

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 ^1H and ^{13}C nmr spectra were recorded in CDCl_3 as solvent at 300 and 75 MHz, respectively, with CHCl_3 (7.26ppm) for ^1H 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 ($\text{Sn}(\text{CH}_3)_4$ as an internal reference) in CDCl_3 . The GC-MS analyses were run on a Varian Saturn 4D instrument(column: 30m, 0.22mm, 0.25 μm 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, $\text{X}=\text{COOCH}_3$) 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* = 25/75¹. Epimerization of the mixture by heating at 120^oC in the presence of sodium methoxide¹ (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 procedures² to yield the *exo* alcohol mixtures¹ (Schemes I and IV). Jones oxidation³ of these alcohols gave the corresponding ketones which, on $\text{NaBH}_4/\text{CH}_3\text{OH}$ reduction, provided the required *endo*

alcohols¹ except for 16-*exo*-OH which led to 19-*endo*-OH and the expected lactone(18) from the other *endo* alcohol(Scheme IV).

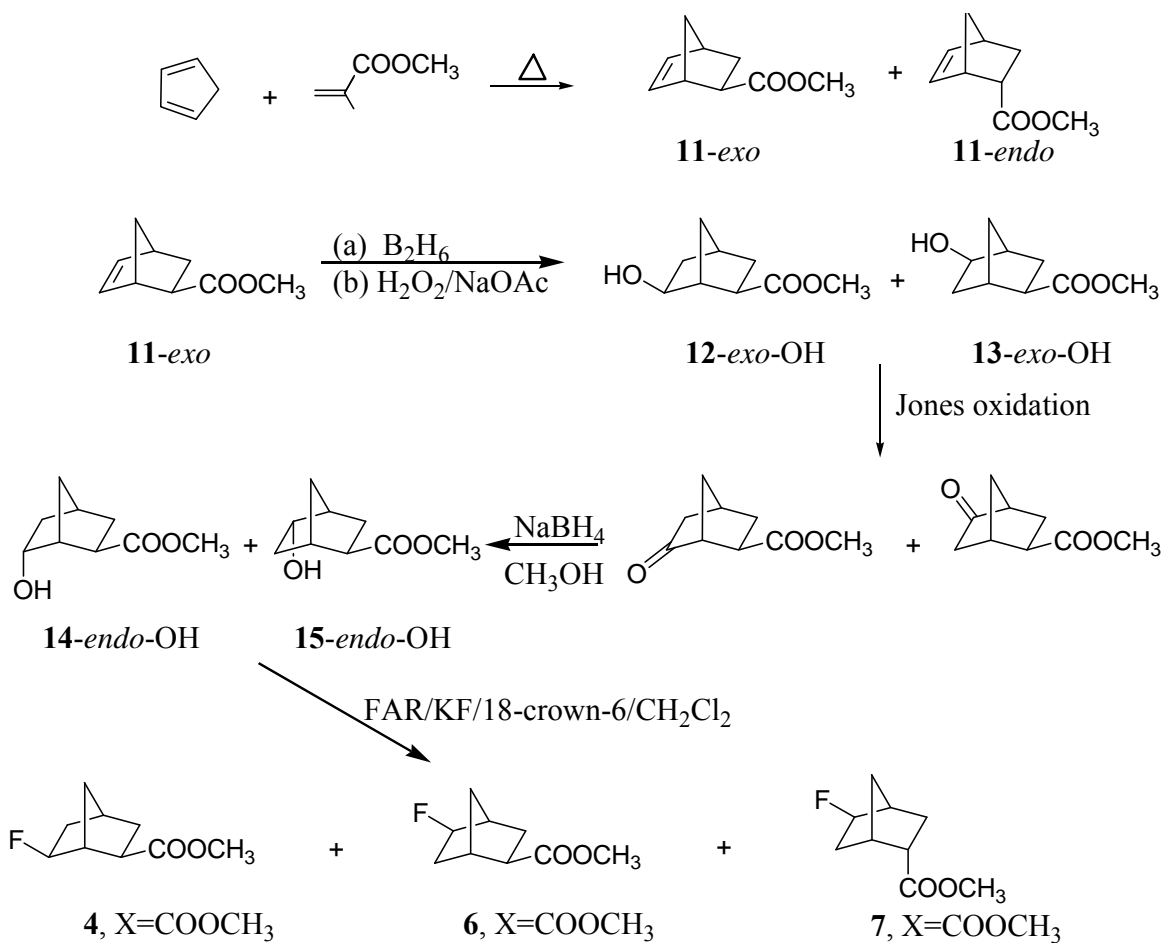
In initial trial fluorination experiments pure 2,6- *exo, exo* and -*exo, endo* ester alcohols(12-*exo*-OH and 14-*exo*-OH, respectively; Scheme I), which were obtained from the aforementioned *exo*- alcohol mixtures (3:2) by literature procedures¹, were treated in a standard way with DAST and 2-chloro-1,2,2-trifluorotriethylamine(FAR = fluoroamine reagent)⁴. Both fluorinating methods gave similar product mixtures. In the case of 12-*exo*-OH five fluoronorbonyl derivatives were identified(4, X=COOCH₃(48%); 6, X=COOCH₃(14%); 7, X=COOCH₃(14%); *endo*-epimer of 1, X=COOCH₃(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 Hanreich⁵ in the preparation of 6-*exo*-fluoro-2-*exo*-norbonyl acetate significantly increased the proportion of 4, X=COOCH₃ in the mixture. Similar fluorination trials on the 14-*exo*-OH isomer gave 5, X=COOCH₃ 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 fluoronorbonyl derivatives in a pure state and, moreover, because the fluoride mixtures could be unambiguously characterized by ¹³C and ¹⁹F NMR in conjunction with GC-MS and VPC analyses, we decided to obtain the ¹⁹F SCS of the various derivatives of 4 and 5 from mixtures rather than homogeneous compounds. Consequently, differently biased mixtures of 4, 5, 6, and 7(X=COOCH₃) (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 Hanreich⁵, 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 CH₂Cl₂(10ml) at 0°C under N₂ 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 CH₂Cl₂(30ml) under N₂ which had been under reflux for 45 min under N₂. After reflux for ca. 20 hrs the reaction mixture was quenched with an ice-cold aqueous NaHCO₃ solution before being thoroughly extracted with diethyl ether. The combined extracts were dried (MgSO₄) 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°C, 0.1 mm Hg) gave a mixture of 4, 6, and 7(X=COOCH₃)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 CFCl₃/CH₂Cl₂(16ml/4ml)was added dropwise to neat FAR⁴(5 equiv.) with stirring maintained at 0°C under N₂. 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

