_B$Ph), 4.34 (d, ^2J(H,H)=13.5 Hz, 1H; CH$_A$$H_B$Ph), 5.25–5.32 (m, 1H; =C*H*CH), 5.42 (dd, ^3J(H,H)=15.8 Hz, ^3J(H,H)= 6.9 Hz, 1H; =C*H*CH), 5.56–5.60 (m, 1H; =C*H*CHP), 5.61–5.65 (m, 1H; =C*H*CHP), 5.78 (d, ^3J(H,H)=11.8 Hz, 1H; =CH), 6.13 (d, ^3J(H,H)= 15.8 Hz, 1H; =CH), 7.23–7.41 ppm (m, 2×5H; CH$_{arom}$, *trans*+*cis*); ^{13}C NMR (75 MHz, CDCl$_3$): δ=22.2 (CH$_3$), 23.2 (CH$_3$), 23.3 (CH$_3$), 28.2 (CH), 31.3 (CH), 53.0 (d, ^2J(C,P)=8.1 Hz; OCH$_3$), 53.1 (d, ^2J(C,P)= 6.9 Hz; OCH$_3$), 53.6 (d, ^2J(C,P)=6.9 Hz; OCH$_3$), 53.8 (d, ^2J(C,P)= 8.1 Hz; OCH$_3$), 59.6 (d, ^3J(C,P)=9.2 Hz; CH$_2$), 60.2 (d, ^3J(C,P)=3.5 Hz; CH$_2$Ph), 60.3 (d, ^3J(C,P)=3.5 Hz; CH$_2$Ph), 62.2 (d, ^3J(C,P)=8.1 Hz; CH$_2$), 68.0 (d, ^1J(C,P)=174.2 Hz; CHP), 68.7 (d, ^1J(C,P)=175.4 Hz; CHP), 119.4 (d, ^2J(C,P)=6.9 Hz; =*C*HCHP), 119.6 (d, ^4J(C,P)=4.6 Hz; = CH), 121.1 (d, ^4J(C,P)=4.6 Hz; =CH), 122.0 ppm (d, ^2J(C,P)=6.9 Hz; = *C*HCHP), 127.0, 128.3, 128.5, 128.6 (CH$_{arom}$, *trans*+*cis*), 139.2 (C$_{q,arom}$), 139.4 (C$_{q,arom}$), 140.5 (d, ^3J(C,P)=12.7 Hz; =C$_q$), 141.1 (d, ^5J(C,P)= 3.5 Hz; =*C*HCH), 141.6 (=CHCH), 141.6 ppm (d, ^3J(C,P)=12.7 Hz; = C$_q$); ^{31}P NMR (121 MHz, CDCl$_3$): δ=24.75, 24.77 ppm; IR (film): $\tilde{\nu}$= 1645 (C=C), 1242 (P=O), 1032 cm^{-1}; MS: m/z (%): 336 [M+H]$^+$ (100), 226 [M+H−PO(OMe)$_2$]$^+$ (46); chromatography (hexane/EtOA*c* 1:4): R_f=0.35; elemental analysis (%) calcd for $C_{18}H_{26}NO_3P$: C 64.46, H 7.81, N 4.18; found: C 64.47, H 7.82, N 4.20.

Synthesis of 2-phosphono pyrroles 13: Aminoalkenyl phosphonate **11** (0.39 mmol), tetrachloroquinone (0.43 mmol), and benzene (10 mL) were added to an oven-dried round-bottomed flask. The solution was refluxed under a nitrogen atmosphere and Grubbs second-generation catalyst **2** (0.02 mmol, 5 mol%) was added to this boiling solution. The reaction mixture was then further refluxed for 16 h. The course of the reaction was conveniently monitored by means of ^{31}P NMR spectroscopic analyses of samples taken directly from the reaction mixture. The product was coated on silica gel by removal of the solvent in vacuo and purified by flash chromatography.

