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Synthesis of 9,10-bis(trifluoromethyl)benzobarrelenes through reaction of hexafluorobut-2-yne and substituted naphthalenes

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ABSTRACT

The cycloadducts 9,10-bis(trifluoromethyl)benzobarrelenes were prepared by the reaction of hexafluorobut-2-yne (**HFB**) with 1- and, 2- substituted naphthalenes in moderate to high yields. In most cases the reaction proceeds with the formation of two isomeric products derived from cycloaddition of **HFB** to different aromatic rings of the naphthalene system. The individual isomers were isolated by column chromatography and fully characterized. The basic hydrolysis of ester derivatives of the various 9,10-bis(trifluoromethyl)benzobarrelenes provided the corresponding acids.

1. Introduction

Benzobarrelenes belong to an interesting class of rigid cage compounds, which have been used as diene ligands for the preparation of transition-metal complexes [1] and also as monomers for ring-opening metathesis polymerization [2]. Their utility however, is limited due the limited number of known examples. Typically these materials are prepared by [4 + 2] cycloaddition of alkynes with naphthalenes. Hexafluorobut-2-yne (**HFB**) is a highly reactive dienophile which undergoes cycloaddition reactions with substrates such as furan [3], anthracene [4] and even electron-rich benzenes [5]. The reactions of **HFB** with naphthalene proceeds at elevated temperature [6,7]. For example, the reaction with naphthalene (225 °C, 1.5 h) resulted in isolation of the corresponding 9,10-bis(trifluoromethyl)benzobarrelene in 37 % yield [7]. The similar reaction of 2,3,6,7-tetrakis-(trifluoromethyl)naphthalene (225 °C, 800 atm pressure over 16 h) gave the cycloaddition product in 79 % yield [7].

It should be pointed out that all previously reported examples of 9,10-bis(trifluoromethyl)benzobarrelenes were derived from the reaction of symmetric naphthalenes and **HFB**.

In continuation of our ongoing studies [8] of HFB chemical behavior we studied the reaction of **HFB** with various non-symmetrical naphthalene derivatives, including 1- and 2-naphthol, 1-acetoxynaphthalene, methyl esters of 1- and 2-naphthylacetic acid, and 1- and 2-naphthyl carboxylic acids. The results of this study are reported in this article.

2. Results and discussion

The reaction of excess **HFB** and naphthalenes was carried out at 195 °C under - autogenous pressure (see Experimental). Various non-symmetrical 1- and 2- substituted naphthalenes (R = −OH, $-CH_2C(O)OMe$ and –C(O)OMe substituents) were subjected to the reaction with excess of **HFB**.

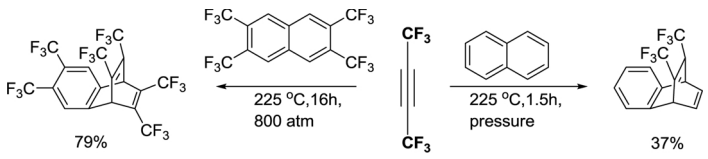

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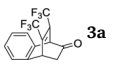
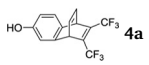
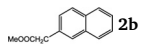
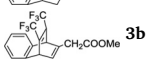
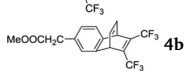
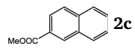
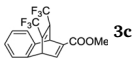
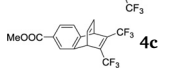
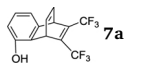
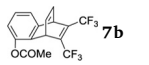
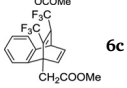
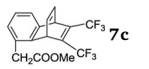
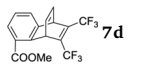
Table 1
Yields and ratios of products derived from cycloaddition of HFB and with 1- and 2- substituted naphthalenes.

Entry	Starting naphthalene (**2**), (**5**)	Product (**3**), (**6**)	Product (**4**), (**7**)	Total yield, % (ratio (**3**)/(**4**) (**6**)/(**7**))	Yield [a] of (**3**), (**6**), %	Yield [a] of (**4**), (**7**), %
1	 **2a**	 **3a**	 **4a**	88 (1 : 1)	29	31
2	 **2b**	 **3b**	 **4b**	71 (1 : 3)	14	25
3	 **2c**	 **3c**	 **4c**	82 (1 : 3)	16	30
4	 **5a**	 **6a**	 **7a**	94 (3 : 1)	40	25
5	 **5b**	 **6b**	 **7b**	89 (1 : 3)	17	41
6	 **5c**	 **6c**	 **7c**	89 (1 : 10)	4	63
7	 **5d**	 **6d**	 **7d**	87 (1 : 0)	87	

[a] Isolated yields (column chromatography followed by crystallization).

In case of naphthalenes carrying a substituent at the 2 position [**2a** (R= −OH), **2b** (R= $-CH_2C(O)OMe$) and **2c** (R= –C(O)OMe)) high yields (71–88%) were obtained for the corresponding isomeric barrelenes **3a-c** and **4a-c**, resulting from cycloaddition of one mole **HFB** to either substituted or non-substituted aromatic ring of naphthalene system. These yields are in contrast to the low yield of **HFB** cycloaddition to unsubstituted naphthalene [7], thus we repeated this experiment, changing time and concentration but the yield of key product was still in the range of 37–39 %. We assume that the specificity of this case, in contrast to all other examples, is the volatility of naphthalene in comparison to substituted derivatives.

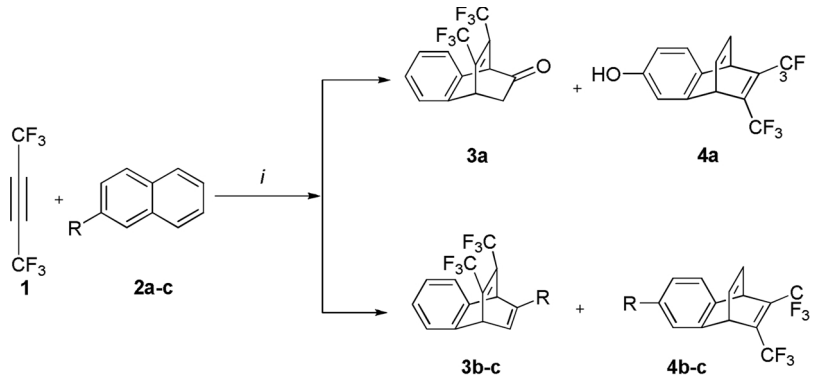
While in case of 2-naphthol (**2a**) the reaction resulted in high yield formation of two isomeric products **3a** and **4a** (ratio 1:1), the cycloaddition of **HFB** to 2-naphthylacetic acid (**2b**) and 2-naphthyl carboxylic acid (**2c**) led to formation of cycloadducts **3b/4b and 3c/4c**, with predominant formation of cycloadducts at the unsubstituted aromatic ring (**4b-c Sch. 1,** Table 1). It is necessary to note that while high reaction temperatures were employed the various functional groups were found to be stable to these reaction conditions (Scheme 1).

The same peculiarities were found in the reaction of naphthalenes with substituents at the 1 position (**Sch. 2**).

