Supporting information

Direct Generation of Ti-enolate of α-CF_3 Ketone: Theoretical Study, and High Yielding and Diastereoselective Aldol Reaction

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General:

^{1}H NMR and ^{13}C NMR were measured on Varian Gemini 2000 (300 MHz) spectrometers and ^{19}F NMR was measured on Varian UNITY INOVA (400 MHz) spectrometers. Chemical shift of ^{1}H NMR was expressed in parts per million downfield from tetramethylsilane as an internal standard (δ=0) in $CDCl_3$. Chemical shifts of ^{13}C NMR were expressed in parts per million downfield from $CDCl_3$ as an internal standard (δ = 77.0) in $CDCl_3$. Chemical shifts of ^{19}F NMR were expressed in parts per million downfield from BTF as an internal standard (δ=-63.24) in $CDCl_3$. Analytical thin layer chromatography (TLC) were performed on a glass plates and /or aluminum sheets pre-coated with silica gel (Merck Kieselgal 60 F_{254}, layer thickness 0.25 and 0.2 mm). Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$ and phosphomolybdic acid. Column chromatography was performed on Merck Kieselgel 60 and KANTO Silica Gel 60N (spherical, neutral), employing hexane ethyl acetate mixture as an eluent unless otherwise noted. All experiments were carried out under argon atmosphere unless otherwise noted. The calculations were performed with a GAUSSIAN 98 and 03 program package.

General Experimental procedure for Ti-enolate formation and the reaction with D_2O or DCl

To a solution of 1,1,1-trifluoro-4,4-dimethyl-5-phenyl-3-pentanone (**1**)(17.1 mg, 0.07 mmol) in dichloromethane (0.7 ml) was added titanium tetrachloride (9.2 µl, 0.084 mmol) at 0 °C and stirred for 10 min under argon atmosphere. Then the reaction mixture was cooled to -78 °C and was added triethylamine (13.7 µl, 0.098 mmol) at the temperature. The reaction mixture was stirred for 15 min and then was quenched with D_2O or 35wt% DCl/D_2O (0.1 ml) and warmed to room temperature. The crude mixture was directly analyzed by ^{19}F NMR using BTF as an internal standard.

General Experimental procedure for Ti-enolate formation and aldol reaction

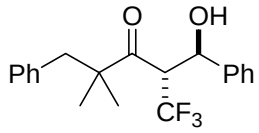
To a solution of 1,1,1-trifluoro-4,4-dimethyl-5-phenyl-3-pentanone (**1**)(17.1 mg, 0.07 mmol) in dichloromethane (0.7 ml) was added titanium tetrachloride (9.2 µl, 0.084 mmol) at 0 °C and stirred for 10 min under argon atmosphere. Then the reaction mixture was cooled to -78 °C and was added triethylamine (13.7 µl, 0.098 mmol) at the temperature. The reaction mixture was stirred for 15 min and then was added benzaldehyde (8.5 µl, 0.084 mmol) and titanium (IV) isopropoxide (24.8 µl, 0.084 mmol). After stirring for 24 h at -78 °C, the reaction was quenched by adding phosphorous buffer (pH=7) at the temperature. The mixture was extracted 3 times with ether. Combined organic layer was washed with brine, dried over anhydrous sodium sulfate and evaporated under reduced pressure. The crude mixture was purified by silica gel

column chromatography (hexane:acetone=10:1 to 6:1). 23.8 mg of 5-Hydroxy-2,2-dimethyl-1,5-diphenyl-4-trifluoromethyl-3-pentanone was obtained (97%).

Determination of the relative stereochemistry of the aldol product

The X-ray analysis of the product of the reaction with benzaldehyde (Table 2, entry 1) revealed that the relative stereochemistry was ***anti***. The product of the reaction with 2-methylpropanal (entry 2) was converted to acetonide and the NMR analysis of the acetonide revealed that this product has also ***anti***-stereochemistry. The stereochemistry of the product of the reaction with 3-phenylpropanal (entry 3) was determined by the analogy of the NMR chemical shift of the above determined compounds to be ***anti***.

