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Tetrahedron: Asymmetry
Tetrahedron: *Asymmetry* 16 (2005) 2319–2327

Fluorous derivatives of (1*R*,2*R*)-diaminocyclohexane as chiral ligands for metal-catalyzed asymmetric reactions

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Received 17 May 2005; accepted 26 May 2005

Abstract—Perfluoroalkyl-substituted, enantiopure diamines derived from (1*R*,2*R*)-diaminocyclohexane were conveniently prepared from readily available precursors. In situ generated metal complexes of these ligands were tested as chiral catalysts in three standard asymmetric reactions (cyclopropanation of styrene, hydrogen transfer reduction of acetophenone, and allylic alkylation of 1,3-diphenyl-2-propenyl acetate) affording enantioselectivities of up to 47% in the copper-catalyzed cyclopropanation of styrene.

1. Introduction

Enantiomerically pure 1,2-diamines, in particular, those possessing C_2-symmetry, and their derivatives have found wide application as chiral auxiliaries and ligands in asymmetric synthesis.[1,2] Moreover, they are valuable building blocks for generating multicomponent organometallic catalysts, such as ruthenium derivatives of dual ligand systems composed of a chiral diamine and a chiral bisphosphine,[3] dendritic catalysts,[4] or hybrid organic–inorganic materials.[5]

An intense research activity is currently devoted to the synthesis of easily recoverable enantiopure 1,2-diamines. As in the case of other families of chiral ligands and catalysts,[6,7] immobilization onto inorganic supports,[5,8] attachment to soluble or insoluble organic polymers,[9,10] and solubilization in water upon introduction of hydrophilic substituents[11] have been explored. Fluorous techniques have recently been introduced in asymmetric synthesis and are rapidly emerging as a convenient alternative for recovering chiral catalysts.[12] In this context, we had previously reported the synthesis of certain enantiopure C_2-symmetric 1,2-diamines bearing perfluoroalkyl substituents and demonstrated their use as ligands in two metal-catalyzed asymmetric reactions, namely transfer hydrogenation of ketones and the cyclopropanation of styrene.[13–15] Herein, we report practical procedures for the functionalization of (1*R*,2*R*)-diaminocyclohexane with readily available fluorinated reactants to give enantiopure fluorous secondary diamines. Preliminary data concerning their use as ligands in metal-catalyzed reactions are also reported.

2. Results and discussion

Most fluorous chiral diamines employed so far as ligands in asymmetric organometallic catalysis are derivatives of commercially available, enantiomerically pure *trans*-1,2-diaminocyclohexane.[12–14] These have been prepared by the condensation of the chiral diamine with two molar equivalents of an aryl aldehyde bearing perfluoroalkyl substituents, followed by reduction of the imino functionalities (Scheme 1). We thus tried to extend this method towards the use of (*F*-alkyl)alkanals ($R_F(CH_2)_mCHO$, $m = 1$–4)[16] in order to attach perfluorinated alkyl chains R_F to the nitrogen atoms of *trans*-1,2-diaminocyclohexane through methylene spacers of various length. Unfortunately, attempted *N*,*N*′-dialkylation by stepwise or in situ reductive amination with $R_F(CH_2)_mCHO$ resulted in the formation of complex product mixtures, containing massive amounts of unknown fluorous by-products which were hardly

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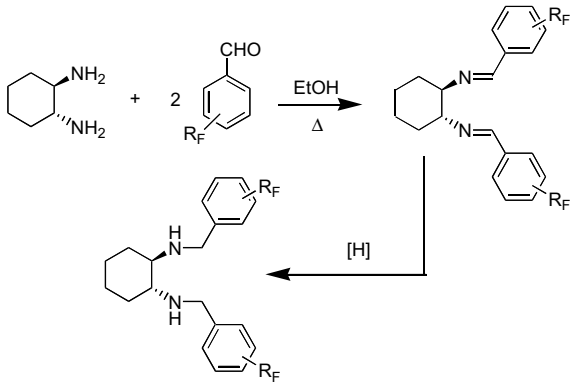
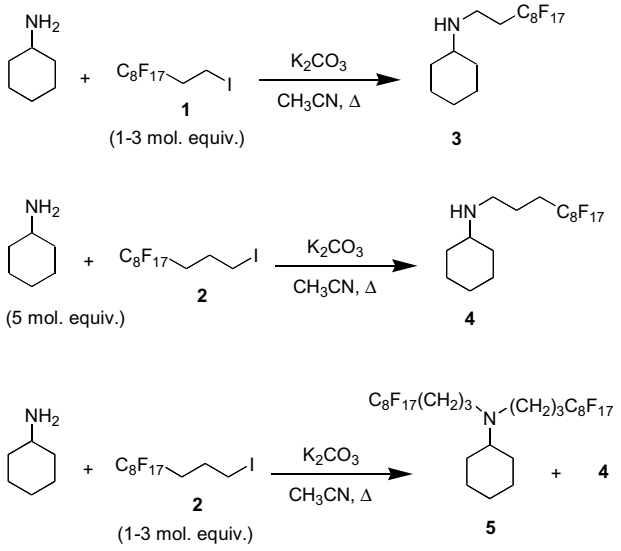
doi:10.1016/j.tetasy.2005.05.040



Scheme 1. Synthesis of fluorous *N*,*N*′-dibenzyl derivatives of (1*R*,2*R*)-diaminocyclohexane.

separable from the desired compounds. Alternative routes to *N*,*N*′-dialkylation, which are consistent with the use of readily available fluorinated starting materials, were therefore examined.

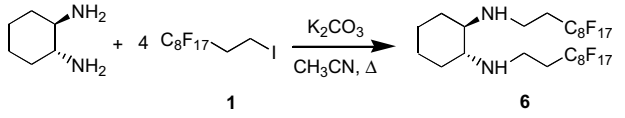
Direct *N*,*N*′-dialkylation using perfluoroalkyl iodides $R_F(CH_2)_mI$ appeared to be worth exploring. It is known that such iodides behave in a different manner from their non-fluorinated analogues when $m = 0$, 1, since the strong electron-withdrawing effect of R_F makes iodine a very bad leaving group in nucleophilic substitutions. For $m \geqslant 2$, the shielding effect of the methylene groups is progressively enhanced and reactivity of iodides such as **1** and **2** (Scheme 2) towards nucleophiles becomes closer to the usual one. Indeed, bis *N*-alkylation of certain primary amines was observed upon reaction with **2**.[17,18] However, in other cases, the reaction stops after the first alkylation step and a secondary amine is obtained as the only product, even under strong conditions.[14]



Scheme 2. *N*-alkylation of cyclohexylamine with fluorous iodides.

