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Reaction of 2,5-bis-trifluoromethyl-1,3,4-oxadiazole with 7-oxanorbornenes revisited: Experimental and quantum-chemical study of reaction stereoselectivity

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ABSTRACT

The stereochemical outcome of reaction of 2,5-bis-trifluoromethyl-1,3,4-oxadiazole with 7-oxanorbornenes under various conditions was investigated. For the first time, microwave irradiation in carrying this type of reactions was used, resulting in comparable yields in significantly shorter reaction times. Regardless on substrate, in all reactions mixtures of the two isomeric O^3-[3]polynorbornanes, bent and linear were obtained, with slight preference for bent structure. In some cases, retro Diels–Alder fragmentation was observed resulting in formation of isobenzofuran species. Reaction mechanism was also studied computationally (RHF/6-31G* method), and the origin of stereoselectivity explained by repulsive lone pair interactions between oxygen bridges in the transition state of the 1,3-dipolar addition.

1. Introduction

Polycyclic rigid molecular scaffolds and platforms are often employed to separate two functionalities at the appropriate distance and orientation [1]. These can be classified as flexible, semi-rigid and rigid systems, of which rigid systems offer the precise effector separation required for instance for photophysical studies of electron and charge transfer [2]. The importance of geometrical features of these polycycles is reflected in the fact that even the small geometrical change between two functionalities could have significant effect on the electron transfer rates and the lifetime of charge-separated species [2].

Synthesis of the functionalized large hetero-bridged, *syn*-facially fused norbornane ([n]polynorbornane) systems by employing Warrener's building BLOCK protocol [3] has a synthetic advantage over consecutive cycloaddition approaches used by Paddon-Row and co-workers [2b], Zimmt and co-workers [2c], Klärner and co-workers [4], Stoddart and co-workers [5], and Lin and co-workers [6]. Using BLOCK protocol, the number of synthetic steps is significantly reduced and often higher yields of products result. A crucial step in the building BLOCK protocols is the connection of two alkene (norbornene) units utilizing cycloaddition reactions. Either Diels–Alder or 1,3-dipolar cycloadditions of small heterocyclic molecules, such as 1,2,4,5-tetrazine [7,8], 1,2,4-triazine [7], 1,3,4-oxadiazole [9,10], phthalazine [11], bis-epoxide [12], or bis-aziridine [13] were used. Using these protocols, a number of functionalized hetero-bridged and polarofacial [n]polynorbornanes was prepared [3,12,14,15]. Amongst heterocyclic 'molecular glues' listed, 2,5-bis-trifluoromethyl-1,3,4-oxadiazole (OD) **1** was recognized as the key reagent for construction of 7-oxabicyclo[2.2.1] moiety at the junction of two norbornene fragments producing *COC*-[3]polynorbornanes (Scheme 1). For instance, OD coupling was used to synthetise 'molecular workbenches', possessing a variety of functionalities at terminal atoms [16]. Thus, it was found that 1,3,4-oxadiazole **1** is an effective coupling reagent of norbornene type compounds and the stereochemical outcome of reaction can be controlled by the nature of norbornene bridging group proximate to the reacting olefin.

While OD reactions of compounds containing methylene bridge adjacent to the reacting π-bond are stereosselective [17,18], giving 2:1 products possessing exclusively linear (*exo*,*exo*-) geometries of *COC*-[3]polynorbornanes **3** (Scheme 1), we noted inconsistencies in results reported for 7-oxanorbornene derivatives. For instance, Warrener and Butler reported that 7-oxabenzonorbornadiene **4** by reacting with 1,3,4-oxadiazole **1** produces exclusively bent (angular, *anti*-facial poly-7-oxanorbornadiene) (*endo*,*exo*-) O^3-[3]polynorbornane product **8** (Table 1) [19]. On the other hand, Warrener reported that *syn*-facial (*exo*,*exo*-) adducts **9** and **11** were prepared alongside *anti*-facial adducts **10** and **12** from 1,3,4-oxadiazoles **5** and **6**, respectively, in which ester groups are substituted for one or both trifluoromethyl groups [3].

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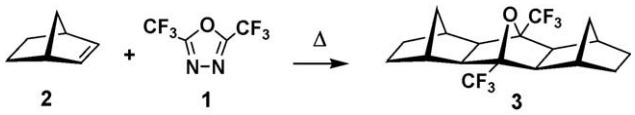
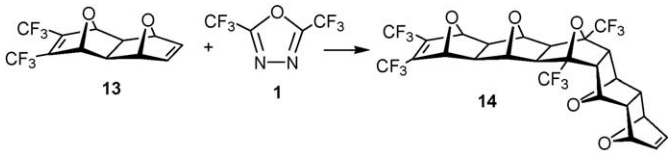


Scheme 1. Oxadiazole coupling reaction.



Scheme 2. OD coupling of substrate **13**.

Furthermore, Warrener and Butler found that polycyclic bis-oxygen bridged polarofacial substrate **13** by treatment with the 1,3,4-oxadiazole **1** produced exclusively bent- geometry of O^5-[5]polynorbornane **14** (Scheme 2) [19].

This finding is in sharp contrast with the Warrener's report on the OD addition to the parent *exo*,*endo*- isomer **15** [20]. In this particular case, reaction is nonstereoselective and yields the mixture of *syn*- and *anti*-facial O^5-[5]polynorbornane *exo*,*exo*- and *exo*,*endo*- adducts **16** and **17** in approximately 2:1 ratio (Scheme 3).

In these publications, the exclusive formation of the *anti*-facial product **8** was attributed to the effect of adverse O,O-orbital/orbital interactions in the transition state of the second step of the coupling process which involves alkene addition to a 1,3-dipolar intermediate. It was also proposed that stereochemical effects should also be taken into account, since the *syn*-facial adducts such **9** and **11** can be prepared from 1,3,4-oxadiazoles **5** and **6** [9].

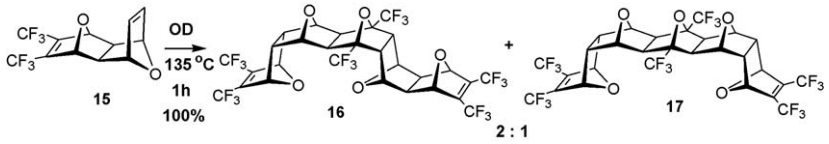
Since the stereochemical results of OD coupling are of the utmost importance for the definition of geometrical and spatial arrangements of two terminal functional groups attached to polynorbornane skeleton, the stereochemical study of model reactions is crucial for understanding of reaction mechanism, prediction and molecular design of large polynorbornane scaffolds. The aims of this paper are: (1) to revisit previously published data, (2) to investigate stereoselectivity of OD coupling reactions with 7-oxanobornenes, (3) to explore the use of microwave heating on reaction efficiency, and (4) to investigate the origin of stereoselectivity of OD couplings by quantum-chemical methods.

