Supporting Information
for DOI: 10.1055/s-0037-1611061
© Georg Thieme Verlag KG Stuttgart · New York 2018
Electronic Supporting Information

Straightforward Synthesis of Triester-Substituted Pyrrolizidines by a Three-Component Reaction of $\beta,\gamma$-Unsaturated $\alpha$-Keto Esters, Proline, and Maleates

Lian-Mei Chen,*, a Zhi-Hui Liu, b Xu-Feng Nie, b Xiao-Qiang Guo a and Tai-Ran Kang*, a, b

a College of Pharmacy and Biological Engineering, Chengdu University,
Chengdu city 610106, P. R. China.
b College of Chemistry and Chemical Engineering, China West Normal University, Nanchong city 637002, P. R. China.

E-mail: Chenlianmei845@163.com; kangtairan@sina.com

Table of Contents

1. General remarks.................................................................S2
2. General procedure.............................................................S3
3. Spectra data of products 4a-n..............................................S4
4. NMR spectra of compounds 4a-n .......................................S9
5. Crystal data for compound 4f.............................................S23
1. General remarks

Unless otherwise noted, all the materials were purchased from commercial suppliers and used as received. Solvents used in the reactions were distilled from appropriate drying agents prior to use. $^1$H NMR and $^{13}$C spectra were recorded respectively at 400 or 600 MHz and 100 MHz or 150 MHz, respectively. Data for $^1$H NMR were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiple), integration, coupling constant (Hz). Data for $^{13}$C NMR were reported in terms of chemical shift. Electrospray mass spectra (ESIMS) were obtained from an LCT Premier XE using electrospray ionization coupled with a time of flight analyzer (ESI-TOF). The β,γ-Unsaturated keto esters used here are known compounds and prepared according to the reported procedure.$^{[1]}$
2. General procedure

2.1 General procedure for synthesis of pyrrolizidine derivatives 4a-n

To a solution of racemic proline 2 (0.12 mmol) in DMF (1 mL) was added $\beta,\gamma$-unsaturated keto ester 1 (0.1 mmol) and maleic acid ester 3 (0.3 mmol). The reaction mixture was stirred at 80 °C until the reaction was complete (monitored by TLC). After cooling to room temperature, 5 mL H$_2$O and 5 mL EtOAc were added and the mixture was well stirred for 5 min. The organic layer was separated and the aqueous layer extracted with EtOAc (2×10 mL). The organic phase was washed with brine and dried over anhydrous Na$_2$SO$_4$, and then evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the pure cycloaddition products 4a-n.

2.2 General procedure for scaled-up synthesis of pyrrolizidine derivative 4f

To a solution of racemic proline 2 (6.0 mmol) in DMF (5 mL) was added methyl (E)-4-(4-bromophenyl)-2-oxobut-3-enoate (5.0 mmol) and maleic acid ester 3 (15.0 mmol). The reaction mixture was stirred at 80 °C until the reaction was complete (monitored by TLC). After cooling to room temperature, 25 mL H$_2$O and 25 mL EtOAc were added and the mixture was well stirred for 5 min. The organic layer was separated and the aqueous layer extracted with EtOAc (2×30 mL). The organic phase was washed with brine and dried over anhydrous Na$_2$SO$_4$, and then evaporated under reduced pressure. The residue was purified by flash column chromatography on silica gel to give the pure cycloaddition product 4f (1.86g, 80% yield).
3. Spectra data of the products 4a-n

**trimethyl 3-styryl-hexahydro-1H-pyrrolizine-1,2,3-tricarboxylate (4a):**

![Chemical structure of 3-styryl-hexahydro-1H-pyrrolizine-1,2,3-tricarboxylate](image)

