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Influence of an Internal Trifluoromethyl Group on the Rhodium(II)-Catalyzed Reactions of Vinyldiazocarbonyl Compounds

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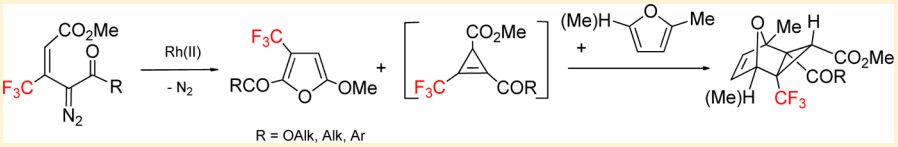
Supporting Information



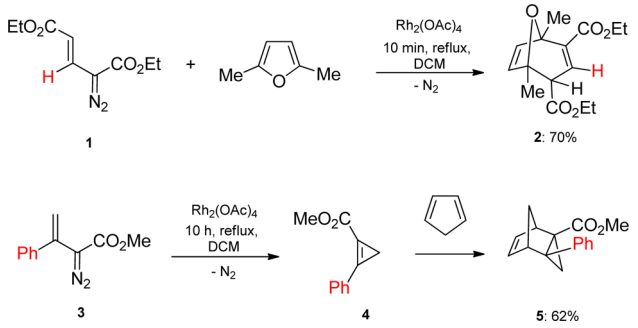
ABSTRACT: Incorporation of a trifluoromethyl group into the structure of 4-(alkoxycarbonyl)vinyldiazocarbonyl compounds greatly decreases the tendency of the carbenoid intermediates formed during Rh(II)-catalyzed reactions to undergo *intermolecular* processes. Instead, they are prone to experience *intramolecular* [1,5]- and [1,3]-electrocyclizations to produce reactive cyclopropenes and furans, and these are capable of further transformations.

INTRODUCTION

Vinyldiazocarbonyl compounds are broadly useful synthons and have been applied to the synthesis of a number of natural and biologically active compounds.[1a−d] The Davies group has demonstrated that one of the synthetically most useful reactions of vinyldiazocarbonyl compounds is their interaction with unsaturated substrates, such as alkenes, alkynes and dienes.[2] Even though with most rhodium-stabilized vinylcarbenoids the reactive site is the carbenoid center, it is possible to cause the carbenoid to display a different reactivity profile. Introduction of a bulky ester substituent or having no substituent at the vinyl terminus can cause attack to occur at the vinylogous position of the vinylcarbenoid, whereas introduction of a bulky internal substituent blocks intermolecular reactions at both the carbenoid and the vinylogous position.[3a,b,4] This behavior has been illustrated in the reaction of vinyldiazocarbonyl compounds with cyclic dienes, such as furan and cyclopentadiene (Scheme 1). Reactions of internally unsubstituted vinyldiazocarbonyl compounds **1** generate [3.2.1]bicyclic products **2** derived from tandem cyclopropanation/Cope rearrangement. In contrast, the reaction of the 3-phenyl-substituted diazocarbonyl **3** generates the cyclopropene **4**, which is rapidly trapped by cyclopentadiene to form the tricyclic product **5**.

The impetus for the collaborative study between the Nikolaev and the Davies groups described herein, arose from attempts to understand the apparently inconsistent reports on the reaction between trifluoromethyl-susbstituted vinyldiazocarbonyl derivatives with furans. The trifluoromethyl group would be expected to sterically limit attack of the furan at the carbene site, leading to greater preference for the formation of cyclopropene derivatives. Zhu and co-workers reported that

Scheme 1. Divergent Reaction Pathways of Vinyldiazocarbonyl Compounds with Cyclic Dienes



trifluoromethyl-substituted 4-(alkoxycarbonyl)vinyl diazoacetate **6** on reaction with 2,5-dimethylfuran gave rise to 8-oxa[3.2.1]bicyclooctadiene **7** and cyclopropene **8** (Scheme 2).[5] The [3.2.1]bicyclic compound **7** would be the expected product of a tandem cyclopropanation/Cope rearrangement between the vinylcarbenoid and the 2,5-dimethylfuran. The relative configuration of the assigned isolated compound **7** was not unambiguously established by the authors [5]; however, according to their speculations they assumed the Cope rearrangement product **7** has to possess an *exo*-configuration.

