Photoreactions of bicyclic aziridines with alkenes and alkynes: a novel synthetic methodology for 8-azabicyclo[3.2.1]octane derivatives†

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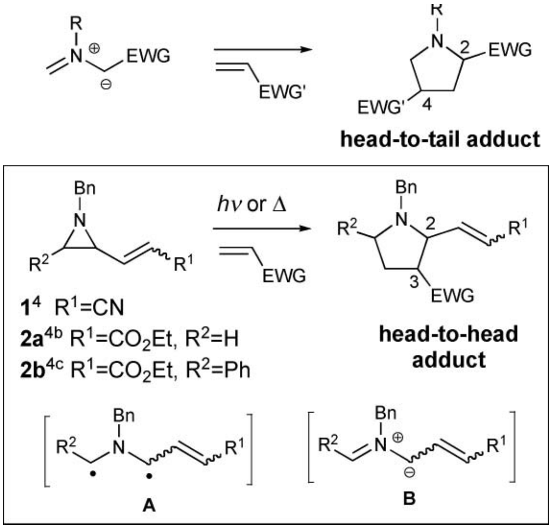
The photochemical C–C bond cleavage of bicyclic aziridines **7** and subsequent [3 + 2] cycloaddition with electron-deficient alkenes and alkynes afforded the novel head-to-head adducts selectively and efficiently. The adducts contain the naturally occurring 8-azabicyclo[3.2.1]octane skeleton (*e.g.* tropane alkaloids). The aziridine **8** fused with a 6-membered ring also afforded the cycloadducts but in poor yields. The methylaziridine **9** reacted with an electron-deficient alkene, affording the head-to-tail adduct **23** in addition to head-to-head adducts **22a** and **22b**. The photoreactions of bicyclic aziridines with alkenes and alkynes indicate a similar behavior to that of aziridines with a linear chain.

Introduction

For the construction of pyrrolidine-containing heterocycles, the 1,3-dipolar cycloaddition of azomethine ylides with alkenes is an important and useful strategy.[1] The aziridine ring is cleaved to give the corresponding azomethine ylide on irradiation or under thermal conditions.[2] In general, the 1,3-dipolar cycloaddition of an azomethine ylide possessing one electron-withdrawing group (EWG) at the ylide carbon and electron-deficient alkenes affords head-to-tail adducts (2,4-disubstituted pyrrolidines).[2b,3]

Recently, we reported that β-aziridinylacrylonitrile **1** or acrylate **2** undergo ring opening by irradiation or heating and subsequent [3 + 2] cycloaddition with electron-deficient alkenes, leading to head-to-head adducts (2,3-disubstituted pyrrolidines) selectively and efficiently (Scheme 1).[4] One of the resonance forms, the biradical intermediate **A**, primarily contributes to the cycloaddition rather than the other resonance form, the azomethine ylide **B**. In contrast, the head-to-tail adducts are also formed only in the thermal reactions of the aziridine **2b** because the stabilization of the azomethine ylide intermediate **B** (R^2 = Ph) is increased by the phenyl substituent.[4c]

We have also reported that the photochemical C–C-bond cleavage of bicyclic epoxide **3** and consequent [3 + 2] cycloaddition with ethyl vinyl ether afforded 8-oxobicyclo[3.2.1]octane **4**.[5] We have considered that the 8-azabicyclo[3.2.1]octane skeleton could be also constructed from bicyclic aziridines. This skeleton occurs naturally in the tropane alkaloids, which possess a wide range of biological activities. The tropane skeletons **6** are mainly synthesized from 3-oxidopyridinium betaines **5** by dipolar cycloaddition (Fig. 1).[6] A synthesis of **6**, involving thermal ring opening of a bicyclic aziridine and cycloaddition, has been reported by only one research group.[7]



Scheme 1

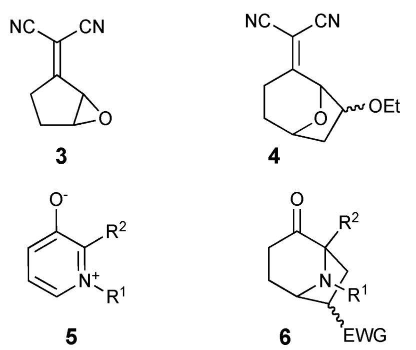


Fig. 1

In this paper, we describe the scope and limitation of the cycloadditions of bicyclic aziridines **7–10** (Fig. 2) with alkenes and alkynes for the construction of the 8-azabicyclo[3.2.1]octane skeleton.

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† Electronic supplementary information (ESI) available: phase-sensitive NOESY of compounds (*E*)-**15a**, (*Z*)-**15a**, (*E*)-**15b**, (*Z*)-**17a**, (*Z*)-**18a**, (*Z*)-**18b** and **c**, (*Z*)-**23** and **25a**. See DOI: 10.1039/b805801f

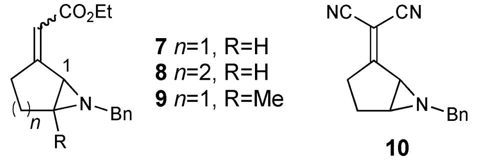
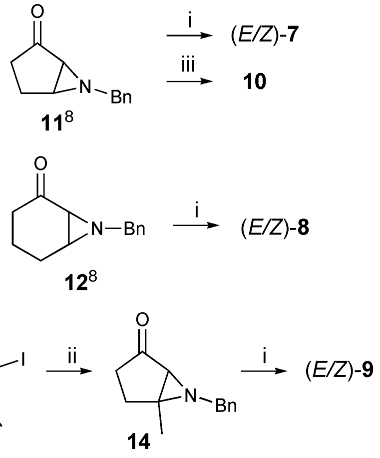


Fig. 2

Results and discussion

Preparation of aziridines

The γ,δ-epimino α,β-unsaturated esters **7** and **8** were prepared by the Horner–Emmons reaction of the ketones **11**[8] and **12**[8] with triethyl phosphonoacetate in 89% (E:Z = 45 : 55) and 68% (E:Z = 35 : 65) yields, respectively. In a similar manner, the δ-methyl γ,δ-epimino α,β-unsaturated ester **9** was obtained from iodoenone **13** by treatment with benzylamine, caesium carbonate and 1,10-phenanthroline (25% yield) and a subsequent Horner–Emmons reaction of the obtained aziridine **14** with triethyl phosphonoacetate in 71% (E:Z = 49 : 51) yield. The (*E*) and (*Z*) configurations of **7–9** were determined by means of the chemical shifts of their ^{1}H NMR spectra (see Experimental); they showed signals due to 1-H of the (*Z*)-isomers at a lower field (δ 3.45–3.69) than those of *E*-isomers (δ 2.06–2.46) because of the deshielding effect of the carboxyl group.[9] The dinitrile **10** was synthesized from the ketone **11** and malononitrile by the Knoevenagel condensation[10] in 69% yield (Scheme 2).



Scheme 2 *Reagents and conditions*: i, $(EtO)_2P(O)CH_2CO_2Et$, NaH, DMF or CH_2Cl_2, rt; ii, $BnNH_2$, Cs_2CO_3, xylene, 95 °C; iii, $CH_2(CN)_2$, NH_4OAc, AcOH, benzene, rt.

Reactions of aziridine 7 with various alkenes and alkynes

Direct irradiation of a solution of the aziridine (*Z*)-**7** with 3 equiv. methyl acrylate in acetonitrile with a low-pressure mercury lamp in a quartz test tube at room temperature afforded the head-to-head *exo*- and *endo*-adducts (*Z*)-**15a** and (*Z*)-**15b** in moderate yields, respectively (Table 1, entry 2). The 1,7-configurations of (*Z*)-**15a** and (*Z*)-**15b** were determined by means of the coupling constant of 1-H in the ^{1}H NMR spectra; they showed a singlet for 1,7-*cis* and a doublet (J 7.0 Hz) for 1,7-*trans*. The coupling constant of 1-H is nearly the same as those of the analogous adducts derived from carbonyl ylides and alkenes.[5b] The aziridine (*E*)-**7** also reacted with methyl acrylate to give the adducts (*E*)-**15a** and (*E*)-**15b** (Table 1, entry 1), whose stereochemistries could not be determined by the coupling constant of 1-H owing to the overlapping with the signal of 3-H. Therefore, the stereochemistries of (*E*)-**15a** and (*E*)-**15b** were primarily deduced from the phase-sensitive NOESY spectra (see ESI†).[11] The (*E*) and (*Z*) configurations of **15** were assigned by the chemical shifts of 1-H, as mentioned for the case of aziridines **7–9**. The photochemical reactions of aziridine **7** with *tert*-butyl acrylate (entry 3), *N*-phenylmaleimide (entries 4 and 5), dimethyl maleate (entry 6), dimethyl fumarate (entry 7), methyl propiolate (entry 8), and dimethyl acetylenedicarboxylate (entries 9 and 10) were performed, and the results are summarized in Table 1 and Fig. 3.

The *exo*-products (*e.g.*, **15a**, **16a** and **17a**) were formed preferentially and independently of the (*E*/*Z*)-configuration of the exocyclic double bond. In the transition state **C** (Fig. 3) the carboxy group of the alkenes is presumably orientated to be outside the ring, because of the steric hindrance of the exocyclic double bond of aziridine ring-cleaved intermediates. (*E*/*Z*)-Isomerization of the exocyclic double bond was not observed during the irradiation, because the isomerization would occur mainly *via* the triplet state of aziridine compounds.[4a,b] The reaction of aziridine **7** with dimethyl maleate afforded the 6,7-*cis* (*Z*)-**18a** and 6,7-*trans* dicarbonyl compounds (*Z*)-**18b** and (*Z*)-**18c** (entry 6). The results may indicate that the cycloaddition proceeds stepwise and/or that the maleate isomerizes to the corresponding fumarate

Table 1 Photochemical reactions of aziridine **7** with various alkenes and alkynes[a]

Entry	Aziridine	Alkene/alkyne	Reaction time/h	Conversion (%)	Products (yield (%)[13])
1	(*E*)	Methyl acrylate	2	100	(*E*)-**15a** (49) and (*E*)-**15b** (22)
2	(*Z*)	Methyl acrylate	3	100	(*Z*)-**15a** (38) and (*Z*)-**15b** (21)
3	(*E*)	*t*-Butyl acrylate	4	94	(*E*)-**16a** (62) and (*E*)-**16b** (3)
4	(*E*)	*N*-Phenylmaleimide	3	80	(*E*)-**17a** (59) and (*E*)-**17b** (20)
5	(*Z*)	*N*-Phenylmaleimide	2	81	(*Z*)-**17a** (60) and (*Z*)-**17b** (12)
6	(*Z*)	Dimethyl maleate	4	99	(*Z*)-**18a** (31), (*Z*)-**18b** (14) and (*Z*)-**18c** (3)
7	(*Z*)	Dimethyl fumarate	3	100	(*Z*)-**18b** (52) and (*Z*)-**18c** (21)
8	(*Z*)	Methyl propiolate	4	80	(*Z*)-**19** (59)
9	(*E*)	Dimethyl acetylenedicarboxylate	1.5	98	(*E*)-**20** (62)
10	(*Z*)	Dimethyl acetylenedicarboxylate	4	100	(*Z*)-**20** (55)

[a] A 0.060 mol dm^{-3} solution of aziridine in acetonitrile with 3 equiv. of alkene or alkyne was irradiated at RT.

