DOI: 10.1002/ejoc.200800620

Lewis Acid Catalyzed Reactions of Donor–Acceptor Cyclopropanes with Anthracenes

Olga A. Ivanova,*[a] Ekaterina M. Budynina,[a] Yuri K. Grishin,[a] Igor V. Trushkov,[a] and Pavel V. Verteletskii[a]

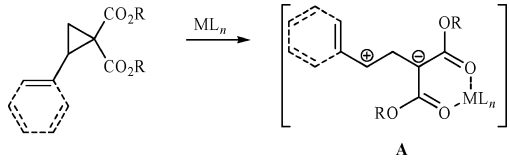
Keywords: Cycloaddition / Aromatic substitution / Cyclopropanes / Dienes / Lewis acids

The reactions of 2-aryl-1,1-cyclopropane diesters with anthracene derivatives were studied for the first time. Three kinds of reaction products are formed depending on the nature of the aryl group and the substituents in the anthracene. The first one is the product of [4+3] cycloaddition of cyclopropane to a diene moiety of anthracene. The second one also has a seven-membered ring and is formed by the Lewis acid catalyzed electrophilic attack of cyclopropane onto the C9 atom of anthracene followed by intramolecular attack of the formed arenonium ion on aryl group of the starting cyclopropane. Lastly, the common Friedel–Crafts products are formed.

Introduction

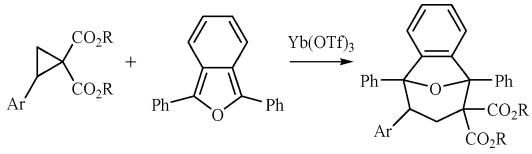
Cyclopropanes have found a wide range of applications in modern organic synthesis.[1] Introduction of various functional groups into the cyclopropane ring extends its reactivity significantly. Thus, cyclopropanes with electron-withdrawing groups are prone to reactions with nucleophiles acting as a homo Michael acceptor similar to electron-deficient alkenes.[2] Cyclopropanes bearing electron-donating groups show increased sensitivity to electrophilic agents.[1,3] Donor–acceptor cyclopropanes have the broadest scope of reactivity.[4] They react with both nucleophiles and electrophiles. However, the most interesting synthetic application of donor–acceptor cyclopropanes is related to their ability to react, under Lewis acid mediated conditions, with double or triple bonds, such as C=C,[5] C≡C,[6] C=O,[7] C=N,[8] C≡N,[9] and N=N[10] through [3+2] cycloaddition reactions to afford five-membered carbo- and heterocycles. In these reactions donor–acceptor cyclopropanes can be considered as 1,3-dipole equivalents of type **A** (Scheme 1). Moreover, donor–acceptor cyclopropanes are able to react with nitrones in the presence of Lewis acids to produce tetrahydro-1,2-oxazine derivatives by [3+3] cycloaddition reactions.[11]

Recently, we reported the first example of a [4+3] cycloaddition of donor–acceptor cyclopropanes. In these $Yb(OTf)_3$-catalyzed reactions, 2-aryl-1,1-cyclopropane diesters added to 1,3-diphenylisobenzofuran as three-carbon dienophiles to form seven-membered skeletons



Scheme 1.

(Scheme 2).[12] Herein we report our results on the reactions of donor–acceptor cyclopropanes with anthracenes as dienes.



Scheme 2.

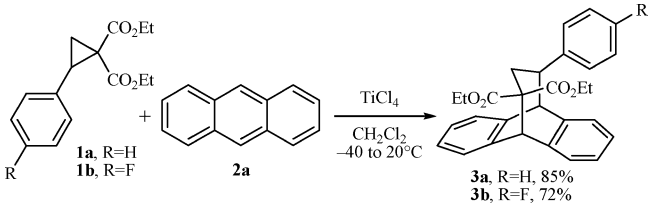
Results and Discussion

Reactions of 2-Aryl-1,1-cyclopropane Diesters with Anthracene

The first process to be studied was the reaction between 2-phenyl-1,1-bis(ethoxycarbonyl)cyclopropane (**1a**) and anthracene (**2a**) (Scheme 3). Earlier we found that the best yields in the [4+3] cycloaddition of 2-aryl-1,1-cyclopropane diesters to 1,3-diphenylisobenzofuran were obtained when reactions were performed in CH_2Cl_2 in the presence of $Yb(OTf)_3$ as a catalyst.[12] Unfortunately, under the same reaction conditions the desired cycloaddition product **3a** was formed from cyclopropane **1a** and anthracene (**2a**) in a

[a] Department of Chemistry, M.V. Lomonosov Moscow State University,
Leninskie gory 1/3, Moscow 119991, Russia
Fax: +7-495-932-8846
E-mail: iv@org.chem.msu.ru

very small amount. At room temperature, conversion was low, and the increase in the reaction temperature led to considerable polymerization of cyclopropane **1a**. Therefore, we examined alternative Lewis acids and found that the best results were obtained when cyclopropane **1a** was added to anthracene (**2a**) at –40 °C in the presence of $TiCl_4$ (1:1.1:1.2 ratio) followed by warming of the reaction mixture to room temperature whilst stirring for 4 h. Under these reaction conditions, [4+3] cycloadduct **3a** was obtained as a single product in 85% yield. Its structure was proved by ^1H and ^{13}C NMR spectroscopy, which confirmed the formation of the bicyclic skeleton. The expected ^3J value for the proton of a bridgehead CH group connected to a CHAr group must be small, as the H–C–C–H dihedral angle is close to 90 °. Indeed, the protons of both bridgehead CH groups give characteristic broadened singlets (δ = 4.06 and 5.02 ppm, cf. Experimental Section). Other alicyclic protons gave an AMX-type spectrum.

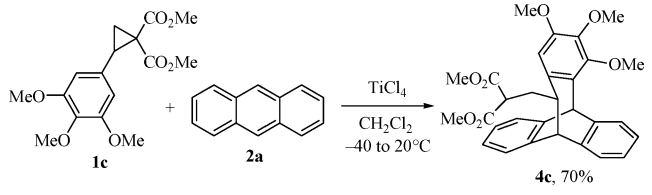


Scheme 3.

