FULL PAPER

Acid-Induced Rearrangement of Cycloadducts from Cyclopropenecarboxylates and 1,3-Diarylisobenzofurans

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Treatment of several *Diels–Alder* adducts of cyclopropenecarboxylates and 1,3-diarylisobenzofurans with a strong acid triggers a skeletal rearrangement resulting in 4,8b-dihydro-3a*H*-indeno[1,2-*b*]furans.

Keywords: Cyclopropenecarboxylates, 1,3-Diarylisobenzofurans, Rearrangements, Indeno[1,2-*b*]furans, *Diels–Alder* adduct.

Introduction

Natural and synthetic products containing an indeno[1,2-*b*]furan framework display a variety of pharmacological effects including antibacterial [1][2] and enzymatic [1] activities. Indenofuran derivatives are also used as a stimulant for the germination of seeds of parasitic weeds belonging to the genera *Striga* and *Orobanche* [3 – 6]. There has been interest in the synthesis of indeno[1,2-*b*]-furan ring systems and several multistage approaches have been reported [4][7][8]. Several approaches to the synthesis of the indeno[1,2-*b*]furan ring system have been developed, including methods such as reaction of ninhydrin with diketones [1][2][9][10], titanocene-catalyzed cyclocarbonylation of *o*-allyl aryl ketones [11], electrochemical reduction of 2,2-dibromo-1,3-diketones in the presence of indene [12], oxidative addition of 1,3-dicarbonyl compounds to indene [13][14]. *Bhuyan* and co-workers have reported a novel synthetic method for the preparation of dihydroindeno[1,2-*b*]furans *via* one-pot three-component reaction of 1,3-indanedione, aromatic aldehyde, and a pyridinium ylide in the presence of Et_3N under MW irradiation [15]. In 2014, *Yang* reported the first example of one-pot three-component condensation reactions of 1,3-indandione, aromatic aldehyde, and cyclohexyl isocyanide with the formation of indeno[1,2-*b*]furan derivatives in good yields [16].

Results and Discussion

It was discovered that the *Diels–Alder* adducts of 1,3-diarylisobenzofurans and cyclopropenecarboxylates on treatment with a strong acid undergo a cascade of cationic rearrangements leading to compounds with an indeno [1,2-*b*]furan skeleton. In this article, we present the synthesis, structural elucidation, and a mechanistic proposal for this rearrangement. Previously, acid-induced rearrangements of 1,3-diphenylisobenzofuran adducts with azirines [17 – 19], maleimides [20 – 23], (*E*)-6,6-dimethoxy-3-hexen-2-one [24], dimethyl maleate [23], cyclooctene [23], cyclopropenes [25 – 27], and *N*-aryl itaconimides [28] have been studied. *Cava* and *Narasimhan* reported that the [4+2] adduct from 1,3-diphenylisobenzofuran and 1,2,3-triphenylcyclopropene by treatment with hydrochloric acid underwent the fragmentation affording the 1,2,3,4-tetraphenylnaphthalene and benzaldehyde [26]. Similar results were obtained by treatment of the *Diels–Alder* adduct from 1,3-diphenylisobenzofuran and 1,2,3-triphenylcyclopropene with $MeSO_3H$ in CH_2Cl_2 at ambient temperature (*our data*).

For this study, we prepared several *Diels–Alder* adducts **3** from 1,3-diarylisobenzofurans **2a**, **2b** and cyclopropenecarboxylates **1a**, **1b**. The reactions of compounds **2a** with **1a**, **1b** and **2b** with **1b** in benzene at 60° resulted in the *exo*-adducts **3a** – **3c** (*Table*). It should be noted that according to the ^{1}H-NMR data, the reaction mixtures contained only the starting compounds and *exo*-adducts **3a** – **3c**. The *endo*-isomer could not be detected. The reaction products were isolated by column chromatography (CC) over silica using a mixture of hexane/AcOEt as the eluent. The structures of adducts **3a** – **3c** were characterized from their ^{1}H- and ^{13}C-NMR, MS, and IR spectra. The ^{1}H-NMR spectra of adducts **3a**, **3b**, and **3c** exhibit signals at δ(H) 3.60, 3.83, and 3.77, respectively, belonging to the cyclopropyl H-atoms. The values of the chemical shifts for cyclopropyl H-atoms indicate their *syn*-position with respect to the O-atom [29 – 31].

The rearrangement of compounds **3** was found in the presence of acids. Of the acids ($MeSO_3H$, H_2SO_4, HCl,

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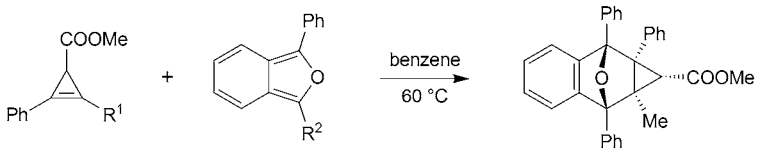
Table. Synthesis of *Diels–Alder* adducts **3a** – **3c**



1a, **1b** **2a**, **2b** **3a – 3c**

Entry	R^1	R^2	Time [h]	Yield of **3** [%][a])
1	Me (**1a**)	Ph (**2a**)	1 h	83 (**3a**)
2	Ph (**1b**)	Ph (**2a**)	3 h	80 (**3b**)
3	Ph (**1b**)	4–BrC_6H_4 (**2b**)	3 h	52 (**3c**)

[a]) Yield of isolated product.

$BF_3{\cdot}OEt_2$) and solvents (CH_2Cl_2, benzene, toluene, THF, Et_2O) screened, the combination of $MeSO_3H$ and CH_2Cl_2 produced the best results for these reactions [20].

