

6 Partition Coefficients Involving Fluorous Solvents

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6.1 Introduction

Partition coefficients quantify the equilibrium distribution of a solute between two immiscible phases, which are most often but not necessarily liquids. They see extensive use throughout chemistry, and their thermodynamic nuances have been analyzed in detail [1].

In order to rationally extract non-fluorous products from reactions involving fluorous solvents, partition coefficients for fluorous/non-fluorous liquid/liquid biphasic systems are necessary. The design and optimization of fluorous catalysts and reagents require analogous data. Such partition coefficients constitute a direct measure of fluorophilicity, a term that is used interchangeably with fluorous phase affinity.

By 1999, only a few partition coefficients involving fluorous and organic phases had been measured [2, 3]. Now there is a wealth of data, to which sophisticated analysis and parameterization methods have been applied [4–6]. The primary aim of this chapter is to summarize the literature reports, and qualitatively interpret the principal trends. Representative procedures for the determination of partition coefficients are also given.

6.2 Literature Data

Some investigators prefer to express partition coefficients as ratios that have been normalized to 100 (e.g., 98.3:1.7), others as ratios with either the less populated phase or the non-fluorous phase set to 1 (e.g., 57.8:1), and still others as logarithmic values. The abbreviation *P* indicates a concentration ratio with the non-fluorous phase in the denominator. The natural logarithm of the $\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene concentration ratio, $\ln\{[c(\text{CF}_3\text{C}_6\text{F}_{11})]/[c(\text{toluene})]\}$, has been given the abbreviation *f*, for fluorophilicity [4].

All partition coefficients measured in the authors' laboratories can be found in Table 6-1. Most of these involve the solvent system $\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene. Many data from other research groups are also included. However, there are undoubtedly inadvertent omissions, for which the authors express their regrets. Since the entries are sorted by functional group, the placement of difunctional molecules is arbitrary. At the end of some sections, cross refer-

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
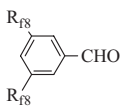
Tab. 6-1. Fluorous/organic liquid/liquid partition coefficients^a

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
I Alkanes					
I-1	CH ₃ (CH ₂) ₈ CH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	5.4:94.6 (P = 0.057)	GLC	1
I-2	CH ₃ (CH ₂) ₉ CH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	4.2:95.8 (P = 0.044)	GLC	1
I-3	CH ₃ (CH ₂) ₁₀ CH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	3.4:96.6 (P = 0.035)	GLC	1, 2
I-4	CH ₃ (CH ₂) ₁₁ CH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	2.4:97.6 (P = 0.025)	GLC	1
I-5	CH ₃ (CH ₂) ₁₂ CH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	1.9:98.1 (P = 0.019)	GLC	1
I-6	CH ₃ (CH ₂) ₁₄ CH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	1.1:98.9 (P = 0.011)	GLC	1
II Alkenes					
II-1	CH ₃ (CH ₂) ₇ CH=CH ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	4.8:95.2 (P = 0.050)	GLC	3
II-2	CH ₃ (CH ₂) ₈ CH=CH ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	3.7:96.3 (P = 0.038)	GLC	3
II-3	CH ₃ (CH ₂) ₉ CH=CH ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	2.5:97.5 (P = 0.026)	GLC	2
II-4	CH ₃ (CH ₂) ₁₀ CH=CH ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	1.9:98.1 (P = 0.019)	GLC	3
II-5	CH ₃ (CH ₂) ₁₁ CH=CH ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	1.6:98.4 (P = 0.016)	GLC	3
II-6	CH ₃ (CH ₂) ₁₃ CH=CH ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	0.9:99.1 (P = 0.009)	GLC	3
II-7 ^c	R _{f8} CH=CH ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	93.5:6.5 (P = 14.4) ^d	GLC	4a
II-8 ^c	<i>E</i> -R _{f6} CH=CHC ₆ H ₁₃	C ₁₀ F ₁₈ ^e :C ₁₆ H ₃₄	63.4:36.6 (P = 1.73)	GLC	5
II-9 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	72.5:27.5 (P = 2.63)	GLC	5
II-10 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	74.9:25.1 (P = 2.98)	GLC	5
II-11 ^c	<i>Z</i> -R _{f6} CH=CHC ₆ H ₁₃	C ₁₀ F ₁₈ ^e :C ₁₆ H ₃₄	62.1:37.9 (P = 1.64)	GLC	5
II-12 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	67.5:32.5 (P = 2.08)	GLC	5
II-13 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	72.6:27.4 (P = 2.65)	GLC	5
II-14 ^c	<i>E</i> -R _{f6} CH=CHC ₈ H ₁₇	C ₁₀ F ₁₈ ^e :C ₁₆ H ₃₄	42:58 (P = 0.72)	GLC	5
II-15 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	49:51 (P = 0.95)	GLC	5
II-16 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	53.1:46.9 (P = 1.13)	GLC	5

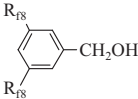
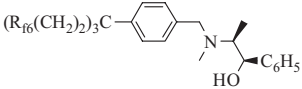
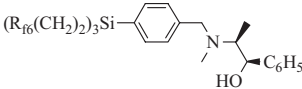
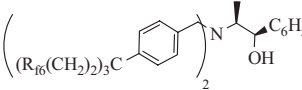
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
II-17 ^c	Z-R _{f6} CH=CHC ₈ H ₁₇	C ₁₀ F ₁₈ :C ₁₆ H ₃₄	50.0:50.0 (P = 1.00)	GLC	5
II-18 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	53.1:46.9 (P = 1.13)	GLC	5
II-19 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	60.0:40.0 (P = 1.50)	GLC	5
II-20 ^c	E-R _{f6} CH=CHC ₁₀ H ₂₁	C ₁₀ F ₁₈ :C ₁₆ H ₃₄	20:80 (P = 0.25)	GLC	5
II-21 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	43:57 (P = 0.74)	GLC	5
II-22 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	44:56 (P = 0.80)	GLC	5
II-23 ^c	Z-R _{f6} CH=CHC ₁₀ H ₂₁	C ₁₀ F ₁₈ :C ₁₆ H ₃₄	28:72 (P = 0.38)	GLC	5
II-24 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	40:60 (P = 0.68)	GLC	5
II-25 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	47:53 (P = 0.88)	GLC	5
II-26 ^c	E-R _{f8} CH=CHC ₆ H ₁₃	C ₁₀ F ₁₈ :C ₁₆ H ₃₄	79.8:20.2 (P = 3.95)	GLC	5
II-27 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	86.0:14.0 (P = 6.13)	GLC	5
II-28 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	86.4:13.6 (P = 6.38)	GLC	5
II-29 ^c	Z-R _{f8} CH=CHC ₆ H ₁₃	C ₁₀ F ₁₈ :C ₁₆ H ₃₄	77.2:22.8 (P = 3.38)	GLC	5
II-30 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	82.0:18.0 (P = 4.55)	GLC	5
II-31 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	83.6:16.4 (P = 5.11)	GLC	5
II-32 ^c	E-R _{f8} CH=CHC ₈ H ₁₇	C ₁₀ F ₁₈ :C ₁₆ H ₃₄	72.5:27.5 (P = 2.63)	GLC	5
II-33 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	76.7:23.3 (P = 3.30)	GLC	5
II-34 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	79.2:20.8 (P = 3.81)	GLC	5
II-35 ^c	Z-R _{f8} CH=CHC ₈ H ₁₇	C ₁₀ F ₁₈ :C ₁₆ H ₃₄	71.5:28.5 (P = 2.51)	GLC	5
II-36 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	76.0:24.0 (P = 3.17)	GLC	5
II-37 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	78.6:21.4 (P = 3.67)	GLC	5
II-38 ^c	E-R _{f8} CH=CHC ₁₀ H ₂₁	C ₁₀ F ₁₈ :C ₁₆ H ₃₄	54.8:45.2 (P = 1.21)	GLC	5
II-39 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	63.1:36.9 (P = 1.71)	GLC	5

Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
II-40 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	70.8:29.2 (P = 2.43)	GLC	5
II-41 ^c	Z-R _{f8} CH=CHC ₁₀ H ₂₁	C ₁₀ F ₁₈ ^e :C ₁₆ H ₃₄	54.1:45.9 (P = 1.18)	GLC	5
II-42 ^c		(C ₄ F ₉ CH=) ₂ :C ₁₆ H ₃₄	56.7:43.3 (P = 1.31)	GLC	5
II-43 ^c		C ₈ F ₁₇ Br:C ₁₆ H ₃₄	65.5:34.5 (P = 1.90)	GLC	5
II-44 ^c	<i>c</i> -C ₅ H ₄ [(CH ₂) ₂ R _{f4}] ₂ ^f	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	55:45 (P = 1.2)	GLC	6
II-45 ^c	<i>c</i> -C ₅ H ₄ [(CH ₂) ₂ R _{f6}] ₂ ^f	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	83:17 (P = 4.9)	GLC	6
II-46 ^c	<i>c</i> -C ₅ H ₄ [(CH ₂) ₂ R _{f8}] ₂ ^f	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	90:10 (P = 8.8)	GLC	6
II-47 ^c	<i>c</i> -C ₅ H ₄ [(CH ₂) ₂ R _{f4}][(CH ₂) ₂ R _{f6}] ^f	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	75:25 (P = 3.0)	GLC	6
II-48 ^c	<i>c</i> -C ₅ H ₄ [(CH ₂) ₂ R _{f4}][(CH ₂) ₂ R _{f8}] ^f	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	82:18 (P = 4.6)	GLC	6
II-49 ^c	<i>c</i> -C ₅ H ₄ [(CH ₂) ₂ R _{f6}][(CH ₂) ₂ R _{f8}] ^f	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	86:14 (P = 6.4)	GLC	6
	for further compounds see XII and XIII				
III	Ketones and Aldehydes				
III-1	cyclohexanone	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	2.2:97.8 (P = 0.022)	GLC	2
III-2	2-cyclohexen-1-one	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	1.7:98.3 (P = 0.017)	GLC	2
III-3	R _{f8} (CH ₂) ₃ -  -C(O)(CH ₂) ₂ R _{f8}	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	84.6:15.4 (P = 5.49)	GLC	7
III-4 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.6:1.4 (P = 73.0) ^d	GLC	4a
IV	Alcohols				
IV-1	cyclohexanol	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	1.6:98.4 (P = 0.016)	GLC	2
IV-2 ^c	CF ₃ CH ₂ OH	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	14.5:85.5 (P = 0.170) ^d	GLC	8
IV-3 ^c	(CF ₃) ₂ CHOH	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	26.7:73.3 (P = 0.364) ^d	GLC	8
IV-4 ^c	R _{f6} (CH ₂) ₂ OH	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	52:48 (P = 1.1) ^d	GLC	8
IV-5 ^c	R _{f6} (CH ₂) ₃ OH	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	44:56 (P = 0.79) ^d	GLC	8

Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (<i>P</i>)	Method	Ref.
IV-6 ^c	R _{f8} (CH ₂) ₂ OH	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	73.5:26.5 (<i>P</i> = 2.77) ^d	GLC	8
IV-7 ^c	R _{f8} (CH ₂) ₃ OH	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	64:36 (<i>P</i> = 1.8) ^d	GLC	8
IV-8 ^c	R _{f10} (CH ₂) ₃ OH	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	80.5:19.5 (<i>P</i> = 4.14) ^d	GLC	8
IV-9 ^g	[R _{f6} (CH ₂) ₂] ₃ COH	C ₆ F ₁₄ :THF	90.9:9.1 (<i>P</i> = 10.0)	–	9
IV-10 ^h		C ₆ F ₁₄ :THF	95.8:4.2 (<i>P</i> = 23.0)	–	9
IV-11 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	97.4:2.6 (<i>P</i> = 38.1) ^d	GLC	4a
IV-12 ^g	[R _{f6} (CH ₂) ₂] ₂ C(OCH ₃)CH(OH)C ₆ H ₅	C ₆ F ₁₄ :THF	19:81 (<i>P</i> = 0.24)	–	9
IV-13 ^g		C ₆ F ₁₄ :CH ₃ CN	88:12 (<i>P</i> = 7.3)	gravimet	10
IV-14 ^g		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	59:41 (<i>P</i> = 1.4)	gravimet	10
IV-15 ^g		C ₆ F ₁₄ :CH ₂ Cl ₂	38:62 (<i>P</i> = 0.61)	gravimet	10
IV-16 ^g		C ₆ F ₁₄ :CH ₃ CN	82:18 (<i>P</i> = 4.6)	gravimet	10
IV-17 ^g		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	48:52 (<i>P</i> = 0.92)	gravimet	10
IV-18 ^g		C ₆ F ₁₄ :CH ₂ Cl ₂	25:75 (<i>P</i> = 0.33)	gravimet	10
IV-19 ^g		C ₆ F ₁₄ :CH ₃ CN	97:3 (<i>P</i> = 32)	gravimet	10
IV-20 ^g		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	97:3 (<i>P</i> = 32)	gravimet	10
IV-21 ^g		C ₆ F ₁₄ :CH ₂ Cl ₂	94:6 (<i>P</i> = 16)	gravimet	10

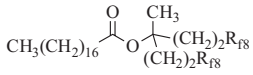
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
V Aliphatic Ethers					
V-1 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.3:1.7 (P = 56.8) ^d	GLC	11
V-2 ⁱ		C ₆ F ₁₄ :CH ₃ CN	88:12 (P = 7.3)	gravimet	12
V-3 ⁱ		C ₆ F ₁₄ :CH ₃ OH	79:21 (P = 3.8)	gravimet	12
V-4 ⁱ		C ₆ F ₁₄ :C ₂ H ₅ OH	78:22 (P = 3.6)	gravimet	12
V-5 ⁱ		C ₆ F ₁₄ :C ₆ H ₆	62:38 (P = 1.6)	gravimet	12
V-6 ⁱ		C ₆ F ₁₄ :CH ₂ Cl ₂	57:43 (P = 1.3)	gravimet	12
V-7 ⁱ		C ₆ F ₁₄ :CH ₃ COCH ₃	52:48 (P = 1.1)	gravimet	12
V-8 ⁱ		C ₆ F ₁₄ :CH ₃ CO ₂ C ₂ H ₅	46:54 (P = 0.85)	gravimet	12
V-9 ⁱ		C ₆ F ₁₄ :CHCl ₃	46:54 (P = 0.85)	gravimet	12
for further compounds see IV, VII and VIII					
VI Carboxylic Acids and Derivatives					
VI-1 ^c	R ₁₇ C(O)OC ₆ H ₅	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	62:38 (P = 1.6) ^d	GLC	4a
VI-2 ^c	R ₁₇ C(O)OCH ₂ C ₆ H ₅	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	89.5:10.5 (P = 8.50) ^d	GLC	4a
VI-3 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	95.9:4.1 (P = 23.3) ^d	GLC	4a
VI-4 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	40:60 (P = 0.68) ^d	GLC	4a
VI-5 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	52:48 (P = 1.1) ^d	GLC	4a
VI-6 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	50:50 (P = 0.99) ^d	GLC	4a
VI-7 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.8:1.2 (P = 85.6) ^d	GLC	4a

