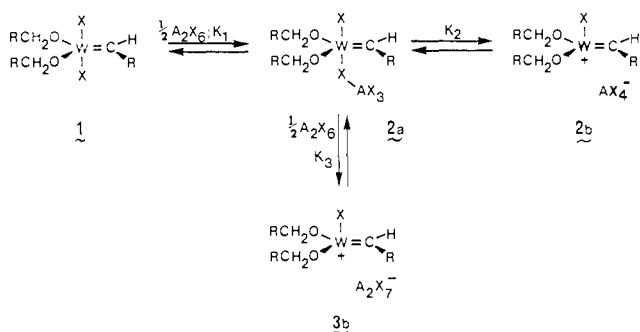
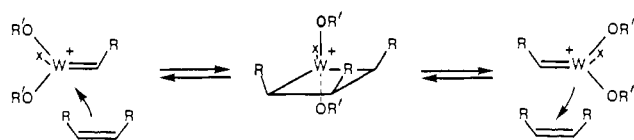


Scheme I



Scheme II



(b) For $n > 1$, further NMR displacements are observed, and many of the plots of chemical shift displacement against n show cusps at $n = 1$, indicating the formation of a second species between **2a** ($A = \text{Ga}$; $X = \text{Br}$) and gallium bromide. The non-linear behavior of these displacements, where limiting values are only achieved at $n > 6$, shows that the corresponding formation constant K_3 is small and is calculated as $5 \pm 1 \text{ mol}^{-1}$ at -35°C .

We propose (Scheme I) that the new complex formed is **3b**, $\text{W}(\text{=CRH})(\text{OCH}_2\text{R})_2\text{Br}^+\text{Ga}_2\text{Br}_7^-$, on the following observations:³ (a) whereas the resonances of $\text{W}=\text{CH}-t\text{-Bu}$ (in ^1H) and $\text{W}=\text{CH}-t\text{-Bu}$ (in ^{13}C) shift in lower field, the $J_{\text{C-H}}$ coupling constant remains essentially unchanged for all values of n . (b) The two $\text{OCH}_2-t\text{-Bu}$ ligand resonances (^1H , ^{13}C) suffer only slight displacements. (c) The conductivity of solutions increases dramatically after $n = 1$, approaching an asymptotic limit (allowing for excess Ga_2Br_6) only at higher values of n , corresponding to a 1:1 electrolyte.

The catalytic activity of this system in the metathesis of *cis*-pent-2-ene (ca. 10^{-2} M carbene, 10^4 mol equiv of olefin, $\text{C}_6\text{H}_5\text{Cl}$, 20°C) follows a similar profile, the initial rates increasing linearly until $n = 1$ ($650 \text{ mol of olefin (mol W)}^{-1} \text{ min}^{-1}$) and then rapidly and nonlinearly with $n > 1$ reaching a limiting value at high values of n ($5000 \text{ mol of olefin (mol W)}^{-1} \text{ min}^{-1}$). This parallel relationship between catalytic activity and the concentration of **3b** implies strongly that this cationic species is the active species for $n > 1$. Further, the initial rate of metathesis for $n = 1$ as well as the conductivity are both ca. 15% of the limiting values found for large n . Thus we propose that the same cationic complex (**2b** = **3b**) is the active species⁴ for all values of n , even for $n < 1$ where **2a** is the major complex in solution. Also the initial ratio ($t = 0$) of *cis*-/*trans*-but-2-ene produced in the metathesis of *cis*-pent-2-ene is the same (1.0 ± 0.1) for all values of n .

The NMR data of **3b** show³ that the two $\text{OCH}_2-t\text{-Bu}$ groups are diastereotopic indicating that irrespective of the precise stereochemistry about W, no rotation about the metal-carbene bond takes place on the NMR time scale and **3b** is chiral.⁵

We thus propose that (a) the olefin interacts with **3b** via the site vacated by the halide ion (Scheme II), this approach allowing

(3) By extrapolation to high n we obtain for **3b** ($\text{C}_6\text{D}_6\text{Br}$, -35°C): ^1H NMR δ 13.15 (s, 1 H, CHCMe_3 , $J_{\text{W-H}} = 12 \text{ Hz}$), 4.72, 4.55 (s, 2 H, OCH_2CMe_3), 1.18 (s, 9 H, CHCMe_3), 0.94, 0.85 (s, 9 H, OCH_2CMe_3); ^{13}C NMR (ppm) 333 (d, $J_{\text{C-H}} = 134 \text{ Hz}$, CHCMe_3), 93.0, 92.5 (t, OCH_2CMe_3), 51.5 (s, CHCMe_3), 35.2, 34.9 (s, OCH_2CMe_3), 32.5 (q, CHCMe_3), 26.7 (q, OCH_2CMe_3).

