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An efficient synthesis of 3-trifluoromethylated 8-oxabicyclo[3.2.1]octa-2,6-dienes

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Abstract—The rhodium(II) acetate catalyzed decomposition of 3-trifluoromethylated vinyldiazomethanes **3** in the presence of furans resulted in the formation of a series of 3-trifluoromethylated 8-oxabicyclo[3.2.1]octa-2,6-dienes. The 4-substituent on the vinyldiazomethanes had great effects on the product distribution and the stereo- and regiochemistry of the [3+4] annulation products. The rhodium(II) acetate catalyzed reaction of 4-carbonyl substituted vinyldiazomethanes **3a–c** with furans resulted in cyclopropenes and [3+4] annulation products, while in the case of cyano-substituted vinyldiazomethanes **3d**, only cycloaddition products were obtained. The reaction was presumed to follow a tandem cyclopropanation/Cope rearrangement mechanism.

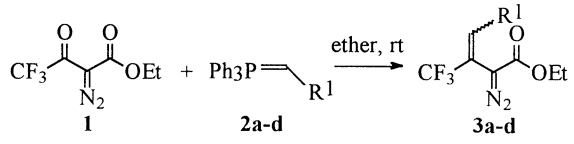
1. Introduction

Growing interest in trifluoromethylated organic compounds in various fields such as medicines, pharmaceuticals and fluoropolymers has led to greater impetus in the quest for facile methods for the introduction of trifluoromethyl groups so as to give useful intermediates or desired substrates.[1] Direct transformations of certain functional groups to the CF_3 group have been employed, while for the synthesis of trifluoromethylated aromatic compounds,[2] however, new approaches that allow access to trifluoromethylated aliphatic compounds under mild conditions and with a wide tolerance different of functionalities are still highly desirable although only a limited number of intermediates are known as useful CF_3-containing building blocks.[3] Therefore, the development of a simple method for the preparation of the trifluoromethylated building blocks and their further utilization for the synthesis of desired CF_3-containing aliphatic compounds are essential to organofluorine chemistry. In the search for new CF_3-containing building blocks, we pay much attention to the wide utilities of rhodium(II)-stabilized vinylcarbenoids.[4] Recent research by Davies Huw M. L. and co-workers found that a formal [3+4] cycloaddition reaction between vinylcarbenes and dienes represented a general and stereoselective method for the synthesis of seven-membered rings.[4] Furthermore, rhodium(II) carboxylate catalyzed decomposition of vinyldiazomethanes in the presence of furans and pyrroles resulted in a general synthesis of 8-oxabicyclo[3.2.1]octa-2,6-diene and tropane derivatives, respectively.[5]

Although the synthesis of stable trifluoromethylated vinyldiazomethanes **3** had been previously reported in 1995, their reaction as carbene precursors in the presence of rhodium(II) acetate has not been reported till now,[6] so our objective is to exploit their reactivities as vinylcarbenoid precursors and use these vinyldiazomethanes to synthesize various trifluoromethyl-containing heterocycles. Since stereochemically well-defined bicyclic derivatives have been extensively used as building blocks for the synthesis of natural products,[5b,7] their trifluoromethylated analogues should have synthetic value. In this paper, we report an efficient synthesis of 3-trifluoromethylated 8-oxabicyclo-[3.2.1]octadienes from the reaction of 3-trifluoromethylated vinyldiazomethanes **3a–d** with 2,5-dimethylfuran **4a** and 2-butylfuran **4b**.

2. Results and discussion

3-Trifluoromethylated vinyldiazomethanes **3** could be readily synthesized by the reaction of 1,1,1-trifluoro-3-diazoacetoacetate **1** with stabilized Wittig reagents **2** in diethyl ether (Scheme 1).[6] One single *E*-isomer was obtained from **2a–c** whilst **2d** gave an isomeric mixture of



1 **2a-d** **3a-d**

Scheme 1. R^1=CO_2Et (**2a**); CO_2Me (**2b**); COMe (**2c**); CN (**2d**).

Keywords: trifluoromethyl; vinyldiazo compounds; furans; carbenoids; rhodium(II) acetate; [3+4] annulation.

