Facile Synthesis of 1,4-Benzodiazepin-5-one Derivatives via Intramolecular Aza-Wittig Reaction. Application to an Efficient Synthesis of *O*-Benzyl DC-81[1]

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The tandem Staudinger/aza-Wittig reaction of *N*-(*o*-azidobenzoyl)-α-amino acid esters gave the corresponding 1,4-benzodiazepin-5-one derivatives in moderate to good yields. This method was applied successfully to a new efficient synthesis of BzlDC-81.

Over the past decade, great progress has been made in the field of heterocyclic synthesis by the aza-Wittig methodology.[2,3] The key intermediate iminophosphoranes can be conveniently generated by the Staudinger reaction from organic azides and phosphorus(III) reagents or by the Kirsanov reaction from primary amines and phosphorus pentahalides.[4] We reported previously on a convenient route to quinazolinone derivatives via intramolecular aza-Wittig reaction of (*o*-azidobenzoyl)-amides and -lactams.[5–7] In this paper, we describe a facile synthetic route to 1,4-benzodiazepinone derivatives by using the intramolecular aza-Wittig reaction of *N*-(*o*-azidobenzoyl)-α-amino acid esters and its application to an efficient synthesis of BzlDC-81.[8]

Results and Discussion

o-Azidobenzoylation of α-amino acid esters (**2a–g**) with acid chloride **1** by standard methods gave the corresponding *N*-*o*-azidobenzoyl derivatives **3a–l** in 70–92% yields (Scheme 1, Table 1).

o-Azidobenzoyl derivatives **3** were treated with a small excess of triphenylphosphine (TPP) and/or tributylphosphine (TBP) at room temperature in xylene or toluene to afford the corresponding iminophosphorane derivatives **4**, which were, without isolation, heated in the same solvent to afford the intramolecular aza-Wittig products **5**, 1,4-benzodiazepin-5-ones (Scheme 1, Table 2). For compounds **3a–g**, the cyclization via aza-Wittig reaction required heating at 140 °C for 16–84 h (entries 1–10 in Table 1). TBP was more effective than TPP (compare entries 3 and 4 and 8 and 9). With TPP, the intermediate iminophosphoranes **4b**, **4f**, and **4k** remained unreacted and could be isolated (entries 4, 9, and 21). The lower reactivity of these TPP-derived iminophosphoranes was apparently due to steric hindrance as was observed previously for the aza-Wittig cyclization of lactam carbonyls.[5] Such steric retardation became large when the substituent of the ester (R^2) became bulky (entries 8 and 10). Only modest yields of cyclization product **5f** and **5g** were obtained even when TBP was employed with prolonged reaction times. Contrary to the results for these NH-containing substrates **3a–g**, *N*-alkyl- or phen-

Scheme 1

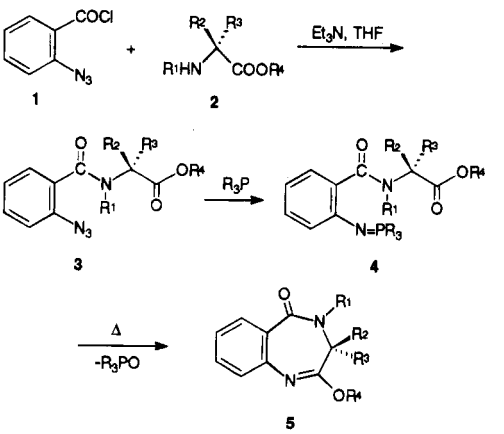

Table 1. *o*-Azidobenzoylation of α-Amino Acid Esters 2a–l[a]

entry	2	R^1	R^2	R^3	R^4	product	yield, %[d]
1	**2a**	H	H	H	Et	**3a**	75
2	**2b**[b]	H	Me	H	Et	**3b**	87
3	**2c**[b]	H	*i*-Bu	H	Et	**3c**	92
4	**2d**[b]	H	Bzl	H	Me	**3d**	87
5	**2e**	H	$(CH_2)_5$	$(CH_2)_5$	Me	**3e**	78
6	**2f**[b]	H	*i*-Pr	H	Et	**3f**	85
7	**2g**[b]	H	*s*-Bu	H	Et	**3g**	82
8	**2h**[b]	$(CH_2)_3$	$(CH_2)_3$	H	Me	**3h**	79
9	**2i**[c]	$(CH_2)_4$	$(CH_2)_4$	H	Et	**3i**	94
10	**2j**	Ph	H	H	Me	**3j**	70
11	**2k**	Me	H	H	Et	**3k**	76
12	**2l**	Me	H	H	Me	**3l**	80

[a] All reactions were performed in THF (see the Experimental Section). [b] L-Isomer was used. [c] A DL-isomer was used. [d] Isolated yield.

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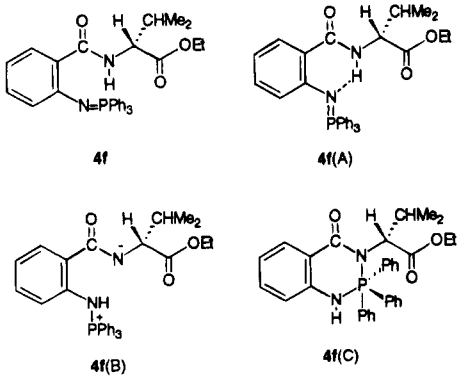
Table 2. Intramolecular Aza-Wittig Reaction of 3[a]

entry	3	P reagent[b]	solvent[c]	temp, °C	time, h[d]	product	yield, %[e]
1	**3a**	PBu_3	xylene	140	16	**5a**	61
2	**3b**	PBu_3	toluene	110	50	**5b**	80
3	**3b**	PBu_3	xylene	140	20	**5b**	84
4	**3b**	PPh_3	xylene	140	62	**5b** (+**4b**)	82 (15)
5	**3c**	PBu_3	xylene	140	24	**5c**	77
6	**3d**	PBu_3	xylene	140	20	**5d**	81
7	**3e**	PBu_3	xylene	140	20	**5e**	55
8	**3f**	PBu_3	xylene	140	60	**5f**	39
9	**3f**	PPh_3	xylene	140	84	**5f** (+**4f**)	9 (80)
10	**3g**	PBu_3	xylene	140	72	**5g**	40
11	**3h**	PBu_3	xylene	20–25	2	**5h**	86
12	**3h**	PPh_3	xylene	140	1.5	**5h**	83
13	**3h**	PPh_3	toluene	110	3	**5h**	86
14	**3i**	PBu_3	toluene	110	1	**5i**	88
15	**3i**	PPh_3	toluene	110	7	**5i**	82
16	**3i**	PPh_3	xylene	140	2	**5i**	90
17	**3j**	PBu_3	toluene	110	1.5	**5j**	90
18	**3j**	PPh_3	xylene	140	2	**5j**	95
19	**3k**	PBu_3	toluene	20–25	6	**5k**	58
20	**3k**	PBu_3	toluene	110	1.5	**5k**	72
21	**3k**	PPh_3	toluene	20–25	20	**5k** (+**4k**)	7 (91)
22	**3k**	PPh_3	xylene	140	1.5	**5k**	70
23	**3l**	PBu_3	toluene	110	1.5	**5l**	77
24	**3l**	PPh_3	xylene	140	2	**5l**	64

[a] All reactions were performed under nitrogen in a sealed tube. [b] A small excess amount was used. [c] Mixed xylene, bp 137–144 °C, was used. [d] Heating time after stirring at 20–25 °C for 1 h was shown. [e] Isolated yield.

yl-substituted substrates **3h–l** cyclized under mild conditions (entries 11–24). For example, the proline ester derivative **3h** gave the cyclized product **5h** in good yields with TBP even at room temperature and also with TPP by short heating (entries 11–13). Aza-Wittig cyclization products of other *N*-alkyl- and phenyl-substituted azido derivatives **3i–l** also underwent cyclization using both TPP and TBP under relatively mild conditions (entries 14–20 and 22–24). Sarcosine ester-derived **3k**, for example, cyclized at room temperature with TBP, but with TPP, cyclization was very slow (entries 19 and 21).