Nikolaev and co-workers reported that trifluoromethyl-substituted 4-(alkoxycarbonyl)vinyldiazoketones **9** revealed distinctly different reactivity under comparable reaction conditions.[6] In the presence of 2,5-dimethylfuran the only isolable products were the tricyclic derivatives **10** and the 2,3,5-

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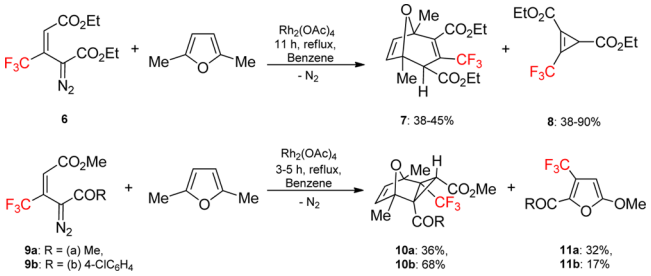
Scheme 2. Reaction of Fluorinated Vinyldiazoacetate 6 and Vinyldiazoketones 9 with 2,5-Dimethylfuran



trisubstituted furans **11** (Scheme 2). The tricyclic adducts **10** would be the expected products of the [4 + 2] cycloaddition between the furan and the cyclopropenes derived from the vinylcarbenoids. In the Zhu example, the cyclopropene is apparently isolable but in the Nikolaev case, the initially formed cyclopropene is trapped by the 2,5-dimethylfuran. In order to understand these apparent inconsistencies, we decided to reanalyze the reactions of trifluoromethyl-substituted 4-(alkoxycarbonyl)vinyldiazocarbonyl derivatives with furans.

RESULTS AND DISCUSSION

The study began by exploring the reaction of vinyl diazoacetate **12**, the methyl ester derivative of the vinyl diazoacetate **6** used by Zhu. The reaction was conducted in cyclohexane as solvent in the absence of a furan trapping agent (Scheme 3). Dirhodium tetraacetate (2 mol %) catalyzed decomposition of the vinyl diazoacetate **12** required relatively vigorous conditions (10 h at 80 °C). This is quite different from nonfluorinated vinyl diazoacetates, which typically react in the presence of a rhodium catalyst at room temperature or below.[3a,b]

Two products were isolated in this reaction, the furan **13** and the tricyclic product **15**, presumably derived from a cycloaddition between the furan **13** and the cyclopropene **14**. The structures of **13** and **15** were confirmed using ^{1}H, ^{13}C, ^{19}F NMR spectroscopy and mass spectrometry. In addition, the structure of compound **15** was unambiguously determined by X-ray crystallographic analysis (the ORTEP Figure 1 for the compound **15** is available in the Supporting Information). The X-ray data also demonstrated that cycloaddition between cyclopropene **14** and the furan **13** occurred stereoselectively to produce only one stereoisomer of tricyclic product **15** with *endo*-configuration[4,7] and regioselectively giving rise to only one regioisomer that had the CF_3 group adjacent to carbon atom C^3 bearing the least bulky substituent (OMe).

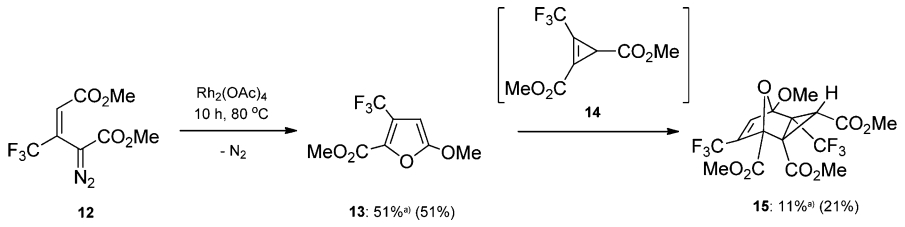
The next series of experiments examined the reaction of vinyl diazoacetate **12** in the presence of 2,5-dimethylfuran. These reactions were carried out with three different catalysts, dirhodium tetraacetate, dirhodium tetraoctanoate, and the chiral catalyst Rh_2(*S*-DOSP)$_4$ (Table 1).

When the reaction was carried out with 2 mol % of catalyst, dirhodium tetraacetate gave a different result to the other two catalysts. The reaction catalyzed by dirhodium tetraacetate gave a mixture of the furan **13** and the cyclopropene cycloadduct **16**, whereas the reaction catalyzed by either dirhodium tetraoctanoate or Rh_2(*R*-DOSP)$_4$ gave only the furan **13**. Dirhodium tetraacetate was only sparingly soluble under the reaction conditions, and it is well-established that dirhodium complexes are capable of catalyzing the rearrangement of cyclopropenes to furans.[10,11] Therefore, as a control experiment, the dirhodium tetraoctanoate catalyzed reaction was repeated with 0.2 mol % of catalyst, and under these conditions a mixture of the furan **13** and the cyclopropene cycloadduct **16** was formed. None of these reactions showed any evidence for the formation of the 8-oxa[3.2.1]bicyclooctane products similar to **8**.[5]

One more series of experiments explored the dirhodium tetraacetate catalyzed reactions of the vinyldiazoketones **9** with furans (Scheme 4). The reactions of **9a** and **9b** with 2,5-dimethylfuran were confirmed[6] to generate a mixture of the cycloadducts **10a** and **10b** and furans **11a** and **11b**, respectively. Similarly, the reaction of the *tert*-butyl vinyldiazoketone **9c** gave a mixture of cycloadduct **10c** and furan **11c**. All three vinyldiazoketones **9a–c** gave similar results in the dirhodium tetraacetate catalyzed reactions with 2-methylfuran. A mixture of the furan **11** and the cycloadduct **17** was formed in each case.