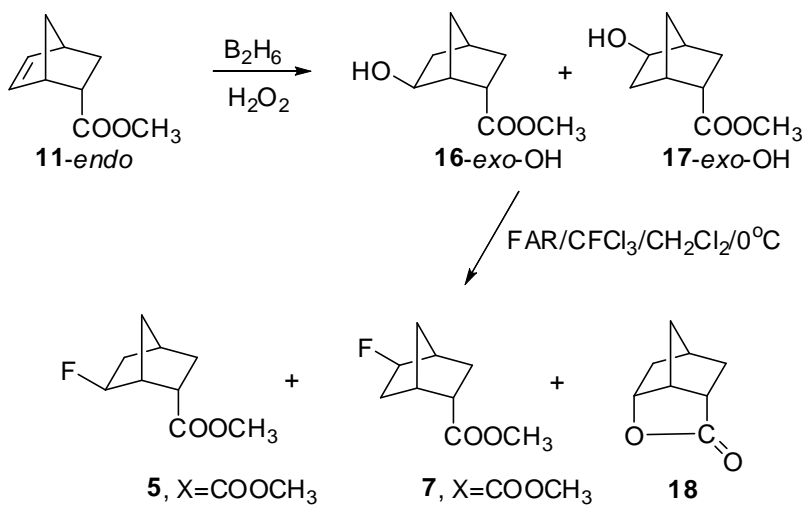
al⁷ for the treatment of norbornene. The mixture was then quenched by pouring into an ice-cold NaHCO₃ solution before being extracted with diethyl ether. The combined extracts were dried (MgSO₄) and the ether removed under vacuum to yield a crude mixture which, after kugelrohr distillation (70°C, 1 mm Hg), gave a mixture of pure 4, 5, 6, and 7(X=COOCH₃) 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/pyridine⁷ (see Scheme V). The *exo/endo* ratios for the Diels-Alder mixtures were 20-*exo*/20-*endo* = 1:2⁸, and 21-*exo*/21-*endo* = 2:3⁵. 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 acid³.

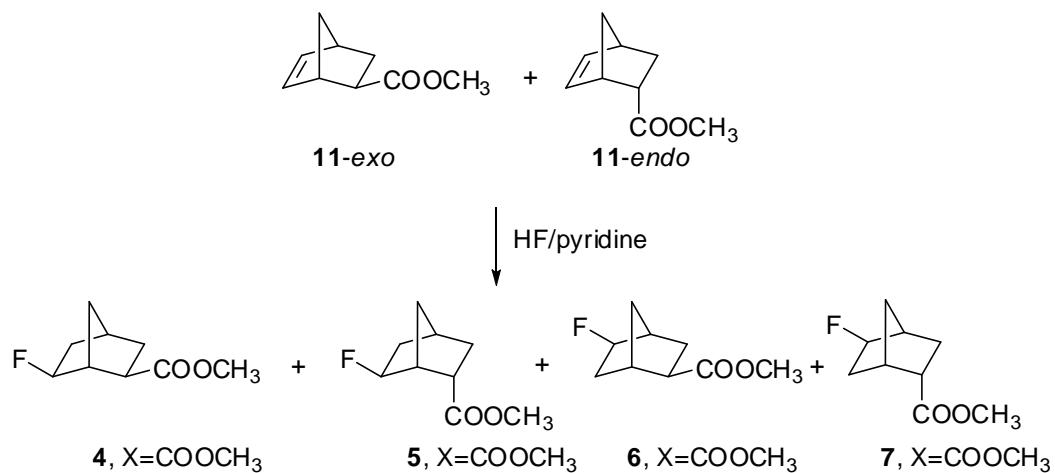
All the fluoride mixtures were unambiguously characterized by ¹³C and ¹⁹F NMR in conjunction with GC-MS and VPC analyses. The ¹³C NMR spectral assignments followed unequivocally from the characteristic ¹³C - ¹⁹F coupling constants in the norbornane skeletal framework⁷ as well as chemical shift additivity and APT technology. The observed and calculated ¹³C 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.



