Two-Stage Synthesis of 3-(Perfluoroalkyl)-Substituted Vinyldiazocarbonyl Compounds and Their Nonfluorinated Counterparts: A Comparative Study

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Abstract: Two approaches for the synthesis of fluorinated (*F*) and nonfluorinated (*H*) 4-(alkoxycarbonyl)-substituted *cis*- and *trans*-vinyldiazocarbonyl compounds with substituents of variable stereoelectronic nature (H, Me, Ph, CF_3, OTBS) at the C-3 atom of the vinyl double bond from the relevant 1,3-dicarbonyl compounds were compared: a pathway using the Wittig reaction followed by a diazo transfer reaction was most efficient for the synthesis of the *H*-vinyldiazocarbonyl compounds (total yields of up to 60%), while the yields of their *F*-analogues under similar conditions did not exceed 16–37%. An approach via diazo transfer followed by the Wittig reaction, in contrast, is more effective for the preparation of *F*-vinyldiazocarbonyl compounds (total yields 37–69%). The configuration of the resulting *F*- and *H*-vinyldiazocarbonyl compounds is evidently controlled by the steric bulk of the substituent at the C-3 atom of the vinyl double bond and, in addition, depends on the specific synthetic pathway.

Key words: (perfluoroalkyl)-containing vinyldiazocarbonyl compounds, diazo transfer, Wittig reaction, 1,3-diketones

In recent years, reactions of α-vinyl-α-diazocarbonyl compounds with the elimination or retention of 'dinitrogen' of the diazo group have gained significant attention and importance for the generation of diversified reactive intermediates, such as metallocarbenes,[1] carbenes,[2] ylides[3] and cyclopropenes.[4] They are also widely used for the synthesis of a great variety of heterocyclic compounds.[5]

During a study of thermal reactions of a series of vinyldiazocarbonyl compounds (VDCC) with retention of the CN_2 moiety, it was recently established that 3-R_F-substituted vinyldiazocarbonyl compounds ($R^1 = CF_3$, C_3F_7) readily take part in tandem Staudinger–diaza-Wittig reactions to produce pyridazines, but do not undergo 1,5-electrocyclization, whereas their nonfluorinated analogues (R^1 = H, Me) easily cyclize to pyrazoles, but remain intact under Staudinger–diaza-Wittig reaction conditions (Scheme 1).[6] It was assumed that the different reactivity of vinyldiazocarbonyl compounds in these processes is due to a different stereochemical arrangement of the CO_2Alk and CN_2 groups (*cis* or *trans*)[7] on the vinyl double bond.[6c]

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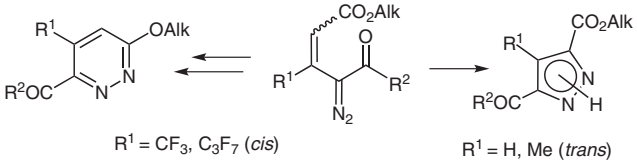


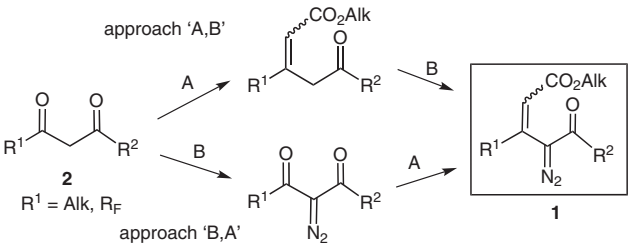
Scheme 1 Assumed stereocontrol in the cyclization of vinyldiazocarbonyl compounds

To experimentally check this assumption, we needed to prepare a series of 4-(alkoxycarbonyl)-substituted 2-vinyldiazocarbonyl compounds with *cis* and *trans* configuration of the vinyl double bond, the synthesis of which is the focus of this research.

Basically, in the chemistry of aliphatic diazo compounds, two fundamentally different approaches are used for the incorporation of the diazo function in a target molecule[8] which, as applied to the synthesis of 2-vinyldiazocarbonyl compounds **1** from 1,3-dicarbonyl compounds **2**, can be stated in the following manner (Scheme 2):

(i) approach 'A,B' involves the initial creation of a 2-vinylcarbonyl compound[9] (A) followed by incorporation of the diazo function (B) using, for example, a diazo transfer reaction;

(ii) approach 'B,A' involves first the preparation of a diazocarbonyl precursor (B), followed by creation of a vinyl moiety adjacent to the diazo group (A) with a certain synthetic protocol.



Scheme 2 Two approaches for the synthesis of 2-vinyldiazocarbonyl compounds **1** from 1,3-dicarbonyl substrates **2**

Each of the reaction protocols 'A' and 'B' has already been used by others for the preparation of a number of vinyldiazocarbonyl compounds;[1,6,10a,b,11] however, a comparative evaluation of the above approaches with respect to their validity for the synthesis of 3-(fluoroalkyl)-con-

taining and nonfluorinated vinyldiazocarbonyl compounds has not been previously realized.

The main goal of our research was to assess the efficacy of the approaches 'A,B' and 'B,A' starting from 1,3-dicarbonyl compounds **2** for the preparation of (fluoroalkyl)-containing (*F*) and nonfluorinated (*H*) 4-(alkoxycarbonyl)-substituted *cis*- and *trans*-vinyldiazocarbonyl compounds **1** bearing various substituents R^1 at the C-3 atom of the vinyl fragment of the molecule.

A series of *H*- and *F*-vinyldiazocarbonyl compounds **1a**–**i** containing a substituent R^1 with various electronic and steric requirements (R^1 = H, Me, R_F, Ph, OTBS) and dissimilar character of the carbonyl group on the diazo carbon atom (CO_2Alk, COAlk) were used for this study, as well as the cyclic diazo compounds **1j**,**k** with fixed *cis* configuration of the compound (Figure 1).

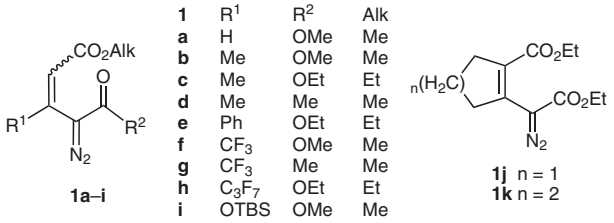


Figure 1 Structures of the vinyldiazocarbonyl compounds **1a**–**k** targeted in this study

Furthermore, the structural variations employed in our research would help to determine the feasibility of both approaches for the synthesis of *F*- and *H*-vinyldiazocarbonyl compounds with different configurations of the vinyl double bond and to estimate the scope and limitations of the reactions studied.

Approach 'A,B'

Stage 'A': Synthesis of the vinylcarbonyl compounds using the Wittig reaction

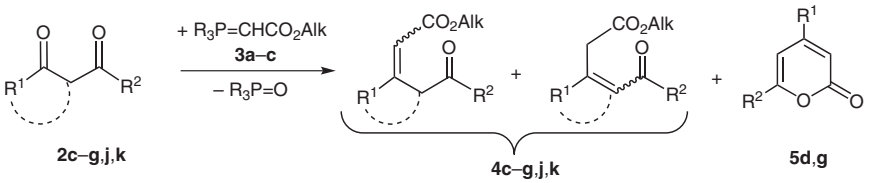
Although there are well-known examples for the synthesis of 3-substituted vinylcarbonyl compounds,[12] there is to the best of our knowledge no common method suitable for the preparation of these compounds. One of the practical approaches for their synthesis that one can envision is the Wittig reaction of rather easily available 1,3-dicarbonyl compounds. However, only one example of this reaction was available in the literature; namely, treatment of acetylacetone with (ethoxycarbonylmethylene)triphenylphosphorane.[13]

We have established that the efficacy and selectivity of the Wittig reaction with 1,3-dicarbonyl compounds **2c**–**g**,**j**,**k** depends considerably on the nature of the carbonyl group and the Wittig reagent used, and the reaction conditions employed.

a) Wittig reaction with nonfluorinated 1,3-dicarbonyl compounds **2c**–**e**: Reaction of the acetoacetate **2c** with phosphoranes **3a**,**b** (**3a**: R = Ph, Alk = Me; **3b**: R = Ph, Alk = Et) (in benzene solution, at 80 °C for 48 h), followed by chromatographic purification, gave vinyl esters **4c**,**c′** in yields of 52–63% (Table 1, entry 1). At the same time, the similar reaction of acetylacetone (**2d**) with triphenylphosphorane **3a** in benzene, dichloromethane, chloroform or dioxane gave very low yields of the targeted vinyl ketone **4d** (5–18%); the most satisfactory yield of **4d** (38%) was obtained by performing the reaction in acetonitrile (Table 1, entry 2).

