

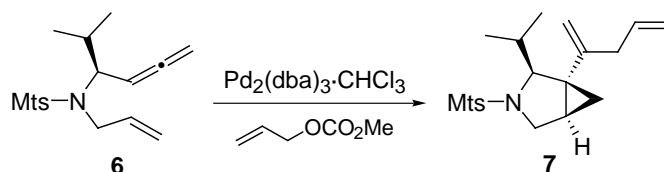
Supporting Information

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

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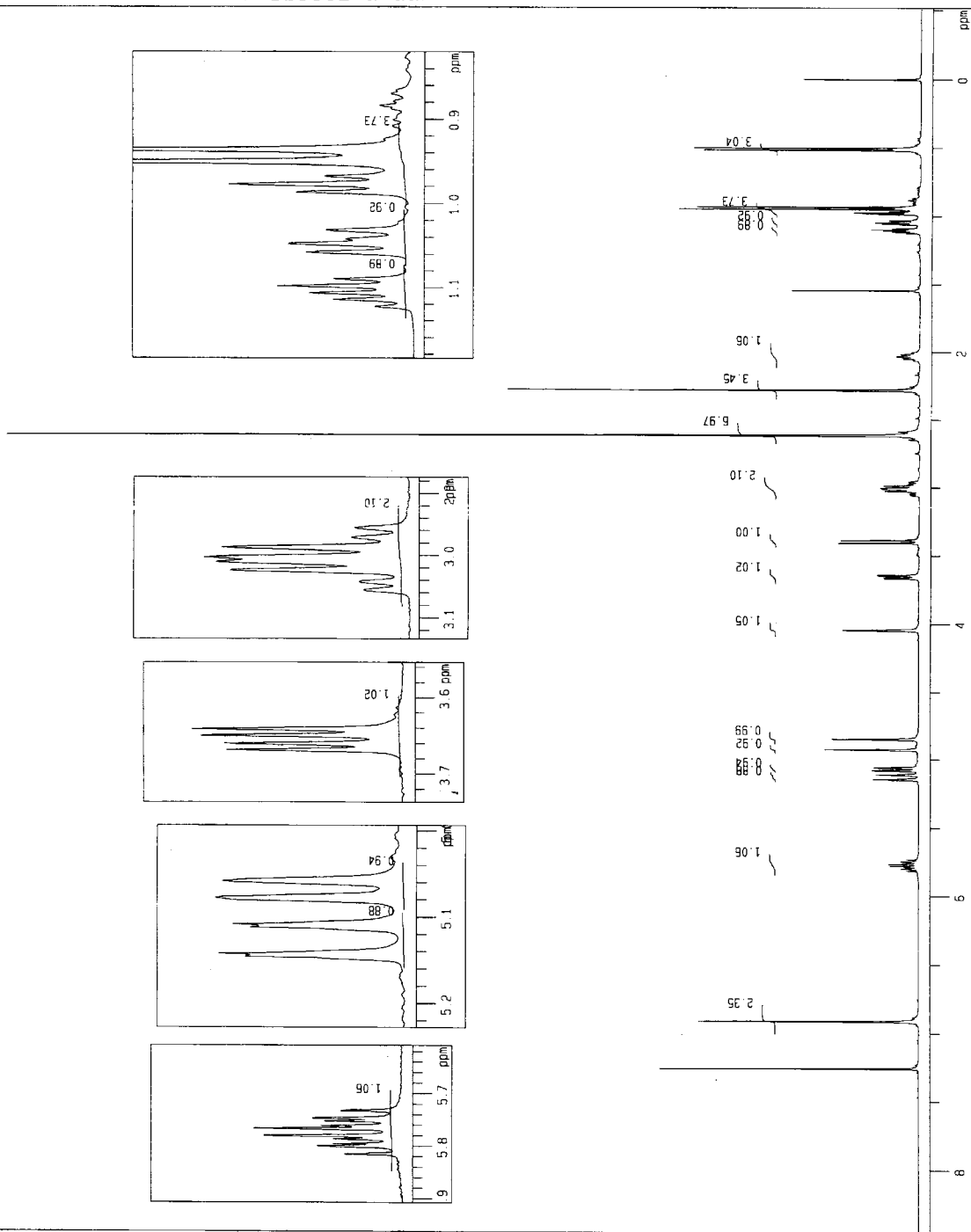
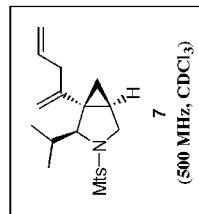
General Methods. Melting points are uncorrected. Nominal (LRMS) and exact mass (HRMS) spectra were recorded on a JEOL JMS-01SG-2 or JMS-HX/HX 