

SUPPLEMENTARY INFORMATION

Regioselective synthesis of pyrrole and indole-fused isocoumarins catalysed by N[^]O chelate ruthenium(II) complex

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General procedure for ruthenium (II) catalyzed annulation of 1-methylpyrrole-2-carboxylic acid and 1-methylindole-3-carboxylic acid with alkynes in DMF

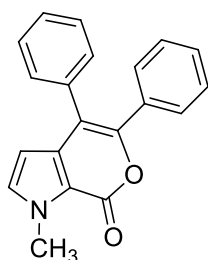
A dried Schlenk tube was loaded with [RuCl(*p*-cymene)(PySO₃)] (0.0306g, 0.05 mmol, 10 mol%), heterocyclic acid (**2** or **3**) (0.5 mmol), Alkyne (0.65 mmol), Cu(OAc)₂H₂O (0.199g, 1.0 mmol). The reaction mixture was stirred in DMF at 80°C for 16 h under air. After which the reaction mixture was rotary evaporated. The residue was purified over silica gel column using petroleum ether and ethyl acetate as eluant to give the compounds **5** and **6** in upto 81% of isolated yield. Spectroscopic data of the compounds are in accordance with those reported values.^[1,2,3]

General procedure for ruthenium (II) catalyzed annulation of 1-methylpyrrole-2-carboxylic acid and 1-methylindole-3-carboxylic acid with alkynes in water

A dried Schlenk tube was loaded with [RuCl(*p*-cymene)(PySO₃)] (0.0306g, 0.05 mmol), heterocyclic acids **2** or **3** (0.5 mmol), alkyne (1 mmol), Cu(OAc)₂H₂O (0.199g, 1.0 mmol). The reaction mixture was stirred in water at 100°C for 20 h under nitrogen. After which the reaction mixture was extracted with ethyl acetate (3 x 20 mL). The organic fractions were combined and treated with sodium sulphate and dried in a rotary evaporator. The residue was purified over silica gel column using petroleum ether and ethyl acetate as eluant to give the compounds **5** and **6**.

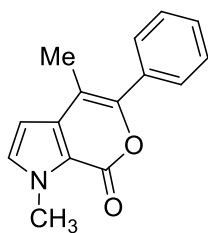
Characterization data for 5a-e to 6a-d

1-methyl-4,5-diphenylpyrano[3,4-b]pyrrol-7(1H)-one (**5a**)



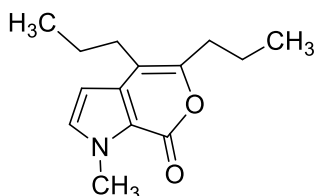
White solid; M.P = 161.2°C; yield: 113.3 mg (76%); FTIR (KBr, cm⁻¹): 3057, 2920, 1718, 1593, 1436; ¹H NMR (300 MHz, CDCl₃): δ 7.35- 7.34 (m, 5H), 7.31-7.30 (m, 2H), 7.23-7.20 (m, 3H), 7.08 (d, 1H, *J* = 2.4), 6.09 (d, 1H, *J* = 2.4), 4.15 (s, 3H); ¹³CNMR (75 MHz, CDCl₃): δ 155.97, 149.41, 135.29, 134.76, 133.25, 133.00, 130.14, 129.24, 128.70, 128.31, 127.81, 127.60, 116.92, 115.29, 103.60, 35.86; ESI-MS: *m/z* 302.1181 (M+H)⁺ calculated for C₂₀H₁₆NO₂, found 302.1981.

1,4-dimethyl-5-phenylpyrano[3,4-b]pyrrol-7(1H)-one (5b)



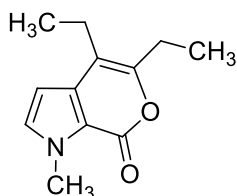
Yellow solid; M.P. = 113.9°C; yield: 103.2 mg (86%); FTIR (KBr, cm^{-1}): 3130, 2983, 1707, 1616, 1446; ^1H NMR (300 MHz, CDCl_3): δ 7.58 (d, 2H, $J = 7.2$), 7.48-7.39 (m, 3H), 7.11 (d, 1H, $J = 2.4$), 6.31(d, 1H, $J = 2.7$), 4.12 (s, 3H), 2.28 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ 156.36, 149.36, 135.30, 133.52, 132.90, 129.10, 128.10, 108.44, 102.25, 35.82, 13.69; ESI-MS: m/z 240.1025 ($\text{M}+\text{H}$) $^+$ calculated for $\text{C}_{15}\text{H}_{14}\text{NO}_2$, found 240.0987.

1-methyl-4,5-dipropylpyrano[3,4-b]pyrrol-7(1H)-one (5c)



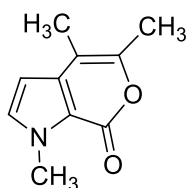
Light yellow liquid; yield: 48.3 mg (41%); FTIR (KBr, cm^{-1}): 3107, 2958, 1712, 1625, 1430; ^1H NMR (300 MHz, CDCl_3): δ 7.03 (d, 1H, $J = 2.4$), 6.19 (d, 1H, $J = 2.7$), 4.06 (s, 3H), 2.49 (m, 4H), 1.65 (m, 4H), 0.98 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 156.95, 152.13, 134.99, 132.62, 116.77, 111.57, 101.51, 35.72, 31.88, 29.30, 22.96, 21.50, 14.01, 13.71; ESI-MS: m/z 234.1494 ($\text{M}+\text{H}$) $^+$ calculated for $\text{C}_{14}\text{H}_{20}\text{NO}_2$, found 234.1452.

4,5-diethyl-1-methylpyrano[3,4-b]pyrrol-7(1H)-one (5d)



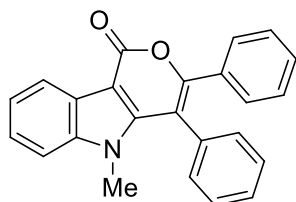
Light brown crystals; M.P. = 53-54 °C; yield: 51.2 mg (50%); FTIR (KBr, cm^{-1}): 3128, 2960, 1714, 1620, 1456; ^1H NMR (300 MHz, CDCl_3): δ 7.03 (d, 1H, $J = 2.4$), 6.20 (d, 1H, $J = 2.7$), 4.05 (s, 3H), 2.54 (m, 4H), 1.26-1.15 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 156.94, 152.96, 134.27, 132.67, 116.86, 112.42, 101.26, 35.69, 23.25, 20.52, 14.50, 12.98; ESI-MS: 206.1181 ($\text{M}+\text{H}$) $^+$ calculated for $\text{C}_{12}\text{H}_{16}\text{NO}_2$, found 206.1126.

1,4,5-trimethylpyrano[3,4-b]pyrrol-7(1H)-one (5e)



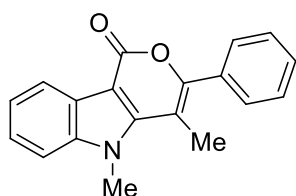
Light brown solid; M.P. = 100-101 °C; yield: 42.8 mg (48%); FTIR (KBr, cm⁻¹): 3087, 2924, 1708, 1636, 1447; ¹H NMR (300 MHz, CDCl₃) δ (ppm) 7.02 (s, 1H), 6.16 (s, 1H), 4.05 (s, 3H), 2.23 (s, 3H), 2.09 (s, 3H); ¹³CNMR (75 MHz, CDCl₃): δ 155.22, 139.34, 124.23, 122.49, 121.17, 109.15, 102.08, 32.22, 17.68, 13.49; ESI-MS: m/z 178.0868 (M+H)⁺ calculated for C₁₀H₁₂NO₂, found 178.0729.

5-methyl-3,4-diphenylpyrano[4,3-b]indol-1(5H)-one(6a)



Light pink solid; M.P. = 208-209 °C; yield: 120.3 mg (69%); FTIR (KBr, cm⁻¹): 3057, 2937, 1720, 1587, 1519, 1428; ¹H NMR (300 MHz, CDCl₃): δ 8.38-8.35 (m 1H), 7.44-7.34 (m, 9H), 7.23-7.20 (m, 4H), 3.21 (s, 3H); ¹³CNMR (75 MHz, CDCl₃): δ 159.34, 155.83, 144.84, 139.96, 133.44, 133.14, 131.73, 129.08, 128.94, 128.78, 124.73, 123.84, 122.83, 121.53, 110.52, 109.36, 100.71, 32.07; ESI-MS: m/z 352.1338 (M+H)⁺ calculated for C₂₄H₁₈NO₂, found 352.1396.

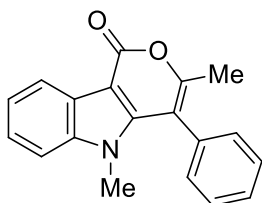
5-methyl-3,4-diphenylpyrano[4,3-b]indol-1(5H)-one (6ba)



White grey solid; M. P. = 258-262 °C; yield: 18.3 mg (13%); FTIR (KBr, cm⁻¹): 3072, 2927, 1708, 1589, 1436; ¹H NMR (300 MHz, CDCl₃): δ 8.32 (d, 1H, J = 7.5), 7.56 (m, 2H), 7.49-7.38 (m, 6H), 4.10 (s, 3H), 2.54 (s, 3H); ¹³CNMR (75 MHz, CDCl₃): δ 159.13, 156.17, 146.89, 139.70, 133.18, 129.67, 129.48, 128.25, 124.62, 123.94, 122.70, 121.51, 109.27,

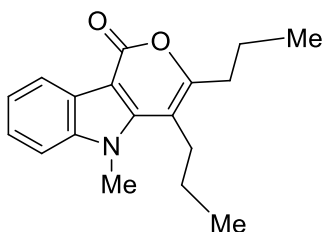
103.27, 101.43, 32.46, 15.24; ESI-MS: m/z 290.1181 (M+H)⁺ calculated for C₁₉H₁₆NO₂, found 290.1203.

3,5-dimethyl-4-phenylpyrano[4,3-b]indol-1(5H)-one (6bb)



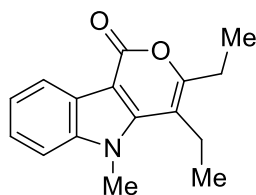
Light pink solid; M.P. = 230-233 °C; yield: 31.6 mg (22%); FTIR (KBr, cm⁻¹): 3057, 2954, 1707, 1525, 1469; ¹H NMR (300 MHz, CDCl₃): δ 8.29 (m, 1H), 7.52 (m, 3H), 7.41-7.30 (m, 4H), 7.29 (m, 1H), 3.17 (s, 3H), 2.16 (s, 3H); ¹³CNMR (75 MHz, CDCl₃): δ 159.76, 157.22, 144.97, 139.41, 133.91, 130.83, 129.26, 128.80, 124.31, 123.97, 122.65, 121.25, 109.79, 109.77, 31.66, 18.18; ESI-MS: m/z 290.1181 [M+H]⁺ calculated for C₁₉H₁₆NO₂, found 290.0995.

5-methyl-3,4-dipropylpyrano[4,3-b]indol-1(5H)-one (6c)



Light orange crystals; M. P. = 157-158 °C; yield: 64.2 mg (45%); FTIR (KBr, cm⁻¹): 3064, 2954, 1712, 1597, 1463; ¹H NMR (300 MHz, CDCl₃): δ 8.25(d, 1H, *J* = 6.9), 7.36-7.34 (m, 3H), 3.97 (s, 3H), 2.75 (t, 2H, *J* = 8.4), 2.64 (t, 2H, *J* = 7.8), 1.80-1.77 (m, 2H), 1.75-1.66 (m, 2H), 1.12-1.00 (m, 6H); ¹³CNMR (75 MHz, CDCl₃): δ 159.97, 159.36, 145.80, 139.51, 124.21, 124.04, 122.45, 121.13, 109.14, 107.18, 101.07, 32.77, 31.80, 28.06, 24.52, 21.60, 13.81. ESI-MS: m/z 284.1651 (M+H)⁺ calculated for C₁₈H₂₂NO₂, found 284.1604.

3,4,5-trimethylpyrano[4,3-b]indol-1(5H)-one (6d)



Colourless solid; M. P. = 162-163 °C; yield: 81.1 mg (64%) ^1H NMR (300 MHz, CDCl_3): δ 8.26 (d, 1H, $J = 6$), 7.36 (m, 3H), 4.00 (s, 3H), 2.84 (m, 2H), 2.68 (m, 2H), 1.31 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 160.37, 160.04, 145.77, 139.48, 124.22, 122.48, 121.17, 109.13, 107.94, 101.10, 31.84, 29.67, 24.15, 19.20, 15.73, 12.86. ESI-MS: m/z 256.1338 ($\text{M}+\text{H}$) $^+$ calculated for $\text{C}_{16}\text{H}_{18}\text{NO}_2$, found 256.1367.

