Supporting Information for the Enantioselective Diels–Alder Reaction of 1,2-Dihydropyridines with α-Acyloxyacroleins Catalyzed by Chiral Primary Ammonium Salt

Kazuaki Ishihara,[*,†,§] Hiroki Yamada[†] and Matsujiro Akakura[‡,§]

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

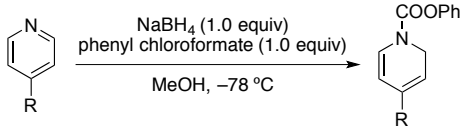
[‡]*Department of Chemistry, Aichi University of Education, Igaya-cho, Kariya, Aichi 448-8542, Japan,*

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

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, 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). 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-H (4.6 mm × 25 cm), Daicel CHIRALCEL OZ-H (4.6 mm × 25 cm), Daicel CHIRALPAK AD-3 (4.6 mm × 25 cm), Daicel CHIRALPAK OD-3 (4.6 mm × 25 cm), Daicel CHIRALPAK IA-3 (4.6 mm × 25 cm). Optical rotations were measured on a RUDOLPH AUTOPOL IV digital polarimeter. 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) 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). In experiments that required dry solvent, tetrahydrofuran (THF), *N*,*N*-dimethylformamide (DMF) and dichloromethane (CH_2Cl_2) were purchased from Kanto, TCI or Wako as the "anhydrous." Nitroethane ($EtNO_2$), and triethylamine (Et_3N) were freshly distilled from calcium hydride. Other simple chemicals were analytical-grade and obtained commercially. Chiral triamine **6**,[1] α-acyloxyacroleins **9**,[1] and 1-phenoxycarbonyl-1,2-dihydropyridine (**8a**)[2] were prepared according to the known procedures.

Synthesis of 4-Substituted 1-Phenoxycarbonyl-1,2-dihydropyridines (8)[2]



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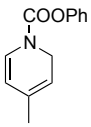
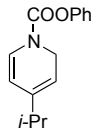
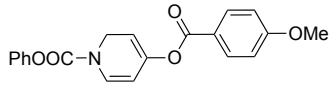


4-Methyl-1-phenoxycarbonyl-1,2-dihydropyridine (8b): To a solution of 4-methyl pyridine (4.7 g, 50 mmol) in MeOH (40 mL) was added $NaBH_4$ (1.9 g, 50 mmol) at –78 ºC, the mixture was stirred for 30 min. Phenyl chloroformate (7.8 g, 50 mmol) was slowly introduced to the mixture, and stirred for 3 h at the same temperature. The reaction was quenched by the successive addition of ice water and the solution was stirred until H_2 bubble stopped and then warmed up to ambient temperature. The mixture was extracted with EtOAc (100 mL × 3). The

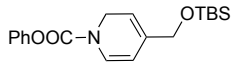
combined organic layers were washed with brine (100 mL × 2), dried over Na_2SO_4, filtrated and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 10:1) to give 4-methyl-*N*-phenoxycarbonyl-1,2-dihydropyridines in 70% yield (7.5 g, 35 mmol). IR ($CHCl_3$) 1726, 1359, 1204, 1174 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (3/2)) δ 1.75 (s, 3H), 4.34–4.43 (m, 1.3H), 4.48–4.58 (m, 0.7H), 5.12 (d, *J* = 7.8 Hz, 0.6H), 5.16 (d, *J* = 7.8 Hz, 0.4H), 5.22–5.28 (m, 0.4H), 5.28–5.33 (m, 0.6H), 6.80 (d, *J* = 7.8 Hz, 0.4H), 6.87 (d, *J* = 7.8 Hz, 0.6H), 7.13 (d, *J* = 7.8 Hz, 2H), 7.19–7.27 (m, 1H), 7.37 (t, *J* =7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5, 44.0 and 44.4, 109.4 and 109.6, 113.54 and 114.1, 121.6 (2C), 124.8, 125.5 and 125.6, 129.3 and 129.4 (2C), 129.7 and 130.2, 150.9 and 151.5; HRMS (FAB) calcd for $C_{13}H_{14}NO_2$ $[M+H]^+$ 216.1019, found 216.1015.



4-Isopropyl-1-phenoxycarbonyl-1,2-dihydropyridine (8c): Compound **8c** was prepared from 4-isopropylpyridine according to the procedure for the synthesis of **8b**. 56% yield. IR ($CHCl_3$) 1727, 1359, 1205 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (3/2)) δ 1.05 (d, *J* = 6.9 Hz, 6H), 2.29 (h, *J* = 6.9 Hz, 1H), 4.41 (d, *J* = 3.7 Hz, 1.3H), 4.55 (d, *J* = 3.7 Hz, 1.3H), 5.19–5.33 (m, 2H), 7.14 (d, *J* = 8.2 Hz, 1H), 7.22 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 21.1 (2C), 32.4, 44.0 and 44.3, 107.3 and 107.6, 110.8 and 111.3, 121.6 (2C), 125.1, 125.6, 125.7 and 125.9, 129.3 (2C), 139.7 and 140.1, 150.9 and 151.4; HRMS (FAB) calcd for $C_{15}H_{18}NO_2$ $[M+H]^+$ 244.1332, found 244.1333.



4-(*p*-Methoxybenzoyloxy)-1-phenoxycarbonyl-1,2-dihydropyridine (8d): Compound **8d** was prepared from 4-(*p*-methoxybenzoyloxy)pyridine[3] according to the procedure for the synthesis of **8b**. 30% yield. White solid; IR (KBr) 1732, 1718, 1602, 1510, 1333, 1283, 1161 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (3/2)) δ 3.88 (s, 3H), 4.66 (d, *J* = 4.1 Hz, 1.2H), 4.81 (d, *J* = 4.1 Hz, 0.8H), 5.19 (dd, *J* = 2.3, 8.7 Hz, 0.6H), 5.21 (dd, *J* = 2.3, 8.7 Hz, 0.4H), 5.32–5.40 (m, 1H), 6.92–6.98 (m, 2.6H), 7.02 (d, *J* =8.2 Hz, 0.4H), 7.15 (d, *J* = 7.8 Hz, 2H), 7.22–7.27 (m, 1H), 7.39 (t, *J* = 7.8 Hz, 2H), 8.05 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 44.0 and 44.4, 55.5, 103.8 and 104.1, 104.6 and 105.0, 113.8 (2C), 112.3 and 121.5 (2C), 125.9, 127.6, 128.5, 129.4 (2C), 132.2 (2C), 144.1 and 144.5, 150.8 and 151.3, 152.0, 152.3, 163.9 and 164.3 ; HRMS (FAB) calcd for $C_{20}H_{17}NO_5$ [M] 351.1107, found 351.1111.

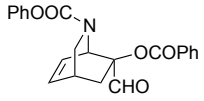


4-(*tert*-Butyldimethylsilyloxy)methyl-1-phenoxycarbonyl-1,2-dihydropyridine (8e): Compound **8e** was prepared from 4-[(*tert*-butyldimethylsilyloxy)methyl]pyridine[4] according to the procedure for the synthesis of **8b**. 47% yield. White participate; IR ($CHCl_3$) 1731, 1353, 1204 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) a

mixture of rotamers (2/1): δ 0.10 (s, 6H), 0.93 (s, 9H), 4.12 (s, 2H), 4.30–4.62 (m, 0.4H), 4.38–4.48 (m, 0.6H), 5.19 (t, *J* = 8.3 Hz, 1H), 5.45–5.55 (m, 1H), 6.84 (d, *J* = 7.8 Hz, 0.3H), 6.91 (d, *J* = 7.8 Hz, 0.7H), 7.13 (d, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.3, 7.3 Hz, 1H), 7.37 (dd, *J* = 7.8, 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ –5.37 (2C), 18.3, 25.9 (2C), 43.9 and 44.3, 105.3 and, 105.4, 112.5 and 113.1, 121.5 (2C), 125.4, 125.6 and 126.1, 129.3 (2C), 133.5 and 133.9, 150.7 and 150.8, 151.4 and 152.5; HRMS (FAB) calcd for $C_{19}H_{28}NO_3Si$ $[M+H]^+$ 346.1833, found 346.1834.

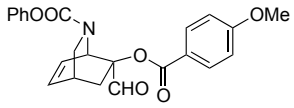
General Procedure for the Enantioselective Diels–Alder Reaction of 1,2-Dihydropyridines with α-(Acyloxy)acroleins (Table 1 (entries 1–4) and Table 2 (entries 1–5). α-(Acyloxy)acrolein (**9**, 0.1 mmol) was added to a solution of chiral triamine (**6**, 3 mg, 0.01 mmol) and $C_6F_5SO_3H$ (6.8 mg, 0.028 mmol) in $EtNO_2$ (0.125 mL) at –78 ºC. After the mixture was stirred at the same temperature for 5 min, 1-phenoxycarbonyl-1,2-dihydropyridine (**8**, 0.15 mmol) was added in one portion. After the reaction mixture was stirred for 1.5 days at 0 ºC or 3.0 days at –20 ºC, the reaction was quenched with Et_3N, the crude mixture was directly purified by chromatography on a silica gel column (hexane/EtOAc 10:1 to 5:2) to give Diels–Alder adducts **10**.

Typical Procedure for the Enantioselective Diels–Alder Reaction of 8a with 9b on Large Scale (Table 1 (entry 5). α-(*p*-Methoxybenzoyloxy)acrolein (**9b**, 500 mg, 2.43 mmol) was added to a solution of **6** (73.6 mg, 0.24 mmol) and $C_6F_5SO_3H$ (165 mg, 0.67 mmol) in $EtNO_2$ (3.0 mL) at –20 ºC and stirred for 5 min at same temperature. After the mixture was stirred at the 0 ºC for 10 min, and cooled to –20 ºC again. The diene **8** (536 mg, 2.67 mmol) was added in one portion at same temperature. After 5 min, the reaction was stirred for 2.5 days at 0 ºC. The reaction was quenched with Et_3N, the crude product was purified directly by chromatography on a silica gel column (hexane/EtOAc 10:1 to 5:2) to give **10ab** in 81% yield, 92% ee (800 mg, 1.97 mmol).

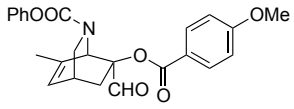


(1*R*,4*R*,7*S*)-(–)-7-Formyl-1-phenoxycarbonyl-2-azabicyclo[2.2.2]oct-5-ene-7-yl Benzoate (10aa, *endo*-isomer, Table 1, entry 1): Colorless oil; $[\alpha]^{19}_D$ –27.6 (c 1.00, $CHCl_3$) for 88% ee; HPLC (Daicel CHIRALPAK OD-3 column, hexane–*i*-PrOH = 9:1, flow rate = 1.0 mL/min) t_R = 23.7 (major) and 28.4 (minor) min; IR ($CHCl_3$) 17.16, 1404, 1290, 1205 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (1/1)) δ 1.78 (dd, *J* = 14.6, 2.3 Hz, 0.5H), 1.85 (dd, *J* = 14.6, 2.3 Hz, 0.5H), 2.54 (dt, *J* = 14.6, 3.2 Hz, 0.5H), 2.62 (dt, *J* = 14.6, 3.2 Hz, 0.5H), 3.03–3.12 (m, 1H), 3.21 (dt, *J* = 10.5, 2.3 Hz, 0.5H), 3.31 (dt, *J* = 10.1, 2.3 Hz, 0.5H), 3.58 (dd, *J* = 10.6, 2.3 Hz, 0.5H), 3.69 (dd, *J* = 10.3, 2.3 Hz, 0.5H), 5.24 (d, *J* = 6.4 Hz, 0.5H), 5.34 (d, *J* = 6.4 Hz, 0.5H), 6.30 (dd, *J* = 7.1, 6.4 Hz, 0.5H), 6.39 (dd, *J* = 7.3, 7.1 Hz, 0.5H), 6.69 (dd, *J* = 14.6, 2.3 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 0.5H), 7.08 (d, *J* = 7.8 Hz, 0.5H), 7.12–7.25 (m, 1H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.37 (dd, *J* = 8.0, 7.8 Hz, 1H), 7.44 (dd, *J* = 7.6, 7.3 Hz, 1H), 7.46 (dd, *J* = 7.6, 7.3 Hz, 1H),

8.05 (d, J = 7.4 Hz, 1H), 8.09 (d, J = 6.9 Hz, 1H), 9.51 (s, 0.5H), 9.55 (s, 0.5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.5 and 30.9, 32.0 and 32.4, 46.8 and 47.0, 49.3 and 50.1, 86.1 and 86.6, 121.4 and 121.7 (2C), 125.3 and 125.5, 127.4 and 127.8, 128.6 (2C), 129.2 and 129.3 (2C), 130.0 and 130.2 (2C), 133.9 and 133.9, 137.8 and 137.8, 151.0 and 151.2, 153.3, 154.4, 166.0 and 166.1, 195.3 and 195.5; HRMS (FAB) calcd for $C_{22}H_{20}NO_5$ $[M+H]^+$ 378.1336, found 378.1340.

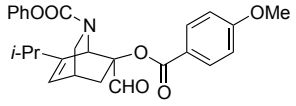


(1*R*,4*R*,7*S*)-(–)-7-Formyl-1-phenoxycarbonyl-2-azabicyclo-[2.2.2]-oct-5-ene-7-yl *p*-Methoxybenzoate (10ab, *endo*-isomer, Table 1, entries 2–4): Colorless oil; $[\alpha]^{21}_D$ –22.4 (*c* 1.00, $CHCl_3$) for 95% ee; HPLC (Daicel CHIRALPAK OD-H column, hexane–*i*-PrOH = 4:1, flow rate = 1.0 mL/min) t_R = 19.3 (minor) and 22.2 (major) min; IR ($CHCl_3$) 1716, 1605, 1404, 1258 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (1/1)) δ 1.76 (dd, J = 14.2, 1.8 Hz, 0.5H), 1.82 (dd, J = 14.5, 1.8 Hz, 1H), 2.52 (d, J = 14.2 Hz, 0.5H), 2.61 (d, J = 14.5 Hz, 1H), 3.02–3.10 (m, 1H), 3.20 (d, J = 10.6 Hz, 0.5H), 3.30 (d, J = 10.6 Hz, 0.5H), 3.58 (d, J = 9.2 Hz, 0.5H), 3.68 (d, J = 9.4 Hz, 0.5H), 5.26 (d, J = 6.0 Hz, 0.5H), 5.31 (d, J = 6.0 Hz, 0.5H), 6.28 (t, J = 6.9 Hz, 0.5H), 6.38 (dd, J = 6.9, 6.9 Hz, 0.5H), 6.62–6.72 (m, 1H), 6.90 (d, J = 7.3 Hz, 1H), 6.92 (d, J = 7.3 Hz, 1H), 7.03 (d, J = 7.8 Hz, 1H), 7.10 (d, J = 7.8 Hz, 1H), 7.19 (dd, J = 7.6, 7.3 Hz, 1H), 7.23 (t, J = 7.3 Hz, 1H), 7.32 (t, J = 7.8 Hz, 1H), 7.38 (t, J = 7.8 Hz, 1H), 7.99 (d, J = 8.7 Hz, 1H), 8.03 (d, J = 8.7 Hz, 1H), 9.50 (s, 0.5H), 9.55 (s, 0.5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.5 and 30.9, 32.0 and 32.5, 46.8 and 47.0, 49.3 and 50.2, 55.5, 85.8 and 86.3, 113.9 and 113.9 (2C), 120.8 and 121.1, 121.5 and 121.7 (2C), 125.3 and 125.5, 127.4 and 127.9, 129.2 and 129.3 (2C), 132.2 and 132.3 (2C), 137.7, 151.0 and 151.2, 153.3 and 154.4, 164.0 and 164.1, 165.7 and 165.9, 195.5 and 195.6; HRMS (FAB) calcd for $C_{22}H_{22}NO_6$ $[M+H]^+$ 408.1442, found 408.1441.

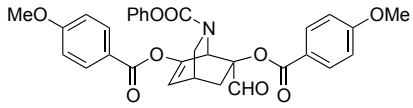


(1*R*,4*R*,7*S*)-(–)-7-Formyl-6-methyl-1-phenoxycarbonyl-2-azabicyclo[2.2.2]oct-5-ene-7-yl *p*-Methoxybenzoate (10bb, *endo*-isomer, Table 2, entry 1): Colorless oil; $[\alpha]^{21}_D$ –41.7(*c* 1.15, $CHCl_3$) for 88% ee; HPLC (Daicel CHIRALPAK OZ-H column, hexane–*i*-PrOH = 4:1, flow rate = 1.0 mL/min) t_R = 40.8 (major), 67.5 (minor) min; IR ($CHCl_3$) 1715, 1606, 1403, 1259, 1206, 1169 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (1/1)) δ 1.73 (dd, J = 14.6, 2.3 Hz, 0.5H), 1.80 (dd, J = 14.2, 2.3 Hz, 0.5H), 1.96 (s, 3H), 2.56 (dt, J = 14.2, 2.8 Hz, 0.5H), 2.63 (dt, J = 14.2, 2.8 Hz, 0.5H), 2.73–2.85 (m, 1H), 3.22 (dt, J = 10.5, 2.3 Hz, 0.5H), 3.32 (dt, J = 10.5, 2.3 Hz, 0.5H), 3.54 (dd, J = 10.5, 1.8 Hz, 0.5H), 3.65 (dd, J = 10.5, 1.8 Hz, 0.5H), 3.86 (s, 1.5H), 3.87 (s, 1.5H), 5.10 (d, J = 6.4 Hz, 0.5H), 5.21 (d, J = 6.4 Hz, 0.5H), 5.86 (d, J = 6.4 Hz, 0.5H), 5.96 (d, J = 6.0 Hz, 0.5H), 6.89 (d, J = 8.7 Hz, 1H), 6.91 (d, J = 8.7 Hz, 1H), 7.19 (dd, J = 7.6, 7.3 Hz, 0.5H), 7.23 (dd, J = 7.8, 7.4 Hz, 0.5H), 7.05 (d, J = 7.8 Hz, 1H), 7.10 (d, J = 7.3 Hz,

1H), 7.33 (dd, *J* = 8.0, 7.8 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 9.48 (s, 0.5H), 9.53 (s, 0.5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 19.7 and 19.8, 31.4 and 32.0, 36.0 and 36.4, 46.4 and 46.6, 50.2 and 51.0, 55.5, 86.0 and 86.6, 113.8 (2C), 119.7 and 120.2, 121.5 and 121.8 (2C), 125.2 and 125.4, 129.2 and 129.3 (2C), 132.1 and 132.3 (2C), 147.7 and 147.9, 151.1 and 151.3, 153.2, 154.3, 164.0 and 164.1, 165.8 and 165.9, 195.5 and 195.8; HRMS (FAB) calcd for $C_{24}H_{24}NO_6$ $[M+H]^+$ 422.1598, found 422.1598.

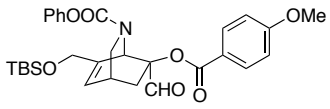


(1*R*,4*R*,7*S*)-(–)-7-Formyl-6-isopropyl-1-phenoxycarbonyl-2-azabicyclo[2.2.2]oct-5-ene-7-yl *p*-Methoxybenzoate (10cb, *endo*-isomer, Table 2, entry 2): Colorless oil; $[\alpha]^{21}_D$ –45.6 (*c* 1.00, $CHCl_3$) for 80% ee; HPLC (Daicel CHIRALPAK AD-3 column, hexane–*i*-PrOH = 4:1, flow rate = 1.0 mL/min) t_R = 21.6 (minor), 38.2 (major) min; IR ($CHCl_3$) 1716, 1605, 1403, 1259 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (1/1)) δ 1.11 (d, *J* = 1.8 Hz, 3H), 1.13 (d, *J* = 1.8 Hz, 3H), 1.75 (dd, *J* = 14.2, 2.3 Hz, 0.5H), 1.82 (dd, *J* = 14.2, 2.3 Hz, 0.5H), 2.44–2.64 (m, 2H), 2.90–3.12 (m, 1H), 3.15 (dt, *J* = 10.5, 2.3 Hz, 0.5H), 3.25 (dt, *J* = 10.1, 2.3 Hz, 0.5H), 3.58 (dd, *J* = 10.5, 1.8 Hz, 0.5H), 3.69 (dd, *J* = 10.1, 2.3 Hz, 0.5H), 3.86 (s, 1.5H), 3.87 (s, 1.5H), 5.15 (d, *J* = 6.4 Hz, 0.5H), 5.25 (d, *J* = 6.4 Hz, 0.5H), 5.80 (d, *J* = 6.8 Hz, 0.5H), 5.90 (d, *J* = 6.8 Hz, 0.5H), 6.89 (d, *J* = 8.7 Hz, 1H), 6.91 (d, *J* = 8.7 Hz, 1H), 7.07 (d, *J* = 7.3 Hz, 1H), 7.11 (d, *J* = 7.3 Hz, 1H), 7.19 (dd, *J* = 7.8, 7.1 Hz, 1H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.34 (dd, *J* = 9.8, 8.2 Hz, 1H), 7.38 (dd, *J* = 8.0, 7.3 Hz, 1H), 7.99 (d, *J* = 8.7 Hz, 1H), 8.04 (d, *J* = 9.2 Hz, 1H), 9.47 (s, 0.5H), 9.52 (s, 0.5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.0, 32.1 and 32.5, 33.4 and 33.8, 47.3 and 47.4, 50.3 and 51.1, 55.5, 86.1 and 86.7, 113.8 (2C), 116.3 and 116.8, 121.0 and 121.1, 121.5 and 121.8 (2C), 125.2 and 125.4, 128.3, 129.2 and 129.3 (2C), 132.2 and 132.3 (2C), 151.1 and 151.3, 153.2 and 154.3, 156.8 and 157.1, 164.0 and 164.1, 165.8 and 165.9, 195.4 and 195.7; HRMS (FAB) calcd for $C_{26}H_{28}NO_6$ $[M+H]^+$ 450.1911, found 450.1915.



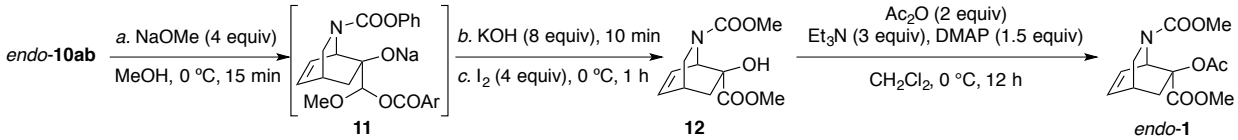
(1*R*,4*R*,7*S*)-(–)-7-Formyl-6-(*p*-methoxybenzoyl)oxy-1-phenoxycarbonyl-2-azabicyclo[2.2.2]oct-5-ene-7-yl *p*-Methoxybenzoate (10db, *endo*-isomer, Table 2, entries 3 and 4): Colorless oil; $[\alpha]^{25}_D$ –47.8 (*c* 0.95, $CHCl_3$) for 95% ee; HPLC (Daicel CHIRALPAK IA-3 column, hexane–*i*-PrOH =1:1, flow rate = 0.5 mL/min) t_R = 44.1 (minor), 60.2 (major) min; IR ($CHCl_3$) 1718, 1605, 1511, 1402, 1259, 1162 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz) a mixture of rotamers (2/1): δ 1.87 (dd, *J* = 14.4, 2.3 Hz, 0.3H), 1.94 (dd, *J* = 14.2, 2.3 Hz, 0.5H), 2.98 (dt, *J* = 10.5, 2.3 Hz, 0.3H), 3.02 (dd, *J* = 11.0, 2.8 Hz, 0.7H), 3.12–3.17 (m, 1H), 3.62–3.66 (m, 1H), 3.71 (d, *J* = 2.3 Hz, 0.3H), 3.74 (d, *J* = 1.8 Hz, 0.7H), 3.81 (dd, *J* = 2.3, 2.3 Hz, 0.7H), 3.84 (dd, *J* = 2.5, 2.3 Hz, 0.3H), 3.87 (s, 1H), 3.88 (s, 2H), 3.40 (s, 3H), 5.35 (d, *J* = 6.9 Hz, 0.7H), 5.42

(d, *J* = 6.9 Hz, 0.3H), 5.93 (dd, *J* = 7.1, 2.8 Hz, 0.7H), 6.06 (dd, *J* = 7.1, 2.8 Hz, 0.3H), 6.90 (d, *J* = 10.6 Hz, 0.7H), 6.92 (d, *J* = 6.9 Hz, 1.3H), 6.98 (d, *J* = 11.5 Hz, 2H), 7.04 (d, *J* = 7.4 Hz, 0.7H), 7.11 (d, *J* = 7.4 Hz, 1.3H), 7.19 (dd, *J* = 7.6, 7.3 Hz, 0.3H), 7.24 (t, *J* = 7.3 Hz, 0.7H), 7.34 (t, *J* = 6.0 Hz, 0.7H), 7.38 (dd, *J* = 7.8, 7.4 Hz, 1.3H), 9.59 (s, 0.7H), 9.65 (s, 0.3H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.1 and 32.7, 35.1 and 35.4, 47.1 and 47.3, 50.9 and 51.7, 55.5 (2C), 85.9 and 86.4, 109.7 and 110.1, 113.9 and 113.9 (4C), 120.6 and 120.8, 121.5 and 121.8 (2C), 125.3 and 125.5 129.2 and 129.3 (2C), 132.2 and 132.3 (4C), 151.0 and 151.2, 153.0, 154.3, 156.6 and 156.8, 164.1 and 164.2, 165.7, 195.4 and 195.7; HRMS (FAB) calcd for $C_{31}H_{28}NO_9$ $[M+H]^+$ 558.1759, found 558.1761.



(1*R*,4*R*,7*S*)-(–)-6-(*tert*-Butyldimethylsilyloxy)methyl-7-formyl-1-phenoxycarbonyl-2-azabicyclo[2.2.2]oct-5-ene-7-yl *p*-Methoxybenzoate (10eb, *endo*-isomer, Table 2, entry 5): Colorless oil; $[\alpha]^{25}_D$ –28.8 (*c* 1.00, $CHCl_3$) for 93% ee; HPLC (Daicel CHIRALPAK OD-3 column, hexane–*i*-PrOH = 20:1, flow rate = 1.0 mL/min) t_R = 32.3 (minor), 40.7 (major) min; IR ($CHCl_3$) 1606, 1404, 1259, cm^{-1}; ^{1}H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (1/1)) δ 0.11 (s, 3H), 0.12 (s, 3H), 0.93 (s, 9H), 1.76 (d, *J* = 13.3 Hz, 0.5H), 1.84 (d, *J* = 14.2 Hz, 0.5H), 2.52 (d, *J* = 14.7 Hz, 0.5H), 2.60 (d, *J* = 14.2 Hz, 0.5H), 2.94 (m, 1H), 3.20 (d, *J* = 10.5 Hz, 0.5H), 3.30 (d, *J* = 10.1 Hz, 0.5H), 3.58 (d, *J* = 10.5 Hz, 0.5H), 3.68 (d, *J* = 10.1 Hz, 0.5H), 3.86 (s, 1.5H), 3.87 (s, 1.5H), 4.31 (s, 2H), 5.20 (d, *J* = 6.4 Hz, 0.5H), 5.31 (d, *J* = 6.4 Hz, 0.5H), 6.07 (d, *J* = 5.5 Hz, 0.5H), 6.17 (d, *J* = 5.0 Hz, 0.5H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.91 (d, *J* = 8.2 Hz, 1H), 7.04 (d, *J* = 7.8 Hz, 1H), 7.09 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 0.5H), 7.23 (dd, *J* = 8.0, 8.7 Hz, 0.5H), 7.33 (t, *J* = 8.2 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.99 (d, *J* = 9.2 Hz, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 9.48 (s, 0.5H), 9.53 (s, 0.5H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ –5.5 and –5.4 (2C), 18.3, 25.8 (3C), 31.8 and 31.8, 32.2 and 32.4, 46.8 and 46.9, 50.1 and 50.9, 55.5, 62.6 and 62.7, 86.1 and 86.6, 113.8 (2C), 118.8 and 119.2, 120.9 and 121.1, 121.5 and 121.8 (2C), 125.2 and 125.4, 129.2 and 129.3 (2C), 132.2 and 132.3 (2C), 150.5 and 150.7, 151.1 and 151.2, 153.2 and 154.3, 164.0 and 164.1, 165.7 and 165.8, 195.3 and 195.6; HRMS (FAB) calcd for $C_{30}H_{38}NO_7Si$ $[M+H]^+$ 552.2412, found 552.2409.

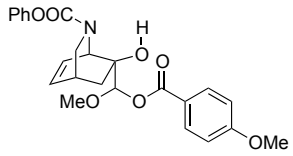
Derivatation of *Endo*-10ab to *Endo*-1 (Scheme 4)[5]



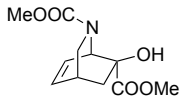
To a solution of *endo*-**10ab** (50 mg, 0.12 mmol) in MeOH (0.25 mL) was added sodium methoxide (26 mg, 0.48 mmol) at 0 ºC and the mixture was stirred for 15 min. KOH (0.25 mL of

1.9 *M* solution in MeOH, 0.96 mmol) and I_2 (122 mg, 0.48 mmol) were added sequentially to the mixture, and stirred for 1 h at same temperature. The reaction was quenched by the successive addition of aqueous sodium thiosulfate, and then reaction mixture was warmed up to ambient temperature. The mixture was extracted with EtOAc (10 mL × 3). The combined organic layers were dried over Na_2SO_4, filtrated and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 1:1 to 0:1) to give **12** (16 mg, 0.067 mmol) in 56% yield.

To a solution of **12** (28 mg, 0.12 mmol), DMAP (21 mg, 0.17 mmol) and triethylamine (48 μL, 0.35 mmol) in CH_2Cl_2 (0.5 mL) was added acetic anhydride (22 μL, 0.23 mmol) at 0 °C and stirred for 12 h at the same temperature. The resultant mixture was directly purified by chromatography on a silica gel column (hexane/EtOAc 1:1) to give *endo*-**1** (29 mg, 0.10 mmol) in 88% yield.

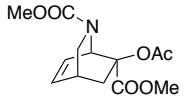


Intermediate (11): IR ($CHCl_3$) 1714, 1605, 1510, 1408, 1259, 1209, 1169 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (4/3) and stereoisomers (2/1)) δ 1.48–1.71 (m, 1.3H), 1.74–1.89 (m, 0.7H), 2.76–2.93 (m, 1.3H), 2.61–2.71 (m, 0.7H), 3.11–3.16 (m, 0.4H), 3.22–3.28 (m, 0.6H), 3.44–3.51 (m, 3H), 3.51–3.60 (m, 0.5H), 3.64–3.72 (m, 0.5H), 3.82–3.90 (m, 3H), 4.71 (d, *J* = 6.0 Hz, 0.3H), 4.76 (d, *J* = 6.4 Hz, 0.1H), 4.86 (d, *J* = 6.4 Hz, 0.4H), 4.88 (d, *J* = 7.8 Hz, 0.2H), 5.71–5.78 (m, 1H), 6.38–6.62 (m, 2H), 6.87–6.98 (m, 2H), 7.08–7.23 (m, 3H), 7.29–7.42 (m, 2H), 7.98–8.12 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.6 and 30.9, 33.4 and 33.5 and 34.8, 46.7 and 47.1, 52.2 and 52.9 and 53.8, 55.5, 55.5, 57.0 and 57.1 and 57.8, 78.8, 99.1 and 99.7, 113.7 and 113.8 (2C), 121.7 and 121.8 (2C), 125.0 and 125.1 and 125.2, 129.1 (2C), 129.2 and 130.0 and 130.5 and 132.1, 135.6 (2C), 136.3 and 136.7, 151.3, 155.2 and 155.5, 164.1; HRMS (FAB) calcd for $C_{24}H_{26}NO_7$ $[M+H]^+$ 440.1704, found 440.1700.



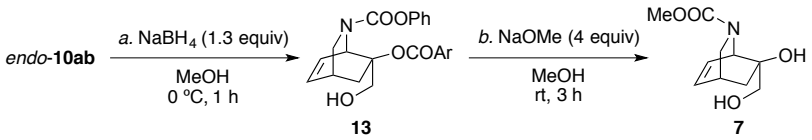
(1*R*,4*R*,7*S*)-Dimethyl 7-Hydroxy-2-azabicyclo[2.2.2]oct-5-ene-2,7- dicarboxylate (**12**): IR ($CHCl_3$) 1737, 1684, 1457, 1399, 1273, 1124 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (2/1)) δ 1.50–1.60 (m, 1H), 2.29–2.40 (m, 1H), 2.82–2.90 (m, 1H), 2.90–3.08 (m, 1H), 3.38–3.48 (m, 1H), 3.71 (s, 2.1H), 3.72 (s, 0.9H), 3.74 (s, 2.1H), 3.75 (s, 0.9 H), 4.73 (d, *J* = 6.4 Hz, 0.3H), 4.87 (d, *J* = 6.0 Hz, 0.7H), 6.27 (dd, *J* = 8.2, 7.8 Hz, 0.3H), 6.29 (dd, *J* = 7.8, 7.3 Hz, 0.7H), 6.47 (t, *J* = 7.3 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 30.5 and 30.7, 34.7 and 35.1, 46.4 and 46.8, 52.6 and 52.7, 52.6 and 52.7, 53.3 and 53.8, 78.1 and 78.2, 129.2 and 129.5, 136.1

and 136.2, 156.4 and 157.4, 173.2; HRMS (FAB) calcd for $C_{11}H_{16}NO_5$ $[M+H]^+$ 242.1023, found 242.1026.



(1*R*,4*R*,7*S*)-(–)-Dimethyl 7-Acetoxy-2-azabicyclo[2.2.2]oct-5-ene-2,7-dicarboxylate (*endo*-1): Clear yellow oil; $[\alpha]^{25}_D$ –37.8 (*c* 1.00, $CHCl_3$) for 91% ee; IR ($CHCl_3$) 1750, 1702, 1451, 1395, 1245, cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (1/1)) δ 1.60–1.70 (m, 1H), 2.06 (s, 3H), 2.33–2.43 (m, 1H), 2.87–2.94 (m, 1H), 2.99–3.07 (m, 1H), 3.33–3.43 (m, 1H), 3.69 (s, 1.5H), 3.69 (s, 1.5H), 3.71 (s, 1.5H), 3.72 (s, 1.5H), 5.03 (d, *J* = 6.4 Hz, 0.5H), 5.16 (d, *J* = 6.4 Hz, 0.5H), 6.23–6.38 (m, 1H), 6.43–6.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 20.5 and 20.6, 30.1 and 30.4, 34.4 and 34.4, 46.1 and 46.4, 50.0 and 50.4, 52.3, 52.4, 81.8 and 81.8, 128.6 and 129.0, 135.3 and 135.7, 155.7 and 156.2, 170.2 and 170.3; HRMS (FAB) calcd for $C_{13}H_{18}NO_6$ $[M+H]^+$ 284.1129, found 284.1128.

