

Supporting Information

Hydroxylamines as Oxygen Atom Nucleophiles in Transition Metal-Catalyzed Allylic Substitution

Hideto Miyabe,^a Kazumasa Yoshida,^a Masashige Yamauchi,^b and Yoshiji Takemoto^{a*}

^a Graduate School of Pharmaceutical Sciences, Kyoto University, Yoshida, Sakyo-ku, Kyoto 606-8501, Japan.

FAX: +81-75-753-4569; E-mail: takemoto@pharm.kyoto-u.ac.jp

^b Faculty of Pharmaceutical sciences, Josai University, Keyakidai, Sakado, Saitama 350-0295, Japan.

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1. Experimental procedure

General. Melting points are uncorrected. ¹H and ¹³C NMR spectra were recorded in CDCl₃ at 500 MHz, and at 125 MHz, respectively; Tetramethylsilane (TMS) was used as an internal standard. Low and high resolution mass spectra were obtained by EI, CI or FAB method. Preparative TLC separations were carried out on precoated silica gel plates (E. Merck 60F₂₅₄). Optical rotations were recorded with a path length of 1 cm; concentrations are quoted in mg (2 mL). [α]^D values are measured in 10⁻¹ deg cm² g⁻¹. The ratios of products were determined by ¹H NMR analysis. Enantiomeric excess was determined by high performance liquid chromatography (HPLC) analysis.

General procedure for iridium-catalyzed reaction of 4A-K with carbonate 1a-d. A mixture of **4A-K** (0.50 mmol), allylic carbonate **1a-d** (0.50 mmol), and [IrCl(cod)]₂ (13.4 mg, 0.020 mmol) in MeCN or CH₂Cl₂ (2.5 mL) was stirred under argon atmosphere at 20 °C. After the reaction was completed, the reaction mixture was concentrated under reduced pressure. The ratio of products and combined yield were determined after rough purification by column chromatography (hexane:AcOEt=1:1). Purification of the residue by preparative TLC (hexane:AcOEt=10:1-20:1, 2-fold development) afforded the products **5Aa-Ca** and **6Aa-Dd**.

General procedure for palladium-catalyzed reaction of 4A-K with carbonate 1a. A mixture of **4A-K**, **5Ba**, or **6Ba** (0.50 mmol), allylic carbonate **1a-d** (0.50 or 1.25 mmol), and Pd(PPh₃)₄ (23.1 mg, 0.020 mmol) in MeCN (2.5 mL) was stirred under argon atmosphere at 20 °C. After the reaction was completed, the reaction mixture was concentrated under reduced pressure. The ratio of products and combined yield were determined after rough purification by column chromatography (hexane:AcOEt=1:1). Purification of the residue by preparative TLC (hexane:AcOEt=10:1-25:1, 2-

fold development) afforded the products **7Ba**, **8Aa-Dd**, **9Ba-Ca**, **10**, and **11**.

General procedure for of 4E with carbonate 1a in the presence of Et₂Zn. To a solution of **4E** (0.50 mmol) in CH₂Cl₂ (1.0 mL) was added Et₂Zn (1.0 M in hexane, 0.50 mL, 0.50 mmol) under argon atmosphere at 20 °C. After being stirred at the same temperature for 10 min, a solution of **1a** (0.75 mmol) and [IrCl(cod)]₂ (13.4 mg, 0.020 mmol) or Pd(PPh₃)₄ (23.1 mg, 0.020 mmol) in CH₂Cl₂ (1.0 mL) was added to the reaction mixture at 20 °C. After the reaction was completed, the reaction mixture was diluted with saturated aqueous potassium sodium (+)-tartrate and then extracted with AcOEt. The organic phase was dried over MgSO₄ and concentrated under reduced pressure. Purification of the residue by preparative TLC (hexane:AcOEt=20:1, 2-fold development) afforded the product **6Ea** and **8Ea**.

General procedure for enantioselective reaction of 4D-I with carbonate 3a-d.

A mixture of **4D-I** (1.0 mmol) and Ba(OH)₂·H₂O (139 mg, 1.0 mmol) in PhCF₃ (2.0 mL) and H₂O (2.0 mL) was stirred under argon atmosphere at 20 °C for 10 min. To the reaction mixture was added a solution of **3a-d** (1.5 mmol), pybox (44 mg 0.12 mmol) and [IrCl(cod)]₂ (40 mg, 0.060 mmol) in PhCF₃ (2.0 mL) at 20 °C. After the reaction was completed, the reaction mixture was diluted with saturated aqueous NH₄Cl and then extracted with AcOEt. The organic phase was dried over MgSO₄ and concentrated under reduced pressure. The ratio of products was determined by ¹H NMR analysis of crude products. Purification of the residue by preparative TLC (hexane:AcOEt=10:1-25:1, 2-fold development) afforded the products.

2. Characterization data of all obtained compounds

N-Benzyl-N-hydroxy-1-phenylprop-2-en-1-amine (5Aa**).¹⁾**

A colorless oil. IR (CHCl₃) 3387, 1741, 1710, 1440 cm⁻¹. ¹H NMR (CDCl₃) δ 7.44-7.23 (10H, m), 6.15 (1H, m), 5.27 (1H, d, *J*=17.4 Hz), 5.22 (1H, d, *J*=10.4 Hz), 4.80 (1H, br s), 4.25 (1H, d, *J*=8.8 Hz), 3.84 (1H, br d, *J*=13.5 Hz), 3.74 (1H, d, *J*=13.5 Hz). ¹³C NMR (CDCl₃) δ 141.1, 138.2, 137.9, 129.3, 128.6, 128.2, 128.0, 127.4, 127.2, 117.7, 75.7, 61.2. MS (Cl⁺) m/z: 240 (M+H⁺, 100). HRMS calcd for C₁₆H₁₈NO (M+H⁺): 240.1388, Found: 240.1382.

tert-Butyl [N-hydroxy-N-(1-phenylallyl)]carbamate (5Ba**).**

A colorless oil. IR (CHCl₃) 3386, 1697, 1453, 1369 cm⁻¹. ¹H NMR (CDCl₃) δ 7.41-7.26 (5H, m), 6.35 (1H, br m), 6.23 (1H, m), 5.61 (1H, d, *J*=6.7 Hz), 5.35 (1H, d, *J*=10.4 Hz), 5.39 (1H, d, *J*=17.4 Hz), 1.46 (9H, s). ¹³C NMR (CDCl₃) δ 157.1, 138.3, 134.5, 128.3, 127.9, 127.6, 118.4, 82.4, 65.2, 28.3. MS (Cl⁺) m/z: 250 (M+H⁺, 40), 194 (100). HRMS calcd for C₁₄H₂₀NO₃ (M+H⁺): 250.1443, Found: 250.1448.

Benzyl [N-hydroxy-N-(1-phenylallyl)]carbamate (5Ca**).**

A colorless oil. IR (CHCl₃) 3530, 1710, 1496, 1453, 1395 cm⁻¹. ¹H NMR (CDCl₃) δ 7.38-7.25 (10H, m), 6.21 (1H, m), 5.73 (1H, d, *J*=6.4 Hz), 5.35 (1H, d, *J*=10.4 Hz), 5.29 (1H, d, *J*=17.4 Hz), 5.19 (2H, s), 4.66 (1H, br s). ¹³C NMR (CDCl₃) δ 157.3, 137.8, 135.7, 134.0, 128.5 (2C), 128.3, 128.1, 128.0, 127.8, 118.8, 68.2, 64.9. MS (Cl⁺) m/z: 284 (M+H⁺, 100). HRMS calcd for C₁₇H₁₈NO₃ (M+H⁺): 284.1287, Found: 284.1293.

tert-Butyl [N-(1-phenylallyloxy)]carbamate (6Ba**).**

A colorless oil. IR (CHCl₃) 3387, 1741, 1440, 1369 cm⁻¹. ¹H NMR (CDCl₃) δ 7.42-7.30 (5H, m),

7.03 (1H, br s), 6.08 (1H, m), 5.33 (1H, d, $J=10.1$ Hz), 5.32 (1H, d, $J=18.0$ Hz), 5.23 (1H, d, $J=7.0$ Hz), 1.47 (9H, s). ^{13}C NMR (CDCl_3) δ 156.4, 138.6, 136.0, 128.5, 128.4, 127.6, 119.2, 88.2, 81.6, 28.2. MS (Cl^+) m/z: 250 ($\text{M}+\text{H}^+$, 35), 194 (100). HRMS calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_3$ ($\text{M}+\text{H}^+$): 205.1443, Found: 250.1446.

Benzyl [*N*-(1-phenylallyloxy)]carbamate (6Ca).

A colorless oil. IR (CHCl_3) 3390, 1748, 1453, 1335 cm^{-1} . ^1H NMR (CDCl_3) δ 7.40-7.30 (10H, m), 6.08 (1H, m), 5.33 (1H, d, $J=10.4$ Hz), 5.31 (1H, d, $J=17.1$ Hz), 5.24 (1H, d, $J=7.0$ Hz), 5.17 (2H, s). ^{13}C NMR (CDCl_3) δ 157.3, 138.2, 135.7, 128.6 (2C), 128.5, 128.4, 128.2, 127.6, 119.6, 88.6, 67.5. One carbon peak was missing due to overlapping. MS (Cl^+) m/z: 284 ($\text{M}+\text{H}^+$, 10), 117 (100). HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_3$ ($\text{M}+\text{H}^+$): 284.1287, Found: 284.1285.

***N*-(1-Phenylallyloxy)-*N*-phenylbenzamide (6Da).**

A colorless oil. IR (CHCl_3) 3490, 1653, 1491, 1362 cm^{-1} . ^1H NMR (CDCl_3) δ 7.53 (2H, d, $J=7.0$ Hz), 7.44-7.13 (14H, m), 5.89 (1H, m), 5.28 (1H, d, $J=10.1$ Hz), 5.27 (1H, d, $J=16.8$ Hz). ^{13}C NMR (CDCl_3) δ 168.7, 140.2, 137.5, 135.7, 135.1, 130.3, 128.9, 128.8, 128.6, 128.4, 127.9, 127.7, 126.9, 125.1, 120.2, 86.8. MS (FAB^+) m/z: 330 ($\text{M}+\text{H}^+$, 22), 117 (100). HRMS calcd for $\text{C}_{22}\text{H}_{20}\text{NO}_2$ ($\text{M}+\text{H}^+$): 330.1494, Found: 330.1488. HPLC (Chiralcel AD-H, hexane/2-propanol=90/10, 0.5 ml/min 254 nm) t_r (*S*) = 24.9 min, t_r (*R*) = 26.9 min. A sample of 88%ee (*S*) by HPLC analysis gave $[\alpha]^{25}_D -20.9$ (*c* 1.8, CHCl_3).

***N*-(1-Phenylallyloxy)-*N*-benzyl(phenyl)methanamine (6Ea).**

A colorless oil. ^1H NMR (CDCl_3) δ 7.35-7.17 (13H, m), 7.13 (2H, br d, $J=6.4$ Hz), 5.76 (1H, ddd, $J=17.1$, 10.4, 7.3 Hz), 5.06 (1H, d, $J=10.4$ Hz), 5.00 (1H, d, $J=17.1$ Hz), 4.55 (1H, d, $J=7.3$ Hz), 3.81 (4H, s). ^{13}C NMR (CDCl_3) δ 140.6, 138.0, 137.8, 129.8, 128.2, 128.1, 127.8, 127.6, 127.2, 117.0, 85.9, 62.6. MS (EI^+) m/z: 329 (M^+ , 1), 117 (100). HRMS calcd for $\text{C}_{23}\text{H}_{23}\text{NO}$: 329.1780, Found: 329.1776.

***N*-(1-Phenylallyloxy)-*N*-phenylacetamide (6Fa).**

A colorless oil. IR (CHCl_3) 1669, 1495, 1376 cm^{-1} . ^1H NMR (CDCl_3) δ 7.47-7.18 (10H, m), 6.11 (1H, m), 5.35 (1H, d, $J=10.4$ Hz), 5.32 (1H, d, $J=17.9$ Hz), 5.17 (1H, br d, $J=4.9$ Hz). ^{13}C NMR (CDCl_3) δ 170.7, 139.0, 137.3, 135.0, 128.7, 128.5, 128.4, 127.8, 126.7, 124.2, 120.4, 85.9, 22.0. MS (EI^+) m/z: 267 (M^+ , 0.4), 93 (100). HRMS calcd for $\text{C}_{17}\text{H}_{17}\text{NO}_2$: 267.1259, Found: 267.1252. HPLC (Chiralcel AD-H, hexane/2-propanol=90/10, 0.5 ml/min 254 nm) t_r (*S*) = 13.8 min, t_r (*R*) = 15.8 min. A sample of 82%ee (*S*) by HPLC analysis gave $[\alpha]^{25}_D -14.1$ (*c* 0.4, CHCl_3).

Benzyl [*N*-(1-phenylallyloxy)-*N*-phenyl]carbamate (6Ga).

A colorless oil. IR (CHCl_3) 1710, 1338 cm^{-1} . ^1H NMR (CDCl_3) δ 7.41-7.25 (15H, m), 6.06 (1H, m), 5.30-5.16 (5H, m). ^{13}C NMR (CDCl_3) δ 155.1, 140.7, 137.9, 136.0, 135.9, 128.5 (2C), 128.4, 128.2, 128.1, 127.9, 126.1, 123.3, 119.9, 87.5, 67.9. One carbon peak was missing due to overlapping. MS (EI^+) m/z: 359 (M^+ , 1), 117 (100). HRMS calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_3$: 359.1521, Found: 359.1518. HPLC (Chiralcel AD-H, hexane/2-propanol=90/10, 0.5 ml/min 254 nm) t_r (*S*) = 15.6 min, t_r (*R*) = 17.5 min. A sample of 68%ee (*S*) by HPLC analysis gave $[\alpha]^{24}_D -0.2$ (*c* 0.9, CHCl_3).

***N*-(1-Phenylallyloxy)-*N*-benzylacetamide (6Ha).**

A colorless oil. IR (CHCl_3) 1655, 1396 cm^{-1} . ^1H NMR (CDCl_3) δ 7.39-7.20 (10H, m), 6.07 (1H,

ddd, $J=17.1, 10.4, 6.4$ Hz), 5.31 (1H, d, $J=10.4$ Hz), 5.25 (1H, d, $J=17.1$ Hz), 5.16 (1H, br d, $J=6.4$ Hz), 4.83 (1H, d, $J=15.6$ Hz), 4.58 (1H, d, $J=15.6$ Hz), 2.09 (3H, s). ^{13}C NMR (CDCl_3) δ 173.5, 138.0, 136.5, 135.5, 128.7, 128.6, 128.4, 127.6, 127.4, 119.7, 87.4, 50.7, 21.0. One carbon peak was missing due to overlapping. MS (Cl^+) m/z: 282 ($\text{M}+\text{H}^+$, 11), 117 (100). HRMS calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_2$ ($\text{M}+\text{H}^+$): 282.1494, Found: 282.1487. HPLC (Chiralcel AD-H, hexane/2-propanol=90/10, 0.5 ml/min 254 nm) t_r (S) = 21.4 min, t_r (R) = 25.8 min. A sample of 82%ee (S) by HPLC analysis gave $[\alpha]^{25}_D -11.5$ (c 1.0, CHCl_3).

***N*-(1-Phenylallyloxy)-*N*-benzylbenzamide (6Ia).**

A colorless oil. IR (CHCl_3) 1635, 1450, 1405 cm^{-1} . ^1H NMR (CDCl_3) δ 7.59 (2H, d, $J=7.3$ Hz), 7.46-7.21 (11H, m), 7.09 (2H, m), 5.72 (1H, m), 5.17 (1H, d, $J=10.4$ Hz), 5.11 (1H, d, $J=17.1$ Hz), 5.06 (1H, br d, $J=7.0$ Hz), 4.93 (1H, d, $J=15.3$ Hz), 4.65 (1H, d, $J=15.3$ Hz). ^{13}C NMR (CDCl_3) δ 170.7, 137.7, 136.4, 135.5, 134.7, 130.4, 128.6, 128.5, 128.4, 128.3, 127.9, 127.8, 127.6, 119.9, 87.6, 52.4. One carbon peak was missing due to overlapping. MS (Cl^+) m/z: 344 ($\text{M}+\text{H}^+$, 3), 117 (100). HRMS calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_2$ ($\text{M}+\text{H}^+$): 344.1650, Found: 344.1647. HPLC (Chiralcel AD-H, hexane/2-propanol=90/10, 0.5 ml/min 254 nm) t_r (S) = 32.5 min, t_r (R) = 35.2 min. A sample of 87%ee (S) by HPLC analysis gave $[\alpha]^{26}_D -25.9$ (c 0.9, CHCl_3).

2-(1-Phenylallyloxy)isoindoline-1,3-dione (6Ja).

A colorless crystal. mp 91-93 °C (AcOEt/hexane). IR (CHCl_3) 1733, 1374 cm^{-1} . ^1H NMR (CDCl_3) δ 7.81 (2H, m), 7.72 (2H, m), 7.57 (2H, br d, $J=7.6$ Hz), 7.44-7.31 (3H, m), 6.27 (1H, m), 5.76 (1H, d, $J=8.5$ Hz), 5.38 (1H, d, $J=17.1$ Hz), 5.34 (1H, d, $J=10.4$ Hz). ^{13}C NMR (CDCl_3) δ 163.9, 136.9, 135.2, 134.4, 129.1, 128.8, 128.6, 127.9, 123.5, 121.5, 90.0. MS (FAB^+) m/z: 280 ($\text{M}+\text{H}^+$, 6), 117 (100). HRMS calcd for $\text{C}_{17}\text{H}_{14}\text{NO}_3$ ($\text{M}+\text{H}^+$): 280.0974, Found: 280.0980. Anal. Calcd for $\text{C}_{17}\text{H}_{13}\text{NO}_3$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.14; H, 4.59; N, 4.86.

1-(1-Phenylallyloxy)pyrrolidine-2,5-dione (6Ka).

A colorless crystal. mp 115-117 °C (AcOEt/hexane). IR (CHCl_3) 1727, 1373 cm^{-1} . ^1H NMR (CDCl_3) δ 7.50 (2H, br d, $J=7.3$ Hz), 7.41-7.33 (3H, m), 6.18 (1H, m), 5.73 (1H, d, $J=8.5$ Hz), 5.38 (1H, d, $J=12.8$ Hz), 5.36 (1H, d, $J=5.8$ Hz), 2.63 (4H, s). ^{13}C NMR (CDCl_3) δ 171.5, 136.5, 135.1, 129.2, 128.6, 127.9, 121.3, 88.8, 25.3. MS (FAB^+) m/z: 232 ($\text{M}+\text{H}^+$, 4), 117 (100). HRMS calcd for $\text{C}_{13}\text{H}_{14}\text{NO}_3$ ($\text{M}+\text{H}^+$): 232.0974, Found: 232.0979. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{NO}_3$: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.67; H, 5.76; N, 6.05.

***N*-(1-(4-Fluorophenyl)allyloxy)-*N*-phenylbenzamide (6Db).**

A colorless oil. IR (CHCl_3) 1654, 1604, 1510, 1489, 1360 cm^{-1} . ^1H NMR (CDCl_3) δ 7.50 (2H, d, $J=7.3$ Hz), 7.43-7.12 (10H, m), 6.94 (2H, br t, $J=8.9$ Hz), 5.90 (1H, m), 5.35-5.24 (3H, m). ^{13}C NMR (CDCl_3) δ 168.6, 162.8 (d, $J=247$ Hz), 140.2, 135.5, 134.9, 133.4, 130.4, 129.8 (d, $J=9.3$ Hz), 128.9, 128.8, 127.8, 127.1, 125.2, 120.2, 115.3 (d, $J=21.7$ Hz), 86.0. MS (Cl^+) m/z: 348 ($\text{M}+\text{H}^+$, 1), 135 (100). HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{FNO}_2$ ($\text{M}+\text{H}^+$): 348.1400, Found: 348.1398. HPLC (Chiralcel AD-H, hexane/2-propanol=95/5, 0.5 ml/min 254 nm) t_r (S) = 47.7 min, t_r (R) = 49.9 min. A sample of 62%ee (S) by HPLC analysis gave $[\alpha]^{25}_D -20.0$ (c 1.3, CHCl_3).

***N*-(1-p-Tolylallyloxy)-*N*-phenylbenzamide (6Dc).**

A colorless oil. IR (CHCl_3) 1653, 1591, 1489, 1360 cm^{-1} . ^1H NMR (CDCl_3) δ 7.55 (2H, d, $J=7.0$ Hz), 7.43 (2H, d, $J=7.6$ Hz), 7.39-7.18 (6H, m), 7.08-7.02 (4H, m), 5.87 (1H, m), 5.27-5.20 (3H, m), 2.31 (3H, s). ^{13}C NMR (CDCl_3) δ 168.7, 140.1, 138.5, 135.7, 135.2, 134.5, 130.2, 129.1, 128.9,

128.8, 127.9, 127.7, 126.8, 124.9, 120.0, 86.6, 21.1. MS (Cl^+) m/z: 344 ($\text{M}+\text{H}^+$, 1), 131 (100). HRMS calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_2$ ($\text{M}+\text{H}^+$): 344.1650, Found: 344.1646. HPLC (Chiralcel AD-H, hexane/2-propanol=90/10, 0.5 ml/min 254 nm) t_r (*S*) = 27.3 min, t_r (*R*) = 35.6 min. A sample of 72%ee (*S*) by HPLC analysis gave $[\alpha]^{25}_D$ -12.6 (*c* 1.8, CHCl_3).

N-(1-(Naphthalen-1-yl)allyloxy)-N-phenylbenzamide (6Dd).

A colorless oil. IR (CHCl_3) 1653, 1598, 1495, 1353 cm^{-1} . ^1H NMR (CDCl_3) δ 7.98 (1H, d, J =8.2 Hz), 7.83-7.76 (2H, m), 7.51 (2H, d, J =7.0 Hz), 7.45-7.15 (12H, m), 6.17 (1H, m), 6.04 (1H, d, J =7.9 Hz), 5.36 (1H, d, J =17.1 Hz), 5.32 (1H, d, J =10.4 Hz). ^{13}C NMR (CDCl_3) δ 168.8, 140.2, 135.8, 135.1, 133.8, 133.6, 131.0, 130.3, 129.3, 128.8, 128.6, 127.8, 127.1, 126.4, 126.2, 125.7, 125.5, 125.1, 124.0, 120.5, 84.6. One carbon peak was missing due to overlapping. MS (Cl^+) m/z: 380 ($\text{M}+\text{H}^+$, 1), 167 (100). HRMS calcd for $\text{C}_{26}\text{H}_{22}\text{NO}_2$ ($\text{M}+\text{H}^+$): 380.1650, Found: 380.1648. HPLC (Chiralcel AD-H, hexane/2-propanol=90/10, 0.5 ml/min 254 nm) t_r (*S*) = 24.9 min, t_r (*R*) = 28.7 min. A sample of 78%ee (*S*) by HPLC analysis gave $[\alpha]^{25}_D$ -5.9 (*c* 1.7, CHCl_3).

tert-Butyl (*N*-cinnamyl-*N*-hydroxy)carbamate (7Ba).

A colorless oil. IR (CHCl_3) 3258, 1693, 1369 cm^{-1} . ^1H NMR (CDCl_3) δ 7.37 (2H, d, J =7.6 Hz), 7.30 (2H, d, J =7.7 Hz), 7.23 (1H, m), 7.20 (1H, br s), 6.57 (1H, d, J =15.9 Hz), 6.25 (1H, dt, J =15.9, 6.1 Hz), 4.22 (2H, d, J =6.1 Hz), 1.47 (9H, s). ^{13}C NMR (CDCl_3) δ 157.3, 136.7, 133.4, 128.5, 127.7, 126.5, 123.5, 82.1, 52.8, 28.2. MS (FAB^+) m/z: 250 ($\text{M}+\text{H}^+$, 13), 117 (100). HRMS calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_3$ ($\text{M}+\text{H}^+$): 250.1443, Found: 250.1448.

tert-Butyl [*N*-(cinnamyl)oxy]carbamate (8Ba).

A colorless oil. IR (CHCl_3) 3385, 1742, 1439, 1369 cm^{-1} . ^1H NMR (CDCl_3) δ 7.42-7.18 (6H, m), 6.64 (1H, d, J =15.9 Hz), 6.33 (1H, dt, J =15.9, 6.8 Hz), 4.49 (2H, d, J =6.8 Hz). ^{13}C NMR (CDCl_3) δ 156.8, 136.3, 135.4, 128.6, 128.0, 126.6, 123.4, 88.2, 81.7, 28.2. MS (FAB^+) m/z: 250 ($\text{M}+\text{H}^+$, 7), 117 (100). HRMS calcd for $\text{C}_{14}\text{H}_{20}\text{NO}_3$ ($\text{M}+\text{H}^+$): 250.1443, Found: 250.1435.

Benzyl [*N*-(cinnamyl)oxy]carbamate (8Ca).

A colorless oil. IR (CHCl_3) 3388, 1745, 1452, 1335 cm^{-1} . ^1H NMR (CDCl_3) δ 7.50 (1H, s), 7.40-7.23 (10H, m), 6.62 (1H, d, J =15.9 Hz), 6.30 (1H, dt, J =15.9, 6.7 Hz), 5.17 (2H, s), 4.50 (2H, d, J =6.7 Hz). ^{13}C NMR (CDCl_3) δ 157.3, 136.1, 135.8, 135.6, 128.7, 128.5, 128.4, 128.2, 128.1, 126.7, 123.0, 77.3, 67.5. MS (Cl^+) m/z: 284 ($\text{M}+\text{H}^+$, 39), 117 (100). HRMS calcd for $\text{C}_{17}\text{H}_{18}\text{NO}_3$ ($\text{M}+\text{H}^+$): 284.1287, Found: 284.1296.

***N*-(Cinnamyl)oxy-*N*-phenylbenzamide (8Da).**

A colorless oil. IR (CHCl_3) 3437, 1655, 1491, 1357 cm^{-1} . ^1H NMR (CDCl_3) δ 7.60 (2H, d, J =7.6 Hz), 7.49 (2H, d, J =7.9 Hz), 7.43-7.20 (11H, m), 6.59 (1H, d, J =15.9 Hz), 6.08 (1H, dt, J =15.9, 6.7 Hz), 4.50 (2H, d, J =6.7 Hz). ^{13}C NMR (CDCl_3) δ 168.4, 139.9, 136.3 (2C), 136.0, 134.9, 128.7, 128.3, 127.9, 127.0, 126.7, 74.9. MS (Cl^+) m/z: 330 ($\text{M}+\text{H}^+$, 100). HRMS calcd for $\text{C}_{22}\text{H}_{20}\text{NO}_2$ ($\text{M}+\text{H}^+$): 330.1494, Found: 330.1483.

N-Benzyl-*N*-(cinnamyl)oxy)(phenyl)methanamine (8Ea).

A colorless oil. ^1H NMR (CDCl_3) δ 7.44-7.16 (15H, m), 6.27 (1H, d, J =15.9 Hz), 5.86 (1H, dt, J =15.9, 7.9 Hz), 3.91 (2H, d, J =7.9 Hz), 3.90 (4H, s). ^{13}C NMR (CDCl_3) δ 137.8, 136.8, 132.9, 129.8, 128.4, 128.2, 127.5, 127.3, 126.5, 125.5, 74.3, 62.9. MS (EI^+) m/z: 329 (M^+ , 1), 117 (100). HRMS calcd for $\text{C}_{23}\text{H}_{23}\text{NO}$: 329.1780, Found: 329.1772.

N-(Cinnamyoxy)-N-phenylacetamide (8Fa).

A colorless oil. IR (CHCl₃) 1670, 1493, 1376 cm⁻¹. ¹H NMR (CDCl₃) δ 7.50 (2H, d, *J*=7.6 Hz), 7.41-7.20 (8H, m), 6.62 (1H, d, *J*=15.9 Hz), 6.28 (1H, dt, *J*=15.9, 6.7 Hz), 4.48 (2H, d, *J*=6.7 Hz), 2.27 (3H, s). ¹³C NMR (CDCl₃) δ 170.1, 138.7, 136.2, 135.8, 128.8, 128.6, 128.5, 128.3, 126.6, 123.3, 121.8, 74.7, 21.8. MS (EI⁺) m/z: 267 (M⁺, 0.4), 117 (100). HRMS calcd for C₁₇H₁₇NO₂: 267.1259, Found: 267.1267.

Benzyl [N-(cinnamyoxy)-N-phenyl]carbamate (8Ga).

A colorless oil. IR (CHCl₃) 1712, 1495, 1338 cm⁻¹. ¹H NMR (CDCl₃) δ 7.49 (2H, d, *J*=7.0 Hz), 7.40-7.12 (13H, m), 6.55 (1H, d, *J*=15.9 Hz), 6.27 (1H, dt, *J*=15.9, 6.7 Hz), 5.24 (2H, s), 4.52 (2H, d, *J*=6.7 Hz). ¹³C NMR (CDCl₃) δ 154.4, 139.9, 136.0, 135.7, 128.6, 128.4, 128.1, 128.0, 127.9, 126.6, 125.8, 122.6, 122.2, 75.3, 67.7. Some carbon peaks were missing due to overlapping. MS (EI⁺) m/z: 359 (M⁺, 1), 117 (100). HRMS calcd for C₂₃H₂₁NO₃: 359.1521, Found: 359.1518.

N-Benzyl-N-(cinnamyoxy)acetamide (8Ha).

A colorless oil. IR (CHCl₃) 1655, 1396 cm⁻¹. ¹H NMR (CDCl₃) δ 7.35-7.22 (10H, m), 6.53 (1H, d, *J*=15.9 Hz), 6.18 (1H, dt, *J*=15.9, 6.7 Hz), 4.82 (2H, s), 4.38 (2H, d, *J*=6.7 Hz), 2.21 (3H, s). ¹³C NMR (CDCl₃) δ 172.5, 136.5, 135.8, 128.6, 128.5, 128.4, 128.3, 127.6, 126.6, 121.9, 106.6, 75.5, 50.0, 20.5. MS (CI⁺) m/z: 282 (M+H⁺, 10), 117 (100). HRMS calcd for C₁₈H₂₀NO₂ (M+H⁺): 282.1494, Found: 282.1491.

N-Benzyl-N-(cinnamyoxy)benzamide (8Ia).

A colorless oil. IR (CHCl₃) 1634, 1405 cm⁻¹. ¹H NMR (CDCl₃) δ 7.69 (2H, d, *J*=7.0 Hz), 7.50-7.17 (13H, m), 6.30 (1H, d, *J*=15.9 Hz), 5.84 (1H, dt, *J*=15.9, 6.7 Hz), 4.95 (2H, s), 4.23 (2H, d, *J*=6.7 Hz). ¹³C NMR (CDCl₃) δ 170.1, 136.4, 135.9, 135.8, 134.4, 130.5, 128.6, 128.5, 128.4, 128.2, 127.9, 127.7, 126.6, 122.0, 75.6, 51.5. One carbon peak was missing due to overlapping. MS (CI⁺) m/z: 344 (M+H⁺, 3), 117 (100). HRMS calcd for C₂₃H₂₂NO₂ (M+H⁺): 344.1650, Found: 344.1645.

2-(Cinnamyoxy)isoindoline-1,3-dione (8Ja).²⁾

A colorless crystal. mp 151-152 °C (AcOEt/hexane). IR (CHCl₃) 1732, 1377 cm⁻¹. ¹H NMR (CDCl₃) δ 7.82 (2H, m), 7.72 (2H, m), 7.44-7.20 (5H, m), 6.67 (1H, d, *J*=15.6 Hz), 6.47 (1H, dt, *J*=15.6, 7.0 Hz), 4.87 (2H, d, *J*=7.0 Hz). ¹³C NMR (CDCl₃) δ 163.9, 137.5, 135.8, 134.5, 128.9, 128.6, 128.5, 126.9, 123.5, 122.0, 78.6. MS (FAB⁺) m/z: 280 (M+H⁺, 10), 117 (100). HRMS calcd for C₁₇H₁₄NO₃ (M+H⁺): 280.0974, Found: 280.0970. Anal. Calcd for C₁₇H₁₃NO₃: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.06; H, 4.70; N, 5.02.

1-(Cinnamyoxy)pyrrolidine-2,5-dione (8Ka).

A colorless crystal. mp 174-175 °C (AcOEt/hexane). IR (CHCl₃) 1727, 1377 cm⁻¹. ¹H NMR (CDCl₃) δ 7.43-7.24 (5H, m), 6.65 (1H, d, *J*=15.9 Hz), 6.37 (1H, dt, *J*=15.9, 7.3 Hz), 4.78 (2H, d, *J*=7.3 Hz), 2.66 (4H, s). ¹³C NMR (CDCl₃) δ 171.6, 137.7, 135.6, 128.7, 128.6, 126.9, 121.6, 77.4, 25.3. MS (FAB⁺) m/z: 232 (M+H⁺, 7), 117 (100). HRMS calcd for C₁₃H₁₄NO₃ (M+H⁺): 232.0974, Found: 232.0978. Anal. Calcd for C₁₃H₁₃NO₃: C, 67.52; H, 5.67; N, 6.06. Found: C, 67.57; H, 5.75; N, 6.01.

N-(4-Fluorocinnamyoxy)-N-phenylbenzamide (8Db).

A colorless oil. IR (CHCl₃) 1655, 1604, 1509, 1489, 1357 cm⁻¹. ¹H NMR (CDCl₃) δ 7.60 (2H, d,

J=7.0 Hz), 7.48 (2H, d, *J*=7.9 Hz), 7.43-7.20 (8H, m), 6.98 (2H, br t, *J*=8.9 Hz), 6.45 (1H, d, *J*=15.9 Hz), 6.00 (1H, dt, *J*=15.9, 7.0 Hz), 4.49 (2H, d, *J*=7.0 Hz). ^{13}C NMR (CDCl_3) δ 168.3, 162.7 (d, *J*=248 Hz), 139.9, 135.0, 134.8, 132.2, 130.5, 129.0, 128.6, 128.3 (d, *J*=8.3 Hz), 127.9, 127.0, 124.5, 122.0, 115.5 (d, *J*=21.7 Hz), 74.8. MS (Cl^+) m/z: 348 ($\text{M}+\text{H}^+$, 1), 135 (100). HRMS calcd for $\text{C}_{22}\text{H}_{19}\text{FNO}_2$ ($\text{M}+\text{H}^+$): 348.1400, Found: 348.1397.

N-(4-Methylcinnamyl)-N-phenylbenzamide (8Dc).

A colorless oil. IR (CHCl_3) 1654, 1591, 1489, 1358 cm^{-1} . ^1H NMR (CDCl_3) δ 7.60 (2H, d, *J*=7.3 Hz), 7.49 (2H, d, *J*=7.9 Hz), 7.42-7.20 (6H, m), 7.18 (2H, d, *J*=8.0 Hz), 7.00 (2H, d, *J*=8.0 Hz), 6.45 (1H, d, *J*=15.9 Hz), 6.02 (1H, dt, *J*=15.9, 6.7 Hz), 4.48 (2H, d, *J*=6.7 Hz), 2.32 (3H, s). ^{13}C NMR (CDCl_3) δ 168.4, 139.9, 138.2, 136.4, 134.9, 133.2, 130.5, 129.3, 128.9, 128.6, 127.9, 126.9, 126.6, 124.4, 121.1, 75.1, 21.1. MS (Cl^+) m/z: 344 ($\text{M}+\text{H}^+$, 1), 131 (100). HRMS calcd for $\text{C}_{23}\text{H}_{22}\text{NO}_2$ ($\text{M}+\text{H}^+$): 344.1650, Found: 344.1645.

