7. A Nonconcerted Intramolecular *Diels-Alder* Reaction of Chiral Allenic-Acid Derivatives

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The reaction between the chiral allenic acid (+)-(*S*)-**1** and the carbodiimides **2a–d** and the keten-imine **6** gives, under mild conditions, the tricyclic compounds **3–5**, **7**, and **8**. Low diastereoselectivity and a partial loss of optical activity are observed. A stepwise mechanistic pathway *via* a biradical intermediate is postulated.

1. Introduction. – The first intramolecular cyclization of allenic amides bearing an aryl substituent at the N-atom has been reported by *Himbert* and *Henn* [1] in 1982. Kinetic measurements of the substituent effect at the aryl ring acting as a diene, performed by the same research group [2], have been interpreted in terms of a concerted mechanism [3].

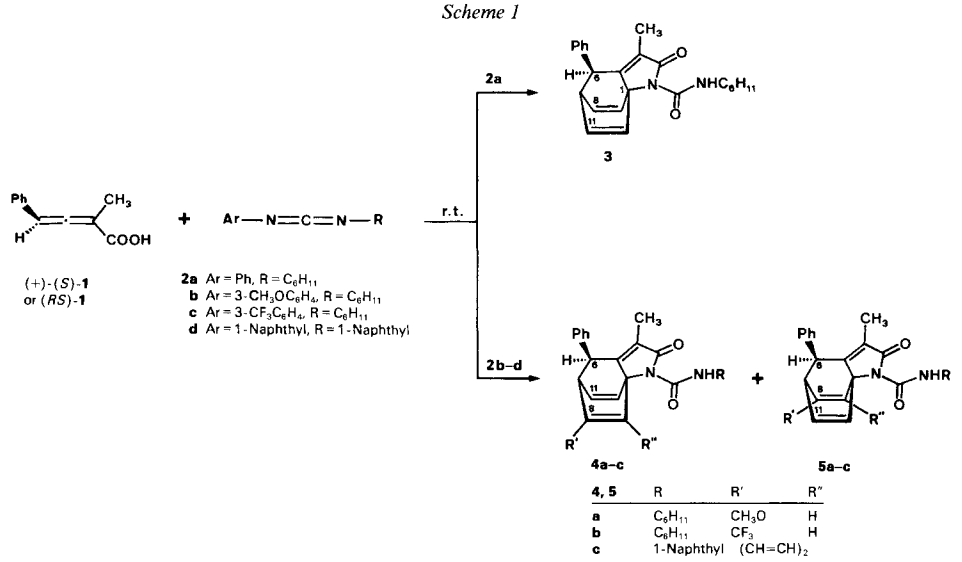
Recently, we have reported on the spontaneous intramolecular cyclization of allenic acylureas in a *Diels-Alder* fashion, the *N*-substituted aryl ring participating as a diene [4].

Among the two possible reaction pathways, the synchronous one would be favoured by the low-lying allenic LUMO orbitals [5]; this would be rendered even more favourable by the phenyl substitution [6] at C(4) of the allene and by the exothermicity of the reaction [7]. On the other hand, a stepwise 4 + 2 cyclization is also theoretically feasible [8]. It can be seen from *Dreiding* models of the intermediate allenic acylureas which undergo intramolecular cyclization that the sp-C-atom is directly sited above the *ipso*-C-atom of the aromatic moiety, while C(4) of the allene is comparatively far from the *p*-C-atom. This implies an unsymmetric transition state. Indeed, it could be expected that the reaction proceeds *via* a nonconcerted mechanism.

The employment of a chiral allene as a probe in the reaction under study could be expected to yield information on the possible intervention of an intermediate. The latter, provided it has a long enough lifetime, could be expected, whether ionic or radical in character, to have a bearing on the optical purity of the products obtained. The retention of optical purity on the hand could be taken as a strong indication of concertedness in bond-breaking and bond-making in the transition state of the [4 + 2] process. We now present the results from the application of the chiral allenic acid **1**, both as an optically pure compound and as a racemate, with the aim to elucidate the concertedness of the reaction.