The reaction of **HFB** with 1-naphthol (**5a**), 1-naphthyl acetate (**5b**), and the methyl ester of 1-naphthylacetic acid (**5c**) led to high yields (89–94 %) of benzobarrelenes **6a-c/7a-c**. Interestingly, in the case of 1-naphthol (**5a**) the isomer **6a** was predominant (**6a/7a** - 3:1, Scheme 2, Table 1), while the cycloaddition of **HFB** to **5b** and **5c** proceeded with predominant formation of isomers **7b** and **7c.** In case of methyl 1-naphthoate (**5d**) the reaction was regioselective, leading to exclusive formation of the adduct **6d** (87 % yield), derived from an addition of the acetylene to the substituted aromatic ring (**see** Table 1). Using column chromatography individual isomers were isolated and in the case of isomers **6b** and **7b** the structures was confirmed by X-ray diffraction.

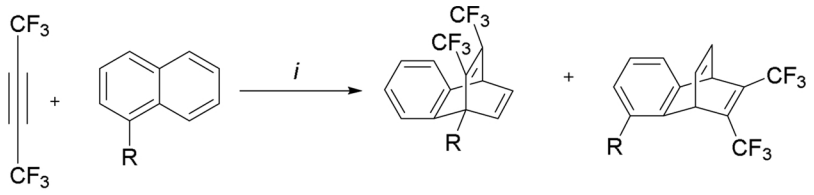
The 2,3-bis(trifluoromethyl)bicyclo(2.2.2)oct-2-ene fragment in **6b** and **7b** (Fig. 1) has very similar geometric parameters. The average interatomic distances and bond angles are typical of those for known hydrocarbon analogues - [9,10] and correlated to standard values typical for corresponding carbon-carbon bonds. For example, the distances between C8 and C9 and C11 and C12 carbons (see Fig. 1) in these compounds have values in the range 1.309(3)-1.333(3) typical for standard C═C double bond in organic compounds. Bond distances and angles for aromatic rings and C_{sp3} hybridized carbon atoms are also within standard values. The notable exception is the significant increase of the C12-C11-C13 and C11-C12-bond angles (124.49(17)-129.43(17)°) caused by the intramolecular CF_3-CF_3 repulsion.

It should be also pointed out, that despite that an excess **HFB** was



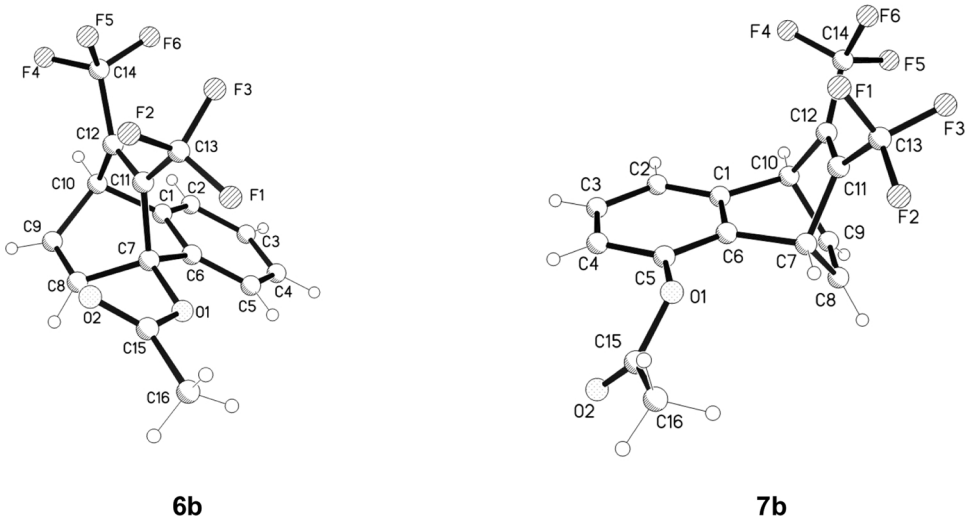
a R = OH (**88%**; ratio **3/4 - 1:1**);
b R = $CH_2C(O)OMe$ **(71%;** ratio **3/4 - 1:3);**
c R = C(O)OMe **(82%;** ratio **3/4 - 1:3)**

Scheme 1. The cycloaddition reaction of **HFB** with 2-substituted naphthalenes. *i*) 195 °C, 16 h.



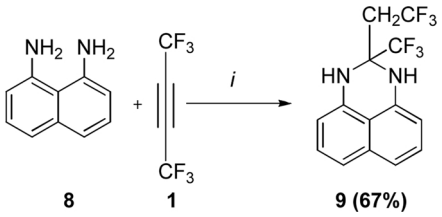
a R = OH (**94%**, ratio **6/7- 3:1**)
b R = OC(O)Me (**89%**, ratio **6/7- 1:3**)
c R = $CH_2C(O)OMe$ (**89%**, ratio **6/7- 1:10**)
d R = C(O)OMe (**87%**, only **6d**)

Scheme 2. The Diels-Alder reaction of **HFB** with 1-substituted naphthalenes. *i*) 195 °C, 16 h.



6b **7b**

Fig. 1. Molecular structure of **6b and 7b.**



Scheme 3. The reaction of **HFB** with 1,8-naphthalenediamine. *i*) 195 °C, 8 h.

used in all experiments involving naphthalenes the formation of double-addition products was never observed in these reactions.

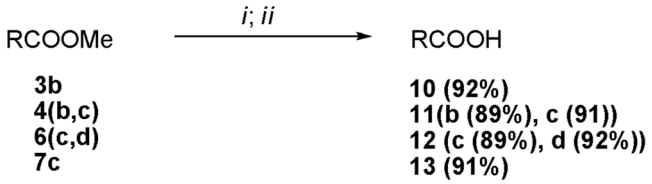
An attempt to react **HFB** with 1,8-naphthalenediamine led to a very different result. This reaction resulted in selective formation of cyclic product **9**, derived from nucleophilic addition of the amino groups of **8** across the electrophilic triple bond of **HFB** (Scheme 3).

Although this type of nucleophilic reactions of fluorinated olefins often results in the formation of seven-membered rings [11], in this particular case the cyclization resulted in the formation of six-membered ring that was proved by NMR data.

Esters of benzobarrelenes **3b, 4(b,c), 6(c,d), 7c** were hydrolyzed to the corresponding acids **10–13** upon treatment with NaOH, followed by acidification (Scheme 4, Table 2).

The hydrolysis of compound **6b** gave alcohol **6a**, prepared from the 1-naphthol (See Scheme 2) which was identified by ^{1}H, ^{19}F NMR spectroscopy. Similarly, the hydrolysis of compound **7b** gave alcohol **7a**, which was identical to the material isolated in the cycloaddition reaction with 1-naphthol **(Sch. 5,** Table 2) (Scheme 5).

Hydrolysis of compound (**3c**) in the mixture NaOH, water, methanol and THF gave product **14** (Scheme 6) as a result of Michael type addition of MeOH to the double bond of either compound **3c** (followed by hydrolysis), or to compound **15.** Noteworthy to mention that acid **15** was isolated in high yield when the hydrolysis was carried out in the absence of methanol (**Sch. 6**).

