Electronic Supplementary Material (ESI) for Chemical Communications


# Supporting Information for

# Enantioselective Direct Aminalization with Primary Carboxamides Catalyzed by Chiral Ammonium 1,1'-Binaphthyl-2,2'-disulfonates

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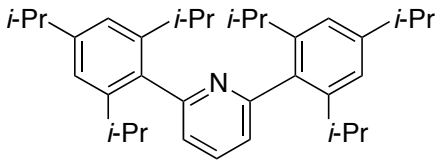
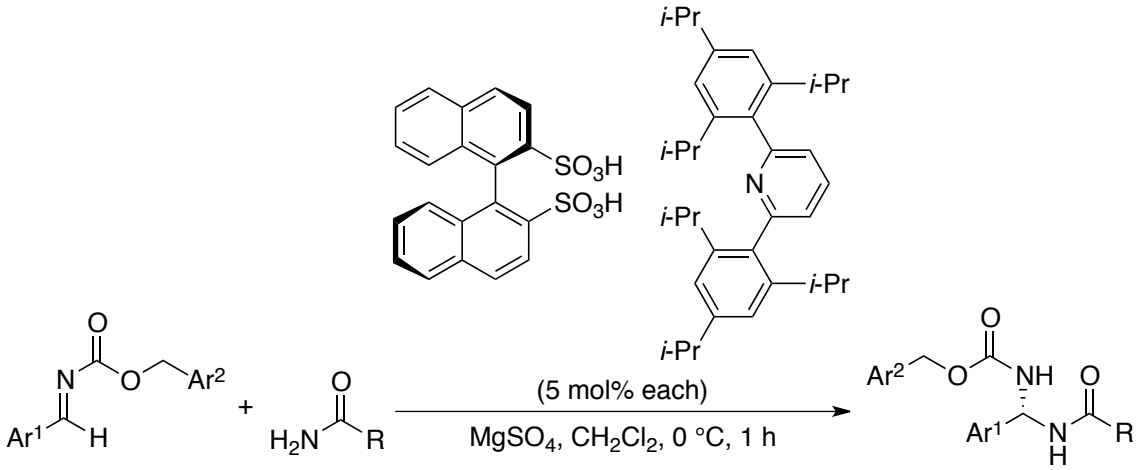
**1. General methods.** $^{1}$H NMR spectra were measured on a JEOL ECS-400 (400 MHz) spectrometer at ambient temperature. Data were recorded as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (s = singlet; d = doublet; t = triplet; q = quartet; m = multiplet; br = broad), coupling constant (Hz), integration, and assignment. $^{13}$C NMR spectra were measured on JEOL ECS-400 (100 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard (deuterochloroform at 77.1 ppm). $^{19}$F NMR spectra were measured on a JEOL ECS-400 (376 MHz) spectrometer. Chemical shifts were recorded in ppm from the solvent resonance employed as the internal standard ($CF_3C_6H_5$ at –63.24 ppm). High resolution mass spectral analyses (HRMS) was performed at Chemical Instrument Center, Nagoya University (JEOL JMS-700). Infrared (IR) spectra were recorded on a JASCO FT/IR 460 plus spectrometer. Optical rotations were measured on Rudolph Autopol IV digital polarimeter. 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, CHIRALPAK; AD-H, AS-H, OD-3, OD-H, OZ-H, and IA. The products were purified by column chromatography on silica gel (E. Merck Art. 9385; Kanto Chemical Co., Inc. 37560). For thin-layer chromatography (TLC) analysis throughout this work, Merck TLC plates (silica gel 60G $F_{254}$ 0.25 mm) were used. Visualization was accomplished by UV light (254 nm), anisaldehyde, $KMnO_4$, and phosphomolybdic acid. In experiments that required dry solvents such as dichloromethane and 1,2-dichloroethane were distilled in prior to use.

**2. Analytucal data of amines (2g).**



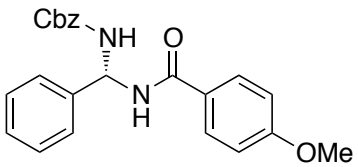

**2,6-Bis(2,4,6-triisopropylphenyl)pyridine (2g):**[1] $^{1}$H NMR (300 MHz, $CDCl_3$) δ 1.09 (d, $J$ = 6.9 Hz, 12H), 1.11 (d, $J$ = 6.9 Hz, 12H), 1.25 (d, $J$ = 6.9 Hz, 12H), 2.58 (septet, $J$ = 6.9 Hz, 4H), 2.90 (septet, $J$ = 6.9 Hz, 2H), 7.02 (s, 2H), 7.26 (s, 4H), 7.75 (t, $J$ = 7.2 Hz, 1H). $^{13}$C NMR (75 MHz, $CDCl_3$) δ 23.7 (4C), 24.2 (4C), 24.7 (4C), 30.5 (4C), 34.5 (2C), 120.5 (4C), 122.9 (2C), 135.3 (2C), 136.9, 146.1 (4C), 148.6 (2C), 160.0 (2C). M.p. >300 °C (incapable measurement). IR(KBr) 2959, 2927, 2866, 1578, 1458 $cm^{-1}$. HRMS(ESI+) calcd for $C_{35}H_{50}N$ $[M+H]^+$ 484.3938, found 484.3938.

**3. General procedure for the catalytic enantioselective aminal synthesis.**



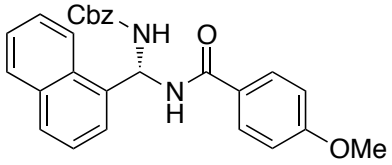

A well-dried pyrex Schlenk tube was charged with (*R*)-BINSA (**1**)[2] (8.3 mg, 0.02 mmol) and 2,6-bis-(2,4,6-triisopropylphenyl)pyridine (**2g**) (9.7 mg, 0.02 mmol) under a nitrogen atmosphere. 2 mL of $CH_3CN$ was added, and the solution was stirred at room temperature for 30 min. The volatiles were removed *in vacuo* at room temperature for 1 h, and then $MgSO_4$ (80 mg, 0.66 mmol), 1.5 mL of $CH_2Cl_2$, and *N*-nucleophile (0.40 mmol) were added. The mixture was cooled to 0 °C and stirred for 30 min. Aldimine (**3**) (0.60 mmol) in $CH_2Cl_2$ (0.5 mL) was added via a cannula. The resultant mixture was then stirred at 0 °C for 1 h. 1 mL of saturated $NaHCO_3$ aqueous solution was poured into the reaction mixture, and the product was extracted with AcOEt (15 mL × 2). The combined extracts were washed with brine (10 mL) and dried over $MgSO_4$. **Method A:** The organic phase was concentrated under reduced pressure and the crude product was purified by silica gel column chromatography (eluent: $CHCl_3$/AcOEt = 100/1 to 5/1), to give the desired product with the original enantioselectivity. **Method B:** Powedered crude was washed with water and ethyl acetate. Recrystallization from chloroform–hexane gave the desired product with the enhanced enantioselectivity. The enantiomeric purity was determined by chiral HPLC analysis.

**4. Products (Tables 1 and 2, and eqns. 1–3).**

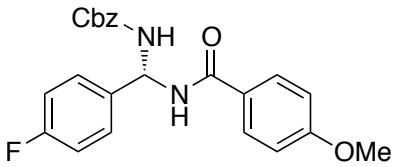



**(*S*)-Benzyl ((4-methoxybenzamido)(phenyl)methyl)carbamate (5a):** $^1$H NMR (400 MHz, $CDCl_3$) δ 3.84 (s, 3H), 5.10 (s, 2H), 6.27 (br, 1H), 6.55 (br, 1H), 6.89 (d, $J$ = 8.1 Hz, 2H), 7.25-7.56 (m, 11H), 7.76 (br, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.4, 60.8, 67.0, 113.8 (2C),

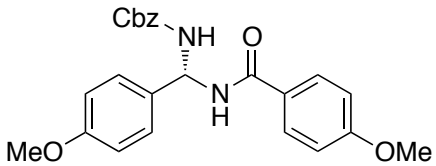
125.8 (2C), 126.0, 128.0 (2C), 128.1, 128.2, 128.4 (2C), 128.6 (2C), 129.0 (2C), 136.1, 139.0, 155.7, 162.6, 166.5. M.p. 190–192 °C. IR (KBr) 3288, 1699, 1634, 1496, 1354, 1256, 1187, 1040 $cm^{-1}$. $[\alpha]_D^{26}$ = –5.2 (*c* 1.0, $CHCl_3$, 78% ee (*S*)). HRMS (FAB+) calcd for $C_{23}H_{23}N_2O_4$ $[M+H]^+$ 391.1658, found 391.1662. HPLC analysis; OD-H, *n*-hexane/*i*-PrOH = 4/1, 0.6 mL/min, $t_R$ = 30.0 min (major, *S*), 41.1 min (minor, *R*).




**(*S*)-Benzyl ((4-methoxybenzamido)(naphthalen-1-yl)methyl)carbamate (5b):** $^1$H NMR (400 MHz, $CDCl_3$) δ 3.78 (s, 3H), 5.08 (s, 2H), 6.09 (br, 1H), 6.76-6.84 (m, 2H), 7.10-7.35 (m, 6H), 7.36-7.44 (m, 2H), 7.45-7.53 (m, 2H), 7.66 (d, *J* = 7.2 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 2H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.86 (m, 1H), 8.02 (m, 1H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.3, 58.7, 67.0, 113.7 (2C), 123.0, 123.4, 125.0, 125.6, 125.9, 126.8, 128.0 (2C), 128.1, 128.4 (2C), 128.8, 129.0 (2C), 129.3, 130.2, 133.9, 134.1, 136.0, 155.3, 162.4, 166.1. M.p. 224–226 °C. IR (KBr) 3305, 1697, 1636, 1606, 1546, 1493, 1251, 1175, 1027 $cm^{-1}$. $[\alpha]_D^{27}$ = 5.3 (*c* 1.0, $CHCl_3$, 81% ee (*S*)). HRMS (FAB+) calcd for $C_{27}H_{25}N_2O_4$ $[M+H]^+$ 441.1814, found 441.1803. HPLC analysis; AS-H, *n*-hexane/*i*-PrOH = 4/1, 1.0 mL/min, $t_R$ = 67.3 min (major, *S*), 91.0 min. (minor, *R*).

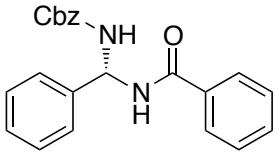



**(*S*)-Benzyl ((4-fluorophenyl)(4-methoxybenzamido)methyl)carbamate (5c):** $^1$H NMR (400 MHz, $CDCl_3$) δ 3.85 (s, 3H), 5.10 (s, 2H), 6.25 (br, 1H), 6.50 (br, 1H), 6.90 (d, *J* = 8.1 Hz, 2H), 7.02 (d, *J* = 8.7 Hz, 2H), 7.26-7.52 (m, 8H), 7.75 (br, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.5, 60.4, 67.2, 113.9 (2C), 115.5 (d, $J_{C-F}$ = 21.9 Hz, 2C), 125.8, 127.8 (d, $J_{C-F}$ = 8.5 Hz, 2C), 128.1 (2C), 128.3, 128.6 (2C), 129.2 (2C), 135.0, 136.1, 155.9, 162.5 (d, $J_{C-F}$ = 246 Hz), 162.7, 166.7. $^{19}$F NMR (376 MHz, $CDCl_3$) δ –114.3. M.p. 202–205 °C. IR (KBr) 3293, 1698, 1639, 1606, 1495, 1253, 1037 $cm^{-1}$. $[\alpha]_D^{28}$ = –3.3 (*c* 1.0, $CHCl_3$, 82% ee (*S*)). HRMS (FAB+) calcd for $C_{23}H_{22}FN_2O_4$ $[M+H]^+$ 409.1564, found 409.1563. HPLC analysis; OD-H, *n*-hexane/*i*-PrOH = 4/1, 0.6 mL/min, $t_R$ = 24.8 min (major, *S*), 42.8 min. (minor, *R*).

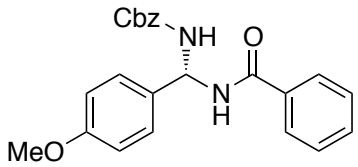



**(*S*)-Benzyl ((4-methoxybenzamido)(4-methoxyphenyl)methyl)carbamate (5d):** $^1$H NMR (400

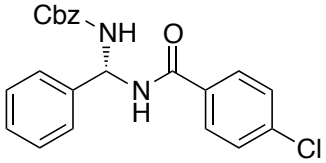
MHz, $CDCl_3$) δ 3.79 (s, 3H), 3.85 (s, 3H), 5.11 (s, 2H), 6.10 (br, 1H), 6.52 (br, 1H), 6.88 (d, $J$ = 8.7 Hz, 2H), 6.91 (d, $J$ = 8.1 Hz, 2H), 7.26-7.42 (m, 8H), 7.76 (br, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.2, 55.4, 60.4, 67.0, 113.7 (2C), 114.0 (2C), 125.8, 127.0 (2C), 128.0 (2C), 128.2, 128.5 (2C), 129.0 (2C), 130.9, 136.0, 155.6, 159.3, 162.5, 166.4. M.p. 189–191 °C. IR (KBr) 3303, 1694, 1635, 1607, 1547, 1511, 1248, 1037 $cm^{-1}$. $[\alpha]_D^{27}$ = 3.2 (*c* 1.0, $CHCl_3$, 87% ee (*S*)). HRMS (FAB+) calcd for $C_{24}H_{25}N_2O_5$ $[M+H]^+$ 421.1763, found 421.1767. HPLC analysis; AD-H, *n*-hexane/*i*-PrOH = 4/1, 1.0 mL/min, $t_R$ = 34.2 min (major, *S*), 49.2 min. (minor, *R*).




**(*S*)-Benzyl (benzamido(phenyl)methyl)carbamate (5e):** $^1$H NMR (400 MHz, $CDCl_3$) δ 5.12 (s, 2H), 6.17 (br, 1H), 6.58 (br, 1H), 7.27-7.56 (m, 14H), 7.80 (br, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 60.8, 67.0, 125.8 (2C), 127.2 (2C), 128.0 (2C), 128.1 (2C), 128.4 (2C), 128.5 (2C), 128.6 (2C), 131.8, 133.7, 136.1, 138.9, 155.7, 166.9. M.p. 182–184 °C. IR (KBr) 3298, 1697, 1644, 1509, 1351, 1245, 1038 $cm^{-1}$. $[\alpha]_D^{26}$ = 13.1 (*c* 1.0, $CHCl_3$, 87% ee (*S*)). HRMS (FAB+) calcd for $C_{22}H_{21}N_2O_3$ $[M+H]^+$ 361.1552, found 361.1554. HPLC analysis; OD-3 + OD-H, *n*-hexane/*i*-PrOH = 9/1, 0.5 mL/min, $t_R$ = 99.2 min (major, *S*), 122.0 min (minor, *R*).

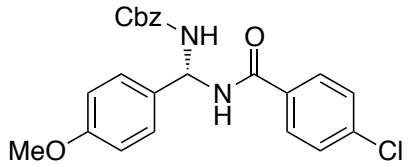



**(*S*)-Benzyl (benzamido(4-methoxyphenyl)methyl)carbamate (5f):** $^1$H NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 5.12 (s, 2H), 6.06 (br, 1H), 6.54 (br, 1H), 6.88 (d, $J$ = 8.7 Hz, 2H), 7.27-7.40 (m, 9H), 7.43 (t, $J$ = 7.8 Hz, 1H), 7.52 (t, $J$ = 7.2 Hz, 1H), 7.80 (br, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.4, 60.7, 67.2, 114.3 (2C), 127.2 (2C), 127.3 (2C), 128.2 (2C), 128.3, 128.6 (2C), 128.7 (2C), 131.1, 132.0, 133.9, 136.2, 155.7, 159.7, 167.0. M.p. 181–185 °C. IR (KBr) 3297, 1695, 1638, 1546, 1509, 1244, 1038 $cm^{-1}$. $[\alpha]_D^{28}$ = 5.9 (*c* 1.0, $CHCl_3$, 89% ee (*S*)). HRMS (FAB+) calcd for $C_{23}H_{23}N_2O_4$ $[M+H]^+$ 391.1658, found 391.1646. HPLC analysis; AS-H, *n*-hexane/*i*-PrOH = 4/1, 0.6 mL/min, $t_R$ = 63.4 min (minor, *R*), 71.8 min (major, *S*).

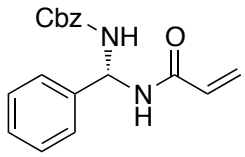



**(*S*)-Benzyl ((4-chlorobenzamido)(phenyl)methyl)carbamate (5g):** $^1$H NMR (400 MHz, $CDCl_3$) δ 5.10 (s, 2H), 6.12 (br, 1H), 6.55 (br, 1H), 7.27-7.45 (m, 13H), 7.72 (br, 2H). $^{13}$C NMR (100

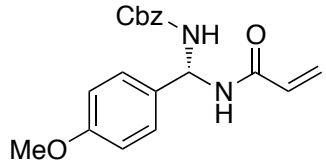
MHz, $CDCl_3$) δ 60.9, 67.1, 125.8 (2C), 128.0 (2C), 128.2, 128.3, 128.5 (2C), 128.6 (2C), 128.7 (2C), 128.8 (2C), 132.1, 136.0, 138.2, 138.6, 155.7, 165.9. M.p. 199–202 °C. IR (KBr) 3297, 1698, 1642, 1595, 1551, 1349, 1247, 1036 $cm^{-1}$. $[\alpha]_D^{26}$ = 6.4 (*c* 1.0, $CHCl_3$, 80% ee (*S*)). HRMS (FAB+) calcd for $C_{22}H_{20}ClN_2O_3$ $[M+H]^+$ 395.1162, found 395.1162. HPLC analysis; AD-H, *n*-hexane/*i*-PrOH = 4/1, 0.6 mL/min, $t_R$ = 35.5 min (minor, *R*), 47.7 min (major, *S*).




**(*S*)-Benzyl ((4-chlorobenzamido)(4-methoxyphenyl)methyl)carbamate (5h):** $^1H$ NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 5.10 (s, 2H), 6.03 (br, 1H), 6.52 (br, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.27-7.38 (m, 8H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.72 (br, 2H). $^{13}C$ NMR (100 MHz, DMSO-$d_6$) δ 55.1, 60.0, 65.6, 113.6 (2C), 127.8 (4C), 128.3 (3C), 128.4 (2C), 129.5 (2C), 132.0, 132.7, 136.2, 136.9, 155.2, 158.8, 164.4. M.p. 197–201 °C. IR (KBr) 3279, 1698, 1637, 1509, 1248, 1035 $cm^{-1}$. $[\alpha]_D^{26}$ = 6.6 (*c* 1.0, DMSO, 75% ee (*S*)). HRMS (FAB+) calcd for $C_{23}H_{22}ClN_2O_4$ $[M+H]^+$ 425.1268, found 425.1257. HPLC analysis; AD-H, *n*-hexane/*i*-PrOH = 4/1, 0.6 mL/min, $t_R$ = 49.7 min (major, *S*), 59.0 min (minor, *R*).

