Chelation-Controlled Diasteroselective Reduction of α-Fluoroketones

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Supporting Information

General Experimental Procedures

All reactions were performed in a flame-dried apparatus under an inert atmosphere of nitrogen. Solvents are dried by passing through a column in a solvent dry system and collected in dry box (Innovative Technology Inc.). MeOH was distilled over anhydrous $MgSO_4$. *N*-fluorobenzene sulfonamide (Accuflour®), 3-fluoro butan-2-one and 1-fluoro-4-hydroxy-1,4-diazoniabicyclo[2,2,2]octane bis(tetrafluoroborate) [Accufluor ™-NFTh] were purchased from Matrix Scientific and SynQuest Laboratories Inc.. ^{19}F NMR, ^{13}C NMR, ^1H NMR spectra were recorded on a 360 MHz (Brucker) or 500 MHz (Brucker) multinuclear spectrometer. ^{19}F NMR spectra are referenced to external $CFCl_3$, ^1H NMR and ^{13}C NMR spectra to TMS. All NMR solvents were stored overnight on 4^0A-molecular sieves prior to use. Gas chromatography was performed on Shimadzu GC-14B. The diastereoselectivities were determined from ^1H, ^{19}F NMR and GC.

NMR solutions used for low temperature experiments are 0.18M in CD_2Cl_2 with respect to substrate and 0.18-0.44M with respect to Ti(IV) Lewis acids. NMR spectra were stacked using MestReC software.

Synthesis of α-Fluoropropiophenone[1]

Lithium diisopropylamide (2M solution) in THF/n-heptane (6.5 mL, 13 mM) was diluted with 6.5 mL THF at a –78^{o}C and allowed to stir for 5 minutes. Propiophenone (1.34 g, 10 mM, dissolved in 5 mL of THF) was added drop wise and the enolate formation was monitored by the color change of the solution from brown to orange (approximately 30 minutes). After formation of the enolate was complete, Accuflour® (3.78 g, 12 mM, dissolved in THF) was injected by syringe and the reaction mixture was allowed to stir at –78 ^{o}C for 1 hour and then slowly warmed to room temperature and stirred overnight. Aqueous NH_4Cl solution was added to the reaction and the mixture was poured into water. The organic layer was extracted with Et_2O (3 x 15 mL) and dried over $MgSO_4$. The solvent was removed under vacuum and the product was purified by Kuglerohr distillation followed by column chromatography {neutral Al_2O_3; pentane:Et_2O (10:1)}.α-Fluoropropiophenone was obtained as clear liquid (yield: 1.06 g, 70%).
GC-MS, m/z (%): 152 (M^+, 6), 107 (43), 79 (100), 77 (96).

Preparation of α-Fluoroindanone[2]

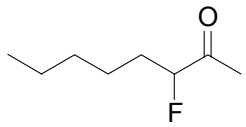
Indanone (2.64 g, 20 mM) and Accufluor® (6.95 g, 22 mM) were dissolved in methanol (50 mL) and attached to a water condenser. The reaction mixture was allowed to reflux for 2h (monitored by GC), cooled to rt and the solvent was removed under vacuum. The crude product was dissolved in CH_2Cl_2 (50 mL) and washed with water (1 × 25 mL). The organic layer was separated out and was dried over $MgSO_4$. After filtration the solvent was again removed under vacuum to yield the crude product as a yellow solid, which was purified by silica gel-column chromatography (3% ethyl acetate in hexane) to produce a pale yellow solid (yield: 2.19 g, 73%).
GC-MS, m/z (%): 150 (M^+, 100), 122 (87.3), 102 (28.7), 76 (37).