Derivatization of *endo*-10ab to (–)-4 (Scheme 5)



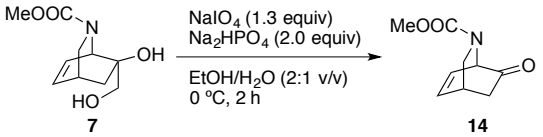
To a solution of Diels–Alder adduct (**10ab**, 615 mg, 1.51 mmol) in MeOH (10 mL) was added $NaBH_4$ (57 mg, 1.7 mmol) portion wise at 0 ºC and stirred for 1 h at same temperature. The reaction mixture was quenched with a saturated NH_4Cl aqueous solution and the solution was stirred until H_2 bubble stopped and then warmed up to ambient temperature. The mixture was extracted with EtOAc (50 mL × 3). The combined organic layers were washed with brine (100 mL × 2), dried over Na_2SO_4, filtrated and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 1:1) to give (1*R*,4*R*,7*S*)-7-hydroxymethyl-1-phenoxycarbonyl-2-azabicyclo[2.2.2]oct-5-ene-7-yl *p*-methoxybenzoate (**13**) in 82% yield (507 mg, 1.24 mmol).

(1*R*,4*R*,7*S*)-7-Hydroxymethyl-1-phenoxycarbonyl-2-azabicyclo-[2.2.2]-oct-5-ene-7-yl *p*-Methoxybenzoate (13): IR ($CHCl_3$) 1710, 1606, 1409, 1257 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (5/1)) δ 1.49 (dt, *J* = 13.8, 2.8 Hz, 0.8H), 1.58 (d, *J* = 8.3 Hz, 0.2H), 1.66 (d, *J* = 7.4 Hz, 0.2H), 1.74 (dd, *J* = 12.2, 2.3 Hz, 0.8H), 2.67 (s, 0.2H), 2.71 (s, 0.8H), 2.87–2.96 (m, 1H), 3.18 (d, *J* = 10.5 Hz, 0.2H), 3.30 (dt, *J* = 10.5, 2.8 Hz, 0.8H), 3.57 (dd, *J* = 10.5, 1.8 Hz, 0.2H), 3.74 (dd, *J* = 10.3, 1.8 Hz, 0.8H), 3.85 (s, 3H), 4.10 (d, *J* = 11.4 Hz, 0.8 H), 4.128 (d, *J* = 11.4 Hz, 0.2H), 4.130 (d, *J* = 11.4 Hz, 0.8H), 4.19 (d, *J* = 5.7 Hz, 0.2H), 4.88 (d, *J* = 6.0 Hz, 0.2H), 4.90 (d, *J* = 6.0 Hz, 0.8H), 6.44–6.55 (m, 2H), 6.90 (d, *J* = 6.9 Hz, 2H), 7.14 (d, *J* = 7.3 Hz, 2H), 7.20 (t, *J* = 7.3 H), 7.36 (t, *J* = 7.8 Hz, 2H), 7.99 (d, *J* = 8.2 Hz, 0.3H), 8.01 (d, *J* = 8.7 Hz, 1.7H); ^{13}C NMR ($CDCl_3$,

100 MHz, major rotamer) δ 31.0, 34.8, 47.0, 52.8, 55.4, 69.1, 76.2, 113.7 (2C), 121.8 (2C), 125.3, 129.2 (2C), 130.7, 131.7, 131.8 (2C), 135.3, 151.3, 155.6, 163.6, 165.9; HRMS (FAB) calcd for $C_{23}H_{24}NO_6$ $[M+H]^+$ 410.1598, found 410.1596.

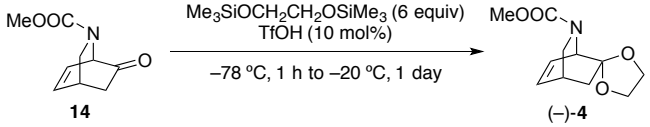
To a solution of alcohol **13** (460 mg, 1.12 mmol) in MeOH (10 mL) was added sodium methoxide (240 mg, 4.5 mmol) at ambient temperature and stirred for 1 h. The resultant mixture was concentrated and the crude product was purified by chromatography on a silica gel column (hexane/EtOAc 1:1 to 0:1) to give diol **7** in 96% yield (229 mg, 1.06 mmol).

Methyl (1*R*,4*R*,7*S*)-7-hydroxy-7-(hydroxymethyl)-2-azabicyclo[2.2.2]oct-5-ene-2-Carboxylate (7): Colorless oil; IR ($CHCl_3$) 1683, 1458, 1400, cm^{-1}; ^1H NMR (CD_3OD, 400 MHz, a mixture of rotamers (1/1)) δ 1.33 (dt, *J* = 4.6, 2.8 Hz, 0.5H), 1.37 (dt, *J* = 4.6, 2.8 Hz, 0.5H), 1.47 (dd, *J* = 4.6, 2.8 Hz, 0.5H), 1.44 (dd, *J* = 4.8, 2.8 Hz, 0.5H), 2.79–2.88 (m, 1H), 3.04 (dt, *J* = 8.7, 2.3 Hz, 0.5H), 3.06 (dt, *J* = 8.7, 2.3 Hz, 0.5H), 3.31–3.32 (m, 2H), 3.42 (dt, *J* = 10.3, 1.8 Hz, 0.5H), 3.45 (dd, *J* = 10.3, 1.8 Hz, 0.5H), 3.71 (s, 1.5H), 3.72 (s, 1.5H), 4.66 (dd, *J* = 4.1, 3.7 Hz, 0.5H), 4.70 (dd, *J* = 5.5, 1.6 Hz, 0.5H), 6.39–6.48 (m, 2H); ^{13}C NMR (CD_3OD, 100 MHz) δ 32.2 and 32.4, 35.5 and 35.6, 47.8 and 48.2, 53.0 and 53.0, 53.7 and 54.1, 68.9, 78.0 and 78.3, 132.2 and 132.3, 135.9 and 135.9, 158.3 and 158.8; HRMS (FAB) calcd for $C_{10}H_{16}NO_4$ $[M+H]^+$ 214.1074, found 214.1071.



To a solution of diol **7** (250 mg, 1.17 mmol), Na_2HPO_4 (400 mg, 2.34 mmol) in EtOH (4 mL) and H_2O (8 mL) was added $NaIO_4$ (330 mg, 1.52 mmol) at 0 ºC and stirred for 2 h at the same temperature. The reaction mixture was quenched by the successive addition of aqueous sodium thiosulfate (20 mL), and then reaction mixture was warmed up to ambient temperature. The mixture was extracted with Et_2O (50 mL × 3). The combined organic layers were washed with Brine (30 mL × 2) and dried over Na_2SO_4, filtrated and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 20:1) to give **14** in 80% yield (170 mg, 0.94 mmol).

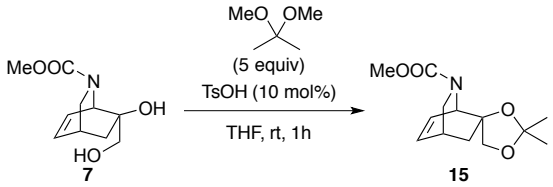
Methyl (1*R*,4*R*)-7-oxo-2-azabicyclo[2.2.2]oct-5-ene-2-carboxylate (14): IR ($CHCl_3$) 1736, 1699, 1448, 1889, 1283, 1113 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (3/2)) δ 2.22 (s, 2H), 3.13–3.23 (m, 2H), 3.43–3.54 (m, 1H), 3.72 (s, 3H), 4.85 (d, *J* = 6.4 Hz, 0.6H), 5.02 (d, *J* = 5.9 Hz, 0.4H), 6.38–6.48 (m, 1H), 6.62–6.72 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 32.0 and 32.2, 36.4 and 36.5, 46.0 and 46.4, 52.8, 57.2 and 57.8, 127.7 and 128.3, 139.1 and 139.7, 155.2, 202.8 and 202.9; HRMS (FAB) calcd for $C_9H_{11}NO_3Na$ $[M+Na]^+$ 204.0631, found 204.0633.



To a solution of ketone **14** (22 mg, 0.12 mmol) and Ethylenedioxybis(trimethylsilane) (177 μL, 0.72 mmol) in CH_2Cl_2 (0.5 mL) was added a solution of TfOH (10 μl, 0.01 mmol) in CH_2Cl_2 (0.5 mL) dropwise at –78 ºC and stirred for 1 h at same temperature.[6] The solution was warmed to –20 ºC and stirred for 1 d. The reaction mixture was quenched by a saturated $NaHCO_3$ aqueous solution (3 mL) and then warmed up to ambient temperature. The mixture was extracted with EtOAc (50 mL × 3). The combined organic layers were washed with brine (100 mL × 2), dried over Na_2SO_4, filtrated and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 1:1) to give acetal **4** in >99% yield (27 mg, 0.12 mmol).

Methyl 2-azaspiro[bicyclo[2.2.2]oct[5]ene-7,2'-[1,3]dioxolane]-2-carboxylate (4):[7] Colorless oil; $[\alpha]^{26}_D$ –65 (c 0.40, $CHCl_3$) for 91% ee; IR ($CDCl_3$) 1696, 1455, 1396 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) a mixture of rotamers (2/1) δ 1.78–1.93 (m, 2H), 2.80–2.89 (m, 1H), 3.00 (dd, *J* = 11.8, 10.1 Hz, 1H), 3.36 (t, *J* = 9.8 Hz, 1H), 3.70 (s, 2H), 3.72 (s, 1H), 3.91–4.01 (m, 2H), 4.01–4.12 (m, 2H), 4.27 (d, *J* = 5.9 Hz, 0.3H), 4.69 (d, *J* = 5.9 Hz, 0.7H), 6.34–6.44 (m, 1H), 6.44–6.54 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 31.1 and 31.3, 37.8, 45.9 and 46.3, 49.8 and 50.5, 52.4, 64.1 and 64.3, 64.8, 111.0, 130.1 and 130.7, 135.3 and 135.8, 155.9 and 156.5; HRMS (FAB) calcd for $C_{11}H_{16}NO_4$ $[M+H]^+$ 226.1074, found 226.1077.

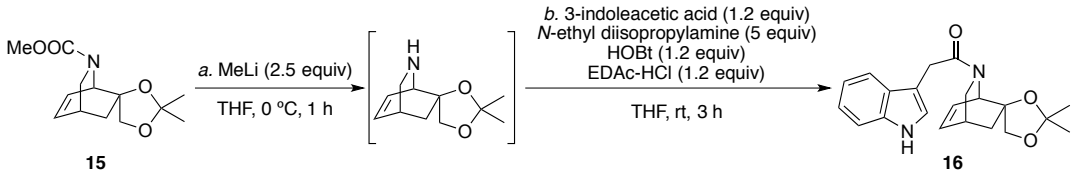
Derivatization of 7 to (+)-5 (Scheme 6)



To a solution of diol **7** (190 mg, 0.89 mmol) and 2,2-dimethoxy propane (560 μL, 4.45 mmol) in THF (5 mL) was added TsOH (15.2 mg, 0.09 mmol) at ambient temperature and stirred for 1 h at the same temperature. The reaction mixture was quenched with a saturated $NaHCO_3$ aqueous solution (10 mL). The mixture was extracted with EtOAc (50 mL × 3). The combined organic layers were dried over Na_2SO_4, filtrated and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 1:1) to give **15** in 86% yield (195 mg, 0.77 mmol).

Methyl (1*R*,2*S*,4*R*)-2',2'-dimethyl-6-azaspiro[bicyclo[2.2.2]octane-2,4'-[1,3]-dioxolan]-7-ene-6-carboxylate (15): IR ($CHCl_3$) 1699, 1451, 1397 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (1/1)) δ 1.33 (s, 1.5H), 1.35 (s, 1.5H), 1.46 (s, 1.5H), 1.53 (s, 1.5H), 1.57–1.66 (m, 1H), 1.81 (dd, *J* = 5.3, 2.3 Hz, 0.5H), 1.84 (dd, *J* = 5.0, 2.3 Hz, 0.5H), 2.75–2.84 (m, 1H), 3.04 (dt, *J* = 10.5, 2.8 Hz, 0.5H), 3.07 (dt, *J* = 10.5, 2.8 Hz, 0.5H), 3.44 (dd, *J* = 10.1, 1.8 Hz,

1H), 3.49 (dd, *J* = 8.7, 4.6 Hz, 1H), 3.69 (s, 3H), 3.82 (t, *J* = 9.2 Hz, 1H), 4.55 (d, *J* = 6.0 Hz, 0.5H), 4.74 (d, *J* = 6.0 Hz, 0.5H), 6.31–6.38 (m, 1H), 6.38–6.48 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 26.0 and 26.2, 27.1 and 27.5, 30.1 and 31.2, 36.1 and 36.3, 46.5 and 46.7, 52.0 and 52.2, 52.4 and 53.1, 73.3 and 73.3, 83.7 and 83.8, 109.4 and 109.5, 130.5 and 131.1, 136.1 and 136.7, 155.9 and 156.3; HRMS (FAB) calcd for $C_{13}H_{20}NO_4$ $[M+H]^+$ 254.1387, found 254.1385.

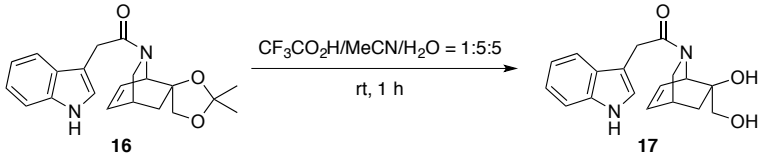


To a solution of **15** (65 mg, 0.26 mmol) in THF (1 mL) was added MeLi (0.56 mL, 1.14 M in Et_2O) at 0 ºC and stirred for 30 min at the same temperature. The reaction mixture was quenched with a saturated NH_4Cl aqueous solution (2 mL) and then warmed up to ambient temperature. To the mixture was added 1 M NaOH aqueous solution untile hydrogen ion concentration reached higher than pH7. The resultant mixture was extracted with Et_2O (10 mL × 3) and CH_2Cl_2 (10 mL× 2). The combined organic layers were dried over Na_2SO_4, filtrated and concentrated.

To a solution of the crude product, *N*,*N*-diisopropylethylamine (88 μL, 0.52 mmol), HOBt (35 mg, 0.26 mmol) and 3-indole acetic acid (45 mg, 0.26 mmol) in THF (2 mL) was added EDAC (49 mg, 0.26 mmol) at 0 ºC and stirred for 3 h at same temperature. The resultant mixture was poured a saturated $NaHCO_3$ aqueous solution (15 mL) and washed with EtOAc (20 mL × 3). The combined organic layers were dried over Na_2SO_4, filtrated and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 1:1 to 0:1) to give **17** in 89% yield (81 mg, 0.23 mmol).

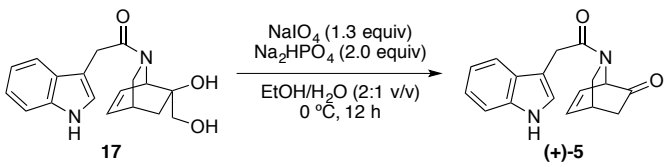
1-((1*R*,2*S*,4*R*)-2',2'-dimethyl-6-azaspiro[bicyclo[2.2.2]octane-2,4'-[1,3]dioxolan]-7-en-6-yl)-2-(1*H*-indol-3-yl)ethan-1-one (16): IR ($CHCl_3$) ^{1}H NMR ($CDCl_3$, 400 MHz, a mixture of rotamers (3/2)) δ 1.36 (s, 1.8H), 1.38 (s, 1,2H), 1.51 (s, 1.2H), 1.54 (s, 1.8H), 1.62 (dt, *J* = 13.8, 2.8 Hz, 0.6H), 1.71 (dt, *J* = 13.3, 2.8 Hz, 0.4H), 1.82 (dd, *J* = 13.7, 2.8 Hz, 0.6H), 1.91 (dd, *J* = 13.7, 2.3 Hz, 0.4H), 2.81–2.88 (m, 0.4H), 2.74–2.81 (m, 0.6H), 3.14–3.23 (m, 1H), 3.49 (d, *J* = 9.2 Hz, 0.5H), 3.56 (d, *J* = 9.2 Hz, 0.5H), 3.58 (d, *J* = 3.2 Hz, 0.6H), 3.61 (d, *J* = 1.8 Hz, 0.6H), 3.72–3.74 (m, 1H), 3.78 (d, *J* = 9.2 Hz, 0.5H), 3.81 (d, *J* = 17.4 Hz, 0.5H), 3.85 (d, *J* = 9.2 Hz, 0.5H), 4.01 (d, *J* = 15.6 Hz, 0.5H), 4.35 (d, *J* = 6.0 Hz, 0.4H), 5.34 (dd, *J* = 6.0, 1.4 Hz, 0.6H), 6.04 (t, *J* = 6.4 Hz, 0.4H), 6.32–6.45 (m, 1.6H), 6.96 (s, 0.4H), 7.07–7.20 (m, 2.6H), 7.31 (d, *J* = 8.2 Hz, 0.6H), 7.32 (d, *J* = 7.8 Hz, 0.4H), 7.56 (d, *J* = 7.1 Hz, 0.6H), 7.58 (d, *J* = 7.6 Hz, 0.4H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 25.7 and 26.5, 27.3 and 27.6, 31.0, 31.6 and 31.8, 36.4 and 38.5, 46.9 and 47.5, 50.3, 56.3, 73.4 and 74.4, 83.5 and 83.7, 108.9 and 109.7, 109.9 and 111.1, 118.6, 119.2 and 119.4, 121.8 and 121.9,

122.6 and 122.8, 127.2 and 127.4, 129.6 and 131.3, 136.1, 136.3 and 137.7, 170.3 and 170.7; HRMS (FAB) calcd for $C_{21}H_{25}N_2O_3$ $[M+H]^+$ 353.1860, found 353.1860.



To a solution of **16** (67 mg, 0.19 mmol) in MeCN (0.5 mL) and H_2O (0.5 mL) was added trifluoroacetic acid (0.5 mL) dropwised at ambient temperature and stirred for 1 h at same temperature. The resultant mixture was quenched with a saturated $NaHCO_3$ aqueous solution. The mixture was washed with EtOAc (20 mL × 3). The combined organic layers were washed with brine (50 mL × 2), dried over Na_2SO_4, filtrated and concentrated. The residue was purified by column chromatography on silica gel (EtOAc–MeOH 1:0 to 5:1) to give **17** in >99% yield (59 mg, 0.19 mmol).

1-((1*R*,4*R*,7*S*)-7-hydroxy-7-(hydroxymethyl)-2-azabicyclo[2.2.2]oct-5-en-2-yl)-2-(1*H*-indol-3-yl)ethan-1-one (17): yellow participate; IR (KBr) 3397, 1606, 1458 cm^{-1}; ^1H NMR (CD_3OD, 400 MHz) a mixture of rotamers (3/2) δ 1.29 (t, *J* = 2.8 Hz, 0.3H), 1.33 (t, *J* = 2.7 Hz, 0.7H), 1.43 (d, *J* = 2.3 Hz, 0.7H), 1.46 (d, *J* = 2.3 Hz, 0.3H), 2.78–2.83 (m, 1H), 3.08 (dt, *J* = 11.4, 2.8 Hz, 0.5H), 3.21–3.28 (m, 2.5H), 3.47 (dd, *J* = 11.7, 1.8 Hz, 0.5H), 3.63 (dd, *J* = 10.8, 1.8 Hz, 0.5H), 3.72 (d, *J* = 15.6 Hz, 0.4H), 3.76 (d, *J* = 2.8 Hz, 1H), 4.16 (d, *J* = 15.6 Hz, 0.6H), 4.66 (d, *J* = 6.0 Hz, 0.6H), 5.21 (dd, *J* = 5.3, 1.8 Hz, 0.4H), 6.05 (ddd, *J* = 7.8, 6.4, 1.4 Hz, 0.5H), 6.33 (t, *J* = 7.4 Hz, 0.5H), 6.38 (dt, *J* = 5.5, 2.8 Hz, 1H), 6.99 (dd, *J* = 7.8, 7.4 Hz, 1H), 7.08 (dd, *J* = 8.7, 7.4 Hz, 1H), 7.06 (s, 0.4H), 7.14 (s, 0.6H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 0.5H), 7.58 (d, *J* = 7.8 Hz, 0.5H); ^{13}C NMR (CD_3OD, 100 MHz) δ 32.0 and 32.2, 32.7, 35.5 and 35.8, 48.1, 51.9, 56.4, 68.8 and 68.9, 77.9 and 78.1, 109.5, 112.2, 119.4 and 119.6, 119.8, 122.5 and 122.6, 124.1 and 124.2, 128.5, 131.4 and 132.0, 136.4 and 138.0, 174.0; HRMS (FAB) calcd for $C_{18}H_{21}N_2O_3$ $[M+H]^+$ 313.1547, found 313.1549.



To a solution of **17** (35 mg, 0.11 mmol) and Na_2HPO_4 (32 mg, 0.22 mmol) in EtOH (0.26 mL) and H_2O (0.52 mL) was added $NaIO_4$ (31 mg, 0.15 mmol) at 0 ºC and stirred for 12 h at same temperature. The reaction mixture was quenched by the successive addition of aqueous sodium thiosulfate, and then reaction mixture was warmed up to ambient temperature. The mixture was

washed with EtOAc (20 mL × 3). The combined organic layers were dried over Na_2SO_4, filtrated and concentrated. The residue was purified by column chromatography on silica gel (hexane–EtOAc 1:1 to 0:1) to give **5** in 85% yield (27 mg, 0.10 mmol). **(1*R*,4*R*)-(+)-2-(2-(1*H*-indol-3-yl)acetyl)-2-azabicyclo[2.2.2]oct-7-en-6-one (5):**[7] yellow participate; $[\alpha]^{24}_{D}$ +88 (*c* 1.20, $CHCl_3$) for 91% ee; IR ($CHCl_3$) 3349, 1716, 1655, 1389, 1229 cm^{-1}; ^1H NMR (CD_2Cl_2, 400 MHz, a mixture of rotamers (3/2)) δ 2.12–2.24 (m, 2H), 3.14–3.21 (m, 1H), 3.23 (d, *J* = 11.5 Hz, 0.4H), 3.35 (d, *J* = 9.2 Hz, 0.6H), 3.55–3.63 (m, 1H), 3.74 (s, 1H), 3.80 (d, *J* = 15.6 Hz, 0.5H), 3.87 (d, *J* = 15.6 Hz, 0.5H), 4.74 (d, *J*= 6.4 Hz, 0.4H), 5.45 (d, *J* = 6.4 Hz, 0.6H), 6.26 (dd, *J*= 7.1, 6.9 Hz, 0.4H), 6.41 (dd, *J*= 7.1, 6.9 Hz, 0.6H), 6.67 (dt, *J* = 6.9, 6.4 Hz, 1H), 7.09 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.17 (dd, *J* = 7.8, 7.6 Hz, 1H), 7.05 (s, 1H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 0.5H), 7.58 (d, *J* = 7.8 Hz, 0.5H); ^{13}C NMR (CD_2Cl_2, 100 MHz) δ 31.1 and 31.4, 31.7 and 32.3, 36.1 and 36.2, 45.9 and 46.6, 55.2, 59.8, 108.1 and 108.5, 110.8 and 110.8, 118.2 and 118.4, 119.0, 121.6 and 121.7, 122.4 and 122.5, 126.8 and 127.8, 135.8, 139.0 and 140.0, 169.8 and 169.8, 202.2 and 202.4; HRMS (FAB) calcd for C17H17N2O3 $[M+H]^+$ 281.1285, found 218.1289.

Computational Methods

The quantum chemical calculations were performed using the Gaussian09[8] suites of programs. The structure in Figure 1 was optimized using density functional theory (DFT) methods employing three nonlocal functionals (B3LYP).[9] The standard 6-31G(d) basis set was used for geometry optimizations of the stable structures. The optimized geometries are also subjected to full frequency analyses at the same level of theory to verify the nature of the stationary points. Equilibrium geometries are characterized by the absence of imaginary frequencies.

Optimized Geometry of Iminium Salt **18**•H_2O

```
Method: B3LYP/6-31+G(d)
SCF Done:  E(RB3LYP) =  -5576.27621811    A.U. after    6 cycles
Imaginary frequencies: 0
 Zero-point correction=                          0.897512 (Hartree/Particle)
 Thermal correction to Energy=                    0.976990
 Thermal correction to Enthalpy=                  0.977934
 Thermal correction to Gibbs Free Energy=         0.770864
 Sum of electronic and zero-point Energies=          -5575.378706
 Sum of electronic and thermal Energies=             -5575.299228
 Sum of electronic and thermal Enthalpies=           -5575.298284
 Sum of electronic and thermal Free Energies=        -5575.505355

                     Standard orientation:

 ---------------------------------------------------------------------
 Center     Atomic     Atomic           Coordinates (Angstroms)
 Number     Number      Type           X          Y          Z
 ---------------------------------------------------------------------
```

1	6	0	2.567748	-1.775695	-4.681694
2	6	0	1.570473	-2.670595	-3.956805
3	6	0	1.940984	-0.366249	-4.574032
4	16	0	-5.375720	0.243593	-0.647843
5	6	0	1.041754	-0.408596	-3.315924
6	7	0	1.164878	-1.822482	-2.775032
7	8	0	-2.309146	0.065240	-2.427135
8	6	0	-0.031899	-2.386106	-2.061311
9	6	0	-0.147601	-2.048382	-0.565949
10	6	0	-1.013021	-3.075459	0.193611
11	7	0	-0.609438	-0.606857	-0.368349
12	6	0	-2.524572	-3.198166	-0.121529
13	6	0	-3.238952	-3.813232	1.094828
14	6	0	-2.834167	-4.035897	-1.374119
15	6	0	-1.002026	-0.242908	1.032387
16	6	0	-1.207647	1.269092	1.215193
17	6	0	-1.230901	1.597218	2.741434
18	7	0	-2.488893	1.668196	0.610934
19	6	0	-1.465418	3.057771	3.045771
20	6	0	-2.853258	2.804730	0.111647
21	8	0	-4.470795	-0.180410	0.482223
22	6	0	-2.736046	3.518569	3.419907
23	6	0	-2.958694	4.874822	3.664643
24	6	0	-1.908995	5.786499	3.537647
25	6	0	-0.635703	5.333557	3.179005
26	6	0	-0.411126	3.979072	2.935214
27	6	0	-2.065424	3.989427	-0.197571
28	8	0	-0.706049	3.912887	-0.474313
29	6	0	-2.664345	5.187929	-0.198468
30	6	0	-0.382285	3.392835	-1.717942
31	8	0	-5.585652	1.706523	-0.668879
32	6	0	0.975548	3.756330	-2.154641
33	8	0	-1.195425	2.752637	-2.357694
34	6	0	1.306022	3.528381	-3.500146
35	6	0	2.570247	3.867841	-3.970318
36	6	0	3.510359	4.425333	-3.098502
37	6	0	3.183507	4.648209	-1.758404
38	6	0	1.916924	4.321100	-1.281376
39	6	0	-6.964426	-0.532373	-0.255474
40	8	0	-4.981664	-0.347927	-1.953809
41	16	0	2.360709	1.088784	0.758291
42	8	0	1.550840	1.057209	-0.517217
43	6	0	-7.051320	-1.928818	-0.270051
44	6	0	-8.236814	-2.593550	0.021359
45	6	0	-9.375055	-1.855938	0.339556
46	6	0	-9.314075	-0.467220	0.365944
47	6	0	-8.116752	0.188585	0.073423
48	9	0	-5.980544	-2.677472	-0.562132
49	9	0	-8.289230	-3.929079	0.000569
50	9	0	-10.518479	-2.481183	0.621234
51	9	0	-10.405626	0.240232	0.675476
52	9	0	-8.135498	1.520204	0.129022
53	8	0	2.224293	2.384294	1.458590
54	6	0	4.097489	1.001450	0.234733
55	8	0	2.116017	-0.115895	1.586551
56	6	0	4.529697	0.970051	-1.092699
57	6	0	5.885111	0.906476	-1.410445
58	6	0	6.838512	0.873515	-0.400389
59	6	0	6.434357	0.906064	0.931527
60	6	0	5.078445	0.966868	1.232617

61	9	0	3.684047	1.018204	-2.130523
62	9	0	6.269281	0.885338	-2.693158
63	9	0	8.136158	0.817709	-0.704534
64	9	0	7.345613	0.877797	1.907261
65	9	0	4.732598	0.979667	2.525319
66	16	0	3.584262	-3.411522	-0.854326
67	8	0	3.474450	-2.007762	-1.419190
68	8	0	2.282558	-4.115169	-0.983658
69	6	0	3.833334	-3.097763	0.927312
70	8	0	4.769685	-4.148490	-1.297993
71	6	0	5.026790	-2.495933	1.335845
72	6	0	5.273570	-2.170596	2.664606
73	6	0	4.312529	-2.449936	3.631521
74	6	0	3.116331	-3.046345	3.253929
75	6	0	2.883494	-3.357854	1.915348
76	9	0	5.975188	-2.182184	0.443513
77	9	0	6.419612	-1.570834	3.010965
78	9	0	4.536455	-2.141893	4.911176
79	9	0	2.179756	-3.307897	4.176280
80	9	0	1.685065	-3.894666	1.635042
81	1	0	2.726718	-2.094603	-5.715062
82	1	0	3.526049	-1.810527	-4.155640
83	1	0	1.972852	-3.609694	-3.573804
84	1	0	0.670457	-2.861839	-4.551952
85	1	0	2.705935	0.407241	-4.481733
86	1	0	1.335910	-0.139530	-5.457722
87	1	0	-0.011764	-0.235411	-3.546211
88	1	0	1.367950	0.277941	-2.536831
89	1	0	2.016351	-1.856869	-2.130577
90	1	0	-3.283372	-0.100571	-2.359775
91	1	0	-1.365911	-0.360781	-1.059637
92	1	0	-2.198053	1.015184	-2.608736
93	1	0	0.085750	-3.467209	-2.115278
94	1	0	-0.918635	-2.083262	-2.622037
95	1	0	0.847315	-2.087539	-0.119710
96	1	0	-0.885812	-2.866344	1.261158
97	1	0	-0.515498	-4.041366	0.046738
98	1	0	0.222205	0.006906	-0.567809
99	1	0	-2.955088	-2.199861	-0.273455
100	1	0	-4.313951	-3.892010	0.909728
101	1	0	-3.099418	-3.202998	1.995338
102	1	0	-2.853727	-4.818241	1.310116
103	1	0	-3.917338	-4.112238	-1.513431
104	1	0	-2.432872	-5.052789	-1.274485
105	1	0	-2.425975	-3.602768	-2.292138
106	1	0	-0.175992	-0.550738	1.675078
107	1	0	-1.909794	-0.786930	1.298251
108	1	0	-0.400261	1.835966	0.753151
109	1	0	-1.994015	0.975447	3.225247
110	1	0	-0.252693	1.282320	3.120295
111	1	0	-3.268898	0.960131	0.678020
112	1	0	-3.919387	2.857656	-0.119175
113	1	0	-3.554340	2.809855	3.529714
114	1	0	-3.946993	5.215719	3.961522
115	1	0	-2.077539	6.842162	3.733635
116	1	0	0.188152	6.037553	3.096730
117	1	0	0.578452	3.627024	2.653132
118	1	0	-2.095158	6.091517	-0.385187
119	1	0	-3.722295	5.281321	0.019427
120	1	0	0.560838	3.097843	-4.161089

121	1	0	2.824640	3.700840	-5.012928
122	1	0	4.499848	4.684657	-3.464955
123	1	0	3.919159	5.070489	-1.080505
124	1	0	1.673686	4.455433	-0.234929