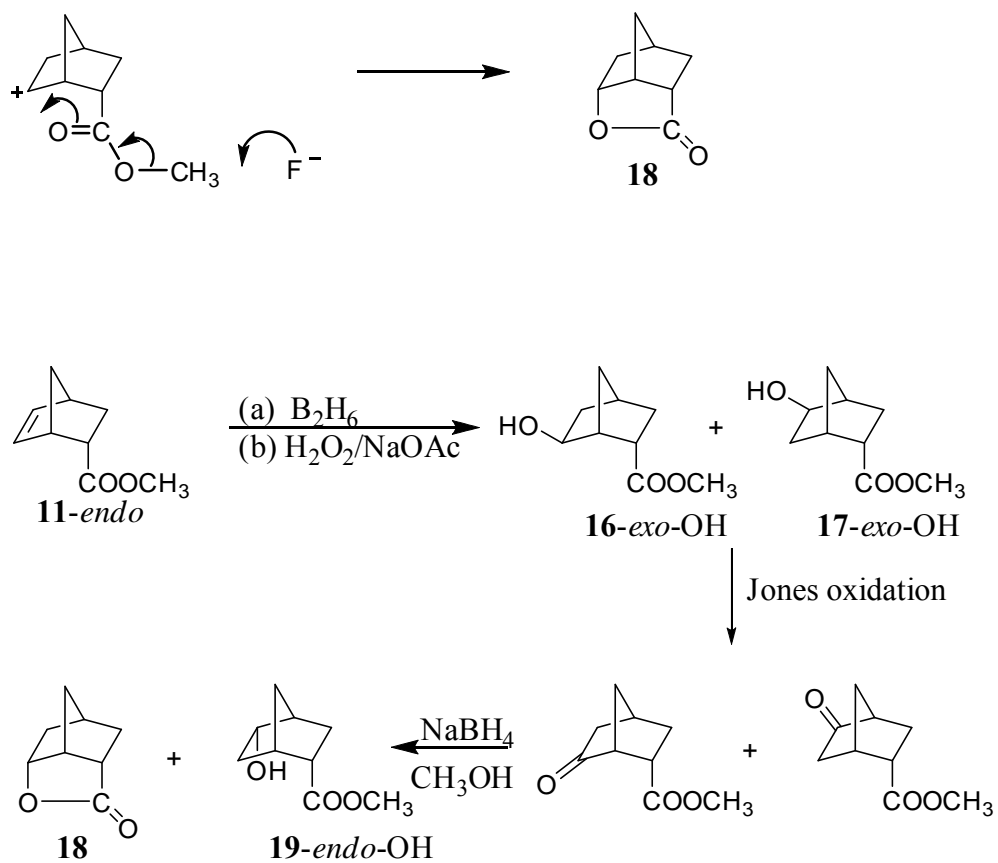
Scheme 1



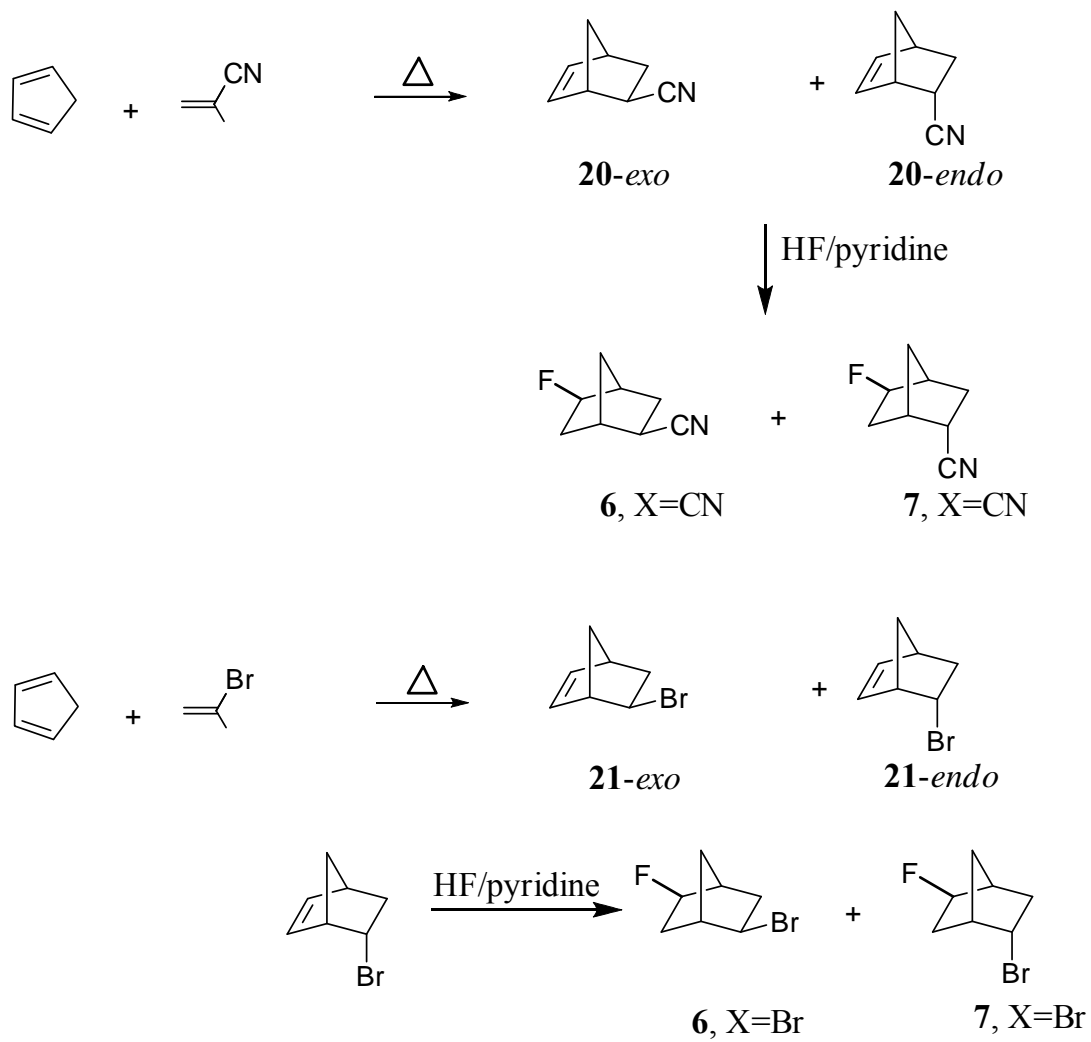
Scheme 2



