The Enantioselectivity and the Stereochemical Course of Copper-Catalyzed Intramolecular CH Insertions of Phenyliodonium Ylides

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The Cu-catalyzed intramolecular CH insertion of phenyliodonium ylide **1b** was investigated at 0° in the presence of several chiral ligands. Enantioselectivities varied in the range 38–72%, and were higher than those resulting from reaction of the diazo compound **1c** at 65°. The intramolecular insertion of the enantiomerically pure methyl diazoacetate (*R*)-**20** and of the corresponding phenyliodonium ylide (*R*)-**21** proceeded to (*R*)-**23** with retention of configuration with [Cu(hfa)$_2$] (hfa = hexafluoroacetylacetone = 1,1,1,5,5,5-hexafluoropentane-2,4-dione) and [Rh$_2$(OAc)$_4$]. These results are consistent with a carbenoid mechanism for the Cu-catalyzed insertion with phenyliodonium ylides. However, the insertion of the perfluorosulfonated phenyliodonium ylide (*R*)-**29** afforded with [Cu(hfa)$_2$] as well as with [Rh$_2$(OAc)$_4$] the cyclopentanone derivative **30** as a *cis*/*trans* mixture with only 56–67% enantiomeric excess.

Introduction. – The decomposition of diazo compounds in the presence of transition metals leads to reactions typical for metal-carbenoid intermediates, such as cyclopropanations, insertions into X–H bonds, and formation of ylides with heteroatoms having lone pairs available. The Cu-catalyzed asymmetric cyclopropanation is probably the most popular application of the transition-metal-catalyzed carbenoid reactions [1]. In addition, Cu-catalyzed decomposition of diazo compounds may also lead to CH bond insertions, although Rh^{II} catalysts are usually more appropriate for these latter transformations [2]. The Rh^{II}-catalyzed insertion proceeds with retention of configuration at the C-atom undergoing the reaction [3], and all the experimental evidence is consistent with a mechanism involving a rhodium-carbenoid as the reactive intermediate [4]. In contrast, the mechanism of the Cu-catalyzed CH insertion has not been investigated systematically, but is assumed to be analogous to that of the reactions catalyzed by Rh^{II}.

Since diazo compounds are potentially explosive, toxic, and cancerogenic [5], the number of their industrial applications is limited [6]. Phenyliodonium ylides are potential substitutes for diazo compounds in metal-carbenoid reactions. Their photochemical [7][8], thermal [8][9], and transition-metal-catalyzed [10] decompositions exhibit analogies to that of diazo compounds, and, accordingly, carbene or carbenoid intermediates are usually assumed to be involved in these reactions [9–11] although little effort has been made to demonstrate the involvement of these putative species. Some years ago, we presented evidence for metal-carbenoid pathways in Rh^{II}-catalyzed cyclopropanation and CH insertion reactions [11].

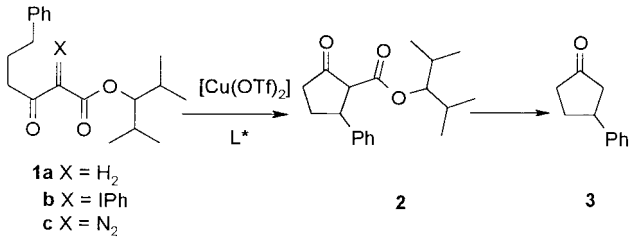
The mechanism of the Cu^{I}-catalyzed decomposition of phenyliodonium ylides is controversial. Originally, *Hayasi et al.* proposed a copper-complexed carbene intermediate in the Cu^{I}-catalyzed decomposition of phenyliodonium ylides derived

from 1,3-diketones [9]. More recently, *Moriarty* reported the CuCl-catalyzed intramolecular cyclopropanation of olefins with phenyliodonium ylides [12]. Surprisingly, the reaction took place even in the absence of catalyst, albeit at lower rate. A mechanism involving electrophilic addition of the iodonium center to the double bond followed by reductive elimination of PhI was proposed for the uncatalyzed transformation. The catalytic effect of Cu^I was tentatively ascribed to electron transfer from the catalyst to the ylide. A carbene or metal-carbenoid mechanism was specifically ruled out.

Recently, we reported the intramolecular cyclopropanation of unsaturated phenyliodonium ylides derived from acetoacetate and malonate esters with $[Cu(OTf)_2]$ (Tf = CF_3SO_2) in the presence of chiral ligands [13]. Enantioselectivities of up to 68% were observed, consistent with a carbenoid mechanism. However, comparison of the enantioselectivities resulting from ylide decomposition with those of the corresponding diazo compounds revealed irregularities, suggesting a competing unselective cyclopropanation mechanism of unknown nature. Since the cycloaddition mechanism of *Moriarty* cannot apply to CH insertions, and since no spontaneous, uncatalyzed CH insertions of phenyliodonium ylides have ever been reported, we have now examined the enantioselectivity and the stereochemistry of intramolecular insertions upon the Cu^I-catalyzed decomposition of phenyliodonium ylides in comparison to that of the corresponding diazo compounds. Some of the results have been reported in preliminary form [14].

Results and Discussion. – *Enantioselective CH Insertion of Phenyliodonium Ylide* **1b** *and Diazo Ester* **1c**. The phenyliodonium ylide **1b** was synthesized by reaction of the hydrocarbon **1a** [15] with $PhI(OAc)_2$ [16] as described previously [11a] (*Scheme 1*). Exposure of **1b** to $[Cu(OTf)_2]$ in CH_2Cl_2 at 0° in the presence of chiral ligands **4**–**11** and **13**–**16** or catalyst **12** (*Fig.*) resulted in intramolecular CH insertion and afforded the cyclopentanone carboxylate **2**. The keto ester **2** was subjected to hydrolysis and decarboxylation (HBr/EtOH) to furnish the ketone **3** on which enantiomeric excess (ee) and the absolute configuration were determined. The diazo compound **1c** corresponding to **1b** was obtained *via* diazo transfer from **1a** with TsN_3. Owing to the low reactivity of the Cu^I catalysts towards diazo compounds, the diazo decomposition had to be carried out in 1,2-dichloroethane at 65°. Unfortunately, the ylide **1b** decomposed at this temperature, and it was impossible to effect the reactions of **1b** and **1c** under identical conditions. The results are summarized in *Table 1*.