α-Fluorotetralone[2]

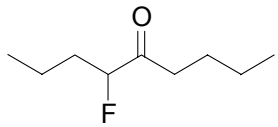
In a 50 mL round bottom flask α-tetralone (0.292 g, 2 mM) and Accufluor® (0.693 g, 2.2 mM) were dissolved in methanol (20 mL), attached to a water condenser and the reaction was refluxed overnight under nitrogen. The reaction was allowed to cool and the solvent was removed under vacuum. The crude product was dissolved in CH_2Cl_2 (50 mL), washed with water, and the organic layer was dried over $MgSO_4$. After filtration the solvent was again removed under vacuum to yield the crude product as a yellow solid, which was purified by column chromatography (SiO_2, 2.5% ethyl acetate in CH_2Cl_2) to produce a white solid (Yield: 0.272 g, 83%).
^{1}H NMR: ($CDCl_3$, 500 MHz): δ 2.22-2.32 (m, 1H), 2.48-2.55 (m, 1H), 3.06-3.08 (dd, *J* = 4.0, 5.2 Hz, 2H), 5.02-5.15 (ddd, *J* = 5.0, 12.5, 47.8 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 8.00 (d, *J* = 8.0 Hz, 1H).
^{13}C NMR: ($CDCl_3$,125 MHz): δ 26.96 (d), 29.98 (d), 91.08 (d), 127.12, 127.82, 128.62, 134.14, 142.97, 193.39 (d).
^{19}F NMR: ($CDCl_3$, 338 MHz): δ -190.958 (dt, *J* = 6.8-9.8, 54.08 Hz)
GC-MS, m/z (%): 164 (M^+, 99.8), 133 (10.6), 118 (100), 90 (91.37).

General Procedure for Preparation of 3-Fluoro-2-octanone and 4-Fluoro-5-nonanone [3]

A mixture of ketone (2 mM) and accufluor ™- NFTh (2.5 mM) in dry acetonitrile (35 mL) is stirred at 80°C until all reagent was dissolved and then heated to reflux 8-12h (reaction was monitored by GC). Heating was stopped, the reaction mixture was cooled to rt and solvent was removed under reduced pressure. The crude reaction mixture was dissolved in CH_2Cl_2 (40 mL), and insoluble materials was filtered off. The filtrate was washed with saturated sodium bicarbonate solution, water and dried over anhydrous $MgSO_4$. Solvent was removed under reduced pressure and the crude product was purified by silica gel-column chromatography using hexane-ether as eluent.



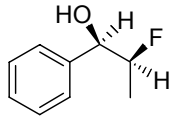
3-Fluoro-2-octanone
Clear liquid, yield: 41%
^{1}H NMR: ($CDCl_3$, 500 MHz): δ 0.81 (t, *J* = 6.0 Hz, 3H), 1.36-1.39 (m, 2H), 1.48-1.51(m, 4H), 2.06 (s, 3H), 2.18 (dd, *J* = 2.0, 5.0 Hz, 2H), 4.65 (dm, *J* = 48.9 Hz, 1H)
^{13}C NMR: ($CDCl_3$,125 MHz): δ 13.78, 22.25, 24.0, 25.69, 31.19, 31.75 (d), 95.84 (d), 208.34 (d).
^{19}F NMR: ($CDCl_3$, 338 MHz): δ - 189.77 (m)
GC-MS, m/z (%): 146 (M^+, 18.4), 99 (3.2), 85 (5.9), 76 (100), 55 (28.0).



4-Fluoro-5-nonanone
Clear Liquid, yield: 49 %
^{1}H NMR: ($CDCl_3$, 500 MHz): δ 0.92 (m, 6H), 1.22-1.32 (m, 4H), 1.42-1.49 (m, 2H), 1.69-1.75 (m, 2H), 2.54-2.56 (dm, *J* = 8. 5 Hz, 2H), 4.70 (dq, *J* = 6.0, 50.1 Hz, 1H).
^{13}C NMR: ($CDCl_3$,125 MHz): δ 13.79, 13.82, 17.89, 22.36, 24.73, 34.01 (d), 37.68, 95.83 (d), 212.5 (d).
^{19}F NMR: ($CDCl_3$, 338MHz): δ -192.3 (m)
GC-MS, m/z (%): 160 (M^+, 14.8), 118 (3.7), 85 (100), 76 (8.3), 57 (81.6).

