

Cu(II)-Hydromagnesite catalyzed synthesis of tetrasubstituted propargylamines and pyrrolo[1,2-a]quinolines via KA2, A3 couplings and their decarboxylative versions

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1. General Remarks

X-ray diffraction (XRD) patterns were recorded on Rigaku Rotaflex spectrometer at 2θ range of $10\text{--}70^\circ$ with Cu K α radiation. Scanning electron microscopy (SEM) measurement was performed on a Philips XL30 electron micrograph. Transmission electron microscopy (TEM), SAED micrographs were obtained on a Joel JEM 2010 transmission electron microscope. The samples were supported on carbon-coated copper grids for the experiment.-Inductively coupled plasma atomic emission spectroscopy (ICP-AES) analysis was obtained from Perkin Elmer, Optima 2000. The elemental composition and electronic structure analysis of Cu/HM was obtained from X-ray photoelectron spectra (XPS) of model SPECS and Omircon electron analyzer (EA125). Fourier transform infrared (FT-IR) spectra were recorded on Perkin Elmer and the samples were prepared by mixing the powdered solids with KBr. The single crystal data for compound (**6db**) was obtained from Xcalibur Sapphire3 diffractometer equipped with graphite monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$). ^1H and ^{13}C NMR spectra were measured on a BruckerAC-200 instrument using C_6D_6 as solvent. Mass spectral data were recorded on a Jeol-Accu TOF JMS-T100LC and micromass LCT Mass Spectrometer/Data system.

The intensity data for compound (**6db**) was collected on Xcalibur Sapphire3 diffractometer equipped with graphite monochromatic Mo-K α radiation ($\lambda = 0.71073 \text{ \AA}$) at $293(2) \text{ K}$ [1]. A multi-scan correction was applied. The structure was solved by the direct methods using SIR-92 and refined by full-matrix least-squares refinement techniques on F^2 using SHELXL97 [2]. The hydrogen atoms were placed into the calculated positions and included in the last cycles of the refinement. All calculations were done using WinGX software package [3].

Table S1. Crystal data collection and structure refinement parameters for compound (**6db**).

Empirical formula	C ₃₀ H ₂₉ N ₃
Formula weight	431.56
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	I 2/a
<i>a</i>	14.2590(15) Å
<i>b</i>	11.0518(19) Å
<i>c</i>	29.807(5) Å
α	90°
β	91.907(13)°
γ	90°
Volume	4694.6(12) Å ³
<i>Z</i>	8
Density (calculated)	1.221 Mg/m ³
Absorption coefficient	0.072 mm ⁻¹
<i>F</i> (000)	1840
Crystal size	0.25 x 0.23 x 0.21 mm ³
Theta range for data collection	3.13 to 25.00°
Index ranges	-16 ≤ <i>h</i> ≤ 16, -11 ≤ <i>k</i> ≤ 13, -35 ≤ <i>l</i> ≤ 34
Reflections collected	15524
Independent reflections	4125 [<i>R</i> (int) = 0.1166]
Completeness to theta = 25.00°	99.8 %
Absorption correction	Multi-scan
Max. and min. transmission	0.9851 and 0.9823
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data / restraints / parameters	4125 / 0 / 299
Goodness-of-fit on <i>F</i> ²	0.966
Final <i>R</i> indices [I>2sigma(I)] ^{a, b}	<i>R</i> ₁ = 0.0786, <i>wR</i> ₂ = 0.1480
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.1880, <i>wR</i> ₂ = 0.2034
Largest diff. peak and hole	0.213 and -0.194 e.Å ⁻³

$$^a R = \sum(\| F_O \| - \| F_C \|)/\sum \| F_O \| ; ^b wR = \{ \sum[w(F_O^2 - F_C^2)^2] / \sum[w(F_O^2)^2] \}^{1/2}$$

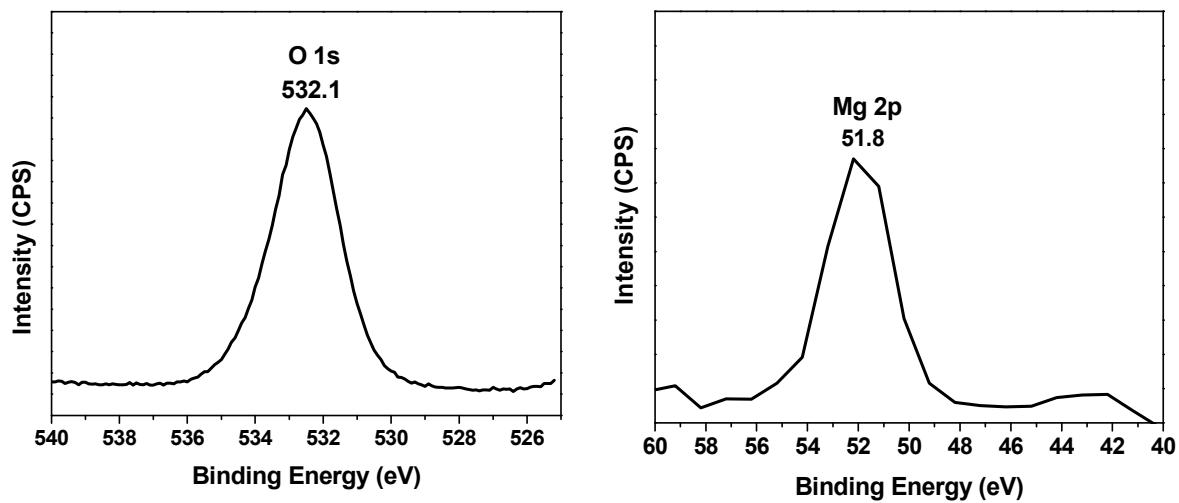


Figure S1: High resolution XPS of O 1s and Mg 2p regions in Cu/HM

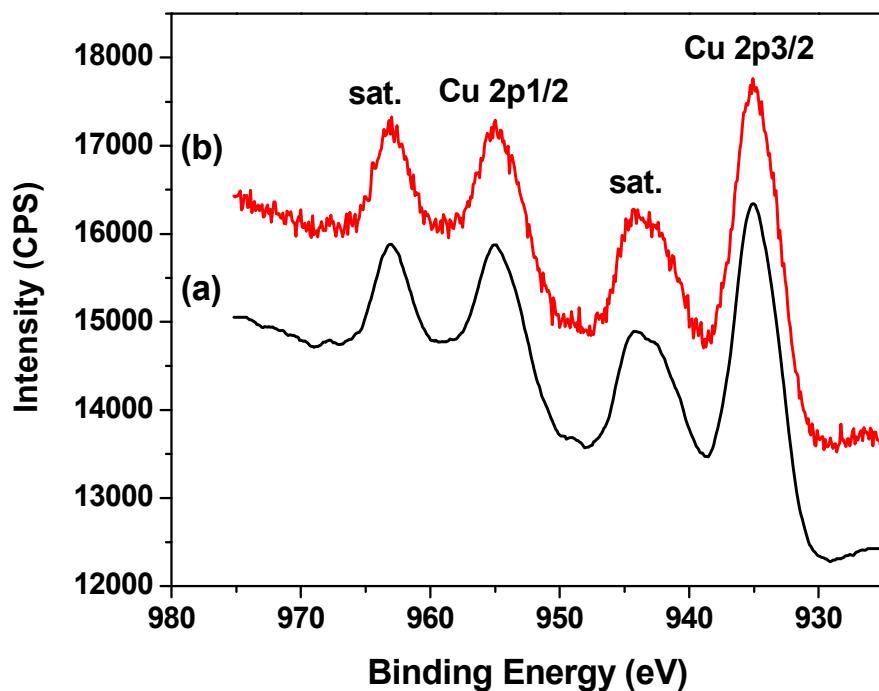


Figure S2: High resolution XPS of (a) fresh and (b) recycled Cu 2p regions of Cu/HM

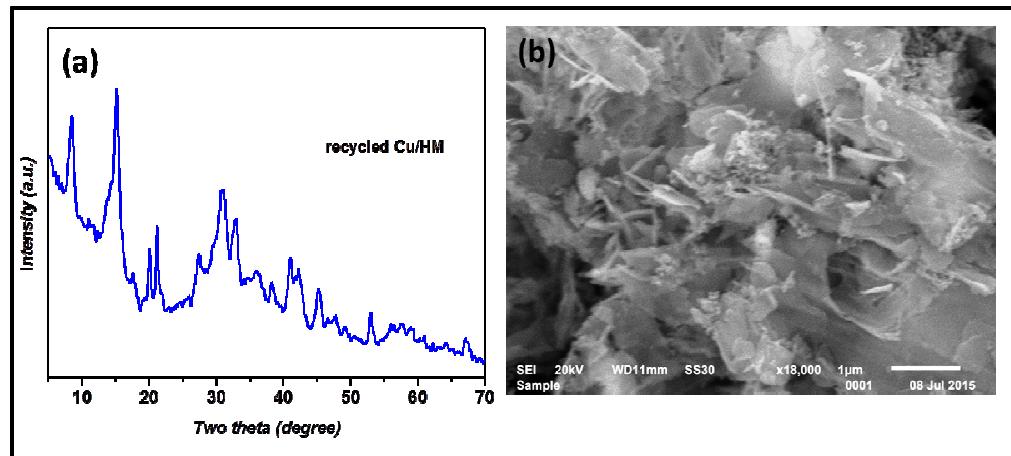
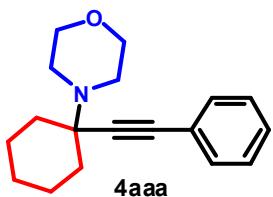
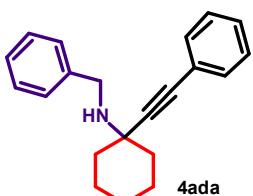


Figure S3: (a) PXRD; (b) SEM of recycled Cu/HM catalyst

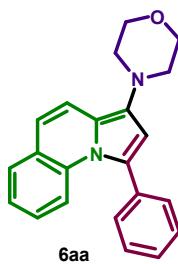
Spectral data of known compounds

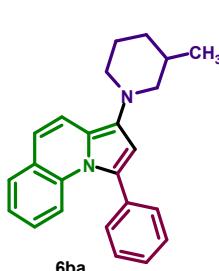


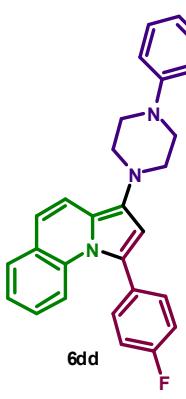
4-(1-(Phenylethynyl)cyclohexyl)morpholine (4aaa) [Ref. 7]: Yellow solid. m. p: 96-97 °C. IR (ν_{max} /cm⁻¹, CHCl₃): 2930, 2855, 2358, 1601, 1270, 1211, 976, 802, 759, 693; ¹H NMR (400 MHz, C₆D₆) δ = 7.44-7.42 (m, 2H), 7.29-7.27 (m, 3H), 3.76 (t, J = 4.6 Hz, 4H), 2.72 (t, J = 4.6 Hz, 4H), 2.03 (d, J = 12.2 Hz, 2H), 1.74-1.70 (m, 2H), 1.61 (d, J = 11.4 Hz, 2H), 1.47 (t, J = 11.4 Hz, 2H), 1.31-1.24 (m, 2H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ = 131.88, 128.37, 127.98, 123.55, 89.97, 86.69, 67.65, 59.07, 46.83, 35.63, 25.83, 22.91 ppm; HRMS (ES): Calcd 269.1780, found 269.1775; Anal. calcd for C₁₈H₂₃NO: C, 80.26; H, 8.61; N, 5.20; found C, 80.26; H, 8.61; N, 5.20.



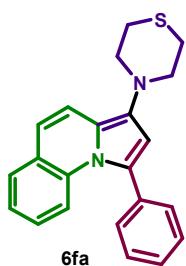
N-Benzyl-1-(phenylethynyl)cyclohexanamine (4ada) [Ref 8]: Yellow oil; ¹H NMR (CDCl₃, 300 MHz): δ = 7.52-7.17 (m, 10H), 3.94 (s, 2H), 2.08-1.92 (m, 2H), 1.79-1.21 (m, 8H) ppm; ¹³C NMR (CDCl₃, 100 MHz): δ = 142.08, 133.67, 129.44, 129.43, 129.28, 128.16, 127.24, 123.35, 92.47, 83.89, 54.41, 48.09, 38.80, 25.72, 22.04 ppm.

3-Morpholin-4-yl-1-phenyl-pyrrolo[1,2-a]quinoline (6aa) [Ref. 4]: Yellow oil.

¹H NMR (400 MHz, C₆D₆) δ = 7.58 (d, *J* = 8.4 Hz, 1H), 7.43 (d, *J* = 9.2 Hz, 1H), 7.34 (d, *J* = 6.8 Hz, 3H), 7.13-7.09 (m, 3H), 6.93 (t, *J* = 7.3 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.72 (d, *J* = 9.9 Hz, 1H), 6.5 (s, 1H), 3.74 (t, *J* = 4.6 Hz, 4H), 2.87 (t, *J* = 4.6 Hz, 4H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ: 136.27, 134.64, 132.29, 129.55, 128.79, 128.70, 126.49, 124.88, 123.60, 118.15, 117.76, 117.21, 109.12, 67.50, 54.72 ppm.

3-(3-Methyl-piperidin-1-yl)-1-phenyl-pyrrolo[1,2-a]quinoline (6ba) [Ref. 7]: Dark yellow oil.

¹H NMR (400 MHz, C₆D₆) δ = 7.59 (t, *J* = 9.9 Hz, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 7.33 (d, *J* = 6.8 Hz, 1H), 7.14-7.07 (m, 3H), 6.93 (t, *J* = 8.4 Hz, 1H), 6.78 (t, *J* = 7.6 Hz, 1H), 6.71 (d, *J* = 8.4 Hz, 1H), 6.59 (s, 1H), 3.24 (t, *J* = 10.7 Hz, 2H), 2.64 (t, *J* = 11.4 Hz, 1H), 2.36 (t, *J* = 10.7 Hz, 1H), 1.95-1.76 (m, 2H), 1.69-1.58 (m, 2H), 0.96-0.89 (m, 1H), 0.84 (d, *J* = 6.9 Hz, 3H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ: 136.44, 134.82, 134.07, 129.54, 128.75, 128.64, 127.55, 126.60, 126.33, 124.88, 123.45, 118.10, 116.86, 109.58, 63.00, 55.25, 33.27, 32.02, 26.48, 19.82 ppm.

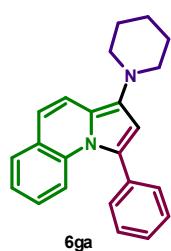
1-(4-Fluoro-phenyl)-3-(4-o-tolyl-piperazin-1-yl)-pyrrolo[1,2-a]quinoline (6dd) [Ref. 7]: Brown oil.

¹H NMR (400 MHz, C₆D₆) δ = 7.48 (d, *J* = 9.2 Hz, 1H), 7.38 (d, *J* = 8.4 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.04-6.99 (m, 3H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.73 (t, *J* = 8.4 Hz, 2H), 6.68 (d, *J* = 9.2 Hz, 1H), 6.43 (s, 1H), 3.06 (t, *J* = 4.6 Hz, 4H), 2.92 (t, *J* = 4.6 Hz, 4H), 2.28 (s, 3H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ = 162.70 (d, ¹J_{C-F} = 249.2 Hz), 152.27, 134.62, 132.98, 132.87, 132.22 (d, ⁴J_{C-F} = 3.8 Hz), 131.49, 131.31, 131.24, 128.74, 127.11, 126.94, 126.49 (d,

$^3J_{C-F} = 7.6$ Hz), 124.86, 123.65, 119.53, 117.87 (d, $^3J_{C-F} = 7.6$ Hz), 117.18, 115.71 (d, $^2J_{C-F} = 22.0$ Hz), 109.34, 54.88, 52.76, 18.22 ppm.



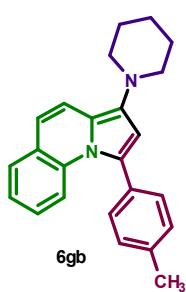
1-Phenyl-3-thiomorpholin-4-yl-pyrrolo[1,2-a]quinoline (6fa) [Ref. 7]:

Yellow oil. 1H NMR (400 MHz, C_6D_6) δ = 7.58 (d, J = 8.4 Hz, 1H), 7.39 (d, J = 9.2 Hz, 1H), 7.35-7.32 (m, 3H), 7.13-7.09 (m, 3H), 6.93 (t, J = 7.6 Hz, 1H), 6.78 (t, J = 7.6 Hz, 1H), 6.72 (d, J = 9.9 Hz, 1H), 6.47 (s, 1H), 3.12 (t, J = 4.6 Hz, 4H), 2.59 (t, J = 4.6 Hz, 4H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 136.01, 134.47, 133.60, 129.30, 128.56, 128.49, 126.31, 126.22, 124.87, 123.37, 117.89, 117.35, 117.17, 109.62, 56.34, 28.48 ppm.



1-Phenyl-3-piperidin-1-yl-pyrrolo[1,2-a]quinoline (6ga) [Ref. 5]: Brown oil. 1H

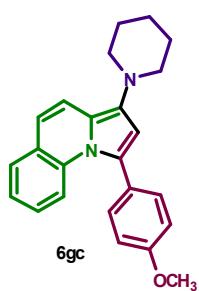
NMR (400 MHz, C_6D_6) δ = 7.52 (d, J = 9.2 Hz, 1H), 7.50 (d, J = 9.2 Hz, 1H), 7.28 (t, J = 7.6 Hz, 3H), 7.08-7.02 (m, 3H), 6.86 (t, J = 7.6 Hz, 1H), 6.71 (t, J = 7.6 Hz, 1H), 6.64 (d, J = 9.2 Hz, 1H), 6.53 (s, 1H), 2.91 (t, J = 5.3 Hz, 4H), 1.62 (quint, 4H), 1.38 (quint, 2H) ppm; ^{13}C NMR (100 MHz, C_6D_6) δ = 136.42, 134.78, 134.39, 129.54, 128.77, 128.65, 127.57, 126.60, 126.32, 124.85, 123.45, 118.14, 116.87, 109.41, 56.01, 27.18, 24.82 ppm.



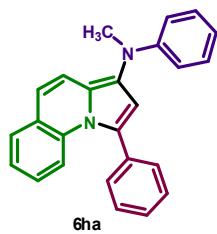
3-Piperidin-1-yl-1-p-tolyl-pyrrolo[1,2-a]quinoline (6gb) [Ref. 6]: Yellow solid.

mp: 136-138 °C. 1H NMR (400 MHz, C_6D_6) δ = 7.67 (d, J = 8.3 Hz, 1H), 7.57 (d, J = 9.2 Hz, 1H), 7.33 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 8.4 Hz, 2H), 6.98 (d, J = 8.4 Hz, 2H), 6.93 (t, J = 7.9 Hz, 1H), 6.81 (t, J = 8.4 Hz, 1H), 6.70 (d, J = 9.2 Hz, 1H), 6.62 (s, 1H), 2.99 (t, J = 5.3 Hz, 4H), 2.12 (s, 3H), 1.68 (quint, 4H), 1.43 (quint, 2H) ppm; ^{13}C

NMR (100 MHz, C₆D₆) δ = 137.25, 134.94, 134.34, 133.64, 129.62, 129.53, 128.66, 126.66, 126.25, 124.67, 123.41, 118.18, 118.11, 116.65, 109.26, 55.86, 27.07, 24.75, 21.35 ppm.

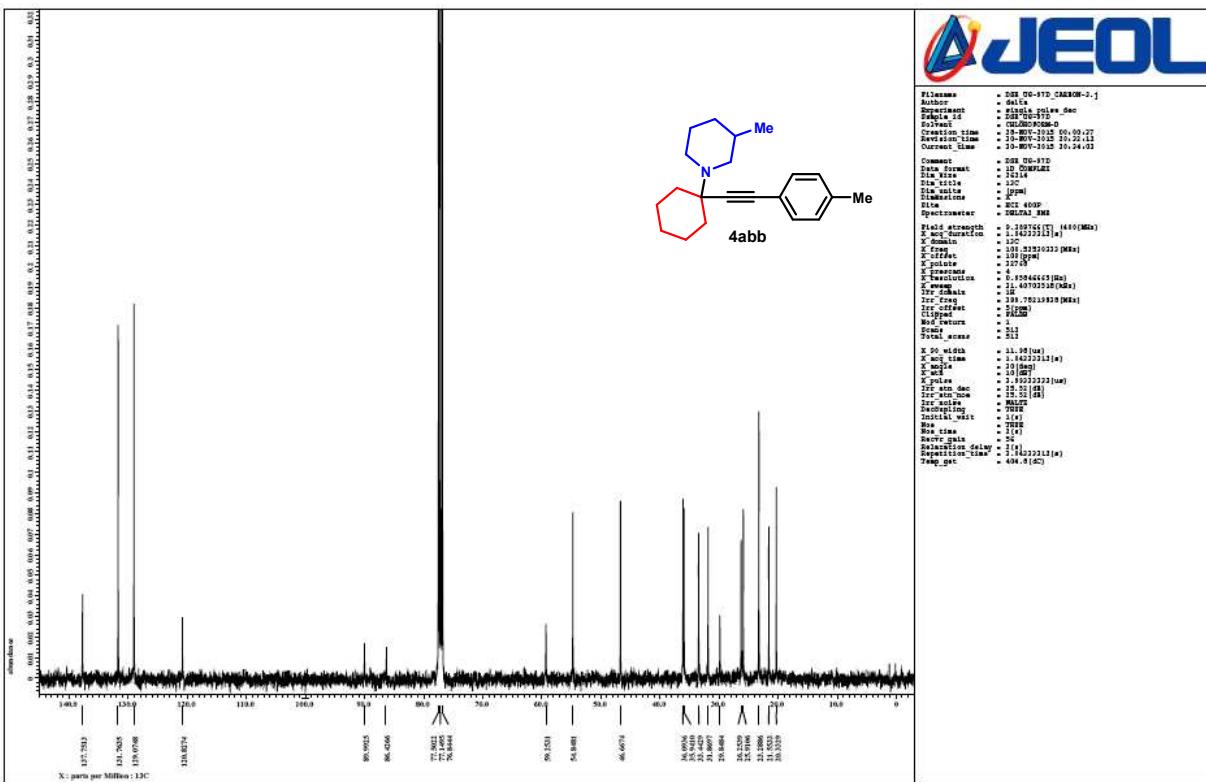
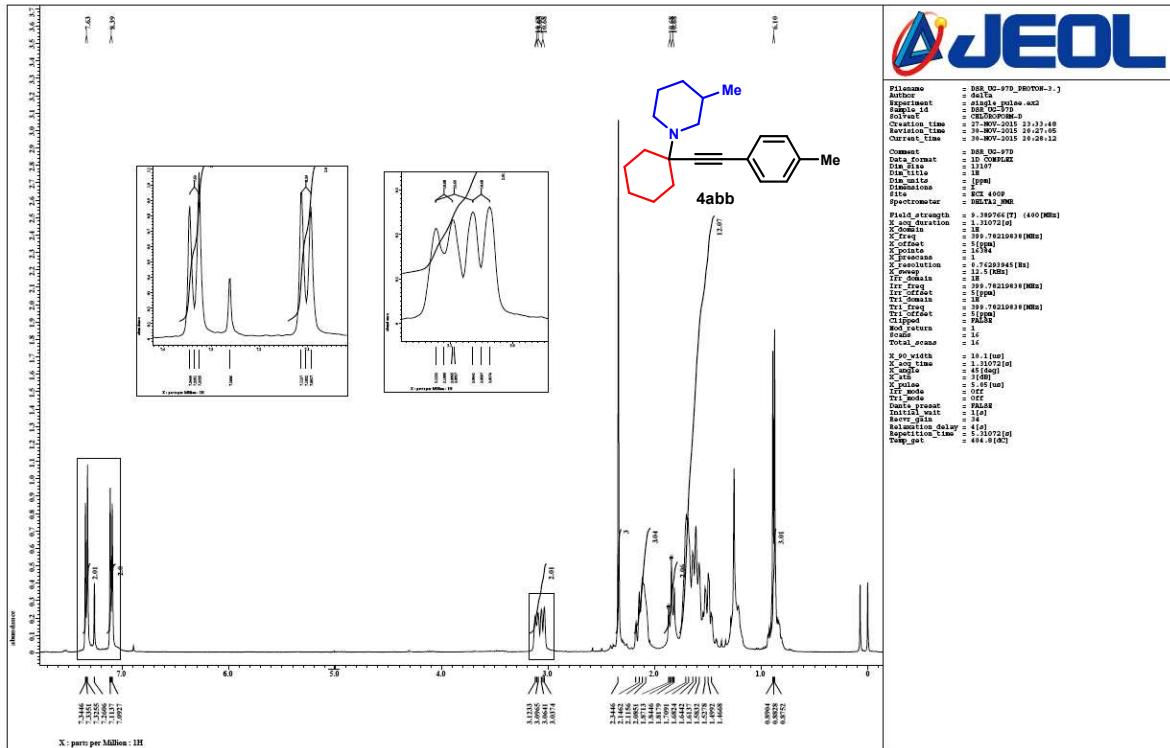


