

SUPPORTING INFORMATION

Polystyrene supported N-phenylpiperazine-Cu(II) complex: An efficient and reusable catalyst for KA²-coupling reaction under solvent-free conditions

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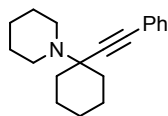
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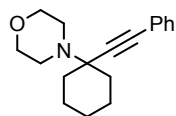
- **General Information**

All reagents were commercial grade materials and were used without further purification. All solvents were dried and distilled by standard methods. Purification of products was carried out by column chromatography using commercial column chromatography grade silica gel (60-120 mesh) using mixture of ethyl acetate and hexane as eluting agent. All known compounds were characterized and compared with the literature reports. The ^1H NMR and ^{13}C NMR spectra were obtained as solutions in CDCl_3 and TMS as the internal standard. IR spectra were obtained using KBr pallets. ESI-MS spectra were determined on a LCQ ion trap mass spectrometer equipped with an ESI source.

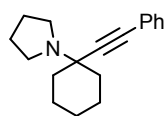
• **Analytical Data**



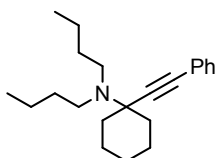
1-(1-(phenylethynyl)cyclohexyl)piperidine (8a): yellow solid, mp 51-54 °C. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.45-7.43 (m, 2H), 7.31-7.25 (m, 3H), 2.67 (s, 4H), 2.10 (d, *J* = 12.51 Hz, 2H), 1.74-1.71 (m, 2H), 1.63-1.58 (m, 7H), 1.52-1.44 (m, 4H), 1.25-1.23 (m, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 131.6, 128.0, 127.5, 123.6, 90.6, 86.0, 59.2, 47.0, 35.6, 26.5, 25.6, 24.6, 23.0; ESI-MS: (M+H) = 268.



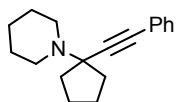
4-(1-(phenylethynyl)cyclohexyl)morpholine (8b): pale yellow solid, mp 93-95 °C. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.45-7.43 (m, 2H), 7.30-7.28 (m, 3H), 3.77 (d, *J* = 4.73 Hz, 4H), 2.73 (d, *J* = 4.57 Hz, 4H), 2.05 (m, 2H), 1.75-1.72 (m, 2H), 1.64-1.61 (m, 2H), 1.52-1.46 (m, 2H), 1.25 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 131.6, 128.1, 127.7, 123.3, 89.6, 86.5, 67.4, 58.9, 46.6, 35.3, 25.6, 22.7; ESI-MS: (M+H) = 270.



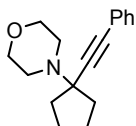
1-(1-(phenylethynyl)cyclohexyl)pyrrolidine (8f): yellow liquid. ¹H NMR (400 MHz, CDCl₃, TMS) δ 7.44-7.42 (m, 2H), 7.30-7.26 (m, 3H), 2.80 (t, *J* = 6.71 Hz, 4H), 2.04 (d, *J* = 11.74 Hz, 2H), 1.80-1.78 (m, 4H), 1.71-1.61 (m, 6H), 1.56-1.50 (m, 2H); ¹³C NMR (100 MHz, CDCl₃) δ 131.6, 128.0, 127.5, 123.5, 90.2, 86.0, 59.2, 46.9, 37.7, 25.6, 23.4, 22.9; ESI-MS: (M+H) = 254.



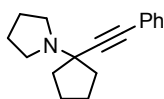
N,N-dibutyl-1-(phenylethynyl)cyclohexanamine (8g): yellow liquid. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.42-7.40 (m, 2H), 7.30-7.25 (m, 3H), 2.64 (t, $J = 8.06$ Hz, 4H), 2.05 (d, $J = 11.86$ Hz, 2H) 1.69-1.59 (m, 4H), 1.54-1.44 (m, 6H), 1.33-1.24 (m, 6H), 0.92 (t, $J = 7.33$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 131.5, 128.1, 127.4, 124.0, 93.0, 84.8, 59.6, 50.0, 37.1, 32.2, 25.7, 23.2, 20.7, 14.1; ESI-MS: (M+H) = 312.



1-(1-(phenylethynyl)cyclopentyl)piperidine (9a): yellow liquid. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.43-7.41 (m, 2H), 7.30-7.25 (m, 3H), 2.65 (s, 4H), 2.15-2.11 (m, 2H), 1.90-1.85 (m, 2H), 1.81-1.71 (m, 4H), 1.65-1.60 (m, 4H), 1.45 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 131.8, 128.3, 127.8, 124.0, 91.7, 85.3, 67.7, 50.5, 40.1, 26.5, 24.6, 23.6; ESI-MS: (M+H) = 254.