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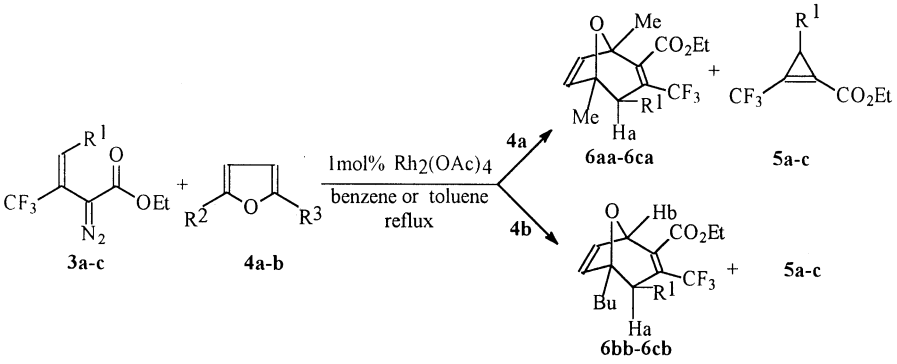


Scheme 2. **3a**: R^1=CO_2Et; **3b**: R^1=CO_2Me; **3c**: R^1=COMe; **4a**: R^2=R^3=Me; **4b**: R^2=H, R^3=Bu.

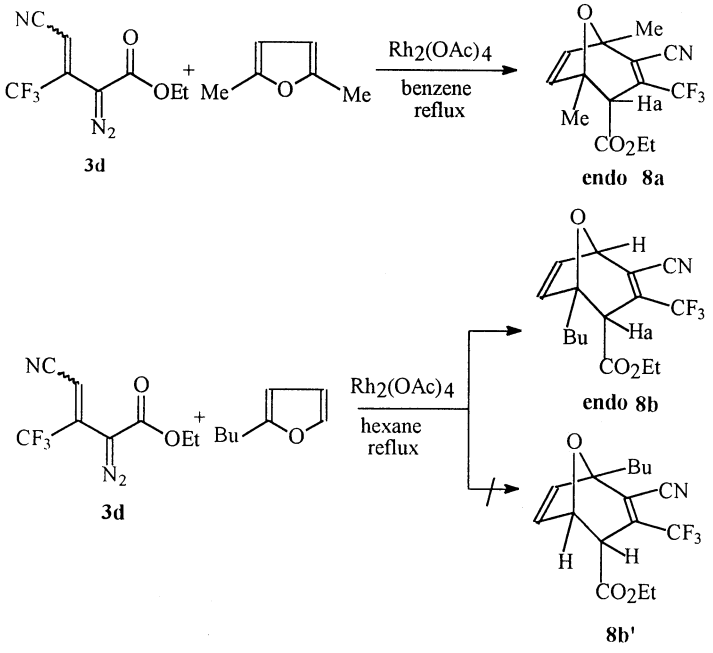
both *E* and *Z* olefins. Although it was well known that non-fluorinated vinyldiazomethanes tended to rearrange spontaneously to 3*H*-pyrazoles,[8] the trifluoromethyl analogues **3a–d** were indefinitely stable at 25°C. That was probably due to the fact that the two adjacent electron withdrawing groups, trifluoromethyl and ethoxycarbonyl, greatly stabilized the vinyldiazomethanes and inhibited the formation of 3*H*-pyrazole.[9]

We first attempted the rhodium(II)-catalyzed reaction of **3a** with furans, and found that **3a** reacted smoothly and cleanly with 2,5-dimethylfuran **4a** and 2-butylfuran **4b** in refluxing benzene giving the desired [3+4] annulation products **6aa°6ab** and intramolecular rearranged cyclopropene **5a** in the presence of 2 mol% of $Rh_2(OAc)_4$. Correspondingly, rhodium(II)-catalyzed reactions of other 4-carbonyl substituted vinyldiazomethanes **3b**,**c** with furans **4a**,**b** gave similar results (Scheme 2). The reaction of **3c** needed to be performed in refluxing toluene because the stronger electron-withdrawing ability of 4-acetyl made the vinyldiazomethane **3c** more stable. Previously, reports in the literature have stared that rhodium(II)-carbenoids derived from

