Supporting Information

Nature of Transmission of Polar Substituent Effects in γ-Disposed Bicyclo[2.2.1]heptane (Norbornane) and Adamantane Ring Systems as Monitored by ^{19}F NMR: A DFT- GIAO and – NBO Analysis

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General Procedures. NMR spectra were recorded on a Gemini-300 spectrometer. The probe temperature of the instrument was 295 ±2 K. All ^{1}H and ^{13}C nmr spectra were recorded in $CDCl_3$ as solvent at 300 and 75 MHz, respectively, with $CHCl_3$ (7.26ppm) for ^{1}H and $CDCl_3$ (77.0ppm) for ^{13}C as the internal reference. The proton-decoupled ^{13}C NMR spectra were obtained employing spectral widths of 18761.7 and 9718.2 Hz (64K/32K data points, digital resolution of 0.60 and 0.30 Hz, respectively. The ^{19}F nmr spectra were obtained under proton-decoupled conditions at 282.328 MHz (64K/32K data points, spectral widths of 69,930.1 Hz and 19,569 Hz) on dilute solutions (ca. 1-2 mg of the compound or mixture and 1-2 mg 1, 1, 2, 2-tetrachloro-3,3, 4,4-tetrafluorocyclobutane(TCTFCB)as an internal reference) in $CDCl_3$ or cyclo-C_6H_{12} (0.6-0.7 ml). The ^{119}Sn NMR spectra were obtained under proton-decoupled conditions at 111.9 MHz with a digital resolution of 0.48Hz on dilute solutions ($Sn(CH_3)_4$ as an internal reference) in $CDCl_3$. The GC-MS analyses were run on a Varian Saturn 4D instrument(column: 30m, 0.22mm, 0.25μm film thickness; 5% phenyl, 95% methylpolysiloxane(J&W DB-5ms)as stationary phase with helium(15psi)as the carrier gas. Analytical vapour-phase chromatographic analyses (VPC) were performed using a 15-m capillary column (RSL-300, 0.53-mm column). All the anhydrous solvents used in this study were dried by standard procedures. Diethylaminosulfurtrifluoride(DAST) was purchased from the Aldrich Chemical Company, Inc.

Syntheses. The syntheses of the precursor compounds (4, 5, 6, and 7, X=$COOCH_3$) for the preparation of the various mixtures of fluoro-norbornyl derivatives were relatively straightforward and are summarized in Schemes I – IV. The *exo*/*endo* ratio for the Diels-Alder mixture was 11-*exo*/11-*endo* = 25/75[1]. Epimerization of the mixture by heating at 120^{O}C in the presence of sodium methoxide[1] (0.05 equivs) gave a mixture more biased in the *exo*-epimer(60/40). The mixture was separated by HPLC (silica gel column/2% ethyl acetate-hexane as the eluent) to provide the respective pure *exo*- and *endo*- epimers. The *exo*- and *endo*-norbornene esters (11-*exo* and 11-*endo*) were hydroborated/oxidized by standard procedures[2] to yield the *exo* alcohol mixtures[1] (Schemes I and IV). Jones oxidation[3] of these alcohols gave the corresponding ketones which, on $NaBH_4/CH_3OH$ reduction, provided the required *endo*

alcohols[1] except for 16-*exo*-OH which led to 19-*endo*-OH and the expected lactone(18) from the other *endo* alcohol(Scheme IV).

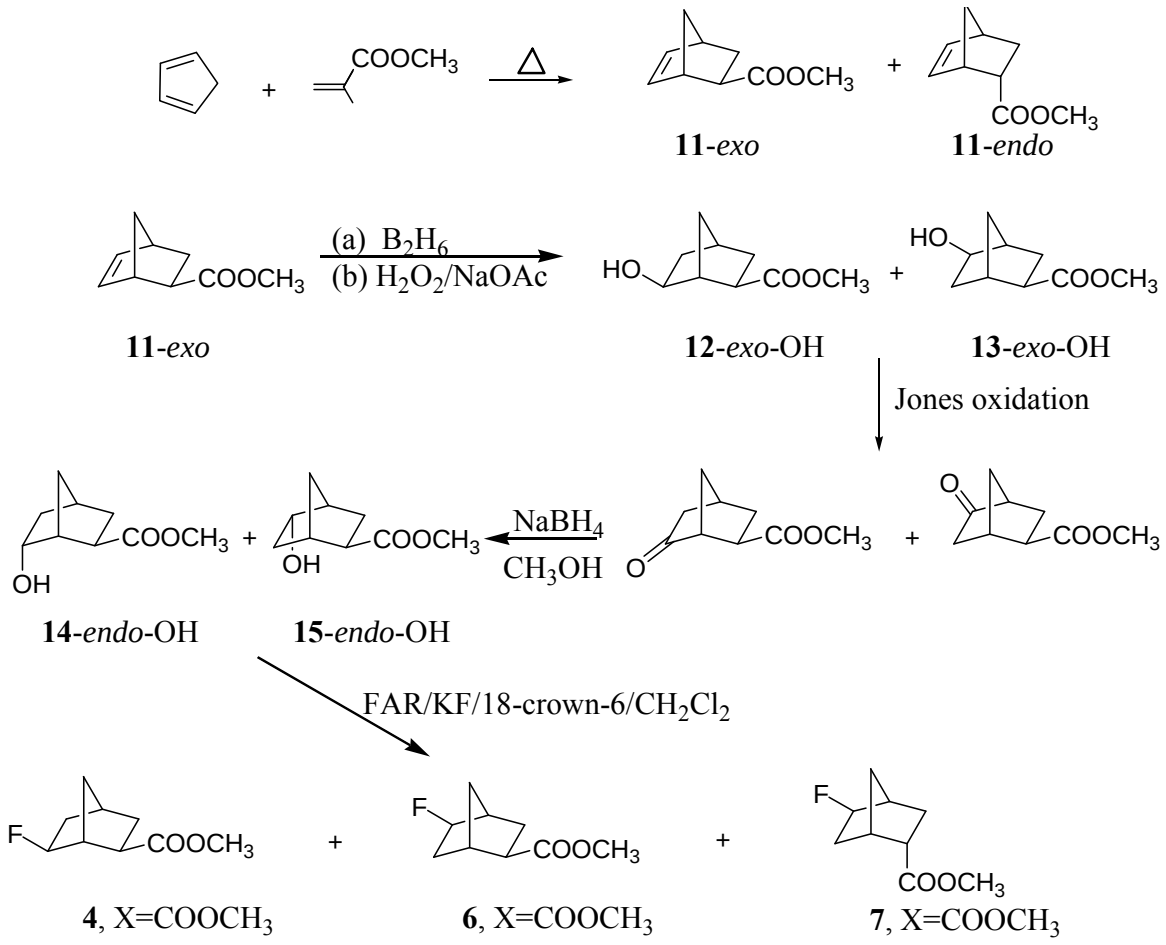
In intial trial fluorination experiments pure 2,6- *exo*, *exo* and -*exo*, *endo* ester alcohols(12-*exo*-OH and 14-*exo*-OH, respectively; Scheme I), which were obtained from the aforementioned *exo*- alcohol mixtures (3:2) by literature procedures[1], were treated in a standard way with DAST and 2-chloro-1,2,2-trifluorotriethylamine(FAR = fluoroamine reagent)[4]. Both fluorinating methods gave similar product mixtures. In the case of 12-*exo*-OH five fluoro-norbornyl derivatives were identified(4, X=$COOCH_3$(48%); 6, X=$COOCH_3$(14%); 7, X=$COOCH_3$(14%); *endo*-epimer of 1, X=$COOCH_3$(18%) plus unidentified residuals(6%)) in the product mixture. Since these fluorination procedures are known to involve cationic mediated pathways, fast 1,2-hydrogen shifts and Wagner- Meerwein rearrangements are clearly implicated. Modification of the use of FAR (FAR/KF/18-crown-6) as described by Hanreich[5] in the preparation of 6-*exo*-fluoro-2-*exo*-norbornyl acetate significantly increased the proportion of 4, X=$COOCH_3$ in the mixture. Similar fluorination trials on the 14-*exo*-OH isomer gave 5, X=$COOCH_3$ with formation of significant amounts of the 2,6-lactone,[6] apparently formed by trapping of the cation as indicated in Scheme IV. The formation of this by-product was found to be minimized by use of an excess of the fluorinating agent (5 equiv of FAR).