N-((E)-3-(Naphthalen-1-yl)allyloxy)-N-phenylbenzamide (8Dd).

A colorless oil. IR (CHCl_3) 1653, 1591, 1489, 1360 cm^{-1} . ^1H NMR (CDCl_3) δ 7.98-7.22 (18H, m), 6.18 (1H, dt, *J*=15.6, 6.7 Hz), 4.62 (2H, d, *J*=6.7 Hz). ^{13}C NMR (CDCl_3) δ 168.4, 140.0, 134.8, 133.6, 133.5, 133.4, 131.0, 130.6, 129.0, 128.7, 128.6, 128.5, 128.0, 127.0, 126.2, 125.9, 125.5 (2C), 124.5, 124.2, 123.5, 75.1. MS (Cl^+) m/z: 380 ($\text{M}+\text{H}^+$, 1), 167 (100). HRMS calcd for $\text{C}_{26}\text{H}_{22}\text{NO}_2$ ($\text{M}+\text{H}^+$): 380.1650, Found: 380.1655.

tert-Butyl [N-cinnamyl-N-(cinnamyl)]carbamate (9Ba).

A colorless oil. IR (CHCl_3) 1701, 1369 cm^{-1} . ^1H NMR (CDCl_3) δ 7.35 (4H, d, *J*=7.7 Hz), 7.30 (4H, t, *J*=7.4 Hz), 7.24 (2H, m), 6.61 (1H, d, *J*=15.9 Hz), 6.57 (1H, d, *J*=15.9 Hz), 6.37-6.23 (2H, m), 4.52 (2H, d, *J*=7.0 Hz), 4.21 (2H, d, *J*=6.4 Hz), 1.51 (9H, s). ^{13}C NMR (CDCl_3) δ 156.7, 136.7, 136.3, 135.0, 133.3, 128.5 (2C), 127.9, 127.6, 126.6, 126.4, 124.0, 123.7, 81.5, 76.0, 52.7, 28.3. MS (Cl^+) m/z: 366 ($\text{M}+\text{H}^+$, 7), 310 (100). HRMS calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_3$ ($\text{M}+\text{H}^+$): 366.2070, Found: 366.2082.

Benzyl [N-cinnamyl-N-(cinnamyl)]carbamate (9Ca).

A colorless oil. IR (CHCl_3) 1706, 1347 cm^{-1} . ^1H NMR (CDCl_3) δ 7.40-7.21 (15H, m), 6.58 (1H, d, *J*=15.9 Hz), 6.57 (1H, d, *J*=15.9 Hz), 6.35-6.22 (2H, m), 5.22 (2H, s), 4.54 (2H, d, *J*=7.0 Hz), 4.28 (2H, d, *J*=6.8 Hz). ^{13}C NMR (CDCl_3) δ 157.3, 136.5, 136.2, 136.0, 135.4, 133.7, 128.5 (2C), 128.2, 128.0, 127.7, 126.6, 126.5, 123.5, 123.3, 76.2, 67.8, 52.7. Some carbon peaks were missing due to overlapping. MS (FAB^+) m/z: 400 ($\text{M}+\text{H}^+$, 6), 117 (100). HRMS calcd for $\text{C}_{26}\text{H}_{26}\text{NO}_3$ ($\text{M}+\text{H}^+$): 400.1913, Found: 400.1922.

tert-Butyl [N-(cinnamyl)-N-(1-phenylallyl)]carbamate (10).

A colorless oil. IR (CHCl_3) 1698, 1369 cm^{-1} . ^1H NMR (CDCl_3) δ 7.42 (2H, d, *J*=7.0 Hz), 7.39-7.20 (8H, m), 6.47 (1H, d, *J*=15.9 Hz), 6.22-6.12 (2H, m), 5.34-5.27 (3H, m), 4.15 (1H, dd, *J*=15.6, 6.4 Hz), 4.03 (1H, br dd, *J*=15.6, 6.0 Hz), 1.52 (9H, s). ^{13}C NMR (CDCl_3) δ 156.9, 139.0, 136.7 (2C), 133.0, 128.4, 128.3 (2C), 127.9, 127.5, 126.4, 124.1, 118.9, 87.6, 81.5, 53.2, 28.3. MS (Cl^+) m/z: 366 ($\text{M}+\text{H}^+$, 9), 310 (100). HRMS calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_3$ ($\text{M}+\text{H}^+$): 366.2070, Found: 366.2078.

tert-Butyl [N-cinnamyl-N-(1-phenylallyloxy)]carbamate (11).

A colorless oil. IR (CHCl_3) 1699, 1368 cm^{-1} . ^1H NMR (CDCl_3) δ 7.43 (2H, d, *J*=7.0 Hz), 7.37-7.20 (8H, m), 6.43 (1H, d, *J*=15.9 Hz), 6.26 (1H, m), 6.11 (1H, br m), 5.58 (1H, d, *J*=6.8 Hz), 5.32 (1H,

d, $J=10.4$ Hz), 5.28 (1H, d, $J=17.4$ Hz), 4.36 (1H, br dd, $J=10.4, 7.0$ Hz), 4.12 (1H, br m), 1.46 (9H, s). ^{13}C NMR (CDCl_3) δ 156.9, 138.8, 136.4, 134.7, 134.6, 128.6, 128.4, 128.2, 127.8, 127.6, 126.6, 123.4, 118.1, 81.6, 77.0, 65.9, 28.2. MS (Cl^+) m/z: 366 ($\text{M}+\text{H}^+$, 10), 310 (100). HRMS calcd for $\text{C}_{23}\text{H}_{28}\text{NO}_3$ ($\text{M}+\text{H}^+$): 366.2070, Found: 366.2065.

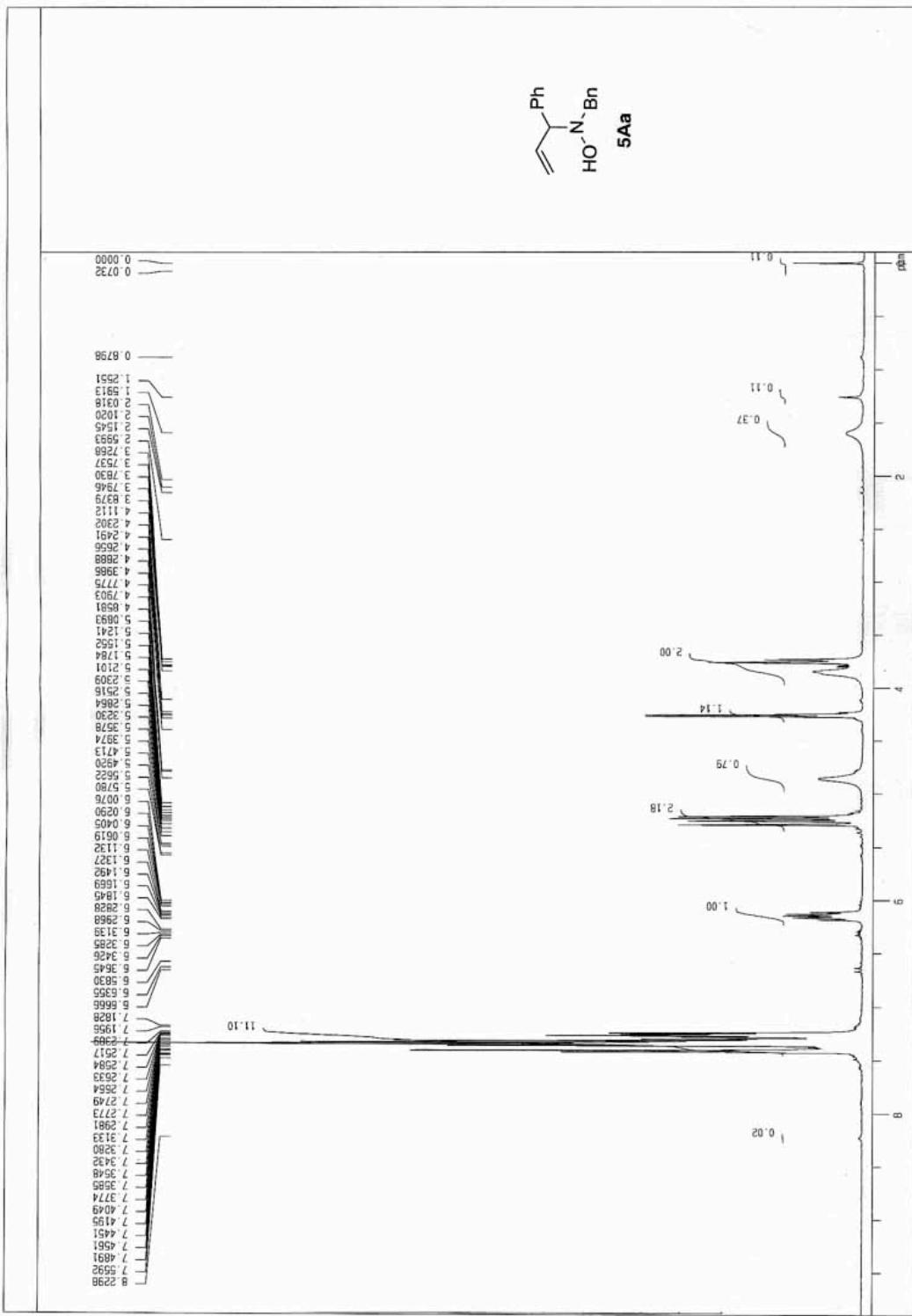
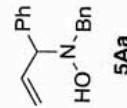
Reduction of **6Da** to Alcohol **12**

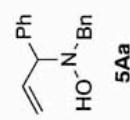
A suspension of oxime ether **6Da** (165 mg, 0.50 mmol) and 20% $\text{Pd}(\text{OH})_2\text{-C}$ (30 mg) in MeOH (2.5 mL) was stirred under a hydrogen atmosphere at 20 °C for 3 h. After the reaction mixture was filtered, the filtrate was concentrated under reduced pressure. Purification of the residue by preparative TLC (hexane:AcOEt=5:1) afforded the product **12** (56 mg, 82%). A colorless oil. IR (CHCl_3) 3428, 2969, 1493, 1455, 1380 cm^{-1} . ^1H NMR (CDCl_3) δ 7.37-7.20 (5H, m) 4.55 (1H, t, $J=6.6$ Hz), 2.12 (1H, br s), 1.84-1.67 (2H, m), 0.89 (3H, t, $J=7.5$ Hz). ^{13}C NMR (CDCl_3) δ 144.6, 128.4, 127.4, 126.0, 75.9, 31.7, 10.0. MS (EI^+) m/z: 136 (M^+ , 9.0), 91 (100). HRMS calcd for $\text{C}_9\text{H}_{12}\text{O}$: 136.0888, Found: 136.0888. A sample of 87%ee gave $[\alpha]^{24}_{\text{D}} -46.3$ (c 1.2, hexane).

References

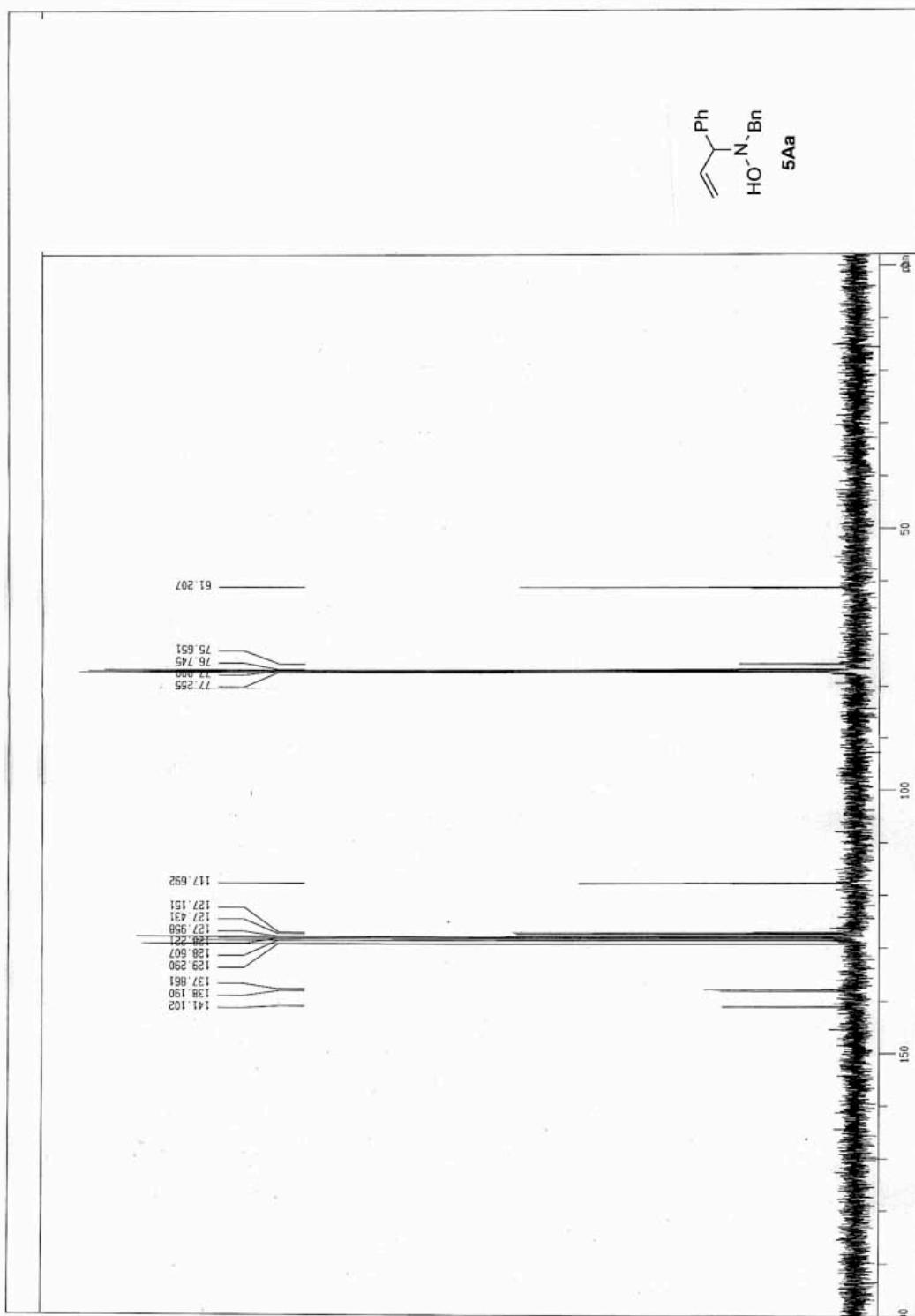
- 1) (a) Davies, S. G.; Fox, J. F.; Jones, S.; Price, A. J.; Sanz, M. A.; Sellers, T. G. R.; Smith, A. D.; Teixeira, F. C. *J. Chem. Soc., Perkin Transactions 1* **2002**, 41, 1757. (b) Le Flohic, A.; Meyer, C.; Cossy, J.; Desmurs, J.-R. *Tetrahedron Lett.* **2003**, 44, 197.
- 2) Kim, S.; Lee, T. A.; Song, Y. *Synlett* **1998**, 471.

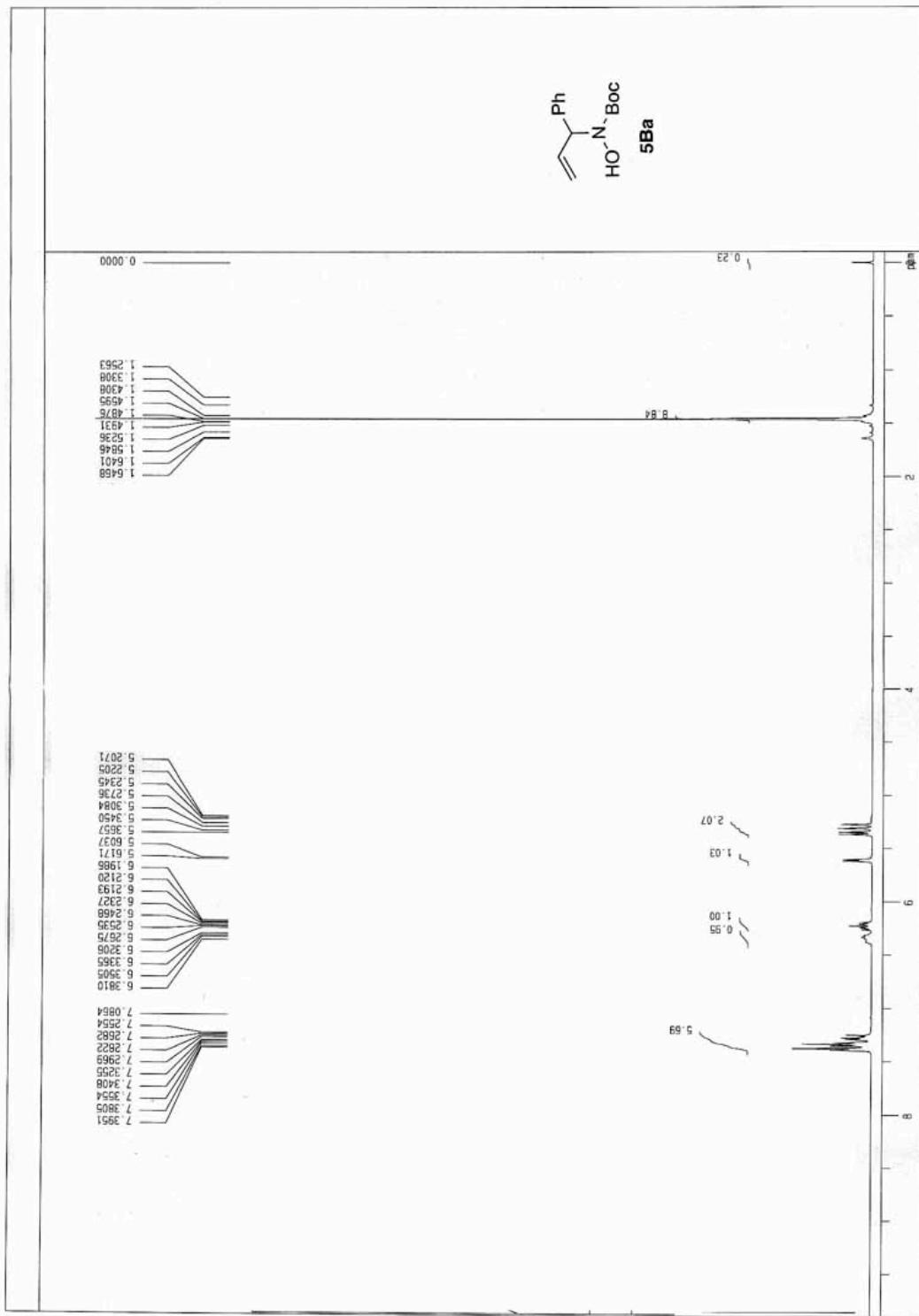
3. Copies of ^1H and ^{13}C NMR spectrum of all obtained compounds

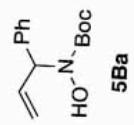




5Aa







26.263

65.163

76.745

77.000

77.255

82.363

118.424

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127.908

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138.314

157.125

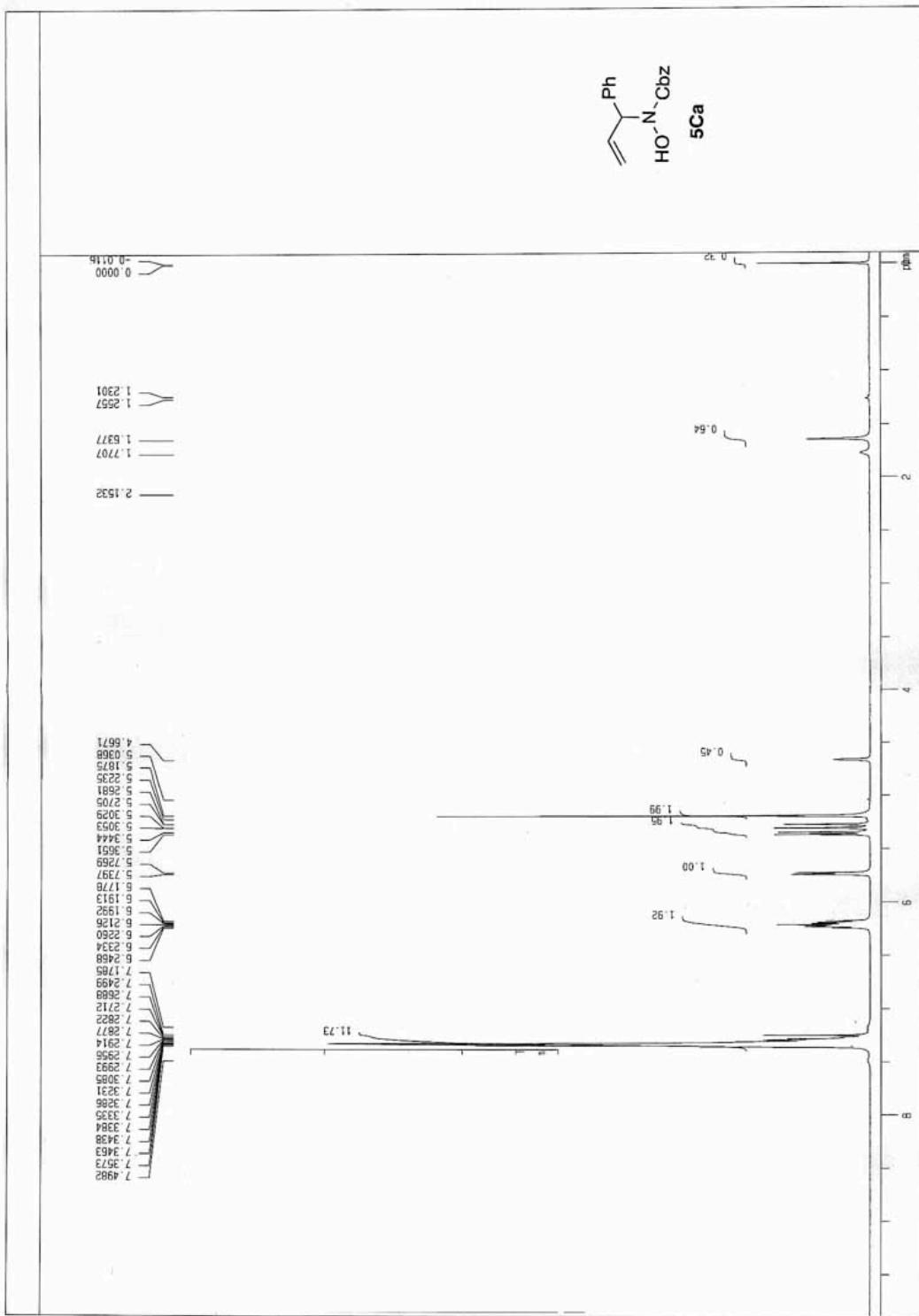
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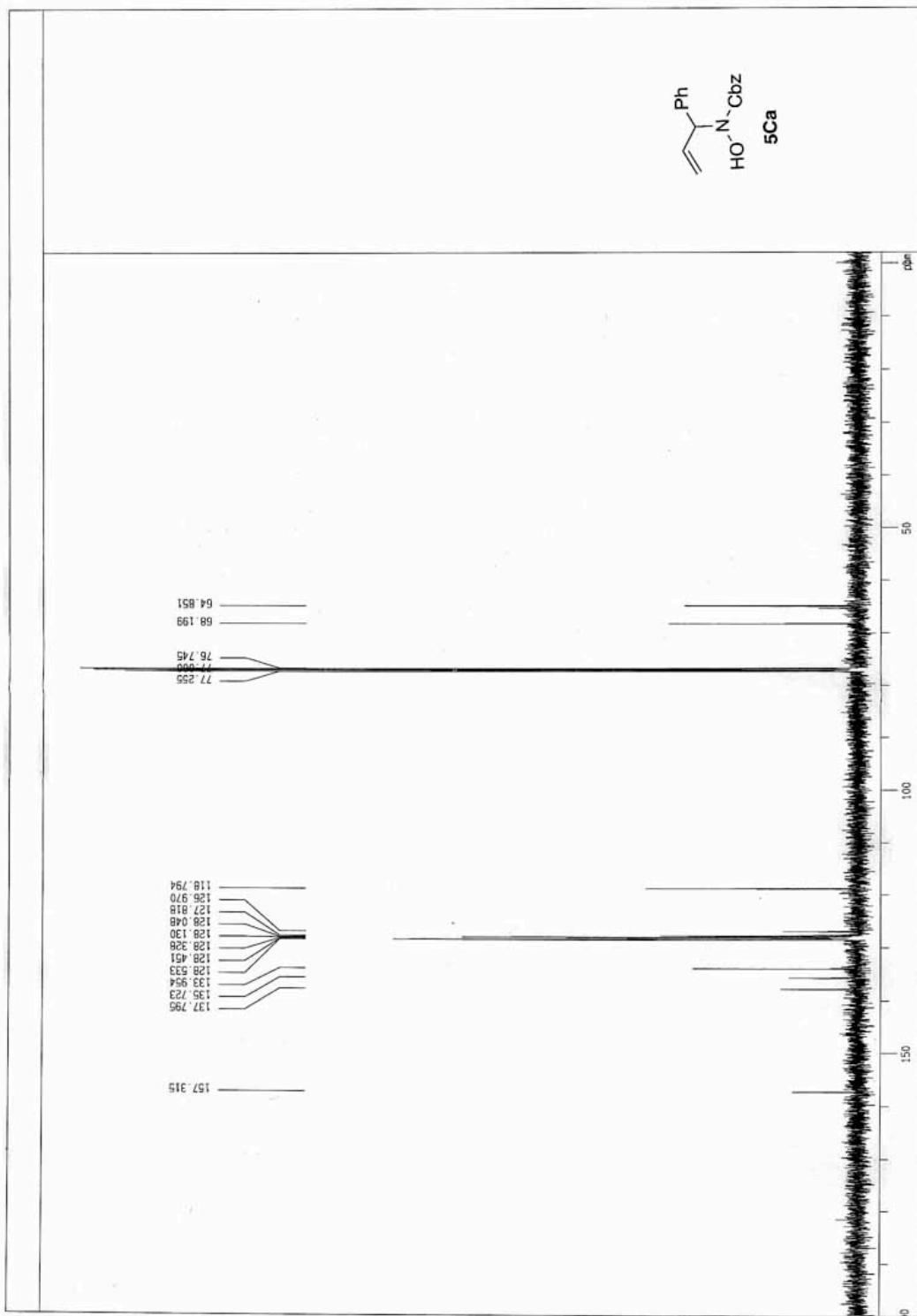
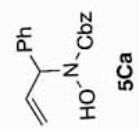
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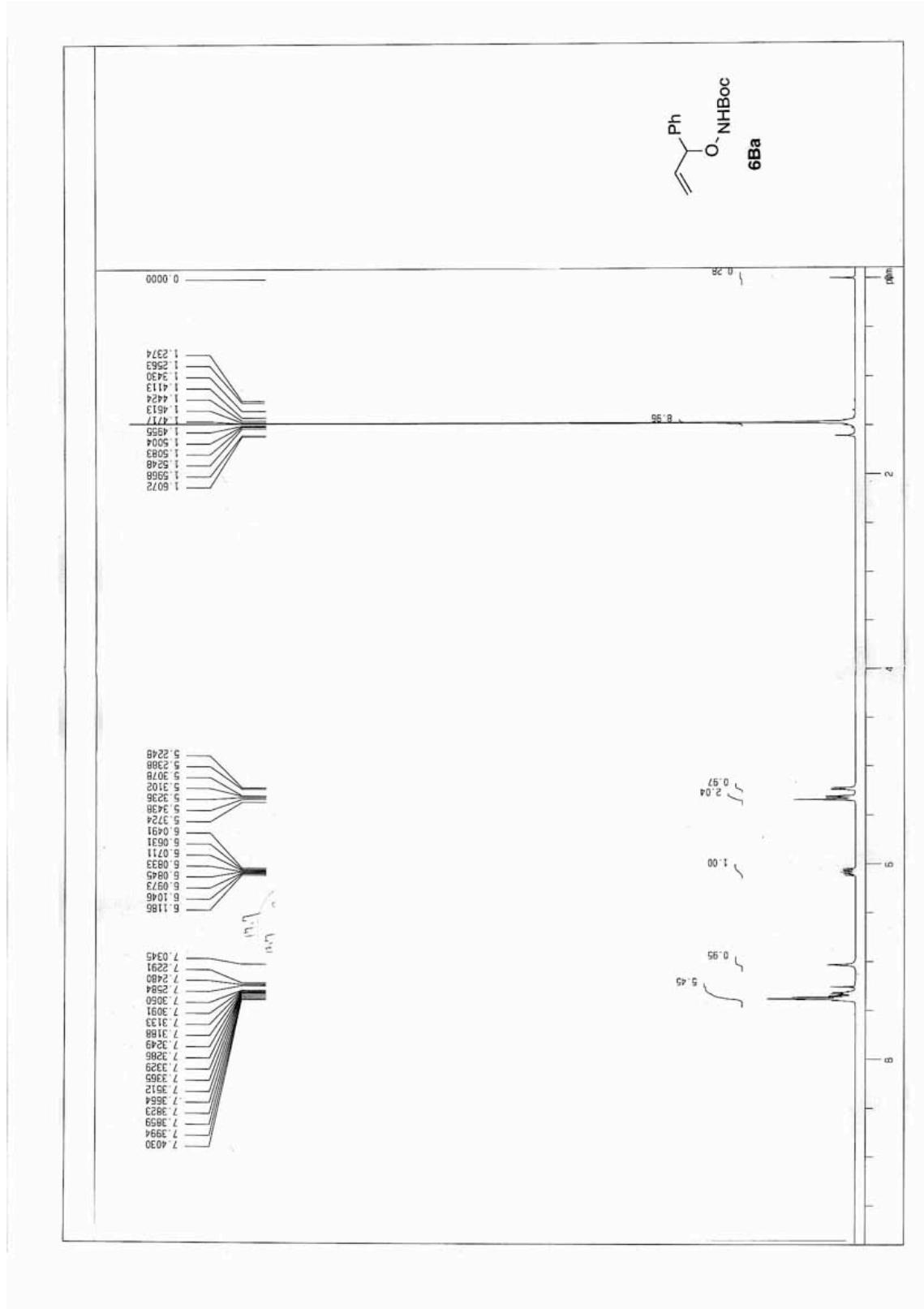
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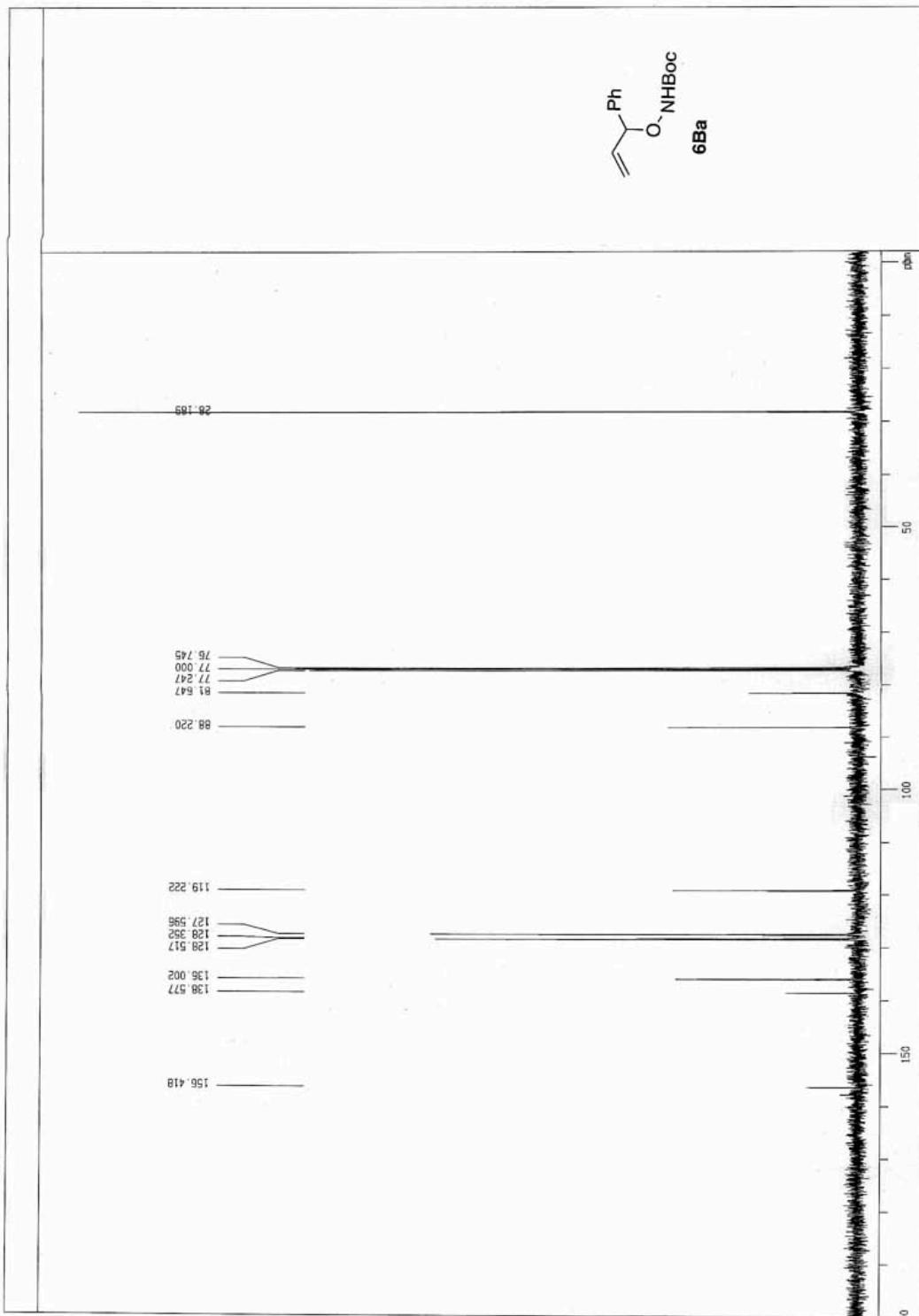
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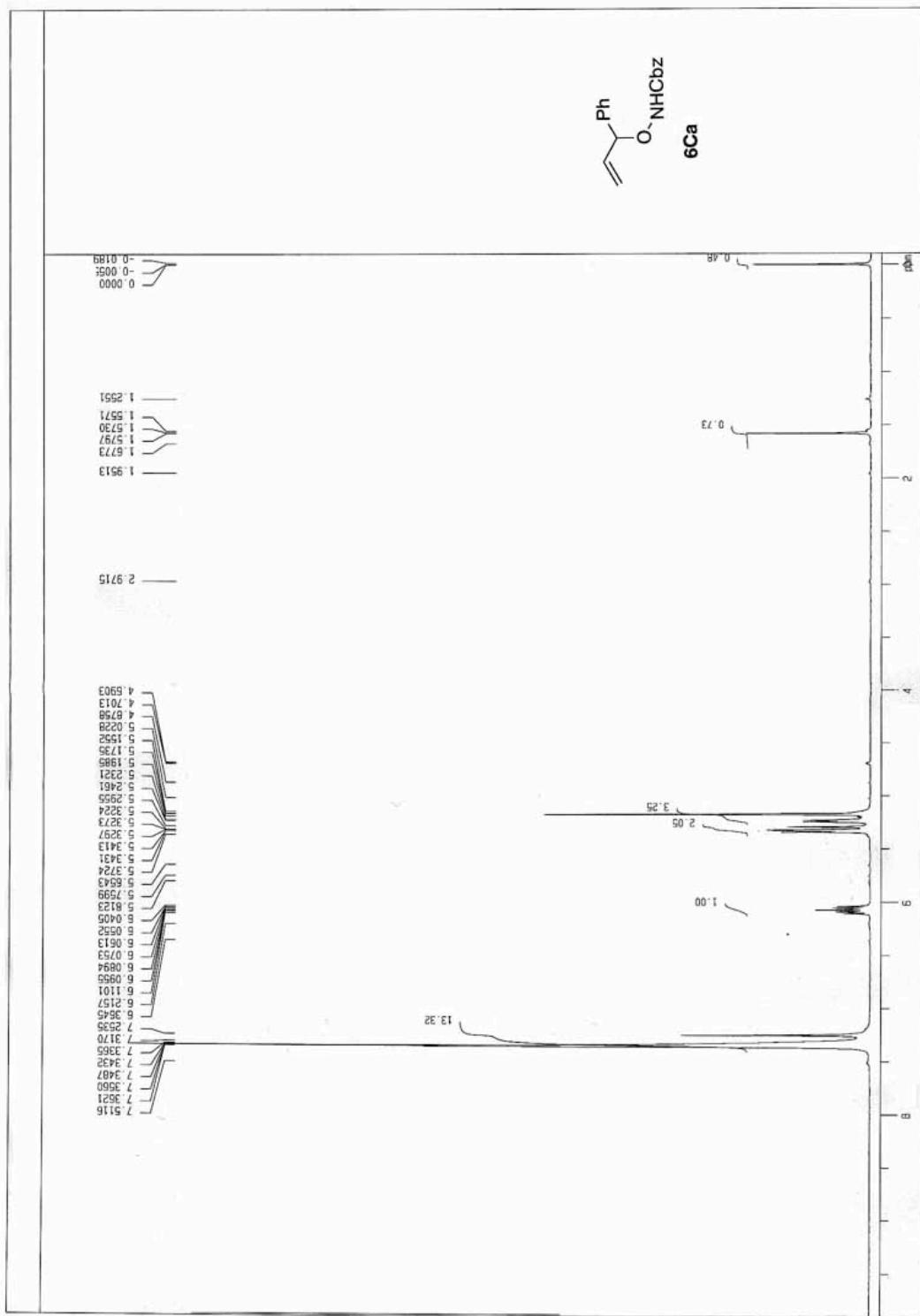
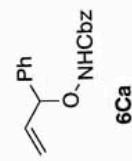
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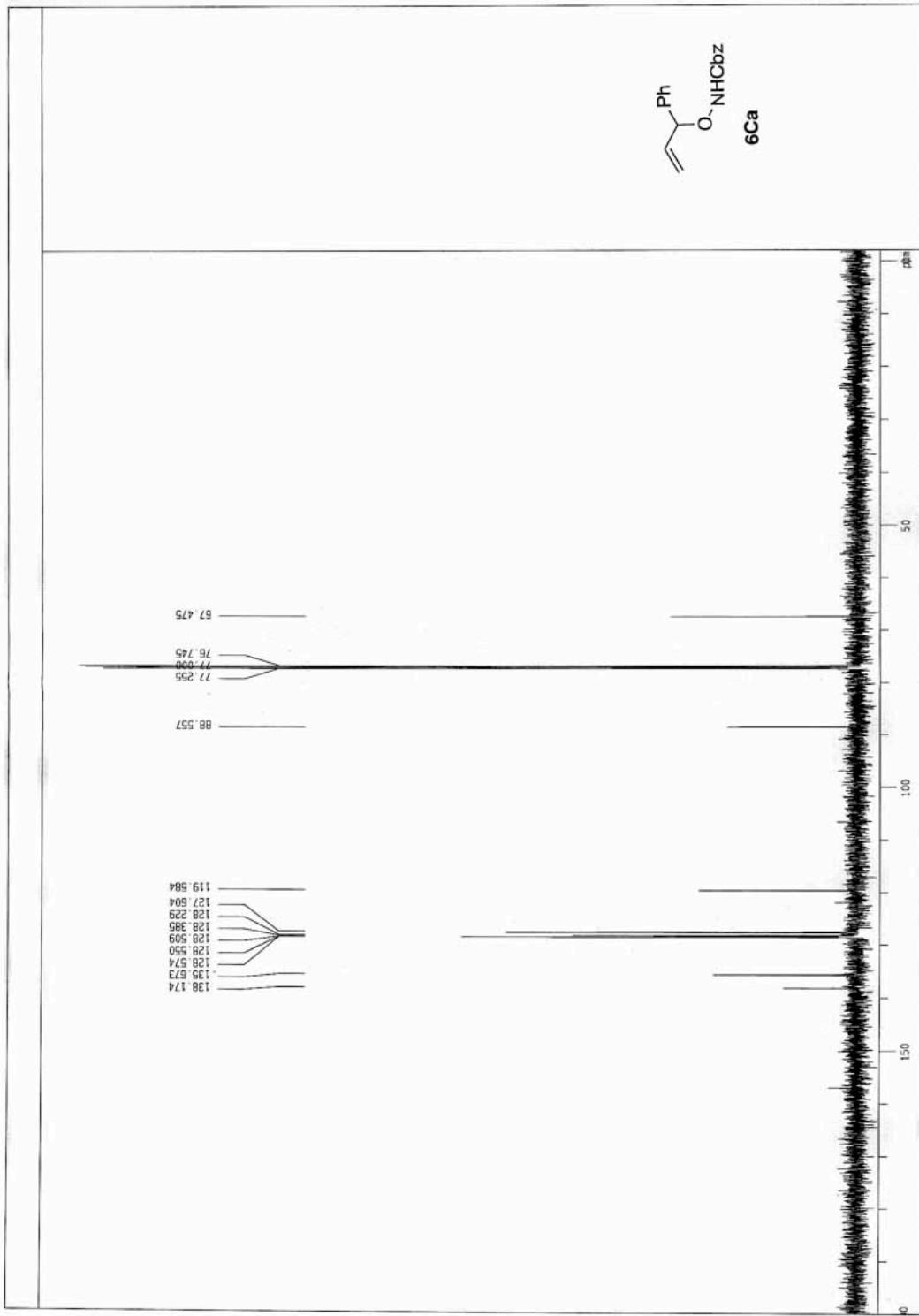
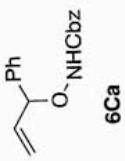


