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SUPPORTING INFORMATION

Title: Hydrolytic Deallylation of *N*-Allyl Amides Catalyzed by Pd^{II} Complexes
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Ref. No.: O200800771

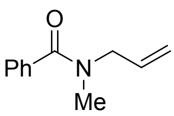
General

^1H and ^{13}C NMR spectra were recorded on a JEOL AL-400 spectrometer. GC analysis was carried out using an Agilent GC 6850 equipped with J & W INNOWax Column (length 30 m, 0.25 mm I.D.). GC-MS analysis was performed with a Thermo Fisher Scientific Polaris Q equipped with a Trace TR-5 Column (length 7 m, 0.32 mm I.D.). HPLC analysis was performed with a JASCO PU-1580 with UV-1575 chromatograph equipped with a DAICEL CHIRALCEL OD-H (eluent: hexane:2-propanol = 20:1). Optical rotations were measured with a Horiba SEPA-300 poralimeter. All compounds are known except for **12** and **19**. Characterization of **12** and **19** is given in following part. Compound **20** was purchased form Wako Chemical. All amide products were commercially available and characterized by GC and GC-MS analysis except for following three compounds. β-Butyrolactam was synthesized by a literature procedure.[1] (*S*)-*N*-(1-Phenylethyl)acetamide was synthesized from (*S*)-1-phenylethylamine and acetyl chloride. (*S*)-2-*tert*-Butoxycarbonylamino-3-phenylpropionic acid methyl ester was synthesized from L-phenylalanine methyl ester and Boc_2O. $H_2{}^{18}O$ was purchased from Taiyo Nippon Sanso (^{18}O: 99 atm%, lot: YEH0027A).

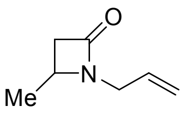
Syntheses of N-allyl amide substrates

Typical procedure for the synthesis of *N*-allyl amides (**1**, **5**–**13**, **15**–**18**): Under N_2 atmosphere, an amide was added to a suspension of sodium hydride (1.1–1.5 equiv.) in THF at 0 °C and stirred for 10–60 min at 0–60 °C. Then allyl bromide (1.1–2.0 equiv.) was added at 0 °C, and the mixture was stirred overnight at 20–85°C. Water was added, and the product was extracted with diethyl ether, then the extracts were dried over sodium sulfate. The solvents were removed and the residue was subjected to column chromatography on silica-gel to afford an *N*-allylamide.

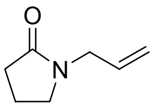
***N*-Allyl-*N*-methylbenzamide** (**1**): prepared from *N*-methylbenzamide (4.05 g, 30 mmol), yield: 5.32 g (quant.). Existing as a 3:2 mixture of rotamers. ^1H NMR ($CDCl_3$, 400 MHz) δ = 2.90 (bs, 3H, minor, CH_3), 3.05 (bs, 3H, major, CH_3), 3.83 (bs, 2H, major, NCH_2), 4.15 (bs, 2H, minor, NCH_2), 5.18–5.25 (m, 2H, $CH{=}CH_2$), 5.68–5.80 (m, 1H, major, $CH{=}CH_2$), 5.80–5.94 (m, 1H, minor, $CH{=}CH_2$), 7.34–7.44 (m, 5H, aromatic).



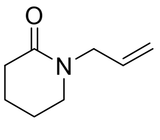
***N*-Allyl-β-butyrolactam** (**5**): prepared from β-butyrolactam (1.67 mL, 20 mmol), yield: 1.55 g (62%). ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.30–1.35 (m, 3H, CH_3), 2.48–2.55 (m, 1H, $CHHCO$), 3.04–3.12 (m, 1H, $CHHCO$), 3.60–3.69 (m, 1H, $NCHH$), 3.69–3.72 (m, 1H, $CHCH_3$), 3.94–4.00 (m, 1H, $NCHH$), 5.16–5.25 (m, 2H, $CH{=}CH_2$), 5.74–5.81 (m, 1H, $CH{=}CH_2$).



