

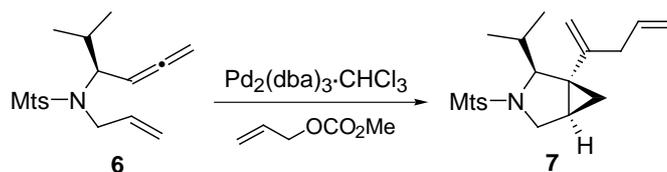
Supporting Information

Novel Synthesis of 3-Azabicyclo[3.1.0]hexanes by Unusual Palladium(0)-Catalyzed Cyclopropanation of Allenenes

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General Methods. Melting points are uncorrected. Nominal (LRMS) and exact mass (HRMS) spectra were recorded on a JEOL JMS-01SG-2 or JMS-HX/HX 110A mass spectrometer. ¹H NMR spectra were recorded in CDCl₃. Chemical shifts are reported in parts per million downfield from internal Me₄Si (s = singlet, d = doublet, dd = double doublet, ddd = doublet of double doublet, t = triplet, q = quartet, m = multiplet). Optical rotations were measured in CHCl₃ with a JASCO DIP-360 digital polarimeter. For flash chromatography, silica gel 60 H (silica gel for thin-layer chromatography, Merck) or silica gel 60 (finer than 230 mesh, Merck) was employed.



General Procedure for Construction of 3-Azabicyclo[3.1.0]hexane by the Palladium-Catalyzed Cyclopropanation of Allenenes. Synthesis of (1*S*,2*S*,5*R*)-2-Isopropyl-3-(mesitylsulfonyl)-1-(1-methylene-3-butenyl)-3-azabicyclo[3.1.0]hexane (7) (Table 1, Entry 5). A mixture of **6** (50 mg, 0.150 mmol), Pd₂(dba)₃-CHCl₃ (15.5 mg, 10 mol%), and allyl methyl carbonate (0.102 mL, 0.90 mmol) was refluxed for 5 h. The mixture was diluted with Et₂O and washed with water, and dried over MgSO₄. The filtrate was concentrated under reduced pressure to give an oily residue, which was purified by flash column chromatography over silica gel with *n*-hexane–EtOAc (20:1) to give **7** (36.1 mg, 64% yield) as colorless crystals: mp 100–102 °C (*n*-hexane–Et₂O); [α]_D²⁵ +20.7 (*c* 1.69, CHCl₃); IR (KBr) cm⁻¹: 1327 (NSO₂), 1153 (NSO₂); ¹H NMR (500 MHz, CDCl₃) δ: 0.51 (d, *J* = 6.7 Hz, 3H, CMe), 0.94 (d, *J* = 6.7 Hz, 3H, CMe), 0.97-0.99 (m, 1H, 6-CHH), 1.03-1.06 (m, 1H, 6-CHH), 1.09-1.12 (m, 1H, 5-H), 2.00-2.06 (m, 1H, Me₂CH), 2.28 (s, 3H, CMe), 2.62 (s, 6H, 2 × CMe), 2.98 (dd, *J* = 15.9, 7.9 Hz, 1H, 2'-CHH), 3.03 (dd, *J* = 15.9, 6.7 Hz, 1H, 2'-CHH), 3.49 (d, *J* = 9.8 Hz, 1H, 4-CHH), 3.65 (dd, *J* = 9.8, 4.3 Hz, 1H, 4-CHH), 4.05 (d, *J* = 2.4 Hz, 1H, 2-H), 4.85 (d, *J* = 1.2 Hz, 1H, C=CHH), 4.93 (s, 1H, C=CHH), 5.07 (d, *J* = 9.8 Hz, 1H, 4'-CHH), 5.13 (dd, *J* = 17.1, 1.7 Hz, 1H, 4'-CHH), 5.73-5.82 (m, 1H, 3'-H), 6.91 (s, 2H, Ph); ¹³C NMR (75 MHz, CDCl₃) δ: 11.9, 16.3, 19.6, 20.1, 20.9, 22.7 (2C), 30.2, 35.0, 39.3, 50.4, 65.8, 113.5, 116.7, 131.8 (2C), 135.2, 136.1, 139.4 (2C), 142.2, 148.4; MS (FAB) *m/z* (%) 374 (MH⁺, 50), 119 (100); HRMS (FAB) Calcd for C₂₂H₃₂NO₂S (MH⁺): 374.2154, found: 374.2154.

