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Diels–Alder reactions of β-trifluoroacetylvinylsulfones

Arkady L. Krasovsky, Valentine G. Nenajdenko* and Elizabeth S. Balenkova

Department of Chemistry, Moscow State University, 119899 Moscow, Russia

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Abstract—Diels–Alder reactions of β-trifluoroacetylvinylsulfones with 1,3-dienes in CH_2Cl_2 afforded corresponding mono- and polycycloadducts. A possibility of stereo- and regioselective cycloaddition was investigated. Elimination of sulfonyl group from cycloadducts leads to α,β-unsaturated trifluoromethylketones in good yields. © 2000 Elsevier Science Ltd. All rights reserved.

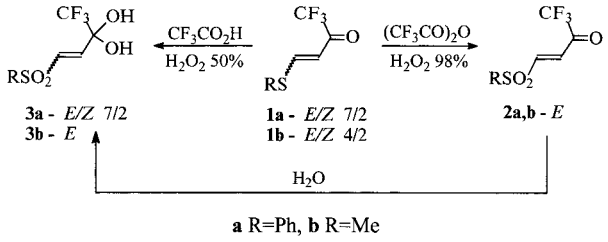
1. Introduction

In recent years, Diels–Alder reactions of vinylsulfones have attracted considerable attention.[1–19] The sulfonyl group is a versatile and flexible functionality that enjoys increasing popularity as an activating group in organic synthesis. It is also convenient, the elimination of sulfonyl group can be easily accomplished resulting in alkene[3–9] or allene[10] formation and the adducts can be transformed into the corresponding anion which can be alkylated.[1] Moreover the sulfonyl group may undergo desulfonylation[11–14] and oxidative desulfonylation with the formation of the corresponding ketones.[15,16]

Introduction of electron-withdrawing substituents in the α or β positions decrease the LUMO energy level and increase the dienophilicity. The addition of dienes to a compound in which the double bond was activated by both a sulfonyl and a carbonyl group has also been reported,[9,17–19] but although β-trifluoroacetylvinylsulfones are expected to be good dienophiles, their reactivity in Diels–Alder cycloadditions have previously not been described in the literature.

2. Results and discussion

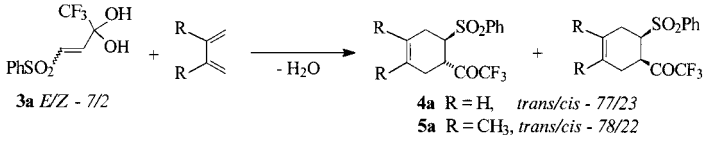
In recent work[20] we have prepared some β-trifluoroacetylvinylsulfones by oxidation of the readily available sulfides **1a**,**b**. We have found that these alkenes **2a**,**b** and **3a**,**b** are very reactive electrophiles, reacting with heteroarenes such as pyrrole, indole and furan. It has been shown that β-trifluoroacetylvinylsulfones **2a**,**b** easily add water to form *gem*-diols. The preparation of pure ketones **2a**,**b** demands water-free conditions, whereas oxidation of **1a**,**b** in aqueous trifluoroacetic acid yields diols **3a**,**b** (Scheme 1).



Scheme 1.

We now report the investigation of the reactivity of β-trifluoroacetylvinylsulfones and their hydrated forms in reaction with 1,3-dienes. We found that both β-trifluoroacetylvinylsulfones and the corresponding hydrates are highly reactive dienophiles. Their reactions with cyclic and linear dienes proceed easily even at room temperature in CH_2Cl_2 to form cycloadducts **4**–**8** in high yield. Only in the case of reaction with 9,10-dimethylanthracene is prolonged reflux in CH_2Cl_2 required.

We started our investigation from interaction of the diols



Scheme 2.

Keywords: Diels–Alder cycloaddition reaction; sulfones; trifluoromethylketone.

* Corresponding author. Tel.: +7-95-939-2276; fax: +7-95-932-88-46; e-mail: nen@acylium.chem.msu.ru

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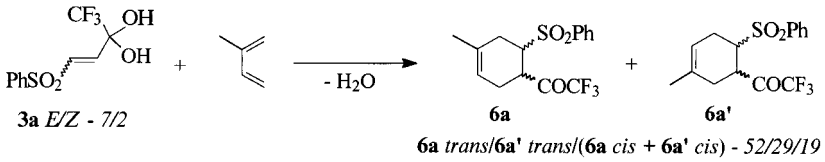
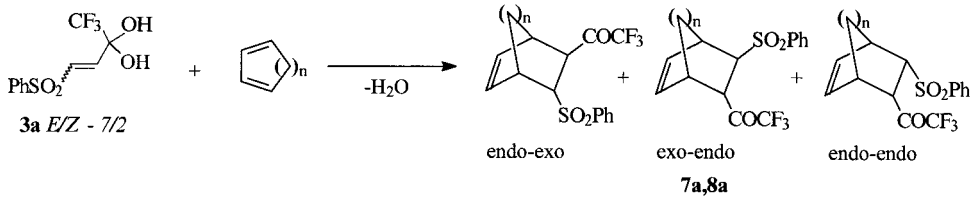


Scheme 3.



Scheme 4.

Table 1. Yields and diastereomeric ratio of cycloadducts **7a**,**8a**

Product	Ratio of isomers (%)			Yield (%)
	endo–exo	*exo–endo*	*endo–endo*	
7a (n=1)	34	46	20	78
8a (n=2)	33	45	22	89

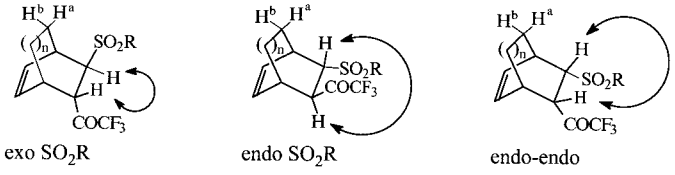
because they are more easily handled. Reaction of 1,3-butadiene and 2,3-dimethylbutadiene with the diol **3a** results in formation of cycloadducts **4a**, **5a** as mixture of *cis* and *trans* isomers. Preferentially *trans* substituted cyclohexenes are formed. We believe that the low stereoselectivity is due to diol **3a** existing as a mixture of *cis* and *trans* isomers (Scheme 2).