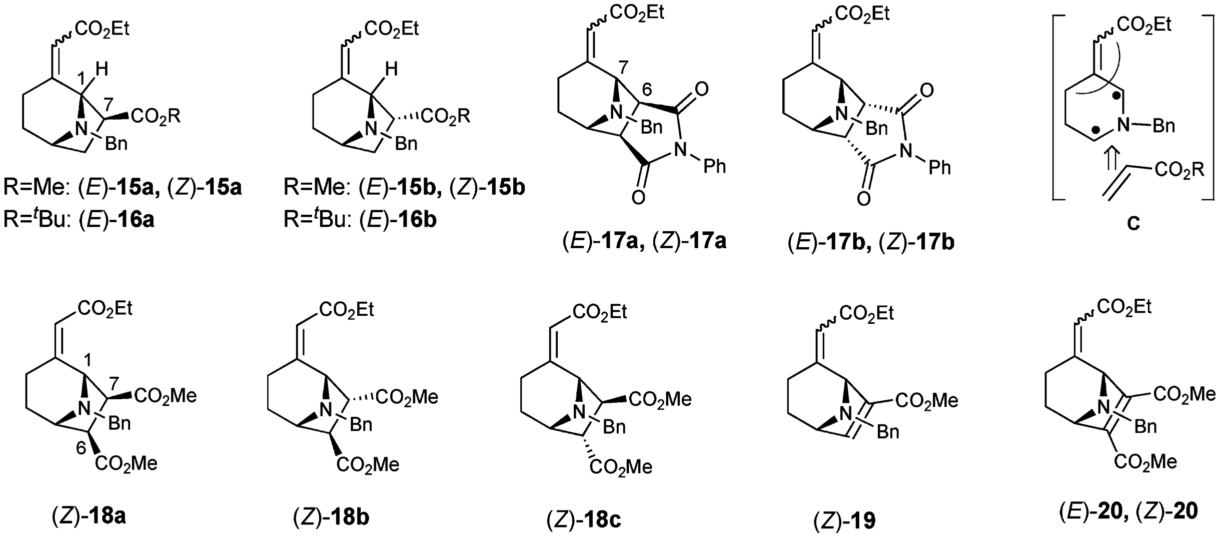


Fig. 3

photochemically. The reactions of aziridine **7** and alkynes also gave the adducts **19** and **20** in moderate yields (entries 8–10). In comparison with the cycloaddition of linear aziridine **1** with dimethyl maleate, dimethyl fumarate, and dimethyl acetylenedicarboxylate,[4b] bicyclic aziridine **7** reacted smoothly with those compounds to afford the corresponding adducts.

The structures of adducts **16–20** were also deduced on the basis of their spectral data. In particular, the stereochemistries of **16–18** were determined by the chemical shift and the multiplicity of the signals at H-C(1) and H-C(7) for **16** and **18** and at H-C(6) and H-C(7) for **17** in the ^{1}H NMR spectra (see Table 2) in comparison with those of the compounds (*E*/*Z*)-**15a** and (*E*/*Z*)-**15b**. Furthermore, the structures of (*Z*)-**17a** and (*Z*)-**18a–c** were also confirmed by phase-sensitive NOESY spectra (see ESI).[11]

Reactions of aziridines 8, 9 and 10 with an alkene and an alkyne

The photochemical reactions of **8–10** with an alkene and an alkyne were performed, and the results are summarized in Table 3 and Fig. 4. In order to study the effects of the fused ring size in the bicyclic aziridine on the [3 + 2] cycloaddition with an alkyne, the aziridine (*Z*)-**8** was irradiated with dimethyl acetylenedicarboxylate. The yield of the adduct (*Z*)-**21** from (*Z*)-**8** drastically decreased (Table 3, entry 1) relative to that of the adduct (*Z*)-**20** from the aziridine (*Z*)-**7** (Table 1, entry 10). The same phenomenon has been also observed in the cycloaddition of 7-membered carbonyl ylide and an alkene (4% yield).[5b,12]

The methyl substituent at the 5-position in aziridine (*Z*)-**9** had an effect on adduct distribution; the irradiation of (*Z*)-**9** with

Table 2 The chemical shift (ppm) and multiplicity of H-C(1) and H-C(7) in the ^{1}H NMR spectra (in $CDCl_3$) for **15–18**, **22** and **25**

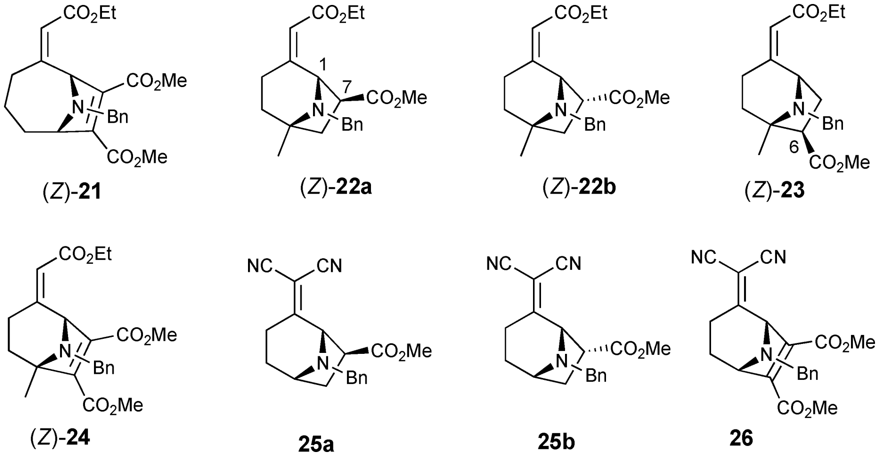
exo-Adduct	$\delta_{H\text{-}C(1)}$	$\delta_{H\text{-}C(7)}$	*endo*-Adduct	$\delta_{H\text{-}C(1)}$	$\delta_{H\text{-}C(7)}$
(*E*)-**15a**	NA[a]	2.88 dd	(*E*)-**15b**	NA	3.39–3.47 br dt
(*Z*)-**15a**	5.31 s	2.88 dd	(*Z*)-**15b**	5.34 d	3.46–3.56 br dt
(*E*)-**16a**	NA	2.78 dd	(*E*)-**16b**	3.55 d	NA
(*E*)-**17a**	NA	3.27 or 3.31 d[b]	(*E*)-**17b**[c]	3.53–3.56 br d[d]	3.17 dd[b]
(*Z*)-**17a**	5.43 s[d]	—	(*Z*)-**17b**	5.72 d[d]	4.03 dd[b]
(*Z*)-**18a**[c]	5.81 s	3.70 d	(*Z*)-**18b**[c]	5.87 d	4.28 t
(*Z*)-**18c**[c]	5.89 s	3.65–3.67 br d			
(*Z*)-**22a**	5.13 s	2.78 dd	(*Z*)-**22b**	5.10 d	3.30–3.39 br dt
25a	4.50 s	2.89 dd	**25b**	4.36 d	3.55–3.64 br dt

[a] The signal overlapped with another signal. [b] Values for H-C(6). [c] Spectra taken in C_6D_6. [d] Values for H-C(7).

Table 3 Photochemical reactions of aziridines **8**, **9** and **10** with an alkene and an alkyne[a]

Entry	Aziridine	Alkene/Alkyne	Reaction time/h	Conversion (%)	Products and yields (%)[13]
1	(*Z*)-**8**	Dimethyl acetylenedicarboxylate	3.5	96	(*Z*)-**21** (17)
2	(*Z*)-**9**	Methyl acrylate	2	69	(*Z*)-**22a** (18), (*Z*)-**22b** (5) and (*Z*)-**23** (5)
3	(*Z*)-**9**	Dimethyl acetylenedicarboxylate	2	100	(*Z*)-**24** (61)
4	**10**	Methyl acrylate	3	100	**25a** (33) and **25b** (13)
5	**10**	Dimethyl acetylenedicarboxylate	2	98	**26** (28)

[a] A 0.060 mol dm^{-3} solution of aziridine in acetonitrile with 3 equiv. of alkene or alkyne was irradiated at RT.



(*Z*)-**21** (*Z*)-**22a** (*Z*)-**22b** (*Z*)-**23**

(*Z*)-**24** **25a** **25b** **26**

Fig. 4

methyl acrylate afforded the head-to-tail adduct (*Z*)-**23** as well as head-to-head adducts (*Z*)-**22a** and (*Z*)-**22b** (Table 3, entry 2). The formation of the head-to-tail adducts has previously been observed in the thermal reactions of phenyl-substituted aziridines **2b** (Scheme 1).[4c] The adduct (*Z*)-**23** formed presumably *via* the azomethine ylide intermediate stabilized by the methyl substituent. The sum of yields for all adducts from (*Z*)-**9** were reduced owing to steric reasons. The reaction of (*Z*)-**9** with dimethyl acetylenedicarboxylate, however, proceeded smoothly, as did that of **7** (Table 1, entries 9 and 10).

The electron-withdrawing inductive effects in the side chain of the bicyclic aziridine on the [3 + 2] cycloaddition with alkenes were studied. In earlier studies of the 1,3-dipolar cycloaddition of carbonyl ylide and alkenes, the carbonyl ylides possessing a stronger electron-withdrawing substituent (*e.g.*, dinitrile) reacted with electron-rich alkenes better than weaker ones (*e.g.*, diester and mononitrile).[5c] Linear dicyanoaziridine reacts with non-electron-deficient alkenes (vinyl acetate and isoprene) to give the adducts.[4c] The reactions of the bicyclic dicyanoaziridine **10** with non-electron-deficient alkenes (vinyl acetate and isoprene) afforded no cycloadducts, and the yields of the reactions of **10** and electron-deficient alkene and alkyne were lower (Table 3, entries 4 and 5) relative to those of (*Z*)-**7** (Table 1, entries 2 and 10).

The stereo- and regiochemistries of **21–25** were deduced on the basis of their spectral data. In particular, (*E*/*Z*)- and *endo*/*exo*-configurations of **22** and **25** were determined by the chemical shift and the multiplicity of the ^{1}H NMR signals at H-C(1) and H-C(7) (see Table 2) in comparison with those of the compounds (*E*/*Z*)-**15a** and (*E*/*Z*)-**15b**. Furthermore, the structure of **25a** was also confirmed by the phase-sensitive NOESY spectrum (see ESI).[11] The regiochemistry of (*Z*)-**23** was determined by the ^{1}H NMR spectrum; the signals at δ 1.83 (dd) and δ 2.51–2.61 (br ddd) due to 2H-C(7) and at δ 4.91 due to H-C(1) were observed. The assignment of the *exo*-configuration of (*Z*)-**23** was deduced from the phase-sensitive NOESY spectrum (see ESI).[11]

Conclusions

The reactions of bicyclic aziridine **7** with electron-deficient alkenes and alkynes selectively and efficiently afforded the novel head-to-head adducts, whose skeleton, 8-azabicyclo[3.2.1]octane, is found in nature (*e.g.*, tropane alkaloids). However, the 7-azabicyclo[4.1.0]heptane **8** reacted with alkyne to give the adduct in low yields. The reactions of 5-methylaziridine **9** with electron-deficient alkenes gave head-to-tail adducts **23** in addition to head-to-head adducts. The dicyanoaziridine **10** reacted also with electron-deficient alkenes, but not with non-electron-deficient alkenes. The photoreactions of bicyclic aziridines and alkenes showed similar behavior to that of linear aziridines (*e.g.*, **1** and **2**). However, the bicyclic aziridines reacted with alkynes better than linear aziridines.