Scheme 1



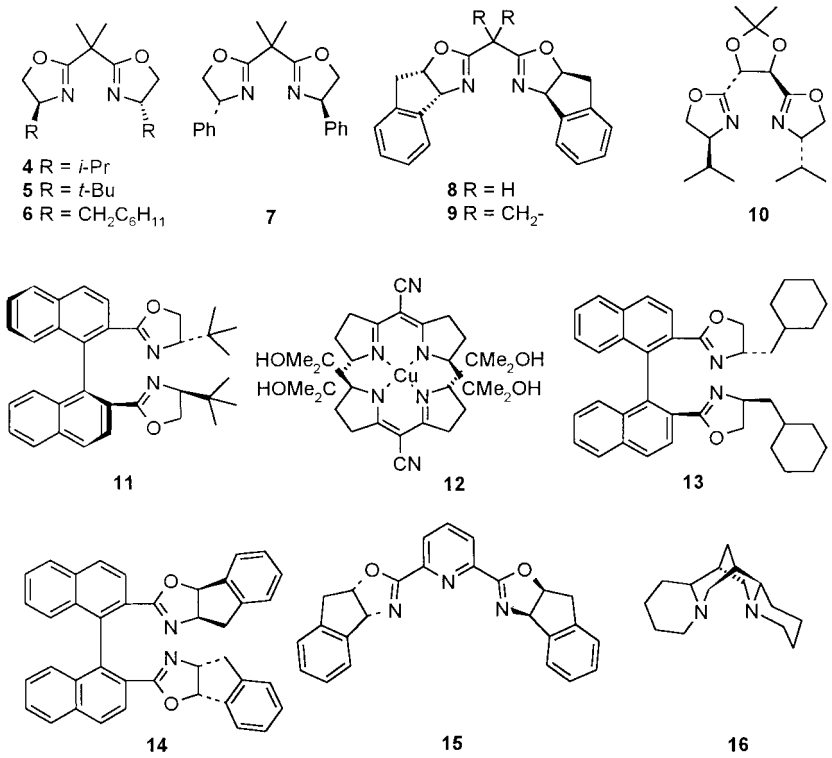


Figure. *Catalyst and Ligands*

Table 1. *Yields and Enantioselectivities* (ee) *in Intramolecular CH Insertions of Phenyliodonium Ylide* **1b** *and Diazo Keto Ester* **1c** *in the Presence of Chiral Ligands* L *and [Cu(OTf)$_2$]*

Run	L	Yield [%] from **1b**[a])	ee [%]	Yield [%] from **1c**[b])	ee [%]	Comment
1	**4**	51	42 (*R*)	38	15 (*R*)	[14]
2	**5**	56	23 (*R*)	–	–	
3	**6**	49	38 (*R*)	32	18 (*R*)	
4	**7**	47	13 (*R*)	–	–	
5	**8**	52	72 (*S*)	14	31 (*S*)	[14]
6	**9**	46	17 (*S*)	55	22	
7	**10**	41	05 (*R*)	–	–	
8	**11**	55	22 (*R*)	–	–	
9	**12**[c])	35	10 (*S*)	–	–	
10	**13**	46	59 (*R*)	35	60 (*R*)	
11	**14**[d])	47	67 (*S*)	17	51 (*S*)	[14]
12	**14**[e])	49	70 (*S*)	–	–	
13	**15**	42	16 (*R*)	–	–	
14	**16**	11	57 (*S*)	32	18 (*S*)	

[a]) In CH_2Cl_2, 0°. [b]) In $ClCH_2CH_2Cl$, 65°. [c]) Reaction with isolated complex **12**. [d]) de of **14** 70%. [e]) de of **14** > 98%.

In general, we find that the Cu-catalyzed insertions proceed with acceptable yields from the ylide. The occurrence of CH insertions upon catalysis with Cu is remarkable in itself, since Cu^{I} complexes are traditionally regarded as the catalysts of choice for cyclopropanations, while CH insertions are better carried out with Rh^{II} catalysts. However, since **1b** and **1c** have no competitive cyclopropanation pathway available, the normally disfavored insertion pathway predominates with Cu^{I} catalysts. Other Cu-catalyzed intramolecular CH insertions of diazo compounds have been reported [17]. The observation that the yields of insertion product **2** resulting from the reaction of the ylide **1b** are generally higher than those of the diazo decomposition is probably a consequence of the notorious low reactivity of diazo esters and diazo ketones derived from β-dicarbonyl compounds, which require temperatures of up to 80° with [Cu^{I}(carboxamidato)] and also with [Rh^{II}(carboxamidato)] catalysts [18]. Phenyliodonium ylides react with these catalysts already at 0°, and their enhanced reactivity constitutes the main aspect of their synthetic interest.

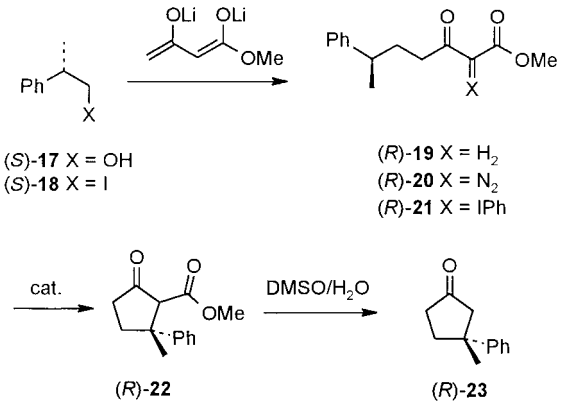
In all cases, the absolute configuration of the major enantiomer of the insertion product **3** obtained from the ylide **1b** is identical with that obtained from the diazo precursor **1c** for a given ligand. Inspection of *Table 1* shows that the enantioselectivity resulting from ylide decomposition (at 0°) is always higher than that from the corresponding diazo decomposition (at 65°), except for **13**, where it is practically equal. It culminates at 72% ee with ligand **8**. The higher selectivity of the ylide **1b** corresponds to expectation on the grounds of the lower temperature of the reactions. In addition, catalyst stability may become a problem in the diazo decomposition. The low ee's observed in some of these reactions may be due to partial degradation of the catalyst at the temperature required for the reaction to occur. Thus, the intriguing irregularities in the enantioselectivities of Cu-catalyzed cyclopropanations of phenyliodonium ylides and diazo compounds do not occur in the CH insertion reactions.

To the best of our knowledge, these are the first enantioselective CH insertions ever observed upon Cu-catalyzed decomposition of phenyliodonium ylides. The results show clearly that the reactions proceed in the intimate vicinity of the chiral catalyst, and that the mechanism proposed by *Moriarty* for intramolecular cyclopropanation of phenyliodonium ylides does not apply to the CH insertions. The less than 100% ee observed for insertion of **1b** under optimized conditions may reasonably be ascribed to an inappropriate choice of catalysts, rather than to a competing reaction of a free carbene. Although thermolysis of phenyliodonium ylides may result in formation of free carbenes capable of CH insertion, this reaction does not occur at 0°, but requires a temperature of 100° [7].