To study the regiochemistry of the cycloaddition we investigated the reaction of diol **3a** with isoprene. We found that a mixture of the four possible cycloadducts **6a** (*trans*/*cis*) and **6a′** (*trans*/*cis*) is formed (Scheme 3).

The *cis*/*trans* isomers ratio for cycloadducts **4a**–**6a** precisely correspond to the ratio of the isomers in the initial diol **3a**. Low stereoselectivity is also observed in the case of reaction of diol **3a** with cyclopentadiene and cyclohexadiene. A mixture of three isomers was isolated (Scheme 4, Table 1).

The diol **3b** is a much less reactive dienophile compared with diol **3a.** Interaction of dienes with diol **3b** at room temperature proceeds very slowly. For instance, the reaction of **3b** with 1,3-cyclohexadiene (2 equiv.) in CH_2Cl_2 at room temperature afforded 50% conversion after 10 days. Reflux in CH_2Cl_2 accelerates the reaction and leads to the stereospecific formation of cycloadducts **4b**–**9b**. Only *trans* substituted cyclohexenes are formed in reaction of diol **3b**.

The stereochemistry of compounds **4**–**8** was established by ^{1}H NMR spectroscopy. Those cycloadducts **4**–**6** having a *trans* arrangement of CH–$COCF_3$ and CH–SO_2R groups, have J^3_{HH} of 10.3–11.0 Hz, while those with a *cis* arrangement have J^3_{HH} of 4–5 Hz. In bicyclic products **7**,**8** $J_{Hexo-Hendo}$ is in the range 5–7 Hz. However, if the sulfonyl group is *exo* arranged a significant difference between signals CH^a and CH^b protons in ^{1}H NMR spectra is observed, contrary to the compounds with sulfonyl group in *endo* position which have close shifts of CH^a and CH^b protons in ^{1}H NMR spectra[21] (Scheme 5, Table 2).



Scheme 5.

Table 2. Proton chemical shifts and coupling constants in cycloadducts **7**,**8**

Product		$^3J_{HH}$, Hz	$\delta H^a - \delta H^b$, ppm
7 (n=0)	*exo* SO_2R	5.1	0.59
	endo SO_2R	5.5	0.07
	endo–endo	Overlap	0.28
8 (n=1)	*exo* SO_2R	6.2	0.52
	endo SO_2R	6.7	Overlap
	endo–endo	10.6	0.09

We supposed that the cycloaddition using the keto form of reagents might proceed more selectively since both ketones **2a**,**b** exist in the *trans* form. In the Diels–Alder reaction of sulfones **2a**,**b** with linear dienes, only *trans* isomers of **4**,**5** were formed in good yield. In the case of the unsymmetrical diene–isoprene, we have obtained a mixture of regioisomers **6a**/**6a′** in 2/1 and **6b**/**6b′** in 2.5/1 ratio, preferentially *para* $COCF_3$ substituted isomers are formed. In the case of cyclic dienes such as cyclopentadiene and 1,3-cyclohexadiene

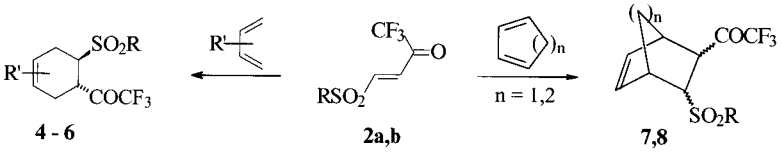
mixture of *exo* and *endo* cycloadducts were formed. So trifluoroacetyl and sulfonyl substituents have similar orientation ability (Scheme 6, Table 3).

We also investigated the influence of a series of Lewis acids, such as BF_3, $TiCl_4$, $Eu(fod)_3$ and $ZnCl_2$ on the regio- and stereochemistry of cycloaddition. In some cases addition of Lewis acid leads to some increase of yield (5–10%), but does not significantly affect the regioisomers ratio. We believe that this can be attributed to the possibility of coordination with both carbonyl and sulfonyl groups with nearly equal probability due to low nucleophilicity of the CF_3CO carbonyl group.

We used semiempirical PM3 calculations to explain the observed reactivity of the reagents **2**,**3**. Frontier molecular orbital theory is one of the most successful approaches in the prediction of the *regio*- and *endo–exo* selectivity for Diels–Alder reactions. We have calculated LUMO energy of reagents **2a**,**b** as well as for analogous CH_3CO-compounds. There is a dramatical difference between LUMO energies of CF_3-containing and non-fluorinated alkenes. The presence of the CF_3 group in the molecule results in a significant decrease in the LUMO energy, and CF_3 ketones are much more electron-deficient and reactive species (Table 4).

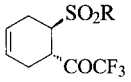
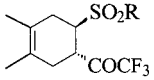
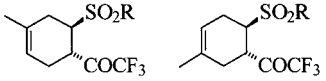
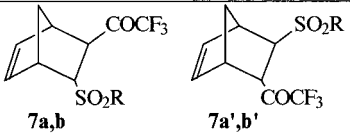
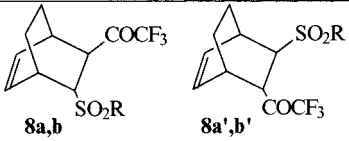
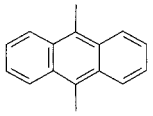
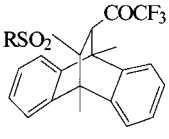
Regio and stereoselectivity of the reactions of **2a**,**b** with dienes can be explained using the LUMO orbital coefficients. The preferential formation of the *para*-$COCF_3$-isomers in the case of reaction with isoprene is in good agreement with 'large–large' molecular orbitals overlapping in the transition state (Scheme 7).

As we have found in the reaction with cyclic 1,3-dienes the cycloadducts have a preference for an *endo*-oriented trifluoroacetyl moiety. As is shown in Table 4, LUMO



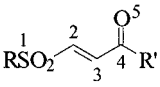
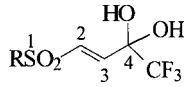
Scheme 6.