Experimental

General

Melting points were measured with a Yanaco MP-3 apparatus and are uncorrected. IR spectra were recorded on a Hitachi 215 spectrometer. ^{1}H NMR spectra were obtained with a JEOL JNM-AL300 (300 MHz), a JEOL JNM-AL400 (400 MHz) or a JEOL JNM-LA500 (500 MHz) spectrometer, and *J* values are given in Hz. ^{13}C NMR spectra were recorded on a JEOL JNM-AL300 (75 MHz), a JEOL JNM-AL400 (100 MHz) or a JEOL JNM-LA500 (125 MHz) spectrometer. Unless otherwise noted, NMR spectra were measured in $CDCl_3$ using tetramethylsilane as an internal standard at rt. Mass spectra (MS) and high-resolution MS (HRMS) were taken on a JEOL JMS-700 spectrometer in the EI mode at ionization potential of 70 eV. Column chromatography was performed with Merck silica gel 60 (230–400 mesh) and preparative TLC with Wakogel B-5F.

An Eikosha 60 W low-pressure mercury lamp was used for irradiation. The photolysis solutions were purged with argon before and during irradiation.

Preparations of aziridines

Ethyl (*E*)-(6-benzyl-6-azabicyclo[3.1.0]hex-2-ylidene)acetate [(*E*)-7] and ethyl (*Z*)-(6-benzyl-6-azabicyclo[3.1.0]hex-2-ylidene)-acetate [(*Z*)-7]. To a suspension of NaH [197 mg, 8.2 mmol; prepared from a NaH dispersion (60%, 329 mg) by washing it twice with hexane (5 cm^3)] in dry DMF (15 cm^3)] was added dropwise triethyl phosphonoacetate (1.65 cm^3, 8.2 mmol) at room temperature. After the mixture had been stirred for 20 min at room temperature, ketone **11**[8] (1.40 g, 7.48 mmol) was added dropwise, and the stirring was continued for 1 h at room temperature. Ice–water was added to the mixture, and the organic phase was extracted with diethyl ether. The ethereal extract was washed with brine, dried with $MgSO_4$, and concentrated *in vacuo*, giving a residue that was subjected to flash column chromatography [methylene chloride–ethyl acetate (29 : 1)] to afford (*E*)-**7** (761 mg, 40%) and (*Z*)-**7** (940 mg, 49%).

(*E*)-**7**, an oil (Found: M$^+$ 257.1422. $C_{16}H_{19}NO_2$ requires *M*, 257.1416); ν_{max} (film)/cm^{-1} 1690 (C=O); δ_H (300 MHz) 1.27 (3 H, t, *J* 7.2, CH_3), 1.73–1.86 (1 H, br dtd, *J* 13, 9 and 3, 4-H), 2.07–2.15 (1 H, br dd, *J* 13 and 8.5, 4-H), 2.24–2.38 (1 H, m, 3-H), 2.46 (1 H, d, *J* 4.4, 1-H), 2.53–2.56 (1 H, br dd, *J* 4 and 3, 5-H), 3.19 (1 H, dd, *J* 18.5 and 9.4, 3-H), 3.51 and 3.58 (2 H, each d, *J* 14.1, $C\mathit{H}_2Ph$), 4.15 (2 H, q, *J* 7.2, OCH_2), 5.96 (1 H, t, *J* 2.2, C=CH) and 7.23–7.34 (5 H, m, Ph); δ_C (75 MHz) 14.3 (q, CH_3), 27.5 (2 t, C-3 and -4), 47.4 and 50.3 (2 d, C-1 and -5), 59.7 and 61.5 (2 t, OCH_2 and $\mathit{C}H_2Ph$), 113.5 (d, C=*C*H), 126.9, 127.4 and 128.3 (3 d, 5 C in Ph), 138.8 (s, 1 C in Ph), 164.0 (s, C-2) and 166.4 (s, CO); *m/z* 257 (M$^+$, 82%), 138 (35), 120 (29) and 91 (100).

(*Z*)-**7**, an oil (Found: M$^+$ 257.1417. $C_{16}H_{19}NO_2$ requires *M*, 257.1416); ν_{max} (film)/cm^{-1} 1695 (C=O); δ_H (300 MHz) 1.25 (3 H, t, *J* 7.2, CH_3), 1.66–1.78 (1 H, m, 4-H), 1.97–2.05 (1 H, br dd, *J* 13 and 8, 4-H), 2.19–2.29 (1 H, br dd, *J* 17 and 9, 3-H), 2.33–2.47 (1 H, m, 3-H), 2.56 (1 H, dd, *J* 4.2 and 3.3, 5-H), 3.40 and 3.76 (2 H, each d, *J* 13.9, $C\mathit{H}_2Ph$), 3.69 (1 H, d, *J* 4.2, 1-H), 4.17 (2 H, q, *J* 7.2, OCH_2), 5.84 (1 H, br s, C=CH) and 7.21–7.37 (5 H, m, Ph); δ_C (75 MHz) 14.3 (q, CH_3), 26.3 and 30.7 (2 t, C-3 and -4), 45.6 and 48.9 (2 d, C-1 and -5), 59.7 and 61.6 (2 t, OCH_2 and $\mathit{C}H_2Ph$), 114.4 (d, C=*C*H), 126.9, 127.6 and 128.2 (3 d, 5 C in Ph), 139.0 (s, C in Ph), 163.5 (s, C-2) and 166.5 (s, CO); *m/z* 257 (M$^+$, 89%), 138 (38), 120 (29) and 91 (100).

Ethyl (*E*)-(7-benzyl-7-azabicyclo[4.1.0]hept-2-ylidene)acetate [(*E*)-8] and ethyl (*Z*)-(7-benzyl-7-azabicyclo[4.1.0]hept-2-ylidene)-acetate [(*Z*)-8]. By analogy with the synthesis of **7**, ketone **12**[8] (2.60 g, 12.9 mmol) was treated with NaH (60%, 568 mg, 14.2 mmol) and triethyl phosphonoacetate (2.83 cm^3, 14.2 mmol) in dry DMF (26 cm^3) at room temperature, and the resulting mixture was stirred for 1 h at room temperature. Flash column chromatography [hexane–ethyl acetate (4 : 1)] of the reaction mixture afforded (*E*)-**8** (848 mg, 24%) and (*Z*)-**8** (1.53 g, 44%).

(*E*)-**8**, an oil (Found: M$^+$ 271.1568. $C_{17}H_{21}NO_2$ requires *M*, 271.1572); ν_{max} (film)/cm^{-1} 1710 (C=O); δ_H (300 MHz) 1.27 (3 H, t, *J* 7.2, CH_3), 1.35–1.46 (1 H, m, 4-H), 1.66–1.77 (2 H, m, 4- and 5-H), 1.93–2.14 (2 H, m, 5- and 6-H), 2.06 (1 H, d, *J* 6.1, 1-H), 2.60–2.72 (1 H, m, 3-H), 2.79–2.89 (1 H, br d, *J* 17, 3-H), 3.47 and 3.67 (2 H, each d, *J* 14.0, $C\mathit{H}_2Ph$), 4.14 (2 H, q, *J* 7.2, OCH_2), 5.85 (1 H, t, *J* 1.8, C=CH) and 7.21–7.33 (5 H, m, Ph); δ_C (100 MHz) 14.5 (q, CH_3), 19.5 (t, C-4), 23.7 and 25.9 (2 t, C-3 and -5), 42.2 and 45.0 (2 d, C-1 and -6), 59.6 and 63.9 (2 t, OCH_2 and $\mathit{C}H_2Ph$), 117.3 (d, C=*C*H), 126.7, 127.3 and 128.1 (3 d, 5 C in Ph), 138.9 (s, C in Ph), 158.3 (s, C-2) and 165.8 (s, CO); *m/z* 271 (M$^+$, 96%), 226 (25), 198 (43), 180 (100), 152 (66), 134 (30), 124 (18), 106 (24), 91 (90) and 58 (35).

(*Z*)-**8**, an oil (Found: M$^+$ 271.1577. $C_{17}H_{21}NO_2$ requires *M*, 271.1572); ν_{max} (film)/cm^{-1} 1710 (C=O); δ_H (300 MHz) 1.27 (3 H, t, *J* 7.2, CH_3), 1.38–1.49 (1 H, m, 4-H), 1.58–1.71 and 1.73–1.84 (2 H, 2 m, 4- and 5-H), 1.94–2.06 (3 H, m, 3-, 5- and 6-H), 2.34 (1 H, dddd, *J* 14.7, 8.1, 3.5 and 1.1, 3-H), 3.27 and 3.12 (2 H, each d, *J* 14.1, $C\mathit{H}_2Ph$), 3.45 (1 H, d, *J* 6.1, 1-H), 4.14 and 4.15 (2 H, each q, *J* 7.2, OCH_2), 5.84–5.85 (1 H, br s, C=CH) and 7.20–7.37 (5 H, m, Ph); δ_C (100 MHz) 14.5 (q, CH_3), 20.9 (t, C-4), 24.2 and 32.2 (2 t, C-3 and -5), 39.3 and 42.0 (2 d, C-1 and C-6), 59.7 and 64.1 (2 t, OCH_2 and $\mathit{C}H_2Ph$), 117.9 (d, C=*C*H), 126.5, 127.5 and 128.0 (3 d, 5 C in Ph), 139.3 (s, C in Ph), 158.1 (s, C-2) and 166.4 (s, CO); *m/z* 271 (M$^+$, 100%), 242 (21), 226 (18), 198 (38), 180 (93), 152 (60), 134 (27), 124 (18), 106 (19) and 91 (90).

Ethyl (*E*)-(6-benzyl-5-methyl-6-azabicyclo[3.1.0]hex-2-ylidene)-acetate [(*E*)-9] and ethyl (*Z*)-(6-benzyl-5-methyl-6-azabicyclo-[3.1.0]hex-2-ylidene)acetate [(*Z*)-9]. To a solution of iodoenone **13** (670 mg, 3.02 mmol) in xylene (6 cm^3) were added benzylamine (0.50 cm^3, 4.53 mmol), caesium carbonate (1.47 g, 4.52 mmol), and 1,10-phenanthroline (543 mg, 3.02 mmol). The reaction mixture was stirred 2 h at 50 °C. After silica gel filtration, preparative TLC [hexane–ethyl acetate (2 : 1)] of the filtrate afforded 6-benzyl-5-methyl-6-azabicyclo[3.1.0]hexan-2-one **14** (150 mg, 25%), an oil (Found: M$^+$ 201.1146. $C_{13}H_{15}NO$ requires *M*, 201.1154); ν_{max} (film)/cm^{-1} 1705 (C=O); δ_H (300 MHz) 1.54 (3 H, s, CH_3), 1.85 (1 H, dt, *J* 12.7 and 9.2, 4-H), 1.96–2.06 (1 H, m, 3-H), 2.04 (1 H, s, 1-H), 2.18–2.27 (1 H, m, 4-H), 2.39–2.51 (1 H, br dt, *J* 17 and 9, 3-H), 3.74 (2 H, s, $C\mathit{H}_2Ph$) and 7.22–7.35 (5 H, m, Ph); δ_C (100 MHz) 13.6 (q, CH_3), 31.5 and 34.3 (2 t, C-3 and -4), 50.0 (s, C-5), 52.8 (d, C-1), 55.3 (t, $\mathit{C}H_2Ph$), 126.1, 127.1 and 128.3 (3 d, 5 C in Ph), 138.8 (s, C in Ph) and 212.7 (s, C-2); *m/z* 201 (M$^+$, 20%), 145 (5), 91 (100), 82 (20) and 65 (7).