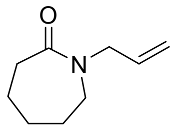
***N*-Allyl-γ-butyrolactam** (**6**): prepared from γ-butyrolactam (4.00 g, 47 mmol), yield: 6.11 g (quant.). ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.98–2.07 (m, 2H, $CH_2CH_2CH_2$), 2.41(t, J = 8.0 Hz, 2H, $COCH_2$), 3.35 (t, J = 7.2 Hz, 2H, NCH_2CH_2), 3.89 (d, J = 6.0 Hz, 2H, $NCH_2CH{=}CH_2$), 5.15–5.18 (m, 1H, $CH{=}CHH$), 5.19–5.21 (m, 1H, $CH{=}CHH$), 5.69–5.78 (ddt, J = 17.2, 10.0, 6.0 Hz, 1H, $CH{=}CH_2$).



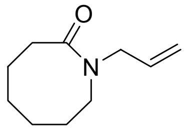
***N*-Allyl-δ-valerolactam** (**7**): prepared from δ-valerolactam (4.66 g, 47 mmol), yield: 6.51 g (99%). ^1H NMR ($CDCl_3$, 400 MHz) δ = 1.77–1.83 (m, 4H, $CH_2(CH_2)_2CH_2$), 2.38–2.42 (m, 2H, $COCH_2$), 3.23–3.25 (m, 2H, NCH_2CH_2), 3.97–4.01 (m, 2H, $NCH_2CH{=}CH_2$), 5.15 (dd, J = 16.8, 1.6 Hz, 1H, $CH{=}CHH$), 5.17 (dd, J = 10.4, 1.6 Hz, 1H, $CH{=}CHH$), 5.76 (ddt, J = 16.8, 10.4, 6.0 Hz, 1H, $CH{=}CH_2$).



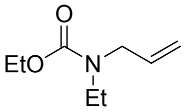
***N*-Allyl-ε-caprolactam** (**8**): prepared from ε-caprolactam (10.62 g, 94 mmol), yield: 6.51 g (99%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.60–1.74 (m, 6H, $CH_2(C\mathit{H}_2)_3CH_2$), 2.53–2.56 (m, 2H, $COC\mathit{H}_2$), 3.29–3.31 (m, 2H, $NC\mathit{H}_2CH_2$), 4.01 (ddd, *J* = 6.0, 1.4, 1.4 Hz, 2H, $NC\mathit{H}_2CH{=}CH_2$), 5.12–5.14 (m, 1H, $CH{=}CH\mathit{H}$), 5.15–5.19 (m, 1H, $CH{=}C\mathit{H}H$), 5.76 (ddt, *J* = 16.8, 10.4, 6.0 Hz, 1H, $C\mathit{H}{=}CH_2$).



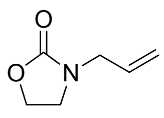
***N*-Allyl-ω-heptanolactam** (**9**): prepared from ω-heptanolactam (3.82 g, 30 mmol), yield: 6.09 g (99%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.45–1.85 (m, 8H, $CH_2(C\mathit{H}_2)_4CH_2$), 2.48–2.54 (m, 2H, $COC\mathit{H}_2$), 3.45–3.48 (m, 2H, $NC\mathit{H}_2CH_2$), 3.99 (d, *J* = 6.0 Hz, 2H, $NC\mathit{H}_2CH{=}CH_2$), 5.13–5.19 (m, 2H, $CH{=}C\mathit{H}_2$), 5.76–5.84 (ddt, *J* = 17.2, 10.4, 6.0 Hz, 1H, $C\mathit{H}{=}CH_2$).



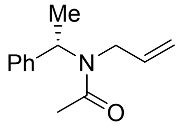
Ethyl *N*-allyl-*N*-ethylcarbamate (**10**): prepared from ethyl *N*-ethylcarbamate (4.78 g, 30 mmol), yield: 4.23 g (67%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.10 (t, *J* = 7.2 Hz, 3H, $NCH_2C\mathit{H}_3$), 1.25 (t, *J* = 7.2 Hz, 3H, $OCH_2C\mathit{H}_3$), 3.27 (bs, 2H, $NC\mathit{H}_2CH_3$), 3.86 (bs, 2H, $NC\mathit{H}_2CH{=}CH_2$), 4.14 (q, *J* = 7.2 Hz, 2H, $OC\mathit{H}_2CH_3$), 5.09–5.18 (m, 2H, $CH{=}C\mathit{H}_2$), 5.73–5.84 (m, 1H, $C\mathit{H}{=}CH_2$).