Table S1. Summary of structure determination and refinement for 1

Empirical formula	C ₁₅ H ₁₈ ClNO ₃ RuS
CCDC	1055202
Formula Weight	428.88
Temperature (K)	100(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	
<i>a</i> (Å)	8.3051(4)
<i>b</i> (Å)	8.7763(4)
<i>c</i> (Å)	12.5555(6)
α (°)	70.028(2)
β (°)	78.317(2)
γ (°)	66.212(2)
Volume (Å ³)	784.81(6)
<i>Z</i>	2
Density (calculated) (Mg/m ³)	1.815 Mg/m ³
Absorption coefficient (mm ⁻¹)	1.313 mm ⁻¹
F(000)	432
θ range for data collection (°)	2.69 to 28.44
index ranges	-11 ≤ <i>h</i> ≤ 11, -11 ≤ <i>k</i> ≤ 11, -16 ≤ <i>l</i> ≤ 16
Reflection collected/unique	41334
Completeness to theta	25.0° to 99.6%
Refinement method	Full-matrix least squares on <i>F</i> ²
Data/restraints/parameters	3915 / 0 / 202
Goodness-of-fit on <i>F</i> ²	1.086
Final <i>R</i> indices	<i>R</i> ₁ = 0.0165, w <i>R</i> ₂ = 0.0415
[<i>I</i> > 2σ(<i>I</i>)]	
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0172, w <i>R</i> ₂ = 0.0419
Largest different peak and hole (eÅ ⁻³)	0.534 and -0.537 eÅ ⁻³

Table S2. Selected bond lengths (Å) and angles(°)

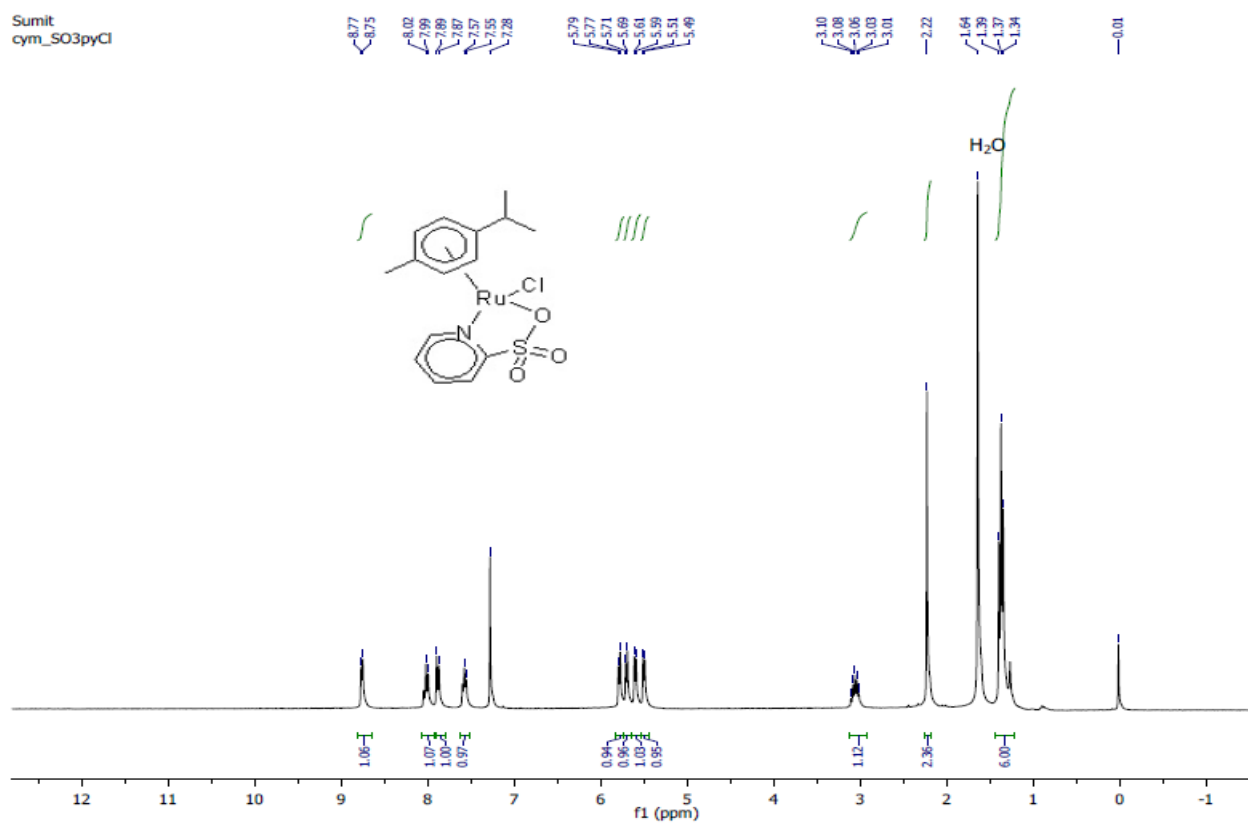
Ru(1)-C(1)	2.1909(13)	Ru(1)-C(2)	2.1673(14)
Ru(1)-C(3)	2.1673(14)	Ru(1)-C(4)	2.1912(14)
Ru(1)-C(5)	2.1829(14)	Ru(1)-C(6)	2.1554(13)
Ru(1)-N(1)	2.1258(12)	Ru(1)-O(1)	2.1488(11)
Ru(1)-Cl(1)	2.3907(4)	S(1)-O(1)	1.4886(11)
S(1)-O(2)	1.4433(11)	S(1)-O(3)	1.4385(11)
N(1)-Ru(1)-O(1)	77.68(4)	N(1)-C(11)-S(1)	113.38(10)
O(1)-S(1)-C(11)	100.09(6)	O(1)-Ru(1)-Cl(1)	86.56(3)

References

- [1] Shimizu, M.; Hirano, K.; Satoh, T.; Miura, M. *J. Org. Chem.* **2009**, *74*, 3478-3483.
- [2] Singh, K. S.; Sawant, S. G.; Dixneuf, P. H. *ChemCatChem.* **2016**, *8*, 1046-1050.
- [3] Villuendas, P.; Urriolabeitia, E. P. *J. Org. Chem.* **2013**, *78*, 5254-5263.

NMR Spectra of compounds

(a)



(b)

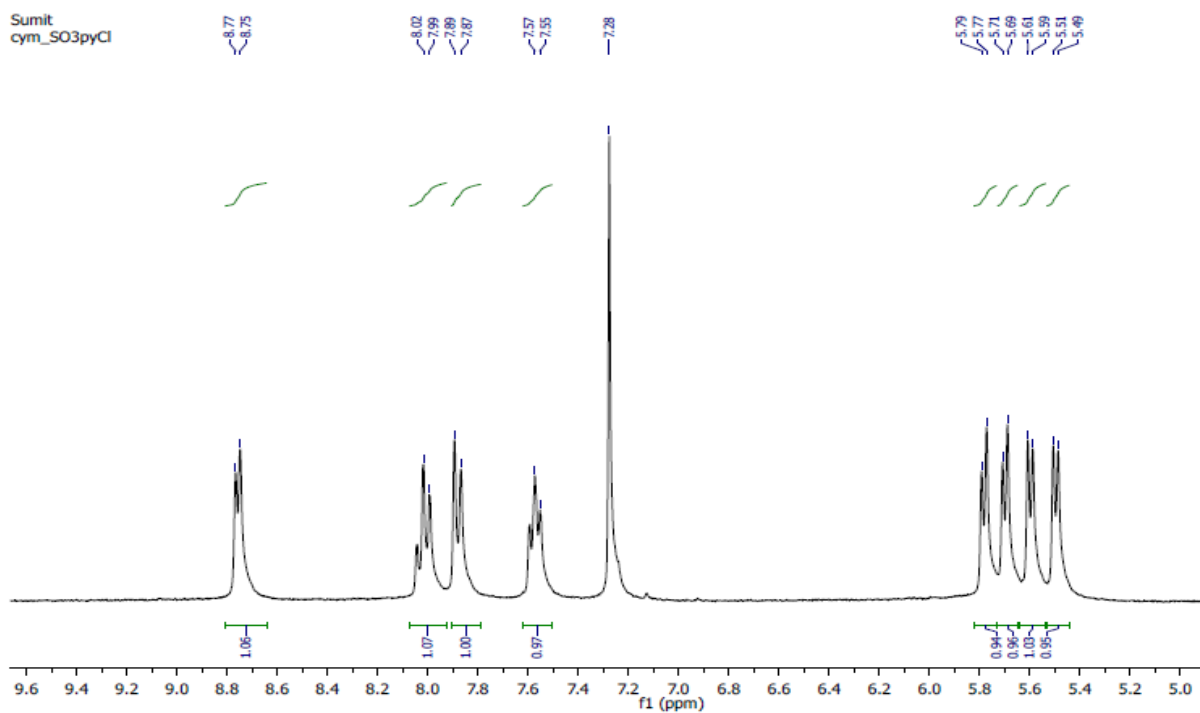


Figure S1. (a) ^1H -NMR spectrum of complex **1**; (b) Expansion of aromatic region.

Sumit
cym_pySO3

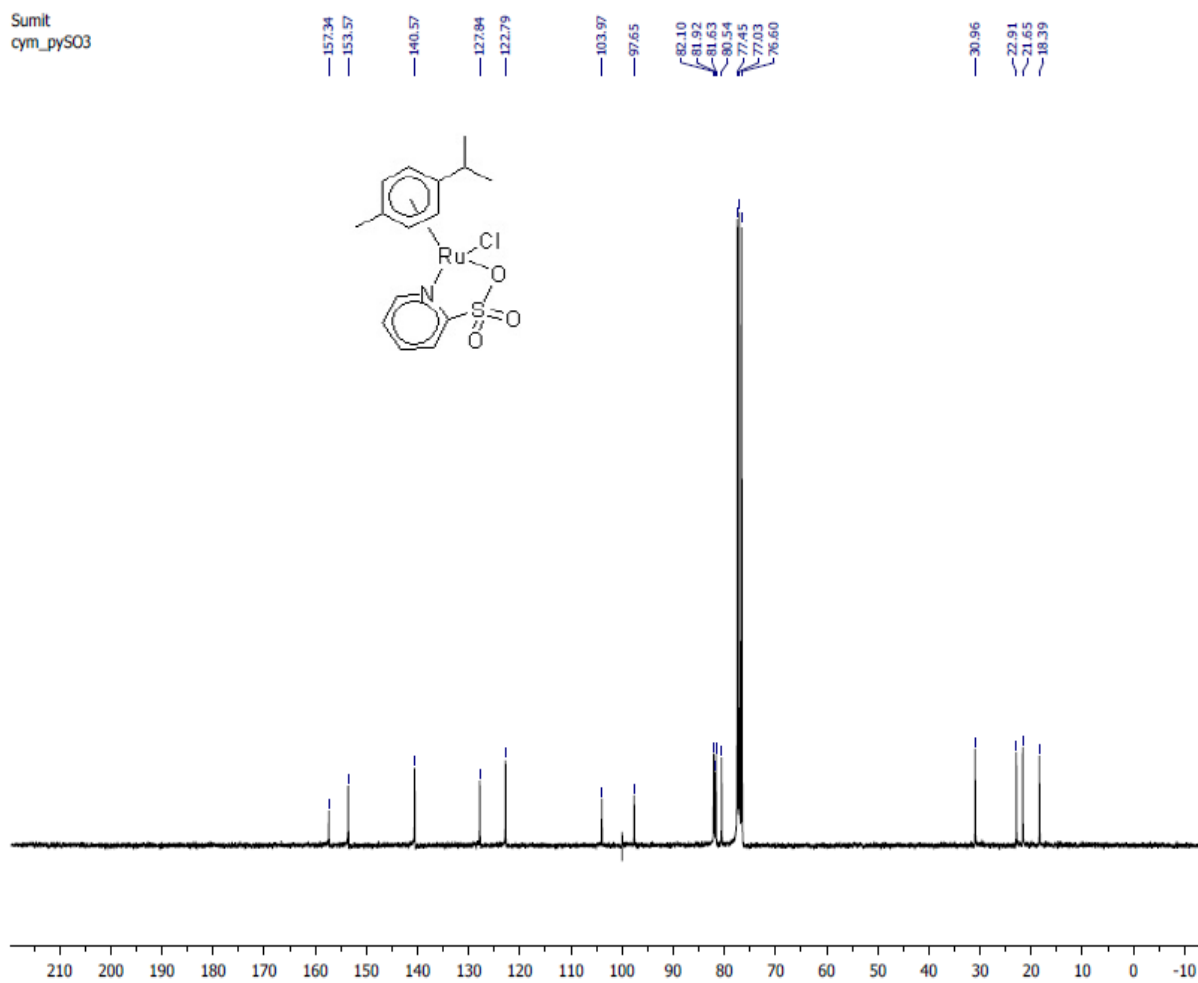
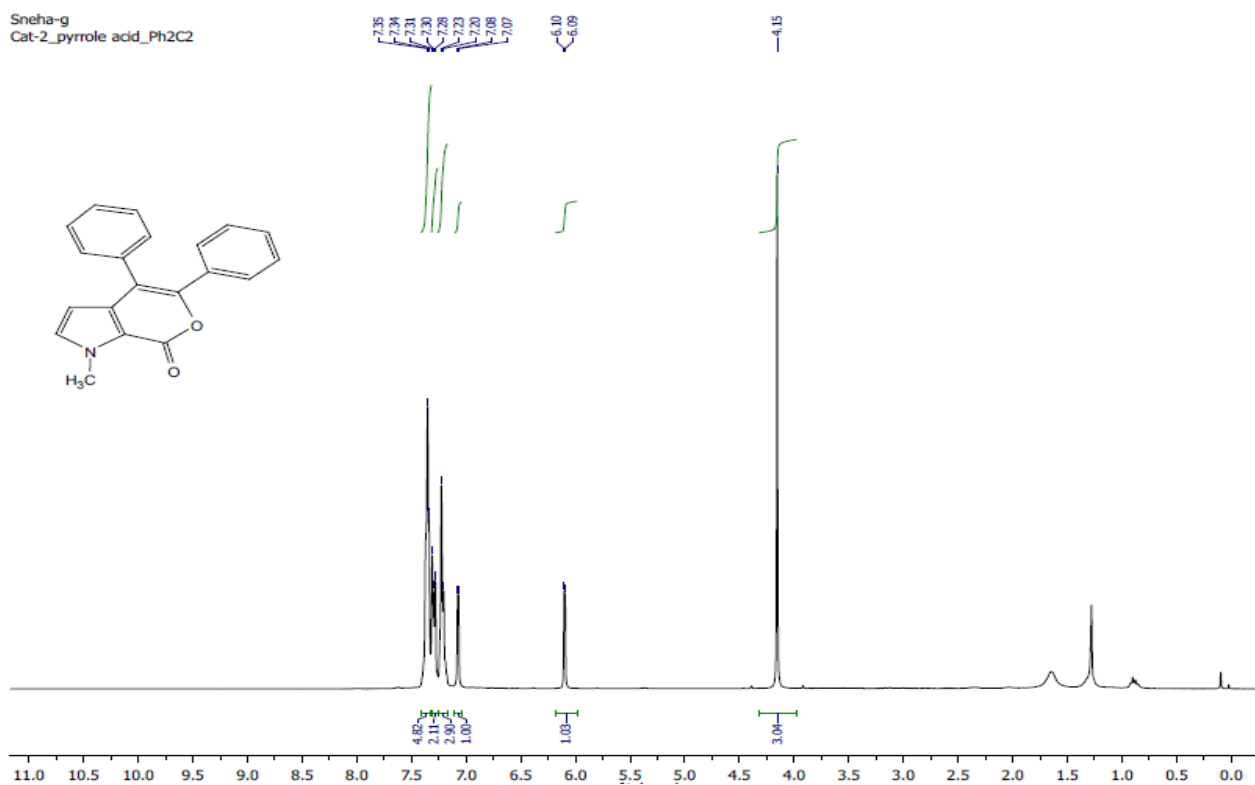


Figure S2. ^{13}C -NMR for complex 1.