110A mass spectrometer. ^1H NMR spectra were recorded in CDCl_3 . Chemical shifts are reported in parts per million downfield from internal Me_4Si (s = singlet, d = doublet, dd = double doublet, ddd = doublet of double doublet, t = triplet, q = quartet, m = multiplet). Optical rotations were measured in CHCl_3 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 (1S,2S,5R)-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), $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (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 Et_2O and washed with water, and dried over MgSO_4 . 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– Et_2O); $[\alpha]_{\text{D}}^{25} +20.7$ (*c* 1.69, CHCl_3); IR (KBr) cm^{-1} : 1327 (NSO₂), 1153 (NSO₂); ^1H NMR (500 MHz, CDCl_3) 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, Me_2CH), 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); ^{13}C NMR (75 MHz, CDCl_3) 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 $\text{C}_{22}\text{H}_{32}\text{NO}_2\text{S}$ (MH^+): 374.2154, found: 374.2154.

1H Line

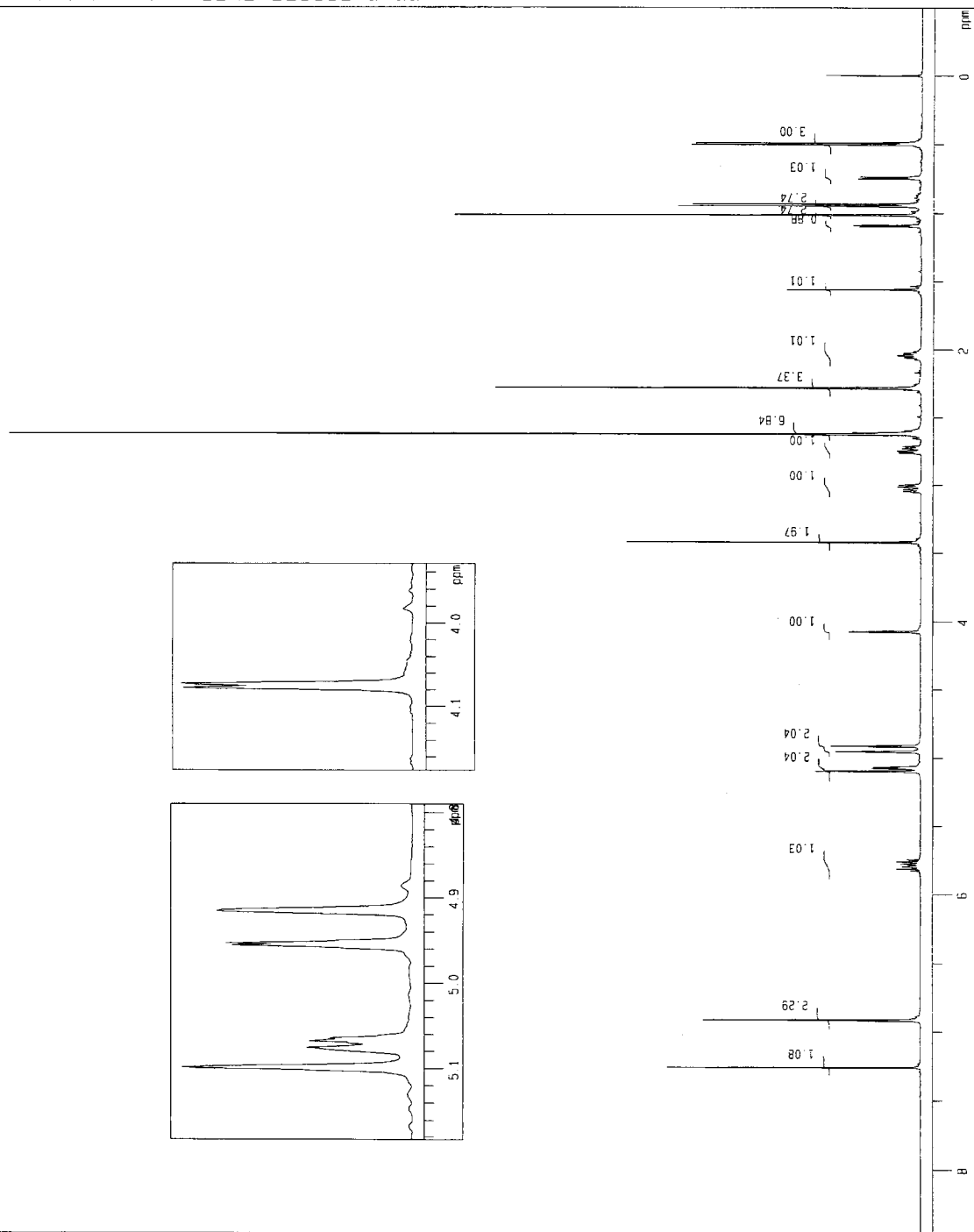
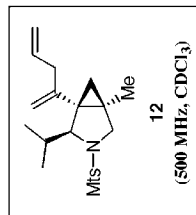