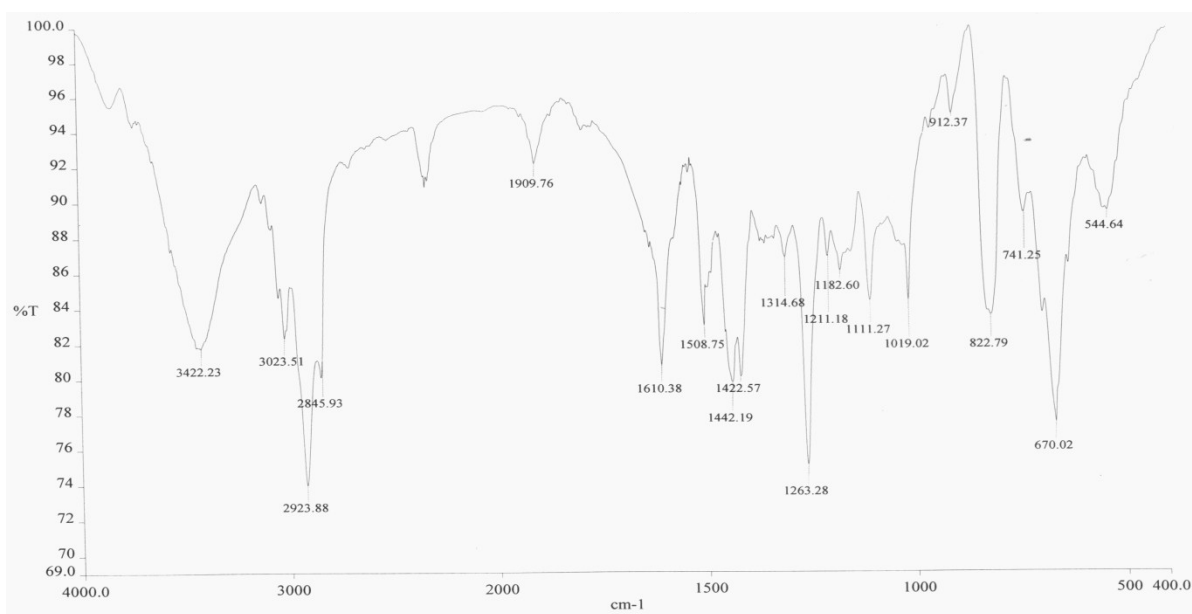


4-(1-(phenylethynyl)cyclopentyl)morpholine (9b): yellow solid, mp 78-80 °C. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.43-7.41 (m, 2H), 7.31-7.28 (m, 3H), 3.77 (t, $J = 4.73$ Hz, 4H), 2.72 (t, $J = 4.88$ Hz, 4H), 2.12-2.08 (m, 2H), 1.91-1.86 (m, 2H), 1.82-1.70 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 131.7, 128.2, 127.7, 123.4, 90.4, 85.6, 67.2, 49.5, 39.3, 29.6, 23.2; ESI-MS: (M+H) = 256.

