

Synthesis of β -Monosubstituted α,β -Unsaturated Amides with *Z*-Selectivity Using Diphenylphosphonoacetamides

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ABSTRACT: The utility of diphenylphosphonoacetamides [(PhO)₂P(O)CH₂CONRR'] as Horner–Wadsworth–Emmons reagents was examined with five different patterns of substitution upon the amide nitrogen atom (**2a**: R, R' = CH₂Ph; **2b**: R = CH₂Ph, R' = H; **2c**: R = Me, R' = OMe; **2d**: R, R' = Ph; **2e**: R, R' = (CH₂)₄). The reaction of **2a** was found to be *Z*-selective for aromatic aldehydes with selectivities up to 95:5. Reagent **2b** led to reasonable selectivity for both benzaldehyde (85:15) and 3-phenylpropionaldehyde (87:13), while **2c** was somewhat effective for only the latter alkyl aldehyde (83:17). Compounds **2d** and **2e** exhibited slightly lower selectivities compared with **2a**. © 2004 Wiley Periodicals, Inc. *Heteroatom Chem* 15:515–523, 2004; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20054

INTRODUCTION

The Wittig reaction and its variants are extremely versatile reagents for the regioselective introduction of unsaturation with concomitant carbon–carbon bond formation [1]. The applicability of α,β -

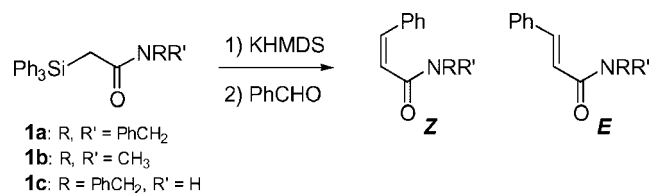
unsaturated carbonyl compounds has made this class of compounds attractive building blocks, i.e., both the carbonyl and the alkene moieties can undergo further modification. The stereochemical outcome of reactions utilizing this class of compounds is frequently dependent upon the geometry of the olefin moiety, and thus it is worthwhile to prepare these compounds with high *E* or *Z*-selectivity. The preparation of disubstituted *E*-alkenes of this type with high selectivity is rather facile. However, for the thermodynamically less stable *Z*-form, only a limited number of methods involving C–C bond formation with high selectivities have been reported, for α,β -unsaturated esters [2–4], carbonitriles [5–8], methyl ketones [9], and amides [7,10]. As for the last subgroup of α,β -unsaturated compounds, i.e., amides, preparation with high *Z*-selectivity was achieved by the use of 10-P-5 phosphoranes [7] and Peterson type reagents **1** [10]. However, there are a few drawbacks with these reagents. For the former, the preparation of the reagent requires the use of rather expensive and unpleasant hexafluoroacetone. For the latter series, applicable bases in the olefination reaction were rather limited, and enolizable 2-phenylpropionaldehyde and hindered 2,2-dimethylpropionaldehyde did not give olefinic products. Furthermore, for the mono-*N*-substituted amide **1c** (see Scheme 1), the mere generation of the amide enolate of **1c** led to decomposition of the reagent. In an attempt to overcome these deficiencies, we have carried out an examination

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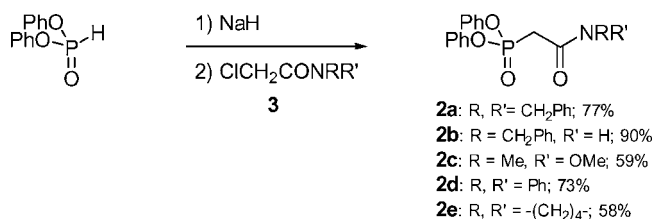
SCHEME 1

of diphenylphosphonoacetamides, prospectively Z-selective Horner–Wadsworth–Emmons (HWE) analogs of the highly successful phosphonoacetates by Ando [3]. As a result, we have found that with these easily prepared reagents, more common bases are applicable and that the reaction proceeds even with an *N*-monoalkyl reagent. Herein we present a full account of results from the reaction of five different amide reagents [11,12].

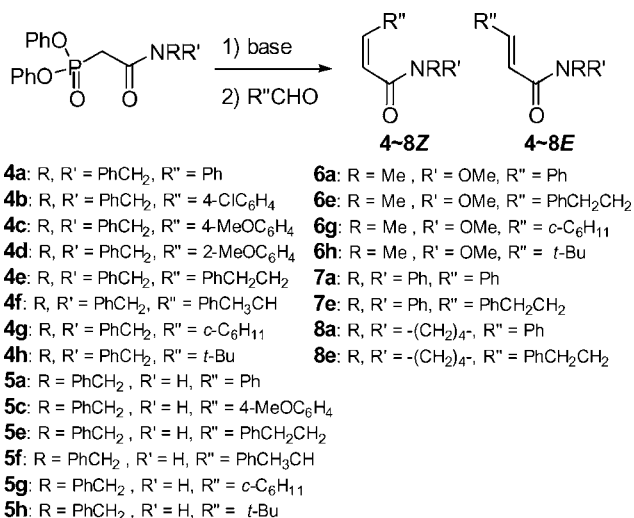
RESULTS AND DISCUSSION

Examined were [(PhO)₂P(O)CH₂CONRR'] with several different patterns of substitution upon the amide nitrogen (**2a**: R, R' = CH₂Ph; **2b**: R = CH₂Ph, R' = H; **2c**: R = Me, R' = OMe; **2d**: R = R' = Ph; **2e**: NRR' = pyrrolidinyl). Compound **2a** was selected as a representative of *N,N*-disubstituted reagents and for comparison with **1**, **2b** as that of *N*-monosubstituted reagents, and **2c** as that having somewhat electronegative character and bearing the potential for further transformation to ketones [13,14]. Two other *N,N*-disubstituted compounds **2d** and **2e** were also briefly examined. The reagents were prepared by the reaction of diphenyl phosphite with the corresponding chloroacetamides **3** in the presence of NaH in fair to good yield (58–90%), as shown in Scheme 2.

The reaction of **2a** with benzaldehyde (see Scheme 3), an aromatic aldehyde, was first examined with representative bases (Table 1, entries 1–4). All the reactions were carried out in THF at –78°C besides those of *n*-BuLi, of which reaction temperature was allowed to gradually warm to 0°C. The counter-



SCHEME 2



SCHEME 3

cation was found to affect the selectivity, with higher selectivity achieved in the order of Li⁺ < Na⁺ < K⁺. Especially for KHMDS, the selectivity was as high as 94:6. This is the same cation propensity observed for the Peterson reagent **1** [10]. It was also found that NaH and *t*-BuOK, which could not be used for **1**, could be used here.