5-Hydroxy-2,2-dimethyl-1,5-diphenyl-4-trifluoromethyl-3-pentanone



^{1}H NMR ($CDCl_3$, 300 MHz)

δ 0.89 (s, 3H), 1.01 (s, 3H), 2.63 (d, ***J***=13.5 Hz, 1H), 2.73 (d, ***J***=13.5, 1H), 3.15 (d, ***J***=5.7 Hz, 1H), 4.18 (dq, ***J***=6.6, 8.1 Hz, 1H), 5.27 (dd, J=6.0, 6.3 Hz, 1H), 7.07~7.10 (m, 2H), 7.16~7.42 (m, 8H)

^{13}C NMR ($CDCl_3$, 75 Hz)

δ 22.9, 23.2, 43.3, 49.4, 54.9 (q, ***J***=24.4 Hz), 72.6 (q, ***J***=2.4 Hz), 123.4 (q, ***J***=282.6 Hz), 126.5, 126.6, 128.0, 128.8, 128.9, 131.1, 137.2, 140.9, 211.2

^{19}F NMR ($CDCl_3$, 376 Hz)

δ -62.6 (d, ***J***=7.9 Hz) (-61.4 (d, ***J***=7.9 Hz) for ***syn*** isomer)

IR (neat)

3484, 3034, 2978, 2932, 1715, 1495, 1470, 1458, 1338, 1241, 1160, 1129, 700

X-ray analysis (CCDC 240382)

Empirical Formula	C20H21F3O2
Formula Weight	350.38
Crystal System	triclinic
Lattice Type	Primitive
Lattice Parameters	a = 6.469(4) Å
	b = 10.934(6) Å
	c = 13.371(9) Å
	a = 73.90(2) o
	b = 88.25(3) o
	g = 76.29(2) o
	V = 882.2(10) Å3
Space Group	P-1 (#2)
Z value	2
Dcalc	1.319 g/cm3
Detector	Rigaku Saturn
Goniometer	Rigaku AFC10

Radiation	MoKa (l = 0.71070 Å) graphite monochromated
Structure Solution	Direct Methods (SIR92)
esiduals: R; Rw	0.096; 0.162
Goodness of Fit Indicator	0.991

Bond lengths (Å)

atom	atom	distance	atom	atom	distance
F(2)	C(15)	1.339(4)	F(3)	C(15)	1.346(4)
F(4)	C(15)	1.331(5)	O(1)	C(20)	1.211(4)
O(2)	C(18)	1.417(3)	C(1)	C(2)	1.398(4)
C(1)	C(7)	1.373(5)	C(1)	C(10)	1.515(4)
C(2)	C(3)	1.389(5)	C(3)	C(4)	1.363(6)
C(4)	C(5)	1.379(5)	C(5)	C(7)	1.385(5)
C(6)	C(8)	1.392(4)	C(6)	C(18)	1.513(3)
C(6)	C(19)	1.380(5)	C(8)	C(13)	1.383(4)
C(9)	C(12)	1.529(4)	C(10)	C(12)	1.547(4)
C(11)	C(15)	1.501(4)	C(11)	C(18)	1.554(4)
C(11)	C(20)	1.545(3)	C(12)	C(16)	1.531(4)
C(12)	C(20)	1.534(4)	C(13)	C(14)	1.376(6)
C(14)	C(21)	1.381(5)	C(19)	C(21)	1.384(4)