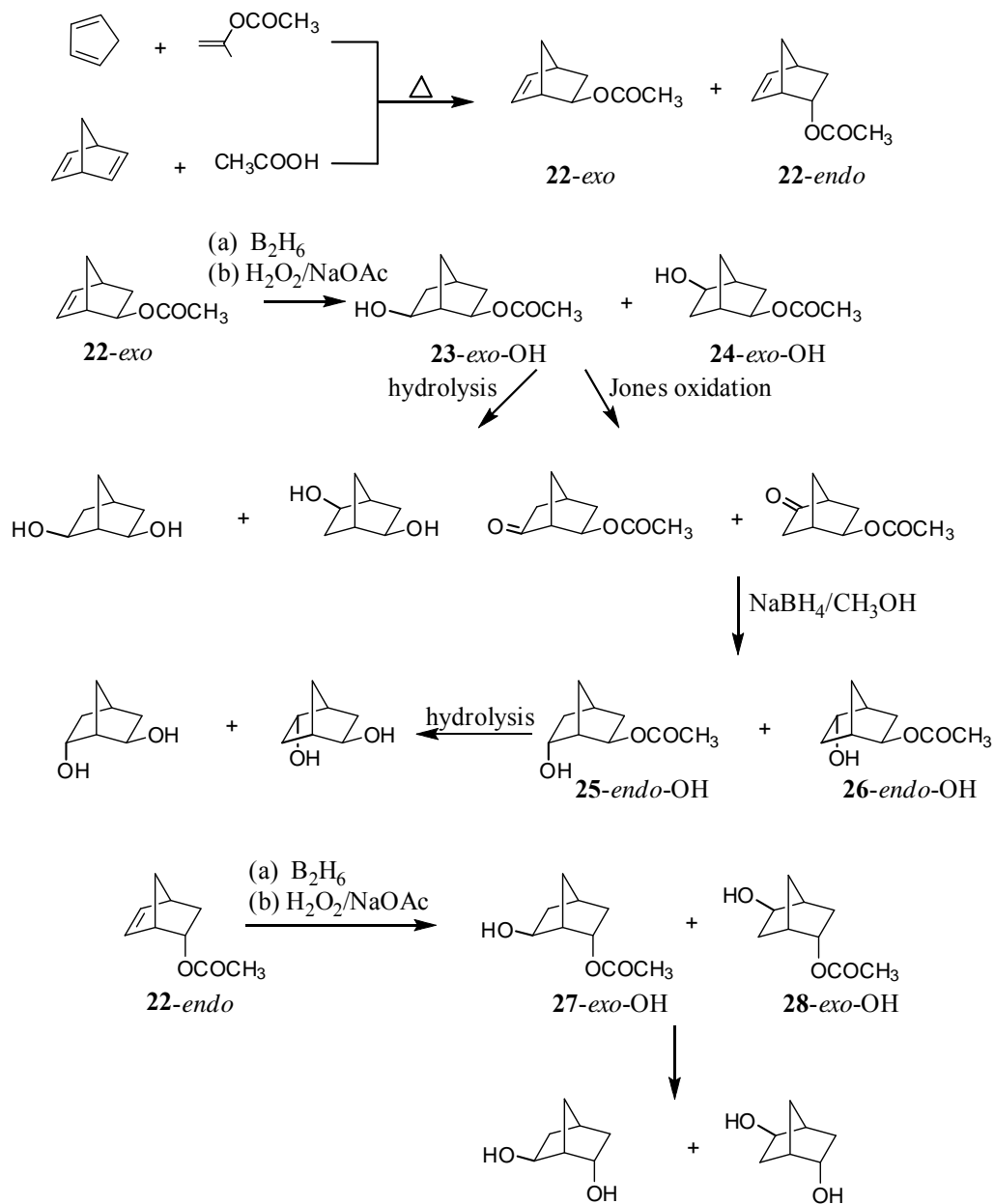
Scheme 3



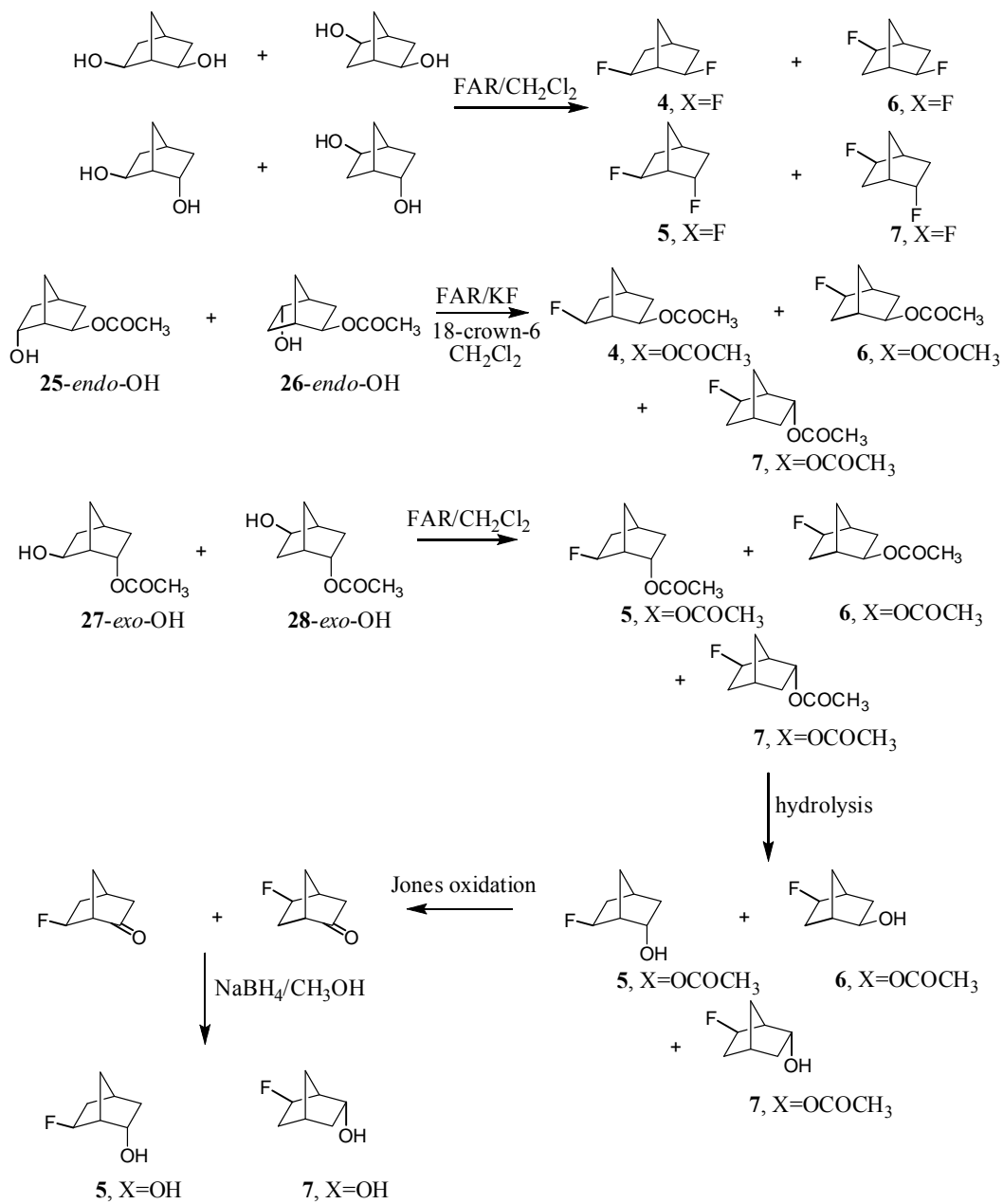
Scheme 4



Scheme 5



Scheme 6



Scheme 7

Table 1. Synthetic Methods for Mixtures of 4-7 from Mixtures of Fluoro-Carboxylic Esters 4-7, X = COOCH₃ (Schemes I, II, and III)

