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Novel metal-free Lewis acid catalysis by phosphonium salts through hypervalent interaction

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Abstract—Phosphonium salts as a novel metal-free Lewis acid catalyst can be considered as organocatalysts. The introduction of a five-membered dioxaphosphacycle to the phosphonium salt is critical to its function as a Lewis acid catalyst for the Diels–Alder reaction. The key to the successful catalysis by the phosphonium salt is the utilization of hypervalent bonding as a strategic interaction for the generation of an active species.
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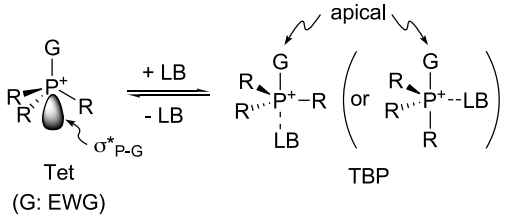
1. Introduction

Over the past half-century, organophosphorus compounds have been extensively utilized in organic synthesis ranging from equimolar to catalytic usage.[1] In particular, their benefits have been widely appreciated in the field of organometallic chemistry and they have become indispensable for versatile organic transformations catalyzed by transition metal complexes. In recent years, the challenges associated with the use of organophosphorus compounds without metal salts as catalysts have received considerable interest[2] from the viewpoint of organocatalysis.[3] Among them, the Morita–Baylis–Hillman reaction has been extensively investigated.[2d,4,5] Catalytic processes have been successfully accomplished by taking advantage of the nucleophilic or Lewis basic nature of organophosphorus compounds.[6] However, little attention has been paid to catalysis on the basis of the electrophilic, and hence the Lewis acidic nature of pentavalent organophosphorus compounds. Herein, we report the use of phosphonium salts as novel Lewis acid catalysts, which offers a new entry to a rapidly growing area in organocatalysis.[3] The key to the success of the catalysis is the utilization of hypervalent bonding as a strategic interaction for the generation of an active species[7,8] by the phosphonium salt (Scheme 1).[9]

The formation of pentacoordinate organophosphorus compounds, namely, hypervalent compounds,[10] which have



Scheme 1. Hypervalent interaction between phosphonium salt and Lewis base.

electronic structures with formal valence shell electrons over octet, are well investigated in terms of their unique structure and reactivity.[11] A hypervalent bond is formed by adding an unshared electron pair of a Lewis base (LB) to a cationic organophosphorus compound, a phosphonium salt, where the lower lying σ^* orbital of the P^+–G bond accepts those electrons.[12] The hypervalent bond thus formed is stabilized when an electron-withdrawing substituent (G) occupies the apical position of a trigonal bipyramidal (TBP) arrangement.

2. Results and discussion

2.1. Preparation of phosphonium salts

As illustrated in Figure 1, several phosphonium salts (**1**–**3**) bearing mono- or bicyclic structures have been synthesized. In order to stabilize the hypervalent bonding,[13] we introduced an oxygenated functionality as the electron-withdrawing group. **1**–**3** were prepared from the corresponding hydroxy phosphine oxide (**4**) or phosphinate (**5**)

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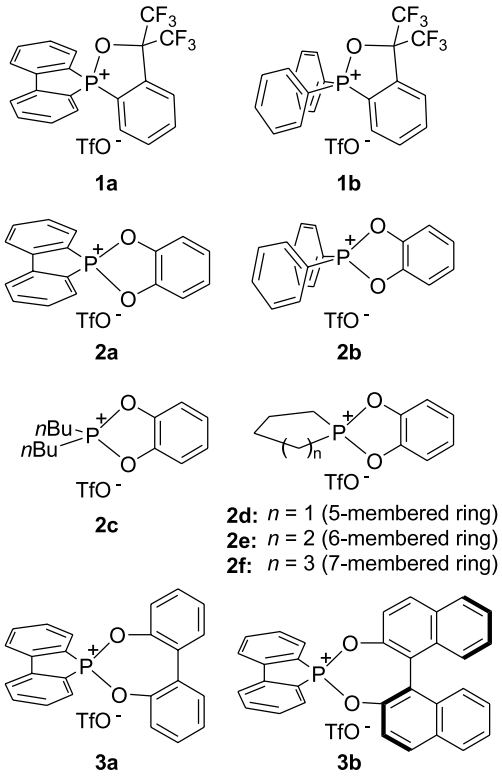
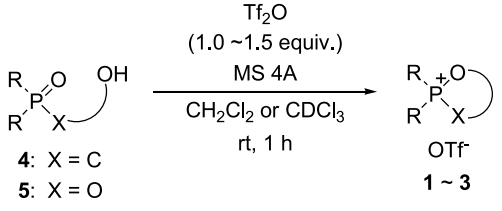


Figure 1. Chemical structures of phosphonium salts (**1**–**3**) prepared.

and trifluoromethanesulfonic anhydride at room temperature for 1 h in the presence of 4 Å molecular sieves (MS) as a desiccant and a base to trap the trifluoromethanesulfonic acid generated (Scheme 2).[14] The generation of phosphonium salts (**1**–**3**) was confirmed by ^{31}P NMR analysis, in which significant downfield shifts were observed.[15] During this transformation, the chemical shift pattern observed in the ^{1}H NMR spectra changed in a symmetric fashion. This can be ascribed to the formation of phosphonium salts with tetrahedral configuration.



Scheme 2. Preparation of phosphonium salts (**1**–**3**) from **4** or **5**.

2.2. Coordination studies

Initially, we attempted ^{31}P NMR analysis to estimate the interaction between phosphonium salts (**1**–**3**) and dimethylformamide (DMF) as a representative carbonyl Lewis base in $CDCl_3$. It is noteworthy that not only the ring size but also the substituent on the phosphorus atom is essential for the coordination of DMF to phosphonium salts (**1**–**3**). Phosphonium salts (**1a**,**b**) derived from the Martin ligand, which is known to stabilize a hypervalent species,[16] exhibited no chemical shift change in the ^{1}H and ^{31}P NMR spectra. In contrast, marked upfield shifts were observed in the spectra of catechol-derived phosphonium salts (**2a**,**b**).[17] Interestingly enough, the spectra of biphenol-derived phosphonium salts (**3a**,**b**) did not show any chemical shift change even though the salts (**3**) had a similar dioxaphosphacycle to **2**. These NMR studies indicate clearly that the five-membered 1,3,2-dioxaphosphacycle is the key structural factor for gaining coordination ability.[18] Detailed analysis of the ^{1}H NMR spectra of the **2**/DMF complex gave further information on the coordination mode of the phosphonium salts (**2**) with DMF (Fig. 2). When bicyclic phosphonium salt (**2a**) was exposed to 3.0 equiv of DMF, two sets of DMF signals were observed along with upfield shifts of the signals in the aromatic region (Fig. 2b). One set of DMF signals appeared significantly downfield compared with the original shift (Fig. 2e vs b). The other set was assigned to uncoordinated DMF because of little chemical shift change. Furthermore, the aromatic region of **2a** showed a more complex shift pattern (Fig. 2a vs b). 2D NMR experiments of the **2a**/DMF complex revealed that the catechol moiety was separated into four signals whereas the dibenzophosphole moiety retained symmetry.[19] These chemical shift changes strongly suggest that phosphonium