(a)



(b)

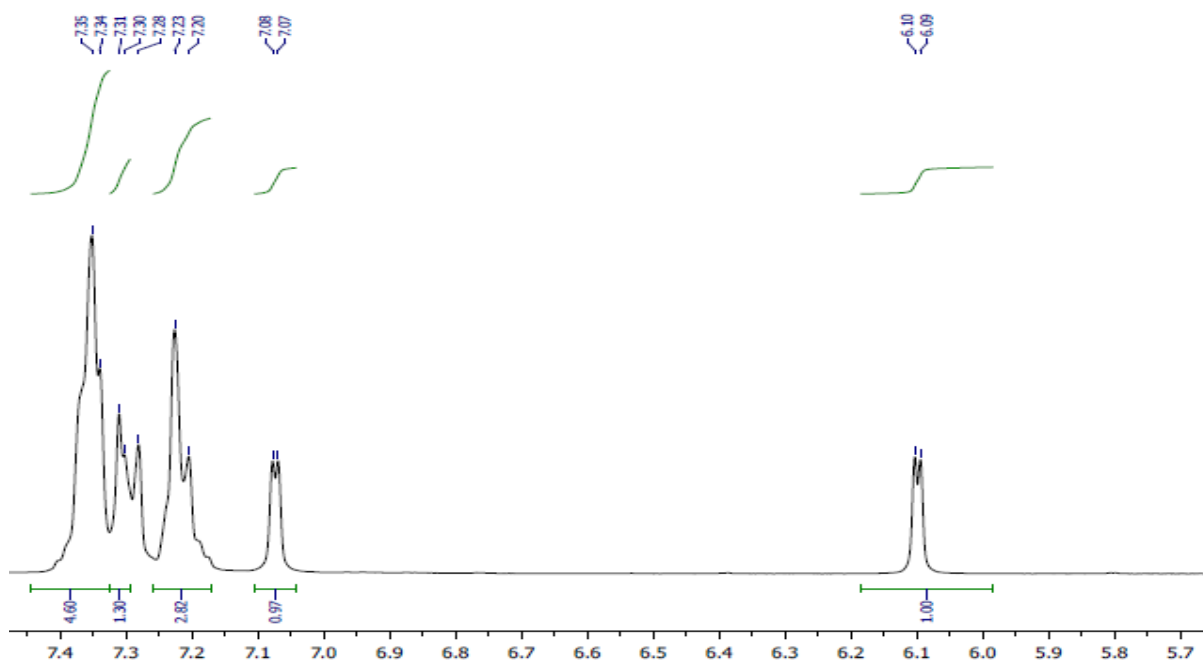


Figure S3. (a) ^1H NMR spectrum of **5a**; (b) Expansion of aromatic region of **5a**.

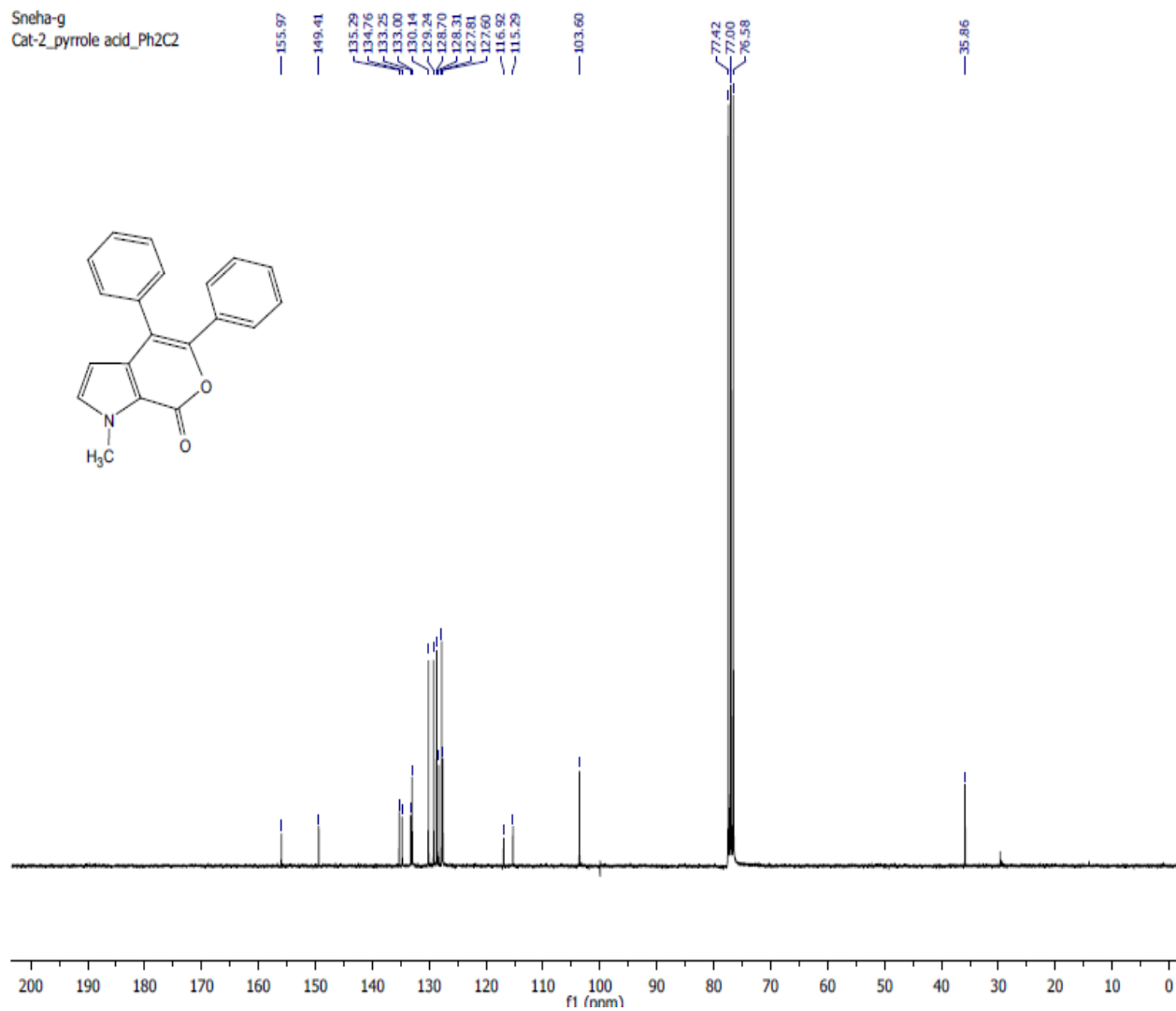
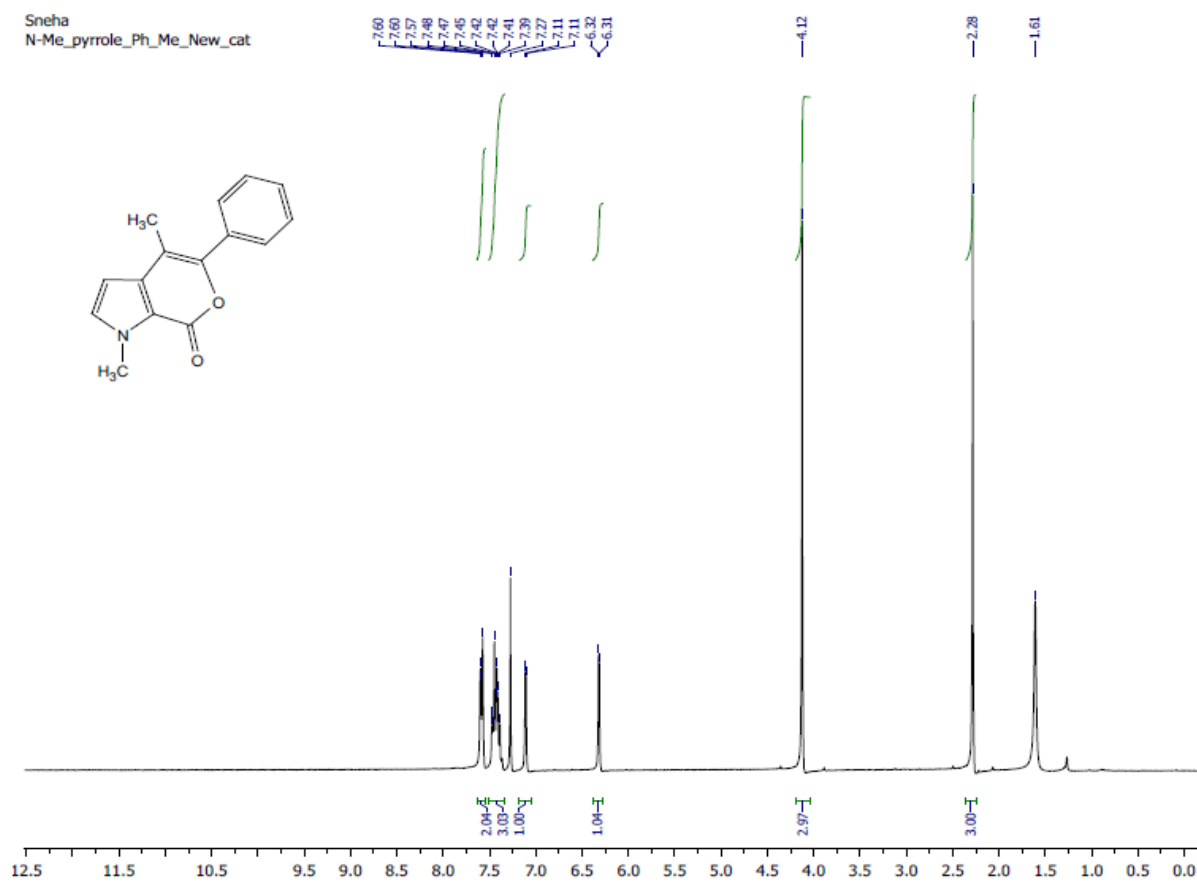


Figure S4. ^{13}C NMR for compound 5a.

(a)



(b)

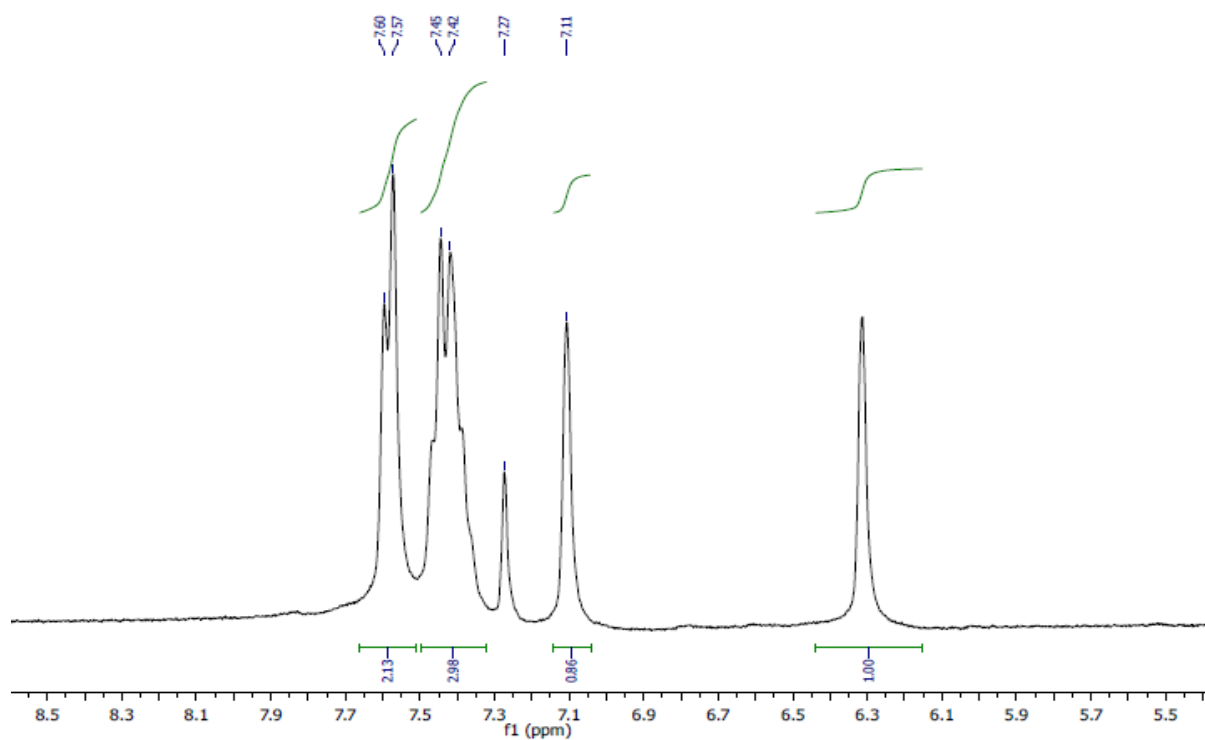


Figure S5. (a) ^1H -NMR spectrum of compound **5b**; (b) Expansion of aromatic region of **5b**.

