

Electronic Supplementary Information

Facile two-step synthesis of 3-substituted indazoles using diazo(trimethylsilyl)methylmagnesium bromide

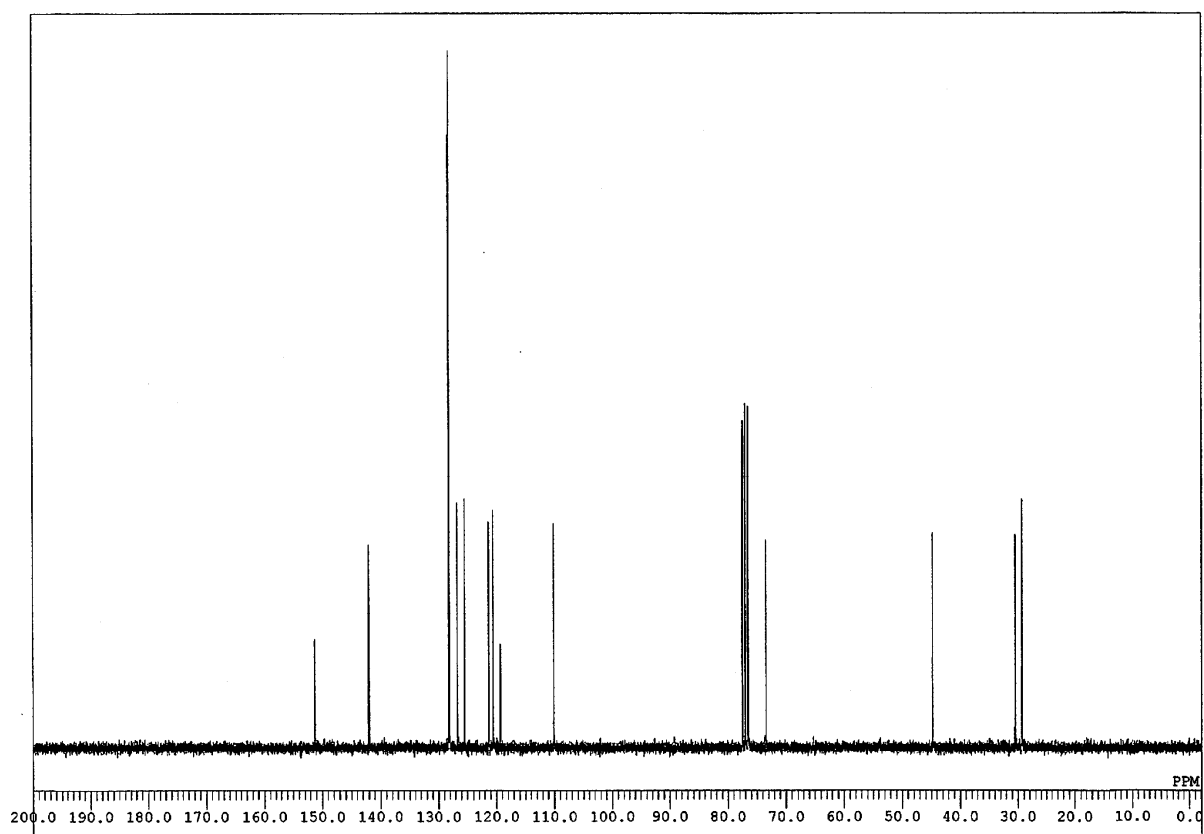
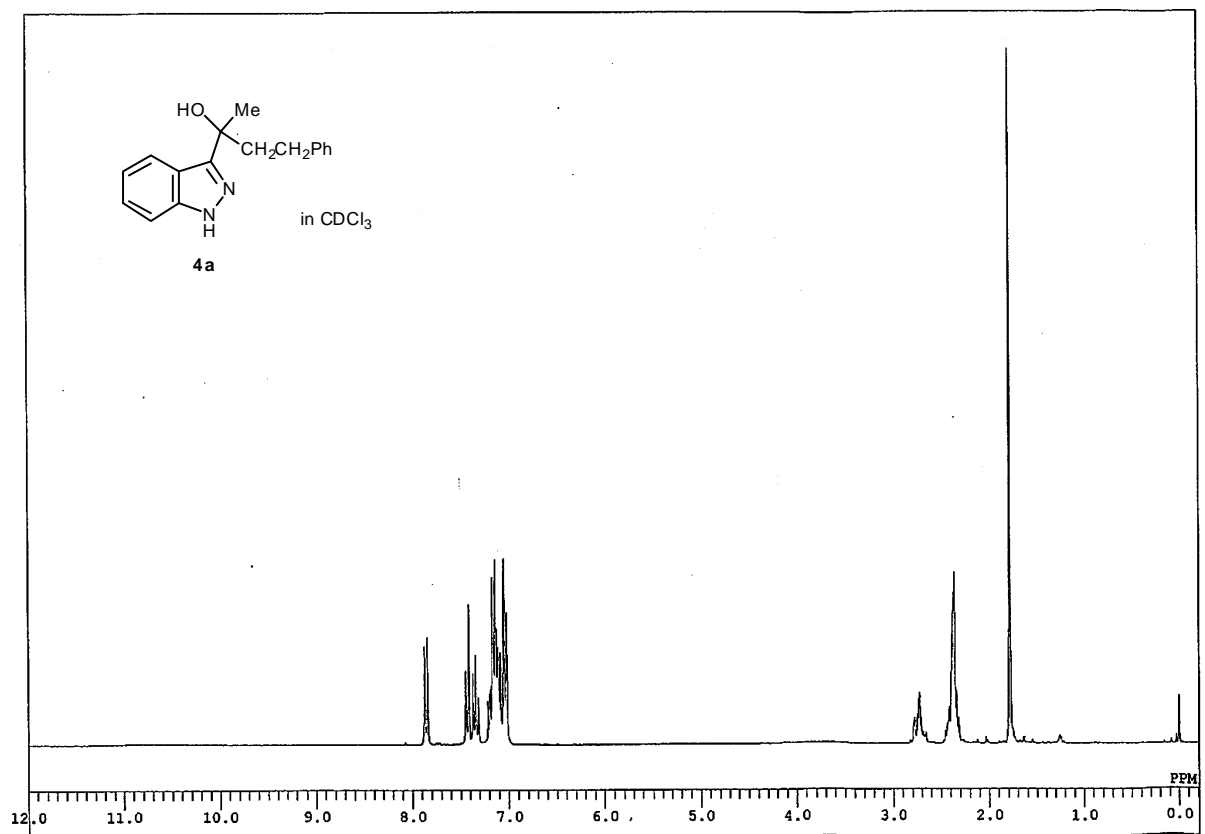
Yoshiyuki Hari,^{*a} Ryosuke Sone^b and Toyohiko Aoyama^{*b}

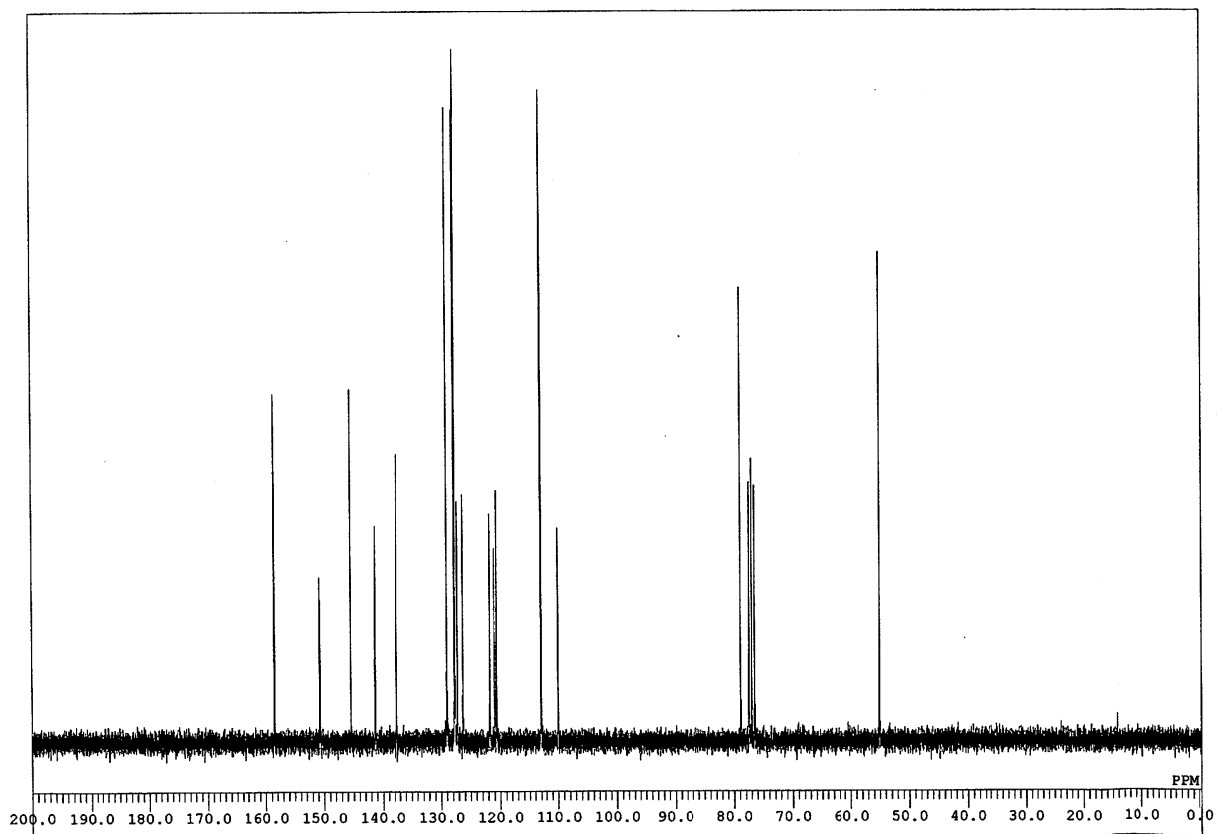
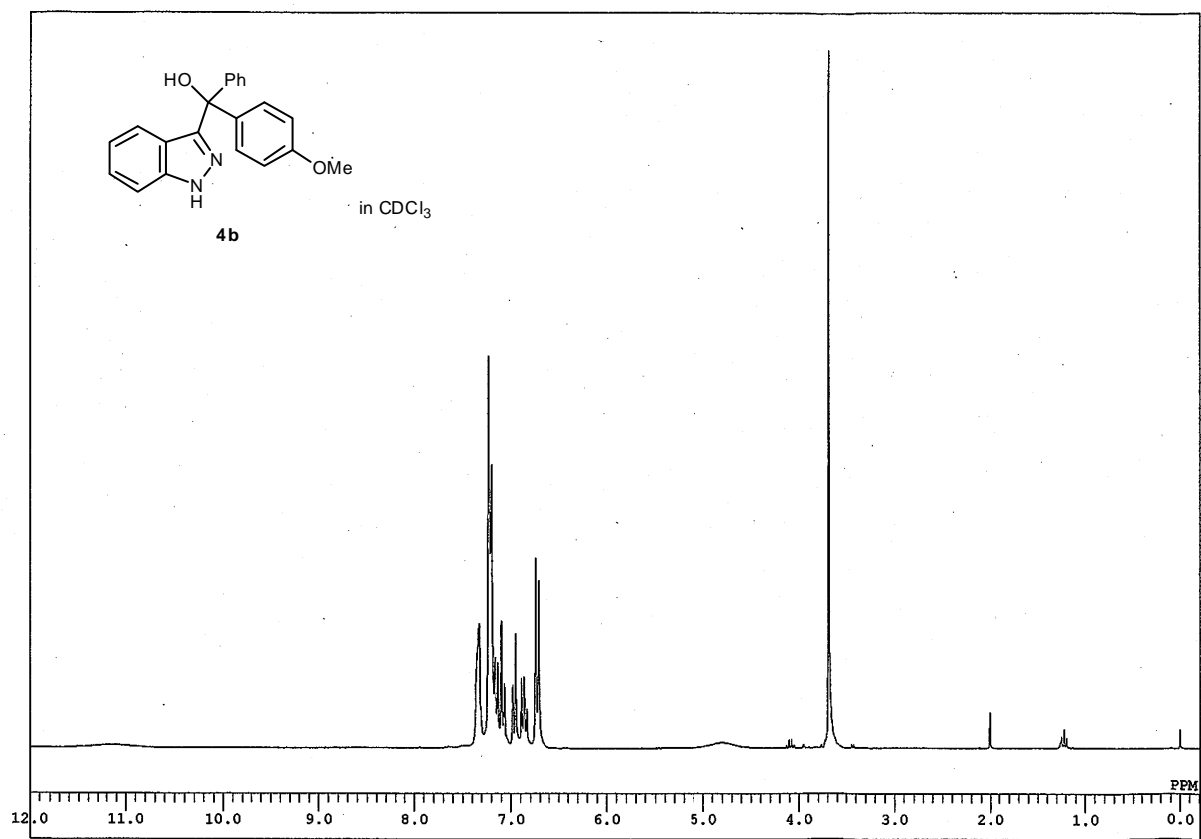
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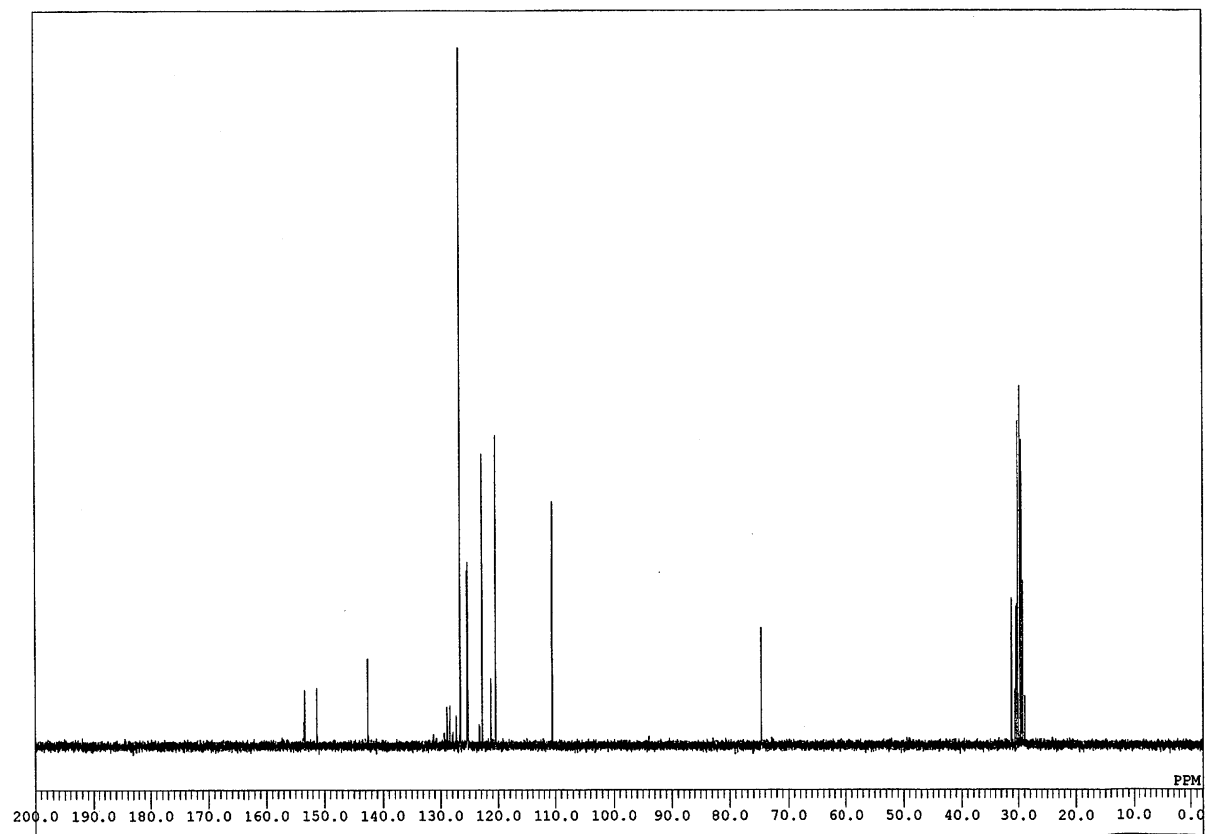
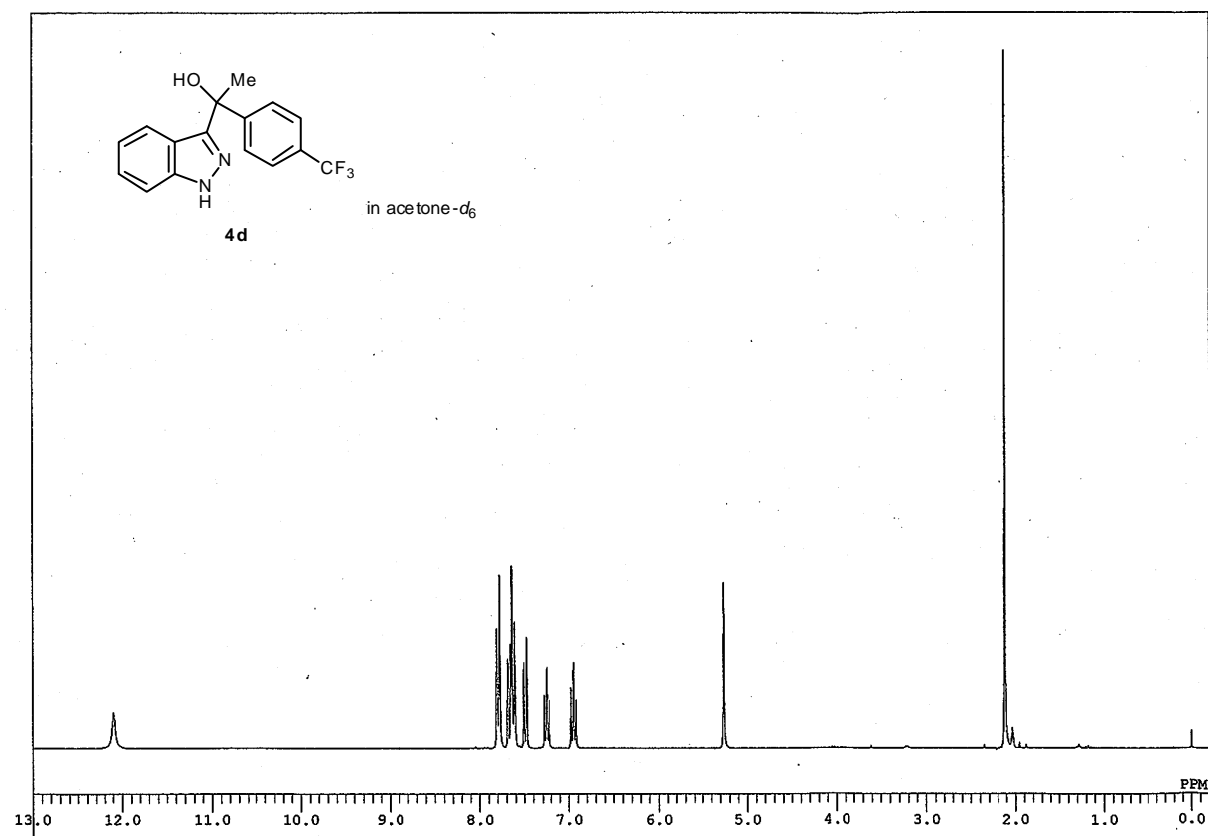
^b*Graduate School of Pharmaceutical Sciences, Nagoya City University, 3-1 Tanabe-dori, Mizuho, Nagoya 467-8603, Japan.*

