An Investigation into Domino-*Heck* Reactions of *N*-Acylamino-Substituted Tricyclic Imides: Synthesis of New Prospective Pharmaceuticals

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Heck and domino-*Heck* reactions of unsaturated *N*-acylamino-substituted tricyclic imides with aryl(heteroaryl) iodides and phenyl- or (trimethylsilyl)acetylene were either carried out in the presence of formate or phenyl- and (trimethylsilyl)acetylene, respectively. The C–C coupling reactions appeared to be completely diastereoselective, giving the corresponding *N*-acylamino-5-*exo*-aryl (heteroaryl)- (**5a**–**c**, **6a**,**b**), *N*-(benzoylamino)-5-*exo*-phenyl-6-*exo*-[(trimethylsilyl)ethynyl]- (**5d**), or 5-*exo*-(4-chlorophenyl)-*N*-(2,2-dimethylpropanoylamino)-6-*exo*-(phenylethynyl)bicyclo[2.2.1]heptane-2-*endo*,3-*endo*-dicarboximide (**6c**) (*Schemes 3* and *4*).

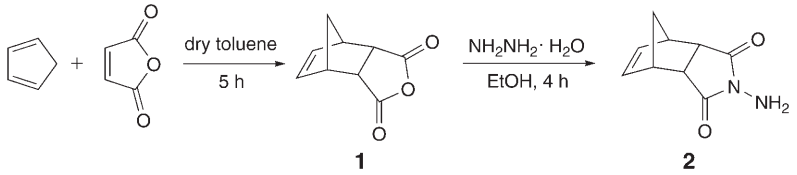
Introduction. – In the last decade, organopalladium-catalyzed C–C bond-formation has become one of the most efficient approaches in the synthesis of organic molecules. The *Heck* reaction, in particular, is widely used as an important method to build biologically active compounds in synthetic chemistry and the pharmaceutical industry [1][2]. As an extension of the *Heck* reaction, Pd-catalyzed hydroarylation of alkynes and alkenes continues to attract research interest in simple coupling processes and cyclization reactions. The research in the field of domino reactions also is attracting considerable attention in synthetic organic chemistry since it enables the rapid assembly of complex molecules in one-pot processes [3][4].

Kaufmann and co-workers have carried out new examples of *Heck* reactions using bicyclic systems aiming at the synthesis of new biologically active compounds [5–7]. Preparations of epibatidine analogues with bi- and tricyclic skeletons in a single synthetic operation *via* reductive *Heck* and additional domino-*Heck* reactions have recently been reported by us [8]. In the present work, we focused on reductive *Heck* reactions of the polyfunctionalized tricyclic molecules **3** and **4** with a strained C=C bond and an acylamino-imide or hydrazide group.

Organic derivatives of substituted hydrazines are extensively used in medicine as pharmacological agents exhibiting tuberculocidal, anticancer, radioprotection, antidepressant, psychotherapeutic, and other kinds of biological activities [9]. *Kas'yan* and co-workers indicated that, in contrast, the hydrazinolysis product of dicarboxyclic acid anhydrides and derivatives of the bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboxylic acids are poorly studied [10]. Furthermore, the synthesis of imide derivatives is important, because such compounds exhibit a wide range of pharmacological effects [11][12].

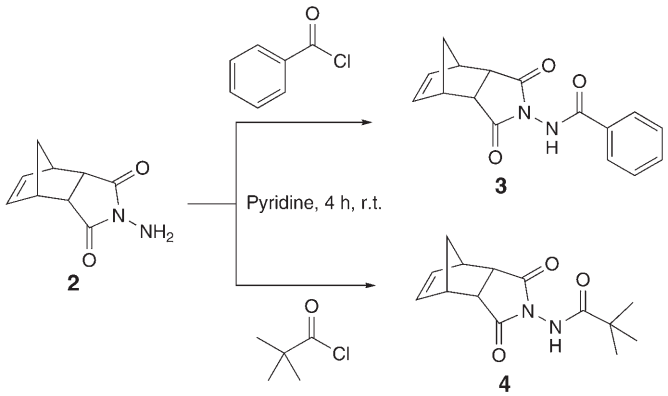
Results and Discussion. – Our synthesis started with the *Diels–Alder* reaction of cyclopentadiene and maleic anhydride. Hydrazinolysis of anhydride **1** was carried out with hydrazine hydrate in EtOH for 5 h to give bicyclic aminoimide **2** by a known procedure [13] (*Scheme 1*).