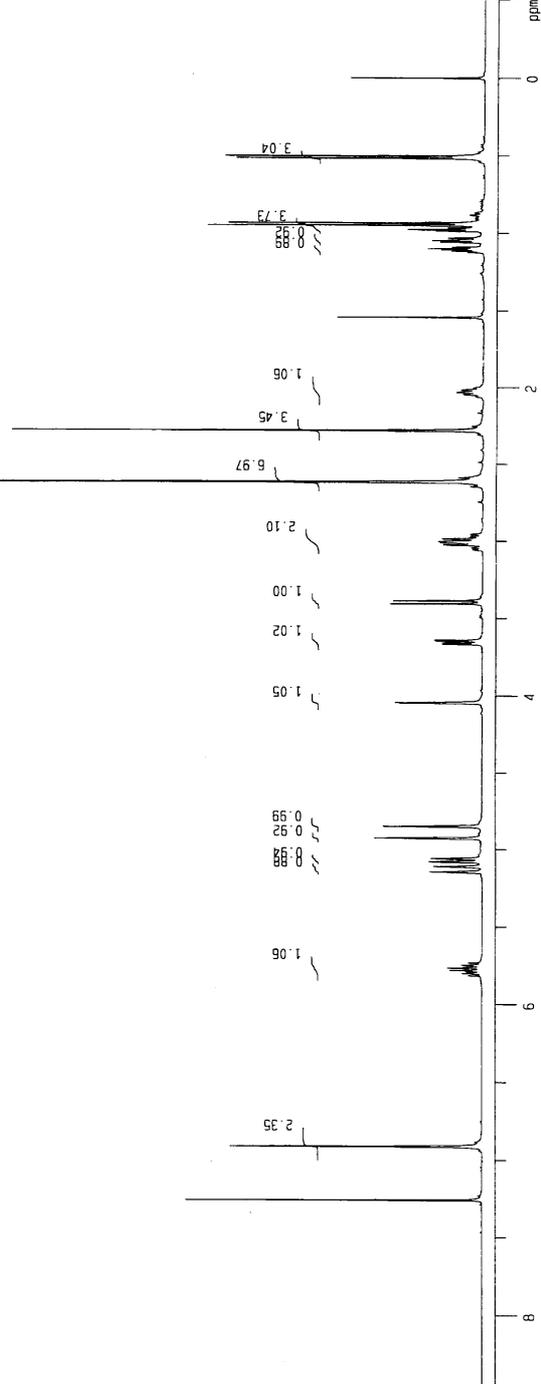
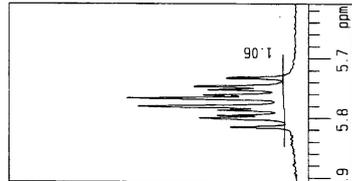
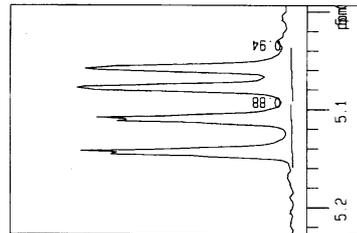
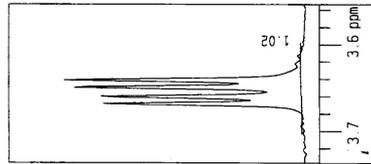
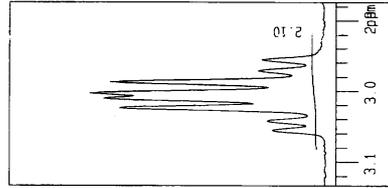