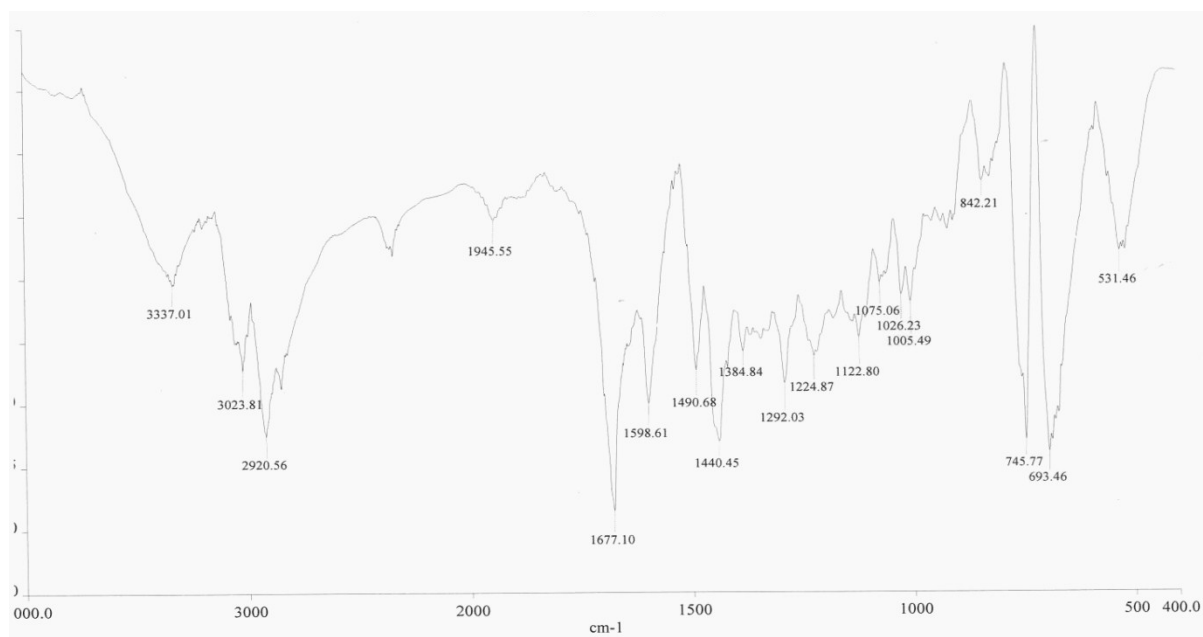


1-(1-(phenylethynyl)cyclopentyl)pyrrolidine (9f): yellow liquid. ^1H NMR (400 MHz, CDCl_3 , TMS) δ 7.41-7.39 (m, 2H), 7.30-7.26 (m, 3H), 2.80-2.77 (m, 4H), 2.07-2.05 (m, 2H), 1.88-1.78 