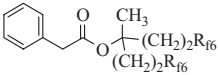
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
VI-8 ^c		C ₆ F ₁₄ : <i>c</i> -C ₆ H ₁₂	89.0:11.0 (P = 8.10)	gravimet	13
VI-9 ^c		CF ₃ C ₆ F ₁₁ : <i>c</i> -C ₆ H ₁₂	90.5:9.5 (P = 9.58)	gravimet	13
VI-10 ^c		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	88.6:11.4 (P = 7.75)	gravimet	13
VI-11 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	86.6:13.4 (P = 6.46)	gravimet	13
VI-12 ^c		C ₆ F ₁₄ :CH ₂ Cl ₂	90.1:9.9 (P = 9.08)	gravimet	13
VI-13 ^c		CF ₃ C ₆ F ₁₁ :CH ₂ Cl ₂	93.8:6.2 (P = 15.4)	gravimet	13
VI-14 ^c		C ₆ F ₁₄ :CHCl ₃	75.4:24.6 (P = 3.06)	gravimet	13
VI-15 ^c		CF ₃ C ₆ F ₁₁ :CHCl ₃	85.6:14.4 (P = 5.93)	gravimet	13
VI-16 ^c		C ₆ F ₁₄ :CH ₃ CO ₂ C ₂ H ₅	72.1:27.9 (P = 2.59)	gravimet	13
VI-17 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ CO ₂ C ₂ H ₅	76.5:23.5 (P = 3.25)	gravimet	13
VI-18 ^c		C ₆ F ₁₄ :THF	73.0:27.0 (P = 2.70)	gravimet	13
VI-19 ^c		CF ₃ C ₆ F ₁₁ :THF	84.0:16.0 (P = 5.26)	gravimet	13
VI-20 ^c		C ₆ F ₁₄ :CH ₃ COCH ₃	76.9:23.1 (P = 3.33)	gravimet	13
VI-21 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ COCH ₃	86.3:13.7 (P = 6.28)	gravimet	13
VI-22 ^c		C ₆ F ₁₄ :CH ₃ CN	86.5:13.5 (P = 6.42)	gravimet	13
VI-23 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ CN	94.4:5.6 (P = 16.9)	gravimet	13
VI-24 ^c		C ₆ F ₁₄ :C ₂ H ₅ OH	80.7:19.3 (P = 4.19)	gravimet	13
VI-25 ^c		CF ₃ C ₆ F ₁₁ :C ₂ H ₅ OH	94.1:5.9 (P = 16.0)	gravimet	13
VI-26 ^c		C ₆ F ₁₄ :CH ₃ OH	82.7:17.3 (P = 4.78)	gravimet	13
VI-27 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ OH	91.5:8.5 (P = 10.8)	gravimet	13
VI-28 ^c		C ₆ F ₁₄ : <i>c</i> -C ₆ H ₁₂	87.0:13.0 (P = 6.72)	gravimet	13
VI-29 ^c		CF ₃ C ₆ F ₁₁ : <i>c</i> -C ₆ H ₁₂	92.5:7.5 (P = 12.4)	gravimet	13

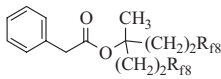
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
VI-30 ^c		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	84.1:15.9 (P = 5.28)	gravimet	13
VI-31 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	94.5:5.5 (P = 17.2)	gravimet	13
VI-32 ^c		C ₆ F ₁₄ :CH ₂ Cl ₂	81.9:18.1 (P = 4.53)	gravimet	13
VI-33 ^c		CF ₃ C ₆ F ₁₁ :CH ₂ Cl ₂	93.2:6.8 (P = 13.6)	gravimet	13
VI-34 ^c		C ₆ F ₁₄ :CHCl ₃	72.5:27.5 (P = 2.63)	gravimet	13
VI-35 ^c		CF ₃ C ₆ F ₁₁ :CHCl ₃	85.2:14.8 (P = 5.74)	gravimet	13
VI-36 ^c		C ₆ F ₁₄ :CH ₃ CO ₂ C ₂ H ₅	73.3:26.7 (P = 2.74)	gravimet	13
VI-37 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ CO ₂ C ₂ H ₅	90.8:9.2 (P = 9.86)	gravimet	13
VI-38 ^c		C ₆ F ₁₄ :THF	63.0:37.0 (P = 1.70)	gravimet	13
VI-39 ^c		CF ₃ C ₆ F ₁₁ :THF	82.7:17.3 (P = 4.79)	gravimet	13
VI-40 ^c		C ₆ F ₁₄ :CH ₃ COCH ₃	74.5:25.5 (P = 2.92)	gravimet	13
VI-41 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ COCH ₃	84.7:15.3 (P = 5.55)	gravimet	13
VI-42 ^c		C ₆ F ₁₄ :CH ₃ CN	91.8:8.2 (P = 11.2)	gravimet	13
VI-43 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ CN	96.8:3.2 (P = 29.9)	gravimet	13
VI-44 ^c		C ₆ F ₁₄ :C ₂ H ₅ OH	85.7:14.3 (P = 5.98)	gravimet	13
VI-45 ^c		CF ₃ C ₆ F ₁₁ :C ₂ H ₅ OH	91.7:8.3 (P = 11.0)	gravimet	13
VI-46 ^c		C ₆ F ₁₄ :CH ₃ OH	89.9:10.1 (P = 8.89)	gravimet	13
VI-47 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ OH	96.5:3.5 (P = 27.3)	gravimet	13
VI-48 ^c		C ₆ F ₁₄ : <i>c</i> -C ₆ H ₁₂	48:52 (P = 0.91)	gravimet	13
VI-49 ^c		CF ₃ C ₆ F ₁₁ : <i>c</i> -C ₆ H ₁₂	74.1:25.9 (P = 2.86)	gravimet	13
VI-50 ^c		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	53.1:46.9 (P = 1.13)	gravimet	13
VI-51 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	79.3:20.7 (P = 3.84)	gravimet	13

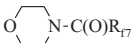
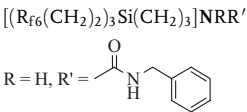
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (<i>P</i>)	Method	Ref.
VI-52 ^c		C ₆ F ₁₄ :CH ₂ Cl ₂	50.0:45.0 (<i>P</i> = 1.22)	gravimet	13
VI-53 ^c		CF ₃ C ₆ F ₁₁ :CH ₂ Cl ₂	82.4:17.6 (<i>P</i> = 4.68)	gravimet	13
VI-54 ^c		C ₆ F ₁₄ :CHCl ₃	35:65 (<i>P</i> = 0.53)	gravimet	13
VI-55 ^c		CF ₃ C ₆ F ₁₁ :CHCl ₃	62.1:37.9 (<i>P</i> = 1.64)	gravimet	13
VI-56 ^c		C ₆ F ₁₄ :CH ₃ CO ₂ C ₂ H ₅	51.5:48.5 (<i>P</i> = 1.06)	gravimet	13
VI-57 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ CO ₂ C ₂ H ₅	67.5:32.5 (<i>P</i> = 2.08)	gravimet	13
VI-58 ^c		C ₆ F ₁₄ :THF	33:67 (<i>P</i> = 0.50)	gravimet	13
VI-59 ^c		CF ₃ C ₆ F ₁₁ :THF	51.0:49.0 (<i>P</i> = 1.04)	gravimet	13
VI-60 ^c		C ₆ F ₁₄ :CH ₃ COCH ₃	63.9:36.1 (<i>P</i> = 1.77)	gravimet	13
VI-61 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ COCH ₃	72.9:27.1 (<i>P</i> = 2.69)	gravimet	13
VI-62 ^c		C ₆ F ₁₄ :CH ₃ CN	93.5:6.5 (<i>P</i> = 14.3)	gravimet	13
VI-63 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ CN	94.3:5.7 (<i>P</i> = 16.4)	gravimet	13
VI-64 ^c		C ₆ F ₁₄ :C ₂ H ₅ OH	89.3:10.7 (<i>P</i> = 8.35)	gravimet	13
VI-65 ^c		CF ₃ C ₆ F ₁₁ :C ₂ H ₅ OH	91.8:8.2 (<i>P</i> = 11.2)	gravimet	13
VI-66 ^c		C ₆ F ₁₄ :CH ₃ OH	95.1:4.9 (<i>P</i> = 19.5)	gravimet	13
VI-67 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ OH	97.1:2.9 (<i>P</i> = 33.7)	gravimet	13
VI-68 ^c		C ₆ F ₁₄ : <i>c</i> -C ₆ H ₁₂	89.2:10.8 (<i>P</i> = 8.26)	gravimet	13
VI-69 ^c		CF ₃ C ₆ F ₁₁ : <i>c</i> -C ₆ H ₁₂	84.3:15.7 (<i>P</i> = 5.37)	gravimet	13
VI-70 ^c		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	64.0:36.0 (<i>P</i> = 1.78)	gravimet	13
VI-71 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	74.2:25.8 (<i>P</i> = 2.87)	gravimet	13
VI-72 ^c		C ₆ F ₁₄ :CH ₂ Cl ₂	38:62 (<i>P</i> = 0.61)	gravimet	13
VI-73 ^c		CF ₃ C ₆ F ₁₁ :CH ₂ Cl ₂	66.2:33.8 (<i>P</i> = 1.96)	gravimet	13

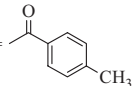
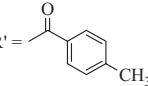
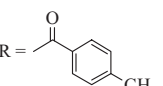
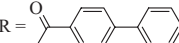
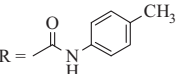
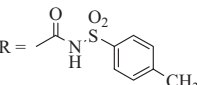
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
VI-74 ^c		C ₆ F ₁₄ :CHCl ₃	41:59 (P = 0.69)	gravimet	13
VI-75 ^c		CF ₃ C ₆ F ₁₁ :CHCl ₃	46:54 (P = 0.86)	gravimet	13
VI-76 ^c		C ₆ F ₁₄ :CH ₃ CO ₂ C ₂ H ₅	22:78 (P = 0.29)	gravimet	13
VI-77 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ CO ₂ C ₂ H ₅	37:63 (P = 0.58)	gravimet	13
VI-78 ^c		C ₆ F ₁₄ :THF	27:73 (P = 0.37)	gravimet	13
VI-79 ^c		CF ₃ C ₆ F ₁₁ :THF	35:65 (P = 0.55)	gravimet	13
VI-80 ^c		C ₆ F ₁₄ :CH ₃ COCH ₃	20:80 (P = 0.25)	gravimet	13
VI-81 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ COCH ₃	36:64 (P = 0.57)	gravimet	13
VI-82 ^c		C ₆ F ₁₄ :CH ₃ CN	77.4:22.6 (P = 3.42)	gravimet	13
VI-83 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ CN	82.8:17.2 (P = 4.81)	gravimet	13
VI-84 ^c		C ₆ F ₁₄ :C ₂ H ₅ OH	76.7:23.3 (P = 3.29)	gravimet	13
VI-85 ^c		CF ₃ C ₆ F ₁₁ :C ₂ H ₅ OH	81.7:18.3 (P = 4.46)	gravimet	13
VI-86 ^c		C ₆ F ₁₄ :CH ₃ OH	82.3:17.7 (P = 4.65)	gravimet	13
VI-87 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ OH	91.7:8.3 (P = 11.1)	gravimet	13
VI-88 ^c		C ₆ F ₁₄ :c-C ₆ H ₁₂	93.6:6.4 (P = 14.62)	gravimet	13
VI-89 ^c		CF ₃ C ₆ F ₁₁ :c-C ₆ H ₁₂	93.3:6.7 (P = 13.92)	gravimet	13
VI-90 ^c		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	84.6:15.4 (P = 5.49)	gravimet	13
VI-91 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	90.5:9.5 (P = 9.53)	gravimet	13
VI-92 ^c		C ₆ F ₁₄ :CH ₂ Cl ₂	80.0:20.0 (P = 4.00)	gravimet	13
VI-93 ^c		CF ₃ C ₆ F ₁₁ :CH ₂ Cl ₂	86.1:13.9 (P = 6.21)	gravimet	13
VI-94 ^c		C ₆ F ₁₄ :CHCl ₃	71.8:28.2 (P = 2.55)	gravimet	13
VI-95 ^c		CF ₃ C ₆ F ₁₁ :CHCl ₃	73.0:27.0 (P = 2.70)	gravimet	13

Tab. 6-1. (continued)

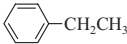





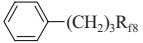
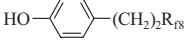
Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (<i>P</i>)	Method	Ref.
VI-96 ^c		C ₆ F ₁₄ :CH ₃ CO ₂ C ₂ H ₅	56.9:43.1 (<i>P</i> = 1.32)	gravimet	13
VI-97 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ CO ₂ C ₂ H ₅	67.1:32.9 (<i>P</i> = 2.04)	gravimet	13
VI-98 ^c		C ₆ F ₁₄ :THF	56.5:43.5 (<i>P</i> = 1.30)	gravimet	13
VI-99 ^c		CF ₃ C ₆ F ₁₁ :THF	75.1:24.9 (<i>P</i> = 3.02)	gravimet	13
VI-100 ^c		C ₆ F ₁₄ :CH ₃ COCH ₃	60.0:40.0 (<i>P</i> = 1.50)	gravimet	13
VI-101 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ COCH ₃	71.1:28.9 (<i>P</i> = 2.46)	gravimet	13
VI-102 ^c		C ₆ F ₁₄ :CH ₃ CN	90.0:10.0 (<i>P</i> = 9.00)	gravimet	13
VI-103 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ CN	94.2:5.8 (<i>P</i> = 16.2)	gravimet	13
VI-104 ^c		C ₆ F ₁₄ :C ₂ H ₅ OH	88.5:11.5 (<i>P</i> = 7.69)	gravimet	13
VI-105 ^c		CF ₃ C ₆ F ₁₁ :C ₂ H ₅ OH	91.1:8.9 (<i>P</i> = 10.24)	gravimet	13
VI-106 ^c		C ₆ F ₁₄ :CH ₃ OH	92.1:7.9 (<i>P</i> = 11.7)	gravimet	13
VI-107 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ OH	95.4:4.6 (<i>P</i> = 20.7)	gravimet	13
VI-108 ^c	R ₇ C(O)NH(CH ₃)	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	55:45 (<i>P</i> = 1.2) ^d	GLC	4a
VI-109 ^c	R ₇ C(O)N(CH ₃) ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	58:42 (<i>P</i> = 1.4) ^d	GLC	4a
VI-110 ^c	 N-C(O)R ₇	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	35:65 (<i>P</i> = 0.54) ^d	GLC	4a
VI-111 ^c	[R _{f8} (CH ₂) ₃] ₂ C(CO ₂ CH ₂ CH ₃) ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	85.1:14.9 (<i>P</i> = 5.70) ^d	gravimet	14
VI-112 ^c	[R _{f8} (CH ₂) ₃] ₂ CH(CO ₂ H)	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	97.1:2.9 (<i>P</i> = 33.1) ^d	gravimet	14
VI-113 ^j		C ₆ F ₁₄ :CHCl ₃	21:79 (<i>P</i> = 0.27)	gravimet or HPLC	15
VI-114 ⁱ		C ₆ F ₁₄ :CH ₃ CN	50.0:50.0 (<i>P</i> = 1.00)	gravimet or HPLC	15
VI-115 ^j		C ₆ F ₁₄ :CH ₃ OH	21:79 (<i>P</i> = 0.27)	gravimet or HPLC	15

Tab. 6-1. (continued)

