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Vinyl Azides Derived from Allenes: Thermolysis Leading to Multisubstituted 1,4-Pyrazines and Mn(III)-Catalyzed Photochemical Reaction Leading to Pyrroles

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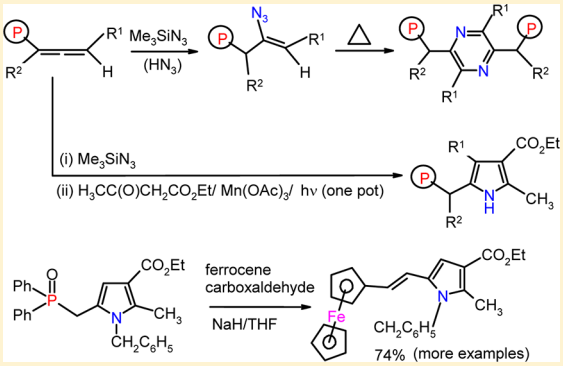
Supporting Information

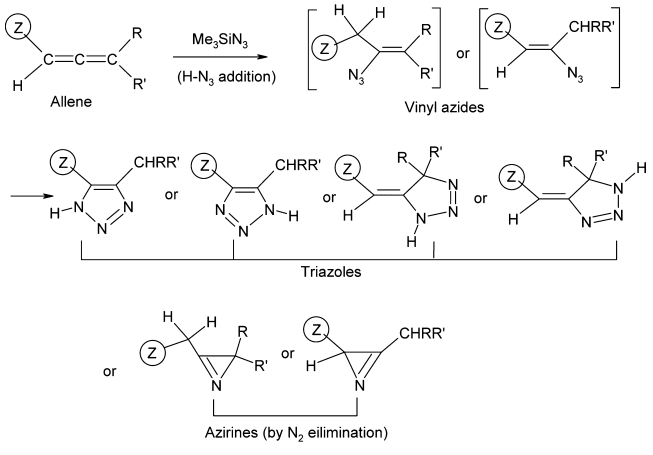
ABSTRACT: Thermolysis of phosphorus-based vinyl azides under solvent- and catalyst-free conditions furnished a new route for 1,4-pyrazines. A simple one-pot, Mn(III)-catalyzed photochemical route has been developed for multisubstituted pyrroles starting from allenes and 1,3-dicarbonyls via in situ-generated vinyl azides. The utility of new phosphorus-based pyrroles is also demonstrated in the Horner reaction. The structures of key products are unequivocally confirmed by X-ray crystallography.



INTRODUCTION

Allenes are interesting substrates among the unsaturated systems because of their high reactivity,[1] and hence they serve as potential precursors for highly complex and strained target molecules of biological and industrial importance.[2] Allenylphosphonates/allenylphosphine oxides are also excellent precursors for the preparation of synthetically important molecules.[3,4] One class of compounds that can be prepared via allenes are vinyl azides. The latter substrates are versatile intermediates for the synthesis of nitrogen heterocycles such as triazoles,[5] azirines,[6] (Scheme 1) or other heterocycles.[7] The intermediate vinyl azides can also be used in the alkyne−azide click reaction to generate a diverse class of triazoles.[5] Recently, there have been two reports on the preparation of pyrroles that involve a vinyl azide and 1,3-dicarbonyl compounds as starting materials.[8] In this direction, we surmised that in situ-generated phosphono-vinyl azides by starting with the corresponding allenes could lead to multisubstituted phosphono-pyrroles. Although there have been many methods for the synthesis of pyrroles,[9] it is still challenging to prepare polysubstituted pyrroles directly from the building blocks such as allenes. Because phosphonylated nitrogen heterocycles constitute an important class of compounds with significant biological potential,[10] new routes toward these molecules are still warranted; only limited reports are available for the synthesis of phosphorus-based pyrroles.[11,12] In the course of our investigations on such a system, we stumbled upon a new reaction of vinyl azides leading to 1,4-pyrazines. This reaction as well as the *one-pot* generation of phosphorus-based pyrroles from the corresponding phosphono-vinyl azides *photochemically under Mn(III)-catalyzed conditions* is described herein. Further synthetic potential of thus derived phosphono-pyrroles in the Horner−Wittig reaction is also highlighted herein. The precursor allenes **1**−**6** (Chart 1) have been prepared for this work by the synthetic routes available in the literature.[13,14]

Scheme 1. Formation of Triazoles or Azirines via Vinyl Azides Generated from Allenes



RESULTS AND DISCUSSION

We shall first discuss the thermolysis of vinyl azides leading to 1,4-pyrazines. This will be followed by the reaction of vinyl azides with 1,3-diketones leading to multisubstituted pyrroles.

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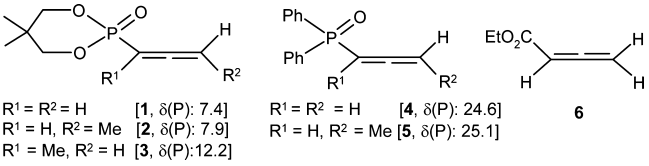
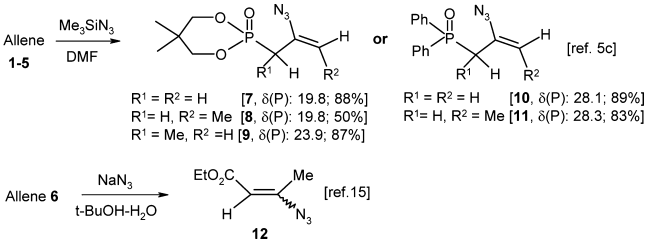
Chart 1. Allene Precursors Used in the Present Study



When the latter contained a $Ph_2P(O)CH_2$ moiety, synthetic utility in Horner reaction is demonstrated.

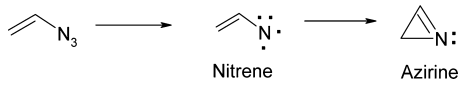
1. Vinyl Azides. Facile Pyrolysis Leading to 1,4-Pyrazines. Vinyl azides **7**−**11** required for the present study are obtained by treatment of allenylphosphonates/allenylphosphine oxides with Me_3SiN_3 in DMF at room temperature (Scheme 2);[5c] the vinyl azide **12** is prepared from allenoate **6**

Scheme 2. Synthesis of Vinyl Azides 7−11 via Allenes 1−6



by using a reported method.[15] Among these, **7** and **9**−**11** are new. Vinyl azides under pyrolysis conditions are known to afford azirines (Scheme 3; also see Scheme 1 shown above).[6]

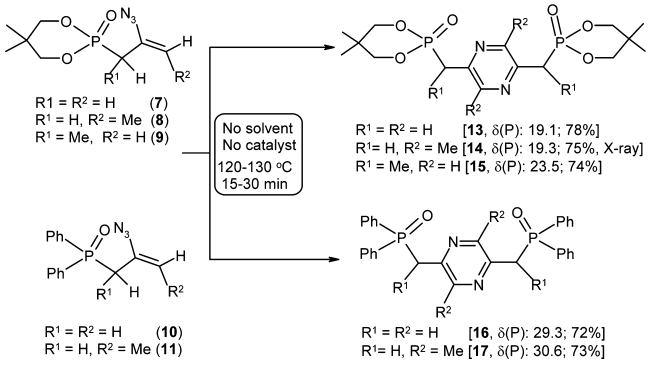
Scheme 3. Generation of Azirines from Vinyl Azides via Nitrenes



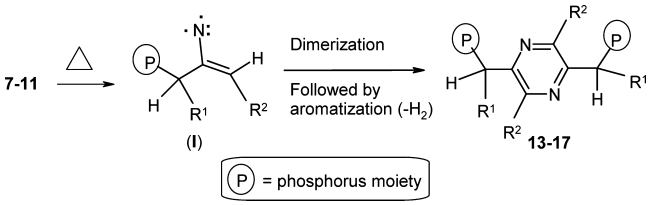
Initially, while checking the melting point of azide **7**, gas evolution at the melting region (of temperature) was observed. Upon further heating, gas evolution stopped resulting in a solid material. To analyze the chemistry behind this, we heated ca. 0.2 g of compound **7** above its melting point (15 min) to get the new solid material **13**. The structure of this compound is ascertained conclusively by single crystal X-ray crystallography of a similar product **14** obtained from the azide **8** (Figure S1 in Supporting Information). Thus, the resulting product upon heating phosphorus-based vinyl azides under neat condition was 1,4-pyrazines (Scheme 4) *and not the expected azirines*. To our knowledge, this reaction is new. In an analogous manner, azides **9**−**11** also led to 1,4-pyrazines **15**−**17** (Scheme 4). Although vinyl azide **12** appears to eliminate gaseous nitrogen, there were many products (TLC) and hence isolation was not attempted.

The above pyrazines are likely to have formed via a radical mechanism via a nitrene intermediate (**I**) as shown in Scheme 5. Involvement of a radical is indicated by the reduction in the yield of the product (to <50% as revealed by ^{31}P NMR) when the reaction was performed in the presence of a radical quencher (20 mol % of *p*-hydroquinone). The dimerization of this intermediate followed by aromatization by the loss of hydrogen leads to the pyrazines **13**−**17**. It is possible that the there is some interaction between phosphorus and the nitrogen

Scheme 4. Formation of 1,4-Pyrazines 13−17 upon Thermal Treatment of Vinyl Azides 7−11



Scheme 5. Possible Pathway for the Formation of 1,4-Pyrazines



in the transition state, but at the moment this is only a speculation. An approximate weight loss of 10% from compound **10** observed in the TGA analysis (Figure 1) also supported the nitrogen gas elimination.

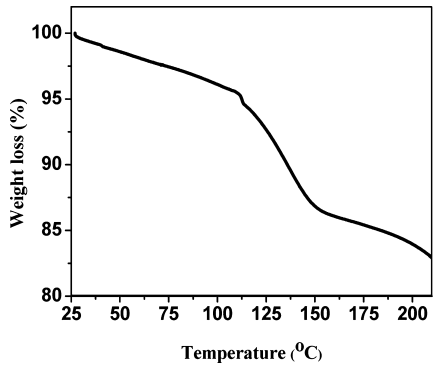


Figure 1. TGA behavior of azide **10**.

2. One Pot Synthesis of Multisubstituted Pyrroles from Allenes and 1,3-Diketones via Vinyl Azides. Mn(III) Catalysis and Photochemical Activation. Our intended target was to synthesize multisubstituted pyrroles by in situ-generated vinyl azides from allenes. To check the feasibility of product formation though, we first treated the azide **7** with ethyl acetoacetate (EAA) in the presence of catalytic amount of $Mn(OAc)_3{\cdot}2H_2O$ (Scheme 6)[8] and were successful in obtaining the *phosphono-pyrrole* **18** in good yield (60%). We could reduce the reaction time from 12 to 4 h and also increase the yield to 80% by using photochemical conditions (λ = 254 nm). As a means of confirmation, the X-ray structure of **18** was determined (Figure S2 in Supporting Information). The presence of the NH group was also revealed by its hydrogen-bonding interaction with the phosphoryl oxygen.