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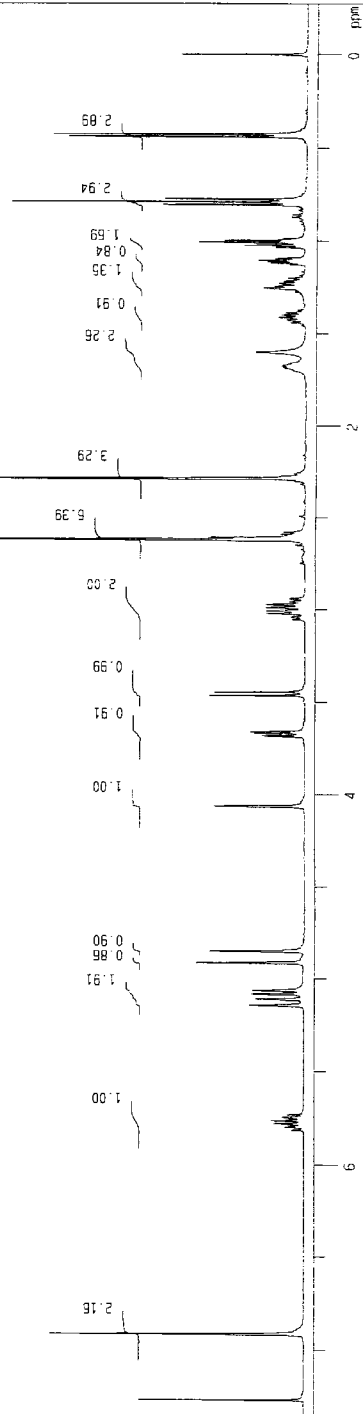
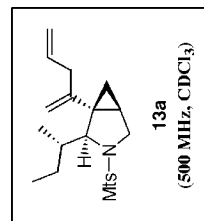
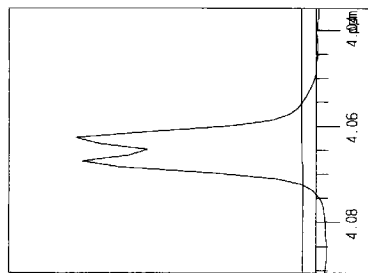
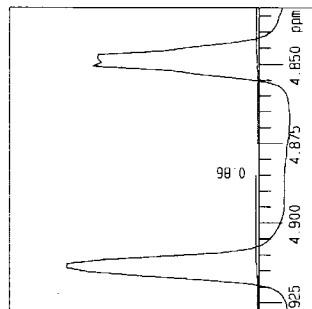
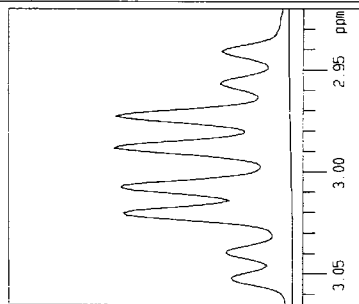
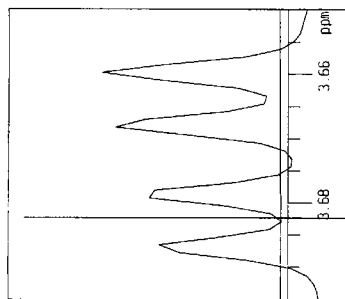
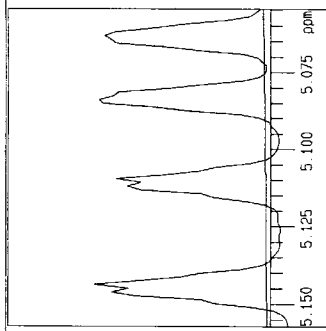
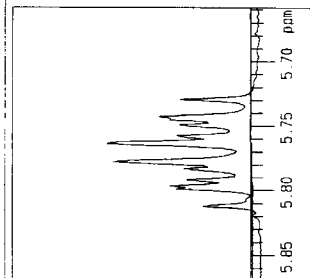
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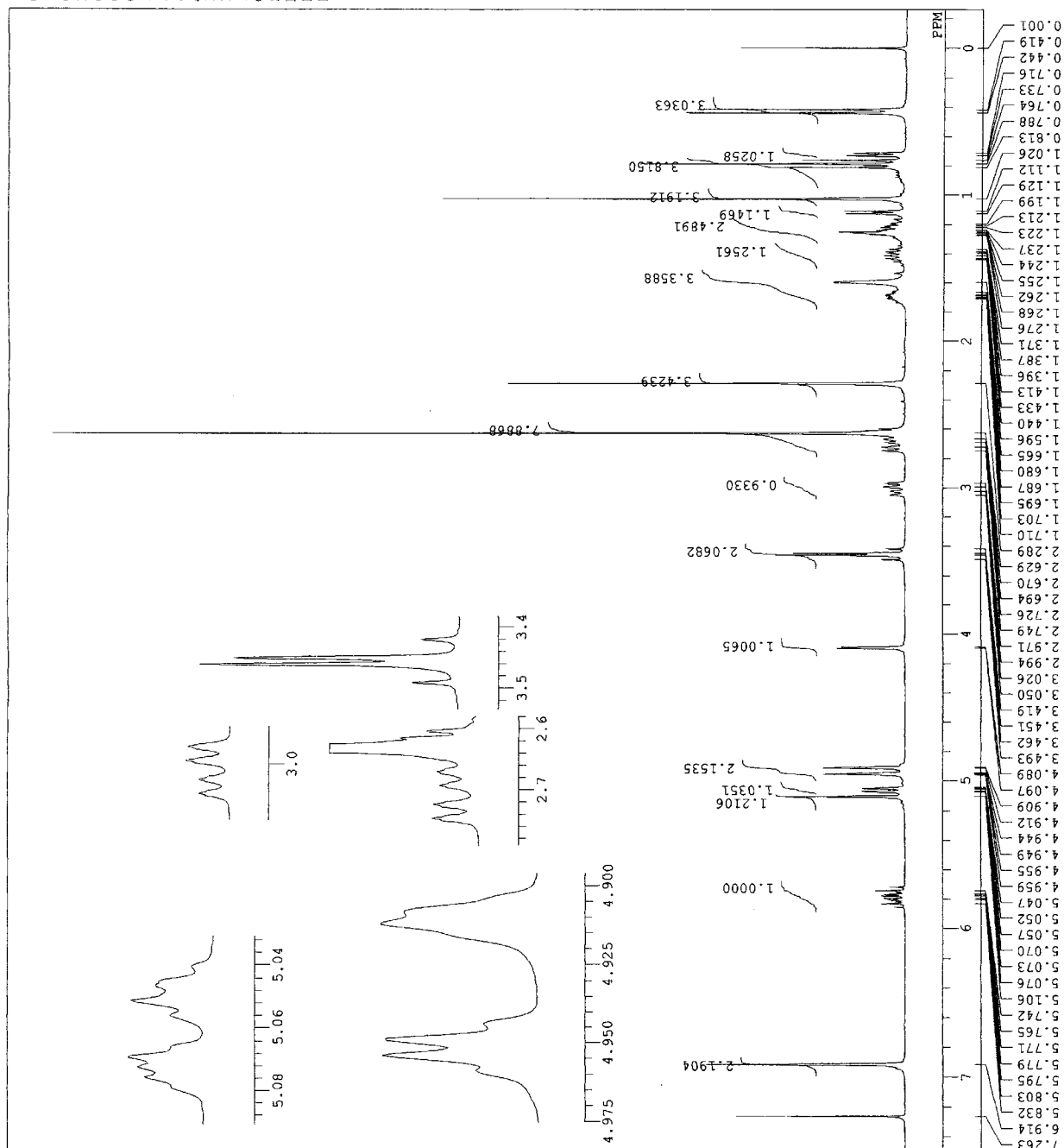
