The transition state of the cyclopropylidene to allene ring opening

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The transition state of the cyclopropyldene to allene ring opening

Sutherland, Robert Jude, Ph.D.

Iowa State University, 1988
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The transition state of the cyclopropylidene
to allene ring opening

by

Robert Jude Sutherland

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
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DOCTOR OF PHILOSOPHY

Department: Chemistry
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INTRODUCTION

In 1958, Doering and LaFlamme (1) demonstrated that olefins 1 may be transformed into allenes 4 in a convenient two step synthesis. A possible intermediate in this work, cyclopropylidene 3, has since been the subject of experimental (2,3) and theoretical (4) efforts. Experimental investigations have probed the stereochemical course of the ring opening, while theoretical efforts have focused on the mapping of the energy surface of the transformation.

\[ \text{CHBr}_2 \xrightarrow{\text{Mg/Na}} \text{cyclopropylidene} \xrightarrow{} \text{allene} \]

In 1954, Doering and Hoffmann (5) reported a synthesis of cyclopropyl geminal dihalides from alkenes, via the reaction of alkoxide ion with a haloform. Later, Doering and LaFlamme (1) converted 1,1-dibromocyclopropanes 2 into allenes by reduction with sodium or magnesium, although sodium was preferred. Sodium was dispersed on alumina and the reaction carried out at reduced pressure, without a solvent. Using this technique, 1,1-dibromo-2-n-propylcyclopropane was converted to 1,2-hexadiene in 64 percent yield.
The reaction was predicted to occur via the free carbene, although the authors considered and dismissed several possibilities (Scheme 1). The prediction of a carbene intermediate stems from the stereospecific addition of methylene iodide, reduced with zinc-copper couple, to cis and trans 2-butene.

Scheme 1
Skattebøl (6) used this technique to synthesize both acyclic and cyclic allenes in good yield. The appropriate olefins were cyclopropanated and subsequently decomposed with alkyl lithium compounds. In the case of 1,1-dibromo-2,3-tetramethylcyclopropane the expected allene was only a trace product (7). Instead, the carbon-hydrogen insertion product predominated (Scheme 2).

Scheme 2
Moore and Hill (8) reported that the ratio of bicyclo-
butane to allene was dependent upon the ability of the
substituents to stabilize the intermediate. They also noted
that insertion into a methylene was highly preferred over a
methyl carbon-hydrogen insertion (Scheme 3). The product
ratios in reactions 2-4 can be rationalized as arising from
steric control of insertion over ring opening. Comparison
of reactions 3 and 5 demonstrates that stabilization by the
anisyl groups favors ring opening.

Jones et al. (9) have generated cyclopropylidenes via
diazocyclopropane intermediates. They prepared
2,2-diphenylcyclopropanecarboxylic acid from diphenyl-
diazo methane and methacrylate, a procedure developed by
Walborsky and Hornyak (10). The acid was then converted to
the N-nitroso urea, which is the precursor of the
diazocyclopropane and ultimately cyclopropylidene (Scheme
4). The N-nitroso urea was then decomposed with a lithium
ethoxide in hydrocarbon solvent to give 1,1-diphenyllallene
in 90 percent yield. When cyclohexene was present they
obtained 18-22 percent yields of the spiropentane product
shown in Scheme 4.
Scheme 3

1. \[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Et} & \quad \text{Et}
\end{align*}
\]

2. \[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

3. \[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

4. \[
\begin{align*}
\text{Br} & \quad \text{Br} \\
\text{Ph} & \quad \text{Ph}
\end{align*}
\]

5. \[
\begin{align*}
\text{MeOPh} & \quad \text{PhOME} \\
\text{PhOME} & \quad \text{MeOPh}
\end{align*}
\]

Yields:

1. 87%

2. 98%

3. 73% 27%

4. 98%

5. 56% 44%
In 1963, Jones et al. (11) demonstrated the stereospecificity of the ring opening. Using the method of D'yakonov et al. (12) they prepared trans-2,3-diphenylcyclopropanecarboxylic acid. After resolving the enantiomeric mixture of acids, they transformed the (−)-trans-2,3-diphenylcyclopropanecarboxylic acid into the N-nitroso urea as before. The N-nitroso urea provided, when decomposed at 0°C, a 79 percent yield of (+)-1,3-diphenyllallene. This finding demands that the transition structure be asymmetric,
but it does not require that free cyclopropylidene be its source.

In order to determine the nature of the allene precursor, Jones et al. (13) sought to elucidate the mechanism of the decomposition of the N-nitroso urea. By a study of the expected side products and/or their stability to the reaction conditions, they were able to identify a very probable mechanism, which is shown in Scheme 5.

Scheme 5
first attacks the N-nitroso nitrogen, whose basic oxygen then deprotonates the amide nitrogen. Isocyanic acid is then generated, followed by loss of either hydroxide or alkoxide ion to give the diazotate. Finally, loss of water or alcohol gives the diazocyclopropane which can decompose to give allene directly or via cyclopropylidene.

This mechanism is complementary to the thermal mode of decomposition, which was studied by Muck and Jones (14). Here they propose that the oxygen, of the N-nitroso nitrogen, abstracts a proton from the amide nitrogen. Loss of isocyanic acid then gives the diazotic acid, which loses water to give the diazo compound (Scheme 6).

Scheme 6

\[
\begin{align*}
\text{R}_2\text{HC-NCONH}_2 & \xrightarrow{\Delta} \text{R}_2\text{HC-N}^\text{O}^\text{N-H} \\
\text{R}_2\text{HC-N}^\text{O}^\text{N-H} & \xrightarrow{\text{-HNCO}} \text{R}_2\text{HC-N}=\text{N}^\text{OH} \\
\text{R}_2\text{HC-N}=\text{N}^\text{OH} & \xrightarrow{\text{-OH}_2} \text{R}_2\text{C}=\text{N}_2
\end{align*}
\]

Jones and Walbrick (15) next looked at the stereochemistry of the allene which was generated in the presence of a cyclopropylidene trap. They found that allene generated in the presence of cyclohexene was of the same optical purity as allene generated without a trapping agent. They argued that it was very unlikely that two different
intermediates would produce allene of the same optical purity. They conclude from this that both the spiropentane and allene have a common intermediate, namely cyclopropylidene.

In perhaps their most interesting discovery, Jones and Krause (16) have shown that the ring opening of cyclopropylidene is affected by the electronic nature of the substituents. They studied para substituted cis-2,3-diaryl-cyclopropylidenes in order to demonstrate this effect. It is reasonable to assume that para substituted phenyl rings are of equal steric bulk; therefore, any optical activity in the products must arise from electronic controls on the mode of ring opening. To minimize any steric effects, they chose to study cis-2-phenyl-3-p-chlorophenylcyclopropylidene, cis-2-p-methylphenyl-3-phenylcyclopropylidene and cis-2-p-bromophenyl-3-p-methylphenylcyclopropylidene (Scheme 7).

Compound 5a, whose acid had a rotation of -5.73°, gave allene with a rotation of +5.95°; compound 5b, whose acid had a rotation of -1.00°, gave allene with a rotation of -8.26°; and compound 5c, whose acid had a rotation of -8.24°, gave allene with a rotation of +101.0°. All of these rotations were collected at 22-23°C, at 436 nanometers. Although the optical yields were low, it is clear that some difference in energy exists between path a and path b for the ring openings.
Miller and Shechter (17) have studied the electronic effects on the rate of decomposition of diaryldiazomethanes. A series of mono and disubstituted diphenyldiazomethanes were studied at 70°C, in a temperature regulated spectrophotometer. Interestingly, all substituents gave rate accelerations over the unsubstituted diphenyldiazomethane. The linear free energy plot showed a parabolic curve, which is usually indicative of a change in mechanism or complex kinetic behavior. Symmetrically disubstituted compounds show a rate reduction compared to the monosubstituted ones, and unsymmetrically disubstituted compounds show a large rate increase over either of monosubstituted ones. These results may be explained by
consideration of the orbital interactions as the transition state is approached (Scheme 8). The results suggest that each aryl ring may align itself with a different carbene orbital. Electron donors would align with the empty orbital and electron acceptors would line up with the filled carbene orbital, such that both groups would stabilize the transition state. Rate reduction occurs when a molecule bears two donors or two acceptors; one may align itself so as to lower the energy of the transition state, but the other is forced into a destabilizing orientation.

A reaction which is analogous to the cyclopropylidene to allene ring opening is the cyclopropyl cation to allyl cation ring opening, both are two pi electrocyclic ring openings, and as such are governed by the same orbital symmetry considerations (18).

Cyclopropanol was first synthesized by Magrane and Cottle (19) in 1942. They reacted 3-chloropropylene oxide
with magnesium bromide, followed by ethylmagnesium bromide
and iron chloride. Since then, many authors have noted the
reluctance with which cyclopropanol derivates under
solvolysis (20,21). In 1966, DePuy et al. (21) reported a
detailed investigation of the relative solvolysis rates of
arylcyclopropyl tosylates. The solvolysis of trans-2-aryl-
cyclopropyl tosylates were run in buffered acetic acid
solutions at 108°C. They studied the phenyl, para chloro-, para methyl- and trifluoromethylphenyl cases, and correlated
the data to standard sigma values. They obtained a rho
value of -2.4±.2 for the trans systems. The evidence points
to a transition state in which partial solvolysis and ring
opening have begun (Figure 1).

Kirmse and Schütte (22) investigated the cyclopropyl
cation problem via the diazonium ion precursor. They used
sodium formate to decompose N-(2-phenylcyclopropyl)-N-
nitroso urea in deuterated methanol. After studying both cis and trans substituted compounds, they concluded that the ring opening was not in concert with nitrogen loss, and that the free cation was a common intermediate. This work is not, in principle, contrary to the solvolysis of cyclopropyl tosylates.

The thermal (23) and solvolytic (24) behavior of cyclopropyl halides has also been investigated. Parham and Yong (25) studied the solvolysis of trans-1,1-dichloro-2,3-dipropylcyclopropane, in ethanol, at 80.8°C. The reactions were carried out in the dark with a silver nitrate catalyst. The product, trans ether 9, supports the idea that ring opening and solvolysis occur in concert (Scheme 9).

Scheme 9

The formation of a single bond between the termini of a linear n-pi electron system, and the reverse process, was defined as an electrocyclic transformation, by Woodward and
Hoffmann (18). For such a reaction to occur, the termini must rotate in either a conrotatory or a disrotatory sense (Figure 2). The rotatory pathway that is followed by a given molecule is dependent upon the number of pi electrons and the mode of activation, i.e., thermal or photochemical. The conservation of orbital symmetry is the guiding principle for these reactions. In a conrotatory process, a two fold axis of rotation ($C_2$) is maintained, whereas a mirror plane ($σ$) is maintained in a disrotatory process. Some predicted modes of ring opening are shown in Figure 3 (26). The generalized rule is that a thermal $(4n+2)\pi$ electrocyclic ring opening will be thermally disrotatory and photolytically conrotatory. A $(4n)\pi$ electrocyclic ring
opening will be thermally conrotatory and photolytically disrotatory. Odd electron species will behave as the even electron species containing one more electron, and charged species will behave as the neutral ones, with the same number of electrons. Note that cyclopropylidene, in its ground singlet state, should behave as cyclopropyl cation, and, in its lowest triplet state, as a cyclopropyl anion.

\[
\begin{align*}
\Delta & \quad h_v \\
\begin{array}{c}
\text{CON} & \quad \text{DIS} \\
\text{DIS} & \quad \text{CON} \\
\text{DIS} & \quad \text{CON} \\
\text{CON} & \quad \text{DIS} \\
\text{CON} & \quad \text{DIS}
\end{array}
\end{align*}
\]

Figure 3. Examples of electrocyclic reactions for thermal (\(\Delta\)) and photochemical (\(h_v\)) modes

The \(\text{C}_3\text{H}_4\) systems in general, and cyclopropylidene in specific, undergo a variety of rearrangements which encompass a great deal of chemistry (27). These include: ring opening and closing, hydrogen shifts, carbon-hydrogen
bond insertions, additions to olefins, etc. Some of these are depicted in Figure 4. The first problem in computing

\[
\begin{align*}
\Delta & \leftrightarrow \equiv \equiv \\
\Uparrow & \downarrow \\
\equiv & \equiv \\
\Delta & \leftrightarrow \\
\end{align*}
\]

Figure 4. Representative species on the C$_3$H$_4$ energy surface

the cyclopropylidene to allene energy surface was to determine the ground state multiplicity and geometry for cyclopropylidene.

In 1978, Pasto et al. (28) reported that the triplet state was 8.4 kcal/mol lower in energy than the lowest singlet. Pasto's calculations employed a restricted Hartree-Fock (RHF) wave function, for the singlet, and an unrestricted Hartree-Fock (UHF) wave function for the triplet. The geometries were optimized with STO-3G and 4-31G basis sets. Baird and Taylor (29), on the other hand, determined that the triplet was 6.4 kcal/mol above the lowest singlet. This work was based on STO-3G basis sets, but used RHF wave functions for both the singlet and triplet energies.
Honjou et al. (27,30) have published the results of their investigation of the C$_3$H$_4$ energy surface. In this study the structures and paths were determined by self-consistent-field (SCF) wave functions, with double zeta plus polarization (DZP) functions used to determine the geometrical parameters. Energies were determined with either one-reference single and double-excitation configuration-interaction (SDCI) with a DZP basis, or a multi-reference SDCI wave function. They found that the singlet lies approximately 12 kcal/mol below the triplet, with an estimated error of ±2 kcal/mole. The resultant relative energies of some C$_3$H$_4$ species are shown in Figure 5.