(4) Wengrovius, J. H.; Schrock, R. R. *Organometallics* **1982**, *1*, 148 (ref 21).

(5) Note: (a) The active species described here are chiral even if all ligands are identical (if $\text{R} \neq \text{H}$). (b) Chiral forms are interchanged, however, if halide exchange occurs between cation and anion ($\mathbf{3} \leftrightarrow \mathbf{1}$). The equivalence of the diastereotopic protons in **2** and **3b** is consistent with such an exchange process occurring at -35°C . The implications in catalysis will be discussed fully elsewhere.

a suprafacial interaction of the olefin and metal carbene π -orbitals leading to metallacycle formation, and (b) the metallacycle so formed whether as an intermediate or transition state must possess a plane of symmetry imposed by the principle of microscopic reversibility.⁶ Hence ligand rearrangement must accompany metallacycle formation, the most feasible mechanism of which is shown in Scheme II. Hence a *cis* olefin reacting to give a *cis* olefin product should occur with inversion of chirality of the carbene and hence the catalyst; a *cis* olefin giving *trans* olefin as product occurs with retention of configuration. Indeed classical catalysts have been shown to exhibit enantiomeric selectivity in the polymerization⁷ of (\pm)-1-methylbicyclo[2.2.1]hept-2-ene.

Acknowledgment. We thank the C.N.R.S. and Rhône-Poulenc for financial aid.

Registry No. **1**, 82958-93-8; **2a**, 86993-74-0; **3b**, 86993-76-2; Ga_2Br_6 , 18897-68-2; *cis*-pent-2-ene, 627-20-3; *cis*-but-2-ene, 590-18-1; *trans*-but-2-ene, 624-64-6.

(6) This argument strictly applies only to degenerate metathesis.

(7) Hamilton, G. J.; Ivin, K. J.; Rooney, J. J.; Waring, L. C. *J. Chem. Soc., Chem. Commun.* **1983**, 159-161.

Dynamics of Micellized Radical Pairs. Measurement of Micellar Exit Rates of Benzylic Radicals by Time-Resolved Flash CIDNP and Optical Spectroscopy

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The dynamics of micellized triplet radical pairs have been investigated recently by time-resolved laser optical flash spectroscopy in several laboratories.¹⁻⁵ Usually, the disappearance of the micellized triplet radical pairs consists of a fast decay in the 1-500-ns time domain and a slow decay in the 500-5000-ns time domain. The fast decay is typically sensitive to applied laboratory magnetic fields, whereas the slow decay is not. The fast decay has been attributed to the competition between hyperfine-induced intersystem crossing to a singlet radical pair, which rapidly undergoes reaction and results in loss of radical absorption, and diffusive separation of the radicals to intra- and extramicellar configurations.^{3,5} The slow decay has been attributed to uncorrelated micellar recombinations of geminate and nongeminate radical pairs.^{3,5} In only one case has a rate constant for micellar exit of a radical been estimated from such experiments.³ In that case, the exit rate of the cyclohexadienyl radical was found to be similar to the exit rate of singlet excited benzene for SDS micelles. We report the direct measurements of exit rates of radicals from sodium dodecyl sulfate (SDS) micelles by two independent methods: time-resolved laser flash spectroscopy and time-resolved chemically induced dynamic nuclear polarization (CIDNP). Our results are consistent with mechanisms that include radical exit from the micelle as a kinetically important process in the slow decay of micellized triplet radical pairs.

We have used the stable nitroxide radical Fremy's salt (FS), a selective water-soluble anionic scavenger, to react with radicals that exit from SDS micelles. Reaction of benzyl radicals with

(1) Turro, N. J.; Chow, M.-F.; Chung, C.-J.; Tanimoto, Y.; Weed, G. C. *J. Am. Chem. Soc.* **1981**, *103*, 4574.

(2) Sakaguchi, Y.; Nagakura, S.; Minoh, A.; Hayashi, H. *Chem. Phys. Lett.* **1981**, *82*, 213.

(3) Scaiano, J. C.; Abuin, E. B.; Stewart, L. C. *J. Am. Chem. Soc.* **1982**, *104*, 5673.