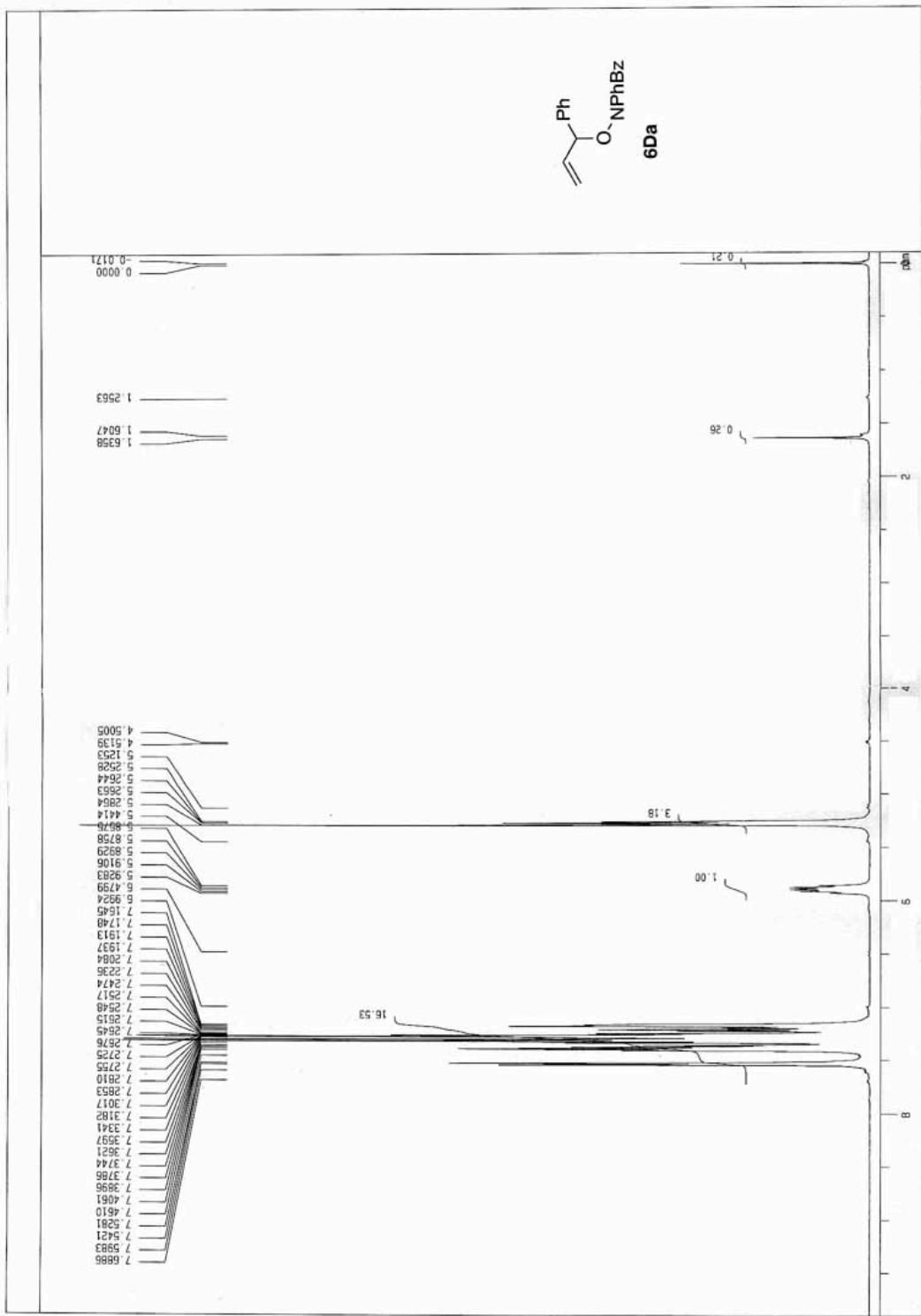


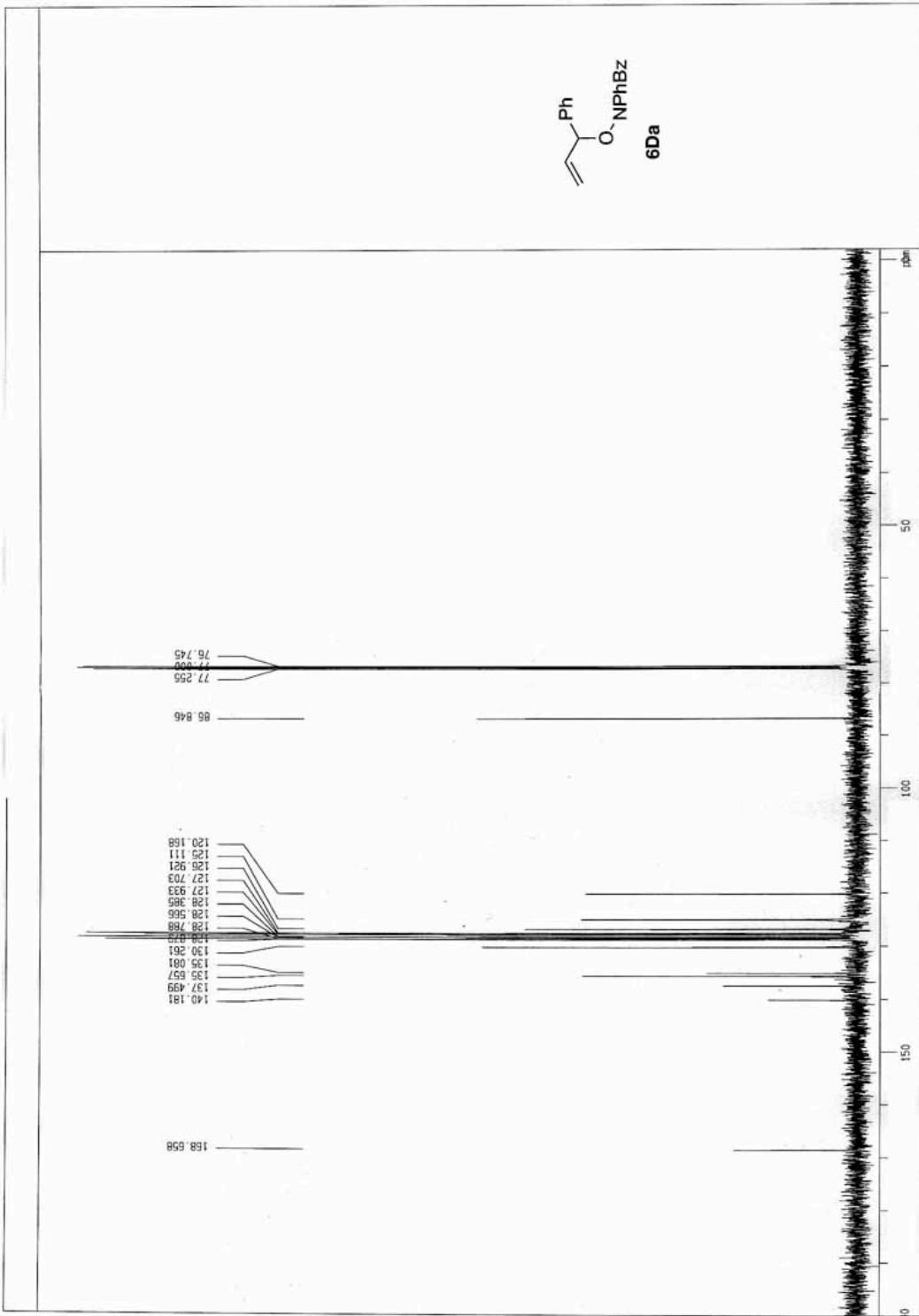


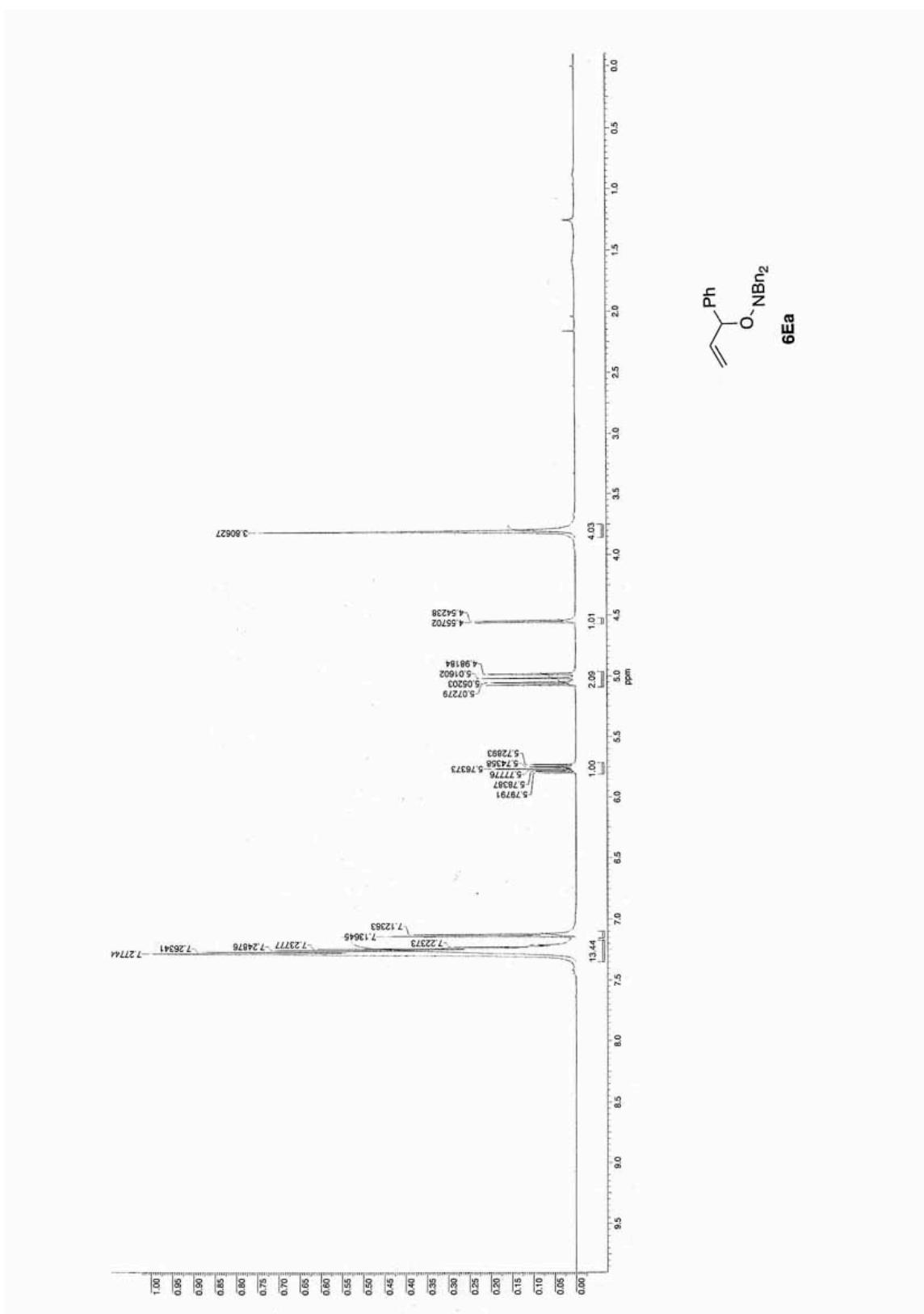


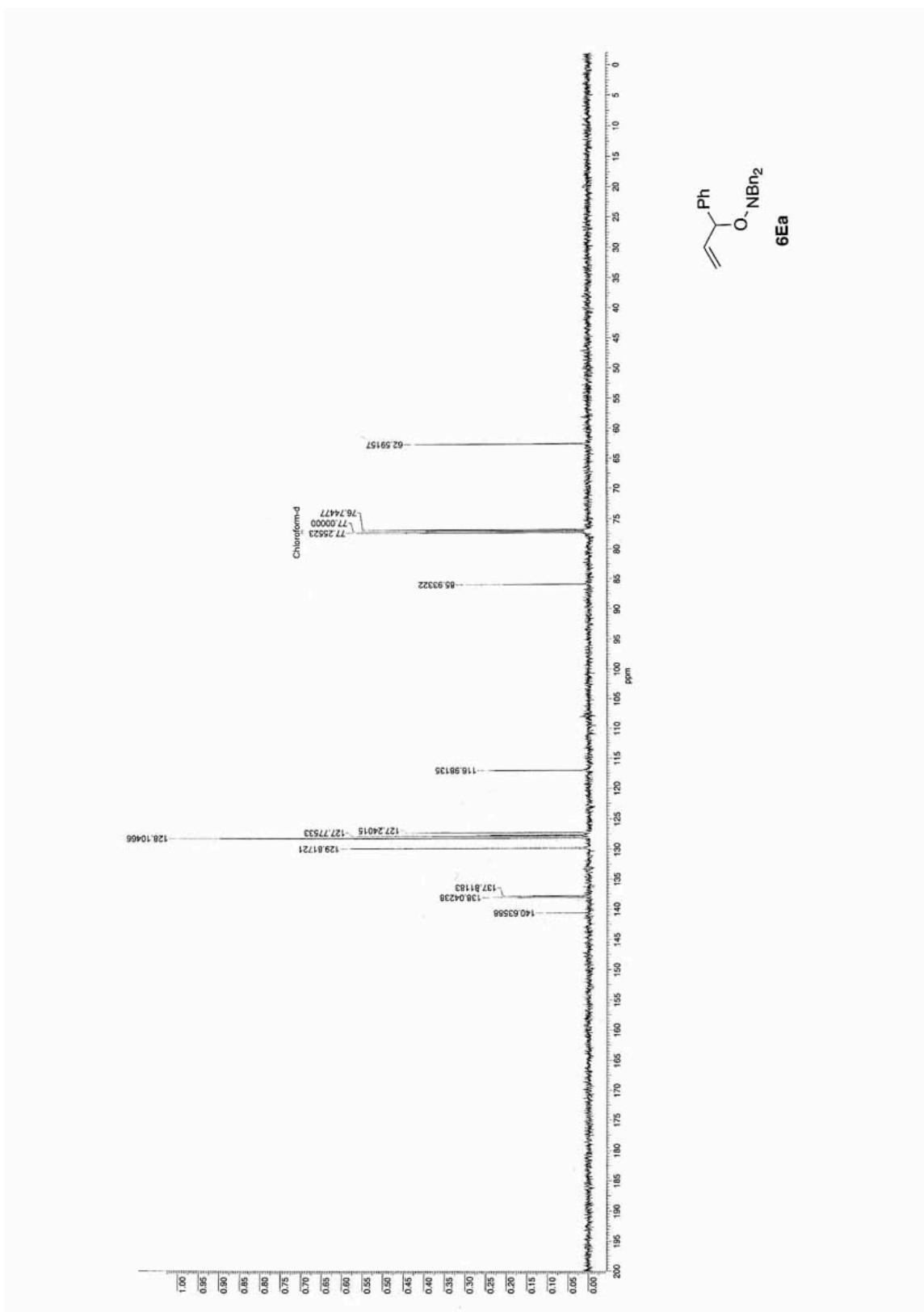


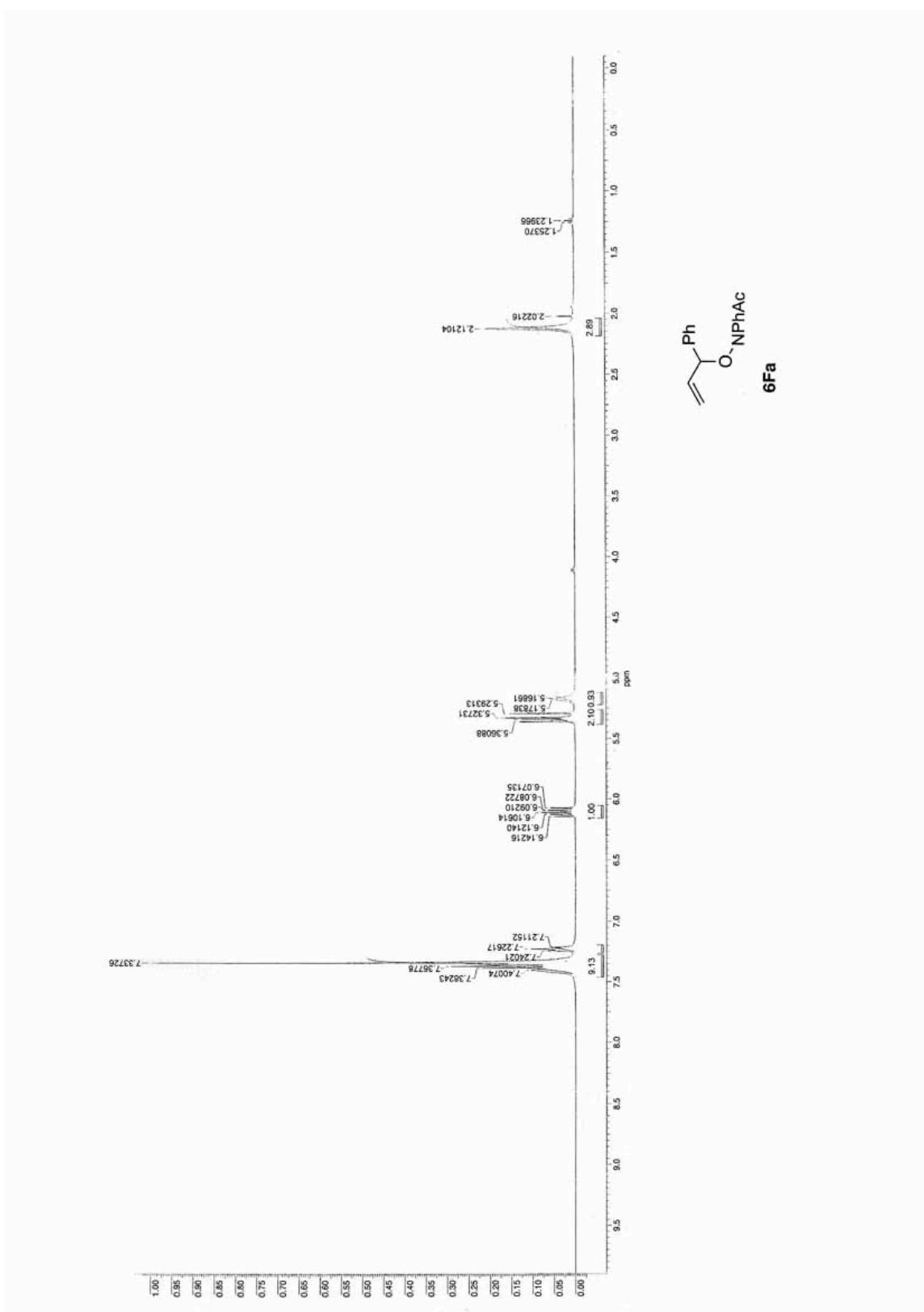


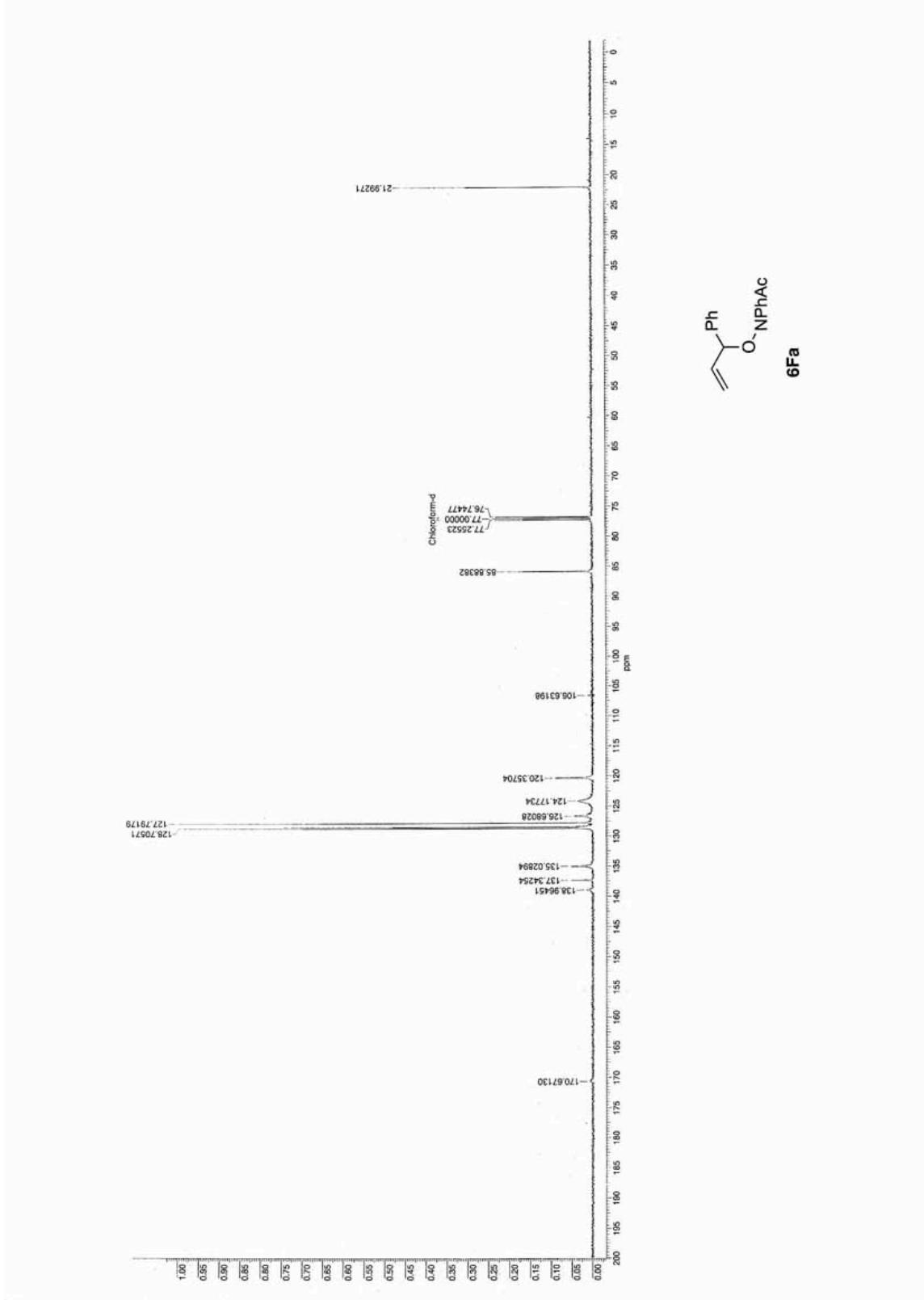


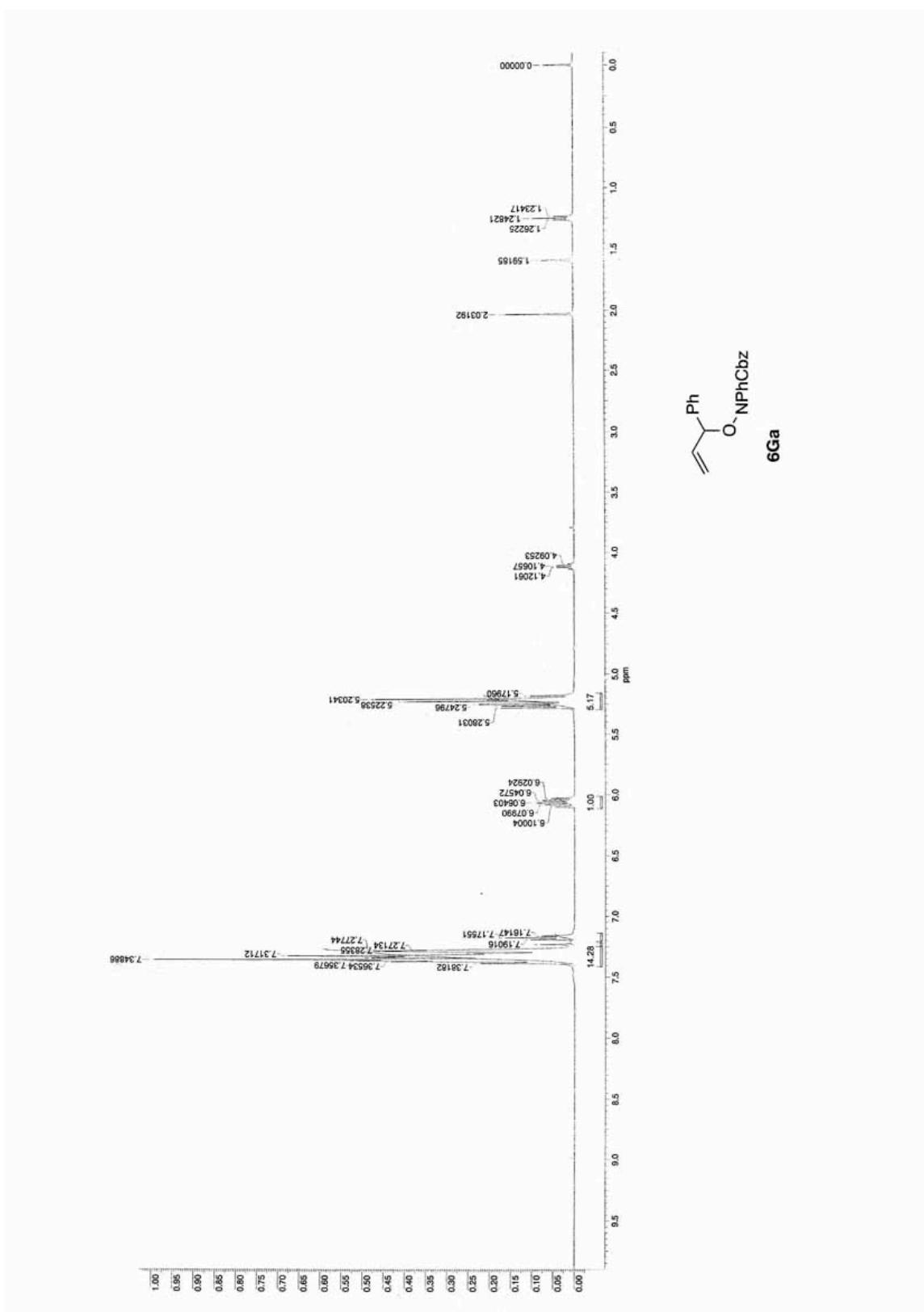


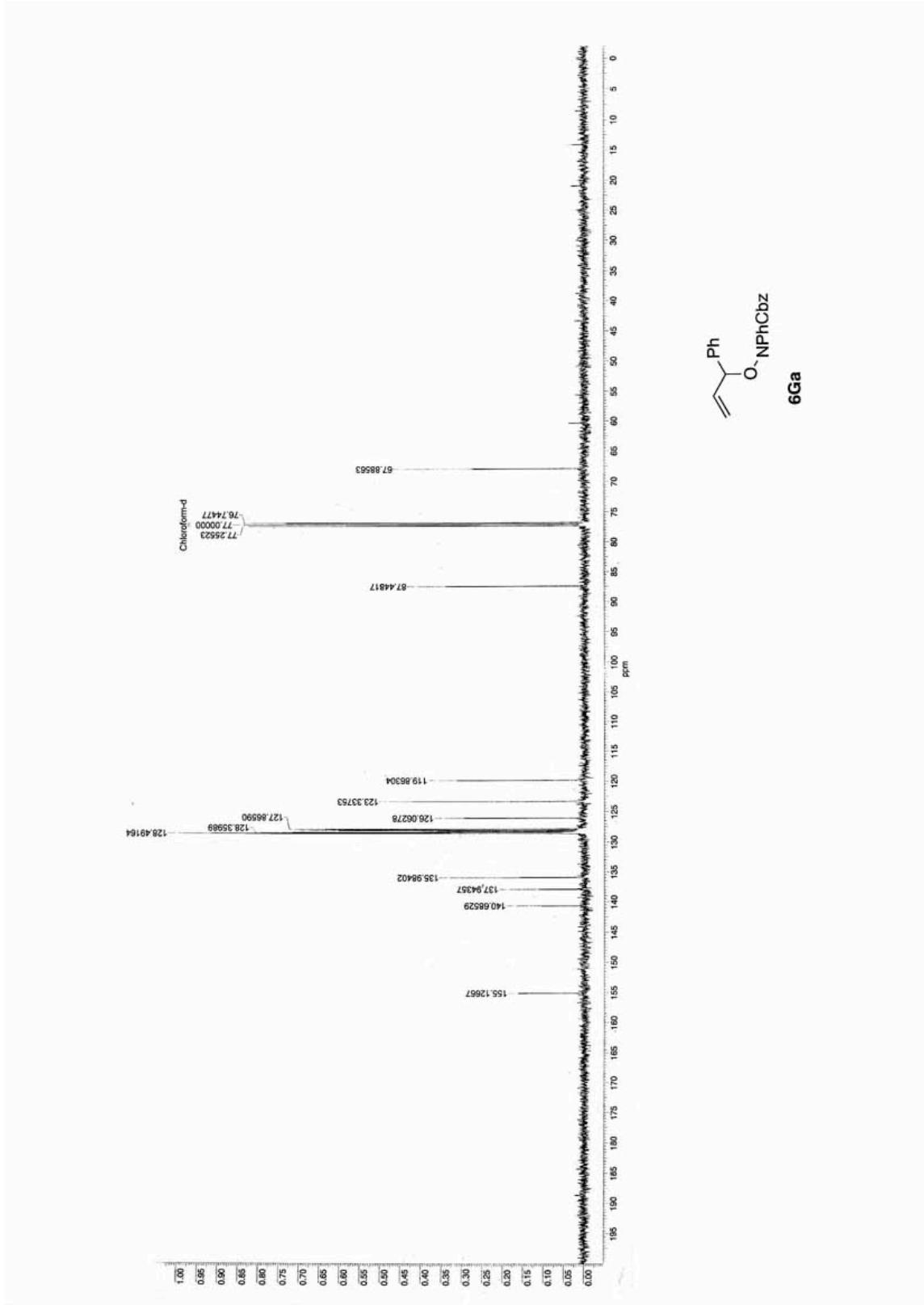


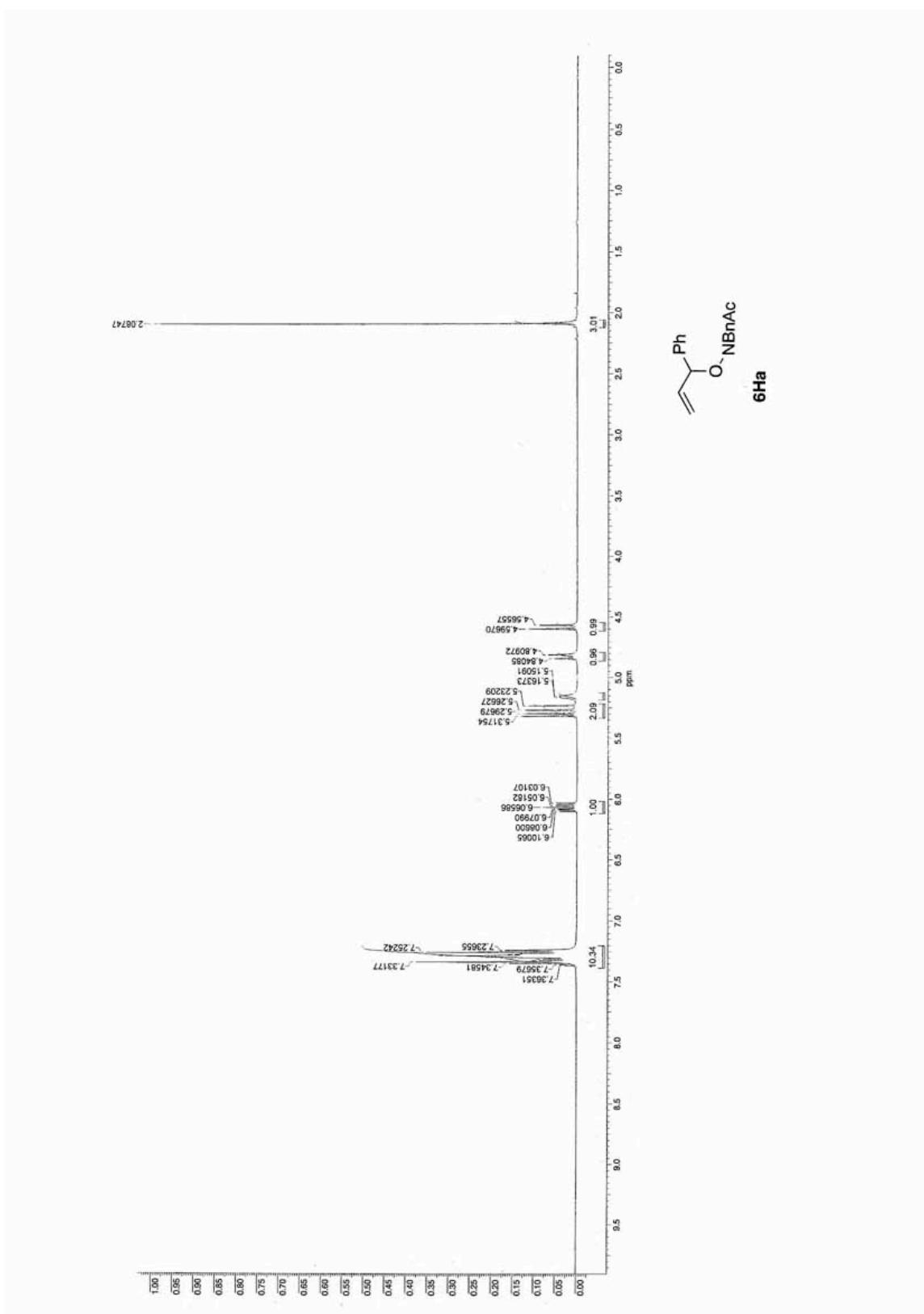


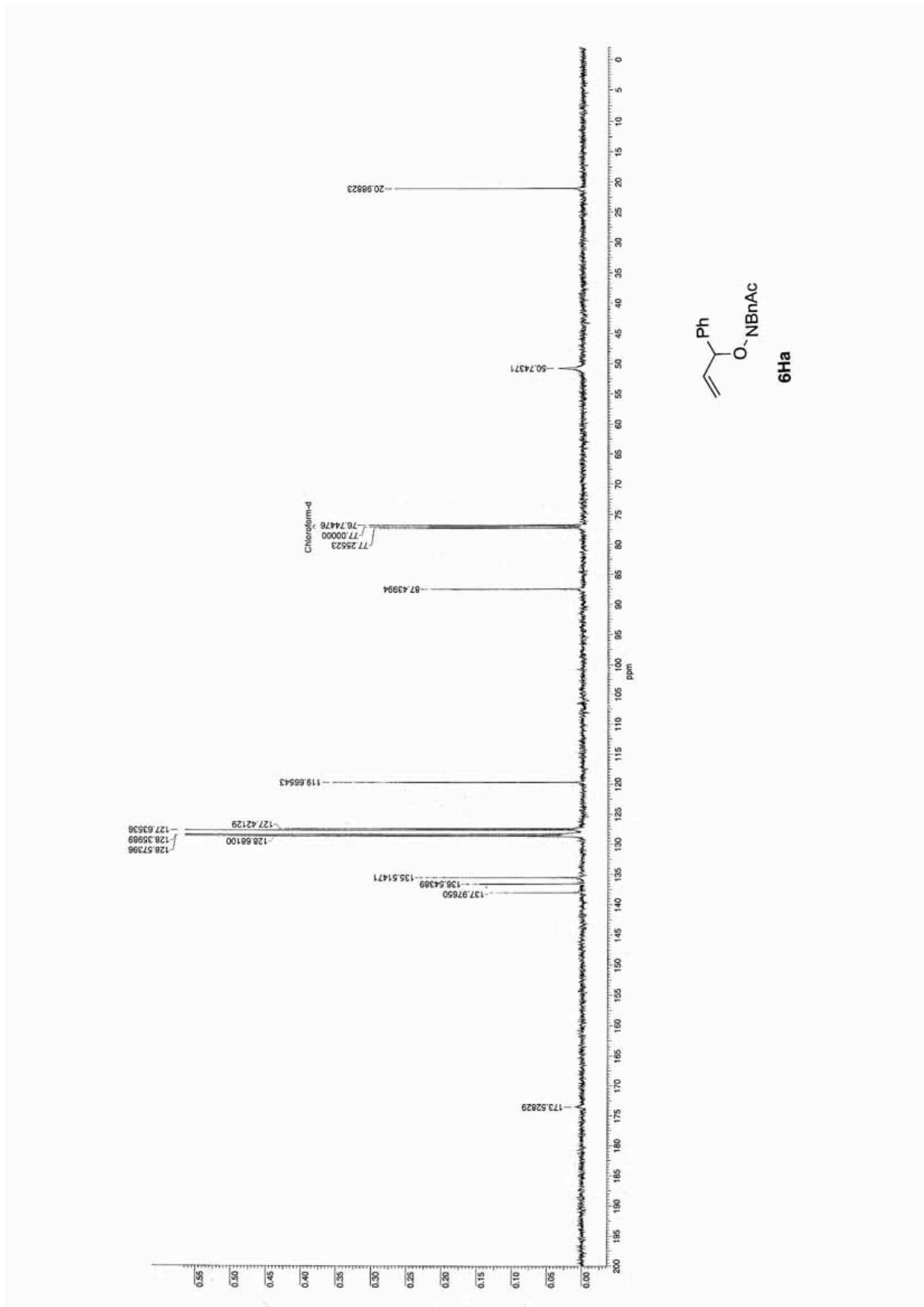