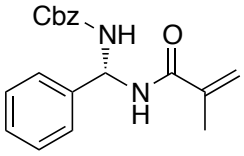



**(*S*)-Benzyl (acrylamido(phenyl)methyl)carbamate (5i):** $^1H$ NMR (400 MHz, $CDCl_3$) δ 5.08 (d, *J* = 12.3 Hz, 1H), 5.12 (d, *J* = 12.3 Hz, 1H), 5.70 (d, *J* = 10.2 Hz, 1H), 6.12 (d, *J* = 16.8 Hz, 1H), 6.14 (m, 1H), 6.33 (d, *J* = 16.8 Hz, 1H), 6.45 (br, 1H), 6.91 (br, 1H), 7.37-7.42 (m, 10H). $^{13}C$ NMR (100 MHz, $CDCl_3$) δ 60.3, 67.0, 125.8 (2C), 127.4, 127.9 (2C), 128.1 (2C), 128.4 (2C), 128.6 (2C), 130.4, 136.1, 138.7, 155.6, 165.1. M.p. 192–194 °C. IR (KBr) 3293, 1697, 1655, 1560, 1261, 1079, 1041 $cm^{-1}$. $[\alpha]_D^{26}$ = 6.5 (*c* 1.0, $CHCl_3$, 77% ee (*S*)). HRMS (FAB+) calcd for $C_{18}H_{19}N_2O_3$ $[M+H]^+$ 311.1396, found 311.1404. HPLC analysis; AD-H, *n*-hexane/*i*-PrOH = 4/1, 0.6 mL/min, $t_R$ = 22.5 min (minor, *R*), 43.1 min (major, *S*).

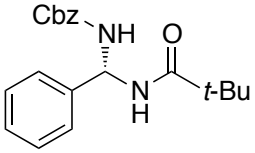



**(*S*)-Benzyl (acrylamido(4-methoxyphenyl)methyl)carbamate (5j):** $^1H$ NMR (400 MHz, $CDCl_3$) δ 3.79 (s, 3H), 5.11 (s, 2H), 5.72 (d, *J* = 10.5 Hz, 1H), 5.94 (br, 1H), 6.10 (dd, *J* = 16.8, 10.5 Hz, 1H), 6.34 (d, *J* = 16.8 Hz, 1H), 6.41 (br, 1H), 6.71 (br, 1H), 6.88 (d, *J* = 8.7 Hz, 2H), 7.27-7.43 (m,

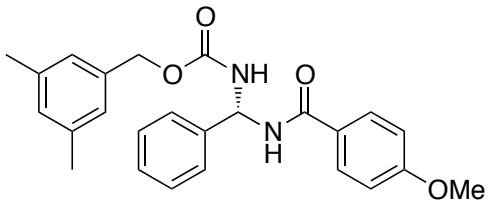
7H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 55.3, 60.3, 67.1, 114.1 (2C), 127.1 (2C), 127.6, 128.1 (2C), 128.2, 128.5 (2C), 130.4, 130.8, 136.1, 155.5, 159.6, 164.9. M.p. 199–203 °C. IR (KBr) 3301, 1691, 1557, 1509, 1251, 1228, 1048 $cm^{-1}$. $[\alpha]_D^{27}$ = 2.0 (*c* 1.0, $CHCl_3$, 89% ee (*S*)). HRMS (FAB+) calcd for $C_{19}H_{21}N_2O_4$ $[M+H]^+$ 341.1501, found 341.1508. HPLC analysis; OZ-H × 2, *n*-hexane/*i*-PrOH = 4/1, 0.6 mL/min, $t_R$ = 70.6 min (minor, *R*), 76.2 min (major, *S*).




**(*S*)-Benzyl (methacrylamido(phenyl)methyl)carbamate (5k):** $^1$H NMR (400 MHz, $CDCl_3$) δ 1.94 (s, 3H), 5.07 (d, *J* = 12.3 Hz, 1H), 5.11 (d, *J* = 12.3 Hz, 1H), 5.36 (s, 1H), 5.73 (s, 1H), 6.22 (br, 1H), 6.42 (br, 1H), 7.17 (br, 1H), 7.20-7.50 (m, 10H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 18.2, 60.4, 67.0, 120.6, 125.7 (2C), 128.0 (2C), 128.1, 128.2, 128.4 (2C), 128.6 (2C), 136.0, 138.7, 139.3, 155.6, 167.8. M.p. 160–164 °C. IR (KBr) 3308, 1696, 1654, 1621, 1550, 1507, 1252, 1040 $cm^{-1}$. $[\alpha]_D^{26}$ = 13.2 (*c* 1.0, $CHCl_3$, 71% ee (*S*)). HRMS (FAB+) calcd for $C_{19}H_{21}N_2O_3$ $[M+H]^+$ 325.1552, found 325.1558. HPLC analysis; IA, *n*-hexane/*i*-PrOH = 4/1, 0.6 mL/min, $t_R$ = 20.9 min (major, *S*), 24.7 min (minor, *R*).

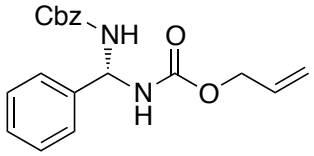



**(*S*)-Benzyl (phenyl(pivalamido)methyl)carbamate (5l):** $^1$H NMR (400 MHz, $CDCl_3$) δ 1.20 (s, 9H), 5.10 (d, *J* = 12.3 Hz, 1H), 5.14 (d, *J* = 12.3 Hz, 1H), 6.00 (br, 1H), 6.33 (br, 1H), 6.89 (br, 1H), 7.28-7.42 (m, 10H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 27.3 (3C), 38.7, 60.1, 66.9, 125.9 (2C), 128.0, 128.1 (2C), 128.2, 128.5 (2C), 128.6 (2C), 136.0, 138.9, 155.6, 178.2. M.p. 102–104 °C. IR (KBr) 3261, 2965, 1698, 1652, 1549, 1498, 1348, 1246, 1027 $cm^{-1}$. $[\alpha]_D^{26}$ = 13.2 (*c* 1.0, $CHCl_3$, 56% ee (*S*)). HRMS (FAB+) calcd for $C_{20}H_{25}N_2O_3$ $[M+H]^+$ 341.1865, found 341.1873. HPLC analysis; OZ-H, *n*-hexane/*i*-PrOH = 9/1, 0.5 mL/min, $t_R$ = 17.0 min (major, *S*), 21.2 min (minor, *R*).



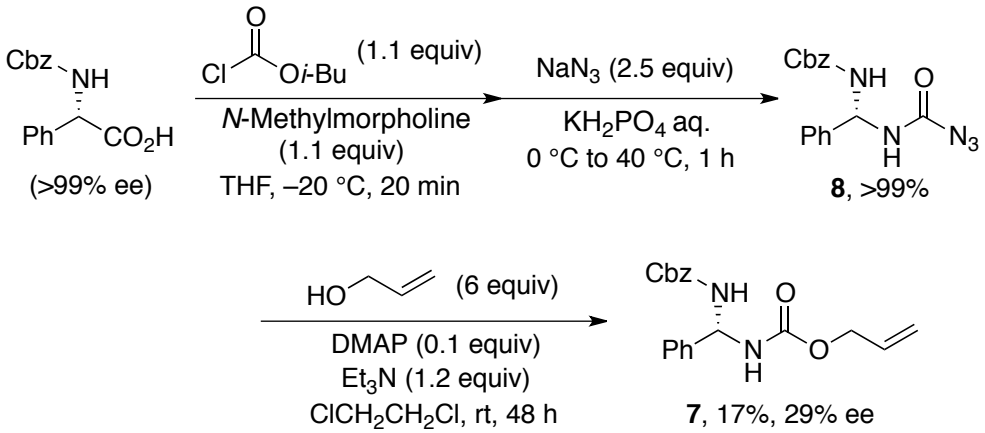

**(*S*)-3,5-Dimethylbenzyl ((4-methoxybenzamido)(phenyl)methyl)carbamate (5m):** $^1$H NMR (400 MHz, $CDCl_3$) δ 2.27 (s, 6H), 3.84 (s, 3H), 5.04 (s, 2H), 6.15 (br, 1H), 6.56 (br, 1H), 6.87-7.00 (m, 5H), 7.27-7.40 (m, 4H), 7.44 (d, *J* = 7.2 Hz, 2H), 7.77 (br, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$)

δ 21.1 (2C), 55.4, 60.8, 67.1, 113.8 (2C), 125.8 (2C), 125.9 (2C), 126.0, 128.0, 128.6 (2C), 129.0 (2C), 129.8, 135.9, 138.1 (2C), 139.1, 155.8, 162.6, 166.4. M.p. 202–204 °C. IR (KBr) 3262, 1699, 1636, 1494, 1256, 1034 $cm^{-1}$. $[\alpha]_D^{26}$ = 3.9 (*c* 1.0, $CHCl_3$, 83% ee (*S*)). HRMS (FAB+) calcd for $C_{25}H_{27}N_2O_4$ $[M+H]^+$ 419.1971, found 419.1990. HPLC analysis; AS-H, *n*-hexane/*i*-PrOH = 4/1, 0.6 mL/min, $t_R$ = 40.0 min (major, *S*), 54.8 min (minor, *R*).




**(*S*)-Allyl benzyl (phenylmethylene)dicarbamate (7):** $^1$H NMR (400 MHz, $CDCl_3$) δ 4.58 (d, *J* = 5.4 Hz, 2H), 5.12 (d, *J* = 12.3 Hz, 1H), 5.13 (d, *J* = 12.3 Hz, 1H), 5.21 (d, *J* = 10.2 Hz, 1H), 5.29 (d, *J* = 16.3 Hz, 1H), 5.70-6.00 (br, 2H), 6.27 (br, 1H), 7.25-7.45 (11H). $^{13}$C NMR (100 MHz, $CDCl_3$) δ 62.0, 66.0, 67.2, 118.1, 125.8 (2C), 128.3 (3C), 128.4, 128.6 (2C), 128.8 (2C), 132.5, 136.1, 138.8, 155.3, 155.4. M.p. 126–130 °C. IR (KBr) 3298, 1708, 1555, 1515, 1239, 1026 $cm^{-1}$. $[\alpha]_D^{28}$ = –3.3 (*c* 1.0, $CHCl_3$, 77% ee (*S*)). HRMS (FAB+) calcd for $C_{19}H_{21}N_2O_4$ $[M+H]^+$ 341.1501, found 341.1498. HPLC analysis; AS-H, *n*-hexane/*i*-PrOH = 4/1, 0.6 mL/min, $t_R$ = 36.4 min (minor, *R*), 48.2 min (major, *S*).

**5. Conventional synthesis of 11 from azide carbonyl compound 10 (eqn. 4).**[3]




*N*-Methylmorpholine (0.24 mL, 2.2 mmol) was slowly added to a stirred solution of *N*-Benzyloxycarbonyl-L-phenylglycine (0.571 g, 2.0 mmol) in THF (12 mL). After 5 min, isobutyl chloroformate (0.285 mL, 2.2 mmol) was slowly added to the previously cooled reaction mixture at –20 °C and stirring was continued for 20 min at that temperature. The reaction mixture was warmed to 0 °C and a solution of $KH_2PO_4$ (0.136 g, 1.0 mmol) in $H_2O$ (1 mL) was added in one portion, after 5 min followed by a solution of $KH_2PO_4$ (1.36 g, 10 mmol) and $NaN_3$ (0.33 g, 5.0 mmol) in $H_2O$ (7 mL). After 1 h, 10 mL of saturated $NaHCO_3$ aqueous solution was poured into the reaction mixture, and the product was extracted with AcOEt (15 mL × 3). The

combined extracts were washed with $NH_4Cl$ aqueous solution (10 mL), brine (10 mL), and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure and the crude product was obtained in quantitative yield. Obtained **8** was used in next step without further purification. $^1$H NMR (400 MHz, THF-$d_4$) δ 5.07 (s, 2H), 6.34 (br, 1H), 7.10-7.55 (m, 11H), 8.00 (br, 1H). $^{13}$C NMR (100 MHz, DMSO-$d_6$) δ 61.5, 65.6, 126.5 (2C), 127.7, 127.9 (2C), 128.0, 128.3 (4C), 136.8, 138.9, 155.0, 155.2. IR (KBr) 3270, 2140, 1702, 1556, 1512, 1234, 1041 cm$^{-1}$. HRMS (FAB+) calcd for $C_{16}H_{16}N_5O_3$ $[M+H]^+$ 326.1253, found 326.1247. The 1,2-dichloroethane solution of **8** (32.5 mg, 0.1 mmol) and 4-(dimethylamino)pyridine (1.2 mg, 0.01 mmol), triethylamine (16.7 μL, 0.12 mmol) and allyl alcohol (40 μL, 0.6 mmol) were added at room temperature. After 48 h, 10 mL of saturated $NaHCO_3$ aqueous solution was poured into the reaction mixture, and the product was extracted with AcOEt (15 mL × 3). The combined extracts were washed with brine (10 mL), and dried over $MgSO_4$. The organic phase was concentrated under reduced pressure and the crude product was purified by preparative thin-layer chromatography (eluent: hexane/AcOEt = 3/1), to give **7** in 17% yield (5.8 mg) with 29% ee (*S*). The absolute stereochemistry of **5** was deduced from that of **7**.

### 6. Relationship between enantioselectivity of (*R*)-1 and that of aminal product 5a.

We examined the relationship between the enantioselectivity of (*R*)-**1** and that of aminal product **5a** (Fig. S1). (*R*)-**1** is a disulfonic acid, and thus not only monomeric but also oligomeric structures of the catalysts in situ might be possible. However, a nonlinear effect was not observed in this catalysis, and a 1 to 1 monomeric complex of (*R*)-**1** and **2g** was strongly suggested.

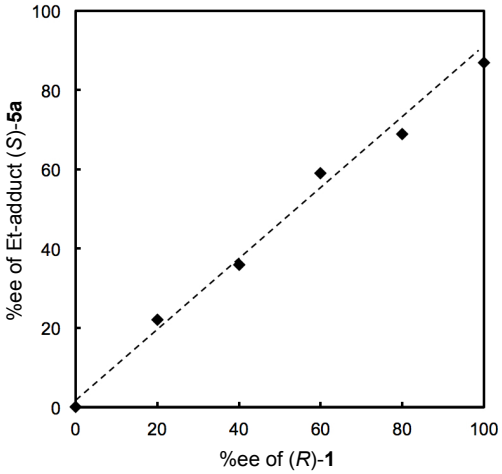



**Fig. S1** Absence of a nonlinear effect between the enantioselectivity of (*R*)-**1** and that of **5a**.

### 7. $^1$H NMR analysis of the catalyst (*R*)-1–2g.

A preliminary $^1$H NMR ($CDCl_3$) analysis of the catalysts generated in situ from (*R*)-**1** (1 equiv) and **2g** (0–2 equiv) was performed (Fig. S2). The catalyst was prepared in $CH_3CN$ according to the general procedure, the volatiles were removed under reduced pressure, and $CDCl_3$ was added.

$^1$H NMR spectra of (*R*)-**1** and **2g** as standard samples are shown in Figs. S2a and S2b, respectively. A mixture of (*R*)-**1** (1 equiv) and **2g** (1 equiv) gave sharp peaks at 6.75–7.80 ppm and a broad peak at 8.45 ppm with upfield shifts compared to the results with (*R*)-**1** or **2g** (Fig. S2c). Moreover, a mixture of (*R*)-**1** (1 equiv) and **2g** (2 equiv) gave peaks similar to those for a mixture of (*R*)-**1** (1 equiv) and **2g** (1 equiv) (Fig. S2d). Although these $^1$H NMR analyses cannot be considered solid evidence for the structure of the ammonium salt, and further studies on the structure are necessary, a 1:1 complex of (*R*)-**1** and **2g** is strongly suggested. Moreover, the absence of a nonlinear effect (Fig. S1) between the enantioselectivity of (*R*)-**1** and that of aminal product **5a** also supports the assumption of a 1:1 monomeric complex. Ammnonium salts in situ might be in equilibrium, as shown in Fig. S3. Therefore, the balance of the complexes might be in favor of a 1:1 monomeric complex.

