Stereoselective Synthesis of Dienic Nitrogen Compounds

Ramzi Aït Youcef,[a] Charlotte Boucheron,[a] Stéphane Guillarme,[a] Stéphanie Legoupy,*[a] Didier Dubreuil,[b] François Huet*[a]

[a] Laboratoire de Synthèse Organique, UCO2M, UMR CNRS 6011, Université du Maine, avenue Olivier Messiaen, 72085 Le Mans cedex 9, France

[b] Laboratoire de Synthèse Organique, UMR CNRS 6513, FR CNRS 2465, 2 rue de la Houssinière, BP 92208, 44322 Nantes cedex 03, France
Fax +33(2)43833902; E-mail: stephanie.legoupy@univ-lemans.fr; E-mail: francois.huet@univ-lemans.fr

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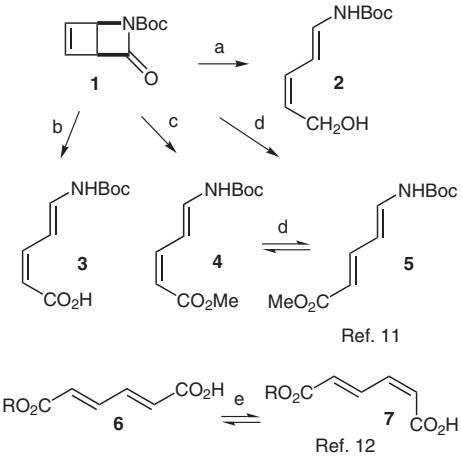
Abstract: Eight dienic nitrogen compounds were prepared starting from cyclobutene lactam **8**. Dienes **12**–**15** were obtained by benzylation or acylation followed by methanolysis, hydrolysis or reduction. The unsubstituted lactam **8** provided diene **16**. The latter was a precursor for the mono and biacylated products **17**–**19**.

Key words: electrocyclic reactions, lactams, ring opening, dienes, torquoselectivity

In the course of the past two decades, dienamides have emerged as reactive dienes in Diels–Alder reactions, especially for the synthesis of alkaloids.[1] Stereocontrolled preparation of dienamides can be achieved by various methods such as acylation of enamines,[2] thermal rearrangement of propargylic trichloroacetamides or Curtius rearrangement of dienyl azides,[3] anionization and alkylation of α-carbamidosulfones,[4] deprotonation and silylation of a vinylogous amide,[5] reaction involving ynamide-titanium alkoxide complexes,[6] condensation of nitrogen compound with an aldehyde,[7] and cross coupling reactions.[8]

The thermal ring opening of cyclobutene derivatives, leading to 1,3-diene compounds, has been studied extensively by both experimentalists and theoreticians. In the case of dissymmetric cyclobutenes, two conrotatory openings are possible each yielding a different geometrical isomer. Houk et al. predicted that π-donors such as nitrogen substituents should exclusively lead to outward rotation.[9] This theoretical prediction was confirmed by experimental work from our laboratory.[10] In more recent work[11] we pointed out new results equally consistent with conrotatory openings of cyclobutene derivatives and exclusive outward rotation of nitrogen substituents in the case of obtaining dienes **2**, **3** and **4** (Scheme 1). In contrast, the *E*,*E*-diene **5** was formed when the ring opening was carried out in basic medium. We suppose that, in this case, diene **4** is the primary product. Then isomerization occurs to the more stable diene **5**, in basic medium. Compound **4** was obtained only in practically neutral medium and we also checked that it isomerized to **5** on basic treatment. On the other hand, isomerization of **2**, which was obtained by reduction with $NaBH_4$, did not occur. This result is coherent with the absence of 'push–pull' character of this diene. As to isomerization of **3** to the *E*,*E*-isomer, it did not occur either. This result is not surprising when taking into account the better stability of 2*Z*,3*E*-dienic diacid monoesters with respect to the 2*E*,2*E*-derivatives showing the preference of a CO_2H group for the 2*Z*-position.[12]



Scheme 1 *Reagents and conditions* : (a) $NaBH_4$, MeOH –20 °C, separation of the reduction products, then heating in refluxing toluene for 10 min; (b) H_2O, LiOH, THF; (c) MeOH, NaN_3, DMF; (d) MeOH, LiOH; (e) H_2O, 80 °C.