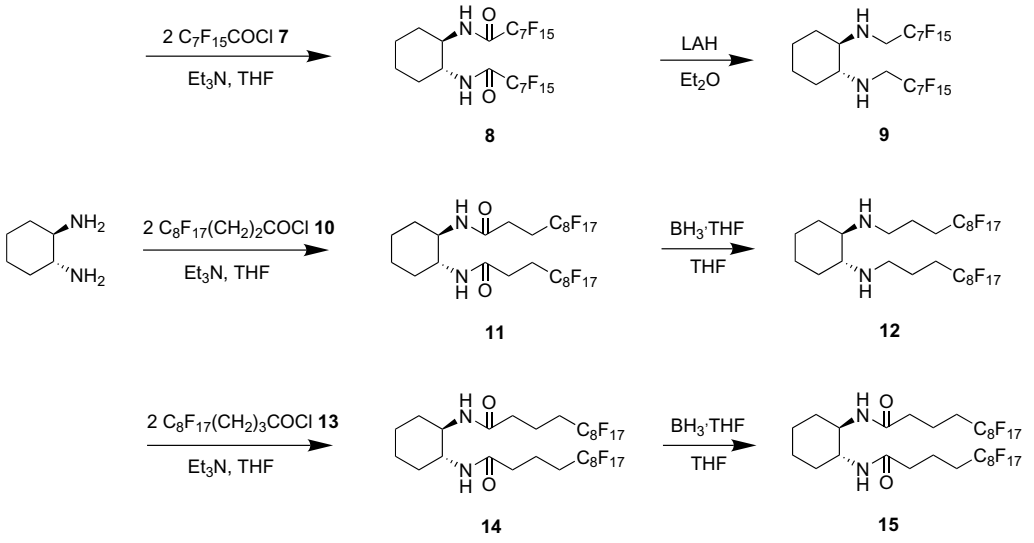
To verify whether direct *N*,*N*′-dialkylation of (1*R*,2*R*)-diaminocyclohexane was feasible, a simpler model reaction, namely *N*-alkylation of cyclohexylamine was first studied (Scheme 2). We were primarily interested in the effect of the molar ratio alkylating agent/primary amine on the outcome of the reaction, so various amounts of commercially available perfluoroalkyl iodides **1** and **2** were reacted with cyclohexylamine in boiling CH_3CN in the presence of K_2CO_3 as a base. ^1H NMR analysis of crude reaction mixtures showed that in the case of **1** only mono *N*-alkylation occurs, even if using a large excess of alkylating agent. This is possibly due to the residual electron withdrawing effect of R_F, which is not completely shielded by two CH_2 spacing units, thus making the secondary amine **3** a poor nucleophile with respect to cyclohexylamine. In the case of **2**, bis-*N*-alkylation of cyclohexylamine could be avoided by using substoichiometric amounts of the iodide, but this would be obviously unpractical if *N*,*N*′-functionalization of a diamine was sought. Mixtures of mono- and bis-*N*-alkylated products **4** and **5** were obtained for **2**/cyclohexylamine molar ratios up to 3, whereas in the presence of a further excess of alkylating agent, the tertiary amine **5** was the only product detected. The insertion of a further CH_2 spacing unit effectively reduces the influence of R_F on the electronic density of the nitrogen atom, so that the secondary amine **4** is still prone to attack by a second molecule of alkylating agent.

With these results in mind, (1*R*,2*R*)-diaminocyclohexane was reacted with four molar equivalents of commercially available iodide **1** in boiling CH_3CN in the presence of K_2CO_3 as a base (Scheme 3). Diamine **6** was isolated in a quite low yield (30%) from the reaction mixture due to the rather awkward work-up required (see Experimental).



Scheme 3. *N*,*N*′-dialkylation of (1*R*,2*R*)-diaminocyclohexane with fluorous iodide **1**.

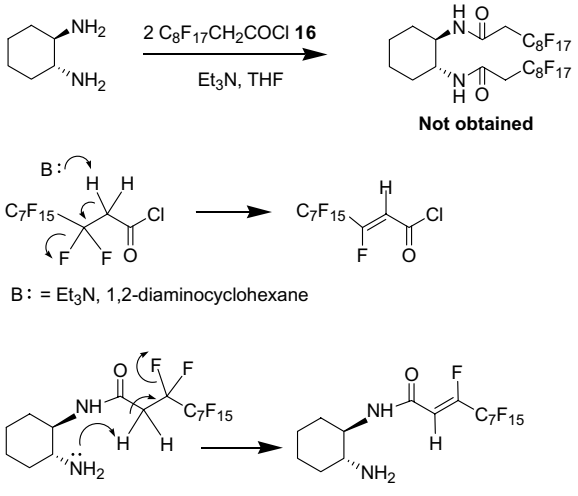
Our attention next turned towards the synthesis of disubstituted diamines by reduction of the corresponding bis-amides, in order to overcome limitations of direct *N*,*N*′-dialkylation.[19] Indeed, (*F*-alkyl)alkanoic acids $R_F(CH_2)_mCOOH$ and their derivatives are readily available and are amongst the most useful building blocks in the synthesis of more elaborated fluorous molecules.[20] Diacylation of (1*R*,2*R*)-diaminocyclohexane was achieved using commercially available $C_7F_{15}COCl$ **7** in the presence of Et_3N as a base (Scheme 4), affording bis-amide **8** in 88% yield. This compound was then reduced with $LiAlH_4$ affording the corresponding diamine **9** featuring a single CH_2 spacing unit between R_F substituents and the nitrogen atoms in 57% yield. Analogously, bis-diamides **11** and **14** were readily obtained in 88% and 96% yield, respectively, using (*F*-alkyl)alkanoyl chlorides **10** and **13** prepared following slightly modified literature methods.[21,22] Reduction of bis-amides **11** and **14** with $LiAlH_4$ went along with partial cleavage of the final product. Better results were



Scheme 4. Synthesis of fluorous *N*,*N*′-diamines **9**, **12**, and **15** by acylation/reduction.

obtained using the milder reducing agent BH_3·THF with diamines **12** and **15** recovered in 93% and 90% yield, respectively.

