Fluorochloro-, Fluorobromo-, and Monofluorocarbene Generation via Organolithium Reagents

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Low temperature (−116 °C) reactions of fluorotrichloromethane and fluorotribromomethane with *n*-butyllithium have been explored as routes to fluorochloro- and fluorobromocyclopropanes and gave moderate yields with tetrasubstituted olefins. Fluorodichloromethyllithium showed little stability even at −116 °C. Fluorodibromomethyllithium gave reasonably good yields of cyclopropanes with tetra-, tri-, and disubstituted olefins. The reactions were stereospecific with *cis*- and *trans*-2-butene. The *Z*/*E* ratios with 2-methyl-2-butene and cyclohexene implicate lithium carbenoid as the reactive species. Except for monosubstituted olefins, this synthetic approach permits a facile synthesis of fluorobromocyclopropanes. Direct attempts at fluorocarbene generation via lithium reagents met with little success. In situ reduction of fluorobromocyclopropanes—from olefin and fluorodibromomethyllithium—gave fluorocyclopropanes in an overall yield of ~20%.

Halogenated carbenes are classically generated via the base hydrolysis of haloforms. Acid–base reactions of the carbon acids generate a trihalomethyl carbanion which subsequently eliminates halide ion to generate the carbene.

$$CHXYZ \xrightarrow{\text{base}} {}^{-}CXYZ \rightarrow [:CXY] + Z^{-}$$

In some cases (i.e., bromodifluoromethane), this process is considered to be concerted.

The role of organolithium reagents in the generation of nonfluorinated halocarbenes has been thoroughly investigated.[1] However, few studies on organolithium generated fluorocarbenes have been reported. Fluorochlorocarbene generation from fluorodichloromethane and *n*-butyllithium appears comparable with generation by other bases.[2] The best preparation of fluorobromocarbene is base hydrolysis of fluorodibromomethane.

A logical improvement to the base hydrolysis of haloforms with organolithium reagents might be expected to be the utilization of lithium–halogen exchange reactions rather than the classic metalation (lithium–proton exchange) reactions. In other systems, lithium–halogen exchange has been shown to be up to several orders of magnitude faster than metalation.[3] In reactions to form vinyl organolithium reagents, increased velocity of lithium–halogen exchange eliminates the problem of side reactions found in metalation.[4] Lithium–halogen exchange has been used in a number of carbene-formation reactions, but no successful fluorochloro- or fluorobromocarbene generation using this method has been reported.

This paper describes the synthetic utility of lithium–halogen exchange reactions in the generation of fluorochloro-, fluorobromo-, and monofluorocarbenes (carbenoids) for cyclopropanation reactions. Fluorobromocyclopropanes and to a lesser extent fluorochlorocyclopropanes can be successfully generated.

Results and Discussion

Fluorotrichloromethane is a convenient and inexpensive fluorochlorocarbene precursor, although lithium–chlorine exchange is generally not greatly faster than the metalation reactions. Generally, lithium carbenoids are stabilized by low reaction temperatures and coordinating solvents. Table I shows the results when an equimolar amount of *n*-butyllithium in hexane is added to olefins and fluorotrichloromethane in THF at −116 °C. The yields are quite similar to those of the reaction of *n*-butyllithium with fluorodichloromethane reported by Schlosser.[2] Although the yield of 2,3-dimethyl-2-butene is moderate, the yields fall drastically for less substituted olefins. Apparently, the electrophilic carbenoid intermediate is effectively trapped only by olefins with high electron density.

The reaction with 2-methyl-2-butene is stereoselective, forming a greater amount of the more sterically hindered *Z* isomer. The *Z*/*E* ratio of 2.4 is similar to that reported in other methods of generation.[5] Reaction with *trans*-2-butene is completely stereospecific, indicating that cyclopropanation probably proceeds via a concerted addition.

Stabilization of the carbenoid intermediate is important in these reactions. When the reaction of 2,3-dimethyl-2-butene is carried out at −78 °C, the yield of cyclopropane drops from 49% to 35%. The temperature, however, is limited to −116 °C on the lower end by the freezing point of the reaction mixture. The solvent is also important in the stabilization of the intermediate. When the reaction of 2,3-dimethyl-2-butene is carried out in hexane rather than THF–hexane, the yield drops to 14%. Highly coordinating reagents also fail to improve the yields. For example, when 2,3-dimethyl-2-butene reacts in hexane with TMEDA coordinated *n*-butyllithium, only 7% cyclopropane is obtained. The reaction in an HMPA–THF–hexane solvent mixture gives only 24%.