2. Results and discussion

2.1. Cycloaddition experiments

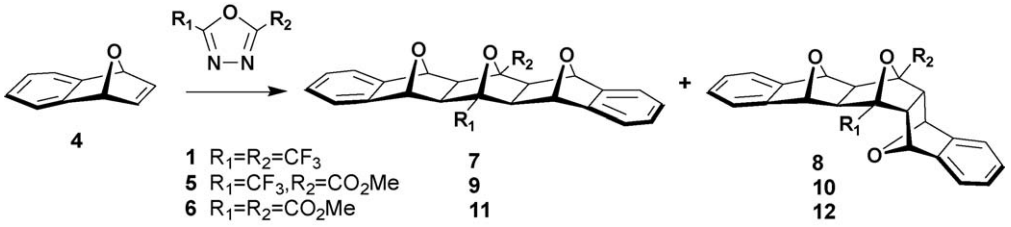
Firstly, reaction of **4** with OD **1** was reexamined. Classical thermal conditions (140 °C, CH_2Cl_2, sealed glass vessel, 24 h), as well as non-classical conditions: high pressure (0.8 GPa, RT, CH_2Cl_2, 18 h) and microwave accelerated (CH_2Cl_2, 170 °C, 45 min) were employed. To the best of our knowledge, this is the first report on use of microwave irradiation for the enhancement of OD coupling reaction, where in significantly shorter times, comparable product yields were obtained. In all reactions, a fivefold excess of OD was used. In contrast to the previous literature reports, mixtures of isomers **7** and **8** were obtained (in ~1:2 ratio), regardless of reaction conditions employed, as indicated by the analysis of ^{1}H NMR spectra of crude reaction mixtures. The individual stereoisomers were separated by chromatography and fully spectroscopically characterized. Two isomers could be easily distinguished on the basis of product symmetry and the characteristic up-field shift of *endo*- protons, which in the case of linear isomer are double-shielded by aromatics. Alongside these main products, small quantity (5%) of side-products **18** and **19** were detected (Scheme 4), which arise from the formation of isobenzofuran **21** by Alder–Rickert fragmentation of intermediate **20** and its subsequent Diels–Alder reaction with **4**.

Subsequently, the same reaction was carried out with the series of 7-oxanorbornene substrates **4**, and **25–30** under microwave conditions. The results are collected in Table 2. Microwave enhanced reactions were proven to be an efficient entry to a variety of O^3-[3]-, O^5-[5]-, and O^7-[7]polynorbornanes. The individual stereoisomers were isolated and their structures characterized spectroscopically. Geometries of new products were deduced with the aid of NMR spectroscopy, based on product symmetry, multiplicities and H–H-couplings in COSY and NOESY spectra. The inspection of these results indicated that regardless of substrate used, two isomers were formed, favoring the (*exo*,*endo*-)

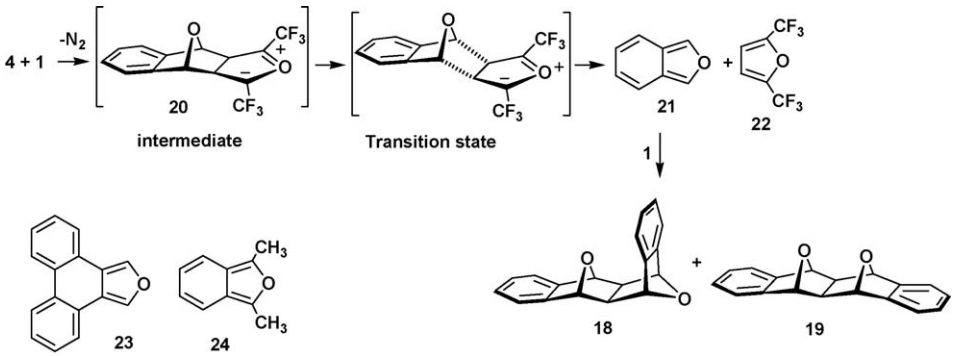


Scheme 3. OD coupling of substrate **15**.

Table 1
Stereochemical outcomes of OD reactions with 7-oxabenzonorbornadienes [3].



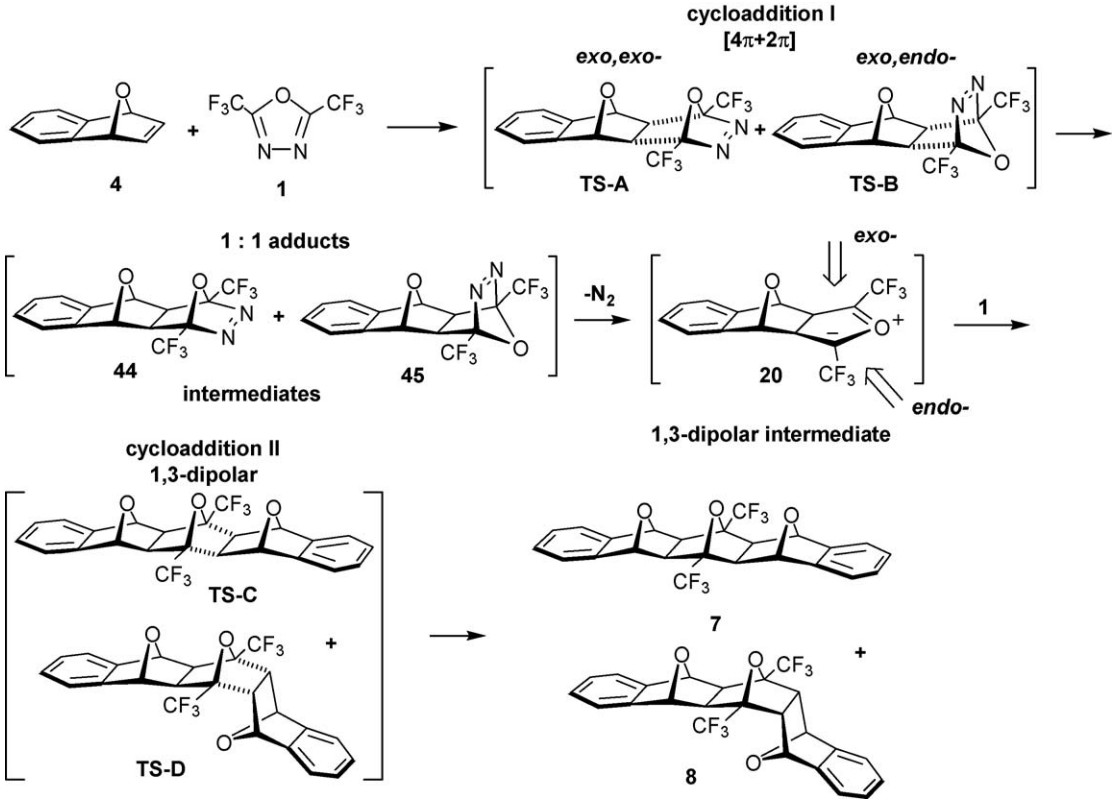
Reactants	Products	Yields (%)	Products	Yields (%)
4+**1**	7	0	8	100
4+**5**	9	55	10	45
4+**6**	11	60	12	40



Scheme 4. Formation of isobenzofurans by Alder–Rickert fragmentation.