Because the separation of the aforementioned mixtures posed a difficult and protracted exercise to obtain the desired fluoronorbornyl derivatives in a pure state and, moreover, because the fluoride mixtures could be unambiguously characterized by ^{13}C and ^{19}F NMR in conjunction with GC-MS and VPC analyses, we decided to obtain the ^{19}F SCS of the various derivatives of 4 and 5 from mixtures rather then homogeneous compounds. Consequently, differently biased mixtures of 4, 5, 6, and 7(X=$COOCH_3$) (see Schemes I - III) were obtained by fluorination of appropriate mixtures of the *exo*- and *endo*-alcohols. The following procedures are typical : (a) Following the protocols of Hanreich[5], FAR (16.4g, 15.5ml; 86 mmoles) was added to a solution of a mixture of 14-*endo*-OH and 15-*endo*-OH(8.8g, 51 mmoles; see Scheme I) in dry CH_2Cl_2(10ml) at 0^OC under N_2 and then allowed to stand for 30 min before being added dropwise with stirring to a refluxing mixture of dry KF(6g) and 18-crown-6(2g) in dry CH_2Cl_2(30ml) under N_2 which had been under reflux for 45 min under N_2. After reflux for ca. 20 hrs the reaction mixture was quenched with an ice-cold aqueous $NaHCO_3$ solution before being thoroughly extracted with diethyl ether. The combined extracts were dried ($MgSO_4$) and the ether removed under vacuum to yield a crude mixture. Removal of residual organics by flash chromatography (silica gel with 10% EtOAc/hexane as the eluent) followed by kugelrohr distillation (40^OC, 0.1 mm Hg) gave a mixture of 4, 6, and 7(X=$COOCH_3$)in the ratio of ca. 6:4:1. (b) A solution of the *exo*-hydroxy-esters (10g, 59 mmoles; 16-*exo*-OH/17-*exo*-OH) in dry $CFCl_3/CH_2Cl_2$(16ml/4ml)was added dropwise to neat FAR[4](5 equiv.) with stirring maintained at 0^OC under N_2. The mixture was then allowed to slowly warm to room temperature(ca. 5hrs) before being worked up as described above in (a) to provide a mixture of 5, 6 and 7(X=COOCH3) in the ratio of ca. 4:1:2. (c) A THF (2.5ml) solution of a mixture of the norbornene esters (11-*exo*/11-*endo*; 1.5g) was treated with pyridine/HF as described by Olah et

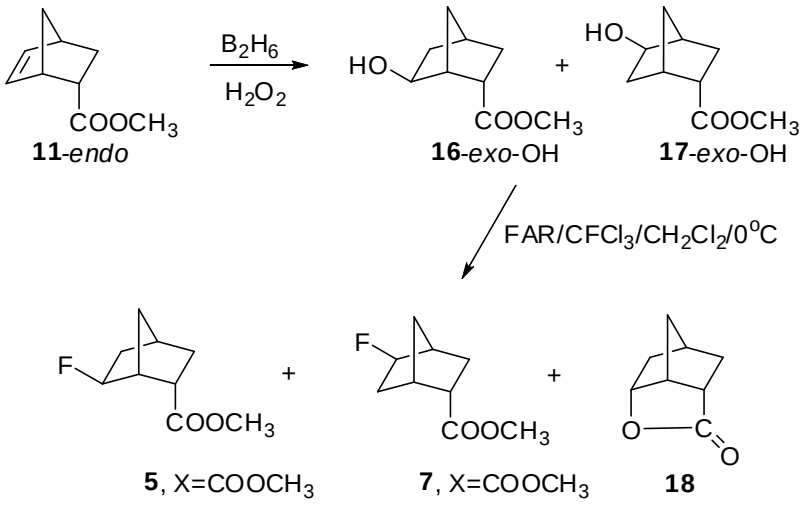
al[7] for the treatment of norbornene. The mixture was then quenched by pouring into an ice-cold $NaHCO_3$ solution before being extracted with diethyl ether. The combined extracts were dried ($MgSO_4$) and the ether removed under vacuum to yield a crude mixture which, after kugelrohr distillation (70^{O}C,1 mm Hg), gave a mixture of pure 4, 5, 6, and 7(X=$COOCH_3$)in the ratio of ca. 2: 0.2: 10: 5.

Most of the fluoride mixtures were obtained from these fluoro-ester mixtures by standard functionalization procedures from the appropriate precursor as indicated in Table 1. Additional mixtures of 6 and 7(X = CN and Br; 1:1 and 45:55, respectively) were obtained from the readily available Diels-Alder adducts by treatment with HF/pyridine[7] (see Scheme V).The exo/endo ratios for the Diels-Alder mixtures were 20-*exo*/20- *endo* = 1:2[8], and 21-*exo*/21-*endo* = 2:3[5]. The latter mixture was separated by HPLC (silica gel column/2% ethyl acetate-hexane as the eluent) to provide the respective pure *exo*- and *endo*- epimers. The remaining mixtures of 4, 5, 6, and 7(X = F, OCOCH3, OH, and OCH3) were derived from the appropriate norbornene precursors (22-*exo* and 22-*endo*) by reaction pathways as shown in Schemes VI and VII. The Diels-Alder mixture of 22-*exo*/22-*endo* (3:7)[5] was separated by HPLC (silica gel column/2% ethyl acetate-hexane as the eluent). A mixture heavily biased in the *exo*-epimer(22-*exo*/22-*endo* = 96/4)was obtained by heating norbornadiene with acetic acid[3].

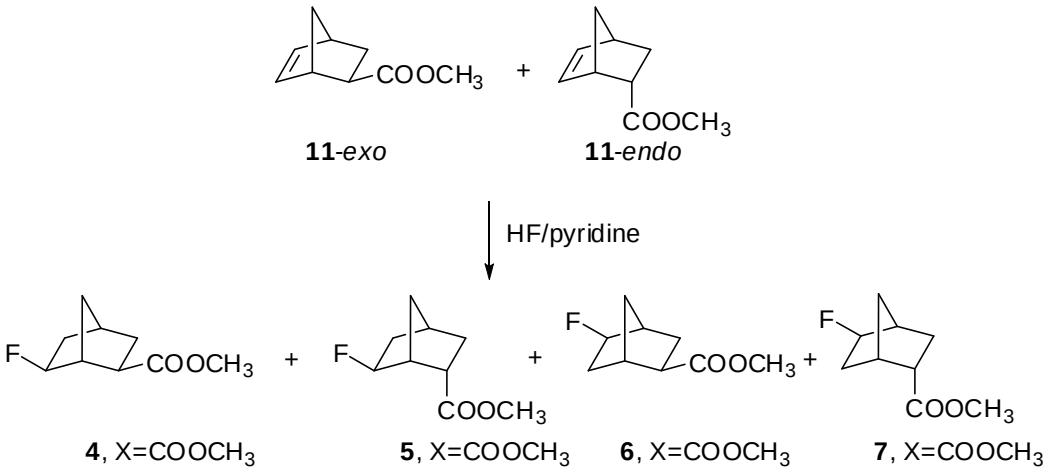
All the fluoride mixtures were unambiguously characterized by ^{13}C and ^{19}F NMR in conjunction with GC-MS and VPC analyses. The ^{13}C NMR spectral assignments followed unequivocally from the characteristic ^{13}C - ^{19}F coupling constants in the norbornane skeletal framework[7] as well as chemical shift additivity and APT technology. The observed and calculated ^{13}C chemical shifts for the various derivatives of 4- 7 are listed in Tables 2-9 below. The chemical shifts and SCS employed in determining the calculated shifts of 4-7 are given in Tables 10 and 11. All spectra were obtained on the same instrument under identical conditions and were generally in accord with literature values. The *exo*- and *endo*-2-substituted (X)-norbornanes are all known compounds and were prepared by standard procedures.