When the reactions are carried out in excess olefin in the absence of solvent (the procedure used by Schlosser for reaction of chlorodifluoromethane) the yields are similar at −78 °C but reduced at −116 °C or at warmer temperatures. No significant improvement is observed to warrant the necessity of the excess olefin. It appears that lithium–chlorine exchange and metalation are quite similar in the generation of fluorodichloromethyllithium.

Attempts to pregenerate the carbenoid have failed. When fluorodichloromethyllithium is generated at −116 °C and then quenched with olefin or hydrogen chloride, none of the expected products were formed. These reactions indicate that the intermediate fluorodichloromethyllithium is not stable under the reaction conditions.

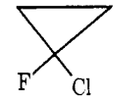
All of the results indicate that the yield of cyclopropane depends on the ability of the olefin to rapidly trap a transient carbenoid intermediate. The low stability of fluorodichloromethyllithium demonstrates the poorer carbanion stabilizing ability of fluorine when compared to chlorine. Trichloromethyllithium is stable to just above −90 °C;[1] however, fluorodichloromethyllithium is quite unstable even at −116 °C in this study.

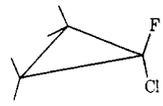
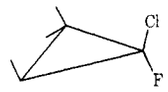
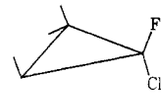
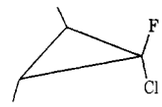
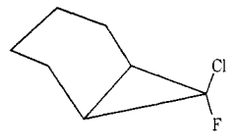
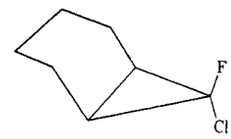
Fluorotribromomethane (**5**), a logical fluorobromocarbene precursor, is commercially available or can be readily prepared by fluorination of carbon tetrabromide.[6]

$$CBr_4 + SbF_3 + Br_2 \xrightarrow[\text{neat}]{125\text{–}150\ ^\circ C} \underset{\mathbf{5}}{CFBr_3}$$

Table I. Preparation of Fluorochlorocyclopropanes in THF–Hexane

$$CFCl_3 + n\text{-BuLi} + \text{olefin} \xrightarrow[\text{THF-hexane}]{-116\ ^\circ C}$$



Olefin	Products	Yield,[a] %	Z/E ratio[a]
2,3-Dimethyl-2-butene	 1	49	
2-Methyl-2-butene	 (Z)-2  (E)-2	32	2.4
trans-2-Butene	 3	8	
Cyclohexene	 (Z)-4  (E)-4	0	

[a] Determined by ^{19}F NMR using benzotrifluoride as internal standard.

Since lithium–bromine exchange is much faster than metalation and bromine is a better carbanion stabilizer than chlorine, we would expect a more stable and more easily formed carbenoid than found with fluorotrichloromethane.

The results of the reaction of olefins with equimolar amounts of *n*-butyllithium and **5** at −116 °C in THF–hexane are recorded in Table II. The yields are recorded for reactions using freshly prepared base with magnetic stirring, freshly prepared base with mechanical stirring, and commercial base with mechanical stirring.

All of the olefins except 1-hexene afforded good yields of cyclopropanes. The monosubstituted 1-hexene is expected to be the least reactive of the olefins surveyed and this method of fluorobromocarbene generation is apparently not applicable for such unreactive olefins.

The reactions are greatly dependent on effective mixing, particularly the less reactive olefins with a relatively high melting point. The drastic change in yields from cyclohexene (from 19% to 57%) emphasizes the importance of efficient mixing at these low temperatures. The problem is underscored by the reactions of 2-methyl-2-butene. With magnetic stirring the yield of **7** is 44% at −116 °C but 59% at −98 °C where the solution is not nearly as viscous. With mechanical stirring, the yield is 71% at −116 °C, indicating that the intermediate carbenoid is more stable at the lower temperature.