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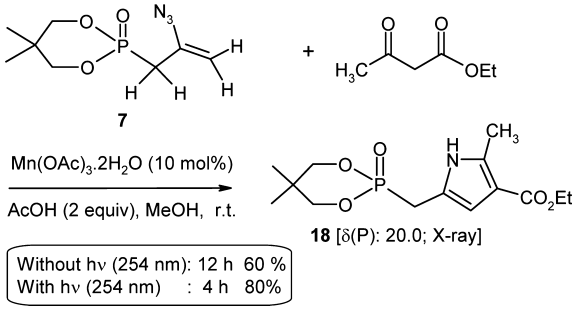
Scheme 6. Mn(III)-Catalyzed Photochemical Conversion of Vinyl Azide 7 to Phosphono-pyrrole 18



To perform the above reaction in *one pot* using allenes **1**−**5** and also to maximize the yield of the products **18**−**32** under photochemical conditions, we have screened various cosolvents and additives. For this optimization, we chose allene **4** and ethyl acetoacetate (EAA) as model reactants; this led to pyrrole **27** via azide **10** (cf. Scheme 7 and Tables 1-2). Formation of azide **10** was straightforward but needed a solvent such as DMF; methanol did not work for this step. For the next step, we added methanol. There was no reaction in the absence of the catalyst [$Mn(OAc)_3{\cdot}2H_2O$] or additive (acetic acid) (cf., Table 1, entries 1 and 2). However, in the presence of the catalyst and additive, the reaction occurred smoothly to give product **27** (entry 3) in excellent yield. The use of EtOH or *i*-PrOH lowered the yield, and in fact there was no reaction in *t*-BuOH (entries 4−6). DMF as a solvent was not effective for the second step (entry 7). Trifluoroacetic acid or trifluoromethane sulfonic acid as an additive worked, but the yield was lower (entries 8 and 9). PTSA was ineffective as an additive (entry 10). Ceric ammonium nitrate (CAN) in place of Mn-$(OAc)_3{\cdot}2H_2O$ also did not work (entry 11). Thus, efforts toward the preparation of the pyrrole by employing the same solvent system (methanol or DMF) in two consecutive steps failed. While DMF facilitates the azide formation, methanol is required for the formation of pyrrole from azide. Hence, we carried out the first step in DMF, and then a solution of ethyl acetoacetate, $Mn(OAc)_3{\cdot}2H_2O$, and acetic acid in methanol was added to the crude azide under photochemical conditions to obtain the product. This procedure was then adapted to other allenes and 1,3-diketones as shown in Table 2. The yields were good to excellent. An interesting point here is that in the reaction of the allenes **1**−**5** with ethyl 4-chloroacetoacetate the Cl atom was exchanged for the OMe group in the products **19**, **22**, **25**, **28**, and **31** (cf., Table 2, entries 2, 5, 8, 11, and 14). This exchange substantiates the radical mechanism proposed in the literature for similar reactions.[8] To confirm the authenticity of our result, compound **20** was also characterized by single crystal X-ray crystallography (Figure S3 in Supporting Information).

Scheme 7. One-Pot Transformation of Allenes 1−5 to Multisubstituted Pyrroles 18−32 via Mn(III)-Catalyzed Reaction

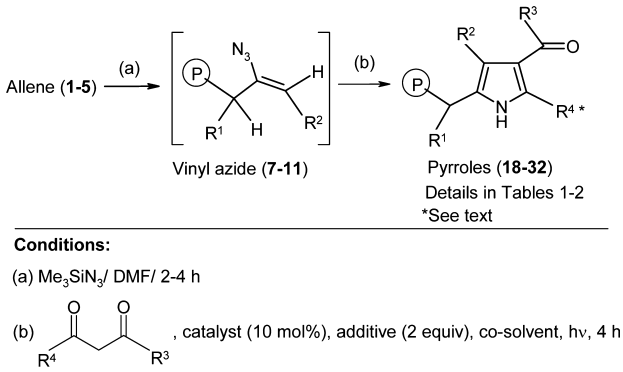
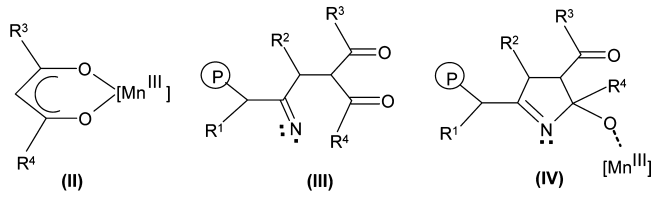


Table 1. Details on the Conditions Shown in Scheme 7b Using Vinyl Azide 10 and Ethyl Acetoacetate [Ⓟ ≡ $Ph_2P(O)$; $R^1 = R^2 = H$; $R^3 = OEt$, $R^4 = Me$] leading to 27[a]

entry	catalyst	additive	cosolvent (i.e., in addition to DMF)	product yield **27** (%)[b]
1	none	acetic acid	MeOH	n.r.
2	$Mn(OAc)_3{\cdot}2H_2O$	–	MeOH	n.r.
3	$Mn(OAc)_3{\cdot}2H_2O$	acetic acid	MeOH	88
4	$Mn(OAc)_3{\cdot}2H_2O$	acetic acid	EtOH	65
5	$Mn(OAc)_3{\cdot}2H_2O$	acetic acid	^{i}PrOH	30
6	$Mn(OAc)_3{\cdot}2H_2O$	acetic acid	^{t}BuOH	n.r.
7	$Mn(OAc)_3{\cdot}2H_2O$	acetic acid	–	n.r.
8	$Mn(OAc)_3{\cdot}2H_2O$	CF_3CO_2H	MeOH	46
9	$Mn(OAc)_3{\cdot}2H_2O$	CF_3SO_3H	MeOH	10
10	$Mn(OAc)_3{\cdot}2H_2O$	PTSA	MeOH	n.r.
11	CAN	acetic acid	MeOH	n.r.

[a]Conditions: To a solution of Me_3SiN_3 (0.5 mmol) in DMF (3 mL) was added allene (0.42 mmol), and the reaction mixture was stirred at rt for 4 h. To this was added a solution of ethyl acetoacetate (0.62 mmol), catalyst (10 mol %), and additive (2 equiv) in cosolvent (1.5 mL), and the mixture was irradiated in a photoreactor (λ = 254 nm) for an additional 4 h. [b]Based on ^{31}P NMR analysis.

The above reactions can be assumed to take place via the vinyl azides. Possible intermediates based on the literature[8] for the formation of **18**−**32** include **II**−**IV**. Similar intermediates are likely to be present in the formation of **33**−**35**. As can be expected, the ring closure from **III** can occur at the carbon close to R^3 also; the choice between the two possibilities should depend on the electronic factors.



3. Utility of Phosphorus-Based Pyrroles in the Horner Reaction. We were interested to see if at least some of the phosphorus-based pyrroles synthesized as above could be utilized further, and in this direction, we felt that the Horner reaction of these products possessing a PCH_2 group should be

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Table 2. Details on Pyrrole Derivatives 18−32 Synthesized from Allenes 1−5, Me_3SiN_3, and 1,3-Dicarbonyls[a]

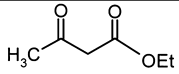
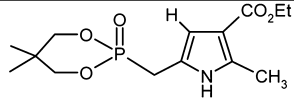
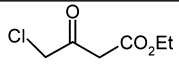
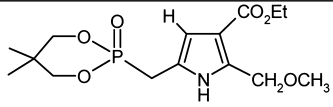
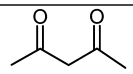
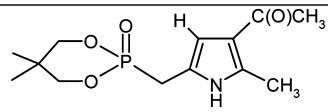
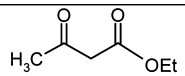
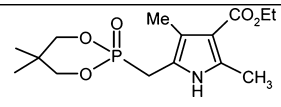
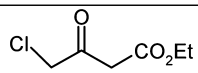
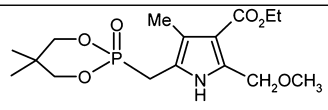
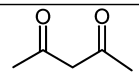
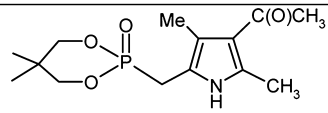
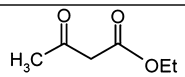
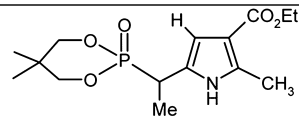
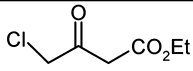
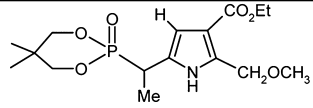
Entry	Allene	1,3-dicarbonyl substrate	Product	Yield[b]	δ(P)
1	**1**		 **18** (X-ray)	80	20.0
2	**1**		 **19**	78	20.5
3	**1**		 **20** (X-ray)	72	20.4
4	**2**		 **21**	81	21.3
5	**2**		 **22**	69	21.3
6	**2**		 **23**	72	21.3
7	**3**		 **24**	79	24.7
8	**3**		 **25**	77	24.8

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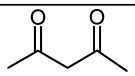
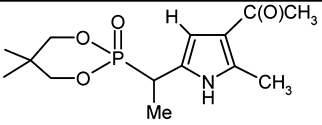
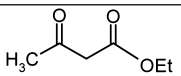
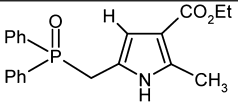
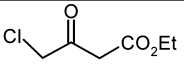
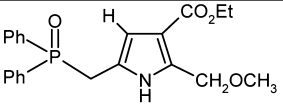
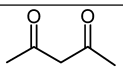
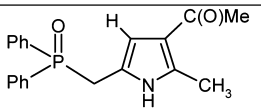
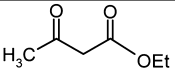
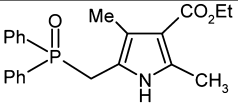
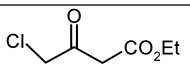
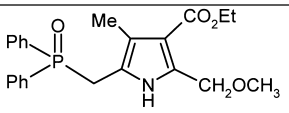
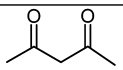
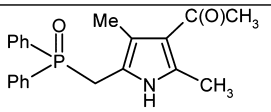
Table 2. continued

Entry	Allene	1,3-dicarbonyl substrate	Product	Yield[b]	δ(P)
9	**3**		 **26**	71	25.1
10	**4**		 **27**	88	30.9
11	**4**		 **28**	80	30.5
12	**4**		 **29**	70	33.0
13	**5**		 **30**	81	30.8
14	**5**		 **31**	77	30.8
15	**5**		 **32**	73	32.0

[a]Conditions: Me_3SiN_3 (1.2 equiv), DMF, allene (1.0 equiv), 2–4 h, then add ethyl acetoacetate (1.5 equiv), $Mn(OAc)_3{\cdot}2H_2O$ (10 mol %) and acetic acid (2 equiv) in MeOH and irradiate (λ = 254 nm) for an additional 4 h. [b]After isolation.