2. Results and Discussion. – When the allenic acid **1** [9] was reacted with the carbodiimides **2a** [10], **2b**, **2c**, and **2d** [11] at room temperature for several days, the tricyclic adducts **3–5** were isolated in moderate yields (22–58%) after prep. TLC separation *(Scheme 1)*. In the case of the carbodiimide **2a**, a single product **3** was obtained, while the

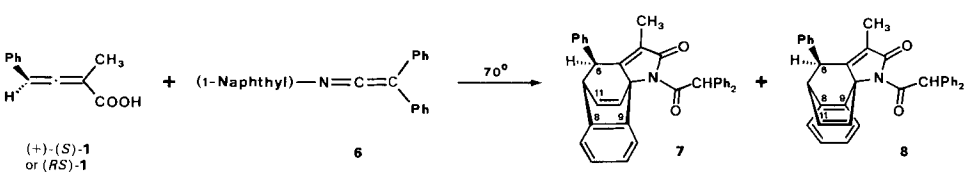
Scheme 1



aryl-*m*-substituted **2b** and **2c** and the (1-naphthyl)carbodiimide **2d** afforded mixtures of two diastereoisomeric products **4a–c** and **5a–c**. The ratio **4**/**5** in the crude reaction mixture was established by means of ^{1}H-NMR spectroscopy to be 56:44, *ca.* 50:50, and 55:45, respectively.

The racemic acid **1**, on heating with *N*-(1-naphthyl)ketenimine **6** *(Scheme 2)*, led to the formation of the diastereoisomers **7** and **8** in a ratio of 62:38. The reason for the preponderance of the more hindered diastereoisomer remains unclear[1]).

Scheme 2



The structures of the adducts **3**, **4**, **5**, **7**, and **8** were established mainly on the basis of their ^{1}H-NMR spectra.

Thus, in all cases, the ^{1}H-NMR signal of H–C(6) appeared as a br. *s* at 3.74–4.07 ppm and that of H–C(7) (*dd* for **7**, *d* for **5c** and **8**, and *m* for the other isomers) at 3.60–4.32 ppm (see *Exper. Part*). The relative configuration of the adducts was based on NOE experiments carried out with the isomers **4**, **5**, **7**, and **8**. An enhancement of the H–C(6) signal on irradiation of the olefinic proton at C(11) was observed only in the case of the isomers **4a–c** and

[1]) There is only one known example of cyclization of an allene derivative having different substituents at C(4) and an asymmetric aromatic moiety [12]: the intramolecular cyclization of a 1-naphthyl penta-2,3-dienoate (bearing a Me group at C(4)) had afforded two isomeric lactone adducts (unknown ratio), to the main of which *'syn'*-configuration had been ascribed on the basis of the upfield-shifted signal of CH_3–C(6) in the ^{1}H-NMR spectrum.

7 with *'syn'*-oriented H–C(6) and H–C(11). This assignment was in accordance with the high-field absorption of H–C(11) in **5a–c** and **8** due to the shielding effect of the phenyl ring at C(6) (see *Exper. Part*). The appearance of the CH_3O signal of **4a** at higher field (3.39 ppm) compared to the one of **5a** (3.56 ppm) has to be attributed to the same cause.

Interestingly, the signal of the *o*-protons of the phenyl group at C(6) in **4c** and **7** appeared at an unusually high field (6.34 and 6.24 ppm, resp.), probably because of the anisotropic effect of the benzo ring at C(8)–C(9).

