3-TRIPHENYLPHOSPHORANYLIDENEAMINO-2-CYCLOALKENONES: REACTION WITH METHYL PROPIOLATE LEADING TO [N](2,6)PYRIDINOPHANES

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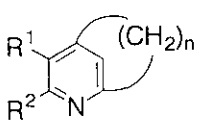
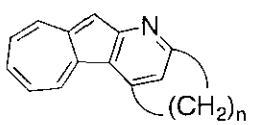
Abstract--The title compounds have been synthesized, and their reaction with methyl propiolate afforded 3-methoxycarbonyl[n](2,6)-pyridinophanes (*n*=9 and 8), along with 5,6-ring annulated 2-methoxypyridines *albeit in* low yields, respectively.

The remarkable chemical and physical properties of strained cyclophanes continue to fascinate many chemists.[1-4] In the field of heterocyclic [n]paracyclophanes,[5,6] the smallest known member is [6](2,5)-pyridinophane.[5] In the [n]metacyclophane series, the metapyridinophanes thus far obtained are 3-halogeno-substituted [6](2,4)pyridinophanes,[7] [n](2,4)pyridinophane (n=9 and 7),[8] [n](2,6)pyridinophane (n=12 and 10-6),[9] [n](3,5)pyridinophane (n=9 and 7),[10] 3-chloro-substituted [n](2,4)quinolinophane (*n*=10, 8, and 6), and [n](2,4)quinolinophane (n=10 and 8).[11,12]

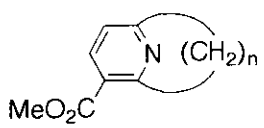
Previously, we worked on a convenient preparation of [n](2,4)pyridinophanes (n=9-6) (**1**)[13,14] and azuleno-annulated [n](2,4)pyridinophane (**3**) (n=9-6),[15] and studied their static and dynamic behavior (Scheme 1). The synthesis consists of an enamine-alkylation process of vinyliminophosphorane or β-amino enones and 2-aminoazulene with 2-cycloalkenones, respectively, subsequent condensation of the



1 (n=9-6)



2 (n=9-6)

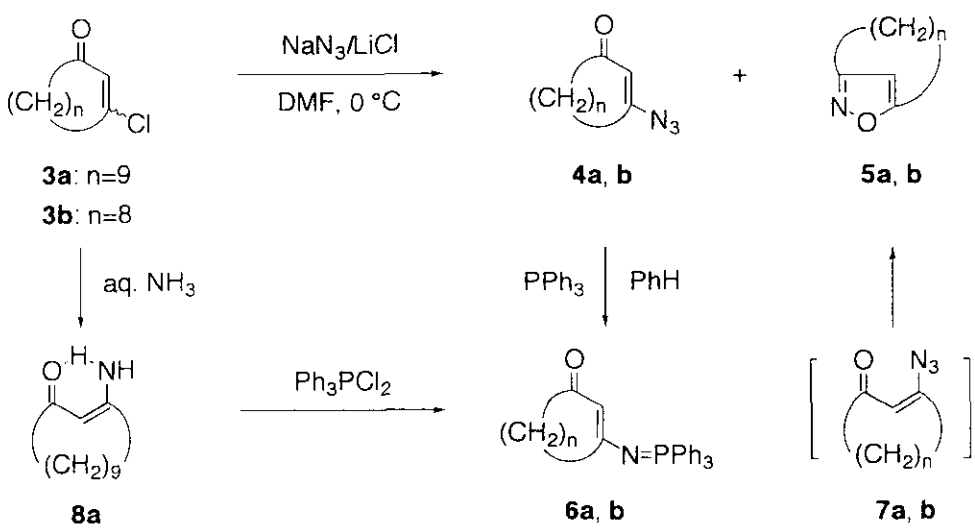


15a, **b** (n=9 and 8)

Scheme 1.

nitrogen moiety with the carbonyl function, and dehydrogenation. The utility of vinyliminophosphoranes as useful building blocks for the synthesis of aza-heterocycles has been demonstrated.[16] In the search for new methodology for synthesizing 3-methoxycarbonyl[n](2,6)pyridinophanes (**15a,b**), which might be promising precursors of chiral nicotinamides,[6b] we studied the preparation of 3-triphenylphosphoranylideneamino-2-cycloalkenones (**6a,b**). The iminophosphoranes (**6a,b**) reacted with methyl propiolate to give the expected 3-methoxycarbonyl[n](2,6)pyridinophanes (**15a,b**) (n=9 and 8), along with 5,6-ring annulated 2-methoxypyridines (**12a,b**), respectively, *albeit in* low yield. We describe herein the results in detail.