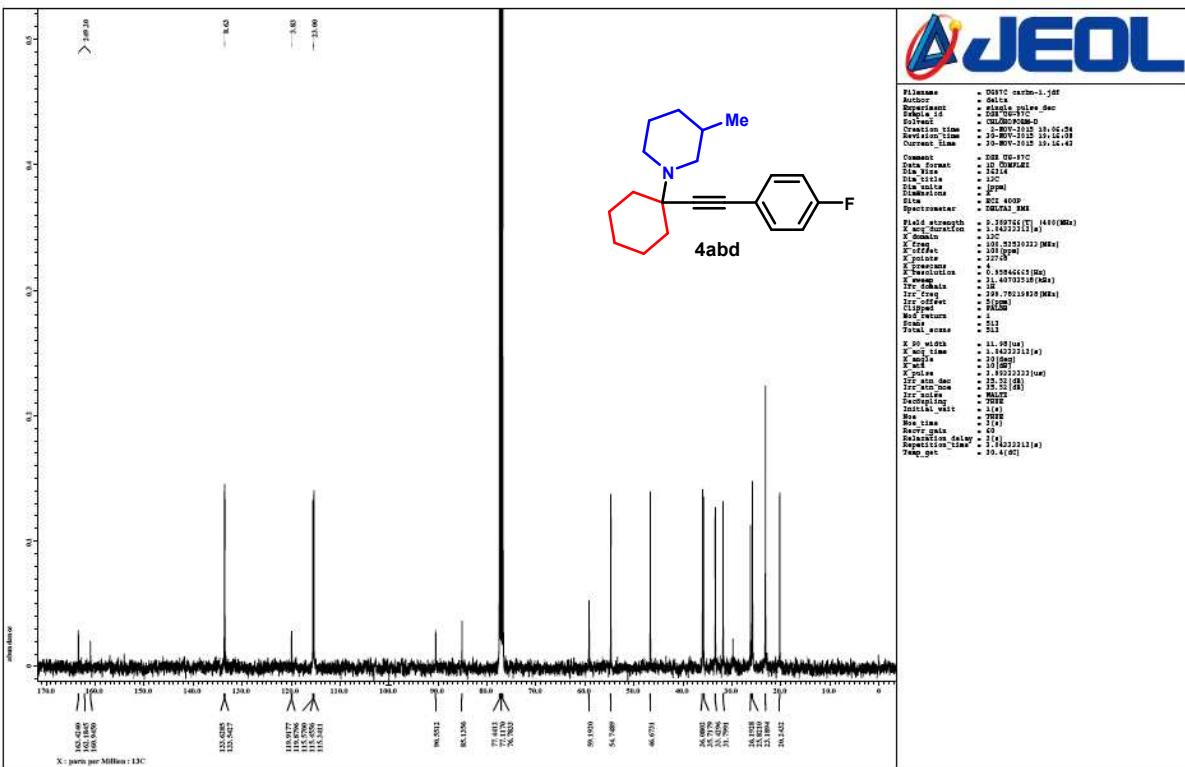
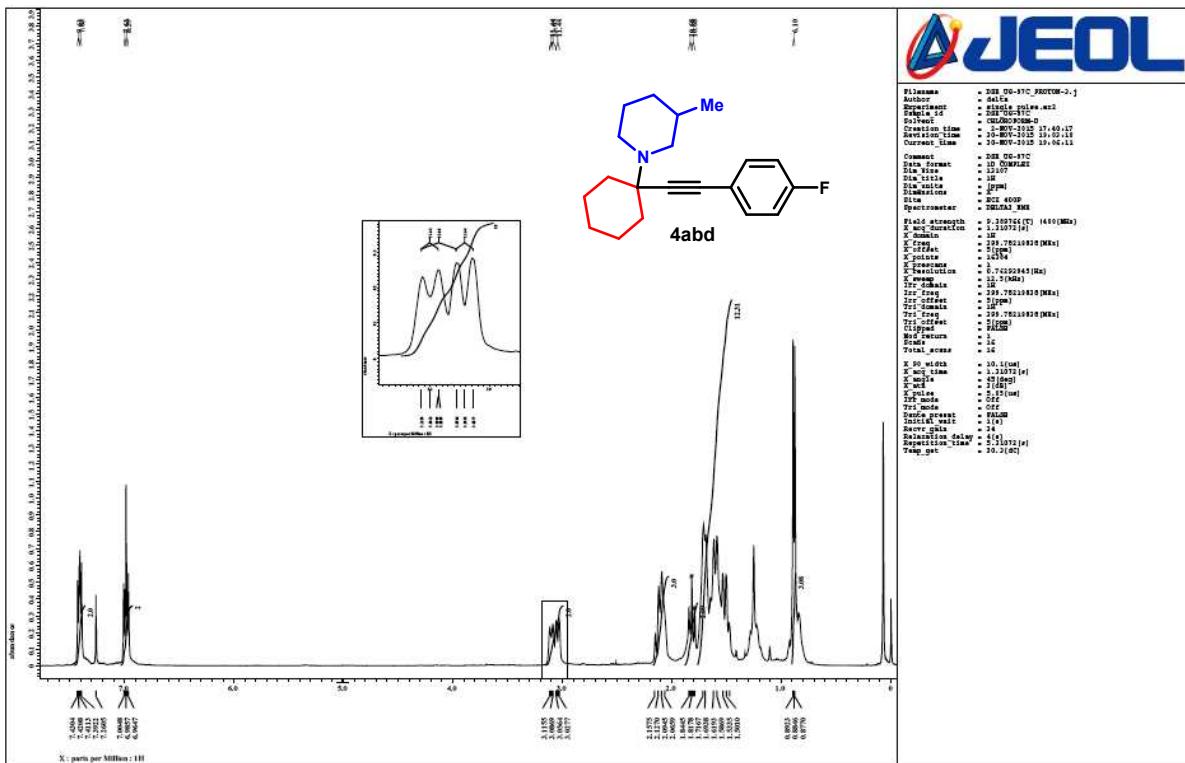
1-(4-Methoxy-phenyl)-3-piperidin-1-yl-pyrrolo[1,2-a]quinoline (6gc) [Ref. 6]: Brown oil. ¹H NMR (400 MHz, C₆D₆) δ = 7.67 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 9.2 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 9.2 Hz, 2H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.83 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 8.4 Hz, 2H), 6.70 (d, *J* = 9.2 Hz, 1H), 6.61 (s, 1H), 3.30 (s, 3H), 2.99 (t, *J* = 5.3 Hz, 4H), 1.68 (quint, 4H), 1.43 (quint, 2H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ = 159.67, 135.05, 134.17, 131.03, 128.81, 128.64, 126.67, 126.27, 124.37, 123.37, 118.18, 117.88, 116.48, 114.32, 108.93, 55.93, 54.91, 27.00, 24.78 ppm.

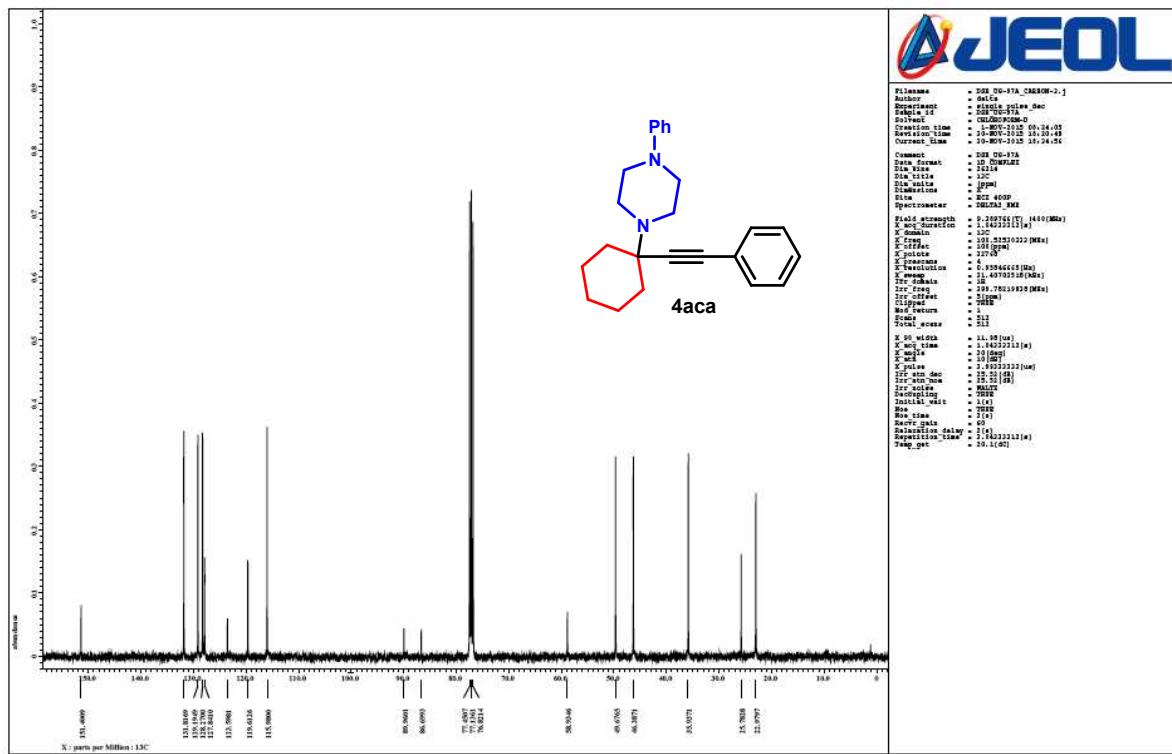
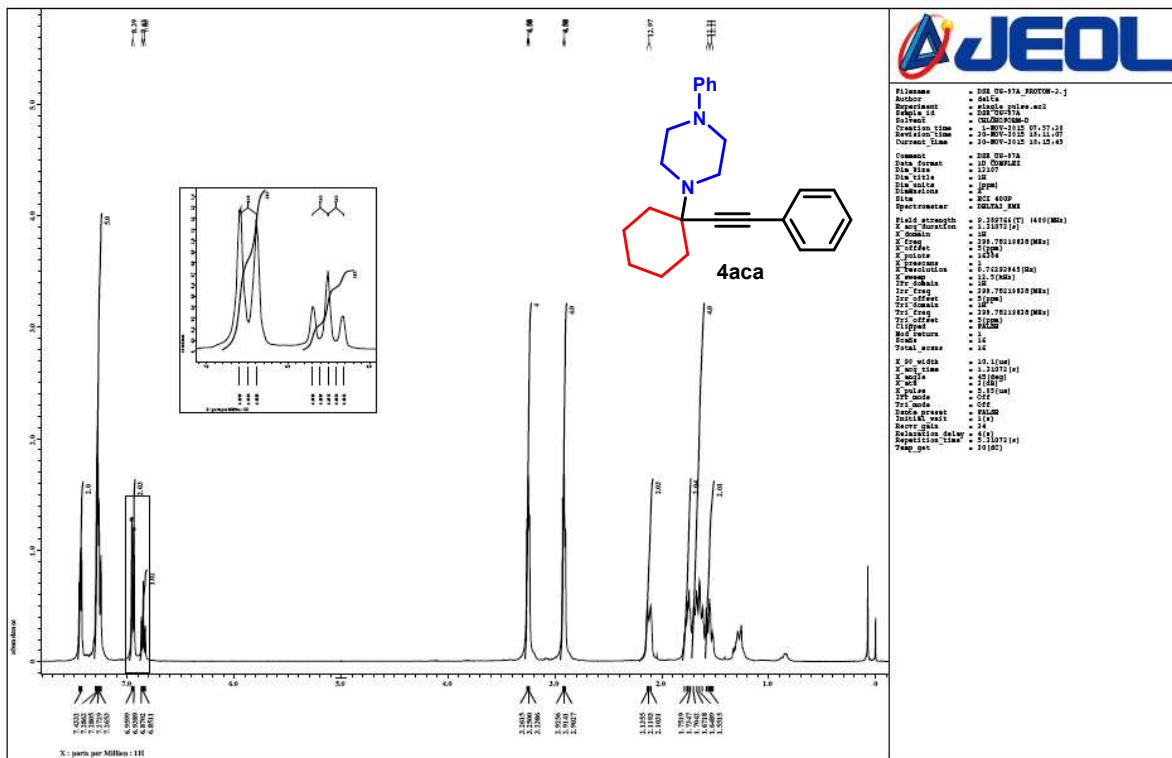


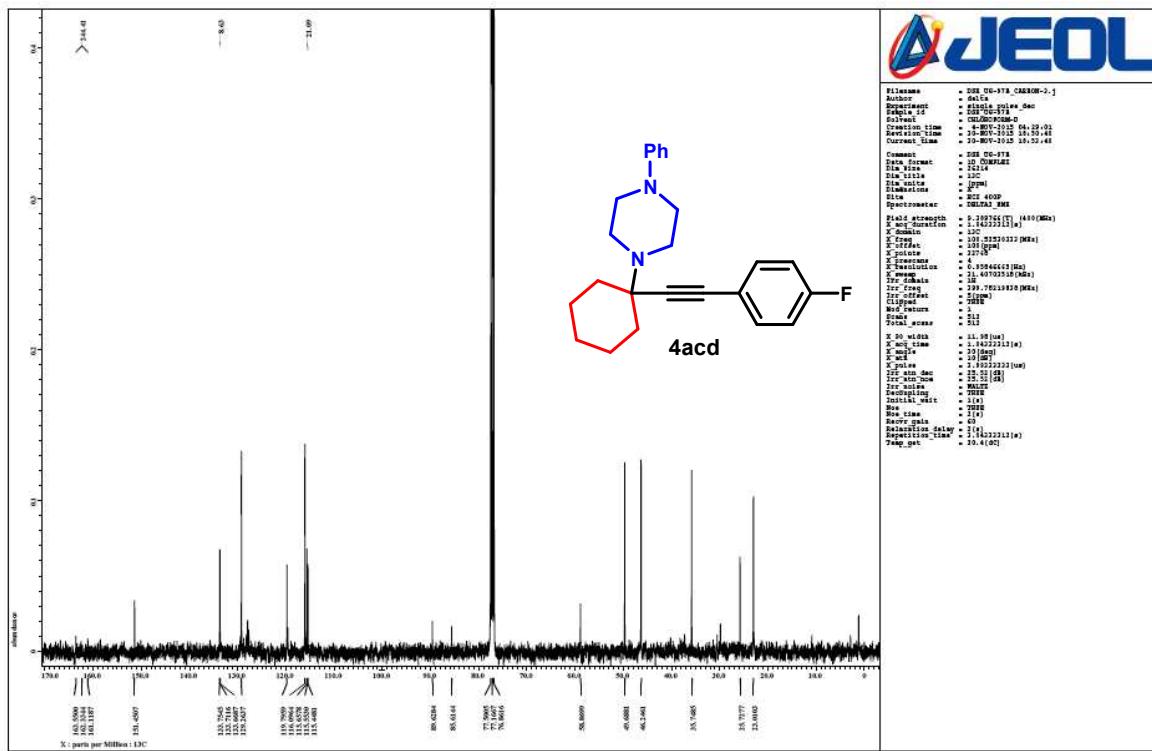
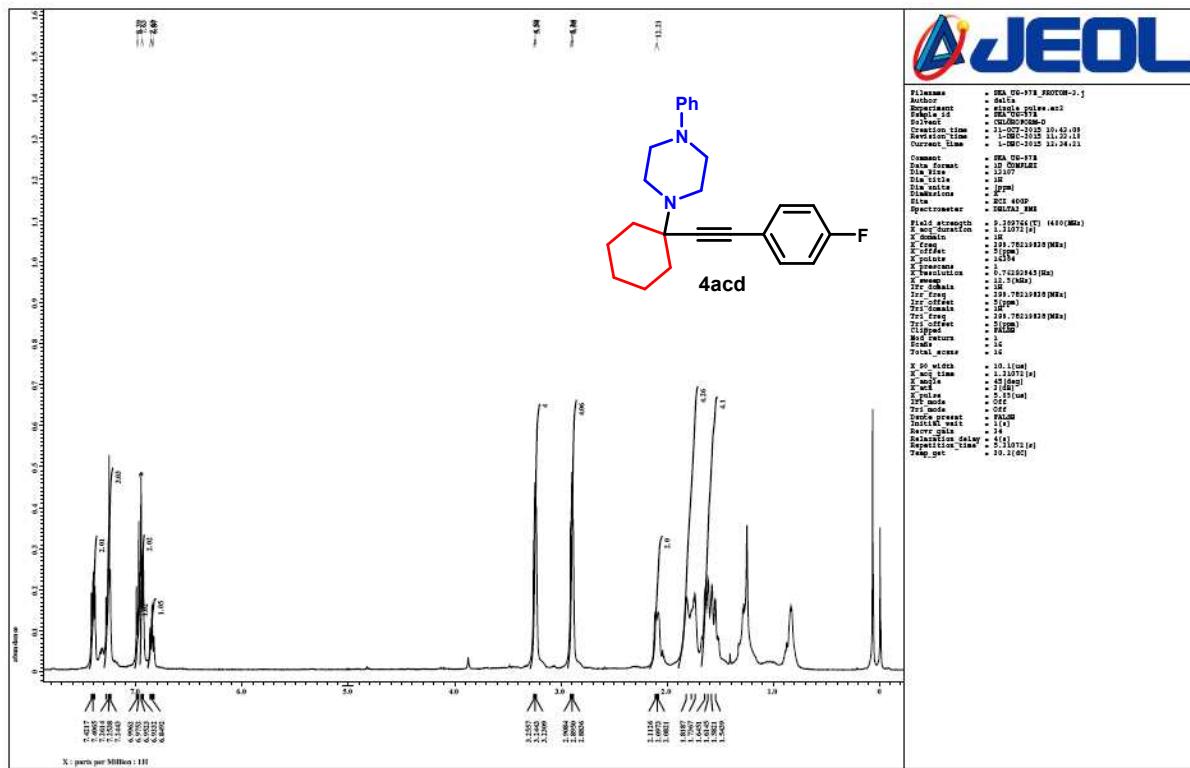
Methyl-phenyl-(1-phenyl-pyrrolo[1,2-a]quinolin-3-yl)-amine (6ha) [Ref. 7]: Orange oil. ¹H NMR (400 MHz, C₆D₆) δ = 7.64 (d, *J* = 8.4 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.6 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 4H), 6.90 (d, *J* = 7.6 Hz, 2H), 6.82 (t, *J* = 7.6 Hz, 2H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.63 (d, *J* = 9.2 Hz, 1H), 6.52 (s, 1H), 3.12 (s, 3H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ = 150.66, 135.93, 134.74, 129.61, 129.36, 128.89, 128.80, 126.80, 126.36, 126.18, 123.72, 119.17, 118.02, 117.75, 117.39, 114.66, 113.94, 40.70 ppm.