Attempted diacylation of (1*R*,2*R*)-diaminocyclohexane with $C_8F_{17}CH_2COCl$ **16** failed to give the desired bisamide because of concurrent HF elimination (Scheme 5). Dehydrofluorination of **16** by acid–base reaction with Et_3N or (1*R*,2*R*)-diaminocyclohexane and intramolecular *E*2 elimination of HF from a monoacylated intermediate are both possible, as pointed out by Selve et al., for the reaction of (*F*-alkyl)ethanoyl chlorides with polyfunctional amines.[21] Since diamine **6** can be obtained by direct *N*,*N*′-dialkylation, its preparation via acylation/reduction was not further investigated.



Scheme 5. Attempted acylation of (1*R*,2*R*)-diaminocyclohexane with **16**.

Next, we studied the equilibrium distribution of the new secondary diamines between two immiscible fluorous/non-fluorous solvents. Partition coefficients *P* ($P = C_{\text{fluorous phase}}/C_{\text{organic phase}}$) for **6**, **9**, **12**, and **15** between perfluoro-1,3-dimethylcyclohexane (PDMC) and standard organic solvents are reported in Table 1. Moderate to good fluorous phase affinities were exhibited by all the new compounds, as a result of the balance between their high fluorine content and the presence of two organophilic amino groups. Fluorophilicity was also influenced by the number of CH_2 spacing units interposed between R_F and the nitrogen atom, as evidenced by the higher *P* values consistently observed for **12** ($3CH_2$) with respect to **15** ($4CH_2$) despite the similar fluorine content of the two compounds (62% vs 61%). Even in the case of PDMC/MeOH biphasic systems, all these secondary diamines are preferentially dissolved in the fluorous phase, in contrast to what was observed with primary fluorous diamines and β-amino alcohols.[23] Fortunately, they are also readily soluble in Et_2O, THF, and at low concentrations, in CH_2Cl_2. This residual affinity for organic solvents greatly simplified the use of these diamines as ligands in asymmetric organometallic catalysis.

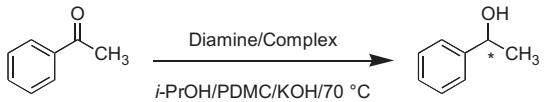
Table 1. Partition coefficients *P* for fluorous diamines between perfluoro-1,3-dimethylcyclohexane (PDMC) and standard organic solvents[a]

Organic solvent	P $[X]_{PDMC}/[X]_{org.\ solv.}$			
	9 (*F* = 65%)	**6** (*F* = 64%)	**12** (*F* = 62%)	**15** (*F* = 61%)
Toluene	5.5	8.0	4.1	2.9
CH_2Cl_2	5.5	8.6	4.4	2.6
CH_3CN	>20	>20	>20	>20
CH_3OH	7.7	4.3	5.3	4.4

[a] In a 50:50 (v:v) mixture of PDMC/organic solvent at 25 °C. Determined gravimetrically (see Experimental).

Fluorous diamines **6**, **9**, **12**, and **15**, in association with $[Ir(COD)Cl]_2$ or $[Ru(p\text{-cymene})Cl_2]_2$, were tested in the asymmetric reduction of acetophenone with isopropanol as the hydride source in the presence of PDMC as the fluorous solvent at 70 °C (Table 2). The reduction was

Table 2. Catalytic hydrogen transfer reduction of acetophenone using fluorous chiral diamines[a]



Entry	Diamine	Complex	*t* (h)	Conversion (%)	ee (%) Config.
1	**9**	$[Ru(p\text{-cymene})Cl_2]_2$	3	98	6 (*R*)
2	**6**	$[Ir(COD)Cl]_2$	0.5	98	—
3	**6**	$[Ru(p\text{-cymene})Cl_2]_2$	20	96	6 (*R*)
4	**12**	$[Ir(COD)Cl]_2$	0.5	98	12 (*S*)
5	**12**	$[Ru(p\text{-cymene})Cl_2]_2$	48	60	5 (*R*)
6	**15**	$[Ir(COD)Cl]_2$	0.5	98	5 (*S*)
7	**15**	$[Ru(p\text{-cymene})Cl_2]_2$	20	99	3 (*R*)

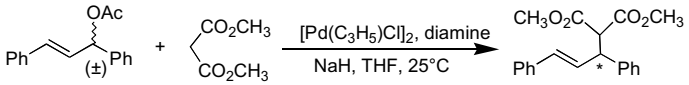
[a] Diamine = 10 mol %; complex = 5 mol %; PDMC/*i*-PrOH = 1:1 v/v; conversion and ee determined by GC (see Experimental for details).

almost quantitative with all the ligands used and whatever the catalyst precursor, except in the case of the combination **12**/$[Ru(p\text{-cymene})Cl_2]_2$ (entry 5). Unfortunately, enantioselectivities (ee max = 12%, entry 4) were much lower than those obtained using enantiopure fluorous *N*,*N*′-dibenzylcyclohexane-1,2-diamines (Scheme 1) associated with the same catalyst precursor (ee up to 69%).[13]

Slightly better results were obtained in the case of the enantioselective allylic alkylation of 1,3-diphenyl-2-propenyl acetate with diethyl malonate catalyzed by Pd(0) (Tsuji–Trost alkylation, Table 3).[24] This reaction was carried out in THF at room temperature, using the fluorous ligand (6 mol %) and $[Pd(C_3H_5)Cl]_2$ (2.5 mol %) in the presence of NaH as a base. Catalytic systems based on diamines **6**, **12**, and **15** afforded the alkylated product in almost quantitative yields, with ees up to 15–20% (entries 3–6), whereas **9** proved to be inadequate as a ligand for this reaction (entries 1 and 2). Efficient enantiopure fluorous bis(oxazolines) had been recently developed for Tsuji–Trost alkylation, affording ees up to 95% in the case of the alkylation of 1,3-diphenyl-2-propenyl acetate.[25] The new fluorous diamines **6**, **12**, and **15** are clearly inferior to those fluorous bidentate nitrogen ligands in terms of enantioselectivity. On the other hand, they compare well with a synthetically demanding fluorous BINAP analogue recently reported by us.[26]