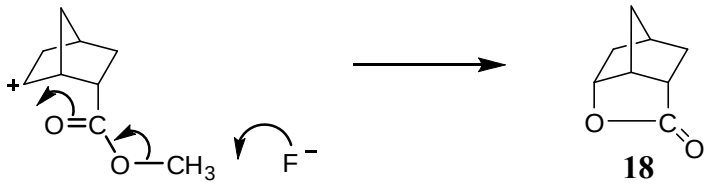
Scheme 1

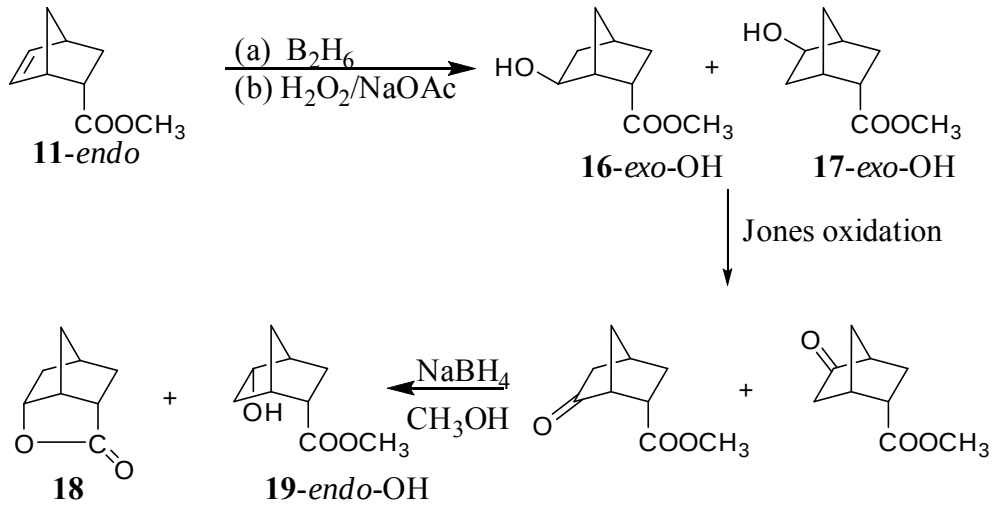


Scheme 2

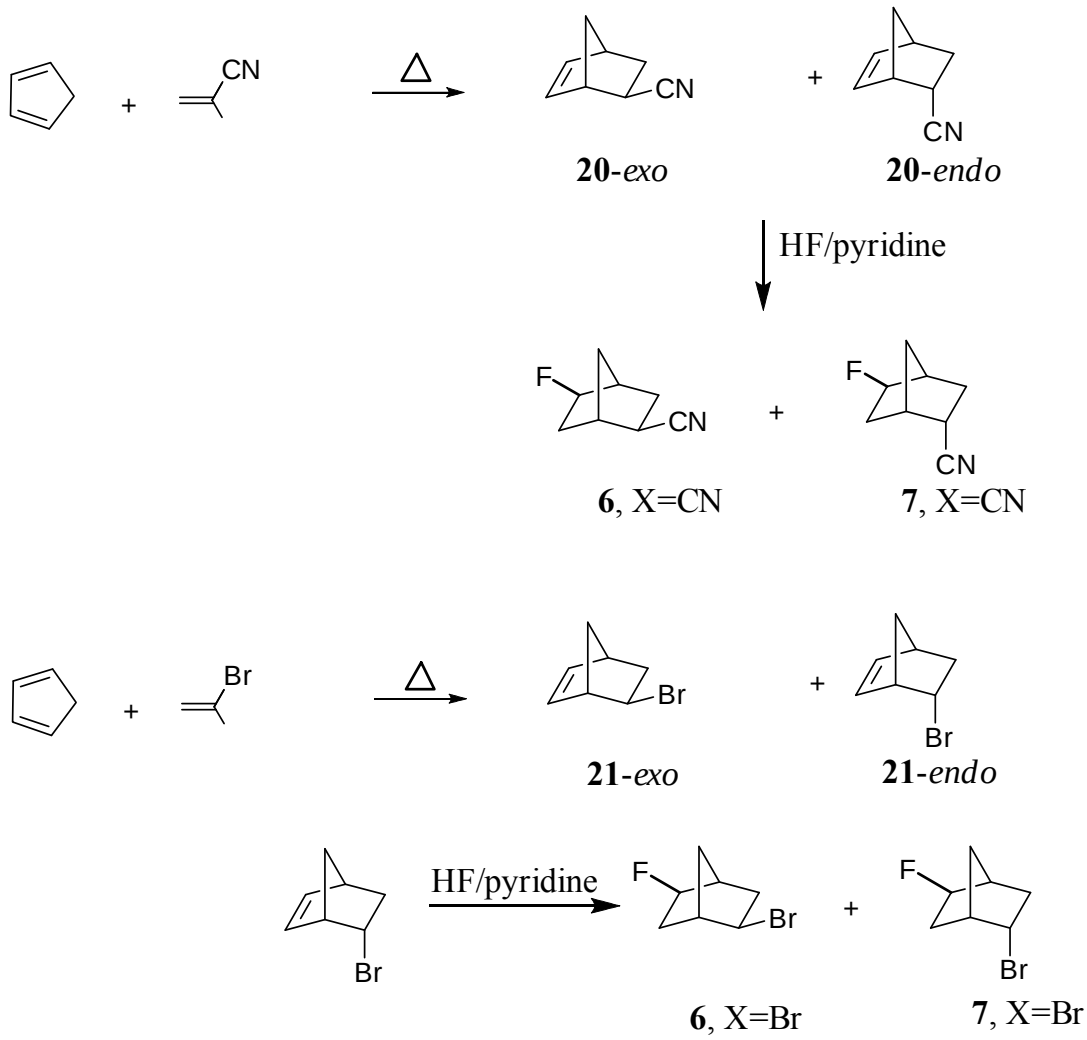


Scheme 3

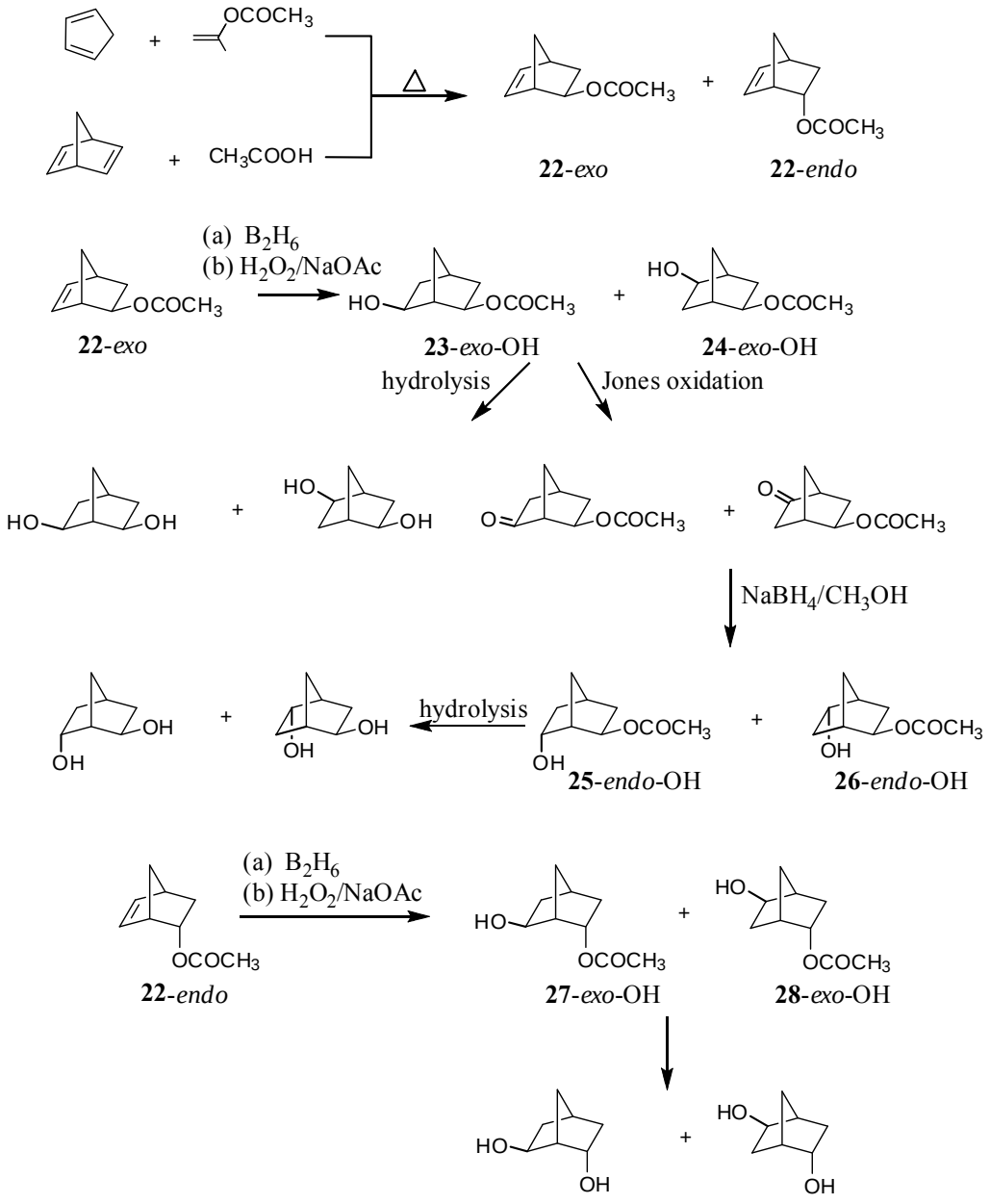




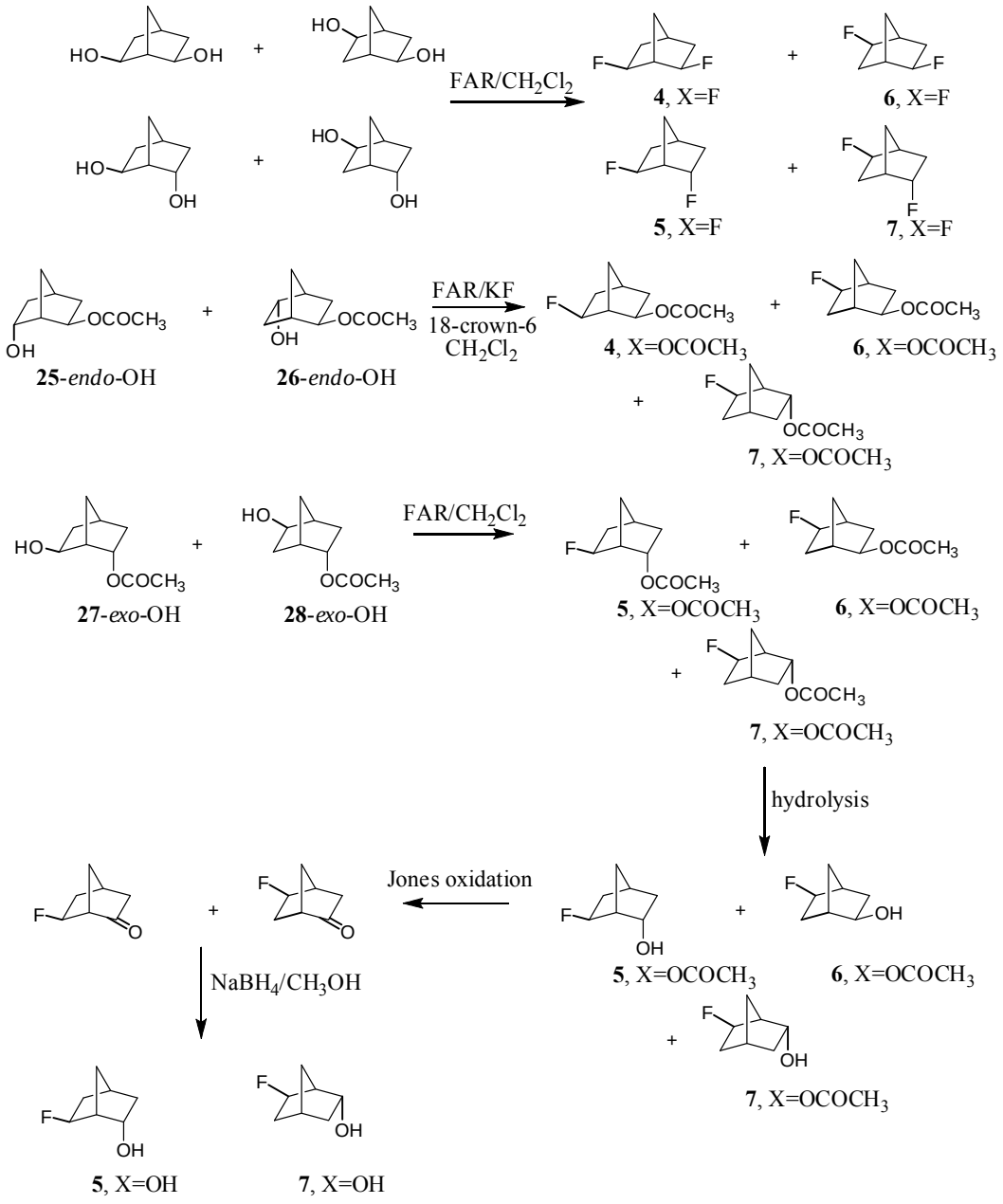
Scheme 4


CN
CN
CN
20-exo
20-endo
HF/pyridine
F
CN
F
CN
6, X=CN
7, X=CN
Br
Br
Br
21-exo
21-endo
Br
HF/pyridine
F
Br
F
Br
6, X=Br
7, X=Br

Scheme 5


OCOCH3
CH3COOH
Δ
22-exo
22-endo
(a) B2H6
(b) H2O2/NaOAc
23-exo-OH
24-exo-OH
hydrolysis
Jones oxidation
NaBH4/CH3OH
25-endo-OH
26-endo-OH
27-exo-OH
28-exo-OH