In our initial studies, the reaction of **3a** with $MeSO_3H$ was investigated (*Scheme 1*). Compound **3a** was reacted with $MeSO_3H$ (6 equiv.) in CH_2Cl_2 at ambient temperature. After stirring for 6 h and extractive workup, the thin-layer chromatography (TLC) analysis indicated the formation of several compounds. Only methyl (3a*SR*,4*RS*,8b*RS*)-4,8b-dihydro-2-methyl-3a,4,8b-triphenyl-3a*H*-indeno[1,2-*b*]furan-3-carboxylate (**4a**) and methyl 3-oxo-2-(1,1,3-triphenyl-1*H*-inden-2-yl)butanoate (**5**) were isolated from the reaction mixture by a CC in 35% and 15% yields, respectively; no other products were isolated in pure form (*Scheme 1*). After reducing the reaction time to 3 h, we could isolate product **4a** in 51% yield. It should be noted that using one or two equivalents of $MeSO_3H$ in the reaction mixture after stirring for 6 h was observed the presence of starting *Diels–Alder* adduct **3a**. According to TLC data, using 1 – 3 equivalents of the $MeSO_3H$ leads to more complex reaction mixtures. The compositions and structures of the products **4a** and **5** were established by elemental and spectroscopic analyses. The ^{1}H-NMR spectrum of indeno[1,2-*b*]furan **4a** exhibits a signal for the CH H-atoms at the C(4) atom at δ(H) 5.7, and a signal for the Me group at the C(2) atom at δ(H) 2.4. The fused tricyclic structure and relative configuration of product **4a** were confirmed by a single-crystal X-ray diffraction (*Fig. 1*). The ^{1}H-NMR spectrum of indene **5** shows *singlet* signals at δ(H) 4.1 and 2.2 belonging to the H-atom in α-position of the ester group and the *Me*CO group, respectively. The ^{13}C-NMR spectrum of compound **5** exhibits a signal for the CO group at δ(C) 208, signals for the Me groups at δ(C) 52 (CO_2*Me*), and 31 (*Me*CO), a signal for the CH C-atom at δ(C) 55 and a signal for C(1) at δ(C) 65. We proposed that indene **5** was formed from indenofuran **4a** under acidic conditions, and when **4a** was treated with $MeSO_3H$ in CH_2Cl_2 the formation of indene **5** was observed.

For the next step in our study, we treated *Diels–Alder* adduct **3b** with $MeSO_3H$ (*Scheme 2*). The reaction proceeded at room temperature producing indeno[1,2-*b*]furan

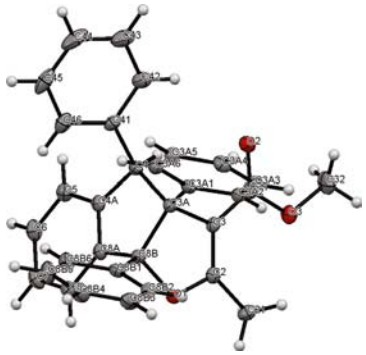
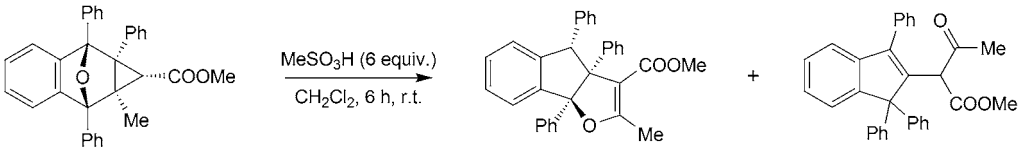


Fig. 1. Molecular structure (ORTEP 50% probability level) of **4a**. Selected interatomic distances [Å] and Angles [°]: O(1)–C(2) 1.3578 (13), O(1)–C(8b) 1.4720(12), C(2)–C(3) 1.3470(15), C(3)–C(3a) 1.5265 (14), C(3a)–C(4) 1.5924(14), C(3a)–C(8b) 1.5990(14), C(4)–C(4a) 1.5094(14), C(4a)–C(8a) 1.3835(15), C(8a)–C(8b) 1.5059(14), C(2)–O (1)–C(8b) 108.35(8), C(3)–C(2)–O(1) 113.25(9), C(3)–C(3a)–C(4) 108.75(8), C(3)–C(3a)–C(8b) 98.64(8).

Scheme 1. Reaction of *Diels–Alder* adduct **3a** with $MeSO_3H$.



3a **4a** (35%) **5** (15%)

4b in 37% yield. Although the TLC analysis indicated the formation of several compounds, isolation of other products from the reaction mixture in a pure form was not possible. The treatment of the unsymmetrically substituted adduct **3c** with $MeSO_3H$ at 20° for 3 h afforded a complex mixture of products (*Scheme 3*). A CC of this mixture made it possible to isolate indeno[1,2-*b*]furan **4c** in 25% yield and indenes **6a**, **6b** in 30% overall yield as inseparable mixtures of isomers. By increasing the reaction time to 3 d, isomeric indenes **6a**, **6b** were isolated in 47% overall yield, indenofuran **4c** (7%) and a mixture of unidentified products. The reaction of indeno[1,2-*b*]furan **4c** with $MeSO_3H$ in CH_2Cl_2 for 2 d led to indene **6a** in 34% yield (*Scheme 4*). The structure of **4c** was established unequivocally by X-ray diffraction analysis (*Fig. 2*). Single crystals of **4c** were obtained by crystallization from CH_2Cl_2/MeOH.