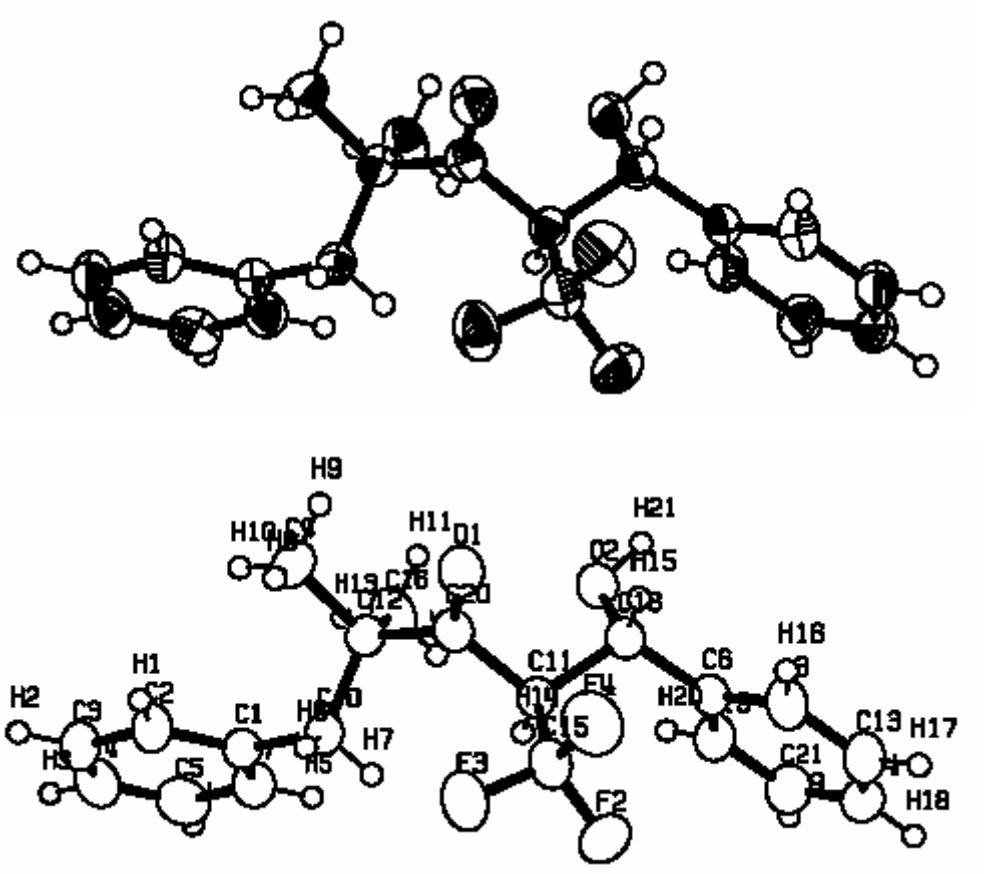
Bond angles (°)

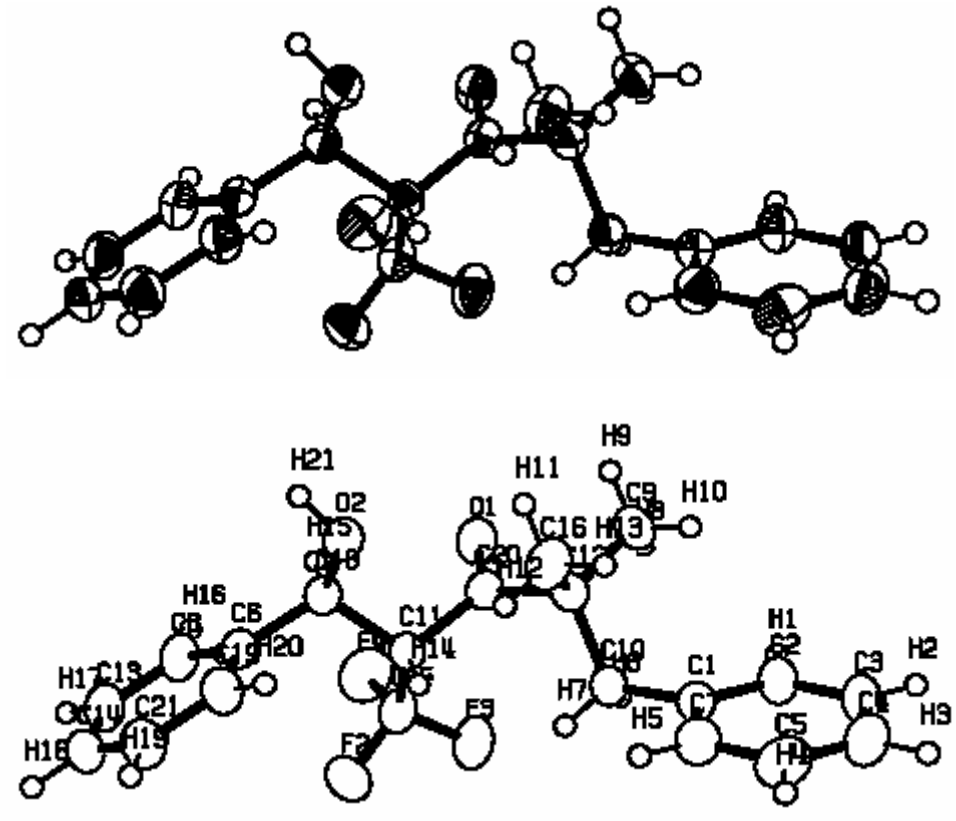
atom	atom	atom	angle	atom	atom	atom	angle
C(2)	C(1)	C(7)	118.3(3)	C(2)	C(1)	C(10)	120.5(3)
C(7)	C(1)	C(10)	121.2(2)	C(3)	C(2)	C(1)	120.2(3)
C(4)	C(3)	C(2)	120.6(3)	C(5)	C(4)	C(3)	119.6(3)
C(7)	C(5)	C(4)	120.1(4)	C(8)	C(6)	C(18)	120.6(3)
C(8)	C(6)	C(19)	119.1(2)	C(18)	C(6)	C(19)	120.3(3)
C(1)	C(7)	C(5)	121.1(3)	C(13)	C(8)	C(6)	120.2(3)
C(12)	C(10)	C(1)	115.5(2)	C(15)	C(11)	C(18)	112.5(2)
C(15)	C(11)	C(20)	109.3(2)	C(18)	C(11)	C(20)	107.9(2)
C(16)	C(12)	C(20)	108.8(2)	C(16)	C(12)	C(9)	110.0(2)
C(16)	C(12)	C(10)	110.6(3)	C(20)	C(12)	C(9)	108.3(3)
C(20)	C(12)	C(10)	108.8(2)	C(9)	C(12)	C(10)	110.2(2)
C(14)	C(13)	C(8)	120.2(3)	C(21)	C(14)	C(13)	120.1(3)
F(2)	C(15)	F(3)	105.3(3)	F(2)	C(15)	F(4)	106.3(2)
F(2)	C(15)	C(11)	112.9(3)	F(3)	C(15)	F(4)	105.6(3)
F(3)	C(15)	C(11)	112.2(2)	F(4)	C(15)	C(11)	113.9(3)
O(2)	C(18)	C(6)	112.0(2)	O(2)	C(18)	C(11)	104.0(2)
C(6)	C(18)	C(11)	113.3(2)	C(21)	C(19)	C(6)	120.7(3)
O(1)	C(20)	C(11)	118.0(2)	O(1)	C(20)	C(12)	121.2(2)
C(11)	C(20)	C(12)	120.8(3)	C(14)	C(21)	C(19)	119.8(4)

