



Supporting Information

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Carbocycle Synthesis through Facile and Efficient Palladium-Catalyzed Allylative Dearomatization of Naphthyl- and Phenanthryl-Allyl Chlorides

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General Methods

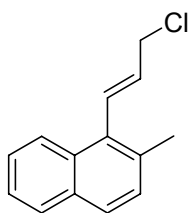
All experiments were carried out under standard Schlenk techniques. Solvents were dried and degassed before use by standard procedures. ^1H and ^{13}C NMR spectra were recorded in CDCl_3 solution on a Varian Inova-400 spectrometer (400 MHz for ^1H , 100 MHz for ^{13}C). The chemical shifts are reported in ppm downfield (δ) from Me_4Si . IR spectra were recorded on a NEXUS FT-IR spectrometer. High resolution mass spectra were recorded on a Q-TOF mass spectrometry (Micromass, England) equipped with Z-spray ionization source. TLC was carried out on SiO_2 (silica gel 60 F₂₅₄, Merck), and the spots were located with UV light, iodoplatinate reagent or 1% aqueous KMnO_4 . Flash chromatography was carried out on SiO_2 (silica gel 60, 200-300 meth) or basic Al_2O_3 (Al_2O_3 90, 100-200 meth).

Representative procedure for the preparation of the starting materials.^[1]

To a solution of 2-methyl-1-naphthaldehyde (1.70 g, 10.0 mmol) in 50 mL of THF at 0 °C under nitrogen atmosphere was added vinylmagnesium bromide (1M in THF, 12 mL) through a drop funnel slowly. After the mixture was stirred for 1 h, 100 mL of water was added. Product was extracted with diethyl ether (50 mL \times 3), and the organic layer was washed with water and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude product was purified by silica gel column chromatography (eluent: hexane:Et₂O = 10:1) to afford pure 1-[1-(2-methylnaphthyl)]homoallyl alcohol in 91% yield (1.80 g).

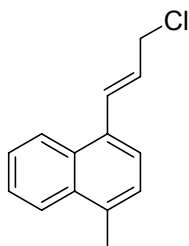
To a mixture of 1-[1-(2-methylnaphthyl)]homoallyl alcohol (198 mg, 1.0 mmol) and *N*-chlorosuccinimide (NCS, 146 mg, 1.1 mmol) in dichloromethane (50 mL) at -78 °C was added a solution of PPh_3 (275 mg, 1.1 mmol) in dichloromethane (15 mL) through a drop funnel slowly. After the mixture was stirred at -78 °C for 10 minutes, the reaction temperature was allowed to enhance to room temperature slowly. And then the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: hexane) to give 1-(3-chloroallyl)-2-methylnaphthalene (**7b**, 153 mg, 71%).

1-(3-chloroallyl)-2-methylnaphthalene (**7b**)



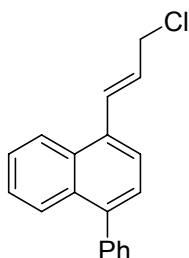
Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 7.97 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 7.6 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.44-7.33 (m, 2H), 7.23 (d, J = 7.6 Hz, 1H), 6.86 (d, J = 16.0 Hz, 1H), 5.90 (dt, J = 8.0 and 16.0 Hz, 1H), 4.23 (d, J = 8.0 Hz, 2H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.3, 132.3, 132.2, 132.08, 132.03, 131.1, 128.9, 128.3, 127.6, 126.2, 125.1, 125.0, 45.5, 20.9; IR (neat) 3049, 2951, 1714, 1594, 1508, 1438, 1246, 971, 811, 743 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{13}\text{Cl}$: 216.0706 $[\text{M}]^+$; found: 216.0702.

1-(3-chloroallyl)-4-methylnaphthalene (**7c**)



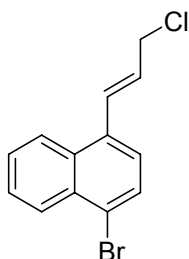
Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.04-8.01 (m, 1H), 7.95-7.92 (m, 1H), 7.48-7.36 (m, 3H), 7.30 (d, $J = 14.8$ Hz, 1H), 7.19 (d, $J = 7.2$ Hz, 1H), 6.22 (dt, $J = 7.2$ and 14.8 Hz, 1H), 4.24 (d, $J = 7.2$ Hz, 2H), 2.60 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.0, 132.7, 131.9, 131.5, 131.2, 127.3, 126.5, 125.9, 125.8, 124.7, 124.2, 124.1, 45.7, 19.7; IR (neat) 3069, 3037, 2946, 2861, 1591, 1513, 1438, 1390, 1245, 962, 821, 754, 675, 542 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{13}\text{Cl}$: 216.0706 $[\text{M}]^+$; found: 216.0710.

1-(3-chloroallyl)-4-phenylnaphthalene (7d)



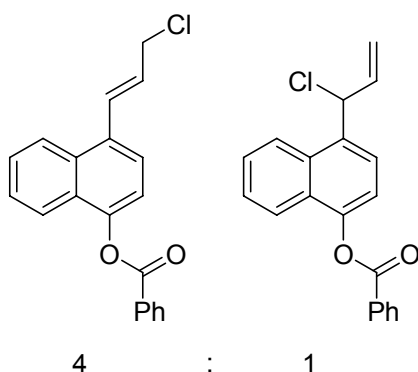
Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (d, $J = 8.4$ Hz, 1H), 7.92 (d, $J = 8.4$ Hz, 1H), 7.64 (d, $J = 7.2$ Hz, 1H), 7.53-7.39 (m, 9H), 6.37 (dt, $J = 6.8$ and 13.6 Hz, 1H), 4.36 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 140.8, 140.6, 133.1, 131.7, 131.39, 131.37, 130.1, 128.3, 128.1, 127.4, 126.77, 126.72, 126.1, 126.0, 123.9, 45.5; IR (neat) 3055, 2924, 2853, 1643, 1583, 1512, 1492, 1443, 1388, 1245, 962, 769, 703 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{15}\text{Cl}$: 278.0862 $[\text{M}]^+$; found: 278.0858.

1-(3-chloroallyl)-4-bromonaphthalene (7e)



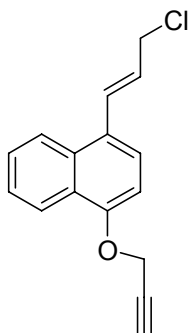
Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.28 (d, $J = 8.4$ Hz, 1H), 8.08 (d, $J = 8.0$ Hz, 1H), 7.76 (d, $J = 7.6$ Hz, 1H), 7.64-7.56 (m, 2H), 7.43 (d, $J = 7.6$ Hz, 1H), 7.36 (d, $J = 15.2$ Hz, 1H), 6.35 (dt, $J = 6.8$ and 15.2 Hz, 1H), 4.33 (d, $J = 6.8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 133.8, 132.2, 131.9, 130.6, 129.7, 128.8, 127.8, 127.3, 127.0, 124.6, 124.1, 123.2, 45.2; IR (neat): 3014, 2922, 2850, 1506, 1378, 1245, 912, 742 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{13}\text{H}_{10}\text{BrCl}$: 279.9654 and 281.9634 $[\text{M}]^+$; found: 279.9650 and 281.9630.

1-(3-chloroallyl)-4-naphthalene benzoate (7f)



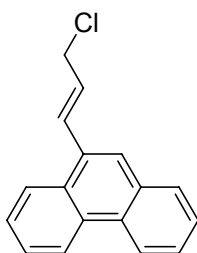
Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 8.8$ Hz, 2H), 8.12 (d, $J = 8.0$ Hz, 1H), 7.97 (d, $J = 8.0$ Hz, 1H), 7.70-7.35 (m, 8H), 6.37 (dt, $J = 7.2$ and 14.4 Hz, 1H), 4.36 (d, $J = 7.2$ Hz, 2H); and ^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 8.8$ Hz, 2H), 8.24 (d, $J = 8.8$ Hz, 1H), 8.05 (d, $J = 8.8$ Hz, 1H), 7.70-7.45 (m, 7H), 6.44-6.38 (m, 1H), 6.23 (d, $J = 6.4$ Hz, 1H), 5.52 (d, $J = 16.8$ Hz, 1H), 5.38 (d, $J = 10$ Hz, 1H) IR (neat) 3071, 2957, 2924, 2854, 1740, 1600, 1512, 1248, 1234, 1150, 1084, 1067, 1022, 761, 707, 542 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{14}\text{H}_{13}\text{Cl}$: 322.0761 $[\text{M}]^+$; found: 322.0758.

1-(3-chloroallyl)-4-propynyloxynaphthalene (7g)



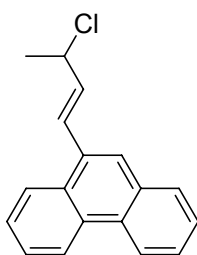
Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.03 (d, $J = 8.0$ Hz, 1H), 8.04 (d, $J = 8.4$ Hz, 1H), 7.56-7.52 (m, 3H), 7.34 (d, $J = 15.2$ Hz, 1H), 6.94 (d, $J = 8.0$ Hz, 1H), 6.27 (dt, $J = 7.6$ and 15.2 Hz, 1H), 4.91 (s, 2H), 4.35 (d, $J = 7.6$ Hz, 2H), 2.56 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.8, 132.3, 131.4, 127.2, 127.1, 126.8, 125.8, 125.6, 124.4, 123.6, 122.8, 105.6, 78.6, 75.9, 56.4, 45.9; IR (neat): 3291, 3055, 2917, 2852, 2118, 1581, 1511, 1275, 1087, 1024, 766 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{13}\text{ClO}$: 256.0655 $[\text{M}]^+$; found: 256.0667.

(E)-9-(3-chloroprop-1-enyl)phenanthrene (7j)



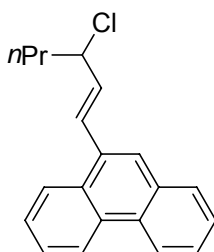
Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.72 (d, $J = 8.0$ Hz, 1H), 8.64 (d, $J = 8.0$ Hz, 1H), 8.11 (d, $J = 7.6$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.82 (s, 1H), 7.69-7.57 (m, 4H), 7.40 (d, $J = 15.6$ Hz, 1H), 6.42 (dt, $J = 7.2$ and 15.6 Hz, 1H), 4.37 (d, $J = 7.2$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.7, 132.2, 131.7, 130.55, 130.53, 130.51, 128.9, 128.7, 127.0, 126.99, 126.9, 126.8, 125.6, 124.7, 123.3, 122.7, 45.5; IR (neat): 3060, 2919, 2849, 1494, 1450, 1246, 962, 907, 746, 723 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{13}\text{Cl}$: 252.0706 $[\text{M}]^+$; found: 252.0710.

(E)-9-(3-chlorobut-1-enyl)phenanthrene (7k)



Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.69 (d, $J = 7.6$ Hz, 1H), 8.63 (d, $J = 8.0$ Hz, 1H), 8.08 (d, $J = 7.6$ Hz, 1H), 7.86 (d, $J = 7.2$ Hz, 1H), 7.80 (s, 1H), 7.68-7.55 (m, 4H), 7.32 (d, $J = 15.2$ Hz, 1H), 6.39 (dd, $J = 8.0$ and 15.2 Hz, 1H), 4.86 (dt, $J = 4.4$ and 8.0 Hz, 1H), 1.79 (d, $J = 4.4$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.6, 132.6, 131.6, 130.44, 130.37, 128.7, 126.9, 126.75, 126.72, 126.6, 125.3, 124.5, 123.1, 122.5, 58.1, 25.5; IR (neat): 3075, 2974, 2924, 1494, 1449, 1375, 1205, 1145, 1011, 962, 746, 723 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{18}\text{H}_{15}\text{Cl}$: 266.0862 $[\text{M}]^+$; found: 266.0851.