Since the pronounced proton affinity of the P=N bond is well-known,[4a,9] the slow cyclization of **4a–g** may have originated from the intramolecular amide NH proton transfer to the imino nitrogen. Thus, for example, the equilibrating zwitterionic tautomer (B) for **4f** may be cyclized to the **4f**(C) form, which cannot react with the carbonyl function. *N*-(Hydroxyphenyl)- and *N*-(aminophenyl)phosphazenes **6**(A) are known to tautomerize to the corresponding zwitterionic **6**(B) and heterocyclic **6**(C) forms (Scheme 2).[10] Therefore, X-ray crystallographic



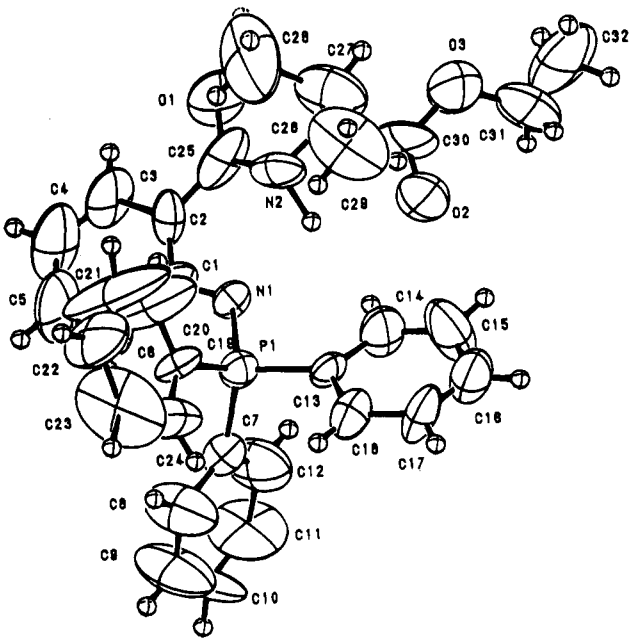


Figure 1. ORTEP diagram of the X-ray structure of **4f** showing the atom-labeling scheme and 50% probability thermal ellipsoids.

Scheme 2

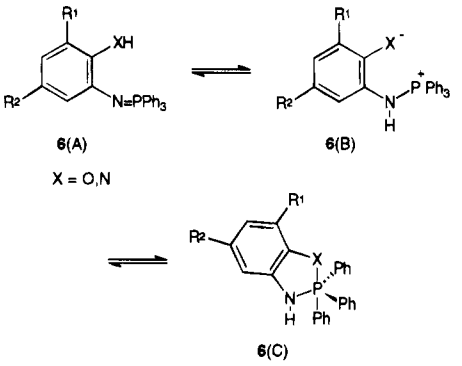


Table 3. Selected Bond Lengths (Å) and Bond Angles (deg) for 4f[a]

P1–N1	1.601(8)	N1–P1–C7	116.7(5)
P1–C7	1.83(1)	N1–P1–C13	105.3(5)
P1–C13	1.75(1)	N1–P1–C19	112.0(5)
P1–C19	1.81(1)	P1–N1–C1	124.0(7)
N1–C1	1.40(1)	O1–C25–N2	120(1)
N2–C25	1.31(2)	O1–C25–C2	124(1)
O1–C25	1.50(2)		

[a] Standard deviations are in parentheses.

analysis of compound **4f** was performed in order to confirm the structure of the phosphazene **4f**. As summarized in Figure 1 and Table 3,[24] the results clearly excluded these possibilities (**4f**(B),(C)). P–N bond length and N–P–C bond angles are in accord with the reported values for (*p*-bromophenyl)iminotriphenylphosphorane which has values of 1.567 Å for the P=N bond length and 124.2° for the P–N–C angle.[11] The betaine P–N bond length is longer.[12] Thus, a large contribution from the covalent structure $Ph_3P{=}NAr$ is supported for **4f** also.

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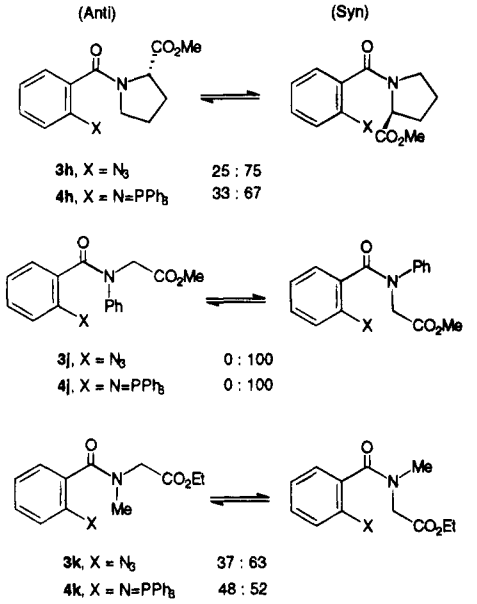
Table 4. Amide NH NMR Data[a]

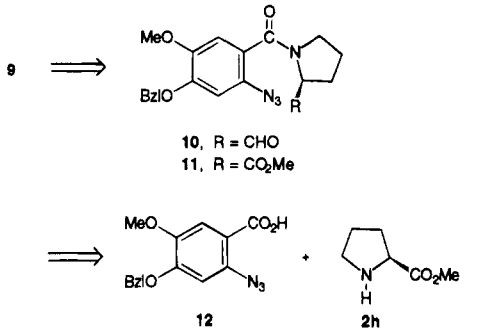
compd	δ_H (multiplet, J in bertz)
3a	8.12 (br s)
3b	8.17 (br s)
3f	8.00 (br d, 8.0)
4a	11.78 (t, 5.8)
4b	11.54 (d, 7.4)
4f	11.52 (d, 8.8)

[a] In $CDCl_3$. For other spectral data, see the Experimental Section.

Scheme 3

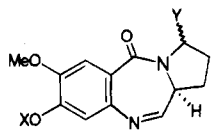


Scheme 4



In the ^1H NMR spectrum ($CDCl_3$), the amide NH of **4f** appeared at a characteristically lower field, δ 11.52 ppm, compared with that (δ 8.0) of the azido derivative **3f**. Such a large shift was also observed between **4a** and **3a** and between **4b** and **3b** (Table 4). The IR spectra of **4a,b** and **4f** had very broad absorptions around 3100 cm^{-1}. These data clearly support a hydrogen bond between the amide NH and the imino nitrogen as explained in **4f**(A). Such hydrogen-bonding stabilization discourages aza-Wittig cyclization due to conformational restriction and lowered nucleophilicity of the imino nitrogen as is actually observed (Table 2). On the other hand, characteristic low-field ^1H NMR signals at δ 8.15–8.19 ppm due to H_6 (peri-H to amide C=O) observed for **3a–g** and **4a–g** were not observed for the *tert*-amides **3h–l** and **4h–l**, in which the lactam C=O deviates from the coplanarity with the azidophenyl ring because of steric crowding. For the latter groups, s-cis and s-trans isomers, in fact, were observed in the ^1H NMR spectra as summarized in Scheme 3 where anti and syn refer to the relative position of X and the ester groups.[13] Because of this equilibrium situation, both isomers can react directly or indirectly in the aza-Wittig cyclization. It is of interest that only the syn isomer was detected for **3j** and **4j** which gave the high yields of the aza-Wittig product **5j**.

1,4-Benzodiazepine derivatives are pharmacologically useful compounds and have been extensively studied since the introduction of chlorodiazepoxide in 1960 and diazepam in 1963.[14,15] Furthermore, the pyrrolo[2,1-*c*][1,4]benzodiazepine ring system[16] is a skeleton characteristic of antitumor antibiotics such as DC-81 (**7**),[17] neothramycins (**9**),[18] anthramycin,[19] etc.[20] We have applied the above aza-Wittig method for a new short step synthesis of BzlDC-81 (**9**) which has previously been converted to DC-81 (**7**) via catalytic transfer hydrogenation.[21] The required compound **12** by the retrosynthetic analysis in Scheme 4 was readily prepared starting from the known 4-(benzyloxy)-5-methoxy-2-nitrobenzoic acid **13**[21] via reduction and diazotization followed by azidation sequences (Scheme 5). Reduction of **13** was examined by following two methods. The reduction with the sodium borohydride–nickel(II) chloride system[22] afforded anthranilic acid derivative **14** in 53% yield, while the reduction with tin(II) chloride in methanol under reflux for 1.2 h gave **14** in 62% yield. In the latter method, 2 h of refluxing yielded only 48% due to side reactions. Diazotization of **14** followed by sodium azide treatment gave the desired 2-azido derivative **12** in 64% yield. The azido carboxylic acid was converted to the acid chloride by thionyl chloride and was treated with L-proline methyl



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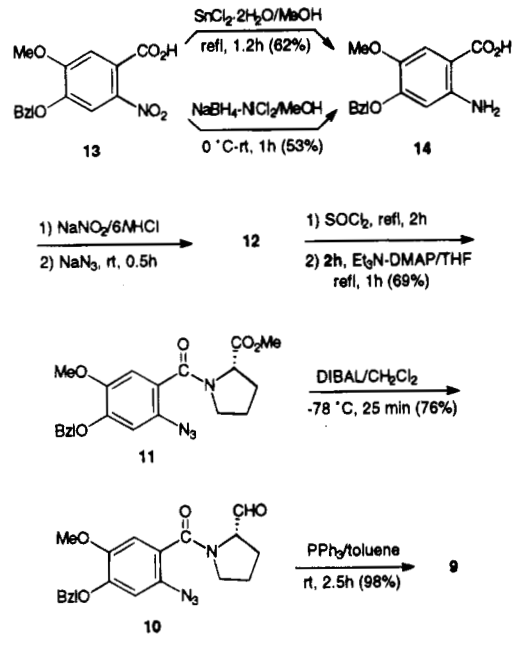
Scheme 5



ester in the presence of Et_3N/DMAP (10 mol %) in THF under reflux for 1 h to afford **11** in 69% yield. Diisobutylaluminum hydride (DIBAL) reduction of **11** at −78 °C for 25 min gave the aldehyde **10** in 76% yield after the usual workup and chromatography. The consecutive Staudinger reaction and intramolecular aza-Wittig reaction with TPP in toluene was carried out under very mild conditions (room temperature, 2.5 h) to afford 8-benzyl DC-81 in 98% yield (Scheme 5).