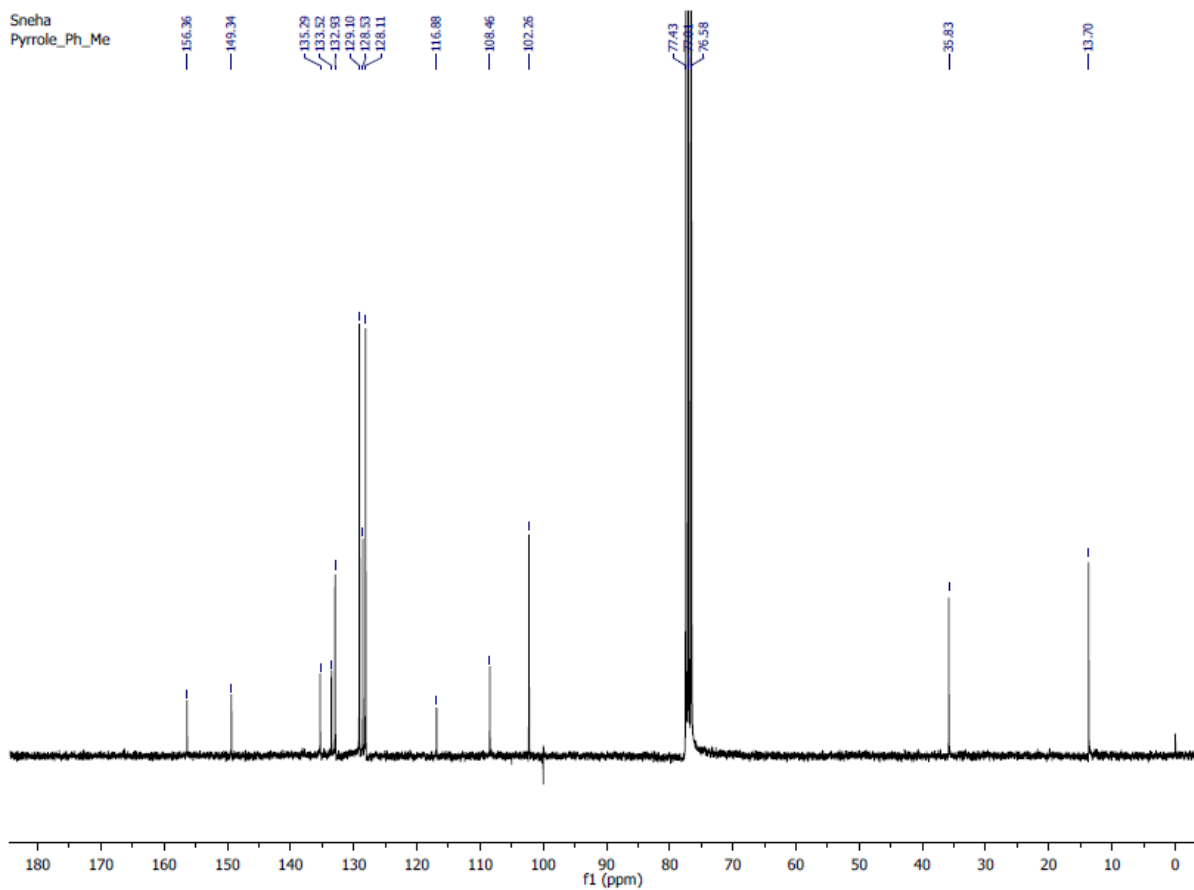


Figure S6. ^{13}C -NMR spectrum of **5b**.

Sneha
Me_pyrole_octyne

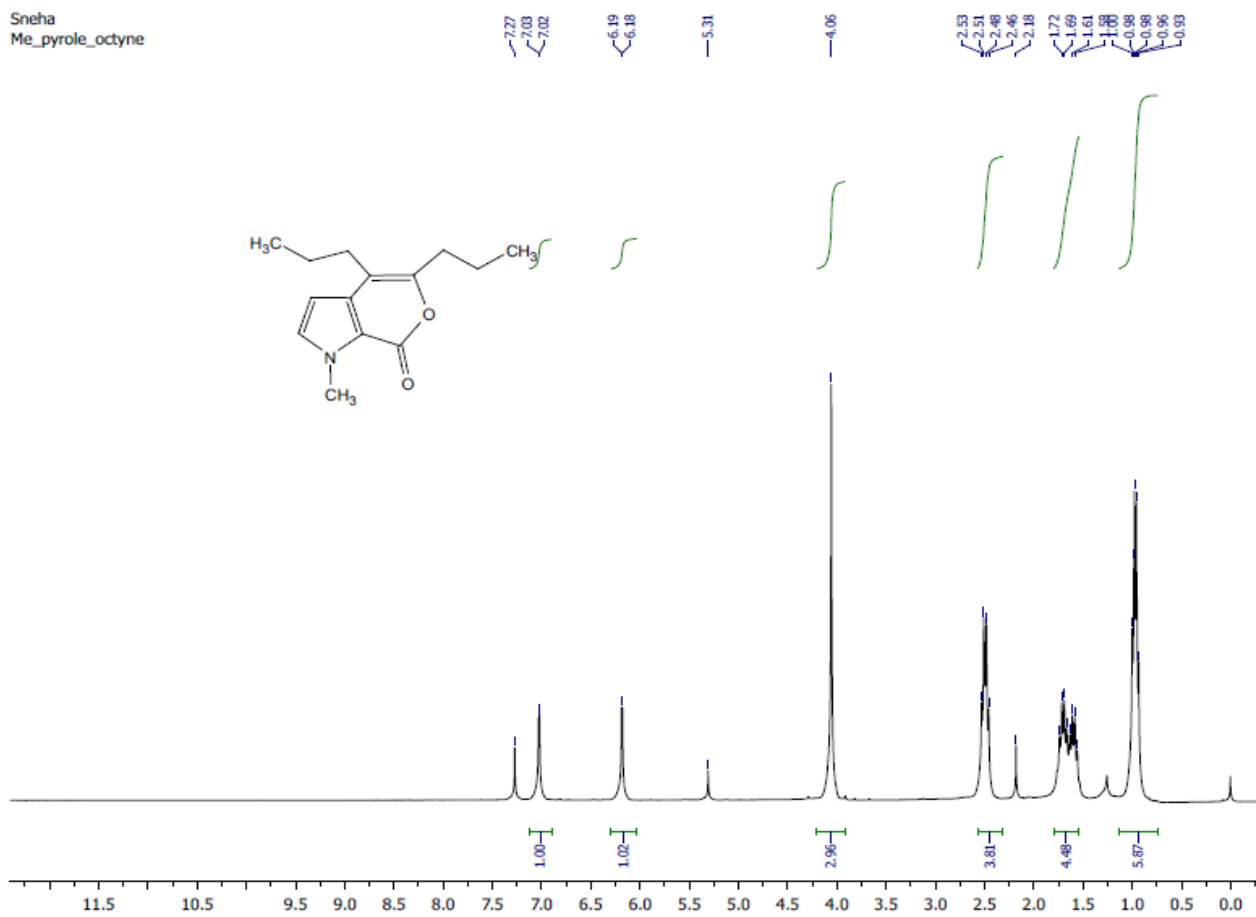


Figure S7. ¹H- NMR of compound **5c**.

Sneha
Me_pyrrole_octyne

156.95

152.13

134.59

132.62

116.77

111.55

101.51

77.43

77.00

76.58

35.72

31.88

29.30

22.96

21.50

14.01

13.71

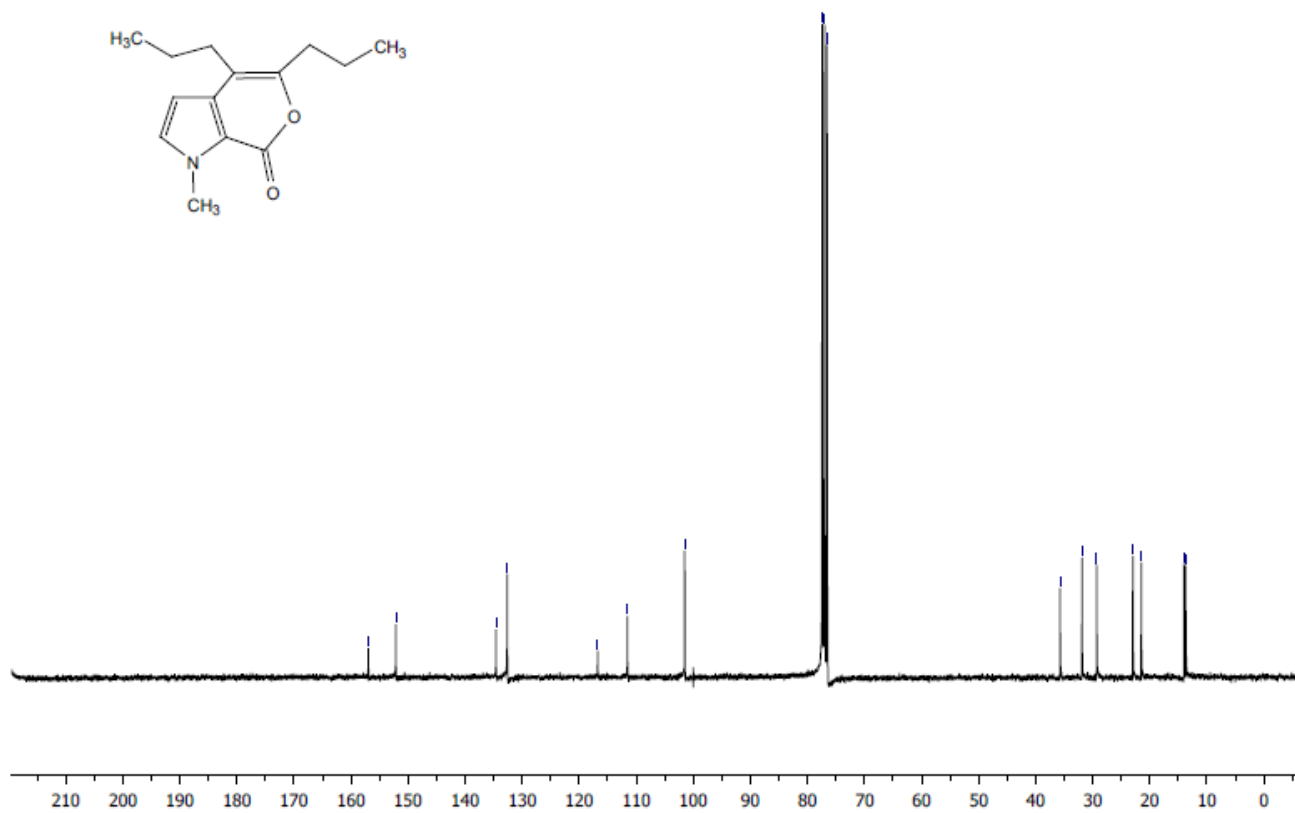


Figure S8. ^{13}C NMR for compound **5c**.

Sneha
me_pyrrole_3-hexyne_Cat 2

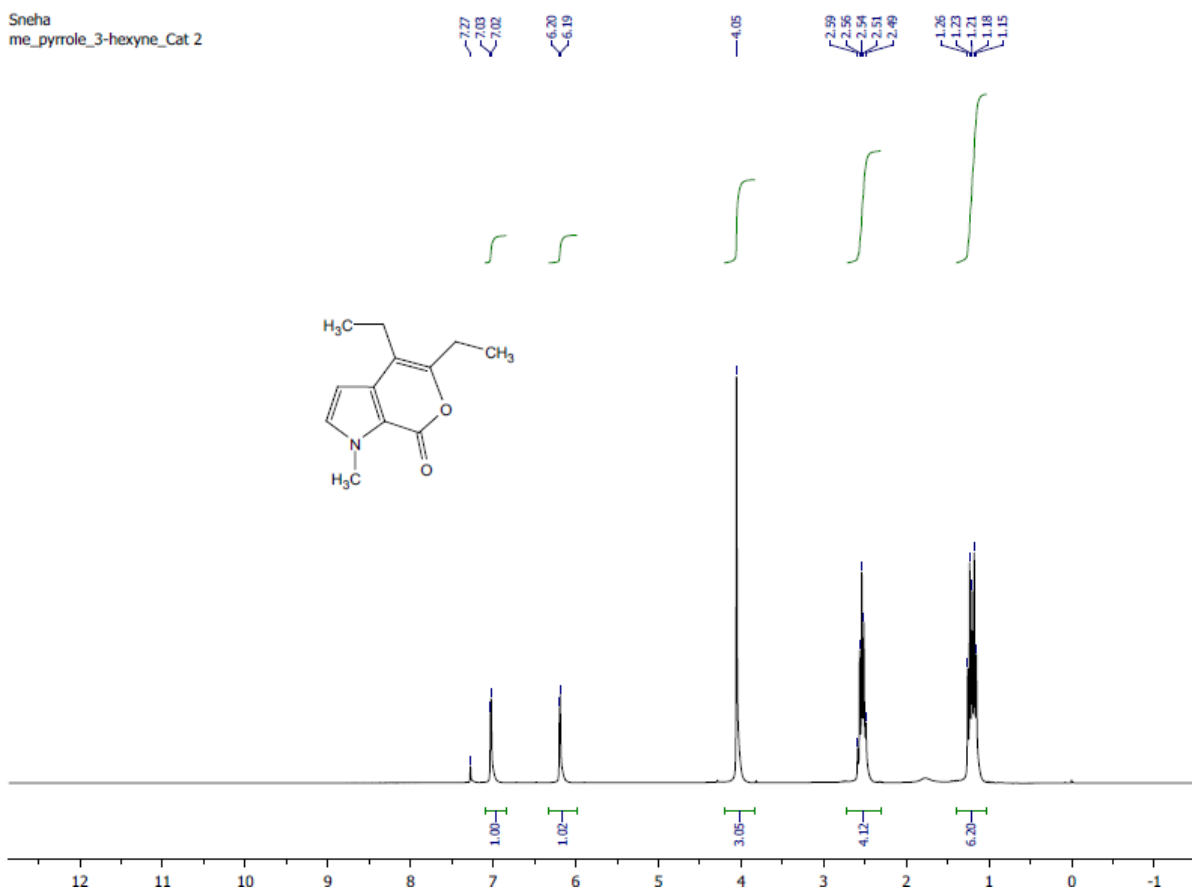


Figure S9. ¹H NMR spectrum of compound 5d.