(E)-9-(3-chlorohex-1-enyl)phenanthrene(7l)



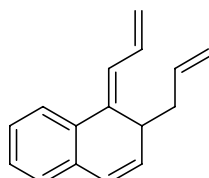
Pale yellow oil; ^1H NMR (400 MHz, CDCl_3) δ 8.71 (d, $J = 8.0$ Hz, 1H), 8.64 (d, $J = 8.0$ Hz, 1H), 8.10 (d, $J = 8.0$ Hz, 1H), 7.88 (d, $J = 8.0$ Hz, 1H), 7.81 (s, 1H), 7.69-7.56 (m, 4H), 7.33 (d, $J = 15.6$ Hz, 1H), 6.34 (dd, $J = 8.4$ and 15.6 Hz, 1H), 4.71 (dt, $J = 8.4$ and 8.4 Hz, 1H), 2.03-1.95 (m, 2H), 1.63-1.54 (m, 2H), 1.01 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 134.1, 132.8, 131.8, 130.60, 130.53, 130.49, 129.7, 128.8, 128.5, 127.0, 126.7, 126.5, 125.4, 124.7, 123.3, 122.7, 63.2, 41.1, 20.1, 13.7; IR (neat): 3075, 2959, 2926, 2871, 1451, 1120, 963, 912, 745, 724, 541 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{19}\text{Cl}$: 294.1175 $[\text{M}]^+$; found: 294.1179.

Representative procedure for the Pd-catalyzed allylative dearomatization of naphthalenes and phenanthrenes bearing allyl chlorides:

To a mixture of $\text{Pd}_2(\text{dba})_3$ (22.8 mg, 0.025 mmol) and PPh_3 (26.2 mg, 0.1 mmol) in dichloromethane (3 mL) at room temperature were added **7a** (101.3 mg, 0.5 mmol) and

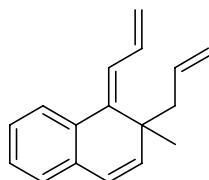
allyltributylstannane (165.6 mg, 0.5 mmol), and then the mixture was stirred for 12 h under a N₂ atmosphere. The reaction progress was monitored by TLC. After the allyltributylstannane consumed, the solvent was removed under the reduced pressure. The product was filtered through a short basic alumina column with pentane to remove palladium residue and then was purified with a basic alumina column with pentane as eluent, giving **8a** in 84% yield (87.5 mg) as a colorless liquid.

(E)-2-allyl-1-allylidene-1,2-dihydronaphthalene (8a)



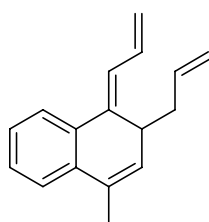
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.53-7.51 (m, 1H), 7.20-7.18 (m, 2H), 7.04-7.02 (m, 1H), 6.75 (ddd, *J* = 10.0, 11.2 and 16.8 Hz, 1H), 6.56 (d, *J* = 11.2 Hz, 1H), 6.44 (d, *J* = 9.6 Hz, 1H), 6.06 (dd, *J* = 6.4 and 9.6 Hz, 1H), 5.80-5.73 (m, 1H), 5.37 (d, *J* = 16.8 Hz, 1H), 5.25 (d, *J* = 10.0 Hz, 1H), 5.00-4.94 (m, 2H), 3.63 (ddd, *J* = 6.4, 6.4 and 6.4 Hz, 1H), 2.23 (ddd, *J* = 6.4, 6.4 and 12.8 Hz, 1H), 2.14 (ddd, *J* = 6.4, 6.4 and 12.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 138.8, 135.6, 134.0, 133.0, 132.4, 131.7, 128.1, 127.8, 127.7, 126.8, 126.6, 124.3, 119.0, 116.8, 40.6, 37.6; IR (neat): 3031, 2923, 2851, 1637, 1480, 1452, 985, 904, 782, 757 cm⁻¹; HRMS (EI) calcd for C₁₆H₁₆: 208.1252 [M]⁺; found: 208.1250.

(E)-2-allyl-1-allylidene-2-methyl-1,2-dihydronaphthalene (8b)



Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 7.63-7.61 (m, 1H), 7.17-7.15 (m, 2H), 7.11-6.98 (m, 2H), 6.82 (d, *J* = 11.6 Hz, 1H), 6.35 (d, *J* = 9.6 Hz, 1H), 5.71-5.60 (m, 1H), 5.57 (d, *J* = 9.6 Hz, 1H), 5.32 (d, *J* = 16.4 Hz, 1H), 5.25 (d, *J* = 10.0 Hz, 1H), 5.01-4.92 (m, 2H), 2.58 (dd, *J* = 7.6 and 14.4 Hz, 1H), 2.25 (dd, *J* = 7.6 and 14.4 Hz, 1H), 1.49 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 140.3, 139.1, 134.9, 134.7, 134.6, 132.6, 128.8, 127.8, 127.6, 126.8, 124.5, 124.4, 119.7, 117.2, 46.5, 42.5, 28.7; IR (neat): 3071, 3026, 2963, 2923, 1610, 1483, 1454, 1413, 1373, 992, 941, 907, 787, 760 cm⁻¹; HRMS (EI) calcd for C₁₇H₁₈: 222.1409 [M]⁺; found: 222.1405.

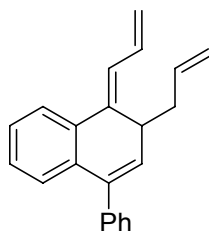
(E)-2-allyl-1-allylidene-4-methyl-1,2-dihydronaphthalene (8c)



Colorless oil; ¹H NMR (400 MHz, CDCl₃): δ 7.52 (d, *J* = 7.2 Hz, 1H), 7.29-7.19 (m, 3H), 6.74 (ddd,

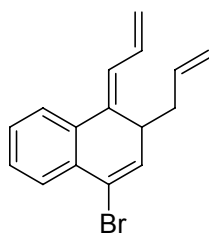
$J = 10.4, 11.2$ and 16.4 Hz, 1H), 6.50 (d, $J = 11.2$ Hz, 1H), 5.91 (d, $J = 5.6$ Hz, 1H), 5.80-5.70 (m, 1H), 5.35 (d, $J = 16.4$ Hz, 1H), 5.23 (d, $J = 10.4$ Hz, 1H), 4.97-4.93 (m, 2H), 3.56 (ddd, $J = 6.8, 6.8$ and 6.8 Hz, 1H), 2.19 (ddd, $J = 6.8, 6.8$ and 13.6 Hz, 1H), 2.16-2.06 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.7, 136.0, 134.5, 134.4, 132.5, 130.8, 128.6, 128.1, 127.5, 127.4, 124.5, 123.4, 118.7, 116.6, 40.2, 37.4, 19.6; IR (neat): 3060, 3028, 2974, 2921, 2857, 1638, 1621, 1479, 1450, 1437, 1413, 1378, 987, 903, 826, 757, 664 cm^{-1} . HRMS (EI) calcd for $\text{C}_{17}\text{H}_{18}$: 222.1409 $[\text{M}]^+$; found: 222.1421.

(E)-2-allyl-1-allylidene-4-phenyl-1,2-dihydronaphthalene (8d)



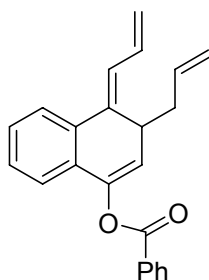
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 7.2$ Hz, 1H), 7.39-7.30 (m, 5H), 7.22 (dd, $J = 6.8$ and 6.8 Hz, 1H), 7.14 (dd, $J = 7.6$ and 7.6 Hz, 1H), 6.98 (d, $J = 7.6$ Hz, 1H), 6.79 (ddd, $J = 10.8, 10.8$ and 16.0 Hz, 1H), 6.58 (d, $J = 11.2$ Hz, 1H), 6.04 (d, $J = 6.0$ Hz, 1H), 5.84-5.75 (m, 1H), 5.39 (d, $J = 16$ Hz, 1H), 5.26 (d, $J = 10.4$ Hz, 1H), 5.03-4.98 (m, 2H), 3.74 (ddd, $J = 6.4, 6.4$ and 6.4 Hz, 1H), 2.31 (ddd, $J = 6.4, 6.4$ and 12.8 Hz, 1H), 2.19 (ddd, $J = 6.4, 6.4$ and 12.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ 140.6, 139.1, 138.6, 135.6, 134.7, 133.7, 132.4, 130.6, 129.2, 128.4, 127.9, 127.8, 127.6, 127.4, 126.0, 125.0, 119.1, 116.9, 40.0, 37.4; IR (neat): 3078, 3057, 3025, 2974, 2925, 1638, 1622, 1599, 1493, 1475, 1443, 985, 907, 760, 701 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{22}\text{H}_{20}$: 284.1565 $[\text{M}]^+$, found: 284.1576.

(E)-2-allyl-1-allylidene-4-bromo-1,2-dihydronaphthalene (8e)



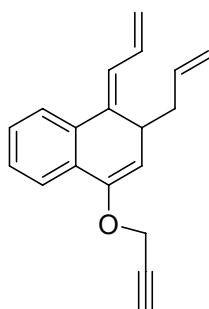
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.0$ Hz, 1H), 7.48 (d, $J = 7.2$ Hz, 1H), 7.31-7.23 (m, 2H), 6.68 (ddd, $J = 11.2, 11.2$ and 16.4 Hz, 1H), 6.51 (d, $J = 11.2$ Hz, 1H), 6.48 (d, $J = 10.4$ Hz, 1H), 5.77-5.66 (m, 1H), 5.39 (d, $J = 16.4$ Hz, 1H), 5.28 (d, $J = 11.2$ Hz, 1H), 5.00-4.95 (m, 2H), 3.65 (ddd, $J = 6.8, 6.8$ and 6.8 Hz, 1H), 2.26 (ddd, $J = 6.8, 6.8$ and 13.6 Hz, 1H), 2.12 (ddd, $J = 6.8, 6.8$ and 13.6 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 137.0, 134.9, 134.7, 133.4, 132.0, 131.5, 129.0, 128.8, 128.4, 127.2, 124.5, 120.8, 120.0, 117.4, 40.0, 39.6; IR (neat): 3079, 3060, 2975, 2926, 1638, 1619, 1469, 1450, 1436, 1414, 1319, 1293, 1183, 984, 960, 908, 878, 831 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{15}\text{Br}$: 286.0357 and 288.0337 $[\text{M}]^+$; found: 286.0364 and 288.0343.

(E)-3-allyl-4-allylidene-3,4-dihydronaphthalen-1-yl benzoate (8f)



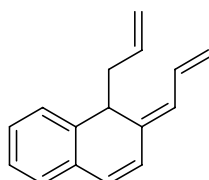
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 8.21 (d, $J = 7.2$ Hz, 2H), 7.66-7.62 (m, 1H), 7.58 (d, $J = 7.6$ Hz, 1H), 7.53-7.50 (m, 2H), 7.27-7.15 (m, 3H), 6.76 (ddd, $J = 11.6, 11.6$ and 16.4 Hz, 1H), 6.59 (d, $J = 11.6$ Hz, 1H), 5.91 (d, $J = 6.0$ Hz, 1H), 5.87-5.77 (m, 1H), 5.41 (d, $J = 16.4$ Hz, 1H), 5.29 (d, $J = 11.6$ Hz, 1H), 5.07-4.98 (m, 2H), 3.82 (ddd, $J = 6.4, 6.4$ and 6.4 Hz, 1H), 2.37 (ddd, $J = 6.4, 6.4$ and 12.8 Hz, 1H), 2.26 (ddd, $J = 6.4, 6.4$ and 12.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.0, 144.6, 137.3, 135.1, 134.9, 133.8, 132.2, 130.3, 129.6, 129.2, 128.8, 128.7, 128.5, 128.1, 124.7, 121.4, 119.7, 119.0, 117.3, 40.7, 30.1; IR (neat): 3070, 2976, 2925, 1739, 1599, 1451, 1262, 1090, 910, 760, 707 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{20}\text{O}_2$: 328.1463 $[\text{M}]^+$; found: 328.1460.