![Figure 5. Relative energies for some C$_3$H$_4$ species](image-url)
The energy surface that contains the transition state of the cyclopropylidene to allene ring opening has received separate attention. Several authors (31-33) have done extensive mapping of the surface for cyclopropylidene to allene, and for the cyclopropyl cation to allyl cation as well (34).

Dillon and Underwood (31) were among the first to attempt to map the cyclopropylidene to allene ring opening surface. Their calculations imposed severe restrictions on the cyclopropylidene geometry, so much so that no minimum could be found. The calculation suggests that an initially disrotatory ring opening leads to a nonrotated transition state, which yields a conrotated product. Dewar et al. (33) have explored the surface using MINDO/2 calculations, from which they find a nonrotatory ring opening to give a planar allene. This, of course, is not consistent with the experimental work of Jones et al. (11).

In 1985, Rauk et al. (35) published a detailed account of the cyclopropyliden to allene ring opening. Geometries were optimized at the Hartree-Fock level with analytical gradient procedures and a split valence 3-21G basis set. The 3-21G structures were then reoptimized at the 6-31G and 6-31G** levels. They found that the transition state occurs when the CCC angle is 96.2°, with an activation barrier of 11.5 kcal/mol. At 95° of opening and 35° of disrotation,
the molecule begins to enter the conrotatory phase as the transition state nears. Although Rauk et al.'s computations are more exact and detailed than are those of Dillon and Underwood, they provide qualitatively the same picture of the energy surface. They both suggest a transition structure which resembles the one depicted in Figure 6.

![Figure 6. Transition state structure for the cyclopropylidene to allene ring opening, as obtained by Rauk et al. (35)](image)

Ruedenberg et al. (36) have also mapped this energy surface in great detail. They used the Fully Optimized Reaction Space (FORS) model, which was introduced by Ruedenberg and Sundberg (37). MCSCF energies were calculated using a minimal basis set (STO-3G). In order to calculate the ground state energy of cyclopropylidene, one would need to optimize the 15 internal coordinates in a 16 dimensional space. In order to simplify the calculation,
Ruedenberg et al. fixed all but three of these variables. The three key coordinates, $\phi$, $\delta_1$ and $\delta_2$ (Figure 7), were varied in order to find important geometries on the energy surface. Then, at each geometry, all 15 coordinates were reoptimized, to provide the best structure. Calculations were performed to test the validity of these approximations, and no discontinuities were found.

Figure 7. The fifteen internal coordinates for cyclopropylidene, as defined by Ruedenberg et al.

The angle $\phi$ was investigated in $5^\circ$ steps from $50^\circ$ to $100^\circ$ and in $1^\circ$ steps from $82^\circ$ to $86^\circ$ (the transition region). At a CCC angle of $80^\circ$ the first bifurcation was reached. This corresponds to the choice between two degenerate,
disrotatory paths that the molecule may take. As the ring continues to open, the transition region was found to lie between 84° and 85°. At 85° a second bifurcation was revealed, which provides a path to each of two enantiomeric geometries. A detailed examination of the transition region gave \( \phi = 84.24°, \delta_+ = 5.94° \) and \( \delta_- = 30.85° \) at the transition state (\( \delta_+ = (\delta_1 + \delta_2)/2 - 90 \) and \( \delta_- = \delta_1 - \delta_2 \)). This is shown in Figure 8. A barrier of approximately 40 kcal/mol was found with these minimal basis calculations. Ruedenberg et al. describe the "transition region," containing the second bifurcation, as relatively flat. With the energy surface calculated in detail, via a minimal basis function, they recalculated key species with an expanded basis set.

These new calculations by Ruedenberg et al. (36) serve the purpose of more carefully defining the activation barrier. The changes made include the use of the Dunning-Hay (38) basis plus polarization functions, and an even-tempered Gaussian basis (39) of double-zeta quality. These changes result in a lowering of the ring opening barrier to
Figure 8. Contour plots of cyclopropylidene before (left) and after (right) the transition state, as calculated by Ruedenberg et al.
13 kcal/mol leaving other features of the surface almost unchanged (Figure 9). A notable change is that the extended basis calculation finds only one transition structure. The second bifurcation comes after the transition state at a valley ridge inflection point; the walls of the valley gradually lower, flatten and invert (the inflection point) as the molecule descends from the transition state. In a further calculation they employed the extended basis set with single and double excitation configuration interactions (SDCI) to yield a value of 7.4 kcal/mol for the ring opening barrier. This value is not corrected for zero point energy differences.

In order to shed some light on the work of Jones and Krause (16) on electronic influences on allene stereochemistry, Ruedenberg et al. (36) calculated some substituted cyclopropylidene to allene surfaces. Due to the overly complex nature of such calculations, they modeled substituent effects by adding long range electrostatic and steric effects to the unsubstituted case. The molecules thus modeled were 2-methylcyclopropylidene, 2,3-dimethylcyclopropylidene and 2-bromo-3-methylcyclopropylidene. The computations indicate that short-range covalent interactions are not involved, and that stereospecificity is determined by long range dipole-dipole interactions as well as by
Figure 9. Cyclopropylidene at $\phi = 100^\circ$ from the minimal basis (left) and extended basis (right) calculations of Ruedenberg et al.
steric effects. A contour plot for the cis-2,3-dimethyl and trans-2,3-dimethyl species is shown in Figure 10.

Figure 10. Contour plot for cis and trans-2,3-dimethyl-cyclopropylidene: $\phi$ vs $\delta$, where $\delta = (\delta_1 + \delta_2)/2$, from calculations by Ruedenberg et al.

The work of Jones and Krause (16) and of Ruedenberg et al. (36) was the source of our interest in the cyclopropylidene to allene ring opening. The nature of the transition state for this ring opening has not been determined experimentally and is quite complex for a detailed theoretical determination, at a high level of theory. The theoretical and experimental evidence to date point towards a transition state which should exhibit cationic character. Such a system should be influenced electronically by
electron donors and acceptors. In order to minimize steric interactions we chose trans diaryl cyclopropylidenes for our study; by substituting these aryl groups in the para position we can also effect the donor/acceptor influence on the transition state of $3'$. Finally, since absolute rates of ring opening are not possible (cyclopropylidene has yet to be isolated) a partitioning trap for cyclopropylidene must be introduced, so that relative rate may be obtained.

Methanol has been chosen as the trapping agent, it provides diffusion control trapping (40) and forms kinetically simple products with cyclopropylidene. It is reasonable that $3'$ may be formed at various methanol concentrations and the relative rates of ring opening and trapping may be correlated with electronic influences from the para substituents.
RESULTS AND DISCUSSION

The preparation of compounds 18a-j was effected by the method of Walbrick et al. (41) with several modifications. The trans-stilbenes 13a-j were prepared via a standard Wittig reaction. The crude product mixture was then isomerized to give only the trans olefins (Scheme 9). The isocyanates 16a-j were prepared from the acids 15a-j in a single step (Scheme 10), using diphenylphosphoryl azide (DPPA) (42) in refluxing benzene. This is a superior method to that of Walbrick et al. in terms of yield, convenience and functionality tolerance. Further, the isocyanates may be converted to the carbamates 17a-j in the same reaction pot, in an overall yield of 50-85 percent. The method of nitrosation of the carbamates was also altered. The amount of acetic acid in the solvent was reduced from 30 percent to a trace, as several of the N-nitroso carbamates (18a-j) proved to be very acid sensitive.

The reaction of 18a (~ 10⁻³ M) with sodium methoxide, in toluene/methanol solution (5-25 M methanol), is illustrative of the reactions of 18a-j (Scheme 11). The principal products are 1,3-diphenylallene, 19a, and trans-2,3-diphenylcyclopropyl methyl ether, 20a. The ring opening of trans-2,3-diphenylcyclopropylidene, 22a, gives the allene and methanol trapping of 22a provides the ether.
Scheme 9

\[(\text{Ph})_3p + \text{Cl}^- \rightarrow \]

\[\text{Cl} \quad \text{Ph} \quad \text{Cl} \quad \text{Ph} \quad \text{Cl} \]

\[\text{Ph} + \text{Ph} \rightarrow \text{Ph} \]

11: a-e
12: a-e

11: a, Y=H, b, Y=Me, c, Y=OMe, d, Y=Cl, e, Y=CF_3
12: a, X=H, b, X=Me, c, X=OMe, d, X=Cl, e, X=CF_3

\[\text{XPh} + \text{PhX} \rightarrow \text{XPh} \]

13: a-j
13': a-j
13: a-j

13: a, X/Y=H/H, b, X/Y=Me/Me, c, X/Y=OMe/OMe, d, X/Y=Cl/Cl, e, X/Y=CF_3/CF_3, f, X/Y=H/Me, g, X/Y=H/Cl, h, X/Y=H/CF_3, i, X/Y=Me/Cl, j, X/Y=Me/CF_3
Scheme 10

\[ \text{DPPA} \quad \overset{\text{EtOH}}{\longrightarrow} \quad \text{NaNO}_2, \text{H}^+ \]

13 \text{ a-j}

14 \text{ a-j}

15 \text{ a-j}

16 \text{ a-j}

17 \text{ a-j}

18 \text{ a-j}

19 \text{ a-j}

20 \text{ a-j}

13-20 \text{ a, X/Y=H/H b, X/Y=Me/Me c, X/Y=OMe/OMe d, X/Y=Cl/Cl e, X/Y=CF}_3/\text{CF}_3 f, X/Y=H/Me g, X/Y=H/Cl h, X/Y=H/CF}_3 i, X/Y=Me/Cl j, X/Y=Me/CF}_3
Scheme 11

18a \rightarrow 21a \rightarrow 22a

\[ \text{Ph} \quad \text{H} \quad \text{Ph} \]

\[ \text{Ph} \quad \text{H} \quad \text{Ph} \]

\[ \text{Ph} \quad \text{H} \quad \text{Ph} \]

\[ \text{OMe} \]

\[ \text{Ph} \quad \text{H} \quad \text{Ph} \]

\[ \text{Ph} \quad \text{Ph} \]

\[ \text{Ph} \quad \text{Ph} \]

\[ \text{Ph} \quad \text{Ph} \]

\[ 25a \]

\[ 20a \]

\[ 19a \]

\[ 24a \]
Independent synthesis of $^{19a}$ was effected by decomposing the corresponding dibromocyclopropane with methyllithium. The ether $^{20a}$ was prepared from trans-stilbene and $\alpha,\alpha$-dichloromethyl methyl ether treated with methyllithium. Both products showed identical spectra and retention times when coinjected on a capillary GLPC column.

When the concentration of base is low, side products of the type $^{25a}$ are generated via diazonium ion chemistry. The reaction path from $^{21a}$ to $^{25a}$ was shown not to cross over to give products $^{19a}$ or $^{20a}$. This was demonstrated in two ways: first, 1,3-diphenylallyl cation was generated from the tosylate, the p-nitrobenzoate, and the action of hydrochloric acid on the alcohol in methanol solution, whereby $^{25a}$ was the only detectable product. Secondly, when high concentrations (> 5 M) of soluble base were used, the diazonium ion pathway was averted (no $^{25a}$ was detected), and the ratio of $^{20a}/^{19a}$ was the same as when $^{25a}$ was observed.

A stirred solution of $^{18a}$ was decomposed by addition of an excess (> 10 equivalents) of solid sodium methoxide. The solutions were stirred for 3-5 minutes although the reaction appeared to be over after about 30 seconds. The reactions were neutralized with ammonium chloride solution and extracted into ether before analysis. The product ratio $^{20a}/^{19a}$ was obtained via capillary GLPC analysis over a range of methanol concentrations (4.9 M to 24.7 M).
Response factor ratios were applied to all data to correct the product ratios to mole ratios. The response factor was that number which when multiplied by the GLPC ratio would give the mole ratio. To obtain these values, an NMR sample was prepared which contained a mixture of 20a and 19a. Mole ratios were determined by integration of a 200 scan 300 MHz NMR spectrum. The NMR sample was then analyzed by GLPC (average of 4 determinations) and Equation (1) was used to calculate the response factor ratio (RF = response factor, PN = proton number to correct to the mole ratio).

\[
\frac{RF(20a)}{RF(19a)} = \left[ \frac{\text{NMR}(20a)}{\text{NMR}(19a)} \times \frac{\text{PN}(19a)}{\text{PN}(20a)} \right] \times \frac{\text{GLPC}(19a)}{\text{GLPC}(20a)}
\] (1)

The results were interpreted in terms of the kinetic model shown in Scheme 12. Equation (2) was derived with presumption that 22a is a common intermediate for the generation of 19a and 20a. This predicts that a plot of 20a/19a versus the concentration of methanol should be linear with a zero intercept. All plots are indeed linear with intercepts which lie within experimental error of zero. The intercepts are consistently positive, which perhaps requires some attention. Several authors (43, 44) have noted that high concentrations (> 1 M) of methanol (as were used in this work) react somewhat faster with carbenes than do submolar concentrations. These small but consistently
positive intercepts, therefore, may be the result of an unfair extrapolation of the data. Further, due to the uncertain nature of condensed phase reactions (45), no attempt has been made to correct the data for monomer, dimer and oligomer concentrations of methanol, or for the dielectric constant of the medium. The data for 18a are collected in Tables 1 and 2; Figures 11-16 display the data graphically.
Table 1. Product ratios\textsuperscript{a} 20a/19a for the reaction of 18a in toluene/methanol solution at 271 K, 297 K and 313 K

<table>
<thead>
<tr>
<th>T(K)</th>
<th>[MeOH], M</th>
<th>4.94</th>
<th>9.88</th>
<th>14.81</th>
<th>19.75</th>
<th>24.69</th>
</tr>
</thead>
<tbody>
<tr>
<td>271</td>
<td>0.11±0.01</td>
<td>0.18±0.01</td>
<td>0.24±0.01</td>
<td>0.35±0.03</td>
<td>0.46±0.02</td>
<td></td>
</tr>
<tr>
<td>297</td>
<td>0.11±0.02</td>
<td>0.17±0.01</td>
<td>0.23±0.01</td>
<td>0.30±0.01</td>
<td>0.41±0.02</td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>0.11±0.01</td>
<td>0.17±0.01</td>
<td>0.21±0.02</td>
<td>0.29±0.01</td>
<td>0.40±0.03</td>
<td></td>
</tr>
</tbody>
</table>

\textsuperscript{a}Product ratios represent the corrected average of at least 4 but not more than 15 kinetic experiments with a tolerance of ± one sample standard deviation.