Optically active adducts with the absolute configuration shown in *Schemes 1* and *2* were isolated in all cases when the above reactions were conducted with (+)-(*S*)-**1**[2]). The chiral solvating agent (−)-1-phenylethylamine failed in the measurement of the ee value of the adducts. However, the chiral lanthanide shift reagent [Eu(tfc)$_3$] was found to be useful and showed the ee value of **3**, **4a**, **5a**, **4b**, and **5b** to be 54, 46, 50, 56, and 56%, respectively. This reagent, unfortunately, did not resolve the signals of the compounds **4c**, **5c**, **7**, and **8**.

Optically active alenic acids are known to be configurationally unstable under basic conditions [13]. For this reason, *i.e.* in order to exclude the possibility of a trivial racemization of (+)-(*S*)-**1** under the reaction conditions prior to cyclization which could lead to the observed decrease in optical purity, a probe of 0.1 mmol of (+)-(*S*)-**1** and 0.2 mmol of (−)-1-phenylethylamine ($pK'_a = 9.78$ [14]) was kept in THF at room temperature for two days. The ^{1}H-NMR analysis of the reaction mixture in $CDCl_3$ showed no measurable racemization. Thus, a stepwise reaction route remains as the only explanation of the observed significant loss of optical purity of the products after cyclization.

We believe that the reaction intermediate is of biradical character [15] on the grounds of the small differences in reaction rates observed with electron-withdrawing and electron-donating groups as reported by *Himbert* and coworkers [2] and indeed as roughly observed by us in the case of compounds **4a**, **5a**, **4b**, and **5b**. The small (3–4 times) differences in reaction rates observed by the former authors in the [4 + 2] cycloaddition reaction when using different substituents are considered to support a concerted mechanism [3]. However, while militating against an ionic stepwise reaction pathway, their data do not exclude a radical mechanism [16].

In the presently studied cases, the partial loss of optical purity and small differences in 4 + 2 cyclization rates shown by the compounds with CH_3O and CF_3 groups allows the conclusion to be drawn that the cycloaddition proceeds in a non-concerted manner through a biradical intermediate.

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[2]) The optical purity of this acid [9] was shown to be $\geq 98\%$ by ^{1}H-NMR analysis of the salt with (−)-1-phenylethylamine in $CDCl_3$. This chiral solvating agent gave $\Delta\delta = 0.0287$ ppm (7.18 Hz) for the signals of the olefinic protons and $\Delta\delta = 0.0320$ ppm (8.00 Hz) for the signals of the Me groups of (±)-**1**.

Experimental Part

General. See [4]. Optical rotations: *Perkin-Elmer-241* instrument. CD spectra: *Mark-III/ISA-Jobin-Yvon* dichrograph. ^{1}H-NMR: NOE experiments on a *Bruker* (400 MHz) apparatus; a rough estimate of the rates of formation of **4a**, **5a**, **4b**, and **5b** was obtained by ^{1}H-NMR monitoring.

General Procedure. A soln. of **1** or (+)-(*S*)-**1** (174 mg, 1 mmol) and **2a–d** or **6** (1 mmol) in dry THF (1 ml) was kept at r.t. for two days (for **2a–d**) or refluxed for 10 h (for **6**). The mixture was chromatographed on prep. TLC plates with petroleum ether/AcOEt/acetone 15:1:1 (3- to 5-fold development). The UV (254 nm)-active zones were eluted with $CHCl_3$ to give after evaporation of the solvent under vacuum crude adducts which were recrystallized from Et_2O/hexane to afford pure compounds.

1. N-*Cyclohexyl*-N′-*(3-methoxyphenyl)carbodiimide* (**2b**) was prepared following the procedure given in [17]: colourless oil (88%) which was used directly for the preparation of **4b** and **5b**. IR ($CHCl_3$): 2955*m*, 2915*m*, 2840*m*, 2120*s*, 1595*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.19 (*t*, *J* = 8.0, 1 arom. H); 6.75–6.65 (*m*, 3 arom. H); 3.78 (*s*, CH_3O); 3.55–3.45 (*m*, CH–N); 2.1–1.1 (*m*, 10 H, C_6H_{11}). MS (70 eV): 231 (7), 230 (23, $M^{+\cdot}$), 207 (3), 206 (3), 149 (100, $M^{+\cdot} - C_6H_{10}$), 83 (13), 81 (10), 55 (26).