The new ligands were finally assessed in the copper-catalyzed cyclopropanation of styrene with ethyl α-diazoacetate. Indeed, catalytic systems based on combinations of bidentate chiral nitrogen ligands and Cu(I) salts operate efficiently in the asymmetric cyclopropanation of styrene derivatives.[27] Positive results were also obtained using enantiopure C_2-symmetric diimines and diamines derived from *trans*-1,2-diphenylethanediamine or related compounds featuring a 1,2-cyclohexanediamine-like skeleton derived from sugars.[28,29] Furthermore, the scope and limitations of enantiopure fluorous *N*,*N*′-dibenzylcyclohexane-1,2-diamines as ligands in the cyclopropanation of styrene has recently been disclosed.[14] Reaction conditions were optimized using diamine **12** (5 mol %) as a model ligand (Table 4). Cyclopropanation of styrene (5 mol equiv) with ethyl α-diazoacetate (1 mol equiv) was carried out at 20 °C in CH_2Cl_2 and the *trans*- and *cis*-cyclopropanes isolated by flash column chromatography (see Experimental). As found for *N*,*N*′-dibenzylcyclohexane-1,2-diamines, the nature of the Cu(I) precursor strongly affected the outcome of the reaction (entries 1–3) while the use of $Cu(CH_3CN)_4PF_6$ (entry 3) led to the highest reaction yield (68%) and ee for both *trans* (47%) and *cis* (47%) diastereoisomers. The ratio of the diamine to the copper is also important, with a 2:1 ratio giving higher enantioselectivities than a 1 to 1 ratio (entry 3 vs 4), whereas increasing the amounts of both ligand and $Cu(CH_3CN)_4PF_6$ with respect to styrene did not result in any improvement (entry 5 vs 3). As often observed with chiral fluorous ligands, lowering the reaction temperature had negative effects on the activity and enantioselectivity of the catalytic system (entry 7). Conversely, performing the reaction at 40 °C instead of 20 °C led

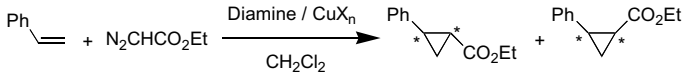
Table 3. Enantioselective allylic alkylation of 1,3-diphenyl-2-propenyl acetate using fluorous diamines[a]



Entry	Diamine	*t* (h)	Conversion (%)	ee (%) Config.
1	**9**	48	8	—
2[b]	**9**	48	17	—
3	**6**	48	100	20 (*R*)
4[b]	**6**	24	99	20 (*R*)
5	**12**	20	98	15 (*R*)
6	**15**	20	100	20 (*S*)

[a] Diamine = 6 mol %; $[Pd(C_3H_5)Cl]_2$ = 2.5 mol %; PDMC/*i*-PrOH = 1:1 v/v; conversion and ee determined by HPLC (see Experimental for details).
[b] T = 50 °C.

Table 4. Asymmetric cyclopropanation of styrene under homogeneous conditions[a]



Entry	Diamine	CuX_n	Yield (%)[b]	*Trans*/*cis*[c]	ee *trans* (%)[d,e]	ee *cis* (%)[d,f]
1	**12**	$Cu(OTf)_2$	29	67/33	38	42
2	**12**	$Cu(CH_3CN)_4BF_4$	48	66/34	38	35
3	**12**	$Cu(CH_3CN)_4PF_6$	68	67/33	47	47
4[g]	**12**	$Cu(CH_3CN)_4PF_6$	17	65/35	28	27
5[h]	**12**	$Cu(CH_3CN)_4PF_6$	68	67/33	46	46
6[i]	**12**	$Cu(CH_3CN)_4PF_6$	63	67/33	36	36
7[j]	**12**	$Cu(CH_3CN)_4PF_6$	18	66/34	36	31
8[k]	**12**	$Cu(CH_3CN)_4PF_6$	75	67/33	44	45
9[l]	**12**	$Cu(CH_3CN)_4PF_6$	37	77/23	30[m]	n.d.
10	**9**	$Cu(CH_3CN)_4PF_6$	23	61/39	16	10
11	**6**	$Cu(CH_3CN)_4PF_6$	39	62/38	39	35
12	**15**	$Cu(CH_3CN)_4PF_6$	37	65/35	32	24

[a] Diamine = 5 mol %; CuX_n = 2.5 mol %; reaction time = 1 h + 1 h; T = 20 °C (see Experimental for details).
[b] Overall isolated yield (*cis* + *trans*).
[c] Determined by GC analysis of the isolated mixture (*cis* + *trans*).
[d] Determined by HPLC analysis.
[e] Configuration (1*R*,2*R*) determined by comparison with an authentic sample.
[f] Configuration (1*S*,2*R*) determined by comparison with an authentic sample.
[g] Diamine **6** = 5 mol%; Cu(I)X = 5 mol %.
[h] Diamine **6** = 10 mol%; Cu(I)X = 5 mol %.
[i] Reaction time = 4 h + 1 h.
[j] T = 0 °C.
[k] T = 40 °C.
[l] Using *tert*-butyl α-diazoacetate instead of ethyl α-diazoacetate.
[m] Configuration of the major enantiomer not determined.

to a modest increase in the isolated yield (entry 8). Attempts to improve the enantioselectivity of the reaction by using more bulky diazoacetates, for example, *tert*-butyl-α-diazoacetate, also proved unsuccessful (entry 9). The presence of the *tert*-butyl group increases the *trans*/*cis* ratio as it makes the *cis*-transition state sterically less favorable. However, the major *trans*-cyclopropane isomer was obtained with an ee of 30% only. Under optimized conditions, results obtained with fluorous diamines **6**, **9**, and **15** were not as good as in the case of **12** (entries 10–12). Enantioselectivities and reaction yields increased with the number m of CH_2 spacing units for m = 1–3, but dropped quite unexpectedly for m = 4. Currently, we have no plausible explanation for this behavior.

