Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Electronic Supporting Information:

Contents

General Considerations

All reactions were carried out in a dry argon or nitrogen atmosphere using standard Schlenk or glove box techniques. Halogenated solvents were dried over P_2O_5, and nonhalogenated solvents were dried over sodium benzophenone ketyl. Deuterated solvents were ordered from Cambridge Isotope Laboratories, vented, stored over molecular sieves and distilled. All chemicals were purchased from commercial sources with purity over 95 % and used without further purification. Polysilazane "KiON HTT 1800" was purchased from Clariant Advanced Materials GmbH, Frankfurt (Germany) and used without further purification. NMR spectra were received using an INOVA 300 or 400 MHz spectrometer at 298 K. Chemical shifts are reported in ppm relative to the deuterated solvent. Elemental analyses were carried out on a Vario elementar EL *III*. X-ray crystal structure analyses were performed with a STOE-STADIVARI diffractometer [λ(Mo-K_α) = 0.71073 Å] equipped with an Oxford Cryostream low-temperature unit. Structure solution and refinement were accomplished with SIR-97 and SHELXL-2014[1,2]. GC analyses were carried out on an Agilent 6890N Network GC system equipped with a HP-5 column (30 m x 0.32 µm x 0.25 µm) using *n*-dodecane as internal standard. GC/MS analyses were carried out on an Agilent 7890A/MSD 5975C system equipped with a HP-5MS column (30 m x 0.32 µm x 0.25 µm). Ceramisation was carried out under nitrogen atmosphere in a high temperature furnace (Gero, Germany). All X-ray powder diffractograms were recorded by using a STOESTADE-P-diffractometer (CuK_α-Strahlung, 1.54178 Å) in θ-2θ-geometry and with a position sensitive detector. Transmission electron microscopy (TEM) was carried out by using a Varian LEO 9220 (200 kV) instrument. The sample was suspended in chloroform and sonicated for 5 min. Subsequently a drop of the suspended sample was placed on a grid (Plano S 166-3) and allowed to dry. High resolution transmission electron microscopy (HR-TEM) was carried out by using a Philips CM300 FEG/UT (300 kV) instrument. The sample was suspended in chloroform and sonicated for 2 min. Subsequently a drop of the suspended sample was placed on a grid with lacy carbon film and allowed to dry. EDX measurements were carried out by using a Zeiss Field-Emission-Scanning-Electron-Microscope (FESEM) „LEO 1530 GEMINI". The acceleration voltage was 1 - 5 kV. FT-IR measurements were performed using a Perkin-Elmer FTIR-spectrum 100. TGA measurements were carried out under nitrogen atmosphere by using a Netzsch

409 C instrument (5 °Cmin^{-1} heating rate up to 1000 °C). Milling of the catalyst was performed in a ball mill “Pulverisette 0” (Fritsch, Germany) for 15 min. ChemBET measurements were carried out by using a ChemBET Pulsar TPR/TPD instrument from Quantachrome. N_2 sorption was measure using a Nova2000e (Quantachrome). ICP-OES measurements were carried out by using a Vista-pro radical model from Varian.

Catalyst Synthesis

Synthesis of (4-methyl-pyridin-2-yl)-(2,4,6-trimethyl-phenyl)-amine $Ap^{TMA}H$ I:

(4-Methyl-pyridin-2-yl)-(2,4,6-trimethyl-phenyl)-amine $Ap^{TMA}H$ was synthesized according to a published procedure.[3] To 13.3 g (105 mmol) of 2-chloro-4-methylpyridine 17.77 g (103.5 mmol) of 2,4,6-trimethylaniline hydrochloride were added to get a mash. After stirring at 180 °C for 26 h the residue was dissolved in 50 mL of water and made alkaline with Na_2CO_3. The mixture was extracted three times with 75 mL of CH_2Cl_2 and dried over Na_2SO_4. Subsequent removing of the solvent yielded a residue which was dissolved in 200 mL of a hot 1:1 mixture of hexane and diethyl ether and filtered. After removal of the solvent the solid was re-crystallized in diethyl ether to give colourless crystals (9.26 g = 40.9 mmol = 39 %).

^{1}H NMR (400 MHz, C_6D_6, 298 K): δ = 8.11 (d, 1H, J_{H-H} = 17 Hz); 6.77 (s, 1H); 6.20 (d, 1H, J_{H-H} = 17 Hz); 5.89 (s, 1H); 2.18 (s, 6H); 2.15 (s, 3H); 1.72 (s, 3H) ppm.

Synthesis of iridium[(4-methyl-pyridin-2-yl)-(2,4,6-trimethyl-phenyl)-amine(cyclooctadiene)] [$IrAp^{TMA}$(cod)] II:

1.657 g (2.5 mmol) bis(1,5-cyclooctadien)-di-μ-methoxydiiridium were added to a solution of 1.132 g (5 mmol) $Ap^{TMA}H$ in 100 mL THF and stirred over night at room temperature. The solvent was removed *in vacuo* and the residue was extracted with either hexane or diethyl ether. The solvent was concentrated *in vacuo* and stored in a freezer at -30 °C yielding [$IrAp^{TMA}$(cod)] as orange crystals. (1.155 g = 2.20 mmol = 88 %).

^{1}H NMR (400 MHz, D_8-THF, 298 K): δ = 7.18 (d, 1H, J_{H-H} = 5.52 Hz); 6.79 (s, 2H); 5.87 (d, 1H, J_{H-H} = 5.52 Hz); 5.08 (s, 1H); 3.84 (m, 2H); 3.51 (m, 2H); 2.30 (s, 6H); 2.14 - 2.24 (m, 7H); 1.97 (s, 3H); 1.46 (m, 4H) ppm. ^{13}C NMR (103 MHz, CD_2Cl_2, 298 K): δ = 178.6, 152.9, 142.8, 139.9, 135.2, 134.2, 129.0, 109.5, 106.2, 65.3, 59.7, 32.7, 22.3, 21.1, 18.6 ppm.

Elemental analysis (%) for $C_{23}H_{29}IrN_2$ calcd: C 52.55, H 5.56, N 5.33; found: C 52.54, H 5.54, N 5.39.

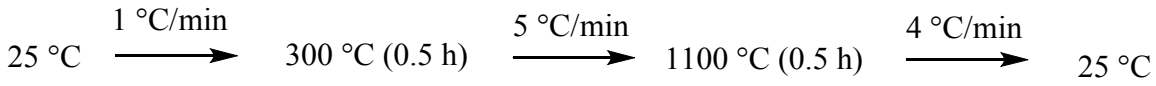
Single X-ray data:

Compound	**[IrAp^{TMA}(cod)]**
Formula	$C_{23}H_{29}IrN_2$
Formula weight	525.68
Crystal system	triclinic
Space group	*P-1*
a [Å]	7.8138(3)
b [Å]	14.5845(5)
c [Å]	19.1054(7)
α [°]	68.745(3)
β [°]	87.157(3)
γ [°]	75.844(3)
Cell volume [Å^3]	1965.70(13)
Z	4
Crystal size [mm^3]	0.211x0.188x0.186
Habit	block
Colour	orange
Density [gcm^{-3}]	1.776
T [K]	133(2)
Theta range	1.555 – 28.973
Unique reflections	41743
Observed reflections [I > 2s(I)]	28827
Parameters	478
wR_2 (all data)	0.1450

CCDC: 1014360

Ceramization:

Under vigorous stirring 1.0 g HTT1800 was added drop wise to a solution of 817 mg (1.55 mmol) [IrAp^{TMA}(cod)] in 15 mL THF. The solvent was removed slowly under reduced pressure and the resulting orange-brown solid was pyrolyzed under N_2 atmosphere with the following program:



The ceramic yield was 72 %. After ball milling for 15 minutes, the catalyst was pre-treated by applying 20 bar H_2 for 3 days in an aqueous suspension.

Characterisation of Ir@SiCN Catalyst

FT-IR measurements:

FT-IR measurements were carried out to study the crosslinking of polysilazane HTT1800 and [IrAp^{TMA}(cod)] (Fig. 1).

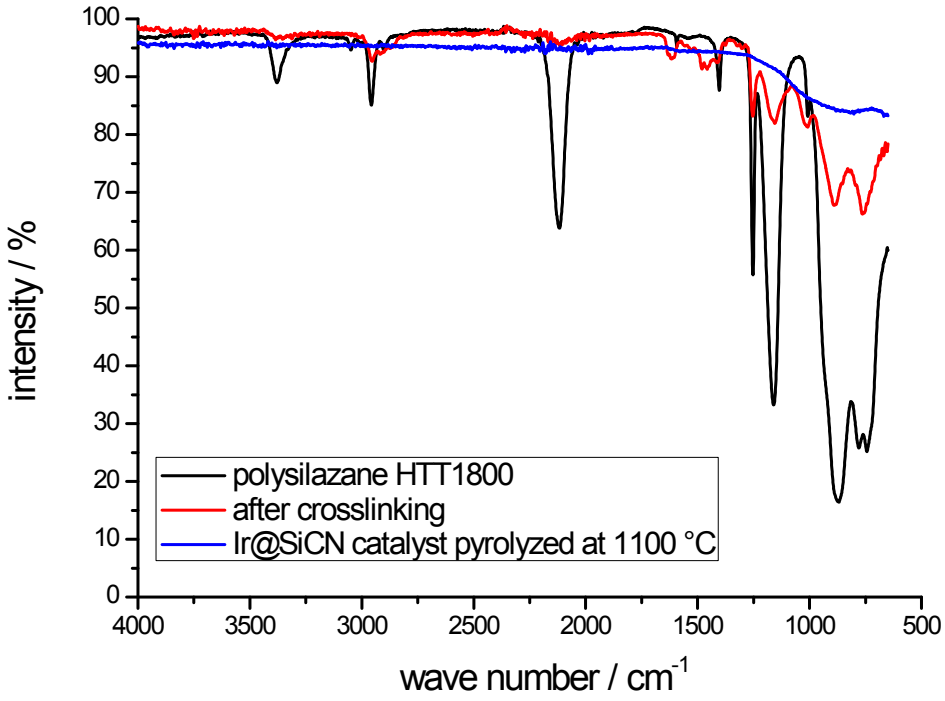


Fig. 1: FT-IR study of the Ir@SiCN nano composite synthesis

^{1}H NMR spectroscopy:

60 mg HTT1800 was added to a solution of 50 mg [IrAp^{TMA}(cod)] in 2 mL THF. The solvent was removed under reduced pressure and the mixture became solid. The "green body" was extracted with 1 mL of C_6D_6. ^{1}H NMR measurement indicate the presence of only traces of HTT1800 and [IrAp^{TMA}(cod)].

TEM measurements:

TEM measurements an overview over the the Ir@SiCN catalyst to show the homogenously distributed very small nanometer sized Ir particles (Fig. 2, left).

Furthermore HR-TEM measurements were performed to verify the metallic nature of the Ir particles by analysis of the FFT (Fig. 2, right).

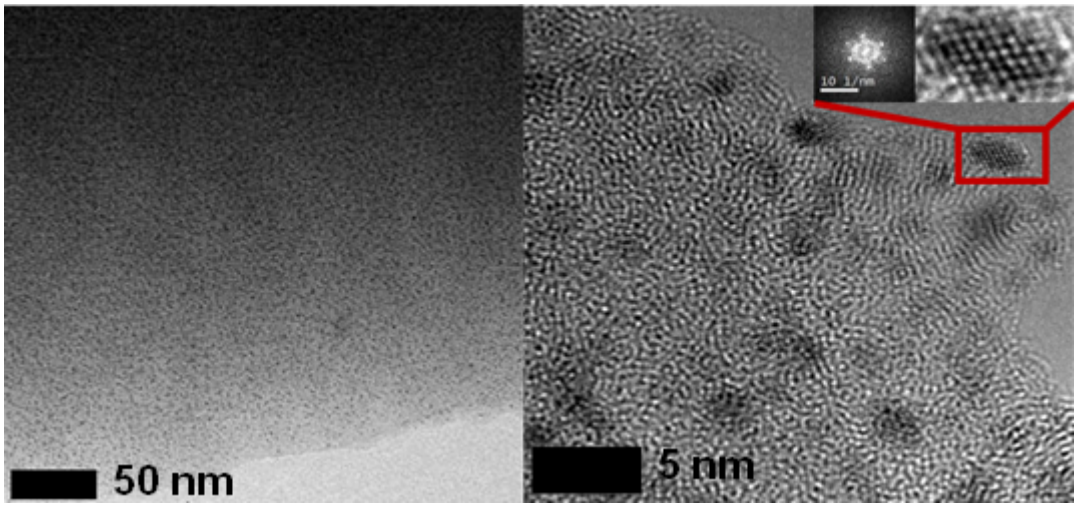


Fig. 2: TEM analysis of the Ir@SiCN catalyst. left: overview; right: HR-TEM.

ICP-OES-analysis:

50 mg of the sample was solved in 1.5 mL HNO_3 (65 %, distilled), 4.5 mL HCl (32 %, p.a.) and 1 mL HF (40 %) and heated in the microwave at 170 °C for 7 min (80 % power), at 180 °C for 7 min (85 % power) and at 195 °C for 20 min (90 % power).

Result: 18.9 wt% Ir content

Powder XRD analysis:

Powder XRD analysis was applied to verify the existence of Ir nanoparticles and to prove the amorphous character of the SiCN support (Fig. 3). Reference card for cubic crystalline Iridium was 00-046-1044.[4]

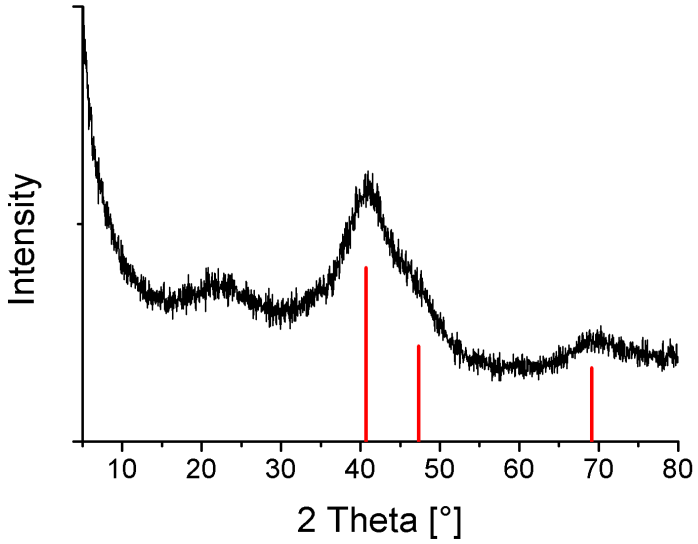


Fig. 3: Powder XRD analysis of the Ir@SiCN catalyst (red: Reflexes of cubic crystalline iridium; reference card: 00-046-1044)

EDX measurement:

Iridium as well as all other elements of the SiCN support could be detected (Fig. 4).

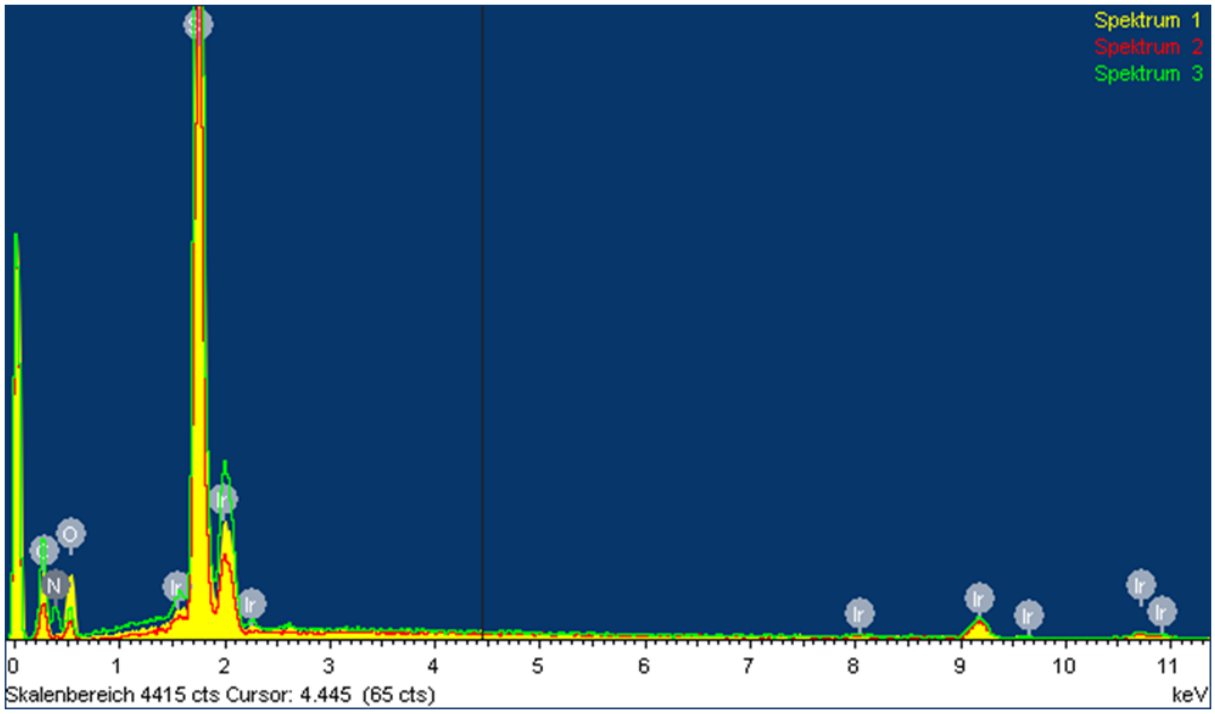


Fig. 4: EDX mapping of the Ir@SiCN catalyst

ChemBET measurements:

182 mg of the Ir@SiCN catalyst was pre-treated under helium and nitrogen atmosphere at 500 °C for 3 hours. After cooling the sample to RT, hydrogen gas was added portion wise using a 50 µl injection loop. Analysis of the results was performed with the free version of the program fytik 0.9.8.[5]

Metal dispersion on surface of Ir@SiCN catalyst: 6.61 %

N_2 sorption

N_2 sorption experiments revealed no porosity of the Ir@SiCN nano composite as synthesized

Reusability of the Ir@SiCN catalyst:

200 mg Ir@SiCN, cycloheptanol (2892 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 4 mL diglyme and KO*t*Bu (1.37 g, 12.0 mmol) were stirred in a pressure tube equipped with a pressure equalization device for 24 h at 120 °C. The mixture was quenched with 3 mL water and extracted 2 times with 15 mL diethyl ether. The extract was dried over Na_2SO_4 and the yield of 2-ethyl-1,5,6,7,8,9-hexahydro-cyclohepta[*b*]pyrrole was determined by GC. The catalyst was recovered by centrifugation, washed with water (1x) and acetone (2x) and used for the next run. The results are shown in Fig. 5.

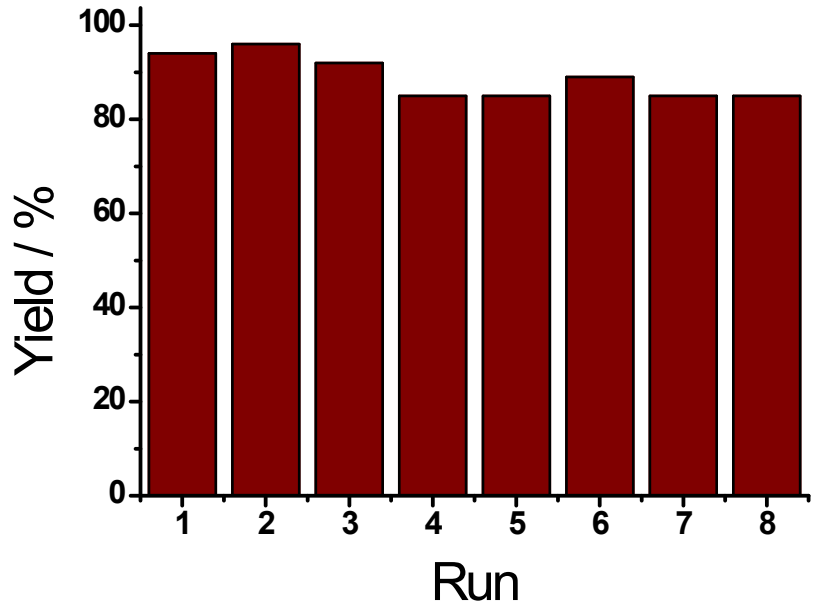


Fig. 5: Reusability of the Ir@SiCN catalyst; the catalyst was recovered after each run

Leaching experiments:

1: 200 mg Ir@SiCN catalyst and 1.374 mg KO*t*Bu were stirred in 6 mL diglyme at 120 °C for 20 h. The solid catalyst was centrifugated and the supernatant basic solution was used as "catalyst" for pyrrole synthesis:

565 µl (6.0 mmol), 2-amino-1-butanol and 2904 µl (24.0 mmol) 1-phenylethanol were added to the centrifugate and stirred at 120 °C (oil bath temperature) for 24 h. After extraction with diethyl ether the product 2-ethyl-5-phenyl-1*H*-pyrrole could not be detected by GC.

2: 50 mg Ir@SiCN catalyst and 300 mg KO*t*Bu were stirred in 3 mL H_2O at 120 °C (pressure tube) for 19 h. The solid catalyst was centrifugated and the supernatant solution analysed by ICP-OES (see ICP-OES analysis). 0.02 % of the applied Iridium could be found.

Use of other (commercial) heterogeneous iridium catalysts

Ir/C (1 wt.-%; 50 % water wet), Ir/Al_2O_3 (1 wt.-%) and $Ir/CaCO_3$ (5 wt.-%) were received from Alfa Aesar and used without further treatment or purification. Ir@MIL101 (5 wt.-%) was prepared in our group by chemical vapour deposition. The amount of active metal was the same as in 200 mg of the above used Ir@SiCN catalyst.

Ir/C:

508 mg Ir/C, 1-phenylethanol (2904 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, and KO*t*Bu (1.37 g, 12.0 mmol) were heated at 120 °C (oil bath temperature) for 24 h. After extraction with diethyl ether the yield was determined by GC. The catalyst was recovered by centrifugation, washed with water (1x) and acetone (2x) and used for one more run.

Ir/Al_2O_3:

254 mg Ir/Al_2O_3, 1-phenylethanol (2904 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, and KO*t*Bu (1.37 g, 12.0 mmol) were heated at 120 °C (oil bath temperature) for 24 h. After extraction with diethyl ether the yield was determined by GC. The catalyst was recovered by centrifugation, washed with water (1x) and acetone (2x) and used for one more run.

$Ir/CaCO_3$:

50 mg $Ir/CaCO_3$, 1-phenylethanol (2904 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, and KO*t*Bu (1.37 g, 12.0 mmol) were heated at 120 °C (oil bath temperature) for 24 h. After extraction with diethyl ether the yield was determined by GC. The catalyst was recovered by centrifugation, washed with water (1x) and acetone (2x) and used for one more run.

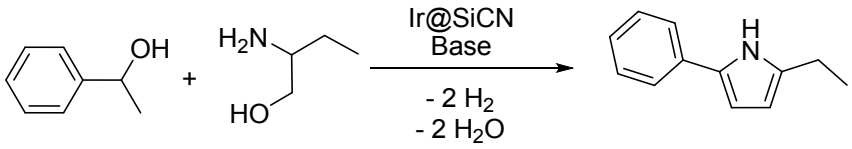
Ir@MIL101:

50.8 mg Ir@MIl101, 1-phenylethanol (2904 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, and KO*t*Bu (1.37 g, 12.0 mmol) were heated at 120 °C (oil bath temperature) for 24 h. After extraction with diethyl ether the yield was determined by GC.

Screening Reactions

General screening procedure:

In a pressure tube catalyst, solvent, alcohol, amino alcohol and base were combined. The pressure tube was closed with a semi-permeable membrane, added to a pressure equalizer, heated to the desired temperaure and stirred for 24 h. The reaction mixture was cooled to room temperature under argon atmosphere and 1 mL of water as well as 5 mL diethyl ether were added. *n*-Dodecane was added as internal standard and after shaking, a small fraction of the organic phase was analyzed by GC. The following reaction was investigated.



Supplementary Table 1: Alcohol ratio

Amino Alcohol / Secondary Alcohol [eq.]	Yield [%]
1 : 3	34
1 : 2	51
1 : 1.5	54
1 : 1.1	53
1.1 : 1	61
1.5 : 1	68
2 : 1	45
3 : 1	55

Reaction conditions: 1.1 eq. KO^{t}Bu (according to secondary alcohol), 1.5 mL diglyme, 50 mg (0.33 mol-%) Ir@SiCN catalyst, 24 h, 120°C (oil bath temperature) (reaction connected to a pressure equalisation). Yields were determined by GC analyses with *n*-dodecane as internal standard.

Supplementary Table 2: Temperature screening

Temperature [°C] (Oil Bath)	Yield [%]
90	33
105	42
120	68
130	68
150	54

Reaction conditions: 1 eq. 2-amino-1-butanol (1 mmol, 94.1 µl), 1.5 eq. 1–phenylethanol (1.5 mmol, 181.4 µl), 1.1 eq. KO^{t}Bu (according to secondary alcohol), 1.5 mL diglyme, 50 mg (0.33 mol-%) Ir@SiCN catalyst, 24 h (reaction connected to a pressure equalisation). Yields were determined by GC analyses with *n*-dodecane as internal standard.

Supplementary Table 3: Solvent screening

Solvent	Yield [%]
THF	12
Diglyme	68
Dioxane	41
Toluene	56
Water	0

Reaction conditions: 1 eq. 2-amino-1-butanol (1 mmol, 94.1 µl), 1.5 eq. 1–phenylethanol (1.5 mmol, 181.4 µl), 1.1 eq. KO^{t}Bu (according to secondary alcohol), 1.5 mL solvent, 50 mg (0.33 mol-%) Ir@SiCN catalyst, 120 °C or reflux, 24 h (reaction connected to a pressure equalisation). Yields were determined by GC analyses with *n*-dodecane as internal standard.

Supplementary Table 4: Solvent Amount

Amount Diglyme [mL]	Yield [%]
3	50
1.5	68
0.5	64

Reaction conditions: 1 eq. 2-amino-1-butanol (1 mmol, 94.1 µl), 1.5 eq. 1–phenylethanol (1.5 mmol, 181.4 µl), 1.1 eq. KO^{t}Bu (according to secondary alcohol), 50 mg (0.33 mol-%) Ir@SiCN catalyst, 120 °C (oil bath temperature), 24 h (reaction connected to a pressure equalisation). Yields were determined by GC analyses with *n*-dodecane as internal standard.

Supplementary Table 5: Base screening

Base	Yield [%]
KO^{t}Bu	68
NaO^{t}Bu	58
KOH	61
KH	45
K_2CO_3	0

Reaction conditions: 1 eq. 2-amino-1-butanol (1 mmol, 94.1 µl), 1.5 eq. 1–phenylethanol (1.5 mmol, 181.4 µl), 1.1 eq. base (according to secondary alcohol), 1.5 mL diglyme, 50 mg (0.33 mol-%) Ir@SiCN catalyst, 120 °C (oil bath temperature), 24 h (reaction connected to a pressure equalisation). Yields were determined by GC analyses with *n*-dodecane as internal standard.

Supplementary Table 6: Amount of KO^{t}Bu

Base Amount According to Secondary Alcohol [eq.]	Yield [%]
2	34
1.5	50
1.1	68
1	73
0.9	72
0.8	66
0.5	57
0.1	12
0	0

Reaction conditions: 1 eq. 2-amino-1-butanol (1 mmol, 94.1 µl), 1.5 eq. 1–phenylethanol (1.5 mmol, 181.4 µl), 1.5 mL diglyme, 50 mg (0.37 mol-%) Ir@SiCN catalyst, 120 °C (oil bath temperature), 24 h (reaction connected to a pressure equalisation). Yields were determined by GC analyses with *n*-dodecane as internal standard.

Supplementary Table 7: Screening of catalyst loading

Catalyst Loading [mol-%]	Yield [%]
0.33	68
0.66	73
1.98	66

Reaction conditions: 1 eq. 2-amino-1-butanol (1 mmol, 94.1 µl), 1.5 eq. 1–phenylethanol (1.5 mmol, 181.4 µl), 1.0 eq. KO^{t}Bu (according to secondary alcohol), 1.5 mL diglyme, 120 °C (oil bath temperature), 24 h (reaction connected to a pressure equalisation). Yields were determined by GC analyses with *n*-dodecane as internal standard.