(E)-2-allyl-1-allylidene-4-(prop-2-ynyloxy)-1,2-dihydronaphthalene (8g)



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.59-7.51 (m, 2H), 7.28-7.23 (m, 2H), 6.76 (ddd, $J = 11.2, 11.2$ and 16.0 Hz, 1H), 6.51 (d, $J = 11.2$ Hz, 1H), 5.82-5.72 (m, 1H), 5.37 (d, $J = 16.0$ Hz, 1H), 5.25 (d, $J = 11.2$ Hz, 1H), 5.19 (d, $J = 6.0$ Hz, 1H), 5.0-4.95 (m, 2H), 4.59 (d, $J = 2.4$ Hz, 2H), 3.69 (ddd, $J = 6.8, 6.8$ and 6.8 Hz, 1H), 2.51 (t, $J = 2.4$ Hz, 1H), 2.2-2.1 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 149.6, 138.6, 135.8, 134.8, 132.4, 130.2, 128.4, 127.9, 127.3, 124.2, 122.1, 119.1, 116.8, 101.0, 78.9, 75.3, 55.3, 41.5, 36.5; IR (neat): 3301, 3071, 3029, 2975, 2917, 2248, 1650, 1343, 1218, 1093, 909, 763, 734 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{19}\text{H}_{18}\text{O}$: 262.1358 $[\text{M}]^+$; found: 262.1365.

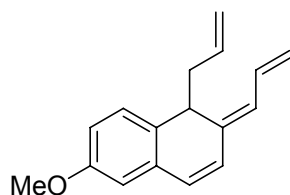
(Z)-1-allyl-2-allylidene-1,2-dihydronaphthalene (8h)



Colorless oil; ^1H NMR (300 MHz, CDCl_3) δ 7.17-7.05 (m, 4H), 6.74 (ddd, $J = 11.7, 11.7$ and 16.5 Hz, 1H), 6.37 (d, $J = 9.6$ Hz, 1H), 6.21 (d, $J = 9.6$ Hz, 1H), 6.12 (d, $J = 11.7$ Hz, 1H), 5.69 (ddt, $J = 7.2, 9.9$ and 17.1 Hz, 1H), 5.30 (d, $J = 16.5$ Hz, 1H), 5.22 (d, $J = 9.9$ Hz, 1H), 4.93-4.82 (m, 2H), 4.07 (t, $J = 6.6$ Hz, 1H), 2.35 (dd, $J = 6.9$ and 6.9 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 139.8, 138.2, 135.2, 133.0, 132.3, 129.8, 128.2, 127.1, 126.8, 126.7, 126.6, 118.5, 116.8, 44.7, 41.3; IR

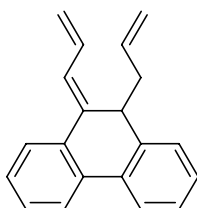
(neat): 3074, 3022, 2978, 2926, 1638, 989, 910, 795, 750, 476 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{16}\text{H}_{16}$: 208.1252 $[\text{M}]^+$; found: 208.1252.

(Z)-1-allyl-2-allylidene-6-methoxy-1,2-dihydronaphthalene (8i)



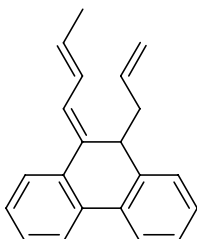
Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.04 (d, $J = 8.4$ Hz, 1H), 6.78 -6.63 (m, 3H), 6.33 (d, $J = 9.2$ Hz, 1H), 6.23 (d, $J = 9.2$ Hz, 1H), 6.12 (d, $J = 11.2$ Hz, 1H), 5.74-5.63 (m, 1H), 5.31 (d, $J = 16.8$ Hz, 1H), 5.22 (d, $J = 10.0$ Hz, 1H), 4.92-4.84 (m, 2H), 4.03 (t, $J = 6.4$ Hz, 1H), 3.80 (s, 3H), 2.35 (dd, $J = 6.8$ and 6.8 Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5, 140.4, 135.5, 134.2, 132.5, 130.7, 130.6, 130.1, 129.3, 127.3, 118.7, 116.9, 112.5, 112.1, 55.4, 45.0, 40.7; IR (neat): 2958, 2922, 2851, 1601, 1463, 1376, 1264, 899, 721 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{17}\text{H}_{18}\text{O}$: 238.1358 $[\text{M}]^+$; found: 238.1350.

(E)-9-allyl-10-allylidene-9,10-dihydrophenanthrene (8j)



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.79 (dd, $J = 8.0$ and 8.0 Hz, 2H), 7.55 (dd, $J = 1.0$ and 7.2 Hz, 1H), 7.38-7.23 (m, 5H), 6.86 (ddd, $J = 10.8$, 10.8 and 16.0 Hz, 1H), 6.52 (d, $J = 10.8$ Hz, 1H), 5.74-5.65 (m, 1H), 5.38 (d, $J = 16.0$ Hz, 1H), 5.25 (d, $J = 10.8$ Hz, 1H), 4.94-4.84 (m, 2H), 4.06 (dd, $J = 6.4$ and 8.8 Hz, 1H), 2.28-2.17 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.3, 139.2, 136.1, 135.3, 133.1, 132.8, 132.6, 128.7, 128.6, 128.2, 127.7, 127.3, 126.0, 124.1, 123.3, 119.1, 116.7, 42.8, 41.3; IR (neat): 3064, 3030, 2975 2928, 1637, 1593, 1494, 1479, 1450, 1442, 987, 907, 758, 731 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{20}\text{H}_{18}$: 258.1409 $[\text{M}]^+$; found: 258.1419.

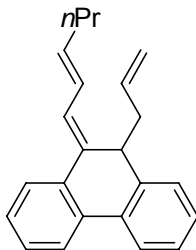
(E)-9-allyl-10-((E)-but-2-enylidene)-9,10-dihydrophenanthrene (8k)



Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 7.78 (dd, $J = 7.6$ and 7.6 Hz, 2H), 7.51 (dd, $J = 0.6$ and 7.6 Hz, 1H), 7.35-7.22 (m, 5H), 6.56-6.45 (m, 2H), 5.88 (dt, $J = 7.2$ and 14.4 Hz, 1H), 5.75-5.68 (m, 1H), 4.94-4.84 (m, 2H), 4.04 (dd, $J = 7.2$ and 8.4 Hz, 1H), 2.25-2.18 (m, 2H), 1.86 (d, $J = 7.2$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 139.4, 136.3, 136.0, 135.8, 133.0, 132.9, 132.1, 128.7, 128.2,

128.1, 127.6, 127.4, 127.2, 127.0, 125.8, 124.1, 123.3, 116.5, 42.7, 41.3, 19.0; IR (neat): 3064, 3024, 2976, 2929, 1638, 1479, 1450, 1375, 1093, 1047, 995, 960, 916, 757, 731, 619, 576 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{21}\text{H}_{20}$: 272.1565 $[\text{M}]^+$, found: 272.1565.

(E)-9-allyl-10-((E)-hex-2-enylidene)-9,10-dihydrophenanthrene (**8l**)

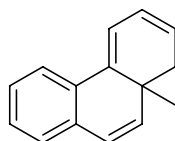


Colorless oil; ^1H NMR (400 MHz, CDCl_3): δ 7.78 (dd, $J = 6.4$ and 6.4 Hz, 2H), 7.53 (dd, $J = 1.2$ and 7.6 Hz, 1H), 7.35-7.23 (m, 5H), 6.56-6.46 (m, 2H), 5.87 (dt, $J = 7.2$ and 14.4 Hz, 1H), 5.75-5.68 (m, 1H), 4.93-4.85 (m, 2H), 4.05 (dd, $J = 6.8$ and 8.4 Hz, 1H), 2.27-2.14 (m, 4H), 1.52-1.42 (m, 2H), 0.92 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (100MHz, CDCl_3) δ 139.4, 137.4, 136.3, 136.1, 135.8, 133.0, 132.9, 128.7, 128.2, 128.1, 127.6, 127.2, 127.1, 126.3, 125.9, 124.1, 123.3, 116.4, 42.7, 41.3, 35.5, 22.8, 13.9; IR (neat): 3064, 3027, 2957, 2929, 2870, 1480, 1450, 996, 964, 913, 758, 732 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{23}\text{H}_{24}$: 300.1878 $[\text{M}]^+$; found: 300.1877.

Procedure for the metathesis reaction of **8b** catalyzed by ruthenium-complex **9**:^[2]

A mixture of catalyst **9** (7.2 mg, 8.8×10^{-2} mmol) and **8b** (488 mg, 2.2 mmol) in dichloromethane (20 mL) was refluxed under nitrogen atmosphere. The reaction progress was monitored by TLC. After the reaction completed, the solvent was removed under reduced pressure, and the residue was filtered through a short basic alumina column with pentane to remove ruthenium residue and then was purified by a basic alumina column with pentane as eluent, giving **10** in 62% yield (264 mg) as a colorless liquid.

10a-methyl-1,10a-dihydrophenanthrene (**10**)



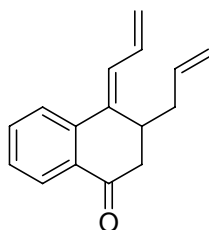
^1H NMR (400 MHz, CDCl_3): δ 7.63-7.61 (m, 1H), 7.21-7.16 (m, 2H), 7.07-7.05 (m, 1H), 6.47 (d, $J = 5.6$ Hz, 1H), 6.36 (d, $J = 9.6$ Hz, 1H), 6.15-6.10 (m, 1H), 5.80-5.76 (m, 1H), 5.71 (d, $J = 9.6$ Hz, 1H), 2.57-2.51 (m, 1H), 2.18 (dd, $J = 6.0$ and 22.0 Hz, 1H), 0.96 (3H, s); ^{13}C NMR (100 MHz, CDCl_3) δ 139.1, 137.1, 132.3, 131.8, 127.7, 127.4, 127.0, 124.7, 123.7, 123.6, 123.5, 117.7, 36.3, 34.6, 22.9; IR (neat): 3037, 2956, 2916, 1636, 1455, 728, 757, 706, 690 cm^{-1} ; HRMS (EI) calcd for $\text{C}_{15}\text{H}_{14}$: 194.1096 $[\text{M}]^+$; found: 194.1098.

Procedure for the hydrolysis reaction of **8f** under basic condition:

A mixture of NaOH aqueous solution (2N, 2 mL), ethanol (2 mL), and compound **8f** (164 mg, 0.5 mmol) was vigorously stirred at room temperature under nitrogen atmosphere. The reaction progress was monitored by TLC. When the starting material **8f** disappeared, the mixture was

extracted with diethyl ether (10 mL×3). The organic layer was washed with saturated brine, and dried over MgSO₄. And then the organic layer was evaporated to give the crude product **11**, which was purified by chromatography on silica gel (eluent: hexane/Et₂O = 10:1) to afford pure **11** in 77% yield (68 mg) as a colorless oil.