In summary, we have demonstrated that the intramolecular aza-Wittig methodology provides a powerful route for the synthesis of a variety of 1,4-benzodiazepine derivatives. This method has also been successfully applied to a short and efficient synthesis of the antitumor antibiotic *O*-benzyl DC-81.

Experimental Section

Melting points were determined with a Yanagimoto micro-melting point hot stage apparatus and are uncorrected. IR spectra were recorded with a JASCO FT/IR-5300 spectrometer. ^1H (200 MHz) and ^{13}C (50 MHz) NMR spectra of $CDCl_3$ solutions were obtained on a Varian Gemni 200 instrument. Chemical shifts are reported in parts per million (ppm) relative to Me_4Si as an internal standard. Electron impact mass spectra (EIMS) were recorded with a JEOL JMS-AX505HA spectrometer at 70 eV. Optical rotations were measured with a ATAGO POLAX-D polarimeter. Microanalyses were performed with a Perkin-Elmer 2400S elemental analyzer. Fuji-Davison BW-300 silica gel was used for column chromatography. All reagents were of commercial quality.

Preparation of *N*-(2-Azidobenzoyl)-α-amino Acid Esters (3a−l). General Procedure. To a stirred solution of α-amino acid ester hydrochloride (**2**) (2.00 mmol) and triethylamine (6.0 mmol) in THF (6 mL) was added dropwise 2-azidobenzoyl chloride (**1**)[23] (2.00 mmol) in THF (9 mL) under nitrogen at room temperature. After stirring was continued for 2 h, the resulting precipitates were removed by filtration. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel, eluting with 1:4 AcOEt/hexane to give the azidobenzoyl derivative **3** (For the yields, see Table 1).

***N*-(2-Azidobenzoyl)glycine ethyl ester (3a):** light yellow powder from 1:4 AcOEt/hexane; mp 87.5−89 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.19 (dd, 1H, J = 1.7, 7.8 Hz), 8.12 (br s, 1H, NH), 7.53 (dt, 1H, J = 1.8, 7.8 Hz), 7.30−7.21 (m, 2H), 4.27 (q, 2H, J = 7.2 Hz), 4.26 (d, 2H, J = 5.0 Hz), 1.32 (t, 3H, J = 7.2 Hz); IR (KBr) 3295, 2124, 1746, 1634, 1535, 1485, 1416, 1377, 1289, 1204, 1096, 1071, 1030 cm^{-1}; MS m/z (relative intensity) 220 (M^+ − 28, 44), 148 (11), 147 (100), 146 (90), 120 (50), 119 (50), 118 (39), 105 (20). Anal. Calcd for $C_{11}H_{12}N_4O_3$: C, 53.22; H, 4.87; N, 22.57. Found: C, 53.42; H, 4.79; N, 22.31.

***N*-(2-Azidobenzoyl)-L-alanine ethyl ester (3b):** white powder from 1:4 AcOEt/hexane; mp 87−87.5 °C; $[\alpha]^{22}_D$ +15.3 (c = 2.62, EtOH); ^1H NMR (200 MHz, $CDCl_3$) δ 8.16 (dd, 1H, J = 1.8, 7.8 Hz), 8.17 (br s, 1H, NH), 7.53 (td, 1H, J = 1.6, 7.8 Hz), 7.3−7.2 (m, 2H), 4.79 (quint, 1H, J = 7.2 Hz), 4.26 (q, 2H, J = 7.2 Hz), 1.54 (d, 3H, J = 7.2 Hz), 1.32 (t, 3H, J = 7.2 Hz); IR (KBr) 3320, 2128, 1752, 1634, 1528, 1483, 1298, 1206, 1175, 756 cm^{-1}; MS m/z (relative intensity) 262 (M^+, 0.8), 234 (85), 162 (16), 161 (100), 160 (87), 146 (54), 132 (17), 130 (36), 120 (75), 119 (40), 118 (22), 105 (16), 104 (48), 103 (46). Anal. Calcd for $C_{12}H_{14}N_4O_3$: C, 54.95; H, 5.38; N, 21.37. Found: C, 55.03; H, 5.36; N, 21.14.

***N*-(2-Azidobenzoyl)-L-leucine ethyl ester (3c):** light yellow oil; $[\alpha]^{23}_D$ −18.7 (c = 2.09, EtOH); ^1H NMR (200 MHz, $CDCl_3$) δ 8.17 (dd, 1H, J = 1.7, 7.8 Hz), 7.94 (br d, 1H, J = 7.0 Hz, NH), 7.52 (td, 1H, J = 1.8, 7.7 Hz), 7.3−7.2 (m, 2H), 4.88−4.77 (m, 1H), 4.23 (q, 2H, J = 7.2 Hz), 1.85−1.62 (m, 3H), 1.31 (t, 3H, J = 7.2 Hz), 1.00 (d, 6H, J = 6.2 Hz); IR (KBr) 3362, 2132, 1740, 1657, 1528, 1481, 1298, 1198, 1165 cm^{-1}; MS m/z (relative intensity) 304 (M^+, 0.8), 276 (38), 248 (13), 231 (10), 203 (48), 202 (21), 161 (20), 160 (21), 147 (99), 146 (81), 134 (23), 131 (11), 120 (100), 119 (48), 118 (29), 105 (26), 104 (14). Anal. Calcd for $C_{15}H_{20}N_4O_3$: C, 59.19; H, 6.62; N, 18.41. Found: C, 59.31; H, 6.87; N, 18.11.

***N*-(2-Azidobenzoyl)-L-phenylalanine methyl ester (3d):** white powder from 1:2 AcOEt/hexane; mp 82−84 °C; $[\alpha]^{24}_D$ −61.1 (c = 1.31, EtOH); ^1H NMR (200 MHz, $CDCl_3$) δ 8.15 (dd, 1H, J = 1.6, 8.0 Hz), 7.98 (br d, 1H, J = 6.6 Hz, NH), 7.50 (ddd, 1H, J = 1.8, 7.4, 8.0 Hz), 7.34−7.15 (m, 7H), 5.07 (td, 1H, J = 6.0, 7.2 Hz), 3.77 (s, 3H), 3.25 (d, 2H, J = 6.2 Hz); IR (KBr) 3301, 2130, 1738, 1644, 1539, 1480, 1443, 1289, 1223, 1177, 752 cm^{-1}; MS m/z (relative intensity) 324 (M^+, 4.5), 296 (14), 238 (19), 206 (26), 174 (14), 163 (51), 162 (12), 148 (16), 147 (74), 146 (32), 137 (12), 135 (56), 132 (17), 122 (26), 121 (100), 120 (29), 119 (26), 106 (17), 105 (32), 104 (13). Anal. Calcd for $C_{17}H_{16}N_4O_3$: C, 62.95; H, 4.97; N, 17.28. Found: C, 62.98; H, 4.96; N, 17.26.

***N*-(2-Azidobenzoyl)-D,L-1-aminocyclohexane carboxylic acid methyl ester (3e):** light yellow powder from 3:1 AcOEt/hexane; mp 116−117 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 8.19 (dd, 1H, J = 1.3, 7.9 Hz), 7.90 (br s, 1H, NH), 7.53 (dt, 1H, J = 1.8, 7.8 Hz), 7.3−7.2 (m, 2H), 3.74 (s, 3H), 2.23−1.31 (m, 10H); IR (KBr) 3345, 2133, 1726, 1651, 1530, 1489, 1447, 1298, 1248, 1165, 1074, 756 cm^{-1}; MS m/z (relative intensity) 302 (M^+, 6.9), 274 (11), 243 (19), 207 (11), 207 (11), 206 (65), 205 (14), 173 (16), 148 (11), 147 (25), 141 (11), 136 (29), 135 (84), 120 (100), 119 (40), 118 (17), 109 (16), 105 (41). Anal. Calcd for $C_{15}H_{18}N_4O_3$: C, 59.59; H, 6.00; N, 18.54. Found: C, 59.55; H, 5.84; N, 18.38.

***N*-(2-Azidobenzoyl)-L-valine ethyl ester (3f):** light yellow oil; $[\alpha]^{21}_D$ +15.0 (c = 2.67, EtOH); ^1H NMR (200 MHz, $CDCl_3$) δ 8.16 (dd, 1H, J = 1.6, 8.2 Hz), 8.00 (br d, 1H, J = 8.0 Hz, NH), 7.53 (dt, 1H, J = 1.8, 8.0 Hz), 7.3−7.2 (m, 2H), 4.77 (dd, 1H, J = 4.8, 8.4 Hz), 4.24 (dq, 2H, J = 1.6, 7.2 Hz), 2.31 (d sept, 1H, J = 4.8, 6.8 Hz), 1.31 (t, 3H, J = 7.2 Hz), 1.03 (dd, 6H, J = 1.8, 6.8 Hz); IR (neat) 3376, 2132, 1738, 1661, 1528, 1481, 1310, 1277, 1202, 1159, 754 cm^{-1}; MS m/z (relative intensity) 290 (M^+, 2.9), 262 (37), 217 (10), 189 (35), 188 (33), 147 (95), 146 (71), 145 (12), 134 (27), 133 (10), 120 (100), 119 (37), 118 (26), 105 (22), 104 (22). Anal. Calcd for $C_{14}H_{18}N_4O_3$: C, 57.92; H, 6.25; N, 19.30. Found: C, 58.14; H, 6.34; N, 18.99.