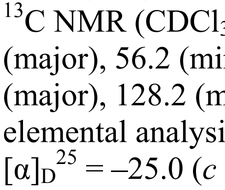
***N*-Allyloxazolidinone** (**11**): prepared from oxazolidinone (3.48 g, 40 mmol), yield: 2.75 g (54%). ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 3.54 (dt, *J* = 1.6, 8.0 Hz, 2H, $NC\mathit{H}_2CH_2$), 3.87 (d, *J* = 6.0 Hz, 2H, $NC\mathit{H}_2CH{=}CH_2$), 4.34 (dt, *J* = 1.2, 8.0 Hz, 2H, $OC\mathit{H}_2$), 5.24–5.32 (m, 2H, $CH{=}C\mathit{H}_2$), 5.75–5.80 (m, 1H, $C\mathit{H}{=}CH_2$).



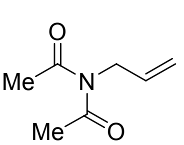
(*S*)-*N*-Allyl-*N*-(1-phenylethyl)acetamide (**12**): prepared from (*S*)-*N*-(1-phenylethyl)acetamide (4.8 g, 30 mmol), yield: 0.98 g (16%). Existing as a 3:1 mixture of rotamers. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.49 (d, *J* = 7.2 Hz, 3H, major, $CHC\mathit{H}_3$), 1.62 (d, *J* = 7.2 Hz, 3H, minor, $CHC\mathit{H}_3$), 2.12 (s, 3H, major, CH_3CO) , 2.22 (s, 3H, minor, CH_3CO), 3.44 (dd, *J* = 6.4, 15.6 Hz, 1H, minor, $NCH\mathit{H}CH{=}CH_2$), 3.54–3.74 (m, 2H, major, $NC\mathit{H}_2CH{=}CH_2$), 4.12 (dd, *J* = 4.8, 15.6 Hz, 1H, minor, $NC\mathit{H}HCH{=}CH_2$), 4.96–5.13 (m, 2H, major and minor, $CH{=}C\mathit{H}_2$, and 1H, minor, $C\mathit{H}CH_3$), 5.56 (ddt, *J* = 17.2, 10.4, 5.2 Hz, 1H, major, $C\mathit{H}{=}CH_2$), 5.77 (ddt, *J* = 16.4, 10.4, 6.0 Hz, 1H, minor, , $C\mathit{H}{=}CH_2$), 6.11 (q, *J* = 7.2 Hz, 1H, major, $C\mathit{H}CH_3$), 7.22–7.38 (m, 5H, aromatic), ^{13}C NMR ($CDCl_3$, 150 MHz) δ = 16.5 (major), 18.6 (minor), 21.9, 45.1 (minor), 46.5 (major), 50.7 (major), 56.2 (minor) 115.7 (minor), 116.1(major), 126.4 (minor), 127.1 (major), 127.3 (minor), 128.0 (major), 128.2 (major), 128.5 (minor), 134.9, 140.5 (minor), 140.8 (major), 170.1(minor), 171.0 (major); elemental analysis: calcd (%) for $C_{13}H_{17}NO$: C 76.81, H 8.43, N 6.89; found: C 76.86, H 8.51, N 6.92; $[\alpha]_D^{25}$ = –25.0 (*c* = 1.00, $CHCl_3$).