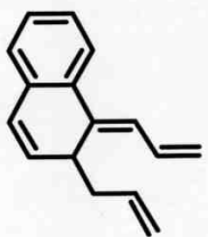
(E)-3-allyl-4-allylidene-3,4-dihydronaphthalen-1(2H)-one (11)



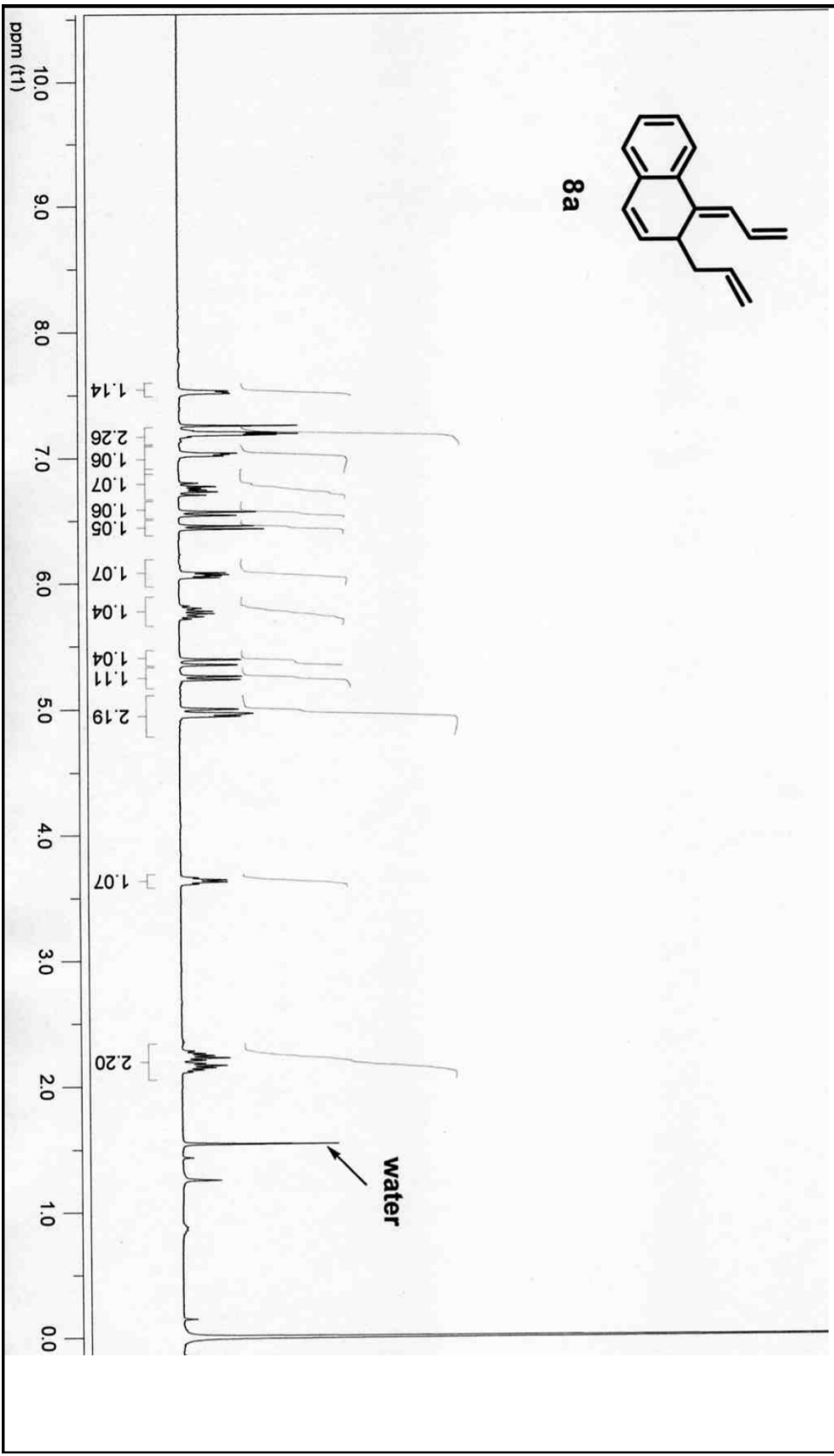
¹H NMR (400 MHz, CDCl₃) δ 8.02 (dd, *J* = 1.2 and 8.0 Hz, 1H), 7.66 (d, *J* = 7.6 Hz, 1H), 7.58-7.54 (m, 1H), 7.39-7.35 (m, 1H), 6.86-6.75 (m, 2H), 5.74-5.64 (m, 1H), 5.53-5.46 (m, 1H), 5.36-5.30 (m, 1H), 5.0-4.91 (m, 2H), 3.49 (tt, *J* = 3.2 and 6.4 Hz, 1H), 2.82 (d, *J* = 3.2 Hz, 2H), 2.19 (dd, *J* = 6.4 and 6.4 Hz, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 197.4, 140.3, 137.5, 135.6, 134.2, 132.5, 131.2, 128.2, 128.0, 126.9, 125.2, 120.7, 117.4, 43.4, 37.9, 36.9; IR (neat): 3064, 2938, 1684, 1595, 1289, 985, 912, 773 cm⁻¹; HRMS (EI) calcd for C₁₆H₁₆O: 224.1201 [M]⁺; found: 224.1208.

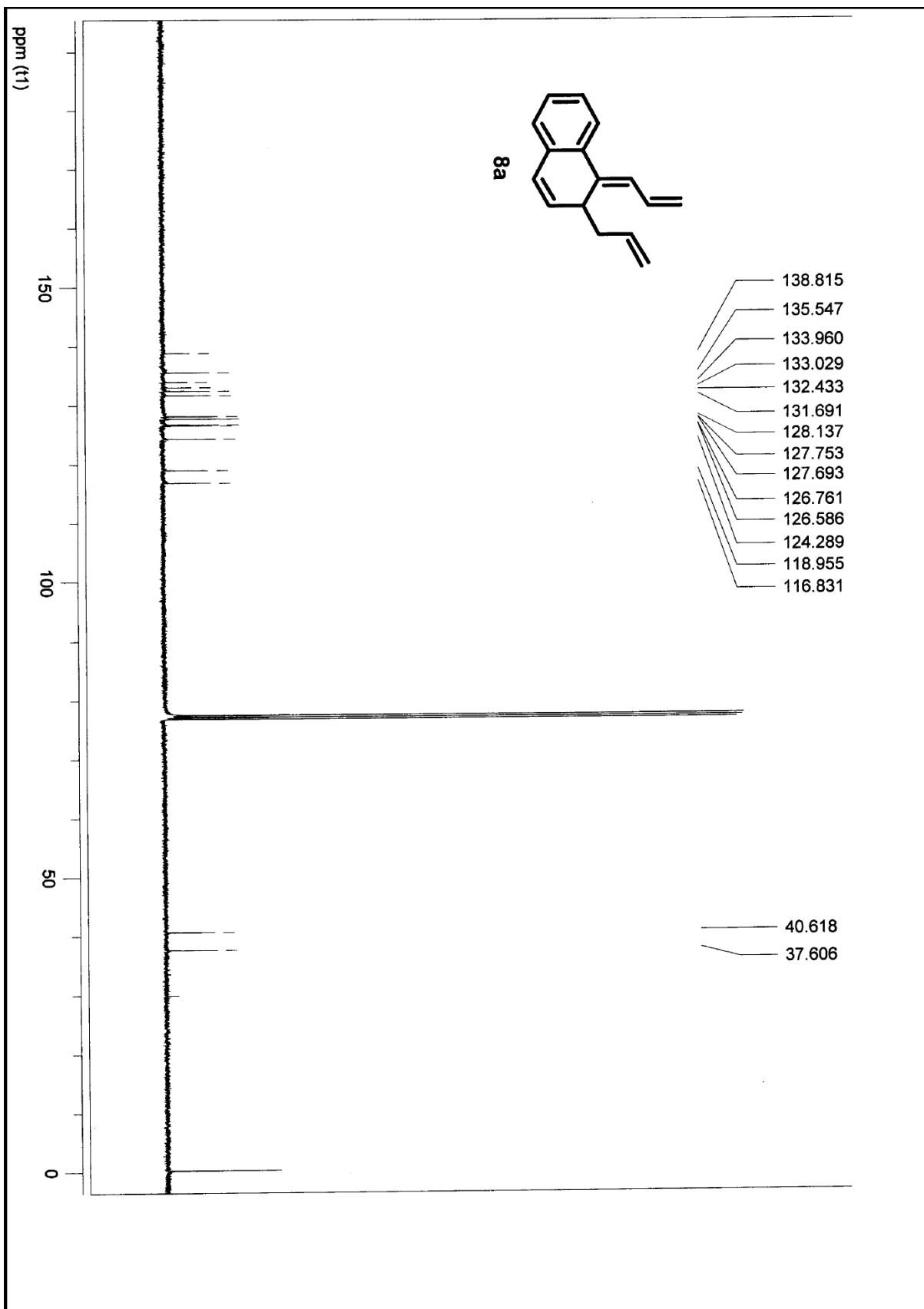
References

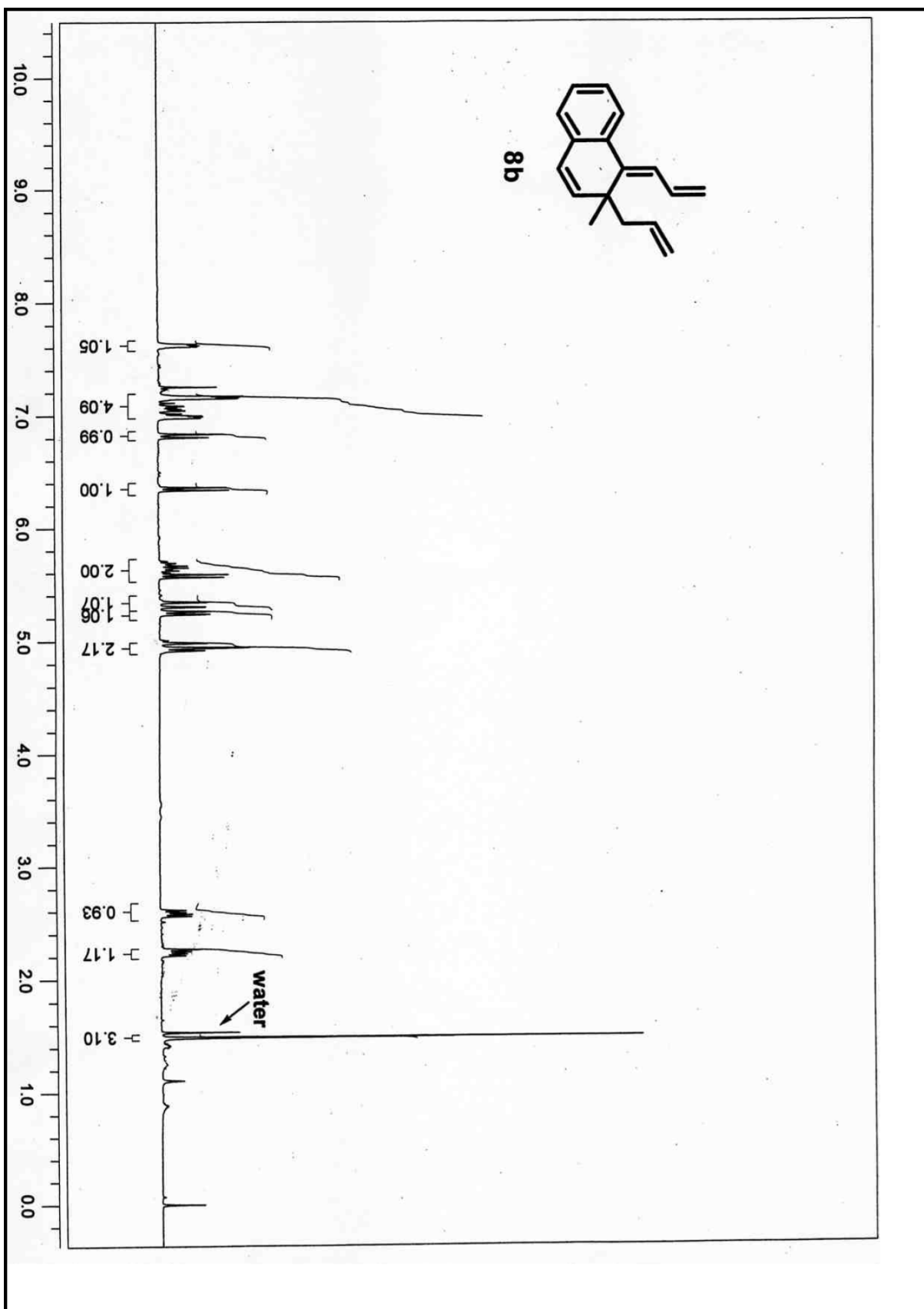
- [1] The starting materials **7a**, **7h**, and **7i** have appeared in the literatures, see: (a) F. Dübner, P. Knochel, *Angew. Chem. Int. Ed.* **1999**, *38*, 379-381. (b) F. Dübner, P. Knochel, *Tetrahedron Lett.* **2000**, *41*, 9233-9237. (c) K. Tissot-Croset, A. Alexakis, *Tetrahedron Lett.* **2004**, *45*, 7375-7378.
- [2] W. Zhang, C. Bai, X. Lu, R. He, *J. Organomet. Chem.* **2007**, *692*, 3563-3567.