Table 2. Eyring data for 18a at 271 K, 297 K and 313 K

<table>
<thead>
<tr>
<th>T(K)</th>
<th>k\textsubscript{2}/k\textsubscript{1}</th>
<th>ΔΔS* (e.u.)</th>
<th>ΔΔH* (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>271</td>
<td>55.56</td>
<td></td>
<td></td>
</tr>
<tr>
<td>297</td>
<td>66.67</td>
<td>11.7 ± 0.3</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>313</td>
<td>71.43</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 11. Plot of $\frac{20a}{19a}$ versus [MeOH] at 271 K

The graph shows a linear relationship with the following characteristics:

- Slope ($m$): 0.018 ± 0.001
- Intercept ($b$): 0.01 ± 0.02
- Temperature ($T$): 271 K
Figure 12. Plot of $\frac{20a}{19a}$ versus [MeOH] at 297 K
Figure 13. Plot of $20\alpha/19\alpha$ versus [MeOH] at 313 K
Figure 14. Eyring plot of $\ln k_{2a}/k_{1a}$ versus $1/T$ (K$^{-1}$)

$\Delta \Delta H^* = 1.0 \pm 0.1 \text{kcal/mol}$

$\Delta \Delta S^* = 11.7 \pm 0.3 \text{ e.u.}$
Figure 15. Entropy diagram $-T(\Delta S^*(\text{allene})-\Delta S^*(\text{ether}))$
Figure 16. Enthalpy diagram -$\Delta H^*$ (allene) - $\Delta H^*$ (ether)
The data were analyzed with the aid of a statistical non-linear least squares (NLLSQ) program (46). The NLLSQ program provides the slope and intercept along with the standard deviation of each. Approximate values for the slope and intercept were obtained by a least squares analysis on a TI-55 programmable hand calculator. From these values, the NLLSQ program provided the final results in an average of only four iterative cycles.

The temperature dependence of the rates of ring opening and trapping of 22a was analyzed with the Eyring equation (Equation (3)). Equation (3) may be written as Equation (4) for use with relative rate constants. Thus

\[
k = \frac{k}{N} \exp(\frac{\Delta S^*/R}{\Delta H^*/RT}) \exp(-\frac{\Delta H^*/RT}{\Delta S^*/R})
\]

\[
k_2/k_1 = \exp(\frac{\Delta S^*_2-\Delta S^*_1}{R}) \exp(\frac{\Delta H^*_1-\Delta H^*_2}{RT})
\]

A plot of \(k_2/k_1\) versus \(1/T\) will provide the relative entropies and enthalpies of activation for allene formation versus ether formation (Table 2).

The remaining systems, \(18b-j\), were analyzed in the same fashion (note that \(18c\) was not prepared and is, therefore, omitted). Tables 3-6 show the kinetic data for \(18b-j\), and Figures 17-44 display the results graphically. For systems \(18b, d, f, h\) for which multi temperature data have
Table 3. The product ratios\(^a\) of \(^{20}/^{19}\) for the reaction of \(^{18}\) (b-d) in toluene/methanol solution

<table>
<thead>
<tr>
<th>T(K)</th>
<th>(20/19)</th>
<th>[MeOH], M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>4.94</td>
</tr>
<tr>
<td>271</td>
<td>b</td>
<td>0.06±0.01</td>
</tr>
<tr>
<td>297</td>
<td>b</td>
<td>0.06±0.01</td>
</tr>
<tr>
<td>313</td>
<td>b</td>
<td>0.05±0.01</td>
</tr>
<tr>
<td>297</td>
<td>c</td>
<td>0.05±0.01</td>
</tr>
<tr>
<td>271</td>
<td>d</td>
<td>0.15±0.02</td>
</tr>
<tr>
<td>297</td>
<td>d</td>
<td>0.16±0.03</td>
</tr>
<tr>
<td>313</td>
<td>d</td>
<td>0.17±0.01</td>
</tr>
</tbody>
</table>

\(^a\)Product ratios represent the corrected average of at least 4 but not more than 15 kinetic experiments with a tolerance of ± one sample standard deviation.
Figure 17. Plot of $\frac{20b}{19b}$ versus [MeOH] at 271 K.
Figure 18. Plot of $\frac{20b}{19b}$ versus [MeOH] at 297 K
Figure 19. Plot of $\frac{20b}{19b}$ versus [MeOH] at 313 K
Figure 20. Plot of $\frac{20c}{19c}$ versus $[\text{MeOH}]$ at 297 K

$m = 0.006 \pm 0.001$

$b = 0.02 \pm 0.01$

$T = 297 \text{ K}$
Figure 21. Plot of $\frac{20d}{19d}$ versus [MeOH] at 271 K

$m = 0.024 \pm 0.002$

$b = 0.03 \pm 0.02$

$T = 271 \text{ K}$
Figure 22. Plot of $^{20d}/^{19d}$ versus [MeOH] at 297 K
Figure 23. Plot of $20d/19d$ versus $[\text{MeOH}]$ at 313 K.
Table 4. Eyring data for 18b and 18d at 271 K, 297 K and 313 K

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$k_2/k_1$</th>
<th>$\Delta S^*$ (e.u.)</th>
<th>$\Delta H^*$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>271</td>
<td>111.11$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>297</td>
<td>142.86$^a$</td>
<td>14.6 ± 0.3$^a$</td>
<td>1.4 ± 0.1$^a$</td>
</tr>
<tr>
<td>313</td>
<td>166.67$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>271</td>
<td>41.67$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>297</td>
<td>47.62$^b$</td>
<td>12 ± 2$^b$</td>
<td>1.4 ± 0.4$^b$</td>
</tr>
<tr>
<td>313</td>
<td>58.82$^b$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Data for 18b.

$^b$Data for 18d.
Figure 24. Eyring plot of $\ln \frac{k_{2b}}{k_{1b}}$ versus $\frac{1}{T}$ (K$^{-1}$)
Figure 25. Entropy diagram for system $b - T (\Delta S^* (\text{allene}) - \Delta S^* (\text{ether}))$
Figure 26. Enthalpy diagram for system $b - (\Delta H^* (\text{allene}) - \Delta H^* (\text{ether}))$
Figure 27. Eyring plot of $\ln \frac{k_{2d}}{k_{1d}}$ versus $1/T$ ($K^{-1}$)

$\Delta \Delta H^* = 1.4 \pm 0.4$ kcal/mol

$\Delta \Delta S^* = 12 \pm 2$ e.u.
Figure 28. Entropy diagram for system $\Delta S^*$ (allene) - $\Delta S^*$ (ether)
Figure 29. Enthalpy diagram for system $\Delta H^*$ (allene) - $\Delta H^*$ (ether)
Table 5. Product ratios\textsuperscript{a} $20/19$ for the reaction of 18 (f-j) in toluene/methanol solution

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$20/19$</th>
<th>[MeOH], M</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>4.94</td>
</tr>
<tr>
<td>271</td>
<td>f</td>
<td>0.08±0.01</td>
</tr>
<tr>
<td>297</td>
<td>f</td>
<td>0.08±0.01</td>
</tr>
<tr>
<td>313</td>
<td>f</td>
<td>0.07±0.01</td>
</tr>
<tr>
<td>297</td>
<td>g</td>
<td>0.17±0.01</td>
</tr>
<tr>
<td>271</td>
<td>h</td>
<td>0.19±0.01</td>
</tr>
<tr>
<td>297</td>
<td>h</td>
<td>0.27±0.01</td>
</tr>
<tr>
<td>313</td>
<td>h</td>
<td>0.27±0.01</td>
</tr>
<tr>
<td>297</td>
<td>i</td>
<td>0.04±0.01</td>
</tr>
<tr>
<td>297</td>
<td>j</td>
<td>0.15±0.01</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Product ratios represent the corrected average of at least 4 but not more than 15 kinetic experiments with a tolerance of ± one sample standard deviation.
Figure 30. Plot of $20f/19f$ versus [MeOH] at 271 K
Figure 31. Plot of $20f/19f$ versus [MeOH] at 297 K.
Figure 32. Plot of $20f/19f$ versus [MeOH] at 313 K
Figure 33. Plot of $\frac{20g}{19g}$ versus [MeOH] at 297 K
Figure 34. Plot of $\frac{20h}{19h}$ versus [MeOH] at 271 K
Figure 35. Plot of $\frac{20h}{19h}$ versus [MeOH] at 297 K.
Figure 36. Plot of $\frac{20h}{19h}$ versus [MeOH] at 313 K

$m = 0.031 \pm 0.002$

$b = 0.08 \pm 0.04$

$T = 313 \text{ K}$
Figure 37. Plot of $\frac{20i}{19i}$ versus [MeOH] at 297 K
Figure 38. Plot of $\frac{20i}{19i}$ versus [MeOH] at 297 K

$m = 0.022 \pm 0.001$

$b = 0.03 \pm 0.02$

$T = 297 \text{ K}$
Table 6. Eyring data for $^{18}$f and $^{18}$h at 271 K, 297 K and 313 K

<table>
<thead>
<tr>
<th>T(K)</th>
<th>$k_2/k_1$</th>
<th>$\Delta S^*$ (e.u.)</th>
<th>$\Delta H^*$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>271</td>
<td>83.33$^a$</td>
<td>11.4 ± 0.5$^a$</td>
<td>0.7 ± 0.1$^a$</td>
</tr>
<tr>
<td>297</td>
<td>90.91$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>313</td>
<td>100.00$^a$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>271</td>
<td>20.41$^b$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>297</td>
<td>30.30$^b$</td>
<td>13 ± 2$^b$</td>
<td>1.8 ± 0.5$^b$</td>
</tr>
<tr>
<td>313</td>
<td>32.26$^b$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^a$Data for $^{18}$f.

$^b$Data for $^{18}$h.
Figure 39. Eyring plot of \( \ln \frac{k_{2f}}{k_{1f}} \) versus \( 1/T \) (K\(^{-1}\))

\[ \Delta \Delta H^* = 0.7 \pm 0.1 \text{ kcal/mol} \]
\[ \Delta \Delta S^* = 11.4 \pm 0.5 \text{ e.u.} \]
Figure 40. Entropy diagram for system $\xi - T (\Delta S^* (\text{allene}) - \Delta S^* (\text{ether}))$
Figure 41. Enthalpy diagram for system $\xi - (\Delta H^*\text{ (allene)} - \Delta H^*\text{ (ether)})$
Figure 42. Eyring plot of $\ln k_{2h}/k_{1h}$ versus $1/T$ (K$^{-1}$)

$\Delta H^* = 1.8 \pm 0.5$ kcal/mol

$\Delta S^* = 13 \pm 2$ e.u.
Figure 43. Entropy diagram for system $h - T (\Delta S^* \text{ (allene)} - \Delta S^* \text{ (ether)})$
Figure 44. Enthalpy diagram for system $h - (\Delta H^* \text{ (allene)} - \Delta H^* \text{ (ether)})$
been collected, Eyring plots were made in order to obtain the relative activation parameters. The thermodynamic data were evaluated with the NLLSQ program in order to obtain the relative entropy and enthalpy of activation along with the sample standard deviations. Although the data were generally well behaved, it is not reasonable to suppose that such limited data would have such small errors. It is, therefore, proposed (although not supported) that errors may be ± 1 kcal/mol for enthalpies and ± 3-5 e.u. for entropies.

The rate constant ratios $k_2 / k_1$, for systems $a - i$, and the Hammett sigma constants (45) are collected in Table 7. When these values are correlated via the Hammett equation (Equation (5)), Equation (6) results, where $k_H$ is the rate constant for the unsubstituted case. Equation (7) may be

$$\log k_x = \log k_H + \rho \sigma$$  \hspace{1cm} (5)

$$\log \frac{k_{2x}}{k_{1x}} = \log \frac{k_{2H}}{k_{1H}} + \rho \sigma$$  \hspace{1cm} (6)

$$\log \left( \frac{k_{2x}}{k_{1x}} \cdot \frac{k_{1H}}{k_{2H}} \right) = \rho \sigma$$  \hspace{1cm} (7)

simplified if one assumes that $k_{1x}$ and $k_{1H}$ are equal.