*Stereochemistry of the Cu-Catalyzed CH Insertion of Phenyliodonium Ylide (*R*)-***21***.* The observation of enantioselective CH insertions upon decomposition of phenyliodonium ylide **1b** in the presence of chiral nonracemic Cu^{I} catalysts is consistent with a mechanism involving a metal-carbenoid as intermediate, but constitutes no proof. The carbenoid mechanism for insertion requires retention of configuration at the C-atom undergoing insertion, and this has been observed in the [$Rh_2(OAc)_4$]-catalyzed diazo decomposition of α-diazo-β-keto esters and α-diazo-β-keto sulfones [3]. We have now investigated the stereochemistry of the Cu^{I}-catalyzed intramolecular CH insertion at the chiral center of the enantiomerically pure diazo ester (*R*)-**20** and the ylide (*R*)-**21**. The required precursors were synthesized starting with commercially available (−)-

(*S*)-phenylpropan-1-ol ((*S*)-**17**), which was converted to the iodide (*S*)-**18** by reaction with I_2 and triphenylphosphine (*Scheme 2*). Condensation with the dianion prepared from methyl acetoacetate with lithium diisopropylamide (LDA) in THF and hexamethylphosphoric triamide (HMPA) as cosolvent gave the substituted keto ester (*R*)-**19** in 62% yield, and diazo transfer with TsN_3/Et_3N in MeCN yielded the diazo precursor (*R*)-**20** (87%). The ylide (*R*)-**21**, in turn was isolated as an unstable oil in 75–90% yield upon reaction of (*R*)-**19** with $PhI(OAc)_2$ in MeOH.

Scheme 2



As expected, the diazo precursor (*R*)-**20** reacted smoothly with $[Rh_2(OAc)_4]$ at 23° to afford the cyclic keto ester (*R*)-**22** in 59% yield (*Table 2*). The steric course of the reaction was determined with the ketone (*R*)-**23**, which was obtained after hydrolysis ($DMSO/H_2O$) and decarboxylation of (*R*)-**22**. The absolute configuration of (*R*)-**23** was determined by comparison of the optical rotation with that reported in [19]. The enantiomeric excess as determined by GC was >98%. This corresponds to an overall retention of configuration for the CH insertion. The ylide (*R*)-**21** reacted with $[Rh_2(OAc)_4]$ at 0° to afford (*R*)-**22** and, subsequently, (*R*)-**23** with the same enantioselectivity. The diazo decomposition of (*R*)-**20** with Cu^I catalysts proceeded only sluggishly even at elevated temperatures. Optimized conditions (2 mol-% of $[Cu(hfa)_2$ (Hhfa = hexafluoroacetylacetone = 1,1,1,5,5,5-hexafluoropentane-2,4-dione)] in 1,2-dichloroethane at 60°, 3 h) resulted in a 54% yield of (*R*)-**22** with retention of configuration. The ylide (*R*)-**21**, in turn, reacted at 0° and furnished (*R*)-**22** with full retention of configuration, albeit with only 36% yield.

Table 2. *Decomposition of Diazo Ester* (R)-**20** *and Ylide* (R)-**21**

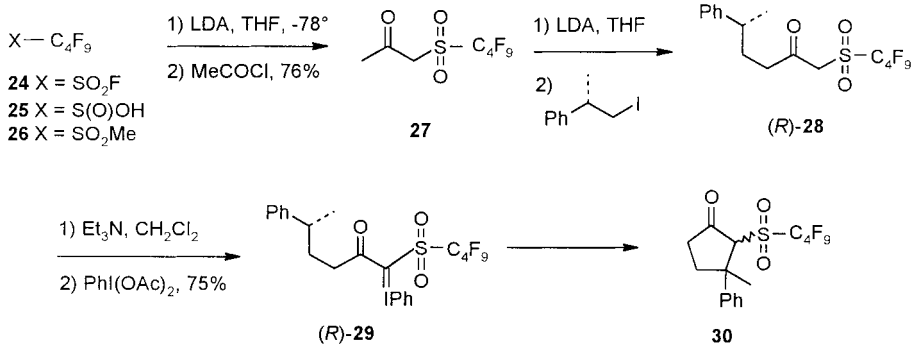
	Catalyst[a])	Solvent, *T* [°]	Time	Yield of (*R*)-**22** [%]	$[\alpha]_D^{20}$[b])	ee [%][c])
(*R*)-**20**	$[Rh_2(OAc)_4]$	CH_2Cl_2, 23	30 min	59	10.2	>98
(*R*)-**20**	$[Cu(hfa)_2]$	$(CH_2Cl)_2$, 60	3 h	54	10.1	>98
(*R*)-**21**	$[Rh_2(OAc)_4]$	CH_2Cl_2, 0	3 h	57	10.0	>98
(*R*)-**21**	$[Cu(hfa)_2]$	CH_2Cl_2, O	3 h	36	10.1	>98

[a]) 2 mol-% with respect to substrate; Hfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dione. [b]) In EtOH, *c* = 1.00–1.20. [c]) by GC.

The observation of retention of configuration in all these reactions provides strong evidence for a carbenoid intermediate, while the observation of enantioselectivity in the insertions pleads in favor of a metal-associated carbene (metal-carbenoid). While metal-carbenoid intermediates have for a long time been assumed in the Cu^I-catalyzed diazo decompositions, retention of configuration has been experimentally observed only once [20]. That the Cu^I-catalyzed ylide decomposition proceeds also with retention of configuration suggests that the same intermediate should be involved in both reactions. The cyclopropanations with ylides follow in principle the same carbenoid pathway; however, an uncatalyzed cyclopropanation may intervene *via* an as yet unknown mechanism, and result in decreased enantioselectivity in comparison to that observed in the corresponding diazo decompositions.

*Stereochemistry of the Intramolecular CH Insertion of (5*R*)-Phenyliodonium 1-[(Nonafluorobutyl)sulfonyl]-2-oxo-5-phenylhexylide.* In view of the low stability of the ylide (*R*)-**21** and the low yield in its Cu^I-catalyzed intramolecular CH insertion, we turned our attention to (perfluoroalkyl)sulfonyl-stabilized phenyliodonium ylides which, according to the literature, are more stable, but may also be decomposed by [Cu(acac)$_2$] (Hacac = pentane-2,4-dione) to afford products derived from carbenoid reactions [21][22]. The required ylide (*R*)-**29** was synthesized as shown in *Scheme 3:* Commercially available nonafluorobutanesulfonyl fluoride (**24**) was reduced with hydrazine [23] to the sulfinic acid **25**, which was alkylated with MeI to afford the sulfone **26**. The sulfone was deprotonated (LDA) and acylated with AcCl to yield the sulfonyl ketone **27**. Double deprotonation of **27** afforded the dianion which was alkylated *in situ* with the iodide (*S*)-**18** to give (*R*)-**28** in 53% yield. While diazo transfer to (*R*)-**28** attempted under a variety of conditions failed, the phenyliodonium ylide (*R*)-**29** was formed smoothly upon treatment of (*R*)-**28** with Et_3N/PhI(OAc)$_2$. The ylide (*R*)-**29** proved to be remarkably stable and survived purification by flash chromatography. Decomposition with [Rh$_2$(OAc)$_4$] at 23° furnished the cyclopentanone **30** in 47% yield as a mixture of stereoisomers having 67 and 68% ee, respectively. The isomers were separable by chromatography, but interconverted slowly upon standing in solution. The relative configuration was assigned by NMR: The *cis*-isomer showed a NOE between the quaternary Me group and the proton at C(2). Decomposition of (*R*)-**29** with [Cu(hfa)$_2$], in turn, afforded **30** in 56% yield (*trans*/*cis* ratio 81:19) with

Scheme 3



enantioselectivities of 67 (*trans*-isomer) and 56% (*cis*-isomer), respectively. Surprisingly, the desulfonation of **30** under a large variety of conditions failed, and the absolute configuration could not be determined.