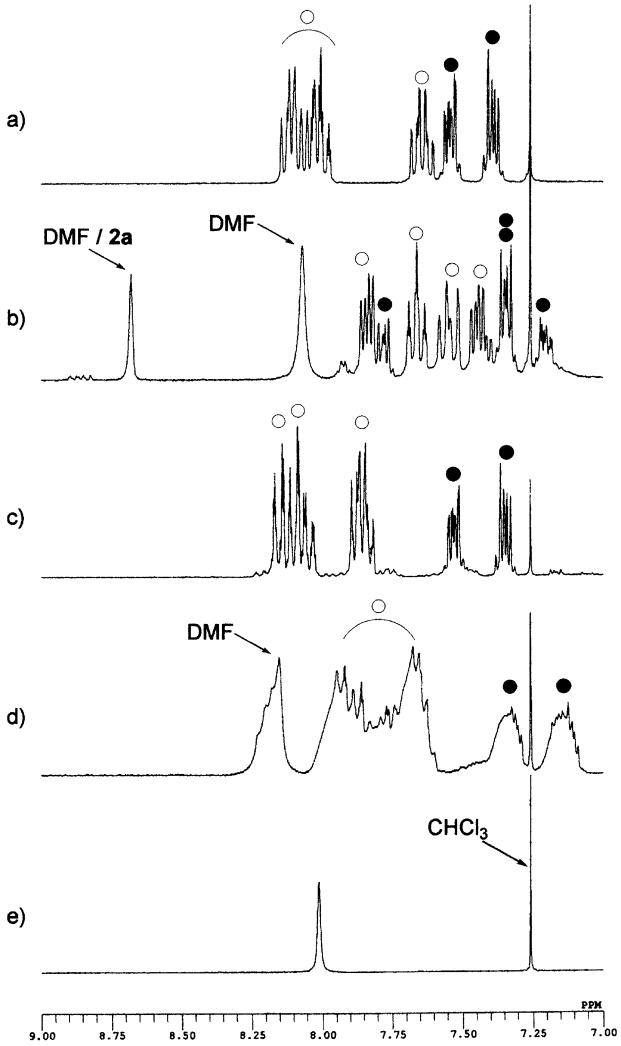


Figure 2. ^{1}H NMR analysis of phosphonium salts (**2**) with or without DMF in $CDCl_3$ (30 mM solution). Solid circles (●) indicate catechol moiety. Hollow circles (○) indicate aromatic substituents of phosphorus atom: (a) **2a**; (b) **2a** with DMF (3.0 equiv); (c) **2b**; (d) **2b** with DMF (3.0 equiv); (e) DMF.

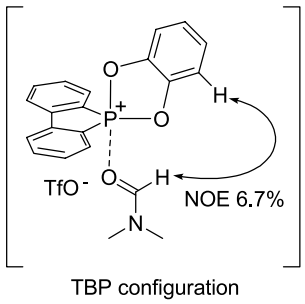


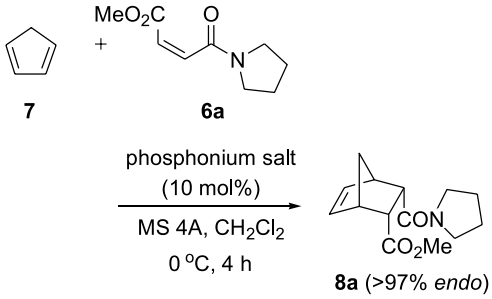
Figure 3. Coordination mode of DMF/phosphonium salt (**2a**) complex.

salt (**2a**) arranged into the TBP configuration upon coordination with DMF and one of the two oxygen atoms of the catechol moiety as well as the carbonyl oxygen of DMF occupied the apical position of the TBP arrangement (Fig. 3). In fact, marked NOE was observed at the C3-proton of the catechol moiety upon irradiation of the formyl proton of DMF, in contrast to little NOE detected at the dibenzophosphole moiety. On the other hand, only one set of DMF signals was observed (Fig. 2e), when monocyclic phosphonium salt (**2b**) was exposed to excess DMF (3.0 equiv). As seen in the spectra for **2a**, signals assigned to the aromatic region shifted upfield but showed significant broadening (Fig. 2c vs d). It is obvious that the complexation between **2b** and DMF is in equilibrium within the NMR timescale at room temperature.

2.3. Lewis acid catalysis by phosphonium salts

In the next phase of our investigation, we focused on Lewis acid catalysis by the phosphonium salts. In order to estimate the catalytic activity, we chose the Diels–Alder reaction as the probe reaction (Table 1). α,β-Unsaturated amides (**6**) were employed as the dienophile because NMR experiments have indicated that phosphonium salts, in particular, catechol derivatives (**2**), function as an activator of amide functionality. The Diels–Alder reaction of unsaturated amide (**6a**) with cyclopentadiene (**7**) catalyzed by 10 mol% phosphonium salts (**1**–**3**), which were prepared in situ from **4** or **5** (10 mol%) and Tf_2O (10 mol%) in the presence of MS 4 Å, was carried out at 0 °C for 4 h. As expected, the catechol-derived phosphonium salts (**2**) gave Diels–Alder product (**8a**) in moderate to good chemical yield (entries 3 and 4).[20] By contrast, under similar reaction conditions, phosphonium salts bearing the Martin ligand (**1**) and biphenol derivatives (**3**) gave **8a** in low chemical yield (entries 1 and 2) and in trace amounts (entries 5 and 6), respectively. These results are consistent with the tendency of the coordination ability observed in ^1H and ^{31}P NMR studies of DMF/phosphonium salt mixtures. Thus, higher catalytic activity is attained with stronger coordination ability of the phosphonium salt to the Lewis base. An increase in the amount of Tf_2O from 1.0 to 1.5 equiv with respect to the amount of the starting phosphinate (**5**) increased the chemical yield (entries 8 and 9). It was confirmed by control experiments that Tf_2O (10 mol%) did not catalyze the reaction at all in the absence of **5** (entry 7). The phosphonium salts (**2c** to **2f**) derived from dialkylphosphinate also worked well (entries 10–13) except for the five-membered phosphacarbocyclic derivative (**2d**) (entry 10). The absence of rate acceleration in the case of **2d** is due to its low solubility in a halogenated solvent. Again, the importance of the five-membered 1,3,2-dioxaphosphacyclic structure in achieving high catalytic efficiency should be emphasized.

