Phosphonite Mediated 1,3-Dipolar Cycloaddition: A Route to Polycyclic 2-Pyrrolines from Imines, Acid Chlorides and Alkenes

Marie S. T. Morin, Sara Aly and Bruce A. Arndtsen*

801 Sherbrooke St. W., Department of Chemistry, McGill University
Montreal, Quebec H3A 2K6 Canada

Supporting Information

I. General Procedures

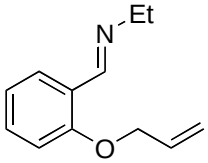
All reactions were performed under an inert nitrogen atmosphere in either a Vacuum Atmospheres 553-2 dry box or using Schlenk techniques. Reagents were purchased from commercial sources and used as received. Solid PPh_3 and PCy_3 were dried by heating at 120˚C under high vaccum. Liquid $P(OCH_2CF_3)_3$, $P(OPh)_3$ and $P(NMe_2)_3$ were dried over 4 A molecular sieves. (2-catechyl)PPh was prepared by a literature procedure.[1] Aldehyde precursors to imines **2a**,**b**,**f-m**,[2] **2c,e**[3] and **2d**[4] were prepared by literature procedures. $CDCl_3$ and CD_3CN were distilled from CaH_2 under nitrogen. Dichloromethane and diethyl ether were dried via filtration through activated molecular sieves (MBraun SPS). ^{1}H and ^{13}C NMR spectra were recorded on Varian Mercury 300 MHz, 400 MHz and Unity 500 MHz spectrometers. The stereochemistry of the pyrroline and pyrrolidine products was determined by NoE NMR experiments (**3a, 3f, 4a** and **4c**), and comparison to literature reported compounds.[6]

II. Imine Synthesis

Typical Procedure

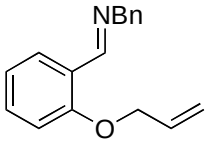
To a solution of 2-(allyloxy)benzaldehyde (405.4 mg, 2.5 mmol) in dichloromethane (10 mL) was added $MgSO_4$ and ethylamine (2.0 M in THF) (1.4 mL, 2.75 mmol). The heterogeneous mixture was stirred at room temperature for 18h. The reaction mixture was filtered, and the solvent and excess amine were evaporated *in vacuo* to provide imine **2a** as a clear oil (402 mg, 85%). In the case of imines **2b, 2i**, **2j**, **2l** and **2m**, exactly 1.0 equivalent of amine was added.

(*E*)-N-(2-(allyloxy)benzylidene)ethanamine **2a**



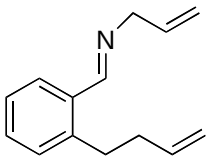
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 7.96 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.34-7.29 (m, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.86 (dd, *J* = 8.4 Hz, 2.1 Hz, 1H), 6.11-6.01 (m, 1H), 5.41 (dt, *J* = 17.3 Hz, 1.6 Hz, 1H), 5.29 (dt, *J* = 10.6 Hz, 1.5 Hz, 1H), 4.58-4.55 (m, 2H), 3.65 (qd, *J* = 7.3 Hz, 1.3 Hz, 2H), 1.30 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz; $CDCl_3$): δ 157.6, 156.3, 133.0, 131.5, 127.3, 125.1, 121.0, 117.5, 112.3, 69.0, 56.2, 16.5. **HRMS** (ESI^+) for $C_{12}H_{16}NO^+$; calculated: 190.12264, found: 190.12231.

(*E*)-*N*-(2-(allyloxy)benzylidene)-1-phenylmethanamine **2b**



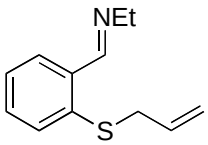
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (s, 1H), 8.06 (dd, *J* = 7.7 Hz, 1.8 Hz, 1H), 7.37-7.35 (m, 5H), 7.30-7.25 (m, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 8.3 Hz, 1H), 6.15-6.05 (m, 1H), 5.44 (dd, *J* = 17.3 Hz, 1.5 Hz, 1H), 5.34-5.31 (m, 1H), 4.86 (s, 2H), 4.62 (d, *J* = 5.1 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 157.9_4, 157.8_6, 139.7, 133.0, 131.9, 128.4, 128.0, 127.5, 126.8, 124.9, 121.0, 117.6, 112.3, 69.1, 65.5 **HRMS** (ESI^+) for $C_{17}H_{18}NO^+$; calculated: 252.13829, found: 252.13766.

(*E*)-*N*-(2-(but-3-en-1-yl)benzylidene)prop-2-en-1-amine **2c**



^{1}H NMR (400 MHz; $CDCl_3$): δ 8.61 (s, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.34 (td, *J* = 7.4 Hz, 1.5 Hz, 1H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.19 (d, *J* = 7.6 Hz 1H), 6.10 (ddt, *J* = 17.1 Hz, 10.4 Hz, 5.6 Hz, 1H), 5.87 (ddt, *J* = 17.0 Hz, 10.3 Hz, 6.7 Hz, 1H), 5.28-5.15 (m, 2H), 5.08-4.99 (m, 2H), 4.29 (dq, *J* = 5.6 Hz, 1.5 Hz, 2H), 2.95 (t, *J* = 7.9 Hz, 2H), 2.35 (q, *J* = 6.8 Hz, 2H). **^{13}C NMR** (126 MHz; $CDCl_3$): δ 160.2, 141.5, 137.6, 136.0, 133.7, 130.3, 130.0, 127.7, 126.4, 115.9, 115.2, 64.0, 36.0, 32.1. **HRMS** ($APCI^+$) for $C_{14}H_{18}N^+$; calculated: 200.14287, found: 200.143338.

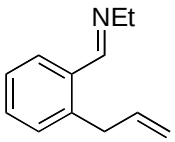
N-(2-(allylthio)benzylidene)ethanamine **2d**



^{1}H NMR (400 MHz; $CDCl_3$): δ 8.85 (s, 1H), 7.92 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.40 (dd, *J* = 7.7 Hz, 1.4 Hz, 1H), 7.31 (td, *J* = 7,5 Hz, 1.7 Hz, 1H), 7.27-7.23 (m, 1H), 5.82 (ddt, *J* = 17.0 Hz, 10.0 Hz, 7.0 Hz, 1H), 5.07-5.01 (m, 2H), 3.67 (qd, *J* = 7.3 Hz, 1.4 Hz, 2H), 3.47 (dt, *J* = 7.0 Hz, 1.1 Hz, 2H), 1.31 (t, *J* = 7.3

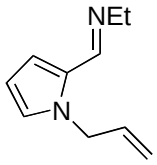
Hz, 3H). **^{13}C NMR** (126 MHz; $CDCl_3$): δ 159.0, 136.6, 136.1, 133.1, 131.8, 130.3, 127.8, 127.1, 118.0, 56.0, 38.3, 16.4. **HRMS** (ESI^+) for $C_{12}H_{16}NS^+$; calculated: 206.09980, found: 206.09928.

N-(2-allylbenzylidene)ethanamine **2e**



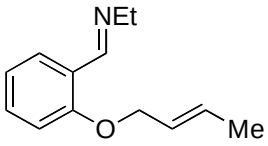
^{1}H NMR (400 MHz, $CDCl_3$) δppm): 8.53 (s, 1H), 7.87 (d, *J* = 7.5 Hz, 1H), 7.29 (t, *J* = 7.5 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 1H), 7.14 (d, *J* = 7.5 Hz, 1H), 6.00-5.92 (m, 1H), 5.03 (d, *J* = 9.0 Hz, 1H), 4.92 (d, *J* = 17.0 Hz, 1H), 3.63-3.57 (m, 4H), 1.27 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δppm): 158.8, 139.0, 137.2, 134.4, 130.3, 130.2, 127.5, 126.8, 116.1, 56.4, 36.9, 16.5. **HRMS** ($APCI^+$) for $C_{12}H_{16}N^+$; calculated: 174.12773, found: 174.12772.

(*E*)-*N*-((1-allyl-1*H*-pyrrol-2-yl)methylene)ethanamine **2f**



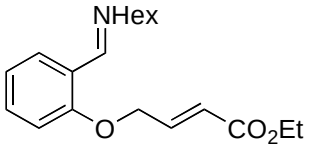
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.12 (s, 1H), 6.75 (t, *J* = 2.2 Hz, 1H), 6.50 (dd, *J* = 3.7 Hz, 1.8 Hz, 1H), 6.17 (dd, *J* = 3.7 Hz, 2.7 Hz, 1H), 6.03-5.94 (m, 1H), 5.14-5.11 (m, 1H), 5.04-4.96 (m, 3H), 3.51 (qd, *J* = 7.3 Hz, 1.2 Hz, 2H), 1.23 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz; $CDCl_3$): δ 151.5, 135.1, 129.4, 126.2, 116.4, 115.8, 108.3, 56.3, 50.6, 16.7. **HRMS** ($APCI^+$) for $C_{10}H_{15}N_2^+$; calculated: 163.12298, found: 163.12271.

N-(2-((*E*)-but-2-en-1-yloxy)benzylidene)ethanamine **2h**



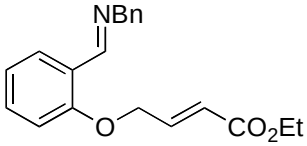
^{1}H NMR (500 MHz, $CDCl_3$): δ 8.75-8.74 (m, 1H), 7.93 (dd, *J* = 7.7 Hz, 1.8 Hz, 1H), 7.34 (ddd, *J* = 8.3 Hz, 7.3 Hz, 1.8 Hz, 1H), 6.98-6.97 (m, 1H), 6.91-6.88 (m, 1H), 5.90-5.83 (m, 1H), 5.79-5.71 (m, 1H), 4.64-4.48 (m, 2H), 3.67-3.62 (m, 2H), 1.78-1.74 (m, 3H), 1.29 (td, *J* = 7.3 Hz, 1.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$), with rotamers: δ 157.8, 156.5, 131.5, 130.3, 128.6, 127.2, 125.9, 125.5, 125.0, 120.9, 120.8, 112.4, 112.2, 69.1, 64.2, 56.1, 17.9, 16.4, 13.4. **HRMS** (ESI^+) for $C_{13}H_{18}NO^+$; calculated: 204.13829, found: 204.13784.

(*E*)-ethyl 4-(2-((*E*)-(hexylimino)methyl)phenoxy)but-2-enoate **2i**



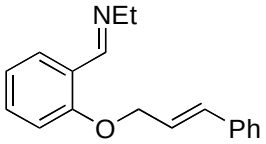
^{1}H NMR (400 MHz, $CDCl_3$) δppm): 8.73 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.33 (t, *J* = 8.4 Hz, 1H), 7.10 (dt, *J* = 4.0, 16.0 Hz, 1H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.18 (d, *J* = 16.0 Hz, 1H), 4.75 (d, *J* = 4.0 Hz, 2H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.63 (t, *J* = 6.8 Hz, 2H), 1.72–1.66 (m, 2H), 1.39–1.29 (m, 9H), 0.89 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (125.7 MHz, $CDCl_3$) δppm): 166.0, 157.0, 156.2, 142.1, 131.5, 127.6, 125.3, 122.2, 121.5, 112.0, 66.8, 62.1, 60.6, 31.7, 31.0, 27.0, 22.6, 14.2, 14.1; **HRMS** (ESI^+) for $C_{19}H_{28}NO_3^+$; calculated: 318.20637, found: 318.20591.

(*E*)-ethyl 4-(2-((*E*)-(benzylimino)methyl)phenoxy)but-2-enoate **2j**



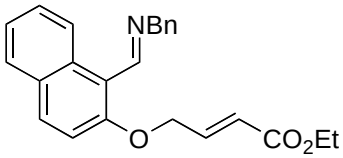
^{1}H NMR (400 MHz; $CDCl_3$): δ 8.88 (s, 1H), 8.05 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.37-7.35 (m, 5H), 7.27-7.24 (m, 1H), 7.11 (dt, *J* = 15.8 Hz, 4.1 Hz, 1H), 7.02 (t, *J* = 7,5 Hz, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.18 (dt, *J* = 15.8 Hz, 2.0 Hz, 1H), 4.86 (d, *J* = 1.2 Hz, 2H), 4.77 (dd, *J* = 4.1 Hz, 2.0 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 165.9, 157.4, 157.2, 142.0, 139.5, 131.9, 128.5, 128.0$_1$, 127.8$_2$, 126.9, 125.0, 122.2, 121.5, 112.1, 66.9, 65.4, 60.6, 14.3. **HRMS** (ESI^+) for $C_{20}H_{22}NO_3^+$; calculated: 324.15942, found: 324.15888.

(*E*)-*N*-(2-(cinnamyloxy)benzylidene)ethanamine **2k**



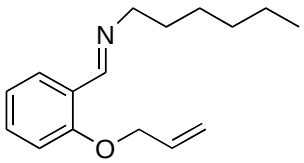
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.00 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.45-7.43 (m, 2H), 7.39-7.34 (m, 3H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.03-6.95 (m, 2H), 6.75 (d, *J* = 16.0 Hz, 1H), 6.45 (dt, *J* = 16.0 Hz, 5.8 Hz, 1H), 4.76 (dd, *J* = 5.8 Hz, 1.1 Hz, 2H), 3.68 (qd, *J* = 7.3 Hz, 1.3 Hz, 2H), 1.33 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$): δ 157.7, 156.4, 136.3, 133.1, 131.6, 128.7, 128.0, 127.4, 126.6, 125.1, 124.2, 121.1, 112.4, 69.1, 56.2, 16.5. **HRMS** (ESI^+) for $C_{18}H_{20}NO^+$; calculated: 266.15394, found: 266.15345.

(*E*)-ethyl 4-((1-((*E*)-(benzylimino)methyl)naphthalen-2-yl)oxy)but-2-enoate **2l**



^{1}H NMR (400 MHz; $CDCl_3$): δ 9.25 (d, *J* = 8.7 Hz, 1H), 9.20 (t, *J* = 1.4 Hz, 1H), 7.87 (d, *J* = 9.1 Hz, 1H), 7.77 (d, *J* = 8.1 Hz, 1H), 7.53 (ddd, *J* = 8.6 Hz, 6.9 Hz, 1.5 Hz, 1H), 7.47 (d, *J* = 8.2 Hz, 2H), 7.41-7.35 (m, 2H), 7.31-7.26 (m, 2H), 7.19-7.11 (m, 2H), 6.23 (dt, *J* = 15.7 Hz, 2.0 Hz, 1H), 4.99 (s, 2H), 4.88 (dd, *J* = 4.0 Hz, 2.0 Hz, 2H), 4.24 (q, *J* = 7.1 Hz, 2H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz; $CDCl_3$): δ 166.0, 159.4, 156.5, 142.1, 139.7, 132.6, 132.1, 129.5, 128.5, 128.2, 128.1, 126.9, 125.9, 124.4, 122.3, 118.2, 113.6, 68.0, 66.8, 60.7, 14.3. **HRMS** (ESI^+) for $C_{24}H_{24}NO_3^+$; calculated: 374.17507, found: 374.17396.

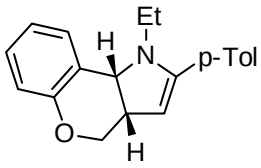
(*E*)-*N*-(2-(allyloxy)benzylidene)hexan-1-amine **2m**



^{1}H NMR (400 MHz; $CDCl_3$): δ 8.74 (s, 1H), 7.96 (dd, *J* = 7.7 Hz, 1.7 Hz, 1H), 7.35-7.31 (m, 1H), 6.98 (t, *J* = 7,5 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.12-6.03 (m, 1H), 5.43 (dd, *J* = 17.3 Hz, 1.6 Hz, 1H), 5.30 (dt, *J* = 10.6 Hz, 1.3 Hz, 1H), 4.59 (td, *J* = 3.4 Hz, 1.7 Hz, 2H), 3.62 (td, *J* = 7.1 Hz, 1.1 Hz, 2H), 1.70 (quintet, *J* = 7.3 Hz, 2H), 1.39-1.30 (m, 6H), 0.89 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (126 MHz; $CDCl_3$): δ 157.6, 156.6, 133.1, 131.5, 127.3, 125.2, 121.0, 117.5, 112.3, 69.1, 62.1, 31.7, 31.0, 27.1, 22.6, 14.1. **HRMS** (ESI^+) for $C_{16}H_{24}NO^+$; calculated: 246.18524, found: 246.18461.

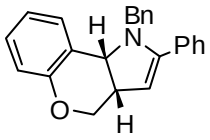
III. Synthesis of Pyrrolines 3

Synthesis and characterization of **3a**.



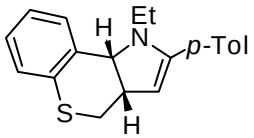
In the glovebox, imine **2a** (37.8 mg, 0.2 mmol) and toluoyl chloride (32.5 mg, 0.21 mmol) were mixed in $CDCl_3$ (ca. 0.5 mL) and allowed to stand 30 min. (2-catechyl)PPh (47.5 mg, 0.22 mmol) was added and after 1h at room temperature, DBU (45.7 mg, 0.3 mmol) was added, and the volume of $CDCl_3$ adjusted to 1.5 mL. The reaction was complete within 10 min at room temperature. The solution was concentrated in vacuo, and the residue dissolved in minimum amount of CH_2Cl_2. The product is purified in a glovebox with small pipette column of alumina using diethyl ether as eluent, affording **3a** as a light yellow oil (49.5 mg, 85%).
^{1}H NMR: (500 MHz, $CDCl_3$) δppm): 7.31 (d, *J* = 7.5 Hz, 1H), 7.26-7.21 (m, 3H), 7.15 (d, *J* = 7.5 Hz, 2H), 6.98-6.93 (m, 2H), 4.79 (d, *J* = 2.0 Hz, 1H), 4.35 (d, *J* = 8.0 Hz, 1H), 4.06 (dd, *J* = 10.5 Hz, 4.5 Hz, 1 H), 3.83 (t, *J* = 10.5 Hz, 1H), 3.32-3.21 (m, 2H), 3.09-3.04 (m, 1H), 2.36 (s, 3H), 0.98 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR**: (125.7 MHz, $CDCl_3$) δppm): 155.5, 155.0, 137.8, 131.3, 130.9, 128.9, 128.7, 127.2, 122.0, 120.4, 117.2, 101.0, 66.3, 57.4, 40.4, 38.6, 21.2, 10.1. **HRMS** (ESI^+) for $C_{20}H_{22}NO^+$; calculated: 292.16959, found: 292.16908.

Synthesis and characterization of **3b**



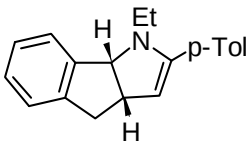
3b was prepared according to the same procedure as **3a**. Isolated yield: 85%.
^{1}H NMR: (500 MHz, CD_3CN) δppm): 7.49 (dd, *J* = 8.15 Hz, 1.42 Hz, 2H), 7.40-7.31 (m, 7H), 7.27 (td, *J* = 6.16 Hz, 3.04 Hz, 1H), 7.17-7.12 (m, 2H), 6.85-6.81 (m, 2H), 5.08 (d, *J* = 2.25 Hz, 1H), 4.41 (d, *J* = 8.30 Hz, 1H), 4.32 (d, *J* = 15.91 Hz, 1H), 4.27 (d, *J* = 15.90 Hz, 1H), 4.05 (dd, *J* = 11.03 Hz, 4.23 Hz, 1H), 3.95 (dd, *J* = 11.02 Hz, 7.63 Hz, 1H), 3.20 (dtd, *J* = 10.21 Hz, 5.03 Hz, 2.86 Hz, 1H). **^{13}C NMR**: (125.7 MHz, CD_3CN) δppm): 161.0, 159.8, 144.2, 138.9, 136.3, 133.8, 133.7, 133.6, 132.4, 132.2, 128.5, 125.9, 122.0, 109.3, 71.6, 63.9, 57.3, 45.3. **HRMS** (ESI^+) for $C_{24}H_{22}NO^+$; calculated: 340.16959, found: 340.16954.

Synthesis and characterization of **3d**



3d was prepared according to the same procedure as **3a**, except the cycloaddition required 2 h to go to completion. Isolated yield: 95%.
^{1}H NMR (400 MHz, $CDCl_3$) δppm): 7.47–7.45 (m, 1H), 7.40–7.35 (m, 3H), 7.22–7.15 (m, 4H), 4.83 (s, 1H), 4.43 (d, *J* = 10.4 Hz, 1H), 3.83–3.78 (m, 1H), 3.15 (sx, *J* = 7.2 Hz, 1H), 2.97–2.88 (m, 2H), 2.58 (dd, *J* = 6.8 Hz, 12.8 Hz, 1H), 2.37 (s, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** (75.5 MHz, $CDCl_3$) δppm): 154.1, 137.9, 137.5, 136.9, 131.0, 130.1, 129.4, 129.0, 127.1, 127.0, 125.4, 104.8, 63.1, 45.8, 42.2, 34.0, 21.3, 10.8. **HRMS** ($APCI^+$) for $C_{20}H_{22}NS^+$; calculated: 308.14675, found: 308.14622.