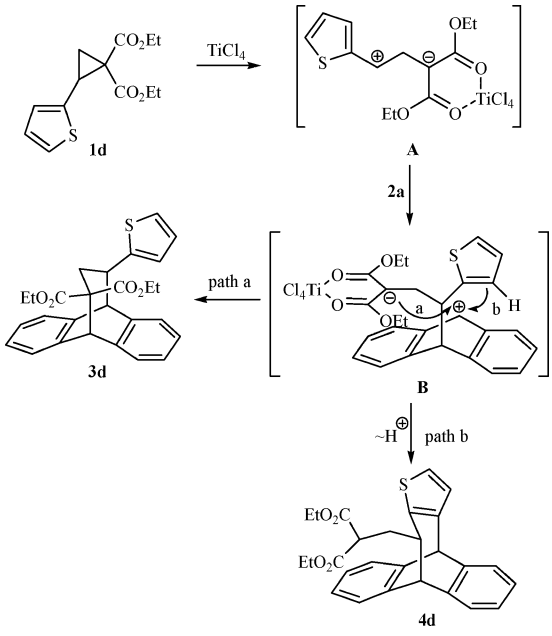
To investigate the scope of this reaction, cyclopropanes **1b**–**d** were studied under the same conditions. Cyclopropane **1b** reacted in a similar manner to produce [4+3] cycloaddition product **3b** (Scheme 3). A single product was also obtained when cyclopropane **1c** with three donor substituents in the phenyl ring was treated with anthracene (**2a**) and $TiCl_4$. However, careful analysis of the ^1H and ^{13}C NMR spectroscopic data showed that a different product, **4c**, was formed in this reaction (Scheme 4). According to the NMR spectroscopic data, **4c** has a tribenzobicyclo[3.2.2]nonane framework with two CH bridgehead groups, an aliphatic $CH_2CH(CO_2Me)_2$ side chain, and an alicyclic CH group.

Similar adduct **4d** was also the major product (71% yield) in the reaction of 2-(2-thienyl)cyclopropane (**1d**; Scheme 5). However, in this case [4+3] cycloadduct **3d** was also formed in low yield (14%).

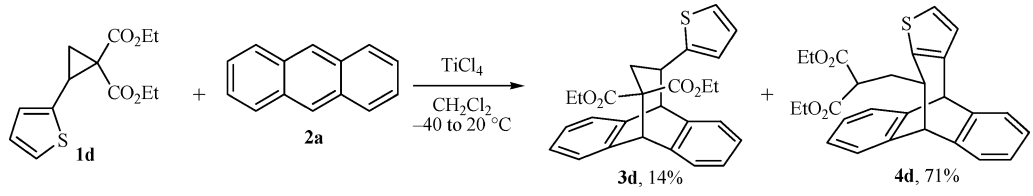
The possible mechanism for the formation of **4** is presented in Scheme 6 for the reaction of **1d**. Lewis acid induces cyclopropane ring opening into 1,3-zwitterionic intermediate **A**, which is stabilized by an electron-enriched aryl group. Electrophilic attack of intermediate **A** at C9 of anthracene leads to intermediate **B**. The new cationic center in **B** can interact with two nucleophilic centers (paths a and b). Attack at the enolate-like C2 atom of the malonyl moiety leads to the [4+3] cycloaddition product **3d** (path a). This path predominates when the aryl group has moderate nucleophilicity. Thiophene is more reactive towards electrophiles than benzene. As a result, the thienyl moiety attacks the cationic center in **B** to give **4d** (path b), which competes efficiently with the [4+3] way of cyclization (path a). The nucleophilicity of 1,2,3-trimethoxybenzene is even higher. Therefore, in the case of cyclopropane **1c**, interaction of the electrophilic center with the electron-enriched aryl group (path b) is the only transformation for intermediate **B**.



Scheme 4.

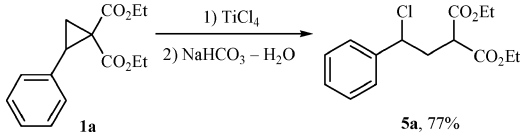


Scheme 6.



Scheme 5.

Thus, the competitive formation of two kinds of products in the reactions of anthracene with cyclopropane **1d** can be explained by the realization of the stepwise mechanism. The direction of cyclization depends on the nucleophilic reactivity of the aryl group in the starting cyclopropane. When the nucleophilicity of the aromatic substituent is low, [4+3] cycloadducts are formed, but when the aryl group is sufficiently nucleophilic, the electrophilic cyclization onto the aromatic moiety becomes the main reaction path. The formation of only **4c** from cyclopropane **1c** is in full accordance with the above mechanism. It is logical to suppose that [4+3] cycloadducts **3a**,**b** are formed in reactions of anthracene with cyclopropanes **1a**,**b** by the same mechanism, but some additional experiments are needed for confirmation of this conclusion. As one of these experiments, we hydrolyzed the reaction mixtures of cyclopropanes **1a**–**d** with anthracene (**2a**) before full conversion of the reagents. We found that open-chain byproducts **5** were obtained after quenching. When cyclopropane **1a** was treated with $TiCl_4$ in the absence of anthracene, chloride **5a** was the only product of the reaction (Scheme 7). The formation of **5a** is circumstantial evidence for the generation of open-chain intermediate **A**.



Scheme 7.

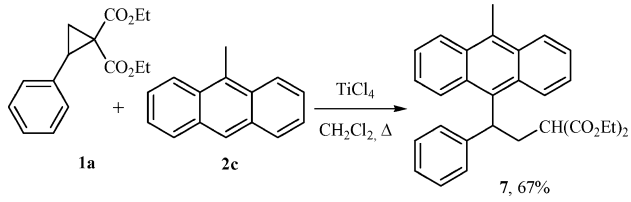
It is well known that 9,10-dimethylanthracene is more reactive in Diels–Alder cycloadditions than anthracene itself. However, for a stepwise reaction we can expect another model of reactivity: the substituents at C2 and C3 of anthracene should not significantly affect the reactivity towards donor–acceptor cyclopropanes, whereas substitution at C9 and C10 leads to stabilization of the intermediate carbocation and induces steric repulsions. Both effects should prevent the formation of both kinds of cycloadducts **3** and **4**. To experimentally test these hypotheses, we studied reactions of donor–acceptor cyclopropanes with tetracene (**2b**) as an example of 2,3-disubstituted anthracenes as well as with 9-methylanthracene (**2c**) and 9,10-dimethylanthracene (**2d**).

Reactions of 2-Phenyl-1,1-cyclopropane Diesters with 2,3-Benzanthracene

We found that 2,3-benzanthracene (**2b**) reacted with donor–acceptor cyclopropanes similarly to anthracene. For example, [4+3] cycloaddition product **6** (Scheme 8) was obtained from tetracene (**2b**) and donor–acceptor cyclopropane **1e** under catalysis by $TiCl_4$ or $SnCl_4$.

Reactions of 2-Aryl-1,1-cyclopropane Diesters with 9-Methylanthracene and 9,10-Dimethylanthracene

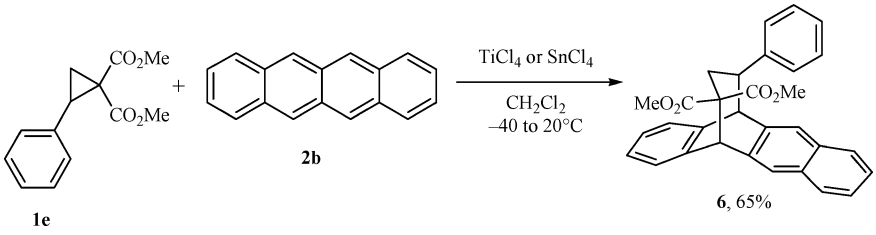
In agreement with our hypothesis, the reactions of cyclopropanes **1a**,**b** with 9-methylanthracene (**2c**) and 9,10-dimethylanthracene (**2d**) failed to produce cycloaddition products **3** and **4**. In these reactions only electrophilic substitutions of the anthracene derivatives were observed. Thus, in the reaction of cyclopropane **1a** with **2c** (Scheme 9), open-chain intermediate **A** attacked the unsubstituted C10 atom by the cationic center to afford product **7** in good yield. When both the C9 and C10 positions were substituted, as it was in **2d**, electrophilic attack was directed to C2 to produce **8a**,**b** (Scheme 10).