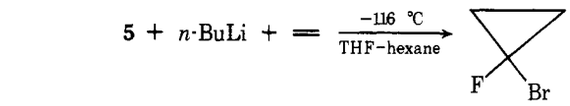
Reactions with *cis* and *trans*-2-butene indicate that cyclopropanation is stereospecific with no cis–trans or trans–cis scrambling, indicating that concerted addition is likely. All reactions of olefins possessing an axis of symmetry produce only one cyclopropane product and unsymmetrical olefins afford two products. The structural assignments of the geometrical isomers are easily made from the ^{19}F NMR.[7,8]

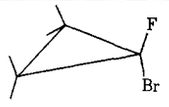
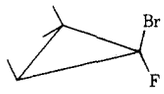
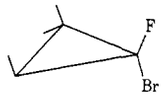
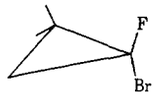
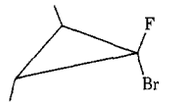
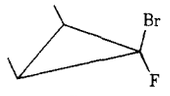
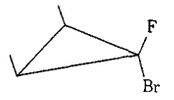
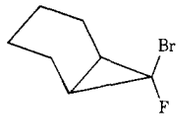
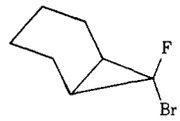
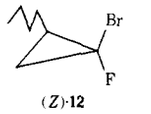
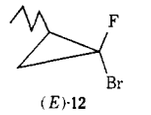
The *Z*/*E* ratios cited in Table II represent an average of at least four reactions. Note that the *Z*/*E* ratio of 1.8 for 2-methyl-2-butene is somewhat smaller than the *Z*/*E* ratio of 2.4 found for the addition of fluorochlorocarbene to the same olefin. This might be expected since, although bromine is more polarizable than chlorine (thus increasing the *Z*/*E* ratio), it is also more sterically hindered (thus decreasing the *Z*/*E* ratio). The difference in *Z*/*E* ratios found here underscores the importance of the balance of electronic and steric factors in determining the stereoselectivity of cyclopropanation reactions. The magnitude of the *Z*/*E* ratio indicates that the reactive species is a carbenoid rather than a free carbene.

Using 10 equiv of each olefin, the relative reactivities of the various olefins toward fluorobromocarbene generated from **5** and *n*-butyllithium were investigated. The internal consistency of the results was not good, and the values obtained from individual competition reactions could not be reproduced accurately. These difficulties probably are a direct result of the reaction solutions at this temperature being quite viscous and at times semisolid. Although mechanical stirring is used, effective stirring may not be achieved and complete solvation of both olefins is not unequivocal. Also, relative reactivities of olefins toward cyclopropanation are temperature dependent in other carbene systems.[5] Lithium–bromine exchange is an exothermic process, and complete temperature control in the reaction flask is difficult when a slush bath is used at such low temperatures. Despite these difficulties and the lack of preciseness of the relative reactivity data, several conclusions can be drawn from the relative reactivity study. The order of relative reactivity of olefins toward fluorobromocarbene is definitely 2,3-dimethyl-2-butene > 2-methyl-2-butene > isobutylene > *cis*-2-butene > *trans*-2-butene > cyclohexene. This order is common to most carbene systems.[5] Similarly to other lithium carbenoids, the fluorobromocarbene precursor investigated here appears to be quite selective in its reactions with olefins, a fact that is reinforced by the failure of cyclopropanation in the case of 1-hexane.

Preparation of fluorocyclopropanes via the generation of monofluorocarbene with *n*-butyllithium has failed. Precursors investigated include fluorodibromomethane, fluorodiiodomethane, difluoromethane, and difluorobromomethane; however, none of the yields were greater than 10%. Fluorocyclopropanes can, however, be formed by in situ reduction of fluorobromocyclopropanes with trimethyltin hydride. The reaction mixture from the preparation of fluorobromocyclopropanes is simply refluxed with lithium aluminum hydride

Table II. Preparation of Fluorobromocyclopropanes



Olefin	Products	Yields,[a] % Mechanical stirring	Commercial n-BuLi	Magnetic stirring	Z/E ratio
2,3-Dimethyl-2-butene	 6	73	61	53	
2-Methyl-2-butene	 (Z)-7  (E)-7	71	70	44	1.8 ± 0.2
Isobutylene	 8	60	55		
trans-2-Butene	 9			57	
cis-2-Butene	 (Z)-10  (E)-10		60	68	2.4 ± 0.4
Cyclohexene	 (Z)-11  (E)-11	57	47	19	2.9 ± 0.8
1-Hexene	 (Z)-12  (E)-12	Trace	Trace	Trace	

[a] Determined by integration of ^{19}F NMR using benzotrifluoride as an internal standard.

and trimethyltin hydride for 24–48 h using this method. 1-Fluoro-2,2,3,3-tetramethylcyclopropane is formed in 21% yield based on starting olefin. Isolation of products from some of the simple olefins (such as butene) can be difficult, since fluorocyclopropanes are generally low boiling and cannot be easily separated from the solvents (ether, hexane, and THF) used in this reaction. While this method is not as simple and does not give comparable yields to the photolysis of fluorodiiodomethane,[9] it does provide a convenient route from 2-substituted olefins which are unreactive via the photolysis method.