Scheme 1



Aminoimide **2** reacted with benzoyl chloride in pyridine as base to afford *N*-(benzoylamino)bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboximide (**3**[1]) [14]. The same reaction occurred with 2,2-dimethylpropanoyl chloride to give *N*-[(2,2-dimethylpropanoyl)amino]bicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboximide (**4**[1]) as a new compound (*Scheme 2*).

Scheme 2



The presence of a strained C=C bond in the *N*-substituted aminoimides **3** and **4** provided the possibility for carrying out *Heck* reactions with aryl(heteroaryl) iodides, in the presence of triphenylarsine ($AsPh_3$) as a ligand and palladium(II) acetate [15]. Treatment of **3** with iodobenzene, 1-chloro-4-iodobenzene, or 2-chloro-5-iodopyridine under reductive *Heck* conditions gave the new compounds **5a–c** as 5-*exo* products after chromatographic separation (*Scheme 3*).

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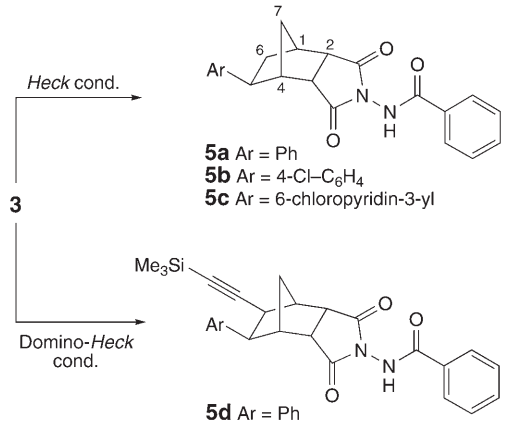
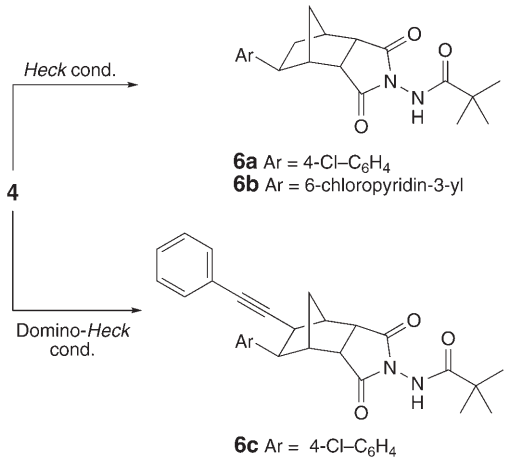
[1]) Trivial atom numbering (*syn*/*anti* relative to the imide); for systematic names, see *Exper. Part.*

Scheme 3[1])



We also synthesized **6a** and **6b** as new 5-*exo* compounds from **4** with 1-chloro-4-iodobenzene or 2-chloro-5-iodopyridine, respectively, under the same conditions (*Scheme 4*). The use of (trimethylsilyl)acetylene with 1-iodobenzene and of phenylacetylene with 1-chloro-4-iodobenzene under domino-*Heck* conditions provided the alkynylated tricyclic systems **5d** and **6c**, respectively. The configuration of the new compounds was inferred from their ^{1}H-NMR and ^{1}H,^{1}H-COSY data. Due to the symmetry of **3** and **4**, after column chromatographic separation, we obtained single diastereoisomers, only. Not surprisingly, the attachments of the phenyl or silylethynyl group took place exclusively from the *exo*-side of the tricyclic alkene moieties of **3** and **4**. The structures of **5d** and **6c** were also assigned by their ^{1}H,^{1}H-COSY and HSQC data in $CDCl_3$.

