Electronic Supplementary Information

"Phosphite–Urea" Cooperative High-Turnover Catalysts for the Highly Selective Bromocyclization of Homogeranylarenes

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

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

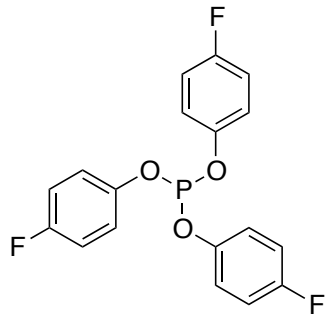
[‡]*Graduate School of Natural Science & Technology, Okayama University, 3-1-1 Tsushima-naka, Kita-ku, Okayama 700-8530, Japan*

[§]*Japan Science and Technology (JST), CREST, Japan*

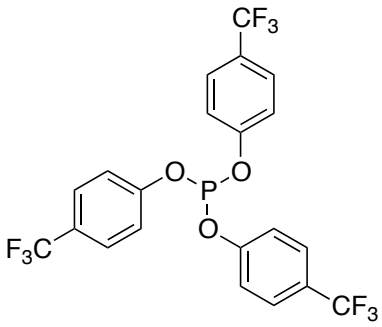
Table of Contents

General Methods. Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. ^{1}H NMR spectra were measured on a JEOL ECS-400 spectrometer (400 MHz) at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet, sep = septet; m = multiplet), coupling constant (Hz), integration, and assignment. ^{13}C NMR spectra were measured on a JEOL ECS-400 spectrometer (100 MHz). Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.00 ppm). ^{19}F NMR spectra (376 MHz) and ^{31}P NMR spectra (162 MHz) were measured on a JEOL ECS-400 spectrometer. The reactions were carried out under an atmosphere of dry nitrogen. For thin-layer chromatography (TLC) analysis throughout this work, Merck precoated TLC plates (silica gel 60 GF_{254} 0.25 mm or silica gel NH_2 F_{254S} 0.25 mm) were used. The products were purified by column chromatography on silica gel (E. Merck Art. 9385). High resolution mass spectral analysis (HRMS) was performed at Chemical Instrumentation Facility, Nagoya University on JEOL JMS-700 spectrometer (for FAB) or JEOL JMS-T100GCV spectrometer (for EI) or Bruker Daltonics micrOTOF-QII (for ESI). HRMS analysis of an arylboronic acid was performed after conversion to its ester with 1,3-propanediol. Dry tetrahydrofuran, diethylether, toluene and dichloromethane were purchased from Kanto as the "anhydrous" and stored under nitrogen. Dry acetonitrile were purchased from Wako as the "anhydrous" and stored under nitrogen. Triethylamine were freshly distilled from calcium hydride. Other simple chemicals were analytical-grade and obtained commercially.

Preparation of Triaryl Phosphites.

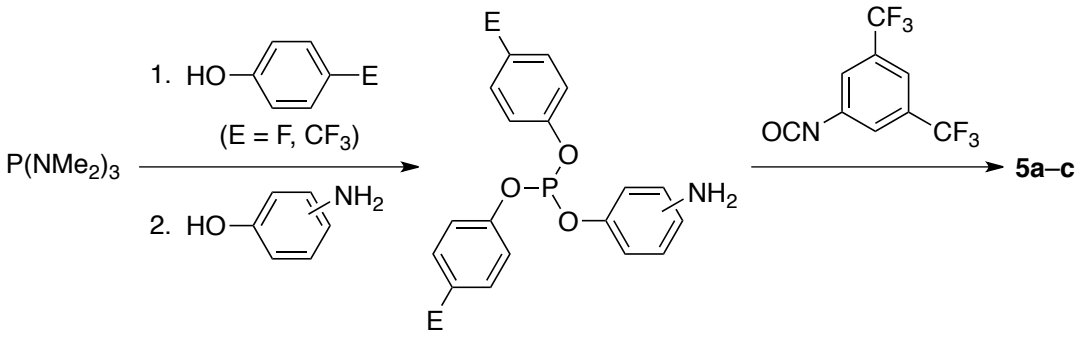


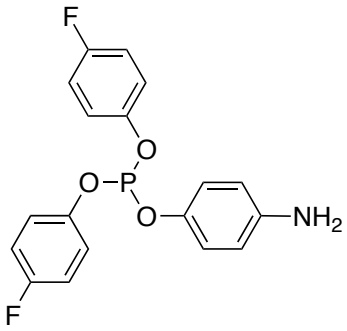
Tris(4-fluorophenyl) phosphite:[1] To a solution of 4-fluorophenol (2.43 g, 21.7 mmol) and Et_3N (3.22 mL, 23.1 mmol) in THF (140 mL) was added PCl_3 (610 μL, 7.0 mmol) dropwise at 0 °C. The mixture was warmed to ambient temperature and stirred for 20 h. The reaction mixture was filtered through a Celite pad and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane–toluene 5:1) to give tris(4-fluorophenyl) phosphite as a colorless oil (1.53 g, 60% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10–6.97 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, $J_{C\text{-}F}$ = 242 Hz, 3C), 147.1 (3C), 121.9 (d, $J_{C\text{-}F}$ = 7.7 Hz, $J_{C\text{-}P}$ = 7.7 Hz, 6C), 116.3 (d, $J_{C\text{-}F}$ = 24.0 Hz, 6C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –118.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 128.0.



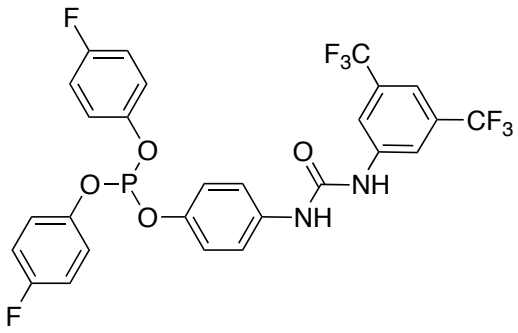
Tris(4-(trifluoromethyl)phenyl) phosphite:[1] Tris(4-(trifluoromethyl)phenyl) phosphite was prepared from PCl_3 and 4-hydroxybenzotrifluoride according to the same manner as tris(4-fluorophenyl) phosphite. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.7 Hz, 6H), 7.23 (d, J = 8.6 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8(3C), 127.3 (q, $J_{C\text{–}F}$ = 3.8 Hz, 6C), 127.0 (q, $J_{C\text{–}F}$ = 33.6 Hz, 3C), 123.9 (q, $J_{C\text{–}F}$ = 271 Hz, 3C), 120.7 (q, $J_{C\text{–}P}$ = 7.7 Hz, 6C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.2.

Preparation of Phosphite–Urea Cooperative Catalysts 5a–c.

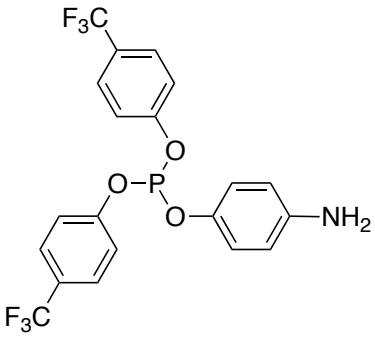




4-Aminophenyl bis(4-fluorophenyl) phosphite: To a solution of 4-fluorophenol (448 mg, 4.0 mmol) in DME (2.0 mL) was added *N*,*N*,*N*',*N*',*N*'',*N*''-hexamethylphosphinetriamine (363 μL, 2.0 mmol) at ambient temperature. The mixture was heated at reflux and stirred for 21 h, and then concentrated *in vacuo*. To a solution of the residue in acetonitrile (10.0 mL) was added 4-aminophenol (284 mg, 2.6 mmol) and *N*-phenylimidazolium trifluoromethanesulfonate salt (647 mg, 2.2 mmol) at ambient temperature. After stirring for 12 h at the same temperature, the reaction mixture was concentrated *in vacuo*. The residue was quickly purified by column chromatography on silica gel (hexane–toluene 1:1). Bulb to bulb distillation by elmination of *p*-fluorophenol (80 °C, 5 mmHg) afforded to 4-aminophenyl bis(4-fluorophenyl) phosphite (347 mg, 48% yield). IR (neat) 3458, 3379, 1871, 1623, 1498, 1186, 1091 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.10–7.04 (m, 4H), 7.04–6.96 (m, 4H), 6.91 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 3.58 (br s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3 (d, $J_{C\text{-}F}$ = 241 Hz, 2C), 147.3 (2C), 143.3 (d, $J_{C\text{-}P}$ = 2.9 Hz), 143.1, 122.0 (dd, $J_{C\text{-}F}$ = 6.7 Hz, $J_{C\text{-}P}$ = 6.7 Hz, 4C), 121.5 (d, $J_{C\text{-}P}$ = 6.7 Hz, 2C), 116.2 (d, $J_{C\text{-}F}$ = 23.8 Hz, 4C), 116.0 (2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –119.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 128.8; HRMS (FAB) calcd for $C_{18}H_{14}F_2NO_3P^+$ [M^+] 361.0679, found 361.0667.

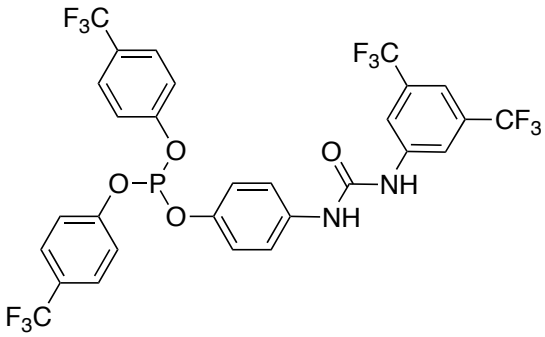


4-(3-(3,5-Bis(trifluoromethyl)phenyl)ureido)phenyl bis(4-fluorophenyl) phosphite (5a): To a solution of 4-aminophenyl bis(4-fluorophenyl) phosphite (347 mg, 0.96 mmol) in CH_2Cl_2 (3.0 mL) was added 3,5-bis(trifluoromethyl)phenyl isocyanate (200 μL, 1.15 mmol) at ambient temperature. After stirring for 3 h at the same temperature, the reaction mixture was diluted with hexane (10.0 ml) and insoluble urea starts to precipitate as a colorless solid. The solid was filtered off and washed with hexane to give **5a** (81% yield) as a product. IR (KBr) 3318, 1657, 1584, 1500, 1475, 1391, 1275, 1189, 1129 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.84 (s, 2H), 7.53 (s, 1H), 7.29 (d, J = 8.7 Hz, 2H), 7.12 (d, J = 8.7 Hz, 2H), 7.10–6.96 (m, 9H), 6.70 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (d, $J_{C\text{-}F}$ = 242 Hz, 2C), 154.2, 148.5, 147.0 (2C), 139.2, 132.9, 132.3 (q, $J_{C\text{-}F}$ = 33.4 Hz, 2C), 123.2 (2C), 123.0 (q, $J_{C\text{-}F}$ = 242 Hz, 2C), 121.8 (dd, $J_{C\text{-}F}$ = 7.6 Hz, $J_{C\text{-}P}$ = 7.6 Hz, 4C), 121.3 (d, $J_{C\text{-}P}$ = 6.7 Hz, 2C), 119.5 (2C), 116.9, 116.3 (d, $J_{C\text{-}F}$ = 22.9 Hz, 4C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –63.1, –118.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 128.0; HRMS (FAB) calcd for $C_{27}H_{18}F_8N_2O_4P^+$ [M+H$^+$] 617.0871, found 617.0874.

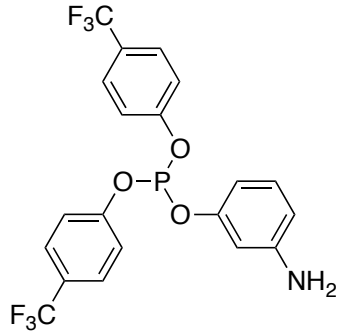


4-Aminophenyl bis(4-(trifluoromethyl)phenyl) phosphite: 4-Aminophenyl bis(4-(trifluoromethyl)phenyl) phosphite was prepared from *N*,*N*,*N*',*N*',*N*'',*N*''-hexamethylphosphinetriamine and 4-hydroxybenzotrifluoride according to the same manner as 4-aminophenyl bis(4-fluorophenyl) phosphite. IR (neat) 3383, 1612, 1507, 1416, 1324, 1207, 1169, 1123, 1067 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 8.7 Hz, 4H), 7.22 (d, J = 8.7 Hz, 4H), 6.92 (d, J = 8.7 Hz, 2H), 6.63 (d, J = 8.7 Hz, 2H), 3.62 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2 (2C), 143.4, 142.9, 127.1 (q, $J_{C\text{-}F}$ = 3.8 Hz, 4C), 126.5 (q, $J_{C\text{-}F}$ = 33.4 Hz, 2C),

124.0 (q, $J_{C\text{-}F}$ = 271 Hz, 2C), 121.5 (d, $J_{C\text{-}P}$ = 5.7 Hz, 2C), 120.7 (d, $J_{C\text{-}P}$ = 6.7 Hz, 4C), 116.1 (2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 127.5; HRMS (FAB) calcd for $C_{20}H_{14}F_6NO_3P^+$ [M^+] 461.0615, found 461.0624.

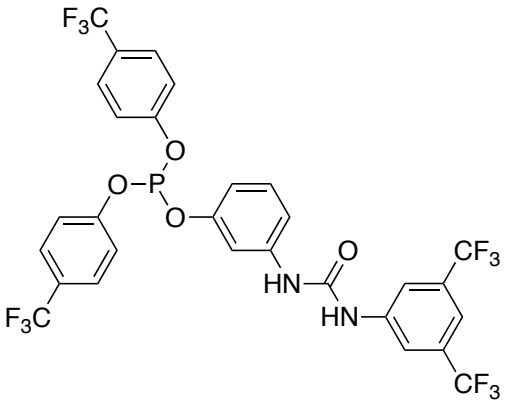


4-(3-(3,5-Bis(trifluoromethyl)phenyl)ureido)-phenyl bis(4-(trifluoromethyl)phenyl) phosphite (5b): Compound **5b** was prepared from 4-aminophenyl bis(4-(trifluoromethyl)phenyl) phosphite and 3,5-bis(trifluoromethyl)phenyl isocyanate according to the same manner as **5a**. IR (KBr) 3344, 1657, 1612, 1571, 1508, 1474, 1388, 1326, 1280, 1168, 1139, 1067 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 2H), 7.62 (d, *J* = 8.7 Hz, 4H), 7.55 (s, 1H), 7.34 (d, *J* = 8.7 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 4H), 7.14 (d, *J* =8.7 Hz, 2H), 6.78 (brs, 1H), 6.52 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.8 (2C), 153.2, 148.2, 139.4, 133.4, 132.3 (q, $J_{C\text{–}F}$ = 33.4 Hz, 2C), 127.2 (q, $J_{C\text{–}F}$ = 3.8 Hz, 4C), 126.8(q, $J_{C\text{–}F}$ = 33.4 Hz, 2C), 123.9 (q, $J_{C\text{–}F}$ = 271 Hz, 2C), 123.4 (2C), 122.9 (q, $J_{C\text{–}F}$ = 271 Hz, 2C), 121.5 (d, $J_{C\text{–}P}$ = 6.7 Hz, 2C), 120.6 (d, $J_{C\text{–}P}$ = 7.6 Hz, 4C), 119.3 (2C), 116.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.0, –63.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.7; HRMS (FAB) calcd for $C_{29}H_{17}F_{12}N_2O_4P^+$ [M^+] 716.0734, found 716.0746.

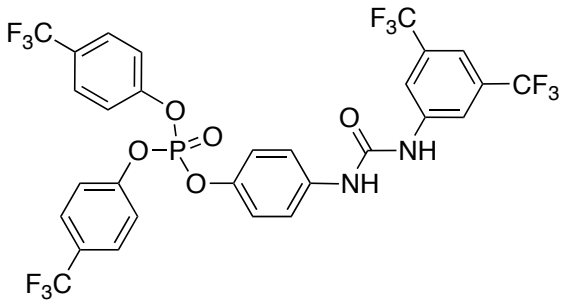


3-Aminophenyl bis(4-(trifluoromethyl)phenyl) phosphite: 3-Aminophenyl bis(4-(trifluoromethyl)phenyl) phosphite was prepared from *N*,*N*,*N*',*N*',*N*'',*N*''-hexamethylphosphinetriamine, 4-hydroxybenzotrifluoride and 3-aminophenol according to the same manner as 4-aminophenyl bis(4-fluorophenyl) phosphite. IR (KBr) 3482, 3392, 1909, 1611, 1510, 1493, 1417, 1321, 1208, 1067 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d,

J = 8.7 Hz, 4H), 7.23(d, *J* = 8.7 Hz, 4H), 7.10 (dd, *J* = 7.8, 7.8 Hz, 1H), 6.51 (*J* = 7.8 Hz, 1H), 6.48 (*J* = 7.8 Hz, 1H), 6.42 (s, 1H), 3.74 (brs, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.0 , 152.1 (d, J_{C-P} = 5.7 Hz, 2C), 148.1, 130.5, 127.2 (q, J_{C-F} = 3.4 Hz, 4C), 126.6 (q, J_{C-F} = 32.4 Hz, 2C), 124.0 (q, J_{C-F} = 271 Hz, 2C), 120.8 (d, J_{C-P} = 7.8 Hz, 4C), 111.5, 110.0 (d, J_{C-P} = 7.6 Hz), 106.8 (d, J_{C-P} = 7.6 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 127.0; HRMS (FAB) calcd for $C_{20}H_{14}F_6NO_3P^+$ [M^+] 461.0615, found 461.0614.



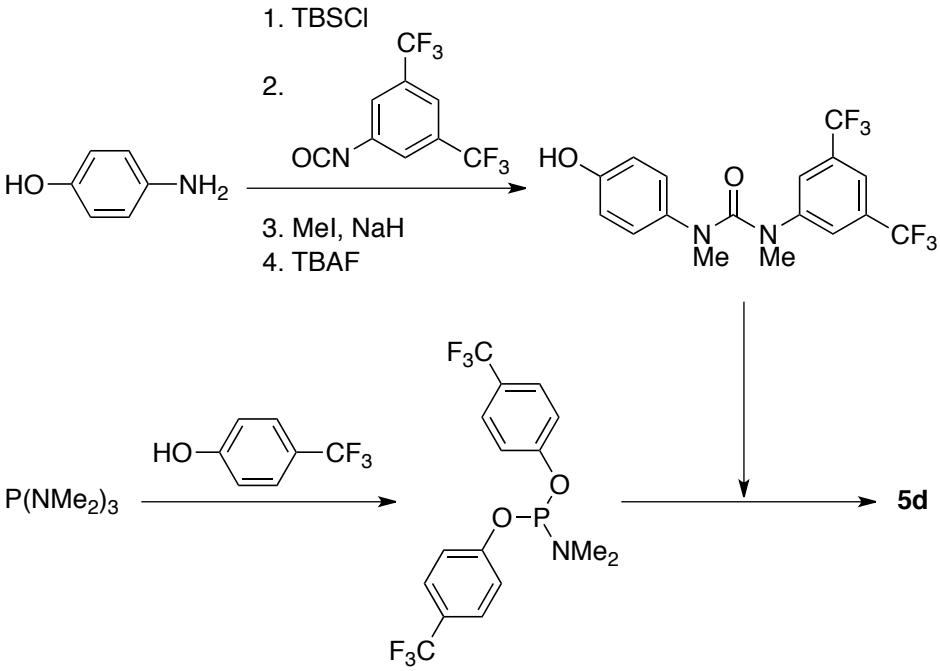
3-(3-(3,5-Bis(trifluoromethyl)phenyl)ureido)phenyl bis(4-(trifluoromethyl)phenyl) phosphite (5c): Compound **5c** was prepared from 3-aminophenyl bis(4-(trifluoromethyl)phenyl) phosphite and 3,5-bis(trifluoromethyl)phenyl isocyanate according to the same manner as **5a**. IR (KBr) 3339, 1657, 1611, 1573, 1389, 1327, 1277, 1170, 1127, 1068 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (s, 2H), 7.55 (d, *J* = 8.7 Hz, 4H), 7.48 (s, 1H), 7.44 (s, 1H), 7.35 (s, 1H), 7.24 (s, 1H), 7.22 (dd, *J* = 7.8, 7.8 Hz, 1H), 7.17 (d, *J* = 8.7 Hz, 4H), 6.93 (d, *J* = 7.8 Hz, 2H), 6.87 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.7 (2C), 153.3, 151.8, 139.1, 138.4, 132.3 (q, J_{C-F} = 33.4 Hz, 2C), 130.5, 127.1 (q, J_{C-F} = 3.8 Hz, 4C), 126.8 (q, J_{C-F} = 33.4 Hz, 2C), 123.8 (q, J_{C-F} = 270 Hz, 2C), 122.8 (q, J_{C-F} = 272 Hz, 2C), 120.6 (d, J_{C-P} = 6.7 Hz, 4C), 119.4 (2C), 117.1, 116.7, 116.5 (d, J_{C-P} = 7.6 Hz), 113.1 (d, J_{C-P} = 6.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.0, –63.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.7; HRMS (FAB) calcd for $C_{29}H_{17}F_{12}N_2O_4P^+$ [M^+] 716.0734, found 716.0735



4-(3-(3,5-Bis(trifluoromethyl)phenyl)ureido)-

phenyl bis(4-(trifluoromethyl)phenyl) phosphate: To a suspension of **5b** (143 mg, 0.2 mmol) in CH_2Cl_2 (5 mL) was added 5.5 M solution of TBHP in nonane (73 μL, 0.4 mmol) 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 recrystallized from CH_2Cl_2–heaxne to give 4-(3-(3,5-bis(trifluoromethyl)phenyl)ureido)phenyl bis(4-(trifluoromethyl)phenyl) phosphate as white solid (109 mg, 74% yield). IR (KBr) 3346, 1651, 1612, 1572, 1509, 1471, 1388, 1326, 1280, 1170, 1146, 1068 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (br s, 1H), 7.77 (s, 2H), 7.68 (d, J = 8.7 Hz, 4H), 7.48 (s, 1H), 7.38 (d, J = 8.7 Hz, 4H), 7.19 (brs, 1H), 7.09 (s, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 152.0 (d, J_{C-P} = 7.6 Hz, 2C), 144.9 (q, J_{C-F} = 7.6 Hz), 140.3, 136.5, 132.1 (q, J_{C-F} = 33.4 Hz, 2C), 129.1 (q, J_{C-F} = 34.3 Hz, 2C), 127.8 (q, J_{C-F} = 3.8 Hz, 4C), 123.3 (q, J_{C-F} = 271 Hz, 2C), 123.1 (q, J_{C-F} = 271 Hz, 2C), 121.8 (2C), 120.3 (d, J_{C-P} = 4.8 Hz, 2C), 120.2 (d, J_{C-P} = 4.8 Hz, 4C), 118.0 (2C), 115.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.4, –63.0; ^{31}P NMR (162 MHz, $CDCl_3$) δ –16.5; HRMS (FAB) calcd for $C_{29}H_{17}F_{12}N_2O_5P^+$ [M^+] 732.0683, found 732.0697.

Preparation of 4-(3-(3,5-bis(trifluoromethyl)phenyl)-1,3-dimethylureido)phenylbis(4-(trifluoromethyl)phenyl) phosphite (5d).



To a solution of 4-aminophenol (1.09 g, 10.0 mmol) and imidazole (2.04 g, 30.0 mmol) in THF

(20.0 mL) was added TBSCl (3.80 g, 15.0 mmol) at 0 °C. After stirring for 3 h at ambient temperature, the reaction was quenched with saturated aqueous $NaHCO_3$. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 50:1) to give 4-(*tert*-butyldimethylsilanyloxa)-phenyl aniline as pale yellow oil (2.17 g, 97% yield).

To a solution of 4-(*tert*-butyldimethylsilanyloxa)-phenyl aniline (2.17 g, 9.7 mmol) in CH_2Cl_2 (20 mL) was added 3,5-bis(trifluoromethyl)phenyl isocyanate (2.47 g, 9.7 mmol) at ambient temperature. After stirring for 1 h at the same temperature, the reaction mixture was diluted with hexane (10.0 mL) and insoluble urea starts to precipitate as a colorless solid. The solid was filtered off and washed with hexane to give 1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)urea a colorless solid (8.54 g, 90% yield).

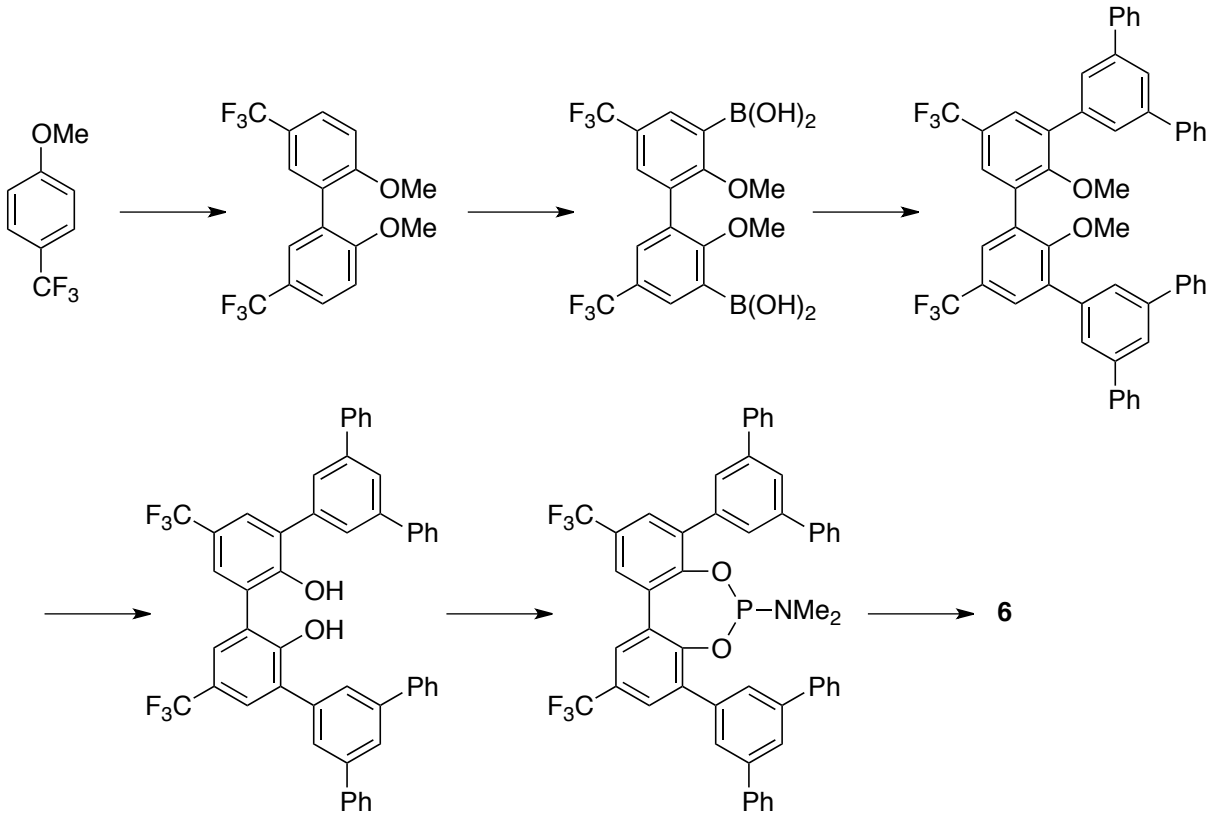
To a solution of 1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-((*tert*-butyldimethylsilyl)oxy)-phenyl)urea (957 mg, 2 mmol) in THF (4.0 mmol) was added NaH (60% dispersion in oil; 160 mg, 4.0 mmol) at 0 °C. After stirring for 0.5 h, CH_3I (249 μL, 4.0 mmol) was added. After stirring for 1 h at ambient temperature, the reaction was quenched with saturated aqueous NH_4Cl. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 50:1) to give 1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-1,3-dimethylurea as pale yellow oil (729 mg, 72% yield).

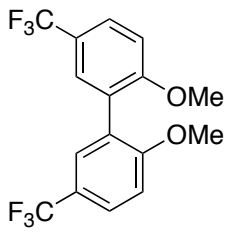
To a solution of 1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-((*tert*-butyldimethylsilyl)oxy)phenyl)-1,3-dimethylurea (729 mg, 1.44 mmol) in THF (7.0 mL) was added a THF solution of TBAF (1 M; 2.16 mL, 2.16 mmol) at ambient temperature. After stirring for 3 h at the same temperature, the reaction mixture was quenched with brine. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 2:1) to give 1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-hydroxyphenyl)-1,3-dimethylurea as a colorless solid (475 mg, 84% yield). ^{1}H NMR (400 MHz, acetone-d_6) δ 7.48 (s, 3H), 6.72 (d, J = 8.2 Hz, 2H), 6.55 (d, J = 8.2 Hz, 2H), 3.82 (s, 1H), 3.19 (s, 3H), 3.16 (s, 3H); 13C NMR (100 MHz, acetone-d_6) δ 160.3, 156.0, 148.2, 137.3, 132.1 (q, J_{C-F} = 33.6 Hz, 2C), 127.8 (2C), 125.0 (2C), 124.0 (q, J_{C-F} = 272 Hz, 2C), 117.3 (2C), 116.2 (2C), 39.8, 38.5.

To a solution of 4-fluorophenol (224 mg, 2.0 mmol) in DME (1.0 mL) was added *N*,*N*,*N*',*N*',*N*'',*N*''-hexamethylphosphinetriamine (181 mL,1.0 mmol) at ambient temperature. The mixture was heated at reflux and stirred for 21 h, and then concentrated *in vacuo*. To a solution of

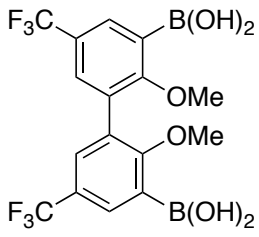
the residue in toluene (2 mL) was added 1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-hydroxyphenyl)-1,3-dimethylurea (510 mg, 1.3 mmol) at reflux. After stirring for 2 h at the same temperature, the reaction mixture was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane–EtOAc 5:1) to give **5d** as colorless oil (156 mg, 21% yield). IR (neat) 1664, 1615, 1504, 1472, 1383, 1278, 1170 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, J = 8.7 Hz, 4H), 7.39 (s, 1H), 7.19 (d, J = 8.7 Hz, 4H), 6.81 (d, J = 8.7 Hz, 2H), 6.73 (d, J =8.7 Hz, 2H), 3.26 (s, 3H), 3.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8 (2C), 153.8, 148.7 (d, J_{C-P} = 3.8 Hz), 146.7, 141.2, 132.1 (q, J_{C-F} = 33.4 Hz, 2C), 127.2 (q, J_{C-F} = 3.8 Hz, 4C), 126.8 (q, J_{C-F} = 32.6 Hz, 2C), 125.0, 123.9 (q, J_{C-F} = 272 Hz, 2C), 122.7 (q, J_{C-F} = 273 Hz, 2C), 120.8 (d, J_{C-P} = 7.7 Hz, 2C), 120.6 (d, J_{C-P} = 7.7 Hz, 4C), 117.8 (4C), 115.4, 39.6, 38.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 126.2; HRMS (FAB) calcd for $C_{31}H_{21}F_{12}N_2O_4P^+$ [M^+] 744.1047, found 744.1071.