Experimental Section

All ^{19}F NMR spectra were recorded with a Varian HA-100 spectrometer operated at 94.075 MHz. Chemical shifts are reported in parts per million upfield from internal $CFCl_3$ and coupling constants are reported in hertz. ^1H NMR spectra were recorded with a Varian A-60 spectrometer. Mass spectra were obtained with a Hitachi Perkin-Elmer RMU-66 spectrometer. Analytical gas chromatography (GLC) was performed on a Hewlett-Packard 5750 chromatograph, and preparative GLC was performed with a Varian Autoprep A-700. The procedure of Jones and Gilman[10] was used for the preparation of *n*-butyllithium and the concentration determined by the method of Gilman and Cartledge.[11]

General Procedure for the Preparation of Fluorochloro- and Fluorobromocyclopropanes. A 50-ml round-bottom flask with septum port is oven dried and thoroughly flushed with argon. If a gaseous olefin is to be reacted, the flask is equipped with a cold-finger condenser which is filled with dry ice–2-propanol and connected to an argon reservoir. If a liquid olefin is to be reacted, the flask is equipped with a glass "T" connected to an argon reservoir. The reaction flask is equipped with a magnetic or mechanical stirrer and cooled in an ethanol slush bath (−116 °C). The flask is charged with 15 ml of dry THF (distilled from benzophenone ketyl) and 1.37 g (10 mmol) of fluorotrichloromethane (Du Pont) or 2.707 g (10 mmol) of fluorotribromomethane (**5**),[12] and 10 mmol of olefin. With vigorous stirring, 10 mmol of *n*-butyllithium in hexane is very slowly (over approximately 20 min) added to the reaction via syringe. The reaction mixture is stirred at −116 °C for approximately 0.25 h after the addition is complete. Then 1 ml of water is added to quench any remaining *n*-butyllithium, the reaction mixture is allowed to warm to room temperature, and 0.438 g (3 mmol) of benzotrifluoride is added for internal ^{19}F NMR standard.

The reaction mixtures are analyzed and yields determined by ^{19}F NMR. The product cyclopropanes are isolated by preparative [10 ft × 0.5 in., 20% silicone gum rubber (SE-30)] or analytical [10 ft × 0.25 in., 20% silicone gum rubber (SE-30)] GLC after the low boiling solvent is removed by fractional distillation through a 2 × 50 mm vacuum-jacketed glass helices column.

1-Fluoro-1-chloro-2,2,3,3-tetramethylcyclopropane (1). ^{19}F NMR ϕ^* 148.0 ppm agrees with previously reported values.[8,13] Mass spectrum *m/e* (rel intensity) 137 [(P + 2) − 15] (1), 135 (P − 15) (2), 115 (27), 114 (100), 99 (90), 97 (14), 85 (13), 79 (45), 77 (32), 73 (21), 61 (11), 59 (26), 55 (11), 53 (45), 51 (17), 42 (12), 41 (34), and 39 (36).

1-Fluoro-1-chloro-2,2,3-trimethylcyclopropane (2). The *Z* and

E isomers could not be separated via glc. ^{19}F NMR (*Z*)-**2** ϕ^* 138.2 ppm, $J_{F,H\text{-cis}}$ = 20.4 Hz. (*E*)-**2** ϕ^* 154.3 ppm agrees with previously reported values.[8,13] Mass spectrum *m/e* (rel intensity) 123 [(P + 2) − 15] (8), 121 (P − 15), 102 (100), 100 (10), 93 (13), 85 (29), 81 (12), 79 (10), 73 (36), 72 (62), 71 (60), 65 (15), 61 (18), 59 (25), 57 (5), 56 (16), 55 (17), 53 (23), and 51 (9).

1-Fluoro-1-chloro-*trans*-2,3-dimethylcyclopropane (3). ^{19}F NMR ϕ^* 145.7 ppm, $J_{F,H\text{-cis}}$ = 22 Hz, agrees with previously reported values.[8,13] Mass spectrum *m/e* (rel intensity) 112 (P) (8), 87 (15), 85 (80), 84 (18), 71 (61), 70 (30), 57 (100), 55 (42), and 55 (26).

