61. Thermal Reaction of Azulenes with Dimethyl Acetylenedicarboxylate in Supercritical Carbon Dioxide

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1,3,4,6,8-Pentamethylazulene (**9**), when heated at 100° in supercritical CO_2 at 150 bar in the presence of 4 equiv. of dimethyl acetylenedicarboxylate (ADM), led to the formation of 16% of a 1:1 mixture of dimethyl 3,5,6,8,10-pentamethylheptalene-1,2-dicarboxylate (**12a**) and its double-bond-shifted isomer **12b** as well as 4% of the corresponding azulene-1,2-dicarboxylate **13** (*Scheme 4*). The formation of the [1 + 2] adduct **11** (*cf. Scheme 2*) was not observed. Similarly, benz[*a*]azulene (**25**) yielded in supercritical CO_2 (150°/170 bar) in the presence of 4 equiv. of ADM dimethyl benzo[*d*]heptalene-6,7-dicarboxylate (**29**; 30%) and dimethyl benzo[*a*]cyclopent[*cd*]azulene-1,2-dicarboxylate (**28**; 22%; *Scheme 5*). The reaction of 5,9-diphenylbenz[*a*]azulene (**26**) and ADM in supercritical CO_2 (100°/150 bar) gave the corresponding benzo[*d*]heptalene-6,7-dicarboxylate **31** (22%) and dimethyl 5,9-diphenyl-4b,10-etheno-10*H*-benz[*a*]azulene-11,12-dicarboxylate (**30**; 25%; *Scheme 5*).

Introduction. – Our studies on the mechanism of the formation of heptalene-1,2-dicarboxylates **4** from azulenes **1** and dimethyl acetylenedicarboxylate (ADM) have shown that the *Diels-Alder* adducts **2** are the crucial intermediates (*cf.* [1] [2]) which rearrange by heterolytic cleavage of the C(1)–C(10) bond *via* corresponding zwitterions (ZI) into tricyclic intermediates **3** which, in turn, on ring opening, yield the heptalenedicarboxylates **4** (*cf. Scheme 1*)[2]). The formation of **4** from **2** is strongly dependent on the temperature, on the polarity of the medium, and on the position of substituents on **2** and, hence, on **1**. For example, 1,3,4,6,8-pentamethylazulene (**9**) and ADM give in apolar media such as decalin at 180° mainly the [1 + 2] adduct **11** and only small amounts of the corresponding heptalene-1,2-dicarboxylate **12a** and azulene-1,2-dicarboxylate **13** [1] (*cf. Scheme 2*).

On the other hand, the Ru^{II}-catalyzed reaction of the corresponding 1,3,4,8-tetramethyl-6-propylazulene (**10**) with ADM in MeCN at 100° leads to the formation of the heptalene-1,2-dicarboxylate **15a** in a yield of 60%, followed by the corresponding azulene-1,2-dicarboxylate **16** in a yield of 14% [5]. A [1 + 2] adduct is not observed under these conditions. We also observed that tricycles of type **2**, which carry no substituents at C(6), do not lead to the formation of heptalene-1,2-carboxylates when heated in MeCN at 110°, but mainly yield (azulen-1-yl)fumarates and cyclopentano-anellated azulene-1,2-dicarboxylates along with the parent azulenes [6] [7] (*cf.* also [4]). The results of the rearrangement of two tricycles of this type are shown in *Scheme 3*.