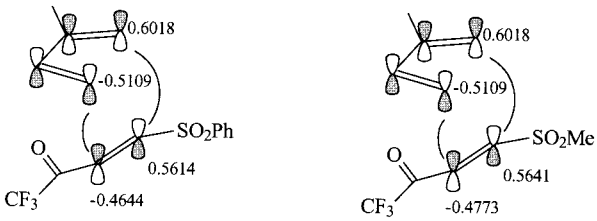
Table 3. Reaction of sulfones **2a**,**b** with dienes; **a**,**a′** R=Ph, **b**,**b′** R=Me

Dienes	Product	Yield, %	
		R = Ph	R = Me
	 **4a,b**	86	88
	 **5a,b**	85	85
	 **6a,b** **6a',b'** **6a/6a'** - 2/1; **6b/6b'** - 2.5/1 *	87	85
	 **7a,b** **7a',b'** **7a/7a'** - 3/4; **7b/7b'** - 2/3	76	80
	 **8a,b** **8a',b'** **8a/8a'** - 3/4; **8b/8b'** - 2/3	81	86
	 **9a,b**	70	72

*Ratio of regioisomer was confirmed by the product of oxidative aromtaization

Table 4. LUMO coefficients at the atoms

						
	R=Ph		R=Me		R=Ph	R=CH_3
	R′=CF_3	R′=CH_3	R′=CF_3	R′=CH_3		
S (1)	0.0986	0.1818	0.0956	0.1712	0.1798	0.1588
C (2)	0.5614	0.5420	0.5641	0.5777	0.4728	0.6308
C (3)	0.4644	0.5469	0.4773	0.6141	0.4951	0.6930
C (4)	0.4708	0.3302	0.4645	0.3249	0.0941	0.1191
O (5)	0.4420	0.3120	0.4396	0.3036	–	–
LUMO, eV	−1.67	−0.83	−1.80	−0.83	−0.85	−0.92



Scheme 7.

orbital coefficients for fluorinated alkenes are considerably greater for the carbonyl group compared with CH_3CO analogues. We suppose that the *endo*-$COCF_3$ selectivity is connected with the secondary *p*-orbital interaction between the π-system of the dienes and the π-system of the carbonyl groups of the reagents **2a**,**b**. Having greater LUMO coefficients at the carbonyl group than at the sulfonyl group, secondary *p*-orbital interactions in the transition state are more probable between the C(4) carbon of the reagents and the π-system of the diene resulting in preferable *endo*-$COCF_3$ stereochemistry. However the regioselectivity of the cycloaddition was not high, both in the case of β-trifluoroacetylvinylsulfones and in the case of the non-fluorinated analogues.[9]

We also investigated the possibility of sulfonyl group removal from cycloadducts. A number of bases, namely NaH, $NaHCO_3$, NaOEt, Et_3N, $Et(i\text{-}Pr)_2N$ and DBU were been used to study the elimination. Best results were obtained for DBU, in dry CH_2Cl_2, which is probably connected with its high basicity and low nucleophilicity. Other bases resulted in formation of tars, or low yield of desirable product. We found that elimination of the sulfonyl group with DBU whilst open to the air leads to instant oxidative aromatization of the product-1,4-dienes to the corresponding trifluoroacetylbenzenes **15**–**17** (Scheme 8).

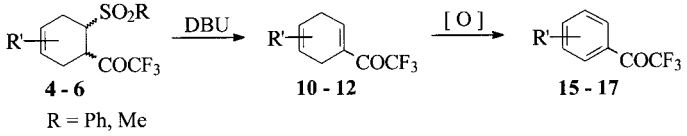
However, under an argon atmosphere 1,4-cyclohexadiene derivatives **10**–**12** can be obtained in quantitative yields. The elimination reaction to form the enone **14** proceeds with high yield, however, prolonged reflux of about 12 h in CH_2Cl_2 is required.

Elimination of the sulfonyl group from cycloadduct **8** yields bicyclic trifluoroacetyl substituted diene **13** in quantitative yield. In contrast, our attempts to prepare the corresponding diene from cyclopentadiene derivatives **7** were unsuccessful, probably due to instability of the forming diene connected with its high strain and the basic conditions of reaction (Scheme 9; Table 5).

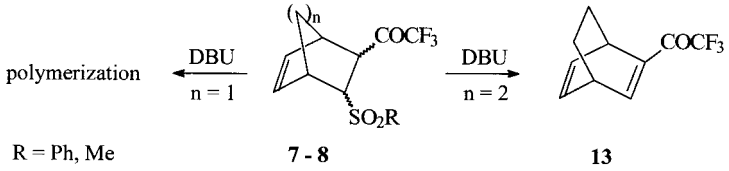
The elimination of the sulfonyl group is rather convenient for preparation of trifluoroacetyl substituted derivatives of 1,4-cyclohexadiene **10**–**12**, and new polycyclic adducts **13**,**14**. Moreover both pure *trans* isomer **4**–**6** and the mixture of *cis*–*trans* isomers give the same product. These products are good building blocks to construct new fused trifluoromethyl substituted heterocycles.

3. Conclusion

We have investigated β-trifluoroacetylvinylsulfones in Diels–Alder reactions. The dienophiles are conveniently prepared reagents which were proven to be good

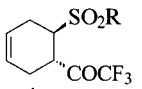
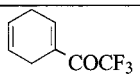
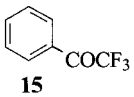
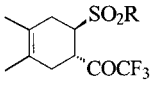
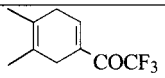
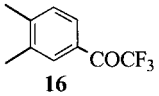
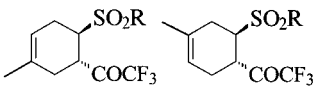
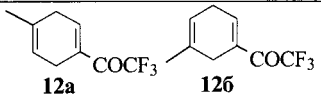
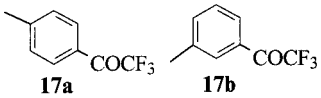
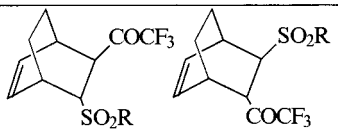
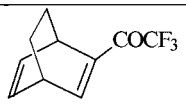
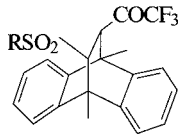
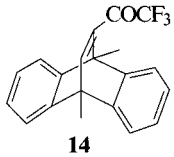


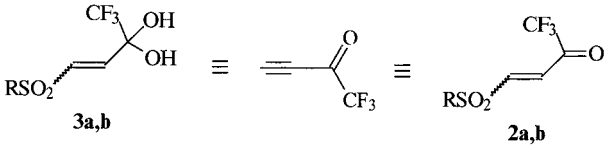
Scheme 8.



Scheme 9.