Table 1. $Rh_2(OAc)_4$ catalyzed reaction of vinyldiazomethanes with furans

Entry	Vinyldiazo compounds	Furans	Solvent	Temperature	Time (h)	Product yield (%)[a]
1	**3a**	**4a**	Toluene	100°C	16	**5a** (45), **6aa** (52)
2	**3b**	**4a**	Benzene	Reflux	14	**5b** (38), **6ba** (43)
3	**3c**	**4a**	Benzene	Reflux	19	**5c** (45), **6ca** (45)
4	**3d**	**4a**	Benzene	Reflux	13	**8a** (90)
5	**3b**	**4b**	Benzene	Reflux	16	**5b** (40), **6bb** (36)
6	**3c**	**4b**	Toluene	Reflux	17	**5c** (40), **6cb** (43)
7	**3d**	**4b**	Hexane	Reflux	12	**8b** (85)

[a] Yield of isolated product.



Scheme 3.

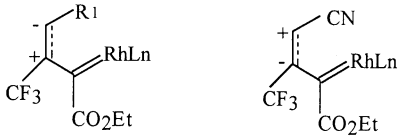


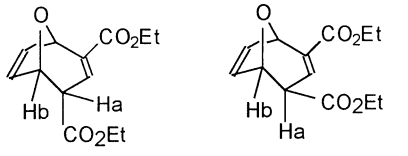
Figure 1. R_1=CO_2Et, CO_2Me, COMe.

vinyldiazomethanes could rearrange to cyclopropene derivatives,[10] but in the presence of furans only [3+4] annulation products were formed and no cyclopropenes were detected.[10a] To the best of our knowledge, this was the first time that the cyclopropenation products could be isolated and identified in the reaction of vinyldiazomethanes with furans. The formation of the cyclopropene was probably due to the fact that steric hindrance of trifluoromethyl groups disfavored intermolecular addition reaction.[10]

However, rhodium(II) acetate catalyzed reactions of **3d** with 2,5-dimethylfuran and 2-butylfuran lead to different results. Only cycloadduct **8a**,**b** was isolated in high yields (Table 1), but no rearranged cyclopropene was observed. Pure **8b** could be obtained by recrystallizing from diethyl ether and petroleum ether since it decomposed partially upon purification by column chromatography (Scheme 3). The reaction results were summarized in Table 1 and all of these new trifluoromethyl-containing compounds were fully characterized by NMR, IR, MS and EA.

The data in Table 1 shows that the 4-substitutent on vinyldiazomethanes has dramatic effects on the product distribution. We ascribe this to the different polarization orientation of double bond of rhodium(II) stabilized carbenoids caused by the different electron-withdrawing ability (COMe>‴ CO_2Me, CO_2Et>CF_3>CN) of the 4-substituent (Fig. 1).[11] In the case of the carbonyl-substituted vinyldiazomethanes **3a**–**c**, the 3-trifluoromethyl somewhat hindered the intramolecular attack of vinylcarbenoids on the furan. Furthermore, the dipolar orientation also facilitated electrophilic attack of carbenoid on the double bond to produce cyclopropene; so two products were isolated. In the case of 4-cyano substituted vinyldiazomethane **3d**, the dipolar orientation of the double bond unfavored intramolecular rearrangement of rhodium(II) carbenoid, consequently, only [3+4] annulation products were obtained.

X-Ray diffraction analysis of the product **8a** showed that it was in a 4-*endo* conformation (Fig. 3). The [3+4] annulation product of **3d** with 4-butylfuran was determined as **8b** as assignment based on the following facts (Scheme 3). The



7a endo — J_{HaHb} = 5.8 Hz — 4 - Ha δ = 3.79 ppm

7b exo — J_{HaHb} = 0 Hz — 4 - Ha δ = 2.81 ppm

Figure 2.

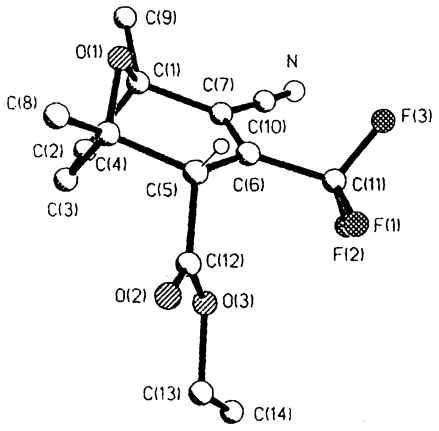


Figure 3. The X-ray crystal structure of **8a**.