The reaction of 3-chloro-2-cycloalkenone (**3a**)[17] with sodium azide in DMF at 0 ℃ afforded a mixture of 3-azido-2-cyclododecenone (**4a**) and [9](3,5)isoxazolophane (**5a**). Since in the mixture of **4a** and **5a**, **4a** undergoes decomposition, the mixture was subsequently reacted with triphenylphosphine (the Staudinger reaction)[18] in benzene to give 3-triphenylphosphoranylideneamino-2-cyclododecenone (**6a**) and **5a**. Similarly, the iminophosphorane (**6b**) was prepared by the reaction of triphenylphosphine with the mixture of 3-azido-2-cycloalkenone (**4b**) and [8](3,5)isoxazolophane (**7b**) (Scheme 2). Since the conversion of **4a,b** to **5a,b** was not observed, the precursors of **5a,b** may be the possible intermediates, *trans*-3-azido-2-cycloalkenones (**7a,b**).[19] In the reaction of **3a**, the isoxazolophane (**5a**) was obtained preferentially over iminophosphorane (**6a**) probably because the *trans*-isomer is more stable than the *cis*-isomer in 2-cyclododecenone.[20,21] The iminophosphorane (**6b**) was obtained preferentially over the [8](3,5)isoxazolophane (**5b**).[20] An alternative, efficient preparation of the iminophosphorane (**6a**) was

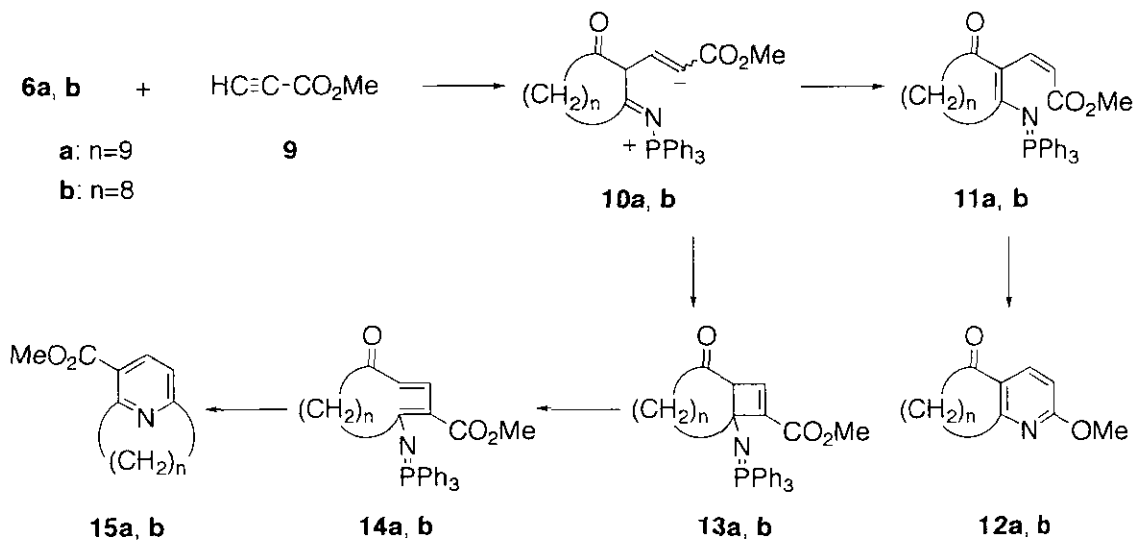


Scheme 2.

accomplished by the reaction of **3a** with aq. NH_3 to give 3-amino-2-cyclododecenone (**8a**) and subsequent treatment of **8a** with phosphonium salt (the Kirsanov reaction) as shown also in Scheme 2.[18]

The compound (**5a**) is known and the ^1H NMR spectrum is in accordance with the reported data.[22] There was good correlation between **5a** and **5b** in the ^1H NMR spectra, and the structure of **5b** was suggested to be [8](3,5)isoxazolophane. The structures of new compounds (**6a,b** and **8a**) were assigned on the basis of the ^1H NMR and ^{13}C NMR spectral data, IR, and MS spectral data, as well as elemental analyses. Regarding **8a**, the IR spectrum and the signal appearing at δ 9.55 (-NH) in the ^1H NMR spectrum suggest hydrogen bond between the -NH proton and carbonyl-oxygen and the *trans*-configuration of 2-cyclododecenone moiety for **8a**. In addition, the triplets appearing at δ 2.16 and δ 2.30 are ascribed to methylene protons at C-4 and C-12 positions and equivalency of these is explained by assuming free inversion of polymethylene chain. Furthermore, the ylides (**6a,b**) consist of only one component, respectively: thus, we prefer *cis*-cycloalkenone skeleton for **6a,b** because of the bulky triphenylphosphoranylideneamino group.

