Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Enantioselective Bromocyclization of 2-Geranylphenols Induced by Chiral Phosphite–Urea Bifunctional Catalysts

Yasuhiro Sawamura,[†] Yoshihiro Ogura[†], Hidefumi Nakatsuji,[†,§]
Akira Sakakura,*[,‡] Kazuaki Ishihara*[,†]

[†]*Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan*

[‡]*Graduate School of Natural Science and Technology, Okayama University, 3-1-1 Tsushimanaka, Kita-ku, Okayama 700-8530, Japan*

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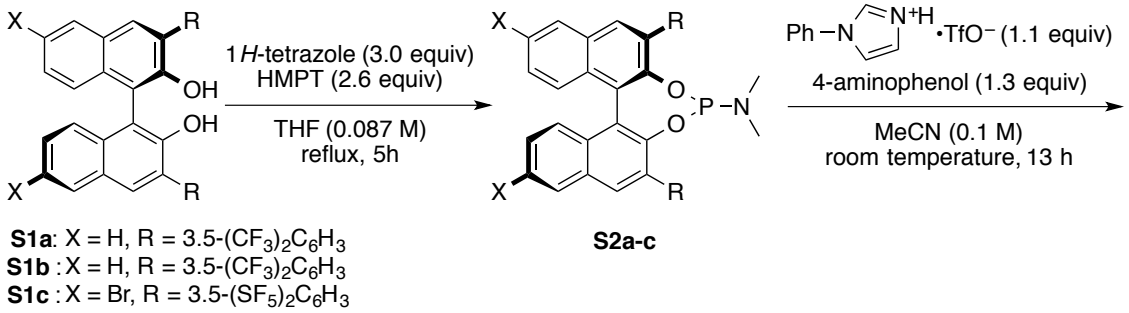
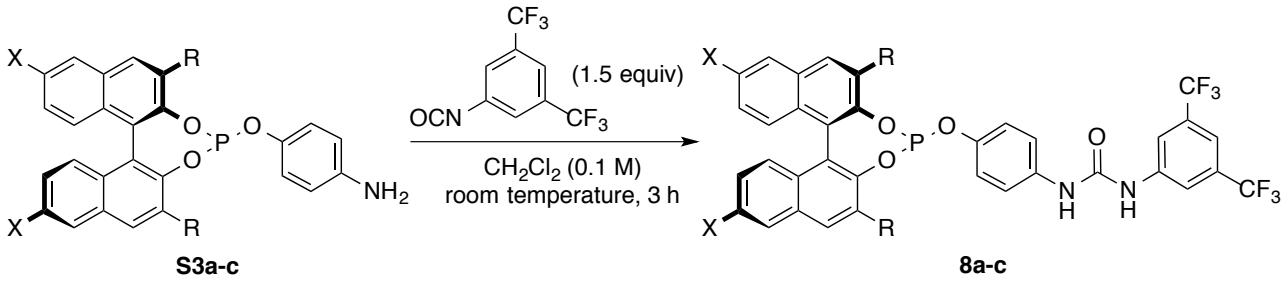
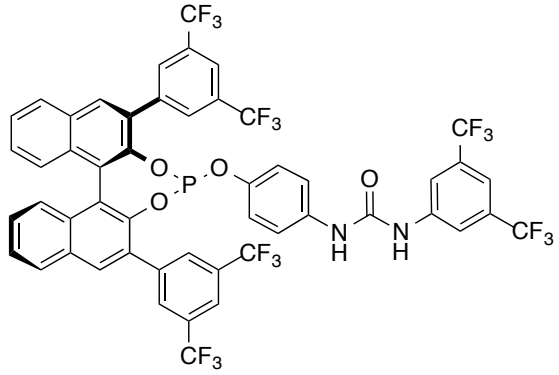
General Methods. IR spectra were recorded on a JASCO FT/IR-460 plus spectrometer. ^{1}H spectra were measured on a JEOL ECS-400 spectrometer (400 MHz) at ambient temperature. Chemical shifts are reported in ppm from the solvent resonance (acetone-d_6: 2.05 ppm, CD_3OD: 3.31 ppm, THF-d_8: 1.73 ppm) or Me_4Si resonance (0.00 ppm; $CDCl_3$) as the internal standard. Data were recorded as follows: chemical shift, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; sept = septet; m = multiplet, br = broad), coupling constant (Hz), and integration. ^{13}C NMR spectra were measured on a JEOL ECS-400 (100 MHz). Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CDCl_3$: 77.00 ppm, acetone-d_6: 29.84 ppm, THF-d_8: 25.30 ppm). ^{19}F NMR spectra (376 MHz) and ^{31}P NMR spectra (162 MHz) were measured on a JEOL ECS-400 spectrometer. High-performance liquid chromatography (HPLC) analysis was conducted using Shimadzu LC-10 AD coupled diode array-detector SPD-MA-10A-VP and chiral column of Daicel Chiralcel OD-3 (4.6 mm × 25 cm), Daicel Chiralcel AD-3 (4.6 mm × 25 cm), or Daicel Chiralpack IB-3 (4.6 mm × 25 cm). For TLC analysis, Merck precoated TLC plates (silica gel 60 F_{254} 0.25 mm) were used. For preparative column chromatography, Merck silica gel 60 (0.040–0.063 mm) was used. High resolution mass spectral analysis (HRMS) was performed at Chemical Instrument Facility, Nagoya University. Dry dichloromethane and tetrahydrofurane were purchased from Kanto as the "anhydrous" and stored under nitrogen. Dry acetonitrile was purchased from Wako as the "anhydrous" and stored under nitrogen. Dry toluene was distilled fractionally from CaH_2 and used immediately. Other materials were obtained from commercial supplies and used without further purification.

Synthesis of Phosphite–Urea Bifunctional Catalysts 8a-8e and 9

Synthesis of **8a-c**



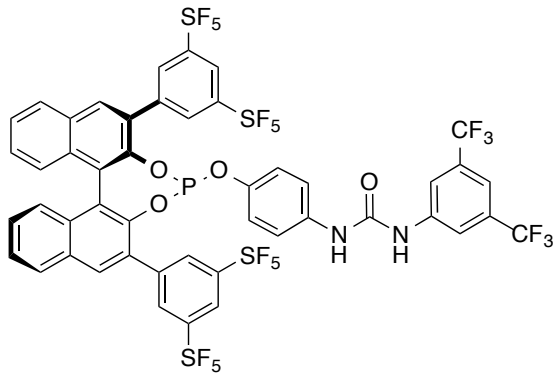




1-(4-(((11b*R*)-2,6-Bis(3,5-bis-(trifluoromethyl)phenyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy)phenyl)-3-(3,5-bis(trifluoromethyl)phenyl)urea (8a): To a suspension of **S1a**[1] (923 mg, 1.3 mmol) and 1*H*-tetrazole (273 mg, 3.9 mmol, 3.0 equiv) in dry THF (15 mL) was added *N*,*N*,*N*',*N*',*N*'',*N*''-hexamethylphosphinetriamine (HMPT) (424 mg, 3.4 mmol, 2.6 equiv). The reaction mixture was heated at reflux for 5 h, cooled to room temperature, and filtered through a Celite pad. The filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane–toluene = 3:1) to give **S2a** (968 mg, 95% yield).

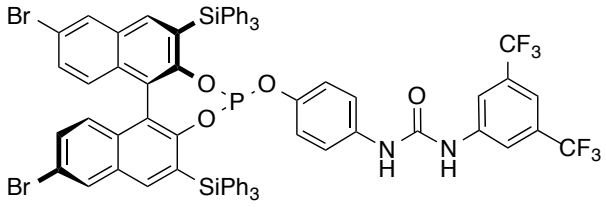
To a solution of **S2a** (392 mg, 0.50 mmol) and *N*-phenylimidazolium trifluoromethanesulfonate salt (162 mg, 0.55 mmol, 1.1 equiv) in dry CH_3CN (5 mL) was added 4-aminophenol (71 mg, 0.65 mmol, 1.3 equiv). The reaction mixture was stirred at room temperature for 13 h, filtered through a Celite pad, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane–toluene = 4:1 → 2:1 → 1:1 → 1:2) to give **S3a** (339 mg, 80% yield).

To a solution of **S3a** (339 mg, 0.4 mmol) in CH_2Cl_2 (4 mL) was added 1-isocyanato-3,5-bis(trifluoromethyl)benzene (153 mg, 0.60 mmol, 1.5 equiv). The reaction mixture was stirred at room temperature and insoluble urea starts to precipitate as a colorless solid. The reaction mixture was diluted with hexane, then the solid was filtered off and washed with hexane to give **8a** (350 mg, 79% yield). Colorless solid; $[\alpha]^{25}_{D}$ –96.8 (*c* 1.00, THF); IR (KBr) 1643, 1577, 1508, 1473, 1381, 1326, 1279, 1176, 1136, 1083, 987 cm^{-1}; ^{1}H NMR (400 MHz, THF-d_8) δ 8.43 (s, 2H), 8.40–8.29 (m, 5H), 8.40–8.18 (m, 6H), 7.99 (s, 1H), 7.62–7.53 (m, 3H), 7.50–7.37 (m, 4H), 7.18 (d, J = 8.7 Hz, 2H), 6.20 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, THF-d_8) δ 152.8, 147.2, 147.1, 145.6 (d, $J_{C–P}$ = 2.9 Hz, 2C), 144.9 (d, $J_{C–P}$ = 2.9 Hz, 2C), 143.1, 141.5, 140.8, 136.9, 130.4, 133.7, 132.8, 132.66, 132.65 (q, $J_{C–F}$ = 33.4 Hz, 2C), 132.4, 132.34 (q, $J_{C–F}$ = 32.4 Hz, 2C), 132.30 (q, $J_{C–F}$ = 32.4 Hz, 2C), 132.0, 131.6 (2C), 131.4(2C), 129.9, 129.8, 128.3, 128.1, 127.6, 127.5, 127.1, 126.9, 126.5, 126.4, 125.2, 124.6 (q, $J_{C–F}$ = 272 Hz, 6C), 122.4, 122.1, 120.7 (2C), 119.9 (d, $J_{C–P}$ = 8.6 Hz, 2C), 118.8 (2C), 115.5; ^{19}F NMR (376 MHz, THF-d_8) δ –63.3, –63.7; ^{31}P NMR (162 MHz, THF-d_8) δ 145.7; HRMS (FAB+) calcd for $C_{51}H_{25}F_{18}N_2O_4P^+$ $[M]^+$ 1102.1265, found 1102.1269.



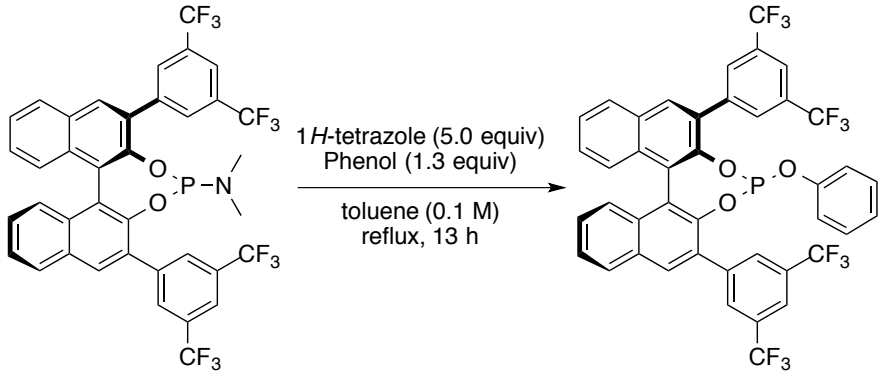
1-(4-(((11b*R*)-2,6-Bis(3,5-bis(pentafluor-o-λ^6-sulfanyl)phenyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy)phenyl)-3-(3,5-bis(trifluoromethyl)phenyl)urea (8b): Compound **8b** was prepared from **S1b**[2] according to the same manner as **8a**. Pale yellow solid; $[\alpha]^{22}_{D}$ –51.8 (*c* 1.00, THF); IR (KBr) 1508, 1388, 1281, 1187, 1139 cm^{-1}; ^{1}H NMR (400 MHz, acetone-d_6) δ 8.72 (s, 1H), 8.64 (d, J = 1.8 Hz, 2H), 8.55 (s, 1H), 8.54 (d, J = 1.8 Hz, 2H), 8.50 (s, 1H), 8.42 (t, J = 1.8 Hz, 1H), 8.38 (s, 1H), 8.34 (t, J = 1.8 Hz, 1H), 8.26 (d, J = 8.2 Hz, 1H), 8.22 (d, J = 8.2 Hz, 1H), 8.18 (s, 2H), 7.70–7.62 (m, 2H), 7.61 (s, 1H), 7.56–7.39 (m, 4H), 7.29 (d, J = 8.7 Hz, 2H), 6.20 (d, J = 8.7 Hz, 2H); ^{13}C NMR (100 MHz, acetone-d_6) δ 153.9 (quintet, $J_{C–F}$ = 18.1 Hz), 153.0, 147.0, 146.9, 145.1 (d, $J_{C–P}$ = 3.8 Hz), 144.4, 142.9, 141.4, 140.8, 136.8, 133.9, 133.7, 133.1, 132.6, 132.5, 132.4 (q, $J_{C–F}$ = 32.4 Hz), 132.2, 132.0, 131.6, 131.5, 130.2, 128.7, 128.6, 127.44, 127.37, 127.3, 127.2, 126.23, 126.17, 125.0, 124.5 (q, $J_{C–F}$ = 271 Hz), 123.8, 123.7, 120.9, 119.4 (d, $J_{C–P}$ = 9.5 Hz),

119.1, 115.6; ^{19}F NMR (376 MHz, acetone-d_6) δ 81.5 (quintet, J = 150 Hz), 63.1, 62.6, –63.5; ^{31}P NMR (162 MHz, acetone-d_6) δ 145.8; HRMS (ESI–) calcd for $C_{47}H_{24}F_{26}N_2O_4PS_4$ $[M–H]^-$ 1332.9947, found 1332.9957.

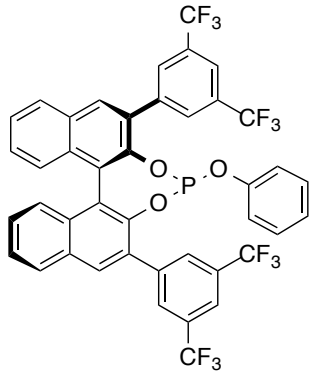


1-(3,5-Bis(trifluoromethyl)phenyl)-3-(4-(((11b*R*)-9,14-dibromo-2,6-bis(triphenylsilyl)dinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy)phenyl)urea (8c): Compound **8c** was prepared from **S1c**[3] according to the same manner as **8a**. Colorless solid; $[\alpha]^{22}_D$ –168.9 (*c* 1.00, $CHCl_3$); IR (KBr) 1560, 1506, 1475, 1429, 1387, 1279, 1184, 1136, 1108 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (s, 2H), 7.91 (d, J = 1.8 Hz, 1H), 7.82 (s, 2H), 7.81 (s, 1H), 7.59–7.48 (m, 13H), 7.38 (dd, J = 9.2, 1.9 Hz, 1H), 7.34 (t, J = 7.3 Hz, 6H), 7.29–7.19 (m, 13H), 7.13 (d, J = 9.2 Hz, 1H), 7.05 (d, J = 9.2 Hz, 1H), 6.83 (s, 1H), 6.69 (d, J = 8.7 Hz, 2H), 6.48 (s, 1H), 5.77 (d, J =8.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 152.2, 152.1, 148.2, 140.2, 139.6, 139.7, 136.7, 136.4, 134.0, 133.1, 132.7, 132.3 (q, $J_{C–F}$ = 33.4 Hz), 132.0, 131.9, 131.4, 130.71, 130.65, 130.5, 129.7, 129.5, 129.2, 128.5, 128.4, 128.3, 128.0, 127.7, 123.1, 123.0, 123.0 (q, $J_{C–F}$ = 272 Hz), 122.9, 122.6, 121.6 (d, $J_{C–P}$ = 6.7 Hz), 119.0, 118.8, 116.5; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 148.3; HRMS (ESI–) calcd for $C_{71}H_{46}Br_2F_6N_2O_4PSi_2^-$ $[M–H]^-$ 1349.1010, found 1349.1021.

Synthesis of **8d**

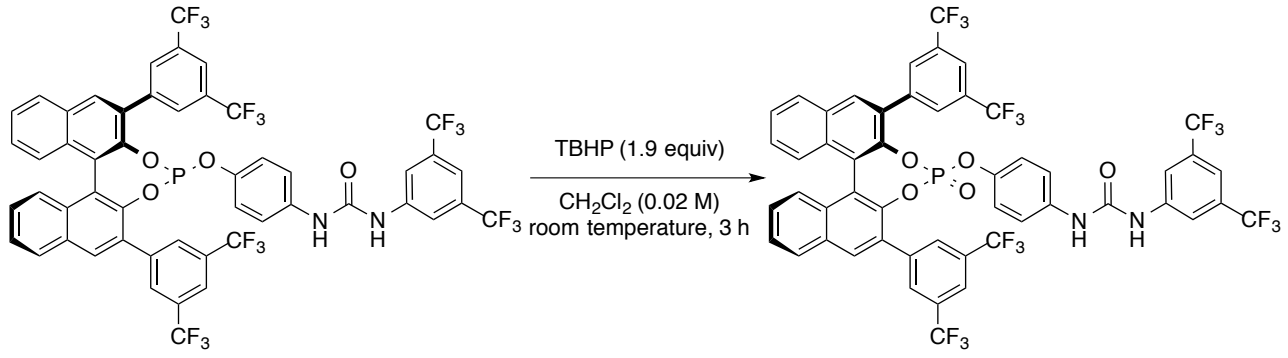


S2a **8d**

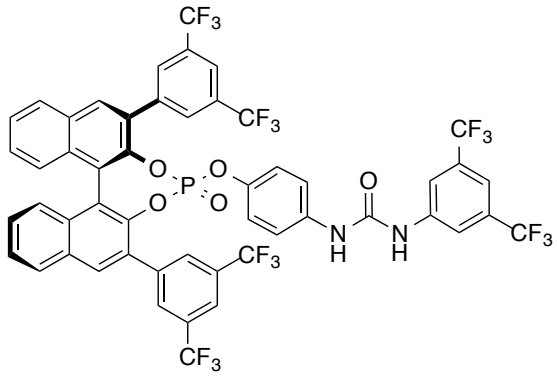


(11b*R*)-2,6-Bis(3,5-bis(trifluoromethyl)phenyl)-4-phenoxydinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepine (8d): To a solution of **S2a** (235 mg, 0.30 mmol) and 1*H*-tatrazole (105 mg, 1.50 mmol, 5.0 equiv) in dry toluene (3 mL) was added phenol (36.7 mg, 0.39 mmol, 1.3 equiv). The reaction mixture was stirred at room temperature for 13 h under reflux condition. After the stirring, the reaction mixture was filtered through a Celite pad, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane–toluene = 15:1) to give **8d** (201 mg, 80% yield). $[\alpha]^{28}_{D}$ –106.9 (*c* 1.00, $CHCl_3$); IR (KBr) 1378, 1280, 1175, 1135, 882 cm^{-1}; ^1H NMR (400 MHz, $CHCl_3$) δ 8.23 (s, 2H), 8.14 (s, 1H), 8.12 (s, 2H), 8.07 (s, 1H),8.06 (d, *J* = 6.8 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.93 (s, 1H),7.83 (s, 1H), 7.61–7.50 (m, 3H), 7.49–7.35 (m, 3H), 7.05–6.92 (m, 3H), 6.26 (d, *J* = 8.0 Hz, 2H); δ ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.0, 150.9, 144.4 (d, $J_{C–P}$ = 3.8 Hz, 2C), 143.7 (d, $J_{C–P}$ = 2.9 Hz, 2C),140.0, 139.2, 133.0, 132.7, 131.8, 131.8 (q, $J_{C–F}$ = 33.3 Hz, 2C),131.6 (q, $J_{C–F}$ = 32.4 Hz, 2C), 131.2, 131.2, 130.9, 130.1 (2C), 130.1 (2C), 129.5 (2C), 128.8, 128.7, 127.5, 127.4, 126.9, 126.8, 126.4, 126.2, 124.4, 124.2, 123.3 (q, $J_{C–F}$ = 271 Hz, 2C), 123.2 (q, $J_{C–F}$ = 272 Hz, 2C), 121.6, 121.1, 118.5 (d, $J_{C–P}$ = 9.5 Hz, 2C),; ^{19}F NMR (376 MHz,$CDCl_3$) δ –62.6, –62.7; ^{31}P NMR (162 MHz, $CDCl_3$) δ –144.4; HRMS (ESI+) calcd for $C_{42}H_{21}F_{12}NaO_3P^+$ $[M+Na]^+$ 855.0929, found 855.0928.

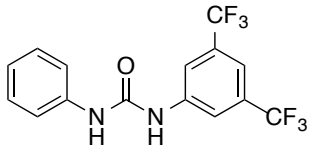
Synthesis of **9**



8a **9**



1-(4-(((11b*R*)-2,6-Bis(3,5-bis(trifluoro-methyl)phenyl)-4-oxidodinaphtho[2,1-*d*:1',2'-*f*][1,3,2]dioxaphosphepin-4-yl)oxy)phenyl)-3-(3,5-bis(trifluoromethyl)phenyl)urea (9): To a solution of **8a** (42 mg, 0.038 mmol) in CH_2Cl_2 (2 mL) was added 5.5 M solution of TBHP in nonane (13 μL, 0.072 mmol, 1.9 equiv) at 0 °C. After stirring for 3 h at ambient temperature, the reaction was quenched with saturated aqueous $Na_2S_2O_3$. The mixture was extracted with EtOAc, and the combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was reprecipitated from EtOAc–hexane to give **9** as a colorless solid (37 mg, 88% yield). $[\alpha]^{23}_D$ –105.8 (*c* 1.00, THF); IR (KBr) 1560, 1508, 1474, 1381, 1324, 1281, 1178, 1136 cm^{-1}; ^1H NMR (400 MHz, THF-d_8) δ 8.51 (s, 1H), 8.42 (s, 1H), 8.40 (s, 1H), 8.35 (s, 2H), 8.18 (t, J = 7.3 Hz, 2H), 8.08 (s, 4H), 8.05 (s, 1H). 7.67–7.58 (m, 2H), 7.57 (s, 1H), 7.48–7.36 (m, 4H), 7.21 (d, J = 8.7 Hz, 2H), 6.54 (d, J = 8.7 Hz, 2H); δ ^{13}C NMR (100 MHz, THF-d_8) δ 152.8, 146.0 (d, $J_{C–P}$ = 5.7 Hz, 2C), 145.4, 145.3, 144.1 (d, $J_{C–P}$ = 8.6 Hz, 2C), 143.0, 140.1, 140.0, 137.6, 133.8, 133.5, 133.4, 132.9, 132.6 (q, $J_{C–F}$ = 32.4 Hz, 2C), 132.4 (q, $J_{C–F}$ = 32.4 Hz, 2C), 132.3 (q, $J_{C–F}$ = 32.4 Hz, 2C), 131.9 (2C), 131.7, 131.4 (3C), 129.9, 129.9, 128.7, 127.8, 127.7 (3C), 124.6 (q, $J_{C–F}$ = 271 Hz, 2C), 124.6 (q, $J_{C–F}$ = 271 Hz, 2C), 124.5 (q, $J_{C–F}$ = 271 Hz, 2C), 123.6, 122.6, 122.5, 120.4 (2C), 119.5 (d, $J_{C–P}$ = 5.7 Hz, 2C), 118.8 (2C), 115.5; ^{19}F NMR (376 MHz, THF-d_8) δ –63.2, –63.7, –63.8; ^{31}P NMR (162 MHz, THF-d_8) δ –4.6; HRMS (ESI+) calcd for $C_{51}H_{25}F_{18}N_2NaO_5P^+$ $[M+Na]^+$ 1141.1106, found 1141.1107.

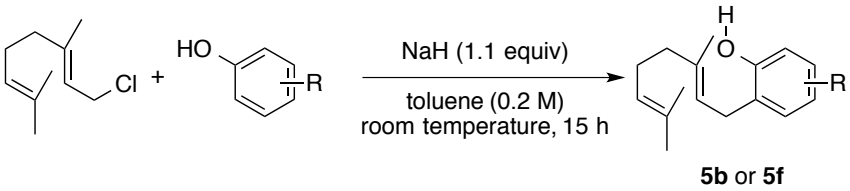


1-(3,5-Bis(trifluoromethyl)phenyl)-3-phenylurea (10)[4]

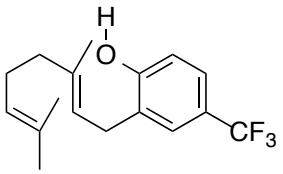
Preparation of Substrate 5a-5f, 14, and 15

2-Geranylphenol (**5a**),[3,5,6] 2-geranyl-4-bromophenol (**5c**),[7] 2-geranyl-4-methoxyphenol (**5d**),[3] 2-geranyl-4-methylphenol (**5e**),[3] geranylbenzene (**17**),[8] were synthesized as reported procedure.

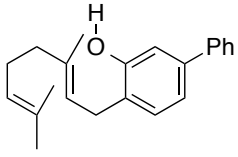
Synthesis of **5b** and **5f**



5b or **5f**



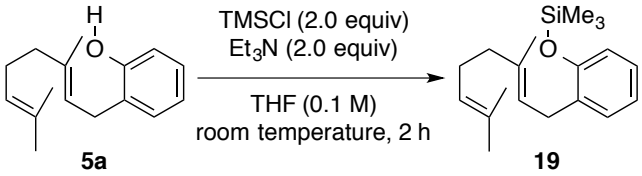
2-Beranyl-4-trifloromethylphenol (5b): To a solution of 4-trifluoromethylphenol (535 mg, 3.3 mmol, 1.1 equiv) in toluene (15 mL) was added NaH (60% in oil, 132 mg, 3.3 mmol, 1.1 equiv) at 0 °C. After stirring for 2 h at ambient temperature, geranylchloride (556 μL, 3.0 mmol) was added and stirred for 15 h. After the stirring, the reaction was quenched with saturated aqueous NH_4Cl. The mixture was extracted with EtOAc, and the combined organic layer was washed with brine, dried over Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (hexane–EtOAc = 50:1 → 20:1) to give **5b** (358 mg, 40% yield). Clear oil; IR (neat) 1616, 1507, 1438, 1329, 1276, 1216, 1160, 1119, 1075 cm^{-1}; δ 7.40–7.32 (m, 2H), 6.88–6.81 (m, 1H), 5.59 (brs, 1H), 5.31 (t, J = 7.1 Hz, 1H), 5.12–5.02 (m, 1H), 3.40 (d, J = 7.3 Hz, 2H), 2.18–2.06 (m, 4H), 1.77 (s, 3H), 1.68 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.2, 139.8, 132.2, 127.3, 127.1 (q, $J_{C–F}$ = 3.8 Hz), 124.9 (q, $J_{C–F}$ = 3.8 Hz), 124.5 (q, $J_{C–F}$ = 269 Hz), 123.6, 122.9 (q, $J_{C–F}$ = 32.4 Hz), 120.5, 115.8, 39.6, 29.7, 26.3, 25.6, 17.7, 16.8; ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.2; HRMS (FAB) calcd for $C_{17}H_{22}F_3O$ $[M+H]^+$ 299.1617, found 299.1620

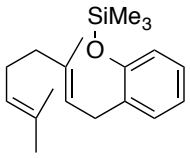


2-Geranyl-4-phenylphenol (5f): Compound **5f** was prepared from geranyl chloride and 3-phenylphenol according to the same manner as **5b**. **5f** (191 mg, 21% yield).; Clear oil; IR (neat) 3451, 2967, 2915, 2853, 1486, 1450, 1411, 1227, 759, 697 cm^{-1}; δ 7.56 (d, J = 7.4 Hz, 2H), 7.41 (dd, J = 7.8, 7.4 Hz, 2H), 7.32 (t, J = 7.8 Hz, 1H), 7.17 (d, J = 7.8 Hz, 1H), 7.10 (dd, J = 7.8, 1.4 Hz, 1H), 7.05 (d, J = 1.4 Hz, 1H), 5.36 (t, J = 7.3 Hz, 1H), 5.22 (s, 1H), 5.08 (t, J = 6.0 Hz,

1H), 3.40 (d, J = 7.3 Hz, 2H), 2.18–2.06 (m, 4H), 1.79 (s, 3H), 1.69 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.7, 140.8, 140.7, 138.8, 132.0, 130.3, 128.7 (2C), 127.2, 126.9 (2C), 125.8, 123.8, 121.5, 119.5, 114.5, 39.7, 29.5, 26.4, 25.7, 17.7, 16.2; HRMS (ESI+) calcd for $C_{22}H_{26Na}O$ $[M+Na]^+$ 329.1876, found 329.1878.