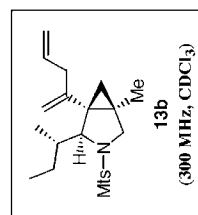


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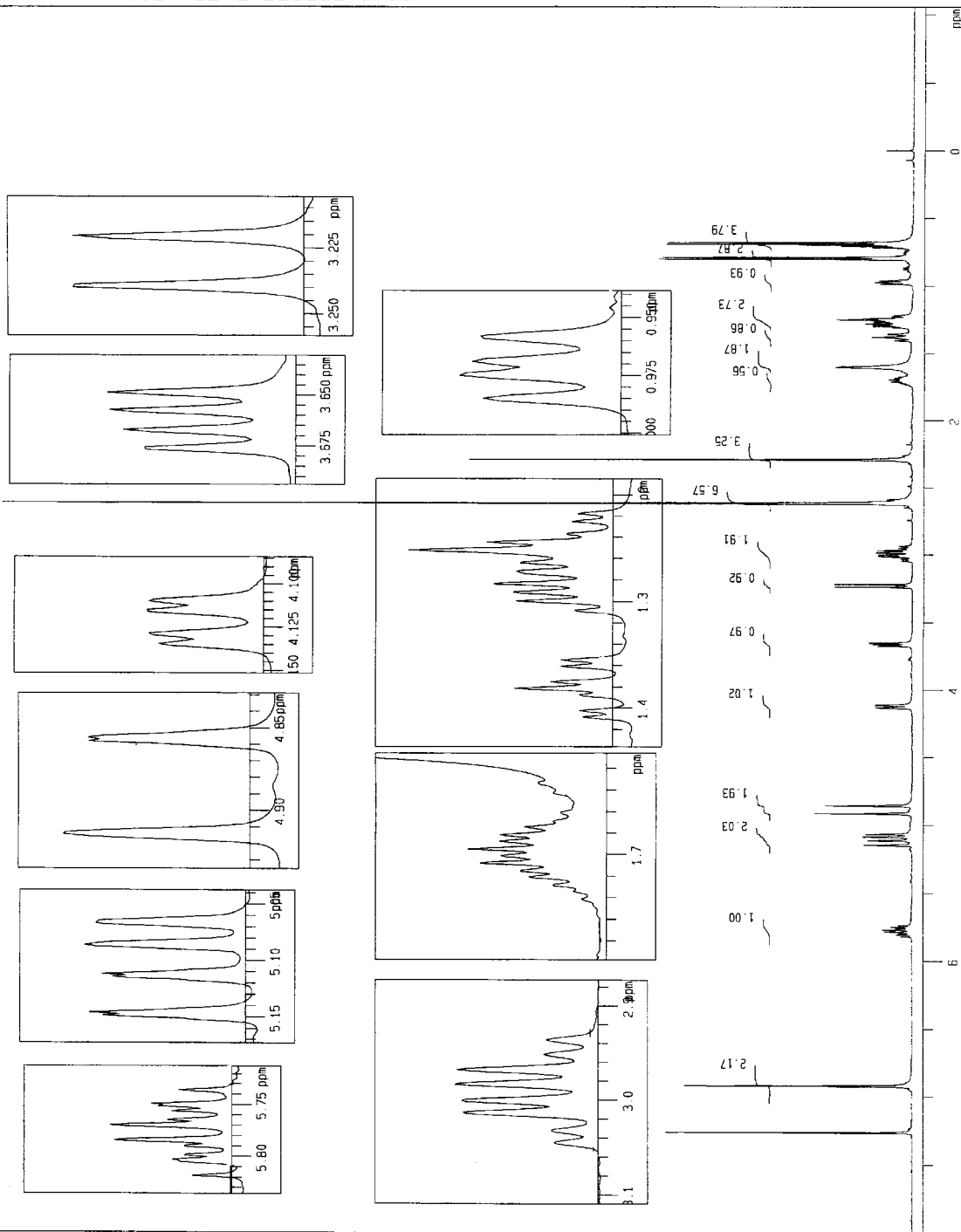
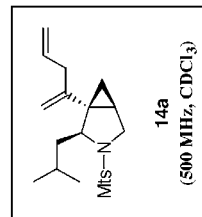
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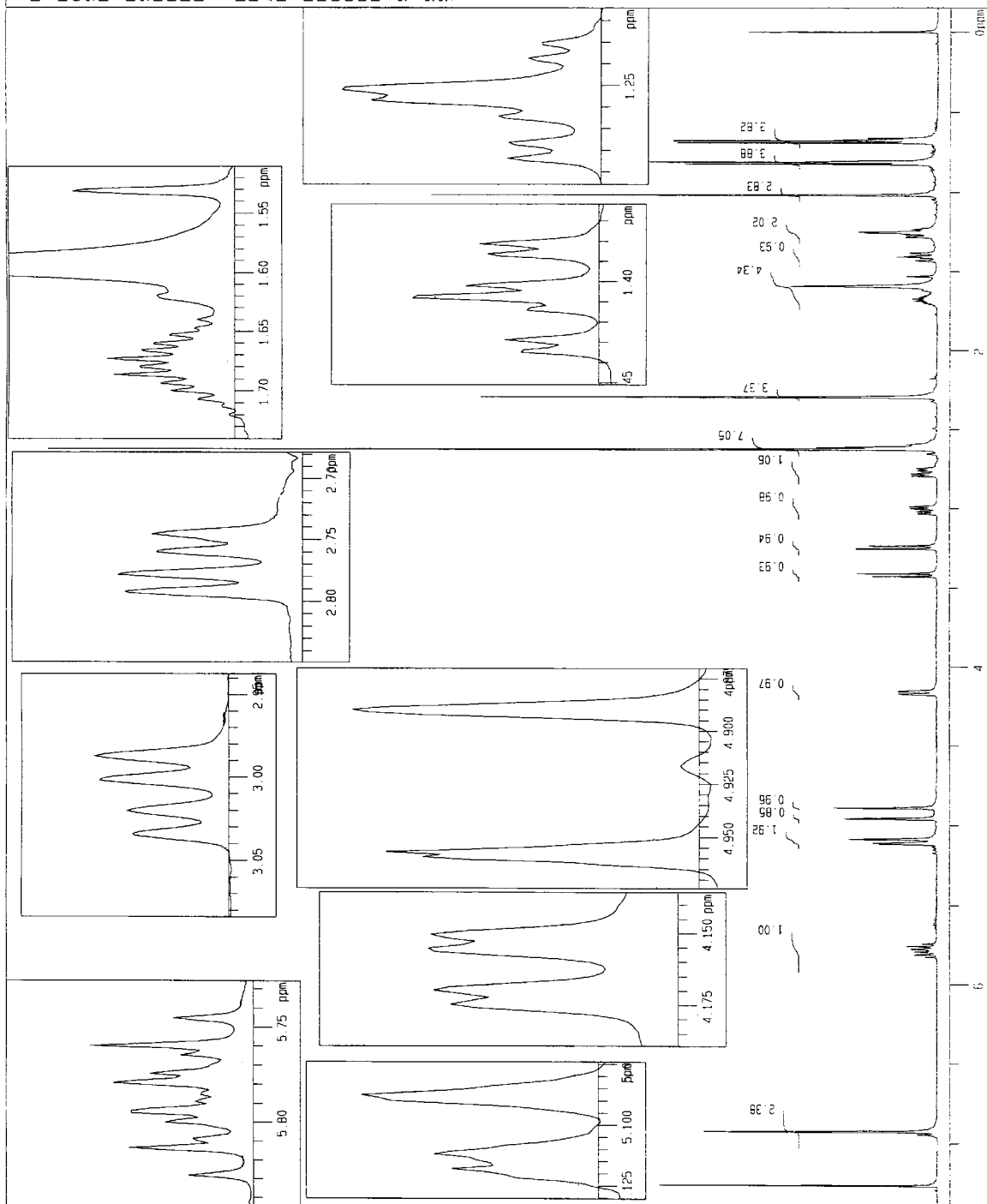
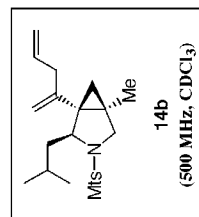
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