yield 85%, (Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1); **1H NMR** (400MHz, CDCl₃): (ppm) 7.26-7.29 (m, 2H), 7.22-7.24 (m, 2H), 7.19-7.21 (m, 1H), 6.45 (d, J = 16.4 Hz, 1H), 6.08 (d, J = 16.4 Hz, 1H), 4.25 (d, J = 11.4 Hz, 1H), 3.78 (s, 3H), 3.65 (s, 3H), 3.60-3.64 (m, 1H), 3.53 (s, 3H), 3.15-3.20 (m, 1H), 2.99-3.06 (m, 1H), 2.73-2.78 (m, 1H), 1.97-2.03 (m, 1H), 1.77-1.84 (m, 2H), 1.64-1.72 (m, 1H); **13C NMR** (100MHz, CDCl₃): (ppm) 172.2, 171.2, 136.2, 133.9, 128.8, 128.2, 126.6, 125.0, 76.7, 73.8, 66.8, 56.6, 52.6, 52.2, 51.1, 47.3, 31.4, 1.02; ESI-HRMS for C_{21}H_{25}NO_{6} (M+H)^+: 388.1682, Found: 388.1755.

**3-ethyl 1, 2-dimethyl 3-styryl-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4b):**

yield 80%, (Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1); **1H NMR** (600MHz, CDCl₃): (ppm) 7.26-7.27 (m, 2H), 7.23-7.26 (m, 2H), 7.17-7.19 (m, 1H), 6.45 (d, J = 16.4 Hz, 1H), 6.08 (d, J = 16.4 Hz, 1H), 4.23-4.25 (m, 1H), 4.19-4.22 (m, 2H), 3.65 (s, 3H), 3.60-3.63 (m, 1H), 3.53 (s, 3H), 3.16-3.20 (m, 1H), 3.00-3.04 (m, 1H), 2.73-2.77 (m, 1H), 1.97-2.01 (m, 1H), 1.77-1.82 (m, 2H), 1.63-1.68 (m, 1H), 1.26 (t, J = 7.2 Hz, 3H); **13C NMR** (150MHz, CDCl₃): (ppm) 172.3, 171.6, 171.3, 136.4, 133.7, 128.6, 128.1, 126.6, 125.3, 73.7, 66.7, 61.5, 56.6, 52.6, 52.2, 51.1, 47.3, 31.6, 14.2; ESI-HRMS for C_{22}H_{27}NO_{6} (M+H)^+: 402.1838, Found: 402.1912.

**3-isopropyl 1,2-dimethyl 3-styryl-hexahydro-1H-pyrrolizine-1,2,3-tricarboxylate (4c):**

yield 70%, (Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1); **1H NMR** (400MHz, CDCl₃): 7.26-7.27 (m, 1H), 7.23-7.25 (m, 2H), 7.17-7.19 (m, 2H), 6.42 (d, J = 16.4 Hz, 1H), 6.08 (d, J = 16.4 Hz, 1H), 5.06-5.10 (m, 1H), 4.13 (d, J = 11.4 Hz, 1H), 3.64 (s, 3H), 3.61-3.63 (m, 1H), 3.53 (s, 3H), 3.16-3.19 (m, 1H), 2.99-3.03 (m, 1H), 2.74-2.76 (m, 1H), 1.96-2.01 (m, 1H), 1.43-1.80 (m, 2H), 1.60-1.65 (m, 1H), 1.25 (d, J = 6.0 Hz, 3H), 1.21 (d, J = 6.0 Hz, 3H); **13C NMR** (100MHz, CDCl₃): 172.3, 171.3, 171.0, 136.5, 133.5, 128.6, 128.0, 126.6, 125.4, 73.6, 69.1, 66.5, 56.4, 52.2, 52.0, 51.2, 47.2, 31.9, 27.1, 21.7, 14.1; ESI-HRMS for C_{23}H_{29}NO_{6} (M+H)^+: 416.1995, Found: 416.2071.
trimethyl 3-(4-fluorostyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4d): yield 86%,

(Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1). \(^1\)H NMR (600MHz, CDCl\(_3\)): (ppm) 7.30-7.33 (m, 2H), 7.00-7.02 (m, 2H), 6.49 (d, \(J = 16.4\) Hz, 1H), 6.07 (d, \(J = 16.4\) Hz, 1H), 4.31 (d, \(J = 11.4\) Hz, 1H ), 3.85 (s, 3H), 3.73 (s, 3H), 3.70-3.72 (m, 1H), 3.61 (s, 3H), 3.22-3.26 (m, 1H), 3.06-3.10 (m, 1H), 2.80-2.84 (m, 1H), 2.06-2.11 (m, 1H), 1.89-1.91 (m, 2H), 1.74-1.78 (m, 1H); \(^{13}\)C NMR (150MHz, CDCl\(_3\)): (ppm) 172.1, 171.2, 163.5, 132.7, 132.4, 128.2, 128.1, 115.7, 115.5, 73.7, 66.8, 56.6, 52.7, 52.3, 52.2, 51.1, 47.3, 31.4, 1.02; ESI-HRMS for C\(_{21}\)H\(_{24}\)FNO\(_6\)(M+H): 406.1667, Found: 406.1667.