Table 5. Elimination of sulfonyl group by DBU from **4–9**; R=Ph, Me

Cycloadduct	Product	Yield, %	
		R=Ph	R=Me
 **4**	 **10**	90	95
	 **15**	80	84
 **5**	 **11**	91	96
	 **16**	84	90
 **6**	 **12a** **12б**	90	94
	 **17a** **17b**	80	85
 **8**	 **13**	75	85
 **9**	 **14**	71	80



a R = Ph, **b** R = Me

Scheme 10.

synthetic equivalents of 1,1,1-trifluoro-3-butyn-2-ones (Scheme 10).

It was found that the cycloaddition with various dienes take place in mild condition. Stereochemistry of reaction was studied.

4. Experimental

All solvents used were dried and distilled according to standard procedures. Silica gel Merck 60 and Merck $60F_{254}$ plates were used for conventional and analytical (TLC) chromatography, respectively.

4.1. Preparation of Diels–Alder cycloadducts 4–9

To a solution of vinylsulfone **2a**,**b** and **3a**,**b** (1 mmol) in CH_2Cl_2 (5 ml) the corresponding diene (2 mmol) was added. The mixture was stirred at room temperature (in the case of the reaction with anthracenes reactions were carried out at 40°C with stirring). Removal of the solvent under reduced pressure afforded products, which were purified by column chromatography over silica gel using hexane as eluent.

4.1.1. ***trans*-2,2,2-Trifluoro-1-[6-(phenylsulfonyl)-3-cyclohexen-1-yl]ethanone (4a).** Yield (274 mg, 86%), colourless oil; [Found: C, 52.59; H, 4.19. $C_{14}H_{13}F_3O_3S$ requires C, 52.83; H, 4.12%]; ν_{max} (film) 1770 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.88–7.84 (2H, m, arom.), 7.72–7.67 (1H, m, arom.), 7.62–7.55 (2H, m, arom.), 5.69 (2H, br s, 2CH=), 3.81 (1H, ddd, *J*=6.3, 10.6, 4.6 Hz, CH-6), 3.58 (1H, ddd, *J*=5.9, 10.6, 4.5 Hz, CH-1), 2.64-2.50 and 2.30–2.19 (4H, m, $2CH_2$); δ_C (100 MHz, $CDCl_3$) 192.3 (*J*=35.4 Hz), 137.2, 134.2, 129.4, 128.5, 128.5, 123.3, 115.6 (*J*=291.8 Hz), 61.2, 38.8, 28.5, 24.3.

The reaction of **3a** with 1,3-butadiene gave a mixture of *trans*- and *cis*-isomers — (77/23), after purification, yield

(277 mg, 87%), colourless oil; [Found for mixture of isomers: C, 52.57; H, 4.17. $C_{14}H_{13}F_3O_3S$ requires C, 52.83; H, 4.12%]; minor isomer ***cis*-2,2,2-trifluoro-1-[6-(phenylsulfonyl)-3-cyclohexen-1-yl]ethanone:** ν_{max} (film) 1770 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.88–7.84 (2H, m, arom.), 7.72–7.67 (1H, m, arom.), 7.62–7.55 (2H, m, arom.), 5.76–5.50 (2H, m, 2CH═), 3.78–3.70 (1H, m, CH-6), 3.60–3.54 (1H, m, CH-1), 2.84–2.76 and 2.58–2.42 (4H, m, $2CH_2$); δ_C (100 MHz, $CDCl_3$) 188.7 (J=35.2 Hz), 137.3, 134.2, 129.3, 128.6, 125.2, 122.0, 115.6 (J=292.0 Hz), 61.7, 36.3, 26.5, 23.5.

4.1.2. *trans*-2,2,2-Trifluoro-1-[6-(methylsulfonyl)-3-cyclohexen-1-yl]ethanone (4b). Yield (226 mg, 88%), white solid; mp 110–115°C; [Found: C, 42.35; H, 4.12. $C_9H_{11}F_3O_3S$ requires C, 42.19; H, 4.33%]; ν_{max} (film) 1775 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 5.78 (2H, br s, 2CH═), 3.75 (1H, ddd, J=8.2, 10.3, 2.1 Hz, CH-6), 3.52 (1H, ddd, J=5.6, 10.3, 4.7 Hz, CH-1), 2.93 (3H, s, CH_3), 2.65–2.20 (4H, m, $2CH_2$); δ_C (100 MHz, $CDCl_3$) 192.3 (J=35.0 Hz), 123.6, 123.4, 115.4 (J=290.0 Hz), 59.6, 40.2, 39.0, 28.5, 24.7.

4.1.3. *trans*-1-[3,4-Dimethyl-6-(phenylsulfonyl)-3-cyclohexen-1-yl]-2,2,2-trifluoroethanone (5a). Yield (295 mg, 85%), colourless oil; [Found C, 55.61; H, 4.91. $C_{16}H_{17}F_3O_3S$ requires C, 55.48; H, 4.95%]; ν_{max} (film) 1770cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.83 (2H, m, arom.), 7.68 (1H, m, arom.), 7.57 (2H, m, arom.), 3.80 (1H, ddd, J=6.4, 10.7, 4.5 Hz, CH-6), 3.56 (1H, ddd, J=6.1, 10.7, 3.5 Hz, CH-1), 2.60–2.00 (4H, m, $2CH_2$), 1.58 (6H, br s, $2CH_3$); δ_C (100 MHz, $CDCl_3$) 192.5 (J=35.3 Hz), 137.3, 134.1, 129.3, 128.5, 122.8, 122.7, 115.5 (J=290.0 Hz), 62.1, 39.8, 34.7, 30.3, 18.4, 18.1.

The reaction of **3a** with 2,3-dimethyl-1,3-butadiene gave a mixture of *trans* and *cis* isomers—(78/22), after purification, yield (302 mg, 87%), colourless oil; [Found for mixture of isomers: C, 55.58; H, 4.89. $C_{16}H_{17}F_3O_3S$ requires C, 55.48; H 4.95%]; minor isomer ***cis*-1-[3,4-dimethyl-6-(phenylsulfonyl)-3-cyclohexen-1-yl]-2,2,2-trifluoroethanone:** ν_{max} (film) 1770 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.83 (2H, m, arom.), 7.68 (1H, m, arom.), 7.57 (2H, m, arom.), 3.70 (1H, ddd, J=6.4, 4.6, 4.5 Hz, CH-6), 3.56 (1H, ddd, J=6.1, 4.6, 3.5 Hz, CH-1), 2.80–2.00 (4H, m, $2CH_2$), 1.58 (3H, s, CH_3), 1.50 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 192.5 (J=35.2 Hz), 137.6, 134.4, 129.2, 128.6, 124.3, 121.4, 115.7 (J=290.0 Hz), 62.5, 37.5, 32.2, 29.1, 18.5, 18.2.