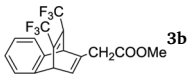
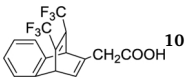
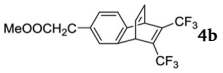
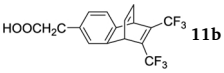
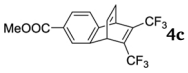
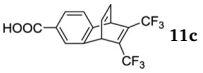
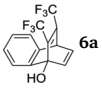
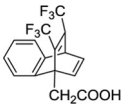
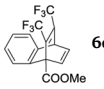
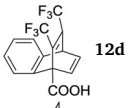
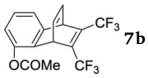
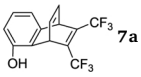
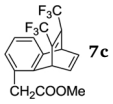
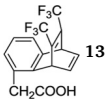


Scheme 4. Hydrolysis of esters**3b, 4(b,c), 6(c,d), 7c**. *i*) NaOH, H_2O/MeOH/THF-1:1:4, r.t.; *ii)* conc. HCl.

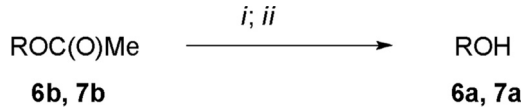
3. Conclusion

Hexafluorobutyne-2 undergoes cycloaddition with various naphthalenes resulting in the formation of 1:1 cycloadducts - the corresponding 9,10-bis(trifluoromethyl)benzobarrelenes isolated tin moderate to high yields It was found that in case of nonsymmetrical naphthalenes the reactions was not regioselective and proceed with formation of two isomeric products as a result of **HFB** cycloaddition to both aromatic rings of the naphthalene system. The ratio of regioisomers varies significantly depending on the naphthalene substitution pattern and character of the substituents.

Table 2
Hydrolysis of esters **3b, 4(b,c), 6(b–d), 7(b,c).**[a]

Entry	Starting ester	Product	Yield, %
1	 **3b**	 **10**	92
2	 **4b**	 **11b**	89
3	 **4c**	 **11c**	90
4	 **6b**	 **6a**	89
5	 **6c**	 **12c**	89
6	 **6d**	 **12d**	92
7	 **7b**	 **7a**	91
8	 **7c**	 **13**	91

[a] Conditions: NaOH (12 mmol), H_2O (5 mL), MeOH (5 mL), THF (20 mL), r.t., 48 h.



Scheme 5. Hydrolysis of esters **6b, 7b**. *i*) NaOH, H_2O/MeOH/THF-1:1:4, r. t.; *ii*) conc. HCl.

4. Experimental

NMR spectra of compounds isolated were recorded on a Varian UNITY- Plus 400 (^{1}H, 399.98 MHz, ^{19}F, 376.49 MHz) and ^{13}C NMR-spectra were recorded on a Bruker AVANCE DRX 500 instrument at 125.71 MHz in $CDCl_3$ (DMSO-d_6 for compounds 10,15) solutions. The chemical shifts are given in units of δ (ppm) using external standards (^{1}H, ^{13}C Me_4Si, ^{19}F: CCl_3F). Melting points were determined using a Stuart melting point apparatus SMP10. Elemental analyses were carried out in the Analytical Laboratory of the Institute of Organic Chemistry, NAS of Ukraine, Kyiv; analytically pure samples were prepared by crystallization of small amount of the product. Purification of products by column chromatography was performed using Silica Gel, (70–230 mesh, Aldrich), column: L = 350 mm, D = 30 mm and hexane/dichloromethane 6:4 (by weight) as eluent. Esters were prepared according to standard procedure from corresponding naphthyl acetic acids and naphthyl carboxylic acids by reflux with methanol in the presence of sulfuric acid.

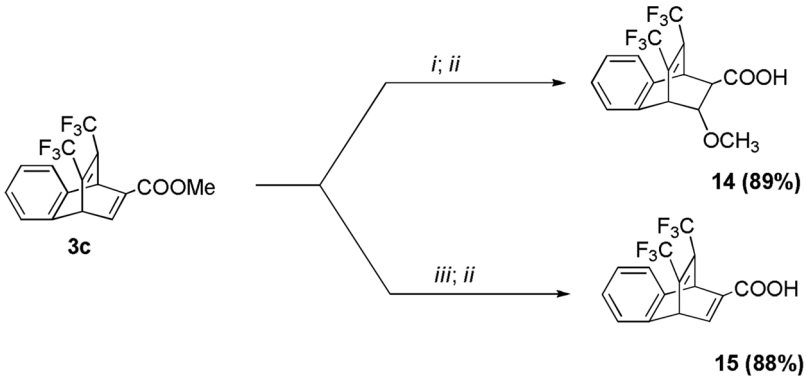
All crystallographic measurements were performed at temperature 173 K on a Bruker Smart Apex II diffractometer operating in the ω scans mode. The structure were solved by direct methods and refined by the full-matrix least-squares technique in the anisotropic approximation for non-hydrogen atoms using the Bruker SHELXTL program package [12]. Full crystallographic details have been deposited at Cambridge Crystallographic Data Centre CCDC. Any request to the CCDC for these materials should quote the full literature citation and reference number CCDC 1,953,290 and CCDC 1,953,291.

4.1. General procedure of 1,4-addition of hexafluorobut-2-yne to naphthalene derivatives

A mixture of 0.03 mol corresponding naphthalene derivative and 0.06 mol of hexafluorobut-2-yne was heated at 190 − 195 °C for 16 h (8 h for 1,8-naphthalenediamine) in a 100 ml stainless steel autoclave fitted with magnetic stirrer under autogenous pressure - given the moles of reagents (0.09 mol total), temperature (195 C), and reactor volume (100 mL) the maximum pressure in the reactor would be 34.5 bar (ca. 525 psig). Autoclave was cooled to ambient temperature and volatile product was removed. The reaction mixture was extracted with dichloromethane and then solvent was removed under reduced pressure. The crude product thus obtained was subjected to separation by column chromatography and the isolated individual isomers were further purified by recrystallization. However, products (**5**) and (**9**) were purified only by crystallization.

4.2. 11,12-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,11-tetraen-9-on (3a)

Colorless crystals, yield 29 %. m.p. 39 − 40 °C. (from pentane); ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.15 (d, 1H, $^2J_{HH}$ = 18 Hz, CH_2), 2.31 (d, 1H, $^2J_{HH}$ = 18 Hz, CH_2), 4.60 (s, 1H, H-8), 4.81 (s, 1H, H-1), 7.35 (m, 4H, arom. H-3,4,5,6). ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 200.0 (s, C-9, C = O), 140.7 (qq, $^2J_{CF}$ = 35.4 Hz, $^3J_{CF}$ = 4 Hz, C-12,(11), CF_3C=), 138.7 (s, 2C, arom. C-2,7), 136.15 (qq, $^2J_{CF}$ = 35.4 Hz, $^3J_{CF}$ = 4 Hz, C-11(12), CF_3C=), 133.9 (s, 2C, arom. C-2,7) 128.7 (s, arom. C), 127.9 (s, arom. C), 125.9 (s, arom. C), 124.3 (s, arom. C), 121.1 (q, $^1J_{CF}$ = 271.8 Hz, CF_3), 120.9 (q, $^1J_{CF}$ = 271.8 Hz, CF_3), 59.0 (s, C-8(1)), 41.58 (s, C-1(8)),



Scheme 6. Hydrolysis of **3c** *i*) NaOH, H_2O/MeOH/THF-1:1:4, r. t.; *ii*) conc. HCl; *iii*) NaOH, H_2O /THF-1:4, r. t.