Preparation of Phosphite–Urea Cooperative Catalyst 6.



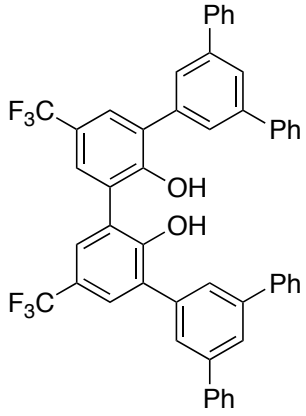


2,2'-Dimethoxy-5,5'-bis(trifluoromethyl)-1,1'-biphenyl: To a suspension of $NiBr_2$ (1.01 g, 4.63 mmol) in THF (25.0 mL) was added PPh_3 (2.43 g, 9.25 mmol) at ambient temperature. The mixture was heated at 80 °C for 0.5 h. After cooling to ambient temperature, Zn (909 mg, 13.9 mmol), Et_4NI (2.38 g, 9.25 mmol) and 2-bromo-1-methoxy-4-(trifluoromethyl)benzene (2.36 g, 9.25 mmol) in THF (5.0 mL) were added. The mixture was stirred at 50 °C for 58 h. After cooling to ambient temperature, 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–EtOAc 10:1) to give 2,2'-dimethoxy-5,5'-bis(trifluoromethyl)-1,1'-biphenyl as a colorless solid (770 mg, 48% yield). IR (KBr) 1609, 1515, 1498, 1345, 1329, 1263, 1105 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.62 (dd, J = 8.7, 1.8 Hz, 2H), 7.49 (d. J = 1.8 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 3.82 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4 (2C), 128.4 (q, J_{C-F} = 3.8Hz, 2C), 126.8 (2C), 126.6 (q, J_{C-F} = 3.8 Hz, 2C), 124.4 (q, J_{C-F} = 271 Hz, 2C), 122.6 (q, J_{C-F} = 32.8 Hz, 2C), 110.8 (2C), 55.8 (2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.3; HRMS (FAB) calcd for $C_{16}H_{12}F_6O_2^+$ [M^+] 350.0741, found 350.0751.



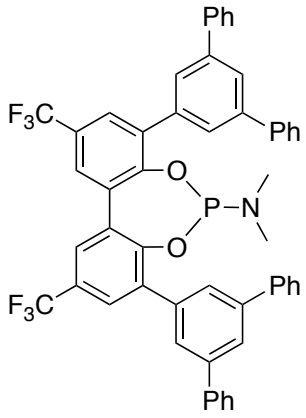
(2,2'-Dimethoxy-5,5'-bis(trifluoromethyl)-[1,1'-biphenyl]-3,3'-diyl)diboronic acid: To a solution of 2,2'-dimethoxy-5,5'-bis(trifluoromethyl)-1,1'-biphenyl (1.05 g, 3.0 mmol) in Et_2O (30.0 mL) were added TMEDA (1.35 mL, 9.0 mmol) and 1.6 M solution of BuLi in hexane (5.6 mL, 9.0 mmol) at ambient temperature. After stirring for 3 h, the reaction mixture was cooled to –78 °C, and then added triethyl borate (3.55 mL, 21.0 mmol) dropwise. The mixture was warmed to ambient temperature and stirred for 11 h. To the mixture was added 1 M HCl (20.0 mL) solution and stirred at ambient temperature for 9 h. The aqueous layer was extracted with EtOAc, and the organic extract was washed with 1 M HCl solution and brine, dried over Na_2SO_4, filtered. The solvent was evaporated to leave a volume of 5 mL. To the residue was added hexane (50 mL), and the resulting solid was filtered and washed with hexane to give (2,2'-dimethoxy-5,5'-bis(trifluoromethyl)-[1,1'-biphenyl]-3,3'-diyl)diboronic acid as pale yellow

solid (990 mg, 75% yield). IR (KBr) 3410, 1606, 1590, 1469, 1431, 1302, 1158, 1123 cm^{-1}; ^1H NMR (400 MHz, THF–d_8) δ 7.96 (d, J = 2.3 Hz, 2H), 7.66 (d, J = 2.3Hz, 2H), 7.52 (s, 4H), 3.53 (s, 6H); ^{13}C NMR (100 MHz, THF–d_8) δ 166.0 (2C), 133.5 (2C), 131.3 (4C), 128.4 (2C), 125.9 (q, J_{C-F} = 32.4 Hz, 2C), 125.5 (q, J_{C-F} = 271 Hz, 2C), 61.7 (2C); ^{19}F NMR (376 MHz, THF–d_8) δ –62.5; HRMS (FAB, ester of (2,2'-dimethoxy-5,5'-bis(trifluoromethyl)-[1,1'-biphenyl]-3,3'-diyl)diboronic acid with 1,3-propanediol) calcd for $C_{22}H_{22}B_2F_6O_6^+$ [M^+] 518.1507, found 518.1488.

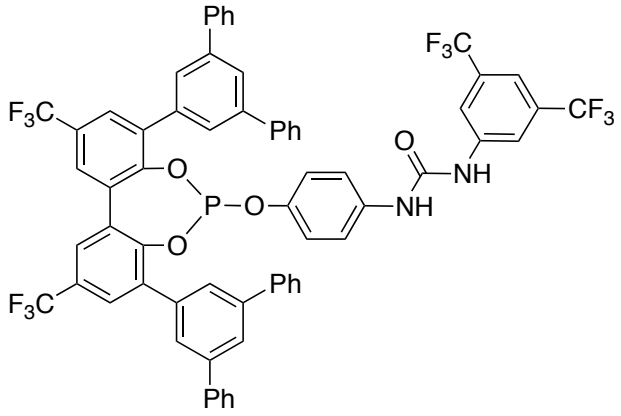


3,3'-Di([1,1':3',1''-terphenyl]-5'-yl)-5,5'-bis(trifluoromethyl)-[1,1'-biphenyl]-2,2'-diol: To a solution of [1,1':3',1"-terphenyl]-5'-ol (4.93 g, 20.0 mmol) and pyridine (3.22 mL, 40.0 mmol) in CH_2Cl_2 (50.0 mL) was added trifluoromethanesulfonic anhydride (4.03 mL, 24.0 mmol) at 0 °C. The mixture was warmed to ambient temperature and stirred for 2 h. The reaction was quenched with saturated aqueous NH_4Cl and extracted with $CHCl_3$. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 5:1) to give [1,1':3',1"-terphenyl]-5'-yl trifluoromethanesulfonate as white solid (7.38 g, 98% yield). To a solution of (2,2'-dimethoxy-5,5'-bis(trifluoromethyl)-[1,1'-biphenyl]-3,3'-diyl)diboronic acid (427 mg, 1.0 mmol) in dioxane–water (16.0 mL, 3:1 v/v) were added [1,1':3',1"-terphenyl]-5'-yl trifluoromethanesulfonate (1.51 g, 4.0 mmol), $Ba(OH)_2{\cdot}8H_2O$ (946 mg, 3.0 mmol), and $Pd(PPh_3)_4$ (58 mg, 0.05 mmol) at ambient temperature. The mixture was stirred at reflux for 19 h. After cooling to ambient temperature, the reaction was quenched with 1 M HCl solution. To the mixture was added THF until a solid was dissolved, then extracted with EtOAc. The combined organic layers were dried over anhydrous Na_2SO_4, filtered and concentrated to give crude coupling products. To a solution of these crude products in CH_2Cl_2 (10.0 mL) was added a 1.0 M solution of BBr_3 in CH_2Cl_2 (4.0 mL, 4.0 mmol) at 0 °C. After stirring for 1 day at 0 °C, the reaction was quenched with water. The mixture was extracted with $CHCl_3$, and 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 10:1) to give 3,3'-di([1,1':3',1''-terphenyl]-5'-yl)-5,5'-bis(trifluoromethyl)-[1,1'-biphenyl]-2,2'-diol as a white solid (493 mg, 63% yield). IR (KBr) 3513, 1594, 1498, 1384, 1310, 1224, 1172, 1119 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (t, J = 1.4 Hz, 2H), 7.76–7.71 (m, 6H), 7.71–7.64 (m, 10H), 7.47 (t, J = 7.3 Hz, 8H), 7.40 (t, J = 7.3 Hz, 4H), 6.12 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.5 (2C), 143.0 (4C), 140.3 (4C), 136.6 (4C), 126.9 (4C), 128.9 (8C), 128.4 (2C), 127.93 (2C), 127.87 (2C), 127.3 (8C), 126.8 (2C), 126.3 (2C), 124.7 (2C), 124.1 (q, J_{C-F} = 271 Hz, 2C), 123.9 (q, J_{C-F} = 32.4 Hz, 2C); ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.3; HRMS (FAB) calcd for $C_{50}H_{32}F_6O_2^+$ [M^+] 778.2306, found 778.2291.

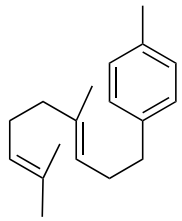


4,8-Di([1,1':3',1''-terphenyl]-5'-yl)-*N*,*N*-dimethyl-2,10-bis(trifluoromethyl)dibenzo[*d*,*f*][1,3,2]dioxaphosphepin-6-amine: To a solution of 3,3'-di([1,1':3',1''-terphenyl]-5'-yl)-5,5'-bis(trifluoromethyl)-[1,1'-biphenyl]-2,2'-diol (493 mg, 0.63 mmol) and 1*H*-tetrazole (132 mg, 1.89 mmol) in THF (6.0 mL) was added *N*,*N*,*N*',*N*',*N*'',*N*''-hexamethylphosphinetriamine (228 μL, 1.26 mmol). The reaction mixture was heated at reflux for 4 h. After cooling to ambient temperature, the mixture was filtered through a Celite pad and a silica gel pad, washed with toluene, and the filtrate was concentrated to give 4,8-di([1,1':3',1''-terphenyl]-5'-yl)-*N*,*N*-dimethyl-2,10-bis(trifluoromethyl)dibenzo[*d*,*f*][1,3,2]dioxaphosphepin-6-amine as a colorless solid (513 mg, 96% yield). IR (KBr) 1596, 1497, 1386, 1312, 1226, 1152, 1122 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88–7.80 (m, 10H), 7.68 (d, J =7.4 Hz, 8H), 7.47 (t, J = 7.4 Hz, 8H), 7.39 (t, J = 7.4 Hz, 4H), 2.16 (s, 3H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2 (2C), 141.9 (4C), 140.7 (4C), 137.4 (4C), 135.6 (4C), 132.1 (2C), 128.9 (8C), 127.9 (2C), 127.7 (2C), 127.24 (10C), 127.19 (q, J_{C-F} = 32.6 Hz, 2C), 126.4 (2C), 125.7 (2C), 123.9 (q, J_{C-F} = 272 Hz, 2C), 34.8, 34.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.5; ^{31}P NMR (162 MHz, $CDCl_3$) δ 151.3; HRMS (FAB) calcd for $C_{52}H_{37}F_6NO_2P^+$ [M+H^+] 852.2461, found 852.2457.



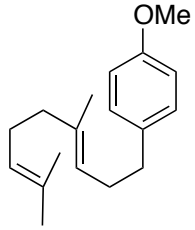
1-(3,5-bis(trifluoromethyl)phenyl)-3-(4-((4,8-di([1,1':3',1''-terphenyl]-5'-yl)-2,10-bis(trifluoromethyl)dibenzo[*d*,*f*][1,3,2]dioxaphosphepin-6-yl)oxy)phenyl)urea (6): To a solution of 4,8-di([1,1':3',1''-terphenyl]-5'-yl)-*N*,*N*-dimethyl-2,10-bis(trifluoromethyl)dibenzo[*d*,*f*][1,3,2]dioxaphosphepin-6-amine (513 mg, 0.60 mmol) and *N*-phenylimidazolium trifluoromethanesulfonate salt (194 mg, 0.66 mmol) in CH_3CN/CH_2Cl_2 (6.0 mL, 1:1) was added 4-aminophenol (75 mg, 0.69 mmol). The mixture was stirred at 60 °C for 9 h, cooled to ambient temperature, and concentrated *in vacuo*. To the residue was added toluene, filtered through a Celite pad, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (hexane–toluene 1:1) to give 4-((4,8-di([1,1':3',1''-terphenyl]-5'-yl)-2,10-bis(trifluoromethyl)dibenzo[*d*,*f*][1,3,2]dioxaphosphepin-6-yl)oxy)aniline (462 mg, 84% yield). To a solution of this aniline (462 mg, 0.50 mmol) in CH_2Cl_2 (2.0 mL) was added 1-isocyanato-3,5-bis(trifluoromethyl)benzene (104 μL, 0.60 mmol) at ambient temperature. After stirring for 0.5 h, the mixture was added hexane, cooled to –78 °C, then an insoluble compound precipitated as a colorless solid. The solid was filtered off and washed with cooled hexane to give **6** as colorless solid (503 mg, 86% yield). IR (KBr) 1507, 1386, 1313, 1280, 1185, 1160, 1129 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.94–7.83 (m, 6H), 7.80–7.72 (m, 6H), 7.62 (d, J = 7.4 Hz, 8H), 7.52 (s, 1H), 7.43 (t, J = 7.4 Hz, 8H), 7.34 (t, J = 7.4 Hz, 4H), 6.70 (d, J = 8.7 Hz, 2H), 6.44 (s, 1H), 6.24 (d, J = 8.7 Hz, 2H), 6.07 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 148.5 (2C), 142.1 (4C), 140.4 (4C), 139.5, 137.0 (4C), 136.2 (4C), 132.7, 132.2 (q, J_{C-F} = 33.4 Hz, 2C), 131.9, 128.9 (10C), 128.33 (q, J_{C-F} = 32.4 Hz, 2C), 128.31 (2C), 127.8 (2C), 127.3 (2C), 127.2 (8C), 126.7 (2C), 125.8 (2C), 124.0 (2C), 123.7 (q, J_{C-F} = 271 Hz, 2C), 123.0 (q, J_{C-F} = 272 Hz, 2C), 120.5 (q, J_{C-P} = 7.6 Hz, 2C), 119.1 (2C), 116.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ –61.8, –62.9; ^{31}P NMR (162 MHz, $CDCl_3$) δ 144.7; HRMS (FAB) calcd for $C_{65}H_{40}F_{12}N_2O_4P^+$ [M+H$^+$] 1171.2529, found 1171.2529.

Preparation of Homogeranylarenes 1.



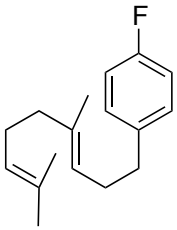
(*E*)-1-(4,8-Dimethylnona-3,7-dien-1-yl)-4-methylbenzene (1a):[2,3]

Compound **1a** was prepared from 4-methylbenzyl magnesium chloride and (*E*)-geranyl diethyl phosphate according to the reported procedure.[3] ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 4H), 5.18 (t, *J* = 7.4 Hz, 1H), 5.09 (t, *J* = 6.9 Hz, 1H), 2.60 (t, *J* = 7.4 Hz, 2H), 2.32 (s, 3H), 2.28 (dt, *J* = 7.4, 7.4 Hz, 2H), 2.06 (dt, *J* = 6.9, 7.8 Hz, 2H), 1.97 (t, *J* = 7.8 Hz, 2H), 1.69 (s, 3H), 1.60 (s, 3H), 1.56 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 135.6, 135.0, 131.3, 128.9 (2C), 128.3 (2C), 124.3, 123.7, 39.7, 35.7, 30.1, 26.7, 25.7, 21.0, 17.7, 16.0.



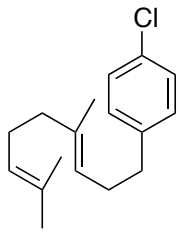
(*E*)-1-(4,8-Dimethylnona-3,7-dien-1-yl)-4-methoxybenzene (1b):[2c]

Compound **1b** was prepared from (4-methoxybenzyl)magnesium chloride and (*E*)-geranyl diethyl phosphate according to the same manner as **1a**. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.7 Hz, 2H), 6.82 (d, *J* = 8.7 Hz, 2H), 5.17 (t, *J* = 7.3 Hz, 1H), 5.09 (t, *J* = 6.9 Hz, 1H), 3.79 (s, 3H), 2.58 (t, *J* = 7.8 Hz, 2H), 2.26 (dt, *J* = 7.3, 7.8 Hz, 2H), 2.06 (dt, *J* = 6.9, 7.3 Hz, 2H), 1.97 (t, *J* = 7.3 Hz, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.55 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.6, 135.6, 134.5, 131.3, 129.3 (2C), 124.3, 123.6, 113.6 (2C), 55.2, 39.7, 35.2, 30.2, 26.7, 25.7, 17.7, 16.0.

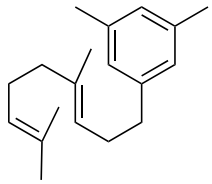


(*E*)-1-(4,8-Dimethylnona-3,7-dien-1-yl)-4-fluorobenzene (1c): Compound **1c** was prepared from (4-fluorobenzyl)magnesium chloride and (*E*)-geranyl diethyl phosphate according to the same manner as **1a**. Colorless liquid; IR (neat) 1602, 1509, 1448, 1376, 1223, 1157 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.13 (dd, J_H = 8.7 Hz, J_{H-F} = 5.7 Hz, 2H), 6.95 (dd, J_H = 8.7 Hz, J_{H-F} = 8.7 Hz, 2H), 5.15 (t, *J* = 7.3 Hz, 1H), 5.08 (t, *J* = 6.9 Hz, 1H), 2.61 (t, *J* = 7.8 Hz, 2H),

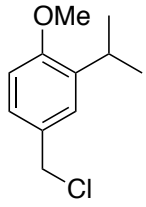
2.27 (dt, J = 7.3, 7.8 Hz, 2H), 2.05 (dt, J = 6.9, 7.3 Hz, 2H), 1.97 (t, J = 7.3 Hz, 2H), 1.68 (s, 3H), 1.61 (s, 3H), 1.53 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.2 (d, J_{C-F} = 242 Hz), 137.9 (d, J_{C-F} = 2.9 Hz), 135.9, 131.3, 129.7 (d, J_{C-F} = 7.6 Hz, 2C), 124.3, 123.3, 114.8 (d, J_{C-F} = 20.0 Hz, 2C), 39.7, 35.2, 30.0, 26.7, 25.6, 17.6, 15.9; HRMS (FAB) calcd for $C_{17}H_{23}F^+$ [M^+] 246.1784, found 246.1805.



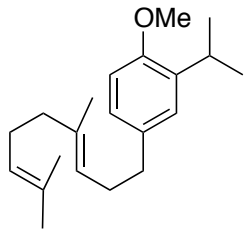
(*E*)-1-(4,8-Dimethylnona-3,7-dien-1-yl)-4-chlorobenzene (1d): Compound **1d** was prepared from (4-chlorobenzyl)magnesium chloride and (*E*)-geranyl diethyl phosphate according to the same manner as **1a**. Colorless liquid; IR (neat) 1638, 1492, 1449, 1406, 1376, 1092 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 8.2 Hz, 2H), 7.10 (d, J = 8.2 Hz, 2H), 5.13 (t, J = 7.3 Hz, 1H), 5.06 (t, J = 7.3 Hz, 1H), 2.59 (t, J = 7.8 Hz, 2H), 2.26 (dt, J = 7.3, 7.8 Hz, 2H), 2.04 (dt, J = 7.3, 7.3 Hz, 2H), 1.96 (t, J = 7.3 Hz, 2H), 1.67 (s, 3H), 1.59 (s, 3H), 1.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.7, 136.1, 131.35, 131.29, 129.8 (2C), 128.2 (2C), 124.2, 123.1, 39.6, 35.4, 29.7, 26.6, 25.7, 17.7, 15.9; HRMS (FAB) calcd for $C_{17}H_{23}Cl^+$ [M^+] 262.1488, found 262.1464.



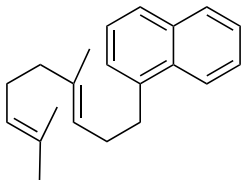
(*E*)-1-(4,8-Dimethylnona-3,7-dien-1-yl)-3,5-dimethylbenzene (1e): Compound **1e** was prepared from (3,5-dimethylbenzyl)magnesium chloride and (*E*)-geranyl diethyl phosphate according to the same manner as **1a**. Colorless liquid; IR (neat) 1606, 1450, 1376 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.82 (s, 3H), 5.19 (t, J = 6.9 Hz, 1H), 5.10 (t, J = 6.9 Hz, 1H), 2.55 (t, J = 6.9 Hz, 2H), 2.31–2.23 (m, 2H), 2.29 (s, 6H), 2.11–2.02 (m, 2H), 2.02–1.94 (m, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 137.6, 135.5, 131.3, 127.3 (2C), 126.3 (2C), 124.3, 123.8, 39.7, 36.0, 30.1, 26.8, 25.7, 21.3 (2C), 17.7, 16.0 ; HRMS (FAB) calcd for $C_{19}H_{29}^+$ [M+H$^+$] 257.2264, found 257.2248.



4-(Chloromethyl)-2-isopropyl-1-methoxybenzene: To the solution of PPh_3 (2.22 g, 8.5 mmol) in CCl_4 (6.0 mL) was added (3-isopropyl-4-methoxyphenyl)methanol (1.17 g, 6.5 mmol) at ambient temperature. The mixture was heated at 90 °C for 1 h. After cooling to ambient temperature, the mixture was added pentane, filtered through Celite, concentrated *in vacuo*. Bulb to bulb distillation by purification (120 °C, 80 Pa) afforded to 4-(chloromethyl)-2-isopropyl-1-methoxybenzene as a colorless oil (908 mg, 70% yield). IR (neat) 1608, 1500, 1464, 1250, 1172, 1116, 1091, 1033 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, J = 1.8 Hz, 1H), 7.19 (dd, J = 8.2, 1.8 Hz, 1H), 6.81 (d, J = 1.8 Hz, 1H), 4.58 (s, 2H), 3.83 (s, 3H), 3.30 (septet, J = 6.9 Hz, 1H), 1.21 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 137.3, 129.4, 127.1, 126.7, 110.3, 55.4, 46.8, 26.7, 22.5 (2C); HRMS (FAB) calcd for $C_{11}H_{15}ClO^+$ [M^+] 198.0811, found 198.0811.

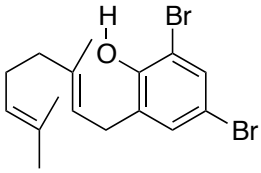


(*E*)-4-(4,8-Dimethylnona-3,7-dien-1-yl)-2-isopropyl-1-methoxybenzene (1f): Compound **1f** was prepared from (3-isopropyl-4-methoxybenzyl)magnesium chloride and (*E*)-geranyl diethyl phosphate according to the same manner as **1a**. Colorless liquid; IR (neat) 1608, 1498, 1463, 1245, 1171, 1091, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.02 (d, J = 2.3 Hz, 1H), 6.97 (dd, J = 2.3, 8.2 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 5.19 (t, J = 7.3 Hz, 1H), 5.10 (t, J = 7.3 Hz, 1H), 3.80 (s, 3H), 3.29 (septet, J = 6.9 Hz, 1H), 2.57 (t, J = 7.8 Hz, 2H), 2.27 (dt, J = 7.3, 7.8 Hz, 2H), 2.06 (dt, J = 7.3, 7.3 Hz, 2H), 1.97 (t, J = 7.3 Hz, 2H), 1.68 (s, 3H), 1.60 (s, 3H), 1.56 (s, 3H), 1.20 (d, J = 6.9 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.8, 136.6, 135.4, 134.3, 131.3, 126.2, 126.1, 124.4, 123.8, 110.2, 55.4, 39.7, 35.5, 30.3, 26.73, 26.65, 25.7, 22.7 (2C), 17.7, 16.0; HRMS (FAB) calcd for $C_{21}H_{32}O^+$ [M^+] 300.2453, found 300.2465.



(*E*)-1-(4,8-Dimethylnona-3,7-dien-1-yl)naphthalene (1g):[4] Compound **1g** was prepared from (naphthalen-1-ylmethyl)magnesium bromide and (*E*)-geranyl acetate according to the reported procedure.[4,5] Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 8.2 Hz, 1H), 7.85 (d, *J* = 8.7 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.54–7.43 (m, 2H), 7.40 (dd, *J* = 7.4, 8.3 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 5.28 (t, *J* = 7.3 Hz, 1H), 5.11 (t, *J* = 6.9 Hz, 1H), 3.10 (t, *J* = 7.8 Hz, 2H), 2.44 (dt, *J* = 7.3, 7.8 Hz, 2H), 2.07 (dt, *J* = 6.9, 7.8 Hz, 2H), 1.99 (t, *J* = 7.8 Hz, 2H), 1.69 (s, 3H), 1.61 (s, 3H), 1.54 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.4, 135.9, 133.8, 131.9, 131.4, 128.7, 126.5, 125.9, 125.6, 125.5, 125.3, 124.3, 123.8, 123.7, 39.7, 33.2, 29.2, 26.7, 25.7, 17.7, 16.0.

Preparation of 2,4-Dibromo-6-geranylphenol.



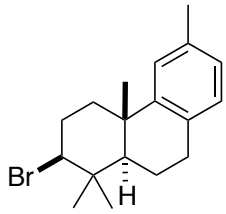
2,4-Dibromo-6-geranylphenol: To a solution of 2,4-dibromophenol (1.39 g, 5.5 mmol) in toluene was added sodium hydride (abt. 60% oil suspension) (220 mg, 5.5 mmol) at 0 °C. After stirring for 2 h, then geranyl chloride (927 μL, 5 mmol) was added. The mixture was warmed to ambient temperature and stirred for 11 h. The reaction was quenched with saturated aquerous $NaHCO_3$. The mixture was extracted with Et_2O, and 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 98:2) to give 2,4-dibromo-6-geranylphenol as a yellow oil (775 mg, 40% yield). IR (neat) 3515, 1457, 1401, 1319, 1234, 1138cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 2.3 Hz, 1H), 7.18 (d, *J* = 2.3 Hz, 1H), 5.60 (s, 1H), 5.27 (t, *J* = 7.3 Hz, 1H), 5.09 (t, *J* = 6.9 Hz, 1H), 3.35 (t, *J* = 7.3 Hz, 2H), 2.16–2.03 (m, 4H), 1.70 (s, 3H), 1.69 (s, 3H), 1.60 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.5, 138.2, 131.8, 131.7, 131.4, 130.9, 123.9, 120.4, 112.3, 110.6, 39.6, 29.0, 26.4, 25.7, 17.7, 16.1; HRMS (EI) calcd for $C_{16}H_{20}Br_2O^+$ [M^+] 385.9881, found 385.9872.

General Procedure for Selective Bromocyclization of Homogeranylarenes 1

To a solution of **6** (1.8 mg, 0.0015 mmol) in toluene (1.5 mL) were added DBH (94.4 mg, 0.33 mmol) and **1** (0.30 mmol) successively at –78 °C, and the mixture was stirred at –78 °C for 0.5 h and then at –60 °C for 24–30 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 yields were evaluated from the ratio of **2a**, *endo*-**3a**, *exo*-**3a** and **4a** which was determined by ^{1}H NMR analysis: δ 4.04 (dd, *J* = 12.4, 4.1 Hz, 1H, **2a**), 4.17 (dd, *J* = 6.9, 9.6 Hz, 1H, *endo*-**3a**), 4.11 (dd, *J* = 4.6, 11.5 Hz, 1H, *exo*-**3a**), and 5.29 (t, *J* = 6.9 Hz, 1H, **4a**).

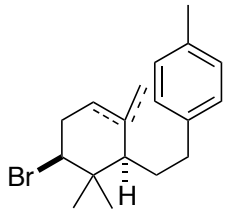
The crude product was purified by column chromatography on silica gel using hexane as an eluent. The resulting mixture of **2**, *endo*-**3** and *exo*-**3** was used for the next cyclization without further separation. To a solution of the resulting mixture of **2**, *endo*-**3** and *exo*-**3**, which were obtained in the above reaction, in *i*-$PrNO_2$ (4.5 mL) were added TFA (230 μL, 3.0 mmol), and 1 M $SnCl_4$ solution in hexane (600 μL, 0.60 mmol) at –78 °C. The mixture was stirred at –40 °C for 24–39 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 residue was purified by column chromatography on silica gel using hexane as an eluent, to give **2**.

The corresponding physical and spectroscopic data for **2** are as follows.

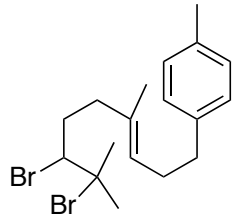


2-Bromo-1,1,4a,6-tetramethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (2a): Pale yellow solid; IR (KBr) 1611, 1500, 1438, 1377, 1261, 1096, 1066, 1032 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.00 (s, 1H), 6.98–6.88 (m, 2H), 4.04 (dd, *J* = 12.4, 4.1 Hz, 1H), 2.96–2.77 (m, 2H), 2.42–2.21 (m, 2H), 2.28 (s, 3H), 1.95 (ddt, *J* = 2.3, 6.9, 13.3 Hz, 1H), 1.85–1.71 (m, 1H), 1.58 (td, *J* = 3.2, 11.9 Hz, 1H), 1.45 (dd, *J* = 2.3, 11.9 Hz, 1H), 1.23 (s, 3H), 1.15 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 135.1, 131.5, 128.9, 126.5, 124.9, 68.9, 51.2, 39.9, 39.8, 37.8, 31.5, 30.5, 30.4, 24.8, 21.2, 20.6, 18.2; HRMS (FAB) calcd for $C_{18}H_{25}Br^+$ [M^+] 320.1140, found 320.1138.

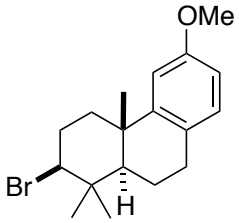
***Cis*-isomer of 2a:** ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.13 (dd, *J* = 5.0, 11.0 Hz, 1H), 1.21 (s, 3H), 1.09 (s, 3H), 0.44 (s, 3H), and other resonances could not be discerned.



1-(2-(5-Bromo-2,6,6-trimethylcyclohex-2-en-1-yl)ethyl)-4-methylbenzene (*endo*-3a), 1-(2-(3-Bromo-2,2-dimethyl-6-methylenecyclohexyl)ethyl)-4-methylbenzene (*exo*-3a): Compounds ***endo*-3a**, and ***exo*-3a** could not be separated by column chromatography on silica gel. ***endo*-3a:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.23 (brs, 1H), 4.17 (dd, *J* = 6.9, 9.6 Hz, 1H), 1.07 (s, 3H), 0.88 (s, 3H). Other resonances could not be discerned for this compound. ***exo*-10:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.99 (s, 1H), 4.76 (s, 1H), 4.11 (dd, *J* = 4.6, 11.5 Hz, 1H), 1.12 (s, 3H), 0.82 (s, 3H). Other resonances could not be discerned for this compound.