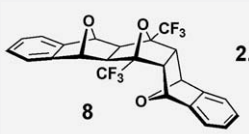
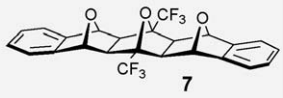
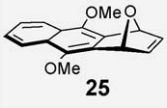
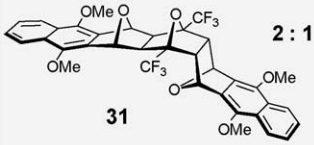
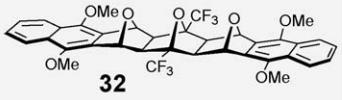
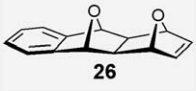
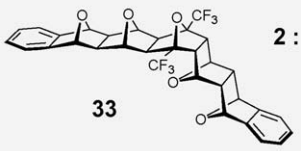
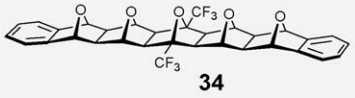
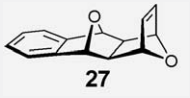
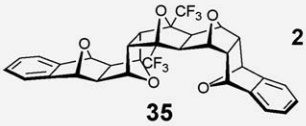
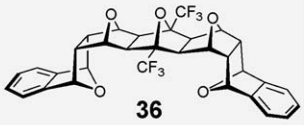
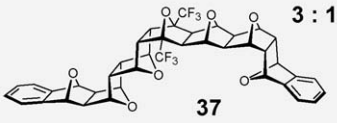
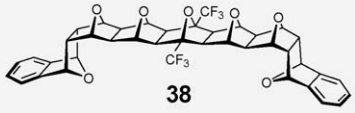
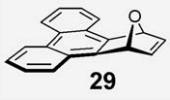
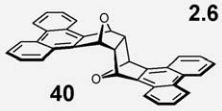
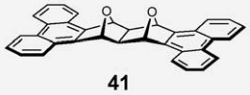
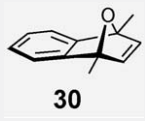
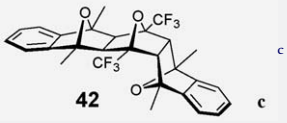
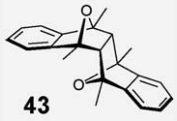
over (*exo*,*exo*-) adducts in approximately 2:1 ratio. These results are in accordance with stereoselectivity attained in reaction of **4** with **1** under classical and high pressure conditions, as well as with those of substrate **15** (Scheme 3). The exceptions of this general trend, however, are encountered in reactions of substrates **29** and **30**. Under MW conditions, substrate **29** affords adducts **40** and **41** (2.6:1 ratio), which indicates that reaction involves facile formation of an intermediate phenanthro[9,10-*c*]furan **23**. Similar side-reaction was previously observed in reaction with **4**. However, in the case of **29**, this retro-Diels–Alder fragmentation to parent isobenzofuran is much more pronounced, presumably due to larger stability of phenanthro[9,10-*c*]furan **23**, which is stable and isolable compound [21]. The presence of low-field singlet at δ 8.09 in ^{1}H NMR spectra confirms this assumption [22]. Finally, substrate **30** presents a special case, due to the increased sterical bulk at the bridgehead positions imposed by methyl substituents. In this particular case, the *exo*,*endo*- adduct of 2,9-dimethylisobenzofuran **24** was formed as a sole product. Adduct **43** is known from literature [23], where steric effects were postulated to govern exclusive formation of bent adduct. These results indicate that increased steric hindrance is a driving force for retro Diels–Alder fragmentation of initially formed 1:1 adduct and formation of 2,9-dimethylisobenzofuran. When the OD coupling was conduced under milder conditions (0.8 GPa, RT, 3 days, CH_2Cl_2), a single stereoisomeric product **42** was formed with *exo*,*endo*- geometry. This clearly demonstrates that substituents have important influence on the outcome of the reaction.

Two separate cycloaddition reactions are now considered to be involved in the coupling process (Scheme 5) [24]. *Cycloaddition I*: a Diels–Alder reaction between the alkene and the 1,3,4-oxadiazole-[4π+2π] addition, a reverse electron-demand process; *Cycloaddition II*: the 1,3-dipolar addition of a second alkene (same or different) with the 1,3-dipolar intermediate **20** (regular electron-demand process). This intermediate is obtained by dinitrogen expulsion from the 1:1 adducts **44** and **45** formed in step I. Facile elimination of dinitrogen from **44** (or **45**) and high reactivity of intermediate **20** precluded isolation and spectroscopic detection of these species.



Scheme 5. Reaction mechanism for OD coupling reaction.

Table 2
MW reactions of 7-oxanorbornene substrates with oxadiazole **1**.

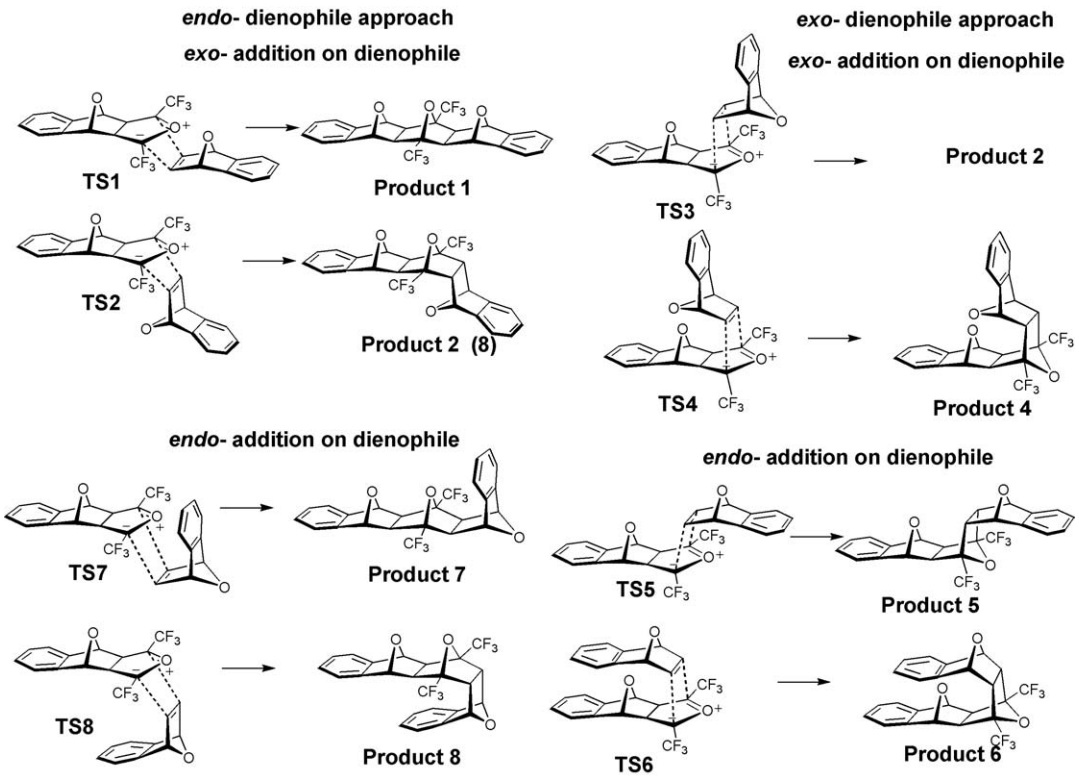
Entry	Substrate	Products (ratios)[a,b]	
1	 **4**	 **8** 2.2 : 1	 **7**
2	 **25**	 **31** 2 : 1	 **32**
3	 **26**	 **33** 2 : 1.1	 **34**
4	 **27**	 **35** 2 : 1	 **36**
5	 **28**	 **37** 3 : 1	 **38**
6	 **29**	 **40** 2.6 : 1	 **41**
7	 **30**	 **42** [c]	
8	30	 **43**	

[a] 170 °C, 45 min, CH_2Cl_2.
[b] Ratios obtained from NMR analysis.
[c] 8 kbar, RT, 12 h, CH_2Cl_2.