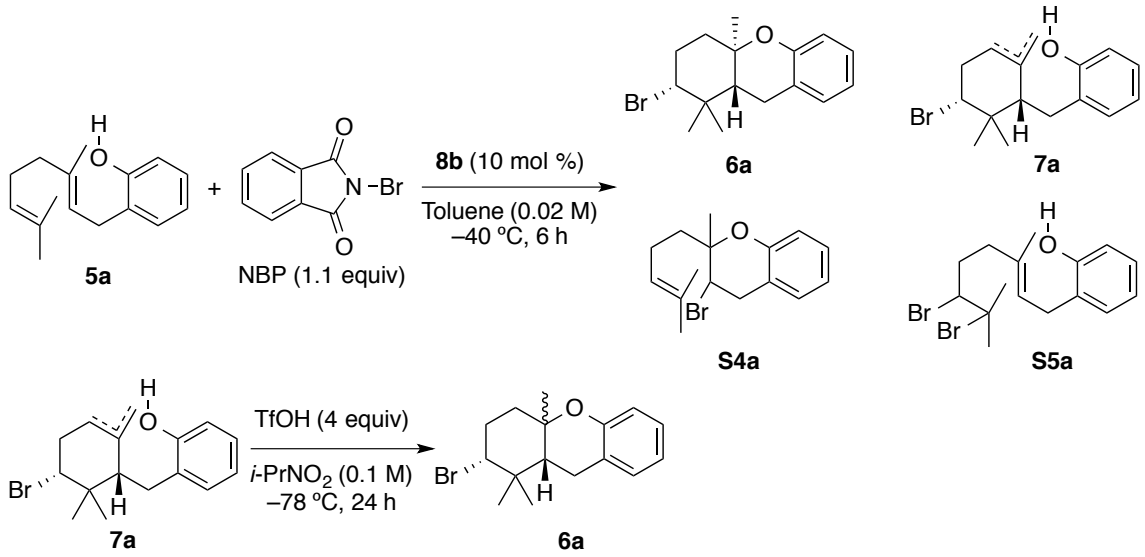
Synthesis of **19**





(*E*)-(2-(3,7-Dimethylocta-2,6-dien-1-yl)phenoxy)trimethylsilane (19): To a solution of **5a** (115 mg, 0.5 mmol) and triethylamine (139 μL, 1.0 mmol) in THF (5 mL) was added trimethylsilyl chloride (126 μL, 1.0 mmol) at 0 °C. After stirring for 2 h at ambient temperature, the mixture was filtered through a Celite pad, washed with Et_2O, and the filtrate was concentrated to give **18** (79 mg, 85% yield) as a pale yellow oil. IR (neat) 1490, 1451, 1253 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (d, J = 7.3 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H), 6.89 (t, J = 7.3 Hz, 1H), 6.77 (d, J = 7.8 Hz, 1H), 5.29 (t, J = 7.3 Hz, 1H), 5.11 (t, J = 6.0 Hz, 1H), 3.29 (d, J = 7.3 Hz, 2H), 2.25–2.01 (m, 4H), 1.69 (s, 6H), 1.60 (s, 3H), 0.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 136.0, 132.3, 131.4, 129.4, 126.6, 124.3, 122.3, 121.3, 118.7, 39.7, 28.4, 26.6, 25.7, 17.7, 16.1 0.5 (3C); HRMS (FAB+) calcd for $C_{19}H_{30}OSi^+$ $[M]^+$ 302.2066, found 302.2069.

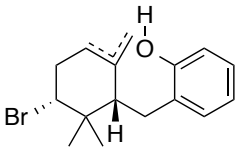
Typical Procedure for the Enantioselective Bromocyclization Induced by Phosphite–Urea Bifunctional Catalysts



To a solution of **5c** (13.3 mg, 0.01 mmol, 10 mol %) in toluene (5.0 mL) were added **5a** (23.0 mg, 0.10 mmol) and NBP (24.9 mg, 0.11 mmol, 1.1 equiv) successively at –78 °C, and the mixture was stirred at –78 °C for 0.5 h and then at –40 °C for 6 h. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (3.0 mL) and extracted with hexane (5.0 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The yield of *trans*-fused brominated AB-ring product **6a** (29%) and *endo*- and *exo*-isomeric A-ring products **7a** (60%) were determined by ^{1}H NMR analysis of the crude mixture using tetrachloroethane (5.2 μL, 0.050 mmol, 0.5 equiv) as an internal standard. [Note: The following assignments of **6a**, **7a**, **S4a**, and **S5a** were used by ^{1}H NMR analysis. δ 4.05 (dd, J = 12.4, 4.1 Hz, 1H of ***trans*-6a**), δ 4.15 (dd, J = 11.0, 1.4 Hz, 1H of **S5a**), δ4.21 (dd, J = 11.0, 4.1 Hz, 1H of ***exo*-7a**), δ 4.27 (dd, J = 9.6, 6.4 Hz, 1H of ***endo*-7a**), δ 4.35 (dd, J = 9.6, 6.0 Hz, 1H of **S4a**).] The crude product was purified by column chromatography on silica gel (hexane–EtOAc = 1000:1 → 500:1 → 20:1) to give **6a** and *endo*- and *exo*-isomeric mixture**7a**.

The *endo*- and *exo*-isomeric mixture **7a** was used for the next cyclization to determine the enantioselectivity. To a solution of the resulting mixture, which were obtained in the above reaction, in *i*-$PrNO_2$ (0.6 mL) was added TfOH (21 mL, 0.24 mmol, 4.0 equiv) at –78 °C. After stirring at –78 °C for 24 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with Et_2O (5 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The diastereomeric ratio (*trans/cis* = 75:25) was determined by ^{1}H NMR analysis of the crude mixture. [Note: The following assignments were used by ^{1}H NMR analysis. δ 0.79 (s, 3H of ***cis*-6a**), δ 1.03 (s, 3H of ***trans*-6a**).] The residue was purified by preparative TLC (hexane–EtOAc = 20:1) to give **6a**.

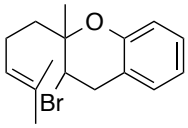
The corresponding physical and spectroscopic data for **7a**, **S4a**, **S5a**, and **7a** are as follows.



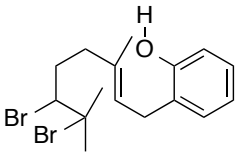
2-((5-Bromo-2,6,6-trimethylcyclohex-2-en-1-yl)methyl)phenol (*endo*-7a) and **2-((3-Bromo-2,2-dimethyl-6-methylenecyclohexyl)methyl)phenol (*exo*-7a)**: Compounds ***endo*-7a** and ***exo*-7a** could not be separated by column chromatography on silica gel.

***endo*-7a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.22 (brs, 1H), 4.27 (dd, *J* = 9.6, 6.4 Hz, 1H), 1.48 (s, 3H), 1.21 (s, 3H), 1.05 (s, 3H); Other resonances could not be discerned for this compound.

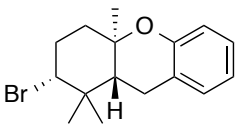
***exo*-7a**: ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.86 (s, 1H),4.74 (s, 1H), 4.21 (dd, *J* = 11.0, 4.1 Hz, 1H), 1.12 (s, 3H), 1.01 (s, 3H); Other resonances could not be discerned for this compound.



3-Bromo-2-methyl-2-(4-methylpent-3-en-1-yl)chroman (S4a):[5] Colorless oil; IR (neat) 1585, 1489, 1456, 1262, 1238 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.01 (d, *J* = 7.3 Hz, 1H), 6.86 (dd, *J* = 7.8, 7.3 Hz, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 5.13 (t, *J* = 7.4 Hz, 1H), 4.35 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.36 (dd, *J* = 16.5, 6.0 Hz, 1H), 3.27 (dd, *J* = 16.5, 9.6 Hz, 1H), 2.24–2.25 (m, 2H), 1.91–1.75 (m, 2H), 1.69 (s, 3H), 1.63 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.8, 132.2, 128.7, 128.0, 123.6, 120.5, 119.9, 117.4, 78.3, 50.6, 39.1, 34.0, 25.7, 21.4, 19.8, 17.6; HRMS (FAB+) calcd for $C_{16}H_{21}BrO^+$ $[M]^+$ 308.0776, found 308.0769.

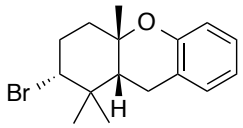


(*E*)-2-(6,7-Dibromo-3,7-dimethyloct-2-en-1-yl)phenol (S5a):[5] Colorless oil; IR (neat) 1591, 1489, 1454, 1370, 1221, 1097 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (d, *J* = 7.4 Hz, 1H), 7.11 (dd, *J* = 7.8, 7.4 Hz, 1H), 6.87 (dd, *J* = 7.4, 7.4 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 5.45 (t, *J* = 7.4 Hz, 1H), 4.97 (s, 1H), 4.15 (dd, *J* = 11.0, 1.4 Hz, 1H), 3.39 (d, *J* = 7.4 Hz, 2H), 2.58 (dddd, *J* = 14.7, 7.8, 7.8, 1.4 Hz, 1H), 2.46–2.38 (m, 1H), 2.29–2.19 (m, 1H), 1.97 (s, 3H), 1.95–1.83 (m, 1H), 1.81 (s, 1H), 1.80 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 135.9, 129.9, 127.5, 126.8, 123.5, 120.8, 115.6, 68.8, 65.7, 37.8, 35.4, 33.7, 29.3, 28.1, 16.1; HRMS (FAB+) calcd for $C_{16}H_{22}Br_2O^+$ $[M]^+$ 388.0037, found 388.0043.



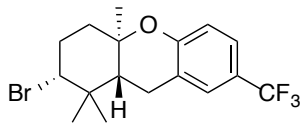
(2*R*,4a*R*,9a*R*)-2-Bromo-1,1,4a-trimethyl-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene

(*trans*-6a): The absolute configuration of ***trans*-6a** was determined by coupling constant of ^{1}H NMR and transformation to ***trans*-11a** and assigned to be (4a*R*,9a*R*) by comparing the reported retention time of HPLC.;[3] Colorless solid; $[\alpha]^{23}_D$ 28.0 (*c* 0.32, $CHCl_3$) for 65% ee (*trans/cis* 75:25); HPLC (Daicel Chiralcel AD-H column, hexane–*i*-PrOH = 1000:1, flow rate = 1.0 mL/min) t_R = 10.6 (minor enantiomer), 13.6 (major enantiomer) min; IR (KBr) 1488, 1454, 1242, 1150 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13–7.03 (m, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 6.75 (d, *J* = 8.2 Hz, 1H), 4.05 (dd, *J* = 12.4, 4.1 Hz, 1H, $C(2)H_{axial}$), 2.83–2.69 (m, 2H), 2.28 (dddd, *J* = 13.7, 4.1, 3.6, 3.6 Hz, 1H), 2.13 (dddd, *J* = 13.7, 13.7, 12.4, 3.7 Hz, 1H), 2.01 (ddd, *J* = 12.8, 3.7, 3.6 Hz, 1H), 1.81 (dd, *J* = 11.9, 6.0 Hz, 1H), 1.78 (ddd, *J* = 13.7, 12.8, 3.6 Hz, 1H), 1.24 (s, 3H), 1.17 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 129.5, 127.3, 121.7, 120.0, 117.0, 75.7, 66.0, 48.0, 40.7, 39.2, 31.5, 29.6, 24.6, 19.8, 16.9; HRMS (FAB) calcd for $C_{16}H_{21}BrO^+$ $[M]^+$ 308.0776, found 308.0774.



(2*R*,4a*S*,9a*R*)-2-Bromo-1,1,4a-trimethyl-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene

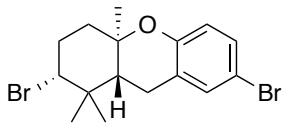
(*cis*-6a): Colorless solid; IR (neat) 1584, 1489, 1455, 1237 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11–7.02 (m, 2H), 6.84 (t, *J* = 7.3 Hz, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 4.09 (dd, *J* = 12.8, 3.3 Hz, 1H, $C(2)H_{axial}$), 3.12 (dd, *J* = 17.9, 7.8 Hz, 1H), 2.84 (d, *J* = 17.9 Hz, 1H), 2.48 (dddd, *J* = 13.7, 12.8, 12.8, 3.6 Hz, 1H), 2.11–2.04 (m, 2H), 1.67 (ddd, *J* = 14.7, 13.7, 4.1 Hz, 1H) 1.57 (d, *J* = 7.8 Hz, 1H), 1.19 (s, 3H), 1.15 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0, 128.7, 127.0, 121.4, 120.3, 117.2, 74.4, 67.5, 45.1, 40.3, 40.2, 30.1, 29.9, 26.5, 27.8, 16.6; HRMS (FAB) calcd for $C_{16}H_{21}BrO^+$ $[M]^+$ 308.0776, found 308.0794.



(2*R*,4a*R*,9a*R*)-2-Bromo-1,1,4a-trimethyl-7-(trifluoromethyl)-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene (6b): Colorless solid; $[\alpha]^{27}_D$ 54.7 (*c* 1.00, $CHCl_3$) for 66% ee (*trans/cis* 74:26); HPLC (Daicel Chiralcel AD-3 column × 2, hexane–*i*-PrOH = 1000:1, flow rate = 0.7 mL/min) t_R = 22.4 (major enantiomer), 26.1 (major enantiomer) min; IR (KBr) 1621, 1505, 1332, 1281, 1150, 1120, 1069 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (s, 1H), 7.33 (dd, *J* = 2.3, 8.7 Hz, 1H), 6.81 (d, *J* = 8.7 Hz, 1H), 4.04 (dd, *J* = 12.8, 4.1 Hz, 1H, $C(2)H_{axial}$), 2.88–2.72 (m, 2H), 2.30 (dddd, *J* = 14.0, 4.4, 3.6, 3.2 Hz, 1H), 2.13 (dddd, *J* = 14.0, 12.8, 12.8, 3.6 Hz, 1H), 2.03 (ddd, *J* = 13.2, 3.6, 3.6 Hz,

1H), 1.80 (dd, J = 10.0, 5.2 Hz, 1H), 1.79 (ddd, J = 13.2, 12.8, 3.2 Hz, 1H),1.25 (s, 3H), 1.18 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.4, 126.9 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.6 (q, $J_{C\text{-}F}$ = 3.8 Hz), 124.5 (q, $J_{C\text{-}F}$ = 270 Hz), 122.2 (q, $J_{C\text{-}F}$ = 32.4 Hz), 121.9, 77.2, 65.3, 47.7, 40.5, 39.2, 31.4, 29.6, 24.5, 19.9, 16.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.2; HRMS (FAB+) calcd for $C_{17}H_{21}BrF_3O^+$ $[M+H]^+$, 377.0722 found 377.0741.

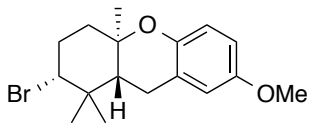
[Note: The following assignments of **7b**, **S4b**, **S5b**, and **6b** were used by ^{1}H NMR analysis. δ 4.04 (dd, J = 12.8, 4.1 Hz, 1H, C(2)H_{axial} of ***trans*-6b**), δ 4.14 (dd, J = 11.6, 1.2 Hz, 1H of **S5b**), δ 4.24 (dd, J = 10.6, 4.4 Hz, 1H of ***exo*-7b**), δ 4.28 (dd, J = 9.0, 6.4 Hz, 1H of ***endo*-7b**), δ 4.33 (dd, J = 8.8, 2.4 Hz, 1H of **S4b**).



(2*R*,4a*R*,9a*R*)-2,7-Dibromo-1,1,4a-trimethyl-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene

(6c): Colorless solid; $[\alpha]^{27}_D$ 54.8 (*c* 1.10, $CHCl_3$) for 71% ee (*trans/cis* 75:25); HPLC (Daicel Chiralcel AD-3 column × 2, hexane–*i*-PrOH = 1000:1, flow rate = 0.8 mL/min) t_R = 22.5 (major enantiomer), 30.7 (minor enantiomer) min; IR (KBr) 1480, 1258, 1240, 1147, 1130, 1070 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.19 (s, 1H), 7.17 (dd, J = 8.7, 2.3 Hz, 1H), 6.63 (d, J = 8.7 Hz, 1H), 4.03 (dd, J = 12.4, 4.1 Hz, 1H, C(2)H_{axial}), 2.80–2.66 (m, 2H), 2.28 (dddd, J = 13.8, 4.1, 4.1, 3.7 Hz, 1H), 2.12 (dddd, J = 13.8, 13.3, 12.4, 3.7 Hz,1 H), 1.99 (ddd, J = 13.3, 3.7, 3.7 Hz, 1H), 1.76 (dd, J = 12.4, 6.4 Hz, 1H), 1.75 (ddd, J = 13.3, 13.3, 4.1 Hz, 1H), 1.22 (s, 3H), 1.16 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 132.0, 130.3, 123.9, 118.8, 112.0, 76.1, 65.5, 47.7, 40.5, 39.2, 31.4, 29.6, 24.4, 19.8, 16.9; HRMS (FAB+) calcd for $C_{16}H_{20}Br_2O^+$ $[M]^+$ 385.9811, found 385.9866.

[Note: The following assignments of **7c**, **S4c**, **S5c**, and **6c** were used by ^{1}H NMR analysis. δ 4.03 (dd, J = 12.4, 4.1 Hz, 1H, C(2)H_{axial} of ***trans*-6c**), δ 4.14 (dd, J = 11.4, 1.6 Hz, 1H of **S5c**), δ 4.22 (dd, J = 10.4, 4.4 Hz, 1H of ***exo*-7c**), δ 4.26 (dd, J = 9.4, 6.4 Hz, 1H of ***endo*-7c**, δ 4.31 (dd, J = 10.8, 2.0 Hz, 1H of **S4c**).)

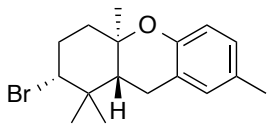


(2*R*,4a*R*,9a*R*)-2-Bromo-7-methoxy-1,1,4a-trimethyl-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene

(6d): Pale yellow solid; $[\alpha]^{27}_D$ 44.0 (*c* 0.85, $CHCl_3$) for 67% ee (*trans/cis* 73:27); HPLC (Daicel Chiralcel AD-3 column × 2, hexane–*i*-PrOH = 1000:1, flow rate = 0.8 mL/min) t_R = 19.5 (major

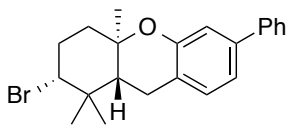
enantiomer), 21.7 (minor enantiomer) min; IR (KBr) 1496, 1260, 1225, 1148, 1123, 1039, cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.69–6.66 (m, 2H), 6.63–6.60 (m, 1H), 4.05 (dd, *J* = 12.8, 4.1 Hz, 1H, $C(2)H_{axial}$), 3.75 (s, 3H), 2.81–2.67 (m, 2H), 2.28 (dddd, *J* = 13.8, 4.1, 3.7, 3.7 Hz, 1H), 2.13 (dddd, *J* = 13.8, 13.8, 12.8, 3.7 Hz, 1H), 1.98 (ddd, *J* = 13.3, 3.7, 3.7 Hz, 1H), 1.80 (dd, *J* = 11.5, 6.4 Hz, 1H), 1.76 (ddd, *J* = 13.8, 13.3, 3.7 Hz, 1H), 1.21 (s, 3H), 1.17 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.2, 146.6, 122.3, 117.5, 114.0, 113.4, 75.4, 66.1, 55.7, 48.1, 40.7, 39.2, 31.5, 29.6, 24.9, 19.7, 16.8; HRMS (FAB+) calcd for $C_{17}H_{23}BrO_2^+$ $[M]^+$ 338.0881, found 338.0892.

[Note: The following assignments of **7d**, **S4d**, **S5d**, and **6d** were used by ^1H NMR analysis. δ 4.05 (dd, *J* = 12.8, 4.1 Hz, 1H, $C(2)H_{axial}$ of ***trans*-6d**), δ 4.13 (dd, *J* = 14.4, 7.2 Hz, 1H of **S5d**), δ 4.21 (dd, *J* = 11.0, 4.1 Hz, 1H of ***exo*-7d**), δ 4.26 (dd, *J* = 9.6, 6.0 Hz, 1H of ***endo*-7d**), δ 4.34 (dd, *J* = 9.2, 6.0 Hz, 1H of **S4d**).]



(2*R*,4a*R*,9a*R*)-2-Bromo-1,1,4a,7-tetramethyl-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene (6e): Pale yellow solid; $[\alpha]^{27}_D$ 45.0 (*c* 0.95, $CHCl_3$) for 67% ee (*trans/cis* 73:27); HPLC (Daicel Chiralpack IB-3 column, hexane–*i*-PrOH = 1000:1, flow rate = 0.8 mL/min) t_R = 13.7 (minor enantiomer), 15.9 (major enantiomer) min; IR (KBr) 1489, 1378, 1241, 1151 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.89 (d, *J* = 7.8 Hz, 1H), 6.88 (s, 1H), 6.65 (d, *J* = 7.8 Hz, 1H), 4.05 (dd, *J* = 12.4, 3.7 Hz, 1H, $C(2)H_{axial}$), 2.83–2.64 (m, 2H), 2.27 (dddd, *J* = 13.8, 4.1, 3.7, 3.7 Hz, 1H), 2.25 (s, 3H), 2.11 (dddd, *J* = 13.8, 13.8, 12.4, 3.7 Hz, 1H), 1.99 (ddd, *J* = 13.3, 3.7, 3.7 Hz, 1H), 1.79 (dd, *J* = 11.5, 6.0 Hz, 1H), 1.77 (ddd, *J* = 13.8, 13.3, 4.1 Hz, 1H), 1.22 (s, 3H), 1.16 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.3, 129.9, 129.2, 128.0, 121.3, 116.7, 75.6, 66.1, 48.2, 40.7, 39.2, 31.5, 29.6, 24.5, 20.5, 19.7, 16.9; HRMS (FAB+) calcd for $C_{17}H_{23}BrO^+$ $[M]^+$ 322.0932, found 322.0937.

[Note: The following assignments of **7e**, **S4e**, **S5e**, and **6e** were used by ^1H NMR analysis. δ 4.05 (dd, *J* = 12.4, 3.7 Hz, 1H, $C(2)H_{axial}$ of ***trans*-6e**), δ 4.13 (dd, *J* = 14.4, 7.2 Hz, 1H of **S5e**), δ 4.23 (dd, *J* = 11.4, 4.0 Hz, 1H of ***exo*-7e**), δ 4.28 (dd, *J* = 9.8, 6.4 Hz, 1H of ***endo*-7e**), δ 4.33 (dd, *J* = 8.4, 2.8 Hz, 1H of **S4e**).]

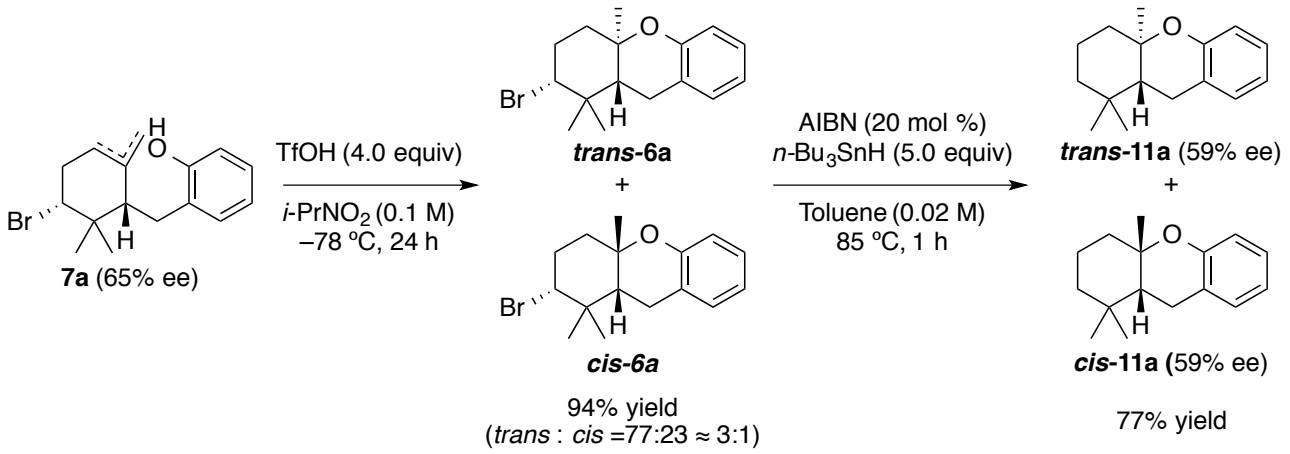


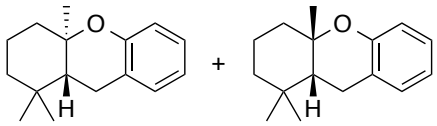
(2*R*,4a*R*,9a*R*)-2-Bromo-1,1,4a-trimethyl-6-phenyl-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene

(6f): Colorless solid; $[\alpha]^{27}_{D}$ 48.9 (*c* 0.95, $CHCl_3$) for 65% ee (*trans/cis* 76:24); HPLC (Daicel Chiralcel AD-3 column, hexane–*i*-PrOH = 1000:1, flow rate = 1.0 mL/min) t_R = 26.6 (major enantiomer), 40.0 (minor enantiomer) min; IR (KBr) 1483, 1305, 1149, 910 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.8, 1.4 Hz, 2H), 7.41 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.31 (t, *J* = 7.8 Hz, 1H), 7.10 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.02 (d, *J* = 1.8 Hz, 1H), 4.07 (dd, *J* = 12.6, 4.2 Hz, 1H, $C(2)H_{axial}$), 2.88–2.73 (m, 2H), 2.30 (dddd, *J* = 13.7, 4.2, 4.1, 3.6 Hz, 1H), 2.16 (dddd, *J* = 12.7, 12.6, 12.8, 3.7 Hz, 1H), 2.04 (ddd, *J* = 13.3, 3.6, 3.7 Hz, 1H), 1.86 (dd, *J* = 12.4, 6.0 Hz, 1H), 1.83 (ddd, *J* = 13.3, 12.8, 4.1 Hz, 1H), 1.28 (s, 3H), 1.19 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 140.7, 140.6, 129.9, 128.6 (2C), 127.1, 126.9 (2C), 120.8, 118.9, 115.5, 76.0, 65.9, 48.1, 40.7, 39.2, 31.5, 29.6, 24.6, 19.9, 16.9; HRMS (ESI+) calcd for $C_{22}H_{25}BrNaO^+$ $[M+Na]^+$ 407.0981, found 407.0981.

[Note: The following assignments were used by ^1H NMR analysis. δ 4.07 (dd, *J* = 12.6, 4.2 Hz, 1H, $C(2)H_{axial}$ of ***trans*-6f**), δ 4.16 (dd, *J* = 12.0, 2.0 Hz, 1H of **S5f**), δ 4.24 (dd, *J* = 10.6, 4.4 Hz, 1H of ***exo*-7f**), δ 4.28 (dd, *J* = 9.8, 6.4 Hz, 1H of ***endo*-7f**), δ 4.34 (dd, *J* = 9.8, 2.8 Hz, 1H of **S4f**).]

Determination of Absolute Configuration



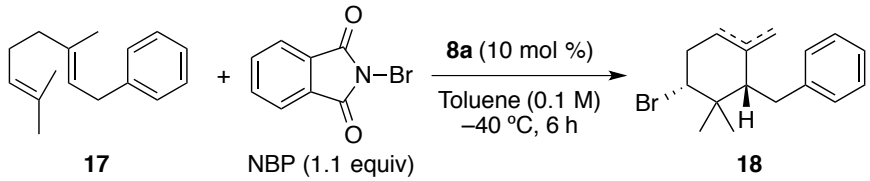


(4a*R*,9a*R*)-1,1,4a-Trimethyl-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene (*trans*-10a) and **(4a*S*,9a*R*)-1,1,4a-Trimethyl-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene (*cis*-10a):** To a solution of the mixture of *endo*- and *exo*-isomeric A-ring products **7a** (33.9 mg, 0.11 mmol) in *i*-$PrNO_2$ (1.1 mL) was added TfOH (21 μL, 0.24 mmol, 4.0 equiv) at –78 °C. After stirring at –78 °C for 24 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with Et_2O (5 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The diastereomeric ratio (*trans/cis* = 75:25) was determined by ^{1}H NMR analysis of the crude mixture. The residue was purified by preparative TLC (hexane–EtOAc = 20:1) to give **6a** (31.9 mg, 94% yield) as a mixture of *cis*-, and *trans*-isomer. The diastereomeric ratio (*trans/cis* = 77:23) was determined by ^{1}H NMR analysis.

To a solution of **6a** (31.9 mg, 0.10 mmol) in toluene (5 mL) were added AIBN (3.2 mg, 0.02 mmol, 20 mol %) and 1.0 M cyclohexane solution of tributyltin hydride (500 μL, 0.5 mmol, 5.0 equiv) at ambient temperature. The mixture was stirred for 1 h under reflux condition. After the stirring, the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane only) to give **11a** (17.8 mg, 77% yield) as a mixture of *cis*-, and *trans*-isomer. Compounds ***trans*-11a** and ***cis*-11a** could not be separated by column chromatography on silica gel. The absolute configuration of ***trans*-11a** was determined assigned to be (4a*R*,9a*R*) by comparing the reported retention time of HPLC.[3]; Spectral data of ^{1}H NMR and ^{13}C NMR of the mixture of *cis*-, and *trans*-isomer were identical to previously reported data.[3]; HPLC (Daicel Chiralcel OD3 column × 2, hexane, flow rate = 0.3 mL/min) t_R = 28.0 (minor enantiomer of ***cis*-11a**) min, 37.6 (major enantiomer of ***cis*-11a**) min, 43.0 (major enantiomer of ***trans*-11a**) min, 77.2 (minor enantiomer of ***trans*-11a**) min.