34.2 (s, C-10, CH_2). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -61.04 (q, 3 F, $^2J_{FF}$ =11.2 Hz, CF_3), -62.64 (q, 3 F, $^2J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 54.98; %H 2.70. $C_{14}H_8F_6O$. Calcd.: %C 54.91; % H 2.63.

4.3. Methyl [11,12-bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-9-yl] acetate (3b)

Colorless oil, yield 14 %; ^1H NMR (400 MHz, $CDCl_3$): **δ** 3.57 (s, 2H, CH_2), 3.68 (s, 3H, CH_3), 5.21 (m, 2H, H-1,8), 6.93 (d, 1H, $^3J_{HH}$ =6 Hz, H-10), 6.99 (m, 2H, arom. H), 7.25 (m, 2H, arom. H). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 170.2 (s, C = O), 146.4 (s, arom. C-2(7)), 144.5 (m, C-11(12), CF_3C=), 144.2 (m, C-12(11), CF_3C=), 143.9 (s, arom. C-2(7)), 143.5 (s, C-9(10), CH=), 135.0 (s, C-10(9), CH=), 125.0 (s, arom. C), 123.5 (s, arom. C), 123.1 (s, arom. C), 122.1 (q, $^1J_{CF}$ =271.8 Hz, $2CF_3$), 52.9 (s, CH_3O), 52.0 (s, C-8(1)), 48.8 (s, C-1(8)), 37.9 (s, CH_2). ^{19}F (376.49 MHz, $CDCl_3$): **δ** -61.78 (q, 3 F, $^2J_{FF}$ 11.2 Hz CF_3,), -61.89 (q., 3 F, CF_3, $^2J_{FF}$ 11,2 Hz). Analysis: Found: %C 56.26; %H 3.04. $C_{17}H_{12}F_6O_2$. Calcd.: %C 56.36; % H 3.34.

4.4. Methyl [11,12-bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-9-yl] carboxylate (3c)

Yellow oil, yield 16 %; ^1H NMR (400 MHz, $CDCl_3$): **δ** (ppm) 3.77 (s, 3H, CH_3), 5.32 (d, 1H, $^3J_{HH}$ =6 Hz, H-1), 5.75 (s, 1H, H-8), 7.06 (m, 2H, arom. H), 7.36(m, 1H, arom. H), 7.41(m, 1H, arom. H), 7.79 (d, 1H, $^3J_{HH}$ =6 Hz, H-10). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 163.2 (C = O), 147.0 (s, arom. C-7(2)), 144.3 (s, arom. C-2(7)), 144-143.4 (m, 2C-11(12), $2CF_3C$=), 142.5 (s, C-9(10), CH=), 141.5 (s, C-10(9), CH=), 125.3 (s, arom. C), 125.1 (s, arom. C), 123.6 (s, arom. C), 123.5 (s, arom. C), 121.3 (q, $^1J_{CF}$ =273.1 Hz, CF_3), 121.2 (q, $^1J_{CF}$ =273.1 Hz, CF_3), 51.7 (s, C, CH_3O), 48.9 (s, C-8(1)), 48.2 (s, C-1(8)). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -61.83 (br. s, 6 F, $2CF_3$). Analysis: Found: %C 55.30; %H 3.03. $C_{16}H_{10}F_6O_2$. Calcd.: %C 55.18; % H 2.89.

4.5. 10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-4-ol (4a)

Colorless crystals, yield 31 % m.p. 72−74 °C (from pentane); ^1H NMR (400 MHz, $CDCl_3$): **δ** 4.76 (br.s, 1H, OH), 5.13 (m, 2H, H-1,8), 6.42 (dd, 1H, $^3J_{HH}$ =7.6 Hz, $^3J_{HH}$ =2.4 Hz, H-5), 6.84 (d, 1H, $^3J_{HH}$ =2.4 Hz, H-3), 6.97 (m, 2H, H-11,12), 7.10 (d, 1H, $^3J_{HH}$ =7.6 Hz, arom, H-6). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 152.9 (s, arom. C), 146.0 (s, arom. C), 144.9 (m, C-9(10), CF_3C=), 144.2 (m, C-10(9), CF_3C=), 139.8 (s, C-11(12), CH=), 138.7 (s, C-12(11), CH=), 136.2 (s, arom.C), 123.0 (s, arom. C), 122.0 (q, $^1J_{CF}$ =272.8 Hz, $2CF_3$), 112.1 (s, arom. C), 110.5 (s, arom. C), 48.9 (s, C-8(1)), 48.3 (s, C-1(8)). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -61.95 (m, 3 F, CF_3), -62.05 (m, 3 F, CF_3). Analysis: Found: %C 54.85; %H 2.58. $C_{14}H_8F_6O$. Calcd.: %C 54.91; % H 2.63.

4.6. Methyl [9,10-bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-4-yl] acetate (4b)

Colorless oil, yield 25 %; ^1H NMR (400 MHz, $CDCl_3$): **δ** 3.30 (s, 2H, CH_2), 3.68 (s, 3H, CH_3), 5.13 (m, 2H, H-1,8), 6.68 (d, 1H, $^3J_{HH}$ =6 Hz, arom. H-3) 7.03 (m, 2H, H-11,12), 7.32 (m, 2H, arom. H-5,6). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 170.2 (s, C = O), 146.4 (s, C-12(11), CH=), 144.26 (m, C-10,9, $2CF_3C$=), 143.9 (s, arom. C-2(7)), 143.5 (s, arom. C-7(2)), 135.0 (s, C-11(12), CH=), 125.24 (s, arom. C), 125.2(s, arom. C), 123.5 (s, arom. C), 123.1 (s, arom. C), 122.0 (q, $^1J_{CF}$ =271.5 Hz, $2CF_3$), 52.9 (s, C-8(1)), 52.0 (s, CH_3), 48.7 (s, C-1(8)), 39.7 (s, CH_2). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -61.43 (q, 3 F, $^2J_{FF}$ =11.2 Hz, CF_3), -62.87 (q, 3 F, $^2J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 56.40; %H 3.48. $C_{17}H_{12}F_6O_2$. Calcd.: %C 56.36; % H 3.34.