straightforward.[5c] Because the NH moiety interfered in the reaction of **27** with 4-nitrobenzaldehyde by using NaH as base (TLC evidence), we protected the pyrrole-NH with CH_2Ph by using a known procedure[16] to obtain the N-benzylated compound **36**. We then performed the olefination using *p*-nitrobenzaldehyde, ferrocene carboxaldehyde, compound **37**,[17] and 9-anthraldehyde, respectively, which led to *phosphorus-free* extended conjugated pyrroles **38**–**41** in good yields (Scheme 9). The ^1H NMR spectra of these compounds suggest that the olefins have an (*E*)-configuration. The structure of one of these compounds **41** is confirmed by X-ray crystallography (Figure S5 in Supporting Information). Thus, this reaction clearly

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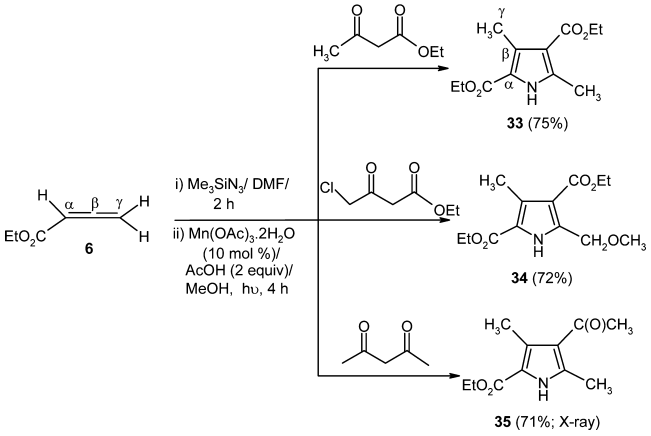
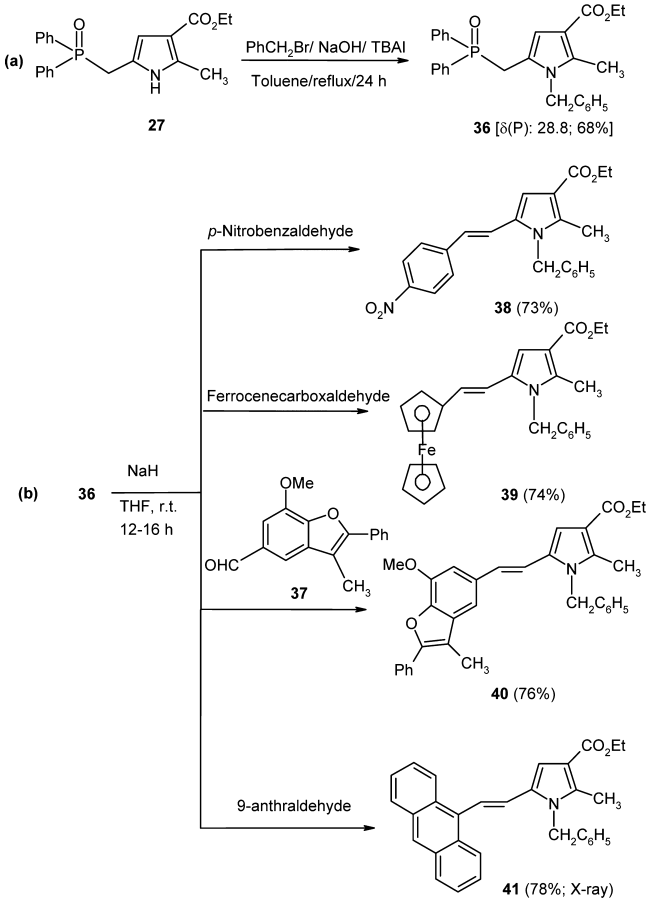
Scheme 8. Synthesis of Multisubstituted Pyrroles by Using Allenoate 6 and 1,3-Dicarbonyls



Scheme 9. Horner Reaction of the Protected Pyrrole 36 Leading to Phosphorus-Free Extended Conjugated Pyrroles 38−41



shows one possible avenue for utililizing these phosphorus-based pyrroles.

CONCLUSION

Thermolysis of phosphorus-based vinyl azides under solvent-free and catalyst-free conditions provided an entirely new route for 1,4-pyrazines **13**−**17**. A simple one-pot method for multisubstituted pyrroles have been obtained starting from allenes via in situ-generated vinyl azides and 1,3-dicarbonyls using $Mn(OAc)_3{\cdot}2H_2O$ as the catalyst under photochemical conditions. In the case of phosphorus-based allenes **1**−**5** the β,γ-carbon atoms of allenes participated in the pyrrole ring formation whereas in allenoate **6**, the α,β-carbon atoms are involved. Finally, utility of the phosphorus-based pyrroles was shown in the Horner reaction that led to multisubstituted phosphorus-free extended conjugated pyrroles **38**−**41**.

EXPERIMENTAL SECTION

1. General Comments. Solvents were dried according to known methods as appropriate.[18] ^1H, ^{13}C, and ^{31}P NMR spectra (^1H, 400 MHz or 500 MHz; ^{13}C, 100 or 125 MHz; ^{31}P, 162 MHz) were recorded using a 400 or 500 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ (δ = 0) or 85% H_3PO_4 (δ = 0). IR spectra were recorded on an FTIR spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Elemental analyses were carried out on a CHN analyzer. Mass spectra were recorded using LCMS or HRMS (ESI-TOF analyzer) instruments.

2. Synthesis of Allenes 1−6. The phosphorus-based allenes **1**−**5**[2b,13] and allenoate **6**[14] were synthesized according to literature procedures.

3. Synthesis of Vinyl Azides 7−12. Compounds **7**−**11** were prepared by a procedure developed in our laboratory.[5c] To a solution of Me_3SiN_3 (0.15 g, 1.3 mmol) in DMF (5 mL) was added the allene **1** (0.21 g, 1.1 mmol), and mixture was stirred at room temperature for 2−4 h. The solvent was removed under reduced pressure to give the crude product **7**, which was purified by column chromatography on silica gel using EtOAc−hexane (3:2) as the eluent. Compounds **8**−**11** were also prepared similarly. Among these, **7** and **9**−**11** are new. The vinyl azide **12** was synthesized from allenoate **6** by using a reported method.[15]

Compound ***7***. Yield 0.22 g (88%); mp 64−66 °C (white solid); IR (KBr, cm^{-1}) 2976, 2101, 1630, 1478, 1265, 1059, 1009, 982; ^1H NMR (400 MHz, $CDCl_3$) δ 1.05 and 1.15 (2 s, 6H), 2.74 (d, J = 21.2 Hz, 2H), 3.87−3.93 and 4.23−4.28 (2 m, 4H), 4.91−4.93 and 5.01−5.02 (2 dd, $J \sim$ 2.0, 5.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.5, 30.5 (d, J = 136.7 Hz), 32.6 (d, J = 6.1 Hz), 75.5, 75.6, 102.7 (d, J = 10.6 Hz), 137.1 (d, J = 11.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.8; LC/MS m/z 232 $[M + 1]^+$; Anal. Calcd for $C_8H_{14}N_3O_3P$: C, 41.56; H, 6.10; N, 18.18. Found: C, 41.63; H, 6.14; N, 18.25.

Compound ***9***. This azide was synthesized from the allene **3** (0.20 g, 1.0 mmol) and was isolated by using ethyl acetate−hexane (3:2) mixture as the eluent. Yield 0.21 g (87%); mp 76−78 °C (white solid); IR (KBr, cm^{-1}) 2967, 2128, 1744, 1476, 1229, 1057, 1013, 853; ^1H NMR (400 MHz, $CDCl_3$) δ 0.99 and 1.12 (2 s, 6H), 1.43 (dd, $J \sim$ 18.2 Hz, $J \sim$ 7.0 Hz, 3H), 2.66−2.77 (m, 1H), 3.78−3.89 and 4.21−4.26 (2 m, 4H), 4.89 and 5.04 (2 br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5 (d, J = 5.5 Hz), 21.4, 21.7, 32.8 (d, J = 5.8 Hz), 35.8 (d, J = 135.7 Hz), 75.1 (d, J = 2.2 Hz), 75.2 (d, J = 2.5 Hz), 101.0 (d, J = 10.0 Hz), 143.3 (d, J = 9.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.9; LC/MS m/z 246 $[M + 1]^+$; Anal. Calcd for $C_9H_{16}N_3O_3P$: C, 44.08; H, 6.58; N, 17.14. Found: C, 44.16; H, 6.51; N, 17.12.

Compound ***10***. This azide was synthesized from the allene **4** (0.50 g, 2.1 mmol) and was isolated by using ethyl acetate−hexane (3:2) mixture as the eluent. Yield 0.52 g (89%); mp 102−104 °C (white solid); IR (KBr, cm^{-1}) 3056, 2124, 1616, 1437, 1186, 1121, 853; ^1H NMR (400 MHz, $CDCl_3$) δ 3.08 (d, J = 13.2 Hz, 2H), 4.79 and 4.90 (2 br, 2H), 7.48−7.54 and 7.74−7.79 (2 m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 36.1 (d, J = 66.4 Hz), 102.9 (d, J = 7.8 Hz), 128.6, 128.7, 131.0, 131.1, 131.9 (d, J = 100.2 Hz), 132.1, 137.5 (d, J = 9.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.1; LC/MS m/z 284 $[M + 1]^+$; Anal. Calcd for $C_{15}H_{14}N_3OP$: C, 63.60; H, 4.98; N, 14.83. Found: C, 63.51; H, 4.91; N, 14.75.

Compound ***11***. This azide was synthesized from the allene **5** (0.41 g, 1.6 mmol) and was isolated by using ethyl acetate−hexane (3:2) mixture as the eluent. Yield 0.39 g (83%); mp 98−100 °C (white solid); IR (KBr, cm^{-1}) 3057, 2116, 1437, 1271, 1177, 1119, 843; ^1H NMR (400 MHz, $CDCl_3$) δ 1.55−1.57 (m, 3H), 3.13 (d, J = 14.0 Hz,

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2H), 5.30−5.35 (m, 1H), 7.46−7.56 and 7.76−7.81 (2 m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 32.3 (d, J = 66.7 Hz), 114.0 (d, J = 8.8 Hz), 128.5, 128.6, 129.2 (d, J = 10.9 Hz), 131.1, 131.2, 132.0, 132.3 (d, J = 99.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.3; LC/MS m/z 298 $[M + 1]^+$; Anal. Calcd for $C_{16}H_{16}N_3OP$: C, 64.64; H, 5.42; N, 14.13. Found: C, 64.51; H, 5.38; N, 14.25.

4. Synthesis of Phosphorus-Based 1,4-Pyrazines 13−17. Azide **7** (0.20 g, 0.80 mmol) was taken in a round-bottomed flask, which was then stoppered and heated at 120 °C for 15 min. The reaction mixture was cooled to rt, and the product **13** was precipitated by adding ethyl acetate (5 mL). Compounds **14**−**17** were also synthesized by following the same method.