Torsion Angles(°)

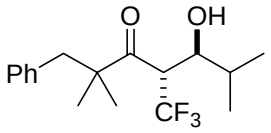
atom1	atom2	atom3	atom4	angle	atom1	atom2	atom3	atom4	angle
C(7)	C(1)	C(2)	C(3)	0.7(4)	C(10)	C(1)	C(2)	C(3)	-177.0(3)
C(2)	C(1)	C(7)	C(5)	-1.4(5)	C(10)	C(1)	C(7)	C(5)	176.3(3)
C(2)	C(1)	C(10)	C(12)	-85.1(3)	C(7)	C(1)	C(10)	C(12)	97.2(3)

C(1) C(2) C(3) C(4) 0.1(5)	C(2) C(3) C(4) C(5) -0.3(5)
C(3) C(4) C(5) C(7) -0.4(5)	C(4) C(5) C(7) C(1) 1.2(5)
C(18) C(6) C(8) C(13) 178.5(3)	C(19) C(6) C(8) C(13) -1.6(5)
C(8) C(6) C(18) O(2) 136.8(3)	C(8) C(6) C(18) C(11) -106.0(3)
C(19) C(6) C(18) O(2) -43.2(4)	C(19) C(6) C(18) C(11) 74.1(3)
C(8) C(6) C(19) C(21) 1.5(5)	C(18) C(6) C(19) C(21) -178.6(3)
C(6) C(8) C(13) C(14) 0.8(5)	C(1) C(10) C(12) C(9) 63.1(3)
C(1) C(10) C(12) C(16) -58.8(3)	C(1) C(10) C(12) C(20)-178.3(2)
C(18) C(11) C(15) F(2) -75.8(4)	C(18) C(11) C(15) F(3) 165.4(3)
C(18) C(11) C(15) F(4) 45.6(3)	C(20) C(11) C(15) F(2) 164.4(3)
C(20) C(11) C(15) F(3) 45.6(4)	C(20) C(11) C(15) F(4) -74.3(3)
C(15) C(11) C(18) O(2) -179.3(2)	C(15) C(11) C(18) C(6) 58.9(3)
C(20) C(11) C(18) O(2) -58.6(3)	C(20) C(11) C(18) C(6) 179.6(2)
C(15) C(11) C(20) O(1) 66.6(3)	C(15) C(11) C(20) C(12) -114.2(3)
C(18) C(11) C(20) O(1) -56.0(3)	C(18) C(11) C(20) C(12) 123.2(3)
C(9) C(12) C(20) O(1) -3.9(4)	C(9) C(12) C(20) C(11) 176.9(2)
C(10) C(12) C(20) O(1) -123.7(3)	C(10) C(12) C(20) C(11) 57.1(3)
C(16) C(12) C(20) O(1) 115.7(3)	C(16) C(12) C(20) C(11) -63.5(3)
C(8) C(13) C(14) C(21) 0.2(5)	C(13) C(14) C(21) C(19) -0.3(5)
C(6) C(19) C(21) C(14) -0.5(5)	