With the aim of increasing the possibilities of stereochemical control, we examined several parameters. The influence of the nature of substituent on the nitrogen atom proved to be determinant. We prepared the suitable precursors from lactam **8**[11,13] (Scheme 2). Acetylation, benzylation and tosylation provided the expected products **9**, **10**, and **11**, in 57, 78 and 64% yield, respectively.

As it was anticipated, hydrolysis of **9** provided diene **12** by a conrotatory process with outward rotation of the nitrogen substituent and preference of CO_2H for the 2*Z*-position. On the other hand, we thought that the *E*,*E*-diene would be formed by methanolysis after isomerization of the primary diene. This isomerization was not observed and we obtained compound **13**. This unexpected result is probably due to a moderate 'push–pull' character of diene **13** in which a strongly electron-withdrawing group is present on nitrogen. In this case, isomerization was slow and stirring in the presence of LiOH in MeOH for 48

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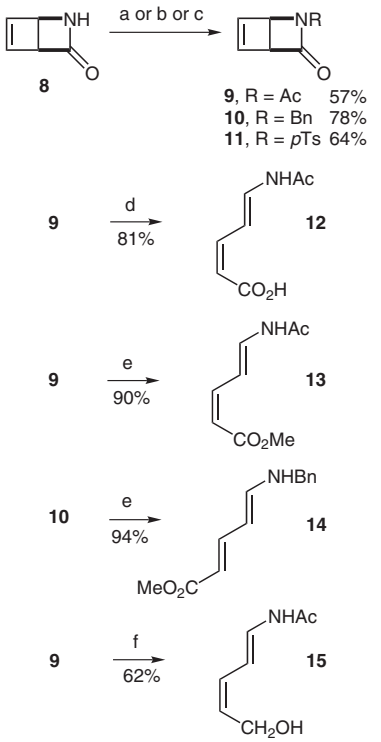
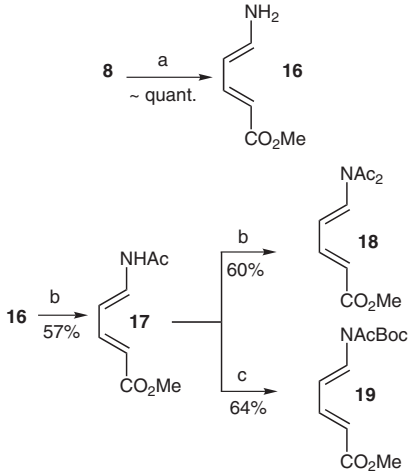


Scheme 2 *Reagents and conditions*: (a) Ac_2O, KOH, THF, –78 °C to r.t.; (b) BnBr, KOH, Bu_4NI, THF, –78 °C to r.t; (c) *p*-Ts_2O, Et_3N, CH_2Cl_2, 0 °C to r.t.; (d) H_2O, LiOH, THF; (e) MeOH, LiOH; (f) $LiAlH_4$, THF, –78 to –20 °C, separation of the reduction products, then heating in refluxing toluene for 40 min.

hours led to a mixture of *Z*,*E*- and *E*,*E*-dienes in a 4:1 ratio, respectively. Logically, when the acetyl group was replaced by a benzyl group, the *E*,*E*-diene **14** was formed. Treatment of **9** with $LiAlH_4$ at low temperature led to a selectivity in favor of reduction of the lactam moiety with respect to the acetyl group. A mixture of *N*-[4-hydroxymethyl)cyclobut-2-enyl]acetamide and diene **15** was thus obtained. The latter was isolated in 62% overall yield after isomerization of the cyclobutene compound by heating in refluxing toluene. Methanolysis and hydrolysis of lactam **11** were also carried out. However, they did not lead to good results and mainly formation of degradation products was observed.