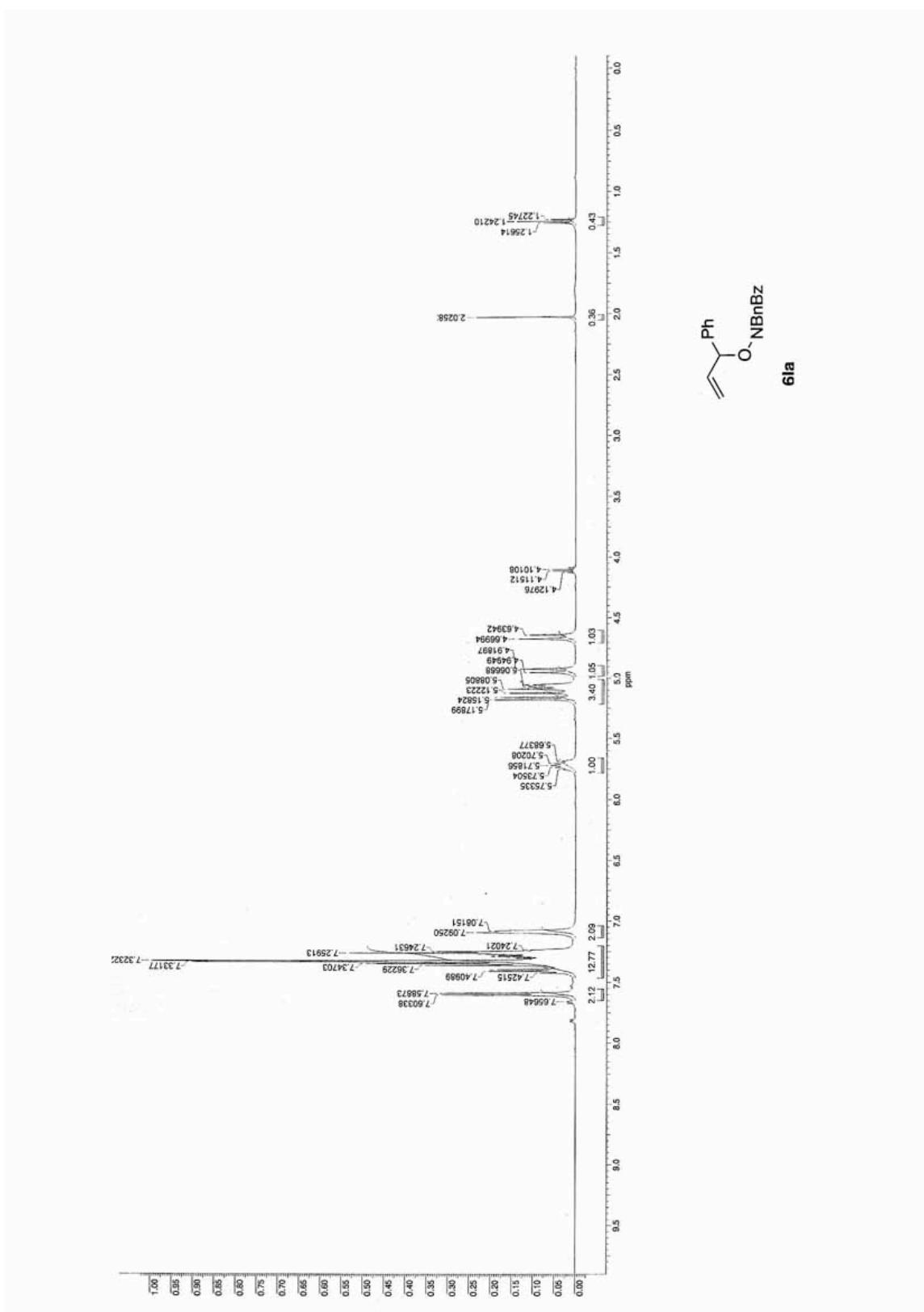


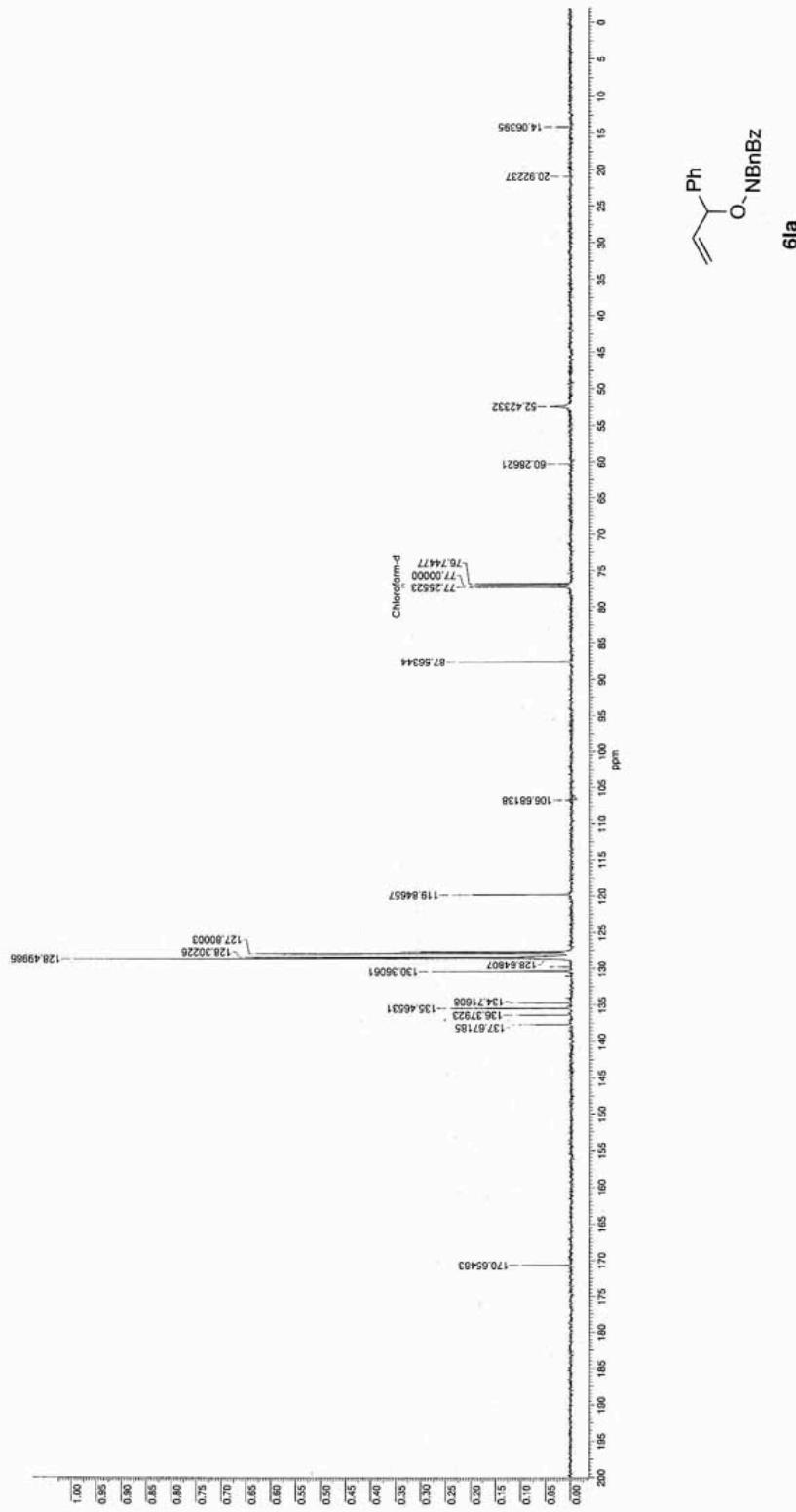


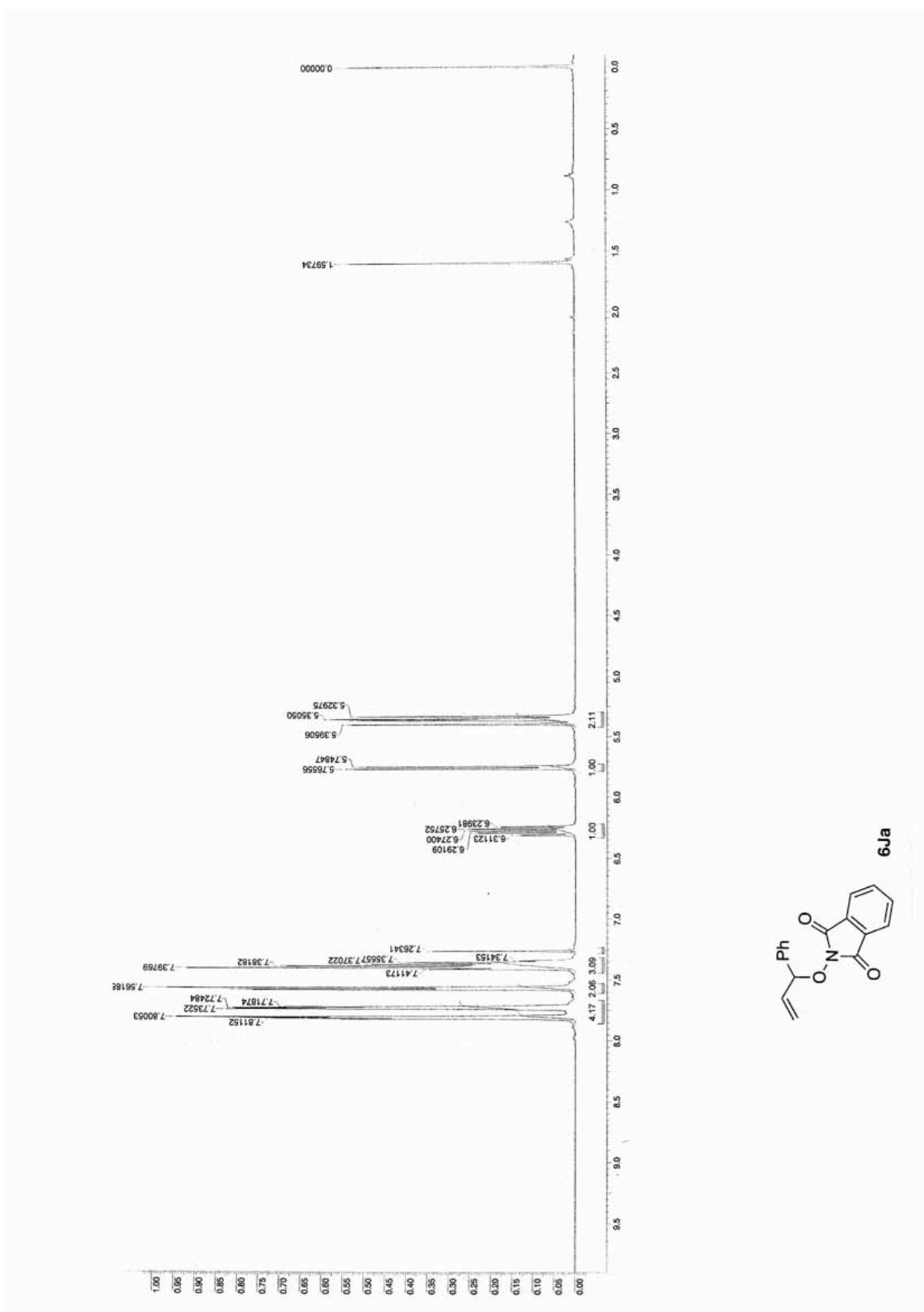


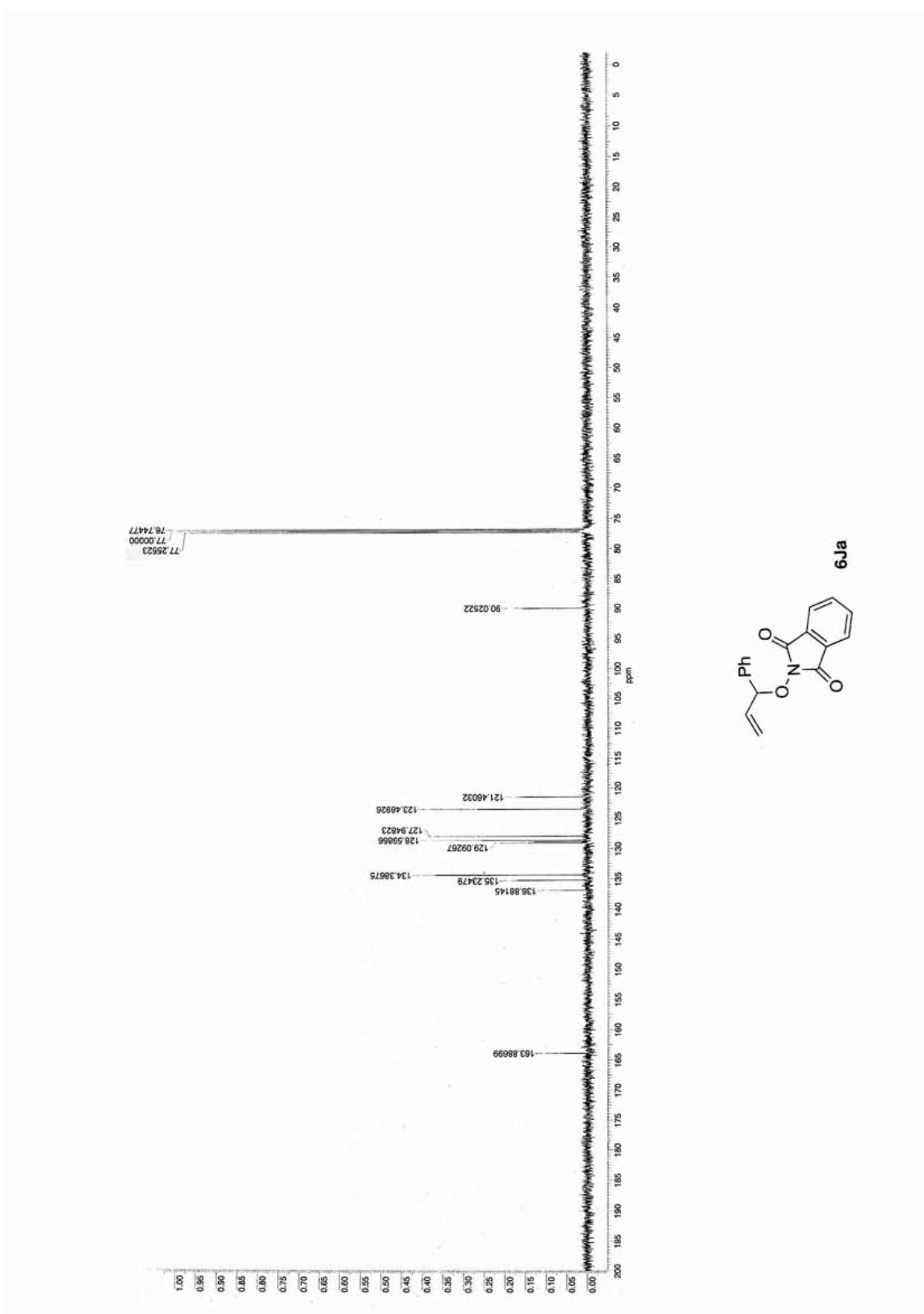


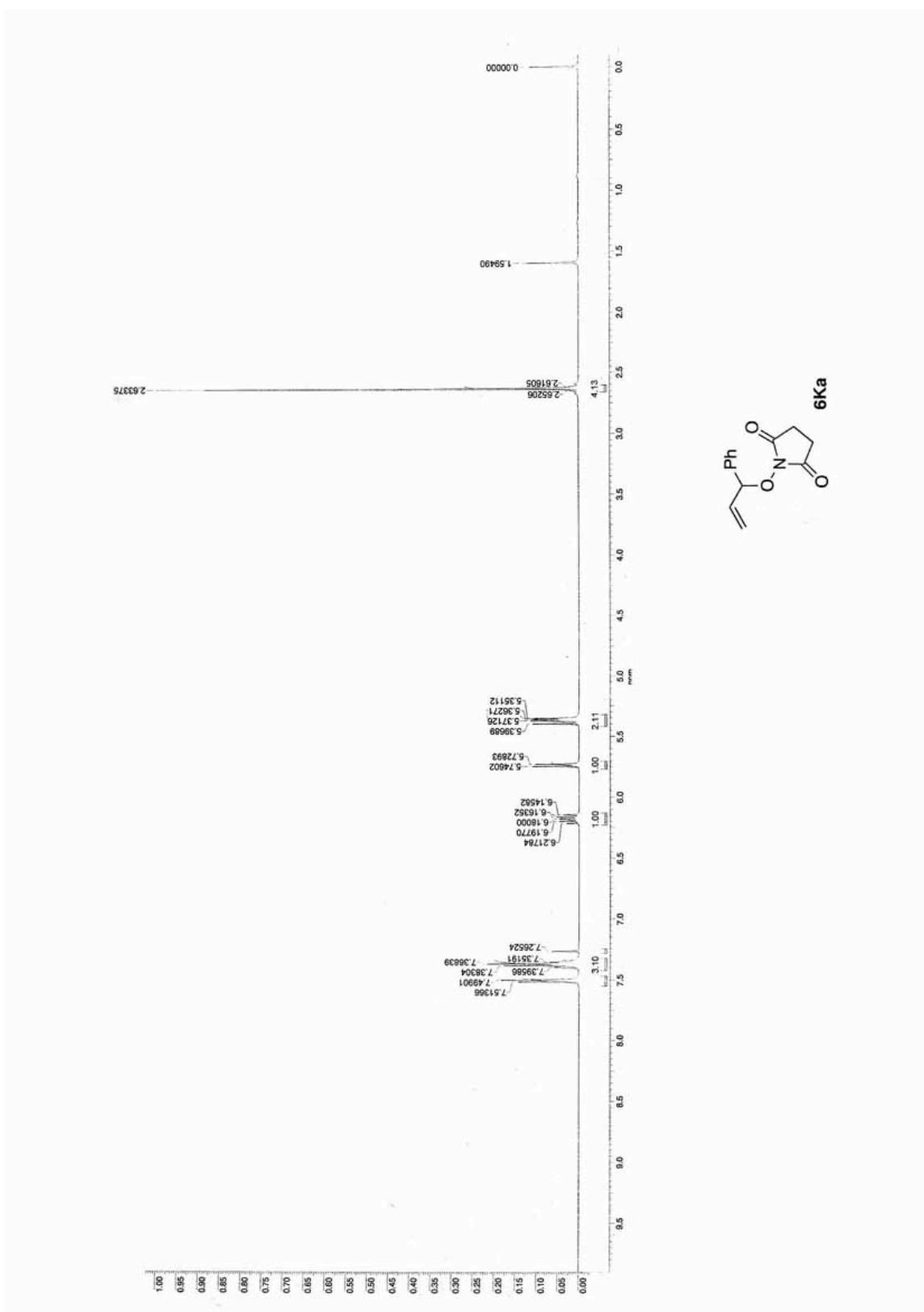


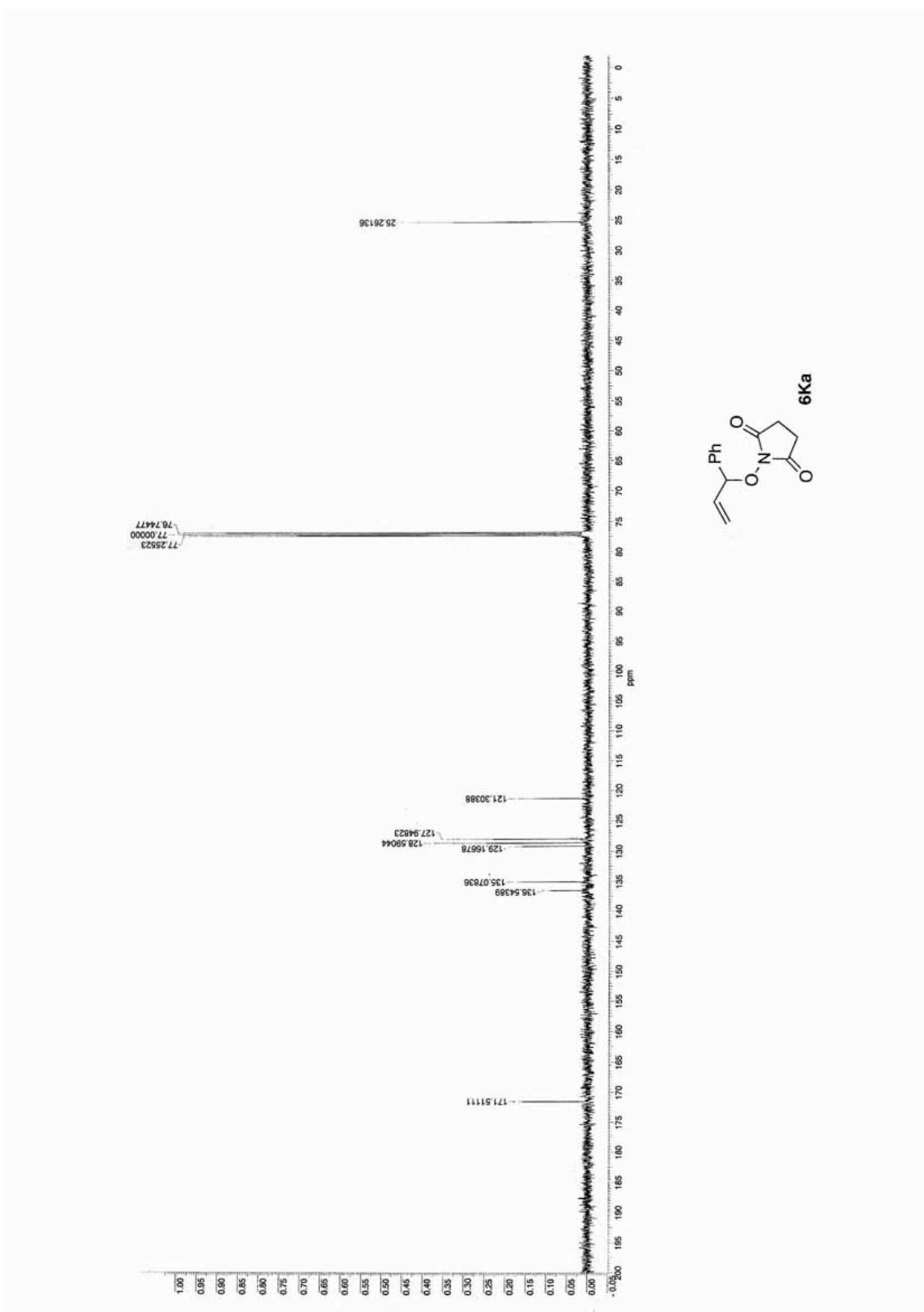


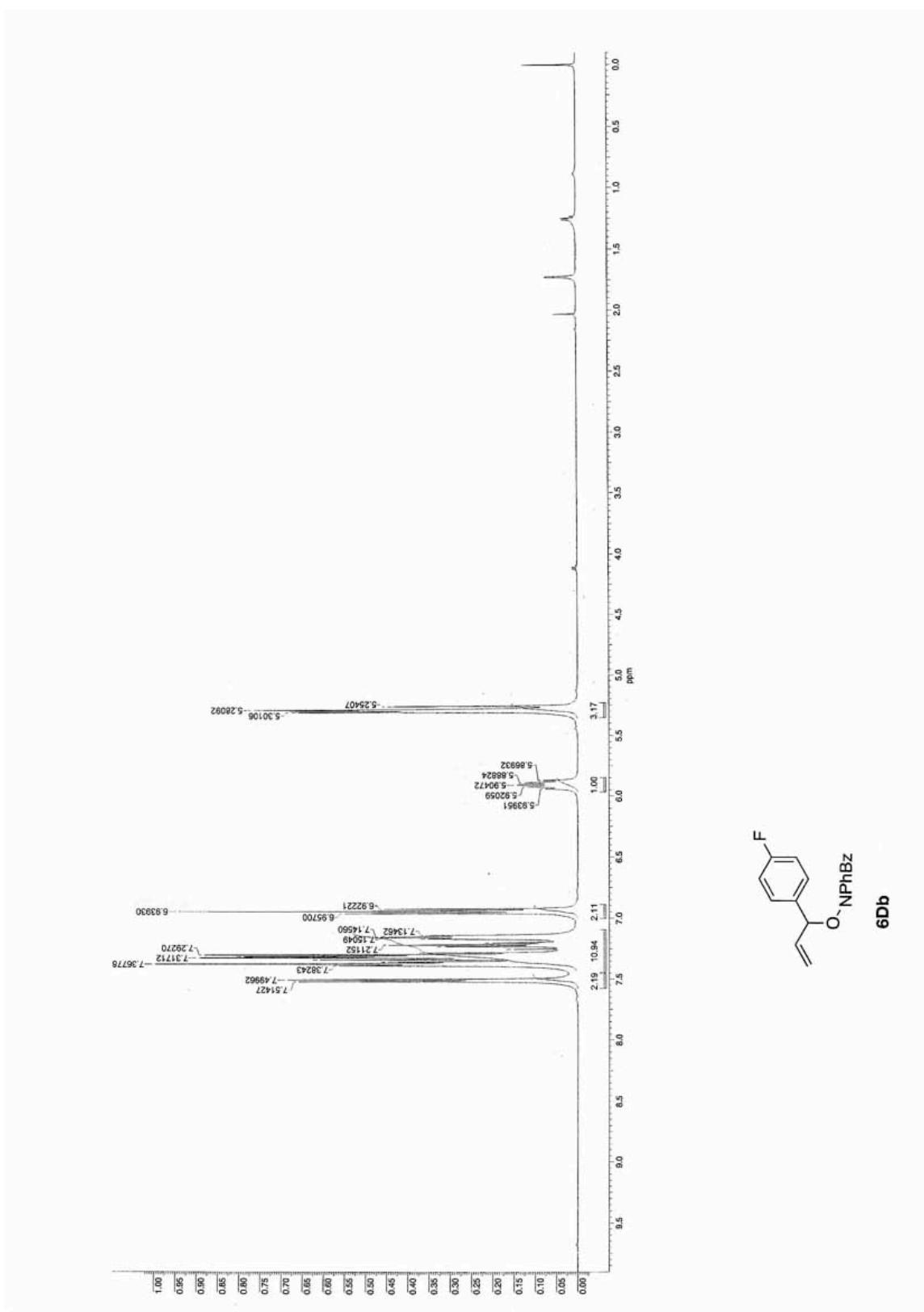


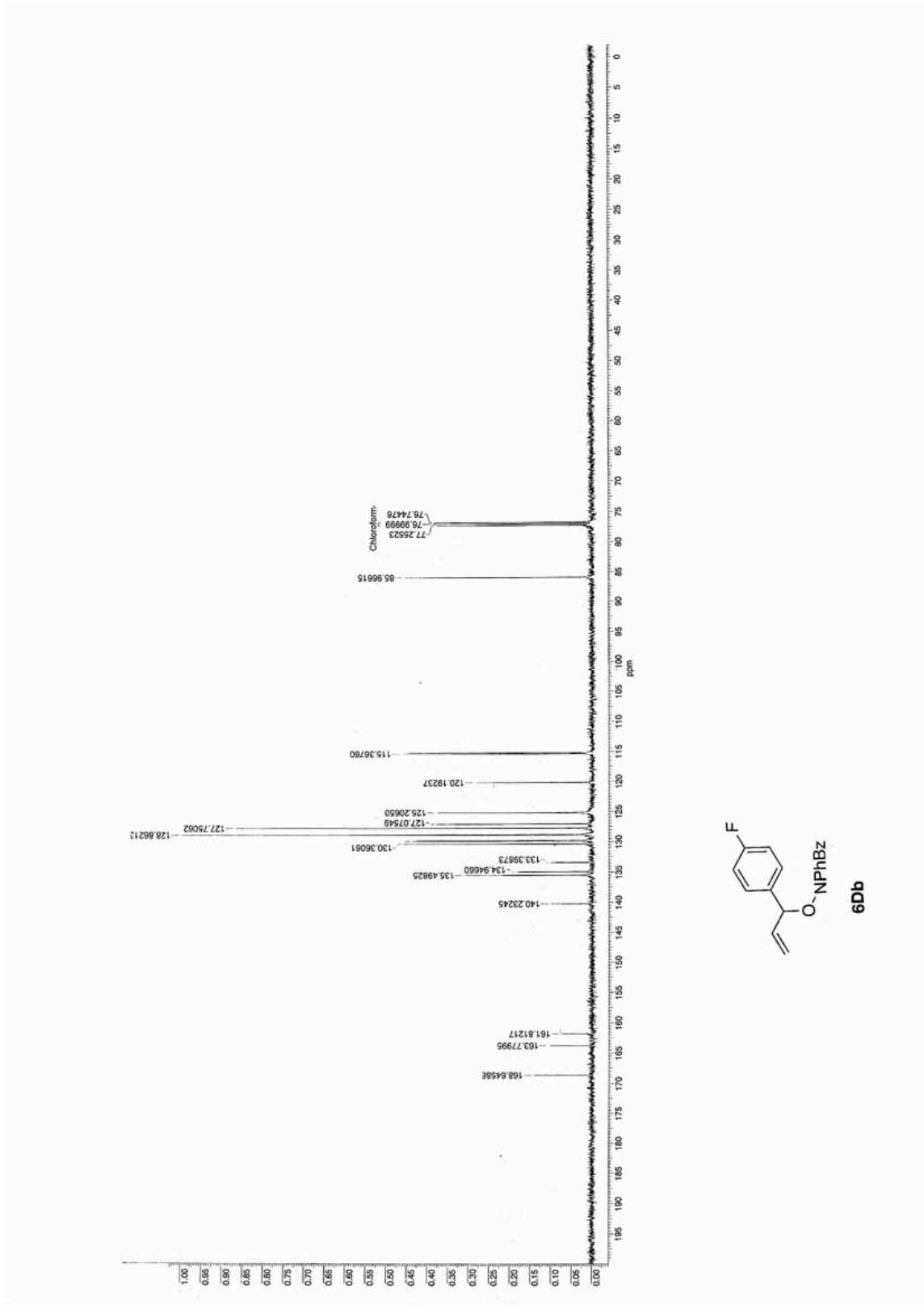


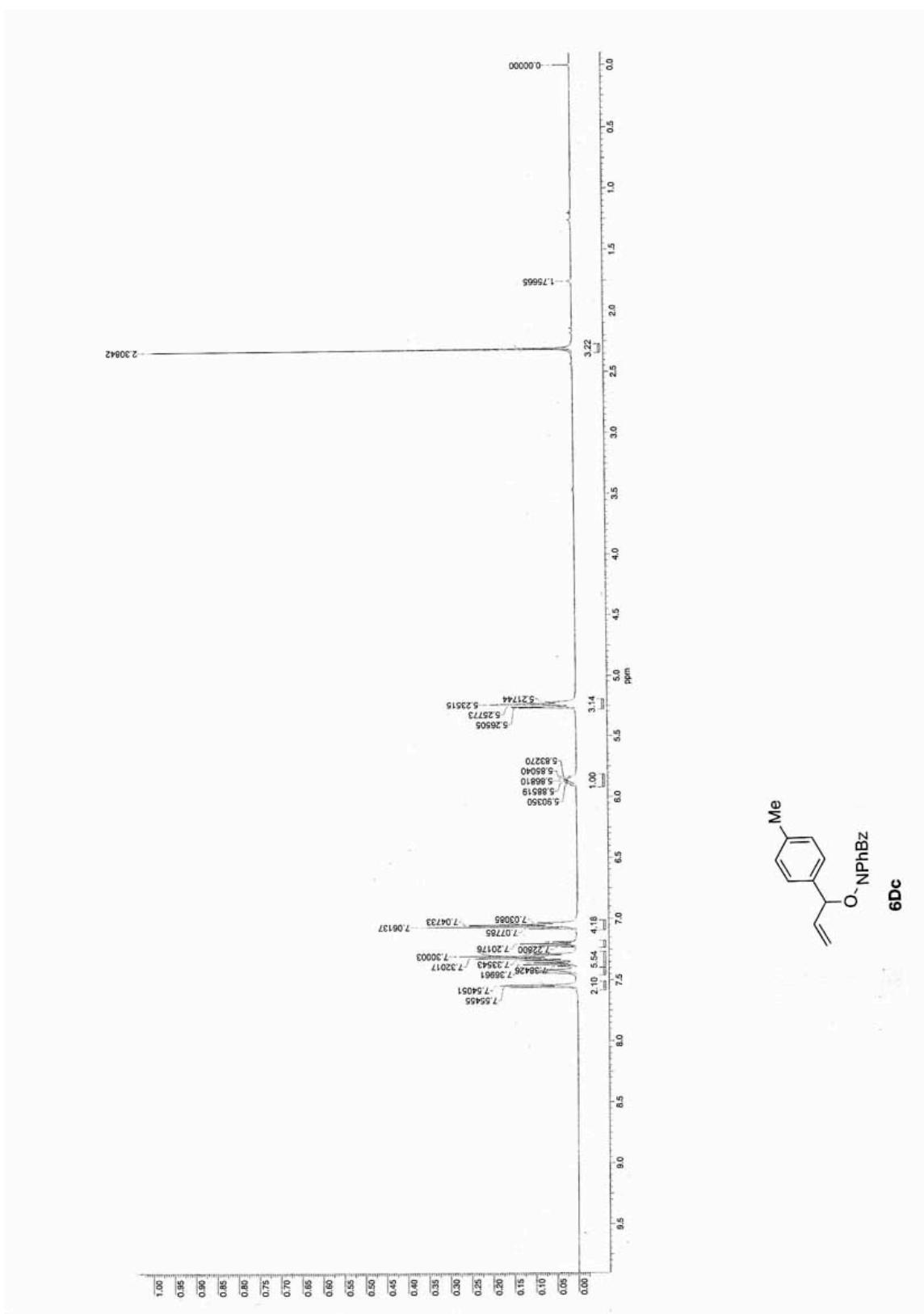


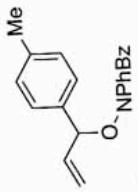