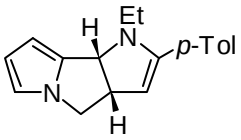
Synthesis and characterization of **3e**



3e was prepared according to the same procedure as **3a**. Isolated yield: 74%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51–7.47 (m, 1H), 7.35–7.31 (m, 2H), 7.29–7.18 (m, 3H), 7.09 (d, *J* = 7.9 Hz, 2H), 5.05 (d, *J* = 2.1 Hz, 1H), 4.79 (d, *J* = 8.3 Hz, 1H), 4.04 (t, *J* = 8.3 Hz, 1H), 3.26 (dd, *J* = 16.2 Hz, 8.3 Hz, 1H), 3.19–3.05 (m, 1H), 2.98 (ddd, *J* = 17.4 Hz, 11.0 Hz, 4.3 Hz, 2H), 2.31 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 151.2, 145.4, 142.0, 137.5, 131.2, 128.8, 127.6, 127.0, 126.5, 125.5, 124.9, 109.6, 72.7, 46.3, 45.9, 38.3, 21.3, 14.3. **HRMS** (ESI^+) for $C_{20}H_{22}N^+$: calculated: 276.17468, found: 276.17430.

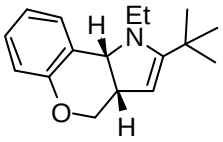
Synthesis and characterization of **3f**



3f was prepared according to the same procedure as **3a** with the exception that CD_3CN was used as solvent. Isolated yield: 76%.

^{1}H NMR (400 MHz, C_6D_6) δ 7.29 (d, *J* = 6.4 Hz, 2H), 6.87 (d, *J* = 7.6 Hz, 2H), 6.57–6.47 (m, 1H), 6.38 (dd, *J* = 2.6 Hz, 1.3 Hz, 1H), 6.22 (dd, *J* = 3.5 Hz, 1.2 Hz, 1H), 4.66 (d, *J* = 2.3 Hz, 1H), 4.52 (d, *J* = 9.5 Hz, 1H), 3.87–3.71 (m, 1H), 3.51 (dd, *J* = 10.1 Hz, 8.2 Hz, 1H), 3.42 (dd, *J* = 10.1 Hz, 4.1 Hz, 1H), 3.11 (dq, *J* = 14.5 Hz, 7.2 Hz, 1H), 2.71 (dq, *J* = 13.9 Hz, 7.0 Hz, 1H), 2.02 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, C_6D_6) δ 153.1, 138.4, 137.5, 131.4, 128.8, 113.6, 113.5, 103.0, 100.7, 65.6, 52.3, 50.1, 45.2, 20.8, 13.8. **HRMS** ($APCI^+$) for $C_{18}H_{21}N_2^+$; calculated: 265.16993, found: 265.16930.

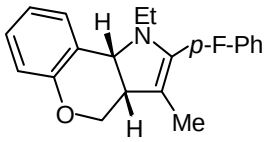
Synthesis and characterization of **3g**



In the glovebox, imine **2a** (37.8 mg, 0.2 mmol) and trimethylacetyl chloride (26.5 mg, 0.22 mmol) were mixed in $CDCl_3$ (ca. 0.5 mL) and allowed to stand 30 min. (2-catechyl)PPh (47.5 mg, 0.22 mmol) was added and after 18h at room temperature, DBU (45.7 mg, 0.3 mmol) was added, and the volume of $CDCl_3$ adjusted to 1.5 mL. The reaction was complete after 10 min at rt. The solution was concentrated in vacuo, and the residue dissolved in minimum amount of CH_2Cl_2. The product is purified in a glovebox with small pipette column of alumina using diethyl ether as eluent, affording **3g** as a light yellow oil (33 mg, 68%).

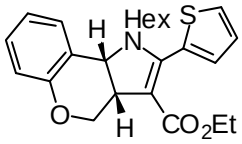
^{1}H NMR (400 MHz; $CDCl_3$): δ 7.28 (dd, *J* = 7.6 Hz, 1.4 Hz, 1H), 7.19 (t, *J* = 8.4 Hz, 1H), 6.94-6.87 (m, 2H), 4.54 (d, *J* = 2.2 Hz, 1H), 4.21 (d, *J* = 7.7 Hz, 1H), 3.97 (dd, *J* = 10.7 Hz, 4.6 Hz, 1H), 3.66 (t, *J* = 10.0 Hz, 1H), 3.51-3.26 (m, 2H), 2.91-2.85 (m, 1H), 1.21 (t, *J* = 6.8 Hz, 3H), 1.16 (s, 9H). **^{13}C NMR** (101 MHz; $CDCl_3$): δ 161.4, 155.6, 130.9, 128.5, 121.8, 120.2, 117.0, 97.7, 66.3, 57.5, 40.7, 37.3, 30.0, 26.5, 11.4. **HRMS** (ESI^+) for $C_{17}H_{24}NO$; calculated: 258.18524 found: 258.18491.

Synthesis and characterization of **3h**



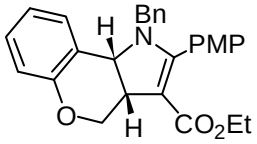
3h was prepared according to the same procedure as **3a**, with the exception that cycloaddition required 1h at 60˚C. Isolated yield: 88%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.32–7.18 (m, 4H), 7.04 (m, 2H), 7.00–6.88 (m, 2H), 4.25 (d, J = 8.0 Hz, 1H), 4.20 (dd, J = 10.8 Hz, 4.4 Hz, 1H), 3.93 (t, J = 10.3 Hz, 1H), 3.20–2.95 (m, 3H), 1.71 (s, 3H), 0.95 (t, J = 7.0 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 161.9 (d, $^1J_{C\text{-}F}$ = 237.5 Hz), 155.5, 145.4, 130.9, 130.4 (d, $^3J_{C\text{-}F}$ = 7.5 Hz), 128.7 (d, $^4J_{C\text{-}F}$ = 3.0 Hz), 128.6, 122.4, 120.5, 117.1, 115.1 (d, $^2J_{C\text{-}F}$ = 15.0 Hz), 110.0, 64.8, 56.1, 42.9, 40.8, 11.8, 10.0. **HRMS** (APCI$^+$) for $C_{20}H_{21}NOF^+$; calculated: 310.16017, found: 310.16097.

Synthesis and characterization of **3i**



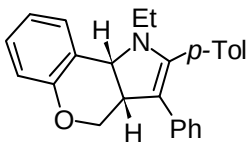
In the glovebox, imine **2i** (63.5 mg, 0.2 mmol) and 2-thiophenecarbonyl chloride (32.2 mg, 0.22 mmol) were mixed in $CDCl_3$ (ca. 0.5 mL) and allowed to stand 30 min. (2-catechyl)PPh (47.5 mg, 0.22 mmol) was added and after 1h at room temperature, DBU (60.8 mg, 0.4 mmol) was added, and the volume of $CDCl_3$ adjusted to 1.5 mL. The reaction was complete within 10 min at room temperature. The product was purified by column chromatography on silica using hexanes/diethyl ether 95/5 as the eluent, affording **3i** as a light yellow oil (65.8 mg, 80%).
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.45 (d, J = 3.9 Hz, 1H), 7.29-7.22 (m, 2H), 7.08-7.03 (m, 2H), 6.98-6.94 (m, 2H), 4.68 (d, J = 8.4 Hz, 1H), 4.33 (dd, J = 4.8 Hz, 10.4 Hz, 1H), 4.05-3.96 (m, 2H), 3.82 (t, J = 10.8 Hz, 1H), 3.41-3.35 (m, 1H), 3.07 (t, J = 8.4 Hz, 2H), 1.72-1.65 (m, 1H), 1.31-1.06 (m, 10H), 0.83 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (75.5 MHz, $CDCl_3$) δppm): 165.2, 156.2, 155.6, 131.1, 131.0, 129.6, 128.7, 127.2, 126.7, 120.5, 118.4, 117.8, 101.4, 65.0, 58.8, 58.5, 44.2, 37.9, 31.2, 27.4, 26.3, 22.4, 14.2, 13.9; **HRMS** (ESI$^+$) for $C_{24}H_{30}NO_3S^+$; calculated: 412.19409 found: 412.19430.

Synthesis and characterization of **3j**



Pyrroline **3j** was prepared according to the same procedure as **3i.** Isolated yield: 89%.
^{1}H NMR (400 MHz, $CDCl_3$) δppm): 7.37 (t, J = 7.6 Hz, 3H), 7.29-7.21 (m, 3H), 7.17 (d, J = 7.6 Hz, 2H), 6.98 (d, J = 7.6 Hz, 1H), 6.94-6.88 (m, 3H), 6.83 (t, J = 7.2 Hz, 1H), 4.79 (d, J = 8.8 Hz, 1H), 4.48 (d, J = 16.8 Hz, 1H), 4.37 (dd, J = 4.8 Hz, 11.2 Hz, 1H), 4.20 (d, J = 16.8 Hz, 1H), 4.11-4.01 (m, 2H), 3.96 (t, J = 10.8 Hz, 1H), 3.79 (s, 3H), 3.56-3.50 (m, 1H), 1.12 (t, J = 6.8 Hz, 3H); **^{13}C NMR** (75.5 MHz, $CDCl_3$) δppm): 165.7, 163.4, 160.1, 156.5, 137.1, 131.3, 130.1, 129.5, 128.8, 127.2, 127.0, 123.6, 120.4, 118.5, 117.7, 113.5, 98.6, 65.9, 58.8, 57.6, 55.2, 47.5, 38.5, 14.4. **HRMS** (ESI$^+$) for $C_{28}H_{28}NO_4^+$; calculated: 442.20128, found: 442.20053.

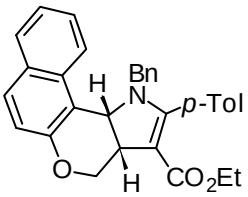
Synthesis and characterization of **3k**



Pyrroline **3k** was prepared according to the same procedure as **3h.** Isolated yield: 91%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.15 (m, 6H), 7.09 (t, *J* = 7.7 Hz, 2H), 7.00-6.94 (m, 5H), 4.50 (d, *J* = 7.9 Hz, 1H), 4.18 (dd, *J* = 10.9 Hz, 4.8 Hz, 1H), 3.91 (t, *J* = 11.0 Hz, 1H), 3.33-3.56 (m, 1H), 3.24–3.04 (m, 2H), 2.41 (s, 3H), 1.01 (t, *J* = 7.0 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.7, 148.7, 138.0, 135.7, 131.1$_3$, 131.0$_8$, 129.6, 129.1, 129.0, 128.1, 126.0, 124.2, 120.7, 120.3, 117.3, 110.6, 65.0, 56.1, 39.9, 38.9, 21.4, 10.5. **HRMS** ($APCI^+$) for $C_{26}H_{26}NO^+$; calculated: 368.20089, found: 368.19963.

Synthesis and characterization of **3l**

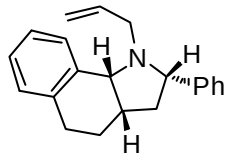


Pyrroline **3l** was prepared according to the same procedure as **3i**. Isolated yield: 75%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.60 (m, 3H), 7.37–7.17 (m, 4H), 7.17–7.07 (m, 6H), 6.69–6.59 (m, 2H), 5.69 (d, *J* = 9.4 Hz, 1H), 4.20–4.10 (m, 3H), 4.07–3.91 (m, 3H), 3.66 (dt, *J* = 9.3 Hz, 5.9 Hz, 1H), 2.33 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.9, 163.6, 156.1, 138.9, 138.4, 133.7, 130.1, 129.2, 128.8, 128.7, 128.0, 126.7, 126.5, 123.5, 122.0, 119.3, 112.3, 98.9, 67.3, 58.6, 55.6, 48.1, 40.3, 21.4, 14.3, 14.1. **HRMS** ($APCI^+$) for $C_{32}H_{30}NO_3^+$; calculated: 476.22202, found: 476.22177.

IV. Synthesis of Pyrrolidines 4

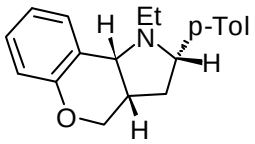
Synthesis and characterization of **4c**



In the glovebox, imine **2c** (39.8 mg, 0.2 mmol) and benzoyl chloride (29.5 mg, 0.21 mmol) were mixed in $CDCl_3$ (ca. 0.5 mL) and allowed to stand 30 min. (2-catechyl)PPh (47.5 mg, 0.22 mmol) was added and after 1h at room temperature, DBU (45.7 mg, 0.3 mmol) was added, and the volume of $CDCl_3$ adjusted to 1.5 mL. The reaction was complete within 10 min at room temperature. To the crude reaction mixture in a 25 mL round bottom flask was added $NaBH(OAc)_3$ (64 mg, 0.3 mmol) followed by HCl, 1M in Et_2O (400 µl, 0.4 mmol). The solution is stirred at rt for 18h and then quenched with 4 mL of 2N NaOH. The product is extracted with dichloromethane, washed with water, then dried with $MgSO_4$, filtered and concentrated. The product is purified by flash column chromatography on silica using petroleum ether/diethyl ether as eluent (90/10), affording **4c** as a white foam (43.4 mg, 75%).

^{1}H NMR (400 MHz; $CDCl_3$): δ 7.39-7.36 (m, 2H), 7.32-7.28 (m, 3H), 7.26-7.22 (m, 4H), 6.03-5.92 (m, 1H), 5.13 (d, *J* = 10.2 Hz, 1H), 5.01 (d, *J* = 17.1 Hz, 1H), 3.90 (d, *J* = 8.8 Hz, 1H), 3.81 (dd, *J* = 9.9 Hz, 6.6 Hz, 1H), 3.20 (dd, *J* = 13.6 Hz, 6.4 Hz, 1H), 3.10-2.98 (m, 2H), 2.63-2.56 (m, 2H), 2.43 (ddd, *J* = 12.4 Hz, 8.5 Hz, 6.4 Hz, 1H), 1.74-1.70 (m, 2H), 1.61 (ddd, *J* = 12.3 Hz, 10.1 Hz, 8.4 Hz, 1H). **^{13}C NMR** (126 MHz; $CDCl_3$): δ 143.5, 141.1, 137.8, 132.9, 129.7, 128.3, 128.0, 127.6, 127.0, 126.7, 125.4, 118.2, 65.4, 62.2, 51.0, 41.9, 34.8, 30.4, 27.0. **HRMS** ($APCI^+$) for $C_{21}H_{24}N^+$; calculated: 290.19033, found: 290.18968.

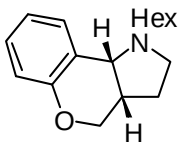
1-ethyl-2-(*p*-tolyl)-1,2,3,3a,4,9b-hexahydrochromeno[4,3-*b*]pyrrole**, 4a**



4a was prepared according to the same procedure as **4c**. Isolated yield: 89%.

^{1}H NMR (500 MHz, $CDCl_3$) δppm): 7.26-7.20 (m, 4H), 7.12 (d, *J* = 8 Hz, 2H), 6.93 (d, *J* = 7.5 Hz, 2H), 4.18 (t, *J* = 10.5 Hz, 1H), 4.05 (dd, *J* = 10.5 Hz, 4.5 Hz, 1H), 3.83 (t, *J* = 8.5 Hz, 1H), 3.70 (d, *J* = 5.5 Hz, 1H), 2.87 (dt, *J* = 14.5 Hz, 7 Hz, 1H), 2.74 (dt, *J* = 14.5 Hz, 7 Hz, 1H), 2.51-2.45 (m, 1H), 2.42-2.35 (m, 1H), 2.33 (s, 3H) 1.31-1.26 (m, 1H), 0.95 (t, *J* = 7 Hz, 3H). **^{13}C NMR** (125.7 MHz, $CDCl_3$) δppm): 155.2, 141.1, 136.5, 131.4, 129.1, 128.6, 127.3, 122.2, 119.9, 116.9, 67.4, 64.1, 57.4, 41.2, 36.1, 33.3, 21.1, 8.2. **HRMS** (ESI^+) for $C_{20}H_{24}NO^+$; calculated: 294.18524, found: 294.18454.

Synthesis and characterization of **4m**

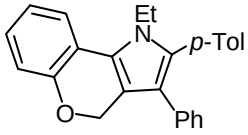


In the glovebox, imine **2m** (49.1 mg, 0.2 mmol) and ethyl chlorothioformate (27.4 mg, 0.22 mmol) were mixed in $CDCl_3$ (ca. 0.5 mL) and allowed to stand 30 min at 50˚C. (2-catechyl)PPh (47.5 mg, 0.22 mmol) was added and after 1h at 50˚C, DBU (60.8 mg, 0.4 mmol) was added, and the volume of $CDCl_3$ adjusted to 1.5 mL. The reaction was complete within 10 min at room temperature. To the crude reaction mixture in a 25 mL round bottom flask was added $NaBH(OAc)_3$ (85 mg, 0.4 mmol) followed by

HCl, 1M in Et_2O (400 µl, 0.4 mmol). The solution is stirred at rt for 18h and then quenched with 4 mL of 2N NaOH. The product is extracted with dichloromethane, washed with water, then dried on $MgSO_4$, filtered and concentrated. The product is purified by flash column chromatography on silica using petroleum ether/diethyl ether as eluent 90/10, affording **4m** as a white foam (19.2 mg, 37%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21–7.16 (m, 2H), 6.91–6.87 (m, 2H), 4.05–3.91 (m, 2H), 3.17-3.13 (m, 1H), 3.08-2.98 (m, 2H), 2.41-2.34 (m, 1H), 2.23-2.19 (m, 2H), 2.08-2.01 (m, 1H), 1.54–1.35 (m, 3H), 1.27-1.24 (m, 6H), 0.86 (t, *J* = 6.6 Hz, 3H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.2, 131.9, 128.6, 121.7, 119.6, 116.8, 67.6, 61.5, 53.3, 50.9, 34.3, 31.8, 28.4, 27.3, 24.6, 22.6, 14.1. **HRMS** ($APCI^+$) for $C_{17}H_{26}NO^+$; calculated: 260.20131, found: 260.20199.

V. Synthesis of Pyrrole 5k



The crude reaction mixture of pyrroline **3k** described above was dissolved in THF (5 mL). To this solution was added 1,4-benzoquinone (75 mg, 0.7 mmol). The solution is refluxed at 90 ˚C for 1 h, followed by the addition of more 1,4-benzoquinone (21.6 mg, 0.2 mmol). This solution was heated at 90 ^{o}C for 3 h. The product was purified by flash column chromatography on silica using hexanes/diethyl ether as eluent 90/10, affording **5k** as a white foam (48 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δppm): 7.48 (d, *J* = 7.6 Hz, 1H), 7.26-7.20 (m, 6H), 7.15-7.10 (m, 2H), 7.05-6.99 (m, 4H), 5.30 (s, 2H), 4.18 (q, *J* = 7.1 Hz, 2H), 2.40 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz; $CDCl_3$): δ 153.6, 137.7, 134.8, 133.4, 131.3, 129.2, 129.1$_7$, 129.1, 128.1, 126.5, 125.4, 122.8, 121.7, 120.6, 119.8, 119.2, 117.4, 115.3, 65.1, 40.1, 21.4, 16.6. **HRMS** ($APCI^+$) for $C_{26}H_{24}NO^+$; calculated: 366.18524, found: 366.18440.