Compound ***13***. Yield 0.27 g (78%); mp 224−226 °C (white solid); IR (KBr, cm^{-1}) 2982, 1487, 1408, 1265, 1065, 1003; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.89 and 1.01 (2 s, 12H), 3.51 (d, J = 20.8 Hz, 4H), 3.85−3.91 and 4.14−4.19 (2 m, 8H), 8.60 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 21.4, 32.2 (d, J = 131.8 Hz), 32.5 (d, J = 5.9 Hz), 75.6, 75.7, 144.8, 146.5 (d, J = 2.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.1; LC/MS m/z 405 $[M + 1]^+$; Anal. Calcd for $C_{16}H_{26}N_2O_6P_2$: C, 47.53; H, 6.48; N, 6.93. Found: C, 47.62; H, 6.52; N, 6.85; HRMS (ESI) Calcd for $C_{16}H_{27}N_2O_6P_2$ $[M + H]^+$ 405.1344, found 405.1344.

Compound ***14***. This product was synthesized from the azide **8** (0.15 g, 0.6 mmol). Yield 0.20 g (75%); mp 222−224 °C (white solid); IR (KBr, cm^{-1}) 2965, 1474, 1377, 1244, 1055, 1015; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 and 1.06 (2 s, 12H), 2.64 (s, 6H), 3.53 (d, J = 20.4 Hz, 4H), 3.89−3.95 and 4.11−4.16 (2 m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.1, 21.5, 21.6, 32.1 (d, J = 131.1 Hz), 32.5 (d, J = 6.5 Hz), 75.7, 75.8, 144.2, 149.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.3; LC/MS m/z 431 $[M - 1]^+$; Anal. Calcd for $C_{18}H_{30}N_2O_6P_2$: C, 50.00; H, 6.99; N, 6.48. Found: C, 50.12; H, 6.92; N, 6.41; HRMS (ESI) Calcd for $C_{18}H_{31}N_2O_6P_2$ $[M + H]^+$ 433.1657, found 433.1657. This compound was crystallized from methanol (2 mL) at 25 °C. The X-ray structure was determined for this sample.

Compound ***15***. This product was synthesized from the azide **9** (0.15 g, 0.6 mmol). Yield 0.20 g (74%); mp 222−224 °C (white solid); IR (KBr, cm^{-1}) 2922, 2114, 1647, 1534, 1269, 1047, 1017; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.91 and 0.96 (2 s, 12H), 1.73 (dd, J = 18.0 Hz, J ∼ 7.2 Hz, 6H), 3.59−3.87 (m, 6H), 4.16−4.25 (m, 4H), 8.64 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.6, 21.3$_9$, 21.4$_5$, 32.6 (br), 37.3 (d, J = 133.1 Hz), 75.1, 75.2, 144.1, 151.3; ^{31}P NMR (162 MHz, $CDCl_3$) δ 23.5; LC/MS m/z 431 $[M - 1]^+$; Anal. Calcd for $C_{18}H_{30}N_2O_6P_2$: C, 50.00; H, 6.99; N, 6.48. Found: C, 49.95; H, 7.06; N, 6.55; HRMS (ESI) Calcd for $C_{18}H_{31}N_2O_6P_2$ $[M + H]^+$ 433.1657, found 433.1657.

Compound ***16***. This product was synthesized from the azide **10** (0.20 g, 0.7 mmol). Yield 0.26 g (72%); mp 258−260 °C (white solid); IR (KBr, cm^{-1}) 3052, 1483, 1437, 1402, 1177, 1121, 1032; ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.87 (d, J = 13.6 Hz, 4H), 7.43−7.55 and 7.69−7.74 (2 m, 20H), 8.42 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 38.3 (d, J = 63.7 Hz), 128.6, 128.6$_6$, 128.7$_2$, 131.0$_2$, 131.0$_7$, 131.1$_2$, 131.8 (d, J = 100.7 Hz), 132.1, 144.9, 146.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 29.3; LC/MS m/z 507 $[M - 1]^+$; Anal. Calcd for $C_{30}H_{26}N_2O_2P_2$: C, 70.86; H, 5.15; N, 5.51. Found: C, 70.73; H, 5.08; N, 5.60; HRMS (ESI) Calcd for $C_{30}H_{26}N_2O_2P_2Na$ $[M + Na]^+$ 531.1367, found 531.1368.

Compound ***17***. This product was synthesized from the azide **11** (0.20 g, 0.7 mmol). Yield 0.26 g (73%); mp 232−234 °C (white solid); IR (KBr, cm^{-1}) 2951, 1435, 1227, 1186, 1121, 1074; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.29 (s, 6H), 3.83 (d, J = 14.0 Hz, 4H), 7.42−7.51 and 7.71−7.75 (2 m, 20H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 37.8 (d, J = 64.0 Hz), 128.3$_1$, 128.3$_7$, 128.4$_3$, 131.2$_5$, 131.3$_1$, 131.9, 132.9, 144.1, 150.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.6; LC/MS m/z 537 $[M + 1]^+$; Anal. Calcd for $C_{32}H_{30}N_2O_2P_2$: C, 71.63; H, 5.64; N, 5.22. Found: C, 71.52; H, 5.68; N, 5.16; HRMS (ESI) Calcd for $C_{32}H_{31}N_2O_2P_2$ $[M + H]^+$ 537.1861, found 537.1861.

5. Synthesis of Multisubstituted Pyrrole Derivatives 18−35. To a solution of Me_3SiN_3 (0.77 g, 6.7 mmol) in DMF (10 mL) was added the allene **1** (1.05 g, 5.6 mmol), and the reaction mixture stirred for 2−4 h. To this was added a solution of ethyl acetoacetate (1.10 g, 8.4 mmol), $Mn(OAc)_3{\cdot}2H_2O$ (0.15 g, 0.56 mmol), and acetic acid (0.67 g, 11.2 mmol) in MeOH (5 mL), and the mixture was irradiated in a photoreactor (λ = 254 nm) for further 4 h. Solvent was removed under reduced pressure and the crude product treated with ethyl acetate (20 mL). The resulting slurry was filtered through a plug of silica pad. Ethyl acetate was removed from the filtrate, and the product **18** was purified by column chromatography (EtOAc−hexane: 7:3). Compounds **19**−**35** were also prepared similarly.

Compound ***18***. Yield 1.42 g (80%); mp 110−112 °C (white solid); IR (KBr, cm^{-1}) 3248, 2969, 1699, 1599, 1263, 1063, 1007; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 and 1.06 (2 s, 6H), 1.30 (t, J ∼ 7.0 Hz, 3H), 2.37 (s, 3H), 3.23 (d, J = 19.6 Hz, 2H), 3.80−3.86 and 4.07−4.12 (m, 4H), 4.21−4.22 (m, 2H), 6.35 (s, 1H), 9.67 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 14.5, 21.3, 21.4, 23.8 (d, J = 136.8 Hz), 32.6 (d, J = 6.4 Hz), 59.3, 75.9, 76.0, 110.1 (d, J = 10.0 Hz), 111.9, 117.7 (d, J = 11.1 Hz), 136.0, 165.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.0; LC/MS m/z 316 $[M + 1]^+$; Anal. Calcd for $C_{14}H_{22}NO_5P$: C, 53.33; H, 7.03; N, 4.44. Found: C, 53.41; H, 6.92; N, 4.62; HRMS (ESI) Calcd for $C_{14}H_{22}NO_5PNa$ $[M + Na]^+$ 338.1134, found 338.1134. This compound was crystallized from dichloromethane−hexane (9:1) at 25 °C. The X-ray structure was determined for this sample.

Compound ***19***. This pyrrole was prepared from allene **1** (0.24 g, 1.3 mmol) and ethyl 4-chloroacetoacetate (0.31 g, 1.9 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.34 g (78%); mp 126−128 °C; IR (KBr, cm^{-1}) 3246, 1699, 1597, 1269, 1055, 1001; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 and 1.01 (2 s, 6H), 1.32 (t, J ∼ 7.0 Hz, 3H), 3.24 (d, J = 20.0 Hz, 2H), 3.43 (s, 3H), 3.77−3.84 and 4.16−4.27 (2 m, 6H), 4.75 (s, 2H), 6.41 (s, 1H), 9.20 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 21.3$_7$, 21.4$_0$, 24.2 (d, J = 138.1 Hz), 32.6 (d, J = 6.3 Hz), 58.6, 59.5, 66.8, 75.6, 75.7, 110.2 (d, J = 9.1 Hz), 112.0, 119.4 (d, J = 10.9 Hz), 135.9, 164.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.5; LC/MS m/z 346 $[M + 1]^+$; Anal. Calcd for $C_{15}H_{24}NO_6P$: C, 52.17; H, 7.01; N, 4.06. Found: C, 52.05; H, 7.11; N, 4.12; HRMS (ESI) Calcd for $C_{15}H_{24}NO_6P$ $[M]^+$ 345.1341, found 345.1341.

Compound ***20***. This pyrrole was prepared from allene **1** (0.17 g, 0.9 mmol) and acetylacetone (0.14 g, 1.4 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.19 g (72%); mp 86−88 °C (white solid); IR (KBr, cm^{-1}) 3221, 2975, 1655, 1258, 1061, 1007; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.99 and 1.05 (2 s, 6H), 2.34 (s, 3H), 2.41 (s, 3H), 3.24 (d, J = 20.0 Hz, 2H), 3.81−3.87 and 4.11−4.16 (2 m, 4H), 6.31 (s, 1H), 9.79 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 21.3, 21.4, 24.0 (d, J = 137.3 Hz), 28.5, 32.6 (d, J = 6.1 Hz), 75.9, 76.0, 110.2 (d, J = 9.4 Hz), 117.7 (d, J = 10.9 Hz), 121.2, 135.7, 194.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.4; LC/MS m/z 284 $[M - 1]^+$; Anal. Calcd for $C_{13}H_{20}NO_4P$: C, 54.73; H, 7.07; N, 4.91. Found: C, 54.65; H, 7.15; N, 4.85; HRMS (ESI) Calcd for $C_{13}H_{21}NO_4P$ $[M + H]^+$ 286.1208, found 286.1208. This compound was crystallized from dichloromethane−hexane (9:1) at 25 °C. X-ray structure was determined for this sample.

Compound ***21***. This pyrrole was prepared from allene **2** (0.38 g, 1.9 mmol) and ethyl acetoacetate (0.38 g, 2.9 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.51 g (81%); mp 162−164 °C (white solid); IR (KBr, cm^{-1}) 3250, 1686, 1262, 1165, 1049, 1001; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 and 1.04 (2 s, 6H), 1.33 (t, J = 7.2 Hz, 3H), 2.18 (d, J = 2.8 Hz, 3H), 2.42 (d, J = 1.2 Hz, 3H), 3.17 (d, J = 19.6 Hz, 2H), 3.76−3.82 (m, 2H), 4.12−4.27 (m, 4H), 9.01 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.1, 13.8, 14.5, 21.2, 21.4, 22.1 (d, J = 135.5 Hz), 32.6 (d, J = 6.1 Hz), 59.0, 75.8, 75.9, 110.7, 114.6 (d, J = 11.5 Hz), 118.7 (d, J = 9.7 Hz), 135.7, 166.2; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.3; LC/MS m/z 330 $[M + 1]^+$; Anal. Calcd for $C_{15}H_{24}NO_5P$: C, 54.71; H, 7.35; N, 4.25. Found: C, 54.91; H, 7.36; N, 4.32; HRMS (ESI) Calcd for $C_{15}H_{24}NO_5PNa$ $[M + Na]^+$ 352.1290, found 352.1290.