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 131.5, 128.0, 127.5, 123.5, 91.0, 84.8, 65.5, 49.1, 40.3, 23.5, 23.4; ESI-MS: (M+H) = 240.

i)

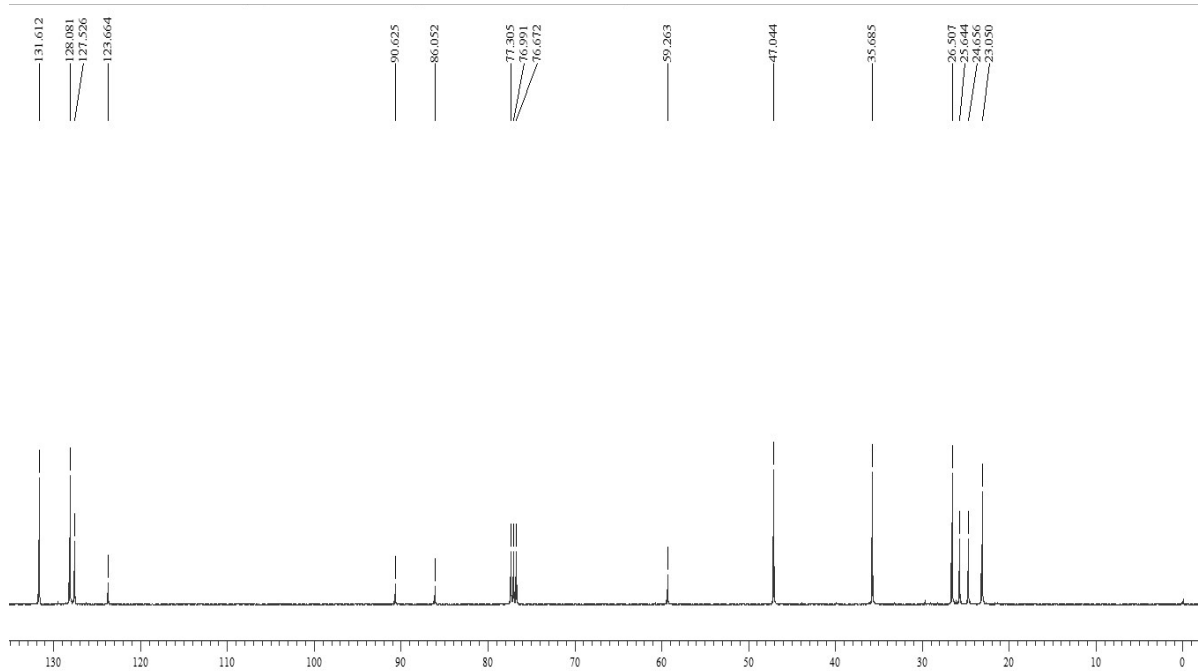
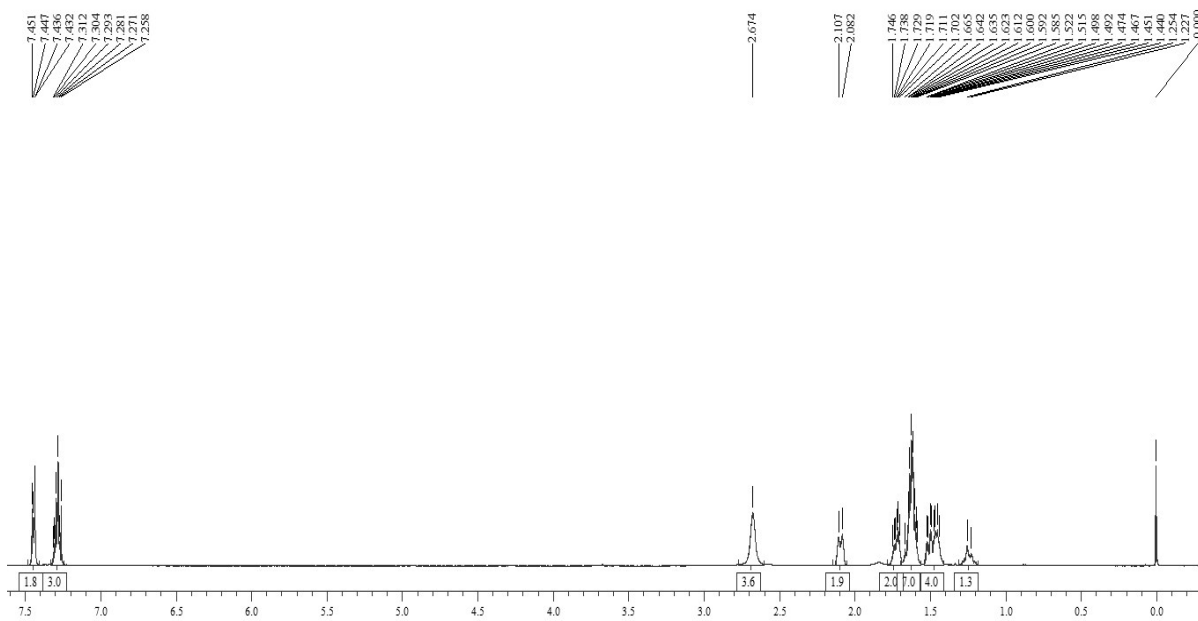
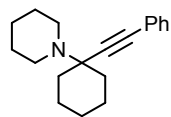