***N*-(2-Azidobenzoyl)-L-isoleucine ethyl ester (3g):** light yellow oil; $[\alpha]^{22}_D$ +26.7 (c = 3.56, EtOH); ^1H NMR (200 MHz, $CDCl_3$) δ 8.16 (dt, 1H, J = 7.8, 0.8 Hz), 8.05 (br d, 1H, J = 7.8 Hz, NH), 7.53 (dt, 1H, J = 1.8, 7.7 Hz), 7.29−7.21 (m, 2H), 4.81 (dd, 1H, J = 4.6, 8.0 Hz), 4.24 (dq, 2H, J = 2.2, 7.2 Hz), 2.14−1.95 (m, 1H), 1.66−1.48 (m, 1H), 1.40−1.18 (m, 1H), 1.32 (t, 3H, J = 7.2 Hz), 1.00 (d, 3H, J = 6.8 Hz), 0.99 (t, 3H, J =

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7.6 Hz); IR (neat) 3376, 2132, 1738, 1661, 1599, 1526, 1481, 1377, 1298, 1200, 1159, 1026 cm^{-1}; MS *m/z* (relative intensity) 304 (M$^+$, 3.9), 276 (47), 231 (219), 202 (23), 174 (11), 173 (17), 148 (12), 147 (100), 146 (65), 145 (26), 135 (32), 134 (70), 121 (21), 120 (100), 119 (46), 116 (12), 104 (15), 103 (18). Anal. Calcd for $C_{15}H_{20}N_4O_3$: C, 59.19; H, 6.62; N, 18.41. Found: C, 59.19; H, 6.72; N, 18.31.

***N*-(2-Azidobenzoyl)-L-proline methyl ester (3h):** white powder from 2:3 AcOEt/hexane; mp 64–67 °C; $[\alpha]^{24}_D$ −108.2 (*c* = 2.24, EtOH); ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.48–7.34 (m, 2H), 7.26–7.10 (m, 2H), 4.69 (dd, 0.75H, *J* = 4.0, 8.0 Hz, syn-NCH), 4.21 (dd, 0.25H, *J* = 2.8, 8.4 Hz, anti-NCH), 3.93–3.70 (m, 0.50H, anti-NCH_2), 3.80 (s, 2.25H, syn-CO_2Me), 3.53 (s, 0.75H, anti-CO_2Me), 3.49–3.27 (m, 1.50H, syn-N-CH_2), 2.42–1.81 (m, 4H); IR (KBr) 2141, 1755, 1630, 1451, 1423, 1368, 1314, 1120, 1167 cm^{-1}; MS *m/z* (relative intensity) 274 (M$^+$, 2.3), 246 (56), 188 (26), 187 (100), 185 (12), 160 (40), 146 (45), 132 (18), 131 (11), 130 (12), 120 (23), 119 (47), 118 (23), 105 (12), 104 (18). Anal. Calcd for $C_{13}H_{14}N_4O_3$: C, 56.92; H, 5.15; N, 20.43. Found: C, 56.86; H, 5.21; N, 20.42.

Ethyl *N*-(2-azidobenzoyl)piperidine-2-carboxylate (3i): light yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.48–7.10 (m, 4H), 5.56 (br t, 0.70H, *J* = 5.0 Hz, syn-NCH), 4.73 (br d, 0.30H, *J* = 13.8 Hz, anti-NCH), 4.45–4.10 (qm, 2H, *J* = 7.2 Hz), 3.45–3.00 (m, 2H), 2.43–1.15 (m, 6H), 1.33 and 1.29 (each t, ca. 2.1H and 0.9H, each *J* = 7.2 Hz, ester methyl of syn and anti isomers); IR (neat) 2130, 1736, 1644, 1580, 1489, 1447, 1426, 1370, 1290, 1206, 1175, 1146, 1024, 1007 cm^{-1}; MS *m/z* (relative intensity) 302 (M$^+$, 0.8), 274 (23), 245 (17), 202 (48), 201 (100), 200 (20), 199 (29), 174 (38), 173 (72), 160 (31), 147 (31), 146 (73), 130 (18), 120 (77), 119 (80), 118 (32), 117 (20), 105 (29), 104 (19). Anal. Calcd for $C_{15}H_{18}N_4O_3$: C, 59.59; H, 6.00; N, 18.54. Found: C, 59.94; H, 5.93; N, 18.26.

***N*-(2-Azidobenzoyl)-*N*-phenylglycine methyl ester (3j):** light yellow powder from 1:2 AcOEt/hexane; mp 104–106 °C; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.28–7.11 (m, 7H), 7.00–6.93 (m, 2H), 4.62 (s, 2H), 3.80 (s, 3H); IR (KBr) 2137, 1759, 1647, 1593, 1493, 1451, 1412, 1389, 1304, 1208, 1175, 768 cm^{-1}; MS *m/z* (relative intensity) 310 (M$^+$, 9.3), 282 (17), 225 (17), 224 (100), 223 (13), 119 (12), 107 (20), 106 (20), 105 (35). Anal. Calcd for $C_{16}H_{14}N_4O_3$: C, 61.93; H, 4.55; N, 18.06. Found: C, 61.96; H, 4.47; N, 17.79.

***N*-(2-Azidobenzoyl)-*N*-methylglycine ethyl ester (3k):** light yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50–7.12 (m, 4H), 4.29 (br s, ca. 0.74H, anti-NCH_2), 4.26 (q, 1.26H, *J* = 7.2 Hz, syn-CO_2CH_2), 4.17 (q, 0.74H, *J* = 7.2 Hz, anti-CO_2CH_2), 3.88 (br d, 1.26H, *J* = 6.4 Hz, syn-NCH_2), 3.16 (s, 1.11H, anti-NCH_3), 2.92 (s, 1.89H, syn-NCH_3), 1.32 (t, 1.89H, *J* = 7.2 Hz, syn-CH_2CH_3), 1.24 (t, 1.11H, *J* = 7.2 Hz, anti-CH_2CH_3); IR (neat) 2132, 1746, 1645, 1599, 1493, 1449, 1399, 1296, 1206, 1105, 1069, 1030, 756 cm^{-1}; MS *m/z* (relative intensity) 262 (M$^+$, 4.0), 234 (20), 162 (18), 161 (100), 148 (12), 147 (52), 146 (18), 133 (11), 132 (39), 120 (52), 119 (49), 105 (14), 104 (13). Anal. Calcd for $C_{12}H_{14}N_4O_3$: C, 54.95; H, 5.38; N, 21.37. Found: C, 55.05; H, 5.46; N, 21.17.

***N*-(2-Azidobenzoyl)-*N*-methylglycine methyl ester (3l):** light yellow oil; ^{1}H NMR (200 MHz, $CDCl_3$) δ 7.50–7.12 (m, 4H), 4.32 (br s, 1.3H, syn-NCH_2), 3.91–3.88 (m, 0.7H, anti-NCH_2), 3.80 (s, 2.0H, syn-$COOCH_3$), 3.72 (s, 1.0H, anti-$COOCH_3$), 3.16 (s, 1.0H, anti-NCH_3), 2.92 (s, 2.0H, syn-NCH_3); IR (neat) 2132, 1750, 1644, 1493, 1443, 1400, 1294, 1213, 1105, 1071 cm^{-1}; MS *m/z* (relative intensity) 248 (M$^+$, 2.0), 220 (34), 161 (68), 148 (11), 147 (100), 146 (13), 133 (14), 132 (20), 120 (31), 119 (40), 118 (14), 106 (21), 105 (19), 104 (14). Anal. Calcd for $C_{11}H_{12}N_4O_3$: C, 53.22; H, 4.87; N, 22.57. Found: C, 53.56; H, 4.90; N, 22.20.

Tandem Staudinger Reaction/Intramolecular Aza-Wittig Reaction of 3a–l. Preparation of 3,4-Dihydro-2-alkoxy-1,4-benzodiazepin-5(5*H*)-ones (5a–l). General Procedure. A mixture of **3** (1.00 mmol) and Bu_3P or Ph_3P (1.07 mmol) in xylene or toluene (5 mL) was stirred at 20–25 °C for 1 h in a heavy-walled sealed tube under argon. The mixture was then heated under the conditions shown in Table 2. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography, eluting with a 0.25–1:1 AcOEt/hexane system. For the yields, see Table 2.