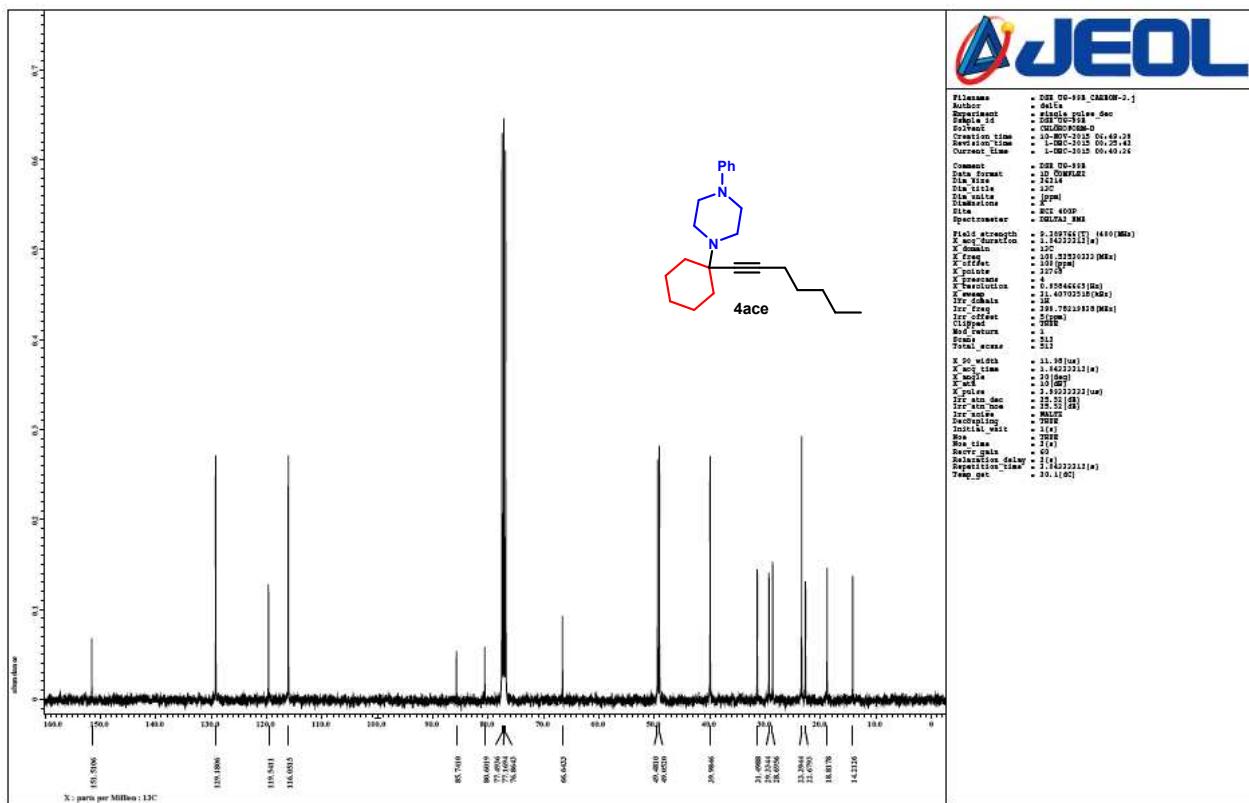
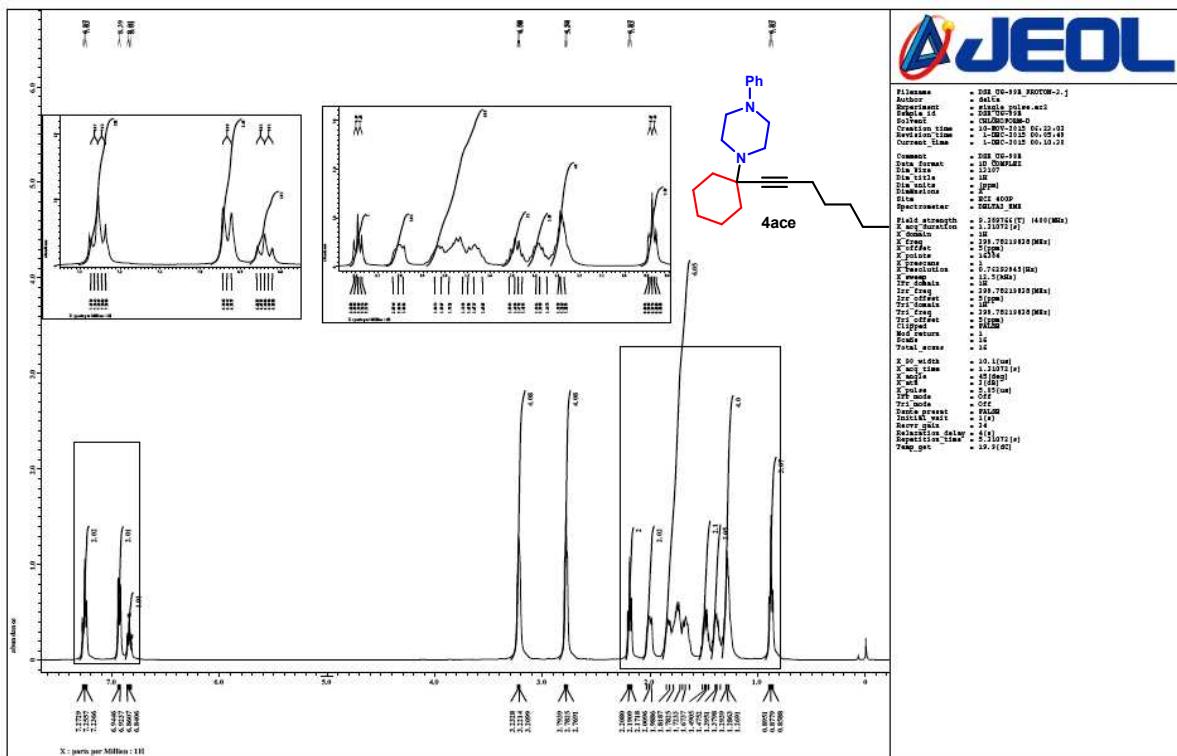
¹H NMR and ¹³C spectra of all tetrasubstituted propargylamines

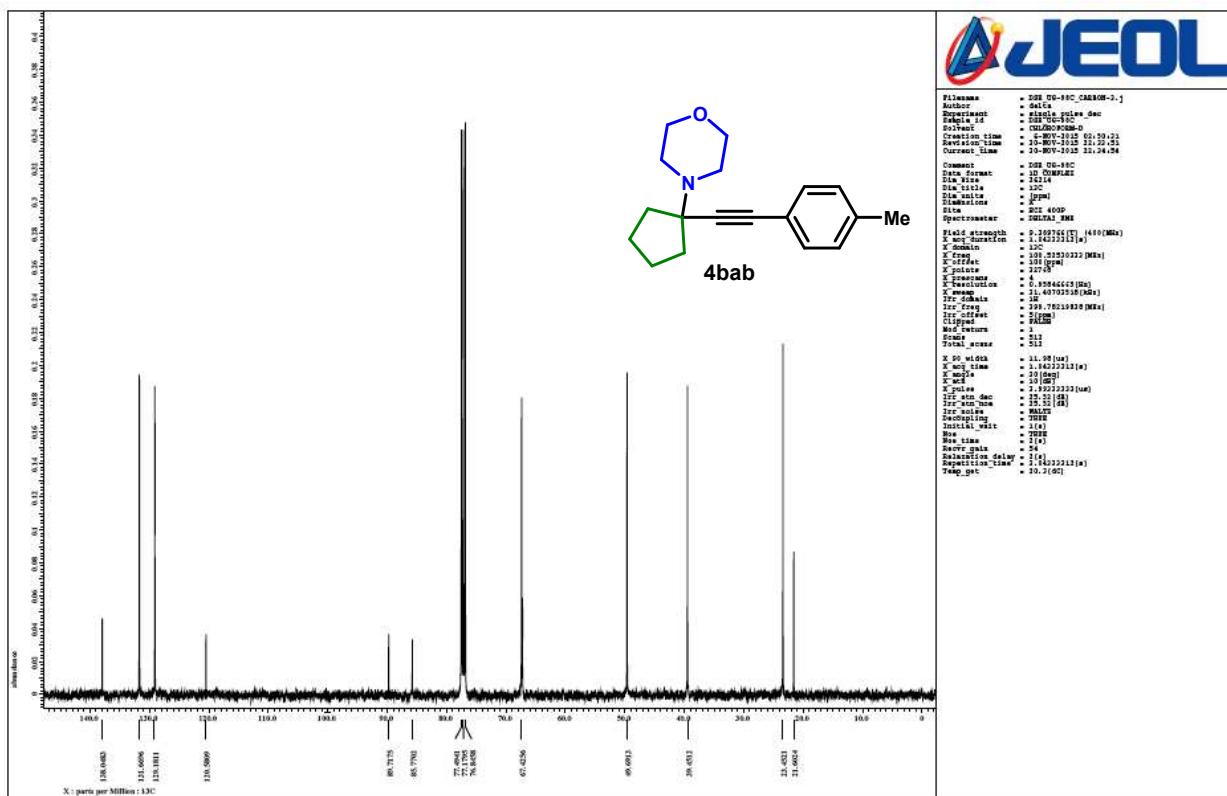
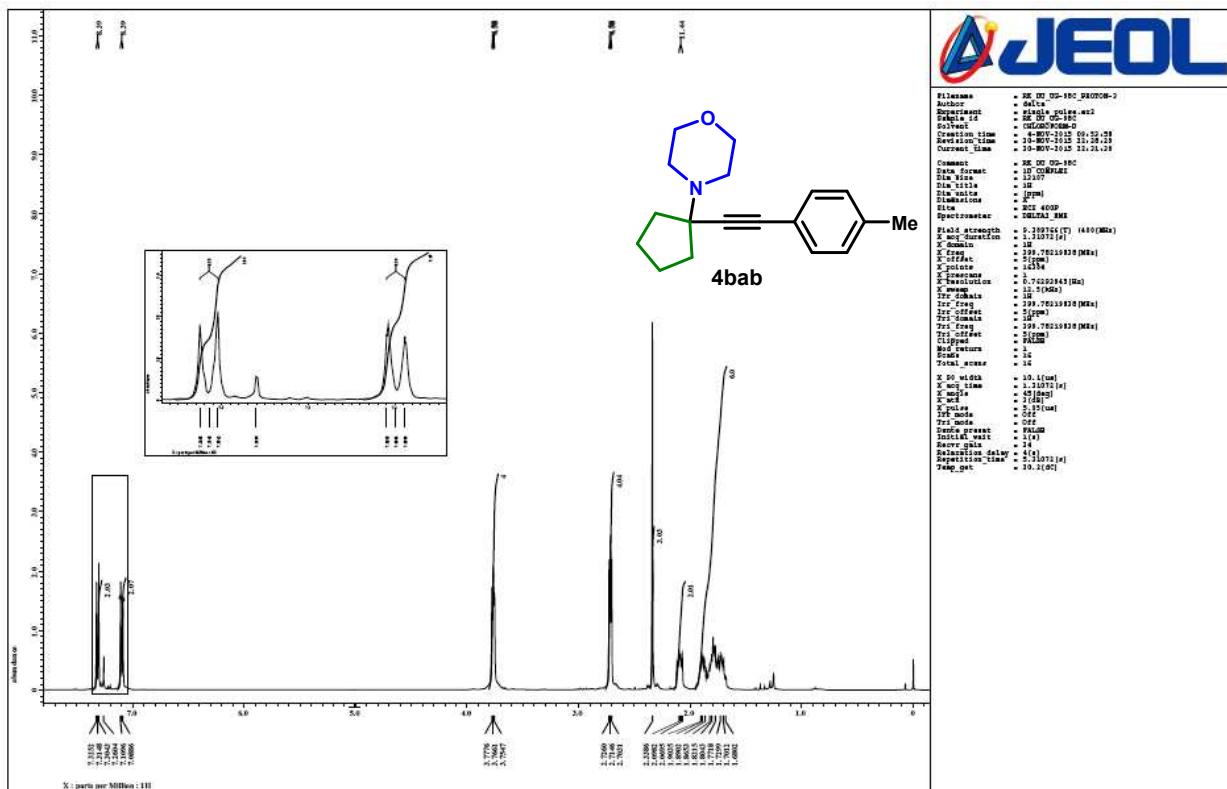


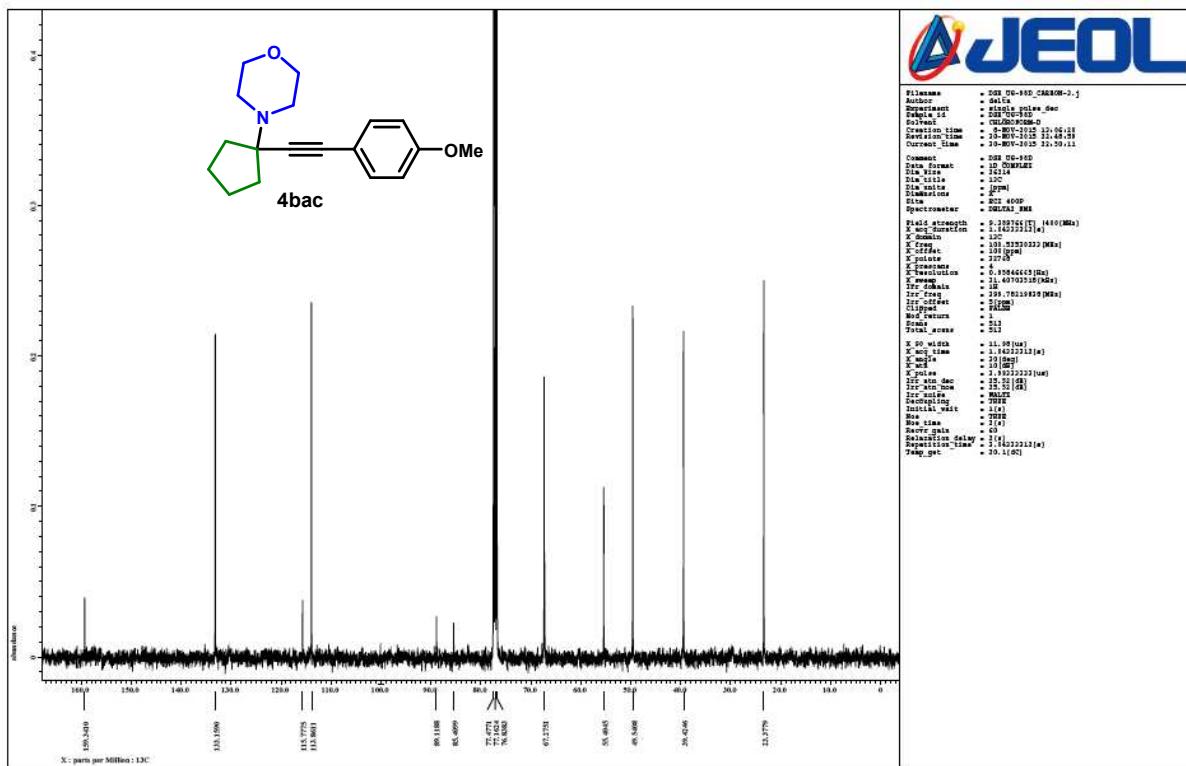
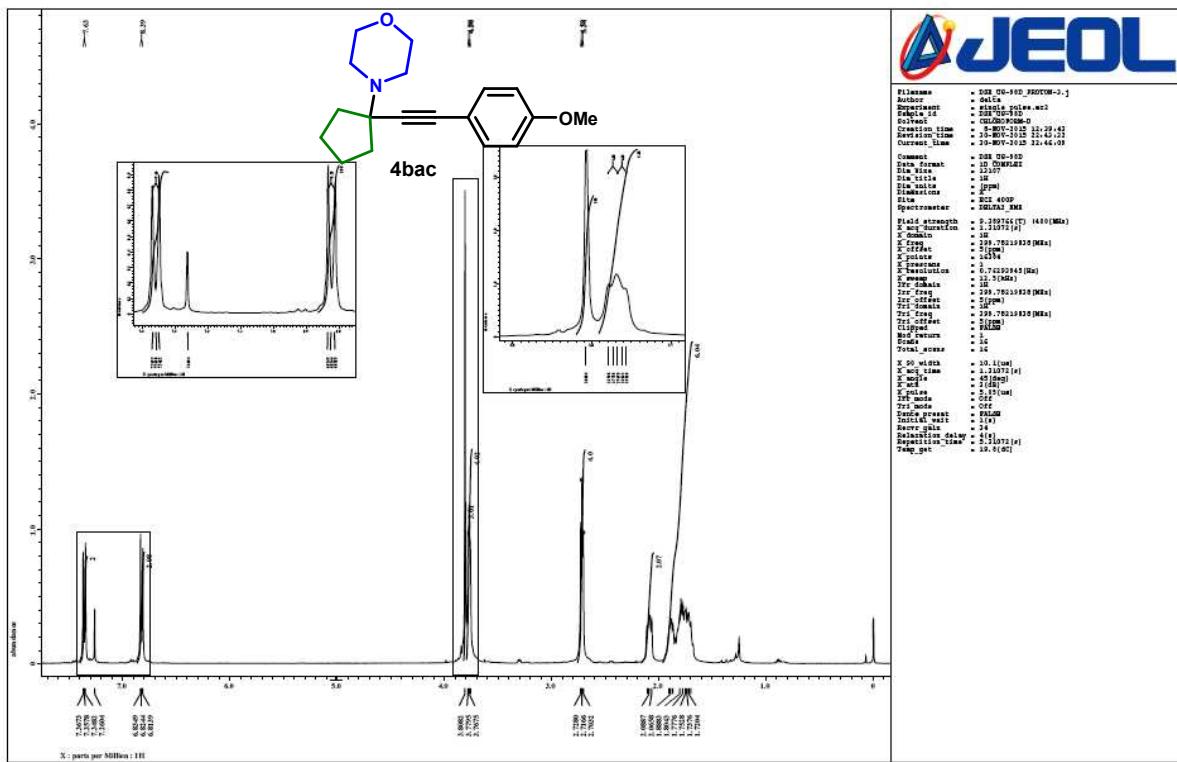


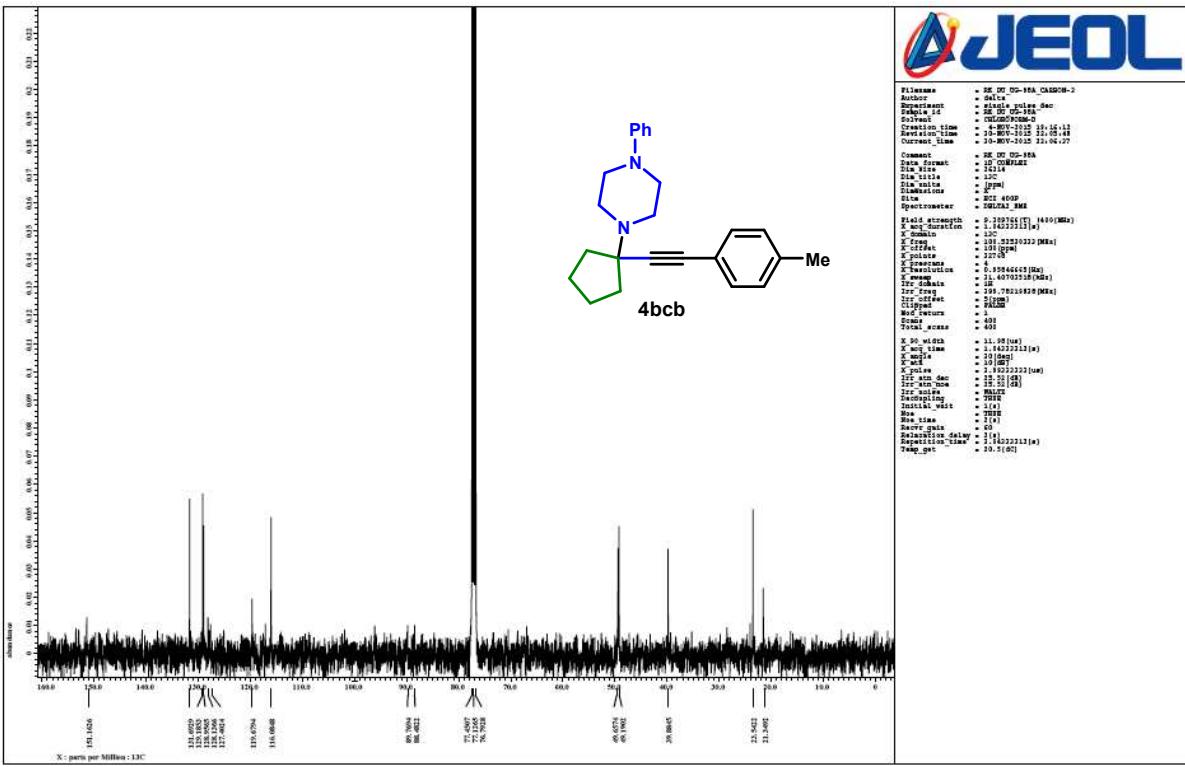
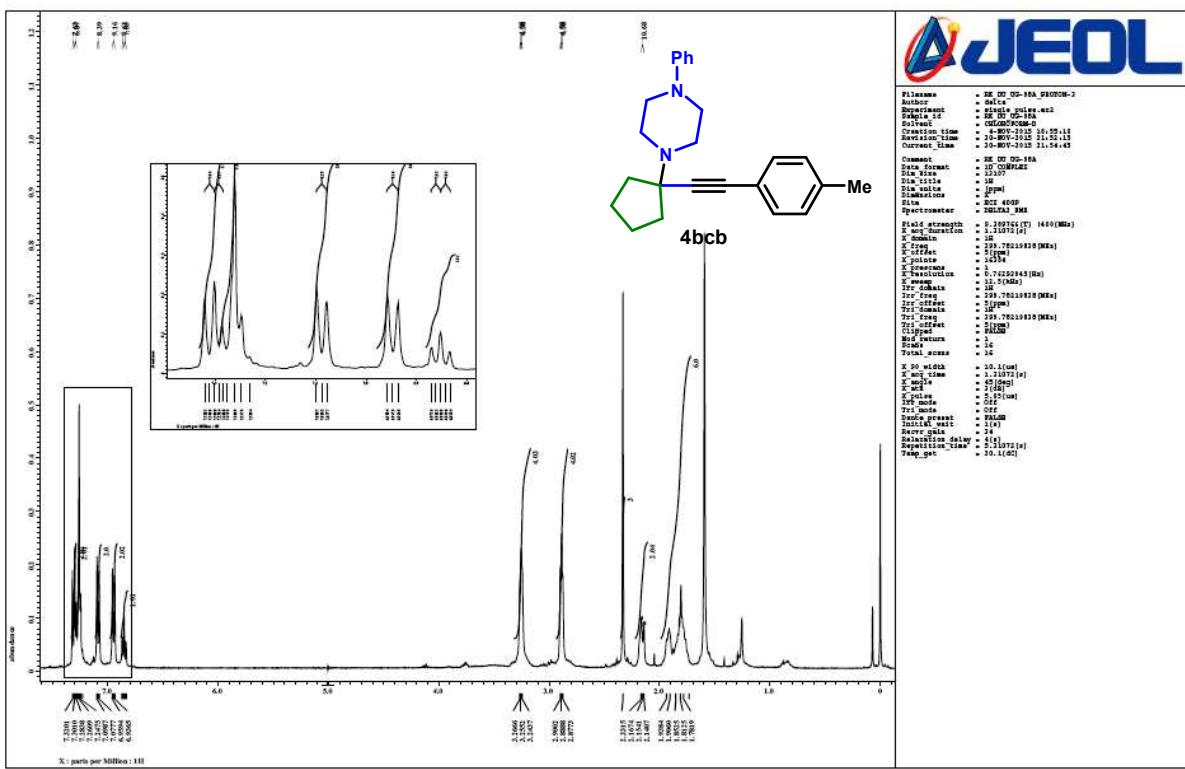