Dimethyl 1-benzyl-4-[(*E*)-2-(2-furyl)vinyl]-1*H*-pyrrol-2-ylphosphonate (13a): Yield: 78%; *trans*/*cis* 75:25; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.61$ (d, $^3J(H,P) = 5.5$ Hz, 3H; OCH_3), 3.62 (d, $^3J(H,P) = 11.6$ Hz, 6H; 2×OCH_3), 3.65 (d, $^3J(H,P) = 5.8$ Hz, 3H; OCH_3), 5.31 (s, 2H; NCH_2Ph), 5.35 (s, 2H; NCH_2Ph), 6.08 (d, $^3J(H,H) = 12.7$ Hz, 1H; OCC*H*), 6.19 (d, 1H, $^3J(H,H) = 12.7$ Hz; OCCHC*H*), 6.21 (d, $^3J(H,H) = 3.3$ Hz, 1H; OCCH), 6.33 (d, $^3J(H,H) = 3.3$ Hz, 1H; OCCH), 6.37 (dd, $^3J(H,H) = 3.3$ Hz, $^3J(H,H) = 1.8$ Hz, 1H; OCHC*H*), 6.60 (d, $^3J(H,H) = 16.2$ Hz, 1H; OCC*H*), 6.84 (d, $^3J(H,H) = 16.2$ Hz, 1H; OCCHC*H*), 6.97 (dd, $^4J(H,H) = 1.7$ Hz, $^4J(H,P) = 5.5$ Hz, 1H; NC*H*), 7.01 (dd, $^4J(H,H) = 1.7$ Hz, $^3J(H,P) = 3.7$ Hz, 1H; NCC*H*), 7.08 (dd, $^4J(H,H) = 1.8$ Hz, $^4J(H,P) = 3.6$ Hz, 1H; NC*H*), 7.11 (dd, $^4J(H,H) = 1.8$ Hz, $^3J(H,P) = 3.6$ Hz, 1H; NCC*H*), 7.14–7.42 ppm (m, 6H; Ph+OCH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 52.6$ (2×NCH_2), 52.9 (d, $^2J(C,P) = 5.8$ Hz; 4×OCH_3), 107.0 (OC*C*H), 109.9 (OC*C*H), 111.4 (OCH*C*H), 111.5 (OCH*C*H), 113.7 (NCHCCH*C*H), 114.5 (NCHCCH*C*H), 119.2 (d, $^2J(C,P) = 17.3$ Hz; 2×NC*C*H), 119.5 (NCHC*C*H), 119.0 (d, $^1J(C,P) = 227.3$ Hz; CP), 119.1 (d, $^1J(C,P) = 227.3$ Hz; CP), 123.06 (d, $^3J(C,P) = 15.0$ Hz; NCH*C*), 123.38 (d, $^3J(C,P) = 13.8$ Hz; NCH*C*), 123.66 (d, $^2J(C,P) = 17.3$ Hz; NC*C*H), 125.99 (2×CH_{arom}), 127.31 (2×CH_{arom}), 127.48 (CH_{arom}), 127.64 (d, $^3J(C,P) = 10.4$ Hz; NCH), 127.89 (CH_{arom}), 128.78 (2×CH_{arom}), 128.69 (2×CH_{arom}), 137.51 (d, $^4J(C,P) = 3.5$ Hz; C_{arom}), 137.86 (C_{arom}), 141.35 (OCH), 141.58 (OCH), 152.84 (OC), 153.64 ppm (OC); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 12.97$, 12.91 ppm; IR (film): $\tilde{\nu} = 1640$, 1252 (P=O), 1027 cm^{-1}; MS: *m*/*z* (%): 358.8 $[M+H]^+$ (100); chromatography (hexane/EtOAc 4:6): $R_f = 0.18$; elemental analysis (%) calcd for $C_{19}H_{20}NO_4P$: C 63.86, H 5.64, N 3.92; found: C 63.56, H 5.83, N 3.93

Dimethyl 1-benzyl-3-methyl-4-[(*E*)-2-phenylvinyl]-1*H*-pyrrol-2-ylphosphonate (13c): Yield: 85%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.38$ (s, 3H; CH_3), 3.56 (d, $^3J(H,P) = 11.6$ Hz, 6H; 2×OCH_3), 5.41 (s, 2H; NCH_2), 6.76 (d, $^3J(H,H) = 16.4$ Hz, 1H; CHPh), 6.97 (d, $^3J(H,H) = 16.4$ Hz, 1H; C*H*CHPh), 7.12–7.44 ppm (m, 11H; 2×Ph+NCH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 10.9$ (CH_3), 52.2 (d, $^2J(C,P) = 4.6$ Hz; 2×OCH_3), 52.7 (NCH_2), 114.8 (d, $^1J(C,P) = 225.0$ Hz; CP), 120.2 (*C*HCHPh), 122.6 (d, $^3J(C,P) = 15.0$ Hz; NCH*C*), 126.0 (2×CH_{arom}), 126.2 (d, $^3J(C,P) = 11.5$ Hz; NCH), 126.4 (CHPh), 127.0 (CH_{arom}), 127.1 (2×CH_{arom}), 127.6 (CH_{arom}), 128.7 (4×CH_{arom}), 131.5 (d, $^2J(C,P) = 18.5$ Hz; *C*CH_3), 138.2 (C_{arom}), 138.2 ppm (NCH_2C_{arom}); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 14.4$ ppm; IR (film): $\tilde{\nu} = 1250$ (P=O), 1046, 1023 cm^{-1}; MS: *m*/*z* (%): 382.2 $[M+H]^+$ (100); chromatography (hexane/EtOAc 2:8): $R_f = 0.46$; elemental analysis (%) calcd for $C_{22}H_{24}NO_3P$: C 69.28, H 6.34, N 3.67; found: C 69.17, H 6.39, N 3.67.