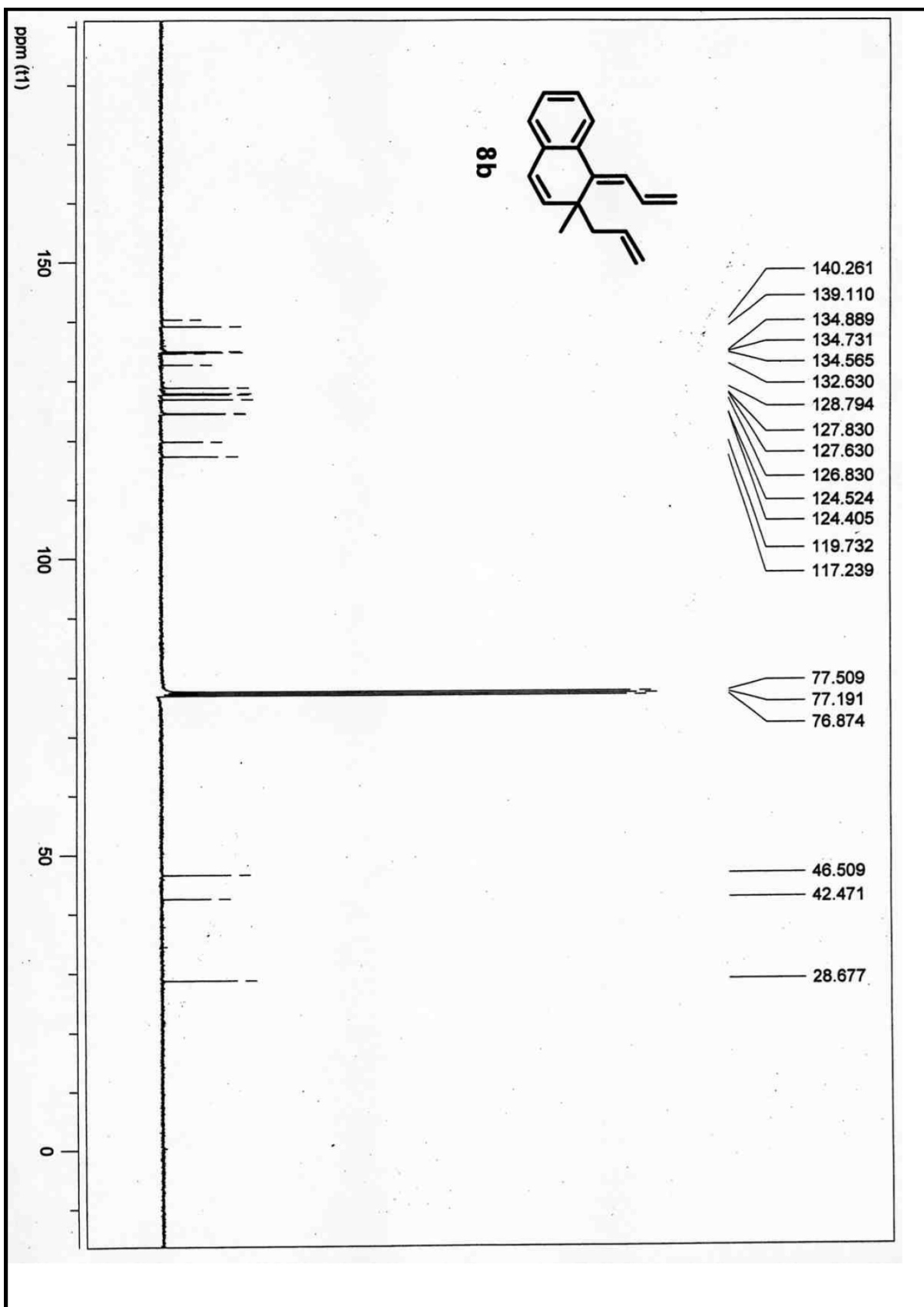


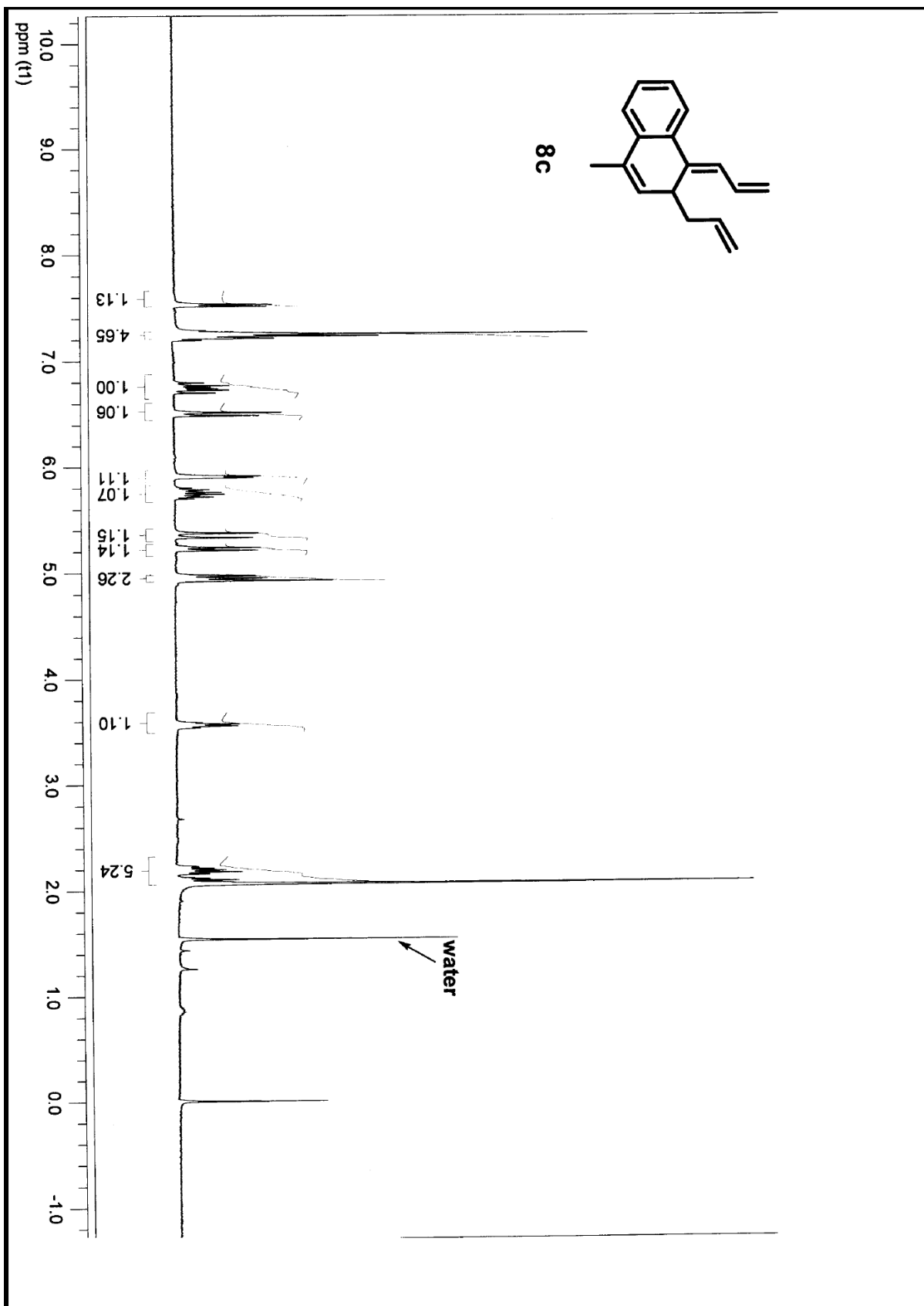
8a

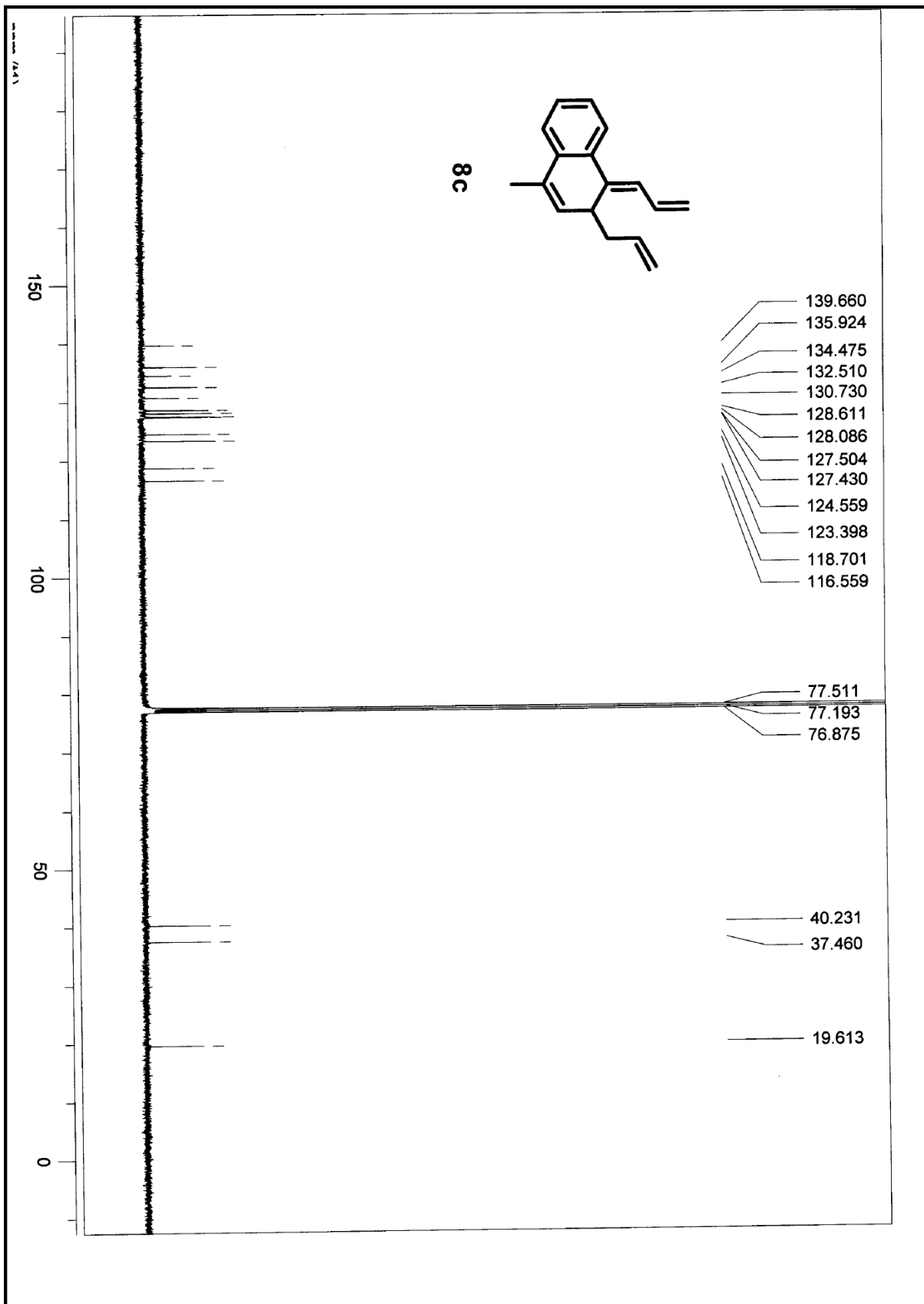