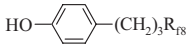
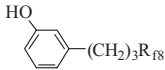
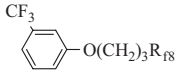
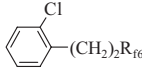
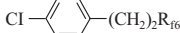
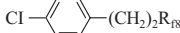
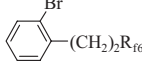
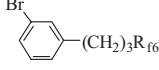
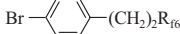
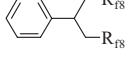
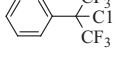
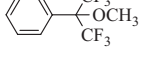
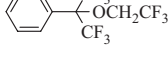
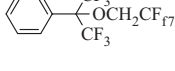
Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
VI-116 ⁱ	R = H, R' = 	C ₆ F ₁₄ :CH ₃ CN	55:45 (P = 1.2)	gravimet or HPLC	15
VI-117 ⁱ		C ₆ F ₁₄ :CH ₃ OH	57:43 (P = 1.3)	gravimet or HPLC	15
VI-118 ⁱ	R = CH ₃ , R' = 	C ₆ F ₁₄ :CH ₃ CN	64:36 (P = 1.8)	gravimet or HPLC	15
VI-119 ⁱ	[(R _{f6} (CH ₂) ₂) ₃ Si(CH ₂) ₃] ₂ NR	C ₆ F ₁₄ :CH ₃ OH	73:27 (P = 2.7)	gravimet or HPLC	15
VI-120 ⁱ	R = 	C ₆ F ₁₄ :CHCl ₃	96:4 (P = 26)	gravimet or HPLC	15
VI-121 ⁱ		C ₆ F ₁₄ :CH ₃ CN	>99.0:<1.0 (P > 100)	gravimet or HPLC	15
VI-122 ⁱ		C ₆ F ₁₄ :CH ₃ OH	>99.0:<1.0 (P > 100)	gravimet or HPLC	15
VI-123 ⁱ		C ₆ F ₁₄ :THF	90:10 (P = 9.0)	gravimet or HPLC	15
VI-124 ⁱ	R = 	C ₆ F ₁₄ :CHCl ₃	86:14 (P = 6)	gravimet or HPLC	15
VI-125 ⁱ		C ₆ F ₁₄ :CH ₃ OH	>99.0:<1.0 (P > 100)	gravimet or HPLC	15
VI-126 ⁱ	R = 	C ₆ F ₁₄ :CHCl ₃	96:4 (P = 27)	gravimet or HPLC	15
VI-127 ⁱ		C ₆ F ₁₄ :CH ₃ CN	>98:<2 (P > 50)	gravimet or HPLC	15
VI-128 ⁱ		C ₆ F ₁₄ :CH ₃ OH	>99.0:<1.0 (P > 100)	gravimet or HPLC	15
VI-129 ⁱ		C ₆ F ₁₄ :THF	92:8 (P = 11)	gravimet or HPLC	15
VI-130 ⁱ	R = 	C ₆ F ₁₄ :CHCl ₃	97:3 (P = 37)	gravimet or HPLC	15
VI-131 ⁱ		C ₆ F ₁₄ :THF	94:6 (P = 16)	gravimet or HPLC	15

for further compounds see X, XIV,
XV and Table 6-2

Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
VII	Arenes, Aryl Halides, Phenols				
VII-1 ^c	C ₆ H ₆	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	6:94 (P = 0.063) ^d	GLC	4a
VII-2	C ₆ HF ₅	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	22.4:77.6 (P = 0.289)	GLC	1
VII-3	C ₆ F ₆	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	28.0:72.0 (P = 0.389)	GLC	1
VII-4		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	1.2:98.8 (P = 0.012)	GLC	1
VII-5		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	0.9:99.1 (P = 0.009)	GLC	1
VII-6 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	12.4:87.6 (P = 0.142) ^d	GLC	4a
VII-7 ⁱ		C ₆ F ₁₄ :CH ₃ CN	12:88 (P = 0.13)	GLC	12
VII-8 ⁱ		C ₆ F ₁₄ :CH ₃ OH	17:83 (P = 0.21)	GLC	12
VII-9 ⁱ		C ₆ F ₁₄ :C ₂ H ₅ OH	15:85 (P = 0.18)	GLC	12
VII-10 ⁱ		C ₆ F ₁₄ :C ₆ H ₆	15:85 (P = 0.18)	GLC	12
VII-11 ⁱ		C ₆ F ₁₄ :CH ₂ Cl ₂	14:86 (P = 0.16)	GLC	12
VII-12 ⁱ		C ₆ F ₁₄ :CH ₃ COCH ₃	7:93 (P = 0.08)	GLC	12
VII-13 ⁱ		C ₆ F ₁₄ :CH ₃ CO ₂ C ₂ H ₅	12:88 (P = 0.13)	GLC	12
VII-14 ⁱ		C ₆ F ₁₄ :CHCl ₃	14:86 (P = 0.16)	GLC	12
VII-15 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	63:37 (P = 1.7) ^d	GLC	4a
VII-16 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	77.5:22.5 (P = 3.46) ^d	GLC	4a
VII-17 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	85.4:14.6 (P = 5.87) ^d	GLC	4a
VII-18		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	49.5:50.5 (P = 0.980)	GLC	1
VII-19		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	20:80 (P = 0.25)	¹ H and ¹⁹ F NMR	16

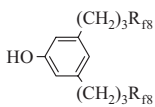
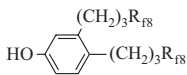
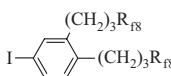
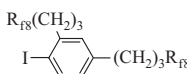
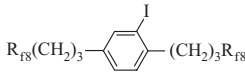
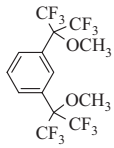
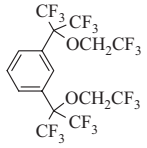
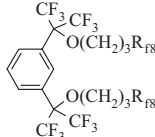
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
VII-20		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	12:88 (P = 0.14)	¹ H and ¹⁹ F NMR	16
VII-21		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	14:86 (P = 0.16)	¹ H and ¹⁹ F NMR	16
VII-22 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	55:45 (P = 1.2) ^d	GLC	11
VII-23 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	35:65 (P = 0.53) ^d	GLC	4a
VII-24 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	26.5:73.5 (P = 0.360) ^d	GLC	4a
VII-25 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	41:59 (P = 0.69) ^d	GLC	4a
VII-26 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	25.9:74.1 (P = 0.350) ^d	GLC	4a
VII-27 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	19.2:80.8 (P = 0.237) ^d	GLC	4a
VII-28 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	18.4:81.6 (P = 0.225) ^d	GLC	4a
VII-29 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	97.9:2.1 (P = 46.6)	GLC	17
VII-30 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	11.5:88.5 (P = 0.130) ^d	GLC	11
VII-31 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	13.8:86.2 (P = 0.160) ^d	GLC	11
VII-32 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	35:65 (P = 0.54) ^d	GLC	11
VII-33 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	87.0:13.0 (P = 6.69) ^d	GLC	11

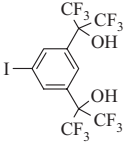
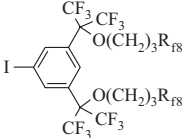
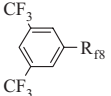
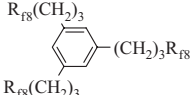
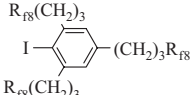
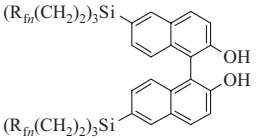
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (<i>P</i>)	Method	Ref.
VII-34 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	81.2:18.8 (<i>P</i> = 4.31) ^d	GLC	11
VII-35 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	80.0:20.0 (<i>P</i> = 4.01) ^d	GLC	11
VII-36 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	76.1:23.9 (<i>P</i> = 3.19) ^d	GLC	11
VII-37 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	81.8:18.2 (<i>P</i> = 4.48) ^d	GLC	4a
VII-38 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	91.5:8.5 (<i>P</i> = 10.7) ^d	GLC	4a
VII-39 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	89.4:10.6 (<i>P</i> = 8.41) ^d	GLC	4a
VII-40 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	99.3:0.7 (<i>P</i> = 145) ^d	GLC	4a
VII-41 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	36:64 (<i>P</i> = 0.57) ^d	GLC	4a
VII-42		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	73.7:26.3 (<i>P</i> = 2.80)	GLC	1
VII-43		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	91.2:8.8 (<i>P</i> = 10.4)	GLC	1
VII-44		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	97.4:2.6 (<i>P</i> = 37.5)	GLC	1
VII-45		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	90.7:9.3 (<i>P</i> = 9.75)	GLC	1
VII-46		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	91.1:8.9 (<i>P</i> = 10.2)	GLC	1

Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
VII-47		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	70:30 (P = 2.3)	¹ H and ¹⁹ F NMR	16
VII-48		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	72:28 (P = 2.6)	¹ H and ¹⁹ F NMR	16
VII-49		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	69.5:30.5 (P = 2.28)	GLC	18
VII-50		CF ₃ C ₆ F ₁₁ :CH ₃ OH	97.0:3.0 (P = 32.3)	GLC	18
VII-51		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	74.7:25.3 (P = 2.95)	GLC	18
VII-52		CF ₃ C ₆ F ₁₁ :CH ₃ OH	98.6:1.4 (P = 70.4)	GLC	18
VII-53		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	73.9:26.1 (P = 2.83)	GLC	18
VII-54		CF ₃ C ₆ F ₁₁ :CH ₃ OH	98.0:2.0 (P = 49.0)	GLC	18
VII-55 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	29:71 (P = 0.41) ^d	GLC	11
VII-56 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	76.7:23.3 (P = 3.29) ^d	GLC	11
VII-57 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	99.1:0.9 (P = 107) ^d	GLC	11

Tab. 6-1. (continued)

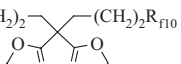
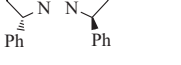
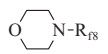
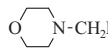
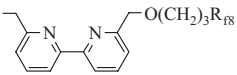
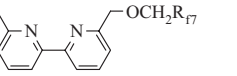
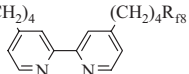
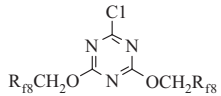
Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
VII-58 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	4:96 (P = 0.044) ^d	GLC	19
VII-59 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.0:2.0 (P = 49.9) ^d	GLC	11
VII-60 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.3:1.7 (P = 58.6) ^d	GLC	4a
VII-61		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	>99.7: <0.3 (P > 332)	GLC	1
VII-62		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.0:2.0 (P = 49.0)	GLC	18
VII-63		CF ₃ C ₆ F ₁₁ :CH ₃ OH	>99.7: <0.3 (P > 332)	GLC	18
VII-64 ^g	n = 6	C ₆ F ₁₄ :CHCl ₃	95:5 (P = 19)	gravimet	20
VII-65 ^g	n = 6	C ₆ F ₁₄ :CH ₃ C ₆ H ₅	98:2 (P = 49)	gravimet	20
VII-66 ^g	n = 8	C ₆ F ₁₄ :CH ₂ Cl ₂	99:1 (P = 99)	gravimet	20
VII-67 ^g	n = 8	C ₆ F ₁₄ :CH ₃ C ₆ H ₅	99:1 (P = 99)	gravimet	20

for further compounds see III, IV, VI,
VIII, X, XI, XIII, XIV, XV and XVI

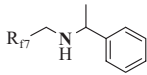
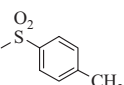
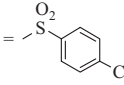
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
VIII Nitrogen Heterocycles					
VIII-1 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	63:37 (P = 1.7) ^d	GLC	4a
VIII-2 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	71:29 (P = 2.4) ^d	GLC	4a
VIII-3 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	69:31 (P = 2.2) ^d	GLC	4a
VIII-4		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	93.8:6.2 (P = 15.1)	GLC	21
VIII-5		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	90.4:9.6 (P = 9.42)	GLC	21
VIII-6		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	93.9:6.1 (P = 15.4)	GLC	21
VIII-7		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	>99.7:<0.3 (P > 332)	GLC	21
VIII-8		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	93.6:6.4 (P = 14.6)	GLC	21
VIII-9		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	79.3:20.7 (P = 3.83)	GLC	21
VIII-10 ^c		C ₈ F ₁₈ :CH ₂ Cl ₂	82:18 (P = 4.7)	gravimet	22
VIII-11 ^c		C ₈ F ₁₈ :CH ₃ CN	94.6:5.4 (P = 17.5)	gravimet	22
VIII-12 ^c		C ₆ F ₁₄ :CH ₂ Cl ₂	14:86 (P = 0.16)	–	23
VIII-13 ^c		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	20:80 (P = 0.25)	–	23

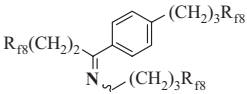
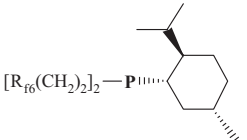
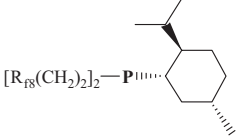
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
VIII-14 ^c	$R_{f10}(CH_2)_2$ 	$C_6F_{14}:CH_2Cl_2$	30:70 ($P = 0.42$)	–	23
VIII-15 ^c		$C_6F_{14}:CH_3C_6H_5$	40:60 ($P = 0.67$)	–	23
VIII-16 ^c		$CF_3C_6F_{11}:CH_3C_6H_5$	71:29 ($P = 2.4$) ^d	GLC	24
VIII-17 ^c		$CF_3C_6F_{11}:CH_3C_6H_5$	55:45 ($P = 1.2$) ^d	GLC	24
VIII-18 ⁱ	$R_{f8}(CH_2)_3O$ 	$n-C_8F_{18}:CH_2Cl_2$	20:80 ($P = 0.25$)	gravimet	25a
VIII-19 ⁱ	$R_{f7}CH_2O$ 	$n-C_8F_{18}:CH_2Cl_2$	51.9:48.1 ($P = 1.08$)	gravimet	25a
VIII-20 ⁱ	$R_{f8}(CH_2)_4$ 	$n-C_8F_{18}:CH_2Cl_2$	40:60 ($P = 0.67$)	gravimet	25a
VIII-21 ^c		$CF_3C_6F_{11}:CH_3C_6H_5$	95.7:4.3 ($P = 22.0$)	gravimet	25b
VIII-22 ^c		$CF_3C_6F_{11}:CH_2Cl_2$	95.2:4.8 ($P = 20.0$)	gravimet	25b
VIII-23 ^c		$CF_3C_6F_{11}:THF$	83.6:16.4 ($P = 5.10$)	gravimet	25b
IX	Aliphatic Halides				
IX-1 ^c	$R_{f6}I$	$CF_3C_6F_{11}:CH_3C_6H_5$	78.8:21.2 ($P = 3.71$) ^d	GLC	4a
IX-2 ^c	$R_{f8}I$	$CF_3C_6F_{11}:CH_3C_6H_5$	88.5:11.5 ($P = 7.69$) ^d	GLC	4a, 24
IX-3 ^c	$R_{f10}I$	$CF_3C_6F_{11}:CH_3C_6H_5$	94.5:5.5 ($P = 17.1$) ^d	GLC	4a
IX-4	$R_{f8}(CH_2)_3I$	$CF_3C_6F_{11}:CH_3C_6H_5$	50.7:49.3 ($P = 1.03$)	GLC	1
	for further compounds see VII				
X	Amines, Imines and related Compounds				
X-1	$R_{f8}(CH_2)_3NH_2$	$CF_3C_6F_{11}:CH_3C_6H_5$	70.0:30.0 ($P = 2.33$)	GLC	4b, 26
X-2	$R_{f8}(CH_2)_4NH_2$	$CF_3C_6F_{11}:CH_3C_6H_5$	63.2:36.8 ($P = 1.72$)	GLC	26

Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
X-3	R _{f8} (CH ₂) ₅ NH ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	56.9:43.1 (P = 1.32)	GLC	26
X-4 ^c	R _{f7} CH ₂ NH(CH ₃)	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	74.5:25.5 (P = 2.92) ^d	GLC	4a, 24
X-5 ^c	R _{f7} 	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	30:70 (P = 0.42) ^d	GLC	24
X-6 ^c	R _{f8} (CH ₂) ₃ NH(CH ₃)	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	71:29 (P = 2.4) ^d	GLC	4b
X-7	[R _{f8} (CH ₂) ₃] ₂ NH	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	96.5:3.5 (P = 27.6)	GLC	4b, 26
X-8	[R _{f8} (CH ₂) ₄] ₂ NH	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	95.1:4.9 (P = 19.4)	GLC	26
X-9	[R _{f8} (CH ₂) ₅] ₂ NH	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	93.0:7.0 (P = 13.3)	GLC	26
X-10 ^c	R _{f7} CH ₂ N(CH ₃) ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	82.2:17.8 (P = 4.62) ^d	GLC	24
X-11 ^c	R _{f8} (CH ₂) ₃ N(CH ₃) ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	79.8:20.2 (P = 3.94) ^d	GLC	4b
X-12 ^c	[R _{f8} (CH ₂) ₃] ₂ N(CH ₃)	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	97.4:2.6 (P = 37.7) ^d	GLC	4b
X-13	[R _{f8} (CH ₂) ₃] ₃ N	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	>99.7: <0.3 (P > 332)	GLC	4b, 26
X-14	[R _{f8} (CH ₂) ₄] ₃ N	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	>99.7: <0.3 (P > 332)	GLC	26
X-15	[R _{f8} (CH ₂) ₅] ₃ N [(R _{f6} (CH ₂) ₂) ₃ Si(CH ₂) ₃]NRR'	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	99.5:0.5 (P = 199)	GLC	26
X-16 ⁱ	R = H, R' = 	C ₆ F ₁₄ :CHCl ₃	42:58 (P = 0.71)	gravimet or HPLC	15
X-17 ⁱ		C ₆ F ₁₄ :CH ₃ CN	27:73 (P = 0.37)	gravimet or HPLC	15
X-18 ⁱ		C ₆ F ₁₄ :CH ₃ OH	67:33 (P = 2.0)	gravimet or HPLC	15
X-19 ⁱ		C ₆ F ₁₄ :THF	5:95 (P = 0.05)	gravimet or HPLC	15
X-20 ⁱ	R = CH ₃ , R' = 	C ₆ F ₁₄ :CHCl ₃	17:83 (P = 0.20)	gravimet or HPLC	15
X-21 ⁱ		C ₆ F ₁₄ :CH ₃ CN	44:56 (P = 0.77)	gravimet or HPLC	15

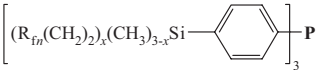
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (<i>P</i>)	Method	Ref.
X-22 ^j		C ₆ F ₁₄ :CH ₃ OH	87:13 (<i>P</i> = 6.5)	gravimet or HPLC	15
X-23 ⁱ		C ₆ F ₁₄ :THF	9:91 (<i>P</i> = 0.10)	gravimet or HPLC	15
X-24	 <p>for further compounds see IV</p>	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.7:1.3 (<i>P</i> = 75.9)	GLC	7, 27
XI	Phosphorus Compounds				
XI-1 ^k	[R _{f6} (CH ₂) ₂] ₃ P	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.8:1.2 (<i>P</i> = 82.3)	GLC	28
XI-2 ^k	[R _{f8} (CH ₂) ₂] ₃ P	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	>99.7:<0.3 (<i>P</i> > 332)	GLC	28
XI-3 ^k	[R _{f10} (CH ₂) ₂] ₃ P	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	>99.7:<0.3 (<i>P</i> > 332)	GLC	28
XI-4 ^k	[R _{f8} (CH ₂) ₃] ₃ P	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.8:1.2 (<i>P</i> = 82.3)	GLC	28
XI-5 ^k	[R _{f8} (CH ₂) ₄] ₃ P	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.9:1.1 (<i>P</i> = 89.9)	GLC	28
XI-6 ^k	[R _{f8} (CH ₂) ₅] ₃ P	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.9:1.1 (<i>P</i> = 89.9)	GLC	29
XI-7 ^k	[R _{f6} (CH ₂) ₂] ₃ P=O	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	>99.7:<0.3 (<i>P</i> > 332)	GLC	28
XI-8 ^k		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	78.4:21.6 (<i>P</i> = 3.63)	GLC	30
XI-9 ^k		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	93.7:6.3 (<i>P</i> = 14.9)	GLC	30
XI-10 ⁱ	(C ₆ H ₅) ₃ P	C ₆ F ₁₄ :C ₅ H ₁₂	<0.5:>99.5 (<i>P</i> < 0.005)	–	31
XI-11	(4-R _{f6} C ₆ H ₄) ₃ P	1,3-(CF ₃) ₂ C ₆ F ₁₀ :CH ₃ C ₆ H ₅	81:19 (<i>P</i> = 4.4)	gravimet	32
XI-12		1,3-(CF ₃) ₂ C ₆ F ₁₀ :THF	69:31 (<i>P</i> = 2.2)	gravimet	32
XI-13	[4-R _{f6} (CH ₂) ₂ C ₆ H ₄] ₃ P	1,3-(CF ₃) ₂ C ₆ F ₁₀ :CH ₃ C ₆ H ₅	47:53 (<i>P</i> = 0.9)	gravimet	32

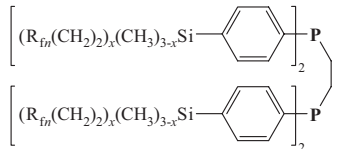
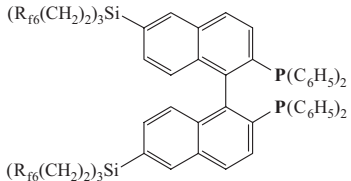
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
XI-14		1,3-(CF ₃) ₂ C ₆ F ₁₀ :THF	17:83 (P = 0.2)	–	32
XI-15 ^g		C ₆ F ₁₄ :CH ₃ OH	96.8:3.2 (P = 30.03)	HPLC	33
XI-16 ^g		C ₆ F ₁₄ :THF	7:93 (P = 0.08)	HPLC	33
XI-17 ^g		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	43:57 (P = 0.75)	HPLC	33
XI-18 ^k	[4-R _{f6} (CH ₂) ₃ C ₆ H ₄] ₃ P	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	19.5:80.5 (P = 0.242)	GLC	34
XI-19 ^k	[4-R _{f8} (CH ₂) ₃ C ₆ H ₄] ₃ P	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	66.6:33.4 (P = 1.99)	GLC	34
XI-20 ^c	[4-R _{f8} (CH ₂) ₃ C ₆ H ₄] ₃ P→BH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	37.3:62.7 (P = 0.595)	³¹ P NMR	17
XI-21 ^c	[4-(R _{f8} CH ₂) ₂ CH(CH ₂) ₃ C ₆ H ₄] ₃ P→BH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	96.6:3.4 (P = 28.4)	¹⁹ F NMR	17
XI-22 ^g	[4-R _{f6} (CH ₂) ₂ C ₆ H ₄] ₂ PC ₆ H ₅	C ₆ F ₁₄ :CH ₃ OH	65.0:35.0 (P = 1.86)	HPLC	33
XI-23 ^g		C ₆ F ₁₄ :THF	5:95 (P = 0.05)	HPLC	33
XI-24 ^g		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	5:95 (P = 0.05)	HPLC	33
XI-25 ^g	4-R _{f6} (CH ₂) ₂ C ₆ H ₄ P(C ₆ H ₅) ₂	C ₆ F ₁₄ :CH ₃ OH	11:89 (P = 0.12)	HPLC	33
XI-26 ^g		C ₆ F ₁₄ :THF	2:98 (P = 0.02)	HPLC	33
XI-27 ^g		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	5:95 (P = 0.05)	HPLC	33
XI-28 ^g	[4-R _{f3} (CF ₃) ₂ CCH ₂ C ₆ H ₄] ₃ P	C ₆ F ₁₄ :CH ₃ OH	94.9:5.1 (P = 18.48)	HPLC	33
XI-29 ^g		C ₆ F ₁₄ :THF	34:66 (P = 0.51)	HPLC	33
XI-30 ^g		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	87.2:12.8 (P = 6.84)	HPLC	33
XI-31 ^g	[4-R _{f3} (CF ₃) ₂ CCH ₂ C ₆ H ₄] ₂ PC ₆ H ₅	C ₆ F ₁₄ :CH ₃ OH	77.0:23.0 (P = 3.34)	HPLC	33
XI-32 ^g		C ₆ F ₁₄ :THF	51.2:48.8 (P = 1.05)	HPLC	33
XI-33 ^g		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	15:85 (P = 0.18)	HPLC	33
XI-34 ^g	4-R _{f3} (CF ₃) ₂ CCH ₂ C ₆ H ₄ P(C ₆ H ₅) ₂	C ₆ F ₁₄ :CH ₃ OH	8:92 (P = 0.09)	HPLC	33
XI-35 ^g		C ₆ F ₁₄ :THF	1:99 (P = 0.01)	HPLC	33
XI-36 ^g		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	11:89 (P = 0.12)	HPLC	33

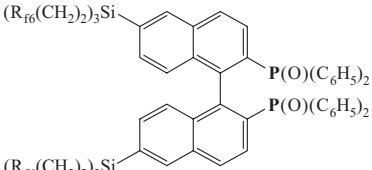
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
XI-37 ⁱ	[4-(CH ₃) ₃ SiC ₆ H ₄] ₃ P	C ₆ F ₁₄ :C ₅ H ₁₂	<4:>96 (P < 0.044)	–	31
XI-38 ⁱ		C ₆ F ₁₄ :n-C ₆ H ₁₄	<1:>90 (P < 0.01)	–	31
					
XI-39 ^m	x = 1, n = 6	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	21:79 (P = 0.26)	ICP-AAS ⁿ	35, 36
XI-40 ^m		CF ₃ C ₆ F ₁₁ :n-C ₈ H ₁₈	52:48 (P = 1.1)	ICP-AAS ⁿ	36
XI-41 ^m		CF ₃ C ₆ F ₁₁ :n-C ₅ H ₁₂	60:40 (P = 1.5)	ICP-AAS ⁿ	36
XI-42 ^m	x = 1, n = 8	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	69:31 (P = 2.2)	ICP-AAS ⁿ	35, 36
XI-43 ^m		CF ₃ C ₆ F ₁₁ :n-C ₈ H ₁₈	82:18 (P = 4.6)	ICP-AAS ⁿ	36
XI-44 ^m		CF ₃ C ₆ F ₁₁ :n-C ₅ H ₁₂	69:31 (P = 2.2)	ICP-AAS ⁿ	36
XI-45 ⁱ		C ₆ F ₁₄ :C ₅ H ₁₂	12:88 (P = 0.14)	–	31
XI-46 ⁱ		C ₆ F ₁₄ :n-C ₆ H ₁₄	43.5:56.5 (P = 0.770)	–	31
XI-47 ^m	x = 2, n = 6	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	89:11 (P = 7.8)	ICP-AAS ⁿ	36
XI-48 ^m		CF ₃ C ₆ F ₁₁ :n-C ₈ H ₁₈	94:6 (P = 17)	ICP-AAS ⁿ	36
XI-49 ^m		CF ₃ C ₆ F ₁₁ :n-C ₅ H ₁₂	85:15 (P = 5.7)	ICP-AAS ⁿ	36
XI-50 ^m	x = 2, n = 8	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	89:11 (P = 7.8)	ICP-AAS ⁿ	36
XI-51 ^m		CF ₃ C ₆ F ₁₁ :n-C ₈ H ₁₈	97:3 (P = 28)	ICP-AAS ⁿ	36
XI-52 ^m		CF ₃ C ₆ F ₁₁ :n-C ₅ H ₁₂	90:10 (P = 9.2)	ICP-AAS ⁿ	36
XI-53 ^m	x = 3, n = 6	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	81:19 (P = 4.3)	ICP-AAS ⁿ	36
XI-54 ^m		CF ₃ C ₆ F ₁₁ :n-C ₈ H ₁₈	90:10 (P = 9.4)	ICP-AAS ⁿ	36
XI-55 ^m		CF ₃ C ₆ F ₁₁ :n-C ₅ H ₁₂	94:6 (P = 15)	ICP-AAS ⁿ	36
XI-56 ^m	x = 3, n = 8	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	68:32 (P = 2.1)	ICP-AAS ⁿ	36
XI-57 ^m		CF ₃ C ₆ F ₁₁ :n-C ₈ H ₁₈	92:8 (P = 12)	ICP-AAS ⁿ	36

Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
XI-58 ^m		CF ₃ C ₆ F ₁₁ :n-C ₅ H ₁₂	95:5 (P = 20)	ICP-AAS ⁿ	36
XI-59 ^m	x = 0	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	0:100 (P = 0.0)	gravimet	37
XI-60 ^m	x = 1, n = 6	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	29:71 (P = 0.4)	gravimet	37
XI-61 ^m	x = 2, n = 6	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	92:8 (P = 12)	gravimet	37
XI-62 ^m	x = 3, n = 6	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	>98:<2 (P > 50)	gravimet	37
XI-63 ^c	(4-R _{f7} CH ₂ OC ₆ H ₄) ₂ PC ₆ H ₅	Galden D-100:C ₂ H ₅ OH	62:38 (P = 1.6)	gravimet or ICP-AES ^o	38
XI-64 ^c	(4-R _{f7} CH ₂ OC ₆ H ₄) ₃ P	Galden D-100:C ₂ H ₅ OH	96.1:3.9 (P = 24.6)	gravimet or ICP-AES ^o	38
XI-65 ^c		Galden D-100:THF	38:62 (P = 0.6)	gravimet or ICP-AES ^o	38
XI-66 ^c		Galden D-100:CH ₃ C ₆ H ₅	91.2:8.8 (P = 10.4)	gravimet or ICP-AES ^o	38
XI-67 ^c		Galden D-100:CH ₃ CN	52:48 (P = 1.1)	gravimet or ICP-AES ^o	38
XI-68 ^c		Galden D-100:CH ₃ CO ₂ C ₂ H ₅	41:59 (P = 0.7)	gravimet or ICP-AES ^o	38
XI-69 ^c	(3-R _{f7} CH ₂ OC ₆ H ₄) ₃ P	Galden D-100:C ₂ H ₅ OH	89:11 (P = 8.0)	gravimet or ICP-AES ^o	38
XI-70 ^c	(2-R _{f7} CH ₂ OC ₆ H ₄) ₃ P	Galden D-100:C ₂ H ₅ OH	89:11 (P = 7.7)	gravimet or ICP-AES ^o	38
XI-71 ^c	[4-R _{f8} (CH ₂) ₃ OC ₆ H ₄] ₃ P	Galden D-100:C ₂ H ₅ OH	94.9:5.1 (P = 18.6)	gravimet or ICP-AES ^o	38
XI-72 ^g		C ₆ F ₁₄ :C ₆ H ₆	74:26 (P = 2.9)	HPLC	20
XI-73 ^g		C ₆ F ₁₄ :C ₆ H ₆	79:21 (P = 3.8)	gravimet	20
XI-74 ^g		C ₆ F ₁₄ :CH ₃ CN	98:2 (P = 49)	HPLC	20
XI-75 ^g		C ₆ F ₁₄ :DMF	98:2 (P = 49)	HPLC	20