(4) Tanimoto, Y.; Itoh, M. *Chem. Phys. Lett.* **1981**, *83*, 626.

(5) Turro, N. J.; Baretz, B. H.; Gould, I. R.; Lehr, G. F. *J. Am. Chem. Soc.*, submitted for publication.

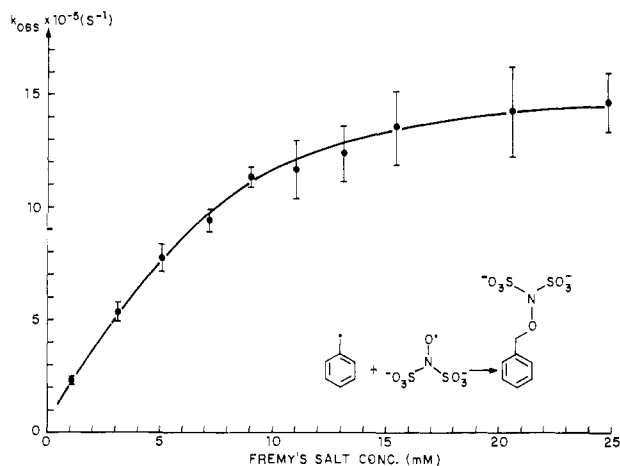
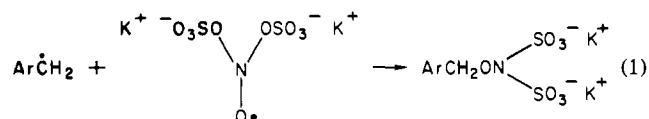


Figure 1. Plot of the rate of decay of benzyl radical absorption (k_{obsd}) in SDS as a function of added Fremy's salt. Error bars represent two standard deviations.

FS decreases the radical absorption lifetime monitored at 317 nm due to formation of hydroxyl amine ethers (HAE) (eq 1).^{6,7}



Electrostatic repulsion prevents the Fremy's salt from reacting with micellized geminate radical pairs, so that only radicals that exit from the micelle are scavenged. At sufficiently high concentrations of Fremy's salt, it is expected that each exiting radical will be scavenged, and above this concentration the effectiveness of scavenging will become independent of scavenger concentration. In this domain the rate of micellar exit determines the radical lifetime.⁸

Triplet micellized benzyl radical pairs were produced by photolysis of dibenzyl ketone (DBK) in SDS micelles.^{6,9} The long-lived decay of benzyl radical absorption follows (pseudo) first-order kinetics (characterized by the pseudo-first-order constant k_{obsd}) in the presence of >1 mM Fremy's salt. Figure 1 shows that k_{obsd} initially varies linearly with Fremy's salt concentration, but at about 8 mM the dependence of k_{obsd} on scavenger concentration diminishes and above 20 mM k_{obsd} becomes independent of scavenger concentration. The extrapolated value of k_{obsd} in the scavenger-independent region is $(1.4 \pm 0.3) \times 10^6 \text{ s}^{-1}$. This value is in excellent agreement with the reported exit rate of toluene from SDS micelles ($1.3 \times 10^6 \text{ s}^{-1}$).¹⁰ Photolysis of methyl benzyl ketone (MBK) was also employed to produce benzyl radicals in SDS micelles. Quenching of the benzyl radical absorption by Fremy's salt follows a behavior identical with that shown in Figure 1. The extrapolated value of k_{obsd} in the scavenger-independent region is $(1.4 \pm 0.4) \times 10^6 \text{ s}^{-1}$. These results provide convincing support¹¹ for the conclusion that the exit rate for benzyl radicals

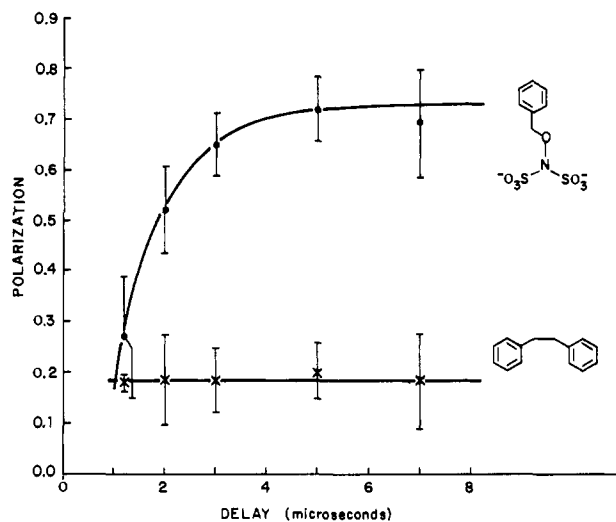


Figure 2. Plot of the polarization intensity of amine ether and diphenylethane coupling products as a function of time after the laser pulse. Error bars represent two standard deviations.

from SDS micelles is ca. $1 \times 10^6 \text{ s}^{-1}$.