In order to confirm unequivocally the structural assignments of the products, the structures of several products (**10a**, **10b**, **11a**, and **17b**) were established by X-ray crystallography (the ORTEP Figures 2–5 for the compounds **10a**, **10b**, **11a**, and **17b** are available in the Supporting Information). The Diels–Alder cycloaddition between the cyclopropene and 2-methylfurans form **17b** as a single regioisomer, in which the bulky CF_3 group is adjacent to the C^5-H from the furan. A pronounced heteronuclear NOE by the CF_3-group to the adjacent position revealed that **17a** and **17c** had the same regiochemical arrangement as **17b**. Usually, the *exo,endo*-stereoselectivity in the Diels–Alder reactions of cyclopropenes with dienes is a function of different variables,[3b,4,8a–c] beginning from the nature and steric bulk of substituents in the structure of cyclopropene and/or diene[3b,4,8a] and up to the pivotal role of the reaction conditions used.[8b,c] Similar to observations by the other authors,[8c] high *endo*-stereoselectivity of the cyclopropenes **18** (Scheme 5) cycloadditions with furans, established in our reactions, is apparently derived from lesser steric repulsion between CF_3- or COR^2 group of cyclopropene **18** and Me-

Scheme 3. Catalytic Decomposition of the Vinyldiazoacetate 12 in the Absence of Trapping agent[a]



[a]Yield of isolated product. The yields determined by ^{1}H NMR spectroscopy are given in parentheses.

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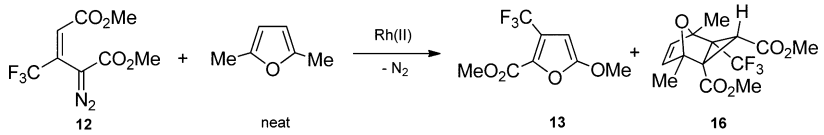
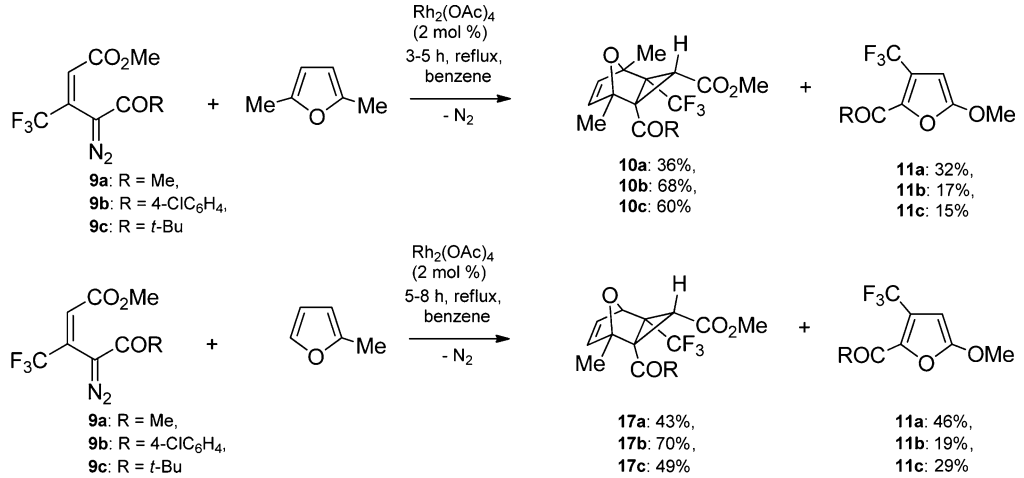
Table 1. Influence of Catalyst Type on Decomposition of Vinyldiazoacetate 12



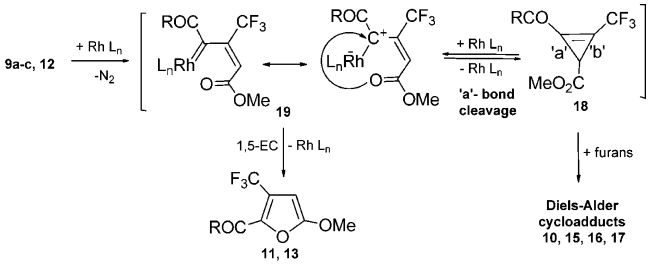
entry	Rh(II)	catalyst loading (mol %)	yield[a] (%) 13	yield[a] (%) 16	procedure
1	$Rh_2(OAc)_4$	2	30 (31)	30 (35)	a
2	$Rh_2(OAc)_4$	2	37 (38)	16 (16)	b
3	$Rh_2(OOct)_4$	2	64	0	a
4	Rh_2(*S*-DOSP)$_4$	2	47 (58)	0	a
5	$Rh_2(OOct)_4$	0.2	(32)	(11)	a

[a]Yields of isolated products. The yields determined by ^{1}H NMR are listed in parentheses. (Rh_2(*S*-DOSP)$_4$ = tetrakis[1-[[4-alkyl(C_{11}–C_{13})phenyl]sulfonyl]-(2*S*)-pyrrolidinecarboxylate]dirhodium(II)).