Scheme 4



In conclusion, the [$Pd(OAc)_2$]-catalyzed hydroarylation of the easily accessible tricyclic unsaturated *N*-(acylamino)-imides **3** and **4**, in the presence of $AsPh_3$ as a ligand, proved to be a stereoselective, versatile and high-yield approach for the synthesis of the aryl and heteroaryl derivatives of imides. Domino-*Heck* sequential C–C couplings with aryl or heteroaryl halides were shown to be feasible in the presence of (trimetylsilyl)acetylene or phenylacetylene.

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Experimental Part

1. *General.* All reactions were conducted under N_2 and carried out in a *Schlenk* system. Column chromatography (CC): silica gel *60*. TLC: silica gel precoated (0.2 mm layer) aluminium sheets (*Merck*). M.p.: *Gallenkamp*-melting-point apparatus; uncorrected. IR Spectra: *Perkin-Elmer FT-IR* spectrometer; KBr pellets; in cm^{-1}. NMR Spectra: *Bruker Digital-FT-NMR-Avance* (400 MHz) and *Varian Inova* (500 MHz) spectrometers; $CDCl_3$ solns.; δ in ppm rel. to $SiMe_4$ as internal standard, *J* in Hz. MS: *Varian Saturn 2100T/GC3900* GC/MS spectrometer; FAB ionization; in *m/z* (rel. %).

2. Heck *Reactions of Compounds* **3** *and* **4**: *General Procedure.* A soln. of [$Pd(OAc)_2$] (5.6 mg, 0.025 mmol) and $AsPh_3$ (33.7 mg, 0.11 mmol) in anh. DMF (3 ml) was stirred under N_2 at 65° for 15 min. Then, **3** or **4** (1 mmol), Et_3N (488 µl, 3.5 mmol), the appropriate aryl or heteroaryl iodide (1.5 mmol), and HCOOH (138 mg, 3 mmol) were added. The mixture was stirred for 8–24 h. After cooling to r.t., AcOEt and brine were added, and the org. layer was dried ($MgSO_4$), the solvent evaporated, and the residue purified by CC.

3. *Domino*-Heck *Reactions of Compounds* **3** *and* **4**: *General Procedure.* [$Pd(OAc)_2$] (5.6 mg, 25 µmol) and $AsPh_3$ (55 µmol) were dissolved in dry DMF (3 ml), and the soln. was stirred at 40° for 15 min. Then, **3** or **4** (1 mmol), the aryl compound (1.5 mmol), Et_3N (488 µl, 3.50 mmol), and (trimethylsilyl)ethyne or phenylethyne (3 mmol) were added rapidly in one portion. The mixture was kept at the same temp. for 24 h. After cooling to r.t., brine (50 ml) was added, the mixture extracted with AcOEt and dried ($MgSO_4$), the solvent evaporated, and the residue purified by CC.

4. rel-*[(3a*R*,4*S*,7*R*,7a*S*)-1,3,3a,4,7,7a-Hexahydro-1,3-dioxo-4,7-methano-2*H*-isoindol-2-yl]benzamide* (**3**) was prepared according to [14] in 85% yield. White crystals. M.p. 104–106°.

N-*(Benzoylamino)-5*-exo-*phenylbicyclo[2.2.1]heptane-2*-endo,*3*-endo-*dicarboximide* (= rel-N-*[(3a*R*,4*S*,5*S*,7*R*,7a*S*)-Octahydro-1,3-dioxo-5-phenyl-4,7-methano-2*H*-isoindol-2-yl]benzamide*; **5a**). CC (AcOEt/hexane 2:1): **5a** (90%). White crystals. M.p. 119–121°. IR: 3274, 3059, 2971, 1785, 1731, 1692, 1189. ^{1}H-NMR (400 MHz): 1.59 (*d*, *J* = 10.6, H_{anti}–C(7)); 1.66–1.80 (*m*, H_{syn}–C(7)); 1.90–1.98 (*m*, CH_2(6)); 2.98 (*d*, *J* = 10.0, H–C(1), H–C(4)); 3.22–3.27 (*m*, H–C(2), H–C(3), H_{endo}–C(5)); 7.20–7.35 (*m*, 5 arom. H); 7.42 (*t*, *J* = 7.4, 2 arom. H); 7.54 (*t*, *J* = 7.4, 1 arom. H); 7.85 (*d*, *J* = 8.4, 2 arom.H); 8.68 (br. *s*, NH). ^{13}C-NMR (100 MHz): 32.61 (CH_2); 39.29 (CH_2); 39.94; 41.64; 45.91; 46.53; 47.15; 126.12; 127.16; 127.73; 128.46; 128.71; 130.49 (*q*); 132.83; 152.68 (*q*); 165.24 (C=O); 175.03 (C=O); 175.33 (C=O). MS: 360 (11.8, $M^{+\cdot}$), 255 (8.2, $[M-COPh]^+$), 191 (25.5, $[M+1-C_{13}H_{14}]^+$), 119 (11.8, $NCOPh^+$), 105 (56.4, $COPh^+$), 77 (16.4, Ph^+), 57 (100, $NNHCO^+$).