VI. References

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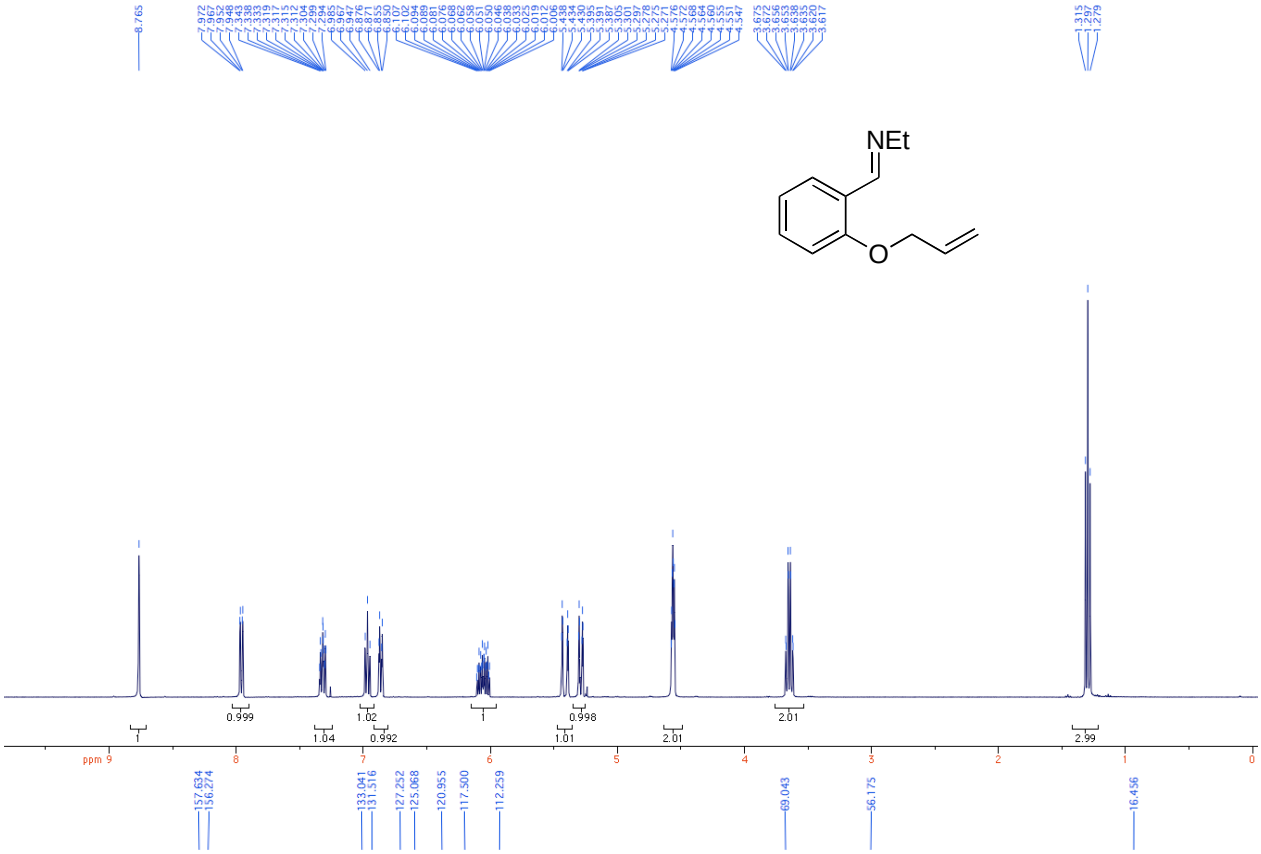
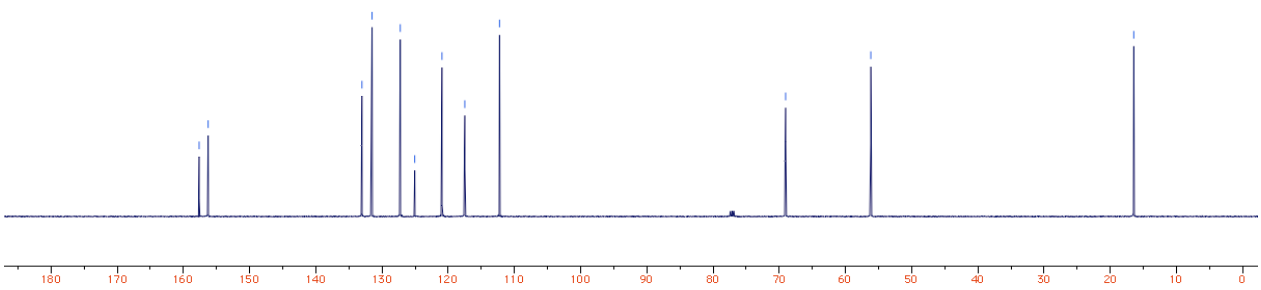
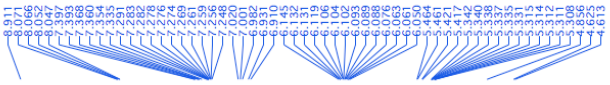
VII. ^{1}H and ^{13}C NMR spectra

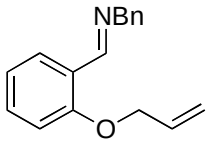
Imine **2a** ($CDCl_3$)

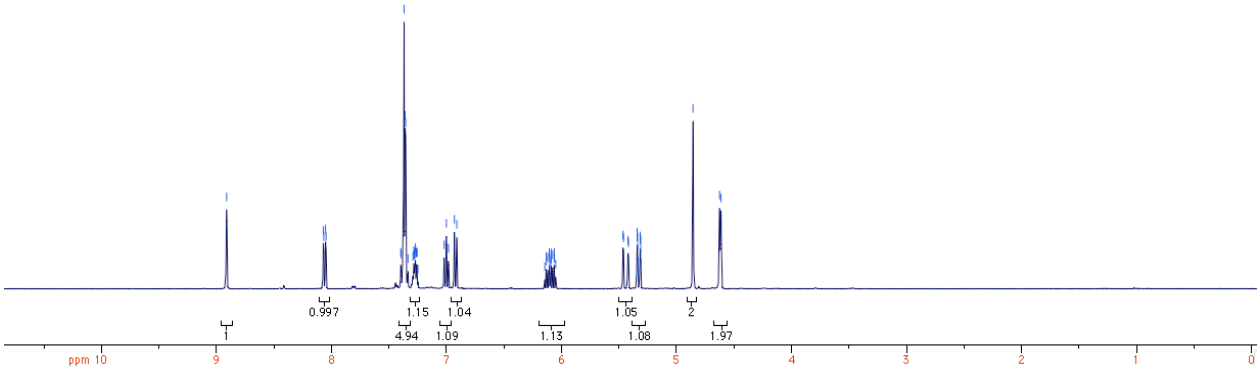


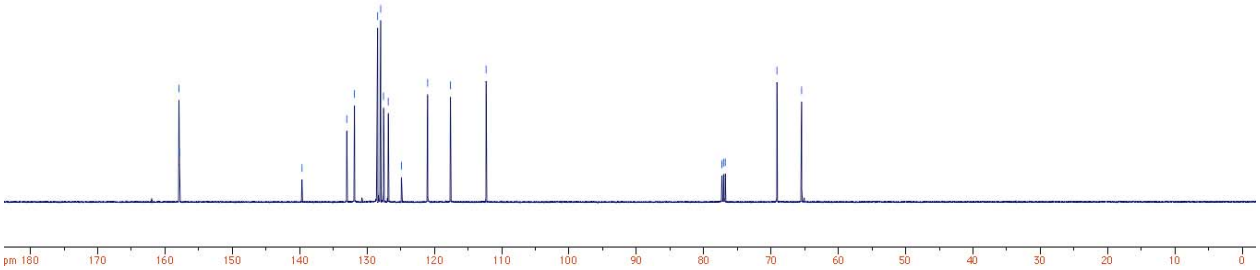


Imine **2b** ($CDCl_3$)

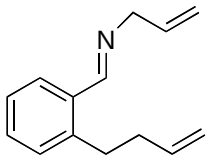


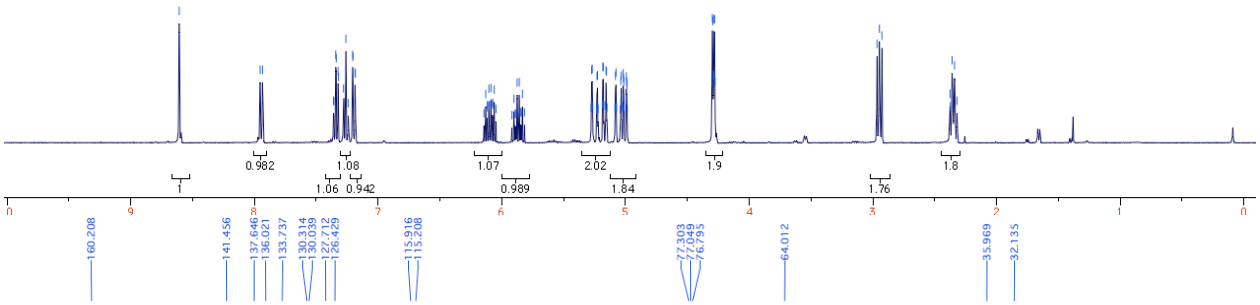


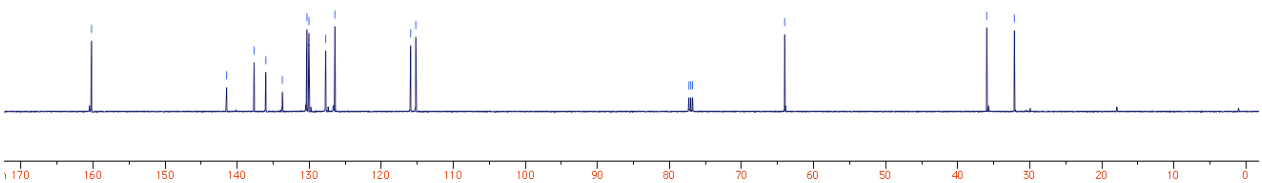




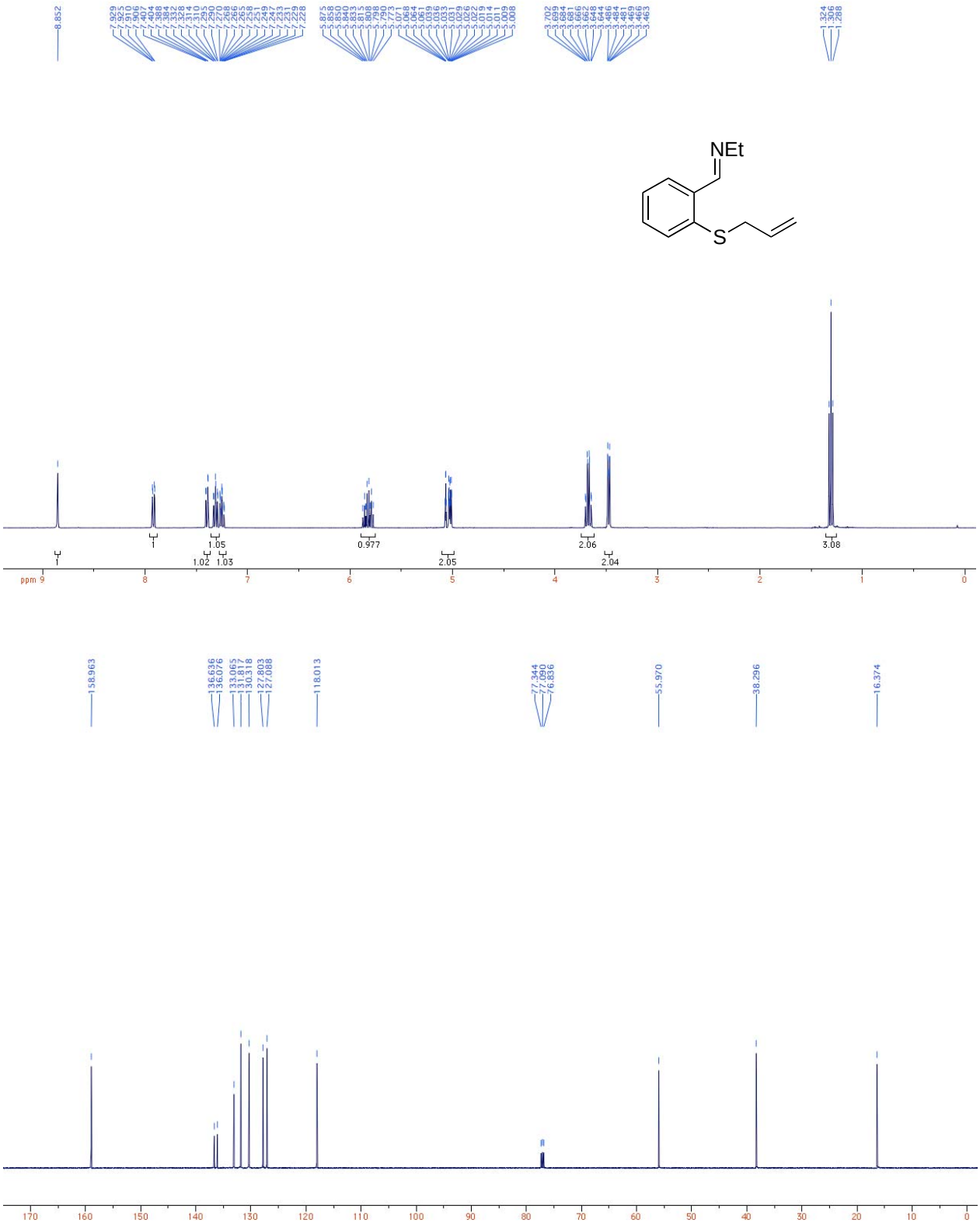
Imine **2c** ($CDCl_3$)



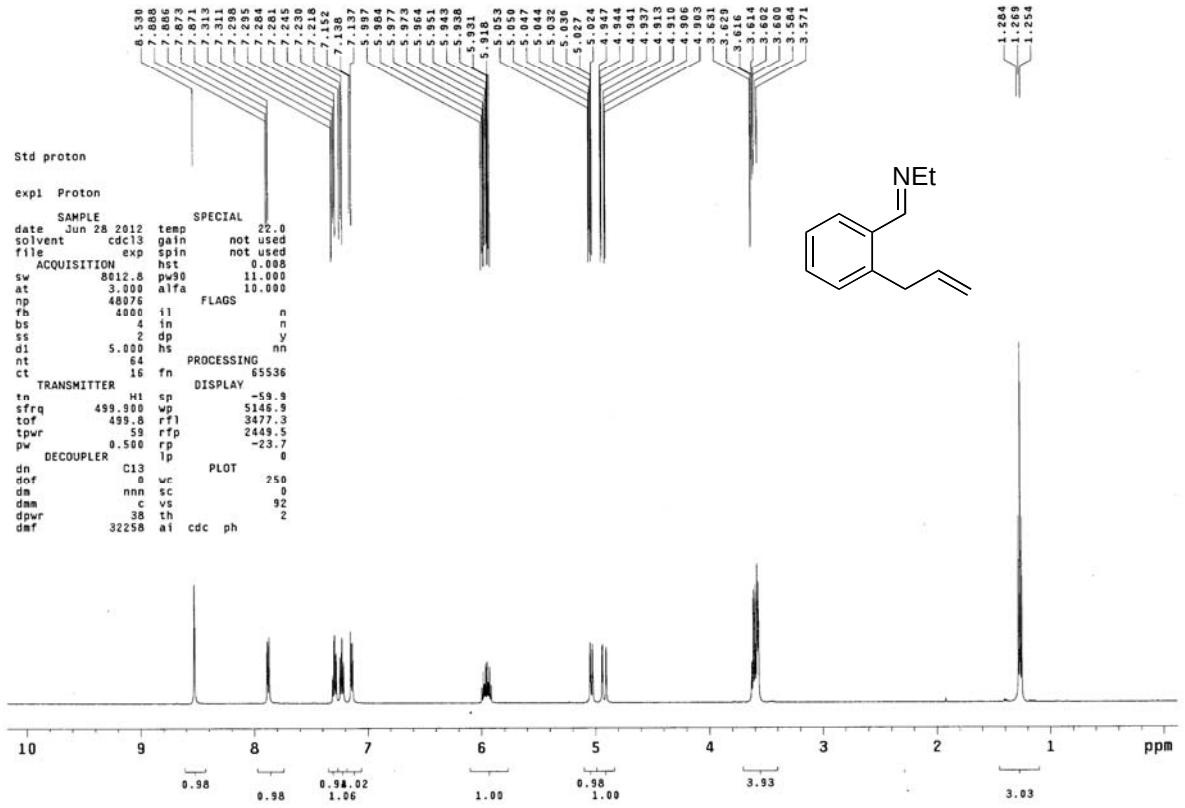


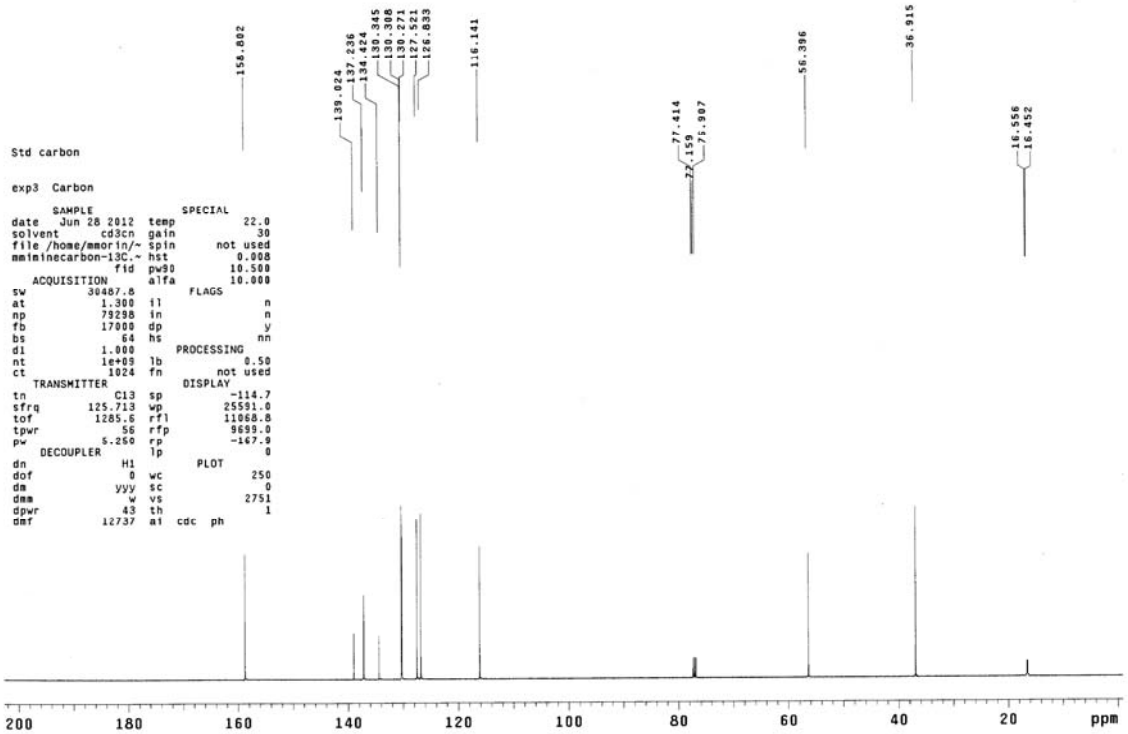


Imine **2d** ($CDCl_3$)

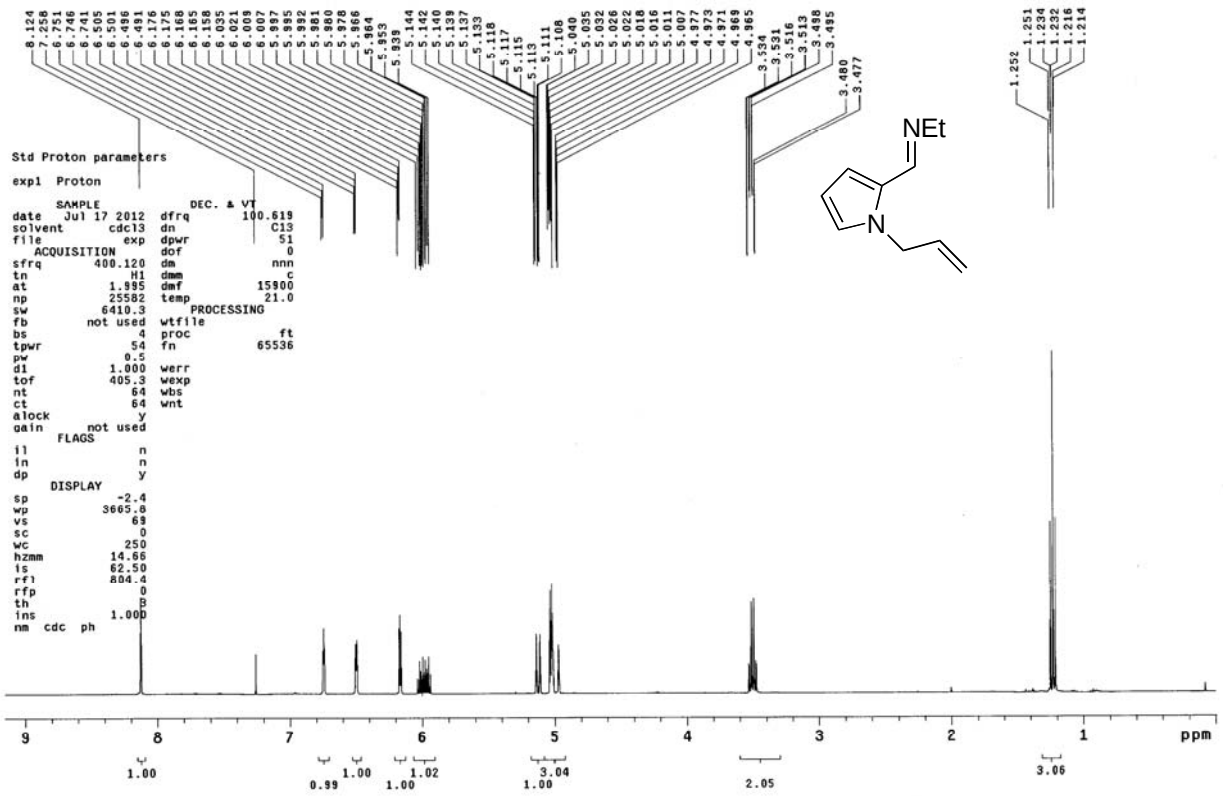


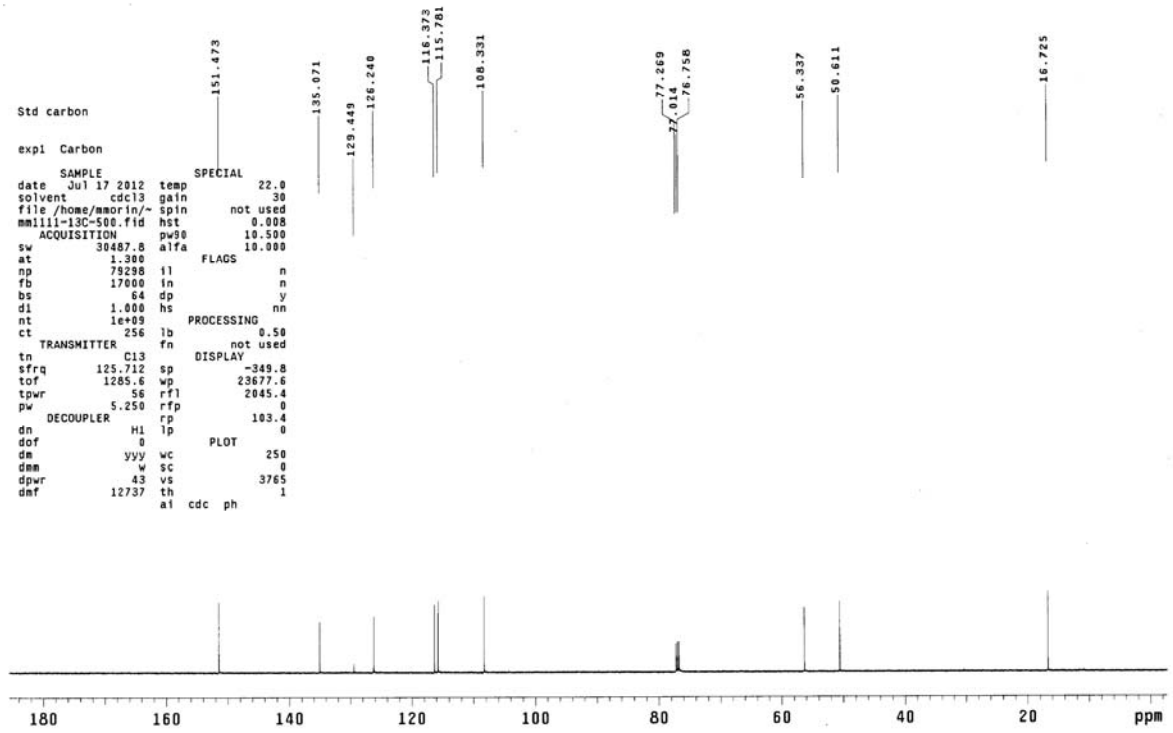
Imine **2e** ($CDCl_3$)