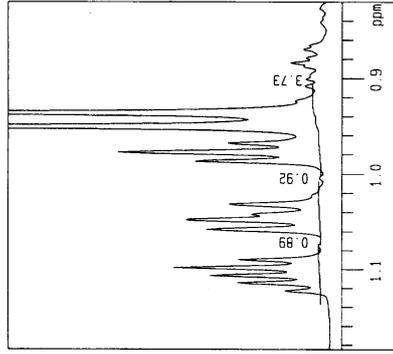
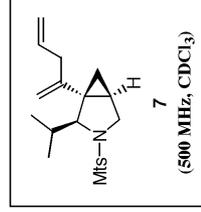
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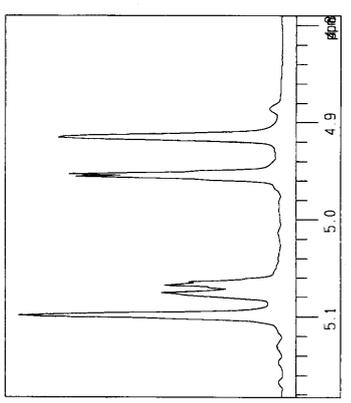
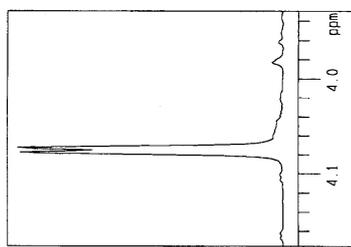