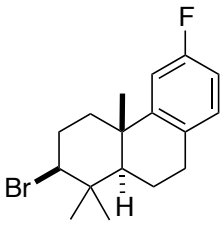
(*E*)-1-(7,8-Dibromo-4,8-dimethylnon-3-en-1-yl)-4-methylbenzene (4a): Colorless solid; IR (neat) 1516, 1456, 1370, 1097 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.09 (s, 4H), 5.29 (t, *J* = 6.9 Hz, 1H), 4.09 (dd, *J* = 0.9, 11.0 Hz, 1H), 2.62 (t, *J* = 7.8 Hz, 2H), 2.46–2.56 (m, 1H), 2.32 (s, 3H), 2.39–2.27 (m, 3H), 2.21–2.12 (m, 1H), 1.96 (s, 3H), 1.89–1.78 (m, 1H), 1.81 (s, 3H), 1.58 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) d 139.1, 135.1, 133.5, 128.9 (2C), 128.3 (2C), 125.7, 68.8, 65.8, 37.7, 35.5, 35.3, 33.7, 30.0, 28.2, 21.0, 15.7; HRMS (FAB) calcd for $C_{18}H_{27}Br_2$ $[M+H]^+$ 401.0474, found 401.0470.



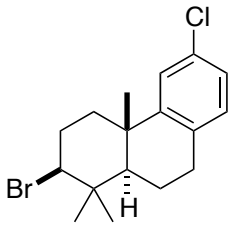
2-Bromo-6-methoxy-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (2b): Colorless solid; IR (KBr) 1612, 1574, 1501, 1264, 1044 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 8.2 Hz, 1H), 6.74 (d, *J* = 2.8 Hz, 1H), 6.68 (dd, *J* = 2.8, 8.2 Hz, 1H), 4.04 (dd, *J* = 4.1, 12.4 Hz, 1H), 3.77 (s, 3H), 2.89 (dd, *J* = 6.9, 12.8 Hz, 1H), 2.80 (ddd, *J* = 7.3, 11.5, 16.9 Hz, 1H), 2.48–2.21 (m, 3H), 1.95 (dd, *J* = 6.9, 12.8 Hz, 1H), 1.78 (dddd, *J* = 6.8, 11.9, 11.9, 12.8 Hz, 1H), 1.60 (td, *J* = 4.1, 11.9 Hz, 1H), 1.45 (dd, *J* = 2.3, 11.9 Hz, 1H), 1.24 (s, 3H), 1.15 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.7, 149.9, 129.8, 126.9, 111.1,

110.2, 68.8, 55.2, 51.2, 40.0, 39.8, 38.0, 31.5, 30.5, 29.9, 24.8, 20.7, 18.3; HRMS (FAB) calcd for $C_{18}H_{25}BrO^+$ [M^+] 336.1089, found 336.1095.

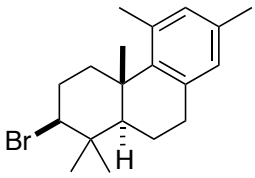
***Cis*-isomer of 2b:** ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.12 (dd, J = 4.1, 11.9 Hz, 1H), 3.79 (s, 3H) 1.12 (s, 3H), 1.09 (s, 3H), 0.45 (s, 3H), and other resonances could not be discerned.



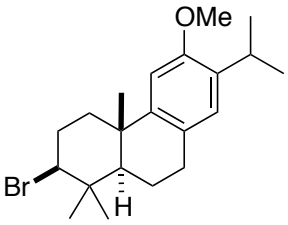
2-Bromo-6-fluoro-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (2c): Colorless solid; IR (KBr) 1610, 1585, 1497, 1473, 1379, 1259, 1176 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.99 (dd, J_H = 8.2 Hz, J_{H-F} = 6.0 Hz, 1H), 6.87 (dd, J_H = 2.8 Hz, J_{H-F} = 11.0 Hz, 1H), 6.78 (ddd, J_H = 2.8, 8.2 Hz, J_{H-F} = 8.2 Hz), 4.03 (dd, J = 4.1, 12.4 Hz, 1H), 2.92 (dd, J = 6.4, 17.0 Hz, 1H), 2.81 (ddd, J = 7.3, 11.4, 17.0 Hz, 1H), 2.35 (qd, J = 3.2, 13.8 Hz, 1H), 2.31–2.18 (m, 2H), 1.97 (ddt, J = 1.8, 7.4, 13.3 Hz, 1H), 1.79 (dddd, J = 6.9, 11.9, 11.9, 13.3 Hz, 1H), 1.63–1.52 (m, 2H), 1.44 (dd, J = 2.3, 8.2 Hz, 1H), 1.23 (s, 3H), 1.16 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.3 (d, J_{C-F} = 240 Hz), 150.6 (d, J_{C-F} = 5.7 Hz), 130.2 (d, J_{C-F} = 7.6 Hz), 130.1 (d, J_{C-F} = 2.9 Hz), 112.6 (d, J_{C-F} = 21.0 Hz), 110.9 (d, J_{C-F} = 21.0 Hz), 68.3, 50.8, 39.84, 39.76, 38.0, 31.3, 30.5, 30.0, 24.7, 20.5, 18.2; HRMS (FAB) calcd for $C_{17}H_{22}BrF^+$ [M^+] 324.0889, found 324.904.



2-Bromo-6-chloro-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (2d): Colorless solid; IR (KBr) 1594, 1488, 1394, 1379, 1215, 1108 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (d, J = 1.8 Hz, 1H), 7.05 (dd, J = 1.8, 8.2 Hz, 1H), 6.97 (d, J = 8.2 Hz, 1H), 4.03 (dd, J = 4.1, 12.8 Hz, 1H), 2.91 (dd, J = 5.5, 17.4 Hz, 1H), 2.81 (ddd, J = 7.3, 11.4, 17.4 Hz, 1H), 2.42–2.18 (m, 3H), 1.97 (dd, J = 7.3, 12.8 Hz, 1H), 1.79 (ddd, J = 6.9, 12.4, 12.4 Hz, 1H), 1.63–1.50 (m, 1H), 1.42 (dd, J = 1.8, 12.8 Hz, 1H), 1.23 (s, 3H), 1.16 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.5, 133.1, 131.4, 130.4, 125.7, 124.6, 68.3, 50.8, 39.8, 38.0, 31.3, 30.5, 30.1, 24.8, 20.4, 18.2; HRMS (FAB) calcd for $C_{17}H_{22}ClBr^+$ [M^+] 340.0593, found 340.0597.

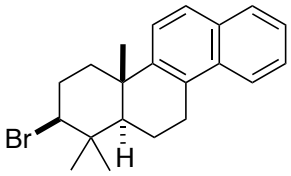


2-Bromo-1,1,4a,5,7-pentamethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (2e): Colorless solid; IR (KBr) 1610, 1475, 1443, 1392, 1375, 1169, 1157 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.76 (s, 1H), 6.75 (s, 1H), 4.04 (dd, *J* = 4.1, 12.8 Hz, 1H), 2.88 (dd, *J* = 6.4, 13.7 Hz, 1H), 2.78 (dt, *J* = 3.7, 13.8 Hz, 1H), 2.44 (s, 3H), 2.32 (qd, *J* = 3.7, 13.8 Hz, 1H), 2.24–2.13 (m, 1H), 2.21 (s, 3H), 1.94–1.87 (m, 1H), 1.70 (dddd, *J* = 6.8, 11.4, 11.9, 13.3 Hz, 1H), 1.47 (td, *J* = 3.7, 13.8 Hz, 1H), 1.40 (dd, *J* = 0.9, 11.9 Hz, 1H), 1.36 (s, 3H), 1.16 (s, 3H), 1.06 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.5, 136.3, 135.7, 134.8, 132.1, 128.5, 68.9, 54.3, 40.3, 40.1, 38.9, 33.1, 31.5, 30.8, 24.7, 20.5 (2C), 20.3, 18.7; HRMS (FAB) calcd for $C_{19}H_{27}Br^+$ [M^+] 334.1296, found 334.1301.



2-Bromo-7-isopropyl-6-methoxy-1,1,4a-trimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene (2f): Colorless liquid; IR (neat) 1614, 1572, 1499, 1463, 1253, 1239, 1207, 1057, 1045 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.85 (s, 1H), 6.64 (s, 1H), 4.04 (dd, *J* = 4.1, 12.8 Hz, 1H), 3.78 (s, 3H), 3.21 (septet, *J* = 6.9 Hz, 1H), 2.87 (dd, *J* = 6.9, 17.0 Hz, 1H), 2.79 (ddd, *J* = 6.9, 11.4, 17.0 Hz, 1H), 2.42–2.21 (m, 3H), 1.95 (dd, *J* = 6.8, 12.8 Hz, 1H), 1.78 (dddd, *J* = 6.8, 11.9, 11.9, 12.8 Hz, 1H), 1.62 (ddd, *J* = 3.2, 11.9, 13.3 Hz, 1H), 1.46 (dd, *J* = 1.8, 11.9 Hz, 1H), 1.25 (s, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 1.17 (d, *J* = 6.9 Hz, 3H), 1.15 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 146.5, 134.7, 126.37, 126.34, 106.3, 69.0, 55.5, 51.4, 40.1, 39.8, 37.9, 31.5, 30.5, 30.2, 26.4, 24.8, 22.8, 22.6, 20.8, 18.2; HRMS (FAB) calcd for $C_{21}H_{31}BrO^+$ [M^+] 378.1558, found 378.1553.

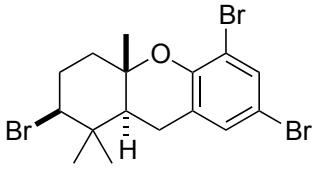
***Cis*-isomer of 2f:** ^1H NMR ($CDCl_3$, 300 MHz) δ 6.82 (s, 1H), 6.68 (s, 1H), 4.13 (dd, *J* = 4.1, 12.4 Hz, 1H), 1.09 (s, 3H), 0.45 (s, 3H), and other resonances could not be discerned.



2-Bromo-1,1,4a-trimethyl-1,2,3,4,4a,11,12,12a-octahydrochrysene

(**2g:** Colorless solid; IR (neat) 1508, 1460, 1440, 1367, 1267, 1143, 1038 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.77 (d, *J* = 8.3 Hz, 1H), 7.66 (*J* = 8.7 Hz, 1H), 7.53–7.41 (m, 2H), 7.39 (d, *J* = 8.7 Hz, 1H), 4.07 (dd, *J* = 4.6, 12.8 Hz, 1H), 3.37 (dd, *J* = 6.4, 17.4 Hz, 1H), 3.20–3.08 (m, 1H), 2.49–2.35 (m, 2H), 2.34–2.26 (m, 1H), 2.18 (dd, *J* = 7.3, 12.8 Hz, 1H), 1.91 (dddd, *J* = 6.4, 12.4, 12.4, 12.8 Hz, 1H), 1.65–1.53 (m, 2H), 1.34 (s, 3H), 1.21 (s, 3H), 1.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 145.3, 132.1, 131.5, 129.3, 128.1, 126.5, 126.0, 125.1, 123.2, 123.1, 68.7, 51.2, 40.1, 39.7, 38.2, 31.5, 30.5, 28.0, 24.3, 20.4, 18.2; HRMS (FAB) calcd for $C_{21}H_{25}Br^+$ [M^+] 356.1140, found 356.1133.

***Cis*-isomer of 2g:** ^1H NMR ($CDCl_3$, 300 MHz) δ 4.19 (dd, *J* = 4.6, 11.4 Hz, 1H), 1.25 (s, 3H), 1.16 (s, 3H), 0.51 (s, 3H), and other resonances could not be discerned.



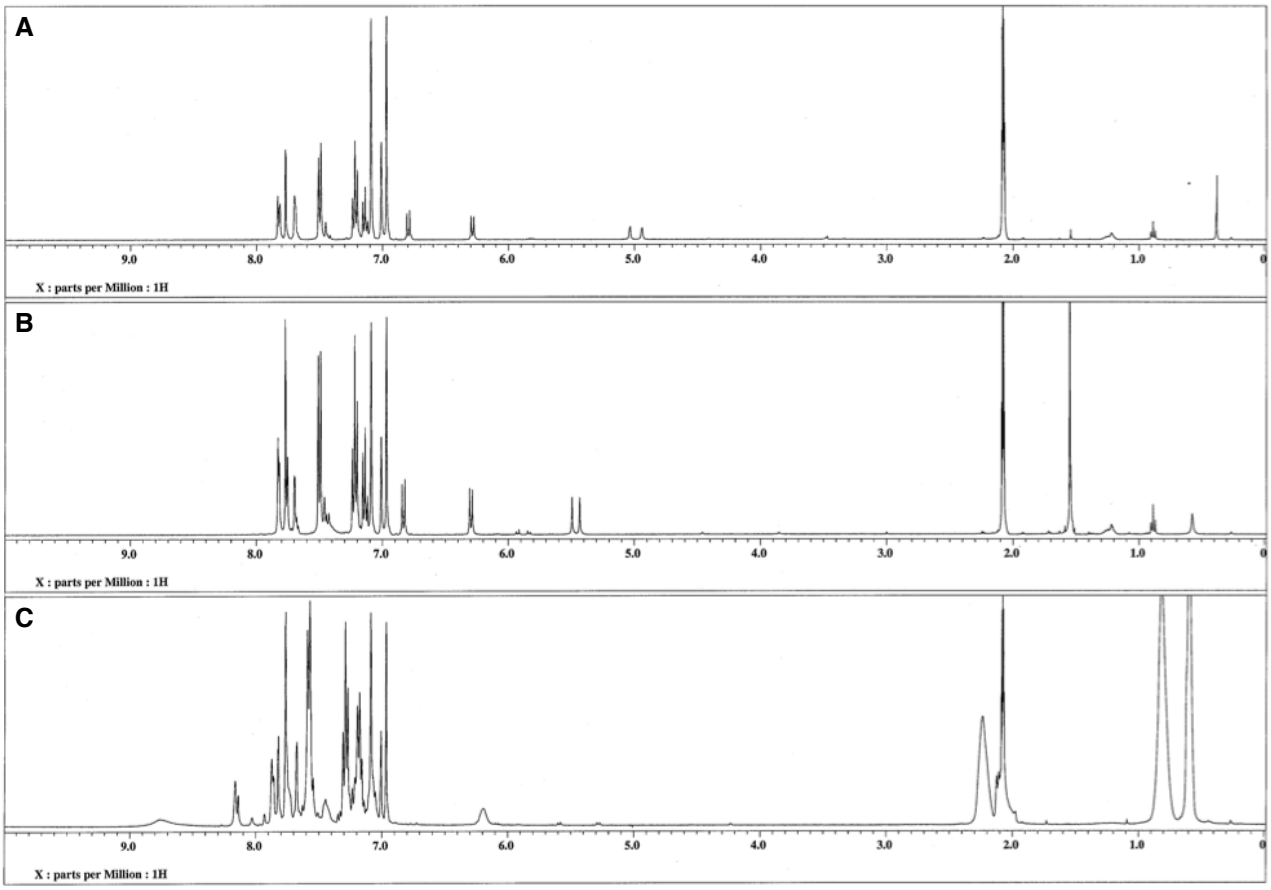
2,5,7-Tribromo-1,1,4a-trimethyl-2,3,4,4a,9,9a-hexahydro-1*H*-xanthene: To a solution of **6** (5.4 mg, 0.0045 mmol) in toluene (1.5 mL) were added DBH (94.4 mg, 0.33 mmol) and 2,4-dibromo-6-geranylphenol (116 mg, 0.30 mmol) successively at –78 °C, and the mixture was stirred at –78 °C for 0.5 h and then at –60 °C for 24 h. The reaction mixture was quenched with saturated aqueous $Na_2S_2O_3$ (3.0 mL) and extracted with Et_2O (5.0 mL × 3). The combined organic layer was dried over Na_2SO_4, filtered and concentrated. The crude product was purified by column chromatography on silica gel using (hexane–EtOAc 20:1) as an eluent. The resulting mixture was used for the next cyclization without further separation. To a solution of the resulting mixture, which were obtained in the above reaction, in *i*-$PrNO_2$ (3.0 mL) was added TfOH (106 μL, 1.2 mmol) at –78 °C. The mixture was stirred 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 residue was purified by column chromatography on silica gel using (hexane–EtOAc 40:1) as an eluent to give 2,5,7-tribromo-1,1,4a-trimethyl-2,3,4,4a,9,9a- hexahydro-1*H*-xanthene as colorless solid. IR (KBr) 1558, 1454, 1391, 1383, 1304, 1289, 1258, 1128, 1066 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 2.3 Hz, 1H), 7.15 (d, *J* = 2.3 Hz, 1H), 4.02 (dd, *J* = 4.1, 12.4 Hz, 1H), 2.83–2.68 (m,

2H), 2.31 (dddd, *J* = 3.2, 3.2, 4.1, 14.6 Hz, 1H), 2.13 (ddd, *J* = 3.2, 13.2, 13.7, 1H), 2.09 (ddd, *J* = 3.2, 3.2, 13.2 Hz, 1H), 1.85 (ddd, *J* = 3.2, 13.7, 14.2 Hz, 1H), 1.79 (dd, *J* = 6.9, 11.0 Hz, 1H), 1.23 (s, 3H), 1.16 (s, 3H), 1.02 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.9, 133.1, 131.2, 124.9, 112.1, 111.7, 77.5, 65.1, 47.5, 40.2, 39.1, 31.3, 29.5, 24.7, 19.9, 16.8; HRMS (EI) calcd for $C_{16}H_{19}Br_3O^+$ [M^+] 463.8986, found 463.8999.

***Cis*-isomer:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, *J* = 1.8 Hz, 1H), 7.15 (d, *J* = 1.8 Hz, 1H), 4.06 (dd, *J* = 3.7, 12.8 Hz, 1H), 3.12 (dd, *J* = 7.8, 18.3 Hz, 1H), 2.83 (d, *J* = 18.3 Hz, 1H), 2.49 (ddd, 3.7, 13.3, 14.2 Hz, 1H), 2.20 (ddd, *J* = 3.6, 4.1, 13.3 Hz, 1H), 2.09 (dddd, *J* = 3.6, 3.7, 3.7, 14.2 Hz, 1H), 1.70 (ddd, *J* = 4.1, 14.2, 14.2 Hz, 1H), 1.59 (d, *J* = 7.8 Hz, 1H), 1.18 (s, 3H), 1.13 (s, 3H), 0.75 (s, 3H).

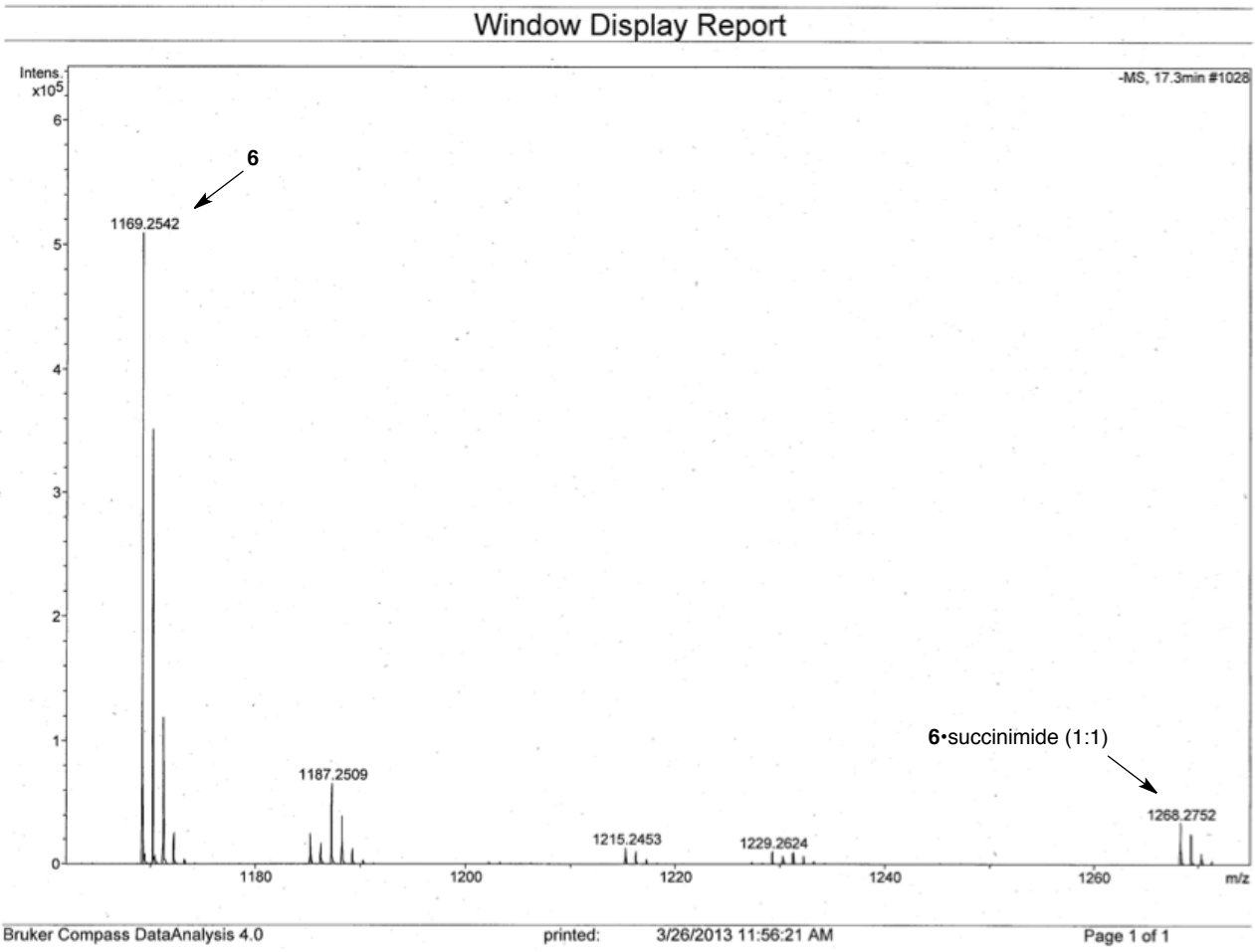
NMR Experiments of a Mixture of Catalyst 6 and Succinimide.

The ^{1}H NMR studies were carried out in toluene-d_8. When catalyst **6** was mixed with succinimide, two signals of urea (δ 5.03, 4.94 ppm, chart **A**) shifted downfield (δ 5.46, 5.40 ppm, chart **B**). Furthermore, signals of urea were observed at δ 8.77, 6.19 ppm when catalyst **6** was mixed with tertabutylammonium salt of succinimide (chart **C**). These results suggested that succinimide anion interacted with the urea group via hydrogen bonding.

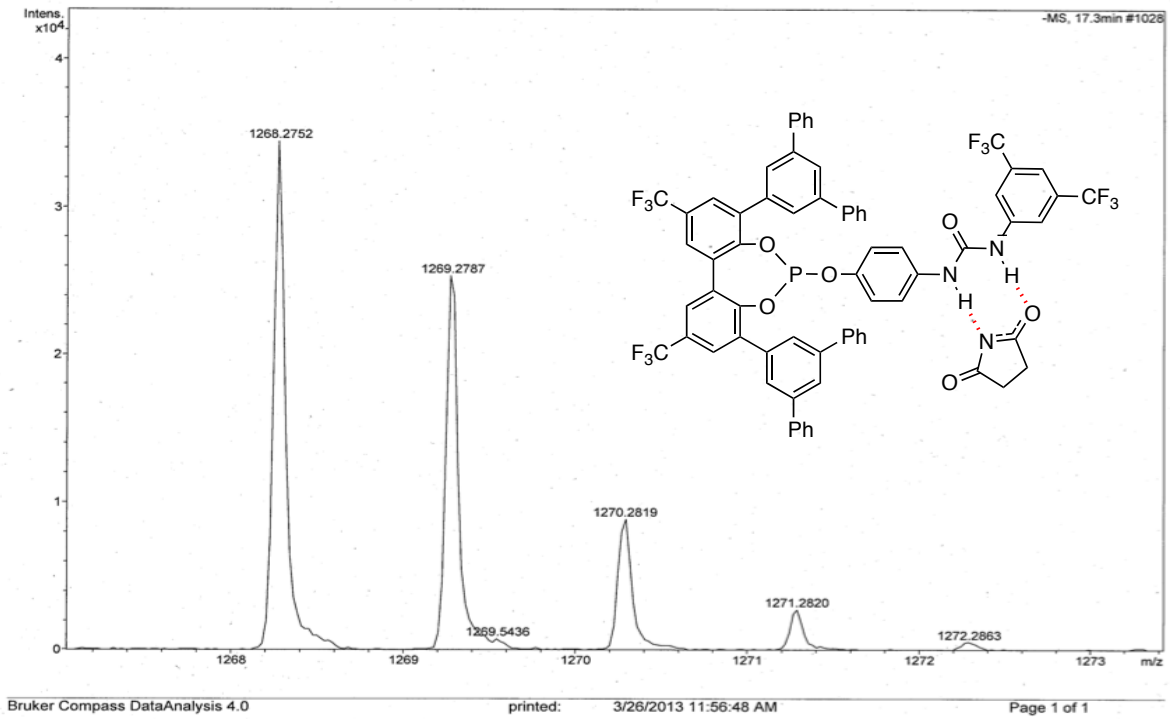


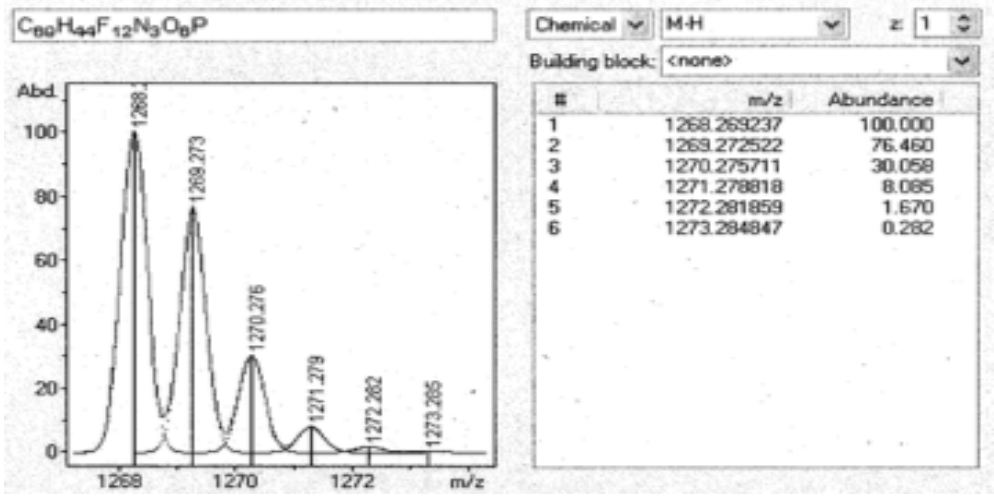
Negative ESI-MS Analysis of a Mixture of Catalyst 6 and Succinimide.

To a solution of catalyst **6** in CH_3CN (10 μM, 1.0 mL, 0.01 μmol) was added tetrabutylammonium succinimide (10 mM in CH_3CN, 1μL, 0.01 μmol). The resulting mixture was passed through a membrane filter (200 mm mesh) just before injection. A MS peak corresponding to a complex of catalyst **6** and succinimide (m/z 1268) was observed by ESI-MS analysis (negative mode).



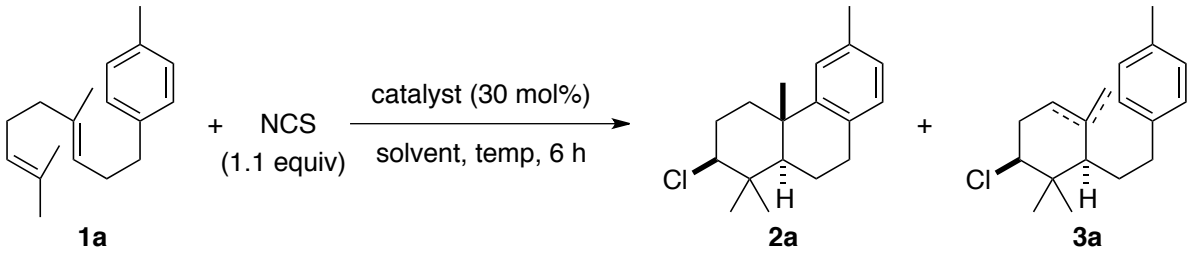
Correlation of theoretical and observed ion distirbution for the peak m/z = 1268 is shown below. For m/z = 1268, $C_{69}H_{44}F_{12}N_3O_6P$ is identified to [catalyst **6** + succinimide] as $[M–H]^-$.