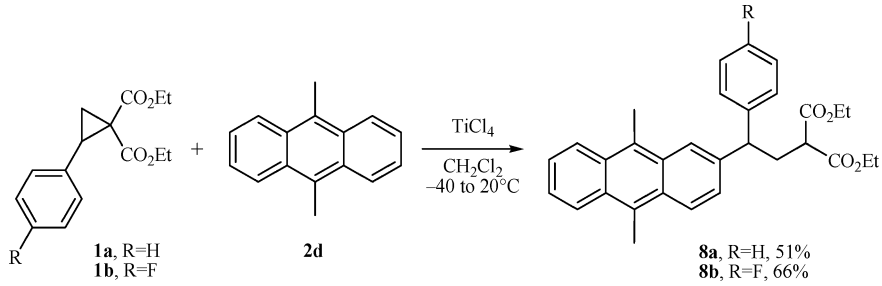
Scheme 9.

Anthrone (**2e**) was also treated with **1a** (Scheme 11) in the presence of a moderate excess of $TiCl_4$ (1.5 equiv.). In this case, we found that Lewis acid can play two roles. The first one is transformation of anthrone into anthracene intermediate **C**. Another one is catalytic cleavage of cyclopropane **1a** into zwitterionic intermediate **A**. The interaction between **A** and **C** leads to the formation of 10-substituted anthrone **9** in high yield.

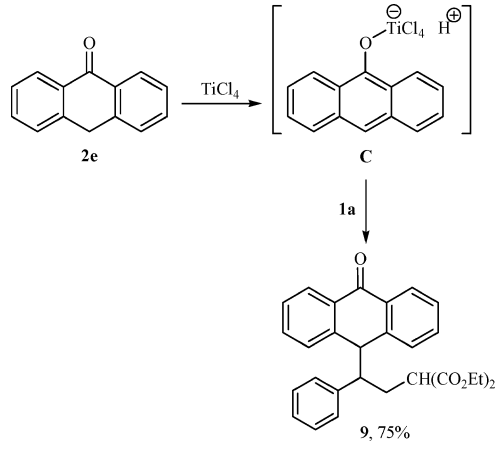
Lewis acid catalyzed formation of Friedel–Crafts adduct was also found in the reaction of 2-phenyl-1,1-cyclopropane diester with 1,3-dimethoxybenzene (**10**; Scheme 12).



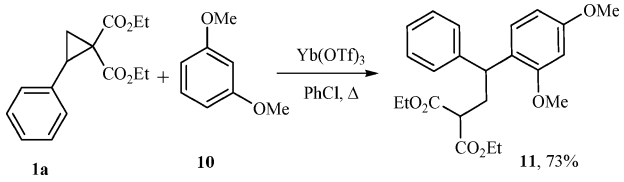
Scheme 8.



Scheme 10.



Scheme 11.



Scheme 12.

There are only two earlier examples of such reactivity of donor–acceptor cyclopropanes towards aromatic compounds, namely, annulation of aryl cyclopropyl ketones and electrophilic substitution in indoles.[13]

Conclusions

2-Aryl-1,1-cyclopropane diesters react with anthracene derivatives under Lewis acid catalysis through a stepwise mechanism, which includes cyclopropane ring opening into 1,3-zwitterionic intermediate **A**, electrophilic attack of this intermediate onto anthracene with formation of intermediate **B**, and finally, transformation of the last intermediate into the reaction products. Three kinds of products are formed depending on the substituents in anthracene and the nature of the aryl group in the donor–acceptor cyclopropane. The common Friedel–Crafts products are formed from 9- and 9,10-substituted anthracenes. For anthracenes without substituents at C9 and C10, two kinds of products resulting from cyclization of intermediate **B** were isolated. When the nucleophilicity of the aromatic substituent is low, [4+3] cycloadducts are formed, but when the aryl group is sufficiently nucleophilic, electrophilic cyclization onto the aromatic moiety becomes the main reaction path. The products of both kinds of cyclization were found in the reactions of 2-(2-thienyl)-1,1-cyclopropane diester, wherein the thienyl group has intermediate reactivity.

Experimental Section

General Remarks: NMR spectra were recorded with a Bruker Avance-400 (400 MHz for ^{1}H and 100 MHz for ^{13}C NMR) spectrometer at room temperature; the chemical shifts (δ) were measured in ppm with respect to the solvent ($CDCl_3$, ^{1}H: δ = 7.26 ppm, ^{13}C: δ = 77.13 ppm). MS were recorded with a Bruker Ultraflex MALDI-TOF mass spectrometer in positive mode (dithranol matrix) or a Finnigan MAT INCOS 50 (the energy of ionizing electrons was 70 eV, direct input or GCMS). Melting points (mp): Electrothermal 9100 capillary melting point apparatus, values uncorrected. Column chromatography was performed on silica gel 60 (230–400 mesh, Merck). $TiCl_4$, $SnCl_4$, $Yb(OTf)_3$, anthracene, benzanthracene, 9-methylanthracene, 9,10-dimethylanthracene, anthrone, and 1,3-dimethoxybenzene are available commercially. 2-Aryl-1,1-cyclopropane diesters **1** were prepared by published procedures.[14] All the reactions were carried out by using freshly distilled and dry solvents from solvent stills.

General Procedure for the $TiCl_4$ or $SnCl_4$ Catalyzed Reaction of Diethyl 2-Arylcyclopropane-1,1-dicarboxylates with Anthracenes: Lewis acid (1.2 mmol) was added to solution of anthracene (1.2 mmol) in dry CH_2Cl_2 (20 mL) at –40 °C under an atmosphere of argon. To the resulting mixture was dropwise added a solution of cyclopropane (1.0 mmol) in CH_2Cl_2 (20 mL) over 10–15 min. The reaction mixture was stirred for 0.5 h at –40 °C, warmed to room temperature, and stirred for the specified time. The solvent was evaporated under vacuum, and the final residue was purified by column chromatography (SiO_2; hexane/$CHCl_3$, 1:1) to yield desired product **3**, **4**, **6**–**9**.