Based on the above results, a plausible mechanism for the formation of compounds **4a** – **4c** is proposed in *Scheme 5*. The acid-catalyzed isomerization of **3** starts from cation **7**, which undergoes rearrangement through a cascade of cations **8** – **10**. The breaking up of an oxygen bridge in cation **7** gives cyclopropyl carbinyl cation **8**. Subsequent rearrangement leads to homoallylic cation **9**. Finally, a v [$_{\pi}2 + {}_{\sigma}2 + {}_{\sigma}2$]-rearrangement occurs in the cation **9** to form cation **10**, which *via* deprotonation gives products **4a** – **4c**.

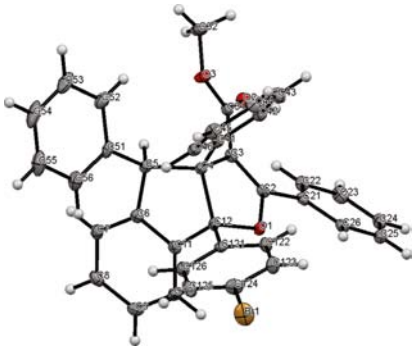
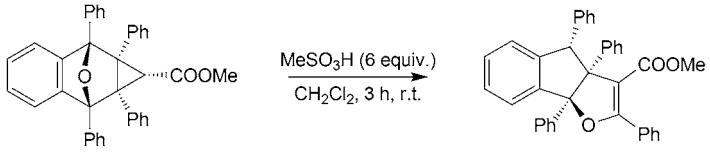


Fig. 2. Molecular structure (ORTEP 50% probability level) of **4c**. Selected interatomic distances [Å] and angles [°]: O(1)–C(2) 1.3682 (18), O(1)–C(12) 1.4597(17), C(3)–C(2) 1.351(2), C(3)–C(4) 1.531 (2), C(4)–C(5) 1.595(2), C(6)–C(5) 1.509(2), C(11)–C(6) 1.382(2), C(4)–C(12) 1.592(2), C(2)–O(1)–C(12) 107.97(11), O(1)–C(12)–C(4) 104.67(11), C(2)–C(3)–C(4) 110.57(13), C(3)–C(4)–C(5) 107.79(12), C(3)–C(4)–C(12) 98.35(11).

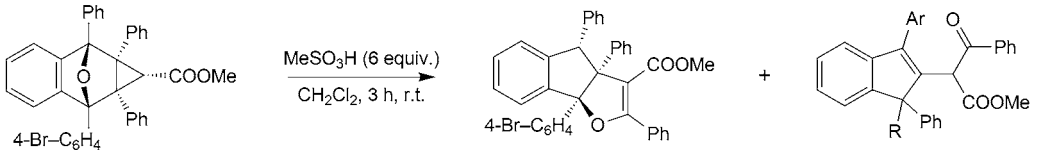
The probable mechanism of formation of indenes **5** and **6** is shown in *Scheme 6*. On the first stage, indenofuran **4** reacts with $MeSO_3H$ giving the protonated form **11**,

Scheme 2. Reaction of *Diels–Alder* adduct **3b** with $MeSO_3H$.



3b **4b** (37%)

Scheme 3. Reaction of *Diels–Alder* adduct **3c** with $MeSO_3H$.

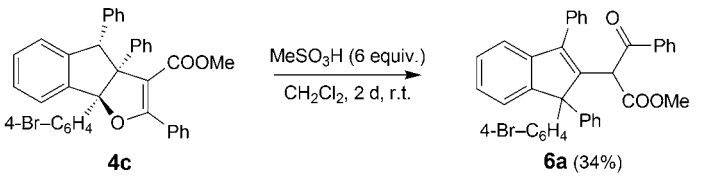


3c **4c** (25%)

Inseparable mixture of isomers (30% overall yield)

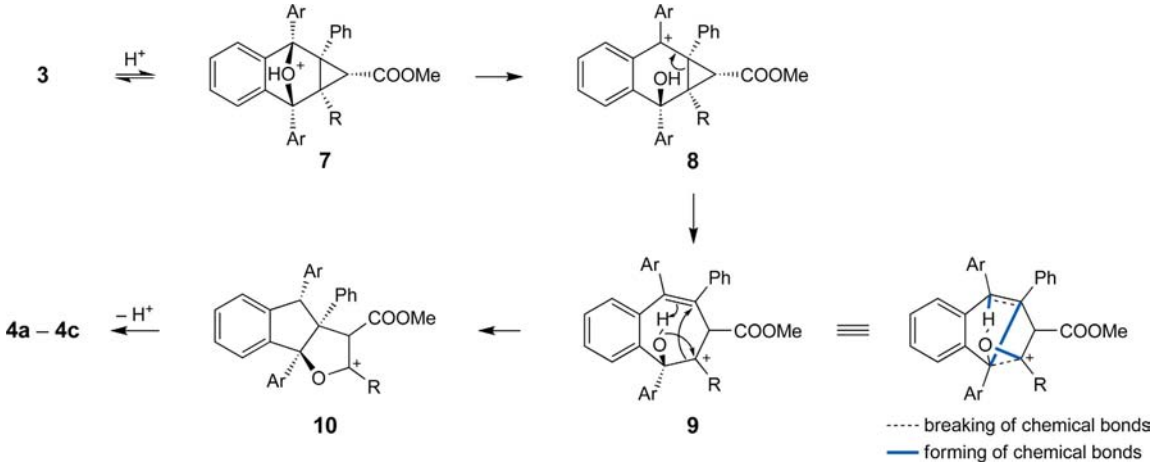
	R	Ar
6a	4-Br–C_6H_4	Ph
6b	Ph	4-Br–C_6H_4

Scheme 4. Reaction of indenofuran adduct **4c** with $MeSO_3H$.