Reaction of iminophosphorane (**6a**) with methyl propiolate (**9**) in refluxing xylene afforded ring-annulated pyridine (**12a**) (11%) and [9](2,6)pyridinophane (**15a**) (9%) (Scheme 3). Similarly, the reaction of **6b** with **9** afforded pyridine (**12b**) (8%) and [8](2,6)pyridinophane (**15b**) (4%). The postulated reaction pathways for the formation of **12a,b** and **15a,b** are also shown in Scheme 3. The enamine-type alkylation of the iminophosphoranes (**6a,b**) to the β-carbon atom of **9** gives **10a,b**. The following hydrogen transfer and cyclobutene-formation in **10a,b** gives **11a,b** and **13a,b**, respectively.[16c,23] The



Scheme 3.

intermediates (**11a,b**) undergo aza-Wittig reaction to produce pyridines (**12a,b**). On the other hand, the intermediates of iminophosphoranes (**13a,b**) undergo cyclobutene-ring-opening to give **14a,b**, which undergo aza-Wittig reaction to give 3-methoxycarbonyl[n](2,6)pyridinophanes (**15a,b**). The ^{1}H NMR and ^{13}C NMR spectra of **12a,b** as well as **15a,b** correlate well, respectively, and are in good accordance with the proposed structures. A characteristic feature of the pyridinophanes (**15a,b**) is the equivalence of geminal hydrogen at the benzylic positions, H-1' and H-n' (see the convenient numbering in structural formulae (**15a,b**) in Figure 1). These protons appear as two triplets at δ 2.90 and δ 3.27 for **15a** and at δ 2.89 and δ 3.28 for **15b**. The splitting pattern is indicative of a rapid flipping of the methylene chain of **15a,b** at room temperature.[13-15]

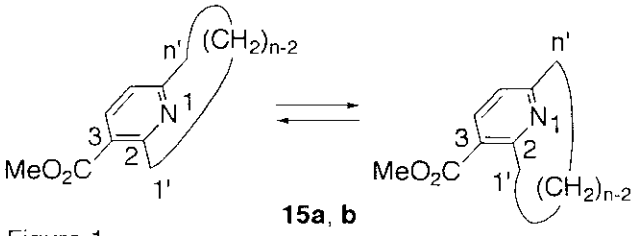
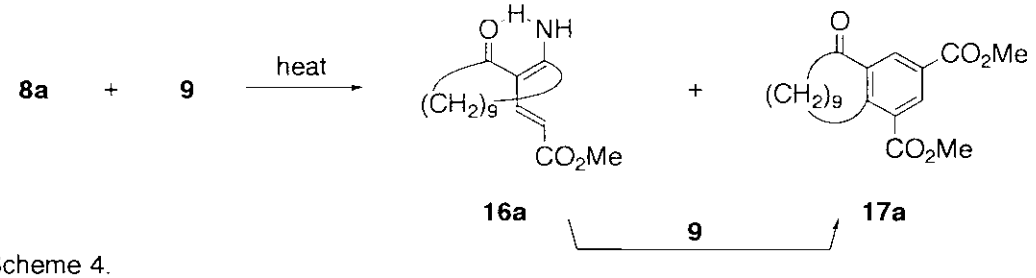


Figure 1.