General Procedure for Reduction of α-Fluoroketones in the presence of a Ti(IV) Lewis Acids

α-Fluoroketone (30 mM, 1.0 equiv) was dissolved in dry diethyl ether (or dichloromethane) and cooled to –78 ^{o}C under N_2. Lewis Acid (38 mM to 100 mM, 1.25 to 3.5 equiv of LA) was added and the reaction mixture was allowed to stir at –78 ^{o}C for 15 minutes. Metal reducing agent (2.0 equiv) was added and the reaction mixture was allowed to stir for 4-7h at -78^{o}C. [In the case of $TiCl_4$ with diethyl ether solvent, after the addition of $TiCl_4$ the reaction mixture turns a brown color. When this occurred, an additional amount of diethyl ether (5 mL) was added to the reaction followed by the metal reducing agent. The change in color had no impact on the outcome of the reaction]. The reaction was quenched with saturated NH_4Cl and then slowly warmed to room temperature. The suspension was poured into water and the organic layer was extracted with Et_2O (or CH_2Cl_2). The combined organic layer was washed with brine, and was dried over $MgSO_4$. After filtration the solvent was removed under vacuum to yield the α-fluoroalcohols.



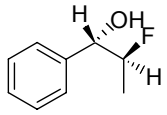
2-Fluoro-1-phenyl-1-propanol

Syn: ^{1}H NMR ($CDCl_3$, 500 MHz) δ1.15-1.21 (dd, *J* = 6.0, 24.0 Hz, 3H), 2.73 (brs, 1H, OH), 4.72-4.78 (ddm, *J* = 6.0-7.0, 45.0 Hz, 1H), 4.83-4.87 (ddd, *J* = 4.0, 6.0, 10.5 Hz, 1H), 7.28-7.33 (Ar, 5H).

^{13}C NMR: ($CDCl_3$,125 MHz): δ 16.95 (d), 77.68 (d), 93.76 (d), 127.04, 128.4, 128.56, 139.

^{19}F-NMR ($CDCl_3$, 338.86 Hz) δ -180.53 (m).

GC-MS, m/z (%): 154 (M^+, 11), 107 (80.5), 79 (100), 77 (75).

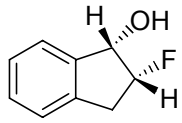


Anti: ^{1}H NMR ($CDCl_3$, 500 MHz) δ1.21-1.27 (dd, *J* = 6.0, 24.0 Hz, 3H), 2.40 (brs, 1H, OH), 4.58-4.67 (dm, *J* = 45.0 Hz, 1H), 4.86-4.89 (brdd, *J* = 3.5, 13.5 Hz, 1H), 7.34-7.36 (ArH, 5H).

^{13}C NMR: ($CDCl_3$,125 MHz): δ 14.56 (d), 75.57 (d), 92.96 (d), 126.45, 127.96, 128.44, 138.95.

^{19} F NMR ($CDCl_3$, 338.86 Hz) δ -180.90 (m).

GC-MS, m/z (%): 154 (M^+, 6), 107 (43), 79 (100), 77 (96).



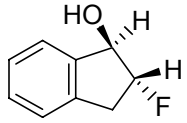
2-Fluoro-1-hydroxyindane[4]

Syn:^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.43 (brs, 1H, O*H*), 2.98 (ddd, *J* = 34.0, 17.3, 4.4 Hz, 1H), 3.14 (dd, *J* = 22.4, 17.3 Hz, 1H), 5.09 (dd, *J* = 4.2, 18.6 Hz, 1H), 5.30 (dm, *J* = 55.5 Hz, 1H), 7.21-7.23 (ArH, 2H), 7.37-7.39 (ArH, 2H).

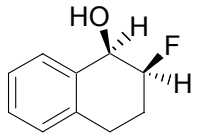
^{13}C NMR: ($CDCl_3$, 125 MHz): δ 36.23 (d), 79.72 (d), 100.22 (d), 124.64, 125.14, 127.62, 129.21, 138.63, 141.44.

^{19} F NMR ($CDCl_3$, 338.86 Hz) δ -186.53 (m).