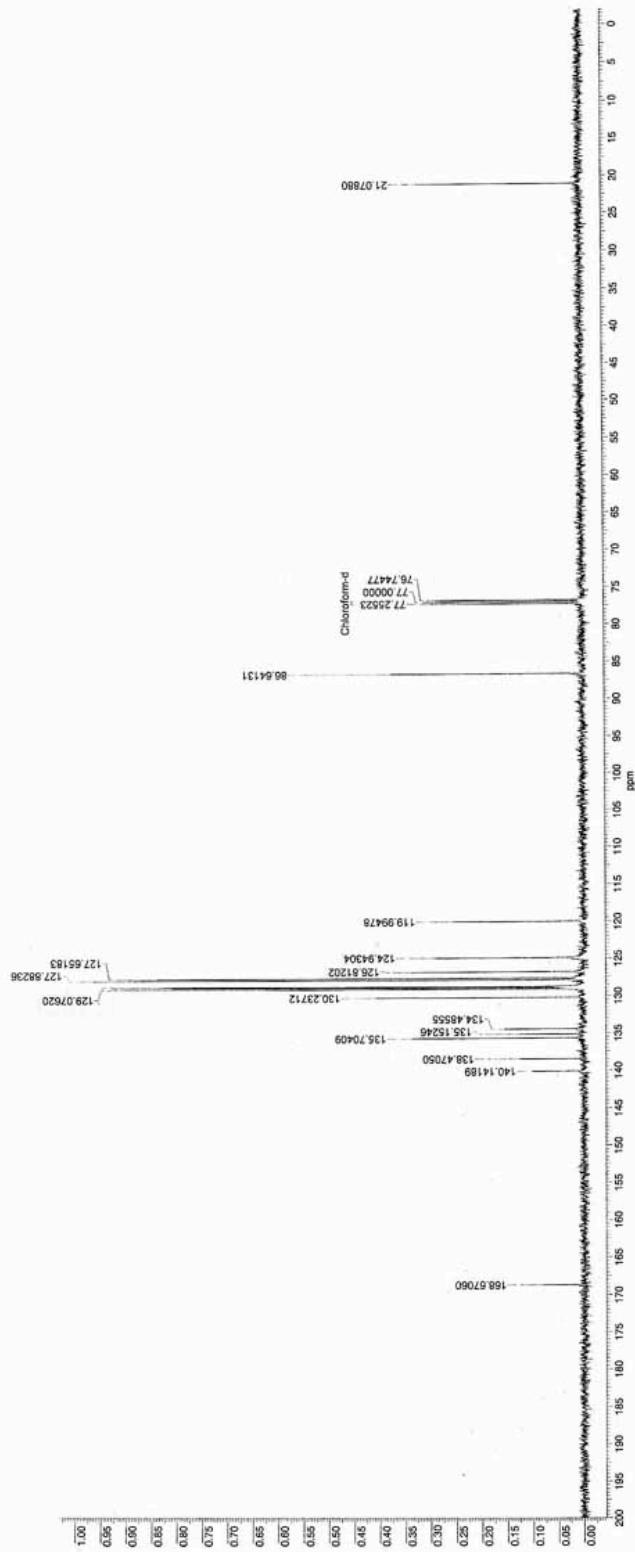




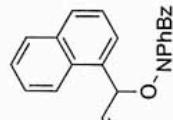
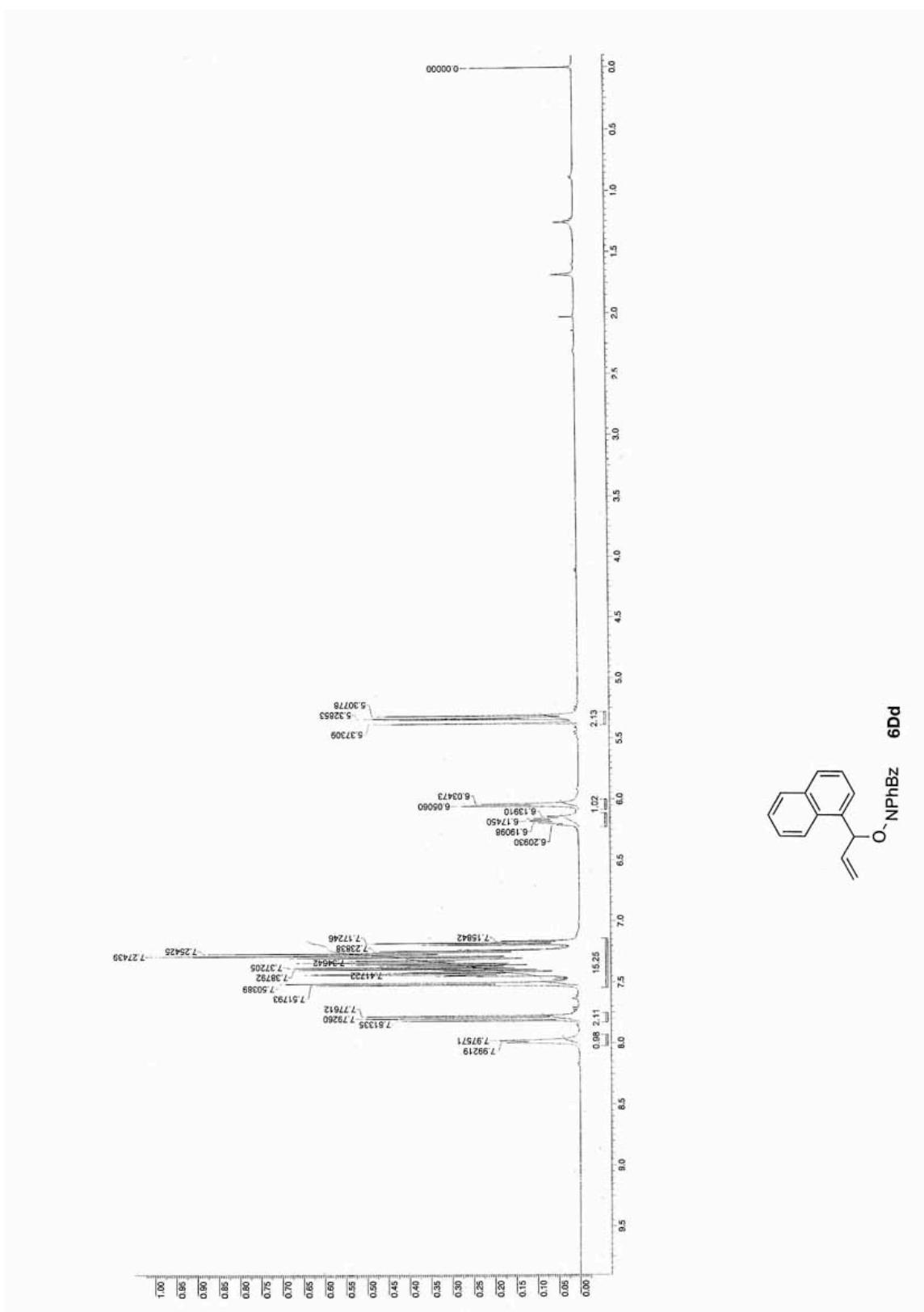




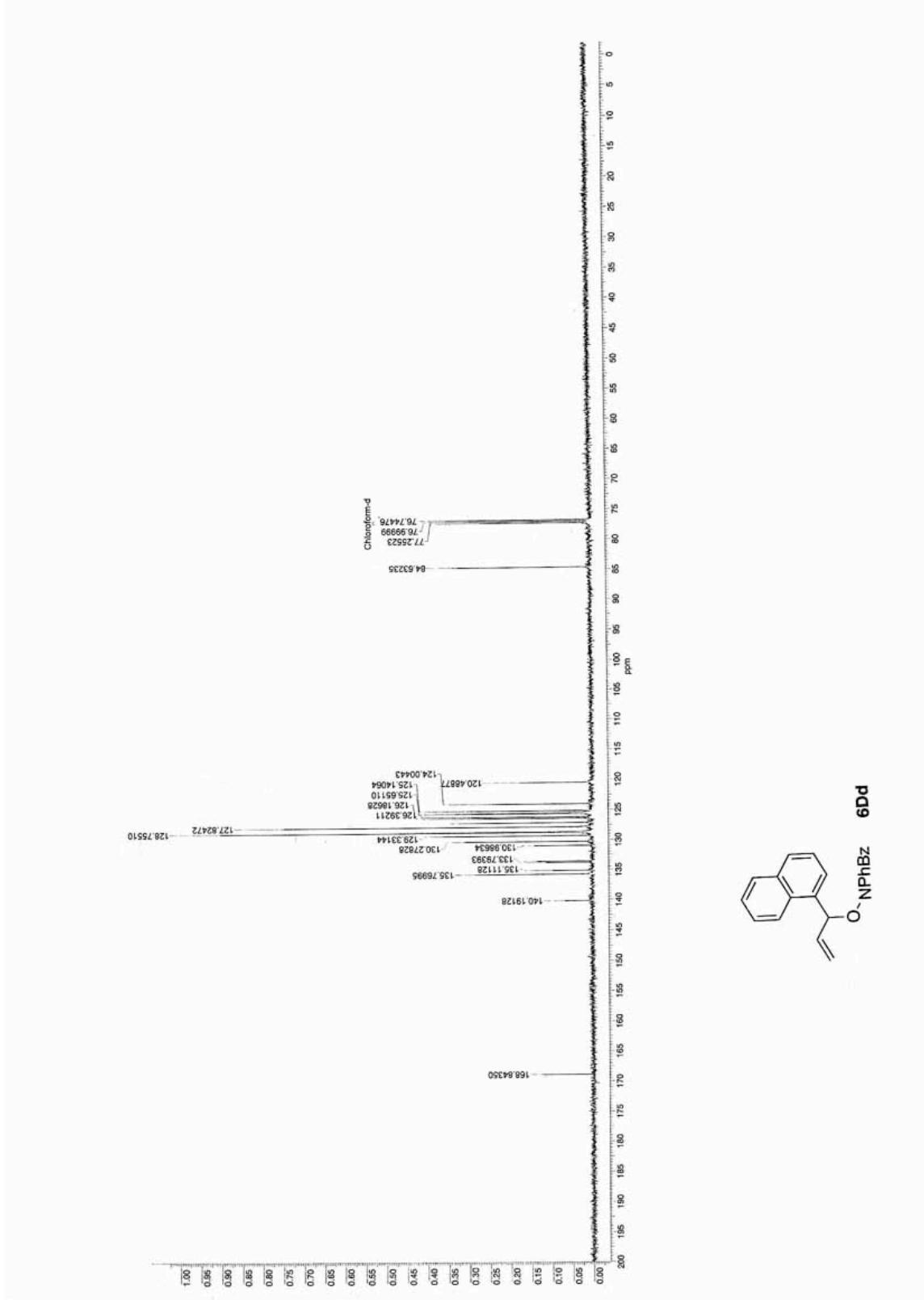




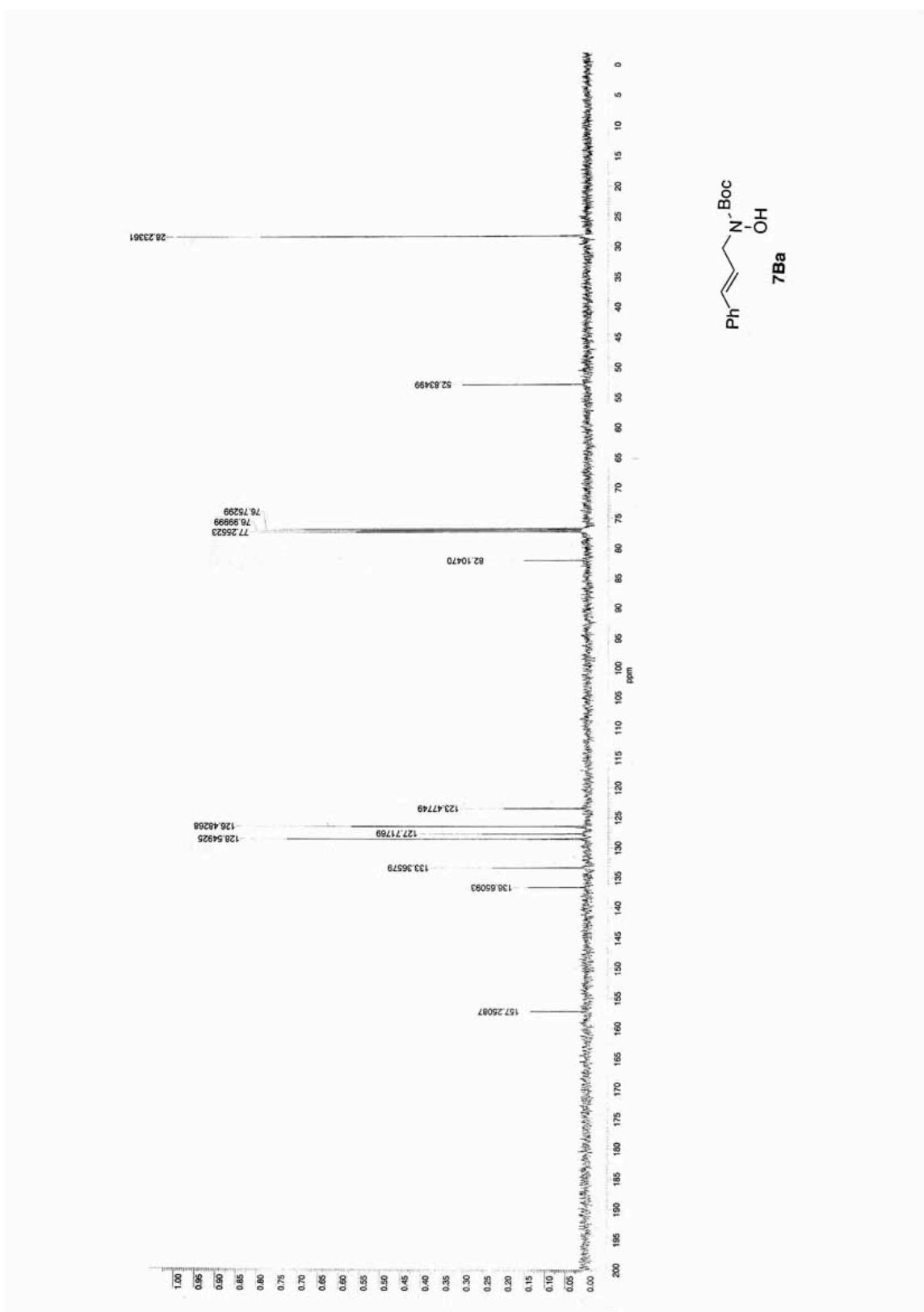
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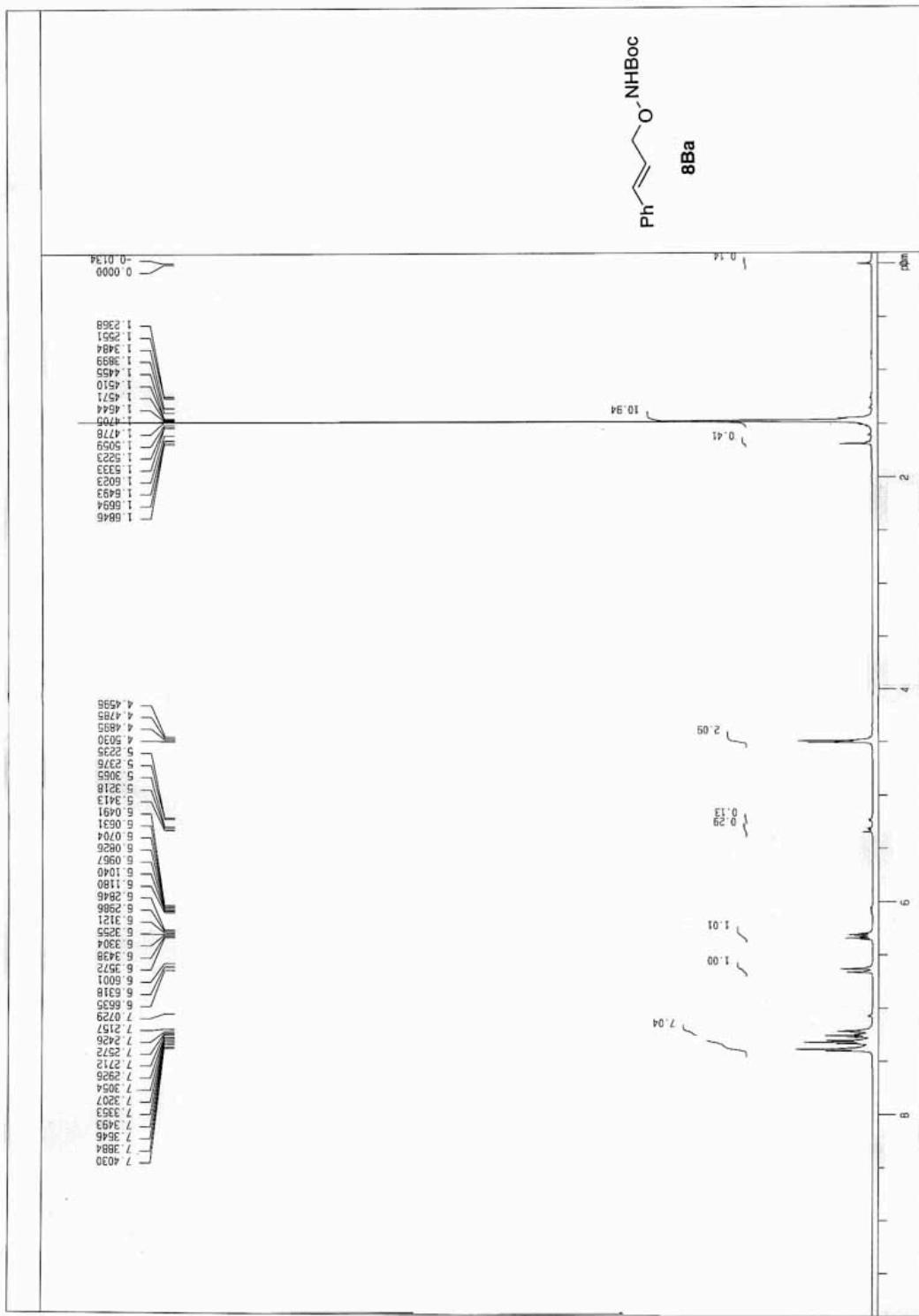


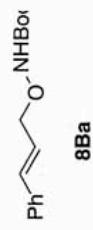
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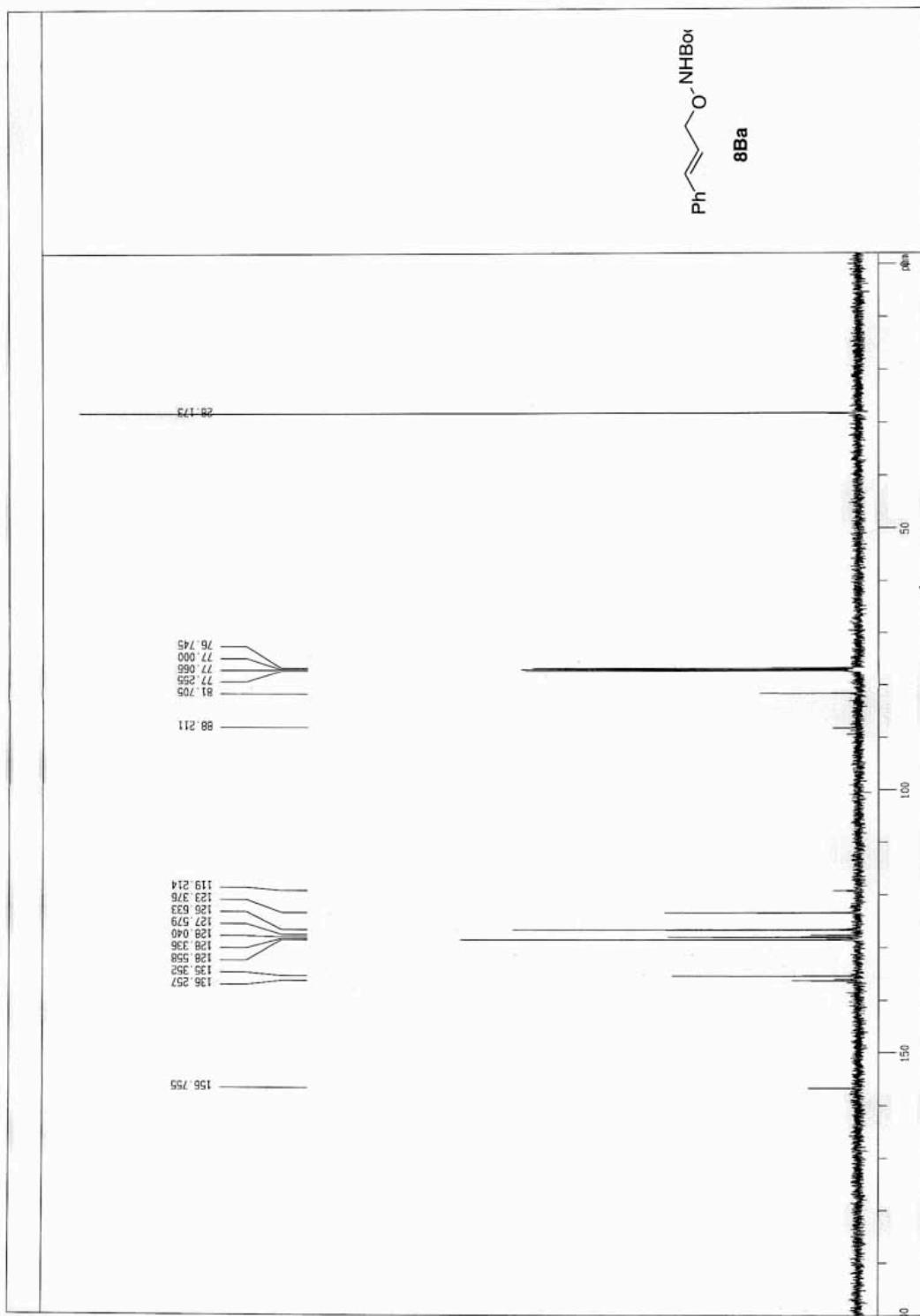