The possibility that the partial racemization of **30** could be due to a ring-opening and ring-closing process after carbenoid insertion was ruled out by redetermination of its enantiomer composition, which remained unchanged even after several weeks. The partial loss of stereochemical integrity on the way from (*R*)-**29** to **30** must, therefore, be attributed to the insertion process itself. Since partial racemization occurs also with Rh^{II} catalysts, the phenomenon should not be ascribed to an effect due to the involvement of the Cu-atom. Furthermore, the presence of the sulfonyl substituent alone should not be responsible for partial racemization, since Rh^{II}-catalyzed insertion of a diazo keto sulfone reportedly proceeds with full retention of configuration [24]. On the other hand, unexpected reactions of (perfluorobutyl)sulfonyl-substituted phenyliodonium ylides involving carbenium ions have been reported: thus, decomposition of the phenyliodonium ylide derived from ethyl [(nonafluorobutyl)sulvonyl]acetate in the presence of $[Cu(OTf)_2]$ and olefins affords lactones, arising from intermediate carbenium ions, rather than the expected cyclopropanes [22]. A few examples of Rh^{II}-catalyzed diazo decompositions proceeding *via* hydride transfer to stabilized carbenium ions have been observed [25], and an alternative mechanism for CH insertion, involving an intermediate zwitterion, subsequent to hydride transfer has been proposed [26]. Conceivably, the presence of the strongly electron-attracting (perfluorobutyl)sulfonyl group could enforce such a mechanism in the case of (*R*)-**29**. However, a radical mechanism cannot be ruled out on the grounds of the present results. At this time, and until contrary evidence becomes available, we believe that the retention mechanism as observed for the Rh^{II}- and Cu^{I}-catalyzed decomposition of (*R*)-**20** and (*R*)-**21** is representative, and the partial racemization occurring in the case of (*R*)-**29** should be considered exceptional.

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Experimental Part

1. *General*. See [27]. TsN_3 was prepared according to the procedure of *McElwee-White* and *Dougherty* [28]. The 2-methyl-1-(1-methylethyl)propyl 3-oxobutanoate was synthesized as described previously [29]. Nonafluoro-4-(methylsulfonyl)butane (**26**) was prepared *via* hydrazine reduction of nonafluorobutanesulfonyl fluoride (*Aldrich*) and alkylation of the resulting sulfinic acid with methyl iodide, as described by *Harzdorf et al.* [23].

2. *Ligands and Catalysts.* The ligands and catalysts were either purchased (sparteine (**16**)) or prepared according to literature procedures: **4**, **5**, and **7**, [30]; **6**, [14]; **8**, [31]; **9**, [32]; **11**, [33]; **12**, [34]; **13** and **14**, [13b]; **15**, [35]; ligand **10** was kindly provided by *P. G. Andersson* [36].

3. *Intramolecular CH Insertion of Phenyliodonium Ylide* **1b** *and Diazo Acetoacetate* **1c**. *2-Methyl-1-(1-methylethyl)propyl 3-Oxo-6-phenylhexanoate* (**1a**) [11a]. To diisopropylamine (8.47 ml, 59.9 mmol) in THF (40 ml) at $-78°$, 1.6M BuLi in hexane (34.3 ml, 54.9 mmol) was added, and the mixture was stirred for 15 min. Then 2-methyl-1-(1-methylethyl)propyl 3-oxobutanoate (5.00 g, 25.0 mmol) in THF (10 ml) was added at $-78°$. After stirring for 30 min, (2-bromoethyl)benzene (13.9 g, 74.9 mmol) in THF (10 ml) was added at once, and stirring was maintained at $-78°$ for 10 min. The mixture was decomposed with 2N HCl (30 ml) with cooling at $0°$. The aq. phase was extracted with CH_2Cl_2 (3×50 ml), the combined org. phase dried ($MgSO_4$), and

evaporated, and the residue distilled to remove the remaining (2-bromoethyl)benzene and then purified by FC (pentane/AcOEt 97:3): **1a** (7.22 g, 95%). Colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.86 (*d*, *J* = 6.9, 6 H); 0.90 (*d*, *J* = 6.9, 6 H); 1.84–1.99 (*m*, 4 H); 2.58 (*t*, *J* = 7.3, 2 H); 2.65 (*t*, *J* = 7.3, 2 H); 3.45 (*s*, 2 H); 4.63 (*dd*, *J* = 6.0, 6.3, 1 H); 7.16–7.32 (*m*, 3 H); 7.26–7.32 (*m*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 17.2 (*q*); 19.5 (*q*); 24.8 (*t*); 29.3 (*d*); 34.8 (*t*); 42.3 (*t*); 49.3 (*t*); 84.1 (*d*); 126.0 (*d*); 128.3 (*d*); 128.4 (*d*); 141.3 (*s*); 172.9 (*s*); 178.3 (*s*); 202.6 (*s*). MS: 189 (18), 188 (34), 148 (9), 147 (78), 128 (12), 105 (13), 104 (100), 102 (19), 99 (14), 98 (16), 91 (40), 84 (16), 83 (10), 73 (12), 57 (94), 55 (12).

Phenyliodonium 1-[2-Methyl-1-(1-methylethyl)propoxy]-1,3-dioxo-6-phenylhexylide (**1b**) [11a]. To KOH (257 mg, 3.94 mmol) in MeOH (5.0 ml) at 0°, **1a** (300 mg, 0.98 mmol) in MeOH (10 ml) was added slowly. $PhI(OAc)_2$ (317 mg, 0.98 mmol) was added in portions. After stirring for 5 min, the mixture was poured on ice/H_2O (10 ml). Extraction with CH_2Cl_2 (2 × 10 ml), drying ($MgSO_4$), and evaporation afforded **1b** (496 mg, 80%). Thick yellow oil. ^{1}H-NMR (200 MHz, $CDCl_3$): 0.80 (*d*, *J* = 6.9, 6 H); 0.85 (*d*, *J* = 6.9, 6 H); 1.80–2.04 (*m*, 4 H); 2.68 (*t*, *J* = 7.3, 2 H); 2.92 (*t*, *J* = 7.3, 2 H); 4.73 (*dd*, *J* = 6.0, 6.4, 1 H); 7.17–7.52 (*m*, 5 H); 7.39–7.77 (*m*, 5 H).