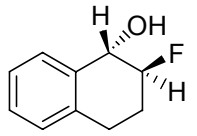
GC-MS, m/z (%): 152 (M^+, 100), 151 (49), 134 (21), 131 (53), 104 (74), 78 (28), 77 (32).



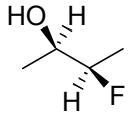
Anti:^{1}H NMR ($CDCl_3$, 500 MHz) δ 2.26 (brs, 1H, OH), 3.30 (dt, *J* = 6.7, 16.0 Hz, 1H), 2.82 (m, 1H), 5.12 (dd, *J* = 20.0, 2.5, Hz, 1H), 5.33 (dm, *J* = 56.0 Hz, 1H), 7.15-7.18 (ArH, 2H), 7.30-7.33 (ArH, 2H).
^{19} F NMR ($CDCl_3$, 338.86 Hz) δ -201.44 (m).
^{13}C NMR: ($CDCl_3$,125 MHz): δ 36.6 (d), 76.36 (d), 94.8 (d), 124.56, 125.2, 127.45, 128.79, 138.31, 140.76.
GC-MS, m/z (%): 152 (M^+, 100), 151 (48), 134 (20), 131 (61), 104 (100), 103 (91), 78 (38), 77 (65).



2-Fluoro-1-tetralol [5]
Syn:^{1}H NMR: ($CDCl_3$, 500 MHz): δ 2.02-2.07 (m, 1H), 2.32-2.39 (m, 1H), 2.44 (brs, 1H, OH), 2.75-2.78 (m, 1H), 3.02-3.05 (m, 1H), 4.77 (dd, *J* = 6.0-7.0, 18.0 Hz, 1H), 4.9-5.03 (ddt, *J* = 49.69, 8.5, 2.9 Hz, 1H), 7.11 (t, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 7.48 (t, 1H).
^{13}C NMR: ($CDCl_3$,125 MHz): δ 24.34 (d), 25.54 (d), 68.91(d), 91.02 (d), 126.5, 128.07, 128.27, 129.14, 135.43, 135.57.
^{19}F NMR: ($CDCl_3$, 338MHz): δ -185.15 (m).
GC-MS, m/z (%): 166 (M^+, 37.2), 148 (85.14), 147 (17.0), 120 (71.9), 119 (100), 91 (44.0).

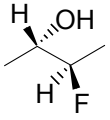


Anti:^{1}H NMR: ($CDCl_3$, 500 MHz): δ 1.95-2.01 (m, 1H) , 2.18-2.25 (m, 1H), 2.59 (brs, 1H, OH), 2.80-2.84 (m, 1H), 2.98-3.01 (m, 1H), 4.7 (dm, *J* = 46.9 Hz, 1H), 4.79-4.81 (dm, *J* = 16-20 Hz, 1H), 7.09 (t, 1H), 7.19 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.5 Hz, 1H), 7.53 (t, 1H).
^{13}C NMR: ($CDCl_3$,125 MHz): δ 25.91(d), 26.28 (d), 71.6 (d), 93.15 (d), 126.6, 127.94, 128.11, 135.18, 135.46, 135.53.
^{19}F NMR: ($CDCl_3$, 338MHz): δ -197.79 (m).
GC-MS, m/z (%): 166 (M^+, 32.0), 148 (80.2), 147 (17.0), 120 (70.3), 119 (100), 91 (41.3).

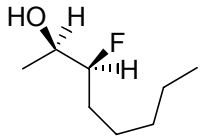


3-Fluoro-2-butanol

Syn: ^{1}H NMR: ($CDCl_3$, 500 MHz): δ 1.1 (d, *J* = 1.0 Hz, 3H), 1.22 (dd, *J* = 2.24, 6.37 Hz, 3H), 2.54 (brs, 1H, OH), 3.65 (ddq, *J* = 4.5, 7.5, 21.5Hz, 1H), 4.35 (dpentate, *J* = 6.0-7.0, 49.0 Hz, 1H).
^{13}C NMR: ($CDCl_3$,125 MHz): δ 15.5 (d), 17.11 (d), 69.28 (d), 93.35 (d).
^{19}F NMR: ($CDCl_3$, 338 MHz): δ -183.18 (m)