4.7. Methyl [9,10-bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-3-yl] carboxylate (4c)

Colorless crystals, yield 30 %; m.p. 96−97 °C (from hexane); ^1H NMR (400 MHz, $CDCl_3$): **δ** 3.85 (s, 3H, CH_3), 5.25 (m, 2H, H-1,8), 6.98 (m, 2H, H-11,12), 7.32 (d, 1H, $^3J_{HH}$ =7.5 Hz arom. H-6), 7.73 (d, 1H, $^3J_{HH}$ =7.5 Hz, arom. H-5), 7.91 (s, 1H, arom. H-3); ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 166.6 (C = O), 148.7 (s, arom. C-7(2)), 144.3 (s, arom. C-2(7)), 144.2 (m, C-9,10, $2CF_3C$=), 139.5 (s, C-12(11), CH=), 139.2 (s, C-11(12), CH=), 127.5 (s, arom. C), 127.4 (s, arom. C), 124.0 (s, arom. C), 123.1 (s, arom. C), 121.7 (q, $^1J_{CF}$ =273.8 Hz, $2CF_3$), 52.1 (s, $C(O)OCH_3$), 49.0 (s, C-8(1)), 48.9 (s, C-1(8)). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -62.42 (br. s, 6 F, $2CF_3$). Analysis: Found: %C 56.31; %H 2.95. $C_{10}H_{10}F_6O_2$. Calcd.: %C 55.18; % H 2.89.

4.8. 9,10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-1-ol (6a)

Colorless crystals yield 40 %, m.p. 62−64 °C (from pentane); ^1H NMR (400 MHz, $CDCl_3$): **δ** 3.33 (br. s, OH), 5.22 (d, 1H, $^3J_{HH}$ =6.0 Hz, H-8), 6.87 (d, 1H, $^3J_{HH}$ = 7.2 Hz, H-11), 7.12 (m, 4H, arom. H-3,4,5,6), 7.51 (d, 1H, $^3J_{HH}$ = 7.2 Hz, H-12). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 145.7 (qq, $^2J_{CF}$ =31 Hz, $^3J_{CF}$ =4 Hz, C-10(9), CF_3C=), 145.0 (s, arom. C), 144.0 (qq., $^2J_{CF}$ =31 Hz, $^3J_{CF}$ =4 Hz, C-9(10), CF_3C=), 143.7 (s, C-12(11), CH=), 141.7 (arom. C), 137.2 (s, C-11(12), CH=), 125.3 (s, arom. C), 125.1 (s, arom. C), 123.0 (s, arom. C), 122.8 (q, $^1J_{CF}$ =278.8 Hz, CF_3), 122.6 (q, $^1J_{CF}$ =272.8 Hz, CF_3), 119.4 (s, arom. C), 84.0 (s, C−OH), 47.0 (s, CH). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -59.20 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3), -60.54 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 54.90; %H 2.67. $C_{14}H_8F_6O$. Calcd.: %C 54.91; % H 2.63.

4.9. 9,10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-1-yl acetate (6b)

Colorless crystals, yield 17 %, m.p. 106−108 °C (from pentane); ^1H NMR (400 MHz, $CDCl_3$): **δ** 2.43 (s, 3H, CH_3), 5.20 (d, 1H, $^3J_{HH}$ =6.6 Hz, H-8), 6.93 (t, 1H, $^3J_{HH}$ =6.9 Hz, 6.6 Hz, arom. H-4), 7.10 (m., 3H, H arom., H-3,5,6), 7.30 (d, 1H, $^3J_{HH}$ = 6.6 Hz, H-11), 7.40 (d, 1H, $^3J_{HH}$ = 6.6 Hz, H-12). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 169.3 (s, C = O), 144.2 (m, 2C, C-10,9, $2CF_3C$=), 142.0 (s, arom. C-7(2)), 141.2 (s, C-11(12), CH=), 141.2 (s, arom. C-2(7)), 134.2 (s, C-12(11), CH=), 125.6 (s, arom. C), 125.06 (s, arom. C), 123.1 (s, arom. C), 121.6 (q, $^1J_{CF}$ =272.8 Hz, CF_3), 121.0 (q, $^1J_{CF}$ =278.8 Hz, CF_3), 120.7 (s, arom. C), 86.2 (s, C-O), 47.4 (s, CH), 21.2 (s, CH_3). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -59.69 (q, 3 F, $^3J_{FF}$ =12.7 Hz, CF_3), -61, 65 (q, 3 F, $^3J_{FF}$ =12.7 Hz, CF_3). Analysis: Found: %C 55.12; %H 2.83. $C_{16}H_{10}F_6O_2$. Calcd.: %C 55.18; % H 2.89.

4.10. Methyl [9,10-bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-1-yl] acetate (6c)

Colorless crystals, yield 4 %; m.p. 72−73 °C (from pentane); ^1H NMR (400 MHz, $CDCl_3$): **δ** 3.60 (d, 1H, H^A, $^2J_{HH}$ =18 Hz, CH_2), 3.77 (d, 1H, H^B, $^2J_{HH}$ =18 Hz, CH_2), 3.80 (s, 3H, CH_3), 5.22 (d, 1H, $^3J_{HH}$ =5.6 Hz, H-8), 7.03 (m., 4H, arom. H-3,4,5,6), 7.23 (d, 1H, $^3J_{HH}$ =7.6 Hz, H-11), 7.31 (d, 1H, $^3J_{HH}$ =7.6 Hz, H-12). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 171.0 (s, C = O), 147.8 (qq, $^2J_{CF}$ =34 Hz, $^3J_{CF}$ =4.1 Hz, C-10(9), CF_3C=), 145.1 (s, arom. C-7(7)), 144.6 (qq, $^2J_{CF}$ =34 Hz, $^3J_{CF}$ =4.1 Hz, C-9(10), CF_3C=), 143.3 (s, C- 12(11), CH=), 137.7 (s, C-11(12), CH=), 125.0 (s, arom. C), 124.9 (s, arom. C), 123.4 (s, arom. C), 122.3 (q, $^1J_{CF}$ =273.4 Hz, CF_3), 122.1 (q, $^1J_{CF}$ =273.4 Hz, CF_3), 121.2 (s, arom. C), 53.9 (s, CH_3O), 52.0 (s, C-8(1)), 48.6 (s, C-1(8)), 34.2 (s, CH_2) ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -57.53 (q, 3 F, $^1J_{FF}$ =11.2 Hz, CF_3), -60.12 (q, 3 F, $^1J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 56.38; %H 3.23. $C_{17}H_{12}F_6O_2$. Calcd.: %C 56.36; % H 3.34.

4.11. Methyl [9,10-bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-1-yl] carboxylate (6d)

Colorless crystals, yield 87 %, m.p. 99−100 °C (from hexane); ^{1}H NMR (400 MHz, $CDCl_3$): **δ** 3.96 (s, 3H, CH_3), 5.27 (d, 1H, $^3J_{HH}$ = 5.2 Hz H-8), 6.68 (d, 1H, $^3J_{HH}$ = 5.2 Hz, H-11), 6.99 (m, 1H, H-12), 7.08 (m, 2H, arom. H-4,5), 7.44 (d, 1H, $^3J_{HH}$ =8 Hz, arom. H-3), 7.65 (d, 1H, $^3J_{HH}$ =8 Hz, arom. H-6); ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 166.7 (s, C = O), 145.8 (s, arom. C-7(2)), 144.25 (s, arom. C) 144.6 (m, 2C, C-9,10, 2CF_3C=), 139.8 (s, C-12(11), CH=), 139.2 (s, C-11(12), CH=), 126.9 (s, arom. C), 126.6 (s, arom. 2C), 125.8 (s, arom. C-2(7)), 124.8 (s, arom. C), 121.9 (q, $^1J_{CF}$ =273.4 Hz, 2CF_3), 52.1 (s, CH_3O), 49.1 (s, C-1(8)), 45.7 (s, C-8(1)). ^{19}F NMR (376.49 MHz, $CDCl_3$): δ -62.36 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3), -62.56 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 55.17; %H 2.94. $C_{16}H_{10}F_6O_2$. Calcd.: %C 55.18; % H 2.89.