Compound ***22***. This pyrrole was prepared from allene **2** (0.36 g, 1.8 mmol) and ethyl 4-chloroacetoacetate (0.44 g, 2.7 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.44 g (69%); mp 170−172 °C (white solid); IR (KBr, cm^{-1}) 3353, 1688, 1472, 1372, 1269, 1169, 1059, 1009; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 and 0.99 (2 s, 6H), 1.34 (t, J ∼ 7.2 Hz, 3H), 2.19 (s,

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3H), 3.20 (d, J = 19.6 Hz, 2H), 3.43 (s, 3H), 3.72−3.81 (m, 2H), 4.16−4.28 (m, 4H), 4.72 (s, 2H), 9.12 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 20.8, 21.4, 21.5, 24.3 (d, J = 138.8 Hz), 32.7 (d, J = 6.3 Hz), 58.6, 59.6, 66.9, 75.6$_7$, 75.7$_2$, 110.3 (d, J = 8.8 Hz), 112.0, 119.5 (d, J = 11.3 Hz), 135.9, 165.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.3; LC/MS m/z 360 $[M + 1]^+$; Anal. Calcd for $C_{16}H_{26}NO_6P$: C, 53.48; H, 7.29; N, 3.90. Found: C, 53.36; H, 7.36; N, 3.82; HRMS (ESI) Calcd for $C_{16}H_{27}NO_6P$ $[M + H]^+$ 360.1576, found 360.1576.

Compound ***23***. This pyrrole was prepared from allene **2** (0.42 g, 2.1 mmol) and acetylacetone (0.32 g, 3.2 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.45 g (72%); mp 178−180 °C (white solid); IR (KBr, cm^{-1}) 3223, 1644, 1478, 1250, 1053, 999; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.03 and 1.07 (2 s, 6H), 2.23 (d, J = 2.8 Hz, 3H), 2.41 (s, 3H), 2.45 (s, 3H), 3.20 (d, J = 19.6 Hz, 2H), 3.80−3.86 and 4.15−4.21 (2 m, 4H), 9.22 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.8, 15.1, 21.4, 21.6 (d, J = 138.0 Hz), 30.9 (d, J = 3.2 Hz), 32.6 (d, J = 6.1 Hz), 75.6, 75.7, 115.0 (d, J = 11.1 Hz), 118.2 (d, J = 9.8 Hz), 121.4, 134.9 (d, J = 7.3 Hz), 195.1 (d, J = 4.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.3; LC/MS m/z 300 $[M + 1]^+$; Anal. Calcd for $C_{14}H_{22}NO_4P$: C, 56.18; H, 7.41; N, 4.68. Found: C, 56.35; H, 7.32; N, 4.81; HRMS (ESI) Calcd for $C_{14}H_{23}NO_4P$ $[M + H]^+$ 300.1364, found 300.1364.

Compound ***24***. This pyrrole was prepared from allene **3** (0.10 g, 0.5 mmol) and ethyl acetoacetate (0.09 g, 0.7 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.13 g (79%); mp 124−126 °C (white solid); IR (KBr, cm^{-1}) 3233, 2922, 1694, 1260, 1061; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 and 1.04 (2 s, 6H), 1.30 (t, $J \sim$ 7.0 Hz, 3H), 1.56 (dd, $J \sim$ 18.2 Hz, J = 7.2 Hz, 3H), 2.39 (s, 3H), 3.28−3.39 (m, 1H), 3.69−3.84 and 4.14−4.24 (2 m, 6H), 6.37 (s, 1H), 9.60 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 14.0, 14.6, 21.4, 21.6, 30.0 (d, J = 137.2 Hz), 32.7 (d, J = 5.9 Hz), 59.2, 75.2 (d, J = 6.6 Hz), 75.4 (d, J = 6.5 Hz), 108.6 (d, J = 9.2 Hz), 111.6 (d, J = 1.4 Hz), 124.3 (d, J = 9.5 Hz), 136.1, 165.6; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.7; LC/MS m/z 330 $[M + 1]^+$; Anal. Calcd for $C_{15}H_{24}NO_5P$: C, 54.71; H, 7.35; N, 4.25. Found: C, 54.81; H, 7.28; N, 4.33; HRMS (ESI) Calcd for $C_{15}H_{25}NO_5P$ $[M + H]^+$ 330.1470, found 330.1470.

Compound ***25***. This pyrrole was prepared from allene **3** (0.24 g, 1.2 mmol) and ethyl 4-chloroacetoacetate (0.30 g, 1.8 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.33 g (77%); mp 134−136 °C (white solid); IR (KBr, cm^{-1}) 3351, 1692, 1468, 1375, 1227, 1059, 1009; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.94 and 1.02 (2 s, 6H), 1.32 (t, J = 7.2 Hz, 3H), 1.59 (dd, J = 18.2 Hz, $J \sim$ 7.4 Hz, 3H), 3.30−3.39 (m, 1H), 3.42 (s, 3H), 3.69−3.80 and 4.20−4.27 (2 m, 6H), 4.75 (s, 2H), 6.42 (s, 1H), 9.43 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 14.5, 21.3, 21.6, 30.1 (d, J = 137.7 Hz), 32.7 (d, J = 5.6 Hz), 58.6, 59.6, 66.8, 75.1, 75.2, 108.7 (d, J = 8.8 Hz), 111.7, 125.9 (d, J = 9.2 Hz), 135.8, 165.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.8; LC/MS m/z 360 $[M + 1]^+$; Anal. Calcd for $C_{16}H_{26}NO_6P$: C, 53.48; H, 7.29; N, 3.90. Found: C, 53.62; H, 7.23; N, 3.81; HRMS (ESI) Calcd for $C_{16}H_{26}NO_6P$ $[M]^+$ 359.1498, found 359.1498.

Compound ***26***. This pyrrole was prepared from allene **3** (0.20 g, 1.0 mmol) and acetylacetone (0.15 g, 1.5 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.21 g (71%); mp 104−106 °C; IR (KBr, cm^{-1}) 3212, 2978, 1649, 1474, 1256, 1065, 1011; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97 and 1.10 (2 s, 6H), 1.59 (dd, J = 18.0 Hz, J = 7.2 Hz, 3H), 2.37 (s, 3H), 2.48 (s, 3H), 3.31−3.36 (m, 1H), 3.74−3.85 and 4.22−4.25 (m, 4H), 6.34 (s, 1H), 9.30 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 14.1 (d, J = 5.1 Hz), 21.3, 21.7, 28.5, 29.9 (d, J = 137.4 Hz), 32.7 (d, J = 5.8 Hz), 75.1, 75.2, 108.9 (d, J = 9.5 Hz), 120.9, 124.2 (d, J = 9.2 Hz), 135.6, 194.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.1; LC/MS m/z 300 $[M + 1]^+$; Anal. Calcd for $C_{14}H_{22}NO_4P$: C, 56.18; H, 7.41; N, 4.68. Found: C, 56.32; H, 7.48; N, 4.61; HRMS (ESI) Calcd for $C_{14}H_{23}NO_4P$ $[M + H]^+$ 300.1364, found 300.1364.

Compound ***27***. This pyrrole was prepared from allene **4** (0.41 g, 1.7 mmol) and ethyl acetoacetate (0.34 g, 2.6 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.55 g (88%); mp 178−180 °C (white solid); IR (KBr, cm^{-1}) 3208, 2924, 1688, 1437, 1331, 1177, 1073; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.28 (t, $J \sim$ 7.0 Hz, 3H), 2.25 (s, 3H), 3.66 (d, J = 11.6 Hz, 2H), 4.17−4.21 (m, 2H), 6.10 (s, 1H), 7.45−7.71 (m, 10H), 10.43 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 14.5, 29.6 (d, J = 68.0 Hz, PCH), 59.2, 109.9, 111.5, 119.0, 128.7, 128.9, 130.9, 131.3, 132.2, 136.1, 165.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.9; LC/MS m/z 368 $[M + 1]^+$; Anal. Calcd for $C_{21}H_{22}NO_3P$: C, 68.66; H, 6.04; N, 3.81. Found: C, 68.56; H, 6.12; N, 3.76; HRMS (ESI) Calcd for $C_{21}H_{22}NO_3PNa$ $[M + Na]^+$ 390.1235, found 390.1235.

Compound ***28***. This pyrrole was prepared from allene **4** (0.29 g, 1.2 mmol) and ethyl 4-chloroacetoacetate (0.31 g, 1.9 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.38 g (80%); mp 182−184 °C (white solid); IR (KBr, cm^{-1}) 3351, 2122, 1703, 1618, 1437, 1285, 1186, 1024; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, $J \sim$ 7.0 Hz, 3H), 3.37 (s, 3H), 3.62 (d, J = 12.8 Hz, 2H), 4.21 (qrt, $J \sim$ 7.0 Hz, 2H), 4.69 (s, 2H), 6.24 (s, 1H), 7.44−7.55 and 7.66−7.70 (2 m, 10H), 9.92 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 29.5 (d, J = 68.2 Hz), 58.5, 59.5, 66.8, 110.2 (d, J = 7.4 Hz), 111.6, 120.9 (d, J = 9.2 Hz), 128.7, 128.8, 130.8, 130.9, 131.8 (d, J = 99.3 Hz), 132.2, 135.9, 165.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.5; LC/MS m/z 398 $[M + 1]^+$; Anal. Calcd for $C_{22}H_{24}NO_4P$: C, 66.49; H, 6.09; N, 3.52. Found: C, 66.59; H, 6.14; N, 3.45; HRMS (ESI) Calcd for $C_{22}H_{24}NO_4PNa$ $[M + Na]^+$ 420.1341, found 420.1341.

Compound ***29***. This pyrrole was prepared from allene **4** (0.29 g, 1.2 mmol) and acetylacetone (0.19 g, 1.9 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.28 g (70%); mp 92−94 °C (white solid); IR (KBr, cm^{-1}) 3289, 1645, 1437, 1175, 1115, 945; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.21 (s, 3H), 2.41 (s, 3H), 4.16 (d, J = 12.4 Hz, 2H), 6.61 (s, 1H), 7.37−7.49 and 7.71−7.76 (2 m, 10H), 10.90 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 28.4, 29.5 (d, J = 68.4 Hz), 110.2 (d, J = 7.8 Hz), 119.2 (d, J = 9.6 Hz), 121.0, 128.7, 128.8, 130.8, 130.9, 131.3, 131.7 (d, J = 99.5 Hz), 131.8 (d, J = 10.9 Hz), 132.3, 135.6, 194.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.0; LC/MS m/z 338 $[M + 1]^+$; Anal. Calcd for $C_{20}H_{20}NO_2P$: C, 71.21; H, 5.98; N, 4.15. Found: C, 71.36; H, 5.88; N, 4.21.