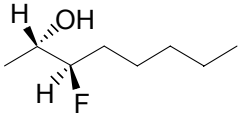


Anti: ^{1}H NMR: ($CDCl_3$, 500 MHz): δ 1.11 (d, *J* = 1.0 Hz, 3H) , 1.26 (dd, *J* = 2.0, 6.5 Hz, 3H), 2.43 (brs, 1H, OH), 3.82 (ddq, *J* = 2.5, 4.5, 22.6 Hz, 1H), 4.49 (ddq, *J* = 2.5, 3.5, 43.8 Hz, 1H).
^{13}C NMR: ($CDCl_3$,125 MHz): δ 16.73 (d), 17.92 (d), 70.95 (d), 94.16 (d).
^{19}F NMR: ($CDCl_3$, 338 MHz): δ -183.54 (m)

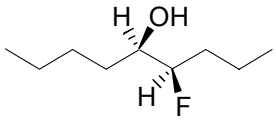


3-Fluoro-2-octanol

Syn: ^{1}H NMR: ($CDCl_3$, 500 MHz): δ 0.79 (t, *J* = 7.0 Hz, 3H) , 1.12 (d, *J* = 6.4 Hz, 3H), 1.25 (m, 4H), 1.3-1.34 (m, 2H), 1.5-1.52 (m, 2H), 3.24 (brs, 1H), 4.08 (dm, *J* = 12.5 Hz, 1H) 4.3 (ddt, *J* = 5.2, 6.4, 50.0 Hz, 1H).
^{19}F NMR: ($CDCl_3$, 338 MHz): δ -192.96 (m)

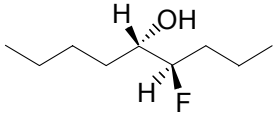


Anti: ^{1}H NMR: ($CDCl_3$, 500 MHz): δ 0.83 (t, *J* = 6.8 Hz, 3H) , 1.15 (d, *J* = 7.2 Hz, 3H), 1.28 (m, 4H), 1.39-1.49 (m, 4H), 3.05 (brs, 1H), 4.11 (dm, *J* = 10.8 Hz, 1H) 4.35 (dt, *J* = 29.5, 6.7 Hz, 1H).
^{19}F NMR: ($CDCl_3$, 338 MHz): δ -195.51 (m)



4-Fluoro-5-nonanol

Syn: ^{1}H NMR: ($CDCl_3$, 500 MHz): δ 0.89 (t, J = 7.0 Hz, 6H) , 1.25-1.56 (m, 8H), 1.69 (m, 2H), 2.0 (brs, 1H), 3.49 (m, 1H), 4.26 (ddm, J = 5.5, 50.0 Hz, 1H).
^{19}F NMR: ($CDCl_3$, 338 MHz): δ -191.25 (m)



Anti: ^{1}H NMR: ($CDCl_3$, 500 MHz): δ 0.93 (t, J = 7.0 Hz, 6H) , 1.17-1.51 (m, 8H), 1.65 (m, 2H), 2.4 (brs, 1H), 3.53 (m, 1H), 4.38 (ddm, J = 2.0, 48.5 Hz, 1H)
^{19}F NMR: ($CDCl_3$, 338 MHz): δ -195.55 (m)

Table 1a.