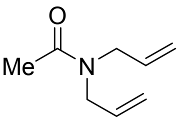
(*S*)-2-(Allyl-*tert*-butoxycarbonylamino)-3-phenylpropionic acid methyl ester (**13**): prepared from (*S*)-2-*tert*-butoxycarbonylamino-3-phenylpropionic acid methyl ester (8.3 g, 30 mmol), using potassium carbonate instead of sodium hydride, yield: 2.14 g (22%). Existing as a 2:1 mixture of rotamers. ^{1}H NMR ($CDCl_3$, 400 MHz) δ = 1.39–1.50 (bs, 9H, major and minor, $C(C\mathit{H}_3)_3$), 3.10–3.40, 3.73–4.12 (m, 2H, major and minor, $PhC\mathit{H}_2$, 2H major and minor, $NC\mathit{H}_2CH{=}CH_2$, and 1H major, $NC\mathit{H}$), 3.70–3.72 (bs, 3H, major and minor, $OC\mathit{H}_3$), 4.37–4.43(m, 1H, minor, $NC\mathit{H}$), 4.96–5.03 (m, 2H, major and minor, $CH{=}C\mathit{H}_2$), 5.45–5.58 (m, 1H, major and minor, $C\mathit{H}{=}CH_2$), 7.13–7.31 (m, 5H, aromatic); $[\alpha]_D^{25}$ = 50.5 (*c* = 1.00, $CHCl_3$).



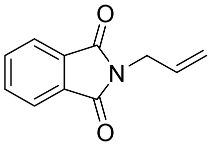
***N*-Allyldiacetamide** (**15**): obtained as a byproduct of **14,** see synthesis of **14** (4.05 g, 30 mmol), yield: 3.74 g (6%). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) $\delta = 2.42$ (s, 6H, $\mathrm{COC}H_3$), 4.34–4.35 (m, 2H, $\mathrm{NC}H_2\mathrm{CH{=}CH_2}$), 5.12 (ddd, *J* = 17.2, 0.8, 0.8 Hz, 1H, $\mathrm{CH{=}C}H\mathrm{H}$), 5.20 (ddd, *J* = 10.4, 0.8, 0.8 Hz, 1H, $\mathrm{CH{=}CH}H$) 5.84 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H, $\mathrm{C}H\mathrm{{=}CH_2}$).



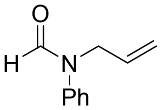
***N,N*-Diallylacetamide** (**16**): prepared from *N*-allylacetamide **14** (4.5 mL, 40 mmol), yield: 1.77 g (31%). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) $\delta = 2.10$ (s, 3H, $\mathrm{COC}H_3$), 3.87 (d, *J* = 4.8 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH{=}CH_2}$), 3.99 (d, *J* = 6.4 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH{=}CH_2}$), 5.10–5.23 (m, 4H, $\mathrm{CH{=}C}H_2$), 5.70–5.83 (m, 2H, $\mathrm{C}H\mathrm{{=}CH_2}$).



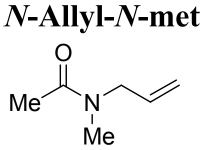
***N*-Allylphthalimide** (**17**): prepared from phthalimide (5.89 g, 40 mmol), yield: 2.14 g (45%) ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) $\delta = 4.28$–4.32 (m, 2H, $\mathrm{NC}H_2\mathrm{CH{=}CH_2}$), 5.18–5.22 (m, 1H, $\mathrm{CH{=}CH}H$), 5.22–5.29 (m, 1H, $\mathrm{CH{=}C}H\mathrm{H}$), 5.85–5.95 (m, 1H, $\mathrm{C}H\mathrm{{=}CH_2}$), 7.72–7.74 (m, 2H, aromatic), 7.85–7.87 (m, 2H, aromatic).



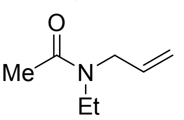
***N*-Allylformanilide** (**18**): prepared from formanilide (4.85 g, 40 mmol), yield: 5.32 g (quant.). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) $\delta = 4.42$ (dd, *J* = 5.6, 0.8 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH{=}CH_2}$), 5.14–5.23 (m, 2H, $\mathrm{CH{=}C}H_2$), 5.80–5.90 (m, 1H, $\mathrm{C}H\mathrm{{=}CH_2}$), 7.18–7.41 (m, 5H, aromatic), 8.48 (s, 1H, $\mathrm{C}H\mathrm{O}$).