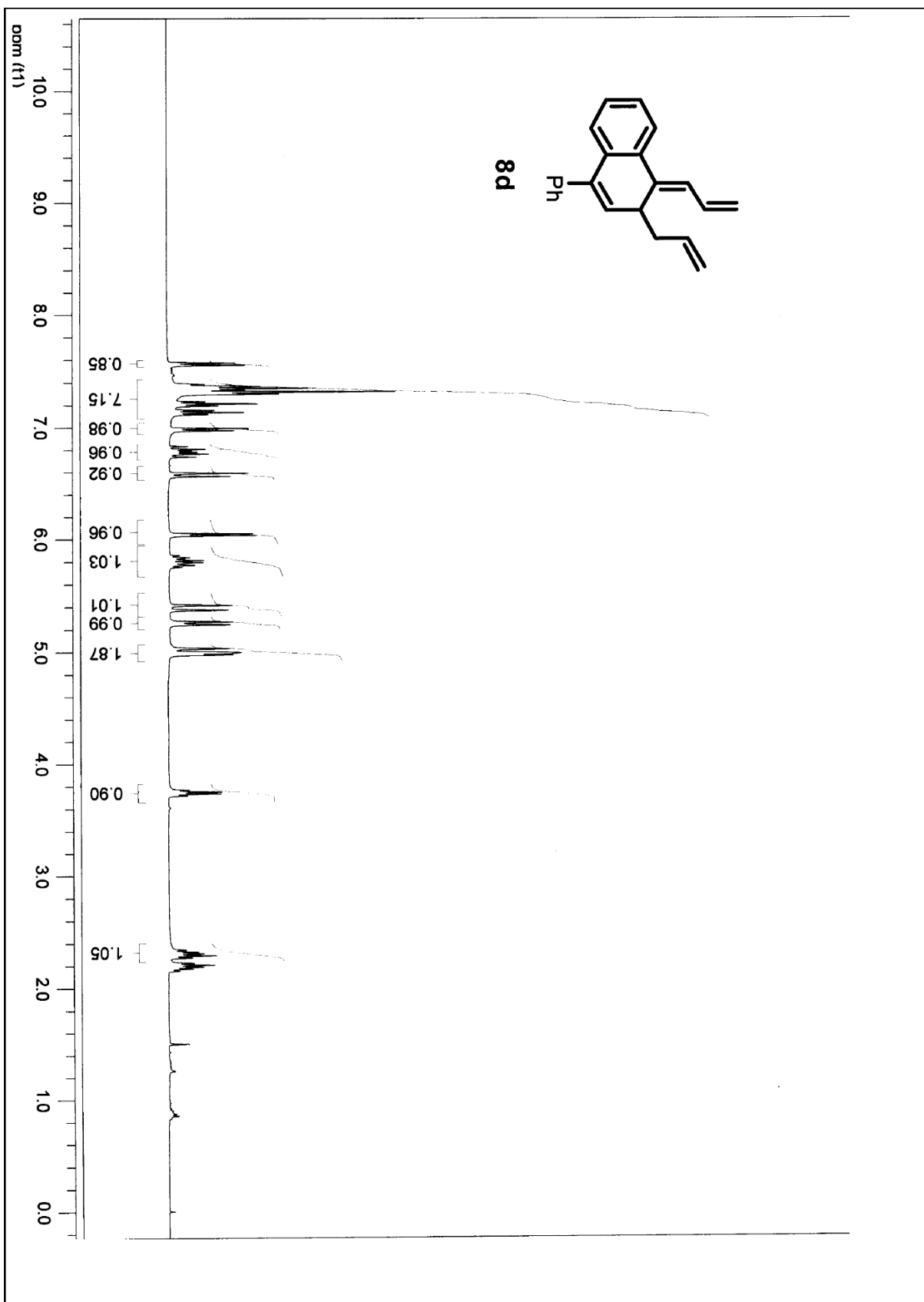


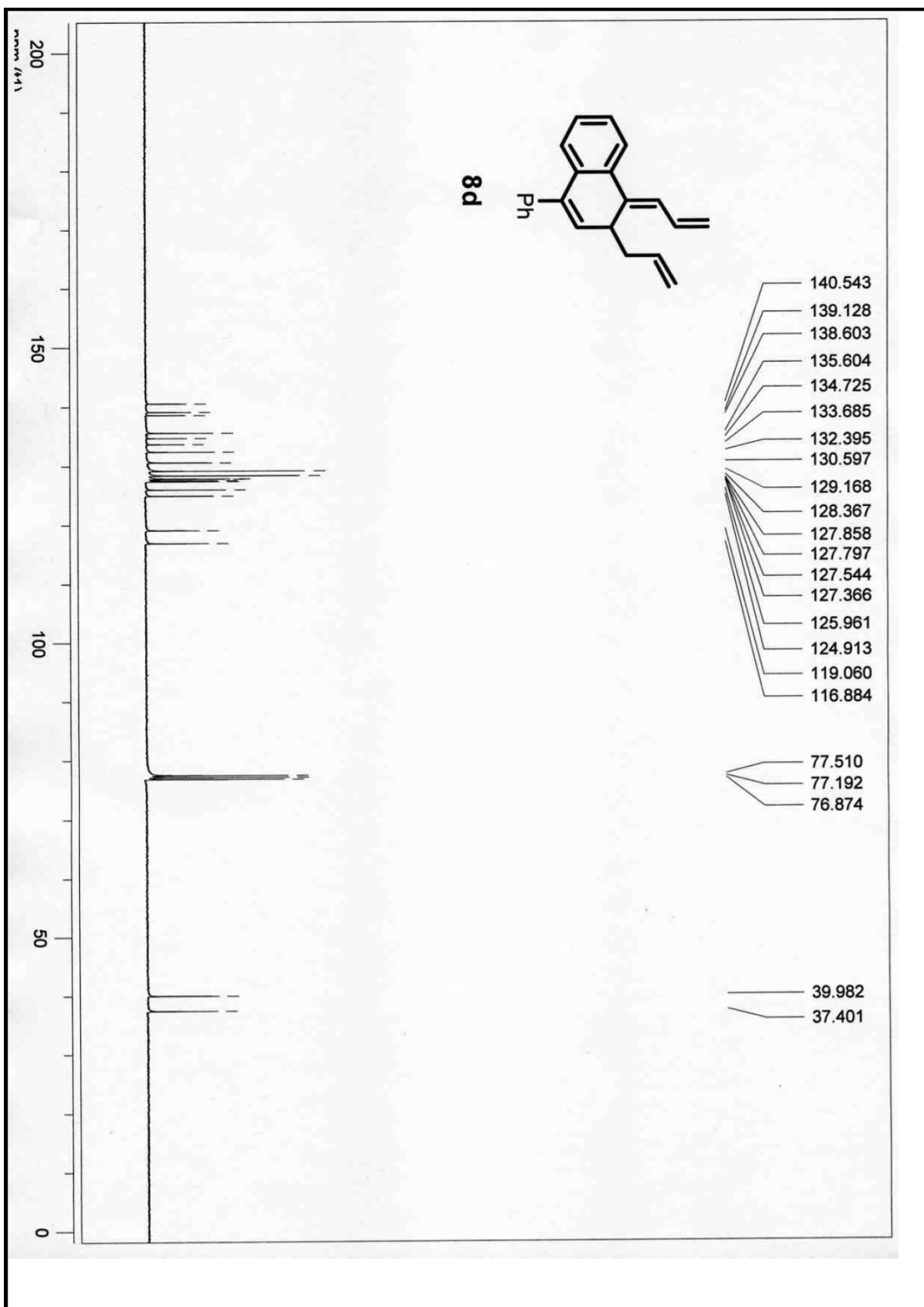


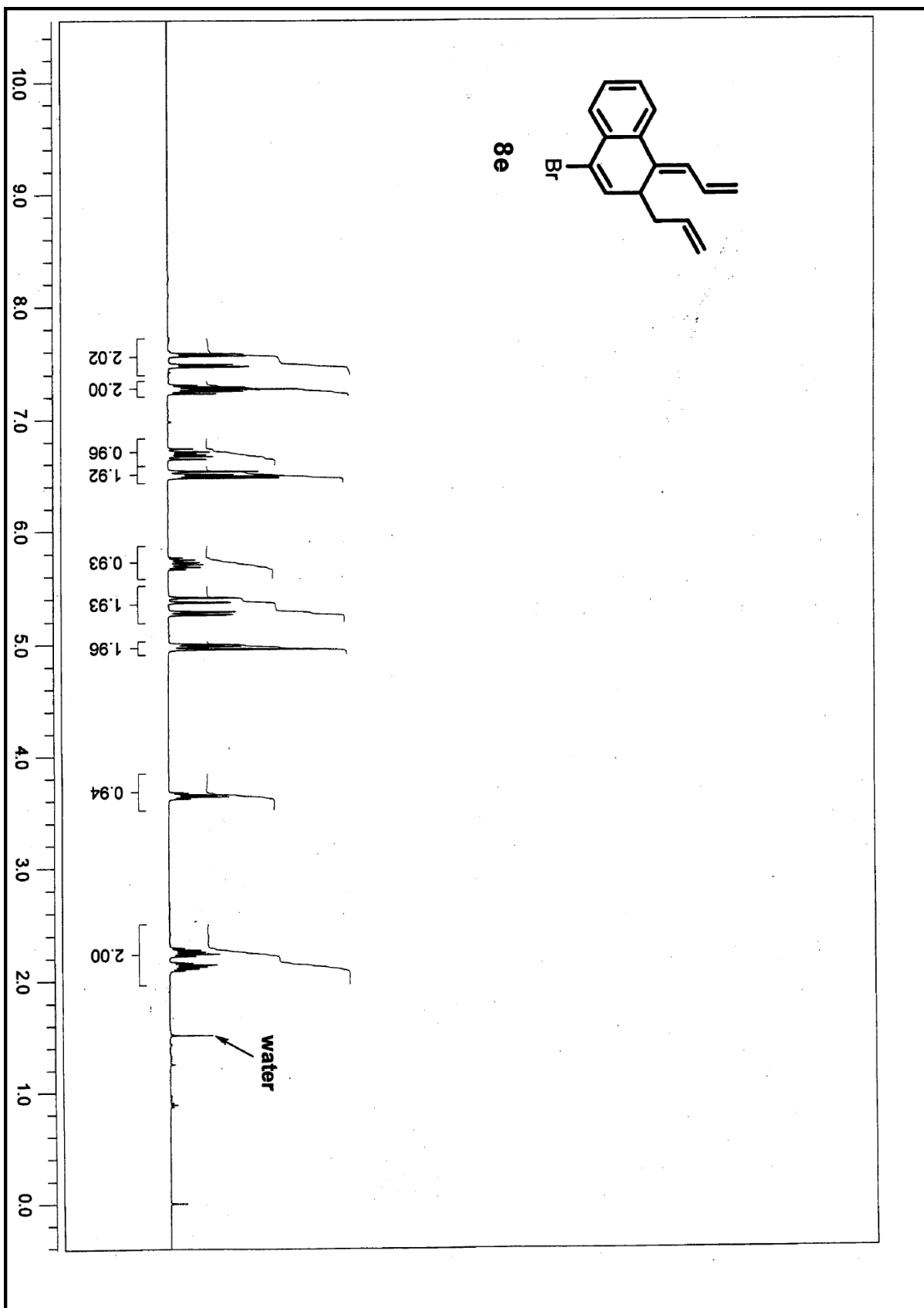


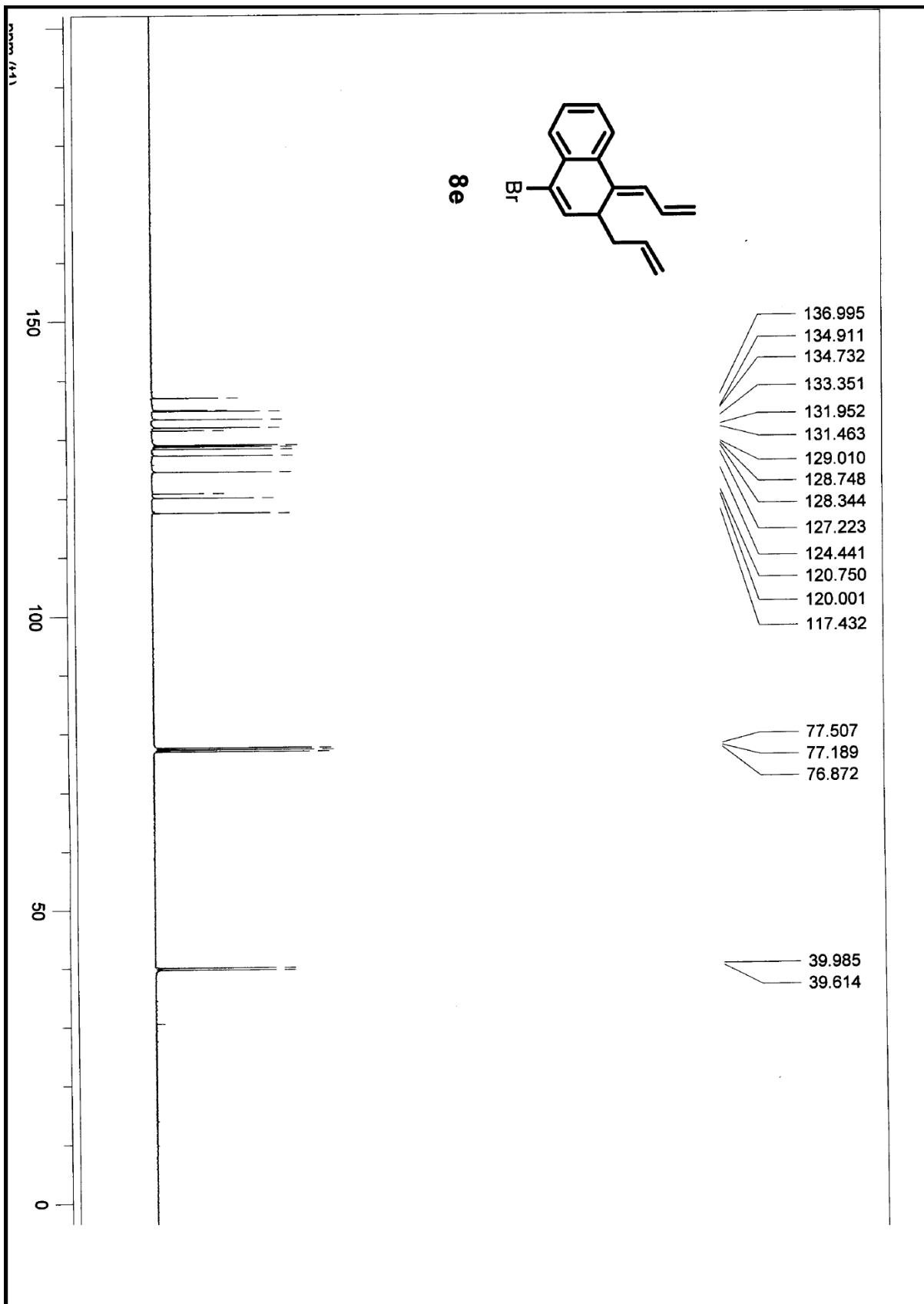