Dimethyl 1-benzyl-4-[(1*E*)-pent-1-enyl]-1*H*-pyrrol-2-ylphosphonate (13d): Yield: 48%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 0.92$ (t, 3H, $^3J(H,H) = 7.2$ Hz; CH_3), 1.45 (sextet, 2H, $^3J(H,H) = 7.2$ Hz; C$H_2$$CH_3$), 2.04–2.30 (m, 2H; CHC$H_2$), 3.60 (d, 6H, $^3J(H,P) = 11.3$ Hz; 2×OCH_3), 5.28 (s, 2H; NCH_2), 5.93 (dt, $^3J(H,H) = 15.7$ Hz, $^3J(H,H) = 7.2$ Hz, 1H; C*H*CH_2), 6.18 (dd, $^3J(H,H) = 15.7$ Hz, $^5J(H,P) = 1.0$ Hz, 1H; *C*HCH), 6.83 (dd, $^4J(H,H) = 1.8$ Hz, $^4J(H,P) = 5.4$ Hz, 1H; NCH), 6.91 (dd, $^4J(H,H) = 1.8$ Hz, $^3J(H,P) = 3.4$ Hz, 1H; NCCH), 7.12–7.15 (m, 2H, 2×CH_{arom}), 7.27–7.35 ppm (m, 3H, 3×CH_{arom}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 13.8$ (CH_3), 22.77 (CH_2CH_3), 35.1 (CH*C*H_2), 52.4 (NCH_2), 52.8 (d, $^2J(C,P) = 5.8$ Hz; 2×OCH_3), 117.7 (d, $^1J(C,P) = 222.2$ Hz; CP), 119.2 (d, $^2J(C,P) = 18.5$ Hz; NC*C*H), 121.6 (*C*HCH), 123.7 (d, $^3J(C,P) = 15.0$ Hz; NCH*C*), 126.4 (d, $^3J(C,P) = 10.4$ Hz; NCH), 127.3 (2×CH_{arom}), 127.8 (*C*HCH_2), 128.5 (CH_{arom}), 128.7 (2×CH_{arom}), 137.8 ppm (C_{arom}); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 13.37$ ppm; IR (film): $\tilde{\nu} = 1673$, 1255 (P=O), 1029 cm^{-1} (P–O); MS: *m*/*z* (%): 334.0 $[M+H]^+$ (100); chromatography (hexane/EtOAc 1:1): $R_f = 0.24$; elemental analysis (%) calcd for $C_{18}H_{24}NO_3P$: C 64.85, H 7.26, N 4.20; found: C 64.60, H 7.29, N 4.41.

Dimethyl 1-benzyl-4-[(*E*)-2-phenylvinyl]-1*H*-pyrrol-2-ylphosphonate (13e): Yield: 82%; *trans*/*cis* 82:18; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 3.54$ (d, $^3J(H,P) = 11.3$ Hz, 6H; 2×OCH_3), 3.63 (d, $^3J(H,P) = 11.3$ Hz, 6H; 2×OCH_3), 5.22 (s, 2H; NCH_2), 5.26 (s, 2H; NCH_2), 6.34 (d, $^3J(H,H) = 12.1$ Hz, 1H; C*H*CHPh), 6.40 (d, $^3J(H,H) = 12.1$ Hz, 1H; CHC*H*Ph), 6.63 (dd, $^4J(H,H) = 1.8$ Hz, $^4J(H,P) = 3.4$ Hz, 1H; NCH), 6.73 (dd, $^4J(H,H) = 1.8$ Hz, $^3J(H,P) = 5.4$ Hz, 1H; NCCH), 6.82 (d, $^3J(H,H) = 16.1$ Hz, 1H; CHC*H*Ph), 6.92 (d, $^3J(H,H) = 16.1$ Hz, 1H; C*H*CHPh), 7.00 (dd, $^4J(H,H) = 1.8$ Hz, $^4J(H,P) = 5.2$ Hz, 1H; NCH), 7.08 (dd, $^4J = 1.8$ Hz, $^3J(H,P) = 3.6$ Hz, 1H; NCCH), 7.15–7.45 ppm (m, 10H; 2×Ph); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 52.5$ (NCH_2), 52.6 (NCH_2), 52.9 (d, $^2J(C,P) = 5.8$ Hz; 2×OCH_3), 119.1 (d, $^3J(C,P) = 226.1$ Hz; CP), 119.4 (d, $^2J(C,P) = 17.3$ Hz; NC*C*H), 120.8 (*C*HCHPh), 121.1 (d, $^3J(C,P) = 15.0$ Hz; NCH*C*), 122.3 (d, $^2J(C,P) = 17.3$ Hz; NC*C*H), 122.7 (*C*HCHPh), 123.4 (d, $^3J(C,P) = 15.0$ Hz; NCH*C*), 126.0 (2×CH_{arom}), 126.3 (CH*C*HPh), 127.0 (CH_{arom}), 127.3 (2×CH_{arom}), 127.6 (d, $^3J(C,P) = 11.5$ Hz; NCH), 127.9 (CH_{arom}), 128.7 (2×CH_{arom}), 128.8 (2×CH_{arom}), 137.5 (C_{arom}), 137.9 ppm (C_{arom}); ^{31}P NMR (121 MHz, $CDCl_3$): $\delta = 12.97$, 13.03 ppm; IR (film): $\tilde{\nu} = 1639$, 1254 (P=O), 1028 cm^{-1} (P-O); MS: *m*/*z* (%): 368.8 $[M+H]^+$ (100); chromatography: (hexane/EtOAc 0:1): $R_f = 0.44$; elemental analysis (%) calcd for $C_{21}H_{22}NO_3P$: C 68.66, H 6.04, N 3.81; found: C 68.41, H 6.16, N 3.71.