5-Hydroxy-2,2-dimethyl-6-methyl-1-phenyl-4-trifluoromethyl-3-heptanone



^{1}H NMR ($CDCl_3$, 300 MHz)

δ 0.94 (s, 3H), 0.97 (s, 3H), 1.14 (d, J=3.3 Hz, 6H), 1.75~1.88 (m, 1H), 2.03 (d, J=5.4 Hz, 1H), 2.78 (d, J=13.2 Hz, 1H), 2.89 (d, J=13.2 Hz, 1H), 3.98~4.11 (m, 2H), 7.12~7.17 (m, 2H), 7.19~7.32 (m, 3H)

^{13}C NMR ($CDCl_3$, 75 Hz)

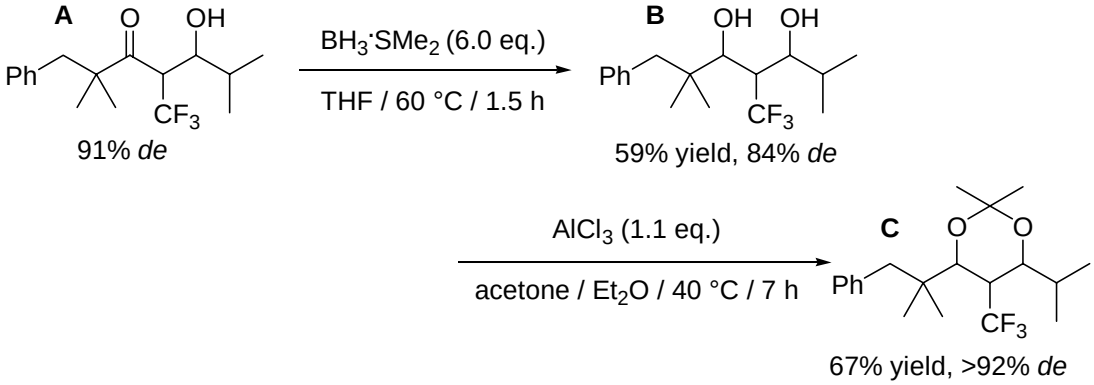
δ 14.8, 19.8, 23.5, 24.1, 30.6, 43.9, 49.6, 51.2 (q, J=24.4 Hz), 74.6 (q, J=2.4 Hz), 123.8 (q, J=280.8 Hz), 126.5, 127.9, 131.0, 137.2, 210.9

^{19}F NMR ($CDCl_3$, 376 Hz)

δ -62.5 (d, *J*=7.2 Hz) (-59.6 (d, *J*=7.9 Hz) for *syn* isomer)

IR (KBr)

3538, 2970, 2880, 1712, 1496, 1468, 1345, 1248, 1144, 1092, 1008, 874, 760, 728, 707



91% *de*

59% yield, 84% *de*

67% yield, >92% *de*

C

^{1}H NMR ($CDCl_3$, 300 MHz)

δ 0.91 (s, 6H), 0.93 (d, J=6.9 Hz, 3H), 1.02 (d, J=6.6 Hz, 3H), 1.30 (s, 3H), 1.39 (s, 3H), 1.83 (qqd, J=6.3, 6.3, 2.4 Hz, 1H), 2.45~2.58 (m, 1H), 2.61 (d, J=12.9 Hz, 1H), 2.74 (d, J=12.9 Hz, 1H), 2.62 (distorted q, J=1.8 Hz, 1H), 3.79 (dd, J=2.7, 6.6 Hz, 1H), 7.13~7.30 (m, 5H)

^{13}C NMR ($CDCl_3$, 75 Hz)

δ 14.5, 19.7, 22.1, 22.8, 25.6, 32.8, 37.0, 44.0, 44.9 (q, J=23.2 Hz), 71.2 (q, J=2.5 Hz), 75.2, 100.9, 125.0, 127.7, 127.8 (q, J=282.0 Hz), 131.2, 138.7

^{19}F NMR ($CDCl_3$, 376 Hz)

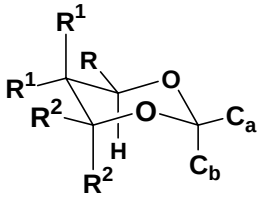
δ -62.2 (d, ***J***=10.2 Hz)

The aldol product (**A**) was converted to acetonide (**C**) by reduction with BH_3•SMe_2 and protection with acetone. NMR analysis of C is as follows.