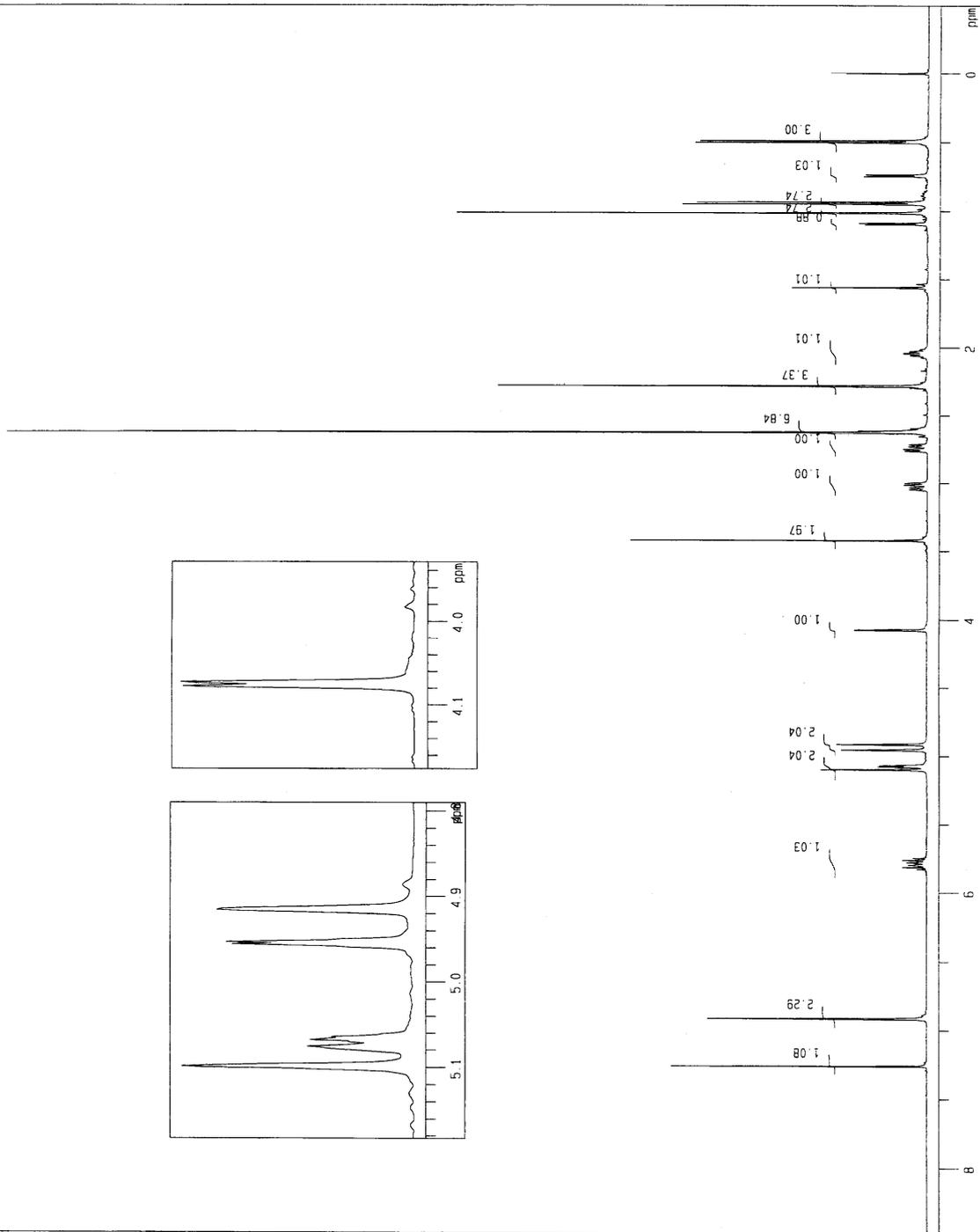
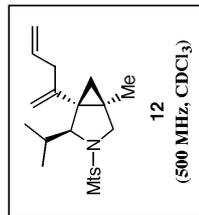


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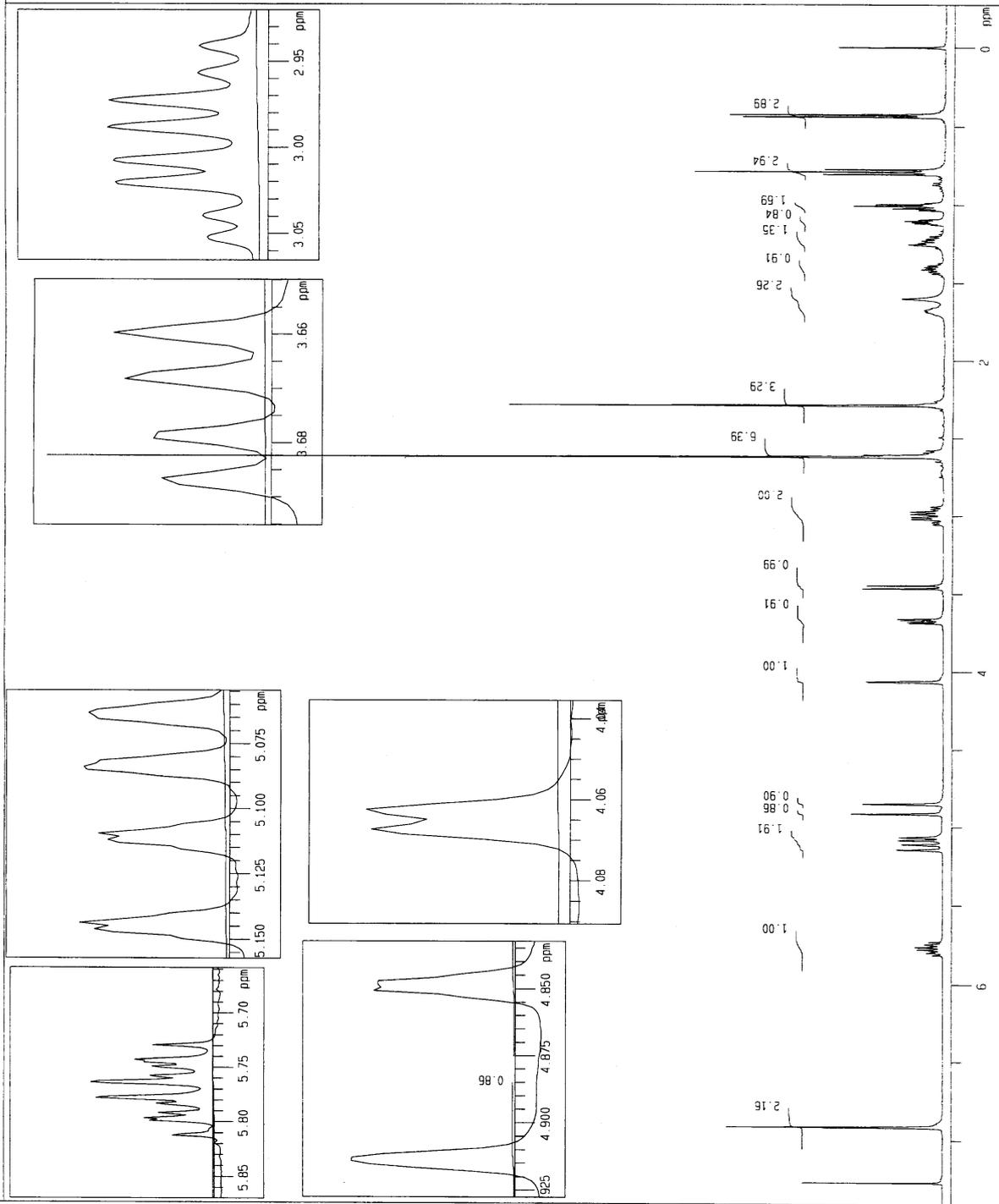