Methanol has been shown to react at a diffusion controlled rate with other carbenes (40). Since theoretical results suggest that carbene orbitals in ground state cyclopropylidene do not interact with other molecular
orbitals, one would expect at least equal reactivity for
cyclopropylidene, relative to other carbenes. Equation (7),
therefore, may reasonably be written as Equation (8).

\[
\frac{k_2x}{k_2H} = \rho \sigma
\]  

Figure 45 shows the correlation plot for the data in
Table 7; rho was found to be \(-0.72 \pm 0.07\) for the seven
points indicated. The two points which do not fit the rest
of the data may require separate treatment.

The rho value of \(-0.72\) may be rationalized in terms of
the transition state structure. The negative sign indicates
that the transition state is stabilized by electron donation
and destabilized by electron withdrawal. This is consistent
with the idea that allyl cation character exists in the
transition state. The magnitude of 0.72 gives an indication
of the extent of electron demand at the transition state.
This demand is tempered in two ways: first the distance
between the aryl ring and the reaction center; and secondly,
the degree of ring opening and consequent conjugation
(orbital rotation affects the ability of the cyclopropyl
orbitals to overlap with those of the carbene center).

When discussing correlation analyses, it is useful to
compare similar systems. In this way relative rho values
may be compared. The solvolysis of aryl substituted
Table 7. Ratio of rate constants $k_{2x}/k_{2H}$ and the corresponding Hammett sigma values

<table>
<thead>
<tr>
<th>$X_1/X_2$</th>
<th>$k_{2x}/k_{2H}^a$</th>
<th>$\sigma_1 + \sigma_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/H</td>
<td>1.000</td>
<td>0.00</td>
</tr>
<tr>
<td>Me/Me</td>
<td>2.143</td>
<td>-0.34</td>
</tr>
<tr>
<td>OMe/OMe</td>
<td>2.500</td>
<td>-0.54</td>
</tr>
<tr>
<td>Cl/Cl(^b)</td>
<td>0.714</td>
<td>+0.46</td>
</tr>
<tr>
<td>H/Me</td>
<td>1.364</td>
<td>-0.17</td>
</tr>
<tr>
<td>H/Cl</td>
<td>0.556</td>
<td>+0.23</td>
</tr>
<tr>
<td>H/CF(_3)</td>
<td>0.455</td>
<td>+0.54</td>
</tr>
<tr>
<td>Me/Cl(^b)</td>
<td>2.143</td>
<td>+0.06</td>
</tr>
<tr>
<td>Me/CF(_3)</td>
<td>0.682</td>
<td>+0.37</td>
</tr>
</tbody>
</table>

\(^a\)Actually $k_{2x}k_{1H}/k_{1x}k_{2H}$; see text for why this has been simplified.

\(^b\)Values were not used to determine the slope of the line.
Figure 45. Correlation plot of $\log k_{2x}/k_{2H}$ versus the sum of substituent sigmas.
cyclopropyl tosylates does show similarities to the cyclopropylidene ring opening. The cyclopropylidene ring opening and the cyclopropyl tosylate solvolysis are both concerted ring openings and develop positive charge in the transition state. One should keep in mind, however, that the solvolysis of cyclopropyl tosylates are assisted by the ring opening; the situation is different for cyclopropylidene (free cyclopropylidene is the sole source of products (15)). The rho value of -0.72 for cyclopropylidene is, therefore, reasonably large when compared to rho = -2.3 for the cyclopropyl tosylate solvolysis. Theoretical calculations had suggested that electronic influences on ring opening of cyclopropylidenes were negligible (36).

In cases where the cyclopropylidene was symmetrically disubstituted, the transition structure could resemble 26. However, the systems that are unsymmetrically substituted
have three possible transition structures 26, 27 and 28. It is clear that 28 does not represent a reasonable geometry, and is higher in energy than 27. Structure 27 may be achieved by a concerted disrotatory ring opening in which C₂ C₃ rotation is not synchronous. This would allow electron withdrawing groups to remain better aligned with the filled carbene orbital, and electron donating groups to be better aligned with the empty carbene orbital.

In seven of the nine systems studied, the sigma values of the substituents appear to be additive and generate a linear correlation. However, 18d and 18i show a marked acceleration in ring opening rates over what was expected based on the results for the other seven cases. Both of these disubstituted systems contain a para chloro substituent which may be the source of the discrepancy. Since chlorine is relatively soft and polarizable, it is tempting to speculate that this polarizability leads to a
net increase in the rate of ring opening. There is, however, no direct evidence to support such a suggestion.

Finally, it is evident from the thermodynamic data that the ring opening of cyclopropylidenes is an entropically favored reaction, relative to methanol trapping. Internal rotational degrees of freedom apparently overcome the C₂-C₃ bond energy in driving the reaction toward allene.

In summary, the following conclusions may be offered:

(i) The cyclopropylidene to allene ring opening rate increases when electron donors are attached to C₂ and/or C₃, and decrease when electron acceptors are similarly attached.

(ii) The transition state is cationic in nature insofar as C₂ and C₃ are concerned, with a fairly large interaction existing between the carbene center and the developing p-orbitals at C₂ and C₃.

(iii) Relative to insertion into methanol, the ring opening of cyclopropylidene is favored entropically, while being disfavored enthalpically.

(iv) It is predicted that at least some unsymmetrically disubstituted cyclopropylidenes pass through ring-opening transition states which are unsymmetrical with respect to the developing p-orbitals. It is further predicted that if these compounds were optically active, they would yield allenes of higher optical purity than symmetrically
disubstituted cyclopropylidenes (this would be reasonable evidence for structure 27 and of electronic control of the stereochemical outcome).
EXPERIMENTAL

General

Infrared spectra were recorded on an IBM FT-IR98 spectrophotometer. The proton and carbon magnetic resonance spectra were obtained on a Nicolet 300 FT-NMR spectrometer, using deuterochloroform, perdeutero-benzene and perdeutero-acetone as solvents. Exact mass and GLPC exact mass spectra were recorded on the High Resolution MS-50 mass spectrometer. GLPC analysis was performed on a Hewlett-Packard HP5890 gas chromatograph, which was fitted with a 30 meter DB-1 capillary column and a flame ionization detector. Melting points were taken on a Thomas-Hoover melting point apparatus and were not corrected.

Synthesis and reactions

Preparation of diphenylphosphoryl azide (21) (Figure 46)

A 250 ml round bottom flask was charged with 94 g of phenol and 76 g of phosphorous oxychloride. The stirred mixture was heated to 180°C for 2 hours, the product was then vacuum distilled. The product diphenylphosphoryl chloride was collected at 130-140°C at 0.15 Torr. The product fraction gave 13.9 g, 40% yield based on 50% conversion. The 13.9 g of diphenylphosphoryl chloride was dissolved in 20 ml of acetone and treated with 6.6 g of sodium azide in 20 ml of water, for 3 hours at room temperature. The product 21 was
extracted into ether and dried over magnesium sulfate. Yield of 21 was 12.8 g, 90% from diphenylphosphoryl chloride.

\[
\begin{align*}
\text{FT-IR (neat): } & 3406 \text{ (w), 3078 \text{ (w), 2172 \text{ (s), 1602 \text{ (s), 1485}} } \\
& \text{s cm}^{-1}.
\end{align*}
\]

\text{Preparation of ethyl diazoacetate} \quad A 500 \text{ ml 3 neck round bottom flask was charged with 70 g of ethyl glycinate hydrochloride in 100 ml of water, 250 ml of methylene chloride and 42 g of sodium nitrite in 80 ml of water. The mechanically stirred solution was then cooled to -20°C and 45 g of 5% sulfuric acid was added over 5 minutes. The reaction was over in 15 minutes and the cold solution was poured into a 1 l separatory funnel. The organic phase was washed with several portions of cold 5% sodium bicarbonate solution. The organic phase was dried over magnesium sulfate and the solvent was removed under reduced pressure. The golden-yellow product was used without further purification.}
Figure 46. FT-IR of 21 neat
General synthesis of para substituted benzyltriphenyl-phosphonium halides (11a-e)

Preparation of benzyltriphenylphosphonium chloride (11a)

A 250 ml round bottom flask was charged with 10 g of benzyl chloride, 100 ml of xylene and 21.6 g of triphenylphosphine. The stirred mixture was refluxed for 18 hours to give 20.1 g of white crystalline precipitate 11a in 70% yield, m.p. > 300°C.

\[
\begin{array}{c}
\text{(Ph)}_3P \\
\text{+ Cl}^- \\
\text{X}
\end{array}
\]

X = H (a), CH₃ (b), OCH₃ (c), Cl (d), CF₃ (e)

p-Methylbenzyltriphenylphosphonium chloride (11b)
Prepared from α-chloro-p-xylene in 86% yield, m.p. > 300°C.

p-Methoxybenzyltriphenylphosphonium chloride (11c)
Prepared from p-methoxybenzyl chloride in 83% yield, m.p. > 300°C.

p-Chlorobenzyltriphenylphosphonium chloride (11d)
Prepared from p-chlorobenzyl chloride in 86% yield, m.p. > 300°C.

p-Trifluoromethylbenzyltriphenylphosphonium bromide (11e)
Prepared from p-trifluoromethylbenzyl bromide in 96% yield, m.p. 245-246°C.
General synthesis of trans-4,4'-disubstituted stilbenes (13a-j)

Preparation of trans-4,4'-dimethylstilbene (13b) (Figures 47, 48) A 250 ml round bottom flask was charged with 34 g of 11b, 100 ml of absolute ethanol and 10 g of p-tolualdehyde. To this was added 10 g of potassium t-butoxide and the reaction stirred for 1 hour. Then 40 ml of water was added and the product was filtered off to give 9.2 g of 13b as a crystalline white solid in 53% yield, m.p. 179-180°C (lit. m.p. 180°C (47)). In cases where the cis isomer is significant it may be isomerized to trans by refluxing the crude reaction mixture in toluene with iodine present.

\[
\begin{array}{c}
\text{X} \\
\text{\textbullet} \\
\text{\textbullet} \\
\text{\textbullet} \\
\text{Y}
\end{array}
\]

13a-j

\[
X/Y = H/H \text{ (a), } CH_3/CH_3 \text{ (b), } OCH_3/OCH_3 \text{ (c), } Cl/Cl \text{ (d), } CF_3/CF_3 \text{ (e), } H/CH_3 \text{ (f), } H/Cl \text{ (g), } H/CF_3 \text{ (h), } CH_3/Cl \text{ (i), } CH_3/CF_3 \text{ (j)}
\]

HRMS: Calculated C_{16}H_{16} m/e 208.12520 measured m/e 208.12520 error 0.0 ppm.
87

$^1$H NMR (CDCl$_3$): $\delta$ 7.38 (d), $\delta$ 7.14 (d), $\delta$ 7.00 (s), $\delta$ 2.35 (s).

FT-IR (CDCl$_3$): 3031 (w), 3000 (w), 2922 (w), 1520 (w), 980 (s), 820 (s) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$): $\delta$ 137.2 (rel. intens. 30), $\delta$ 134.7 (29), $\delta$ 129.3 (60), $\delta$ 127.6 (40), $\delta$ 126.3 (100), $\delta$ 21.3 (20).

**Trans-stilbene (13a)** The commercial product was used without further purification.

**Trans-4,4'-dimethoxystilbene (13c) (Figures 49, 50)**
Prepared from 11c and p-methoxybenzaldehyde in 87% yield, m.p. 207-210°C (lit. m.p. 214-215°C (48)).

HRMS: Calculated C$_{16}$H$_{16}$O$_2$ m/e 240.11503 measured 240.11519 error 0.7 ppm.

$^1$H NMR (CDCl$_3$): $\delta$ 7.40 (d), $\delta$ 6.91 (s), $\delta$ 6.87 (d), $\delta$ 3.81 (s).

FT-IR (CDCl$_3$): 2969 (w), 2953 (w), 2938 (w), 1544 (w), 1508 (m), 1410 (m), 1009 (s) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$): $\delta$ 159.0 (rel. intens. 40), $\delta$ 130.5 (38), $\delta$ 127.4 (100), $\delta$ 126.2 (60), $\delta$ 114.1 (100), $\delta$ 55.3 (80).

**Trans-4,4'-dichlorostilbene (13d) (Figures 51, 52)**
Prepared from 11d and p-chlorobenzaldehyde in 78% yield, isomerized with iodine in refluxing toluene, m.p. 173-174°C (lit. m.p. 177-178°C (49)).
Trans-4,4'-bis(trifluoromethyl)stilbene (13e) (Figures 53, 54)
Prepared from 11e and p-trifluoromethylbenzaldehyde, isomerized with iodine in refluxing toluene in 76% yield, m.p. 133-133.5°C (lit. m.p. 124-127°C (50)).

HRMS: Calculated C_{14}H_{10}Cl_2 m/e 248.01596
measured m/e 248.01629 error 1.3 ppm.

^1H NMR (CDCl_3): δ 7.41 (d), δ 7.31 (d), δ 6.99 (s).
FT-IR (CDCl_3): 3000 (w), 1610 (w), 1500 (m), 1408 (m),
980 (s), 810 (s) cm\(^{-1}\).

^13C NMR (CDCl_3): δ 135.5 (rel. intens. 30), δ 133.4 (30),
δ 128.9 (100), δ 128.0 (60), δ 127.7 (80).