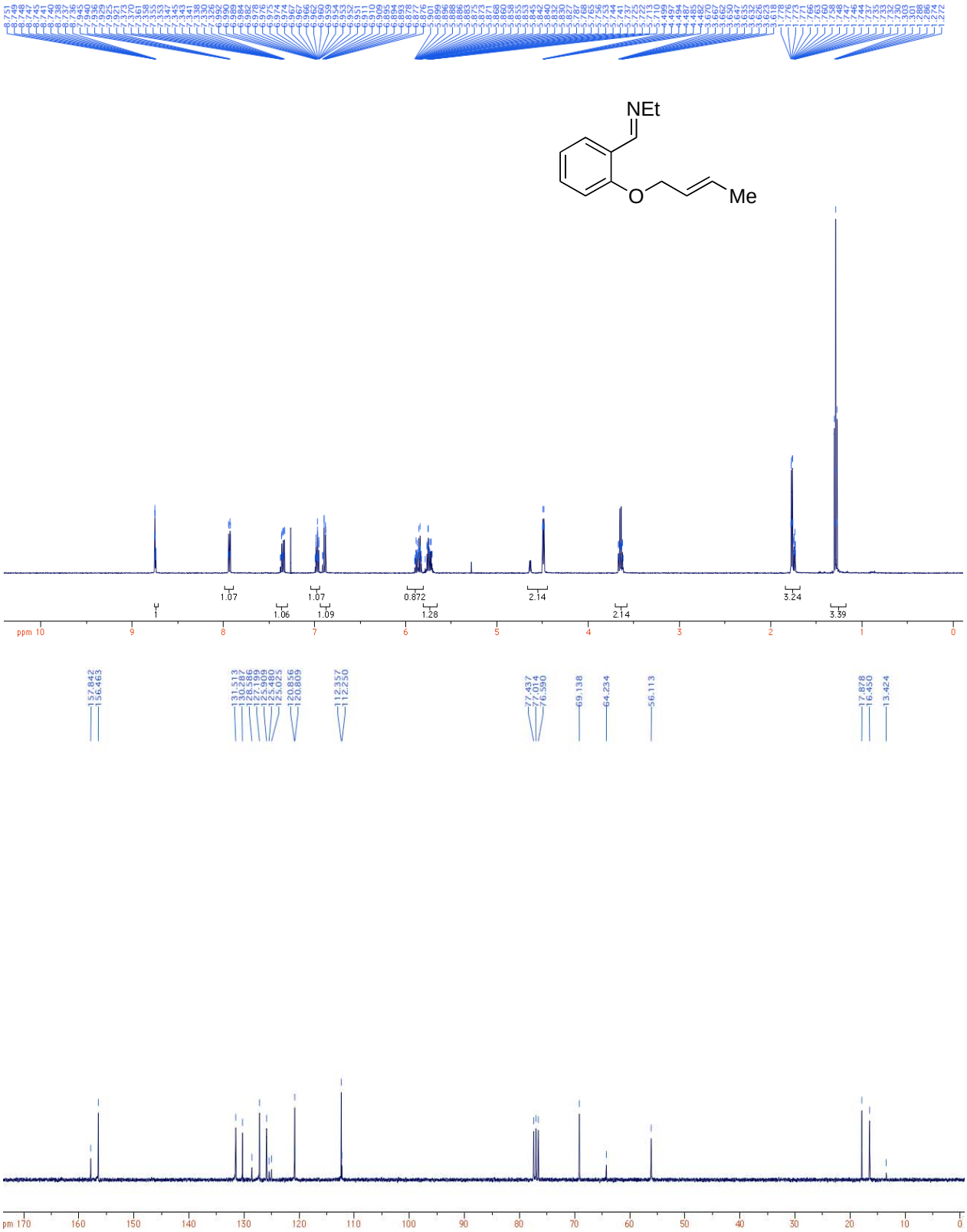


Imine **2f** ($CDCl_3$)

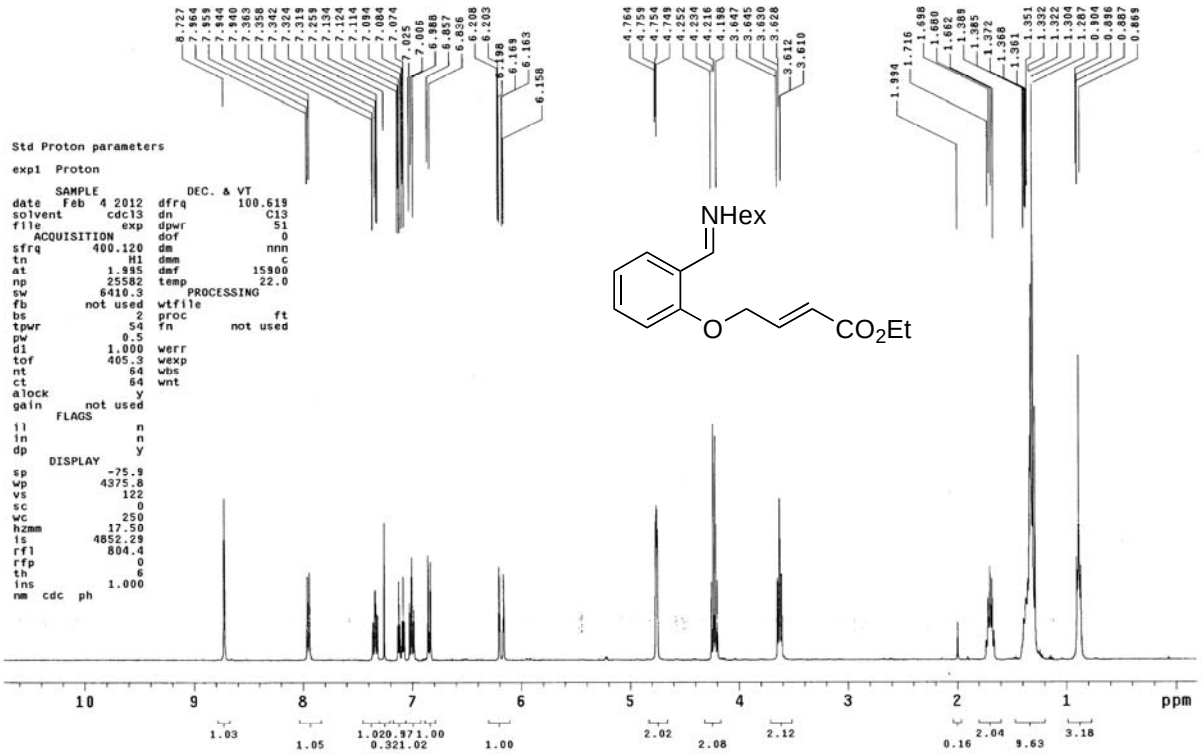


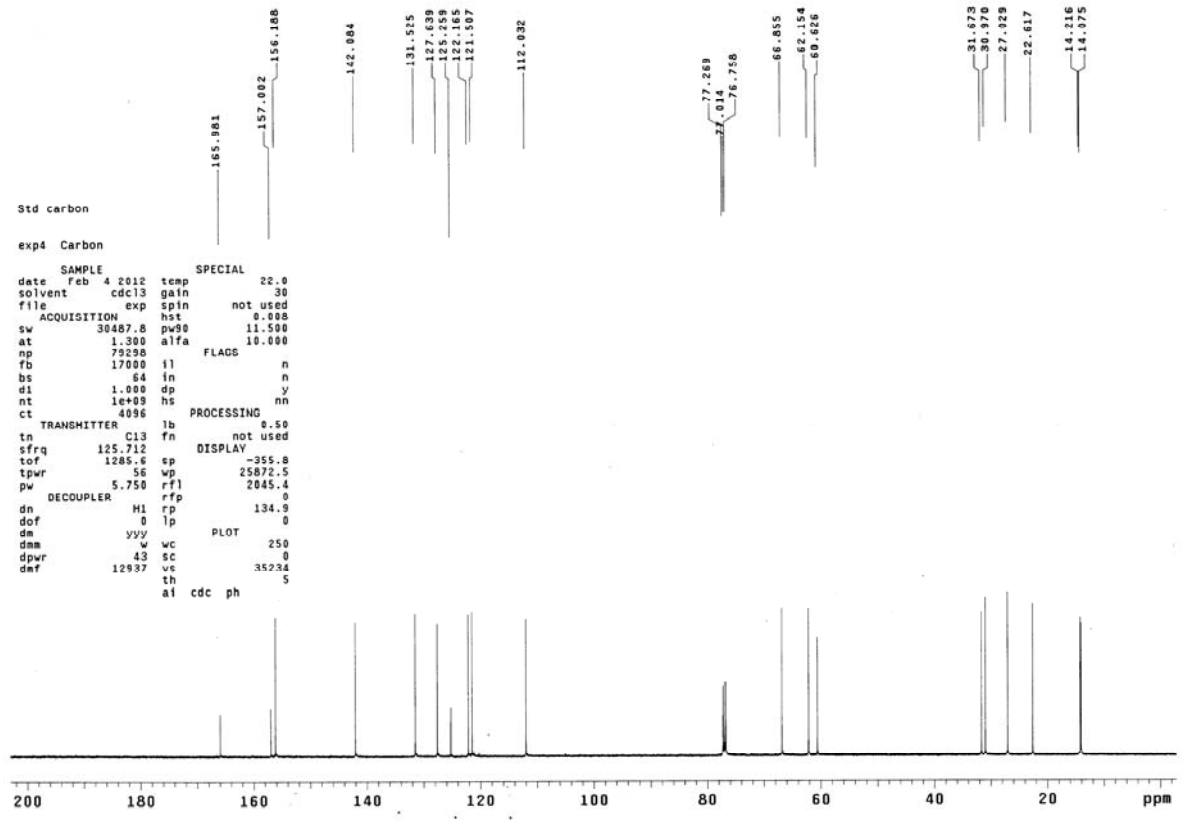


Imine **2h** ($CDCl_3$)

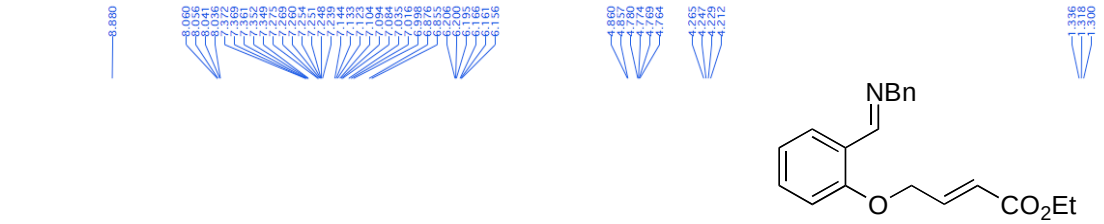


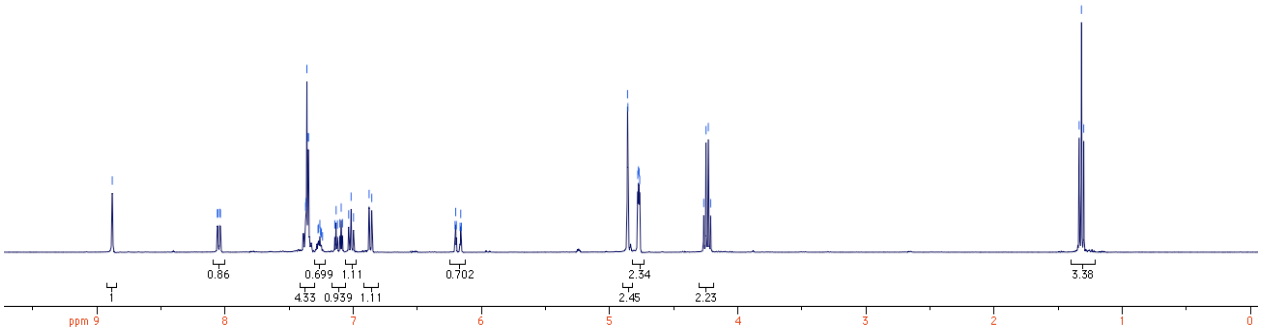
Imine **2i** ($CDCl_3$)

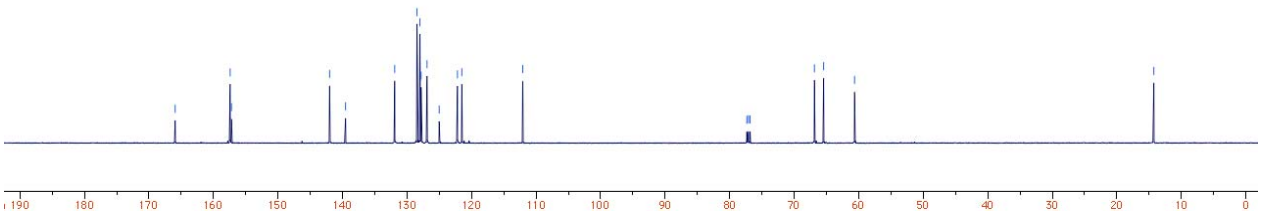




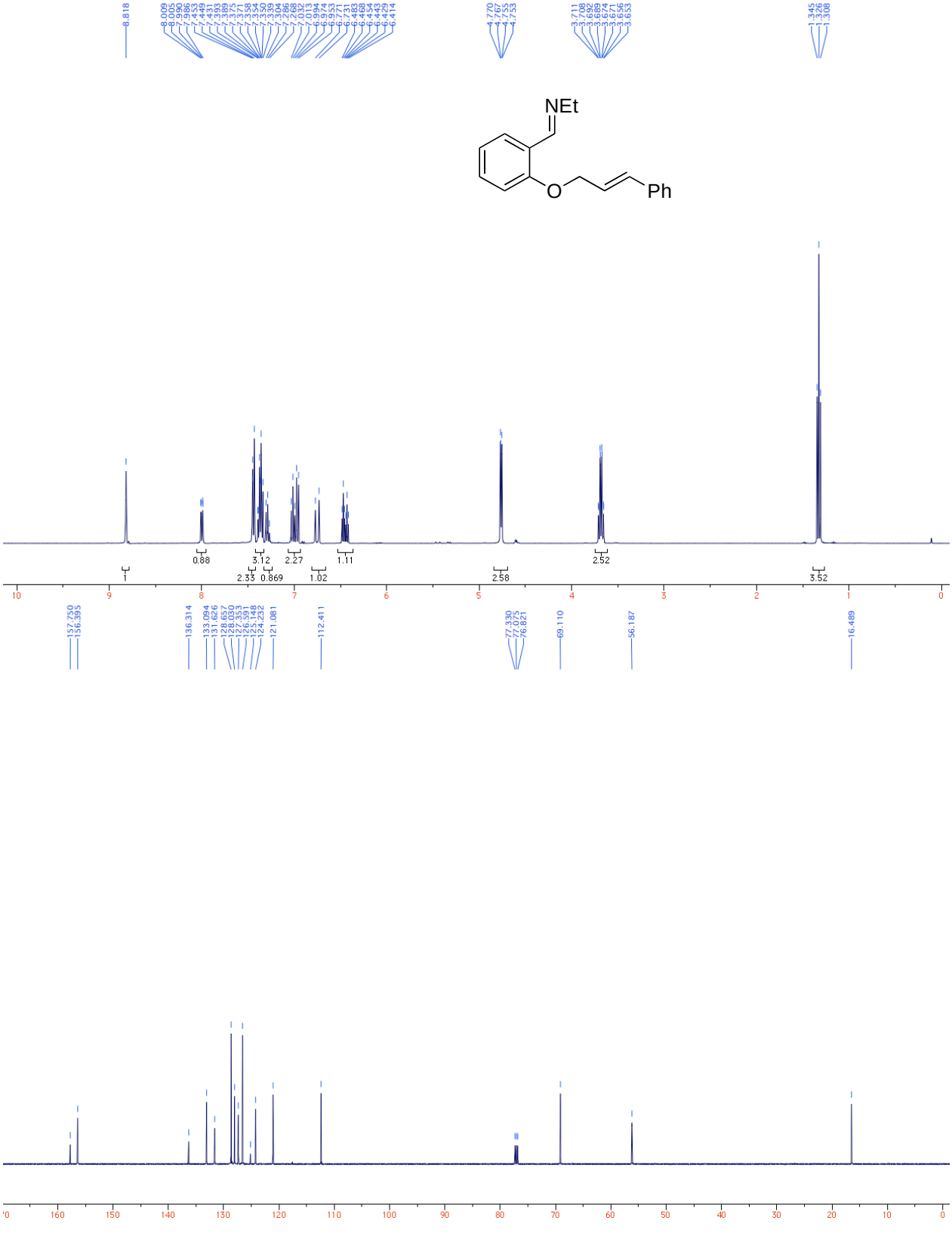
Imine **2j** ($CDCl_3$)



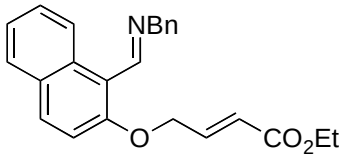


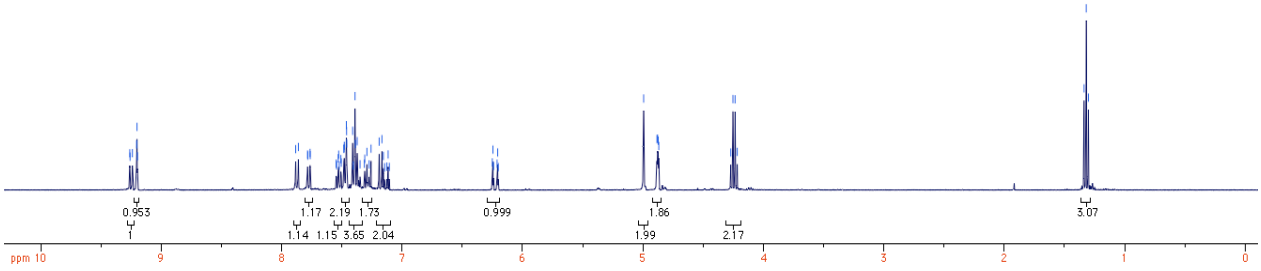


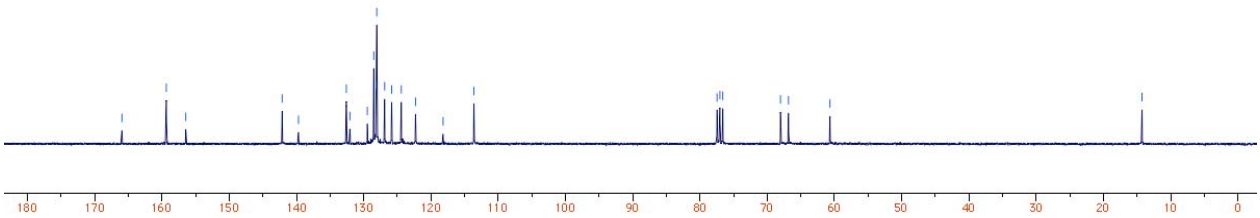
Imine **2k** ($CDCl_3$)