Wittig reaction of keto esters **2c** with phosphoranes **3a**,**b** proceeded chemoselectively on the acetyl carbonyl group ($COCH_3$), as demonstrated by the disappearance of the signal for the carbonyl C-atom of the *H*-acyl group at around 190–200 ppm in the ^{13}C NMR spectra of the isolated compounds **4c**,**c′**. Also, based on ^{1}H and ^{13}C NMR spectroscopic data, the reactions of acetoacetate **2c′** and

Table 1 Synthesis of the α-Vinylcarbonyl Compounds **4c**–**g**,**j**,**k** Using the Wittig Reaction



Entry	**2**	R^1	R^2	Yield (%) of **4** and **5** R = Ph	R = *n*-Bu	Alk	**4**	**5d**,**g**
1	**c**	Me	OEt	52–63		Et (Me)	**c** (**c′**)	
2	**d**	Me	Me	5–38		Me	**d**	13–35
3	**e**	Ph	OEt	–	85	Et	**e**	
4	**f**	CF_3	OMe	83–86		Me (Et)	**f** (**f′**)	
5	**g**	CF_3	Me	75–85		Me	**g**	5–23
6	**j**	$(CH_2)_3$	OEt	57–60		Et	**j**	
7	**k**	$(CH_2)_4$	OEt	50		Et	**k**	

acetylacetone (**2d**) with Wittig reagent **3a** produced a mixture of isomers of vinyl ester **4c′** (Alk = Me) and vinyl ketone **4d** in a ratio of 3:3:2:2 and 2:1:7:2, respectively (two stereoisomers of each regioisomer, Table 1), while with phosphorane **3b** (Alk = Et) the reaction with **2c** gave two stereoisomers of 3-methylglutaconate **4c** in the ratio 5:3. Since at the next stage 'B' (diazo transfer reaction), under the action of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), one would expect generation of the same intermediate anion A from all four (or two) isomers of vinylcarbonyl compounds **4c**,**d**,**g** (see Table 2), separation of the mixtures of regio- and stereoisomers of vinyl compounds **4c**,**d**,**g** was not undertaken. On prolonged heating of the reaction mixture with vinyl ketones **4d**,**g**, self-condensation occurred and considerable amounts of the α-pyranones **5d**,**g**[12a,b,14] were formed, significantly diminishing the yields of the target compounds **4d**,**g**.

Ethyl benzoylacetate (**2e**) did not react with phosphorane **3b** (Alk = Et) under similar reaction conditions. In this connection, for olefination of the keto ester **2e**, the tri-*n*-butylphosphorane **3c** was used, which has been shown to be a more active olefination agent than triphenylphosphoranes in some cases.[15] The reaction of keto ester **2e** with tri-*n*-butyl(ethoxycarbonylmethylene)phosphorane (**3c**) in toluene under reflux for 23 hours gave 3-phenyl-substituted glutaconate **4e** in high yield (85%), as a single stereoisomer based on ^{1}H and ^{13}C NMR spectroscopic analysis (Table 1, entry 3).

Reaction of carbocyclic keto esters **2j**,**k** with phosphorane **3b** gives rise to thermodynamically more stable regioisomers with an endocyclic double bond in the vinyl esters **4j**,**k** (Table 1, entries 6 and 7).

b) Wittig reaction with fluorine-containing 1,3-dicarbonyl compounds **2f**,**g**: The reaction of *F*-**2f**,**g** with phosphorane **3a** (in benzene at 80 °C, within 30 min) produced vinylcarbonyl compounds *F*-**4f**,**f′**,**g** in yields of 75–86% (Table 1, entries 4 and 5). According to ^{1}H and ^{13}C NMR spectra, vinyl ester *F*-**4f′** (Alk = Et) and vinyl ketone *F*-**4g** were found to be mixtures of two isomers in a ratio of 1:1 and 2:1, respectively. On using phosphorane **3a** instead of the ethyl analogue **3b**, only one isomer of vinyl acetate *F*-**4f** was obtained.

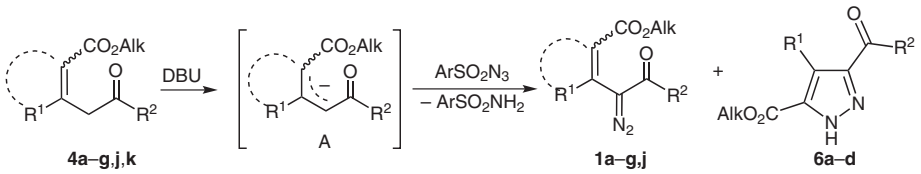
Wittig reaction of phosphorane **3a** with dicarbonyl compounds *F*-**4f**,**g** took place chemoselectively on the perfluoroacetyl carbonyl group, as evidenced by the disappearance of the distinctive quartet for the *F*-acyl group carbonyl C-atom at around 160–175 ppm and the growth of signals for the C-3–CF_3 fragment at around 138–139 ppm in the ^{13}C NMR spectra.

*Stage 'B': Synthesis of the 2-vinyldiazocarbonyl compounds **1a–g,j***

Vinyldiazocarbonyl compounds **1a–g**,**j** were prepared from the corresponding vinyl ketones and esters **4b–g**,**j** obtained at stage 'A', as well as from commercially available dimethyl glutaconate (**4a**, mixture of *trans*/*cis*-isomers ~8:2), using a diazo transfer reaction[3a,7] with 4-acetamidobenzenesulfonyl azide (*p*-ABSA) and DBU[6b,c,10a] (Table 2).

a) Synthesis of *H*-vinyldiazocarbonyl compounds **1a–e**,**j**,**k**: The yields of the nonfluorinated diazo compounds *H*-**1a–e**,**j** at this stage generally exceeded 50%, based on the ^{1}H and ^{13}C NMR spectra, and all vinyl compounds *H*-**4a–e**,**j** gave rise to only one isomer of the target diazo compounds *H*-**1a–e**,**j**. In the reaction mixtures of *H*-vinyl

Table 2 Results of the Diazo Transfer Reaction with α-Vinylcarbonyl Compounds **4a–g**,**j**,**k**



4a–g,j,k 1a–g,j 6a–d

Entry	R^1	R^2	Alk	**1**	Yield (%)	**6**	Yield (%)
1	H	OMe	Me	**a**	63–85	**a**	3–10
2	Me	OMe	Me	**b**	56	**b**	27
3	Me	OEt	Et	**c**	73	**c**	15
4	Me	Me	Me	**d**	45–60	**d**	35–52
5	Ph	OEt	Et	**e**	72		
6	CF_3	OMe	Me	**f**	18[a]		
7	CF_3	Me	Me	**g**	23–43		
8	$(CH_2)_3$	OEt	Et	**j**	60		
9	$(CH_2)_4$	OEt	Et	**k**	–		

[a] Based on ^{1}H NMR spectroscopic data.

diazo compounds **4a**–**d**, pyrazoles **6a**–**d** were usually also identified (3–52%, based on ^{1}H NMR spectra).

The diazo transfer reaction with carbocyclic vinyl ester *H*-**4j** also gave rise to the anticipated vinyldiazo ester **1j** in good yield (60%); however, a similar reaction with its homologue **4k** did not produce the desired diazo ester **1k** independent of the base employed in the diazo transfer process (DBU or Et_3N, 72 h). From the reaction mixture after workup, only starting carbocyclic vinyl ester **4k** was recovered. Application of triisopropylbenzenesulfonyl azide (TIPBSA), which is usually employed in diazo transfer reactions with sterically demanding substrates,[3a,16] also failed.

b) Synthesis of (fluoroalkyl)-containing vinyl diazo compounds **1f**,**g**: Compounds *F*-**1f**,**g** were obtained similarly to their nonfluorinated analogues *H*-**1a**–**d**; however, in contrast to the vinyl diazo acetates *H*-**1a**–**c**, where the yields were up to 85%, the efficacy of the diazo transfer reaction with vinylcarbonyl compounds *F*-**4f**,**g** was much lower. Under optimized reaction conditions, the yields of vinyl diazo ketone *F*-**1g** and vinyl diazo ester *F*-**1f** were 43% and 18%, respectively (Table 2, entries 7 and 6). Vinyl diazo ketone *F*-**1g**, in contrast to vinyl diazo acetate *F*-**1f**, was found to be a mixture of stereoisomers (1:1).

Low yields of the fluorinated diazo compounds *F*-**1f**,**g** most likely are a consequence of a slow diazo transfer reaction with vinylcarbonyl compounds *F*-**4f**,**g** compared to their *H*-analogues, with reaction of the azide with DBU proceeding much faster than the diazo transfer reaction. Moreover, the yield of vinyl ketone *F*-**1g**, apparently, was decreased due to the parallel formation of pyranone **5g** from the initial vinyl ester *F*-**4g** (Table 1, entry 5).

Approach 'B,A'

*Stage 'B': Synthesis of diazodicarbonyl compounds **7b,c,e–i***

Nonfluorinated diazodicarbonyl compounds *H*-**7b**,**c**,**e**,**e′**,**i** employed in this study were obtained using the general diazo transfer procedure with triethylamine as a base[10a] (Table 3, entries 1, 2 and 6). Fluorinated analogues *F*-**7f**–**h** were prepared with DBU using our previously developed procedure for the synthesis of *F*-diazodicarbonyl compounds[10c,d] (Table 3, entries 3–5).

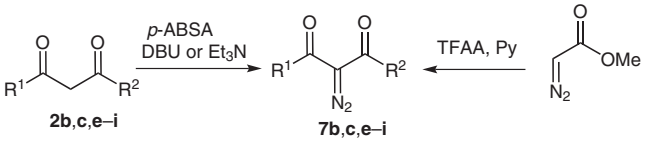
The methyl ester of 2-diazo-4,4,4-trifluoro-3-oxobutanoic acid (**7f**, R^2 = OMe) was also prepared via acylation of methyl diazoacetate with trifluoroacetic anhydride,[17] which provided better yields of *F*-diazo keto ester **7f** than the diazo transfer reaction (Table 3, entry 3).