3,4-Dihydro-2-ethoxy-1,4-benzodiazepin-5(5*H*)-one (5a): white solid from 1:1 AcOEt/hexane; mp 126.5–128.5 °C; ^{1}H NMR (200 MHz, C_6D_6) δ 9.03 (br s, 1H, NH), 8.32 (dd, 1H, *J* = 1.2, 8.0 Hz), 7.25 (dd, 1H, *J* = 1.2, 8.0 Hz), 7.21–7.12 (m, 1H), 6.95 (ddd, 1H, *J* = 1.6, 6.8, 7.8 Hz), 3.99 (q, 2H, *J* = 7.2 Hz), 3.09 (d, 2H, *J* = 5.6 Hz), 0.97 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (50 MHz, C_6D_6) δ 171.49, 164.16, 146.47, 132.46, 131.77, 127.58, 127.29, 124.63, 63.16, 41.00, 13.94; IR (KBr) 3171, 1659, 1601, 1474, 1404, 1296, 1252, 1225, 1038, 617 cm^{-1}; MS *m/z* (relative intensity) 204 (M$^+$, 39), 176 (36), 160 (23), 148 (15), 147 (39), 146 (100), 139 (10), 133 (14), 120 (34), 119 (44), 105 (14), 104 (11), 102 (16). Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.93; H, 6.02; N, 13.34.

3,4-Dihydro-2-ethoxy-3(*S*)-methyl-1,4-benzodiazepin-5(5*H*)-one (5b): white solid from 2:3 AcOEt/hexane; mp 132–135 °C; $[\alpha]^{23}_D$ +577.3 (*c* = 1.10, EtOH); ^{1}H NMR (200 MHz, C_6D_6) δ 9.24 (d, 1H, *J* = 4.0 Hz, NH), 8.35 (ddd, 1H, *J* = 0.6, 1.8, 8.0 Hz), 7.27 (ddd, 1H, *J* = 0.6, 1.8, 8.0 Hz), 7.22 (dd, 1H, *J* = 1.6, 6.8 Hz), 7.00 (ddd, 1H, *J* = 1.8, 6.8, 7.8 Hz), 4.04 (dq, 1H, *J* = 7.2, 11.0 Hz), 3.81 (dq, 1H, *J* = 7.2, 11.0 Hz), 1.23 (d, 3H, *J* = 6.8 Hz), 0.91 (t, 3H, *J* = 7.2 Hz); ^{13}C NMR (50 MHz, C_6D_6) δ 170.76, 164.62, 146.20, 132.37, 131.42, 127.75, 127.08, 124.35, 63.20, 46.70, 13.96, 13.81; IR (KBr) 3167, 1661, 1607, 1466, 1385, 1304, 1254, 1182, 1055, 760 cm^{-1}; MS *m/z* (relative intensity) 218 (M$^+$, 19), 190 (9.5), 189 (6.6), 173 (7.8), 148 (8.0), 147 (22), 146 (100), 120 (8.0), 119 (16), 102 (8.3). Anal Calcd for $C_{12}H_{14}N_2O_2$: C, 66.03; H, 6.47; N, 12.84. Found: C, 66.12; H, 6.41; N, 12.82.

3(*S*)-Isobutyl-3,4-dihydro-2-ethoxy-1,4-diazepin-5(5*H*)-one (5c): white solid from 1:2 AcOEt/hexane; mp 36–38 °C; $[\alpha]^{28}_D$ −6.7 (*c* = 2.97, EtOH); ^{1}H NMR (200 MHz, C_6D_6) δ 9.64 (d, 1H, *J* = 3.6 Hz, NH), 8.38 (dd, 1H, *J* = 1.6, 7.9 Hz), 7.30 (dd, 1H, *J* = 1.2, 8.0 Hz), 7.19 (dd, 1H, *J* = 1.6, 7.0 Hz), 6.94 (ddd, 1H, *J* = 1.4, 7.2, 7.8 Hz), 4.09 (dq, 1H, *J* = 7.0, 11.0 Hz), 3.87 (dq, 1H, *J* = 7.0, 11.0 Hz), 3.85–3.75 (m, 1H), 1.92–1.58 (m, 3H), 0.79 (d, 3H, *J* = 6.2 Hz), 0.60 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (50 MHz, C_6D_6) δ 171.20, 164.76, 146.21, 132.63, 131.45, 127.84, 127.12, 124.56, 63.35, 50.30, 37.33, 25.03, 23.17, 21.85, 13.96; IR (KBr) 3173, 1651, 1603, 1468, 1372, 1314, 1257, 1208, 1167, 1028, 766 cm^{-1}; MS *m/z* (relative intensity) 260 (m$^+$, 21), 217 (14), 176 (10), 148 (21), 147 (21), 146 (100), 106 (71), 105 (34). Anal. Calcd for $C_{15}H_{20}N_2O_2$: C, 69.20; H, 7.74; N, 10.76. Found: C, 69.24; H, 7.66; N, 10.80.

3(*S*)-Benzyl-3,4-dihydro-2-methoxy-1,4-benzodiazepin-5(5*H*)-one (5d): white solid from 2:3 AcOEt/hexane; mp 65.5–68.5 °C; $[\alpha]^{25}_D$ +147.7 (*c* = 0.88, EtOH); ^{1}H NMR (200 MHz, C_6D_6) δ 8.86 (br s, 1H, NH), 8.28 (ddd, 1H, *J* = 0.4, 1.6, 7.8 Hz), 7.26 (ddd, 1H, *J* = 0.4, 1.4, 8.0 Hz), 7.20–7.11 (m, 1H), 7.06–6.87 (m, 6H), 3.90 (dt, 1H, *J* = 5.8, 7.6 Hz), 3.36 (s, 3H), 2.95 (dd, 2H, *J* = 7.6, 10.0 Hz); ^{13}C NMR (50 MHz, C_6D_6) δ 170.46, 164.56, 145.66, 137.68, 132.73, 131.63, 129.17, 127.79, 127.13, 124.82, 54.29, 53.47, 34.90; IR (KBr) 3179, 1653, 1603, 1456, 1319, 1256, 1017, 768 cm^{-1}; MS *m/z* (relative intensity) 280 (m$^+$, 19), 189 (46), 163 (11), 162 (100), 146 (19), 130 (29), 102 (10). Anal. Calcd for $C_{17}H_{16}N_2O_2$: C, 72.83; H, 5.75; N, 10.00. Found: C, 73.10; H, 5.92; N, 9.55.

Spiro[3,4-dihydro-2-methoxy-1,4-benzodiazepin-5(5*H*)-one-3,1′-cyclohexane] (5e): white solid from 1:1 AcOEt/hexane; mp 175.5–177.5 °C; ^{1}H NMR (200 MHz, C_6D_6) δ 8.98 (s, 1H, NH), 8.39 (dd, 1H, *J* = 1.4, 7.8 Hz), 7.26 (dd, 1H, *J* = 1.4, 7.8 Hz), 7.20–7.11 (m, 1H), 6.91 (ddd, 1H, *J* = 1.4, 7.0, 7.8 Hz), 3.44 (s, 3H), 1.82–0.95 (m, 10H); ^{13}C NMR (50 MHz, C_6D_6) δ 169.73, 164.62, 146.20, 132.37, 131.42, 127.75, 127.08, 124.35, 63.20, 46.70, 13.96, 13.81; IR (KBr) 3170, 1649, 1600, 1458, 1391, 1300, 1246 cm^{-1}; MS *m/z* (relative intensity) 258 (M$^+$, 35), 243 (14), 162 (28), 147 (10), 146 (100), 130 (11). Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.85. Found: C, 69.95; H, 6.91; N, 10.63.

3,4-Dihydro-2-ethoxy-3(*S*)-isopropyl-1,4-benzodiazepin-5(5*H*)-one (5f): white solid from 1:2 AcOEt/hexane; mp 133–135 °C; $[\alpha]^{23}_D$ +28.9 (*c* = 1.13, EtOH); ^{1}H NMR (200 MHz, C_6D_6) δ 9.67 (d, 1H, *J* = 6.6 Hz, NH), 8.36 (dd, 1H, *J* = 1.4, 8.0 Hz), 7.28 (dd, 1H, *J* = 1.0, 8.0 Hz), 7.20–7.12 (m, 1H), 6.92 (d, 1H, *J* = 1.4, 7.2, 8.0 Hz), 4.03 (dq, 2H, *J* = 2.2, 7.0 Hz), 3.30 (dd, 1H, *J* = 6.8, 10.6 Hz), 2.14–1.95 (m, 1H), 0.97 (t, 3H, *J* = 7.0 Hz), 0.83 (d, 3H, *J* = 6.6 Hz), 0.67 (d, 3H, *J* = 6.4 Hz); ^{13}C NMR (50 MHz, C_6D_6) δ 170.87, 164.83, 145.88, 132.68,

131.51, 128.76, 127.07, 124.49, 63.14, 59.82, 27.55, 19.88, 19.37, 14.05; IR (KBr) 3170, 1655, 1603, 1458, 1375, 1318, 1215, 1028, 770 cm^{-1}; MS m/z (relative intensity) 246 (M^+, 16), 203 (15), 176 (12), 175 (12), 148 (58), 147 (21), 146 (100), 120 (12), 119 (10), 102 (12). Anal. Calcd for $C_{14}H_{18}N_2O_2$: C, 68.27; H, 7.37; N, 11.38. Found: C, 68.39; H, 7.35; N, 11.03.