2. N-*Cyclohexyl*-N′-*[3-(trifluoromethyl)phenyl]carbodiimide* (**2c**). Following the above procedure, **2c** was obtained in quant. yield as colourless oil which was not purified. IR ($CHCl_3$): 2935*m*, 2840*w*, 2130*s*, 2110*s*, 1650*m*, 1605*m*, 1585*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.5–7.2 (*m*, 4 arom. H); 3.60–3.45 (*m*, CH–N); 2.1–1.0 (*m*, 10 H, C_6H_{11}). MS (70 eV): 268 (12, $M^{+\cdot}$), 220 (4), 187 (16), 186 (100, $M^{+\cdot} - C_6H_{10}$), 145 (4), 83 (16), 82 (12), 81 (8), 67 (20), 55 (50).

3. *(6RS)-2-(*N-*Cyclohexylcarbamoyl)-4-methyl-6-phenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**3**). Oil (27%). UV (CH_3CN): *ca.* 214 (sh, 9400). IR ($CHCl_3$): 3300*m*, 2920*m*, 2850*m*, 1700*s*, 1670*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.51 (*d*, *J* = 8.0, NH); 7.3–7.2 (*m*, 3 arom. H); 7.1–7.0 (*m*, 2 arom. H); 6.65–6.50 (*m*, H–C(8), H–C(9), H–C(10)); 6.14 (*t*, *J* = 7.2, H–C(11)); 4.05–3.95 (*m*, H–C(7)); 3.95–3.80 (*m*, CH–N); 3.74 (br. *s*, H–C(6)); 2.1–1.2 (*m*, 10 H, C_6H_{11}); 1.44 (*d*, *J* = 1.2, CH_3). MS (70 eV): 375 (9), 374 (25, $M^{+\cdot}$), 250 (22), 249 (100, $M^{+\cdot} - C_6H_{11}NCO$), 248 (48), 234 (30), 129 (42), 128 (33), 55 (38).

4. *(−)-(6S)-2-(*N-*Cyclohexylcarbamoyl)-4-methyl-6-phenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* ((−)-**3**). Oil $[\alpha]_D^{25} = -112.1$ (*c* = 0.340, $CHCl_3$). Ee 54%. CD (CH_3CN, $c = 1.08 \cdot 10^{-3}$, r.t.): 270 (+2.2), 265 (+2.5), 258 (+1.4), 247 (−1.1), 240 (−1.8), 234 (−1.2), 229 (−0.7), 215 (−8.4), 210 (−8.9), 205 (−9.4), 201 (−8.9), < 200 (neg.).

5. *(1RS,6RS,7SR)-2-(*N-*Cyclohexylcarbamoyl)-8-methoxy-4-methyl-6-phenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**4a**). Colourless crystals (10%). M.p. 160.0–162.5°. UV (CH_3CN): 216 (12200), *ca.* 250 (sh, 5600). IR (KBr): 3310*m*, 2945*m*, 2870*w*, 1725*s*, 1685*m*, 1645*m*, 1560*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.56 (*d*, *J* = 7.5, NH); 7.45–7.25 (*m*, 3 arom. H); 7.20–7.00 (*m*, 2 arom. H); 6.61 (*d*, *J* = 6.5, H–C(10)); 6.52 (*t*, *J* = 6.5, H–C(11); NOE with H–C(6) at 3.81, H–C(7) at *ca.* 3.65, and H–C(10) at 6.61); 5.20 (*d*, *J* = 2.0, H–C(9)); 4.00–3.80 (*m*, CH–N); 3.81 (br. *s*, H–C(6)); 3.70–3.60 (*m*, H–C(7)); 3.39 (*s*, CH_3O); 2.1–1.2 (*m*, 10 H, C_6H_{11}); 1.48 (br. *s*, CH_3). MS (70 eV): 405 (10), 404 (30, $M^{+\cdot}$), 280 (20), 279 (100, $M^{+\cdot} - C_6H_{11}NCO$), 278 (13), 264 (16), 129 (8), 128 (6).