7-Fluoro-7-chloronorcarane (4). ^{19}F NMR analysis of the reaction solution indicates that **4** was not produced.

1-Fluoro-1-bromo-2,2,3,3-tetramethylcyclopropane (6). Owing to thermal instability **6** could not be isolated but was identified by enhancement of a NMR with an authentic sample[13] and also reduction of 1-fluoro-2,2,3,3-tetramethylcyclopropane. ^{19}F NMR ϕ^* 141.2 ppm (reported 140.4 ppm[13]).

1-Fluoro-1-bromo-2,2,3-trimethylcyclopropane (7). The *Z* and *E* isomers could not be efficiently separated by GLC. ^{19}F NMR (*Z*)-**7** ϕ^* 132.1 ppm, $J_{F,H\text{-cis}}$ = 20 Hz (reported 129.6 ppm, *J* = 23.5 Hz[14]). (*E*)-**7** ϕ^* 149.5 ppm. Mass spectrum *m/e* (rel intensity) 167 [(P + 2) − 15] (3), 165 (P − 15) (3), 146 (7), 101 (66), 100 (67), 99 (6), 86 (10), 85 (100), 81 (11), 79 (19), 77 (15), 73 (30), 72 (87), 71 (83), 65 (22), 61 (14), 59 (45), 57 (39), 56 (19), 55 (17), 53 (25), and 51 (17).

1-Fluoro-1-bromo-2,2-dimethylcyclopropane (8). ^{19}F NMR ϕ^* 137.0 ppm, $J_{F,H\text{-cis}}$ = 19 Hz. Mass spectrum *m/e* (rel intensity) 168 (P + 2) (1), 166 (P) (1), 153 (38), 151 (40), 87 (100), 86 (20), 85 (14), 71 (16), 67 (11), 59 (38), 51 (16), 41 (46), and 39 (26). These data agree well with the previously published values.[15]

1-Fluoro-1-bromo-*trans*-2,3-dimethylcyclopropane (9). ^{19}F NMR ϕ^* 141.9 ppm, $J_{F,H\text{-cis}}$ = 21 Hz (reported 142.2 ppm, *J* = 21 Hz[16]). Mass spectrum *m/e* (rel intensity) 168 (P + 2) (2), 166 (P) (2), 153 (10), 151 (10), 88 (10), 87 (100), 86 (11), 85 (18), 72 (11), 71 (21), 67 (20), 65 (11), 59 (69), and 57 (28).

1-Fluoro-1-bromo-*cis*-2,3-dimethylcyclopropane (10). The *Z* and *E* isomers could not be effectively separated by GLC. ^{19}F NMR (*Z*)-**10** ϕ^* 121.0 ppm, $J_{F,H\text{-cis}}$ = 22 Hz (reported 121.2 ppm, *J* = 20 Hz[16]), (*E*)-**10** ϕ^* 162.0 ppm (reported 161.9 ppm[16]). Mass spectrum *m/e* (rel intensity) 168 (P + 2) (3), 166 (P) (3), 153 (10), 151 (10), 87 (100), 85 (12), 72 (68), 71 (73), 67 (25), 65 (10), 59 (59), 57 (30), 56 (13), and 51 (11).

7-Fluoro-7-bromonorcarane (11). The two isomers could not be separated by GLC. ^{19}F NMR (*Z*)-**11** ϕ^* 118.0 ppm, $J_{F,H\text{-cis}}$ = 20 Hz (reported 117.6 ppm, *J* = 21 Hz[14]), (*E*)-**11** ϕ^* 155.2 ppm (reported 152.6 ppm[14]). Mass spectrum *m/e* (rel intensity(96 (P − Br) (8), 86 (7), 85 (39), 84 (9), 71 (30), 70 (15), 57 (38), 56 (21), 55 (13), 43 (100), 42 (15), 41 (38), and 39 (11).

1-Fluoro-1-bromo-2-*n*-butylcyclopropane (12). Owing to the small quantities produced, **12,** was not isolated, but only observed in solution. ^{19}F NMR (*Z*)-**12** ϕ^* 126.5 ppm, (*E*)-**12** ϕ^* 149.4 ppm.