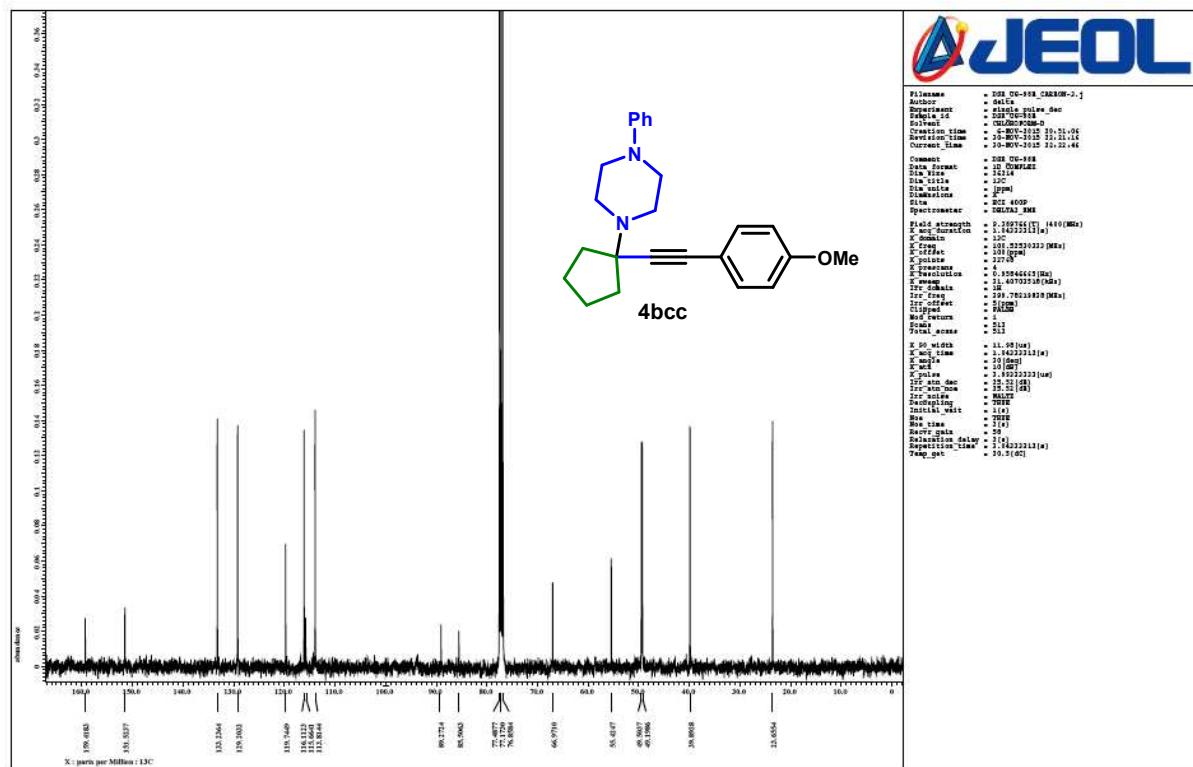
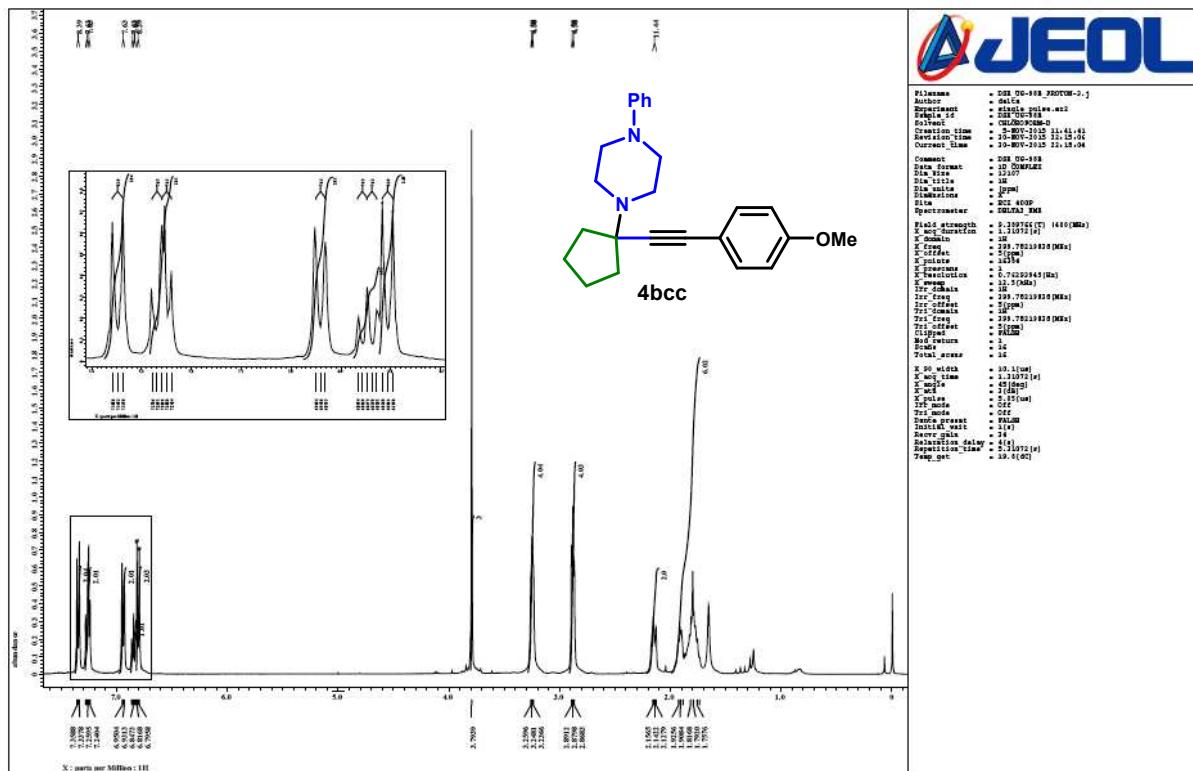


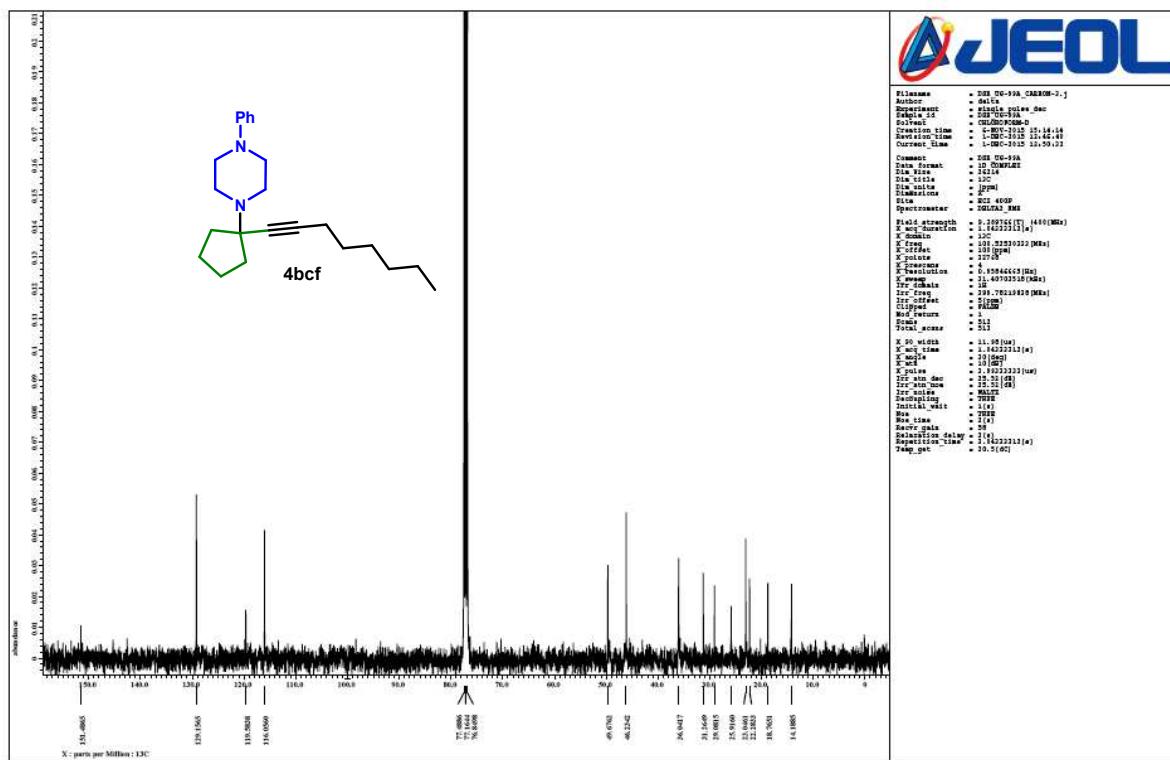
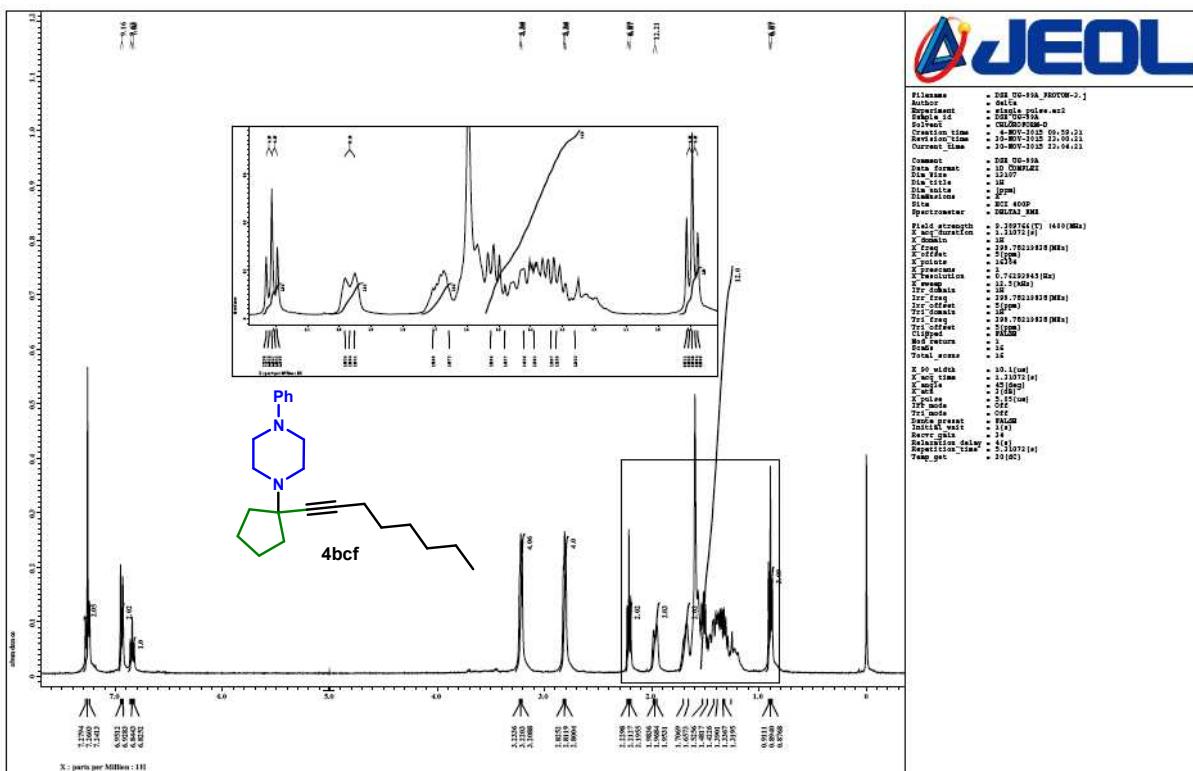




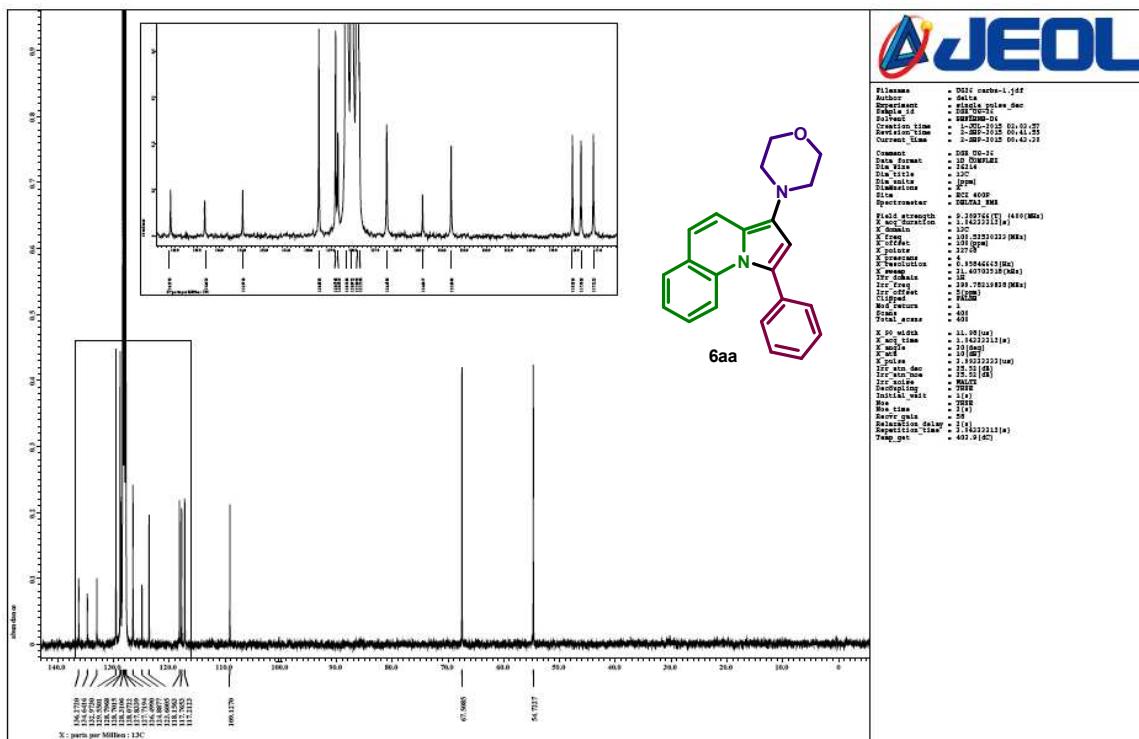
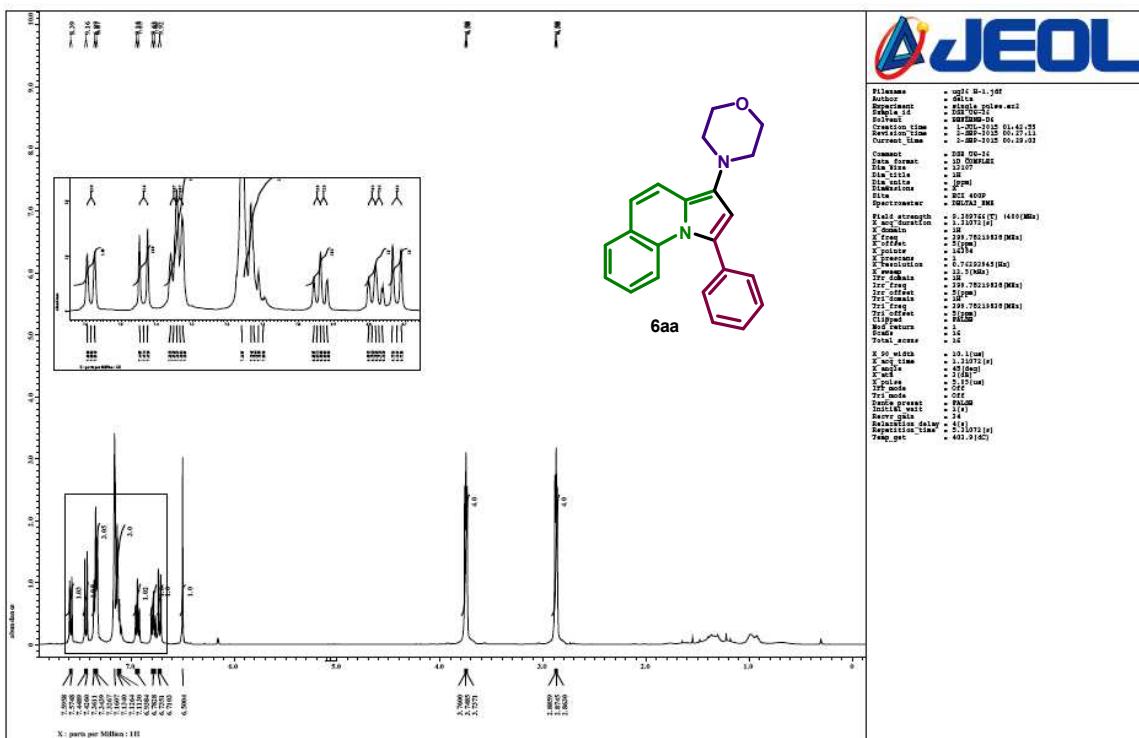


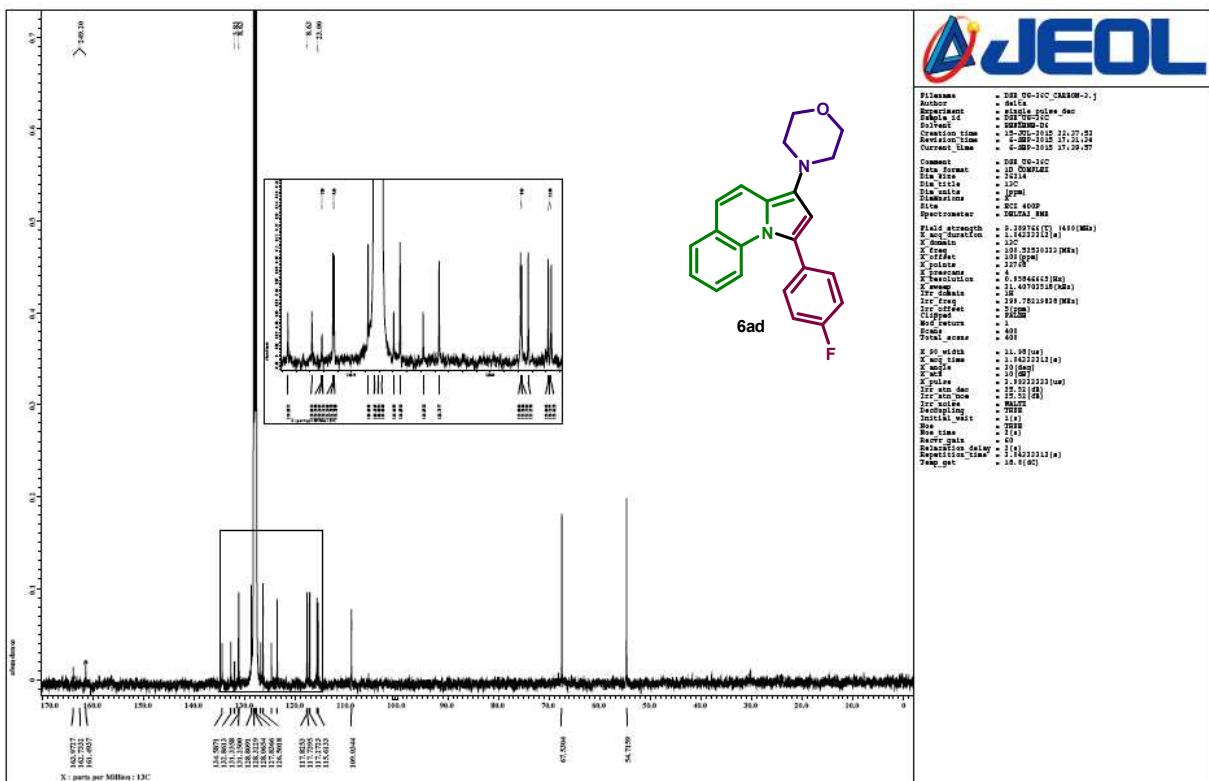
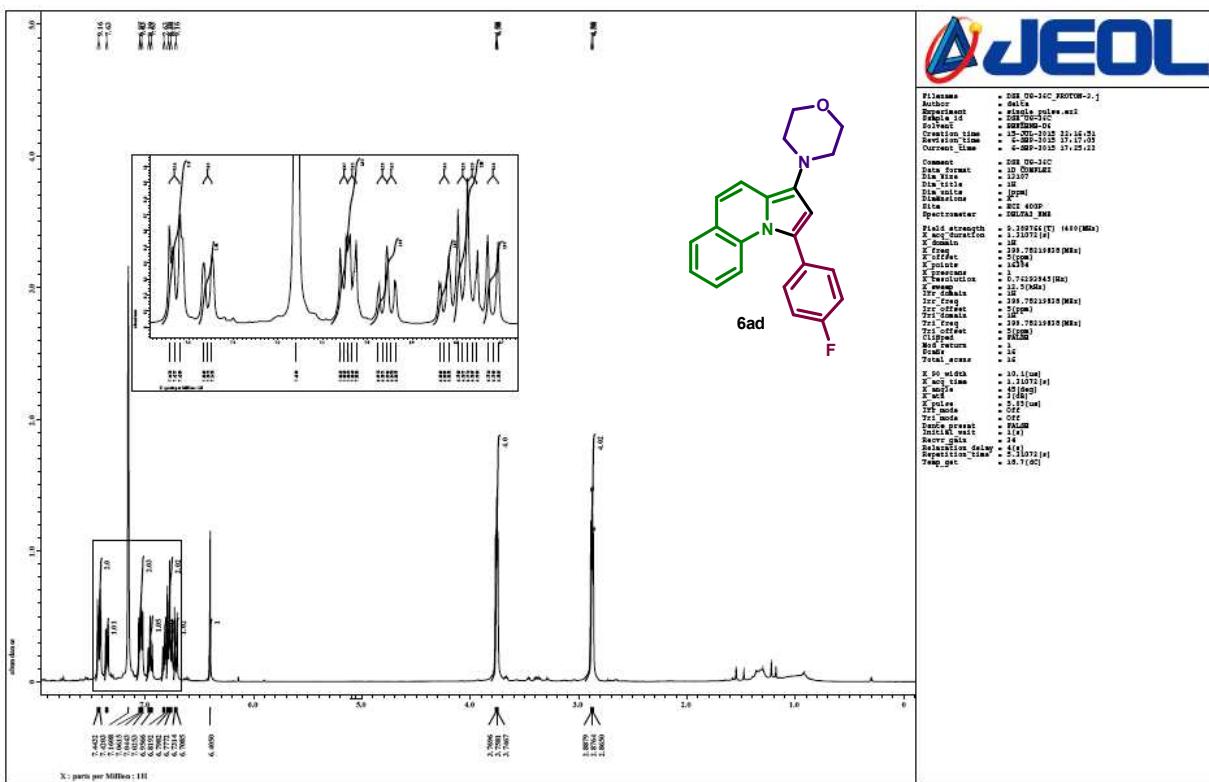