It was clarified that β-amino ester reacts with methyl propiolate (**9**) to give condensed cyclobutene (cf. **13a,b**), which undergoes ring enlargement reaction.[24] An attempted reaction of β-amino enone (**8a**) with **9** in benzene for 11 h, however, afforded **16a** (88%) and **17a** (6%). Furthermore, prolonged heating of **8a** with excess amount of **9** under similar conditions resulted in the formation of only **17a** in 68% yield. Thus compound (**17a**) seems to arise from the primary adduct (**16a**). The structures of **16a** and **17a** were confirmed on the basis of the spectral characteristics. Regarding **16a**, the IR spectrum and the signal appearing at δ 10.18 (NH) in the ^{1}H NMR spectrum suggest hydrogen bond between the NH proton and carbonyl-oxygen, and thus, the *trans*-configuration of 2-cyclododecenone moiety was confirmed for **16a**. Unlike in the case of **8a**, the four methylene protons at C-4 and C-12 of **16a** appear at different chemical shifts: thus, inversion of the methylene chain is fixed at room temperature. This feature is ascribed to the bulky substituent of methyl acrylate moiety.



Scheme 4.

In summary, this work shows for the first time that easily accessible 3-triphenylphosphoranylideneamino-

2-cycloalkenones react with methyl propiolate to give novel 3-methoxycarbonyl[n](2,6)pyridinophanes (*n*=9 and 8), which might be promising precursors of chiral nicotinamide, *albeit in* low yields.

EXPERIMENTAL

IR spectra were recorded on a Perkin-Elmer FT-IR1640 or a Horiba FT-710 spectrophotometer. UV-vis spectra were recorded on a Shimadzu UV-3101PC spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-GSX400 and a JEOL JNM-LA500 spectrometers using $CDCl_3$ as a solvent, and the chemical shifts are given relative to internal $SiMe_4$ standard: J-values are given in Hz. MS spectra and HRMS spectra were run on a *JEOL Automass 150 and a JEOL JMS-SX102A spectrometers, respectively.* Mps were measured on a Yamato MP-21 apparatus and are uncorrected. All the reactions were carried out under dry nitrogen atmosphere. 3-Chloro-2-cyclododecenone (**3a**) and 3-chloro-2-cycloundecenone (**3b**) were prepared according to the literature procedure.[17]

Preparation of 3-triphenylphosphoranylideneamino-2-cycloalkenones (6a,b) along with [n](3,5)isoxazolophanes (5a,b). A solution of **3a,b** (5 mmol), sodium azide (650 mg, 10 mmol), and lithium chloride (106 mg, 2.5 mmol) in DMF (35 mL) was stirred at 0 ℃ for 47 h. The reaction mixture was poured into ice-water, extracted with hexane-AcOEt (5/1), and the extract was dried over Na_2SO_4. After evaporation of the solvent, the residue was dissolved in benzene (10 mL) and a solution of triphenylphosphine (1.3 g, 5 mmol) in benzene (5 mL) was added and the mixture was stirred for 3 h at rt. To the reaction mixture, hexane (30 mL) was added and the precipitate was collected by filtration to give (**6a**) (571 mg, 25%) and (**6b**) (1.128 g, 51%). Then the filtrate was separated by column chromatography on silica gel (hexane-AcOEt : 9/1) to give (**5a**) (550 mg, 57%) and (**5b**) (80 mg, 9%).

For 3-triphenylphosphoranylideneamino-2-cyclododecenone (**6a**): colorless prisms; mp 191-192 ℃ (from benzene-hexane); ^{1}H NMR (400 MHz) δ 1.00-1.17 (6H, m), 1.17-1.40 (6H, m), 1.82 (2H, br s), 1.90 (2H, t, J=6.1), 3.03 (2H, br s), 5.07 (1H, d, J_{PH}=1.1), 7.48 (6H, ddd, J=7.7, 7.2, J_{PH}=2.8), 7.56 (3H, td, J=7.7, J_{PH}=1.3), 7.78 (6H, dd, J=7.2, J_{PH}=11.9); ^{13}C NMR (100.5 MHz) δ 23.5, 23.7, 23.8, 25.1, 25.2, 26.0, 26.4, 32.2 (J_{PC}=21.3), 43.2, 110.7 (J_{PC}=13.2), 128.7 (J_{PC}=11.7), 129.0 (J_{PC}=99.0), 132.1 (J_{PC}=2.9), 132.8 (J_{PC}=9.5), 170.4 (J_{PC}=6.6), 200.5; IR ($CHCl_3$) 1625, 1490, 1440, 1360, 1330, 1110 cm^{-1}; MS (*m/z*) 455 (M^+, 30%), 183 (100). *Anal.* Calcd for $C_{30}H_{34}NOP$: C, 79.09; H, 7.52; N, 3.07. Found: C, 78.96; H, 7.41; N, 3.03.