Similar investigations of 4-methylbenzyl radicals (from photolysis of 4,4'-dimethyldibenzyl ketone) and of *sec*-phenethyl radicals (from photolysis of α,α' -dimethyldibenzyl ketone) in SDS micelles yielded extrapolated values for k_{obsd} of $(2.4 \pm 0.4) \times 10^6 \text{ s}^{-1}$ and $(3.0 \pm 0.6) \times 10^5 \text{ s}^{-1}$, respectively. The latter smaller values of k_{obsd} relative to that for benzyl radicals, are consistent with the more hydrophobic character of these radicals. Furthermore, these values of k_{obsd} compare favorably with the reported exit rate of xylene from SDS micelles ($4.4 \times 10^5 \text{ s}^{-1}$).¹⁰

Steady-state CIDNP investigations of the DBK-Fremy's salt system demonstrated polarization in the DBK, in the cage product diphenylethane (DPE) and in the micelle exit product HAE. Time-resolved laser flash CIDNP studies allowed the measurement of product polarization intensities as a function of time after laser pulse. The generation of CIDNP occurs in the micellized primary triplet benzyl/phenacyl pair and is complete within 1 μs of formation of the pair by the laser pulse.¹² According to the conclusions reached from the time-resolved laser flash spectroscopic studies described above, the kinetics of HAE polarization development will depend on the exit rate of benzyl radicals from SDS micelles, and at sufficiently high scavenger concentration, the rate of development of this polarization will equal that of radical exit.

The kinetics of the appearance of product polarization follows the expression $A[1 - \exp(-k(t - c))]$. For the DBK system with 10 mM FS (Figure 2) $k_{\text{app}} = (1.0 \pm 0.2) \times 10^6 \text{ s}^{-1}$, in excellent agreement with the exit rate of benzyl radicals from SDS micelles derived from the optical studies.^{14,15} In an analogous fashion the rate constant for appearance of polarization of scavenged products for 4-methylbenzyl radicals was found to be $k_{\text{app}} = (2.6 \pm 0.5) \times 10^5 \text{ s}^{-1}$, in excellent agreement with the exit rate of 4-methylbenzyl radicals from SDS micelles.

The results of our investigation demonstrate that exit rates for substituted benzyl radicals from SDS micelles are nearly identical with the exit rates of their saturated analogues. Additionally, the

(6) Robbins, W. K.; and Eastman, R. H. *J. Am. Chem. Soc.* **1970**, *92*, 6077.

(7) (a) in acetonitrile/water (50:50) we have determined a rate constant of $2 \times 10^8 \text{ mol}^{-1} \text{ s}^{-1}$ for addition of FS to benzyl radicals. (b) The rate of FS exit from water pools in water in oil emulsions has been reported: Atik, S. S. Thomas, J. K. *J. Am. Chem. Soc.* **1981**, *103*, 3543; *Chem. Phys. Lett.* **1981**, *79*, 351.

(8) For the analogous case of micellized phosphorescent species, see: Bolt, J. D. Turro, N. J. *J. Phys. Chem.* **1981**, *85*, 4029.

(9) Experiments were performed by using argon purged solutions of ketone (10^{-3} M) and SDS (0.05 M) in the presence of 6×10^{-3} M sodium carbonate to stabilize the Fremy's salt at 28 °C. A Lambda Physik Excimer laser (308 nm, 15 ns) was used with a conventional transient absorption apparatus for the optical absorption experiments and with a Bruker WP-80 FT NMR (80 MHz proton) for the time-resolved CIDNP experiments.

(10) Almgren, M.; Grieser, F.; and Thomas J. K. *J. Am. Chem. Soc.* **1979**, *101*, 279.

(11) Since k_{obsd} is independent of the radical pair precursor, k_{obsd} must reflect a property of a single benzyl radical.

(12) Decarbonylation of the primary phenacyl radical occurs at $5 \times 10^6 \text{ s}^{-1}$ (ref 13); therefore, after 1 μs >99% of the phenacyl radicals have decarbonylated. Benzyl-benzyl radical pairs are incapable of generating net CIDNP.