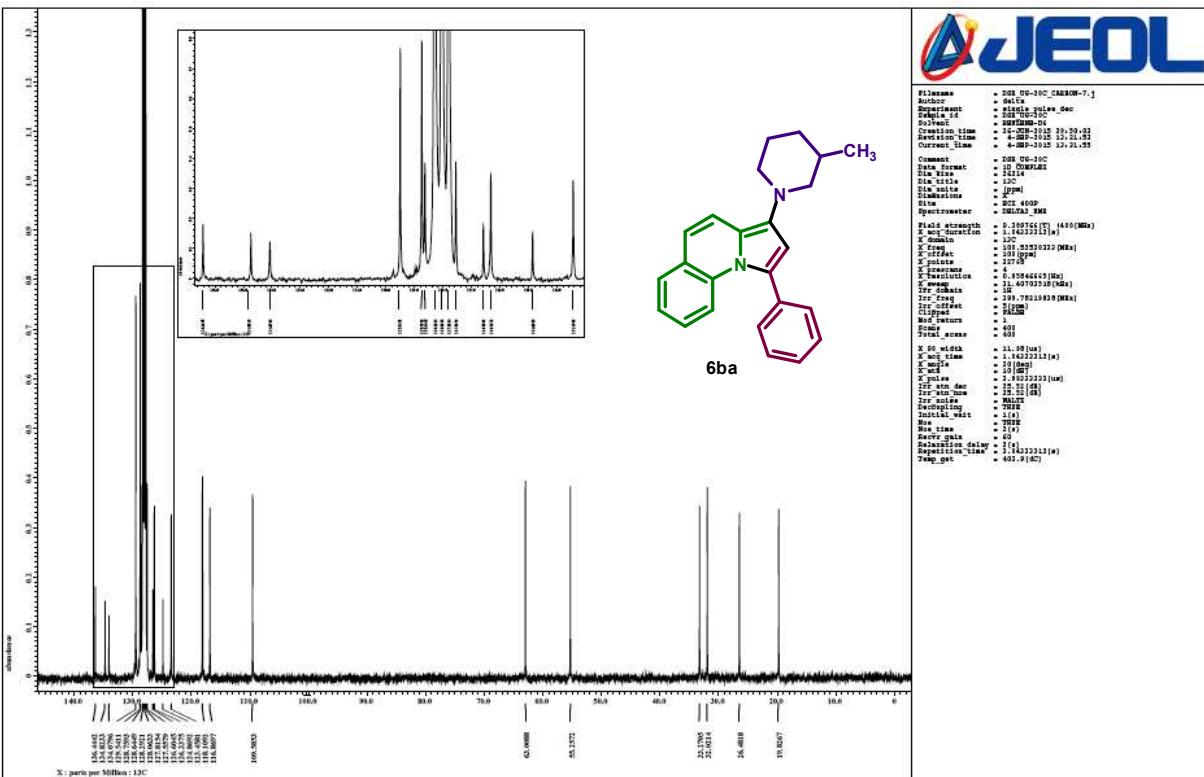
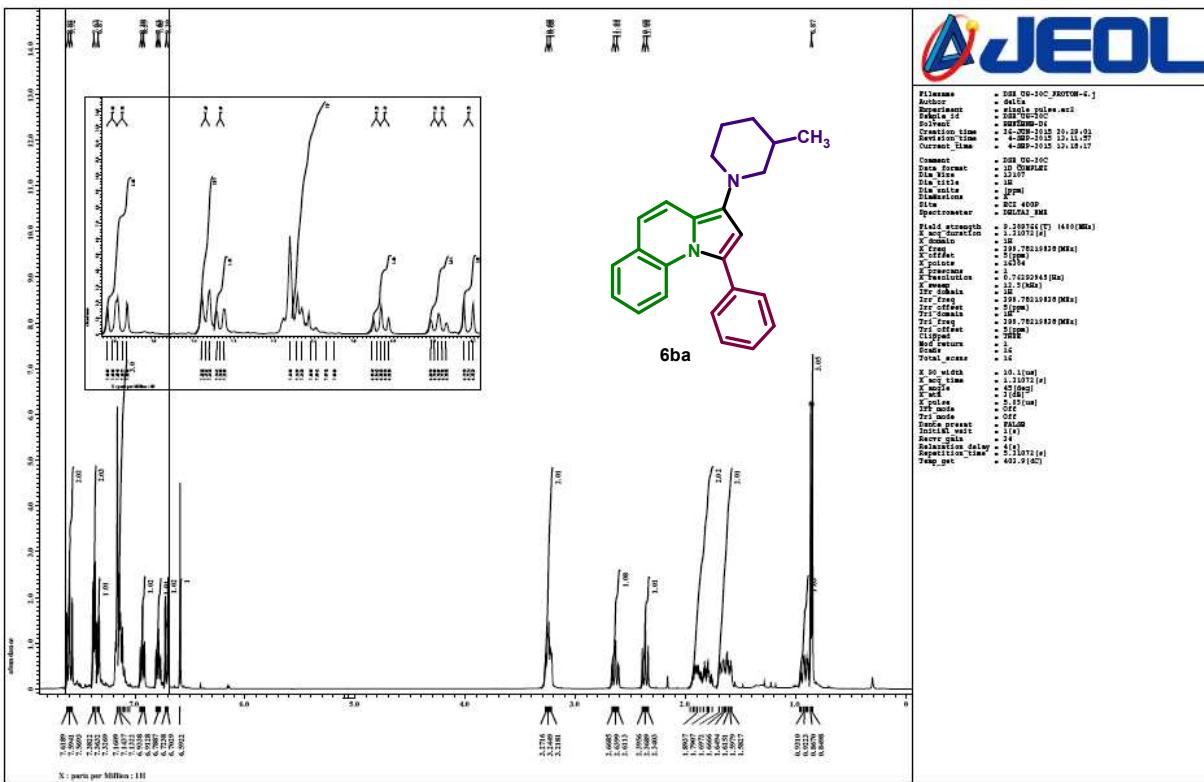


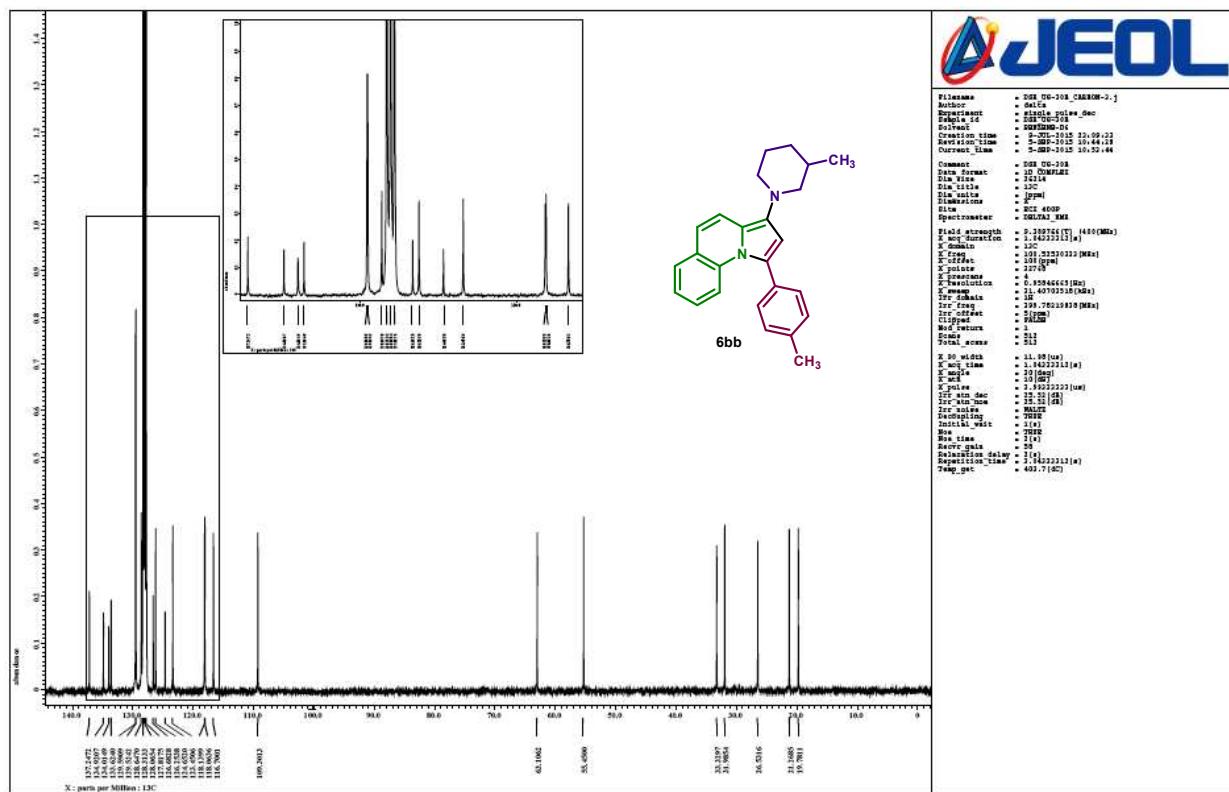
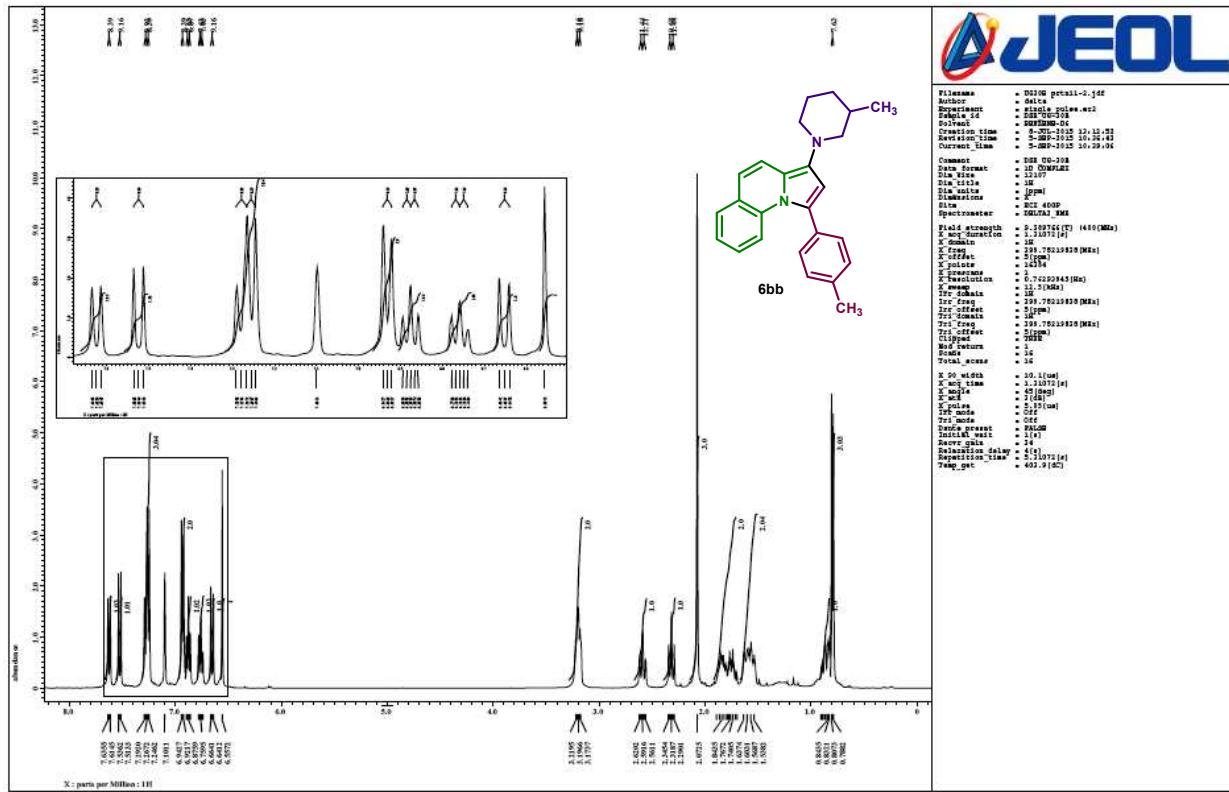


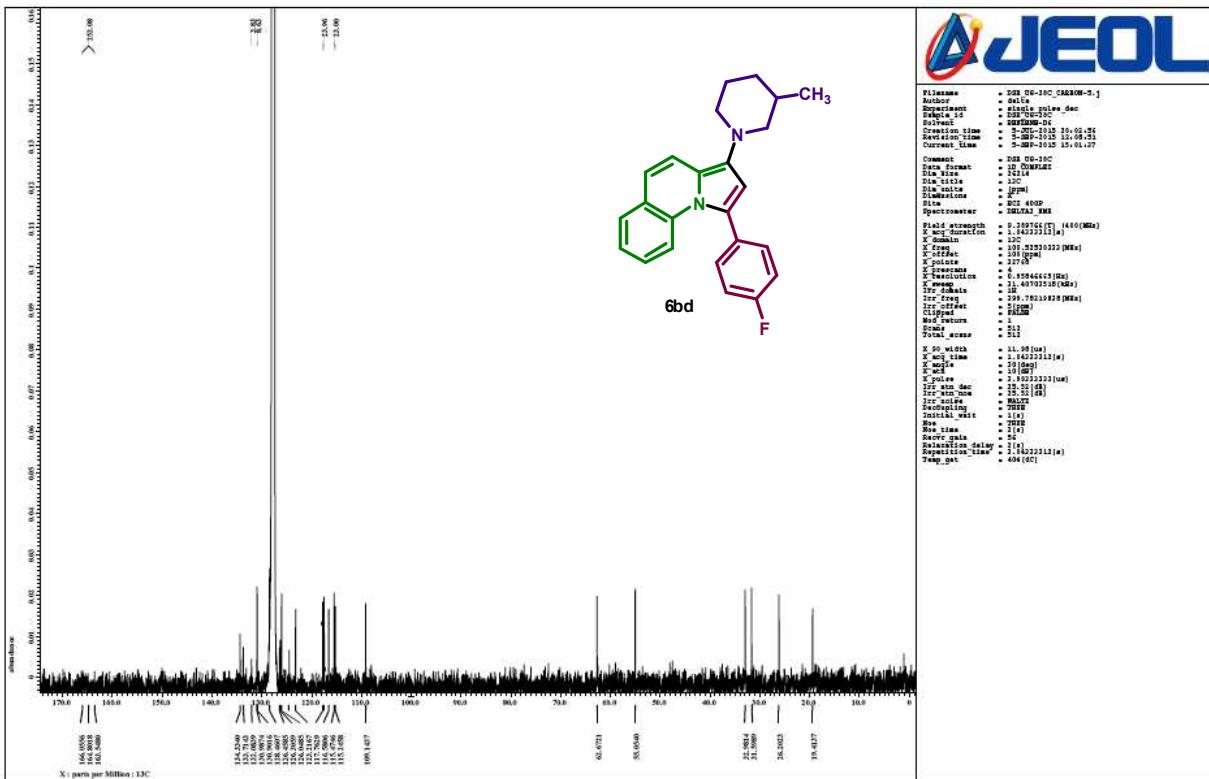
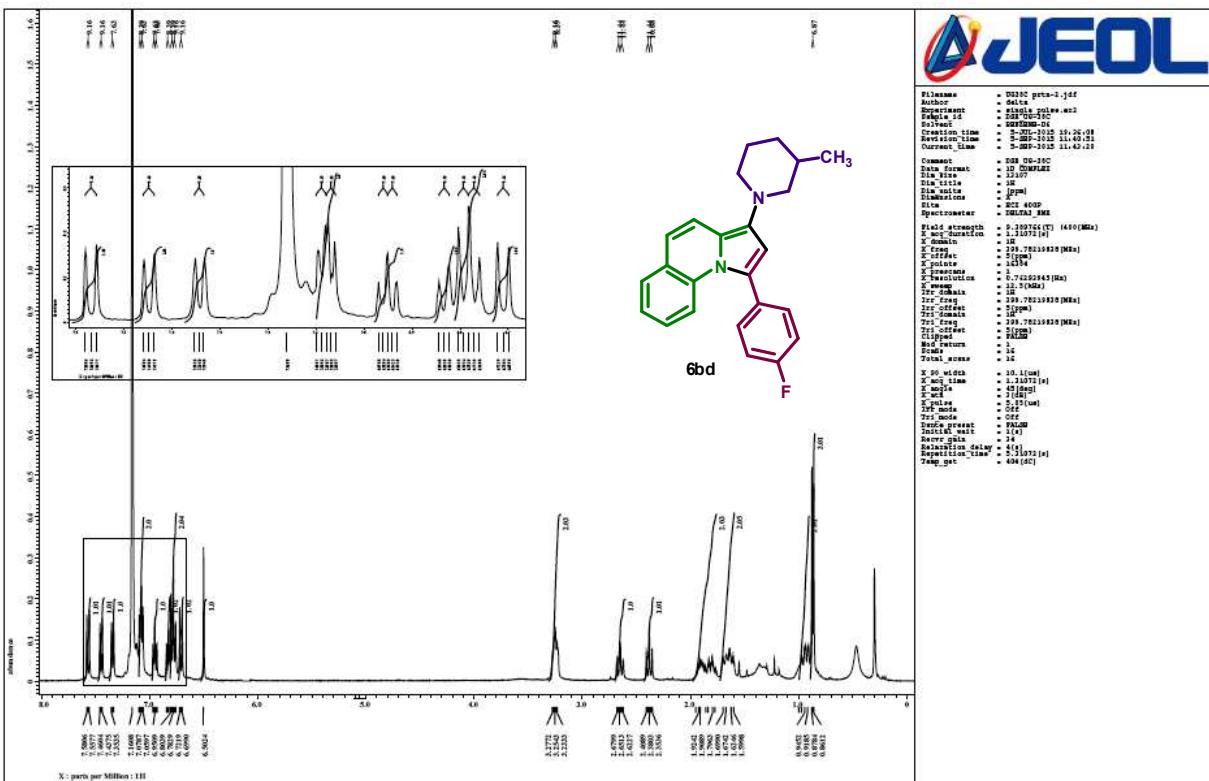
¹H NMR and ¹³C spectra of all pyrrolo[1,2-a]quinolines

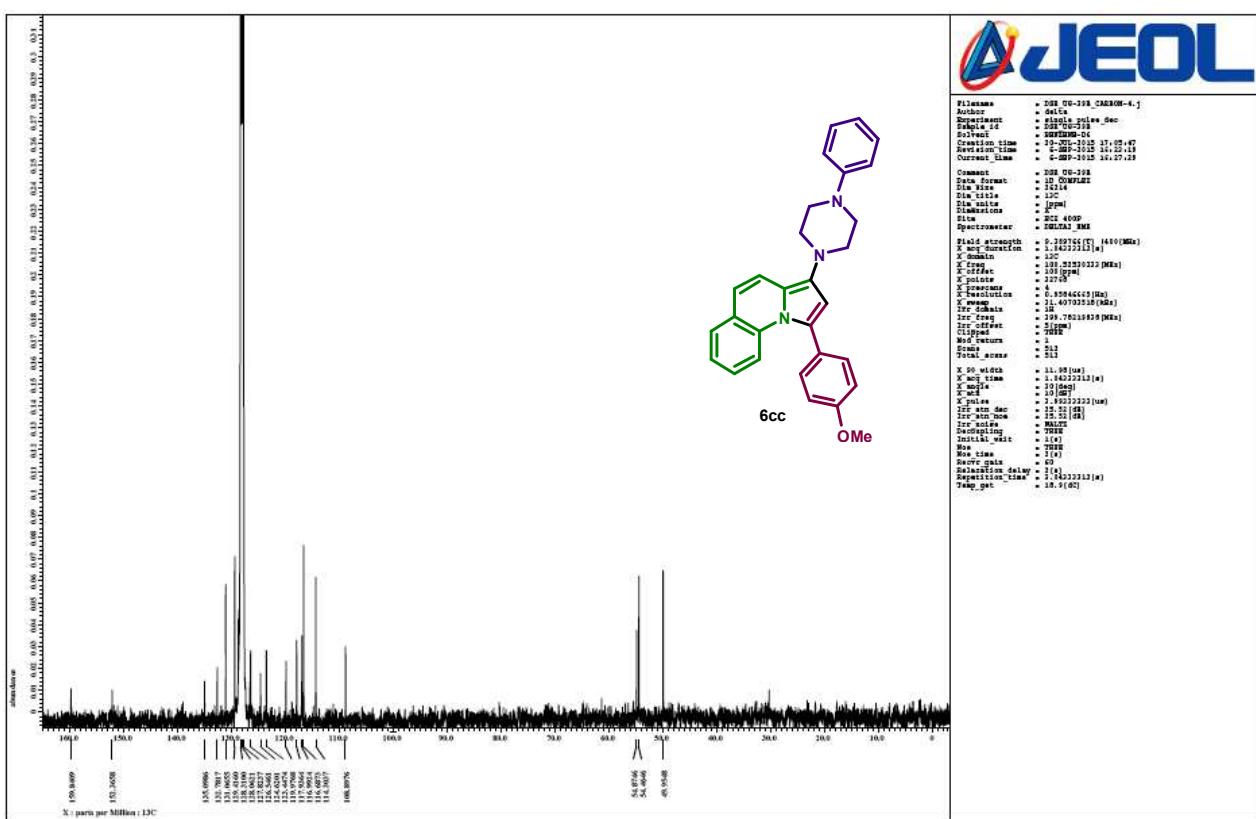
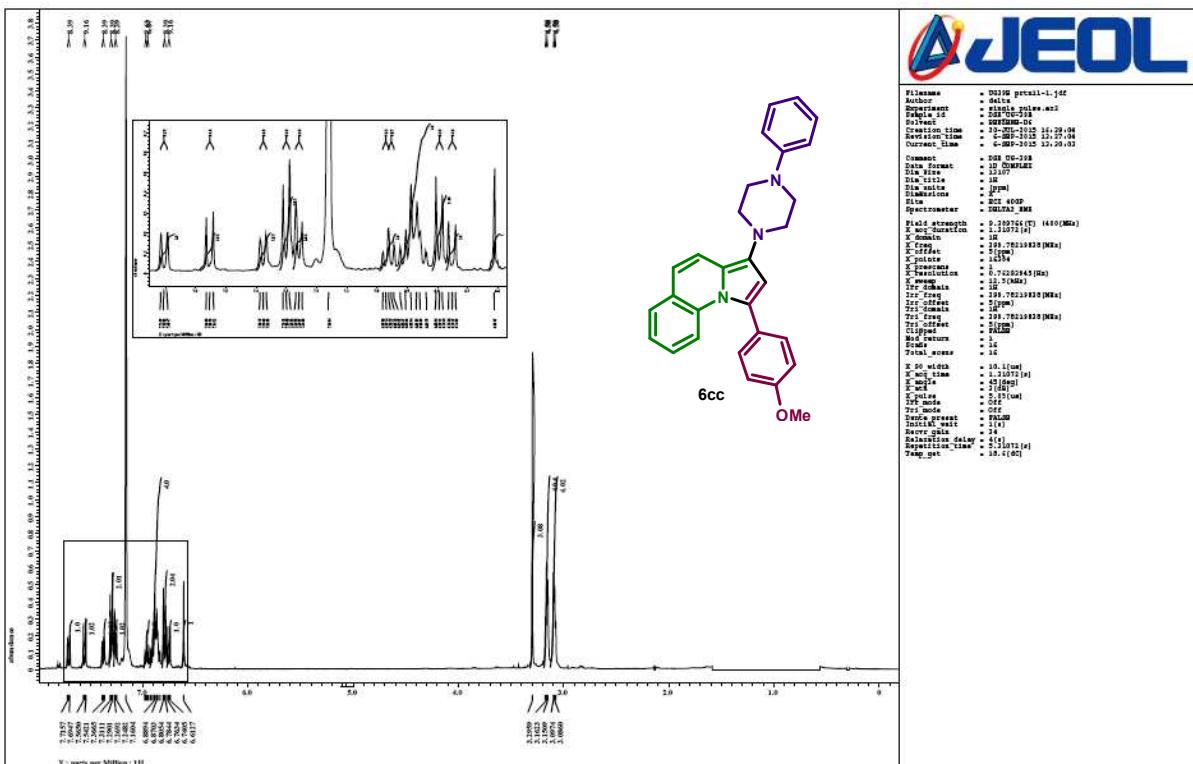