Trans-4-methylstilbene (13f) (Figures 55, 56)
Prepared from 11a and p-tolualdehyde, isomerized with iodine in refluxing toluene in 75% yield, m.p. 116-118°C (lit. m.p. 120°C (51)).

HRMS: Calculated C_{16}H_{10}F_6 m/e 316.06868
measured m/e 316.06820 error -1.5 ppm.

^1H NMR (CDCl_3): δ 7.61 (s), δ 7.18 (s).
FT-IR (CDCl_3): 1612 (m), 1333 (s), 1178 (m), 1111 (s),
1067 (s) cm\(^{-1}\).

^13C NMR (CDCl_3): δ 140.1 (rel. intens. 50), δ 129.6 (80),
δ 126.8 (100), δ 125.7 (80).
FT-IR (CDCl₃): 3000 (w), 1590 (w), 1000 (m), 920 (s), 805 (s), 750 (s), cm⁻¹.

¹³C NMR (CDCl₃): δ 137.5 (rel. intens. 30), δ 137.4 (30), δ 134.5 (15), δ 129.3 (95), δ 128.6 (90), δ 127.6 (40), δ 127.3 (40), δ 126.4 (100), δ 21.2 (25).

Trans-4-chlorostilbene (13g) (Figures 57, 58)
Prepared from 11d and benzaldehyde, isomerized with iodine in refluxing toluene in 66% yield, m.p. 126-128°C (lit. m.p. 130°C (52)).

HRMS: Calculated C₁₄H₁₁Cl m/e 214.05493 measured m/e 214.05513 error 0.9 ppm.

¹H NMR (Acetone-d₆):
δ 7.6-7.5 (m), δ 7.4-7.3 (m),
δ 7.3-7.2 (m).

FT-IR (CDCl₃): 3000 (w), 1420 (m), 1400 (m), 982 (s), 809 (s) cm⁻¹.

¹³C NMR (CDCl₃): δ 136.9 (rel. intens. 40), δ 135.8 (39), δ 133.1 (20), δ 129.3 (60), δ 128.8 (100), δ 128.6 (90), δ 127.8 (60), δ 127.3 (50), δ 126.5 (65).

Trans-4-trifluoromethylstilbene (13h) (Figures 59, 60)
Prepared from 11a and p-trifluoromethylbenzaldehyde, isomerized with iodine in refluxing toluene in 65% yield, m.p. 127-130°C (lit. m.p. 132-133°C (53)).
HRMS: Calculated $C_{15}H_{11}F_3$ m/e 248.08129  
measured m/e 248.08146 error 0.7 ppm.

$^1$H NMR (CDCl$_3$): $\delta$ 7.2-6.6 (m).

FT-IR (CDCl$_3$): 3000 (w), 1600 (w), 1380 (m), 1115 (s),  
806 (m) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$): $\delta$ 140.8 (rel. intens. 20), $\delta$ 136.5 (30),  
$\delta$ 132.1 (10), $\delta$ 132.0 (10), $\delta$ 131.2 (60),  
$\delta$ 128.7 (90), $\delta$ 128.2 (70), $\delta$ 127.1 (50),  
$\delta$ 126.7 (95), $\delta$ 126.5 (100), $\delta$ 125.6 (50),  
$\delta$ 125.5 (40).

**Trans-4-chloro-4'-methylstilbene (13i) (Figures 61, 62)**

Prepared from 1ld and p-tolualdehyde in 70% yield, m.p.  
200-204°C (lit. m.p. 203-204°C (54)).

HRMS: Calculated $C_{15}H_{13}Cl$ m/e 228.07058  
measured m/e 228.07082 error 1.0 ppm.

$^1$H NMR (CDCl$_3$): $\delta$ 7.5-7.1 (m), $\delta$ 7.01 (q), $\delta$ 2.35 (s).

FT-IR (CDCl$_3$): 3000 (w), 908 (m), 810 (s) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$): $\delta$ 136.0 (rel. intens. 30), $\delta$ 134.2 (40),  
$\delta$ 129.4 (100), $\delta$ 129.2 (30), $\delta$ 128.8 (90),  
$\delta$ 127.5 (90), $\delta$ 126.4 (95), $\delta$ 126.3 (50),  
$\delta$ 21.3 (5).

**Trans-4-methyl-4'-trifluoromethylstilbene (13j) (Figures 63, 64)**

Prepared from 1lb and p-trifluoromethylbenzaldehyde, isomerized with iodine in refluxing toluene in 83% yield, m.p. 187-189°C.
Figure 47. $^1$H NMR of 13b in CDCl$_3$
Figure 48. FT-IR of 13b in CDCl₃
Figure 49. $^1$H NMR of 13c in CDCl$_3$
Figure 50. FT-IR of $\text{13C}$ in CDC$_3$
Figure 51. $^1$H NMR of 13d in CDCl$_3$
Figure 52. FT-IR of \textsuperscript{13}C in CDCl\textsubscript{3}
Figure 53. $^1$H NMR of 13e in CDCl$_3$
Figure 54. FT-IR of 13e in CDC\textsubscript{3}
Figure 55. $^1$H NMR of 13F in CDCl$_3$
Figure 56. FT-IR of 13f in CDCl$_3$
Figure 57. $^1$H NMR of 13g in d-6 acetone
Figure 58. FT-IR of \textit{13g} in CDCl$_3$. 
Figure 59. $^1$H NMR of 13b in CDCl$_3$.
Figure 60. FT-IR of 13h in CDCl₃
Figure 61. $^1H$ NMR of $^{131}$ in CDCl$_3$
Figure 62. FT-IR of 13i in CDC$_3$. 
Figure 63. $^1$H NMR of 13j in CDCl$_3$
Figure 64. FT-IR of 13j in CDCl$_3$
HRMS: Calculated $\text{C}_{16}\text{H}_{13}\text{F}_3$ m/e 262.09694 measured m/e 262.09713 error 0.7 ppm.

$^1\text{H NMR (CDCl}_3$): $\delta$ 7.085 (d), $\delta$ 6.91 (s), $\delta$ 6.9-6.7 (m), $\delta$ 2.03 (s).

FT-IR (CDCl$_3$): 3030 (w), 2400 (w), 1610 (w), 1545 (m), 906 (s), 765 (s) cm$^{-1}$.

$^{13}\text{C NMR (CDCl}_3$): $\delta$ 140.9 (rel. intens. 15), $\delta$ 138.3 (25), $\delta$ 133.8 (20), $\delta$ 132.0 (10), $\delta$ 131.1 (45), $\delta$ 129.5 (100), $\delta$ 126.7 (95), $\delta$ 126.4 (70), $\delta$ 126.1 (50), $\delta$ 125.5 (40), $\delta$ 21.3 (30).

General synthesis of trans-2,3-diarylcyclopropanecarboxylic acids (15a-j)

Preparation of trans-2,3-diphenylcyclopropanecarboxylic acid (15a) (Figures 65, 66) A 250 ml round bottom flask was charged with 15 g of 13a, 0.75 g of anhydrous copper sulfate, and 100 ml of dry benzene. The mechanically stirred mixture was heated to 75°C and treated with 23.7 g (2.5 eq.) of ethyl diazoacetate over 4 hours. The cooled reaction mixture was filtered to remove the catalyst and the benzene was removed under reduced pressure. The crude product mixture was dissolved in 100 ml of 70% ethanol. A second filtration removed the unreacted 13a. The crude ester was then saponified with sodium hydroxide to give the acid 15a. The basic solution was extracted twice with 50 ml portions of ether and acidified to precipitate the acid.
The crude 15a was then recrystallized from ethanol and water to give 3.3 g of 15a as a white crystalline solid in 21% yield based on starting olefin. m.p. 153-154°C (lit. m.p. 153-154°C (9)).

\[
\begin{align*}
Y & \quad \text{Ph} \\
H & \quad \text{CO}_2\text{H} \\
& \quad \text{H} \\
& \quad \text{PhX} \\
& \quad \text{H}
\end{align*}
\]

15a-j X/Y = H/H (a), CH₃/CH₃ (b), OCH₃/OCH₃ (c), Cl/Cl (d), CF₃/CF₃ (e), H/CH₃ (f), H/Cl (g), H/CF₃ (h), CH₃/Cl (i), CH₃/CF₃ (j)

HRMS: Calculated C₁₆H₁₄O₂ m/e 238.09938 measured m/e 238.09956 error 0.8 ppm.

\(^1\)H NMR (CDCl₃): δ 7.4-7.19 (m), δ 3.16 (d,d), δ 2.97 (dd), δ 2.36 (dd).

FT-IR (CDCl₃): 3000 (m), 1688 (s), 1480 (m), 1190 (m) cm⁻¹.

\(^{13}\)C NMR (CDCl₃): δ 176.0 (rel. intens. 40), δ 139.3 (25), δ 135.3 (30), δ 129.3 (75), δ 129.1 (90),
Trans-2,3-bis(p-methylphenyl)cyclopropanecarboxylic acid (15b) (Figures 67, 68)

*Prepared from 13b in 71% yield, m.p. 137-139°C.*

HRMS: Calculated $C_{18}H_{18}O_2$ m/e 266.13055
measured m/e 266.13068 error -0.5 ppm.

$^1$H NMR (CDCl$_3$): δ 7.3-7.1 (m), δ 3.23 (dd), δ 3.03 (dd),
δ 2.44 (dd), δ 2.45 (s), δ 2.44 (s).

FT-IR (CDCl$_3$): 3024 (s), 1697 (s), 1518 (m), 1456 (m),
1227 (m), 908 (s), 735 (s) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$): δ 175.6 (rel. intens. 20), δ 136.4 (30),
δ 136.2 (45), δ 132.5 (40), δ 129.2 (80),
δ 128.9 (82), δ 128.8 (100), δ 126.6 (81),
δ 58.4 (15), δ 34.8 (50), δ 30.7 (40),
δ 30.0 (45), δ 21.1 (35), δ 21.0 (40).

Trans-2,3-bis(p-methoxyphenyl)cyclopropanecarboxylic acid (15c) (Figures 69, 70)

*Prepared from 13c in 50% yield, m.p. 159-160°C.*

HRMS: Calculated $C_{18}H_{18}O_4$ m/e 298.12051
measured m/e 298.12029 error -0.7 ppm.

$^1$H NMR (CDCl$_3$): δ 7.23 (d), δ 7.13 (d), δ 6.82 (t), δ 3.78 (s), δ 3.72 (s), δ 3.08 (dd), δ 2.86 (dd),
δ 2.25 (dd).
FT-IR (CDCl₃): 3000 (w), 1693 (s), 1612 (w), 1514 (s), 1248 (s), 1178 (m), 1034 (m) cm⁻¹.

¹³C NMR (CDCl₃): δ 176.0 (rel. intens. 40), δ 158.5 (50), δ 131.2 (20), δ 130.1 (80), δ 127.8 (100), δ 127.5 (42), δ 114.0 (75), δ 113.5 (85), δ 55.3 (45), δ 55.2 (50), δ 34.4 (45), δ 30.6 (30), δ 29.8 (35).

**Trans-2,3-bis(p-chlorophenyl)cyclopropanecarboxylic acid (15d) (Figures 71, 72)**  Prepared from 13d in 50% yield, m.p. 189-192°C.

HRMS: Calculated C₁₆H₁₂Cl₂O₂ m/e 306.02144 measured m/e 306.02121 error -0.8 ppm.

¹H NMR (CDCl₃): δ 7.3-7.1 (m), δ 3.10 (dd), δ 2.88 (dd), δ 2.33 (dd).

FT-IR (CDCl₃): 3000 (w), 1700 (m), 1500 (m), 902 (s), 750 (s) cm⁻¹.

¹³C NMR (CDCl₃): δ 175.0 (rel. intens. 50), δ 137.1 (45), δ 133.5 (55), δ 130.3 (70), δ 128.9 (100), δ 128.3 (98), δ 128.0 (70), δ 34.3 (50), δ 30.7 (40), δ 29.6 (39).

**Trans-2,3-bis(trifluoromethylphenyl)cyclopropanecarboxylic acid (15e)** The reaction of 13e with 5 eq. of ethyl diazoacetate gave less than 1% of the product, which was not isolated.
Trans-2-(p-methylphenyl)-3-phenylcyclopropanecarboxylic acid (15f) (Figures 73, 74) Prepared from 13f in 30% yield, m.p. 125-135°C.

HRMS: Calculated $C_{17}H_{16}O_2$ m/e 252.11503 measured m/e 252.11519 error 0.6 ppm.

$^1$H NMR (CDCl$_3$): $\delta$ 7.5-7.0 (m), $\delta$ 3.13 (dd), $\delta$ 2.94 (dd), $\delta$ 2.35 (dd), $\delta$ 2.32 (s), $\delta$ 2.31 (s).

FT-IR (CDCl$_3$): 3020 (m), 1696 (s), 1480 (m), 1250 (m), 900 (m) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$): $\delta$ 176.44 (rel. intens. 39), $\delta$ 176.40 (40), $\delta$ 139.1 (50), $\delta$ 136.4 (49), $\delta$ 136.3 (50), $\delta$ 135.9 (20), $\delta$ 135.5 (50), $\delta$ 132.3 (55), $\delta$ 129.2 (90), $\delta$ 129.0 (95), $\delta$ 128.9 (85), $\delta$ 128.8 (100), $\delta$ 128.5 (85), $\delta$ 128.0 (70), $\delta$ 126.9 (60), $\delta$ 126.5 (100), $\delta$ 126.48 (110), $\delta$ 35.0 (50), $\delta$ 34.9 (55), $\delta$ 30.74 (48), $\delta$ 30.7 (50), $\delta$ 30.2 (60), $\delta$ 29.9 (60), $\delta$ 21.0 (50), $\delta$ 20.9 (50).