6. *(−)-(1S,6S,7R)-2-(*N-*Cyclohexylcarbamoyl)-8-methoxy-4-methyl-6-phenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* ((−)-**4a**). M.p. 159.0–161.5°. $[\alpha]_D^{28} = -2.5$ (*c* = 0.485, $CHCl_3$). Ee 46%.

7. *(1RS,6SR,7SR)-2-(*N-*Cyclohexylcarbamoyl)-8-methoxy-4-methyl-6-phenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**5a**). Oil (12%) which solidified at −15°. M.p. 80.0–86.0°. UV (CH_3CN): 214 (12600). IR (KBr): 3300*m*, 2931*s*, 2854*m*, 1713*s*, 1676*m*, 1637*m*, 1591*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.55 (*d*, *J* = 7.9, NH); 7.40–7.20 (*m*, 3 arom. H); 7.10–7.00 (*m*, 2 arom. H); 6.61 (*d*, *J* = 6.8, H–C(10)); 6.11 (*dd*, *J* = 7.1, 6.2, H–C(11)); 5.16 (*d*, *J* = 2.5, H–C(9)); 4.00 (br. *s*, H–C(6)); 3.95–3.80 (*m*, CH–N); 3.70–3.60 (*m*, H–C(7)); 3.56 (*s*, CH_3O); 2.05–1.10 (*m*, 10 H, C_6H_{11}); 1.46 (*d*, *J* = 1.1, CH_3). MS (70 eV): 405 (6), 404 (26, $M^{+\cdot}$), 280 (16), 279 (100, $M^{+\cdot} - C_6H_{11}NCO$), 278 (13), 264 (16), 129 (12), 128 (10).

8. *(−)-(1R,6S,7S)-2-(*N-*Cyclohexylcarbamoyl)-8-methoxy-4-methyl-6-phenyl-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* ((−)-**5a**). Oil. $[\alpha]_D^{28} = -25.7$ (*c* = 0.380, $CHCl_3$). Ee 50%. CD (CH_3CN, $c = 0.88 \cdot 10^{-3}$, r.t.): 316 (sh, +0.3), 312 (+0.4), 304 (+0.5), 294 (+0.5), 268 (+0.6), 262 (+0.8), 255 (+0.9), 240 (+1.7), 231 (+2.0), 221 (+0.9), 215 (+0.5), < 210 (neg.).

9. *(1RS,6RS,7SR)-2-(N-Cyclohexylcarbamoyl)-4-methyl-6-phenyl-8-(trifluoromethyl)-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**4b**). Colourless prisms (18%). M.p. 180.0–183.0°. UV (CH_3CN): *ca.* 215 (sh, 22200), *ca.* 250 (sh, 9200). IR (KBr): 3309*m*, 2937*m*, 2850*m*, 1716*s*, 1680*m*, 1539*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.42 (*d*, *J* = 7.2, NH); 7.35–7.20 (*m*, 3 arom. H); 7.05 (br. *s*, H–C(9)); 7.00–6.90 (*m*, 2 arom. H); 6.63 (*t*, *J* = 6.5, H–C(11); NOE with H–C(6) at 3.88, H–C(7) at *ca.* 4.10, and H–C(10) at 6.54); 6.54 (*d*, *J* = 6.8, H–C(10)); 4.15–4.05 (*m*, H–C(7)); 4.00–3.80 (*m*, CH–N); 3.88 (*s*, H–C(6)); 2.10–1.20 (*m*, 10 H, C_6H_{11}); 1.52 (br. *s*, CH_3). MS (70 eV): 443 (28), 442 (100, M^+), 414 (8), 361 (4), 360 (20), 359 (8), 318 (16), 317 (83, $M^+ - C_6H_{11}NCO$), 316 (25), 302 (16), 248 (4), 187 (5), 174 (25), 130 (8), 129 (50), 128 (16), 127 (8), 115 (8), 91 (8), 83 (16), 55 (28).