The scope of the reagent was next examined with several aromatic aldehydes (Table 1, entries 1–9). As a result, 4-substituted aromatic aldehydes gave high selectivity with K⁺ as the countercation, with selectivity in the order of 4-MeO (95:5) > H (94:6) > 4-Cl (89:11) (Table 1, entries 4, 6, and 8).

TABLE 1 Reaction of **2a** with R''CHO in THF

Entry	R''	Base	Product	Z:E	Yield (%)
1	Ph	<i>n</i> -BuLi ^a	4a	73:27	95
2	Ph	NaH	4a	88:12	71
3	Ph	<i>t</i> -BuOK	4a	92:8	65
4	Ph	KHMDS	4a	94:6	96
5	4-ClC ₆ H ₄	<i>n</i> -BuLi ^a	4b	75:25	96
6	4-ClC ₆ H ₄	KHMDS	4b	89:11	100
7	4-MeOC ₆ H ₄	<i>n</i> -BuLi ^a	4c	56:44	100
8	4-MeOC ₆ H ₄	KHMDS	4c	95:5	93
9	2-MeOC ₆ H ₄	KHMDS	4d	79:21	100
10	Ph(CH ₂) ₂	NaH	4e	67:33	77
11	Ph(CH ₂) ₂	<i>t</i> -BuOK	4e	60:40	39
12	Ph(CH ₂) ₂	KHMDS	4e	50:50	80
13	Ph(CH ₂)CH	NaH	4f	29:71	96
14	Ph(CH ₂)CH	KHMDS	4f	17:83	66
15	<i>c</i> -C ₆ H ₁₁	NaH	4g	50:50	50
16	<i>c</i> -C ₆ H ₁₁	KHMDS	4g	35:65	92
17	<i>t</i> -Bu	NaH ^a	4h	47:53	83
18	<i>t</i> -Bu	KHMDS ^a	4h	41:59	44

^aReaction temperature was gradually raised to 0°C.

The tendency for the electron rich aldehyde to give higher Z-selectivity has also been observed with **1** [4-MeO (>97:3)=H (>97:3)>4-Cl (88:12)]. A decrease in selectivity was observed for the sterically more hindered 2-substituted aromatic aldehyde, 2-anisaldehyde (Table 1, entry 9). Reactions using *n*-BuLi showed an opposite trend as compared with reactions with **1** [4-MeO (69:31)>H (54:46)>4-Cl (43:57)]. Here, the more electrophilic aromatic aldehyde gave rise to higher selectivity [4-Cl (75:25)>H (73:27)>4-MeO (56:44)] (Table 1, entries 1, 5, and 7). This may be due to the higher reversibility of the initial adduct for the electron-rich aldehydes compared with electron-poor aldehydes, although the difference in reversibility is probably very small. Thus, as a whole, the Peterson reagent **1** gives higher selectivity than **2a**. However, considering the availability of the reagent and range of usable bases in the olefin-forming reaction, it can be considered that **2a** scores fairly with **1** for reactions involving aromatic aldehydes.

For 3-phenylpropionaldehyde, a typical unbranched aliphatic aldehyde, the selectivity was found to be only modest, with a maximum of ca. 2:1 (Table 1, entries 10–12). In this case, though the difference was rather small, the use of Na⁺ as the counteranion provide to be best. This unique phenomenon concerning the counteranion has previously been pointed out for corresponding ester-based reagents by Ando, although the reason for this behavior is not yet clear [3]. As for α -branched aldehydes (Table 1, entries 13–18), however, the Z-selectivity was even lower, resulting in the preference for the opposite *E*-olefin in some cases. This is in contrast with corresponding phosphonoacetates in general, where branched and thus hindered aldehydes usually give higher Z-selectivity than unbranched substrates [1–3]. A similar decrease in Z-selectivity with size was also observed with the Peterson reagent **1**. This could be associated with the fact that the reaction becomes somewhat sluggish compared with corresponding ester-based reagents. Although not marked, reactions using NaH were again more Z-selective. Nonetheless, the fact that 2-phenylpropionaldehyde reacted (although with low selectivity) at all as opposed to the reaction of **1** implies that Peterson-type reagents such as **1** are quite sensitive to the acidity of the substrate aldehyde.

The reaction of **2b** with benzaldehyde in the presence of either 1 or 2 equiv of base was found to proceed with selectivities up to 85:15 (Table 2, entries 1–5). The use of 2 equiv in some cases was to assure full conversion in the presence of product bearing a somewhat acidic amide group. The reaction of 3-phenylpropionaldehyde also proceeded with a rela-

TABLE 2 Reaction of **2b** with R''CHO in THF

Entry	R''	Base	Product	Z:E	Yield (%)
1	Ph	NaH ^b	5a	85:15	55
2	Ph	NaH ^c	5a	68:32	84
3	Ph	<i>t</i> -BuOK ^c	5a	78:22	91
4	Ph	KHMDS ^b	5a	81:19	77
5	Ph	KHMDS ^c	5a	76:24	93
6	4-MeOC ₆ H ₄	<i>t</i> -BuOK ^c	5c	69:31	75
7	Ph(CH ₂) ₂	<i>n</i> -BuLi ^{a,b}	5e	84:16	82
8	Ph(CH ₂) ₂	NaH ^b	5e	87:13	44
9	Ph(CH ₂) ₂	NaH ^c	5e	86:14	77
10	Ph(CH ₂) ₂	KHMDS ^b	5e	80:20	52
11	Ph(CH ₂) ₂	KHMDS ^c	5e	74:26	52
12	Ph(CH ₃)CH	NaH ^c	5f	88:12	78
13	Ph(CH ₃)CH	<i>t</i> -BuOK ^c	5f	74:26	62
14	<i>c</i> -C ₆ H ₁₁	NaH ^d	5g	75:25	73
15	<i>c</i> -C ₆ H ₁₁	KHMDS ^b	5g	73:27	50
16	<i>t</i> -Bu	NaH ^c	5h	84:16	63
17	<i>t</i> -Bu	<i>t</i> -BuOK ^c	5h	60:40	37

^aReaction temperature was gradually raised to 0°C.

^b1 equiv of base was used.