HRMS (ESI⁻) calcd for $C_{69}H_{43}F_{12}N_3O_6P$ $[M–H]^-$ 1268.2692, found 1268.1752

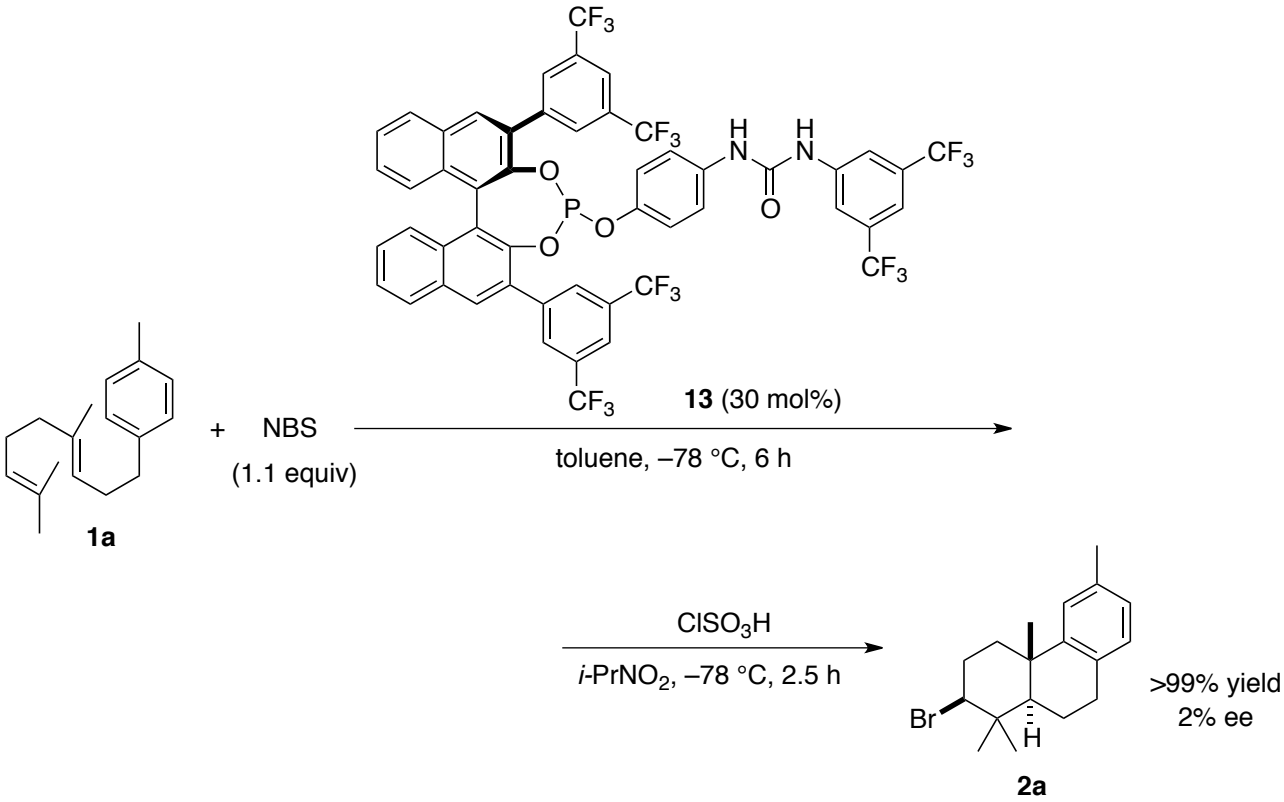
Chlorocyclization of 1a with NCS Using Nucleophilic Phosphite Catalysts



1a **2a** **3a**

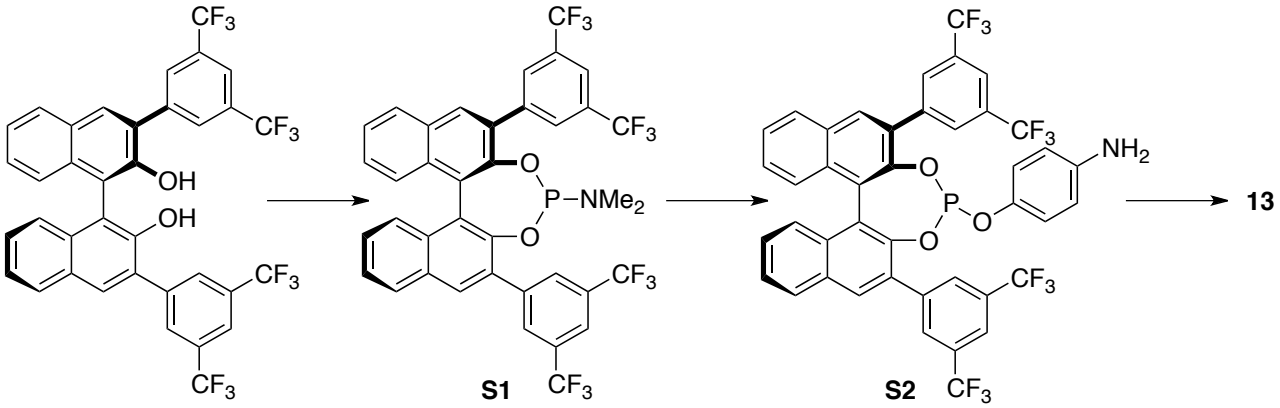
catalyst	solvent	temp	yield of **2a** + **3a**
$P(OPh)_3$	CH_2Cl_2	–78 °C	0%
$P(OPh)_3$	toluene	–40 °C	0%
$P(OC_6H_4\text{-}4\text{-}F)_3$	CH_2Cl_2	–78 °C	0%
$P(OC_6H_4\text{-}4\text{-}F)_3$	toluene	–40 °C	0%

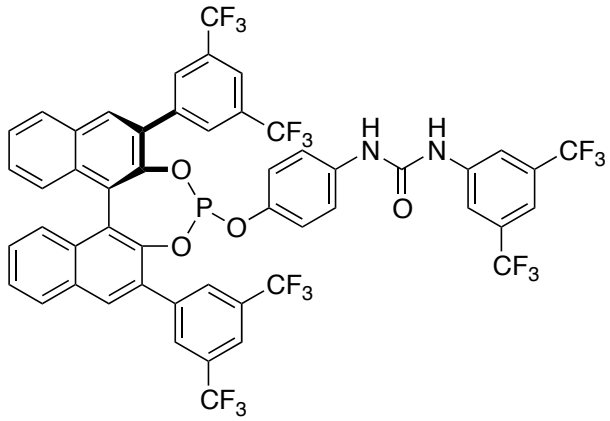
Bromocyclization of 1a Using Chiral Phosphite–Urea Cooperative Catalyst 13



To a solution of **13** (33.1 mg, 0.03 mmol) in toluene (1.0 mL) were added NBS (0.11 mmol) and **1a** (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 crude product was purified by column chromatography on silica gel using hexane as an eluent to give mixture of **2**, *endo*-**3** and *exo*-**3**. To a solution of the mixture of **2a**, *endo*-**3a** and *exo*-**3a** in *i*-$PrNO_2$ (2.0 mL) was added $ClSO_3H$ (50 μL) at –78 °C. The mixture was stirred at –78 °C for 2.5 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 residue was purified by column chromatography on silica gel using hexane as an eluent, to give **2a**. The enantiomeric excess of **2a** was determined to be 2% by HPLC analysis (Shimadzu LC-10 AD coupled diode array-detector SPD-MA-10A-VP, chiral column of Daicel CHIRALPACK AS-H (4.6 mm × 25 cm) and AS-3 (4.6 mm × 25 cm), hexane,, flow rate = 1.0 mL/min, t_R= 48.0, 51.9 min.).

Synthesis of Chiral Phosphite–Urea Cooperative Catalyst 13





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 13: To the suspension of (*R*)-3,3'-bis(3,5-bis(trifluoromethyl)phenyl)-2,2'-binaphthol (923 mg, 1.3 mmol) and tetrazole (273 mg, 3.9 mmol) in dry THF (15 mL) was added *N*,*N*,*N*',*N*',*N*'',*N*''-hexamethylphosphinetriamine (424 mg 3.4 mmol). The reaction mixture was heated at reflux for 5 h and cooled to room temperature, filtered through a Celite pad, and the filtrate was concentrated *in vacuo*. The residue was purified by column chromatography on silica gel to give **S1** (95% yield). To the solution of **S1** (392 mg, 0.50 mmol) and *N*-phenylimidazolium trifluoromethanesulfonate salt[19] (162 mg, 0.55 mmol) in dry CH_3CN was added 4-aminophenol (71 mg, 0.65 mmol). 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 to give **S2** (80% yield). To the solution of **S2** (339 mg, 0.4 mmol) in CH_2Cl_2 was added 1-isocyanato-3,5-bis(trifluoromethyl)benzene (153 mg, 0.60 mmol). The reaction mixture was stirred at room temperature and insoluble urea starts to precipitate as a white solid. The reaction mixture was diluted with hexane, then the solid was filtered off and washed with hexane to give **13** (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 ^{13}C NMR (100 MHz, THF-D_8) δ 152.8, 147.1(d, $J_{C–P}$ = 10.5 Hz), 145.6 (d, $J_{C–P}$ = 2.9 Hz), 144.9 (d, $J_{C–P}$ = 2.9 Hz), 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), 132.5 (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, 131.4, 129.9, 129.8, 128.3, 128.1, 127.6, 127.5, 127.1, 126.9, 126.4 (d, $J_{C–P}$ = 4.8 Hz), 125.2, 124.6 (q, $J_{C–F}$ = 272 Hz, 6C), 122.4 (2C), 122.1 (2C), 120.7 (2C), 120.0, 199.9, 118.8 (2C), 115.5; ^{19}F NMR (376 MHz, THF-d_8) δ –63.3, –63.7; HRMS (FAB) calcd for $C_{51}H_{18}N_2O_4P^+$ [M^+] 1102.1265, found 1102.1269.

References

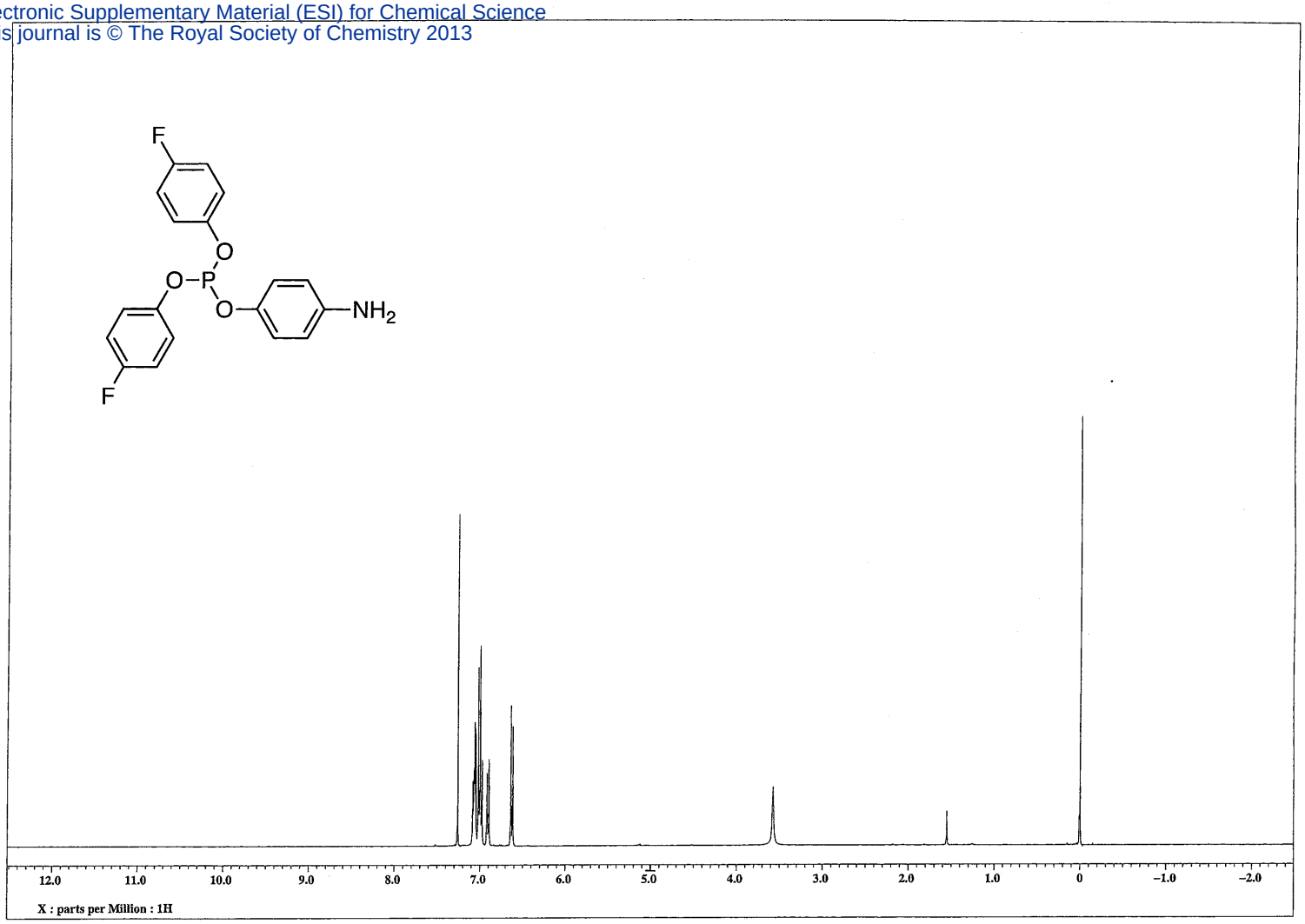
1 M. Oba, Y. Okada, K. Nishiyama, Ando, W. *Org*. *Lett*. **2009**, *11,* 1879.

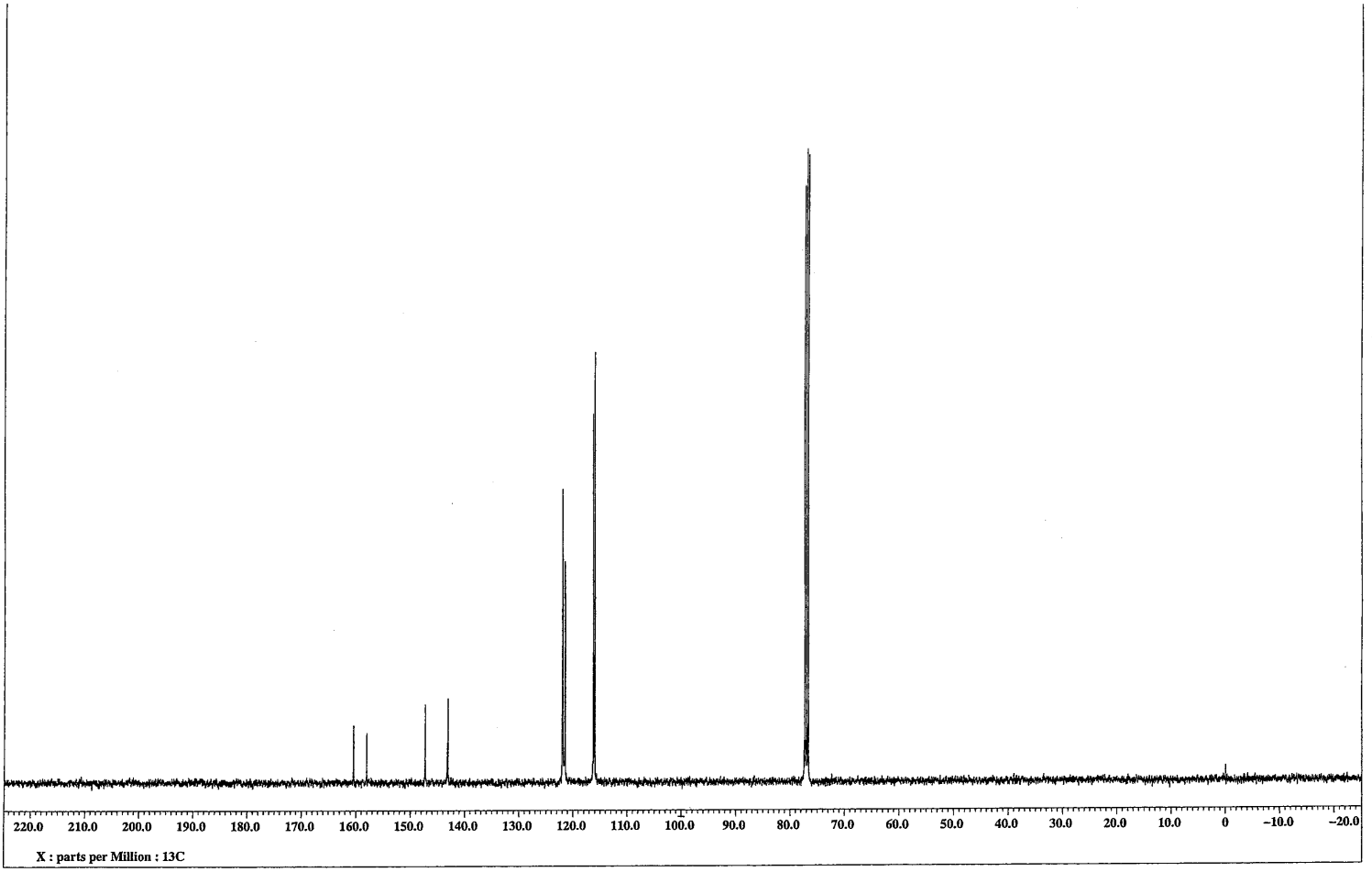
2 (a) H. Ishibashi, K. Ishihara, H. Yamamoto, *J*. *Am*. *Chem*. *Soc*. **2004**, *126*, 11122; (b) K. Kumazawa, K. Ishihara, H. Yamamoto, *Org*. *Lett*. **2004**, *6,* 2551; (c) A. Sakakura, A. Ukai, K. Ishihara, *Nature*, **2007,** *445*, 900.

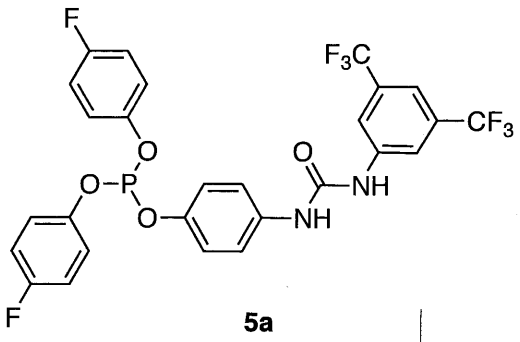
3 S. Araki, T. Sato, Y. Butsugan, *J*. *Chem*. *Soc*. *Chem*. *Commun*. **1982**, 285.

4 S. Karavadhi, E. J. Corey, *J*. *Am*. *Chem*. *Soc*. **2012**, *134*, 11992.

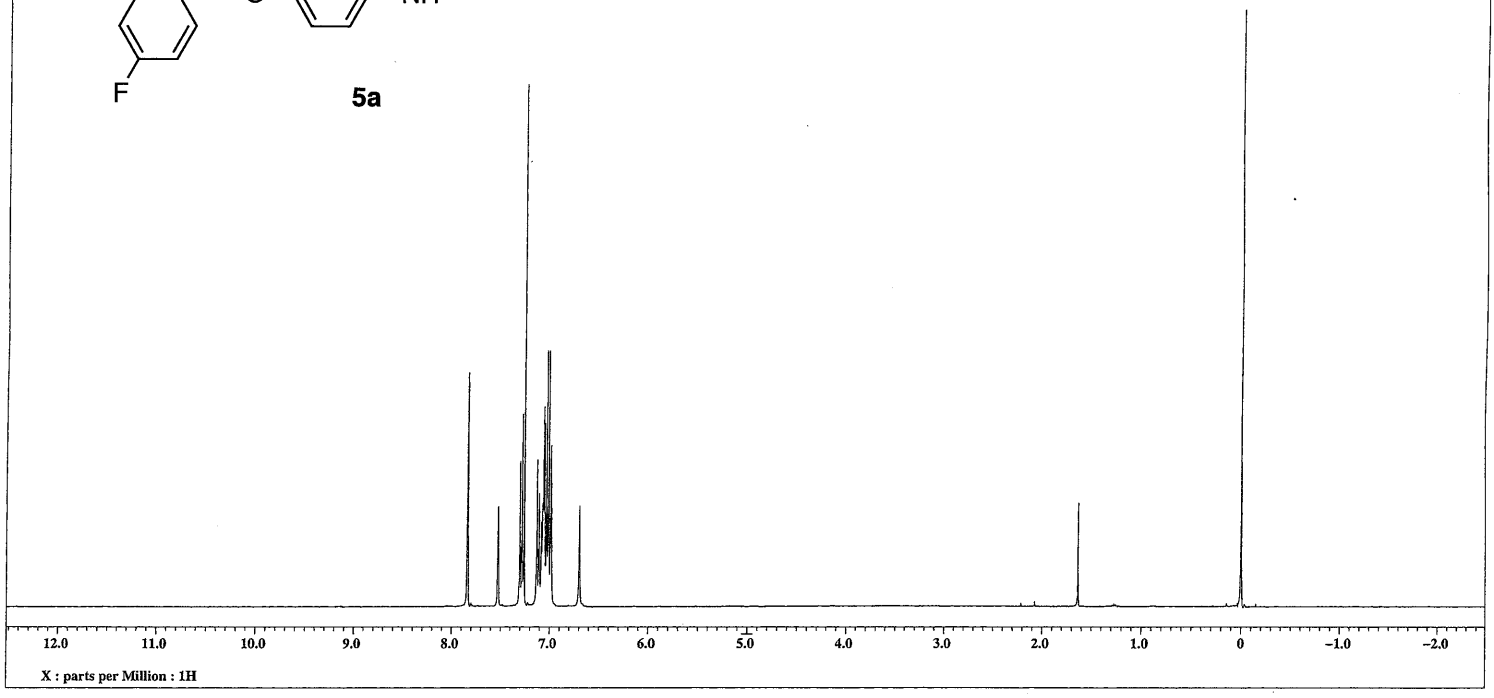
5 A. Gansauer, J. Justicia, A. Rosales, D. Worgull, B. Rinker, J. M. Cuerva, J. E. Oltra, *Eur*. *J*. *Org*. *Chem*. **2006**, 4115.