10. *(–)-(1S,6S,7R)-2-(N-Cyclohexylcarbamoyl)-4-methyl-6-phenyl-8-(trifluoromethyl)-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* ((–)-**4b**). M.p. 181.0–186.0°. $[\alpha]_D^{22} = -91.4$ (*c* = 0.525, $CHCl_3$). Ee 56%. CD (CH_3CN, $c = 0.892 \cdot 10^{-3}$, r.t.): 269 (sh, +2.4), 264 (+3.3), 258 (+2.8), 253 (sh, +1.9), 247 (sh, +1.1), 240 (+0.8), 235 (+0.6), 215 (–11.7), < 210 (neg.).

11. *(1RS,6SR,7SR)-2-(N-Cyclohexylcarbamoyl)-4-methyl-6-phenyl-8-(trifluoromethyl)-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**5b**). Colourless prisms (17%). M.p. 153.0–155.0°. UV (CH_3CN): *ca.* 215 (sh, 25100), *ca.* 250 (sh, 12300). IR (KBr): 3311*m*, 2930*m*, 2852*m*, 1714*s*, 1674*m*, 1535*m*. ^{1}H-NMR (250 MHz, $CDCl_3$): 8.42 (*d*, *J* = 7.8, NH); 7.40–7.20 (*m*, 3 arom. H); 7.15–6.95 (*m*, 2 arom. H, H–C(9)); 6.59 (*d*, *J* = 7.0, H–C(10)); 6.22 (*dd*, *J* = 7.0, 6.2, H–C(11)); 4.15–4.05 (*m*, H–C(7)); 3.95–3.80 (*m*, CH–N); 3.82 (*s*, H–C(6)); 2.00–1.20 (*m*, 10 H, C_6H_{11}); 1.48 (*d*, *J* = 1.2, CH_3). MS (70 eV): 443 (28), 442 (100, M^+), 414 (8), 360 (20), 318 (16), 317 (66, $M^+ - C_6H_{11}NCO$), 316 (25), 302 (16), 248 (8), 187 (8), 174 (28), 130 (12), 129 (33), 128 (21), 115 (8), 91 (8), 83 (16), 55 (28).

12. *(–)-(1R,6S,7S)-2-(N-Cyclohexylcarbamoyl)-4-methyl-6-phenyl-8-(trifluoromethyl)-2-azatricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* ((–)-**5b**). Colourless prisms. M.p. 150.0–154.0°. $[\alpha]_D^{22} = -75.7$ (*c* = 0.515, $CHCl_3$). Ee 56%. CD (CH_3CN, $c = 1.008 \cdot 10^{-3}$, r.t.): 269 (sh, +2.5), 263 (+3.9), 257 (+4.2), 235 (sh, –8.0), 228 (sh, –12.0), 221 (–15.7), 207 (sh, –5.0), 194 (+2.0), < 192 (neg.).