^c2 equiv of base was used.

^d1.5 equiv of base was used.

tively high selectivity of 87:13 using NaH (Table 2, entries 8 and 9). The use of Li⁺ as counter cation is usually unfavorable from the point of selectivities in HWE reactions. However, as it turns out, in this case with the aliphatic substrate, the extent of decline was minimal and selectivity was actually a bit better than K⁺ (Table 2, entries 7, 8, and 10). In contrast to **2a**, which bears two alkyl substituents upon the nitrogen atom, reactions with branched alkyl aldehydes were Z-selective, with selectivities as high as 88:12 for 2-phenylpropionaldehyde (Table 2, entries 12–17). A general trend was that the use of 2 equiv of base compared to 1 equiv gave higher yield but somewhat lower selectivity, and NaH turned out to be more suitable than potassium bases for both aromatic and aliphatic aldehydes. The decrease in selectivity upon using larger amounts of base could be due to a higher degree of base (nucleophile) induced isomerization of the product olefins.

The selectivity of the reaction of Weinreb type HWE reagent **2c** with benzaldehyde was found to be rather disappointing (ca. 2:1) with similar ratios regardless of which base was used (Table 3, entries 1–4). However, the reaction of 3-phenylpropionaldehyde proceeded with a reasonable selectivity of 83:17 using NaH (Table 3, entry 6). Here again for the aliphatic aldehyde, Na⁺ was the optimum counter cation. For the branched cyclohexanecarboxaldehyde there was again a drop in selectivity (Table 3, entry 9). The bulky pivalaldehyde required higher temperature for reaction to proceed at all, although

TABLE 3 Reaction of **2c** with R''CHO in THF

Entry	R''	Base	Product	Z:E	Yield (%)
1	Ph	<i>n</i> -BuLi ^a	6a	67:33	49
2	Ph	NaH	6a	71:29	79
3	Ph	<i>t</i> -BuOK	6a	69:31	85
4	Ph	KHMDS	6a	72:28	67
5	Ph(CH ₂) ₂	<i>n</i> -BuLi ^a	6e	75:25	90
6	Ph(CH ₂) ₂	NaH	6e	83:17	83
7	Ph(CH ₂) ₂	<i>t</i> -BuOK	6e	65:35	85
8	Ph(CH ₂) ₂	KHMDS	6e	67:33	92
9	<i>o</i> -C ₆ H ₁₁	NaH	6g	64:36	78
10	<i>t</i> -Bu	NaH ^b	6h	82:18	45

^aReaction temperature was gradually raised to 0°C.^bReaction temperature was 0°C.

selectivity was maintained over 4:1 (Table 3, entry 10).

The reaction of **2d** with benzaldehyde gave the corresponding α,β -unsaturated amide in fairly good yields (Table 4, entry 1–3). In contrast with similarly *N,N*-disubstituted **2a**, NaH was found to give the highest selectivity even with this aromatic aldehyde. Or, another way to put it is that a significant drop in selectivity was observed for reactions involving K⁺. The same trend in selectivity (decrease with K⁺ and practically no change with Na⁺), although not as distinct, was also observed with **2e** (Table 5, entries 1–3). In the case of **2e**, the reactions were somewhat messy, thus leading to lower reaction yields. With both compounds (**2d** and **2e**), the reaction with 3-phenylpropionaldehyde gave disappointing results as anticipated from the results of **2a**.

Recent sophisticated theoretical calculations on phosphonoacetates support the widely accepted assumption that at the point of the initial C–C formation, the relative conformations of the reacting aldehydes and the phosphonoester enolates have the aldehyde carbonyl oxygen, the P=O oxygen, and the enolate oxide oxygen aligned in the same direction owing to electrostatic and/or chelation effects involving the countercation metal [15]. Thus, the primary factor governing selectivity becomes the steric preference between the two models depicted

TABLE 4 Reaction of **2d** with R''CHO in THF

Entry	R''	Base	Product	Z:E	Yield (%)
1	Ph	NaH	7a	87:13	98
2	Ph	<i>t</i> -BuOK	7a	74:26	73
3	Ph	KHMDS	7a	77:23	76
4	Ph(CH ₂) ₂	NaH	7e	61:39	81
5	Ph(CH ₂) ₂	<i>t</i> -BuOK	7e	56:44	95

TABLE 5 Reaction of **2e** with R''CHO in THF

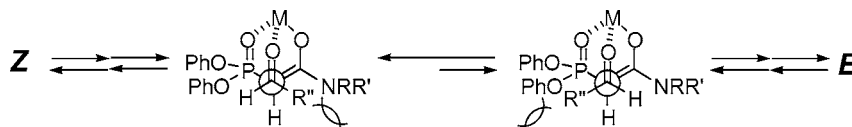
Entry	R''	Base	Product	Z:E	Yield (%)
1	Ph	NaH	8a	89:11	45
2	Ph	<i>t</i> -BuOK	8a	85:15	44
3	Ph	KHMDS	8a	85:15	46
4	Ph(CH ₂) ₂	<i>t</i> -BuOK	8e	56:44	9

in Scheme 4, with the one on the left being favored in the case of phosphonoacetates (Scheme 4). Since the amide group is generally bulkier than the ester group, contribution of the right-hand side model should become relatively larger as compared with ester reagents. Thus, the lower selectivity observed as a whole for reactions involving amide reagents compared with phosphonoacetate counterparts is to some extent inevitable. As for the higher selectivity achieved with Na⁺ in comparison with K⁺, this may be because Na⁺ is smaller in size and thus gives rise to a more compact transition state.

In summary, we have found that the HWE reaction of *N,N*-dibenzyl(diphenylphosphono)-acetamides with aromatic aldehydes gives rise to α,β -unsaturated amides with high *Z*-selectivities. The NH amide compound was also found to be *Z*-selective, while the Weinreb amide-type compound was selective only for alkyl aldehydes. Transformational applications of the products are currently under investigation.