By analogy with the synthesis of **7**, ketone **14** (252 mg, 1.25 mmol) was treated with NaH (60%, 55 mg, 1.38 mmol) and triethyl phosphonoacetate (0.27 cm^3, 1.38 mmol) in dry methylene chloride (3 cm^3) at room temperature, and the resulting mixture was stirred for 1 h at room temperature. Flash column chromatography [cyclohexane–ethyl acetate (3 : 1)] of the reaction mixture afforded (*E*)-**9** (117.8 mg, 35%) and (*Z*)-**9** (121.3 mg, 36%).

(*E*)-**9**, an oil (Found: M$^+$ 271.1574. $C_{17}H_{21}NO_2$ requires *M*, 271.1572); ν_{max} (film)/cm^{-1} 1705 (C=O); δ_H (300 MHz) 1.27 (3 H, t, *J* 7.2, CH_3), 1.50 (3 H, m, 5-CH_3), 1.72 (1 H, dt, *J* 12.8 and 9.2, 4-H), 2.08 (1 H, dd, *J* 12.8 and 9.0, 4-H), 2.22 (1 H, s, 1-H), 2.36 (1 H, dtd, *J* 18.4, 9.2 and 2.8, 3-H), 3.21 (1 H, dd, *J* 18.4 and 9.0, 3-H), 3.67 and 3.81 (2 H, each d, *J* 14.8, $C\mathit{H}_2Ph$), 4.15 (2 H, q, *J* 7.2, OCH_2), 5.88 (1 H, br s, C=CH) and 7.19–7.34 (5 H, m, Ph); δ_C (100 MHz) 13.4 (q, CH_3), 14.4 (q, 5-CH_3), 28.1 (t, C-4), 34.9 (t, C-3), 50.8 (s, C-5), 55.4 (t, $\mathit{C}H_2Ph$), 55.6 (d, C-1), 59.6 (t, OCH_2), 112.5 (d, C=*C*H), 126.4, 126.9 and 128.1 (3 d, 5 C in Ph), 139.4 (s, C in Ph), 165.6 (s, C-2) and 166.1 (s, CO); *m/z* 271 (M$^+$, 100%), 226 (20), 180 (58), 152 (75), 134 (73), 106 (21) and 91 (66).

(*Z*)-**9**, an oil (Found: M$^+$ 271.1575. $C_{17}H_{21}NO_2$ requires *M*, 271.1572); ν_{max} (film)/cm^{-1} 1705 (C=O); δ_H (300 MHz) 1.25 (3 H, t, *J* 7.2, CH_3), 1.49 (3 H, m, 5-CH_3), 1.59–1.71 (1 H, m, H-4), 1.94–2.02 (1 H, br dd, *J* 13 and 8.5, 4-H), 2.18–2.27 (1 H, br dd, *J* 17 and 8.5, 3-H), 2.39–2.52 (1 H, m, 3-H), 3.49 (1 H, s, 1-H), 3.74, 3.84 (2 H, each d, *J* 14.7 Hz, $C\mathit{H}_2Ph$), 4.16 (2 H, q, *J* 7.2 Hz, OCH_2), 5.80 (1 H, br s, C=CH) and 7.18–7.38 (5 H, m, Ph); δ_C (100 MHz) 13.7 and 14.5 (2 q, 2 CH_3), 31.5 and 33.7 (2 t, C-3 and -4), 51.2 (d, C-1), 52.4 (s, C-5), 55.6 and 59.7 (2 t, OCH_2 and $\mathit{C}H_2Ph$), 113.4 (d, C=*C*H), 126.4, 127.1 and 128.0 (3 d, 5 C in Ph), 139.8 (s, C in Ph), 165.2 (s, C-2) and 166.4 (s, CO); *m/z* 271 (M$^+$, 100%), 226 (18), 180 (55), 152 (74), 134 (70), 106 (20) and 91 (62).

(6-Benzyl-6-azabicyclo[3.1.0]hex-2-ylidene)malononitrile (10). To a suspension of the ketone **11**[8] (850 mg, 4.55 mmol) in dry benzene (1.7 cm^3) was added malononitrile (0.29 cm^3, 4.55 mmol), ammonium acetate (70 mg, 0.91 mmol) and acetic acid (0.26 cm^3, 4.55 mmol). The reaction mixture was stirred for 5 h at room temperature. The reaction was quenched with water and the organic phase was extracted with ether. The organic extract was washed with aqueous sat. $NaHCO_3$ and brine, dried with $MgSO_4$, and concentrated *in vacuo*, giving a residue that was subjected to flash column chromatography [hexane–ether (1 : 1)] to afford **10** (733 mg, 69%) as an oil (Found: M$^+$ 235.1104. $C_{15}H_{13}N_3$ requires *M*, 235.1109); ν_{max} ($CHCl_3$)/cm^{-1} 2360 (C≡N); δ_H (400 MHz) 1.96 (1 H, dtd, *J* 13.4, 9.0 and 2.8, 4-H), 2.20 (1 H, ddd, *J* 13.4, 8.3 and 1.1, 4-H), 2.50–2.63 (1 H, br td, *J* 19 and 9, 3-H), 2.74–2.84 (1 H, br dd, *J* 19 and 9, 3-H), 2.93–2.98 (2 H, m, 1- and 5-H), 3.49 and 3.74 (2 H, each d, *J* 13.4, C*H*$_2$Ph) and 7.27–7.40 (5 H, m, Ph); δ_C (100 MHz) 27.5 and 31.1 (2 t, C-3 and -4), 48.0 and 51.4 (2 d, C-1 and -5), 61.8 (t, *C*H$_2$Ph), 81.8 [s, *C*(CN)$_2$], 111.4 and 111.5 (2 s, 2 CN), 127.5, 127.6 and 128.5 (3 d, 5 C in Ph), 137.2 (s, C in Ph) and 186.0 (s, C-2); *m/z* 235 (M$^+$, 7%), 104 (2), 91 (100), 77 (2) and 65 (8).

Reactions of aziridines 7–10 with alkenes and alkynes

A 0.060 mol dm^{-3} solution of aziridines **7–10** in dry acetonitrile with 3 equiv. of with alkenes and alkynes was irradiated with a low-pressure mercury lamp in a quartz test tube at room temperature. After removal of the solvent, flash column chromatography afforded the adducts. The results are summarized in Tables 1 and 3 and Fig. 3 and 4.

Ethyl (*E*,1*RS*,5*RS*,7*RS*)-(8-benzyl-7-methoxycarbonyl-8-azabicyclo[3.2.1]oct-2-ylidene)acetate [(*E*)-15a]. An oil (Found: M$^+$ 343.1779. $C_{20}H_{25}NO_4$ requires *M*, 343.1784); ν_{max} ($CHCl_3$)/cm^{-1} 1720 sh, 1710 (C=O); δ_H (300 MHz) 1.28 (3 H, t, *J* 7.1, CH_3), 1.42–1.50 and 2.01–2.09 (2 H, each m, 4-H$_2$), 2.05 (1 H, dd, *J* 12.9 and 9.8 Hz, 6-H), 2.15–2.25 (1 H, m, 3-H), 2.55–2.63 (1 H, br quintet, *J* 6, 6-H), 2.88 (1 H, dd, *J* 9.8 and 5.1, 7-H), 3.38–3.42 (1 H, m, 5-H), 3.65–3.76 (4 H, m, 1-H, 3-H and C*H*$_2$Ph), 3.71 (3 H, s, OCH_3), 4.15 and 4.16 (2 H, each q, *J* 7.1, OCH_2), 5.54 (1 H, br d, *J* 2.2, C=CH) and 7.20–7.33 (5 H, m, Ph); δ_C (100 MHz) 14.4 (q, CH_3), 21.7 (t, C-4), 27.3 (t, C-3), 31.6 (t, C-6), 47.4 (d, C-7), 52.2 (q, OCH_3), 52.3 (t, *C*H$_2$Ph), 57.3 (d, C-5), 59.8 (t, OCH_2), 68.8 (d, C-1), 114.9 (d, C=*C*H), 126.7, 128.0 and 128.1 (3 d, 5 C in Ph), 138.7 (s, C in Ph), 157.9 (s, C-2) and 166.1 and 174.5 (2 s, 2 CO); *m/z* 343 (M$^+$, 54%), 314 (11), 298 (11), 257 (100), 138 (18), 120 (12) and 91 (90).

Ethyl (*E*,1*RS*,5*RS*,7*SR*)-(8-benzyl-7-methoxycarbonyl-8-azabicyclo[3.2.1]oct-2-ylidene)acetate [(*E*)-15b]. An oil (Found: M$^+$ 343.1776. $C_{20}H_{25}NO_4$ requires *M*, 343.1784); ν_{max} (film)/cm^{-1} 1720 sh and 1710 (C=O); δ_H (300 MHz) 1.28 (1 H, t, *J* 7.2, CH_3), 1.48–1.56 and 1.98–2.11 (2 H, each m, 4-H$_2$), 2.26 (1 H, dd, *J* 12.7 and 6.6, 6-H), 2.27–2.42 (2 H, m, 3- and 6-H), 3.33–3.38 (1 H, m, 5-H), 3.39–3.47 (1 H, br dt, *J* 11 and 7, 7-H), 3.55–3.66 (2 H, m, 1- and 3-H), 3.69 (2 H, s, C*H*$_2$Ph), 3.60 (3 H, s, OCH_3), 4.14 (2 H, q, *J* 7.2, OCH_2), 5.47 (1 H, d, *J* 2.6, C=CH) and 7.17–7.37 (5 H, m, Ph); δ_C (100 MHz) 14.4 (q, CH_3), 21.4 (t, C-4), 27.9 (t, C-3), 29.3 (t, C-6), 47.3 (d, C-7), 51.9 (q, OCH_3), 53.2 (t, *C*H$_2$Ph), 57.4 (d, C-5), 59.7 (t, OCH_2), 68.7 (d, C-1), 116.8 (d, C=*C*H), 126.9, 128.2 and 128.4 (3 d, 5 C in Ph), 138.5 (s, C in Ph), 156.8 (s, C-2) and 165.8 and 172.4 (2 s, 2 CO); *m/z* 343 (M$^+$, 59%), 314 (11), 298 (12), 257 (100), 138 (12) and 91 (76).