At this point of our work, access to *E*,*E*-dienes was limited. We thought that, if our hypotheses were good, it would be possible to prepare one of them from the unsubstituted lactam **8**, as in this case there would not be restriction to isomerization. We were pleased to obtain the anticipated result and diene **16**, which is poorly stable, was available in nearly quantitative yield by treatment with MeOH, LiOH (Scheme 3). This good result made it possible to selectively prepare an *E*,*E*-aminodiene **17** bearing an electron-withdrawing group on the nitrogen atom by a strategy based on acetylation after, instead of before, the ring-opening process. This diene, an isomer of **13**, was available by acetylation of **16**. We also showed that it was possible to introduce a second group [Ac (**18**) or Boc (**19**)] on nitrogen atom of dienamide **17**.



Scheme 3 *Reagents and conditions*: (a) LiOH, MeOH; (b) Ac_2O, DMAP, Et_3N, CH_2Cl_2, 0 °C to r.t.; (c) Boc_2O, DMAP, Et_3N, CH_2Cl_2, 0 °C to r.t.

Stereochemical assignments for dienes **12**–**16** were based on ^1H NMR analyses. When the differences between the coupling constants for a *trans*- and a *cis*-relationship were not sufficient, the structures were confirmed by NOE or NOESY experiments.

In conclusion we have found efficient conditions to prepare *E*,*E*- as well as *Z*,*E*-nitrogen dienes. We also propose an interpretation of our previous results as well as of these new ones. Synthetic application of the products is now in progress.

All moisture-sensitive reactions were carried out in oven-dried glassware (100 °C) under N_2. Commercially available reagents and solvents were purified and dried, when necessary, by standard methods just prior to use. IR spectra were scanned on a FTIR spectrophotometer. All melting points are uncorrected. ^1H and ^{13}C NMR spectra were recorded at 400 and 100.6 MHz, respectively. Chemical shifts are reported in ppm downfield from TMS which was used as an internal reference. Elemental analyses were obtained from the Service de Microanalyse, CNRS ICSN, Gif-sur-Yvette. High-resolution mass measurements were performed at the CRMPO, Rennes.

***N*-Acetyl-2-azabicyclo[2.2.0]hex-5-en-3-one (9)**

Ac_2O (0.45 mL, 4.76 mmol), and KOH (0.285 g, 5.07 mmol), were added to a solution of lactam **8** (0.300 g, 3.15 mmol) in anhyd THF (15 mL) at –78 °C. The mixture was stirred for 16 h while the temperature was slowly allowed to warm to 20 °C. A solution of 1 M aq HCl (3 mL) was then added, and the solvents were evaporated. The residue was dissolved in CH_2Cl_2 (10 mL), successively washed with H_2O (5 mL) and brine (5 mL), dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (silica gel, cyclohexane–EtOAc, 7:3) to give compound **9** (0.246 g, 57%) as a colorless oil.

IR (KBr): 3014, 1702, 1544, 1310 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 6.66 (dd, 1 H, H-5, *J* = 2.7, 1.0 Hz), 6.59–6.56 (m, 1 H, H-6), 4.75 (dd, 1 H, H-1, *J* = 2.7, 2.2 Hz), 4.21–4.18 (m, 1 H, H-4), 2.36 (s, 3 H, $COCH_3$).

^{13}C NMR ($CDCl_3$): δ = 168.7, 166.7, 142.3, 140.3, 56.7, 51.9, 23.1.

HRMS (EI): *m*/*z* calcd for $[(C_7H_7NO_2) - CH_2CO]^+$: 95.0371; found: 95.0374.

N-Benzyl-2-azabicyclo[2.2.0]hex-5-en-3-one (10)

Benzyl bromide (0.217 g, 1.26 mmol), KOH (0.095 g, 1.26 mmol), and Bu_4NI (0.040 g, 0.11 mmol) were added to a solution of lactam **8** (0.100 g, 1.05 mmol) in anhyd THF (8 mL) at –78 °C. The mixture was stirred for 16 h while the temperature was slowly allowed to warm to 20 °C. A solution of 1 M aq HCl (2 mL) was then added, and the solvent was evaporated. The residue was dissolved in CH_2Cl_2 (10 mL), successively washed with H_2O (1 mL) and brine (1 mL), dried ($MgSO_4$) and concentrated. The residue was purified by column chromatography (silica gel, cyclohexane–EtOAc, 3:2) to give compound **10** (0.151 g, 78%) as an orange oil.