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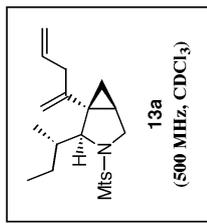
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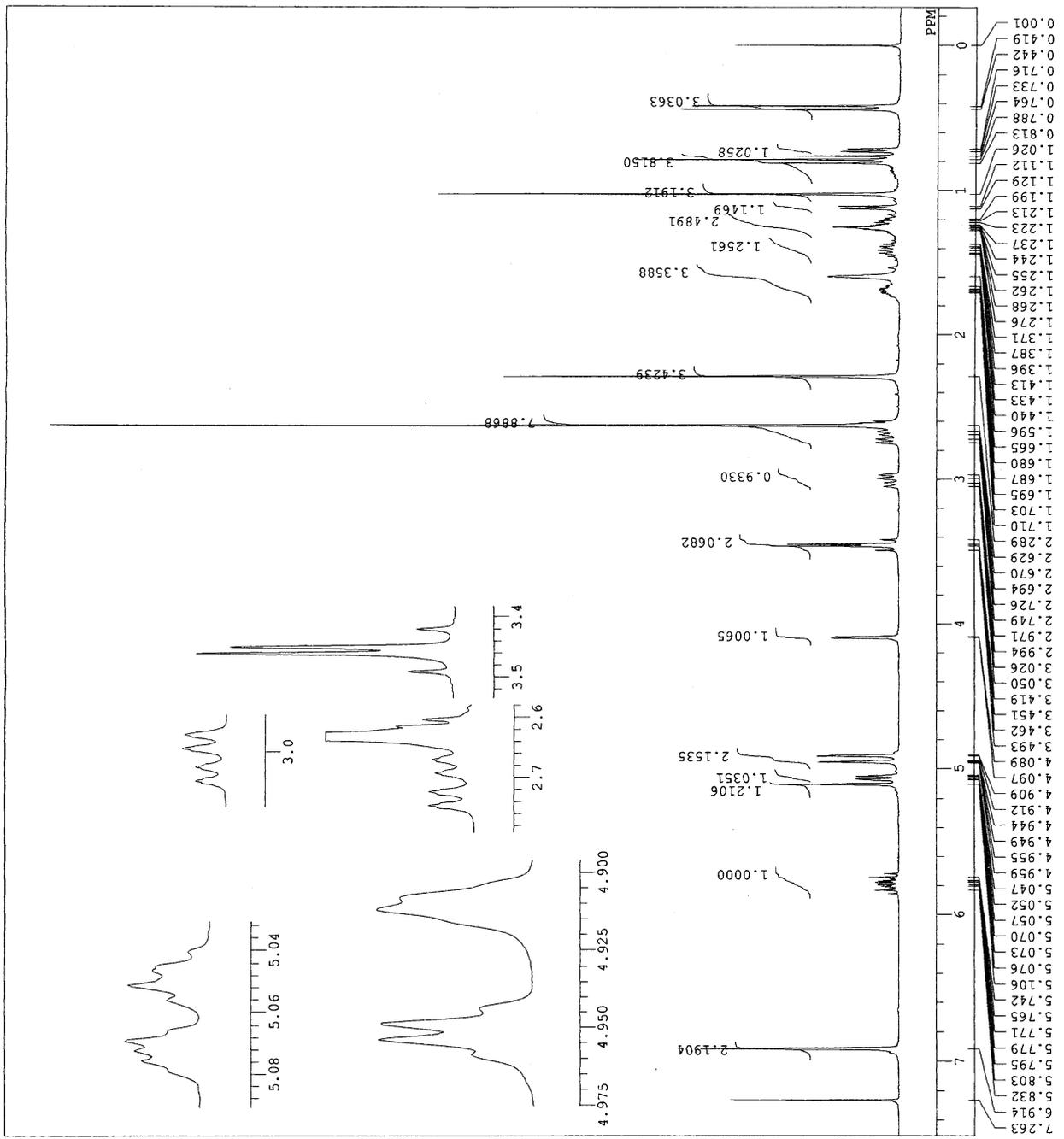