Screen-Up & Optimization of Base to Alcohol ratio:

The consumption of 1-phenylethanol in conjunction with high amounts of base was always 90-100 %. Therefore the base to alcohol ratio had to be optimized to increase

the yield of the desired product. Therefore the amount of KO^{t}Bu was decreased to 0.5 eq. according to the alcohol:

Supplementary Table 8: Temperature screening II

Temperature [°C] (Oil Bath)	Yield [%]
100 (42 h)	20
120	68
130	72

Reaction conditions: 1 eq. 2-amino-1-butanol (6 mmol, 565 µl), 1.5 eq. 1–phenylethanol (9 mmol, 1088 µl), 0.5 eq. KO^{t}Bu (according to secondary alcohol), 300 mg (0.33 mol-%) Ir@SiCN catalyst, 9 mL diglyme, 24 h (reaction connected to a pressure equalisation). Yields were determined by GC analyses with *n*-dodecane as internal standard. The increase in conversion from 120 to 130 °C seemed minor and a temperature of 120 °C was regarded as optimal in terms of a good functional group tolerance.

Supplementary Table 9: Solvent Amount II

Amount Diglyme [mL]	Yield [%]
6	74
9	68
12	53

Reaction conditions: 1 eq. 2-amino-1-butanol (6 mmol, 565 µl), 1.5 eq. 1–phenylethanol (9 mmol, 1088 µl), 0.5 eq. KO^{t}Bu (according to secondary alcohol), 300 mg (0.33 mol-%) Ir@SiCN catalyst, 120 °C (oil bath temperature), 24 h (reaction connected to a pressure equalisation). Yields were determined by GC analyses with *n*-dodecane as internal standard.

Supplementary Table 10: Screening of catalyst loading II

Catalyst Loading [mol-%]	Yield [%]
0.12	58
0.33	68
0.50	75

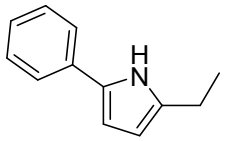
Reaction conditions: 1 eq. 2-amino-1-butanol (6 mmol, 565 µl), 1.5 eq. 1–phenylethanol (9 mmol, 1088 µl), 0.5 eq. KO^{t}Bu (according to secondary alcohol), 120 °C (oil bath temperature), 6 mL diglyme, 24 h (reaction connected to a pressure equalisation). Yields were determined by GC analyses with *n*-dodecane as internal standard. A catalyst loading of 0.33 mol% seemed the optimum in terms of high conversion and low catalyst loading.

Supplementary Table 11: Alcohol ratio

Amino Alcohol / Secondary Alkohol [eq.]	Yield [%]
1.5 : 1	68
2 : 1	74
4 : 1	96

Reaction conditions: 0.5 eq. KO^{t}Bu (according to secondary alcohol), 200 mg (0.33 mol-%) Ir@SiCN catalyst, 120 °C (oil bath temperature), 6 mL diglyme, 24 h (reaction connected to a pressure equalisation). Yields were determined by GC analyses with *n*-dodecane as internal standard.

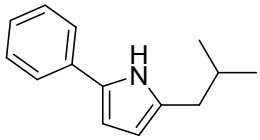
Characterisation of the Pyrrole Products



1a: 2-ethyl-5-phenyl-1*H*-pyrrole:

200 mg Ir@SiCN, 1-phenylethanol (2904 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 40:1 pentane: Et_2O; Yield: 0.887 g = 5.18 mmol = 86 % as colourless solid. M($C_{12}H_{13}N$) = 171.24 gmol^{-1}.

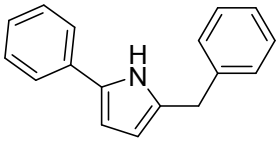
^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.25 (s_br, 1H), 7.48-7.44 (m, 2H), 7.40-7.34 (m, 2H), 7.22-7.16 (m, 1H), 6.44-6.42 (m, 1H), 6.00-5.98 (m, 1H), 2.70 (q, *J* = 7.5 Hz, 2H), 1.30 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 136.3, 133.6, 130.8, 129.4, 126.1, 123.7, 106.7, 106.5, 21.5, 14.1 ppm. MS (EI, m/z): 171.1 (M^+).



1b: 2-isobutyl-5-phenyl-1*H*-pyrrole:

200 mg Ir@SiCN, 1-phenylethanol (2904 µL, 24.0 mmol), 2-amino-4-methylpentan-1-ol (767 µL, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 50:1 pentane: Et_2O; Yield: 1.113 g = 5.58 mmol = 93 % as colourless solid. M($C_{14}H_{17}N$) = 199.29 gmol^{-1}.

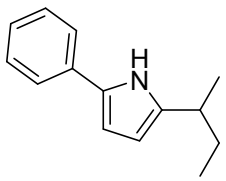
^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.19 (s, br, 1H), 7.46-7.43 (m, 2H), 7.37-7.32 (m, 2H), 7.19-7.14 (m, 1H), 6.42-6.40 (m, 1H), 5.96-5.94 (m, 1H), 2.51 (d, *J* = 7.2 Hz, 2H), 1.96-1.83 (m, 1H), 0.97 (d, *J* = 6.6 Hz, 6H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 133.9, 133.6, 130.7, 129.4, 126.0, 123.6, 108.5, 106.6, 37.8, 29.8, 22.7 ppm. MS (EI, m/z): 199.2 (M^+).



1c: 2-benzyl-5-phenyl-1*H*-pyrrole:

200 mg Ir@SiCN, 1-phenylethanol (2904 µL, 24.0 mmol), 2-amino-3-phenylpropan-1-ol (907 mg, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 80:1 → 10:1 pentane: Et_2O; Yield: 1.234 g = 5.29 mmol = 88 % as colourless solid. M($C_{17}H_{15}N$) = 233.31 gmol^{-1}.

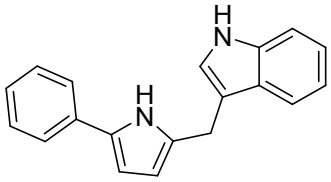
^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.18 (s_br, 1H), 7.42-7.38 (m, 2H), 7.35-7.23 (m, 7H), 7.18-7.13 (m, 1H), 6.43-6.41 (m, 1H), 6.03-6.01 (m, 1H), 4.02 (s, 2H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 140.2, 133.3, 132.9, 131.8, 129.3, 129.1, 129.1, 127.0, 126.3, 123.8, 109.0, 106.6, 34.7 ppm. MS (EI, m/z): 233.2 (M^+).



1d: 2-sec-butyl-5-phenyl-1*H*-pyrrole:

200 mg Ir@SiCN, 1-phenylethanol (2904 µL, 24.0 mmol), 2-amino-3-methylpentan-1-ol (703 mg, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 50:1 pentane: Et_2O; Yield: 1.025 g = 5.14 mmol = 86 % as colourless oil. M($C_{14}H_{17}N$) = 199.29 gmol^{-1}.

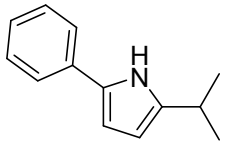
^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.24 (s_br, 1H), 7.51-7.47 (m, 2H), 7.42-7.36 (m, 2H), 7.24-7.18 (m, 1H), 6.48-6.46 (m, 1H), 6.03-6.01 (m, 1H), 2.82-2.71 (m, 1H), 1.80-4.57 (m, 2H), 1.33 (d, *J* = 6.9 Hz, 3H), 0.98 (t, *J* = 7.2 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 139.9, 133.7, 130.6, 129.4, 126.1, 123.7, 106.4, 106.2, 35.0, 30.8, 20.6, 12.2 ppm. MS (EI, m/z): 199.1 (M^+).



1e: 3-(5-phenyl-1*H*-pyrrol-2-ylmethyl)-1*H*-indole:

200 mg Ir@SiCN, 1-phenylethanol (2892 µL, 24.0 mmol), 2-amino-3-(1*H*-indol-3-yl)-propan-1-ol (1.14 g, 6.0 mmol), 6 mL diglyme, KO^{t}Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 15:1 → 8:1 → 4:1 pentane: Et_2O; Yield: 0.964 g = 3.54 mmol = 59 % as colourless solid. M($C_{19}H_{16}N_2$) = 272.34 gmol^{-1}.

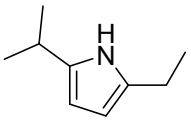
^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.24 (s_br, 1H), 8.13 (s_br, 1H), 7.57-7.54 (m, 1H), 7.41-7.35 (m, 3H), 7.32-7.27 (m, 2H), 7.22-7.06 (m, 4H), 6.45-6.43 (m, 1H), 6.10-6.08 (m, 1H), 4.17 (s, 2H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 137.1, 133.5, 133.3, 131.2, 129.3, 127.8, 126.1, 123.7, 123.0, 122.7, 120.0, 119.3, 114.2, 111.7, 108.3, 106.6, 24.5 ppm. MS (EI, m/z): 272.2 (M^+).



1f: 2-isopropyl-5-phenyl-1*H*-pyrrole:

200 mg Ir@SiCN, 1-phenylethanol (2904 µL, 24.0 mmol), 2-amino-3-methyl-butan-1-ol (619 mg, 6.0 mmol), 6 mL diglyme, KO^{t}Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 90:1 → 25:1 pentane: Et_2O; Yield: 0.998 g = 5.39 mmol = 90 % as colourless oil. M($C_{13}H_{15}N$) = 185.26 gmol^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.23 (s_br, 1H), 7.49-7.45 (m, 2H), 7.40-7.35 (m, 2H), 7.22-7.16 (m, 1H), 6.44-6.42 (m, 1H), 6.00-5.98 (m, 1H), 3.06-2.93 (m, 1H), 1.33 (d, *J* = 6.9 Hz, 6H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 141.0, 133.6, 130.7, 129.4, 126.1, 123.8, 106.4, 105.5, 27.8, 23.1 ppm. MS (EI, m/z): 185.2 (M^+).

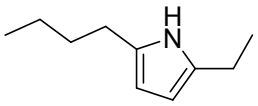


1g: 2-ethyl-5-isopropyl-1*H*-pyrrole:

200 mg Ir@SiCN, 3-methyl-butan-2-ol (2580 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 40:1→ 20:1 pentane: Et_2O; Yield: 0.446 g = 3.25 mmol = 54 % as colourless oil. M($C_9H_{15}N$) = 137.22 $gmol^{-1}$.

^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.65 (s_br, 1H), 5.82-5.80 (m, 2H), 2.95-2.86 (m, 1H), 2.62 (q, *J* = 7.8 Hz, 2H), 1.28-1.23 (m, 9H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 298 K): δ = 137.4, 132.5, 103.6, 102.6, 27.0, 22.7, 20.8, 13.5 ppm. MS (EI, m/z): 137.2 (M^+).

elemental analysis (%) for $C_9H_{15}N$ calcd: C 78.77, H 11.02, N 10.21; found: C 79.21, H 11.44, N 10.30.

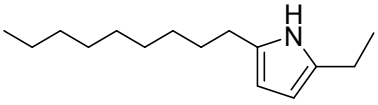


1h: 2-ethyl-5-butyl-1*H*-pyrrole:

200 mg Ir@SiCN, 2-hexanol (3024 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 100:1 → 20:1 pentane: Et_2O; Yield: 0.734 g = 4.85 mmol = 81 % as colourless oil. M($C_{10}H_{17}N$) = 151.25 $gmol^{-1}$.

^1H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.70 (s_br, 1H), 5.76-5.74 (m, 2H), 2.63-2.54 (m, 4H), 1.65-1.55 (m, 2H), 1.47-1.34 (m, 2 H), 1.24 (t, *J* = 7.5 Hz, 3H), 0.97 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 133.0, 131.7, 105.1, 104.4, 32.7, 28.0, 23.1, 21.4, 14.3, 14.2 ppm. MS (EI, m/z): 151.1 (M^+).

elemental analysis (%) for $C_{10}H_{77}N$ calcd: C 79.41, H 11.33, N 9.26; found: C 79.81, H 11.10, N 8.71.

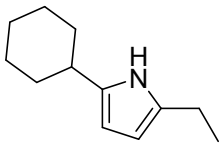


1i: 2-ethyl-5-nonyl-1*H*-pyrrole:

200 mg Ir@SiCN, 2-undecanol (4992 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 70:1 → 30:1 pentane: Et_2O; Yield: 0.867 g = 3.92 mmol = 65 % as colourless solid. M($C_{15}H_{27}N$) = 221.38 gmol^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.66 (s_br, 1H), 5.73-5.70 (m, 2H), 2.61-2.50 (m, 4H), 1.63-1.54 (m, 2H), 1.40-1.24 (m, 12H), 1.21 (t, *J* = 7.8 Hz, 3H), 0.90 (t, *J* = 6.9 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 132.9, 131.7, 105.0, 104.3, 32.5, 30.5, 30.2, 30.1, 30.0, 29.9, 28.3, 23.3, 21.4, 14.5, 14.2 ppm. MS (EI, m/z): 221.2 (M^+).

elemental analysis (%) for $C_{15}H_{27}N$ calcd: C 81.38, H 12.29, N 6.33; found: C 81.37, H 12.78, N 6.38.

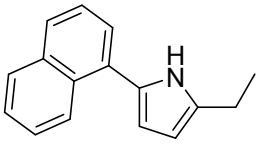


1j: 2-ethyl-5-cyclohexyl-1*H*-pyrrole:

200 mg Ir@SiCN, 1-cyclohexyl-1-ethanol (3316 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 80:1 → 20:1 pentane : Et_2O; Yield: 0.663 g = 3.74 mmol = 63 % as light yellow oil. M($C_{12}H_{19}N$) = 177.29 gmol^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.68 (s_br, 1H), 5.73-5.69 (m, 2H), 2.57 (q, *J* = 7.5 Hz, 2H), 2.51-2.45 (m, 1H), 2.00-1.90 (m, 2H), 1.84-1.68 (m, 3H), 1.45-1.26 (m, 5 H), 1.21 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 137.1, 132.6, 104.1, 103.1, 37.4, 34.0, 27.0, 26.8, 21.4, 14.1 ppm. MS (EI, m/z): 177.2 (M^+).

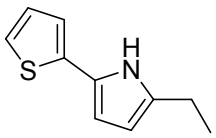
elemental analysis (%) for $C_{12}H_{19}N$ calcd: C 81.30, H 10.80, N 7.90; found: C 81.27, H 10.71, N 8.05.



1k: 2-ethyl-5-(naphthalene-1-yl)-1*H*-pyrrole:

200 mg Ir@SiCN, (±)-1-(1-naphthyl)ethanol (4.13 g, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 5 mL diglyme, KO^{t}Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 10:1 → 2:1 pentane : Et_2O; Yield: 0.942 g = 4.26 mmol = 71 % as yellow oil. M($C_{16}H_{15}N$) = 221.12 gmol^{-1}.

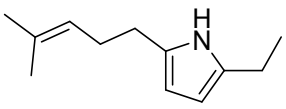
^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.41-8.36 (m, 1H), 8.23 (s_br, 1H), 7.93-7.88 (m, 1H), 7.82-7.76 (m, 1H), 7.55-7.47 (m, 4H), 6.42-6.40 (m, 1H), 6.10-6.08 (m, 1H), 2.75 (q, *J* = 7.5 Hz, 2H), 1.34 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 135.9, 134.7, 132.4, 131.7, 129.2, 128.9, 127.4, 126.7, 126.4, 126.3, 126.1, 125.9, 110.2, 106.2, 21.5, 14.1 ppm. MS (EI, m/z): 222.1 (M^+).
elemental analysis (%) for $C_{16}H_{15}N$ calcd: C 86.84, H 6.83, N 6.33; found: C 87.03, H 6.96, N. 6.66.



1l: 2-ethyl-5-(thiophen-2-yl)-1*H*-pyrrole:

200 mg Ir@SiCN, 1-(thiophen-yl)ethanol (2643 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, KO^{t}Bu (1.37 g, 12.0 mmol), 24 h at 130 °C (oil bath temperature). Purification by column chromatography 20:1 →15:1 pentane: Et_2O; Yield: 0.511 g = 2.90 mmol = 48 % as yellow oil. M($C_{10}H_{11}NS$) = 177.27 gmol^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.11 (s_br, 1H), 7.13-7.10 (m, 1H), 7.02-6.97 (m, 2H), 6.28-6.26 (m, 1H), 5.92-5.90 (m, 1H), 2.65 (q, *J* = 7.5 Hz, 2 H), 1.27 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 137.3, 136.1, 128.2, 125.5, 122.4, 120.4, 107.2, 106.6, 21.4, 14.1 ppm. MS (EI, m/z): 177.1 (M^+).
elemental analysis (%) for $C_{10}H_{11}NS$ calcd: C 67.76, H 6.25, N 7.90; found: C 68.18, H 6.57, N 7.86.

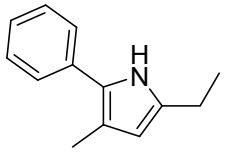


1m: 2-ethyl-5-(4-methyl-pent-3-enyl)-1*H*-pyrrole:

200 mg Ir@SiCN, 6-methyl-5-hepten-2-ol (3664 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, KO^{t}Bu (1.37 g, 12.0 mmol), 24 h at 130 °C (oil

bath temperature). Purification by column chromatography 70:1 → 30:1 pentane: Et_2O; Yield: 0.834 g = 4.70 mmol = 78 % as light yellow oil. M($C_{12}H_{19}N$) = 177.29 gmol^{-1}.

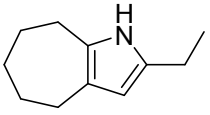
^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.70 (s_br, 1H), 5.73-5.69 (m, 2H), 5.23-5.17 (m, 1H), 2.60-2.53 (m, 4H), 2.27 (q, *J* = 7.5 Hz, 2H), 1.71 (s, 3H), 1.60 (s, 3H), 1.20 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 133.1, 132.9, 131.4, 105.2, 104.4, 29.0, 28.4, 26.0, 21.4, 18.0, 14.2 ppm. MS (EI, m/z): 177.2 (M^+).
elemental analysis (%) for $C_{12}H_{19}N$ calcd: C 81.30, H 10.80, N 7.90; found: C 81.49, H 10.78, N 8.11.



2a: 5-ethyl-3-methyl-2-phenyl-1*H*-pyrrole:

200 mg Ir@SiCN, 1-phenylpropanol (3288 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, KO^{t}Bu (1.37 g, 12.0 mmol), 24 h at 135 °C (oil bath temperature). Purification by column chromatography 50:1 → 20:1 pentane : Et_2O; Yield: 0.740 g = 3.99 mmol = 67 % as colourless oil. M($C_{13}H_{15}N$) = 185.26 gmol^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.91 (s_br, 1H), 7.41-7.35 (m, 4H), 7.22-7.16 (m, 1H), 5.83-5.82 (m, 1H), 2.63 (q, *J* = 7.5 Hz, 2H), 2.22 (s, 3H), 1.25 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 134.7, 134.6, 129.2, 126.7, 126.2, 125.8, 116.8, 109.2, 21.4, 14.1, 13.0 ppm. MS (EI, m/z): 185.1 (M^+).
elemental analysis (%) for $C_{13}H_{15}N$ calcd: C 84.28, H 8.16, N 7.56; found: C 84.76, H 7.63, N 7.13.

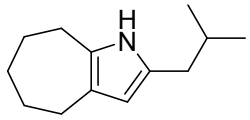


2b: 2-ethyl-1,5,6,7,8,9-hexahydro-cyclohepta[*b*]pyrrole:

800 mg Ir@SiCN, cycloheptanol (11568 µL, 96.0 mmol), 2-amino-butan-1-ol (2260 µL, 24.0 mmol), 16 mL diglyme, KO^{t}Bu (5.48 g, 48.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 40:1 → 20:1 pentane:

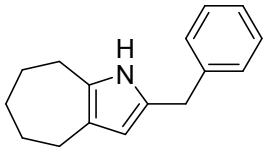
Et_2O; Yield: 3.516 g = 21.54 mmol = 90 % as colourless solid. M($C_{11}H_{17}N$) = 163.26 gmol^{-1}.

^{1}H NMR (300 MHz, C_6D_6, 298 K): δ = 6.45 (s_br, 1H), 5.80 (d, *J* = 3.0 Hz, 1H), 2.66-2.62 (m, 2H), 2.39-2.27 (m, 4H), 1.71-1.64 (m, 4H), 1.63-1.56 (m, 2H), 1.07 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, C_6D_6, 298 K): δ = 129.1, 127.9, 121.2, 107.1, 32.6, 30.0, 29.4, 29.1, 28.7, 21.1, 14.3 ppm. MS (EI, m/z): 163.1 (M^+).



2c: 2-isobutyl-1,5,6,7,8,9-hexahydro-cyclohepta[*b*]pyrrole:

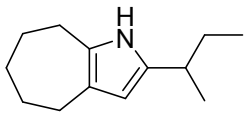
200 mg Ir@SiCN, cycloheptanol (2892 µL, 24.0 mmol), 2-amino-4-methylpentan-1-ol (767 µL, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 50:1→15:1 pentane: Et_2O; Yield: 0.913 g = 4.77 mmol = 80 % as colourless solid. M($C_{13}H_{21}N$) = 191.31 gmol^{-1}.
^{1}H NMR (300 MHz, CD_2Cl_2, 298 K: δ = 7.40 (s_br, 1H), 5.57 (d, *J* = 2.7 Hz, 1H), 2.62-2.58 (m, 2H), 2.50-2.46 (m, 2H), 2.33 (d, *J* = 6.9 Hz, 2H), 1.81-1.72 (m, 3H), 1.70-1.59 (m, 4H), 0.91 (d, *J* = 6.6 Hz, 6H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 128.8, 127.6, 121.6, 108.5, 37.6, 32.6, 30.1, 29.9, 29.6, 29.0, 28.9, 22.8 ppm. MS (EI, m/z): 191.2 (M^+).



2d: 2-benzyl-1,5,6,7,8,9-hexahydro-cyclohepta[*b*]pyrrole:

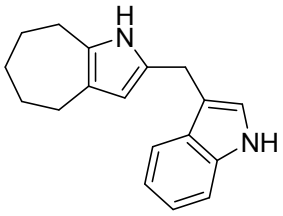
200 mg Ir@SiCN, cycloheptanol (2892 µL, 24.0 mmol), 2-amino-3-phenylpropan-1-ol (907 mg, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 30:1 → 10:1 pentane: Et_2O; Yield: 1.007 g = 4.47 mmol = 75 % as colourless solid. M($C_{16}H_{19}N$) = 225.33 gmol^{-1}.
^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.40 (s_br, 1H), 7.36-7.31 (m, 2H), 7.27-7.22 (m, 3H), 5.66-5.64 (m, 1H), 3.86 (s, 2H), 2.61-2.51 (m, 4H), 1.81-1.78 (m, 2H), 1.70-1.63 (m, 4H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 141.0, 129.9, 129.1,

129.0, 126.8, 126.7, 121.8, 109.0, 34.6, 32.6, 30.1, 29.6, 28.9, 28.8 ppm. MS (EI, m/z): 225.2 (M^+).



2e: 2-sec-butyl-1,5,6,7,8,9-hexahydro-cyclohepta[*b*]pyrrole:

200 mg Ir@SiCN, cycloheptanol (2892 µL, 24.0 mmol), 2-amino-3-methylpentan-1-ol (703 mg, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 50:1→15:1 pentane: Et_2O; Yield: 0.881 g = 4.61 mmol = 77 % as colourless solid. M($C_{13}H_{21}N$) = 191.31 gmol^{-1}.
^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.44 (s_br, 1H), 5.59 (d, *J* = 3.0 Hz, 1H), 2.64-5.59 (m, 2H), 2.57-2.48 (m, 3H), 1.83-1.75 (m, 2H), 1.70-1.60 (m, 4H), 1.58-1.41 (m, 2H), 1.19 (d, *J* = 7.2 Hz, 3H), 0.90 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 133.7, 128.6, 121.3, 106.2, 34.6, 32.6, 30.8, 30.1, 29.7, 29.1, 28.9, 20.5, 12.3 ppm. MS (EI, m/z): 191.2 (M^+).
elemental analysis (%) for $C_{13}H_{21}N$ calcd: C 81.61, H 11.06, N 7.32; found: C 81.38, H 11.00, N 7.34.

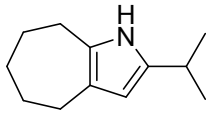


2f: 2-((1H-indol-3-yl)methyl)-1,4,5,6,7,8-hexahydrocyclohepta[b]pyrrole:

200 mg Ir@SiCN, cycloheptanol (2904 µL, 24.0 mmol), 2-amino-3-(1*H*-indol-3-yl)-propan-1-ol (1.14 g, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 10:1 → 2:1 pentane: Et_2O and removement of cycloheptanol by vacuum distillation at 90 °C; Yield: 0.694 g = 2.63 mmol = 44 % as orange solid. M($C_{18}H_{20}N_2$) = 264.36 gmol^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.06 (s_br, 1H), 7.58-7.55 (m, 1H), 7.45 (s_br, 1H), 7.39-7.37 (m, 1H), 7.22-7.17 (m, 1H), 7.12-7.04 (m, 2H), 5.75-5.74 (m, 1H), 4.01 (s, 2H), 2.56-2.50 (m, 4H), 1.82-1.74 (m, 2H), 1.70-1.59 (m, 4H) ppm.

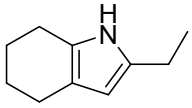
^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 137.0, 129.3, 127.9, 127.0, 122.8, 122.5, 121.7, 119.8, 119.4, 114.8, 111.7, 108.2, 32.6, 30.1, 29.6, 29.0, 28.8, 24.1 ppm. MS (EI, m/z): 264.1 (M^+).



2g: 2-isopropyl-1,5,6,7,8,9-hexahydro-cyclohepta[*b*]pyrrole:

200 mg Ir@SiCN, cycloheptanol (2904 µL, 24.0 mmol), 2-amino-3-methyl-butan-1-ol (619 mg, 6.0 mmol), 6 mL diglyme, KO^{t}Bu (1.37 g, 6.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 60:1 → 40:1 pentane: Et_2O; Yield: 0.863 g = 4.87 mmol = 81 % as colourless solid. M($C_{12}H_{19}N$) = 177.29 gmol^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.47 (s_br, 1H), 5.59 (d, *J* = 3.0 Hz, 1H), 2.88-2.74 (m, 1H), 2.63-5.59 (m, 2H), 2.51-2.47 (m, 2H), 1.86-1.75 (m, 2H), 1.69-1.60 (m, 4H), 1.20 (d, *J* = 6.9 Hz, 6H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 134.8, 128.7, 121.3, 105.6, 32.6, 30.1, 29.6, 29.0, 28.8, 27.4, 23.2 ppm. MS (EI, m/z): 177.2 (M^+).

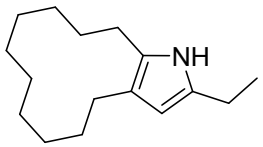


2h: 2-ethyl-1,5,6,7,8-pentahydro-cyclohexa[*b*]pyrrole:

200 mg Ir@SiCN, cyclohexanol (2529 µL, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, KO^{t}Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 40:1→10:1 pentane: Et_2O; Yield: 0.710 g = 4.76 mmol = 79 % as colourless oil. M($C_{10}H_{15}N$) = 149.23 gmol^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.45 (s_br, 1H), 5.59 (d, *J* = 2.4 Hz, 1H), 2.56-5.50 (m, 4H), 2.45-2.41 (m, 2H), 1.83-1.68 (m, 4H), 1.20 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 132.7, 125.4, 117.0, 103.9, 24.6, 24.2, 23.5, 23.2, 21.4, 14.5 ppm. MS (EI, m/z): 149.1 (M^+).

elemental analysis (%) for $C_{10}H_{15}N$ calcd: C 80.48, H 10.13, N 9.39; found: C 80.52, H 10.25, N 9.10.