4.1.4. *trans*-1-[3,4-Dimethyl-6-(methylsulfonyl)cyclohex-3-en-1-yl]-2,2,2-trifluoroethanone (5b). Yield (242 mg, 85%), white solid; mp 115–120°C; [Found: C, 46.13; H, 5.47. $C_{11}H_{15}F_3O_3S$ requires C, 46.27; H, 5.32%]; ν_{max} (film) 1775 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 3.73 (1H, ddd, J=6.4, 10.4, 4.0 Hz, CH-6), 3.47 (1H, ddd, J=5.6, 10.4, 5.2 Hz, CH-1), 2.90 (3H, s, CH_3SO_2), 2.60–2.15 (4H, m, $2CH_2$), 1.69 (3H, s, CH_3), 1.65 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 192.9 (J=35.0 Hz), 123.3, 122.9, 115.5 (J=290.0 Hz), 60.5, 40.5, 40.3, 34.7, 30.5, 18.6, 18.3.

The reaction of **2a** with isoprene gave a mixture of regioisomers ***trans*-2,2,2-trifluoro-1-[4-methyl-6-(phenylsulfonyl)-3-cyclohexen-1-yl]ethanone (6a) and *trans*-2,2,2-trifluoro-1-[3-methyl-6-(phenylsulfonyl)-3-cyclohexen-1-yl]ethanone (6a′)**—(2/1), after purification, yield (289 mg, 87%), colourless oil; [Found for mixture of isomers: C, 54.47; H, 4.43. $C_{15}H_{15}F_3O_3S$ requires C, 54.21; H, 4.55%]; ν_{max}(film) 1765 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.85 (2H, m, arom.), 7.67 (1H, m, arom.), 7.56 (2H, m, arom.), 5.40 (1H, m, CH═, 6a), 5.34 (1H, m, CH═, 6a′), 3.90–3.45 (2H, m, CH-1, CH-6), 2.60–2.05 (4H, m, $2CH_2$), 1.70–1.61 (3H, br s, CH_3); δ_C (100 MHz, $CDCl_3$) for major isomer (**6a**): 192.6 (J=35.2 Hz), 137.4, 134.2, 131.1, 129.4, 128.5, 117.5, 115.6 (J=290.0 Hz), 62.0, 38.9, 28.9, 22.7, 18.3.

The reaction of **3a** with isoprene gave a mixture of isomers *cis*+*trans* (**6a**), and *cis*+*trans* (**6a′**), yield (282 mg, 85%), colourless oil; [Found for mixture of isomers: C, 54.35; H, 4.49. $C_{15}H_{15}F_3O_3S$ required C, 54.21; H, 4.55%]; ν_{max} (film) 1768 cm^{-1}.

The reaction of **2b** (or **3b**) with isoprene gave a mixture of regioisomers ***trans*-2,2,2-trifluoro-1-[4-methyl-6-(methylsulfonyl)-3-cyclohexen-1-yl]ethanone (6b)** and ***trans*-2,2,2-trifluoro-1-[3-methyl-6-(methylsulfonyl)-3-cyclohexen-1-yl]ethanone (6b′)**—(2.5/1) after purification, yield (230 mg, 85%), white solid; mp 105–110°C; [Found for mixture of isomers: C, 44.70; H, 4.80. $C_{10}H_{13}F_3O_3S$ required C, 44.44; H, 4.85%]; ν_{max} (film) 1775 cm^{-1}.

Major isomer (**6b**): δ_H (400 MHz, $CDCl_3$) 5.45 (1H, br s, CH═), 3.69 (1H, ddd, J=7.5, 10.6, 3.1 Hz, CH-6), 3.47 (1H, ddd, J=5.9, 10.6, 4.4 Hz, CH-1), 2.90 (3H, s, CH_3SO_2), 2.60–2.20 (4H, m, $2CH_2$), 1.75 (3H, s, CH_3). δ_C (100 MHz, $CDCl_3$) 192.7 (J=35.1 Hz), 131.2, 117.2, 115.3 (J=290.0 Hz), 59.6, 39.5, 38.9, 32.9, 24.7, 22.4.

Minor isomer (**6b′**): δ_H (400 MHz, $CDCl_3$) 5.45 (1H, br s, CH═), 3.79 (1H, ddd, J=6.7, 10.5, 3.7 Hz, CH-6), 3.47 (1H, ddd, J=5.7, 10.5, 4.8 Hz, CH-1), 2.91 (3H, s, CH_3SO_2), 2.60–2.20 (4H, m, $2CH_2$), 1.80 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 192.8 (J=35.1 Hz), 131.0, 117.6, 115.3 (J=290.0 Hz), 60.2, 40.0, 38.9, 28.9, 28.7, 22.6.

The reaction of **2a** with cyclopentadiene gave a mixture of stereoisomers **1-[3-(*endo*-phenylsulfonyl)bicyclo[2.2.1]-hept-5-en-2-yl]-*exo*-2,2,2-trifluoro-ethanone (7a)** and **1-[3-(*exo*-phenylsulfonyl)bicyclo[2.2.1]hept-5-en-2-yl]-*endo*-2,2,2-trifluoro-ethanone (7a′)**—(3/4) after purification, yield (251 mg, 76%), colourless oil; [Found for mixture of isomers: C, 54.70; H, 3.85. $C_{15}H_{13}F_3O_3S$ required C, 54.54; H, 3.97%]; ν_{max} (film) 1765 cm^{-1}.

(7a): δ_H (400 MHz, $CDCl_3$) 7.90–7.50 (5H, m, arom.), 6.44 (1H, dd, J=2.8, 5.6 Hz, CH═), 6.41 (1H, dd, J=3.0, 5.6 Hz, CH═), 4.19 (1H, dd, J=3.1, 5.5 Hz, CH-3), 3.34 (1H, br s, CH), 3.28 (1H, br s, CH), 3.24 (1H, br d, J=5.5 Hz, CH-2), 1.55 (1H, br d, J=9.5 Hz, CH-7), 1.48 (1H, br d, J=9.5 Hz, CH-7).