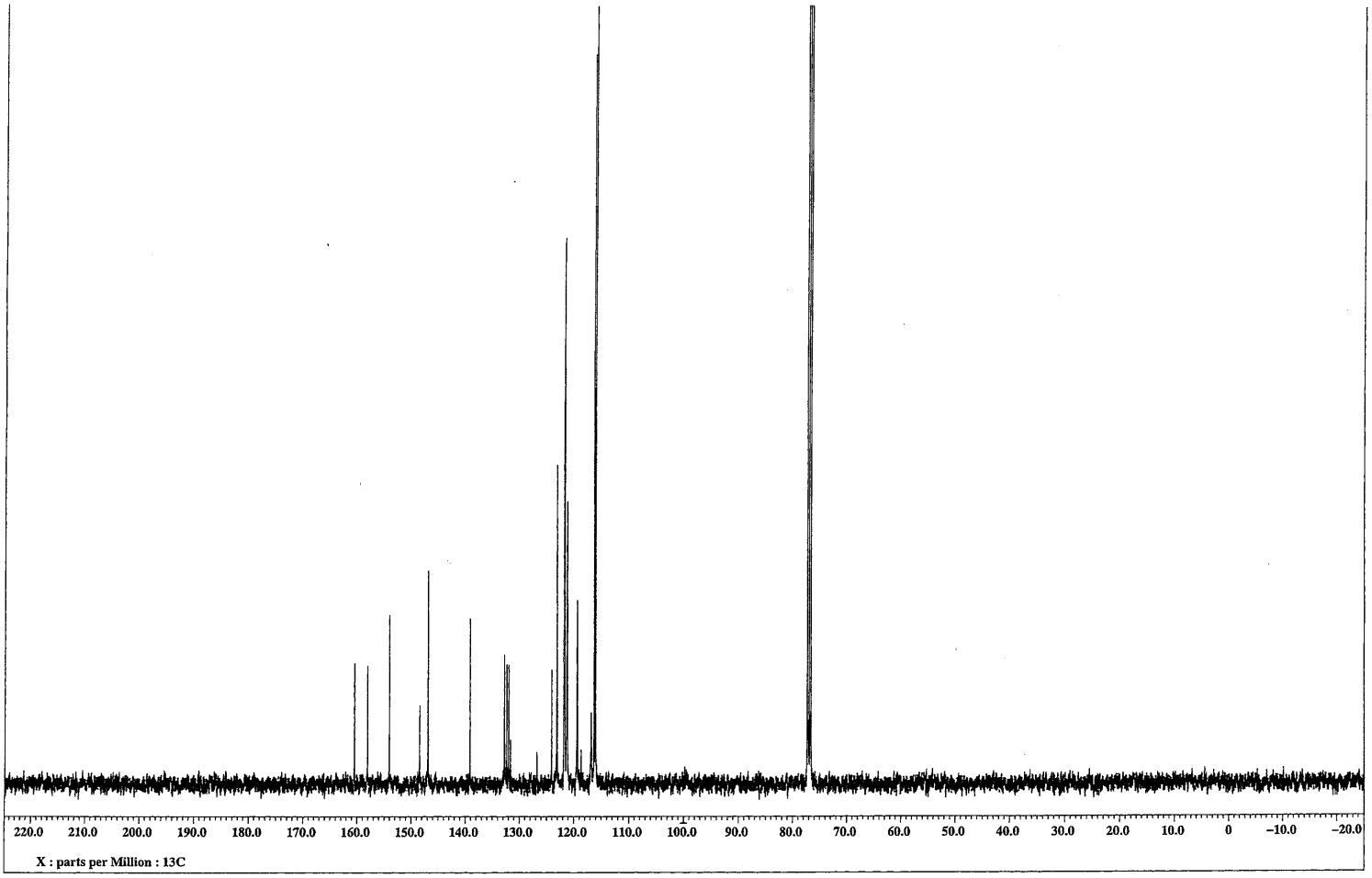


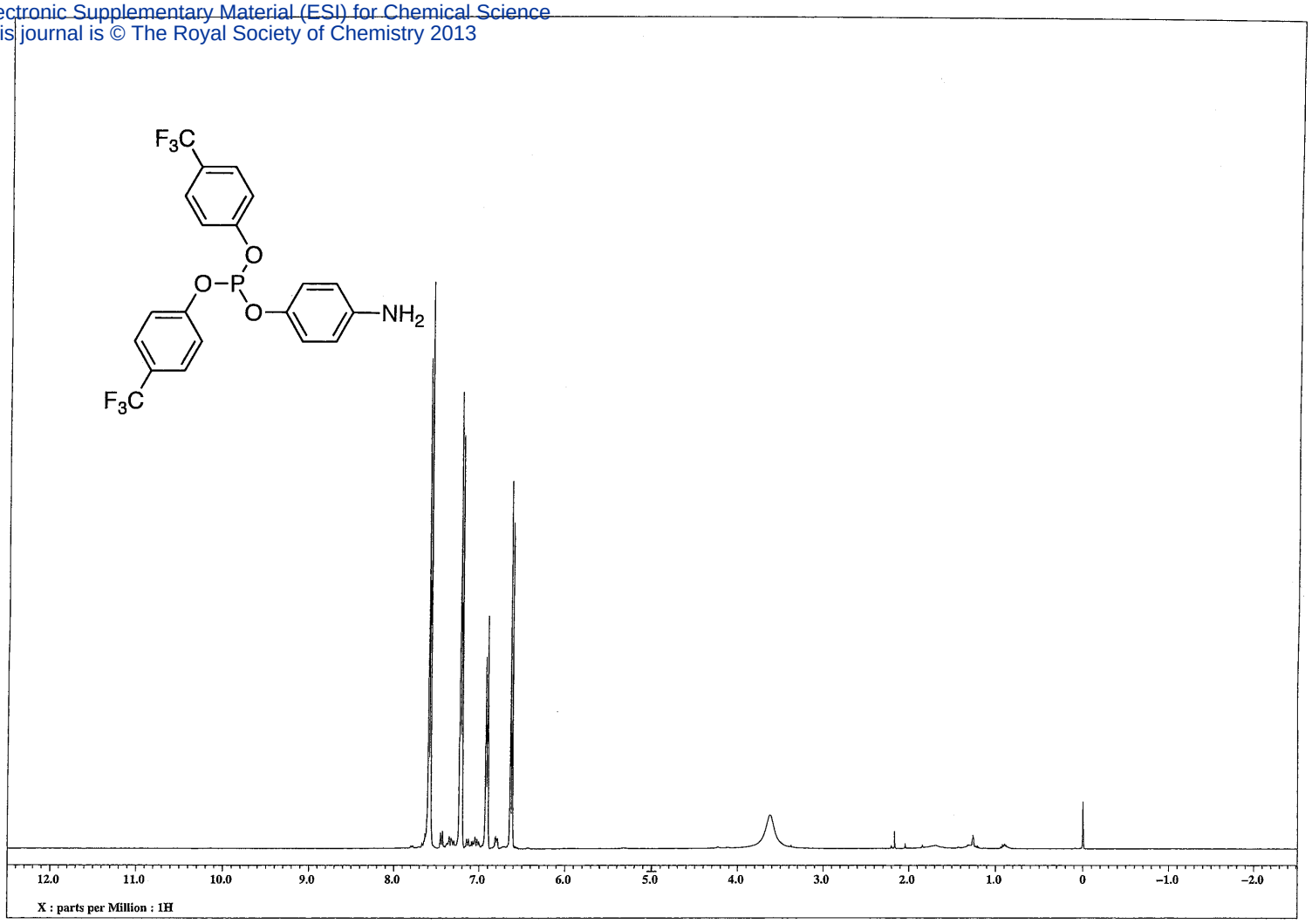


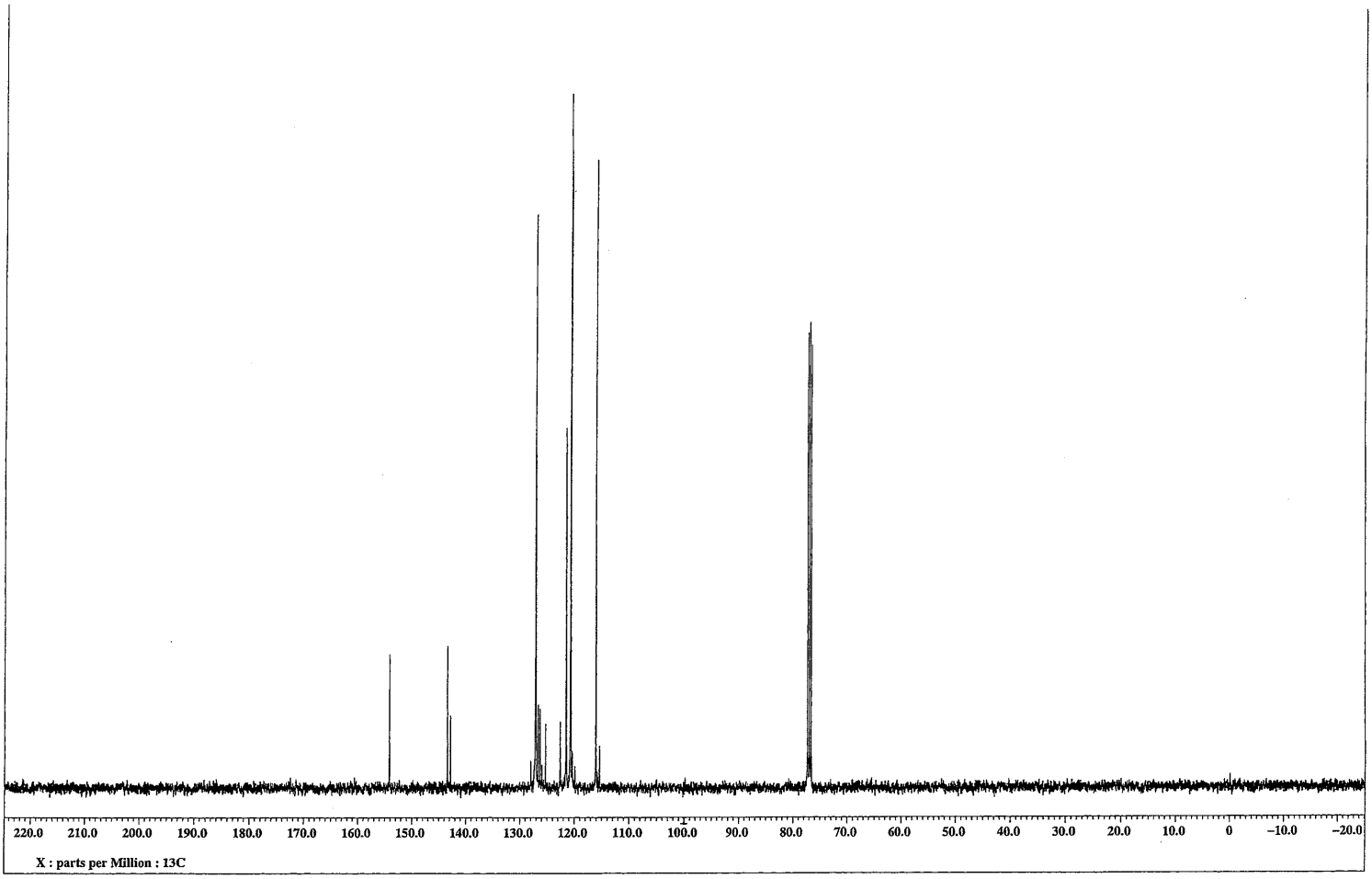


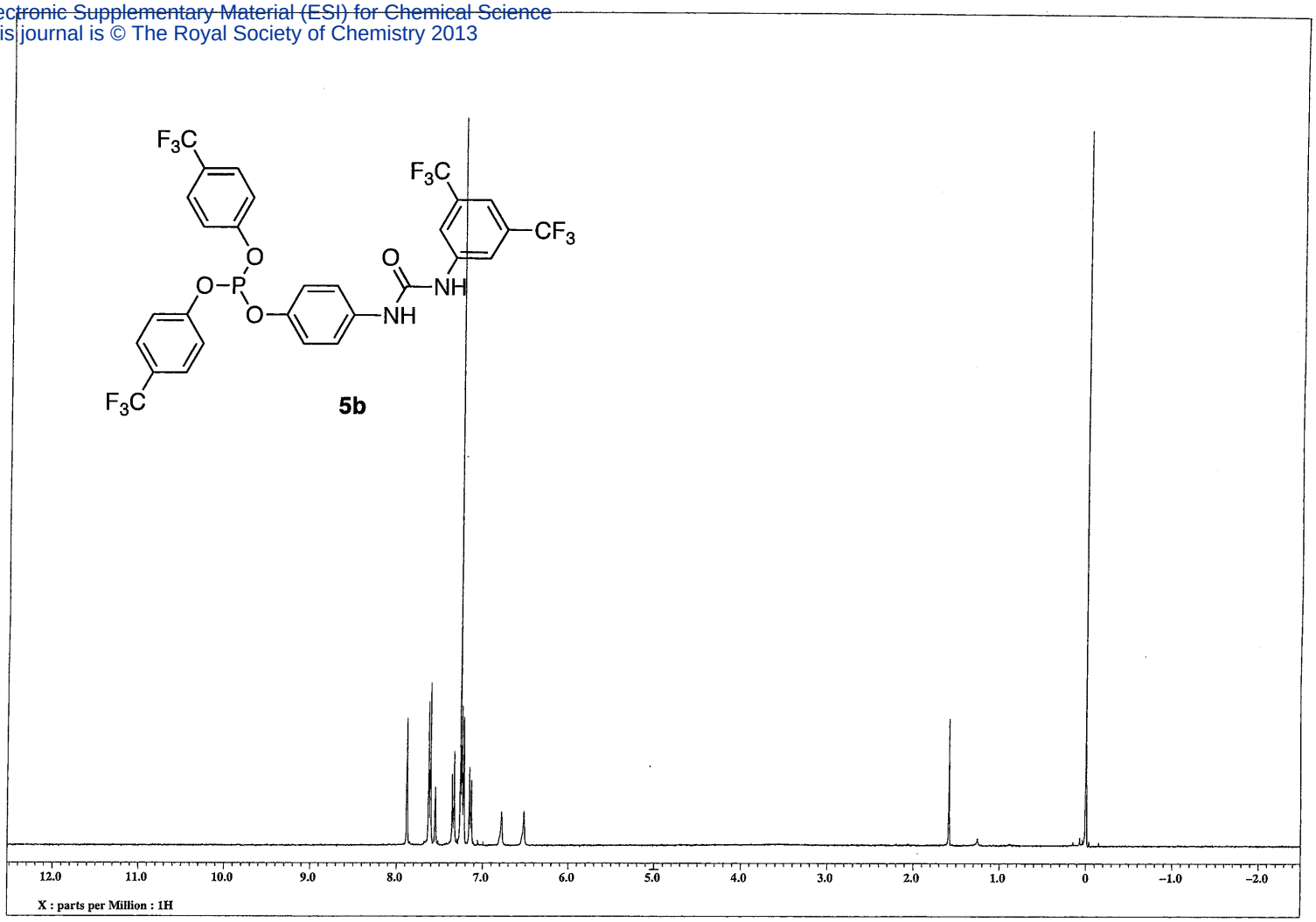
5a

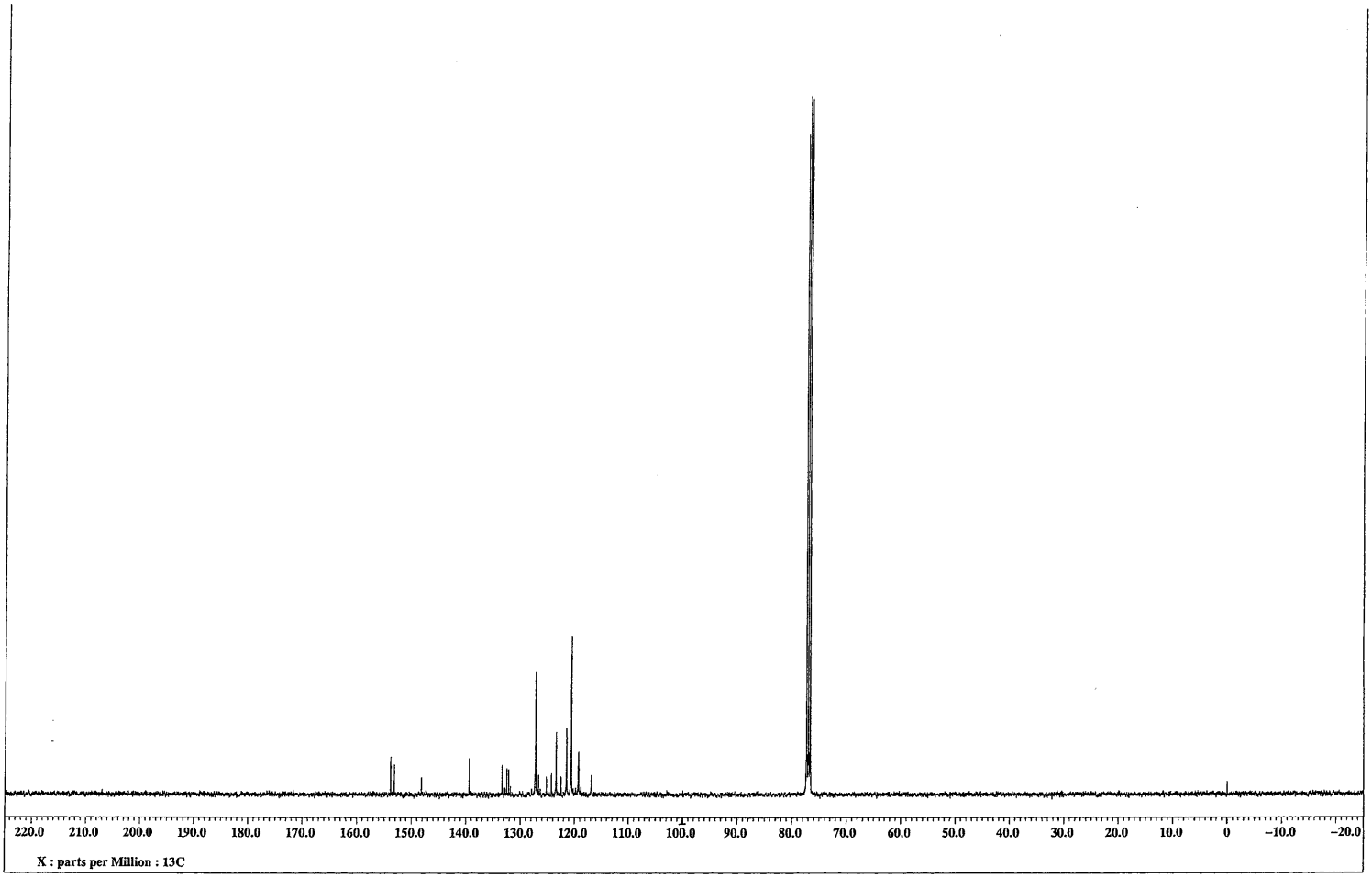


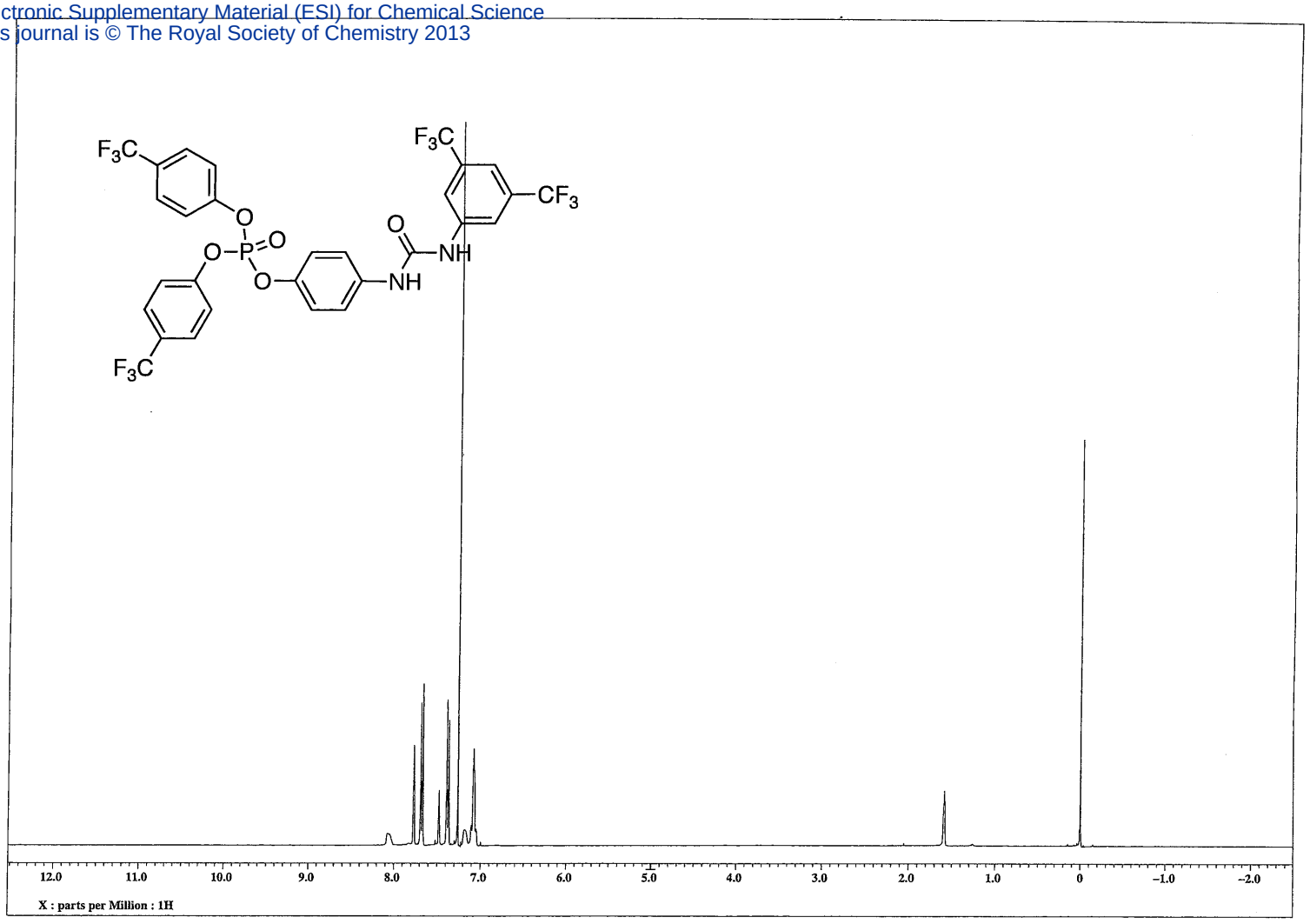


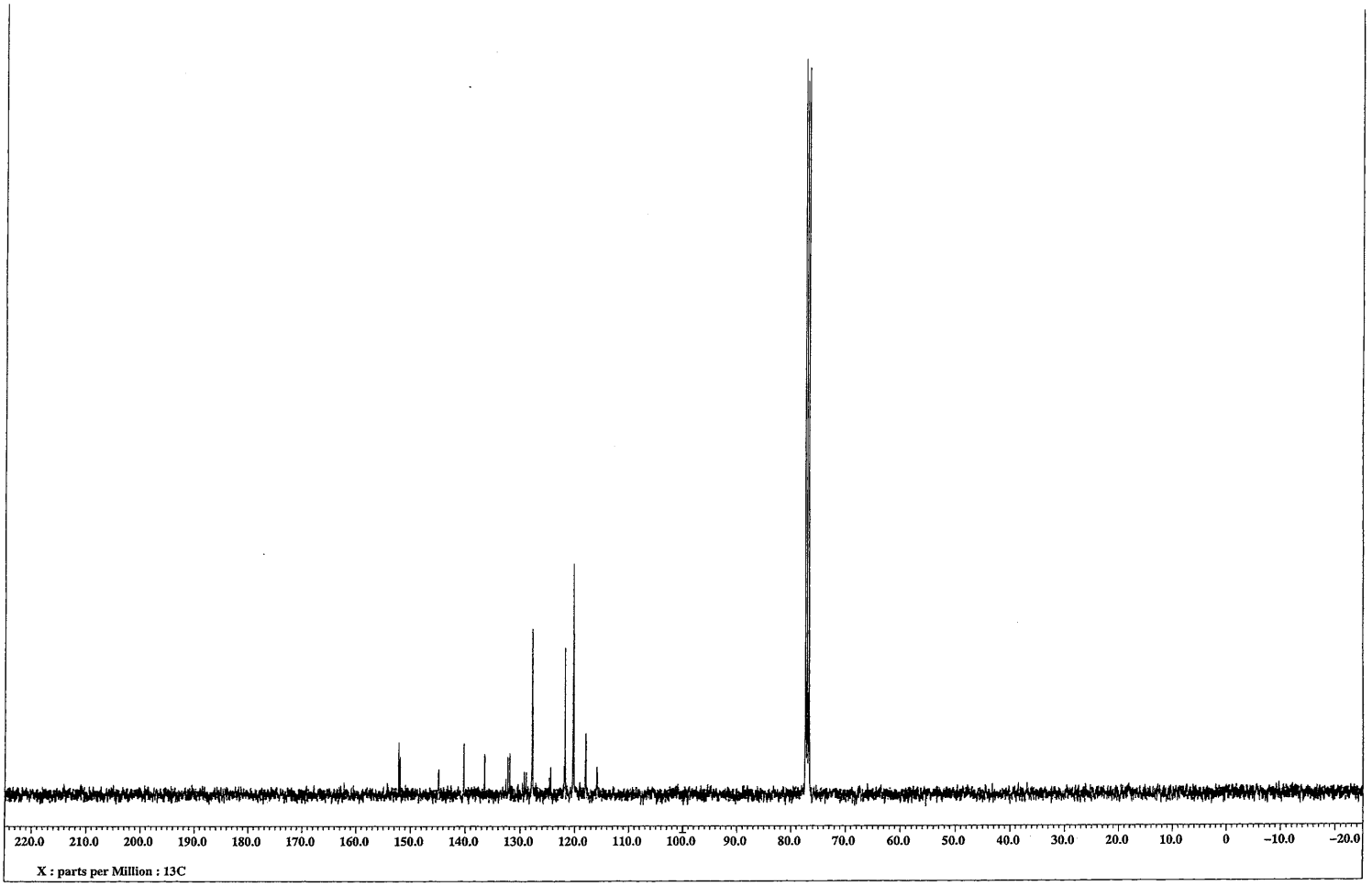


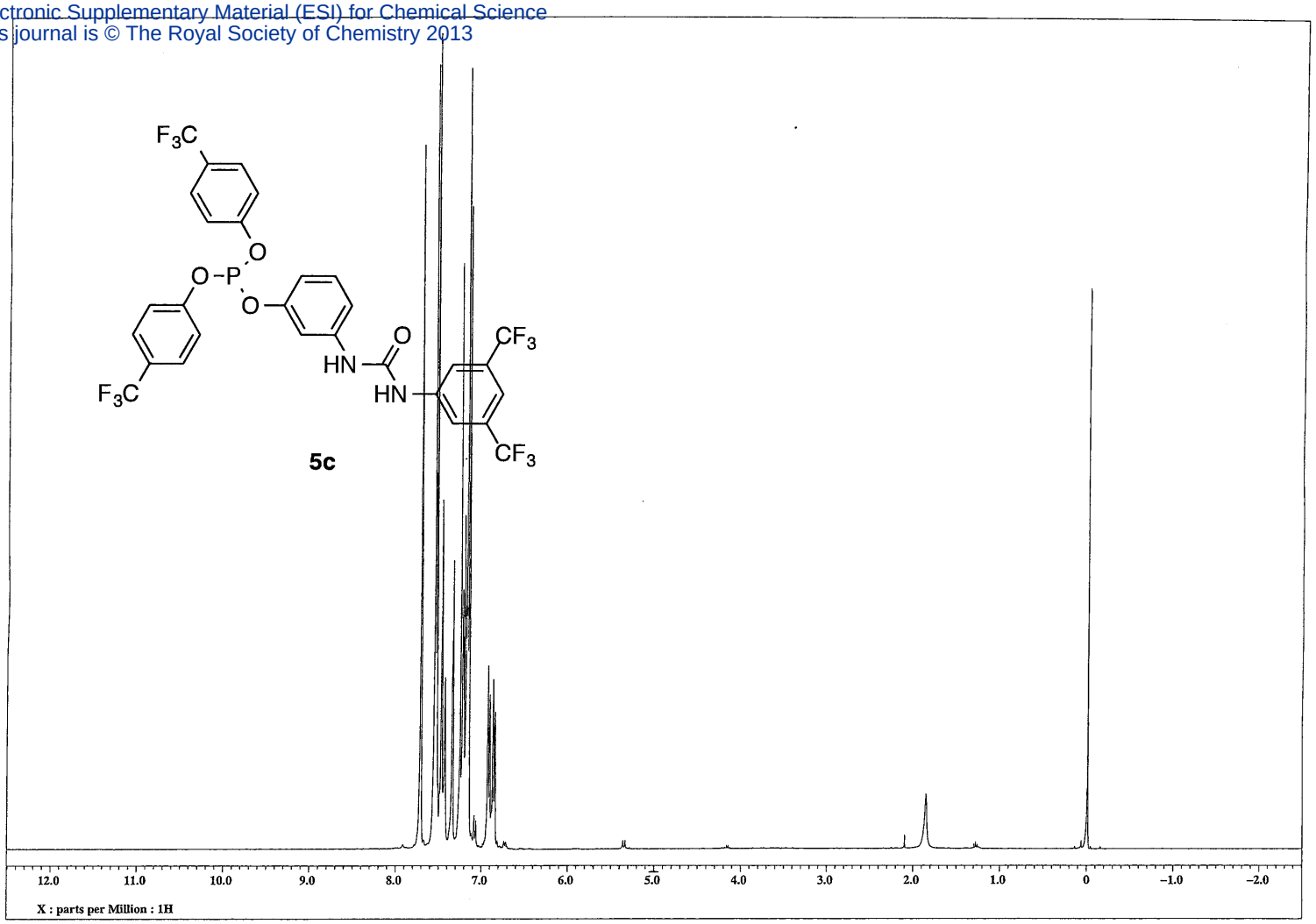


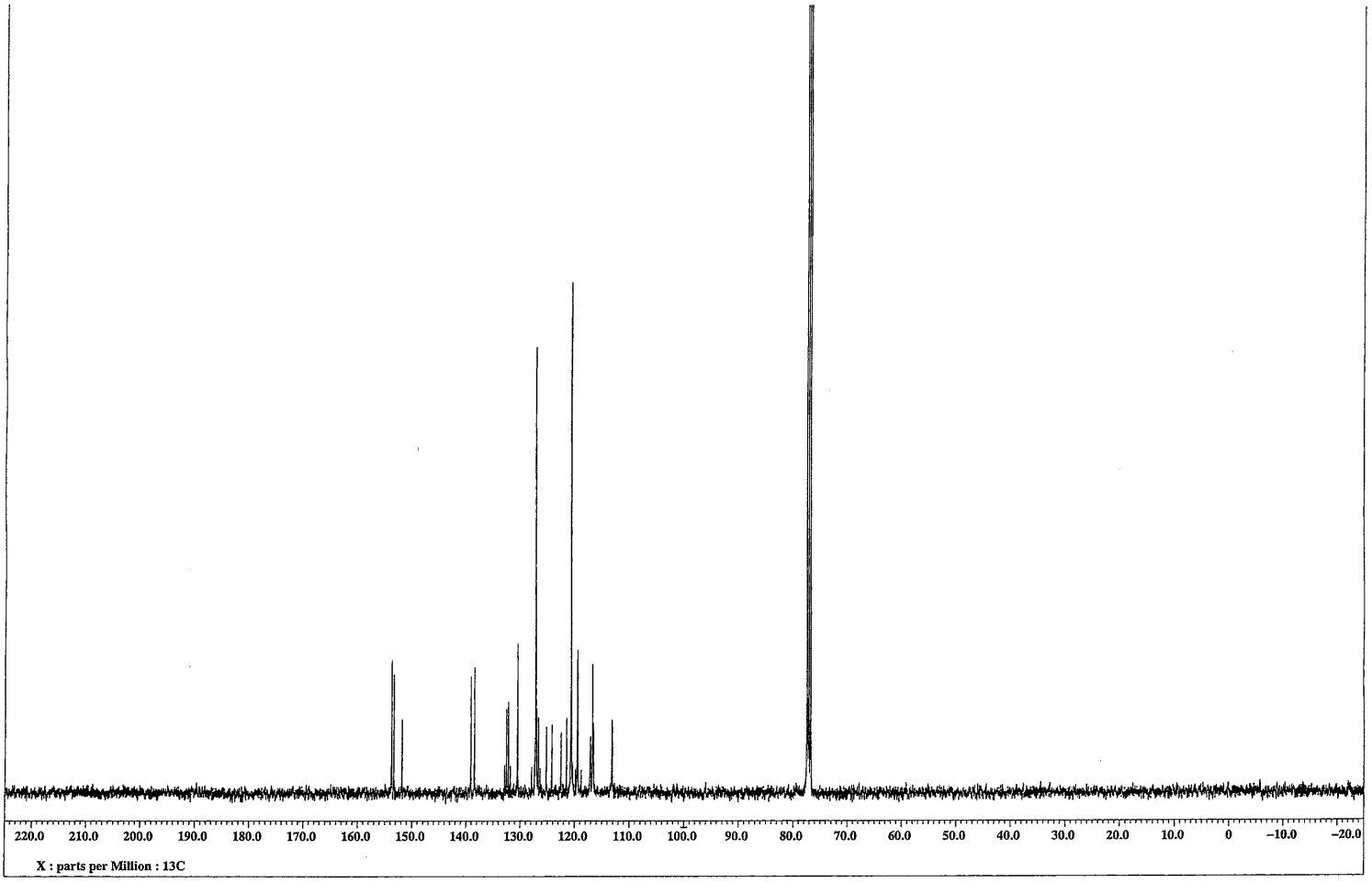


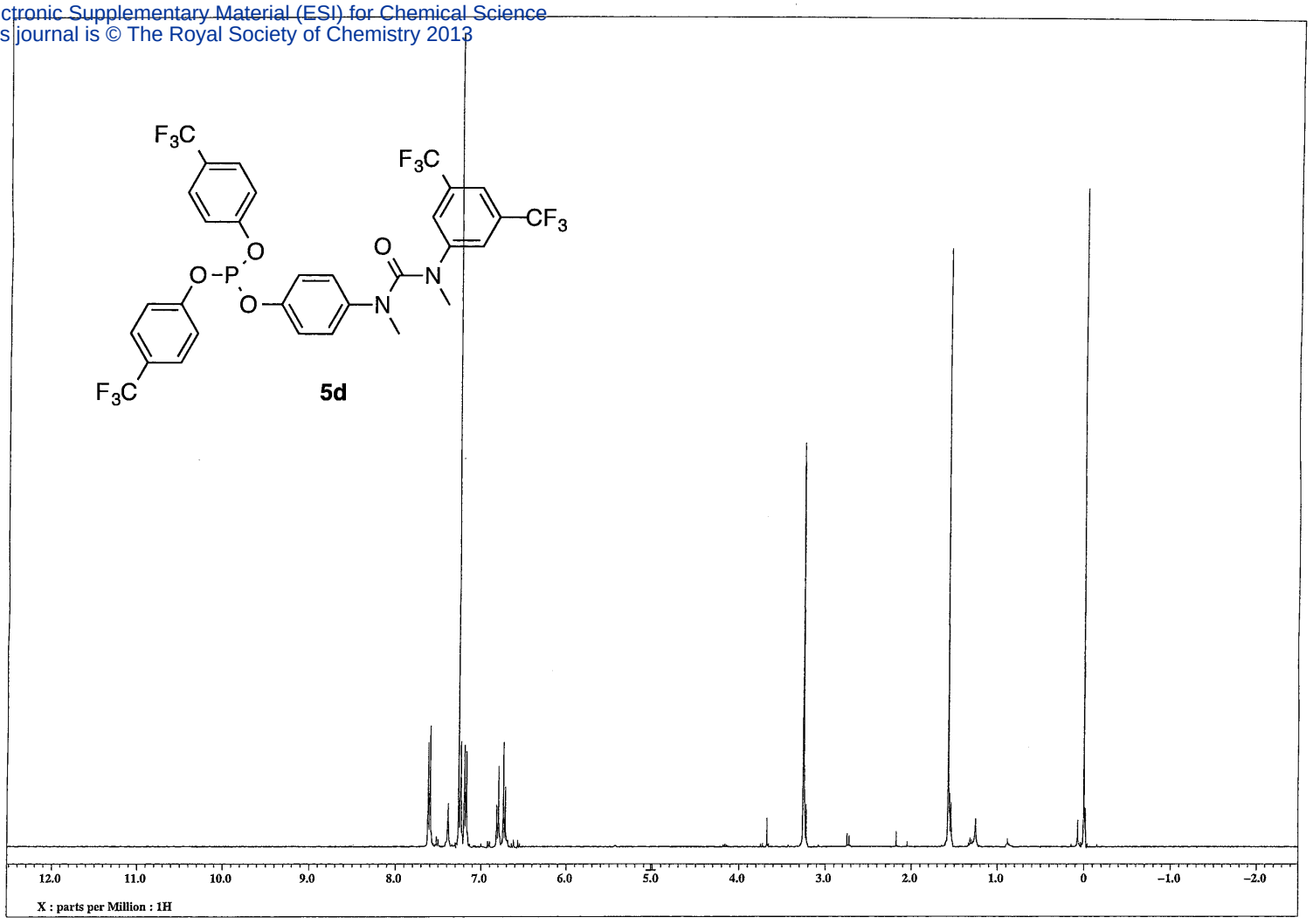


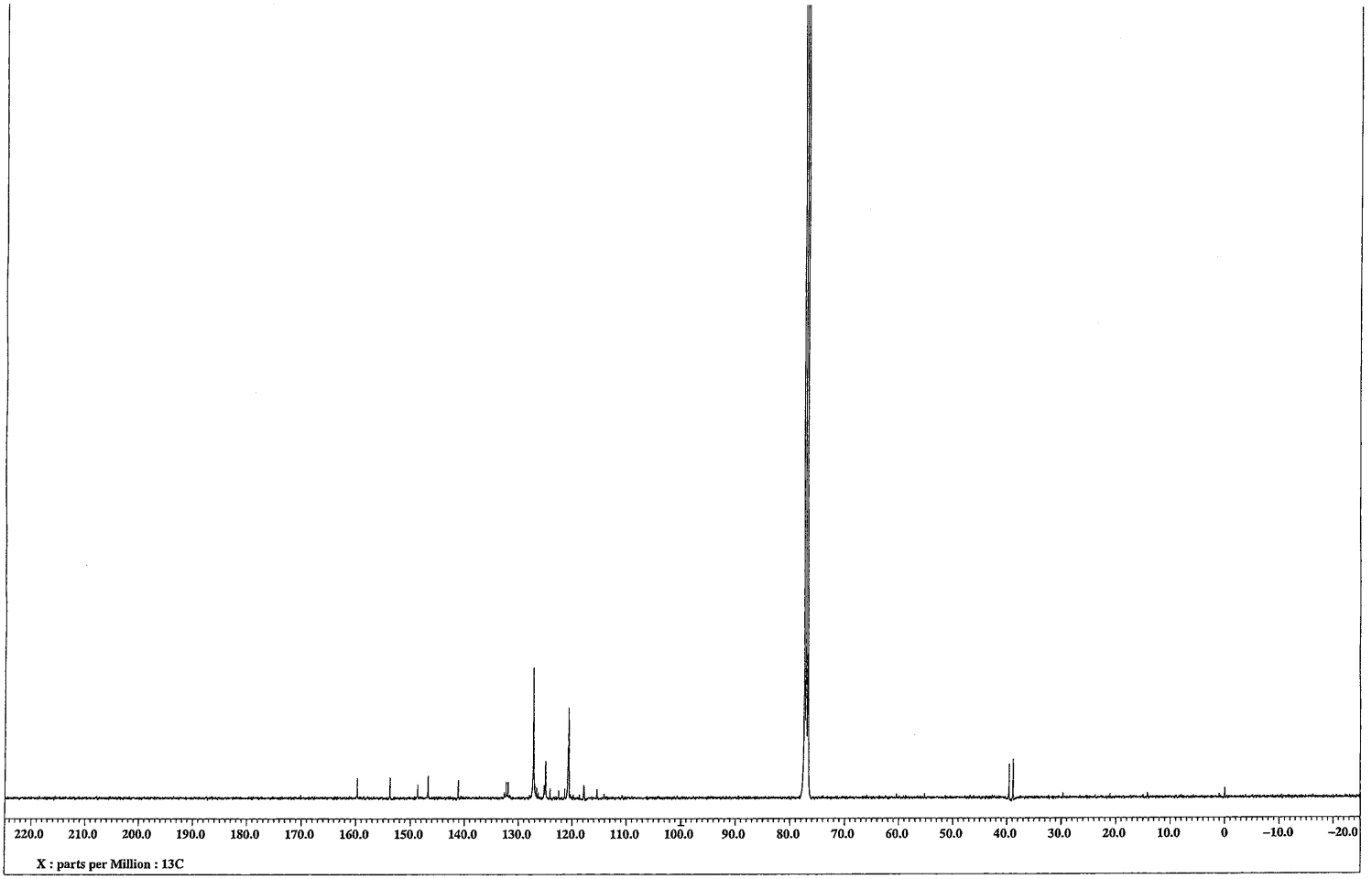


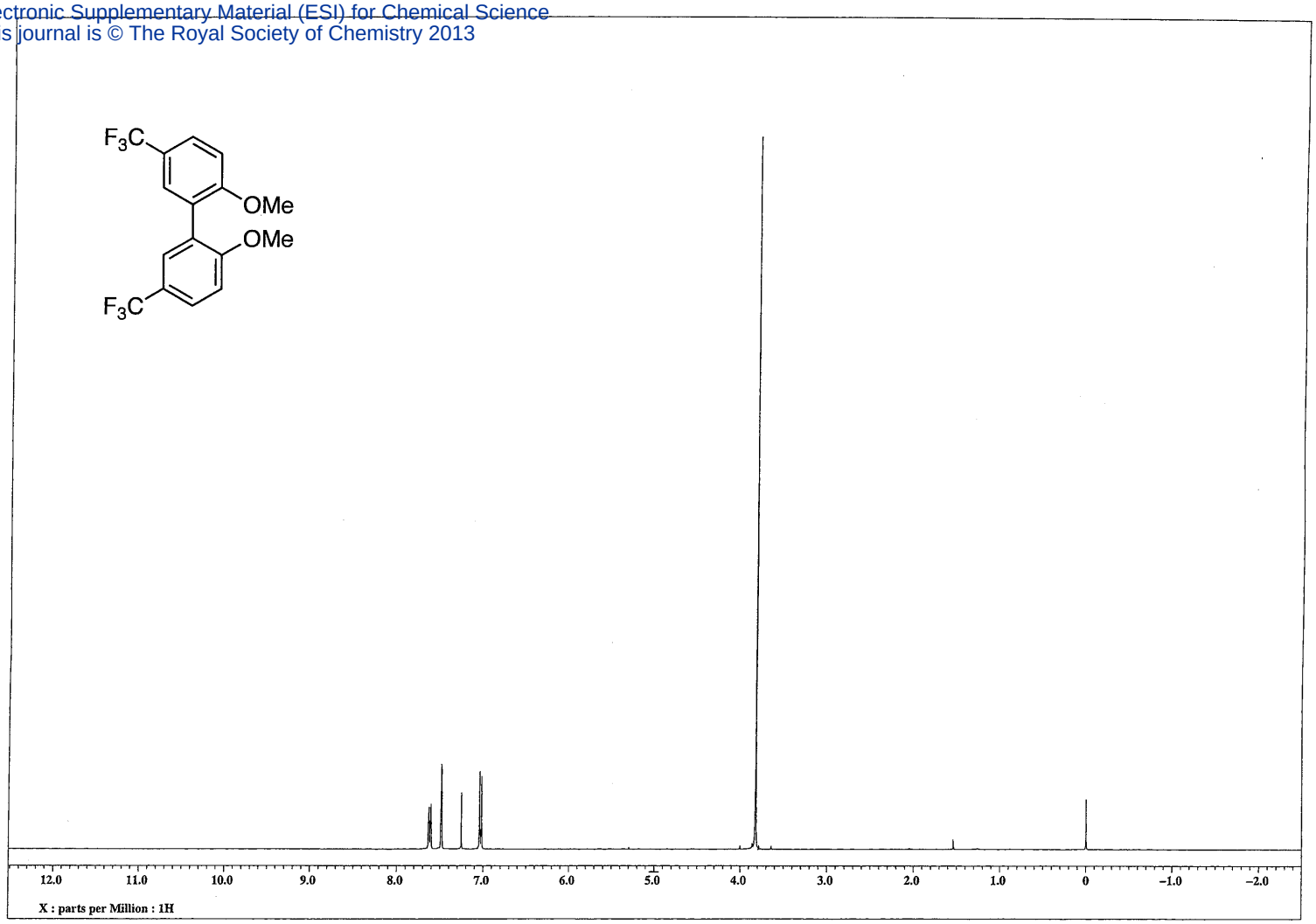