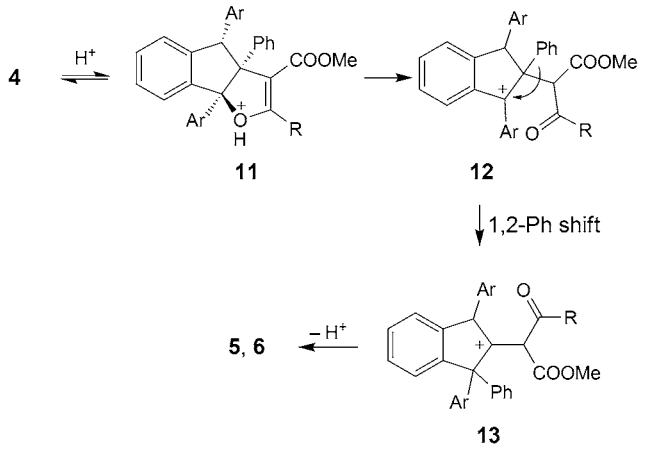


4c **6a** (34%)

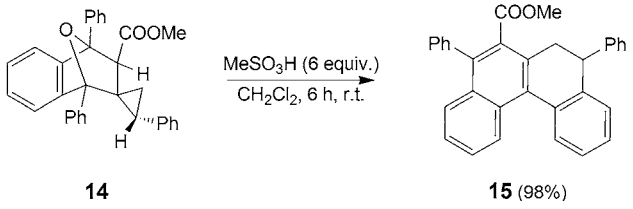
Scheme 5. Proposed reaction mechanism for the formation of products **4a** – **4c**.



Scheme 6. Proposed reaction mechanism for the formation of indenes **5** and **6**.



Scheme 7. Reaction of *Diels–Alder* adduct **14** with $MeSO_3H$.



which is converted into cation **12** through the opening of the furan ring. The latter undergoes a 1,2-phenyl shift with formation of intermediate **13**, which is further transformed into products **5** and **6**.

The choice of spiro-adduct **14** as starting material in this reaction appeared particularly interesting in order to expand the synthetic utility of this methodology (*Scheme 7*). An adduct **14** was prepared by heating of a mixture of methyl (*E*)-2-(2-phenylcyclopropylidene)acetate and isobenzofuran **2a** in toluene (3 h, 110°). Synthesis, and spectroscopic, analytical, and X-ray characterization data for *Diels–Alder* adduct **14** were previously reported by our group [32]. Compound **14** was reacted with $MeSO_3H$ (6 equiv.) in CH_2Cl_2 at ambient temperature. After stirring for 6 h and extractive workup, the TLC analysis indicated the formation of only one compound. The methyl 5,8-diphenyl-7,8-dihydrobenzo[*c*]phenanthrene-6-carboxylate (**15**) was isolated from the reaction mixture by the preparative TLC in 98% yield. The structure of the benzo[*c*]phenanthrene **15** was characterized by ^1H- and ^{13}C-NMR, MS, and IR spectra. The structure of compound **15** was confirmed additionally by the X-ray diffraction analysis (*Fig. 3*).

A plausible mechanism for the formation of compound **15** is proposed in *Scheme 8*. The *Diels–Alder* adduct **14**, under acidic conditions, undergoes subsequent conversion into cations **16** and **17**. The latter is converted to the benzyl cation **18** as result a cyclopropane ring opening. Finally, an intramolecular *Friedel–Crafts* reaction occurs in the intermediate **18** to form product **15**.

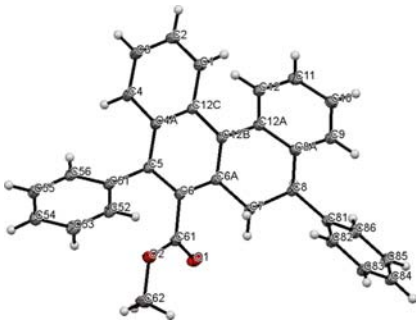
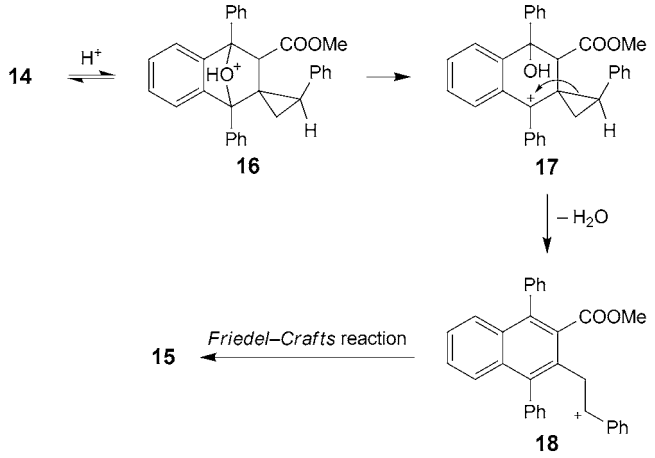


Fig. 3. Molecular structure (ORTEP 50% probability level) of **15**. Selected interatomic distances [Å] and angles [°]: C(6a)–C(7) 1.5142 (17), C(6a)–C(12b) 1.3935(17), C(7)–C(8) 1.5393(17), C(8)–C(8a) 1.5236(17), C(8a)–C(12a) 1.4208(17), C(12a)–C(12b) 1.4910(17), C(12b)–C(6a)–C(7) 118.73(10), C(8a)–C(8)–C(7) 107.28(10), C(6a)–C(12b)–C(12a) 117.34(11), C(12)–C(12a)–C(12b) 123.15(11), C(6)–C(6a)–C(7) 120.97(11).

Scheme 8. Proposed reaction mechanism for the formation of product **15**.