(1) Since substituent R is bulky, it should be in equatorial orientation.

(2) The difference of 13C NMR chemical shift of Ca and Cb is 2.8. Therefore, two hydroxyl groups in 1,3-diol (B) should be ***anti***.[1]

(3) Analysis of two coupling constants showed clear ***anti*** conformation of the aldol product.



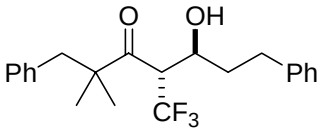
R=$C(CH_3)_2$Bn

(1) **R**: bulky ⟶ eqatorial

(2) $|\delta_{Ca}-\delta_{Cb}|$ =2.8 ppm ⟶ *anti*-1,3-diol (**B**)

(3) ($^{3}J_{HR1}$, $^{3}J_{R1R2}$)=(~0, 6.6) (Hz) ⟶ anti-aldol (**A**)

5-Hydroxy-2,2-dimethyl-1,7-diphenyl-4-trifluoromethyl-3-heptanone



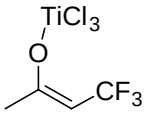
^{1}H NMR ($CDCl_3$, 300 MHz)

δ 1.14 (s, 3H), 1.15 (s, 3H), 1.69~1.81 (m, 1H), 1.83~1.97 (m, 1H), 2.27 (d, ***J***=6.9 Hz, 1H), 2.55~3.00 (m, 4H), 3.90 (qd, ***J***=7.8, 7.8 Hz, 1H), 4.11~4.22 (m, 1H), 7.09~7.33 (m, 10H)

^{13}C NMR ($CDCl_3$, 75 Hz)
δ 23.4, 23.9, 31.4, 36.8, 43.7, 49.6, 53.8 (q, *J*=23.2 Hz), 69.6 (q, 2.4 Hz), 123.8 (q, *J*=282.0 Hz), 126.3, 126.7, 128.1, 128.5, 128.7, 131.1, 137.2, 141.1, 211.1
^{19}F NMR ($CDCl_3$, 376 Hz)
δ -62.28 (d, *J*=9.0 Hz)(-60.27 (d, *J*=8.3 Hz) for *syn*-isomer)
IR (neat)
3508, 3030, 2976, 2932, 1713, 1497, 1470, 1456, 1334, 1257, 1156, 1125, 702