(13) (a) Turro, N. J.; Gould, I. R.; Baretz, B. H. *J. Phys. Chem.* **1983**, *87*, 531. (b) Lunazzi, L.; Ingold, K. U.; and Scaiano, J. C. *Ibid.* **1983**, *87*, 529.

(14) At this concentration of FS, k_{obsd} is identical with k_{app} . At higher concentrations of FS, k_{obsd} approaches a higher value; thus the CIDNP experiment yields a lower limit for the rate of radical micellar escape.

(15) The intensity of the polarization observed in diphenylethane, a cage recombination product, is invariant after 1- μs delay (Figure 2). This result implies that recombination reactions of the benzyl radicals do not contribute significantly to k_{obsd} or k_{app} .

measured rate constants place the rate of micellar exit in the time domain of the slow decay for micellized triplet radical pairs.

Acknowledgment. We thank the National Science Foundation for its generous support of this research. M.B.Z. thanks the National Science Foundation for a predoctoral research fellowship. Invaluable advice and aid from Dr. C. E. Doubleday, Jr., and Dr. E. V. Sitzmann are gratefully acknowledged.

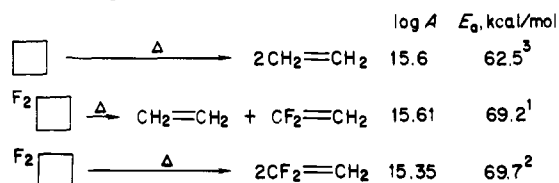
Thermal Isomerizations of 2,2,3,3-Tetrafluorobicyclopentanes. The Kinetic Effect of Fluorine Substituents on Cyclobutane Bond Homolysis

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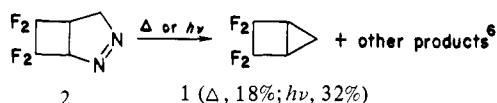
Received June 9, 1983

In 1980 Frey examined the thermal fragmentation reactions of 1,1-difluorocyclobutane and 1,1,2,2-tetrafluorocyclobutane, demonstrating that these fragmentations were significantly inhibited by the presence of the fluorine substituents.^{1,2} It was not

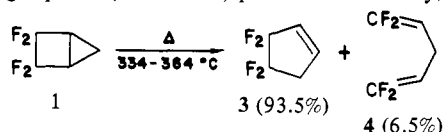


possible, however to dissect unambiguously from these results the relative ease of breaking the CH₂-CH₂ bond of each of these molecules. In view of the fact that the strength of CH₂-CH₂ bonds in cyclopropane can be drastically affected by geminal difluoro substitution, we were interested to determine if similar effects might be present in cyclobutane systems. It is well-known that perfluorocyclobutane is very much stabilized to fragmentation (E_a = 74.2 kcal/mol)⁵, and as seen above in the difluoro and tetrafluoro cases, fluorine substitution definitely stabilizes the cyclobutane ring to overall fragmentation.

The system with which we have initially tested such effects is the 2,2,3,3-tetrafluorobicyclo[2.1.0]pentane system, the parent (1) of which was synthesized by the thermal or photochemical deazotation of pyrazoline 2.⁶



Thermal isomerization of 1 to 3,3,4,4-tetrafluorocyclopentene (3) in the gas phase (10-30 torr) proceeded smoothly, following



excellent first-order kinetics with only a small amount of competitive fragmentation of 4 being observed. The Arrhenius

(1) Conlin, R. T.; Frey, H. M. *J. Chem. Soc., Faraday Trans. 1*, 1979, 75, 2556.

(2) Conlin, R. T.; Frey, H. M. *J. Chem. Soc., Faraday Trans. 1* 1980, 76, 322.

(3) Gerberich, H. R.; Walters, W. D. *J. Am. Chem. Soc.* 1961, 83, 4884, 3935.

(4) Dolbier, W. R., Jr. *Acc. Chem. Res.* 1981, 14, 195.

(5) Butler, J. N. *J. Am. Chem. Soc.* 1962, 84, 1393.

(6) Dolbier, W. R., Jr.; Al-Fekri, D. *Tetrahedron Lett.*, in press.

(7) The relative rate of formation of 4 from 1 was 0.069 at 334 °C, a rate that corresponds to a ΔG[‡] of 3.1 kcal/mol.

(8) (a) Halberstadt, M. L.; Chesick, J. P. *J. Am. Chem. Soc.* 1962, 84, 2688. (b) Steel, C.; Zand, C.; Hurwitz, P.; Cohen, S. G. *Ibid.* 1964, 86, 679.