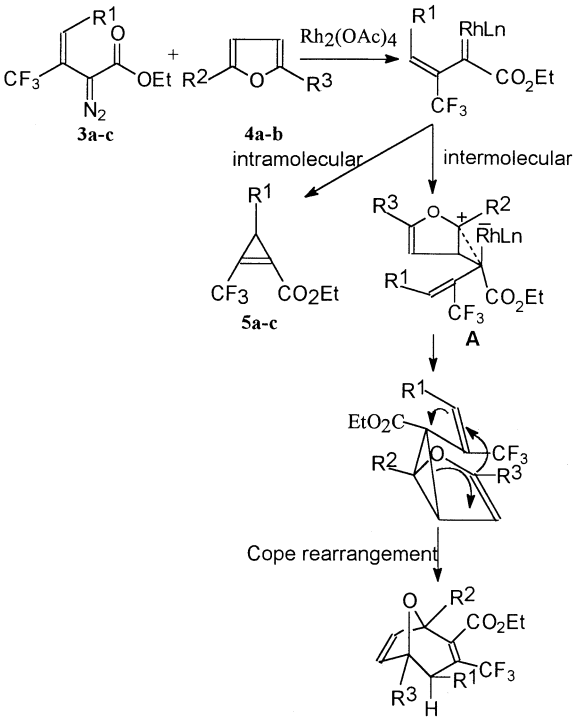
IR spectrum showed a strong resonance for a conjugated cyano group absorption at 2221 cm^{-1}. Comparison of the NMR data with that of the related compound such as **7a** and **b** was also useful (Fig. 2).[9] In the *exo*-isomer **7a**, J_{HaHb}= 0 Hz, while in the *endo*-isomer **7b**, J_{HaHb}=5.8 Hz. The regioisomer as **8b′** was excluded since there was no coupling between the two protons at proton shift 3.60 and 3.20 in the proton NMR of the product **8b**. The proton shift of 4-H (3.60) was approximate to that of **8a** (3.56) determining **8b** as a *endo* product similar to **8a** because *endo*- and *exo*-isomers would exhibit obvious differences generated by the shielding effect of the furan ring.[9]

There existed two problems about the determination of the stereochemistry of **6aa**–**6cb**, the regioisomer of the double bond and the stereochemistry of Ha. These two problems were solved by careful analysis of their spectroscopic data and comparing the data with that of the related compounds **8a**,**b** and **7a**,**b**. Selected ^{1}H NMR and ^{19}F NMR data for **6aa**–**6cb** and **8a**,**b** are summarized in Table 2. First, all the IR spectra of **6aa**–**6cb** indicated the carbonyl frequency of a conjugated ester at 1716–1730 cm^{-1}, and the IR spectra of **6ca** and **6cb** exhibited no frequency for unsaturated ketone at 1650–1700 cm^{-1}, so there should exist a double bond between trifluoromethyl and ester group. Secondly, the proton shift of Ha in **6aa**–**6cb** appeared at 3.19–3.22 ppm, nearly 0.3 ppm upfield (300 MHz, $CDCl_3$) than that of **8a**,**b** (Table 2), which indicated that **6aa**–**6cb** adopted *exo* configurations,[9] since in the related compounds **7a** and **b**, Ha of the *exo* isomer **7a** appears at higher field from that of the *endo* isomer **7b** due to the shielding effect of the double

Table 2. Selected ^{1}H NMR and ^{19}F NMR data for derivatives **6aa**–**6cb** and **8a**,**b**

Compounds	^{1}H NMR (ppm)[a]	^{19}F NMR (ppm)[b]
6aa	3.22	−21.4
6ba	3.22	−21.4
6ca	3.22	−21.7
6bb	3.19	−21.1
6cb	3.20	−21.4
8a	3.56	−15.6
8b	3.60	−16.0

[a] ^{1}H NMR (300 MHz, $CDCl_3$) of Ha.
[b] ^{19}F NMR (56.4 MHz, $CDCl_3$) with CF_3CO_2H as an external signal.