Since both intermediates **44** and **45** afford the same 1,3-dipole **20** by dinitrogen elimination, it follows that the stereochemical outcome of OD coupling reaction is determined in the second cycloaddition step (as shown in Scheme 5). Eight different approaches of two reactants are feasible (Scheme 6). Four modes of dienophile approach are possible from the bottom (*endo*-) π-face of intermediate diene **20** (**TS1**, **TS2**, **TS7** and **TS8**) and four approaches are from the top (*exo*-) π-face of **20** (**TS3**–**TS6**), defined in respect to the norbornene moiety. They give rise to seven stereoisomeric products, since **TS2** and **TS3** produce identical isomer. Interestingly, only two of these products were experimentally identified.

2.2. Quantum-chemical calculations

In order to get further insight into factors determining experimentally observed stereoselectivity of OD coupling reaction with 7-oxanorbornenes we applied quantum-chemical calcula-



Scheme 6. Stereochemical outcomes of OD reaction with 7-oxanorbornenes.

Table 3
Calculated relative activation energies (E_a) for cycloaddition reactions of 1:1 adduct with 7-oxabenzonorbornene – the second cycloaddition step (in kJ mol^{-1}).[a].

	RHF/ 6-31G*	RHF/ 6-31G* +ZPE	B3LYP// 6-31G*	BMK// 6-31G*	MP2// 6-31G*
TS1	4.6	4.6	6.3	7.5	4.6
TS2	0	0	0	0	0
TS3	35.1	34.3	32.2	32.2	35.1
TS4	64.0	64.9	69.9	66.9	64.0
TS5	89.1	89.5	72.4	69.0	89.1
TS6	142.3	142.3	125.9	128.0	142.3
TS7	53.1	53.9	39.3	41.8	53.1
TS8	52.7	53.6	37.2	35.9	52.7

[a] B3LYP//6-31G* = B3LYP/6-31G*//RHF/6-31G*; BMK//6-31G* = BMK/6-31G*//RHF/6-31G*; MP2//6-31G* = MP2/6-31G*//RHF/6-31G*.

tions. For this purpose, *ab initio* RHF/6-31G* method was employed, followed by single point energy calculations using DFT (B3LYP and BMK) [25] and MP2 methods. Reaction of OD with 7-oxabenzonorbornadiene **4** was used as a model system and activation energies estimated, performing transition state (TS) calculations [26]. The results of calculations for eight dienophile/dipolarophile orientations presented in Scheme 6 are summarized in Table 3. Computational results indicate that cycloaddition reaction proceeds under kinetic control, as deduced from the activation energy of the process.

The calculated transition state geometries are compatible with concerted, synchronous cycloaddition mechanism, as illustrated in Fig. 1 for **TS1** and **TS2**. The most interesting feature of the calculated geometries is the length of the newly formed bonds between the dipole and dipolarophile. Survey of the data reveals that the newly forming C···C bonds are in the range of 2.310–2.680 Å, what is slightly longer than calculated in a number of hydrocarbon pericyclic reactions [26]. The calculated TS structures possess almost planar five-membered 1,3-dipole moiety (oxygen atom is tilted away from planarity by $\alpha = 9.2^\circ$ and 15.8°).

The results show that the absolute activation energy values depend on the employed computational methods [27–29]. However, what is more important, the relative activation energies (E_a) are similar regardless of the computational level employed

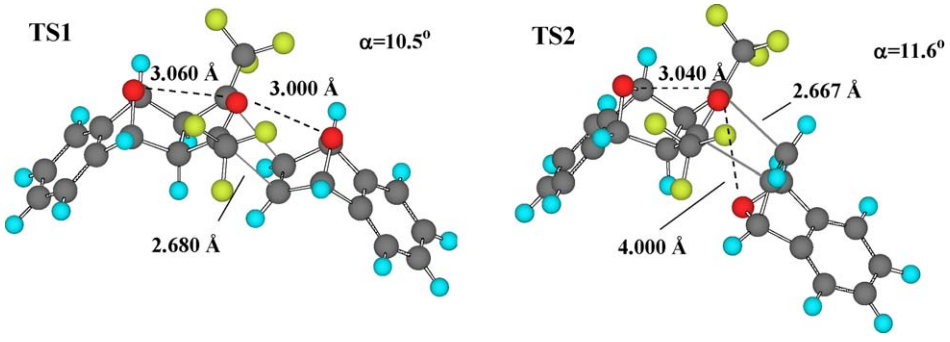


Fig. 1. RHF/6-31G* optimized structures of **TS1** and **TS2**.

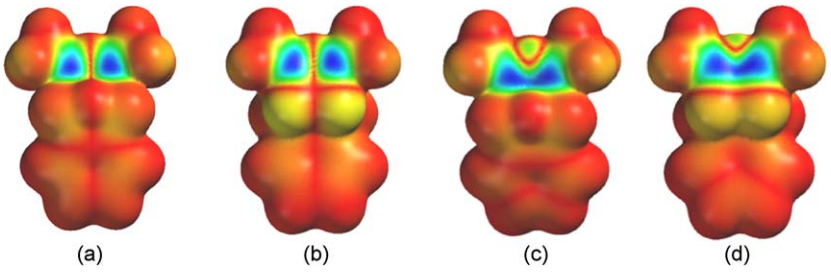


Fig. 2. FMOs of **20** plotted on electron density isosurface (isovalue = 0.002 electrons/a.u.^{3}): (a) HOMO *exo*- face, (b) HOMO *endo*- face, (c) LUMO *exo*- face, and (d) LUMO *endo*- face.

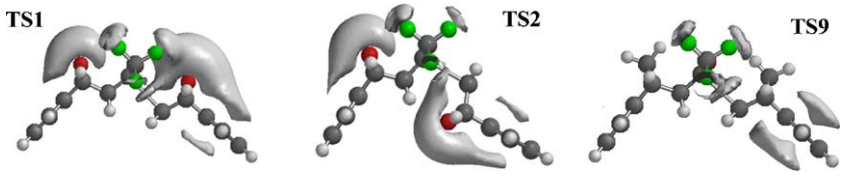


Fig. 3. Electrostatic potential surface for **TS1**, **TS2** and **TS9** (isovalue = −20 a.u.).