The recovery of fluorous diamine **12** was then studied (Table 5). First, the ligand was released from the copper cation by decomplexation with cyanide ions, carried out on the crude reaction mixture obtained after evaporation of CH_2Cl_2 and styrene in excess. Ligand **12** was recovered in 77% yield by fluorous liquid-liquid extraction of the mixture using PDMC and could be reused with moderate success in a second run (entries 1 and 2). Unlike to what we found using fluorous *N*,*N*′-dibenz- ylcyclohexane-1,2-diamines, the performance of di-amine **12** is better under homogeneous conditions than in a Fluorous Biphasic System. In the latter case, the catalyst derived from ligand **12** and $Cu(CH_3CN)_4PF_6$ was extracted into the organic layer during the reaction and could not be recovered by phase

Table 5. Asymmetric cyclopropanation of styrene: attempted recycling using diamine **12**[a]

Entry	Solvent	CuX_n	Yield (%)[b]	*Trans*/*cis*[c]	ee *trans* (%)[d,e]	ee *cis* (%)[d,f]
1	CH_2Cl_2	$Cu(CH_3CN)_4PF_6$	68	67/33	47	47
2[g]	CH_2Cl_2	$Cu(CH_3CN)_4PF_6$	43	63/37	24	22
3	CH_2Cl_2/PDMC	$Cu(CH_3CN)_4PF_6$	40	67/33	33	35
4	CH_2Cl_2/PDMC	$Cu(OTf)_2$	37	67/33	31	32
5[h]	CH_2Cl_2/PDMC	$Cu(OTf)_2$	18	70/30	30	32

[a] Diamine **12** = 5 mol %; CuX_n = 2.5 mol %; reaction time = 1 h + 1 h; T = 20 °C (see Experimental for details).
[b] Overall isolated yield (*cis* + *trans*).
[c] Determined by GC analysis of the isolated mixture (*cis* + *trans*).
[d] Determined by HPLC analysis.
[e] Configuration (1*R*,2*R*) determined by comparison with an authentic sample.
[f] Configuration (1*S*,2*R*) determined by comparison with an authentic sample.
[g] Using diamine **12** recovered from the previous run by decomplexation.
[h] Using the complex recovered from the previous run.

separation (entry 3). On the other hand, the catalytic species obtained from ligand **12** and $Cu(OTf)_2$ (entry 4) turned out to be preferentially soluble in the fluorous layer, as shown by the color of the two phases, which were easily separated at the end of the reaction. The green-blue fluorous phase containing the catalyst was used in a subsequent run (entry 5). Although enantioselectivity remained unchanged, a drop in yield was unfortunately observed in the second run consistent with a loss of catalyst into the organic layer.

3. Conclusion

Unsophisticated fluorous derivatives of (1*R*,2*R*)-diaminocyclohexane have conveniently been prepared from readily available precursors and used as chiral ligands in the hydrogen transfer reduction of acetophenone, the allylic alkylation of 1,3-diphenyl-2-propenyl acetate, and the cyclopropanation of styrene. Catalytic systems based on these new ligands showed similar activities, but lower enantioselectivities than those achieved using more synthetically demanding fluorous chiral ligands such as fluorous bis(oxazolines). Best results were obtained in the copper-catalyzed cyclopropanation of styrene in the presence of diamine **12** (yield = 68%, *trans*/*cis* = 67:33, ee of the *trans* and *cis* isomers = 47%). The application of these fluorous enantiopure compounds in other catalytic reactions is currently under investigation in our laboratories, as well as their use as building blocks in the synthesis of enantiomerically pure tetrasubstituted diamines and P,N-ligands.

4. Experimental

4.1. General

Solvents were purified by standard methods and dried if necessary, except for perfluoro-(1,3-dimethylcyclohexane) (PDMC) (Apollo Scientific Ltd., UK), which was used as received. 1-Iodo-1*H*,1*H*,2*H*,2*H*-perfluorodecane **1**, 1-iodo-1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecane **2**, and pentadecafluorooctanoyl chloride **7** were purchased from Fluka and used as received. 2*H*,2*H*-Perfluorodecanoyl chloride **16** was prepared as described in the literature.[21] 2*H*,2*H*,3*H*,3*H*-Perfluoroundecanoyl chloride **10**,[30] and 2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorododecanoyl chloride **13**,[22] are known compounds. The original synthetic procedures have been conveniently modified as described below. Column chromatography was performed on silica gel 60 (230–240 mesh, Merck). Melting points (uncorrected) were determined with a capillary melting point apparatus Büchi SMP-20. Optical rotations were recorded using a Perkin–Elmer 241 polarimeter. The NMR spectra (^{1}H: 300 MHz, ^{13}C: 75.4 MHz, ^{19}F: 282 MHz) were recorded on a Bruker AC 300 MHz instrument with Me_4Si, $CDCl_3$, and $CFCl_3$ as the internal standard, respectively. Reactions involving organometallic catalysis were carried out in Schlenk tube under an inert atmosphere. Absolute configurations of the enantiomers were determined by comparison of GC and HPLC retention times with those of authentic samples.

4.2. (1*R*,2*R*)-*N*,*N*′-Bis(1*H*,1*H*,2*H*,2*H*-perfluorodecyl)-cyclohexane-1,2-diamine 6

A mixture of (1*R*,2*R*)-diaminocyclohexane (0.23 g, 2 mmol), K_2CO_3 (1.11 g, 8 mmol), and $C_8F_{17}CH_2CH_2I$ **1** (4.59 g, 8 mmol) in dry CH_3CN (20 mL) was refluxed with stirring under nitrogen for 48 h. The suspension was cooled to rt, treated with H_2O (10 mL) and extracted three times with Et_2O (40 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. After filtration, gaseous HCl was bubbled into the ice-cold solution. The white solid precipitate was recovered and recrystallized from EtOH to give pure **6·(HCl)$_2$** (0.65 g, 30%). Mp 188–195 °C; $[\alpha]_D^{20} = -18.7$ (*c* 0.2, CH_3OH); ^{1}H NMR (CD_3OD): δ 1.35–1.67 (4H, m), 1.84–1.99 (2H, m), 2.32–2.47 (2H, m), 2.64–3.10 (4H, m), 3.36–3.47 (4H, m), 3.56–3.65 (2H, m); ^{13}C NMR (CD_3OD): δ 25.5, 29.9, 30.8 (t, J = 21.6 Hz, $R_FCH_2CH_2$), 40.7, 61.6, 106.0–121.0 (C_8F_{17}, m); ^{19}F NMR (CD_3OD): δ −125.3 (4F, m), −122.4 (4F, m), −121.8 (4F, m), −120.9 (8F, m), −120.7 (4F, m), −112.8 (4F, m), −80.4 (6F, t, J = 10.3 Hz); IR (KBr): 2700–3000, 1100–1300 cm^{-1}. Anal. Calcd for $C_{26}H_{22}F_{34}N_2Cl_2$: C, 28.93; H, 2.05; N, 2.60. Found: C, 29.13; H, 2.15; N, 2.72.