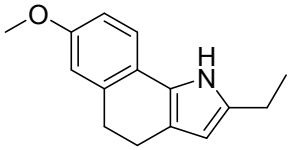


2i: 2-ethyl-4,5,6,7,8,9,10,11,12,13-decahydro-1H-cyclododeca[b]pyrrole:

200 mg Ir@SiCN, cyclododecanol (4.42 g, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 120 °C (oil bath temperature). Purification by column chromatography 40 : 1 pentane : Et_2O; Yield: 0.477 g = 2.04 mmol = 34 % as colourless oil. M($C_{16}H_{27}N$) = 233.39 gmol^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 7.44 (s_br, 1H), 5.68-5.67 (m, 1H), 2.63-2.56 (m, 4H), 2.41 (t, *J* = 6.0 Hz, 2H), 1.72-1.62 (m, 4H), 1.53-1.39 (m, 8H), 1.34-1.29 (m, 4H), 1.25 (t, *J* = 7.5 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 132.8, 127.0 120.4, 104.6, 29.7, 28.8, 25.5, 25.3, 25.3, 25.2, 23.0, 23.0, 22.6, 21.5, 21.5, 14.2 ppm. MS (EI, m/z): 233.2 (M^+).

elemental analysis (%) for $C_{16}H_{27}N$ calcd: C 82.34, H 11.66, N 6.00; found: C 82.34, H 11.59, N 6.09.



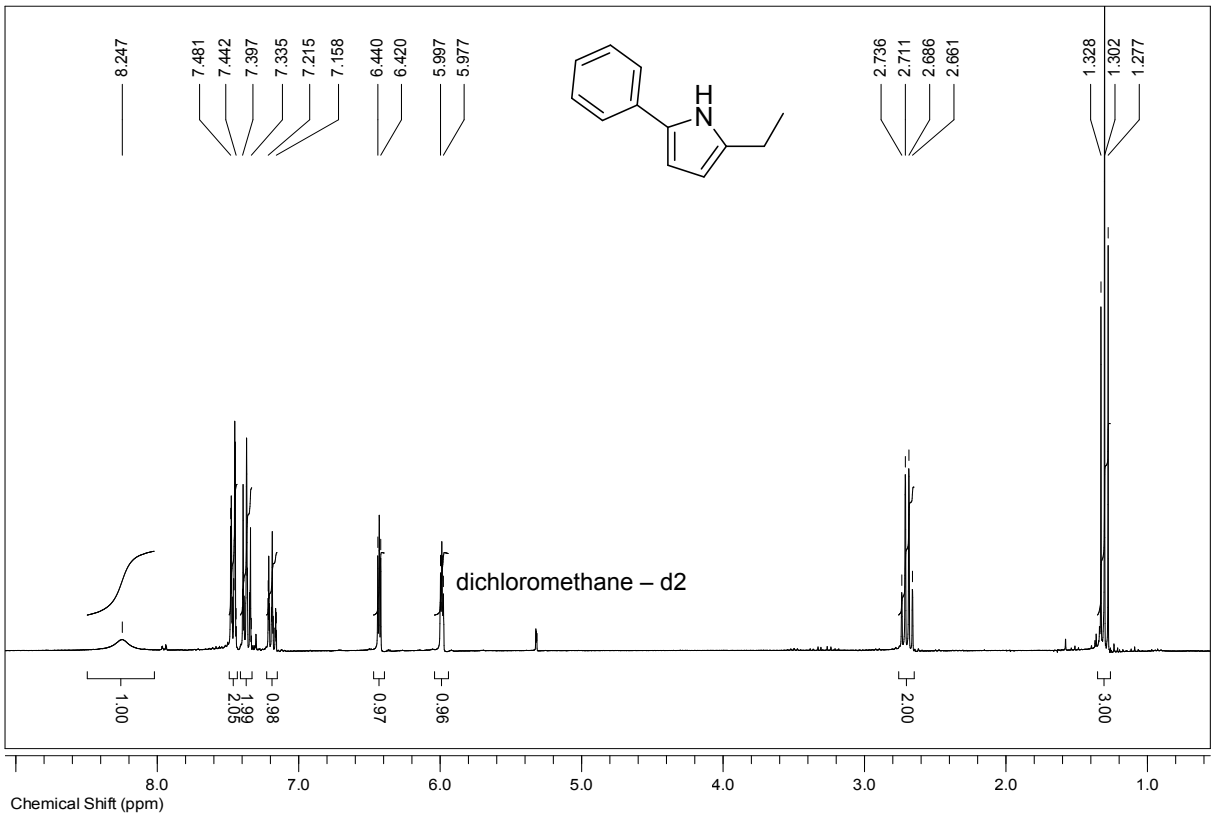
2j: 2-ethyl-7-methoxy-4,5-dihydro-1*H*-benzo[*g*]indole:

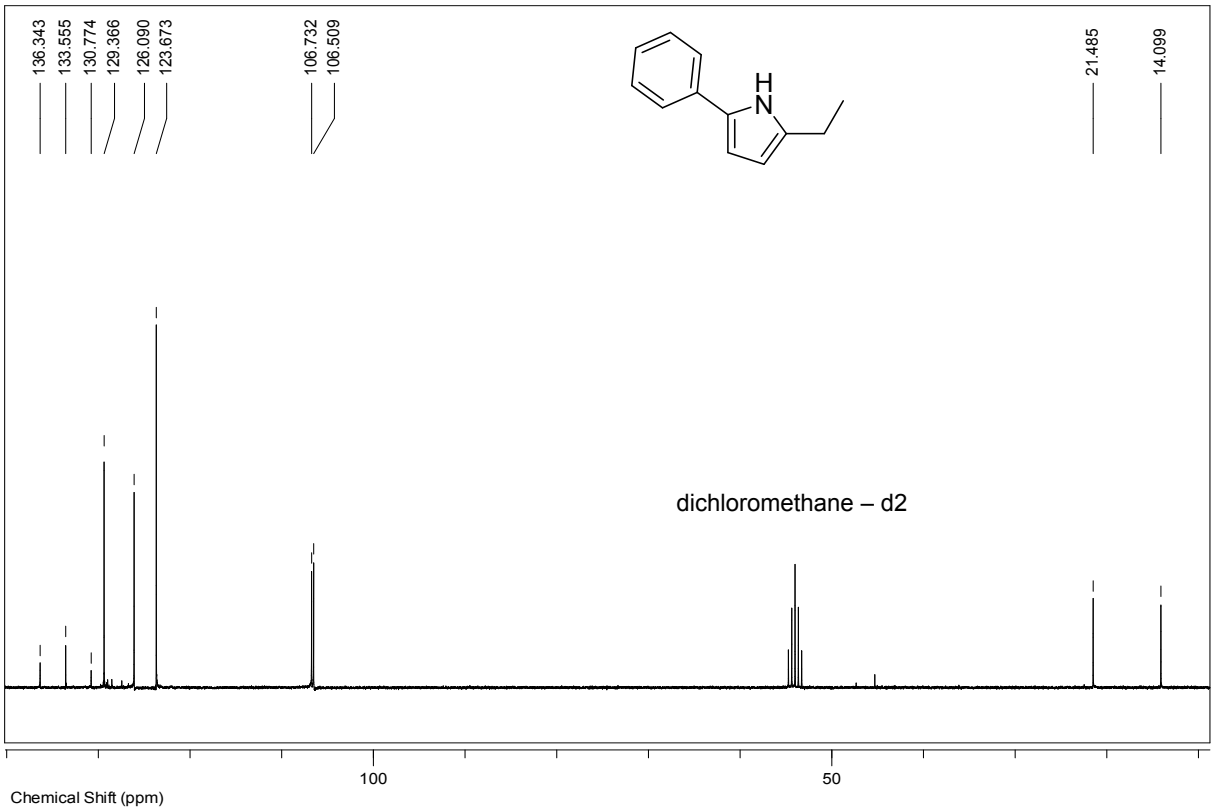
200 mg Ir@SiCN, 6-methoxy-1,2,3,4-tetrahydronaphthalene-1-ol (4.28 g, 24.0 mmol), 2-amino-butan-1-ol (565 µL, 6.0 mmol), 6 mL diglyme, KO*t*Bu (1.37 g, 12.0 mmol), 24 h at 125 °C (oil bath temperature). Purification by column chromatography pentane : Et_2O 20:1 → 2:1; Yield: 0.492 g = 2.16 mmol = 36 % as viscous yellow oil. M($C_{15}H_{17}NO$) = 227.30 gmol^{-1}.

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K): δ = 8.27 (s_br, 1H), 7.11-7.08 (m, 1H), 6.92-6.91 (m, 1H), 6.80-6.77 (m, 1H), 5.94-5.93 (m, 1H), 3.87 (s, 3H), 3.01-2.96 (m, 2H), 2.81-2.70 (m, 4H), 1.37 (t, *J* = 7.8 Hz, 3H) ppm. ^{13}C NMR (75 MHz, CD_2Cl_2, 298 K): δ = 157.5, 136.9, 135.1, 126.7, 123.8, 119.3, 119.2, 115.3, 111.7, 104.9, 55.7, 31.1, 22.6, 21.7, 14.4 ppm. MS (EI, m/z): 227.0 (M^+).

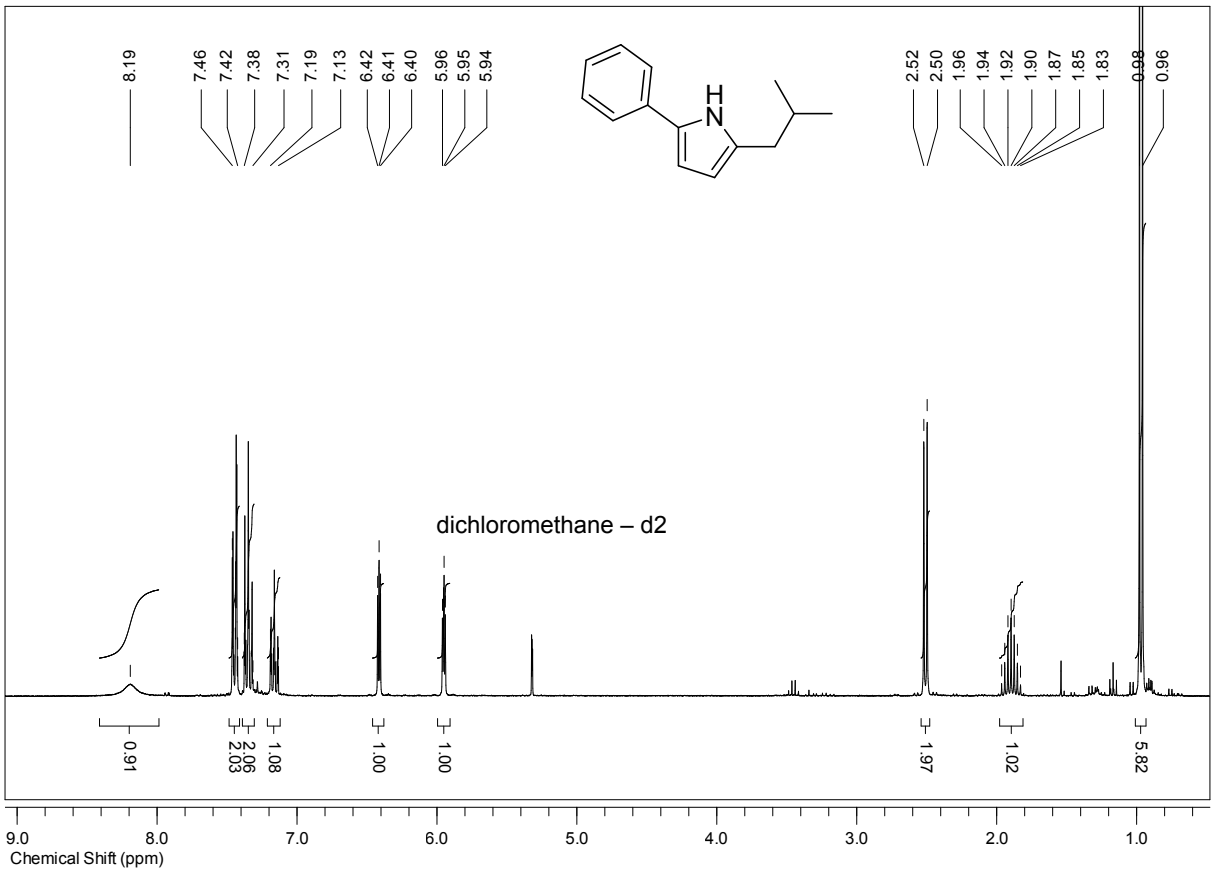
elemental analysis (%) for $C_{15}H_{17}NO$ calcd: C 79.26, H 7.54, N 6.16; found: C 79.32, H 7.28, N 5.35.

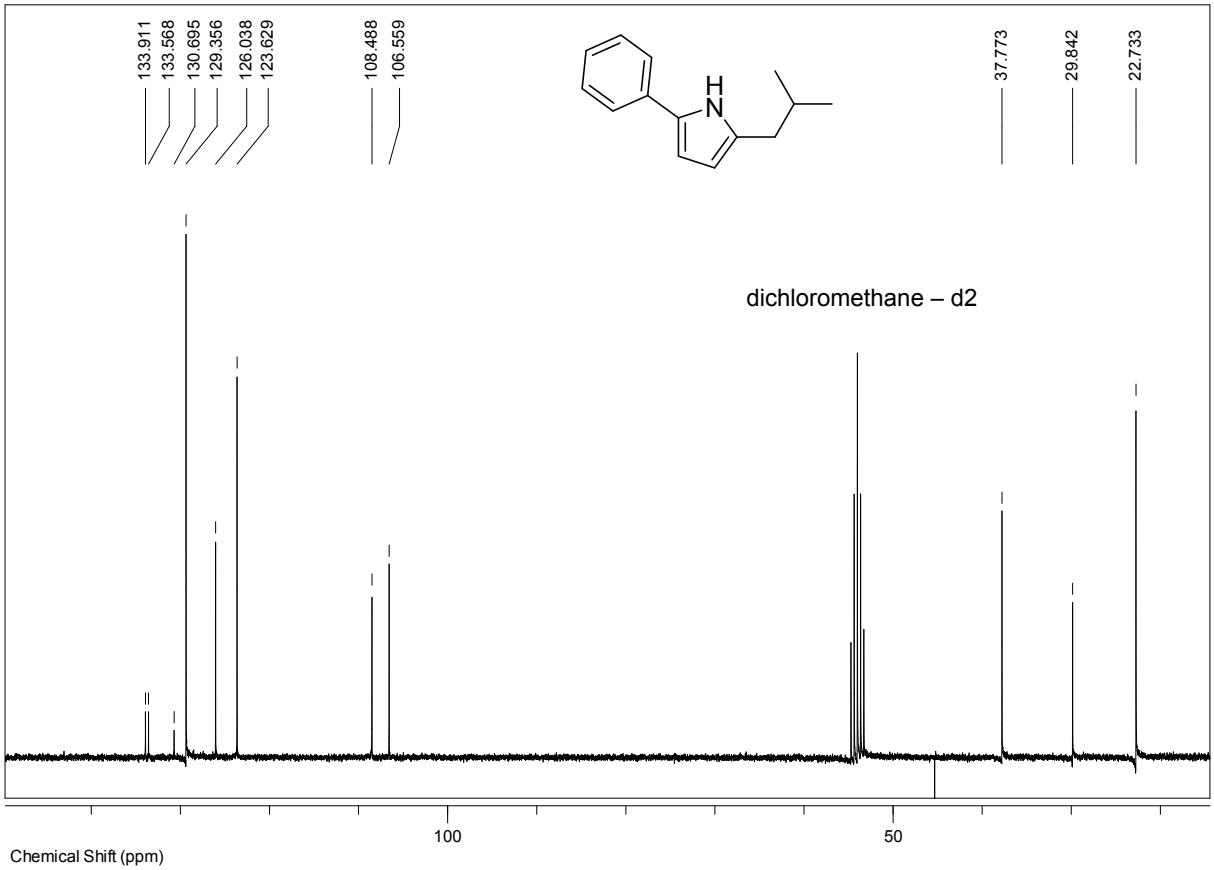
1a:


8.247
7.481
7.442
7.397
7.335
7.215
7.158
6.440
6.420
5.997
5.977
2.736
2.711
2.686
2.661
1.328
1.302
1.277
H
N
dichloromethane – d2
1.00
2.05
1.89
0.98
0.97
0.96
2.00
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

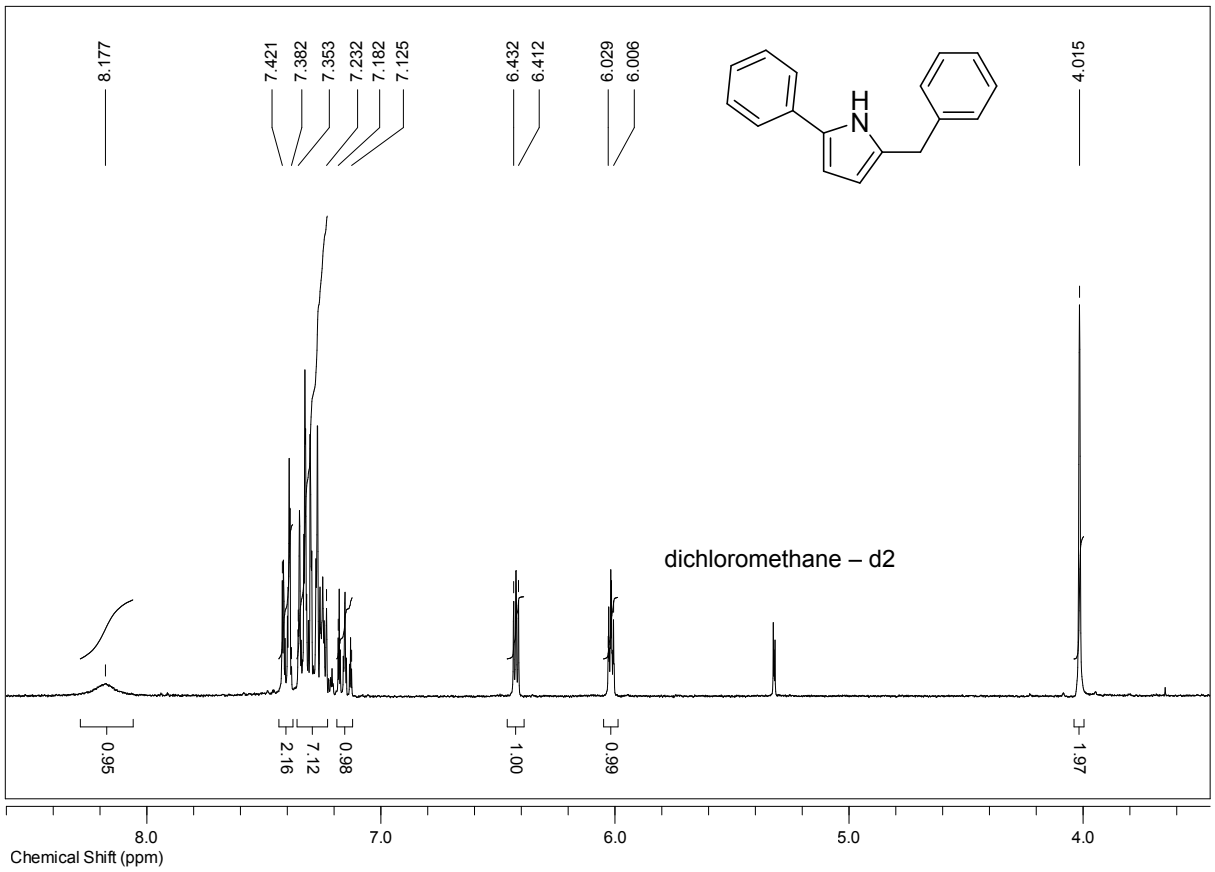

136.343
133.555
130.774
129.366
126.090
123.673
106.732
106.509
21.485
14.099
H
N
dichloromethane – d2
100
50
Chemical Shift (ppm)

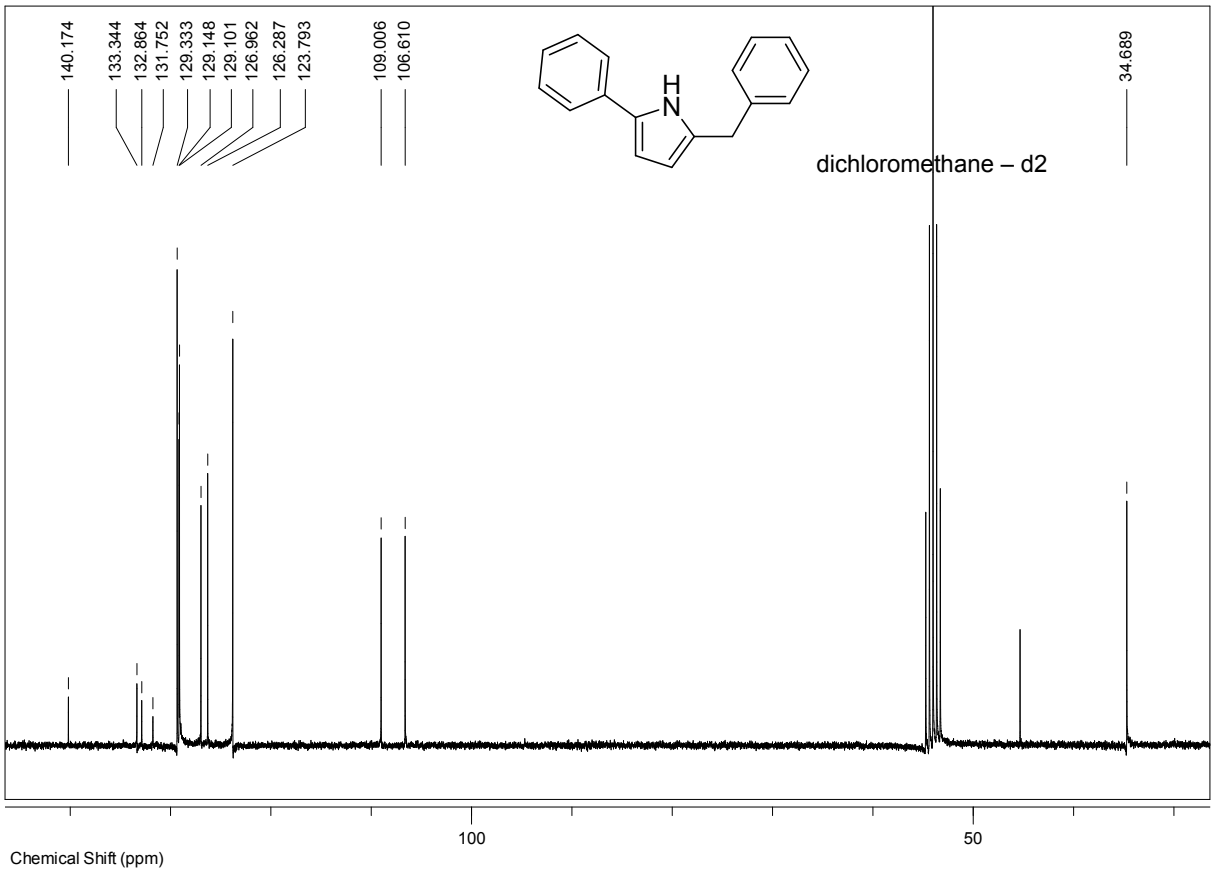
1b:


8.19
7.46
7.42
7.38
7.31
7.19
7.13
6.42
6.41
6.40
5.96
5.95
5.94
2.52
2.50
1.96
1.94
1.92
1.90
1.87
1.85
1.83
0.98
0.96
dichloromethane – d2
0.91
2.03
2.06
1.08
1.00
1.00
1.97
1.02
5.82
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

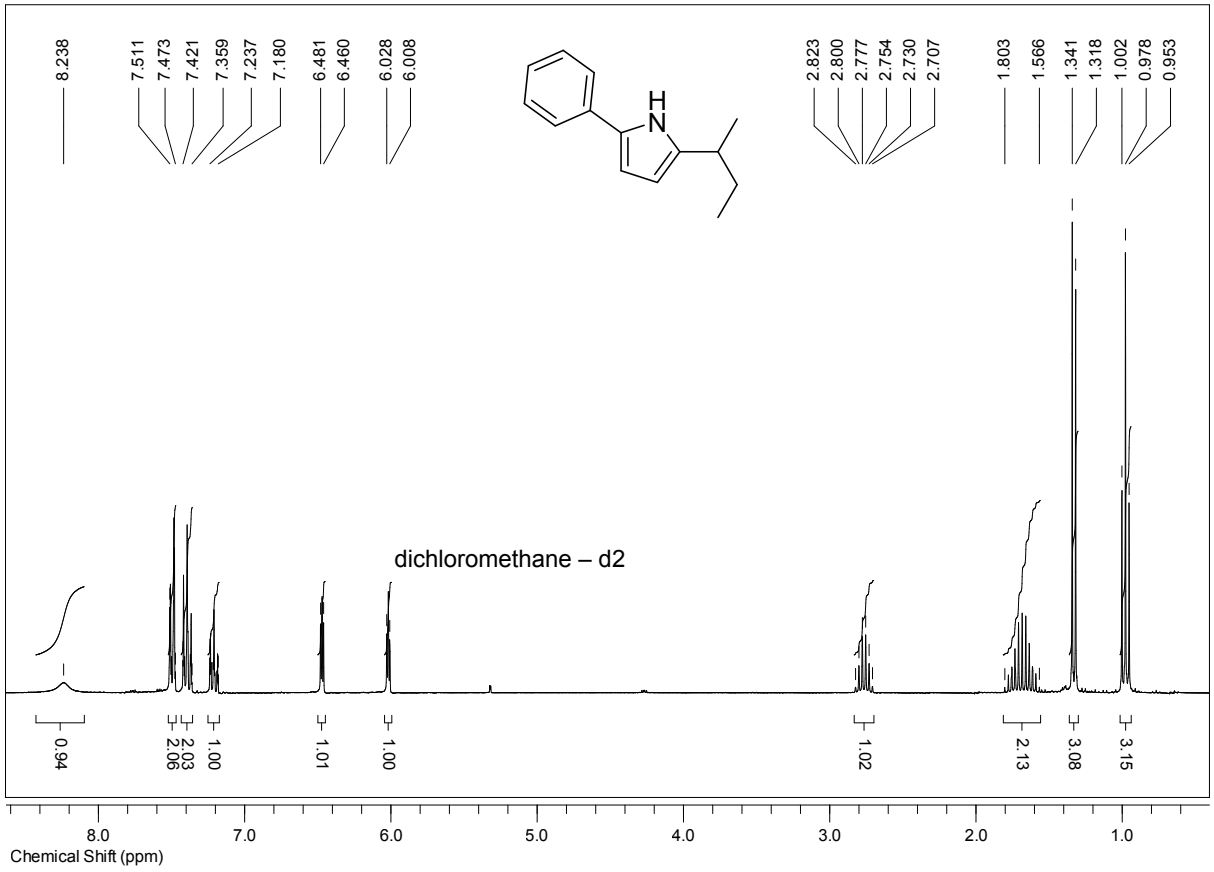

133.911
133.568
130.695
129.356
126.038
123.629
108.488
106.559
37.773
29.842
22.733
dichloromethane – d2
100
50
Chemical Shift (ppm)

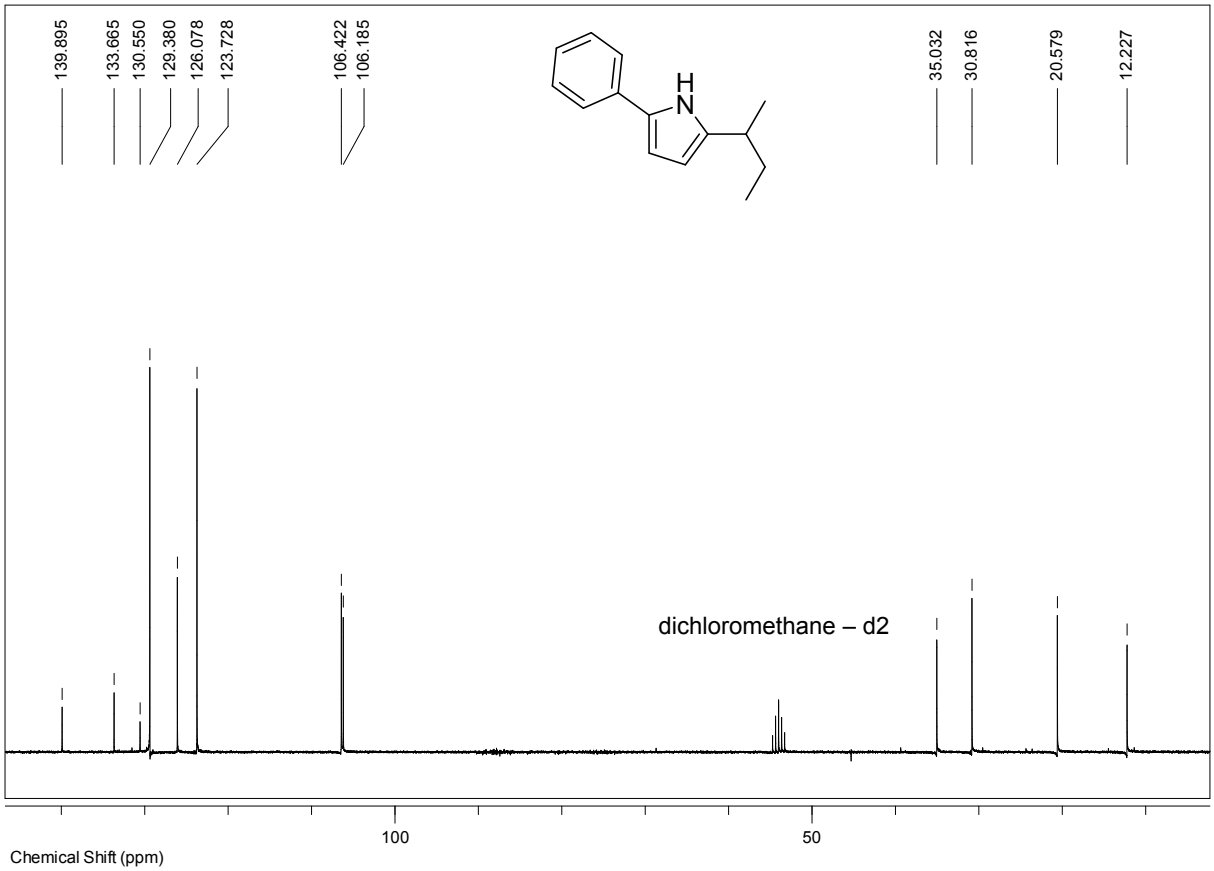
1c:


8.177
7.421
7.382
7.353
7.232
7.182
7.125
6.432
6.412
6.029
6.006
4.015
H
N
dichloromethane – d2
0.95
2.16
7.12
0.98
1.00
0.99
1.97
8.0
7.0
6.0
5.0
4.0
Chemical Shift (ppm)

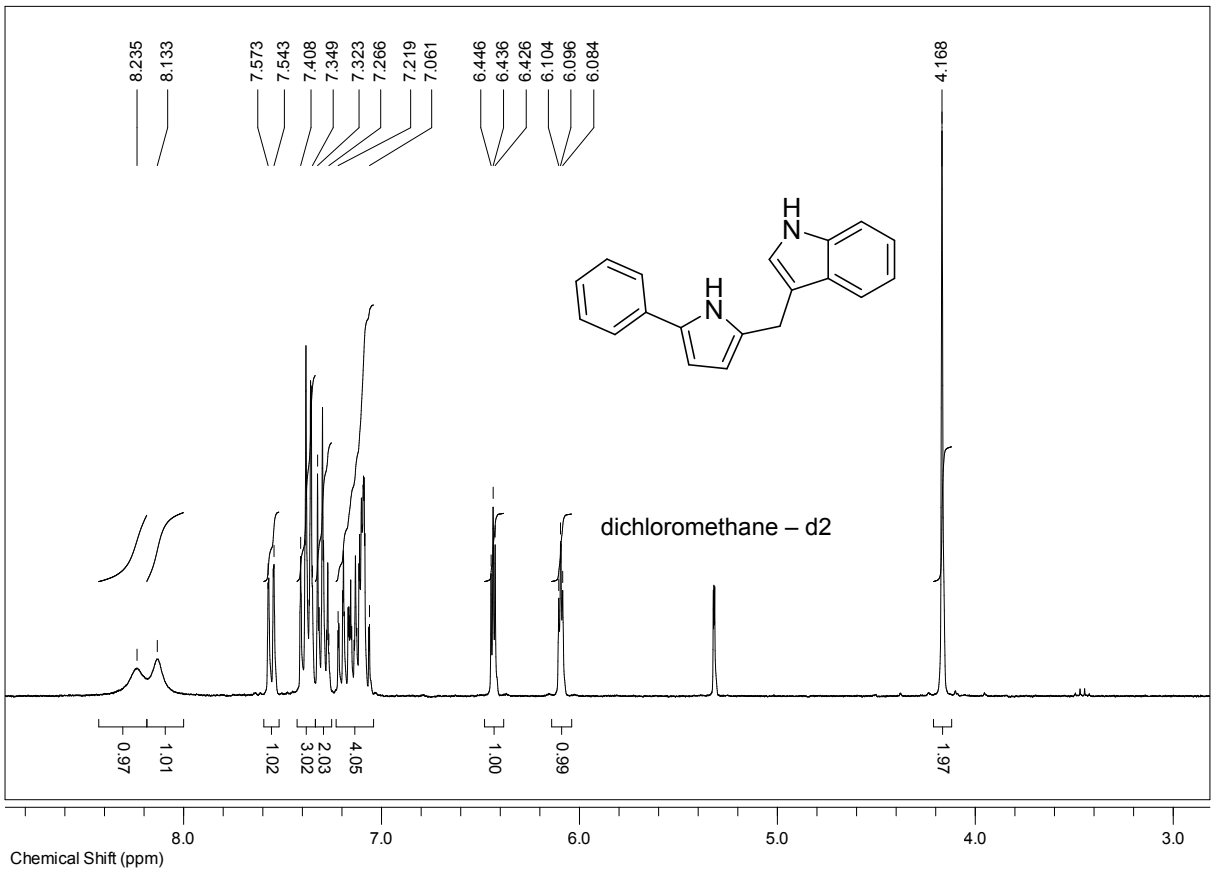

140.174
133.344
132.864
131.752
129.333
129.148
129.101
126.962
126.287
123.793
109.006
106.610
34.689
H
N
dichloromethane – d2
100
50
Chemical Shift (ppm)

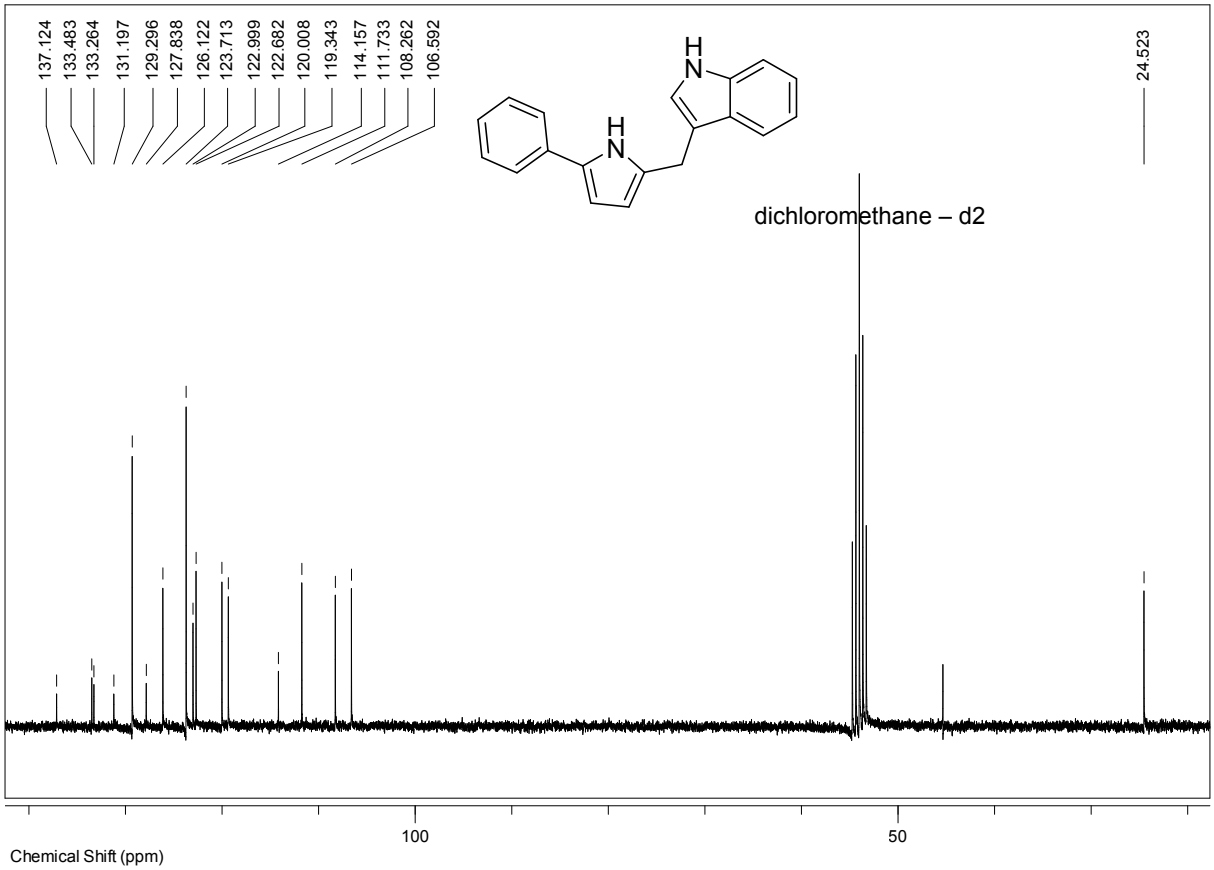
1d:


8.238
7.511
7.473
7.421
7.359
7.237
7.180
6.481
6.460
6.028
6.008
2.823
2.800
2.777
2.754
2.730
2.707
1.803
1.566
1.341
1.318
1.002
0.978
0.953
H
N
dichloromethane – d2
0.94
2.08
2.03
1.00
1.01
1.00
1.02
2.13
3.08
3.15
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

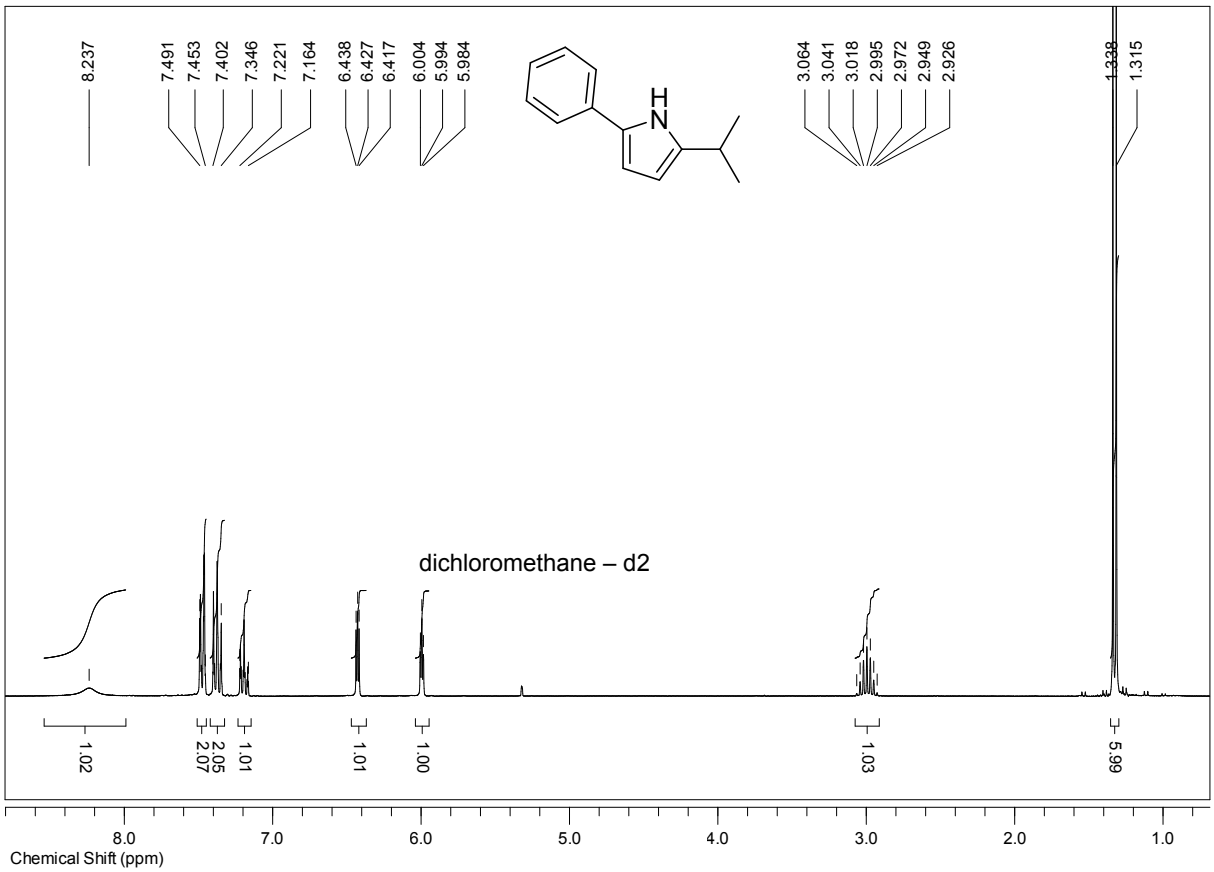

139.895
133.665
130.550
129.380
126.078
123.728
106.422
106.185
35.032
30.816
20.579
12.227
H
N
dichloromethane – d2
100
50
Chemical Shift (ppm)

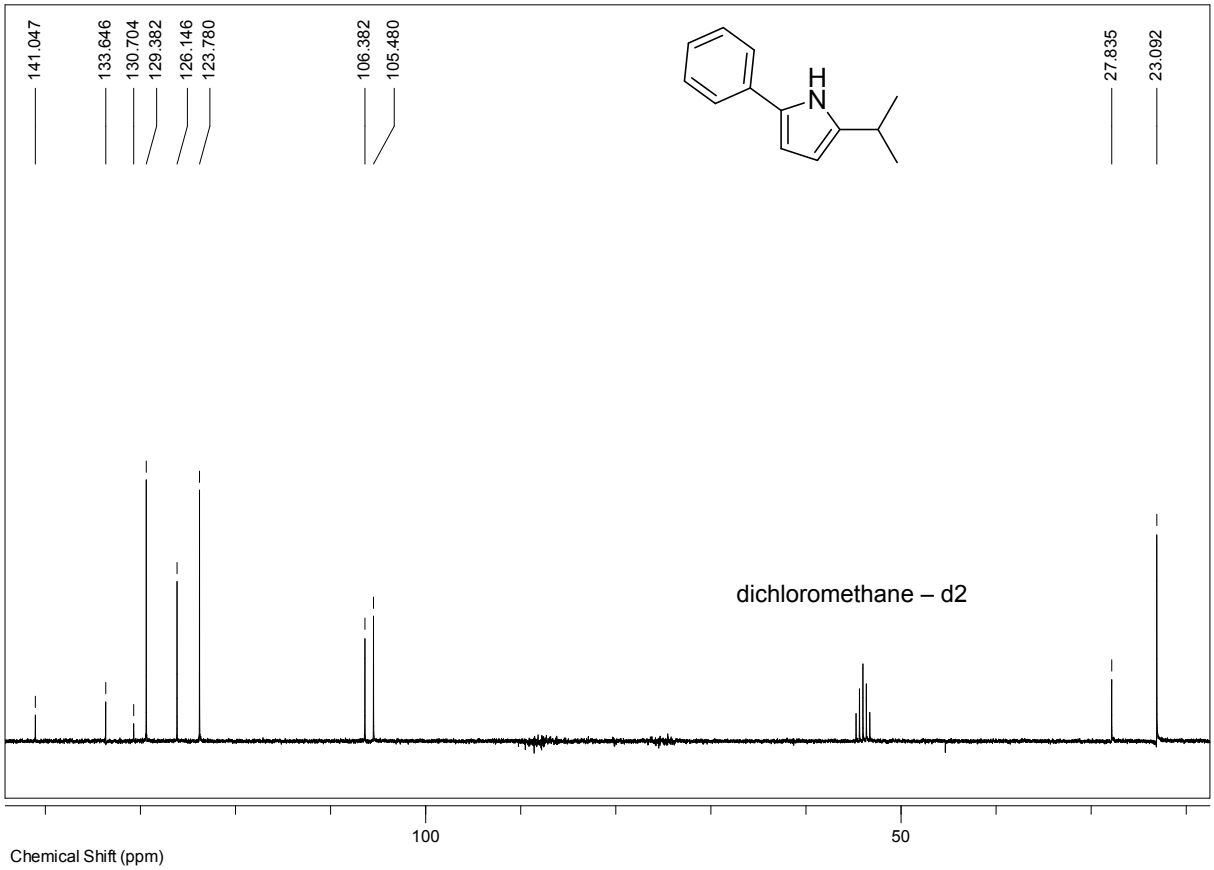
1e:


8.235
8.133
7.573
7.543
7.408
7.349
7.323
7.266
7.219
7.061
6.446
6.436
6.426
6.104
6.096
6.084
4.168
dichloromethane – d2
0.97
1.01
1.02
2.03
2.02
4.05
1.00
0.99
1.97
8.0
7.0
6.0
5.0
4.0
3.0
Chemical Shift (ppm)

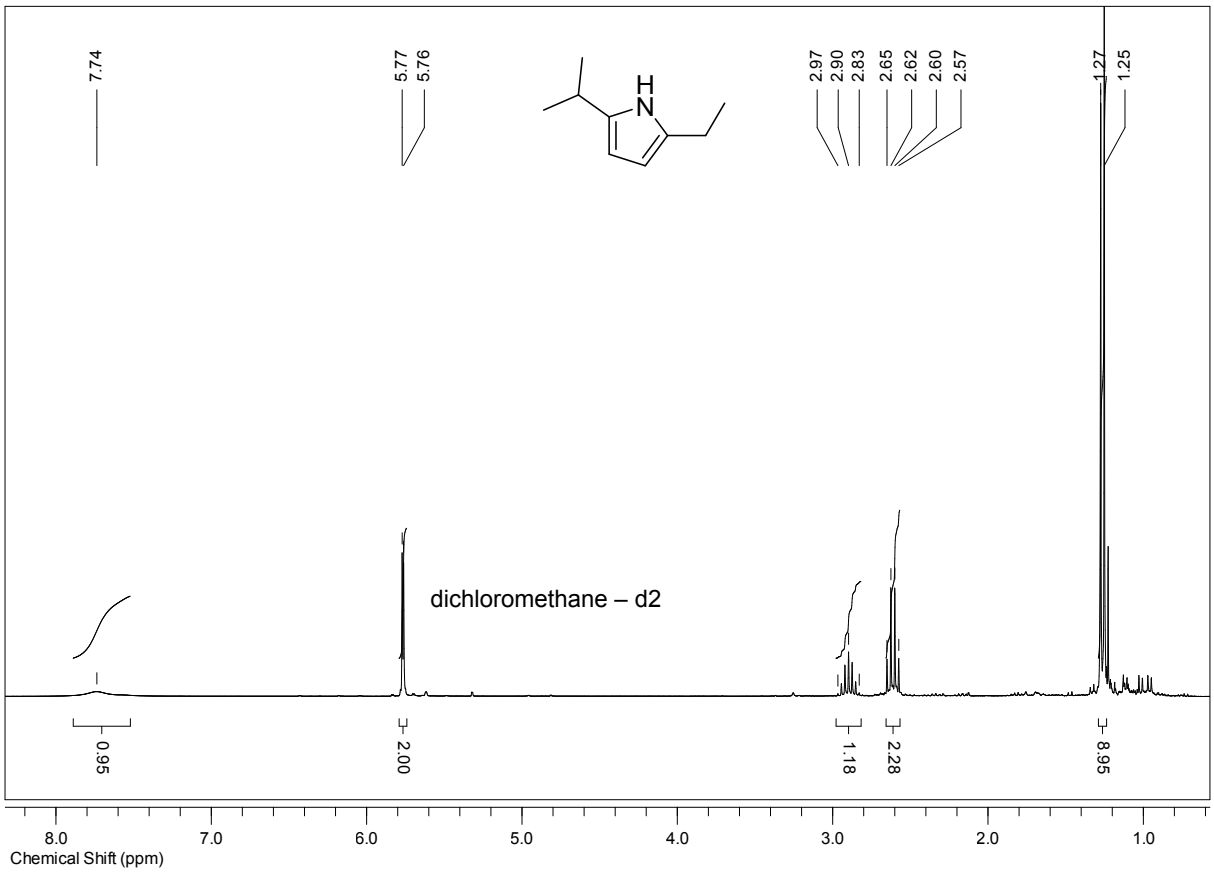

137.124
133.483
133.264
131.197
129.296
127.838
126.122
123.713
122.999
122.682
120.008
119.343
114.157
111.733
108.262
106.592
24.523
dichloromethane – d2
100
50
Chemical Shift (ppm)

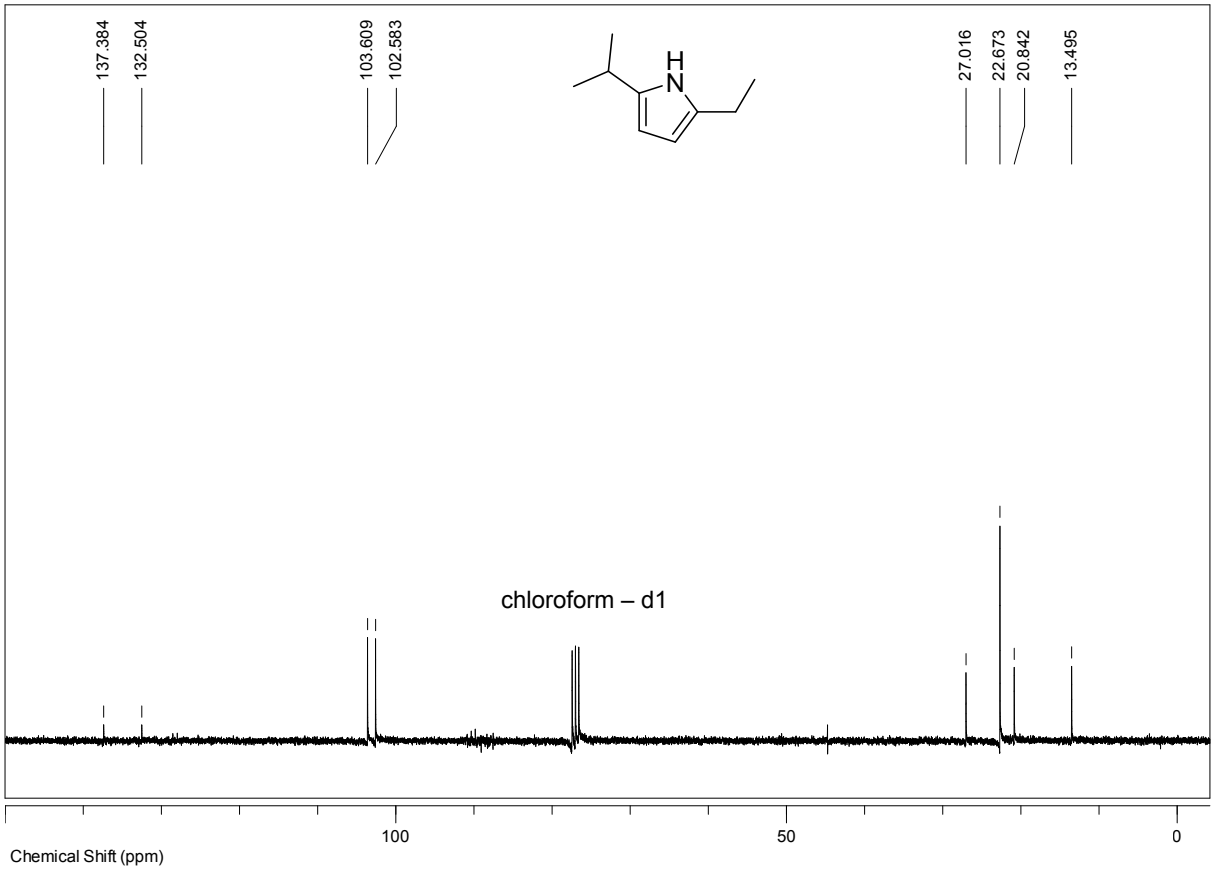
1f:


8.237
7.491
7.453
7.402
7.346
7.221
7.164
6.438
6.427
6.417
6.004
5.994
5.984
3.064
3.041
3.018
2.995
2.972
2.949
2.926
1.338
1.315
H
N
dichloromethane – d2
1.02
2.07
2.05
1.01
1.01
1.00
1.03
5.99
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

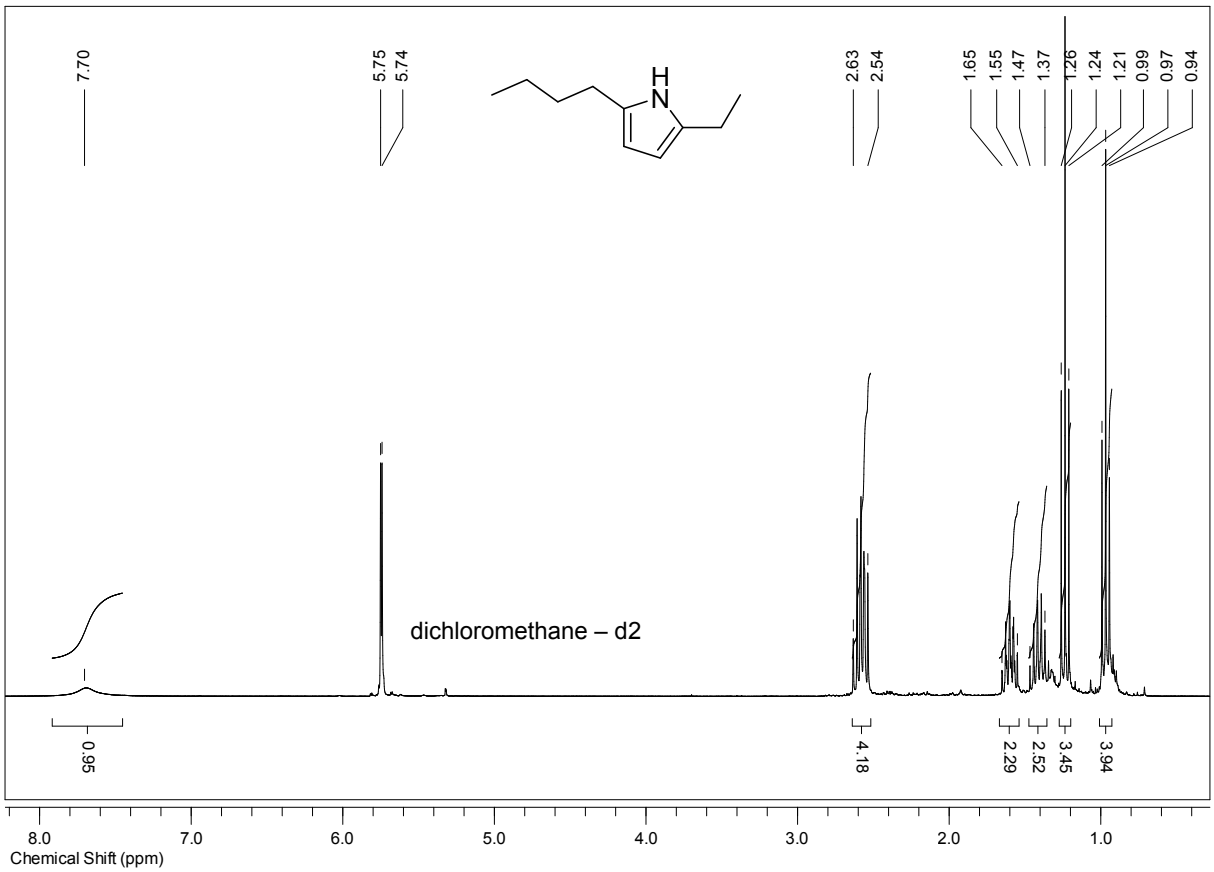

141.047
133.646
130.704
129.382
126.146
123.780
106.382
105.480
27.835
23.092
H
N
dichloromethane – d2
100
50
Chemical Shift (ppm)