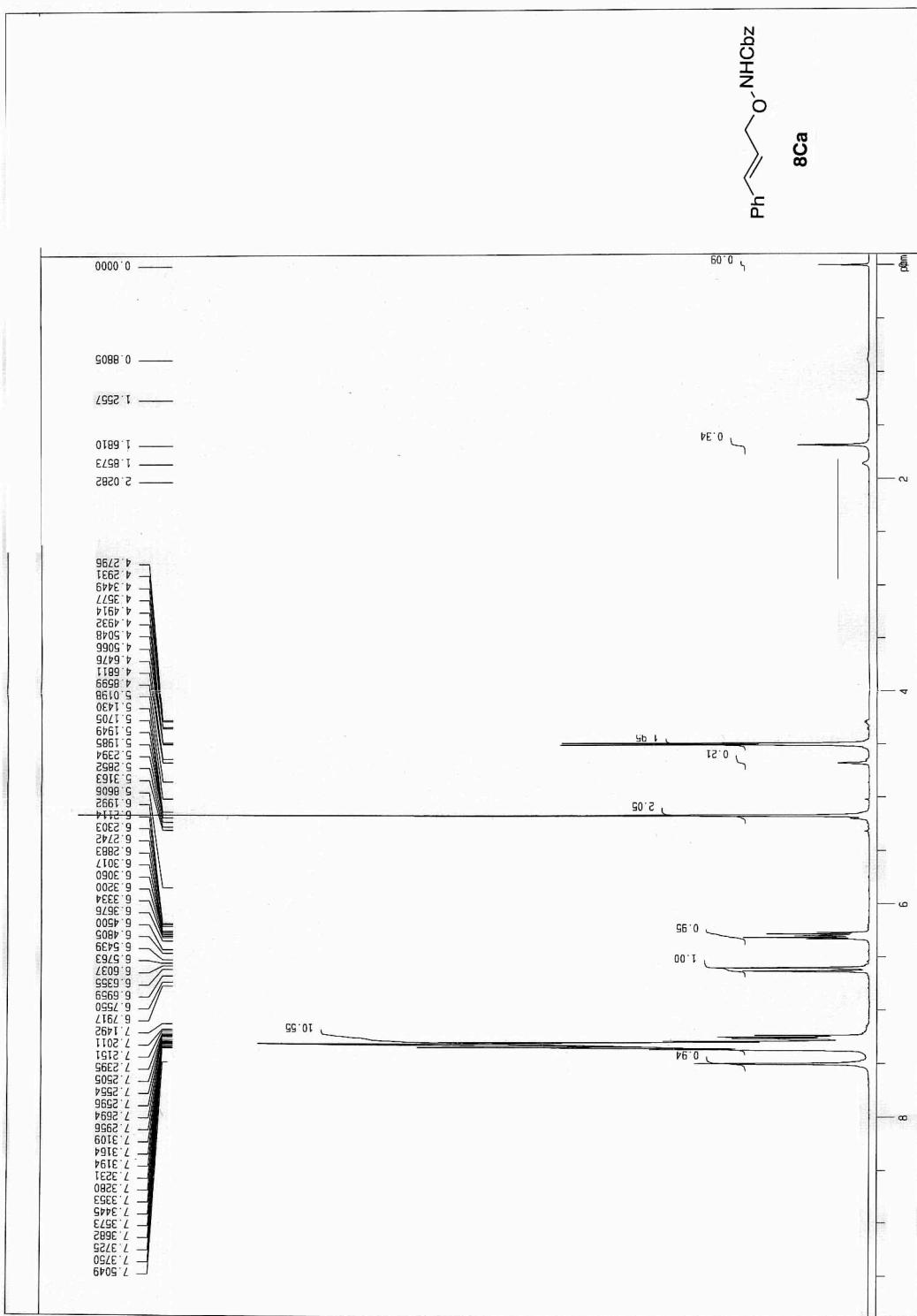


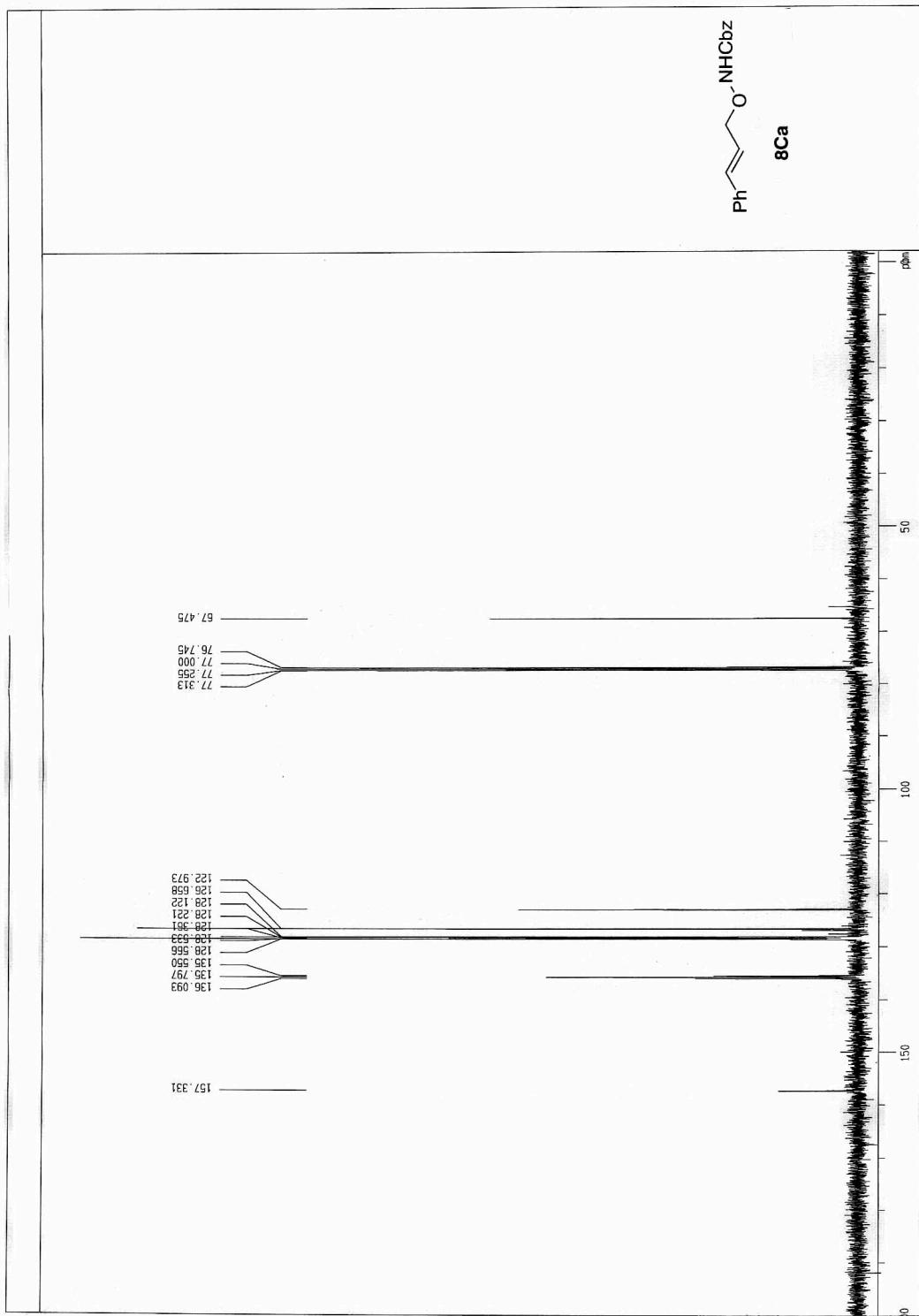


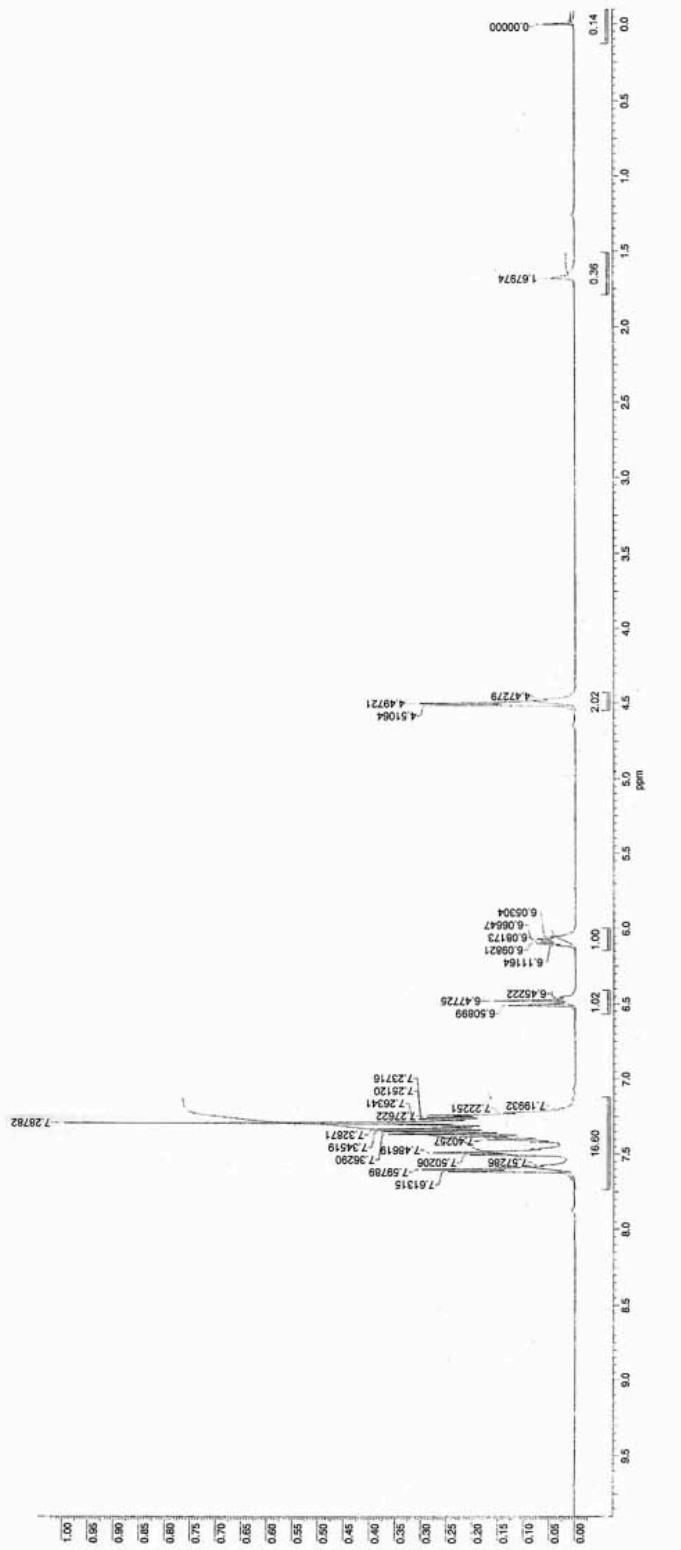


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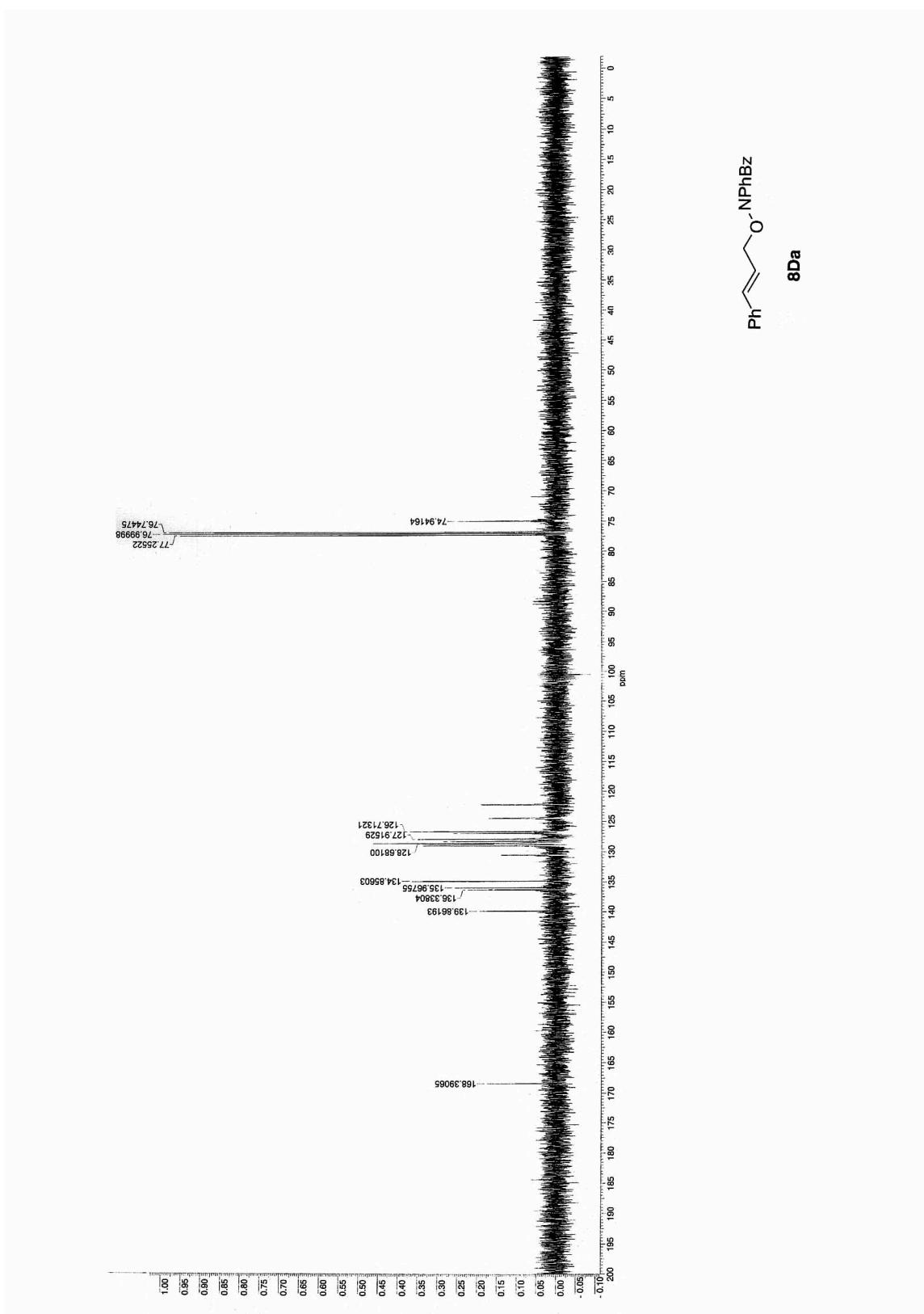


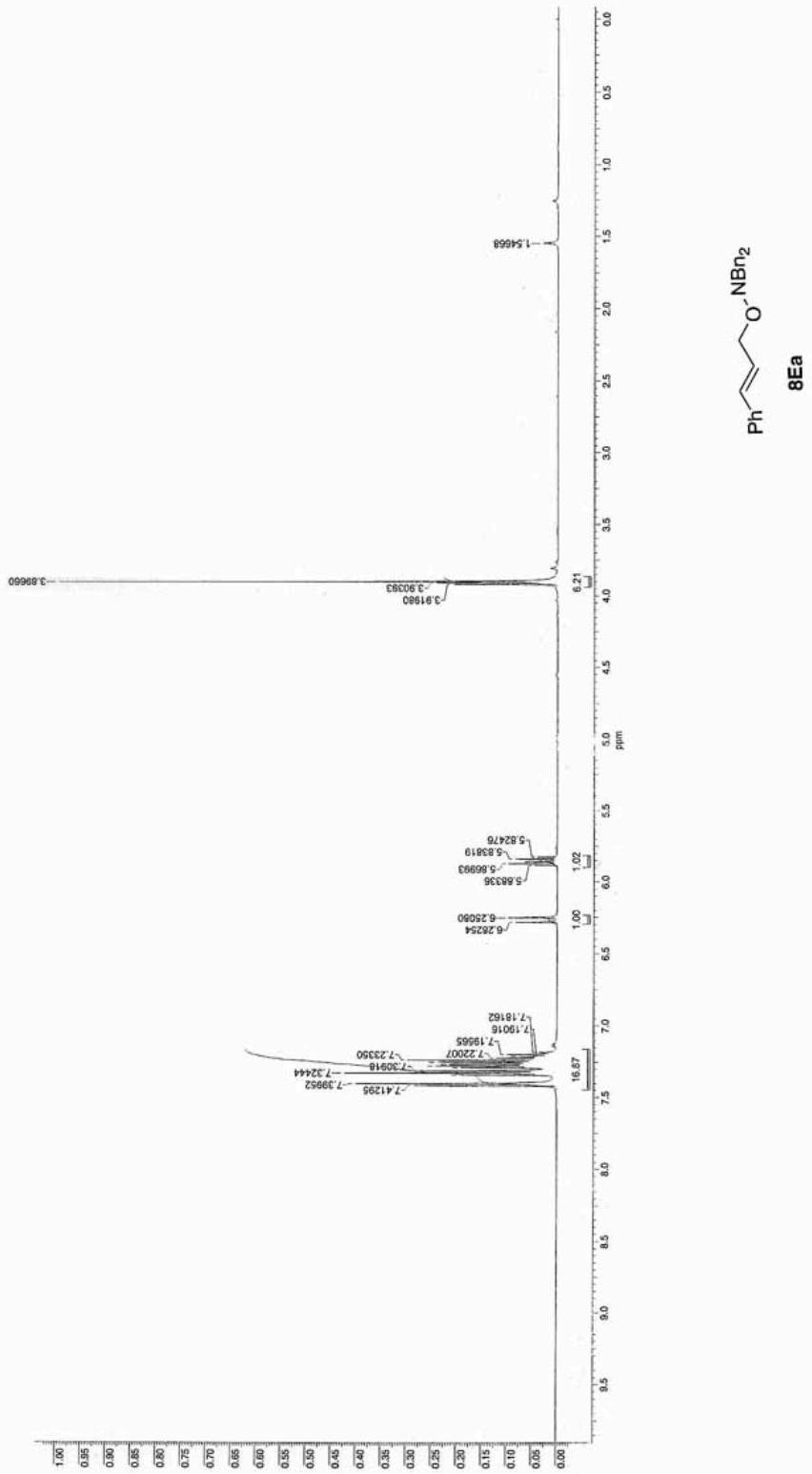


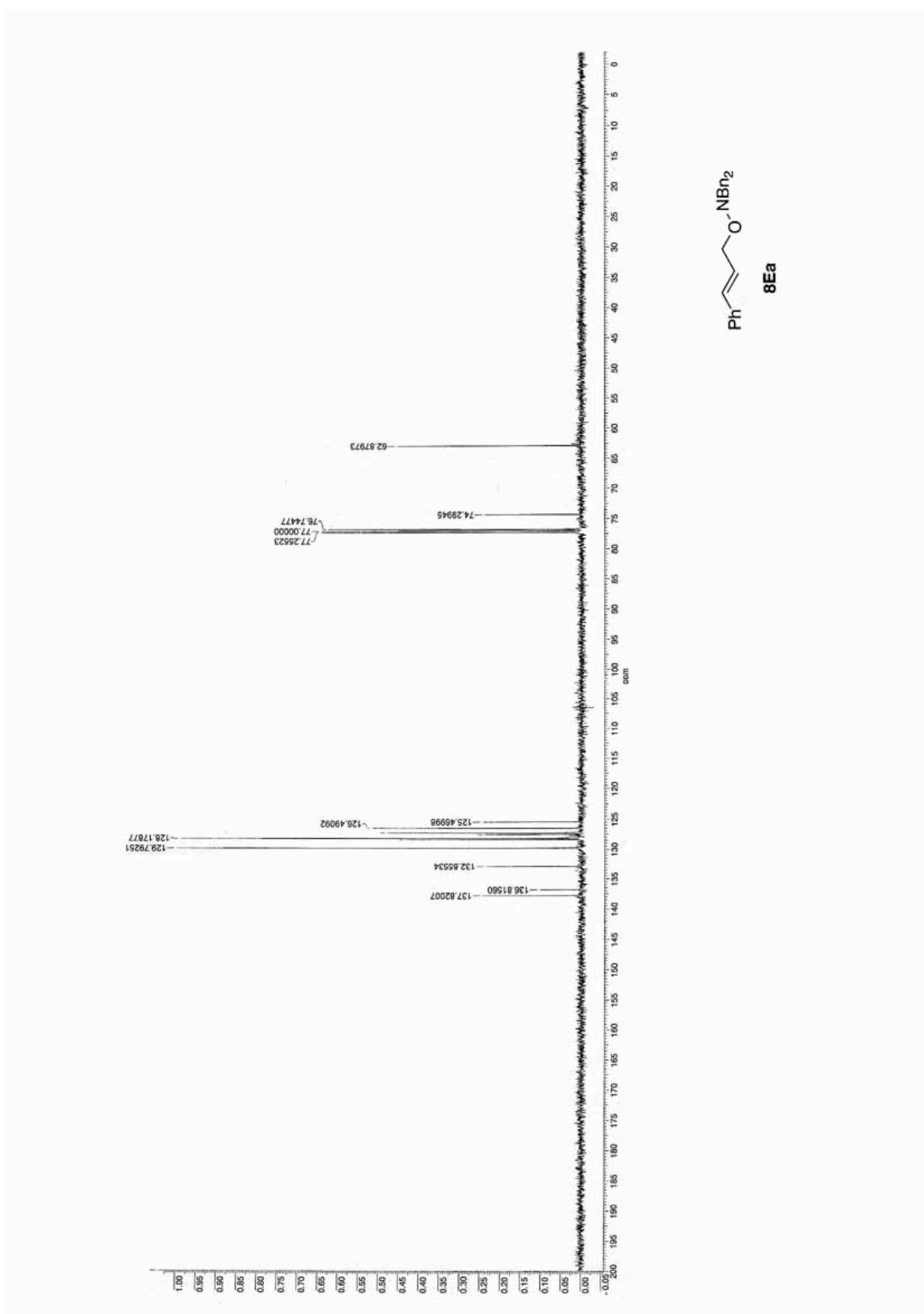


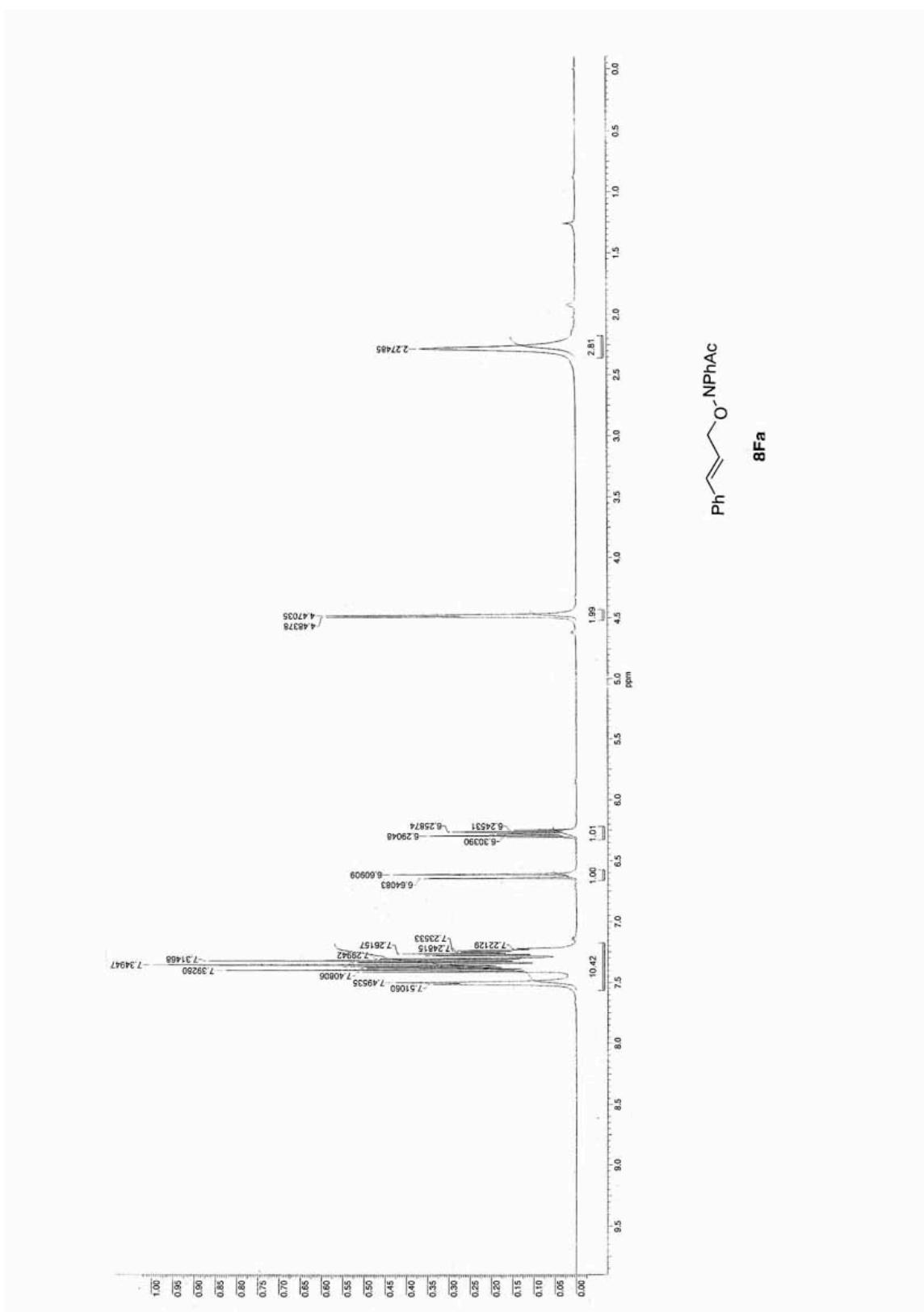


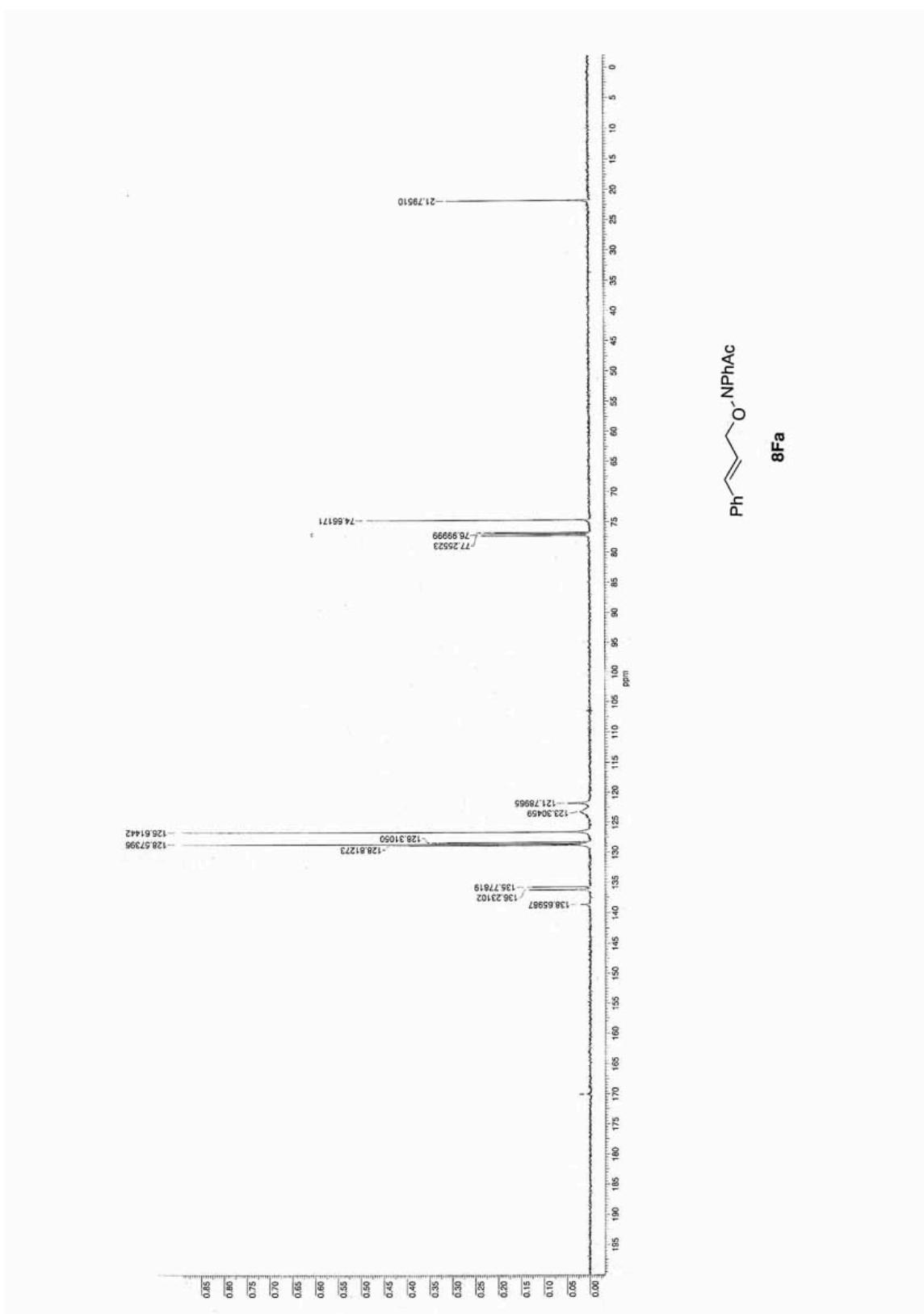
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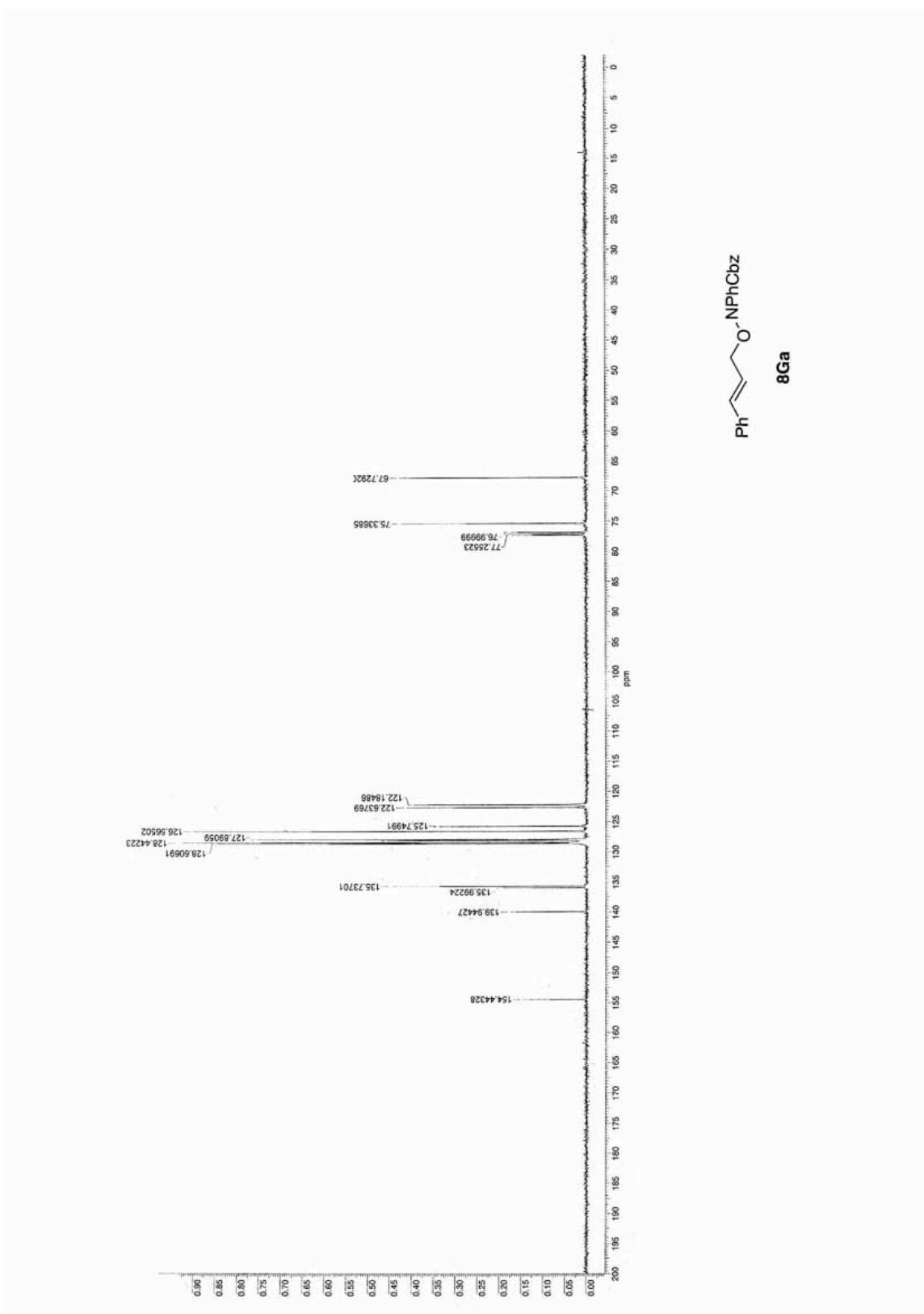