Diethyl 13-Phenyl-9,10-dihydro-9,10-propanoanthracene-11,11-dicarboxylate (3a): $TiCl_4$, 4 h. White foam. Yield: 0.37 g (85%). R_f = 0.50 ($CHCl_3$). M.p. 135–136 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.28 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.62 (dd, ^2J = 14.2 Hz, ^3J = 12.4 Hz, 1 H, CH_2), 2.48 (dd, ^2J = 14.2 Hz, ^3J = 4.0 Hz, 1 H, CH_2), 3.68 (dd, ^3J = 4.0 Hz, ^3J = 12.4 Hz, 1 H, CHPh), 3.97 (dq, ^2J = 10.8 Hz, ^3J = 7.2 Hz, 1 H, CH_2O), 4.06 (br. s, 1 H, CH), 4.02–4.19 (m, 2 H, CH_2O), 4.27 (dq, ^2J = 10.8 Hz, ^3J = 7.2 Hz, 1 H, CH_2O), 5.02 (br. s, 1 H, CH), 7.13–7.39 (m, 12 H), 7.82 (br. d, ^3J = 7.6 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.03 (2×CH_3), 35.70 (CH_2), 42.24

(CHPh), 49.42 (CH), 53.29 (CH), 56.71 (C), 61.13 (CH_2O), 61.56 (CH_2O), 125.33 (CH), 125.76 (CH), 126.45 (CH), 126.67 (CH), 126.70 (CH), 127.41 (3×CH), 127.61 (CH), 128.19 (CH), 128.65 (2×CH), 129.19 (CH), 138.1 (C), 139.0 (C), 139.6 (C), 146.3 (C), 146.67 (C), 169.8 (CO_2Et), 171.1 (CO_2Et) ppm. GC–MS: *m*/*z* (%) = 440 (2) $[M]^+$, 262 (4), 178 (100), 170 (7), 115 (6). $C_{29}H_{28}O_4$ (440.53): calcd. C 79.09, H 6.36; found C 79.26, H 6.55.

Diethyl 13-(4-Fluorophenyl)-9,10-dihydro-9,10-propanoanthracene-11,11-dicarboxylate (3b): $TiCl_4$, 4 h. White crystals. Yield: 0.33 g (72%). R_f = 0.80 ($CHCl_3$). M.p. 104–105 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.28 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.54 (dd, ^2J = 14.2 Hz, ^3J = 12.4 Hz, 1 H, CH_2), 2.42 (dd, ^2J = 14.2 Hz, ^3J = 4.0 Hz, 1 H, CH_2), 3.65 (dd, ^3J = 4.0 Hz, ^3J = 12.4 Hz, 1 H, CHPh), 3.95 (dq, ^2J = 10.8 Hz, ^3J = 7.2 Hz, 1 H, CH_2O), 3.98 (br. s, 1 H, CH), 4.06–4.17 (m, 2 H, OCH_2), 4.27 (dq, ^2J = 10.8 Hz, ^3J = 7.2 Hz, 1 H, OCH_2), 4.99 (br. s, 1 H, CH), 6.98–7.34 (m, 11 H, Ph), 7.81 (br. d, ^3J = 7.4 Hz, 1 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.00 (2×CH_3), 35.76 (CH_2), 41.41 (CH-*p*-FPh), 49.27 (CH), 53.35 (CH), 56.65 (C), 61.15 (CH_2O), 61.60 (CH_2O), 115.30 (d, $^2J_{CF}$ = 21 Hz, 2×CH, *p*-FPh), 125.30 (CH), 125.80 (CH), 126.51 (CH), 126.70 (CH), 127.43 (2×CH), 128.13 (CH), 128.74 (d, $^3J_{CF}$ = 7 Hz, 2×CH, *p*-FPh), 129.20 (CH), 137.98 (C), 138.87 (C), 139.26 (C), 142.32 (C), 146.00 (C), 161.60 (d, $^1J_{CF}$ = 244 Hz, C-F), 169.69 (CO_2Et), 171.00 (CO_2Et) ppm. GC–MS: *m*/*z* (%) = 458 (1) $[M]^+$, 280 (1), 235 (4), 178 (100), 133 (5). $C_{29}H_{27}FO_4$ (458.52): calcd. C 75.96, H 5.94; found C 75.70, H 5.89.

2-[2,2-Bis(methoxycarbonyl)ethyl]-5,6,7-trimethoxypentacyclo-[7.6.6.0^{3,8}.0^{10,15}.0^{16,21}]henicosa-3,5,7,10,12,14,16,18,20-nonaene (4c): $TiCl_4$, 18 h. White foam. Yield: 0.35 g (70%). R_f = 0.20 ($CHCl_3$). M.p. 72–73 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 2.12 (m, 1 H, CH_2), 2.46 (m, 1 H, CH_2), 3.05 (br. d, ^3J = 11.3 Hz, 1 H, CH), 3.79 (s, 3 H, CH_3), 3.80 (s, 3 H, CH_3), 3.89 (s, 3 H, CH_3), 3.90 (s, 3 H, CH_3), 4.00 [dd, ^3J = 4.0 Hz, ^3J = 11.6 Hz, 1 H, $CH(CO_2Et)_2$], 4.08 (s, 3 H, CH_3), 4.20 (d, ^3J = 11.3 Hz, 1 H, CH), 5.63 (s, 1 H, CH), 6.61 (s, 1 H, CH), 7.15–7.50 (m, 8 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 36.07 (CH_2), 42.59 (CH), 43.66 (CH), 47.83 (CH), 49.89 (CH), 52.76 (2×CH_3), 55.88 (CH_3), 60.80 (CH_3), 61.55 (CH_3), 111.50 (CH), 124.98 (CH), 125.91 (CH), 126.16 (CH), 126.26 (CH), 126.39 (CH), 126.55 (CH), 126.80 (CH), 127.90 (CH), 133.44 (C), 138.38 (C), 140.40 (2×C), 144.67 (C), 145.44 (C), 149.29 (C), 151.89 (C), 153.24 (C), 169.69 (CO_2Et), 169.78 (CO_2Et) ppm. GC–MS: *m*/*z* (%) = 502 (27) $[M]^+$, 370 (8), 324 (25), 281 (11), 265 (13), 207 (32), 178 (100). $C_{30}H_{30}O_7$ (502.56): calcd. C 71.70, H 6.02; found C 71.50, H 5.91.