Conclusion

We have shown that treatment of the *Diels–Alder* adducts of cyclopropenecarboxylates and 1,3-diarylisobenzofurans with a strong acid triggers a skeletal rearrangement resulting in 4,8b-dihydro-3a*H*-indeno[1,2-*b*]furans. Under similar conditions, the *Diels–Alder* adduct of methyl (*E*)-2-(2-phenylcyclopropylidene)acetate and 1,3-diphenylisobenzofuran is converted to benzo[*c*]phenanthrene derivative.

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Experimental Part

General

Hexane and AcOEt for the chromatography were distilled before use. Cyclopropenes and 1,3-diarylisobenzofurans were prepared following known procedures [33 – 36]. Reactions were monitored by the TLC analysis using *Silufol UV-254* plates. The CC was performed on silica gel (SiO_2; 70 – 230 mesh; *Merck*), eluted with AcOEt/hexane. M.p.: *Boetius* instrument; uncorrected. IR Spectra: *Bruker Tensor 27* spectrophotometer. ^{1}H- and ^{13}C-NMR spectra: in $CDCl_3$ using a *Bruker Avance 400* or a *Bruker DPX-300* spectrometer. HR-ESI-MS: *Bruker-microTOF* and *Bruker-maXis* (QTOF) instrument. The X-ray diffraction data were performed by a *Bruker APEX-II CCD* diffractometer with MoK_α X-ray radiation.

General Procedure for the Synthesis of Diels–Alder Adducts **3b** *and* **3c**

A soln. containing 1 mmol of cyclopropenecarboxylate **1b** and 1.2 mmol 1,3-diarylisobenzofuran **2a**, **2b** in 5 ml of dry benzene was heated at 60° for 3 h. The mixture was concentrated under reduced pressure and the residue was subjected to SiO_2 chromatography using a hexane/AcOEt mixture as eluent.

The reaction of *Diels–Alder* adducts **3a** – **3c** and **14** with $MeSO_3H$ (*General Procedure*). $MeSO_3H$ (6 equiv.) was added at r.t. to a soln. of **3** (1 equiv.) in CH_2Cl_2 (5 ml). After 3 h (TLC-control), 5 ml of Na_2CO_3 (aq.) were added carefully to the mixture. The aq. layer was extracted with CH_2Cl_2 (3 × 5 ml), the org. layers were combined, dried ($MgSO_4$), and evaporated to dryness. The residue was then purified by a CC using a mixture of hexane/AcOEt as eluent.

Methyl (1*RS*,1a*RS*,2*SR*,7*RS*,7a*RS*)-1a,2,7,7a-Tetrahydro-1a-methyl-2,7,7a-triphenyl-1*H*-2,7-epoxycyclopropa[*b*]-naphthalene-1-carboxylate (**3a**). A soln. containing 3.0 mmol of cyclopropenecarboxylate **1a** and 3.0 mmol 1,3-diphenylisobenzofuran (**2a**) in 50 ml of dry benzene was heated at reflux for 1 h. The mixture was concentrated under reduced pressure and the residue was subjected to SiO_2 chromatography (using hexane/AcOEt mixture as the eluent) to give the product **3a**. Yield: 1.17 g (83%). Colorless crystals. M.p. 120 – 122 °C. IR ($CHCl_3$): 1050, 1085, 1150, 1175, 1280, 1320, 1345, 1400, 1450, 1490, 1710, 2860, 3020. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.38 (*s*, Me); 3.60 (br. *s*, COOMe + C$H_{cycloprop.}$); 6.28 (*d*, *J* = 8, 2 $H_{arom.}$); 7.16 – 7.40 (*m*, 11 $H_{arom.}$); 7.50 – 7.60 (*m*, 4 $H_{arom.}$); 7.85 (*d*, *J* = 8, 2 $H_{arom.}$). ^{13}C-NMR (100 MHz, $CDCl_3$): 10.0 (Me); 32.1 (CH); 41.4 ($C_{cycloprop.}$); 51.0 ($C_{cycloprop.}$); 51.5 (COO*Me*); 90.5 (*C*–O); 90.7 (*C*–O); 122.1; 122.2; 126.0; 126.5; 126.8 (2 C); 127.4 (2 C); 127.5; 127.86; 127.94 (2 C); 128.4; 128.8 (2 C); 128.9 (2 C); 129.0; 132.0 (2 C); 134.3; 134.8; 147.5; 147.9; 169.9 (CO). HR-ESI-MS: 481.1774 ($C_{32}H_{26}NaO_3^+$, $[M + Na]^+$; calc. 481.1780).

Methyl (1a*RS*,2*RS*,7*SR*,7a*SR*)-1a,2,7,7a-Tetrahydro-1a,2,7,7a-tetraphenyl-1*H*-2,7-epoxycyclopropa[*b*]naphthalene-1-carboxylate (**3b**). Yield: 469 mg (80%). Colorless crystals. M.p. 265 – 267 °C. IR ($CHCl_3$): 1175, 1195, 1303, 1330, 1447, 1496, 1737, 2950, 3053. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.33 (*s*, COOMe); 3.83 (*s*, C$H_{cycloprop.}$); 6.67 (*d*, *J* = 8, 4 $H_{arom.}$); 7.13-7.40 (*m*, 20 $H_{arom.}$). ^{13}C-NMR (100 MHz, $CDCl_3$): 32.7 (C$H_{cycloprop.}$); 51.1 (COO*Me*); 54.8 (2 $C_{cycloprop.}$); 90.2 (2**C*–O); 122.5 (2 C); 126.3 (2 C); 126.7 (4 C); 127.2 (4 C); 127.3 (2 C); 127.89 (4 C); 127.92 (2 C); 131.9 (2 C); 132.2 (4 C); 134.6 (2 C); 147.5 (2 C); 169.3 (CO). HR-ESI-MS: 543.1931 ($C_{37}H_{28}NaO_3^+$, $[M + Na]^+$; calc. 543.1936).