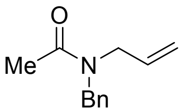


***N*-Allyl-*N*-methylacetamide** (**2**): *N*-Allylacetamide **14** (2.3 mL, 20 mmol) was added to a suspension of sodium hydride (1.8 g, 45 mmol) in THF at 0 °C and stirred for 1 h, and then methyl iodide (25.0 mL, 400 mmol) was added to this solution at 0 °C. Then, the mixture was refluxed overnight. Water was added, and the product was extracted with ethyl acetate. The extracts were dried over sodium sulfate, the solvents were removed, and the residue was subjected to column chromatography on silica-gel. The elution with ethylacetate-hexane mixture (10:1) afforded **2** (3.58 g, 99%). ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) $\delta = 2.01$–2.11 (m, 3H, $\mathrm{COC}H_3$), 2.85–2.96 (m, 3H, $\mathrm{NC}H_3$), 3.83–4.00 (m, 2H, $\mathrm{NC}H_2\mathrm{CH{=}CH_2}$), 5.05–5.24 (m, 2H, $\mathrm{CH{=}C}H_2$), 5.65–5.84 (m, 1H, $\mathrm{C}H\mathrm{{=}CH_2}$).

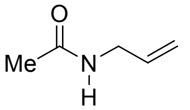


***N*-Allyl-*N*-ethylacetamide** (**3**): *N*-Allylacetamide **14** (4.5 mL, 40 mmol) was added to a suspension of sodium hydride (1.8 g, 48 mmol) in THF at 0 °C and stirred for 1 h, and then ethyl iodide (6.4 mL, 80 mmol) was added to this solution at 0 °C. Then the mixture was refluxed overnight at 80 °C. Water was added, and the product was extracted with diethylether. The extracts were dried over sodium sulfate, the solvents were removed, and the residue was subjected to column chromatography on silica-gel. The elution with diethylether-hexane mixture (10:1) afforded **3** (1.60 g, 31%). Existing as a 1:1 mixture of rotamers. ^{1}H NMR ($\mathrm{CDCl_3}$, 400 MHz) $\delta =$ 1.11, 1.17 (two sets of t, *J* = 7.2 Hz, 3H, $\mathrm{NCH_2C}H_3$), 2.06, 2.12 (two sets of s, 3H, $\mathrm{COC}H_3$), 3.31, 3.39 (two sets of q, *J* = 7.2 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH_3}$), 3.88, 3.98 (two sets of d, *J* = 6.0 Hz, 2H, $\mathrm{NC}H_2\mathrm{CH{=}CH_2}$), 5.12–5.23 (m, 2H, $\mathrm{CH{=}C}H_2$), 5.72–5.84 (m, 1H, $\mathrm{C}H\mathrm{{=}CH_2}$).



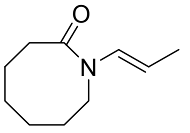


_N_-Allyl-_N_-benzylacetamide (**4**): *N*-Allylacetamide **14** (4.5 mL, 40 mmol) was added to a suspension of sodium hydride (1.8 g, 45 mmol) in THF at 0 °C and stirred for 1 h, and then benzyl bromide (6.5 mL, 55 mmol) was added to this solution at 0 °C. Then the mixture was refluxed overnight at 75 °C. Water was added, and the product was extracted with ethyl acetate. The extracts were dried over sodium sulfate, the solvents were removed, and the residue was subjected to column chromatography on silica-gel. The elution with diethylether-hexane mixture (2:1) afforded **4** (6.63 g, 78 %). Existing as a 3:2 mixture of rotamers. ^{1}H NMR (CDCl$_3$, 400 MHz), δ = 2.14 (s, 3H, minor, COC*H*$_3$), 2.15 (s, 3H, major, COC*H*$_3$), 3.81 (d, *J* = 4.4 Hz, 2H, major, NC*H*$_2$CH=CH$_2$), 4.01 (d, *J* = 6.0 Hz, 2H, minor, NC*H*$_2$CH=CH$_2$), 4.50 (s, 1H, minor, PhC*H*$_2$), 4.59 (s, 1H, major, PhC*H*$_2$), 5.07–5.23 (m, 2H, major and minor, CH=C*H*$_2$), 5.67–5.83 (m, 1H, major and minor, C*H*=CH$_2$), 7.15–7.38 (m, 5H, aromatic).