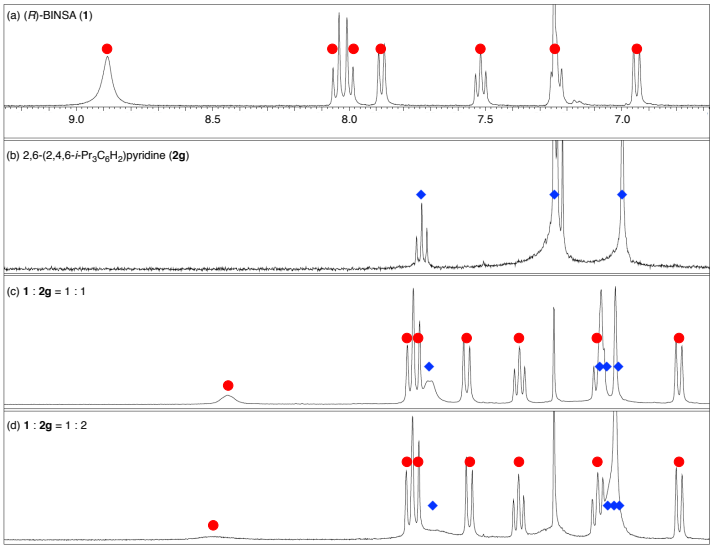



**Fig. S2** $^1$H NMR ($CDCl_3$) analysis of the catalyst (*R*)-**1**–**2g**.

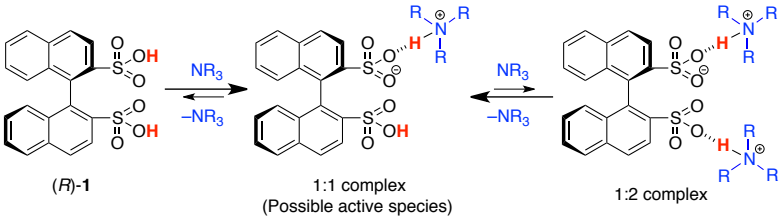


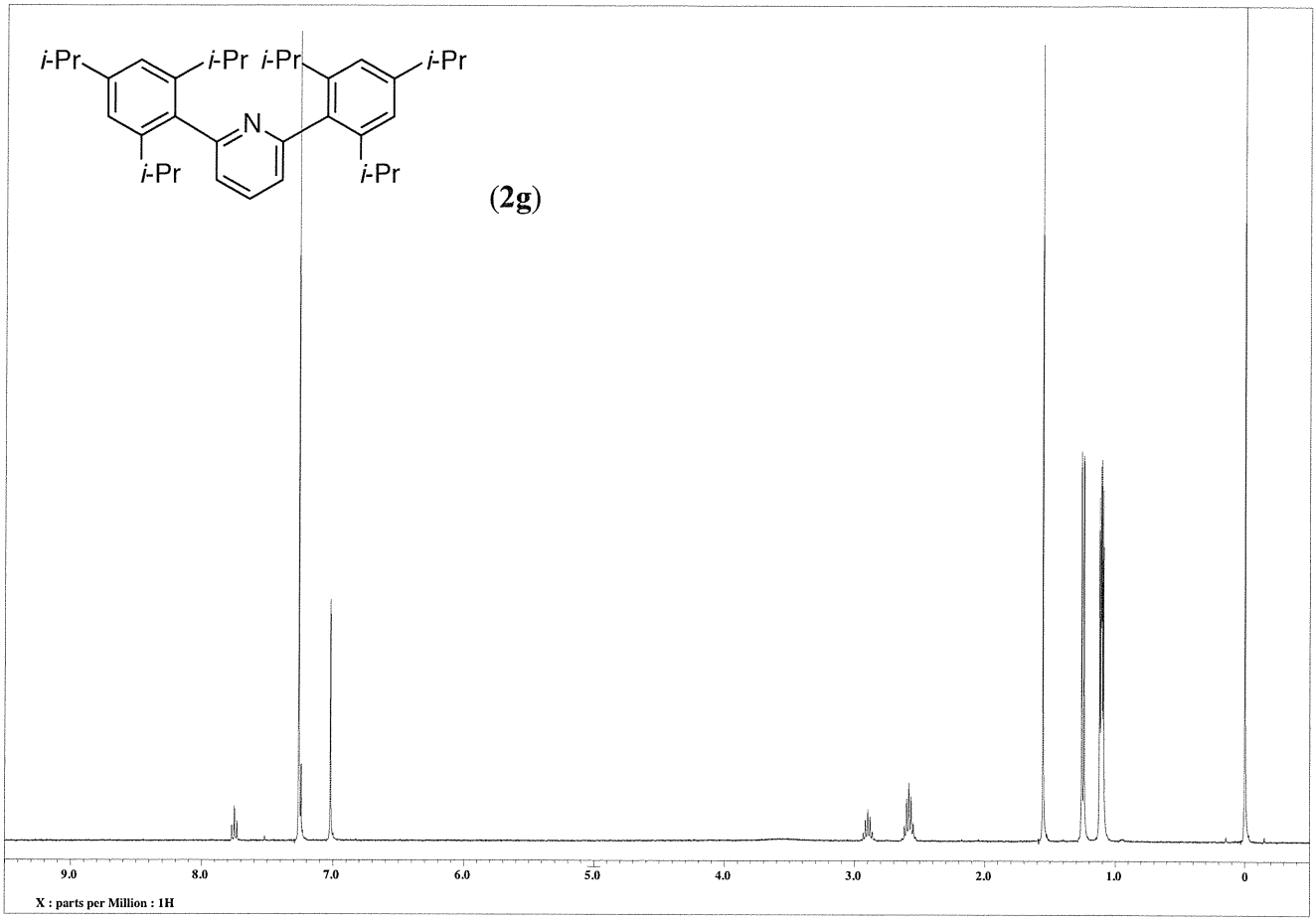

**Fig. S3** $^1$H NMR analysis of the catalyst (*R*)-**1**–**2g**.

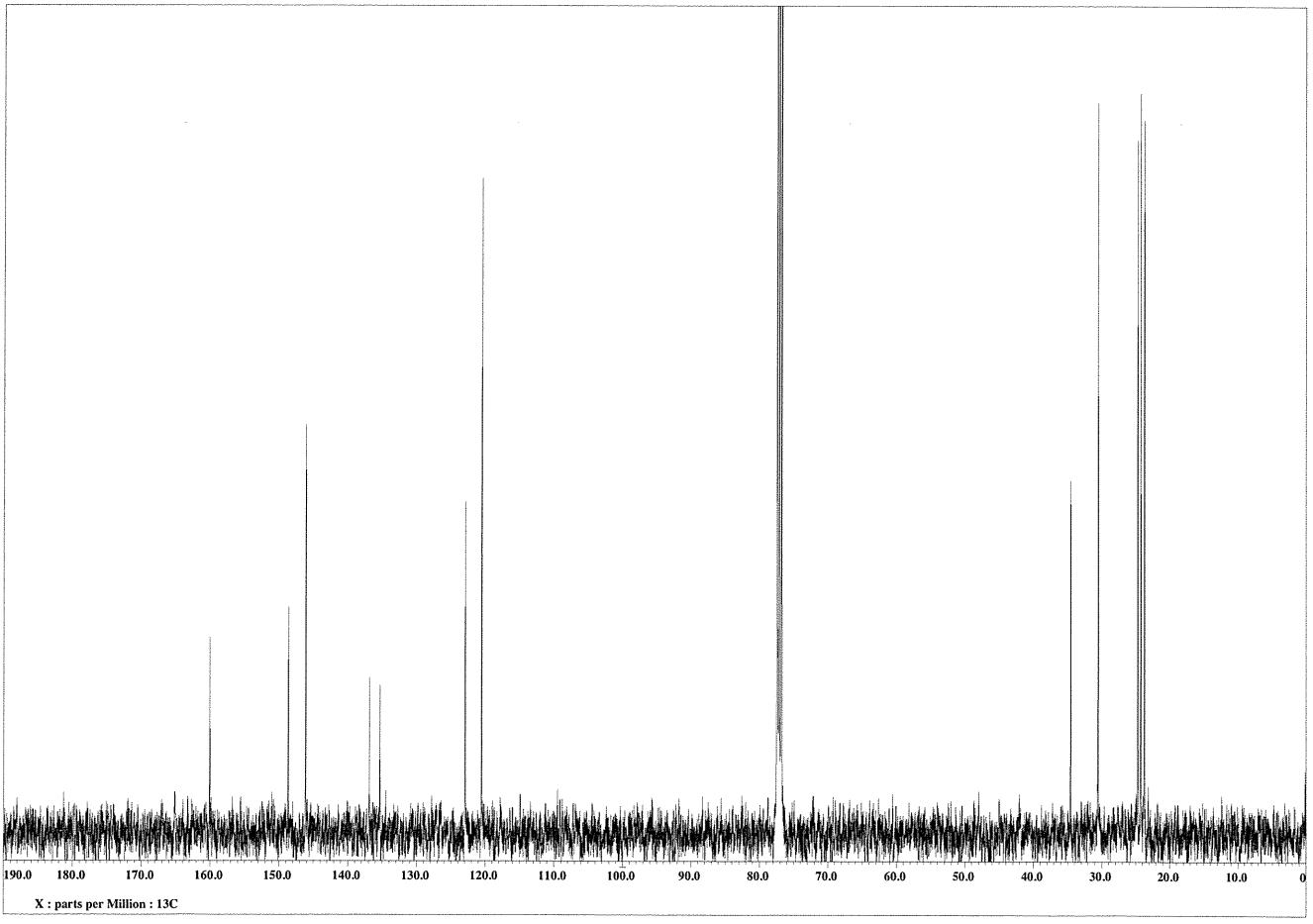
## 8. References.

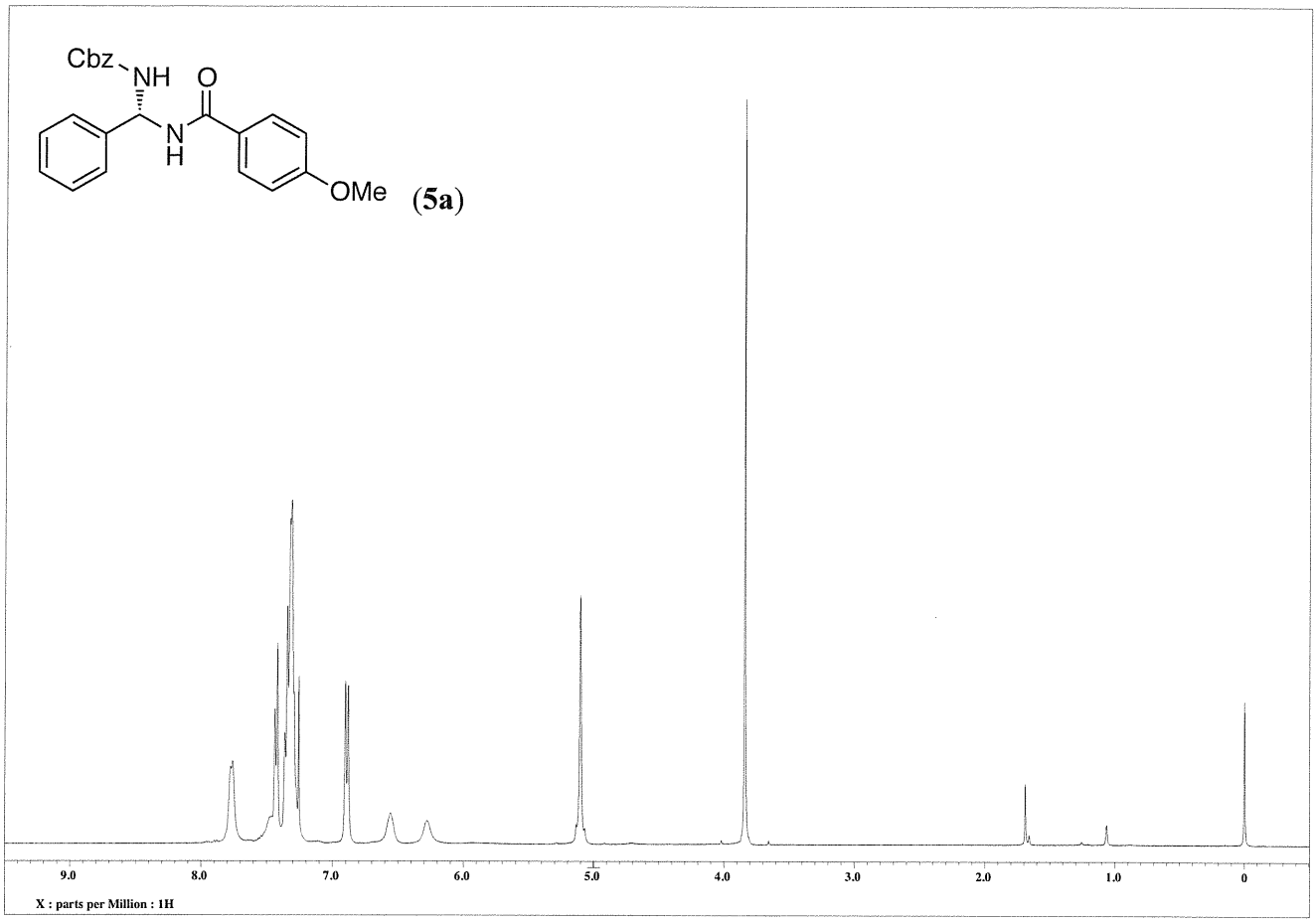
(1) T. Pell, D. P. Mills, A. J. Blake, W. Lewis and S. T. Liddle, *Polyhedron*, **29**, 120 (2010).

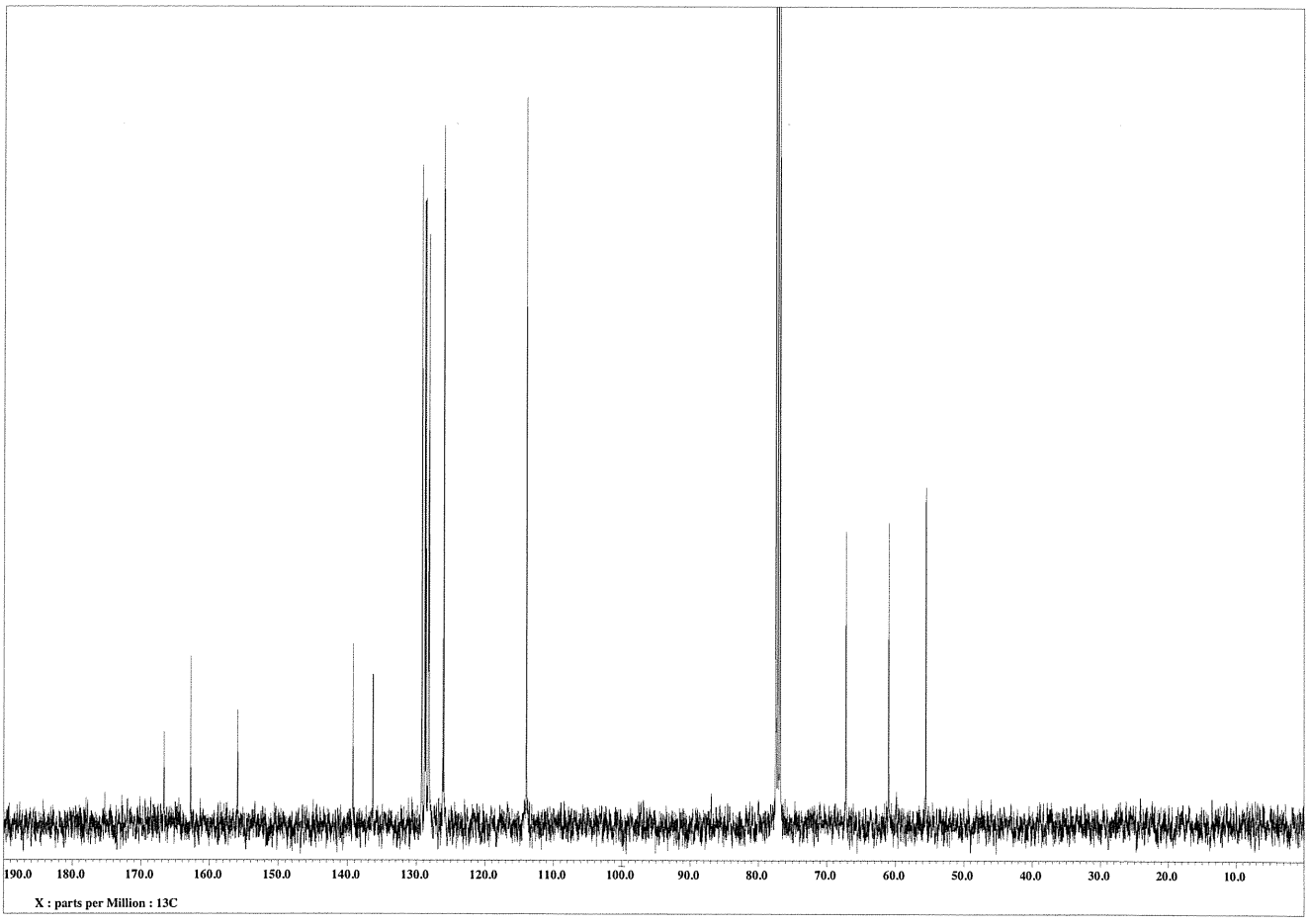
(2) M. Hatano, T. Maki, K. Moriyama, M. Arinobe and K. Ishihara, *J. Am. Chem. Soc.*, **130**, 16858 (2008).

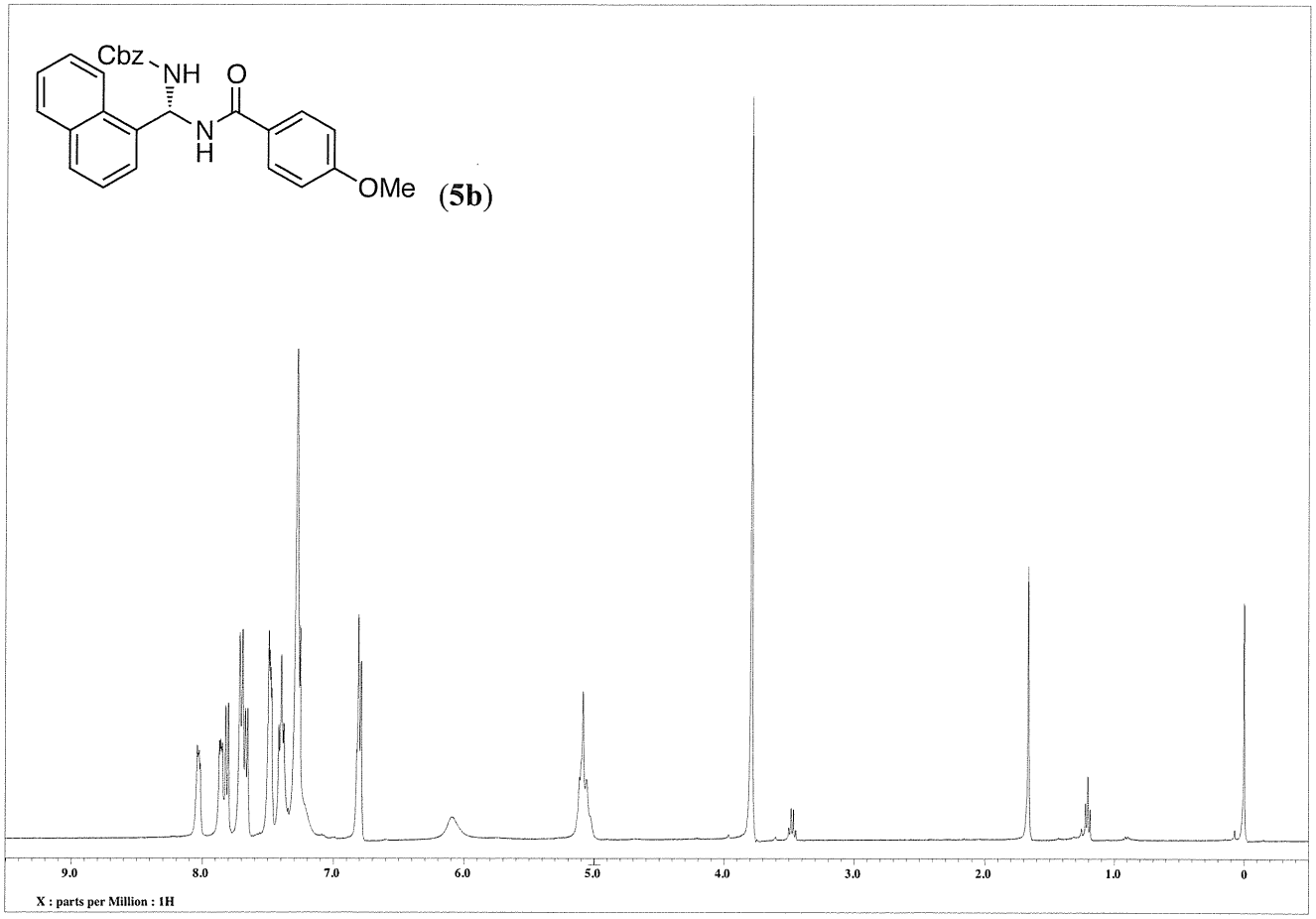
(3) G. Verardo, C. D. Venneri, G. Esposito and P. Strazzolini, *Eur. J. Org. Chem.*, 1376 (2011).