References and Notes

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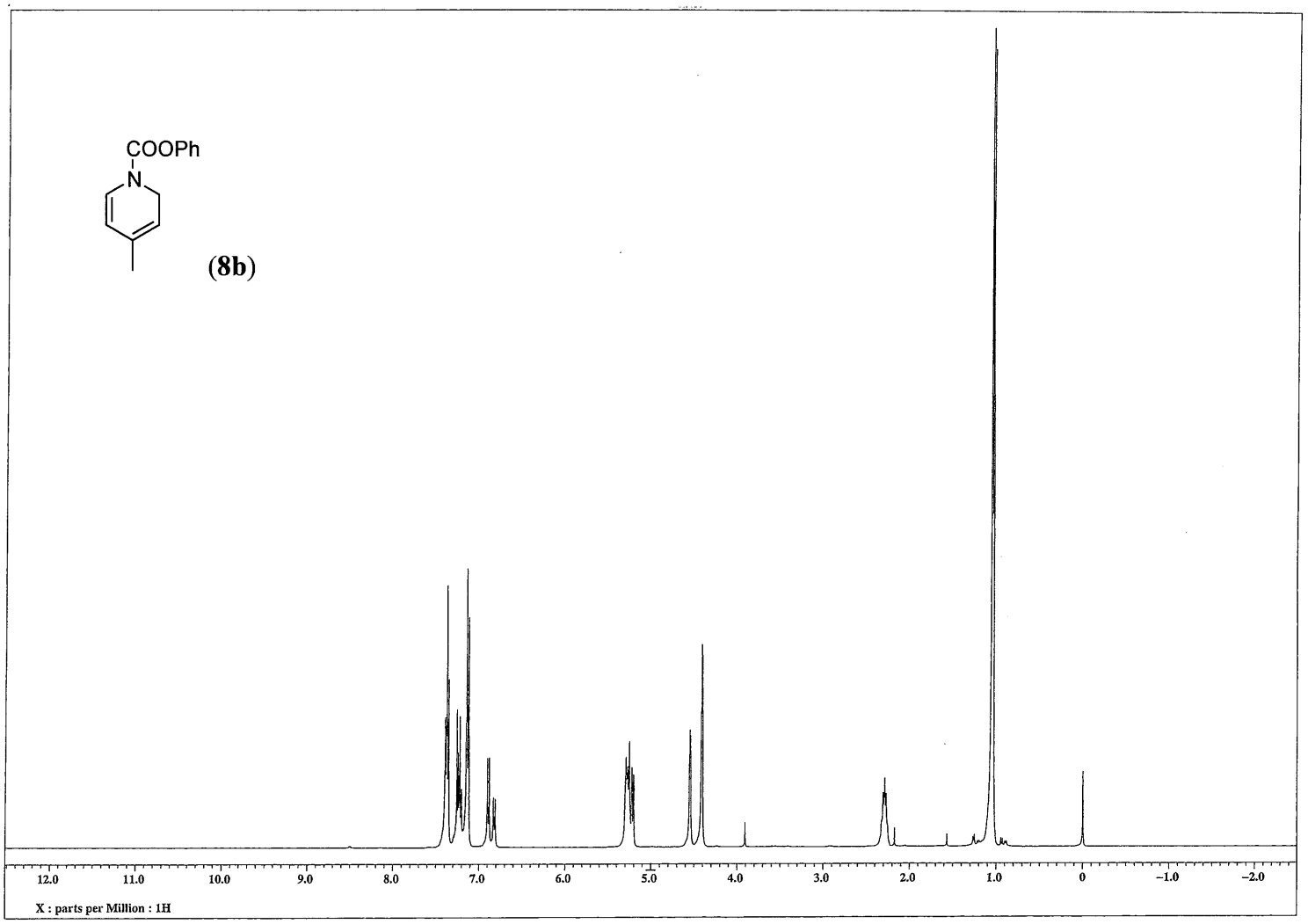
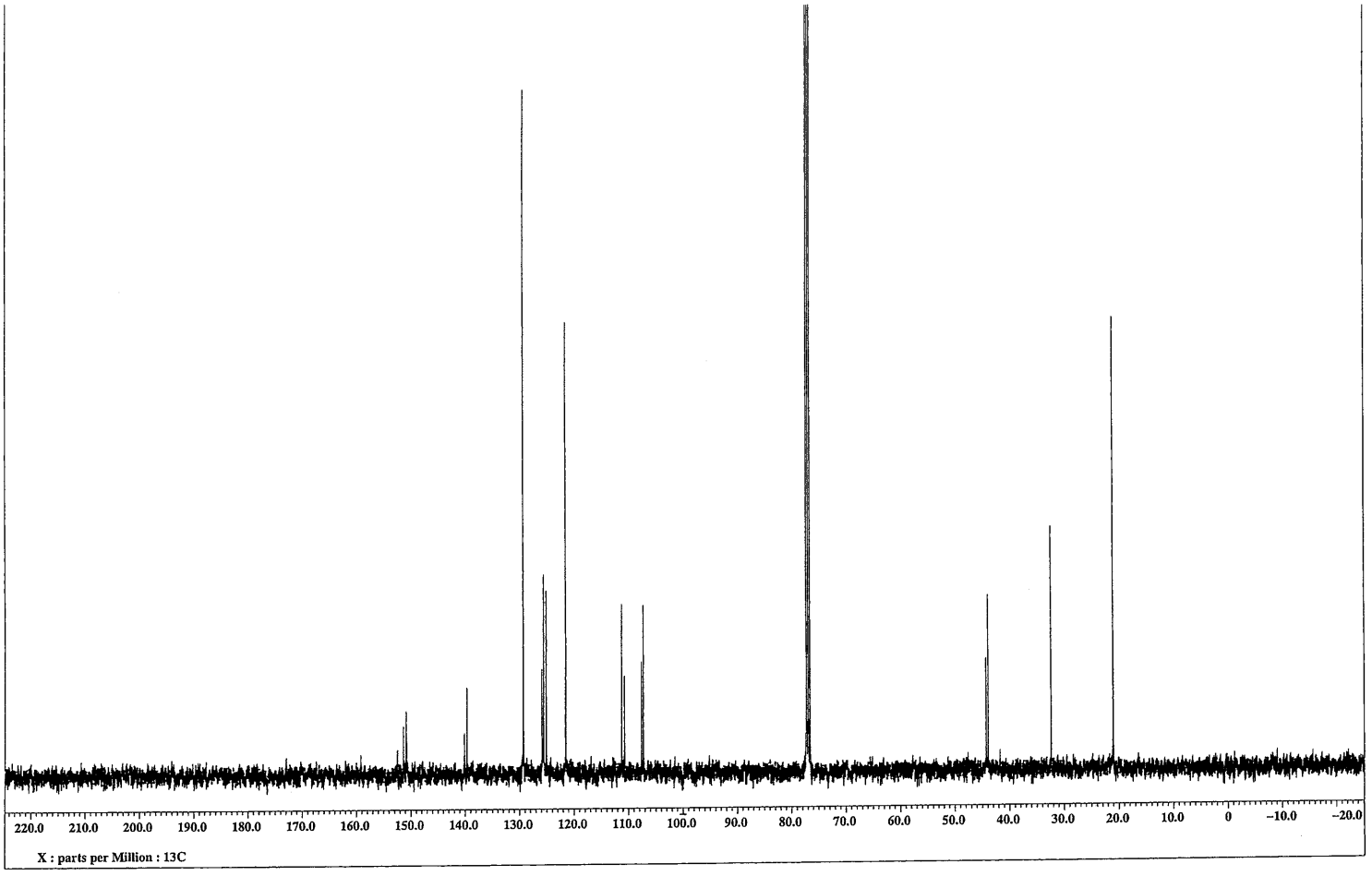

COOPh
N
(8b)
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
X : parts per Million : 1H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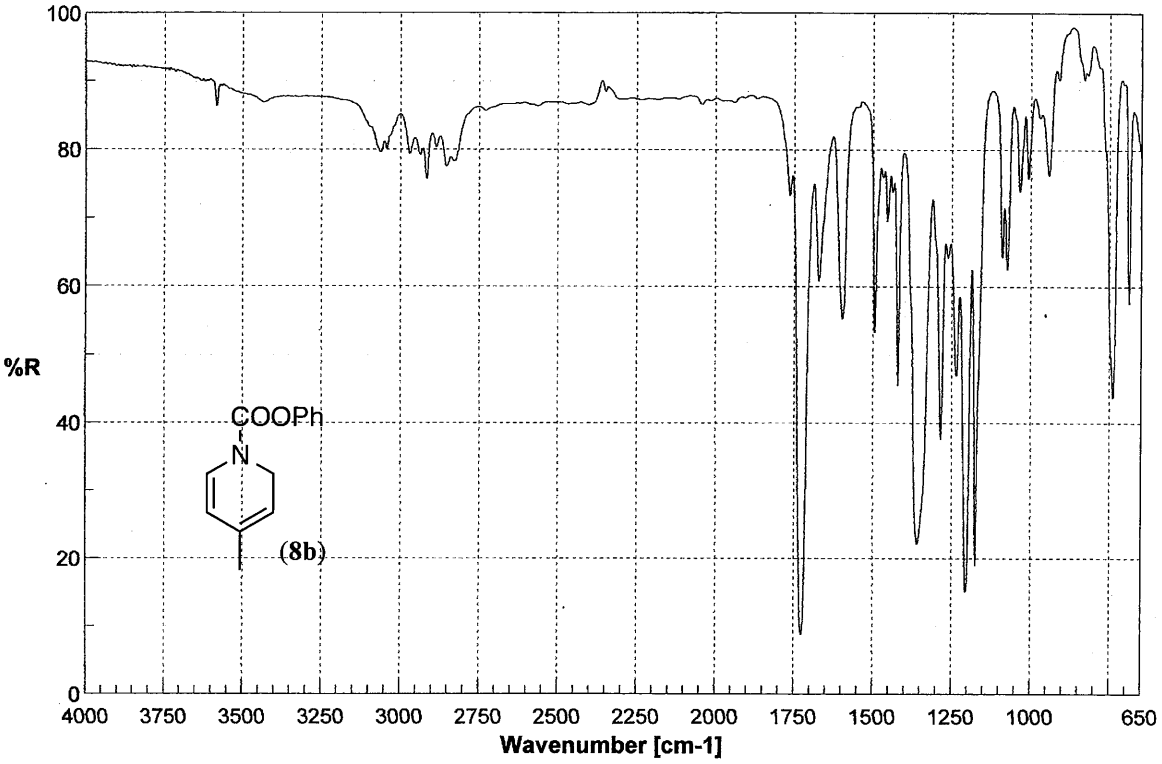
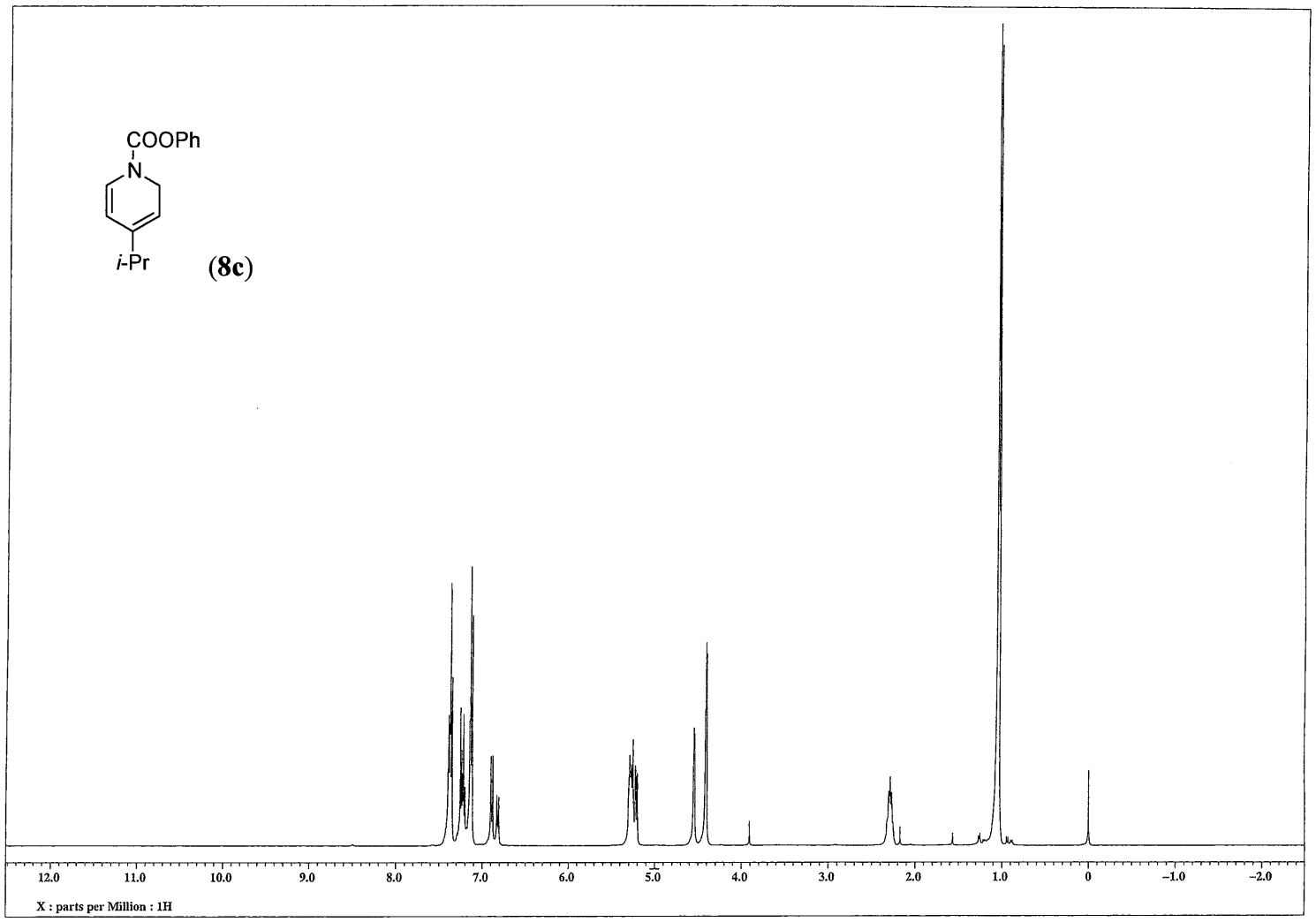
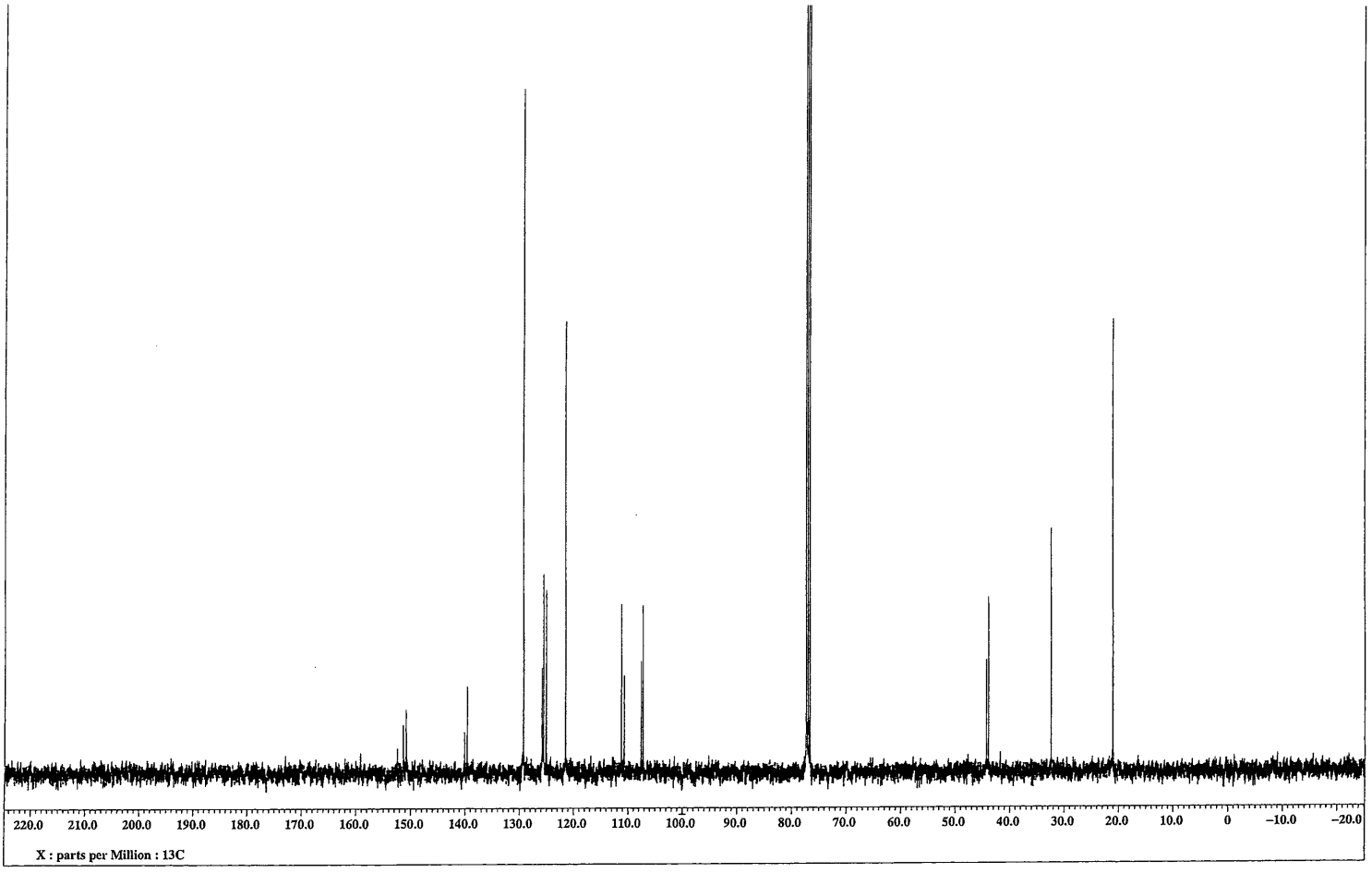
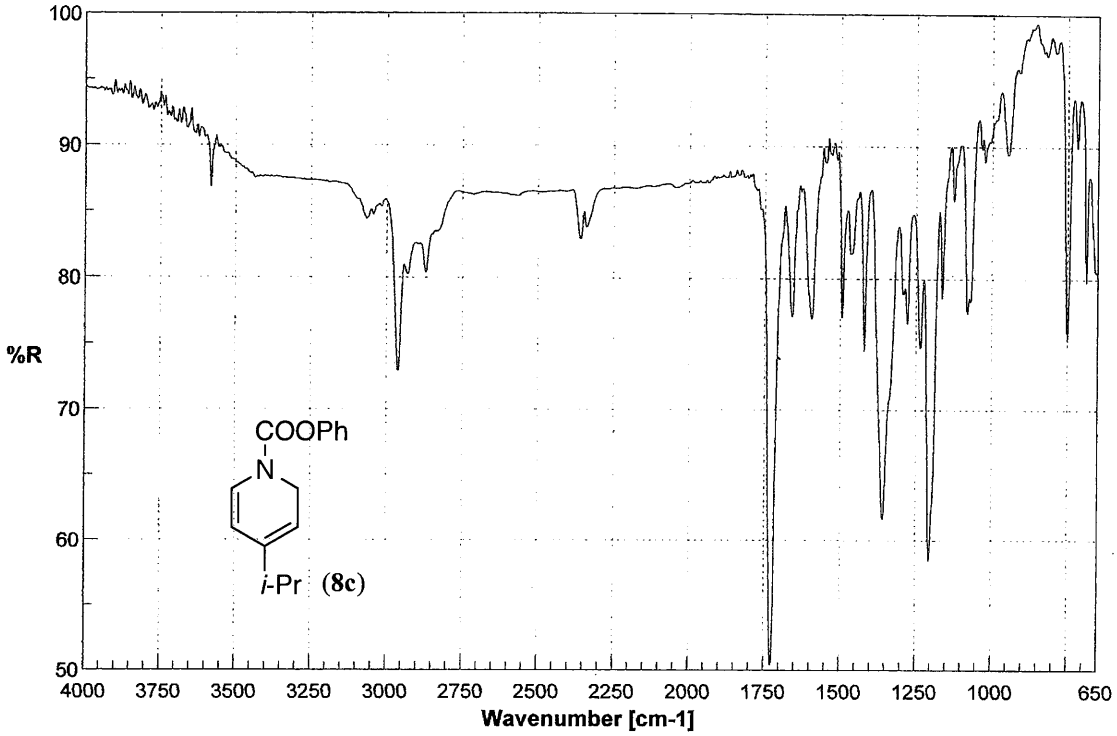
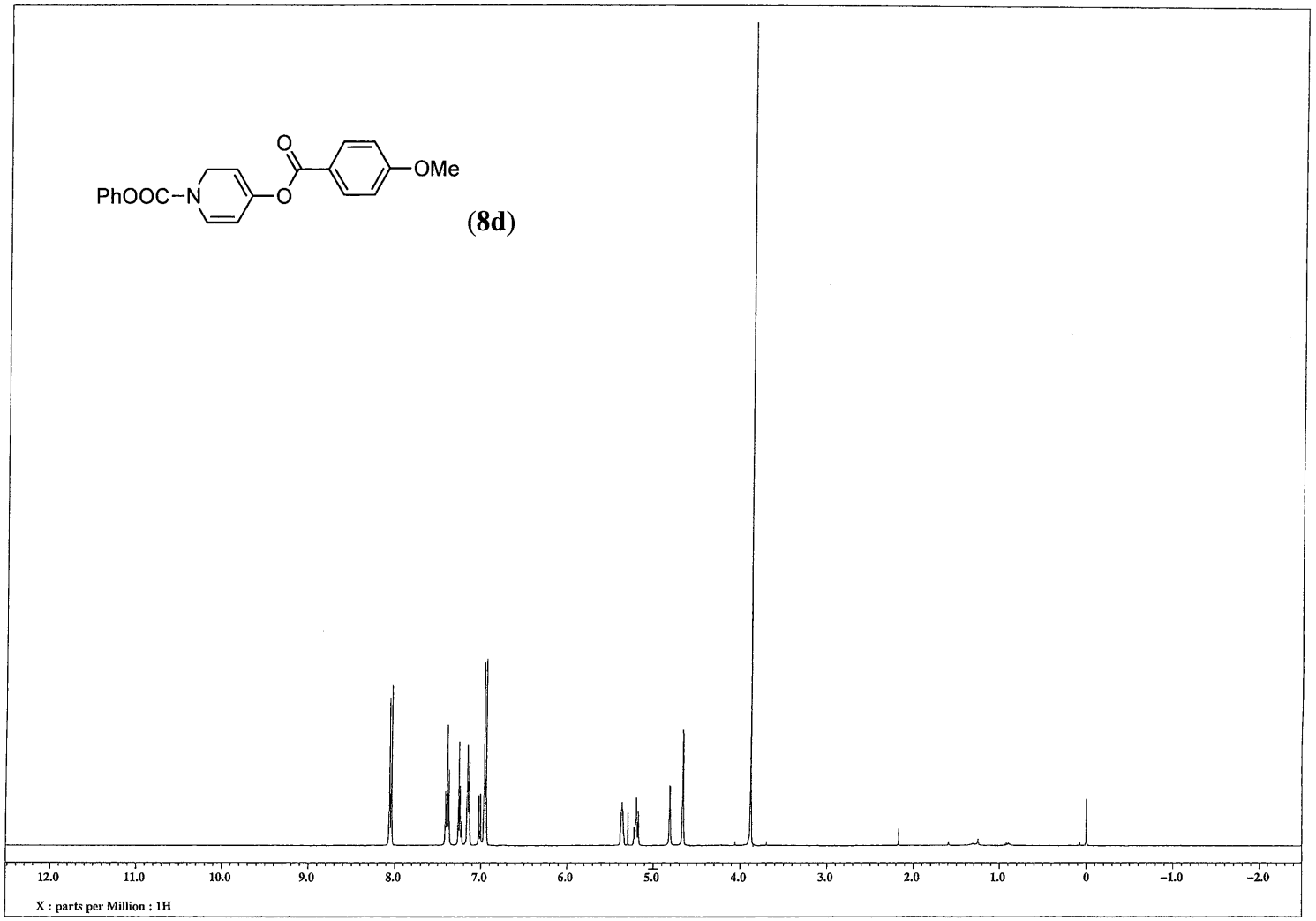
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
X : parts per Million : 13C


100
80
60
40
20
0
%R
COOPh
N
(8b)
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]

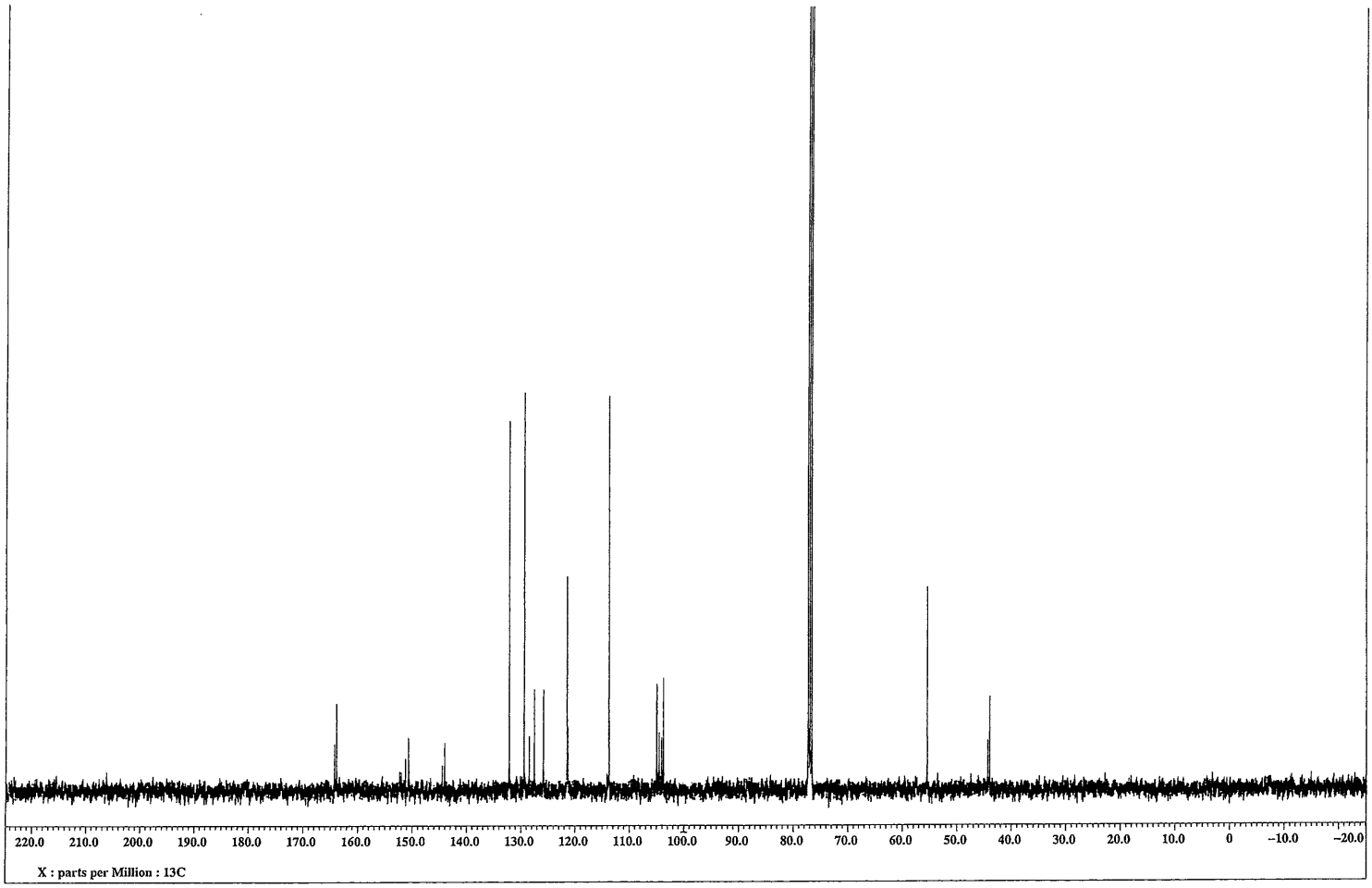

COOPh
N
i-Pr
(8c)
12.0 11.0 10.0 9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0 −1.0 −2.0
X : parts per Million : 1H


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
X : parts per Million : 13C


100
90
80
%R
70
60
50
COOPh
N
i-Pr (8c)
4000 3750 3500 3250 3000 2750 2500 2250 2000 1750 1500 1250 1000 650
Wavenumber [cm-1]


PhOOC–N
O
O
OMe
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
X : parts per Million : 1H

(8d)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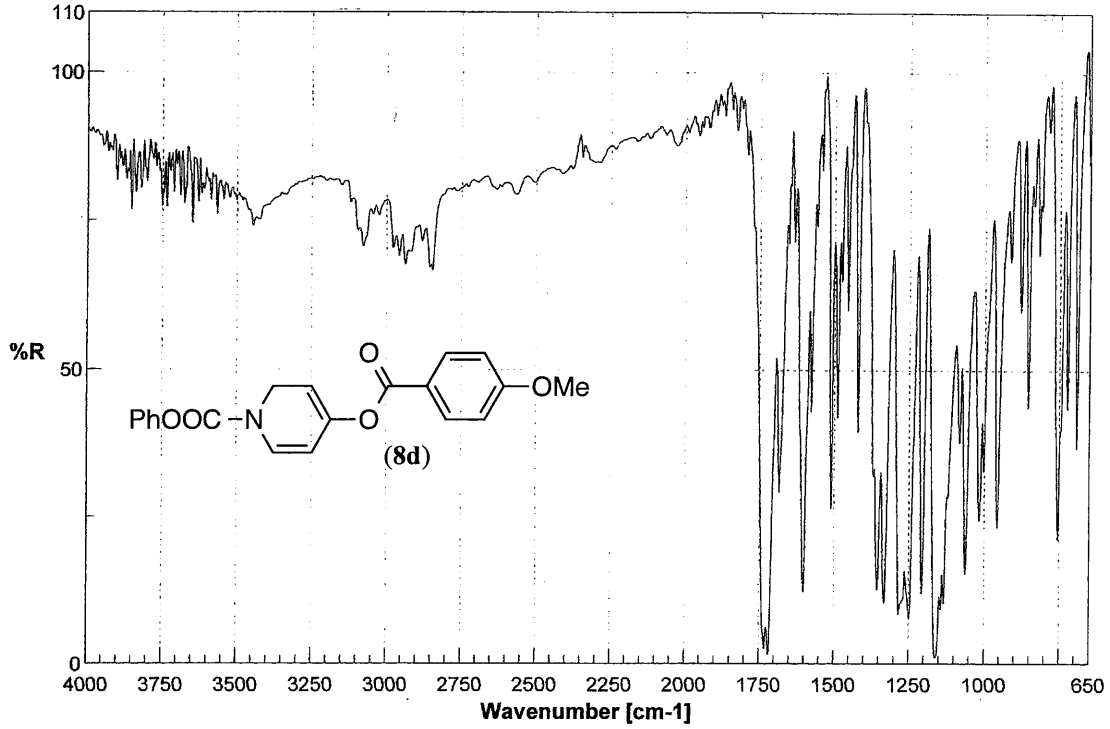
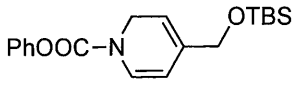
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
–10.0
–20.0
X : parts per Million : 13C


110
100
%R
50
0
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]
PhOOC
N
O
O
OMe
(8d)


PhOOC–N
OTBS

(8e)

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10.0
9.0
8.0
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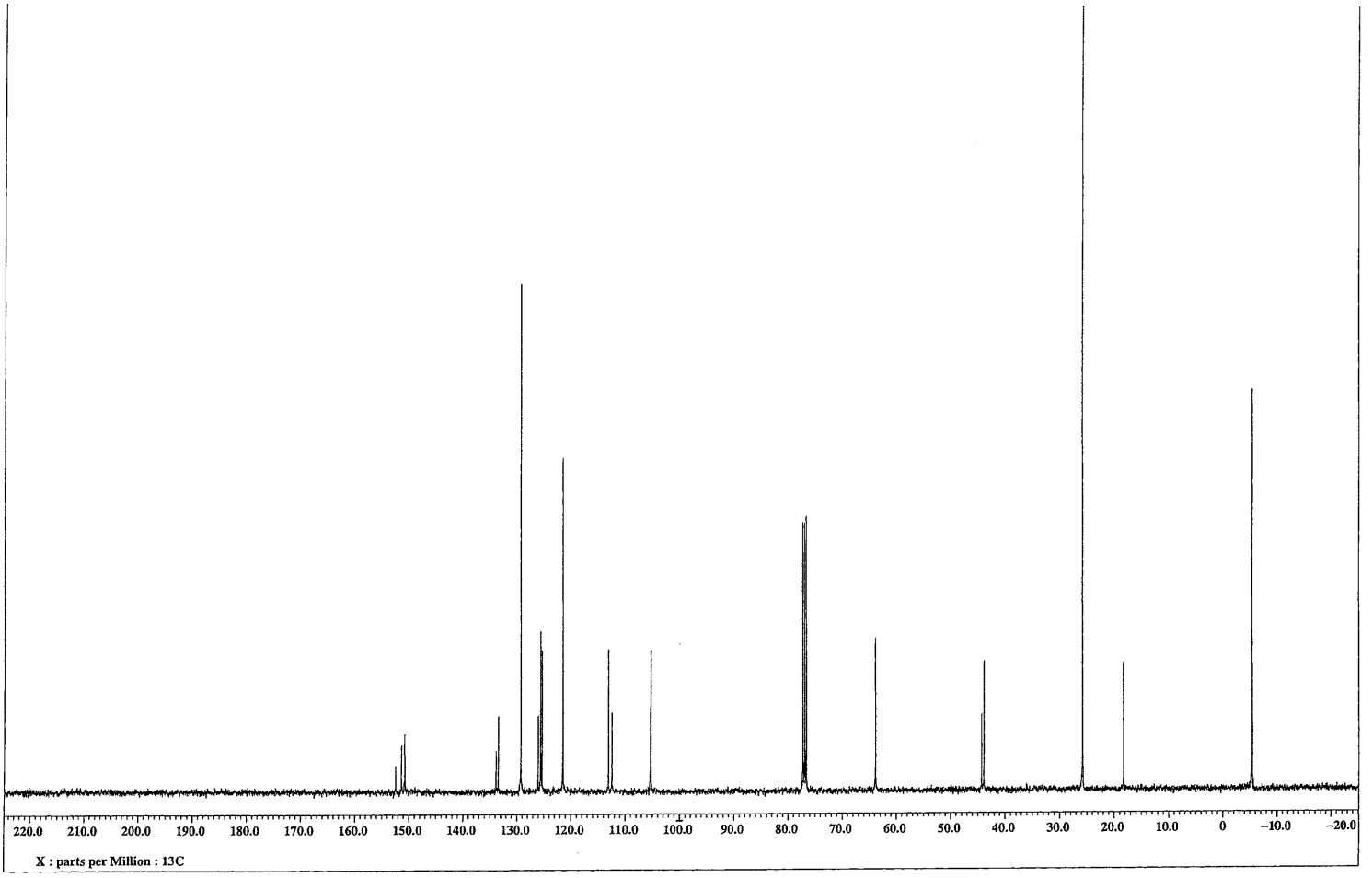
6.0
5.0
4.0
3.0
2.0
1.0
0
–1.0
–2.0
X : parts per Million : 1H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160.0
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120.0
110.0
100.0
90.0
80.0
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50.0
40.0
30.0
20.0
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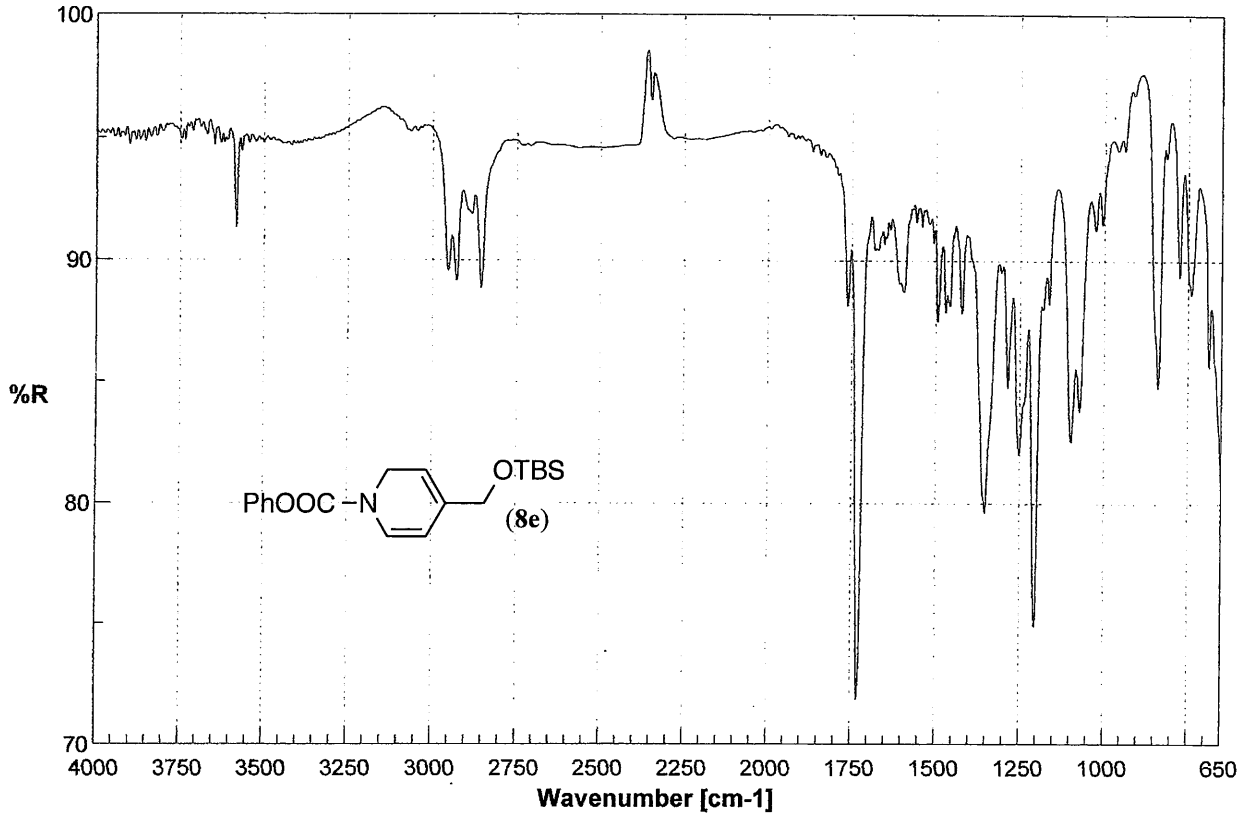
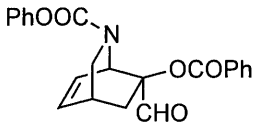
0
–10.0
–20.0
X : parts per Million : 13C