Competition Reactions. Reactions to determine the relative reactivities of various olefins toward fluorobromocarbene are carried out according to the following procedure. A 100-ml three-neck flask, equipped with rubber septum, mechanical stirrer, and cold-finger condenser filled with dry ice–2-propanol and connected to an argon reservoir, is oven dried and thoroughly flushed with argon. The flask is charged with 15 ml of dry THF and 2.707 g (10 mmol) of **5** and cooled to −116 °C in an ethanol slush bath. Each of the two olefins (100 mmol) is added to the reaction via syringe or condensation through the cold-finger condenser. With vigorous stirring, 10 mmol of freshly prepared *n*-butyllithium in hexane is slowly added to the reaction via syringe. The reaction mixture is stirred at −116 °C for approximately 0.25 h and then allowed to warm to room temperature. The reaction solution is too dilute for accurate analysis by ^{19}F NMR. Therefore, low-boiling olefins and solvent are removed by vacuum distillation through a 2 × 150 mm vacuum jacketed glass helices column. The temperature during distillation is maintained below 40 °C to minimize any thermal degradation.

The concentrated reaction mixture is analyzed using ^{19}F NMR. The relative yields are calculated by integration of the ^{19}F NMR peaks by cut and weigh. The order of relative reactivity is 2,3-dimethyl-2-butene > 2-methyl-2-butene > isobutylene > *cis*-2-butene > *trans*-2-butene > cyclohexene. While this order is consistent, the reactivity values calculated are not internally consistent and are not reproducible.

Preparation of Fluorocyclopropanes by in Situ Reduction. 1-Fluoro-2,2,3,3-tetramethylcyclopropane (13). In a typical procedure, a 50-ml three-neck flask equipped with septum port, mechanical stirrer, and water-cooled condenser connected to an argon reservoir through a glass "T" is oven dried and thoroughly flushed with argon. The flask is charged with 10 ml of dry THF, 2.707 g (10 mmol) of **5,** and 0.842 g (10 mmol) of 2,3-dimethyl-2-butene, and cooled to −116 °C in an ethanol slush bath. With vigorous stirring, 11 mmol of *n*-butyllithium in hexane is slowly added to the reaction via syringe. After the addition is complete, the reaction mixture is allowed to slowly warm to room temperature.

The reaction mixture is cooled to 0 °C in an ice–water bath, and 11 mmol of lithium aluminum hydride ($LiAlH_4$) in diethyl ether is added to the reaction via syringe after the mechanical stirrer has been replaced by a magnetic stirrer. After the addition is complete, the reaction mixture is allowed to warm to room temperature and is stirred for several hours.

Then 11 mmol of additional $LiAlH_4$ in diethyl ether is added to the reaction mixture via syringe. While the reaction mixture is protected from the atmosphere by a blanket of argon, 2.19 g (11 mmol) of trimethyltin chloride (Alfa) is added to the reaction mixture and the reaction mixture is stirred at room temperature overnight.

The reaction mixture is cooled in an ice–water bath and slowly hydrolyzed with 10 ml of distilled water after which 0.292 g (2 mmol) of benzotrifluoride is added to the reaction solution for an internal ^{19}F NMR standard. The organic layer is separated from the aqueous layer.

Analysis of the reaction solution by ^{19}F NMR indicates that **13** is formed in 21% yield. The product is identified by comparison of GLC and ^{19}F NMR data with an authentic sample synthesized by photolysis of fluorodiiodomethane in the presence of 2,3-dimethyl-2-butene.[9] ^{19}F NMR ϕ^* 224.2 ppm, $J_{F,H\text{-gem}}$ = 62 Hz.

Registry No.—**1,** 1727-63-5; (*Z*)-**2,** 16496-04-1; (*E*)-**2,** 16496-05-2; **3,** 16496-08-5; **5,** 353-54-8; **6,** 34636-25-4; (*Z*)-**7,** 34217-06-6; (*E*)-**7,** 34217-07-7; **8,** 34636-24-3; **9,** 41391-59-7; (*Z*)-**10,** 41391-58-6; (*E*)-**10,** 41391-72-4; (*Z*)-**11,** 19144-90-2; (*E*)-**11,** 19144-91-3; (*Z*)-**12,** 58413-57-3; (*E*)-**12,** 58413-59-5; **13,** 17370-50-2; fluorotrichloromethane, 75-69-4; *n*-butyllithium, 109-72-8; 2,3-dimethyl-2-butene, 563-79-1; 2-methyl-2-butene, 513-35-9; *trans*-2-butene, 624-64-6; cyclohexene, 110-83-8; isobutylene, 115-11-7; *cis*-2-butene, 590-18-1; 1-hexene, 592-41-6.

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