2-Methyl-1-(1-methylethyl) 2-Diazo-3-oxo-6-phenylhexanoate (**1c**) [11a]. The soln. of **1a** (3.00 g, 9.85 mmol) in MeCN (10 ml) was added to TsN_3 (1.94 g, 9.85 mmol) and Et_3N (2.75 ml, 19.7 mmol) at r.t. The mixture was stirred overnight. It was poured into aq. NaOH soln. (10 ml), the aq. layer extracted with Et_2O (3 × 20 ml), and the combined org. phase dried (Na_2SO_4) and evaporated. FC (pentane/AcOEt 99:1) of the residue yielded **1c** (3.26 g, 89%). Yellow oil. IR (NaCl): 3025*w*, 2967*m*, 2135*s*, 1709*s*, 1645*m*, 1372*m*, 1121*m*, 985*w*. ^{1}H-NMR (500 MHz, $CDCl_3$): 0.89 (*d*, *J* = 6.7, 6 H); 0.93 (*d*, *J* = 6.9, 6 H); 1.92–2.04 (*m*, 4 H); 2.68 (*t*, *J* = 7.3, 2 H); 2.90 (*t*, *J* = 7.3, 2 H); 4.71 (*dd*, *J* = 6.0, 6.3, 1 H); 7.17–7.22 (*m*, 3 H); 7.26–7.31 (*m*, 2 H). ^{13}C-NMR (125 MHz, $CDCl_3$): 17.2 (*q*); 19.5 (*q*); 25.9 (*t*); 29.4 (*d*); 35.2 (*t*); 39.7 (*t*); 84.3 (*d*); 125.9 (*d*); 128.3 (*d*); 128.4 (*d*); 141.7 (*s*); 161.6 (*s*); 192.8 (*s*). MS: 226 (15), 204 (38), 187 (49), 186 (47), 159 (13), 158 (17), 147 (35), 128 (29), 117 (12), 104 (19), 99 (18), 98 (15), 91 (74), 83 (42), 65 (11), 58 (10), 57 (100), 55 (16).

3-Phenylcyclopentanone (**3**) via *Decomposition of* **1b**. A soln. of (*p*)-2,2′-([1,1′-binaphthalene]-2,2′-diyl)bis[(4*S*)-4-(cyclohexylmethyl)-4,5-dihydrooxazole] (**13**; 7.4 mg, 11 μmol) and $[Cu(OTf)_2]$ (3.9 mg, 11 μmol) in CH_2Cl_2 (6.0 ml), was stirred for 1 h at r.t. The ylide **1b** (0.54 mmol) in CH_2Cl_2 (6.0 ml) was added at 0°, and the mixture was stirred overnight at 0°. The solvent was evaporated and the residue purified by FC (pentane/AcOEt 97:3) to give crude keto ester **2** (77 mg, 47%) as colorless oil. The crude **2** (77 mg) was refluxed in a mixture of HBr (2.5 ml) and EtOH (8.0 ml). After cooling, the mixture was extracted with CH_2Cl_2 (3 × 10 ml), the org. phase washed with H_2O (2 × 10 ml), dried ($MgSO_4$), and evaporated, and the residue purified by FC (pentane/AcOEt 90:10): **3** [11a] (26 mg, 64%) of 67% ee. Colorless oil. GC (*Lipodex B* (*Macherey-Nagel*), 130°): t_R 12.1 ((*S*)-**3**) and 13.7 ((*R*)-**3**). $[\alpha]_D^{20} = +69.1$ (*c* = 1.04, $CHCl_3$) for 67% ee ([15a]: $[\alpha]_D^{22} = +69.4$ (*c* = 1.42, $CHCl_3$) for (*R*)-**3** with 76% ee). ^{1}H-NMR (200 MHz, $CDCl_3$): 1.87–2.11 (*m*, 1 H); 2.18–2.55 (*m*, 4 H); 2.66 (*dd*, *J* = 18.8, 15.5, 1 H); 3.30–3.52 (*m*, 1 H); 7.18–7.42 (*m*, 5 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 31.0 (*t*); 38.6 (*t*); 42.0 (*d*); 45.6 (*t*); 126.6 (*d*); 128.5 (*d*); 143.0 (*s*); 217.7 (*s*).

3-Phenylcyclopentanone (**3**) via *Diazo Decomposition of* **1c**. Ligand **13** (4.2 mg, 7.2 μmol) and $[Cu(OTf)_2]$ (2.2 mg, 6.0 μmol) in $ClCH_2CH_2Cl$ (3.0 ml) was stirred at r.t. for 1 h, then heated to 65°. The diazo ester **1c** (100 mg, 0.30 mmol) in $ClCH_2CH_2Cl$ (3.0 ml) was added at once, and the mixture was stirred at 65° for 1 d. After evaporation, the crude keto ester **2** (32 mg, 35%) was obtained, which was converted to **3** as described above in 70% yield and with 60% ee. $[\alpha]_D^{20} = +65.4$ (*c* = 1.06) for 60% ee.

4. *Intramolecular CH Insertion with (*R*)-***20*** and (*R*)-***21***. (*S*)-(2-Iodo-1-methylethyl)benzene* ((*S*)-**18**). To Ph_3P (30.8 g, 117 mmol) and 1*H*-imidazole (8.00 g, 117 mmol) in Et_2O (100 ml) and MeCN (40 ml), I_2 (22.4 g, 88.1 mmol) was added in portions at r.t. The resulting suspension was stirred for 1 h, and (−)-(*S*)-2-phenylpropanol ((*S*)-**17**; 4.00 g, 29.4 mmol) in Et_2O (40 ml) was added dropwise. The mixture was stirred for 3 h, after which it was diluted with petroleum ether (500 ml). The soln. was filtered, the filtrate evaporated, and the residue purified by distillation (103–105°/4 Torr): (*S*)-**18** (6.12 g, 85%). Colorless oil. $[\alpha]_D^{20} = -31.8$ (*c* = 1.67, $CHCl_3$). IR (NaCl): 3026*m*, 2964*s*, 2866*m*, 1494*m*, 1451*m*, 1376*m*, 1179*s*, 759*s*, 698*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.44 (*d*, *J* = 6.9, 3 H); 3.01–3.11 (*m*, 1 H); 3.34 (*dd*, *J* = 7.9, 9.3, 1 H); 3.42 (*dd*, *J* = 6.4, 9.4, 1 H); 7.19–7.38 (*m*, 5 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 14.7 (*t*); 21.6 (*q*); 42.4 (*d*); 126.7 (*d*); 126.9 (*d*); 128.6 (*d*); 144.4 (*s*). MS: 246 (3, $M^{+\bullet}$), 120 (9), 119 (88), 105 (26), 104 (13), 103 (9), 92 (8), 91 (100), 79 (8), 78 (7), 77 (11), 51 (10). HR-MS: 245.9894 ($C_9H_{11}I^+$; calc. 245.9905).