Stage 'A'

a) Interaction of *H*-diazodicarbonyl compounds with Wittig reagents:

Attempts to perform the Wittig reaction with *H*-diazodicarbonyl compounds failed. Thus, after prolonged (7–10 d) reflux of the diazo compounds *H*-**7c**,**e** with phosphorane **3b** in diethyl ether, none of the expected *H*-vinyldiazocarbonyl compounds **1c**,**e** or the corresponding pyrazoles *H*-**6c**,**e** was formed. Reaction under more severe conditions was not undertaken, since at elevated temperature the diazodicarbonyl compounds are thermally rather unstable.[18]

Table 3 Synthesis of Diazodicarbonyl Compounds **7b**,**c**,**e–i**



Entry	**2**	R^1	R^2	**7**	Yield (%)
1	**b** (**c**)	Me	OMe (OEt)	**b** (**c**)	75–85
2	**e** (**e′**)	Ph	OMe (OEt)	**e** (**e′**)	89–90
3	**f** (**f′**)	CF_3	OMe (OEt)	**f** (**f′**)	66, 85[a]
4	**g**	CF_3	Me	**g**	43–55
5	**h**	C_3F_7	OEt	**h**	61
6	**i**	CH_2CO_2Me	OMe	**i**	72

[a] By acylation of methyl diazoacetate with TFAA.

b) Olefination of *F*-diazodicarbonyl compounds:

Wittig reaction of (fluoroalkyl)-containing diazodicarbonyl compounds **7f**–**h**, on the other hand, proceeded easily under very mild conditions, at room temperature, and in high yields (64–93%) (Table 4). Reaction was chemoselective and occurred only at the *F*-acyl carbonyl group, while *H*-acetyl or alkoxycarbonyl groups remained intact in the reactions with phosphoranes **3a**,**b**.

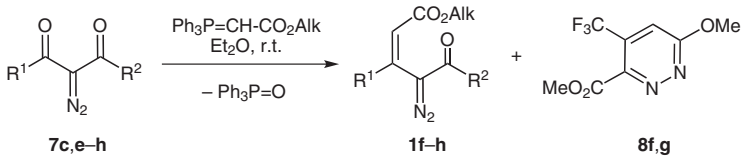
c) Alternative ways to create a vinyl group in the structure of the diazocarbonyl compound:

(i) Cross-coupling of ethyl diazoacetate: Diethyl *cis*-diazoglutaconate (**1a**) was obtained via cross-coupling of ethyl 3-iodoacrylate with ethyl diazoacetate using $Pd(PPh_3)_4$.[19] The diazoacetate is not stable enough in the presence of the palladium catalyst used, producing diethyl fumarate due to decomposition; however, employing a 2–3-fold excess of the diazo compound provided a way for the preparation of the vinyl diazo ester **1a** in yields up to 58–64%.

(ii) Dehydration of diazo alcohols as an alternative pathway for the preparation of vinyldiazocarbonyl compounds[20] was tested with the 3-methyl- and 3-phenyl-substituted diazo alcohols **9c′**,**e′** (R = Me, Ph) prepared by condensation of the diazodicarbonyl compounds **7c**,**e** (ethyl esters) with methyl lithioacetate, followed by dehydration of the resulting diazo alcohols (Table 5).[20b–d]

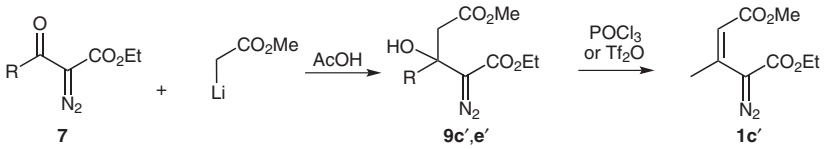
A positive result for the dehydration of the pure diazo alcohols **9** was achieved only with the 3-methyl-substituted diazo compound **7c** (33% of **1c′** using $POCl_3$ as the dehydrating agent). A one-pot reaction of diazo alcohols **9c′**,**e′** (by addition of Tf_2O, or TFAA, or TsCl directly to the reaction mixture with the lithium salt of the diazo alcohols

Table 4 Olefination of Diazodicarbonyl Compounds **7c**,**e–h** via the Wittig Reaction



Entry	**7c**,**e–h**	R^1	R^2	Yield (%) of **1f–h**	Yield (%) of **8f**,**g**
1	**c**	Me	OEt	–	–
2	**e**	Ph	OEt	–	–
3	**f**	CF_3	OMe	87–93	5–11
4	**g**	CF_3	Me	64–68	14–18
5	**h**	C_3F_7	OEt	83	–

Table 5 Attempts to Synthesize the Vinyl Diazo Esters **1c′**,**e′** via Diazo Alcohols **9c′**,**e′**



Entry	**7**	R	Yield (%) of **9**	Dehydration agent	Yield (%) of **1**
1	**c**	Me	79–99	$POCl_3$	33
2	**e**	Ph	78–83	Tf_2O	–

9c′,**e′** at the condensation step) was also only successful for the synthesis of vinyl diazo ester **1c′** (yield: 37%).

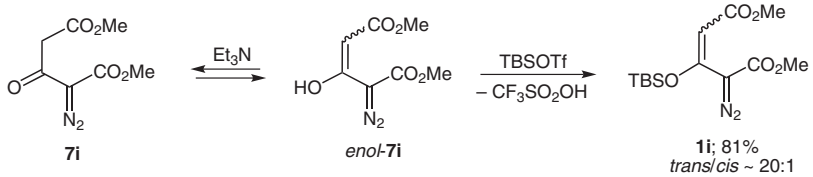
(iii) Silylation of the enol form of the diazocarbonyl compound **7i**: The reaction of dimethyl 2-diazo-3-oxopentanedioate (**7i**) with *tert*-butyldimethylsilyl trifluoromethanesulfonate (TBSOTf) in the presence of triethylamine[21] gave rise through *enol*-**7i** to a mixture of the *trans*/*cis*-isomers (~20:1) of vinyl diazo compound **1i** in more than 80% total yield (Scheme 3).

The silyl group of the vinyl diazo ester **1i** is very sensitive to even traces of water. Thus, only the sole use of completely anhydrous silica gel and eluents for chromatography permitted isolation and full characterization of both isomers by spectroscopic methods.

d) Attempts to olefinate the *H*-diazo keto esters **7b**,**e** via the Horner–Wadsworth–Emmons (HWE) and Peterson reactions:

Since the Wittig reaction was found to be ineffective for the synthesis of the *H*-vinyldiazocarbonyl compounds using the approach 'B,A', attempts were undertaken to create the olefinic fragment in the carbonyl substrate with the help of the HWE[22] and Peterson[23] methods. In these experiments, diazo keto esters **7b**,**e** were employed as model carbonyl compounds.

HWE reaction with diazo keto esters **7b**,**e** and butyllithium or lithium diisopropylamide as a base[24] proved to be not advantageous. Application of the Still–Gennari modification[25] of the HWE reaction also failed, though fluoroalkyl groups in the structure of the Still–Gennari reagent, as compared to alkyl substituents, usually favors the formation of alkenes in this process.[26] The employment of the Masamune adaptation[27] of the HWE reaction, used by Guillaume and co-workers for the synthesis of *F*-vinyl diazo acetates,[11a] in the olefination reactions of the nonfluorinated diazodicarbonyl compounds *H*-**7b**,**e** with *N*-ethyldiisopropylamine or DBU as the base was also found to be ineffective. Similarly, attempts to carry out olefination of the diazo keto esters *H*-**7b**,**e** via the Peterson procedure[28] were also not successful.



Scheme 3 Silylation of the diazodicarbonyl compound **7i**

With repect to the stereochemistry of the *H*- and *F*-vinyldiazocarbonyl compounds **1a–i**, the configuration of the obtained compounds **1a–d**,**f–h** has been established previously by NMR spectroscopy, and X-ray crystal structure analysis of diazo compounds and derived phosphazines (**1a**,[6c,20a] **1b–d**,[6c] **1f**,**g**[6c,11c]). The stereochemistry of the 2-vinyldiazocarbonyl compounds **1e**,**i**, prepared in our current work, was also elucidated by NMR spectroscopy.

Thus, vinyl diazo ester *H*-**1e**, possessing a bulky phenyl substituent on the vinyl double bond, has *cis* configuration which is clearly evident from the NOE between the *ortho* protons of the phenyl group and the 4-H atom of the double bond (Figure 2).

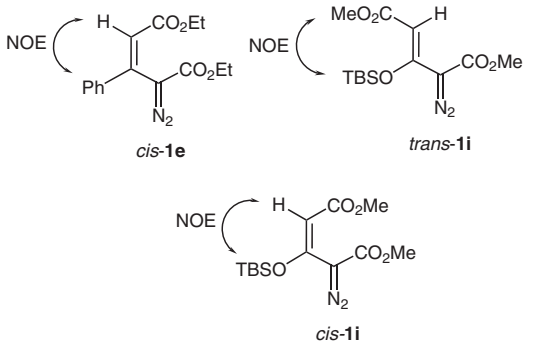


Figure 2 The structures of *cis*- and *trans*-vinyl diazo esters **1e** and **1i** as revealed by NOE studies

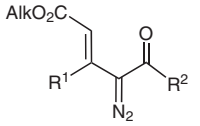
The NOE studies of major isomer **1i** indicated interaction of the protons of the methoxycarbonyl and *tert*-butylsilyl groups on the vinyl double bond, enabling assignment with confidence of the stereochemistry of the major silylation product of the diazo keto ester **7i** to the *trans*-**1i** configuration. At the same time, the minor isomer was ascribed the *cis*-**1i** configuration, since studies revealed an NOE between the 4-H atom of the vinyl double bond and the protons of the *tert*-butylsilyl group (Figure 2).