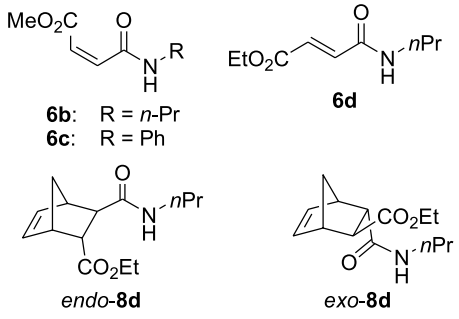
Table 1. Diels–Alder reaction catalyzed by various phosphonium salts[a]



Entry	Phosphonium salt	Yield (%)
1	**1a**	34
2	**1b**	7
3	**2a**	75
4	**2b**	41
5	**3a**	No reaction
6	**3b**	Trace
7[b]	—	Trace
8[c]	**2a**	91
9[c]	**2b**	88
10[c]	**2c**	89
11[c]	**2d**	Trace
12[c]	**2e**	91
13[c]	**2f**	85

[a] The reactions were carried out under the conditions shown in Section 4 unless otherwise noted. Phosphonium salts were prepared from **4** or **5** (10 mol%) and Tf_2O (10 mol%).
[b] The reaction was carried out in the presence of Tf_2O (10 mol%) without phosphonium salts.
[c] Phosphonium salts were prepared from phosphinate (**5**) (10 mol%) and Tf_2O (15 mol%).

Table 2. Diels–Alder reaction of amide dienophiles (**6**)[a]



Entry	2	6	Conditions	Yield (%)	*Endo*/*exo*
1	**2a**	**6b**	0 °C, 2 h	99	>99:<1
2	**2e**	**6b**	0 °C, 2 h	99	>99:<1
3	**2a**	**6c**	−20 °C, 1 h	99	>99:<1
4	**2e**	**6c**	−20 °C, 4 h	87	>99:<1
5	**2a**	**6d**	0 °C, 4 h	31	1:5.3
6	**2e**	**6d**	0 °C, 4 h	46	1:6.7
7[b]	—	**6d**	Room temperature, 17 h	82	1.9:1
8[c]	—	**6d**	0 °C, 4 h	74	1:3.6

[a] The reactions were carried out under the conditions shown in Section 4 unless otherwise noted. Phosphonium salts were prepared from phosphinate (**5**) (10 mol%) and Tf_2O (15 mol%).
[b] The reaction was carried out in the absence of a catalyst.
[c] TfOH (5 mol%) was employed as the catalyst without MS 4 Å.

As listed in Table 2, phosphonium salts **2a** and **2e** are applicable to the reaction of several dienophiles (**6**) with amide functionality.[21] When *Z*-dienophile (**6b**, **6c**) was employed, either **2a** or **2e** gave the product (**8b**, **8c**) in high chemical yield with extremely high *endo* selectivity (entries 1–4). On the other hand, in the reaction with *E*-dienophile (**6d**), *exo*-**8d** was obtained predominantly in moderate chemical yield (entries 5 and 6).[22] The *exo* selectivity thus achieved is in contrast to the reaction yielding *endo*-**8d** as the major product under thermal conditions (entry 7). The difference in *endo*/*exo* selectivity suggests that phosphonium salts activate the amide carbonyl functionality of dienophile (**6d**). In the transition state, the amide moiety coordinates with phosphonium salts oriented to the *endo* direction to increase secondary orbital interactions, which leads to the formation of *exo*-**8d** as the major stereoisomer. In order to rule out the possibility of the catalysis by adventitious acids, we employed TfOH as a catalyst and observed the *endo*/*exo* selectivity (entry 8). The TfOH catalyst exhibited lower *exo* selectivity than that of phosphonium salts (**2a** and **2e**). The differences in *endo*/*exo* selectivity thus observed clearly indicate that the Diels–Alder reaction of the dienophiles (**6**) bearing an amide functionality is accelerated by phosphonium salts.

3. Conclusion

In summary, we have demonstrated novel Lewis acid catalysis by phosphonium salts in which the five-membered dioxaphosphacycle is critical for the salt to function efficiently as a Lewis acid catalyst. The Diels–Alder reaction of α,β-unsaturated amides was markedly accelerated by a catalytic amount of catechol-derived phosphonium salt to afford the products in high chemical yield. We have also concluded that hypervalent interaction is essential for activating the amide functionality based on observations of the interaction between phosphonium salt and the Lewis base.

4. Experimental

4.1. General

Infrared spectra were recorded on a Shimazu FTIR-8200PC spectrometer. ^{1}H NMR spectra were recorded on a JEOL GSX-270 (270 MHz) or Brüker AM-600 (600 MHz) spectrometer. Chemical shifts are reported in ppm from the solvent resonance as the internal standard. Data are reported as follows: chemical shift, integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, quin=quintet, sex=sextet, br=broad, m=multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a JEOL GSX-270 (67.8 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from the solvent resonance as the internal standard. ^{31}P NMR spectra were recorded on a Brüker Avance 400 (162 MHz) spectrometer with complete proton decoupling. Chemical shifts are reported in ppm from H_3PO_4 resonance as the external standard. Mass spectra analysis was performed at the Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University. Analytical thin-layer chromatography (TLC) was performed on Merck precoated TLC plates (silica gel 60 GF_{254}, 0.25 mm). Flash column chromatography was performed on silica gel 60 N (spherical, neutral, 100–210 μm; Kanto Chemical Co., Inc.). All reactions were carried out under a nitrogen (N_2) atmosphere in dried glassware. All substrates were purified by column chromatography or distillation prior to use. Dichloromethane and THF were supplied from Kanto Chemical Co., Inc. as 'Dehydrated solvent system'. Chloroform-*d*1 was dried over activated molecular sieves 4 Å and used under nitrogen atmosphere. Molecular sieves 4 Å activated powder was purchased from Aldrich (Catalogue no. 23,366-8) and activated at 300 °C for 3 h under reduced pressure prior to use. Other solvents and other simple chemicals were purchased and used as such. 5-Chloro-5*H*-benzo[*b*]-phosphindole 5-oxide was prepared by the literature method.[23] *Z*-dienophiles (**6a–c**)[24] and *E*-dienophiles (**6d**)[25] were prepared according to the literature procedure, respectively.