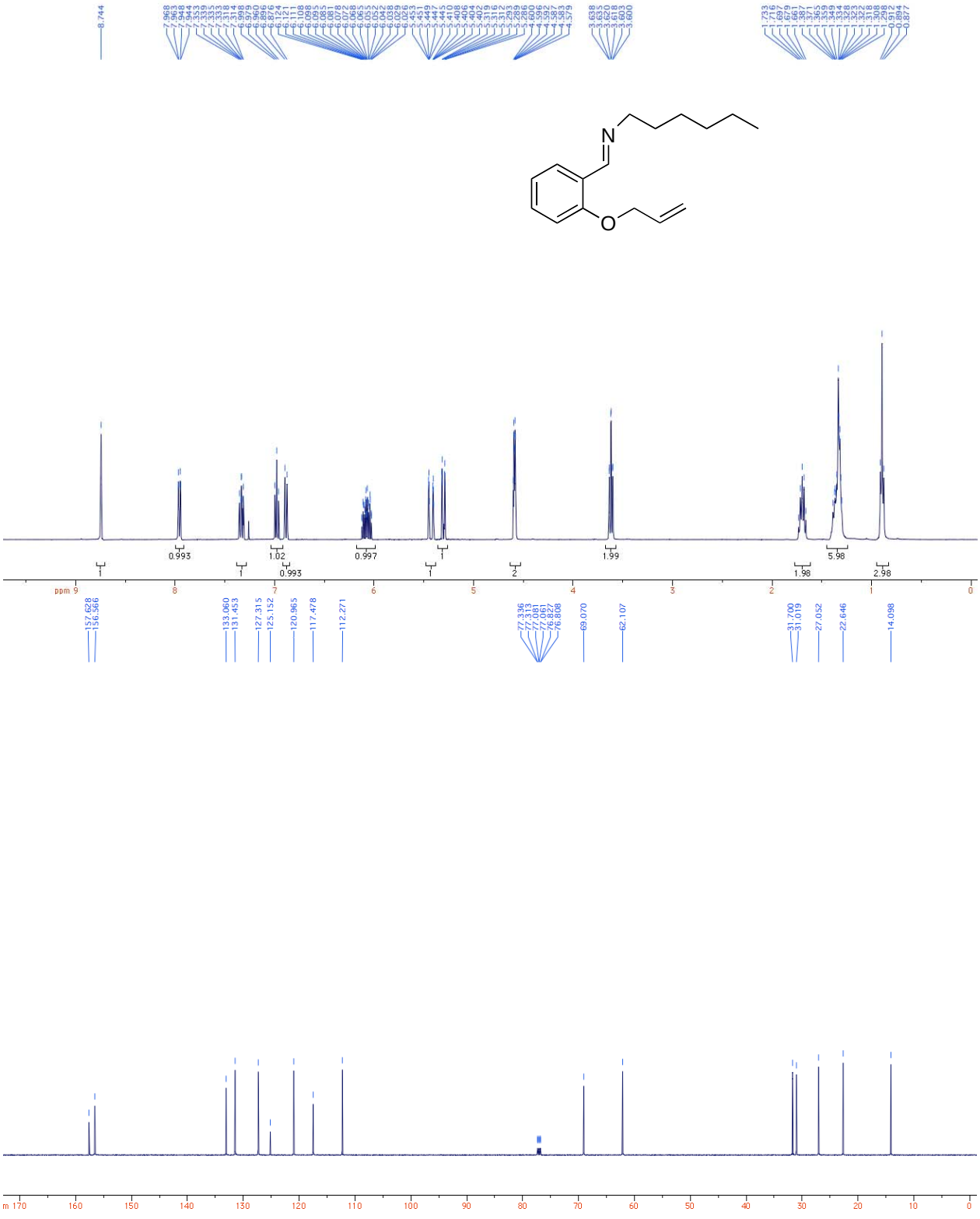
Imine **2l** ($CDCl_3$)



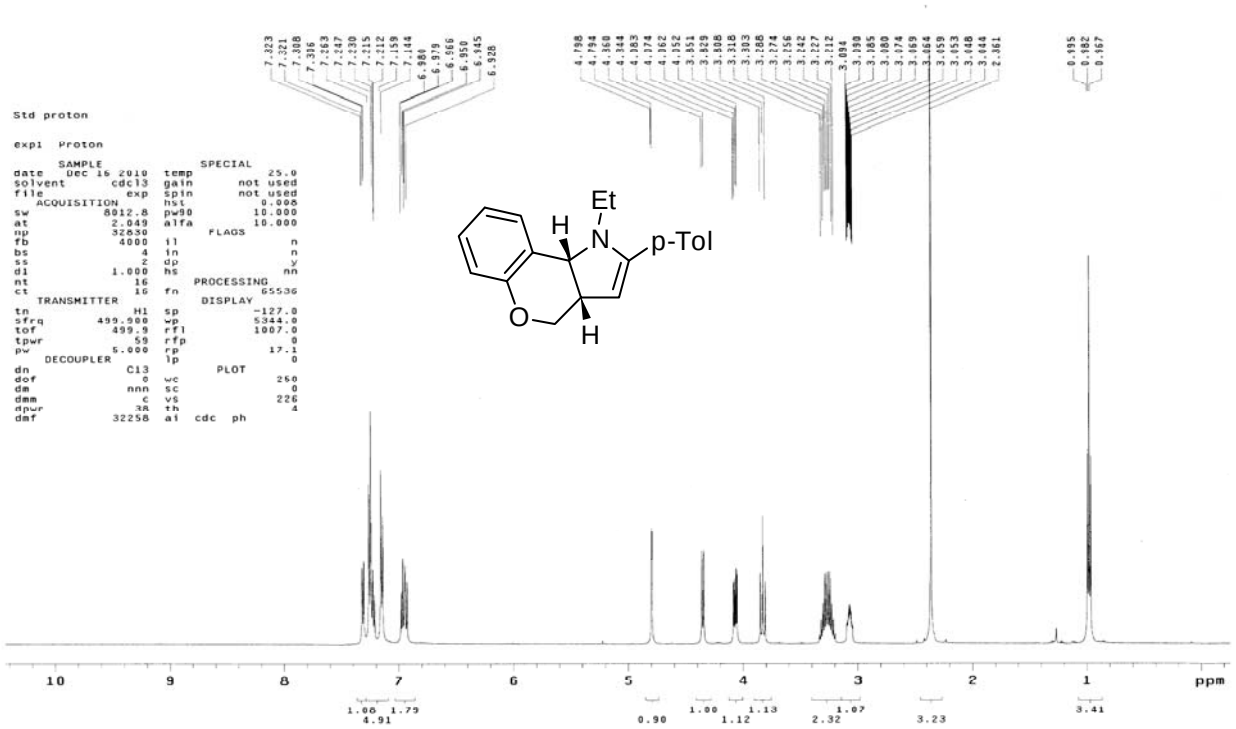


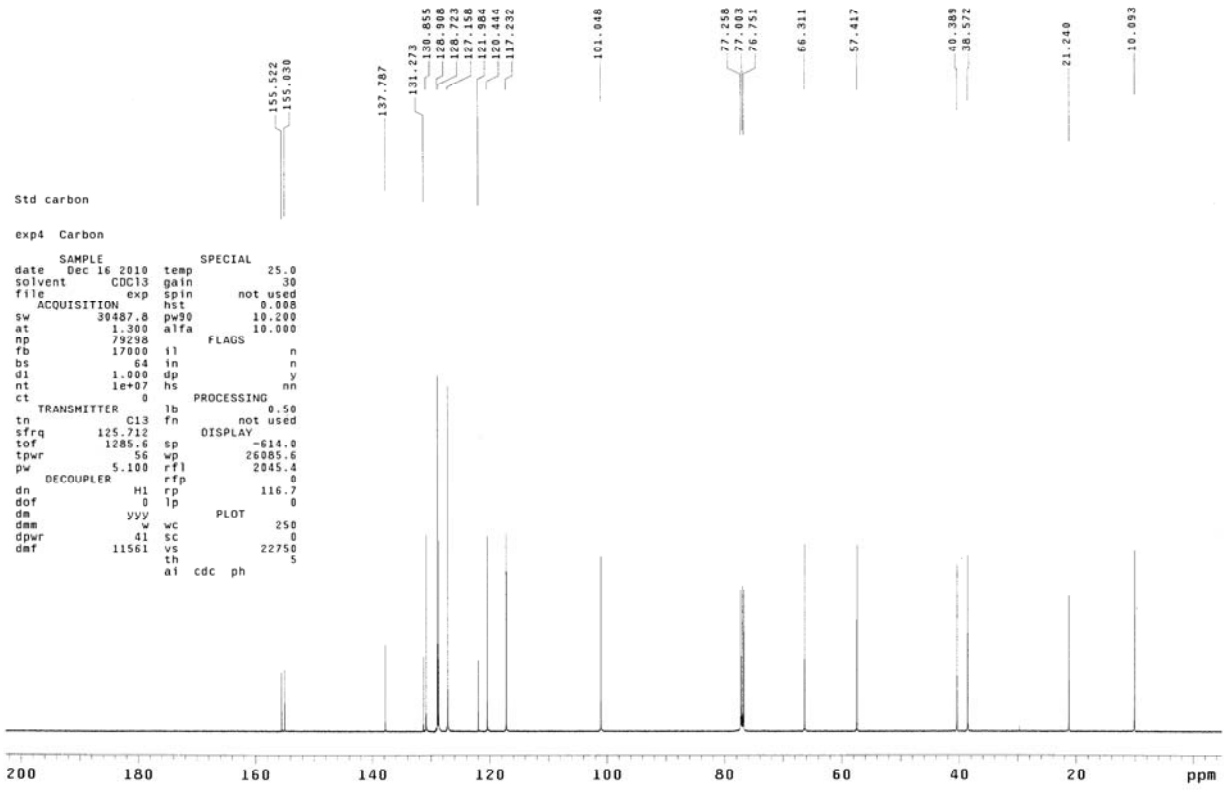


imine **2m** ($CDCl_3$)

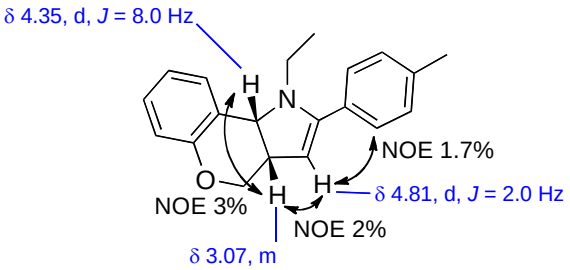


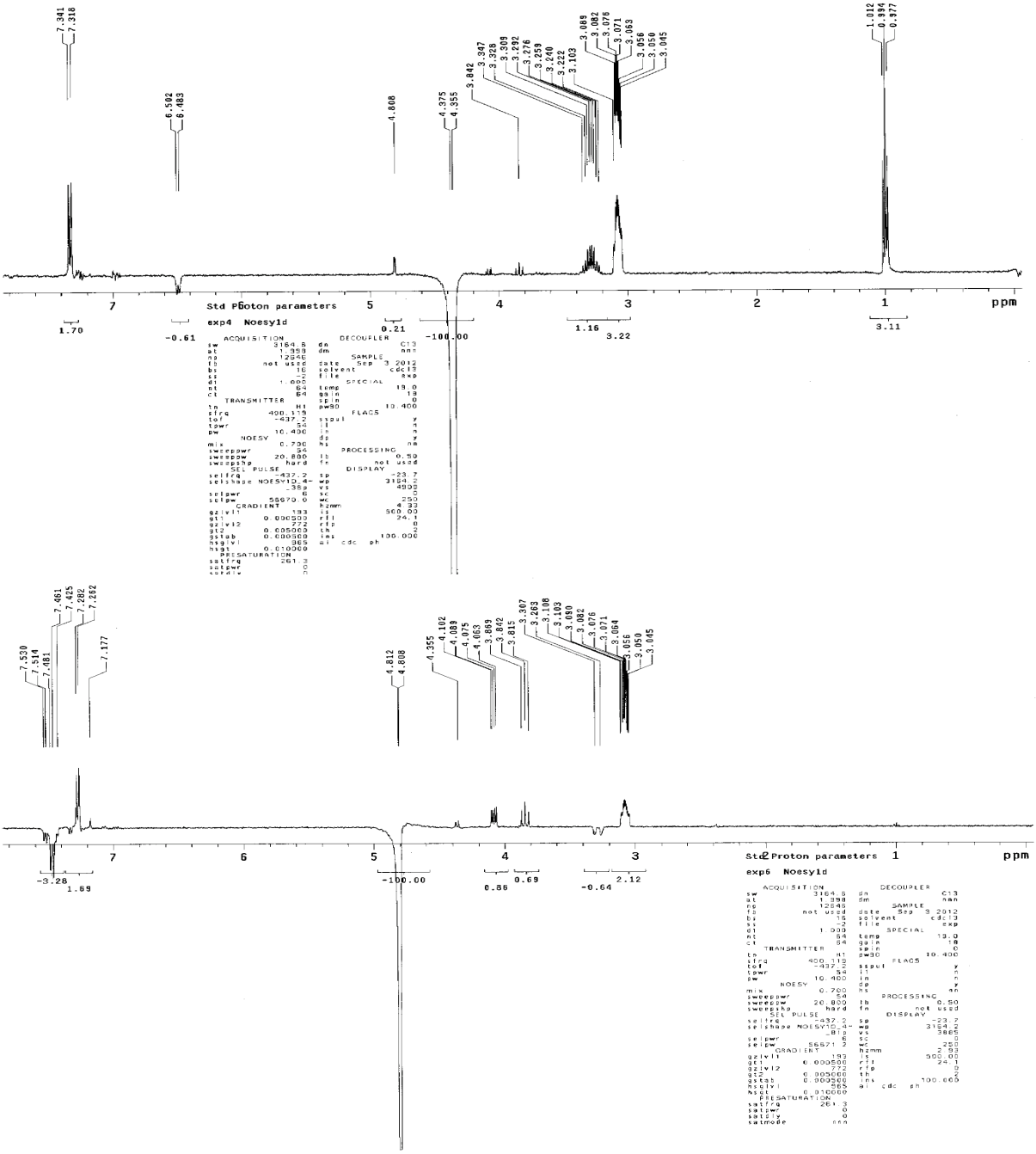
Pyrroline **3a** ($CDCl_3$)



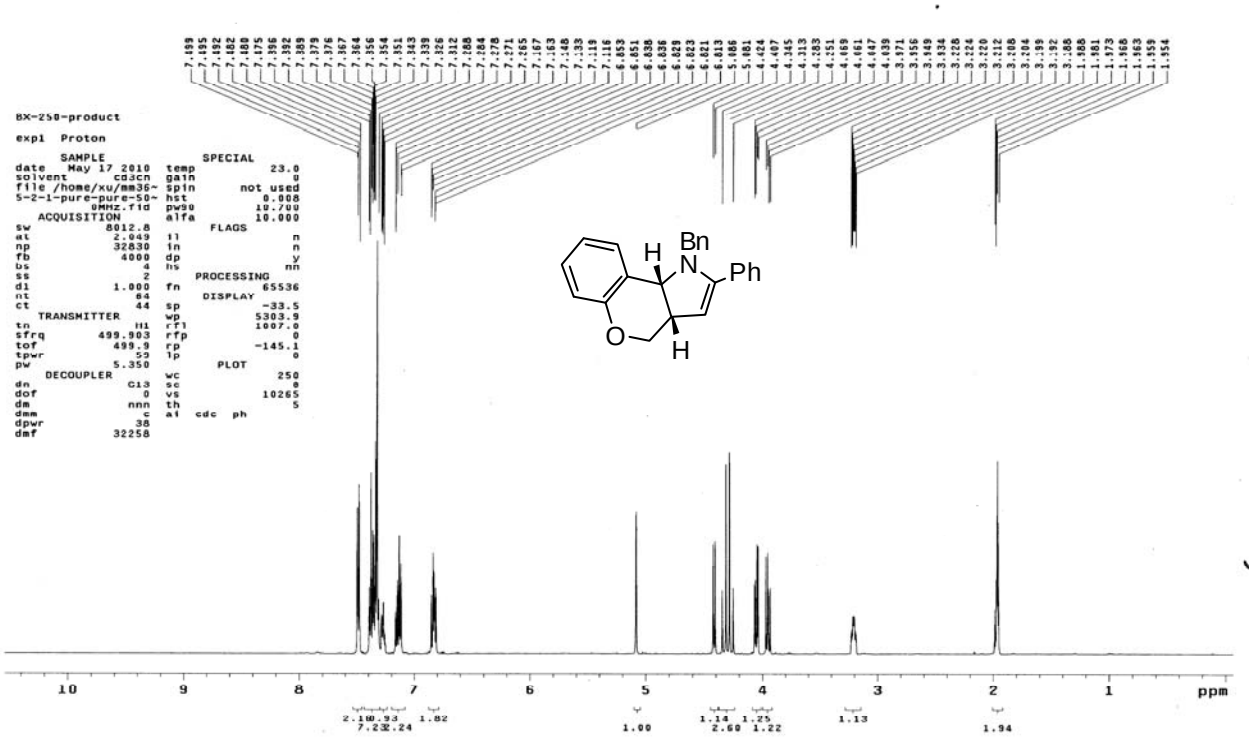


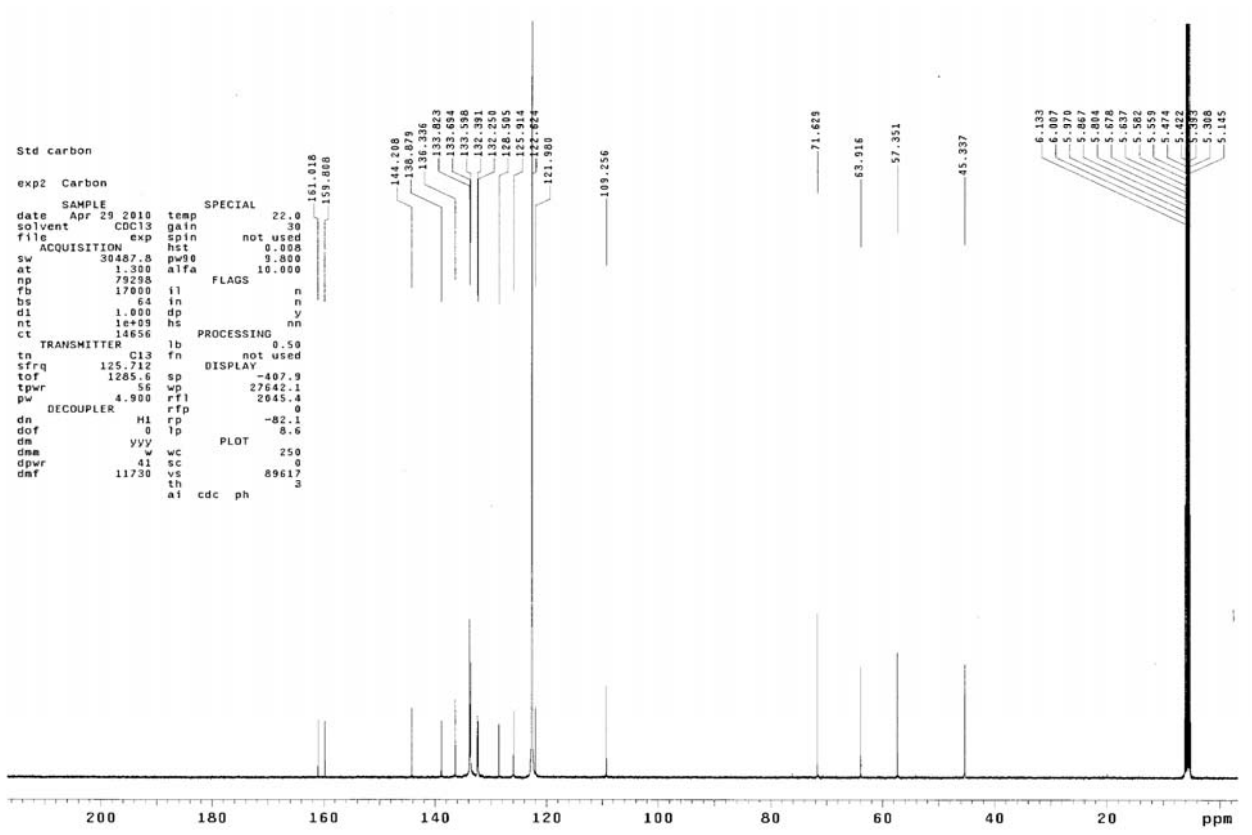
NOE of key correlation in $CDCl_3$



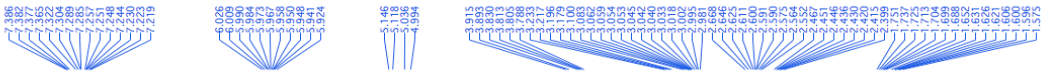


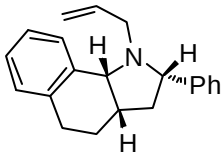
Pyrroline **3b** (CD_3CN)