Scheme 4. Reactions of the Vinyldiazoketones 9 with Furans



Scheme 5. Mechanistic Proposals for Catalytic Decomposition of Fluorinated Vinyldiazoketones 9 and 12 with Furans



groups of furans **3c,d** in the *endo*-activated complex as compared to the *exo*-isomer.

Having obtained a definitive structural assignment for the furan **11a** by X-ray crystallography, a spectral comparison was made between the assigned furan products **11a–c** and **13** and the assigned "cyclopropene **8**".[5] The basic spectral characteristics (^{1}H and ^{13}C) of the furans **11a–c** and **13** are very consistent (Table 2). Most diagnostic is the furan proton C^4-H at 5.59–5.73 that is in the typical range for furans[14a–d] and quite distinct from the sp^3 proton of a trisubstituted cyclopropene, which is normally localized in the area of 2.25–2.45 ppm.[15a–d] Although only ^{1}H NMR data were available from Zhu's studies,[5] the values for the "cyclopropene **8**" are very similar to furan **13**. Therefore, it is very likely that a furan product was generated in the above-mentioned research and the compound was missassigned as cyclopropene **8**. Similarly, we saw no evidence for the formation of 8-oxa[3.2.1]bicyclooctadienes and the spectral data reported in the article[5] for the assigned 8-oxa[3.2.1]bicyclooctadienes **7** is very similar to the spectra of the unambiguously assigned cyclopropene cycloadducts **10**, **15**, and **17** observed in this current study.

These studies demonstrate that cyclopropene and furan products are generated in the Rh(II)-catalyzed reactions of the 3-CF_3-vinyl diazoacetate **12** and vinyldiazoketones **9a–c** (Scheme 5). The cyclopropene products **18** are highly reactive under the reaction conditions and undergo a facile [4 + 2] cycloaddition with furans to give Diels–Alder cycloadducts **10**, **15**, **16**, and **17** and are susceptible to dirhodium-catalyzed ring expansion to produce trisubstituted furans **11** and **13**. When typical loadings of catalyst are used (2 mol %) in the presence of a furan trapping agent, only the trisubstituted furan derived from the vinylcarbenoid **19** is isolated. When a low catalyst loading (0.2 mol %) or the sparingly soluble dirhodium tetracetate catalyst is used, the cyclopropene cycloadduct is also obtained. Presumably in the presence of 2 mol % of catalyst cyclopropene **18** formed rearranges to the furan before the cycloaddition can occur but with low catalyst loading, cycloaddition competes with the cyclopropene rearrangement to the trisubstituted furan.

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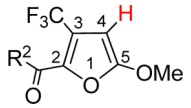
Table 2. Key Parameters of the NMR ^{1}H, ^{13}C, and ^{19}F Spectra (Chemical Shifts) of the Furans 11a−c and 13



11a-c, 13

	^{1}H NMR			^{13}C NMR ($^3J_{C-F}$ or $^4J_{C-F}$)			^{19}F NMR
compd	R^2	C^4-H	OCH_3	C^3-CF_3	C^4-H	CF_3	CF_3
11a	Me	5.63	3.98	124.4 (39.6)	84.2 (4.0)	121.4	−60.1
11b	4-ClC_6H_4	5.73	4.00	126.7 (39.3)	84.1 (3.4)	121.0	−60.3
11c	*t*-Bu	5.60	3.98	125.9 (39.2)	83.8 (br s)	122.4	−60.3
13	OMe	5.59	3.98	125.7 (38.9)	82	120.9	−61.5
"cyclopropene **8**"	OMe	5.59	4.00	NA	NA	NA	NA

Conversion of cyclopropenes into isomeric furans is well-documented process in the transition-metal-catalyzed chemistry of cyclopropenes.[9,12,13] It is assumed that ring-opening of cyclopropene occurs by the attack of electrophilic Rh(II)-catalyst on the carbon atoms C^1 or C^2 of cyclopropene from the less hindered side of the ring, providing the observed regioselectivity of the subsequent cyclization into furan.[14a−c] The most bulky substituent in the structure of the cyclopropenes **C**′ is CF_3-group at the atom C^1 and so attack of the Rh(II)-catalyst has to be directed on the atom C^2 of the carbocycle double bond. The succeeding processes in accordance with the known literature speculations[14a−c] should give rise to predominant formation of the regioisomers **11** and **13**, as was actually demonstrated in the current research.