4-Methyl-*N*-prop-2-ynylbenzenesulfonamide (15): Propargylamine (1.97 g, 36.4 mmol) and dry dichloromethane (25 mL) were added to an oven-dried round-bottomed flask. Tosyl chloride (6.58 g, 34.5 mmol) and pyridine (3.16 g, 40 mmol) were then added to this solution. The reaction mixture was stirred for 16 h at room temperature and was then poured into a separating funnel and washed with aq HCl (×3, 5 mL, 0.5 M). The combined aqueous layers were extracted once with CH_2Cl_2 (10 mL) and the combined organic phases were dried by using $MgSO_4$. 4-Methyl-*N*-prop-2-ynylbenzenesulfonamide was obtained as a white solid after filtration and evaporation of the solvent. Yield: 92%; m.p. 76°C (lit.[33] m.p. 76°C); ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.05$ (dt, $^4J(H,H) = 2.5$ Hz, $^5J(H,H) = 0.6$ Hz, 1H; CH), 2.44 (s, 3H; CH_3), 3.82 (dd, $^4J(H,H) = 2.5$ Hz, $^3J(H,H) = 0.8$ Hz, 1H; NCH_AH_B), 3.84 (dd, $^4J(H,H) = 2.5$ Hz, $^3J(H,H) = 0.8$ Hz, 1H; NCH$_A$$H_B$), 4.76 (br s, 1H; NH), 7.32 (d, $^3J(H,H) = 8.4$ Hz, 2H; 2×CH_{arom}), 7.78 ppm (d, $^3J(H,H) = 8.4$ Hz, 2H; 2×CH_{arom}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.7$ (CH_3), 33.0 (NCH_2), 73.1 (CH), 78.0 (C), 127.5 (2×CH_{arom}), 129.8 (2×CH_{arom}), 136.6 (CH_3C_q), 144.0 ppm (SC_q); IR (KBr): $\tilde{\nu} = 1596$ (C=C), 2131 (alkyne), 3270 cm^{-1} (NH); MS: *m*/*z* (%): 227.7 $[M+NH_4]^+$ (100), 210.7 $[M+H]^+$ (18).

***N*-[(2*Z*)-4-Chlorobut-2-enyl]-4-methyl-*N*-prop-2-ynylbenzenesulfonamide (16g)**: Yield: 62%; 4-methyl-*N*-prop-2-ynylbenzenesulfonamide (0.50 g, 2.39 mmol) and acetone (25 mL) were added to an oven-dried round-bottomed flask. (2*Z*)-1,4-Dichloro-2-butene (0.45 g, 3.58 mmol) and K_2CO_3 (1.32 g, 9.56 mmol) were then added to this solution and the reaction mixture was refluxed for 16 h. After this time, the reaction mixture was cooled and filtered. The product was coated on silica gel by removal of the solvent in vacuo and purified by flash chromatograhy. *N*-4-Methyl-*N*-[(2*E*)-3-phenylprop-2-enyl]-*N*-prop-2-ynylbenzenesulfonamide was obtained as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.05$ (t, $^4J(H,H) = 2.6$ Hz, 1H; CH_{alkyne}), 2.44 (s, 3H; CH_3), 3.92 (dd, $^3J(H,H) = 7.3$ Hz, $^4J(H,H) = 1.3$ Hz, 2H; CH_2Cl), 4.09 (d, $^4J(H,H) = 2.6$ Hz, 2H; NCH_2C), 4.11 (dd, $^3J(H,H) = 8.2$ Hz, $^4J(H,H) = 0.8$ Hz, 2H; NCH_2), 5.58 (dtt, $^3J(H,H) = 10.7$ Hz, $^3J(H,H) = 8.2$ Hz, $^4J(H,H) = 1.3$ Hz, 1H; NCH_2CH), 5.88 (dtt, $^3J(H,H) = 10.7$ Hz, $^3J(H,H) = 7.3$ Hz, $^4J(H,H) = 0.8$ Hz, 1H; C*H*CH_2Cl), 7.31 (d, $^3J(H,H) = 8.1$ Hz, 2H; 2×CH_{arom}), 7.73 ppm (d, $^3J(H,H) = 8.1$ Hz, 2H; 2×CH_{arom}); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.7$ (CH_3), 36.1 (NCH_2C), 38.5 (NCH_2), 42.6 (CH_2Cl), 74.2 (CH_{alkyne}), 76.4 (C_{alkyne}), 127.7 (NCH_2CH), 127.9 (2×CH_{arom}), 129.7 (2×CH_{arom}), 131.1 ($HCCH_2Cl$), 135.7 (CH_3C_q), 143.9 ppm (SC_q); IR (film): $\tilde{\nu} = 1598$ (C=C), 2120.8 cm^{-1} (alkyne); MS: *m*/*z* (%): 298.7/300.7 $[M+H]^+$ (100); chromatography: (hexane/EtOAc 7:3); $R_f = 0.51$; elemental analysis (%) calcd for $C_{14}H_{16}ClNO_2S$: C 56.46, H 5.42, N 4.70; found: C 56.50, H 5.30, N 4.81.