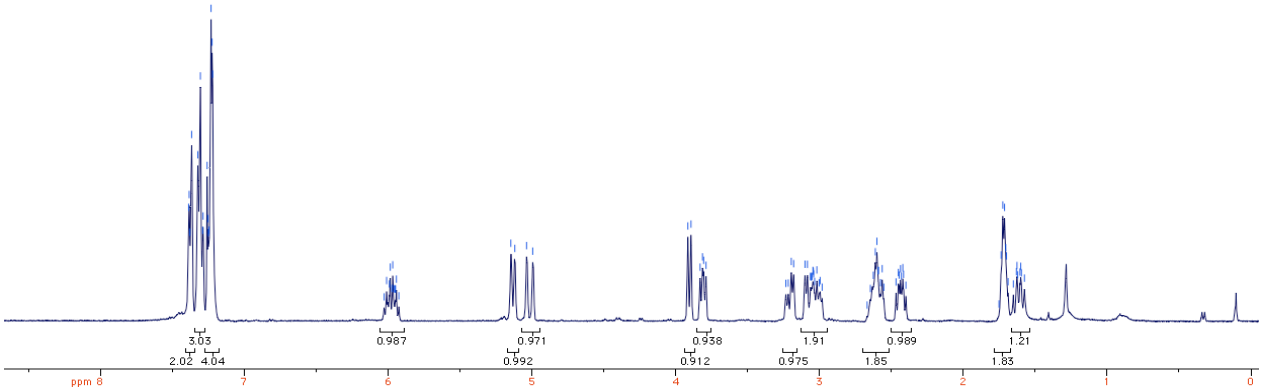


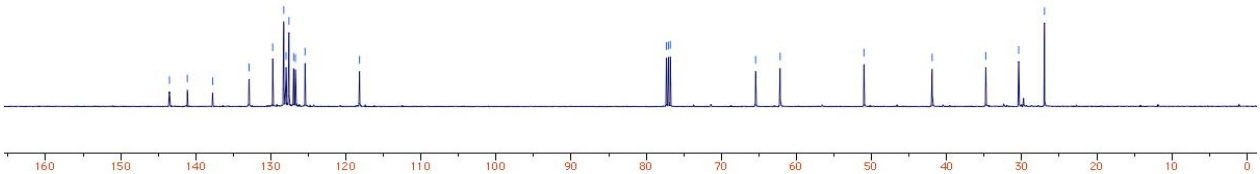


Pyrrolidine **4c** ($CDCl_3$)

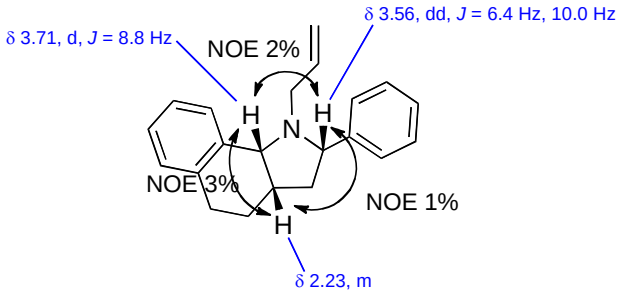


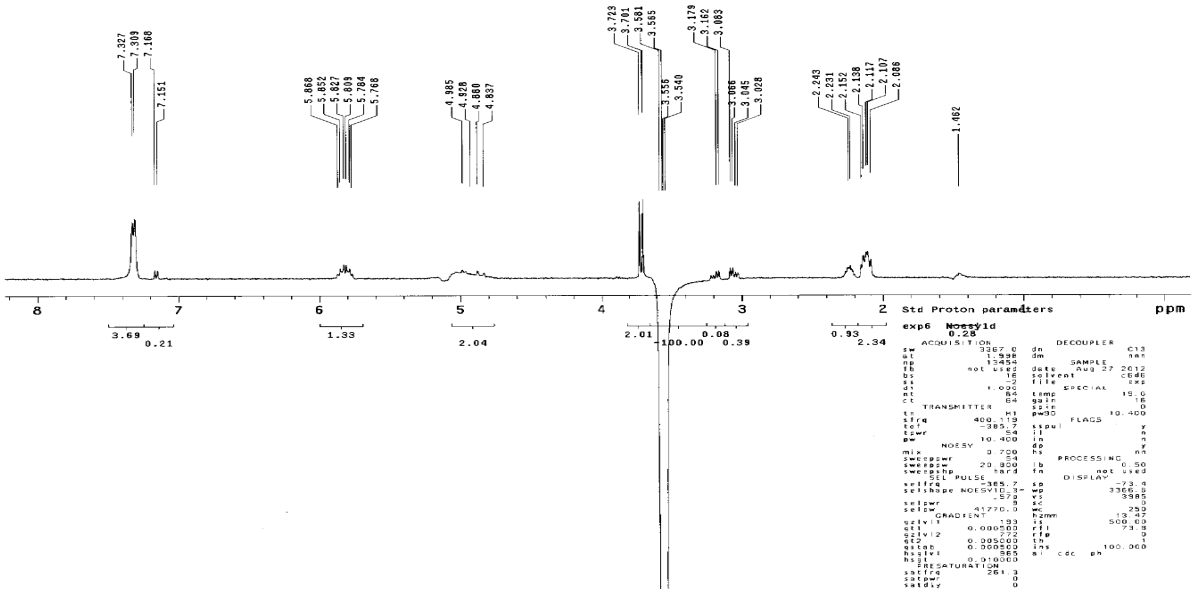


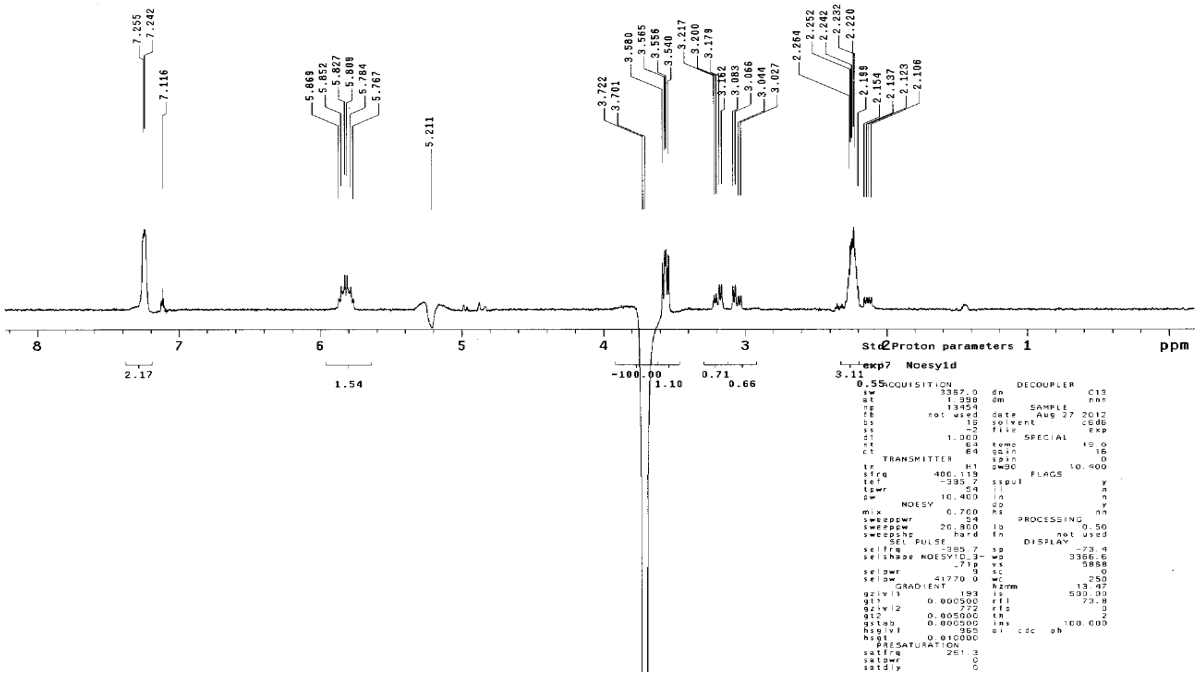




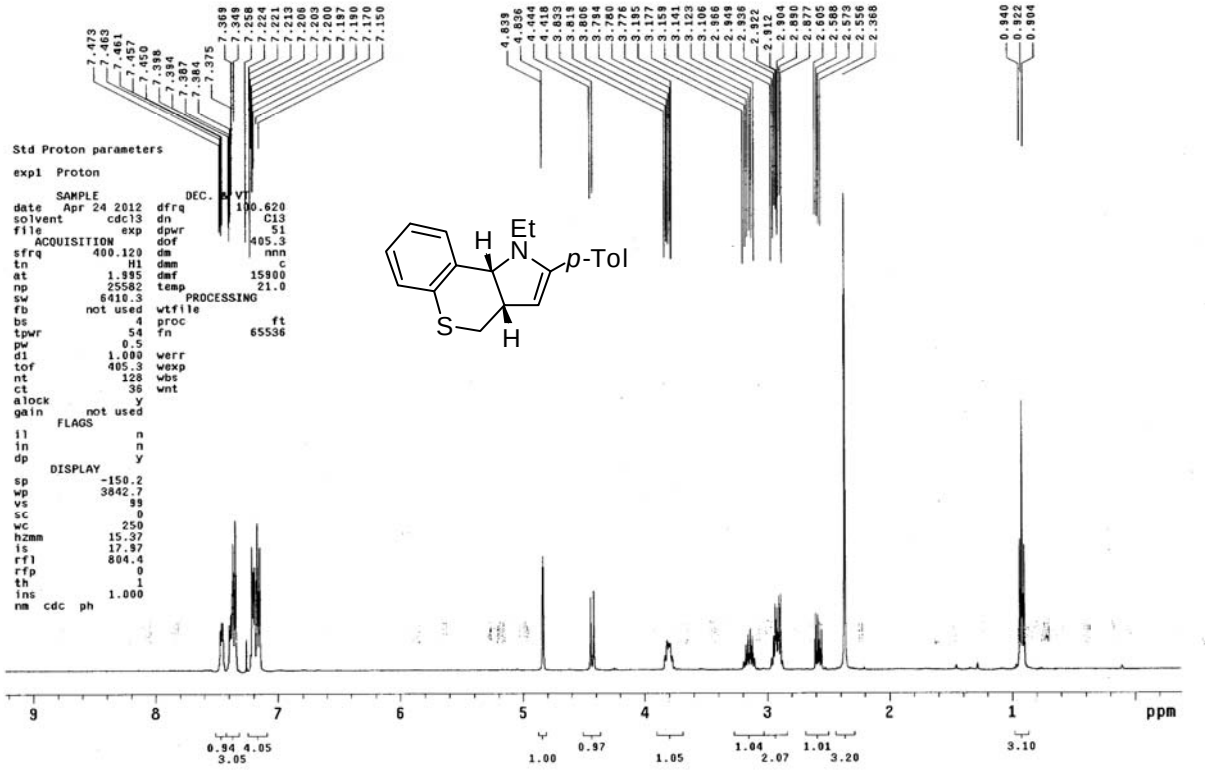
Summary of NOEs of key correlations in C_6D_6

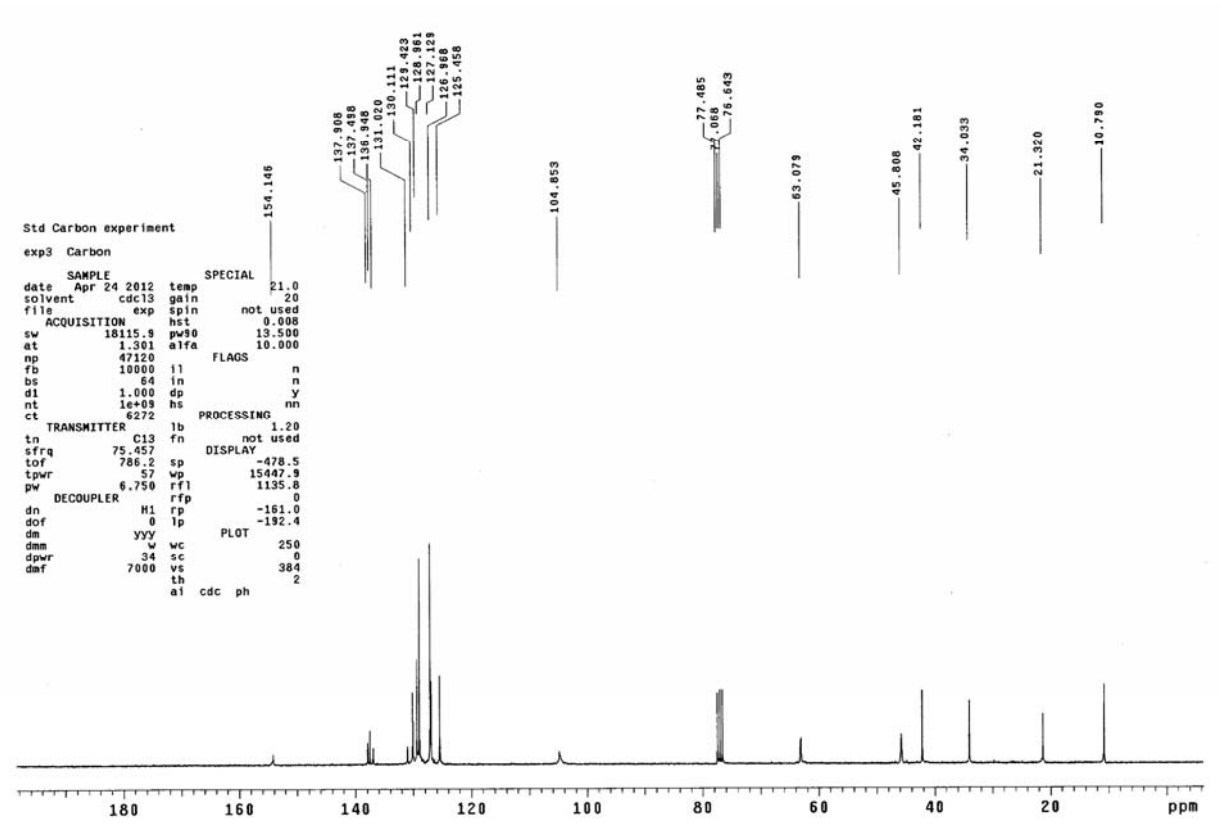




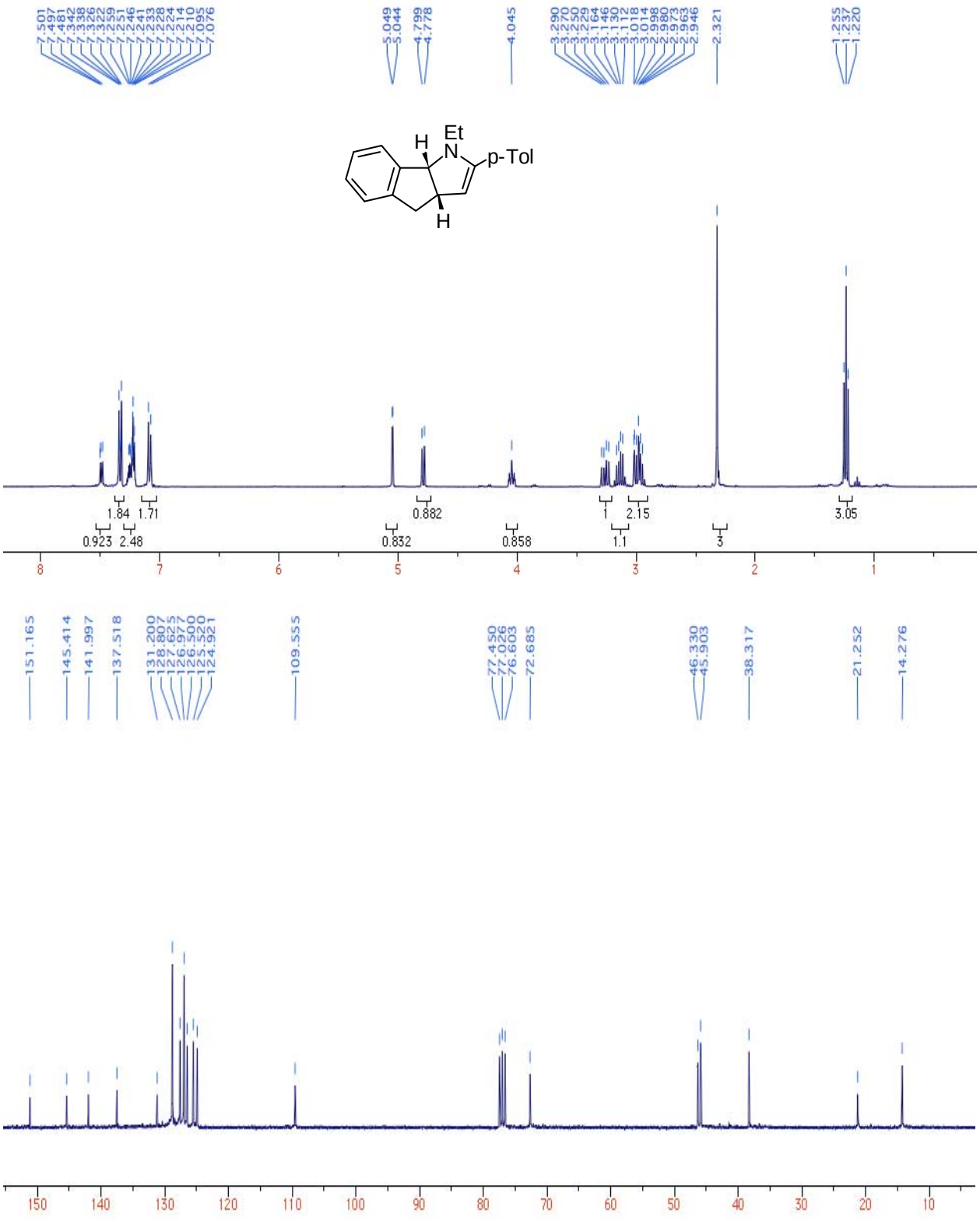


Pyrroline **3d** ($CDCl_3$)

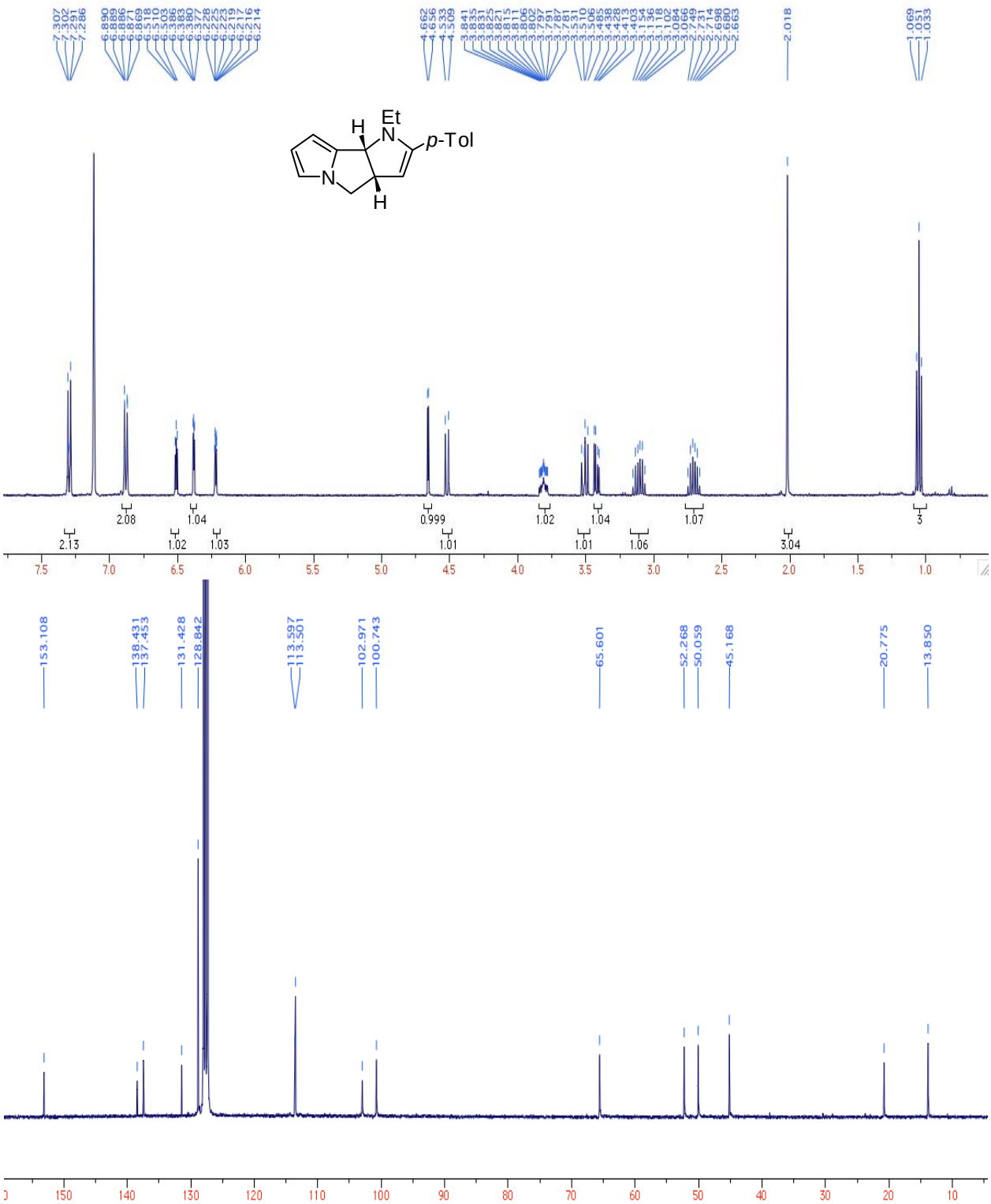




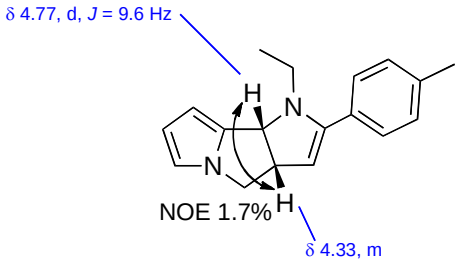
Pyrroline **3e** ($CDCl_3$)