Scheme 4. 4a: R^2=R^3=Me; **4b**: R^2=H, R^3=Bu.

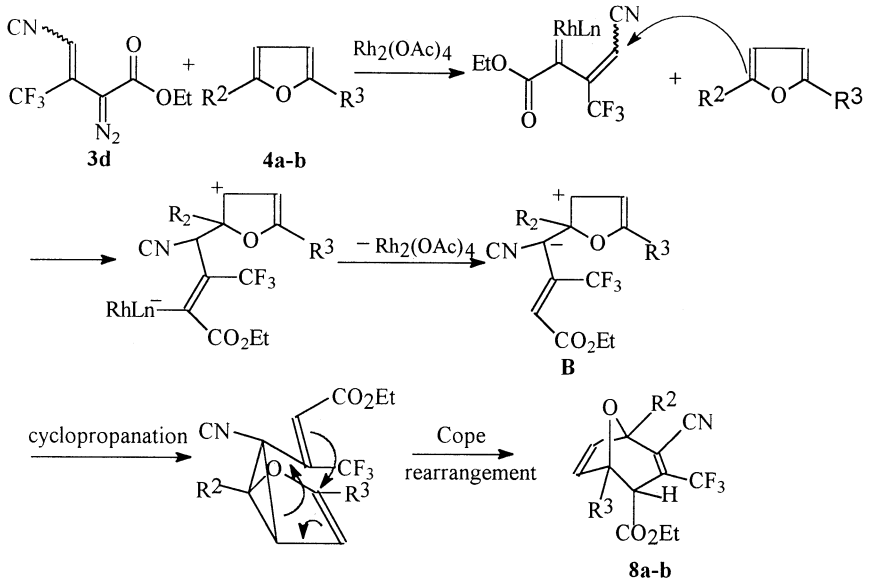
bond derived from the furan. All the cycloadducts **6aa**–**6ca** are determined as *exo* isomers since the proton chemical shifts of H-a were very close to each other (Table 2).

The mechanism of [3+4] annulation reactions of 4-carbonyl substituted vinydiazomethanes **3a**–**c** with furans was anticipated as shown in Scheme 4. The stable rhodium(II) carbenoids could proceed via two reaction pathways. One was rearrangement to cyclopropenes **5a**–**c**, while the other was that the carbenoid terminus attacked at the less hindered position of furans followed by cyclopropanation to produce intermediate **A**, which then underwent Cope rearrangement to afford [3+4] annulation products **6aa**–**6cb**. This tandem cyclopropanation/Cope rearrangement mechanism had been previously demonstrated in lots of studies.[4,5]

The reactions of **8a** and **b** with furans occurred through a different pathway (Scheme 5). Unlike the reaction mechanism of **6a**–**c**, the carbenoid produced from **3d** was nucleophilically attacked by furans on the vinyl terminus which was favored by the polar orientation of double bond (Fig. 1). The resulting zwitterionic structure **B** would undergo a tandem cyclopropanation/Cope rearrangement to generate products **8a**,**b**. Previously, several reports have illustrated that the vinyl terminus of vinylcarbenoid could become susceptible to nucleophilic attack, especially those with no substituent on the vinyl terminus.[12] Using polar solvent and catalyst with an electron-withdrawing ligands also strengthened this trend. However, during our experiments, the vinylogous position of carbenoid became susceptible to nucleophilic attack in nonpolar solvent catalyzed by an ordinary catalyst $Rh_2(OAc)_4$. We assumed that the polar orientation of double bond made the vinyl terminus of the carbenoid somewhat electronically positive and therefore liable to be nucleophilically attacked.

3. Conclusions

In summary, this work provides a practical approach for the synthesis of trifluoromethylated 8-oxabicyclo[3.2.1]octadienes from rhodium(II) acetate catalyzed [3+4] annulation reactions between vinyldiazomethanes and furans. These bicyclic compounds represent valuable building blocks in organic synthesis. Furthermore, the studies also illustrate that the 4-substitutent on the vinyldiazomethanes has great electronic effects on the product distribution and the reaction pathway. The mechanism of the reaction was also discussed and presumed to follow a tandem cyclopropanation/Cope rearrangement mechanism.