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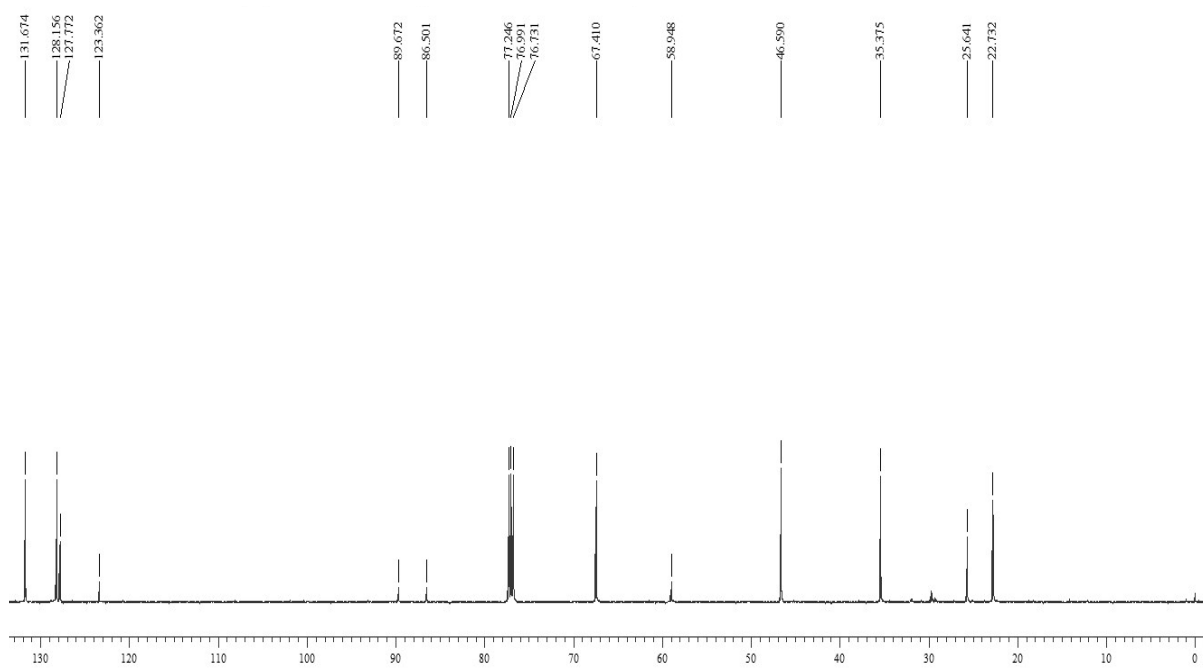
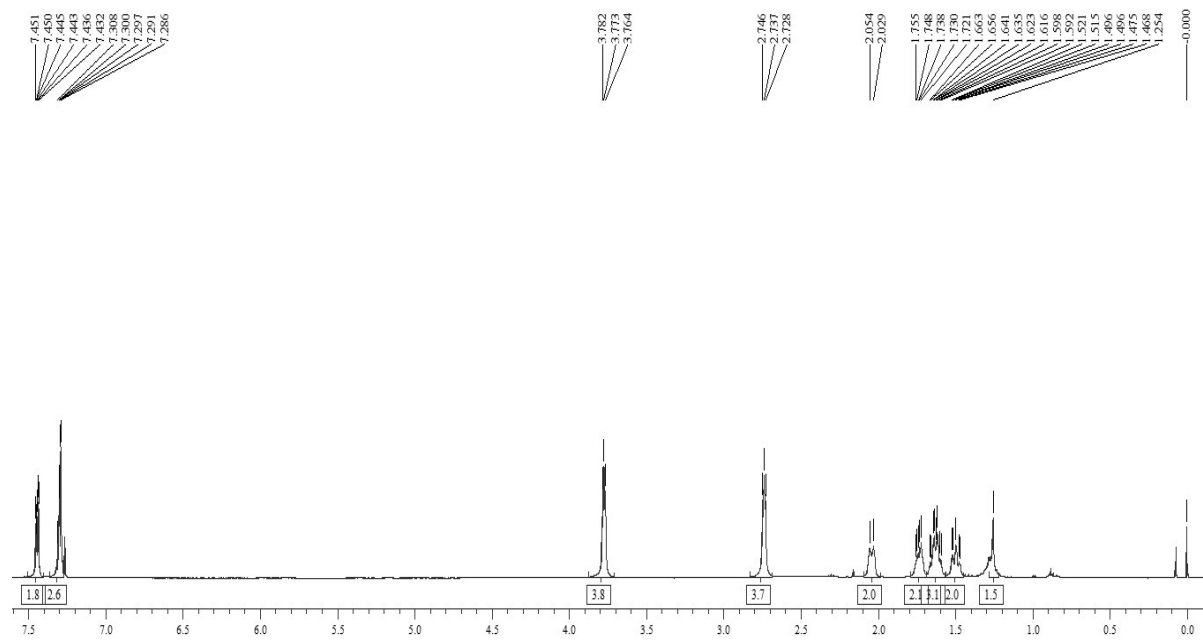
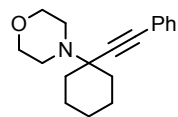