The title compound **6** was quantitatively obtained as a white solid by neutralization of a suspension of **6·(HCl)$_2$** in Et_2O with aqueous 2.5% NaOH. Mp 40.0–41.5 °C; $[\alpha]_D^{20} = -28.1$ (*c* 0.2, CH_3OH); ^{1}H NMR ($CDCl_3$): δ 0.90–1.15 (2H, m), 1.18–1.29 (2H, m), 1.68–1.81 (2H, m), 2.08–2.20 (6H, m), 2.20–2.39 (4H, m), 2.70–2.83 (2H, m), 3.01–3.15 (2H, m); ^{13}C NMR ($CDCl_3$): δ 25.3, 31.9, 32.4 (t, J = 21.3 Hz, $R_FCH_2CH_2$), 38.9, 62.0, 107.0–122.4 (C_8F_{17}, m); ^{19}F NMR ($CDCl_3$): δ −126.6 (4F, m), −124.1 (4F, m), −123.2 (4F, m), −122.4 (8F, m), −122.2 (4F, m), −113.9 (4F, m), −81.3 (6F, t, J = 10.3 Hz); IR (KBr): 3296.9, 1100–1300 cm^{-1}. Anal. Calcd for $C_{26}H_{20}F_{34}N_2$: C, 31.03; H, 2.00; N, 2.78. Found: C, 31.46; H, 1.82; N, 3.01.

4.3. (1*R*,2*R*)-1,2-Bis(perfluorooctylamido)cyclohexane 8

(1*R*,2*R*)-Diaminocyclohexane (0.23 g, 2 mmol) and Et_3N (1.15 mL, 8 mmol) were dissolved in dry THF (10 mL) and the solution cooled to 0 °C under nitrogen. $C_7F_{15}COCl$ **7** (1.00 mL, 4 mmol) dissolved in dry THF (10 mL) was added dropwise over 15 min. After being stirred for 1.5 h at 0 °C, the solution was allowed to warm up and stirred overnight at rt. Saturated aqueous NH_4Cl (10 mL) was added and the mixture was extracted three times with Et_2O. The combined organic layers were washed with H_2O, brine, and dried over Na_2SO_4. The solvent was removed under vacuum affording bis-amide **8** (1.61 g, 88%) as a white solid, which was used for the next step without further purification. Analytical samples were obtained by recrystallization from hexane. Mp 143–144 °C; $[\alpha]_D^{20} = +2.5$ (*c* 0.2, $(CH_3)_2CO$); ^{1}H NMR ($(CD_3)_2CO$): δ 1.30–1.44 (2H, m), 1.62–1.66 (2H, m), 1.79–1.85 (2H, m), 1.99–2.04 (2H,

m), 3.93–4.01 (2H, m), 8,57 (2H, br s); ^{13}C NMR ($(CD_3)_2CO$): δ 25.3, 32.2, 53.7, 105.0–118.0 (m, C_8F_{17}), 203.7; ^{19}F NMR ($(CD_3)_2CO$): δ −126.4 (4F, m), −122.9 (4F, m), −122.6 (4F, m), −122.3 (4F, m), −121.8 (4F, m), −119.7 (4F, m), −81.3 (6F, t, J = 10.3 Hz); IR (KBr): 3319.3, 1692.5, 1545.8, 1100–1300 cm^{-1}. Anal. Calcd for $C_{22}H_{12}F_{30}N_2O_2$: C, 29.15; H, 1.33; N, 3.09. Found: C, 28.78; H, 1.15; N, 3.25.

4.4. (1*R*,2*R*)-*N*,*N*′-Bis(1*H*,1*H*-perfluorooctyl)-cyclohexane-1,2-diamine 9

Bis-amide **8** (1.80 g, 2 mmol) was slowly added under nitrogen to a stirred suspension of LAH (0.70 g, 18 mmol) in dry THF (30 mL). The reaction mixture was refluxed under nitrogen for 8 h, and then stirred at rt for a further 18 h. The suspension was cooled to 0 °C and carefully hydrolyzed with H_2O (3 mL), aqueous 10% NaOH (3 mL) and then H_2O (3 mL). The grey slurry was stirred for 1 h and then extracted three times with Et_2O. The combined organic layers were washed with saturated aqueous NH_4Cl, dried over Na_2SO_4, and evaporated to leave a residue which was purified by flash column chromatography (silica gel, $(i\text{-Pr})_2O$/hexane 1:4) yielding **9** (1.00 g, 57%) as a white solid. Mp 35.5–37.5 °C; $[\alpha]_D^{20} = -27.1$ (c 0.2, Et_2O); ^{1}H NMR ($CDCl_3$): δ 1.00–1.04 (2H, m), 1.19–1.26 (2H, m), 1.68–1.82 (4H, m), 2.03–2.08 (2H, m), 2.25–2.28 (2H, m), 3.17 (2H, q J = 14.9 Hz), 3.36 (2H, q, J = 14.9 Hz); ^{13}C NMR ($(CD_3)_2CO$): δ 25.5, 32.0, 47.7 (t, J = 22.9 Hz, R_FCH_2N), 62.6; ^{19}F NMR ($(CD_3)_2CO$): δ −126.4 (4F, m), −122.9 (8F, m), −122.1 (8F, m), −117.6 (4F, m), −81.4 (6F, t, J = 10.3 Hz); IR (KBr): 3320.6, 1100–1300 cm^{-1}. Anal. Calcd for $C_{22}H_{16}F_{30}N_2$: C, 30.08; H, 1.84; N, 3.19 Found: C, 30.46; H, 1.77; N, 3.00.