*(*R*)-Methyl 3-Oxo-6-phenylheptanoate* ((*R*)-**19**). A soln. of 1.6M BuLi in hexane (29.0 ml, 46.5 mmol, 4 equiv.) was added to diisopropylamine (6.90 ml, 48.8 mmol, 4.2 equiv.) in THF (50 ml) at 0°. After 20 min, the mixture was cooled to −25°, and methyl 3-oxobutanoate (2.50 ml, 23.2 mmol, 2 equiv.) was added. The temp. was raised to 0°, the mixture was stirred for 30 min, and HMPA (8.13 ml, 46.5 mmol, 4 equiv.) was added. After

5 min, the soln. was added to (*S*)-**18** (2.86 mg, 11.6 mmol) in THF (10 ml) at 0°. After stirring at r.t. for 1 h, the mixture was neutralized with sat. NH_4Cl soln. The aq. layer was extracted with AcOEt (3 × 100 ml) and the combined org. layer dried ($MgSO_4$) and evaporated to give (*R*)-**19** (2.05 g, 54%) after FC (petroleum ether/AcOEt 95:5). $[\alpha]_D^{20} = -18.3$ (*c* = 1.00, $CHCl_3$). IR (NaCl): 3026*m*, 2956*s*, 2872*m*, 1748*s*, 1716*s*, 1452*m*, 1436*m*, 1319*m*, 1192*m*, 764*m*, 702*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.28 (*d*, *J* = 6.8, 3 H); 1.81–2.01 (*m*, 2 H); 2.33–2.51 (*m*, 2 H); 2.66–2.77 (*m*, 1 H); 3.37 (*s*, 2 H); 3.72 (*s*, 3 H); 7.16–7.25 (*m*, 3 H); 7.27–7.35 (*m*, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 22.2 (*q*); 31.4 (*t*); 39.1 (*d*); 41.1 (*t*); 48.9 (*t*); 52.2 (*q*); 126.1 (*d*); 126.9 (*d*); 128.4 (*d*); 146.1 (*s*); 167.5 (*s*); 202.5 (*s*). MS: 234 (1, $M^{+\bullet}$), 216 (11), 161 (16), 142 (15), 119 (25), 118 (100), 117 (19), 116 (29), 106 (7), 105 (71), 104 (6), 103 (11), 101 (8), 91 (22), 84 (11), 79 (12), 78 (9), 77 (15), 69 (7), 59 (16), 55 (8), 51 (6). HR-MS: 234.1274 ($C_{14}H_{18}O_3^+$; calc. 234.1256).

*(*R*)-Methyl 2-Diazo-3-oxo-6-phenylheptanoate* ((*R*)-**20**). The soln. of (*R*)-**19** (300 mg, 1.28 mmol) in MeCN (10 ml) was added to TsN_3 (954 mg, 4.83 mmol) and Et_3N (37 µl, 0.26 mmol) in MeCN, and the mixture was stirred overnight. It was then poured into 10% NaOH soln. (10 ml). The aq. phase was extracted with Et_2O (3 × 20 ml), the combined org. layer dried (Na_2SO_4) and evaporated, and the residue purified by FC (petroleum ether/AcOEt 97:3): (*R*)-**20** (292 mg, 88%). Yellow oil. $[\alpha]_D^{20} = -21.6$ (*c* = 1.52, $CHCl_3$). IR (NaCl): 3027*m*, 2958*s*, 2930*m*, 2135*s*, 1723*s*, 1657*s*, 1494*m*, 1436*s*, 1378*s*, 1310*s*, 1216*m*, 701*s*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.28 (*d*, *J* = 6.9, 3 H); 1.89–1.97 (*m*, 2 H); 2.65–2.86 (*m*, 3 H); 3.80 (*s*, 3 H); 7.17–7.23 (*m*, 3 H); 7.26–7.33 (*m*, 2 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 22.1 (*q*); 32.6 (*t*); 38.4 (*t*); 39.4 (*d*); 52.1 (*q*); 126.1 (*d*); 127.0 (*d*); 128.4 (*d*); 146.5 (*s*); 161.7 (*s*); 192.6 (*s*). MS: 232 (4, $[M - N_2]^+$), 217 (23), 185 (69), 155 (10), 142 (38), 129 (13), 123 (12), 118 (31), 117 (21), 115 (10), 113 (10), 106 (11), 105 (100), 104 (11), 103 (18), 101 (17), 99 (15), 91 (50), 79 (18), 77 (28), 69 (10), 59 (21), 55 (22). HR-MS: 232.1105 ($C_{14}H_{16}O_3^+$; calc. 232.1099).

*(*R*)-Phenyliodonium 1-Methoxy-1,3-dioxo-6-phenylheptylide* ((*R*)-**21**). To KOH (112 mg, 1.71 mmol) in MeOH (1.5 ml) at −20°, (*R*)-**19** (100 mg, 0.43 mmol) in MeOH (1.0 ml) and $PhI(OAc)_2$ (137 mg, 0.43 mmol) in MeOH (1.5 ml) were slowly added. The mixture was stirred for 10 min at 0° and then poured into H_2O, and the aq. phase was extracted with CH_2Cl_2 (3 × 10 ml). The combined org. phase was dried ($MgSO_4$) and evaporated: 187 mg (76%) of (*R*)-**21**. Yellow oil. ^{1}H-NMR (200 MHz, $CDCl_3$): 1.27 (*d*, *J* = 6.9, 1 Me); 1.87–2.01 (*m*, 2 H); 2.65–3.10 (3 H); 3.60 (*s*, 1 Me); 7.07–7.42 (8 H, CH); 7.43–7.80 (2 H, CH).