100
90
80
70
%R
PhOOC –N
OTBS
(8e)
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]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N
OCOPh
CHO

(10aa)

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8.0
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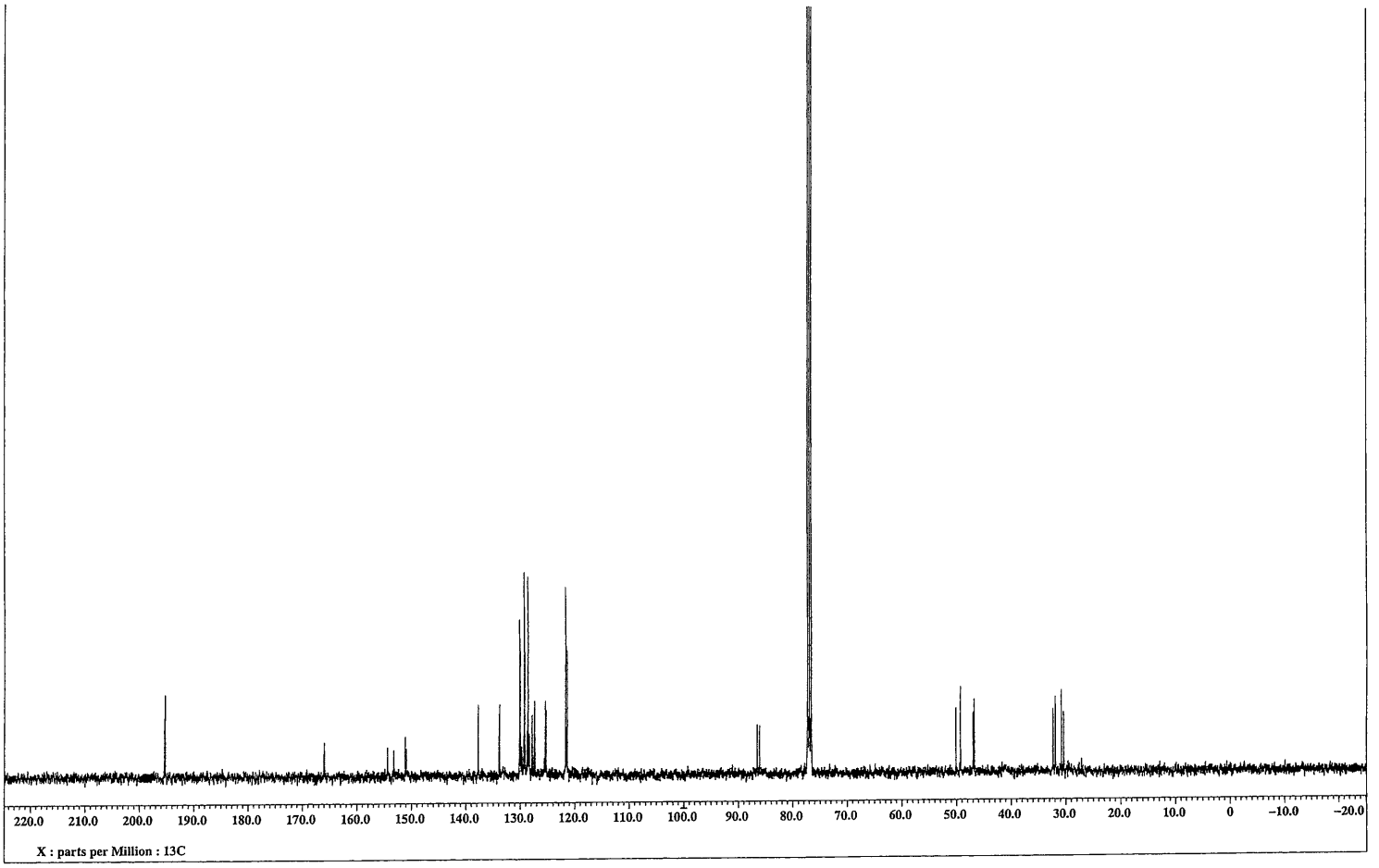
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : 1H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100.0
90.0
80.0
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50.0
40.0
30.0
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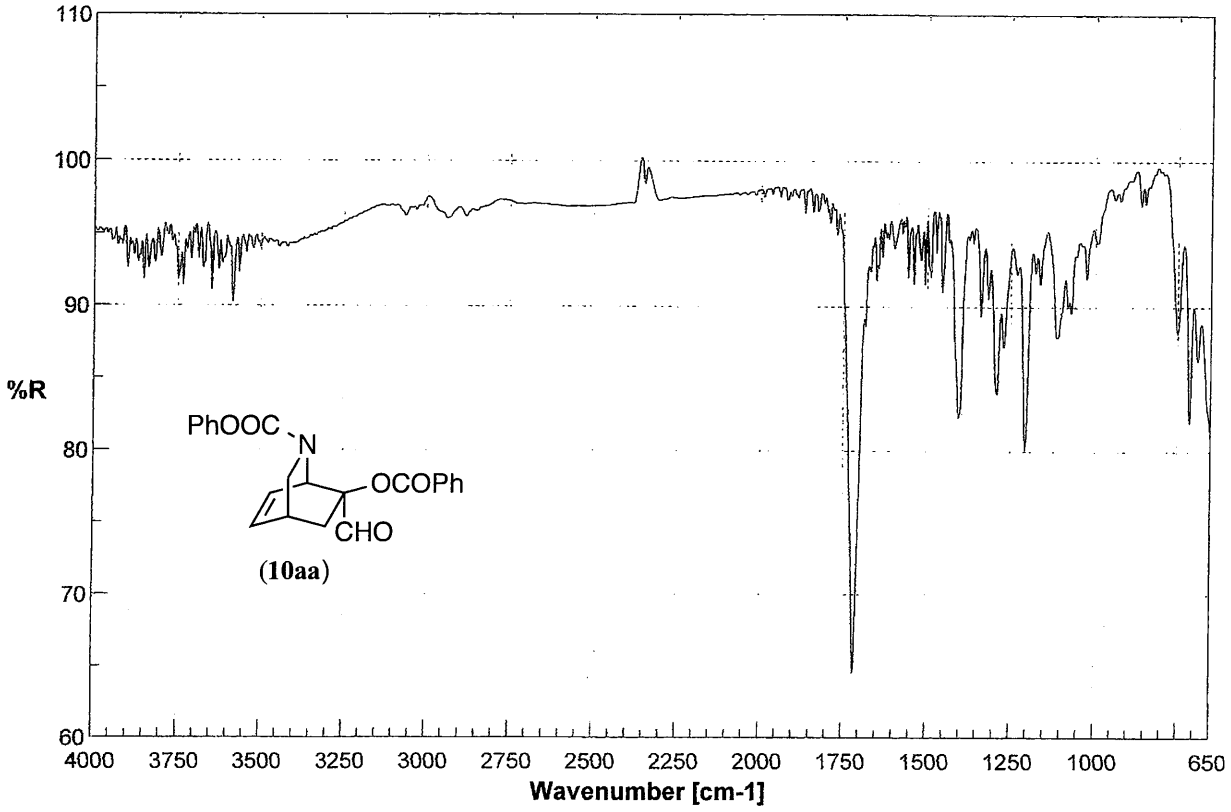
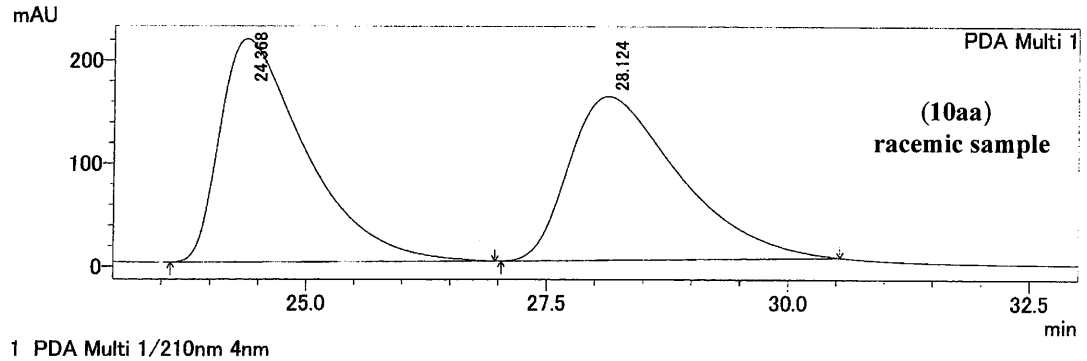
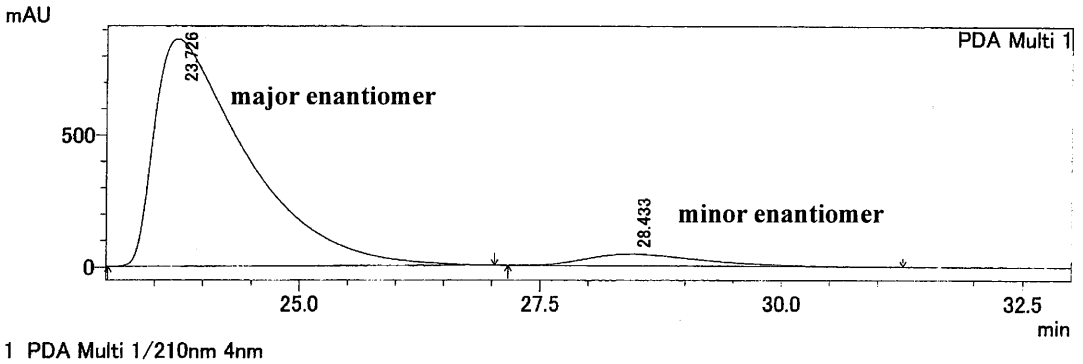
10.0
0
-10.0
-20.0
X : parts per Million : 13C





1 PDA Multi 1/210nm 4nm



1 PDA Multi 1/210nm 4nm

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%
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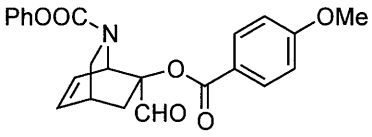
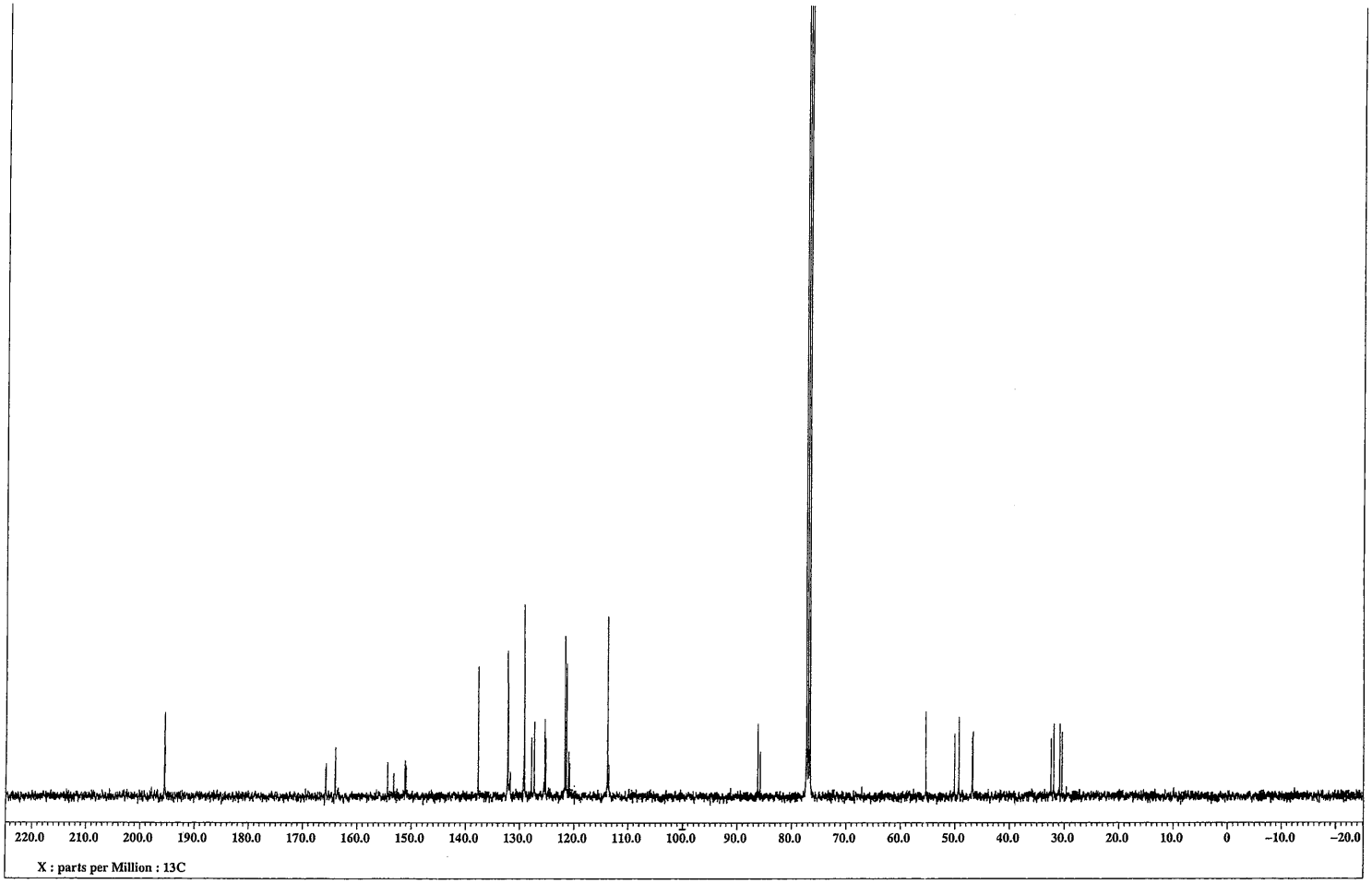
2	28.433	3683188	6.082
合計			100.000


PhOOC
N
O
CHO
O
OMe

(10ab)

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
X : parts per Million : 1H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100.0
90.0
80.0
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40.0
30.0
20.0
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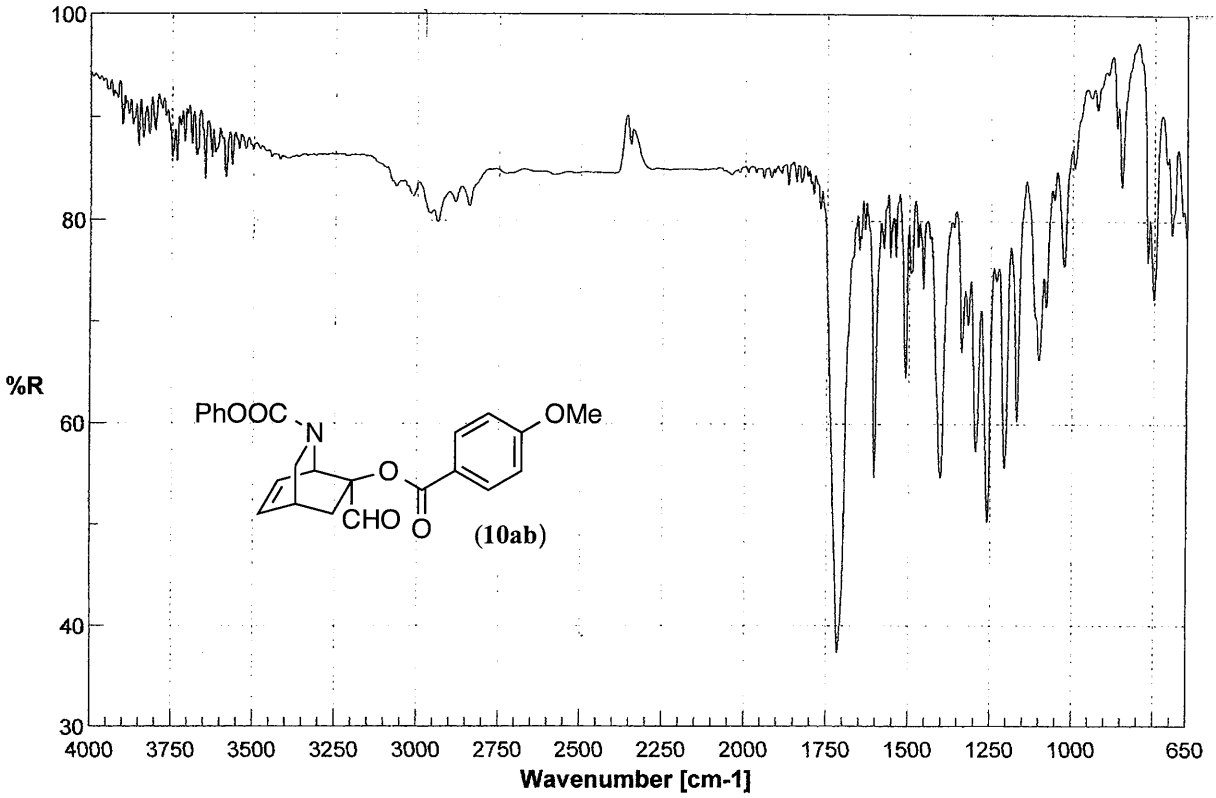
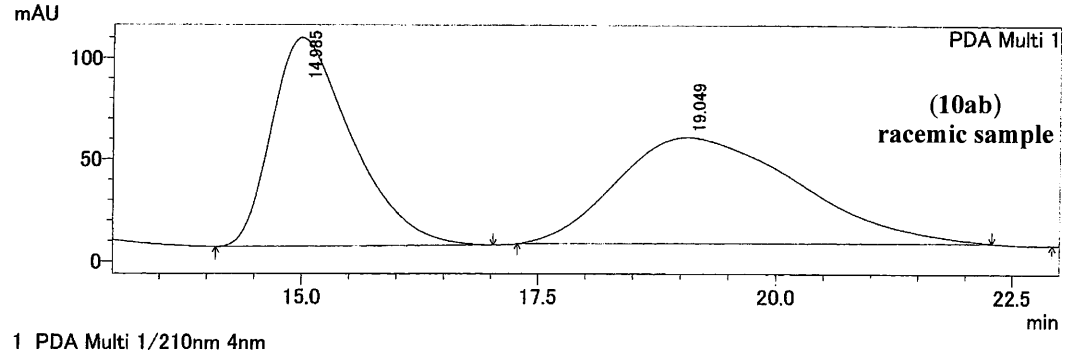
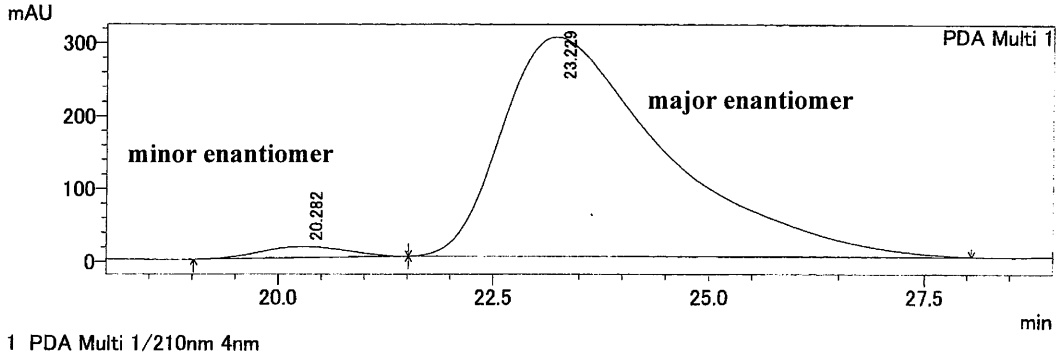
0
-10.0
-20.0
X : parts per Million : 13C





1 PDA Multi 1/210nm 4nm



1 PDA Multi 1/210nm 4nm

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%
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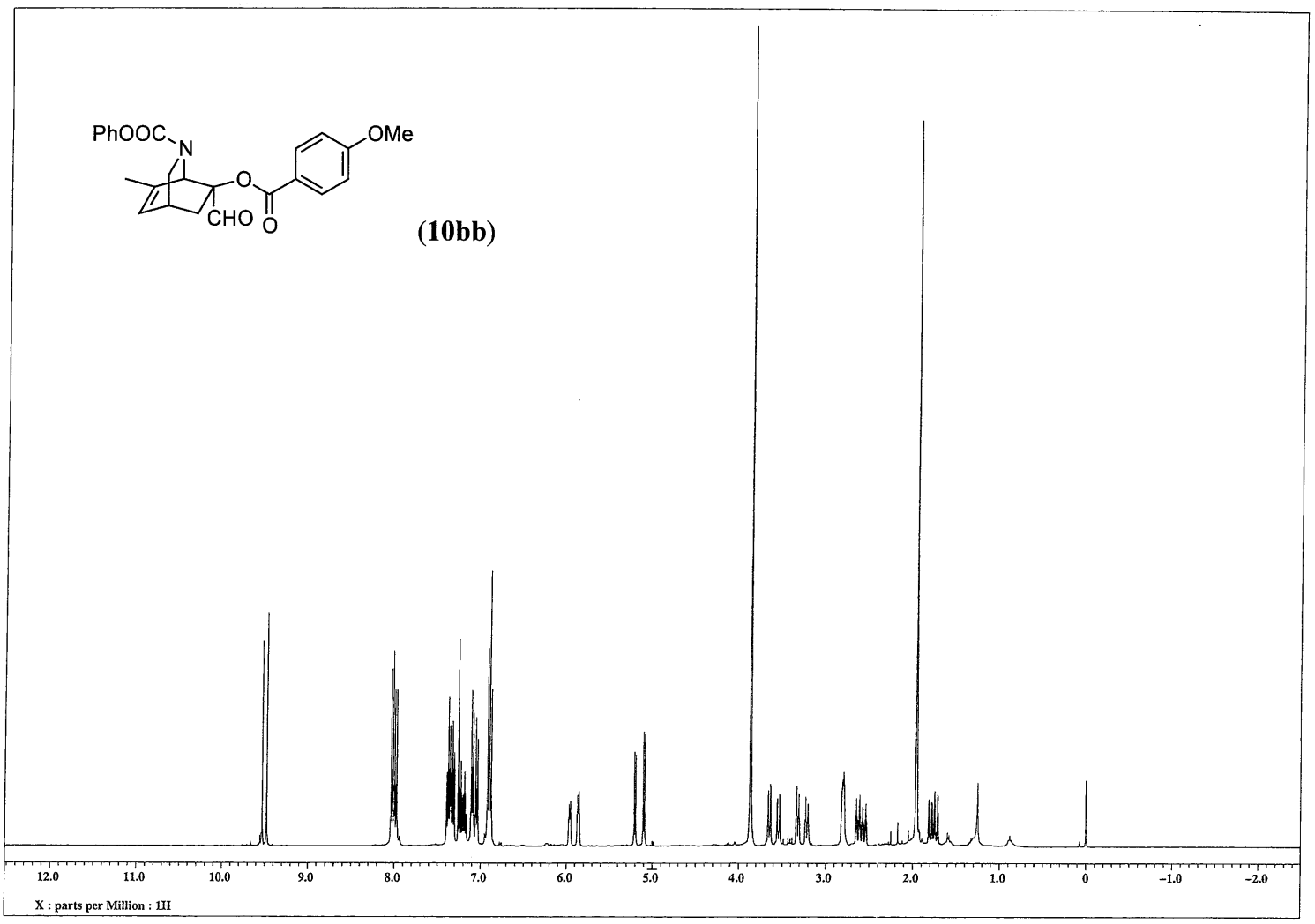
2	23.229	39535742	97.421
合計			100.000


PhOOC
N
O
CHO
O
OMe
12.0
11.0
10.0
9.0
8.0
7.0
6.0
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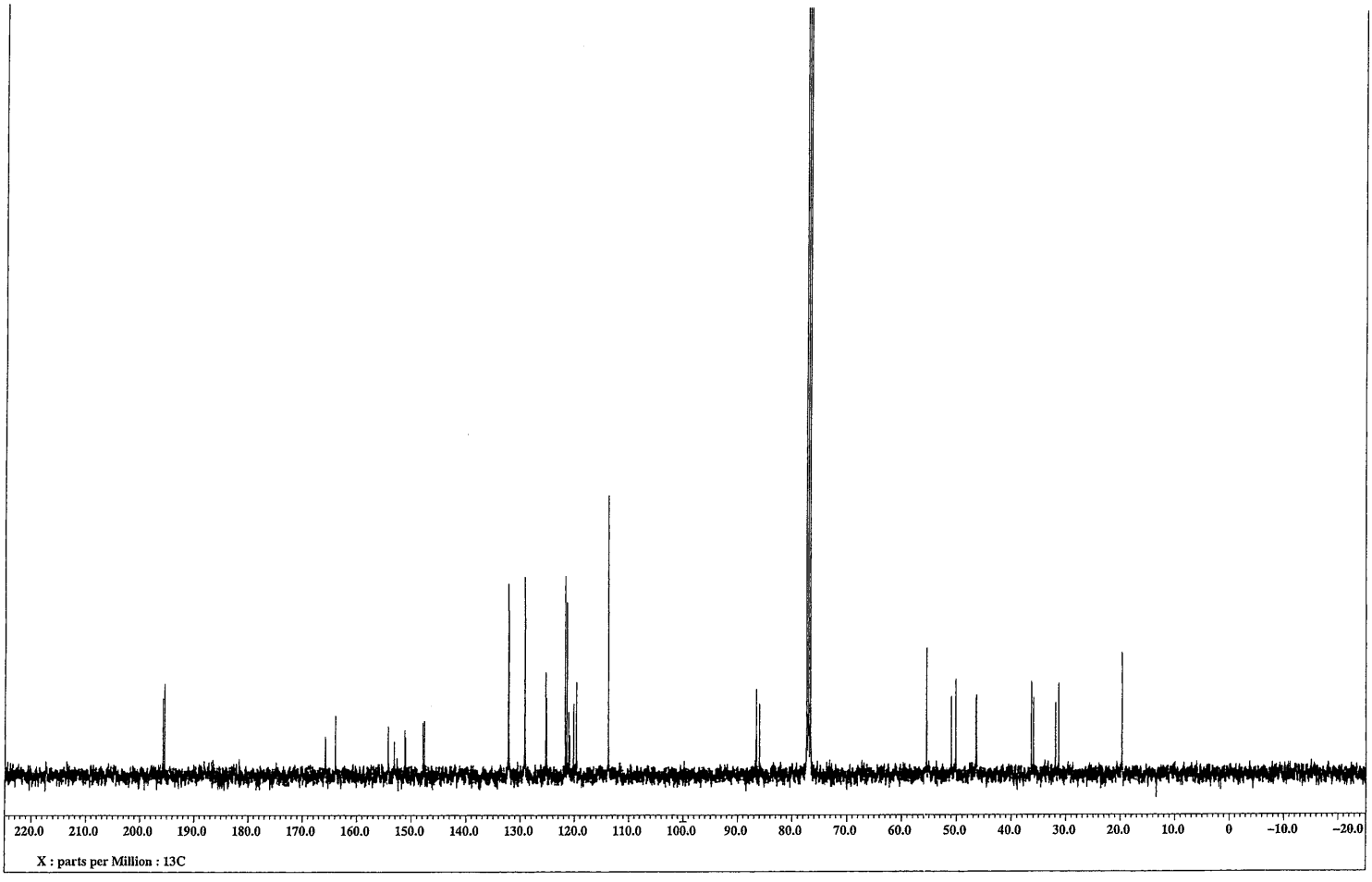
4.0
3.0
2.0
1.0
0
−1.0
−2.0
X : parts per Million : 1H

(10bb)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120.0
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100.0
90.0
80.0
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50.0
40.0
30.0
20.0
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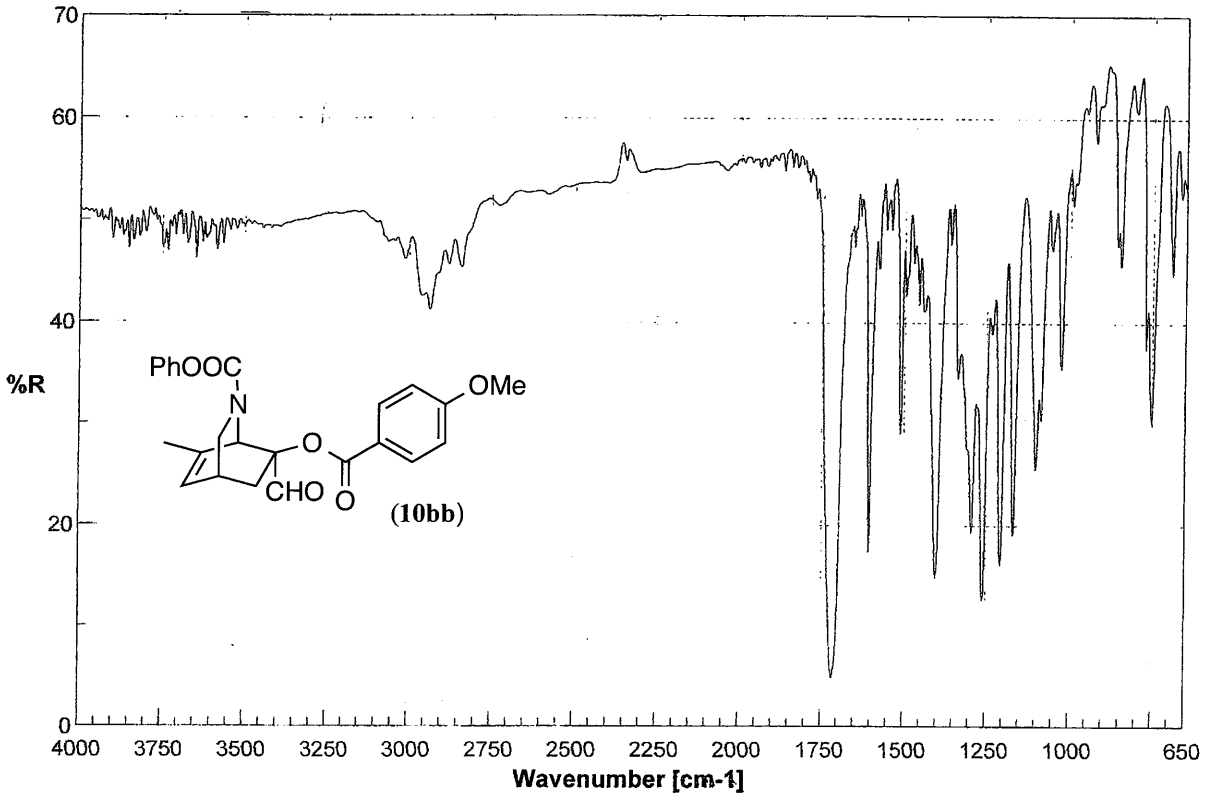
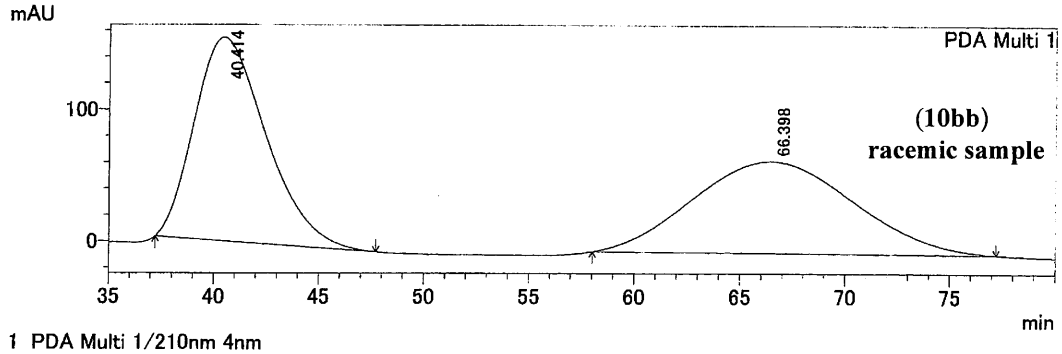
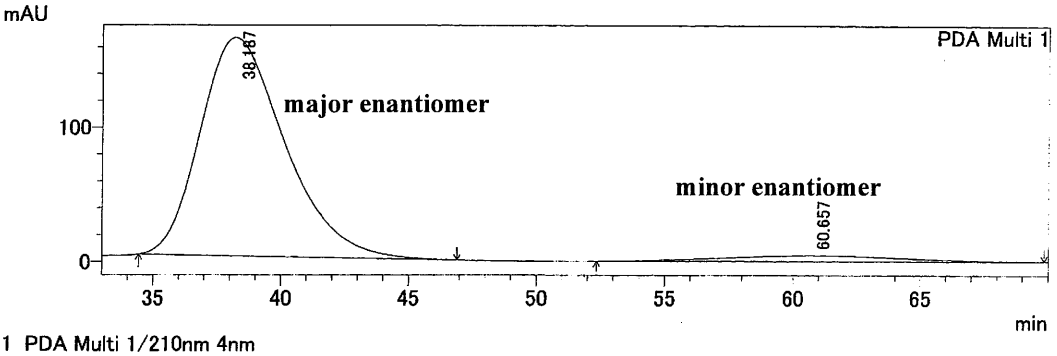
0
−10.0
−20.0
X : parts per Million : 13C