4.5. 2*H*,2*H*,3*H*,3*H*-Perfluoro undecanoyl chloride 10

A solution of $KMnO_4$ (1.77 g, 11.3 mmol) in H_2O (30 mL) was added dropwise to a warm solution of 1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoro undecan-1-ol[31] (3.57 g, 7.5 mmol) and Bu_4NHSO_4 (0.35 g, 0.13 mmol) in toluene (23 mL). The biphasic mixture was vigorously stirred for 4 h at 70 °C, then cooled to rt and acidified with aqueous 10% HCl. Saturated aqueous $Na_2S_2O_3$ was added until the mixture became colorless. The aqueous layer was extracted three times with $(i\text{-Pr})_2O$. The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated to dryness. The residue was recrystallized from $CHCl_3$ yielding 2*H*,2*H*,3*H*,3*H*-perfluoroundecanoic acid (3.01 g, 82%) as a white crystalline solid (physical data in agreement with those reported in the literature).[30]

To the acid placed in a flame dried round-bottomed flask equipped with a condenser $SOCl_2$ (1.75 mL, 24 mmol) was added. The mixture was stirred for 2 h at 100 °C, the condenser was replaced with a Vigreux distilling column and the excess $SOCl_2$ was distilled off at 80 °C, ambient pressure. Distillation was continued under reduced pressure to recover the acyl chloride **10** (2.10 g, 70%) as a colorless liquid (physical data in agreement with those reported in the literature).[30]

4.6. (1*R*,2*R*)-1,2-Bis(2*H*,2*H*,3*H*,3*H*-perfluoroundecanoylamido)cyclohexane 11

(1*R*,2*R*)-Diaminocyclohexane (0.23 g, 2 mmol) and Et_3N (1.15 mL, 8 mmol) were dissolved in dry THF (10 mL) and the solution was cooled to 0 °C under nitrogen. $C_8F_{17}CH_2CH_2COCl$ **10** (2.04 g, 4 mmol) dissolved in dry THF (10 mL) was added dropwise over 15 min. The mixture was stirred at 0 °C for 1.5 h, then allowed to warm up to rt and left overnight under stirring. After filtration on a Büchner funnel, the precipitate was washed with ice-cold hexane, H_2O, and dried under vacuum affording bis-amide **11** (1.95 g, 88%) as a white solid, insoluble in organic and fluorous solvents, which was used for the next step without further purification. Mp 186–192 °C; IR (KBr): 3299.5, 1645.5, 1551.1, 1100–1300 cm^{-1}. Anal. Calcd for $C_{28}H_{20}F_{34}N_2O_2$: C, 31.65; H, 1.90; N, 2.64. Found: C, 32.19; H, 2.24; N, 2.71.

4.7. (1*R*,2*R*)-*N*,*N*′-Bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*-perfluoroundecyl)-cyclohexane-1,2-diamine 12

To a suspension of bis-amide **11** (0.85 g, 0.8 mmol) in dry THF (8 mL) cooled at 0 °C, BH_3·THF 1M in THF (4.00 mL, 4 mmol) was added dropwise over 30 min. The mixture was refluxed for 2 h under stirring and complete disappearance of the solid was observed. The solution was cooled to rt, carefully acidified with aqueous 10% HCl (~1 mL) and refluxed for 1 h, then cooled to rt and treated with aqueous 10% NaOH (~1 mL) to adjust pH to 11. The solution was diluted with Et_2O, washed with H_2O, brine, and dried over Na_2SO_4. The solvent was evaporated to yield **12** as a white solid (0.77 g, 93%). Mp 44–45 °C; $[\alpha]_D^{20} = -29.5$ (c 0.2, Et_2O); ^{1}H NMR ($CDCl_3$): δ 0.90–1.11 (2H, m), 1.15–1.29 (2H, m), 1.50 (2H, br s), 1.65–1.81 (6H, m), 2.05–2.26 (8H, m), 2.51 (2H, dt, J = 11.7 Hz, 6.7 Hz), 2.82 (2H, dt, J = 11.7 Hz, 6.7 Hz); ^{13}C NMR ($CDCl_3$): δ 21.7, 25.4. 29.2 (t, J = 22.1 Hz, $R_FCH_2CH_2CH_2$), 32.2, 46.2, 62.0, 106.0–120.0 (C_8F_{17}, m); ^{19}F NMR ($CDCl_3$): δ −126.7 (4F, m), −124.0 (4F, m), −123.3 (4F, m), −122.5 (8F, m), −122.3 (4F, m), −114.9 (4F, m), −81.3 (6F, t, J = 10.3 Hz); IR (KBr): 3296.9, 1100–1300 cm^{-1}. Anal. Calcd for $C_{28}H_{24}F_{34}N_2$: C, 32.51; H, 2.34; N, 2.71. Found: C, 32.51; H, 2.36; N, 2.76.

4.8. 2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-Perfluorododecanoyl chloride 13

To 2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorododecanoic acid $C_8F_{17}CH_2CH_2CH_2COOH$ (3.04 g, 6 mmol)[22] placed in a flame dried round-bottomed flask equipped with a condenser, $SOCl_2$ (1.75 mL, 24 mmol) was added. The mixture was stirred for 2 h at 100 °C, the condenser was replaced with a Vigreux distilling column and the excess $SOCl_2$ distilled off at 80 °C, at ambient pressure. Distillation was continued under reduced pressure to recover acyl chloride **13** (2.12 g, 67%) as a colorless

liquid (physical data in agreement with those reported in the literature).[22]

4.9. (1*R*,2*R*)-*N*,*N*′-Bis(2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorododecanoylamido)cyclohexane 14

(1*R*,2*R*)-Diaminocyclohexane (0.23 g, 2 mmol) and Et_3N (1.15 mL, 8 mmol) were dissolved in dry THF (15 mL) and the solution was cooled to 0 °C under nitrogen. $C_8F_{17}CH_2CH_2CH_2COCl$ **13** (2.10 g, 4 mmol) dissolved in dry THF (15 mL) was added dropwise over 15 min. The mixture was stirred at 0 °C for 1.5 h then allowed to warm up to rt and left overnight under stirring. After filtration on a Büchner funnel, the precipitate was washed with ice-cold hexane, H_2O, and dried under vacuum affording bis-amide **14** (2.00 g, 96%) as a white solid, insoluble in organic and fluorous solvents, which was used for the next step without further purification. Mp 189–192 °C; IR (KBr): 3296.9, 1643.2, 1548.0, 1100–1300 cm^{-1}. Anal. Calcd for $C_{30}H_{24}F_{34}N_2O_2$: C, 33.04; H, 2.22; N, 2.57. Found: C, 33.27; H, 2.29; N, 2.80.