X	Precursor	Synthetic Method
COOH	COOCH ₃	THF/H ₂ O/H ₂ SO ₄ /Δ ^a
CONH ₂	COOH	CH ₂ Cl ₂ /SOCl ₂ /NH ₃ ^a
CN	CONH ₂	(CF ₃ CO) ₂ /dioxane/pyridine ^b
NH ₂	COOH	1. CH ₂ Cl ₂ /SOCl ₂ 2. acetone/NaN ₃ /H ₂ O 3. CH ₂ Cl ₂ /CF ₃ COOH/Δ ^c 4. CH ₃ OH/H ₂ O/K ₂ CO ₃ /N ₂ /Δ ^c
NO ₂	NH ₂	m-ClC ₆ H ₄ COOH/ClCH ₂ CH ₂ Cl/Δ ^d
CH ₂ OH	COOH	(C ₂ H ₅) ₂ O/LiAlH ₄ /Δ
CH ₂ OTosyl	CH ₂ OH	p-CH ₃ C ₆ H ₄ SO ₂ Cl/pyridine
CH ₂ Br	CH ₂ OTosyl	THF/LiBr/Δ
CH ₃	CH ₂ OTosyl	NaBH ₄ /HMPA
Cl	COOH	1. NHTP ^e /CH ₂ Cl ₂ /DCC ^f 2. PTOC ester ^g /CF ₃ CCl ₃ /hv ^h
Br	COOH	1. NHTP ^e /CH ₂ Cl ₂ /DCC ^f 2. PTOC ester ^g /CF ₃ CHClBr/hv ^h
I	COOH	1. NHTP ^e /CH ₂ Cl ₂ /DCC ^f 2. PTOC ester ^g /CF ₃ CH ₂ I/hv ^h
I	COOH	C ₆ H ₆ /Pb(OCOCH ₃) ₄ /I ₂ /Δ/hv ⁱ
Sn(CH ₃) ₃	Br	(CH ₃) ₃ SnLi/THF ^h

^aRef. 9. ^bRef. 10. ^cRef. 11. ^dRef. 12. ^eNHTP = N-hydroxy-2-thiopyridone. ^fDCC = N, N-dicyclohexylcarbodiimide. ^gBarton PTOC ester = O-acyl-N-hydroxy-2-thiopyridone. ^hRef. 13. ⁱRef. 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 (19.5)	96.21 (181.5)	39.91 (19.6)	34.65	28.00 (1.2)	22.39 (10.5)	34.57	
NO ₂	49.17 (24.4)	91.32 (186.4)	38.85 (20.6)	34.43	36.22	82.70 (12.6)	32.63	
CN	46.83 (23.4)	93.36 (184.4)	38.81 (20.4)	34.84	34.92	25.31 (13.3)	33.77	122.14 (3.9)
COOH	46.13 (22.2)	94.88 (183.5)	39.14 (20.6)	34.67	32.43	40.18 (10.5)	33.12	181.11 (4.4)
COOCH ₃	46.25 (21.8)	94.85 (183.8)	39.17 (20.2)	34.61	32.94	40.06 (10.4)	33.45	175.26 (4.6)
CONH ₂	46.81 (21.4)	95.17 (183.8)	39.29 (20.0)	34.61	33.25	40.89 (9.4)	33.14	177.1 (3.5)
F	49.42 (21.8)	91.62 (183.0)	38.95 (19.0)	33.70	38.95 (19.0)	91.62 (183.0)	30.96	
Cl	52.30 (21.8)	93.06 (185.0)	38.87 (20.3)	35.25	42.37	55.59 (14.8)	32.01	
Br	52.69 (21.9)	93.05 (186.4)	38.78 (20.3)	35.73	42.54	45.27 (14.0)	32.31	
I	53.91 (21.6)	92.47 (187.0)	39.82 (20.2)	36.65	43.63	18.28 (12.9)	32.97	
NH ₂	51.74 (19.9)	94.23 (181.5)	38.84 (20.0)	34.72	40.77	48.99 (12.1)	31.21	
OH	51.19 (19.9)	93.17 (181.5)	38.99 (20.1)	34.21	41.03	69.54 (14.3)	31.39	
OCH ₃	47.03 (20.1)	93.45 (181.8)	39.34 (20.2)	33.92	31.67	78.87 (13.9)	38.29	56.20
OCOCH ₃	48.23 (21.8)	92.45 (183.1)	38.93 (20.1)	34.10	32.10	72.23 (15.8)	38.56	170.46 (21.10)
CH ₃	48.90 (18.4)	95.99 (180.8)	40.38 (19.8)	35.47	38.11 (0.9)	29.42 (9.7)	31.54	21.20 (2.8)
CH ₂ OH	44.19 (19.4)	95.83 (182.6)	39.50 (20.0)	34.70	32.51	38.08 (9.1)	31.84	65.85
Sn(CH ₃) ₃ ^c	44.84 (17.6)	97.07 (187.2)	39.56 (19.7)	35.55	32.51 (1.5)	17.87 (13.9)	34.64	-10.70 ^c

^aJ_{C-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 ¹¹⁹Sn NMR(CDCl₃, relative to internal SnMe₄): δ 14.1ppm, J_{Sn-F} =57.2 Hz.