Procedure for Control Experiment with 17 or 19

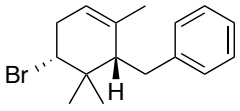
Control Experiment with **17**



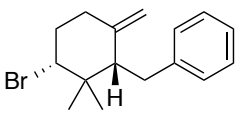
17 NBP (1.1 equiv) **18**

To a solution of **8a** (11 mg, 0.01 mmol, 10 mol %) in toluene (1.0 mL) were added **17** (21.4 mg, 0.10 mmol) and NBP (24.9 mg, 0.11 mmol, 1.1 equiv) and successively at –78 °C, and the mixture was stirred at –78 °C for 0.5 h and then at –40 °C for 6 h. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (3.0 mL) and extracted with hexane (5.0 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel using (hexane–EtOAc 1000:1) as an eluent. The yield of *endo*-**18** and *exo*-**18** (87%) was determined by ^{1}H NMR analysis of the crude mixture using tetrachloroethane (5.2 μL, 0.050 mmol, 0.5 equiv) as an internal standard. The ee of *endo*-**18** and *exo*-**18** mixture was determined by HPLC analysis (Daicel Chiralpack IB-3 column, hexane, flow rate = 1.0 mL/min) t_R= 7.1, 10.8 min.

The corresponding physical and spectroscopic data for *endo*-**18** and *exo*-**18** are as follows.

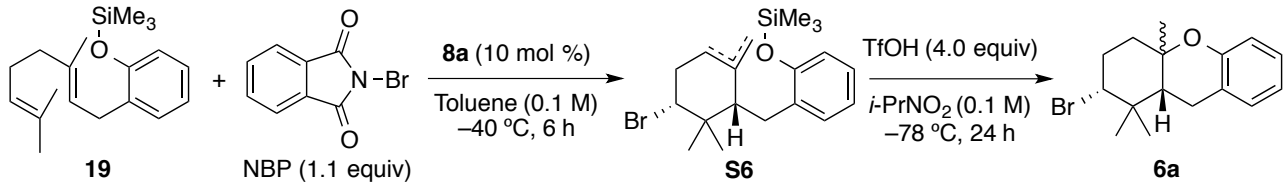


5-Bromo-2,6,6-trimethylcyclohex-2-en-1-yl)methyl)benzene (*endo*-18): IR (neat) 1649, 1604, 1496, 1453, 1389, 1369, 1225, 1206, 1146 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.13 (m, 5H), 5.20 (brs, 1H), 4.27 (dd, *J* = 9.6, 6.4 Hz, 1H), 3.09 (d, *J* = 14.7 Hz, 1H), 2.62–2.46 (m, 4H), 1.45 (s, 3H), 1.25 (s, 3H), 1.01 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.0, 141.6, 128.5 (2C), 128.2 (2C), 125.6, 110.7, 67.1, 53.4, 42.0, 37.1, 35.8, 32.8, 28.7, 16.9; HRMS (FAB+) calcd for $C_{16}H_{21}Br^+$ $[M]^+$ 292.0827, found 292.0826.



3-Bromo-2,2-dimethyl-6-methylenecyclohexyl)methyl)benzene (*exo*-18): IR (neat) 1603, 1496, 1453, 1388, 1368 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28–7.22 (m, 2H), 7.19–7.12 (m, 3H), 4.87 (s, 1H) 4.67 (s, 1H), 4,22 (dd, *J* = 11.4, 4.6 Hz, 1H), 3.04 (dd, *J* = 15.2, 2.3 Hz, 1H), 2.85 (dd, *J* = 15.2, 10.6 Hz, 1H), 2.36–2.25 (m, 3H), 2.16–2.02 (m, 2H), 1.28 (s, 3H), 0.98 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.2, 137.0, 128.4 (2C), 128.3 (2C), 125.7, 120.6, 64.9, 51.2, 38.9, 35.7, 35.3, 28.7, 23.2, 16.0; HRMS (FAB+) calcd for $C_{16}H_{21}Br^+$ $[M]^+$ 292.0827, found 292.0842.

Control Experiment with **19**



To a solution of **8a** (11 mg, 0.01 mmol) in toluene (1.0 mL) were added NBP (24.9 mg, 0.11 mmol) and **19** (30.3 mg, 0.10 mmol) successively at –78 °C, and the mixture was stirred at –78 °C for 0.5 h and then at –40 °C for 6 h. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (3.0 mL) and extracted with hexane (5.0 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The yield (64%) was determined by ^{1}H NMR analysis of the crude mixture using tetrachloroethane (5.2 μL, 0.050 mmol, 0.5 equiv) as an internal standard. The crude product was purified by column chromatography on silica gel using (hexane–EtOAc 20:1) as an eluent to give the mixture of *endo*- and *exo*-isomeric A-ring products **S6**.

The resulting mixture of *endo*- and *exo*-isomeric A-ring products **S6** was used for the next cyclization to determine the enantioselectivity. To a solution of the resulting mixture, which were obtained in the above reaction, in *i*-$PrNO_2$ (1.0 mL) was added TfOH (35 μL, 0.4 mmol) at –78 °C. After stirring at –78 °C for 24 h, the reaction mixture was quenched with saturated aqueous $NaHCO_3$, and extracted with Et_2O (5 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The diastereomeric ratio (*trans/cis* = 75 : 25) was determined by ^{1}H NMR analysis of the crude mixture. The crude mixture was purified by preparative TLC using (hexane–EtOAc = 20:1) as an eluent to give **6a** as a mixture of *cis*-, and *trans*-isomer. The ee of mixture of *cis*-, and *trans*-isomer **6a** was determined by HPLC analysis.

Author Information

Corresponding Authors

*E-mail: ishihara@cc.nagoya-u.ac.jp

*E-mail: sakakura@okayama-u.ac.jp

Present Address

[§](H.N.) Graduate School of Science and Technology, Kwansei Gakuin University.

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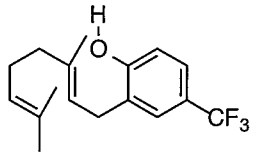
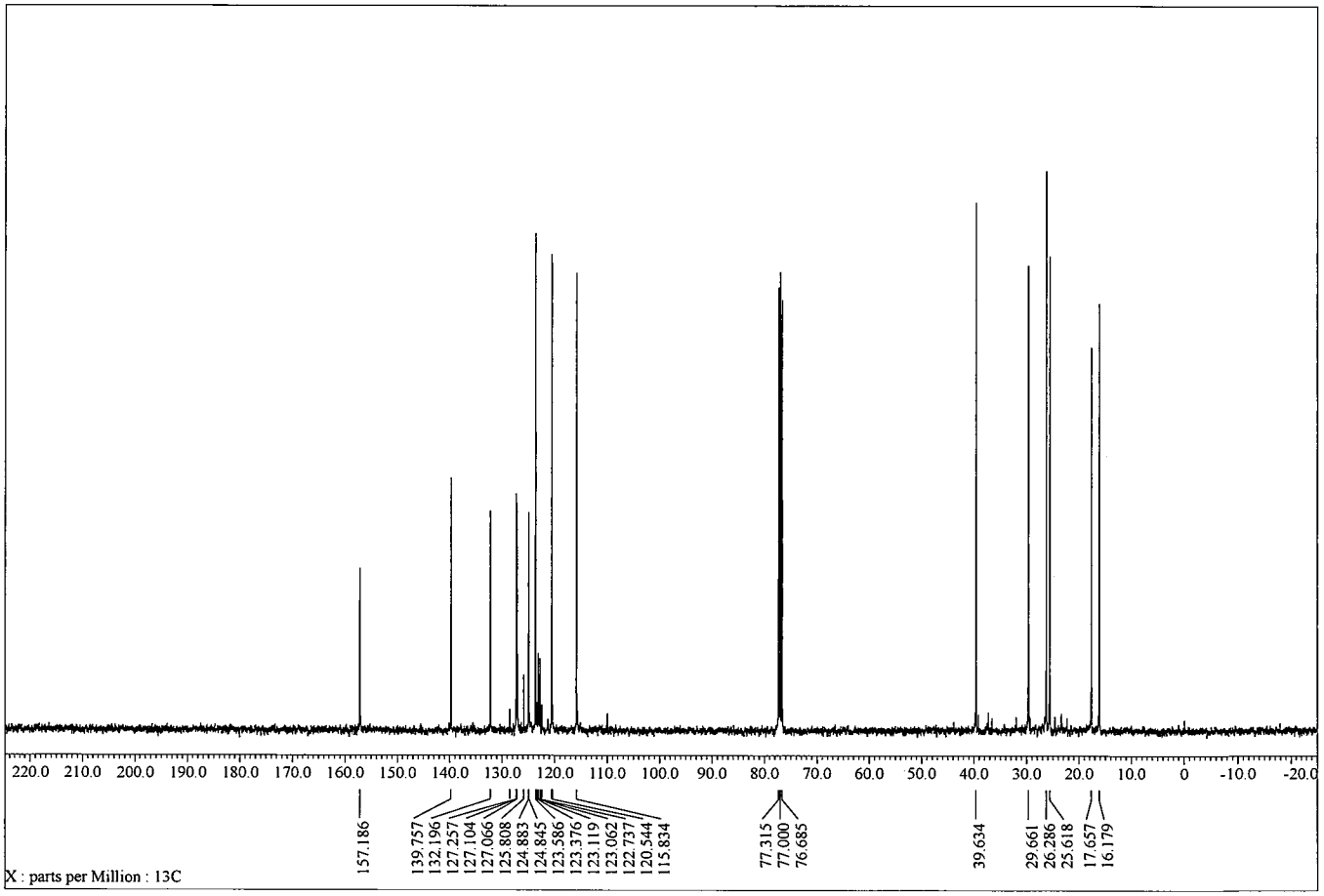
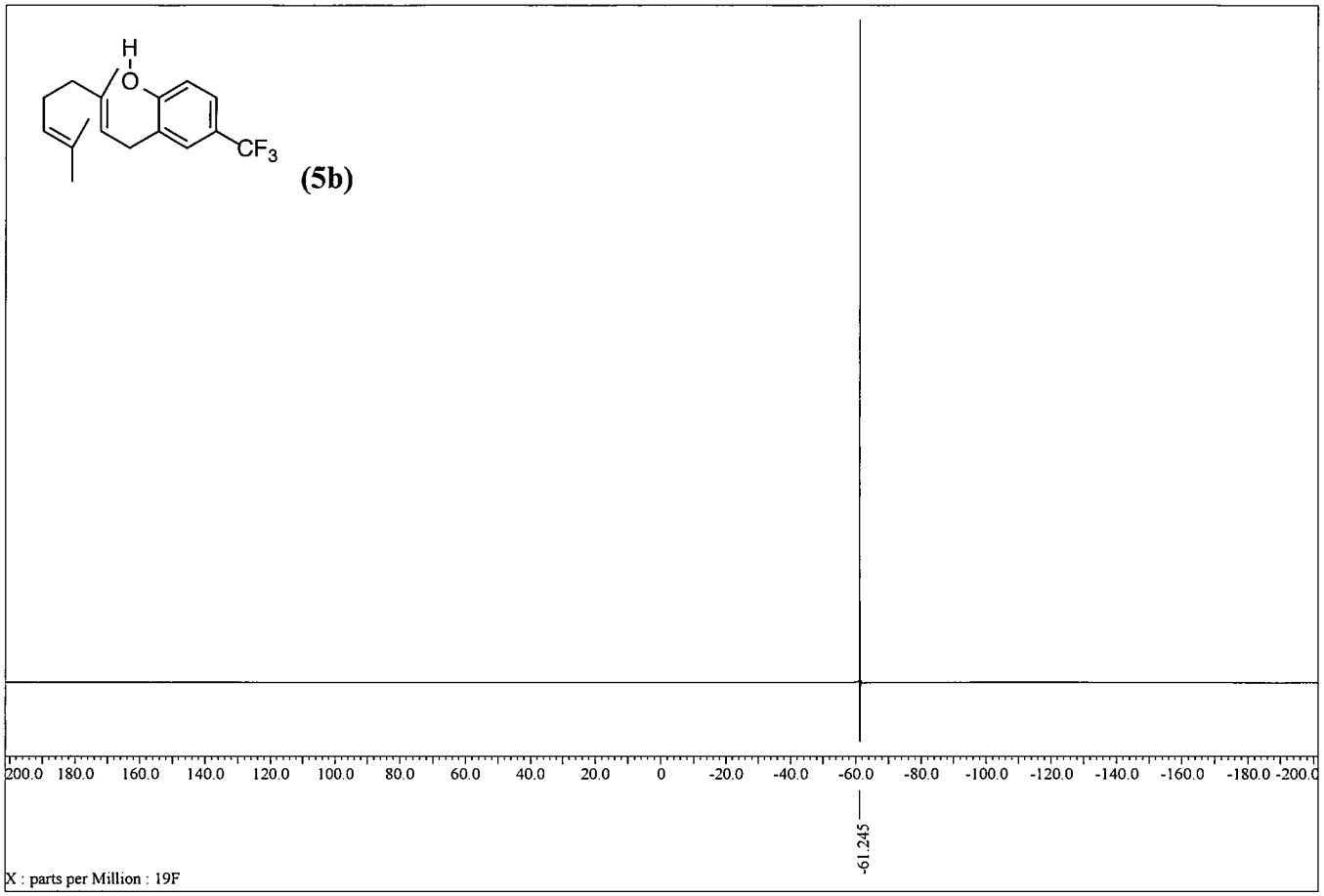
^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR Charts



(5b)

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O
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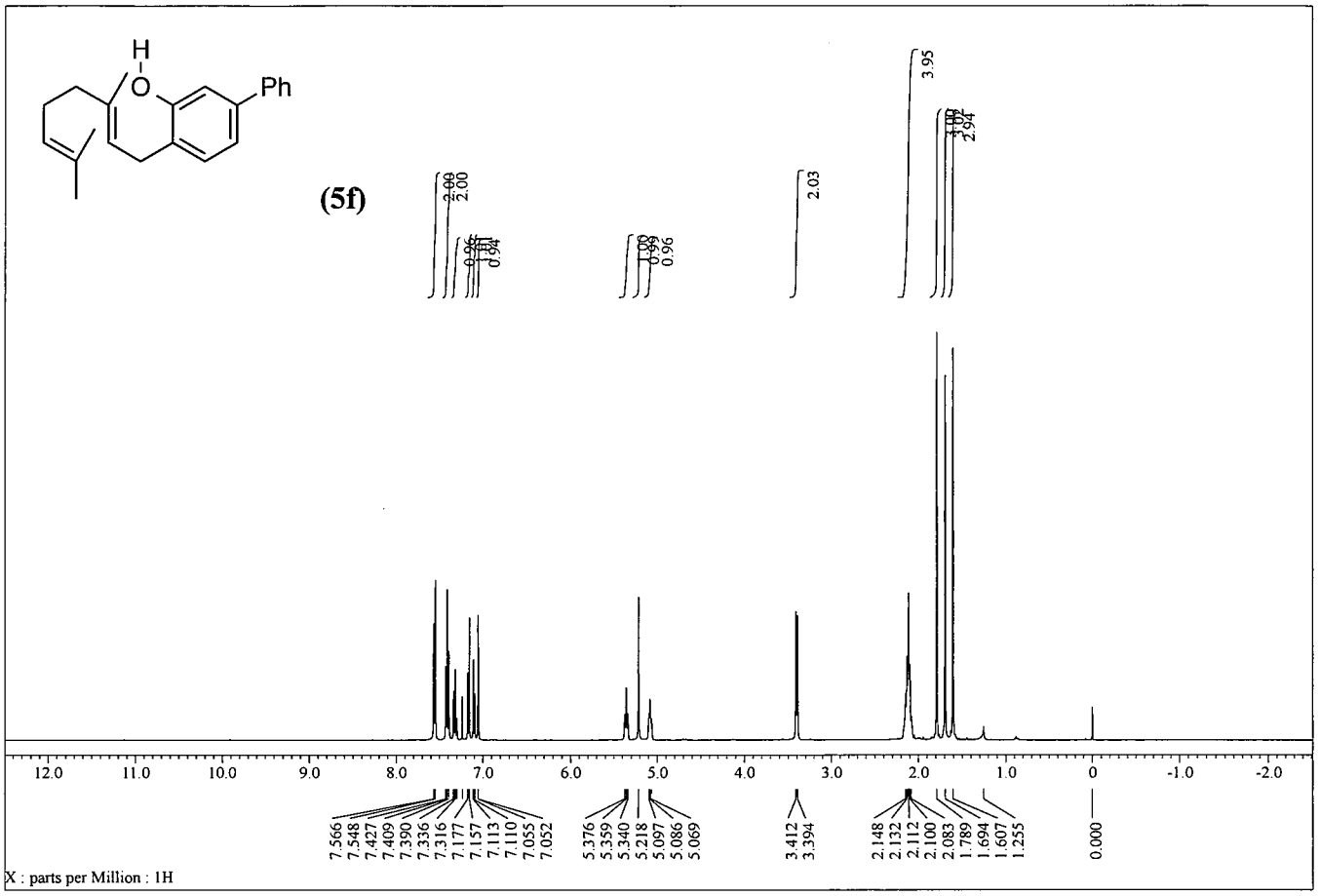
-61.245
X : parts per Million : 19F