Diethyl 13-(2-Thienyl)-9,10-dihydro-9,10-propanoanthracene-11,11-dicarboxylate (3d): $TiCl_4$, 22 h. White crystals. Yield: 63 mg (14%). R_f = 0.75 ($CHCl_3$). M.p. 134–135 °C. ^1H NMR (400 MHz, $CDCl_3$): δ = 1.23 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.25 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.50 (dd, ^2J = 14.0 Hz, ^3J = 12.5 Hz, 1 H, CH_2), 2.58 (dd, ^2J = 14.0 Hz, ^3J = 4.2 Hz, 1 H, CH_2), 3.93 (dq, ^2J = 10.7 Hz, ^3J = 7.1 Hz, 1 H, CH_2O), 3.98 (dd, ^3J = 4.2 Hz, ^3J = 12.5 Hz, 1 H, CHTh), 4.04–4.15 (m, 2 H, CH_2O), 4.12 (br. s, 1 H, CH), 4.26 (dq, ^2J = 10.6 Hz, ^3J = 7.1 Hz, 1 H, CH_2O), 4.96 (br. s, 1 H, CH), 6.85 (d, ^3J = 3.3 Hz, 1 H, Th), 6.99 (dd, ^2J = 3.3 Hz, ^3J = 5.0 Hz, 1 H, Th), 7.13 (t, ^3J = 7.2 Hz, 1 H), 7.18 –7.32 (m, 7 H), 7.73 (br. d, ^3J = 7.4 Hz, 1 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.99 (2×CH_3), 36.67 (CH_2), 37.83 (CH), 49.13 (CH), 53.87 (CH), 56.84 (C), 61.16 (CH_2O), 61.61 (CH_2O), 123.09 (CH), 123.25 (CH), 125.61 (CH), 125.92 (CH), 126.59 (3×CH), 127.42 (CH), 127.79 (CH), 128.00 (CH), 128.87 (CH), 137.98 (C), 138.59 (C), 138.67 (C), 145.15 (C), 149.64 (C, Ph), 169.64 (CO_2Et), 170.80 (CO_2Et) ppm. GC–MS: *m*/*z* (%) = 446 (5) $[M]^+$, 268 (2), 222 (5), 178 (100), 121 (4). $C_{27}H_{26}O_4S$ (446.56): calcd. C 72.62, H 5.87; found C 72.55, H 5.64.

2-[2,2-Bis(methoxycarbonyl)ethyl]-4-thiapentacyclo-[6.6.6.0^{3,7}.0^{9,14}.0^{15,20}]icosa-3(7),5,9,11,13,15,17,19-octaene (4d): $TiCl_4$, 22 h. Light-yellow oil. Yield: 0.32 g (71%). R_f = 0.59 ($CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.34 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.37 (t, ^3J = 7.1 Hz, 3 H, CH_3), 2.22 (ddd, ^2J = 14.4 Hz, ^3J = 5.2 Hz, ^3J = 10.1 Hz, 1 H, CH_2), 2.37 (ddd, ^2J = 14.4 Hz, ^3J = 4.0 Hz, ^3J = 10.1 Hz, 1 H, CH_2), 3.18–3.25 (m, 1 H, CHTh), 4.01 [dd, ^3J = 5.2 Hz, ^3J = 10.1 Hz, 1 H, $CH(CO_2Et)_2$], 3.85–3.96 (m, 2 H, CH_2O), 4.25–4.39 (m, 5 H, 2×CH_2O, CH), 4.91 (s, 1 H, CH), 6.93 (d, ^3J = 5.1 Hz, 1 H, Th), 7.02 (d, ^3J = 5.1 Hz, 1 H, Th), 7.10–7.23 (m, 4 H), 7.28–7.41 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.16 (CH_3), 14.27 (CH_3), 35.81 (CH_2), 41.36 (CH), 48.32 (CH), 48.63 (CH), 50.26 (CH), 61.76 (2×CH_2O), 122.37 (CH), 124.35 (CH), 124.87 (CH), 126.12 (CH), 126.43 (CH), 126.47 (CH), 126.69 (3×CH), 128.56 (CH), 136.52 (C), 136.91 (C), 139.56 (C), 139.96 (C), 145.55 (C), 146.67 (C), 169.01 (CO_2Et), 169.13 (CO_2Et) ppm. GC–MS: *m*/*z* (%) = 446 (12) $[M]^+$, 286 (100), 271 (44), 178 (9). $C_{27}H_{26}O_4S$ (446.56): calcd. C 72.62, H 5.87; found C 72.52, H 5.91.

Diethyl (2-Chloro-2-phenylethyl)malonate (5a): $TiCl_4$ (0.23 g, 0.13 mL, 1.2 mmol) was added to a solution of cyclopropane **1a** (0.27 g, 1.0 mmol) in dry CH_2Cl_2 (10 mL) at –25 °C under an atmosphere of argon. The reaction mixture was stirred for 0.5 h at –25 °C, warmed to room temperature, and stirred for an additional 20 h. The solvent was evaporated under vacuum, and the final residue was purified by column chromatography (SiO_2; hexane/$CHCl_3$, 1:1). Colorless oil. Yield: 0.23 g (77%). R_f = 0.66 ($CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.27 (t, ^3J = 7.1 Hz, 3 H, CH_3), 2.64 (t, ^3J = 7.4 Hz, 2 H, CH_2), 3.62 [t, ^3J = 7.4 Hz, 1 H, $CH(CO_2Et)_2$], 4.17–4.26 (m, 4 H, OCH_2), 4.98 (t, ^3J = 7.4 Hz, 1 H, CH), 7.30–7.42 (m, 5 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.02 (2×CH_3), 38.77 (CH_2), 49.76 (CH), 60.91 (CH), 61.66 (2×CH_2), 126.93 (2×CH, Ph), 128.64 (CH, Ph), 128.77 (2×CH, Ph), 140.60 (C), 168.53 (CO_2Et), 168.68 (CO_2Et) ppm. GC–MS: *m*/*z* (%) = 300/298 (3/8) $[M]^+$, 263 (3), 189 (6), 160 (100), 143 (11), 140/138 (4/12), 133 (44), 115 (42), 104 (19). $C_{15}H_{19}ClO_4$ (298.76): calcd. C 60.30, H 6.41; found C 60.47, H 6.51.

Diethyl 21-Phenylpentacyclo[10.6.3.0^{2,11}.0^{4,9}.0^{13,18}]henicosa-2,4,6,8,10,13,15,17-octaene-19,19-dicarboxylate (6): $SnCl_4$, 23 h. White foam. Yield: 0.30 g (65%). R_f = 0.58 ($CHCl_3$). M.p. 112–113 °C. ^1H NMR (400 MHz, $CDCl_3$, for a mixture of isomers **A**/**B** 55:45): δ = 1.64 (dd, ^2J = 14.2 Hz, ^3J = 12.8 Hz, 1 H, CH_2, **A**), 1.67 (dd, ^2J = 14.2 Hz, ^3J = 12.8 Hz, 1 H, CH_2, **B**), 2.49 (dd, ^2J = 14.2 Hz, ^3J = 4.0 Hz, 1 H, CH_2, **A**), 2.50 (dd, ^2J = 14.2 Hz, ^3J = 4.0 Hz, 1 H, CH_2, **B**), 3.57 (s, 3 H, CH_3, **A**), 3.64 (s, 3 H, CH_3, **B**), 3.70 (s, 3 H, CH_3, **B**), 3.73 (s, 3 H, CH_3, **A**), 3.75 (dd, ^3J = 12.8 Hz, ^3J = 4.0 Hz, 1 H, CH, **A**), 3.78 (dd, ^3J = 12.8 Hz, ^3J = 4.0 Hz, 1 H, CH, **B**), 4.19 (br. s, 1 H, CH, **B**), 4.23 (br. s, 1 H, CH, **A**), 5.18 (s, 1 H, CH, **A**), 5.19 (s, 1 H, CH, **B**), 7.15–7.54 (m, 10 H, **A**+11 H, **B**), 7.45 (s, 1 H, **B**), 7.73 (s, 1 H, **A**), 7.75 (s, 1 H, **A**), 7.81–7.86 (m, 2 H, **A**+1 H, **B**), 7.96–7.99 (m, 1 H, **A**), 8.25 (s, 1 H, **B**) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, for a mixture of isomers **A**/**B** 55:45): δ = 35.36 (CH_2, **B**), 35.49 (CH_2, **A**), 42.98 (CH, **B**), 43.32 (CH, **A**), 49.71 (CH, **B**), 49.76 (CH, **A**), 52.12 (2×CH), 52.81 (2×CH_3O), 53.45 (CH_3O, **A**), 53.52 (CH_3O, **B**), 57.52 (C, **B**), 57.67 (C, **A**), 123.39 (CH), 125.57 (CH), 125.68 (CH), 125.73 (CH), 125.92 (CH), 125.95 (CH), 126.11 (2×CH), 126.77 (4×CH), 127.09 (CH), 127.41 (4×CH), 127.47 (2×CH), 127.59 (CH), 127.76 (2×CH),