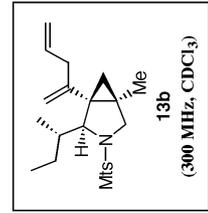
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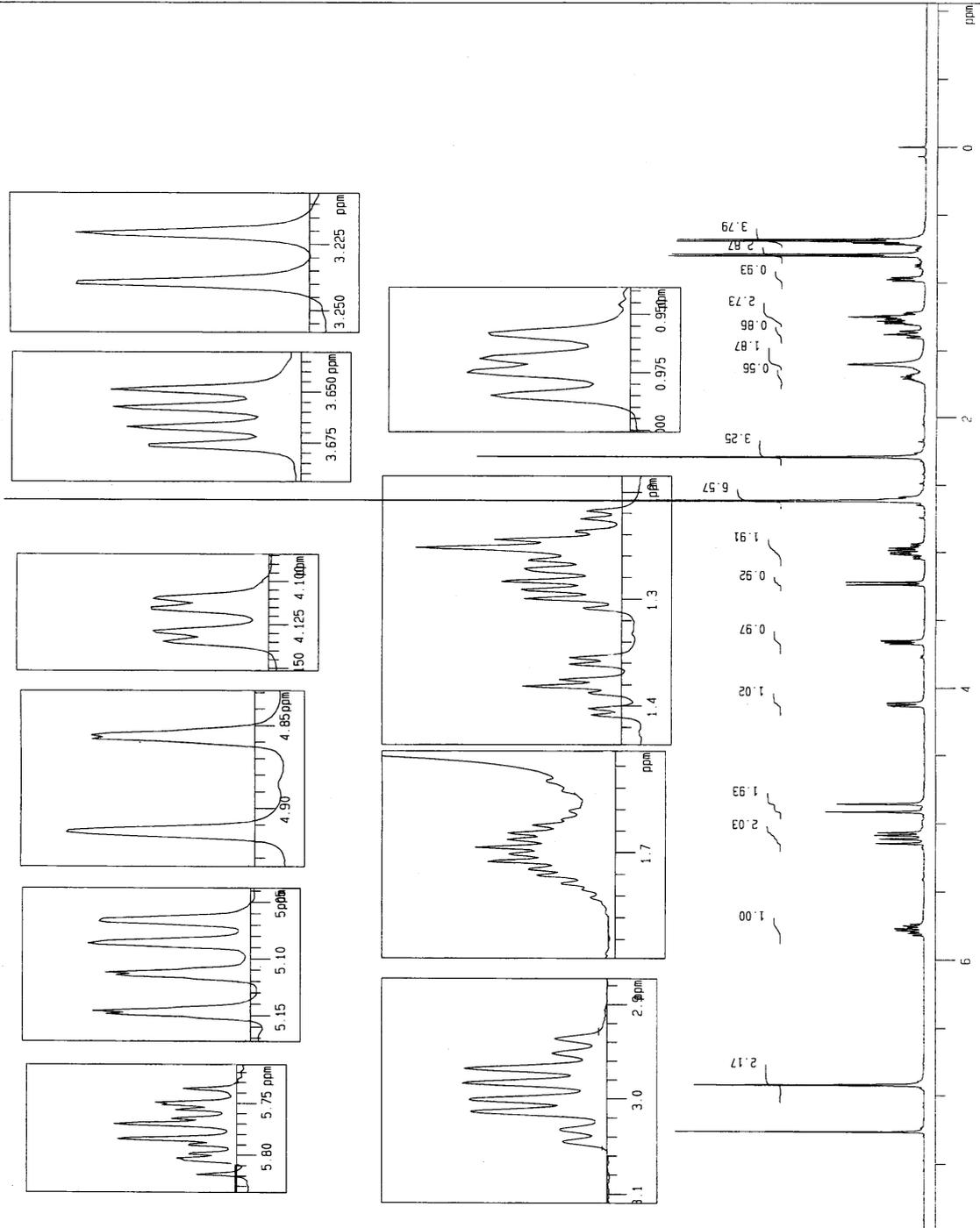
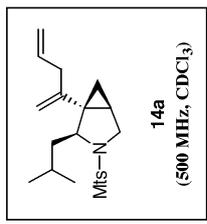


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