(Hartree–Fock, DFT, or Møller–Plesset) and predict the same stereochemical preference with almost identical energy differences [30]. Comparison of computational results with available experimental data indicates that the 6-31G* basis set is adequate for obtaining quantitative answers in term of relative activation energies. The hybrid density functionals B3LYP and BMK and *ab initio* MP2 calculations are in good accord with RHF/6-31G* results. Therefore, we may conclude with confidence that **TS2** has the smallest E_a, while the relative activation energies increase in the following order: E_a(**TS2**) < E_a(**TS1**) < E_a(**TS3**) < E_a(**TS8**) < E_a(**TS7**) < E_a(**TS4**) < E_a(**TS5**) < E_a(**TS6**). Energy differences between **TS1** and **TS2** are smaller than 8.4 kJ mol^{-1}, which is practically not enough to achieve stereoselective cycloadditions. Therefore one should expect formation of the mixture of two isomers experimentally. This conclusion is in full accord with our experimental results. The severe steric congestions are found in the case of **TS4** and **TS6**, accordingly, their E_as are much higher than for **TS1**. It is interesting to mention that E_as calculated with new BMK/6-31G* DFT method, which is specifically designed for accurate reaction energetics are very close to those estimated by B3LYP functional.

The inclusion of solvent effects into calculations by means of IPCM/B3LYP/6-311+G**//RHF/6-31G* method revealed no influence on **TS2**/**TS1** E_a difference. For water, acetonitrile and tetrahydrofuran, **TS2**/**TS1** E_a differences were calculated to be 7.1, 7.5 and 8.4 kJ mol^{-1}, respectively. These values are therefore fully consistent with gas-phase calculations and also with experimentally observed non-sensitivity of OD reactions to solvent polarity [31].

It is evident from Table 3 that the cycloaddition reaction on the *exo*- π-face of approaching 7-oxabenzonorbornadiene (dipolarophile) is greatly favored over the *endo*- π-face attack. This prediction is in good accordance with previously published experimental and theoretical results on norbornene π-facial selectivity [11,28,32–34]. Furthermore, dipolarophile favorably approaches 1,3-dipole **20** from its *endo*- π-face. Plausible explanation for preferred *endo*- approach to **20** is offered by Fukui's non-equivalent π-orbital extension [35]. Fig. 2 depicts FMOs for **20**, plotted on electron density isosurface and their inspection reveals that there is orbital non-equivalency between the *exo*- and *endo*- π-faces. There is a slightly larger electron density located on the *endo*- face of 1,3-dipole moiety, which in the combination with the steric hindrance caused by methylene bridge on the *exo*- face causes preference for the *endo*- face of 2-oxacyclopenta-1,3-diene system [36].

The replacement of the oxygen bridge in dipolarophile **4** with methylene group (CH_2) has significant influence on the activation energies for **TS1** and **TS2**. The RHF/6-31G* method estimated **TS2**/**TS1** E_a difference is 24.7 kJ mol^{-1}, what is almost twice as much as the value calculated for the oxygen bridge systems, indicating larger preference for formation of linear cycloadducts. We assume that this difference mainly arises from the repulsive interactions of oxygen–oxygen lone pairs, as shown in Fig. 3 for **TS1** and **TS2**. Evidently, oxygen lone pairs in linear TS strongly interact, while in the case of CH_2 bridges **TS9** (leading to formation of *exo,exo-COC*-[3]polynorbornane), the interaction is solely steric in nature. Calculations of the parent 1,3,4-oxadiazoles, where one or both trifluoromethyl groups are replaced with carbomethoxy groups (**5** and **6**) also show preference for formation of bent products **10** and **12**, by 6.7 and 7.9 kJ mol^{-1}, respectively (RHF/6-31G* level). These results strongly predict that steric interference introduced in oxadiazoles is less important in determining of stereoselectivities than oxygen lone pair repulsions.

3. Conclusion

This is the first report of microwave irradiation for the enhancement on OD coupling reaction, where in significantly shorter times, comparable product yields were obtained. Importance of synthetic role of 2,5-bis-trifluoromethyl-1,3,4-oxadiazole in polynorbornane chemistry was stressed. The literature reports on stereochemical outcomes of reaction of 2,5-bis-trifluoromethyl-1,3,4-oxadiazole with 7-oxanorbornenes were reexamined. Regardless of starting alkene, formation of bent structures was favored. Quantum-chemical studies indicate that the repulsive lone pair interactions in the molecules with oxygen bridges are the main reason for observed stereoselectivities.

4. Experimental details

The NMR spectra were recorded in $CDCl_3$ solutions containing tetramethylsilane as internal standard on Bruker AMX 300 or 600 MHz instruments. Melting points were determined using a

Gallenkamp digital melting point apparatus and are uncorrected. The high-resolution mass spectra were recorded on a Micromass Platform II single quadrupole AutoSpec instrument (ESMS, electrospray mass spectrometry in CH_2Cl_2). Radial chromatography was carried out with a chromatotron, Model No. 79245T, using 1 mm plates with silica gel $60F_{254}$ as the stationary phase. High pressure reactions were performed using a high pressure piston cylinder apparatus, in Teflon cells, and pentane as piezotransmitter liquid.

Known procedures were used to prepare 1,3,4-oxadiazoles **1** [37], **5** [38], and **6** [39].

4.1. General procedure for microwave reactions

Mixtures of OD (60 mg, 0.25 mmol, excess), substrate (50–100 mg, 0.05 mmol) in CH_2Cl_2 (0.5 mL) were subjected to MW reaction at 170 °C, for 45 min. Reactions were conducted in CEM Discover®LabmateTH/ExplorerPLS® single mode microwave reactor using closed reaction vessel technique (power = 125 W). Radial chromatography (with petroleum ether-ethyl acetate) was used to isolate pure products. Excess of solvent was removed *in vacuo* and products analysed by either by TLC, GC or ^{1}H NMR spectroscopy. All new compounds gave ^{1}H and ^{13}C NMR spectra and high-resolution mass spectra corresponding to their assigned structures.

4.2. Selected analytical data of products in Tables 1 and 2

4.2.1. Reaction of 1 with 4

1,12-Bis-trifluoromethyl-(1α,2α,3β,10β,11α,12α,13β,14α,21α,22β)-23,24,25-trioxa-octacyclo [10.10.1.1^{3,10}.1^{14,21}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]pentacosa-4,6,8,15,17,19-hexaene (**7**) and 1,12-bis-trifluoromethyl-(1α,2α,3β,10β,11α,12α,13β,14α,21α,22β)-23,24,25-trioxa-octacyclo [10.10.1.1^{3,10}.1^{14,21}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]pentacosa-4,6,8,15, 17,19-hexaene (**8**).

7: (mp 145–146 °C, 28%). ^{1}H ($CDCl_3$), δ/ppm: 2.28 (4H, s), 5.73 (2H, s), 7.14 (4H, dd, *J* = 5.5 Hz, *J* = 2.9 Hz); 7.24 (4H, dd, *J* = 5.5 Hz, *J* = 2.9 Hz); ^{13}C ($CDCl_3$), δ/ppm: 54.7, 79.4, 85.5 (q, $^2J_{C,F}$ = 34.1 Hz), 119.1, 126.1 (q, $^1J_{C,F}$ = 279.4 Hz), 127.4, 145.2; HRMS (*m*/*z*): calcd. for $C_{24}H_{16}O_3F_6$: 466.1004; found: 466.1012.

8 [19]: (45%), ^{1}H ($CDCl_3$), δ/ppm: 2.73 (2H, s), 2.91 (2H, s), 5.15 (2H, s), 5.67 (2H, m), 7.15 (2H, dd, *J* = 5.7 Hz, *J* = 3.1 Hz), 7.19 (2H, dd, *J* = 5.3 Hz, *J* = 3.0 Hz), 7.23 (2H, dd, *J* = 5.7 Hz, *J* = 3.1 Hz), 7.29 (2H, dd, *J* = 5.3 Hz, *J* = 3.0 Hz); 48.6, 54.0, 76,8, 78.9, 81.7 (q, $^2J_{C,F}$ = 33.4 Hz), 119.1, 119.2, 123.5 (q, $^1J_{C,F}$ = 280.9 Hz), 126.8, 126.9, 144.7, 144.9.