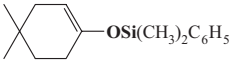

Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
XI-76 ^g	 $(R_{16}(CH_2)_2)_3Si$	$C_6F_{14}:CH_2Cl_2$	76:24 (P = 3.2)	gravimet	20
XI-77 ^g		$C_6F_{14}:C_6H_6$	90:10 (P = 9.0)	gravimet	20
XI-78 ^g	$[2-R_{f8}(CH_2)_2C_6H_4O]_3P$	$C_8F_{17}H:C_8H_{17}CH=CH_2$	95:5 (P = 19)	GLC	39
XI-79 ^g	$[4-R_{f8}(CH_2)_2C_6H_4O]_3P$	$C_8F_{17}H:C_8H_{17}CH=CH_2$	95:5 (P = 19)	GLC	39
XI-80 ^g	$[2,4-(R_{f8}(CH_2)_2)_2C_6H_3O]_3P$	$C_8F_{17}H:C_8H_{17}CH=CH_2$	99:1 (P = 99)	GLC	39
XI-81	$[3,5-(R_{f8}(CH_2)_2)_2C_6H_3O]_3P$	$CF_3C_6F_{11}:CH_3C_6H_5$	92:8 (P = 12)	¹ H and ¹⁹ F NMR	16
XII	Tin Compounds				
XII-1 ^g	$[CH_3(CH_2)_3]_3SnH$	$C_6F_{14}:CH_3CN$	<0.7:>99.3 (P < 0.007)	gravimet	40
XII-2 ^g		$C_6F_{14}:C_6H_6$	<0.3:>99.7 (P < 0.003)	gravimet	40
XII-3 ^g	$[R_{f4}(CH_2)_2]_3SnH$	$C_6F_{14}:CH_3CN$	85:15 (P = 5.8)	gravimet	40
XII-4 ^g		$C_6F_{14}:C_6H_6$	91.3:8.7 (P = 10.5)	gravimet	40
XII-5 ⁱ	$[R_{f6}(CH_2)_2]_3SnH$	$CF_3C_6F_{11}:C_6H_6$	97.8:2.2 (P = 44.5)	gravimet	41
XII-6 ^j		$CF_3C_6F_{11}:CH_3OH$	97.0:3.0 (P = 32.3)	gravimet	41
XII-7 ⁱ		$CF_3C_6F_{11}:CH_2Cl_2$	95.3:4.7 (P = 20.3)	gravimet	41
XII-8 ^j		$CF_3C_6F_{11}:CH_3CO_2C_2H_5$	89.6:10.4 (P = 8.62)	gravimet	41
XII-9 ⁱ		$CF_3C_6F_{11}:CHCl_3$	85.9:14.1 (P = 6.09)	gravimet	41
XII-10 ^g		$C_6F_{14}:CH_3CN$	99.4:0.6 (P = 160)	gravimet	40
XII-11 ^g		$C_6F_{14}:C_6H_6$	98:2 (P = 45)	gravimet	40
XII-12 ^g	$[R_{f4}(CH_2)_2]_3SnH$	$C_6F_{14}:CH_3CN$	70:30 (P = 2.3)	gravimet	40
XII-13 ^g		$C_6F_{14}:C_6H_6$	55:45 (P = 1.2)	gravimet	40

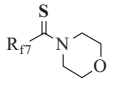
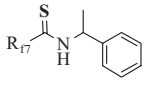
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
XII-14 ⁸	[R _{f6} (CH ₂) ₃ SnH	C ₆ F ₁₄ :CH ₃ CN	86:14 (P = 6.4)	gravimet	40
XII-15 ⁸		C ₆ F ₁₄ :C ₆ H ₆	90.9:9.1 (P = 10.0)	gravimet	40
XII-16 ⁸	[R _{f6} (CH ₂) ₂ Sn(CH ₃) ₂ H	C ₆ F ₁₄ :CH ₃ CN	71:29 (P = 2.4)	GLC	40
XII-17 ⁸		C ₆ F ₁₄ :C ₆ H ₆	41:59 (P = 0.7)	GLC	40
XII-18 ⁸	[R _{f8} (CH ₂) ₂ Sn(CH ₃) ₂ H	C ₆ F ₁₄ :CH ₃ CN	93:7 (P = 14)	GLC	40
XII-19 ⁸		C ₆ F ₁₄ :C ₆ H ₆	71:29 (P = 2.5)	GLC	40
XII-20 ⁸	[R _{f10} (CH ₂) ₂ Sn(CH ₃) ₂ H	C ₆ F ₁₄ :CH ₃ CN	98:2 (P = 48)	GLC	40
XII-21 ⁸		C ₆ F ₁₄ :C ₆ H ₆	82:18 (P = 4.7)	GLC	40
XII-22 ⁱ	[R _{f4} (CH ₂) ₂] ₃ SnCH ₂ CH=CH ₂	C ₆ F ₁₄ :CH ₃ CN	86:14 (P = 6)	gravimet	42
XII-23 ⁱ		C ₆ F ₁₄ :C ₆ H ₆	90:10 (P = 9)	gravimet	42
XII-24 ⁱ	[R _{f6} (CH ₂) ₂] ₃ SnCH ₂ CH=CH ₂	C ₆ F ₁₄ :CH ₃ CN	99:1 (P = 96)	gravimet	42
XII-25 ⁱ		C ₆ F ₁₄ :C ₆ H ₆	98:2 (P = 48)	gravimet	42
XII-26 ⁱ	[R _{f4} (CH ₂) ₃] ₃ SnCH ₂ CH=CH ₂	C ₆ F ₁₄ :CH ₃ CN	93:7 (P = 14)	gravimet	42
XII-27 ⁱ		C ₆ F ₁₄ :C ₆ H ₆	80:20 (P = 4)	gravimet	42
XII-28 ⁱ	[R _{f6} (CH ₂) ₃] ₃ SnCH ₂ CH=CH ₂	C ₆ F ₁₄ :CH ₃ CN	98:2 (P = 47)	gravimet	42
XII-29 ⁱ		C ₆ F ₁₄ :C ₆ H ₆	96:4 (P = 25)	gravimet	42
XII-30 ⁱ	[R _{f6} (CH ₂) ₂] ₂ SnO	C ₆ F ₁₄ :CH ₂ Cl ₂	63.0:37.0 (P = 1.70)	–	43
XII-31 ⁱ		C ₆ F ₁₄ :CH ₃ CN	22:78 (P = 0.28)	–	43
XII-32 ⁱ		C ₆ F ₁₄ :CH ₃ C ₆ H ₅	65.5:34.5 (P = 1.90)	–	43
XII-33 ⁱ	[Cl(R _{f6} (CH ₂) ₂) ₂ Sn] ₂ O	C ₆ F ₁₄ :CH ₃ C ₆ H ₅	99:1 (P = 99)	–	44
XII-34 ⁱ		C ₆ F ₁₄ :CH ₂ Cl ₂	99:1 (P = 99)	–	44
XII-35 ⁱ		C ₆ F ₁₄ :CH ₃ OH	98:2 (P = 49)	–	44

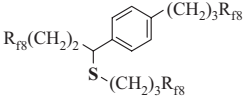
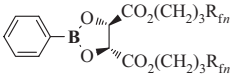
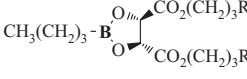
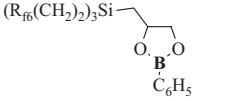
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
XIII Silicon Compounds					
XIII-1	HSi(CH ₃) ₂ C ₆ H ₅	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	3.6:96.4 (P = 0.037)	GLC	45a
XIII-2 ^m	R _{f6} (CH ₂) ₂ Si(CH ₃) ₂ Cl	C ₆ F ₁₄ :CH ₃ C ₆ H ₅	66:34 (P = 1.9)	ICP-AAS ⁿ	46
XIII-3 ^m	R _{f8} (CH ₂) ₂ Si(CH ₃) ₂ Cl	C ₆ F ₁₄ :CH ₃ C ₆ H ₅	83:17 (P = 4.8)	gravimet	46
XIII-4 ^m	R _{f10} (CH ₂) ₂ Si(CH ₃) ₂ Cl	C ₆ F ₁₄ :CH ₃ C ₆ H ₅	95:5 (P = 18)	gravimet	46
XIII-5 ^m	R _{f6} (CH ₂) ₂ Si(CH ₃)Cl ₂	C ₆ F ₁₄ :CH ₃ C ₆ H ₅	74:26 (P = 2.8)	ICP-AAS ⁿ	46
XIII-6 ^m	R _{f6} (CH ₂) ₂ SiCl ₃	C ₆ F ₁₄ :CH ₃ C ₆ H ₅	83:17 (P = 4.8)	ICP-AAS ⁿ	46
XIII-7		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	0.6:99.4 (P = 0.006)	GLC	45a
XIII-8		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	0.8:99.2 (P = 0.008)	GLC	45b
XIII-9 ^P	ROSi[CH(CH ₃) ₂] ₂ (CH ₂) ₂ R' R = 2-(2-naphthyl)ethyl; R' = R _{f8}	C ₆ F ₁₄ :CH ₃ OH	48:52 (P = 0.92)	HPLC	47
XIII-10 ^P		C ₆ F ₁₄ :C ₂ H ₅ OH	48:52 (P = 0.91)	HPLC	47
XIII-11 ^P		C ₆ F ₁₄ :CH ₃ CN	43:57 (P = 0.74)	HPLC	47
XIII-12 ^P		C ₆ F ₁₄ :DMF	28:72 (P = 0.38)	HPLC	47
XIII-13 ^P		C ₆ F ₁₄ :CH ₂ Cl ₂	12:88 (P = 0.14)	HPLC	47
XIII-14 ^P		C ₆ F ₁₄ :THF	3:97 (P = 0.035)	HPLC	47
XIII-15 ^P	R = 2-(2-naphthyl)ethyl; R' = R _{f10}	C ₆ F ₁₄ :CH ₃ OH	73:27 (P = 2.7)	HPLC	47
XIII-16 ^P	R = 2-(2-naphthyl)ethyl; R' = R _{f6}	C ₆ F ₁₄ :CH ₃ OH	28:72 (P = 0.39)	HPLC	47
XIII-17 ^P	R = 2-(2-naphthyl)ethyl; R' = R _{f4}	C ₆ F ₁₄ :CH ₃ OH	11:89 (P = 0.12)	HPLC	47
XIII-18 ^P	R = (S)-(-)-1-(2-naphthyl)ethyl; R' = R _{f8}	C ₆ F ₁₄ :CH ₃ OH	60:40 (P = 1.5)	HPLC	47
XIII-19 ^P	R = C ₆ H ₅ CH=CHCH ₂ ; R' = R _{f8}	C ₆ F ₁₄ :CH ₃ OH	57:43 (P = 1.3)	HPLC	47
XIII-20 ^P	R = C ₆ H ₅ (CH ₂) ₆ ; R' = R _{f8}	C ₆ F ₁₄ :CH ₃ OH	42:58 (P = 0.72)	HPLC	47

Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
XIII-21 ^P	R = CH ₃ (CH ₂) ₁₁ ; R' = R _{f8}	C ₆ F ₁₄ :CH ₃ OH	89:11 (P = 8.2)	gravimet	47
XIII-22 ^P	R = cholestanyl; R' = R _{f8}	C ₆ F ₁₄ :CH ₃ OH	83:17 (P = 5.0)	HPLC	47
XIII-23 ^P	R = 2-adamantylethyl; R' = R _{f8}	C ₆ F ₁₄ :CH ₃ OH	85:15 (P = 5.7)	gravimet	47
XIII-24 ^P	R = 2-adamantylethyl; R' = R _{f6}	C ₆ F ₁₄ :CH ₃ OH	66:34 (P = 1.9)	gravimet	47
XIII-25 ^P	R = mappicine; R' = R _{f8}	C ₆ F ₁₄ :CH ₃ OH	10:90 (P = 0.11)	HPLC	47
XIII-26 ^m	R _{f6} (CH ₂) ₂ Si(OCH ₃) ₃	C ₆ F ₁₄ :CH ₃ C ₆ H ₅	52:48 (P = 1.1)	gravimet	46
	for further compounds see IV, VI, VII, X, XI, XV and XVI				
XIV	Sulfur Compounds				
XIV-1 ^c	HS(CH ₂) ₂ C(O)OCH ₂ CH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	0.5:99.5 (P = 0.0054) ^d	GLC	24
XIV-2 ^c	R _{f8} (CH ₂) ₃ SH	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	56:44 (P = 1.3) ^d	GLC	4a
XIV-3 ^c	R _{f6} S(CH ₂) ₂ C(O)OCH ₂ CH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	34:66 (P = 0.51) ^d	GLC	4a
XIV-4 ^c	R _{f8} S(CH ₂) ₂ C(O)OCH ₂ CH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	50:50 (P = 1.0) ^d	GLC	24
XIV-5 ^c	CF ₃ SC ₆ H ₅	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	8:92 (P = 0.086) ^d	GLC	4a
XIV-6 ^c	CF ₃ S(3-C ₆ H ₄ CF ₃)	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	17.1:82.9 (P = 0.206) ^d	GLC	4a
XIV-7 ^c	R _{f8} SC ₆ H ₅	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	64:36 (P = 1.8) ^d	GLC	4a
XIV-8 ^c	R _{f7} C(O)SCH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	76.1:23.9 (P = 3.19) ^d	GLC	24
XIV-9 ^c	R _{f7} C(S)OCH ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	74.6:25.4 (P = 2.94) ^d	GLC	24
XIV-10 ^c	R _{f7} C(S)N(CH ₃) ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	34:66 (P = 0.52) ^d	GLC	24
XIV-11 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	17.4:82.6 (P = 0.210) ^d	GLC	24
XIV-12 ^c		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	13.7:86.3 (P = 0.159) ^d	GLC	24
XIV-13	[R _{f8} (CH ₂) ₂] ₂ S	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.7:1.3 (P = 75.9)	GLC	48

Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (<i>P</i>)	Method	Ref.
XIV-14	$[\text{R}_{18}(\text{CH}_2)_3]_2\text{S}$	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	96.6:3.4 (<i>P</i> = 28.4)	GLC	48
XIV-15		$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	99.5:0.5 (<i>P</i> = 199)	GLC	7
	for further compounds see VI and X				
XV	Boron Compounds				
					
XV-1 ^c	<i>n</i> = 6	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	11.6:88.4 (<i>P</i> = 0.131) ^d	GLC	19
XV-2 ^c	<i>n</i> = 8	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	24.4:75.6 (<i>P</i> = 0.323) ^d	GLC	19
XV-3 ^c	<i>n</i> = 10	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	39:61 (<i>P</i> = 0.63) ^d	GLC	19
					
XV-4 ^c	<i>n</i> = 6	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	21.6:78.4 (<i>P</i> = 0.275) ^d	GLC	19
XV-5 ^c	<i>n</i> = 8	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	46:54 (<i>P</i> = 0.86) ^d	GLC	19
XV-6 ^c	<i>n</i> = 10	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	76.1:23.9 (<i>P</i> = 3.19) ^d	GLC	19
XV-7 ^l		$\text{FC-77}:\text{CH}_3\text{CN}$	93.0:7.0 (<i>P</i> = 13.3)	–	49
XV-8 ^l		$\text{FC-77}:\text{CH}_2\text{Cl}_2$	88.3:11.7 (<i>P</i> = 7.53)	–	49
XV-9 ^l		$\text{FC-77}:\text{CHCl}_3$	84.4:15.6 (<i>P</i> = 5.43)	–	49
XV-10 ^l		$\text{FC-77}:\text{C}_6\text{H}_{14}$	86.7:13.3 (<i>P</i> = 6.50)	–	49
XV-11 ^l		$\text{FC-77}:\text{CH}_3\text{CO}_2\text{C}_2\text{H}_5$	47:53 (<i>P</i> = 0.88)	–	49
XV-12 ^l		$\text{FC-77}:\text{CH}_3\text{COCH}_3$	73.2:26.8 (<i>P</i> = 2.73)	–	49