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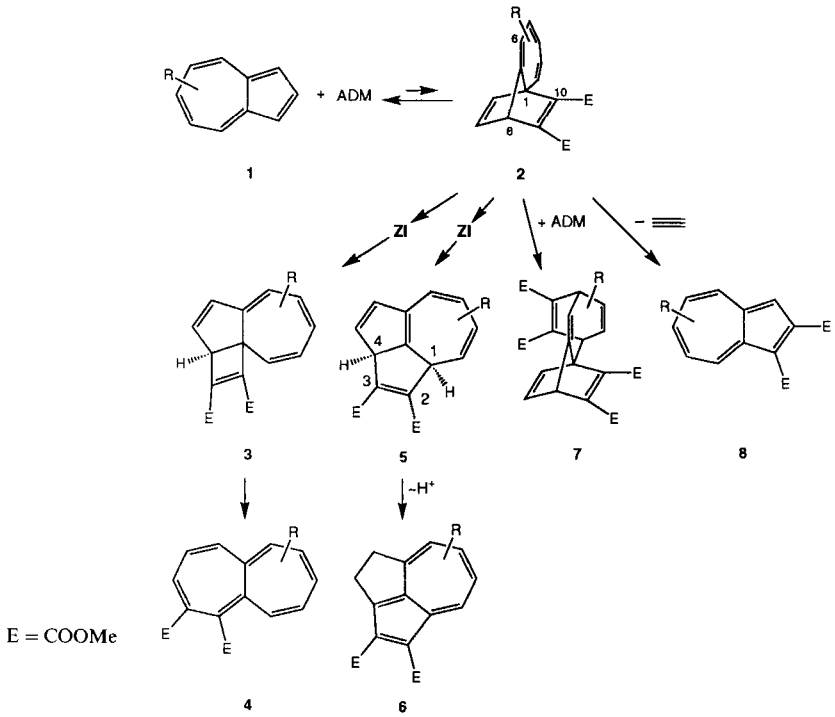
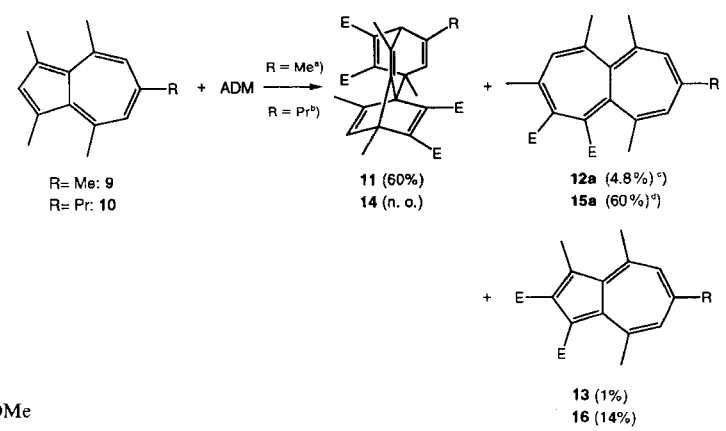
[1]) Part of the planned Ph. D. thesis of *R. H.*, University of Zurich.

[2]) Recently, we succeeded in the isolation of a tricyclic intermediate of type **3** from the reaction mixture of **26** and ADM (*cf. Scheme 5*) [3]. (For heptalene skeleton, the C-atom numbering according to the IUPAC Recommendations, 1979 ('Blue Book'), is retained, in line with our previous communications.)

Scheme 1

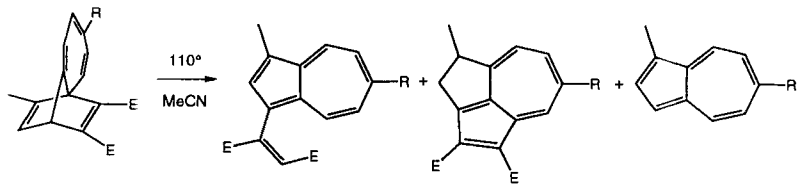


Scheme 2



[a]) 180°, Decalin, 3.4 equiv. of ADM.
[b]) 100°, MeCN, 2 mol-% of $[RuH_2(PPh_3)_4]$, 3 mol-equiv. of ADM [4].
[c]) *Ca.* 1:1 mixture of **12a** and its double-bond-shifted (DBS) isomer **12b.**
[d]) 1:1 mixture of **15a** and its DBS isomer **15b.**

Scheme 3



R= H: **17** R= Me: **18**

(*E*)-**19** (64%)[a] (*E*) -**22** (63%)

20 (26%) **23** (18%)

21 (10%) **24** (19%)

E = COOMe

[a]) In protic solvents, only (*E*)/(*Z*)-**19** (or (*E*)/(*Z*)-**22**) and **21** (or **24**) are observed.

There is little doubt that the tricyclic compounds of type **5** are intermediates in the formation of the cyclopentano-anellated azulene-1,2-dicarboxylates of type **6** (*cf. Scheme 1*)[3]), and that their intramolecular disproportionation takes place by prototropic shifts, *i.e.*, the disproportionation reaction is favored in polar media. On the other hand, the formation of **5** in comparison to **3**, after heterolytic cleavage of the C(1)–C(10) bond in **2**, is also favored in polar media due to the better stabilization of ZI in these media.