N-*(Benzoylamino)-5*-exo-*(4-chlorophenyl)bicyclo[2.2.1]heptane-2*-endo,*3*-endo-*dicarboximide* (= rel-N-*[(3a*R*,4*S*,5*S*,7*R*,7a*S*)-5-(4-Chlorophenyl)-octahydro-1,3-dioxo-4,7-methano-2*H*-isoindol-2-yl]-benzamide*; **5b**). CC (AcOEt/hexane 2:1): **5b** (83%). White crystals. M.p. 122–124°. IR: 3263, 3060, 2970, 1786, 1730, 1692, 1189. ^{1}H-NMR (400 MHz): 1.63 (*d*, *J* = 10.6, H_{anti}–C(7)); 1.68–1.72 (*m*, H_{syn}–C(7)); 1.83–1.89 (*m*, H_{exo}–C(6)); 1.93 (*d*, *J* = 10.6, H_{endo}–C(6)); 2.95 (*d*, *J* = 5.2, H–C(1)); 2.99 (br. *s*, H–C(4)); 3.22–3.31 (*m*, H–C(2), H–C(3), H_{endo}–C(5)); 7.19 (*d*, *J* = 8.4, 2 arom. H); 7.27–7.30 (*m*, 2 arom. H); 7.45 (*t*, *J* = 7.6, 2 arom. H); 7.58 (*t*, *J* = 7.2, 1 arom. H); 7.87 (*d*, *J* = 8.4, 2 arom. H); 8.44 (br. *s*, NH). ^{13}C-NMR (100 MHz): 32.91 (CH_2); 39.30 (CH_2); 39.95; 41.10; 45.78; 46.42; 47.08; 127.73; 128.51; 128.79; 130.53 (*q*); 131.82 (*q*); 132.96; 143.32 (*q*); 165.38 (C=O); 174.82 (C=O); 174.96 (C=O).

MS: 394 (11.8, $M^{+\bullet}$), 359 (0.9, $[M-Cl]^+$), 289 (5.5, $[M-COPh]^+$), 274 (0.9, $[M-NHCOPh]^+$), 178 (3.6, $C_{11}H_{11}Cl^+$), 138 (5.9, $C_8H_7Cl^+$), 105 (100, $COPh^+$), 77 (30, Ph^+).