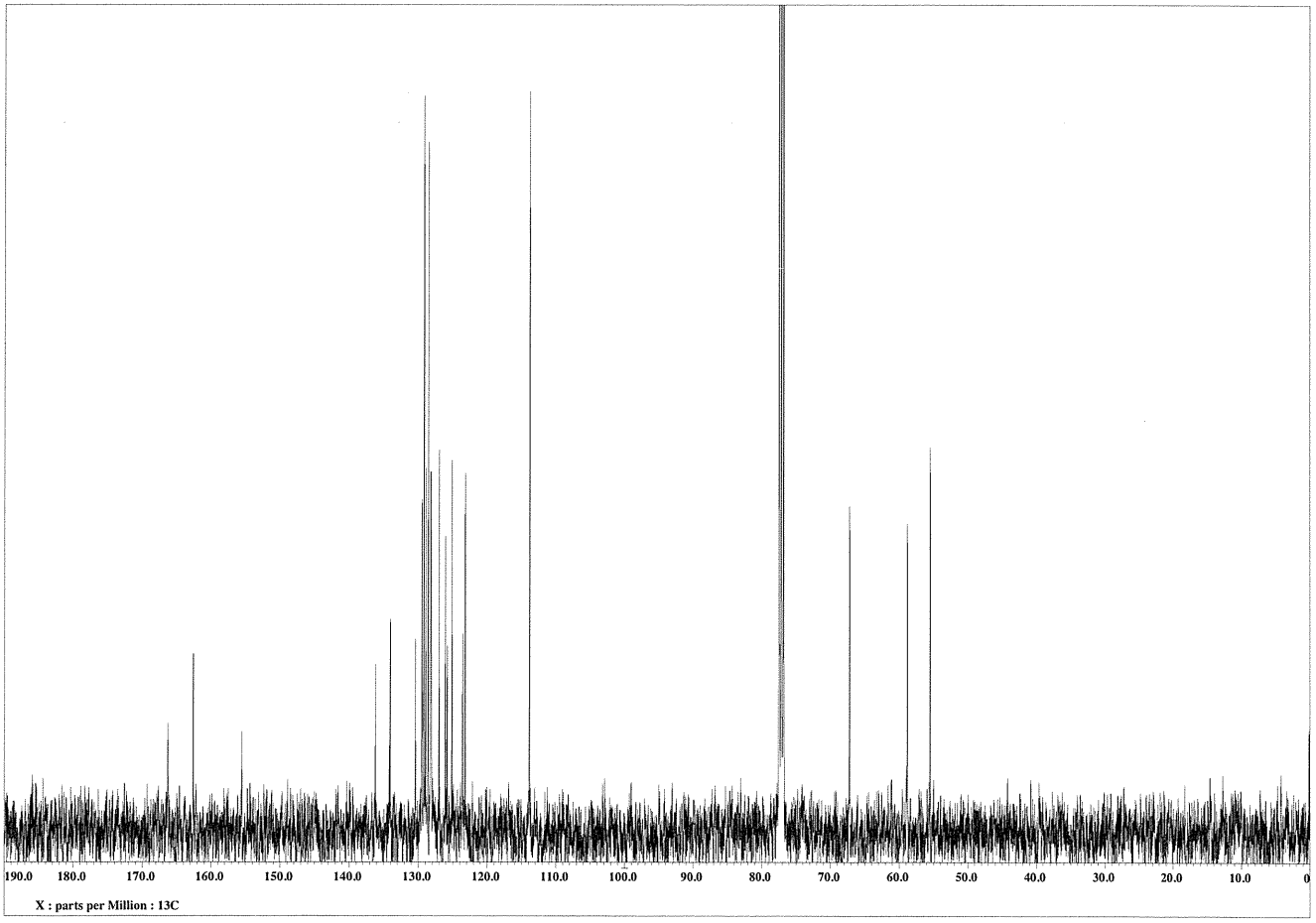


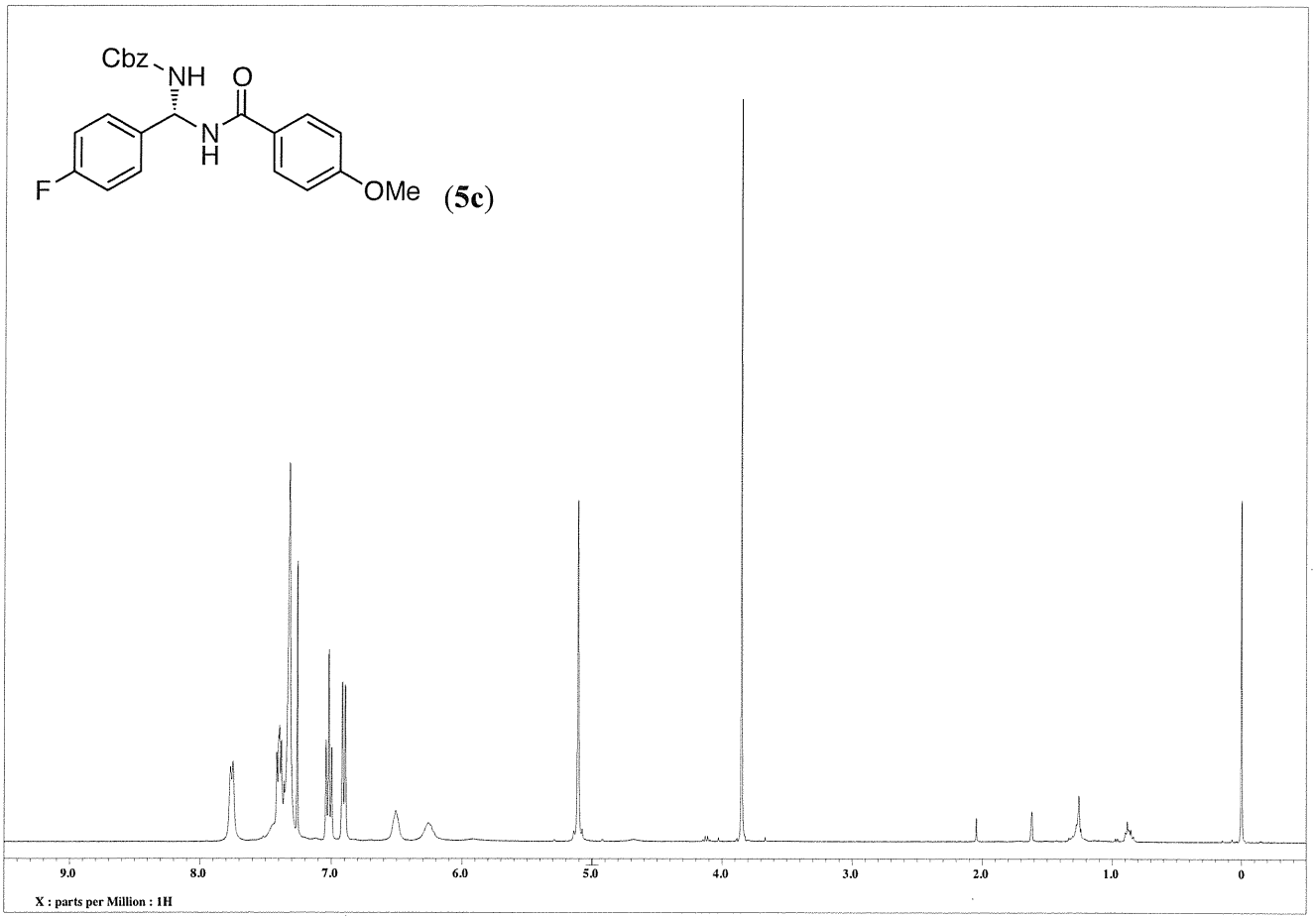



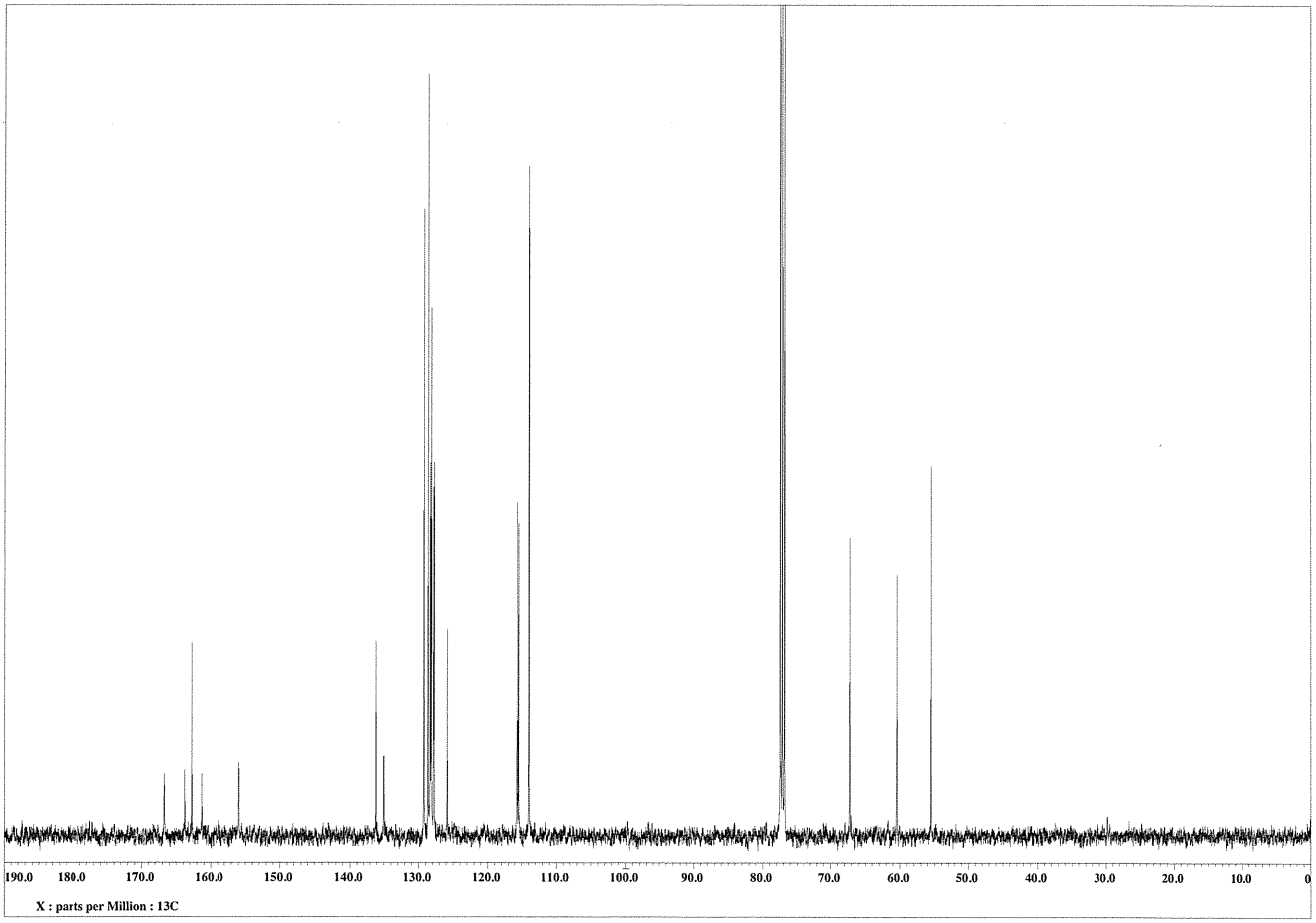


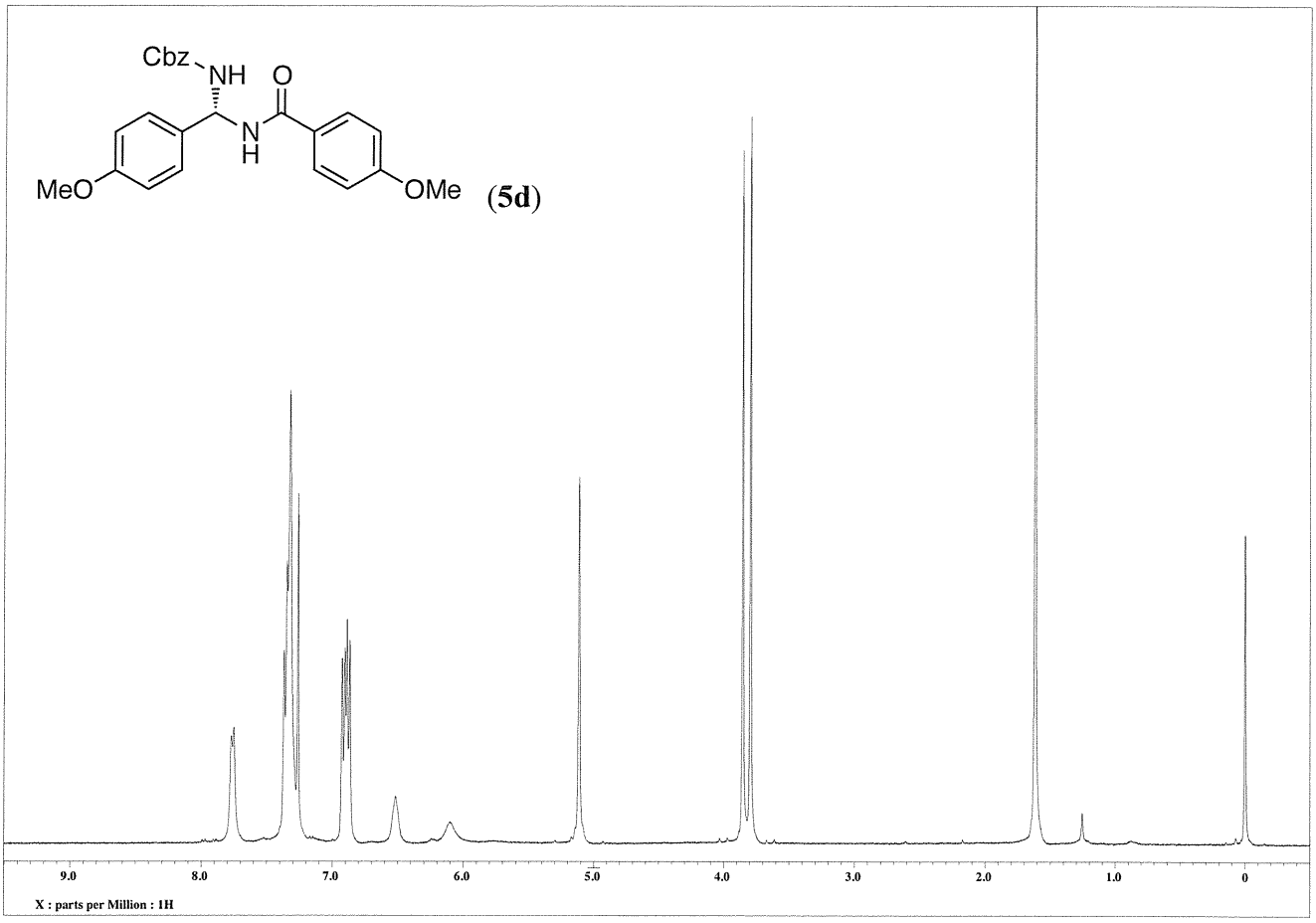



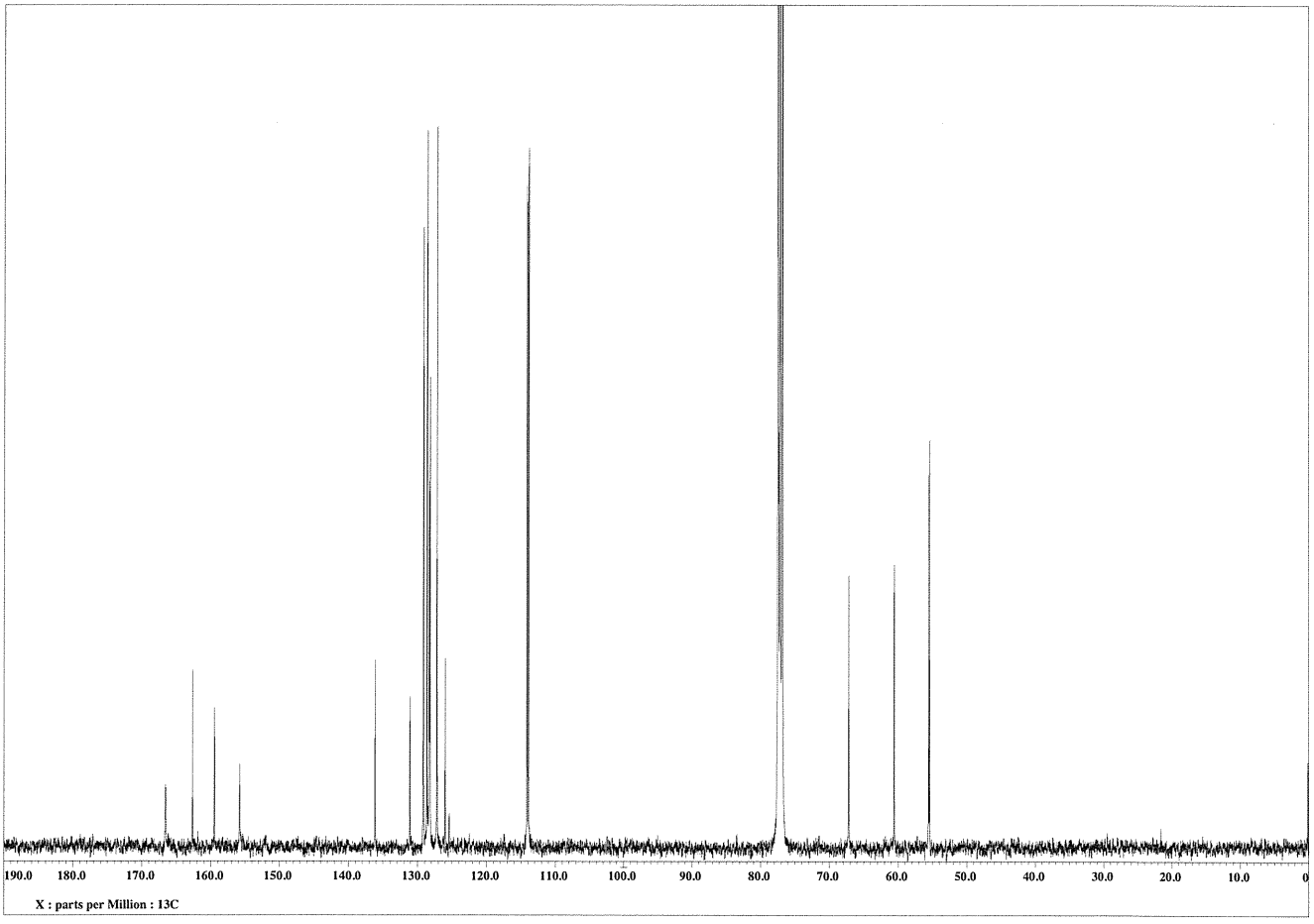


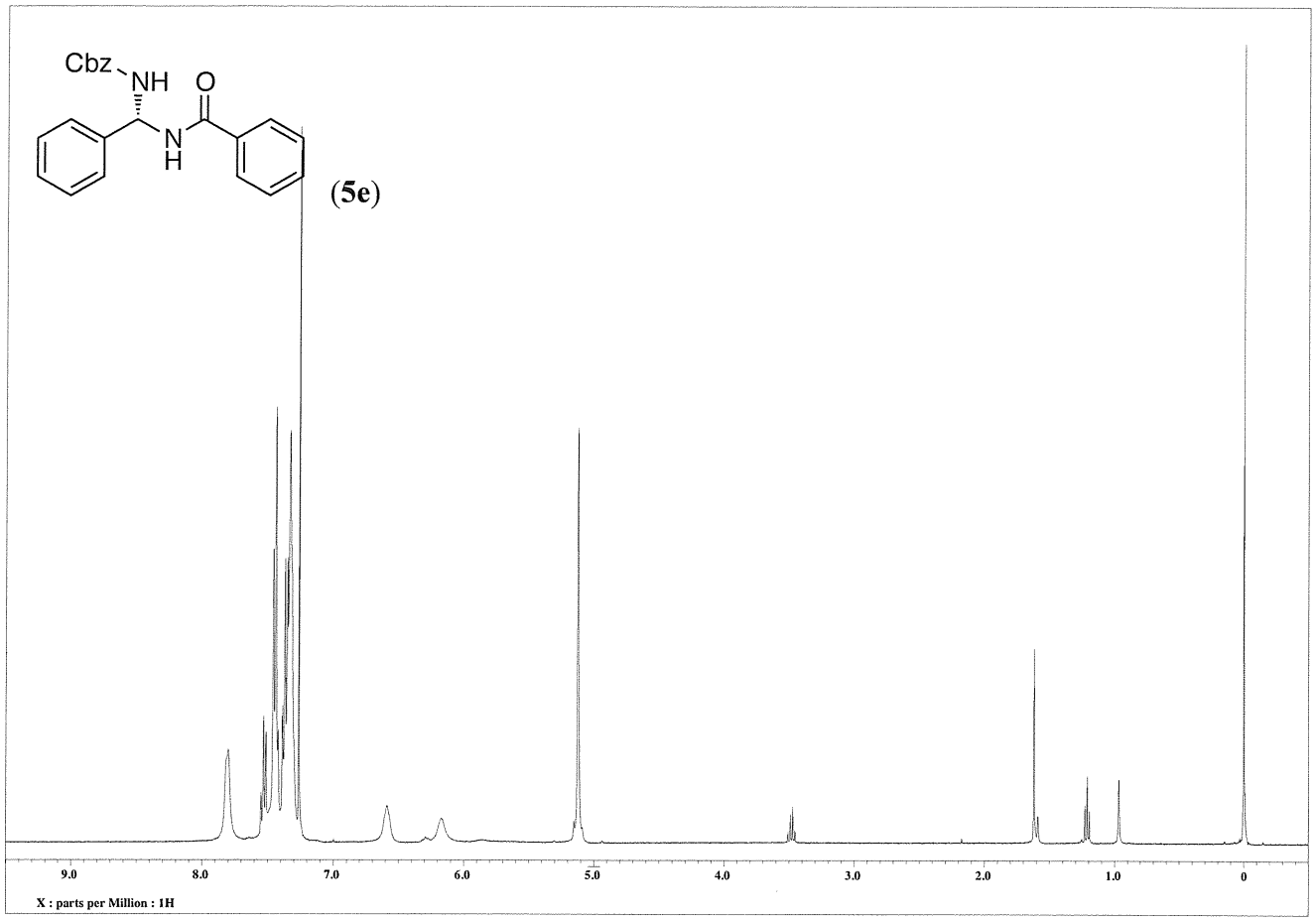





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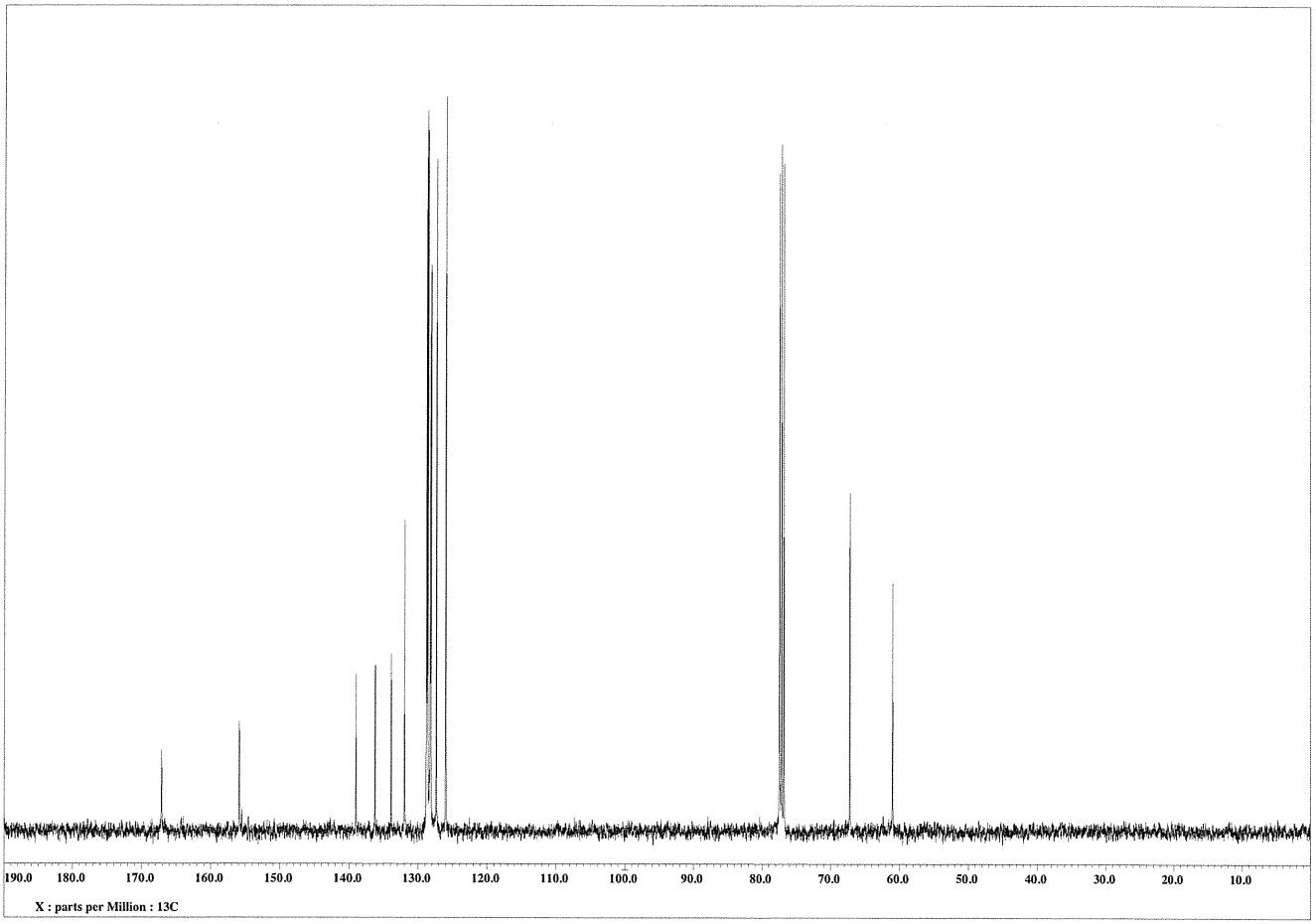