1 PDA Multi 1/210nm 4nm



1 PDA Multi 1/210nm 4nm

PDA Ch1 210nm 4nm

ピーク#	保持時間	面積	面積%
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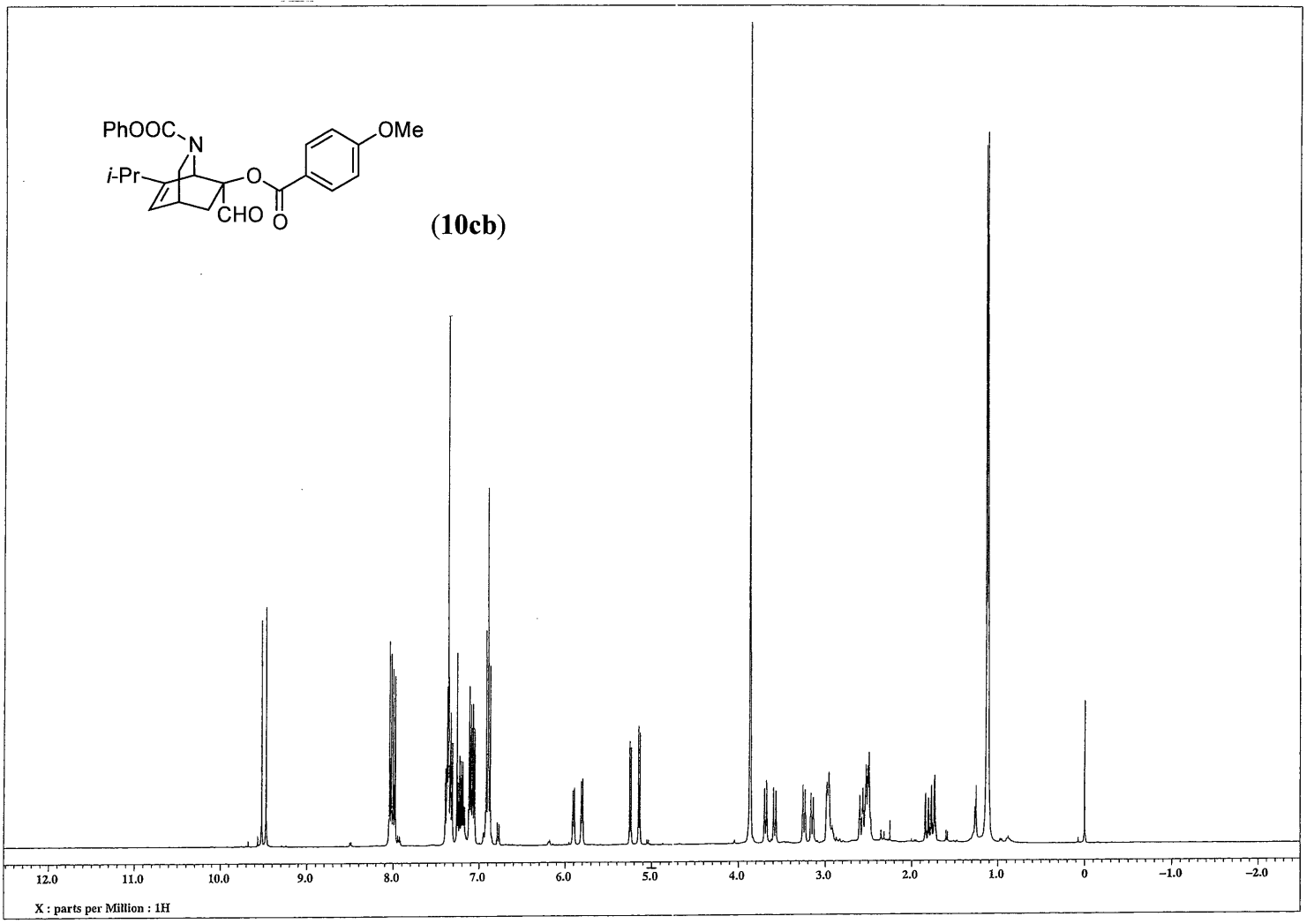
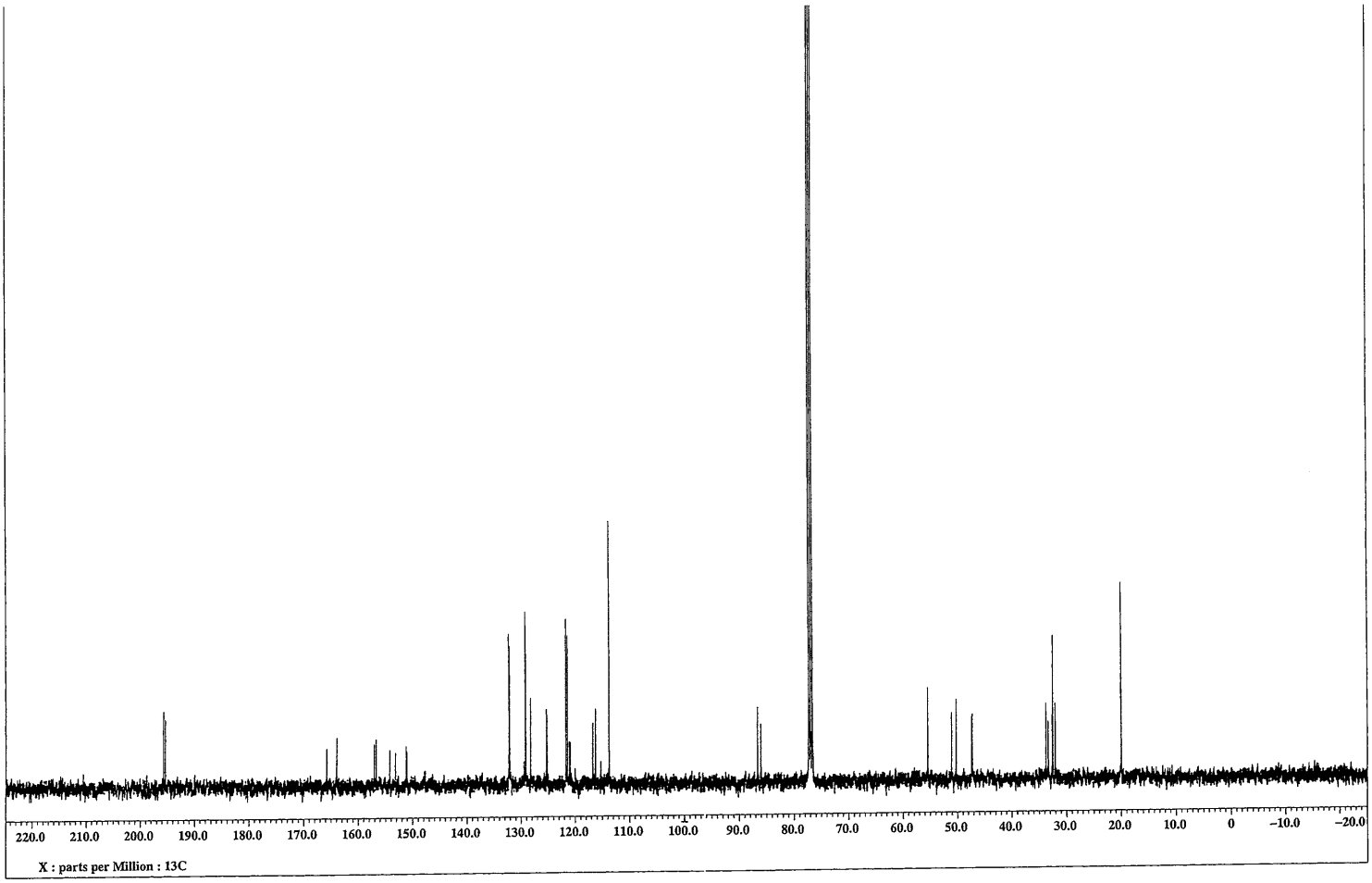
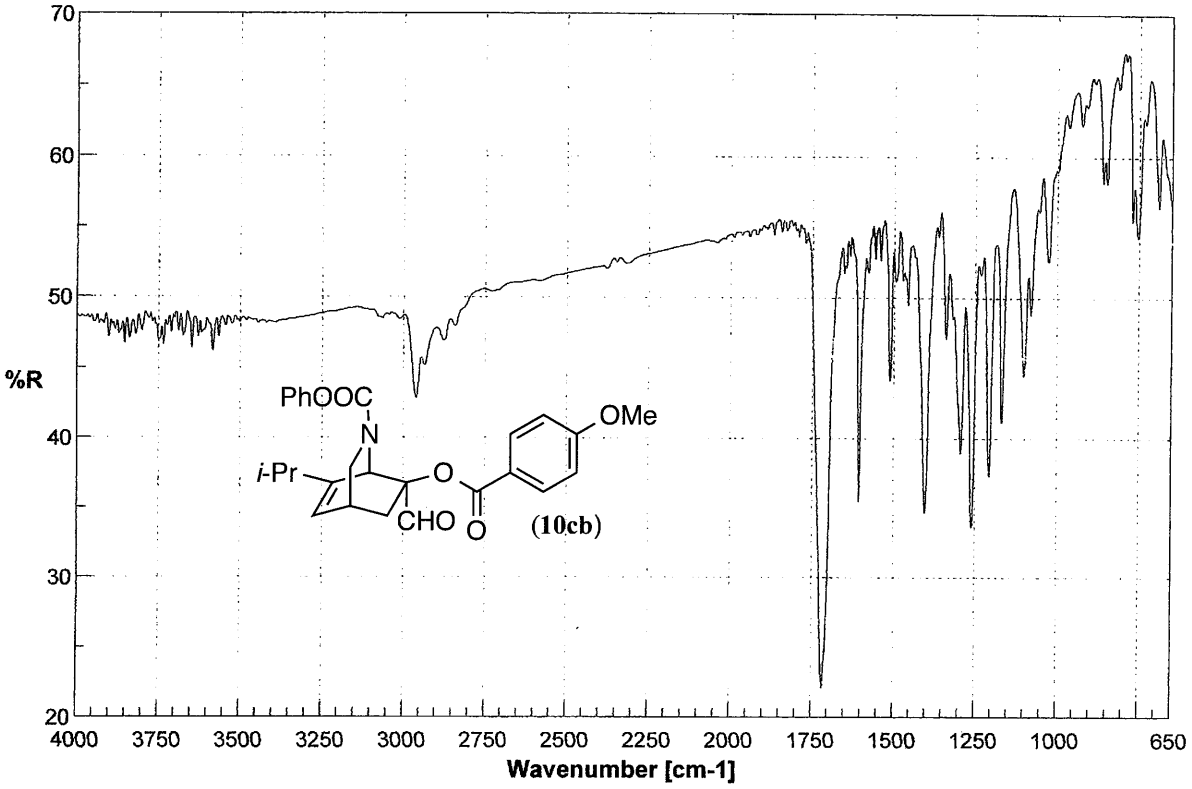
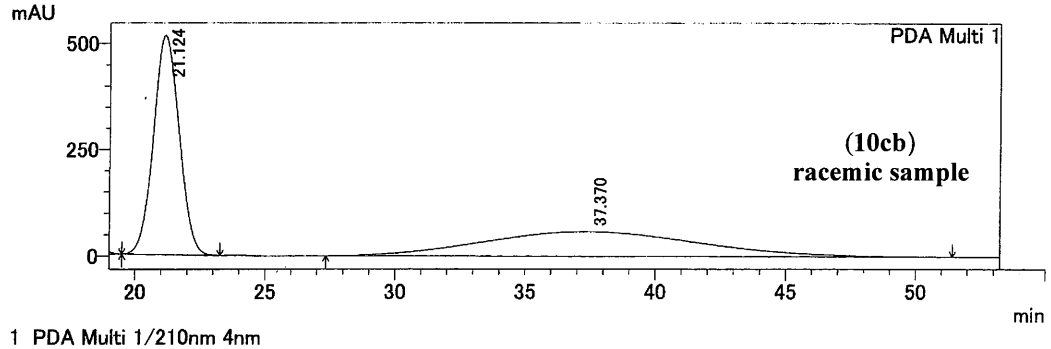
2	60.657	2120392	5.349
合計			100.000


PhOOC
N
i-Pr
O
CHO
O
OMe
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
X : parts per Million : 1H

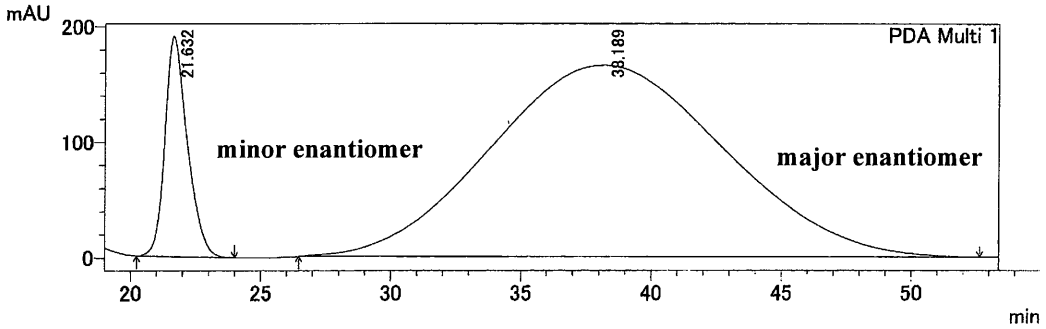
(10cb)


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
X : parts per Million : 13C





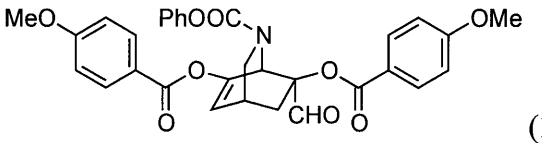
1 PDA Multi 1/210nm 4nm



1 PDA Multi 1/210nm 4nm

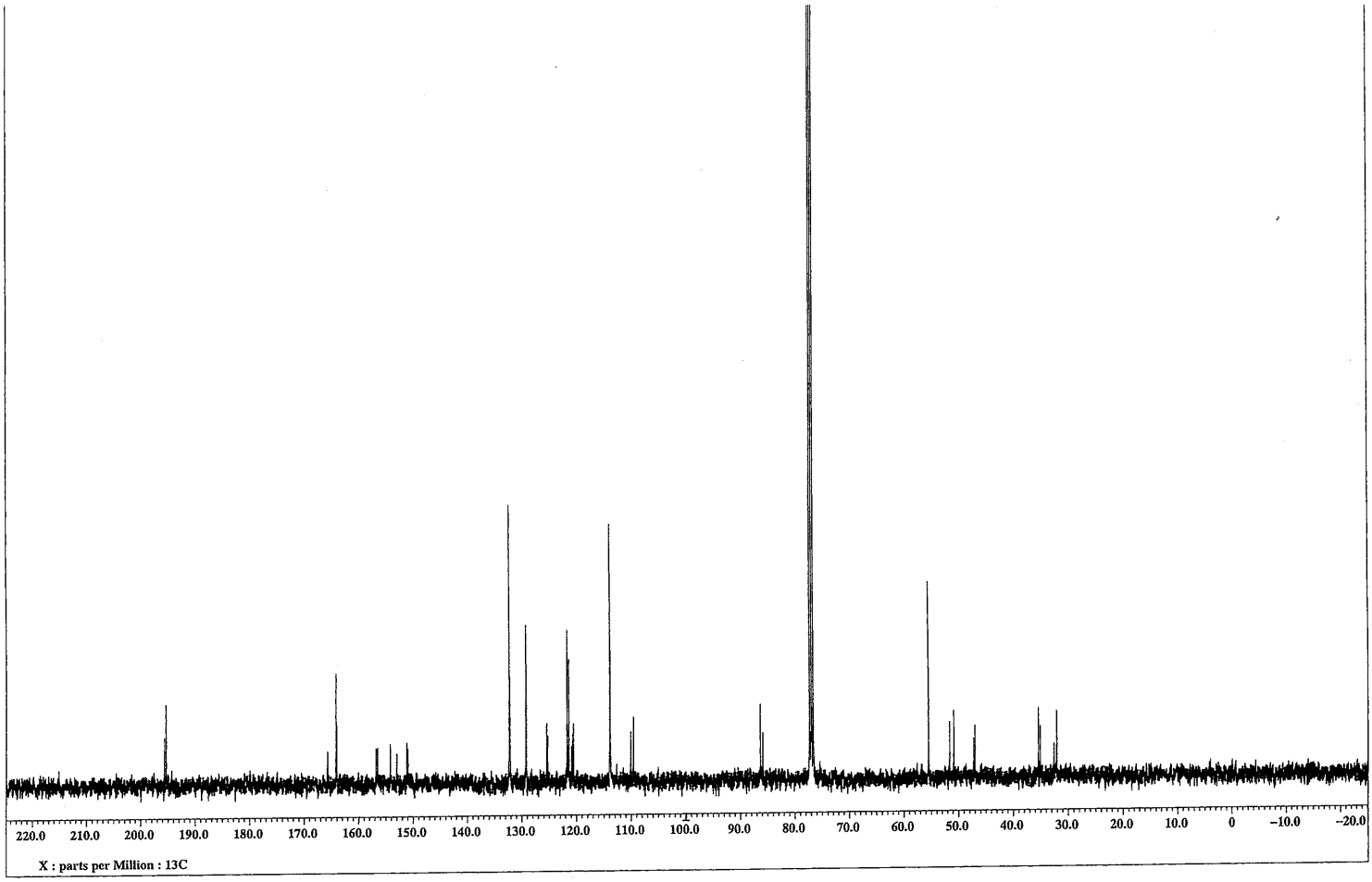
PDA Ch1 210nm 4nm

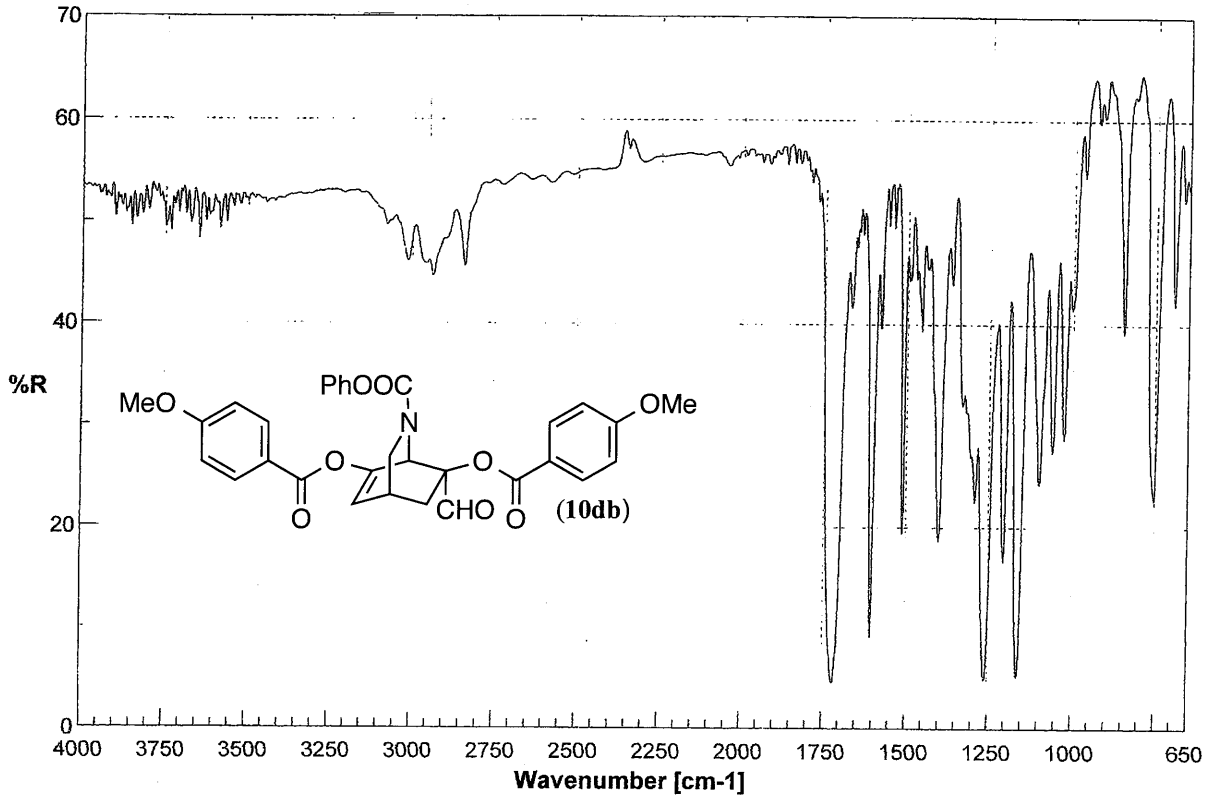
ピーク#	保持時間	面積	面積%
1	21.632	11464183	10.040
2	38.189	102722855	89.960
合計			100.000

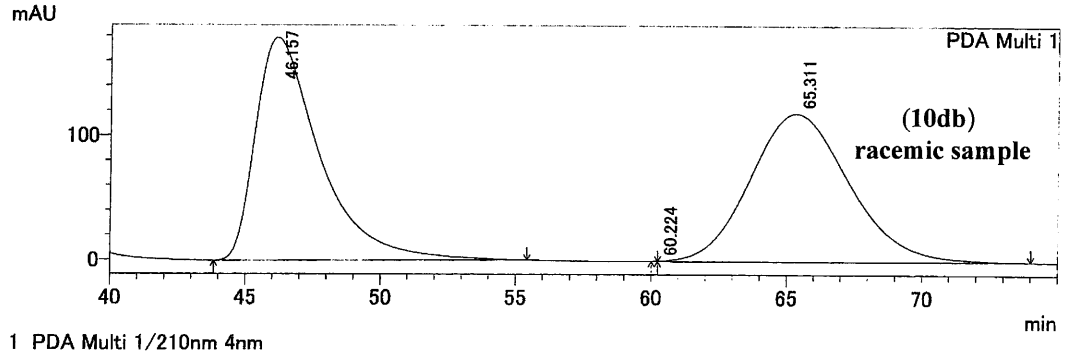

MeO
PhOOC
N
OMe
O
O
O
O
CHO

(10db)

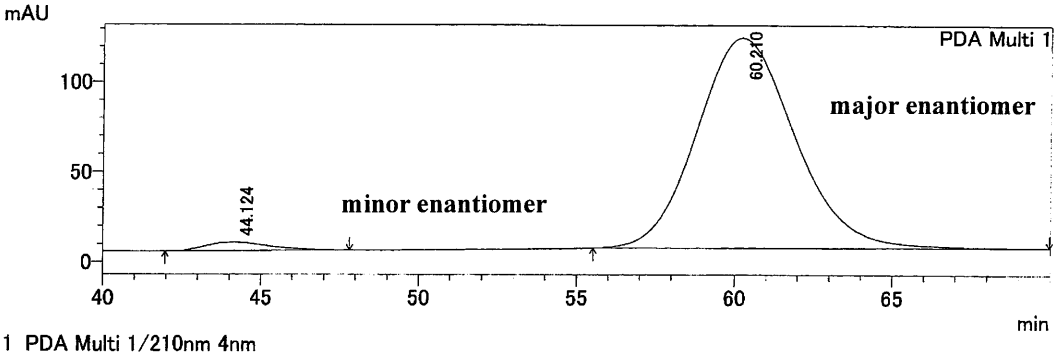
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : 1H


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
X : parts per Million : 13C





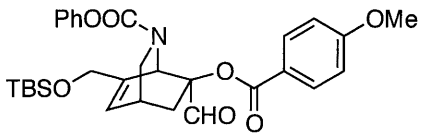
1 PDA Multi 1/210nm 4nm



1 PDA Multi 1/210nm 4nm

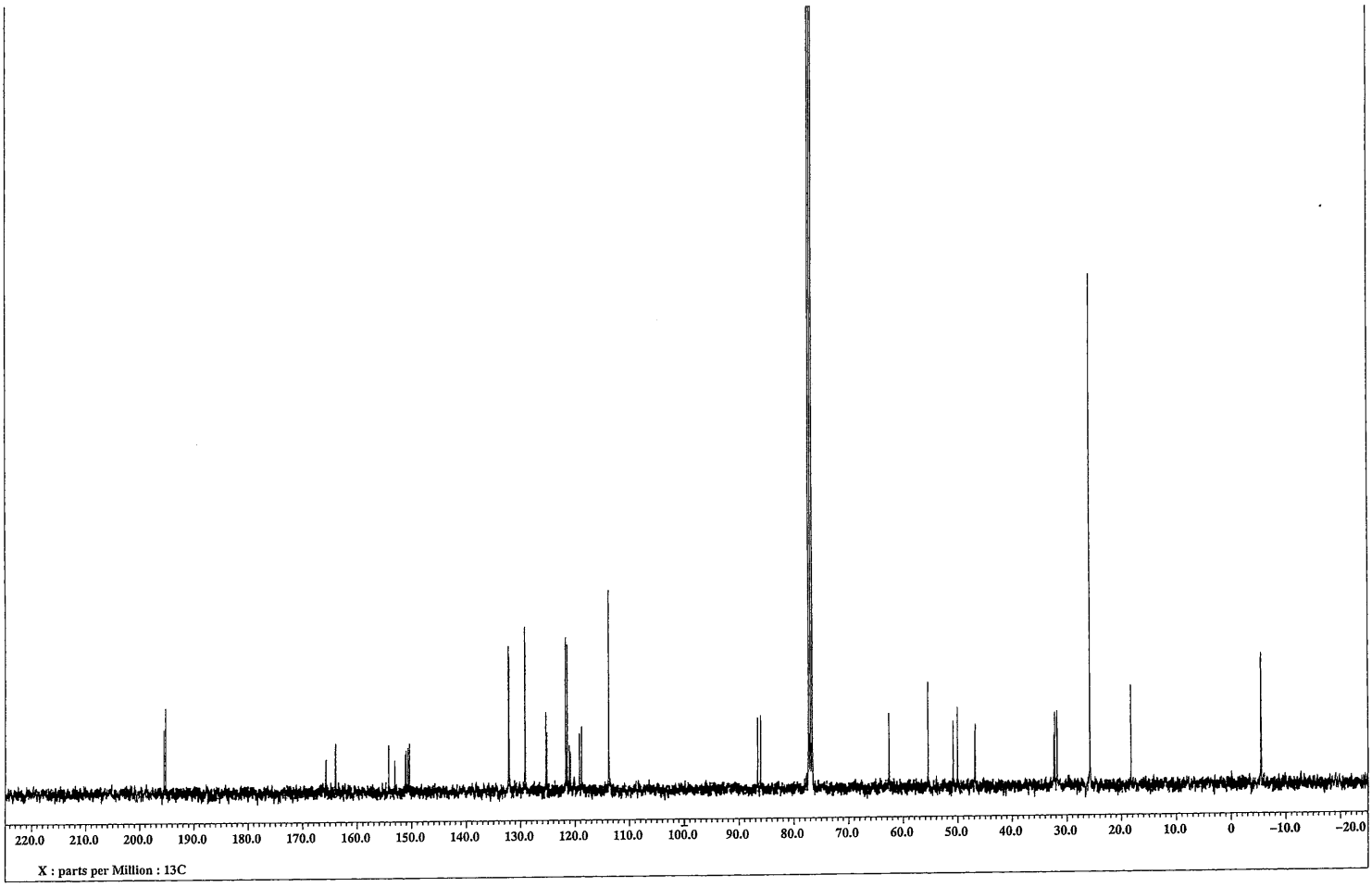
PDA Ch1 210nm 4nm

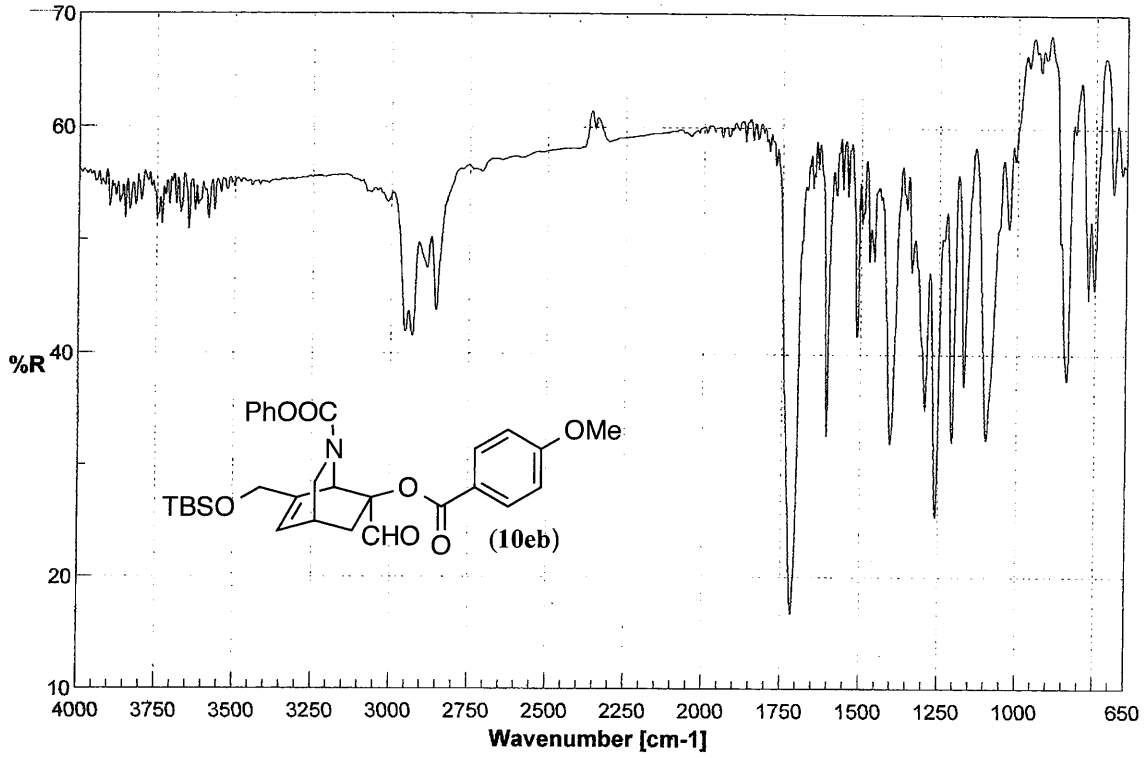
ピーク#	保持時間	面積	面積%
1	44.124	663551	2.556
2	60.210	25295534	97.444
合計			100.000

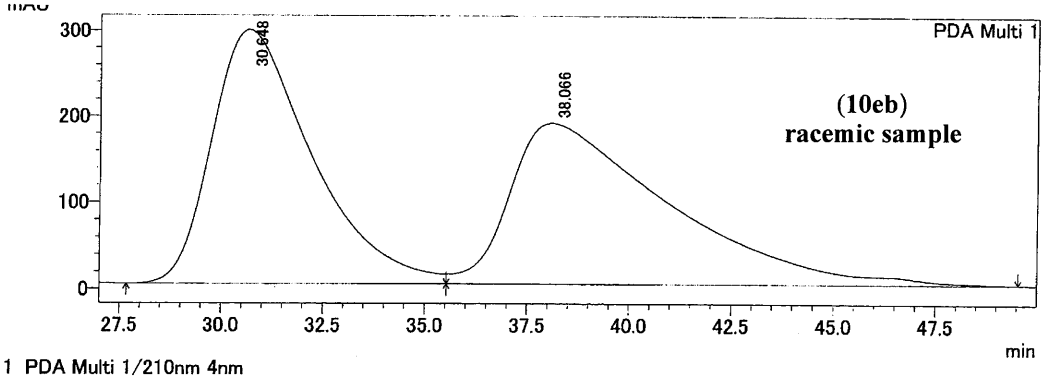

PhOOC
N
OMe
TBSO
O
CHO
O

(10eb)

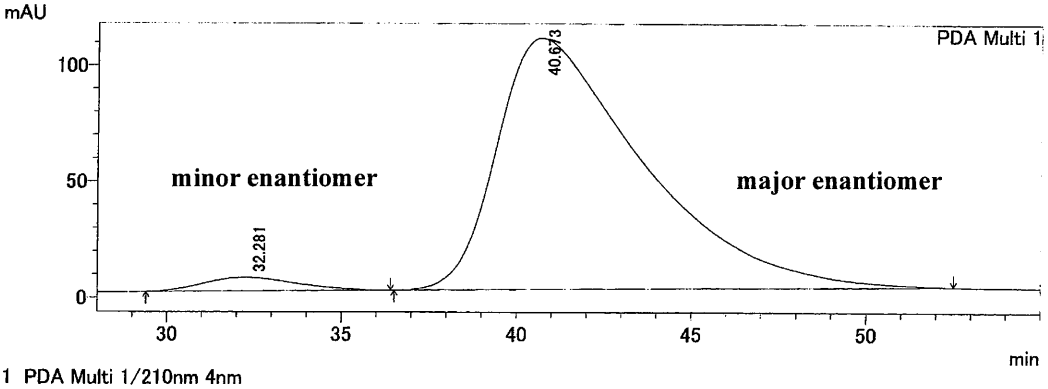
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
X : parts per Million : 1H


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
X : parts per Million : 13C