Sneha
me_pyrrole_3-hexyne_Cat 2

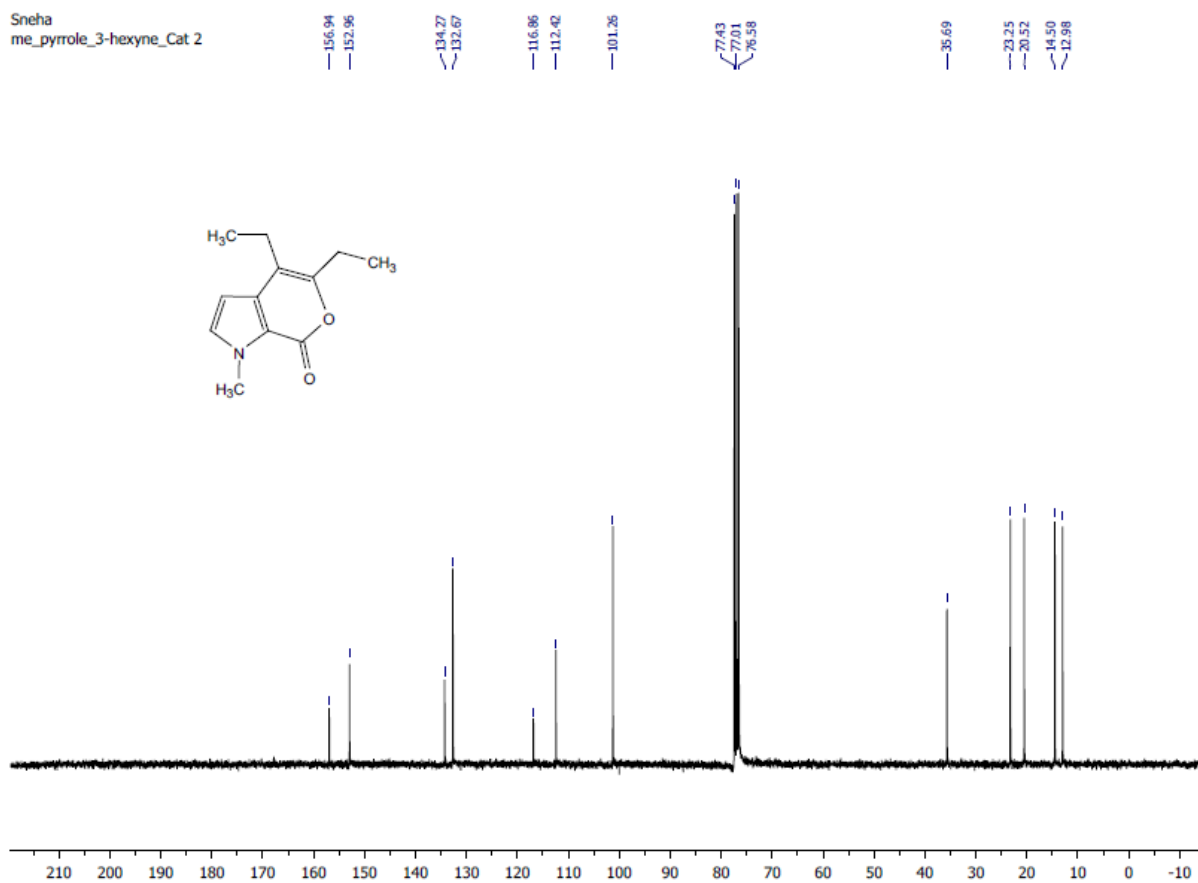


Figure S10. ^{13}C -NMR spectrum of compound **5d**.

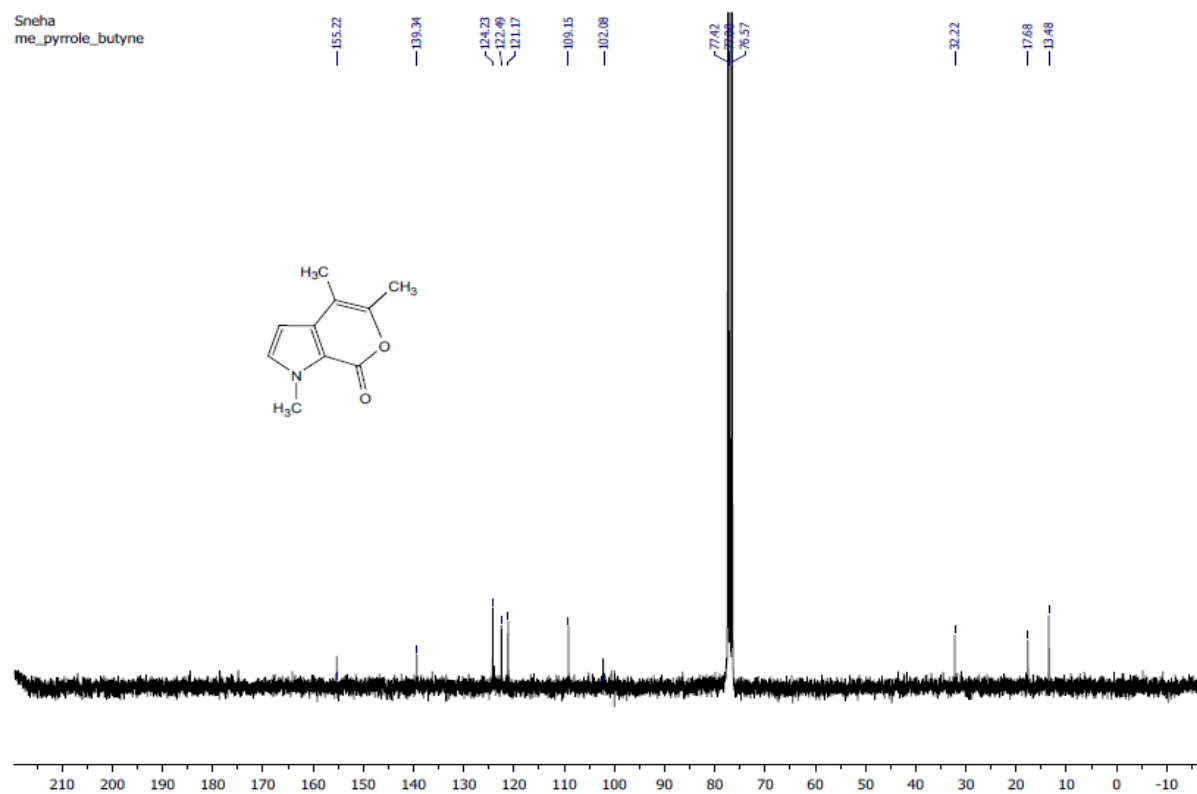
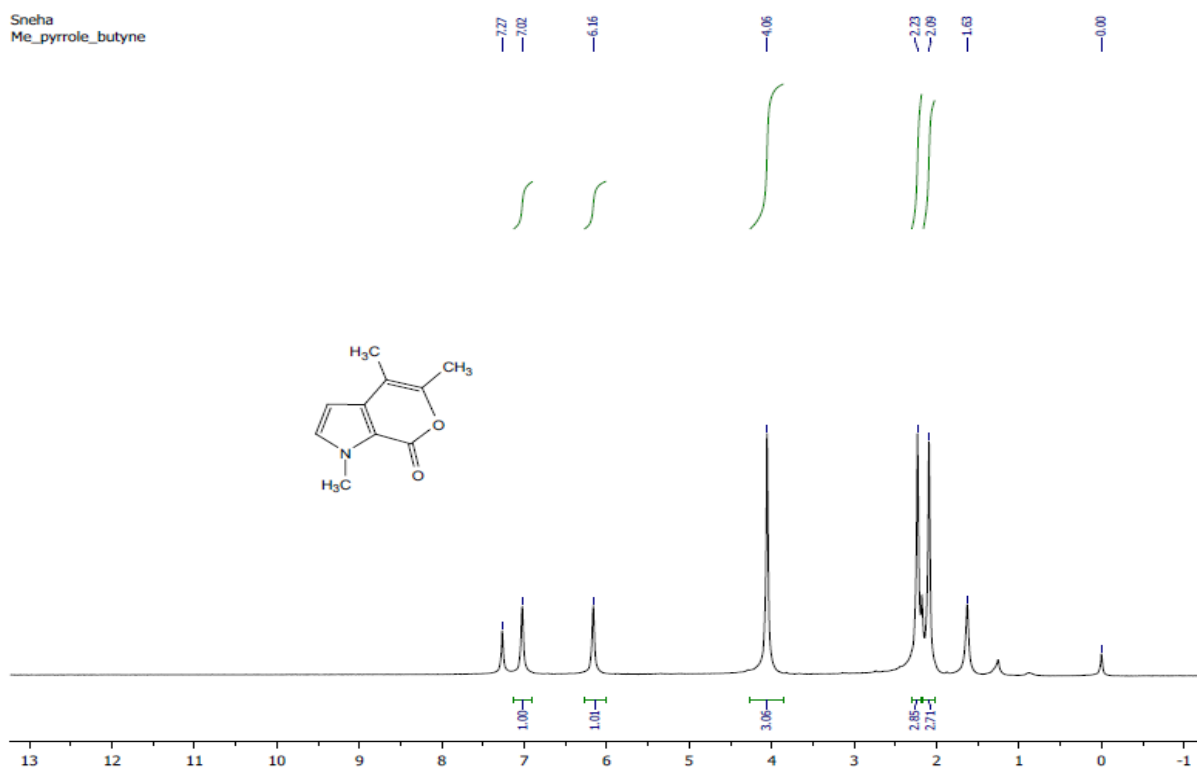
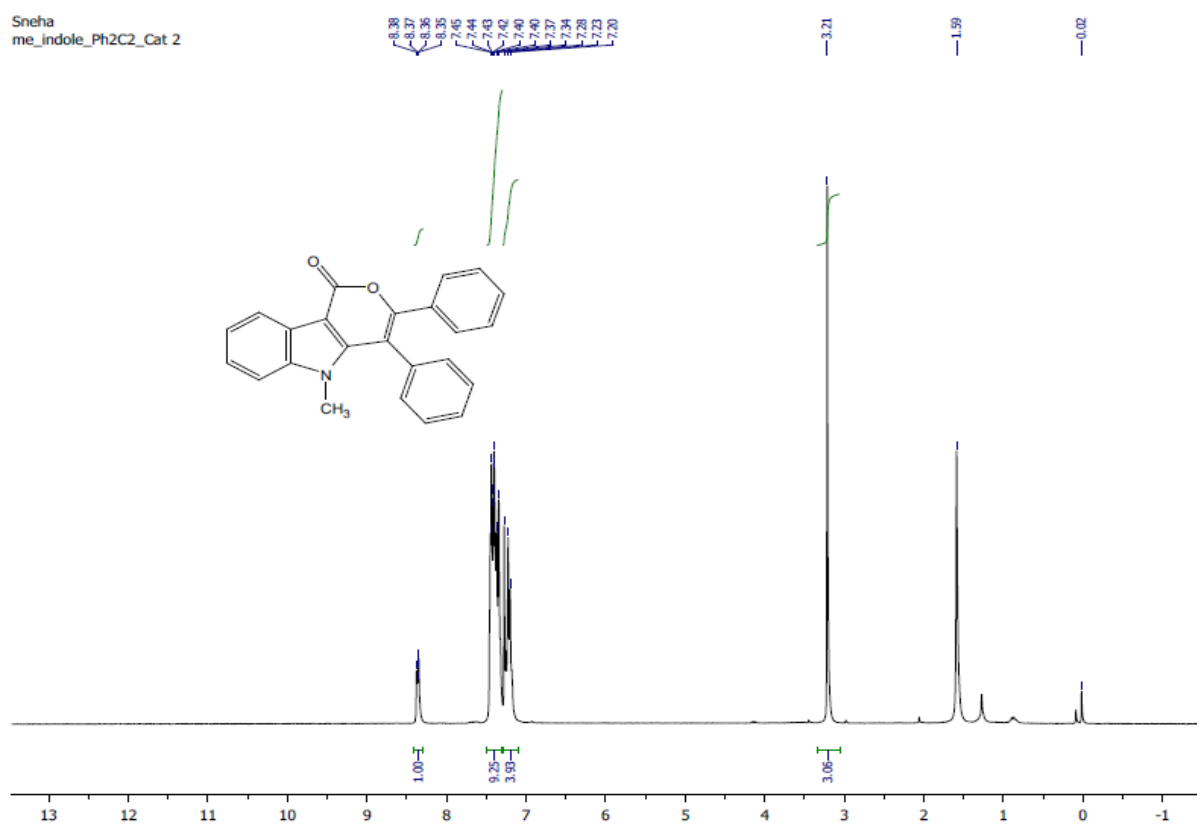


Figure S11. ^1H and ^{13}C NMR spectra of compound **5e**.