(5b)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O
Ph
(5f)
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8.0
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5.0
4.0
3.0
2.0
1.0
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-2.0
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7.548
7.427
7.409
7.390
7.336
7.316
7.177
7.157
7.113
7.110
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5.069
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3.394
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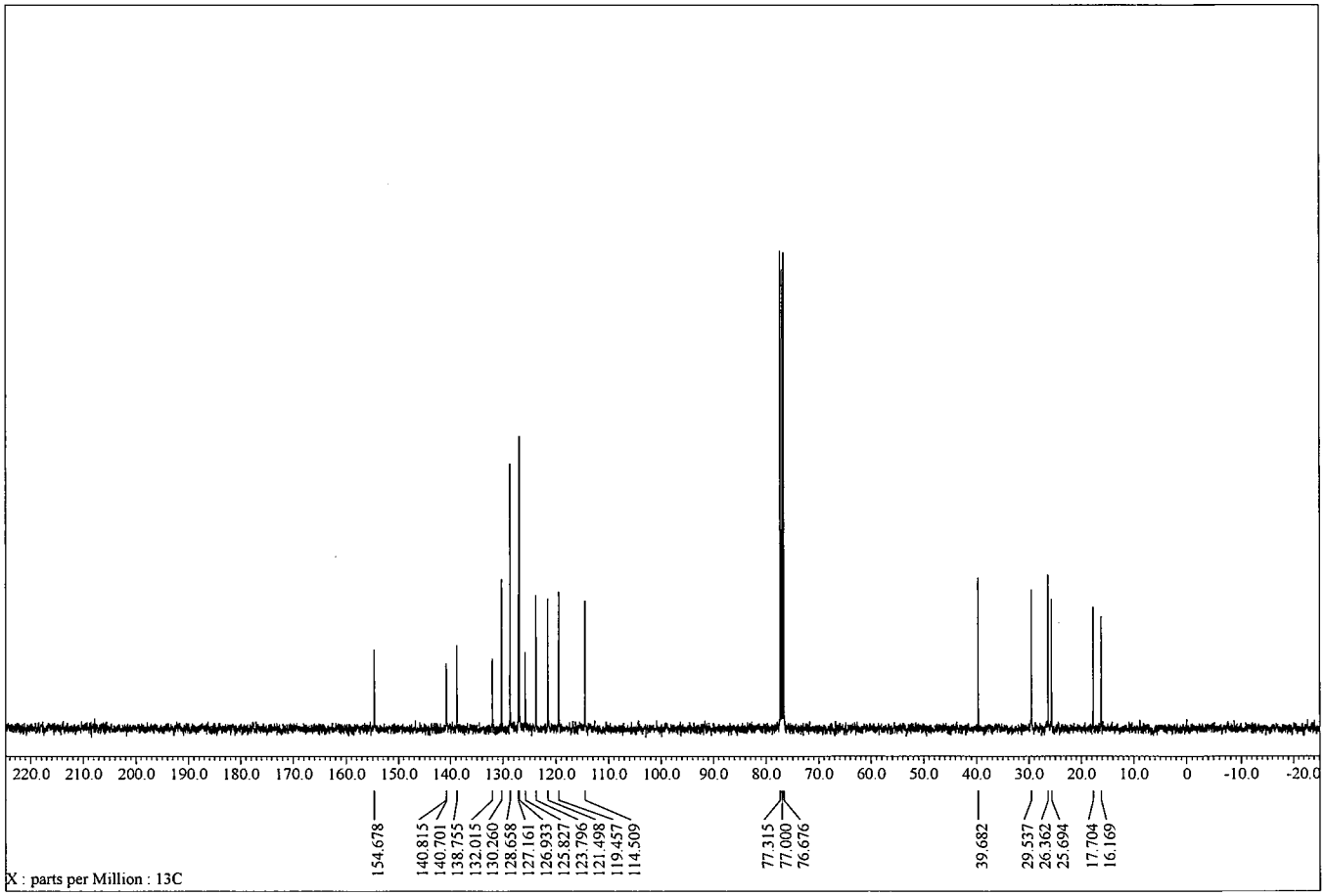
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90.0
80.0
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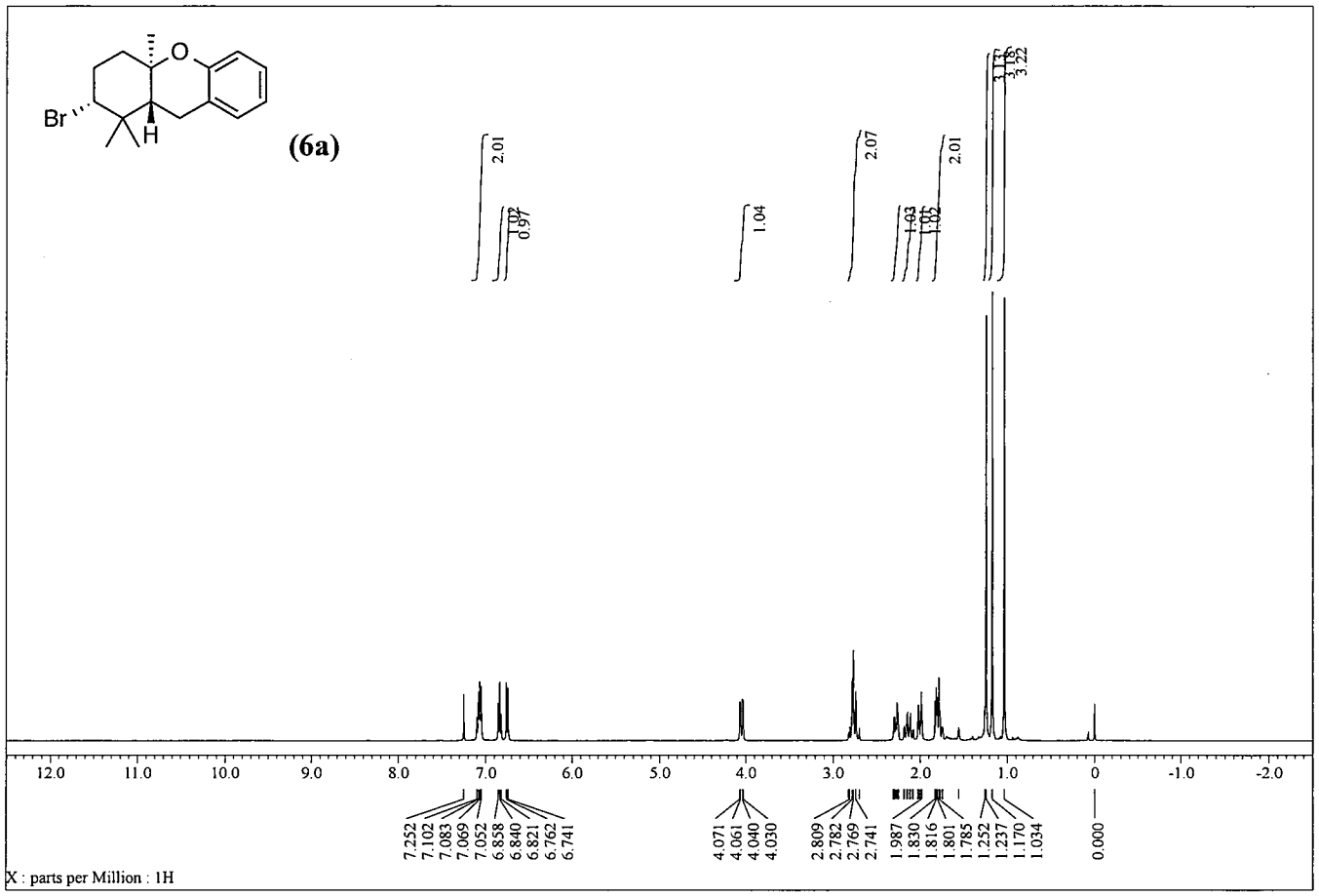
Br
O
H
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0.97
1.04
2.07
2.01
3.22
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.252 7.102 7.083 7.069 7.052 6.858 6.840 6.821 6.762 6.741
4.071 4.061 4.040 4.030
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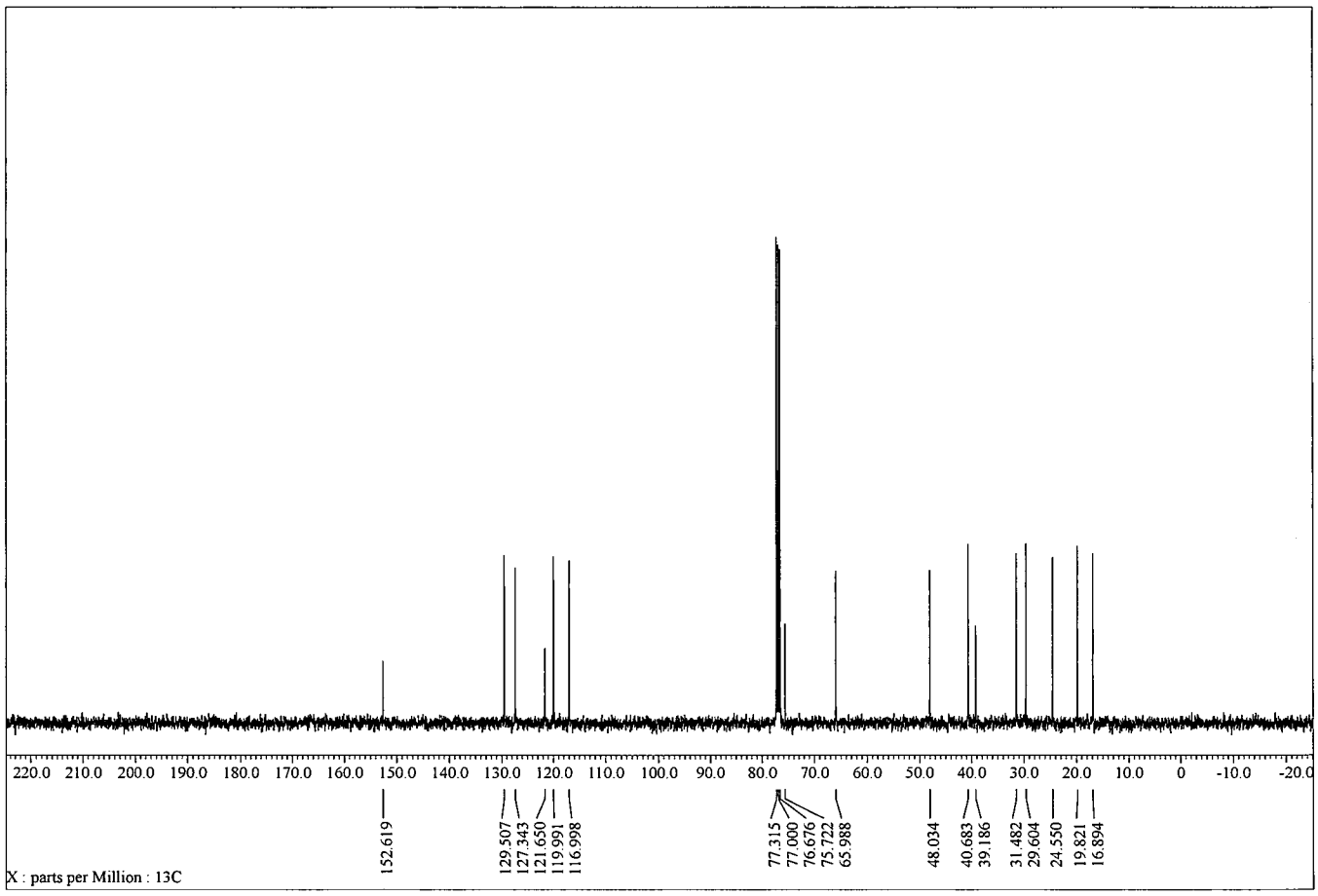
0.000
X : parts per Million : 1H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152.619
129.507 127.343 121.650 119.991 116.998
77.315 77.000 76.676 75.722 65.988
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40.683 39.186
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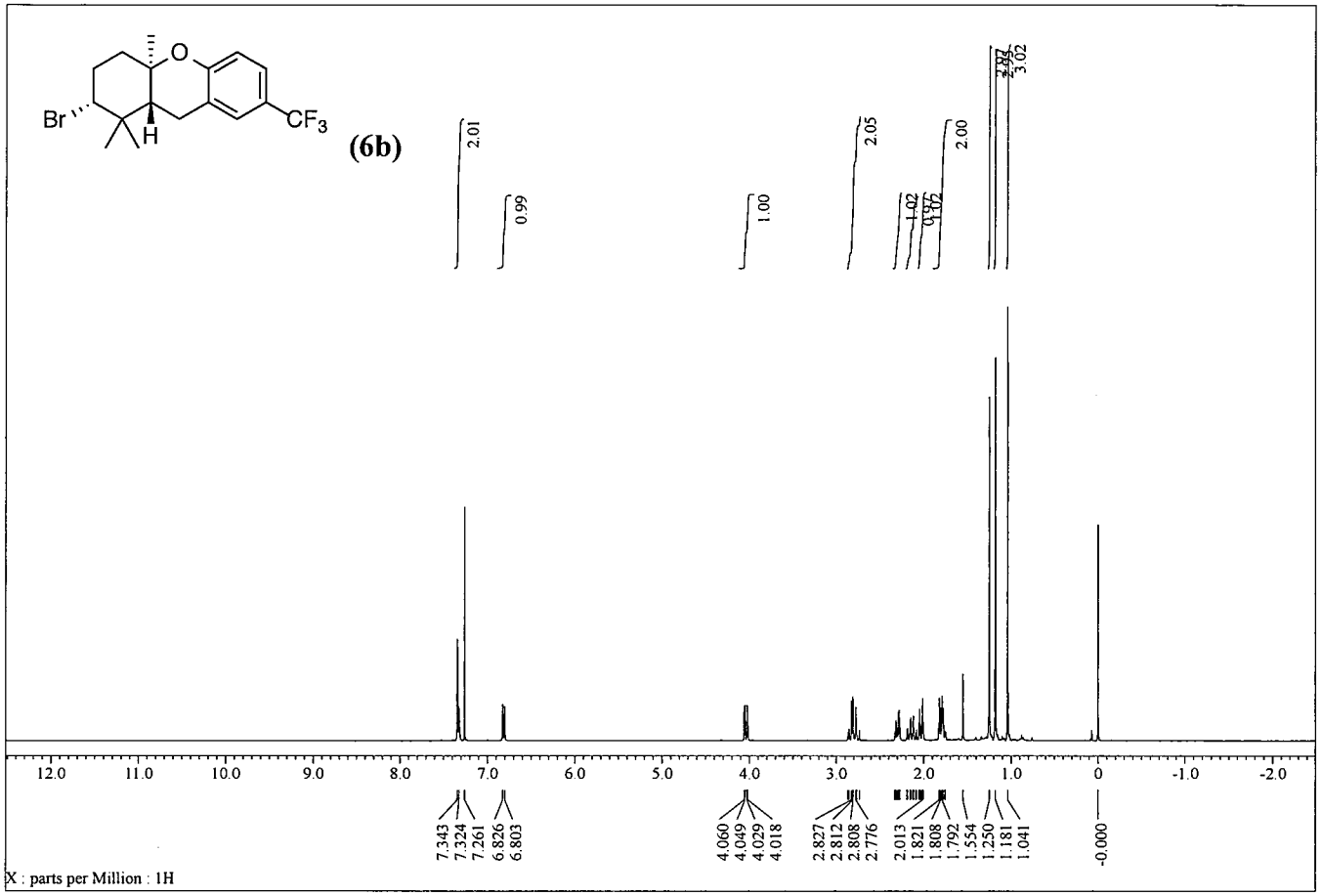
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O
H
CF3
(6b)
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0.99
1.00
2.05
1.02
0.97
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2.00
2.99
3.02
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.343 7.324 7.261 6.826 6.803
4.060 4.049 4.029 4.018
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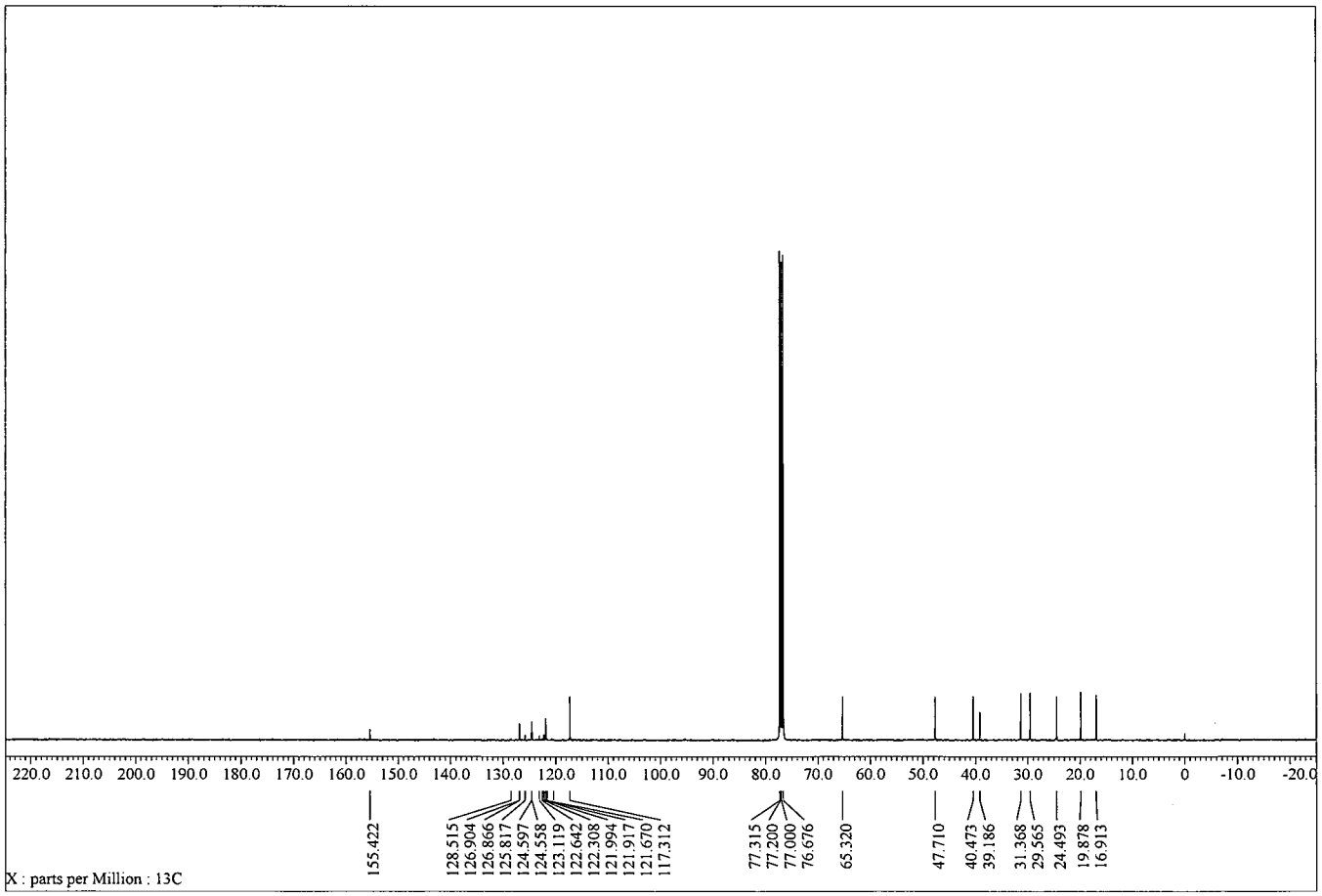
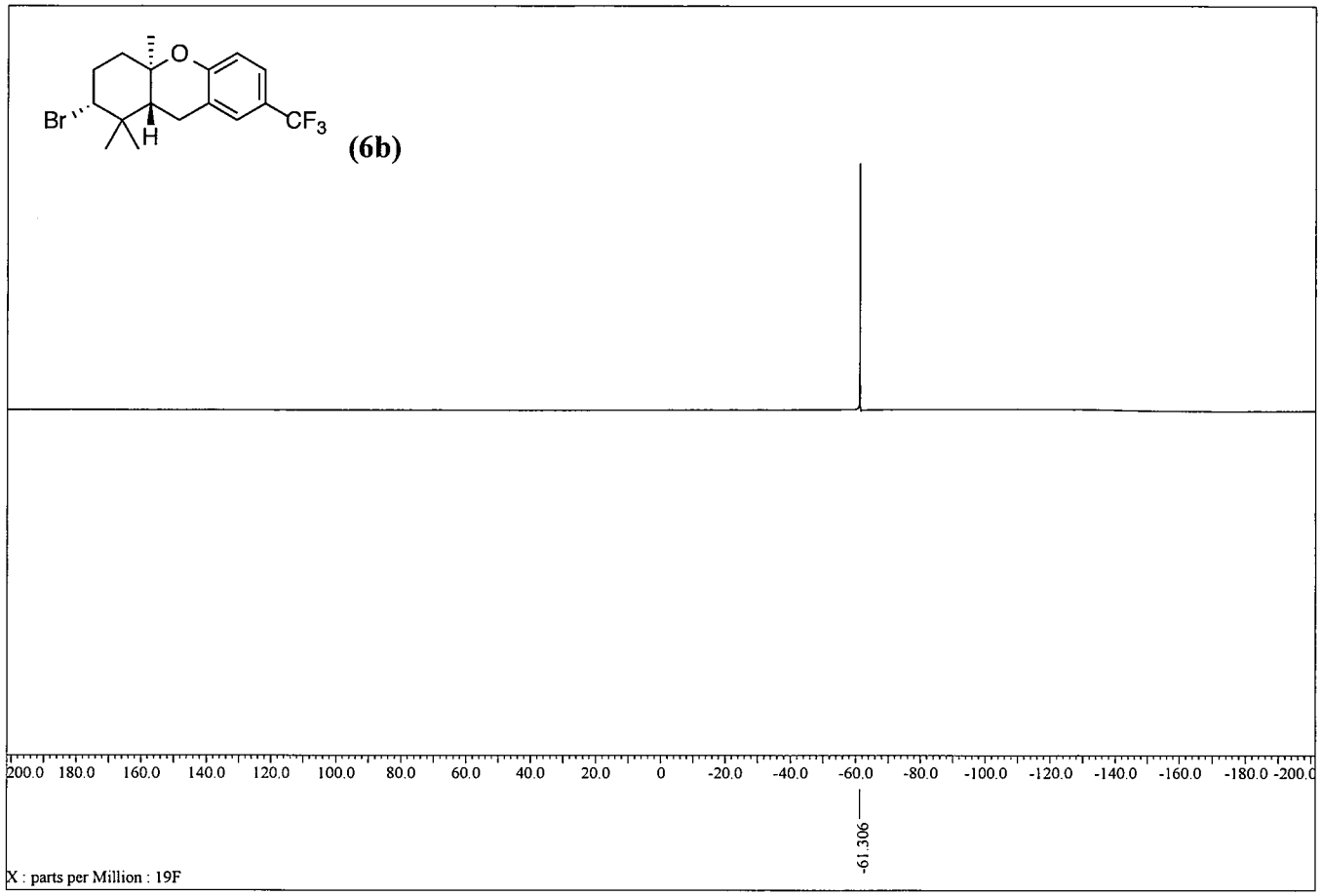
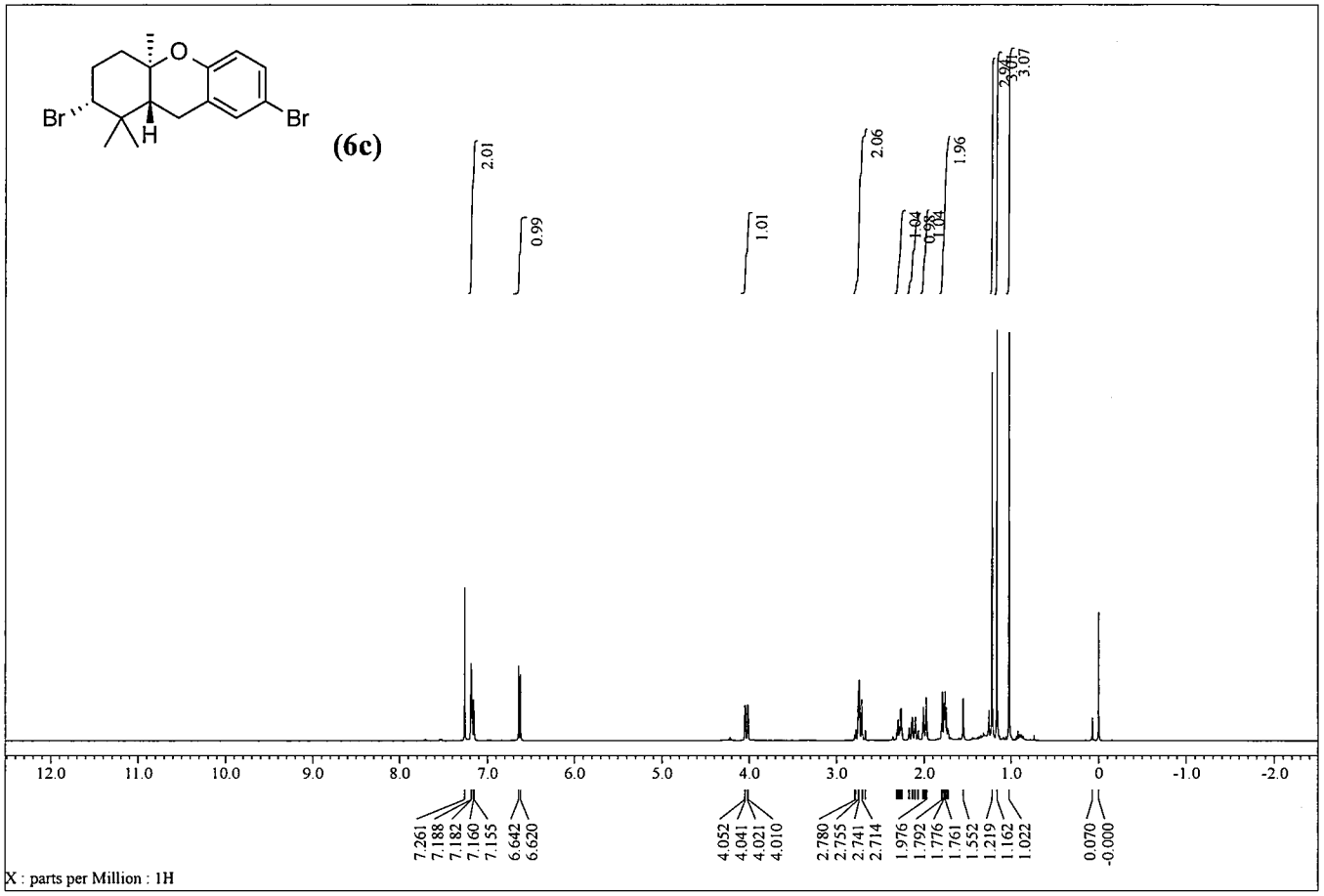
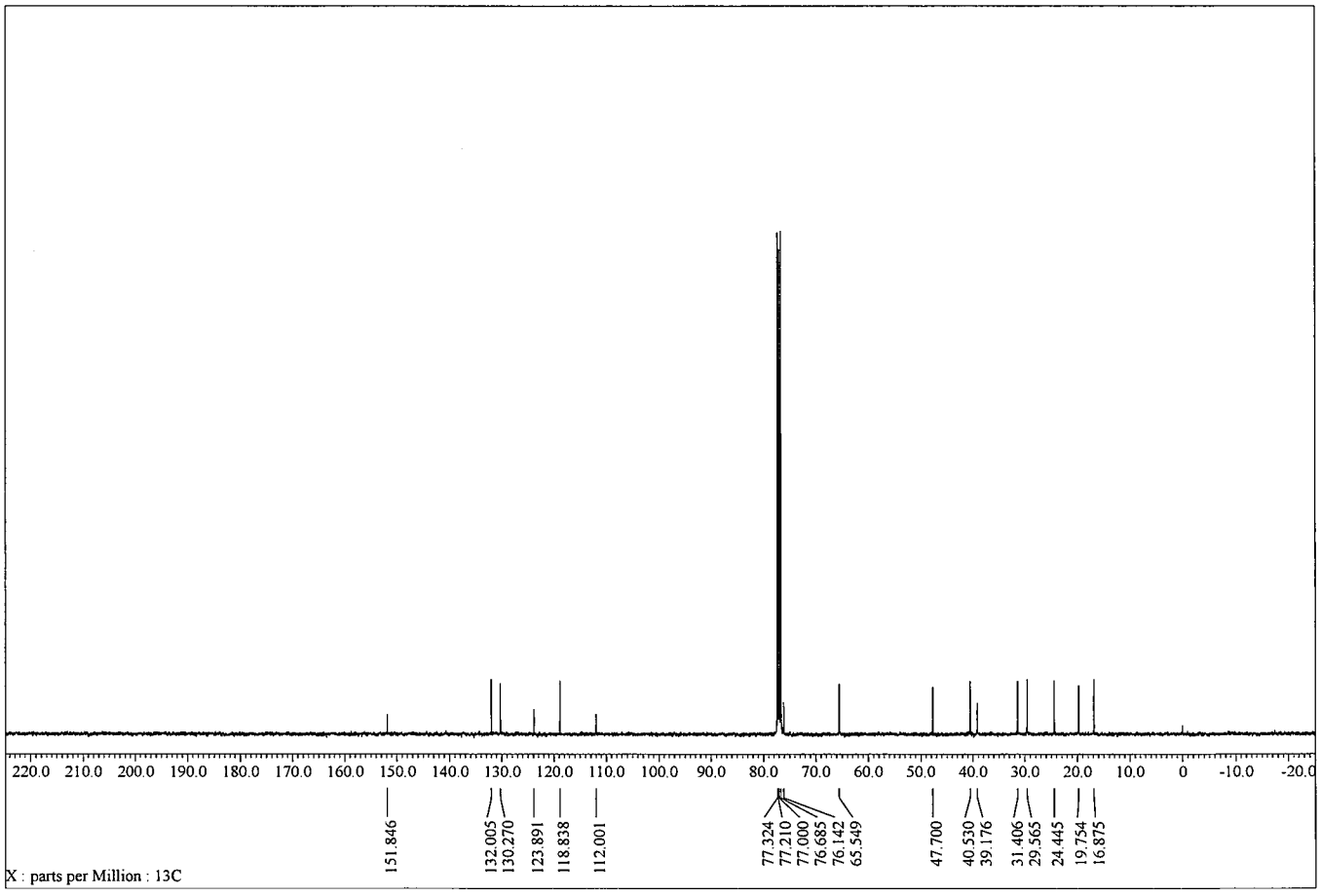
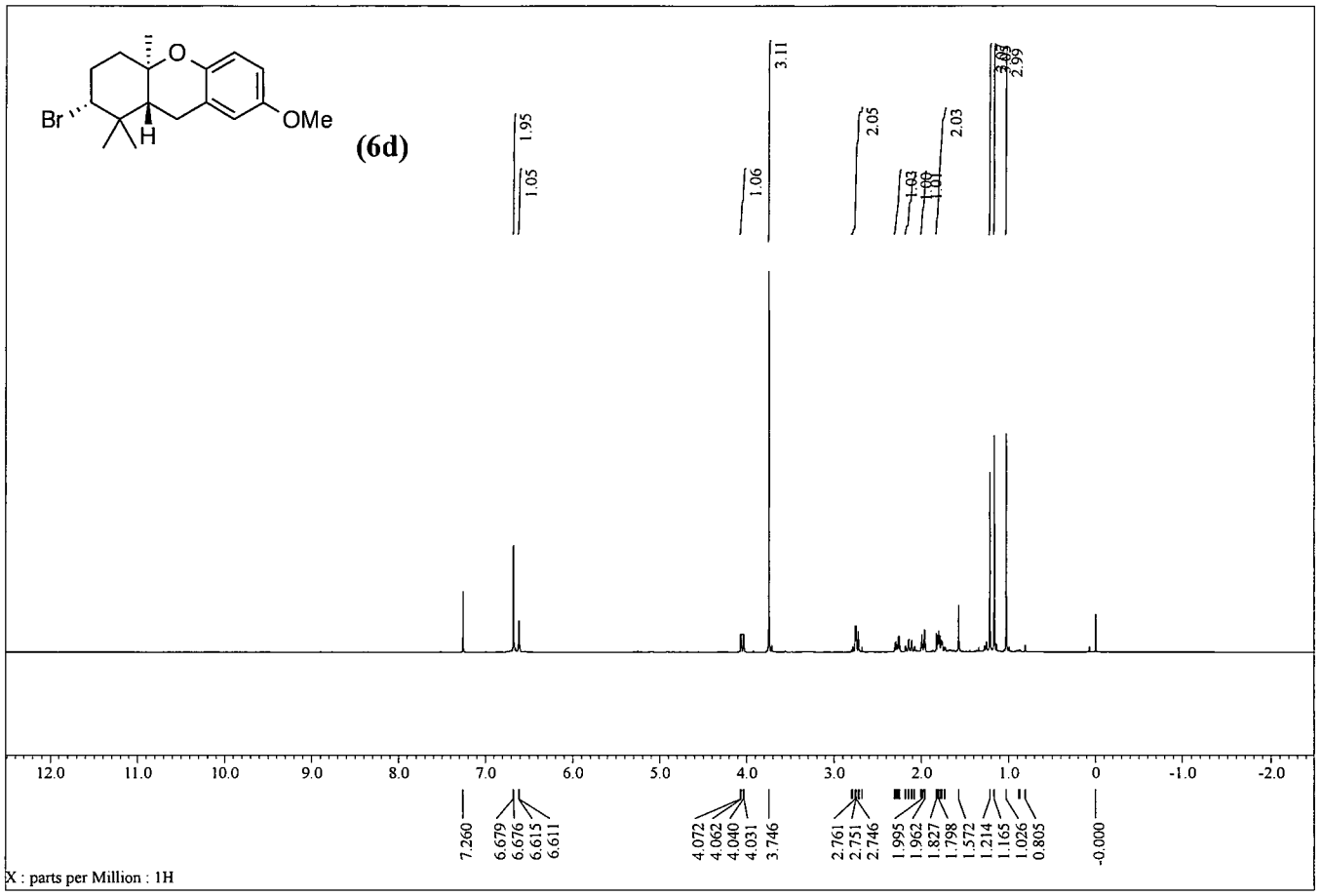
X : parts per Million : 1H

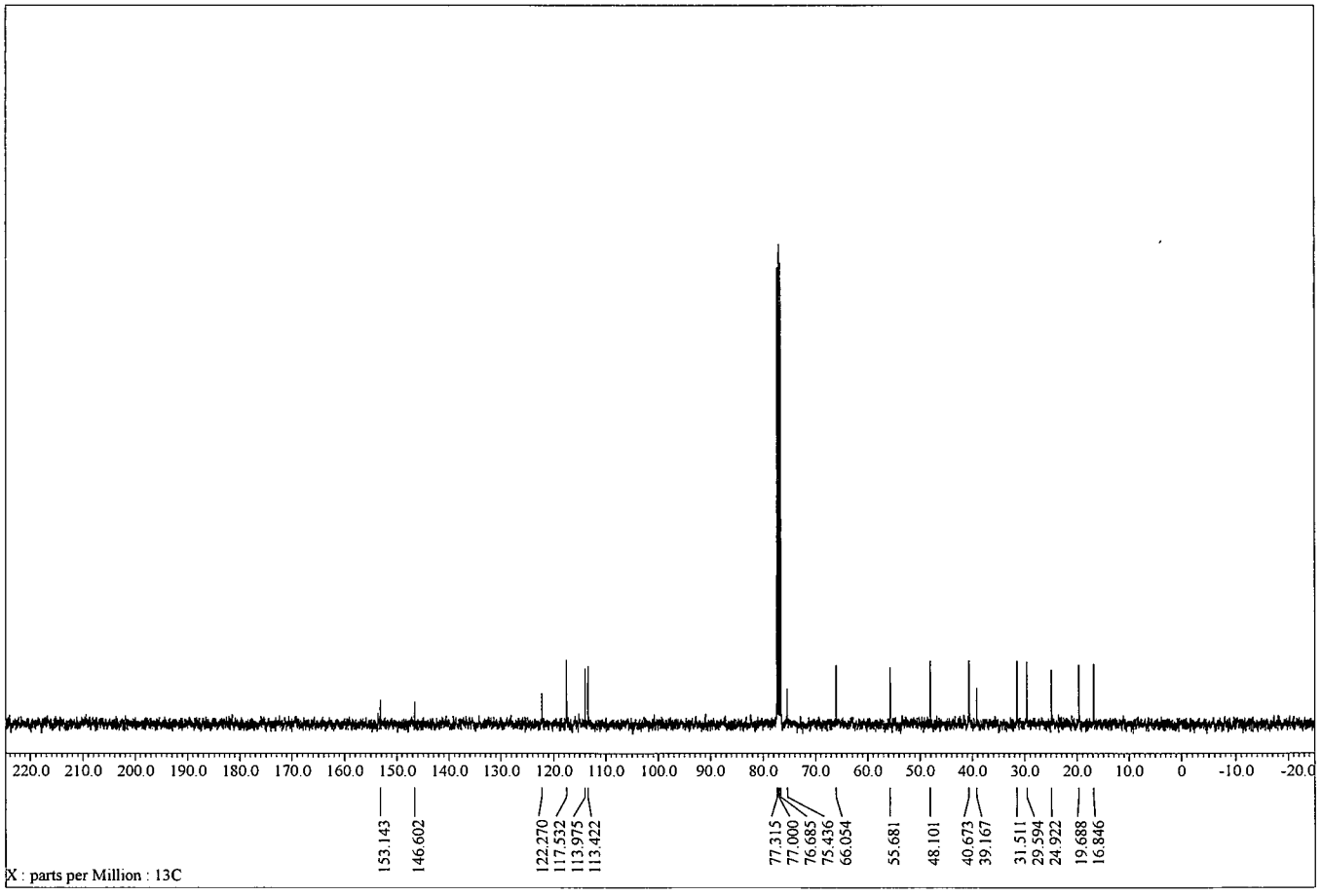

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
155.422
128.515 126.904 126.866 125.817 124.597 124.558 123.119 122.642 122.308 121.994 121.917 121.670 117.312
77.315 77.200 77.000 76.676
65.320
47.710
40.473 39.186
31.368 29.565
24.493
19.878
16.913
X : parts per Million : 13C

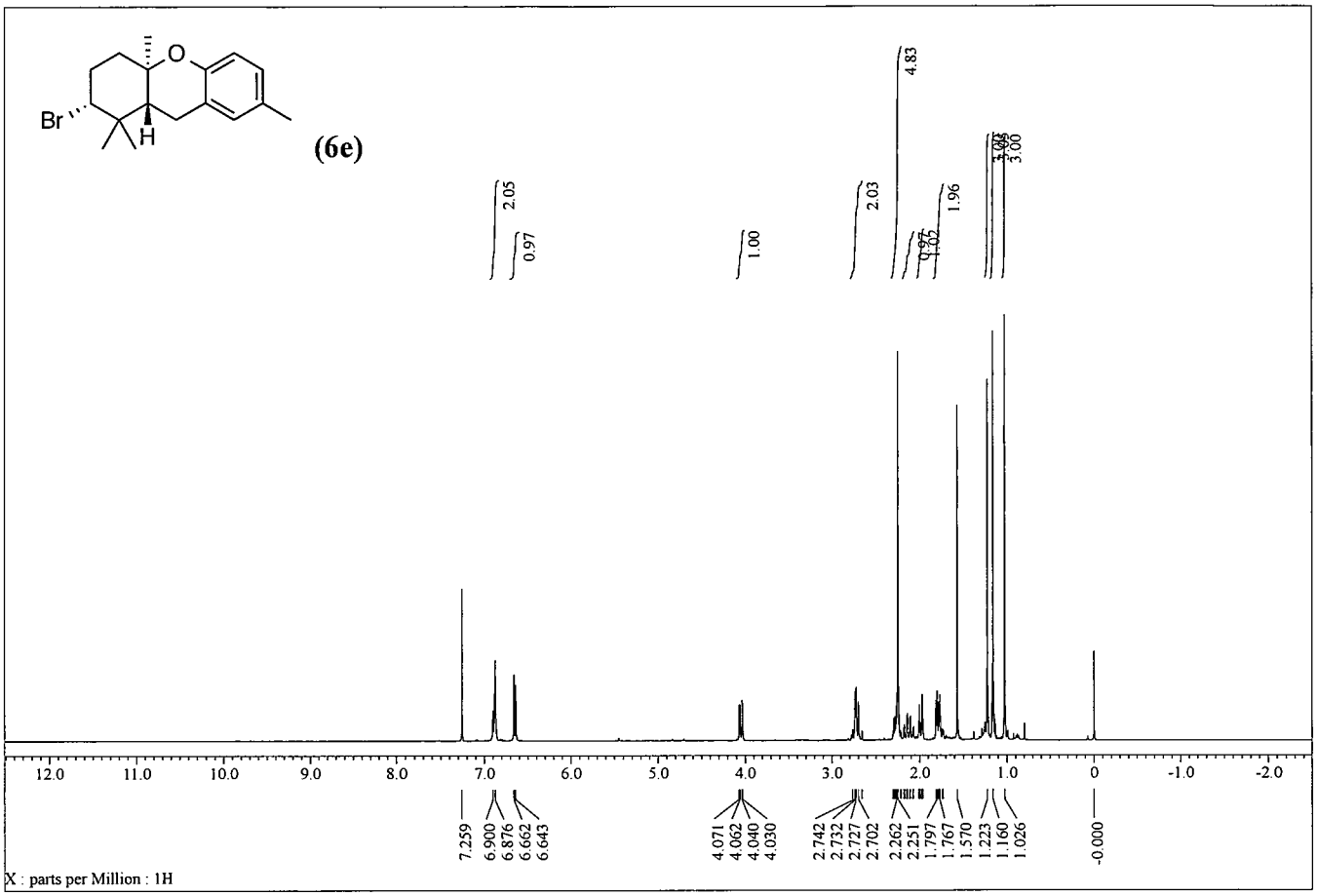

Br
H
O
CF3
(6b)
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
-61.306
X : parts per Million : 19F