Scheme 6


FAR/CH2Cl2
4, X=F
6, X=F
5, X=F
7, X=F
FAR/KF
18-crown-6
CH2Cl2
25-endo-OH
26-endo-OH
4, X=OCOCH3
6, X=OCOCH3
7, X=OCOCH3
27-exo-OH
28-exo-OH
5, X=OCOCH3
6, X=OCOCH3
7, X=OCOCH3
hydrolysis
Jones oxidation
NaBH4/CH3OH
5, X=OCOCH3
6, X=OCOCH3
7, X=OCOCH3
5, X=OH
7, X=OH

Scheme 7

Table 1. Synthetic Methods for Mixtures of **4-7** from Mixtures of Fluoro-Carboxylic Esters **4-7**, X = $COOCH_3$ (Schemes I, II, and III)

X	Precursor	Synthetic Method
COOH	$COOCH_3$	THF/H2O/H2SO4/Δ[a]
$CONH_2$	COOH	$CH_2Cl_2/SOCl_2/NH_3$[a]
CN	$CONH_2$	$(CF_3CO)_2$/dioxane/pyridine[b]
NH_2	COOH	1. $CH_2Cl_2/SOCl_2$
		2. acetone/NaN_3/H_2O
		3. $CH_2Cl_2/CF_3COOH/\Delta$[c]
		4. $CH_3OH/H_2O/K_2CO_3/N_2/\Delta$[c]
NO_2	NH_2	m-$ClC_6H_4COOH/ClCH_2CH_2Cl/\Delta$[d]
CH_2OH	COOH	$(C_2H_5)_2O/LiAlH_4/\Delta$
$CH_2OTosyl$	CH_2OH	p-$CH_3C_6H_4SO_2Cl$/pyridine
CH_2Br	$CH_2OTosyl$	THF/LiBr/Δ
CH_3	$CH_2OTosyl$	$NaBH_4$/HMPA
Cl	COOH	1. NHTP[e]/CH_2Cl_2/DCC[f]
		2. PTOC ester[g]/$CF_3CCl_3/h\upsilon$[h]
Br	COOH	1. NHTP[e]/CH_2Cl_2/DCC[f]
		2. PTOC ester[g]/$CF_3CHClBr/h\upsilon$[h]
I	COOH	1. NHTP[e]/CH_2Cl_2/DCC[f]
		2. PTOC ester[g]/$CF_3CH_2I/h\upsilon$[h]
I	COOH	$C_6H_6/Pb(OCOCH_3)_4/I_2/\Delta/h\upsilon$[i]
$Sn(CH_3)_3$	Br	$(CH_3)_3SnLi$/THF[h]

[a]Ref. 9. [b]Ref. 10. [c]Ref. 11. [d]Ref. 12. [e]NHTP = N-hydroxy-2-thiopyridone. [f]DCC = N, N-dicyclohexylcarbodiimide. [g]Barton PTOC ester = O-acyl-N-hydroxy-2-thiopyridone. [h]Ref. 13. i. Ref. 14.

Table 2. Observed ^{13}C chemical shifts of *exo*-6-substituted(X)-*exo*-2-fluorobicyclo- [2.2.1]heptanes (**4**)[a,b]

X	C1	C2	C3	C4	C5	C6	C7	Others
H	41.98	96.21	39.91	34.65	28.00	22.39	34.57	
	(19.5)	(181.5)	(19.6)		(1.2)	(10.5)		
NO_2	49.17	91.32	38.85	34.43	36.22	82.70	32.63	
	(24.4)	(186.4)	(20.6)			(12.6)		
CN	46.83	93.36	38.81	34.84	34.92	25.31	33.77	122.14
	(23.4)	(184.4)	(20.4)			(13.3)		(3.9)
COOH	46.13	94.88	39.14	34.67	32.43	40.18	33.12	181.11
	(22.2)	(183.5)	(20.6)			(10.5)		(4.4)
$COOCH_3$	46.25	94.85	39.17	34.61	32.94	40.06	33.45	175.26
	(21.8)	(183.8)	(20.2)			(10.4)		(4.6)
								51.9
$CONH_2$	46.81	95.17	39.29	34.61	33.25	40.89	33.14	177.1
	(21.4)	(183.8)	(20.0)			(9.4)		(3.5)
F	49.42	91.62	38.95	33.70	38.95	91.62	30.96	
	(21.8)	(183.0)	(19.0)		(19.0)	(183.0)		
		(16.0)	(1.5)		(1.5)	(16.0)		
Cl	52.30	93.06	38.87	35.25	42.37	55.59	32.01	
	(21.8)	(185.0)	(20.3)			(14.8)		
Br	52.69	93.05	38.78	35.73	42.54	45.27	32.31	
	(21.9)	(186.4)	(20.3)			(14.0)		
I	53.91	92.47	39.82	36.65	43.63	18.28	32.97	
	(21.6)	(187.0)	(20.2)			(12.9)		
NH_2	51.74	94.23	38.84	34.72	40.77	48.99	31.21	
	(19.9)	(181.5)	(20.0)			(12.1)		
OH	51.19	93.17	38.99	34.21	41.03	69.54	31.39	
	(19.9)	(181.5)	(20.1)			(14.3)		
OCH_3	47.03	93.45	39.34	33.92	31.67	78.87	38.29	56.20
	(20.1)	(181.8)	(20.2)			(13.9)		
$OCOCH_3$	48.23	92.45	38.93	34.10	32.10	72.23	38.56	170.46
	(21.8)	(183.1)	(20.1)			(15.8)		21.10
CH_3	48.90	95.99	40.38	35.47	38.11	29.42	31.54	21.20
	(18.4)	(180.8)	(19.8)		(0.9)	(9.7)		(2.8)
CH_2OH	44.19	95.83	39.50	34.70	32.51	38.08	31.84	65.85
	(19.4)	(182.6)	(20.0)			(9.1)		
$Sn(CH_3)_3$[c]	44.84	97.07	39.56	35.55	32.51	17.87	34.64	-10.70[c]
	(17.6)	(187.2)	(19.7)		(1.5)	(13.9)		

[a] $J_{C\text{-}F}$ (Hz), in parenthesis. [b] ^{13}C NMR (CDCl3, relative to Me4Si, δ) of 6-Fluoro-2-norbornanone: 58.55(21.7Hz, C1), 214.40(12.2Hz, C2), 44.76(C3), 34.65(C4), 38.86 (21.0Hz, C5), 90.89

(192.1Hz, C6), 35.19(C7). [c] ^{119}Sn NMR($CDCl_3$, relative to internal $SnMe_4$): δ 14.1ppm, J_{Sn-F} =57.2 Hz.

Table 3. Calculated ^{13}C chemical shifts of *exo*-6-substituted(X)-*exo*-2-fluoro-bicyclo[2.2.1]heptanes (**4**)

X	C1	C2	C3	C4	C5	C6	C7
NO_2	49.20	92.66	38.12	34.21	35.09	80.62	30.93
CN	48.00	94.96	38.80	35.05	34.60	23.75	33.60
COOH	46.63	95.06	39.68	34.56	32.30	39.09	32.77
$COOCH_3$	46.59	95.11	39.70	34.58	32.41	39.01	33.01
$CONH_2$	47.20	95.00	40.00	34.50	34.80	41.20	30.60
F^C	47.74	88.75	38.25	33.49	38.25	88.75	30.90
Cl	52.40	93.25	38.40	35.20	41.90	55.10	31.40
Br	52.30	94.14	38.45	35.74	42.26	46.76	31.85
I	53.74	95.06	38.80	36.40	43.30	22.00	32.40
NH_2	51.20	92.80	38.90	34.50	40.70	47.90	29.90
OH	51.30	93.10	39.10	34.30	41.20	69.70	31.40
OCH_3	45.60	91.10	38.75	33.75	33.00	76.90	35.60
$OCOCH_3$	46.68	90.44	38.00	33.56	33.12	69.85	35.49
CH_3	49.20	95.60	40.50	35.90	38.45	29.45	31.25
CH_2OH	44.20	95.80	40.51	35.15	32.75	37.80	32.85
$Sn(CH_3)_3$	45.80	99.80	39.60	36.00	33.0	20.11	34.70

[a]Calculated ^{13}C NMR of 6-Fluoro-2-norbornanone: 58.10(C1), 213.80(C2), 44.70(C3), 34.80(C4), 39.00(C5), 90.90(C6), 35.00(C7).