trimethyl 3-(4-chlorostyryl)-hexahydro-1H-pyrrolizine-1,2,3-tricarboxylate (4e): yield 78%,

(Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1); \(^1\)H NMR (600MHz, CDCl\(_3\)): (ppm) 7.28-7.31 (m, 2H), 7.26-7.28 (m, 2H), 6.48 (d, \(J = 16.4\) Hz, 1H), 6.13 (d, \(J = 16.4\) Hz, 1H), 4.31 (d, \(J = 11.0\) Hz, 1H ), 3.85 (s, 3H), 3.73 (s, 3H), 3.67-3.71 (m, 1H), 3.60 (s, 3H), 3.22-3.25 (m, 1H), 3.04-3.08 (m,1H), 2.79-2.83 (m, 1H), 2.05-2.10 (m, 1H), 1.86-1.91 (m, 2H), 1.72-1.78 (m, 1H); \(^{13}\)C NMR (150MHz, CDCl\(_3\)): (ppm) 172.1, 171.1, 134.7, 133.9, 132.6, 128.9, 127.8; 125.9, 73.6, 66.8, 56.7, 52.7, 52.3, 51.0, 47.2, 31.4, 1.02; ESI-HRMS for C\(_{21}\)H\(_{24}\)ClNO\(_6\)(M+H): 422.1292, Found: 422.1373 (100.0%). (100.0%). (\(^{37}\)Cl) Calculated: 424.1341, Found: 424.1380 (32.0%)

trimethyl 3-(4-bromostyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4f): yield 80%,

(Flash column chromatography eluent, petroleum ether: ethylacetate = 4:1). \(^1\)H NMR (600MHz, CDCl\(_3\)): (ppm) 7.37 (d, \(J = 8.4\) Hz, 2H), 7.13 (d, \(J = 8.4\) Hz, 2H), 6.38 (d, \(J = 16.2\) Hz, 1H), 6.06 (d, \(J = 16.4\) Hz, 1H), 4.23 (d, \(J = 11.0\) Hz, 1H ), 3.77 (s, 3H), 3.65 (s, 3H), 3.59-3.62 (m, 1H), 3.52 (s, 3H), 3.13-3.17 (m, 1H), 2.96-3.00 (m, 1H), 2.70-2.74 (m, 1H), 1.98-2.00 (m, 1H), 1.78-1.84 (m, 2H), 1.65-1.69 (m, 1H); \(^{13}\)C NMR (150MHz, CDCl\(_3\)): (ppm) 172.1, 172.0, 171.2, 135.2, 132.6, 131.8, 128.1, 126.1, 122.1, 73.5, 66.8, 56.8, 52.7, 52.3, 52.2, 51.0, 47.1, 31.4, 1.01; ESI-HRMS for C\(_{21}\)H\(_{24}\)BrNO\(_6\)(M+H): 466.0865, Found: 466.0806 (100.0%). (100.0%). (\(^{80}\)Br) Calculated: 468.0845, Found: 468.0866 (97.3%)
trimethyl 3-(4-cyanostyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4g): yield 77%, (Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1). ¹H NMR (600MHz, CDCl₃): (ppm) 7.62 (d, J = 8.2 Hz, 2H), 7.44 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 16.2 Hz, 1H), 6.31 (d, J = 16.2 Hz, 1H), 4.31 (d, J = 11.1 Hz, 1H ), 3.86 (s, 3H), 3.75 (s, 3H), 3.70-3.74 (m, 1H), 3.61 (s, 3H), 3.22-3.25 (m, 1H), 3.01-3.05 (m, 1H), 2.79-2.85 (m, 1H), 2.04-2.13 (m, 1H), 1.88-1.94 (m, 2H), 1.70-1.79 (m, 1H); ¹³C NMR (150MHz, CDCl₃): (ppm) 171.9, 171.8, 171.0, 140.7, 132.5, 132.0, 129.5, 127.1, 118.7, 111.5, 73.1, 66.8, 56.9, 52.8, 52.3, 50.9, 46.9, 31.3, 26.9; ESI-HRMS for C₂₂H₂₄N₂O₆(M+H)⁺: 413.1634, Found: 413.1705.