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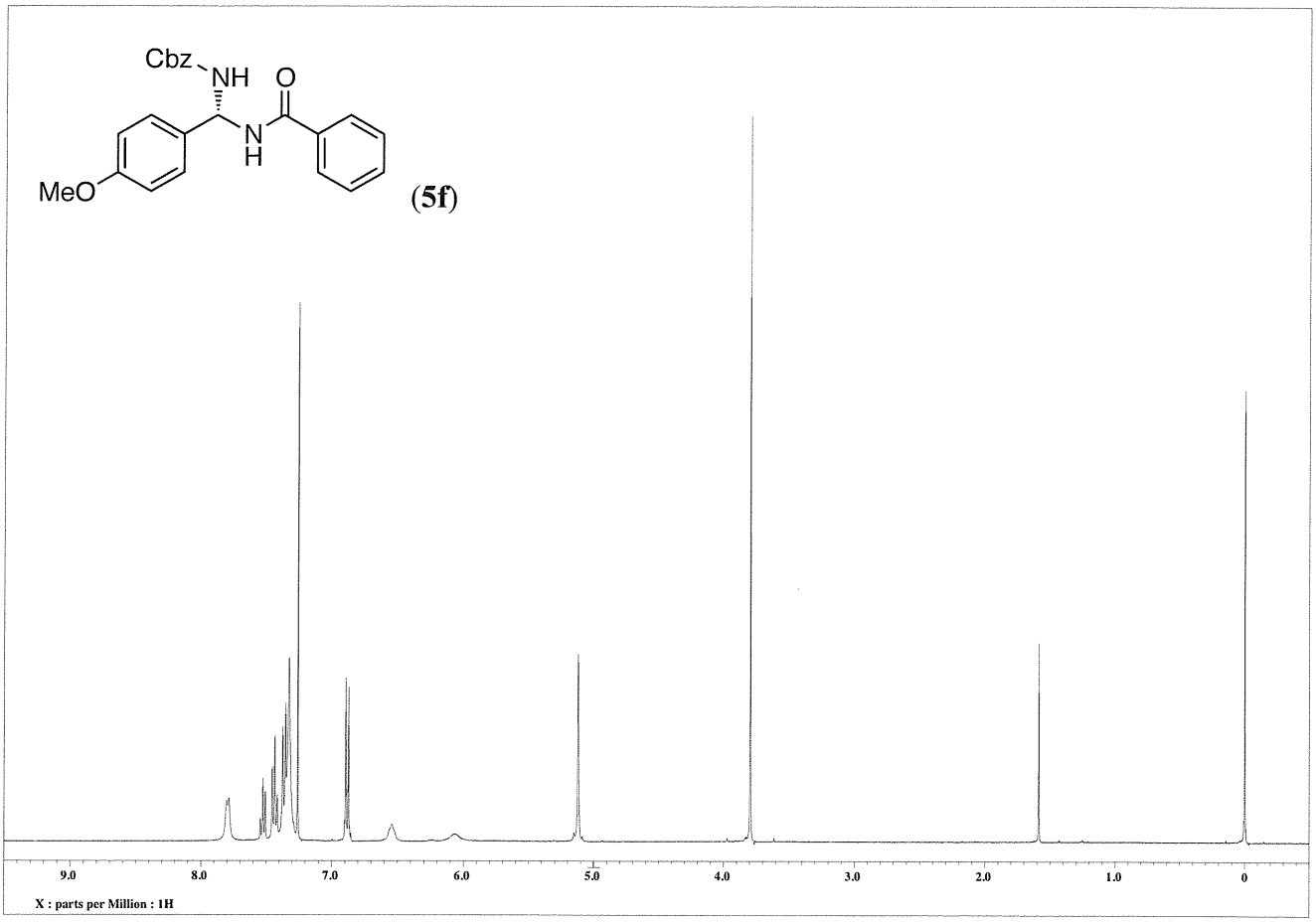
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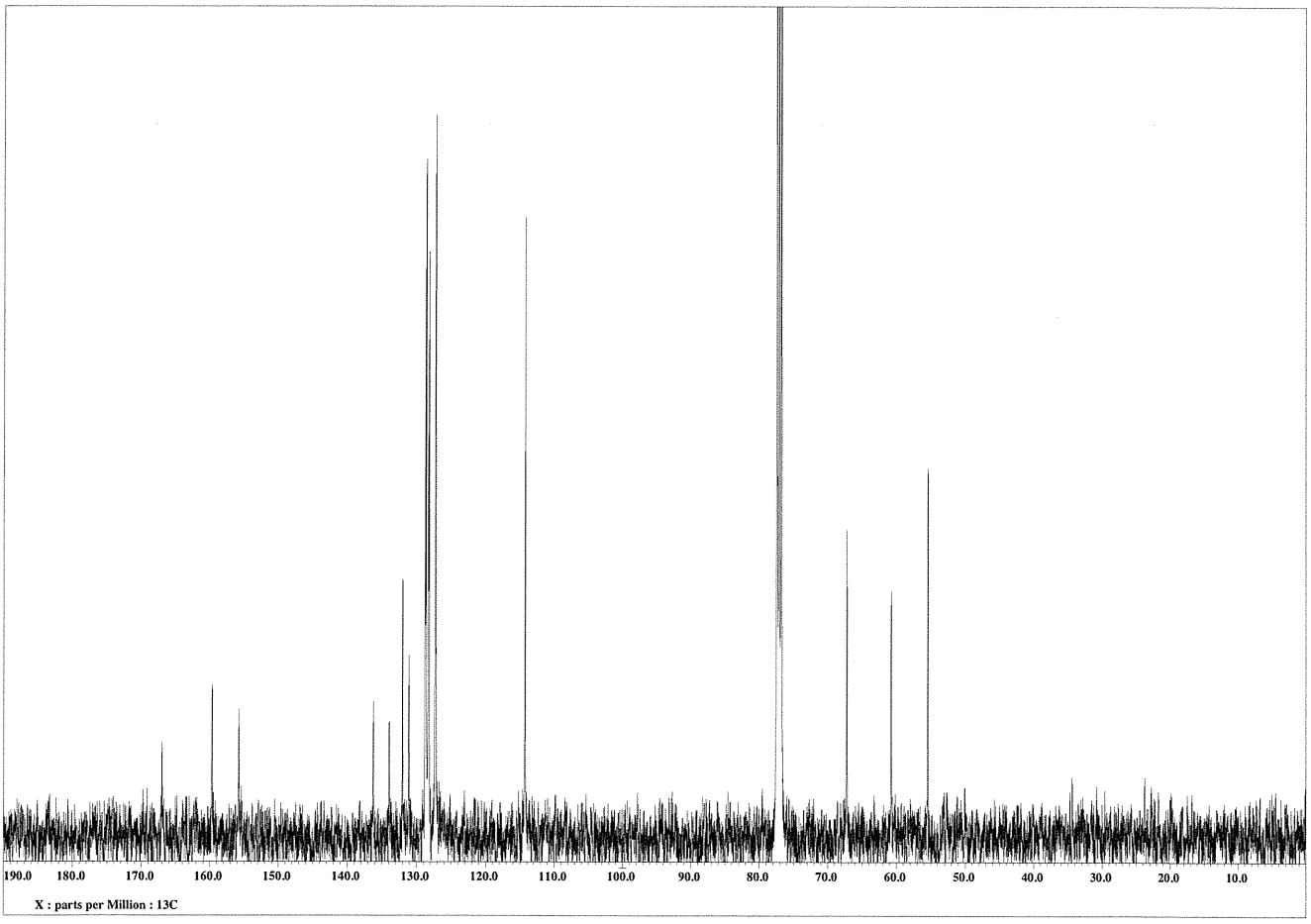
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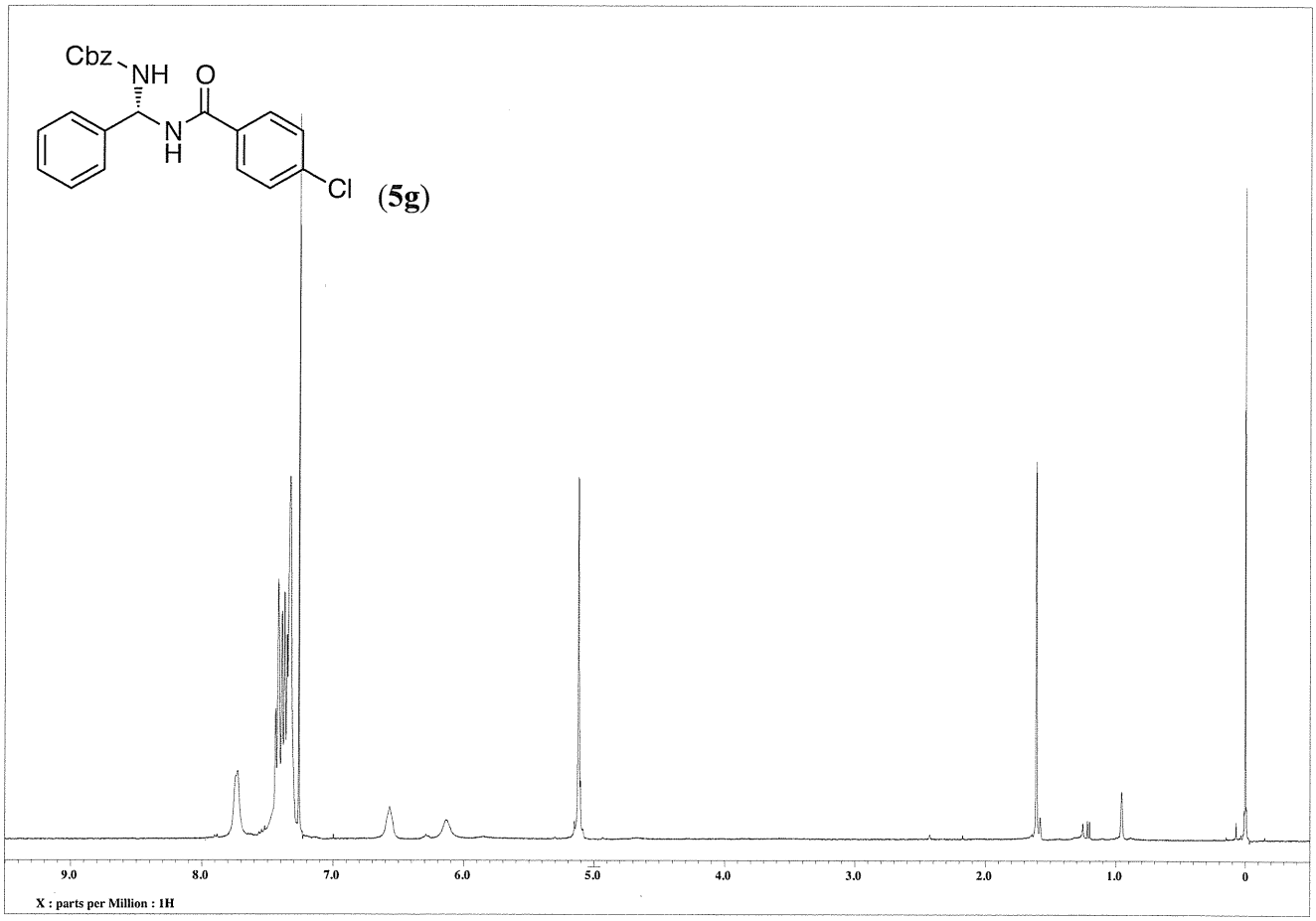
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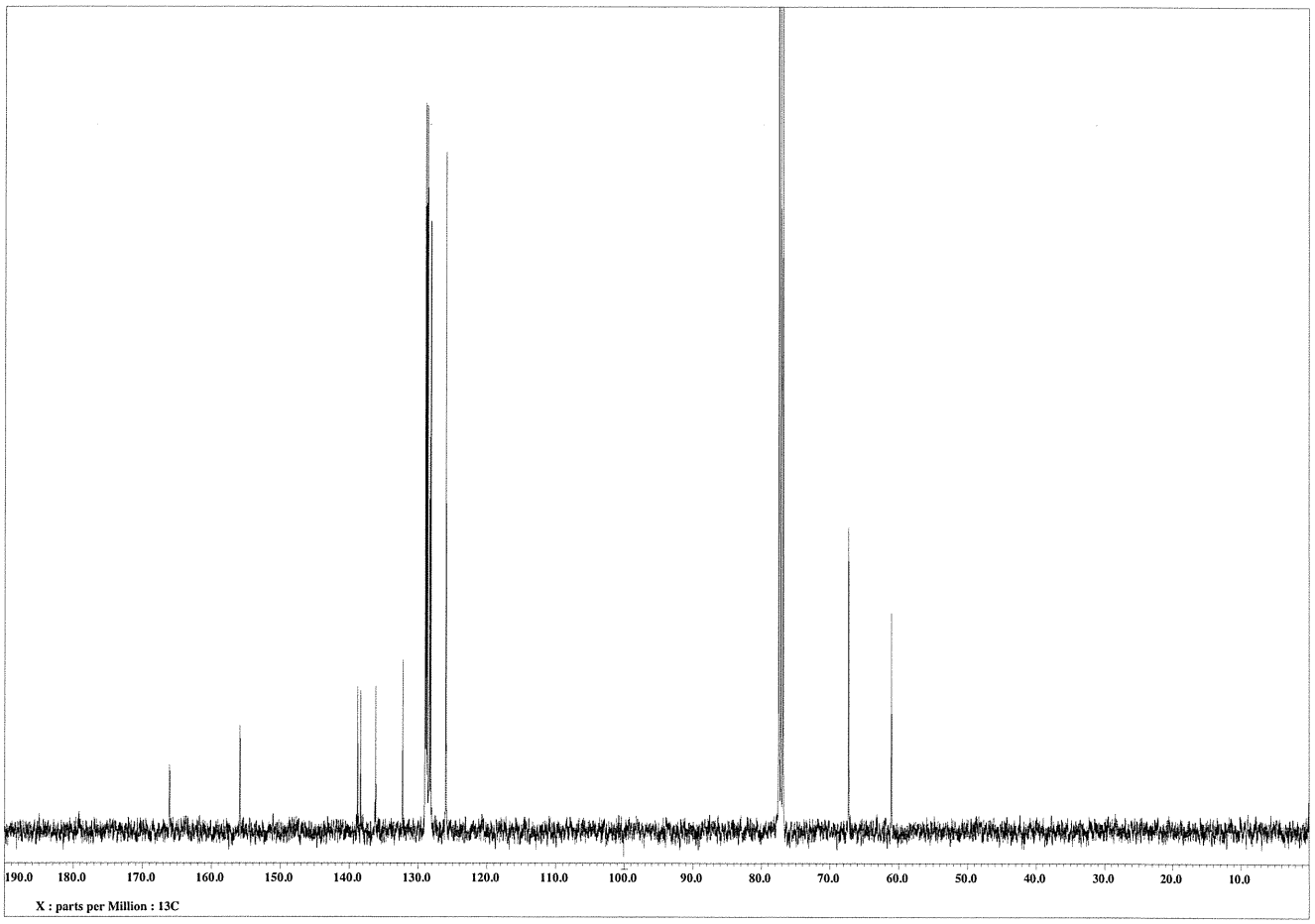
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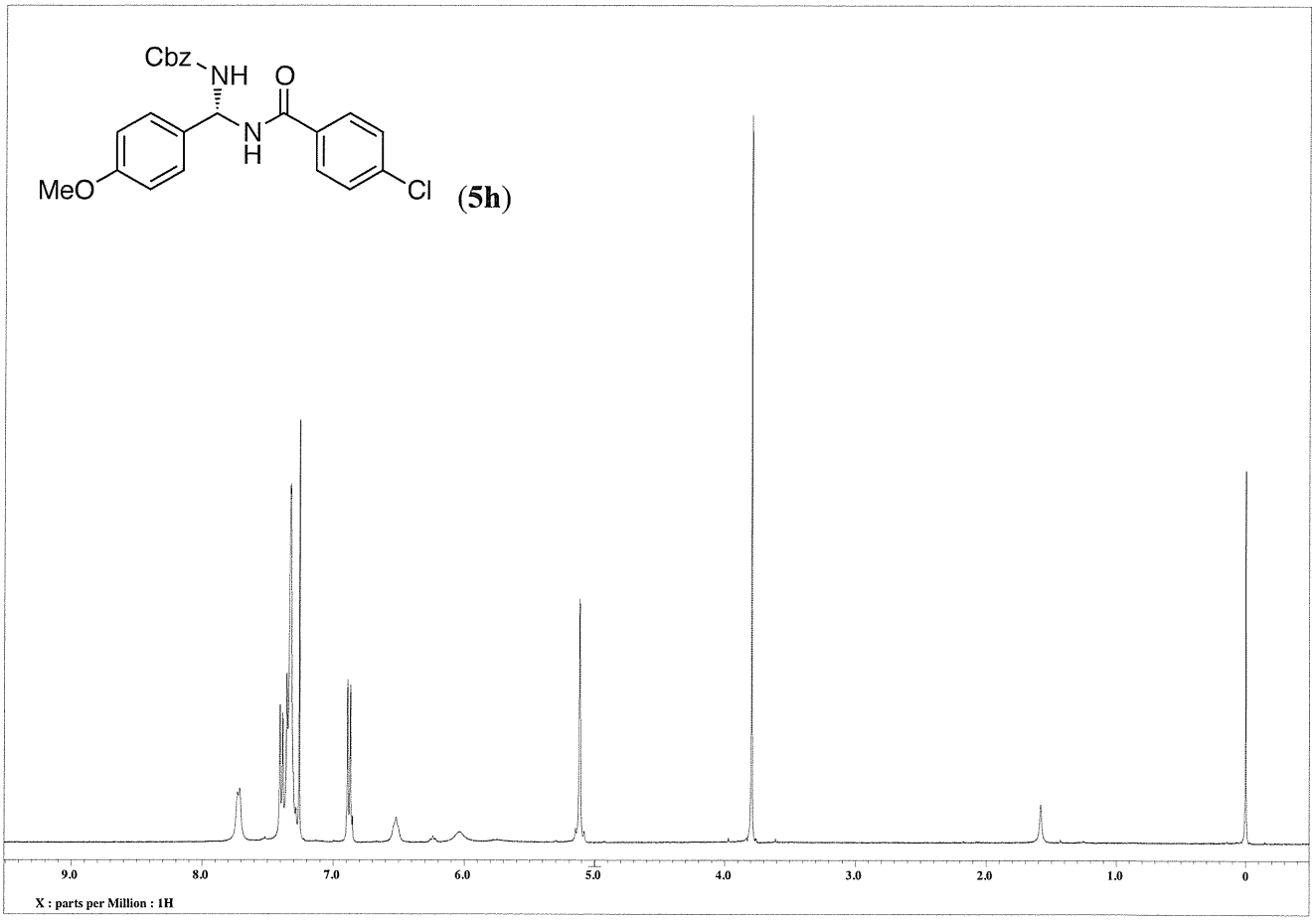