127.84 (CH), 127.96 (CH), 128.08 (CH), 128.68 (2×CH), 128.72 (2×CH), 129.25 (CH), 132.17 (C, **A**), 132.53 (C, **B**), 132.56 (C, **B**), 132.99 (C, **A**), 136.12 (C, **A**), 136.53 (C, **B**), 137.42 (C, **B**), 137.62 (C, **B**), 138.24 (C, **A**), 139.23 (C, **A**), 143.44 (C, **A**), 145.79 (C, **B**), 146.42 (C, **B**), 146.59 (C, **A**), 169.92 (*C*O_2Me, **B**), 170.01 (*C*O_2Me, **A**), 171.29 (*C*O_2Me, **B**), 171.43 (*C*O_2Me, **A**) ppm. HRMS (MALDI-TOF): calcd. for $C_{31}H_{26}O_4$ $[M]^+$ 462.5357; found 462.5362.

Diethyl [2-(10-Methyl-9-anthryl)-2-phenylethyl]malonate (7): $TiCl_4$, 3 h, reflux. Yellow crystals. Yield: 0.30 g (67%). R_f = 0.26 ($CHCl_3$). M.p. 69–70 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.06 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.07 (t, ^3J = 7.1 Hz, 3 H, CH_3), 2.79 [dd, ^3J = 4.5 Hz, ^3J = 10.4 Hz, 1 H, $CH(CO_2Et)_2$], 3.18 (s, 3 H, CH_3), 3.19–3.25 (m, 1 H, CH_2), 3.43–3.49 (m, 1 H, CH_2), 3.85–3.96 (m, 2 H, CH_2O), 4.06–4.30 (m, 2 H, CH_2O), 5.82 (dd, ^3J = 5.2 Hz, ^3J = 10.6 Hz, 1 H, CHPh), 7.14–7.61 (m, 9 H, Ph), 8.20–8.45 (m, 4 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.79 (2×CH_3), 14.59 (CH_3), 32.34 (CH_2), 39.78 (CHPh), 50.14 [*C*$H(CO_2Et)_2$], 61.32 (2×CH_2O), 124.72 (3×CH), 125.64 (3×CH), 125.87 (CH), 127.01 (3×CH), 128.16 (C), 128.51 (3×CH), 128.70 (C), 128.80 (C), 130.03 (C), 130.30 (C), 132.38 (C), 144.60 (C), 169.23 (*C*O_2Et), 169.35 (*C*O_2Et) ppm. GC–MS: *m*/*z* (%) = 455 (1) $[M + H]^+$, 365 (8), 281 (29), 207 (100), 191 (10). $C_{30}H_{30}O_4$ (454.21): calcd. C 79.27, H 6.65; found C 79.40, H 6.70.

Diethyl [2-(9,10-Dimethyl-2-anthryl)-2-phenylethyl]malonate (8a): $TiCl_4$, 24 h. Yellow oil. Yield: 0.24 g (51%). R_f = 0.52 ($CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.25 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.30 (t, ^3J = 7.2 Hz, 3 H, CH_3), 2.81–2.91 (m, 2 H, CH_2), 3.07 (s, 3 H, CH_3), 3.12 (s, 3 H, CH_3), 3.35–3.42 (m, 1 H, CH), 4.14–4.19 (m, 1 H, CH), 4.20–4.29 (m, 4 H, 2×OCH_2), 7.02–7.13 (m, 2 H, Ph), 7.20–7.42 (m, 4 H, Ph), 7.48–7.57 (m, 2 H, Ph), 8.21 (br. s, 1 H, Ph), 8.23–8.37 (m, 3 H, Ph) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.05 (4×CH_3), 34.01 (CH_2), 49.06 (CH), 50.41 (CH), 61.43 (2×CH_2O), 123.35 (CH), 124.61 (CH), 124.79 (CH), 125.30 (2×CH), 125.46 (CH), 126.03 (CH), 126.65 (CH), 127.45 (C), 127.99 (C), 128.11 (2×CH, Ph), 128.65 (2×CH, Ph), 128.90 (C), 129.82 (C), 130.23 (C), 139.11 (C), 143.34 (C), 169.45 (2×*C*O_2Et) ppm. MS (EI): *m*/*z* (%) = 305 (28), 263 (22), 209 (94), 152 (57), 115 (62), 105 (100), 77 (68). $C_{31}H_{32}O_4$ (468.58): calcd. C 79.46, H 6.88; found C 79.26, H 6.53. HRMS (MALDI-TOF): calcd. for $C_{31}H_{32}O_4$ $[M]^+$ 468.5834; found 468.5842.

Diethyl [2-(9,10-Dimethyl-2-anthryl)-2-(4-fluorophenyl)ethyl]malonate (8b): $TiCl_4$, 3 h. Orange-red oil. Yield: 0.32 g (66%). R_f = 0.52 ($CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.29 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.34 (t, ^3J = 7.1 Hz, 3 H, CH_3), 2.84–2.99 (m, 2 H, CH_2), 3.07 (s, 3 H, CH_3), 3.15 (s, 3 H, CH_3), 3.41–3.47 (m, 1 H, CH), 4.20–4.24 (m, 1 H, CH), 4.25–4.33 (m, 4 H, CH, 2×OCH_2), 7.02–7.13 (m, 2 H), 7.32–7.45 (m, 3 H), 7.50–7.57 (m, 2 H), 8.25 (br. s, 1 H), 8.22–8.39 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.17 (4×CH_3), 34.18 (CH_2), 48.38 (CH), 50.41 [$CH(CO_2Et)_2$], 61.56 (2×CH_2O), 115.50 (d, $^2J_{CF}$ = 21 Hz, 2×CH, *p*-FPh), 123.36 (CH), 124.73 (CH), 124.93 (CH), 125.29 (2×CH), 125.34 (CH), 126.25 (CH), 128.05 (C), 128.38 (C), 128.92 (C), 129.64 (d, $^3J_{CF}$ = 8 Hz, 2×CH, *p*-FPh), 129.79 (C), 129.93 (C), 130.30 (C), 138.89 (C), 139.19 (d, $^4J_{CF}$ = 2.9 Hz, C, *p*-FPh), 161.68 (d, $^1J_{CF}$ = 244 Hz, C-F, *p*-FPh), 169.43 (2×*C*O_2Et) ppm. $C_{31}H_{31}FO_4$ (486.57): calcd. C 76.52, H 6.42; found C 76.66, H 6.43.