IR (KBr): 3022, 1742, 1597, 1455 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.37–7.27 (m, 3 H, C_6H_5), 7.26–7.22 (m, 2 H, C_6H_5), 6.46–6.43 (m, 1 H, H-5), 6.13 (t, 1 H, H-6, *J* = 2.5 Hz), 4.33 (AB system, 2 H, C*H*$_2$Ph, *J* = 3.4 Hz), 4.20 (t, 1 H, H-1, *J* = 2.5 Hz), 4.17–4.15 (m, 1 H, H-4).

^{13}C NMR ($CDCl_3$): δ = 169.4, 141.2, 138.8, 134.9, 128.7, 128.3, 127.8, 57.7, 53.8, 47.6.

HRMS (EI): *m*/*z* calcd for $[C_{12}H_{11}NO]^+$: 185.0841; found: 185.0846.

N-Tosyl-2-azabicyclo[2.2.0]hex-5-en-3-one (11)

Et_3N (1.31 mL, 9.42 mmol) and *p*-toluenesulfonic anhydride (2.250 g, 6.90 mmol) were added to a cooled (0 °C) solution of lactam **8** (0.580 g, 6.10 mmol) in CH_2Cl_2 (25 mL). The mixture was stirred for 3 h at r.t. and then diluted with CH_2Cl_2 (10 mL). The solution was successively washed with 1 M aq HCl (3 mL), H_2O (4 mL), and brine (4 mL), dried ($MgSO_4$), and concentrated. The residue was purified by column chromatography (silica gel, cyclohexane–EtOAc, 85:15, then 80:20) to give compound **11** (0.979 g, 64%) as a white powder; mp 106–108 °C.

IR (KBr): 3090, 1788, 1594, 1545, 1169, 1101 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.84 (d, 2 H, C_6H_5, *J* = 8.6 Hz), 7.34 (d, 2 H, C_6H_5, *J* = 8.6 Hz), 6.41 (dd, 1 H, H-5, *J* = 2.5, 1.2 Hz), 6.37–6.34 (m, 1 H, H-6), 4.74 (dd, 1 H, H-1, *J* = 3.0, 2.2 Hz), 4.27–4.25 (m, 1 H, H-4), 2.45 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$): δ = 164.5, 145.3, 141.2, 138.1, 134.9, 129.9, 127.5, 57.9, 55.1, 21.6.

Anal. Calcd for $C_{12}H_{11}NSO_3$: C, 57.82; H, 4.45; N, 5.62. Found: C, 57.71; H, 4.35; N, 5.61.

(2*Z*,4*E*)-5-Acetylaminopenta-2,4-dienoic Acid (12)

LiOH (0.026 g, 1.09 mmol) was added to a solution of compound **9** (0.05 g, 0.36 mmol) in THF (2 mL) and H_2O (1.5 mL). The mixture was stirred at r.t. for 16 h, and the solvent was removed in vacuo. The aqueous layer was acidified with AcOH to pH 4 and extracted with EtOAc (3 mL). The combined extracts were washed with brine (2 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by recrystallization (MeOH) to give compound **12** (0.045 g, 81%) as a yellow powder; mp 183–185 °C.

IR (KBr): 3279, 1683, 1604, 1515, 1213, 994 cm^{-1}.

^1H NMR (DMSO-d_6): δ = 11.97 (s, 1 H, OH), 10.50 (d, 1 H, NH, *J* = 10.7 Hz), 7.32–7.02 (m, 2 H, H-4 and H-5), 6.70 (t, 1 H, H-3, *J* = 11.1 Hz), 5.37 (d, 1 H, H-2, *J* = 11.1 Hz), 1.95 (s, 3 H, $COCH_3$).