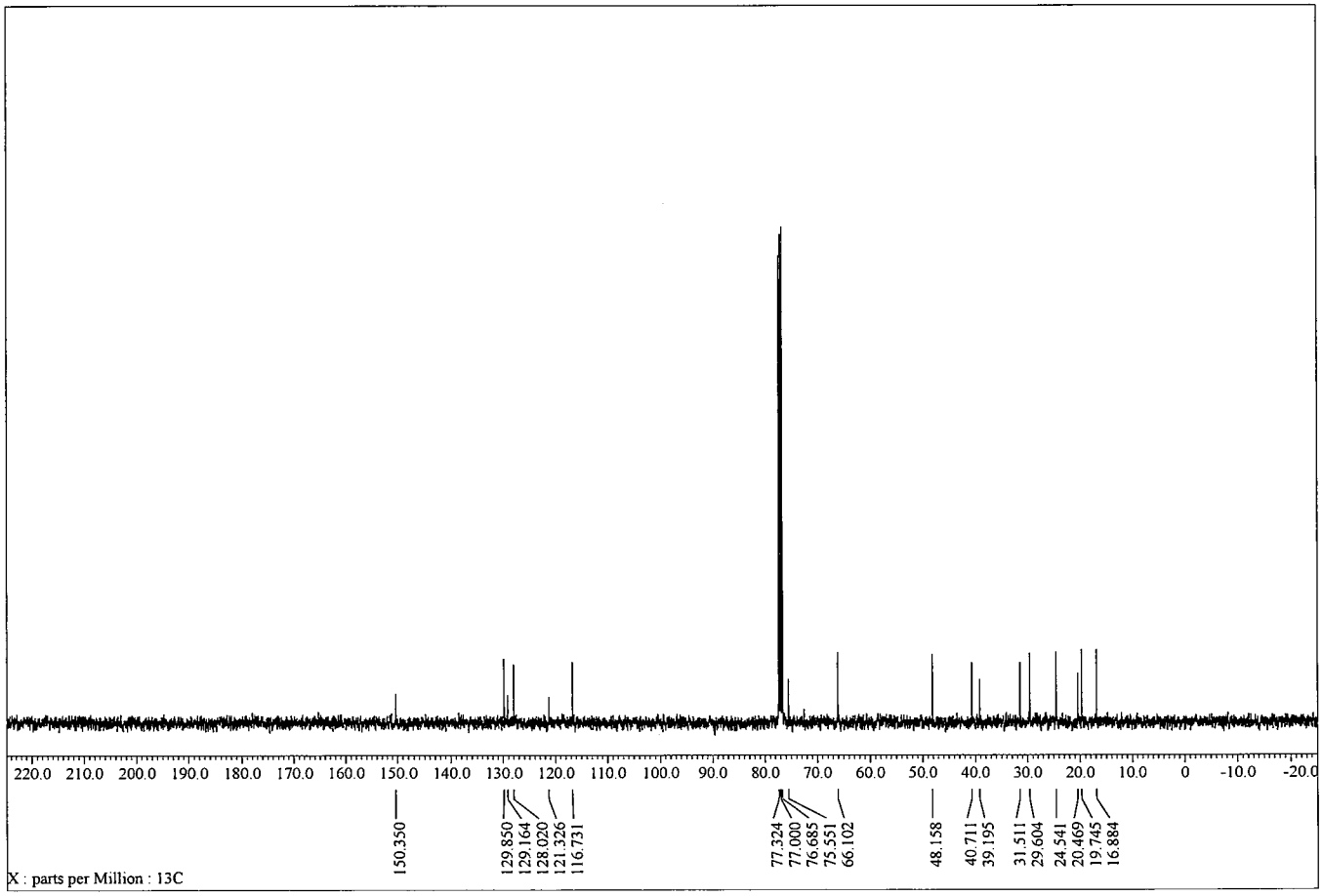

Br
O
H
Br
(6c)
2.01
0.99
1.01
2.06
1.96
3.07
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.261
7.188
7.182
7.160
7.155
6.642
6.620
4.052
4.041
4.021
4.010
2.780
2.755
2.741
2.714
1.976
1.792
1.776
1.761
1.552
1.219
1.162
1.022
0.070
-0.000
X : parts per Million : 1H

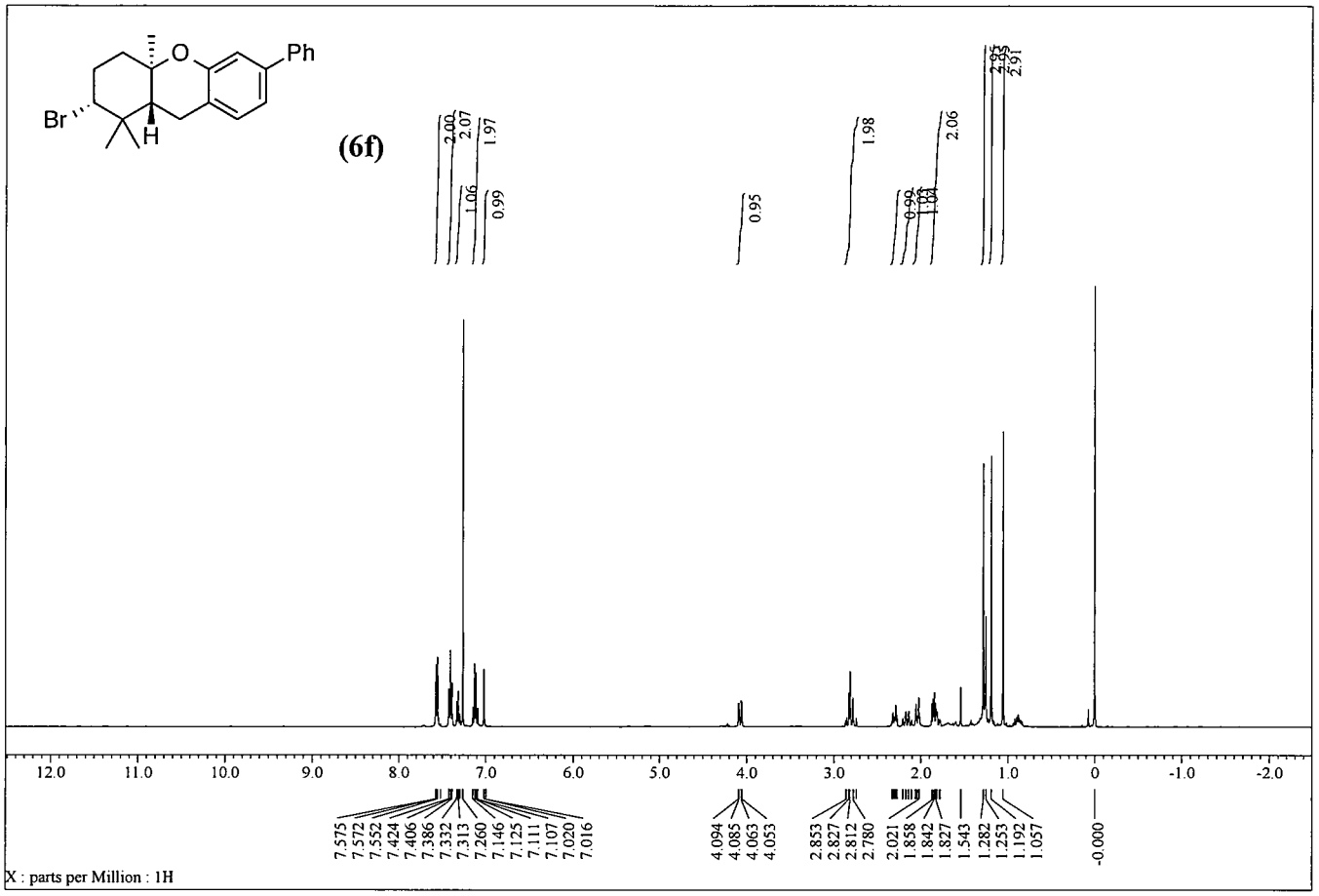

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
151.846
132.005
130.270
123.891
118.838
112.001
77.324
77.210
77.000
76.685
76.142
65.549
47.700
40.530
39.176
31.406
29.565
24.445
19.754
16.875
X : parts per Million : 13C

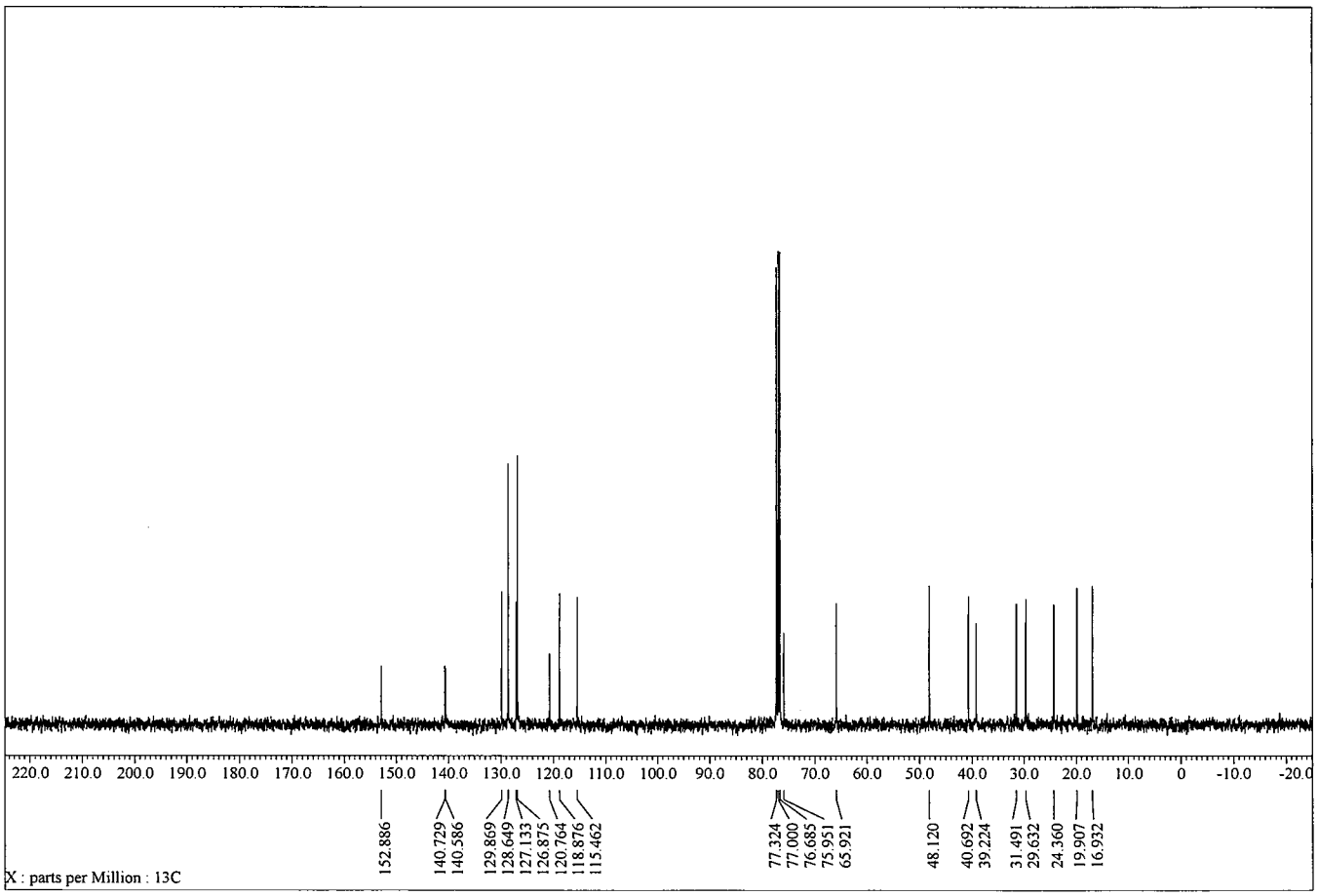

Br
O
OMe
H
(6d)
X : parts per Million : 1H

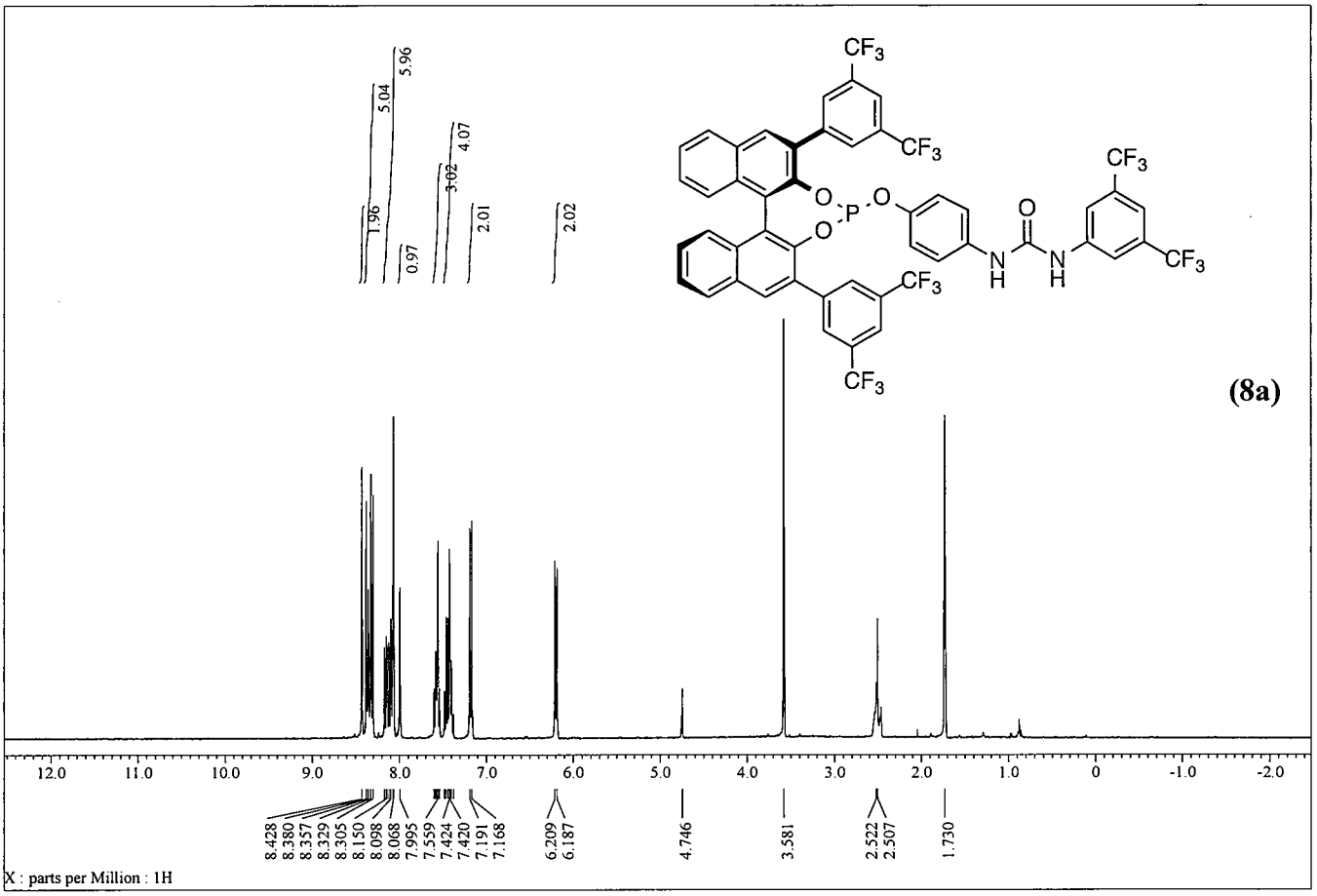

X : parts per Million : 13C

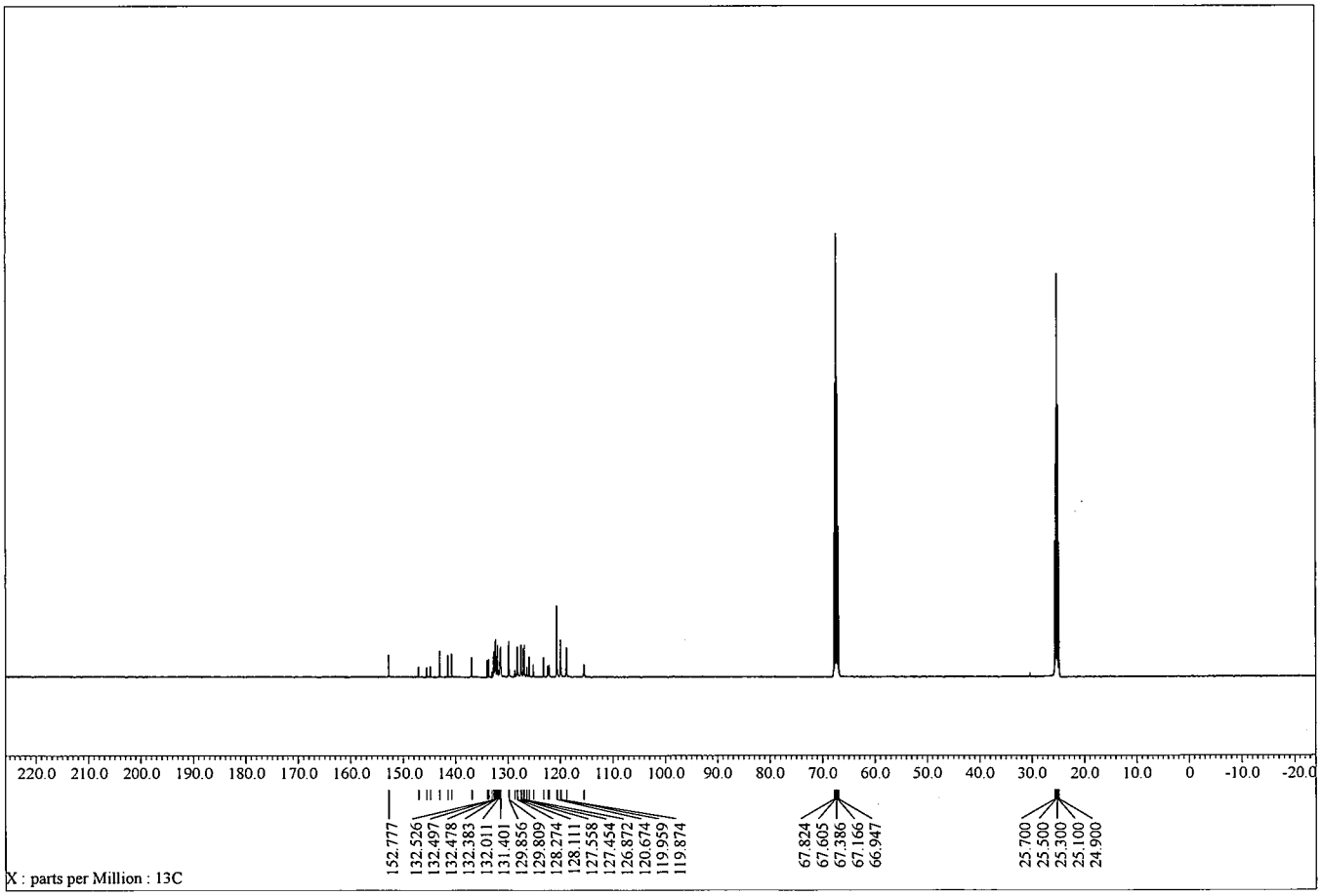

Br
O
H
(6e)
2.05
0.97
1.00
2.03
4.83
1.96
3.00
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.259
6.900
6.876
6.662
6.643
4.071
4.062
4.040
4.030
2.742
2.732
2.727
2.702
2.262
2.251
1.797
1.767
1.570
1.223
1.160
1.026
-0.000
X : parts per Million : 1H

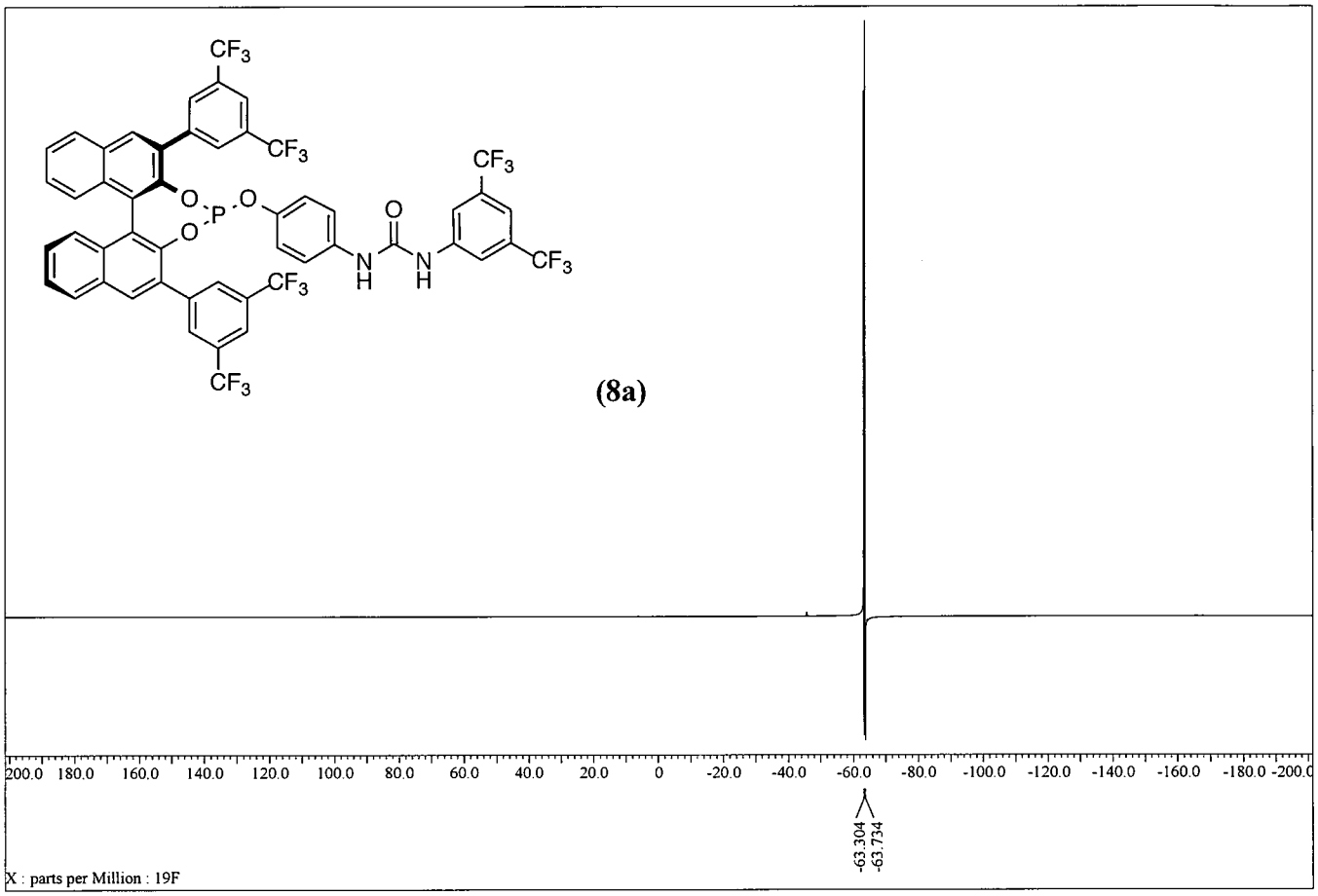

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
150.350
129.850
129.164
128.020
121.326
116.731
77.324
77.000
76.685
75.551
66.102
48.158
40.711
39.195
31.511
29.604
24.541
20.469
19.745
16.884
X : parts per Million : 13C


Br
O
Ph
H
(6f)
2.00
2.07
1.97
1.06
0.99
0.95
1.98
2.06
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.575
7.572
7.552
7.424
7.406
7.386
7.332
7.313
7.260
7.146
7.125
7.111
7.107
7.020
7.016
4.094
4.085
4.063
4.053
2.853
2.827
2.812
2.780
2.021
1.858
1.842
1.827
1.543
1.282
1.253
1.192
1.057
-0.000
X : parts per Million : 1H

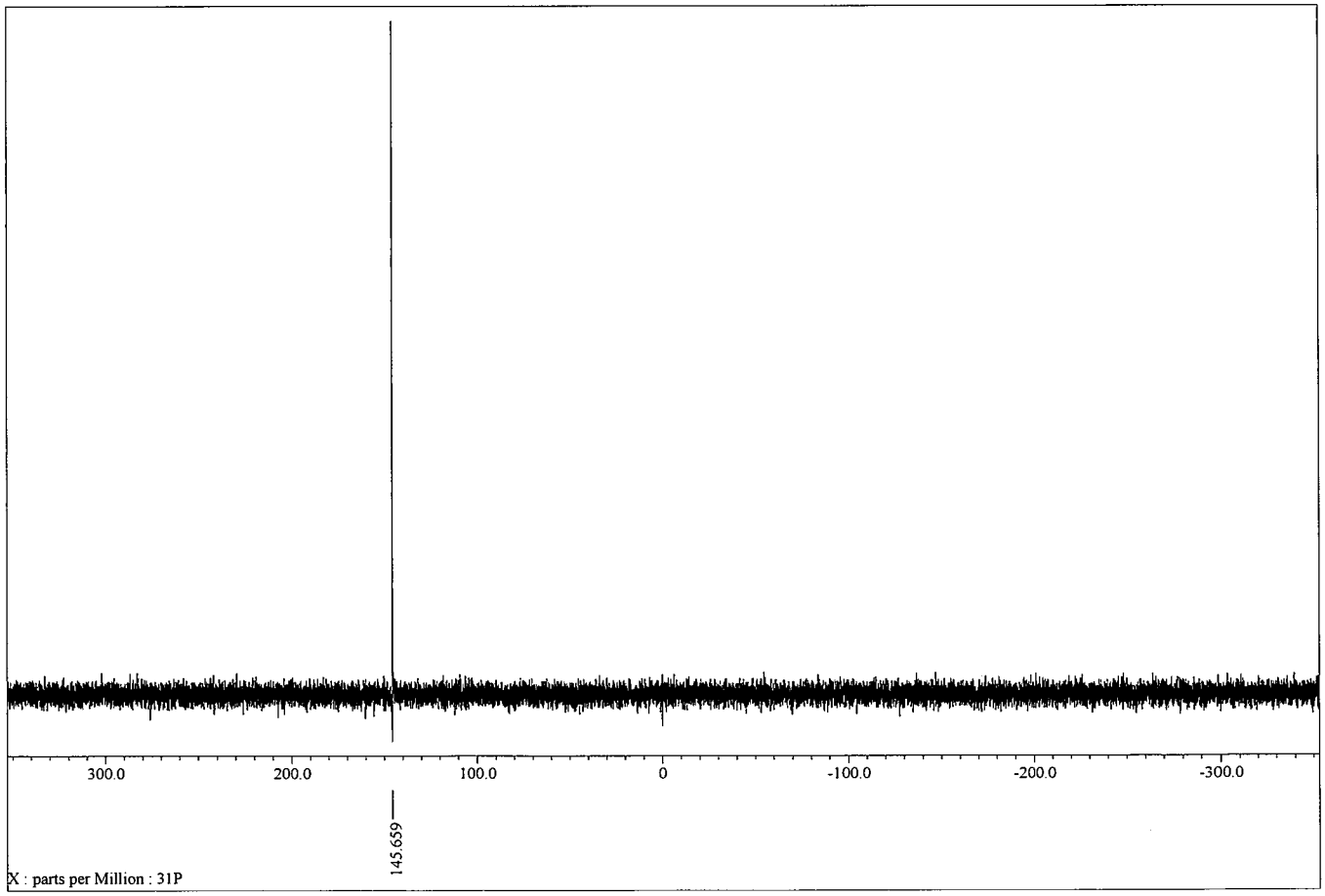

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
152.886
140.729
140.586
129.869
128.649
127.133
126.875
120.764
118.876
115.462
77.324
77.000
76.685
75.951
65.921
48.120
40.692
39.224
31.491
29.632
24.360
19.907
16.932
X : parts per Million : 13C