Diethyl [2-(10-Oxo-9,10-dihydroanthracen-9-yl)-2-phenylethyl]-malonate (9): $TiCl_4$ (1.5 equiv.), 6 h, reflux. Light-yellow crystals. Yield: 0.34 g (75%). R_f = 0.35 ($CHCl_3$). M.p. 104–105 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.14 (t, ^3J = 7.2 Hz, 3 H, CH_3), 1.17 (t, ^3J = 7.2 Hz, 3 H, CH_3), 2.31 (ddd, ^2J = 14.0 Hz, ^3J = 12.8 Hz, ^3J = 4.4 Hz, 1 H, CH_2), 2.56 (ddd, ^2J = 14.0 Hz, ^3J = 10.5 Hz, ^3J = 3.8 Hz, 1 H, CH_2), 3.05 [dd, ^3J = 4.4 Hz, ^3J = 10.5 Hz, 1 H, $CH(CO_2Et)_2$], 3.12–3.17 (m, 1 H, CHPh), 3.97–4.18 (m, 4 H, OCH_2), 4.46 (d, ^3J = 3.8 Hz, 1 H, CH), 6.07 (d, ^3J = 7.8 Hz, 2 H, Ph), 6.91 (t, ^3J = 7.8 Hz, 2 H, Ph), 7.08 (t, ^3J = 7.8 Hz, 1 H), 7.28–7.56 (m, 6 H), 7.92 (d, ^3J = 7.8 Hz, 1 H), 8.02 (d, ^3J = 7.8 Hz, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 13.93 (CH_3), 14.06 (CH_3), 31.78 (CH_2), 49.81 (CH), 50.15 (CH), 54.17 (CH), 61.33 (CH_2O), 61.44 (CH_2O), 126.44 (CH), 126.73 (CH), 127.12 (CH), 127.33 (CH), 127.43 (CH), 127.68 (2×CH), 128.21 (CH), 128.67 (CH), 129.07 (2×CH), 131.72 (CH), 132.29 (CH), 133.19 (C), 134.16 (C), 136.15 (C), 140.84 (C), 143.63 (C), 169.06 (*C*O_2Et), 169.18 (*C*O_2Et), 183.78 (CO) ppm. MS (EI): *m*/*z* (%) = 263 (45), 208 (32), 193 (37), 189 (24), 165 (43), 115 (62), 57 (100). $C_{29}H_{28}O_5$ (456.53): calcd. C 76.30, H 6.18; found C 76.46, H 6.25.

Diethyl [2-(2,4-Dimethoxyphenyl)-2-phenylethyl]malonate (11): 1,3-Dimethoxybenzene (**10**; 110 mg, 0.8 mmol), 2-phenyl-1,1-dicarboethoxycyclopropane (**1a**; 210 mg, 0.8 mmol), and $Yb(OTf)_3$ (25 mg, 0.04 mmol) were dissolved in dry chlorobenzene (4 mL) and stirred with activated 4 Å molecular sieves under an argon atmosphere at reflux for 6 h. The reaction mixture was filtered, the solvent was evaporated under vacuum, and the final residue was purified by column chromatography (SiO_2; hexane/$CHCl_3$, 1:1). Colorless liquid. Yield: 0.23 g (73%). R_f = 0.20 ($CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.26 (t, ^3J = 7.1 Hz, 3 H, CH_3), 1.27 (t, ^3J = 7.1 Hz, 3 H, CH_3), 2.57–2.73 (m, 2 H, CH_2), 3.30 [t, ^3J = 7.3 Hz, 1 H, $CH(CO_2Et)_2$], 3.74 (s, 3 H, OCH_3), 3.77 (s, 3 H, OCH_3), 4.10–4.25 (m, 4 H, OCH_2), 4.40 (t, ^3J = 8.1 Hz, 1 H, CH), 6.45 (d, ^4J = 2.4 Hz, 1 H), 6.48 (dd, ^3J = 8.4 Hz, ^4J = 2.4 Hz, 1 H), 7.10–7.35 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 14.08 (2×CH_3), 33.86 (CH_2), 40.59 (CH), 50.51 (CH), 55.24 (CH_3O), 55.35 (CH_3O), 61.25 (2×CH_2O), 98.73 (CH, Ph), 104.30 (CH, Ph), 126.11 (CH, Ph), 128.05 (2 × CH, Ph), 128.27 (3 × CH, Ph), 143.98 (C), 158.08 (C), 159.46 (C), 169.41 (*C*O_2Et), 169.60 (*C*O_2Et) ppm. $C_{23}H_{28}O_6$ (400.46): calcd. C 68.98, H 7.05; found C 68.94, H 7.13.

[1] a) Z. Rappoport (Ed.), *The Chemistry of the Cyclopropyl Group*, Wiley, New York, **1987**, vol. 1; b) Z. Rappoport (Ed.), *The Chemistry of the Cyclopropyl Group*, Wiley, New York, **1995**, vol. 2.

[2] For reviews, see: a) S. Danishefsky, *Acc. Chem. Res.* **1979**, *12*, 66–72; b) R. Verhe, N. de Kimpe in *The Chemistry of the Cyclopropyl Group* (Ed.: Z. Rappoport), Wiley, New York, **1987**, vol. 1, pp. 445–564; c) S. Angerer, "Carbocyclic Three- and Four-membered Ring Compounds" in *Houben-Weyl, Methods of Organic Chemistry* E 17c (Ed.: A. de Meijere), Thieme, Stuttgart, **1997**, pp. 2041–2120.

[3] For examples, see: a) E. Wenkert, *Acc. Chem. Res.* **1980**, *13*, 27–31; b) C. Brueckner, H.-U. Reissig, *J. Org. Chem.* **1988**, *53*, 2440–2450; c) J. Lee, P. H. Lee, *Tetrahedron Lett.* **1996**, *37*, 9305–9306; d) T. Iwama, H. Matsumoto, T. Kataoka, *J. Chem. Soc. Perkin Trans. 1* **1997**, 835–843.

[4] For reviews on the chemistry of donor–acceptor cyclopropanes, see: a) H.-U. Reissig, *Top. Curr. Chem.* **1988**, *144*, 73–135; b) H.-U. Reissig, R. Zimmer, *Chem. Rev.* **2003**, *103*, 1151–1191; c) M. Yu, B. L. Pagenkopf, *Tetrahedron* **2005**, *61*, 321–347.