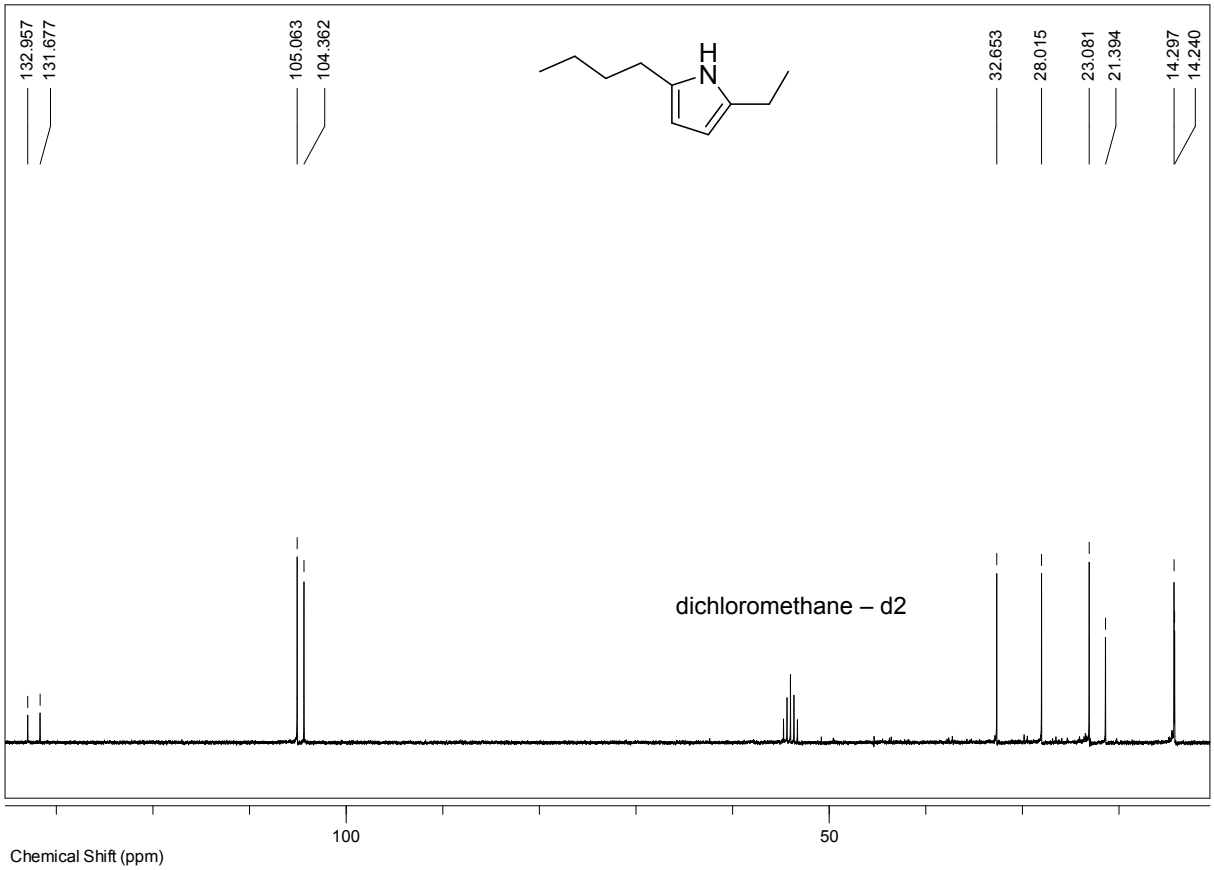
1g:


7.74
5.77
5.76
2.97
2.90
2.83
2.65
2.62
2.60
2.57
1.27
1.25
dichloromethane – d2
0.95
2.00
1.18
2.28
8.95
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

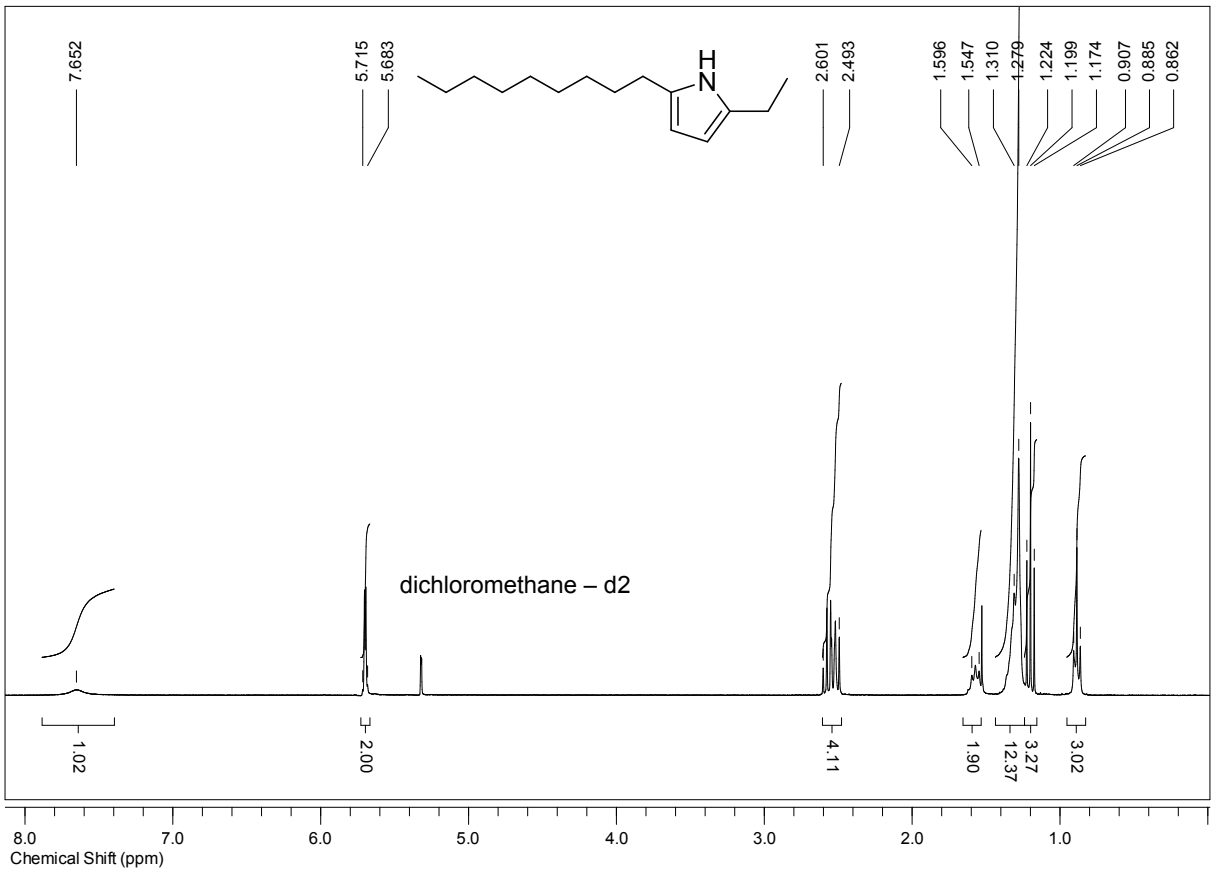

137.384
132.504
103.609
102.583
27.016
22.673
20.842
13.495
chloroform – d1
100
50
0
Chemical Shift (ppm)

1h:


7.70
5.75
5.74
2.63
2.54
1.65
1.55
1.47
1.37
1.26
1.24
1.21
0.99
0.97
0.94
H
N
dichloromethane – d2
0.95
4.18
2.29
2.52
3.45
3.94
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)


132.957
131.677
105.063
104.362
H
N
32.653
28.015
23.081
21.394
14.297
14.240
dichloromethane – d2
100
50
Chemical Shift (ppm)

1i: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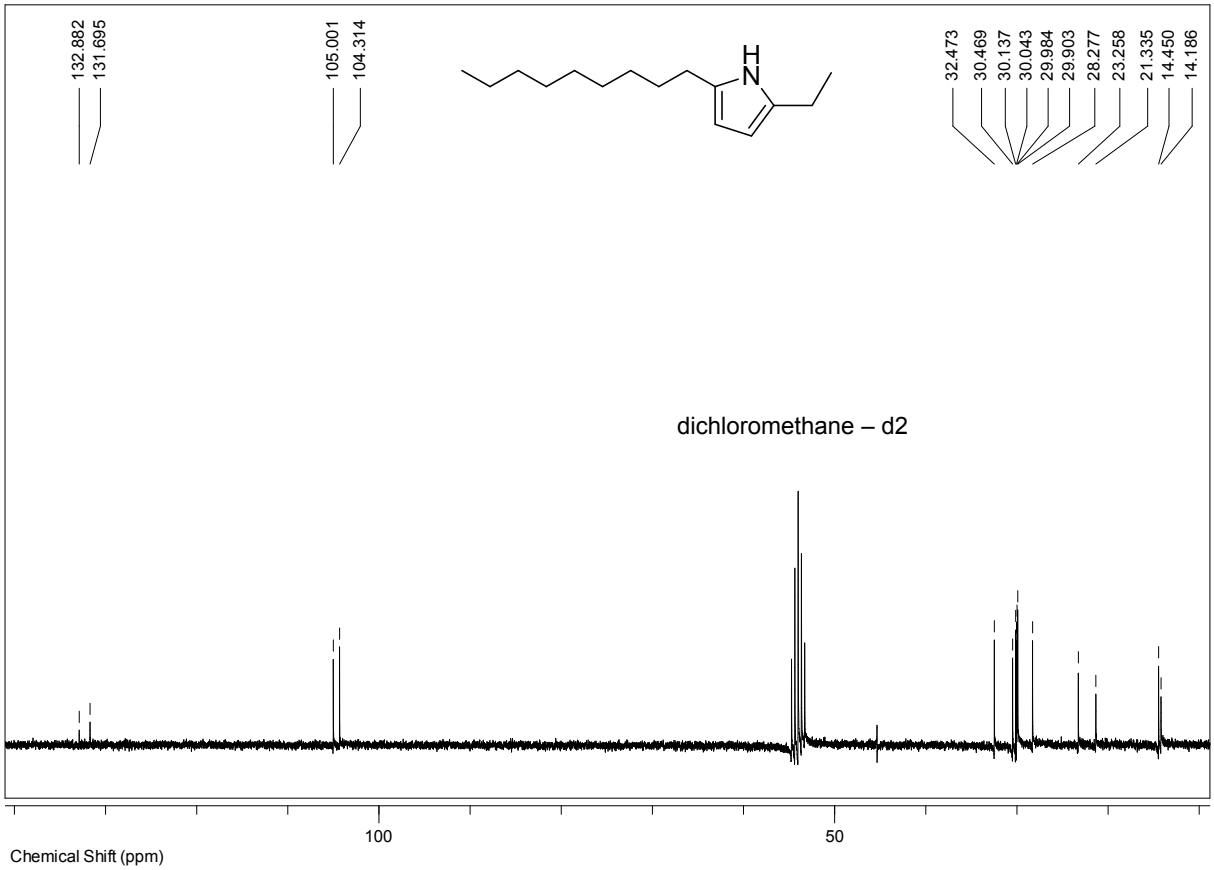
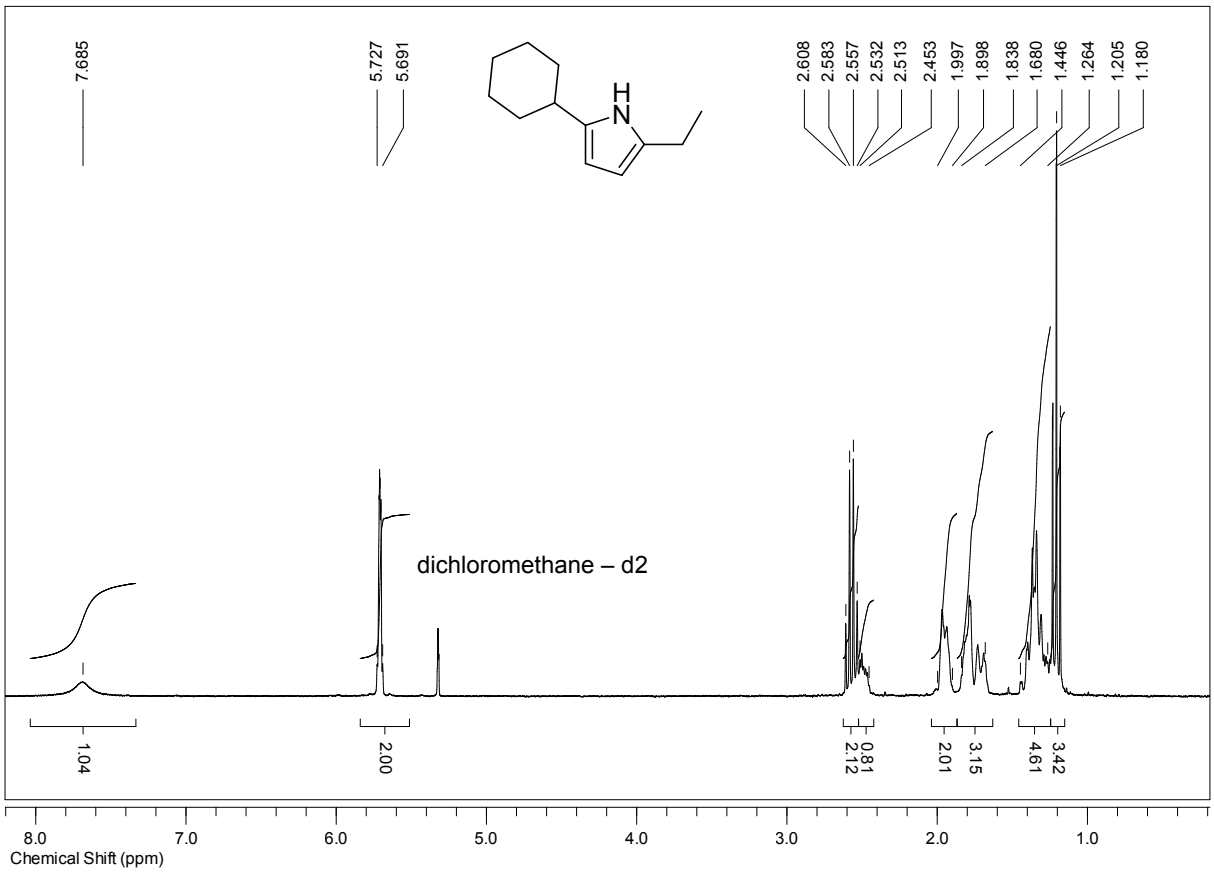
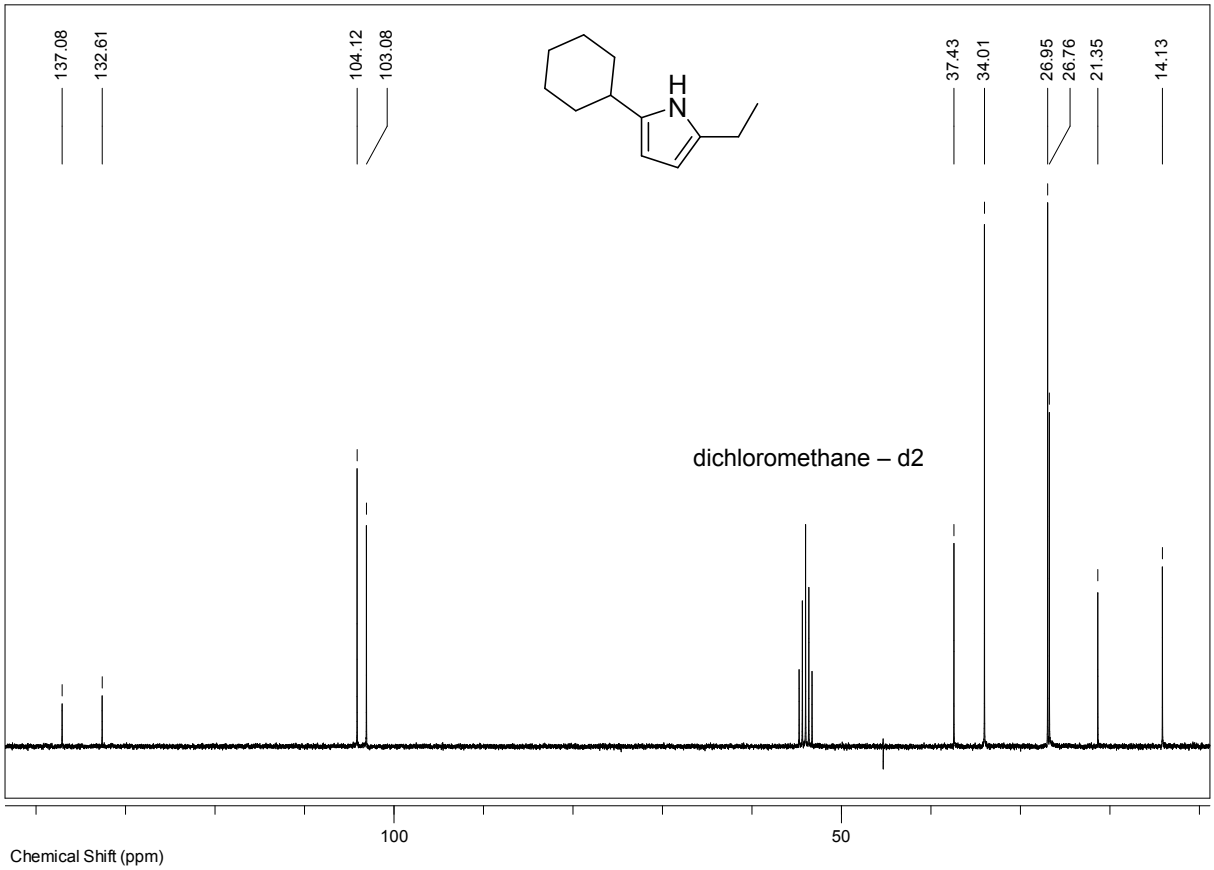
5.715
5.683
2.601
2.493
1.596
1.547
1.310
1.279
1.224
1.199
1.174
0.907
0.885
0.862
dichloromethane – d2
1.02
2.00
4.11
1.90
12.37
3.27
3.02
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

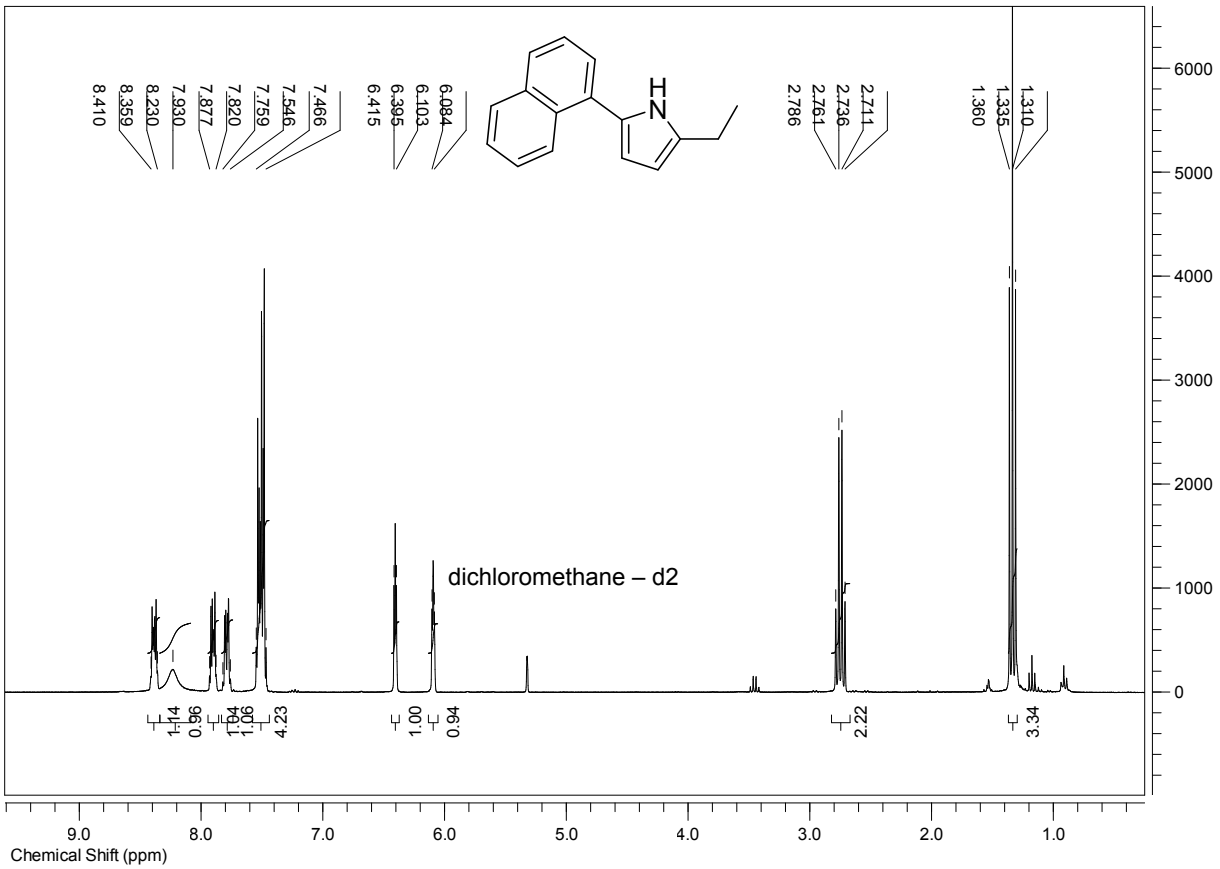

132.882
131.695
105.001
104.314
32.473
30.469
30.137
30.043
29.984
29.903
28.277
23.258
21.335
14.450
14.186
dichloromethane – d2
100
50
Chemical Shift (ppm)

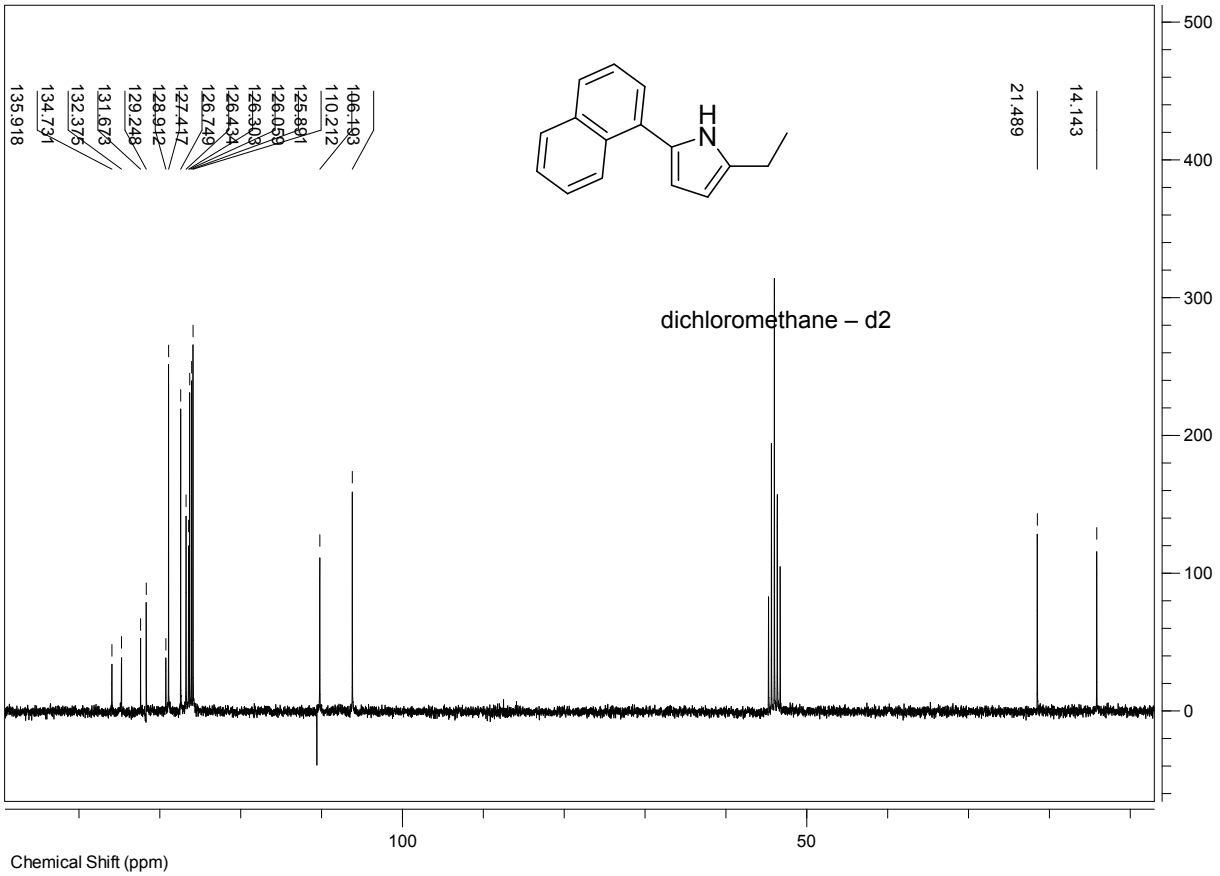
1j:


7.685
5.727
5.691
2.608
2.583
2.557
2.532
2.513
2.453
1.997
1.898
1.838
1.680
1.446
1.264
1.205
1.180
H
N
dichloromethane – d2
1.04
2.00
0.81
2.12
2.01
3.15
4.61
3.42
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

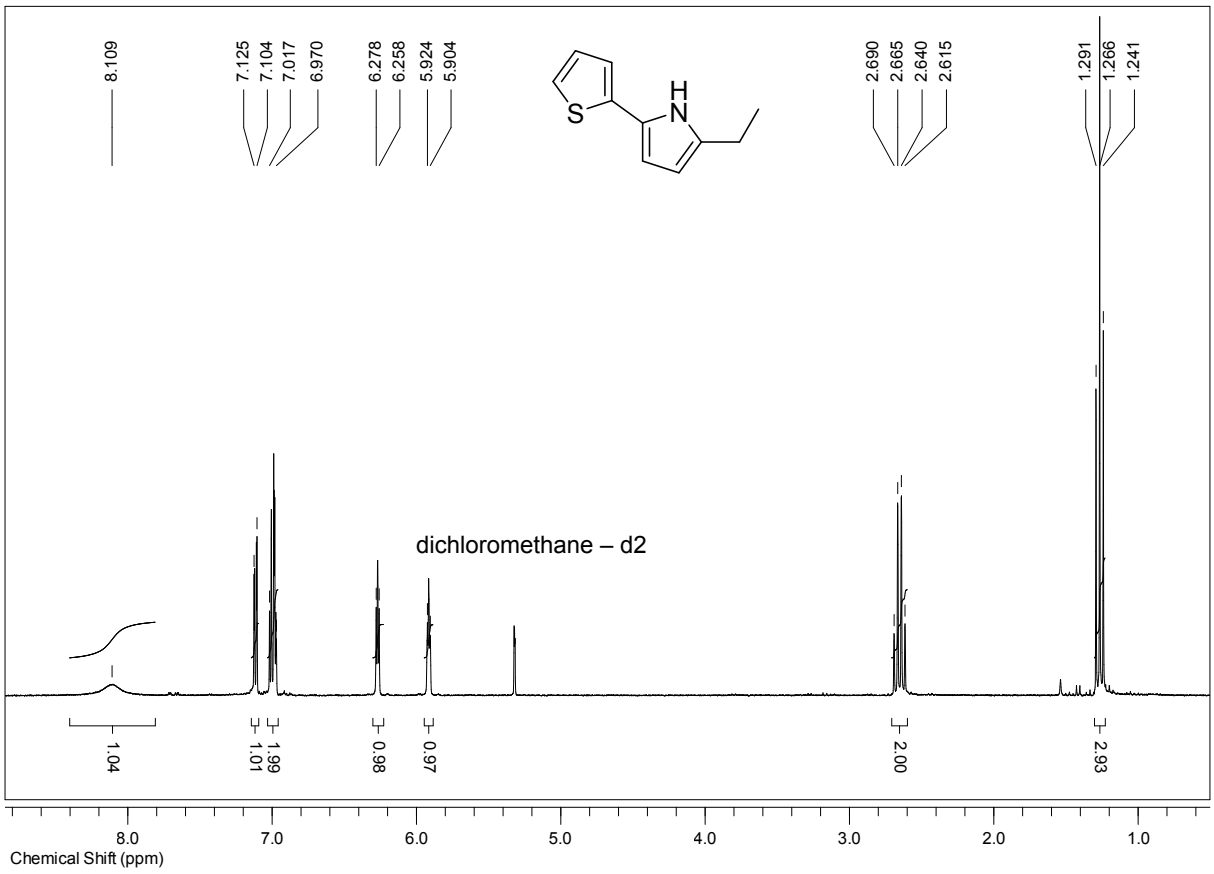

137.08
132.61
104.12
103.08
37.43
34.01
26.95
26.76
21.35
14.13
H
N
dichloromethane – d2
100
50
Chemical Shift (ppm)