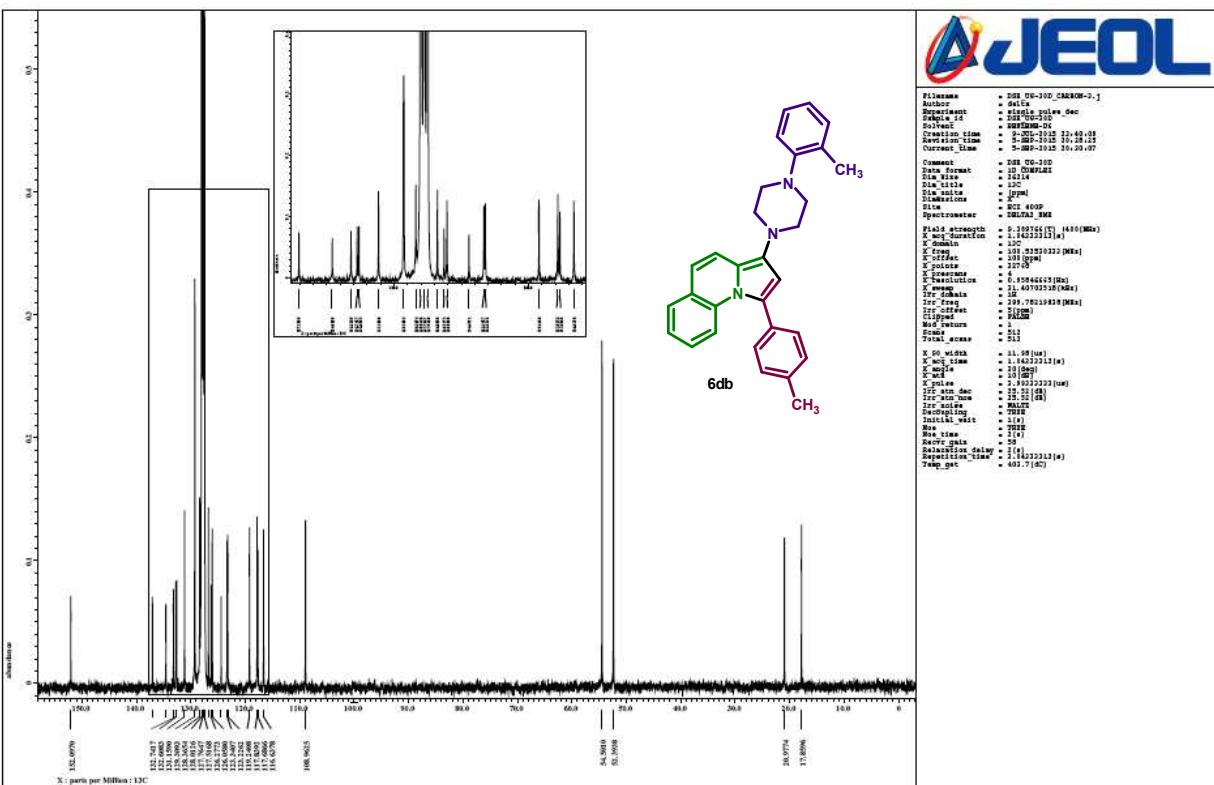
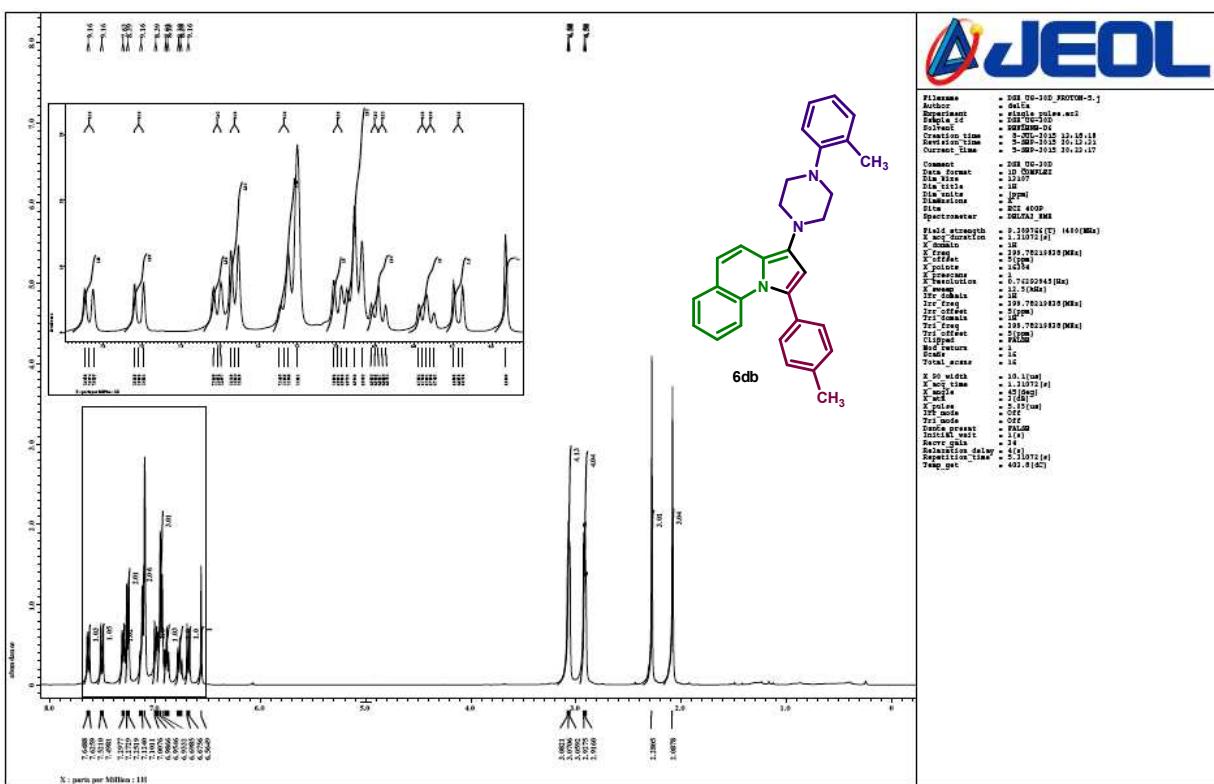


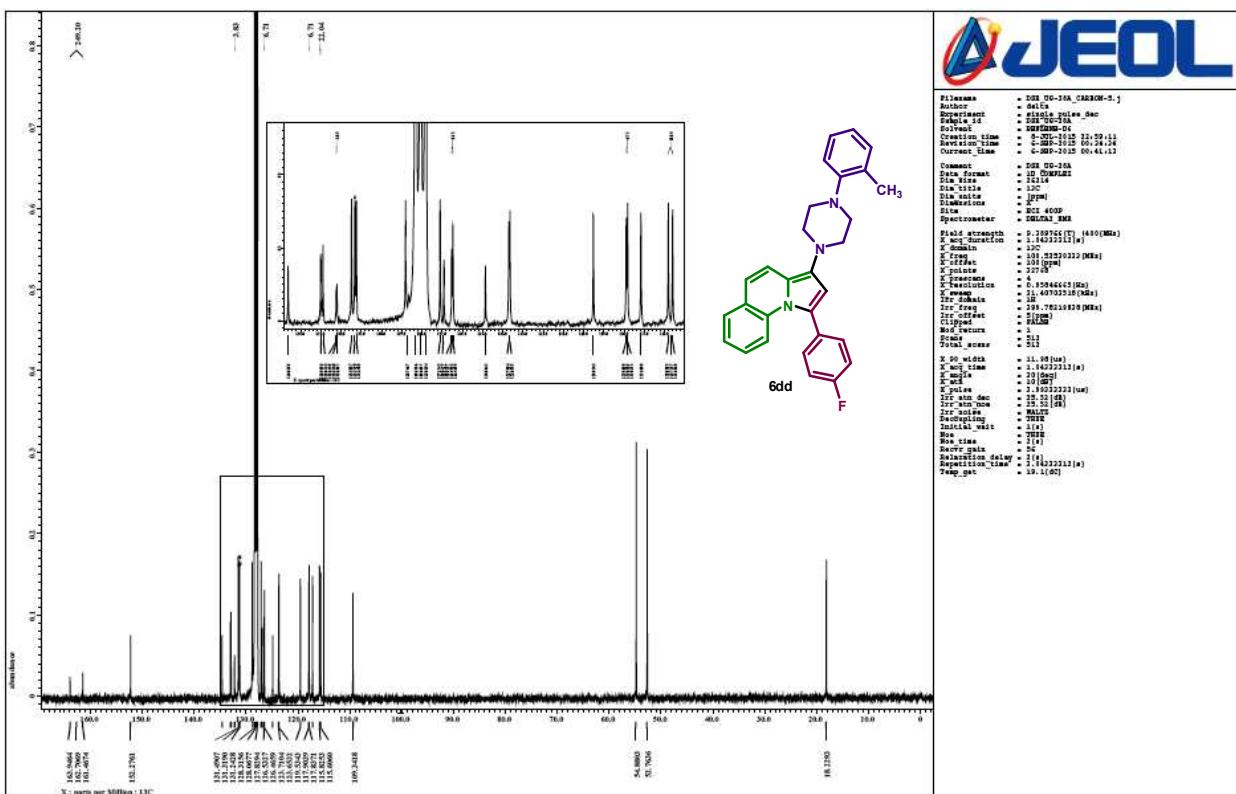
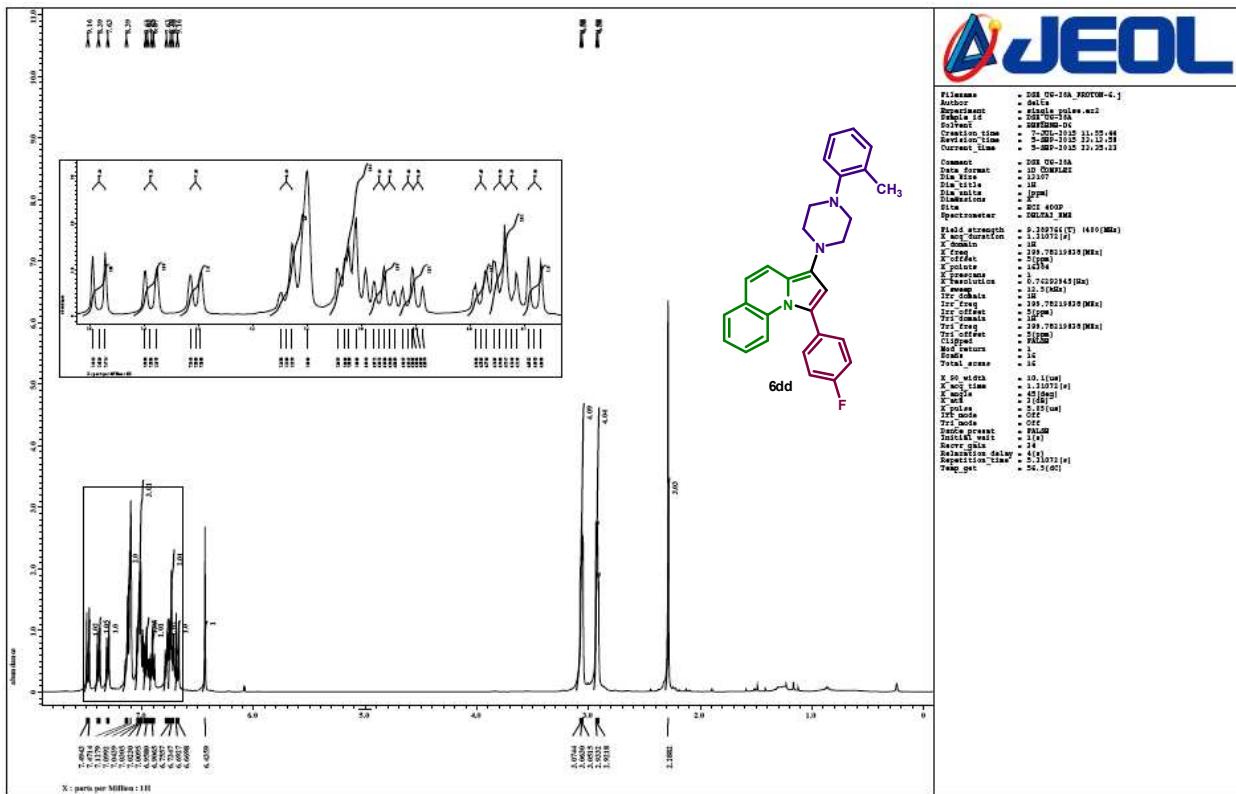


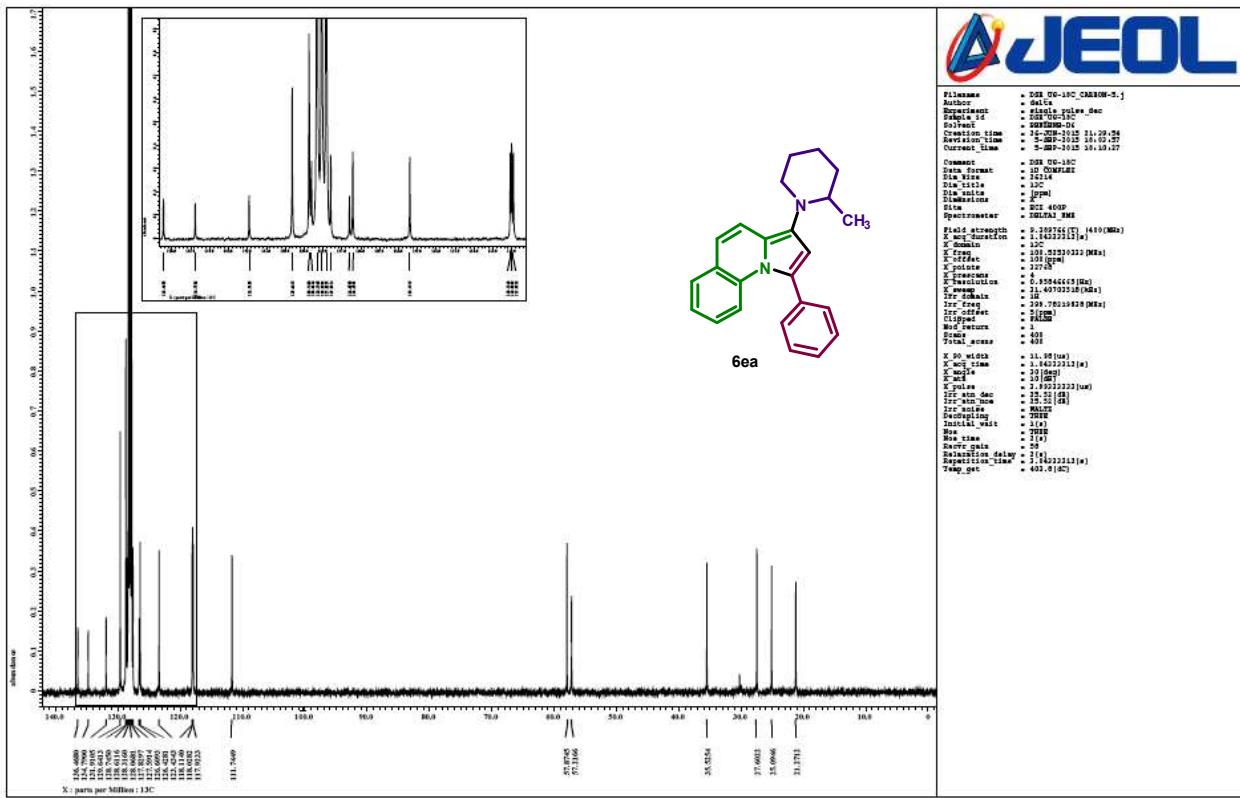
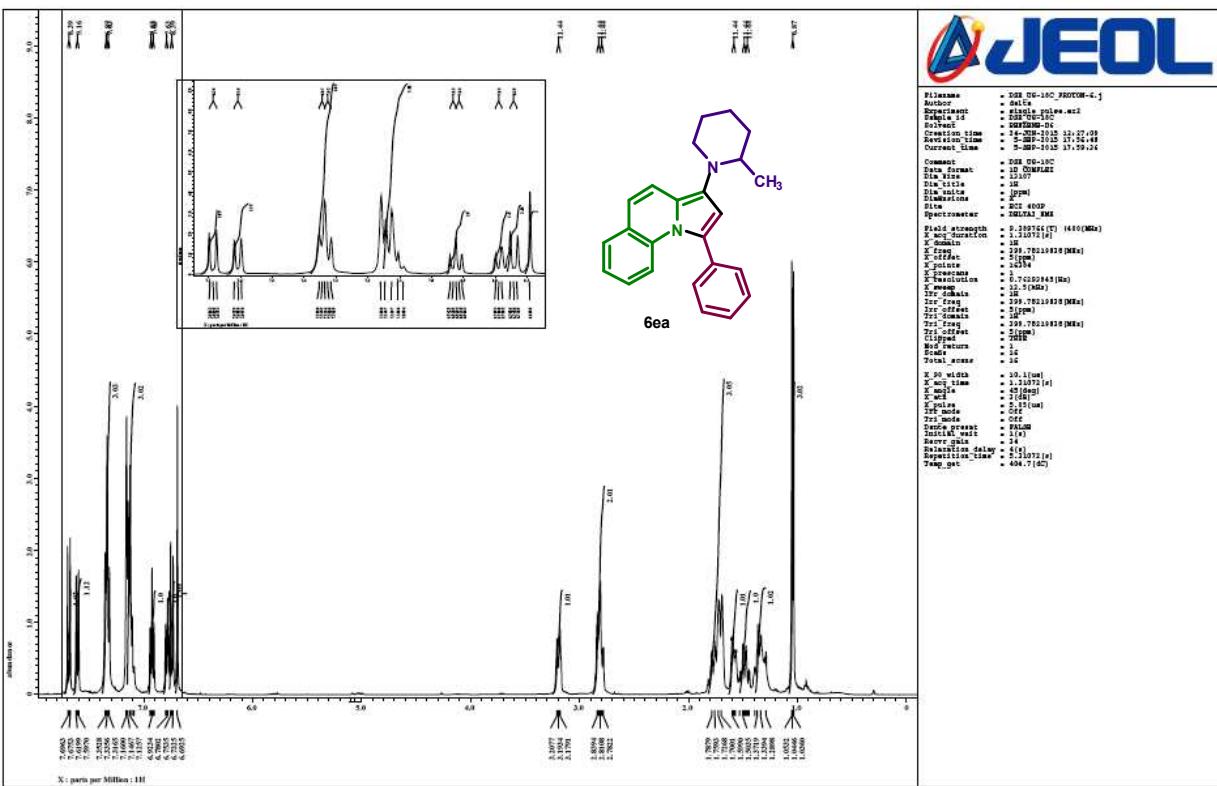


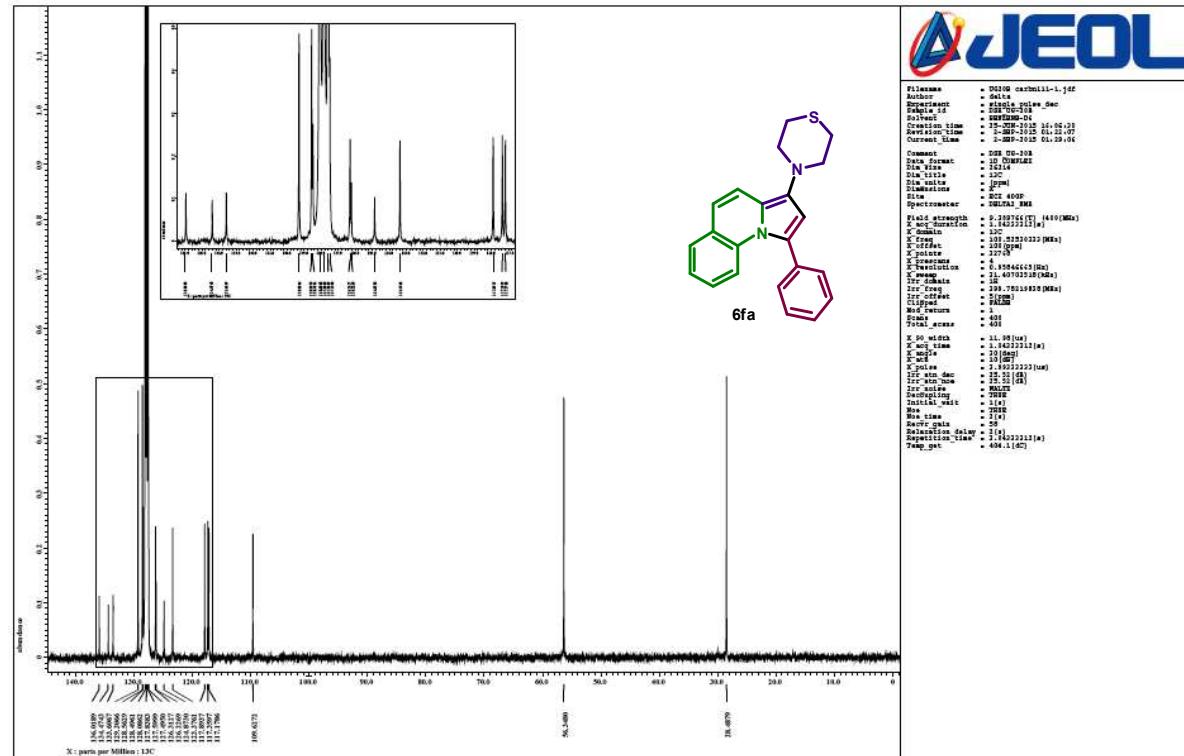
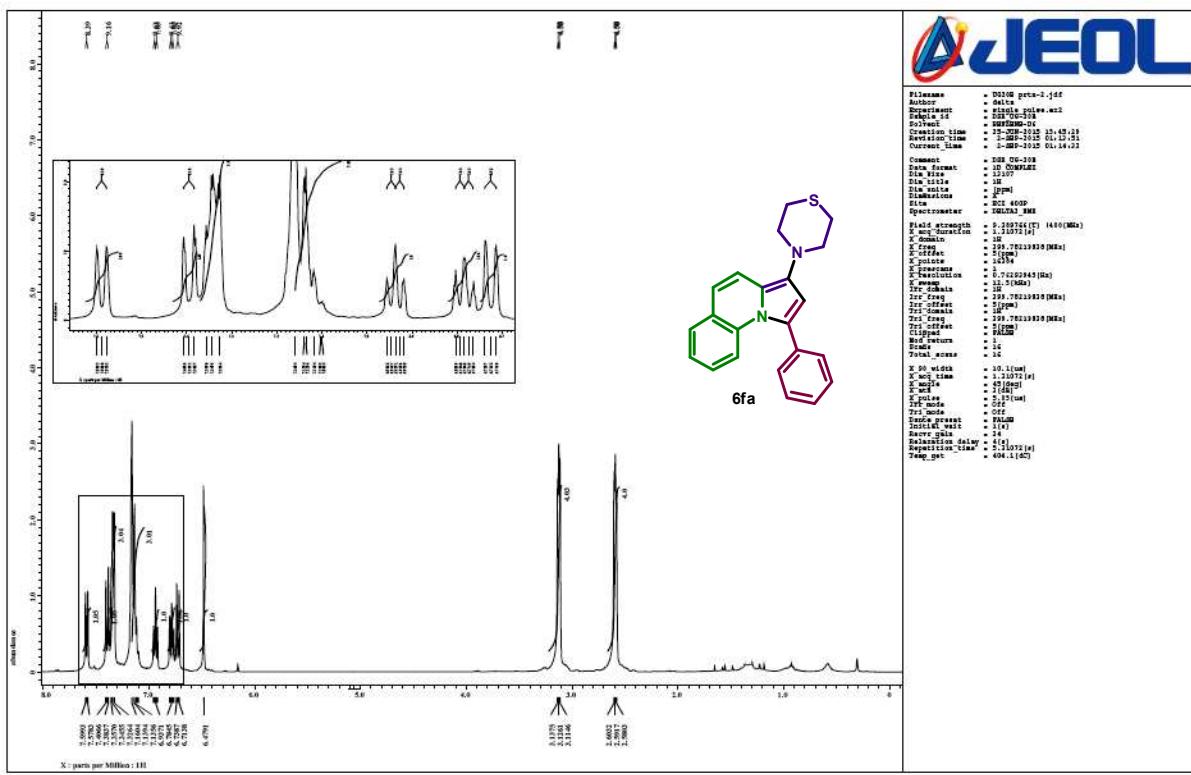