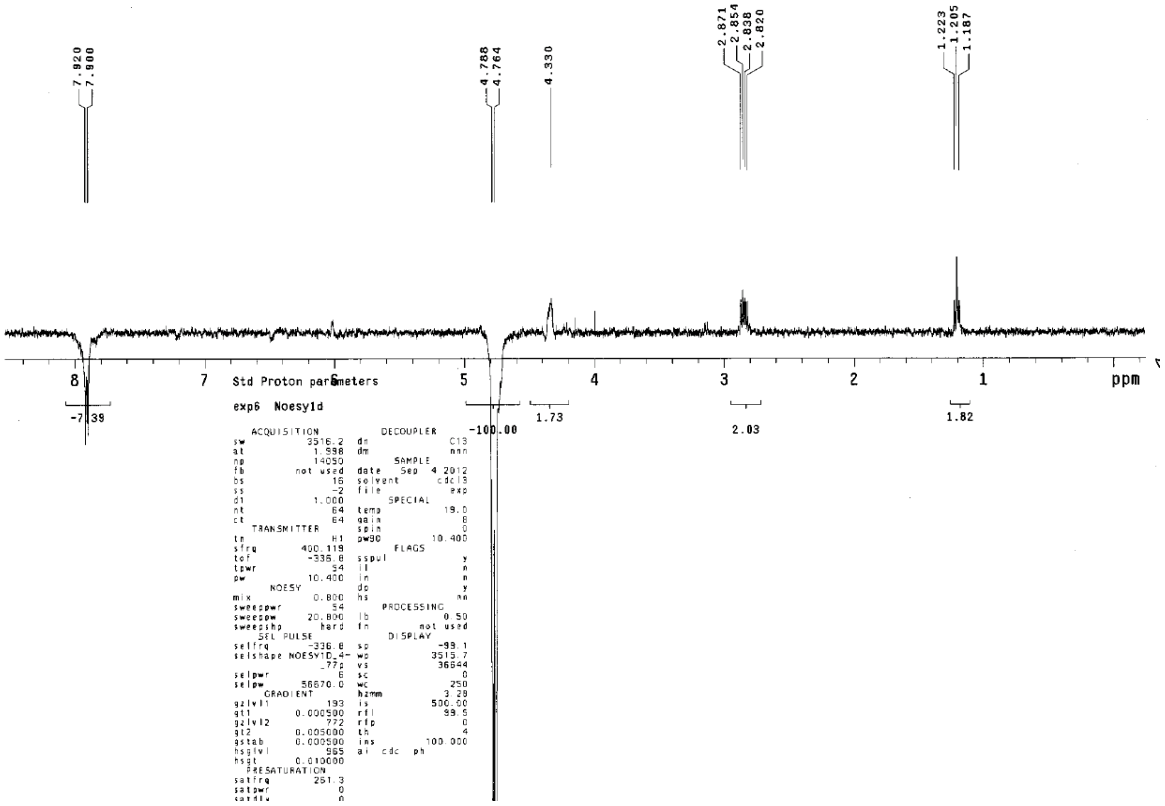


Pyrroline **3f** (C_6D_6)

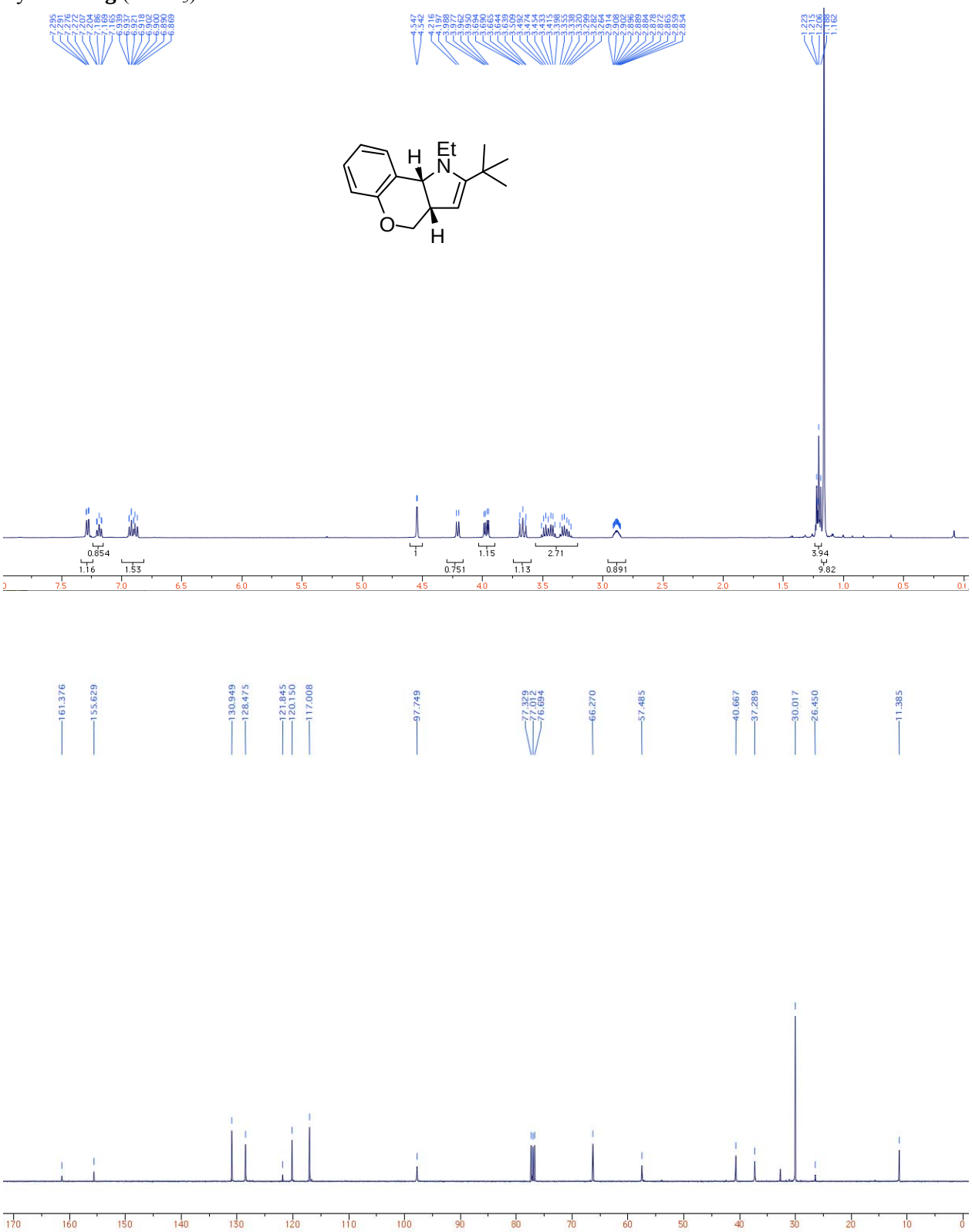


NOE of key correlation in $CDCl_3$

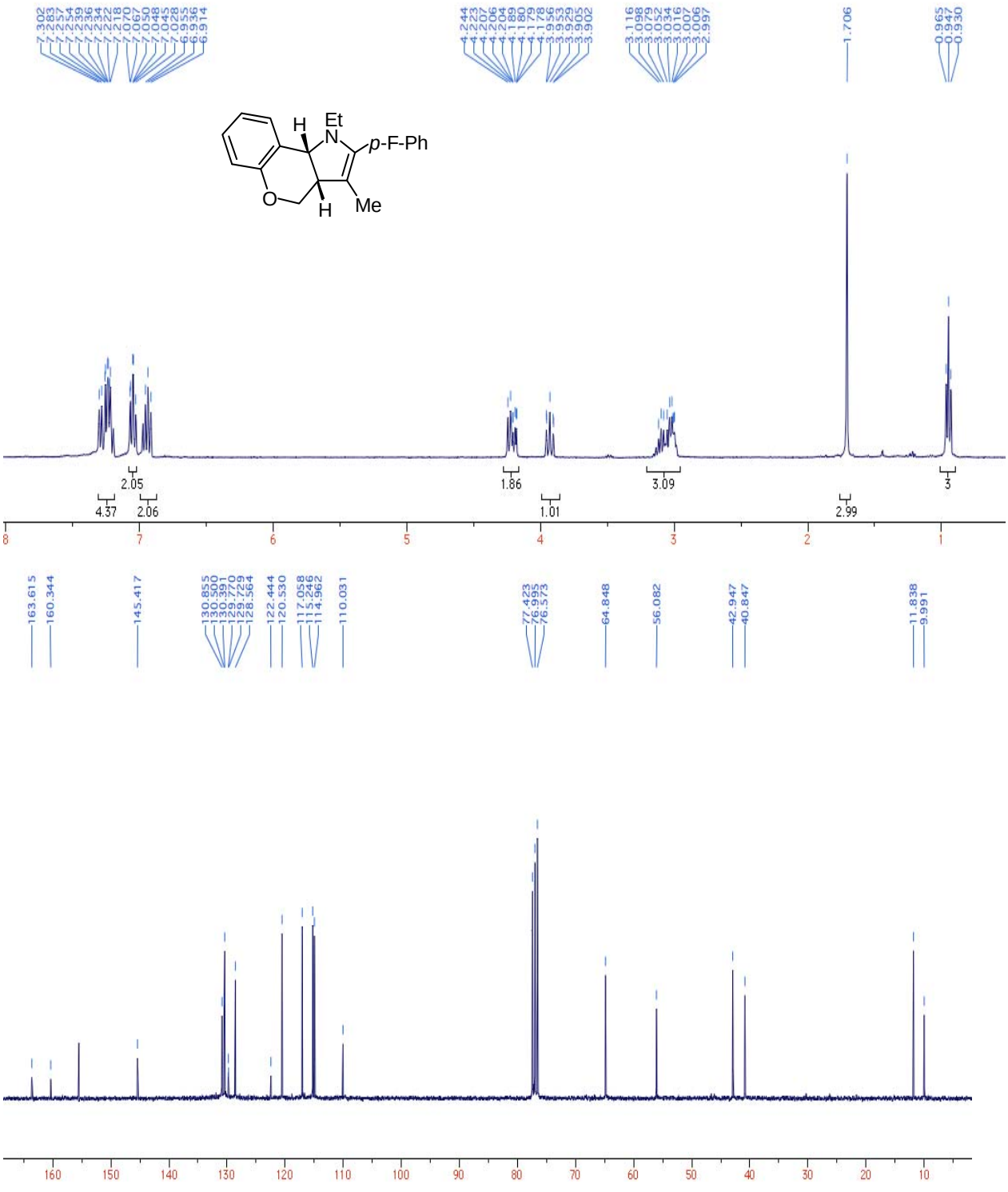




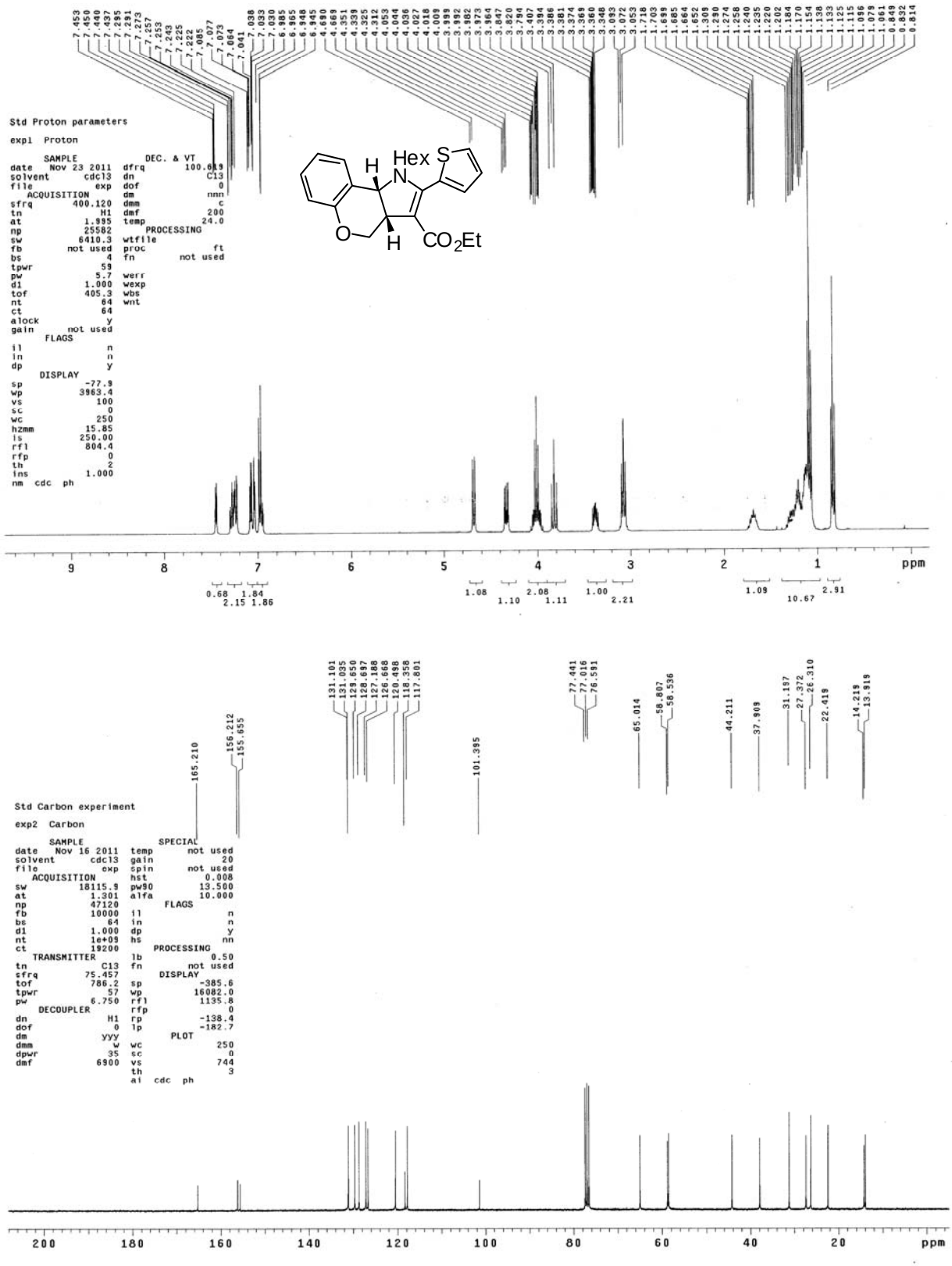
Pyrroline **3g** ($CDCl_3$)



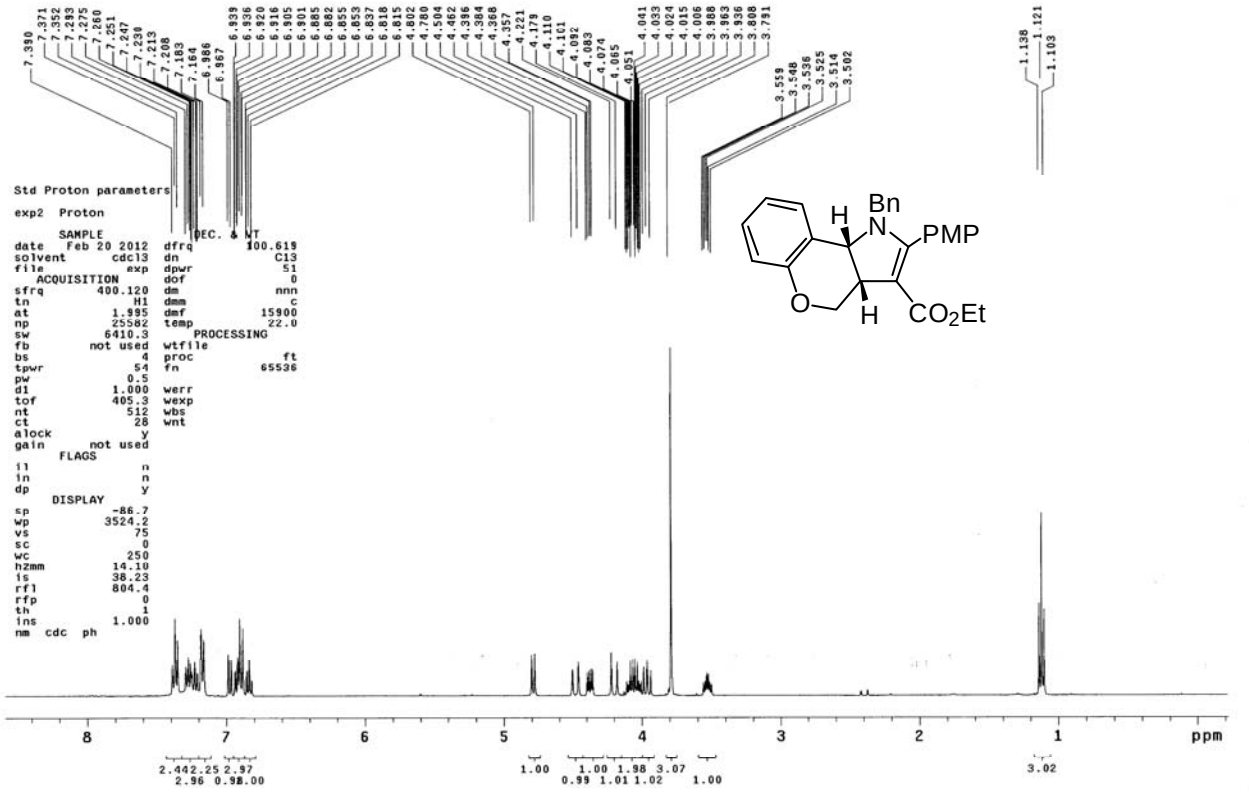
Pyrroline **3h** ($CDCl_3$)

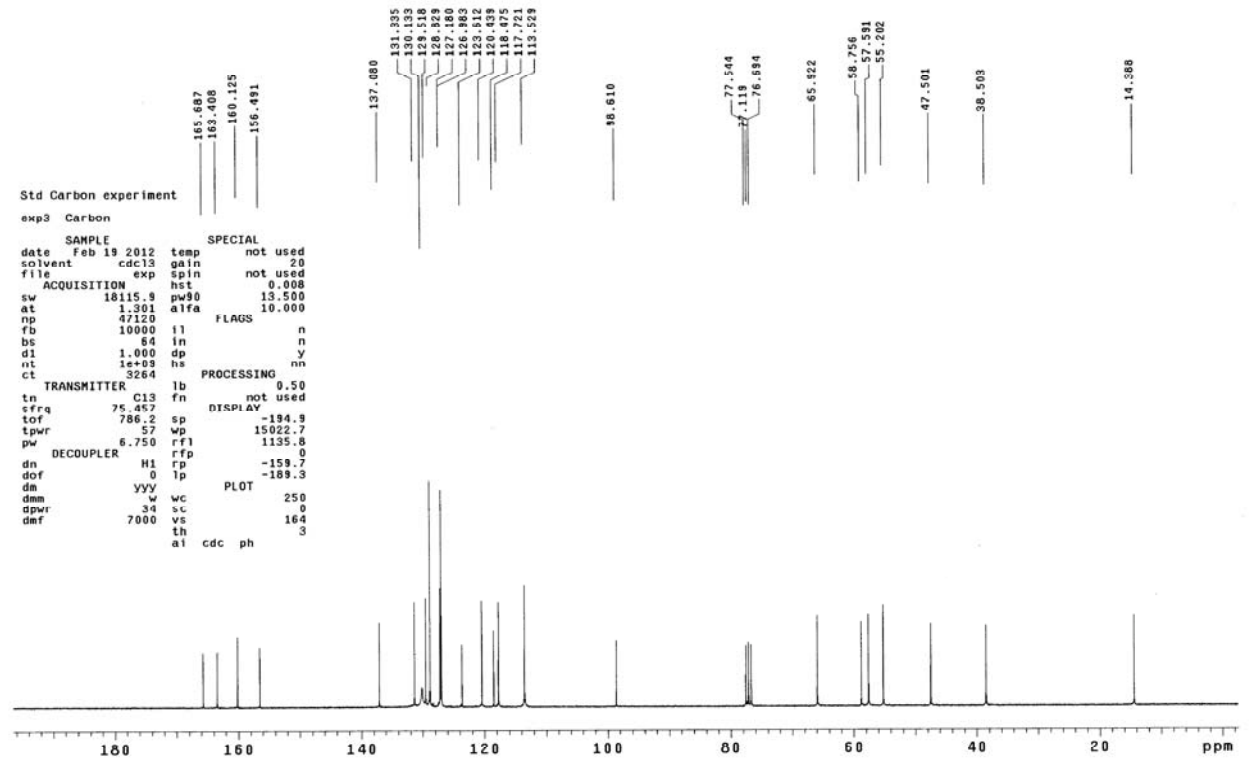


Pyrroline **3i** ($CDCl_3$)