4.10. (1*R*,2*R*)-*N*,*N*′-Bis(1*H*,1*H*,2*H*,2*H*,3*H*,3*H*,4*H*,4*H*-perfluorododecyl)-cyclohexane-1,2-diamine 15

To a suspension of bis-amide **14** (0.87 g, 0.8 mmol) in dry THF (8 mL) cooled at 0 °C, BH_3·THF 1M in THF (4 mL, 4 mmol) was added dropwise over 30 min. The mixture was refluxed for 2 h under stirring and complete disappearance of the solid observed. The solution was cooled to rt, carefully acidified with aqueous 10% HCl (~1 mL) and refluxed for 1 h, then cooled to rt and treated with aqueous 10% NaOH (~1 mL) to adjust the pH to 11. The solution was diluted with Et_2O, washed with H_2O, brine, and dried over Na_2SO_4. The solvent was evaporated to yield **15** as a white solid (0.76 g, 90%). Mp 51.0–52.5 °C; $[\alpha]_D^{20} = -27.1$ (*c* 0.2, Et_2O); ^1H NMR ($CDCl_3$): δ 0.92–1.11 (2H, m), 1.18–1.29 (2H, m), 1.46–1.71 (10H, m), 1.85 (2H, br s), 1.96–2.14 (8H, m), 2.46 (2H, dt, $J = 11.5$ Hz, 6.9 Hz), 2.79 (2H, dt, $J = 11.5$ Hz, 6.9 Hz); ^{13}C NMR ($CDCl_3$): δ 18.4, 25.5, 30.3, 31.2 (t, $J = 22.6$ Hz, $R_FCH_2CH_2CH_2CH_2$), 32.1, 46.7, 62.1, 106.0–120.0 (C_8F_{17}, m); ^{19}F NMR ($CDCl_3$): δ −126.7 (4F, m), −124.0 (4F, m), −123.3 (4F, m), −122.5 (12F, m), −115.1 (4F, m), −81.3 (6F, t, $J = 10.3$ Hz); IR (KBr): 3283.2, 1100–1300 cm^{-1}. Anal. Calcd for $C_{30}H_{28}F_{34}N_2$: C, 33.91; H, 2.66; N, 2.64. Found: C, 34.57; H, 2.60; N, 2.75.

4.11. Determination of partition coefficients *P*

A 10 mL vial equipped with a magnetic stirrer was charged with the fluorous diamine (50 mg), PDMC (2 mL) and the organic solvent (2 mL). The mixture was thermostatted at 25 °C and vigorously stirred for 4 h. A 1 mL sample was taken out of each phase, evaporated to dryness, and weighed on an analytical balance. The partition coefficient *P* was determined as the ratio between the weight of the fluorous phase residue and the weight of the organic phase residue.

4.12. Hydrogen transfer reduction of acetophenone

The catalyst was prepared in a Schlenk tube by stirring $[Ir(COD)Cl]_2$ (10.3 mg, 20 μmol), or Ru (*p*-cymene)$Cl_2]_2$ (12.2 mg, 20 μmol) and the fluorinated diamine (40 μmol) in degassed PDMC (5 mL) at 70 °C for 3 h. To this solution cooled to rt was added a solution of acetophenone (48 mg, 0.4 mmol) and KOH (5.6 mg, 0.1 mmol) in *i*-PrOH (5 mL). The mixture was stirred at 70 °C. The conversion and enantiomeric excess were determined by GC analysis using a capillary Quadrex OV1 column (30 m × 0.25 mm) and a capillary Cyclodex-β column (30 m × 0.25 mm), respectively.

4.13. Alkylation of 1,3-diphenyl-2-propenyl acetate

The catalyst was prepared in a Schlenk tube by stirring $[Pd(C_3H_5)Cl]_2$ (45.6 mg, 12.5 μmol) and the fluorinated diamine (30 μmol) in degassed THF (1.5 mL) at 50 °C for 1 h. 1,3-Diphenyl-2-propenyl acetate (126 mg, 0.5 mmol) dissolved in THF (1.5 mL) was added and the solution stirred for a further 20 min after which it was transferred under nitrogen into another Schlenk tube containing a solution of NaH (36 mg, 1.5 mmol) and dimethyl malonate (198 mg, 1.5 mmol) in THF (2 mL). The solution was stirred at the desired temperature for the time indicated in Table 3. The conversion was determined by GC using a Quadrex OV1 column (30 m × 0.25 mm) and the enantioselectivity by HPLC on a chiral stationary phase (column: Chiralpak AD; eluent hexane/*i*-PrOH 60:40).

4.14. Cyclopropanation of styrene

4.14.1. Homogeneous conditions. Fluorous diamine (25 μmol) and CuX_n (12.5 μmol) were stirred together in degassed CH_2Cl_2 (3 mL) for 1 h at rt. When $Cu(OTf)_2$ was used, phenylhydrazine (1.5 μL) was also added in order to reduce Cu(II) to Cu(I). Styrene (260 mg, 2.5 mmol.) was added to the reaction mixture which was allowed to stir for a further 10 min. Ethyl α-diazoacetate (57 mg, 0.5 mmol) dissolved in CH_2Cl_2 (2 mL) was added dropwise over 1 h using a syringe pump and the mixture was stirred for a further hour. The volatiles were then evaporated under vacuum to leave a thick oil, an aliquot of which was analyzed by GC (HP-1 100% dimethylpolysiloxane 30 m × 320 μm × 0.25 μm column) to determine the *trans*/*cis* ratio. The residue was purified by flash column chromatography (silica gel, hexane/EtOAc 95:5) to give a mixture of the two diastereoisomers. The enantiomeric excesses of *trans*- and *cis*-cyclopropane were determined by HPLC analysis on a chiral stationary phase (column: Chiralcel OJ-H; eluent: hexane/*i*-PrOH 99.5:0.5).

4.14.2. Fluorous biphasic conditions. Diamine **12** (25 μmol) and CuX_n (12.5 μmol) were stirred together in a mixture of degassed CH_2Cl_2 (3 mL) and degassed PDMC (4 mL) for 1 h at rt. When $Cu(OTf)_2$ was used, phenylhydrazine (1.5 μL) was also added to reduce Cu(II) to Cu(I). Styrene (260 mg, 2.5 mmol) was added to the reaction mixture that was allowed to stir for a further 10 min. Ethyl α-diazoacetate (57 mg, 0.5 mmol) dis-

solved in CH_2Cl_2 (2 mL) was added dropwise over 1 h using a syringe pump. After the addition, the mixture was allowed to stir for a further hour, then the CH_2Cl_2 layer removed and the fluorous phase extracted with CH_2Cl_2 (2 mL). The combined organic layers were evaporated under vacuum to leave the crude products, which were separated and analyzed as described above.

Acknowledgements

The support of the COST Action D29 'New Fluorous Media and Processes for Cleaner and Safer Chemistry' is gratefully acknowledged. L.M. and O.H. thank ISTM-CNR for a studentship. J.B. thanks the French Ministry of Education for a fellowship.

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