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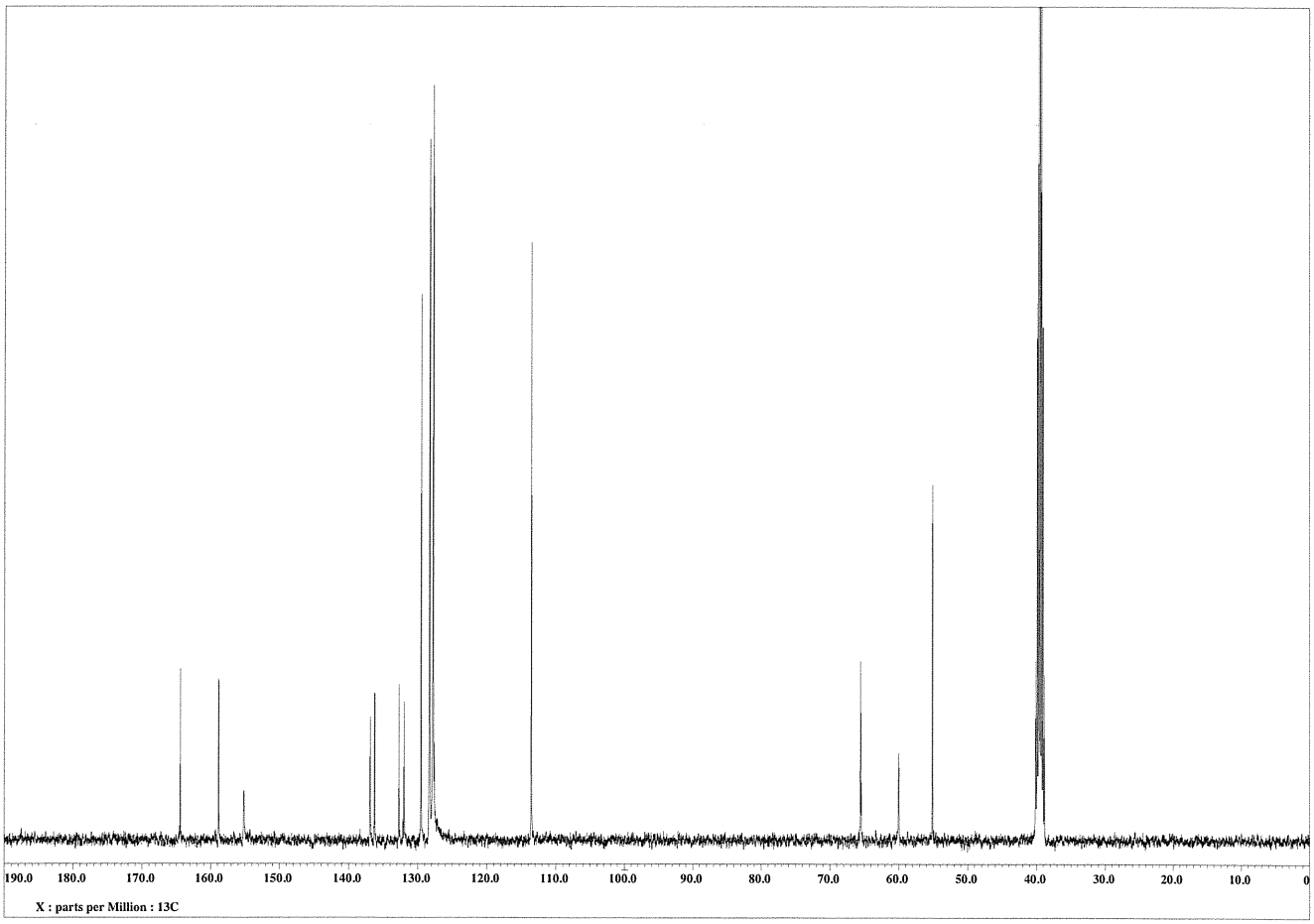
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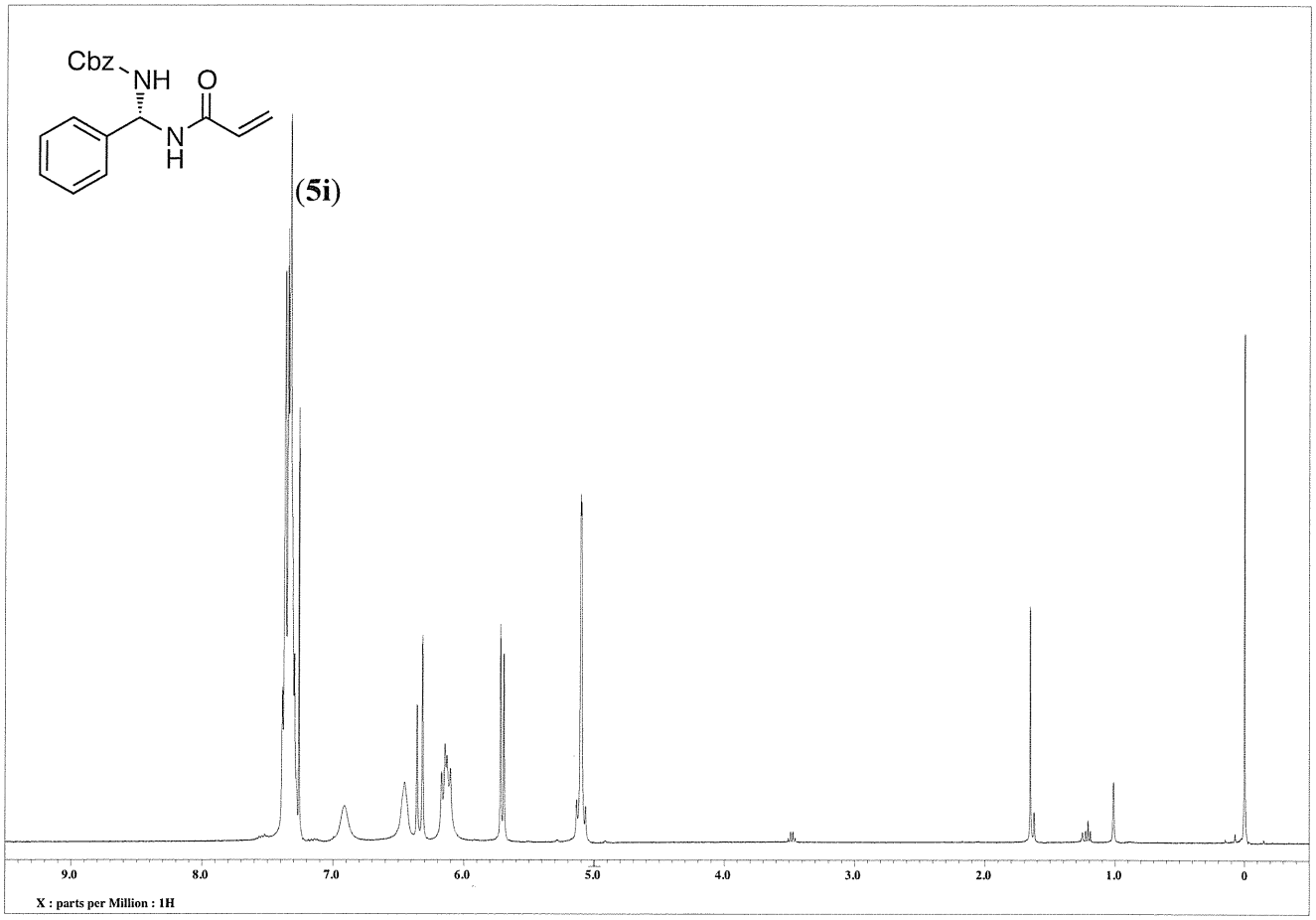
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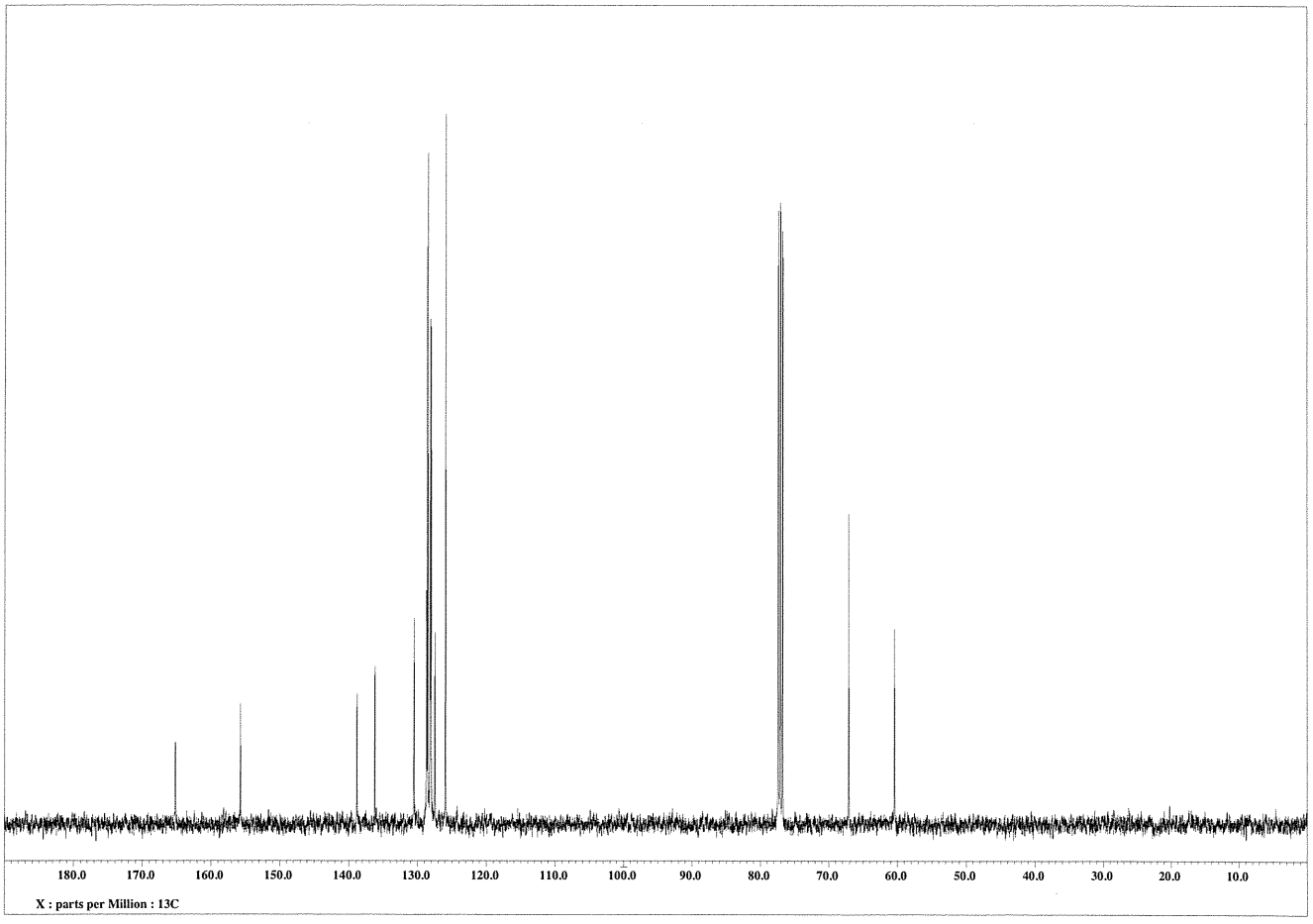
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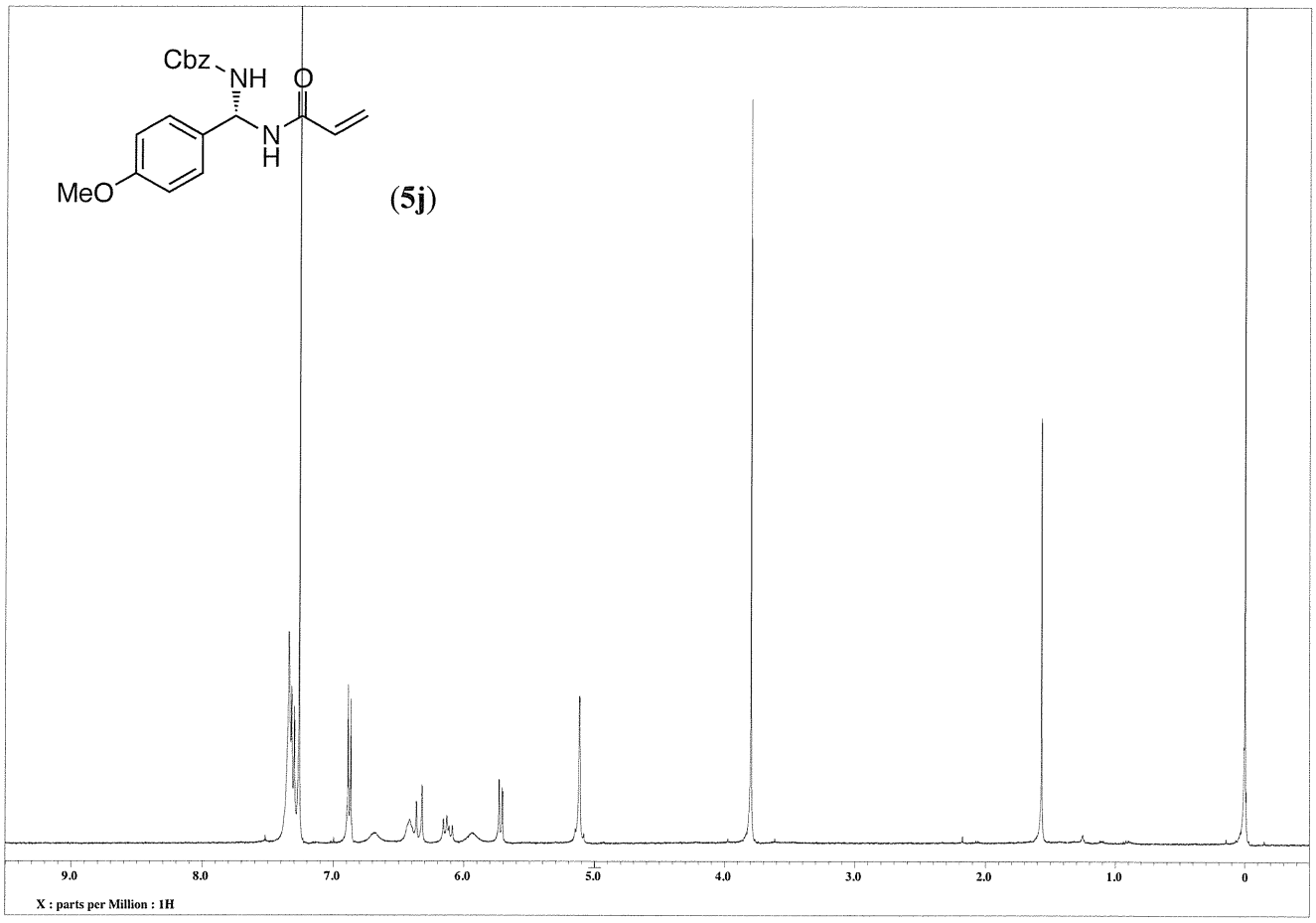