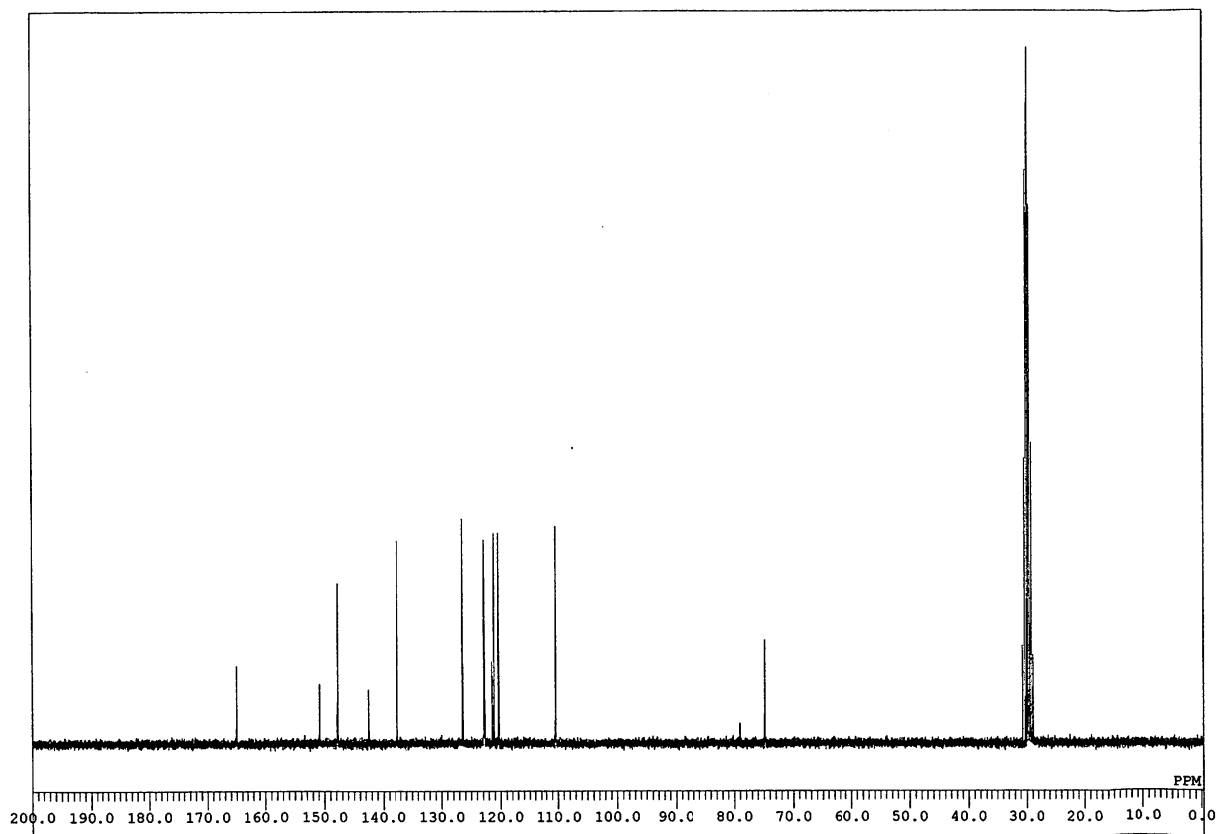
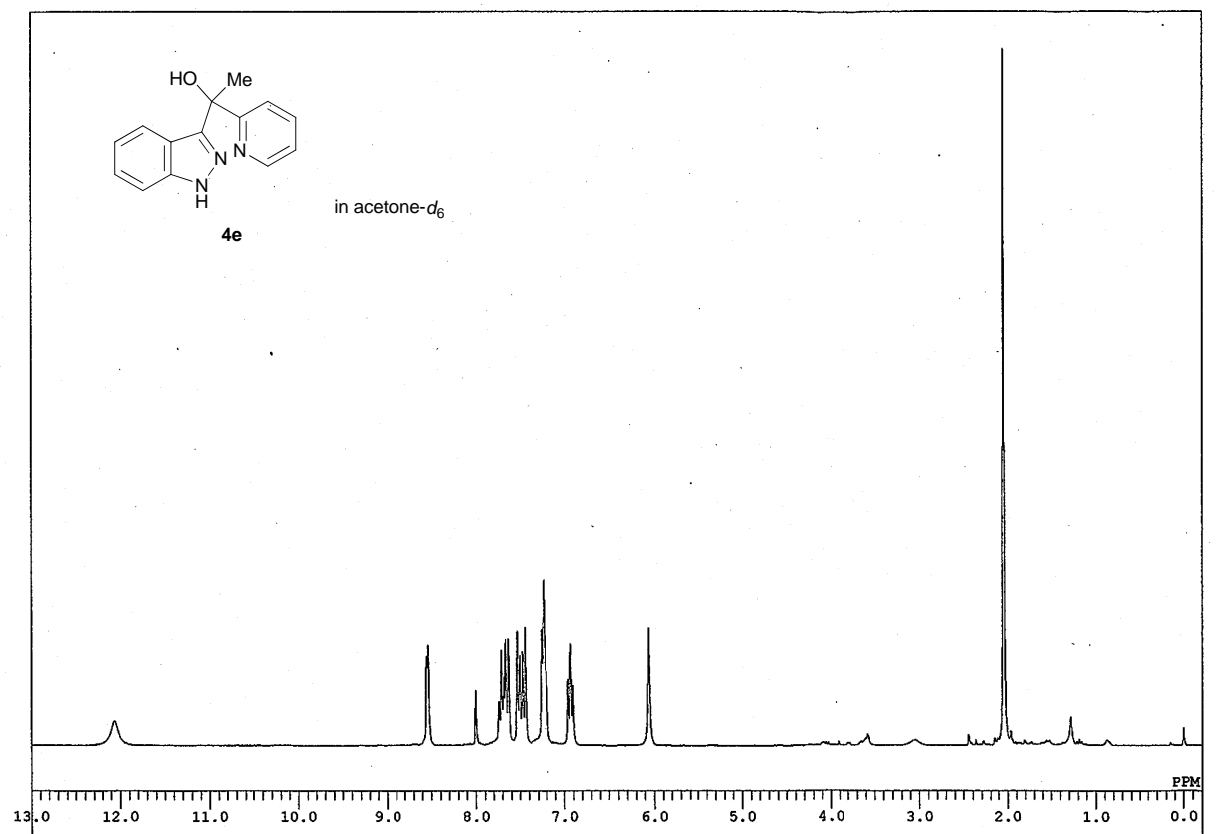
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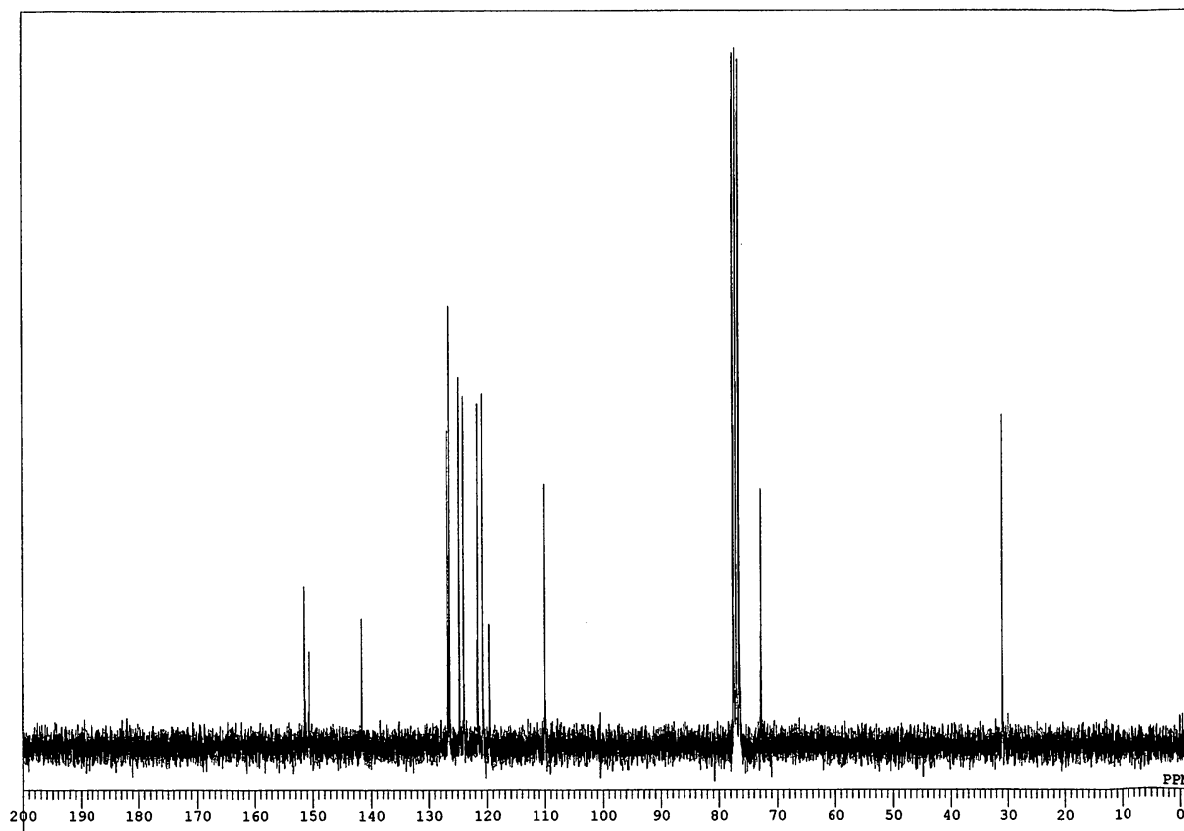
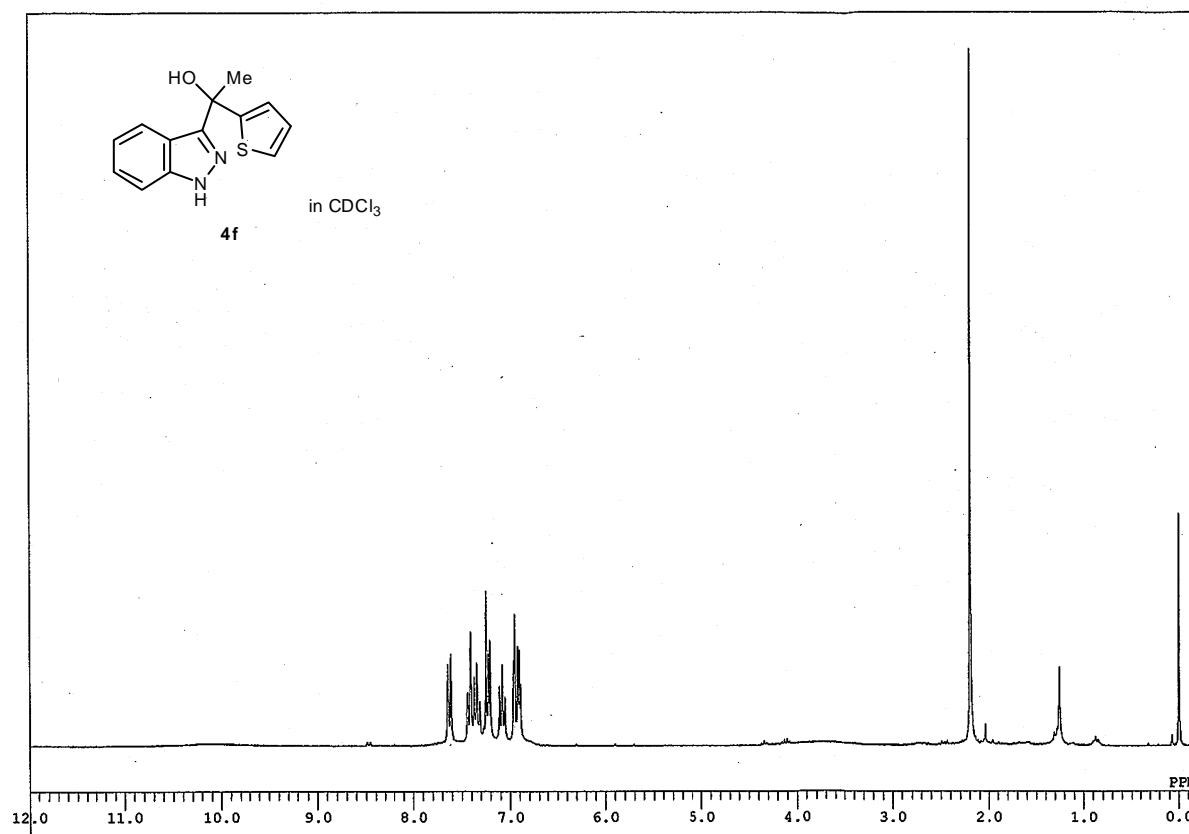
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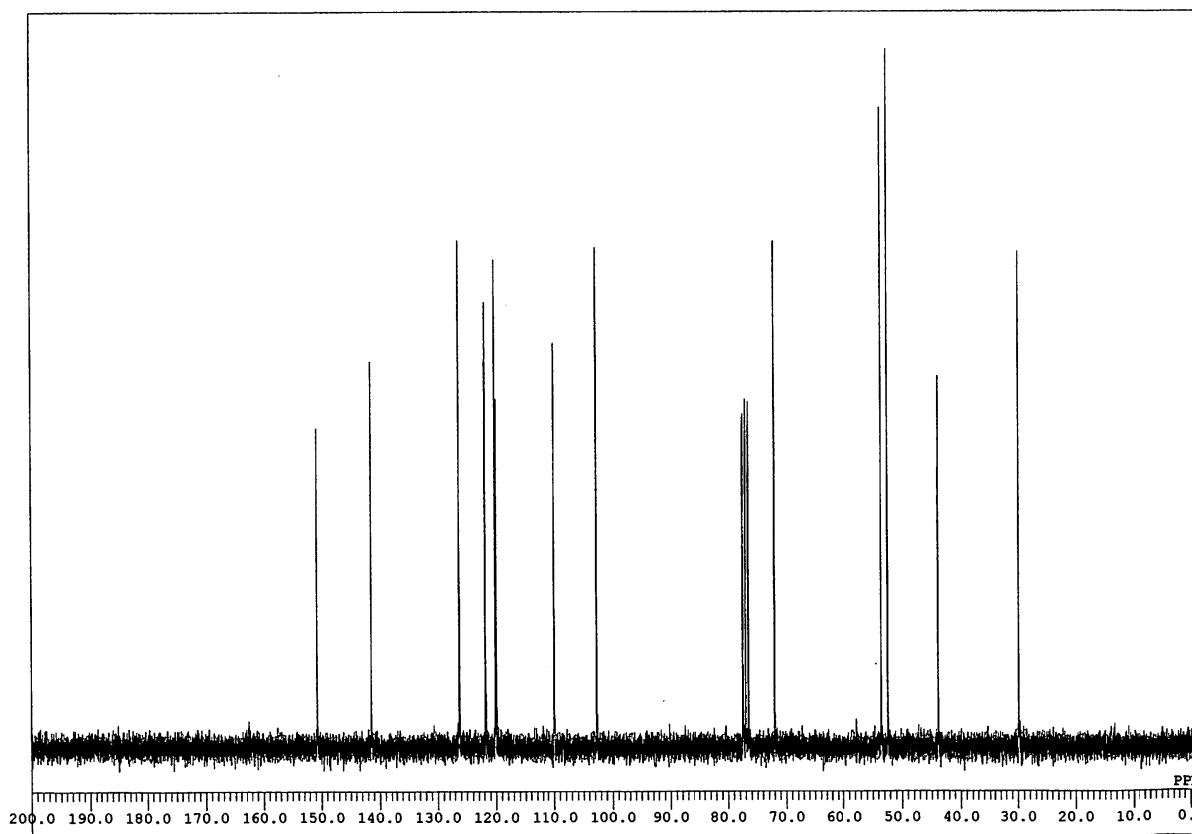
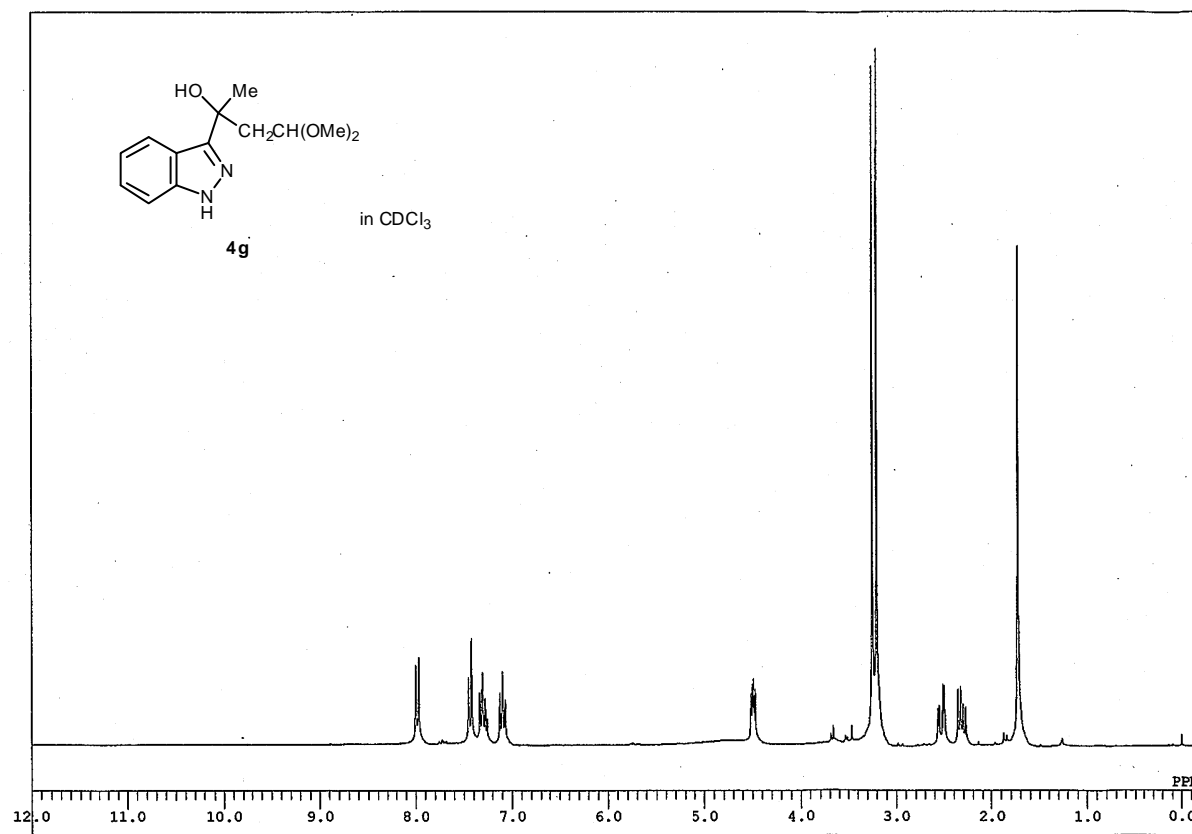