N-*(Benzoylamino)-5*-exo-*(6-Chloropyridin-3-yl)bicyclo[2.2.1]heptane-2*-endo,*3*-endo-*dicarboximide* (= rel-N-*[(3a*R,*4*S,*5*S,*7*R,*7a*S*)-5-(6-Chloropyridin-3-yl)-octahydro-1,3-dioxo-4,7-methano-2*H-*isoindol-2-yl]benzamide*; **5c**). CC (AcOEt/hexane 5:1): **5c** (68%). Yellow crystals. M.p. 90–93°. IR: 3263, 3054, 2971, 1783, 1730, 1690, 1186. ^{1}H-NMR (500 MHz): 1.63 (*d*, *J* = 11.0, H_{anti}–C(7)); 1.72–1.78 (*m*, H_{syn}–C(7), H_{exo}–C(6)); 1.85 (*d*, *J* = 11.0, H_{endo}–C(6)); 2.95 (*d*, *J* = 5.2, H–C(1)); 2.98 (br. *s*, H–C(4)); 3.21–3.31 (*m*, H–C(2), H–C(3), H_{endo}–C(5)); 7.25 (*d*, *J* = 8.4, 2 arom. H); 7.43–7.59 (*m*, 3 arom. H); 7.89 (*d*, *J* = 7.2, 2 arom. H); 8.22 (*s*, 1 arom. H); 8.83 (br. *s*, NH). ^{13}C-NMR (125 MHz): 32.94 (CH_2); 38.95; 39.36 (CH_2); 39.98; 45.25; 46.22; 46.97; 124.01; 127.80; 128.81; 130.53 (*q*); 133.01; 139.28 (*q*); 148.25; 149.13 (*q*); 165.69 (C=O); 174.60 (C=O); 174.62 (C=O). MS: 395 (31.8, $M^{+\bullet}$), 179 (11.8, $C_{10}H_{10}ClN^+$), 105 (100, $COPh^+$), 77 (51.8, Ph^+).

N-*(Benzoylamino)-5*-exo-*phenyl-6*-exo-*[(trimethylsilyl)ethynyl]bicyclo[2.2.1]heptane-2*-endo,*3*-endo-*dicarboximide* (= rel-N-*{(3a*R,*4*S,*5*R,*6*S,*7*R,*7a*S*)-Octahydro-1,3-dioxo-5-phenyl-6-[2-(trimethylsilyl)-ethynyl]-4,7-methano-2*H-*isoindol-2-yl}benzamide*; **5d**). CC (AcOEt/hexane 2:1): **5d** (76%). Light yellow crystals. M.p. 124–127°. IR: 3297, 3063, 2958, 2176, 1789, 1728, 1693, 1190. ^{1}H-NMR (500 MHz): 0.24 (*s*, Me_3Si); 1.93 (*d*, *J* = 10.7, H_{anti}–C(7)); 2.66 (*d*, *J* = 10.3, H_{syn}–C(7)); 3.18 (*d*, *J* = 4.9, H–C(4)); 3.32 (*d*, *J* = 3.9, H–C(1)); 3.39–3.46 (*m*, H–C(2), H–C(3), H_{endo}–C(5)); 3.51 (br. *s*, H_{endo}–C(6)); 7.32–7.44 (*m*, 5 arom. H); 7.57 (*t*, *J* = 7.8, 2 arom. H); 7.70 (*t*, *J* = 8.8, 1 arom. H); 7.99 (*d*, *J* = 7.3, 2 arom. H); 8.61 (br. *s*, NH). ^{13}C-NMR (125 MHz): –0.03 (Me); 38.89 (CH_2); 40.46; 44.15; 46.10; 46.22; 46.89; 47.78; 89.92, 106.60 (C≡C); 126.55; 128.10; 128.14; 128.71; 129.06; 129.17; 130.77; 133.16 (*q*); 141.70 (*q*); 165.62 (C=O); 174.85 (C=O); 174.91 (C=O). MS: 456 (4.5, $M^{+\bullet}$), 441 (20.9, $[M-Me]^+$), 383 (1.8, $[M-SiMe_3]^+$), 322 (4.5, $[M-NNHCOPh]^+$), 120 (0.9, $NHCOPh^+$), 105 (100, $COPh^+$), 77 (31.8, Ph^+), 73 (18.2, Me_3Si^+).