4.2. Preparation of hydroxy phosphine oxide (4) and phosphinate (5)

4.2.1. General procedure for the synthesis of hydroxy phosphine oxide (4). To a stirred solution of *n*-butyllithium (12.4 mL of an 1.6 M *n*-hexane solution, 22 mmol) was added TMEDA (0.66 mL, 4.4 mmol). The mixture was stirred at room temperature for 15 min until it become cloudy. The mixture was then cooled to 0 °C and 1,1,1,3,3,3-hexafluoro-2-phenyl-2-propanol (1.68 mL, 10 mmol), dissolved in 1.5 mL of THF, was then added dropwise to the mixture. After being stirred for 30 min, the ice bath was removed and the mixture was stirred for 12 h at ambient temperature. Diarylphosphinic chloride (9 mmol), dissolved in 5 mL of THF, was added dropwise to the solution of lithium reagent at −78 °C. After being stirred for 30 min at −78 °C, the reaction mixture was gradually warmed up to room temperature and stirring was continued for additional 8 h at ambient temperature. The mixture was quenched by adding 30 mL of saturated NH_4Cl solution. Following extraction with ethyl acetate (3×30 mL), the combined organic layers were washed with 0.5 M HCl solution and brine. The resultant organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to give crude product (**4**). Purification by silica-gel column chromatography and recrystallization gave pure product (**4**) as a colorless solid in 60–70% yield.

4.2.1.1. 2-(5-Oxido-5*H*-benzo[*b*]phosphindol-5-yl)-α,α-bis(trifluoromethyl)benzenemethanol (precursor of 1a). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.17–7.30 (2H, m), 7.44 (2H, td, *J*=7.3, 3.8 Hz), 7.65–7.65 (3H, m), 7.83 (2H, dd, *J*=7.3, 3.2 Hz), 7.97–8.04 (3H, m), 10.22 (1H, br s); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 79.40 (quin, J_{F-}=29.5 Hz, J_{P-}=2.4 Hz), 121.42 (d, J_{P-}=10.8 Hz), 123.04 (q, J_{F-}=287.8 Hz), 129.48 (d, J_{P-}=13.8 Hz), 129.74 (dd, J_{P-}=8.8 Hz, J_{F-}=3.9 Hz), 129.78 (d, J_{P-}=11.3 Hz), 130.34 (d, J_{P-}=94.3 Hz), 131.57 (d, J_{P-}=111.5 Hz), 131.42 (d, J_{P-}=8.9 Hz), 132.40 (d, J_{P-}=1.4 Hz), 132.89 (d, J_{P-}=14.7 Hz), 134.02 (d, J_{P-}=2.4 Hz), 137.99 (d, J_{P-}=5.4 Hz), 141.71 (d, J_{P-}=23.5 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 46.2; IR (KBr): 3082, 2925, 1442, 1271, 1245, 1205, 1193, 1164,

1151, 1130, 954, 931, 856, 759, 729, 715, 704, 551 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{14}F_6O_2P$ ($[M+H]^+$) 443.0636. Found 443.0630.

4.2.1.2. 2-(Diphenylphosphinyl)-α,α-bis(trifluoromethyl)benzenemethanol (precursor of 1b). ^1H NMR (270 MHz, $CDCl_3$): δ 7.24 (1H, dd, $J=16.2$, 7.6 Hz), 7.39 (1H, t, $J=7.6$ Hz), 7.44–7.66 (9H, m), 7.98 (1H, t, $J=5.7$ Hz), 10.57 (1H, br s); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 79.51 (quind, $J_{F-}=29.0$ Hz, $J_{P-}=2.5$ Hz), 122.88 (q, $J_{F-}=289.3$ Hz), 128.69 (d, $J_{P-}=12.3$ Hz), 128.73 (d, $J_{P-}=13.3$ Hz), 130.30 (dd, $J_{P-}=8.3$ Hz, $J_{F-}=3.9$ Hz), 130.85 (d, $J_{P-}=95.8$ Hz), 131.96 (d, $J_{P-}=2.5$ Hz), 131.23 (d, $J_{P-}=109.0$ Hz), 132.11 (d, $J_{P-}=9.8$ Hz), 132.57 (d, $J_{P-}=2.5$ Hz), 136.03 (d, $J_{P-}=12.7$ Hz), 138.07 (d, $J_{P-}=3.9$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 46.3; IR (KBr): 3043, 2925, 1436, 1267, 1240, 1195, 1153, 1126, 954, 933, 866, 758, 727, 696, 542 cm^{-1}; HRMS (ESI) Calcd for $C_{21}H_{16}F_6O_2P$ ($[M+H]^+$) 445.0792. Found 445.0787.

4.2.2. General procedure for the synthesis of hydroxy phosphinate (5). To a stirred solution of diol (1.8 mmol) in CH_2Cl_2 (5 mL) was added triethylamine (0.56 mL, 4 mmol). The mixture was cooled to 0 °C and the corresponding phosphinic chloride (2 mmol), dissolved in 1.5 mL of CH_2Cl_2, was added dropwise to the mixture. After being stirred for 30 min, the ice bath was removed and the mixture was stirred for 3 h at ambient temperature. The mixture was quenched by adding 10 mL of water. Following extraction with CH_2Cl_2 (3×15 mL), the combined organic layers were washed with 0.5 M HCl solution and saturated $NaHCO_3$ solution. The resultant organic phase was dried over $MgSO_4$ and concentrated under reduced pressure to give a crude product (**5**). Purification by silica-gel column chromatography and recrystallization gave pure product (**5**) as a colorless solid in 45–83% yield.

4.2.2.1. *o*-[(5-Oxido-5*H*-benzo[*b*]phosphindol-5-yl)oxy]phenol (precursor of 2a). ^1H NMR (270 MHz, $CDCl_3$): δ 6.70–6.80 (2H, m), 7.08–7.16 (2H, m) 7.39 (2H, td, $J=7.6$, 4.1 Hz), 7.58–7.67 (4H, m), 7.82 (2H, dd, $J=7.8$, 4.1 Hz), 8.60 (1H, s); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 119.67 (d, $J_{P-}=1.5$ Hz), 120.66 (d, $J_{P-}=1.5$ Hz), 121.37 (d, $J_{P-}=12.7$ Hz), 122.27 (d, $J_{P-}=3.9$ Hz), 126.10 (d, $J_{P-}=139.5$ Hz), 126.85 (d, $J_{P-}=1.5$ Hz), 129.30 (d, $J_{P-}=11.9$ Hz), 129.45 (d, $J_{P-}=15.3$ Hz), 134.41 (d, $J_{P-}=2.5$ Hz), 139.46 (d, $J_{P-}=9.8$ Hz), 140.47 (d, $J_{P-}=30.0$ Hz), 148.08 (d, $J_{P-}=2.9$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 48.9; IR (KBr): 3177, 1590, 1515, 1460, 1291, 1238, 1224, 1179, 1132, 1106, 936, 928, 832, 759, 749, 727, 552 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{14}O_3P$ ($[M+H]^+$) 309.0681. Found 309.0685.