Trans-2-(p-chlorophenyl)-3-phenylcyclopropanecarboxylic acid (15g) (Figures 75, 76) Prepared from 13g in 14% yield, m.p. 135-137°C.

HRMS: Calculated $C_{16}H_{13}ClO_2$ m/e 272.06041 measured m/e 272.06004 error -1.4 ppm.

$^1$H NMR (CDCl$_3$): $\delta$ 7.4-7.1 (m), $\delta$ 3.12 (dd), $\delta$ 2.92 (dd), $\delta$ 2.35 (dd).
Trans-2-phenyl-3-(p-trifluoromethylphenyl)cyclopropane-carboxylic acid (15h) (Figures 77, 78) Prepared from 13h in 8% yield, obtained as a brown oil.

\[
\text{HRMS: Calculated } C_{17}H_{13}F_3O_2 \text{ m/e 306.08677 measured m/e 306.08709 error 1.0 ppm.}
\]

\[
\text{FT-IR (CDCI}_3\text{): 3000 (m), 1698 (s), 1340 (s), 1120 (s) cm}^{-1}.
\]

\[
\text{13C NMR (CDCI}_3\text{): } \delta 175.5 \text{ (rel. intens. 20), } \delta 175.4 \text{ (19), } \delta 143.2 \text{ (20), } \delta 139.6 \text{ (18), } \delta 138.4 \text{ (15), } \delta 134.8 \text{ (30), } \delta 132.0 \text{ (10), } \delta 129.4 \text{ (90), } \delta 128.9 \text{ (85), } \delta 128.7 \text{ (75), } \delta 128.2 \text{ (80), } \delta 127.2 \text{ (60), } \delta 126.9 \text{ (75), } \delta 126.5 \text{ (100), } \delta 125.5 \text{ (65), } \delta 125.0 \text{ (68), } \delta 35.3 \text{ (30),}
\]
Trans-2-(p-chlorophenyl)-3-(p-methylphenyl)cyclopropane-carboxylic acid (15j) (Figures 79, 80)
Prepared from 13i in 50% yield, m.p. 131-138°C.

HRMS: Calculated C_{17}H_{15}ClO_2 m/e 286.07606
measured m/e 286.07615 error 0.3 ppm.

$^1H$ NMR (CDCl$_3$):
$\delta$ 7.3-7.0 (m), $\delta$ 3.11 (dd), $\delta$ 2.39 (dd),
$\delta$ 2.33 (s), $\delta$ 2.32 (s), $\delta$ 2.30 (dd).

FT-IR (CDCl$_3$):
3000 (m), 1700 (s), 1510 (m), 1215 (m) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$):
$\delta$ 136.7 (rel. intens. 30), $\delta$ 135.6 (30),
$\delta$ 134.1 (30), $\delta$ 132.0 (28), $\delta$ 130.4 (90),
$\delta$ 129.3 (70), $\delta$ 128.9 (100), $\delta$ 128.7 (50),
$\delta$ 128.2 (90), $\delta$ 128.0 (50), $\delta$ 126.5 (80),
$\delta$ 34.9 (30), $\delta$ 34.3 (33), $\delta$ 30.8 (20),
$\delta$ 30.1 (30), $\delta$ 29.6 (28), $\delta$ 21.1 (20),
$\delta$ 21.0 (25).

Trans-2-(p-methylphenyl)-3-(p-trifluoromethylphenyl)cyclopropanecarboxylic acid (15j) (Figures 81, 82)
Prepared from 13i in 6% yield, m.p. 105-111°C.

HRMS: Calculated C$_{18}$H$_{15}$F$_3$O$_2$ m/e 320.10242
measured m/e 320.10193 error 1.5 ppm.

$^1H$ NMR (CDCl$_3$):
$\delta$ 11.61 (s), $\delta$ 7.7-7.2 (m), $\delta$ 3.30 (m),
$\delta$ 3.08 (m), $\delta$ 2.52 (m), $\delta$ 2.45 (s),
Figure 65. $^1\text{H NMR of 15a in CDCl}_3$
Figure 66. FT-IR of 15a in CDCl$_3$
Figure 67. $^1$H NMR of 15b in CDCl$_3$
Figure 68. FT-IR of 15b in CDCl₃
Figure 69. $^1$H NMR of 15c in CDCl$_3$
Figure 70. FT-IR of 15c in CDCl₃
Figure 71. $^1H$ NMR of 15d in CDCl$_3$
Figure 72. FT-IR of 15d in CDCl₃
Figure 73. $^1$H NMR of 15f in CDCl$_3$
Figure 74. FT-IR of 15f in CDCl₃
Figure 75. $^1H$ NMR of 15g in CDCl$_3$
Figure 76. FT-IR of 15g in CDC3
Figure 77. $^1H$ NMR of 15h in CDCl$_3$
Figure 78. FT-IR of 15h in CDC$_3$. 
Figure 79. $^1$H NMR of 15i in CDCl$_3$
Figure 80. FT-IR of 15i in CDC\textsubscript{3}
Figure 81. $^1$H NMR of J in CDCl$_3$
Figure 82. FT-IR of 15j in CDCl₃
\( \delta 2.43 \) (s).

**FT-IR (CDCl\(_3\))**: 3000 (m), 1696 (s), 1603 (m), 1450 (m), 1367 (s), 1130 (s) cm\(^{-1}\).

\(^{13}\)C NMR (CDCl\(_3\)):

\( \delta 176.1 \) (rel. intens. 25), \( \delta 175.9 \) (27),
\( \delta 148.3 \) (25), \( \delta 139.6 \) (28), \( \delta 136.84 \) (15),
\( \delta 136.79 \) (35), \( \delta 135.2 \) (40), \( \delta 131.7 \) (30),
\( \delta 129.5 \) (60), \( \delta 129.3 \) (100), \( \delta 128.94 \)
(62), \( \delta 128.90 \) (62), \( \delta 128.8 \) (70), \( \delta 128.1 \)
(50), \( \delta 126.8 \) (65), \( \delta 126.5 \) (65), \( \delta 125.5 \)
(40), \( \delta 124.9 \) (40), \( \delta 122.3 \) (10), \( \delta 120.4 \)
(10), \( \delta 35.2 \) (40), \( \delta 34.5 \) (50), \( \delta 31.0 \)
(40), \( \delta 30.8 \) (50), \( \delta 30.1 \) (60), \( \delta 29.7 \)
(50), \( \delta 21.02 \) (50), \( \delta 20.97 \) (65).

**General synthesis of ethyl N-(trans-2,3-diarylcylopropyl)-carbamates 17(a-j)**

**Preparation of ethyl N-(trans-2,3-diphenylcyclopropyl)-carbamate (17a) Figures (83, 84)**

A 250 ml round bottom flask was charged with 100 mg of 15a, 100 ml of dry benzene, 60 mg of triethylamine and 120 mg of diphenylphosphoryl azide (DPPA). The stirred mixture was heated to reflux and the reaction progress was monitored via GLPC. When isocyanate formation was complete (~ 5 hrs), a large excess of ethanol (50 ml) was added, and the mixture was refluxed an additional 3 hours. The product mixture was washed with 30 ml of 5% citric acid and 30 ml of saturated sodium
bicarbonate solution. The product was recrystallized from ethanol and water to give 71 mg of white crystalline solid 17a in 60% yield, m.p. 60-62°C.

\[ \text{H} \quad \text{NHCO}_2\text{Et} \]
\[ \text{YPh} \quad \text{H} \quad \text{PhX} \]

\[ \text{17(a-j)} \]
\[ \text{X/Y} = \text{H/H (a), CH}_3/\text{CH}_3 (b), \text{OCH}_3/\text{OCH}_3 (c), \text{Cl/Cl (d),} \]
\[ \text{H/CH}_3 (f), \text{H/Cl (g), H/CF}_3 (h), \text{CH}_3/\text{Cl (i), CH}_3/\text{CF}_3 (j) \]

HRMS: Calculated \( \text{C}_{18}\text{H}_{19}\text{NO}_2 \) m/e 281.14158
measured m/e 281.14117 error -1.5 ppm.

\(^1\text{H NMR (CDCl}_3): \delta 7.5-7.0 (m), \delta 4.5 (s), \delta 4.1 (q), \]
\[ \delta 3.3 (m), \delta 2.7 (m), \delta 2.6 (m), \delta 1.2 (t) \]

\(^{13}\text{C NMR (CDCl}_3): \delta 139.7 (\text{rel. intens. 20}), \delta 128.7 (50), \]
\[ \delta 128.5 (95), \delta 128.4 (100), \delta 127.1 (40), \]
\[ \delta 128.8 (30), \delta 126.4 (40), \delta 37.6 (15), \]
\[ \delta 31.1 (15). \]

\[^{13}\text{C NMR (CDCl}_3): \delta 139.7 (\text{rel. intens. 20}), \delta 128.7 (50), \]
\[ \delta 128.5 (95), \delta 128.4 (100), \delta 127.1 (40), \]
\[ \delta 128.8 (30), \delta 126.4 (40), \delta 37.6 (15), \]
\[ \delta 31.1 (15). \]
Ethyl N-(trans-2,3-bis-(p-methylphenyl)cyclopropyl)-carbamate (17b) (Figures 85, 86) Prepared from 15b in 70% yield, m.p. 76-78°C.

HRMS: Calculated C_{20}H_{23}NO_2 m/e 309.17288 measured m/e 309.17271 error -0.6 ppm.

$^1$H NMR (CDCl$_3$): $\delta$ 7.5-7.0 (m), $\delta$ 4.5 (s), $\delta$ 4.1 (q), $\delta$ 3.1 (m), $\delta$ 2.6 (m), $\delta$ 2.4 (m), $\delta$ 2.34 (s), $\delta$ 2.32 (s), $\delta$ 1.2 (t).

FT-IR (CDCl$_3$): 3300 (w), 3000 (w), 1733 (s), 1535 (s) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$): $\delta$ 136.7 (rel. intens. 40), $\delta$ 136.4 (20), $\delta$ 135.9 (35), $\delta$ 129.2 (90), $\delta$ 129.1 (100), $\delta$ 128.6 (50), $\delta$ 127.1 (37), $\delta$ 60.8 (10), $\delta$ 59.0 (8), $\delta$ 37.3 (20), $\delta$ 30.5 (15), $\delta$ 21.0 (30), $\delta$ 14.6 (17).

Ethyl N-(trans-2,3-bis-(p-methoxyphenyl)cyclopropyl)-carbamate (17c) (Figures 87, 88) Prepared from 15c in 80% yield, m.p. 79-81°C.

HRMS: Calculated C_{20}H_{23}NO_4 m/e 341.16271 measured m/e 341.16339 error 2.0 ppm.

$^1$H NMR (CDCl$_3$): $\delta$ 7.2 (m), $\delta$ 6.8 (m), $\delta$ 4.6 (s), $\delta$ 4.1 (m), $\delta$ 3.8 (s), $\delta$ 3.7 (s), $\delta$ 3.1 (m), $\delta$ 2.5 (m), $\delta$ 2.4 (m), $\delta$ 1.2 (m).

FT-IR (CDCl$_3$): 3400 (w), 3000 (w), 1720 (m), 1518 (s), 1244 (s) cm$^{-1}$.
$^{13}$C NMR (CDCl$_3$): \( \delta 158.4 \) (rel. intens. 50), \( \delta 158.2 \) (30), \\
\( \delta 157.1 \) (10), \( \delta 131.8 \) (40), \( \delta 129.7 \) (60), \\
\( \delta 128.3 \) (50), \( \delta 127.5 \) (8), \( \delta 113.9 \) (100), \\
\( \delta 113.8 \) (98), \( \delta 60.8 \) (10), \( \delta 55.2 \) (80), \\
\( \delta 37.1 \) (30), \( \delta 29.9 \) (25), \( \delta 14.5 \) (25).

**Ethyl N-(trans-2,3-bis-(p-chlorophenyl)cyclopropyl)-carbamate (17d)** Figures 89, 90) Prepared from 15d in 60% yield, m.p. 88-91°C.

HRMS: Calculated C$_{18}$H$_{17}$Cl$_2$NO$_2$ m/e 349.06364 measured m/e 349.06376 error 0.3 ppm.

$^1$H NMR (CDCl$_3$): \( \delta 7.3 \) (m), \( \delta 4.5 \) (s), \( \delta 4.1 \) (q), \( \delta 3.1 \) (m), \( \delta 2.5 \) (m), \( \delta 2.48 \) (m), \( \delta 1.2 \) (t).

FT-IR (CDCl$_3$): 3400 (w), 3000 (w), 1700 (m), 1500 (s), 1100 (m) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$): \( \delta 156.9 \) (rel. intens. 25), \( \delta 137.8 \) (30), \\
\( \delta 133.7 \) (10), \( \delta 132.8 \) (30), \( \delta 132.3 \) (15), \\
\( \delta 129.9 \) (40), \( \delta 128.6 \) (99), \( \delta 128.58 \) \\
(100), \( \delta 61.1 \) (10), \( \delta 37.6 \) (15), \( \delta 30.6 \) \\
(14), \( \delta 30.57 \) (12), \( \delta 14.5 \) (8).