Ethyl (*Z*,1*RS*,5*RS*,7*RS*)-(8-benzyl-7-methoxycarbonyl-8-azabicyclo[3.2.1]oct-2-ylidene)acetate [(*Z*)-15a]. An oil (Found: M$^+$ 343.1777. $C_{20}H_{25}NO_4$ requires *M*, 343.1784); ν_{max} ($CHCl_3$)/cm^{-1} 1710 (C=O); δ_H (300 MHz) δ 1.12 (3 H, t, *J* 7.2, CH_3), 1.42–1.51 and 2.05–2.13 (2 H, each m, 4-H$_2$), 1.99 (1 H, dd, *J* 13.2 and 9.7, 6-H), 2.15–2.24 and 2.36–2.49 (2 H, each m, 3-H$_2$), 2.58–2.67 (1 H, br quintet, *J* 6.5, 6-H), 2.89 (1 H, dd, *J* 9.7 and 5.3, 7-H), 3.36–3.41 (1 H, m, 5-H), 3.70 and 3.75 (2 H, each d, *J* 14, C*H*$_2$Ph), 3.73 (3 H, s, OCH_3), 3.91 and 4.02 (2 H, each dq, *J* 10.8 and 7.2, OCH_2), 5.31 (1 H, s, 1-H), 5.66 (1 H, d, *J* 2.2, C=CH) and 7.17–7.33 (5 H, m, Ph); δ_C (100 MHz) 14.2 (q, CH_3), 28.5, 28.8 and 32.0 (3 t, C-3, -4 and -6), 46.9 (d, C-7), 52.2 (q, OCH_3), 52.3 (t, *C*H$_2$Ph), 57.0 (d, C-5), 59.9 (t, OCH_2), 61.2 (d, C-1), 115.1 (d, C=*C*H), 126.6, 127.9 and 128.1 (3 d, 5 C in Ph), 139.1 (s, C in Ph), 156.3 (s, C-2) and 165.6 and 174.8 (2 s, 2 CO); *m/z* 343 (M$^+$, 65%), 314 (15), 298 (13), 257 (100), 138 (11) and 91 (78).

Ethyl (*Z*,1*RS*,5*RS*,7*SR*)-(8-benzyl-7-methoxycarbonyl-8-azabicyclo[3.2.1]oct-2-ylidene)acetate [(*Z*)-15b]. An oil (Found: M$^+$ 343.1793. $C_{20}H_{25}NO_4$ requires *M*, 343.1784); ν_{max} ($CHCl_3$)/cm^{-1} 1720 and 1710 sh (C=O); δ_H (300 MHz) 1.19 (3 H, t, *J* 7.2, CH_3), 1.47–1.57 (1 H, m, 4-H), 2.02–2.23 (3 H, m, 3-, 4- and 6-H), 2.27–2.39 (1 H, m, 6-H), 2.55–2.68 (1 H, m, 3-H), 3.27–3.33 (1 H, m, 5-H), 3.46–3.56 (1 H, br dt, *J* 12 and 7, 7-H), 3.59 (3 H, s, OCH_3), 3.71 (2 H, s, C*H*$_2$Ph), 4.02, 4.08 (1 H, each dq, *J* 10.8 and 7.2, OCH_2), 5.34 (1 H, d, *J* 7.0, 1-H), 5.69 (1 H, d, *J* 2.2, C=CH) and 7.19–7.33 (5 H, m, Ph); δ_C (100 MHz) 14.4 (q, CH_3), 27.9, 29.1 and 29.6 (3 t, C-3, -4 and -6), 46.8 (d, C-7), 51.7 (q, OCH_3), 53.4 (t, *C*H$_2$Ph), 56.7 (d, C-5), 59.7 (t, OCH_2), 61.1 (d, C-1), 116.7 (d, C=*C*H), 126.8, 128.1 and 128.4 (3 d, 5 C in Ph), 138.8 (s, C in Ph), 155.9 (s, C-2) and 165.4 and 173.0 (2 s, 2 CO); *m/z* 343 (M$^+$, 62%), 314 (11), 298 (12), 257 (100), 138 (11) and 91 (65).

Ethyl (*E*,1*RS*,5*RS*,7*RS*)-(8-benzyl-7-*tert*-butoxycarbonyl-8-azabicyclo[3.2.1]oct-2-ylidene)acetate [(*E*)-16a]. An oil (Found: M$^+$ 385.2256. $C_{23}H_{31}NO_4$ requires *M*, 385.2253); ν_{max} (film)/cm^{-1} 1705 (C=O); δ_H (300 MHz) 1.29 (3 H, t, *J* 7.2, CH_3), 1.43 (9 H, s, O^{t}Bu), 1.37–1.50 and 2.01–2.09 (2 H, each m, 4-H$_2$), 1.93 (1 H, dd, *J* 13 and 9.7, 6-H), 2.13–2.26 (1 H, m, 3-H), 2.55–2.64 (1 H, br quintet, *J* 6, 6-H), 2.78 (1 H, dd, *J* 9.7 and 5.1, 7-H), 3.39–3.43 (1 H, m, 5-H), 3.65 and 3.75 (2 H, each d, *J* 13.9, C*H*$_2$Ph), 3.62–3.72 (2 H, m, 1- and 3-H), 4.15 and 4.16 (2 H, each q, *J* 7.2, OCH_2), 5.50 (1 H, d, *J* 2.4, C=CH) and 7.20–7.33 (5 H, m, Ph); δ_C (100 MHz) 14.5 (q, CH_3), 21.8 (t, C-4), 27.6 (t, C-3), 28.1 (q, 3 CH_3), 31.2 (t, C-6), 48.6 (d, C-7), 52.3 (t, *C*H$_2$Ph), 57.9 (d, C-5), 59.8 (t, OCH_2), 68.9 (d, C-1), 80.4 [s, *C*(CH$_3$)$_3$], 114.7 (d, C=*C*H), 126.6, 128.0 and 128.1 (3 d, 5 C in Ph), 138.8 (s, C in Ph), 158.3 (s, C-2) and 166.1 and 173.2 (2 s, 2 CO); *m/z* 385 (M$^+$, 41%), 328 (35), 312 (21), 257 (100) and 91 (68).

Ethyl (*E*,1*RS*,5*RS*,7*SR*)-(8-benzyl-7-*tert*-butoxycarbonyl-8-azabicyclo[3.2.1]oct-2-ylidene)acetate [(*E*)-16b]. An oil (Found: M$^+$ 385.2258. $C_{23}H_{31}NO_4$ requires *M*, 385.2253); ν_{max} ($CHCl_3$)/cm^{-1} 1715 (C=O); δ_H (300 MHz) 1.26 (3 H, t, *J* 7.1, CH_3), 1.35 (9 H, s, O^{t}Bu), 1.40–1.56 and 1.98–2.11 (2 H, each m, 4-H$_2$), 2.17 (1 H, dd, *J* 13.0 and 6.2, 6-H), 2.23–2.38 (2 H, m, 3- and 6-H), 3.28–3.39 (2 H, m, 5- and 7-H), 3.55 (1 H, d, *J* 6.6, 1-H), 3.54–3.65 (1 H, m, 3-H), 3.70 (2 H, s, C*H*$_2$Ph), 4.13 and 4.19 (2 H, each dq, *J* 11.0 and 7.1 Hz, OCH$_2$), 5.50 (1 H, d, *J* 2.6, C=CH) and 7.21–7.33 (5 H, m, Ph); δ_C (100 MHz) 14.5 (q, CH$_3$), 21.6 (t, C-4), 28.0 (t, C-3), 28.0 (q, 3CH$_3$), 29.3 (t, C-6), 47.9 (d, C-7), 53.1 (t, *C*H$_2$Ph), 57.5 (d, C-5), 59.7 (t, OCH$_2$), 68.6 (d, C-1), 80.7 [s, *C*(CH$_3$)$_3$], 117.1 (d, C=*C*H), 126.8, 128.2 and 128.4 (3 d, 5 C in Ph), 138.7 (s, C in Ph), 156.9 (s, C-2) and 165.8 and 171.3 (2 s, 2CO); *m*/*z* 385 (M$^+$, 49%), 312 (18), 257 (100) and 91 (56).

Ethyl (*E*,1*RS*,2*SR*,6*RS*,7*RS*)-(11-benzyl-3,5-dioxo-4-phenyl-4,11-diazatricyclo[5.3.1.0^{2,6}]undec-8-ylidene)acetate [(*E*)-17a]. An oil (Found: M$^+$ 430.1887. $C_{26}H_{26}N_2O_4$ requires *M*, 430.1893); ν_{max} (CHCl$_3$)/cm^{-1} 1710 (C=O); δ_H (300 MHz) 1.31 (3 H, t, *J* 7.1, CH$_3$), 1.65–1.70 (1 H, br d, *J* 8, 10-H), 2.13–2.39 (2 H, m, 9- and 10-H), 3.27 and 3.31 (2 H, each d, *J* 7.6, 2- and 6-H), 3.75–3.93 (5 H, m, 1-H, 7-H, 9-H and C*H*$_2$Ph), 4.19 and 4.22 (2 H, each dq, *J* 11.0 and 7.1, OCH$_2$), 5.72 (1 H, br s, C=CH) and 7.18–7.55 (10 H, m, 2 Ph); δ_C (100 MHz) 14.4 (q, CH$_3$), 22.1 (t, C-9), 25.0 (t, C-10), 48.8 and 49.5 (2 d, C-2 and -6), 50.1 (t, *C*H$_2$Ph), 60.1 (t, OCH$_2$), 60.7 (d, C-1), 68.0 (d, C-7), 117.3 (d, C=*C*H), 126.3, 127.2, 127.8, 128.4, 128.6 and 129.1 (6 d, 10 C in 2 Ph), 132.0 and 137.6 (2 s, 2 C in 2 Ph), 153.8 (s, C-8), 165.5 (s, CO) and 176.6 and 177.5 (2 s, C-3 and -5); *m*/*z* 430 (M$^+$, 92%), 385 (14), 257 (100) and 91 (66).

Ethyl (*E*,1*RS*,2*RS*,6*SR*,7*RS*)-(11-benzyl-3,5-dioxo-4-phenyl-4,11-diazatricyclo[5.3.1.0^{2,6}]undec-8-ylidene)acetate [(*E*)-17b]. White crystals; mp 168–170 °C (hexane–ethyl acetate) (Found: C, 72.44; H, 6.29; N, 6.34. $C_{26}H_{26}N_2O_4$ requires C, 72.54; H, 6.09; N, 6.51%); ν_{max} (CHCl$_3$)/cm^{-1} 1715 (C=O); δ_H (300 MHz) 1.28 (1 H, t, *J* 7.1, CH$_3$), 1.90–1.97 (1 H, br dd, *J* 14 and 9, 10-H), 2.05–2.16 (1 H, m, 10-H), 2.17–2.28 (1 H, m, 9-H), 3.67 (1 H, dd, *J* 19.0 and 8.1, 9-H), 3.76 (2 H, s, C*H*$_2$Ph), 3.74–3.80 (1 H, m, 1-H), 3.85–3.97 (3 H, m, 2-, 6- and 7-H), 4.14 (2 H, q, *J* 7.1, OCH$_2$), 5.67 (1 H, d, *J* 2.4, C=CH) and 7.21–7.52 (10 H, m, 2Ph); δ_H (400 MHz; C_6D_6) 0.91 (3 H, t, *J* 7.1, CH$_3$), 1.64–1.78 (2 H, m, 10-H$_2$), 2.32–2.43 (1 H, m, 9-H), 3.10 (1 H, dd, *J* 10.3 and 7.3, 2-H), 3.17 (1 H, dd, *J* 10.3 and 7.6, 6-H), 3.24–3.29 (1 H, m, 1-H), 3.27 (2 H, s, C*H*$_2$Ph), 3.53–3.56 (1 H, br d, *J* 7, 7-H), 3.77–3.84 (1 H, br dd, *J* 19 and 7, 9-H), 3.88 and 3.96 (2 H, each dq, *J* 11.0 and 7.1, OCH$_2$), 5.72 (1 H, d, *J* 2.7, C=CH) and 7.05–7.40 (10 H, m, 2 Ph); δ_C (100 MHz) 14.4 (q, CH$_3$), 22.1 and 22.2 (2 t, C-9 and -10), 48.6 (d, C-2), 50.3 (d, C-6), 53.5 (t, *C*H$_2$Ph), 58.8 (d, C-1), 60.0 (t, OCH$_2$), 67.2 (d, C-7), 119.0 (d, C=*C*H), 125.9, 127.4, 128.36, 128.41, 128.6 and 129.1 (6 d, 10 C in 2 Ph), 131.5 and 137.3 (2 s, 2 C in 2 Ph), 152.5 (s, C-8), 165.4 (s, CO) and 174.0 and 175.3 (2 s, C-3 and -5); EI-MS *m*/*z* 430 (M$^+$, 97%), 385 (13), 257 (100) and 91 (52).