Intramolecular Insertion of Diazo Ester (*R*)-**20**: *(*R*)-3-Methyl-3-phenylcyclopentanone* ((*R*)-**23**). To $[Cu(hfa)_2]$ (5.0 mg, 0.01 mmol) in $ClCH_2CH_2Cl$ (2.0 ml) at 60°, (*R*)-**20** (130 mg, 0.50 mmol) in $ClCH_2CH_2Cl$ (2.0 ml) was added. The mixture was stirred at 60° for 3 h. After evaporation of the solvent, the residue was purified by FC (petroleum ether/AcOEt 90:10) to give (*R*)-**22** (63 mg, 54%), which was heated to reflux in DMSO (500 µl) and H_2O (4.0 ml) for 1 d. After cooling, the mixture was extracted with CH_2Cl_2 (3 × 7 ml) and the combined org. layer washed with H_2O (2 × 5 ml), dried ($MgSO_4$), and evaporated: (*R*)-**23** (32 mg, 68%) with > 98% ee. Colorless oil. GC (*Supelco Gamma-DEX*, 100°): t_R 147.6 ((*R*)-**23**), 150.8 ((*S*)-**23**). $[\alpha]_D^{20} = +10.1$ (*c* = 1.05, EtOH) ([19]: $[\alpha]_D^{20} = +10$ (*c* = 1.1, EtOH)). IR (NaCl): 2958*m*, 1742*s*, 1496*m*, 1445*m*, 1406*m*, 1159*m*, 767*s*, 701*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.40 (*s*, 3 H); 2.24–2.35 (*m*, 2 H); 2.35–2.49 (*m*, 2 H); 2.49 (*d*, *J* = 17.6, 1 H); 2.67 (*d*, *J* = 17.3, 1 H); 7.22–7.28 (*m*, 1 H); 7.29–7.33 (*m*, 2 H); 7.33–7.38 (*m*, 2 H). ^{13}C-NMR (125 MHz): 29.4 (*q*); 35.8 (*t*); 36.7 (*t*); 43.8 (*s*); 52.2 (*t*); 125.5 (*d*); 126.3 (*d*); 128.6 (*d*); 148.5 (*s*); 218.5 (*s*). MS: 174 (81), 159 (23), 145 (15), 132 (8), 131 (24), 119 (14), 118 (100), 117 (42), 116 (9), 115 (15), 104 (7), 103 (17), 91 (26), 78 (12), 77 (15), 65 (7), 58 (11), 57 (9), 56 (25), 51 (14). HR-MS: 174.1044 ($C_{12}H_{14}O^+$; calc. 174.1045).

Decomposition of (*R*)-**20** with $[Rh_2(OAc)_4]$ in CH_2Cl_2 at r.t., followed by hydrolysis as above afforded (*R*)-**23** in 65% yield and with > 98% ee. $[\alpha]_D^{20} = +10.2$ (*c* = 1.00, EtOH).

*Intramolecular Insertion of Phenyliodonium Ylide (*R*)-**21***. A soln. of $[Cu(hfa)_2]$ (3.0 mg, 60 µmol) in CH_2Cl_2 (2.0 ml) was added, at 0°, to (*R*)-**21** (131 mg, 0.30 mmol) in CH_2Cl_2 (2.0 ml). After 3 h, the solvent was evaporated and the keto ester (*R*)-**22** decarboxylated as described above to afford (*R*)-**23** (13 mg, 64%) with > 98% ee. $[\alpha]_D^{20} = +10.1$ (*c* = 1.20, EtOH).

Under the same conditions, ylide (*R*)-**21** (131 mg, 0.30 mmol) reacted in the presence of $[Rh_2(OAc)_4]$ (2.9 mg, 6.0 µmol) to afford (*R*)-**23** (21 mg, 69%) with > 98% ee. $[\alpha]_D^{20} = +10.0$ (*c* = 1.10, EtOH).

5. *Intramolecular Insertion with [(Nonafluorobutyl)sulfonyl]-Substituted Ylide (*R*)-**29**. 1-[(Nonafluorobutyl)sulfonyl]propan-2-one* (**27**). BuLi (56.2 ml, 1.6M, 90 mmol) in hexane was added, at −78°, to diisopropylamine (13.9 ml, 98.1 mmol) in THF (60 ml). The mixture was warmed to 0° for 30 min and cooled again to −78°. Sulfone **26** (12.2 g, 40.9 mmol) in THF (60 ml) was added slowly, and stirring was continued for 30 min. Freshly distilled acetyl chloride (2.90 ml, 36.7 mmol) was added dropwise at −78°. After 1 h of stirring, the mixture was warmed to r.t. within 1 h. The solvent was evaporated, the residue dissolved in Et_2O (100 ml), and 1M HCl added. The aq. layer was extracted with Et_2O (3 × 150 ml), the combined org. layer washed (H_2O), dried ($MgSO_4$), and evaporated, and the residue distilled (122°/20 Torr): **27** (10.5 g, 76%). Colorless solid. IR

($CHCl_3$): 3013*w*, 1737*m*, 1378*s*, 1241*s*, 1202*m*, 1143*s*, 1115*m*, 784*m*, 742*m*. ^{1}H-NMR (500 MHz, $CDCl_3$): 2.50 (*s*, 3 H); 4.30 (*s*, 2 H). ^{13}C-NMR (125 MHz): 31.5 (*q*); 61.8 (*t*); 191.3 (*s*). ^{19}F-NMR (532 MHz, $CDCl_3$): 37.8–37.9 (*m*, 2 F); 42.6–42.7 (*m*, 2 F); 52.1–52.2 (*m*, 2 F); 83.0–83.1 (*m*, 3 F). ESI-MS (pos.): 338.9 ($[M-H]^+$, $C_7H_4F_9O_3S^+$; calc. 338.9).

*(*R*)-1-[(Nonafluorobutyl)sulfonyl]-5-phenylhexan-2-one* ((*R*)-**28**). A soln. of 1.6M BuLi in hexane (23.9 ml, 38.2 mmol) was added to diisopropylamine (5.67 ml, 40.1 mmol) in THF (40 ml) at 0°. After stirring for 20 min, the mixture was cooled to −25°, and **27** (6.50 g, 19.1 mmol) in THF (20 ml) was added slowly. After 30 min of stirring, HMPA (6.69 ml, 38.2 mmol) was added at 0°. Subsequently the dianion resulting from double deprotonation of **27** was added to the iodide (*S*)-**18** (2.35 g, 9.55 mmol) at 0°, and the mixture was stirred at r.t. for 1 h. After evaporation of the solvent, the residue was dissolved in Et_2O (200 ml), and 1M HCl was added until pH 1 was reached. The aq. phase was extracted with Et_2O, the combined org. phase washed (H_2O), dried ($MgSO_4$), and evaporated, unreacted **27** removed by distillation (122°/20 Torr), and the residue purified by FC (pentane/AcOEt 90:10) followed by recrystallization: (*R*)-**28** (2.90 g, 53%). Colorless solid. $[\alpha]_D^{20} = -7.2$ ($c = 1.11$, $CHCl_3$). IR ($CHCl_3$): 3014*s*, 1730*w*, 1602*w*, 1378*m*, 1241*s*, 1210*s*, 1143*m*, 778*s*, 754*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.30 (*d*, $J = 7.0$, 3 H); 1.86–1.96 (*m*, 1 H); 1.96–2.05 (*m*, 1 H); 2.59 (*ddd*, $J = 8.5, 18.6, 27.1$, 1 H); 2.61 (*ddd*, $J = 8.5, 18.6, 27.1$, 1 H); 2.69–2.78 (*m*, 1 H); 4.13 (*s*, 2 H); 7.17 (*d*, $J = 6.9$, 2 H); 7.23 (*dd*, $J = 7.2, 7.5$, 1 H); 7.32 (*dd*, $J = 7.2, 7.8$, 2 H). ^{13}C-NMR (125 MHz): 22.3 (*q*); 31.3 (*t*); 39.0 (*d*); 42.9 (*t*); 60.8 (*t*); 126.5 (*d*); 127.0 (*d*); 128.7 (*d*); 146.5 (*s*); 193.8 (*s*). ^{19}F-NMR (532 MHz, $CDCl_3$): 37.8–37.9 (*m*, 2 F); 42.5–42.7 (*m*, 2 F); 52.0–52.1 (*m*, 2 F); 83.1 (*t*, $J = 9.7$, 3 F). ESI-MS (pos.): 492.8 ($[M+Cl]^+$, $C_{16}H_{15}F_9O_3S^+$; calc. 493.0). Anal. calc. for $C_{16}H_{15}F_9O_3S$: C 41.93, H 3.30; found: C 41.86, H 3.43.