Ab initio calculations

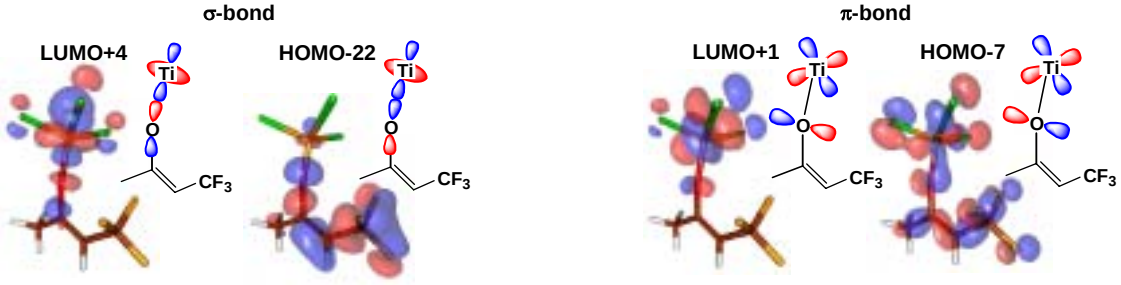
$TiCl_3$-enolate of α-CF_3 acetone

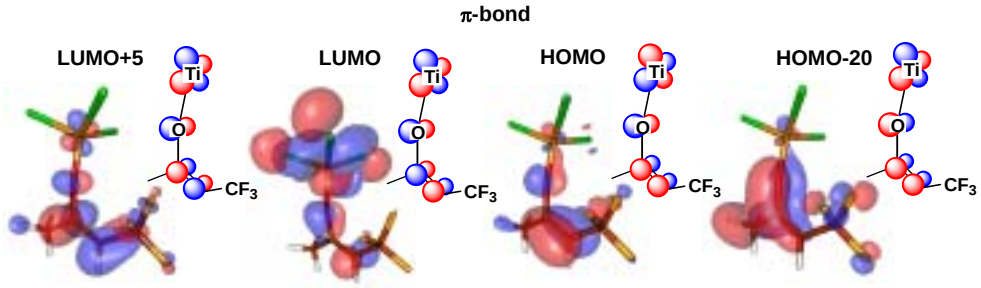


E(B3LYP/631LAN) = -1968.48494129 hartree

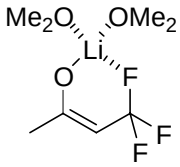
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.108527	0.945609	-0.173877
2	6	0	1.241256	1.687280	-0.094167
3	6	0	2.440350	1.092514	-0.002359
4	22	0	-1.284791	-0.121002	-0.004801
5	6	0	2.642523	-0.390578	-0.005337
6	1	0	3.337027	1.697635	0.046831
7	6	0	1.000373	3.166721	-0.123089
8	9	0	1.846416	-1.027965	0.890538
9	9	0	3.918451	-0.689039	0.307366
10	9	0	2.378904	-0.940792	-1.212584
11	17	0	-3.047065	0.974617	-0.693115
12	17	0	-1.047381	-1.918290	-1.211432
13	17	0	-1.550654	-0.623546	2.100165
14	1	0	0.361290	3.462873	0.716937
15	1	0	0.482160	3.447264	-1.047294
16	1	0	1.942448	3.716682	-0.063515

$TiCl_3$-enolate has triple bond nature at Ti-O bond. Analysis of molecular orbital showed clear interaction between lone electron pair of oxygen and empty d orbital of Ti which causes Ti-O triple bond.





Li-enolate of α-CF_3 acetone

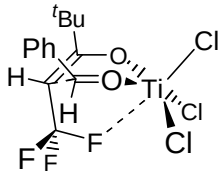


E(B3LYP/631LAN) = -847.272733894 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.468444	0.984952	1.169893
2	6	0	1.656935	1.240669	0.736229
3	6	0	2.287983	0.565099	-0.290919
4	3	0	-0.754844	0.072175	0.159242
5	6	0	1.684506	-0.585053	-0.939024
6	1	0	3.282998	0.826975	-0.624866
7	6	0	2.387726	2.385429	1.416753
8	9	0	1.488323	-1.699597	-0.149713
9	9	0	2.351137	-1.008418	-2.024584
10	9	0	0.344197	-0.348238	-1.400976
11	8	0	-1.437604	-1.602996	0.945157
12	6	0	-1.606692	-2.780473	0.163717
13	6	0	-0.824776	-1.869638	2.210191
14	8	0	-2.193098	1.282907	-0.400597
15	6	0	-3.242660	1.064491	-1.329434
16	6	0	-1.973752	2.663568	-0.109079
17	1	0	-4.192932	1.460986	-0.945401
18	1	0	-3.335677	-0.015017	-1.469709
19	1	0	-3.019146	1.539284	-2.295235
20	1	0	-1.134596	2.696034	0.587329
21	1	0	-2.870738	3.103658	0.347872
22	1	0	-1.724378	3.215764	-1.025674
23	1	0	-2.097216	-2.485578	-0.767316
24	1	0	-2.241343	-3.506128	0.690596
25	1	0	-0.635471	-3.235675	-0.065804
26	1	0	-1.498766	-2.468764	2.837088
27	1	0	-0.627139	-0.903489	2.676045
28	1	0	0.124840	-2.400072	2.071545

29	1	0	2.478352	2.171996	2.488630
30	1	0	1.799096	3.306442	1.323814
31	1	0	3.386178	2.559886	1.004593

TS of the aldol reaction (*anti*-aldol)