4.2.2.2. Diphenylphosphinic acid 2-hydroxyphenyl ester (precursor of 2b). ^1H NMR (270 MHz, $CDCl_3$): δ 6.66–6.72 (1H, m), 6.85 (1H, d, $J=8.1$ Hz), 6.96–7.05 (2H, m), 7.45–7.62 (6H, m), 7.89 (4H, dd, $J=12.7$, 7.0 Hz), 9.00 (1H, s); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 119.70 (d, $J_{P-}=1.5$ Hz), 120.41 (d, $J_{P-}=1.0$ Hz), 122.38 (d, $J_{P-}=4.4$ Hz), 126.38 (d, $J_{P-}=1.5$ Hz), 128.65 (d, $J_{P-}=137.1$ Hz), 128.74 (d, $J_{P-}=13.2$ Hz), 131.86 (d, $J_{P-}=10.8$ Hz), 133.11 (d, $J_{P-}=3.0$ Hz), 139.03 (d, $J_{P-}=9.8$ Hz), 148.04 (d, $J_{P-}=3.0$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 39.1; IR (KBr): 3123, 1518, 1460, 1439, 1292, 1240, 1215, 1176, 1134, 1103, 943, 932, 748, 729, 546 cm^{-1}; HRMS (ESI) Calcd for $C_{18}H_{16}O_3P$ ($[M+H]^+$) 311.0837. Found 311.0832.

4.2.2.3. Dibutylphosphinic acid 2-hydroxyphenyl ester (precursor of 2c). ^1H NMR (270 MHz, $CDCl_3$): δ 0.89 (6H, t, $J=7.3$ Hz), 1.40 (4H, sext, $J=7.3$ Hz), 1.50–1.78 (4H, m), 1.82–1.99 (4H, m), 6.76–6.85 (1H, m), 6.94 (1H, d, $J=7.8$ Hz), 6.99–7.07 (2H, m), 9.09 (1H, br s); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 23.41 (d, $J_{P-}=1.0$ Hz), 23.56, 23.72 (d, $J_{P-}=15.3$ Hz), 26.71 (d, $J_{P-}=86.9$ Hz), 119.85 (d, $J_{P-}=1.5$ Hz), 120.37 (d, $J_{P-}=0.1$ Hz), 121.80 (d, $J_{P-}=4.4$ Hz), 126.29 (d, $J_{P-}=0.9$ Hz), 139.28 (d, $J_{P-}=9.8$ Hz), 147.94 (d, $J_{P-}=2.9$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 67.4; IR (neat): 3074, 2958, 2933, 1494, 1460, 1294, 1242, 1164, 1101, 931, 923, 752, 732 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{24}O_3P$ ($[M+H]^+$) 271.1463. Found 271.1458.

4.2.2.4. *o*-[(1-Oxido-1-phospholanyl)oxy]phenol (precursor of 2d). ^1H NMR (270 MHz, $CDCl_3$): δ 1.72–2.09 (8H, m), 6.80–6.87 (1H, m), 6.94 (1H, d, $J=8.1$ Hz), 7.04–7.12 (2H, m), 8.77 (1H, br s); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 22.91 (d, $J_{P-}=12.8$ Hz), 23.36 (d, $J_{P-}=87.9$ Hz), 120.05 (d, $J_{P-}=1.5$ Hz), 120.61 (d, $J_{P-}=1.5$ Hz), 121.88 (d, $J_{P-}=4.4$ Hz), 126.67 (d, $J_{P-}=1.5$ Hz), 139.37 (d, $J_{P-}=10.3$ Hz), 148.17 (d, $J_{P-}=2.9$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 91.3; IR (KBr): 3109, 1508, 1458, 1290, 1274, 1234, 1168, 1099, 920 cm^{-1}; HRMS (ESI) Calcd for $C_{10}H_{14}O_3P$ ($[M+H]^+$) 213.0681. Found 213.0675.

4.2.2.5. *o*-[(1-Oxido-1-phosphorinanyl)oxy]phenol (precursor of 2e). ^1H NMR (270 MHz, $CDCl_3$): δ 1.36–1.41 (1H, m), 1.78–2.18 (9H, m), 6.79–6.88 (1H, m.), 6.99–7.11 (3H, m), 9.06 (1H, s); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 23.76 (d, $J_{P-}=5.9$ Hz), 25.77 (d, $J_{P-}=8.9$ Hz), 26.17 (d, $J_{P-}=82.5$ Hz), 120.04, 120.40, 121.80 (d, $J_{P-}=4.4$ Hz), 126.51 (d, $J_{P-}=1.4$ Hz), 138.76 (d, $J_{P-}=9.8$ Hz), 148.15 (d, $J_{P-}=3.0$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 60.8; IR (KBr): 3070, 2953, 1516, 1460, 1294, 1242, 1184, 1163, 1103, 916, 825, 760 cm^{-1}; HRMS (ESI) Calcd for $C_{11}H_{16}O_3P$ ($[M+H]^+$) 227.0837. Found 227.0832.

4.2.2.6. *o*-[(1-Oxido-1-phosphepanyl)oxy]phenol (precursor of 2f). ^1H NMR (270 MHz, $CDCl_3$): δ 1.73–2.22 (12H, m), 6.78–6.84 (1H, m), 6.95 (1H, d, $J=8.4$ Hz), 7.01–7.09 (2H, m), 9.09 (1H, br s); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 20.68 (d, $J_{P-}=1.5$ Hz), 28.44 (d, $J_{P-}=83.1$ Hz), 29.54, 119.95 (d, $J_{P-}=0.1$ Hz), 120.41 (d, $J_{P-}=1.0$ Hz), 122.04 (d, $J_{P-}=3.9$ Hz), 126.41 (d, $J_{P-}=1.5$ Hz), 139.02 (d, $J_{P-}=9.8$ Hz), 148.20 (d, $J_{P-}=2.9$ Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 73.9; IR (KBr): 3074, 2931, 1508, 1458, 1380, 1290, 1240, 1197, 1178, 1153, 937, 918, 781 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{18}O_3P$ ($[M+H]^+$) 241.0994. Found 241.0988.