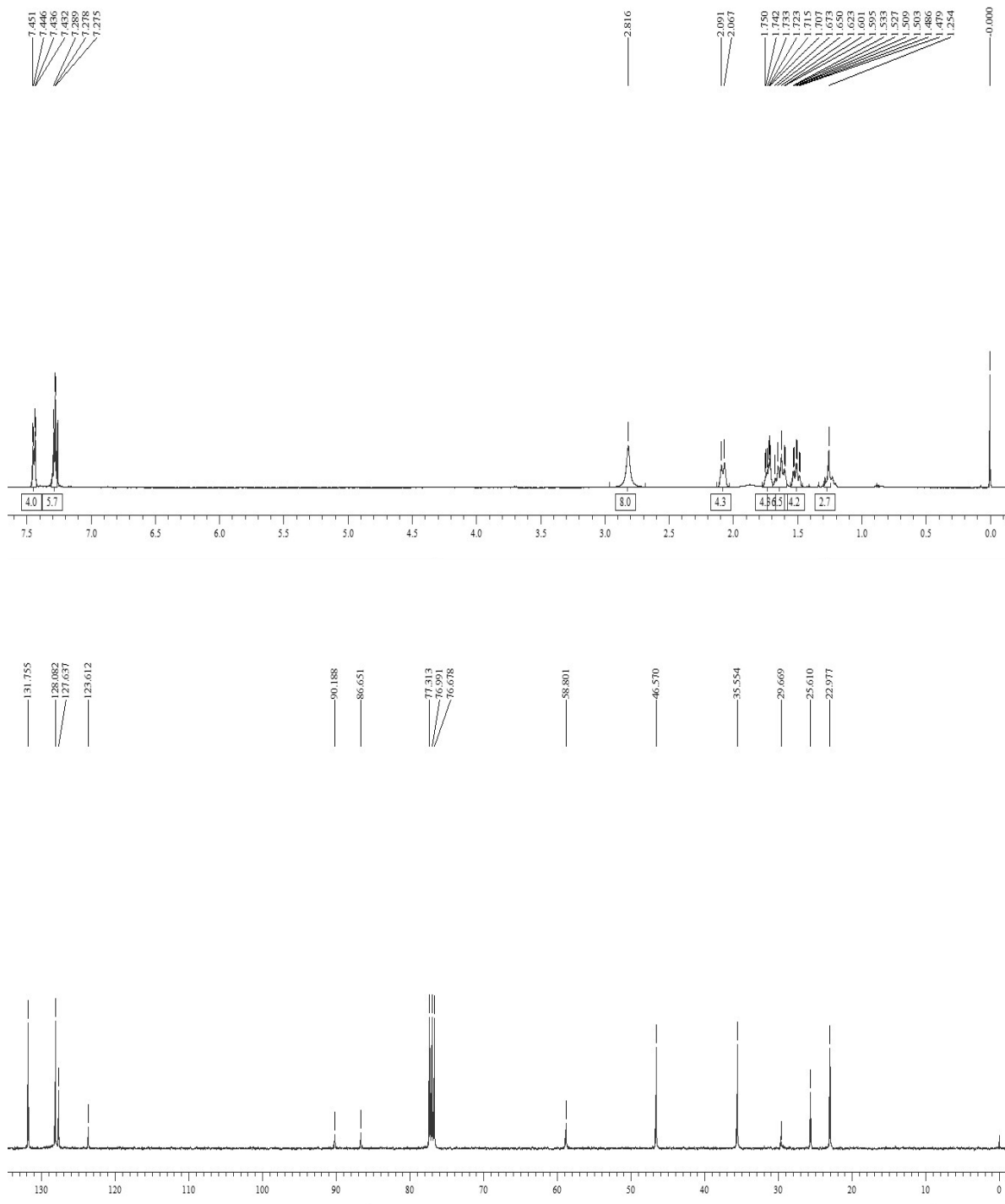
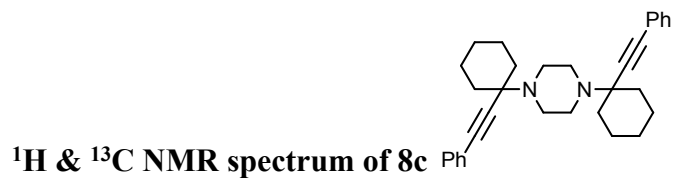
FT-IR spectra of: (i) chloromethylated polystyrene (ii) Polystyrene supported N-phenylpiperazine-Cu(II) complex (**4c**).