Compound ***30***. This pyrrole was prepared from allene **5** (0.53 g, 2.1 mmol) and ethyl acetoacetate (0.40 g, 3.1 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.64 g (81%); mp 116−118 °C (white solid); IR (KBr, cm^{-1}) 3229, 1699, 1439, 1267, 1175, 953; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.30 (t, $J \sim$ 7.0 Hz, 3H), 1.85 (d, J = 2.0 Hz, 3H), 2.31 (s, 3H), 3.57 (d, J = 12.0 Hz, 2H), 4.20 (qrt, $J \sim$ 7.0 Hz, 2H), 7.41−7.54 and 7.64−7.69 (2 m, 10H), 10.19 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.8, 14.0, 14.5, 27.6 (d, J = 69.1 Hz), 58.9, 110.4, 115.9 (d, J = 9.6 Hz), 118.6 (d, J = 7.3 Hz), 128.7, 128.8, 130.8, 131.0, 132.0 (d, J = 98.3 Hz), 132.2, 136.0, 166.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.8; LC/MS m/z 382 $[M + 1]^+$; Anal. Calcd for $C_{22}H_{24}NO_3P$: C, 69.28; H, 6.34; N, 3.67. Found: C, 69.12; H, 6.29; N, 3.75.

Compound ***31***. This pyrrole was prepared from allene **5** (0.43 g, 1.7 mmol) and ethyl 4-chloroacetoacetate (0.41 g, 2.5 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.54 g (77%); mp 120−122 °C (white solid); IR (KBr, cm^{-1}) 3250, 2926, 1698, 1437, 1181, 1100; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32 (t, $J \sim$ 7.0 Hz, 3H), 2.01 (s, 3H), 3.40 (s, 3H), 3.53 (d, J = 12.4 Hz, 2H), 4.22 (qrt, $J \sim$ 7.0 Hz, 2H), 4.70 (s, 2H), 7.46−7.56 and 7.65−7.69 (2 m, 10H), 9.65 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.5, 14.5, 27.3 (d, J = 68.9 Hz), 58.6, 59.2, 67.6, 110.1, 117.7 (d, J = 9.0 Hz), 118.9 (d, J = 7.4 Hz), 128.7, 128.8, 130.7$_6$, 130.8$_3$, 132.0$_6$ (d, J = 98.6 Hz), 132.1$_1$, 132.1$_3$, 135.9, 165.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.8; LC/MS m/z 412 $[M + 1]^+$; Anal. Calcd for $C_{23}H_{26}NO_4P$: C, 67.14; H, 6.37; N, 3.40. Found: C, 67.25; H, 6.41; N, 3.34; HRMS (ESI) Calcd for $C_{23}H_{26}NO_4PNa$ $[M + Na]^+$ 434.1497, found 434.1497.

Compound ***32***. This pyrrole was prepared from allene **5** (0.33 g, 1.3 mmol) and acetylacetone (0.19 g, 1.9 mmol). It was isolated by using ethyl acetate−hexane (7:3) mixture as the eluent. Yield 0.33 g (73%); mp 180−182 °C (white solid); IR (KBr, cm^{-1}) 3148, 1630, 1437, 1169, 1116, 965; ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.01 (s, 3H), 2.05 (s, 3H), 2.34 (s, 3H), 4.10 (d, J = 12.8 Hz, 2H), 7.41−7.47 and 7.75−7.79 (2 m, 10H), 9.51 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ

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11.0, 15.3, 27.7 (d, J = 69.1 Hz, PCH_2), 30.4, 109.2 (d, J = 9.5 Hz), 120.6, 126.7 (d, J = 6.7 Hz), 128.0, 128.1, 131.4, 131.5, 132.8, 133.0 (d, J = 96.2 Hz), 195.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 32.0; LC/MS m/z 352 $[M + 1]^+$; Anal. Calcd for $C_{21}H_{22}NO_2P$: C, 71.78; H, 6.31; N, 3.99. Found: C, 71.65; H, 6.39; N, 3.89.

Compound **33**. This pyrrole was prepared from allene **6** (0.11 g, 1.0 mmol) and ethyl acetoacetate (0.20 g, 1.6 mmol). It was isolated by using ethyl acetate−hexane (1:4) mixture as the eluent. Yield 0.18 g (75%); mp 90−92 °C (white solid); IR (KBr, cm^{-1}) 3289, 1669, 1445, 1215, 1157, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.36−1.41 (m, 6H), 2.54 and 2.58 (2 s, 6H), 4.29−4.38 (m, 4H), 9.00 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.9, 14.3, 14.4, 14.5, 59.5, 60.3, 113.7, 117.9, 130.9, 138.7, 161.6, 165.4; LC/MS m/z 240 $[M + 1]^+$; Anal. Calcd for $C_{12}H_{17}NO_4$: C, 60.24; H, 7.16; N, 5.85. Found: C, 60.32; H, 7.08; N, 5.81; HRMS (ESI) Calcd for $C_{12}H_{18}NO_4$ $[M + H]^+$ 240.1236, found 240.1236.

Compound **34**. This pyrrole was prepared from allene **6** (0.35 g, 3.1 mmol) and ethyl 4-chloroacetoacetate (0.76 g, 4.6 mmol). It was isolated by using ethyl acetate−hexane (1:4) mixture as the eluent. Yield 0.60 g (72%); mp 110−112 °C (white solid); IR (KBr, cm^{-1}) 3366, 1651, 1429, 1155, 1030; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.32−1.36 (m, 6H), 2.42 (s, 3H), 3.43 (s, 3H), 4.26−4.33 (m, 4H), 4.65 (s, 2H), 8.73 (br, 1H); ^{13}C NMR: (100 MHz, $CDCl_3$) δ 12.5, 14.3, 58.5, 60.1$_6$, 60.2$_1$, 66.4, 112.4, 112.7, 132.8, 133.1, 164.7, 165.3; LC/MS m/z 270 $[M + 1]^+$; Anal. Calcd for $C_{13}H_{19}NO_5$: C, 57.98; H, 7.11; N, 5.20. Found: C, 57.85; H, 7.16; N, 5.31.

Compound **35**. This pyrrole was prepared from allene **6** (0.45 g, 4.0 mmol) and acetylacetone (0.58 g, 5.8 mmol). It was isolated by using ethyl acetate−hexane (1:4) mixture as the eluent. Yield 0.59 g (71%); mp 122−124 °C (white solid); IR (KBr, cm^{-1}) 3281, 1649, 1556, 1281, 1202, 1022; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (t, J = 7.2 Hz, 3H), 2.45 (s, 3H), 2.53 (s, 3H), 2.59 (s, 3H), 4.31−4.37 (m, 2H), 9.21 (br, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 14.5, 15.2, 31.4, 60.4, 118.0, 123.6, 129.4, 138.2, 161.7, 195.6; LC/MS m/z 210 $[M + 1]^+$; Anal. Calcd for $C_{11}H_{15}NO_3$: C, 63.14; H, 7.23; N, 6.69. Found: C, 63.06; H, 7.31; N, 6.75; HRMS (ESI) Calcd for $C_{11}H_{15}NO_3Na$ $[M + Na]^+$ 232.0950, found 232.0951. This compound was crystallized from ethyl acetate−hexane (9:1) at 25 °C. The X-ray structure was determined for this sample.

6. Utility of Phosphorus-Based Pyrrole in the Horner Reaction: Synthesis of Phosphorus-Free Extended Conjugated Pyrroles 38−41. *a. Synthesis of N-Benzylated Pyrrole* **36**. Pyrrole **27** (0.20 g, 0.54 mmol) was added to toluene (5 mL) and aq NaOH (2 mL 50% solution). To this suspension were added tetrabutylammonium iodide (2.00 mg, 0.01 mmol) and benzyl bromide (0.09 g, 0.54 mmol). The mixture was heated under reflux for 24 h. The solvent was removed under reduced pressure, and water (10 mL) was added. The mixture was extracted with ethyl acetate (3 × 10 mL), dried (Na_2SO_4), and filtered, and the solvent was removed from the filtrate to give the crude product. Pure compound **36** was obtained by column chromatography (silica gel, ethyl acetate−hexane, 1:1) as a white solid. Yield 0.17 g (68%); mp 162−164 °C (white solid); IR (KBr, cm^{-1}) 2926, 1696, 1437, 1184, 1069; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.31 (t, J = 7.2 Hz, 3H), 2.45 (s, 3H), 3.50 (d, J = 12.0 Hz, 2H), 4.22 (qrt, J = 7.2 Hz, 2H), 5.29 (s, 2H), 6.17 (s, 1H), 6.85 (d, J = 6.8 Hz, 2H), 7.25−7.32 (m, 3H), 7.45−7.57 (m, 6H), 7.65−7.70 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 14.5, 29.6 (d, J = 68.6 Hz), 47.0, 59.3, 111.4 (d, J = 4.5 Hz), 111.9, 121.2 (d, J = 6.7 Hz), 125.6, 127.3, 128.5, 128.7, 128.9, 131.0, 131.1, 131.4, 131.5, 131.9 (d, J = 98.4 Hz), 132.0$_0$ (d, J = 98.6 Hz), 132.0$_1$, 132.0$_3$, 136.8, 137.1, 165.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 28.8; LC/MS m/z 457 $[M - 1]^+$; Anal. Calcd for $C_{28}H_{28}NO_3P$: C, 73.51; H, 6.17; N, 3.06. Found: C, 73.45; H, 6.22; N, 3.12; HRMS (ESI) Calcd for $C_{28}H_{29}NO_3P$ $[M + H]^+$ 458.1885, found 458.1885.

b. Synthesis of Phosphorus-Free Extended Conjugated Pyrroles **38−41**. The phosphonate **36** (0.14 g, 0.30 mmol) was dissolved in dry THF (5 mL) and added dropwise (10 min) to a suspension of NaH (0.014 g, 0.60 mmol) in THF (5 mL) at 0 °C with stirring. The mixture was stirred further at this temperature for 0.5 h. Then 4-nitrobenzaldehyde (0.05 g, 0.30 mmol) in THF (2 mL) was added and the mixture stirred for 12 h at room temperature. Water (10 mL) was added and the aqueous layer thoroughly extracted with diethyl ether (3 × 20 mL). The organic layer was collected, dried (Na_2SO_4), and filtered, and the solvent removed from the filtrate to give a residue that was purified by column chromatography [silica gel, ethyl acetate−hexane (1:4)] to furnish **38**. Compounds **39**−**41** were also synthesized in a manner similar to that for compound **38**.

Compound **38**. Yield 0.09 g (73%); mp 124−126 °C (yellow solid); IR (KBr, cm^{-1}) 2963, 1703, 1588, 1343, 1262, 1020; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, J = 7.2 Hz, 3H), 2.54 (s, 3H), 4.32 (qrt, J = 7.2 Hz, 2H), 5.24 (s, 2H), 6.95−7.01 (m, 3H), 7.08 (s, 1H), 7.30−7.46 (m, 6H), 8.12−8.15 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.5, 14.5, 47.0, 59.7, 109.6, 113.6, 120.6, 124.2, 124.6, 125.6, 126.2, 127.9, 128.1, 128.6, 129.2, 130.4, 136.5, 138.4, 144.0, 165.1; LC/MS m/z 391 $[M + 1]^+$; Anal. Calcd for $C_{23}H_{22}N_2O_4$: C, 70.75; H, 5.68; N, 7.17. Found: C, 70.68; H, 5.75; N, 7.22; HRMS (ESI) Calcd for $C_{23}H_{22}N_2O_4Na$ $[M + Na]^+$ 413.1477, found 413.1478.