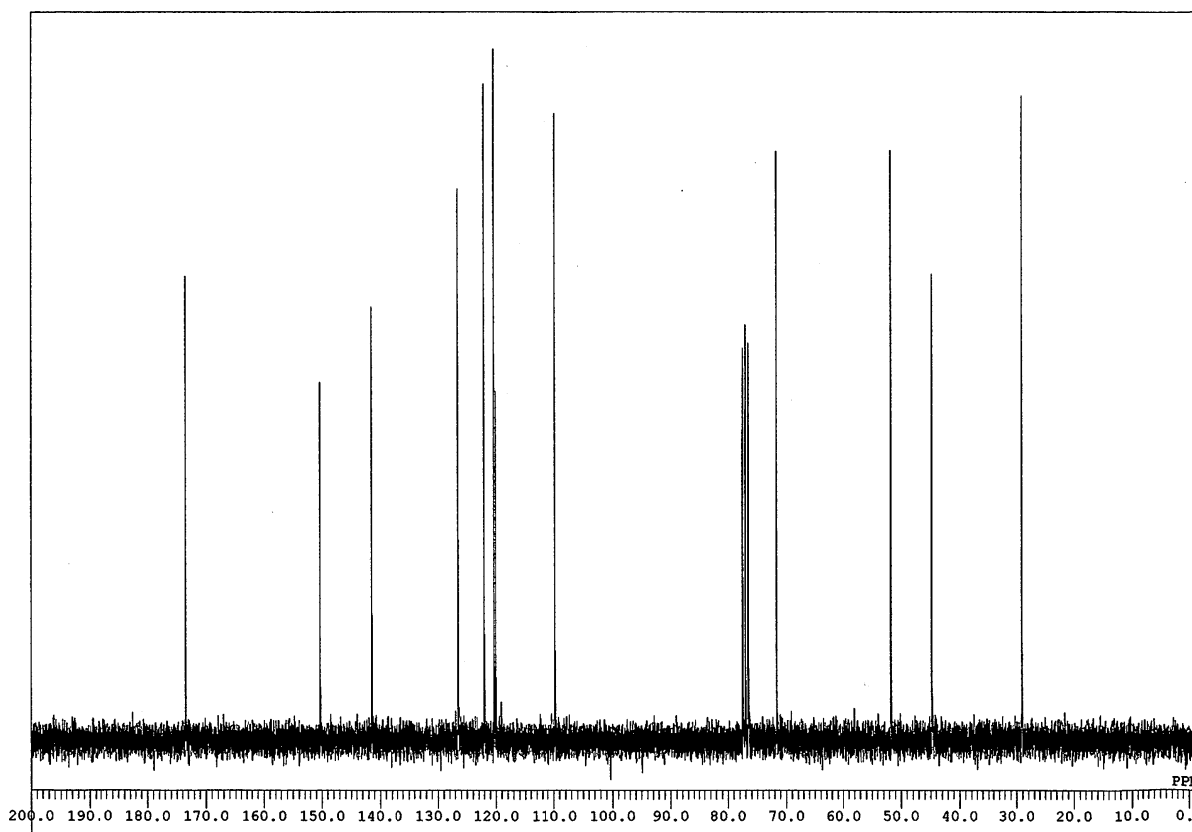
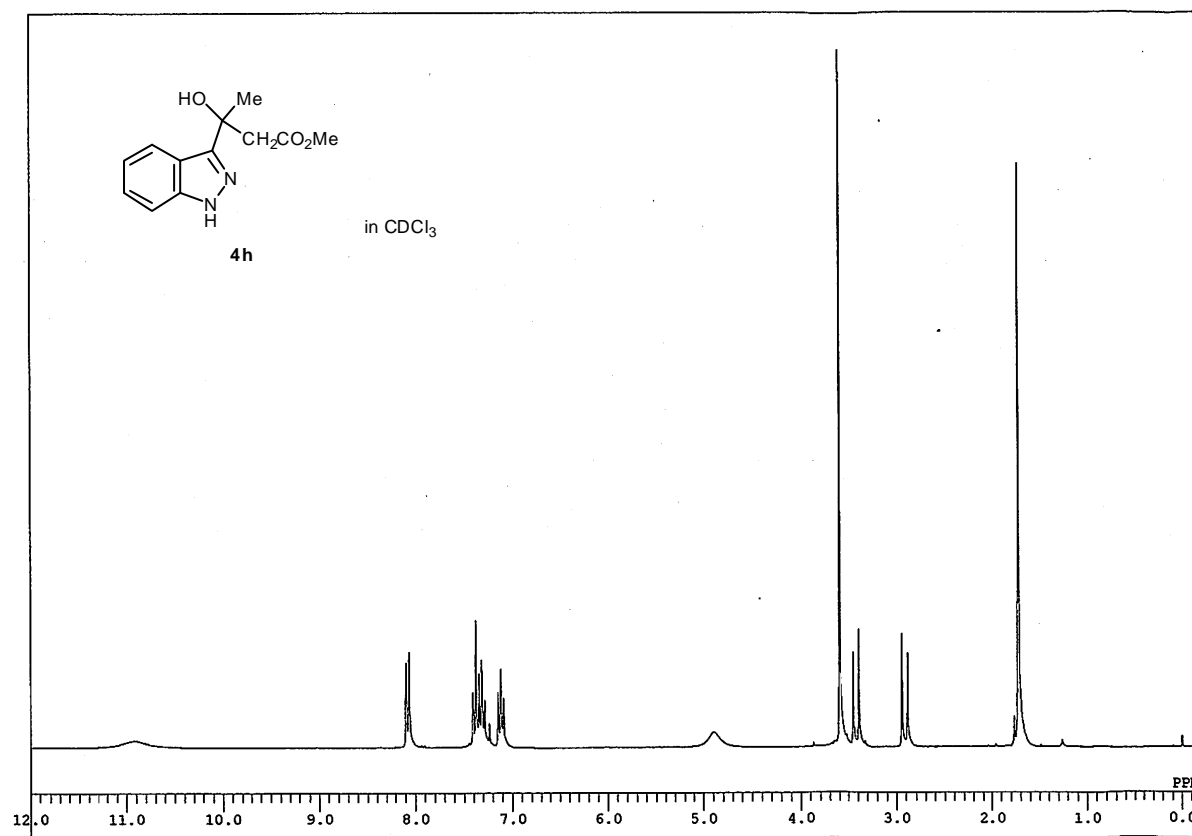


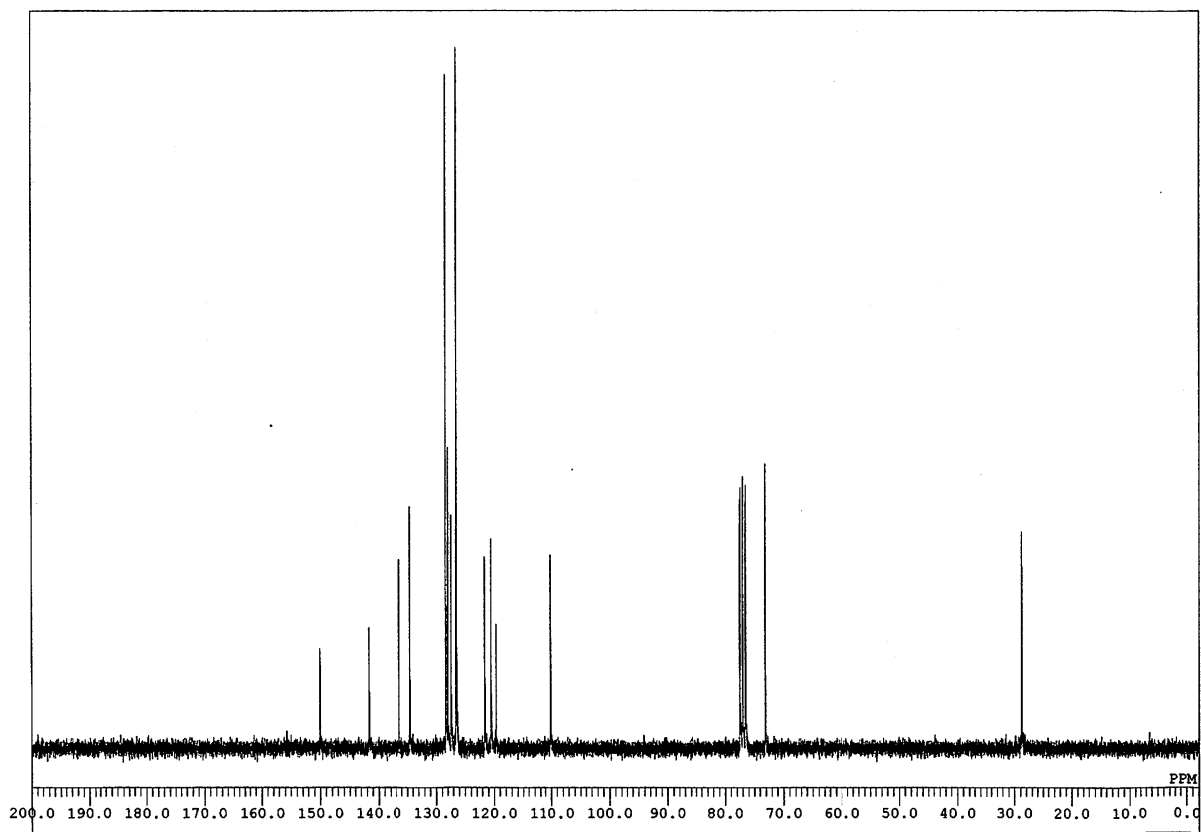
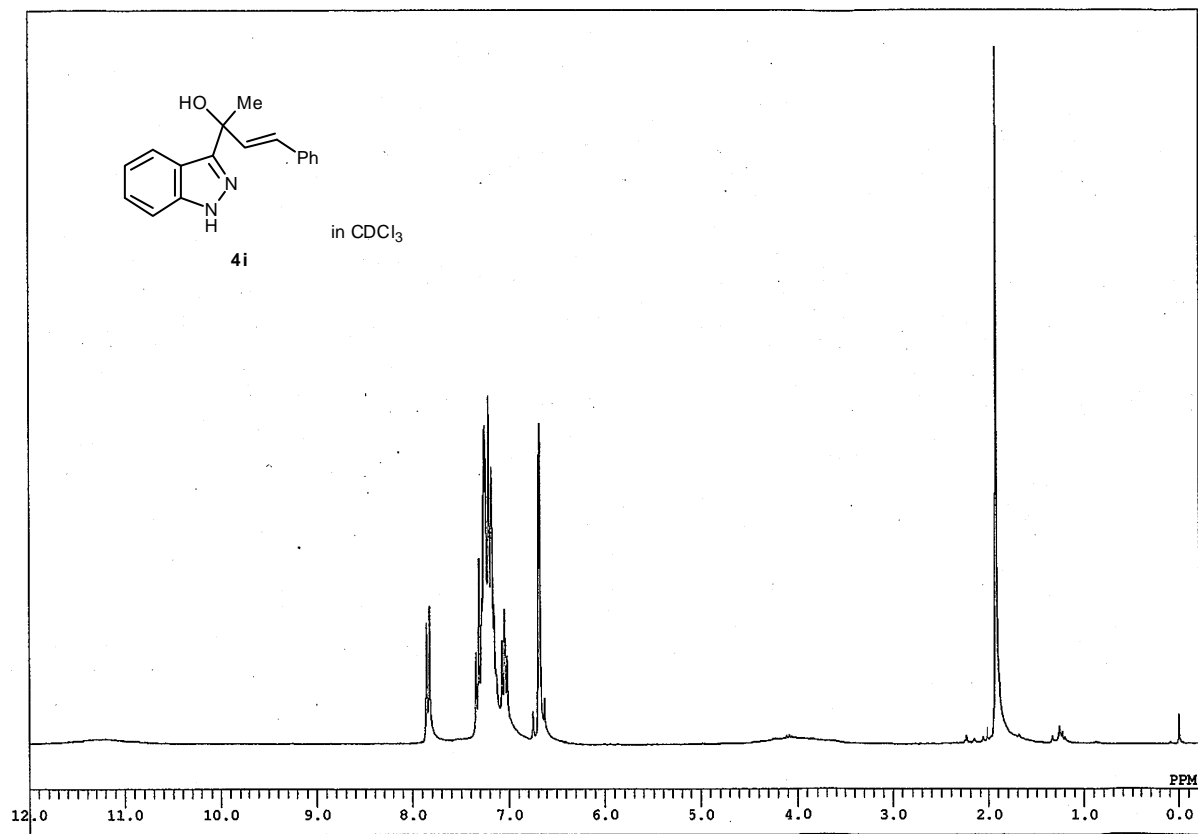