For [9](3,5)isoxazolophane (**5a**): colorless oil; ^{1}H NMR spectrum is identical with the reported data.[22]

For 3-triphenylphosphoranylideneamino-2-cycloundecenone (**6b**): colorless prisms; mp 202-203 ℃ (from benzene-hexane); ^{1}H NMR (500 MHz) δ 0.99-1.13 (8H, m), 1.34-1.42 (2H, m), 1.75 (2H, br s), 1.83 (2H, t, J=6.1), 3.04 (2H, br s), 5.09 (1H, d, J_{PH}=1.6), 7.49 (6H, ddd, J=7.3, 7.0, J_{PH}=3.0), 7.56 (3H, tq, J=7.3, 1.4, J_{PH}=1.4), 7.79 (6H, ddd, J=7.0, 1.4, J_{PH}=12.1); ^{13}C NMR (125.8 MHz) δ 23.1, 23.4, 24.8, 25.9, 26.3, 28.5, 32.6 (J_{PC}=20.7), 44.6, 112.3 (J_{PC}=13.4), 128.7 (J_{PC}=12.4), 129.0 (J_{PC}=99.3), 132.2 (J_{PC}=3.1), 132.8 (J_{PC}=10.3), 169.8 (J_{PC}=7.2), 202.1; IR (KBr) 1627, 1507, 1439, 1363, 1330, 1119 cm^{-1}; MS (*m/z*) 441 (M^+, 94%), 261 (100). *Anal.* Calcd for $C_{29}H_{32}NOP$: C, 78.89; H, 7.30; N, 3.17. Found: C, 78.86; H, 7.31; N, 3.12.

For [8](3,5)isoxazolophane (**5b**): colorless oil; ^{1}H NMR (500 MHz) δ 0.01 (1H, br s), 0.46 (1H, br s), 0.87-0.96 (1H, m), 0.97-1.10 (2H, m), 1.21-1.40 (4H, m), 1.43-1.52 (1H, m), 1.82-1.91 (2H, m), 2.50 (1H, ddd, J=13.4, 9.6, 5.1), 2.57 (1H, ddd, J=13.8, 11.7, 4.9), 2.86 (1H, dt, J=13.4, 5.3), 2.89 (1H, dt, J=13.8, 4.3), 6.06 (1H, s); ^{13}C NMR (125.8 MHz) δ 24.3, 25.2, 26.1, 27.0, 27.1, 27.4, 28.2, 29.4, 106.6, 164.5, 172.6; IR (film) 2934, 2862, 1604, 1459, 1428 cm^{-1}; MS (*m/z*) 179 (M^+, 4%), 111 (100). HRMS Calcd for $C_{11}H_{17}NO$: 179.1310. Found: 179.1307.

Preparation of 3-amino-2-cyclododecenone (8a) and iminophosphorane (6a). A solution of **3a** (1.29g, 6.0 mmol) and 28% aqueous NH_3 (7.20 g, 119 mmol) in dioxane (36 mL) was heated in an autoclave at 100 ℃ for 12 h. The reaction mixture was then poured into water and extracted with ether and the ether extract was dried over $MgSO_4$. After evaporation of the solvent, the residue was crystallized from CCl_4 to give **8a** (1.11 g, 95%): colorless prisms; mp 131-132 ℃ (from AcOEt); ^{1}H NMR (500 MHz) δ 1.20-1.27 (2H, m), 1.27-1.34 (6H, m), 1.34-1.41 (2H, m), 1.60-1.66 (2H, m), 1.69 (2H, quint, J=6.5), 2.16 (2H, t, J=6.5), 2.30 (2H, t, J=6.5), 5.01 (1H, br s), 5.28 (1H, s), 9.55 (1H, br s); ^{13}C NMR (125.8 MHz) δ 24.4, 24.5, 25.3, 25.4, 25.9, 26.0, 26.4, 36.3, 42.1, 96.6, 163.8, 200.4; IR (KBr) 3292, 3136, 1599, 1529 cm^{-1}; MS (*m/z*) 195 (M^+, 96%), 110 (100). *Anal.* Calcd for $C_{12}H_{21}NO$: C, 73.80; H, 10.84; N, 7.17. Found: C, 73.69; H, 10.76; N, 7.15.