Compound **39**. This compound was prepared from **36** (0.34 g, 0.75 mmol) and ferrocene carboxaldehyde (0.16 g, 0.75 mmol). It was isolated by using hexane as the eluent. Yield 0.24 g (74%); mp 118−120 °C (violet solid); IR (KBr, cm^{-1}) 3372, 2926, 1696, 1427, 1240, 1211, 1161, 1028; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, J = 7.2 Hz, 3H), 2.52 (s, 3H), 4.02 (s, 5H), 4.21−4.30 (m, 6H), 5.16 (s, 2H), 6.39 (d, $J \sim$ 15.8 Hz, 1H), 6.66 (d, $J \sim$ 15.8 Hz), 6.84 (s, 1H), 6.99−7.01 (m, 2H), 7.29−7.36 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.3, 14.6, 46.9, 59.4, 66.5, 68.9, 69.2, 83.4, 106.3, 112.6, 114.0, 125.8, 126.6, 127.6, 128.9, 131.9, 136.4, 137.1, 165.5; LC/MS m/z 452 $[M - 1]^+$; Anal. Calcd for $C_{27}H_{27}NO_2Fe$: C, 71.53; H, 6.00; N, 3.09. Found: C, 71.42; H, 6.08; N, 3.15; HRMS (ESI) Calcd for $C_{27}H_{28}NO_2Fe$ $[M + H]^+$ 454.1469, found 454.1469.

Compound **40**. This compound was prepared from **36** (0.14 g, 0.3 mmol) and compound **37**[15] (0.08 g, 0.3 mmol). It was isolated by using ethyl acetate−hexane (1:4) mixture as the eluent. Yield 0.11 g (76%); mp 120−122 °C (white solid); IR (KBr, cm^{-1}) 2976, 2930, 1694, 1597, 1453, 1215, 1100, 1055; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39 (t, $J \sim$ 7.0 Hz, 3H), 2.45 (s, 3H), 2.53 (s, 3H), 4.03 (s, 3H), 4.32 (qrt, $J \sim$ 7.0 Hz, 2H), 5.23 (s, 2H), 6.76−6.79 (m, 2H), 6.96 (s, 1H), 7.02−7.09 (m, 4H), 7.27−7.38 (m, 4H), 7.45−7.49 (m, 2H), 7.80−7.82 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.7, 11.4, 14.6, 47.1, 56.3, 59.5, 105.1, 107.2, 109.9, 111.6, 112.8, 115.4, 125.9, 126.8, 127.6, 128.0, 128.6, 128.8, 129.0, 131.1, 131.6, 133.1, 136.9$_6$, 137.0$_3$, 142.8, 145.1, 151.5, 165.5. LC/MS m/z 506 $[M + 1]^+$; Anal. Calcd for $C_{33}H_{31}NO_4$: C, 78.39; H, 6.18; N, 2.77. Found: C, 78.26; H, 6.21; N, 2.71.

Compound **41**. This compound was prepared from **36** (0.30 g, 0.7 mmol) and 9-anthraldehyde (0.14 g, 0.7 mmol). It was isolated by using ethyl acetate−hexane (1:4) mixture as the eluent. Yield 0.23 g (78%); mp 128−130 °C (yellow solid); IR (KBr, cm^{-1}) 2986, 2928, 1698, 1443, 1242, 1211, 1169, 1069 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43 (t, $J \sim$ 7.0 Hz, 3H), 2.61 (s, 3H), 4.37 (qrt, $J \sim$ 7.0 Hz, 2H), 5.21 (s, 2H), 6.68 (d, $J \sim$ 16.2 Hz, 1H), 6.98−6.99 (m, 2H), 7.21 (s, 1H), 7.28−7.45 (m, 7H), 7.72 (d, $J \sim$ 16.2 Hz, 1H), 7.95−7.97 (m, 2H), 8.08−8.10 (m, 2H), 8.34 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 11.4, 14.6, 47.0, 59.6, 107.8, 112.9, 123.6, 125.1, 125.4, 125.7, 125.8, 126.0, 126.3, 127.6, 128.6, 129.0, 129.6, 131.2, 131.4, 132.6, 136.8, 137.3, 165.5; LC/MS m/z 446 $[M + 1]^+$; Anal. Calcd for $C_{31}H_{27}NO_2$: C, 83.57; H, 6.11; N, 3.14. Found: C, 83.45; H, 6.17; N, 3.19; HRMS (ESI) Calcd for $C_{31}H_{28}NO_2$ $[M + H]^+$ 446.2120, found 446.2120. This compound was crystallized from ethyl acetate−hexane (9:1) at 25 °C. X-ray structure was determined for this sample.

7. X-ray Data. X-ray data for compounds **14**, **18**, **20**·H_2O, **35**, and **41** were collected on an X-ray diffractometer using Mo K_α (λ = 0.71073 Å) radiation. The structures were solved and refined by standard methods.[19] CCDC numbers are CCDC 892102−892106.

8. Crystal Data. 14: $C_{18}H_{30}N_2O_6P_2$, M = 432.38, monoclinic, space group $P2(1)/c$, a = 15.587(2), b = 6.0979(8), c = 11.5256(15) Å, β = 103.146(2)°, V = 1066.8(2) Å^3, Z = 2, μ = 0.240 mm^{-1}, data/restraints/parameters: 1886/0/130, R indices ($I > 2\sigma(I)$): R1 = 0.0385, $wR2$ (all data) = 0.1021. CCDC no. 882102.

18: $C_{14}H_{22}NO_5P$, M = 315.30, orthorhombic, space group $Pna2(1)$, a = 22.0358(19), b = 6.0237(5), c = 24.783(2) Å, V = 3289.6(5) Å^3, Z = 8, μ = 0.186 mm^{-1}, data/restraints/parameters: 5788/4/384, R indices ($I > 2\sigma(I)$): R1 = 0.0802, $wR2$ (all data) = 0.2050. CCDC no. 882103.

20·H_2O: $C_{13}H_{22}NO_5P$, M = 303.29, triclinic, space group P-1, a = 5.5991(8), b = 10.8370(15), c = 13.4812(18) Å, α = 104.942(12)°, β = 99.962(11)°, γ = 96.168(11)°, V = 768.43(18) Å^3, Z = 2, μ = 0.197 mm^{-1}, data/restraints/parameters: 2604/0/189, R indices ($I > 2\sigma(I)$): R1 = 0.0483, $wR2$ (all data) = 0.1337. CCDC no. 882104.

35: $C_{11}H_{15}NO_3$, M = 209.24, monoclinic, space group $P2(1)/c$, a = 8.0841(11), b = 6.8413(9), c = 20.348(3) Å, β = 103.655(5)°, V = 1093.6(3) Å^3, Z = 4, μ = 0.093 mm^{-1}, data/restraints/parameters: 1921/0/140, R indices ($I > 2\sigma(I)$): R1 = 0.0548, $wR2$ (all data) = 0.1447. CCDC no. 882105.

41: $C_{31}H_{27}NO_2$, M = 445.54, monoclinic, space group $P2(1)/c$, a = 11.605(3), b = 20.308(5), c = 10.711(3) Å, β = 106.598(5)°, V = 2419.1(11) Å^3, Z = 4, μ = 0.076 mm^{-1}, data/restraints/parameters: 4220/0/309, R indices ($I > 2\sigma(I)$): R1 = 0.1027, $wR2$ (all data) = 0.1973. CCDC no. 882106.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Materials including ORTEP drawings; copies of $^1H/^{13}C$ NMR spectra of all new products; CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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■ REFERENCES

(1) (a) Ma, S. *Acc. Chem. Res.* **2003**, *36*, 701. (b) Krause, N.; Hashmi, A. S. K. *Modern Allene Chemistry*; Wiley-VCH: Weinheim, 2004; pp 760−787. (c) Ma, S. *Chem. Rev.* **2005**, *105*, 2829. (d) Ma, S. *Acc. Chem. Res.* **2009**, *42*, 1679. (e) Shi, M.; Shao, L.-X.; Lu, J.-M.; Wei, Y.; Mizuno, K.; Maeda, H. *Chem. Rev.* **2010**, *110*, 5883. (f) Deagostino, A.; Prandi, C.; Tabasso, S.; Venturello, P. *Molecules* **2010**, *15*, 2667. (g) Back, T. G.; Clary, K. N.; Gao, D. *Chem. Rev.* **2010**, *110*, 4498. (h) Alcaide, B.; Almendros, P.; Aragoncillo, C. *Chem. Soc. Rev.* **2010**, *39*, 783. (i) Guan, X.-Y.; Wei, Y.; Shi, M. *Org. Lett.* **2010**, *12*, 5024. (j) Sun, Y.-W.; Guan, X.-Y.; Shi, M. *Org. Lett.* **2010**, *12*, 5664. (k) Wu, L.; Shi, M. *J. Org. Chem.* **2010**, *75*, 2296. (l) Krause, N.; Winter, C. *Chem. Rev.* **2011**, *111*, 1994. (m) Bandini, M. *Chem. Soc. Rev.* **2011**, *40*, 1358. (n) López, F.; Mascareñas, J. L. *Chem.—Eur. J.* **2011**, *17*, 418. (o) Zhang, X.-C.; Cao, S.-H.; Wei, Y.; Shi, M. *Org. Lett.* **2011**, *13*, 1142. (p) Wan, B.; Jiang, X.; Jia, G.; Ma, S. *Eur. J. Org. Chem.* **2012**, 4373. (q) Muñoz, M. P. *Org. Biomol. Chem.* **2012**, *10*, 3584.

(2) (a) Zimmer, R.; Dinesh, C. U.; Nandanan, E.; Khan, F. A. *Chem. Rev.* **2000**, *100*, 3067. (b) Jiang, X.; Kong, W.; Chen, J.; Ma, S. *Org. Biomol. Chem.* **2008**, *6*, 3606. (c) Yu, F.; Lian, X.; Zhao, J.; Yu, Y.; Ma, S. *J. Org. Chem.* **2009**, *74*, 1130. (d) Han, X.; Zhong, F.; Wang, Y.; Lu, Y. *Angew. Chem., Int. Ed.* **2012**, *51*, 767. (e) Yu, S.; Ma, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 3074. (f) Alcaide, B.; Almendros, P.; Alonso, J. M.; Fernandez, I. *Chem. Commun.* **2012**, *48*, 6604.