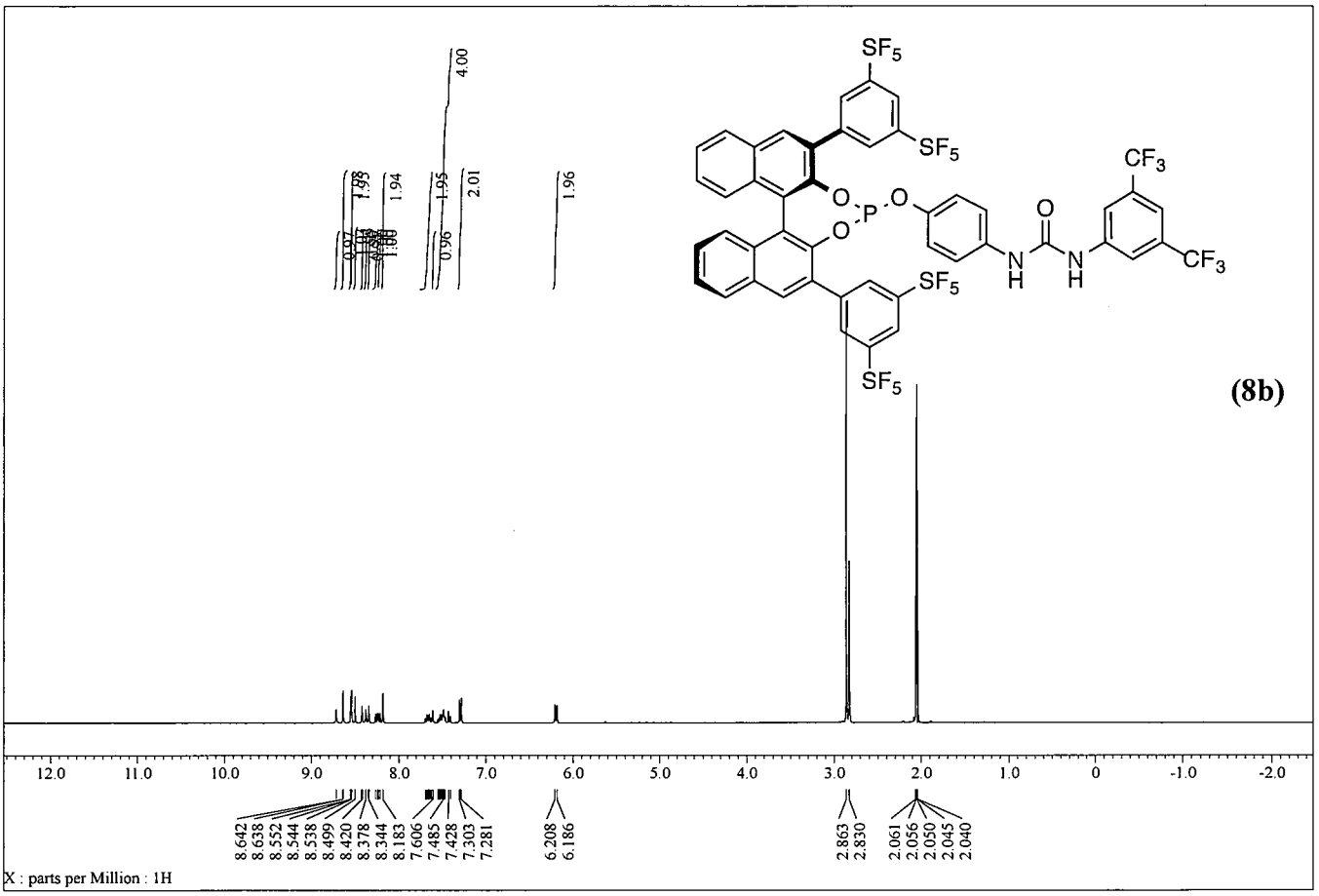

CF3
CF3
CF3
CF3
CF3
CF3
O
P
O
O
O
N
H
N
H
(8a)
1.96
5.04
5.96
0.97
3.02
4.07
2.01
2.02
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.428
8.380
8.357
8.329
8.305
8.150
8.098
8.068
7.995
7.559
7.424
7.420
7.191
7.168
6.209
6.187
4.746
3.581
2.522
2.507
1.730
X : parts per Million : 1H

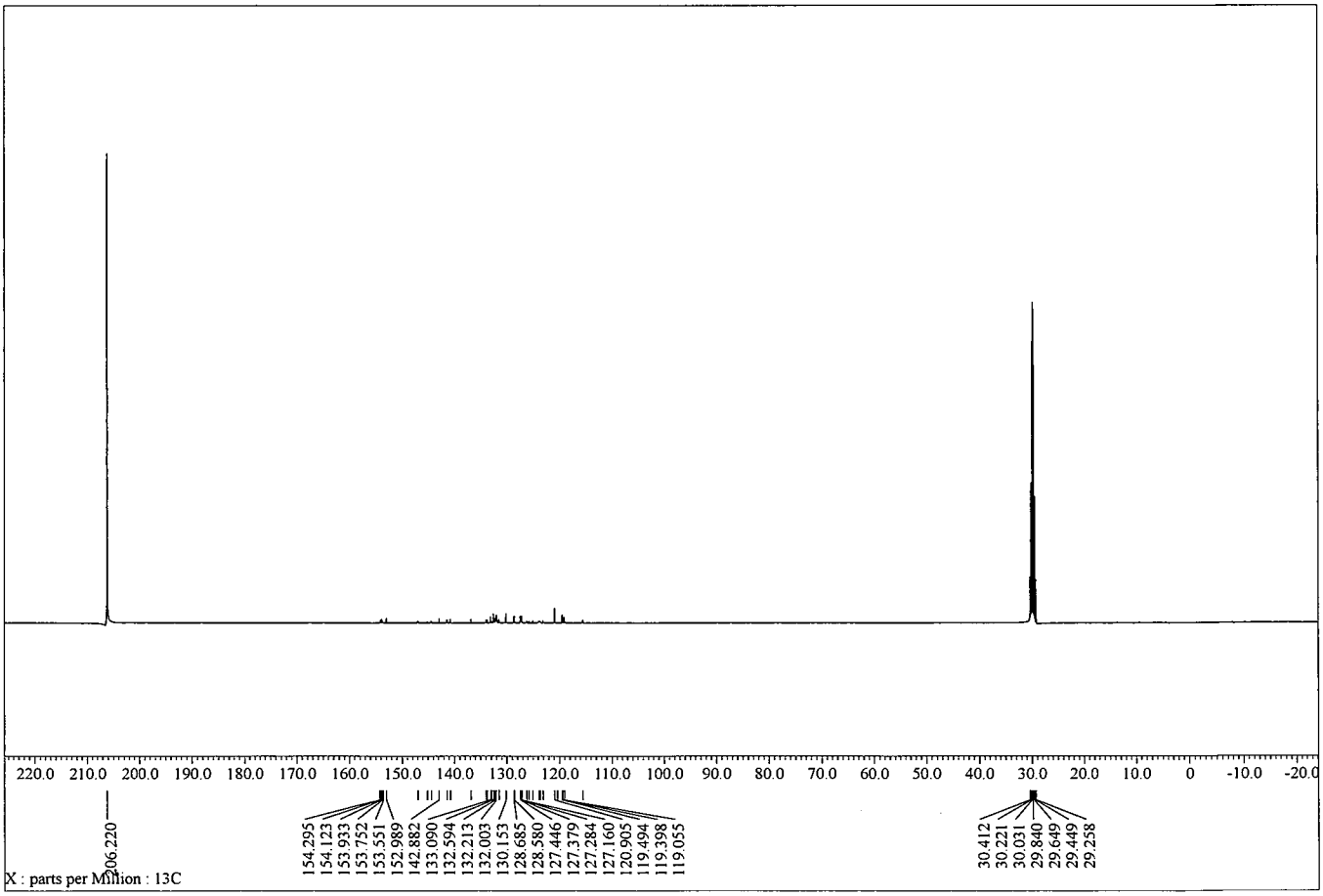

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
152.777
132.526
132.497
132.478
132.383
132.011
131.401
129.856
129.809
128.274
128.111
127.558
127.454
126.872
120.674
119.959
119.874
67.824
67.605
67.386
67.166
66.947
25.700
25.500
25.300
25.100
24.900
X : parts per Million : 13C

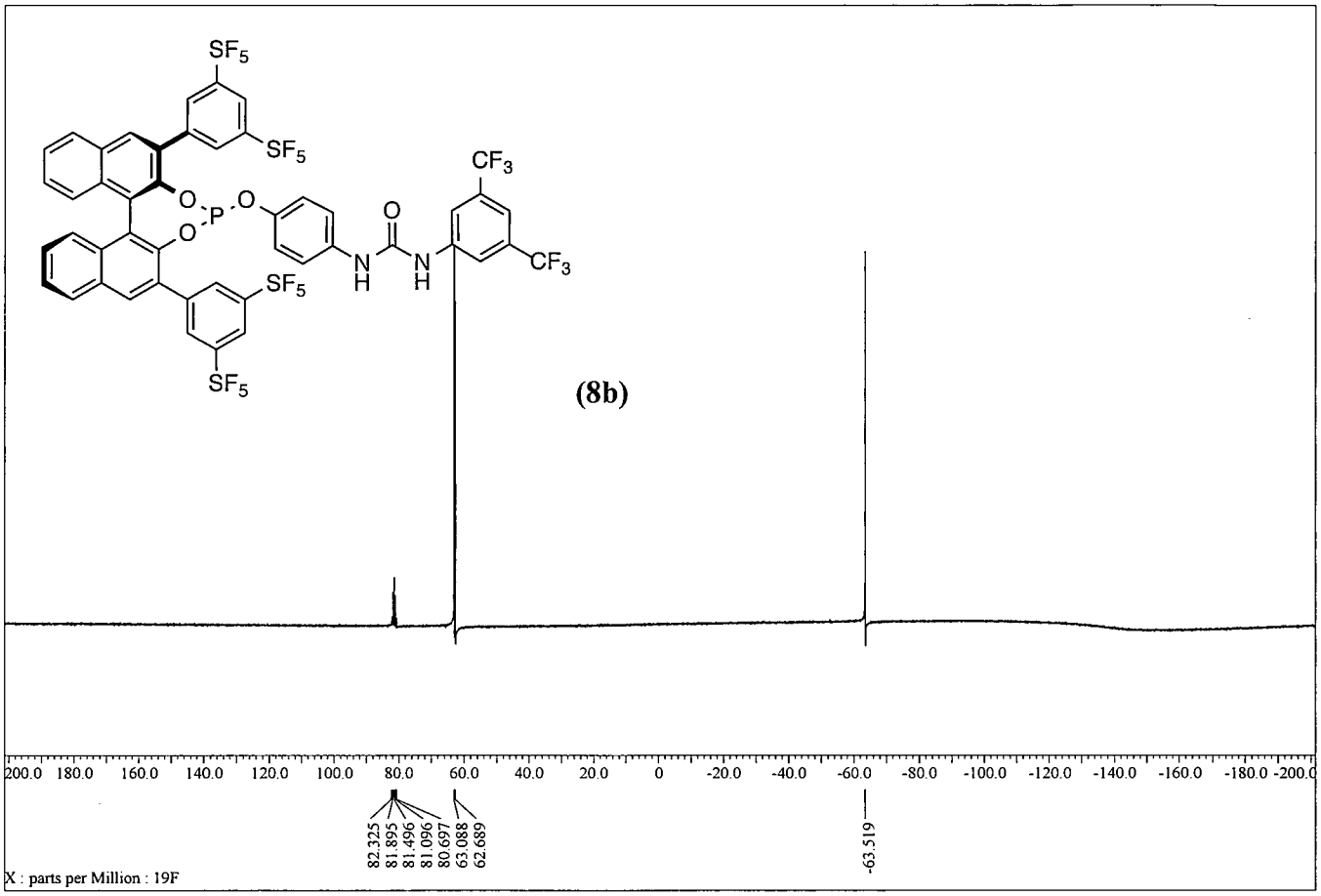

CF3
CF3
CF3
CF3
CF3
CF3
O
P
O
O
O
N
H
N
H
O
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
-63.304
-63.734
X : parts per Million : 19F

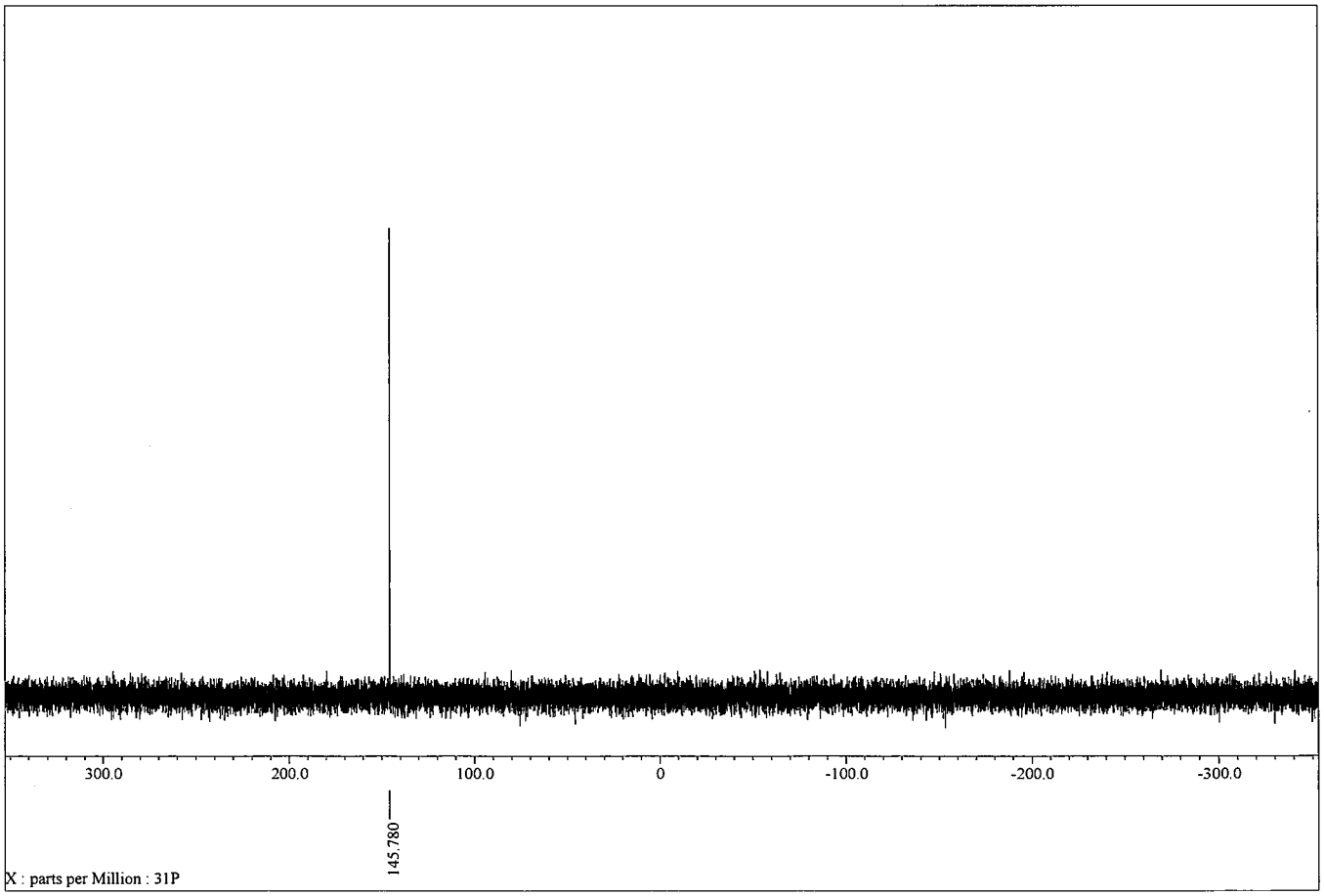
(8a)

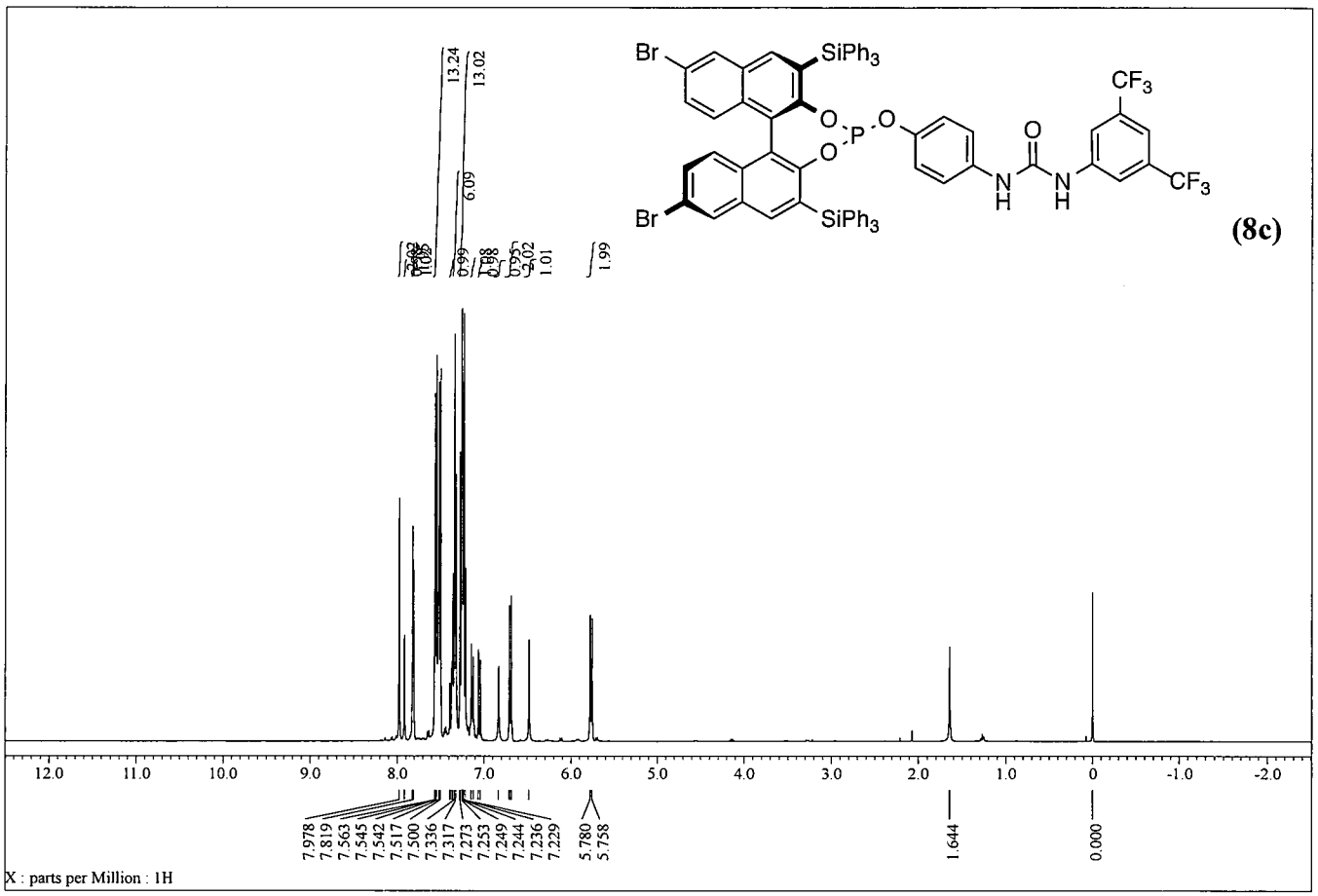

300.0 200.0 100.0 0 -100.0 -200.0 -300.0
145.659
X : parts per Million : 31P

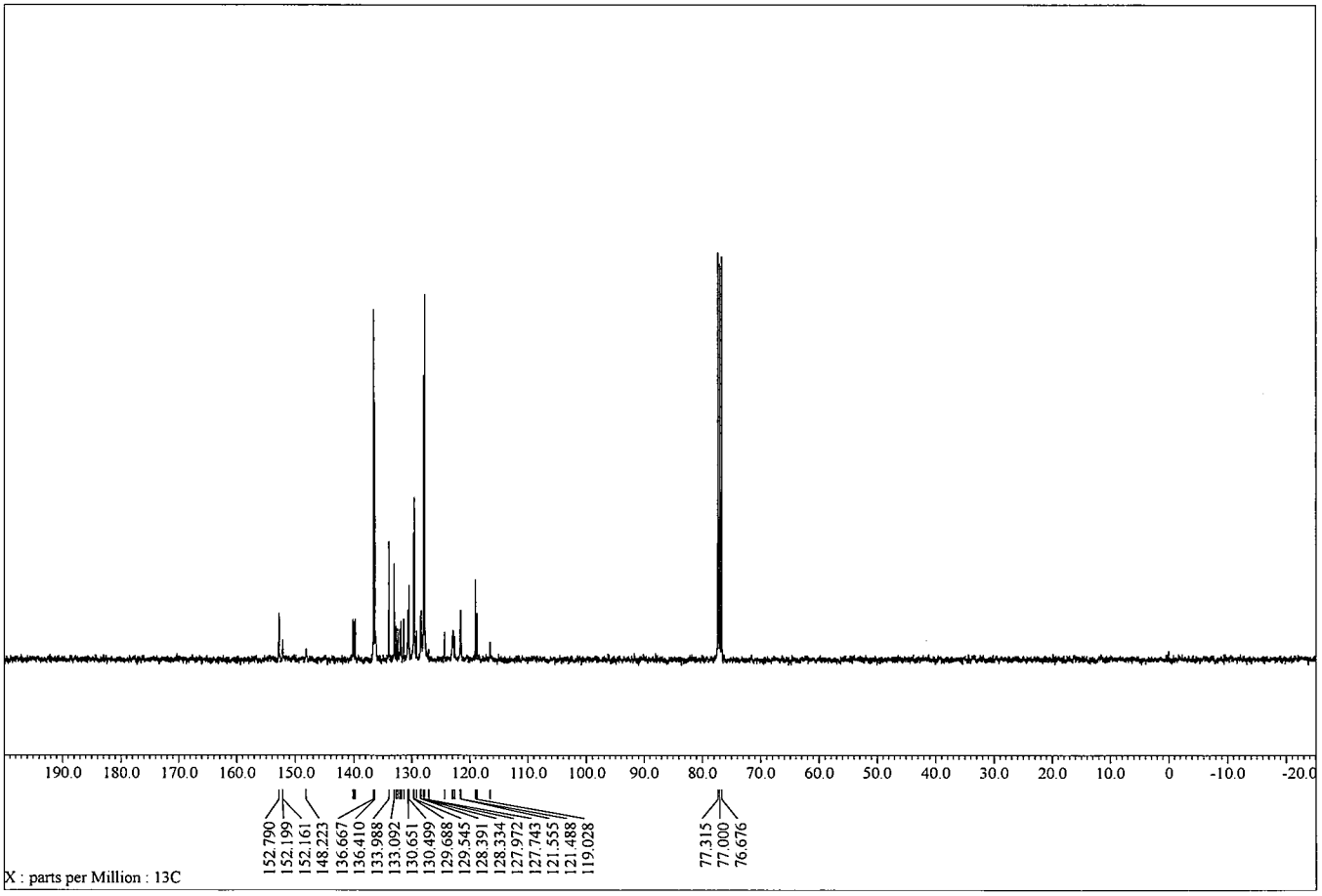

SF5
SF5
CF3
O
P
O
O
O
N
H
N
H
CF3
SF5
SF5
(8b)
4.00
1.94
1.95
2.01
1.96
0.96
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
8.642
8.638
8.552
8.544
8.538
8.499
8.420
8.378
8.344
8.183
7.606
7.485
7.428
7.303
7.281
6.208
6.186
2.863
2.830
2.061
2.056
2.050
2.045
2.040
X : parts per Million : 1H

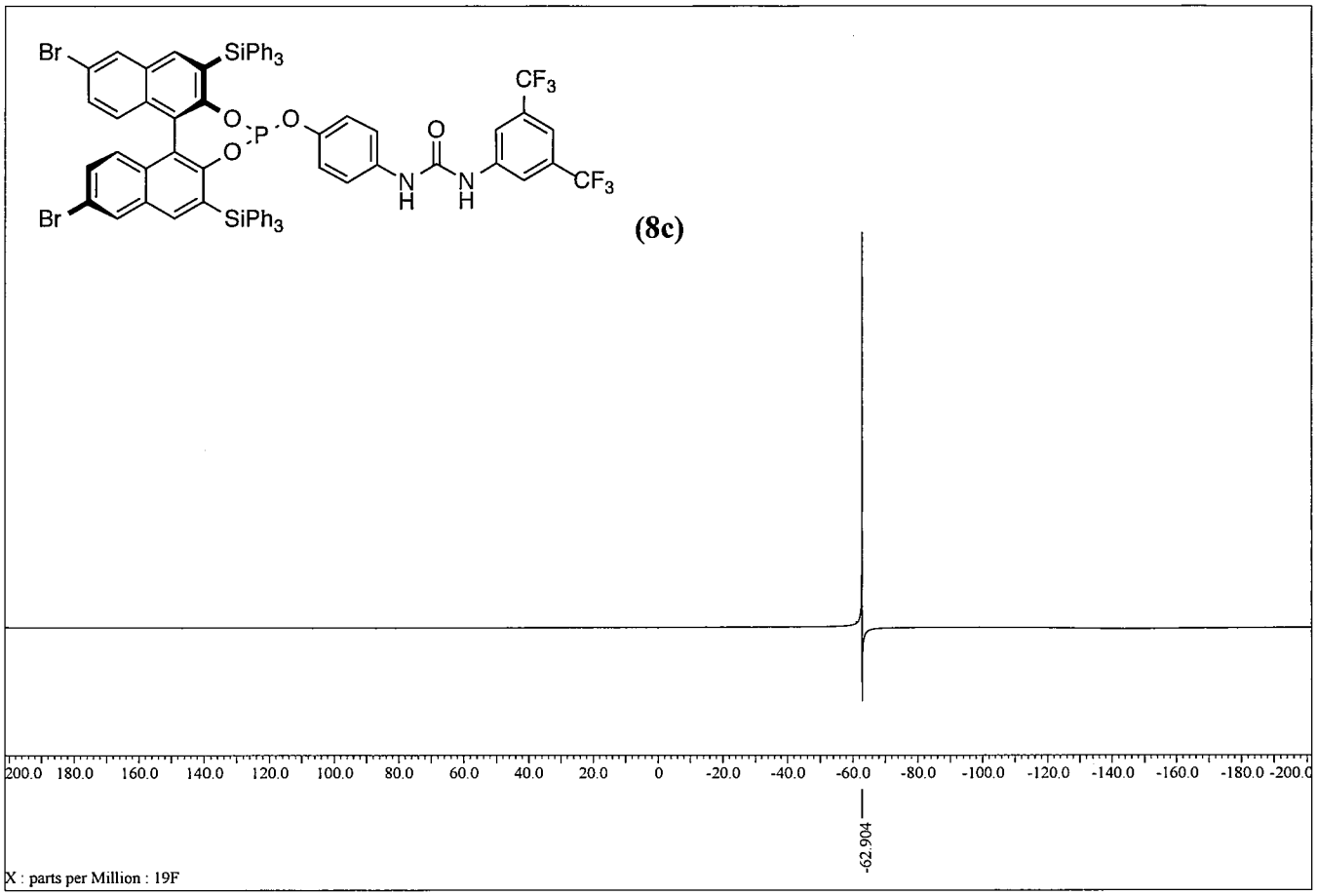

220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
206.220
154.295
154.123
153.933
153.752
153.551
152.989
142.882
133.090
132.594
132.213
132.003
130.153
128.685
128.580
127.446
127.379
127.284
127.160
120.905
119.494
119.398
119.055
30.412
30.221
30.031
29.840
29.649
29.449
29.258
X : parts per Million : 13C

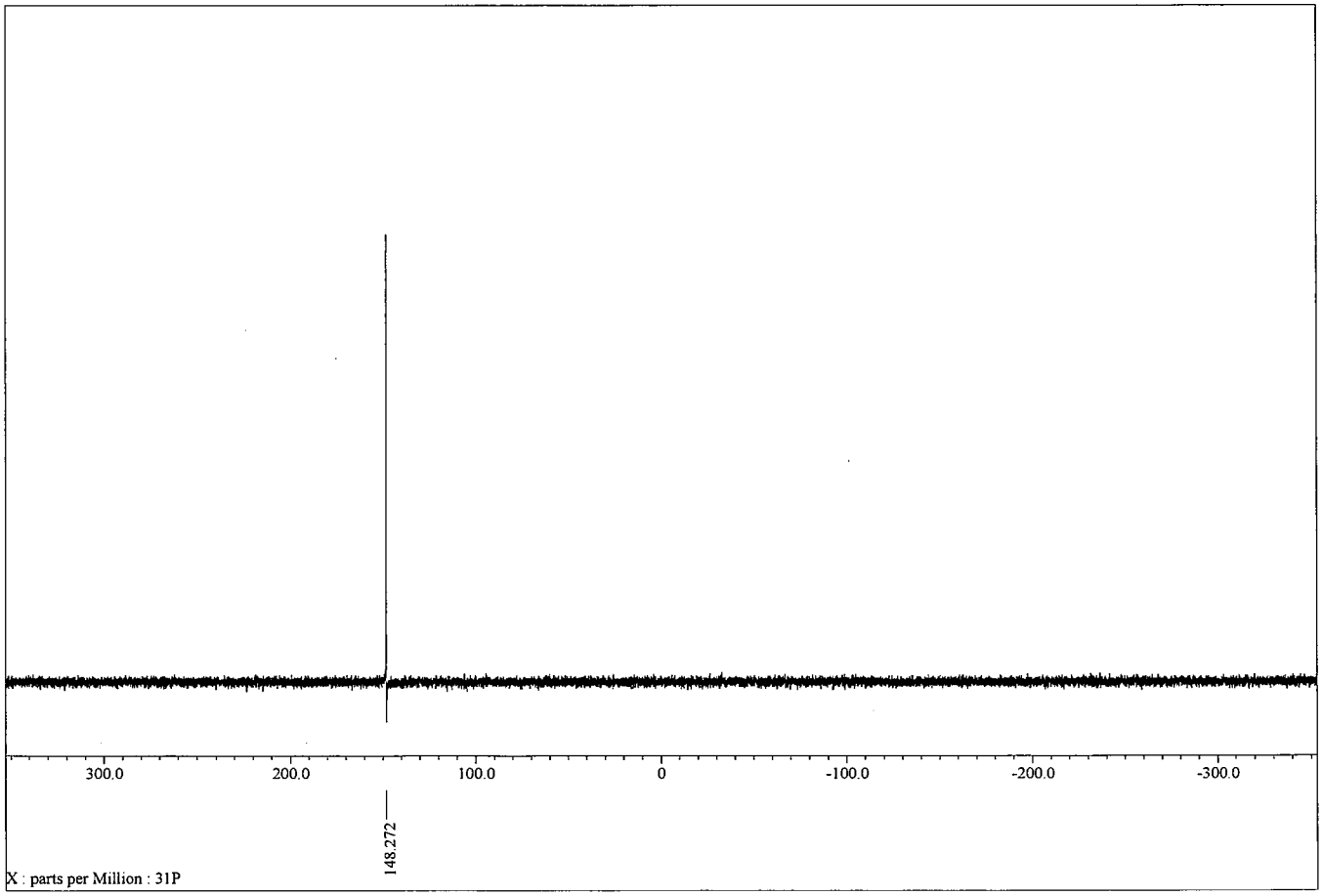

SF5
SF5
SF5
SF5
O
P
O
O
O
N
H
O
N
H
CF3
CF3
(8b)
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
82.325
81.895
81.496
81.096
80.697
63.088
62.689
-63.519
X : parts per Million : 19F