Since we have recently measured the E_T values (*cf.* [8]) of supercritical CO_2 (sc-CO_2) at temperatures between 40 and 120° and at pressures up to 1000 bar [9] and found that sc-CO_2 in the so-called bulk region (*cf. e.g.* [10]) reaches the polarity of hexane only at (880 ± 65) bar (polarity indicator: phenol blue; *cf.* [11]), we were interested in the thermal formation of heptalene-1,2-dicarboxylates from azulenes **1** and ADM in sc-CO_2 as the most apolar medium so far used in heptalene formation[4]). As model azulenes, for a first study, we selected **9**, benz[*a*]azulene (**25**; *cf.* [18]), and its 5,9-diphenyl derivative **26** (*cf.* [19] [20]).

Results and Discussions. – When azulene **9** was reacted with a four-fold molar amount of ADM in an autoclave in sc-CO_2 at 100° and 150 bar[5]), the formation of 16% of a mixture of dimethyl 3,5,6,8,10-pentamethylheptalene-1,2-dicarboxylate (**12a**) and its DBS isomer **12b** beside 4% of the corresponding azulene-1,2-dicarboxylate **13** was observed. The [1 + 2] adduct **11** was not formed under these conditions (*Scheme 4*). The isolated compounds were identified by their spectroscopic data (*cf.* [1]). In comparison to the thermal reaction in decalin at 180°, the reaction in sc-CO_2 takes place already at 100° at a pressure of 150 bar. The formation of the [1 + 2] adduct **11** (*cf. Scheme 2*) is no longer observed, indicating that the *Diels-Alder* reaction of the primary intermediate of type **2** (*cf. Scheme 1*) with ADM occurs only at higher temperatures and is not critically dependent on the pressure.

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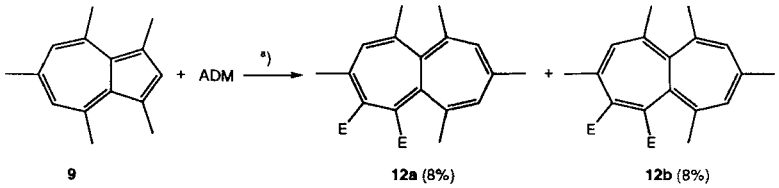
[3]) Compounds of type **5** have so far not been observed in reactions of **1** with ADM. However, there prototropic forms with H–C(4) linked to C(2) have been isolated [3] [7].

[4]) Investigations that deal with sc-CO_2 as medium for reactions increase steadily, including enzymatic reactions (*cf.* lit. cited in [10] [12–17]). *Ikushima et al.* [10] have shown that the ratio of regioisomers, formed in *Diels-Alder* reactions, may change substantially, especially in the near critical region of CO_2.

[5]) The progress of the reaction was followed by UV/VIS spectroscopy through a sapphire window. However, the reaction conditions with respect to the yields were not optimized in this and the other experiments (*cf. Exper. Part*).

Scheme 4



9 **12a** (8%) **12b** (8%)

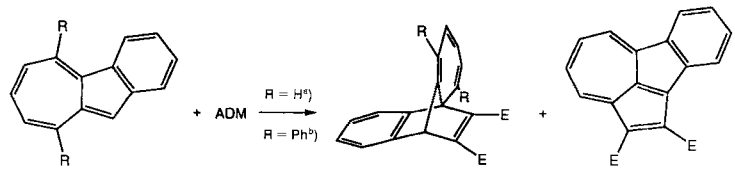
13 (4%)

E = COOMe

a) 150 bar CO_2, 100°, 20 h, with a four-fold molar amount of ADM; 6% of **9** were recovered.

In a second experiment, we investigated the thermal reaction of benz[*a*]azulene (**25**) with ADM in sc-CO_2 at 150° and 170 bar. In this case, we observed the formation of the corresponding benzo[*d*]heptalene-6,7-dicarboxylate **29** in a yield of 30%, accompanied by the diester **28** in 22% yield (*Scheme 5*). No other products could be observed[6]). In earlier experiments, we have reacted **25** with ADM in MeCN under $[RuH_2(PPh_3)_4]$ catalysis [19]. Under these conditions, we did not observe the formation of **29**. However, its tricyclic precursor **27** and dimethyl benzo[*a*]cyclopent[*cd*]azulene-1,2-dicarboxylate (**28**) were obtained. Thermal rearrangement of **27** in MeCN led only to the formation of the latter compound. Very recently, *Yasunami et al.* [21] reported that the thermal

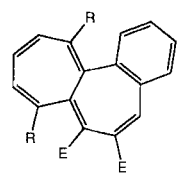
Scheme 5



R= H: **25**
R= Ph: **26**

27 (n. o.)[c])
30 (25%)