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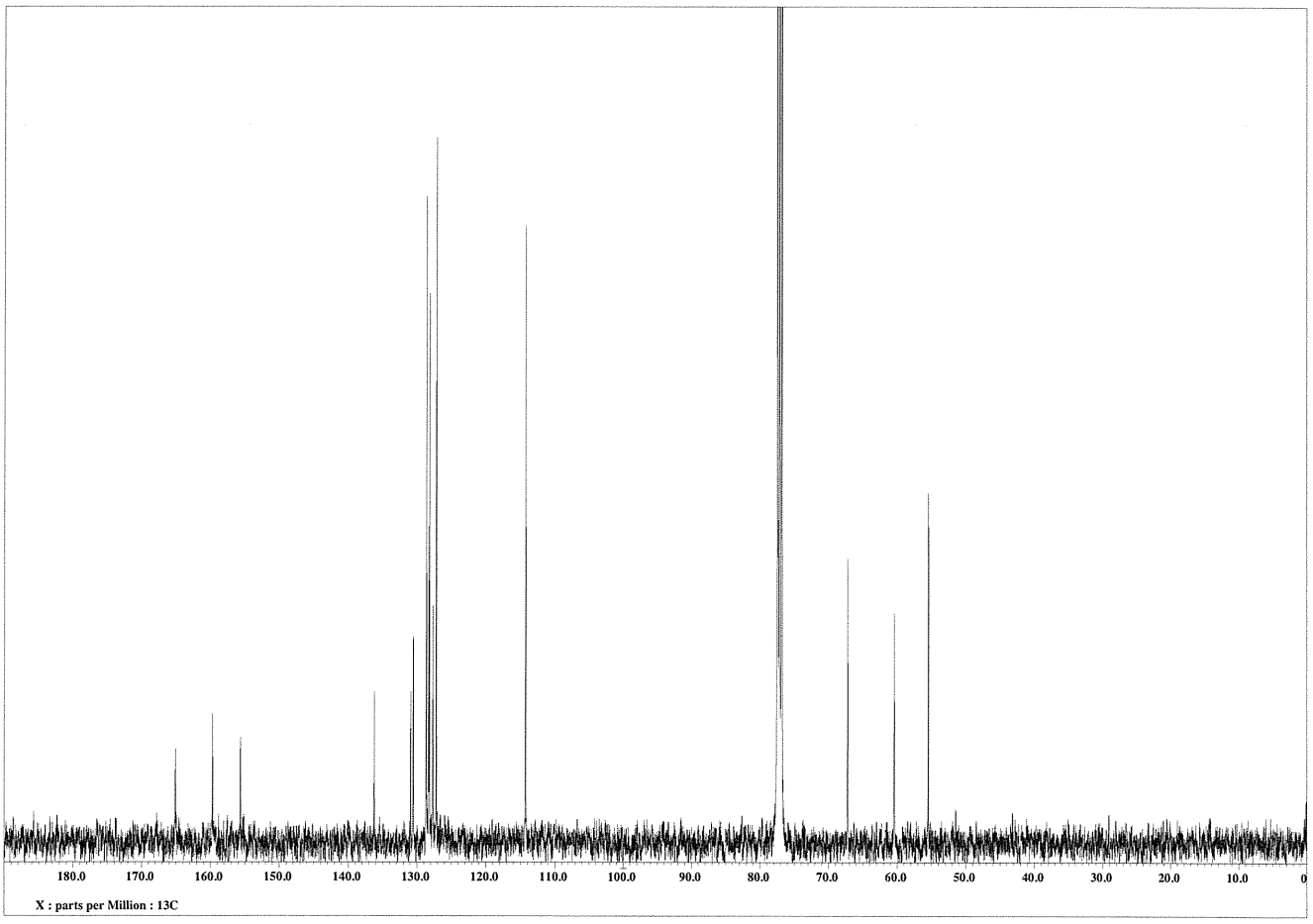
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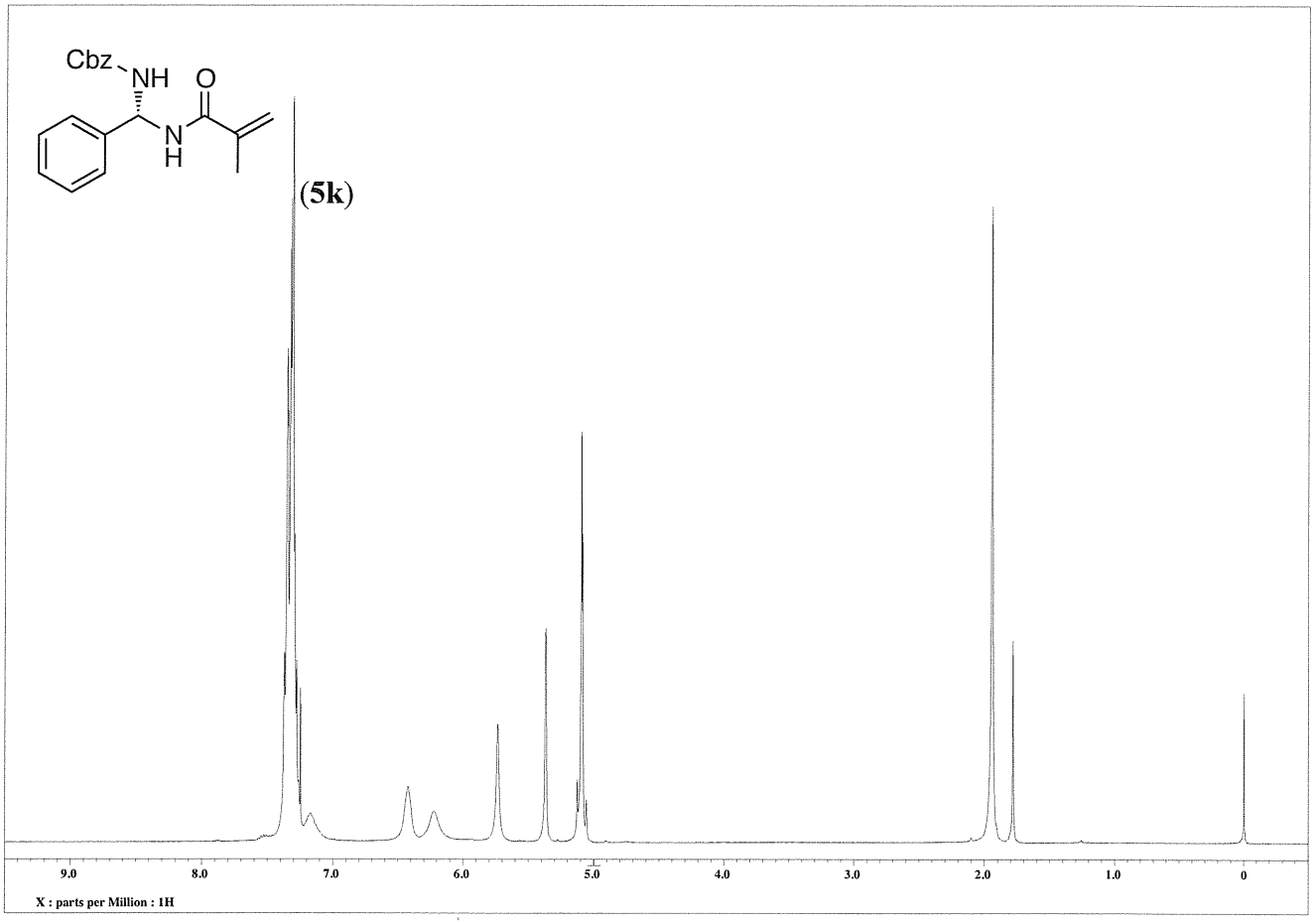
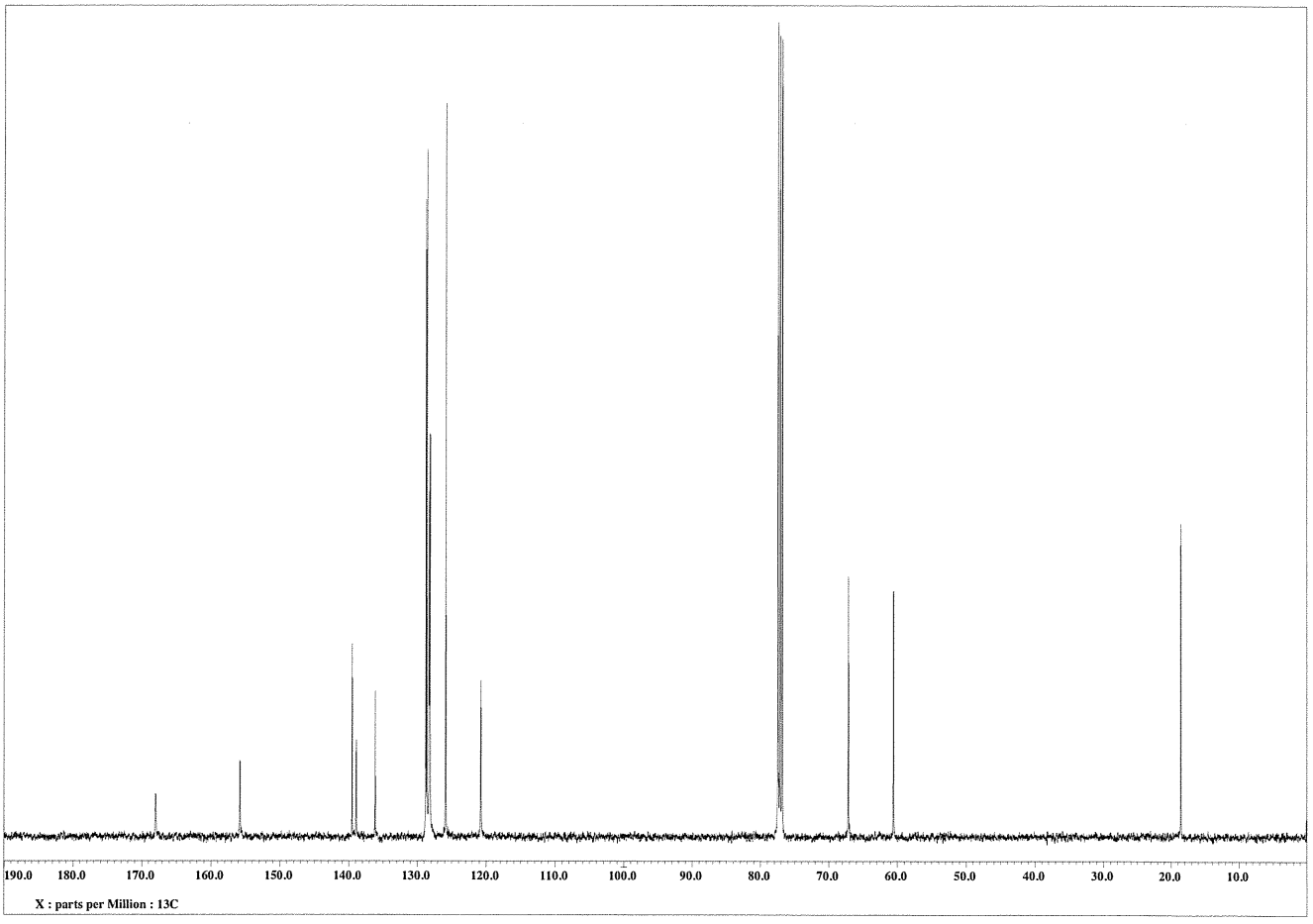
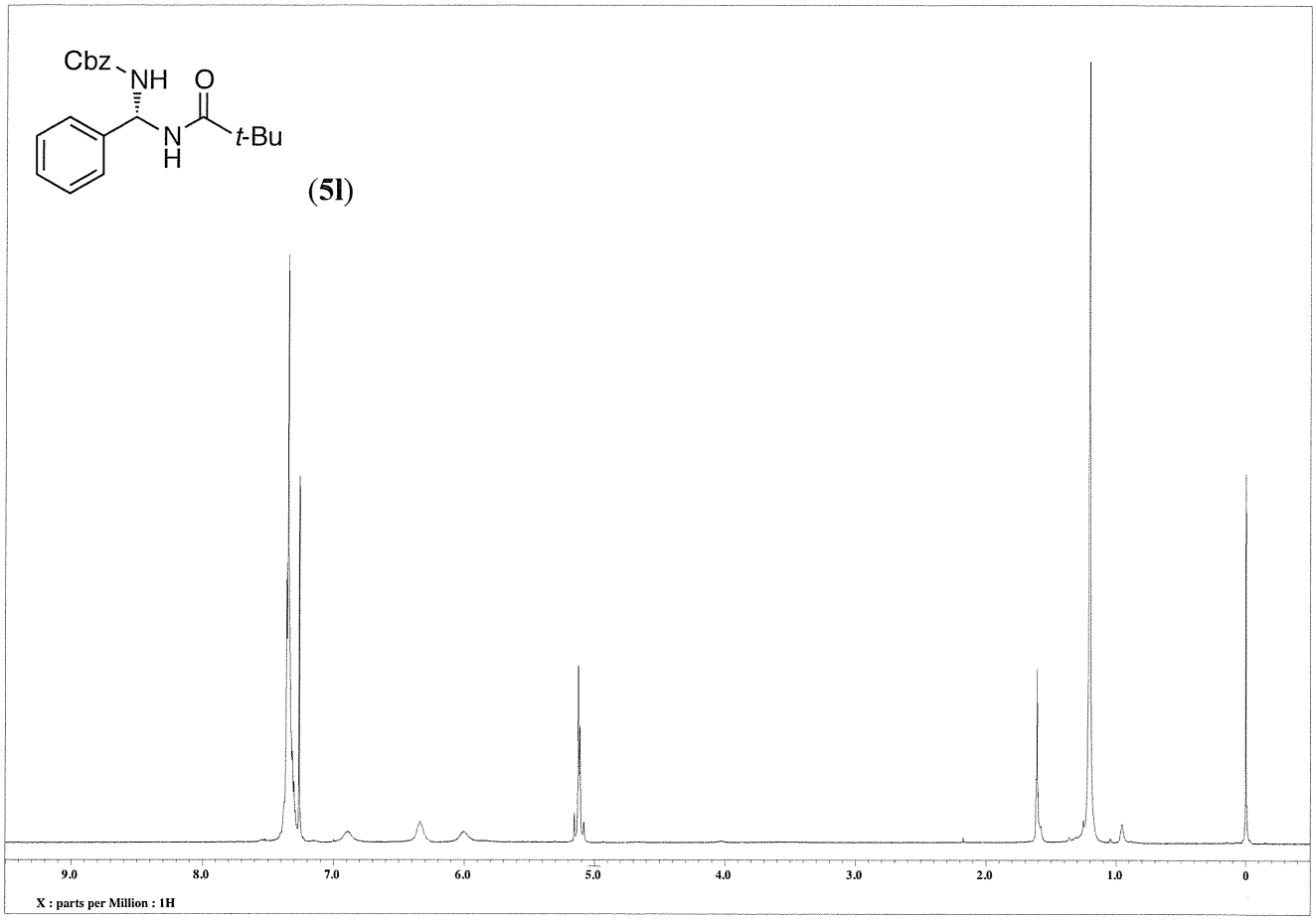
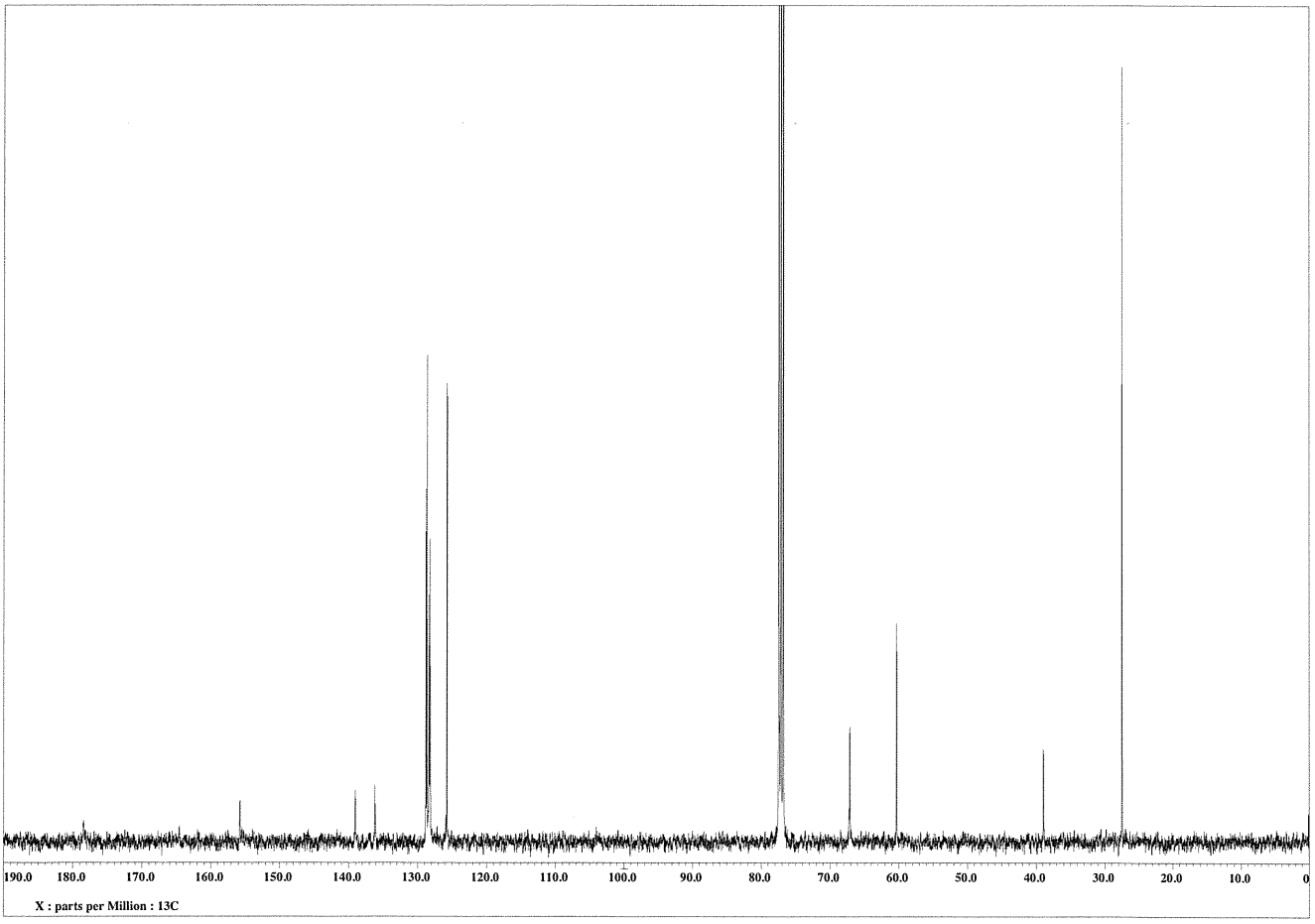
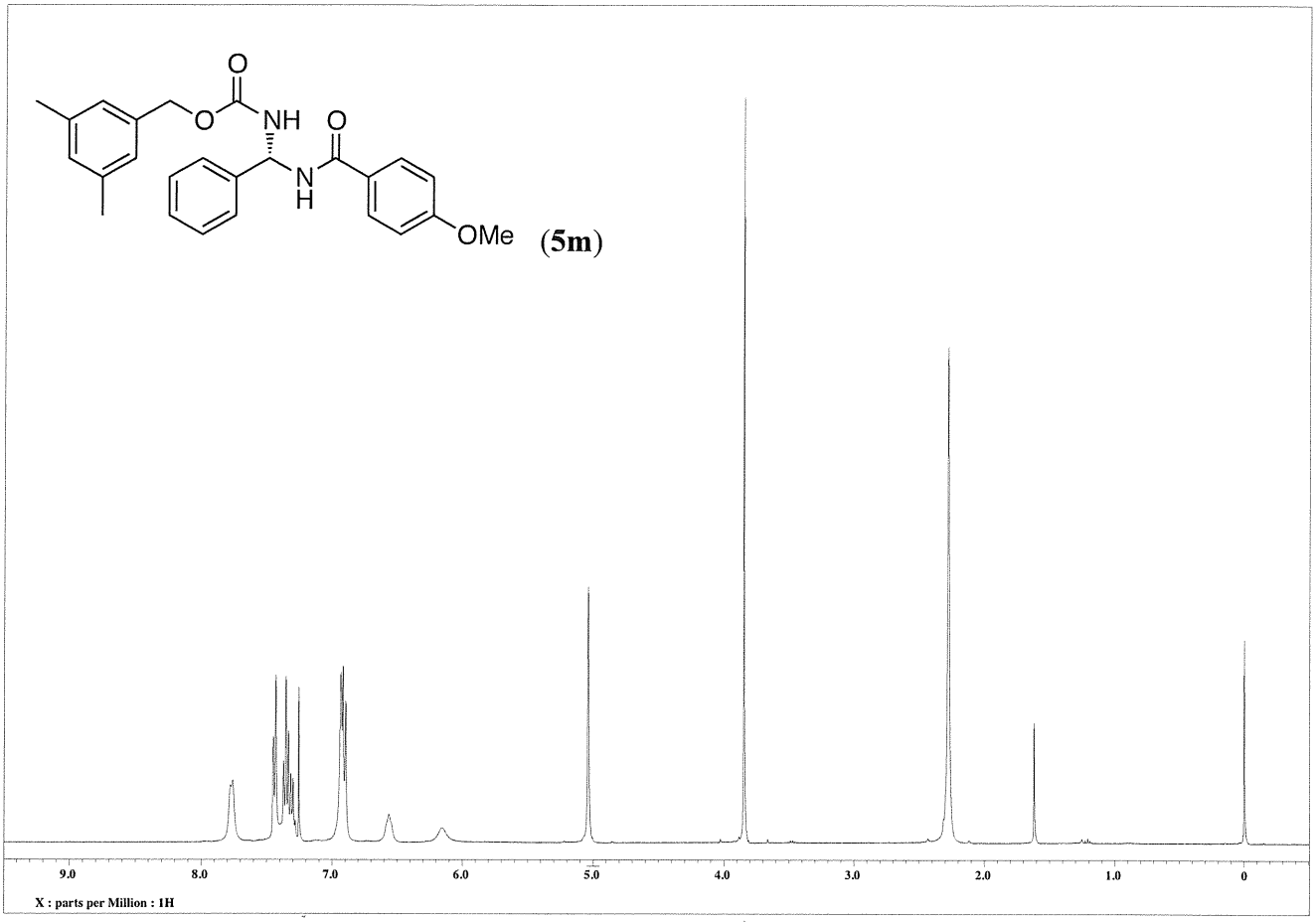
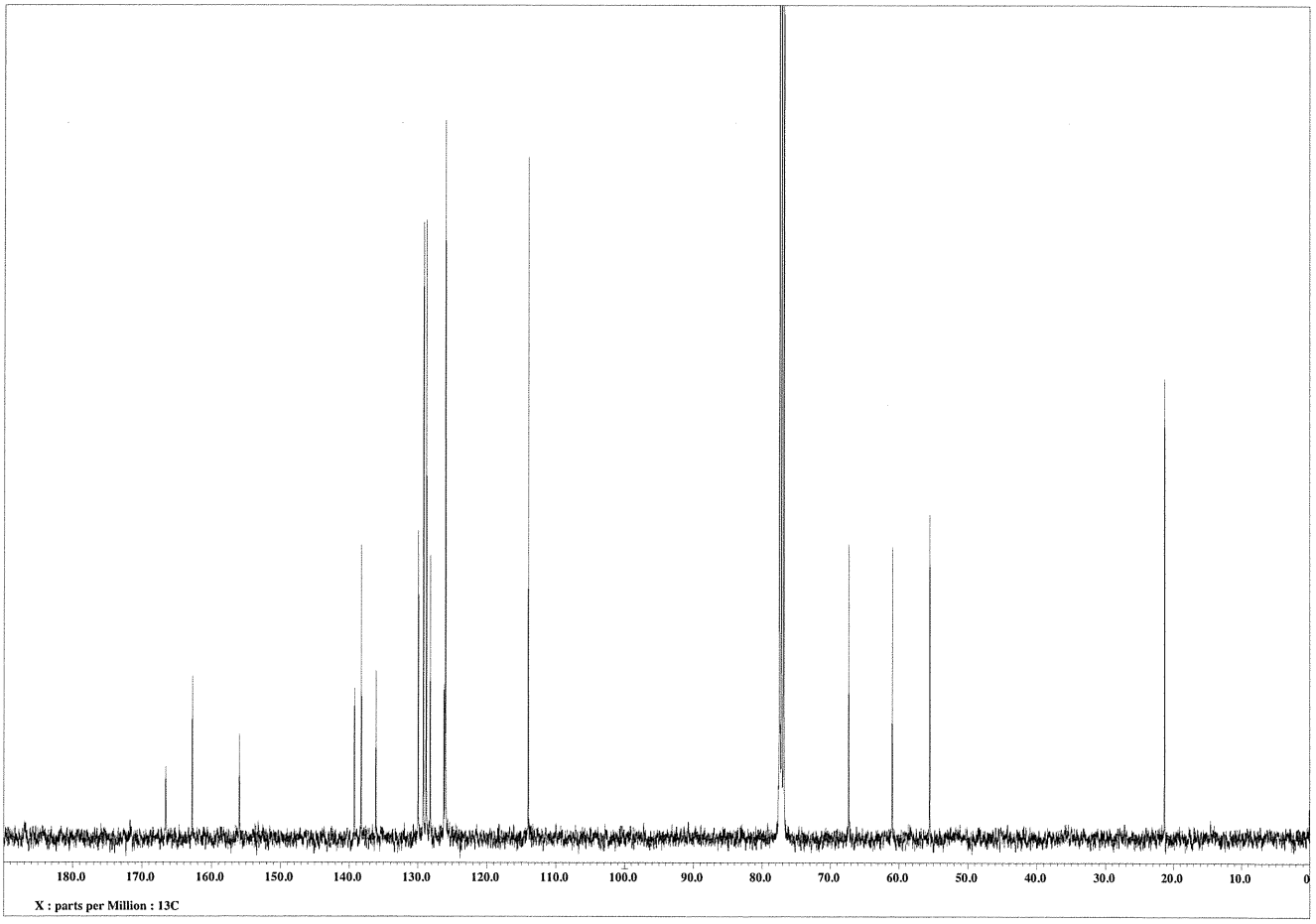