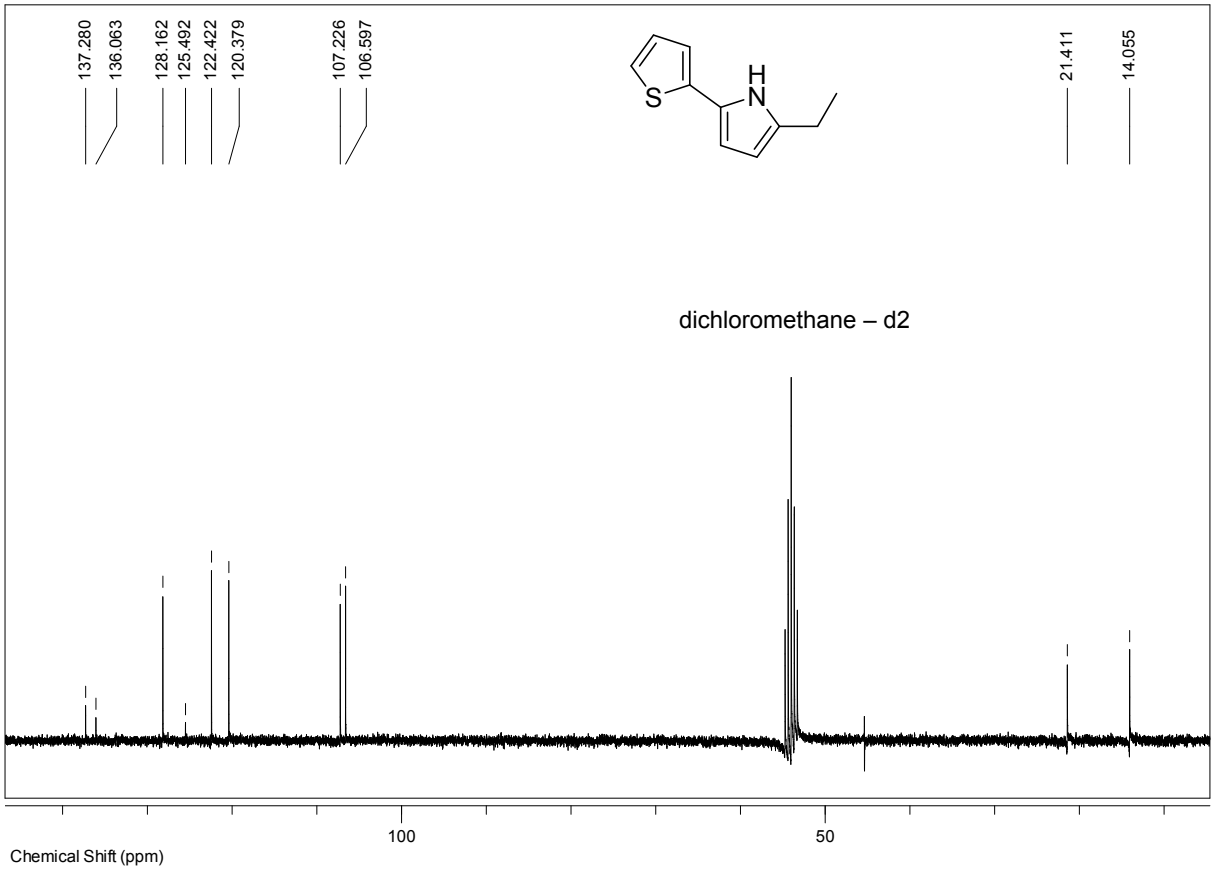
1k:


8.410
8.359
8.230
7.930
7.877
7.820
7.759
7.546
7.466
6.415
6.395
6.103
6.084
2.786
2.761
2.736
2.711
1.360
1.335
1.310
dichloromethane – d2
1.14
0.96
1.04
1.06
2.23
1.00
0.94
2.22
3.34
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

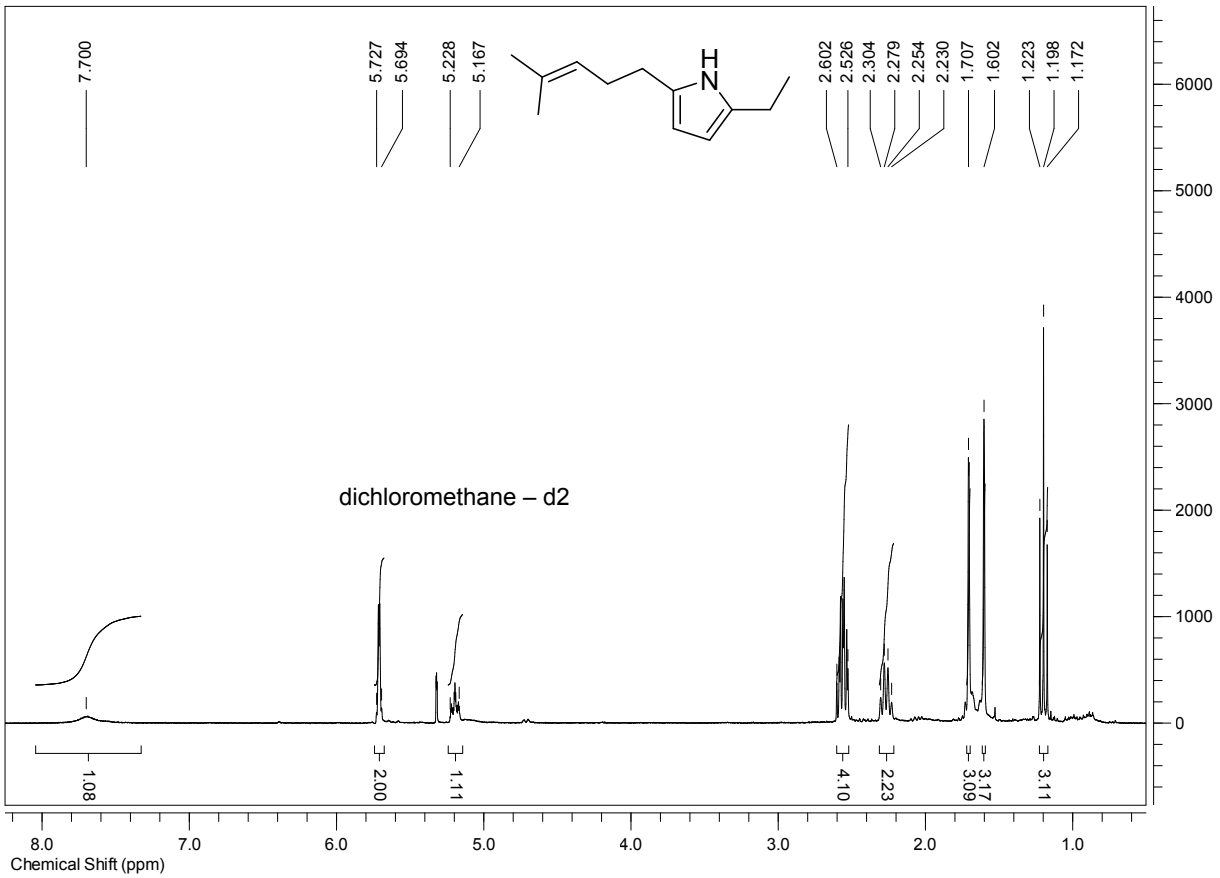

135.918
134.731
132.375
131.673
129.248
128.912
127.417
126.749
126.434
126.303
126.059
125.891
110.212
106.193
21.489
14.143
dichloromethane – d2
100
50
Chemical Shift (ppm)

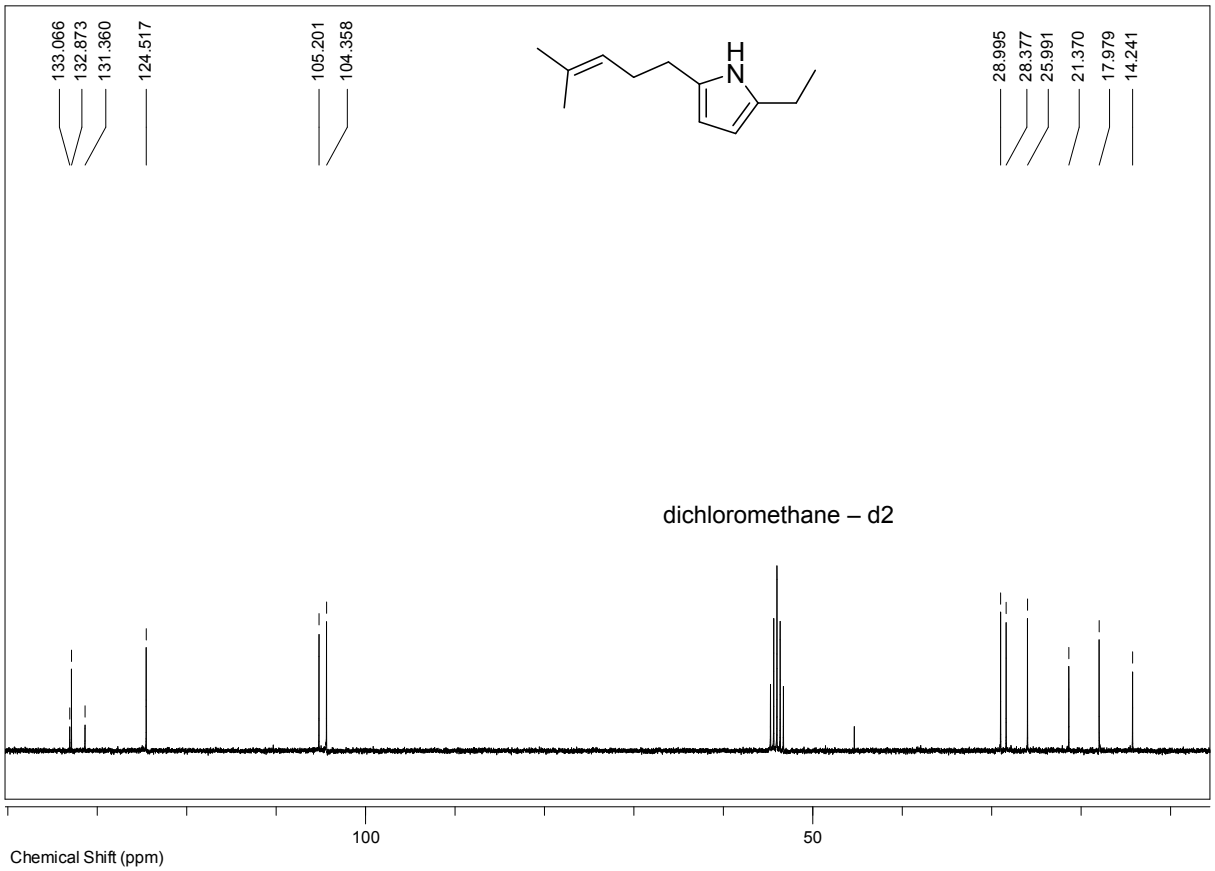
1l:


8.109
7.125
7.104
7.017
6.970
6.278
6.258
5.924
5.904
2.690
2.665
2.640
2.615
1.291
1.266
1.241
S
H
N
dichloromethane – d2
1.04
1.01
1.99
0.98
0.97
2.00
2.93
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

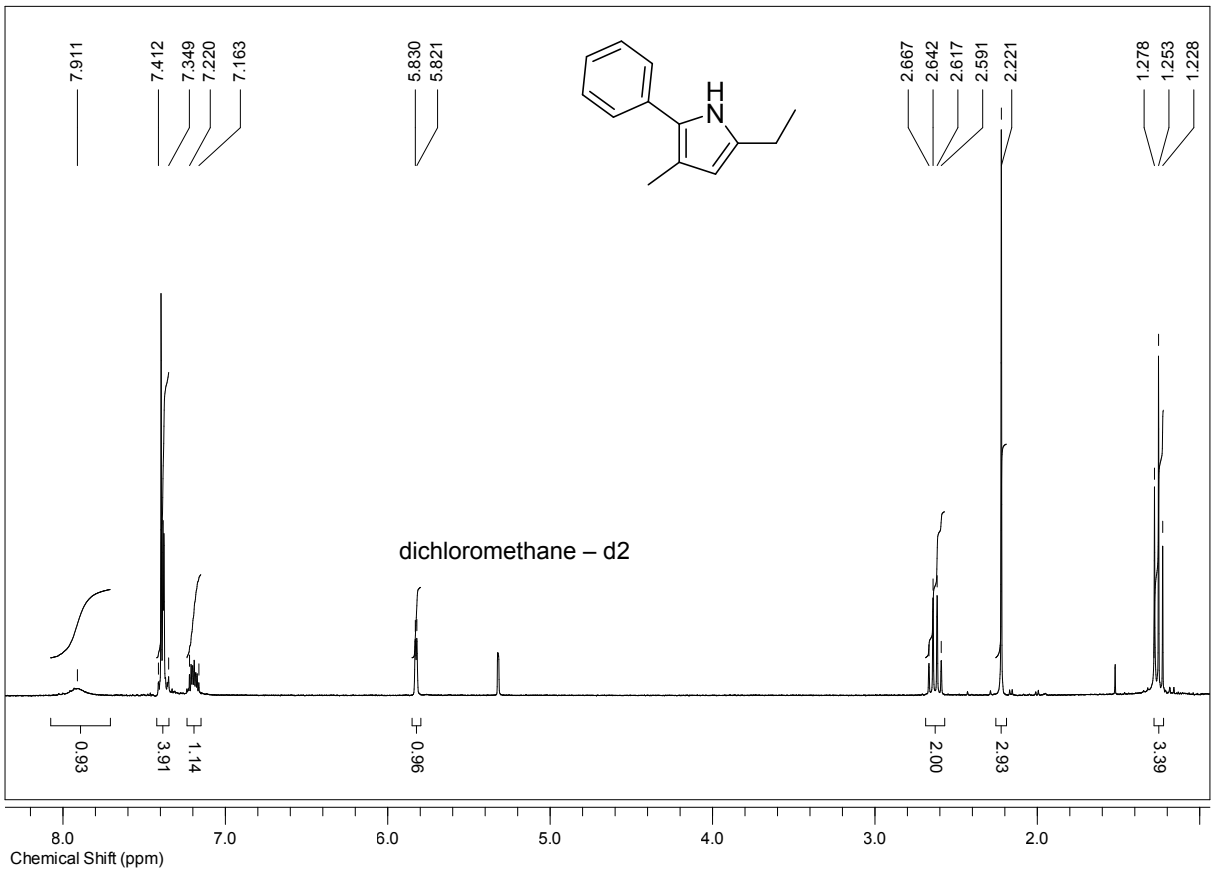

137.280
136.063
128.162
125.492
122.422
120.379
107.226
106.597
21.411
14.055
S
H
N
dichloromethane – d2
100
50
Chemical Shift (ppm)

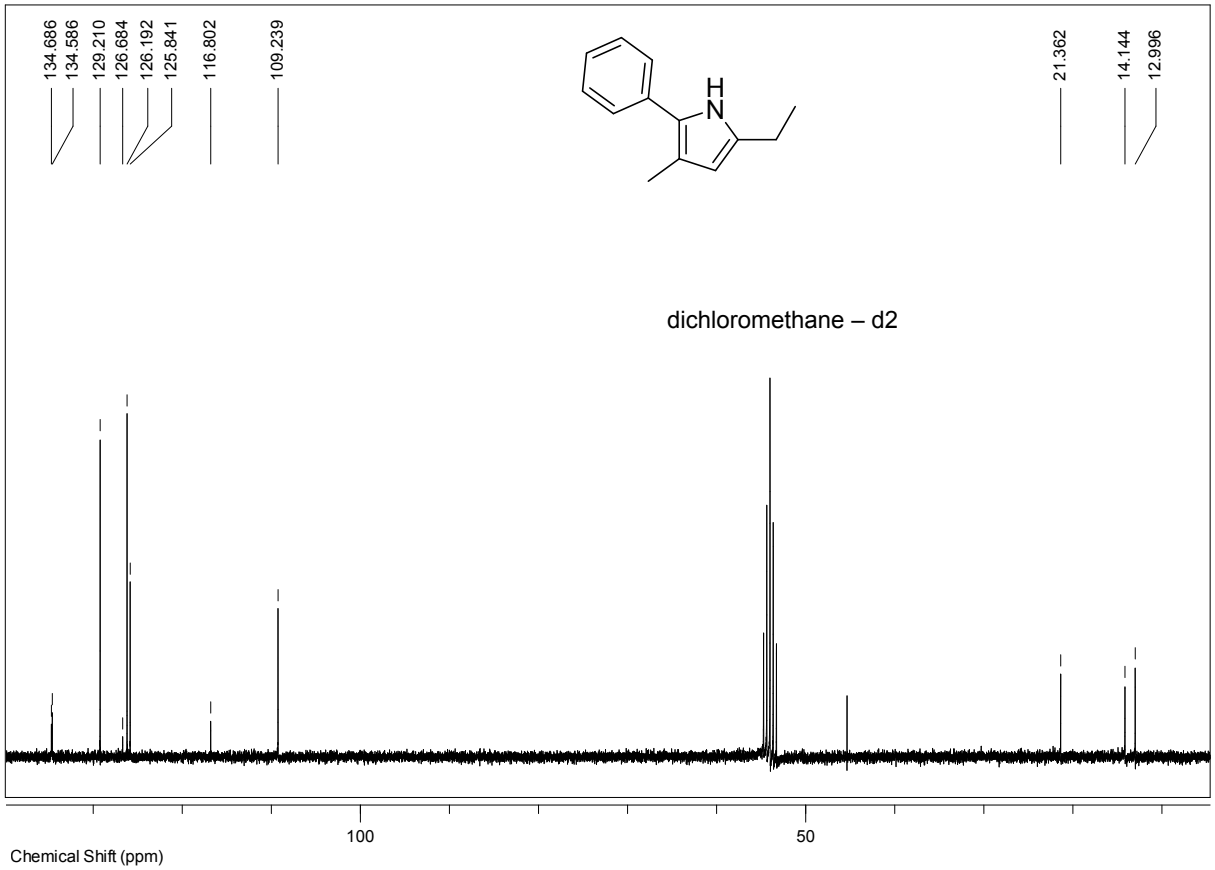
1m:


7.700
5.727
5.694
5.228
5.167
2.602
2.526
2.304
2.279
2.254
2.230
1.707
1.602
1.223
1.198
1.172
H
N
dichloromethane – d2
1.08
2.00
1.11
4.10
2.23
3.17
3.09
3.11
Chemical Shift (ppm)

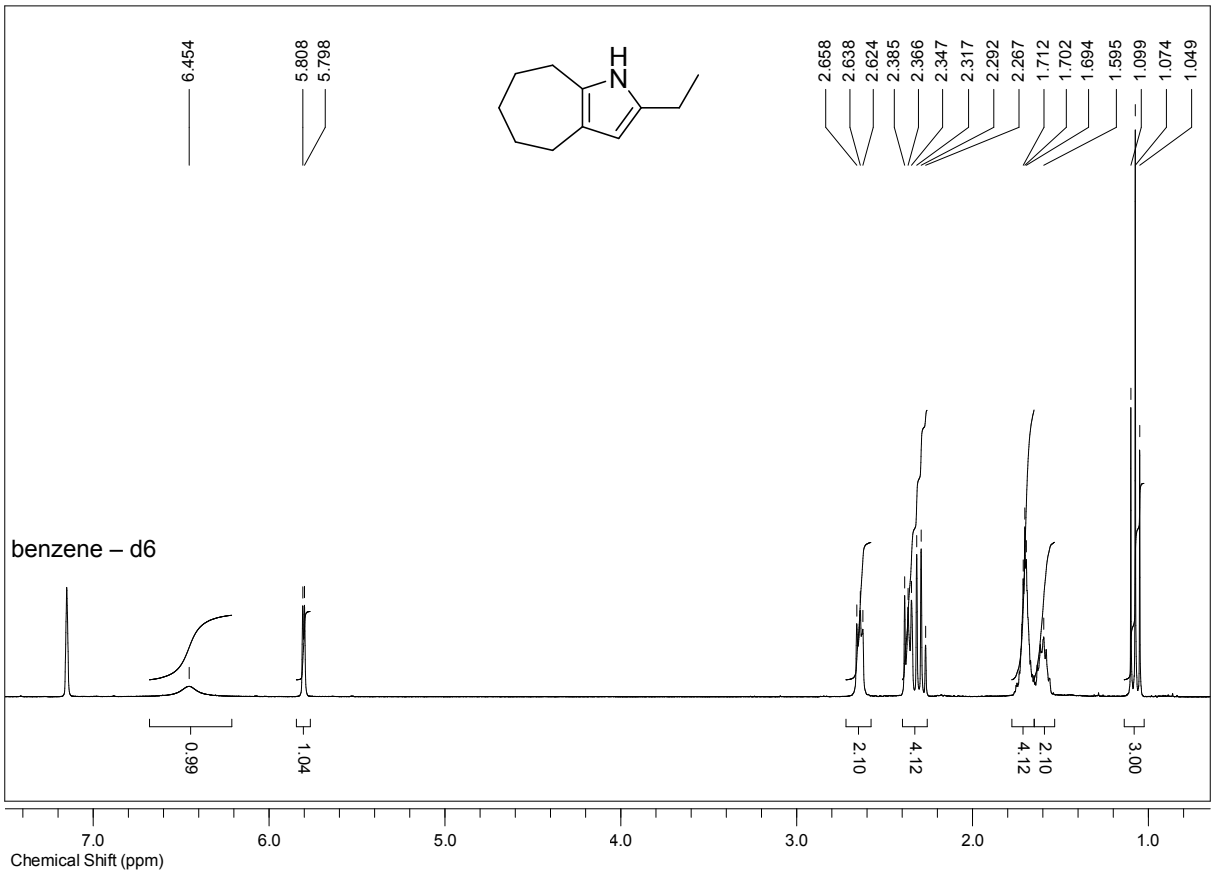

133.066
132.873
131.360
124.517
105.201
104.358
28.995
28.377
25.991
21.370
17.979
14.241
H
N
dichloromethane – d2
Chemical Shift (ppm)

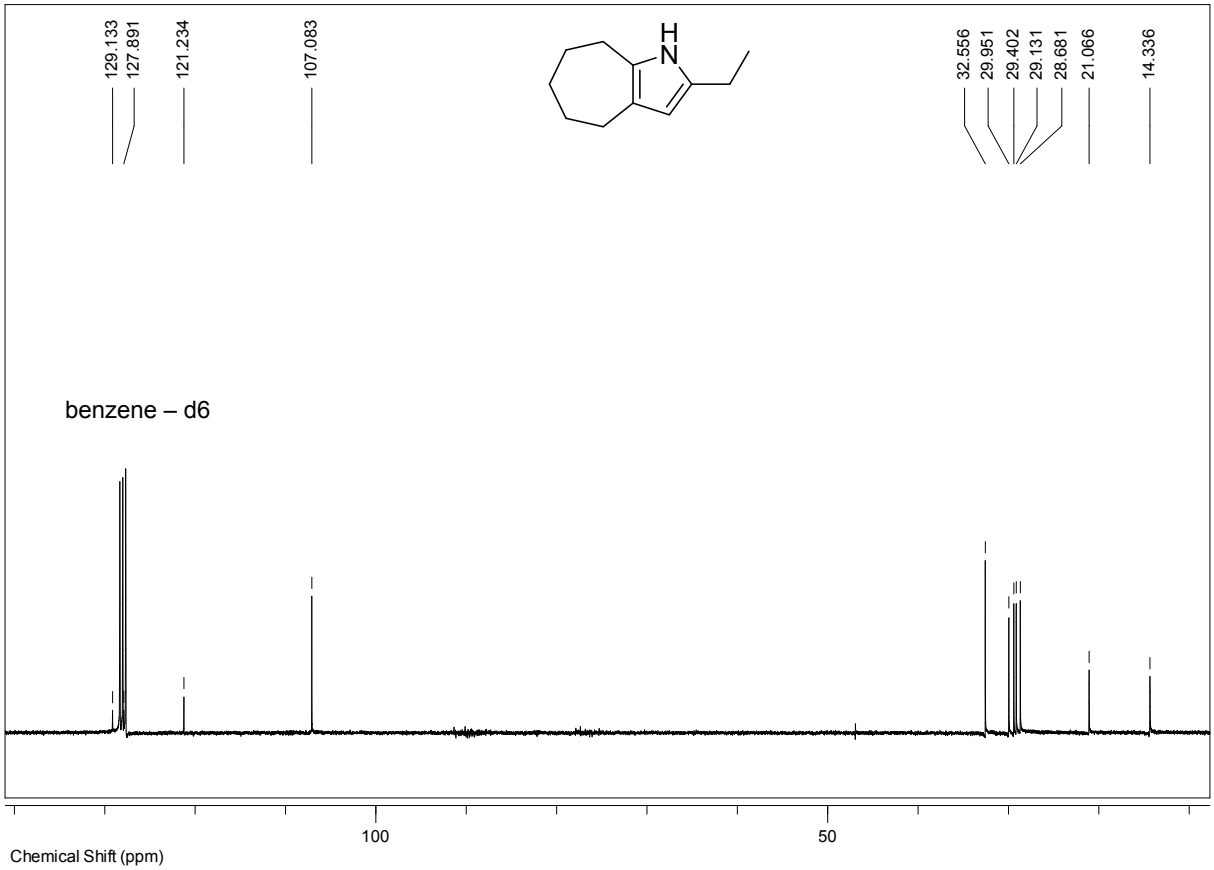
2a:


7.911
7.412
7.349
7.220
7.163
5.830
5.821
2.667
2.642
2.617
2.591
2.221
1.278
1.253
1.228
H
N
dichloromethane – d2
0.93
3.91
1.14
0.96
2.00
2.93
3.39
8.0
7.0
6.0
5.0
4.0
3.0
2.0
Chemical Shift (ppm)

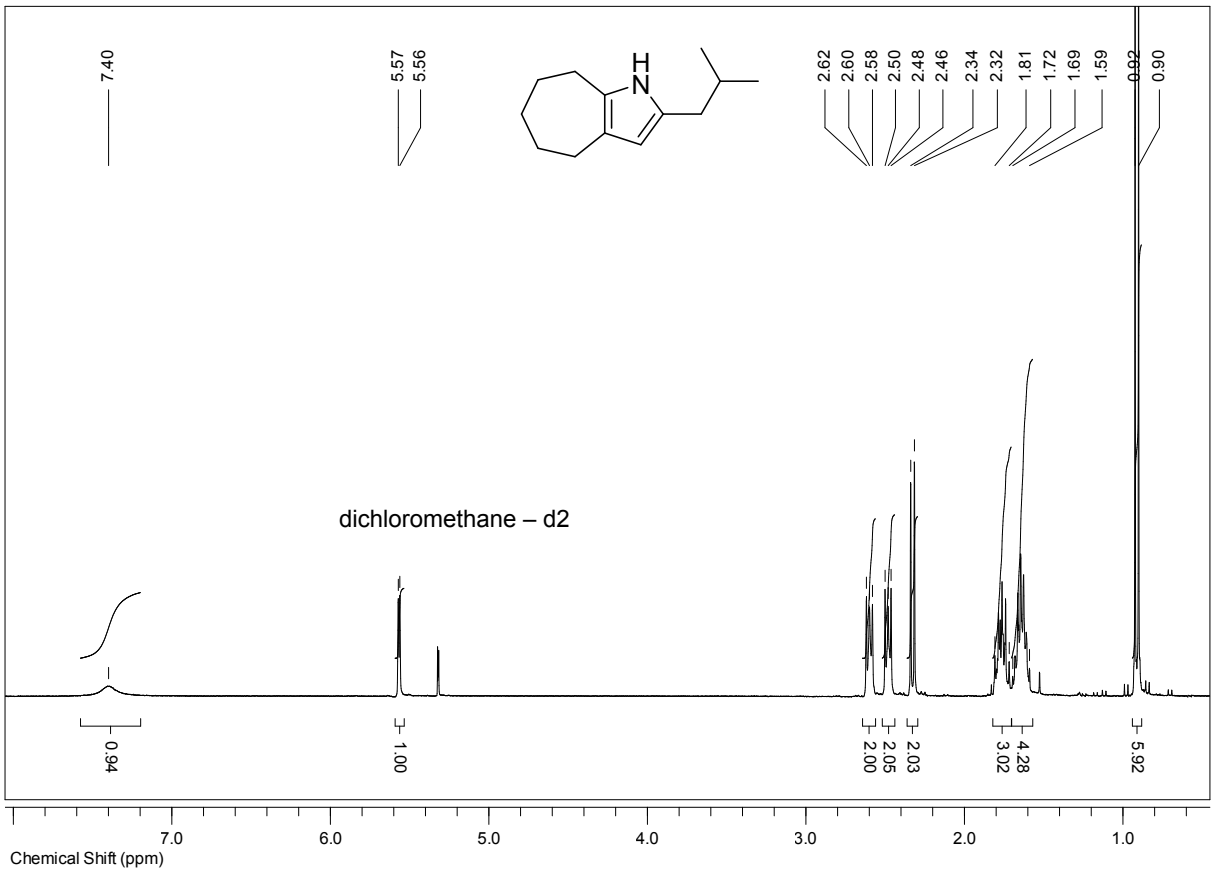

134.686
134.586
129.210
126.684
126.192
125.841
116.802
109.239
21.362
14.144
12.996
H
N
dichloromethane – d2
100
50
Chemical Shift (ppm)