^{1}H-NMR of α-Fluoropropiophenone and $TiCl_4$-Complexes

LA/Solvent	H	δ	Δδ	mult	*J*/Hz
No LA/CD_2Cl_2	C*H*$_3$	1.58		dd	J_{HH} = 6.7, J_{HF} = 24.4
	C*H*F	5.96		dq	J_{HH} = 6.7, J_{HF} = 49.0
	Ar*H*	7.50		t	J_{HH} = 7.2
		7.60		t	J_{HH} =7.5
		7.87		d	J_{HH} = 7.9
$TiCl_4$/CD_2Cl_2					
	C*H*$_3$	2.15	0.57	dd	J_{HH} = 6.4, J_{HF} = 28.8
	C*H*F	6.82	0.86	brdd	J_{HH} = 5.8, J_{HF} = 50.4
	Ar*H*	7.74	0.24	t	J_{HH} = 7.2
		8.00	0.40	t	J_{HH} = 6.9
		8.15	0.28	d	J_{HH} = 7.00
Ti(O^{i}Pr) / CD_2Cl_2					
	C*H*$_3$	1.66	0.08	dd	J_{HH} = 6.8, J_{HH} = 23.7
	C*H*F	5.89	-0.07	dq	J_{HH} = 6.7, J_{HF} = 48.4
	Ar*H*	7.52	0.02	t	J_{HH} = 7.6
		7.65	0.05	t	J_{HH} = 7.6
		7.99	0.12	d	J_{HH} = 7.6

Table 1b.

^{13}C-NMR of α-Fluoropropiophenone and $TiCl_4$-Complexes

LA/Solvent	C	δ	Δδ	mult	*J*/Hz
No LA / CD_2Cl_2	*C*H_3	18.11		d	*J* = 22.76
	*C*HF	90.93		d	*J* = 178.84
	*C*O	196.17		d	*J* = 19.1
	Ar	129.0, 129.12, 134.07, 134.47			
$TiCl_4/CD_2Cl_2$					
	CH_3	20.12	2.01	d	*J* = 21.87
	*C*HF	98.36	7.43	d	*J* = 173.16
	*C*O	205.8	9.64	brs	
	Ar	129.0, 130.7, 132.23, 140.33			
$Ti(O^iPr)_4/CD_2Cl_2$					
	CH_3	18.15	0.04	d	*J* = 22.76
	*C*HF	90.5	-0.43	d	*J* = 178.95
	*C*O	196.47	0.3	d	*J* = 19.24
	Ar	128.89, 129.11, 129.15, 134.09, 134.51			

Table 1c

^{19}F-NMR of α-Fluoropropiophenone and $TiCl_4$-Complexes

LA/Solvent	F	δ	Δδ	mult
No LA / CD_2Cl_2	CH*F*	-187.0		m
$TiCl_4/CD_2Cl_2$	CH*F*	-174.82	13.18	m
$Ti(O^iPr)_4/CD_2Cl_2$	CH*F*	-186.54	0.46	m

Table 2a

^{1}H-NMR of Propiophenone and $TiCl_4$-Complexes$^{\tau}$

LA/Solvent	H	δ	Δδ	mult	*J*/Hz
No LA/CD_2Cl_2	C*H*$_3$	1.1		t	J_{HH} = 7.0
	C*H*$_2$	3.03		q	J_{HH} = 7.1
	Ar*H*	7.46		t	J_{HH} = 6.8
		7.56		t	J_{HH} = 7.0
		7.96		d	J_{HH} = 7.5

table **2a** continued

$TiCl_4/CD_2Cl_2$

C*H*$_3$	1.49	0.39	t	J_{HH} = 7.5
C*H*$_2$	3.49	0.46	q	J_{HH} = 7.5
Ar*H*	7.69	0.23	t	J_{HH} = 6.4
	7.87	0.21	t	J_{HH} = 7.5
	8.27	0.31	d	J_{HH} = 8.0

Table 2b.

^{13}C-NMR of Propiophenone and $TiCl_4$-Complexes$^{\tau}$

LA/Solvent	**C**	**δ**	**Δδ**
No LA / CD_2Cl_2	*C*H$_3$	8.31	
	*C*H$_2$	32.08	
	*C*O	200.81	
	Ar	128.2, 128.88, 133.12, 137.44	
$TiCl_4/CD_2Cl_2$			
	*C*H$_3$	11.93	3.62
	*C*H$_2$	33.01	0.93
	*C*O	217.84	17.03
	Ar	130.23, 132.71, 133.67, 139.02	

$^{\tau}$ ^{1}H-NMR of propiophenone and propiophenone-$TiCl_4$ complex are recorded at -78^{o}C.