4.12. 9,10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-3-ol (7a)

Colorless crystals, yield 25 %, m.p.100−101 °C (from pentane); ^{1}H NMR (400 MHz, $CDCl_3$): **δ** 4.80 (br. s, 1H, OH), 5.22 (t, 1H, $^3J_{HH}$ =2.0 Hz, H-8), 5.65 (t, 1H, J_{HH} =2.0 Hz, H-1), 6.47 (d, 1H, $^3J_{HH}$ =8.0 Hz, H-11), 6.87 (t, 1H, $^3J_{HH}$ = 7.6 Hz, H-4), 6.94 (d, 1H, $^3J_{HH}$ =8.0 Hz, H-12), 7.0 (t, 3H, J_{HH} =2.4 Hz, arom. H-5,6). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 150.0 (s, arom. C-7(2)), 146.9 (s, arom. C-2(7)), 144.6 (m, 2C, C-9,10, 2CF_3C=), 139.5 (s, C-12(11), CH=), 139.1 (s, C-11(12), CH=), 129.5 (s, arom. C), 126.1 (s, arom. C), 122.0 (q, $^1J_{CF}$ =272.8 Hz, 2CF_3), 116.6 (s, arom. C), 113.9 (s, arom. C), 49.2 (s, C-8(1)), 42.6 (s, C-1(8)). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -61.50 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3,), -62.07 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 54.97; %H 2.74. $C_{14}H_8F_6O$. Calcd.: %C 54.91; % H 2.63.

4.13. 9,10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-3-yl acetate (7b)

Colorless crystals, yield 41 %, m.p. 69−70 °C (from pentane). ^{1}H NMR (400 MHz, $CDCl_3$): **δ** 2.39 (s, 3H, CH_3), 5.27 (d, 1H, $^3J_{HH}$ =5.6 Hz, H-8), 5.30 (d, 1H, $^3J_{HH}$ =5.6 Hz, H-1), 6.78 (d, 1H, $^3J_{HH}$ =8.0 Hz, H-11), 7.0 (m, 3H, arom. H-4,5,6), 7.19 (d, 1H, $^3J_{HH}$ =8.0 Hz, H-12). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 169.0 (s, C = O), 147.8 (qq, $^2J_{CF}$ =35.9 Hz, $^3J_{CF}$ =4 Hz, C-10(9), CF_3C=), 146.2 (s, arom. C-3), 145.4 (s, arom. C-2(7)), 145.0 (qq, $^2J_{CF}$ =35.9 Hz, $^3J_{CF}$ =4 Hz, C-9(10), CF_3C=), 139.8 (s, C-12(11), CH=), 135.4 (s, C-11(12), CH=), 135.4 (s, arom. C-7(2)), 126.2 (s, arom. C), 122.0 (q, $^1J_{CF}$ =271.3 Hz, CF_3), 121.8 (q, $^1J_{CF}$ =271.3 Hz, CF_3), 120.9 (s, arom. C), 119.1 (s, arom. C), 48.99 (s, C-1(8)), 43.5 (s, C-8(1)), 20.7 (s, CH_3) ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -62.0 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3), -62.64 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 55.38; %H 2.97. $C_{16}H_{10}F_6O_2$. Calcd.: %C 55.18; % H 2.89.

4.14. Methyl [9,10-bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-3-yl] acetate (7c)

Colorless oil, yield 63 %; ^{1}H NMR (400 MHz, $CDCl_3$): **δ** 3.70 (s, 3H, CH_3), 3.72 (d, 1H^A, $^2J_{HH}$ =15.6 Hz, CH_2), 3.80 (d, 1H^B, $^2J_{HH}$ =15.6 Hz, CH_2), 5.24 (d, 1H, $^3J_{HH}$ = 5.2 Hz, H-8), 5.53 (d, 1H, $^3J_{HH}$ = 5.2 Hz, H-1), 6.95 (m, 2H, arom. H), 7.05 (m, 2H, H-11,12), 7.25(d, 1H, J_{HH} = 7.2 Hz arom. H). ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 171.3 (s, C = O), 144.7 (qq, $^2J_{CF}$ =35.4 Hz, $^3J_{CF}$ =4.0 Hz, C-10(9), *CF_3C*=), 144.5 (s, arom. C-7(2)), 143.9 (qq, $^2J_{CF}$ =34 Hz, $^3J_{CF}$ =4.1 Hz, C-9(10), CF_3C=), 143.1 (s, arom. C-2(7)), 139.5 (s, C-12(11), CH=), 139.0 (s, C-11(12), CH=), 128.6 (s, arom. C), 126.8 (s, arom. C), 125.1 (s, arom. C), 122.7 (s, arom. C), 122.0 (q, $^1J_{CF}$ =273.4 Hz, 2CF_3), 52.2 (s, CH_3O), 49.3 (s, C-8(1)), 46.0 (s, C-8(1)), 38.1 (s, CH_2). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -61.79 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3), -62.20 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 56.47; %H 3.25. $C_{17}H_{12}F_6O_2$. Calcd.: %C 56.36; % H 3.34.

4.15. 2-(2,2,2-Trifluoroethenyl)-2-(trifluoromethyl)-2,3-dihydro-1H-perimidine (9)

Yellow crystals, yield 67 %, m.p. 128−129 °C (from hexane); ^{1}H NMR (400 MHz, $CDCl_3$): **δ** 2.73 (d, 1H^A, $^2J_{HH}$ =10 Hz, CH_2), 2.77 (d, 1H^B, $^2J_{HH}$ =10 Hz, CH_2), 4.68 (br. s, 2H, 2NH), 6.58 (d, 2H, $^3J_{HH}$ =7 Hz, arom. H), 7.26 (m, 4H, arom. H). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 136.5 (s, arom. C), 133.9 (s, arom. C), 127.1 (s, arom. C), 124.6 (q, $^1J_{CF}$ =277.7 Hz, *CF_3*), 124.7 (q, $^1J_{CF}$ =277.7 Hz, *CF_3*), 118.5 (s, arom. C), 105.8 (s, arom. C), 67.2 (q, $^2J_{CF}$ =28.9 Hz, CN), 38.4 (q, $^2J_{CF}$ =28.9 Hz, CH_2). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -59.68 (s, 3F, *C-CF_3*), -83.23 (s, 3F, *CH_2CF_3*). Analysis: Found: %C 52.46; %H 3.13, %N 8.70. $C_{14}H_{10}F_6N_2$. Calcd.: %C 52.51; % H 3.15; %N 8.75.