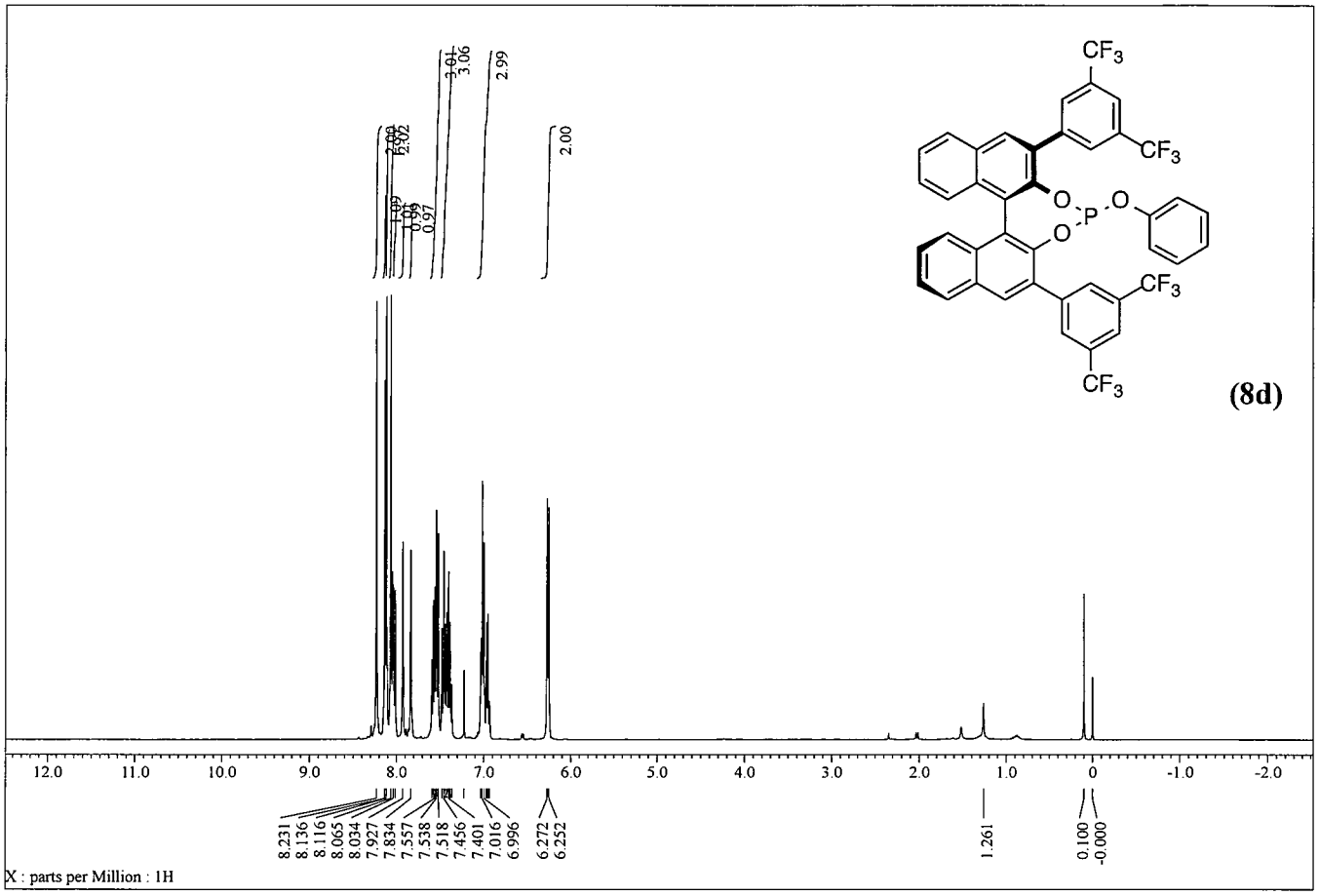

300.0 200.0 100.0 0 -100.0 -200.0 -300.0
145.780
X : parts per Million : 31P

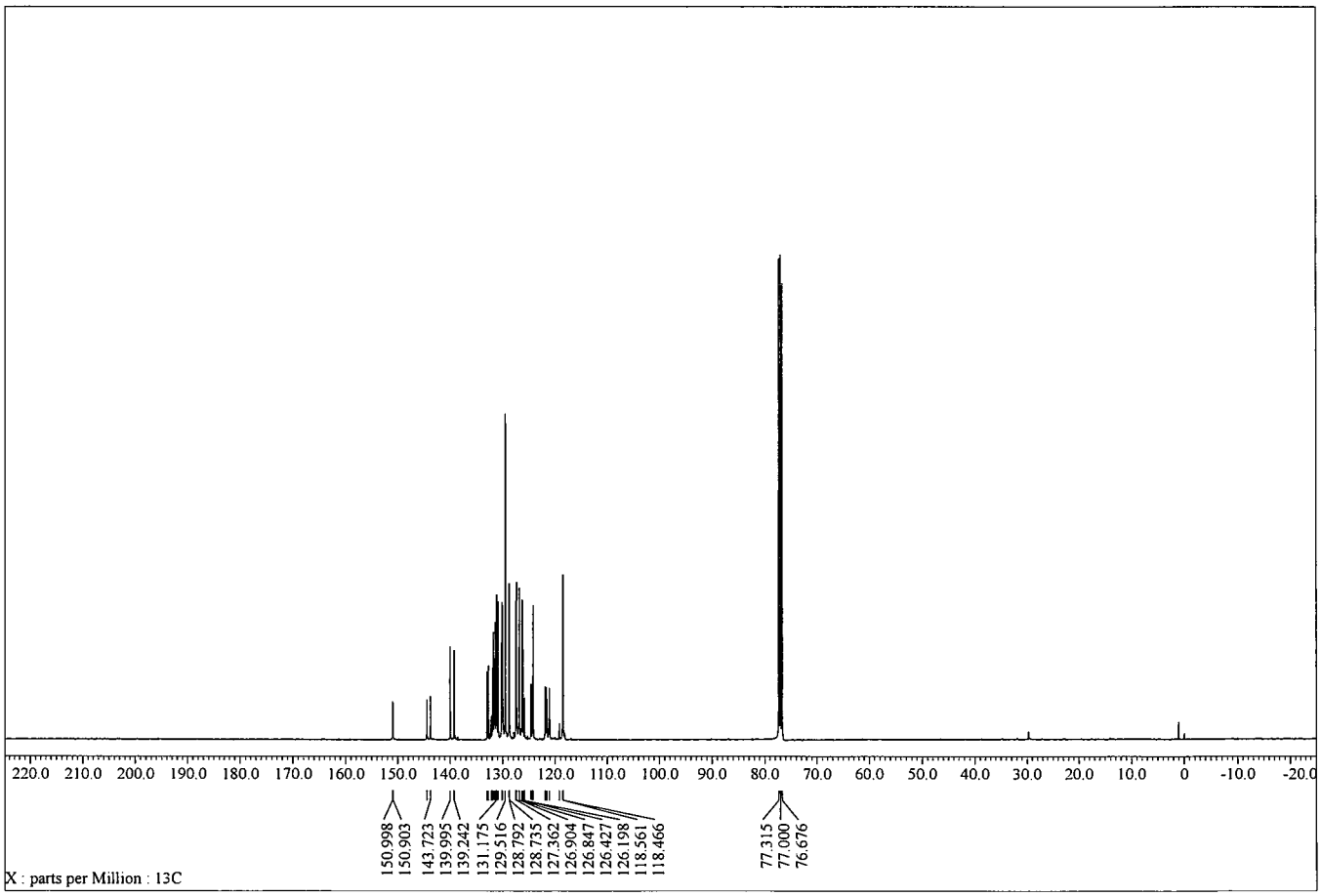

Br
SiPh3
O
P
O
O
O
N
H
N
H
CF3
CF3
Br
SiPh3
(8c)
13.24
13.02
6.09
1.01
1.99
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.978
7.819
7.563
7.545
7.542
7.517
7.500
7.336
7.317
7.273
7.253
7.249
7.244
7.236
7.229
5.780
5.758
1.644
0.000
X : parts per Million : 1H

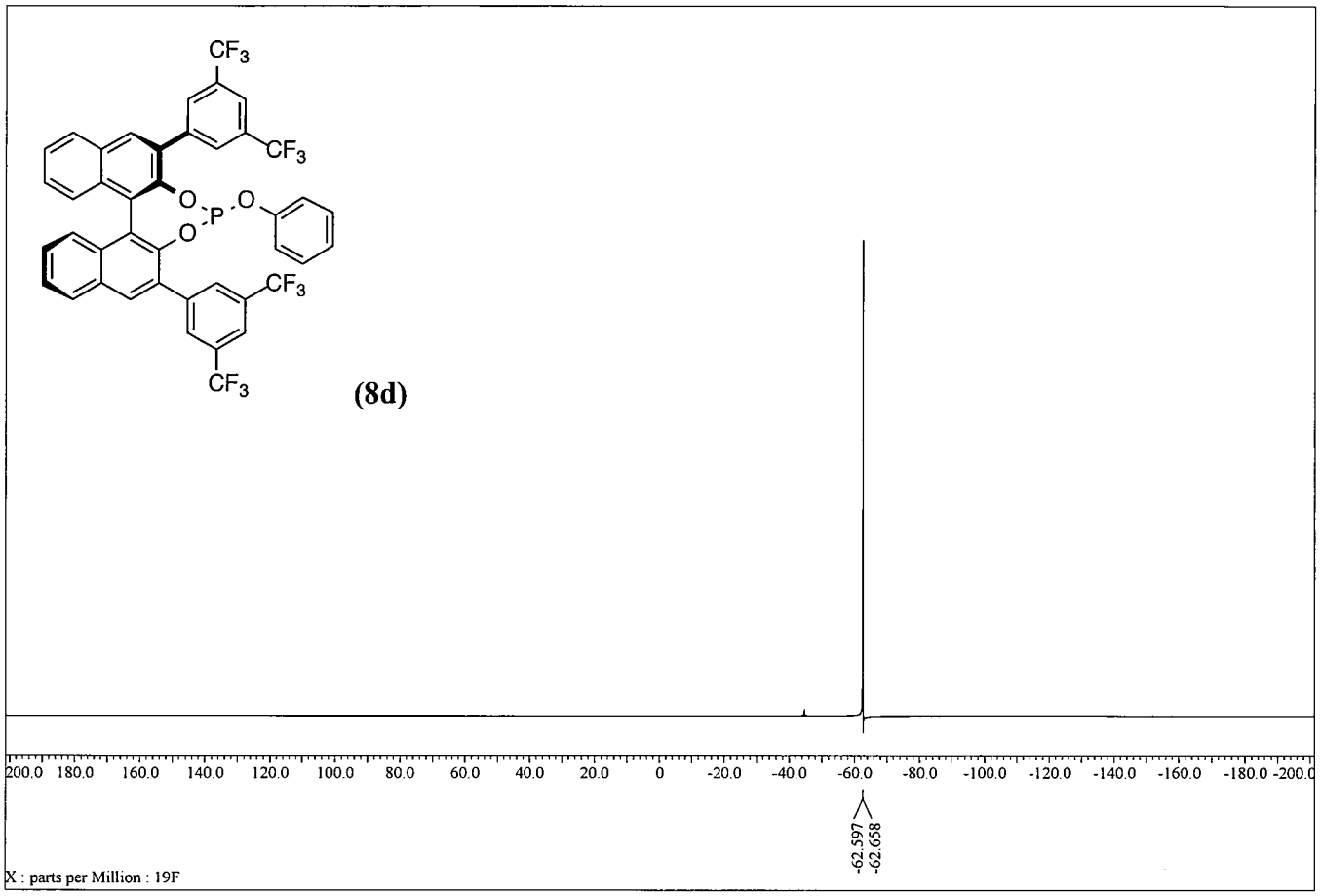

190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
152.790
152.199
152.161
148.223
136.667
136.410
133.988
133.092
130.651
130.499
129.688
129.545
128.391
128.334
127.972
127.743
121.555
121.488
119.028
77.315
77.000
76.676
X : parts per Million : 13C


Br
SiPh3
O
P
O
O
O
N
H
O
N
H
CF3
CF3
Br
SiPh3
(8c)
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
-62.904
X : parts per Million : 19F

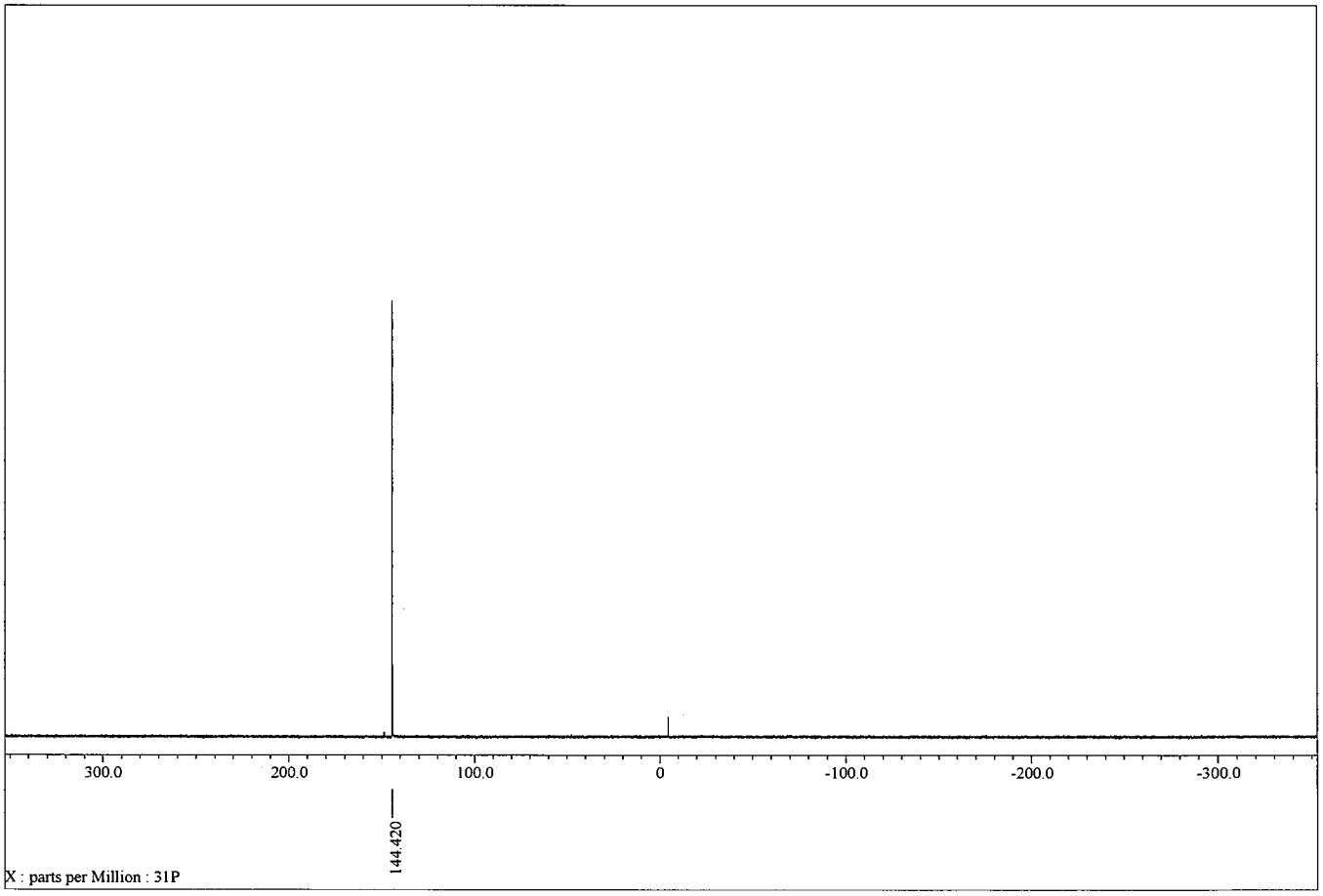

300.0 200.0 100.0 0 -100.0 -200.0 -300.0
148.272
X : parts per Million : 31P

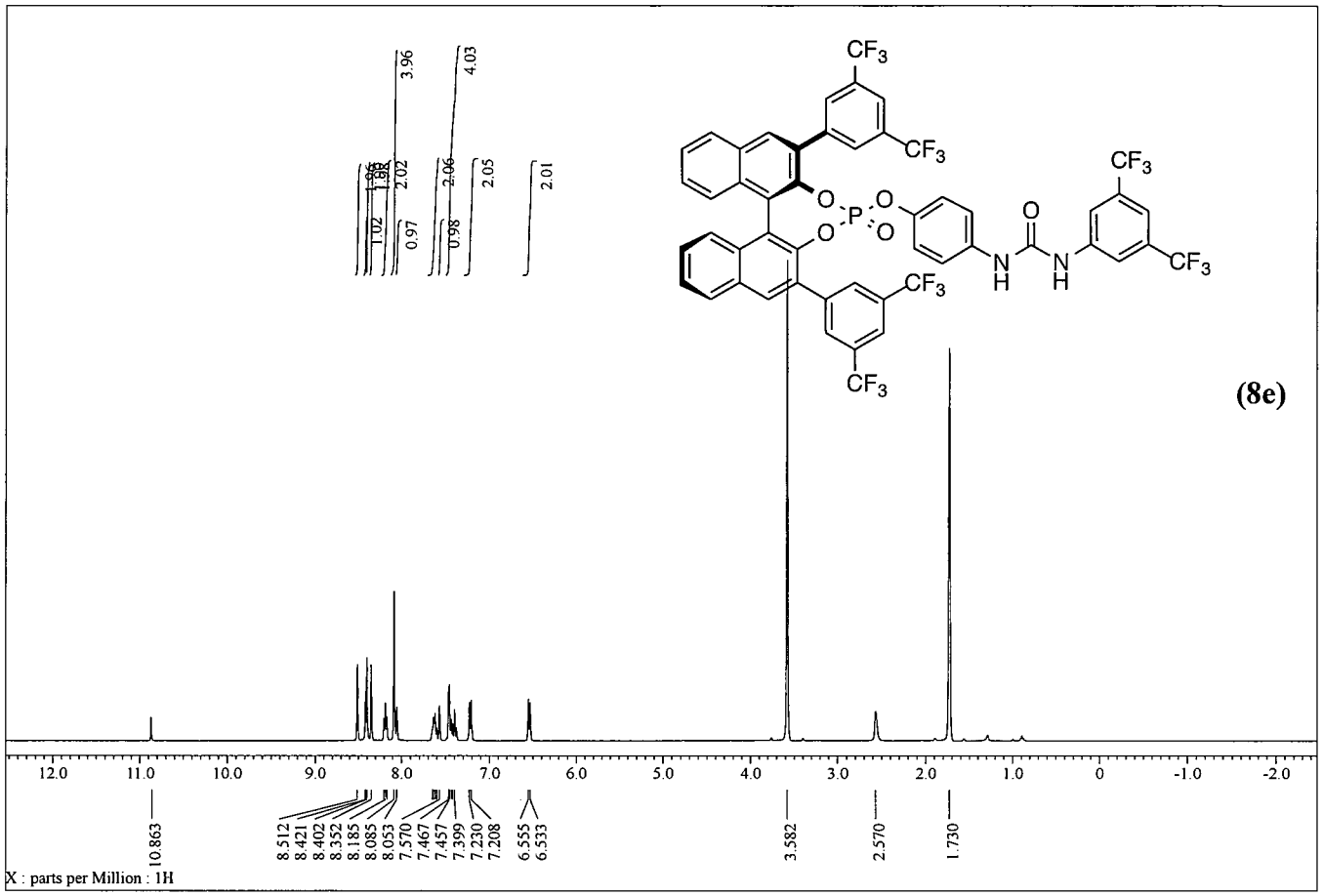

CF3
CF3
CF3
CF3
O
P
O
O
(8d)
2.00
2.99
3.01
3.06
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
8.231
8.136
8.116
8.065
8.034
7.927
7.834
7.557
7.538
7.518
7.456
7.401
7.016
6.996
6.272
6.252
1.261
0.100
-0.000
X : parts per Million : 1H

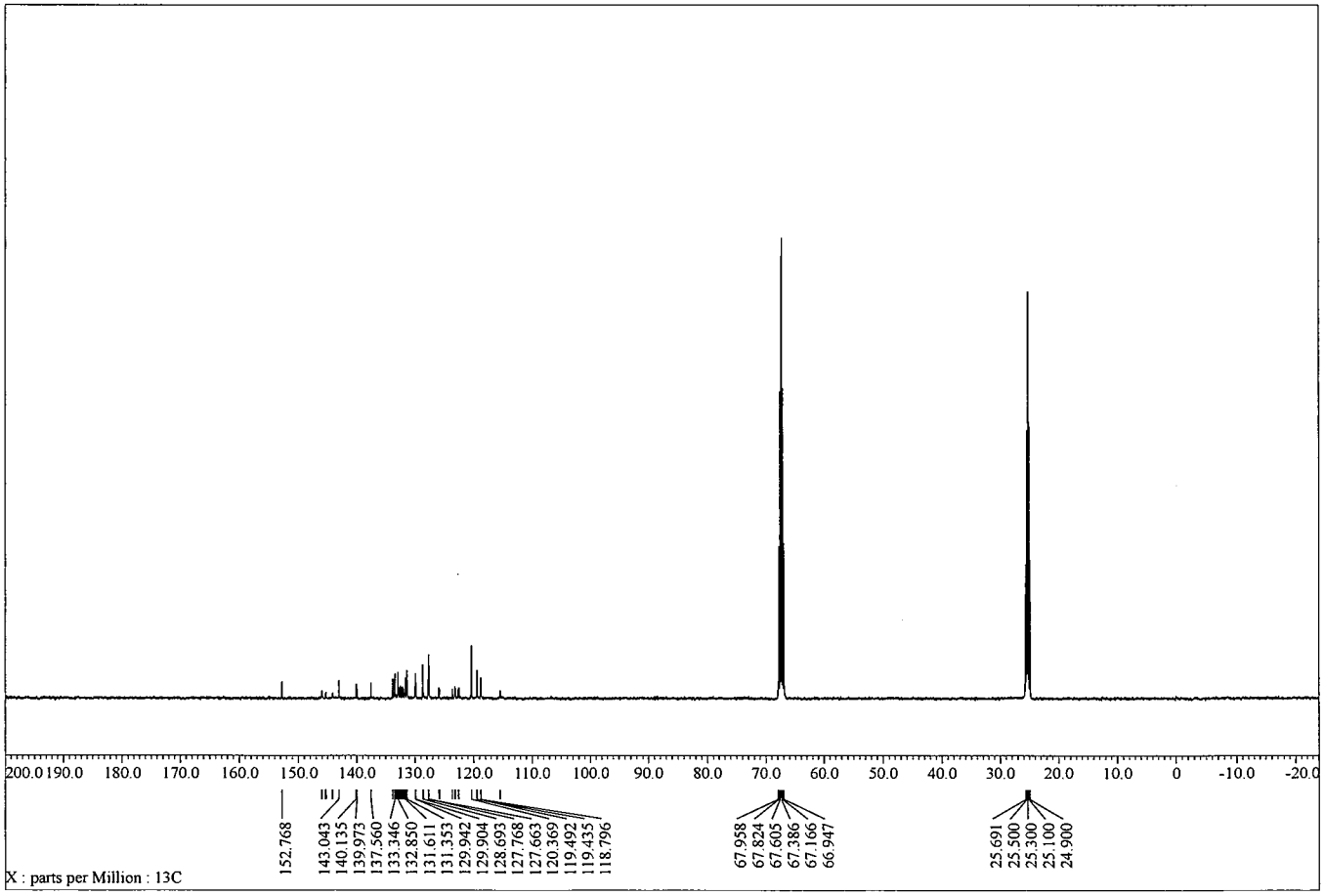

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
150.998
150.903
143.723
139.995
139.242
131.175
129.516
128.792
128.735
127.362
126.904
126.847
126.427
126.198
118.561
118.466
77.315
77.000
76.676
X : parts per Million : 13C

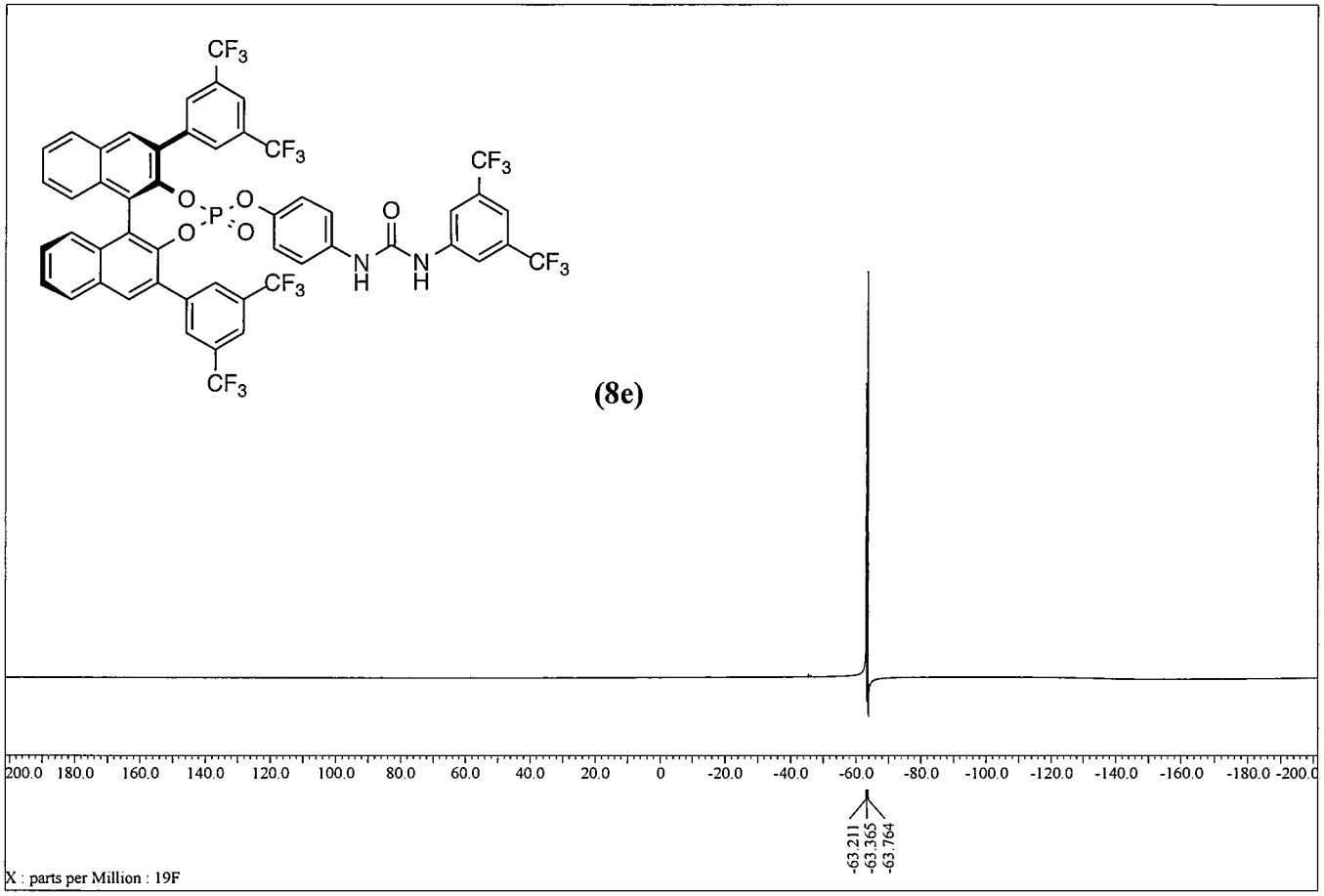

CF3
CF3
O
P
O
O
CF3
CF3
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
-62.597
-62.658
X : parts per Million : 19F