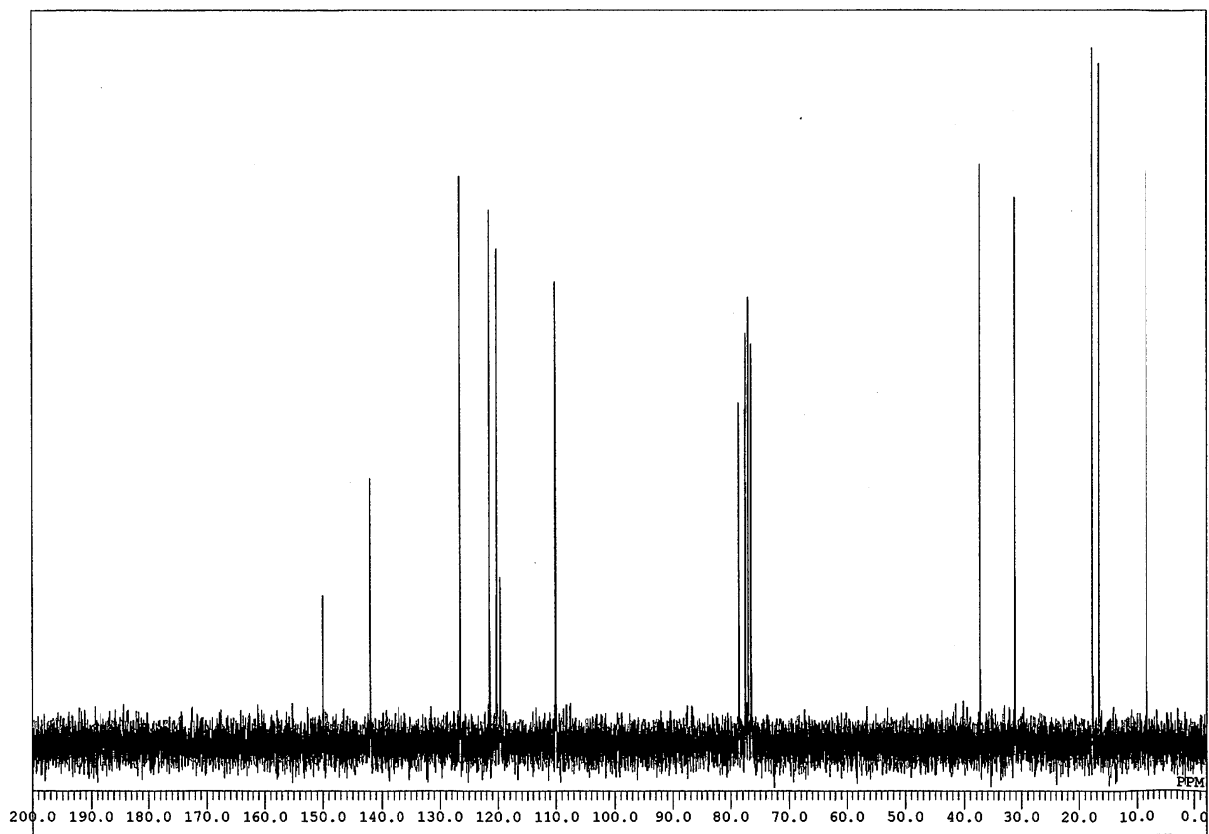
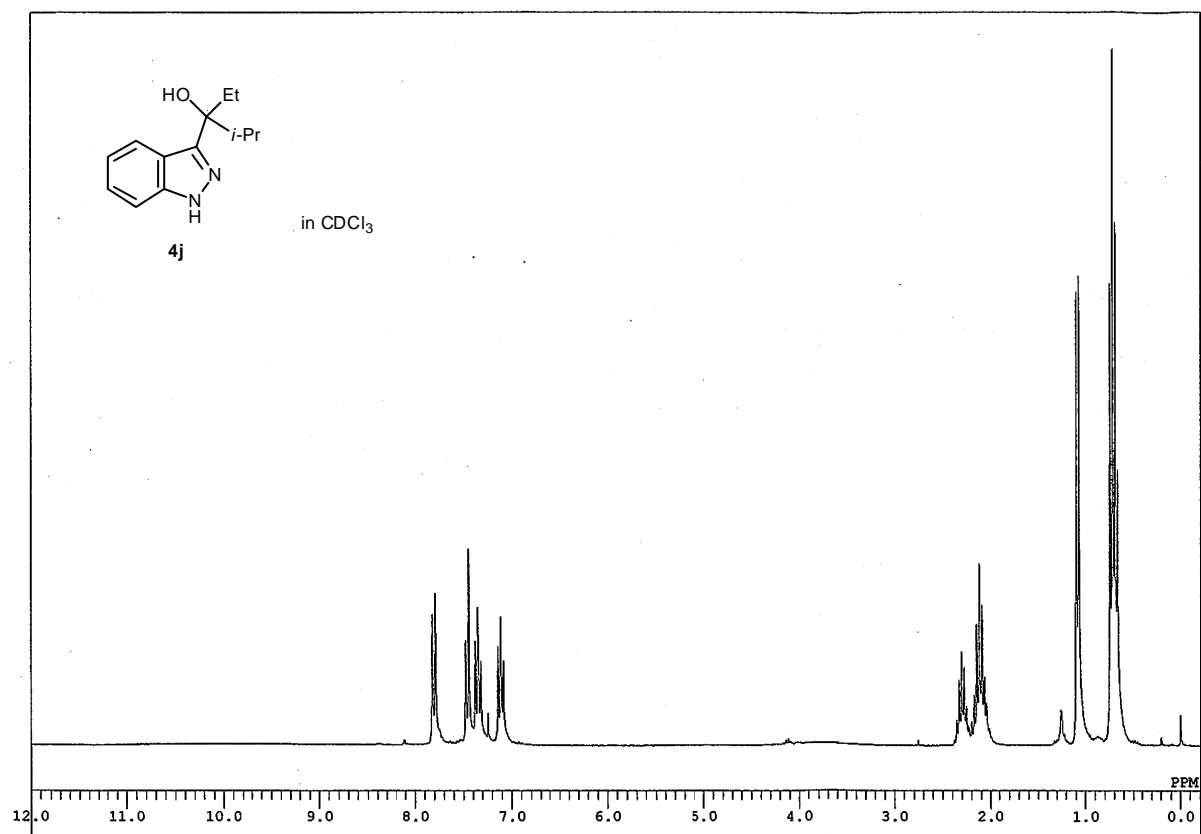


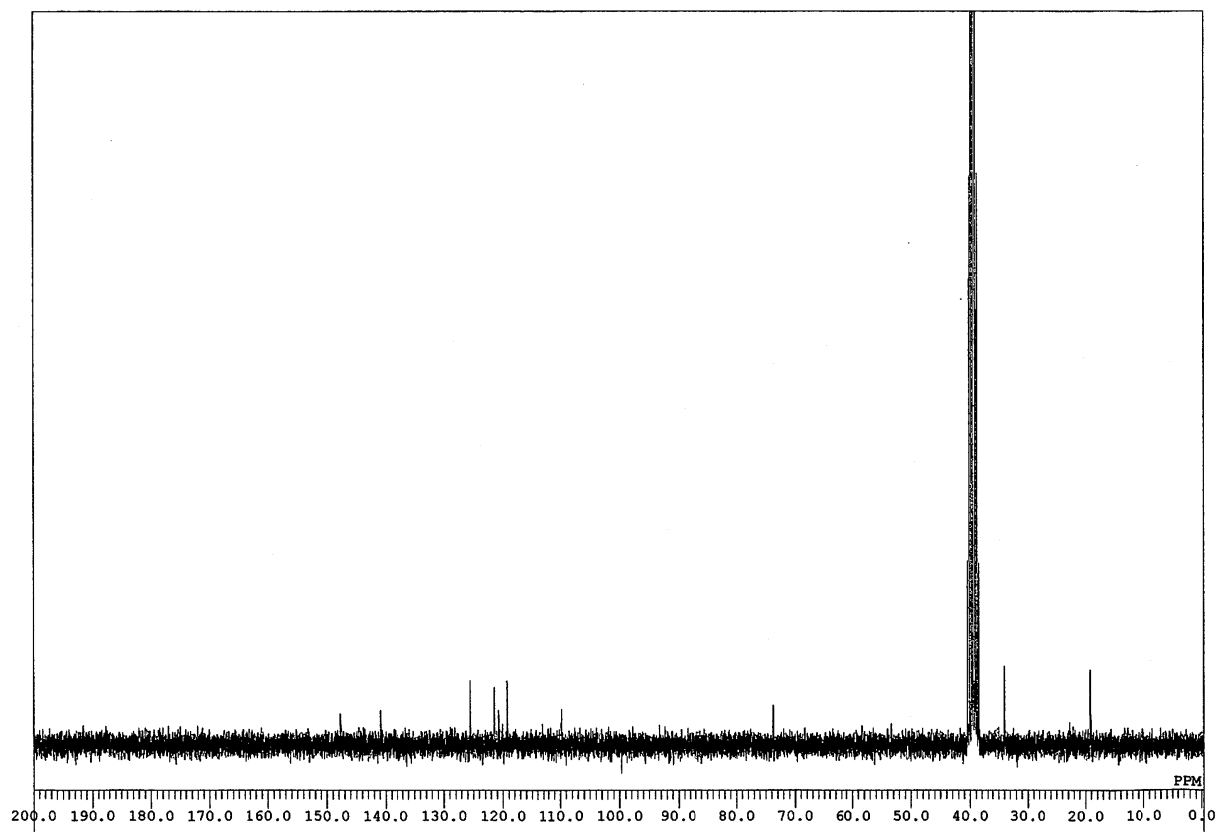
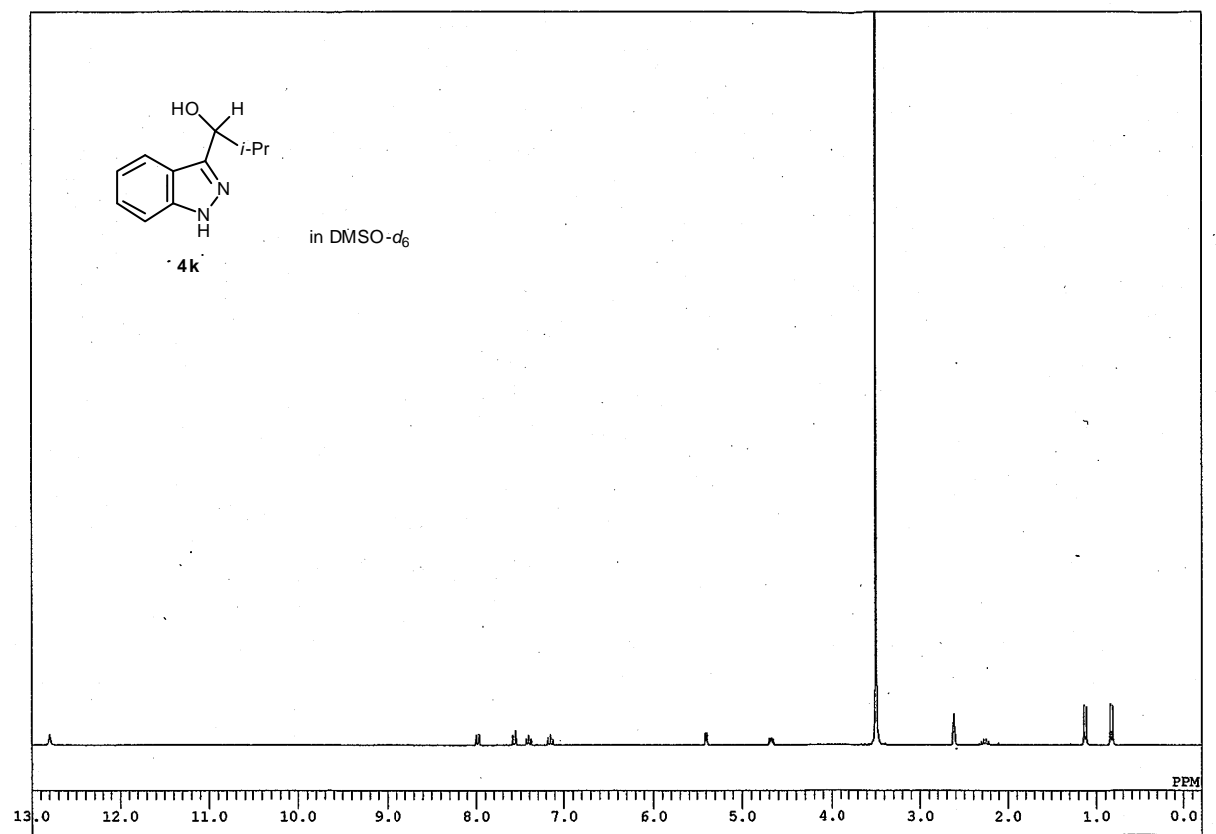


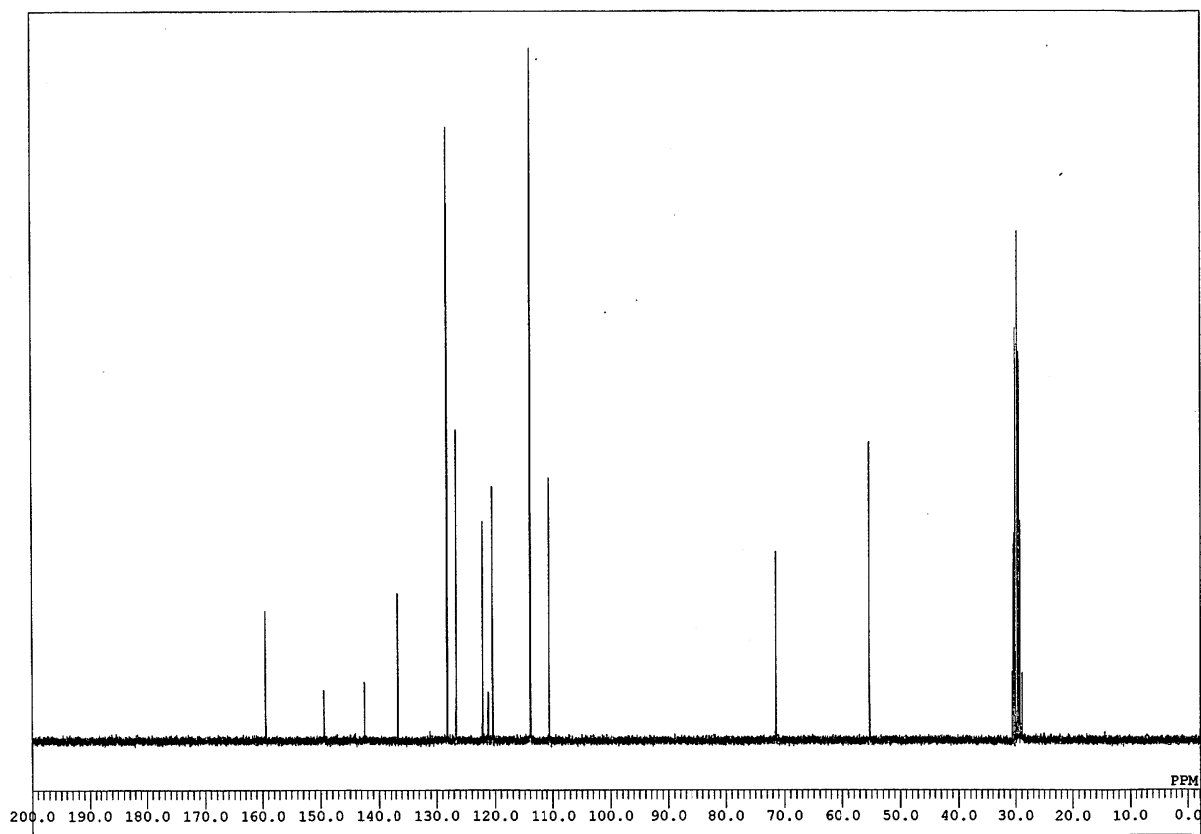
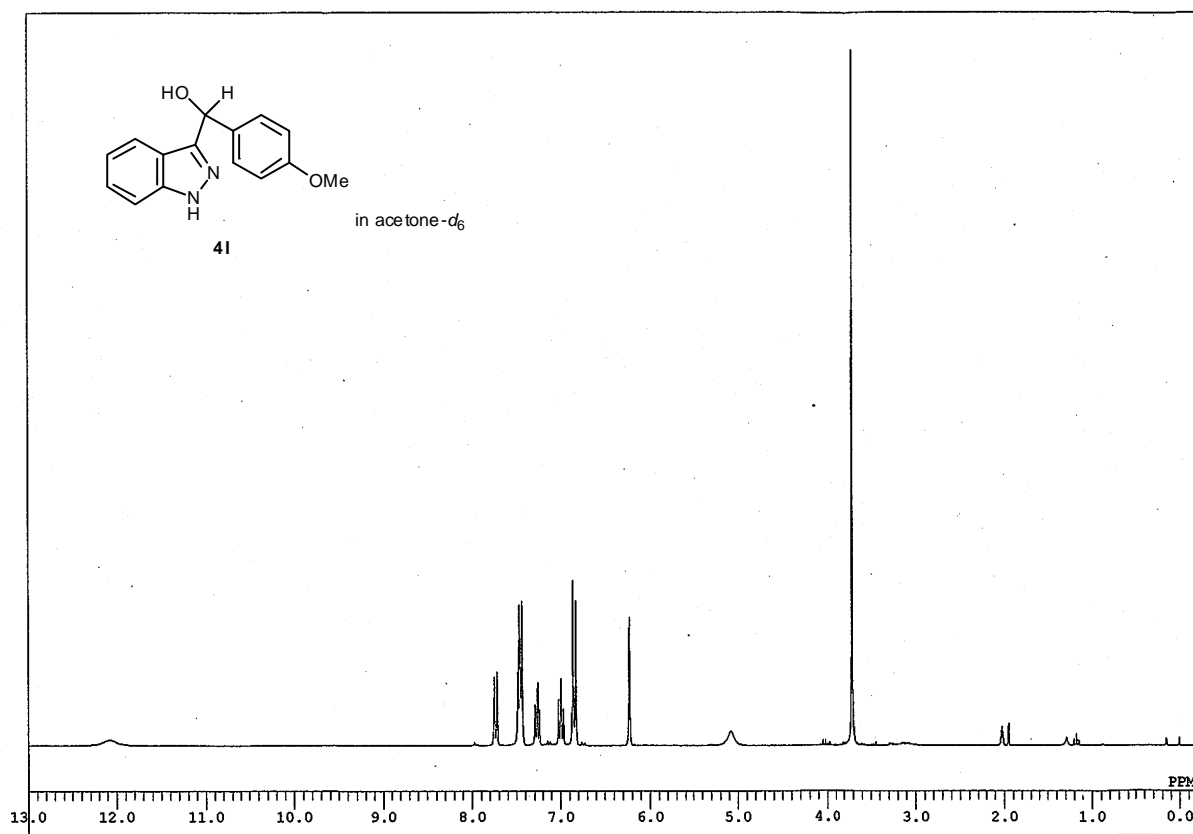