trimethyl 3-(4-methoxystyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4h): yield 65%, (Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1). ¹H NMR (600MHz, CDCl₃): (ppm) 7.20 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.4 Hz, 2H), 6.37 (d, J = 16.2 Hz, 1H), 5.92 (d, J = 16.2 Hz, 1H), 4.23 (d, J = 10.8 Hz, 1H ), 3.76 (s, 3H), 3.73 (s, 3H), 3.65 (s, 3H), 3.58-3.63 (m, 1H), 3.52 (s, 3H), 3.15-3.18 (m, 1H), 3.00-3.04 (m, 1H), 2.72-2.75 (m, 1H), 1.98-2.01 (m, 1H), 1.77-1.81 (m, 2H), 1.65-1.70 (m, 1H); ¹³C NMR (150MHz, CDCl₃): (ppm) 172.4, 172.3, 171.4, 159.7, 133.3, 129.0, 127.8, 122.7, 114.1, 74.0, 66.8, 56.6, 55.3, 52.6, 52.2, 51.2, 47.3, 31.4, 1.02; ESI-HRMS for C₂₂H₂₄N₂O₇(M+H)⁺: 418.1788, Found: 418.1855.

trimethyl 3-(3-chlorostyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4i): yield 74%, (Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1). ¹H NMR (600MHz, CDCl₃): (ppm) 7.19-7.25 (m, 1H), 7.13-7.19 (m, 3H), 6.39 (d, J = 16.2 Hz, 1H), 6.09 (d, J = 16.2 Hz, 1H), 4.24 (d, J = 11.1 Hz, 1H ), 3.77 (s, 3H), 3.65 (s, 3H), 3.61-3.65 (m, 1H), 3.53 (s, 3H), 3.10-3.17 (m, 1H), 2.96-3.00 (m, 1H), 2.71-2.75 (m, 1H), 1.98-2.02 (m, 1H), 1.79-1.84 (m, 2H), 1.64-1.70 (m, 1H); ¹³C NMR (150MHz, CDCl₃): (ppm) 172.1, 172.0, 171.1, 138.1, 134.6, 132.5, 129.9, 128.1, 126.8, 126.4, 124.8, 73.4, 66.8, 56.8, 52.7, 52.2, 50.9, 47.1, 31.4, 1.00; ESI-HRMS for C₂₁H₂₃ClNO₆(M+H)⁺: 422.1292, Found: 422.1357.
trimethyl 3-(3-bromostyril)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4j): yield 73%,

(Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1). $^1$HNMR (600MHz, CDCl$_3$): (ppm) 7.41 (s, 1H), 7.31 (d, $J = 7.9$ Hz, 1H), 7.18 (d, $J = 8.8$ Hz, 1H), 7.10-7.13 (m, 1H), 6.38 (d, $J = 16.4$ Hz, 1H), 6.08 (d, $J = 16.4$ Hz, 1H), 4.24 (d, $J = 11.0$ Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 3.60-3.62 (m, 1H), 3.59-3.64 (m, 1H), 3.53 (s, 3H), 3.16-3.19 (m, 1H), 3.00-3.04 (m, 1H), 2.71-2.75 (m, 1H), 1.98-2.03 (m, 1H), 1.80-1.84 (m, 2H), 1.64-1.69 (m, 1H); $^{13}$C NMR (150MHz, CDCl$_3$): (ppm) 172.1, 172.0, 171.1, 138.4, 132.3, 131.0, 130.2, 129.4, 126.8, 125.2, 122.8, 73.4, 66.8, 56.8, 52.7, 52.3, 50.9, 47.1, 31.4, 1.01; ESI-HRMS for C$_{21}$H$_{24}$BrNO$_6$ (M+H)$^+$: 466.0787, Found: 466.084.