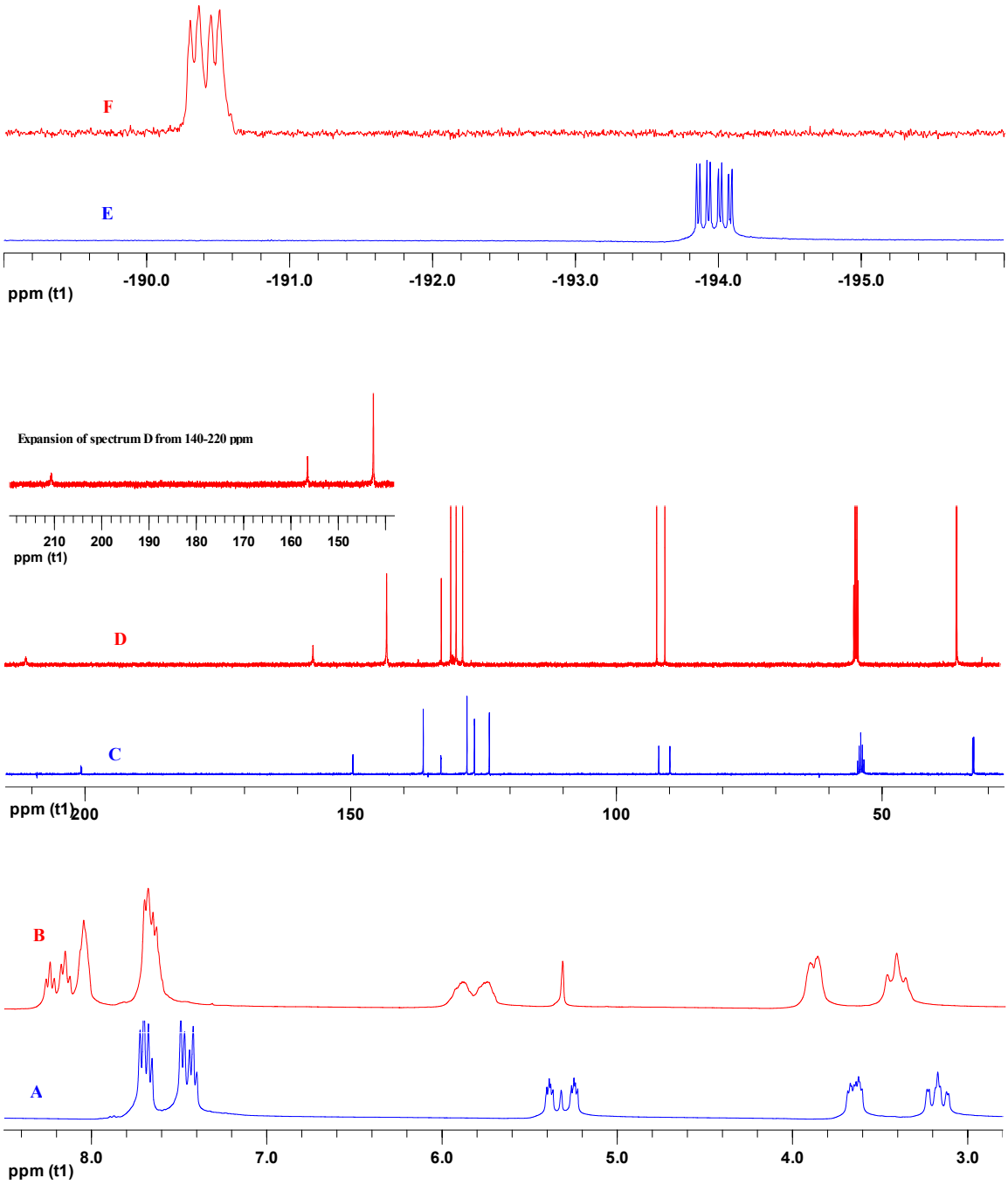


Figure 1. **A, C,** and **E** are the ^{1}H, ^{13}C, and ^{19}F nmr spectra of α-fluoroindanone in CD_2Cl_2 at -78 ^{o}C. **B**, **D,** and **F** are the respective ^{1}H, ^{13}C, and ^{19}F nmr spectra of α-fluoroindanone containing 1.25 equiv of $TiCl_4$ in CD_2Cl_2 at $-78^{0}C$. In ^{1}H-NMR spectra, the peak at δ 5.32 is due to trace amounts of $CHDCl_2$ in CD_2Cl_2 where as in ^{13}C-NMR spectra, the peak at δ 54.0 is due to CD_2Cl_2.

Table 3a

^{1}H-NMR of α-Fluoroindanone and $TiCl_4$-Complexes

LA/Solvent	H	δ	Δδ	mult	*J*/Hz
No LA/CD_2Cl_2	C*H*$_2$	3.17		m	
	C*H*$_2$	3.65		m	
	C*H*F	5.31		dq	J_{HH} = 4.8, J_{HF} = 50.4
	Ar*H*	7.42		t	J_{HH} = 7.2
		7.48		d	J_{HH} = 7.6
		7.66		t	J_{HH} = 7.6
		7.71		d	J_{HH} = 7.9
$TiCl_4/CD_2Cl_2$					
	C*H*$_2$	3.42	0.25	t	J_{HF} = 18.0
	C*H*$_2$	3.89	0.24	brdd	J_{HF} = 10.8, J_{HH} = 3.6
	C*H*F	5.82	0.31	brdq	J_{HH} = 3.2, J_{HF} = 46.8
	Ar*H*	7.67	0.25	brm	
		8.05	0.57	brs	
		8.12	0.28	t	J_{HH} = 7.9
		8.24	0.53	t	J_{HH} = 8.28

Table 3b.

^{13}C-NMR of α-Fluoroindanone and $TiCl_4$-Complexes

LA/Solvent	C	δ	Δδ	mult	*J*/Hz