4.16. General procedure of hydrolysis of compounds (3–7)

A mixture of 0.006 mol of corresponding ester, 0.012 mol of NaOH in 5 ml of water, 5 ml methanol [for preparation of acid (15) without methanol] and 20 ml THF was stirred at ambient temperature for 48 h. The reaction mixture was evaporated under reduced pressure to 30 % of starting volume and was added to 20 ml of water. The mixture was washed with diethyl ether (2 × 10 ml). Water extract was acidified to pH 3–4 and organic acid was extracted with diethyl ether. The ether solution was dried with $MgSO_4$ and solvent was removed under reduced pressure. The product was purified by crystallization.

4.17. 9,10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-1-ol (6a)

Colorless crystals, 89 % yield, m.p. 62−64 °C (from pentane).

4.18. 9,10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-3-ol (7a)

Colorless crystals, 91 % yield, m.p.100−101 °C (from pentane).

4.19. [11,12-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-9-yl] acetic acid (10)

Colorless crystals, 92 % yield, m.p. 110−111 °C (from hexane); ^{1}H NMR (400 MHz, DMSO-d_6): **δ** 3.58 (s, 2H, CH_2), 5.21 (m, 2H, H-1,8), 6.92 (d, 1H, $^3J_{HH}$ = 7.2 Hz, H-10), 6.99 (m, 2H, arom. H), 7.25 (m, 2H, arom. H). ^{13}C NMR (125.71 MHz, DMSO-d_6): **δ** 177.8 (s, C = O), 145.0 (s, arom., C-7(2)), 144.3 (m, 2C, C-11,12, 2CF_3C=), 143.1 (s, arom. C-2(7)), 139.2 (s, C-10(9), CH=), 139.1 (s, C-9(10), CH=), 130.2(s, arom. C), 126.0(s, arom. C), 124.5(s, arom. C), 123.0(s, arom. C), 122.1 (q, $^1J_{CF}$ =278.1 Hz, 2CF_3), 48.9 (s, C-8(1)), 48.7 (s, C-1(8)), 40.6 (s, CH_2). ^{19}F NMR (376.49 MHz, DMSO-d_6): **δ** -62.59 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3), -62.67 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 55.09; %H 2.99. $C_{16}H_{10}F_6O_2$. Calcd.: %C 55.18; %H 2.89.

4.20. [9,10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-4-yl] acetic acid (11b)

Colorless crystals, 89 % yield, m.p. 177–178 °C (from benzene); ^{1}H NMR (400 MHz, $CDCl_3$): **δ** 2.75 (d, 1H^A, $^2J_{HH}$ =16 Hz, CH_2), 2.8 (d, 1H^B, $^2J_{HH}$ =16 Hz, CH_2), 4.57 (s, 1H, H-8), 4.89 (s, 1H, H-1), 7.07 (s, arom. H-3), 7.22 (m, 2H, arom. H-5,6), 7.34 (m, 2H, H-11,12), 11.43 (br. s, 1H, OH). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 171.8 (s, C = O), 157.6 (s, C-12(11), CH=), 140.95 (qq, $^2J_{CF}$ =35.4 Hz, $^3J_{CF}$ =3.5 Hz, C-

10(9), $CF_3C=$), 139.9 (s, arom. C-7(2)), 136.8 (qq, $^2J_{CF}$ =35.4 Hz, $^3J_{CF}$ =3.5 Hz, C-9(10), $CF_3C=$), 136.7 (s, arom. C-2(7)), 127.7 (s, arom. C), 127.4 (s, arom. C), 121.2 (q, $^1J_{CF}$ =272.3 Hz, CF_3), 121.0 (q, $^1J_{CF}$ =272.3 Hz, CF_3), 115.2 (s, C-12(11), CH=), 52.12 (s, C-8(1)), 41.9 (s, C-1(8)), 35.1 (s, CH_2). ^{19}F NMR (376.49 MHz, $CDCl_3$) **δ** -60.89 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3), -61.88 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 55.23; %H 2.99. $C_{16}H_{10}F_6O_2$. Calcd.: %C 55.18; %H 2.89.

4.21. [9,10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-4-yl] carboxylic acid (11c)

Colorless crystals, 91 % yield, m.p. 189−190 °C (from benzene); ^{1}H NMR (400 MHz, $CDCl_3$) **δ** 5.35 (m, 2H, H-8(1)), 7.1 (m, 2H, H-12(11)), 7.4(d, 1H, $^3J_{HH}$ =7.6 Hz, arom. H-6), 7.9 (d, 1H, $^3J_{HH}$ =7.6 Hz, arom., H-5), 8.0 (s, arom. H-6). ^{13}C NMR (125.71 MHz, $CDCl_3$): δ 167.4 (s, C = O), 149.1 (s, C-7(2)), 144.9 (s, C-2(7)), 144.5 (m, 2C, C-10(9), $2CF_3C=$), 140.0 (s, C-12(11), CH=), 139.4 (s, C-11(12), CH=), 128.0 (s, arom. C), 127.5 (s, arom. C), 124.4 (s, arom. C), 123.9 (s, arom. C), 122.2 (q, $^1J_{CF}$ =272.3 Hz, $2CF_3$), 48.7 (s, C-8(1)), 48.6 (s, C-1(8)). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -62.22 (br. s, $2CF_3$). Analysis: Found: %C 53.99; %H 2.62. $C_{15}H_8F_6O_2$. Calcd.: %C 53.91; %H 3.41.

4.22. [9,10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-1-yl] acetic acid (12c)

Colorless crystals, 89 % yield m.p. 169−170 °C (from benzene); ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (d, 1H^A, $^2J_{HH}$ =18 Hz, CH_2), 3.83 (d, 1H^B, $^2J_{HH}$ =18 Hz, CH_2), 5.23 (d, 1H, $^3J_{HH}$ =5.6 Hz, H-8), 7.47 (m, 4H, arom. H-3,4,5,6), 7.26 (d, 1H, $^3J_{HH}$ =6.4 Hz, H-11), 7.34 (d, 1H, $^3J_{HH}$ =6.4 Hz H-12), 10.87 (br. s, 1H, OH). ^{13}C NMR (125.71 MHz, DMSO-D_6): **δ** 172.5 (s, C = O), 147.2 (qq, $^2J_{CF}$ =34.5 Hz, $^3J_{CF}$ =4.4 Hz, C-10(9), $CF_3C=$), 145.7 (qq, $^2J_{CF}$ =34.5 Hz, $^3J_{CF}$ =4.4 Hz, C-9(10), $CF_3C=$), 145.7 (s, arom. C-7(2)), 145.5 (s, arom. C), 144.9 (s, C-12(11), CH=), 137.1 (s, C-11(12), CH=), 125.2 (s, arom. 2C), 124.0 (s, arom. C), 122.9 (q, $^1J_{CF}$ =274.6 Hz, CF_3), 122.6 (q, $^1J_{CF}$ =274.6 Hz, CF_3), 122.3 (s, arom. C), 54.5 (s, C-8(1)), 48.2 (s, C-1(8)), 34.7 (s, CH_2). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -57.31 (q, 3 F, $^3J_{FF}$ =11.3 Hz, CF_3), -60.22 (q, 3 F, $^3J_{FF}$ =11.3 Hz, CF_3). Analysis: Found: %C 55.11; %H 3.00. $C_{16}H_{10}F_6O_2$. Calcd.: %C 55.18; %H 2.89.