28 (22%)



29 (30%)
31 (22%)

E = COOMe

a) 170 bar CO_2, 150°, 7 h, with a four-fold molar amount of ADM.

b) 150 bar CO_2, 100°, 15 h, with a four-fold amount of ADM; 44% of **26** were recovered.

c) *Cf. Footnote 6.*

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6) In a further run, at 700 bar/150°, only traces of **29** could be observed. However, in the fractions that contained **29**, we also observed the presence of small amounts of the corresponding tricyclic precursor **27** by ^{1}H-NMR spectroscopy (H–C(10) at 4.50 ppm in C_6D_6; *cf.* [19]).

reaction of **25** and ADM in tetralin at 200° gives mainly **29** (58%) and only small amounts (4%) of **28**[7]). We suppose that the formation of **28** is mainly due to wall catalysis which may strongly act in the stainless steel autoclave we used for the reaction in sc-CO_2.

The reaction of 5,9-diphenylbenz[*a*]azulene (**26**) with ADM in sc-CO_2 (100°/150 bar) gave the corresponding tricyclic intermediate **30** and the benzo[*d*]heptalene-6,7-dicarboxylate **31** (*Scheme 5*), *i.e.*, the same products which we also observed in the Ru^{II}- and in the Rh^{I}-catalyzed reaction in MeCN [3] [19] as well as in the purely thermal reaction in DMF [7] [19]. The work is continued.

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Experimental Part

General. See [1] [19].

Thermal Reactions of the Azulenes with ADM in sc-CO_2. All reactions were performed in a 60-ml stainless steel autoclave equipped with a sapphire window and attached to an *Otsuka* spectrophotometer (model *MCPD 1100*; see [23]). The used CO_2 was of technical grade (purity: 99.5%) and pressurized with a *Hofer*-compressor (model *MKZ 80-100*). After the reactions the autoclave was cooled to r.t. and CO_2 expanded through a steel tube which ended in a vessel filled with glass beads. Afterwards, the autoclave and the beads were washed with the appropriate solvent.

1. *1,3,4,6,8-Pentamethylazulene* (**9**). The azulene (0.110 g; 0.55 mmol) and ADM (0.315 g; 2.22 mmol) were heated at 100° in sc-CO_2 at 150 bar during 20 h. The mixture was subjected to CC (15 g silica gel; hexane/Et_2O 3:2) and separated into three fractions: *1*) azulene **9** (6.5 mg; 6%), *2*) 1:1 mixture of *dimethyl 3,5,6,8,10-pentamethylheptalene-1,2-dicarboxylate* (**12a**) and its DBS isomer **12b** (28.9 mg; 16%), and *3*) *dimethyl 3,4,6,8-tetramethylazulene-1,2-dicarboxylate* (**13**; 6.6 mg; 4%). Both heptalenes, **12a** and **12b**, were separated by HPLC (*cf.* [1]; hexane/i-PrOH 98:2).

Data of **12a**: Identical with those reported in [1]. ^{1}H-NMR ($CDCl_3$, 300 MHz): 6.15 (*s*, H–C(7)); 6.06 (*s*, H–C(4)); 5.99 (*s*, H–C(9)); 3.67, 3.63 (2*s*, 2 COOMe); 2.26 (*s*, Me–C(3)); 2.05 (*s*, Me–C(8)); 1.98 (*s*, Me–C(10)); 1.94 (*s*, Me–C(5)); 1.77 (*s*, Me–C(6)).

Data of **12b**: Identical with those reported in [1]. ^{1}H-NMR ($CDCl_3$, 300 MHz): 6.44 (*d*, ^4J = 1.3, H–C(2)); 6.12 (*s*, H–C(7)); 6.01 (*s*, H–C(9)); 3.89, 3.67 (2*s*, 2 COOMe); 2.03 (*d*, ^4J = 1.3, Me–C(3)); 2.00 (*d*, ^4J = 1.3, Me–C(8)); 1.98 (*d*, ^4J = 1.3, Me–C(10)); 1.77 (*s*, Me–C(1)); 1.64 (*s*, Me–C(6)).

Data of **13**: Identical with those reported in [1]. ^{1}H-NMR ($CDCl_3$, 300 MHz): 6.99 (*s*, H–C(5,7)); 3.91 (*s*, 2 COOMe); 3.02, 2.88 (2s, Me–C(4,8)); 2.78 (*s*, Me–C(3)); 2.54 (*s*, Me–C(6)).