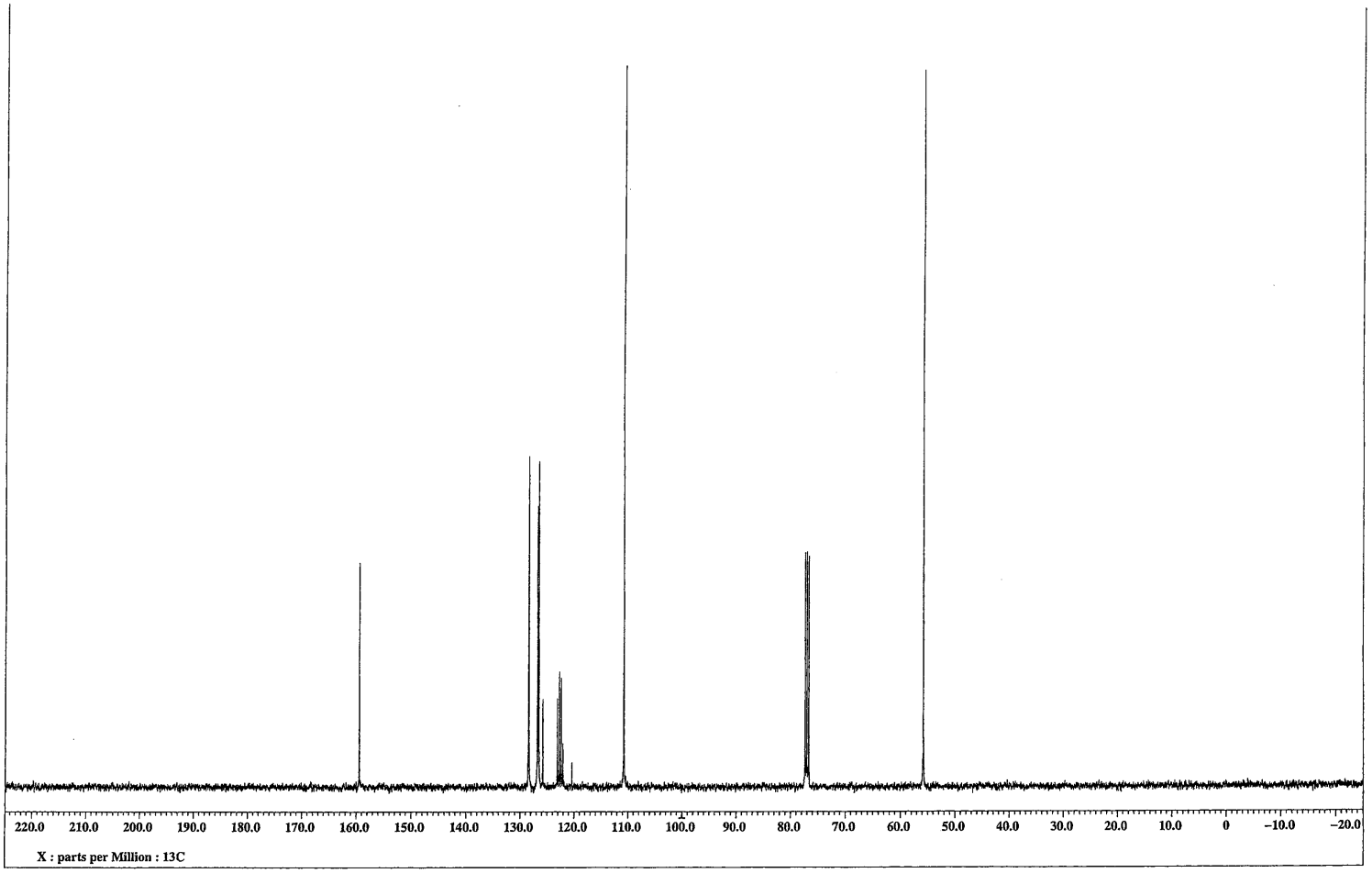


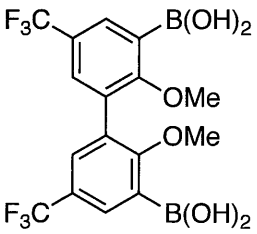


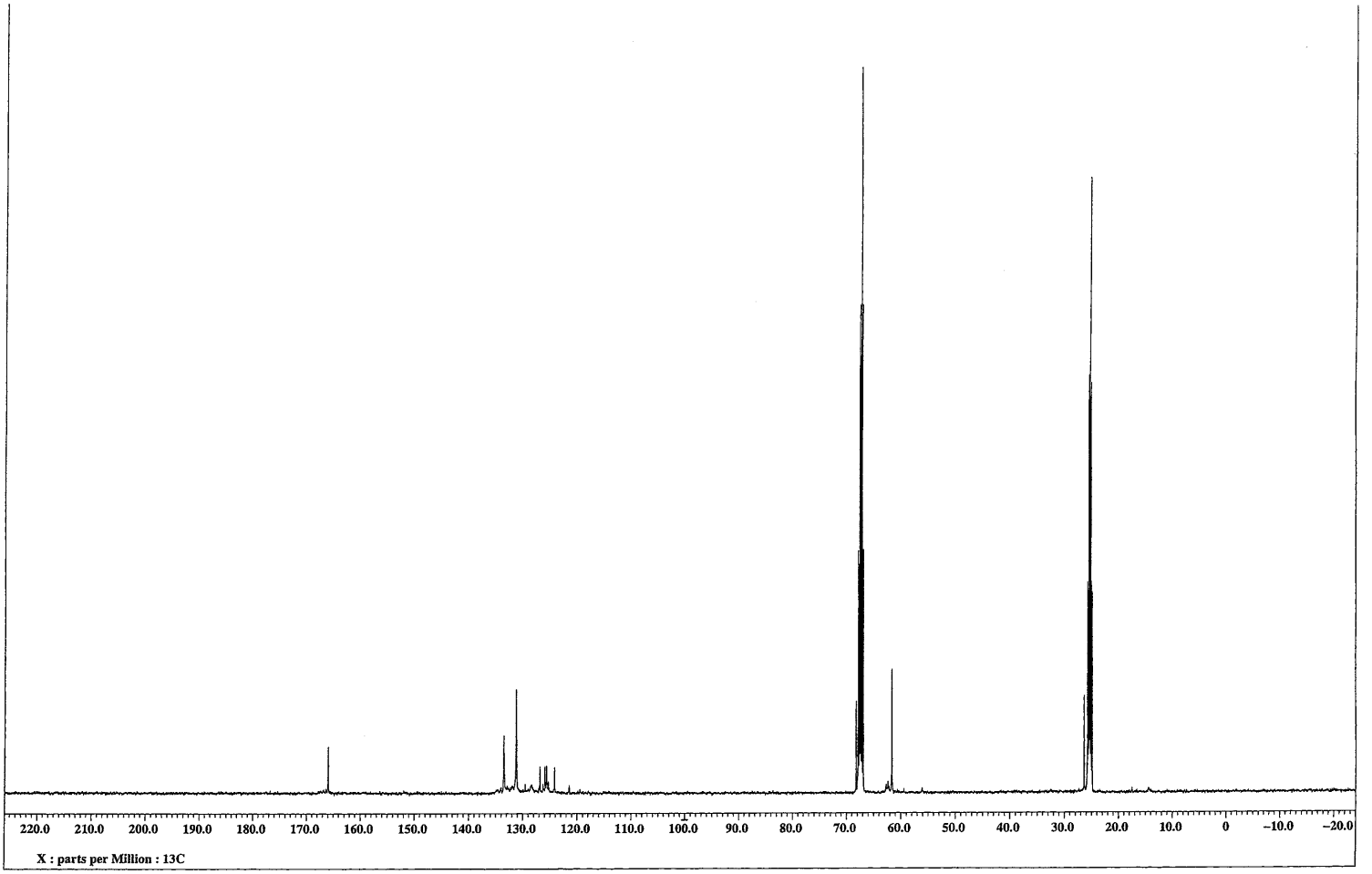


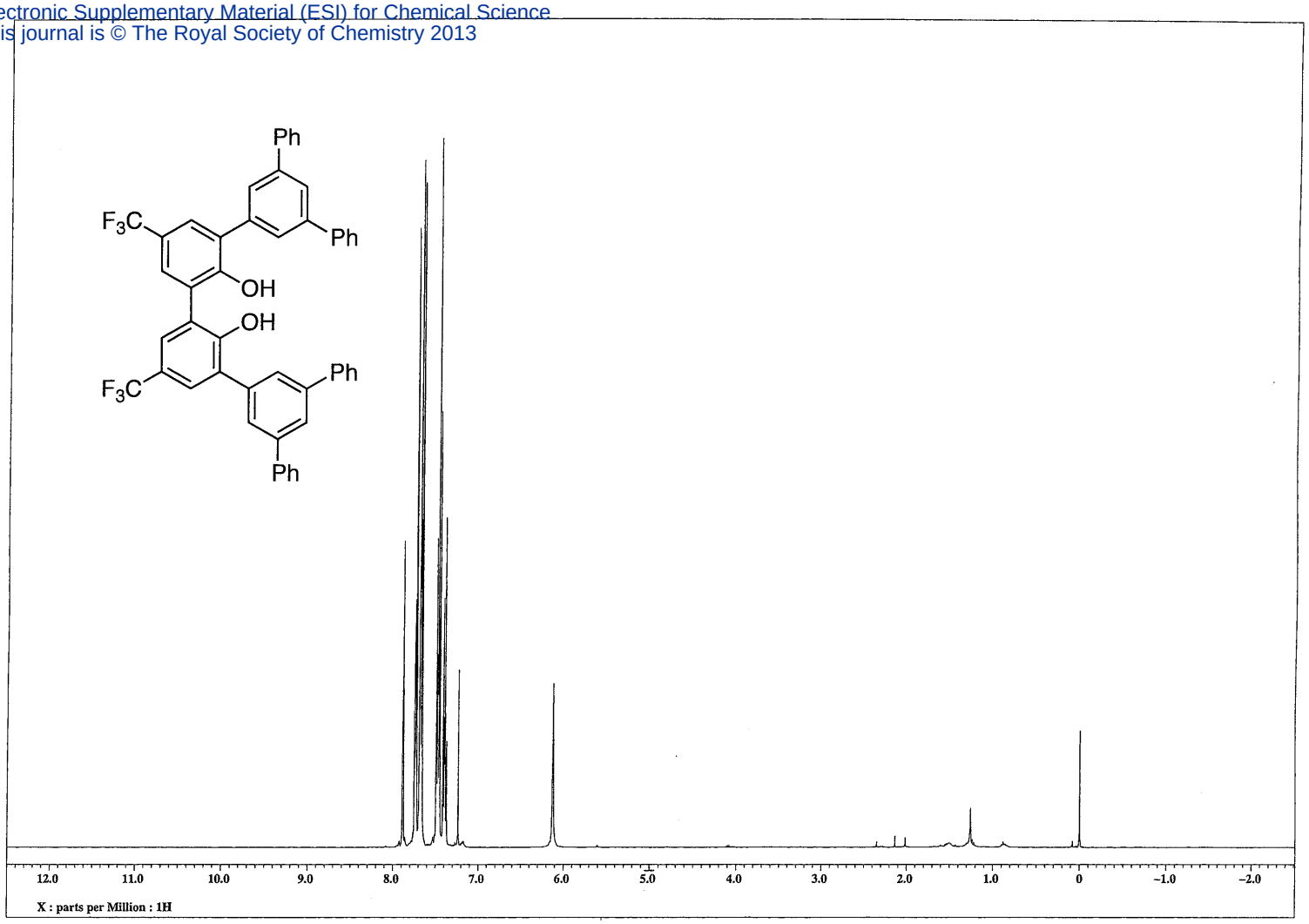


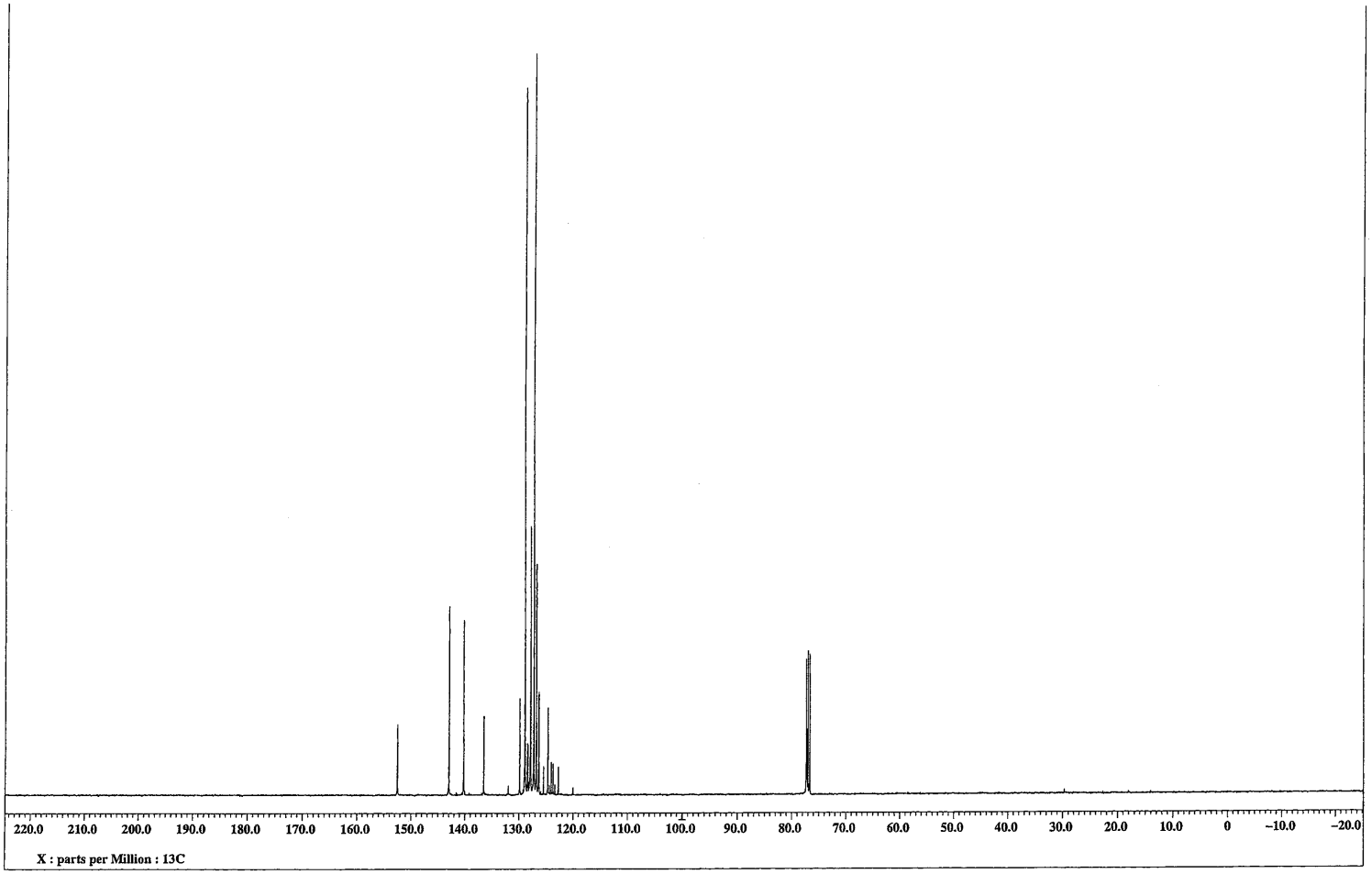


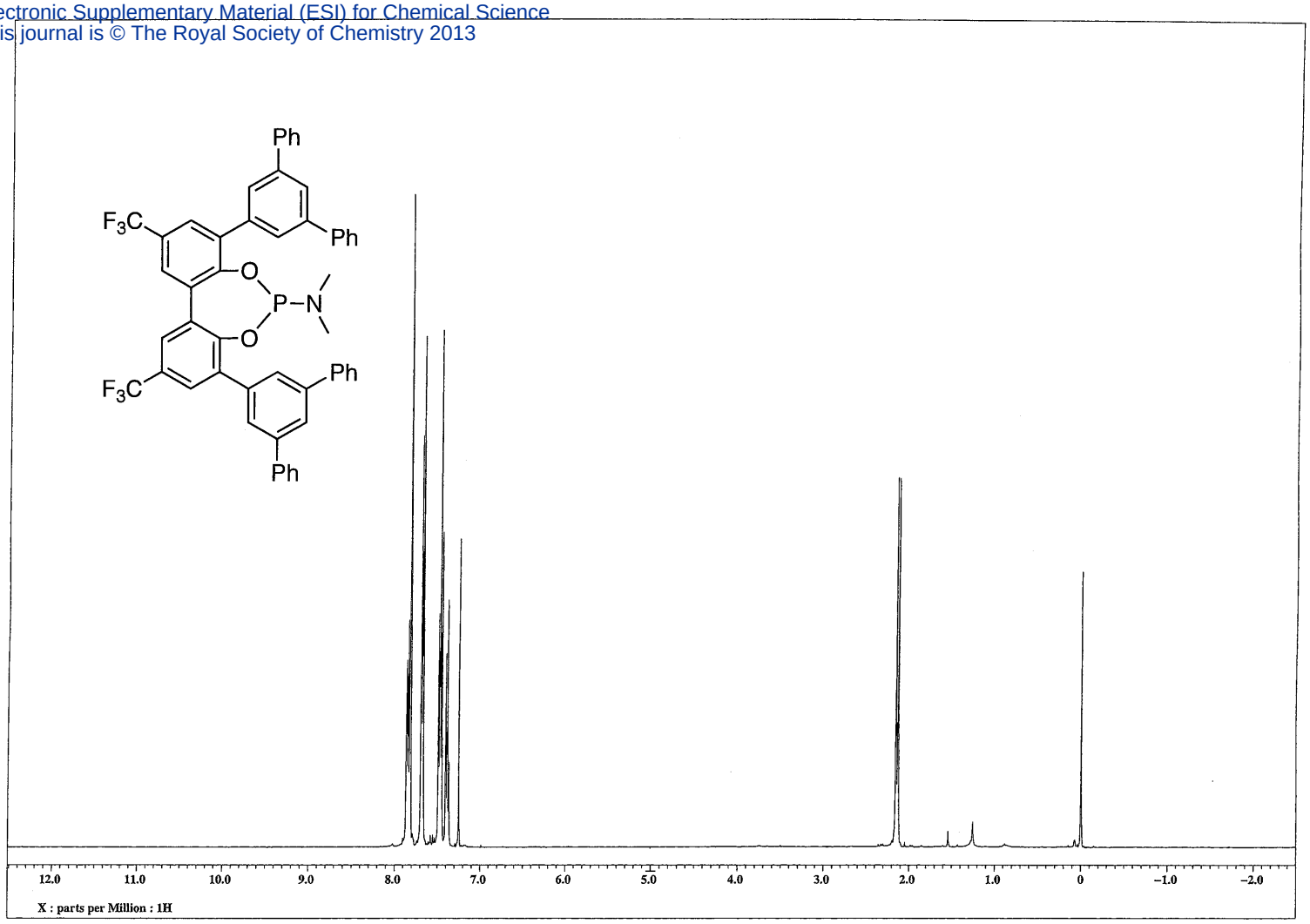


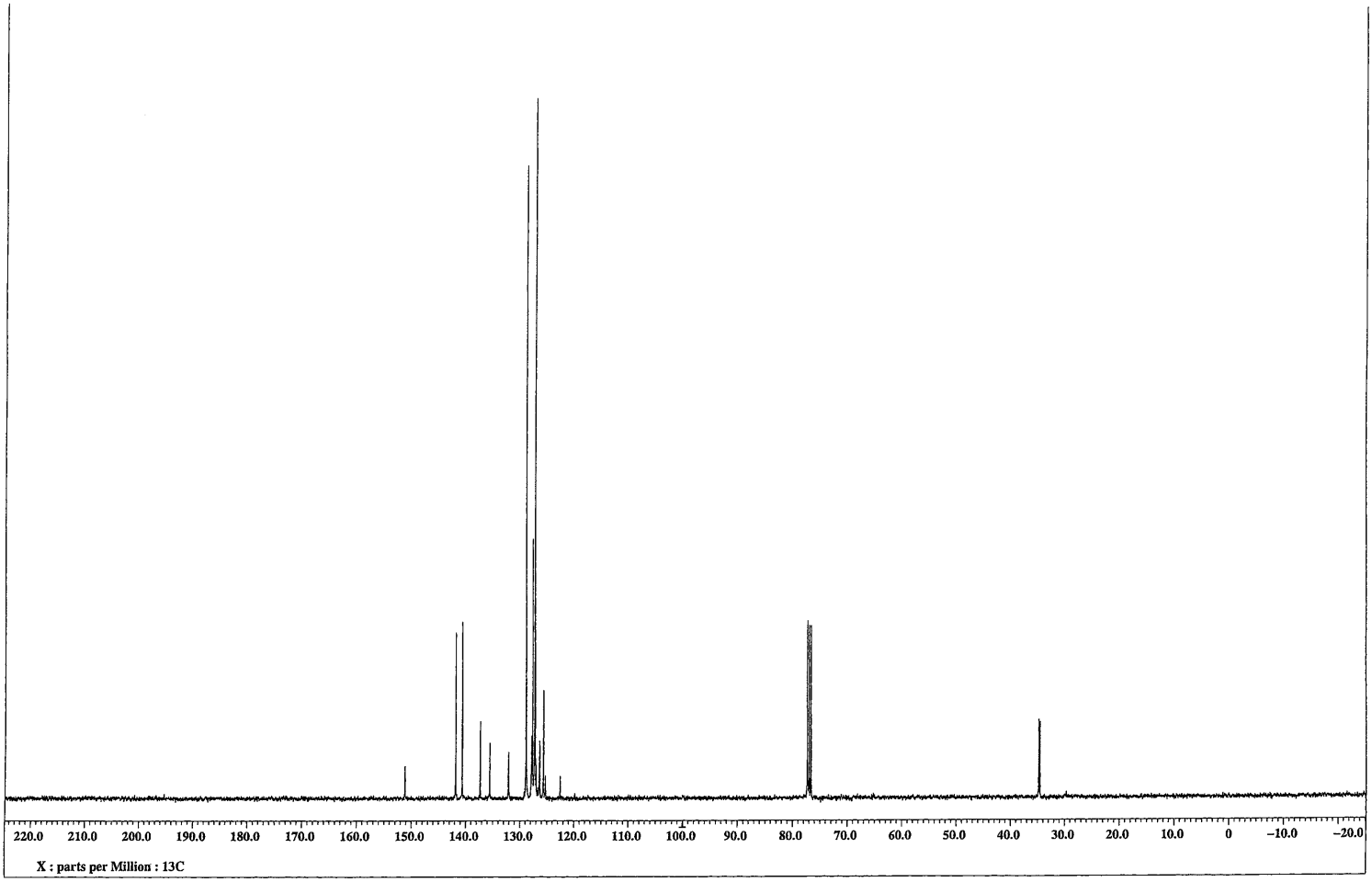


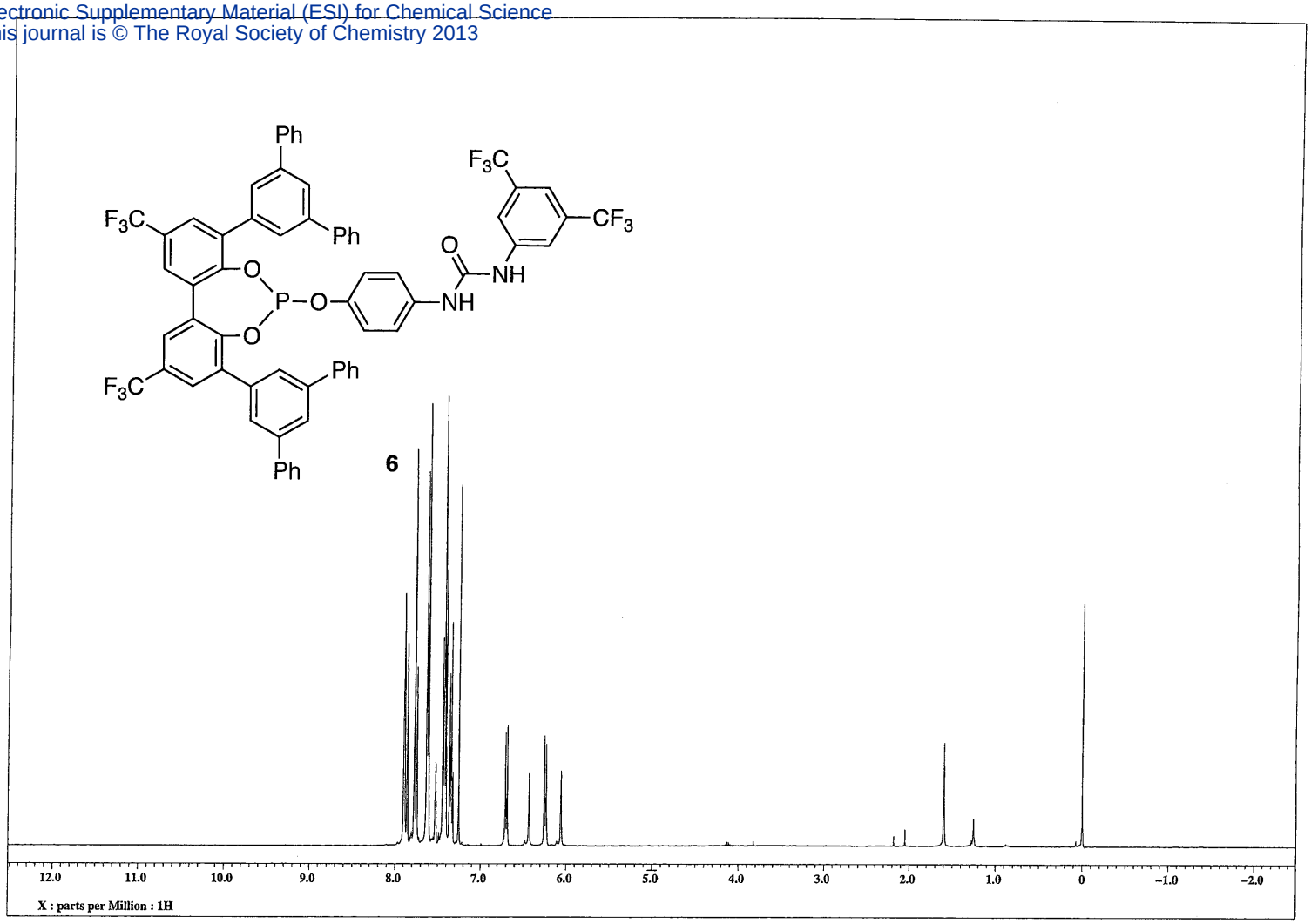


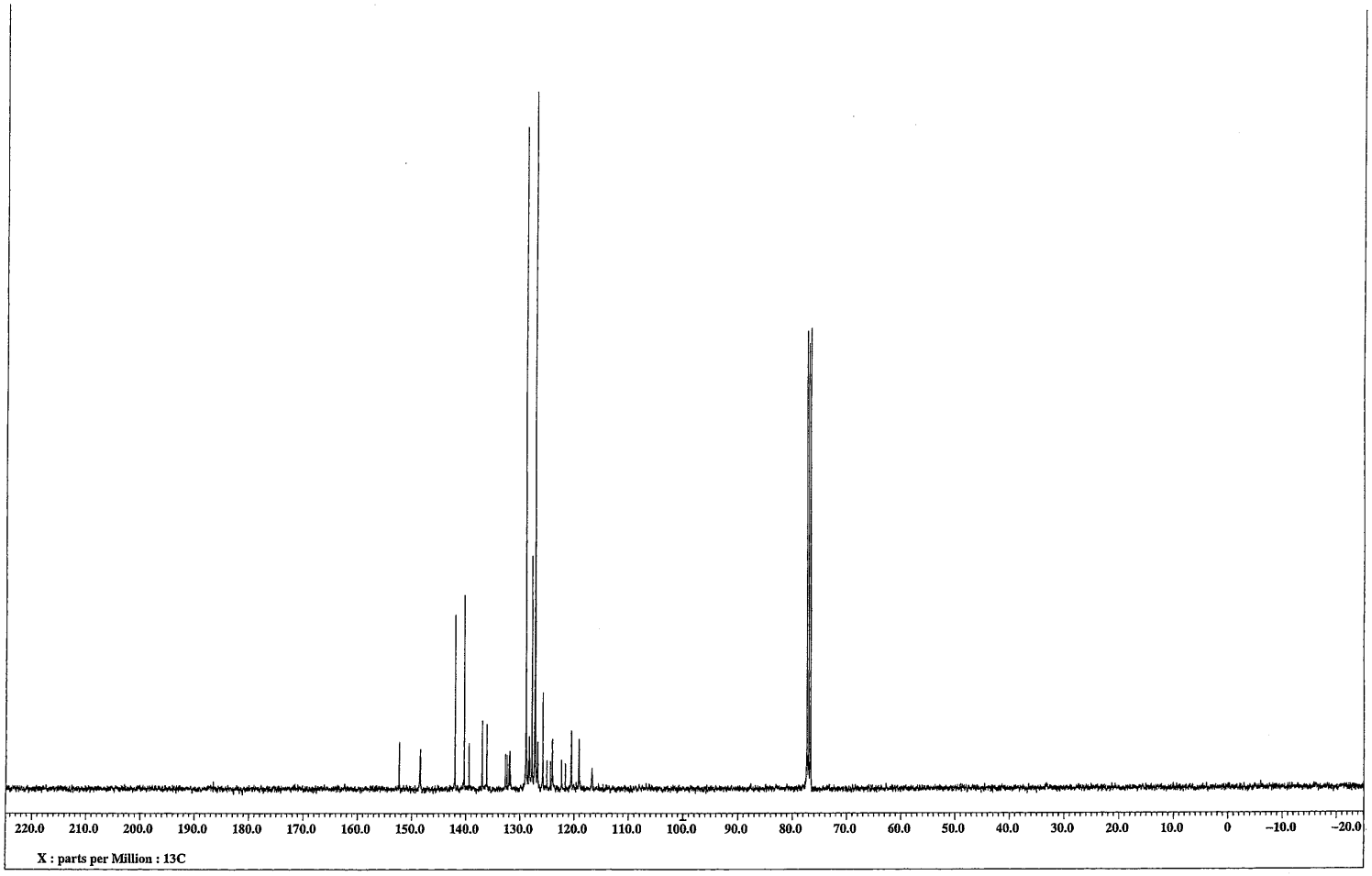


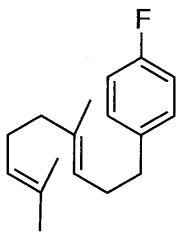




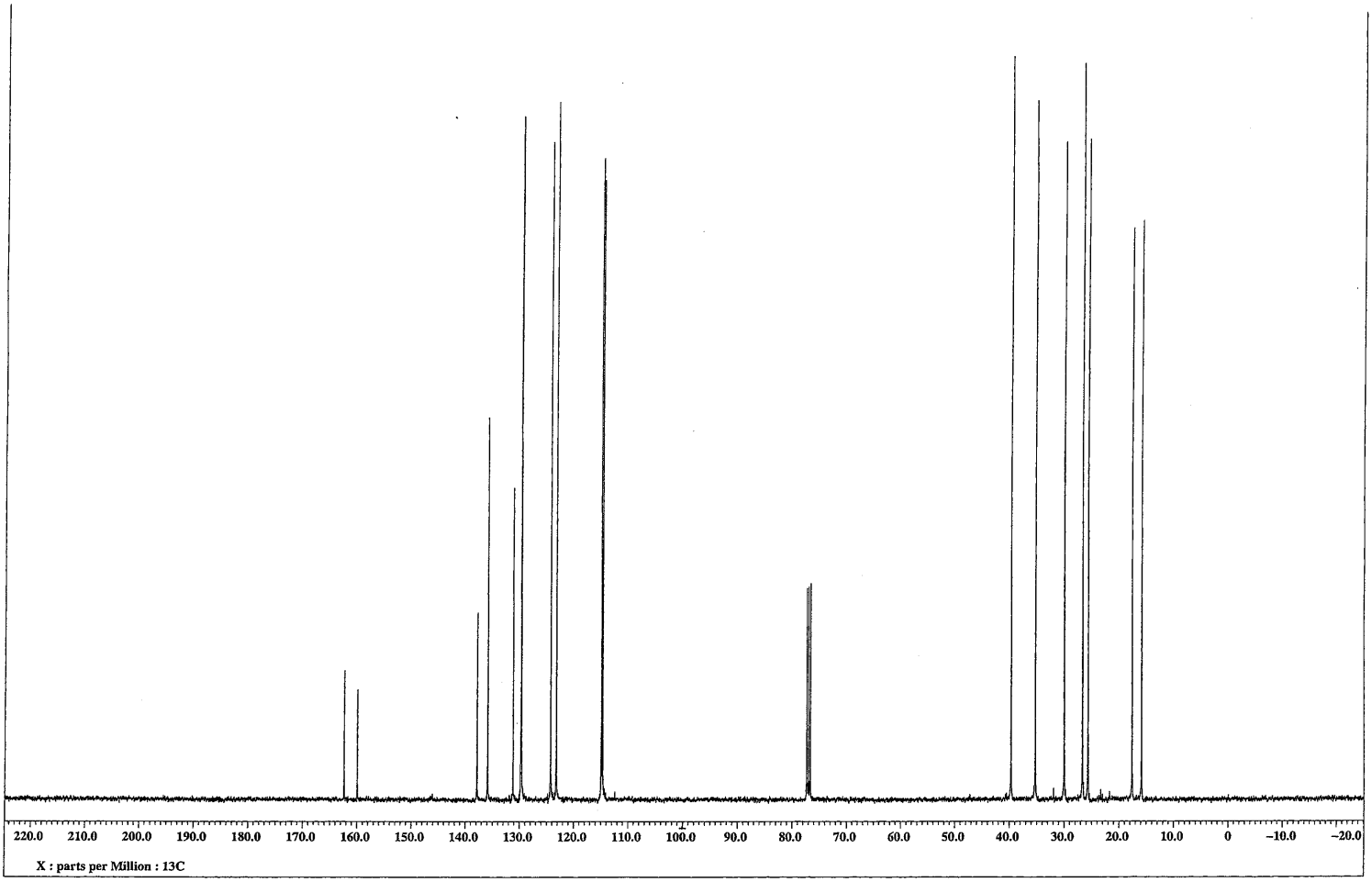


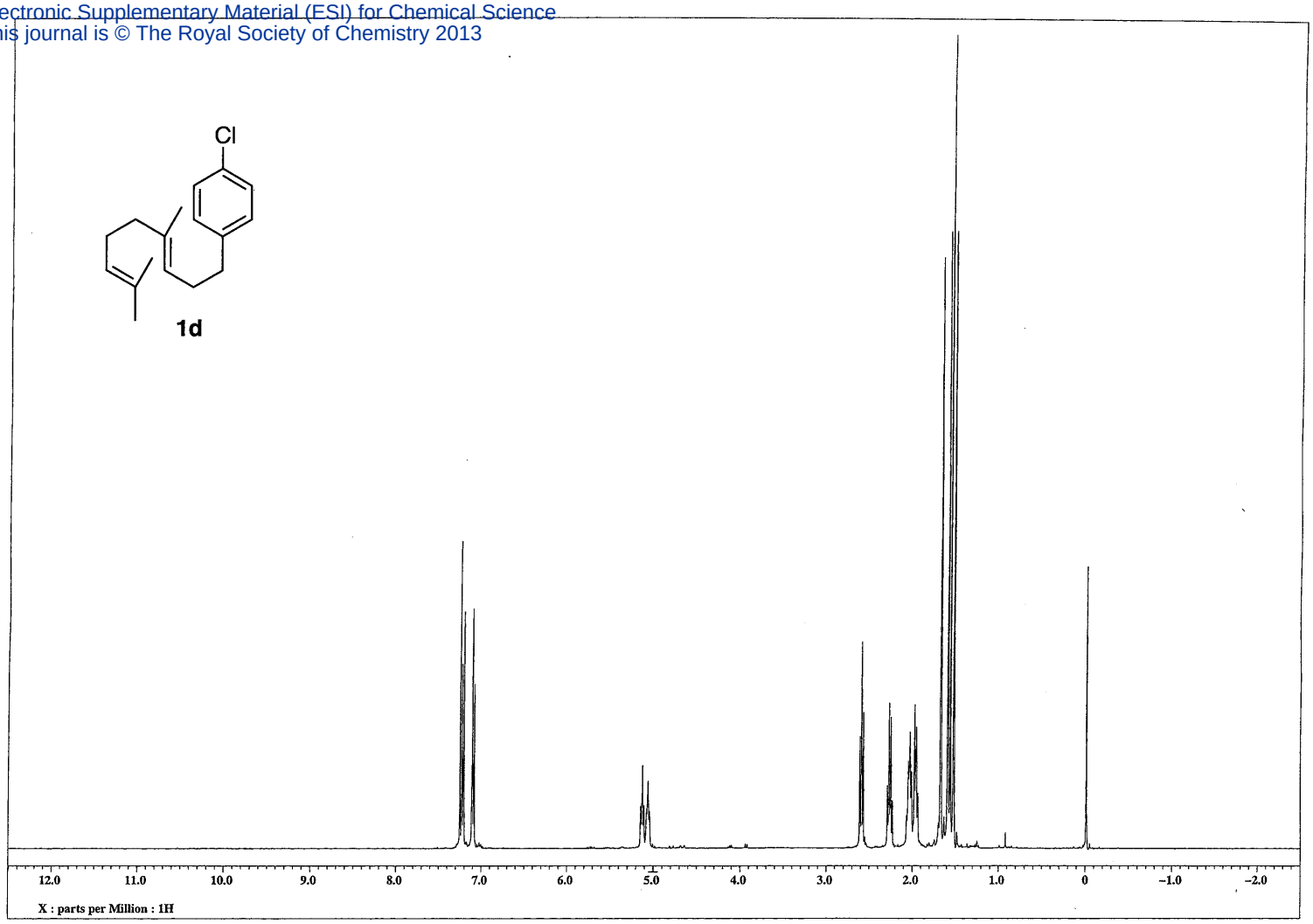


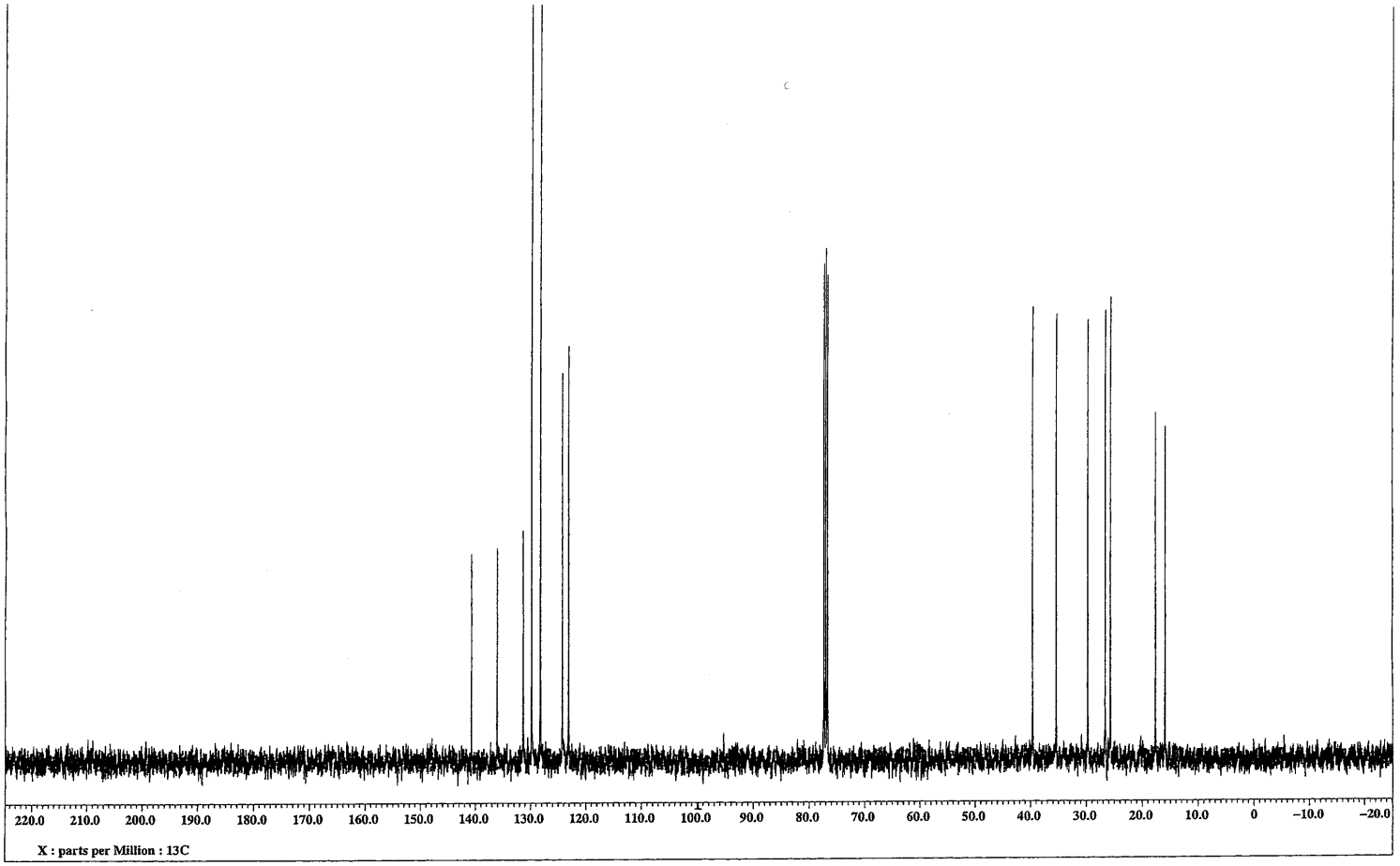