_N_-Allylacetamide (**14**): Allylamine (33 mL, 430 mmol) was added dropwise with stirring to acetic anhydride (70 mL, 735 mmol) at 0 °C. After the addition was completed (~1 h) the temperature was raised to 100 °C for 1.5 h. The solvents were removed, and the residue was subjected to column chromatography on silica-gel. The elution with dichloromethane-hexane mixture (10:1) afforded **14** (41.7 g, 98%). ^{1}H NMR (CDCl$_3$, 400 MHz) δ = 2.01 (s, 3H, COC*H*$_3$), 3.86–3.88 (m, 2H, NC*H*$_2$CH=CH$_2$), 5.13 (d, *J* = 10.4 Hz, 1H, CH=CH*H*), 5.19 (d, *J* = 16.8 Hz, 1H, CH=C*H*H), 5.75 (bs, 1H, N*H*), 5.84 (ddt, *J* = 16.8, 10.4, 5.6 Hz, 1H, C*H*=CH$_2$).

Ru-catalyzed isomerization of 9



_N_-((_E_)-1-Propenyl)-ω-heptanolactam (**19**): *N*-Allyl-ω-heptanolactam **9** (1.8 mL, 10 mmol) and toluene (10 mL) were placed into a dry nitrogen filled 50 mL Schlenk tube, and the vessel was degassed by three freeze-thaw cycles. To this was added RuCl$_2$(PPh$_3$)$_3$ under N$_2$ atmosphere. The mixture was refluxed for 20 h at 110 °C. The solvents were removed, and residue was subjected to column chromatography on silica-gel. The elution with diethylether-hexane mixture (1:1) afforded **19** (1.60 g, 96%). The olefin geometry was determined by coupling constants of ^{1}H NMR. ^{1}H NMR (CDCl$_3$, 400 MHz) δ = 1.42–1.87 (m, 8H, CH$_2$(C*H*$_2$)$_4$CH$_2$), 1.73 (dd, *J* = 6.4, 1.6 Hz, 3H, C*H*$_3$), 2.55–2.60 (m, 2H, COC*H*$_2$), 3.74 (t, *J* = 6.0 Hz, 2H, NC*H*$_2$), 5.09 (dq, *J* = 14.4, 6.4 Hz, 1H, C*H*CH$_3$), 7.19 (dd, *J* = 14.4, 1.6 Hz, 1H, NC*H*=CH); ^{13}C NMR (CDCl$_3$, 150 MHz) δ = 15.2, 23.8, 26.2, 27.7, 28.8, 34.3, 43.5, 105.9, 125.7, 172.8; elemental analysis: calcd (%) for $C_{10}H_{17}NO$: C 71.81, H 10.25, N 8.37; found: C 71.84, H 10.28, N 8.27.

^{18}O-labeled experiment

Hydrolytic deallylation with $H_2{}^{18}O$ was carried out with **8**: propanal was analyzed by GC-MS: *m*/*z* calcd for $C_3H_7{}^{18}O$: 61.1 [*M*+H]$^+$; found 61.0; *m*/*z* calcd for $C_3H_5{}^{18}O$: 59.0 [*M*–H]$^+$; found 59.0. cf. the reaction with H_2O; GC-MS: *m*/*z* calcd for C_3H_7O: 59.0 [*M*+H]$^+$; found 59.0; *m*/*z* calcd for C_3H_5O: 57.0 [*M*–H]$^+$; found 57.0. In both cases, same fragments 42.3 (C_3H_6) and 40.1 (C_3H_4) was observed.

Reference

[1] M. F. Loewe, R. J. Cvetovich, G. G. Hzen, *Tetrahedron Lett.* **1991**, *32*, 2299–2302.