^{13}C NMR (DMSO-d_6): δ = 173.2, 173.1, 149.7, 140.1, 118.5, 113.5, 27.9.

Anal. Calcd for $C_7H_9O_3N{\cdot}0.05H_2O$: C, 53.88; H, 5.88; N, 8.98. Found: C, 54.17; H, 6.26; N, 8.41.

(2*Z*,4*E*)-5-Acetylaminopenta-2,4-dienoic Acid Methyl Ester (13)

LiOH (0.039 g, 1.63 mmol) was added to a solution of lactam **9** (0.065 g, 0.47 mmol) in MeOH (5 mL). The mixture was stirred at r.t. for 3 h, and the solvent was removed in vacuo. The residue was dissolved in EtOAc (5 mL), successively washed with H_2O (2 mL) and brine (2 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, cyclohexane–EtOAc, 3:2) to give compound **13** (0.072 g, 90%) as a yellow oil.

IR (KBr): 3352, 1683, 1578, 1433, 1250, 1128 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 8.32 (d, 1 H, NH, *J* = 10.8 Hz), 7.33 (dd, 1 H, H-5, *J* = 14.2, 10.8 Hz), 7.18 (dd, H, H-4, *J* = 14.2, 11.3 Hz), 6.62 (t, 1 H, H-3, *J* = 11.3 Hz), 5.57 (d, 1 H, H-2, *J* = 11.3 Hz), 3.71 (s, 3 H, OCH_3), 2.12 (s, 3 H, $COCH_3$).

^{13}C NMR ($CDCl_3$): δ = 168.1, 167.6, 144.1, 133.8, 113.7, 109.2, 51.1, 23.3.

Anal. Calcd for $C_8H_{11}NO_3{\cdot}0.1H_2O$: C, 56.20; H, 6.60; N, 8.19. Found: C, 55.01; H, 6.63; N, 8.19.

(2*E*,4*E*)-5-Benzylaminopenta-2,4-dienoic Acid Methyl Ester (14)

LiOH (0.156 g, 6.53 mmol) was added to a solution of lactam **10** (0.400 g, 2.18 mmol) in anhyd MeOH (30 mL). The mixture was stirred at r.t. for 4 h, and the solvent was removed in vacuo. The residue was dissolved in EtOAc (10 mL), successively washed with H_2O (4 mL) and brine (4 mL), dried ($MgSO_4$), and concentrated in vacuo to give compound **14** (0.444 g, 94%) as an orange solid (^1H NMR estimated purity >95%). Degradation was observed in the course of column chromatography on silica gel; mp 72–74 °C.

IR (KBr): 3362, 1732, 1615, 1455 cm^{-1}.

^1H NMR ($CDCl_3$): δ = 7.41–7.27 (m, 6 H, 5 H_{arom} and H-3), 6.80 (dd, 1 H, H-5, *J* = 12.6, 7.6 Hz), 5.48 (d, 1 H, H-2, *J* = 14.8 Hz), 5.35 (dd, 1 H, H-4, *J* = 12.6, 11.6 Hz), 4.46 (d, 1 H, NH, *J* = 7.6 Hz), 4.23 (AB system, 2 H, CH_2 benzyl, *J* = 5.5 Hz), 3.68 (s, 3 H, CH_3).

^{13}C NMR ($CDCl_3$): δ = 169.1, 147.6, 146.3, 137.5, 128.5, 127.7, 127.5, 108.0, 97.8, 50.8, 48.5.

HRMS: *m*/*z* calcd for $[(C_{13}H_{15}NO_2]^+$: 217.1102; found: 217.1101.