Table I. Rates of Thermal Isomerization of 1 to 3

T (±0.1), °C	10 ⁵ k, s ⁻¹
334.5	2.46 ± 0.01
340.0	3.95 ± 0.02
346.0	6.01 ± 0.04
352.0	8.50 ± 0.05
358.0	16.6 ± 0.2
364.5	20.9 ± 0.1

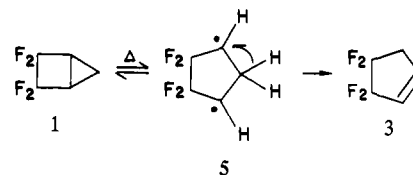
Table II. Rates of Thermal Interconversion of 6 and 7

T (±0.1), °C	10 ⁵ k ₁	10 ⁵ k ₋₁
209.0	3.33	0.171
217.0	6.65	0.368
223.5	10.40	0.575
230.5	20.07	1.14
236.5	30.55	1.79
243.0	49.56	3.004

equation was obtained by the method of least squares from a plot of the rate data in Table I: log k/s⁻¹ = 14.9 ± 0.4 - (54.2 ± 1.1 kcal/mol)/RT ln 10.

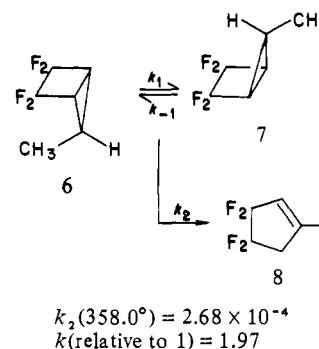
If one compares the activation parameters for conversion of 1 to 3 with those for the analogous rearrangement of the hydrocarbon system (log A = 14.6, E_a = 46.6 kcal/mol), one can see that the rearrangement of 1 is significantly inhibited (ΔE_a = 7.6 kcal/mol) relative to the hydrocarbon rearrangement.

The mechanism of the rearrangement of 1 is presumed to proceed via the intermediacy of the 4,4,5,5-tetrafluorocyclopentane-1,3-diyl species (5).⁹ A significant remaining question



then is whether the observed increase in activation energy is due to an increase in the C₁-C₄ bond-dissociation energy of 1 or whether it is due to a decrease in the rate of the subsequent 1,2-hydrogen shift process of diyl intermediate 5.

In order to answer that question, the *endo*- and *exo*-5-methyl-2,2,3,3-tetrafluorobicyclo[2.1.0]pentanes 6 and 7 were



synthesized in a manner analogous to 1, and their thermal in-

(9) A secondary deuterium isotope effect determination (1-1,4-d₂ → 3-2,5-d₂) at 334.5 °C (kH/kD = 0.97) led to no clear additional mechanistic information.

(10) NMR spectra (300 MHz) of 6: ¹H δ 1.38 (d, J_{HH} = 6.8 Hz, 3 H), 1.76 (m, J_{HH}) = 6.9, 7.0, J_{HF} = 2.3 Hz, 1 H), 2.52 (m, J_{HH} = 7.0, J_{HF} = 9.7, 3.7 Hz, 2 H); ¹⁹F δ 111.5 (midpoint of AB, J_{AB} = 216.1 Hz, Δν = 4726.0 Hz); ¹³C δ 11.49 (s, CH₃), 19.35 (t, J_{CF} = 3.85 Hz, C₃H), 28.18 (d, J_{CF} = 32.5 Hz, C₁H), 114.95 (t, J_{CF} = 264.15 Hz, CF₂).

(11) NMR spectra (300 MHz) of 7: ¹H δ 1.1 (d of t, J_{HH} = 6.2, 1.13, J_{HF} = 1.15 Hz, 3 H), 1.68 (quartet, J_{HH} = 6.3, 1.5, J_{HF} = 0.8 Hz, 1 H), 2.32 (dtd, J_{HF} = 11.8, 3.8, J_{HH} = 1.5 Hz, 2 H); ¹⁹F δ 116.3 (midpoint of AB, J_{AB} = 210.1 Hz, Δν = 4438.5 Hz, downfield F's, d, J_{FH} = 11.9 Hz); ¹³C δ 13.86 (s, CH₃), 15.49 (t, J_{CF} = 2.7 Hz, C₃H), 29.50 (t, J_{CF} = 31.4 Hz, C₁H), 115.17 (t, J_{CF} = 274.94 Hz, CF₂).