3(*S*)-*sec*-Butyl-3,4-dihydro-2-ethoxy-1,4-benzodiazepin-5(5*H*)-one (5g): colorless oil; $[\alpha]^{23}_D$ −323.2 (c = 1.64, EtOH); ^1H NMR (200 MHz, C_6D_6) δ 9.66 (d, 1H, J = 6.8 Hz, NH), 8.37 (dd, 1H, J = 1.4, 7.9 Hz), 7.31 (dd, 1H, J = 1.2, 8.0 Hz), 7.21−7.13 (m, 1H), 6.94 (ddd, 1H, J = 1.2, 7.1, 7.8 Hz), 4.06 (q, 2H, J = 7.0 Hz), 3.49 (dd, 1H, J = 6.8, 10.9 Hz), 2.00−1.79 (m, 1H), 1.71−1.51 (m, 1H), 1.14−0.87 (m, 1H), 1.01 (t, 3H, J = 7.0 Hz), 0.72 (d, 3H, J = 6.6 Hz), 0.65 (t, 3H, J = 7.4 Hz); ^{13}C NMR (50 MHz, C_6D_6) δ 170.63, 164.81, 145.72, 132.67, 131.41, 128.70, 127.00, 124.47, 63.08, 58.38, 33.32, 25.59, 15.97, 14.03, 10.35; IR (KBr) 3181, 1651, 1601, 1464, 1373, 1341, 1314, 1256, 1208, 1154, 1028, 766 cm^{-1}; MS m/z (relative intensity) 260 (M^+, 58), 232 (31), 203 (48), 176 (32), 175 (20), 148 (100), 147 (34), 146 (16), 120 (27). Anal. Calcd for $C_{15}H_{20}N_2O_2$: C, 69.20; H, 7.74; N, 10.76. Found: C, 69.22; H, 8.09; N, 10.39.

(11a*S*)-1,2,3,11a-Tetrahydro-5*H*-pyrrolo[2,1-*c*]-1,4-benzodiazepin-5-one (5h): white solid from 1:1 AcOEt/hexane; mp 57−59 °C; $[\alpha]^{25}_D$ +537.8 (c = 1.41, EtOH); ^1H NMR (200 MHz, C_6D_6) δ 8.46 (dd, 1H, J = 1.6, 7.8 Hz), 7.30 (dd, 1H, J = 1.6, 8.0 Hz), 7.23 (dd, 1H, J = 1.6, 6.9 Hz), 7.00 (ddd, 1H, J = 1.6, 6.9, 7.8 Hz), 3.71−3.61 (m, 1H), 3.46 (s, 3H), 3.32−3.17 (m, 2H), 2.11−1.97 (m, 1H), 1.59−1.34 (m, 1H), 1.30−1.11 (m, 2H); ^{13}C NMR (50 MHz, C_6D_6) δ 165.72, 163.31, 145.22, 131.94, 131.64, 128.77, 127.34, 124.81, 54.28, 47.04, 26.64, 23.92; IR (KBr) 1651, 1632, 1601, 1460, 1416, 1325, 1258, 1184, 1146, 1094, 1001, 764 cm^{-1}; MS m/z (relative intensity) 230 (M^+, 32), 161 (17), 147 (8.2), 146 (100), 139 (11), 102 (5.7). Anal. Calcd for $C_{13}H_{14}N_2O_2$: C, 67.81; H, 6.13; N, 12.17. Found: C, 67.60; H, 6.20; N, 11.94.

1,2,3,4,12a-Pentahydro-5*H*-piperidino[2,1-*c*]-1,4-benzodiazepin-5-one (5i): light yellow oil; ^1H NMR (200 MHz, C_6D_6) δ 8.28 (dd, 1H, J = 1.4, 7.8 Hz), 7.27 (dd, 1H, J = 1.4, 8.0 Hz), 7.19−7.14 (m, 2H), 6.97 (ddd, 1H, J = 1.6, 6.8, 7.8 Hz), 4.56 (dddd, 1H, J = 1.4, 3.1, 4.6, 13.8 Hz), 4.10 (q, 2H, J = 7.2 Hz), 3.73 (dd, 1H, J = 2.6, 6.6 Hz), 2.76 (ddd, 1H, J = 4.0, 11.7, 13.8 Hz), 1.67−0.98 (m, 6H), 1.00 (t, 3H, J = 7.2 Hz); ^{13}C NMR (50 MHz, C_6D_6) δ 169.09, 164.92, 145.66, 131.68, 131.56, 129.74, 126.36, 124.73, 62.91, 49.40, 40.13, 23.51, 23.02, 19.95, 14.12; IR (neat) 1642, 1601, 1468, 1453, 1397, 1372, 1323, 1281, 1240, 1144, 1101, 1026, 764 cm^{-1}; MS m/z (relative intensity) 259 (14), 258 (M^+, 18), 230 (13), 229 (39), 175 (38), 147 (59), 146 (100), 118 (19). Anal. Calcd for $C_{15}H_{18}N_2O_2$: C, 69.74; H, 7.02; N, 10.85. Found: C, 69.82; H, 7.21; N, 10.62.

3,4-Dihydro-5-methoxy-4-phenyl-1,4-benzodiazepin-5(5*H*)-one (5j): coloress oil; ^1H NMR (200 MHz, C_6D_6) δ 8.33 (ddd, 1H, J = 0.5, 1.6, 7.9 Hz), 7.39−6.89 (m, 8H), 3.56 (s, 2H), 3.47 (s, 3H); ^{13}C NMR (50 MHz, C_6D_6) δ 167.07, 164.18, 145.85, 144.05, 132.55, 132.36, 129.46, 129.35, 127.02, 126.96, 126.55, 125.19, 54.38, 49.16; IR (neat) 1651, 1599, 1493, 1454, 1439, 1397, 1346, 1314, 1267, 1208, 1165, 1020, 760 cm^{-1}; MS m/z (relative intensity) 266 (M^+, 6.3), 146 (3.3), 120 (13), 107 (9.4), 106 (100), 105 (77), 104 (10), 103 (12), 102 (3.4). Anal. Calcd for $C_{16}H_{14}N_2O_2$: C, 72.16; H, 5.30; N, 10.52. Found: C, 72.12; H, 5.55; N, 10.30.

3,4-Dihydro-2-ethoxy-4-methyl-1,4-benzodiazepin-5(5*H*)-one (5k): faintly yellowish solid from 2:3 AcOEt/hexane; mp 78−80 °C; ^1H NMR (200 MHz, C_6D_6) δ 8.34 (dd, 1H, J = 1.6, 7.9 Hz), 7.26 (dd, 1H, J = 1.6, 7.9 Hz), 7.21−7.12 (m, 1H), 6.96 (ddd, 1H, J = 1.6, 7.0, 7.9 Hz), 4.06 (q, 2H, J = 7.0 Hz), 3.02 (s, 2H), 2.82 (s, 3H), 1.01 (t, 3H, J = 7.0 Hz); ^{13}C NMR (50 MHz, C_6D_6) δ 167.76, 163.32, 145.90, 132.06, 131.86, 128.68, 126.77, 124.83, 63.20, 48.10, 35.84, 14.05; IR (KBr) 1651, 1601, 1470, 1431, 1404, 1372, 1346, 1314, 1262, 1231, 1150, 1034, 770 cm^{-1}; MS m/z (relative intensity) 218 (M^+, 15), 190 (9.9), 189 (9.3), 147 (6.5), 146 (100), 119 (20), 105 (6.2), 90 (69). Anal. Calcd for $C_{12}H_{14}N_2O_2$: C, 66.03; H, 6.47; N, 12.84. Found: C, 65.88; H, 6.53; N, 12.85.

3,4-Dihydro-2-methoxy-4-methyl-1,4-benzodiazepin-5(5*H*)-one (5l): white solid from 2:3 AcOEt/hexane; mp 117.5−119.5 °C; ^1H NMR (200 MHz, C_6D_6) δ 8.03 (ddd, 1H, J = 0.6, 1.6, 7.9 Hz), 7.24 (ddd, 1H, J = 0.4, 1.4, 8.0 Hz), 7.18−7.10 (m, 1H), 6.94 (ddd, 1H, J = 1.6, 7.0, 7.9 Hz), 3.46 (s, 3H), 2.98 (s, 2H), 2.77 (s, 3H), 1.01 (t, 3H, J = 7.0 Hz); ^{13}C NMR (50 MHz, C_6D_6) δ 167.74, 163.80, 145.70, 132.09, 131.91, 128.77, 126.82, 124.96, 54.19, 47.86, 35.85; IR (KBr) 1657, 1601, 1462, 1437, 1397, 1358, 1316, 1262, 1231, 1150, 1026, 768 cm^{-1}; MS m/z (relative intensity) 204 (M^+, 42), 189 (5.1), 161 (12), 147 (9.7), 146 (100), 90 (58), 84 (34). Anal. Calcd for $C_{11}H_{12}N_2O_2$: C, 64.69; H, 5.92; N, 13.72. Found: C, 64.49; H, 5.92; N, 13.72.