In summary, a comparison of the efficacy of the two approaches 'A,B' and 'B,A' for the synthesis of 4-(alkoxycarbonyl)-substituted *H*- and *F*-vinyldiazocarbonyl compounds has enabled us to come to the following conclusions (Table 6):

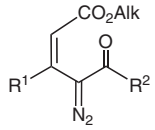
Approach 'A,B' is most adequate for the preparation of the nonfluorinated vinyl diazo compounds *H*-**1a–e**,**j**, providing a pathway for their synthesis with total yields of up to 61% in two stages, while the yields of the *F*-vinyldiazocarbonyl compounds under similar conditions do not exceed 16–37%.

Approach 'B,A', in contrast, is much more efficient for the synthesis of the *F*-vinyldiazocarbonyl compounds, where the total yields in two stages of this process are in the range of 37–69%. At the same time, the approach 'B,A' with *H*-vinyldiazocarbonyl compounds was not successful, since at moderate temperatures the starting *H*-diazodicarbonyl compounds did not react with phosphoranes (stage 'B'), while increasing the temperature of the reaction mixture resulted in the notable decomposition of these diazo compounds. The successful olefination of these diazocarbonyl compounds using the Wittig reaction apparently requires the availability of a rather strong electron-withdrawing substituent adjacent to the reacting carbonyl group, such as a perfluoroalkyl[11a,c,d] or α-carbonyl[11b]

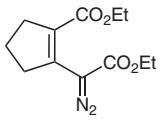
Table 6 Overall Results of the Synthesis of the *trans*- and *cis*-2-Vinyldiazocarbonyl Compounds **1a–j** Using Approaches 'A,B' and 'B,A'



trans-**1a–d**,**g**,**i**



cis-**1a**,**e–j**



1j

trans-**1**	R^1, R^2, Alk	Approach; yield (%)	*cis*-**1**	R^1, R^2, Alk	Approach; yield (%)
a	H, OMe, Me	85[a]	**a**	H, OEt, Et	B,A;[b] 49–64
b,**c**	Me, OAlk, Alk	A,B; 29–46	**e**	Ph, OEt, Et	A,B; 61
c′	Me, OEt, Me	B,A;[c] 33–37	**f**	CF_3, OMe, Me	B,A; 57–69
d	Me, Me, Me	A,B; 23	**g**	CF_3, Me, Me	B,A; 28–37
g	CF_3, Me, Me	A,B; 16–37[d]	**h**	C_3F_7, OEt, Et	B,A; 51
i	OTBS, OMe, Me	B,A;[e] 46	**i**	OTBS, OMe, Me	B,A;[e] 2
			j	cycloalkyl, OEt, Et	A,B; 34–36

[a] Yield of diazo transfer (stage 'B') with commercial dimethyl glutaconate.
[b] Olefination (stage 'A') via cross-coupling with diazocarbonyl compound.
[c] Olefination (stage 'A') via dehydration of diazo alcohol.
[d] Mixture of *cis*- and *trans*-stereoisomers (1:1).
[e] Olefination (stage 'A') using silylation of diazodicarbonyl compound.

group. In this connection, the realization of the pathway 'B,A' with the nonfluorinated diazodicarbonyl compounds, which do not have such an additional activation of the carbonyl group, failed. Analogously, the attempts to olefinate *H*-diazodicarbonyl compounds with the help of HWE, Peterson and Still–Gennari procedures also proved unsuccessful.

The main limitation of the approach 'A,B' for the preparation of *H*-vinyldiazocarbonyl compounds is 1,5-electrocyclization to the respective pyrazoles **6**, but carrying out the reaction under reduced temperature (0–5 °C) permits considerable minimization of this side reaction.

The major side reaction of the fluoroalkyl-containing diazocarbonyl compounds *F*-**1** with the Wittig reagent was found to be the formation of pyridazines **8**. The occurrence of this process is most likely derived from the partial addition of phosphorane **3a** on the terminal N-atom of the diazo function of compounds *F*-**1**, followed by dissociation of this adduct onto triphenylphosphine and the corresponding azine.[29] The subsequent reactions of the phosphine with the *F*-vinyldiazocarbonyl compounds *cis*-**1f**,**g** and intramolecular diaza-Wittig cyclization of phospazine formed via a tandem process gives rise to the pyridazines **8** in the reaction mixture.[6c,11]

The configuration of the resulting *F*- and *H*-vinyldiazocarbonyl compounds is evidently governed by the steric bulk and/or the nature of the substituent at the C-3 atom of the 4-(alkoxycarbonyl)-substituted vinyldiazocarbonyl compounds **1**. Thus, diazo transfer on the vinylcarbonyl compounds **4** or olefination of the diazodicarbonyl compounds **7** with a relatively less bulky substituent (H, Me) at the C-3 atom of the molecule normally produced the *trans*-isomer of the vinyl diazo compounds **1**, while more bulky substituents (Ph, CF_3) at the C-3 position of the vinylcarbonyl compound led to the formation of the *cis*-isomer of the vinyldiazocarbonyl compounds **1**.

At the same time, the relative configuration of the formed vinyldiazo compounds evidently depends in some cases on the specific synthetic pathway. Thus, Wittig olefination of the diazo keto ester *F*-**7g** using phosphorane **3a** (stage 'A' of the approach 'B,A') stereoselectively furnished only one isomer, the *cis*-isomer of vinyl diazo ketone *F*-**1g**, while the diazo transfer reaction with the vinylcarbonyl compound *F*-**4g** (stage 'B' of the approach 'A,B') gave rise to the same vinyldiazo compound *F*-**1g**, but as a mixture of the *cis*- and *trans*-stereoisomers (in a 1:1 ratio).

^{1}H, ^{13}C and ^{19}F NMR spectra were recorded in $CDCl_3$ solution using TMS or $CHCl_3$ as internal standards at 300 or 400 MHz (^{1}H), 75 or 100 MHz (^{13}C), and 375 MHz (^{19}F) with Varian Gemini-300, Bruker DPX-300, or Bruker DRX-400 NMR spectrometers. Microanalysis was performed on a Heraeus CHN Rapid Analyzer. IR spectra were recorded on an ATI Mattson Genesis Series FTIR spectrophotometer. MS data were measured on a micrOTOF 10223 mass spectrometer. All reactions were carried out in carefully purified and dried solvents and were monitored by thin-layer chromatography (TLC) on plates of Silufol UV/VIS 254 nm (Kavalier) using UV light and iodine as visualizing agents. Preparative column chromatography was carried out on neutral silica gel (Chemapol, L 40/100 or Merck 70–230 mesh) with petroleum ether (PE; 40–70 °C) and Et_2O as eluents in gradient regime.

H- and *F*-Vinylcarbonyl Compounds 4b–d,f,g,j,k Using the Wittig Reaction (Approach 'A,B', Stage 'A', Table 1)

Protocol a: A mixture of phosphorane **3a** (12.2 mmol, 1 equiv) and 1,3-dicarbonyl compound **2d** (183.0 mmol, 15 equiv) in CH_2Cl_2 (40 mL) was kept under reflux for 2–6 d, until the completion of the reaction (by TLC and ^{1}H NMR spectroscopy). The reaction mixture was extracted with 5% aq NaOH to remove the excess dicarbonyl compound, and the organic layer was washed with water and dried with $MgSO_4$. The solvent was removed under reduced pressure, the resulting orange solid was triturated with PE–Et_2O (1:1) and removed by filtration, the filtrate was concentrated, and the residue was distilled under reduced pressure.

Protocol b: The reaction and workup procedure were performed as in protocol a, with benzene as the reaction solvent at 80 °C for 48 h. The residue was separated by column chromatography on silica gel (PE–EtOAc).

Protocol c: The reaction and workup procedure were run similarly to protocol a, using MeCN, $CHCl_3$ or dioxane as the reaction solvent at 70 °C for 20 h.

Protocol d: A mixture of a phosphorane **3a**,**b** (42–77 mmol, 1.2 equiv) and a 1,3-dicarbonyl compound **2** (35–64 mmol, 1 equiv) in benzene (30–60 mL) was kept under reflux until disappearance of the phosphorane **3a**,**b** (by TLC and ^{1}H NMR spectroscopy). The solvent was removed under reduced pressure, the resulting orange solid was triturated with PE–Et_2O (1:1) and removed by filtration, the filtrate was concentrated, and the residue was distilled under reduced pressure.

Ethyl Methyl 3-Methylpent-2-enedioate (4c′, Alk = Me)[30]

Obtained from (methoxycarbonylmethylene)triphenylphosphorane (**3a**, 42 mmol) and ethyl acetoacetate (**2c**, 35 mmol) using protocol b, followed by purification with column chromatography on silica gel (20 g, hexane–EtOAc).

Yield: 4.1 g (63%); colorless oil; mixture of isomers (3:3:2:2).