5. N-*[(2,2-Dimethylpropanoyl)amino]bicyclo[2.2.1]hept-5-ene-2*-endo,*3*-endo-*dicarboximide* (= rel-N-*[(3a*R,*4*S,*7*R,*7a*S*)-1,3,3a,4,7,7a-Hexahydro-1,3-dioxo-4,7-methano-2*H-*isoindol-2-yl]-2,2-dimethylpropanamide*; **4**). *N*-Aminobicyclo[2.2.1]hept-5-ene-2-*endo*,3-*endo*-dicarboximide (**2**; 600 mg, 3.3 mmol), which was prepared according to [10], and 2,2-dimethylpropanoyl chloride (411 mg, 3.3 mmol) were stirred in pyridine (5 ml) at r.t. for 4 h. After TLC control, the pyridine was removed *i.v.* The residue was purified by CC (AcOEt/hexane 1:1): **4** (90%). White crystals. M.p. 253–255°. IR: 3251, 3071, 2980, 1785, 1724, 1669, 1201. ^{1}H-NMR (500 MHz): 1.30 (*s*, 3 Me); 1.55 (*d*, *J* = 8.8, H_{syn}–C(7)); 1.76 (*d*, *J* = 9.8, H_{anti}–C(7)); 3.33 (br. *s*, H–C(1), H–C(4)); 3.44 (br. *s*, H–C(2), H–C(3)); 6.19 (*s*, H–C(5), H–C(6)); 7.31 (br. *s*, NH). ^{13}C-NMR (125 MHz): 26.26 (Me); 37.53 (CH_2); 43.29; 43.92; 50.81 (*q*); 133.78; 172.82 (C=O); 175.30 (C=O). MS: 262 (4.5, $M^{+\bullet}$), 247 (0.9, $[M-Me]^+$), 197 (11.8, $[M+1-C_5H_6]^+$), 178 (63.6, $[M+1-COCMe_3]^+$), 114 (49.1, $NNHCOCMe_3^+$), 92 (5.5, $C_7H_8^+$), 57 (100, Me_3C^+).

5-exo-*(4-Chlorophenyl)*-N-*[(2,2-dimethylpropanoyl)amino]bicyclo[2.2.1]heptane-2*-endo,*3*-endo-*dicarboximide* (= rel-N-*[(3a*R,*4*S,*5*S,*7*R,*7a*S*)-5-(4-Chlorophenyl)-octahydro-1,3-dioxo-4,7-methano-2*H-*isoindol-2-yl]-2,2-dimethylpropanamide*; **6a**). CC (AcOEt/hexane 5:1): **6a** (86%). Yellow crystals. M.p. 92–95°. IR: 3316, 3049, 2971, 1786, 1729, 1695, 1191. ^{1}H-NMR (400 MHz): 1.33 (*s*, 3 Me); 1.56 (*d*, *J* = 11.2, H_{anti}–C(7)); 1.63 (*s*, H_{syn}–C(7)); 1.76–1.87 (*m*, CH_2(6)); 2.8 (*d*, *J* = 5.6, H–C(1)); 2.93 (br. *s*, H–C(4)); 3.14–3.25 (*m*, H–C(2), H–C(3), H_{endo}–C(5)); 7.13 (*d*, *J* = 8.4, 2 arom. H); 7.23 (*d*, *J* = 8.6, 2 arom. H); 7.43 (br. *s*, NH). ^{13}C-NMR (100 MHz): 27.35 (Me); 32.63 (CH_2); 38.62 (*q*); 39.23 (CH_2); 39.84; 41.06; 45.79; 46.38; 46.95; 128.42; 128.56; 129.87 (*q*); 131.74 (*q*); 174.51 (C=O); 174.61 (C=O); 174.64 (C=O). MS: 374 (20.9, $M^{+\bullet}$), 290 (18.2, $[M+1-COCMe_3]^+$), 274 (5.5, $[M-NHCOCMe_3]^+$), 178 (21.8, $C_{11}H_{11}Cl^+$), 138 (11.8, $C_8H_7Cl^+$), 114 (13.6, $NNHCOCMe_3^+$), 85 (14.5, $COCMe_3^+$), 57 (100, Me_3C^+).