**Ethyl N-(trans-2-(p-methylphenyl)-3-phenylcyclopropyl)-carbamate (17f)** (Figures 91, 92) Prepared from 15f in 70% yield, m.p. 4-8°C.

HRMS: Calculated C$_{19}$H$_{21}$NO$_2$ m/e 295.15727 measured m/e 295.15692 error -1.1 ppm.
$^1$H NMR (CDCl$_3$): δ 7.2 (m), δ 4.6 (s), δ 4.1 (m), δ 3.2 (m), δ 2.6 (m), δ 2.5 (m), δ 2.36 (s), δ 2.35 (s), δ 1.2 (m).

FT-IR (CDCl$_3$): 3400 (m), 3000 (m), 1710 (s), 1500 (s), 1230 (s), 1070 (s) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$): δ 157.0 (rel. intens. 20), δ 156.9 (18), δ 139.8 (30), δ 136.6 (35), δ 136.3 (15), δ 135.9 (20), δ 129.2 (80), δ 129.0 (100), δ 128.6 (50), δ 128.4 (90), δ 126.9 (60), δ 126.6 (40), δ 126.2 (45), δ 60.9 (10), δ 60.8 (20), δ 37.4 (30), δ 31.0 (25), δ 30.7 (23), δ 30.5 (21), δ 20.9 (35), δ 14.5 (32).

Ethyl N-(trans-2-(p-chlorophenyl)-3-phenylcyclopropyl)-carbamate (17g) (Figures 93, 94) Prepared from 15g in 72% yield, m.p. 89-92°C.

HRMS: Calculated C$_{18}$H$_{18}$ClNO$_2$ m/e 315.10261 measured m/e 315.10218 error -1.4 ppm.

$^1$H NMR (CDCl$_3$): δ 7.2 (m), δ 4.6 (s), δ 4.1 (m), δ 3.3 (m), δ 2.5 (m), δ 2.4 (m), δ 1.2 (m).

FT-IR (CDCl$_3$): 3400 (w), 3000 (w), 1705 (s), 1490 (s), 1250 (m), 1090 (m), 1075 (m) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$): δ 156.95 (rel. intens. 20), δ 156.86 (20), δ 139.2 (50), δ 138.2 (18), δ 134.2 (15), δ 132.4 (30), δ 131.9 (25), δ 129.9 (35),
Ethyl N-(trans-2-phenyl-3-(p-trifluoromethylphenyl)-cyclopropyl)carbamate (17h) (Figures 95, 96)

Prepared from 15h in 60% yield, m.p. 92-99°C.

HRMS:

Calculated $\text{C}_{19}\text{H}_{18}\text{F}_3\text{NO}_2$ m/e 349.12897
 measured m/e 349.12896 error 0.03 ppm.

$^1$H NMR (CDCl$_3$):

$\delta$ 7.2 (m), $\delta$ 4.6 (m), $\delta$ 4.1 (m), $\delta$ 3.3 (m), $\delta$ 2.7 (m), $\delta$ 1.2 (m).

FT-IR (CDCl$_3$):

3400 (w), 3000 (w), 1712 (s), 1530 (m), 1350 (s), 1190 (s), 1130 (s), 1090 (s) cm$^{-1}$.

$^{13}$C NMR (CDCl$_3$):

$\delta$ 139.0 (rel. intens. 30), $\delta$ 128.7 (100), $\delta$ 126.7 (60), $\delta$ 125.3 (40), $\delta$ 38.1 (15), $\delta$ 30.9 (10), $\delta$ 14.5 (30).

Ethyl N-(trans-2-(p-chlorophenyl)-3-(p-methyIphenyl)-cyclopropyl)carbamate (17i) (Figures 97, 98)

Prepared from 15i in 55% yield, m.p. 85-88°C.

HRMS:

Calculated $\text{C}_{19}\text{H}_{20}\text{ClNO}_2$ m/e 329.11826
 measured m/e 329.11792 error -1.0 ppm.

$^1$H NMR (CDCl$_3$):

$\delta$ 7.2 (m), $\delta$ 4.6 (s), $\delta$ 4.1 (m); $\delta$ 3.1 (m), $\delta$ 2.5 (m), $\delta$ 2.46 (m), $\delta$ 2.34 (s), $\delta$ 2.32 (s), $\delta$ 1.2 (m).
FT-IR (CDCl₃): 3400 (w), 3000 (w), 1702 (s), 1520 (m), 1500 (s), 1230 (m), 1120 (m) cm⁻¹.

¹³C NMR (CDCl₃): δ 138.3 (rel. intens. 18), δ 136.2 (20), δ 136.1 (20), δ 132.5 (20), δ 132.1 (20), δ 130.0 (20), δ 129.3 (60), δ 129.2 (90), δ 128.5 (100), δ 126.9 (30), δ 37.5 (20), δ 30.3 (15), δ 21.0 (30), δ 14.5 (25).

Ethyl N-(trans-2-(p-methylphenyl)-3-(p-trifluoromethylphenyl)cyclopropyl)carbamate (17j) (Figures 99, 100)
Prepared from 15j in 50% yield, as a yellow oil.

GC-HRMS: Calculated C₂₀H₂₀F₃NO₂ m/e 363.14462 measured m/e 363.14529 error 1.8 ppm.

¹H NMR (CDCl₃): δ 7.6-7.2 (m), δ 4.91 (s), δ 4.75 (s), δ 4.11 (m), δ 3.55 (q), δ 3.26 (m), δ 2.65 (m), δ 2.42 (s), δ 2.40 (s), δ 1.28 (m).

FT-IR (CDCl₃): 3315 (m), 3000 (m), 1711 (s), 1519 (s), 1325 (s), 1068 (s) cm⁻¹.

¹³C NMR (CDCl₃): δ 157.1 (rel. intens. 20), δ 150.3 (15), δ 144.1 (40), δ 140.3 (20), δ 136.7 (25), δ 136.2 (42), δ 135.9 (40), δ 129.7 (70), δ 129.3 (100), δ 129.2 (90), δ 128.7 (50), δ 128.4 (60), δ 127.2 (40), δ 126.8 (45), δ 125.5 (43), δ 125.3 (45), δ 125.1 (43), δ 120.1 (50), δ 65.7 (70), δ 60.9 (40), δ 37.9 (35), δ 37.7 (3), δ 31.5 (16),
Figure 83. $^1$H NMR of 17a in CDCl$_3$
Figure 84. FT-IR of 17a in CDCl$_3$
Figure 85. $^1$H NMR of 17b in CDCl$_3$
Figure 86. FT-IR of 17b in CDCl₃
Figure 87. $^1$H NMR of 17c in CDCl$_3$
Figure 88. FT-IR of 17c in CDCl$_3$
Figure 89. $^1$H NMR of 17g in CDCl$_3$
Figure 90. FT-IR of 17d in CDCl₃
Figure 91. $^1\text{H}$ NMR of 17E in CDCl$_3$
Figure 92. FT-IR of 17f in CDCl$_3$
Figure 93. $^1\text{H}$ NMR of 17g in CDCl$_3$
Figure 94. FT-IR of 17g in CDCl$_3$
Figure 95. $^1$H NMR of $^{17}h$ in CDCl$_3$
Figure 96. FT-IR of 17h in CDCl₃
Figure 97. $^1$H NMR of 17i in CDCl$_3$
Figure 98. FT-IR of 17j in CDCl$_3$.
Figure 99. $^1H$ NMR of 17j in CDCl$_3$
Figure 100. FT-IR of $^{17}$J in CDCl$_3$
General synthesis of ethyl N-nitroso N-(trans-2,3-diaryl-
cyclopropyl)carbamates (18a-j)

Preparation of ethyl N-nitroso N-(trans-2,3-diphenyl-
cyclopropyl)carbamate (18a) Figures 101, 102

A 25 ml round bottom flask was charged with 100 mg of \( \text{17a} \), 5 ml of acetic anhydride, 10 equivalents of sodium nitrite and 50 \( \mu \)l of glacial acetic acid. The reaction was cooled in an ice/water bath and allowed to stir for 2 hours. The product mixture was then poured into 250 ml of ice water and 200 ml of water was then decanted off. The organic phase was then dissolved in 150 ml of hexanes, this layer was washed with cold 5% sodium bicarbonate solution until it was slightly basic. The organic layer was then washed with water and the solvent was removed under reduced pressure. The product was dried on a high vacuum line as it reacts with magnesium sulfate. The product 18a was obtained as a yellow oil which was acid, base and heat sensitive.
\[ \text{18(a-j)} \]

\[ \text{X/Y} = \text{H/H (a), CH}_3/\text{CH}_3 \text{ (b), OCH}_3/\text{OCH}_3 \text{ (c), Cl/Cl (d), } \]
\[ \text{H/CH}_3 \text{ (e), H/Cl (g), H/CF}_3 \text{ (h), CH}_3/\text{Cl (i), CH}_3/\text{CF}_3 \text{ (j)} \]

\[ ^1H \text{ NMR (CDCl}_3\]): \delta 7.2 \text{ (m), } \delta 4.3 \text{ (m), } \delta 4.2 \text{ (m), } \delta 2.9 \text{ (m), } \delta 1.2 \text{ (t).} \]

\[ \text{FT-IR (CDCl}_3\): 3000 \text{ (w), 1784 \text{ (s), 1500 \text{ (m), 1200 \text{ (m), 700 \text{ (s) cm}^{-1}.}}} \]

\text{Ethyl N-nitroso N-(trans-2,3-bis(p-methylphenyl)cyclopropyl)carbamate (18b) (Figures 103, 104) Prepared from 17b as a yellow oil.}

\[ ^1H \text{ NMR (CDCl}_3\): \delta 7.4-6.8 \text{ (m), } \delta 4.3 \text{ (m), } \delta 4.2 \text{ (m), } \delta 2.8 \text{ (m), } \delta 2.32 \text{ (s), } \delta 2.27 \text{ (s), } \delta 1.2 \text{ (t).} \]

\[ \text{FT-IR (CDCl}_3\): 3000 \text{ (w), 1764 \text{ (s), 1520 \text{ (s), 1190 \text{ (m), 740 \text{ (s) cm}^{-1.}}}} \]
Ethyl N-nitroso N-(trans-2,3-bis(p-methoxyphenyl)-cyclopropyl)carbamate (18c) (Figures 105, 106) Prepared from 17c as a yellow oil.

$^1$H NMR (CDCl$_3$): δ 7.26 (m), δ 6.95 (d), δ 6.86 (d), δ 6.77 (d), δ 4.3 (m), δ 4.2 (m), δ 3.8 (s),
δ 3.75 (s), δ 2.76 (t), δ 1.2 (t).

FT-IR (CDCl$_3$): 3000 (w), 1768 (s), 1512 (s), 1240 (s) cm$^{-1}$.

Ethyl N-nitroso N-(trans-2,3-bis(p-chlorophenyl)-cyclopropyl)carbamate (18d) (Figures 107, 108) Prepared from 17d as a yellow oil.

$^1$H NMR (CDCl$_3$): δ 7.5-7.0 (m), δ 4.3 (m), δ 4.2 (m), δ 2.7 (m), δ 1.2 (m).

FT-IR (CDCl$_3$): 3000 (w), 1730 (s), 1500 (s), 1084 (s) cm$^{-1}$.

Ethyl N-nitroso N-(trans-2-(p-methylphenyl)-3-phenyl-cyclopropyl)carbamate (18f) (Figures 109, 110) Prepared from 17f as a yellow oil.

$^1$H NMR (CDCl$_3$): δ 7.5-7.0 (m), δ 4.2 (m), δ 4.1 (m), δ 2.8 (m), δ 2.33 (s), δ 2.3 (m), δ 2.28 (s),
δ 1.2 (m).

FT-IR (CDCl$_3$): 3000 (w), 2904 (s), 1770 (s), 1540 (s),
1240 (s) cm$^{-1}$. 


Ethyl N-nitroso N-(trans-2-(p-chlorophenyl)-3-phenyl-cyclopropyl)carbamate (18g) (Figures 111, 112) Prepared from 17g as a yellow oil.

$^1$H NMR (CDCl$_3$): $\delta$ 7.4-7.2 (m), $\delta$ 7.1-6.9 (m), $\delta$ 4.3 (m), $\delta$ 2.8 (m), $\delta$ 1.2 (m).

FT-IR (CDCl$_3$): 3006 (w), 1757 (s), 1494 (m), 1381 (s), 1338 (m), 1186 (s), 1012 (m) cm$^{-1}$.

Ethyl N-nitroso N-(trans-2-phenyl-3-(p-trifluoromethyl-phenyl)cyclopropyl)carbamate (18h) (Figures 113, 114)

Prepared from 17h as a yellow oil.

$^1$H NMR (CDCl$_3$): $\delta$ 7.6-7.0 (m), $\delta$ 4.3 (m), $\delta$ 2.9 (m), $\delta$ 1.2 (m).

FT-IR (CDCl$_3$): 3000 (w), 1765 (s), 1341 (s), 1120 (s) cm$^{-1}$.

Ethyl N-nitroso N-(trans-2-(p-chlorophenyl)-3-(p-methyl-phenyl)cyclopropyl)carbamate (18i) (Figures 115, 116)

Prepared from 17i as a yellow oil.