(a)



(b)

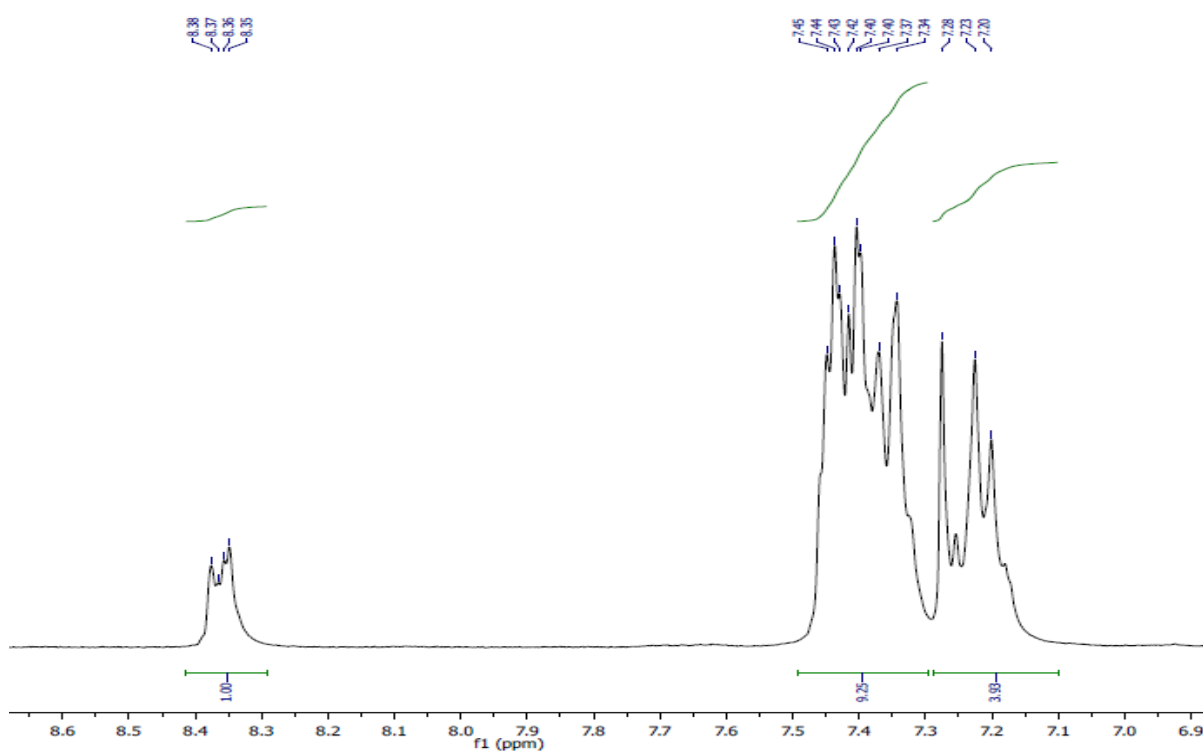


Figure S12. ¹H - NMR spectrum of compound 6a.

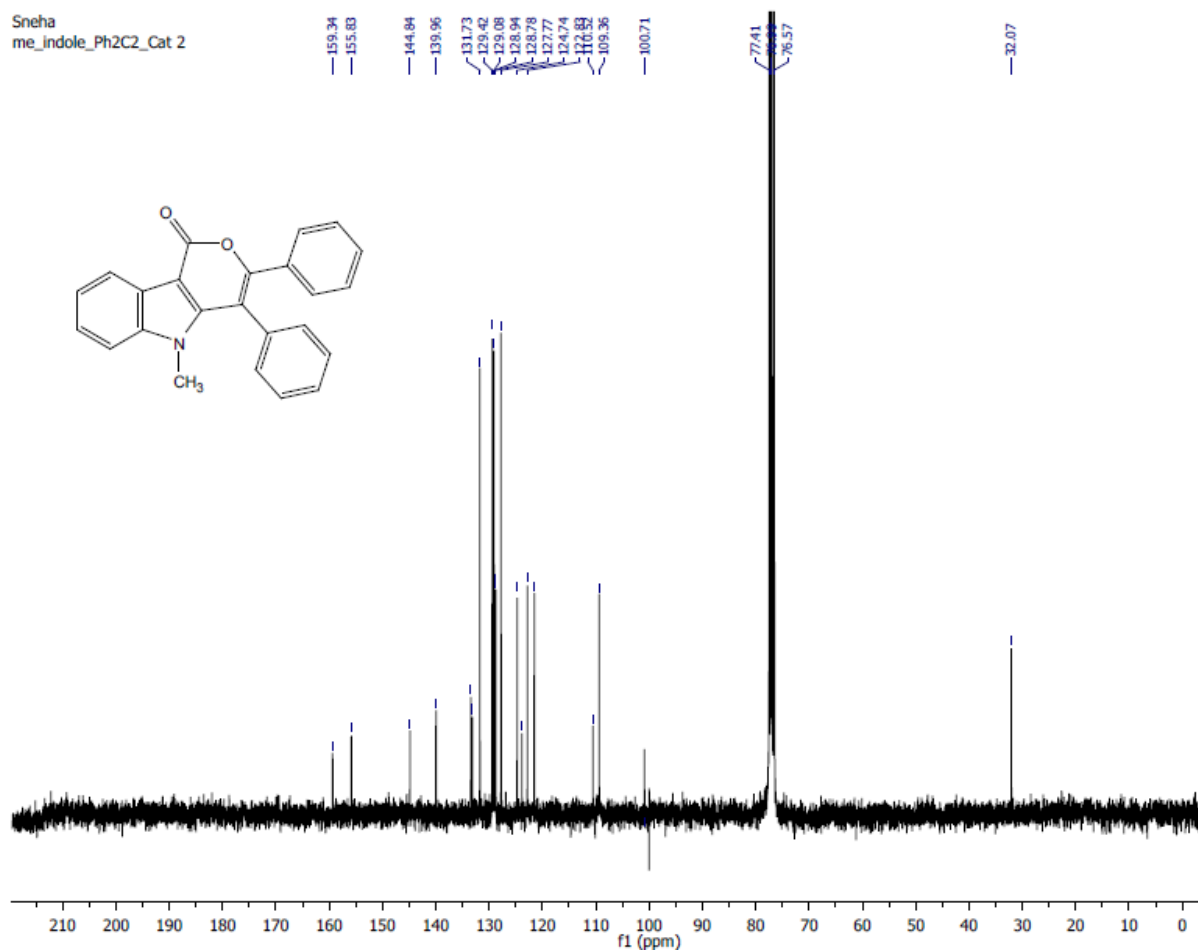


Figure S13. ^{13}C -NMR spectrum of compound **6a**.

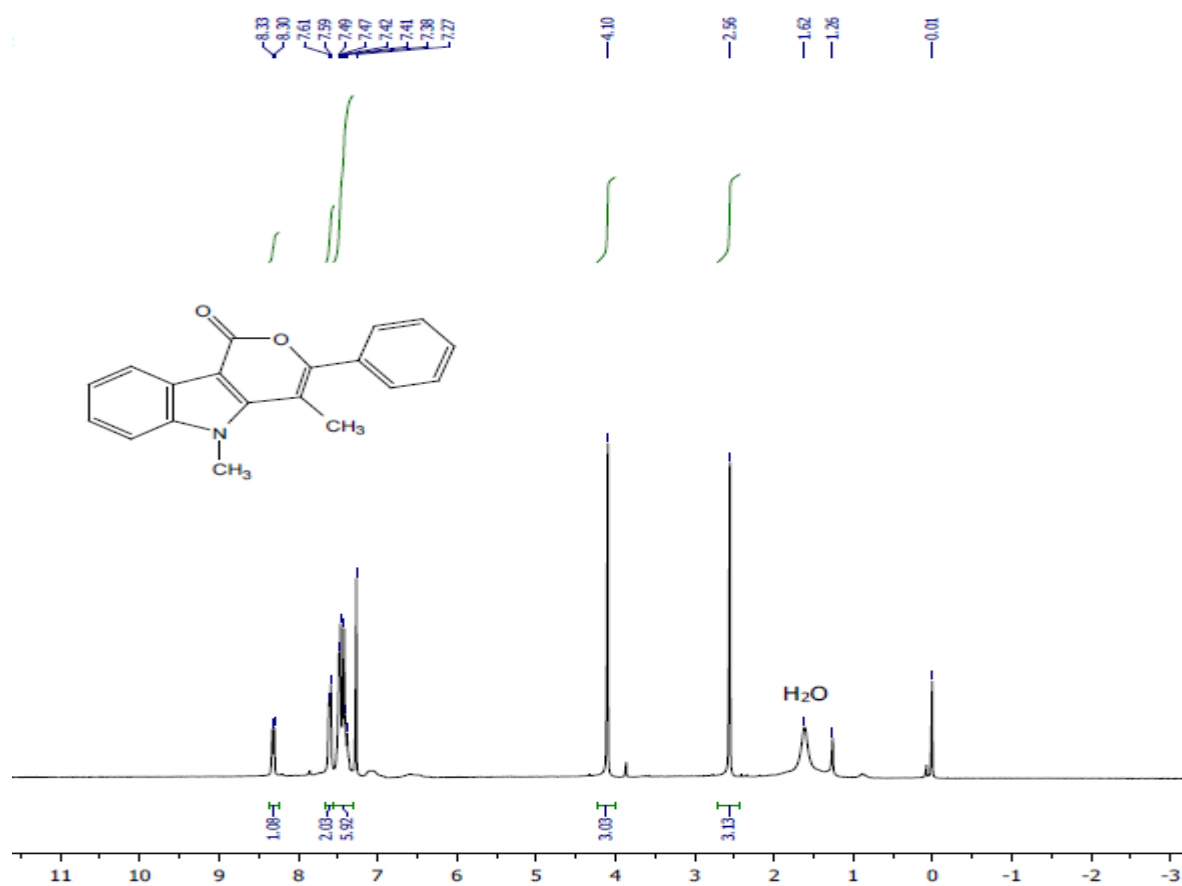


Figure S14. ¹H-NMR spectrum for compound **6ba**.

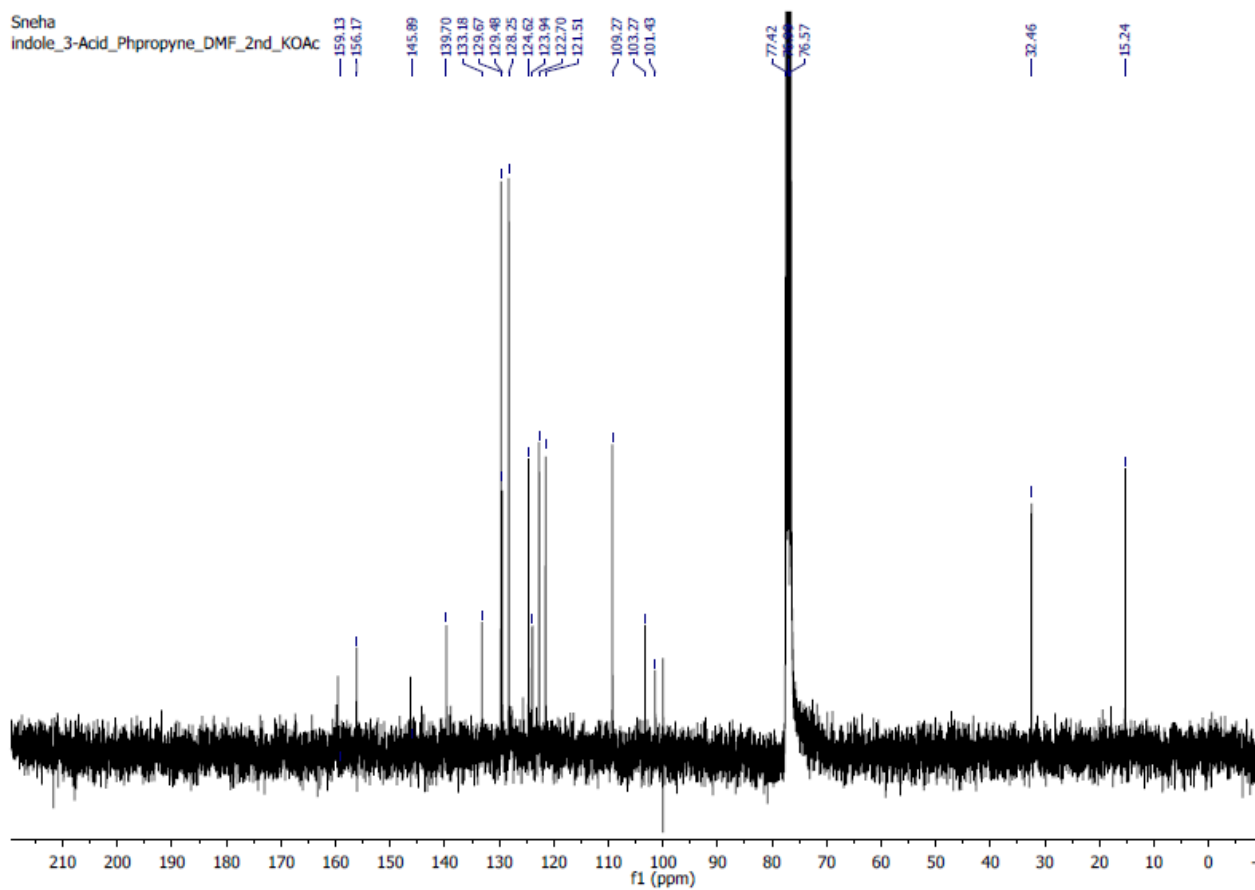
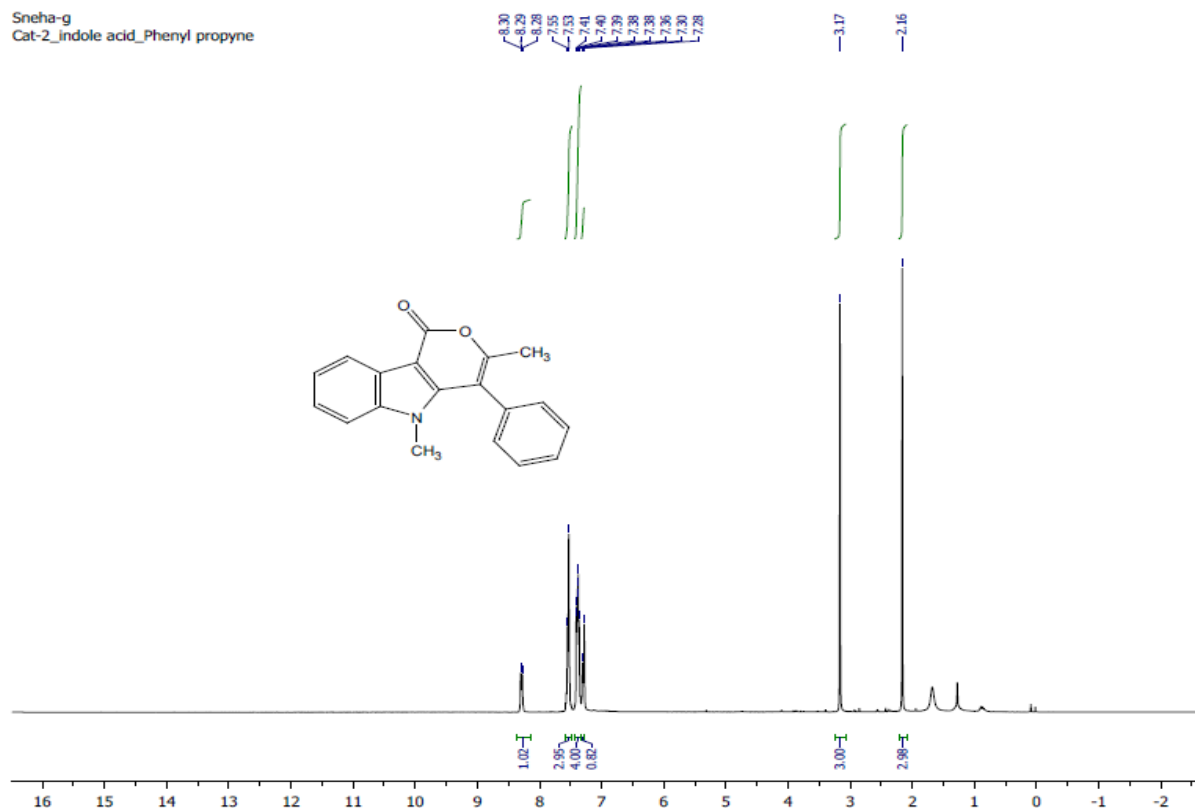