4.2.2.7. 2′-[(5-Oxido-5*H*-benzo[*b*]phosphindol-5-yl)oxy][1,1′-biphenyl]-2-ol (precursor of 3a). ^1H NMR (270 MHz, $CDCl_3$): δ 6.14 (1H, s), 6.84–6.97 (3H, m), 7.23–7.35 (7H, m), 7.52 (2H, t, $J=7.3$ Hz), 7.63 (2H, dd, $J=7.3$, 3.8 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 117.24, 120.84 (d, $J_{P-}=9.8$ Hz), 121.10, 121.68 (d, $J_{P-}=3.4$ Hz), 125.84, 126.08 (d, $J_{P-}=2.0$ Hz), 127.43 (d, $J_{P-}=139.5$ Hz), 128.81 (d, $J_{P-}=8.8$ Hz), 129.25, 129.41 (d, $J_{P-}=2.0$ Hz), 129.54 (d, $J_{P-}=1.4$ Hz), 131.08, 131.63 (d, $J_{P-}=3.9$ Hz), 132.42

(d, J_{P-}=1.5 Hz), 133.89 (d, J_{P-}=2.4 Hz), 140.09, 140.53, 153.53; ^{31}P NMR (162 MHz, $CDCl_3$): δ 42.9; IR (KBr): 3134, 1560, 1508, 1440, 1222, 1205, 1188, 1130, 1068, 920, 758, 748 cm^{-1}; HRMS (ESI) Calcd for $C_{24}H_{18}O_3P$ ([M+H]$^+$) 385.0994. Found 385.0988.

4.2.2.8. 2′-[(5-Oxido-5*H*-benzo[*b*]phosphindol-5-yl)oxy][1,1′-binaphthalen]-2-ol (precursor of 3b). ^{1}H NMR (270 MHz, $CDCl_3$): δ 6.43 (1H, dd, J=11.3, 7.6 Hz), 6.91 (1H, d, J=8.4 Hz), 6.99–7.14 (3H, m), 7.24–7.41 (6H, m), 7.45–7.57 (3H, m), 7.62–7.69 (3H, m), 7.86 (1H, d, J=8.1 Hz), 7.96 (1H, d, J=6.8 Hz), 7.99 (1H, d, J=8.4 Hz), 8.09 (1H, d, J=8.9 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 117.24, 120.03 (d, J_{P-}=2.0 Hz), 120.57, 120.71 (d, J_{P-}=13.3 Hz), 121.18 (d, J_{P-}=12.8 Hz), 123.54, 124.47, 124.90 (d, J_{P-}=4.4 Hz), 125.93, 126.44 (d, J_{P-}=93.4 Hz), 126.60, 127.66 (d, J_{P-}=22.6 Hz), 128.12 (d, J_{P-}=1.0 Hz), 128.65 (d, J_{P-}=8.2 Hz), 129.18 (d, J_{P-}=4.4 Hz), 129.39, 129.40 (d, J_{P-}=11.8 Hz), 130.12, 130.84 (d, J_{P-}=1.4 Hz), 131.84 (d, J_{P-}=1.5 Hz), 133.90 (d, J_{P-}=2.0 Hz), 133.96 (d, J_{P-}=2.4 Hz), 140.18 (d, J_{P-}=2.9 Hz), 140.62 (d, J_{P-}=2.4 Hz), 146.68 (d, J_{P-}=9.4 Hz), 152.59; ^{31}P NMR (162 MHz, $CDCl_3$): δ 44.1; IR (KBr): 3195, 1624, 1593, 1438, 1230, 1203, 1132, 1070, 985, 956, 840, 817, 756, 721 cm^{-1}; HRMS (ESI) Calcd for $C_{32}H_{22}O_3P$ ([M+H]$^+$) 485.1307. Found 485.1301.

4.3. ^{1}H and ^{31}P NMR analysis of phosphonium salt (1–3)

To a suspension of an activated MS 4 Å (100 mg: activated at 300 °C for 3 h under reduced pressure) and hydroxy phosphineoxide (**4**) or hydroxy phosphinate (**5**) (0.03 mmol) in anhydrous deuterated chloroform (0.9 mL) was added trifluoromethanesulfonic anhydride (0.03 mmol) under nitrogen atmosphere at room temperature. After stirring for 1 h at ambient temperature, the resultant suspension was centrifuged to separate MS 4 Å and the supernatant solution was replaced to an NMR tube under nitrogen atmosphere. The sample thus prepared was measured by ^{1}H and ^{31}P NMR at room temperature.

4.3.1. 1,3-Dihydro-3,3-bis(trifluoromethyl)spiro[5*H*-dibenzophospholium-2,1-benzoxaphospholium] salt with trifluoromethanesulfonic acid (1a). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.52–7.63 (4H, m), 7.95–8.02 (2H, m), 8.06–8.26 (5H, m), 8.59 (1H, dd, J=12.4, 7.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 92.3.

4.3.2. 1,3-Dihydro-1,1-diphenyl-3,3-bis(trifluoromethyl)-2,1-benzoxaphospholium salt with trifluoromethanesulfonic acid (1b). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.73–7.81 (4H, m), 7.88–7.97 (7H, m), 8.10–8.25 (2H, m), 9.11–9.17 (1H, m); ^{31}P NMR (162 MHz, $CDCl_3$): δ 92.7.

4.3.3. Spiro[5*H*-dibenzophospholium-1,3,2-benzodioxaphospholium] salt with trifluoromethanesulfonic acid (2a). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.36–7.42 (2H, m), 7.51–7.56 (2H, m), 7.64 (2H, tdd, J=7.6, 4.1, 1.1 Hz), 7.97–8.14 (6H, m); ^{31}P NMR (162 MHz, $CDCl_3$): δ 100.5.

4.3.4. 2,2-Diphenyl-1,3,2-benzodioxaphospholium salt with trifluoromethanesulfonic acid (2b). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.33–7.39 (2H, m), 7.45–7.55 (2H, m), 7.82–7.90 (4H, m), 8.03–8.16 (6H, m); ^{31}P NMR (162 MHz, $CDCl_3$): δ 97.2.

4.3.5. 2,2-Dibutyl-1,3,2-benzodioxaphospholium salt with trifluoromethanesulfonic acid (2c). ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.91 (6H, t, J=7.3 Hz), 1.48 (4H, td, J=14.6, 7.3 Hz), 1.59–1.74 (4H, m), 3.13 (4H, dd, J=15.9, 9.2 Hz), 7.23–7.28 (2H m), 7.32–7.37 (2H, m); ^{31}P NMR (162 MHz, $CDCl_3$): δ 142.6.