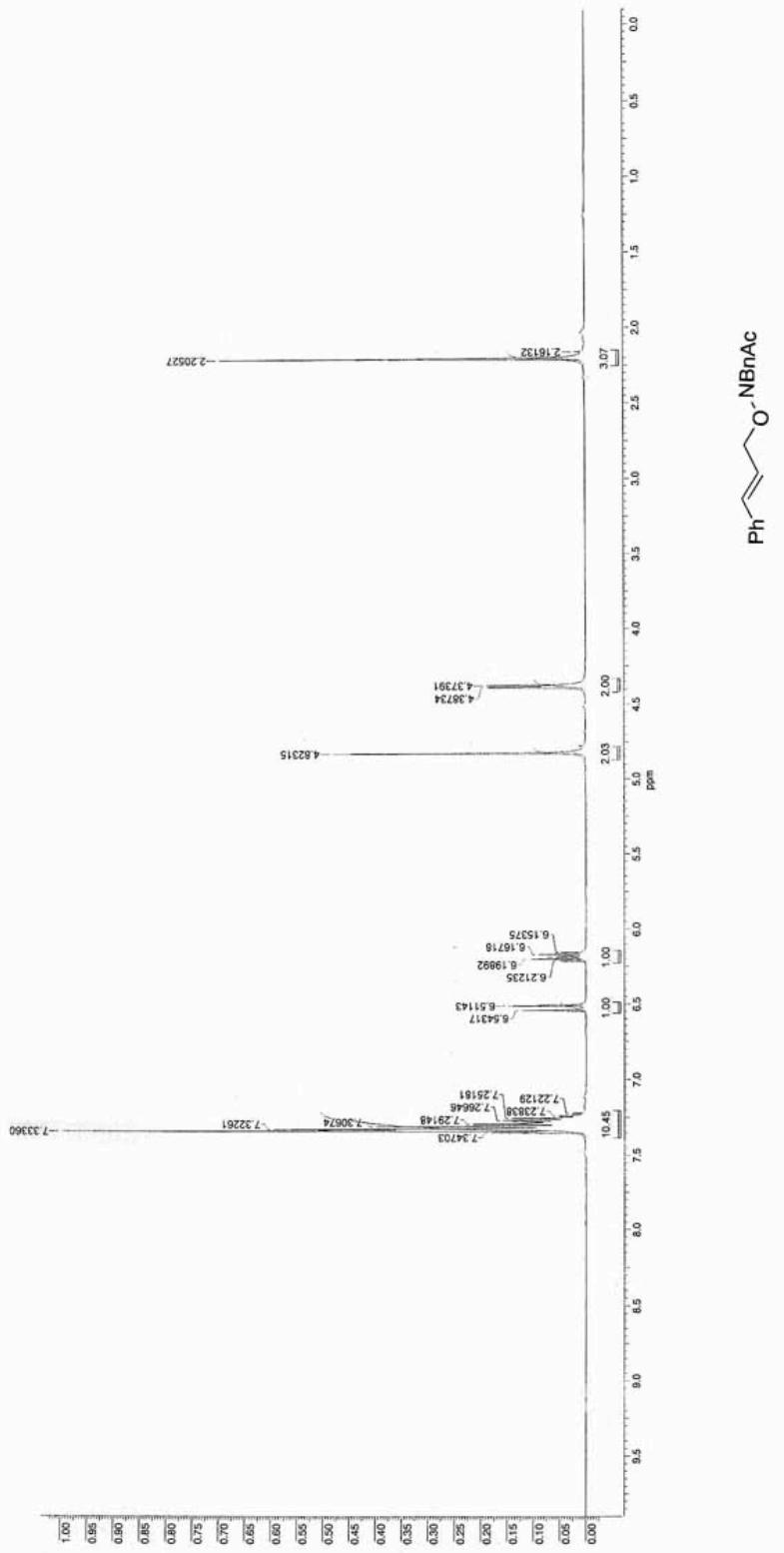


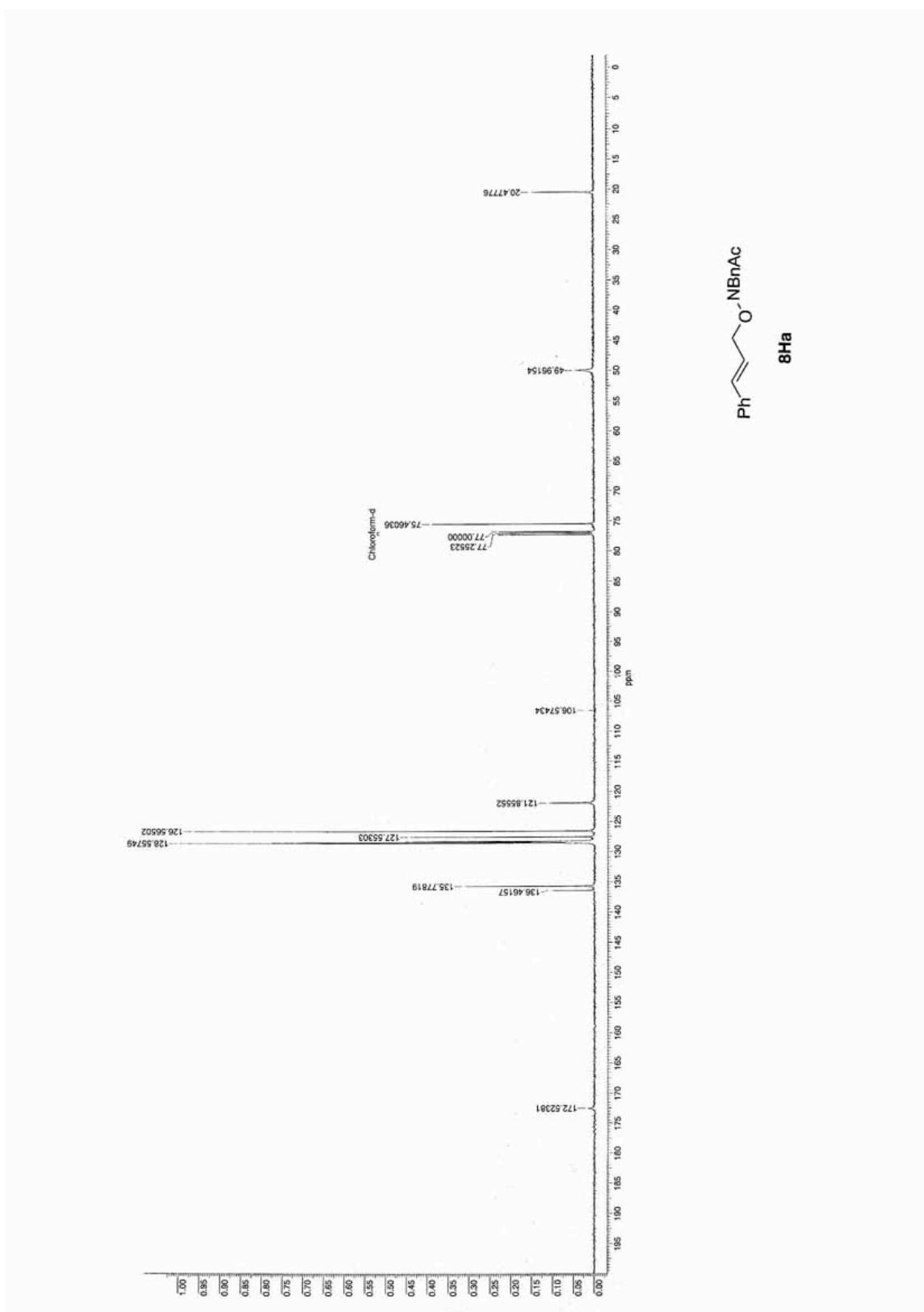


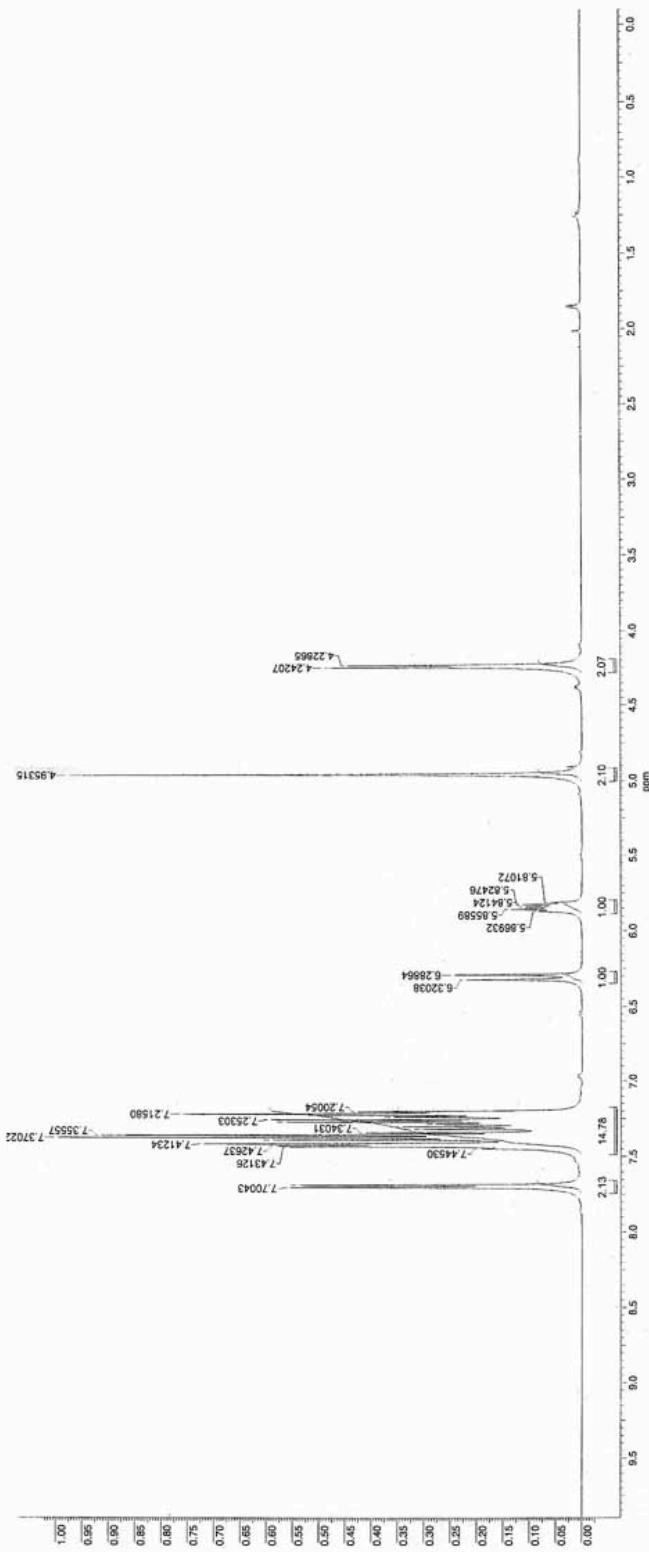




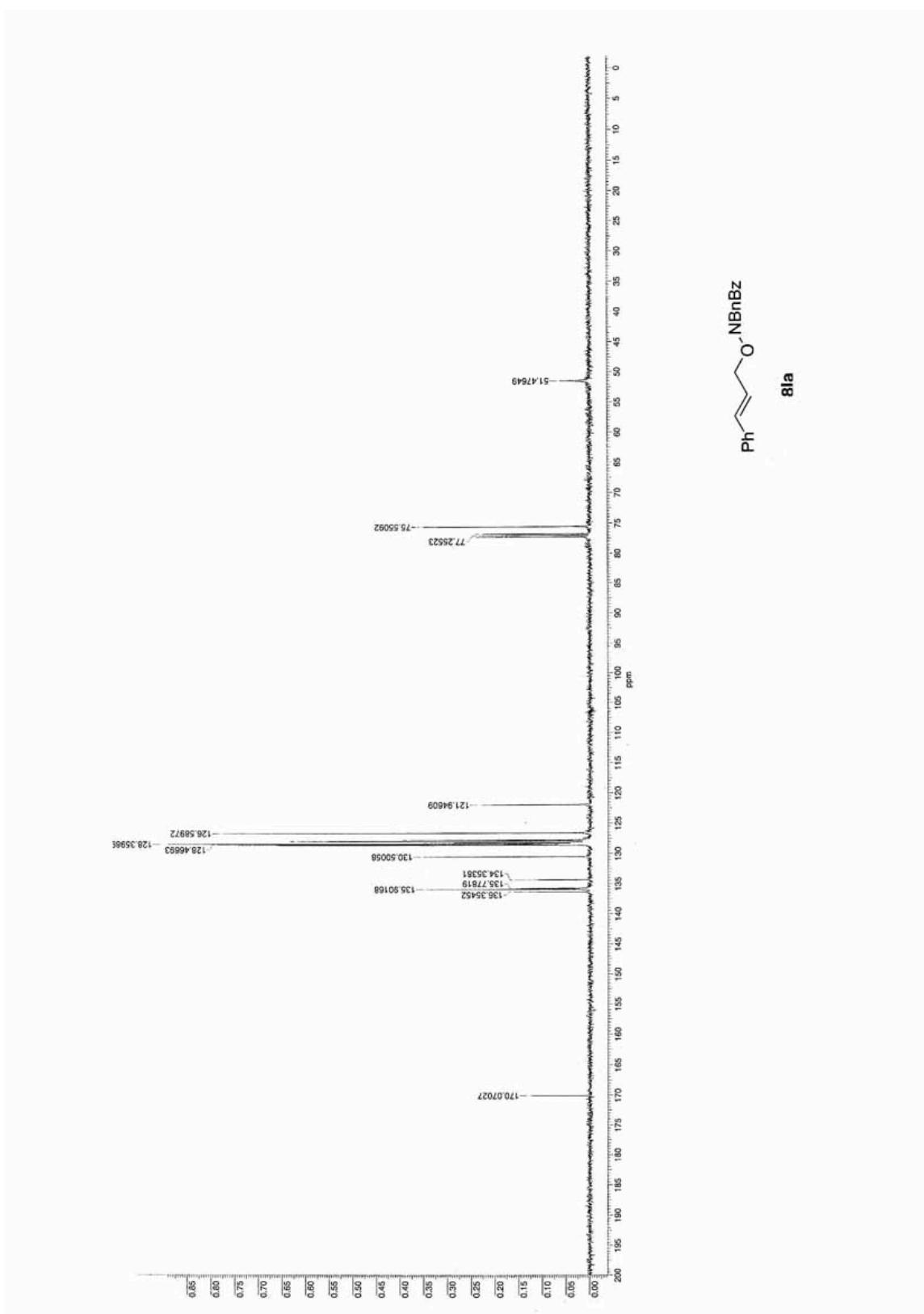


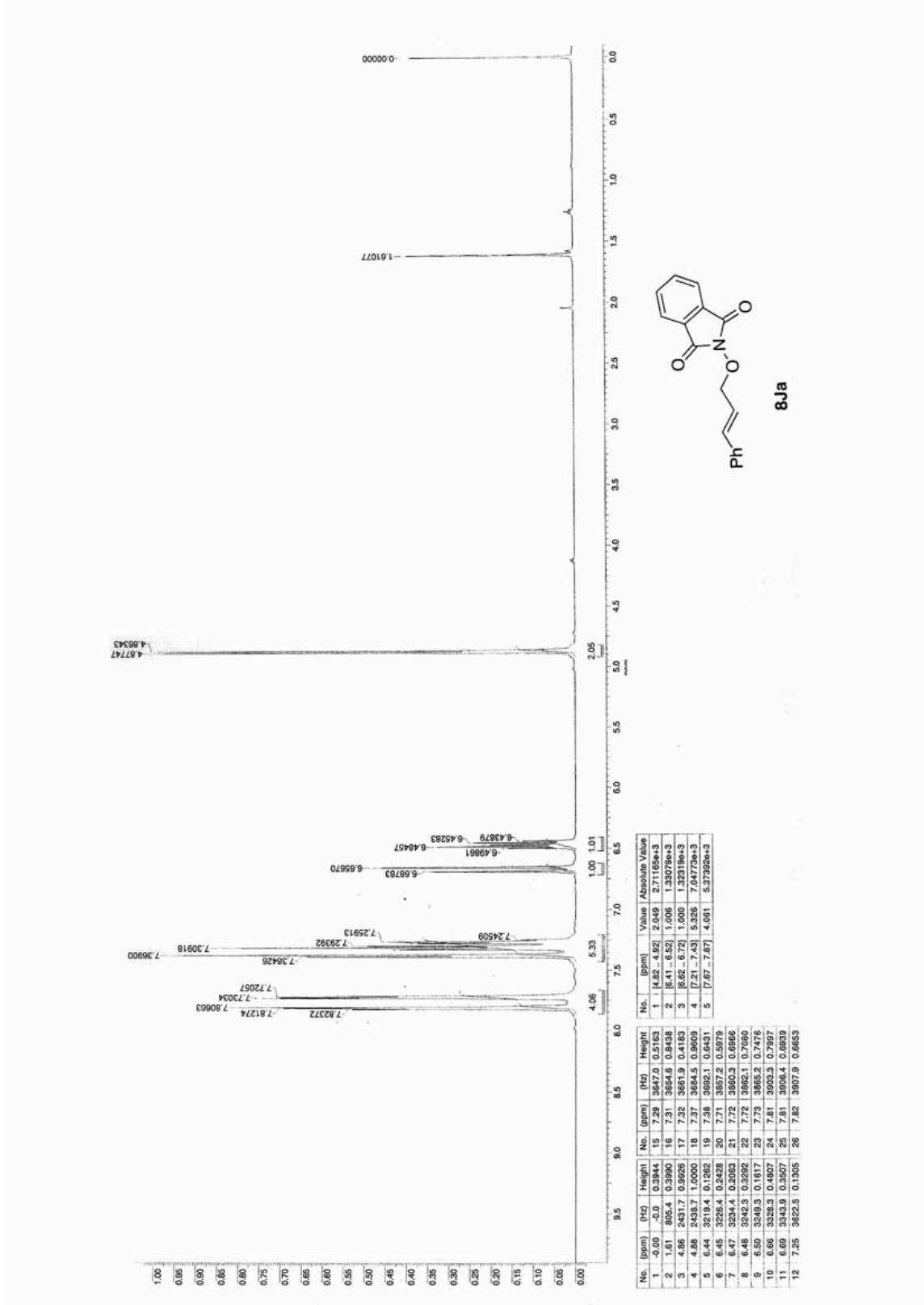


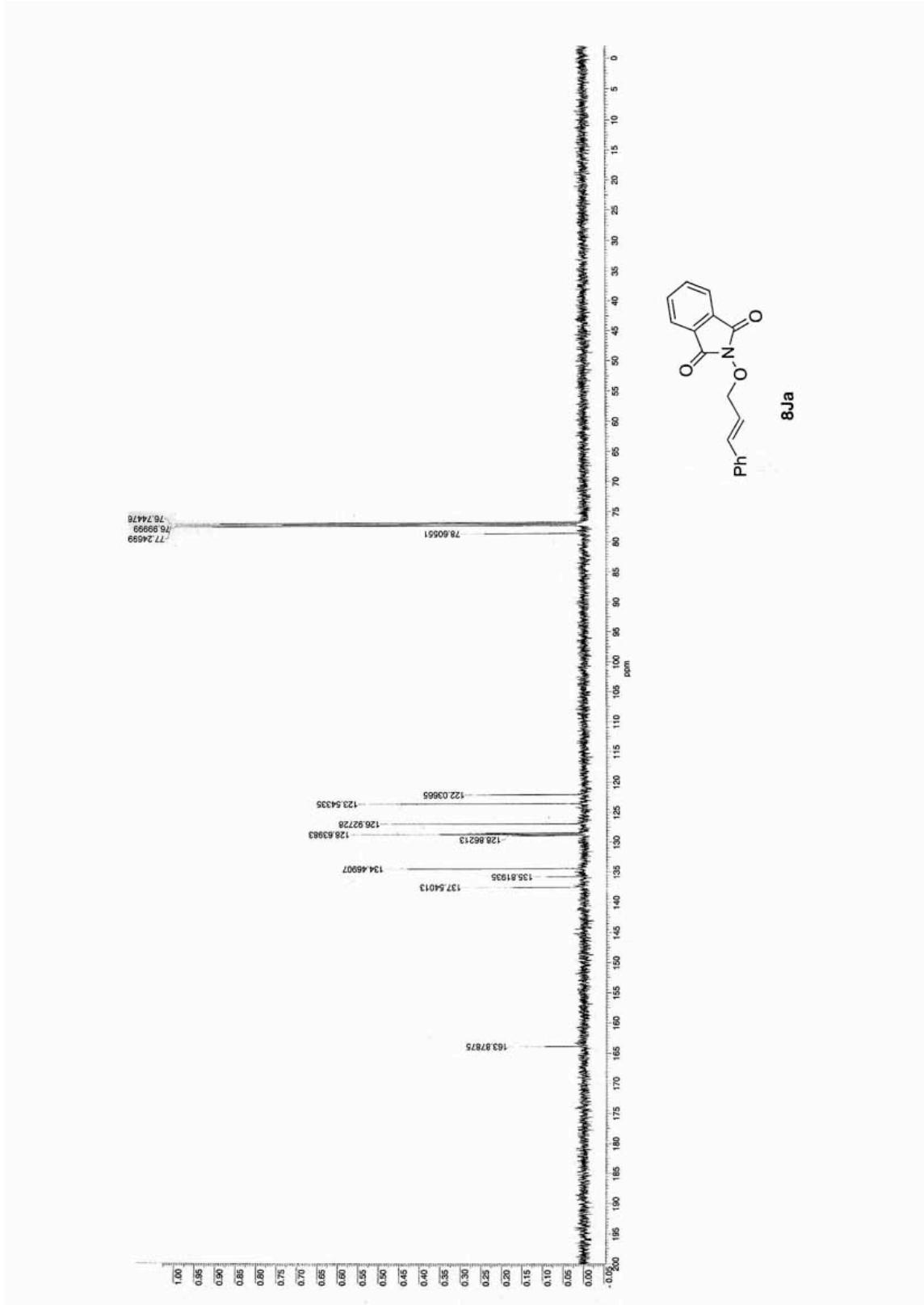


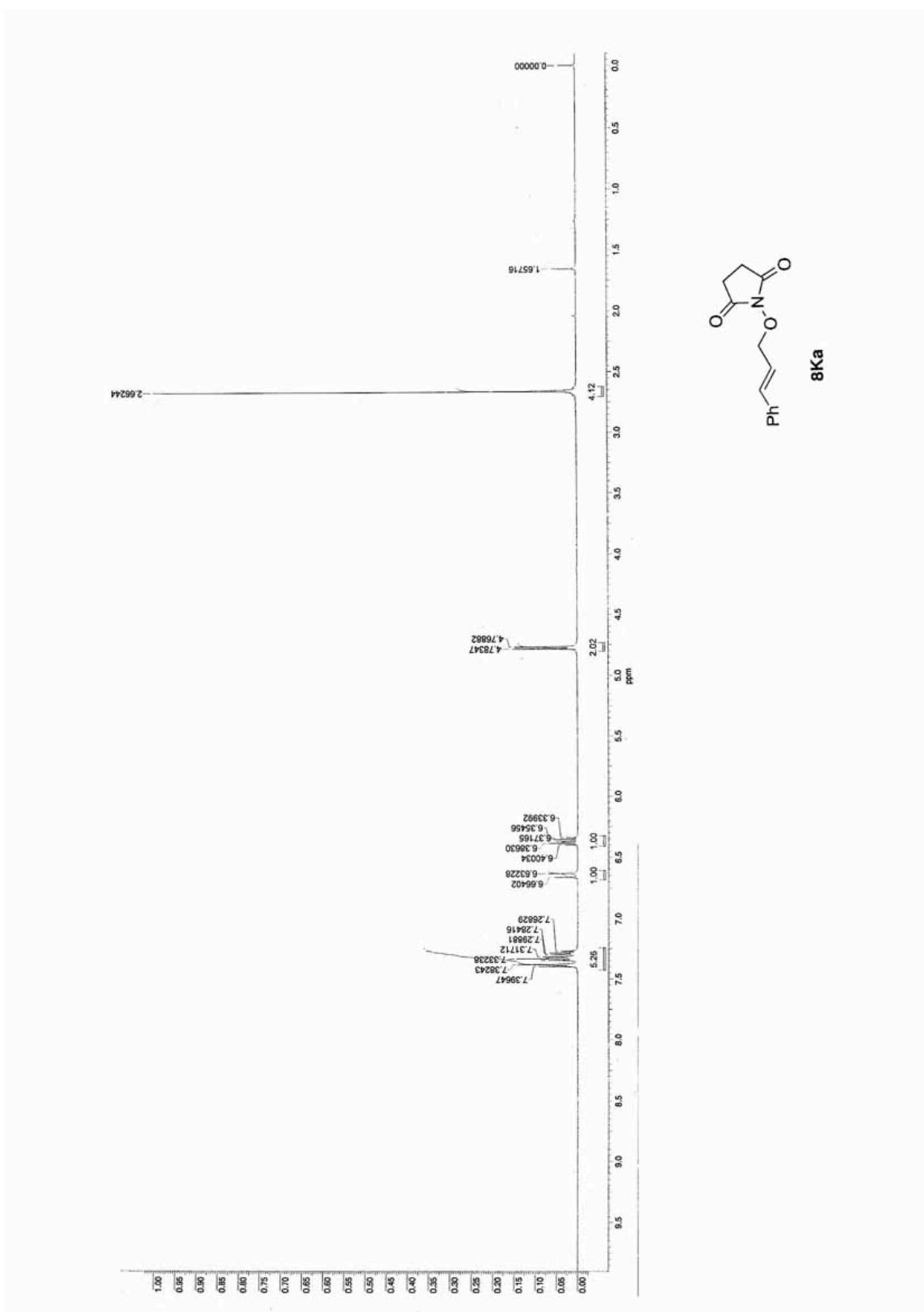


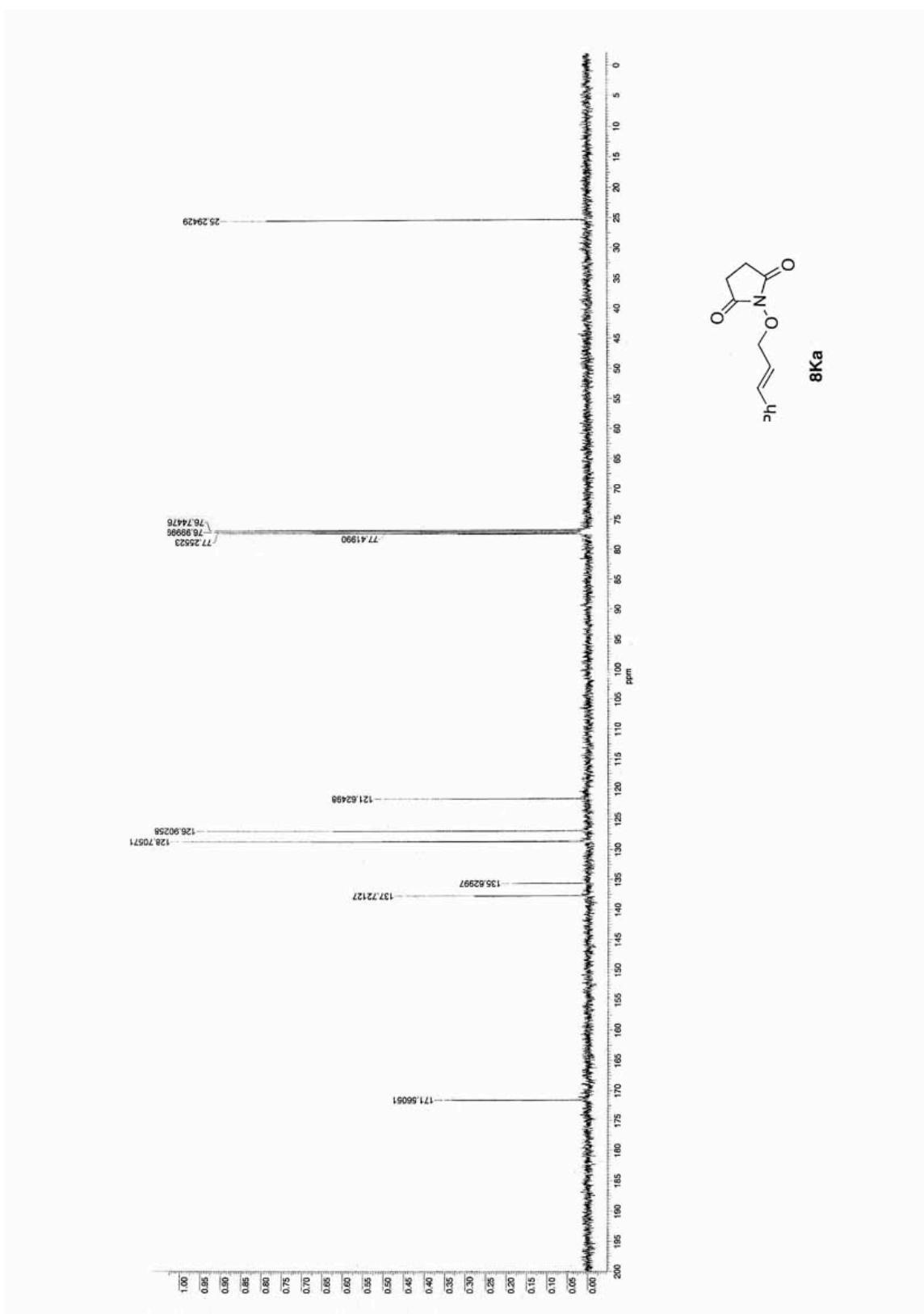
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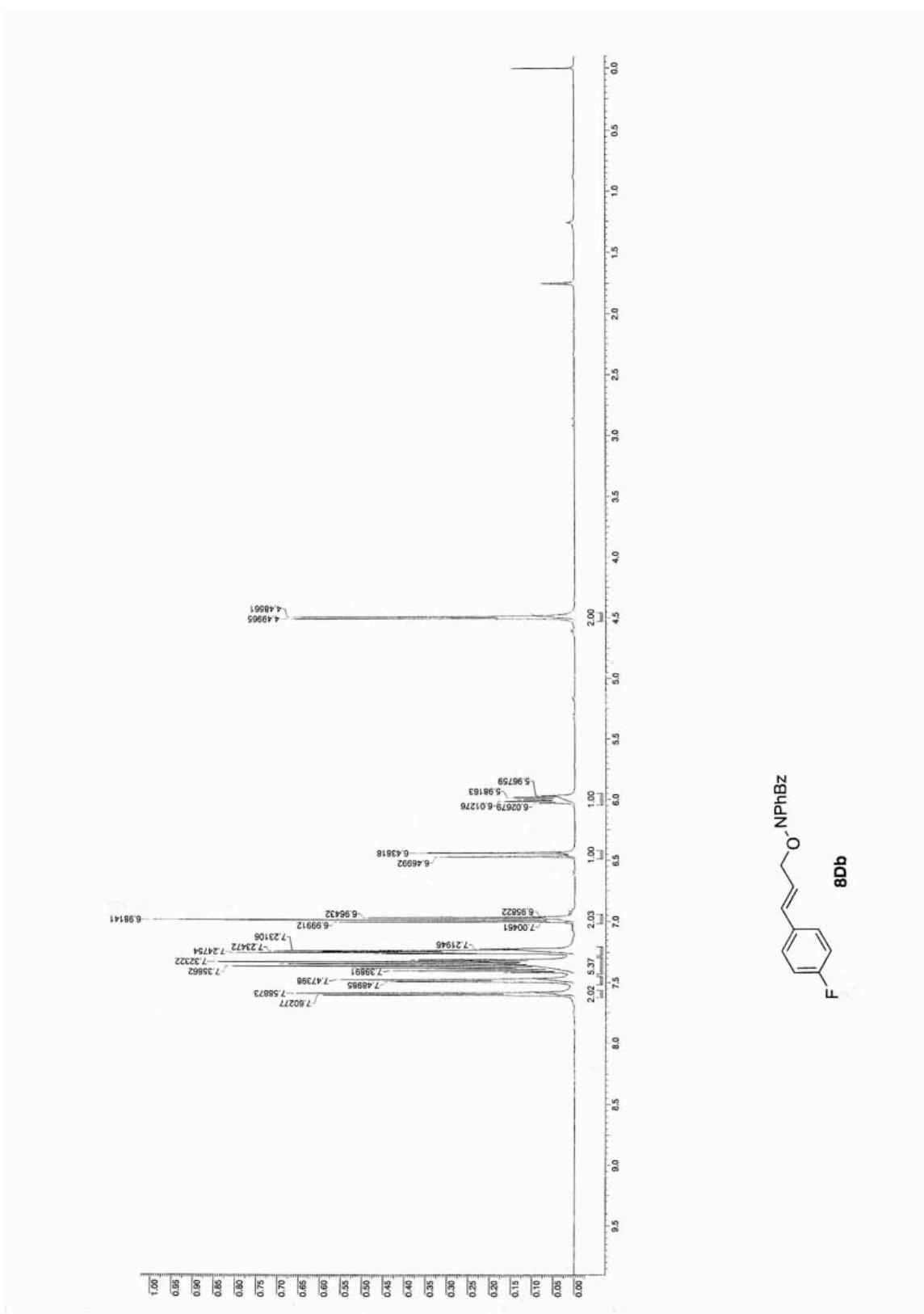