***N*-[(2*Z*)-4-Bromobut-2-enyl]-4-methyl-*N*-prop-2-ynylbenzenesulfonamide (16h)**: 4-Methyl-*N*-prop-2-ynylbenzenesulfonamide (0.50 g, 2.39 mmol) and acetone (25 mL) were added to an oven-dried round-bottomed flask. (2*Z*)-1,4-Dibromo-2-butene (0.77 g, 3.58 mmol) and K_2CO_3 (1.32 g, 9.56 mmol) were then added to this solution and the reaction mixture was refluxed for 16 h. After this time, the reaction mixture was cooled and filtered. The product was coated on silica gel by removal of the solvent in vacuo and was then purified by flash chromatography. *N*-[(2*Z*)-4-Bromobut-2-enyl]-4-methyl-*N*-prop-2-ynylbenzenesulfonamide was obtained as a solid. Yield: 73%; ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 2.04$ (t, $^4J(H,H) = 2.5$ Hz, 1H; CH_{alkyne}), 2.43 (s, 3H; CH_3), 3.84 (d, $^3J(H,H) = 6.7$ Hz, 2H; NCH_2), 3.92 (d, $^3J(H,H) = 7.5$ Hz, 2H; CH_2Br), 4.08 (d,

^4J(H,H) = 2.5 Hz, 2H; NCH_2C), 5.69 (dt, ^3J(H,H) = 6.7 Hz, ^3J(H,H) = 15.1 Hz, 1H; NCH_2CH), 5.94 (dt, ^3J(H,H) = 7.5 Hz, ^3J(H,H) = 15.1 Hz, 1H; $CHCH_2Br$), 7.30 (d, ^3J(H,H) = 8.5 Hz, 2H; $2\times CH_{arom}$), 7.95 ppm (d, ^3J(H,H) = 8.5 Hz, 2H; $2\times CH_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.8 (CH_3), 31.3 (CH_2Br), 36.2 (NCH_2C), 47.5 (NCH_2), 74.1 (CH_{alkyne}), 76.5 (C_{alkyne}), 127.8 ($2\times CH_{arom}$), 128.8 (NCH_2CH), 129.7 ($2\times CH_{arom}$), 131.5 ($HCCH_2Br$), 135.9 (CH_3C_q), 143.8 ppm (SC_q); IR (film): $\tilde{\nu}$ = 1597 (C=C), 2120.8 cm^{-1} (alkyne); MS: *m*/*z* (%): 342.3/344.3 $[M+H]^+$ (100); chromatography: (hexane/EtOAc 7:3); R_f = 0.44; elemental analysis (%) calcd for $C_{14}H_{16}BrNO_2S$: C 49.13, H 4.71, N 4.09; found: C 48.99, H 5.03, N 4.19.

***N*-[(2*Z*)-4-(4-Chlorophenoxy)but-2-enyl]-4-methyl-*N*-prop-2-ynylbenzenesulfon amide (16i)**: 4-Methyl-*N*-prop-2-ynylbenzenesulfonamide (0.50 g, 2.39 mmol) and acetone (25 mL) were added to an oven-dried round-bottomed flask. (2*Z*)-4-Chlorobut-2-enyl 4-chlorophenyl ether (0.78 g, 3.58 mmol) and K_2CO_3 (1.32 g, 9.56 mmol) were then added to this solution and the reaction mixture was refluxed for 16 h. After this time, the reaction mixture was cooled and filtered. The product was coated on silica gel by removal of the solvent in vacuo and purified by flash chromatography. *N*-[(2*Z*)-4-(4-chlorophenoxy)but-2-enyl]-4-methyl-*N*-prop-2-ynylbenzenesulfonamide was obtained as an oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.98 (t, ^4J(H,H) = 2.5 Hz, 1H; CH_{alkyne}), 2.43 (s, 3H; CH_3), 3.94 (br d, 2H, ^3J(H,H) = 7.3 Hz; NCH_2), 4.11 (d, ^4J(H,H) = 2.5 Hz, 2H; NCH_2C), 4.59 (dd, ^3J(H,H) = 6.0 Hz, ^4J(H,H) = 1.1 Hz, 2H; OCH_2), 5.63 (dtt, ^3J(H,H) = 10.6 Hz, ^3J(H,H) = 7.3 Hz, ^4J(H,H) = 1.5 Hz, 1H; NCH_2CH), 5.93 (dtt, ^3J(H,H) = 10.6 Hz, ^3J(H,H) = 6.0 Hz, ^4J(H,H) = 1.1 Hz, 1H; $CHCH_2O$), 6.77–6.84 (m, 2H; CH_{arom}), 7.30 (d, ^3J(H,H) = 8.1 Hz, 2H; $2\times CH_{Tos}$), 7.32–7.36 (m, 2H; CH_{arom}), 7.73 ppm (d, *J* = 8.1 Hz, 2H; $2\times CH_{Tos}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.67 (CH_3), 36.09 (NCH_2C), 43.28 (NCH_2), 63.86 (OCH_2), 74.09 ($C_{q,alkyne}$), 77.36 (CH_{alkyne}), 116.05 ($2\times CH_{arom}$), 125.97 (C_qCl), 127.25 (NCH_2CH), 127.88 ($2\times CH_{arom}$), 129.44 ($2\times CH_{arom}$), 129.70 ($2\times CH_{arom}$), 130.64 ($HCCH_2O$), 135.74 (CH_3C_q), 143.90 (SC_q), 157.01 ppm (OC_q); IR (film): $\tilde{\nu}$ = 1596 cm^{-1} (C=C); MS: *m*/*z* (%): 390.2/392.3 $[M+H]^+$ (100); chromatography: (hexane/EtOAc 7:3): R_f = 0.38; elemental analysis (%) calcd for $C_{20}H_{20}ClNO_3S$: C 61.61, H 5.17, N 3.59; found: C 61.47, H 5.06, N 3.61. Yield: 81%.