CONCLUSIONS

The comparison study of Rh(II)-catalyzed reactions of 3-(fluoroalkyl)-containing 4-(alkoxycarbonyl)vinyl diazoacetate **12** and vinyldiazoketones **9a−c** with furans enables us to conclude that reactivity of these diazo compounds is virtually alike and solely intramolecular [1,5]- and [1,3]-cyclizations of intermediate Rh(II)-vinyloxocarbenoids are observed. Introduction of the 3-CF_3-group in the structure of 4-(alkoxycarbonyl)vinyl diazocarbonyl compounds gives rise to a dramatic lowering the tendency of intermediate vinyloxocarbenoids toward intermolecular reactions.

EXPERIMENTAL SECTION

General Methods. ^{1}H, ^{13}C, and ^{19}F NMR spectra were recorded at 200, 300, and 600 MHz (^{1}H), 50, 75, 150 MHz (^{13}C), 188, 282 MHz (^{19}F), and 81 MHz (^{31}P) in $CDCl_3$ solution using TMS, $CHCl_3$, or H_3PO_4 as internal standards. Single crystals of the CF_3-group containing compounds **10a**, **10b**, **11a**, **15**, and **17b** suitable for X-ray diffraction were selected from analytical samples. Crystallographic measurements were made using an IPDS1 diffractometer [graphite monochromated Mo−Kα radiation (λ 0.71073 Å)]. The structures were solved by direct methods using the program *SIR*2002[16a] and were refined using anisotropic approximation for the non-hydrogen atoms using SHELX-90 software.[16b] All hydrogen atoms were calculated and refined in riding modus. CCDC 912997 for **10a**, 912998 for **10b**, 912996 for **11a**, and 912996 for **17b** contain the supplementary crystallographic data. Commercially available catalysts $Rh_2(OOct)_4$ and Rh_2(*S*-DOSP)$_4$ were used without additional purification, $Rh_2(OAc)_4$ from Aldrich was carefully purified and dried or newly prepared according to the known procedure.[17] Fluorinated vinyldiazocarbonyl compounds **12** and **9a−c** were prepared using the described protocols,[18a−d] and cyclohexane, 2-methylfuran, 2,5-dimethylfuran, and benzene were distilled over P_2O_5. All reactions were monitored by thin-layer chromatography (TLC) on the plates Silufol UV/vis 254 nm using UV light and iodine as visualizing agents. Preparative column chromatography was carried out on the neutral silica gel (70−230 mesh) with petroleum (40−70 °C) and diethyl ether as eluents in gradient regime.

*General Procedures of Rh(II)-Catalyzed Reactions of Vinyldiazocarbonyl Compounds **12** and **9a−c** in the Presence of Cyclohexane and 2-Methyl- and 2,5-Dimethylfurans. Procedure **a**.* A mixture of vinyl diazoacetate **12** or diazoketone **9a−c** (1−4 mmol, 1 equiv), Rh_2L_4 catalyst (0.1−2% mol), and furan or cyclohexane (10−40 mmol, 10 equiv) was placed into a flame-dried 20 mL flask and stirred under reflux and argon atmosphere over 1−15 h until ^{1}H, ^{19}F NMR or TLC indicated completion of the reaction. The mixture was concentrated under reduced pressure and separated using flash chromatography (eluent hexane/EtOAc) on silica gel.

*Procedure **b**.* To a flame-dried 10−20 mL flask containing Rh_2L_4 (2% mol) and 2-methylfuran or 2,5-dimethylfuran (10−40 mmol, 10 equiv) in dry benzene (5−10 mL) under argon atmosphere was added a solution of vinyl diazoacetate **12** or diazoketone **9a−c** (1−4 mmol, 1.0 equiv) in dry benzene (3−6 mL) by syringe pump over 3−5 h under reflux. The resulting reaction mixture was heated for an additional 2−5 h under reflux until ^{1}H, ^{19}F NMR or TLC indicated completion of the reaction and then worked up similarly to procedure **a**.

*Rh(II)-Catalyzed Decomposition of Vinyl Diazoacetate **12** in the Presence of Cyclohexane.* The reaction was carried out according to procedure **a** with vinyl diazoacetate **12** (1 g, 4 mmol, 1 equiv), $Rh_2(OAc)_4$ (36 mg, 2% mol), and cyclohexane (4 mL, 40 mmol, 10 equiv) during 10 h at 80−81 °C. After separation of the reaction mixture using column chromatography (eluent hexane/EtOAc) on silica gel (50 g) and recrystallization of the main fractions from hexane with Et_2O furan **13** and tricyclooctane **15** were isolated.