4.2.2. Reaction of 1 with 9

Methyl-12-trifluoromethyl-(1α,2α,3β,10β,11α,12α,13β,14α,21α,22β)-23,24,25-trioxa-octacyclo [10.10.1.1^{3,10}.1^{14,21}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]pentacosa-4,6,8,15,17,19-hexaene-1-carboxylate (**9**) and methyl-12-trifluoromethyl-(1α,2α,3β,10β,11α,12α,13β,14α, 21α,22 β)-23,24,25-trioxa-octacyclo [10.10.1.1^{3,10}.1^{14,21}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}] pentacosa-4,6,8,15,17,19-hexaene-1-carboxylate (**10**).

Microwave conditions: yields: **9** (20%), **10** (6%).

Thermal reaction: a solution of **4** (200 mg, 1.388 mmol) and **9** (170 mg, 1.388 mmol) in dichloromethane (0.5 mL) was heated at 140 °C overnight in a sealed tube. The reaction mixture was allowed to cool to room temperature. Solvent was removed under reduced pressure and mixture was subjected to three consecutive radial chromatographies (petroleum ether:ethyl acetate 5:1, then the solvent polarity was gradually increased to 1:1) to afford products **9** and **10**.

9: (mp 266–269 °C, 17%) ^{1}H ($CDCl_3$), δ/ppm: 2.19 (d, 2H, *J* = 3.27 Hz); 2.33 (d, 2H, *J* = 3.27 Hz); 4.04 (s, 3H); 5.26 (s, 2H); 5.68 (s, 2H); 7.10–7.15 (m, 4H); 7.17–7.22 (m, 4H); ^{13}C ($CDCl_3$), δ/ppm: 52.9; 53.5; 56.2; 79.7 (q, $^4J_{C,F}$ = 3.11 Hz); 79.9; 85.5 (q, $^2J_{C,F}$ = 31.98 Hz); 88.1; 119.1; 119.6; 124.6 (q, $^1J_{C,F}$ = 277. 9 Hz); 127.1; 127.3; 144.9; 145.7; 169.4; MS (*m*/*e*): 119 (9.7%); 118 (IBF, 100%); 115 (2.4%); 90 (5.0%); 89 (2.9%); 456 (M^+, 0.2%); HRMS (*m*/*z*): calcd. for $C_{25}H_{19}O_5F_3$: 456.1185; found: 456.1189.

10: (mp 230–234 °C, 5%). ^{1}H ($CDCl_3$), δ/ppm: 2.66 (d, 1H, *J* = 3.16 Hz); 2.75 (d, 1H, *J* = 4.68 Hz); 2.81 (d, 1H, *J* = 3.13 Hz); 2.85 (d, 1H, *J* = 4.67 Hz); 3.98 (s, 3H); 5.13 (s, 1H); 5.25 (s, 1H); 5.27 (s, 1H); 5.65 (s, 1H); 7.13-7.30 (m, 8H); ^{13}C ($CDCl_3$), δ/ppm: 48.6; 51.2; 52.9; 54.3 (q, $^3J_{C,F}$ = 2.1 Hz); 57.6; 77.2; 77.8; 79.7 (q, $^4J_{C,F}$ = 2.66 Hz); 80.2; 85.7 (q, $^2J_{C,F}$ = 31.5 Hz); 85.3; 119.3; 119.6; 119.7; 119.7; 124.3 (q, $^1J_{C,F}$ = 278.17 Hz); 127.1; 127.1; 127.2; 145.2; 145.4; 145.5; 145.9; 169.8; HRMS (*m*/*z*): calcd. for $C_{25}H_{19}O_5F_3$: 456.1185; found: 456.1191.

4.2.3. Reaction of 1 with 4

Dimethyl (1α,2α,3β,10β,11α,12α,13β,14α,21α,22β)-23,24,25-trioxa-octacyclo [10.10.1.1^{3,10}.1^{14,21}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]pentacosa-4,6,8,15,17,19-hexaene-1,12-dicarboxylate (**11**) and dimethyl-(1α, 2α,3β,10β,11α,12α,13β,14α,21α,22β)-23,24,25-trioxa- octacyclo [10.10.1.1^{3,10}.1^{14,21}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]pentacosa-4,6,8,15,17,19-hexaene-1,12-dicarboxylate (**12**).

Microwave conditions: yields: **11** (44%), **12** (36%).

Thermal reaction: A mixture of **4** (100 mg, 0.694 mmol) and **6** (20 mg, 0.108 mmol) was heated at 140 °C for 2 h in a sealed tube. The reaction mixture was allowed to cool to room temperature to afford after solvent evaporation under reduced pressure a yellow colored oily residue, which was separated by radial chromatography.

Thermal conditions: yields: **11** (45%), **12** (35%).

High pressure reaction: a solution of **4** (100 mg, 0.694 mmol) and **6** (20 mg, 0.108 mmol) in dichloromethane (0.5 mL) was subjected to high pressure (14 kbar) for 16 h at room temperature. Evaporation of solvent in vacuo gave a yellow colored oily residue, which was separated by radial chromatography.

High pressure conditions: yields: **11** (40%), **12** (30%).

11 [12]: ^{1}H NMR ($CDCl_3$, δ/ppm): 2.13 (s, 4H); 4.02 (s, 6H); 5.28 (s, 4H); 7.02–7.35 (m, 8H).

12 [12]: ^{1}H NMR ($CDCl_3$, δ/ppm): 2.72 (s, 2H); 2.78 (s, 2H); 3.97 (s, 6H); 5.25 (s, 2H); 5.28 (s, 2H); 7.03–7.35 (m, 8H).

4.2.4. Reaction of 1 with 25

1,16-Bis-trifluoromethyl-5,12,20,27-tetramethoxy-(1α,2β,3α,4β,5α, 12α,13β,14α,15β,16α,17α,18β,19α, 20β,27β, 28α,29β,30α)-31,32,33-trioxadodecacyclo[14.14.1.1^{3,14} 1.^{15,12}.1^{18,29}.1^{20,27}.0^{2,15}.0^{4,13}.0^{6,11}.0^{17,30}.0^{19,28}.0^{21,26}]pentatriaconta-4,6,8,10,12,19,21,23,25,27-decaene (**31**) and 1,16-bis-trifluoromethyl-5,12,20,27-tetramethoxy-(1α,2β,3α,4β,5α,12α,13β, 14α,15β,16α, 17β,18α,19β,20α,27α,28β,29α,30β)-31,32,33-trioxadodecacyclo[14.14.1.1^{3,14} 1.^{15,12}.1^{18,29}.1^{20,27}.0^{2,15}.0^{4,13}.0^{6,11}.0^{17,30}.0^{19,28}.0^{21,26}]pentatriaconta-4,6,8,10,12,19,21,23, 25,27-decaene (**32**).