2. *Benz[a]azulene* (**25**). The azulene (0.026 g; 0.14 mmol) and ADM (0.080 g; 0.56 mmol) were heated for 7 h at 150° in sc-CO_2 at 170 bar. CC (10 g of silica gel; pentane/Et_2O 3:1) yielded in a first fraction *dimethyl benzo[d]heptalene-6,7-dicarboxylate* (**29**; 0.014 g; 30%) and in a second one *dimethyl benzo[a]cyclopent[cd]-azulene-1,2-dicarboxylate* (**28**; 0.0094 g; 22%).

Data of **29** (*cf.* [21]): M.p. 151° (pentane/AcOEt; [21]: 152° (hexane/AcOEt)). UV (MeOH): λ_{max}: 337 (sh, 3.68), 326 (sh, 3.71), 291 (4.00), 277 (4.02), 254 (4.03), 241 (4.02). λ_{min}: 285 (3.99), 270 (4.00), 260 (4.03), 246 (4.02). IR (KBr): 3019*w*, 2944*w*, 1703*s*, 1616*w*, 1582*w*, 1445*w*, 1388*w*, 1376*w*, 1432*m*, 1303*s*, 1282*s*, 1268*s*, 1239*s*, 1227*s*, 1215*s*, 1162*m*, 1124*m*, 1105*m*, 1059*m*, 1013*m*, 994*w*, 958*w*, 908*m*, 896*m*, 884*s*, 872*m*, 868*m*, 844*m*, 784*w*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.01 (*s*, H–C(5)); 7.48–7.34 (partially superimposed *td* (H–C(2)), *td* (H–C(3)), and *dt* (H–C(4))); 7.01 (*dt*, $^3J(1,2)$ = 6.9, $^4J(1,3) \approx 2 \cdot {}^5J(1,4)$, H–C(1)); 6.68 (*ddt*, $^3J(11,10)$ = 10.9, $^3J(11,12)$ = 6.4, $^3J(11,9) \approx {}^5J(11,8) \approx 1$, H–C(11)); 6.63 (*ddt*, $^3J(10,11)$ = 10.9, $^3J(10,9)$ = 6.2, $^4J(10,12) \approx {}^4J(10,8) \approx 1$, H–C(10)); 6.43 (*ddd*, $^3J(9,8)$ = 10.9, $^3J(9,10)$ = 6.2, $^4J(9,11) \approx 1$, $^5J(9,12) < 1$, H–C(9)); 6.25 (br. *d*, $^3J(8,9)$ = 11.0, H–C(8)); 6.09 (br. *d*, $^3J(12,11)$ = 6.1, H–C(12)); 3.76, 3.67 (2*s*, 2 COOMe). ^{1}H-NOE ($CDCl_3$, 400 MHz): 6.09 (*d*, H–C(12))→7.01 (*s*, H–C(1)), 6.68 (*s*, H–C(11)). ^{1}H-DR ($CDCl_3$, 400 MHz): 6.09 (*d*, H–C(12))→6.68 (br. *d*,

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[7]) In control experiments, we reacted **25** with ADM under our standard conditions (three-fold molar amount of ADM, decalin, 180–200°) and observed the formation of 69% of **29** and 18% of **28** [22].

^3J = (11,10) = 11.0, H–C(11)); 6.25 (*d*, H–C(8))→6.43 (br. *d*, ^3J(9,10) = 6.0, H–C(9)). EI-MS: 320 (100, $M^{+\cdot}$), 289 (16), 261 (13), 229 (10), 202 (16), 189 (16), 178 (49, $[M - ADM]^{+\cdot}$).