*Methyl 5-Methoxy-3-(trifluoromethyl)-2-furoate (**13**).* Yield: 230 mg (51%). Colorless solid. Mp: 35−36 °C. R_f 0.37 (petroleum ether/Et_2O 3:1). IR (neat): 1728, 1567, 1437 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.59 (s, 1H), 3.98 (s, 3H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 161.8, 157.1, 131.6, 125.7 (q, $^2J_{C-F}$ 38.9 Hz), 120.9 (q, $^1J_{C-F}$ 269.3 Hz), 82.9 (q, $^3J_{C-F}$ 3.0 Hz), 58.3, 52.1. HRMS (ESI-GCT): calcd for $C_8H_8O_4F_3$ $(M + H)^+$ 225.0374, found 225.0398.

*Trimethyl 5-Methoxy-4,7-bis(trifluoromethyl)-8-oxatricyclo-[3.2.1.0^{2,4}]oct-6-ene-1,2,3-tricarboxylate (**15**).* Yield: 120 mg (11%). Colorless solid. Mp: 67−68 °C. R_f 0.20 (hexane/Et_2O 2:1). IR (neat): 1750 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.16−7.13 (m, 1H), 3.90 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 3.61 (s, 3H), 3.21 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 34.6, 43.0 (q, $^2J_{C-F}$ 36.2 Hz), 50.1, 52.8, 53.0, 53.5, 55.1, 82.6, 111.2, 120.4 (q, $^1J_{C-F}$ 270.1 Hz), 123.0 (q, $^1J_{C-F}$ 275.4 Hz), 142.5, 143.9 (q, $^2J_{C-F}$ 38.2 Hz), 162.7, 163.2, 164.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −58.40, −61.63. HRMS (ESI-GCT): calcd for $C_{16}H_{14}O_8F_6Na$ $(M + Na)^+$ 471.0491, found 471.0496.

*Reaction of Vinyl Diazoacetate **12** with 2,5-Dimethylfuran.* The reaction was carried out according to procedure **a** or **b** with vinyl diazoacetate **1** (0.5−4 mmol, 1 equiv), Rh_2L_4 (0.2−2% mol), and dimethylfuran (5−40 mmol, 10 equiv) during 2−19 h at 80−94 °C. After separation of reaction mixtures by column chromatography on silica gel (10−25 g; eluent hexane/EtOAc) furan **13** (105−277 mg,

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30−47%) and cycloadduct **16** were isolated. More details of the specific experiments are given in Scheme 4.

*Dimethyl 1,5-Dimethyl-4-(trifluoromethyl)-8-oxatricyclo-[3.2.1.0^{2,4}]oct-6-ene-2,3-dicarboxylate (**16**).* Yield: 101−387 mg (16−30%). Colorless oil. R_f 0.38 (hexane/Et_2O 2:1). IR (neat): 1742 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 6.55 (d, $^3J_{H-H}$ 5.4 Hz, 1H), 6.47 (dq, $^3J_{H-H}$ 5.4 Hz, $^5J_{H-F}$ 2.9 Hz, 1H), 3.73 (s, 3H), 3.72 (s, 3H), 3.21 (s, 1H), 1.60 (br. s, 3H), 1.59 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 14.9, 15.1, 34.1 (q, $^2J_{C-F}$ 3.5 Hz), 50.2 (q, $^2J_{C-F}$ 34.1 Hz), 51.1, 52.3, 52.5, 86.8, 87.6, 124.4 (q, $^1J_{C-F}$ 275.0 Hz), 141.3, 165.8, 166.1. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −57.22. HRMS (ESI-GCT): calcd for $C_{14}H_{15}O_5F_3Na$ $(M + Na)^+$ 343.0769, found 343.0770.

*Catalytic Reactions of Vinyl Diazoketones **9a−c** in the Presence of Furans.* The reactions were carried out using procedure **b** (the details of individual experiments are given in the Scheme 5). To a boiling solution of 2-methylfuran or 2,5-dimethylfuran (10 mmol) and benzene (5 mL) with 9 mg of $Rh_2(OAc)_4$ was added dropwise a solution of vinyldiazoketone **9a−c** in 1.5 mL of benzene during 3−4 h. The reaction mixture was refluxed 3−8 h more until disappearance of the initial diazo compound (by TLC), benzene and furan were completely removed in vacuo, and the obtained residue was separated by column chromatography on silica gel (using petroleum and diethyl ether as eluents) to give furans **11a−c** and Diels−Alder cycloadducts **10a−c** and **17a−c**.