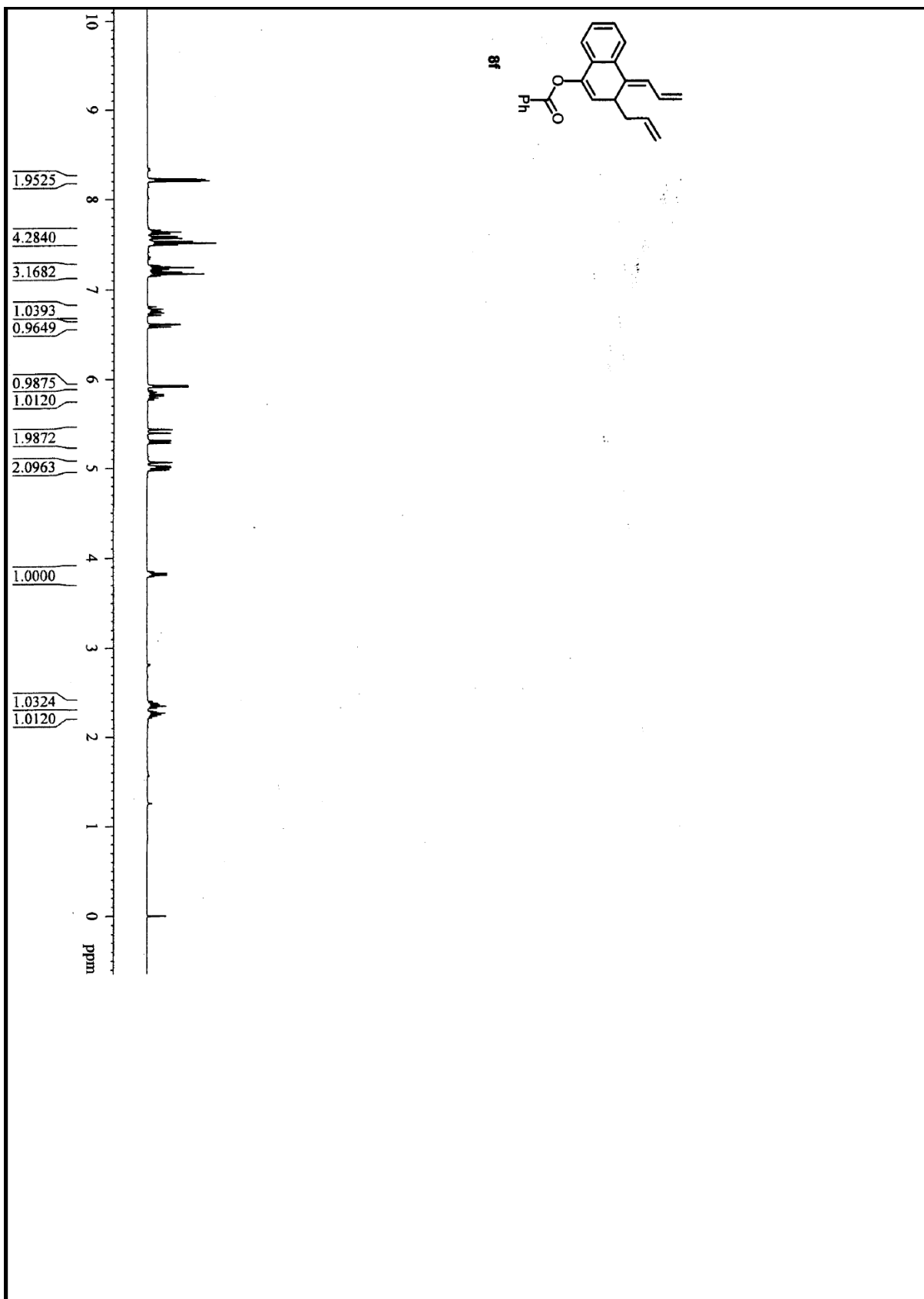


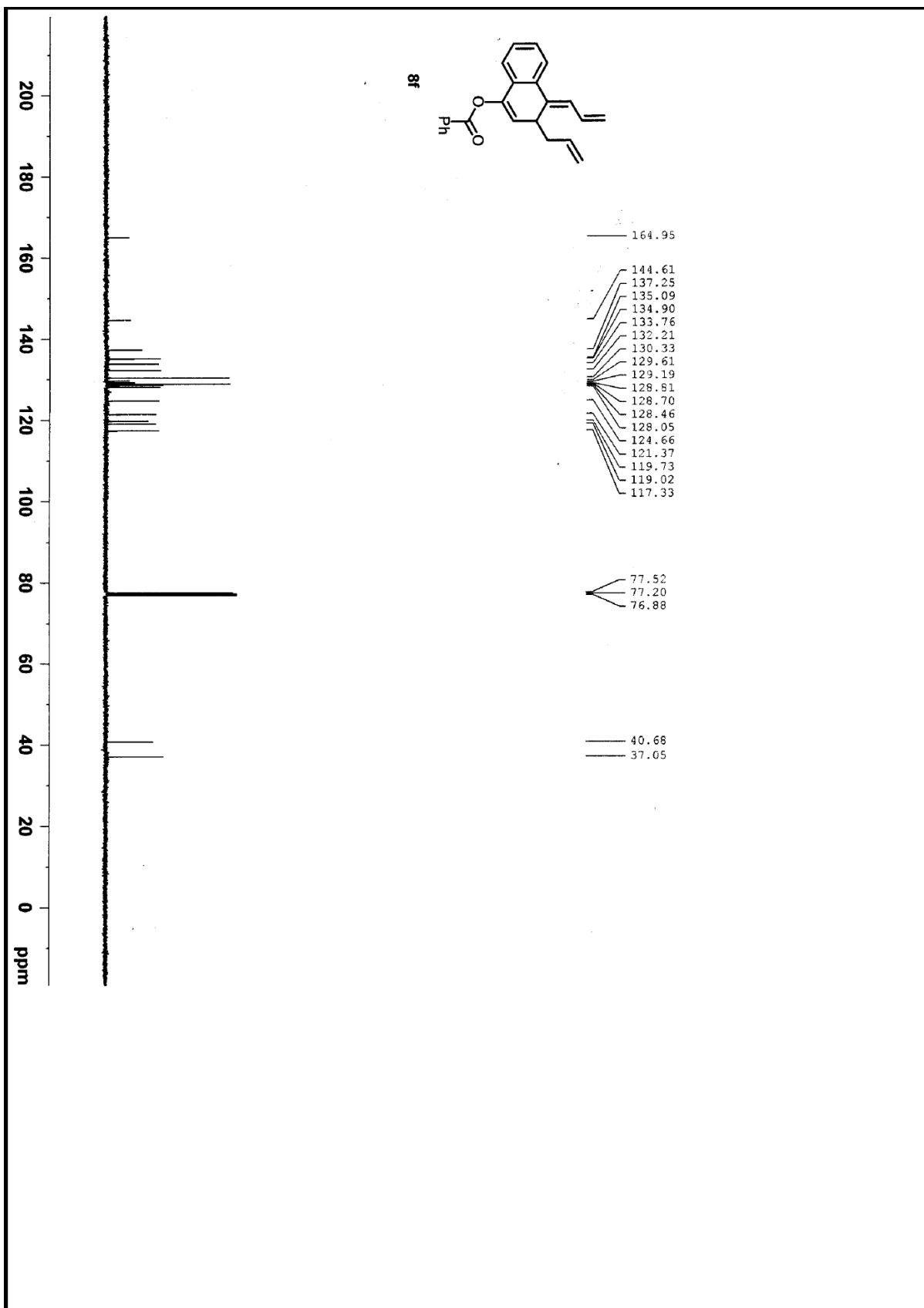


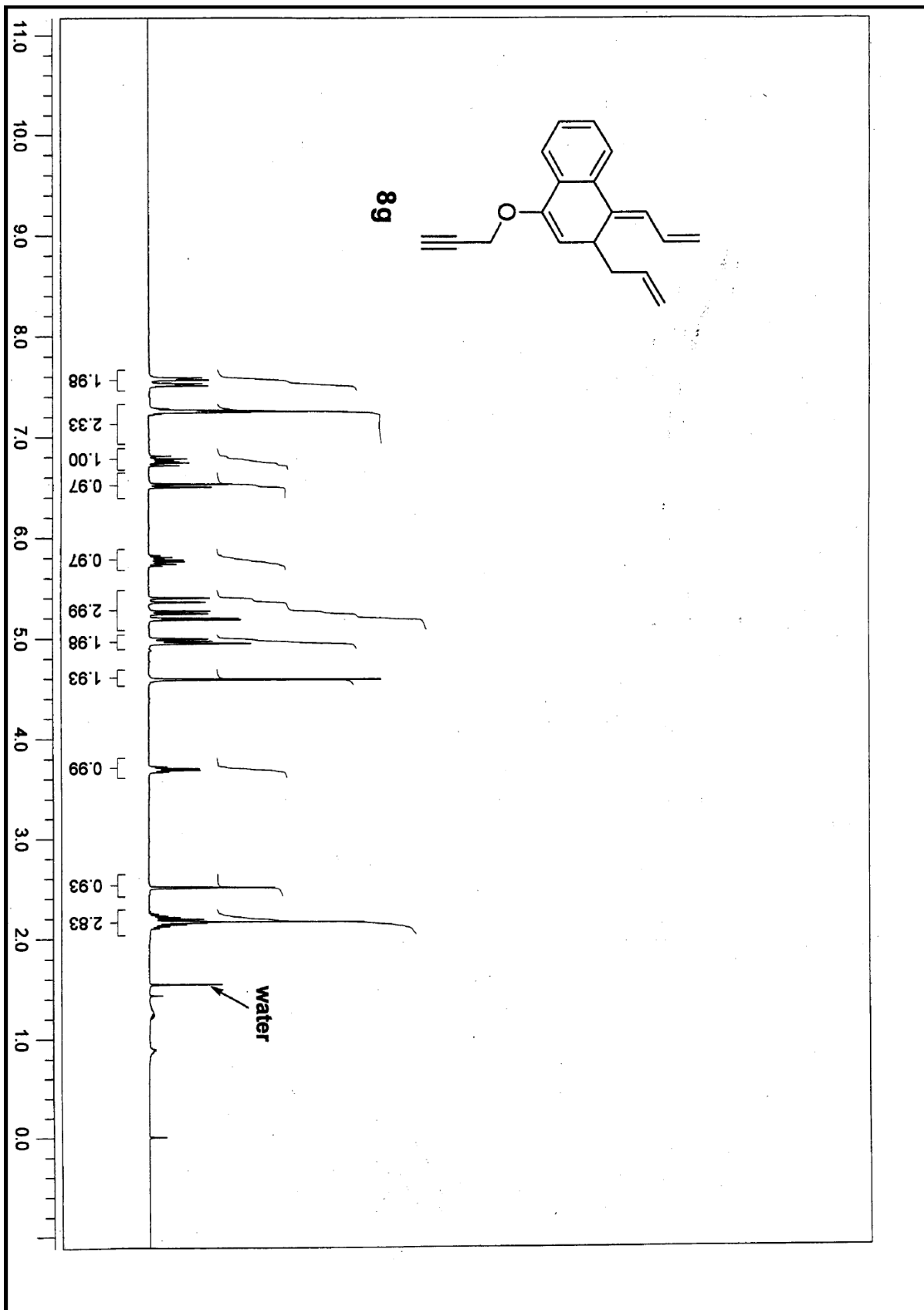