Table 4. Observed ^{13}C chemical shifts of *endo*-6-substituted(X)-exo-2-fluoro-bicyclo[2.2.1]heptanes (**5**)[a,b]

X	C1	C2	C3	C4	C5	C6	C7	Others
NO_2	47.61	90.90	39.13	35.68	35.60	83.31	32.56	
	(24.1)	(182.0)	(20.1)			(9.7)		
CN	44.80	91.8	39.59	35.41	34.24	24.76	35.22	120.98
	(23.3)	(182.6)	(20.3)			(9.7)		
COOH	45.66	93.09	39.64	35.85	30.70	41.28	36.50	180.80
	(22.1)	(180.0)	(19.6)			(10.2)		
$COOCH_3$	45.72	93.05	39.62	35.86	30.81	41.29	36.47	174.30
	(21.6)	(180.8)	(19.5)	(0.5)	(1.1)	(9.7)		51.70
$CONH_2$	46.33	93.03	39.67	35.97	30.45	42.38	37.01	175.10
	(21.2)	(179.0)	(19.4)			(10.1)		
F	47.47	90.76	39.72	35.48	36.26	91.95	33.91	
	(21.5)	(178.0)	(20.2)		(21.7)	(184.0)	(3.9)	
	(16.0)	(14.0)				(10.0)		
Cl	48.97	92.15	42.00	36.78	39.85	55.59	34.58	
	(22.5)	(179.1)	(20.7)			(14.8)		
Br	49.44	93.94	39.71	35.75	40.25	46.45	34.90	
	(16.2)	(179.8)	(20.0)			(13.7)		
I	49.23	94.45	39.97	35.39	41.87	21.31	33.87	
	(22.8)	(183.7)	(20.1)			(16.6)		
NH_2	48.55	92.46	40.41	36.43	38.45	49.68	35.46	
	(19.2)	(176.5)	(19.4)			(10.5)		
OH	48.66	92.03	40.27	37.05	37.33	69.81	34.53	
	(19.7)	(176.2)	(19.7)			(10.7)		
OCH_3	45.62	91.81	40.28	35.62	34.14	79.13	35.89	57.19
	(20.0)	(176.8)	(19.6)			(10.1)		
$OCOCH_3$	46.32	91.25	39.90	35.47	35.95	72.10	34.10	170.30
	(21.1)	(178.4)	(18.1)			(10.0)		21.00
CH_3	47.42	93.13	40.69	36.86	40.51	30.62	36.70	17.01
	(18.6)	(176.9)	(19.4)	(3.9)		(10.7)		
CH_2OH	42.39	95.62	40.28	34.19	31.39	36.67	38.30	66.35
	(19.7)	(176.8)	(20.0)			(10.9)		
$Sn(CH_3)_3$[c]	46.13	92.81	40.35	35.02	31.79	20.56	36.87	-10.30
	(19.6)	(184.0)	(19.5)			(13.5)		[243.0]
						[376.0]		[233.0]
						[359.0]		[55.4]

[a] $J_{C\text{-}F}$ (Hz), in parenthesis. [b] $J_{C\text{-}Sn}$(Hz), in brackets. [c] ^{119}Sn NMR($CDCl_3$,relative to internal $SnMe_4$): δ 2.42ppm, $J_{Sn\text{-}F}$ = 0.0 Hz.

Table 5. Calculated ^{13}C chemical shifts of *endo*-6-substituted(X)-*exo*-2-fluoro-bicyclo[2.2.1]heptanes (**5**)

X	C1	C2	C3	C4	C5	C6	C7
NO_2	48.52	89.48	38.42	35.24	37.07	80.07	29.52
CN	45.88	91.66	39.62	35.55	33.84	22.85	34.93
COOH	46.22	91.30	39.30	35.60	28.93	38.67	36.48
$COOCH_3$	46.10	91.31	39.26	35.51	30.14	38.53	36.35
$CONH_2$	46.67	90.83	39.46	35.58	29.72	41.48	36.79
F	47.70	89.80	39.15	35.35	36.15	90.35	30.75
Cl	50.00	89.20	40.21	36.30	39.50	54.65	34.53
Br	50.78	91.06	39.82	35.75	39.94	46.35	34.03
I	50.48	95.01	39.87	35.89	42.60	25.07	32.40
NH_2	49.10	86.40	40.70	36.10	37.80	45.90	35.60
OH	48.80	86.85	40.50	36.25	37.85	65.15	34.05
OCH_3	44.80	86.15	40.80	35.50	34.15	73.75	33.35
$OCOCH_3$	45.98	87.50	39.71	35.25	35.35	68.30	33.25
CH_3	47.80	88.90	40.80	36.70	39.00	27.25	35.20
CH_2OH	44.20	91.70	39.70	35.50	32.30	35.50	37.30
$Sn(CH_3)_3$	46.20	96.50	40.30	35.25	31.86	21.10	36.80

Table 6. Observed ^{13}C chemical shifts of *exo*-5-substituted(X)-*exo*-2-fluorobicyclo- [2.2.1]heptanes (**6**)[a-c]

X	C1	C2	C3	C4	C5	C6	C7	Others
NO_2	41.48	93.65	36.59	42.08	86.34	29.57	31.96	
	(21.3)	(184.5)	(18.2)			(10.6)		
CN	41.57	93.76	38.73	40.23	29.81	28.98	33.56	122.76
	(21.2)	(184.8)	(20.6)		(1.7)	(11.0)		
COOH	41.80	95.08	39.60	39.53	45.05	26.69	32.60	180.30
	(19.6)	(183.00)	(21.0)			(11.70)		
$COOCH_3$	41.85	95.12	40.22	39.83	44.98	26.79	32.59	175.60
	(20.5)	(182.48)	(20.8)		(1.6)	(11.0)		51.80
$CONH_2$	41.74	95.27	39.98	40.25	45.95	26.77	32.56	177.50
	(20.5)	(182.4)	(20.6)			(11.1)		
F	40.59	94.11	32.83	40.59	94.11	32.83	30.79	
	(21.2)	(182.8)	(16.4)	(21.2)	(182.8)	(16.4)		
Cl	41.96	94.13	37.04	44.54	60.23	36.10	31.45	
	(20.7)	(183.5)	(21.2)		(2.9)	(10.6)		
Br	42.58	94.18	37.85	45.01	51.11	36.29	31.92	
	(20.6)	(183.8)	(21.4)		(1.5)	(10.5)		
I	42.34	93.49	38.62	46.52	26.45	38.62	32.89	
	(20.6)	(182.6)	(20.7)		(2.3)	(10.7)		
NH_2	41.74	95.18	37.11	43.65	53.43	34.61	30.52	
	(20.2)	(181.9)	(20.5)			(9.7)		
OH	39.85	94.94	34.80	42.71	73.13	34.70	30.61	
	(18.2)	(181.6)	(21.2)		(2.1)	(11.1)		
OCH_3	40.88	95.11	34.89	38.39	82.41	32.00	42.49	56.10
	(20.2)	(182.5)	(21.0)		(2.9)	(11.3)		
$OCOCH_3$	41.05	94.37	34.69	39.92	75.64	32.30	39.70	170.60
	(20.6)	(182.5)	(19.7)		(2.5)	(11.0)		21.10
CH_3	42.68	96.04	39.21	41.48	34.95	32.18	31.00	21.90
	(19.8)	(181.5)	(19.8)		(0.95)	(11.1)		(1.5)
CH_2OH	42.36	95.61	39.50	36.70	43.40	26.77	31.32	65.60
	(20.0)	(182.4)	(19.9)			(11.3)		
$Sn(CH_3)_3$[d]	43.05	96.27	44.16	38.72	25.91	27.20	34.78	-10.70
	(19.6)	(181.4)	(18.9)	[7.1]		(10.1)		[298.0, 312]