***N*-4-methyl-*N*-[(2*E*)-3-phenylprop-2-enyl]-*N*-prop-2-ynylbenzenesulfonamide (16j)**: 4-Methyl-*N*-prop-2-ynylbenzenesulfonamide (0.50 g, 2.39 mmol) and acetone (25 mL) were added to an oven-dried round-bottomed flask. Cinnamylbromide (0.71 g, 3.58 mmol) and K_2CO_3 (1.32 g, 9.56 mmol) were then added to this solution and the reaction mixture was refluxed for 16 h. After this time, the reaction mixture was cooled and filtered. The product was coated on silica gel by removal of the solvent in vacuo and purified by flash chromatography. *N*-4-Methyl-*N*-[(2*E*)-3-phenylprop-2-enyl]-*N*-prop-2-ynylbenzenesulfon amide is obtained as a solid. Yield: 71%; m.p. 73–74 °C, lit.[34] m.p. 79–81 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.05 (t, ^4J(H,H) = 2.5 Hz, 1H; CH_{alkyne}), 2.42 (s, 3H; CH_3), 3.99 (d, ^3J(H,H) = 6.9 Hz, 2H; NCH_2CH), 4.13 (d, ^4J(H,H) = 2.5 Hz, 2H; NCH_2C), 6.07 (dt, ^3J(H,H) = 15.7 Hz, ^3J(H,H) = 6.9 Hz, 1H; NCH_2CH), 6.57 (d, ^3J(H,H) = 15.7 Hz, 1H; $CHPh$), 7.23–7.35 (m, 7H; CH_{arom}), 7.76 ppm (d, ^3J(H,H) = 8.5 Hz, 2H; $2\times CH_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.7 (CH_3), 36.0 (NCH_2C), 48.7 (NCH_2), 74.0 (CH_{alkyne}), 76.7 (C_{alkyne}), 123.0 (NCH_2CH), 126.7 ($2\times CH_{arom}$), 127.9 ($2\times CH_{arom}$), 128.2 (CH_{arom}), 128.7 ($2\times CH_{arom}$), 129.7 ($2\times CH_{arom}$), 135.0 ($HCPh$), 136.1 ($C_{q,arom}$), 136.2 ($C_{q,arom}$), 143.8 ppm (SC_q); IR (KBr): $\tilde{\nu}$ = 1598 (C=C), 2116 cm^{-1} (alkyne); MS: *m*/*z* (%): 326.4 $[M+H]^+$ (100); chromatography: (hexane/EtOAc 6:4): R_f = 0.58.

4-Methyl-*N*-{(2*Z*)-4-[prop-2-ynyl-(toluene-4-sulfonyl)amino]but-2-enyl}-*N*-prop-2-ynylbenzenesulfonamide (32): Yield: 89%; 4-Methyl-*N*-prop-2-ynylbenzenesulfonamide (0.50 g, 2.39 mmol) and acetone (25 mL) were added to an oven-dried round-bottomed flask. (2*Z*)-1,4-Dibromo-2-butene (0.27 g, 1.19 mmol) and K_2CO_3 (1.32 g, 9.56 mmol) were then added to this solution and the reaction mixture was refluxed for 16 h. After this time, the reaction mixture was cooled and filtered. The residue was dissolved in a minimal amount of warm THF and placed in the freezer. 4-Methyl-*N*-{(2*Z*)-4-[prop-2-ynyl(toluene-4-sulfonyl)amino]but-2-enyl}-*N*-prop-2-ynylbenzenesulfonamide was obtained as a solid. M.p. 160–161 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.01 (t, ^4J(H,H) = 2.5 Hz, 2H; $2\times CCH$), 2.43 (s, 6H; $2\times CH_3$), 3.93 (d, ^3J(H,H) = 4.7 Hz, 4H; $2\times NCH_2$), 4.07 (d, ^4J(H,H) = 2.5 Hz, 4H; $2\times NCH_2C$), 5.61 (t, ^3J(H,H) = 4.7 Hz, 2H; $2\times NCH_2CH$), 7.26–7.73 ppm (m, 8H; $8\times CH_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 ($2\times CH_3$), 36.4 ($2\times NCH_2C$), 43.2 ($2\times NCH_2CH$), 74.0 ($2\times CH_{alkyne}$), 76.9 ($2\times C_{alkyne}$), 127.9 ($4\times CH_{arom}$), 129.1 ($2\times NCH_2CH$), 129.6 ($4\times CH_{arom}$), 135.9 ($2\times C_{q,arom}$), 143.8 ppm (SC_q); IR (KBr): $\tilde{\nu}$ = 1598 (C=C), 2119 cm^{-1} (alkyne); MS: *m*/*z* (%): 471.3 $[M+H]^+$ (100); elemental analysis (%) calcd for $C_{24}H_{26}N_2O_4S_2$: C 61.25, H 5.57, N 5.95; found: C 61.21, H 5.56, N 6.24.