13. *(1RS,6RS,7SR)-4-Methyl-2-[N-(1-naphthyl)carbamoyl]-6-phenyl-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**4c**). Colourless crystals (32%). M.p. 257.0–261.0°. UV (CH_3CN): 270 (sh, 6250), 276 (sh, 7100), 304 (9600), 332 (sh, 6250). IR (KBr): 3650–3350*w* (br.), 3230*w*, 3070*w*, 1730*s*, 1680*m*, 1640*m*, 1580*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 11.65 (*s*, NH); 8.45 (*d*, *J* = 7.6, 1 arom. H); 8.28 (*d*, *J* = 8.0, 1 arom. H); 7.91 (*d*, *J* = 7.6, 1 arom. H); 7.70–7.50 (*m*, 4 arom. H); 7.40–7.00 (*m*, 6 arom. H); 6.89 (*d*, *J* = 7.8, H–C(10)); 6.85–6.75 (*m*, H–C(11), 1 arom. H; NOE with H–C(6) at 4.07, H–C(7) at *ca.* 4.20, and H–C(10) at 6.89); 6.34 (*d*, *J* = 7.0, H_o of C_6H_5); 4.25–4.15 (*m*, H–C(7)); 4.07 (*s*, H–C(6)); 1.49 (*s*, CH_3). MS (70 eV): 469 (20), 468 (50, M^+), 300 (20), 299 (100, $M^+ - C_{10}H_7NCO$), 298 (40), 170 (12), 169 (70, $C_{10}H_7NCO^+$), 141 (25), 140 (20), 129 (37), 128 (29), 115 (25).

14. *(+)-(1S,6S,7R)-4-Methyl-2-[N-(1-naphthyl)carbamoyl]-6-phenyl-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* ((+)-**4c**). Colourless crystals. M.p. 228.0–235.0° (partial melting at *ca.* 190°). $[\alpha]_D^{28} = +86.3$ (*c* = 0.575, $CHCl_3$). CD (CH_3CN, $c = 0.87 \cdot 10^{-3}$, r.t.): 300 (sh, +5.2), 270 (+11.9), 263 (+13.3), 260 (+13.1), 238 (+16.0), 219 (–37.0), 205 (–36.3), 202 (–41.2).

15. *(1RS,6SR,7SR)-4-Methyl-2-[N-(1-naphthyl)carbamoyl]-6-phenyl-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**5c**). Colourless crystals. M.p. 220.0–225.0°. UV (CH_3CN): 270 (sh, 8200), 276 (sh, 9800), 303 (12800), 322 (sh, 8200). IR (KBr): 3650–3350*m* (br.), 3250*w*, 3080*w*, 1732*s*, 1687*m*, 1640*m*, 1580*s*. ^{1}H-NMR (250 MHz, $CDCl_3$): 11.64 (*s*, NH); 8.45 (*d*, *J* = 8.0, 1 arom. H); 8.28 (*d*, *J* = 7.7, 1 arom. H); 7.91 (*d*, *J* = 8.0, 1 arom. H); 7.70–7.15 (*m*, 13 arom. H); 6.90 (*d*, *J* = 7.7, H–C(10)); 6.44 (*dd*, *J* = 7.5, 6.1, H–C(11)); 4.32 (*d*, *J* = 6.4, H–C(7)); 3.90 (*s*, H–C(6)); 1.55 (*s*, CH_3). MS (70 eV): 469 (25), 468 (70, M^+), 300 (25), 299 (91, $M^+ - C_{10}H_7NCO$), 298 (62), 170 (25), 169 (100, $C_{10}H_7NCO^+$), 141 (37), 129 (54), 128 (50), 115 (54).

16. *(–)-(1R,6S,7S)-4-Methyl-2-[N-(1-naphthyl)carbamoyl]-6-phenyl-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* ((–)-**5c**). Colourless crystals. M.p. 195.0–205.0°. $[\alpha]_D^{25} = -31.9$ (*c* = 0.260, $CHCl_3$). CD (CH_3CN, $c = 0.90 \cdot 10^{-3}$, r.t.): 324 (–0.1), 311 (–0.2), 277 (–0.5), 267 (–0.45), < 240 (neg.).