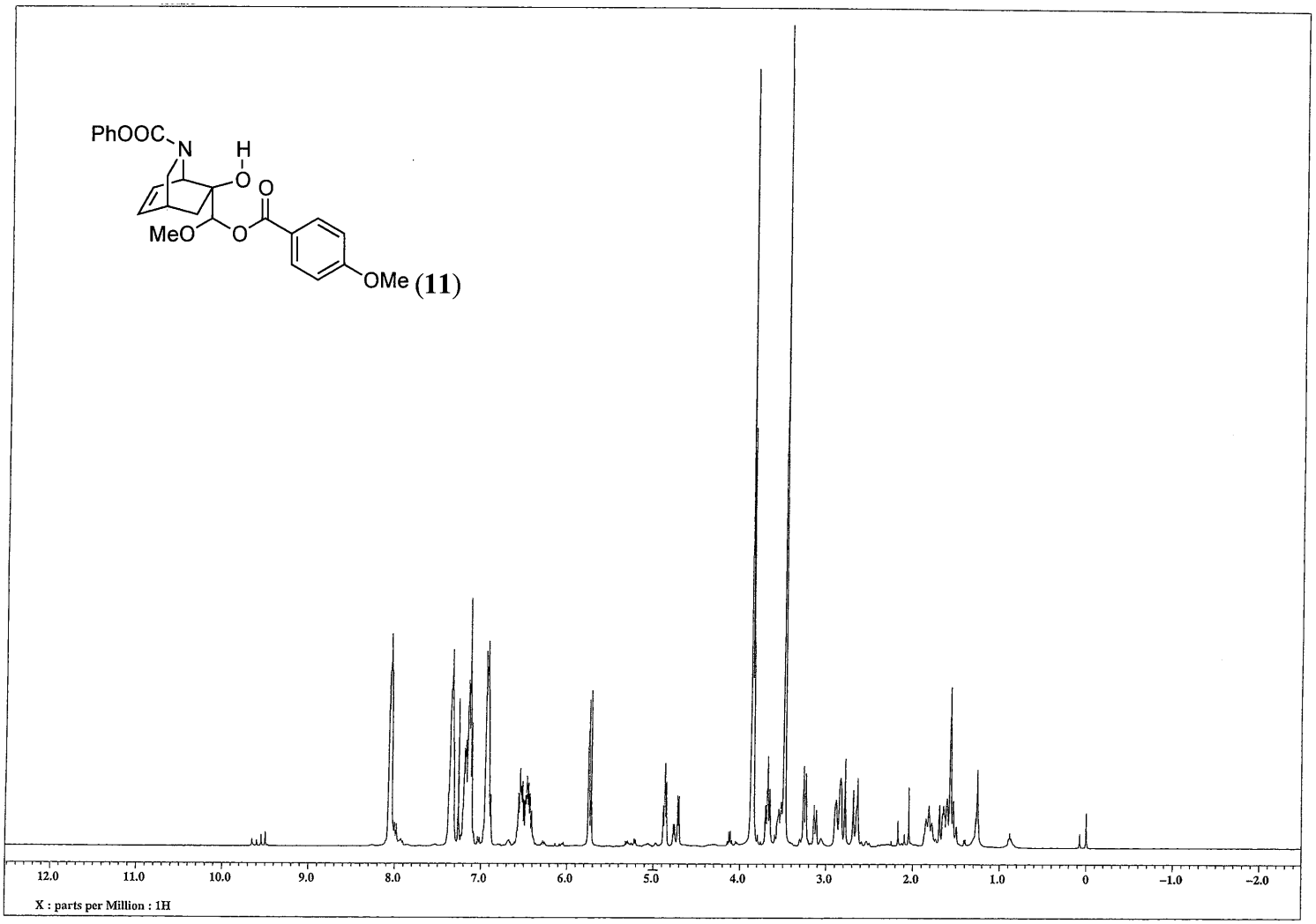
1 PDA Multi 1/210nm 4nm



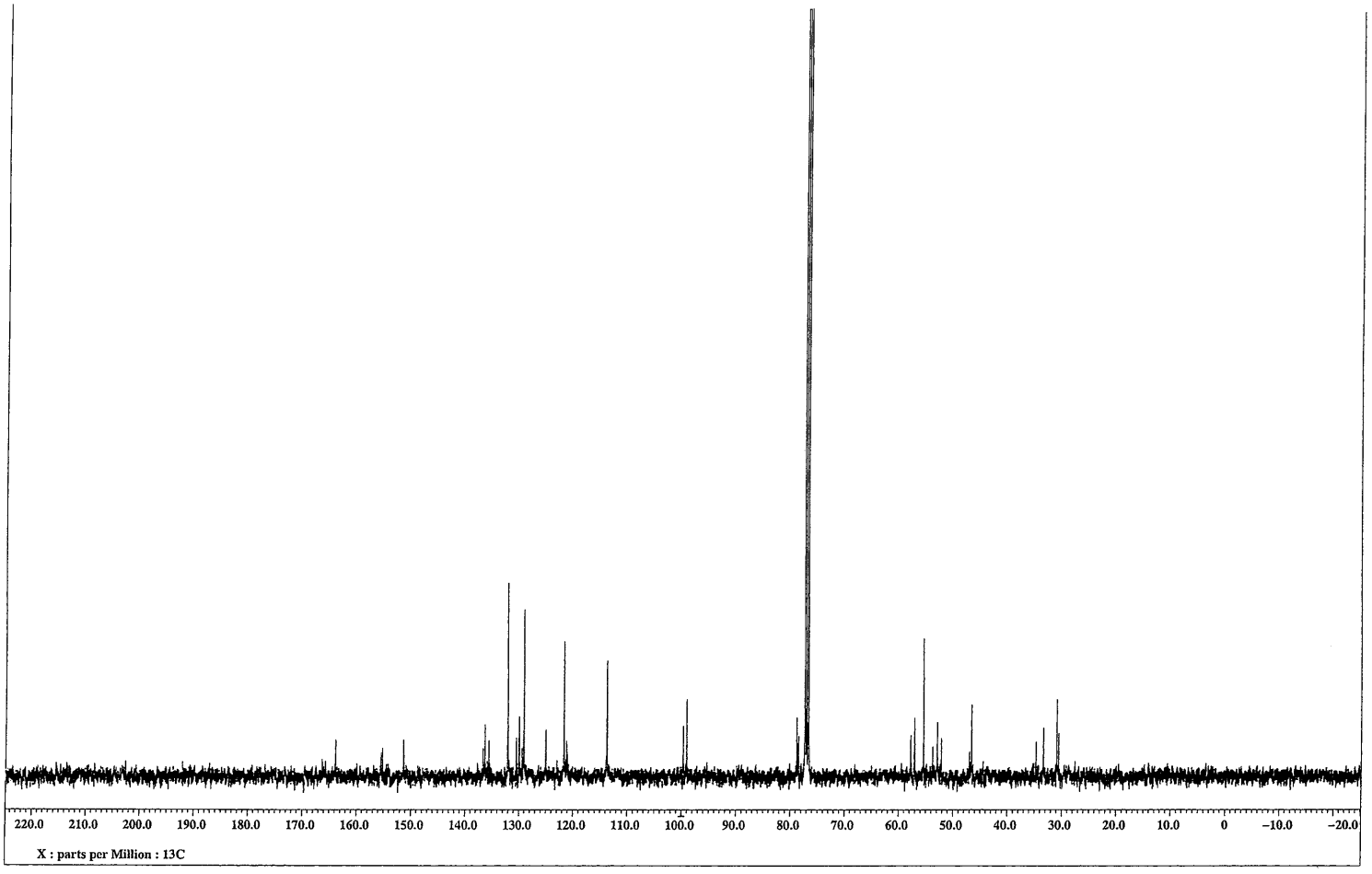
1 PDA Multi 1/210nm 4nm

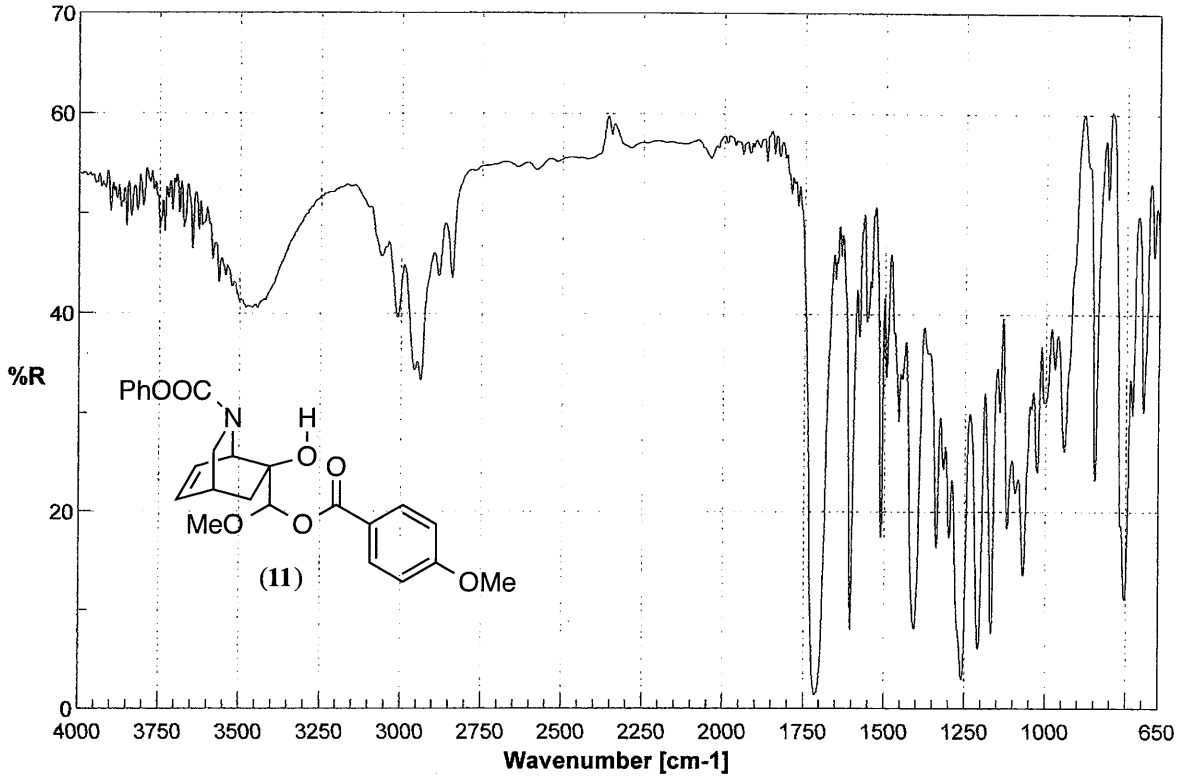
PDA Ch1 210nm 4nm

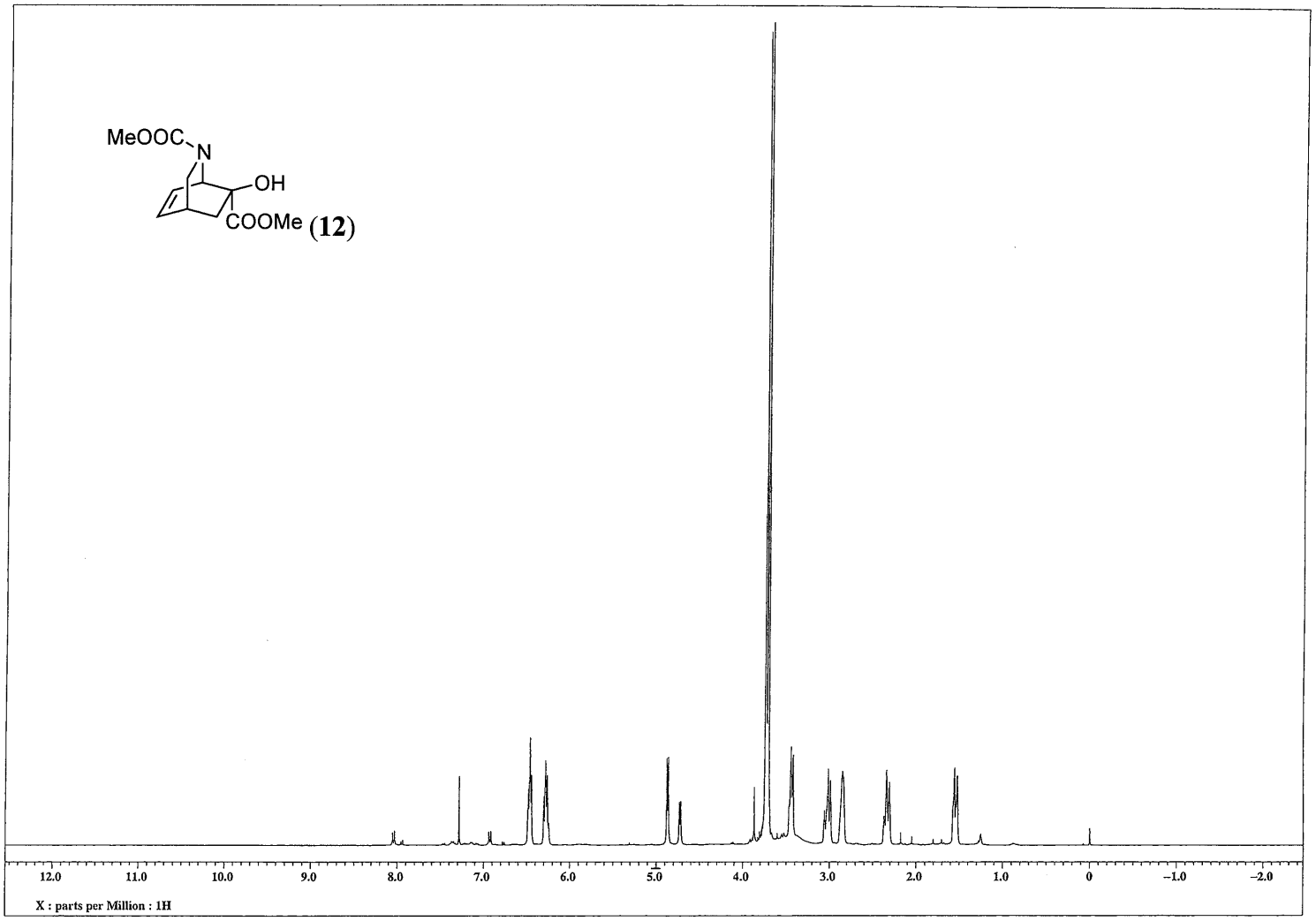
ピーク#	保持時間	面積	面積%
1	32.281	1045696	3.217
2	40.673	31463799	96.783
合計		32509495	100.000


PhOOC
N
H
O
O
MeO
O
OMe
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
X : parts per Million : 1H

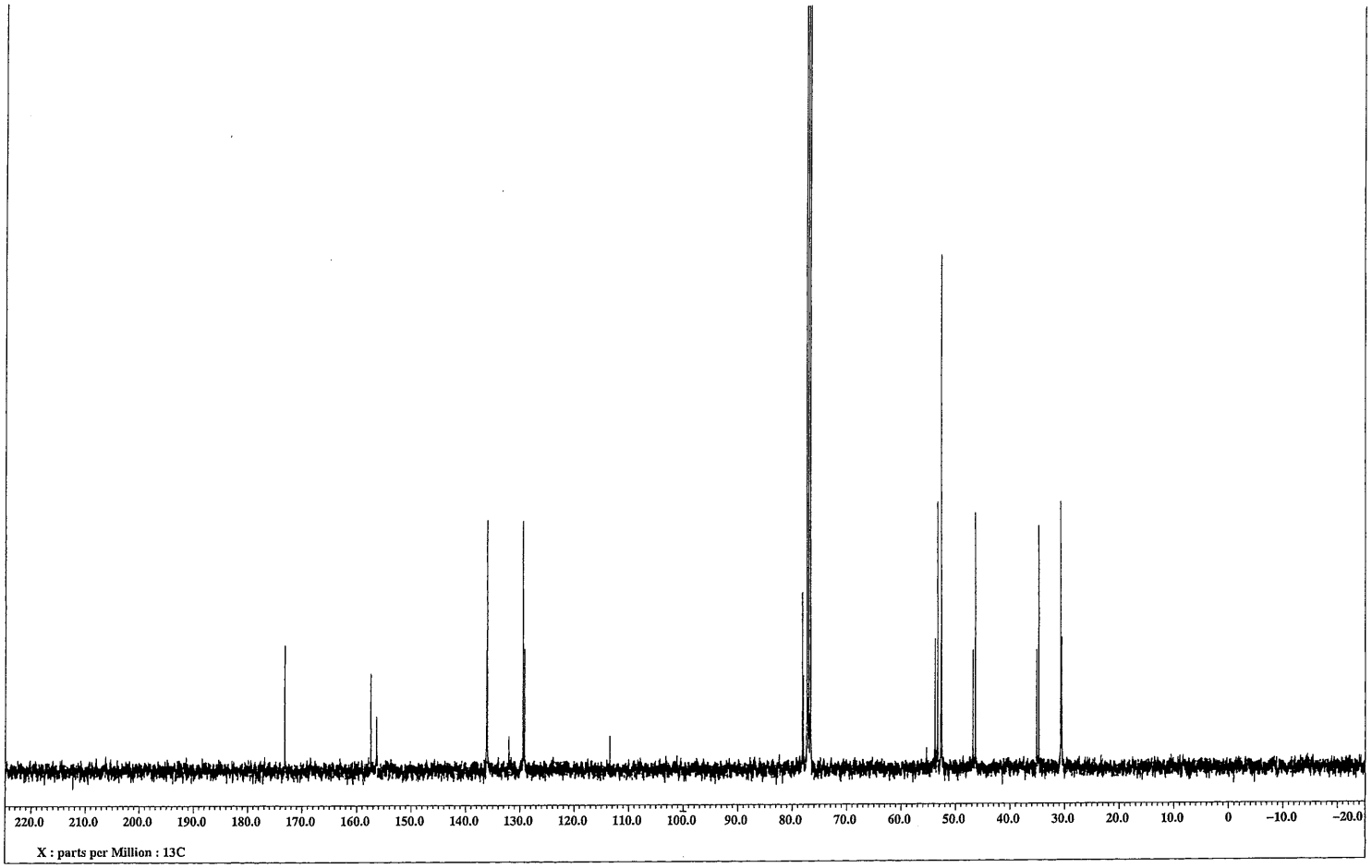
(**11**)

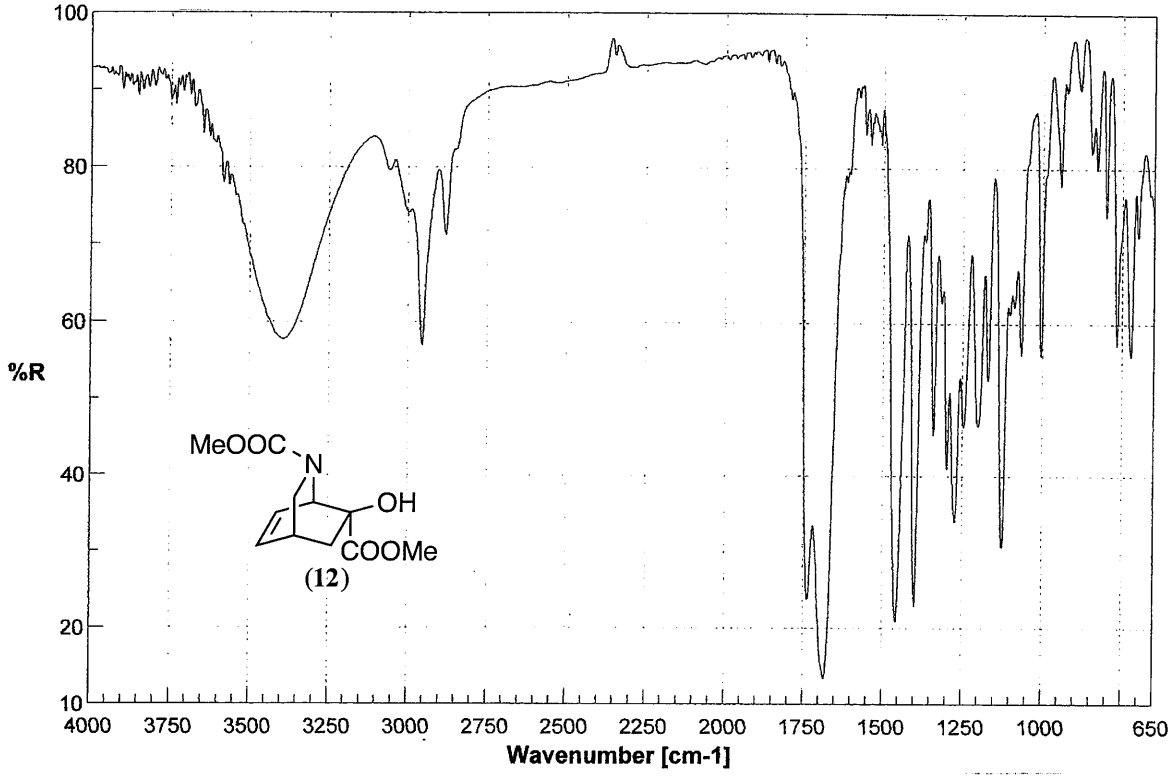

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
X : parts per Million : 13C

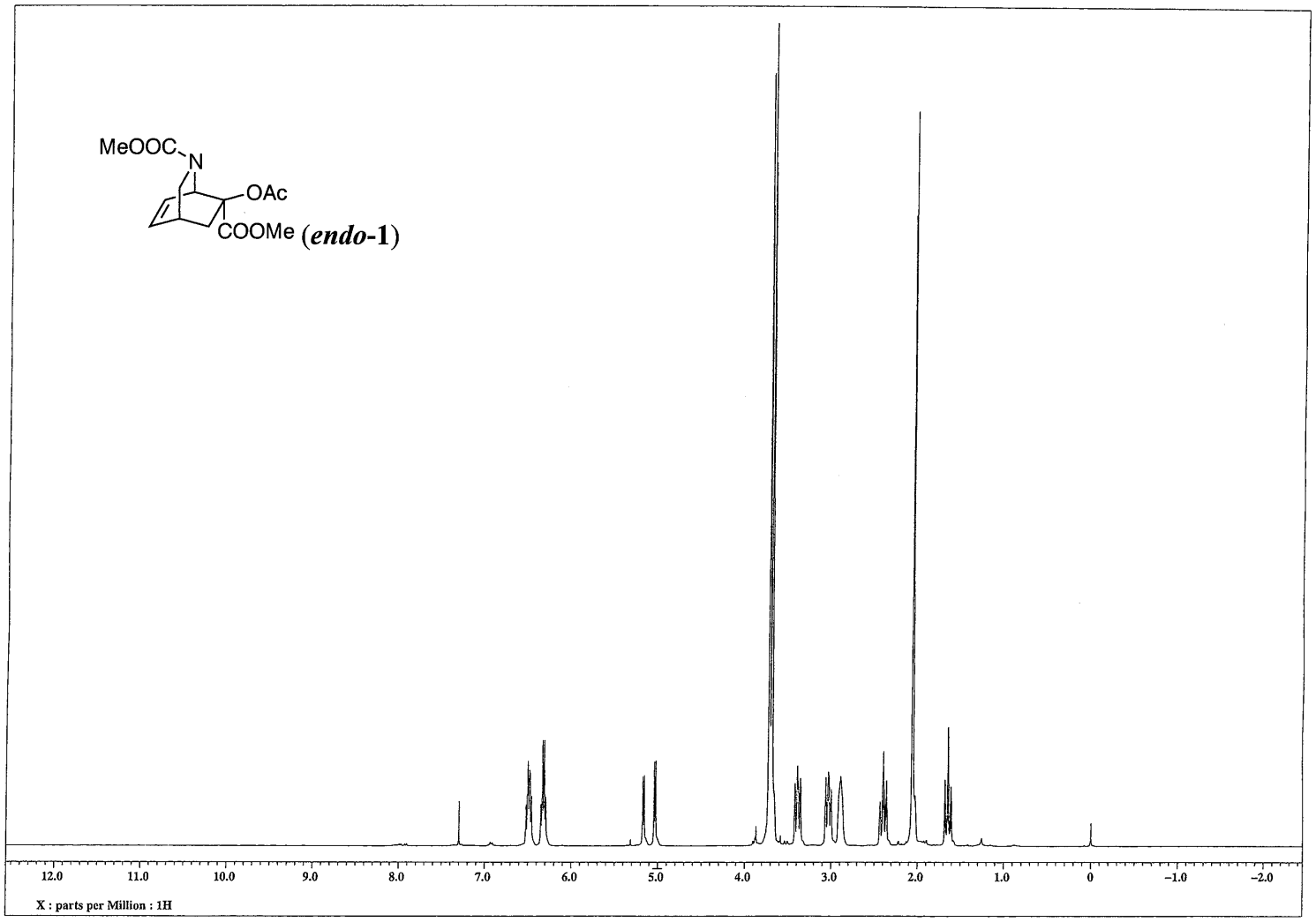

70
60
40
20
0
%R
PhOOC
N
H
O
O
MeO
O
OMe
(11)
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]

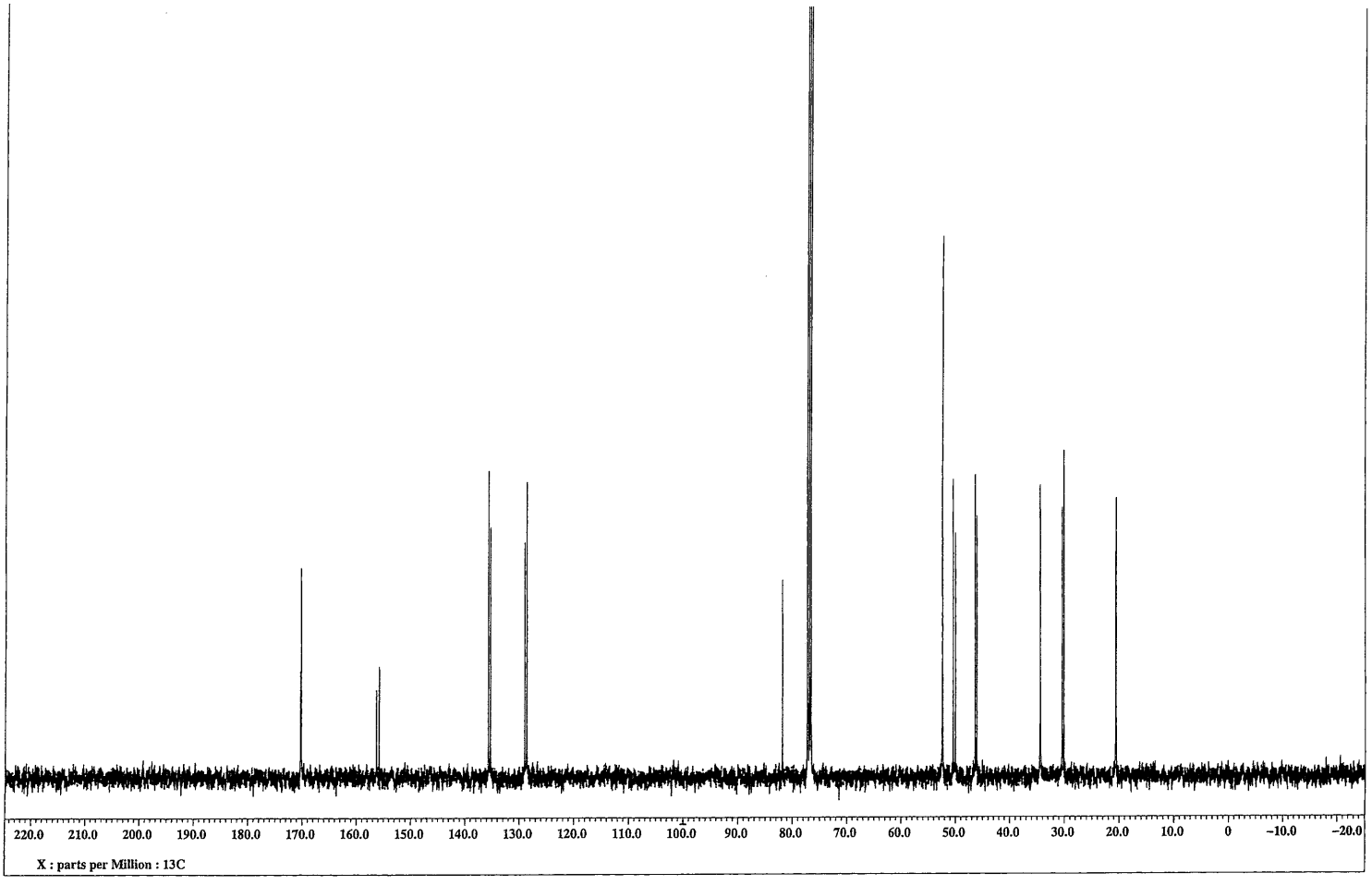

MeOOC
N
OH
COOMe
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
X : parts per Million : 1H

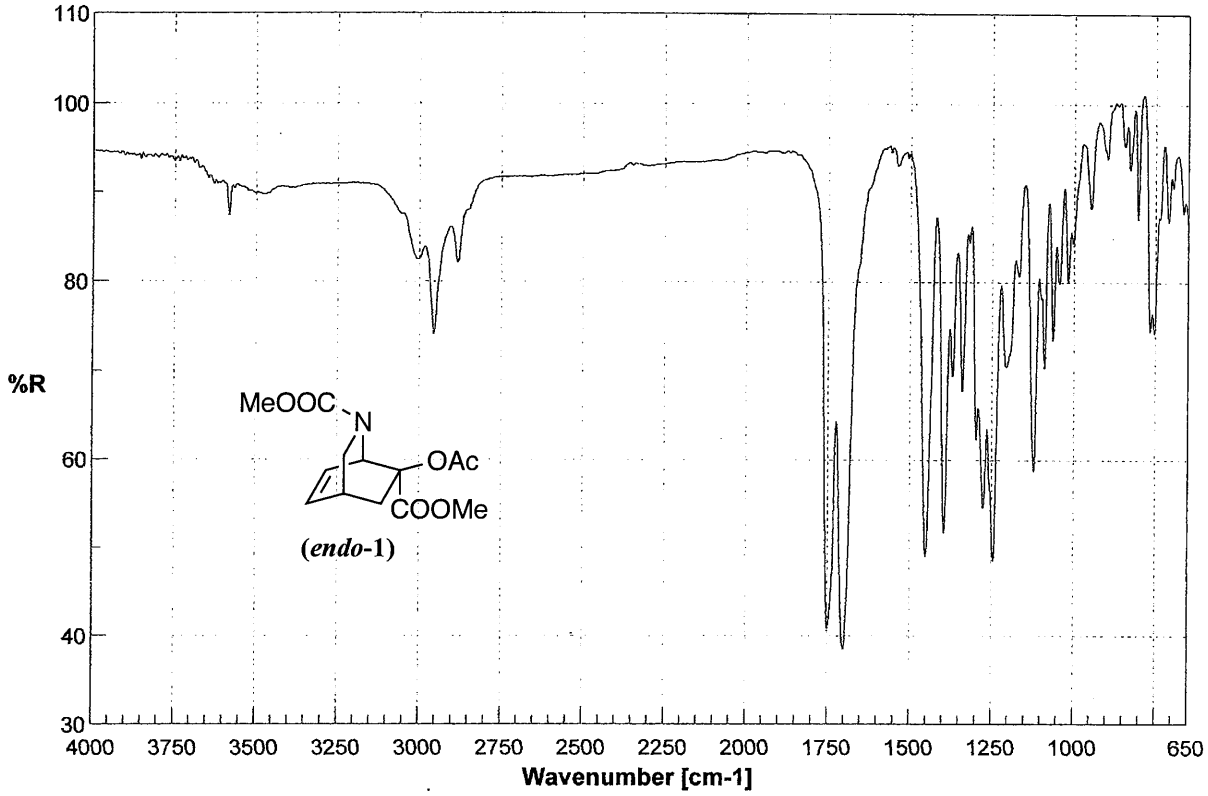
(**12**)

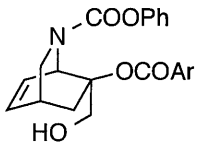

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
X : parts per Million : 13C


100
80
60
40
20
10
%R
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]
MeOOC
N
OH
COOMe
(12)


MeOOC
N
OAc
COOMe
(endo-1)
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
X : parts per Million : 1H

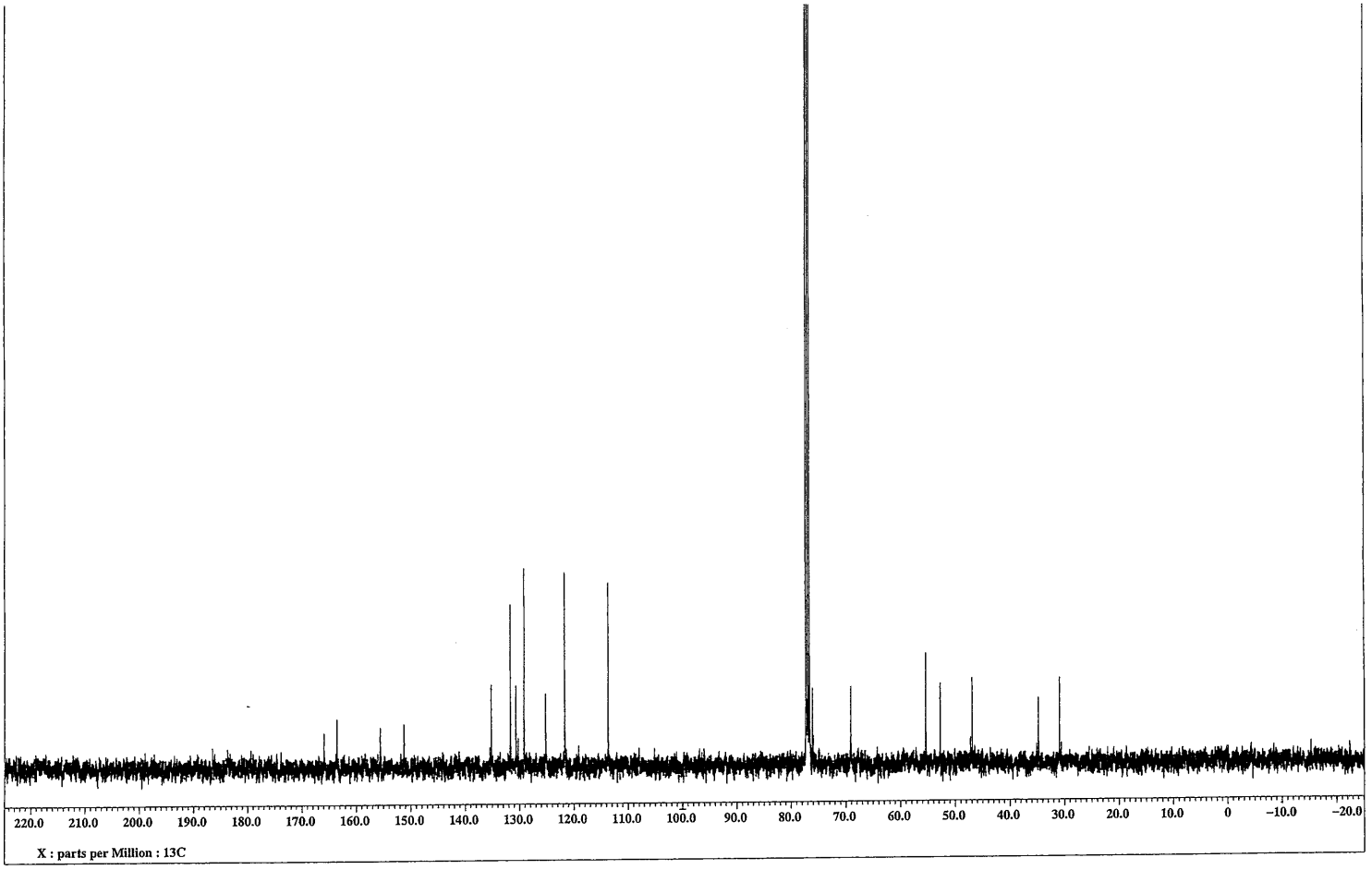

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
X : parts per Million : 13C