EXPERIMENTAL

Melting points were measured on a Yanaco micro melting point apparatus and are uncorrected. ¹H and ¹³C NMR spectra were measured on either a JEOL JNM-LA500 or JEOL GSX-270 spectrometer with CDCl₃ as solvent. ¹H NMR chemical shifts are given in relative ppm from either internal TMS (δ = 0.0) or residual CHCl₃ (δ = 7.26). ¹³C NMR chemical shifts are given in relative ppm from internal CDCl₃ (δ = 77.0). High-resolution mass spectra were measured on a JEOL JMS-SX102A spectrometer under electron ionization (70 eV) or FAB(+) conditions. Elemental analyses (CHN) were carried out on a Perkin–Elmer 2400CHN elemental analyzer. All reactions were carried under N₂. THF was freshly distilled from Na-benzophenone prior to use. Liquid aldehydes and other reagents were distilled prior to use. Silica gel column chromatography was carried out using Merck 7734 (63–200 mesh) or 9385 (230–400 mesh). Preparative thin layer chromatography was carried out with plates prepared with Merck 7730. All chloroacetamides were prepared



SCHEME 4

from the corresponding amine and chloroacetyl chloride. Compounds **4a–e**, **g** have been reported [10].

N,N-Bis(phenylmethyl)-2-(diphenylphosphono)acetamide (**2a**)

To a suspension of prewashed sodium hydride (60% in mineral oil, 579 mg, 14.5 mmol) in THF (5 mL) was added diphenyl phosphite (2.75 mL, 14.3 mmol) at 0°C under N₂. After stirring at 0°C for 30 min, 2-chloro-*N,N*-bis(phenylmethyl)acetamide (1.93 g, 7.05 mmol) in THF (3 mL) was added to this clear solution. The reaction mixture was allowed to warm at room temperature and stirring was continued overnight. The solution was quenched with saturated NH₄Cl, and the organic solvent was removed under reduced pressure. The aqueous layer was extracted with CH₂Cl₂, and the combined organic layer was washed with water followed by brine, dried over MgSO₄, and evaporated. The crude product was chromatographed (hexane/EtOAc = 4/1) to afford **2a** in 87% yield (2.90 g) as a colorless solid. Mp: 68–69°C. ¹H NMR (CDCl₃): δ 7.43–7.06 (m, 20H), 4.69 (s, 2H), 4.65 (s, 2H), 3.42 (d, J = 22.5 Hz, 2H). ¹³C NMR (CDCl₃): δ 164.52 (J_{CP} = 6 Hz), 149.98 (J_{CP} = 10 Hz), 136.50, 135.84, 129.69, 129.00, 128.59, 127.91, 127.73, 127.37, 126.22, 125.39, 120.75 (J_{CP} = 4 Hz), 50.91, 48.90, 33.38 (J_{CP} = 137 Hz). HRMS (EI): Calcd for C₂₈H₂₆NO₄P 471.1599, found 471.1621. Anal. Calcd for C₂₈H₂₆NO₄P: C, 71.33%; H, 5.56%; N, 2.97%. Found: C, 71.28%; H, 5.73%; N, 3.00%.

N-Phenylmethyl-2-(diphenylphosphono)acetamide (**2b**)

According to the procedure for **2a**, diphenyl phosphite (3.00 mL, 15.7 mmol), NaH (60% in mineral oil, 628 mg, 15.7 mmol), and *N*-benzylchloroacetamide (2.37 g, 13.0 mmol) were reacted. After aqueous workup, the crude product was directly recrystallized from hexane-AcOEt to give **2b** in 90% (4.43 g) yield as a white solid. Mp: 150–151°C. ¹H NMR (CDCl₃): δ 7.34–7.13 (m, 15H), 7.10–7.00 (bs, 1H), 4.43 (d, J = 5.8 Hz, 2H), 3.20 (d, J = 20.7 Hz, 2H). ¹³C NMR (CDCl₃): δ 162.56, 149.80, 137.56, 129.91, 128.69, 127.67, 127.48, 125.73 (d, J_{CP} = 2

Hz), 120.62 (d, J_{CP} = 5 Hz), 44.0, 34.9 (d, J_{CP} = 131 Hz). HRMS (EI): Calcd for C₂₁H₂₀NO₄P 381.1130, found 381.1132. Anal. Calcd for C₂₁H₂₀NO₄P: C, 66.14%; H, 5.11%; N, 3.50%. Found: C, 66.25%; H, 5.11%; N, 3.50%.

N-Methoxy-*N*-methyl-2-(diphenylphosphono)acetamide (**2c**)

According to the procedure for **2a**, diphenyl phosphite (2.80 mL, 14.6 mmol), NaH (63% in mineral oil, 565 mg, 14.8 mmol), and 2-chloro-*N*-methoxy-*N*-methylacetamide (1.85 g, 13.4 mmol) were reacted. The crude product was chromatographed (hexane/EtOAc = 4/1) to afford **2c** in 61% (2.72 g) as a pale yellow oil. ¹H NMR (CDCl₃): δ 7.36–7.14 (m, 10H), 3.74 (s, 3H), 3.48 (d, J = 21.9 Hz, 2H), 3.24 (s, 3H). ¹³C NMR (CDCl₃): δ 164.85 (J_{CP} = 6 Hz), 150.08 (J_{CP} = 8 Hz), 129.68, 125.31, 120.70 (J_{CP} = 4 Hz), 61.46, 32.19, 31.15 (J_{CP} = 141 Hz). HRMS (EI): Calcd for C₁₆H₁₈NO₅P 335.0922, found 335.0909. Anal. Calcd for C₁₆H₁₈NO₅P: C, 57.31%; H, 5.41%; N, 4.18%. Found: C, 57.40%; H, 5.44%; N, 3.88%.

N,N-Diphenyl-2-(diphenylphosphono)acetamide (**2d**)

According to the procedure for **2a**, diphenyl phosphite (2.70 mL, 14.2 mmol), NaH (60% in mineral oil, 570 mg, 14.2 mmol), and *N,N*-diphenylchloroacetamide (1.70 mL, 6.94 mmol) were reacted. After aqueous workup, the crude product was directly recrystallized from hexane-AcOEt to give **2d** in 73% (2.24 g) yield as a white solid. Mp: 134–135°C. ¹H NMR (CDCl₃): δ 7.50–7.00 (m, 20H), 3.31 (d, J = 22 Hz, 2H). ¹³C NMR (CDCl₃): δ 163.91, 150.09 (d, J_{CP} = 8 Hz), 129.97, 129.72, 129.02, 128.70, 126.45, 125.32, 120.79 (d, J_{CP} = 4 Hz), 33.58 (d, J_{CP} = 138 Hz). ³¹P NMR (CDCl₃): δ 14.7. HRMS (EI): Calcd for C₂₆H₂₂O₄NP 443.1286, found 443.1248. Anal. Calcd for C₂₆H₂₂O₄NP: C, 70.42%; H, 5.00%; N, 3.16%. Found: C, 70.61%; H, 4.76%; N, 3.00%.