A solution of **8a** (977 mg, 5 mmol), triphenylphosphine (1.31 g, 5 mmol), hexachloroethane (1.18 g, 5 mmol), and triethylamine (2.02 g, 20 mmol) in benzene (25 mL) was heated under reflux for 30 min. After the reaction mixture was filtered, the filtrate was concentrated and the residue was crystallized from benzene-hexane (1/2) to give **6a** (2.00 g, 88%). The spectral data are identical with those of the authentic

specimen.

Preparation of [n](2,6)pyridinophanes (15a,b) and pyridines (12a,b). A solution of **6a,b** (1 mmol) and **9** (252 mg, 3 mmol) in xylene (3 mL) was heated under reflux for 48 h. After the reaction mixture was concentrated *in vacuo*, the residue was separated by TLC on alumina (hexane-AcOEt: 10/1) to give pyridines (**12a**) (28 mg, 11%) and (**12b**) (19 mg, 8%), along with [n](2,6)pyridinophanes (**15a**) (23 mg, 9%) and (**15b**) (10 mg, 4%), respectively.

For 7,8,9,10,11,12,13,14-octahydro-2-methoxycyclododeca[*b*]pyridin-5(6*H*)-one (**12a**): colorless oil; ^{1}H NMR (400 MHz) δ 0.92-1.02 (2H, m), 1.12-1.34 (6H, m), 1.43 (2H, quint, J=7.0), 1.70-1.85 (4H, m), 2.89 (2H, t, J=6.2), 2.98 (2H, t, J=6.2), 3.95 (3H, s), 6.55 (1H, d, J=8.6), 7.65 (1H, d, J=8.6); ^{13}C NMR (100.5 MHz) δ 22.9, 23.1, 23.3, 23.6 (two carbons overlapping), 25.7, 27.7, 30.7, 39.9, 53.5, 107.0, 130.3, 137.4, 160.0, 164.0, 205.0; IR ($CHCl_3$) 3017, 2934, 2865, 1711, 1588, 1364, 1303 cm^{-1}; MS (*m/z*) 261 (M^+, 17%), 55 (100). HRMS Calcd for $C_{16}H_{23}NO_2$: 261.1729. Found: 261.1730.

For 3-methoxycarbonyl[9](2,6)pyridinophane (**15a**): colorless oil; ^{1}H NMR (400 MHz) δ 1.00-1.12 (4H, m), 1.17-1.33 (6H, m), 1.87 (2H, quint, J=6.1), 1.90 (2H, quint, J=6.1), 2.90 (2H, t, J=6.1), 3.27 (2H, t, J=6.1), 3.90 (3H, s), 7.02 (1H, d, J=8.0), 8.07 (1H, d, J=8.0); ^{13}C NMR (100.5 MHz) δ 25.0, 25.1, 25.3, 25.4, 25.5, 25.9, 26.2, 35.7, 37.1, 52.0, 120.3, 122.7, 138.7, 162.5, 164.7, 167.3; IR ($CHCl_3$) 3017, 2934, 2858, 1710, 1588, 1434, 1363, 1278 cm^{-1}; UV(MeCN) (log ε) 232 (3.96), 270 (3.65) nm; MS (*m/z*) 261 (M^+, 58%), 176 (100). HRMS Calcd for $C_{16}H_{23}NO_2$: 261.1729. Found: 261.1710.

For 5*H*-6,7,8,9,10,11,12,13-octahydro-2-methoxycycloundeca[*b*]pyridin-5-one (**12b**): colorless oil; ^{1}H NMR (500 MHz) δ 1.05-1.12 (2H, m), 1.12-1.21 (4H, m), 1.38-1.40 (2H, m), 1.79 (2H, quint, J=6.3), 1.79 (2H, quint, J=6.1), 2.74-2.79 (2H, m), 3.08 (2H, t, J=6.3), 3.96 (3H, s), 6.56 (1H, d, J=8.5), 7.65 (1H, d, J=8.5); ^{13}C NMR (125.8 MHz) δ 23.2, 24.1, 25.0, 25.3, 26.9, 27.6, 31.2, 42.5, 53.5, 107.0, 130.2, 138.0, 160.9, 164.3, 206.8; IR (CCl_4) 2934, 2865, 1683, 1586, 1564, 1559, 1474, 1304, 1239 cm^{-1}; MS (*m/z*) 247 (M^+, 89%), 162 (100). HRMS Calcd for $C_{15}H_{21}NO_2$: 247.1572. Found: 247.1584.