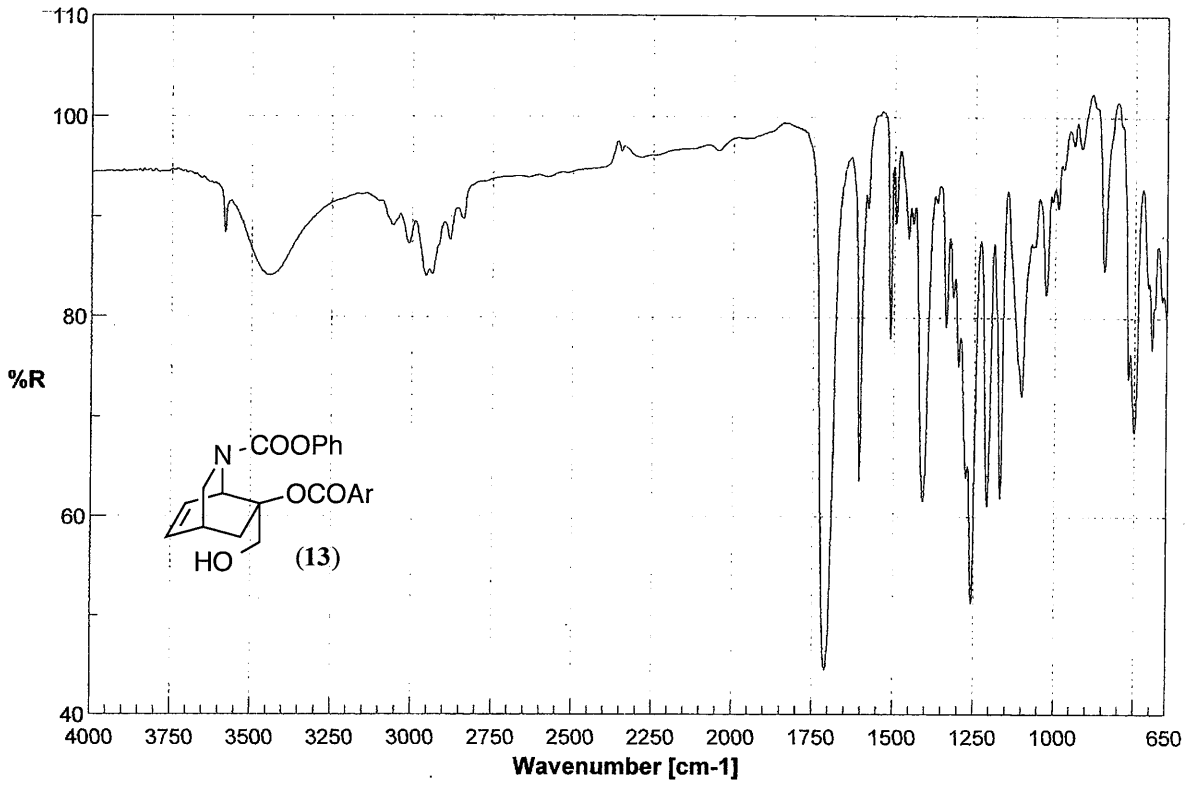

110
100
80
60
40
30
%R
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]
MeOOC
N
OAc
COOMe
(endo-1)

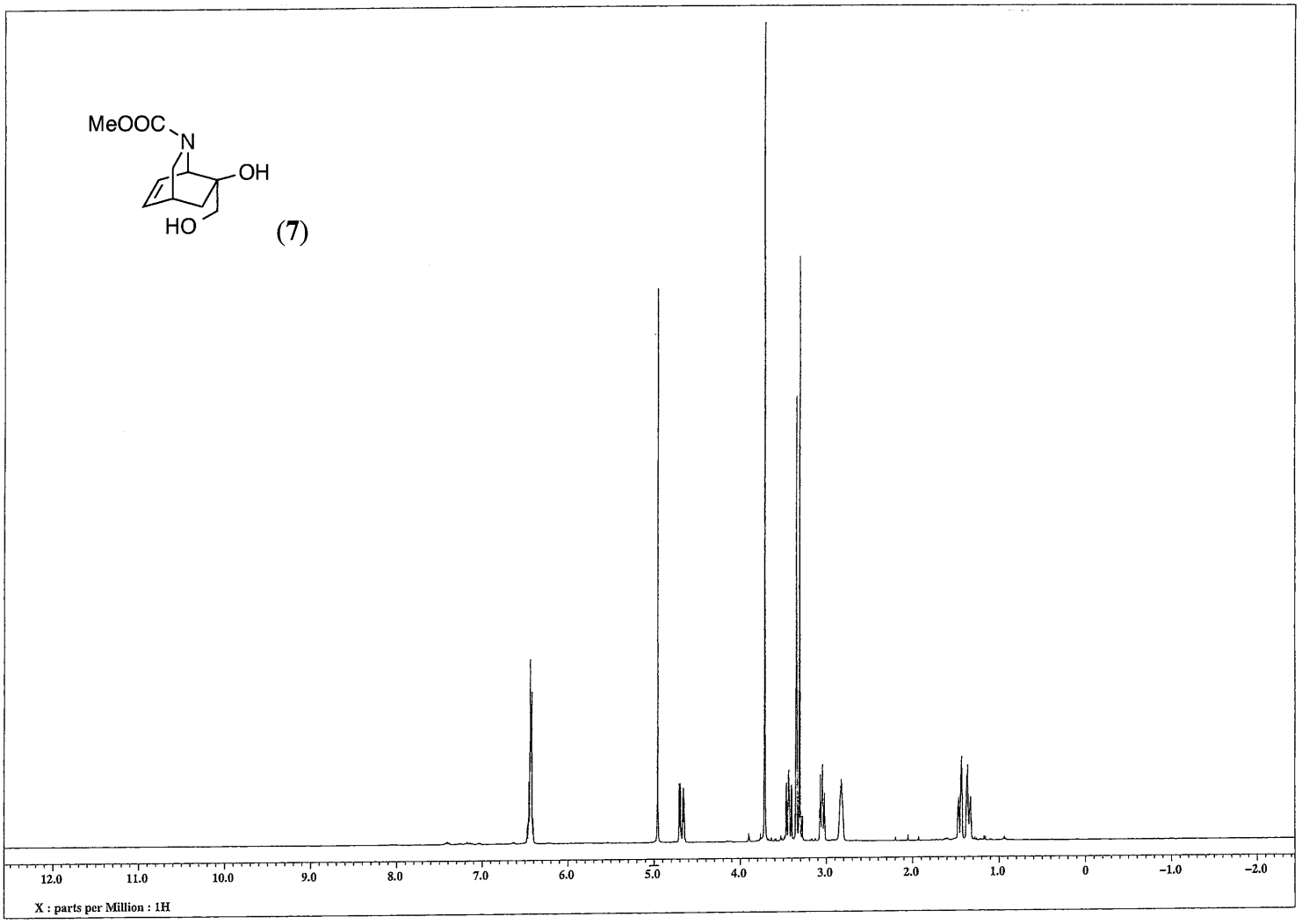

COOPh
N
OCOAr
HO

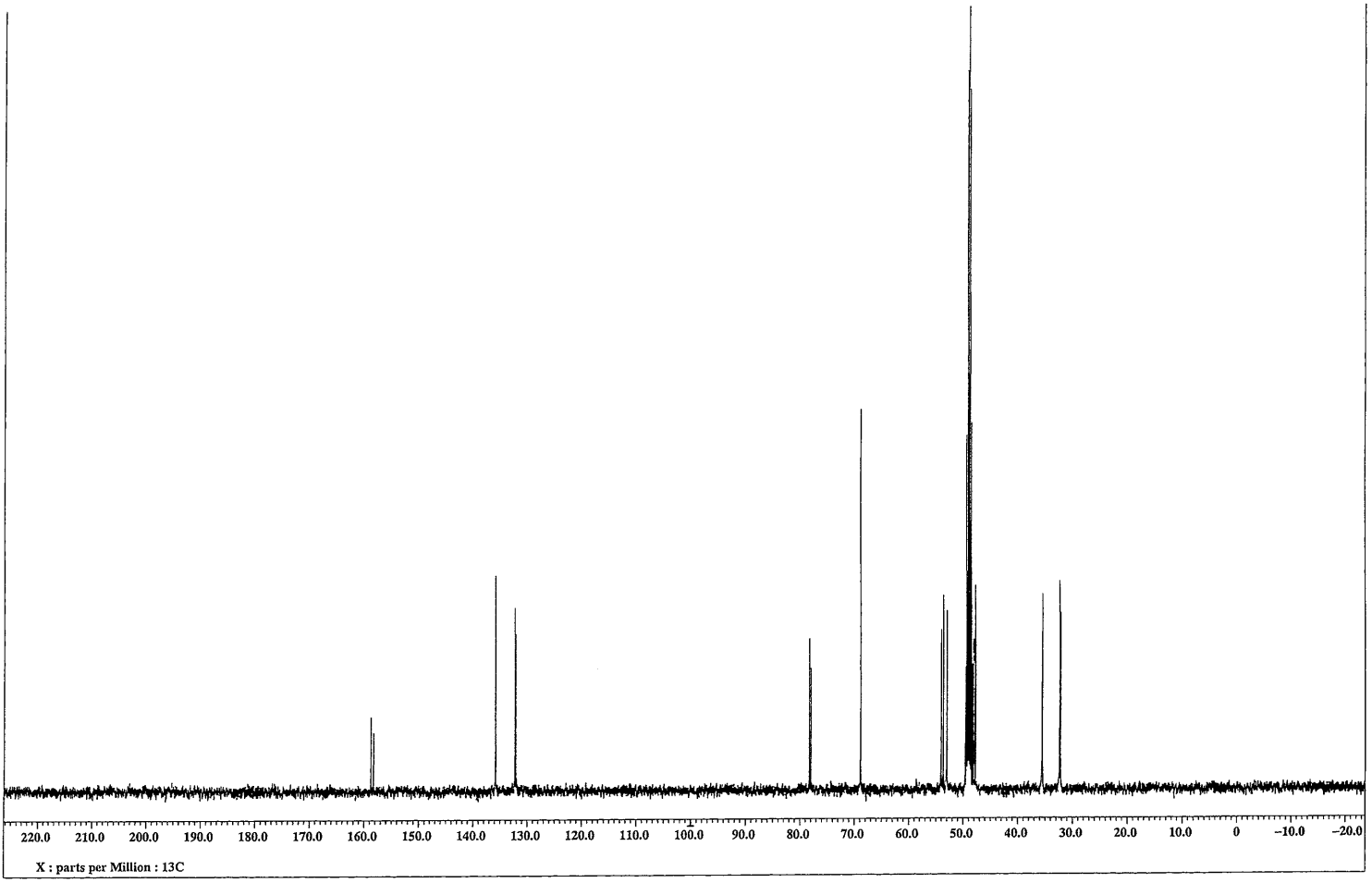
(**13**)

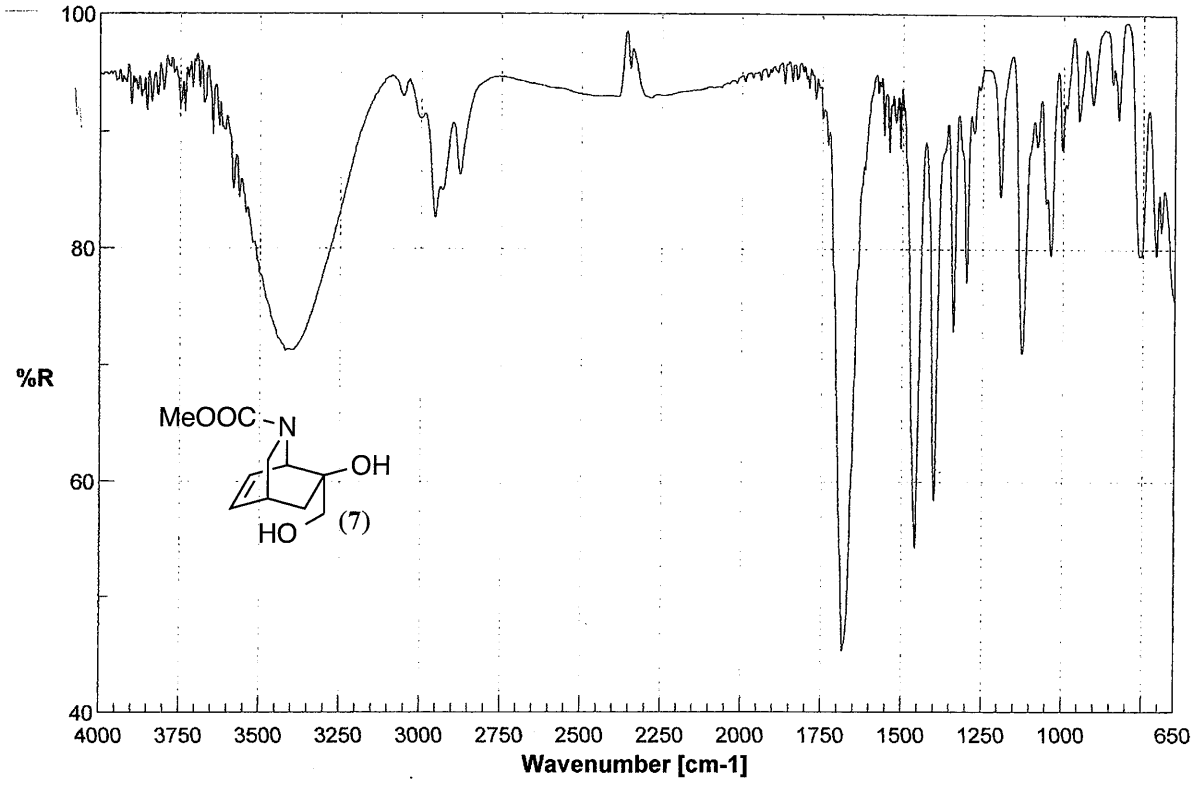
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
-1.0
-2.0
X : parts per Million : 1H

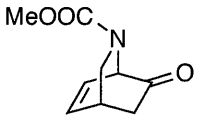

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : 13C


110
100
80
60
40
%R
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]
N
COOPh
OCOAr
HO
(13)

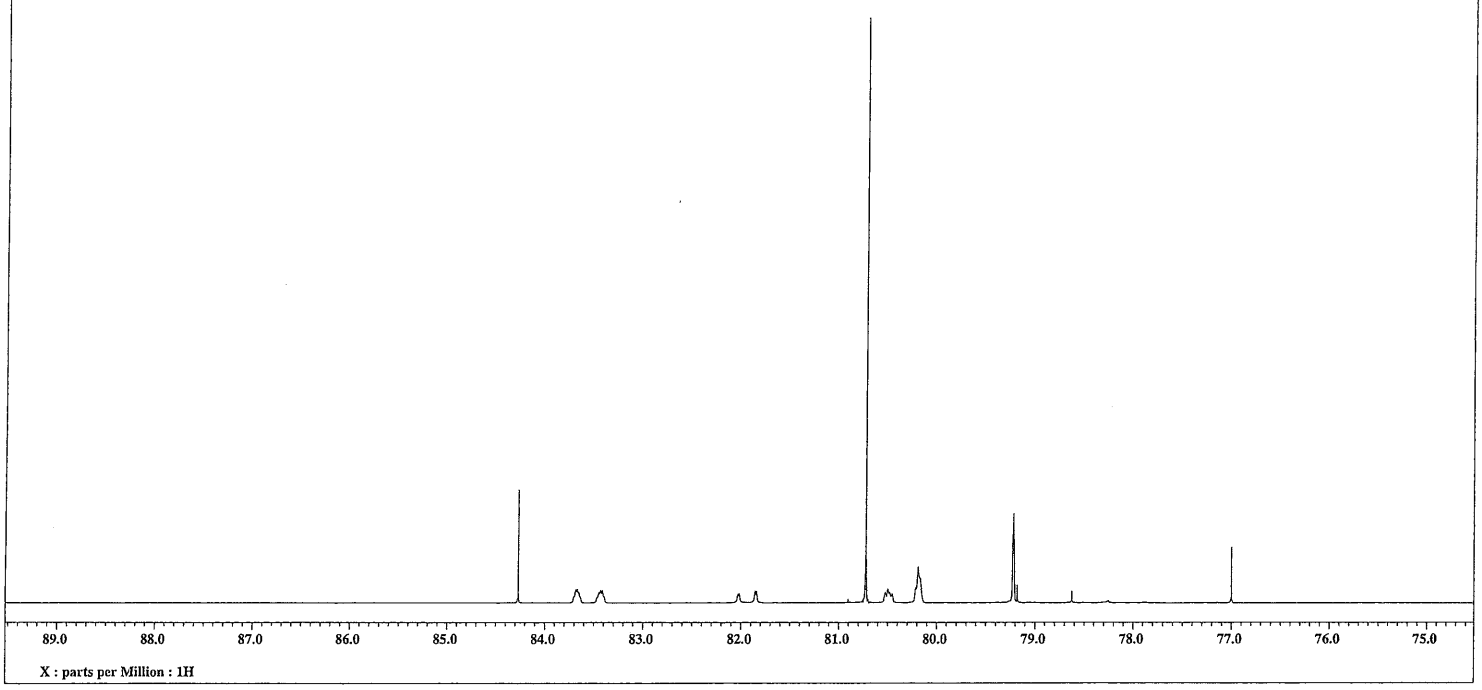

MeOOC
N
OH
HO
(7)
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
−1.0
−2.0
X : parts per Million : 1H

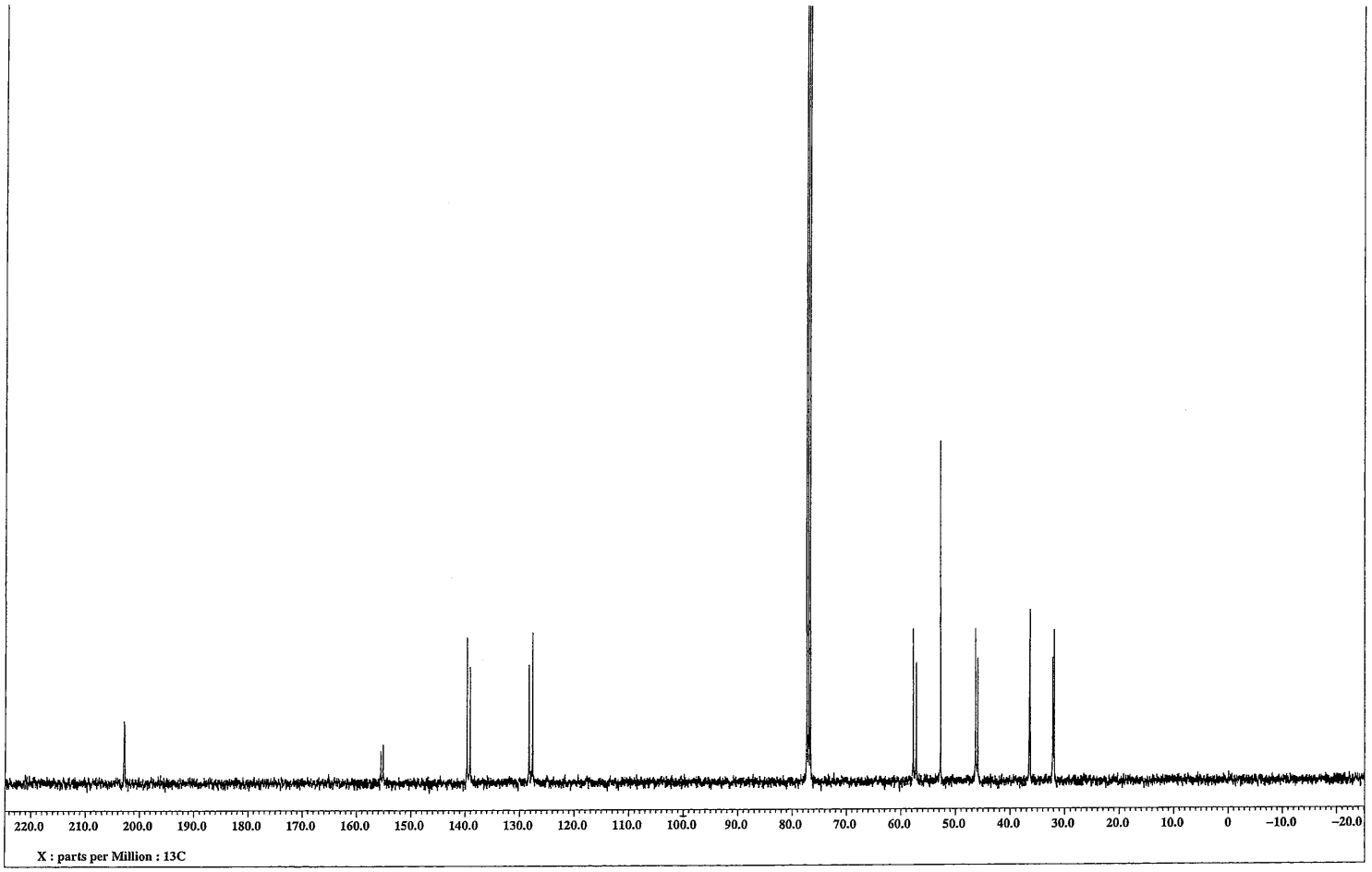

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
X : parts per Million : 13C

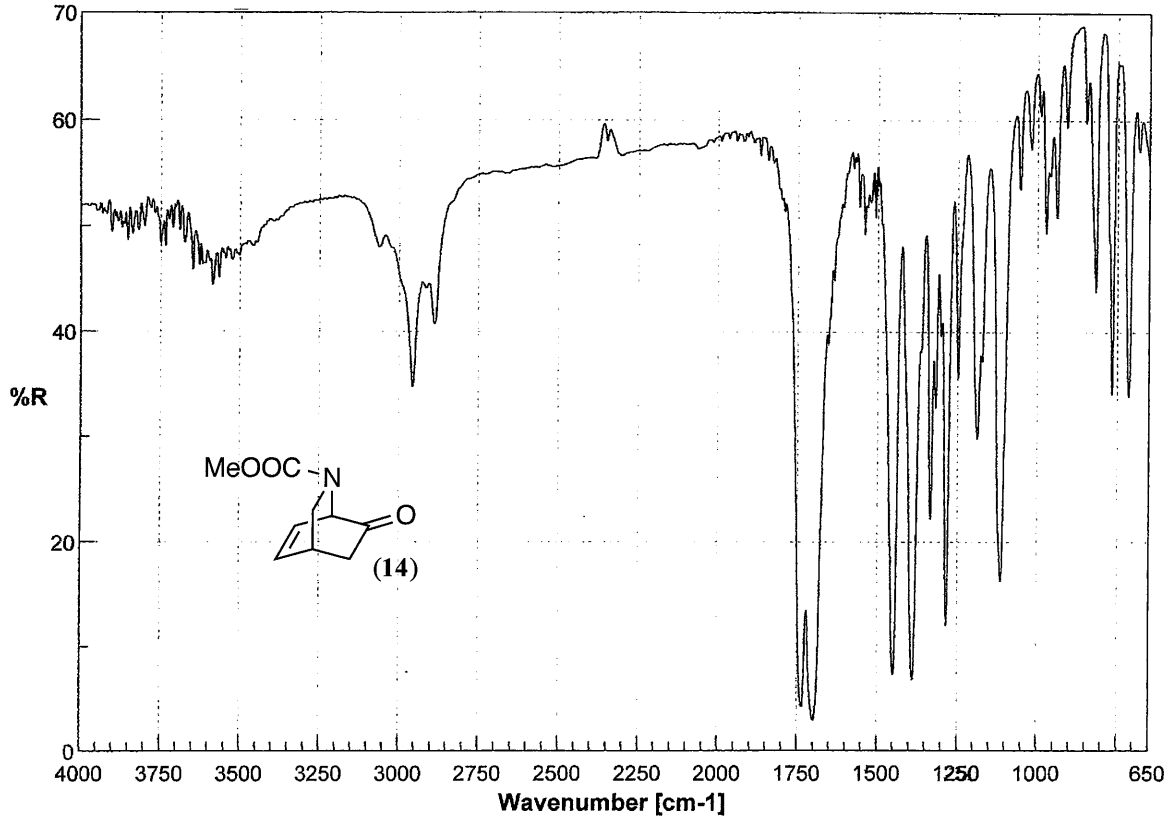

100
80
60
40
%R
MeOOC
N
OH
HO
(7)
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]

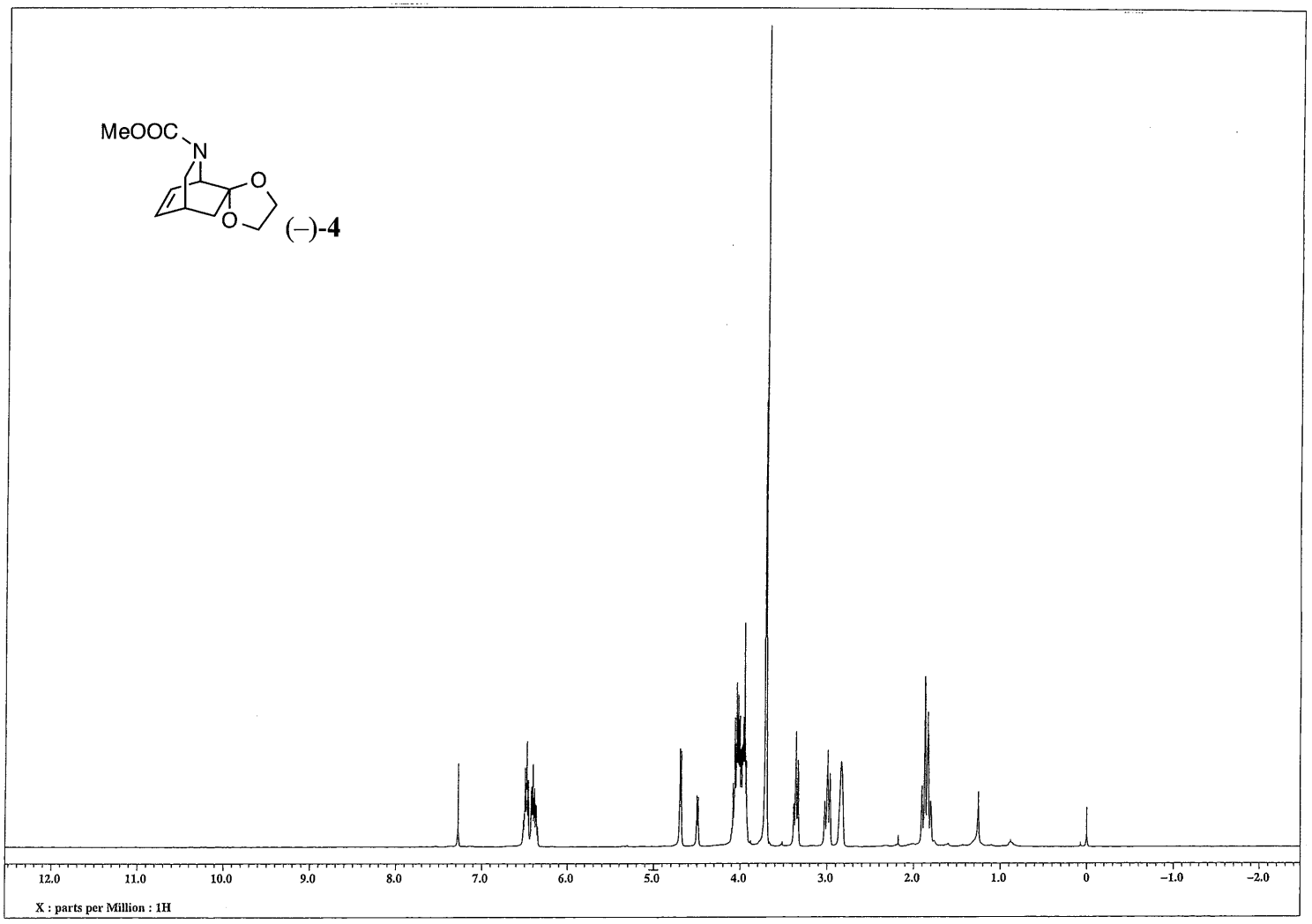

MeOOC
N
O

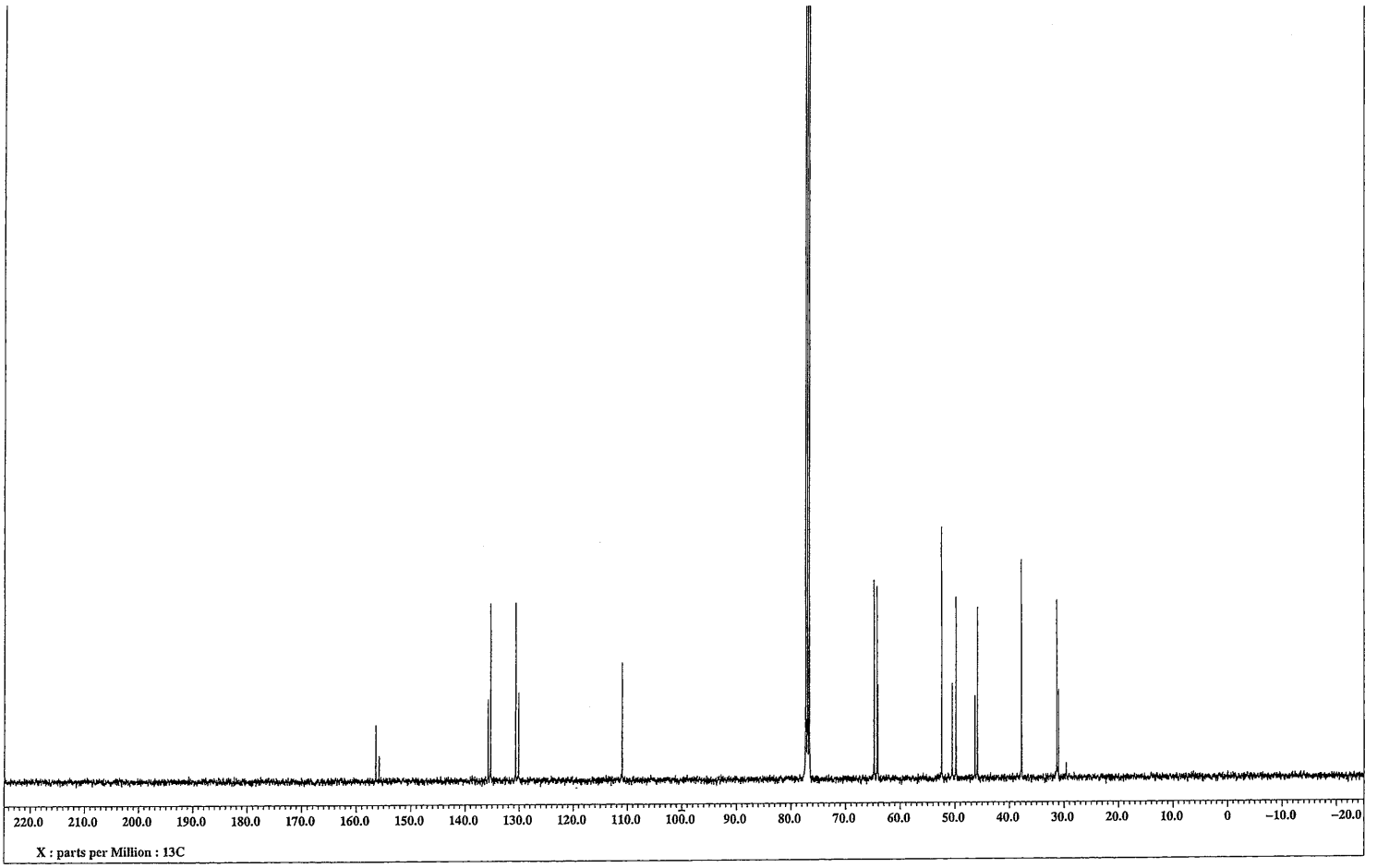
(14)