4.3.6. Spiro[1,3,2-benzodioxaphospholium-2,2′-phospholanium] salt with trifluoromethanesulfonic acid (2d). Not available due to low solubility of **2d** in $CDCl_3$.

4.3.7. Spiro[1,3,2-benzodioxaphospholium-2,2′-phosphorinanium] salt with trifluoromethanesulfonic acid (2e). ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.93–2.02 (2H, m), 2.27–2.45 (4H, m), 3.07 (2H, t, J=6.7 Hz), 3.14 (2H, t, J=6.7 Hz), 7.23–7.30 (2H, m), 7.32–7.39 (2H, m); ^{31}P NMR (162 MHz, $CDCl_3$): δ 137.7.

4.3.8. Spiro[1,3,2-benzodioxaphospholium-2,2′-phosphepanium] salt with trifluoromethanesulfonic acid (2f). ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.88–1.90 (4H, m), 2.11–2.25 (4H, m), 3.13 (2H, t, J=6.5 Hz), 3.19 (2H, t, J=6.5 Hz), 7.20–7.27 (2H, m), 7.29–7.36 (2H, m); ^{31}P NMR (162 MHz, $CDCl_3$): δ 146.8.

4.3.9. Spiro[dibenzo[*d*,*f*][1,3,2]dioxaphosphepinium-5*H*-dibenzophospholium] salt with trifluoromethanesulfonic acid (3a). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.38–7.43 (2H, m), 7.49–7.74 (8H, m), 7.77–7.82 (2H, m), 8.04 (2H, tt, J=7.8, 1.4 Hz), 8.26 (2H, dd, J=7.8, 5.4 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 83.0.

4.3.10. Spiro[dinaphto[2,1-*d*:1′,2′-*f*][1,3,2]dioxaphosphepinium-5*H*-dibenzophospholium] salt with trifluoromethanesulfonic acid (3b). ^{1}H NMR (270 MHz, $CDCl_3$): δ 7.30 (2H, m), 7.46–7.50 (4H, m), 7.53–7.61 (4H, m), 7.69 (2H, ddd, J=8.1, 5.7, 2.4 Hz), 8.04 (2H, t, J=7.8 Hz), 8.15 (2H, d, J=8.4 Hz), 8.27 (2H, dd, J=7.8, 5.4 Hz), 8.32 (1H, d, J=9.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$): δ 83.5.

4.4. Typical procedure for the Diels–Alder reaction

To a suspension of activated MS 4 Å (100 mg: activated at 300 °C for 3 h under reduced pressure) and hydroxy phosphinate (**5**) (0.06 mmol) in anhydrous dichloromethane (1.8 mL) was added trifluoromethanesulfonic anhydride (0.06 or 0.09 mmol) under nitrogen atmosphere at room temperature. The mixture was stirred for 1 h at ambient temperature and then cooled to the indicated temperature. A dienophile (**6**) (0.6 mmol) was added to the suspension at that temperature. After stirring for 30 min, a ca. 3.0 M solution of cyclopentadiene (**7**) (ca. 1.5 mmol) in dichloromethane was added to the suspension. Stirring was continued under the indicated conditions and the reaction mixture was quenched with sodium bicarbonate. Conventional workup followed by silica-gel column chromatography purification gave pure product (**8**).

4.4.1. 2-*endo*-Methoxycarbonyl-3-*endo*-(pyrrolidin-1-yl)carbonylbicyclo[2.2.1]hept-5-ene (8a). ^{1}H NMR

(270 MHz, $CDCl_3$): δ 1.14 (1H, d, J=8.1 Hz), 1.23 (1H, d, J=8.6 Hz), 1.69 (2H, td, J=13.5, 6.5 Hz), 1.70–1.79 (2H, m), 2.91 (1H, br s), 2.96 (1H, br s), 3.06 (2H, dd, J=10.0, 3.2 Hz), 3.14–3.21 (3H, m); 3.30 (1H, t, J=6.5 Hz), 3.37 (3H, s), 6.04 (1H, dd, J=8.1, 2.7 Hz), 6.10 (1H, dd, J=8.1, 2,7 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 23.60, 25.54, 45.15, 45.55, 45.63, 45.69, 47.42, 47.88, 48.03, 60.69, 133.32, 134.85, 169.80, 172.22; IR (neat): 3462, 2972, 2949, 2871, 1739, 1643, 1434, 1352, 1340, 1251, 1195, 1149, 1076, 1041, 914, 723, 707 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{20}NO_3$ ($[M+H]^+$) 250.1443. Found 250.1438.

4.4.2. 2-*endo*-Methoxycarbonyl-3-*endo*-(*N*-propylcarbamoyl)bicyclo[2.2.1]hept-5-ene (8b). ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.85 (3H, t, J=7.6 Hz), 1.29 (1H, d, J=8.4 Hz), 1.39–1.47 (3H, m), 3.04–3.12 (4H, m), 3.19–3.20 (2H, m), 3.54 (3H, s), 5.68 (1H, br s), 6.10 (1H, dd, J=5.7, 3.0 Hz), 6.44 (1H, dd, J=5.7, 3.0 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 11.24, 22.68, 41.13, 45.64, 47.11, 48.92, 49.05, 50.21, 51.29, 133.36, 136.47, 171.43, 173.44; IR (KBr): 3321, 3003, 2952, 2877, 1720, 1647, 1556, 1440, 1336, 1263, 1226, 1197, 1151, 1035, 792, 690, 615 cm^{-1}; HRMS (ESI) Calcd for $C_{13}H_{20}NO_3$ ($[M+H]^+$) 238.1443. Found 238.1438.

4.4.3. 2-*endo*-Methoxycarbonyl-3-*endo*-(*N*-phenylcarbamoyl)bicyclo[2.2.1]hept-5-ene (8c). ^{1}H NMR (270 MHz, $CDCl_3$): δ 1.35 (1H, d, J=8.6 Hz), 1.50 (1H, dt, J=8.6, 1.6 Hz), 3.18 (1H, br s), 3.19 (1H, br s), 3.23 (1H, dd, J=10.3, 1.6 Hz), 3.39 (1H, dd, J=10.3, 3.0 Hz), 3.54 (3H, s), 6.22 (1H, dd, J=5.7, 3.0 Hz); 6.55 (1H, dd, J=5.7, 3.0 Hz), 7.05 (1H, t, J=7.3 Hz), 7.26 (2H, t, J=7.3 Hz), 7.46 (2H, d, J=7.8 Hz), 7.63 (1H, br s); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 45.76, 47.40, 49.12, 49.35, 51.03, 51.59, 119.67, 123.96, 128.81, 133.49, 136.76, 137.97, 170.09, 173.44; IR (KBr): 3342, 1716, 1685, 1600, 1542, 1490, 1442, 1307, 1255, 1213, 1176, 754, 696 cm^{-1}; HRMS (ESI) Calcd for $C_{16}H_{18}NO_3$ ($[M+H]^+$) 272.1287. Found 272.1281.