[a] J_{C-F} (Hz), in parenthesis. [b] J_{C-Sn}(Hz), in parenthesis. [c] ^{13}C NMR(CDCl3, relative to Me4Si, δ) of 5-Fluoro-2-norbornanone: 48.25(C1), 215.05(C2), 38.06(12.4Hz, C3), 41.33(21.7Hz,C4), 93.43(184.3Hz, C5), 33.76(21.8Hz, C6), 33.77(C7). [d] ^{119}Sn NMR ($CDCl_3$, relative to internal $SnMe_4$): δ 7.21ppm, J_{Sn-F} =20.8 Hz.

Table 7. Calculated ^{13}C chemical shifts of *exo*-5-substituted(X)-*exo*-2-fluoro-bicyclo[2.2.1]heptanes (**6**)

X	C1	C2	C3	C4	C5	C6	C7
NO_2	41.30	94.37	36.83	42.06	86.21	29.50	31.92
CN	42.20	95.01	38.50	40.00	29.30	29.05	33.70
COOH	41.71	95.93	38.82	39.50	44.68	26.70	32.76
$COOCH_3$	41.71	95.95	38.86	39.47	44.61	26.82	33.01
$CONH_2$	41.70	96.20	38.90	40.00	44.70	29.15	30.60
F	40.82	94.51	32.61	40.82	94.51	32.61	30.92
Cl	42.30	94.60	36.99	44.55	60.50	36.30	31.40
Br	42.87	94.70	37.89	45.17	52.35	36.67	31.85
I	43.70	95.20	38.70	46.50	28.30	38.00	32.40
NH_2	41.90	94.70	37.00	43.80	53.60	35.00	29.90
OH	41.20	94.90	34.90	42.70	73.10	34.80	30.60
OCH_3	40.85	95.00	34.84	38.45	82.55	27.35	35.60
$OCOCH_3$	40.68	94.26	34.20	39.60	75.45	27.53	35.49
CH_3	43.00	96.70	39.30	42.05	35.05	32.85	31.25
CH_2OH	42.30	96.90	39.60	37.15	43.45	27.15	32.85
$Sn(CH_3)_3$	43.10	95.80	43.50	38.60	25.70	27.40	34.70

[a]Calculated ^{13}C NMR of 5-Fluoro-2-norbornanone: 47.95(C1), 214.34(C2), 37.25(C3), 40.78(C4), 93.46(C5), 33.82(C6), 33.43(C7).

Table 8. Observed ^{13}C chemical shifts of *endo*-5-substituted(X)-*exo*-2-fluoro-bicyclo[2.2.1]heptanes (**7**)[a,b]

X	C1	C2	C3	C4	C5	C6	C7	Others
NO_2	42.32	93.57	33.61	41.44	85.23	29.56	32.56	
	(21.1)	(184.2)	(21.5)			(11.1)		
CN	41.99	94.04	35.49	38.64	28.82	28.50	38.75	121.80
	(21.2)	(184.4)	(21.2)			(10.3)		
COOH	42.63	95.03	35.16	39.00	44.12	25.40	36.50	180.80
	(20.0)	(183.2)	(20.3)			(10.5)		
$COOCH_3$	42.61	94.82	35.14	38.94	44.05	25.54	36.37	174.57
	(20.2)	(182.8)	(20.4)		(1.2)	(9.8)		51.66
$CONH_2$	42.66	95.17	34.74	39.13	44.80	25.10	36.91	177.30
	(20.1)	(182.0)	(20.4)			(10.5)		
F	40.59	94.29	-	39.61	-	-	32.76	
	(21.2)	(183.7)		(17.4)			(4.8)	
	(1.6)							
Cl	41.95	94.60	33.00	42.81	60.10	34.34	34.20	
	(20.7)	(179.10)	(20.5)			(10.6)		
Br	42.60	94.49	35.04	42.49	51.20	34.92	33.95	
	(20.0)	(183.40)	(20.7)			(10.2)		
I	41.12	97.53	39.19	43.50	31.12	36.28	33.41	
	(20.5)	(180.60)	(21.1)			(9.9)		
NH_2	43.00	93.26	31.04	41.40	50.80	33.22	35.28	
	(20.3)	(175.60)	(19.7)			(10.4)		
OH	42.77	95.46	30.77	40.95	70.55	32.32	33.42	
	(20.4)	(180.5)	(19.9)			(10.2)		
OCH_3	42.17	95.37	30.88	37.67	79.77	30.73	33.41	56.10
	(20.3)	(182.10)	(19.9)			(10.5)		
$OCOCH_3$	42.11	94.72	31.76	38.69	73.40	30.57	33.14	170.60
	(20.6)	(183.2)	(20.5)			(10.2)		20.94
CH_3	43.36	96.04	32.65	40.29	32.44	31.49	36.46	16.90
	(19.4)	(181.5)	(19.6)			(10.1)		
CH_2OH	42.02	95.83	33.08	38.53	40.81	26.81	38.18	64.10
	(20.1)	(182.8)	(19.9)			(11.3)		
$Sn(CH_3)_3$[c]	42.38	96.13	40.04	39.02	26.15	26.55	36.87	-10.40
	(19.2)	(182.7)	(19.9)		(1.2)	(10.1)		[326]
								[316]

[a]$J_{C\text{-}F}$ (Hz), in parenthesis. [b]$J_{C\text{-}Sn}$(Hz), in parenthesis [c]^{119}Sn NMR ($CDCl_3$,relative to internal $SnMe_4$): δ -1.06 ppm, $J_{Sn\text{-}F}$ = 0.00Hz.

Table 9. Calculated ^{13}C chemical shifts of *endo*-5-substituted(X)-*exo*-2-fluoro-bicyclo[2.2.1]heptanes (**7**)

X	C1	C2	C3	C4	C5	C6	C7
NO_2	42.37	94.67	33.22	41.37	85.76	31.48	29.48
CN	38.75	28.44	28.24	42.68	95.86	35.42	34.95
COOH	42.72	95.54	35.06	39.10	44.26	24.34	36.48
$COOCH_3$	42.63	95.51	35.10	38.98	44.12	24.55	36.35
$CONH_2$	42.71	95.71	34.59	39.54	45.06	24.14	36.81
F	42.20	95.25	33.80	40.70	95.80	30.80	31.70
Cl	43.50	96.46	32.90	42.80	60.20	34.00	34.50
Br	43.88	96.06	34.82	42.65	51.94	34.35	34.03
I	42.67	96.12	38.76	43.36	31.64	36.00	32.40
NH_2	43.50	96.50	30.60	41.70	51.70	32.10	35.60
OH	42.40	94.90	30.40	40.60	70.30	32.50	33.00
OCH_3	42.70	97.05	29.90	37.65	79.35	28.55	33.35
$OCOCH_3$	42.40	95.90	31,20	38.85	74.00	29.75	33.25
CH_3	43.88	97.06	32.60	40.75	32.85	33.35	35.10
CH_2OH	43.40	96.70	33.10	37.05	41.10	26.70	37.30
$Sn(CH_3)_3$	42.30	96.60	40.20	39.10	26.70	26.30	36.80