Scheme 5. 4a: R^2=R^3=Me; **4b**: R^2=H, R^3=Bu.

4. Experimental

4.1. General

Unless otherwise noted, all manipulations were carried out under an inert atmosphere (dry nitrogen) in flame-dried glassware. All reaction solvents were dried according to literature procedure immediately prior to use.[13] Reagents were purchased from Aldrich or Acros Chemical Co. at the highest grade available and used without further purification unless otherwise noted. The catalyst $Rh_2(OAc)_2$ was prepared using a literature procedure[14] and stored under argon. NMR spectra were recorded as follows: ^1H at 300 MHz, ^{19}F at 56.4 or 300 MHz, all in $CDCl_3$ containing 0.03% TMS. Analytical thin layer chromatography was performed on silica gel plates with an F-254 indicator, and visualization accomplished with UV light, $KMnO_4$ solution. Column chromatography was carried out with silica gel H(10–40 μm).

4.2. Typical experimental procedure for the [3+4] annulation reactions

A solution of **3b** (260 mg, 1 mmol) in benzene (1.5 mL) was added to a stirring, refluxing solution of $Rh_2(OAc)_4$ (9 mg, 2 mol%) in a mixture of 2,5-dimethylfuran (0.53 mL, 10 mmol) and benzene (5 mL) during 6 h. The resulting solution was heated for another 8 h at refluxing until ^{19}F NMR indicated completion of the reaction. Solvent was removed in vacuum and the residue was chromatographed on silica gel using light petroleum (60–90°C)–ethyl acetate (20:1) as eluent, giving a pale yellow liquid **5b** (90 mg, 38%) and light yellow liquid 6ba (144 mg, 43%).

4.2.1. Ethyl (*E*)-2-diazo-4-methoxycarbonyl-3-trifluoromethylbut-3-enoate (3b). Bright-yellow liquid. ^1H NMR ($CDCl_3$) δ 6.46 (s, 1H), 4.22 (q, 2H, J=7.0 Hz), 3.84 (s, 3H), 1.40 (t, 3H, J=7.0 Hz). ^{19}F NMR ($CDCl_3$) δ −12.3 (s, 3F). IR (neat) cm^{-1}: 2112, 1715, 1370–1144. MS *m/z* (EI) 238 (M^+-N_2, 33), 193 (M^+-N_2–OEt, 26), 179 (M^+-N_2–CO_2Me, 100). Anal. calcd for $C_9H_9N_2F_3O_4$: C, 40.60; H, 3.38; N, 10.52. Found: C, 40.89; H, 3.55; N, 10.22.

4.2.2. Diethyl 2-trifluoromethylcyclopropene-1,3-dicarboxylate (5a). Pale-yellow liquid. ^1H NMR ($CDCl_3$) δ 5.47 (s, 1H), 4.12–4.44 (m, 4H), 1.24–1.54 (m, 6H). ^{19}F NMR ($CDCl_3$) δ −19.4 (s, 3F). IR (neat) cm^{-1}: 1725, 1560, 1330–1100. MS *m/z* (EI) 252 (M^+, 22), 207 (M^+–OEt, 11), 179 (M^+–CO_2Et, 35). Anal. calcd for $C_{10}H_{11}O_4F_3$: C, 47.62; H, 4.37. Found: C, 47.52; H, 4.47.

4.2.3. Diethyl 1,5-dimethyl-3-trifluoromethyl-8-oxabicyclo[3.2.1]octa-2,6-diene-2,4-dicarboxylate (6aa). Pale-yellow liquid. ^1H NMR($CDCl_3$) δ 6.08 (d, 1H, J=5.4 Hz), 5.99 (t, 1H, J=2.5 Hz), 4.20 (m, 4H), 3.22 (s, 1H), 1.63 (s, 3H), 1.62 (s, 3H), 1.28 (m, 6H). ^{19}F NMR ($CDCl_3$) δ −21.4 (s, 3F). IR (neat) cm^{-1}: 1743, 1730, 1448, 1429, 1344–1184. MS *m/z* (EI) 349 (MH^+, 17), 303 (M^+−OEt, 42), 43 ($C_3H_7^+$, 100). Anal. calcd for $C_{16}H_{19}O_5F_3$; C, 55.17; H, 5.46. Found: C, 55.06; H, 5.41.