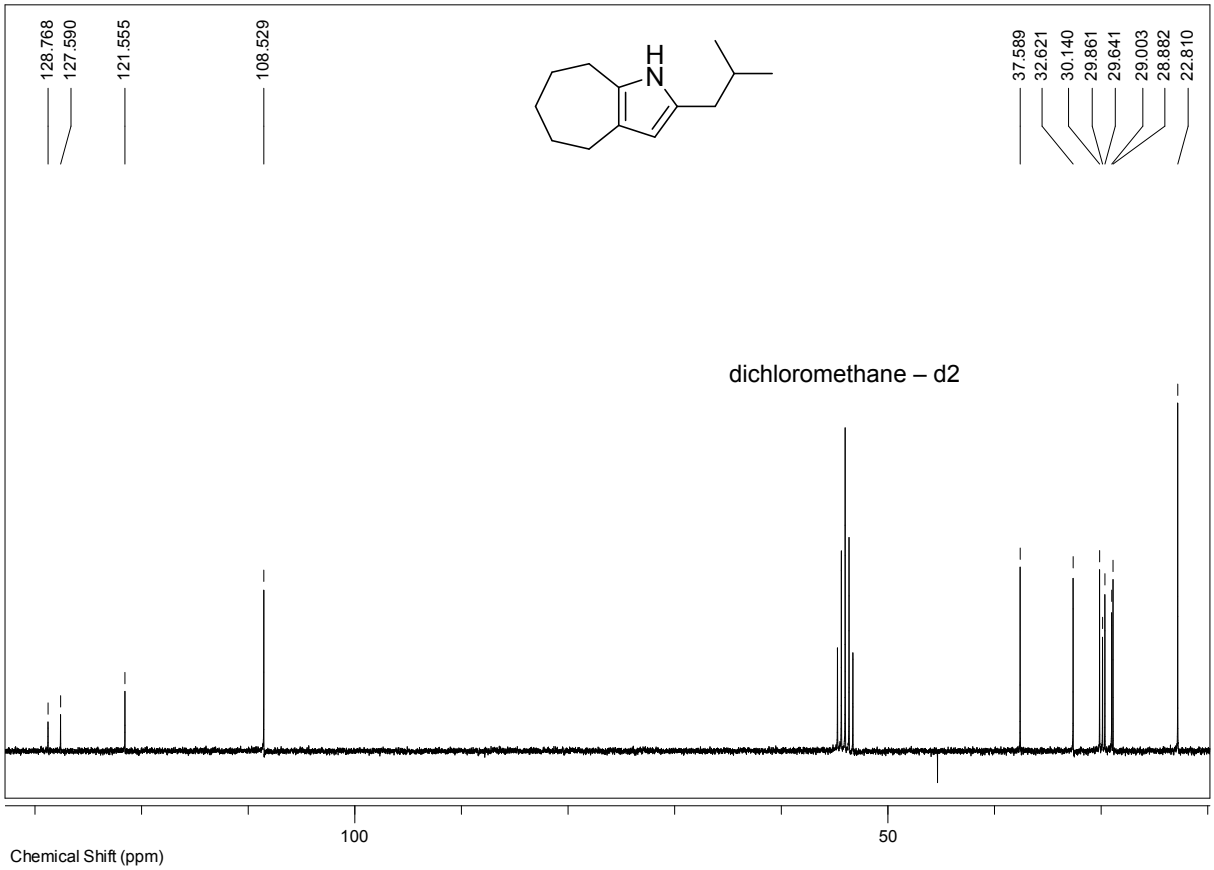
2b:


6.454
5.808
5.798
H
N
2.658
2.638
2.624
2.385
2.366
2.347
2.317
2.292
2.267
1.712
1.702
1.694
1.595
1.099
1.074
1.049
benzene – d6
0.99
1.04
2.10
4.12
4.12
2.10
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

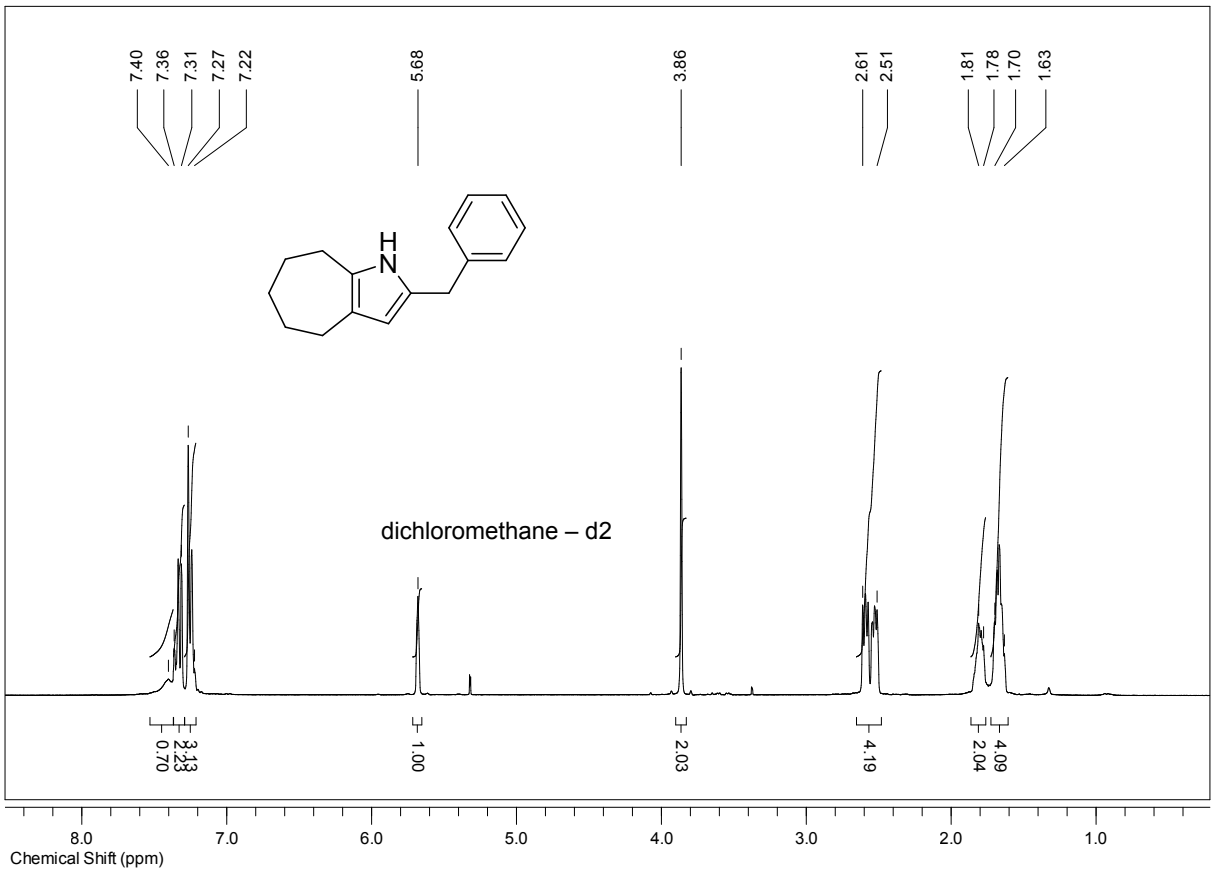

129.133
127.891
121.234
107.083
H
N
32.556
29.951
29.402
29.131
28.681
21.066
14.336
benzene – d6
100
50
Chemical Shift (ppm)

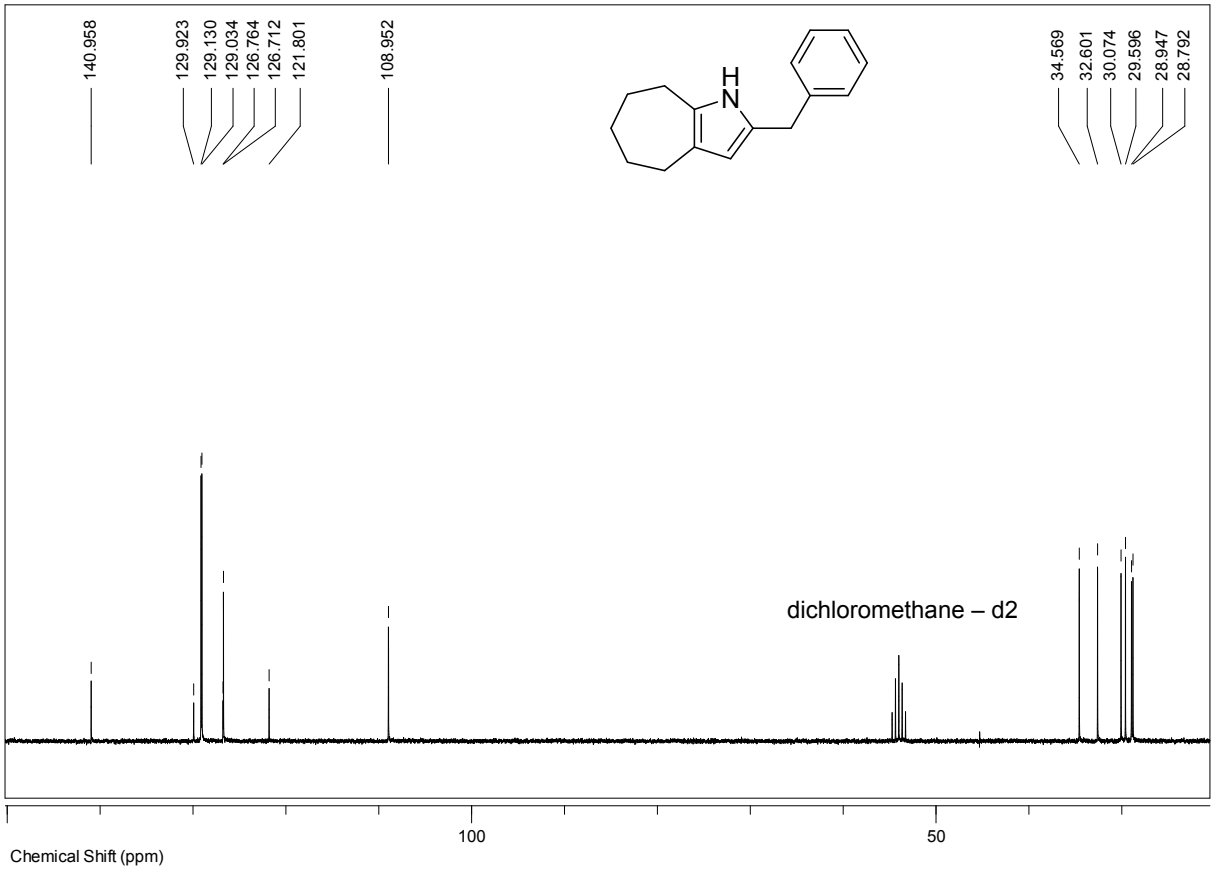
2c:


7.40
5.57
5.56
2.62
2.60
2.58
2.50
2.48
2.46
2.34
2.32
1.81
1.72
1.69
1.59
0.92
0.90
dichloromethane – d2
0.64
1.00
2.00
2.05
2.03
3.02
4.28
5.92
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

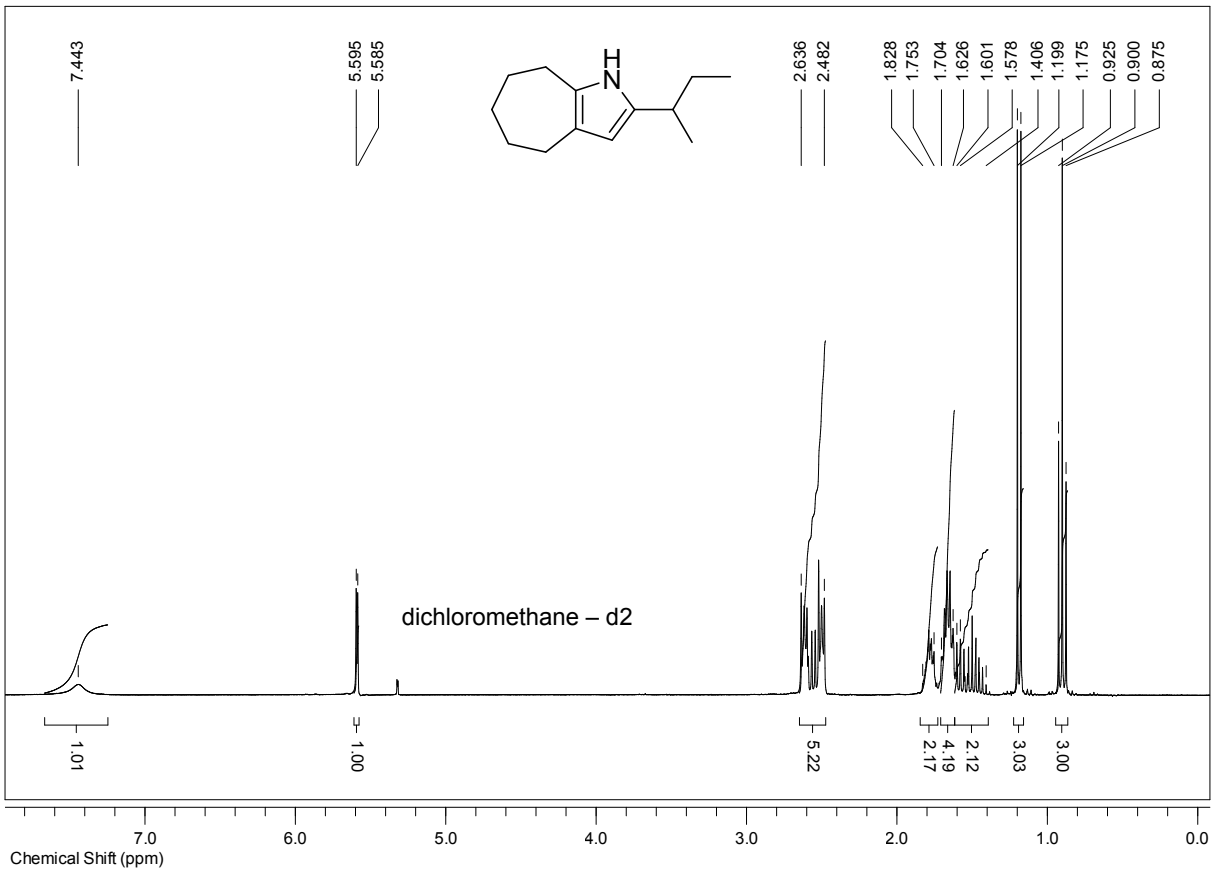

128.768
127.590
121.555
108.529
37.589
32.621
30.140
29.861
29.641
29.003
28.882
22.810
dichloromethane – d2
100
50
Chemical Shift (ppm)

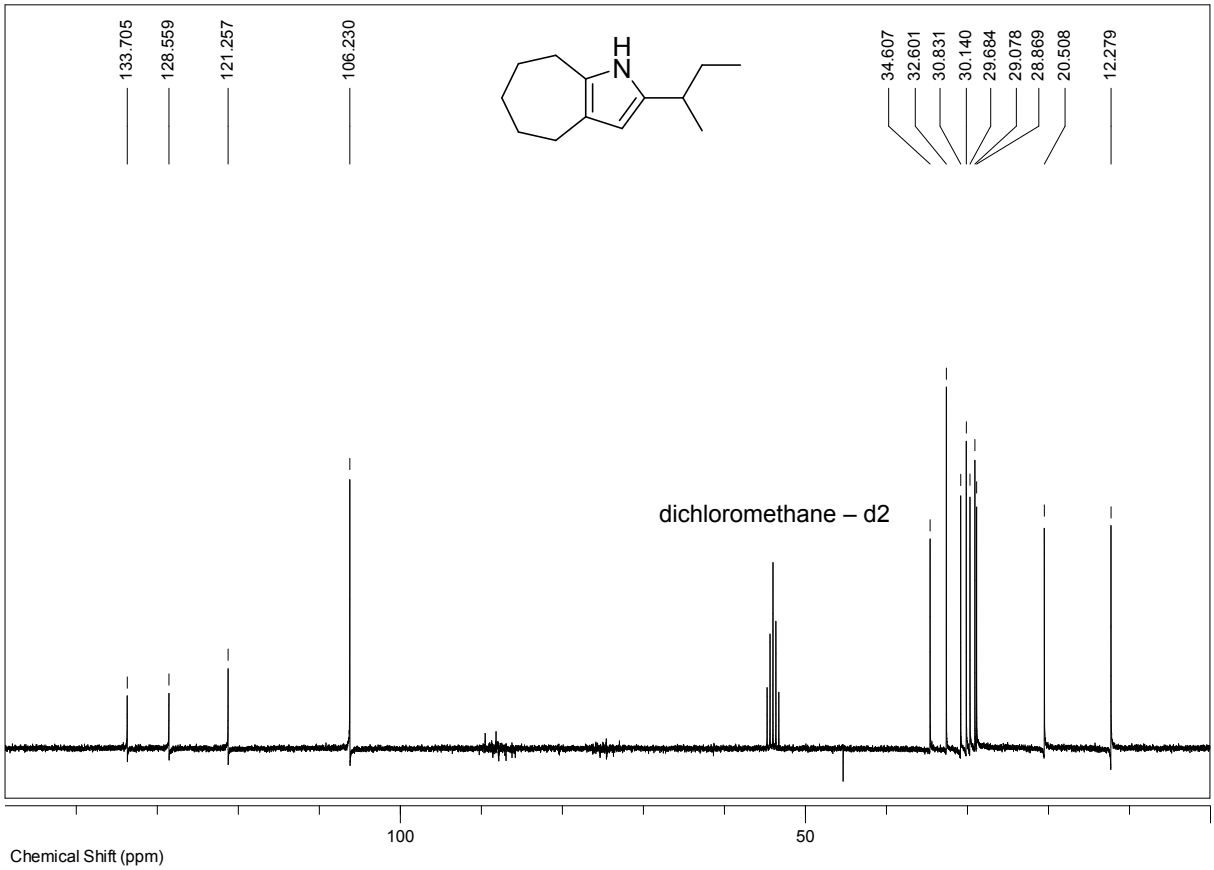
2d:


7.40
7.36
7.31
7.27
7.22
5.68
3.86
2.61
2.51
1.81
1.78
1.70
1.63
H
N
dichloromethane – d2
0.70
3.13
3.23
1.00
2.03
4.19
2.04
4.09
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

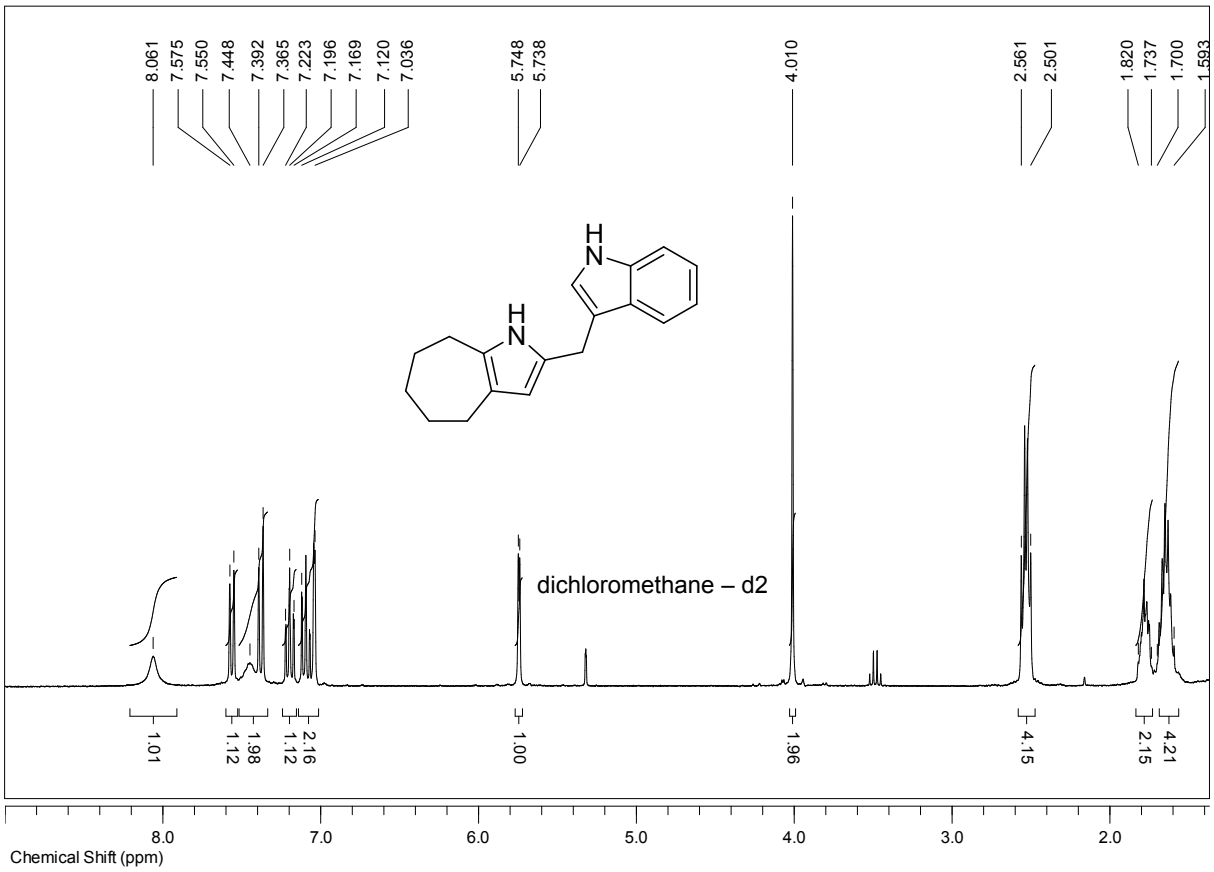

140.958
129.923
129.130
129.034
126.764
126.712
121.801
108.952
H
N
34.569
32.601
30.074
29.596
28.947
28.792
dichloromethane – d2
100
50
Chemical Shift (ppm)

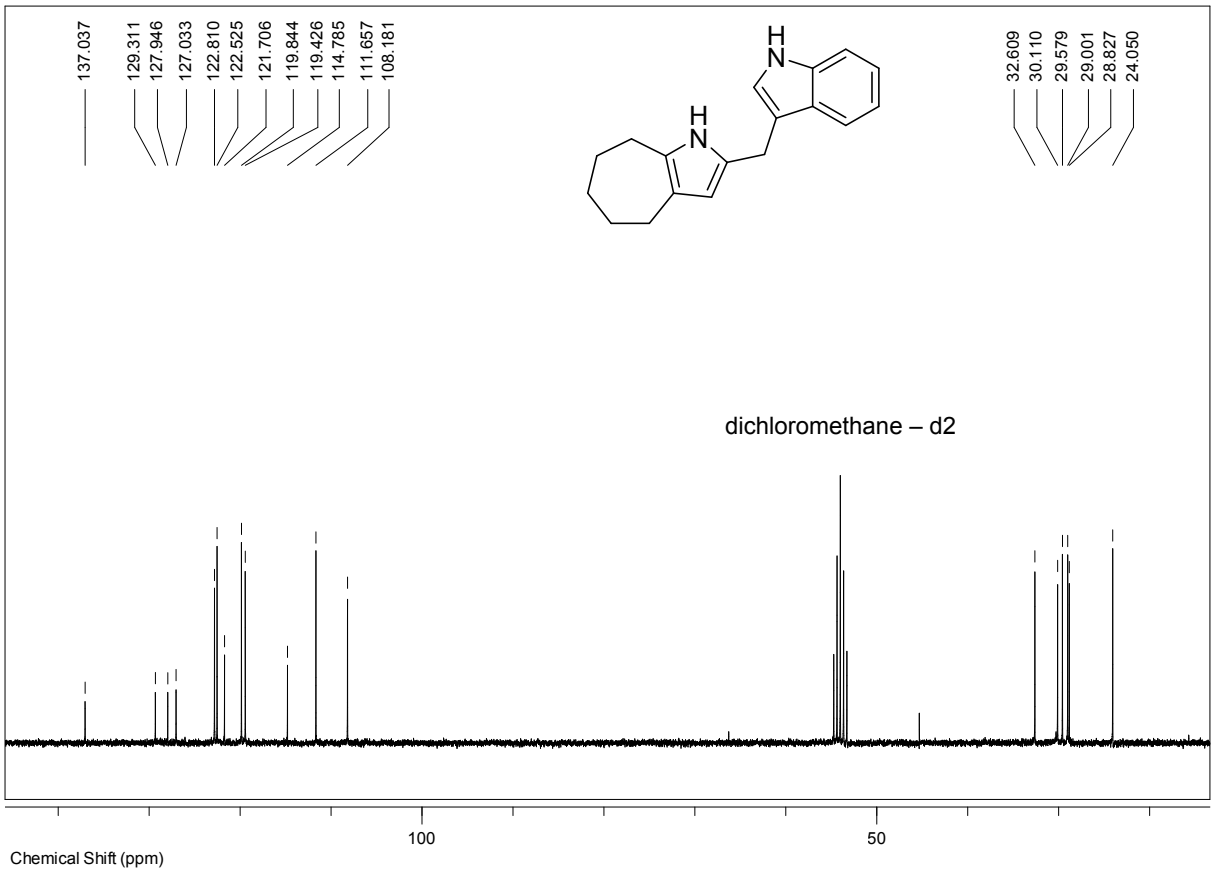
2e:


7.443
5.595
5.585
2.636
2.482
1.828
1.753
1.704
1.626
1.601
1.578
1.406
1.199
1.175
0.925
0.900
0.875
dichloromethane – d2
1.01
1.00
5.22
2.17
4.19
2.12
3.03
3.00
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
Chemical Shift (ppm)

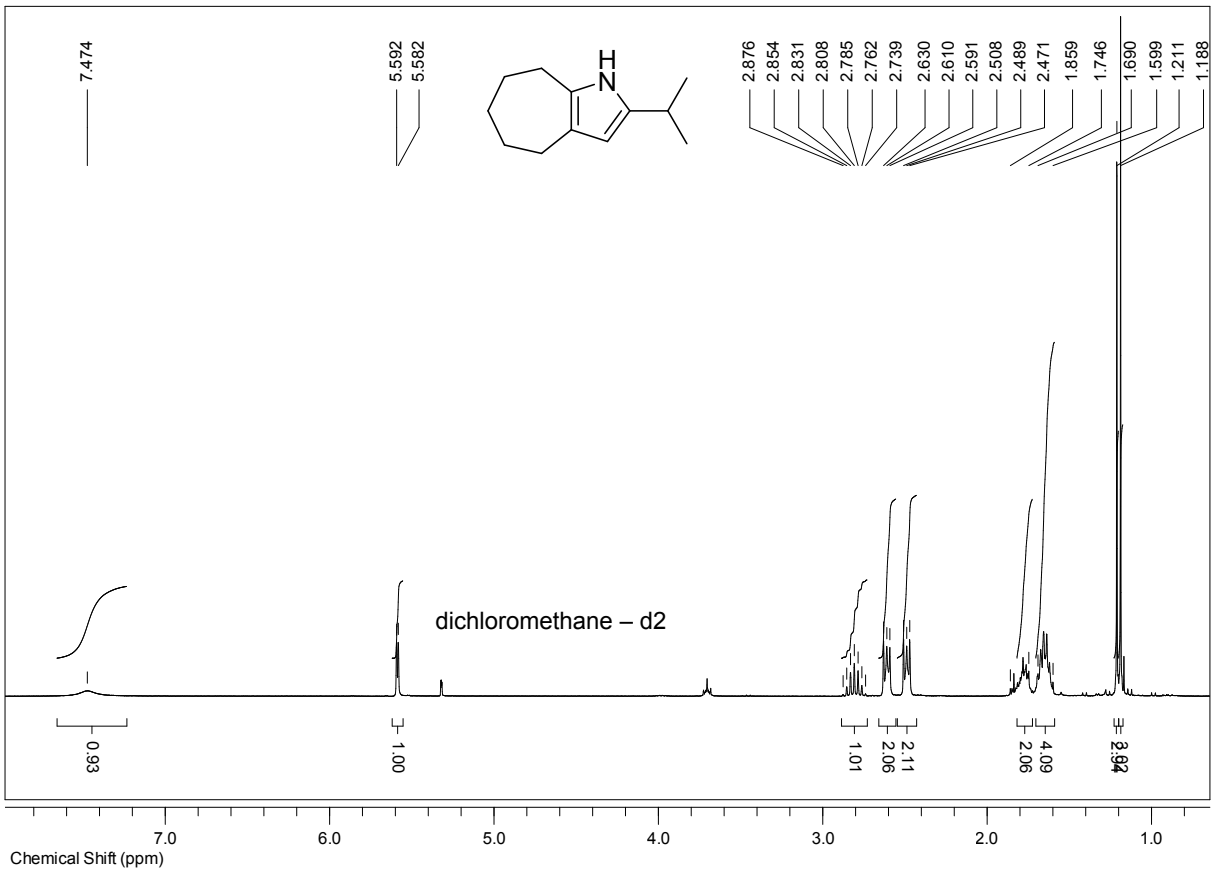

133.705
128.559
121.257
106.230
34.607
32.601
30.831
30.140
29.684
29.078
28.869
20.508
12.279
dichloromethane – d2
100
50
Chemical Shift (ppm)