Ethyl (*Z*,1*RS*,2*SR*,6*RS*,7*RS*)-(11-benzyl-3,5-dioxo-4-phenyl-4,11-diazatricyclo[5.3.1.0^{2,6}]undec-8-ylidene)acetate [(*Z*)-17a]. White crystals; mp 152–154 °C (hexane–ethyl acetate) (Found: C, 72.25; H, 6.01; N, 6.46. $C_{26}H_{26}N_2O_4$ requires C, 72.54; H, 6.09; N, 6.51%); ν_{max} (CHCl$_3$)/cm^{-1} 1710 (C=O); δ_H (300 MHz) 1.13 (3 H, t, *J* 7.1, CH$_3$), 1.67–1.73 (1 H, m, 10-H), 2.25–2.37 (2 H, m, 9- and 10-H), 2.42–2.49 (1 H, m, 9-H), 3.29 (2 H, s, 2- and 6-H), 3.74–3.78 (1 H, br s, 1-H), 3.75 and 3.82 (2 H, each d, *J* 13.7, C*H*$_2$Ph), 3.69 and 4.07 (2 H, each dq, *J* 10.7 and 7.1 Hz, OCH$_2$), 5.43 (1 H, s, 7-H), 5.85 (1 H, d, *J* 2.0, C=CH) and 7.16–7.53 (5 H, m, 2 Ph); δ_C (100 MHz) 14.1 (q, CH$_3$), 26.4 and 29.0 (2 t, C-9 and -10), 49.1 and 49.2 (2 d, C-2 and -6), 49.9 (t, *C*H$_2$Ph), 60.2 and 60.6 (2 d, C-1 and -7), 60.4 (t, OCH$_2$), 118.0 (d, C=*C*H), 126.3, 127.1, 127.7, 128.4, 128.5 and 129.1 (6 d, 10 C in 2 Ph), 132.1 and 138.0 (s, 2 C in 2 Ph), 152.0 (s, C-8), 165.2 (s, CO) and 176.5 and 177.6 (2 s, C-3 and -5); *m*/*z* 430 (M$^+$, 84%), 401 (14), 385 (13), 357 (11), 257 (100), 185 (10), 138 (11) and 91 (79).

Ethyl (*Z*,1*RS*,2*RS*,6*SR*,7*RS*)-(11-benzyl-3,5-dioxo-4-phenyl-4,11-diazatricyclo[5.3.1.0^{2,6}]undec-8-ylidene)acetate [(*Z*)-17b]. White crystals; mp 130–140 °C (Found: M$^+$ 430.1897. $C_{26}H_{26}N_2O_4$ requires *M*, 430.1893); ν_{max} (CHCl$_3$)/cm^{-1} 1705 (C=O); δ_H (300 MHz) 1.22 (1 H, t, *J* 7.2, CH$_3$), 1.84–1.96 (1 H, m, 10-H), 2.12–2.37 (2 H, m, 9- and 10-H), 2.37–2.48 (1 H, m, 9-H), 3.67–3.72 (1 H, m, 1-H), 3.74 and 3.80 (2 H, each d, *J* 13.4, C*H*$_2$Ph), 3.88 (1 H, dd, *J* 10.3 and 7.7, 2-H), 4.05 (1 H, dd, *J* 10.3 and 7.9, 6-H), 4.05–4.16 (2 H, m, OCH$_2$), 5.72 (1 H, d, *J* 7.9, 7-H), 5.80 (1 H, d, *J* 1.8, C=CH) and 7.21–7.49 (10 H, m, 2 Ph); δ_C (100 MHz) 14.3 (q, CH$_3$), 23.6 and 27.3 (2 t, C-9 and -10), 48.9 (d, C-2), 49.9 (d, C-6), 53.9 (t, *C*H$_2$Ph), 58.0 (d, C-1), 60.0 (t, OCH$_2$), 60.2 (d, C-7), 118.6 (d, C=*C*H), 125.7, 127.3, 128.3, 128.4 and 129.0 (5 d, 10 C in 2 Ph), 131.7 and 137.6 (s, 2 C in 2 Ph), 152.3 (s, C-8), 165.1 (s, CO) and 173.9 and 175.4 (2 s, C-3 and -5); *m*/*z* 430 (M$^+$, 92%), 385 (14), 257 (100), 138 (10) and 91 (61).

Dimethyl (*Z*,1*RS*,5*RS*,6*SR*,7*RS*)-8-benzyl-2-ethoxycarbonylmethylene-8-azabicyclo[3.2.1]octane-6,7-dicarboxylate [(*Z*)-18a]. An oil (Found: M$^+$ 401.1837. $C_{22}H_{27}NO_6$ requires *M*, 401.1838); ν_{max} (film)/cm^{-1} 1740 (C=O); δ_H (C_6D_6; 300 MHz) 0.78–0.85 (1 H, m, 4-H), 0.90 (3 H, t, *J* 7.2, CH$_3$), 1.61–1.80 (3 H, m, 3-H$_2$ and 4-H), 2.91 (1 H, d, *J* 10.3, 6-H), 3.07 (1 H, d, *J* 10.3, 7-H), 3.41 and 3.43 (6 H, each s, 2 OCH$_3$), 3.66 (1 H, br s, 5-H), 3.75 and 3.91 (2 H, each d, *J* 14.1, C*H*$_2$Ph), 3.83 and 3.91 (2 H, each dq, *J* 10.8 and 7.2, OCH$_2$), 5.62 (1 H, br s, C=CH), 5.81 (1 H, s, 1-H), 7.07 (1 H, t, *J* 7.3, Ph), 7.18–7.23 (2 H, br t, *J* 7, Ph) and 7.52–7.56 (2 H, br d, *J* 7, Ph); δ_C (C_6D_6; 100 MHz) 14.0 (q, CH$_3$), 27.6 and 28.1 (2 t, C-3 and -4), 50.7 (2 d, C-6 and -7), 51.3 and 51.4 (2 q, 2 OMe), 51.9 (t, *C*H$_2$Ph), 59.7 (d, C-5), 59.7 (t, OCH$_2$), 61.3 (d, C-1), 115.9 (d, C=*C*H), 126.7, 128.0 and 128.4 (3 d, 5 C in Ph), 139.2 (s, C in Ph), 155.2 (s, C-2) and 164.9, 171.6 and 172.0 (3 s, 3 CO); *m*/*z* 401 (M$^+$, 61%), 370 (18), 342 (15), 257 (100) and 91 (79).

Dimethyl (*Z*,1*RS*,5*RS*,6*SR*,7*SR*)-8-benzyl-2-ethoxycarbonylmethylene-8-azabicyclo[3.2.1]octane-6,7-dicarboxylate [(*Z*)-18b]. An oil contaminated with *ca.* 30% of (***Z***)-**18c**; δ_H (C_6D_6; 500 MHz) 0.93 (1 H, t, *J* 7.0, CH$_3$), 1.19–1.25 (1 H, m, 4-H), 1.72–1.82 (2 H, m, 3- and 4-H), 2.48–2.59 (1 H, m, 3-H), 3.29 and 3.31 (6 H, each s, 2 OCH$_3$), 3.58 (1 H, d, *J* 6.7, 6-H), 3.59 and 3.70 (2 H, each d, *J* 13.7, C*H*$_2$Ph), 3.63 (1 H, br s, 5-H), 3.91 and 3.95 (2 H, each dq, *J* 11.0 and 7.0, OCH$_2$), 4.28 (1 H, t, *J* 7, 7-H), 5.70 (1 H, d, *J* 2.4, C=CH), 5.87 (1 H, d, *J* 7.0, 1-H), 7.04–7.09 (1 H, m, Ph), 7.12–7.16 (2 H, m, Ph) and 7.29–7.33 (2 H, m, Ph); δ_C (C_6D_6; 125 MHz) 14.2 (q, CH$_3$), 28.1 and 29.0 (2 t, C-3 and -4), 49.1 and 50.6 (2 d, C-6 and -7), 51.6 and 51.7 (2 q, 2 OMe), 53.6 (t, *C*H$_2$Ph), 59.6 (t, OCH$_2$), 61.4 (d, C-5), 62.3 (d, C-1), 117.6 (d, C=*C*H), 127.3, 128.5 and 128.8 (3 d, 5 C in Ph), 139.0 (s, C in Ph), 154.8 (s, C-2) and 165.3, 172.0 and 174.3 (3 s, 3CO).

Dimethyl (*Z*,1*RS*,5*RS*,6*RS*,7*RS*)-8-benzyl-2-ethoxycarbonylmethylene-8-azabicyclo[3.2.1]octane-6,7-dicarboxylate [(*Z*)-18c]. An oil contaminated with *ca.* 70% of (***Z***)-**18b**; δ_H (C_6D_6; 500 MHz) δ 0.93 (3 H, t, *J* 7.0, CH$_3$), 1.25–1.31 (1 H, m, 4-H), 1.72–1.82

(2 H, m, 3- and 4-H), 2.48–2.59 (1 H, m, 3-H), 3.24 and 3.33 (6 H, each s, 2 OCH_3), 3.46–3.50 (1 H, m, 5-H), 3.67 and 3.77 (2 H, each d, *J* 13.4, C*H*$_2$Ph), 3.65–3.67 (1 H, br d, *J* 7, 7-H), 3.84–4.00 (2 H, m, OCH_2), 4.18 (1 H, t, *J* 6.7, 6-H), 5.64 (1 H, d, *J* 2.1, C=CH), 5.89 (1 H, s, 1-H), 7.04–7.09 (1 H, m, Ph), 7.12–7.16 (2 H, m, Ph), and 7.29–7.33 (2 H, m, Ph); δ_C (C_6D_6; 125 MHz) 14.2 (q, CH_3), 25.7 and 28.2 (2 t, C-3 and -4), 49.8 and 50.0 (2 d, C-6 and -7), 51.5 and 51.9 (2 q, 2 OMe), 53.4 (t, *C*H$_2$Ph), 59.7 (t, OCH_2), 60.1 (d, C-5), 62.4 (d, C-1), 115.3 (d, C=*C*H), 128.3, 128.5 and 128.7 (3 d, 5 C in Ph), 139.0 (s, C in Ph), 156.5 (s, C-2) and 165.4, 172.4 and 174.0 (3 s, 3 CO).