Table 10. Observed ^{13}C Substituent Chemical Shifts(SCS) of *exo*-2-Substituted (X) Norbornanes[a]

X	C1	C2	C3	C4	C5	C6	C7	Others
H[b]	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO_2	7.11	58.24	7.12	-1.05	-1.82	-3.54	-2.71	
CN	5.91	1.35	6.65	0.11	-1.15	-1.25	-1.02	123.00
COOH	4.56	16.69	4.30	-0.36	-0.29	-1.15	-1.89	183.00
$COOCH_3$	4.52	16.62	4.43	-0.36	-0.27	-1.10	-1.94	51.60
								0.00
$CONH_2$	5.07	17.73	6.79	-0.40	0.00	-1.07	-4.05	178.00
F[c]	5.68	66.46	10.16	-1.74	-1.75	-7.36	-3.85	
	(19.5)	(181.5)	(19.6)			(10.5)		
Cl	9.70	32.69	13.89	0.20	-1.56	-2.94	-3.28	
Br	10.23	24.36	14.28	0.80	-1.52	-2.08	-2.80	
I	11.75	0.58	15.54	1.68	-0.93	-1.24	-2.02	
NH_2	8.71	25.65	12.75	0.01	-0.85	-2.75	-4.12	
OH	8.11	44.65	12.65	-0.59	-0.95	-4.85	-3.82	
OCH_3	3.54	54.51	15.01	-1.22	-1.20	-5.14	0.93	55.90
$OCOCH_3$	4.65	47.46	5.13	-1.39	-1.94	-5.76	0.83	21.40
CH_3	7.11	7.05	10.45	0.91	0.55	-0.65	-3.42	22.30
CH_2OH	2.21	15.45	14.75	0.21	0.55	-0.35	-3.02	66.40
$Sn(CH_3)_3$[d]	3.75	-2.25	15.09	1.06	-0.30	4.17	0.08	-10.85
	(9.8)	(407.4)	(23.4)	(12.7)		(67.4)		(306.3)

[a]Defined as the difference (in ppm) between the ^{13}C chemical shift of the substituted compound and that of the parent compound(X=H). A positive and negative sign denotes deshielding(downfield shift) and shielding (upfield shift), respectively. Solvent, $CDCl_3$. 2-Norbornanone, ^{13}C SCS: 13.01(C1), 186.35(C2), 14.85(C3), -1.29(C4), -2.75(C5), -6.15(C6), -1.25(C7). b. X=H, ^{13}C NMR(CDCl3, relative to Me4Si) δ 36.39(C1,4), 29.75(C2, 3, 5, and 6), 38.43(C7). c. J_{C-F} (Hz), in parenthesis. d. J_{C-Sn}(Hz), in parenthesis.

Table 11. Oberved ^{13}C Substituent Chemical Shifts (SCS) of *endo*-2-Substituted (X) Norbornanes[a]

X	C1	C2	C3	C4	C5	C6	C7	Others
H	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO_2	6.45	57.69	9.05	0.30	-1.53	-6.73	-5.20	
CN	3.81	0.45	5.85	0.61	-0.35	-4.55	0.28	123.00
COOH	4.15	16.27	1.94	0.65	-0.69	-4.91	1.82	183.00
$COOCH_3$	4.03	16.13	2.16	-0.03	-0.70	-4.86	1.76	52.00
$CONH_2$	4.60	17.08	1.74	0.64	-0.50	-5.38	2.14	
F	5.67	67.95	8.15	0.41	-0.85	-6.40	-3.92	
	(16.3)	(185.0)	(22.0)			(12.0)	(4.0)	
Cl	7.91	32.25	11.55	1.41	0.25	-7.05	-0.12	
Br	7.62	23.95	11.95	0.81	-0.15	-5.15	-0.62	
I	8.42	2.67	13.61	0.61	-0.08	-1.19	-2.08	
NH_2	7.21	23.65	10.81	1.71	0.95	-9.15	0.69	
OH	6.10	43.18	9.61	0.87	0.01	-9.81	-0.85	
OCH_3	2.71	51.35	6.15	0.61	0.85	-10.05	-1.32	56.00
$OCOCH_3$	3.91	45.95	7.35	0.31	-0.25	-8.75	-1.42	21.00
CH_3	5.40	4.39	10.62	1.36	0.54	-7.63	0.10	22.00
CH_2OH	2.11	13.15	4.35	0.81	0.55	-6.85	1.58	66.00
$Sn(CH_3)_3$	4.19	-1.26	3.93	0.28	0.40	0.31	2.08	-10.20
	(10.0)	(432.0)		(23.4)		(36.0)	(56.6)	(306.3)

[a]See footnotes a-d of Table 1.

Table 12. Some NBO calculated molecular parameters for systems **3**-**5** and **8**-**10**

X	System	n_F[a]	Q_n[b]	σ_{CF}*(occup)[c]
H	3	1.97487	-0.39392	0.05002
NO2	3	1.97346	-0.38406	0.0488
CN	3	1.97379	-0.38519	0.0476
NC	3	1.9738	-0.38578	0.04874
CF3	3	1.97405	-0.38724	0.04818
COOH	3	1.97431	-0.38954	0.04928
F	3	1.97397	-0.38887	0.05138
Cl	3	1.97389	-0.38772	0.05027
HO	3	1.97447	-0.39207	0.05236
O-	3	1.97898	-0.43274	0.07538
NH2	3	1.97474	-0.3932	0.05055
NH-	3	1.97856	-0.42682	0.06331
CH3	3	1.97494	-0.39434	0.05058
Si(CH3)3	3	1.9751	-0.39461	0.05061
Li	3	1.97644	-0.40595	0.05696
H	4	1.97953	-0.413	0.03818
NO2	4	1.97836	-0.40192	0.03434
CN	4	1.97845	-0.40342	0.03453
NC	4	1.97866	-0.40332	0.03392
CF3	4	1.97854	-0.40531	0.03539
COOH	4	1.97894	-0.40779	0.03601
F	4	1.97918	-0.40559	0.03452
Cl	4	1.9788	-0.4049	0.03457
HO	4	1.97939	-0.40858	0.03482
O-	4	1.98304	-0.44617	0.05593
NH2	4	1.9794	-0.41058	0.03607
NH-	4	1.98282	-0.44686	0.06125
CH3	4	1.97949	-0.41283	0.03769
Si(CH3)3	4	1.97924	-0.41394	0.04123
Li	4	1.98053	-0.42926	0.05589
H	5	1.97953	-0.413	0.03818
HO	5	1.98926	-0.41375	0.03504
O-	5	1.98367	-0.4507	0.05155
NH2	5	1.97993	-0.41164	0.03702
NH-	5	1.9837	-0.45037	0.0508
H	8	1.98693	-0.40992	0.05444
HO	8	1.97743	-0.4071	0.0539
0	8	1.98063	-0.44075	0.07513
NH2	8	1.97763	-0.4071	0.05321
NH-	8	1.98049	-0.43948	0.07399
H	9	1.97915	-0.41346	0.03824
HO	9	1.97901	-0.41044	0.03768
0	9	1.9825	-0.44667	0.06007
NH2	9	1.97907	-0.41183	0.03704
NH-	9	1.98197	-0.44176	0.0503
H	10	1.97915	-0.41346	0.03824
HO	10	1.9796	-0.41437	0.03626

O-	10	1.98285	-0.44944	0.05155
NH2	10	1.97929	-0.41211	0.03767
NH-	10	1.98286	-0.44913	0.04987

[a]n_F = average occupation numbers of the fluorine lone pairs.[b]Q_n = fluorine natural charge. [c]σ_{CF}* = occupancy of the C-F antibonding orbital.

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