Methyl (1*SR*,1a*SR*,2*SR*,7*RS*,7a*RS*)-2-(4-Bromophenyl)-1a,2,7,7a-tetrahydro-1a,7,7a-triphenyl-1*H*-2,7-epoxycyclopropa[*b*]naphthalene-1-carboxylate (**3c**). Yield: 310 mg (52%). Colorless crystals. M.p. 209 – 211 °C. IR ($CHCl_3$):

1009, 1168, 1331, 1397, 1445, 1493, 1602, 1745, 2948, 3053. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.34 (*s*, COOMe); 3.80 (*s*, $CH_{cycloprop.}$); 6.65 (*d*, *J* = 7, 4 $H_{arom.}$); 7.16-7.40 (*m*, 17 $H_{arom.}$); 7.50 (*d*, *J* = 8, 2 $H_{arom.}$). ^{13}C-NMR (100 MHz, $CDCl_3$): 32.5 ($CH_{cycloprop.}$); 51.2 (COO*Me*); 54.8 (2 $C_{cycloprop.}$); 90.0 (*C*–O); 90.6 (*C*–O); 122.1; 122.3; 122.6; 126.3; 126.4; 126.6 (2 C); 127.2 (2 C); 127.3 (2 C); 127.4; 127.5; 127.9 (2 C); 128.0; 128.3 (2 C); 131.1 (2 C); 131.6; 131.7; 132.1 (4 C); 133.5; 134.3; 147.1; 147.4; 169.1 (CO). HR-ESI-MS: 621.1036 ($C_{37}H_{27}{}^{79}BrNaO_3^+$, $[M + Na]^+$; calc. 621.1041), 623.1015 ($C_{37}H_{27}{}^{81}BrNaO_3^+$, $[M + Na]^+$; calc. 623.1015).

Methyl (3a*SR*,4*RS*,8b*RS*)-4,8b-Dihydro-2-methyl-3a,4,8b-triphenyl-3a*H*-indeno[1,2-*b*]furan-3-carboxylate (**4a**) and **Methyl 3-Oxo-2-(1,1,3-triphenyl-1*H*-inden-2-yl)butanoate** (**5**). Following the *General Procedure*, *Diels–Alder* adduct **3a** (0.76 mmol) and $MeSO_3H$ (4.5 mmol) were reacted in CH_2Cl_2. CC gave **4a** (121 mg, 35%) and **5** (51 mg, 15%).

Data of **4a**: Colorless crystals. M.p. 198 – 200 °C. IR ($CHCl_3$): 1096, 1131, 1193, 1243, 1375, 1446, 1496, 1634, 1683, 3053. ^{1}H-NMR (300 MHz, $CDCl_3$): 2.41 (*s*, Me); 3.88 (*s*, COOMe); 5.67 (*s*, CH); 6.05 (*d*, *J* = 6, 2 $H_{arom.}$); 6.56 – 6.80 (*m*, 5 $H_{arom.}$); 6.90 – 7.15 (*m*, 8 $H_{arom.}$); 7.38 – 7.55 (*m*, 4 $H_{arom.}$). ^{13}C-NMR (100 MHz, $CDCl_3$): 16.1 (Me); 51.3 (COO*Me*); 60.0 (CH); 71.2; 106.3; 110.3; 125.3; 125.8 (2 C); 126.8; 127.0 (3 C); 127.2 (2 C); 127.6; 127.9 (2 C); 128.5 (3 C); 130.1; 130.5; 130.6 (2 C); 138.7; 140.5; 143.1; 144.0; 146.1; 167.5 (=*C*–O); 168.7 (CO). HR-ESI-MS: 481.1774 ($C_{32}H_{26}NaO_3^+$, $[M + Na]^+$; calc. 481.1780).

Crystallographic Data for **4a**. $C_{32}H_{26}O_3$, M_r 458.53, monoclinic, $P2_1/c$ (no. 14), a = 9.76434(9), b = 9.59139(11), c = 25.5371(3) Å, β = 95.6193(9)°, V = 2380.15(4) Å^3, Z = 4, D_x = 1.280 g cm^{-3}, $F(000)$ = 968, radiation, CuK_α (λ = 1.54184 Å), $3.48 \le 2\theta \le 76.60$, intensity data were collected at 293(2) K with a *Bruker APEX-II CCD* diffractometer, and by employing a $w/2\theta$ scanning technique, in the range of $-12 \le h \le 1$, $-12 \le k \le 12$, $-32 \le l \le 29$; the structure was solved by a direct method; all non-H-atoms were positioned, and anisotropic thermal parameters were refined from 5001 observed reflections with R(into) = 0.0140 by a full-matrix least-squares technique converged to R = 0.0371 and R_w = 0.0925 [$I > 2\sigma(I)$]. *CCDC* No.: 1057280.

Data of **5**: White crystals. M.p. 182 – 184 °C. IR ($CHCl_3$): 1032, 1043, 1070, 1090, 1118, 1154, 1193, 1230, 1246, 1346, 1432, 1445, 1479, 1491, 1596, 1726, 3056. ^{1}H-NMR (400 MHz, $CDCl_3$): 2.24 (*s*, Me); 3.75 (*s*, COOMe); 4.07 (*s*, CH); 6.59 – 7.40 (*m*, 19 $H_{arom.}$). ^{13}C-NMR (100 MHz, $CDCl_3$): 31.0 (Me); 52.0 (COO*Me*); 54.6 (CH); 64.5; 125.8; 126.5; 126.8; 127.5 (2 C); 127.6 (2 C); 127.8 (2 C); 127.9 (3 C); 128.0 (2 C); 128.4 (2 C); 128.6 (2 C); 130.4; 133.3; 135.1; 137.9; 138.7; 139.0; 140.7; 141.3; 172.2 (CO); 208.2 (CO). HR-ESI-MS: 481.1774 ($C_{32}H_{26}NaO_3^+$, $[M + Na]^+$; calc. 481.1780).