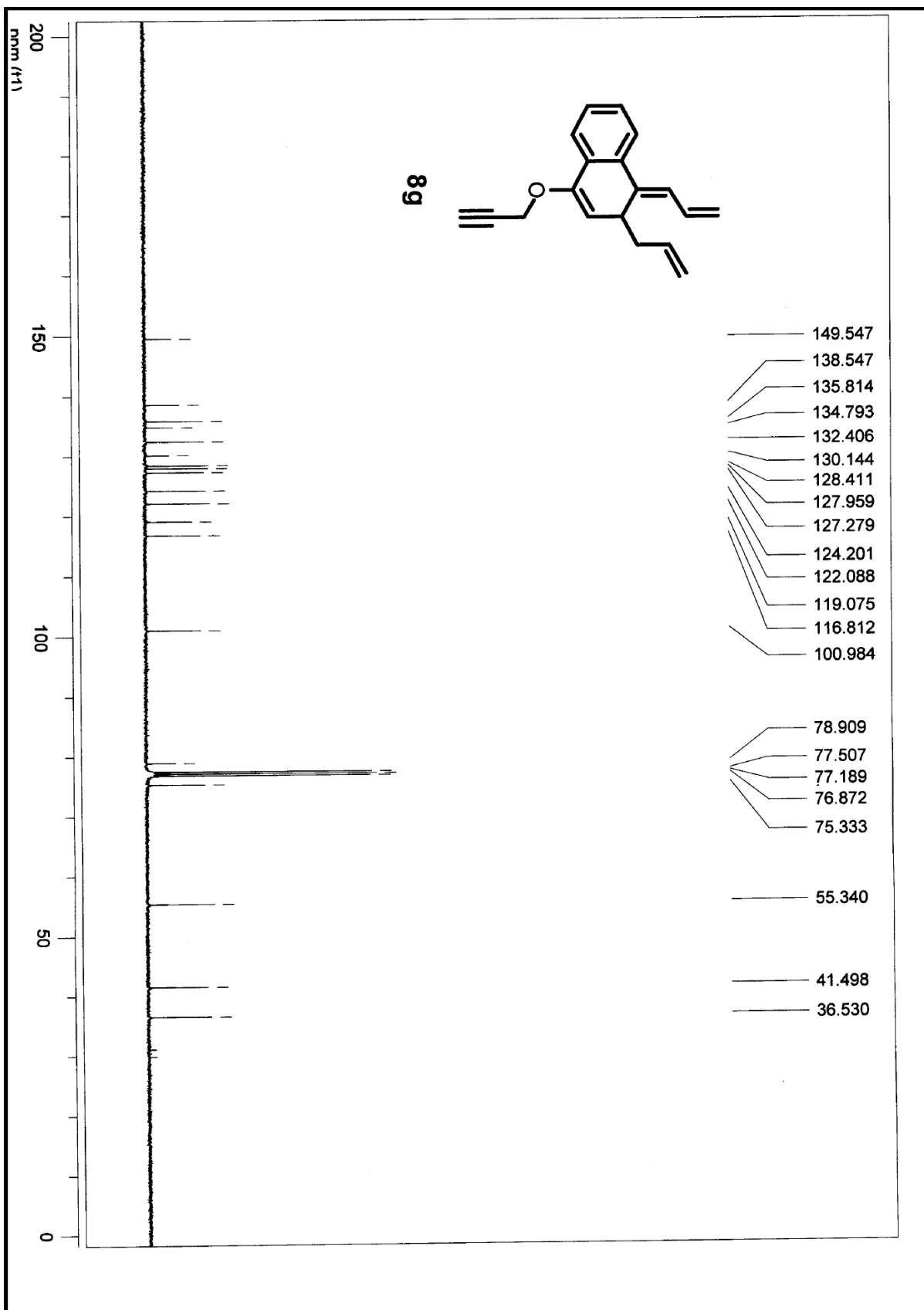


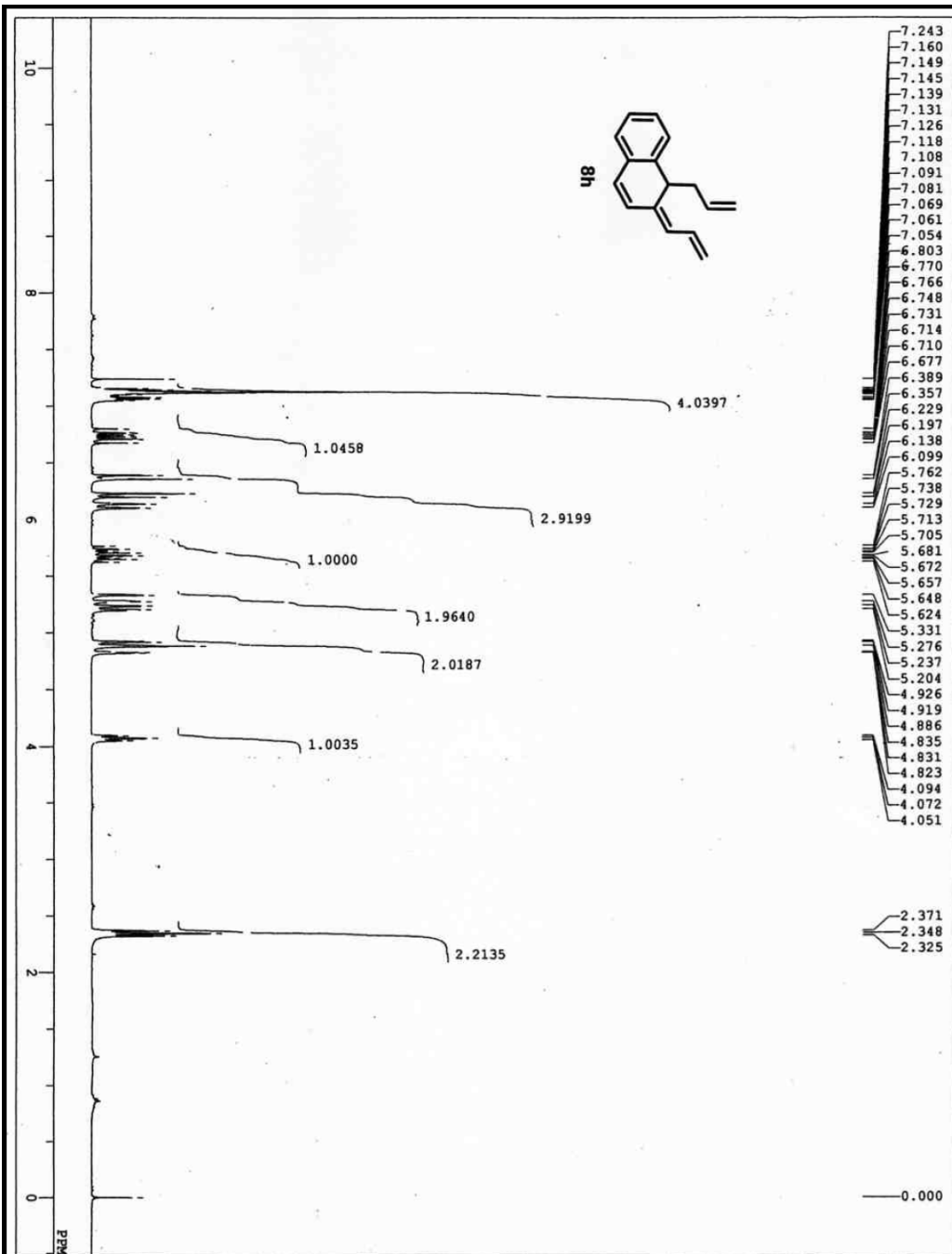












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