Table 3. Calculated ¹³C 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 ₂ OH	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

^aCalculated ¹³C 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**)^{ab}

X	C1	C2	C3	C4	C5	C6	C7	Others
NO ₂	47.61 (24.1)	90.90 (182.0)	39.13 (20.1)	35.68	35.60	83.31 (9.7)	32.56	
CN	44.80 (23.3)	91.8 (182.6)	39.59 (20.3)	35.41	34.24	24.76 (9.7)	35.22	120.98
COOH	45.66 (22.1)	93.09 (180.0)	39.64 (19.6)	35.85	30.70	41.28 (10.2)	36.50	180.80
COOCH ₃	45.72 (21.6)	93.05 (180.8)	39.62 (19.5)	35.86 (0.5)	30.81 (1.1)	41.29 (9.7)	36.47	174.30 51.70
CONH ₂	46.33 (21.2)	93.03 (179.0)	39.67 (19.4)	35.97	30.45	42.38 (10.1)	37.01	175.10
F	47.47 (21.5) (16.0)	90.76 (178.0) (14.0)	39.72 (20.2)	35.48	36.26 (21.7)	91.95 (184.0) (10.0)	33.91 (3.9)	
Cl	48.97 (22.5)	92.15 (179.1)	42.00 (20.7)	36.78	39.85	55.59 (14.8)	34.58	
Br	49.44 (16.2)	93.94 (179.8)	39.71 (20.0)	35.75	40.25	46.45 (13.7)	34.90	
I	49.23 (22.8)	94.45 (183.7)	39.97 (20.1)	35.39	41.87	21.31 (16.6)	33.87	
NH ₂	48.55 (19.2)	92.46 (176.5)	40.41 (19.4)	36.43	38.45	49.68 (10.5)	35.46	
OH	48.66 (19.7)	92.03 (176.2)	40.27 (19.7)	37.05	37.33	69.81 (10.7)	34.53	
OCH ₃	45.62 (20.0)	91.81 (176.8)	40.28 (19.6)	35.62	34.14	79.13 (10.1)	35.89	57.19
OCOCH ₃	46.32 (21.1)	91.25 (178.4)	39.90 (18.1)	35.47	35.95	72.10 (10.0)	34.10	170.30 21.00
CH ₃	47.42 (18.6)	93.13 (176.9)	40.69 (19.4)	36.86 (3.9)	40.51	30.62 (10.7)	36.70	17.01
CH ₂ OH	42.39 (19.7)	95.62 (176.8)	40.28 (20.0)	34.19	31.39	36.67 (10.9)	38.30	66.35
Sn(CH ₃) ₃ ^c	46.13 (19.6)	92.81 (184.0)	40.35 (19.5)	35.02	31.79	20.56 (13.5) [376.0] [359.0]	36.87	-10.30 [243.0] [233.0] [55.4]

^aJ_{C-F} (Hz), in parenthesis. ^bJ_{C-Sn}(Hz), in brackets. ^c¹¹⁹Sn NMR(CDCl₃, relative to internal SnMe₄): δ 2.42ppm, J_{Sn-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 ₂ OH	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 (21.3)	93.65 (184.5)	36.59 (18.2)	42.08	86.34	29.57 (10.6)	31.96	
CN	41.57 (21.2)	93.76 (184.8)	38.73 (20.6)	40.23	29.81 (1.7)	28.98 (11.0)	33.56	122.76
COOH	41.80 (19.6)	95.08 (183.00)	39.60 (21.0)	39.53	45.05	26.69 (11.70)	32.60	180.30
COOCH ₃	41.85 (20.5)	95.12 (182.48)	40.22 (20.8)	39.83	44.98 (1.6)	26.79 (11.0)	32.59	175.60 51.80
CONH ₂	41.74 (20.5)	95.27 (182.4)	39.98 (20.6)	40.25	45.95	26.77 (11.1)	32.56	177.50
F	40.59 (21.2)	94.11 (182.8)	32.83 (16.4)	40.59 (21.2)	94.11 (182.8)	32.83 (16.4)	30.79	
Cl	41.96 (20.7)	94.13 (183.5)	37.04 (21.2)	44.54	60.23 (2.9)	36.10 (10.6)	31.45	
Br	42.58 (20.6)	94.18 (183.8)	37.85 (21.4)	45.01	51.11 (1.5)	36.29 (10.5)	31.92	
I	42.34 (20.6)	93.49 (182.6)	38.62 (20.7)	46.52	26.45 (2.3)	38.62 (10.7)	32.89	
NH ₂	41.74 (20.2)	95.18 (181.9)	37.11 (20.5)	43.65	53.43	34.61 (9.7)	30.52	
OH	39.85 (18.2)	94.94 (181.6)	34.80 (21.2)	42.71	73.13 (2.1)	34.70 (11.1)	30.61	
OCH ₃	40.88 (20.2)	95.11 (182.5)	34.89 (21.0)	38.39	82.41 (2.9)	32.00 (11.3)	42.49	56.10
OCOCH ₃	41.05 (20.6)	94.37 (182.5)	34.69 (19.7)	39.92	75.64 (2.5)	32.30 (11.0)	39.70	170.60 21.10
CH ₃	42.68 (19.8)	96.04 (181.5)	39.21 (19.8)	41.48	34.95 (0.95)	32.18 (11.1)	31.00	21.90 (1.5)
CH ₂ OH	42.36 (20.0)	95.61 (182.4)	39.50 (19.9)	36.70	43.40	26.77 (11.3)	31.32	65.60
Sn(CH ₃) ₃ ^d	43.05 (19.6)	96.27 (181.4)	44.16 (18.9)	38.72 [7.1]	25.91	27.20 (10.1)	34.78	-10.70 [298.0, 312]