Methyl (3a*S*,4*R*,8b*R*)-4,8b-Dihydro-2,3a,4,8b-tetraphenyl-3a*H*-indeno[1,2-*b*]furan-3-carboxylate (**4b**). 29 mg (37%) was obtained using *General Procedure* from *Diels–Alder* adduct **3b** (77 mg). White crystals. M.p. 225 – 227 °C. IR ($CHCl_3$): 1075, 1180, 1330, 1420, 1470, 1620, 1720, 3055. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.75 (*s*, COOMe); 5.67 (*s*, CH); 6.19 (*d*, *J* = 8, 2 $H_{arom.}$); 6.64 (*t*, *J* = 8, 2 $H_{arom.}$); 6.78 – 6.85 (*m*, 3 $H_{arom.}$); 6.95 – 7.10 (*m*, 5 $H_{arom.}$); 7.12 – 7.14 (*m*, 3 $H_{arom.}$); 7.40 – 7.47 (*m*, 4 $H_{arom.}$); 7.50 – 7.67 (*m*, 3 $H_{arom.}$); 7.69 (*d*, *J* = 8, 2 $H_{arom.}$). ^{13}C-NMR (100 MHz, $CDCl_3$): 51.0 (COO*Me*); 59.5 (CH); 72.3; 105.6; 110.3; 125.3; 125.6 (2 C); 126.5 (2 C); 126.7; 127.0 (2 C); 127.5; 127.6 (2 C); 127.8 (2 C); 128.3; 128.4 (2 C); 129.4 (2 C); 129.9; 130.36; 130.41 (2 C); 130.6 (2 C); 130.9; 138.3; 140.0; 142.5; 143.5; 145.6; 165.5 (=*C*–O); 166.2 (CO). HR-ESI-MS: 543.1931 ($C_{37}H_{28}NaO_3^+$, $[M + Na]^+$; calc. 543.1936).

Methyl (3a*SR*,4*RS*,8b*RS*)-8b-(4-Bromophenyl)-4,8b-dihydro-2,3a,4-triphenyl-3a*H*-indeno[1,2-*b*]furan-3-carboxylate (**4c**), **Methyl 2-[1-(4-Bromophenyl)-1,3-diphenyl-1*H*-inden-2-yl]-3-oxo-3-phenylpropanoate** (**6a**), and **Methyl 2-[3-(4-Bromophenyl)-1,1-diphenyl-1*H*-inden-2-yl]-3-oxo-3-phenylpropanoate** (**6b**). Following the *General Procedure*, *Diels–Alder* adduct **3c** (0.5 mmol) and $MeSO_3H$ (3.0 mmol) were reacted in CH_2Cl_2. The column chromatography gave **4c** (75 mg, 25%) and **6a**/**6b** (91 mg, 30% overall yield).

$MeSO_3H$ (6 equiv.) was added at r.t. to a soln. of adduct **4c** (1 equiv.) in CH_2Cl_2 (7 ml). After 2 d of the reaction (TLC-control), the 7 ml of Na_2CO_3 (aq.) was added carefully to the mixture. The aq. layer was extracted with CH_2Cl_2 (3 × 5 ml), the org. layers were combined, dried over $MgSO_4$, and evaporated to dryness. The residue was then purified by a CC using a mixture of hexane/AcOEt as eluent. The residue was subjected to SiO_2 CC (using hexane/AcOEt mixture as the eluent) to give the product **6a** in 34% yield.

Data of **4c**: White crystals. M.p. 177 – 179 °C. IR ($CHCl_3$): 1101, 1155, 1187, 1251, 1283, 1327, 1395, 1444, 1489, 1572, 1596, 1610, 1704, 3053. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.75 (*s*, COOMe); 5.67 (*s*, CH); 6.19 (*d*, *J* = 8, 2 $H_{arom.}$); 6.65 – 7.70 (*m*, 21 $H_{arom.}$). ^{13}C-NMR (100 MHz, $CDCl_3$): 51.0 (COO*Me*); 59.4 (CH); 72.3; 105.0; 110.5; 125.6; 125.9 (2 C); 126.3; 126.7; 126.8; 127.66; 127.70 (2 C); 127.8 (2 C); 128.5; 129.4 (3 C); 130.1 (2 C); 130.2 (2 C); 130.3 (2 C); 130.5; 130.6 (2 C); 130.7; 138.0; 139.2; 142.3; 143.0; 145.6; 165.3 (=*C*–O); 206.0 (CO). HR-ESI-MS: 621.1036 ($C_{37}H_{27}{}^{79}BrNaO_3^+$, $[M + Na]^+$; calc. 621.1041), 623.1021 ($C_{37}H_{27}{}^{81}BrNaO_3^+$, $[M + Na]^+$; calc. 623.1015).

Crystallographic Data for **4c**. $C_{37}H_{27}BrO_3$, M_r 599.50, triclinic, $P\bar{1}$ (no. 2), a = 9.2308(3), b = 12.6850(4), c = 13.0536(5) Å, α = 86.634(3), β = 81.895(3), γ = 71.113(3)°, V = 1431.60(8) Å^3, Z = 2, D_x = 1.391 g cm^{-3}, $F(000)$ = 616, radiation, CuK_α (λ = 1.54184 Å), $3.65 \le 2\theta \le 76.49$, intensity data were collected at 100(2) K with a *Bruker APEX-II CCD* diffractometer, and employing $w/2\theta$ scanning technique, in the range of $-9 \le h \le 11$, $-15 \le k \le 15$, $-15 \le l \le 15$; the structure was solved by a direct method; all non-H-atoms were positioned, and anisotropic thermal parameters were refined from 5375 observed reflections with R(into) = 0.0194 by a full-matrix least-squares technique converged to R = 0.0307 and R_w = 0.0703 [$I > 2\sigma(I)$]. CCDC-1057421.