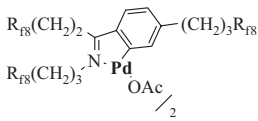
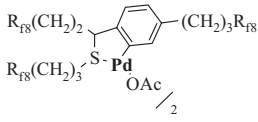
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
XV-13 ^l		FC-77:CH ₃ C ₆ H ₅	88.5:11.5 (P = 7.69)	–	49
XV-14 ^l		FC-77:THF	74.4:25.6 (P = 2.91)	–	49
	for further compounds see XI and XVI				
XVI	Transition Metal Compounds				
XVI-1 ^j	Rh ₂ (O ₂ CR _{f7}) ₄	CF ₃ C ₆ F ₁₁ :Et ₂ O	83:17 (P = 4.9)	gravimet	50
XVI-2 ^j		CF ₃ C ₆ F ₁₁ :CH ₂ Cl ₂	94.9:5.1 (P = 18.7)	gravimet	50
XVI-3 ^j		CF ₃ C ₆ F ₁₁ :C ₆ H ₁₄	96.7:3.3 (P = 29.4)	gravimet	50
XVI-4 ^j		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	95.0:5.0 (P = 18.9)	gravimet	50
XVI-5 ⁱ	Rh ₂ (O ₂ CCH ₂ R _{f6}) ₄	CF ₃ C ₆ F ₁₁ :Et ₂ O	38:62 (P = 0.6)	gravimet	50
XVI-6 ^j		CF ₃ C ₆ F ₁₁ :CH ₂ Cl ₂	89:11 (P = 8.5)	gravimet	50
XVI-7 ^j		CF ₃ C ₆ F ₁₁ :C ₆ H ₁₄	96.6:3.4 (P = 28.7)	gravimet	50
XVI-8 ^j		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	96.3:3.7 (P = 25.7)	gravimet	50
XVI-9 ^k	[(R _{f6} (CH ₂) ₂) ₃ P] ₃ RhCl	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	99.86:0.14 (P = 713)	ICP-AES ^o	51
XVI-10 ^k	[(R _{f8} (CH ₂) ₂) ₃ P] ₃ RhCl	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	99.88:0.12 (P = 832)	ICP-AES ^o	51
XVI-11 ^k	[(R _{f6} (CH ₂) ₂) ₃ P] ₃ Rh(H)(CO)	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	99.5:0.5 (P = 190) ^d	GLC	4a, 52a
	(Ar ₃ P) ₃ RhCl				
XVI-12 ^m	Ar = 4-C ₆ H ₄ Si(CH ₃) ₂ (CH ₂) ₂ R _{f6}	CF ₃ C ₆ F ₁₁ : <i>n</i> -C ₈ H ₁₈	99.7:0.3 (P = 293)	ICP-AAS ⁿ	35
XVI-13 ^c		CF ₃ C ₆ F ₁₁ : <i>n</i> -C ₈ H ₁₈	98.7:1.3 (P = 76)	ICP-AAS ⁿ	35
XVI-14 ^m	Ar = 4-C ₆ H ₄ Si(CH ₃) ₂ (CH ₂) ₂ R _{f8}	CF ₃ C ₆ F ₁₁ : <i>n</i> -C ₈ H ₁₈	99.9:0.1 (P = 887)	ICP-AAS ⁿ	35
XVI-15 ⁱ	[R _{f10} (CH ₂) ₂ C ₅ H ₄]Rh(CO) ₂	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	44:56 (P = 0.8)	ICP-AES ^o	52a
XVI-16 ⁱ	[R _{f10} (CH ₂) ₂ C ₅ H ₄]Rh(CO)[P((CH ₂) ₂ R _{f6}) ₃]	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	96.7:3.3 (P = 29)	ICP-AES ^o	52a
	[Rh(COD)(Ar ₂ P(CH ₂) ₂ PAr ₂)] ⁺ X ⁻				
XVI-17 ^m	Ar = C ₆ H ₅ X ⁻ = [B(3,5-C ₆ H ₃ (R _{f6}) ₂) ₄] ⁻	CF ₃ C ₆ F ₁₁ :THF	<1:>99 (P < 0.01)	ICP-AAS ⁿ	53
XVI-18 ^m		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	41:59 (P = 0.7)	ICP-AAS ⁿ	53

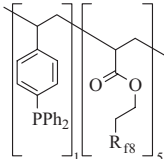
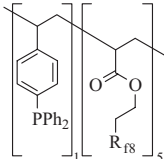
Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
XVI-19 ^m	Ar = 4-C ₆ H ₄ [Si(CH ₃) ₂ (CH ₂) ₂ R _{f6}] X ⁻ = [B(3,5-C ₆ H ₃ (R _{f6}) ₂) ₄] ⁻	CF ₃ C ₆ F ₁₁ :THF	68:32 (P = 2.1)	ICP-AAS ⁿ	53
XVI-20 ^m		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	97.1:2.9 (P = 34)	ICP-AAS ⁿ	53
XVI-21 ^m	Ar = 4-C ₆ H ₄ [Si(CH ₃) ₂ (CH ₂) ₂ R _{f6}] X ⁻ = BF ₄ ⁻	CF ₃ C ₆ F ₁₁ :THF	89:11 (P = 8.1)	ICP-AAS ⁿ	53
XVI-22 ^m		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.4:1.6 (P = 61)	ICP-AAS ⁿ	53
XVI-23 ^m	Ar = 4-C ₆ H ₄ [Si(CH ₃) ₂ (CH ₂) ₂ R _{f6}] X ⁻ = [B(4-C ₆ H ₄ R _{f6}) ₄] ⁻	CF ₃ C ₆ F ₁₁ :THF	86:14 (P = 6.4)	ICP-AAS ⁿ	53
XVI-24 ^m		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.5:1.5 (P = 65)	ICP-AAS ⁿ	53
XVI-25 ^m	Ar = 4-C ₆ H ₄ Si(CH ₂) ₂ R _{f6} ₃ X ⁻ = BF ₄ ⁻	CF ₃ C ₆ F ₁₁ :THF	97.1:2.9 (P = 34)	ICP-AAS ⁿ	53
XVI-26 ^m		CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.5:1.5 (P = 66)	ICP-AAS ⁿ	53
XVI-27 ⁱ	[R _{f10} (CH ₂) ₂ C ₅ H ₄]Mn(CO) ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	64:36 (P = 1.8)	IR	52b
XVI-28 ^g	[(CH ₃ (CH ₂) ₇) ₃ P] ₂ Ir(Cl)(CO)	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	<0.3:>99.7 (P < 0.003)	³¹ P NMR	54
XVI-29 ^g	[(CH ₃ (CH ₂) ₇) ₃ P] ₂ Ir(Cl)(CO)	CF ₃ C ₆ F ₁₁ :THF	<0.3:>99.7 (P < 0.003)	³¹ P NMR	54
XVI-30 ^g	[(R _{f6} (CH ₂) ₂) ₃ P] ₂ Ir(Cl)(CO)	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	>99.7:<0.3 (P > 332)	³¹ P NMR	54
XVI-31 ^g		CF ₃ C ₆ F ₁₁ :CH ₃ COCH ₃	>99.7:<0.3 (P > 332)	³¹ P NMR	54
XVI-32 ^g		CF ₃ C ₆ F ₁₁ :CH ₂ Cl ₂	>99.7:<0.3 (P > 332)	³¹ P NMR	54
XVI-33 ^g		CF ₃ C ₆ F ₁₁ :THF	>99.7:<0.3 (P > 332)	³¹ P NMR	54
XVI-34 ⁱ	[(R _{f6} (CH ₂) ₂) ₃ P] ₂ NiCl ₂ NiCl ₂ [Ar ₂ P(CH ₂) ₂ PAr ₂]	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	98.8:1.2 (P = 83)	ICP-AES ^o	52a
XVI-35 ^m	Ar = 4-C ₆ H ₄ Si(CH ₃) ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	0:100 (P = 0.0)	gravimet	55
XVI-36 ^m	Ar = 4-C ₆ H ₄ [Si(CH ₃) ₂ (CH ₂) ₂ R _{f6}]	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	62:38 (P = 1.6)	gravimet	55
XVI-37 ^m	Ar = 4-C ₆ H ₄ [Si(CH ₃) ₂ (CH ₂) ₂ R _{f8}]	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	79:21 (P = 3.7)	gravimet	55
XVI-38 ^m	Ar = 4-C ₆ H ₄ [Si(CH ₃) ₂ (CH ₂) ₂ R _{f6}]	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	89:11 (P = 8)	gravimet	55
XVI-39 ^m	Ar = 4-C ₆ H ₄ Si(CH ₂) ₂ R _{f6} ₃	CF ₃ C ₆ F ₁₁ :CH ₃ C ₆ H ₅	95.8:4.2 (P = 23)	gravimet	55
XVI-40 ⁱ	Fe[C ₅ H ₄ (CH ₂) ₂ R _{f10}] ₂	C ₇ F ₁₆ :CH ₃ C ₆ H ₅	95.2:4.8 (P = 20)	gravimet	52b

Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
XVI-41 ^c	$\text{Fe}[\text{C}_5\text{H}_3((\text{CH}_2)_2\text{R}_{f4})_2]_2^a$	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	90.9:9.1 (P = 10)	ICP-AAS ⁿ	6
XVI-42 ^c	$\text{Fe}[\text{C}_5\text{H}_3((\text{CH}_2)_2\text{R}_{f6})_2]_2^a$	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	98.6:1.4 (P = 72)	ICP-AAS ⁿ	6
XVI-43 ^c	$\text{Fe}[\text{C}_5\text{H}_3((\text{CH}_2)_2\text{R}_{f4})(\text{CH}_2)_2\text{R}_{f6}]_2^a$	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	94.4:5.6 (P = 17)	ICP-AAS ⁿ	6
XVI-44 ^c	$\text{Fe}[\text{C}_5\text{H}_3((\text{CH}_2)_2\text{R}_{f4})(\text{CH}_2)_2\text{R}_{f8}]_2^a$	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	95.7:4.3 (P = 22)	ICP-AAS ⁿ	6
XVI-45 ^c	$\text{Fe}[\text{C}_5\text{H}_3((\text{CH}_2)_2\text{R}_{f6})(\text{CH}_2)_2\text{R}_{f8}]_2^a$	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	95.7:4.3 (P = 22)	ICP-AAS ⁿ	6
XVI-46 ^g	$[\text{R}_{f6}(\text{CH}_2)_2\text{C}_5\text{H}_4]_2\text{ZrCl}_2$	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	95.4:4.6 (P = 20.7)	gravimet	56
XVI-47 ^g	$[\text{R}_{f6}(\text{CH}_2)_2\text{C}_5\text{H}_4]_2\text{Zr}(\text{CH}_3)_2$	$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	87.5:12.5 (P = 7.00)	gravimet	56
XVI-48		$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	95.5:4.5 (P = 21.2)	HPLC	7, 27
XVI-49		$\text{C}_8\text{F}_{17}\text{Br}:\text{DMF}$	95.9:4.1 (P = 23.4)	HPLC	7, 27
XVI-50		$\text{CF}_3\text{C}_6\text{F}_{11}:\text{CH}_3\text{C}_6\text{H}_5$	90.7:9.3 (P = 9.8)	HPLC	7
XVI-51		$\text{C}_8\text{F}_{17}\text{Br}:\text{DMF}$	91.4:8.6 (P = 10.6)	HPLC	7
XVII	Supramolecular Complexes and Polymers				
XVII-1 ^c	$[\text{R}_{f6}(\text{CH}_2)_2\text{NHCONHCH}(\text{CH}_3)_2]\cdot\text{HO}_2\text{CR}_{f6}$	$\text{C}_6\text{F}_{14}:\text{CH}_2\text{Cl}_2$	40:60 (P = 0.7)	gravimet	57
XVII-2 ^c	$[(\text{CF}_3\text{CH}_2\text{NH})_2\text{CO}]\cdot\text{HO}_2\text{CR}_{f6}$	$\text{C}_6\text{F}_{14}:\text{CH}_2\text{Cl}_2$	77:23 (P = 3.4)	gravimet	57
XVII-3 ^c	$[(\text{CF}_3\text{CH}_2\text{NH})_2\text{CO}]\cdot\text{HO}_2\text{CR}_{f17}$	$\text{C}_6\text{F}_{14}:\text{CH}_2\text{Cl}_2$	83:17 (P = 4.9)	gravimet	57
XVII-4 ^c	$[(\text{R}_{f4}(\text{CH}_2)_2\text{NH})_2\text{CO}]\cdot\text{HO}_2\text{CR}_{f6}$	$\text{C}_6\text{F}_{14}:\text{CH}_2\text{Cl}_2$	96:4 (P = 24)	gravimet	57
XVII-5 ^c	$[(\text{R}_{f6}(\text{CH}_2)_2\text{NH})_2\text{CO}]\cdot\text{HO}_2\text{CR}_{f6}$	$\text{C}_6\text{F}_{14}:\text{CH}_2\text{Cl}_2$	99:1 (P = 99)	gravimet	57
XVII-6 ^c		$\text{C}_6\text{F}_{14}:\text{CHCl}_3$	96:4 (P = 24)	gravimet	57

Tab. 6-1. (continued)

Entry	Solute ^b	Solvent system	Partitioning fluorous: organic (P)	Method	Ref.
XVII-7 ^c		C ₆ F ₁₄ :CH ₃ CN	90:10 (P = 9.0)	gravimet	57
XVII-8 ^c	[(R _{f6} (CH ₂) ₂ NH) ₂ CO]·HO ₂ CCH ₂ R _{f6}	C ₆ F ₁₄ :CH ₂ Cl ₂	98:2 (P = 49)	gravimet	57
XVII-9 ^c	[(R _{f6} (CH ₂) ₂ NH) ₂ CO]·HO ₂ C(CH ₂) ₂ R _{f8}	C ₆ F ₁₄ :CH ₂ Cl ₂	95:5 (P = 19)	gravimet	57
XVII-10		1,3-(CF ₃) ₂ C ₆ F ₁₀ :CH ₃ C ₆ H ₅	96.4:3.6 (P = 26.9)	gravimet	32
XVII-11		1,3-(CF ₃) ₂ C ₆ F ₁₀ :THF	96.5:3.5 (P = 27.7)	gravimet	32

^aAll measurements obtained at 24 °C unless otherwise stated.

^bR_{fn} = (CF₂)_{n-1}CF₃. ^c25 °C. ^dCalculated from ln P. ^ePerfluorodecalin.

^fMixture of isomers. ^gAmbient temperature implied. ^h-45 °C. ⁱ20 °C.

^jT not given. ^k27 °C. ^l10 °C. ^m0 °C. ⁿInductively coupled plasma – atomic absorption spectrometry. ^oInductively coupled plasma – atomic emission spectrometry. ^p23 °C. ^qMixture of regioisomers.

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ences to other sections are given. The abbreviation $R_{fn}[(CF_2)_{n-1}CF_3]$ is used throughout, except for trifluoromethyl groups (formally R_{f1}).

The partition coefficients are listed *both* as ratios normalized to 100, *and* as *P* values. As some rounding is necessary, the value originally reported in the literature is indicated in **bold type**. When a *P* value has been calculated from an $\ln P$ or *f* value, this is indicated by a footnote. All data from the authors' groups are believed to be correctly represented with respect to the number of significant digits.

GLC (gas-liquid chromatography), HPLC (high-performance liquid chromatography), and ICP-AAS/AES measurements are generally the most reliable. Gravimetric determinations where only a very small amount of the solute is present in one phase are subject to greater errors. Importantly, ICP methods give the total amount of a given *element* in a given phase. Hence, the decomposition of a solute to a species with a different partition coefficient (e.g., by oxidation), even to a small extent, can introduce error. Since GLC and HPLC assay a *molecular* characteristic, they are not subject to this problem.