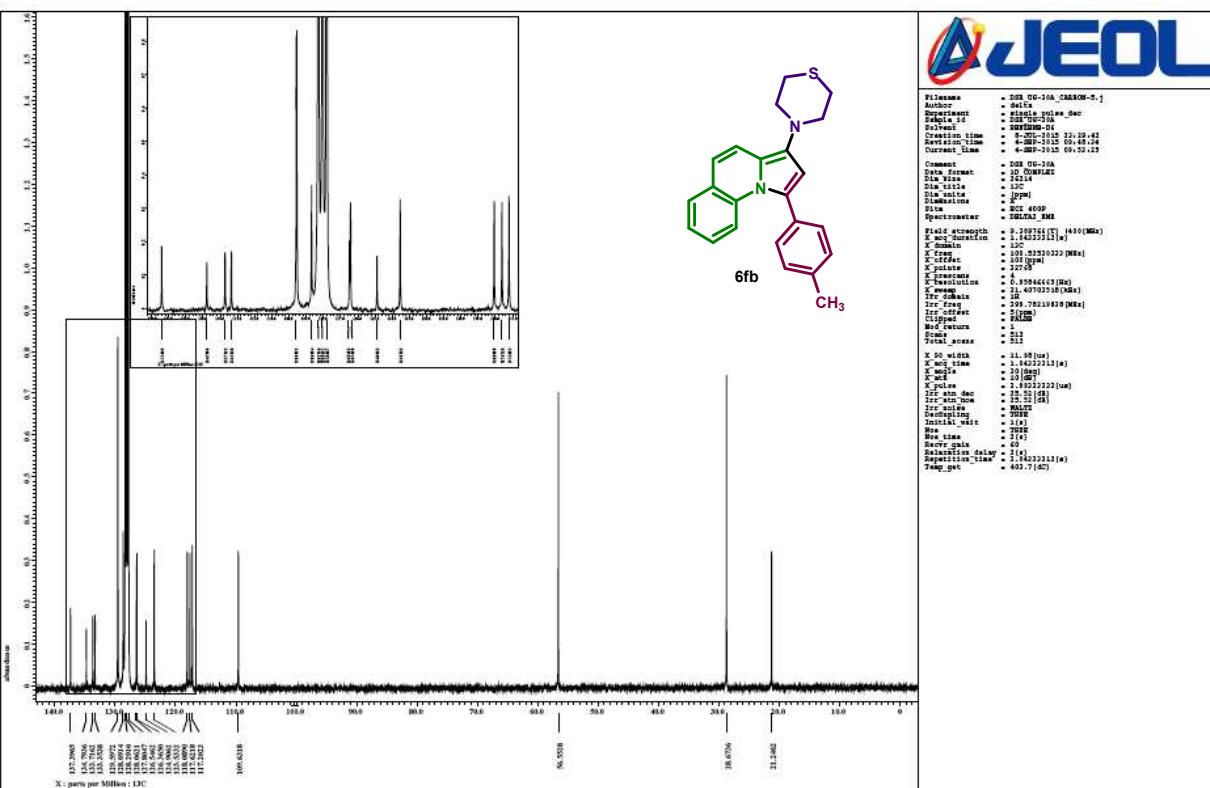
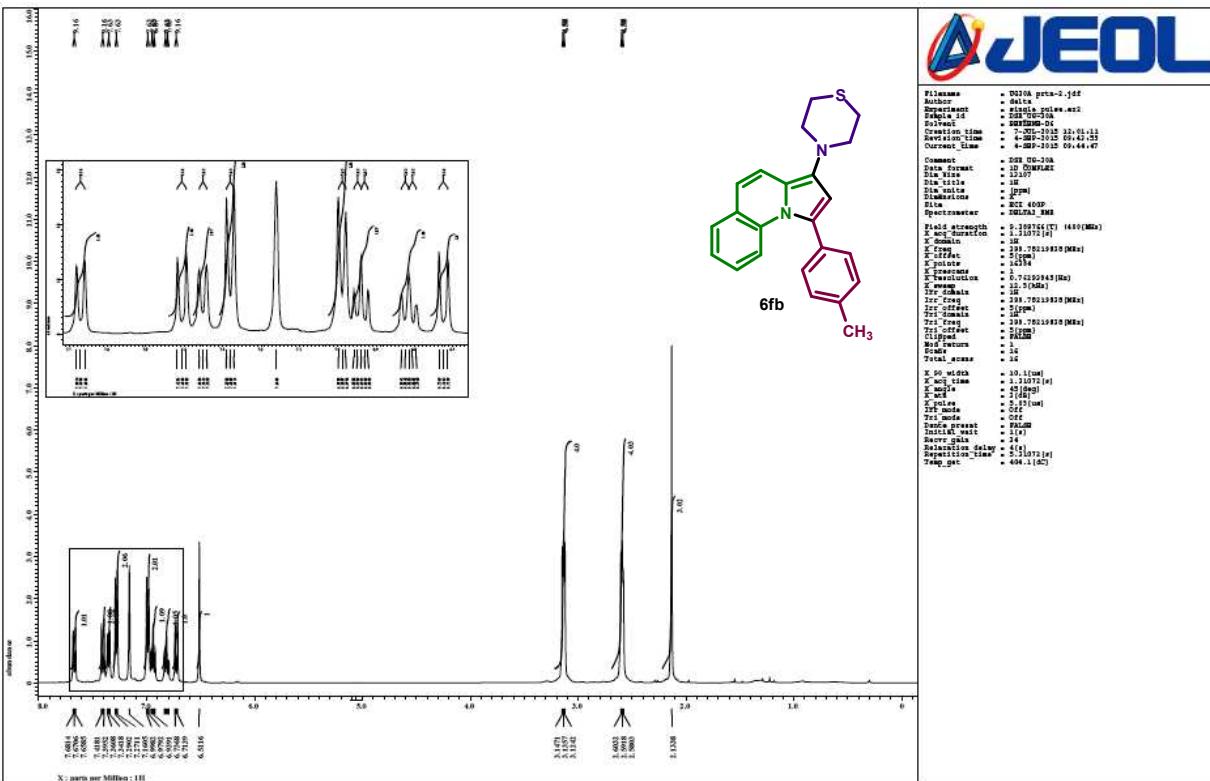


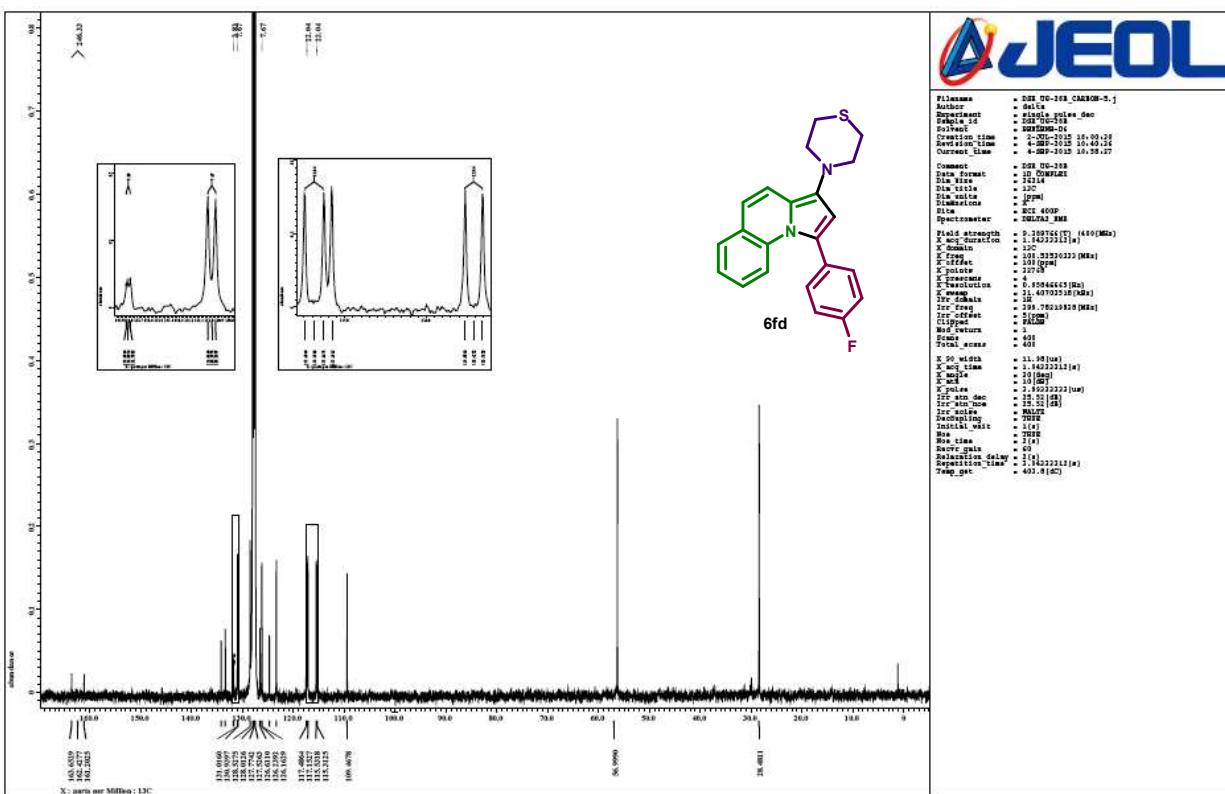
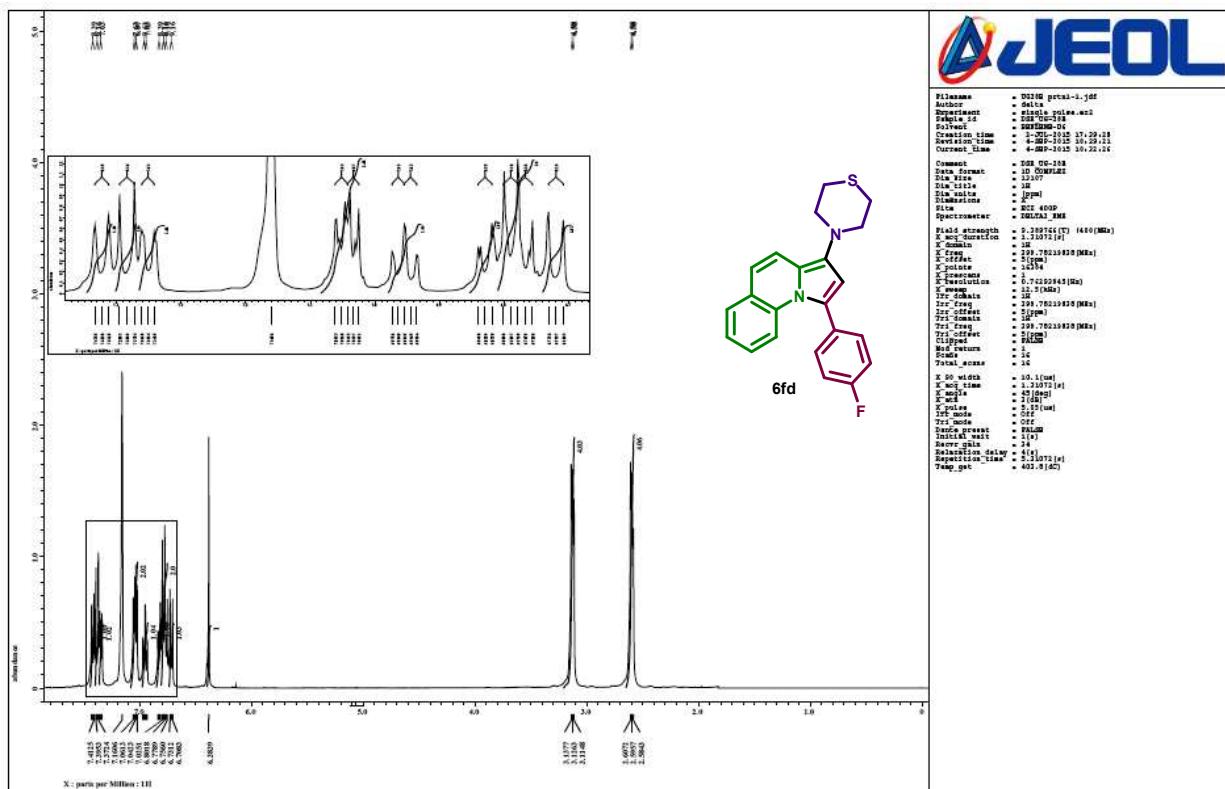


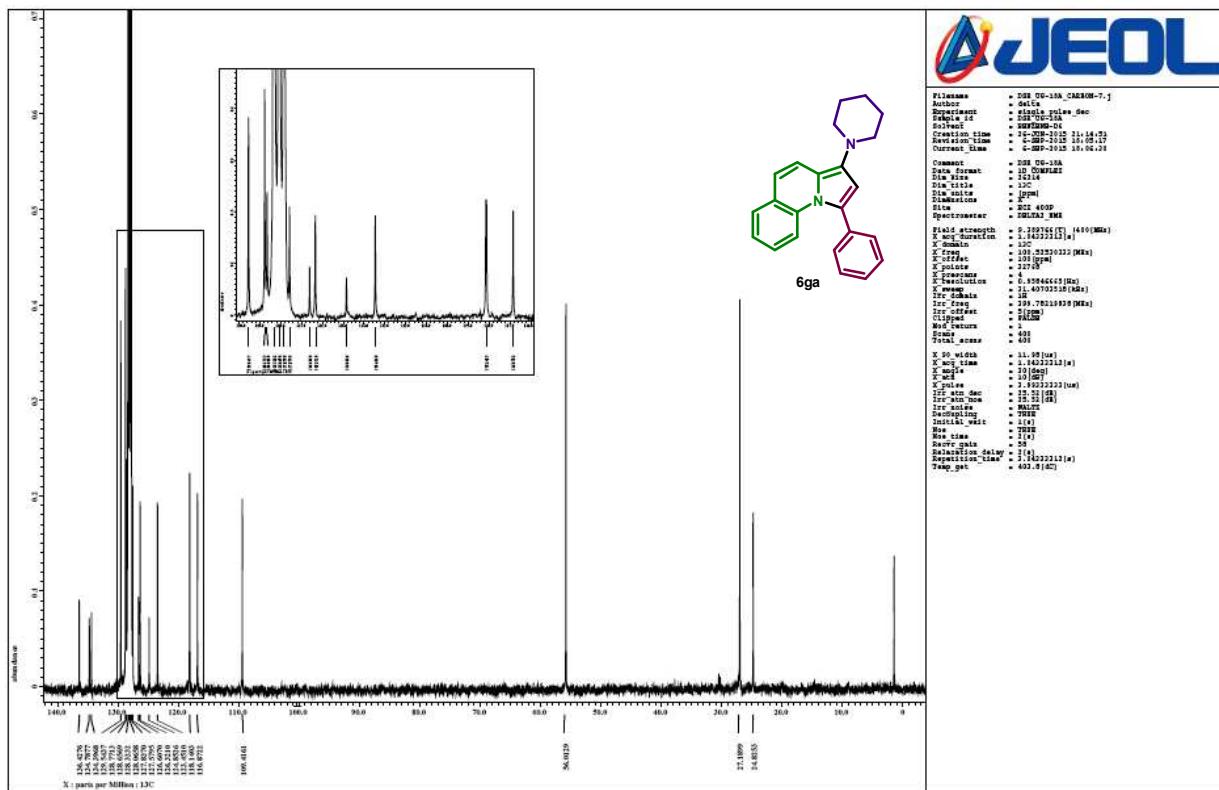
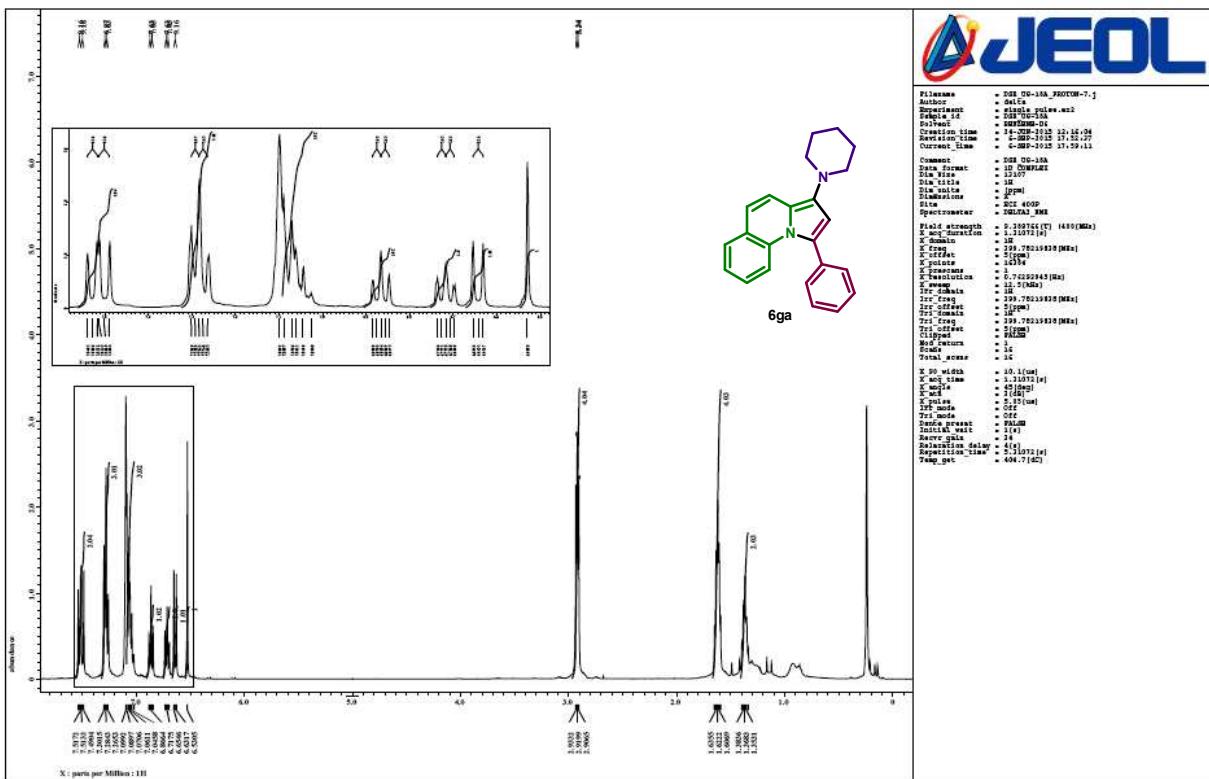