(2*Z*,4*E*)-5-Acetylaminopenta-2,4-dienol (15)

A solution of compound **9** (0.295 g, 2.15 mmol) in anhyd THF (2 mL) was added to a suspension of $LiAlH_4$ (0.245 g, 6.45 mmol) in anhyd THF (10 mL) at –78 °C. The mixture was stirred for 6 h while the temperature was slowly allowed to warm to –20 °C. An aq solution of 2 M KOH (2.5 mL) was then added while the temperature was slowly allowed to warm to 20 °C and then the salts were filtered, and successively rinsed with Et_2O (5 mL) and CH_2Cl_2 (5 mL). The solvents were concentrated in vacuo and the residue was dissolved in CH_2Cl_2 (5 mL) then dried ($MgSO_4$). The solvent was concentrated under reduced pressure. The mixture of *N*-[4-(hydroxymethyl)cyclobut-2-enyl]acetamide and **15** in a 1:1 ratio was refluxed in toluene for 40 min to totally convert the cyclobutene compound into diene **15**. Purification by column chromatography on silica gel (CH_2Cl_2–MeOH, 95:5) provided compound **15** (0.188 g, 62%) as a pale yellow powder; mp 120–122 °C.

IR (KBr): 3310–3100, 1670, 1614, 1529, 1380 cm^{-1}.

^1H NMR (CD_3OD): δ = 6.91 (d, 1 H, H-5, *J* = 13.8 Hz), 6.16 (dd, 1 H, H-4, *J* = 13.8, 11.2 Hz), 6.03 (dd, 1 H, H-3, *J* = 11.2, 11.1 Hz), 5.51–5.37 (m, 1 H, H-2), 4.19 (d, 2 H, CH_2, *J* = 6.8 Hz), 2.00 (s, 3 H, $COCH_3$).

^{13}C NMR (CD_3OD): δ = 172.2, 130.7, 130.0, 129.8, 111.4, 60.5, 24.2.

Anal. Calcd for $C_7H_{11}NO_2$: C, 59.56; H, 7.85; N, 9.92. Found: C, 59.21; H, 7.65; N, 9.68.

(2*E*,4*E*)-5-Aminopenta-2,4-dienoic Acid Methyl Ester (16)

LiOH (0.549 g, 22.9 mmol) was added to a solution of lactam **8** (0.630 g, 6.62 mmol) in anhyd MeOH (40 mL). The mixture was stirred at r.t. for 4 h, and the solvent was removed in vacuo. The residue was dissolved in EtOAc (10 mL), successively washed with H_2O (5 mL) and brine (5 mL), dried ($MgSO_4$), and concentrated in vacuo to give compound **16** (0.840 g, 99%) as a yellow oil (^{1}H NMR estimated purity >95%) which was immediately used in the next step (degradation was observed in the course of column chromatography on silica gel).

IR (KBr): 3352, 1683, 1578, 1433, 1250, 1128 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.32–7.28 (m, 1 H, H-2), 6.70 (dt, 1 H, H-5, *J* = 12.8, 10.3 Hz), 5.50–5.48 (m, 1 H, H-3), 5.47–5.45 (m, 1 H, H-4), 4.18 (br s, 2 H, NH_2), 3.69 (s, 3 H, OCH_3).

^{13}C NMR ($CDCl_3$): δ = 169.0, 146.8, 144.5, 109.1, 101.7, 51.0.

This poorly stable compound was identified based on the NMR data and to the full identification of its acetyl derivative **17.**

(2*E*,4*E*)-5-Acetylaminopenta-2,4-dienoic Acid Methyl Ester (17)

Et_3N (0.06 mL, 0.43 mmol), Ac_2O (0.15 mL, 1.5 mmol), and DMAP (0.052 g, 0.43 mmol) were added to a cooled (0 °C) solution of diene **16** (0.110 g, 0.86 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was stirred at r.t. for 4 h and then diluted with CH_2Cl_2 (1 mL). The solution was successively washed with 1 M aq HCl (1 mL), H_2O (1 mL) and brine (1 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, cyclohexane–EtOAc, 3:2) to give compound **17** (0.083 g, 57%) as a yellow powder; mp 130–132 °C.

IR (KBr): 3304, 1710, 1681, 1614, 1252, 1238, 1136 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 8.40 (d, 1 H, NH, *J* = 10.8 Hz), 7.39–7.23 (m, 2 H, H-3 and H-5), 5.91 (dd, 1 H, H-4, *J* = 14.3, 11.3 Hz), 5.75 (d, 1 H, H-2, *J* = 15.3 Hz), 3.73 (s, 3 H, OCH_3), 2.12 (s, 3 H, $COCH_3$).