$^1$H NMR (CDCl$_3$): $\delta$ 7.3-6.9 (m), $\delta$ 4.3 (m), $\delta$ 2.8 (m), $\delta$ 2.33 (s), $\delta$ 2.28 (s), $\delta$ 1.3 (m).

FT-IR (CDCl$_3$): 3000 (w), 1753 (s), 1518 (s), 1494 (s), 1182 (s) cm$^{-1}$.

Ethyl N-nitroso N-(trans-2-(p-methylphenyl)-3-(p-trifluoromethylphenyl)cyclopropyl)carbamate (18j) (Figures 117, 118)

Prepared from 17j as a yellow oil.

$^1$H NMR (CDCl$_3$): $\delta$ 7.2 (m), $\delta$ 3.90 (m), $\delta$ 2.79 (t), $\delta$ 2.54
Figure 101. $^1$H NMR of 18a in CDCl$_3$
Figure 102. FT-IR of \textit{18a} in CDCl$_3$
Figure 103. $^1$H NMR of 18b in CDCl$_3$
Figure 104. FT-IR of 18b in CDC$_3$.
Figure 105. $^1$H NMR of $^{18}O$ in CDCl$_3$
Figure 106. FT-IR of 18c in CDCl₃
Figure 107. $^{1}H$ NMR of 18d in CDCl$_3$
Figure 108. FT-IR of 18d in CDCl$_3$
Figure 109. $^1H$ NMR of 18f in CDCl$_3$
Figure 110. FT-IR of \( \text{18f} \) in CDCl\(_3\)
Figure 111. $^1$H NMR of 18g in CDCl$_3$
Figure 112. FT-IR of 18g in CDC$_3$. 
Figure 113. $^1$H NMR of 18h in CDCl$_3$
Figure 114. FT-IR of 18h in CDCl$_3$
Figure 115. $^1H$ NMR of 18i in CDCl$_3$
Figure 116. FT-IR of 18i in CDC$_3$
Figure 117. $^1$H NMR of 18j in CDCl$_3$
Figure 118. FT-IR of 18j in CDC$_3$
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(m), δ 2.45 (m), δ 2.15 (s), δ 2.04 (s),
δ 0.80 (m).

FT-IR (CDCl₃): 3000 (w), 1770 (m), 1500 (m), 1350 (s),
1100 (s) cm⁻¹.

General reactions of 18 (a-j) in toluene/methanol solutions

Reaction of 18a in toluene/methanol solution (Figures 119-121)

A 1 dram vial was charged with 0.5 ml of toluene/methanol solution (concentrations of 20-100% methanol were used), and 2-3 mg of 18a. The stirred solution was immersed in a constant temperature bath (temperatures of 271k, 297k and 313k were used) and treated with 10 mg of sodium methoxide. Evolution of nitrogen began immediately and stopped within 30 seconds, the reactions were stirred for 3 minutes to insure complete reaction. The mixture was quenched with 1 ml of 50% ammonium chloride solution and 0.5 ml of either was used to extract the organic products. The products 19a and 20a were analyzed rapidly by capillary GLPC. The response factor ratio of 20a/19a = 0.76 was used to correct the data to mole ratios.
\[
\begin{align*}
19 \ (a-j) & \\
X/Y = H/H \ (a), \ CH_3/CH_3 \ (b), \ OCH_3/OCH_3 \ (c), \ Cl/Cl \ (d), \\
H/CH_3 \ (e), \ H/Cl \ (g), \ H/CF_3 \ (h), \ CH_3/Cl \ (i), \ CH_3/CF_3 \ (j) \\
\end{align*}
\]

GC-HRMS: 
- \(19a\): Calculated \(C_{15}H_{12}\) \(m/e\) 192.09390
- measured \(m/e\) 192.09490 error 5.2 ppm
- \(20a\): Calculated \(C_{16}H_{16}O\) \(m/e\) 224.12012
- measured \(m/e\) 224.12065 error 2.4 ppm

\(^1\)H NMR (CDCl\(_3\)): 
- \(19a\): \(\delta\) 7.2 (m), \(\delta\) 6.7 (s)
- \(20a\): \(\delta\) 7.2 (m), \(\delta\) 3.7 (dd), \(\delta\) 3.26 (s),
  - \(\delta\) 2.5 (dd), \(\delta\) 2.37 (dd)

GC-FT-IR: 
- \(19a\): 3030 (s), 1945 (m), 1600 (m),
  - 1494 (m) \(cm^{-1}\)
- \(20a\): 3030 (s), 1608 (s), 1500 (s),
  - 1220 (s), 1140 (s) \(cm^{-1}\)

Reaction of \(18b\) in toluene/methanol solution (Figures 122-124) 
The response factor ratio for \(20b/19b = 0.45\). 

GC-HRMS: 
- \(19b\): Calculated \(C_{17}H_{16}\) \(m/e\) 220.12520
- measured \(m/e\) 220.12475 error 2.0 ppm
$^{20b}$: Calculated $C_{18}H_{20}O$ m/e 252.15142
measured m/e 252.15043 error -3.9 ppm

$^1H$ NMR

(acetone-$d_6$): $^{19b}$: $\delta$ 7.2 (m), $\delta$ 6.64 (s), $\delta$ 2.24 (s)
$^{20b}$: $\delta$ 7.2 (m), $\delta$ 3.65 (dd), $\delta$ 3.19 (s),
$\delta$ 2.8 (s), $\delta$ 2.5 (m)

GC-FT-IR:
$^{19b}$: 3030 (m), 1954 (w), 1500 (s),
1090 (s) cm$^{-1}$
$^{20b}$: 3030 (m), 1580 (m), 1100 (s) cm$^{-1}$

Reaction of $^{18c}$ in toluene/methanol solution (Figures 125, 126)
The response factor ratio for $^{20c}/^{19c} = 0.13$.

GC-HRMS: $^{19c}$: Calculated m/e 252.11503
measured m/e 252.11557 error 2.1 ppm
$^{20c}$: Calculated m/e 284.14125
measured m/e 284.14233 error 3.8 ppm

$^1H$ NMR (CDCl$_3$): $^{19c}$: $\delta$ 7.2 (m), $\delta$ 6.47 (s), $\delta$ 3.28 (s)
$^{20c}$: $\delta$ 7.2 (m), $\delta$ 3.40 (dd), $\delta$ 3.35 (s),
$\delta$ 3.34 (s), $\delta$ 3.1 (s), $\delta$ 2.50 (dd),
$\delta$ 2.16 (dd)

FT-IR: $^{19c}$ and $^{20c}$: 2960 (m), 2050 (w), 1932 (w), 1886
(w), 1720 (m), 1606 (m), 1514 (s),
1464 (m), 1248 (s), 1175 (m), 1034
(m), 833 (m) cm$^{-1}$
Reaction of 18d in toluene/methanol solution (Figures 127-128) The response factor ratio for 20d/19d = 0.48.

GC-HRMS: 19d: Calculated C_{15}H_{10}Cl_2 m/e 260.01596 measured m/e 260.01614 error 0.7 ppm
20d: Calculated C_{16}H_{14}Cl_2O m/e 292.04218 measured m/e 292.03680 error 5.9 ppm

^1H NMR (CDCl_3): 19d: δ 7.2 (m), δ 6.54 (s)
20d: δ 7.2 (m), δ 3.63 (dd), δ 3.24 (s), δ 2.44 (dd), δ 2.29 (dd)

FT-IR: 19d and 20d: 2925 (m), 1940 (w), 1900 (w), 1726 (m), 1591 (s), 1495 (m), 1261 (m), 1217 (m), 1094 (s), 1012 (s), 827 (s) cm^{-1}

Reaction of 18f in toluene/methanol solution (Figures 129, 130) The response factor ratio for 20f/19f = 0.58.

GC-HRMS: 19f: Calculated C_{16}H_{14} m/e 206.10955 measured m/e 206.10857 error -4.8 ppm
20f: Calculated C_{17}H_{18}O m/e 238.13577 measured m/e 238.13664 error 3.7 ppm

^1H NMR (CDCl_3): 19f: δ 7.2 (m), δ 6.44 (q), δ 2.05 (s)
20f: δ 7.2 (m), δ 3.45 (dd), δ 3.00 (s), δ 2.98 (s), δ 2.55 (m), δ 2.1 (m)

FT-IR: 19f and 20f: 3030 (m), 2926 (m), 1933 (w), 1900 (w), 1514 (s), 1495 (s), 1454 (m),
Reaction of 18g in toluene/methanol solution (Figures 131-133) The response factor ratio for 20g/19g = 0.77.

**GC-HRMS:**
- **19g:** Calculated $C_{15}H_{15}Cl$ m/e 226.05493
  - Measured m/e 226.05300 error -8.5 ppm
- **20g:** Calculated $C_{16}H_{15}ClO$ m/e 258.08115
  - Measured m/e 258.08154 error 1.5 ppm

**$^1$H NMR (CDCl$_3$):**
- **19g:** $\delta$ 7.2 (m), $\delta$ 6.55 (q)
- **20g:** $\delta$ 7.2 (m), $\delta$ 3.65 (dd), $\delta$ 3.23 (s),
  - $\delta$ 2.47 (dd), $\delta$ 2.30 (dd)

**GC-FT-IR:**
- **19g:** 3030 (s), 1955 (w), 1630 (m),
  - 1500 (m), 1210 (s), 670 (s) cm$^{-1}$
- **20g:** 3000 (w), 1500 (s), 1105 (s) cm$^{-1}$

Reaction of 18h in toluene/methanol solution (Figures 134-136) The response factor ratio for 20h/19h = 1.01.

**GC-HRMS:**
- **19h:** Calculated $C_{16}H_{15}F_3$ m/e 260.08129
  - Measured m/e 260.08125 error -0.2 ppm
- **20h:** Calculated $C_{17}H_{15}F_3O$ m/e 292.10751
  - Measured m/e 292.10803 error 1.8 ppm

**$^1$H NMR (CDCl$_3$):**
- **19h:** $\delta$ 7.2 (m), $\delta$ 6.27 (q)
- **20h:** $\delta$ 7.2 (m), $\delta$ 3.4 (m), $\delta$ 2.9 (s),
  - $\delta$ 2.8 (s), $\delta$ 2.4 (m), $\delta$ 2.05 (m)

**GC-FT-IR:**
- **19h:** 3000 (w), 1952 (w), 1320 (s),
  - 1190 (m) cm$^{-1}$
Reaction of 18i in toluene/methanol solution (Figures 137, 138) The response factor ratio for 20i/19i = 0.20.

**GC-HRMS:**
- **19i:** Calculated C\textsubscript{16}H\textsubscript{13}Cl m/e 240.07058
  measured m/e 240.06992 error -2.8 ppm
- **20i:** Calculated C\textsubscript{17}H\textsubscript{17}ClO m/e 272.09680
  measured m/e 272.09492 error -6.9 ppm

**\textsuperscript{1}H NMR (CDCl\textsubscript{3})**:
- **19i:** \( \delta 7.2 \) (m), \( \delta 6.32 \) (q), \( \delta 2.07 \) (s)
- **20i:** \( \delta 7.2 \) (m), \( \delta 3.34 \) (dd), \( \delta 3.25 \) (dd),
  \( \delta 2.92 \) (s), \( \delta 2.90 \) (s), \( \delta 2.4 \) (m),
  \( \delta 2.2-2.0 \) (m)

Reaction of 18j in toluene/methanol solution (Figures 139-141) The response factor ratio for 20j/19j = 0.70.

**GC-HRMS:**
- **19j:** Calculated C\textsubscript{17}H\textsubscript{17}F\textsubscript{3} m/e 274.09694
  measured m/e 274.09668 error -1.0 ppm
- **20j:** Calculated C\textsubscript{18}H\textsubscript{17}F\textsubscript{3}O m/e 306.12316
  measured m/e 306.12104 error -6.9 ppm

**\textsuperscript{1}H NMR (CDCl\textsubscript{3})**:
- **19j:** \( \delta 7.2 \) (m), \( \delta 6.32 \) (q), \( \delta 2.05 \) (s)
- **20j:** \( \delta 7.2 \) (m), \( \delta 3.31 \) (m), \( \delta 3.00 \) (s),
  \( \delta 2.87 \) (s), \( \delta 2.40 \) (m), \( \delta 2.42 \) (m),
  \( \delta 2.16 \) (s), \( \delta 2.13 \) (s)
Figure 119. $^1$H NMR of 19a and 20a in CDCl$_3$
Figure 120. GC-FT-IR of 19a
Figure 121. GC-FT-IR of 20a
Figure 122. $^1$H NMR of 19b and 20b in acetone-d6
Figure 123. GC-FT-IR of 19b
Figure 124. GC-FT-IR of 20b
Figure 125. $^1$H NMR of 19c and 20c in CDCl$_3$
Figure 126. Ft-IR of 19c and 20c neat
Figure 127. $^1$H NMR of 19d and 20d in CDCl$_3$
Figure 128. FT-IR of 19d and 20d neat
Figure 129. $^1\text{H NMR of 19f and 20f in CDCl}_3$
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Figure 131. $^1$H NMR of $19g$ and $20g$ in CDCl$_3$
Figure 132. GC-FT-IR of 19g
Figure 133. GC-FT-IR of 20g
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Figure 135. GC-FT-IR of 19h
Figure 136. GC-FT-IR of 20h
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