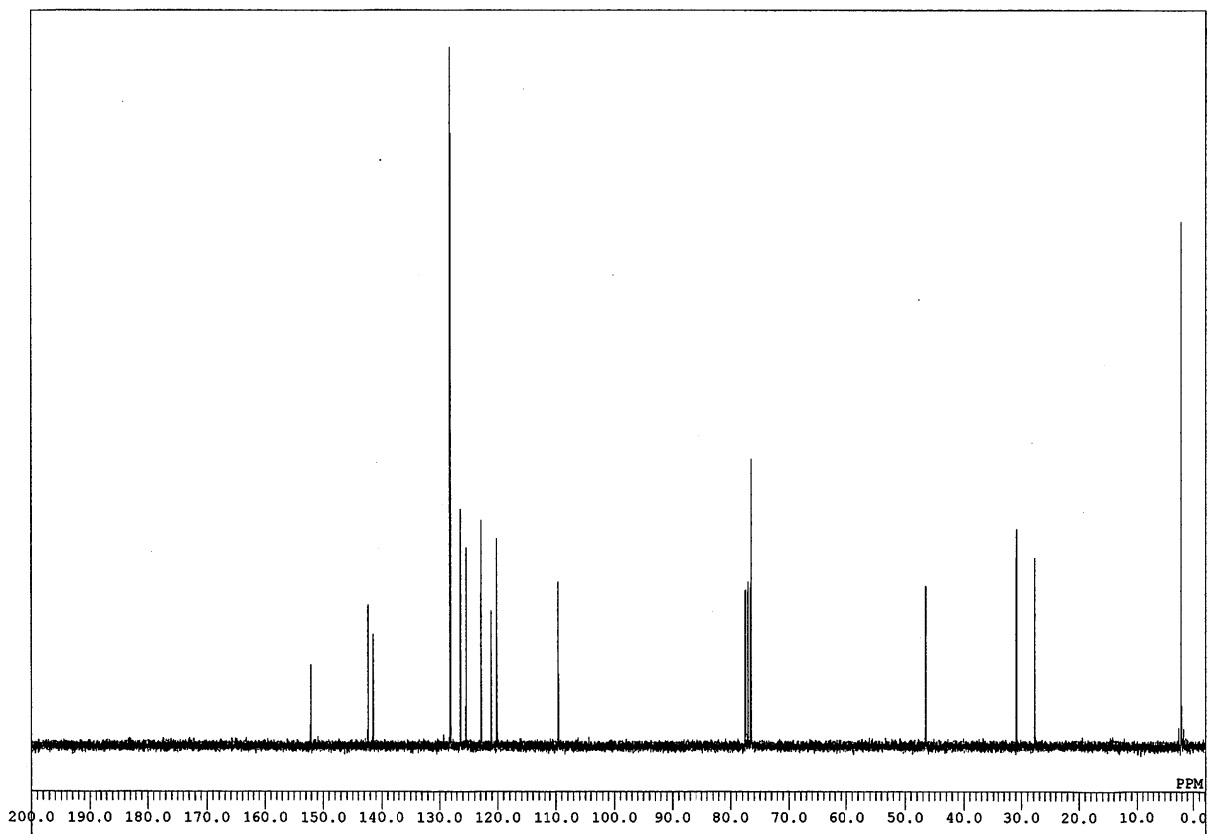
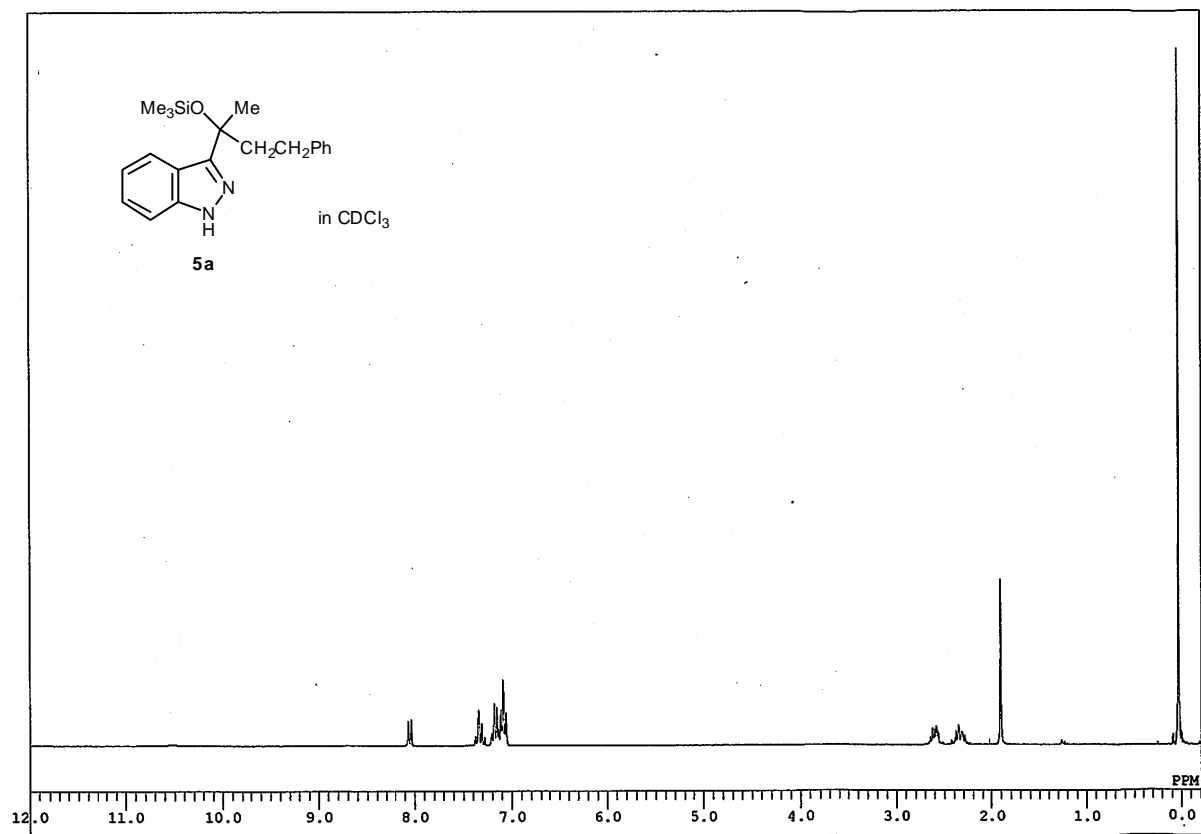


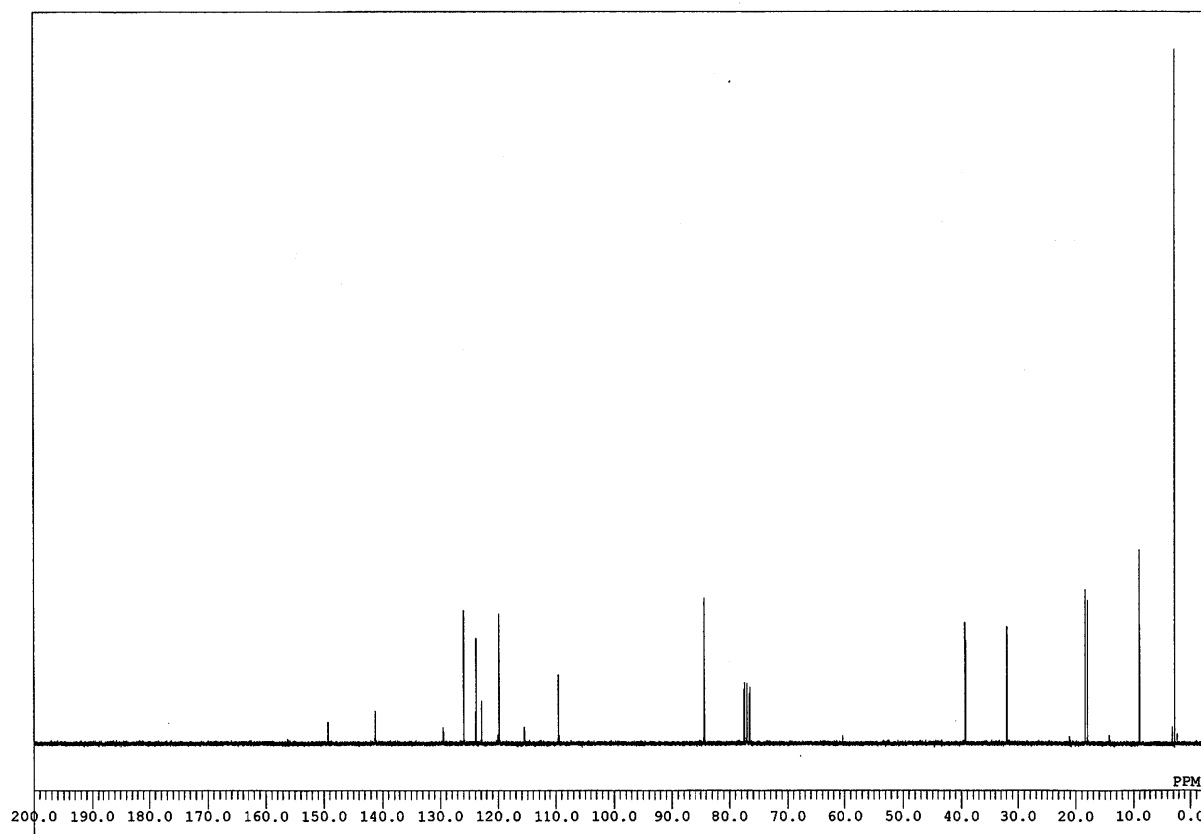
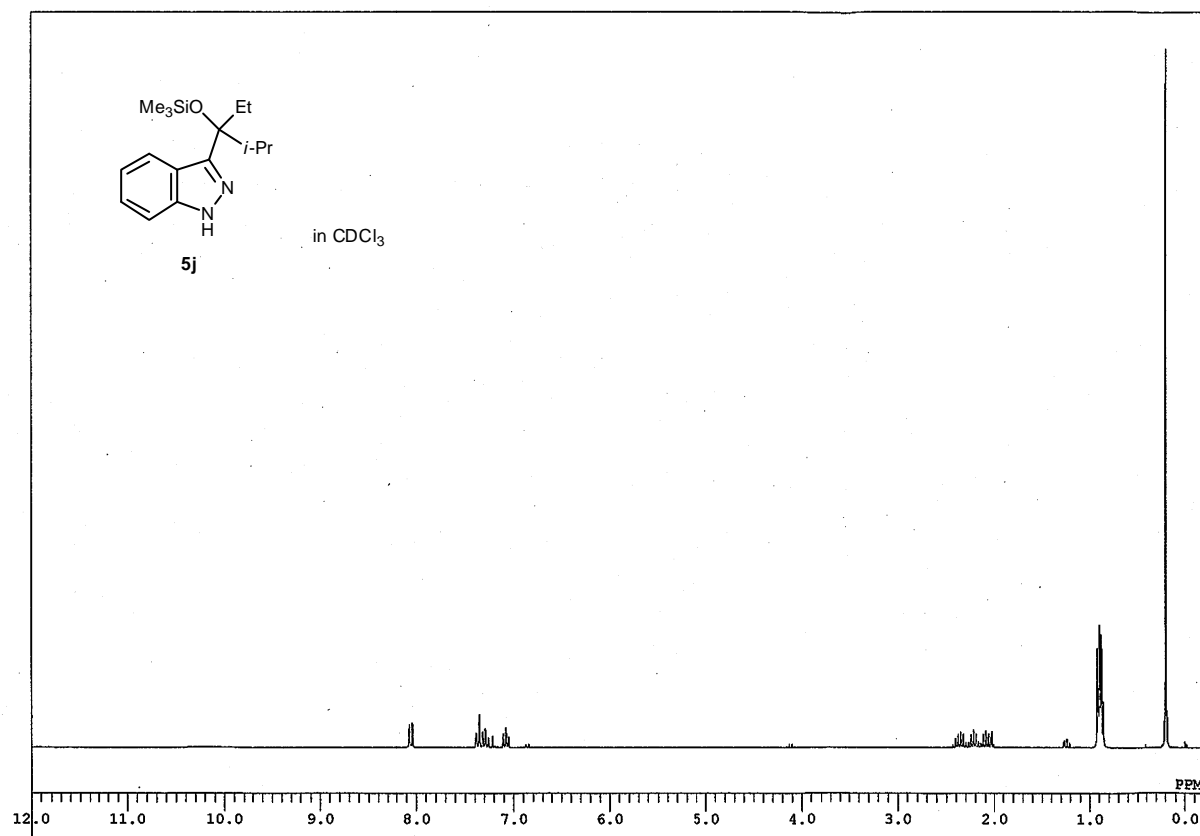