*5-Acetyl-2-methoxy-4-(trifluoromethyl)furan (**11a**).*[6] Yield: 0.096 g (46%) (in reaction with 2-methylfuran), 0.067 g (32%) (with 2,5-dimethylfuran). Colorless solid. Mp: 58−60 °C (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.43 (s, 3H), 3.98 (s, 3H), 5.63 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 185.3, 161.8, 140.1, 124.4 (q, $^2J_{C-F}$ 39.6 Hz), 121.4 (q, $^1J_{C-F}$ 269.0 Hz), 84.2 (q, $^3J_{C-F}$ 4.0 Hz), 58.8, 26.9. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −60.14. MS (EI, 70 eV): m/z = 208.1 $(M)^+$. Anal. Calcd for $C_8H_7F_3O_3$: C, 46.17; H, 3.39. Found: C, 46.06; H, 3.17.

*Methyl 2-Acetyl-1-methyl-4-trifluoromethyl-8-oxatricyclo-[3.2.1.0^{2,4}]oct-6-en-3-oate (**17a**).* Yield: 0.125 g (43%). Pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.62 (s, 3H), 2.29 (s, 3H), 3.21 (s, 1H), 3.73 (s, 3H), 4.91 (d, *J* 2 Hz, CH), 6.50 (d, *J* 6 Hz, 1H), 6.72 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 200.0, 166.9, 140.7, 139.5, 124.9 (q, $^1J_{C-F}$ 274.5 Hz), 89.7, 78.5 (q, $^3J_{C-F}$ 2 Hz), 58.7, 52.9, 48.0 (q, $^2J_{C-F}$ 34.8 Hz), 35.0, 31.2, 15.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −57.48. MS (EI, 70 eV): m/z = 290.1 $(M)^+$. Anal. Calcd for $C_{13}H_{13}F_3O_4$: C, 53.80; H, 4.51. Found: C, 53.55; H, 4.63.

*5-(4-Chlorobenzoyl)-2-methoxy-4-(trifluoromethyl)furan (**11b**).*[6] Yield: 0.058 g (19%) (in reaction with 2-methylfuran), 0.052 g (17%) (with 2,5-dimethylfuran). Colorless solid. Mp: 67−70 °C (petroleum ether). ^{1}H NMR (300 MHz, $CDCl_3$) δ: 4.00 (s, 3H), 5.73 (s, 1H), 7.43−7.45 (m, 2H), 7.90−7.93 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ:: 178.8, 161.7, 143.8, 139.3, 134.7, 130.9, 128.7, 126.7 (q, $^2J_{C-F}$ 39.3 Hz), 121.0 (q, $^1J_{C-F}$ 269.3 Hz), 84.1 (q, $^3J_{C-F}$ 3.4 Hz), 58.5. ^{19}F NMR (188 MHz, $CDCl_3$) δ: −60.25. MS (EI, 70 eV): m/z = 305.1 $(M)^+$. Anal. Calcd for $C_{13}H_8ClF_3O_3$: C, 51.25; H, 2.65. Found: C, 51.23; H, 2.69.

*Methyl 2-(4-Chlorobenzoyl)-1-methyl-4-trifluoromethyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-en-3-oate (**17b**).* Yield: 0.271 g (70%). Colorless solid. Mp: 75−81 °C (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.49 (s, 3H), 3.51 (s, 3H), 3.61 (s, 1H), 5.12 (d, *J* 2 Hz, 1H), 6.45 (d, *J* 5 Hz, 1H), 6.81 (m, 1H), 7.55 (m, 2H), 8.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 189.9, 166.4, 140.4, 139.3, 139.1, 136.5, 131.3, 128.7, 125.1 (q, $^1J_{C-F}$ 274.3 Hz), 90.0, 78.4 (q, $^3J_{C-F}$ 2 Hz), 52.03, 51.9, 46.9 (q, $^2J_{C-F}$ 34.6 Hz), 36.2, 16.3. ^{19}F NMR (188 MHz, $CDCl_3$) δ: −58.23. MS (EI, 70 eV): m/z = 387.1$(M)^+$. Anal. Calcd for $C_{18}H_{14}ClF_3O_4$: C, 55.90; H, 3.65. Found: C, 55.82; H, 3.53.

*5-(tert-Butylcarbonyl)-2-methoxy-4-(trifluoromethyl)furan (**11c**).* Yield: 0.073 g (29%) (in reaction with 2-methylfuran), 0.038 g (15%) (with 2,5-dimethylfuran). Pale yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 1.32 (s, 9H), 3.98 (s, 3H), 5.60 (s, 1H). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 192.6, 161.9, 140.0, 125.9 (q, $^2J_{C-F}$ 39.2 Hz), 122.4 (q, $^1J_{C-F}$ 266.0 Hz), 83.8, 59.4, 43.8, 29.8. ^{19}F NMR (282 MHz, $CDCl_3$) δ: −60.33. MS (EI, 70 eV): m/z = 250.0 $(M)^+$. Anal. Calcd for $C_{11}H_{13}F_3O_3$: C, 52.80; H, 5.24. Found: C, 52.91; H, 5.27.