(7a′): δ_H (400 MHz, $CDCl_3$) 7.90–7.50 (5H, m, arom.), 6.33 (1H, dd, J=3.3, 5.6 Hz, CH═), 5.95 (1H, dd, J=2.8, 5.6 Hz, CH═), 3.84 (1H, dd, J=3.4, 5.1 Hz, CH-3), 3.52 (1H, br s, CH), 3.48 (1H, dd, J=1.7, 5.1 Hz, CH-2), 3.37

(1H, br s, CH), 2.25 (1H, br d, J=9.2 Hz, CH-7), 1.66 (1H, br d, J=9.2 Hz, CH-7); δ_C (100 MHz, $CDCl_3$) for mixture of isomers: 189.5 (J=34.8 Hz), 188.5 (J=34.4 Hz), 138.9, 138.5, 135.6, 135.5, 134.7, 134.2, 134.0, 133.9, 129.4, 129.3, 127.9, 127.8, 115.3 (J=292.2 Hz), 115.2 (J=292.3 Hz), 66.2, 64.7, 49.0, 48.9, 48.7, 47.9, 47.0, 46.4, 44.9, 44.7.

The reaction of **3a** with cyclopentadiene gave a mixture of stereoisomers **1-[3-(*endo*-phenylsulfonyl)bicyclo[2.2.1]-hept-5-en-2-yl]-*exo*-2,2,2-trifluoro-ethanone (7a)** and **1-[3-(*exo*-phenylsulfonyl)bicyclo[2.2.1]hept-5-en-2-yl]-*endo*-2,2,2-trifluoro-ethanone (7a′)** and **1-[3-(*endo*-phenylsulfonyl)bicyclo[2.2.1]hept-5-en-2-yl]-*endo*-2,2,2-trifluoro-ethanone**—(34/46/20) after purification, yield (258 mg, 78%), colourless oil. [Found for mixture of isomers: C, 54.67; H, 3.89. $C_{15}H_{13}F_3O_3S$ required C 54.54, H 3.97%]; ν_{max} (film) 1770 cm^{-1}.

Minor isomer *endo–endo*: δ_H (400 MHz, $CDCl_3$) 7.90–7.50 (5H, m, arom.), 6.35 (1H, dd, J=3.1, 5.6 Hz, CH═), 6.14 (1H, dd, J=2.8 Hz, J=5.6 Hz, CH═), 1.86 (1H, br d, J=9.0 Hz, CH-7,), 1.58 (1H, br d, J=9.0 Hz, CH-7). Other ^1H NMR, ^{13}C NMR signals are overlapped by the signals of major isomer.

The reaction of **2b** (or **3b**) with cyclopentadiene gave a mixture of stereoisomers **1-[3-(*endo*-methylsulfonyl)bicyclo[2.2.1]hept-5-en-2-yl]-*exo*-2,2,2-trifluoro-ethanone (7b)** and **1-[3-(*exo*-methylsulfonyl)bicyclo[2.2.1]hept-5-en-2-yl]-*endo*-2,2,2-trifluoro-ethanone (7b′)**—(2/3), after purification, yield (215 mg, 80%), colourless oil; [Found for mixture of isomers: C, 44.68; H, 4.31. $C_{10}H_{11}F_3O_3S$ requires C, 44.77; H, 4.13%]; ν_{max} (film) 1770 cm^{-1}.

(7b): δ_H (400 MHz, $CDCl_3$) 6.45–6.38 (2H, m, CH═), 3.84 (1H, dd, J=3.2, 5.1 Hz, CH-3), 3.49 (1H, br s, CH), 3.38 (1H, br s, CH), 3.27 (1H, br d, J=5.1 Hz, CH-2), 2.85 (3H, s, CH_3SO_2), 1.64 (1H, br d, J=9.5 Hz, CH-7), 1.55 (1H, br d, J=9.5 Hz, CH-7).

(7b′): δ_H (400 MHz, $CDCl_3$) 6.41 (1H, dd, J=3.1, 5.4 Hz, CH═), 6.06 (1H, dd, J=2.6, 5.4 Hz, CH═), 3.88 (1H, dd, J=3.6, 4.8 Hz, CH-3), 3.64 (1H, br s, CH), 3.49 (1H, br s, CH), 3.24 (1H, br d, J=4.8 Hz, CH-2), 2.91 (3H, s, CH_3SO_2), 2.20 (1H, br d, J=9.5 Hz, CH-7), 1.68 (1H, br d, J=9.5 Hz, CH-7). δ_C (100 MHz, $CDCl_3$) for mixture of isomers 189.4 (J=34.8 Hz), 188.7 (J=34.6 Hz), 139.8, 136.0, 135.3, 134.8, 116.0 (J=292.4 Hz), 115.8 (J=292.4 Hz), 64.2, 62.4, 48.6, 48.0, 47.9, 47.2, 46.5, 46.2, 44.6, 44.5, 40.7, 40.4.

The reaction of **2a** with cyclohexa-1,3-diene gave a mixture of stereoisomers **1-[3-(*endo*-phenylsulfonyl)bicyclo-[2.2.2]oct-5-en-2-yl]-*exo*-2,2,2-trifluoro-ethanone (8a)** and **1-[3-(*exo*-phenylsulfonyl)bicyclo[2.2.2]oct-5-en-2-yl]-*endo*-2,2,2-trifluoro-ethanone (8a′)**—(3/4), after purification, yield (279 mg, 81%), colourless oil; [Found for mixture of isomers: C, 55.95; H, 4.37. $C_{16}H_{15}F_3O_3S$ requires C, 55.81; H, 4.39%]; ν_{max}(film) 1760 cm^{-1}.

(8a): δ_H (400 MHz, $CDCl_3$) 7.90–7.50 (5H, m, arom.), 6.39–6.30 (2H, m, CH═), 3.84 (1H, br d, J=6.7 Hz, CH-3), 3.48 (1H, br d, J=6.7 Hz, CH-2), 3.16 (1H, br s, CH), 3.07 (1H, br s, CH), 1.6–1.2 (4H, m, CH_2).