Isolated Iminophosphoranes 4. *N*-[2-(Triphenylphosphoranylidene)aminobenzoyl]glycine ethyl ester (4a): white solid from 1:1 AcOEt/hexane; mp 53−56 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 11.74 (t, 1H, J = 5.8 Hz, NH), 8.26 (dt, 1H, J = 2.2, 7.8 Hz), 7.80−7.69 (m, 6H), 7.63−7.43 (m, 9H), 6.92 (ddd, 1H, J = 2.0, 7.0, 8.0 Hz), 6.74 (ddd, 1H, J = 1.2, 7.0, 7.8 Hz), 6.45 (dt, 1H, J = 1.2, 8.0 Hz), 4.20 (d, 1H, J = 5.8 Hz), 4.12 (q, 2H, J = 7.2 Hz), 1.20 (t, 3H, J = 7.2 Hz); IR (KBr) 3441 (br), 1748, 1642, 1591, 1528, 1470, 1439, 1333, 1269, 1120, 1109, 1013, 760, 720, 694, 525 cm^{-1}. Anal. Calcd for $C_{29}H_{27}N_2O_3P$: C, 72.18; H, 5.64; N, 5.81. Found: C, 72.26; H, 5.88; N, 5.49.

***N*-[2-(Triphenylphosphoranylidene)aminobenzoyl]-L-alanine ethyl ester (4b):** light yellow solid from 1:1 AcOEt/hexane; mp 51−53 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 11.54 (d, 1H, J = 7.4 Hz, NH), 8.25 (dt, 1H, J = 2.2, 7.8 Hz), 7.81−7.44 (m, 15H), 6.94−6.69 (m, 2H), 6.44 (d, 1H, J = 8.0 Hz), 4.83 (quint, 1H, J = 7.4 Hz), 4.09 (dq, 2H, J = 1.2, 7.2 Hz), 1.19 (d, 3H, J = 7.4 Hz), 1.18 (t, 3H, J = 7.2 Hz); IR (KBr) 1738, 1642, 1591, 1526, 1468, 1437, 1329, 1269, 1109 cm^{-1}. Anal Calcd for $C_{30}H_{29}N_2O_3P$: C, 72.56; H, 5.89; N, 5.64. Found: C, 72.79; H, 6.07; N, 5.23.

***N*-[2-(Triphenylphosphoranylidene)aminobenzoyl]-L-valine ethyl ester (4f):** white crystalline solid from 1:2 AcOEt/hexane; mp 179−182 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 11.52 (d, 1H, J = 8.8 Hz, NH), 8.29 (dt, 1H, J = 2.2, 8.0 Hz), 7.83−7.71 (m, 6H), 7.62−7.42 (m, 9H), 6.92−6.68 (m, 2H), 6.44 (d, 1H, J = 8.0 Hz), 4.76 (dd, 1H, J = 6.6, 8.8 Hz), 4.14 (q, 1H, J = 7.2 Hz), 4.12 (q, 1H, J = 7.2 Hz), 1.98−1.81 (m, 1H), 1.22 (t, 3H, J = 7.2 Hz), 0.83 (d, 3H, J = 6.8 Hz), 0.58 (d, 3H, J = 6.8 Hz); IR (KBr) 1736, 1640, 1591, 1528, 1470, 1439, 1327, 1263, 1109, cm^{-1}. Anal. Calcd for $C_{32}H_{33}N_2O_3P$: C, 73.26; H, 6.34; N, 5.34. Found: C, 73.56; H, 5.77; N, 5.61.

***N*-[2-(Triphenylphosphoranylidene)aminobenzoyl]-L-proline methyl ester (4h):** white solid from 1:1 AcOEt/hexane; mp 52−61 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.81−7.39 (m, 15H), 7.26−7.10 (m, 1H), 6.93−6.80 (m, 1H), 6.71−6.55 (m, 1H), 6.40 (t, 1H, J = 8.4 Hz), 4.85−4.71 (m, 1H), 4.01−3.38 (br m, ca. 2H), 3.90, 3.79 (each s, 2.01H, CO_2Me of two conformers of the syn isomer), 3.42 (s, 0.99H, CO_2Me of the anti isomer), 2.4−1.6 (m, 4H); IR (KBr) 1744, 1628, 1591, 1478, 1456, 1437, 1410, 1343, 1198, 1111, 752, 720, 696 cm^{-1}. Anal. Calcd for $C_{31}H_{29}N_2O_3P$: C, 73.21; H, 5.75; N, 5.51. Found: C, 73.15; H, 5.79; N, 5.50.

***N*-Phenyl-*N*-[2-(triphenylphosphoranylidene)aminobenzoyl]glycine methyl ester (4j):** white solid from 1:2 AcOEt/hexane; mp 63−74 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.90−7.38 (m, 12H), 7.24−6.86 (m, 4H), 6.70 (br t, 1H, J = 7.4 Hz), 6.47 (br t, 1H, J = 7.4 Hz), 6.16 (br d, 1H, J = 7.4 Hz), 4.73 (br s, 2H), 3.76 (s, 3H); IR (KBr) 1753, 1655, 1589, 1481, 1439, 1346, 1206, 1111 cm^{-1}. Anal. Calcd for $C_{34}H_{29}N_2O_3P$: C, 74.98; H, 5.37; N, 5.15. Found: C, 74.86; H, 5.60; N, 5.03.

***N*-Methyl-*N*-[2-(triphenylphosphoranylidene)aminobenzoyl]glycine ethyl ester (4k):** light yellow solid; mp 46−51.5 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.80−7.68 (m, 6H), 7.57−7.39 (m, 9H), 7.25−7.16 (m, 1H), 6.95−6.81 (m, 1H), 6.65 (q, 1H, J = 7.2 Hz), 6.39 (t, 1H, J = 7.6 Hz), 5.00, 4.50 (each br d, ca. 1H, J = 18 Hz, NCH_2 of the syn isomer), 4.24 (q, ca. 1H, J = 7.2 Hz), 4.02 (q, ca. 1H, J = 7.2 Hz), 3.77 (br t, ca. 1H, J = 20 Hz, NCH_2 of the anti isomer), 3.24 (s, 1.54H, NMe of the anti isomer), 2.98 (s, 1.56H, NMe of the syn isomer), 1.30 (t, 1.56H, J = 7.2 Hz), 1.16 (t, 1.54 H, J = 7.2 Hz); IR (KBr) 1748, 1638, 1589, 1480, 1437, 1395, 1348, 1202, 1111, 1073, 1049, 1024, 752, 718 cm^{-1}. Anal. Calcd for $C_{30}H_{29}N_2O_3P$: C, 72.56; H, 5.89; N, 5.64. Found: C, 72.40; H, 5.89; N, 5.63.

2-Amino-4-(benzyloxy)-5-methoxybenzoic Acid (14). Method A. A mixture of 4-(benzyloxy)-5-methoxy-2-nitrobenzoic acid[20] (**13**) (1.213 g, 4.00 mmol) and $SnCl_2/2H_2O$ (3.630 g, 16.09 mmol) in MeOH (12 mL) was heated to reflux for 1.2 h (monitored by TLC, 1:9 MeOH/$CHCl_3$). After removal of the solvent, the residual orange liquid was diluted with AcOEt and 5% aqueous $NaHCO_3$ and stirred vigorously for 1 h. The precipitates were removed by filtration, and the organic layer was separated. The aqueous layer was extracted with AcOEt (50 mL × 2). The combined organic layer and extracts were dried (Na_2SO_4). The removal of the solvent gave a solid residue (820 mg, 75%) which was recrystallized from AcOEt to afford **14** as dark green prisms (675 mg, 62%): mp 160–162 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 7.46–7.28 (m, 6H), 6.16 (s, 1H), 5.17 (s, 2H), 3.84 (s, 3H); IR (KBr) 3700–2400 (br), 1659 1593, 1562, 1514, 1421, 1254, 1219, 1204, 1177 cm^{-1}. Anal. Calcd for $C_{15}H_{15}NO_4$: C, 65.92; H, 5.53; N, 5.13. Found: C, 65.73; H, 5.50; N, 5.16.

Method B. To a stirred and ice-cooled mixture of **13** (608 mg, 2.00 mmol) and $NiCl_2/6H_2O$ (953 mg, 4.01 mmol) in MeOH (8 mL) was added portionwise $NaBH_4$ (303 mg, 8.01 mmol). After stirring was continued for 0.5 h, the MeOH was removed. The residue was dissolved in 6 N HCl, basified with concentrated aqueous ammonia to pH 8, and extracted with AcOEt (40 mL × 6). The combined extracts were dried (Na_2SO_4) and evaporated to give a crystalline residue which was recrystallized from AcOEt to afford the amine **14** as dark green prisms (290 mg, 53%).