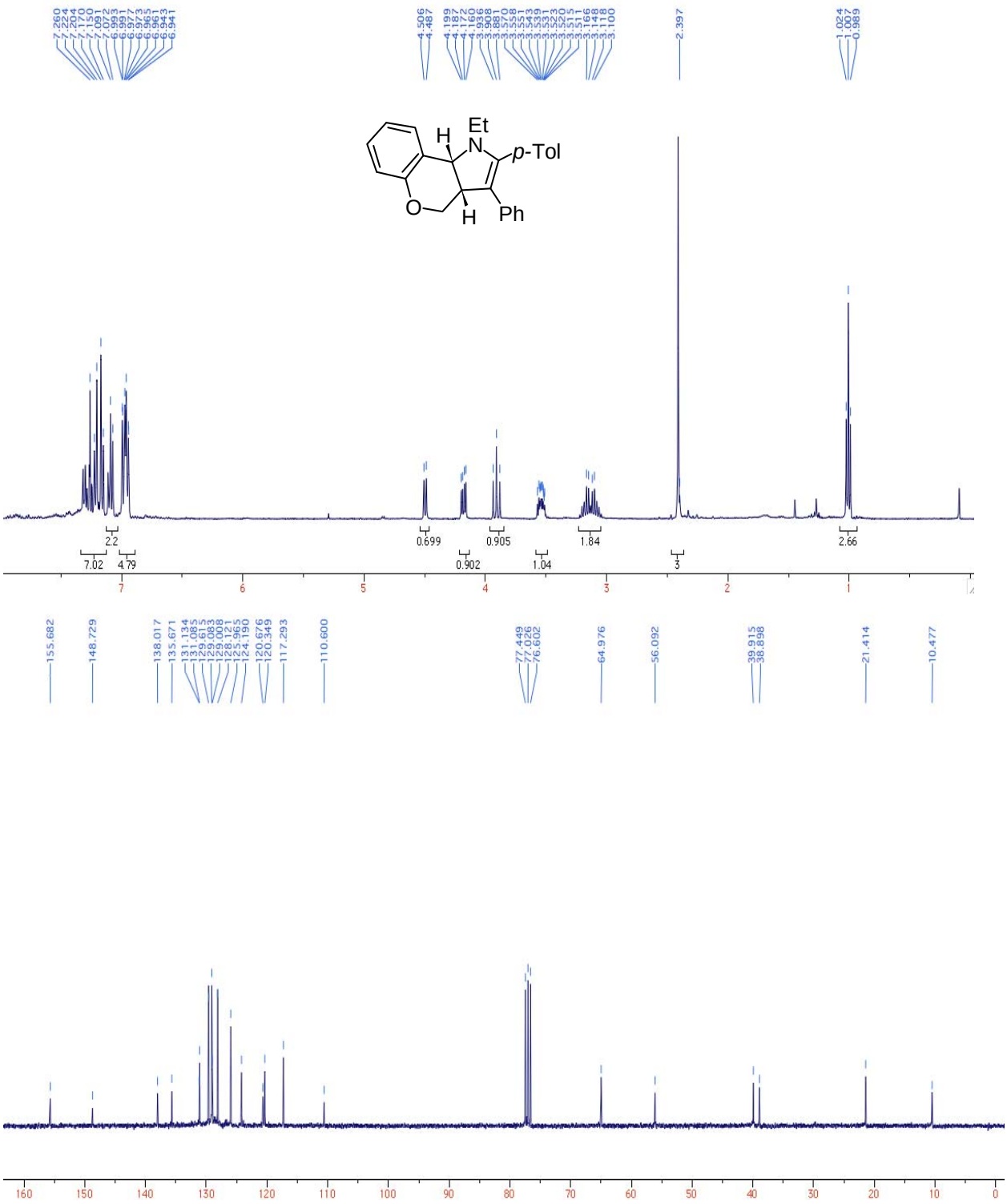


Pyrroline **3j** ($CDCl_3$)

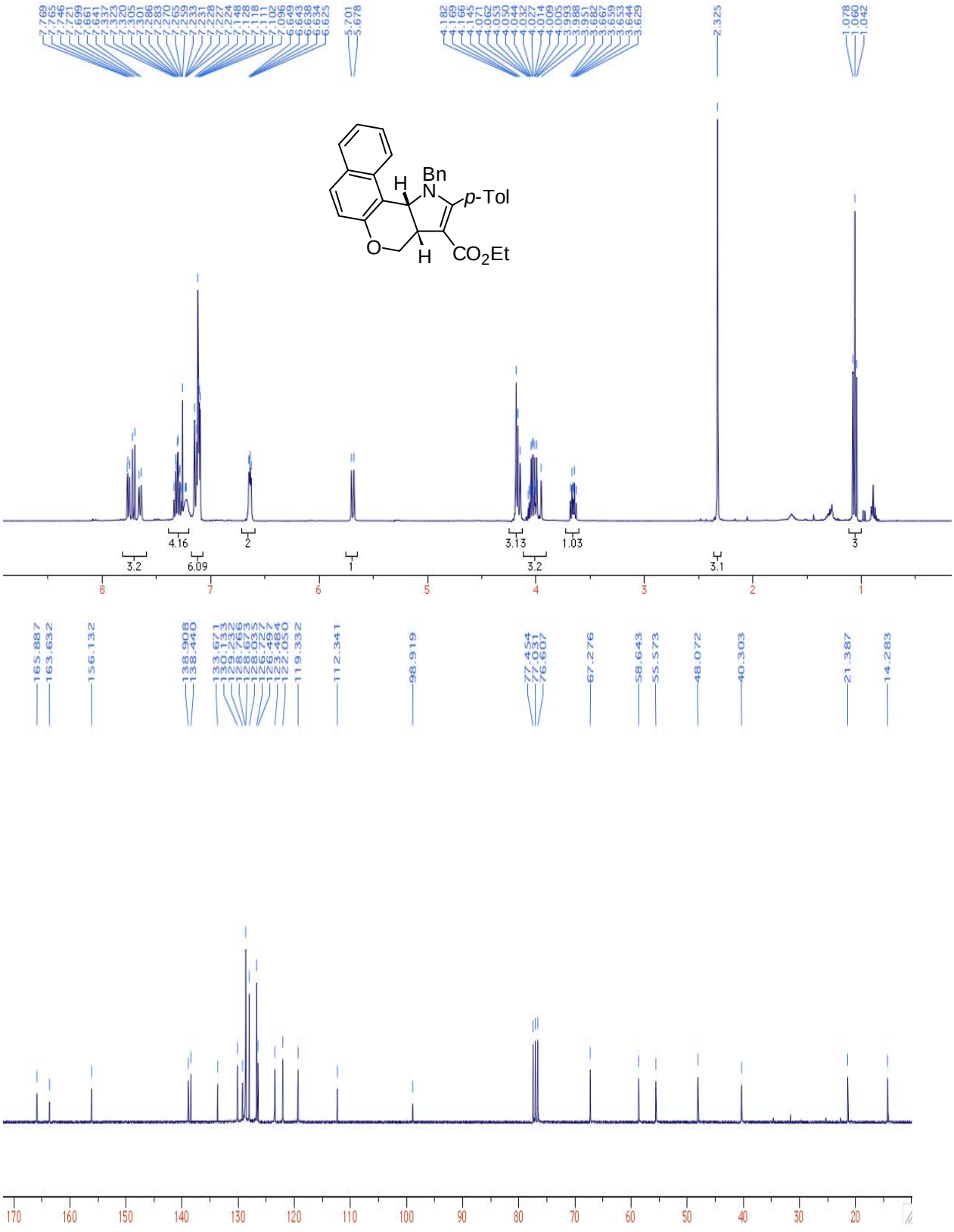




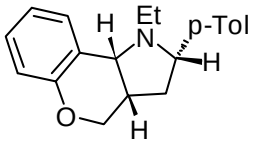
Pyrroline **3k** ($CDCl_3$)

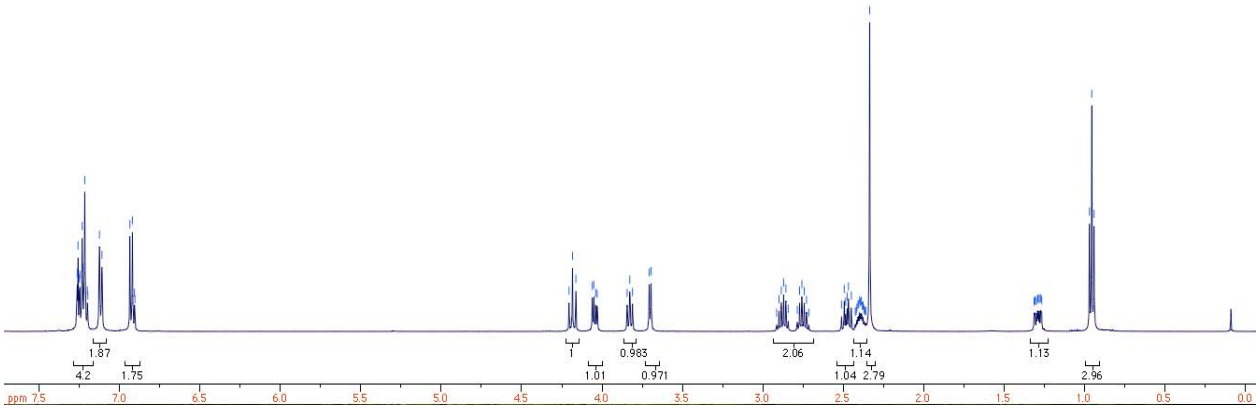


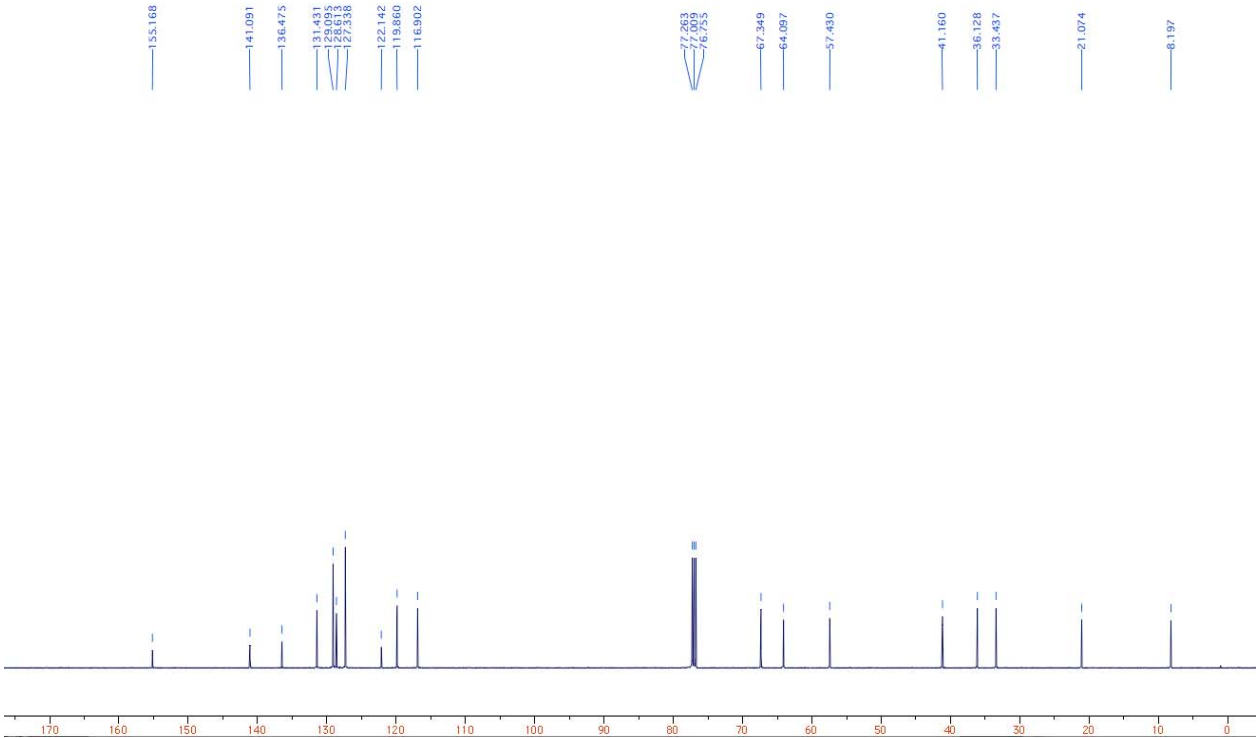
Pyrroline **3l** ($CDCl_3$)



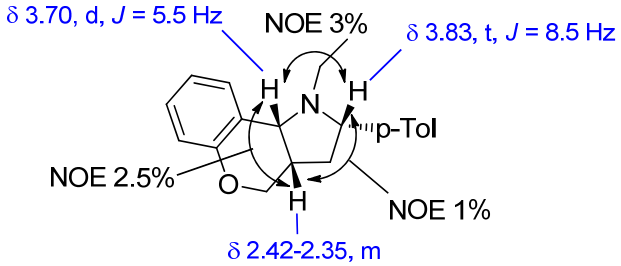
Pyrrolidine **4a** ($CDCl_3$)

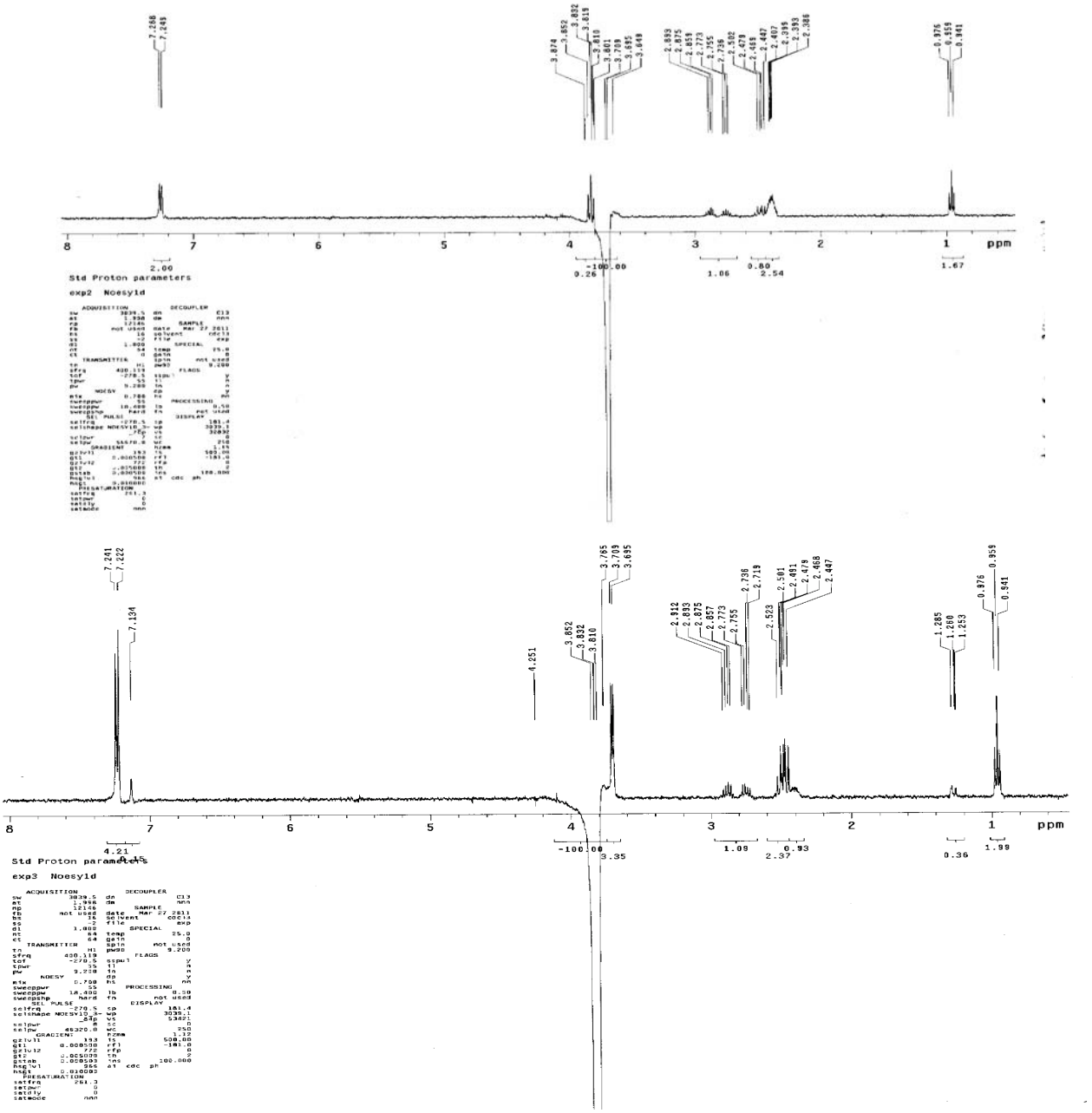




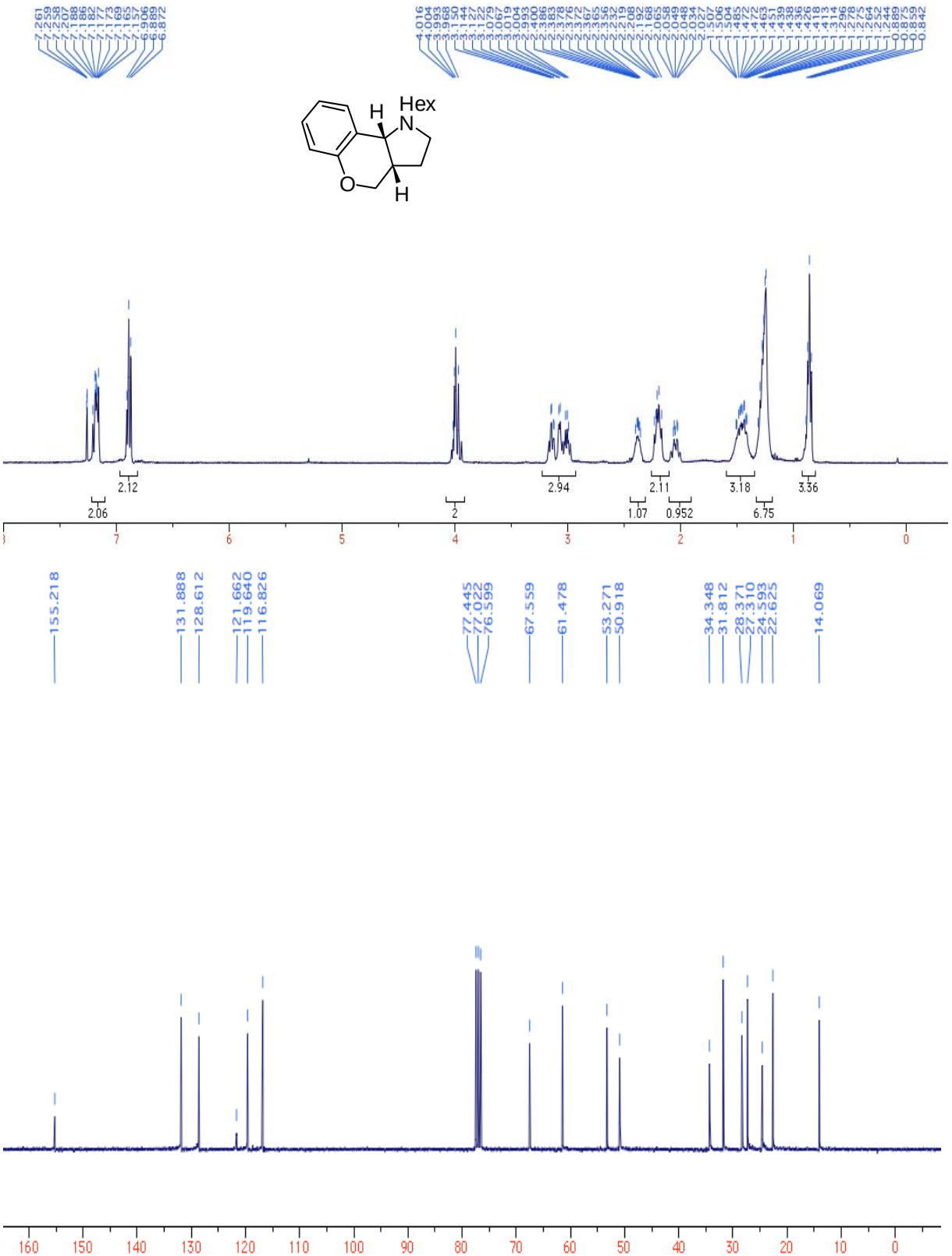


NOEs of key correlations





Pyrrolidine **4m** ($CDCl_3$)



Pyrrole **5k**