Figure S15. ^{13}C -NMR spectrum of compound **6ba**.

(a)

Sneha-g
Cat-2_indole acid_Phenyl propyne



(b)

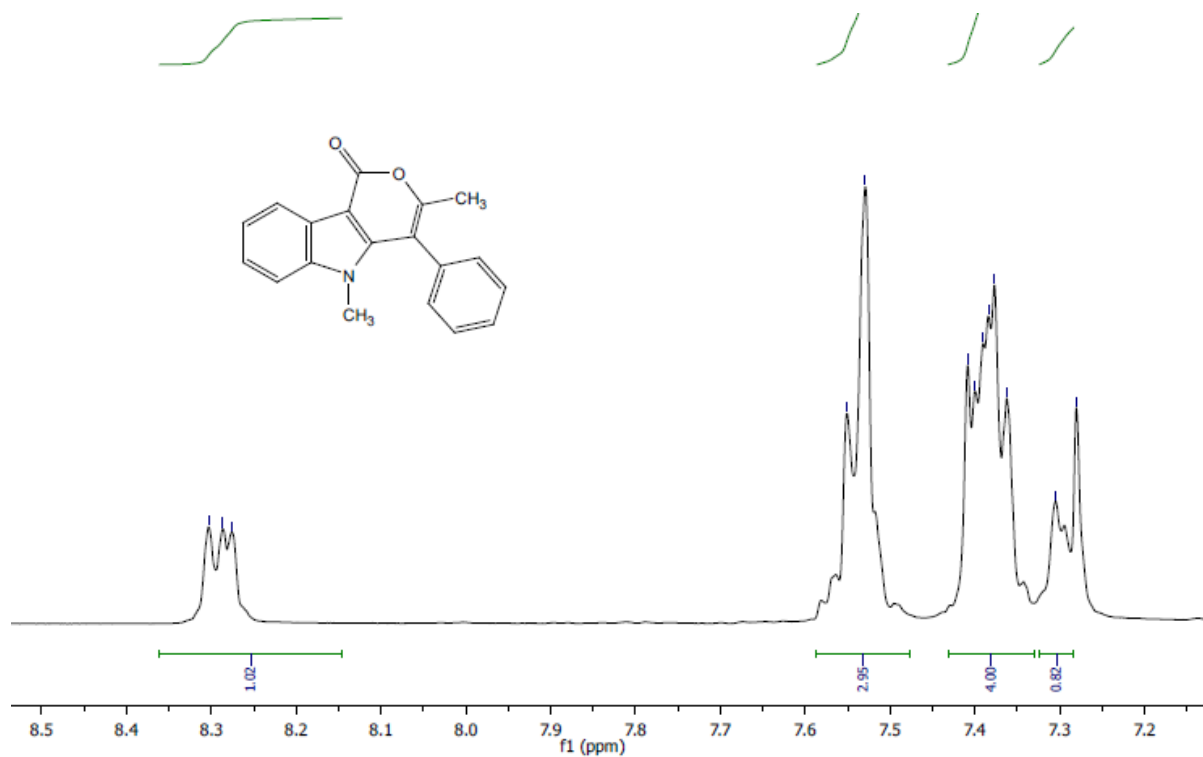


Figure S16. (a) ¹H - NMR spectrum of compound **6bb**; (b) Spectrum with expansion of aromatic region.

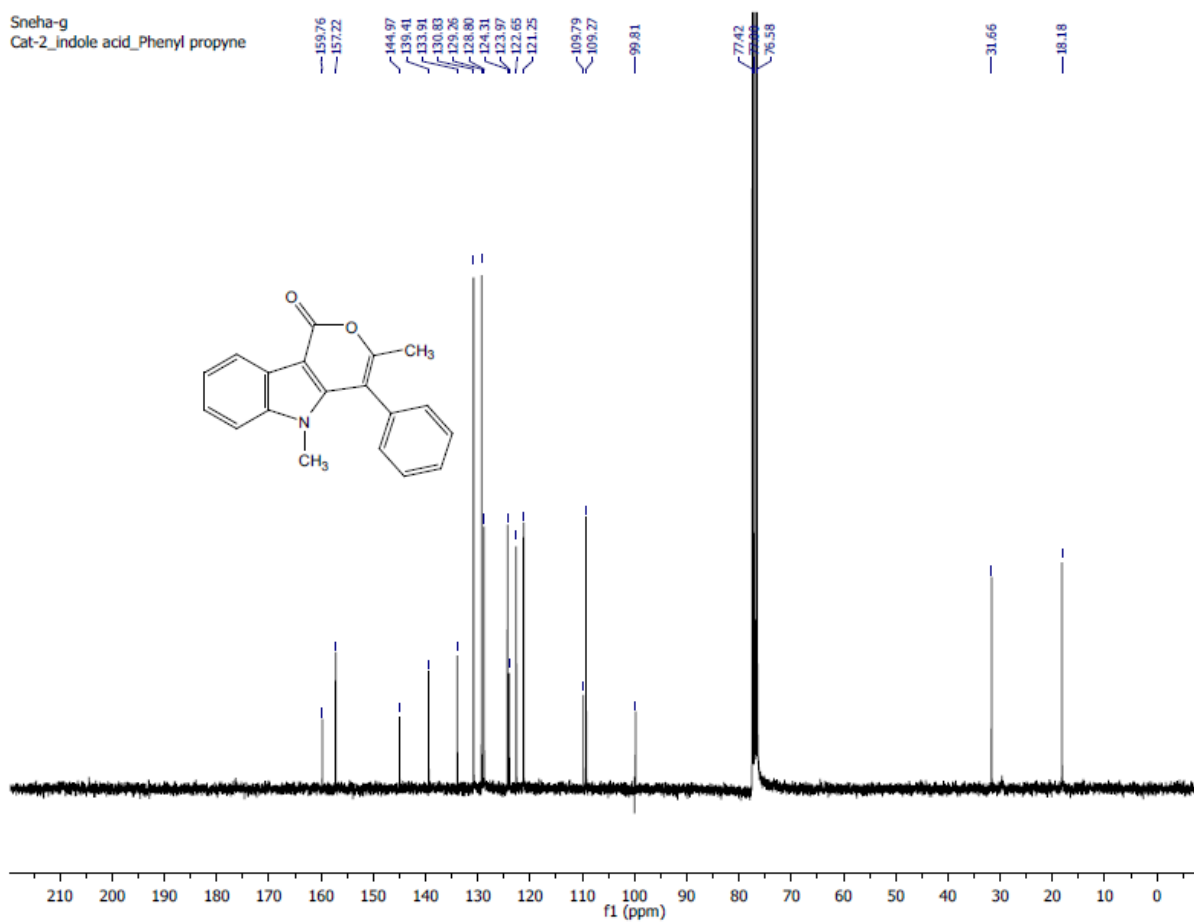


Figure S17. ^{13}C -NMR spectrum of compound 6bb.

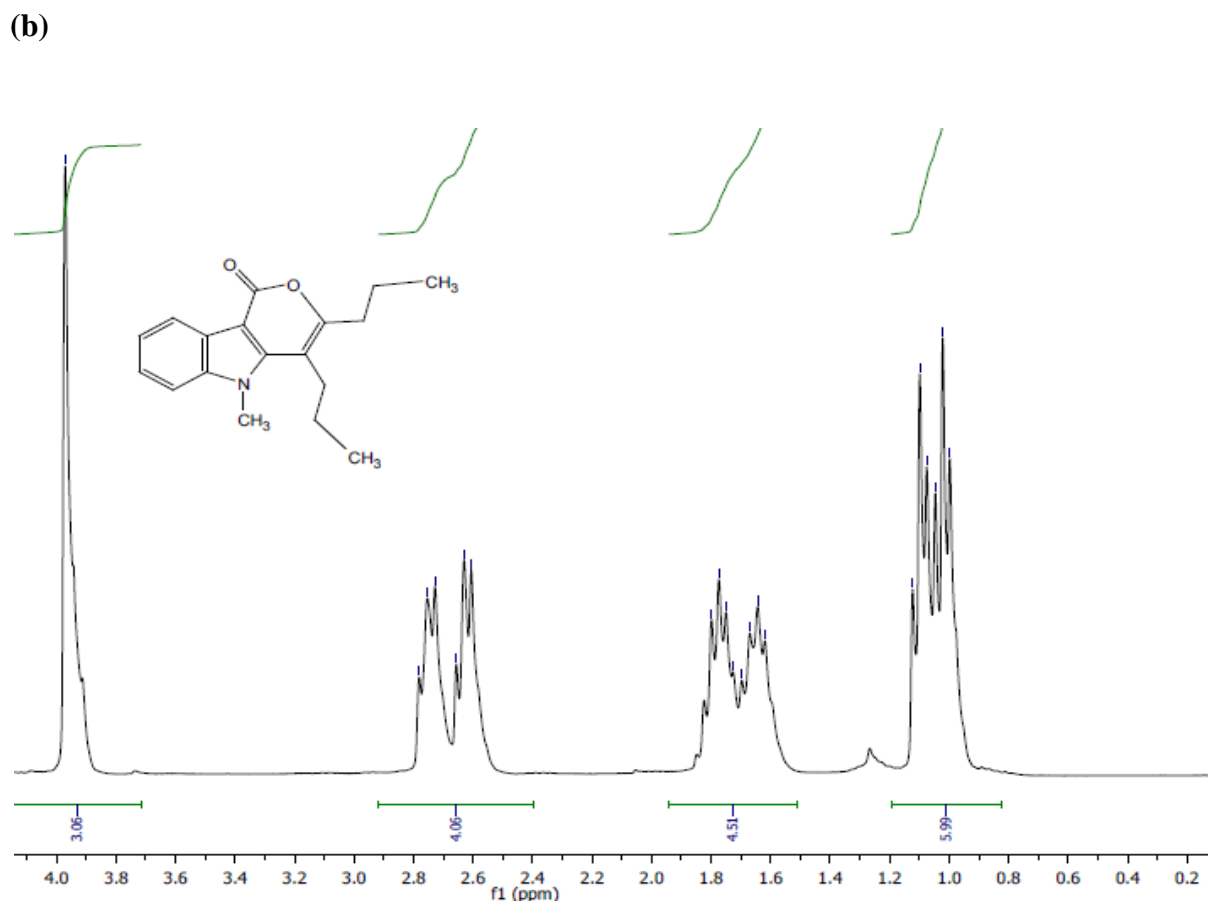
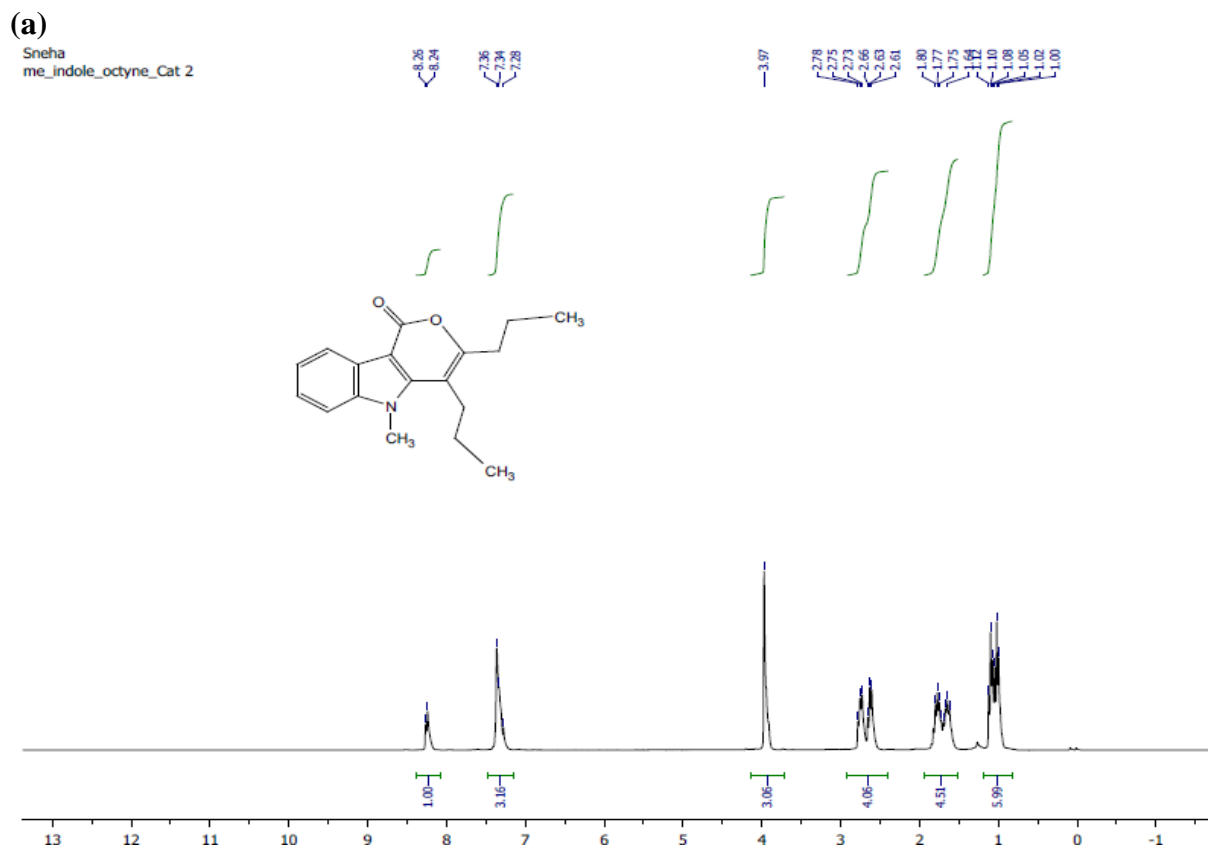