1-[(Diphenylphosphono)acetyl]pyrrolidine (**2e**)

According to the procedure for **2a**, diphenyl phosphite (5.70 mL, 29.9 mmol), NaH (60% in mineral oil,

1.20 g, 30.0 mmol), and *N*-(chloroacetyl)pyrrolidine (4.39 g, 29.7 mmol) were reacted. After aqueous workup, the crude product was directly recrystallized from hexane-AcOEt to give **2e** in 58% (5.90 g) yield as a white solid. Mp: 89–90°C. ¹H NMR (CDCl₃): δ 7.50–7.10 (m, 10H), 3.73–3.39 (m, 4H), 3.30 (d, *J* = 20.4 Hz, 2H), and 2.20–1.80 (m, 4H). ¹³C NMR (CDCl₃): δ 161.8, 150.1 (d, *J*_{CP} = 8 Hz), 129.7, 125.3, 120.7 (d, *J*_{CP} = 4 Hz), 47.6, 46.2, 34.5 (d, *J*_{CP} = 136 Hz), 26.0, 24.4. ³¹P NMR (CDCl₃): δ 15.0. HRMS (EI): Calcd for C₁₈H₂₀O₄NP 345.1130, found 345.1144. Anal. Calcd for C₁₈H₂₀O₄NP: C, 62.61%; H, 5.84%; N, 4.06%. Found: C, 62.54%; H, 6.04%; N, 4.06%.

*General Procedure for the Reaction of the Phosphonoamides (Example Using 2d, Benzaldehyde, and *t*-BuOK)*

A solution of **2d** (229 mg, 0.517 mmol) in THF (5.0 mL) was added dropwise to a suspension of *t*-BuOK (58.0 mg, 0.517 mmol) in THF (3.0 mL) at –78°C under N₂, and the resulting mixture was stirred at 0°C for 0.5 h. Benzaldehyde (50.0 mg, 0.470 mmol) in THF (1.5 mL) was then added at –78°C, and the mixture was stirred at the same temperature for 3 h. The solution was quenched with saturated NH₄Cl and extracted with ether. The combined organic layer was washed with water followed by brine, dried over Na₂SO₄, and evaporated. The residue was purified by preparative TLC (silica gel, hexane-AcOEt = 5:1) to give **7a** in 73% (98.8 mg, mixture of geometric isomers, *Z*/*E* = 74/26) combined yield. In reactions using NaH, the phosphonate solution was added to the suspension containing the base as in the case of *t*-BuOK. In the case of KHMDS and *n*-BuLi, the base was directly added to the solution of the phosphonate. Furthermore, in reactions using *n*-BuLi, the reaction mixture was allowed to gradually warm to 0°C.

4-Phenyl-N,N-bis(phenylmethyl)-2-pentenamide (4f)

¹H NMR (CDCl₃) (*Z*-isomer): δ 7.36–7.17 (m, 13H), 7.11 (d, *J* = 7.0 Hz, 2H), 6.11–6.01 (m, 2H), 4.75 (d, *J* = 14.6 Hz, 1H), 4.52–4.33 (m, 4H), 1.43 (d, *J* = 7.0 Hz, 3H). (*E*-isomer): δ 7.39–7.09 (m, 16H), 6.21 (dd, *J* = 14.9, 1.2 Hz, 1H), 4.72–4.55 (m, 2H), 4.46 (s, 2H), 3.58 (quint, *J* = 7.0 Hz, 1H), 1.38 (d, *J* = 7.0 Hz, 3H). ¹³C NMR (CDCl₃) (*Z*-isomer): δ 167.99, 152.03, 146.99, 144.95, 136.43, 128.86, 128.63, 128.55, 128.37, 127.62, 127.44, 127.07, 126.73, 126.27, 119.99, 50.37, 47.32, 38.72, 21.25. (*E*-isomer): δ 167.54, 151.35, 143.65, 129.44, 128.85,

128.56, 128.54, 128.37, 127.59, 127.41, 127.25, 126.58, 126.50, 119.18, 115.44, 50.12, 48.84, 42.30, 20.62. HRMS (EI) (*Z*-isomer): Calcd for C₂₅H₂₅NO 355.1936, found 355.1950. (*E*-isomer): Calcd for C₂₅H₂₅NO 355.1936, found 355.1953.

4,4-Dimethyl-N,N-bis(phenylmethyl)-2-pentenamide (4h)

¹H NMR (CDCl₃) (*Z*-isomer): δ 7.39–7.14 (m, 10H), 5.83 (d, *J* = 13.1 Hz, 1H), 5.68 (d, *J* = 13.1 Hz, 1H), 4.57 (s, 2H), 4.49 (s, 2H), 1.12 (s, 9H). (*E*-isomer): δ 7.39–7.14 (m, 10H), 7.05 (d, *J* = 15.2 Hz, 1H), 6.16 (d, *J* = 15.2 Hz, 1H), 4.65 (s, 2H), 4.51 (s, 2H), 1.03 (s, 9H). ¹³C NMR (CDCl₃) (*Z*-isomer): δ 169.61, 147.15, 136.77, 136.28, 129.02, 128.85, 128.45, 127.62, 127.44, 127.00, 119.98, 50.64, 46.59, 34.51, 29.54. (*E*-isomer): δ 167.86, 157.62, 137.42, 136.87, 128.83, 128.55, 128.40, 127.59, 127.35, 126.67, 115.35, 50.12, 48.71, 33.76, 28.83. HRMS (EI) (mixture of *Z*- and *E*-isomers): Calcd for C₂₁H₂₅NO 307.1936, found 307.1921.

3-Phenyl-N-phenylmethyl-2-propenamide (5a)

¹H NMR (CDCl₃) (*Z*-isomer): δ 7.6–7.0 (m, 10H), 6.77 (d, *J* = 12.5 Hz, 1H), 6.01 (d, *J* = 12.5 Hz, 1H), 5.8 (bs, 1H), 4.40 (d, *J* = 6.1 Hz, 2H). (*E*-isomer): δ 7.68 (d, *J* = 15.5 Hz, 1H), 7.6–7.2 (m, 10H), 6.41 (d, *J* = 15.5 Hz, 1H) and 5.9 (bs, 1H) and 4.58 (d, *J* = 5.8 Hz, 2H). ¹³C NMR (CDCl₃) (*Z*-isomer): δ 166.84, 137.57, 136.44, 134.88, 128.86, 128.56, 128.49, 128.37, 127.91, 127.42, 124.65, 43.52. (*E*-isomer): δ 165.99, 140.98, 138.17, 134.71, 129.50, 128.65, 128.53, 127.68, 127.66, 127.30, 120.66, 43.61. HRMS (EI) (*Z*-isomer): Calcd for C₁₆H₁₅NO 237.1154, found, 237.1141. (*E*-isomer): Calcd for C₁₆H₁₅NO 237.1154, found, 237.1188.