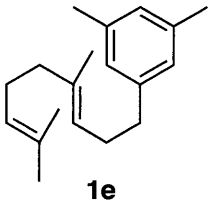


1c

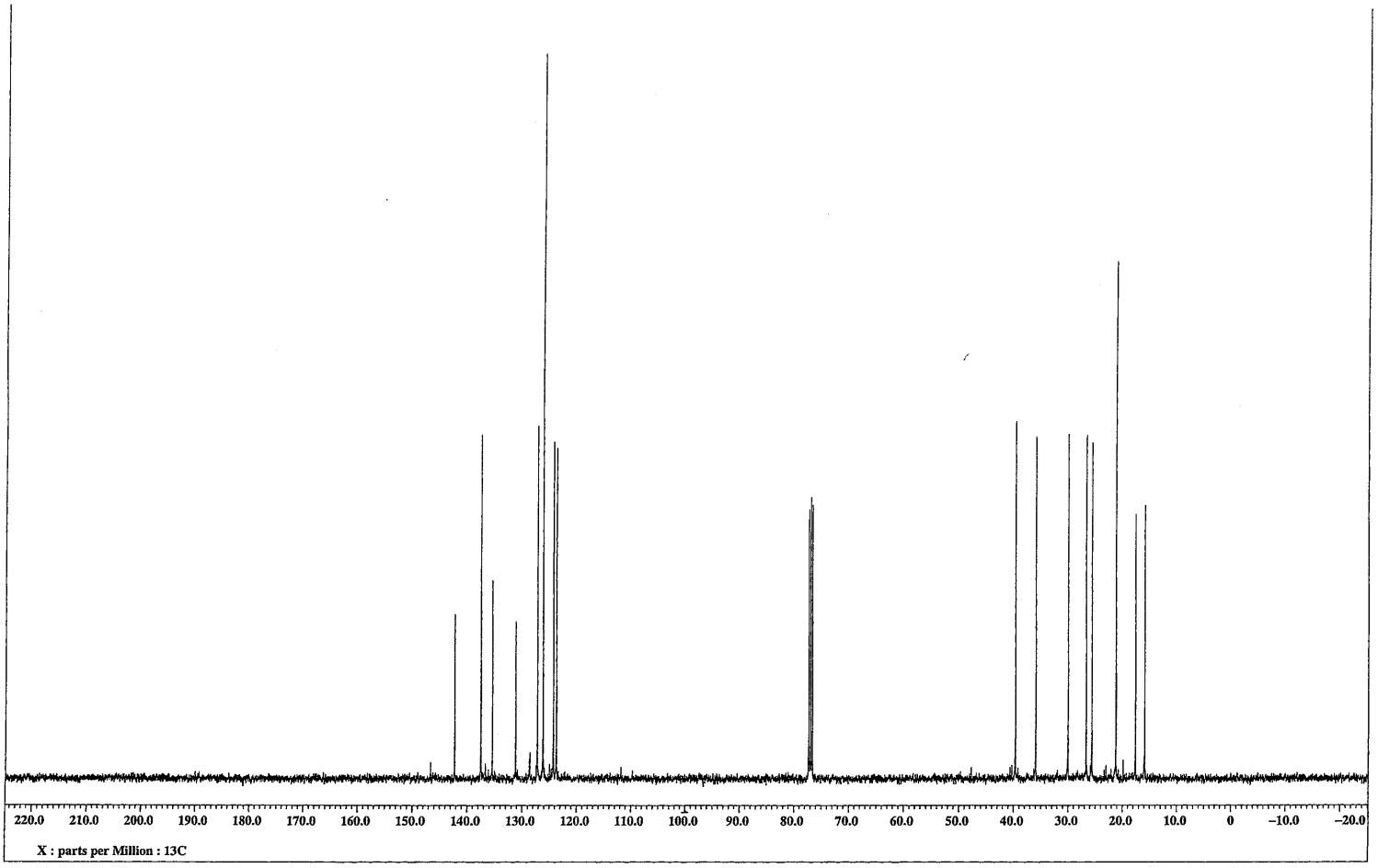


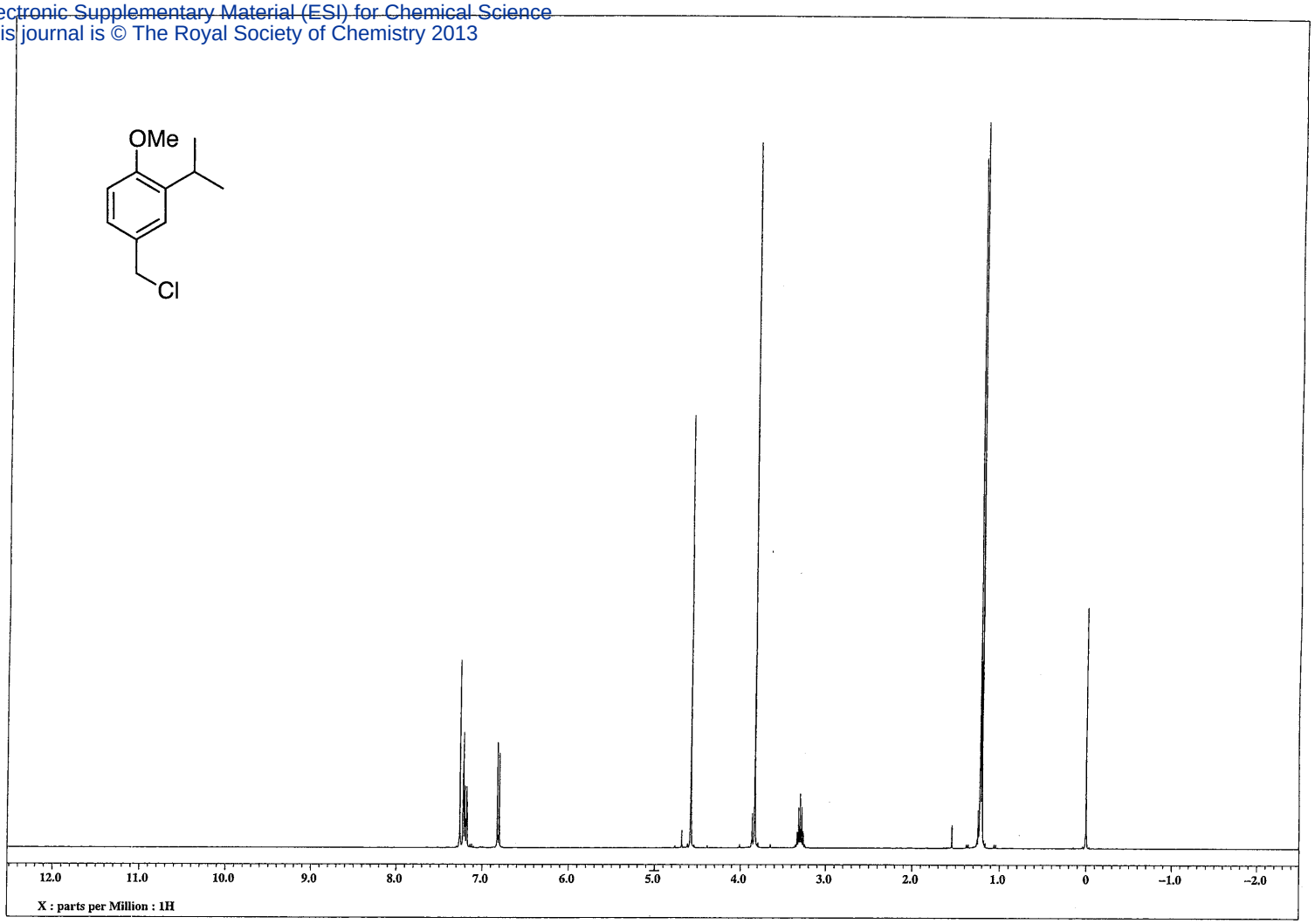


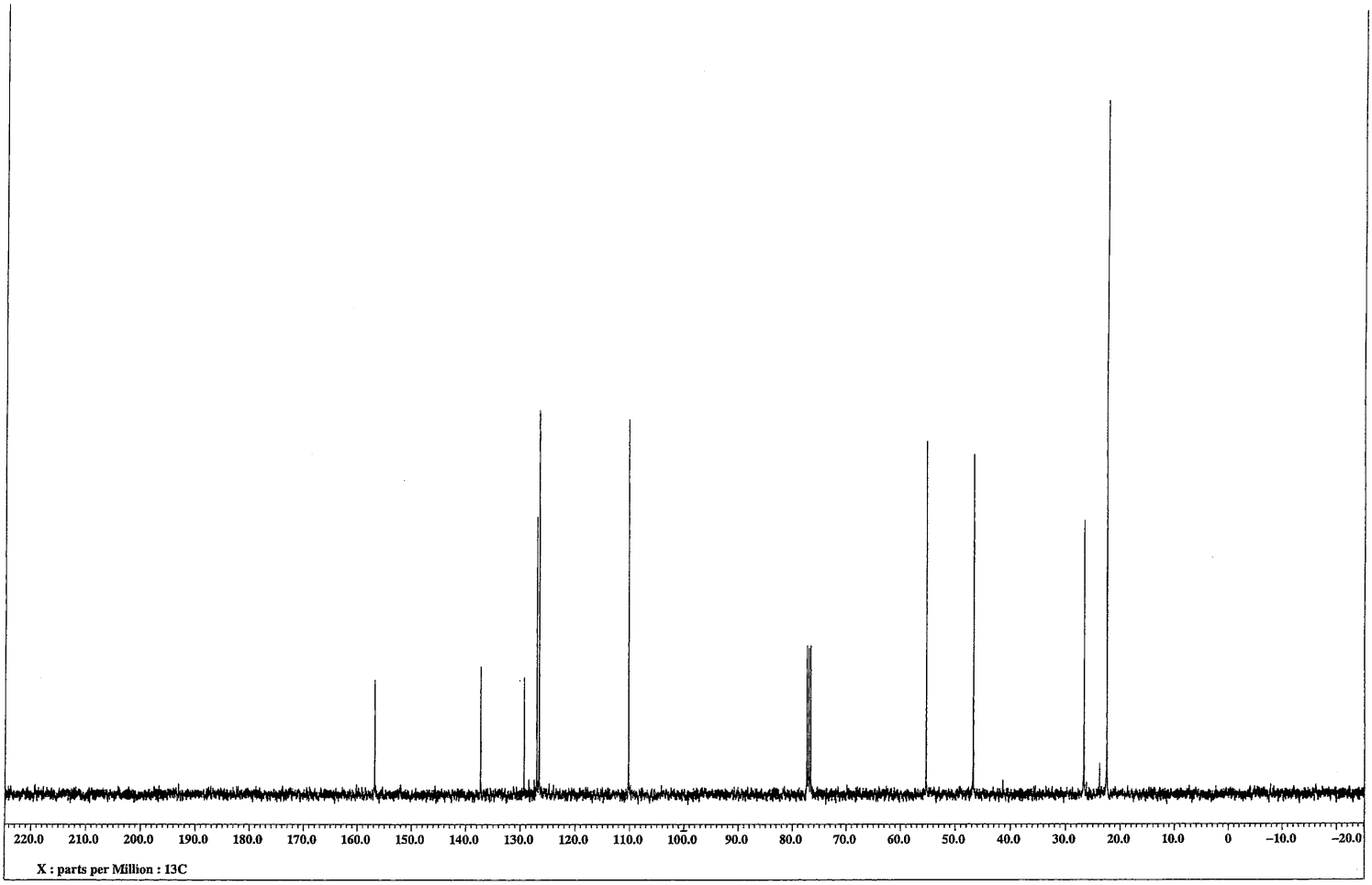


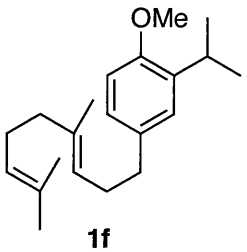


1e

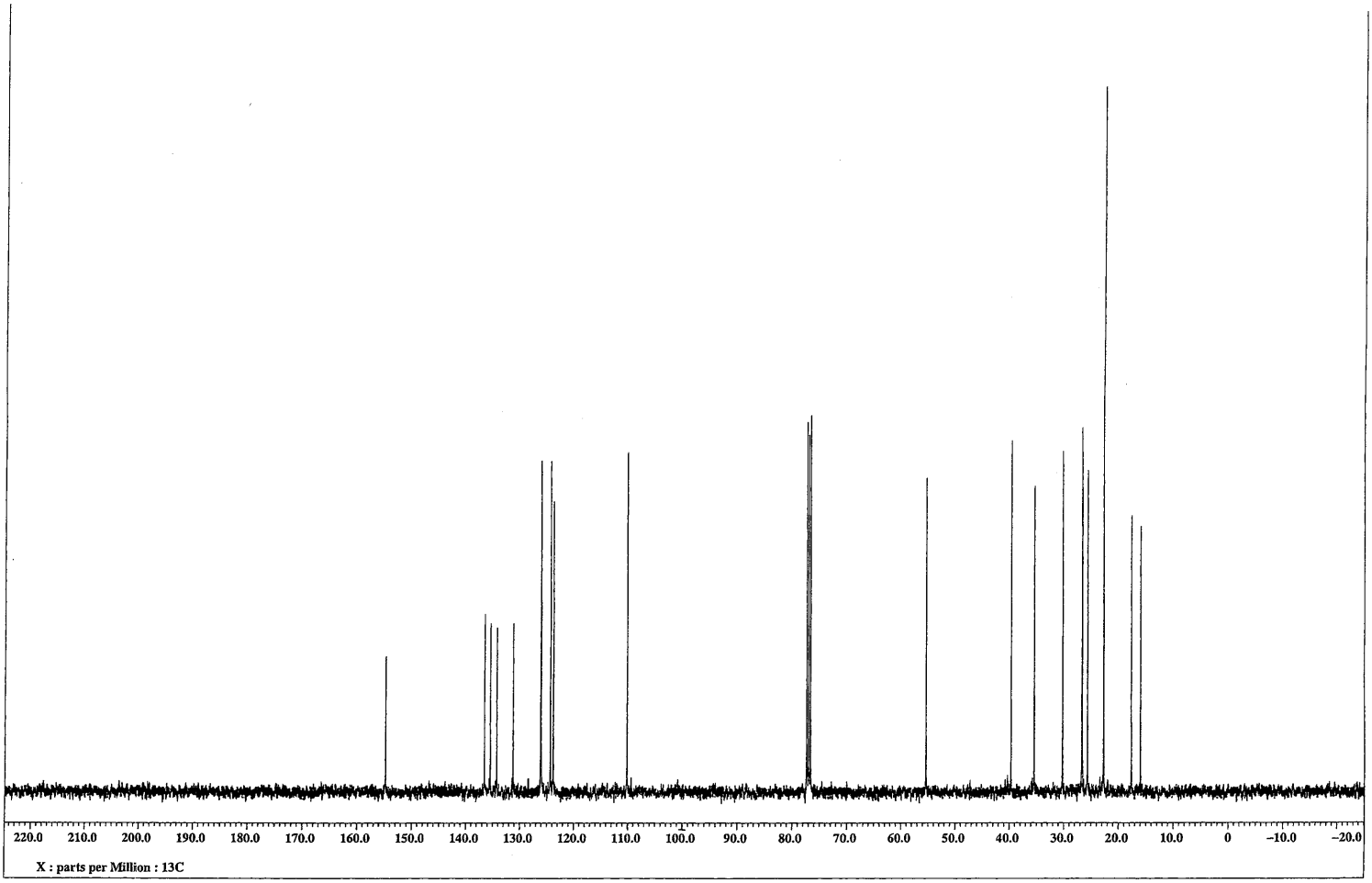


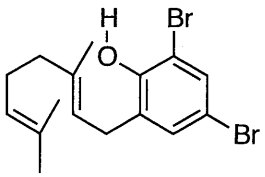


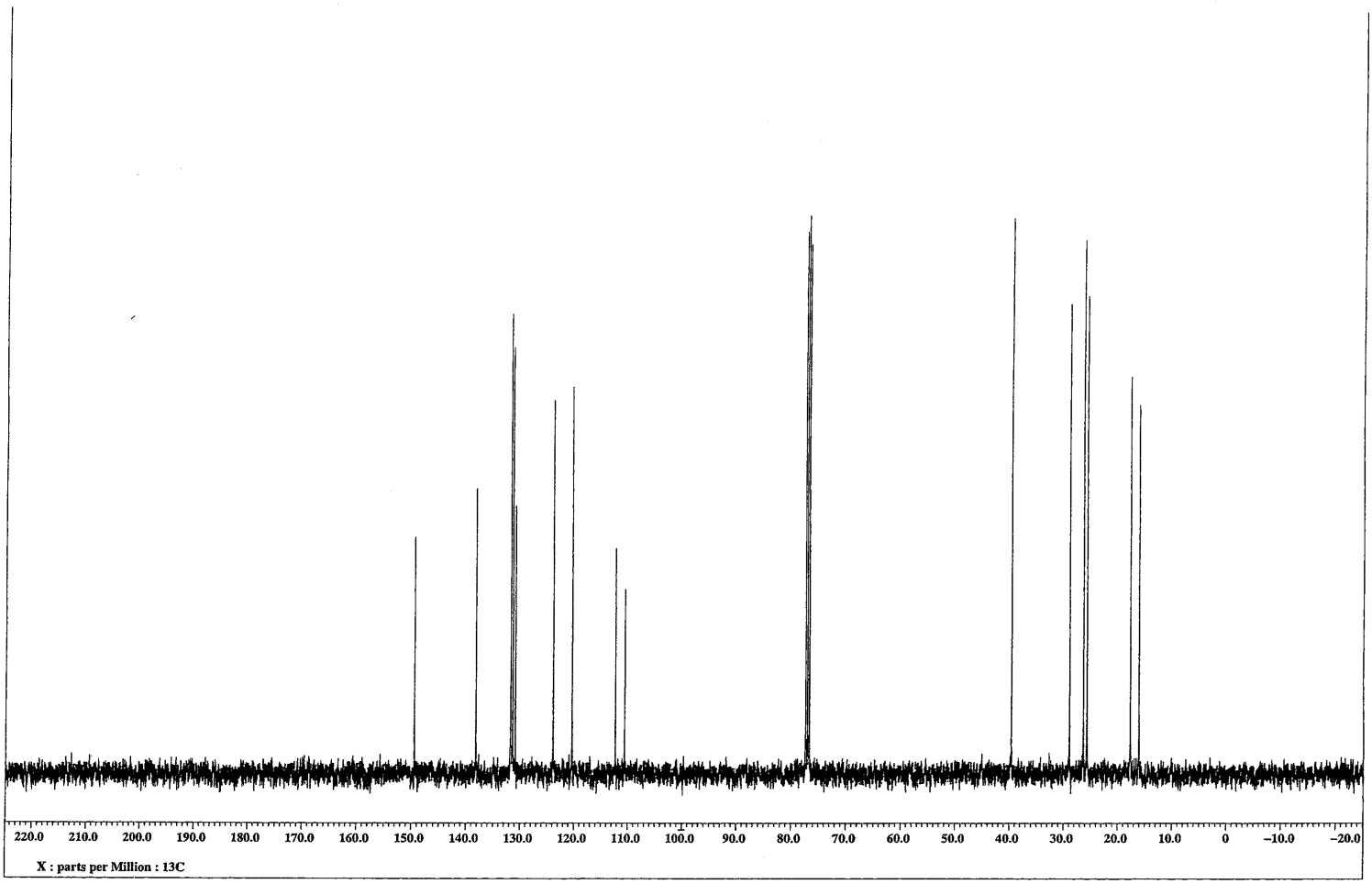


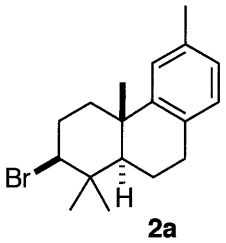


1f

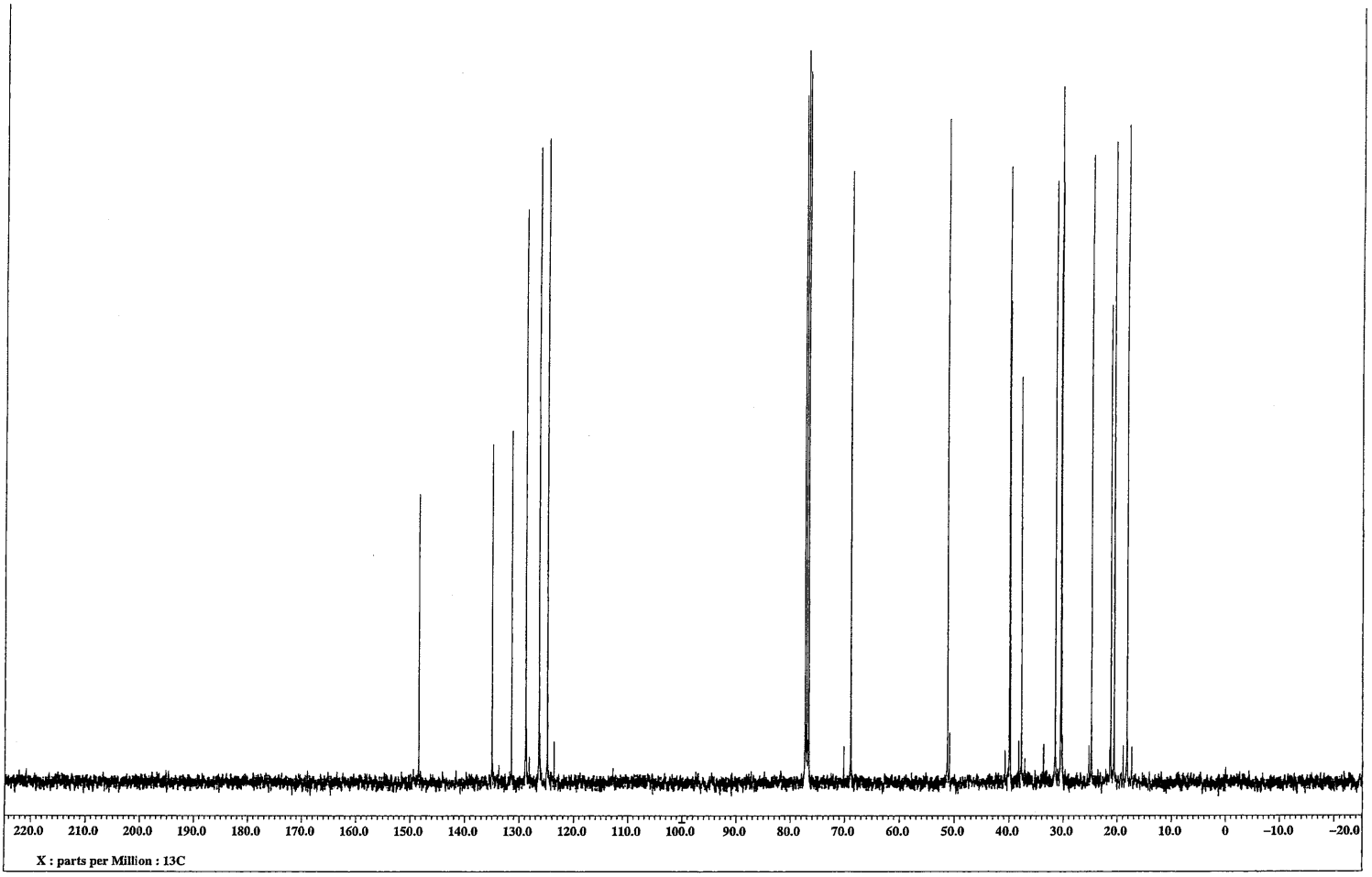


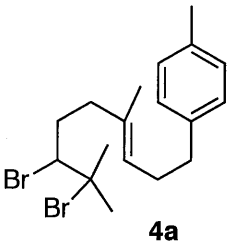




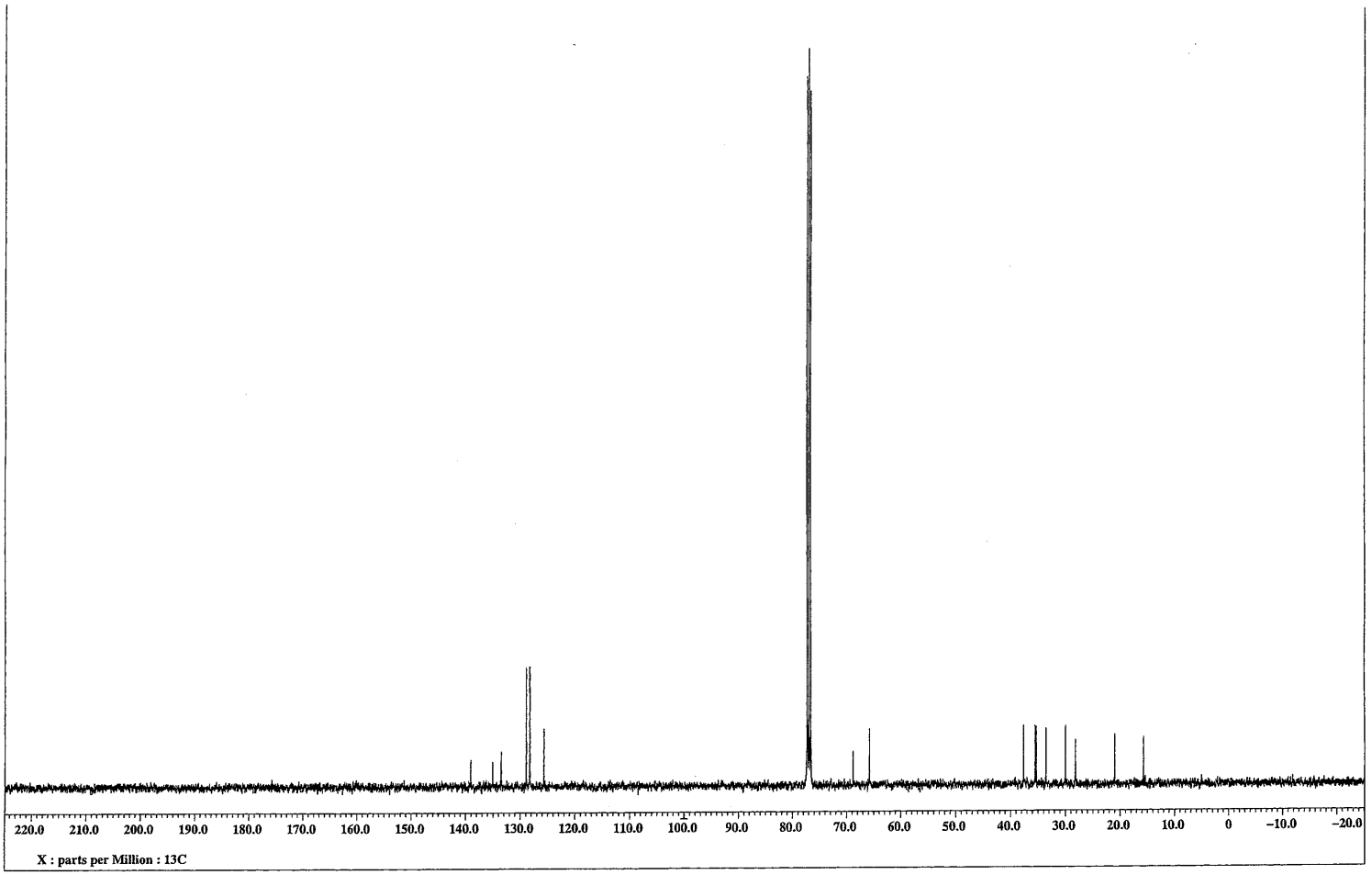