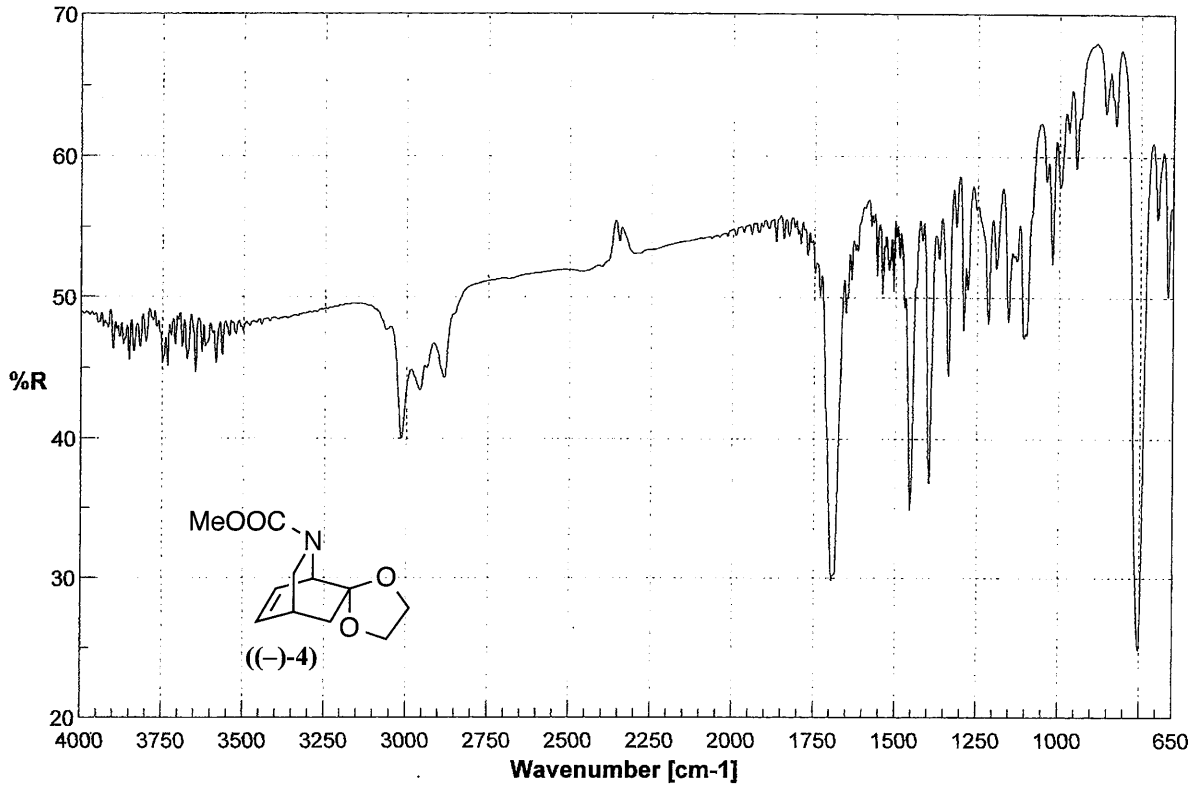

89.0
88.0
87.0
86.0
85.0
84.0
83.0
82.0
81.0
80.0
79.0
78.0
77.0
76.0
75.0
X : parts per Million : 1H

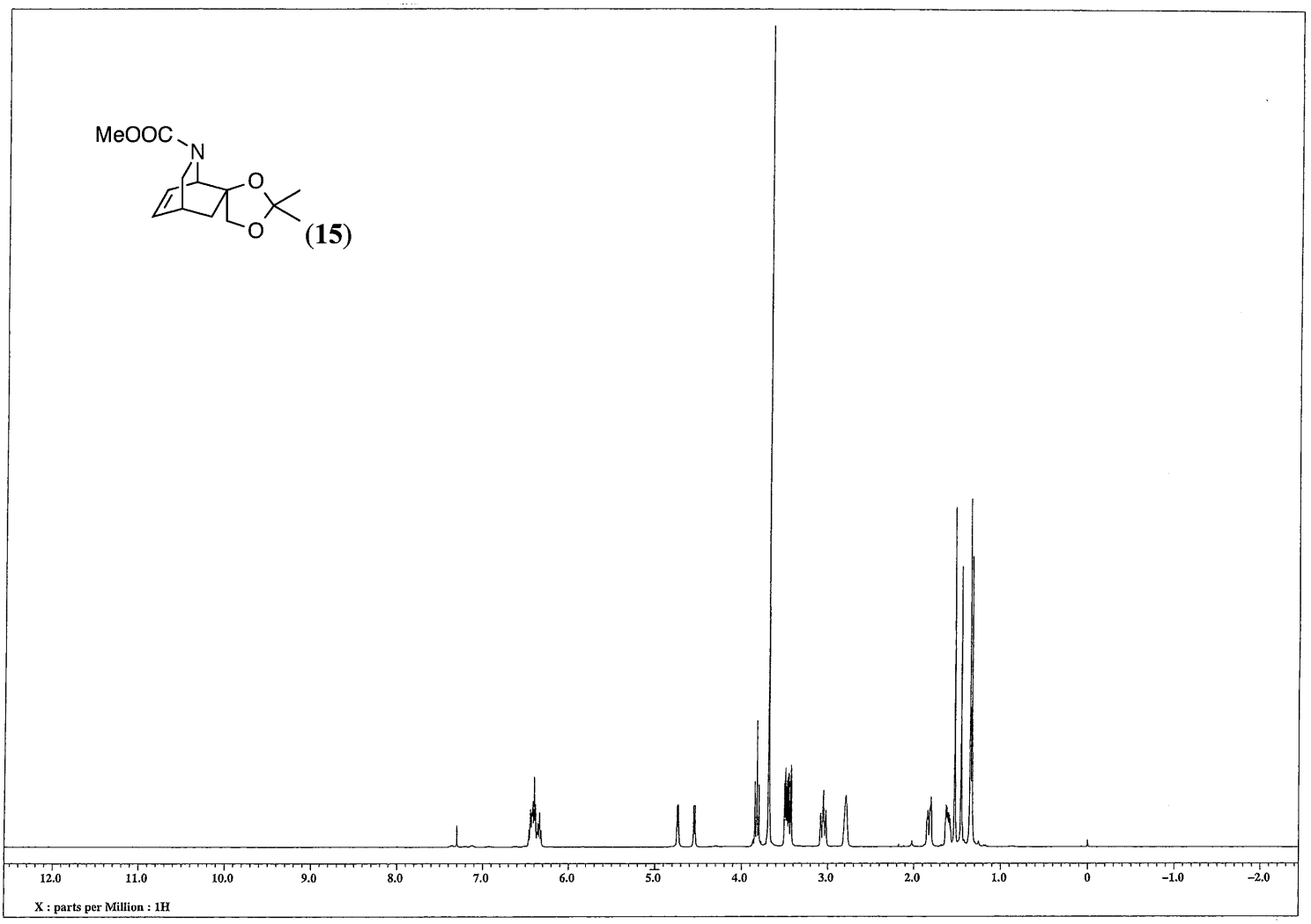

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
-10.0
-20.0
X : parts per Million : 13C

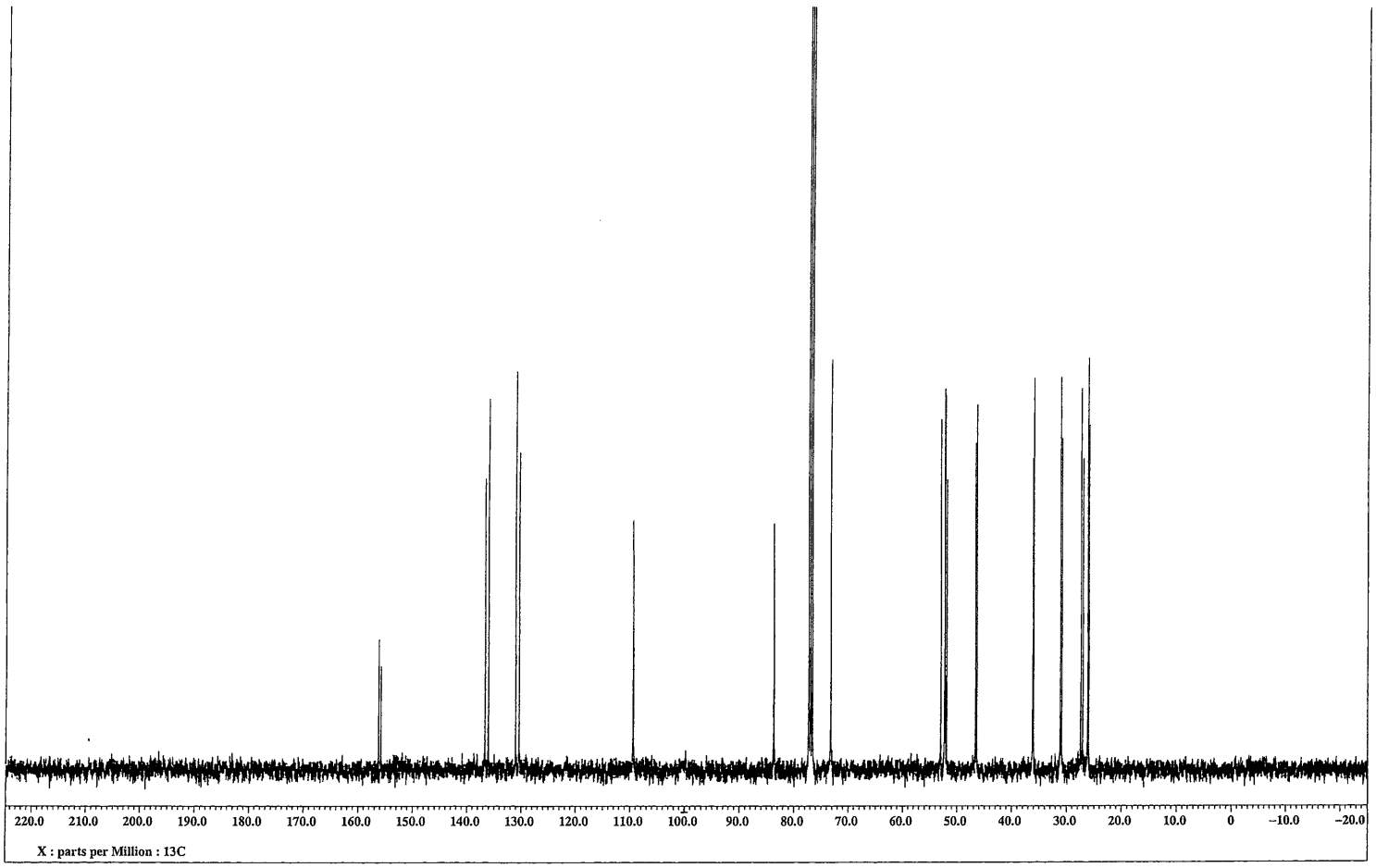

70
60
40
20
0
%R
MeOOC
N
O
(14)
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]

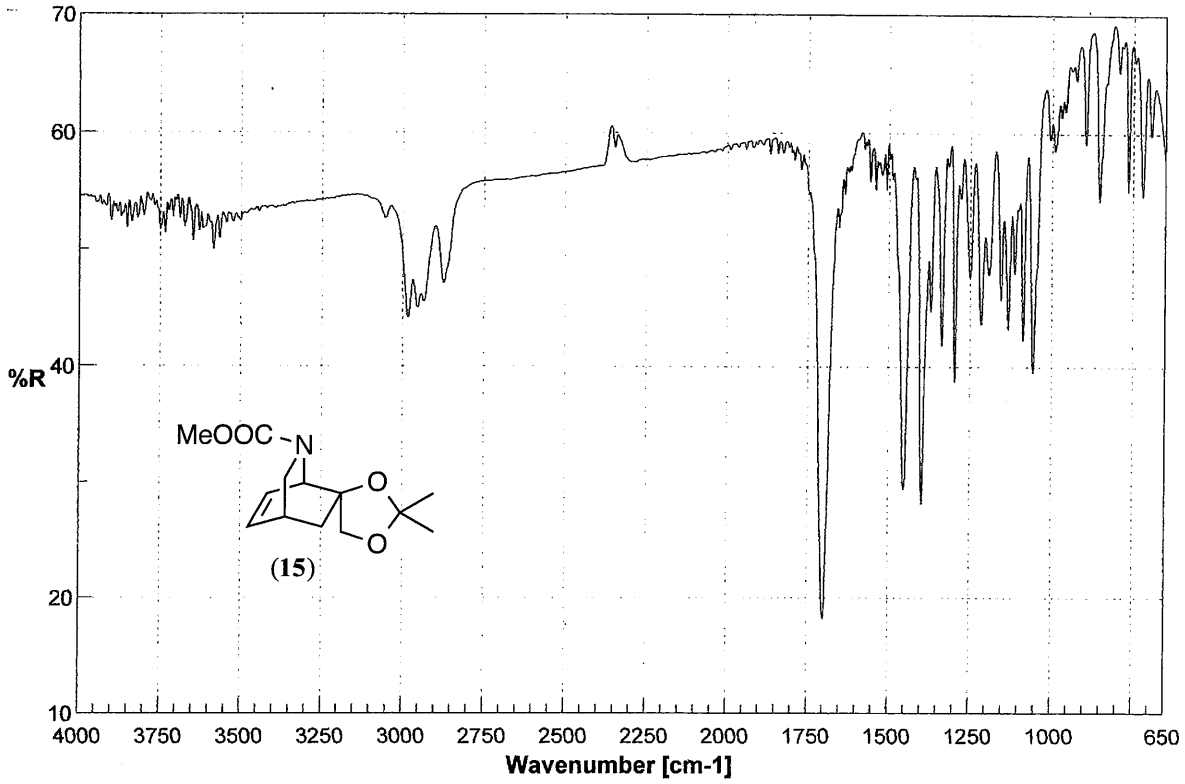

MeOOC
N
O
O
(–)-4
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
–1.0
–2.0
X : parts per Million : 1H


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
X : parts per Million : 13C

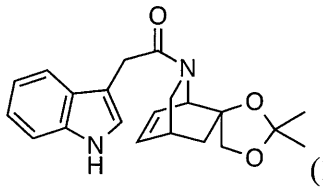

70
60
50
40
30
20
%R
MeOOC
N
O
O
((–)-4)
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]


MeOOC
N
O
O
(15)
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
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
X : parts per Million : 13C

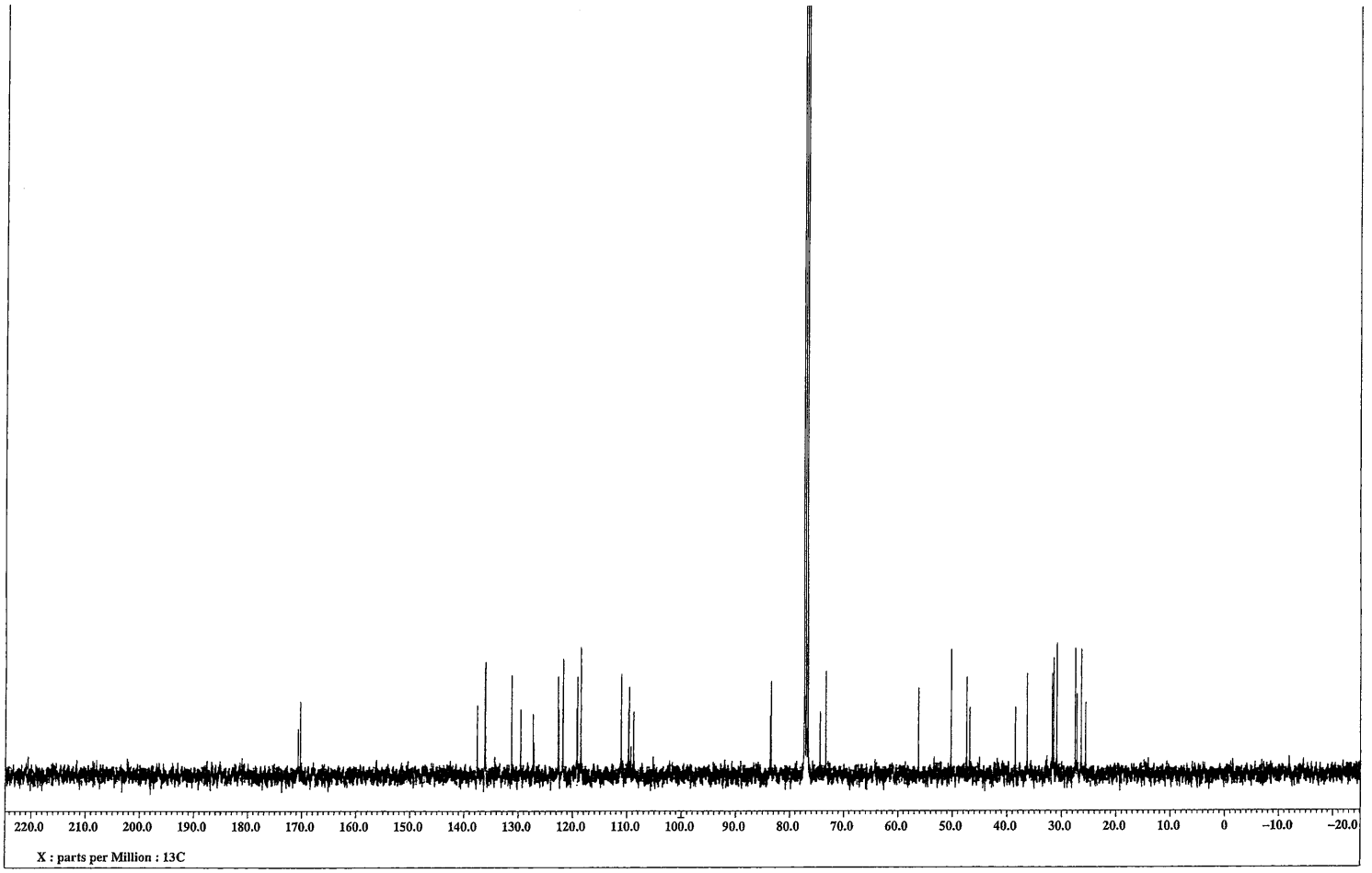

70
60
40
20
10
%R
MeOOC
N
O
O
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]

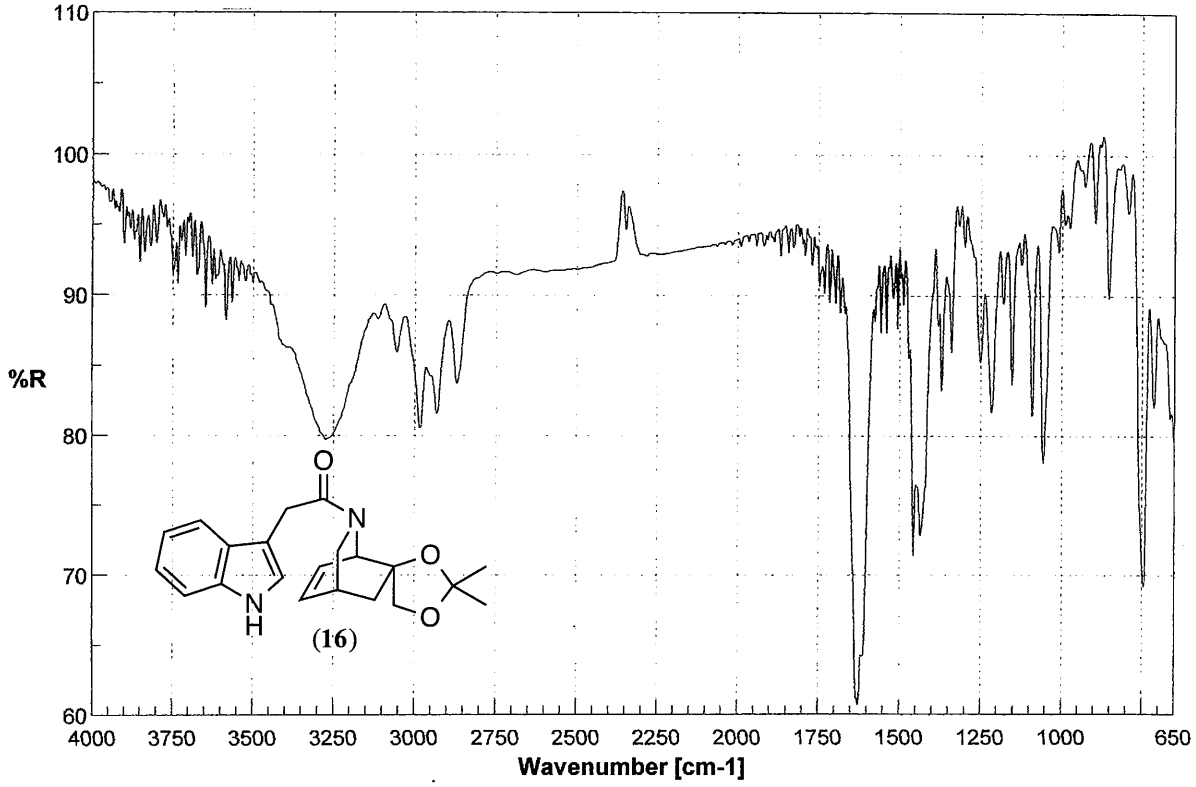
(15)



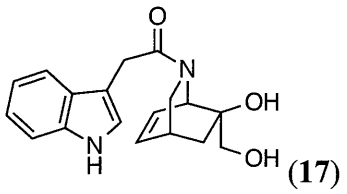
(16)

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
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
X : parts per Million : 13C

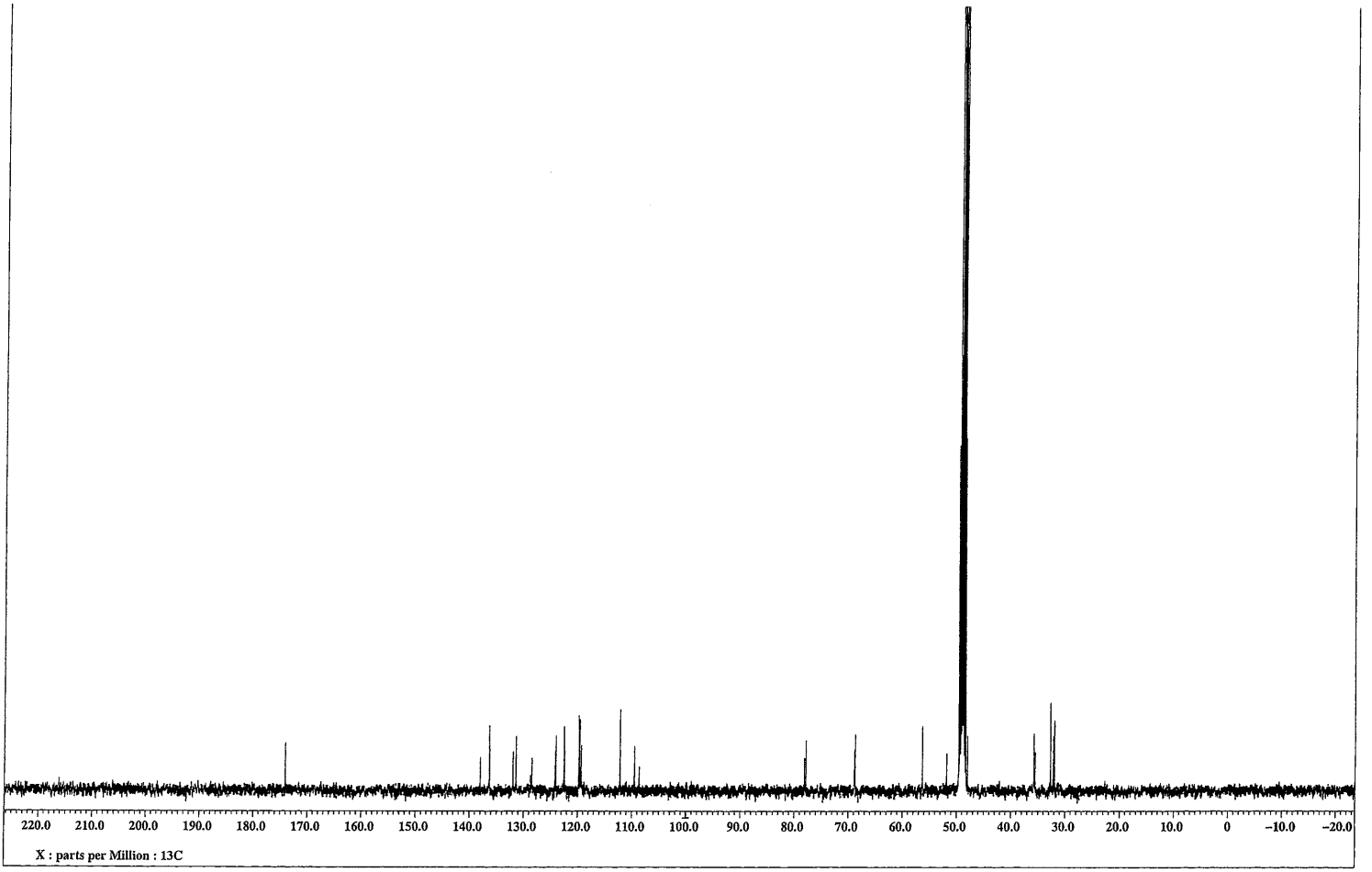

110
100
90
80
70
60
%R
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]
O
N
O
O
N
H

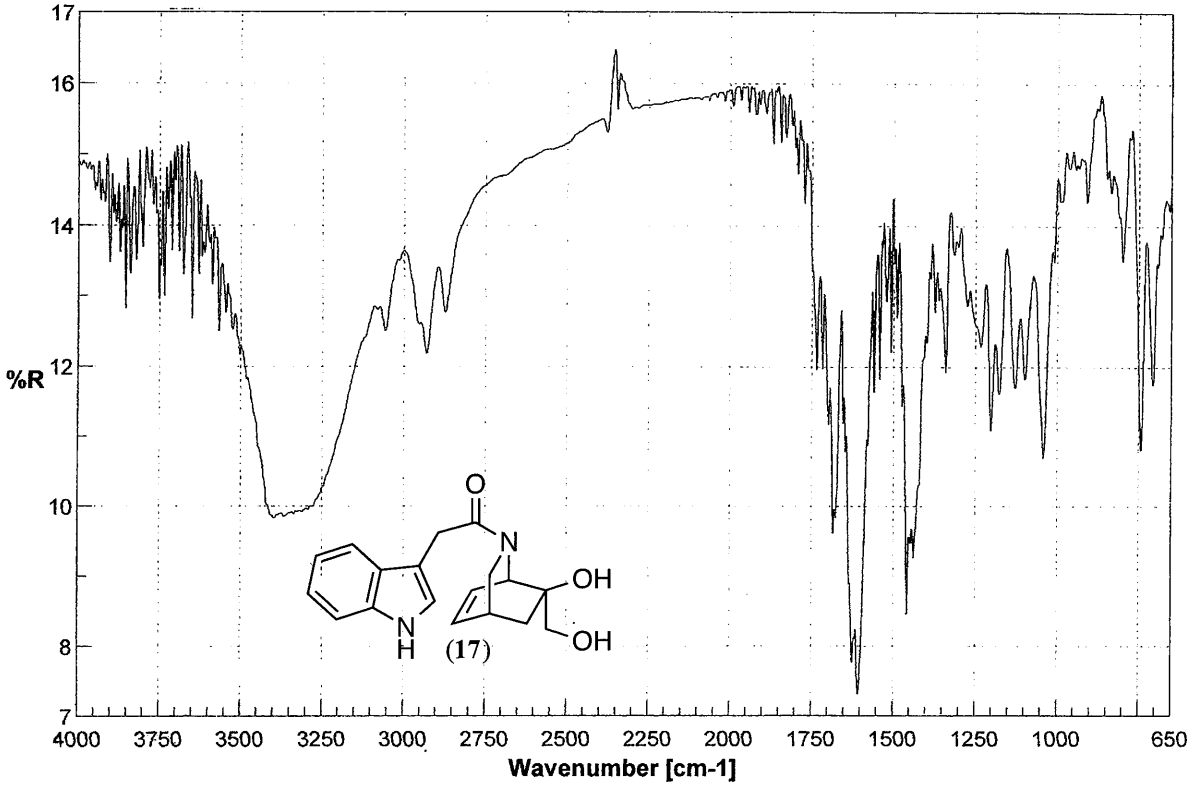
(16)

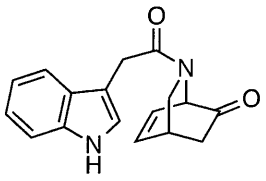

O
N
OH
OH
N
H

(17)

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
X : parts per Million : 1H

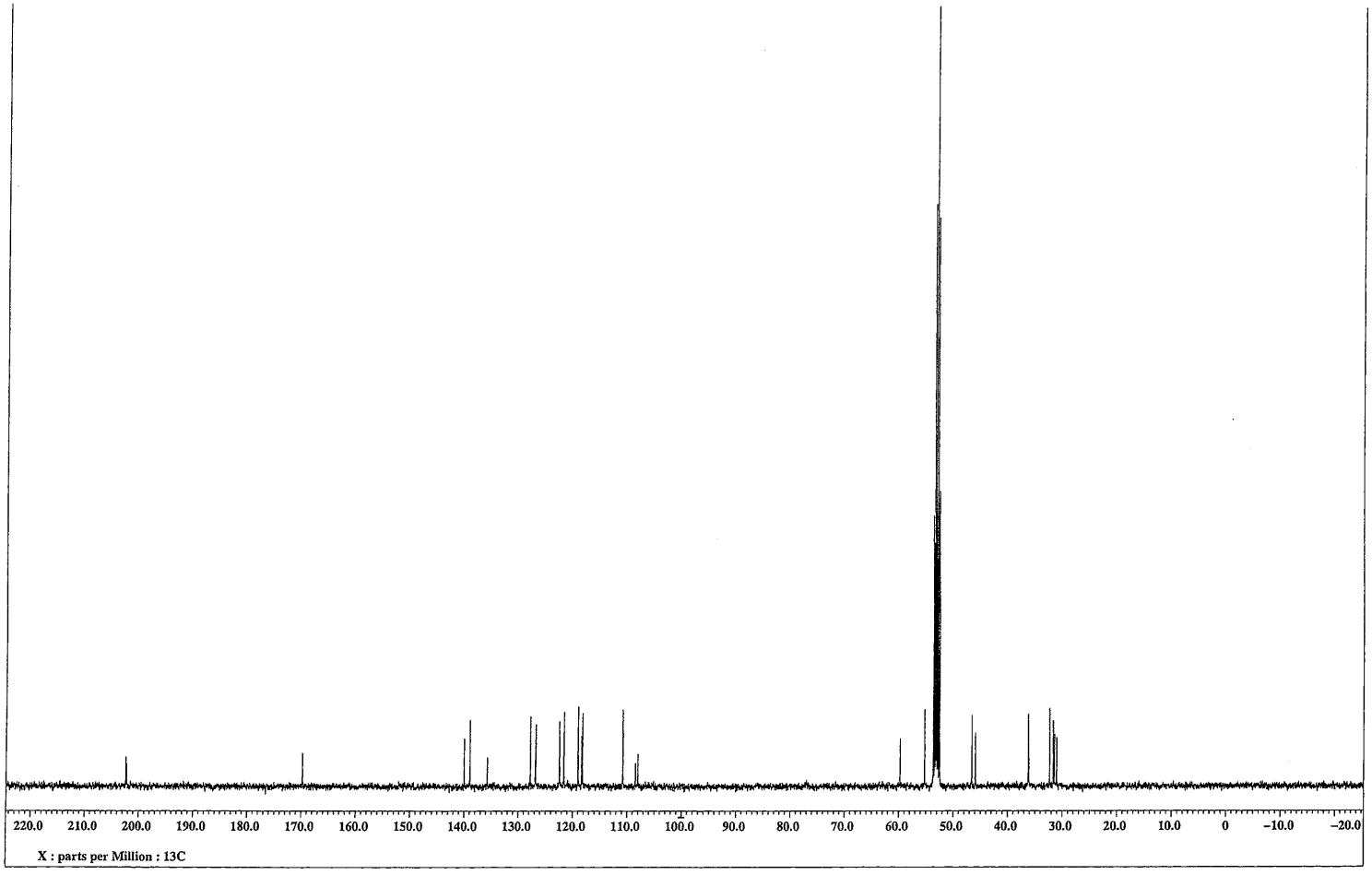

220.0
210.0
200.0
190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
0
−10.0
−20.0
X : parts per Million : 13C

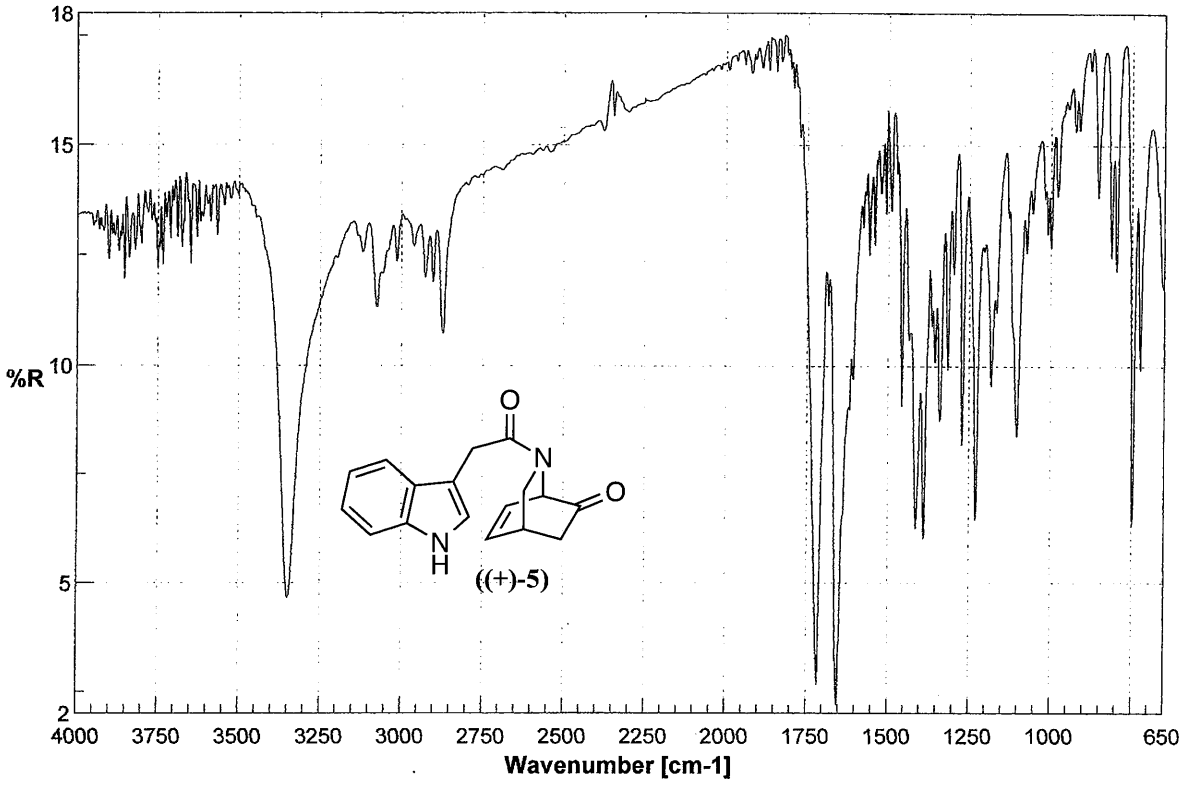

17
16
14
12
10
8
7
%R
4000
3750
3500
3250
3000
2750
2500
2250
2000
1750
1500
1250
1000
650
Wavenumber [cm-1]
O
N
OH
OH
N
H
(17)



(+)-**5**

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
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
X : parts per Million : 13C


18
15
%R 10
5
2
4000 3750 3500 3250 3000 2750 2500 2250 2000 1750 1500 1250 1000 650
Wavenumber [cm-1]
O
N
O
N
H
((+)-5)