Cbz
NH
O
N
H
(5k)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H

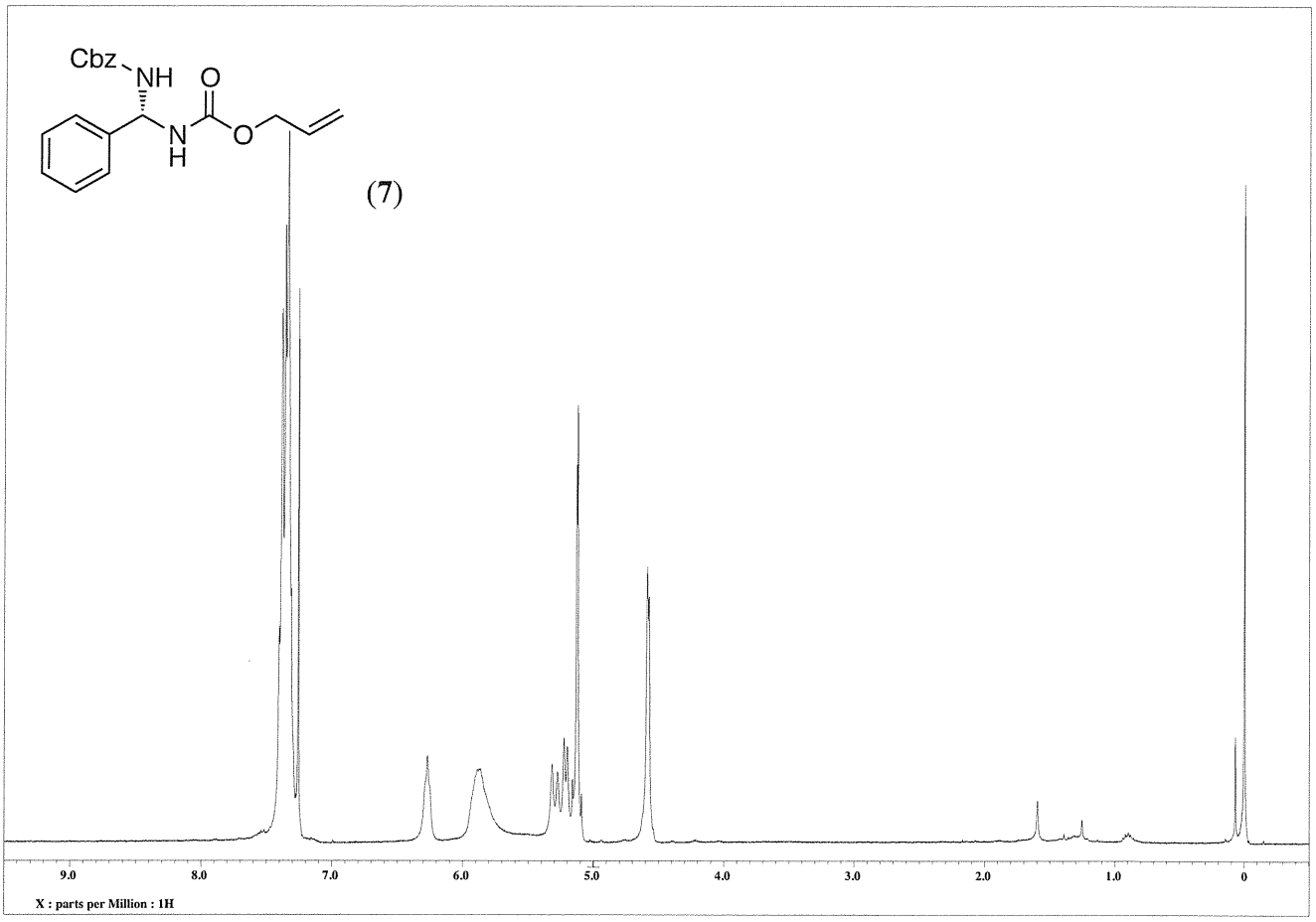

190.0
180.0
170.0
160.0
150.0
140.0
130.0
120.0
110.0
100.0
90.0
80.0
70.0
60.0
50.0
40.0
30.0
20.0
10.0
X : parts per Million : 13C

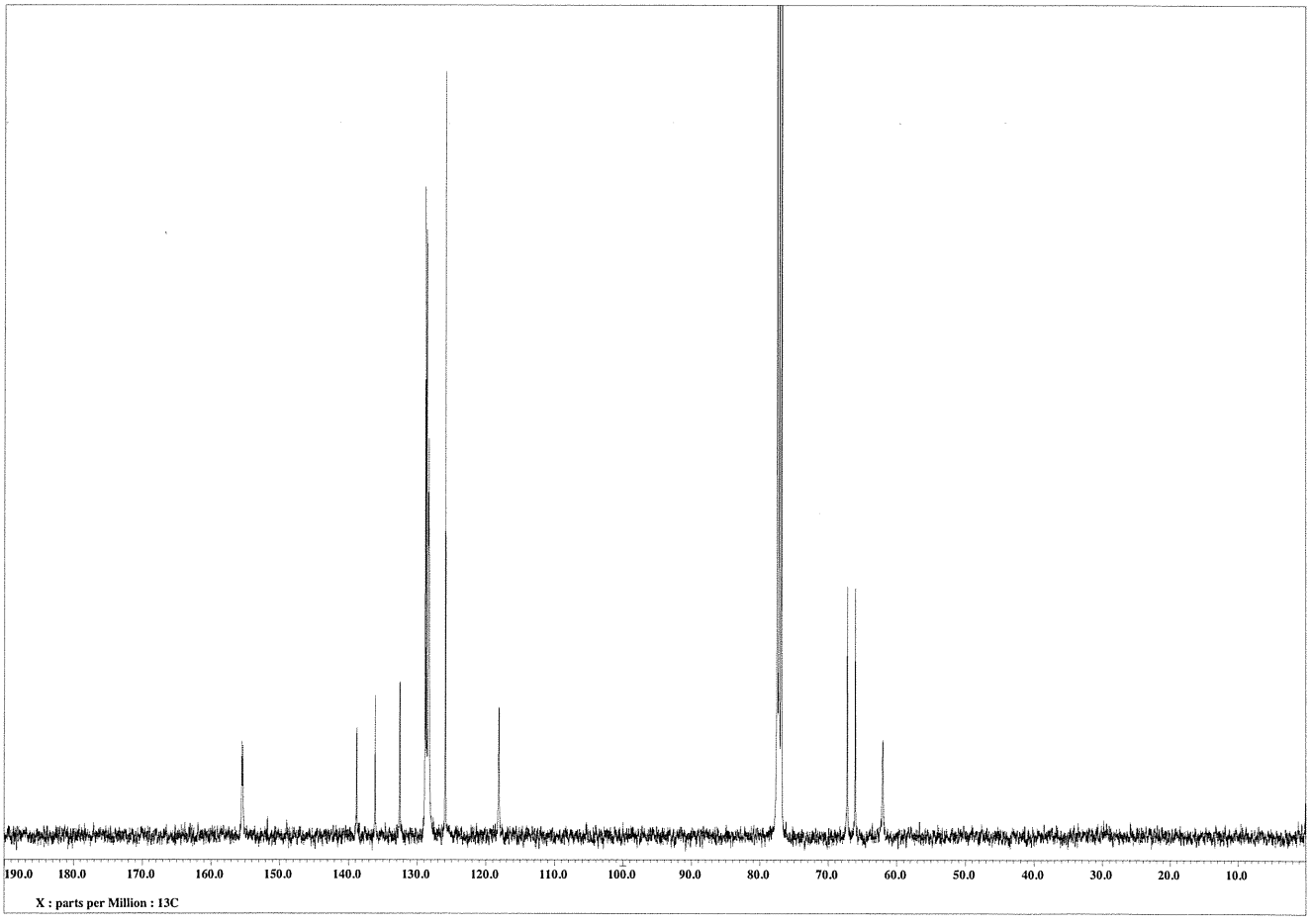

Cbz
NH
O
N
H
t-Bu
(5l)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


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


O
O
NH
O
N
H
OMe
(5m)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


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
X : parts per Million : 13C


Cbz
NH
O
N
H
O
(7)
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
X : parts per Million : 1H


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