No LA / CD_2Cl_2	*C*H$_2$	32.85		d	*J* = 28.55
	*C*HF	90.97		d	*J* = 263.33
	*C*O	200.65		d	*J* = 20.86
	Ar	123.91, 126.72, 128.1, 133.01, 136.33, 149.53 (d, *J* = 8.8 Hz)			
$TiCl_4/CD_2Cl_2$					
	*C*H$_2$	35.22	2.37	d	*J* = 21.38
	*C*HF	91.06	0.09	d	*J* = 195.82
	*C*O	210.86	10.21	brs	
	Ar	128.42, 129.65, 130.67, 132.45, 142.78, 156.66 (d, *J* = 2.6 Hz)			

Table 3c

^{19}F-NMR of α- α-Fluoroindanone and $TiCl_4$-Complexes

LA/Solvent	F	δ	Δδ	mult/Hz
No LA / CD_2Cl_2	CH*F*	-194.03		ddd (J_{HH} = 7.45, J_{HF} = 50.79, 23.7)
$TiCl_4$/CD_2Cl_2	CH*F*	-190.41	3.92	dd (J_{HF} = 49.1, 20.32)

References

1. Enders, D.; Faure, S.; Potthoff, M.; Rundsink, J. *Synthesis* **2001,** 2307-2319.
2. Stavber, S.; Jereb, M.; Zupan, M. *Synthesis* **2002,** 2609-2615.
3. Stavber, S.; Zupan, M. *Tetrahedron Lett.* **1996**, *37*, 3591-3594.
4. Shellhamer, D. F.; Carter, D. L.; Chiaco, M. C.; Harris, T. E.; Henderson, R. D.; Low, W. S. C.; Metcalf, B. T.; Willis, M. C.; Heasley, V. L.; Chapman, R. D. *J. Chem. Soc, Perkin Trans 2*, **1991**, 401-403.
5. Baur, M.A; Riahi, A.; He´nina, F.; Muzarta, J. *Tetrahedron Asymmetry* **2003**, *14,* 2755-2761.