Partition coefficients are temperature dependent, as illustrated by entries IV-9/IV-10 and XVI-12/XVI-13 of Table 6-1. The fluorous phase affinity of a fluorous solute is enhanced at lower temperature. However, most of the values in Table 6-1 were determined between 20 and 27 °C, as specified in the footnotes, and should not vary substantially within this range. In the most rigorous work, partition coefficients are determined over a range of concentrations and extrapolated to infinite dilution [1]. However, the concentrations used in the authors' experiments are close to those encountered in "real-life" fluorous/organic liquid/liquid biphasic separations, and the values for various classes of molecules are believed to have excellent cross-comparability.

6.3 Trends with Respect to Functional Groups

6.3.1

Non-Aromatic Hydrocarbons

Entries I-1 to I-6 in Table 6-1 give partition coefficients ($\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene) for *n*-alkanes (decane through hexadecane), and entries II-1 to II-6 give data for the corresponding terminal alkenes. The alkanes, although very non-polar, show high affinities for the toluene phase. These increase monotonically with alkane size (5.4:94.6 for decane to 1.1:98.9 for hexadecane). This is in accord with the general trends for absolute solubilities in fluoruous solvents, as discussed in Chapter 3.5. Non-fluorous solutes are thought to occupy cavities, and smaller guests are always better accommodated.

The *n*-alkenes have slightly higher toluene phase affinities, consistent with their slightly greater polarities. A comparable monotonic size trend is found (4.8:95.2 for 1-decene to 0.9:99.1 for 1-hexadecene). When the side-chain of 1-decene is perfluorinated to give $\text{R}_{f8}\text{CH}=\text{CH}_2$, the partition coefficient nearly reverses, to 93.5:6.5 (entry II-7). A variety of hemifluorinated disubstituted alkenes, $\text{R}_{fn}\text{CH}=\text{CH}(\text{CH}_2)_m\text{CH}_3$, have been analyzed (entries II-8 to II-43). As would be expected, they exhibit intermediate fluorophilicities.

6.3.2

Non-Aromatic Monofunctional Compounds

Entries III-1 and III-2 give partition coefficients ($\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene) for the ketones cyclohexanone and 2-cyclohexen-1-one – species more polar than alkanes and alkenes but somewhat “smaller” than specific examples discussed above. Their toluene phase affinities are also high (2.2:97.8 and 1.7:98.3). The toluene phase affinity of cyclohexanol (entry IV-1, 1.6:98.4) is higher than that of cyclohexanone, and the corresponding dimethylphenyl silyl ether is higher still (entry XIII-8, 0.8:99.2).

Section IV of Table 6-1 contains several simple fluoruous alcohols. The short-chain species in entries IV-2 and IV-3 show poor fluorophilicities [7]. As the perfluoroalkyl segment lengthens in the series $\text{R}_{f6}(\text{CH}_2)_3\text{OH}$, $\text{R}_{f8}(\text{CH}_2)_3\text{OH}$, and $\text{R}_{f10}(\text{CH}_2)_3\text{OH}$ (entries IV-5, IV-7, IV-8), the fluoruous phase affinities increase from 44:56 to 64:36 to 80.5:19.5 ($\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene). As would be expected, when a methylene group is removed from the first two compounds, the fluorophilicities also increase (52:48 and 73.5:26.5; entries IV-4 and IV-6). Similar trends are found with all other functional groups in Table 6-1.

The thiol $\text{R}_{f8}(\text{CH}_2)_3\text{SH}$ (entry XIV-2), iodide $\text{R}_{f8}(\text{CH}_2)_3\text{I}$ (entry IX-4), and primary amine $\text{R}_{f8}(\text{CH}_2)_3\text{NH}_2$ (entry X-1) exhibit $\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene partition coefficients (56:44, 50.7:49.3, and 70.0:30.0) roughly comparable to that of the corresponding alcohol (64:36). Thus, more than one R_{f8} -containing ponytail is clearly needed to achieve higher fluorophilicities with simple monofunctional organic compounds.

The effect of the number of ponytails is clearly seen in amines of the formula $[\text{R}_{f8}(\text{CH}_2)_3]_x\text{NH}_{3-x}$ (entries X-1, X-7, and X-13). As *x* increases from one to three, the fluoruous phase affinities increase monotonically from 70.0:30.0 to 96.5:3.5 to the point where no GLC-detectable concentration in toluene remains ($>99.7:<0.3$). Thus, $[\text{R}_{f8}(\text{CH}_2)_3]_3\text{N}$ repre-

sents a highly immobilized fluorous base. When the number of the methylene groups in each ponytail is increased to five, a small amount of the amine can again be detected in the toluene phase (99.5:0.5; entry X-15).

Similar trends are observed with fluorous trialkylphosphines. Here, the lengths of the R_{fn} as well as the $(CH_2)_m$ segments have been varied (entries XI-1 to XI-6), and very high fluorous phase affinities can be achieved $\{>99.7:<0.3$ for $[R_{f8}(CH_2)_2]_3P$ and $[R_{f10}(CH_2)_2]_3P$. Where comparisons are possible, fluorophilicities are slightly lower than for analogous amines. Counter-intuitively from a polarity standpoint, oxidation to a phosphine oxide slightly *increases* the fluorous phase affinity (entry XI-7 vs. XI-1).

As shown in Section XII of Table 6-1, appropriately designed trialkyltin hydrides can also be highly fluorophilic. Although the solvent systems used are slightly different, partition coefficients for the compounds $[R_{fn}(CH_2)_2]_3SnH$ are comparable to those of the corresponding phosphines (entries XII-5 and XII-11 for $n = 6$; $n = 10$ is still more fluorophilic but due to solubility limitations an accurate value could not be determined) [8]. Another triply-branched system is the tertiary alcohol $[(R_{f6}(CH_2)_2)_3COH$. The C_6F_{14}/THF partition coefficient is 90.9:9.1 at ambient temperature or 95.8:4.2 at $-45^\circ C$ (entries IV-9 and IV-10).

Thioethers, which can only accommodate two ponytails around the central heteroatom, possess fluorous phase affinities slightly lower than those of comparable amines and phosphines. For example, the $CF_3C_6F_{11}/$ toluene partition coefficients for $[R_{f8}(CH_2)_2]_2S$ and $[R_{f8}(CH_2)_3]_2S$ are 98.7:1.3 and 96.6:3.4 (entries XIV-13 and XIV-14).

6.3.3

Simple Monoarenes

Data for simple arenes are collected in Section VII of Table 6-1, and the $CF_3C_6F_{11}/$ toluene partition coefficients can be analyzed as follows. Both pentafluorobenzene and hexafluorobenzene preferentially partition into toluene (22.4:77.6 and 28.0:72.0; entries VII-2 and VII-3), consistent with their non-fluorous nature as described in Chapter 3.2.2. Benzene exhibits an even greater toluene phase affinity (6:94; entry VII-1). However, the introduction of a single ponytail of formula $R_{f8}(CH_2)_3$ evens the playing field, and a partition coefficient of 49.5:50.5 is obtained (entry VII-18). This value is similar to those obtained when an $R_{f8}(CH_2)_3$ moiety is capped with an iodide or thiol. The compound $R_{f8}C_6H_5$ (entry VII-16), which lacks methylene spacers, is more fluorophilic still (77.5:22.5), but the electronic properties of the arene ring are strongly perturbed.

As shown in entries VII-43, VII-45, and VII-46, benzenes with two ponytails of formula $R_{f8}(CH_2)_3$ exhibit appreciable fluorophilicities, with partition coefficients of 91.2:8.8 to 90.7:9.3. The substitution pattern has little influence. As seen with other compounds above, when the perfluoroalkyl segment of the ponytail is shortened, the fluorous phase affinity decreases [73.7:26.3 for $R_{f6}(CH_2)_3$; entry VII-42], and when it is lengthened the fluorous phase affinity increases [97.4:2.6 for $R_{f10}(CH_2)_3$; entry VII-44]. Importantly, benzenes with three ponytails of formula $R_{f8}(CH_2)_3$ partition (within detection limits) completely into $CF_3C_6F_{11}$, at least when arrayed in a 1,3,5-pattern (entry VII-61).

Entries VII-49 through to VII-54, VII-62, and VII-63 feature monoiodide derivatives of some of the preceding fluorous benzenes. In all cases, the fluorophilicities decrease. Only for entry VII-62, a triply ponytailed compound, is a highly biased $CF_3C_6F_{11}/$ toluene partition

coefficient maintained (98.0:2.0). When the more polar non-fluorous solvent methanol is employed, relative fluorous phase affinities increase. Regardless, it is clear that with mono-functional benzenes, at least three ponytails of the formula $R_{f8}(CH_2)_3$ are required for high degrees of fluorous phase immobilization. Entries III-4, IV-11, and VI-7 – a benzaldehyde, benzyl alcohol, and methyl benzoate – show that two ponytails of formula R_{f8} (i.e., without spacers) are essentially as effective ($CF_3C_6F_{11}$ /toluene partition coefficients 98.6:1.4, 97.4:2.6 and 98.8:1.2).

6.3.4

Triarylphosphines

These points are further illustrated by some of the *para*-substituted fluorous triarylphosphines in Section XI of Table 6-1. With one ponytail of the formula $R_{f6}(CH_2)_3$ per ring, the $CF_3C_6F_{11}$ /toluene partition coefficient is 19.5:80.5 (entry XI-18). When the per-fluoroalkyl segment is lengthened, giving $R_{f8}(CH_2)_3$, the fluorophilicity increases (66.6:33.4; entry XI-19). When the methylene segment is shortened, giving $R_{f6}(CH_2)_2$, the fluorophilicity should also increase. Accordingly, the C_6F_{14} /toluene partition coefficient is 43:57 (entry XI-17). When toluene is replaced by the much more polar solvent methanol, the fluorous phase affinity becomes much higher (96.8:3.2, entry XI-15).

Entries XI-30 and XI-28 provide analogous data for a phosphine with a single methylene spacer and a branched R_{f6} moiety. In C_6F_{14} /toluene, the fluorous phase affinity is lower (87.2:12.8), but in C_6F_{14} /methanol, slightly higher (94.9:5.1). When the phenyl groups bear only *p*- R_{f6} substituents (no methylene spacers), the partition coefficient in 1,3- $(CF_3)_2C_6F_{10}$ /toluene is 81:19 (entry XI-11).

It has proved problematic to attach additional ponytails directly onto the aryl moieties of fluorous triarylphosphines. Thus, there are no readily available compounds of the formula $\{[R_{fn}(CH_2)_m]_xC_6H_{5-x}\}_3P$ ($m > 0$) with truly high fluorous phase affinities. However, a clever way around this dilemma has been developed [9]. Namely, silicon-based ponytails of the formula $[R_{fn}(CH_2)_2]_xSi(CH_3)_{3-x}$ have been used as anchors for as many as three R_{f6} or R_{f8} groups per ring [10]. As summarized in entries XI-47 through to XI-58, this gives triarylphosphines with much higher fluorous phase affinities (up to 95:5 for $x = 3$ and $n = 8$ in $CF_3C_6F_{11}/n-C_5H_{12}$). When the exact values are carefully analyzed, some non-monotonic trends are obvious, and this point is treated further below.

Note that the analogous dppe derivative in entry XI-62, which contains two fluorous arenes on each phosphorus atom, gives a $CF_3C_6F_{11}$ /toluene partition coefficient of $>98:<2$. The related BINAP derivative in entries XI-72 through to XI-75 features only a single fluorous arene on each phosphorus atom, and the C_6F_{14}/C_6H_6 partition coefficient is only 74:26 (HPLC).

6.3.5

Pyridines

The R_{f8} -monosubstituted pyridines in entries VIII-1 through to VIII-3, which are *ortho*, *meta*, and *para* isomers, give $CF_3C_6F_{11}$ /toluene partition coefficients in the narrow range of

63:37 to 71:29. The $R_{f8}(\text{CH}_2)_3$ -disubstituted pyridine in entry VIII-5 is rigorously comparable to the benzenoid analog in entry VII-45 (N/CH exchange), and gives an essentially identical partition coefficient (90.4:9.6 vs. 90.7:9.3). Hence, the polar pyridine nitrogen has little influence. Entry VIII-7 shows that three ponytails of the formula $R_{f8}(\text{CH}_2)_2$ provide essentially complete fluororous phase immobilization ($>99.7:<0.3$). The hydrogenation of the pyridine in entry VIII-5 to the piperidine in entry VIII-8 slightly increases fluorophilicity (90.4:9.6 vs. 93.6:6.4). This secondary amine can in turn be compared to $\text{HN}[(\text{CH}_2)_5R_{f8}]_2$ (entry X-9) which has one less CH_n group and a very similar fluororous phase affinity (93.0:7.0).

6.3.6

Metal Complexes

Section XVI of Table 6-1 features a variety of metal complexes, the majority of which have been engineered to have high fluorophilicities. As illustrated by entries XVI-40 through to XVI-45, a ferrocene appears slightly more difficult to immobilize than a benzene ring. Two ponytails of the formula $R_{f10}(\text{CH}_2)_2$ or four ponytails of the formula $R_{f4}(\text{CH}_2)_2$ suffice for $\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene partition coefficients of $>91:<9$. The fluororous zirconocenes ($\eta^5\text{-C}_5\text{H}_4(\text{CH}_2)_2R_{f6}$) $_2\text{ZrX}_2$ exhibit $\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene partition coefficients of 95.4:4.6 ($\text{X} = \text{Cl}$, entry XVI-46) and 87.5:12.5 ($\text{X} = \text{CH}_3$, entry XVI-47).

Compounds that are catalyst precursors are of particular interest. The rhodium complexes in entries XVI-9 and XVI-10, which feature three phosphine ligands of the formula $\text{P}[(\text{CH}_2)_2R_{fn}]_3$, exhibit very high fluorophilicities ($\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene partition coefficients 99.86:0.14, $n = 6$, and 99.88:0.12, $n = 8$). Those of similar square planar iridium and nickel complexes with two such phosphine ligands are slightly lower (entries XVI-30 through to XVI-34). Salts should normally have poor fluororous phase affinities. However, entries XVI-20 and XVI-24 show that when appropriate cationic fluororous rhodium complexes and fluororous anions are combined, $\text{CF}_3\text{C}_6\text{F}_{11}$ /toluene partition coefficients of 97.1:2.9 to 98.5:1.5 can be achieved. Although partition coefficients have not yet been reported, polyoxometalate salts with fluororous tetralkylammonium cations can exhibit similar fluorophilicities [11].

Entry XVI-12 illustrates an interesting effect. The central rhodium is surrounded by three fluororous triarylphosphines that have only one ponytail per ring, and a $\text{CF}_3\text{C}_6\text{F}_{11}/n\text{-C}_8\text{H}_{18}$ partition coefficient of 52:48 at 0 °C (entry XI-40). Nonetheless, the rhodium complex is highly fluorophilic, with a partition coefficient of 99.7:0.3 under analogous conditions. Similar phenomena, in which the “sum is greater than the parts”, have been observed with other compounds that are aggregates of fluororous building blocks. Two effects are probably at work. Firstly, the ponytails are deployed in a maximally efficient way around the periphery of the molecule. Secondly, the molar volume increases, the influence of which is discussed in Section 6.5 below.