(8a′): δ_H (400 MHz, $CDCl_3$) 7.90–7.50 (5H, m, arom.), 6.43 (1H, dd, J=7.4, 7.4 Hz, CH═), 5.98 (1H, dd, J=7.4, 7.4 Hz, CH═), 3.62 (1H, br d, J=6.2 Hz, CH-3), 3.58 (1H, dd, J=6.2 Hz, CH-2), 3.20 (1H, br s, CH), 3.17 (1H, br s, CH), 2.43 (1H, m, CH_2), 1.91 (1H, m, CH_2), 1.6–1.2 (2H, m, CH_2). δ_C (100 MHz, $CDCl_3$) for mixture of isomers 189.2 (J=35.0 Hz), 188.9 (J=35.1 Hz), 138.2, 137.0, 136.0, 134.0, 133.9, 132.8, 132.2, 131.7, 130.3, 129.4, 129.1, 128.6, 115.4 (J=292.1 Hz), 115.2 (J=292.2 Hz), 63.2, 61.5, 47.7, 46.3, 32.7, 31.9, 29.4, 29.0, 25.0, 24.9, 24.4, 24.2.

The reaction of **3a** with cyclohexa-1,3-diene gave a mixture of stereoisomers **1-[3-(*endo*-phenylsulfonyl)bicyclo[2.2.2]-oct-5-en-2-yl]-*exo*-2,2,2-trifluoro-ethanone (8a)** and **1-[3-(*exo*-phenylsulfonyl)bicyclo[2.2.2]oct-5-en-2-yl]-*endo*-2,2,2-trifluoro-ethanone (8a′)** and **1-[3-(*endo*-phenylsulfonyl)bicyclo[2.2.2]oct-5-en-2-yl]-*endo*-2,2,2-trifluoroethanone**—(33/45/22) after purification, yield (306 mg, 89%), colourless oil. [Found for mixture of isomers: C, 55.99; H, 4.30. $C_{16}H_{15}F_3O_3S$ requires C, 55.81; H, 4.39%]; ν_{max} (film) 1770 cm^{-1}.

Minor isomer *endo–endo*: δ_H (400 MHz, $CDCl_3$) 7.90–7.50 (5H, m, arom.), 6.35 (1H, dd, J=7.3, 7.3 Hz, CH═), 6.11 (1H, dd, J=7.3, 7.3 Hz, CH═), 3.94 (1H, br d, J=10.6 Hz, CH-3), 3.58 (1H, dd, J=10.6 Hz, CH-2), 2.94 (1H, br s, CH), 2.85 (1H, br s, CH), 1.6–1.3 (4H, m, CH_2). ^{13}C NMR signals are overlapped by the signals of major isomer.

The reaction of **2b** (or **3b**) with cyclohexa-1,3-diene gave a mixture of stereoisomers **1-[3-(*endo*-methylsulfonyl)bicyclo[2.2.2]oct-5-en-2-yl]-*exo*-2,2,2-trifluoro-ethanone (8b)** and **1-[3-(*exo*-methylsulfonyl)bicyclo[2.2.2]oct-5-en-2-yl]-*endo*-2,2,2-trifluoro-ethanone (8b′)**—(38/62), after purification, yield (243 mg, 86%), white solid; mp 78–80°C; [Found for mixture of isomers: C, 46.66; H, 4.39. $C_{11}H_{13}F_3O_3S$ requires C, 46.80; H, 4.64%]; ν_{max} (film) 1760 cm^{-1}.

(8b): δ_H (400 MHz, $CDCl_3$) 6.56–6.47 (2H, m, CH═), 3.81 (1H, br d, J=6.8 Hz, CH-3), 3.38 (1H, br d, J=6.8 Hz, CH-2), 3.29 (1H, br s, CH), 3.19 (1H, br s, CH), 2.80 (3H, s, CH_3SO_2), 1.8–1.2 (4H, m, CH_2).

(8b′): δ_H (400 MHz, $CDCl_3$) 6.44 (1H, dd, J=7.5, 7.3 Hz, CH═), 6.11 (1H, dd, J=7.5, 7.4 Hz, CH═), 3.63 (1H, br d, J=6.0 Hz, CH-3), 3.58 (1H, br d, J=6.0 Hz, CH-2), 3.27 (1H, br s, CH), 3.19 (1H, br s, CH), 2.84 (3H, s, CH_3SO_2), 2.27 (1H, m, CH_2), 1.88 (1H, m, CH_2), 1.8–1.2 (2H, m, CH_2). δ_C (100 MHz, $CDCl_3$) for mixture of isomers 189.5 (J=34.8 Hz), 189.2 (J=35.2 Hz), 135.5, 132.4, 132.3, 130.3, 115.2 (J=292.2 Hz), 115.1 (J=292.2 Hz), 62.1, 59.6, 47.1, 46.2, 40.5, 38.6, 32.1, 31.5, 29.4, 29.3, 25.1, 24.7, 22.2, 17.9.

4.1.5. *trans*-1-[1,8-Dimethyl-16(phenylsulfonyl)tetracyclo-[6.6.2.0^{2,7}.0^{9,14}]-hexadeka-2,4,6, 10,12,14-hexaen-15-yl]-2,2,2-trifluoro-1-ethanone (9a). Yield (329 mg, 70%), yellow solid; mp 150–153°C; [Found: C, 66.22; H, 4.61.

$C_{26}H_{21}F_3O_3S$ requires C, 66.37; H, 4.50%]; ν_{max} (film) 1758 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.80–7.10 (13H, m, arom.), 3.96 (1H, d, J=7.2 Hz, CH), 3.82 (1H, d, J=7.2 Hz, CH), 2.20 (3H, s, CH_3), 2.10 (3H, s, CH_3). δ_C (100 MHz, $CDCl_3$) 192.8 (J=36.1 Hz), 140.0–108.0 (18C, arom.), 116.0 (J=291.0 Hz), 74.4, 53.9, 46.0, 43.0, 18.5, 16.0.

The reaction of **3a** with 9,10-dimethylanthracene gave a mixture of *trans* and *cis* isomers (77/23), after purification; yield (339 mg, 72%), yellow solid; mp 141–144°C. [Found: C, 66.30; H, 4.66. $C_{26}H_{21}F_3O_3S$ requires C, 66.37; H, 4.50%]; ν_{max} (film) 1758 cm^{-1}.