R_f = 0.81 (PE–EtOAc, 3:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.81, 5.80, 5.74, 5.73 (s, 4 CH=CR^1, 3:3:2:2), 4.13 (q, J = 7.0 Hz, 2 CH_2), 4.11 (q, J = 7.0 Hz, 2 CH_2), 3.70, 3.69 (s, 2 CH_2), 3.64 (br s, 2 CH_2), 3.66 (s, 4 OCH_3), 2.19, 1.93 (s, 4 CH_3), 1.23 (t, J = 7.0 Hz, 2 CH_3), 1.22 (t, J = 7.0 Hz, 2 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.8, 170.4, 170.2, 169.8, 166.6, 166.5, 166.1, 166.0, 151.5, 151.3, 150.8, 150.7, 119.7, 119.4, 119.2, 118.8, 61.0, 60.8, 59.9, 59.8, 52.1, 51.9, 51.1, 51.1, 46.0, 45.7, 38.6, 38.3, 25.7, 25.6, 18.9, 18.8, 14.3, 14.2.

Diethyl 3-Methylpent-2-enedioate (4c, Alk = Et)[31]

Prepared from (ethoxycarbonylmethylene)triphenylphosphorane (**3b**, 42 mmol) and ethyl acetoacetate (**2c**, 35 mmol) via protocol b (reaction time: 20 h), followed by purification with column chromatography on silica gel (20 g, hexane–EtOAc).

Yield: 3.64 g (52%); colorless oil; mixture of isomers (5:3).

R_f = 0.81 (PE–EtOAc, 3:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.85, 5.77 (s, 2 CH=CR^1, 5:3), 4.16 (q, J = 7.0 Hz, CH_2), 4.13 (q, J = 7.0 Hz, CH_2), 3.74, 3.13 (s, 2 CH_2, 5:3), 2.23, 1.97 (s, 2 CH_3, 3:5), 1.28 (t, J = 7.0 Hz, CH_3), 1.26 (t, J = 7.0 Hz, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.7, 170.3, 166.5, 166.4, 151.3, 151.1, 119.9, 119.6, 61.2, 60.2, 46.4, 35.9, 26.0, 19.2, 14.6, 14.5.

Methyl 3-Methyl-5-oxohex-2-enoate (4d)[12c]

Derived from (methoxycarbonylmethylene)triphenylphosphorane (**3a**, 12.2 mmol) and acetylacetone (**2d**, 183 mmol), using protocol

c with MeCN for 20 h. After separation of the reaction mixture by column chromatography on silica gel (25 g, hexane–EtOAc), vinyl ketone **4d** and pyranone **5d** were isolated.

Yield of vinyl ketone **4d**: 0.1–0.72 g (5–38%); colorless oil; bp 52–53 °C/0.1–0.2 mmHg; mixture of isomers (2:1:7:2).

R_f = 0.27 (PE–EtOAc, 3:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.24, 6.14, 5.85, 5.73 (s, 4 CH=CR^1, 2:1:7:2), 3.80, 3.66 (br s, 4 CH_2), 3.65 (br s, 4 OCH_3), 2.21, 2.17, 1.92, 1.91 (s, 4 CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 204.7, 204.6, 198.4, 198.2, 170.8, 170.6, 166.7, 166.5, 152.6, 152.0, 149.0, 148.9, 126.9, 126.3, 119.5, 118.2, 55.2, 52.1, 51.9, 51.0, 48.2, 45.8, 31.8, 31.6, 30.0, 29.7, 26.9, 25.9.

4,6-Dimethyl-2*H*-pyran-2-one (5d)[14]
Yield: 0.2–0.53 g (13–35%); white solid; mp 48–50 °C.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.90 (s, 1 H), 5.82 (s, 1 H), 2.18 (s, 3 H), 2.08 (s, 3 H).

Dimethyl 3-(Trifluoromethyl)pent-2-enedioate (4f, Alk = Me)
Obtained from (methoxycarbonylmethylene)triphenylphosphorane (**3a**, 71 mmol) and methyl 4,4,4-trifluoro-3-oxobutanoate (**2f**, 59 mmol)[32] using protocol d (reaction time: 30 min), and purification by distillation.

Yield: 11.47 g (86%); colorless oil; bp 79–82 °C/10 mmHg.

R_f = 0.67 (PE–EtOAc, 3:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.55 (s, 1 H), 3.78 (s, 3 H), 3.76 (s, 2 H), 3.73 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.9, 165.1, 138.5 (q, $^2J_{C\text{-}F}$ = 30.9 Hz), 125.2 (q, $^3J_{C\text{-}F}$ = 6.0 Hz), 123.0 (q, $^1J_{C\text{-}F}$ = 274.3 Hz), 52.8, 52.5, 32.1.

MS (EI, 70 eV): *m*/*z* = 226.2 [M]$^+$.

Ethyl Methyl 3-(Trifluoromethyl)pent-2-enedioate (4f′, Alk = Et)
Prepared from (ethoxycarbonylmethylene)triphenylphosphorane (**3b**, 39 mmol) and methyl 4,4,4-trifluoro-3-oxobutanoate (**2f**, 32 mmol) using protocol b (reaction time: 30 min), followed by distillation.

Yield: 6.61 g (83%); colorless oil; bp 101–102 °C/20 mmHg; mixture of isomers (1:1).

R_f = 0.67 (PE–EtOAc, 3:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.55 (br s, 2 CH=CR^1), 4.23 (q, *J* = 7.2 Hz, CH_2), 4.21 (q, *J* = 7.2 Hz, CH_2), 3.79 (s, 2 OCH_3), 3.76, 3.74 (s, 2 CH_2, 1:1), 1.31 (t, *J* = 7.2 Hz, CH_3), 1.27 (t, *J* = 7.2 Hz, CH_3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.9, 168.3, 165.1, 164.6, 138.8 (q, $^2J_{C\text{-}F}$ = 31.9 Hz), 138.4 (q, $^2J_{C\text{-}F}$ = 31.9 Hz), 125.7 (q, $^3J_{C\text{-}F}$ = 6.0 Hz), 125.1 (q, $^3J_{C\text{-}F}$ = 6.0 Hz), 123.1 (q, $^1J_{C\text{-}F}$ = 275.3 Hz), 123.0 (q, $^1J_{C\text{-}F}$ = 275.3 Hz), 61.8, 61.7, 52.8, 52.5, 32.4, 32.1, 14.4.

MS (EI, 70 eV): *m*/*z* = 240.2 [M]$^+$.

Methyl 5-Oxo-3-(trifluoromethyl)hex-2-enoate (4g)
Derived from (methoxycarbonylmethylene)triphenylphosphorane (**3a**, 47 mmol) and 1,1,1-trifluoropentane-2,4-dione (**2g**, 39 mmol) using protocol d (reaction time: 10–30 min). After separation of the reaction mixture by column chromatography on silica gel (25 g, hexane–EtOAc), vinyl ketone **4g** and pyranone **5g** were obtained.

Yield of vinyl ketone **4g**: 6.15–6.97 g (75–85%); colorless oil; bp 25–30 °C/1 mmHg; mixture of isomers (1:2).

R_f = 0.41 (PE–EtOAc, 3:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.83, 6.56 (s, 2 CH=CR^1, 1:2), 3.85, 3.65 (s, 2 CH_2), 3.76, 3.72 (s, 2 OCH_3), 2.35, 2.27 (s, 2 CH_3, 1:2).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 201.0, 198.0, 168.9, 165.3, 139.2 (q, $^2J_{C\text{-}F}$ = 31.9 Hz), 135.1 (q, $^2J_{C\text{-}F}$ = 30.9 Hz), 130.1 (q, $^3J_{C\text{-}F}$ = 5.0 Hz), 124.7 (q, $^3J_{C\text{-}F}$ = 5.0 Hz), 123.2 (q, $^1J_{C\text{-}F}$ = 274.3 Hz), 121.0 (q, $^1J_{C\text{-}F}$ = 274.3 Hz), 52.7, 52.4, 32.2, 31.9, 41.4, 32.0.

MS (EI, 70 eV): *m*/*z* = 210.2 [M]$^+$.

6-Methyl-4-(trifluoromethyl)-2*H*-pyran-2-one (5g)
Yield: 0.29–1.31 g (5–23%); white solid; mp 41–42 °C; sublimed at 25–30 °C/1 mmHg.

R_f = 0.44 (PE–EtOAc, 2:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.38 (s, 1 H), 6.05 (s, 1 H), 2.26 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.8, 160.7, 144.6 (q, $^2J_{C\text{-}F}$ = 34.4 Hz), 121.0 (q, $^1J_{C\text{-}F}$ = 274.3 Hz), 110.6 (q, $^3J_{C\text{-}F}$ = 4.5 Hz), 98.5 (q, $^3J_{C\text{-}F}$ = 2.0 Hz), 20.0.

Anal. Calcd for $C_7H_5F_3O_2$: C, 47.2; H, 2.8. Found: C, 46.92, 47.35; H, 2.81, 2.82.

Ethyl 2-(Ethoxycarbonyl)cyclopent-1-ene-1-acetate (4j)[12e]
Obtained from (ethoxycarbonylmethylene)triphenylphosphorane (**3b**, 72–77 mmol) and ethyl 2-oxocyclopentanecarboxylate (**2j**, 60–64 mmol) using protocol d (reaction time: 48 h), followed by purification by distillation.

Yield: 7.73–8.69 g (57–60%); colorless oil; bp 65–75 °C/0.5–1 mmHg.