Dirhodium tetracarboxylates $\text{Rh}_2[\text{O}_2\text{C}(\text{CH}_2)_mR_{fn}]_4$ with very high fluororous phase affinities are also available (entries XVI-1 through to XVI-8), although for some reason $\text{CF}_3\text{C}_6\text{F}_{11}$ /ether gives much less biased partition coefficients than $/\text{CH}_2\text{Cl}_2$, $/\text{C}_6\text{H}_{14}$, or $/\text{toluene}$ mixtures. The fluororous nitrogen and sulfur palladacycles in entries XVI-48 through to XVI-51

contain three ponytails of the formula $R_{f8}(CH_2)_m$ ($m = 2$ or 3) per arene ring. The $CF_3C_6F_{11}$ /toluene partition coefficients (95.5:4.5 and 90.7:9.3) indicate fluorophilicities somewhat lower than those of the free non-palladated ligands (98.7:1.3 and 99.5:0.5, entries X-24 and XIV-15).

6.4

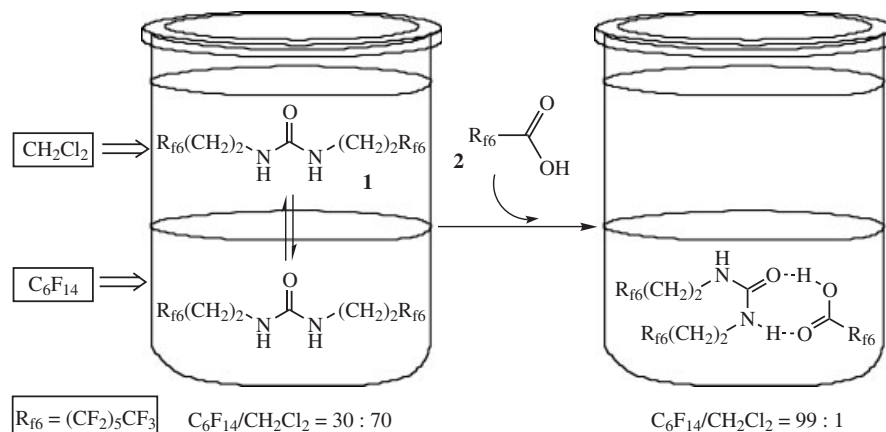
General Trends and Special Situations

Table 6-1 shows that, with only a very few exceptions, the introduction of longer ponytails or additional ponytails leads to higher fluororous phase affinities. When additional methylene spacers are introduced, while keeping the perfluoroalkyl segments constant, fluororous phase affinities decrease. In the authors' view, compounds with $CF_3C_6F_{11}$ /toluene partition coefficients of $>90:<10$ have high fluorophilicities, and those with partition coefficients of $>99:<1$ possess very high fluorophilicities. When the ratio exceeds $>99.7:<0.3$, the compounds can be viewed as "immobilized".

In general, simple monofunctional organic compounds, including arenes, require two ponytails of the formula $(CH_2)_mR_{f8}$ ($m = 2, 3$) for high fluorophilicities. Three such ponytails lead to very high fluorophilicities, and often essentially complete immobilization. An early rule of thumb stated that for a molecule to be preferentially soluble in a fluororous liquid phase (partition coefficient $>50:<50$), 60% of the molecular weight should be fluorine-derived [12]. However, Table 6-1 contains exceptions to all of these generalizations, and selected cases are now examined in turn.

In compounds that already contain a long perfluoroalkyl segment, the introduction of a CF_3 group or a "pigtail" sometimes imparts a fluorophilicity significantly greater than might be expected. For example, the R_{f8} -monosubstituted benzene in entry VII-16 can be compared with the R_{f8}/CF_3 - and R_{f8}/R_{f8} -disubstituted benzenes in entries VII-37 through to VII-40 and the $R_{f8}/CF_3/CF_3$ -trisubstituted benzene in entry VII-60. Although the $CF_3C_6F_{11}$ /toluene partition coefficients for the R_{f8}/CF_3 compounds [91.5:8.5 (*meta*), 89.4:10.6 (*para*), 81.8:18.2 (*ortho*)] indicate fluorophilicities less than that of the R_{f8}/R_{f8} compound (99.3:0.7), they are in two cases distinctly greater than that of the R_{f8} -monosubstituted compound (77.5:22.5). The $R_{f8}/CF_3/CF_3$ compound (98.3:1.7) is nearly as fluorophilic as the R_{f8}/R_{f8} compound. Thus, although trifluoromethylbenzene itself has a very poor fluororous phase affinity (entry VII-6, 12.4:87.6), CF_3 groups represent legitimate design elements for enhancing fluorophilicities once a ponytail is in place. Other compounds that appear to show similar effects can be found in entries VII-33 through to VII-36 and VII-55 through to VII-59.

A possibly related effect, already noted in Section 6.3.6, is as follows. Some compounds that can be viewed as aggregates of fluororous building blocks give partition coefficients distinctly higher than the individual building blocks. For example, the fluorophilicity of the rhodium tris(phosphine) complex in entry XVI-12 is much greater than that of the phosphine ligand (entry XI-40). Another manifestation of this phenomenon, but in a supramolecular context, is illustrated in Scheme 6-1 [13]. The fluororous N,N' -dialkyl urea **1** is not very fluorophilic (C_6F_{14}/CH_2Cl_2 partition coefficient 30:70). However, the addition of an equivalent of the fluororous carboxylic acid **2** gives a highly fluorophilic 1:1 complex (partition coefficient 99:1). Although the partition coefficient of **2** is not known, it could well be



Scheme 6-1. Effect of supramolecular complex formation upon a partition coefficient

somewhat lower due to the polar acidic functional group. In this event, two more polar solutes combine to give a less polar and more fluorophilic complex. Additional examples are provided in entries XVII-1 through to XVII-9 of Table 6-1.

In such compounds or complexes, three main effects are probably operating. Firstly, polar acidic and basic sites (either Brønsted or Lewis) combine to give less polar moieties. Secondly, the ponytails are directed around the outer perimeter of the molecule in an efficient manner such that solvation in non-fluorous media is impeded. One wonders whether a “Maginot line” (or perhaps more accurately, a “Maginot sphere”) of CF_3 -pigtailes, accompanied by a smattering of ponytails, might constitute a particularly staunch defender of the fluorous character. Thirdly, the molar volume increases, the effect of which is discussed in the following section.

The most puzzling exceptions to the generalizations regarding ponytail length and quantity and fluorous phase affinities involve silicon-substituted triarylphosphines of the formula $\text{P}\{p\text{-C}_6\text{H}_4\text{Si}(\text{CH}_3)_{3-x}[(\text{CH}_2)_2\text{R}_{f_n}]_x\}_3$ (entries XI-39 through to XI-58). The partition coefficients were carefully measured in several solvent systems [9a]. The values in $\text{CF}_3\text{C}_6\text{F}_{11}/n$ -pentane show the expected monotonic trend, with fluorophilicities increasing in the order $x/n = 1/6 < 1/8 < 2/6 < 2/8 < 3/6 < 3/8$. However, in $\text{CF}_3\text{C}_6\text{F}_{11}/n$ -octane the phosphines with three ponytails show *lower* fluorous phase affinities than those with two ponytails ($x/n = 1/6 < 1/8 < 3/6 < 3/8 < 2/6 < 2/8$). The situation is similar in $\text{CF}_3\text{C}_6\text{F}_{11}/$ toluene, but now with some of compounds with R_{f6} ponytails showing fluorous phase affinities equal to or *greater* than the homologs with R_{f8} ponytails ($x/n = 1/6 < 1/8 < 3/8 < 3/6 < 2/8 = 2/6$).

The preceding trends cannot be rationalized by any of the qualitative fluorophilicity models, but yet are real and must have an explanation. Apart from questioning the models, it should be noted that for measurements made in solution, there is always the possibility that certain fluorous solutes, but not others, might aggregate in some way. Gel formation is not uncommon, and micelles are certainly conceivable. As noted in Section 6.2, in the most

Tab. 6-2. Effect of fluorous solvent on partition coefficients with toluene^{a,b}

Solvent	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_2R_{f8}$	$\text{CH}_3(\text{CH}_2)_2\text{CH}(\text{CH}_3)\text{CO}_2(\text{CH}_2)_7R_{f8}$
$(\text{CF}_3)_3\text{CC}(\text{CF}_3)_3^c$	39:61 (0.64)	32:68 (0.48)
<i>n</i> -C ₆ F ₁₄	50:50 (0.98)	40:60 (0.68)
CF ₃ C ₆ F ₁₁	55:45 (1.23)	49:51 (0.95)
perfluoroperhydrofluorene ^d	53:47 (1.13)	49:51 (0.97)
perfluorodecalin ^d	61:39 (1.59)	56:44 (1.28)

^a Fluorous solvent: toluene (*P* value as originally determined). ^b 25 °C unless noted. ^c 40 °C. ^d Mixtures of *cis/trans* isomers.

rigorous studies, the concentration dependences of partition coefficients are determined. The data are then extrapolated to infinite dilution, where aggregates become impossible. Perhaps some of these non-monotonic trends reflect non-ideal solution behavior.

For many compounds in Table 6-1, partition coefficients were measured with more than one non-fluorous solvent. Although there are a few curious exceptions (e.g., ether vs. toluene or hexane in entries XVI-1 through to XVI-8), the more polar the non-fluorous solvent, the greater the fraction of the fluorous solute in the fluorous phase.

In contrast, only a few compounds have been probed with more than one fluorous solvent. Naturally, it is of interest to know which ones give the most biased partition coefficients. This has been investigated with two test solutes and toluene as summarized in Table 6-2 [14]. The best results were obtained with perfluorodecalin, and all cyclic solvents tested were superior to *n*-C₆F₁₄. Entries of VI-8 through to VI-107 of Table 6-1 also feature many parallel measurements involving CF₃C₆F₁₁ and *n*-C₆F₁₄. In nearly all cases, the former gives the more biased partition coefficient.

6.5 Quantitative Analysis and Prediction of Partition Coefficients

There have been several efforts to parameterize the above data such that fluorophilicities can be predicted [4–6]. One approach makes use of 3D QSAR descriptors and neural networks [4]. A host of parameters was considered: percent fluorine, molecular volume, molecular surface, globularity, solvent accessible surface, solvent extended surface, solvent extended volume, calculated polarizability, calculated dipole moment, calculated Hildebrand parameter, degree of chemical bond rotational freedom, and others. In the end, very good agreement between measured and predicted partition coefficients in the test group of 60 molecules was realized.

Another parameterization effort involving a test group of 90 molecules found fluorine content, dispersion, and hydrogen bond acidity factors to be most important [4]. Polarity, hydrogen bond basicity, and size effects played much smaller roles.

The most definitive work to date involves Mobile Order and Disorder (MOD) theory [6, 15]. This has been applied to other types of liquid/liquid partition coefficients, using a five-term expression. With aprotic fluoruous biphasic systems, the expression reduces to two terms. One involves the molar volumes of the fluoruous and organic solvents and the solute. The other involves the corresponding cohesion parameters. Once the solvent properties have been measured, the partition coefficients are a function of only two solute variables, one of which (the molar volume) is easily calculated from group increments. The investigators use a small amount of the data in Table 6-1 to back-calculate the solute cohesion parameter and derive a second set of group increments. This allows the partition coefficients of approximately 50 additional compounds to be predicted with good accuracy.

6.6

Future Directions

On the computational side, the prediction of partition coefficients is certain to attract further attention. To better interpret raw data, fluoruous solutes will be increasingly scrutinized for non-ideal behavior in solution. Naturally, there will be many new entries for Table 6-1, as well as increased focus on supramolecular assemblies. However, there are some likely directions for future research that are not straightforward extensions of themes discussed above.

For example, partition coefficients for fluoruous liquid/non-fluorous solid biphasic systems are of interest from several standpoints. Recently, the partitioning of small organic molecules from both fluoruous and non-fluorous solvents as well as mixtures into highly cross-linked, macroporous, and insoluble organic polymers has been studied [16]. One goal is to enhance access of organic substrates to imbedded catalyst sites. Presumably due to a fluorophobic effect, fluoruous/organic solvent mixtures give up to 200-fold increases in local concentrations relative to pure organic solvents. Under catalytic conditions, turnover frequencies are greatly enhanced.

6.7

Sample Experimental Determinations

The following procedures illustrate recommended procedures for determining partition coefficients by GLC, HPLC, and ^{19}F NMR. All correspond to entries in Table 6-1.

A [17]. A 10 mL vial was charged with 3,4-($\text{R}_{\text{f}8}\text{CH}_2\text{CH}_2\text{CH}_2$) $_2\text{C}_6\text{H}_3\text{I}$ (entry VII-50; 0.0156 g, 0.0138 mmol), $\text{CF}_3\text{C}_6\text{F}_{11}$ (2.000 mL), and MeOH (2.000 mL), fitted with a mini-inert valve, vigorously shaken (2 min), and immersed (cap-level) in a 35 °C oil bath. After 12 h, the bath was removed. After 12–24 h, a 0.500 mL aliquot of each layer was added to 0.250 mL of a standard 0.0244 M solution of eicosane in hexane. The samples were diluted with ether and GLC analysis (average of 7–8 injections) showed that 0.00325 mmol of 3,4-($\text{R}_{\text{f}8}\text{CH}_2\text{CH}_2\text{CH}_2$) $_2\text{C}_6\text{H}_3\text{I}$ was in the $\text{CF}_3\text{C}_6\text{F}_{11}$ aliquot and 0.000101 mmol in the MeOH aliquot (97.0:3.0; a 2.000/0.500 scale factor gives a total mass recovery of 0.0150 g, 97%).

B [18]. A 10 mL vial was charged with the imine palladacycle from entry XVI-48; (0.0104 g, 0.0031 mmol), $\text{CF}_3\text{C}_6\text{F}_{11}$ (2.000 mL), and toluene (2.000 mL), fitted with a mini-inert valve,

and vigorously shaken (2 min). After 2 h (24 °C), a 0.250 mL aliquot of the fluoruous phase and a 0.750 mL aliquot of the non-fluoruous phase were removed. The solvents were evaporated and the residues dried by oil pump vacuum (1 h). Each residue was taken up in CF₃C₆H₅/EtOH (9:1 v/v; 0.500 mL) and analyzed by HPLC (average of 5 injections, 200 × 4 mm Nucleosil 100-5 column, UV/visible detector). The relative peak intensities were (after normalization to the aliquot volumes) 95.5:4.5.

C [19]. A 5 mL flask was charged with H₃B·P[*p*-C₆H₄(CH₂)₃CH(CH₂R_{f8})₂]₃ (entry XI-21; 0.0368 g, 0.0121 mmol) and CF₃C₆F₁₁ (2.00 mL). After complete dissolution, toluene (2.00 mL) was added and the mixture was vigorously shaken (20 min). The flask was kept at 25 °C for 48 h. Then aliquots (each of 0.500 mL) were taken from both phases. The CF₃C₆F₁₁ aliquot was evaporated to dryness. A solution of the internal standard C₆F₆ (0.0738 g, 0.397 mmol) in CF₃C₆H₅ (12.7016 g) was prepared. Portions of this standard solution were added gravimetrically to the above aliquots (CF₃C₆F₁₁: 0.6413 g solution, 0.0199 mmol C₆F₆; toluene: 0.0596 g solution, 0.00185 mmol C₆F₆). Then C₆D₆ was added (0.05 mL each) and the samples were analyzed by ¹⁹F NMR (integration of CF₃ signal against C₆F₆). The procedure was repeated, giving an average partition coefficient of 96.6:3.4 {0.00840 g of H₃B·P[*p*-C₆H₄(CH₂)₃CH(CH₂R_{f8})₂]₃ in 0.500 mL of CF₃C₆F₁₁; 0.000292 g of H₃B·P[*p*-C₆H₄(CH₂)₃CH(CH₂R_{f8})₂]₃ in 0.500 mL of toluene}. A 2.00/0.500 scale factor gives a total mass recovery of 0.0348 g (95%).

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