4.23. [9,10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-1-yl] carboxylic acid (12d)

Colorless crystals, 92 % yield, m.p. 203−205 °C (from benzene); ^{1}H NMR (400 MHz, DMSO-D_6): **δ** 5.62 (d, 1H, $^3J_{HH}$ = 5.2 Hz, H-8), 6.72 (d, 1H, $^3J_{HH}$ = 5.2 Hz, H-11), 7.16 (m, 2H, arom. H-4,5), 7.23 (m, 1H, H-12), 7.57 (d, 1H, $^3J_{HH}$ =8 Hz, arom. H-6), 7.67 (d, 1H, $^3J_{HH}$ = 7.2 Hz, arom. H-3). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 167.9 (s, C = O), 146.2 (s, arom. C-7(2)), 145.5 (s, arom. C-2(7)), 144.6 (m, 2C, C-9,10, $CF_3C=$), 140.7 (s, C-12(11), CH=), 139.4 (s, C-11(12), CH=), 127.6 (s, arom. C), 127.0 (s, arom. C), 126.7 (s, arom. C), 125.4 (s, arom. C), 122.2 (q, $^1J_{CF}$ =273.1 Hz, $2CF_3$), 48.8 (s, C-8(1)), 45.8 (s, C-1(8)). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -61.92 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3), -62.04 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 53.88; %H 2.52. $C_{15}H_8F_6O_2$. Calcd.: %C 53.91; %H 2.41.

4.24. [9,10-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-3-yl] acetic acid (13)

Colorless crystals, 91 % yield, m.p. 130−131 °C (from benzene); ^{1}H NMR (400 MHz, $CDCl_3$): **δ** 3.73 (d, 1H^A, $^2J_{HH}$ =16 Hz, CH_2), 3.83 (d, 1H^B, $^2J_{HH}$ =16 Hz, CH_2), 5.24 (d, 1H $^3J_{HH}$ = 5.2 Hz, H-8), 5.46 (d, 1H, $^3J_{HH}$ = 5.2 Hz, H-1), 6.92 (d, 1H, $^3J_{HH}$ = 7.2 Hz, H-11), 7.00 (m, 3H, arom. H-4,5,6), 7.26 (d, 1H, $^3J_{HH}$ = 7.2 Hz, H-12), 11.02 (br. s, 1H, OH). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 177.1 (s, C = O), 143.2 (qq, $^2J_{CF}$ =35 Hz, $^3J_{CF}$ =3.8 Hz, C-10(9), $CF_3C=$), 144.1 (s, arom. C-7(2)), 143.4 (qq, $^2J_{CF}$ =35 Hz, $^3J_{CF}$ =3.8 Hz, C-9(10), $CF_3C=$), 142.7 (s, arom. C-2(7)), 139.0 (s, C-12(11), CH=), 138.4 (s, C-11(12), CH=), 127.2 (s, arom. C), 126.4 (s, arom. C), 124.7 (s, arom. C), 122.4 (s, arom. C), 121.5 (q, $^1J_{CF}$ =271.6 Hz, $2CF_3$), 48.8 (s, C-8(1)), 45.5 (s, C-1(8)), 37.5 (s, CH_2). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -61.70 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3), -62.27 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 55.14; %H 3.00. $C_{16}H_{10}F_6O_2$. Calcd.: %C 55.18; %H 2.89.

4.25. [10-(Methoxy)-11,12-bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7}) dodeca-2,4,6,11-butaen-9-yl] carboxylic acid (14)

Colorless crystals, 89 % yield, m.p. 137−138 °C (from hexane); ^{1}H NMR (400 MHz, $CDCl_3$): **δ** 2.66 (s, 1H, H¯9), 3.43 (s, 3H, OCH_3),): 3.88 (s, 1H, H-10), 4.59 (s, 1H, H-8), 4.67 (s, 1H, H-1), 7.28 (m, 4H, arom. H). ^{13}C NMR (125.71 MHz, $CDCl_3$): **δ** 176.7 (s, C = O), 139.4 (qq, $^2J_{CF}$ =32.4 Hz, $^3J_{CF}$ =3.5 Hz, C-12(11), $CF_3C=$), 138.2 (qq, $^2J_{CF}$ =32.4 Hz, $^3J_{CF}$ =3.5 Hz, C-11(12), $CF_3C=$), 137.3 (s, arom. C-7(2)), 136.8 (s, arom. C-2(7)), 127.4 (s, 2C, arom. C), 125.4 (s, arom. C), 124.9 (s, arom. C), 121.3 (q, $^1J_{CF}$ =273.3 Hz, $2CF_3$), 81.6 (s, C-10), 57.2 (s, OCH_3), 51.6 (s, C-9), 45.6 (s, C-8(1)), 42.5 (s, C-1(8)). ^{19}F NMR (376.49 MHz, $CDCl_3$): **δ** -61.13 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3), -62.24 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 52.74; %H 3.42. $C_{16}H_{11}F_6O_3$. Calcd.: %C 52.60; % H 3.01.

4.26. [11,12-Bis(trifluoromethyl)tricyclo(6.2.2.0^{2,7})dodeca-2,4,6,9,11-pentaen-9-yl] carboxylic acid (15)

Colorless crystals, 88 % yield, m.p. 187−188 °C (from benzene); ^{1}H NMR (400 MHz, DMSO-d_6): **δ** 5.36 (d, 1H, $^3J_{HH}$ = 5.6 Hz, H-1), 5.72 (s, 1H, H-8), 7.08 (s, 2H, arom. H-3,6), 7.39 (m, 2H, arom. H-4,5), 7.94 (d, 1H, $^3J_{HH}$ =5.6 Hz, H-10). ^{13}C NMR (125.71 MHz, DMSO-d_6): **δ** 169.0 (s, C = O), 148.8 (s, C-10(9), CH=), 145.2 (s, C-9(10), CH=), 145.06 (m, 2C, C-11,12, $2CF_3C=$), 144.8 (s, arom. C), 143.4 (s, arom. C-7(2)), 142.8 (s, arom. C-2(7)), 126.0 (s, arom. C), 124.8 (s, arom. C), 124.5 (s, arom. C), 122.1 (q, $^1J_{CF}$ =271.3 Hz, $2CF_3$), 49.3 (s, C-8(1)), 48.8 (s, C-1(8)). ^{19}F NMR (376.49 MHz, DMSO-d_6): **δ** -62.22 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3), -62.35 (q, 3 F, $^3J_{FF}$ =11.2 Hz, CF_3). Analysis: Found: %C 53.90; %H 2.68. $C_{15}H_8F_6O_2$. Calcd.: %C 53.91; % H 2.41.

Declaration of competing interest and authorship conformation form

Please check the following as appropriate:

- All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.
- This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.
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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.jfluchem.2020.109450.

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