3-(4-Methoxyphenyl)-N-phenylmethyl-2-propenamide (5c)

¹H NMR (CDCl₃) (*Z*-isomer): δ 7.42 (dt, *J* = 8.5, 2.0 Hz, 2H), 7.3–7.2 (m, 5H), 6.78 (dt, *J* = 8.5, 2.0 Hz, 2H), 6.69 (d, *J* = 12.9 Hz, 1H), 5.88 (d, *J* = 12.9 Hz, 1H), 5.8 (bs, 1H), 4.44 (d, *J* = 5.8 Hz, 1H), 3.79 (s, 3H). (*E*-isomer): δ 7.63 (d, *J* = 15.5 Hz, 1H), 7.45 (d, *J* = 8.8 Hz, 2H), 7.4–7.25 (m, 5H), 6.78 (d, *J* = 8.8 Hz, 2H), 6.28 (d, *J* = 15.5 Hz, 1H), 5.8 (bs, 1H), 4.58 (d, *J* = 5.2 Hz, 2H), 3.83 (s, 3H). ¹³C NMR (CDCl₃) (*Z*-isomer): δ 167.02, 159.86, 137.78, 136.57, 130.80, 128.59, 128.00, 127.42, 127.38, 122.38, 113.69, 55.21, 43.50. (*E*-isomer): δ 160.90, 140.99, 138.33, 130.79, 129.33, 128.70, 127.89, 127.50, 118.02, 114.23, 113.73, 55.32,

43.80. HRMS (EI) (*Z*-isomer): Calcd for $C_{17}H_{17}NO_2$, 267.1259, found 267.1229. (*E*-isomer): Calcd for $C_{17}H_{17}NO_2$, 267.1259, found 267.1258.

5-Phenyl-*N*-phenylmethyl-2-pentenamide (**5e**)

1H NMR ($CDCl_3$) (*Z*-isomer): δ 7.4–7.1 (m, 10H), 6.01 (dt, $J = 11.6, 7.6$ Hz, 1H), 5.71 (d, $J = 11.6$ Hz, 1H), 5.5 (bs, 1H), 4.42 (d, $J = 5.8$ Hz, 2H), 2.98 (tdd, $J = 7.5, 7.5, 1.5$ Hz, 2H), 2.77 (t, $J = 7.5$ Hz, 2H). (*E*-isomer): δ 7.4–7.1 (m, 11H), 6.93 (dt, $J = 15.5, 7.0$ Hz, 1H), 5.79 (d, $J = 15.5$ Hz, 1H), 5.6 (bs, 1H), 4.51 (d, $J = 5.8$ Hz, 1H), 2.77 (t, $J = 7.8$ Hz, 2H), 2.51 (tdd, $J = 7.8, 7., 1.0$ Hz, 2H). ^{13}C NMR ($CDCl_3$) (*Z*-isomer): δ 166.19, 143.87, 141.18, 138.24, 128.56, 128.50, 128.26, 127.76, 127.35, 125.88, 122.84, 43.18, 35.14, 30.23. (*E*-isomer): δ 165.67, 143.97, 140.93, 138.25, 128.66, 128.41, 128.32, 127.82, 127.48, 126.67, 123.90, 43.53, 34.53, 33.77. HRMS (EI) (*Z*-isomer): Calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1456. (*E*-isomer): Calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1454.

4-Phenyl-*N*-phenylmethyl-2-pentenamide (**5f**)

1H NMR ($CDCl_3$): (*Z*-isomer) δ 7.3–7.0 (m, 10H), 6.09 (dd, $J = 11.3, 10.4$ Hz, 1H), 5.77 (bs, 1H), 5.65 (d, $J = 11.3$ Hz, 1H), 4.97 (qd, $J = 10.4, 6.7$ Hz, 1H), 4.49 (d, $J = 5.7$ Hz, 2H), 1.40 (d, $J = 6.7$ Hz, 3H). (*E*-isomer): δ 7.2–7.1 (m, 10H), 7.05 (dd, $J = 15.2$ Hz, 6.4, 1H), 5.69 (d, $J = 15.2$ Hz, 1H), 5.69 (bs, 1H), 4.49 (d, $J = 5.8$ Hz, 2H), 3.60 (qd, $J = 7.0, 6.4$ Hz, 2H), 1.42 (d, $J = 7.0$ Hz, 3H). ^{13}C NMR ($CDCl_3$) (*Z*-isomer): δ 165.97, 149.66, 145.09, 138.15, 128.65, 128.51, 127.81, 127.45, 127.02, 126.22, 120.15, 43.33, 37.39, 21.23. (*E*-isomer): δ 165.75, 148.75, 143.61, 138.18, 128.64, 128.56, 127.87, 127.46, 127.35, 126.58, 122.29, 43.62, 41.81, 20.47. HRMS (EI) (*Z*-isomer): Calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1439. (*E*-isomer): Calcd for $C_{18}H_{19}NO$ 265.1467, found 265.1458.