5-exo-*(6-Chloropridin-3-yl)*-N-*[(2,2-dimethylpropanoyl)amino]bicyclo[2.2.1]heptane-2*-endo,*3*-endo-*dicarboximide* (= rel-N-*[(3a*R,*4*S,*5*S,*7*R,*7a*S*)-5-(6-Chloropyridin-3-yl)-octahydro-1,3-dioxo-4,7-methano-2*H-*isoindol-2-yl]-2,2-dimethylpropanamide*; **6b**). CC (AcOEt): **6b** (62%). White crystals. M.p. 238–240°. IR (KBr): 3263, 3086, 2975, 1786, 1732, 1699, 1194. ^{1}H-NMR (400 MHz): 1.37 (*s*, 3 Me); 1.66 (*d*, *J* = 11.6, H_{anti}–C(7)); 1.74 (*s*, H_{syn}–C(7)); 1.77–1.83 (*m*, H_{exo}–C(6)); 1.89 (*d*, *J* = 12.0, H_{endo}–C(6)); 2.94 (*d*, *J* = 4.4, H–C(1)); 3.02 (br. *s*, H–C(4)); 3.21–3.32 (*m*, H–C(2), H–C(3), H_{endo}–C(5)); 7.27 (*d*, *J* = 8.4, 1 arom. H); 7.51–7.53 (*dd*, *J* = 2.5, 10.8, 1 arom. H); 7.62 (br. *s*, NH); 8.28 (*d*, *J* = 2.4, 1 arom. H). ^{13}C-NMR (100 MHz): 27.34 (Me); 32.68 (CH_2); 38.61 (*q*); 38.93; 39.30 (CH_2);

39.90; 45.35; 46.17; 46.86; 123.91; 138.02; 139.21 (*q*); 148.38; 149.18 (*q*); 174.28 (C=O); 174.37 (C=O); 176.77 (C=O). MS: 375 (96.4, $M^{+\cdot}$), 291 (35.5, $[M+1-COCMe_3]^+$), 205 (6.4, $C_{12}H_{12}ClN^+$), 179 (31.8, $C_{10}H_{10}ClN^+$), 139 (8.2, $C_7H_6ClN^+$), 85 (7.3, $COCMe_3^+$), 57 (92.7, Me_3C^+).

5-exo-*(4-Chlorophenyl)*-N-*[(2,2-dimethylpropanoyl)amino]-6*-exo-*(phenylethynyl)bicyclo[2.2.1]-heptane-2*-endo,*3*-endo-*dicarboximide* (= rel-N-*[(3a*R,*4*S,*5*R,*6*S,*7*R,*7a*S*)-5-(4-Chlorophenyl)-octahydro-1,3-dioxo-6-(2-phenylethynyl)-4,7-methano-2*H-*isoindol-2-yl]-2,2-dimethylpropanamide*; **6c**). CC (AcOEt/hexane 2:1): **6c** (68%). Light yellow crystals. M.p. 116–119°. IR: 3345, 3060, 2973, 2225, 1787, 1733, 1699, 1192. ^{1}H-NMR (500 MHz): 1.36 (*s*, 3 Me); 1.79 (*d*, *J* = 10.7, H_{anti}–C(7)); 2.48 (*d*, *J* = 10.3, H_{syn}–C(7)); 3.09 (*d*, *J* = 3.9, H–C(4)); 3.14 (*d*, *J* = 3.9, H–C(1)); 3.26–3.28 (*m*, H–C(2), H–C(3)); 3.51 (*d*, *J* = 7.3, H_{endo}–C(6)); 3.58 (br. *s*, H_{endo}–C(5)); 6.84 (*d*, *J* = 7.3, 2 arom. H); 7.13–7.20 (*m*, 5 arom. H); 7.27 (*d*, *J* = 7.3, 2 arom. H); 7.41 (br. *s*, NH). ^{13}C-NMR (125 MHz): 26.33 (Me); 37.10 (CH_2); 37.60 (*q*); 39.07; 42.60; 44.34; 44.65; 45.41; 46.26; 84.77, 88.65 (C≡C); 122.21; 126.59; 126.88; 127.00; 128.68; 130.21 (*q*); 130.92; 133.77 (*q*); 139.15 (*q*); 172.84 (C=O); 172.93 (C=O); 175.64 (C=O). MS: 474 (9.1, $M^{+\cdot}$), 389 (14.5, $[M-COCMe_3]^+$), 374 (2.7, $[M-NHCOCMe_3^+]$), 304 (2.7, $C_{21}H_{17}Cl^+$), 278 (23.6, $C_{19}H_{15}Cl^+$), 238 (7.3, $C_{16}H_{11}Cl^+$), 114 (4.5, $NNHCOCMe_3^+$), 57 (59.1, CMe_3^+).

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