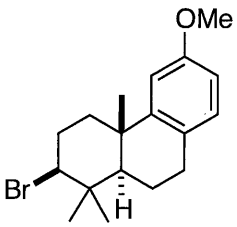
2a



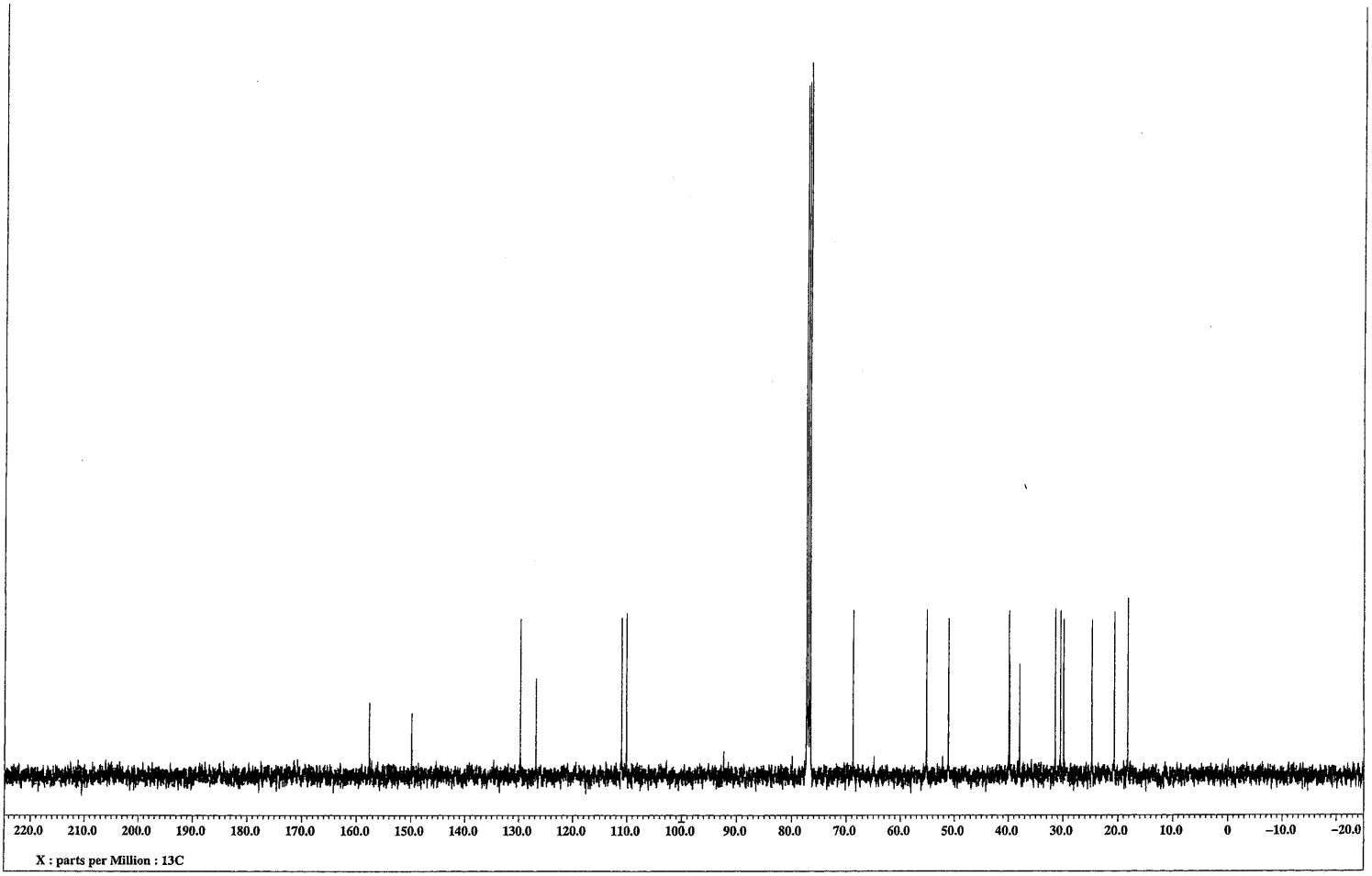


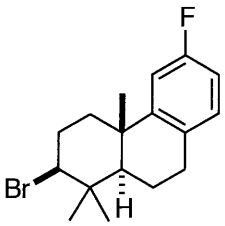
4a



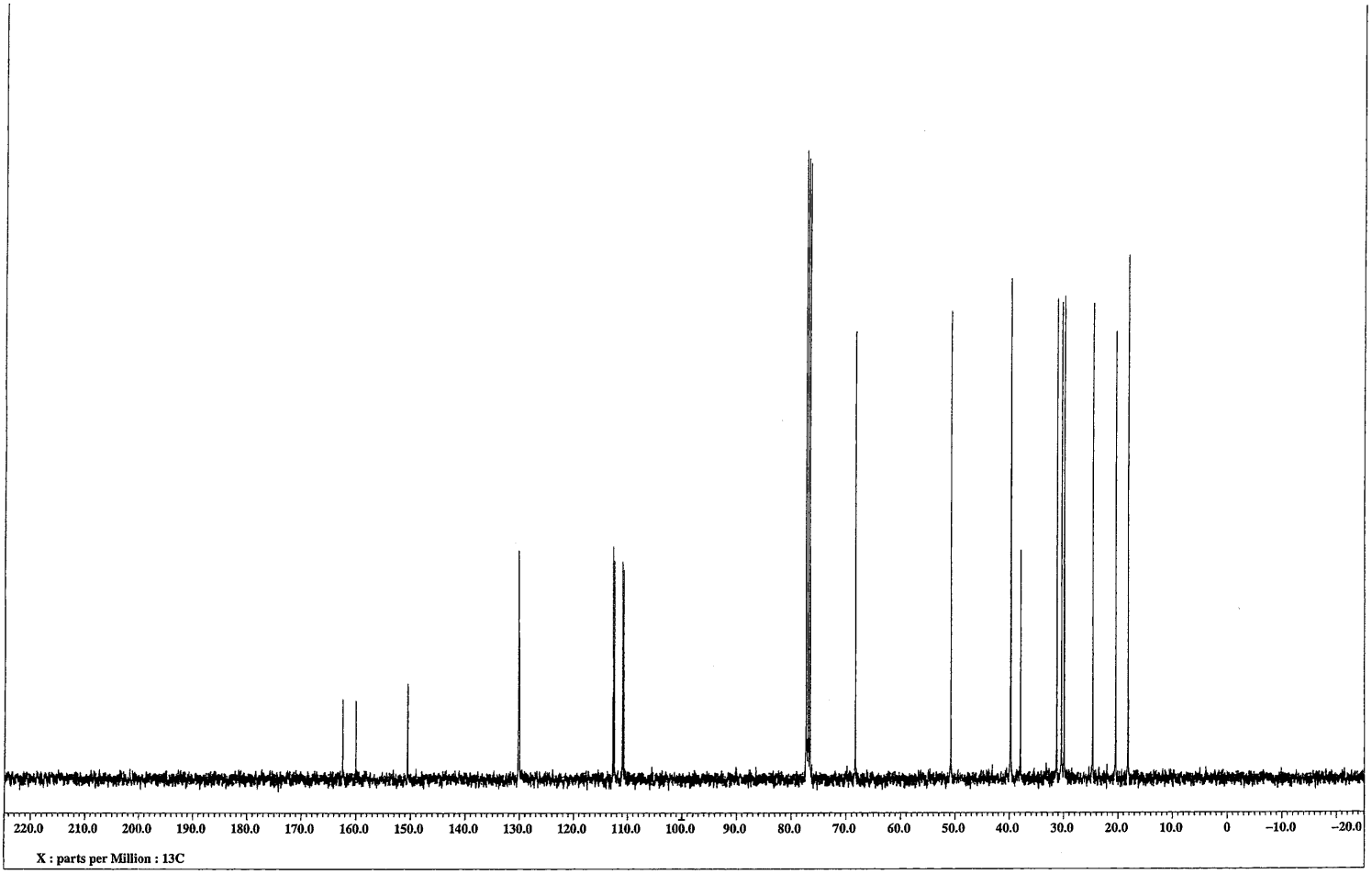


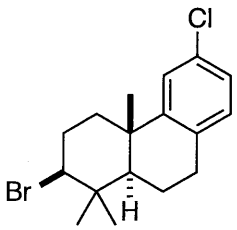
2b



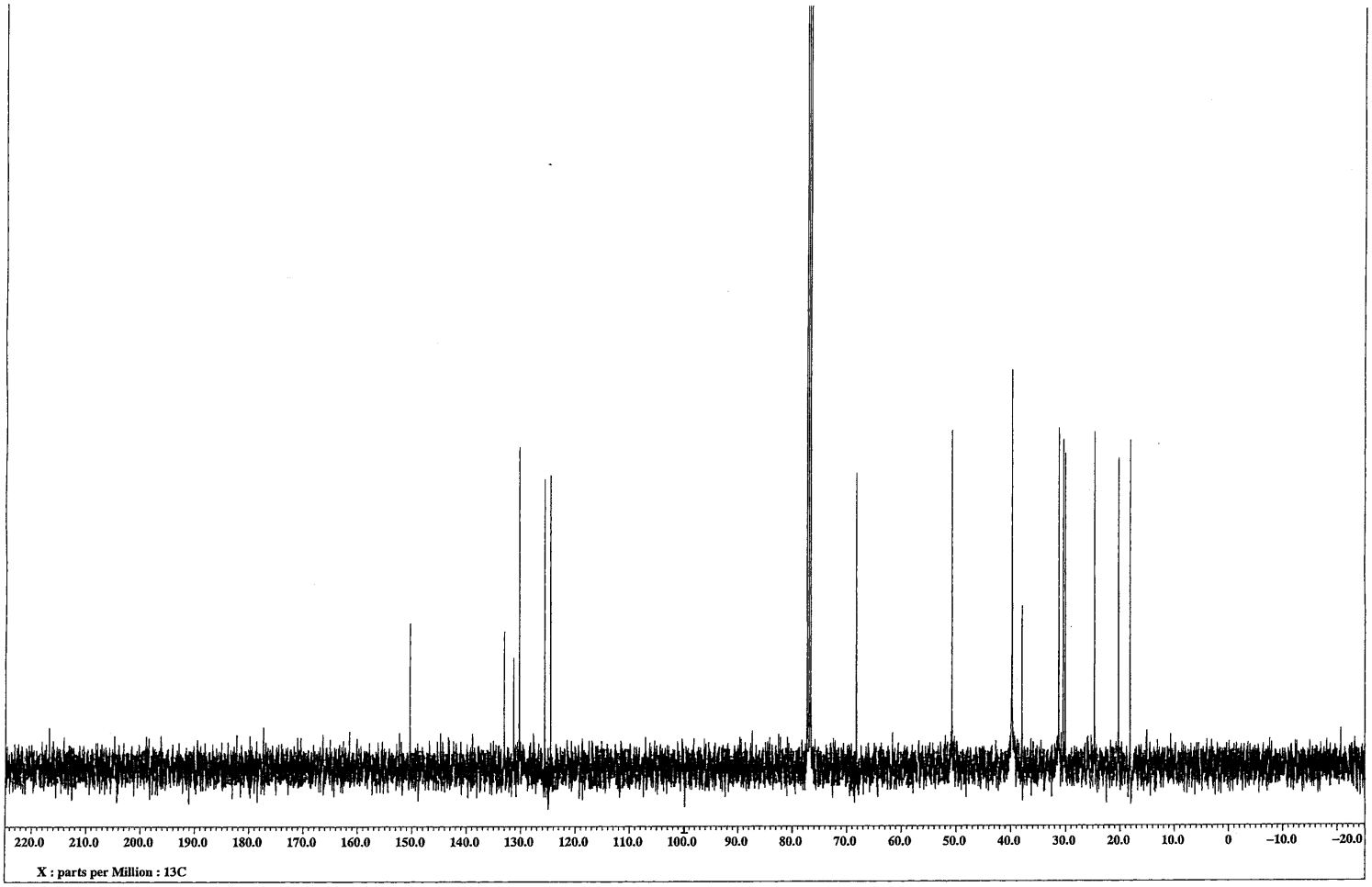


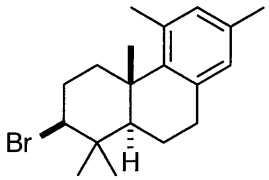
2c



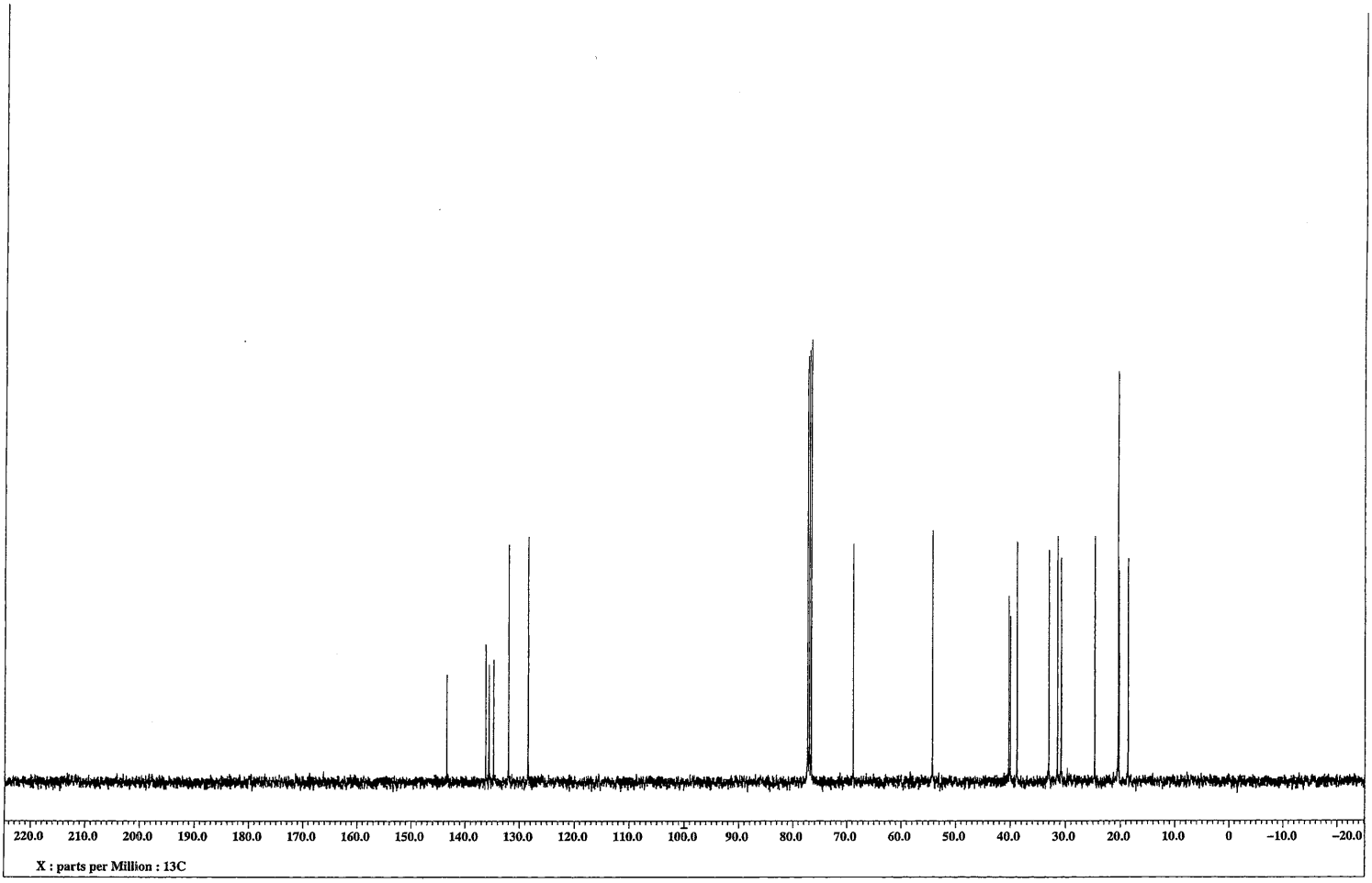


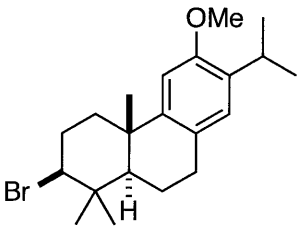
2d



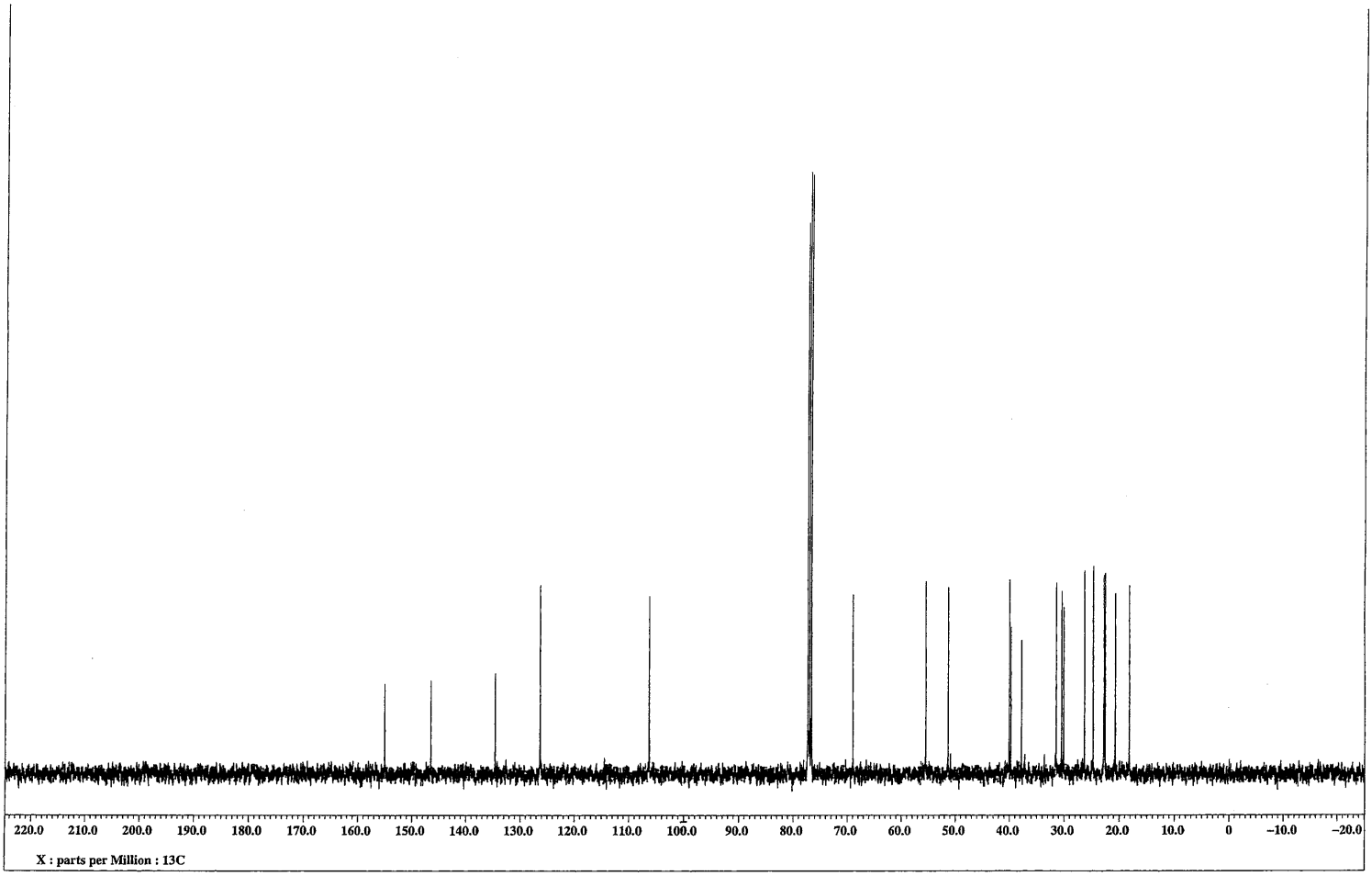


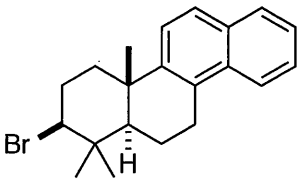
2e





2f





2g