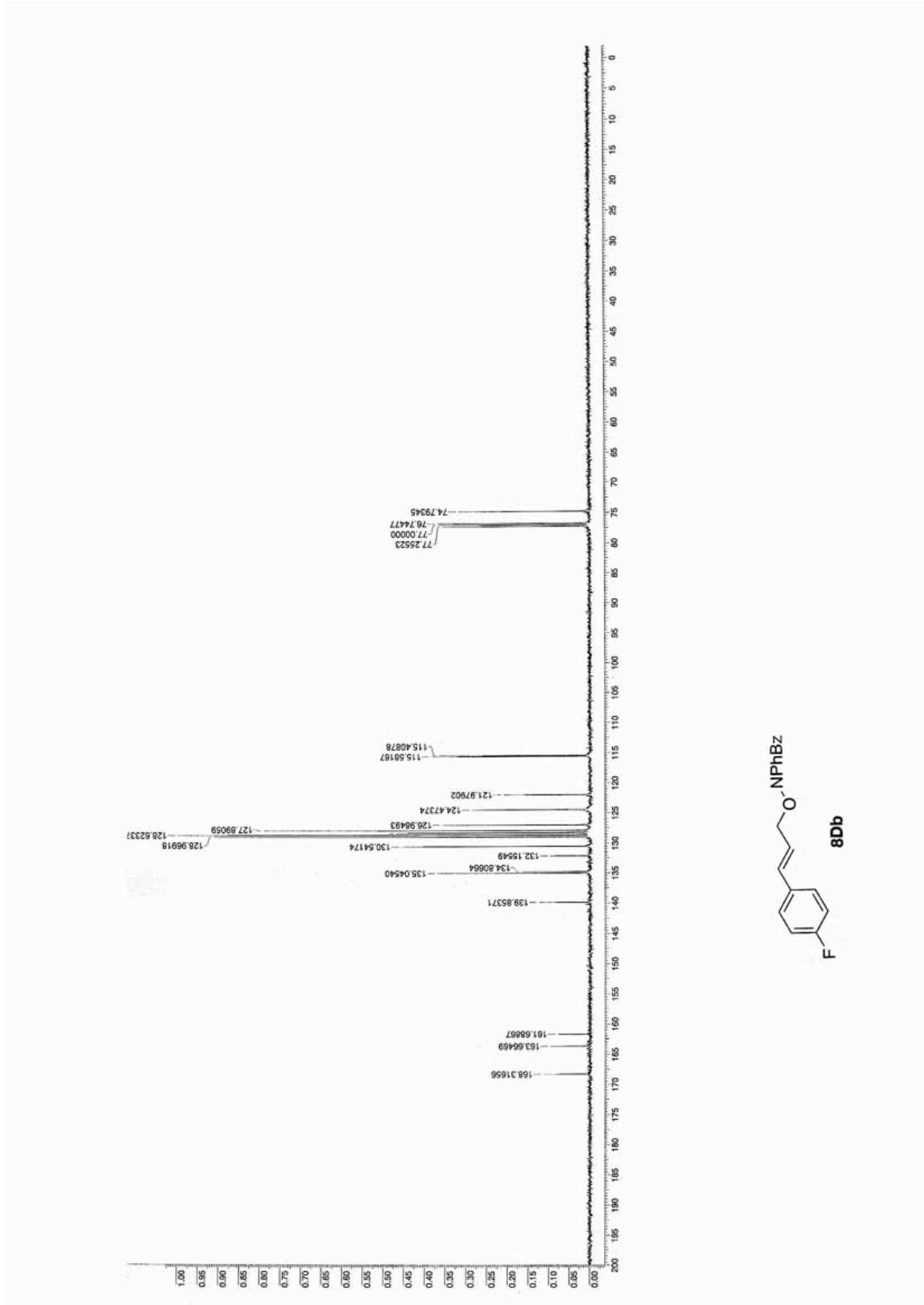


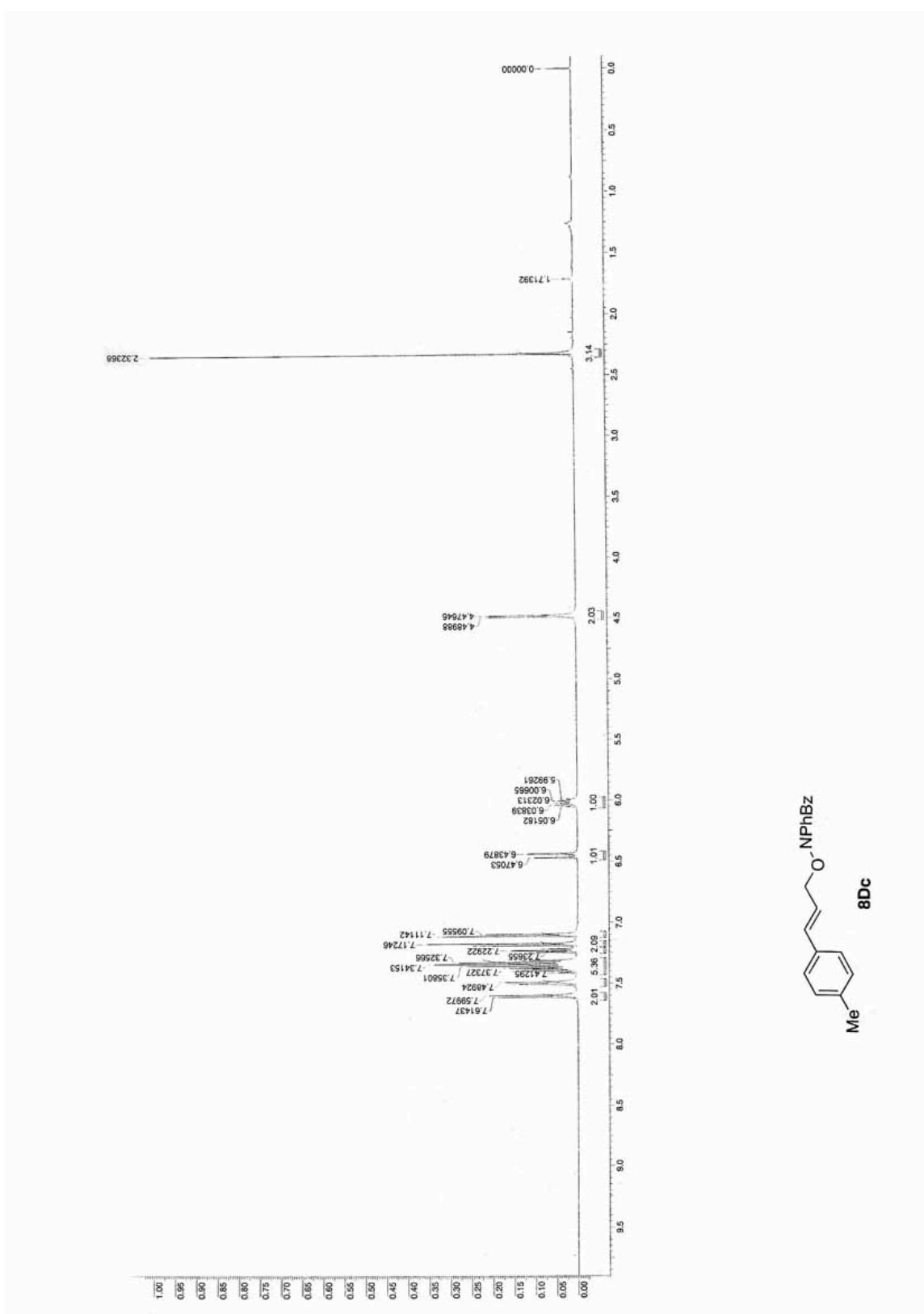


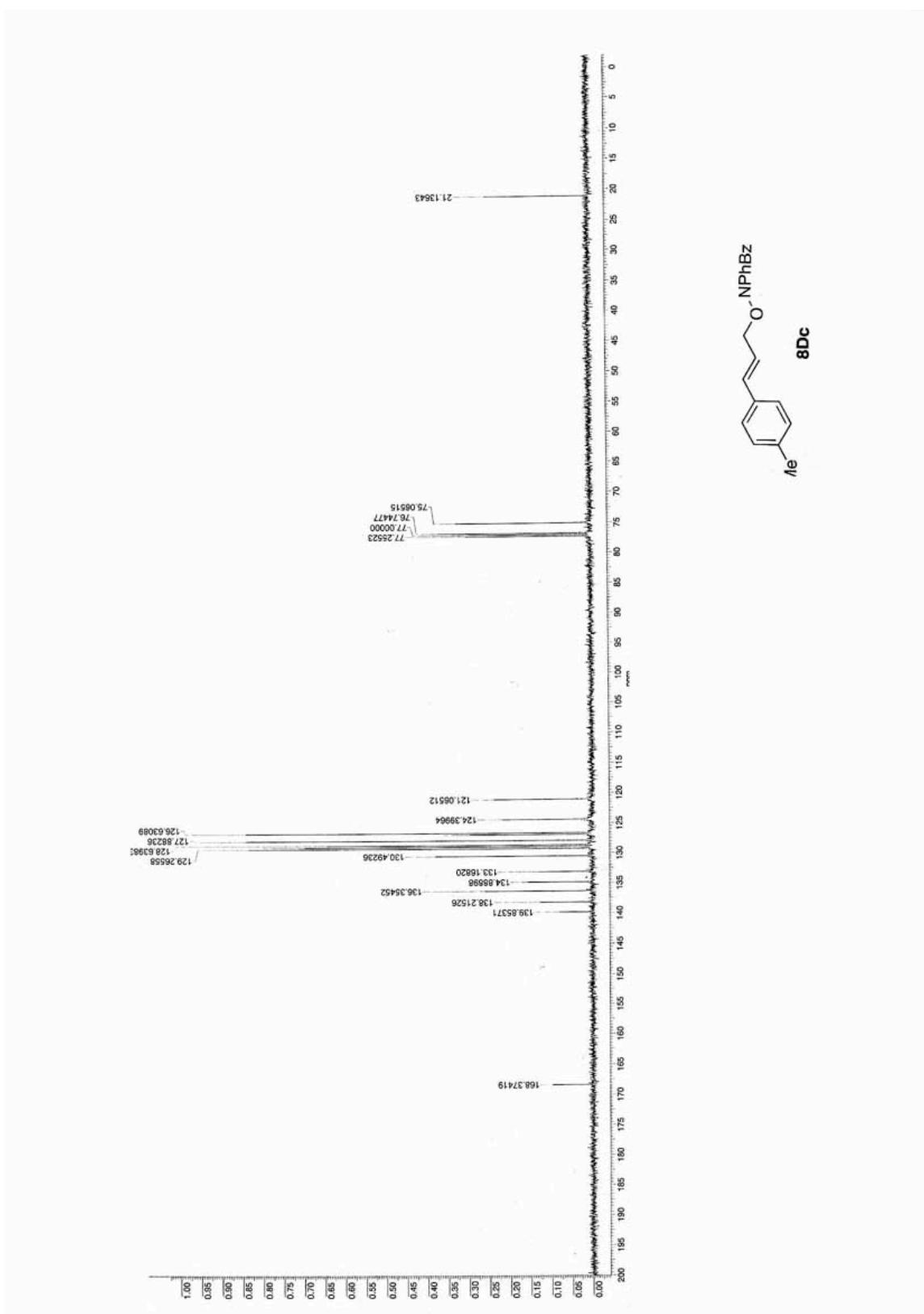


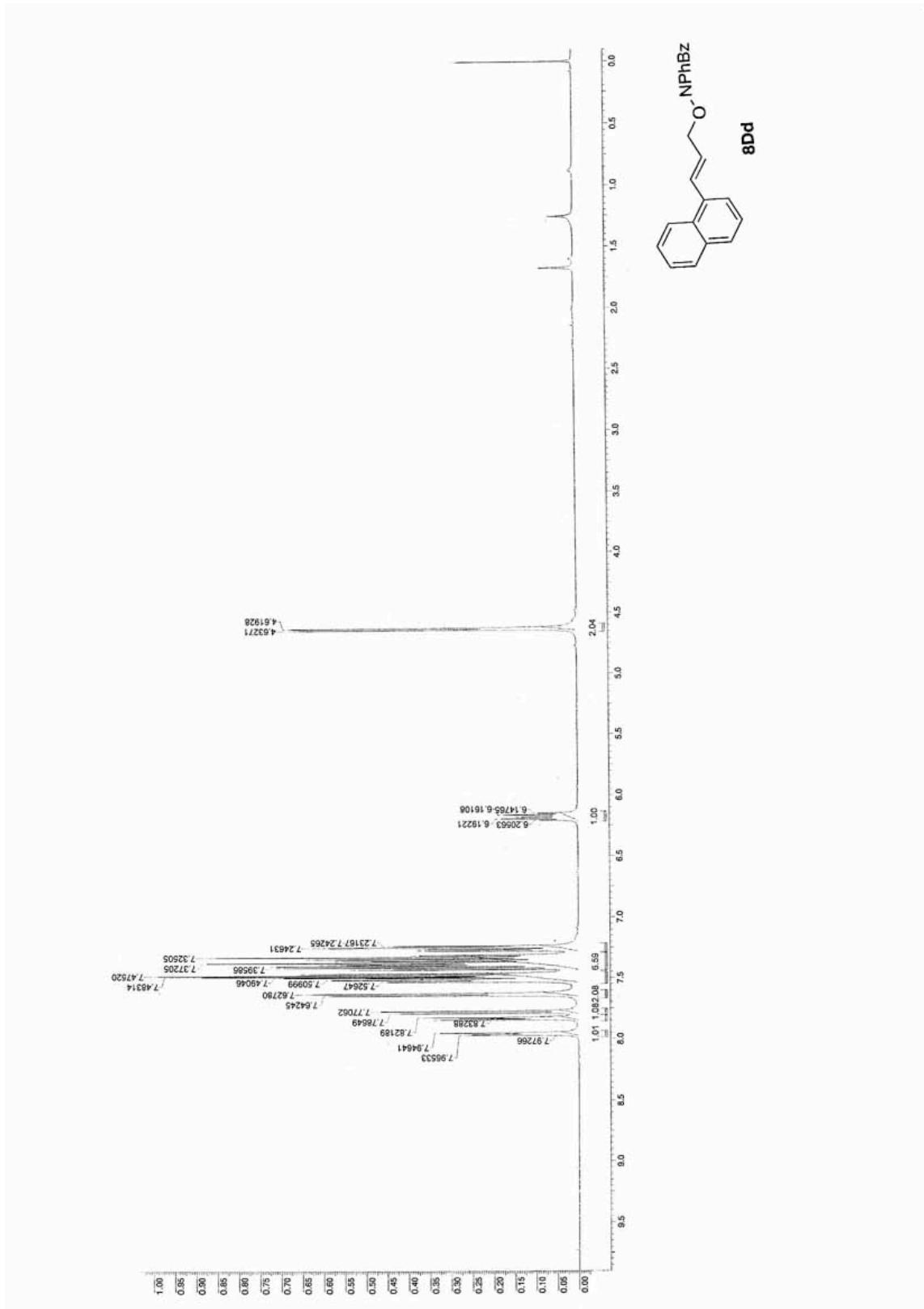


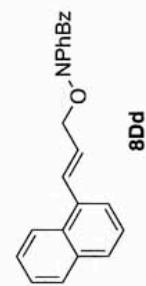
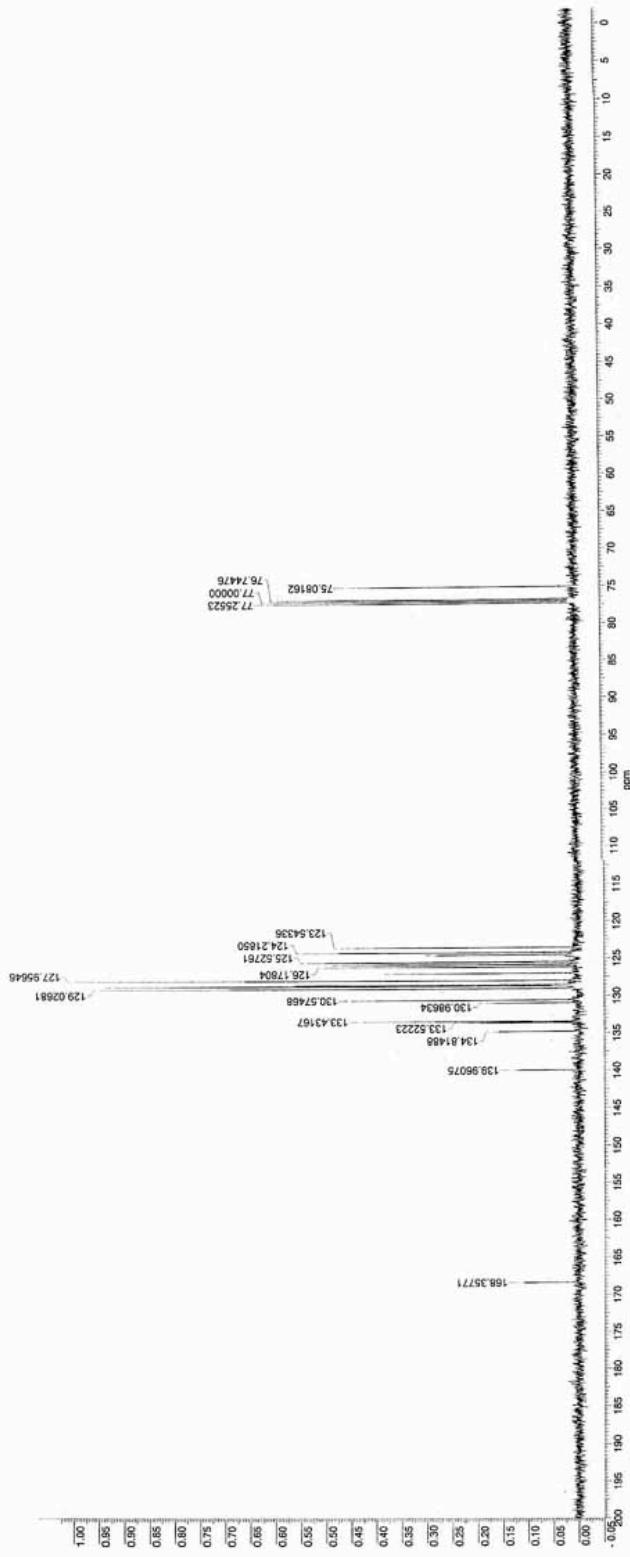


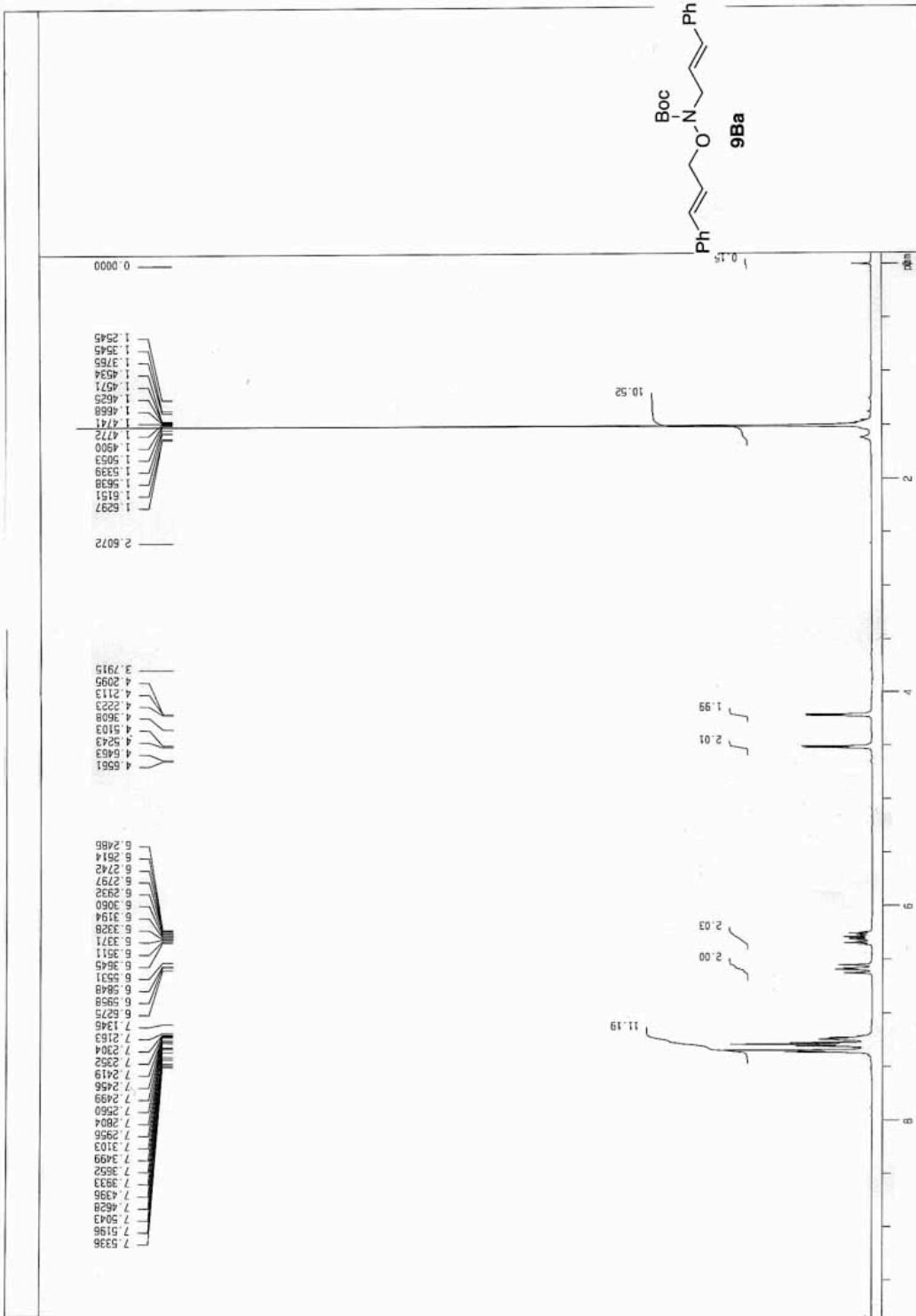


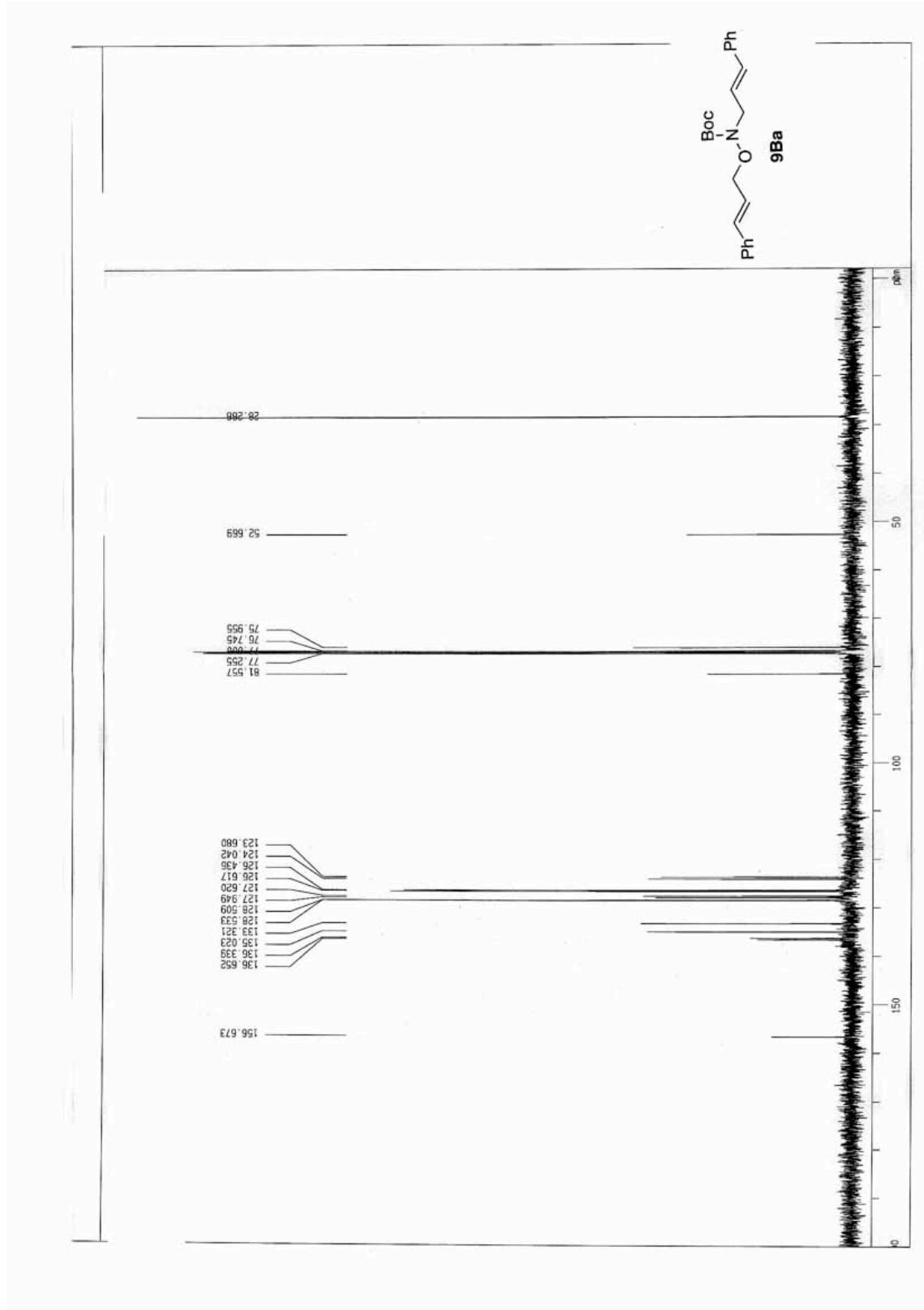
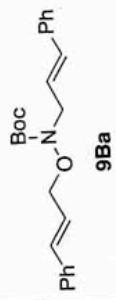


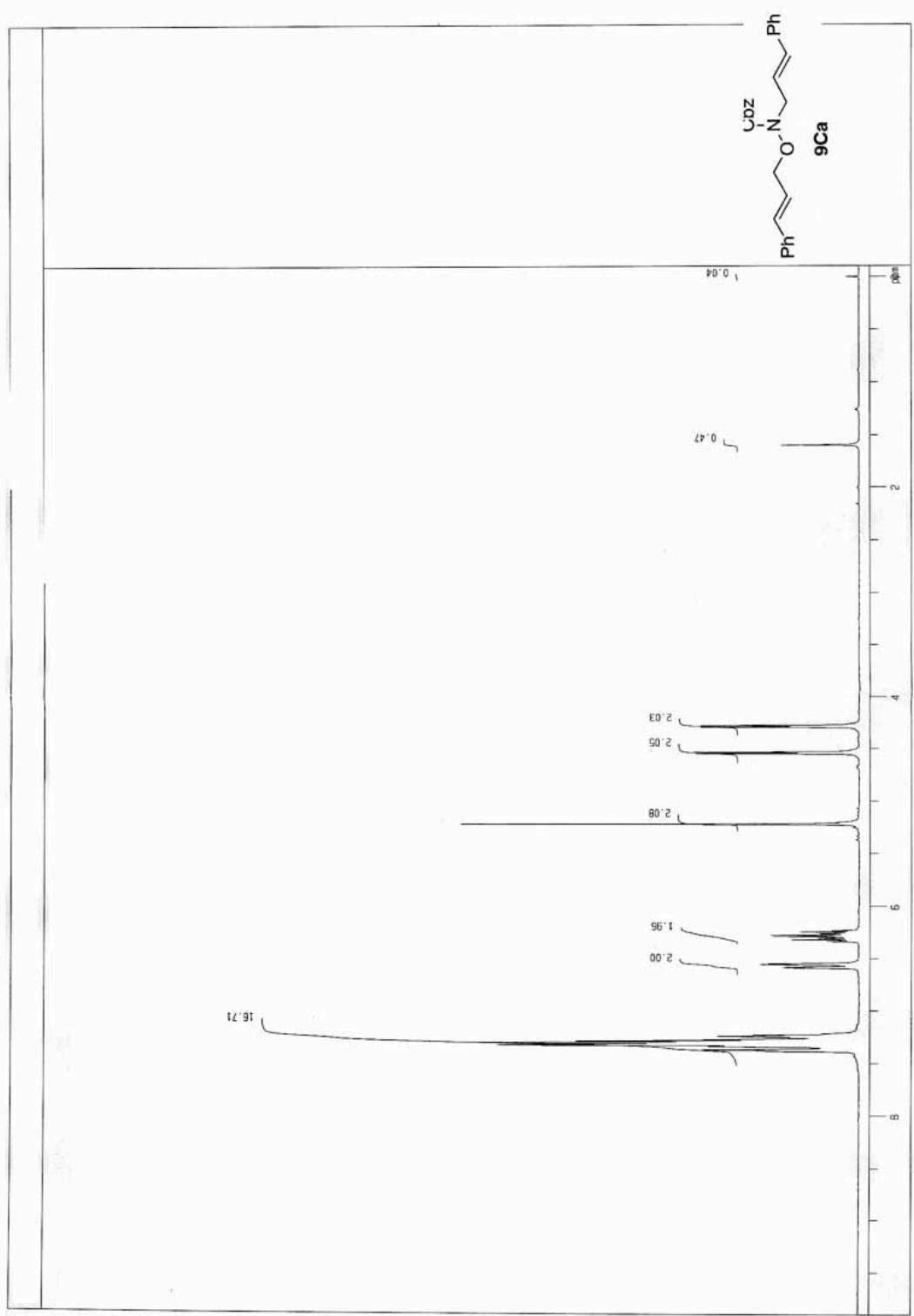


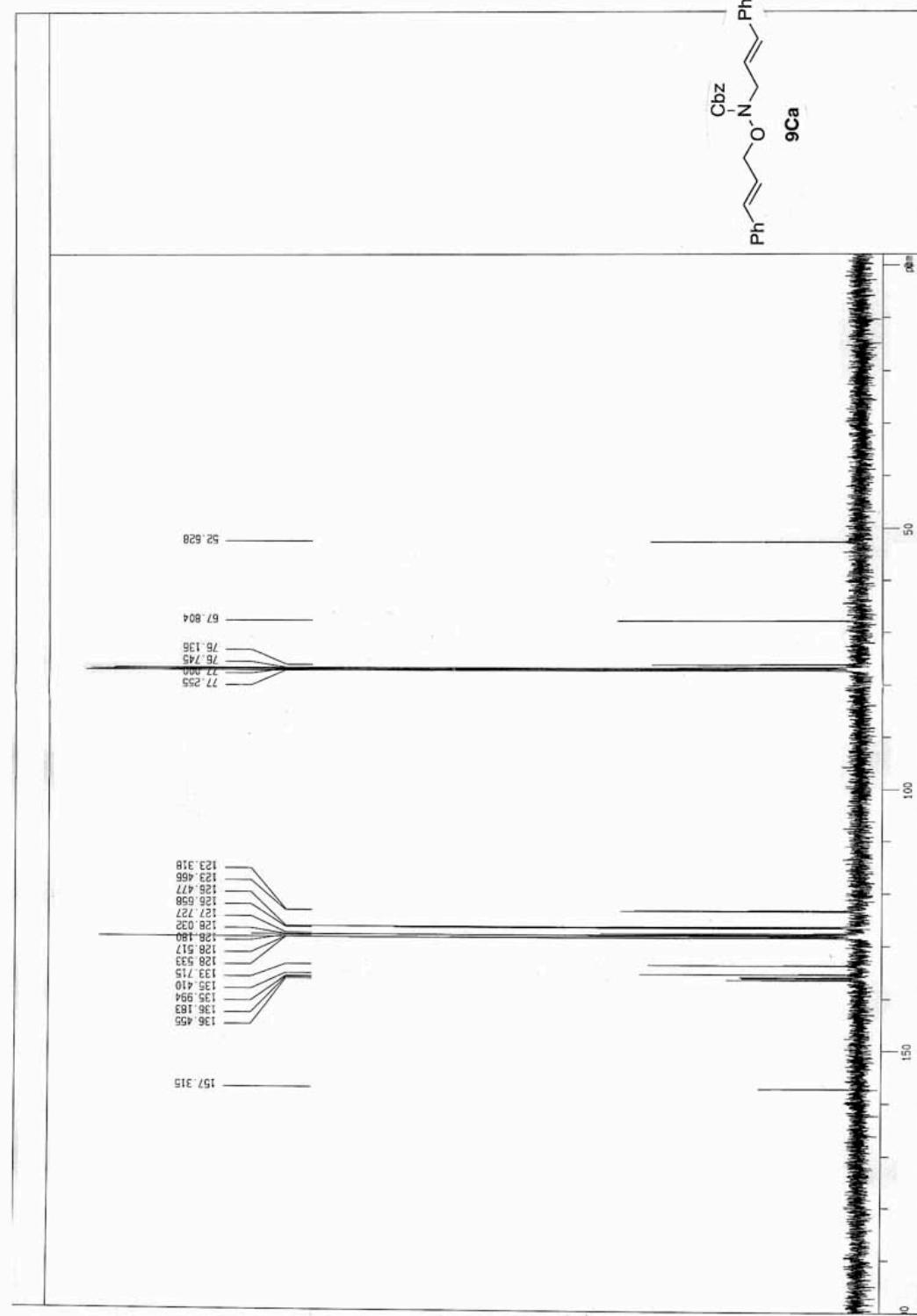
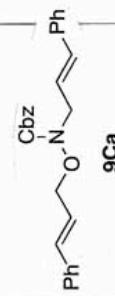


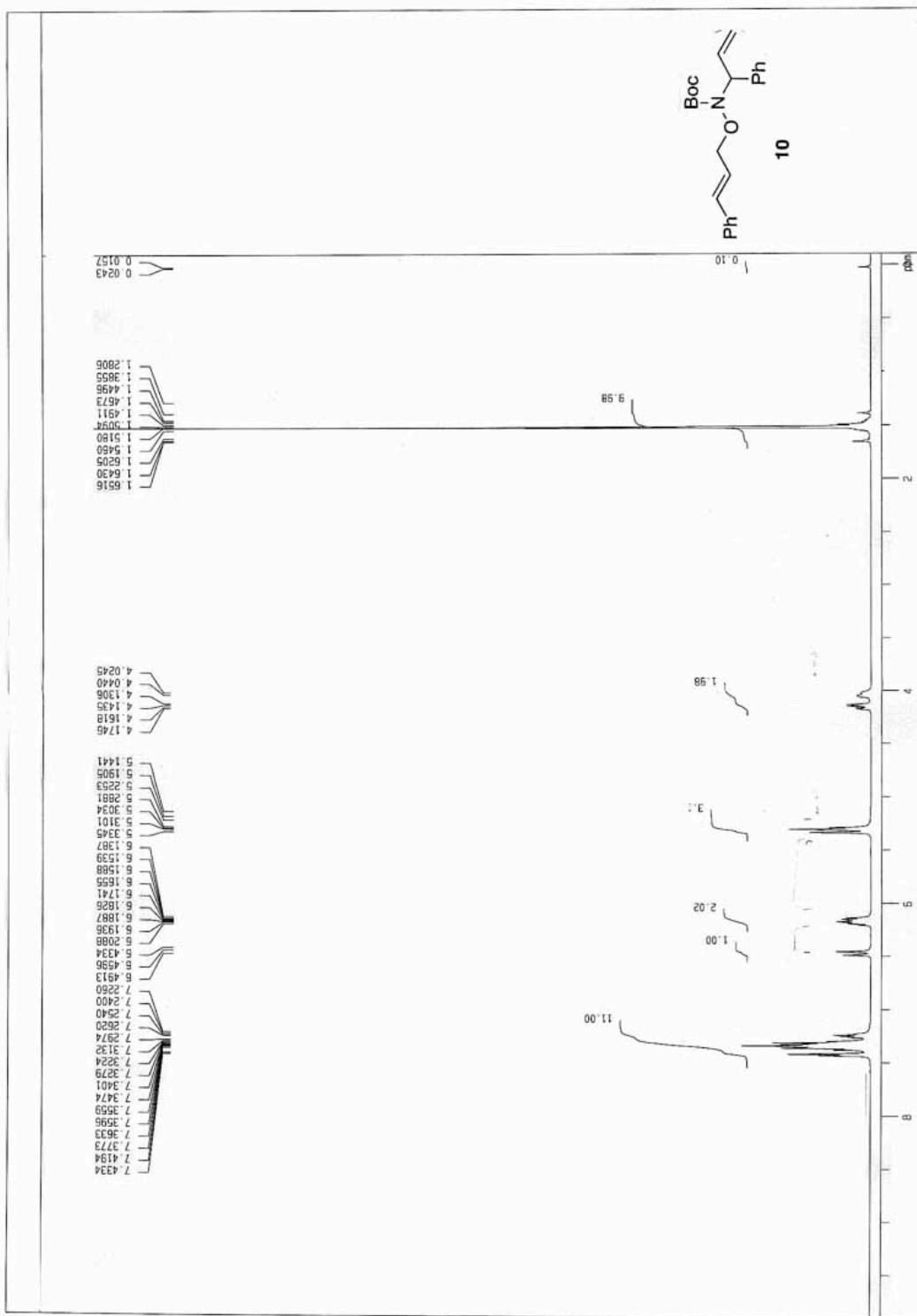
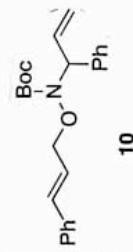


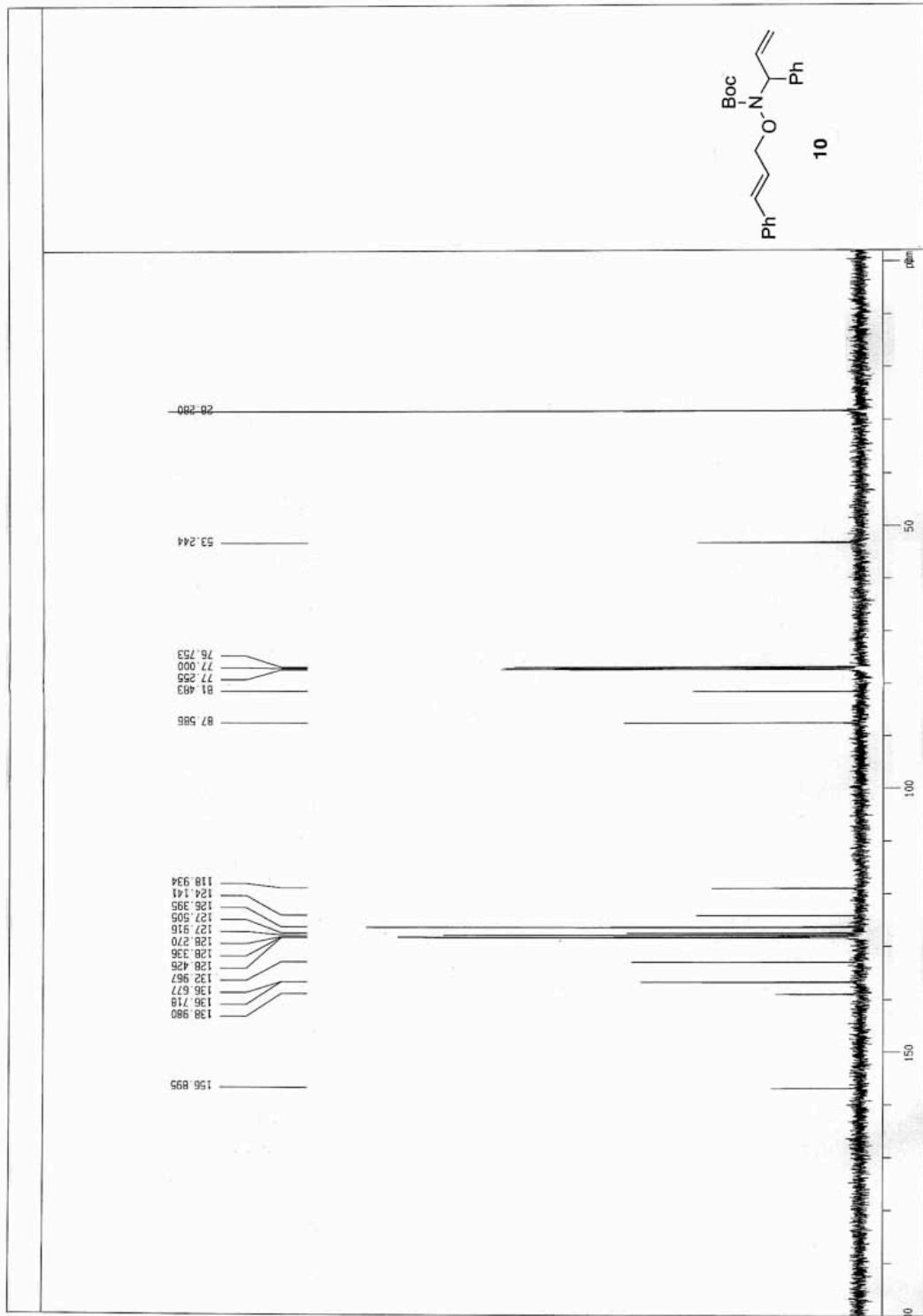
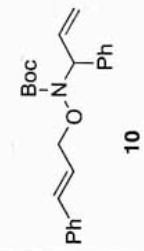


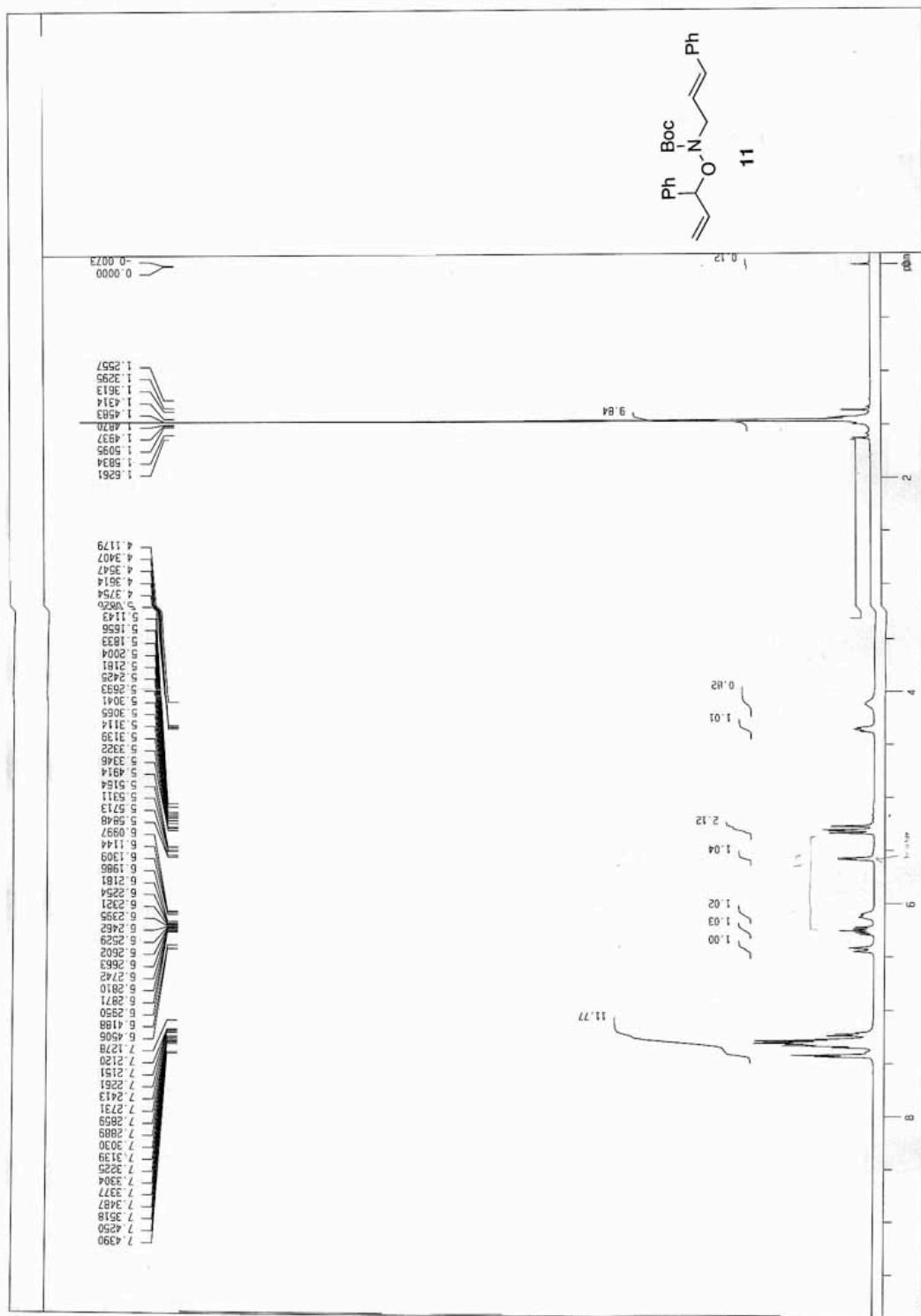
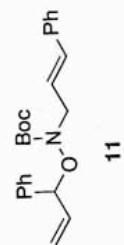


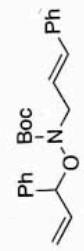












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