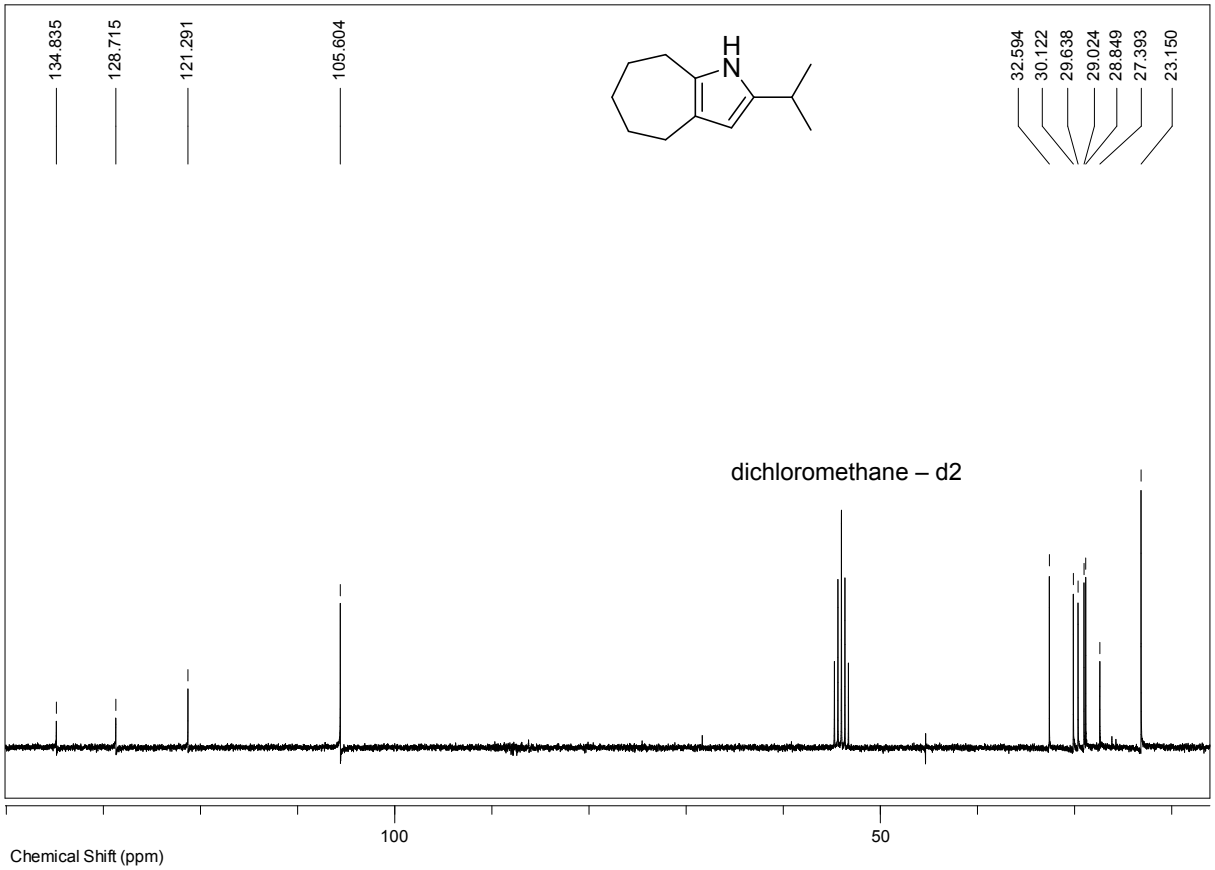
2f:


8.061
7.575
7.550
7.448
7.392
7.365
7.223
7.196
7.169
7.120
7.036
5.748
5.738
4.010
2.561
2.501
1.820
1.737
1.700
1.593
dichloromethane – d2
1.01
1.12
1.98
1.12
2.16
1.00
1.96
4.15
2.15
4.21
8.0
7.0
6.0
5.0
4.0
3.0
2.0
Chemical Shift (ppm)

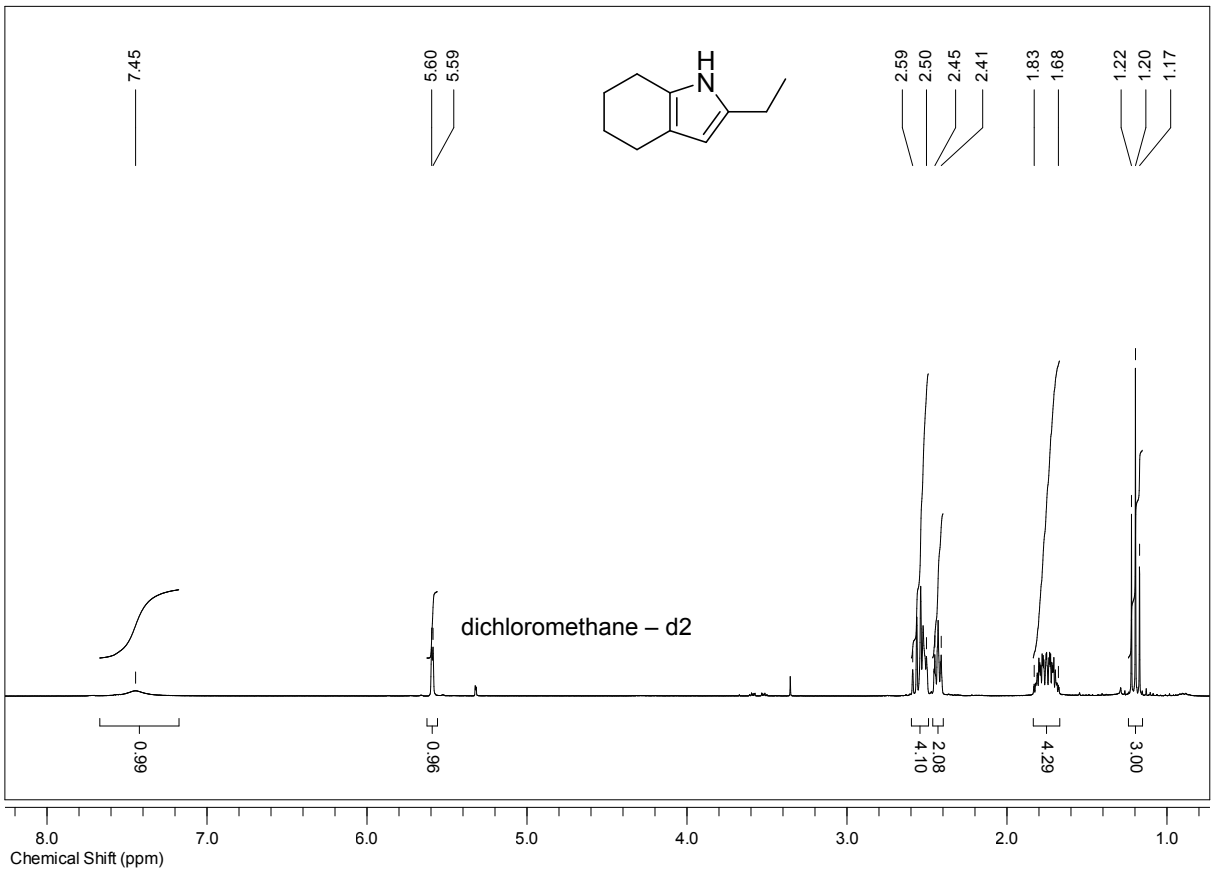

137.037
129.311
127.946
127.033
122.810
122.525
121.706
119.844
119.426
114.785
111.657
108.181
32.609
30.110
29.579
29.001
28.827
24.050
dichloromethane – d2
100
50
Chemical Shift (ppm)

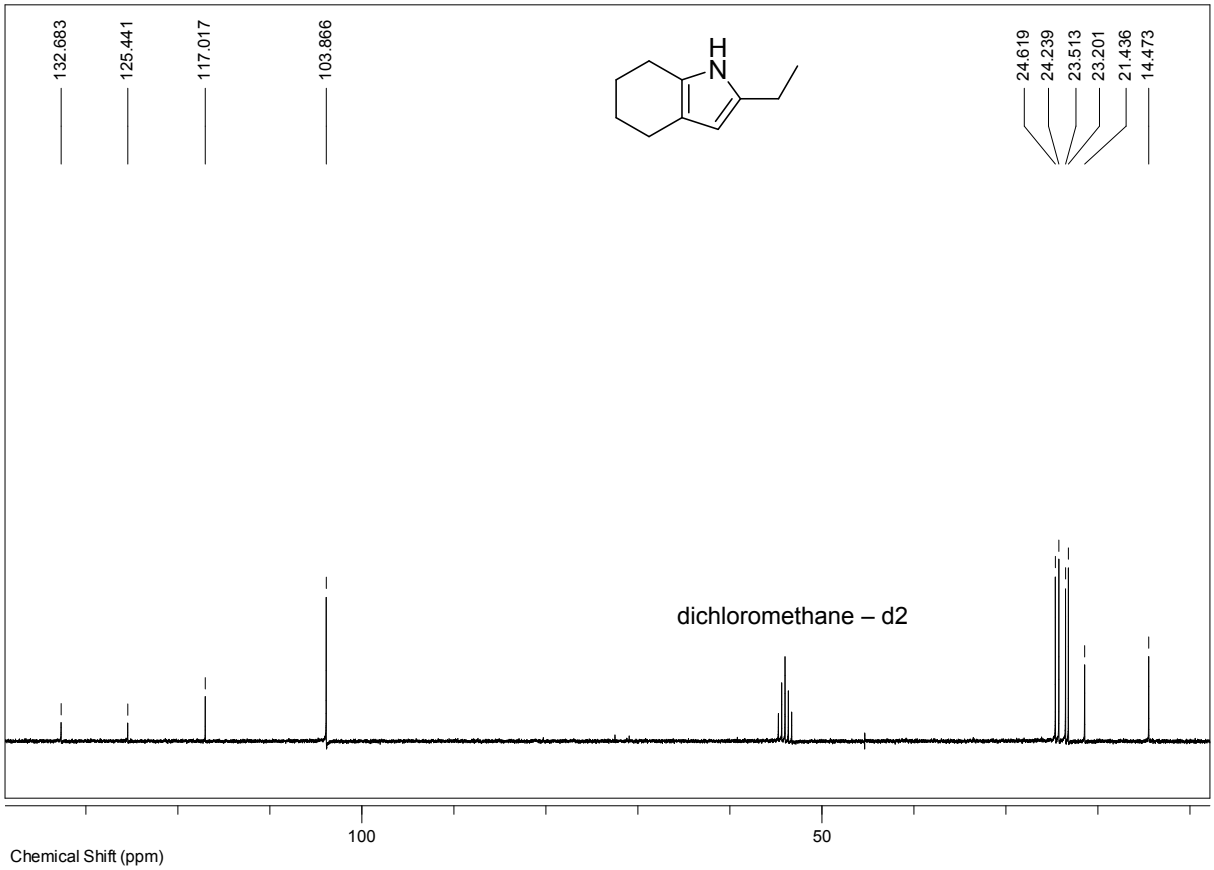
2g:


7.474
5.592
5.582
2.876
2.854
2.831
2.808
2.785
2.762
2.739
2.630
2.610
2.591
2.508
2.489
2.471
1.859
1.746
1.690
1.599
1.211
1.188
dichloromethane – d2
0.93
1.00
1.01
2.06
2.11
2.06
4.09
3.04
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

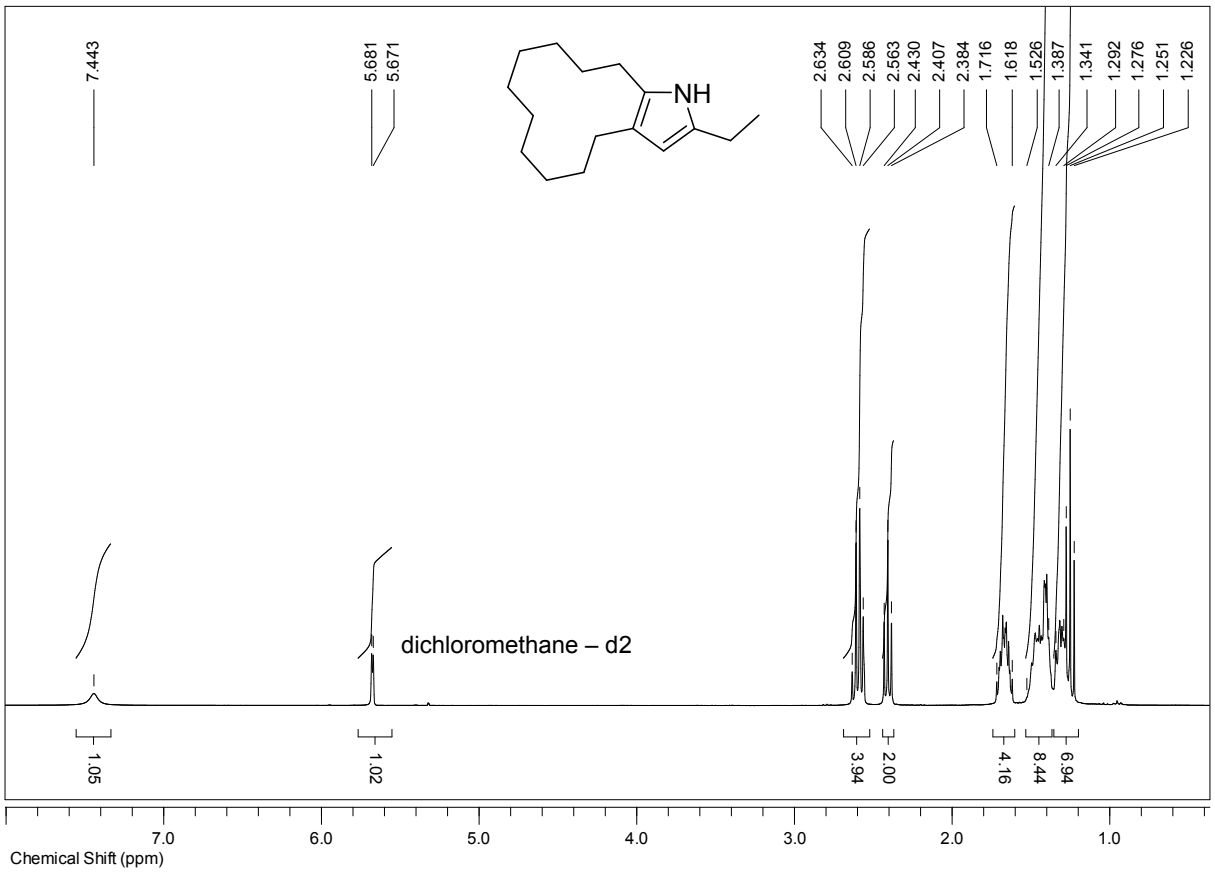

134.835
128.715
121.291
105.604
32.594
30.122
29.638
29.024
28.849
27.393
23.150
dichloromethane – d2
100
50
Chemical Shift (ppm)

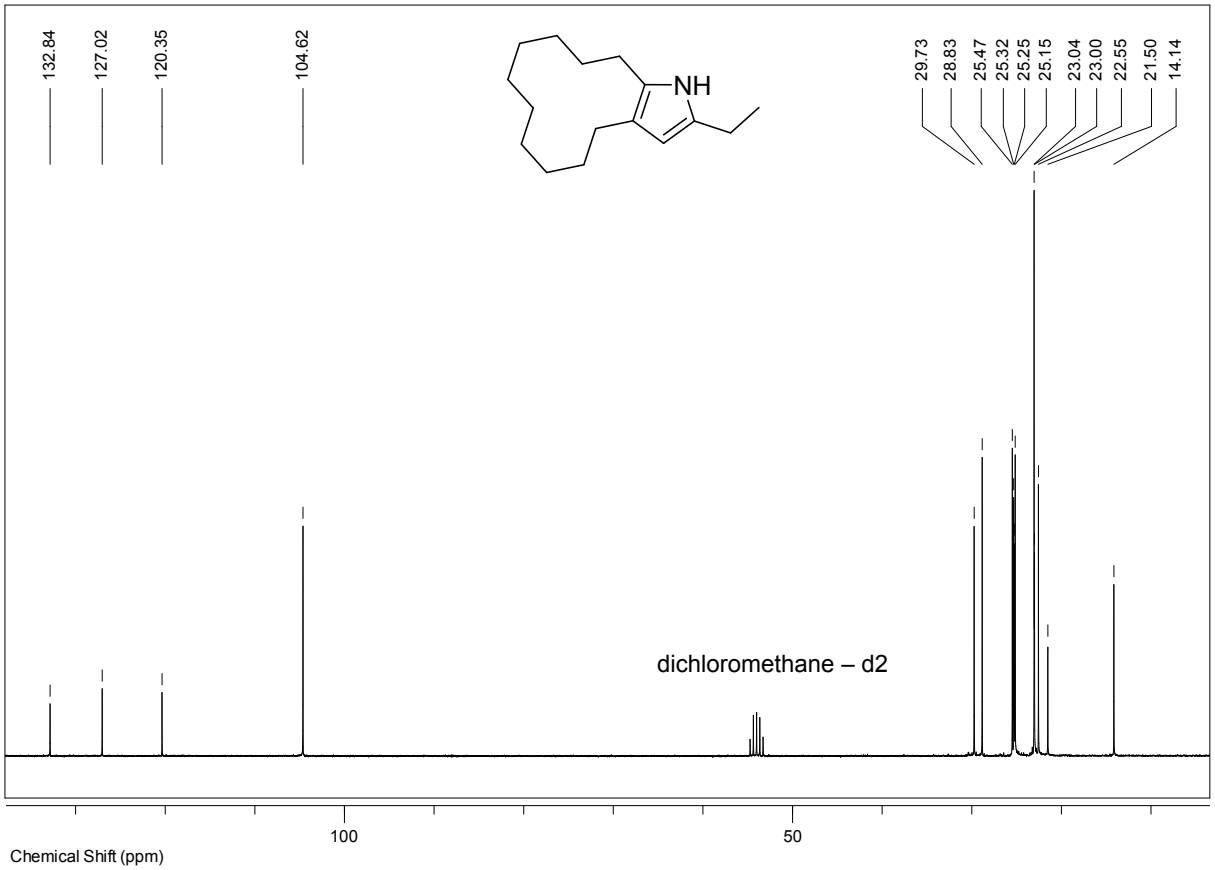
2h:


7.45
5.60
5.59
2.59
2.50
2.45
2.41
1.83
1.68
1.22
1.20
1.17
dichloromethane – d2
0.99
0.99
4.10
2.08
4.29
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)

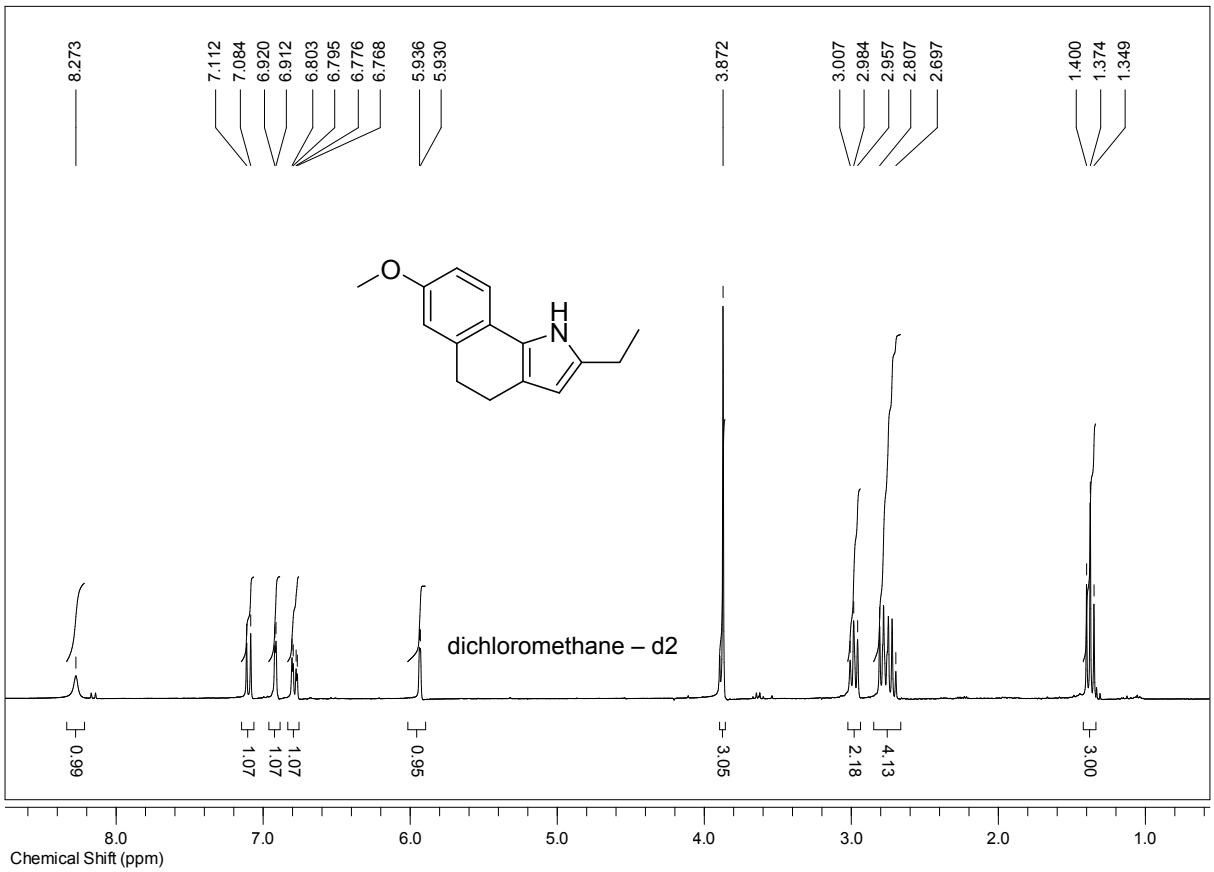

132.683
125.441
117.017
103.866
24.619
24.239
23.513
23.201
21.436
14.473
dichloromethane – d2
100
50
Chemical Shift (ppm)

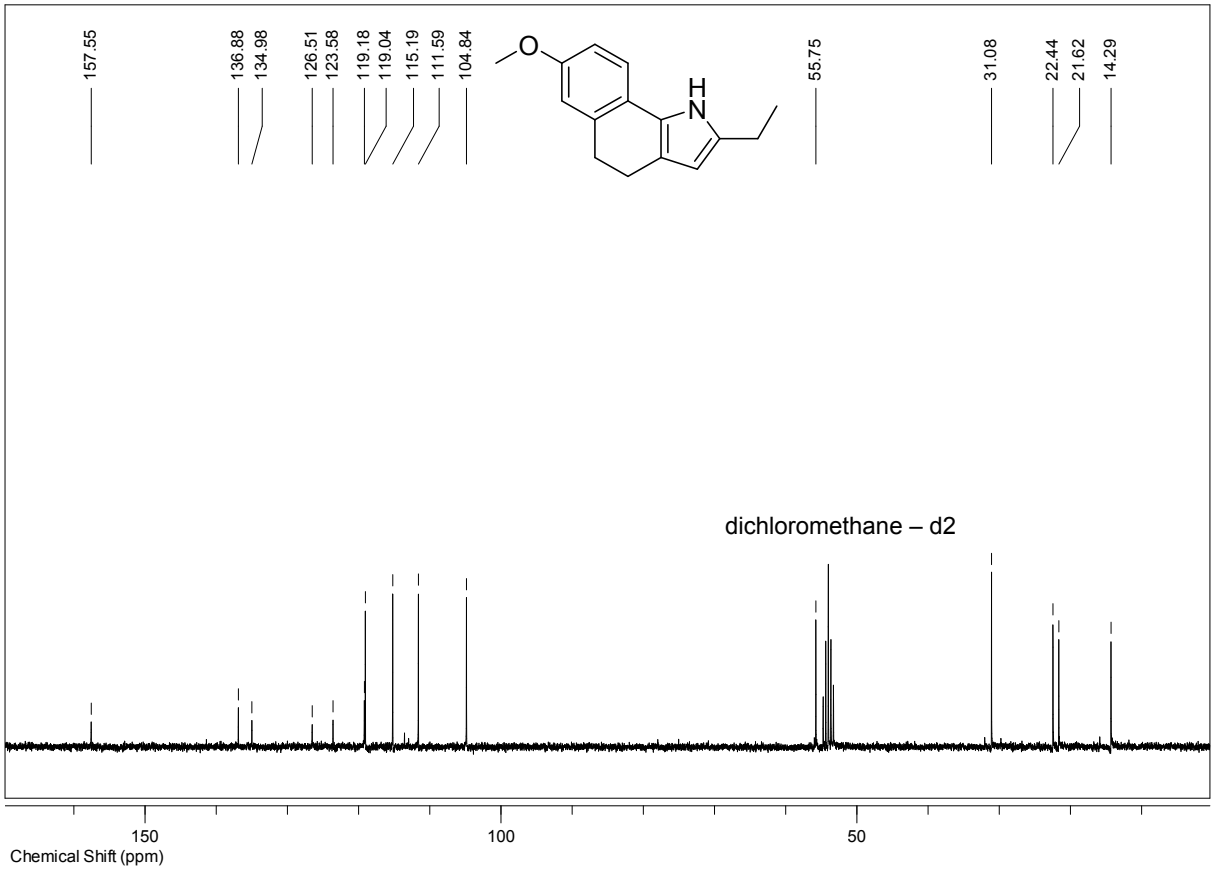
2i:


7.443
5.681
5.671
NH
2.634
2.609
2.586
2.563
2.430
2.407
2.384
1.716
1.618
1.526
1.387
1.341
1.292
1.276
1.251
1.226
dichloromethane – d2
1.05
1.02
3.94
2.00
4.16
8.44
6.94
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)


132.84
127.02
120.35
104.62
NH
29.73
28.83
25.47
25.32
25.25
25.15
23.04
23.00
22.55
21.50
14.14
dichloromethane – d2
100
50
Chemical Shift (ppm)

2j:


8.273
7.112
7.084
6.920
6.912
6.803
6.795
6.776
6.768
5.936
5.930
3.872
3.007
2.984
2.957
2.807
2.697
1.400
1.374
1.349
O
H
N
dichloromethane – d2
0.99
1.07
1.07
1.07
0.96
3.05
2.18
4.13
3.00
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
Chemical Shift (ppm)


157.55
136.88
134.98
126.51
123.58
119.18
119.04
115.19
111.59
104.84
O
H
N
55.75
31.08
22.44
21.62
14.29
dichloromethane – d2
150
100
50
Chemical Shift (ppm)

References

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[2] G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found Crystallogr.*, 2008, **64**, 112.

[3] G. Glatz, T. Irrgang, R. Kempe, *Z. Kristallogr. NCS*, 2007, **222**, 265.

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