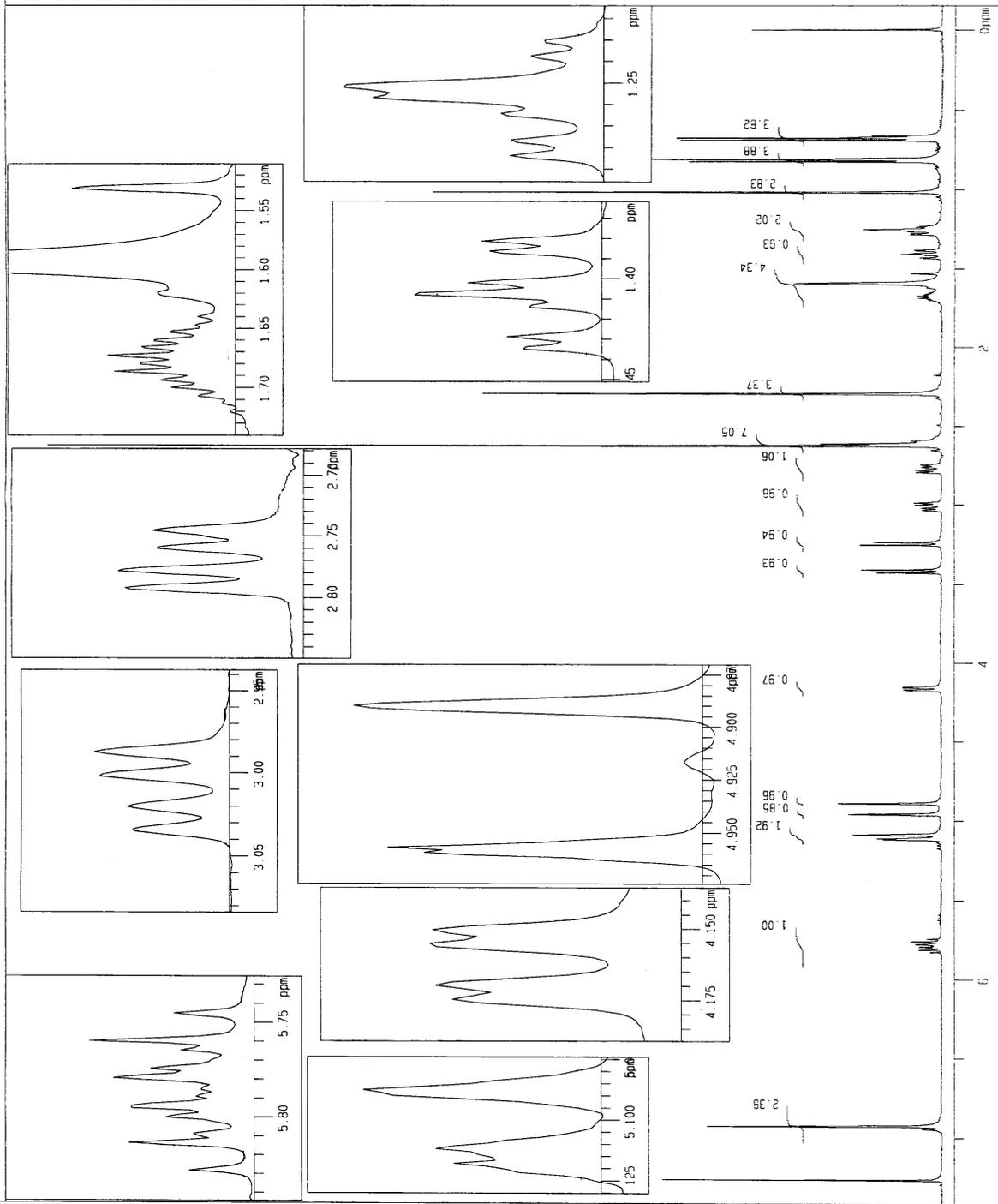


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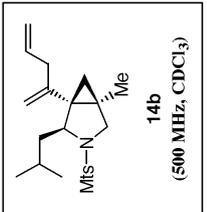
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