3-Cyclohexyl-*N*-phenylmethyl-2-propenamide (**5g**)

1H NMR ($CDCl_3$) (*Z*-isomer): δ 7.4–7.2 (m, 5H), 5.8 (bs, 1H), 5.82 (dd, $J = 11.3, 10.1$ Hz, 1H), 5.59 (d, $J = 11.3$ Hz, 1H), 4.46 (d, $J = 5.5$ Hz, 2H), 3.5–3.3 (m, 1H), 1.8–1.6 (m, 5H), 1.4–1.3 (m, 2H), 1.3–1.0 (m, 3H). (*E*-isomer): δ 7.4–7.2 (m, 5H), 6.83 (dd, $J = 15.5, 6.7$ Hz, 1H), 5.72 (dd, $J = 15.5, 1.2$ Hz, 1H), 5.7–5.6 (bs, 1H), 4.51 (d, $J = 5.5$ Hz, 2H), 2.2–2.0 (m, 1H), 1.8–1.7 (m, 4H), 1.7–1.6 (m, 1H), 1.4–1.2 (m, 2H), 1.2–1.1 (m, 3H). ^{13}C NMR ($CDCl_3$) (*Z*-isomer): δ 166.39, 151.63, 138.50, 128.81, 127.95, 127.59,

120.10, 43.45, 37.16, 32.81, 26.09, 25.61. (*E*-isomer): δ 166.30, 150.40, 138.42, 128.76, 127.98, 127.57, 120.93, 43.73, 40.33, 31.99, 26.04, 25.84. HRMS (EI) (*Z*-isomer): Calcd for $C_{16}H_{21}NO$ 243.1623, found 243.1632. (*E*-isomer): Calcd for $C_{16}H_{21}NO$ 243.1623, found 243.1629.

4,4-Dimethyl-*N*-phenylmethyl-2-pentenamide (**5h**)

1H NMR ($CDCl_3$) (*Z*-isomer): δ 7.4–7.2 (m, 5H), 5.75 (d, $J = 12.9$ Hz, 1H), 5.68 (d, $J = 12.9$ Hz, 1H), 5.8–5.6 (bs, 1H), 4.52 (d, $J = 5.7$ Hz, 2H), 1.17 (s, 9H). (*E*-isomer): δ 7.5–7.2 (m, 5H), 6.87 (d, $J = 15.6$ Hz, 1H), 5.8–5.6 (bs, 1H), 5.65 (d, 15.6, 1H), 4.49 (d, $J = 5.7$ Hz, 2H), 1.02 (s, 9H). ^{13}C NMR ($CDCl_3$) (*Z*-isomer): δ 167.60, 149.52, 138.20, 128.68, 127.98, 127.53, 121.13, 43.60, 34.18, 29.83. (*E*-isomer): δ 166.29, 155.08, 138.32, 128.67, 127.92, 127.48, 118.58, 43.67, 33.44, 28.82. HRMS (EI) (*Z*-isomer): Calcd for $C_{14}H_{19}NO$ 217.1467, found 217.1467. (*E*-isomer): Calcd for $C_{14}H_{19}NO$ 217.1467, found 217.1482.

N-Methoxy-*N*-methyl-3-phenyl-2-propenamide (**6a**)

1H NMR ($CDCl_3$) (*Z*-isomer): δ 7.6–7.2 (m, 5H), 6.76 (d, $J = 12.5$ Hz, 1H), 6.28 (bs, 1H), 3.66 (s, 3H), 3.25 (s, 3H). (*E*-isomer): δ 7.74 (d, $J = 15.8$ Hz, 1H), 7.6–7.2 (m, 5H), 7.04 (d, $J = 15.8$ Hz, 1H), 3.77 (s, 3H), 3.32 (s, 3H). ^{13}C NMR ($CDCl_3$) (*Z*-isomer): δ 168.02, 137.63, 135.12, 128.98, 128.49, 128.17, 120.51, 61.59, 32.13. (*E*-isomer): δ 166.86, 143.33, 135.07, 129.73, 128.69, 127.92, 115.72, 61.76, 32.42. HRMS (EI): Calcd for $C_{11}H_{13}NO_2$ 191.0946, found 191.0938.

N-Methoxy-*N*-methyl-5-phenyl-2-pentenamide (**6e**)

1H NMR ($CDCl_3$) (*Z*-isomer): δ 7.4–7.1 (m, 5H), 6.24 (br d, $J = 10.7$ Hz, 1H), 6.12 (dt, $J = 11.6, 7.3$ Hz, 1H), 3.59 (s, 3H), 3.18 (s, 3H), 2.96 (q, $J = 7.3$ Hz, 2H), 2.77 (t, $J = 7.3$ Hz, 2H). (*E*-isomer): δ 7.3–7.1 (m, 5H), 7.01 (dt, $J = 15.2, 7.0$ Hz, 1H), 6.38 (d, $J = 15.2$ Hz, 1H), 3.62 (s, 3H), 3.22 (s, 3H), 2.79 (t, $J = 7.9$ Hz, 2H), 2.60–2.52 (m, 2H). ^{13}C NMR ($CDCl_3$) (*Z*-isomer): δ 167.23, 145.96, 141.32, 128.43, 128.18, 125.75, 118.69, 61.32, 35.16, 31.91, 30.36. (*E*-isomer): δ 166.78, 146.46, 140.91, 128.32 (two peaks overlap), 125.96, 119.26, 61.54, 34.48, 34.06, 32.26. HRMS (EI) (*Z*-isomer): Calcd for $C_{13}H_{17}NO_2$ 219.1259, found 219.1261. (*E*-isomer): Calcd for $C_{13}H_{17}NO_2$ 219.1259, found 219.1249.

3-Cyclohexyl-N-methoxy-N-methyl-2-propenamide (6g)

^1H NMR (CDCl_3) (Z-isomer): δ 6.13 (d, $J = 11.6$ Hz, 1H), 5.92 (dd, $J = 11.6, 9.8$ Hz, 1H), 3.68 (s, 3H), 3.22 (s, 3H), 3.3–3.1 (m, 1H), 1.8–1.5 (m, 5H), 1.4–1.2 (m, 2H), 1.2–1.0 (m, 3H). (E-isomer): δ 6.93 (dd, $J = 15.5, 7.0$ Hz, 1H), 6.34 (d, $J = 15.5$ Hz, 1H), 3.70 (s, 3H), 3.24 (s, 3H), 2.2–2.0 (m, 1H), 1.9–1.6 (m, 5H), 1.3–1.2 (m, 2H), 1.2–1.1 (m, 3H). ^{13}C NMR (CDCl_3) (Z-isomer): δ 167.42, 152.72, 116.02, 61.40, 37.31, 32.56, 32.02, 25.97, 25.46. (E-isomer): δ 167.58, 153.08, 116.34, 61.73, 40.87, 32.57, 32.13, 26.12, 25.91. HRMS (EI) (Z-isomer): Calcd for $\text{C}_{11}\text{H}_{19}\text{NO}_2$ 197.1416, found 197.1411. (FAB+) (E-isomer): Calcd for $\text{C}_{11}\text{H}_{19}\text{NO}_2$ 198.1494, found 198.1495.