Data of **6a**: White solid. M.p. 232 – 233 °C. IR ($CHCl_3$): 1035, 1070, 1195, 1275, 1400, 1435, 1470, 1600, 1725, 3060. ^{1}H-NMR (400 MHz, $CDCl_3$): 3.40 (*s*, COOMe); 4.86 (*s*, CH); 6.34 – 7.75 (*m*, 23 $H_{arom.}$). ^{13}C-NMR (100 MHz, $CDCl_3$): 67.3; 72.7; 121.4 (2 C); 126.9 (2 C); 127.1; 127.3 (2 C); 127.6 (2 C); 127.7; 127.9; 128.7 (2 C); 129.5 (2 C); 130.2; 130.7 (2 C); 130.8; 131.3; 131.6 (2 C); 131.9; 132.1; 132.5; 132.9; 141.3; 141.5; 142.5; 142.7; 142.9; 143.1; 143.6; 168.9 (CO); 206.6 (CO). HR-ESI-MS: 621.1032 ($C_{37}H_{27}{}^{79}BrNaO_3^+$, $[M + Na]^+$; calc. 621.1041), 623.1017 ($C_{37}H_{27}{}^{81}BrNaO_3^+$, $[M + Na]^+$; calc. 623.1015).

Data of **6b**: ^{1}H-NMR (400 MHz, $CDCl_3$): 3.40 (*s*, COOMe); 4.86 (*s*, CH); 6.34 – 7.75 (*m*, 23 $H_{arom.}$). ^{13}C-NMR (100 MHz, $CDCl_3$): 52.2; 67.5; 73.1; 121.1 (4 C); 126.9 (2 C); 127.0; 127.1; 127.2; 127.25 (2 C); 127.34 (2 C); 127.6 (2 C); 127.7; 127.9 (2 C); 128.7 (4 C); 129.5 (2 C); 131.1; 131.2; 132.8; 133.0; 140.3; 140.8; 141.2; 143.4; 168.6 (CO); 206.5 (CO). HR-ESI-MS: 621.1036 ($C_{37}H_{27}{}^{79}BrNaO_3^+$, $[M + Na]^+$; calc. 621.1041). HR-ESI-MS: 623.1015 ($C_{37}H_{27}{}^{81}BrNaO_3^+$, $[M + Na]^+$; calc. 623.1015).

Methyl 5,8-Diphenyl-7,8-dihydrobenzo[*c*]phenanthrene-6-carboxylate (**15**). A quantity of 113 mg (98%) was obtained using *General Procedure* (reaction time 6 h) from *Diels–Alder* adduct **14** (120 mg). Yield 98%. White crystals. M.p. 156 – 158 °C. IR ($CHCl_3$): 1053, 1142, 1201, 1273, 1378, 1436, 1493, 1599, 1725, 3058. ^{1}H-NMR (300 MHz, $CDCl_3$): 3.12 – 3.19 (*m*, 1 H of CH_2); 3.31 – 3.40 (*m*, 1 H of CH_2); 3.53 (*s*, COOMe); 4.15 – 4.25 (*m*, CH); 6.98 (*d*, J = 6, 1 $H_{arom.}$); 7.25 – 7.60 (*m*, 15 $H_{arom.}$); 7.73 (*d*, J = 9, 1 $H_{arom.}$); 8.00 (*d*, J = 9, 1 $H_{arom.}$); 8.64 (*d*, J = 9, 1 $H_{arom.}$). ^{13}C-NMR (75 MHz, $CDCl_3$): 34.9 (CH_2); 45.01 (CH_2); 52.3 (COO*Me*); 126.1; 126.3; 126.5; 127.3 (2 C); 127.6; 127.8; 127.9; 128.1; 128.4; 128.6; 129.1 (3 C); 129.4 (2 C); 129.6; 130.5; 130.6; 130.8; 131.8; 132.0; 132.6; 133.9; 137.5; 138.5; 142.4; 142.6; 170.2 (CO). HR-ESI-MS: 463.1669 ($C_{32}H_{24}NaO_2^+$, $[M + Na]^+$; calc. 463.1674).

Crystallographic Data for **15**. $C_{32}H_{24}O_2$, M_r 440.51, triclinic, $P\bar{1}$ (no. 2), a = 5.7200(2), b = 10.3268(4), c = 19.9208(8) Å, α = 92.798(3), β = 98.090(3), γ = 94.860 (3)°, V = 1158.60(8) Å^3, Z = 2, D_x = 1.263 g cm^{-3}, F(000) = 464, radiation, MoK_α (λ = 0.71073 Å), 2.78 ≤ 2θ ≤ 31.87, intensity data were collected at 100(2) K with a *Bruker APEX-II CCD* diffractometer, and by employing a $w/2\theta$ scanning technique, in the range of $-7 \le h \le 8$, $-15 \le k \le 15$, $-27 \le l \le 28$; the structure was solved by a direct method; all non-H-atoms were positioned, and anisotropic thermal parameters were refined from 7174 observed reflections with R(into) = 0.0357 by a full-matrix least-squares technique converged to R = 0.0536 and R_w = 0.1205 [$I > 2\sigma(I)$]. CCDC-1057274.

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