Synthesis of 1-[(4-Methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrroles 17: Sulfonamide **16** (0.70 mmol) and benzene (10 mL) were added to an oven-dried round-bottomed flask. The solution was refluxed under a nitrogen atmosphere and Grubbs second-generation catalyst **2** (0.034 mmol, 5 mol%) was added. The reaction mixture was then further refluxed for 1 h. The product was coated on silica gel by removal of the solvent in vacuo and purified by flash chromatography.

3-[(1*E*)-3-Chloroprop-1-enyl]-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole (17g): Yield: 86%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3H; CH_3), 4.09 (d, ^3J(H,H) = 7.3 Hz, 2H; CH_2Cl), 4.19 (s, 4H; CH_2NCH_2), 5.59 (dt, ^3J(H,H) = 7.3 Hz, ^3J(H,H) = 15.7 Hz, 1H; $CHCH_2Cl$), 5.66 (s, 1H; CH=C), 6.33 (d, ^3J(H,H) = 15.7 Hz, 1H; HC=CH), 7.33 (d, ^3J(H,H) = 8.1 Hz, 2H; $2\times CH_{arom}$), 7.73 ppm (d, ^3J(H,H) = 8.1 Hz, 2H; $2\times CH_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 44.6 (CH_2Cl), 53.7 (NCH_2), 55.1 (NCH_2), 125.0 (HC=C), 127.1 (CH=CH), 127.5 ($2\times CH_{arom}$), 127.8 (CH_2ClCH), 130.0 ($2\times CH_{arom}$), 134.0 (C=CH), 136.0 (CH_3C_q), 143.8 ppm (SC_q); IR (film): $\tilde{\nu}$ = 1597 cm^{-1} (C=C); MS: *m*/*z* (%): 298.3/300.3 $[M+H]^+$ (100); chromatography: (hexane/EtOAc 8:2): R_f = 0.19; elemental analysis (%) calcd for $C_{14}H_{16}ClNO_2S$: C 56.46, H 5.42, N 4.70; found: C 56.40, H 5.07, N 4.69.

3-[(1*E*)-3-Bromoprop-1-enyl]-1-[(4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole (17h): Yield: 76%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3H; CH_3), 3.99 (d, ^3J(H,H) = 7.7 Hz, 2H; CH_2Br), 4.18 (s, 4H; CH_2NCH_2), 5.66 (dt, ^3J(H,H) = 7.7 Hz, ^3J(H,H) = 15.6 Hz, 1H; $CHCH_2Br$), 5.66 (s, 1H; CH=C), 6.31 (d, ^3J(H,H) = 15.6 Hz, 1H; HC=CH), 7.33 (d, ^3J(H,H) = 8.4 Hz, 2H; $2\times CH_{arom}$), 7.73 ppm (d, ^3J(H,H) = 8.4 Hz, 2H; $2\times CH_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 (CH_3), 32.3 (CH_2Br), 53.6 (NCH_2), 55.1 (NCH_2), 125.2 (HC=C), 127.5 (HC=CH+$2\times CH_{arom}$), 128.2 (CH_2BrCH), 130.0 ($2\times CH_{arom}$), 134.0 (C=CH), 136.0 (CH_3C_q), 143.8 ppm (SC_q); IR (film): $\tilde{\nu}$ = 1597 cm^{-1} (C=C); MS: *m*/*z* (%): 342.3/344.3 $[M+H]^+$ (100); chromatography: (hexane/EtOAc 7:3): R_f = 0.28; elemental analysis (%) calcd for $C_{14}H_{16}BrNO_2S$: C 49.13, H 4.71, N 4.09; found: C 49.25, H 4.92, N 4.31.

3-[(*E*)-2-(4-Chlorophenoxy)vinyl]-1-[4-methylphenyl)sulfonyl]-2,5-dihydro-1*H*-pyrrole (17i *trans*/*cis* 63:37): Yield: 73%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.43 (s, 3H; CH_3), 2.45 (s, 3H; CH_3), 4.19–4.23 (m, 8H; CH_2NCH_2), 4.53 (br d, 2H, ^3J(H,H) = 5.7 Hz; CH_2O), 4.56 (br d, 2H, ^3J(H,H) = 6.5 Hz; CH_2O), 5.58 (br s, 1H; HC=C), 5.63 (br s, 1H; HC=C), 5.66 (dt, ^3J(H,H) = 16.0 Hz, ^3J(H,H) = 5.7 Hz, 1H; OCH_2CH), 5.79 (dt, ^3J(H,H) = 11.8 Hz, ^3J(H,H) = 6.5 Hz, 1H; OCH_2CH), 6.02 (d, ^3J(H,H) = 11.8 Hz, 1H; HC=CH), 6.39 (d, ^3J(H,H) = 16.0 Hz, 1H; HC=CH), 6.74–6.85 (m, 4H; $4\times CH_{arom}$), 7.14–7.38 (m, 4H; $4\times CH_{arom}$), 7.69–7.77 ppm (m, 4H; $4\times CH_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.6 ($2\times CH_3$), 53.8 (NCH_2), 54.8 (NCH_2), 55.2 (NCH_2), 55.9 (NCH_2), 65.0 (OCH_2), 68.2 (OCH_2), 116.1 ($2\times CH_{arom}$), 116.8 ($2\times CH_{arom}$), 124.2 (HC=C), 124.6 (HC=CH), 125.9 (HC=C), 126.0 (HC=CH), 126.1 ($2\times C_qCl$), 127.0 (OCH_2CH), 127.5 ($2\times CH_{arom}$), 128.7 (OCH_2CH), 129.5 ($2\times CH_{arom}$), 130.0 ($2\times CH_{arom}$), 134.1 (C=CH), 135.1 (C=CH), 136.3 ($2\times CH_3C_q$), 143.7 (SC_q), 143.8 (SC_q), 156.8 (OC_q), 157.0 ppm (OC_q); IR (film): $\tilde{\nu}$ = 1581 (C=C), 1596 cm^{-1} (C=C); MS: *m*/*z* (%): 390.2/392.3 $[M+H]^+$ (100); chromatography: (hexane/EtOAc 7:3): R_f = 0.17; elemental analysis (%) calcd for $C_{20}H_{20}ClNO_3S$: C 61.61, H 5.17, N 3.59; found: C 61.77, H 5.37, N 3.62.