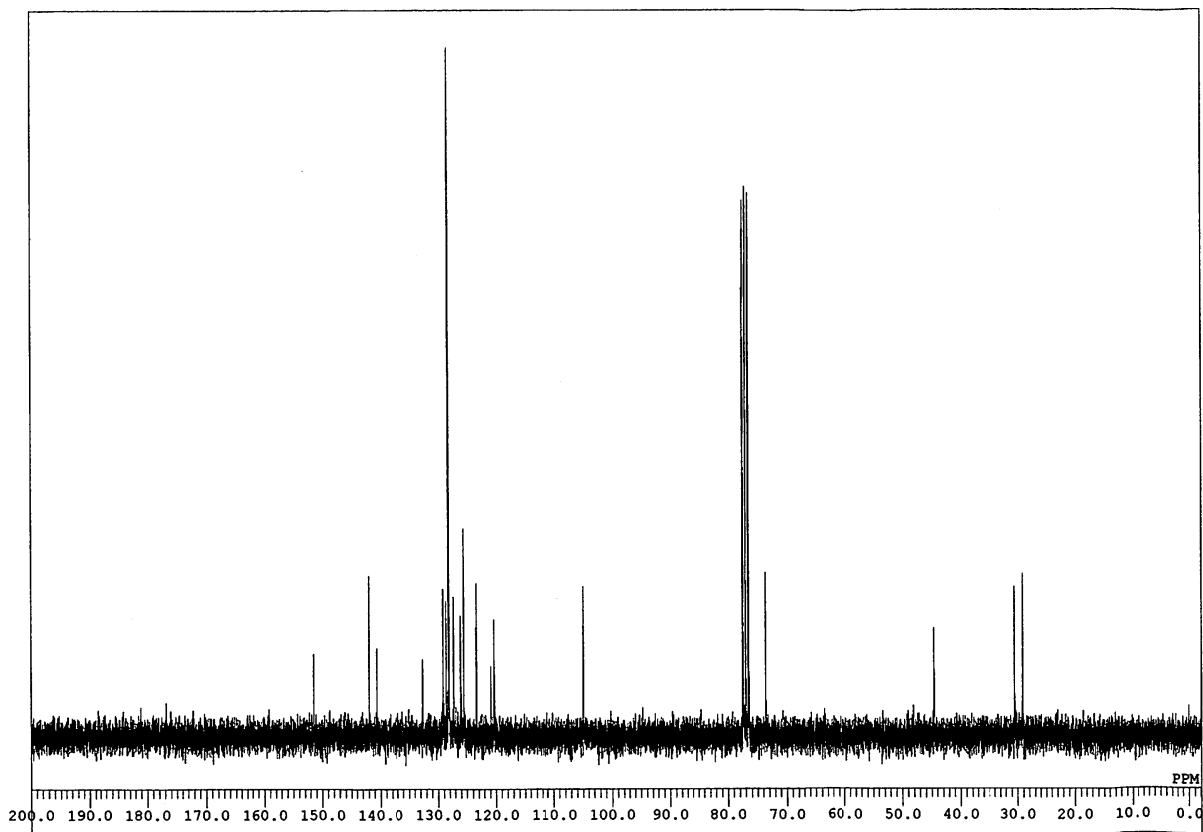
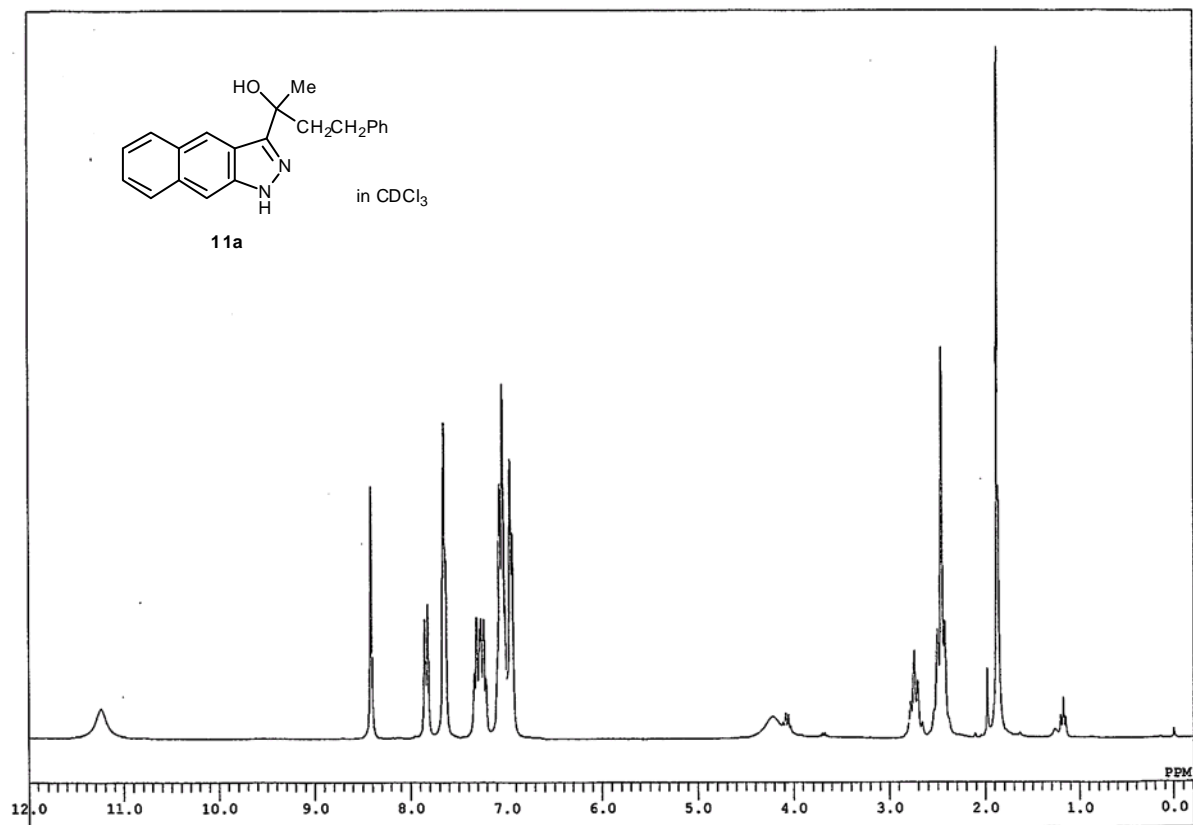


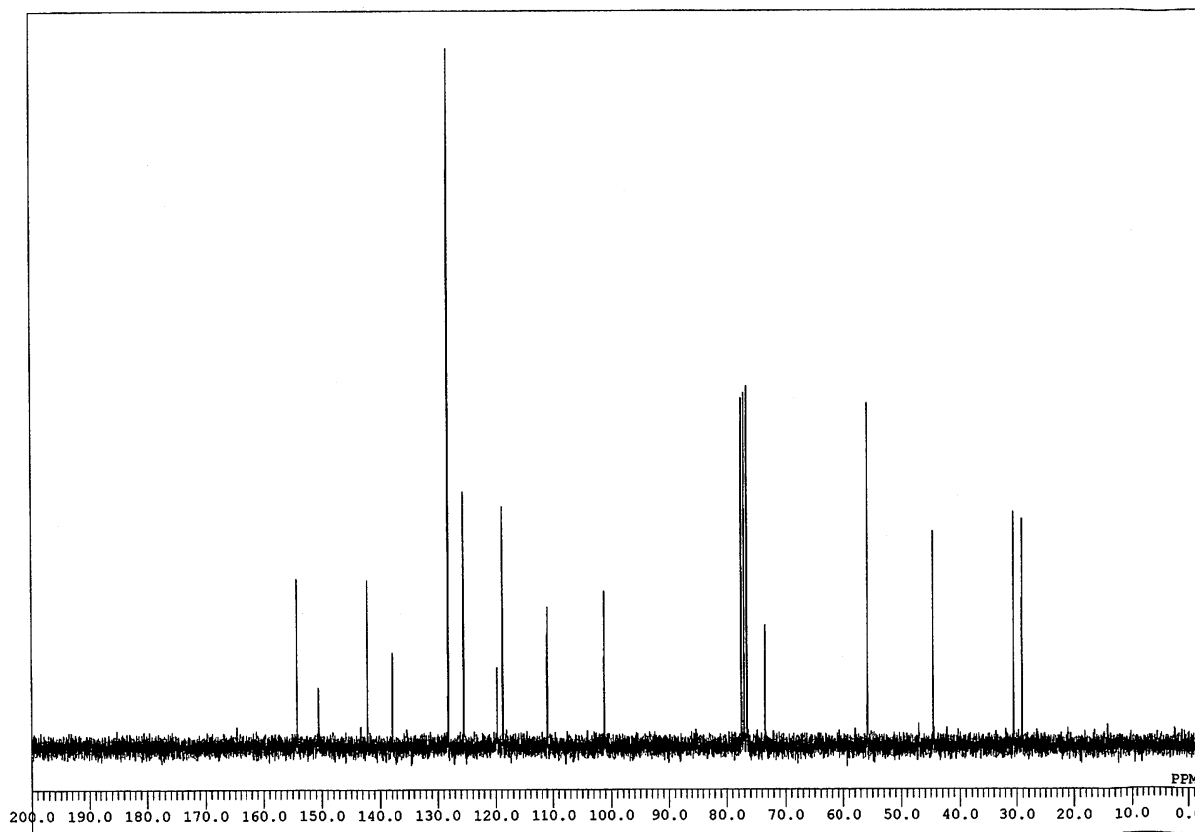
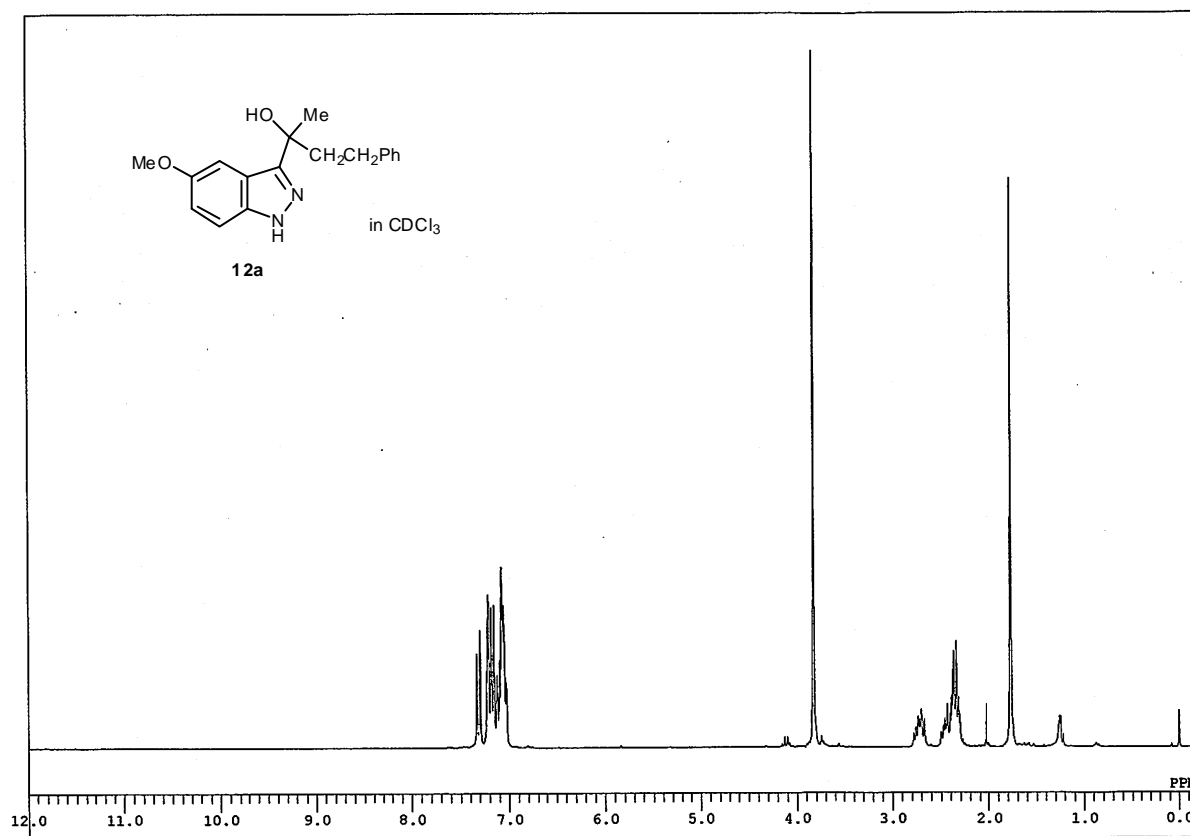


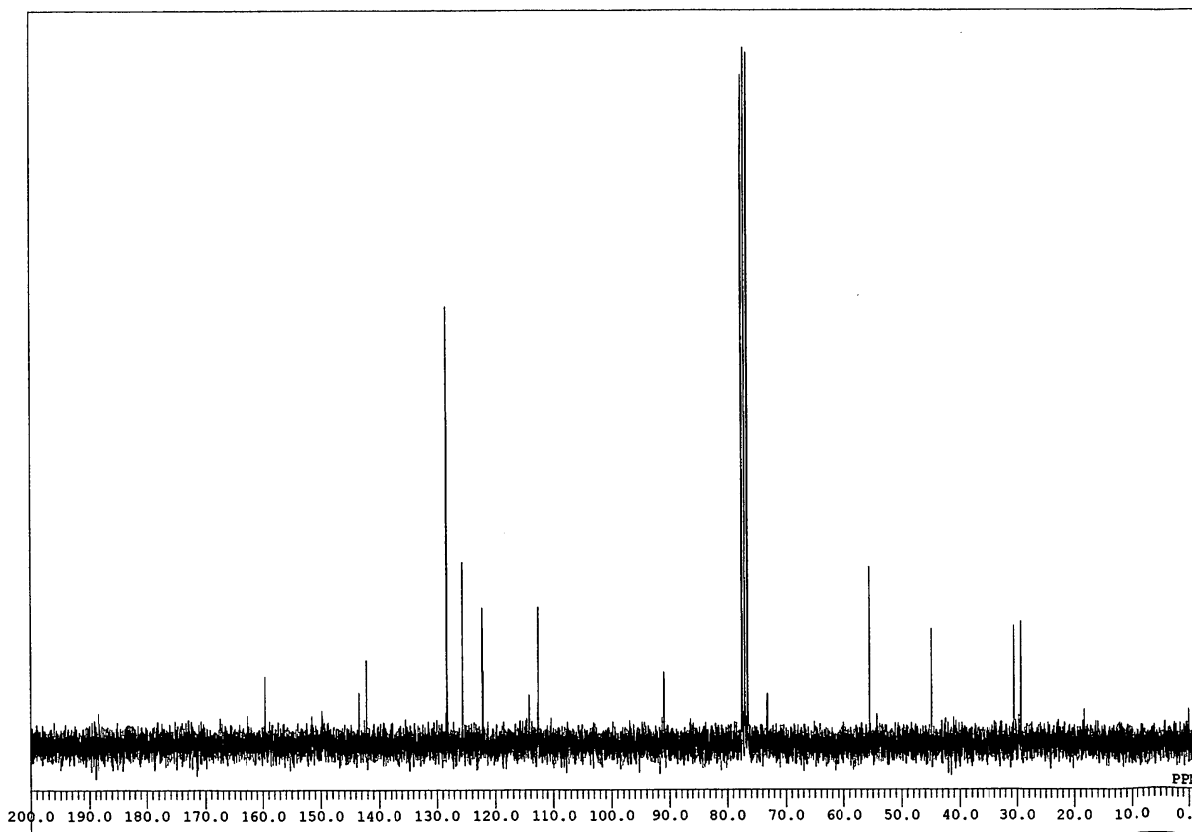
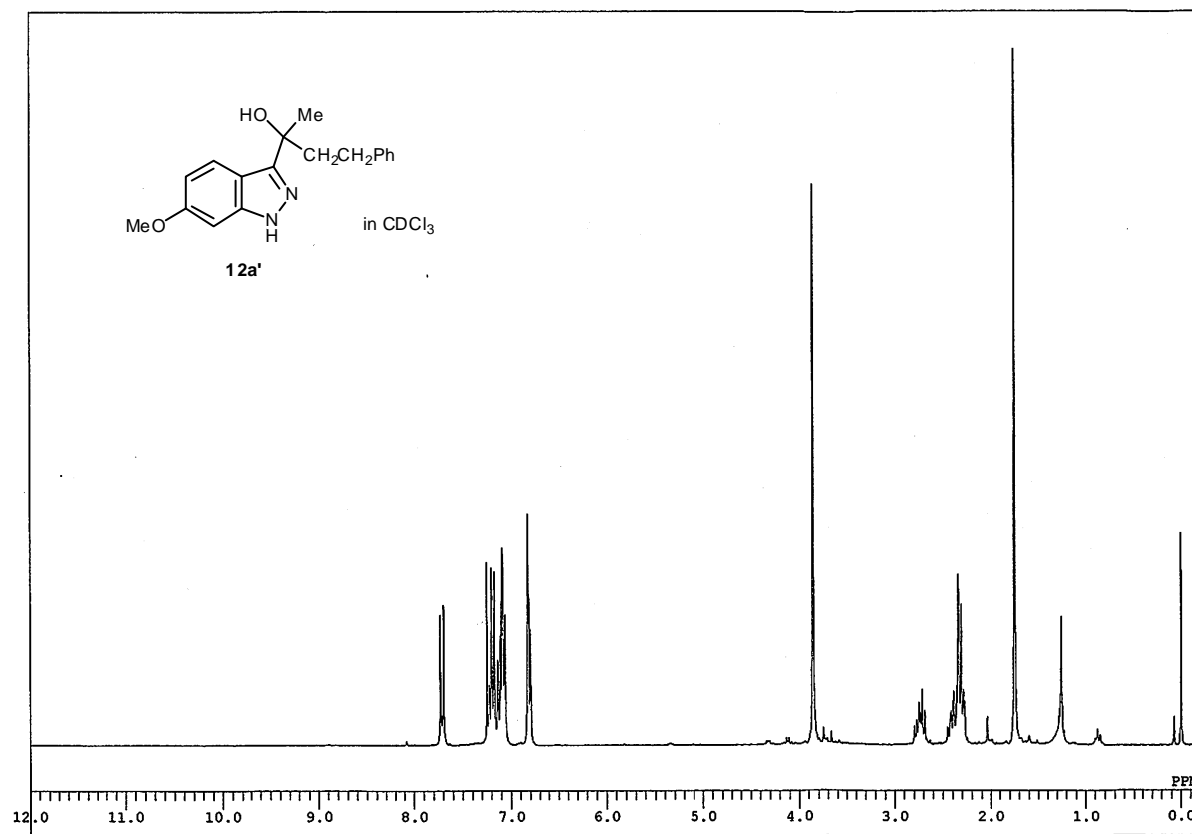