Data of **28** (*cf.* [19] [21]): M.p. 188° (AcOEt; [21]: 188–190° (AcOEt)). UV/VIS (MeOH): λ_{max}: 657 (2.65), 447 (3.16), 418 (3.12), 386 (3.29), 352 (3.56), 337 (3.53), 276 (4.40); λ_{min}: 432 (3.14), 409 (3.10), 375 (3.25), 343 (3.51), 331 (3.50). IR (KBr): 2945*w*, 1739*s*, 1684*s*, 1607*m*, 1595*m*, 1479*m*, 1452*s*, 1431*s*, 1380*s*, 1360*s*, 1329*m*, 1316*m*, 1259*s*, 1202*s*, 1180*s*, 1115*s*, 1047*s*, 1040*s*, 986*m*, 779*s*, 747*s*, 736*m*. ^{1}H-NMR ($CDCl_3$, 300 MHz): 9.36 (*d*, ^3J(9,10) = 9.5, H–C(10)); 8.37 (*d*, ^3J(7,8) = 9.2, H–C(7)); 8.29 (*t*, $\Sigma\,^3J$(7,8) + ^3J(8,9) = 19.5, *i.e.*, ^3J(8,9) = 10.3, H–C(8)); 8.04 (*td*, $\Sigma\,^3J$(8,9) + ^3J(9,10) = 19.8, ^3J(8,9) = 10.3, ^3J(9,10) = 9.5, ^4J(7,9) ≈ 1, H–C(9)); 7.97 (*dt*-like, ^3J(5,6) = 7.5, ^4J(4,6) ≈ 2·^5J(3,6) ≈ 1, H–C(6)); 7.63 (*dt*-like, ^3J(3,4) = 7.5, ^4J(3,5) ≈ 2·^5J(3,6) ≈ 1, H–C(3)); 7.45 (*td*, $\Sigma\,^3J$(4,5) + ^3J(3,4) = 15.1, *i.e.*, ^3J(4,5) = 7.6, ^4J(4,6) = 1.0, H–C(4)); 7.25 (*td*, $\Sigma\,^3J$(4,5) + ^3J(5,6) = 15.1, *i.e.*, ^3J(4,5) = 7.6, H–C(5)); 4.11, 3.97 (2*s*, 2 COOMe). EI-MS: 318 (100, $M^{+\cdot}$), 287 (63), 260 (15), 200 (42).

3. *5,9-Diphenylbenz[*a*]azulene* (**26**). The azulene (0.016 g; 0.048 mmol) and ADM (0.027 g; 0.192 mmol) were heated for 15 h at 100° in sc-CO_2 at 150 bar. The mixture was chromatographed (CC, 7 g of silica gel; hexane/Et_2O 5:1) and separated into 3 fractions: *1*) azulene **26** (7 mg, 44%), *2*) *dimethyl (4b*SR,*10*RS*)-5,9-diphenyl-4b,10-etheno-10*H*-benz[*a*]azulene-11,12-dicarboxylate* (**30**; 1.8 mg; 14%), and *3*) *dimethyl (7a*PM,*12a*MP*)-8,12-diphenylbenzo[*d*]heptalene-6,7-dicarboxylate* (**31**; 1.6 mg; 12.5%). Traces of the intermediate *dimethyl (9a*SR,*10*RS*)-5,9-diphenyl-9a,10-etheno-10*H*-benz[*a*]azulene-11,12-dicarboxylate* were recognizable in the original reaction mixture by the ^{1}H-NMR signal at 4.39 ppm (*s*, H–C(8)) [3].

Data of **30**: Identical with those reported in [19] (*cf.* [3]). ^{1}H-NMR ($CDCl_3$, 300 MHz): 7.70–7.67 (*m*, 2 arom. H); 7.48 (*d*, J_o = 7.5, H–C(4)); 7.38–7.28 (*m*, 8 arom. H); 7.12–7.04 (*m*, 3 arom. H); 6.60 (*d*, ^3J(6,7) = 8.7, H–C(6)); 5.78 (*dd*, ^3J(7,6) = 8.7, ^3J(7,8) = 11.9, H–C(7)); 5.60 (*d*, ^3J(8,7) = 11.9, H–C(8)); 4.51 (*s*, H–C(10)); 3.69 (*s*, MeOCO–C(12)); 3.13 (*s*, MeOCO–C(11)).

Data of **31**: Identical with those reported in [19] (*cf.* [3]). ^{1}H-NMR ($CDCl_3$, 300 MHz): 8.42 (*s*, H–C(5)); 7.57 (*d*, ^3J(4,3) = 7.6, H–C(4)); 7.31 (*td*, ^3J(3,4) = 7.5, ^3J(3,2) = 7.6, ^4J(3,1) = 1.1, H–C(3)); 7.19–7.03 (*m*, H–C(2), arom. H); 6.95–6.83 (*m*, H–C(9), H–C(10), 2 arom. H); 6.69 (*dd*, ^3J(11,10) = 10.8, ^4J(11,9) = 0.9, H–C(11)); 6.61 (*d*, ^3J(1,2) = 7.3, H–C(1)); 3.77 (*s*, MeOCO–C(6)); 3.22 (*s*, MeOCO–C(7)).

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