For 3-(methoxycarbonyl)[8](2,6)pyridinophane (**15b**): colorless oil; ^{1}H NMR (500 MHz) δ 0.94 (2H, quint, J=6.4), 1.02 (2H, quint, J=6.4), 1.45-1.55 (4H, m), 1.87 (2H, quint, J=6.4), 1.89 (2H, quint, J=6.4), 2.89 (2H, t, J=6.4), 3.28 (2H, t, J=6.4), 3.89 (3H, s), 6.98 (1H, d, J=7.9), 8.08 (1H, d, J=7.9);

^{13}C NMR (125.8 MHz) δ 23.0, 23.6, 24.3, 24.7 (two carbons overlapping), 25.0, 34.4, 35.4, 51.9, 120.1, 122.3, 138.9, 161.8, 163.8, 167.2; IR (CCl_4) 2950, 2856, 1729, 1588, 1562, 1458, 1434, 1272 cm^{-1}; UV (MeCN) (log ε) 231 (3.99), 271 (3.65) nm; MS (*m/z*) 247 (M^+, 98%), 204 (100). HRMS Calcd for $C_{15}H_{21}NO_2$: 247.1572. Found: 247.1560.

Reaction of β-amino enone (8a) with methyl propiolate (9). A solution of **8a** (98 mg, 0.5 mol) and **9** (63 mg, 0.75 mmol) in benzene (1.5 mL) was heated at 140 ℃ in an autoclave for 11 h. After evaporation of the solvent, the residue was purified by TLC on silica gel (hexane-AcOEt : 2/1) to give **16a** (123 mg, 88%) and **17a** (10 mg, 6%).

A solution of **8a** (78 mg, 0.4 mol) and **9** (102 mg, 1.2 mmol) in dioxane (1.2 mL) was heated at 140 ℃ in an autoclave for 44 h. Workup similar to the described above afforded **17a** (94 mg, 68%).

For 3-amino-2-(2-methoxycarbonylvinyl)-2-cyclododecenone (**16a**): colorless prisms; mp 153-154 ℃ (from benzene); ^{1}H NMR (500 MHz) δ 1.02-1.46 (10H, m), 1.53-1.63 (1H, m),1.63-1.76 (2H, m), 1.87-1.97 (2H, m), 2.20 (1H, ddd, J=13.7, 9.2, 5.0), 3.14-3.22 (1H, m), 3.26 (1H, ddd, J=13.7, 7.3, 4.5), 3.75 (3H, s), 5.50 (1H, br s), 5.66 (1H, d, J=15.7), 7.88 (1H, d, J=15.7), 10.18 (1H, br s); ^{13}C NMR (125.8 NHz) δ 24.1, 24.3, 24.6, 25.1, 25.5, 25.9, 26.2, 35.3, 41.5, 51.3, 106.7, 111.1, 142.2, 166.7, 168.8, 203.5; IR (KBr) 3337, 3188, 2941, 2856, 1684, 1616, 1582, 1463, 1434, 1337, 1266, 1209, 1195 cm^{-1}; MS (*m/z*) 279 (M^+, 68%), 220 (100). *Anal.* Calcd for $C_{16}H_{25}NO_3$: C, 68.79; H, 9.02; N, 5.01. Found: C, 68.60; H, 9.07; N, 4.86.

For 7,8,9,10,11,12,13,14-octahydro-1,3-bis(methoxycarbonyl)benzocyclododecen-5(6*H*)-one (**17a**): colorless prisms; mp 94-95 ℃ (from MeOH); ^{1}H NMR (500 MHz) δ 1.25-1.45 (8H, m), 1.51-1.63 (4H, m), 1.77-1.87 (2H, m), 3.04 (2H, t, J=6.5), 3.15 (2H, t, J=7.4), 3.93 (3H, s), 3.94 (3H, s), 8.08 (1H, d, J=1.8), 8.46 (1H, d, J=1.8); ^{13}C NMR (125.8 MHz) δ 22.1, 23.1, 23.5, 25.0, 26.0, 26.5, 27.0, 30.3, 41.2, 52.4, 52.5, 127.5, 129.6, 132.6, 132.7, 144.0, 147.2, 165.6, 167.4, 206.2; IR (KBr) 2925, 2857, 1725, 1701, 1468, 1432, 1321, 1223, 1206, 1192 cm^{-1}; MS (*m/z*) 346 (M^+, 83%), 261 (100). *Anal.* Calcd for $C_{20}H_{26}O_5$: C, 69.34; H, 7.57. Found: C, 69.08; H, 7.39.

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