(3) (a) Gu, Y.; Hama, T.; Hammond, G. B. *Chem. Commun.* **2000**, 395. (b) Scheufler, F.; Maier, M. E. *Eur. J. Org. Chem.* **2000**, 3945. (c) Zapata, A. J.; Gu, Y.; Hammond, G. B. *J. Org. Chem.* **2000**, *65*, 227. (d) Kitagaki, S.; Okumura, Y.; Mukai, C. *Tetrahedron* **2006**, *62*, 10311. (e) Yu, F.; Lian, X.; Ma, S. *Org. Lett.* **2007**, *9*, 1703. (f) He, G.; Guo, H.; Qian, R.; Guo, Y.; Fu, C.; Ma, S. *Tetrahedron* **2009**, *65*, 4877. (g) He, G.; Fu, C.; Ma, S. *Tetrahedron* **2009**, *65*, 8035. (h) He, G.; Yu, Y.; Fu, C.; Ma, S. *Eur. J. Org. Chem.* **2010**, 101. (i) Xin, N.; Ma, S. *Eur. J. Org. Chem.* **2012**, 3806. (j) Rama Suresh, R.; Kumara Swamy, K. C. *J. Org. Chem.* **2012**, 6959.

(4) (a) Srinivas, V.; Sajna, K. V.; Kumara Swamy, K. C. *Chem. Commun.* **2011**, *47*, 5629. (b) Sajna, K. V.; Kotikalapudi, R.; Chakravarty, M.; Bhuvan Kumar, N. N.; Kumara Swamy, K. C. *J. Org. Chem.* **2011**, *76*, 920. (c) Phani Pavan, M.; Kumara Swamy, K. C. *Synlett* **2011**, 1288. (d) Srinivas, V.; Sajna, K. V.; Kumara Swamy, K. C. *Tetrahedron Lett.* **2011**, *52*, 5323. (e) Sajna, K. V.; Kumara Swamy, K. C. *J. Org. Chem.* **2012**, *77*, 5345.

(5) Selected references: (a) Fotsing, J. R.; Banert, K. *Eur. J. Org. Chem.* **2005**, 3704. (b) Mayot, E.; Lemière, P.; Gérardin-Charbonnier, C. *Eur. J. Org. Chem.* **2008**, 2232. (c) Chakravarty, M.; Bhuvan Kumar, N. N.; Sajna, K. V.; Kumara Swamy, K. C. *Eur. J. Org. Chem.* **2008**, 4500. (d) Kumar, R.; Pradhan, P.; Zajc, B. *Chem. Commun.* **2011**, *47*, 3891. (e) Pei Jian, Ng, P.; Wang, Y.-F.; Hui, B. W.-Q.; Lapointe, G.; Chiba, S. *Tetrahedron* **2011**, *67*, 7728. (f) Lal, S.; Díez-González, S. *J. Org. Chem.* **2011**, *76*, 2367. (g) Wang, D.; Zhao, M.; Liu, X.; Chen, Y.; Li, N.; Chen, B. *Org. Biomol. Chem.* **2012**, *10*, 229.

(6) Selected references: (a) L'abbe, G. *Chem. Rev.* **1969**, *69*, 345. (b) L'abbe, G.; Mathys, G. *J. Org. Chem.* **1974**, *39*, 1778. (c) Gallagher, T. C.; Storr, R. C. *Tetrahedron Lett.* **1981**, *22*, 2905. (d) Abramovitch, R. A.; Konieczny, M.; Pennington, W.; Kanamathareddy, S.; Vedachalam, M. *J. Chem. Soc., Chem. Commun.* **1990**, 269. (e) Pinho e Melo, T. M. V. D.; d'A. Roeha Gonsalves, A. M.; Lopes, C. S. J. *Tetrahedron Lett.* **1999**, *40*, 789. (f) Banert, K.; Köhler, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 174. (g) Brel, V. K. *Synthesis* **2002**, 1829. (h) Timén, A. S.; Risberg, E.; Somfai, P. *Tetrahedron Lett.* **2003**, *44*, 5339. (i) Brase, S.; Gil, C.; Knepper, K.; Zimmermann, V. *Angew. Chem., Int. Ed.* **2005**, *44*, 5188. (j) Banert, K.; Meier, B. *Angew. Chem., Int. Ed.* **2006**, *45*, 4015.

(7) Selected references: (a) Feldman, K. S.; Iyer, M. R. *J. Am. Chem. Soc.* **2005**, *127*, 4193. (b) Gorin, D. J.; Davis, N. R.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 11260. (c) Minozzi, M.; Nanni, D.; Spagnolo, P. *Chem.—Eur. J.* **2009**, *15*, 7830. (d) Chen, W.; Hu, M.; Wu, J.; Zou, H.; Yu, Y. *Org. Lett.* **2010**, *12*, 3863. (e) Wang, Y.-F.; Toh, K. K.; Lee, J.-Y.; Chiba, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 5927. (f) Hu, J.; Cheng, Y.; Yang, Y.; Rao, Y. *Chem. Commun.* **2011**, *47*, 10133. (g) Wang, Y.-F.; Toh, K. K.; Pei Jian, N. P.; Chiba, S. *J. Am. Chem. Soc.* **2011**, *133*, 6411. (h) Pei Jian, N. P.; Wang, Y.-F.; Chiba, S. *Synlett* **2011**, 783.

(8) (a) Chiba, S.; Wang, Y.-F.; Lapointe, G.; Narasaka, K. *Org. Lett.* **2008**, *10*, 313. (b) Wang, Y.-F.; Toh, K. K.; Chiba, S.; Narasaka, K. *Org. Lett.* **2008**, *10*, 5019.

(9) Selected references: (a) Dhawan, R.; Arndtsen, B. A. *J. Am. Chem. Soc.* **2004**, *126*, 468. (b) Reisser, M.; Maas, G. *J. Org. Chem.* **2004**, *69*, 4913. (c) Bharadwaj, A. R.; Scheidt, K. A. *Org. Lett.* **2004**, *6*, 2465. (d) Alcaide, B.; Almendros, P.; Redondo, M. *Chem. Commun.* **2006**, 2616. (e) Binder, J. T.; Kirsch, S. F. *Org. Lett.* **2006**, *8*, 2151. (f) Cyr, D. J. S.; Martin, N.; Arndtsen, B. A. *Org. Lett.* **2007**, *9*, 449. (g) Rodriguez Rivero, M.; Buchwald, S. L. *Org. Lett.* **2007**, *9*, 973. (h) Shindo, M.; Yoshimura, Y.; Hayashi, M.; Soejima, H.; Yoshikawa, T.; Matsumoto, K.; Shishido, K. *Org. Lett.* **2007**, *9*, 1963. (i) Fantauzzi, S.; Gallo, E.; Caselli, A.; Piangiolino, C.; Ragaini, F.; Re, N.; Cenini, S. *Chem.—Eur. J.* **2009**, *15*, 1241. (j) Estevez, V.; Villacampa, M.; Menendez, J. C. *Chem. Soc. Rev.* **2010**, *39*, 4402. (k) Maiti, S.; Biswas, S.; Jana, U. *J. Org. Chem.* **2010**, *75*, 1674. (l) Yan, R.-L.; Luo, J.; Wang, C.-X.; Ma, C.-W.; Huang, G.-S.; Liang, Y.-M. *J. Org. Chem.* **2010**, *75*, 5395. (m) Ngwerume, S.; Camp, J. E. *J. Org. Chem.* **2010**, *75*, 6271. (n) Benedetti, E.; Lemiere, G.; Chapellet, L.-L.; Penoni, A.; Palmisano, G.; Malacria, M.; Goddard, J.-P.; Fensterbank, L. *Org. Lett.* **2010**, *12*, 4396. (o) Lopes, S. M. M.; Nunes, C. M.; Pinho e Melo, T. M. V. D. *Tetrahedron* **2010**, *66*, 6078. (p) Ribeiro Laia, F. M.; Cardoso, A. L.;

Beja, A. M.; Silva, M. R.; Pinho e Melo, T. M. V. D. *Tetrahedron* **2010**, *66*, 8815. (q) Wang, Y.; Bi, X.; Li, D.; Liao, P.; Wang, Y.; Yang, J.; Zhang, Q.; Liu, Q. *Chem. Commun.* **2011**, *47*, 809. (r) Frolova, L. V.; Evdokimov, N. M.; Hayden, K.; Malik, I.; Rogelj, S.; Kornienko, A.; Magedov, I. V. *Org. Lett.* **2011**, *13*, 1118.

(10) (a) Woodward, R. M.; Polenzani, L.; Miledi, R. *Mol. Pharmacol.* **1992**, *41*, 89. (b) Woodward, R. M.; Polenzani, L.; Miledi, R. *Mol. Pharmacol.* **1992**, *42*, 165. (c) Woodward, R. M.; Polenzani, L.; Miledi, R. *Mol. Pharmacol.* **1993**, *43*, 609. (d) Moonen, K.; Laureyn, I.; Stevens, C. V. *Chem. Rev.* **2004**, *104*, 6177. (e) Van der Jeught, S.; Stevens, C. V. *Chem. Rev.* **2009**, *109*, 2672.

(11) (a) Griffin, C. E.; Peller, R. P.; Peters, J. A. *J. Org. Chem.* **1965**, *30*, 91. (b) Palacios, F.; de Retana, A. M. O.; de Marigorta, E. M.; Rodriguez, M.; Pagalday, J. *Tetrahedron* **2003**, *59*, 2617. (c) Moonen, K.; Dieltiens, N.; Stevens, C. V. *J. Org. Chem.* **2006**, *71*, 4600.

(12) (a) Demir, A. S.; Tural, S. *Tetrahedron* **2007**, *63*, 4156. (b) Broomfield, L. M.; Wright, J. A.; Bochmann, M. *Dalton Trans.* **2009**, 8269.

(13) (a) Patois, C.; Richard, L.; Savignac, P. *J. Chem. Soc., Perkin Trans. 1* **1990**, 1577. (b) Chakravarty, M.; Kumara Swamy, K. C. *J. Org. Chem.* **2006**, *71*, 9128. (c) Bhuvan Kumar, N. N.; Chakravarty, M.; Satish Kumar, N.; Sajna, K. V.; Kumara Swamy, K. C. *J. Chem. Sci.* **2009**, *121*, 23. (d) Yu, S.; Ma, S. *Chem. Commun.* **2011**, *47*, 5384.

(14) Guo, H.; Xu, Q.; Kwon, O. *J. Am. Chem. Soc.* **2009**, *131*, 6318.

(15) Huang, X.; Shen, R.; Zhang, T. *J. Org. Chem.* **2007**, *72*, 1534.

(16) Barra, E. D.; Hoz, A. D. L.; Migallón, A. S.; Loupy, A. *J. Heterocycl. Chem.* **1994**, *31*, 1715.

(17) Phani Pavan, M.; Chakravarty, M.; Kumara Swamy, K. C. *Eur. J. Org. Chem.* **2009**, 5927.

(18) Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*; Pergamon: Oxford, 1986.

(19) (a) Sheldrick, G. M. *SADABS, Siemens Area Detector Absorption Correction*; University of Göttingen, Germany, 1996. (b) Sheldrick, G. M. *SHELX-97- A program for crystal structure solution and refinement*; University of Göttingen, 1997. (c) Sheldrick, G. M. *SHELXTL NT Crystal Structure Analysis Package*, version 5.10; Bruker AXS, Analytical X-ray System, Madison, WI, 1999.