4.2.4. Ethyl 1-trifluoromethyl-3-methoxycarbonylcyclopropene-2-carboxylate (5b). Pale-yellow liquid. ^1H NMR ($CDCl_3$) δ 5.59 (s, 1H), 4.40 (q, 2H, J=7.0 Hz), 4.0 (s, 3H), 1.37 (t, 3H, J=7.0 Hz). ^{19}F NMR ($CDCl_3$) δ −19.2 (s, 3F). IR (neat) cm^{-1}: 1720, 1562, 1320–1100. MS *m/z* (EI) 238 (M^+, 71), 193 (M^+−OEt, 74), 166 (MH^+-CO_2Et, 100). Anal. calcd for $C_9H_9O_4F_3$: C, 45.38; H, 3.78. Found: C, 45.23; H, 3.69.

4.2.5. Ethyl 1,5-dimethyl-3-trifluoromethyl-4-methoxycarbonyl-8-oxabicyclo[3.2.1]octa-2,6-diene-2-carboxylate (6ba). Pale-yellow liquid. ^1H NMR ($CDCl_3$) δ 6.49 (m, 1H), 6.61 (d, 1H, J=5.4 Hz), 4.17 (q, 2H, J=7.0 Hz), 3.22 (s, 1H), 3.7 (s, 3H), 1.61 (s, 3H), 1.60 (s, 3H), 1.22 (t, 3H, J=7.0 Hz). ^{19}F NMR ($CDCl_3$) δ −21.4 (s, 3F). IR (KBr) cm^{-1}: 1747, 1730, 1440, 1388–1159. MS *m/z* (EI) 335 (MH^+, 39), 289 (M^+−OEt, 34), 96 ($C_6H_8O^+$, 100). Anal. calcd for $C_{15}H_{17}O_5F_3$: C, 53.57; H, 5.06. Found: C, 53.71; H, 5.00.

4.2.6. Ethyl 1-trifluoromethyl-3-acetylcyclopropene-2-carboxylate (5c). Pale-yellow liquid. ^1H NMR ($CDCl_3$) δ 6.32 (s, 1H), 4.40 (q, 2H, J=7.0 Hz), 2.40 (s, 3H), 1.35(t, 3H, J=7.0 Hz,). ^{19}F NMR ($CDCl_3$) δ −19.6 (s, 3F). IR(neat) cm^{-1}: 1729, 1414, 1324–1122. MS *m/z* (EI) 223 (M^+H, 67), 222 (M^+, 79), 177 (M^+−OEt, 100). Anal. calcd for $C_9H_9O_3F_3$: C, 48.65; H, 4.05. Found: C, 48.67; H, 4.13.

4.2.7. Ethyl 5-dimethyl-3-trifluoromethyl-4-acetyl-8-oxabicyclo[3.2.1]octa-2,6-diene-2-carboxylate (6ca). Pale-yellow liquid. ^1H NMR ($CDCl_3$) δ 6.38 (m, 1H), 6.56 (d, 1H, J=5.4 Hz), 4.12 (q, 2H, J=7.0 Hz), 3.22 (s, 1H), 2.25 (s, 3H), 1.53 (s, 6H), 1.13 (t, 3H, J=7.0 Hz). ^{19}F NMR ($CDCl_3$) δ −21.7 (s, 3F). IR (neat) cm^{-1}: 1716, 1449, 1440, 1388–1186. MS *m/z* (EI) 319 (MH^+, 95), 245 (M^+-CO_2Et, 16), 43 ($C_3H_7^+$, 100). Anal. calcd for $C_{15}H_{17}O_4F_3$: C, 56.60; H, 5.35. Found: C, 56.30; H, 5.33.