N-Methoxy-N,4,4-trimethyl-2-pentenamide (6h)

^1H NMR (CDCl_3) (Z-isomer): δ 5.87 (bs, 1H), 5.78 (d, $J = 12.5$ Hz, 1H), 3.67 (s, 3H), 3.22 (s, 3H), 1.15 (s, 9H). (E-isomer): δ 7.00 (d, $J = 15.5$ Hz, 1H), 6.30 (d, $J = 15.5$ Hz, 1H), 3.71 (s, 3H), 3.25 (s, 3H), 1.10 (s, 9H). ^{13}C NMR (CDCl_3) (Z-isomer): δ 169.29, 149.35, 118.50, 61.09, 34.14, 32.16, 29.57. (E-isomer): δ 167.50, 157.73, 113.75, 61.53, 33.72, 32.42, 28.82. HRMS (EI) (Z-isomer): Calcd for $\text{C}_7\text{H}_{11}\text{O}[(\text{M}-\text{NMeOMe})^+]$ 111.0810, found 111.0814. (E-isomer): Calcd for $\text{C}_9\text{H}_{17}\text{NO}_2$ 171.1259, found 171.1264.

N,N,3-Triphenyl-2-propenamide (7a)

^1H NMR (CDCl_3) (Z-isomer): δ 7.6–7.5 (m, 2H), 7.4–7.1 (m, 11H), 7.1–6.9 (m, 2H), 7.51 (d, $J = 12.5$ Hz, 1H), 5.95 (d, $J = 12.5$ Hz, 1H). (E-isomer): δ 7.70 (d, $J = 15.5$ Hz, 1H), 7.4–7.1 (m, 15H), and 6.48 (d, $J = 15.5$ Hz, 1H). ^{13}C NMR (CDCl_3) (Z-isomer): δ 167.44, 142.59, 142.40, 136.50, 135.38, 129.68, 129.23, 128.96, 128.70, 128.56, 128.19, 127.94, 127–126 (br), 126.29, 124.21, 119.77. (E-isomer): δ 166.18, 142.78, 142.62, 135.09, 129.70, 129.24, 128.72, 127.96, 127–126 (br), 119.78. HRMS (EI) (Z-isomer): Calcd for $\text{C}_{21}\text{H}_{17}\text{NO}$ 229.1310, found 229.1358. (E-isomer): Calcd for $\text{C}_{21}\text{H}_{17}\text{NO}$ 229.1310, found 229.1328.

N,N,5-Triphenyl-2-pentenamide (7e)

^1H NMR (CDCl_3) (Z-isomer): δ 7.4–7.0 (m, 15H), 5.97 (dt, $J = 11.6, 7.5$ Hz, 1H), 5.71 (d, $J = 11.6$ Hz, 1H), 3.02 (tdd, $J = 7.3, 7.3, 1.5$ Hz, 2H), 2.78 (t, $J = 7.5, 2\text{H}$). (E-isomer): δ 7.4–7.1 (m, 15H), 7.04 (td, $J = 6.8, 14.9$ Hz, 2H), 5.82 (d, $J = 14.9$ Hz, 1H), 2.70 (t, $J = 7.3$ Hz, 2H), 2.44 (td, $J = 6.7, 7.0$ Hz, 2H). ^{13}C NMR (CDCl_3) (Z-isomer): δ 166.41, 145.23, 142.57, 141.35, 129.21, 129.01, 128.51, 128.19, 128–126 (br)

125.80, 122.84, 35.06, 30.27. (E-isomer): δ 165.92, 145.77, 142.71, 140.90, 129.08, 128.34, 128.33, 128–126 (br), 125.94, 123.13, 34.40, 33.98. HRMS (EI) (Z-isomer): Calcd for $\text{C}_{23}\text{H}_{21}\text{NO}$ 327.1623, found, 327.1609. (E-isomer): Calcd for $\text{C}_{23}\text{H}_{21}\text{NO}$ 327.1623, found, 327.1640.

1-(1-Oxo-3-phenyl-2-propenyl)pyrrolidine (8a) [16]

^1H NMR (CDCl_3) (Z-isomer): δ 7.5–7.1 (m, 5H), 6.63 (d, $J = 12.8$ Hz, 1H), 6.06 (d, $J = 12.8$ Hz, 1H), 3.51 (t, $J = 6.7$ Hz, 2H), 3.18 (t, $J = 6.7$ Hz, 2H), 1.9–1.6 (m, 4H). (E-isomer): δ 7.77 (d, $J = 15.5$ Hz, 1H), 7.5–7.1 (m, 5H), 6.74 (d, $J = 15.5$ Hz, 1H), 3.7–3.5 (m, 4H), 2.1–1.8 (m, 4H). HRMS (EI): Calcd for $\text{C}_{13}\text{H}_{15}\text{NO}$ 201.1154, found 201.1162.

1-(1-Oxo-5-phenyl-2-pentenyl)pyrrolidine (8e)

^1H NMR (CDCl_3) (Z-isomer): δ 7.4–7.0 (m, 5H), 6.1–5.9 (m, 2H), 3.48 (t, $J = 6.4$ Hz, 2H), 3.30 (t, $J = 6.4$ Hz, 2H), 3.0–2.8 (m, 2H), 2.76 (t, $J = 6.8$ Hz, 2H), 2.0–1.8 (m, 4H). (E-isomer) [17]: δ 7.4–6.8 (m, 5H), 6.96 (dt, $J = 15.1, 6.8$ Hz, 1H), 6.09 (d, $J = 15.1$ Hz, 1H), 3.52 (t, $J = 6.8$ Hz, 2H), 3.45 (t, $J = 6.6$ Hz, 2H), 2.78 (t, $J = 7.3$ Hz, 2H), 2.51 (td, $J = 7.3, 6.8$ Hz, 2H), 2.0–1.8 (m, 4H). ^{13}C NMR (CDCl_3) (Z-isomer): δ 165.70, 142.31, 141.44, 128.53, 128.14, 125.73, 122.40, 46.72, 45.21, 35.19, 30.38, 26.04, 24.27. (E-isomer): δ 164.71, 144.22, 141.09, 128.34, 128.32, 125.95, 122.33, 46.40, 45.70, 34.68, 34.04, 26.04, 24.25. HRMS (EI) (Z-isomer): Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$ 229.1467, found 229.1490. (E-isomer): Calcd for $\text{C}_{15}\text{H}_{19}\text{NO}$ 229.1467, found 229.1493.

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