^{13}C NMR ($CDCl_3$): δ = 168.1, 167.8, 143.9, 133.1, 117.5, 110.2, 51.5, 23.3.

Anal. Calcd for $C_8H_{11}NO_3 \cdot 0.1H_2O$: C, 56.20; H, 6.60; N, 8.19. Found: C, 56.06; H, 6.41; N, 7.89.

(2*E*,4*E*)-5-Diacetylaminopenta-2,4-dienoic Acid Methyl Ester (18)

Et_3N (0.015 mL, 0.10 mmol), Ac_2O (0.024 mL, 0.24 mmol), and DMAP (0.012 g, 0.10 mmol) were added to a cooled (0 °C) solution of diene **17** (0.035 g, 0.20 mmol) in CH_2Cl_2 (3 mL). The reaction mixture was stirred at r.t. for 4 h and then diluted with CH_2Cl_2 (1 mL). The solution was successively washed with 1 M aq HCl (1 mL), H_2O (1 mL), and brine (1 mL), dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by column chromatography (silica gel, cyclohexane–EtOAc, 3:2) to give compound **18** (0.025 g, 60%) as a yellow solid; mp 59–61 °C.

IR (KBr): 2955, 1708, 1633, 1427, 1367, 1323 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.36 (dd, 1 H, H-3, *J* = 15.2, 11.2 Hz), 6.84 (d, 1 H, H-5, *J* = 14.0 Hz), 6.19 (dd, 1 H, H-4, *J* = 14.0, 11.2 Hz), 5.96 (d, 1 H, H-2, *J* = 15.2 Hz), 3.77 (s, 3 H, OCH_3), 2.39 (s, 6 H, 2 $COCH_3$).

^{13}C NMR ($CDCl_3$): δ = 172.1, 166.8, 140.7, 134.0, 126.4, 122.7, 51.7, 26.0.

Anal. Calcd for $C_{10}H_{13}NO_4$: C, 56.87; H, 6.20; N, 6.63. Found: C, 56.52; H, 6.04; N, 6.41.

(2*E*,4*E*)-5-(Acetyl-*tert*-butoxycarbonylamino)penta-2,4-dienoic Acid Methyl Ester (19)

Et_3N (0.021 mL, 0.15 mmol), Boc_2O (0.063 g, 0.29 mmol), and DMAP (0.018 g, 0.15 mmol) were added to a cooled (0 °C) solution of diene **17** (0.040 g, 0.23 mmol) in CH_2Cl_2 (2 mL). The reaction mixture was stirred at r.t. for 16 h and then diluted with CH_2Cl_2 (2 mL). The solution was successively washed with 1 M aq HCl (1 mL), H_2O (1 mL) and brine (1 mL), dried ($MgSO_4$), and concentrated in vacuo. The residue was purified by column chromatography (silica gel, cyclohexane–EtOAc, 7:3) to give compound **19** (0.040 g, 64%) as a white powder; mp 84–86 °C.

IR (KBr): 2978, 1712, 1629, 1332, 1143 cm^{-1}.

^{1}H NMR ($CDCl_3$): δ = 7.31 (dd, 1 H, H-3, *J* = 15.2, 11.3 Hz), 7.04 (d, 1 H, H-5, *J* = 14.2 Hz), 6.40 (dd, 1 H, H-4, *J* = 14.2, 11.3 Hz), 5.88 (d, 1 H, H-2, *J* = 15.2 Hz), 3.74 (s, 3 H, OCH_3), 2.44 (s, 3 H, $COCH_3$), 1.57 [s, 9 H, $C(CH_3)_3$].

^{13}C NMR ($CDCl_3$): δ = 171.0, 167.3, 151.6, 143.4, 132.9, 120.0, 118.7, 85.2, 51.5, 27.8, 26.0.

Anal. Calcd for $C_{13}H_{19}NO_5$: C, 57.98; H, 7.11; N, 5.20. Found: C, 57.94; H, 7.03; N, 4.94.

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