2-Azido-4-(benzyloxy)-5-methoxybenzoic Acid (12). To a stirred and ice-cooled solution of the amine **14** (546 mg, 2.00 mmol) in 6 N aqueous HCl (8 mL) was added portionwise $NaNO_2$ in water (3 mL), and stirring was continued for 0.5 h. This solution was then added dropwise to a stirred solution of NaOAc (3.954 g, 48.2 mmol) and NaN_3 (139 mg, 2.12 mmol) in water (8 mL). After stirring was continued for a further 0.5 h, the precipitates were filtered, washed with water, dissolved in chloroform, and dried (Na_2SO_4). Solvent removal under reduced pressure gave crystalline residue (470 mg, 79%) which was recrystallized from toluene to afford the azide **12** as grayish crystals (385 mg, 64%): mp 139–141 °C dec; ^1H NMR (200 MHz, $CDCl_3$) δ 7.66 (s, 1H), 7.49–7.31 (m, 5H), 6.69 (s, 1H), 5.25 (s, 2H), 3.92 (s, 3H); IR (KBr) 3700–2400 (br), 2108, 1686, 1605, 1678, 1522, 1458, 1416, 1395, 1258, 1209, 1182 cm^{-1}; MS *m/z* (relative intensity) 299 (M^+, 22), 272 (21), 271 (100), 258 (15), 242 (42), 227 (46), 154 (18), 136 (53), 108 (41), 107 (21). Anal. Calcd for $C_{15}H_{13}N_3O_4$: C, 60.19; H, 4.38; N, 14.04. Found: C, 60.31; H, 4.38; N, 14.02.

***N*-[2-Azido-4-(benzyloxy)-5-methoxybenzoyl]-L-proline Methyl Ester (11).** A mixture of azidobenzoic acid **12** (299 mg, 1.00 mmol) and thionyl chloride (1.1 mL, 15 mmol) was heated to relfux for 2 h. The excess reagent was removed under reduced pressure, and the residue was dissolved in THF (9 mL). This chloride solution was added dropwise to a stirred solution of L-proline methyl ester hydrochloride (186 mg, 1.12 mmol), Et_3N (0.45 mL, 3.23 mmol), and DMAP (13 mg, 0.11 mmol) in THF (9 mL), and the mixture was heated to reflux for 1 h. The resulting precipitates were removed by filtration, and the filtrate was concentrated under reduced pressure. Flash chromatography, eluting with 1:1 AcOEt/hexane, afforded the (azidobenzoyl)proline ester **11** as a crystalline solid (280 mg, 68%): mp 92–95 °C; $[\alpha]^{26}_D$ −67.2 (*c* = 0.67, $CHCl_3$); ^1H NMR (200 MHz, $CDCl_3$) δ 7.48–7.30 (m, 5H), 6.86, 6.76 (each s, 0.7H and 0.3H, Ar H of syn and anti isomers), 6.67, 6.63 (each s, 0.7H and 0.3H, Ar H of syn and anti isomers), 5.18, 5.17 (each s, 0.7H and 0.3H), 4.68, 4.25 (each dd, 0.7 H and 0.3H, *J* = 4.1, 8.7 Hz, *J* = 2.8, 8.4 Hz, NCH of syn and anti isomers), 3.88, 3.83 (each s, 7.0:0.30 ratio, 3H, ArOMe of syn and anti isomers), 3.79, 3.53 (each, s, 7.0:3.0 ratio, 3H, COOMe of syn and anti isomers), 3.94–3.73 (m, ca. 0.3H, NCH_2 of the anti isomer), 3.49–3.32 (m, 0.7H, NCH_2 of the syn isomer), 2.41–1.83 (m, 4H); IR (KBr) 2112, 1744, 1638, 1605, 1512, 1453, 1427, 1387, 1246 cm^{-1}; MS *m/z* (relative intensity) 382 (M^+ − 28, 18), 324 (13), 323 (60), 232 (10), 231 (17), 91 (100). Anal. Calcd for $C_{21}H_{22}N_4O_5$: C, 61.45; H, 5.40; N, 13.65. Found: C, 61.85; H, 5.42; N, 13.24.

(2*S*)-*N*-[2-Azido-4-(benzyloxy)-5-methoxybenzoyl]tetrahydropyrrole-2-carboxaldehyde (10). To a stirred solution of **11** in CH_2Cl_2 (8 mL) was added dropwise 1.0 M solution of DIBAL-H in hexane (0.40 mL, 0.40 mmol) at −78 °C. After stirring was continued for 25 min, the mixture was diluted with MeOH (1 mL) and was allowed to come to room temperature while being stirred. The mixture was filtered, and the filtrate was concentrated and subjected to flash chromatography (3:2 AcOEt/hexane) to afford **10** as a light yellow solid: mp 39–41 °C; ^1H NMR (200 MHz, $CDCl_3$) δ 9.70, 9.31 (each d, 8:2 ratio, 1H, each *J* = 2.0 Hz, CHO of syn and anti isomers), 7.50–7.34 (m, 5H), 6.88, 6.80 (each s, 8:2 ratio, 1H, Ar H of syn and anti isomers), 6.69, 6.61 (each s, 8:2 ratio, 1H, Ar H of syn and anti isomers), 5.19, 5.16 (each s, 8:2 ratio, 2H, CH_2O of syn and anti isomers) 4.63 (ddd, 0.8H, *J* = 1.8, 5.6, 8.2 Hz, NCH of the syn isomer), 4.26–4.19 (m, 0.2H, NCH of the anti isomer), 3.89, 3.84 (each s, 8:2 ratio, 3H, ArOMe), 3.95–3.72, 3.53–3.32 (both m, ca. 2:8 ratio, 2H, NCH_2 of anti and syn isomers), 2.29–1.84 (m, 4H); IR (KBr) 2112, 1732, 1630, 1512, 1454, 1429, 1383, 1246, 1209 cm^{-1}; MS *m/z* (relative intensity) 352 (M^+ − 28, 14), 336 (5.4), 324 (6.1), 323 (26), 322 (5.6), 232 (4.8), 231 (13), 92 (7.7), 91 (100). Anal. Calcd for $C_{20}H_{20}N_4O_4$: C, 63.14; H, 5.30; N, 14.73. Found: C, 63.32; H, 5.52; N, 14.33.

8-Benzyl DC-81 (9). To a stirred solution of **10** (39 mg, 0.10 mmol) in toluene (8 mL) was added slowly PPh_3 (37 mg, 0.14 mmol) in toluene (3 mL) under nitrogen at room temperature. Stirring was continued for 2.5 h at the same temperature until TLC indicated that the reaction was complete, and the solvent was removed under reduced pressure. The residue was subjected to flash chromatography, eluting with 9:1 AcOEt/hexane to afford 8-benzyl DC-81 (**9**) as a light yellow oil (34 mg, 98%) as judged by the following data: $[\alpha]^{20}_D$ +611.1 (*c* = 0.18, $CHCl_3$) [lit.[21] $[\alpha]^{23}_D$ +629.6 (*c* = 0.0108, $CHCl_3$)]; ^1H NMR (200 MHz, $CDCl_3$) δ 7.65 (d, 1H, *J* = 4.4 Hz, N=CH), 7.54 (s, $1H_{arom}$), 7.48–7.31 (m, $5H_{arom}$), 6.85 (s, $1H_{arom}$), 5.20 (d, 2H, *J* = 2.8 Hz, OCH_2), 3.97 (s, 3H, OMe), 3.90–3.51 (m, 3H), 2.37–1.96 (m, 4H); IR (neat) 3339 (very br, OH for carbinol amine form), 2932, 2870, 1700 (very weak), 1626 (sh), 1601, 1504, 1454, 1431, 1381, 1261, 1217, 1200 (sh), 1178 (sh), 1124, 1091, 1022, 755, 735, 698 cm^{-1}; MS *m/z* (relative intensity) 337 (M + 1, 12), 336 (M^+, 53), 245 (21), 217 (11), 91 (100).

X-ray Crystal Structure Analysis of 4f.[24] Crystal data of **4f**: $C_{32}H_{33}N_2O_3P$, *M* = 524.58, orthorhombic, $P2_12_12_1$, *a* = 31.760(3) Å, *b* = 10.501(3) Å, *c* = 8.683(4) Å, *V* = 2896(1) Å^3, *Z* = 4.0, D_c = 1.203 g cm^{-3}. A colorless prism from chloroform/hexane (0.360 × 0.400 × 0.660 mm) was mounted on a Rigaku-AFC5S diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.710 69 Å). Data collection using the ω scan technique to a maximum 2θ value of 55.1° gave 6724 reflections, 3581 unique (R_{int} = 0.077), of which 1283 with $I > 3.00\sigma(I)$ reflections were used in calculations. The structure was solved by direct method and refined by full-matrix least squares technique (TEXSAN system[25] as the computer program and MITHRIL[26] as the structure solution method). The non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included by calculation and were not refined. The unweighted and weighted values were 0.081 and 0.090, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited.[24]

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(24) The authors have deposited atomic coordinates for **4f** with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

(25) *TEXSAN TEXRAY, Structure Analysis Package*; Molecular Structure Corp., 1984.

(26) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.