¹H & ¹³C NMR spectrum of 8a

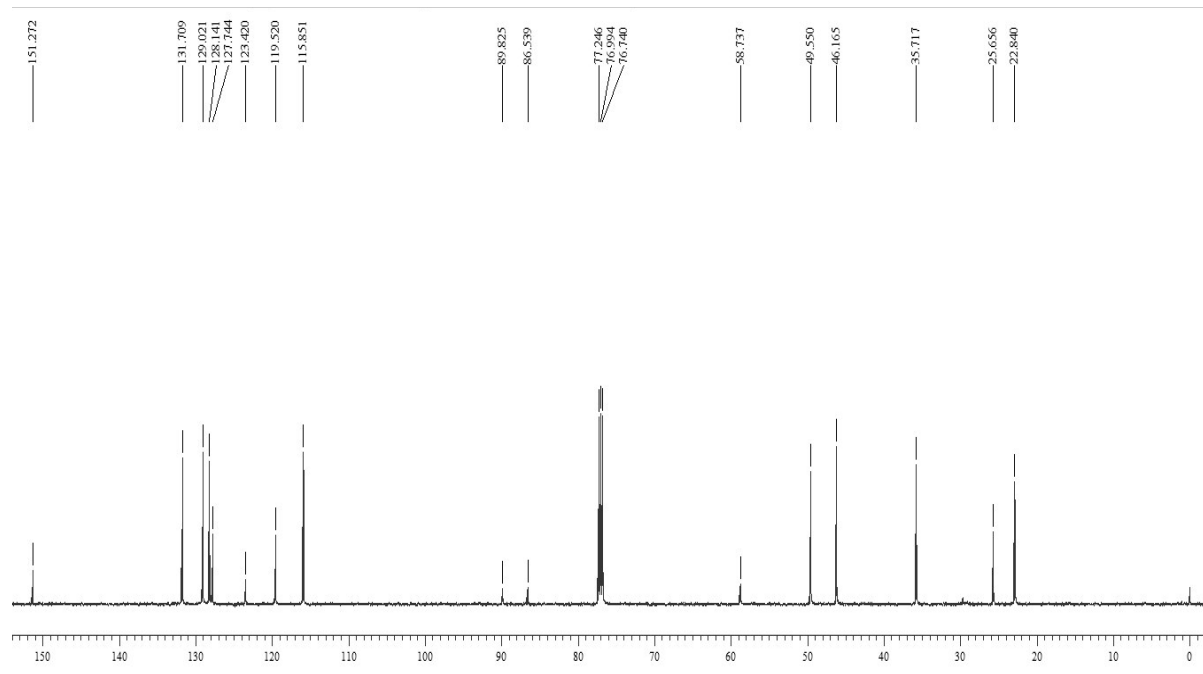
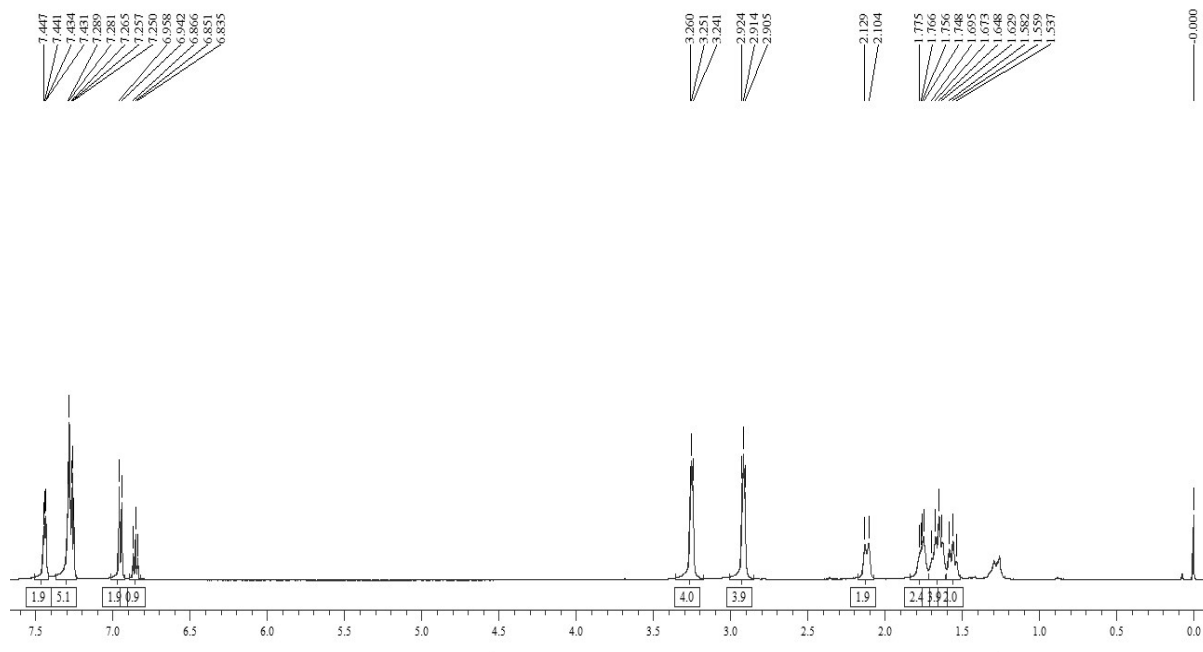
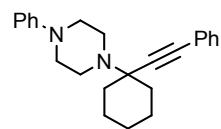