Minor isomer ***cis*-1-[1,8-dimethyl-16(phenylsulfonyl)-tetracyclo[6.6.2.0^{2,7}.0^{9,14}]-hexadeka-2,4,6,10,12,14-hexaen-15-yl]-2,2,2-trifluoro-1-ethanone:** δ_H (400 MHz, $CDCl_3$) 7.80–7.10 (13H, m, arom.), 3.93 (1H, d, J=3.6 Hz, CH), 3.83 (1H, d, J=3.6 Hz, CH), 2.20 (3H, s, CH_3), 2.10 (3H, s, CH_3). δ_C (100 MHz, $CDCl_3$) 192.7 (J=36.1 Hz), 140.0–108.0 (18C, arom.), 115.9 (J=291.0 Hz), 74.5, 53.7, 46.5, 43.3, 18.5, 15.9.

4.1.6. *trans*-1-[1,8-Dimethyl-16(methylsulfonyl)tetracyclo[6.6.2.0^{2,7}.0^{9,14}]-hexadeka-2,4,6,10,12,14-hexaen-15-yl]-2,2,2-trifluoro-1-ethanone (9b). Yield (294 mg, 72%), yellow solid; mp 130–135°C; [Found: C, 61.60; H, 4.47. $C_{21}H_{19}F_3O_3S$ requires C, 61.75; H, 4.69%]; ν_{max} (film) 1760 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.6–6.7 (8H, m, arom.), 3.71 (1H, d, J=7.3 Hz, CH), 3.50 (1H, d, J=7.3 Hz, CH), 2.37 (3H, s, CH_3), 2.27 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 192.6 (J=36.0 Hz), 140.0–108.0 (12C arom.), 114.9 (J=292.7 Hz), 74.4, 53.9, 45.8, 43.4, 42.0, 18.5, 16.0.

4.2. General procedure for the elimination of sulfonyl group

To a solution of cycloadduct (1 mmol) in CH_2Cl_2 (5 ml), DBU (1.1 mmol) was added. The mixture was stirred at room temperature. The product was purified by column chromatography over silica gel using hexane as eluent.

4.2.1. 1-Cyclohexa-1,4-dien-1-yl-2,2,2-trifluoroethanone (10). Colourless oil; ν_{max} (film) 1715 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.12 (1H, br s, CH═), 5.75–5.68 (1H, m, CH═), 5.60–5.54 (1H, m, CH═), 3.00–2.65 (4H, m, $2CH_2$); δ_C (100 MHz, $CDCl_3$) 189.2 (J=33.8 Hz), 146.2, 144.1, 128.2, 122.6, 117.3 (J=291.2 Hz), 33.5, 29.0.

4.2.2. 1-(4,5-Dimethylcyclohexa-1,4-dien-1-yl)-2,2,2-trifluoroethanone (11). Colourless oil; ν_{max} (film) 1720 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.10 (1H, br s, CH═), 2.90 (2H, br s, CH_2), 2.75 (2H, m, CH_2), 1.65 (3H, s, CH_3), 1.60 (3H, s, CH_3). δ_C (100 MHz, $CDCl_3$) 181.3 (J=33.5 Hz), 146.7, 146.1, 126.2, 121.2, 117.1 (J=291.4 Hz), 34.6, 30.3, 19.7, 17.8.

The reaction of **6a/6a′** with DBU gave a mixture of regioisomers **12a/12b** — 2/1 after purification, yield (171 mg, 90%), colourless oil. The reaction of **6b/6b′** with DBU gave a mixture of regioisomers **12a/12b**—2.5/1 after purification, yield (179 mg, 94%), colourless oil.

4.2.3. 2,2,2-Trifluoro-1-(4-methylcyclohexa-1,4-dien-1-yl)ethanone (12a). ν_{max}(film) 1720 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.10 (1H, br s, CH═), 5.42 (1H, br s, CH═), 2.95–2.65 (4H, m, $2CH_2$), 1.60 (3H, s, CH_3). δ_C (100 MHz, $CDCl_3$) 181.4 (J=33.6 Hz), 146.5, 137.1, 131.0, 118.7, 117.1 (J=291.0 Hz), 32.5, 28.9, 22.6.

4.2.4. 2,2,2-Trifluoro-1-(5-methylcyclohexa-1,4-dien-1-yl)ethanone (12b). ν_{max}(film) 1710 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.10 (1H, br s, CH═), 5.3 (1H, br s, CH═), 2.95–2.65 (4H, m, $2CH_2$), 1.65 (3H, s, CH_3). δ_C (100 MHz, $CDCl_3$) 181.4 (J=33.6 Hz), 146.0, 137.1, 129.6, 118.7, 117.0 (J=291.0 Hz), 32.5, 28.1, 22.0.

4.2.5. 1-Bicyclo[2.2.2]octa-2,5-dien-2-yl-2,2,2-trifluoroethanone (13). White solid; mp 78–80°C; [Found: C, 59.25; H, 4.47. $C_{10}H_9F_3O$ requires C, 59.41; H, 4.49%]; ν_{max}(film) 1715 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.66 (1H, m, CH═), 6.41 (1H, m, CH═), 6.32 (1H, m, CH═), 4.37 (1H, br s, CH), 3.90 (1H, br s, CH), 1.50–1.15 (4H, m, $2CH_2$); δ_C (100 MHz, $CDCl_3$) 176.8 (J=34.2 Hz), 154.2, 140.6, 134.4, 132.9, 116.5 (J=291.6 Hz), 38.5, 34.9, 24.1, 24.0.

4.2.6. 1-[1,8-Dimethyl-16-en-tetracyclo[6.6.2.0^{2,7}.0^{9,14}]-hexadeka-2,4,6,10,12,14-hexa en-15-yl]-2,2,2-trifluoro-1-ethanone (14). Yellow solid; mp 102–107°C; [Found: C, 73.23; H, 4.51. $C_{20}H_{15}F_3O$ requires C, 73.16; H, 4.60%]; ν_{max} (film) 1715 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.81 (1H, s, CH═), 7.40–67.0 (8H, m, arom.), 2.48 (3H, s, CH_3), 2.26 (3H, s, CH_3); δ_C (100 MHz, $CDCl_3$) 177.9 (J=34.1 Hz), 163.8, 147.8, 146.2, 146.0, 145.2, 143.8, 125.2, 125.1, 124.9, 124.8, 122.3, 121.1, 120.7, 120.4, 116.0 (J=293.3 Hz), 50.7, 49.9, 15.2, 14.4.

Compounds **15–17** was obtained from corresponding cycloadducts **4–6** in air conditions. The product was purified by column chromatography over silica gel using hexane as eluent. The proton NMR data were in agreement with the literature.[22]

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