*(*R*)-Phenyliodonium 1-[(Nonafluorobutyl)sulfonyl]-2-oxo-5-phenylhexylide* ((*R*)-**29**). To (*R*)-**28** (356 mg, 0.78 mmol) in CH_2Cl_2 (7.0 ml) at r.t., Et_3N (61.0 µl, 0.44 mmol) and $PhI(OAc)_2$ (248 mg, 0.78 mmol) were added slowly. After 10 min of stirring, the mixture was evaporated and the crude product purified by FC (pentane/AcOEt 70:30): (*R*)-**29** (385 mg, 75%). Yellow oil. $[\alpha]_D^{20} = -11.1$ ($c = 1.13$, $CHCl_3$). IR ($CHCl_3$): 3014*s*, 1730*w*, 1602*w*, 1378*m*, 1241*s*, 1210*s*, 1143*m*, 778*s*, 754*s*. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.25 (*d*, $J = 7.0$, 3 H); 1.80–2.04 (*m*, 2 H); 2.52–3.03 (*m*, 3 H); 7.16 (*d*, $J = 7.9$, 1 H); 7.17 (*d*, $J = 7.9$, 2 H); 7.23–7.29 (*m*, 2 H); 7.41–7.47 (*m*, 2 H); 7.59–7.64 (*m*, 1 H, CH); 7.95 (*d*, $J = 7.6$). ^{13}C-NMR (125 MHz, $CDCl_3$): 21.9 (*q*); 34.3 (*t*); 34.5 (*t*); 39.5 (*d*); 114.0 (*s*); 125.9 (*d*); 127.0 (*d*); 128.3 (*d*); 131.9 (*d*); 132.6 (*d*); 134.6 (*d*); 146.8 (*s*); 189.5 (*s*). ^{19}F-NMR (532 MHz, $CDCl_3$): 37.8–37.9 (*m*, 2 F); 43.0–43.1 (*m*, 2 F); 50.5–52.8 (*m*, 2 F); 83.0 (*t*, $J = 9.7$, 3 F). Anal. calc. for $C_{22}H_{18}F_9IO_3S$: C 40.02, H 2.96; found: C 40.29, H 2.96.

*Intramolecular Insertion with Ylide (*R*)-***29***: (*R*)-3-Methyl-2-[(nonafluorobutyl)sulfonyl]-3-phenylcyclopentanone* (**30**). To $[Cu(hfa)_2]$ (2.9 mg, 5.8 µmol) in CH_2Cl_2 (7.0 ml) at r.t., ylide (*R*)-**29** (192 mg, 0.29 mmol) in CH_2Cl_2 (7.0 ml) was added. After stirring for 2 h, the mixture was evaporated and the residue purified by FC (petroleum ether/AcOEt 95:5): **30** (74 mg, 56%) in a *trans*/*cis* ratio of 81:19. GC (*trans*-**30** (67% ee); *Supelco Beta-DEX*, 130°): t_R 149.3 and 151.9. GC (*cis*-**30** (56% ee); *Supelco Beta-DEX*, 150°): t_R 119.2 and 121.4. IR (NaCl): 3018*s*, 1732*w*, 1605*w*, 1384*m*, 1240*s*, 1215*s*, 1141*m*, 781*s*, 756*s*. Anal. calc. for $C_{16}H_{13}F_9O_3S$: C 42.11, H 2.87; found: C 41.90, H 3.51.

Data of trans-**30**: Colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.76 (*s*, 3 H); 2.30–2.37 (*m*, 1 H); 2.44–2.52 (*m*, 1 H); 3.08–3.17 (*m*, 1 H); 3.36–3.46 (*m*, 1 H); 5.72 (*s*, 1 H); 7.27–7.31 (2 H); 7.32–7.37 (*m*, 1 H); 7.38–7.42 (*m*, 2 H). ^{13}C-NMR (125 MHz): 28.4 (*q*); 31.0 (*d*); 36.6 (*d*); 90.1 (*t*); 94.4 (*t*); 124.0 (*d*); 128.0 (*d*); 128.8 (*d*); 142.8 (*s*); 182.9 (*s*). ^{19}F-NMR (532 MHz, $CDCl_3$): 37.7–37.8 (*m*, 2 F); 42.4–42.7 (*m*, 2 F); 49.3–49.4 (*m*, 2 F); 83.0 (*t*, $J = 9.7$, 3 F).

Data of cis-**30**: Colorless oil. ^{1}H-NMR (500 MHz, $CDCl_3$): 1.77 (*s*, 3 H); 2.29–2.38 (*m*, 1 H); 2.44–2.51 (*m*, 1 H); 2.81–2.90 (*m*, 1 H); 2.95–3.04 (*m*, 1 H); 5.25 (*s*, 1 H); 7.29–7.34 (*m*, 1 H); 7.35–7.40 (*m*, 4 H). ^{13}C-NMR (125 MHz): 28.7 (*q*); 33.5 (*d*); 35.9 (*d*); 87.6 (*t*); 96.9 (*t*); 124.0 (*d*); 127.9 (*d*); 128.7 (*d*); 142.9 (*s*); 178.3 (*s*). ^{19}F-NMR (532 MHz, $CDCl_3$): 37.6–37.9 (*m*, 2 F); 42.3–42.5 (*m*, 2 F); 49.2–49.6 (*m*, 2 F); 83.0 (*t*, $J = 9.7$, 3 F). MS: 441 (2), 239 (6), 238 (14), 237 (100), 173 (24), 172 (9), 171 (28), 170 (7), 157 (15), 155 (6), 142 (6), 131 (31), 130 (9), 129 (23), 128 (7), 117 (16), 116 (7), 115 (15), 105 (25), 103 (8), 91 (31), 89 (6), 77 (15), 69 (14), 55 (16), 53 (6), 51 (8). HR-MS: 441.0157 ($[C_{16}H_{13}F_9SO_3 - Me]^+$; calc. 441.0207).

The same procedure, starting with (*R*)-**29** (192 mg, 0.29 mmol) and $[Rh_2(OAc)_4]$ (2.8 mg, 5.8 µmol) afforded **30** in 47% yield, ee (*trans*) = 67%, ee (*cis*) = 68%.

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