31: (mp 181–182 °C, 57%). ^{1}H ($CDCl_3$), δ/ppm: 3.00 (2H, s), 3.20 (2H, s), 3.92 (6H, s), 4.18 (6H, s), 5.64 (2H, s), 6.17 (2H, s), 7.49 (2H, dd, *J* = 6.4 Hz, *J* = 3.3 Hz), 7.52 (2H, dd, *J* = 6.4 Hz, *J* = 3.3 Hz), 8.07 (2H, dd, *J* = 6.4 Hz, *J* = 3.4 Hz), 8.18 (2H, dd, *J* = 6.4 Hz, *J* = 3.4 Hz); ^{13}C ($CDCl_3$), δ/ppm: 54.6, 54.7, 60.2, 60.3, 75.3, 77.5, 86.2 (q, $^2J_{C,F}$ = 33.8 Hz), 122.0, 122.1, 1123.5 (q, $^1J_{C,F}$ = 280.3 Hz), 125.8, 126.2, 126.9, 127.7, 127.8, 127.9, 142.4, 142.7; HRMS (*m*/*z*): calcd. for $C_{36}H_{28}O_7F_6$: 686.1739; found: 686.1731.

32: (mp 175–176 °C, 22%). ^{1}H ($CDCl_3$), δ/ppm: 2.56 (4H, s), 4.08 (12H, s), 6.21 (4H, s), 7.01–7.14 (4H, m), 8.05–8.18 (4H, m); ^{13}C ($CDCl_3$), δ/ppm: 55.3, 61.2, 77.9 (q, $^2J_{C,F}$ = 31.5 Hz), 80.3, 121.0, 122.3, 122.5, 126.3 (q, $^1J_{C,F}$ = 276.8 Hz), 140.8; HRMS (*m*/*z*): calcd. for $C_{36}H_{28}O_7F_6$: 686.1739, found: 686.1731.

4.2.5. Reaction of **1** *with* **26**

1,16-Bis-trifluoromethyl-(1α,2β,3α,4β,5α,12α,13β,14α,15-β,16α,17α,18β, 19α,20β,27β,28α,29β,30α)-31,32,33,34,35-pentaoxadodecacyclo [14.14.1.1^{3,14}.1^{5,12}.1^{18,29}.1^{20,27}.0^{2,15}.0^{4,13}.0^{6,11}.0^{17,30}.0^{19,28}.0^{21,26}] pentatriaconta-6,8,10,21,23,25-hexaene (**33**) and 1,16-bis-trifluoromethyl-(1α,2β,3α,4β,5α,12α,13β,14α,15-β,16α,17β,18α, 19β,20α,27α,28β,29α,30β)31,32,33,34,35-pentaoxadodecacyclo[14.14.1.1^{3,14}.1^{5,12}.1^{18,29}.1^{20,27}.0^{2,15}.0^{4,13}.0^{6,11}.0^{17,30}.0^{19,28}.0^{21,26}]pentatriaconta-6,8,10,21,23,25-hexaene (**34**).

33: (mp 201–202 °C, 22%). ^{1}H ($CDCl_3$), δ/ppm: 1.78 (2H, s), 1.84 (2H, s), 2.36 (2H, s), 2.47 (2H, s), 4.41 (2H, s), 4.78 (2H, s), 5.16 (2H, s), 5.19 (2H, s), 6.99 (2H, dd, *J* = 5.5 Hz, *J* = 2.9 Hz); 7.10 (2H, dd, *J* = 5.5 Hz, *J* = 2.9 Hz), 7.18 (2H, dd, *J* = 5.5 Hz, *J* = 2.9 Hz), 7.19 (2H, dd, *J* = 5.5 Hz, *J* = 2.9 Hz); HRMS (*m*/*z*): calcd. for $C_{32}H_{24}O_5F_6$: 602.1528; found: 602.1522.

34: (mp 214–216 °C, 10%). ^{1}H ($CDCl_3$), δ/ppm: 1.70 (4H, s), 1.96 (4H, s), 4.88 (2H, s), 5.18 (2H, s), 7.13 (4H, dd, *J* = 5.6 Hz, *J* = 2.8 Hz), 7.17 (4H, dd, *J* = 5.6 Hz, *J* = 2.8 Hz); δ/ppm: HRMS (*m*/*z*): calcd. for $C_{32}H_{24}O_5F_6$: 602.1528; found: 602.1524.

4.2.6. Reaction of **1** *with* **27**

1,16-Bis-trifluoromethyl-(1α,2α,3β,4α,5β,12β,13α,14-β,15α,16α,17α,18β, 19α,20β,27β,28α,29β,30α)-31,32,33,34,35-pentaoxadodecacyclo[14.14.1.1^{3,14}.1^{5,12}.1^{18,29}.1^{20,27}.0^{2,15}.0^{4,13}.0^{6,11}.0^{17,30}.0^{19,28}.0^{21,26}]pentatriaconta-6,8,10,21,23,25-hexaene (**35**) and 1,16-bis-trifluoromethyl-(1α,2β,3α,4α,5β,12β,13α,14α, 15β,16α,17α, 18β, 19α,20β,27β,28α,29β,30α)-31,32,33,34,35-pentaoxadodecacyclo [14.14.1.1^{3,14}.1^{5,12}.1^{18,29}.1^{20,27}.0^{2,15}.0^{4,13}.0^{6,11}.0^{17,30}.0^{19,28}.0^{21,26}]pentatriaconta-6,8,10,21,23,25-hexaene (**36**).

35: (mp 188–191 °C, 16%). ^{1}H ($CDCl_3$), δ/ppm: 2.49 (2H, dd, *J* = 3.7 Hz, *J* = 2.1 Hz), 2.52 (2H, dd, *J* = 3.7 Hz, *J* = 2.1 Hz), 2.96 (2H, s), 3.14 (2H, s), 4.54–456 (2H, m), 4.83 (2H, br s), 5.14 (2H, s), 5.17 (2H, s), 7.10–7.14 (4H, m), 7.19–7.22 (4H, m); HRMS (*m*/*z*): calcd. for $C_{32}H_{24}O_5F_6$: 602.1528; found: 602.1533.

36: (mp 167–168 °C, 7%). ^{1}H ($CDCl_3$), δ/ppm: 2.42 (4H, dd, *J* = 3.9 Hz, *J* = 2.0 Hz); 2.82 (4H, s), 4.94 (4H, br s), 5.15 (4H, s), 7.07–7.10 (4H, m), 7.16–7.19 (4H, m); HRMS (m/z): calcd. for $C_{32}H_{24}O_5F_6$: 602.1528; found: 602.1529.

4.2.7. Reaction of **1** *with* **28**

1,20-Bis-trifluoromethyl-(1α,2β,3α,4β,5α,6α,7β,14β,15α, 16α,17β,18α,19β,20α,21α, 22β, 23α,24β,25β,26α,33α, 34β,35β,36α,37β,38α)-39,40,41,42,43,44,45-heptaoxa hexadecacyclo[18.18.1.1^{3,18}.1^{5,16}.1^{7,14}.1^{22,37}.1^{24,35}.1^{26,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,38}.0^{23,36}.0^{25,34}.0^{27,32}]pentatetraconta-8,10,12,27,29,31-hexaene (**37**) and 1,20-bis-trifluoromethyl-(1α,2β,3α,4β, 5α,6α, 7β,14β,15α,16α,17β,18α,19β,20α,21β,22α,23β,24α,25α, 26β, 33β,34α,35α,36β,37α,38β)-39,40,41,42,43,44,45-heptaoxahexadecacyclo [18.18.1.1^{3,18}.1^{5,16}.1^{7,14}.1^{22,37}.1^{24,35}.1^{26,33}.0^{2,19}.0^{4,17}.0^{6,15}.0^{8,13}.0^{21,38}.0^{23,36}.0^{25,34}.0^{27,32}]pentatetraconta-8,10,12,27,29,31-hexaene (**38**).