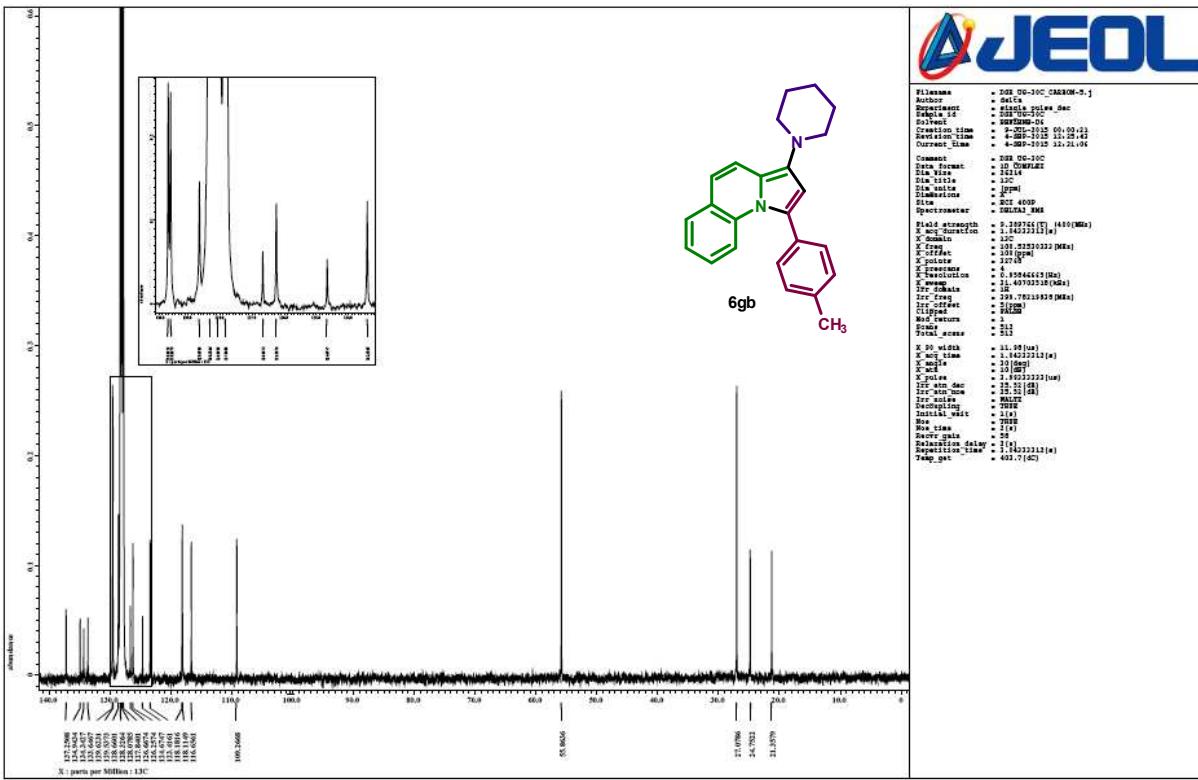
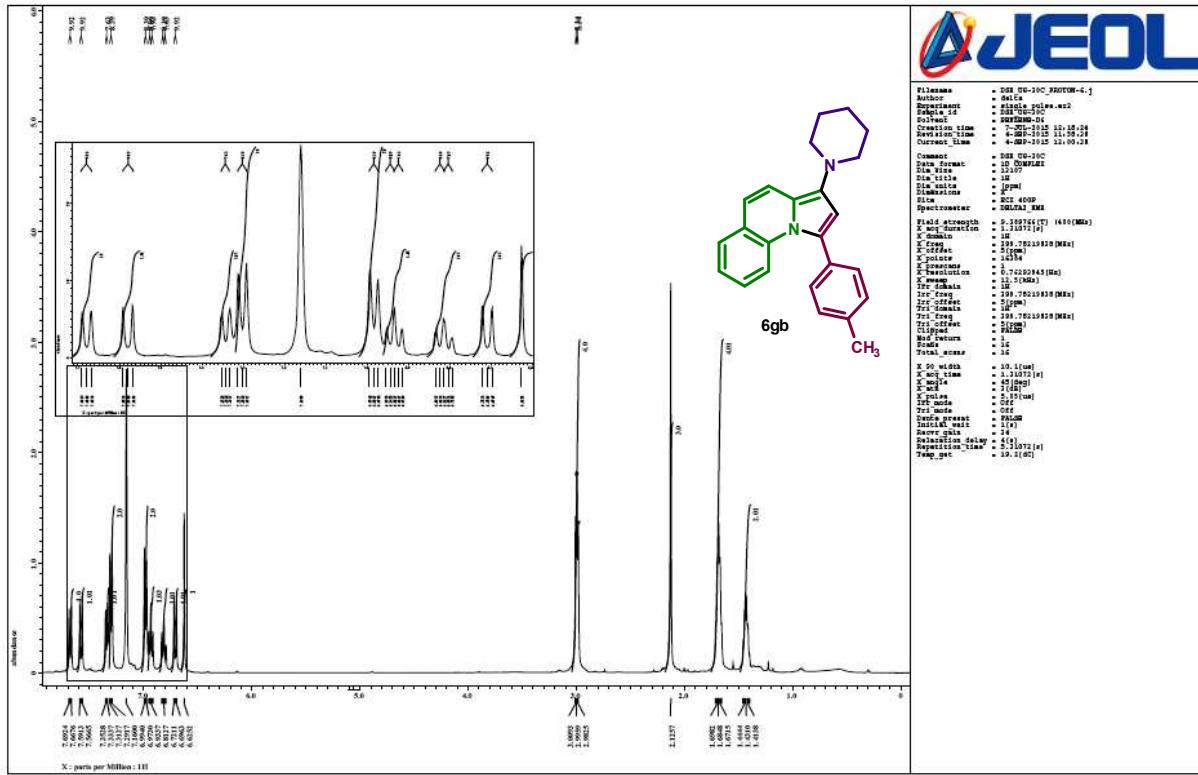


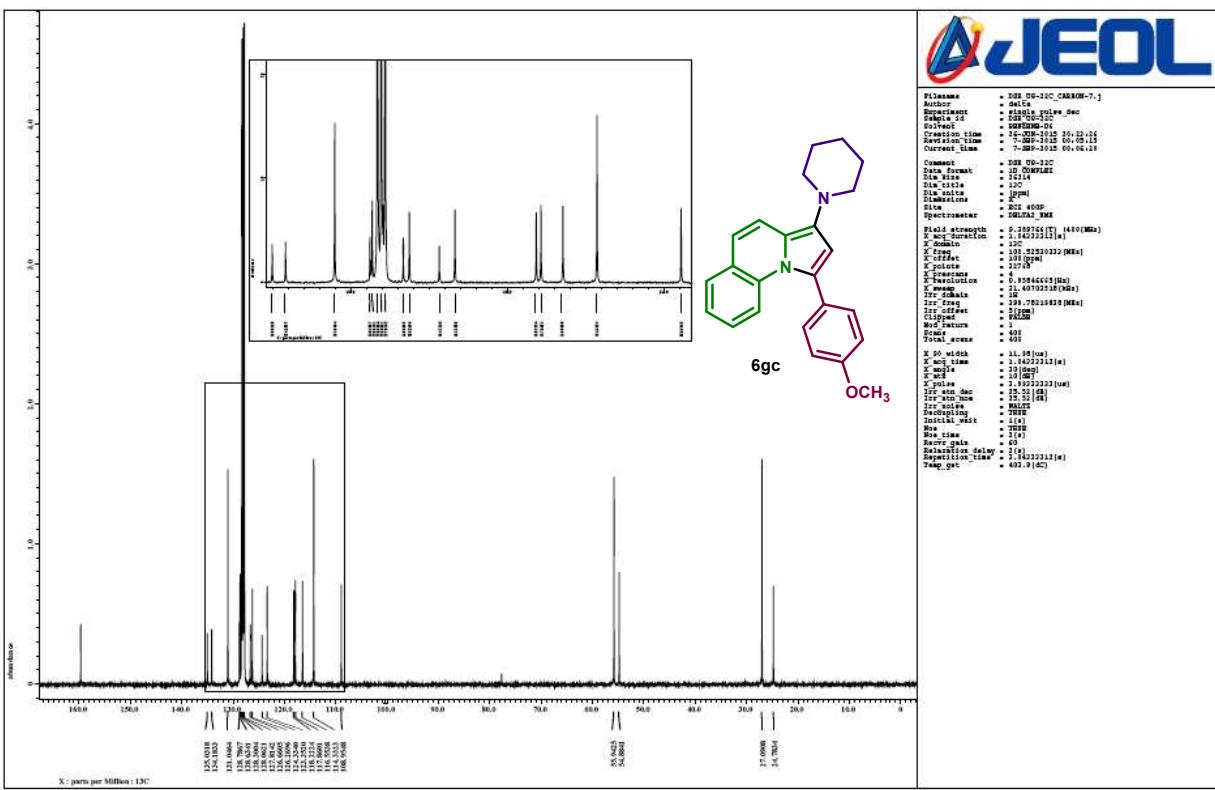
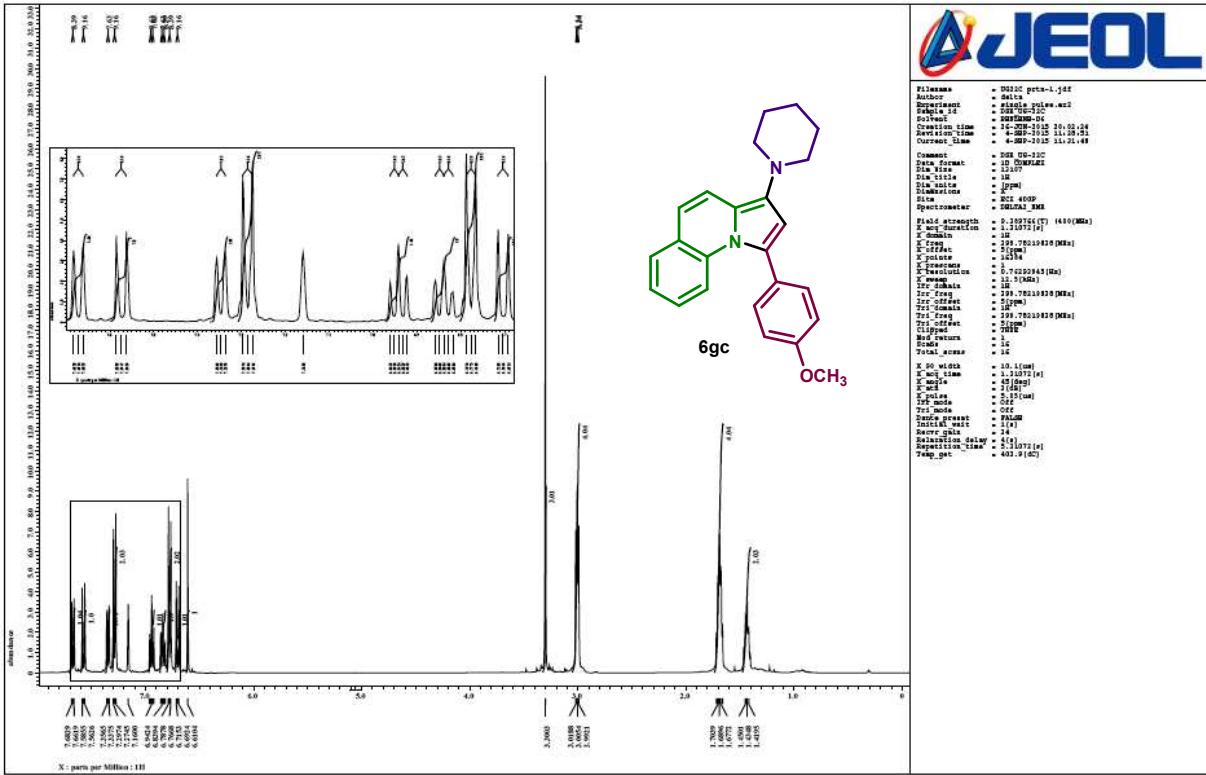


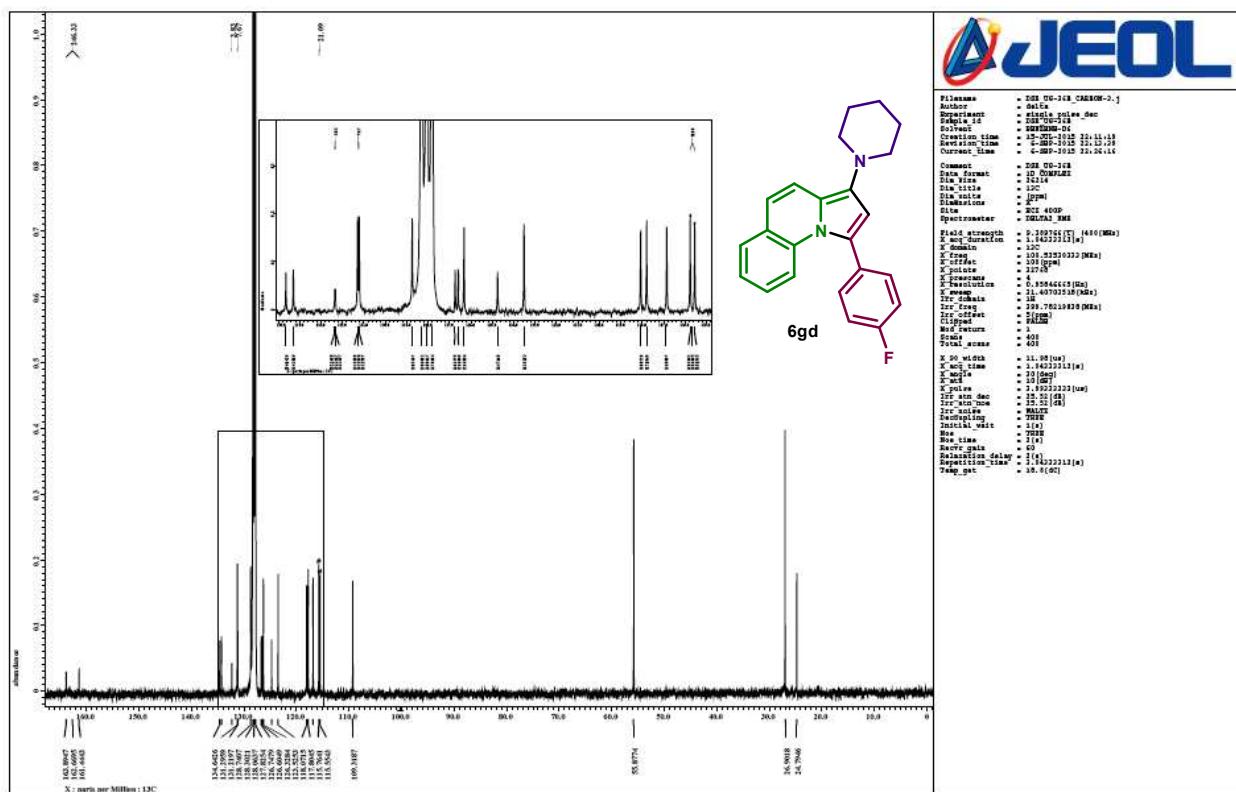
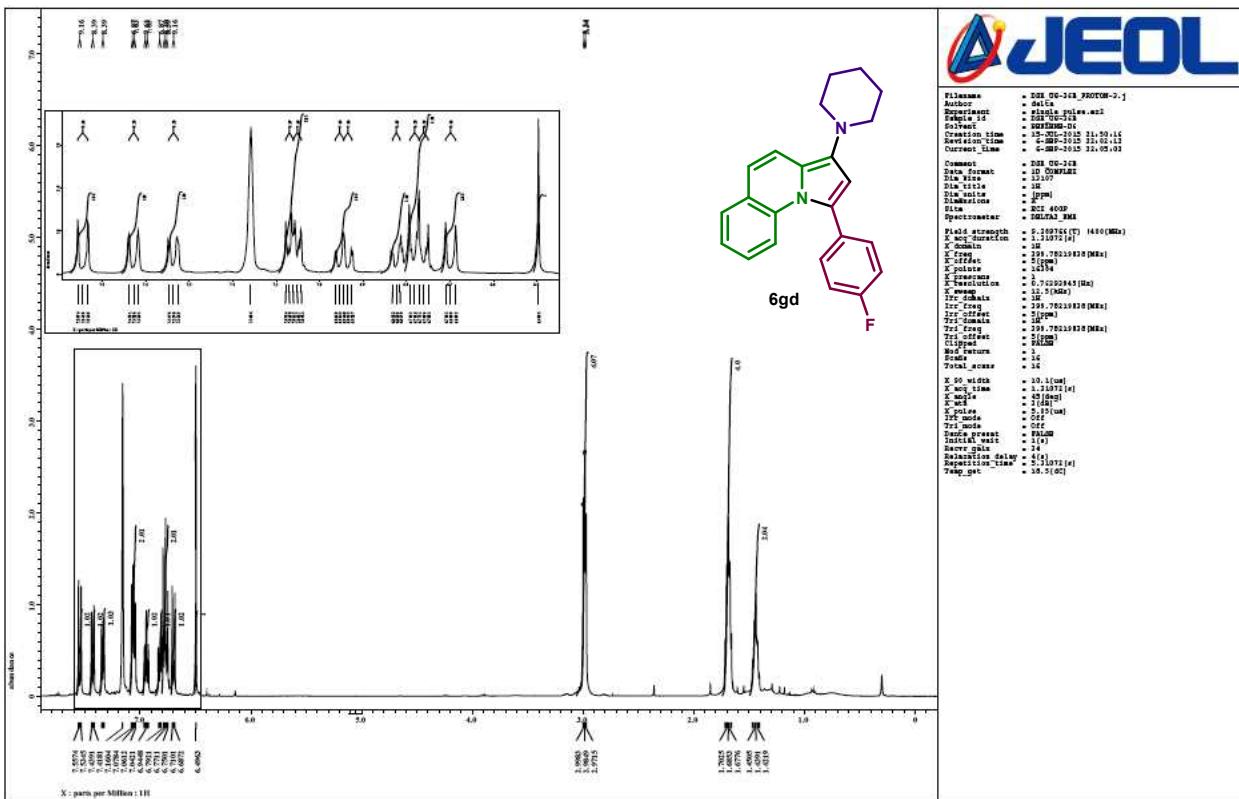


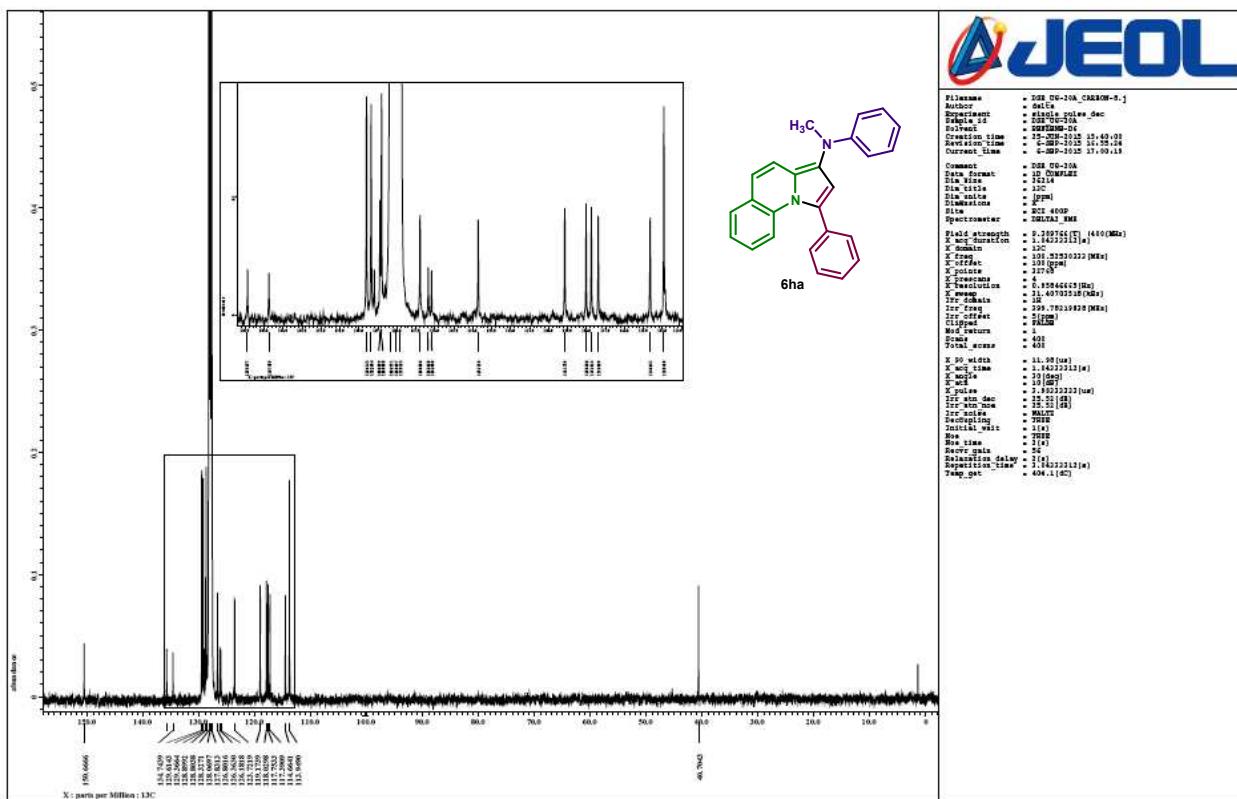
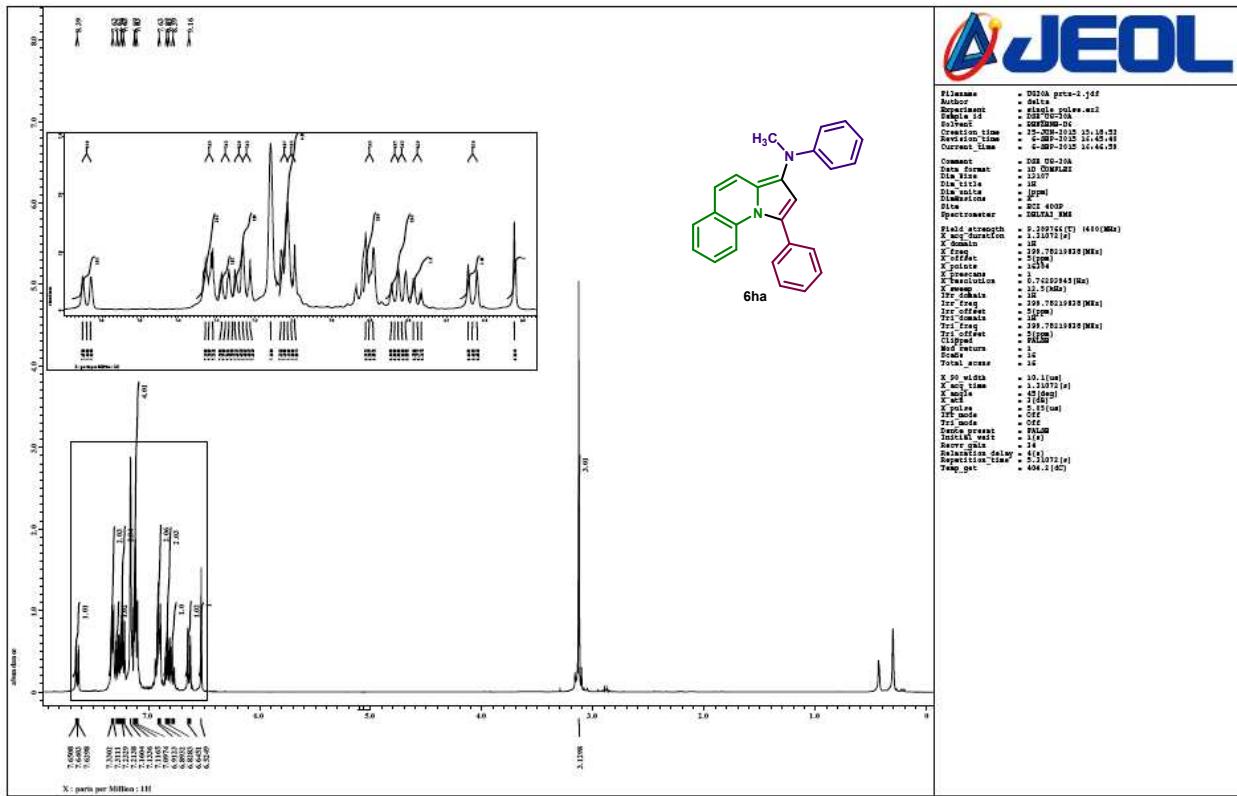












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