4.4.4. 2-*endo*-Ethoxycarbonyl-3-*exo*-(*N*-propylcarbamoyl)bicyclo[2.2.1]hept-5-ene (*endo*-8d). ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.88 (3H, t, J=7.3 Hz), 1.16–1.25 (3H, m), 1.41–1.56 (3H, m), 1.82 (1H, d, J=7.0 Hz), 2.32 (1H, d, J=4.9 Hz), 2.99 (1H, s), 3.15–3.23 (4H, m), 4.02–4.14 (2H, m); 5.99 (3H, br s), 6.06 (1H, dd, J=5.4, 2.4 Hz), 6.21 (1H, dd, J=5.4, 3.0 Hz); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 11.28, 14.17, 22.84, 41.22, 44.76, 46.76, 47.55, 48.42, 49.41, 60.63, 135.30, 137.87, 173.91, 174.11; IR (neat): 3311, 2970, 2939, 1733, 1645, 1544, 1458, 1315, 1269, 1209, 1190, 1116, 1033, 864, 729, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{22}NO_3$ ($[M+H]^+$) 252.1600. Found 252.1594.

4.4.5. 2-*exo*-Ethoxycarbonyl-3-*endo*-(*N*-propylcarbamoyl)bicyclo[2.2.1]hept-5-ene (*exo*-8d). ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.85–0.92 (3H, m), 1.17–1.31 (3H, m), 1.43–1.55 (4H, m), 2.54 (1H, dd, J=4.9, 1.4 Hz), 3.08–3.20 (5H, m), 4.12–4.19 (2H, m), 5.95 (1H, br s), 6.17–6.21 (2H, m); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 11.29, 14.19, 22.87, 41.13, 45.45, 46.66, 47.60, 48.37, 49.67, 60.93, 135.69, 136.37, 172.53, 175.03; IR (KBr): 3317, 2970, 2937, 1726, 1641, 1552, 1458, 1382, 1325, 1276, 1242, 1213, 1172, 1033, 873, 698 cm^{-1}; HRMS (ESI) Calcd for $C_{14}H_{22}NO_3$ ($[M+H]^+$) 252.1600. Found 252.1594.

4.5. Stereochemical assignment of 8d

4.5.1. Transformation to hexahydro-6-iodo-2-oxo-*N*-propyl-3,5-methano-2*H*-cyclopenta[*b*]furan-7-carboxamide (9). To a stirred solution of **8d** (40.0 mg, 0.16 mmol: one diastereomer obtained from the major product of Table 2 entry 7) in methanol (1.0 mL) was added dropwise 2 M NaOH solution (0.5 mL) at 0 °C. After being stirred for 15 min, the ice bath was removed and the mixture was stirred for 1 h at room temperature. The resultant mixture was quenched by adding 1 M HCl solution (2 mL). Following extraction with CH_2Cl_2 (4×15 mL), the combined organic layers were concentrated under reduced pressure to give crude carboxylic acid. The crude material thus obtained was used for the next lactonization without further purification. To a stirred solution of crude carboxylic acid in CH_2Cl_2 (1.0 mL) at room temperature was added $NaHCO_3$ (67.2 mg, 0.8 mmol), water (2.0 mL), KI (265 mg, 1.60 mmol), and I_2 (142 mg, 0.56 mmol) in this order. After being stirred for 3 h at ambient temperature, the reaction mixture was quenched by adding saturated $Na_2S_2O_3$ solution. Following extraction with CH_2Cl_2 (3×10 mL), the combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure to give crude lactone (**9**). Purification by silica-gel column chromatography gave pure lactone (**9**) (52.1 mg, 92% form **8d**), ^{1}H NMR (270 MHz, $CDCl_3$): δ 0.91 (3H, t, J=7.6 Hz), 1.51 (2H, sex, J=7.6 Hz), 2.28 (2H, m), 2.61 (1H, s), 2.84 (1H, s), 3.05 (1H, d, J=3.5 Hz), 3.14–3.21 (3H, m), 3.85 (1H, d, J=1.6 Hz), 5.12 (1H, d, J=4.9 Hz), 5.91 (1H, br s); ^{13}C NMR (67.8 MHz, $CDCl_3$): δ 11.40, 22.72, 28.66, 35.11, 41.52, 41.77, 46.21, 51.55, 51.69, 88.89, 169.45, 178.49; IR (neat): 3327, 2964, 2933, 1781, 1651, 1539, 1458, 1346, 1305, 1247, 1172, 1116, 1006, 985, 912, 840, 736 cm^{-1}; HRMS (ESI) Calcd for $C_{12}H_{16}INNaO_3$ ($[M+Na]^+$) 372.0067. Found 372.0067.

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tet.2005.09.075. This comprises a scanned image of the ^{1}H NMR spectra of phosphonium salts (**1**), table of ^{31}P NMR chemical shifts of **1**–**5**, and scanned image of 2D (COSY) and NOE spectra of **2a**/DMF complex.

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(from δ 46.2); **1b**: δ 92.7 (from δ 46.3); **2a**: δ 100.5 (from δ 48.9); **2b**: δ 97.2 (from δ 39.1); **2c**: δ 142.6 (from δ 67.4); **2d**: δ (low solubility in $CDCl_3$) (from δ 91.3); **2e**: δ 137.7 (from δ 60.8); **2f**: δ 146.8 (from δ 73.9); **3a**: δ 83.0 (from δ 42.9); **3b**: δ 83.5 (from δ 44.1).

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20. When **2a** was exposed to 2 equiv of dienophile (**6a**), several peaks [42.4 (major), 41.5 (minor), −26.5 (minor)] with marked upfield shifts were observed in the ^{31}P NMR spectrum, and a significant broadening of the peak assigned to phosphonium salt (**2a**) was observed in the ^{1}H NMR spectrum.
21. In all cases, the thermal reaction gave no or a trace amount (less than 5%) of the Diels–Alder products under the same conditions except for the absence of phosphonium salt.
22. The stereochemistry of **8d** was confirmed via conventional operations. Ester hydrolysis of **8d** followed by iodolactonization gave five-membered lactone (**9**) that was assigned to be the *endo*-stereoisomer by IR measurement [C═O(lactone); 1781 cm^{-1}].
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