R_f = 0.51 (EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.17 (q, *J* = 7.0 Hz, 2 H), 4.13 (q, *J* = 6.6 Hz, 2 H), 3.66 (br s, 2 H), 2.67–2.63 (m, 2 H), 2.58–2.55 (m, 2 H), 1.90–1.82 (m, 2 H), 1.27 (t, *J* = 6.6 Hz, 3 H), 1.25 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 170.3, 165.5, 149.9, 130.7, 60.6, 59.8, 38.5, 35.4, 33.3, 21.3, 14.6, 14.5.

Ethyl 2-(Ethoxycarbonyl)cyclohex-1-ene-1-acetate (4k)
Synthesized from (ethoxycarbonylmethylene)triphenylphosphorane (**3b**, 60 mmol) and ethyl 2-oxocyclohexanecarboxylate (**2k**, 72 mmol) using protocol d (reaction time: 48 h), followed by purification by distillation.

Yield: 7.21 g (50%); colorless oil; bp 80–85 °C/0.5 mmHg.

R_f = 0.51 (EtOAc).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 4.15 (q, *J* = 7.0 Hz, 2 H), 4.13 (q, *J* = 7.0 Hz, 2 H), 3.42 (br s, 2 H), 2.34–2.31 (m, 2 H), 2.21–2.18 (m, 2 H), 1.65–1.61 (m, 4 H), 1.26 (t, *J* = 7.0 Hz, 3 H), 1.25 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.2, 168.1, 142.1, 127.7, 60.5, 60.1, 40.6, 32.8, 26.3, 22.1, 22.0, 14.6, 14.5.

MS (EI, 70 eV): *m*/*z* = 194.1 [M – 46.2]$^+$.

***H*-Vinylcarbonyl Compound 4e (Diethyl 3-Phenylpent-2-enedioate)**
A mixture of tri-*n*-butyl(ethoxycarbonylmethylene)phosphorane (**3c**,[33] 0.12 mol) and ethyl benzoylacetate (**2e**, 0.1 mol) in toluene (20 mL) was kept under reflux for 23 h, until the completion of the reaction (by TLC and ^{1}H NMR spectroscopy). The mixture was concentrated under reduced pressure and separated by flash chromatography on silica gel (200 g; hexane–Et_2O, 1:4). The resulting vinyl acetate **4e** was distilled.

Yield: 22.3 g (85%); colorless oil; bp 130–140 °C/0.1 mmHg.

R_f = 0.42 (hexane–Et_2O, 2:1).

IR (neat): 1734, 1708, 1629, 1446 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.46–7.43 (m, 2 H), 7.37–7.35 (m, 3 H), 6.27 (s, 1 H), 4.20 (q, *J* = 7.3 Hz, 2 H), 4.16 (s, 2 H), 4.12 (q, *J* = 7.3 Hz, 2 H), 1.30 (t, *J* = 7.3 Hz, 3 H), 1.18 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 170.0, 166.0, 150.8, 140.5, 129.0, 128.5, 126.3, 119.8, 60.6, 60.0, 36.8, 14.0, 13.9.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{15}H_{19}O_4^+$: 263.1283; found: 263.1287.

Vinyldiazocarbonyl Compounds 1a–g,j via a Diazo Transfer Reaction (Approach 'A,B', Stage 'B', Table 2); General Procedure

To a stirred soln of a vinylcarbonyl compound **4a–g**,**j**,**k** (12–21 mmol, 1 equiv) and *p*-ABSA (13.2–23.1 mmol, 1.1 equiv) in CH_2Cl_2 (10–30 mL) at 0 °C, DBU (12–21 mmol, 1 equiv) was added dropwise. The reaction mixture was stirred at r.t. for 2–3 h, then filtered through a short plug of silica gel (5–10 g) eluting with CH_2Cl_2 or Et_2O–PE (1:1, 25–50 mL). The solvents from the combined organic eluates were removed under reduced pressure and the residue was distilled (in the case of **1g**) or purified by chromatography on silica gel (**1a–f**,**j**) to give vinyldiazocarbonyl compounds **1**.

Dimethyl *trans*-4-Diazopent-2-enedioate (1a)[6b,34]

Yield: 1.88 g (85%); yellow solid; mp 72–73 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.33 (d, $^3J_{H-H}$ = 16.2 Hz, 1 H), 5.73 (d, $^3J_{H-H}$ = 16.2 Hz, 1 H), 3.85 (s, 3 H), 3.75 (s, 3 H).

UV/Vis (EtOH): λ_{max} (log ε) = 259 (3.91), 297 nm (3.92).

UV/Vis (MeCN): λ_{max} (log ε) = 259 (4.04), 294 nm (4.10).

UV/Vis (hexane): λ_{max} (log ε) = 255 (3.9), 293 nm (4.0).

Dimethyl *trans*-4-Diazo-3-methylpent-2-enedioate (1b)[6b]

Yield: 1.33 g (56%); yellow oil.

R_f = 0.35 (PE–EtOAc, 5:1).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.51 (q, $^4J_{H-H}$ = 1.2 Hz, 1 H), 3.81 (s, 3 H), 3.69 (s, 3 H), 2.36 (d, $^4J_{H-H}$ = 1.2 Hz, 3 H).

Diethyl *trans*-4-Diazo-3-methylpent-2-enedioate (1c)

Yield: 1.98 g (73%); yellow solid; mp 15–18 °C.

R_f = 0.35 (PE–EtOAc, 5:1).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.51 (s, 1 H), 4.28 (q, *J* = 7.3 Hz, 2 H), 4.15 (q, *J* = 7.3 Hz, 2 H), 2.36 (s, 3 H), 1.31 (t, *J* = 7.3 Hz, 3 H), 1.27 (t, *J* = 7.3 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.0, 163.8, 140.6, 112.1, 69.3, 61.6, 60.0, 14.7.

MS (EI, 70 eV): *m*/*z* = 198.2 $[M - 28]^+$.

Methyl *trans*-4-Diazo-3-methyl-5-oxohex-2-enoate (1d)

Yield: 2.3 g (60%); yellow solid; mp 55–57 °C.

R_f = 0.64 (PE–EtOAc, 3:1).

IR (KBr): 2087, 1716, 1662 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.66 (s, 1 H), 3.69 (s, 3 H), 2.32 (s, 6 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.9, 167.0, 139.8, 113.9, 66.1, 51.1, 27.7, 15.9.

MS (EI, 70 eV): *m*/*z* = 182.1 $[M]^+$.

UV/Vis (MeCN): λ_{max} (log ε) = 216 (4.05), 282 nm (3.97).

Diethyl *cis*-4-Diazo-3-phenylpent-2-enedioate (1e)

Yield: 2.49 g (72%); yellow oil.

R_f = 0.40 (hexane–Et_2O, 2:1).

IR (neat): 2112, 1704, 1592, 1493 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.47–7.45 (m, 2 H), 7.40–7.37 (m, 3 H), 6.02 (s, 1 H), 4.23 (q, *J* = 7.2 Hz, 2 H), 4.10 (q, *J* = 7.2 Hz, 2 H), 1.30 (t, *J* = 7.2 Hz, 3 H), 1.09 (t, *J* = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 164.4, 164.0, 143.4, 138.2, 129.7, 128.4, 127.8, 116.0, 63.9, 61.0, 60.1, 14.1, 13.9.

HRMS (ESI): *m*/*z* $[M - 28 + H]^+$ calcd for $C_{15}H_{17}O_4^+$: 261.1127; found: 261.1127.

Methyl *cis*- and *trans*-4-Diazo-5-oxo-3-(trifluoromethyl)hex-2-enoate (1g)[6c,11c]

Yield: 3.57 g (43%); yellow oil; bp 45–50 °C/1–2 mmHg; mixture of stereoisomers (1:1).

R_f = 0.34 (PE–Et_2O, 2:1).

***cis*-Isomer 1g**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.60 (s, 1 H), 3.81 (s, 3 H), 2.25 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.1, 163.6, 128.0 (q, $^2J_{C-F}$ = 34.5 Hz), 126.8 (q, $^3J_{C-F}$ = 4.6 Hz), 122.7 (q, $^1J_{C-F}$ = 275.8 Hz), 65.4, 52.6, 25.7.

***trans*-Isomer 1g**

^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.01 (s, 1 H), 3.82 (s, 3 H), 2.34 (s, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 188.9, 164.8, 127.6 (q, $^2J_{C-F}$ = 34.5 Hz), 127.4 (q, $^3J_{C-F}$ = 4.6 Hz), 121.6 (q, $^1J_{C-F}$ = 275.8 Hz), 66.2, 60.7, 26.7.

Ethyl α-Diazo-2-(ethoxycarbonyl)cyclopent-1-ene-1-acetate (1j)

Yield: 3.18 g (60%); yellow solid; mp 52–53 °C.

R_f = 0.64 (hexane–EtOAc, 1:1).

IR (neat): 2108, 1696, 1593 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.25 (q, *J* = 7.0 Hz, 2 H), 4.20 (q, *J* = 7.0 Hz, 2 H), 2.96–2.91 (m, 2 H), 2.73–2.68 (m, 2 H), 1.95–1.87 (m, 2 H), 1.30 (t, *J* = 7.0 Hz, 3 H), 1.29 (t, *J* = 7.0 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 164.6, 164.4, 141.3, 124.8, 63.5, 61.0, 60.1, 37.3, 33.5, 22.1, 14.4, 14.3.