*Methyl 2-(tert-Butylcarbonyl)-1-methyl-4-trifluoromethyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-en-3-oate (**17c**).* Yield: 0.163 g (49%). Pale yellow oil. ^{1}H NMR (400 MHz, acetone-d_6) δ: 1.28 (s, 9H), 1.73 (s, 3H), 3.29 (s, 1H), 3.72 (s, 3H), 4.88 (d, *J* 1 Hz, CH), 6.28 (d, *J* 6 Hz, 1H), 6.71 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 208.4, 167.0, 139.5, 139.3, 124.6 (q, $^1J_{C-F}$ 274.3 Hz), 90.5, 77.8 (q, $^3J_{C-F}$ 2 Hz), 56.1, 52.7, 46.8 (q, $^2J_{C-F}$ 34.6 Hz), 45.3, 35.7, 28.0, 18.0. ^{19}F NMR (188 MHz, $CDCl_3$) δ: −57.46. MS (EI, 70 eV): m/z = 332.1$(M)^+$. Anal. Calcd for $C_{16}H_{19}F_3O_4$: C, 57.83; H, 5.76. Found: C, 57.95; H, 5.73.

*Methyl 2-Acetyl-1,5-dimethyl-4-trifluoromethyl-8-oxatricyclo-[3.2.1.0^{2,4}]oct-6-en-3-oate (**10a**).*[6] Yield: 0.110 g (36%). Colorless solid. Mp: 48−50 °C (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.56 (s, 3H), 1.62 (s, 3H), 2.27 (s, 3H), 3.18 (s, 1H), 3.73 (s, 3H), 6.48 (d, *J* 6 Hz, 1H), 6.55 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 199.7, 166.8, 142.4, 140.9, 124.7 (q, $^1J_{C-F}$ 274.9 Hz), 88.2, 87.2, 58.7, 52.6, 50.6 (q, $^2J_{C-F}$ 33.9 Hz), 34.0, 30.8, 15.6, 15.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ: −56.76. MS (EI, 70 eV): m/z = 304.0 $(M)^+$. Anal. Calcd for $C_{14}H_{15}F_3O_4$: C, 55.26; H, 4.97. Found: C, 55.38; H, 4.89.

*Methyl 2-(4-Chlorobenzoyl)-1,5-dimethyl-4-trifluoromethyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-en-3-oate (**10b**).*[6] Yield: 0.273 g (68%). Colorless solid. Mp: 85−89 °C (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.45 (s, 3H), 1.65 (s, 3H), 3.51 (s, 3H), 3.61 (s, 1H), 6.41 (d, *J* 6 Hz, 1H), 6.64 (m, 1H), 7.55 (m, 2H), 8.07 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 190.4, 167.0, 142.7, 141.6, 139.8, 137.0, 132.0, 129.3, 125.9 (q, $^1J_{C-F}$ 274.8 Hz), 89.5, 87.8, 56.3, 52.5, 49.8 (q, $^2J_{C-F}$ 34.0 Hz), 36.6, 17.1, 15.4. ^{19}F NMR (188 MHz, $CDCl_3$) δ: −57.10. MS (EI, 70 eV): m/z = 401.0 $(M+H)^+$. Anal. Calcd for $C_{19}H_{16}ClF_3O_4$: C, 56.94; H, 4.02. Found: C, 55.79; H, 4.05.

*Methyl 2-(tert-Butylcarbonyl)-1,5-dimethyl-4-trifluoromethyl-8-oxatricyclo[3.2.1.0^{2,4}]oct-6-en-3-oate (**10c**).* Yield: 0.208 g (60%). Colorless solid. Mp: 67−70 °C (petroleum ether). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.27 (s, 9H), 1.57 (s, 3H), 1.69 (s, 3H), 3.31 (s, 1H), 3.72 (s, 3H), 6.33 (d, *J* 6 Hz, 1H), 6.54 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 206.10, 167.8, 142.4, 141.1, 125.8 (q, $^1J_{C-F}$ 274.7 Hz), 90.2, 87.0, 57.8, 52.8, 49.7 (q, $^2J_{C-F}$ 33.2 Hz), 45.4, 35.8, 28.2, 18.0, 15.4. ^{19}F NMR (188 MHz, $CDCl_3$) δ: −56.58. MS (EI, 70 eV): m/z = 346.1 $(M)^+$. Anal. Calcd for $C_{17}H_{21}F_3O_4$: C, 58.95; H, 6.11. Found: C, 58.76; H, 6.19.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Spectroscopic data for the compounds **10a**, **11a**, **11b**, **13**, **15**, **16**, **17a** and crystallographic data for the compounds **10a**, **10b**, **11a**, **15**, and **17b** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org. The X-ray data is avaiable from the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk/data_request/cif).

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Notes

The authors declare no competing financial interest.

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