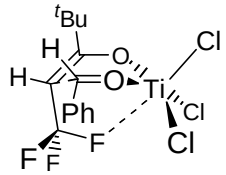


E(B3LYP/631LAN) = -2431.98683106 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	0.897642	0.855532	0.770506
2	6	0	-0.222301	1.419230	0.510840
3	6	0	-0.737464	1.380401	-0.799653
4	6	0	-0.946813	-0.802637	-0.902069
5	8	0	0.024712	-1.234682	-0.178255
6	22	0	1.876504	-0.772536	0.241333
7	1	0	-0.763846	-0.700969	-1.973630
8	6	0	0.156946	1.559116	-1.988506
9	6	0	-2.340503	-1.111576	-0.522300
10	1	0	-1.708883	1.828065	-0.972242
11	6	0	-0.953782	2.045130	1.702142
12	9	0	0.648299	2.810864	-2.075003
13	9	0	-0.529778	1.321191	-3.132495
14	9	0	1.231715	0.718850	-2.000228
15	6	0	-2.633318	-1.765421	0.684173
16	6	0	-3.954224	-2.077467	1.000907
17	6	0	-4.986642	-1.738853	0.120925
18	17	0	2.126654	-1.844803	2.135235
19	17	0	2.530186	-2.233562	-1.313544
20	17	0	3.717800	0.483603	0.139483
21	6	0	-0.995382	1.041801	2.875579
22	6	0	-2.382514	2.499013	1.354734
23	6	0	-0.104254	3.279702	2.107010
24	6	0	-4.697563	-1.094655	-1.086222
25	6	0	-3.378700	-0.786389	-1.409865
26	1	0	-1.820562	-2.042162	1.348037
27	1	0	-4.178976	-2.591776	1.930854
28	1	0	-6.014960	-1.984121	0.371232
29	1	0	-5.498207	-0.840881	-1.774851
30	1	0	-3.145717	-0.289775	-2.349219
31	1	0	0.005674	0.689709	3.136222
32	1	0	-1.615147	0.171943	2.633137
33	1	0	-1.430515	1.529722	3.754689
34	1	0	-2.851221	2.921168	2.249914
35	1	0	-3.007711	1.664615	1.017837

36	1	0	-2.392366	3.278095	0.584269
37	1	0	-0.571608	3.773829	2.966083
38	1	0	-0.041006	4.006598	1.289128
39	1	0	0.911216	2.983389	2.384626

TS of the aldol reaction (*syn*-aldol)



E(B3LYP/631LAN) = -2431.98036301 hartree

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	8	0	-1.545264	0.688230	0.183883
2	6	0	-0.753648	1.698302	0.165911
3	6	0	0.564898	1.553824	0.624072
4	6	0	1.081218	0.284637	-1.149590
5	8	0	0.145883	-0.596818	-1.125597
6	6	0	2.483440	-0.070961	-0.867576
7	6	0	0.864128	0.666705	1.796068
8	1	0	0.949175	1.117144	-1.850088
9	1	0	1.222625	2.413395	0.591557
10	6	0	-1.318553	2.980152	-0.452796
11	6	0	2.828458	-1.344640	-0.385713
12	6	0	4.168966	-1.665058	-0.187603
13	6	0	5.167532	-0.726042	-0.462373
14	9	0	0.261874	1.113051	2.921015
15	9	0	2.184953	0.622563	2.045130
16	9	0	0.445028	-0.626590	1.635804
17	22	0	-1.452502	-1.237218	-0.205570
18	17	0	-2.827033	-1.434641	-1.900999
19	17	0	-0.522460	-3.271852	-0.056859
20	17	0	-2.813870	-1.528447	1.539461
21	6	0	-1.903875	2.660801	-1.847238
22	6	0	-0.270368	4.099889	-0.568766
23	6	0	-2.459957	3.441786	0.491412
24	6	0	4.827999	0.540251	-0.949903
25	6	0	3.491230	0.865232	-1.155397
26	1	0	2.049305	-2.073398	-0.190871
27	1	0	4.436439	-2.652075	0.178063
28	1	0	6.211411	-0.982976	-0.305291
29	1	0	5.604327	1.266135	-1.173473
30	1	0	3.222261	1.846174	-1.541696
31	1	0	-2.642987	1.857623	-1.795308
32	1	0	-1.121479	2.358593	-2.553984
33	1	0	-2.390443	3.554652	-2.252699
34	1	0	-0.736746	4.985524	-1.012838
35	1	0	0.568891	3.815427	-1.215028

36	1	0	0.128612	4.394412	0.408089
37	1	0	-2.918983	4.350846	0.087204
38	1	0	-2.080328	3.668289	1.494202
39	1	0	-3.230305	2.671206	0.580553

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1 Rychnovsky, D. D.; Rogers, B.; Yang, G. ***J. Org. Chem.*** **1993**, *58*, 3511-3515.