^aJ_{C-F} (Hz), in parenthesis. ^bJ_{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 (CDCl₃, relative to internal SnMe₄): 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 ₂ OH	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

^aCalculated ^{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 (21.1)	93.57 (184.2)	33.61 (21.5)	41.44	85.23	29.56 (11.1)	32.56	
CN	41.99 (21.2)	94.04 (184.4)	35.49 (21.2)	38.64	28.82	28.50 (10.3)	38.75	121.80
COOH	42.63 (20.0)	95.03 (183.2)	35.16 (20.3)	39.00	44.12	25.40 (10.5)	36.50	180.80
COOCH ₃	42.61 (20.2)	94.82 (182.8)	35.14 (20.4)	38.94	44.05 (1.2)	25.54 (9.8)	36.37	174.57 51.66
CONH ₂	42.66 (20.1)	95.17 (182.0)	34.74 (20.4)	39.13	44.80	25.10 (10.5)	36.91	177.30
F	40.59 (21.2) (1.6)	94.29 (183.7)	-	39.61 (17.4)	-	-	32.76 (4.8)	
Cl	41.95 (20.7)	94.60 (179.10)	33.00 (20.5)	42.81	60.10	34.34 (10.6)	34.20	
Br	42.60 (20.0)	94.49 (183.40)	35.04 (20.7)	42.49	51.20	34.92 (10.2)	33.95	
I	41.12 (20.5)	97.53 (180.60)	39.19 (21.1)	43.50	31.12	36.28 (9.9)	33.41	
NH ₂	43.00 (20.3)	93.26 (175.60)	31.04 (19.7)	41.40	50.80	33.22 (10.4)	35.28	
OH	42.77 (20.4)	95.46 (180.5)	30.77 (19.9)	40.95	70.55	32.32 (10.2)	33.42	
OCH ₃	42.17 (20.3)	95.37 (182.10)	30.88 (19.9)	37.67	79.77	30.73 (10.5)	33.41	56.10
OCOCH ₃	42.11 (20.6)	94.72 (183.2)	31.76 (20.5)	38.69	73.40	30.57 (10.2)	33.14	170.60 20.94
CH ₃	43.36 (19.4)	96.04 (181.5)	32.65 (19.6)	40.29	32.44	31.49 (10.1)	36.46	16.90
CH ₂ OH	42.02 (20.1)	95.83 (182.8)	33.08 (19.9)	38.53	40.81	26.81 (11.3)	38.18	64.10
Sn(CH ₃) ₃ ^c	42.38 (19.2)	96.13 (182.7)	40.04 (19.9)	39.02	26.15 (1.2)	26.55 (10.1)	36.87	-10.40 [326] [316]

^aJ_{C-F} (Hz), in parenthesis. ^bJ_{C-Sn} (Hz), in parenthesis ^c¹¹⁹Sn NMR (CDCl₃, relative to internal SnMe₄): δ -1.06 ppm, J_{Sn-F} = 0.00 Hz.

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 ₂ OH	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 (19.5)	66.46 (181.5)	10.16 (19.6)	-1.74	-1.75	-7.36 (10.5)	-3.85	
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 ₂ OH	2.21	15.45	14.75	0.21	0.55	-0.35	-3.02	66.40
Sn(CH ₃) ₃ ^d	3.75 (9.8)	-2.25 (407.4)	15.09 (23.4)	1.06 (12.7)	-0.30	4.17 (67.4)	0.08	-10.85 (306.3)

^aDefined 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, CDCl₃. 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. Observed ^{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 ₂ OH	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)

^aSee 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	$\sigma_{CF}^*(\text{occup})^c$
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
O	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
O	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

^an_F = average occupation numbers of the fluorine lone pairs. ^bQ_n = fluorine natural charge. ^cσ_{CF}* = occupancy of the C-F antibonding orbital.

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