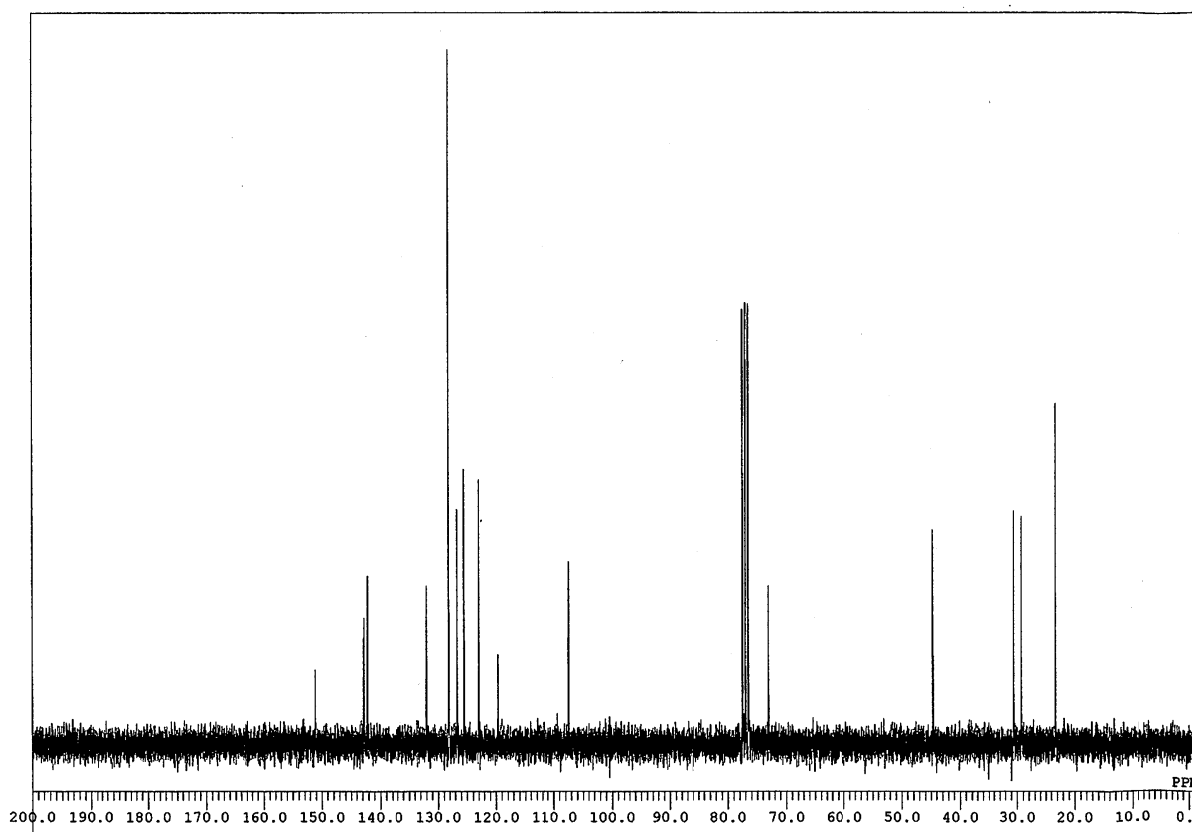
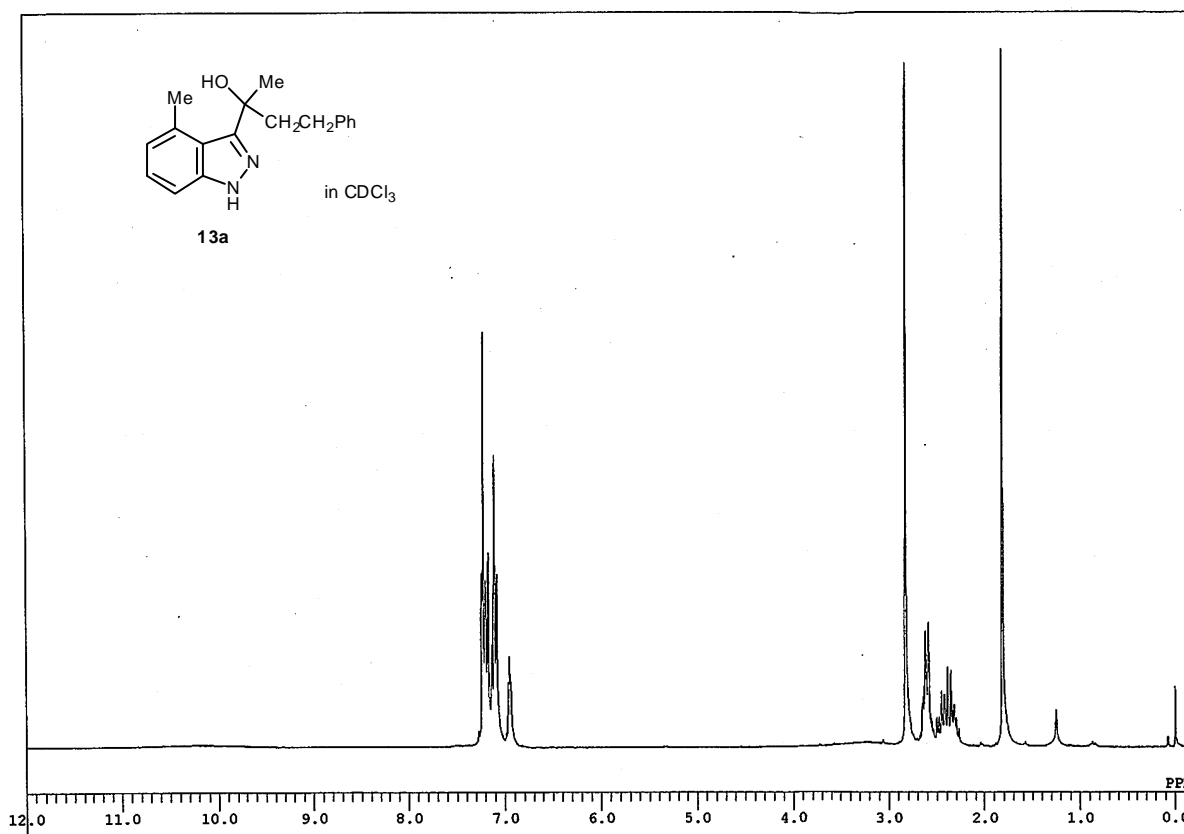


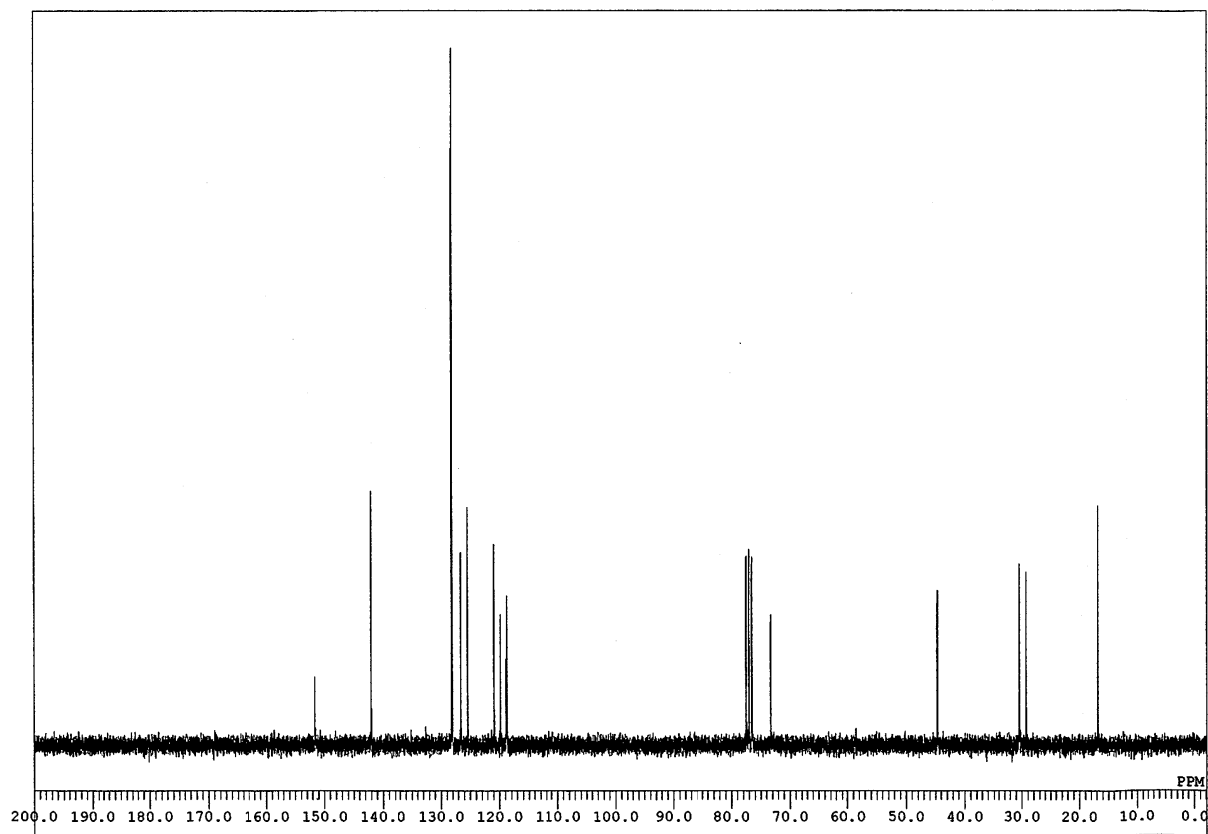
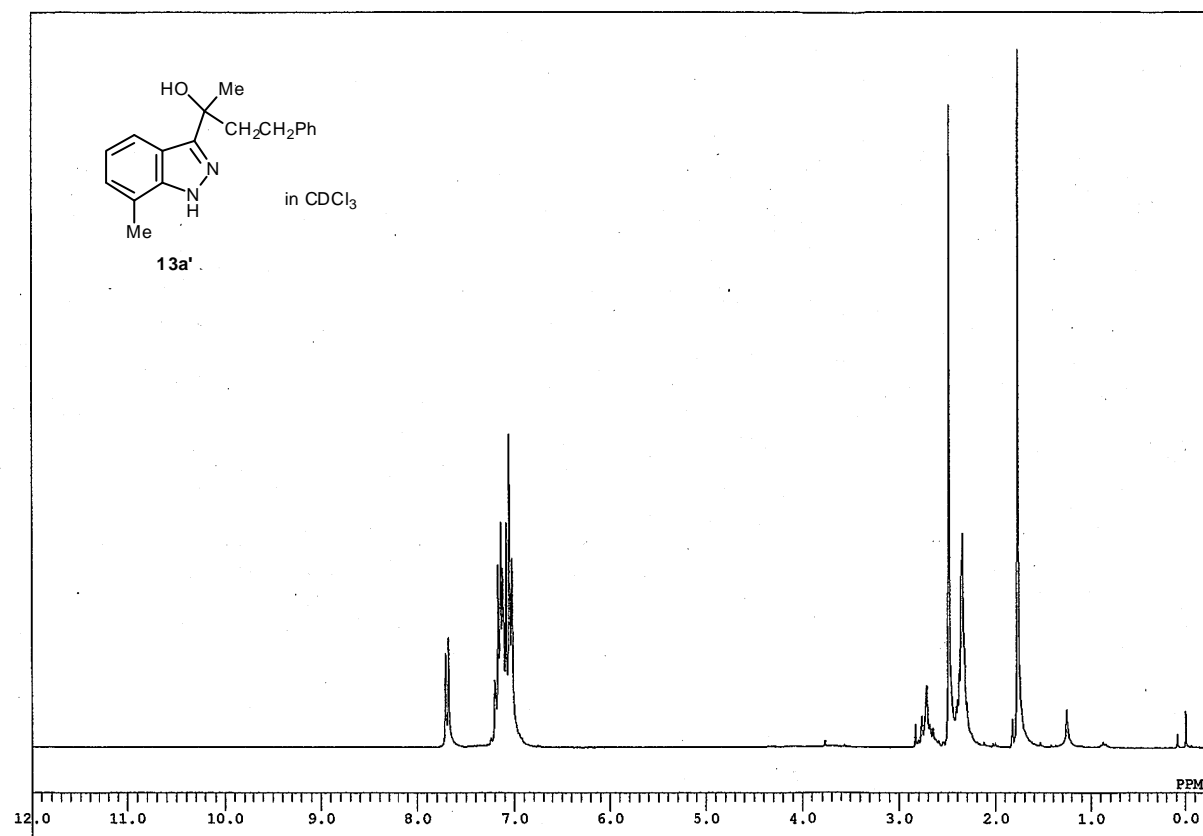


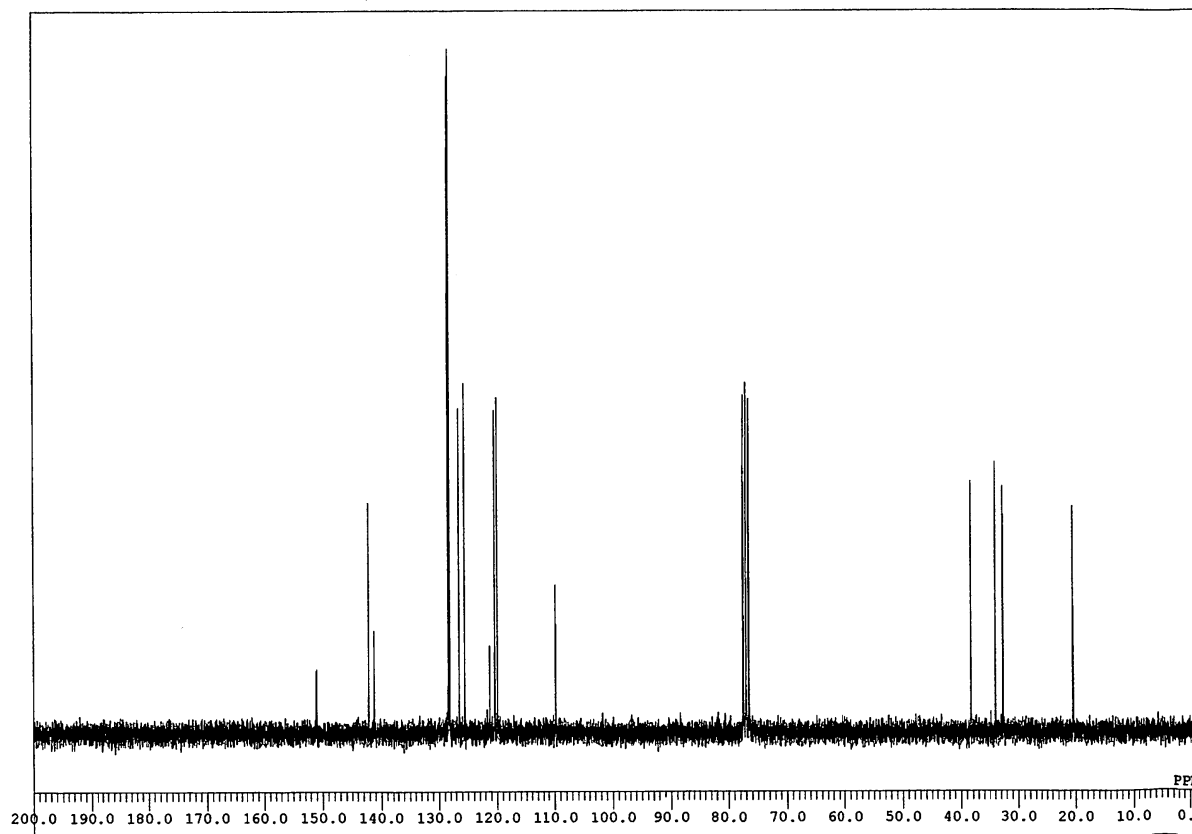
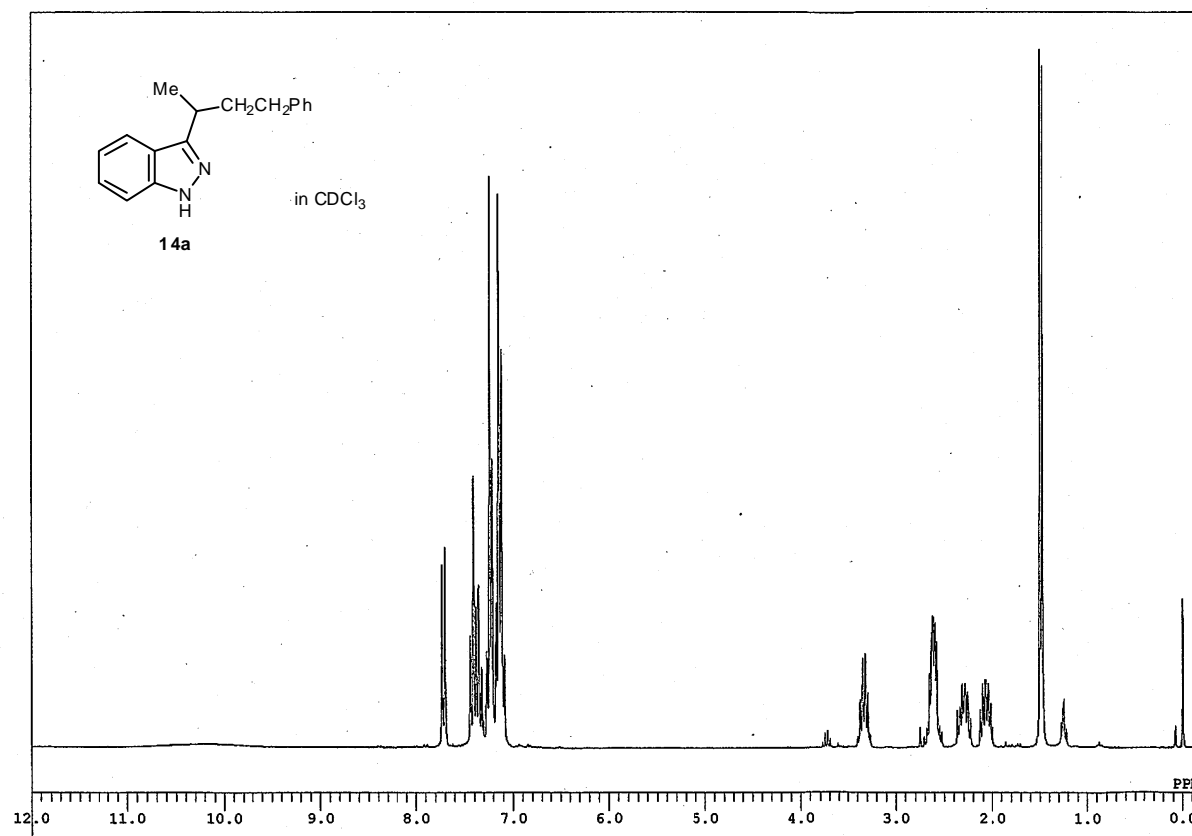