17. *(1RS,6RS,7SR)-2-(Diphenylacetyl)-4-methyl-6-phenyl-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**7**). Colourless crystals (19%). M.p. 199.0–203.0°. UV (CH_3CN): 252 (5500), 268 (sh, 3300), 273 (sh, 2800). IR (KBr): 3080*m*, 1730*s*, 1700*m* (sh). ^{1}H-NMR (250 MHz, $CDCl_3$): 7.64 (*d*, *J* = 7.6, 2 arom. H); 7.54 (*d*, *J* = 7.5, 2 arom. H); 7.45–6.90 (*m*, 11 arom. H, CHCO); 6.81 (*d*, *J* = 7.3, 1 arom. H); 6.73 (*d*, *J* = 7.7, 1 arom. H); 6.71 (*t*, *J* = 6.3, H–C(11); NOE with H–C(6) at 3.95, H–C(7) at 4.12, and H–C(10) at 6.59); 6.59 (*dd*, *J* = 7.5, 1.5, H–C(10)); 6.24 (*d*, *J* = 6.8, 2 H_o of C_6H_5); 4.12 (*dd*, *J* = 6.0, 1.5, H–C(7)); 3.95 (br. *s*, H–C(6)); 1.35 (*d*, *J* = 1.2,

CH_3). MS (70 eV): 494 (12), 493 (32, M^+), 300 (8), 299 (15, $M^+ - Ph_2C{=}C{=}O$), 298 (25), 194 (100, $Ph_2C{=}C{=}O^+$), 167 (38, Ph_2CH^+), 166 (20), 165 (18).

18. *(+)-(1S,6S,7R)-2-(Diphenylacetyl)-4-methyl-6-phenyl-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* ((+)-**7**). Colourless crystals. M.p. 165.0–167.0°. $[\alpha]_D^{28} = +118.9$ ($c = 0.535$, $CHCl_3$). CD (CH_3CN, $c = 0.84 \cdot 10^{-3}$, r.t.): 307 (+1.0), 270 (+16.6), 256 (+19.1), 250 (+19.0), 243 (+18.9), 235 (+15.5), < 225 (neg.).

19. *(1RS,6SR,7SR)-2-(Diphenylacetyl)-4-methyl-6-phenyl-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* (**8**). Colourless crystals (11%). M.p. 227.0–229.0°. UV (CH_3CN): 252 (10000), 268 (4700), 274 (sh, 4200). IR (KBr): 3062*w*, 1720*s*, 1686*s*, 1600*w*. ^{1}H-NMR (250 MHz, $CDCl_3$): 7.62 (*d*, $J = 7.5$, 2 arom. H); 7.57 (*d*, $J = 7.5$, 2 arom. H); 7.50–7.05 (*m*, 14 arom. H); 6.98 (*s*, Ph_2CH); 6.74 (*d*, $J = 7.3$, 1 arom. H); 6.62 (*d*, $J = 7.7$, H–C(10)); 6.34 (*t*, $J = 7.0$, H–C(11)); 4.22 (*d*, $J = 6.3$, H–C(7)); 3.78 (*s*, H–C(6)); 1.40 (*s*, CH_3). MS (70 eV): 494 (13), 493 (33, M^+), 300 (10), 299 (47, $M^+ - Ph_2C{=}C{=}O$), 298 (8), 194 (100, $Ph_2C{=}C{=}O^+$), 167 (64, Ph_2CH^+), 166 (33), 165 (33).

20. *(–)-(1R,6S,7S)-2-(Diphenylacetyl)-4-methyl-6-phenyl-2-azabenzo[8,9]tricyclo[5.2.2.0^{1,5}]undeca-4,8,10-trien-3-one* ((–)-**8**). Colourless crystals. M.p. 260.0–264.0°. $[\alpha]_D^{28} = -288.6$ ($c = 0.405$, $CHCl_3$). CD (CH_3CN, $c = 0.74 \cdot 10^{-3}$, r.t.): 293 (+0.4), 275 (–15.0), 268 (–16.4), 252 (–22.0), 229 (+18.4), 216 (–30.8), 203 (–1.7), 196 (+19.1), < 193 (neg.).

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