HRMS (ESI): *m*/*z* $[M - 28]^+$ calcd for $C_{12}H_{16}O_4^+$: 224.1048; found: 224.1038.

Diazodicarbonyl Compounds 7b,e–i (Approach 'B,A', Stage 'B', Table 3)

The diazo transfer reaction with nonfluorinated 1,3-diketones and esters *H*-**2b**,**e**,**i** was carried out in the usual manner;[8] the same reaction with ***F***-dicarbonyl compounds **2f–h** was performed in oven-dried equipment, excluding entry of moisture in the system at all stages of the process.[8c,d,11d]

Methyl 2-Diazoacetoacetate (7b)[35a]

Prepared from methyl acetoacetate (5.2 g, 45 mmol), *p*-ABSA (9.6 g, 40 mmol) and Et_3N (8.1 g, 11 mL, 80 mmol) in CH_2Cl_2 (90 mL) for 2 h.

Yield: 4.8 g (85%).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 3.83 (s, 3 H), 2.47 (s, 3 H).

Ethyl 2-Diazoacetoacetate (7c)[11d]

Prepared from ethyl acetoacetate (4.16 g, 32 mmol), *m*-$O_2NC_6H_4SO_2N_3$ (7.75 g, 32 mmol) and Et_3N (6.4 g, 8.8 mL, 64 mmol) in CH_2Cl_2 (70 mL) for 2 h.

Yield: 4.29 g (86%); bp 40–42 °C/0.6 mmHg.

Ethyl 2-Diazobenzoylacetate (7e, R^2 = OEt)[35b]

Prepared from ethyl benzoylacetate (2.7 g, 14 mmol), *m*-$O_2NC_6H_4SO_2N_3$ (3.4 g, 14 mmol) and Et_3N (2.8 g, 3.9 mL, 28 mmol) in CH_2Cl_2 (40 mL) for 4 h.

Yield: 2.7 g (90%); bp 95–99 °C/1 mmHg.

Methyl 2-Diazobenzoylacetate (7e′, R^2 = OMe)[35a]
Prepared from methyl benzoylacetate (3.7 g, 20 mmol), *p*-ABSA (5.0 g, 20 mmol) and Et_3N (4.0 g, 5.6 mL, 40 mmol) in CH_2Cl_2 (35 mL) for 5 h.

Yield: 3.6 g (89%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.64–7.61 (m, 2 H), 7.55–7.51 (m, 1 H), 7.44–7.41 (m, 2 H), 3.79 (s, 3 H).

Ethyl 2-Diazo-4,4,4-trifluoro-3-oxobutanoate (7f′, R^2 = OEt)[11d]
Prepared from ethyl 4,4,4-trifluoro-3-oxobutanoate (3.9 g, 21 mmol), *m*-$O_2NC_6H_4SO_2N_3$ (4.9 g, 21 mmol) and DBU (3.2 g, 21 mmol) in CH_2Cl_2 (50 mL) for 0.5 h.

Yield: 4.2 g (66%); bp 35–37 °C/0.6 mmHg.

3-Diazo-1,1,1-trifluoropentane-2,4-dione (7g)[10d]
Prepared from 1,1,1-trifluoropentane-2,4-dione (10.8 g, 70 mmol), *p*-ABSA (18.6 g, 77 mmol) and DBU (5.3 g, 5.3 mL, 35 mmol) in CH_2Cl_2 (80 mL) for 1 h.

Yield: 6.93 g (55%); bp 55 °C/18 mmHg.

Ethyl 2-Diazo-4,4,5,5,6,6,6-heptafluoro-3-oxohexanoate (7h)[11d]
Prepared from ethyl 4,4,5,5,6,6,6-heptafluoro-3-oxohexanoate (3.76 g, 13 mmol), *m*-$O_2NC_6H_4SO_2N_3$ (3.03 g, 13 mmol) and DBU (2.0 g, 13 mmol) in CH_2Cl_2 (40 mL) for 0.5 h.

Yield: 2.47 g (61%); bp 44–48 °C/0.6 mmHg.

Dimethyl 2-Diazo-3-oxopentanedioate (7i)[35c]
Prepared from dimethyl 3-oxopentanedioate (4.4 g, 25 mmol), *p*-ABSA (5 g, 20 mmol) and Et_3N (4 g, 5.6 mL, 40 mmol) in CH_2Cl_2 (50 mL) for 1.5 h.

Yield: 2.85 g (72%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.87 (s, 2 H), 3.84 (s, 3 H), 3.73 (s, 3 H).

Methyl 2-Diazo-4,4,4-trifluoro-3-oxobutanoate (7f, R^2 = OMe) via Acylation of Methyl Diazoacetate with Trifluoroacetic Anhydride
TFAA (20 mL, 0.146 mol) in CH_2Cl_2 (20 mL) was added dropwise at 0 °C during 30 min to a soln of methyl diazoacetate (~0.14 mol) in CH_2Cl_2 (140 mL) (obtained according to the literature[34] and used without any further purification) with added pyridine (11.2 mL, 0.146 mol). The reaction mixture was stirred at r.t. for 12 h, then concentrated at atmospheric pressure to a volume of ~120 mL and treated with pentane–Et_2O (1:1, 100 mL). The precipitate was removed by filtration, and the filtrate was washed with sat. NaCl soln (20 mL) and dried with $MgSO_4$ overnight. The solvents were removed under reduced pressure; distillation of the residue gave the methyl ester **7f**.

Yield: 23.3 g (85%); yellow liquid; bp 55–60 °C/10 mmHg.

R_f = 0.38 (hexane–Et_2O, 2:1).

IR (neat): 2146, 1750, 1675 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.90 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.1 (q, $^2J_{C-F}$ = 40.1 Hz), 159.0, 115.6 (q, $^1J_{C-F}$ = 288.8 Hz), 62.5, 53.1.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –74.56.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_5H_4N_2O_3F_3^+$: 197.0174; found: 197.0171.

Interaction of *H*- and *F*-Diazodicarbonyl Compounds 7c,e–h with Phosphoranes 3a,b (Approach 'B,A', Stage 'A', Table 4); General Procedure
To a stirred suspension of a triphenylphosphorane **3a**,**b** (16.6–20 mmol, 1.0 equiv) in Et_2O (50–60 mL), a soln of a diazodicarbonyl compound **7c**,**e**–**h** (16.6–20 mmol, 1.0 equiv) was added in one portion (*H*-**7c**,**e**) or dropwise (*F*-**7f**–**h**). After the diazodicarbonyl compounds *H*-**7c**,**e** with phosphorane **3b** were refluxed for 7 and 10 d, respectively, there was no indication of the formation of the *H*-vinyl diazo acetates **1c**,**e** or the associated pyrazoles **6c**,**e** (by TLC and ^{1}H NMR spectroscopy of the reaction mixtures). In the case of the Wittig reactions with *F*-diazodicarbonyl compounds **7f**–**h**, after complete disappearance of **7f**–**h** in the reaction mixture (1–2 h), the solid matter was removed by filtration, and the resultant filtrate was concentrated under reduced pressure. The residue was purified by column chromatography (hexane–Et_2O) or by distillation to furnish the vinyldiazocarbonyl compounds **1f**–**h** and pyridazines **8f**,**g**.

Dimethyl *cis*-4-Diazo-3-(trifluoromethyl)pent-2-enedioate (1f)
Prepared from methyl 2-diazo-4,4,4-trifluoro-3-oxobutanoate (**7f**; 4.0 g, 20 mmol) and (methoxycarbonylmethylene)triphenylphosphorane (**3a**; 8.36 g, 25 mmol).

Yield: 4.65 g (93%); yellow oil; bp 65–70 °C/1 mmHg.

R_f = 0.38 (hexane–Et_2O, 2:1).

IR (neat): 2109, 1720 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.44 (s, 1 H), 3.80 (s, 3 H), 3.78 (s, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 163.7, 163.4, 128.3 (q, $^2J_{C-F}$ = 33.2 Hz), 123.8, 121.9 (q, $^1J_{C-F}$ = 276.1 Hz), 58.2, 52.5, 52.2.

^{19}F NMR (376 MHz, $CDCl_3$): δ = –66.13.

HRMS (ESI): *m*/*z* $[M - 28 + H]^+$ calcd for $C_8H_8O_4F_3^+$: 225.0374; found: 225.0374.

Methyl 6-Methoxy-4-(trifluoromethyl)pyridazine-3-carboxylate (8f)[11d]
Yield: 519 mg (11%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (s, 1 H), 4.25 (s, 3 H), 4.03 (s, 3 H).

Methyl *cis*-4-Diazo-5-oxo-3-(trifluoromethyl)hex-2-enoate (1g)[11c]
Prepared from 3-diazo-1,1,1-trifluoropentane-2,4-dione (**7g**; 3.4 g, 22 mmol) and (methoxycarbonylmethylene)triphenylphosphorane (**3a**; 9.0 g, 27 mmol).

Yield: 3.68 g (93%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.52 (s, 1 H), 3.72 (s, 3 H), 2.16 (s, 3 H).

3-Acetyl-6-methoxy-4-(trifluoromethyl)pyridazine (8g)[6a]
Yield: 872 mg (18%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.29 (s, 1 H), 4.24 (s, 3 H), 2.76 (s, 3 H).