1-[(4-Methylphenyl)sulfonyl]-3-[(*E*)-2-phenylvinyl]-2,5-dihydro-1*H*-pyrrole (17j): Yield: 89%; ^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.42 (s, 3H; CH_3), 4.18–4.25 (m, 2H; NCH_2), 4.32–4.43 (m, 2H; NCH_2), 5.69 (br s, 1H; NCH_2CH), 6.33 (d, ^3J(H,H) = 16.4 Hz, 1H; HC=CH), 6.76 (d, ^3J(H,H) = 16.4 Hz, 1H; HC=CH), 7.22–7.39 (m, 7H; $7\times CH_{arom}$), 7.76 ppm (d, ^3J(H,H) = 8.3 Hz, 2H; $2\times CH_{arom}$); ^{1}H NMR (300 MHz,

C_6D_6): $\delta = 1.85$ (s, 3H; CH_3), 4.04–4.06 (m, 2H; NCH_2), 4.27–4.31 (m, 2H; NCH_2), 4.97 (brs, 1H; NCH_2CH), 6.04 (d, $^3J(H,H) = 16.2$ Hz, 1H; *HC*=CH), 6.39 (d, $^3J(H,H) = 16.2$ Hz, 1H; HC=*CH*), 6.77 (d, $^3J(H,H) = 8.1$ Hz, 2H; $2\times CH_{arom}$), 7.00–7.15 (m, 5H; Ph), 7.79 ppm (d, $^3J(H,H) = 8.1$ Hz, 2H; $2\times CH_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.6$ (CH_3), 53.9 (NCH_2), 55.3 (NCH_2), 121.6 (*HC*=C), 123.5 (NCH_2CH), 126.6 ($2\times CH_{arom}$), 127.6 ($2\times CH_{arom}$), 128.3 (CH_{arom}), 128.8 ($2\times CH_{arom}$), 129.9 ($2\times CH_{arom}$), 131.5 (*C*HPh), 134.2 (*C*=CH), 136.5 (CH_3C_q), 137.3 ($C_{q,arom}$), 143.7 (SC_q); IR (film): $\tilde{\nu} = 1596\ cm^{-1}$ (C=C); MS: *m*/*z* (%): 326.3 $[M+H]^+$ (100); elemental analysis (%) calcd for $C_{19}H_{19}NO_2S$: C 70.12, H 5.88, N 4.30; found: C 70.24, H 6.09, N 4.48.

1-[(4-Methylphenyl)sulfonyl]-3-{(*E*)-2-[1-(4-methylphenyl)sulfonyl)-2,5-dihydro-1*H*-pyrrol-3-yl]vinyl}-2,5-dihydro-1*H*-pyrrole (40): Yield: 74%; m.p. 180–200°C (decomp); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 2.42$ (s, 6H; $2\times CH_3$), 4.18 (s, 8H; $2\times CH_2NCH_2$), 5.66 (s, 2H; $2\times NCH_2CH$), 5.99 (s, 2H; C*H*=C*H*), 7.31 (d, $^3J(H,H) = 8.1$ Hz, 4H; $4\times CH_{arom}$), 7.71 ppm (d, $^3J(H,H) = 8.1$ Hz, 4H; $4\times CH_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 21.6$ ($2\times CH_3$), 53.5 ($2\times NCH_2$), 55.3 ($2\times NCH_2$), 124.2 (*HC*=CH), 125.0 ($2\times$ H*C*=C), 127.5 ($4\times CH_{arom}$), 129.9 ($4\times CH_{arom}$), 134.1 ($2\times HC=C$), 136.7 ($2\times CH_3C_q$), 143.7 ppm ($2\times SC_q$); IR (KBr): $\tilde{\nu} = 1597\ cm^{-1}$ (C=C); MS: *m*/*z* (%): 471.3 $[M+H]^+$ (100); chromatography: (hexane/EtOAc 1:1): $R_f = 0.49$; elemental analysis (%) calcd for $C_{24}H_{26}N_2O_4S_2$: C 61.25, H 5.57, N 5.95; found: C 61.39, H 5.60, N 5.99.

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