37: (mp 212–214 °C, 11%). ^{1}H ($CDCl_3$), δ/ppm: 2.25 (2H, s), 2.30 (2H, s), 2.32 (2H, dd, *J* = 3.0 Hz, *J* = 2.2 Hz); 2.40 (2H, dd, *J* = 3.0 Hz, *J* = 2.2 Hz); 2.57 (2H, s), 2.73 (2H, s), 4.40 (2H, s), 4.32 (2H, dd, *J* = 3.0 Hz, *J* = 2.2 Hz); 4.56 (2H, dd, *J* = 3.0 Hz, *J* = 2.2 Hz); 4.99 (2H, s), 5.08 (2H, s); 7.08 (2H, dd, *J* = 5.1 Hz, *J* = 2.1 Hz); 7.11 (2H, dd, *J* = 5.3 Hz, *J* = 2.2 Hz); 7.17 (2H, dd, *J* = 5.1 Hz, *J* = 2.1 Hz); 7.20 (2H, dd, *J* = 5.3 Hz, *J* = 2.2 Hz); ^{13}C ($CDCl_3$), δ/ppm: 48.4, 48.6, 48.8, 52.6, 52.8, 54.1, 76.7, 76.8, 77.0, 79.1, 80.1, 80.3, 86.7 (q, $^2J_{C,F}$ = 31.5 Hz), 123.5 (q, $^1J_{C,F}$ = 276.8 Hz), 126.1, 126.3, 128.3, 130.4, 145.9, 146.2; HRMS (*m*/*z*): calcd. for $C_{42}H_{32}O_7F_6$: 762.2052; found: 762.2047.

38: (mp 231–233 °C, 3%). ^{1}H ($CDCl_3$), δ/ppm: 2.19 (2H, s), 2.34 (2H, s), 2.35 (2H, dd, *J* = 3.0 Hz, *J* = 2.2 Hz); 4.47 (2H, dd, *J* = 3.6 Hz, *J* = 2.2 Hz); 4.77 (2H, s), 5.04 (2H, s); HRMS (*m*/*z*): calcd. for 762.2052; found: 762.2049.

4.2.8. Reaction of **1** *with* **29**

(1α,2β,3β,18β,19β,20α)-35,36-Trioxa-decacyclo[18.14.1.1^{3,18}.0^{2,19}.0^{4,17}.0^{5,10}.0^{11,16}.0^{21,34}.0^{22,27}.0^{28,33}]hexatriaconta-4,6,8,10,12,14,16,21,23,25,27,29,31,33-tetradecaene (**40**) and (1α,2β,3α, 18α,19β,20α)-35,36-trioxa-decacyclo[18.14.1.1^{3,18}.0^{2,19}.0^{4,17}.0^{5,10}.0^{11,16}.0^{21,34}.0^{22,27}.0^{28,33}]hexatriaconta-4,6,8,10,12,14,16,21,23,25,27,29,31,33-tetradecaene (**41**).

40: (mp 141–144 °C, 36%). ^{1}H ($CDCl_3$), δ/ppm: 3.07 (2H, dd, *J* = 3.2 Hz, *J* = 1.6 Hz); 6.06 (2H, dd, *J* = 3.2 Hz, *J* = 1.6 Hz); 6.41 (2H, s); 7.65–7.85 (8H, m); 7.94–7.99 (2H, m); 8.16 (2H, dd, *J* = 8.9 Hz, *J* = 1.7 Hz); 8.65 (2H, d, *J* = 8.9 Hz); 8.82 (2H, d, *J* = 8.9 Hz); HRMS (*m*/*z*): calcd. for $C_{34}H_{22}O_2$: 462.1619; found: 462.1622.

41: (mp 156–157 °C, 11%). ^{1}H ($CDCl_3$), δ/ppm: 2.22 (2H, s); 6.15 (4H, s), 7.60–7.85 (8H, m); 7.93 (4H, dd, *J* = 8.8 Hz, *J* = 2.2 Hz); 8.62 (4H, dd, *J* = 8.9 Hz, *J* = 2.1 Hz); HRMS (*m*/*z*): calcd. for $C_{34}H_{22}O_2$: 462.1619; found: 462.1623.

4.2.9. Reaction of **1** *with* **30**

1,12-Bis-trifluoromethyl-3,10,14,21-tetramethyl-(1α,2α,3β, 10β,11α, 12α,13β,14α,21α, 22β)-23,24,25-trioxa-octacyclo [10.10.1.1^{3,10}.1^{14,21}.0^{2,11}.0^{4,9}.0^{13,22}.0^{15,20}]pentacosa-4,6,8,15, 17,19-hexaene (**42**) and 1,3,10,12-tetramethyl-(1α,2α, 3β,10β,11α,12α)-19,20-dioxa-hexacyclo[10.6.1.1^{3,10}.0^{2,11}.0^{4,9}.0^{13,18}]icosa-4,6,8,13,15,17-hexaene (**43**).

Microwave reaction:

42: (mp 181–183 °C, 56%). ^{1}H ($CDCl_3$), δ/ppm: 1.74 (6H, s), 2.03 (6H, s), 2.92 (2H, s), 3.12 (2H, s), 7.10 (2H, dd, *J* = 5.0 Hz, *J* = 3.1 Hz), 7.15–7.7.17 (4H, m); 7.24 (2H, dd, *J* = 5.0 Hz, *J* = 3.1 Hz); HRMS (*m*/*z*): calcd. for $C_{28}H_{24}O_3F_6$: 522.1629; found: 522.1631.

High pressure reaction: A solution of **30** and **1** in dichloromethane (0.5 mL) was subjected to high pressure (8 kbar) for 12 h at room temperature. Evaporation of solvent in vacuo gave a yellow colored oily residue, which was separated by radial chromatography.

43 [23]: (26%). ^{1}H ($CDCl_3$), δ/ppm: 1.51 (6H, s), 1.71 (6H, s), 2.25 (2H, s), 6.94–6.96 (2H, dd, *J* = 7.1 Hz, *J* = 4.3 Hz), 7.02–7.03 (2H, dd, *J* = 7.1 Hz, *J* = 4.3 Hz), 7.15–7.21 (4H, m).

5. Computational details

All geometrical optimizations were carried out employing RHF/6-31G* method, followed by single point energy estimations with B3LYP[25], BMK and MP2 methods employing 6-31G* basis set. Calculations were performed using *Gaussian03* suite of programs [40], implemented on dual core Opteron 240 personal computer under Linux operating system and computer cluster Isabella at the Computing center of the University of Zagreb. Harmonic vibration frequencies were calculated for all localized stationary structures to verify whether they are minima or transition states.

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