Figure S18. (a) ^1H -NMR of compound 6c; (b) expansion of aliphatic region.

Sneha
me_indole_octyne_Cat 2

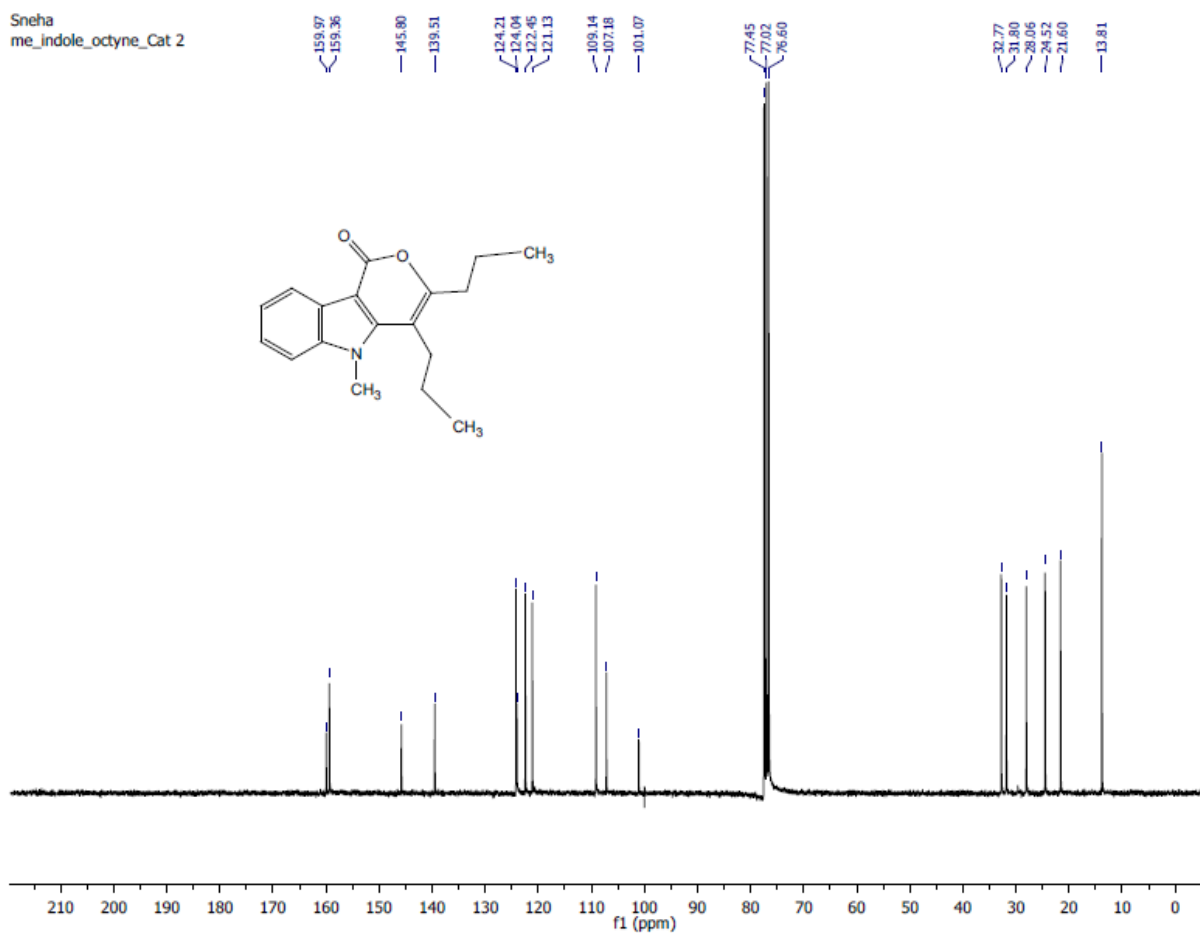
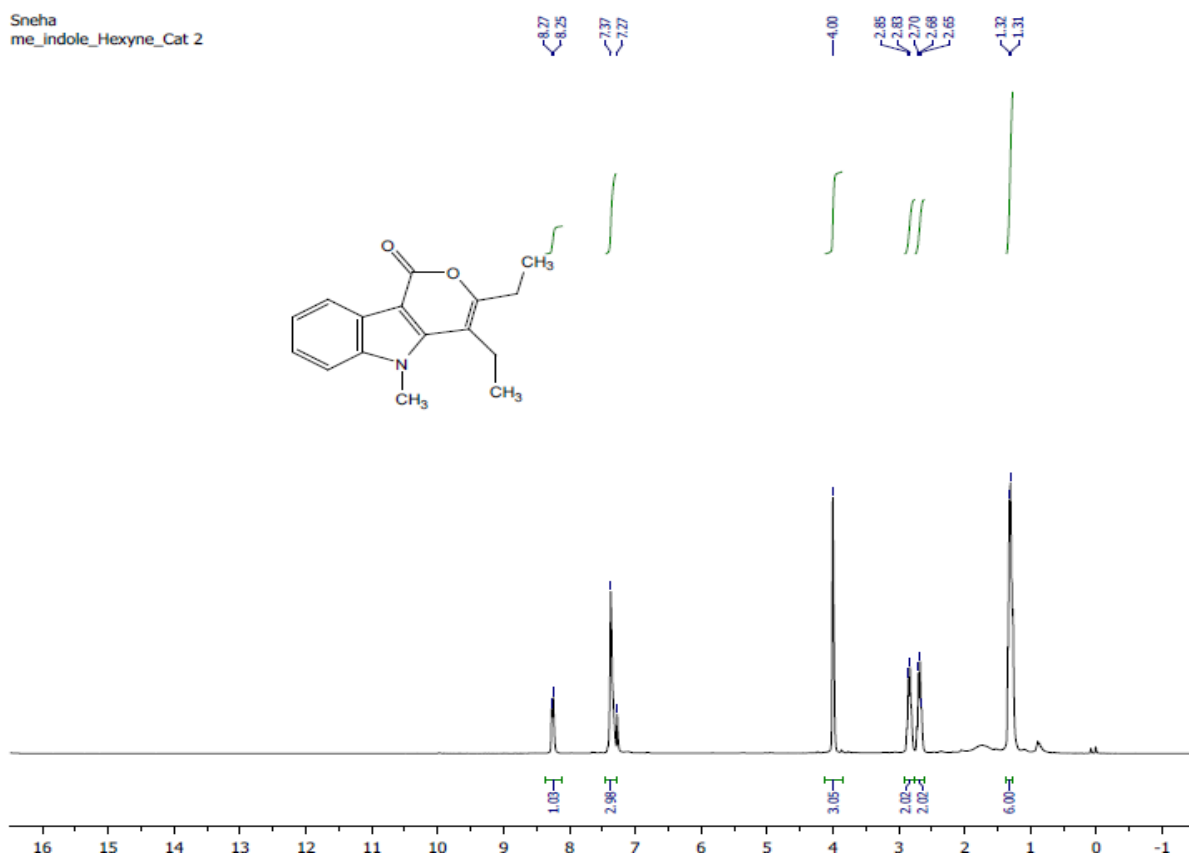


Figure S19. ¹³C-NMR spectrum of compound 6c.

Sneha
me_indole_Hexyne_Cat 2



Sneha
me_indole_Hexyne_Cat 2

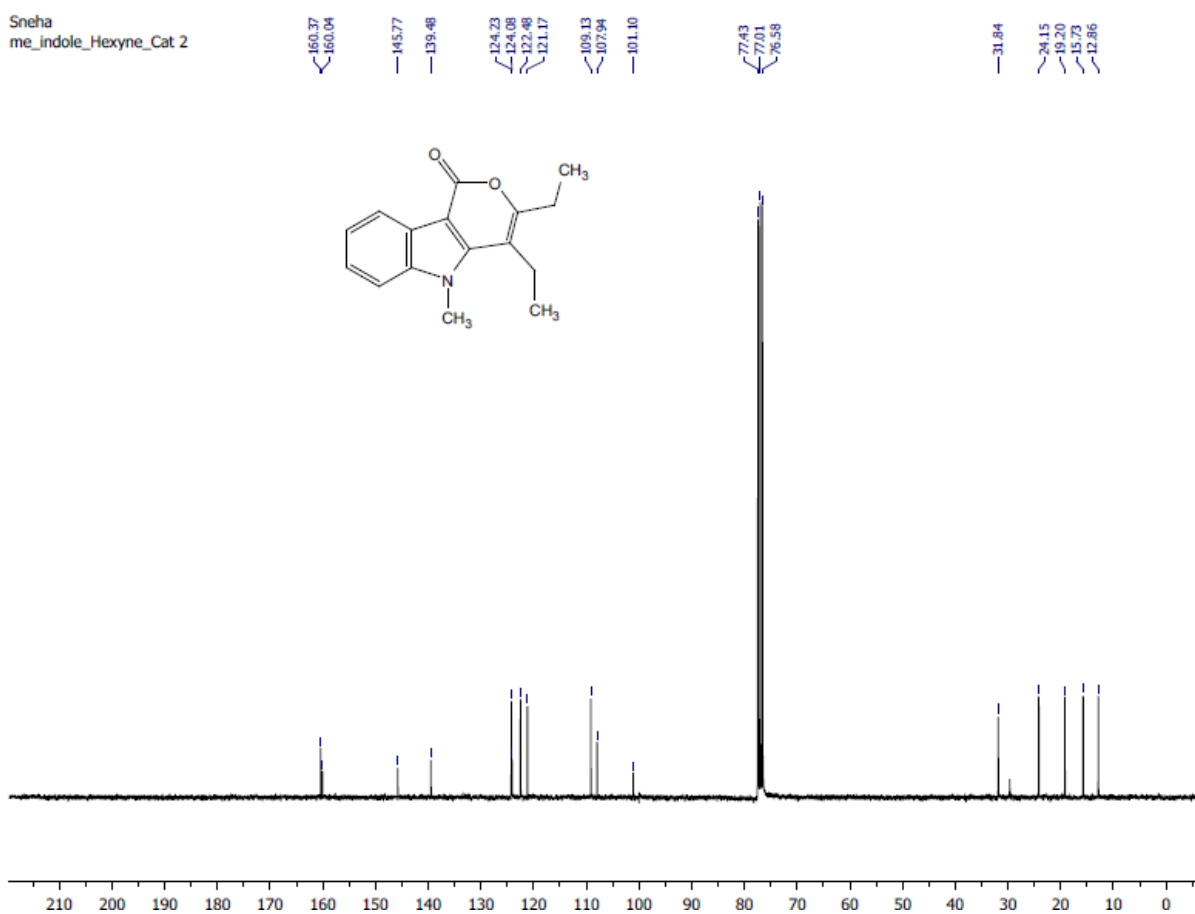


Figure S20. ¹H and ¹³C-NMR spectra of compound 6d.