Ethyl (*Z*,1*RS*,5*SR*)-(8-benzyl-7-methoxycarbonyl-8-azabicyclo-[3.2.1]oct-6-en-2-ylidene)acetate [(*Z*)-19]. An oil (Found: M$^+$ 341.1631. $C_{20}H_{23}NO_4$ requires *M*, 341.1627); ν_{max} (film)/cm^{-1} 1715 (C=O); δ_H (300 MHz) 1.20 (1 H, t, *J* 7.2, CH_3), 1.49 (1 H, ddd, *J* 13.2, 7.5 and 2.2, 4-H), 2.03 (1 H, dddd, *J* 13.2, 10.6, 6.8 and 3.9, 4-H), 2.13–2.21 (1 H, br dd, *J* 16 and 7, 3-H), 2.47 (1 H, dddd, *J* 16.1, 10.6, 8 and 2.5, 3-H), 3.63 and 3.71 (2 H, each d, *J* 13.4, C*H*$_2$Ph), 3.71–3.76 (1 H, m, 5-H), 3.73 (3 H, s, OCH_3), 4.05 and 4.13 (2 H, each dq, *J* 10.8 and 7.2, OCH_2), 5.64 (1 H, br d, *J* 2, C=CH), 5.75 (1 H, s, H-1), 7.05 (1 H, d, *J* 2.4, 6-H) and 7.19–7.34 (5 H, m, Ph); δ_C (C_6D_6; 100 MHz) 14.3 (q, CH_3), 24.0 and 27.2 (2 t, C-3 and -4), 51.7 (q, OMe), 55.5 (t, *C*H$_2$Ph), 59.8 (t, OCH_2), 63.6 (d, C-5), 64.2 (d, C-1), 115.9 (d, C=*C*H), 126.8, 128.1 and 128.6 (3 d, 5 C in Ph), 137.0 and 138.2 (2 s, C-7 and C in Ph), 143.8 (d, C-6), 152.3 (s, C-2) and 163.9 and 165.4 (2 s, 2 CO); *m/z* 341 (M$^+$, 15%), 282 (32), 268 (14), 250 (64), 236 (32), 204 (24) and 91 (100).

Dimethyl (*E*,1*RS*,5*SR*)-8-benzyl-2-ethoxycarbonylmethylene-8-azabicyclo[3.2.1]oct-6-ene-6,7-dicarboxylate [(*E*)-20]. An oil (Found: M$^+$ 399.1683. $C_{22}H_{25}NO_6$ requires *M*, 399.1682); ν_{max} (film)/cm^{-1} 1720 (C=O); δ_H (300 MHz) 1.27 (3 H, t, *J* 7.2, CH_3), 1.72–1.81 (1 H, br dd, *J* 13 and 8, 4-H), 1.89–2.01 (1 H, m, 4-H), 2.30–2.45 and 3.59–3.69 (2 H, each m, 3-H_2), 3.66 (2 H, s, C*H*$_2$Ph), 3.77 and 3.83 (6 H, each s, 2 OCH_3), 3.92–3.95 (1 H, br t, *J* 3, 5-H), 4.06 (1 H, s, 1-H), 4.14 (2 H, q, *J* 7.2, OCH_2), 5.62 (1 H, d, *J* 2.4, C=CH) and 7.23–7.35 (5 H, m, Ph); δ_C (100 MHz) 14.4 (q, CH_3), 21.2 and 23.0 (2 t, C-3 and -4), 52.3 and 52.4 (2 q, 2 OMe), 56.2 (t, *C*H$_2$Ph), 59.9 (t, OCH_2), 67.5 (d, C-5), 74.2 (d, C-1), 116.1 (d, C=*C*H), 127.2, 128.3 and 128.6 (3 d, 5 C in Ph), 137.4, 137.9 and 142.4 (3 s, C-6, C-7 and C in Ph), 151.9 (s, C-2) and 163.3, 164.7 and 165.9 (3 s, 3 CO); *m/z* 399 (M$^+$, 10%), 367 (9), 340 (65), 308 (55), 294 (21), 276 (25), 262 (10) and 91 (100).

Dimethyl (*Z*,1*RS*,5*SR*)-8-benzyl-2-ethoxycarbonylmethylene-8-azabicyclo[3.2.1]oct-6-ene-6,7-dicarboxylate [(*Z*)-20]. An oil (Found: M$^+$ 399.1683. $C_{22}H_{25}NO_6$ requires *M*, 399.1682); ν_{max} ($CHCl_3$)/cm^{-1} 1705 (C=O); δ_H (300 MHz) 1.19 (3 H, t, *J* 7.1, CH_3), 1.72–1.81 (1 H, br dd, *J* 13 and 9 Hz, 4-H), 1.95–2.07 (1 H, m, 4-H), 2.29 (1 H, dd, *J* 16 and 6 Hz, 3-H), 2.55 (1 H, dddd, *J* 16.3, 10.4, 8.1 and 2.2, 3-H), 3.64 and 3.73 (2 H, each d, *J* 13.3, C*H*$_2$Ph), 3.78 and 3.80 (6 H, each s, 2 OCH_3), 3.90–3.93 (1 H, br t, *J* 3, 5-H), 4.03 and 4.10 (2 H, each dq, *J* 10.8 and 7.1, OCH_2), 5.65 (1 H, d, *J* 2.2, C=CH), 5.82 (1 H, s, 1-H) and 7.21–7.34 (5 H, m, Ph); δ_C (100 MHz) 14.3 (q, CH_3), 25.1 and 27.2 (2 t, C-3 and -4), 52.28 and 52.31 (2 q, 2 OMe), 56.4 (t, *C*H$_2$Ph), 59.9 (t, OCH_2), 66.2 (d, C-5), 67.8 (d, C-1), 116.0 (d, C=*C*H), 127.0, 128.2 and 128.6 (3 d, 5 C in Ph), 137.8 (s, C in Ph), 140.1 and 140.4 (2 s, C-6 and -7), 150.9 (s, C-2) and 164.0, 164.3 and 165.3 (3 s, 3 CO); *m/z* 399 (M$^+$, 10%), 367 (13), 340 (48), 308 (60), 294 (42), 276 (33), 262 (17) and 91 (100).

Dimethyl (*Z*,1*RS*,6*SR*)-9-benzyl-2-ethoxycarbonylmethylene-9-azabicyclo[4.2.1]non-7-ene-7,8-dicarboxylate [(*Z*)-21]. An oil (Found: M$^+$ 413.1836. $C_{23}H_{27}NO_6$ requires *M*, 413.1838); ν_{max} ($CHCl_3$)/cm^{-1}1720 (C=O); δ_H (300 MHz) 1.22 (3 H, t, *J* 7.2, CH_3), 1.37–1.54 (1 H, m, 4-H), 1.69–1.85 (1 H, m, 4- and 5-H), 1.88–1.98 (1 H, m, 5-H), 2.30–2.39 (1 H, br dd, *J* 14 and 7, 3-H), 2.96–3.07 (1 H, br t, *J* 14, 3-H), 3.71 and 3.77 (6 H, each s, 2 OCH_3), 3.75 and 3.83 (2 H, each d, *J* 13.4, C*H*$_2$Ph), 4.02 and 4.10 (2 H, each dq, *J* 10.8 and 7.2, OCH_2), 4.06–4.12 (1 H, m, 6-H), 5.71–5.74 (1 H, m, C=CH), 5.76 (1 H, br s, 1-H) and 7.21–7.38 (5 H, m, Ph); δ_C (100 MHz) 14.4 (q, CH_3), 23.0 (t, C-4), 34.2 and 38.7 (2 t, C-3 and -5), 52.1 and 52.3 (2 q, 2 OMe), 59.9 (t, OCH_2), 61.0 (t, *C*H$_2$Ph), 70.7 (d, C-6), 73.6 (d, C-1), 115.3 (d, C=*C*H), 126.9, 128.2 and 128.3 (3 d, 5 C in Ph), 132.5, 139.0 and 145.9 (3 s, C-7, C-8 and C in Ph) and 160.4, 163.0, 165.8 and 166.0 (4 s, C-2 and 3 CO); *m/z* 413 (M$^+$, 5%), 381 (47), 354 (23), 322 (22), 308 (53), 280 (53) and 91 (100).

Ethyl (*Z*,1*RS*,5*RS*,7*RS*)-(8-benzyl-7-methoxycarbonyl-5-methyl-8-azatricyclo[3.2.1]oct-2-ylidene)acetate [(*Z*)-22a]. An oil (Found: M$^+$ 357.1940. $C_{21}H_{27}NO_4$ requires *M*, 357.1940); ν_{max} (film)/cm^{-1} 1710 (C=O); δ_H (300 MHz) 0.97 (3 H, t, *J* 7.2, CH_3), 1.21 (3 H, s, 5-CH_3), 1.51 (1 H, dd, *J* 13.4 and 7, 4-H), 1.86–1.99 (1 H, m, 4-H), 2.14 (1 H, dd, *J* 13.0 and 9.7, 6-H), 2.15–2.24 (1 H, br dd, *J* 15 and 6, 3-H), 2.34 (1 H, ddd, *J* 13.0, 5.0 and 1.7, 6-H), 2.42–2.55 (1 H, m, 3-H), 2.78 (1 H, dd, *J* 9.7 and 5.0, 7-H), 3.42 and 3.76 (2 H, each d, *J* 14.2, C*H*$_2$Ph), 3.68 (3 H, s, OCH_3), 3.72 and 3.90 (2 H, each dq, *J* 10.8 and 7.2, OCH_2), 5.13 (1 H, s, 1-H), 5.73 (1 H, d, *J* 2.2, C=CH) and 7.21–7.29 (5 H, m, Ph); δ_C (100 MHz) 13.9 (q, CH_2*C*H$_3$), 24.7 (q, 5-CH_3), 29.7, 33.9 and 39.9 (3 t, C-3, −4 and -6), 44.7 (d, C-7), 47.3 (t, *C*H$_2$Ph), 52.1 (q, OMe), 59.9 (s, C-5), 60.0 (t, OCH_2), 60.6 (d, C-1), 116.9 (d, C=*C*H), 126.4, 127.8 and 127.9 (3 d, 5 C in Ph), 139.8 (s, C in Ph), 154.3 (s, C-2) and 165.5 and 174.6 (2 s, 2 CO); *m/z* 357 (M$^+$, 53%), 298 (60), 284 (38), 271 (27), 252 (56), 234 (49), 220 (30), 188 (21) and 91 (100).