[5] a) R. B. Beal, M. A. Dombroski, B. B. Snider, *J. Org. Chem.* **1986**, *51*, 4391–4399; b) K. Saigo, S. Shimada, T. Shibasaki, M. Hasegawa, *Chem. Lett.* **1990**, 1093–1096; c) M. Komatsu, I. Suehiro, Y. Horiguchi, I. Kuwajima, *Synlett* **1991**, 771–773; d) Y. Sugita, K. Kawai, H. Hosoya, I. Yokoe, *Heterocycles* **1999**, *51*, 2029–2033; e) M. A. Kerr, R. G. Keddy, *Tetrahedron Lett.* **1999**, *40*, 5671–5675; f) Y. Sugita, C. Kimura, I. Yokoe, *Heterocycles* **2001**, *55*, 855–859; g) Y. Sugita, S. Yamadoi, H.

Hosoya, I. Yokoe, *Chem. Pharm. Bull.* **2001**, *49*, 657–658; h) D. B. England, T. D. O. Kuss, R. G. Keddy, M. Kerr, *J. Org. Chem.* **2001**, *66*, 4704–4709; i) Y. Sugita, C. Kimura, H. Hosoya, S. Yamadoi, I. Yokoe, *Tetrahedron Lett.* **2001**, *42*, 1095–1098; j) V. K. Yadav, V. Sriramurthy, *Org. Lett.* **2004**, *6*, 4495–4498; k) C. Venkatesh, P. P. Singh, H. Ila, H. Junjappa, *Eur. J. Org. Chem.* **2006**, 5378–5386.

[6] a) K. S. Feldman, C. J. Burns, *J. Org. Chem.* **1991**, *56*, 4601–4602; b) M. L. Graziano, M. R. Iesce, F. Cermola, G. Cimminiello, *J. Chem. Res. (S)* **1992**, 4–5; c) V. K. Yadav, V. Sriramurthy, *Angew. Chem.* **2004**, *116*, 2723–2725; *Angew. Chem. Int. Ed.* **2004**, *43*, 2669–2671.

[7] a) S. Shimada, Y. Hashimoto, A. Sudo, M. Hasegawa, K. Saigo, *J. Org. Chem.* **1992**, *57*, 7126–7133; b) S. Shimada, Y. Hashimoto, K. Saigo, *J. Org. Chem.* **1993**, *58*, 5226–5234; c) S. Shimada, Y. Hashimoto, T. Nagashima, M. Hasegawa, K. Saigo, *Tetrahedron* **1993**, *49*, 1589–1604; d) P. D. Pohlhaus, J. S. Johnson, *J. Org. Chem.* **2005**, *70*, 1057–1059; e) P. D. Pohlhaus, J. S. Johnson, *J. Am. Chem. Soc.* **2005**, *127*, 16014–16015; f) K. Fuchibe, Y. Aoki, T. Akiyama, *Chem. Lett.* **2005**, *34*, 538–539.

[8] a) M. L. Graziano, M. R. Iesce, *J. Chem. Res. (S)* **1987**, 362–363; b) K. Saigo, S. Shimada, M. Hasegawa, *Chem. Lett.* **1990**, 905–908; c) M. L. Graziano, G. Cimminiello, *J. Chem. Res. (S)* **1989**, 42–43; d) C. A. Carson, M. A. Kerr, *J. Org. Chem.* **2005**, *70*, 8242–8244; e) R. P. Wurz, A. B. Charette, *Org. Lett.* **2005**, *7*, 2313–2316; f) Y.-B. Kang, Y. Tang, X.-L. Sun, *Org. Biomol. Chem.* **2006**, *4*, 299–301; g) S. D. R. Christie, R. J. Davoile, R. S. F. Jones, *Org. Biomol. Chem.* **2006**, *4*, 2683–2684.

[9] a) M. Yu, B. L. Pagenkopf, *Org. Lett.* **2003**, *5*, 5099–5101; b) M. Yu, B. L. Pagenkopf, *J. Am. Chem. Soc.* **2003**, *125*, 8122–8123.

[10] a) M. H. Chang, R. Jain, D. A. Dougherty, *J. Am. Chem. Soc.* **1984**, *106*, 4211–4217; b) S. Huenig, M. Schmitt, *Tetrahedron Lett.* **1987**, *28*, 4521–4524; c) M. L. Graziano, M. R. Iesce, F. Cermola, *J. Chem. Res. (S)* **1996**, 82–83; d) V. S. Korotkov, O. V. Larionov, A. Hofmeister, J. Magull, A. de Meijere, *J. Org. Chem.* **2007**, *72*, 7504–7510.

[11] a) I. S. Young, M. A. Kerr, *Angew. Chem.* **2003**, *115*, 3131–3134; *Angew. Chem. Int. Ed.* **2003**, *42*, 3023–3026; b) M. D. Ganton, M. A. Kerr, *J. Org. Chem.* **2004**, *69*, 8554–8557; c) I. S. Young, M. A. Kerr, *Org. Lett.* **2004**, *6*, 139–141; d) I. S. Young, J. L. Williams, M. A. Kerr, *Org. Lett.* **2005**, *7*, 953–955; e) F. Cardona, A. Goti, *Angew. Chem.* **2005**, *117*, 8042–8045; *Angew. Chem. Int. Ed.* **2005**, *44*, 7832–7835; f) M. P. Sibi, Z. Ma, C. P. Jasperse, *J. Am. Chem. Soc.* **2005**, *127*, 5764–5765; g) Y.-B. Kang, X.-L. Sun, Y. Tang, *Angew. Chem.* **2007**, *119*, 3992–3995; *Angew. Chem. Int. Ed.* **2007**, *46*, 3918–3921; h) C. A. Carson, I. S. Young, M. A. Kerr, *Synthesis* **2008**, *3*, 485–489; i) K. Sapeta, M. A. Kerr, *J. Org. Chem.* **2007**, *72*, 8597–8599; j) A. Karadeolian, M. A. Kerr, *J. Org. Chem.* **2007**, *72*, 10251–10253.

[12] O. A. Ivanova, E. M. Budynina, Yu. K. Grishin, I. V. Trushkov, P. V. Verteletskii, *Angew. Chem.* **2008**, *120*, 1123–1126; *Angew. Chem. Int. Ed.* **2008**, *47*, 1107–1110.

[13] a) W. S. Murphy, S. Wattanasin, *J. Chem. Soc. Perkin Trans. 1* **1982**, 1029–1035; b) K. Hantawong, W. S. Murphy, N. Russell, *Tetrahedron Lett.* **1984**, *25*, 999–1000; c) P. Harrington, M. A. Kerr, *Tetrahedron Lett.* **1997**, *38*, 5949–5952.

[14] a) E. J. Corey, M. Chaykovsky, *J. Am. Chem. Soc.* **1965**, *87*, 1353–1364; b) W. Fraser, C. J. Suckling, H. C. S. Wood, *J. Chem. Soc. Perkin Trans. 1* **1990**, 3137–3144.

Received: June 24, 2008
Published Online: September 30, 2008