(8d)

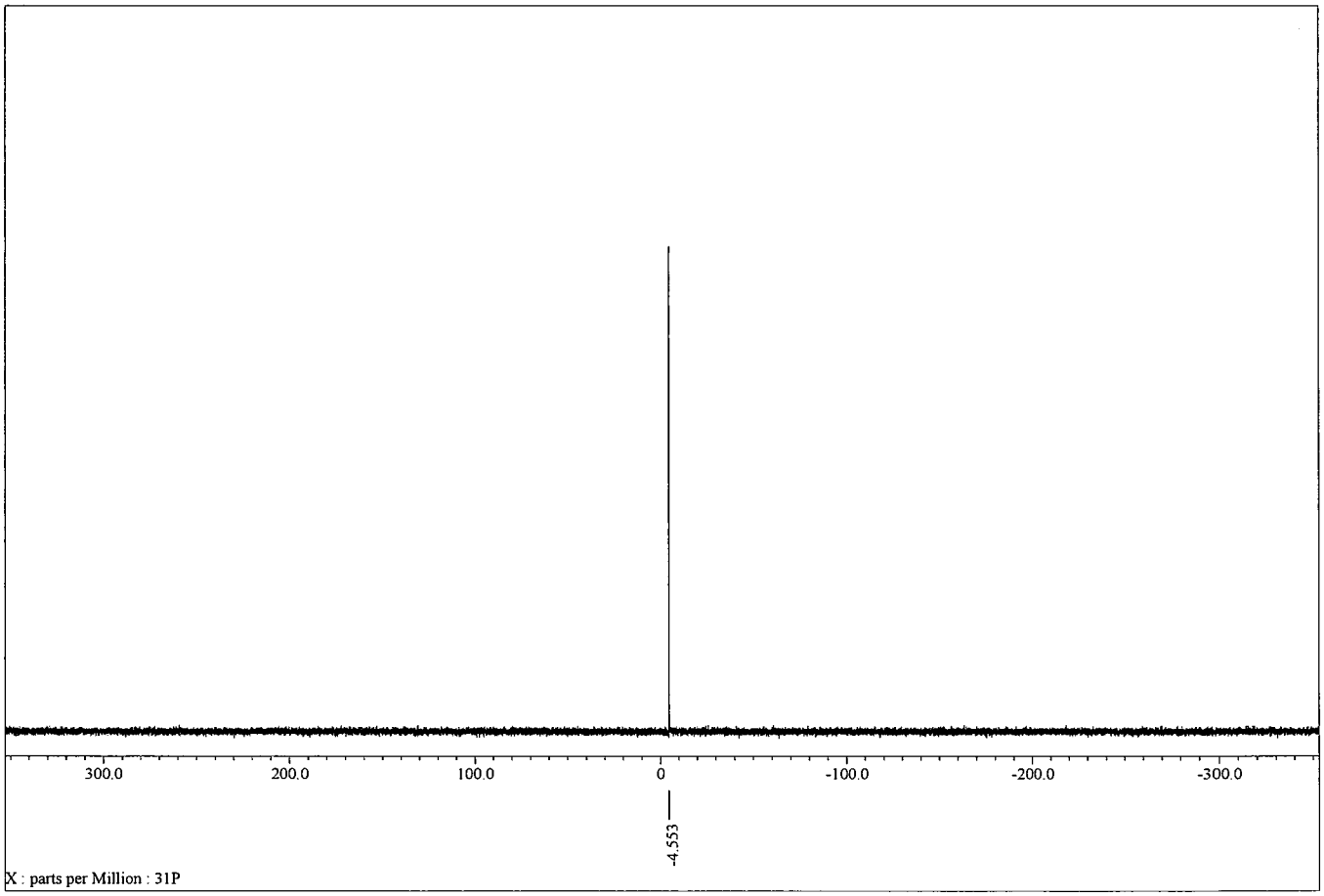

300.0 200.0 100.0 0 -100.0 -200.0 -300.0
144.420
X : parts per Million : 31P

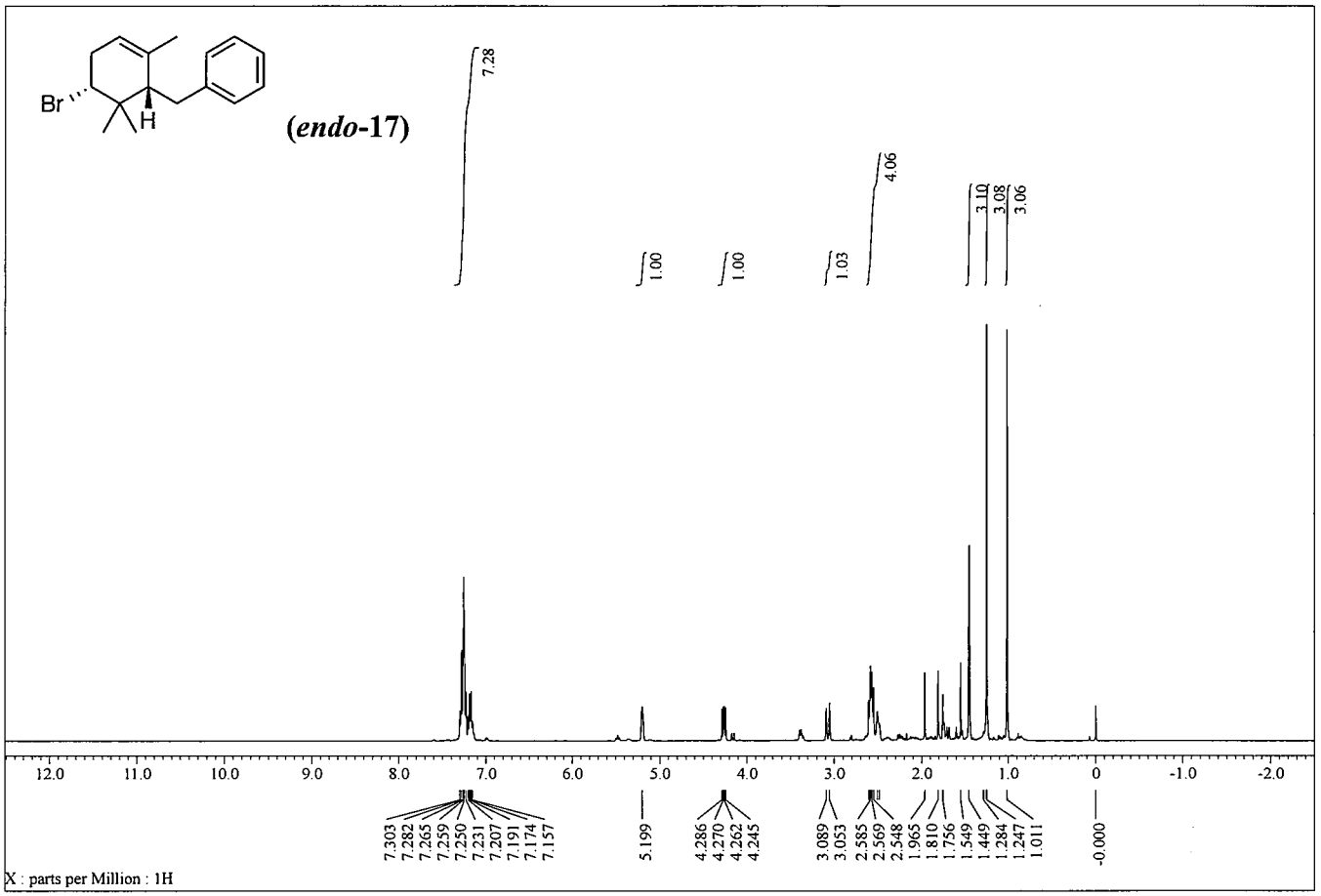

(8e)
X : parts per Million : 1H

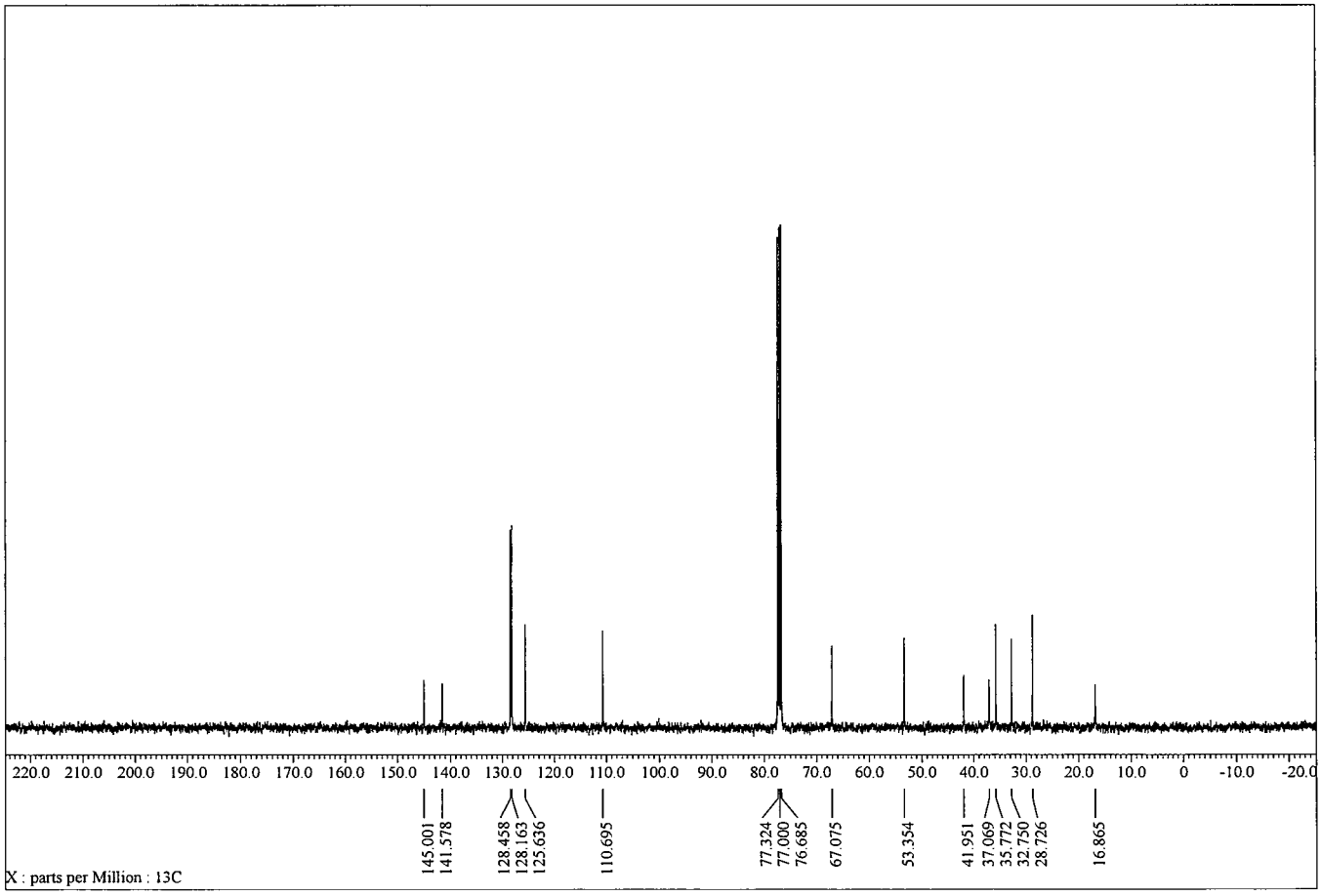

X : parts per Million : 13C

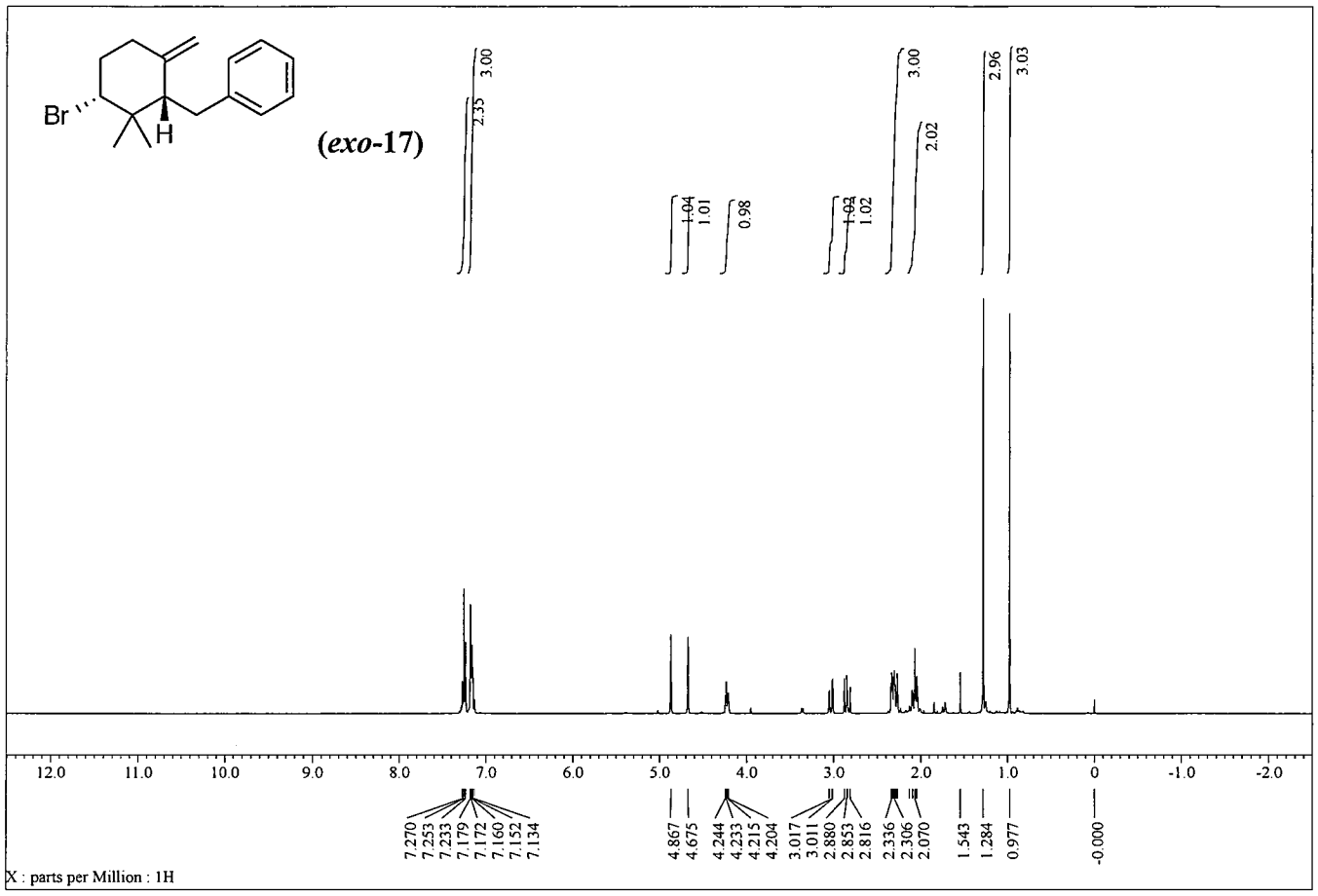

CF3
CF3
CF3
CF3
CF3
CF3
O
P
O
O
O
N
H
O
N
H
200.0 180.0 160.0 140.0 120.0 100.0 80.0 60.0 40.0 20.0 0 -20.0 -40.0 -60.0 -80.0 -100.0 -120.0 -140.0 -160.0 -180.0 -200.0
-63.211
-63.365
-63.764
X : parts per Million : 19F

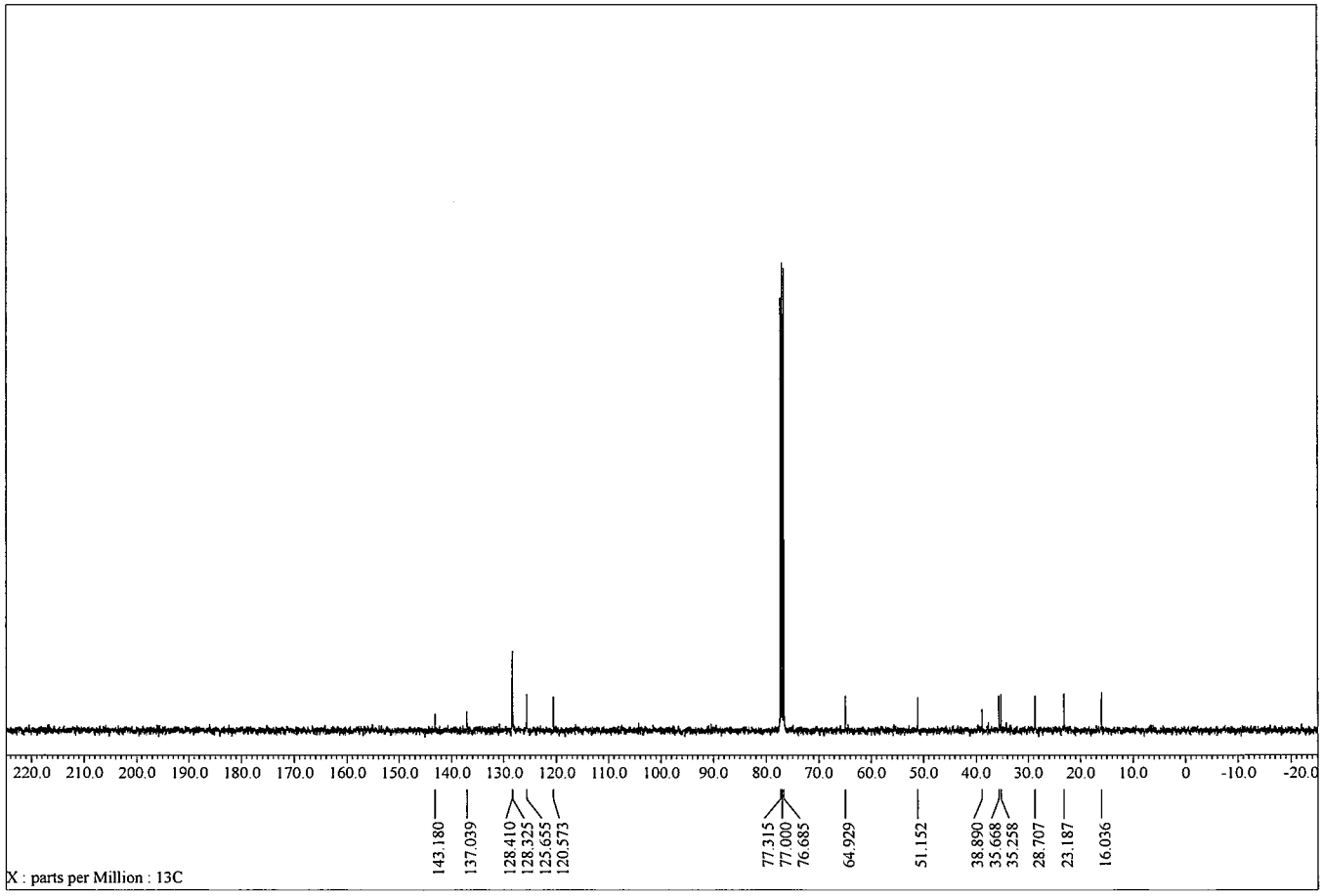
(8e)

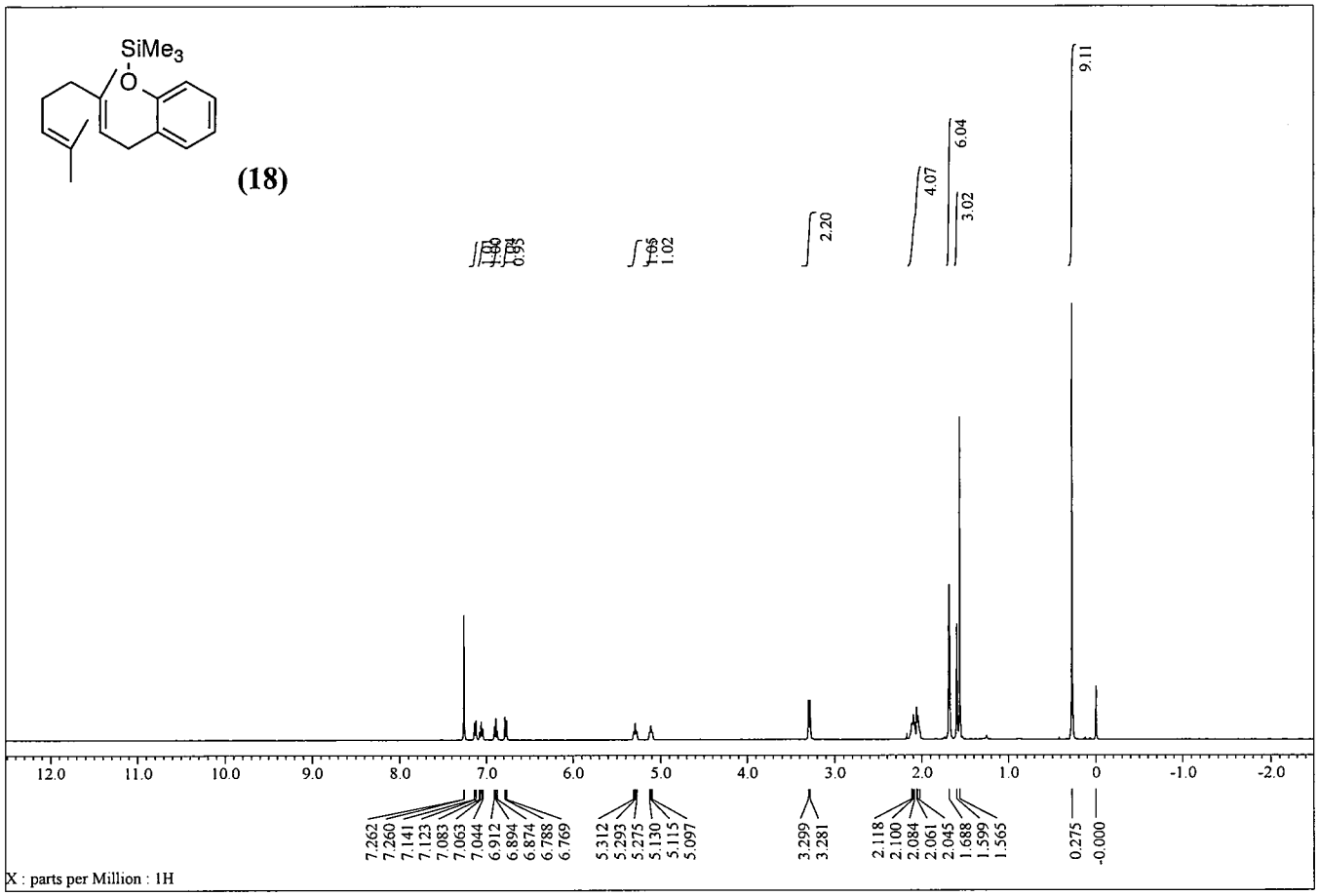

300.0 200.0 100.0 0 -100.0 -200.0 -300.0
-4.553
X : parts per Million : 31P

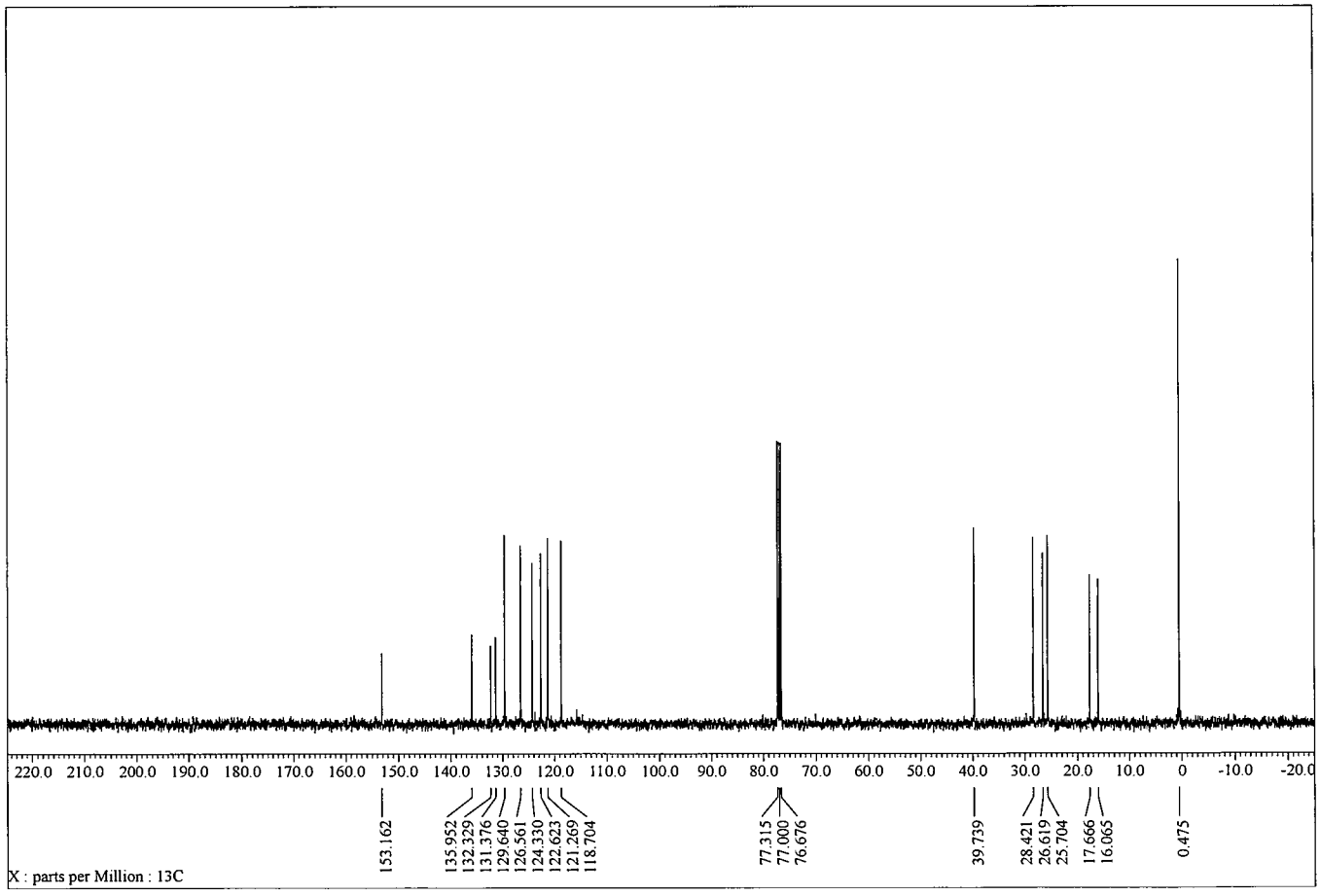

Br
H
(endo-17)
7.28
4.06
3.10
3.08
3.06
1.00
1.00
1.03
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.303 7.282 7.265 7.259 7.250 7.231 7.207 7.191 7.174 7.157
5.199
4.286 4.270 4.262 4.245
3.089 3.053
2.585 2.569 2.548
1.965 1.810 1.756 1.549 1.449 1.284 1.247 1.011
-0.000
X : parts per Million : 1H


220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
145.001 141.578
128.458 128.163 125.636
110.695
77.324 77.000 76.685
67.075
53.354
41.951 37.069 35.772 32.750 28.726
16.865
X : parts per Million : 13C


Br
H
(exo-17)
3.00
2.35
1.04
1.01
0.98
1.02
3.00
2.02
2.96
3.03
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 -1.0 -2.0
7.270 7.253 7.233 7.179 7.172 7.160 7.152 7.134
4.867 4.675 4.244 4.233 4.215 4.204
3.017 3.011 2.880 2.853 2.816
2.336 2.306 2.070
1.543 1.284 0.977
-0.000
X : parts per Million : 1H


220.0 210.0 200.0 190.0 180.0 170.0 160.0 150.0 140.0 130.0 120.0 110.0 100.0 90.0 80.0 70.0 60.0 50.0 40.0 30.0 20.0 10.0 0 -10.0 -20.0
143.180
137.039
128.410
128.325
125.655
120.573
77.315
77.000
76.685
64.929
51.152
38.890
35.668
35.258
28.707
23.187
16.036
X : parts per Million : 13C


SiMe3
O
(18)
9.11
6.04
4.07
3.02
2.20
1.02
0.95
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
7.262
7.260
7.141
7.123
7.083
7.063
7.044
6.912
6.894
6.874
6.788
6.769
5.312
5.293
5.275
5.130
5.115
5.097
3.299
3.281
2.118
2.100
2.084
2.061
2.045
1.688
1.599
1.565
0.275
-0.000
X : parts per Million : 1H


220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
153.162
135.952
132.329
131.376
129.640
126.561
124.330
122.623
121.269
118.704
77.315
77.000
76.676
39.739
28.421
26.619
25.704
17.666
16.065
0.475
X : parts per Million : 13C