trimethyl 3-(3-methylstyril)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4k): yield 67%,

(Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1). $^1$HNMR (600MHz, CDCl$_3$): (ppm) 7.16 (d, $J = 7.8$ Hz, 2H), 7.05 (d, $J = 7.8$ Hz, 2H), 6.41 (d, $J = 16.4$ Hz, 1H), 6.01 (d, $J = 16.4$ Hz, 1H), 4.24 (d, $J = 10.8$ Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 3.59-3.64 (m, 1H), 3.53 (s, 3H), 3.16-3.19 (m, 1H), 3.00-3.04 (m, 1H), 2.72-2.76 (m, 1H), 2.97 (s, 3H), 1.98-2.00 (m, 1H), 1.78-1.81 (m, 2H), 1.66-1.71 (m, 1H); $^{13}$C NMR (150MHz, CDCl$_3$): (ppm) 172.1, 171.3, 138.1, 133.7, 133.5, 129.3, 126.5, 73.9, 66.9, 56.8, 52.6, 52.2, 51.1, 47.3, 31.4, 29.7, 26.7, 21.2; ESI-HRMS for C$_{22}$H$_{27}$NO$_6$ (M+H)$^+$: 402.1838, Found: 402.1898.

trimethyl 3-(2-methylstyril)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4l):

yield 65%, (Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1). $^1$HNMR (600MHz, CDCl$_3$): (ppm) 7.36 (m, 1H), 7.14-7.20 (m, 3H), 6.74 (d, $J = 16.4$ Hz, 1H), 6.01 (d, $J = 16.4$ Hz, 1H), 4.35 (d, $J = 11.1$ Hz, 1H), 3.86 (s, 3H), 3.74 (s, 3H), 3.70-3.72 (m, 1H), 3.64 (s, 3H), 3.24-3.27 (m, 1H), 3.13-3.15 (m, 1H), 2.83-2.87 (m, 1H), 2.31 (s, 3H), 2.07-2.11 (m, 1H), 1.87-1.92 (m, 2H), 1.74-1.79 (m, 1H); $^{13}$C NMR (150MHz, CDCl$_3$): (ppm) 172.2, 171.2, 135.8, 130.2, 128.1, 126.3, 125.9, 73.9, 66.9, 56.5, 52.6, 52.2, 51.1, 47.3, 31.4, 29.7, 26.7, 19.7; ESI-HRMS for C$_{22}$H$_{27}$NO$_6$(M+H)$^+$: 402.1838, Found: 402.1911.
trimethyl 3-(2-(furan-2-yl) vinyl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4m): yield 72%, (Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1). $^1$H NMR (600MHz, CDCl$_3$): (ppm) 7.35 (s, 1H), 6.35-6.37 (m, 2H), 6.26 (s, 1H), 6.08 (d, $J = 16.2$ Hz, 1H), 4.33 (d, $J = 10.8$ Hz, 1H ), 3.84 (s, 3H), 3.72 (s, 3H), 3.66-3.70 (m, 1H), 3.61 (s, 3H), 3.20-3.24 (m, 1H), 3.07-3.08 (m, 1H), 2.77-2.79 (m, 1H), 2.05-2.08 (m, 1H), 1.87-1.91 (m, 2H), 1.74-1.78 (m, 1H); $^{13}$C NMR (150MHz, CDCl$_3$): (ppm) 172.3, 171.0, 170.7, 136.3, 133.8, 128.1, 128.6, 125.1, 73.8, 66.9, 61.0, 56.6, 52.6, 51.3, 47.3, 31.4, 26.8, 14.2, 14.1; ESI-HRMS for C$_{19}$H$_{23}$NO$_7$ (M+H)$^+$: 378.1475, Found: 378.1550.