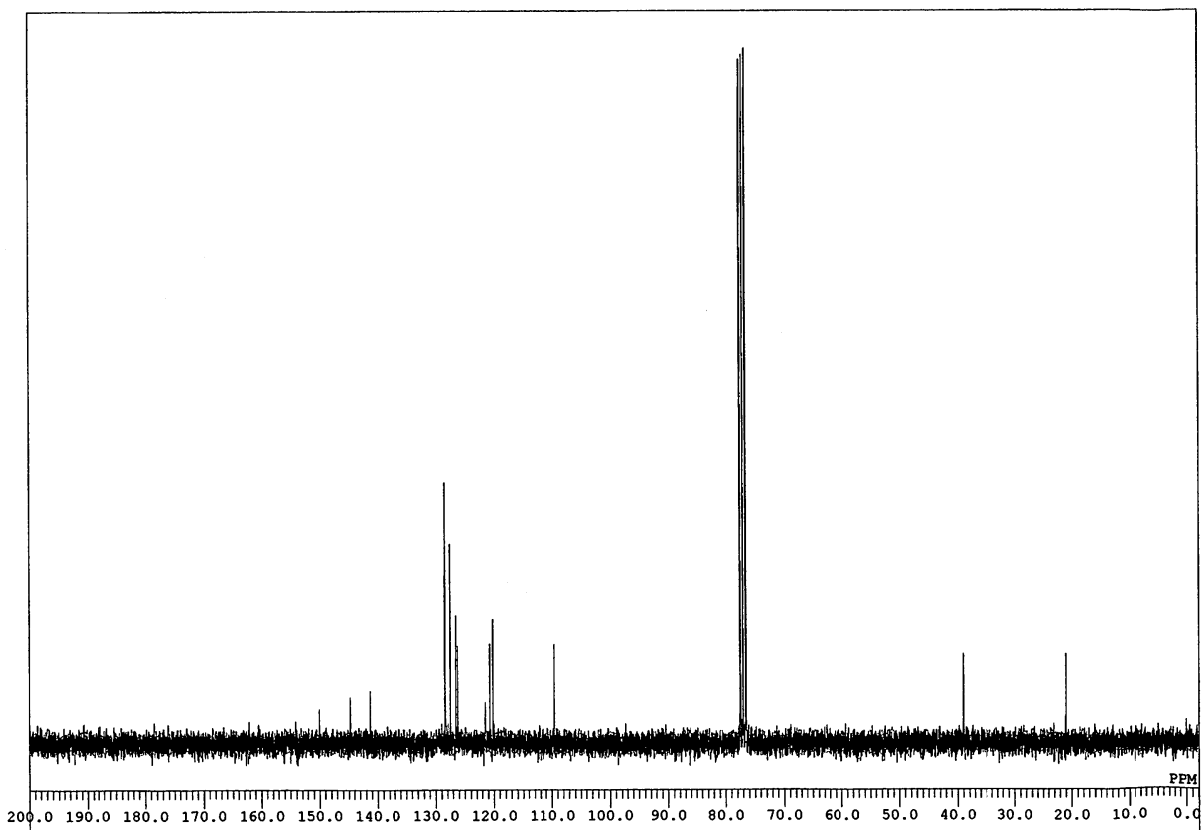
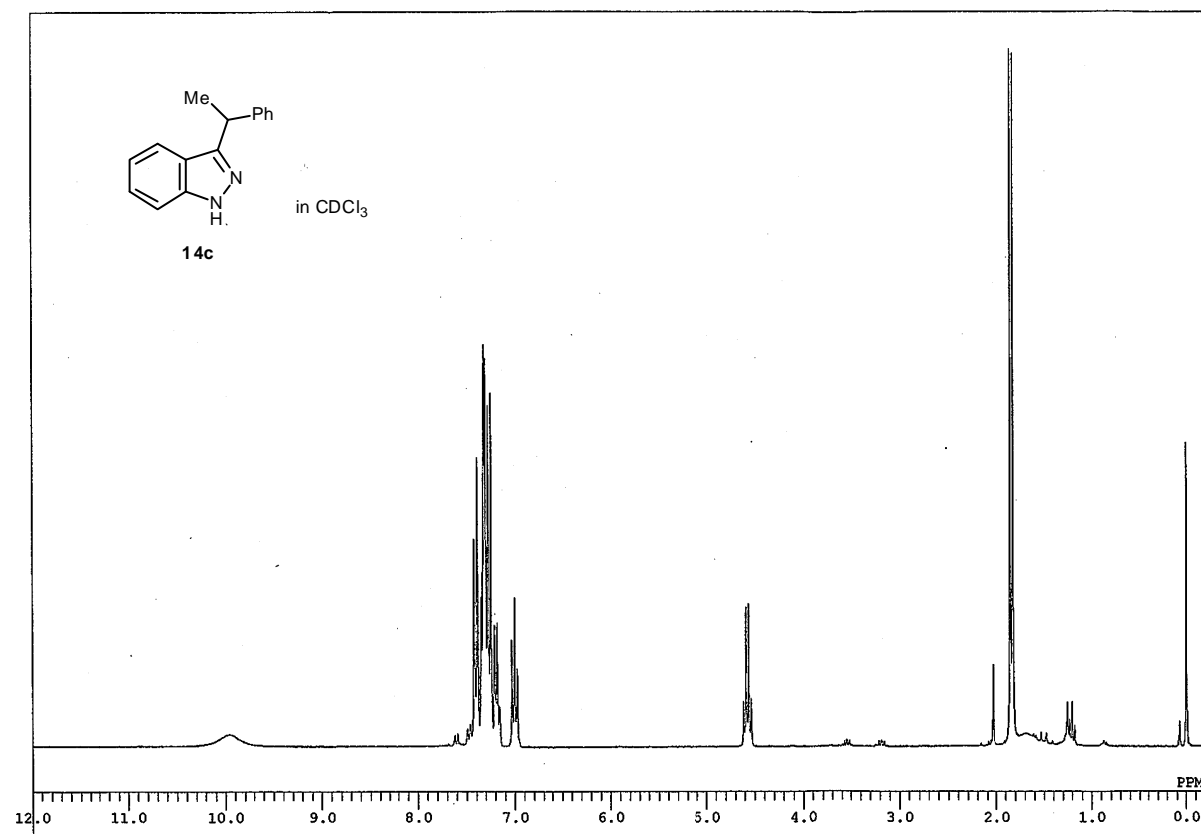












1-Diazo-2-methyl-4-phenyl-1-(trimethylsilyl)butan-2-ol (2a)¹⁾**2-Diazo-1-(4-methoxyphenyl)-1-phenyl-2-(trimethylsilyl)ethanol (2b)**

Orange oil. ¹H-NMR (CD₂Cl₂) δ : 0.17 (s, 9H), 3.01 (br s, 1H), 3.79 (s, 3H), 6.90 (d, 2H, *J* = 8.5 Hz), 7.31-7.43 (m, 5H), 7.50 (d, 2H, *J* = 7.0 Hz). ¹³C-NMR (CD₂Cl₂) δ : -0.46, 55.23, 80.74, 113.36, 126.70, 127.34, 128.03, 128.17, 137.82, 145.97, 158.90. IR (neat) ν : 3477, 2041 cm⁻¹. MS (EI): *m/z* = 298 (M⁺-N₂, 96.2), 135 (bp). HRMS (EI): calcd for C₁₈H₂₂O₂Si (M⁺-N₂), 298.1389, found, 298.1389.

2-Diazo-1-phenyl-2-(trimethylsilyl)ethanol (2c)¹⁾**1-Diazo-2-(4-trifluoromethylphenyl)-1-(trimethylsilyl)propan-2-ol (2d)**

Yellow oil. ¹H-NMR (CD₂Cl₂) δ : 0.07 (s, 9H), 1.74 (s, 3H), 2.41 (br s, 1H), 7.62 (d, 2H, *J* = 8.5 Hz), 7.65 (d, 2H, *J* = 8.5 Hz). ¹³C-NMR (CD₂Cl₂) δ : -0.62, 31.26, 44.44, 75.88, 124.38 (q, ¹*J*_{C-F} = 271 Hz), 125.04 (q, ³*J*_{C-F} = 4 Hz), 125.95, 128.68, 129.03 (q, ²*J*_{C-F} = 32 Hz), 151.44 (q, ⁴*J*_{C-F} = 1 Hz). IR (neat) ν : 3443, 2044 cm⁻¹. MS (EI): *m/z* = 274 (M⁺-N₂, 7.5), 75 (bp). HRMS (EI): calcd for C₁₃H₁₇F₃OSi (M⁺-N₂), 274.1001, found, 274.1003.

1-Diazo-2-(pyridin-2-yl)-1-(trimethylsilyl)propan-2-ol (2e)

Orange solid. ¹H-NMR (CD₂Cl₂) δ : 0.02 (s, 9H), 1.67 (s, 3H), 5.68 (br s, 1H), 7.22 (dd, 1H, *J* = 5.0, 7.5 Hz), 7.43 (d, 1H, *J* = 8.0 Hz), 7.73 (dd, 1H, *J* = 7.5, 8.0 Hz), 8.47 (d, 1H, *J* = 5.0 Hz). ¹³C-NMR (CD₂Cl₂) δ : -0.77, 28.89, 73.84, 119.97, 122.38, 137.22, 146.89, 164.05. IR (neat) ν : 3373, 2039 cm⁻¹. MS (EI): *m/z* = 207 (M⁺-N₂, 29.6), 192 (bp). HRMS (EI): calcd for C₁₁H₁₇NOSi (M⁺-N₂), 207.1080, found, 207.1086.

1-Diazo-2-(thiophen-2-yl)-1-(trimethylsilyl)propan-2-ol (2f)

Yellow oil. ¹H-NMR (CD₂Cl₂) δ : 0.16 (s, 9H), 1.82 (s, 3H), 2.74 (br s, 1H), 6.93-6.99 (m, 2H), 7.23 (d, 1H, *J* = 5.0 Hz). ¹³C-NMR (CD₂Cl₂) δ : -0.53, 31.49, 45.22, 74.27, 123.25, 124.38, 126.57, 152.37. IR (neat) ν : 3435, 2042 cm⁻¹. MS (EI): *m/z* = 240 (M⁺, 2.6), 212 (M⁺-N₂, 14.6), 75 (bp). HRMS (EI): calcd for C₁₀H₁₆N₂OSSi (M⁺), 240.0753, found, 240.0741.

1-Diazo-4,4-dimethoxy-2-methyl-1-(trimethylsilyl)butan-2-ol (2g)

Yellow oil. ¹H-NMR (CD₂Cl₂) δ : 0.18 (s, 9H), 1.35 (s, 3H), 1.90 (d, 2H, *J* = 6.0 Hz), 3.30 (s, 1H), 3.36 (s, 1H), 4.01 (br s, 1H), 4.61 (t, 1H, *J* = 6.0 Hz). ¹³C-NMR (CD₂Cl₂) δ : -0.33, 29.61, 42.66, 52.69, 53.80, 70.78, 103.21. IR (neat) ν : 3481, 2033 cm⁻¹. MS (EI): *m/z* = 246 (M⁺, 3.4), 218 (M⁺-N₂, 2.9), 75 (bp). HRMS (EI): calcd for C₁₀H₂₂N₂O₃Si (M⁺), 246.1400, found, 246.1414.

Methyl 4-diazo-3-hydroxy-3-methyl-4-(trimethylsilyl)butanoate (2h)

Yellow oil. ¹H-NMR (CD₂Cl₂) δ : 0.18 (s, 9H), 1.41 (s, 3H), 2.60, 2.69 (AB, 2H, *J* = 16.0 Hz), 3.68 (s, 3H), 4.08 (br s, 1H). ¹³C-NMR (CD₂Cl₂) δ : -0.43, 28.69, 44.92, 51.89, 71.22, 172.58. IR (neat) ν : 3481, 2039, 1717 cm⁻¹. MS (EI): *m/z* = 202 (M⁺-N₂, 2.1), 187 (M⁺-N₂-Me, 18.5), 73 (bp). HRMS (EI): calcd for C₉H₁₈O₃Si (M⁺-N₂), 202.0988, found, 202.1025.

(E)-2-[(Trimethylsilyl)diazomethyl]-4-phenylbut-3-en-2-ol (2i)

Yellow oil. ¹H-NMR (CD₂Cl₂) δ : 0.22 (s, 9H), 1.60 (s, 3H), 2.23 (br s, 1H), 6.32 (d, 1H, *J* = 16.0 Hz), 6.66 (d, 1H, *J* = 16.0 Hz), 7.24-7.42 (m, 5H). IR (neat) ν : 3412, 2041 cm⁻¹. MS (EI): *m/z* = 232 (M⁺-N₂, 53.1), 73 (bp). HRMS (EI): calcd for C₁₄H₂₀OSi (M⁺-N₂), 232.1284, found, 232.1265.

3-Diazo(trimethylsilyl)methyl-2-methylpentan-3-ol (2j)

Yellow oil. ¹H-NMR (CD₂Cl₂) δ : 0.19 (s, 9H), 0.91-0.98 (m, 9H), 1.48 (br s, 1H), 1.66 (q, 2H, *J* = 7.5 Hz), 1.87 (sept, 1H, *J* = 7.0 Hz). ¹³C-NMR (CD₂Cl₂) δ : -0.16, 8.21, 16.69, 17.68, 30.79, 37.18, 78.26. IR (neat) ν : 3560, 2035 cm⁻¹. MS (EI): *m/z* = 186 (M⁺-N₂, 4.3), 171 (bp). HRMS(EI): calcd for C₁₀H₂₂OSi (M⁺-N₂), 186.1440, found, 186.1465.

1-Diazo-3-methyl-1-(trimethylsilyl)butan-2-ol (2k)

Yellow oil. $^1\text{H-NMR}$ (CD_2Cl_2) δ : 0.17 (s, 9H), 0.91 (d, 3H, $J = 6.8$ Hz), 1.01 (d, 3H, $J = 6.8$ Hz), 1.73-1.86 (m, 1H), 1.92 (br s, 1H), 3.62 (d, 1H, $J = 8.1$ Hz). $^{13}\text{C-NMR}$ (CD_2Cl_2) δ : -1.43, 18.94, 19.35, 34.01, 75.93. IR (neat) ν : 3385, 2042 cm^{-1} . MS (EI): $m/z = 158$ ($\text{M}^+ - \text{N}_2$, 2.3), 73 (bp). HRMS (EI): calcd for $\text{C}_8\text{H}_{18}\text{OSi}$ ($\text{M}^+ - \text{N}_2$), 158.1127, found, 158.1105.

2-Diazo-1-(4-methoxyphenyl)-2-(trimethylsilyl)ethanol (2l)¹⁾

References

- 1) Hari, Y.; Tsuchida, S.; Sone, R.; Aoyama, T. *Synthesis* **2007**, 3371-3375.