4.2.8. Ethyl 1,5-dimethyl-3-trifluoromethyl-2-cyano-8-oxabicyclo[3.2.1]octa-2,6-diene-4-carboxylate (8a). White solid, mp 74–76°C. ^1H NMR ($CDCl_3$) δ 6.30 (d, 1H, J=5.7 Hz), 5.70 (d, 1H, J=5.4 Hz), 4.11 (q, 2H, J=7.0 Hz), 3.45 (s, 1H), 1.72 (s, 3H), 1.70 (s, 3H), 1.19 (t, 3H, J=7.0 Hz). ^{19}F NMR ($CDCl_3$) δ −15.6 (s, 3F). IR (neat) cm^{-1}: 2221, 1729, 1621, 1389–1137. *m/z* (EI) 301 (M^+, 2), 227 (M^+-CO_2Et, 7), 43 ($C_3H_7^+$, 100). Anal. calcd for $C_{14}H_{14}NO_3F_3$: C, 55.81; H, 4.65; N, 4.65. Found: C, 55.93; H, 4.64; N, 4.63.

4.2.9. Ethyl 5-butyl-3-trifluoromethyl-4-methoxycarbonyl-8-oxabicyclo[3.2.1]octa-2,6-diene-2-carboxylate (6bb). Pale-yellow liquid. ^1H NMR ($CDCl_3$) δ 6.63 (t, 1H), 6.57 (d, 1H, J=5.6 Hz), 4.89 (d, 1H, J=1.4 Hz), 4.17 (t, 2H, J=7.0 Hz), 3.74 (s, 3H), 3.19 (s, 1H), 1.30–1.53 (m, 6H), 1.23 (t, 3H, J=7.0 Hz), 0.92 (t, 3H, J=7.0 Hz). ^{19}F NMR ($CDCl_3$) – −20.9 (s, 3F). IR (neat) cm^{-1}: 1747, 1740, 1635, 1184–1353. MS *m/z* (EI) 363 (MH^+, 22), 331 (M^+−OMe, 38), 317 (M^+−OEt, 30), 288 (M^+-1-CO_2Et, 52). Anal. calcd for $C_{15}H_{17}O_5F_3$: C, 56.35; H, 5.80. Found: C, 56.44; H, 6.07.

4.2.10. Ethyl 5-butyl-3-trifluoromethyl-4-methylcarbonyl-8-oxabicyclo[3.2.1]octa-3,6-diene-2-carboxylate (6cb). White solid, mp 28–29°C. ^1H NMR ($CDCl_3$) δ 6.61 (dd, 1H, J=4.6, 2.0 Hz), 6.56 (d, 1H, J=5.6 Hz), 4.89 (d,

1H, J=1.4 Hz), 4.18 (q, 2H, J=7.1 Hz), 3.29 (s, 1H), 2.31 (s, 3H), 1.29–1.55 (m, 6H), 1.22 (t, 3H, J=7.0 Hz), 0.92 (t, 3H, J=7.0 Hz). ^{19}F NMR ($CDCl_3$) δ −21.4 (s, 3F). IR (KBr) cm^{-1}: 1722, 1419, 1084–1317. MS m/z (EI) 347 (MH^+, 7), 289 (M^+-OEt, 19), 43 ($MeCO^+$, 100). Anal. calcd for $C_{17}H_{21}O_4F_3$: C, 58.96; H, 6.07. Found: C, 59.04; H, 6.10.

4.2.11. Ethyl 5-butyl-2-cyano-3-trifluoromethyl-8-oxabicyclo[3.2.1]octa-2,6-diene-2-carboxylate (8b). White solid, mp 67–69°C. ^{1}H NMR ($CDCl_3$) δ 6.66 (dd, 1H, J=5.8, 1.9 Hz), 6.47 (d, 1H, J=5.8 Hz), 5.34 (d, 1H, J=1.9 Hz), 4.28 (q, 2H, J=7.0 Hz), 3.60 (s, 1H), 2.17 (s, 1H), 1.25–1.52 (m, 9H), 0.94 (t, 3H, J=7.0 Hz). ^{19}F NMR ($CDCl_3$) δ −16.1 (s, 3F). IR (KBr) cm^{-1}: 2221, 1737, 1623, 1144–1348. MS m/z (EI) 330 (MH^+, 3), 329 (M^+, 5). Anal. calcd for $C_{16}H_{18}NO_3F_3$: C, 58.36; H, 5.47; N, 4.26. Found: C, 58.24; H, 5.69; N, 4.22.

5. Supplementary material

Further details on the structure are available on request from Cambridge Crystallographic Data Center, 12 Union Road, Cambridge, UK on quoting the depository number CCDC 158451.

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