Ethyl *cis*-2-Diazo-3-[(ethoxycarbonyl)methylene]-4,4,5,5,6,6,6-heptafluorohexanoate (1h)[11d]
Prepared from ethyl 2-diazo-4,4,5,5,6,6,6-heptafluoro-3-oxohexanoate (**7h**; 0.40 g, 1.3 mmol) and (ethoxycarbonylmethylene)triphenylphosphorane (**3b**; 0.68 g, 1.95 mmol).

Yield: 415 mg (83%); bp 38–40 °C/0.5 mmHg.

Alternative Preparations of Vinyldiazocarbonyl Compounds 1a,c′,i

Diethyl *cis*-4-Diazopent-2-enedioate (Diethyl *cis*-Diazoglutaconate, 1a)
Compound **1a** was prepared by cross-coupling of ethyl 3-iodoacrylate with ethyl diazoacetate;[19] prepared from ethyl (2*Z*)-3-iodoacrylate (452 mg, 2 mmol), ethyl diazoacetate (570 mg, 5 mmol), Et_3N (304 mg, 3 mmol), TBAB (644 mg, 2 mmol) and $Pd(PPh_3)_4$ (104 mg, 0.1 mmol) in acetone (10 mL) for 2 h at 35 °C.

Yield: 270 mg (64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.52 (d, $^3J_{H-H}$ = 12.1 Hz, 1 H), 5.63 (d, $^3J_{H-H}$ = 12.1 Hz, 1 H), 4.29 (q, *J* = 7.4 Hz, 2 H), 4.15 (q, *J* = 7.0 Hz, 2 H), 1.31 (t, *J* = 7.0 Hz, 3 H), 1.27 (t, *J* = 7.4 Hz, 3 H).

Ethyl *trans*-4-Diazo-3-methyl-4-(methoxycarbonyl)but-2-enoate (1c′) via Dehydration of Diazo Alcohol 9c′ (Table 5)

1-Ethyl 2-Diazo-3-hydroxy-3-methyl-4-(methoxycarbonyl)butanoate (9c′, Alk = Me)

To a flame-dried 10–20-mL flask with methyl acetate (0.5 g, 7 mmol, 2.0 equiv) in anhyd THF (15 mL), a soln of 2 M LDA in hexane (3.5 mL, 2 equiv) was added under argon atmosphere, and the mixture was stirred at –78 °C for 1 h. A soln of diazo keto ester **7c** (0.55 g, 3.5 mmol, 1.0 equiv) in THF (5 mL) was added to the reaction mixture during 5 min so that the temperature did not rise above –70 °C, and the mixture was stirred for an additional 1.5 h until the reaction was completed (monitored by TLC). Then, a soln of glacial AcOH (7 mmol, 2 equiv) in abs THF (5 mL) was added dropwise, the reaction mixture was heated to r.t. and stirred for an additional 20 min, and was then filtered through neutral alumina (10 g) and washed with Et_2O (30–40 mL). The obtained solution was dried with $MgSO_4$ and the solvents were completely removed under reduced pressure to give the diazo alcohol **9c′** (of 99% purity by ^1H NMR spectroscopy), which was purified by column chromatography on silica gel.

Yield: 0.81 g (99%); yellow oil.

R_f = 0.33 (PE–MTBE, 1:1).

^1H NMR (400 MHz, $CDCl_3$): δ = 4.64 (br s, 1 H), 4.20 (q, $^3J_{H-H}$ = 7.2 Hz, 2 H), 3.70 (s, 3 H), 3.05 (d, $^2J_{H-H}$ = 16.4 Hz, 1 H), 2.83 (d, $^2J_{H-H}$ = 16.4 Hz, 1 H), 1.53 (s, 3 H), 1.26 (t, $^3J_{H-H}$ = 7.2 Hz, 3 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 171.8, 166.2, 68.0, 63.4, 60.7, 51.4, 43.9, 26.3, 13.8.

HRMS (ESI): *m*/*z* $[M - 28 + H]^+$ calcd for $C_9H_{15}O_5^+$: 203.0919; found: 203.0921.

Ethyl 2-Diazo-3-hydroxy-4-(methoxycarbonyl)-3-phenylbutanoate (9e′, Alk = Me)

Prepared from methyl acetate (0.60 g, 8.0 mmol, 2.0 equiv), 2 M LDA in hexane (4 mL, 2 equiv) and diazo keto ester **7e** (0.87 g, 4.0 mmol, 1.0 equiv).

Yield: 0.97 g (83%); yellow oil.

R_f = 0.35 (PE–MTBE, 1:1).

^1H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.53 (m, 2 H), 7.40–7.31 (m, 3 H), 5.33 (br s, 1 H), 4.20 (q, $^3J_{H-H}$ = 7.1 Hz, 2 H), 3.71 (s, 3 H), 3.58 (d, $^2J_{H-H}$ = 16.7 Hz, 1 H), 3.07 (d, $^2J_{H-H}$ = 16.7 Hz, 1 H), 1.26 (t, $^3J_{H-H}$ = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 173.2, 166.1, 143.9, 128.9, 128.5, 125.5, 73.0, 65.9, 61.1, 52.5, 43.7, 14.7.

Anal. Calcd for $C_{14}H_{16}N_2O_5$: C, 57.53; H, 5.52; N, 9.58. Found: C, 57.95, 57.56; H, 5.73, 5.72; N, 9.54, 9.23.

Ethyl *trans*-4-Diazo-3-methyl-4-(methoxycarbonyl)but-2-enoate (1c′)

To a soln of diazo alcohol **9c′** (0.3 g, 1.3 mmol, 1.0 equiv) and Et_3N (0.39 g, 3.9 mmol, 3 equiv) in anhyd CH_2Cl_2 (5 mL), a soln of $POCl_3$ (0.40 g, 2.6 mmol, 2 equiv) in anhyd CH_2Cl_2 (5 mL) was added at 0 °C during 5 min. The mixture was stirred at r.t. until the dehydration was finished (reaction time: 20 h, monitored by TLC and ^1H NMR spectroscopy); during the process, the mixture became dark and a precipitate was formed. The reaction mixture was filtered through silica gel (5 g) and washed with Et_2O (10 mL), the solvents were removed under reduced pressure and the residue was recrystallized (Et_2O–PE) to provide **1c′** as a yellow solid; yield: 85 mg (33%); mp 55–56 °C.

R_f = 0.46 (PE–MTBE, 1:1).

^1H NMR (300 MHz, $CDCl_3$): δ = 6.54 (q, $^4J_{H-H}$ = 1.1 Hz, 1 H), 4.29 (q, $^3J_{H-H}$ = 7.1 Hz, 2 H), 3.69 (s, 3 H), 2.37 (d, $^4J_{H-H}$ = 1.1 Hz, 3 H), 1.31 (t, $^3J_{H-H}$ = 7.1 Hz, 3 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 167.4, 163.8, 141.0, 111.5, 69.4, 61.6, 51.3, 15.9, 14.7.

Anal. Calcd for $C_9H_{12}N_2O_4$: C, 50.94; H, 5.70; N, 13.20. Found: C, 51.12, 51.14; H, 5.68, 5.67; N, 13.19, 13.30.

Compound 1i via Silylation of the Diazodicarbonyl Compound 7i (Scheme 3)

To a soln of dimethyl 2-diazo-3-oxopentanedioate (**7i**; 1.62 g, 8.1 mmol) and Et_3N (9.8 g, 9.8 mmol) in anhyd CH_2Cl_2 (25 mL), which was placed in a flame-dried 50-mL flask, TBSOTf (2.1 g, 9.8 mmol) was added dropwise under argon atmosphere at 0–5 °C. The reaction mixture was stirred at 0–5 °C for 1 h, then filtered through silica gel (2 g) and eluted with hexane–Et_2O (5:1, 100 mL). The resultant filtrate was concentrated under reduced pressure to give **1i** as a mixture of *cis*- and *trans*-stereoisomers [total yield: 2.1 g (81%)], which was separated by column chromatography on silica gel (hexane–Et_2O, 1:100 to 1:10).

Dimethyl *cis*-3-(*tert*-Butyldimethylsilyloxy)-4-diazopent-2-enedioate (*cis*-1i)

Yield: 76 mg (3%); bright yellow-orange oil.

R_f = 0.55 (hexane–EtOAc, 1:1).

^1H NMR (400 MHz, $CDCl_3$): δ = 5.26 (s, 1 H), 3.75 (s, 3 H), 3.65 (s, 3 H), 0.92 (s, 9 H), 0.24 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.9, 163.4, 155.5, 99.8, 65.2, 52.1, 50.7, 25.4, 18.2, –4.8.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{23}N_2O_5Si$: 315.1376; found: 315.1371.

Dimethyl *trans*-3-(*tert*-Butyldimethylsilyloxy)-4-diazopent-2-enedioate (*trans*-1i)

Yield: 1.63 g (64%); bright yellow-orange oil.

R_f = 0.55 (hexane–EtOAc, 1:1).

IR (neat): 2115, 1716, 1604 cm^{-1}.

^1H NMR (400 MHz, $CDCl_3$): δ = 6.07 (s, 1 H), 3.81 (s, 3 H), 3.64 (s, 3 H), 0.97 (s, 9 H), 0.21 (s, 6 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 165.3, 162.9, 149.9, 97.8, 68.6, 52.1, 50.5, 25.5, 18.3, –4.5.

HRMS (ESI): *m*/*z* $[M + H]^+$ calcd for $C_{13}H_{23}N_2O_5Si$: 315.1376; found: 315.1371.

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Supporting Information for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis.

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