Ethyl (*Z*,1*RS*,5*RS*,7*SR*)-(8-benzyl-7-methoxycarbonyl-5-methyl-8-azatricyclo[3.2.1]oct-2-ylidene)acetate [(*Z*)-22b]. An oil (Found: M$^+$ 357.1944. $C_{21}H_{27}NO_4$ requires *M*, 357.1940); ν_{max} ($CHCl_3$)/cm^{-1} 1720 (C=O); δ_H (300 MHz) 1.10 (3 H, t, *J* 7.2, CH_3), 1.22 (s, 3H, 5-CH_3), 1.49–1.58 (1 H, br dd, *J* 13 and 8, 4-H), 1.88–1.96 (1 H, br dd, *J* 13 and 7, 4-H), 2.00 (1 H, ddd, *J* 13.2, 12 and 1.5, 6-H), 2.11–2.21 (1 H, br dd, *J* 16 and 7, 3-H), 2.37 (1 H, dd, *J* 13.2 and 6.4, 6-H), 2.59–2.73 (1 H, m, 3-H), 3.30–3.39 (1 H, br dt, *J* 12 and 7, 7-H), 3.44 and 3.70 (2 H, each d, *J* 13.6, C*H*$_2$Ph), 3.55 (3 H, s, OCH_3), 3.89 and 3.99 (2 H, each dq, *J* 10.8 and 7.2, OCH_2), 5.10 (1 H, d, *J* 7.0, 1-H), 5.78 (1 H, d, *J* 2.4, C=CH) and 7.21–7.27 (5 H, m, Ph); δ_C (100 MHz) 14.3 (q, CH_2*C*H$_3$), 25.3 (q, 5-CH_3), 29.4 (t, C-3), 33.8 (t, C-4), 38.1 (t, C-6), 45.4 (d, C-7), 48.0 (t, *C*H$_2$Ph), 51.6 (q, OMe), 59.7 (t, OCH_2), 59.9 (s, C-5), 60.0 (d, C-1), 118.5 (d, C=*C*H), 126.5, 127.9 and 128.3 (3 d, 5 C in Ph), 139.8 (s, C in Ph), 154.5 (s, C-2) and 165.2 and 173.0 (2 s, 2 CO); *m/z* 357 (M$^+$, 77%), 298 (39), 284 (66), 271 (61), 252 (33), 234 (46), 220 (27), 188 (25) and 91 (100).

Ethyl (*Z*,1*RS*,5*RS*,6*SR*)-(8-benzyl-6-methoxycarbonyl-5-methyl-8-azatricyclo[3.2.1]oct-2-ylidene)acetate [(*Z*)-23]. An oil

(Found: M^+ 357.1947. $C_{21}H_{27}NO_4$ requires *M*, 357.1940); ν_{max} ($CHCl_3$)/cm^{-1} 1710 (C=O); δ_H (300 MHz) 1.04 (3 H, t, *J* 7.2, CH_3), 1.12 (3 H, s, 5-CH_3), 1.60 (1 H, dd, *J* 13.2 and 6.8, 4-H), 1.83 (1 H, dd, *J* 13.2 and 9.4, 7-H), 1.91–2.02 (1 H, br td, *J* 13 and 6 Hz, 4-H), 2.15–2.23 (1 H, br dd, *J* 16 and 6, 3-H), 2.45–2.52 (1 H, m, 3-H), 2.51–2.61 (1 H, br ddd, *J* 13, 7 and 6, 7-H), 2.97 (1 H, dd, *J* 9.4 and 5.8, 6-H), 3.50 and 3.75 (2 H, each d, *J* 14.1, C*H*$_2$Ph), 3.73 (3 H, s, OCH_3), 3.82 and 3.92 (2 H, each dq, *J* 10.8 and 7.2, OCH_2), 4.91 (1 H, d, *J* 7.0, 1-H), 5.71 (1 H, d, *J* 2.0, C=CH) and 7.15–7.32 (5 H, m, Ph); δ_C (100 MHz) 14.1 (q, CH$_2$*C*H$_3$), 21.7 (q, 5-CH_3), 29.3 (t, C-3), 31.5 (t, C-7), 36.1 (t, C-4), 47.7 (t, *C*H$_2$Ph), 51.4 (d, C-6), 51.6 (q, OMe), 57.1 (d, C-1), 59.9 (t, OCH_2), 63.3 (s, C-5), 116.1 (d, C=*C*H), 126.4 (d, C in Ph), 127.9 (d, 4 C in Ph), 140.1 (s, C in Ph), 156.5 (s, C-2) and 165.6 and 175.2 (2 s, 2 CO); *m*/*z* 357 (M^+, 39%), 312 (21), 298 (22), 284 (41), 271 (54), 266 (40), 220 (100), 188 (28) and 91 (89).

Dimethyl (*Z*,1*RS*,5*RS*)-8-benzyl-2-ethoxycarbonylmethylene-5-methyl-8-azabicyclo[3.2.1]oct-6-ene-6,7-dicarboxylate [(*Z*)-24]. An oil (Found: M^+ 413.1843. $C_{23}H_{27}NO_6$ requires *M*, 413.1838); ν_{max} (film)/cm^{-1} 1720 (C=O); δ_H (300 MHz) 1.05 (3 H, t, *J* 7.2, CH_3), 1.32 (3 H, s, 5-CH_3), 1.77–1.86 (1 H, br dd, *J* 13 and 7, 4-H), 1.95 (1 H, ddd, *J* 13.4, 10.5 and 6.6, 4-H), 2.22–2.30 (1 H, br dd, *J* 16 and 6, 3-H), 2.53–2.66 (1 H, m, 3-H), 3.59 and 3.66 (2 H, each d, *J* 13.6, C*H*$_2$Ph), 3.70 and 3.86 (6 H, each s, 2 OCH_3), 3.81 and 3.97 (2 H, each dq, *J* 10.8 and 7.2, OCH_2), 5.55 (1 H, d, *J* 7.0, 1-H), 5.74 (1 H, d, *J* 2.4, C=CH) and 7.18–7.31 (5 H, m, Ph); δ_C (100 MHz) 14.1 (q, CH$_2$*C*H$_3$), 20.0 (q, 5-CH_3), 28.3 (t, C-3), 29.5 (t, C-4), 49.0 (t, *C*H$_2$Ph), 52.0 and 52.3 (2 q, 2 OMe), 59.8 (t, OCH_2), 62.9 (d, C-1), 69.1 (s, C-5), 118.5 (d, C=*C*H), 126.7, 128.0 and 128.4 (3 d, 5 C in Ph), 136.4 and 138.2 (2 s, C-7 and C in Ph), 147.5 and 150.0 (2 s, C-2 and -6) and 162.7, 164.9 and 165.4 (3 s, 3 CO); *m*/*z* 413 (M^+, 24%), 354 (82), 322 (39), 308 (36), 262 (22) and 91 (100).

Methyl (1*RS*,5*RS*,7*RS*)-8-benzyl-2-dicyanomethylene-8-azatricyclo[3.2.1]octane-7-carboxylate (25a). An oil (Found: M^+ 321.1473. $C_{19}H_{19}N_3O_2$ requires *M*, 321.1477); ν_{max} ($CHCl_3$)/cm^{-1} 2240 (C≡N) and 1730 (C=O); δ_H (300 MHz) 1.68–1.77 (1 H, br dd, *J* 13 and 8, 4-H), 2.05 (1 H, dd, *J* 13.6 and 9.7, 6-H), 2.12–2.25 (1 H, m, 4-H), 2.49 (1 H, ddd, *J* 16.7, 11.4 and 7.9, 3-H), 2.65–2.74 (1 H, m, 6-H), 2.89 (1 H, dd, *J* 9.7 and 5.3, 7-H), 2.90–3.00 (1 H, br ddd, *J* 17, 8 and 1, 3-H), 3.44–3.49 (1 H, m, 5-H), 3.72 (2 H, s, C*H*$_2$Ph), 3.76 (3 H, s, OCH_3), 4.50 (1 H, s, 1-H) and 7.24–7.37 (5 H, m, Ph); δ_C (100 MHz) 26.6 (t, C-3), 29.8 (t, C-4), 31.4 (t, C-6), 47.0 (d, C-7), 52.7 (q, OMe), 53.1 (t, *C*H$_2$Ph), 56.7 (d, C-5), 65.4 (d, C-1), 82.9 [s, *C*(CN)$_2$], 111.0 and 111.1 (2 s, 2 CN), 127.5, 128.1 and 128.4 (3 d, 5 C in Ph), 137.0 (s, C in Ph), 172.8 (s, CO) and 180.0 (s, C-2); *m*/*z* 321 (M^+, 52%), 290 (13), 262 (15), 235 (27) and 91 (100).

Methyl (1*RS*,5*RS*,7*SR*)-8-benzyl-2-dicyanomethylene-8-azatricyclo[3.2.1]octane-7-carboxylate (25b). An oil (Found: M^+ 321.1479. $C_{19}H_{19}N_3O_2$ requires *M*, 321.1477); ν_{max} ($CHCl_3$)/cm^{-1} 2230 (C≡N) and 1730 (C=O); δ_H (300 MHz) 1.71–1.80 (1 H, br dd, *J* 13 and 8, 4-H), 2.14–2.26 (2 H, m, 4- and 6-H), 2.65–2.74 (1 H, br td, *J* 13 and 7, 6-H), 2.54–2.67 (1 H, br ddd, *J* 17, 11 and 8, 3-H), 2.86–2.96 (1 H, br dd, *J* 17 and 7, 3-H), 3.38–3.44 (1 H, m, 5-H), 3.55–3.64 (1 H, br dt, *J* 12 and 6, 7-H), 3.70 (3 H, s, OCH_3), 3.71 (2 H, s, C*H*$_2$Ph), 4.36 (1 H, d, *J* 6.4, 1-H) and 7.23–7.38 (5 H, m, Ph); δ_C (100 MHz) 26.3 (t, C-3), 29.5 and 29.8 (2 t, C-4 and -6), 47.1 (d, C-7), 52.4 (q, OMe), 53.4 (t, *C*H$_2$Ph), 56.4 (d, C-5), 65.7 (d, C-1), 84.5 [s, *C*(CN)$_2$], 110.5 and 111.1 (2 s, 2 CN), 127.6, 128.3 and 128.5 (3 d, 5 C in Ph), 136.9 (s, C in Ph), 171.5 (s, CO) and 179.6 (s, C-2); *m*/*z* 321 (M^+, 40%), 290 (9), 235 (28) and 91 (100).

Dimethyl (1*RS*,5*SR*)-8-benzyl-2-dicyanomethylene-8-azatricyclo[3.2.1]oct-6-ene-6,7-dicarboxylate (26). Pale yellow crystals; mp 131–133 °C (hexane–ethyl acetate) (Found: C, 66.96; H, 5.24; N, 10.95. $C_{21}H_{19}N_3O_4$ requires C, 66.83; H, 5.07; N, 11.13%); ν_{max} ($CHCl_3$)/cm^{-1} 2240 (C≡N) and 1730 (C=O); δ_H (300 MHz) 1.88–1.95 and 2.14–2.26 (2 H, 2 m, 4-H$_2$), 2.56–2.66 (1 H, br quintet, *J* 9, 3-H), 2.94–3.01 (1 H, m, 3-H), 3.72 (2 H, br s, C*H*$_2$Ph), 3.83 and 3.87 (6 H, 2 s, 2 OCH_3), 4.03 (1 H, br s, 5-H), 4.78 (1 H, s, 1-H) and 7.26–7.38 (5 H, m, Ph); δ_C (100 MHz) 23.4 and 25.4 (2 t, C-3 and -4), 52.8, (2 q, 2 OMe), 56.4 (t, *C*H$_2$Ph), 66.9 and 70.0 (2 d, C-1 and -5), 84.4 [s, *C*(CN)$_2$], 110.2 and 110.8 (2 s, 2 CN), 127.8, 128.5 and 128.6 (3 d, 5 C in Ph), 135.1, 136.0 and 144.6 (3 s, C-6, C-7 and C in Ph), 161.9 and 163.8 (2 s, 2 CO) and 172.9 (s, C-2); *m*/*z* 377 (M^+, 18%), 318 (22), 286 (26), 254 (13), 242 (34) and 91 (100).

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12 The cycloaddition of the 6-membered carbonyl ylide derived from the epoxide **3** and ethyl vinyl ether afforded the adduct **4** in 44% yield (see ref. 5*b*).

13 Yields for compounds are based on converted starting material.