1, 2-diethyl 3-methyl 3-styryl-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4n): yield 83%, (Flash column chromatography eluent, petroleum ether: ethyl acetate = 4:1). $^1$H NMR (600MHz, CDCl$_3$): (ppm) 7.26-7.28 (m, 1H), 7.23-7.25 (m, 2H), 7.17-7.19 (m, 2H); 6.45 (d, $J = 16.2$ Hz, 1H), 6.09 (d, $J = 16.2$ Hz, 1H), 4.19 (d, $J = 10.8$ Hz, 1H), 4.09-4.13 (m, 2H), 3.98-4.00 (m, 2H), 3.77 (s, 3H), 3.62-3.64 (m, 1H), 3.13-3.17 (m, 1H), 3.01-3.03 (m, 1H), 2.74-2.76 (m, 1H), 1.97-2.02 (m, 1H), 1.77-1.81 (m, 2H), 1.66-1.69 (m, 1H), 1.19-1.21 (m, 3H), 1.06 (t, $J = 7.2$ Hz, 3H); $^{13}$C NMR (150MHz, CDCl$_3$): (ppm) 172.3, 171.8, 170.7, 136.3, 133.8, 128.6, 128.1, 126.6, 125.1, 73.8, 66.9, 61.0, 56.6, 52.6, 51.3, 47.3, 31.4, 26.8, 14.2, 14.1; ESI-HRMS for C$_{23}$H$_{29}$NO$_6$ (M+H)$^+$: 416.1995, Found: 416.2071.

Reference
4. Spectra data of the products 4a-n

trimethyl 3-styryl-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4a)
3-ethyl 1, 2-dimethyl 3-styryl-hexahydro-1H-pyrrolylizine-1, 2, 3-tricarboxylate (4b)
3-isopropyl 1,2-dimethyl 3-styryl-hexahydro-1H-pyrrolizine-1,2,3-tricarboxylate (4c)
trimethyl 3-(4-fluorostyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4d)
trimethyl 3-(4-chlorostyryl)-hexahydro-1H-pyrrrolizine-1, 2, 3-tricarboxylate (4e)
trimethyl 3-(4-bromostyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4f)
trimethyl 3-(4-cyanostyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4g)
trimethyl 3-(4-methoxystyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4h)
trimethyl 3-(3-chlorostyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4i)
trimethyl 3-(3-bromostyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4j)
trimethyl 3-(3-methylstyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4k)
trimethyl 3-(2-methylstyryl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4l)
trimethyl 3-(2-(furan-2-yl) vinyl)-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (4m)
1, 2-diethyl 3-methyl 3-styryl-hexahydro-1H-pyrrolizine-1, 2, 3-tricarboxylate (3n)
5. X-ray crystallographic data of 4f

Compound 4f (CCDC 1472726) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge on application to the Director, CCDC 12 Union Road, Cambridge CB2 1EZ, UK (fax (+44) 1223-336033; or e-mail deposit@ccdc.cam.uk) or via www.ccdc.cam.ac.uk/data_request/cif

![Chemical structure of 4f]

**Table.** Crystal data and structure refinement for Compound 4f.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identification code</td>
<td>4f</td>
</tr>
<tr>
<td>Empirical formula</td>
<td>C_{21}H_{24}BrNO_{6}</td>
</tr>
<tr>
<td>Formula weight</td>
<td>466.32</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>290 (2)</td>
</tr>
<tr>
<td>Wavelength (Å)</td>
<td>1.54184</td>
</tr>
<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>space group</td>
<td>P 21/c</td>
</tr>
<tr>
<td>Unit cell dimensions (Å)</td>
<td>a = 12.2790(2)</td>
</tr>
<tr>
<td></td>
<td>b = 13.8053(2)</td>
</tr>
<tr>
<td></td>
<td>c = 12.5691(2)</td>
</tr>
<tr>
<td></td>
<td>α = 90</td>
</tr>
<tr>
<td></td>
<td>β = 91.1000(10)</td>
</tr>
<tr>
<td></td>
<td>γ = 90</td>
</tr>
<tr>
<td>Volume (Å³)</td>
<td>2130.26(6)</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Calcd. density (Mg/m³)</td>
<td>1.454</td>
</tr>
<tr>
<td>F(000)</td>
<td>960</td>
</tr>
<tr>
<td>Limiting indices</td>
<td>-14 ≤ h ≤ 14</td>
</tr>
<tr>
<td></td>
<td>-15 ≤ k ≤ 16</td>
</tr>
<tr>
<td></td>
<td>-7 ≤ l ≤ 14</td>
</tr>
<tr>
<td>CCDC Deposit number</td>
<td>1472726</td>
</tr>
</tbody>
</table>