¹H & ¹³C NMR spectrum of 8b

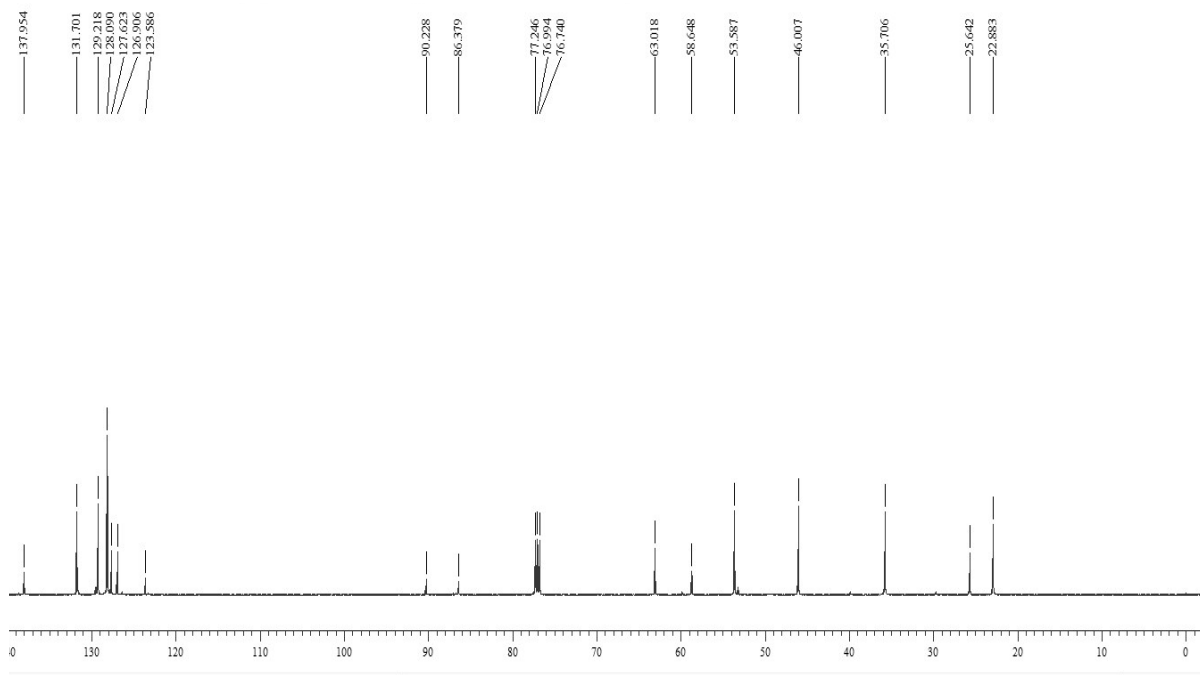
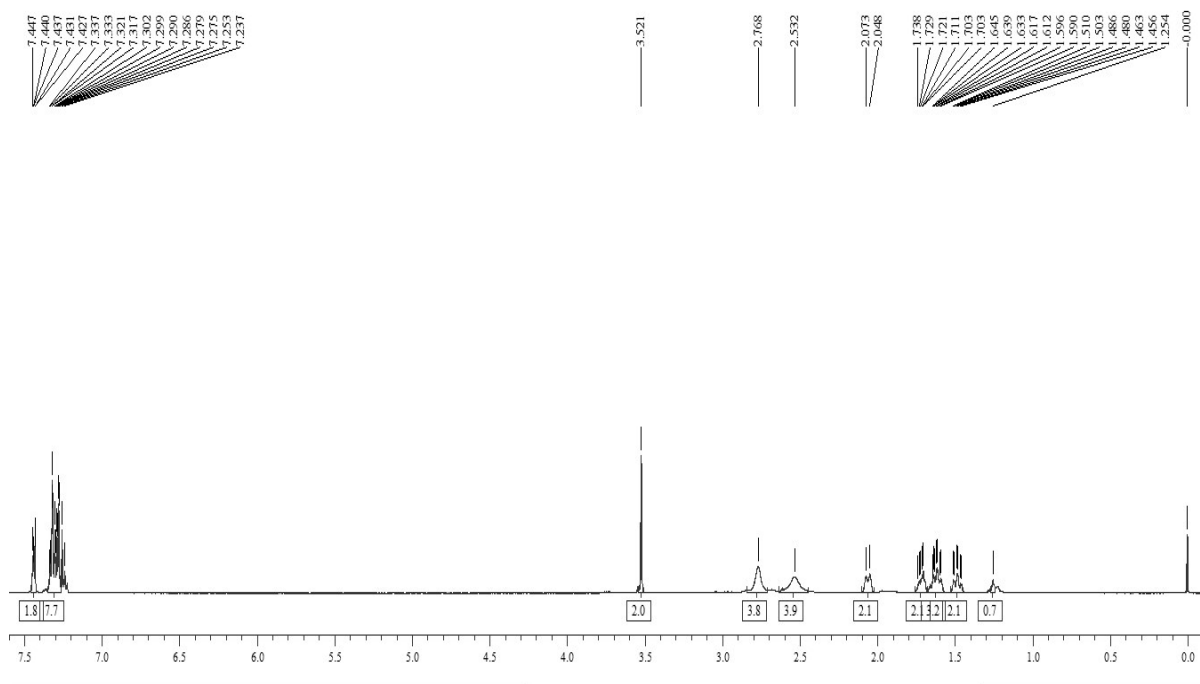
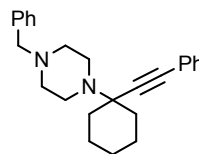




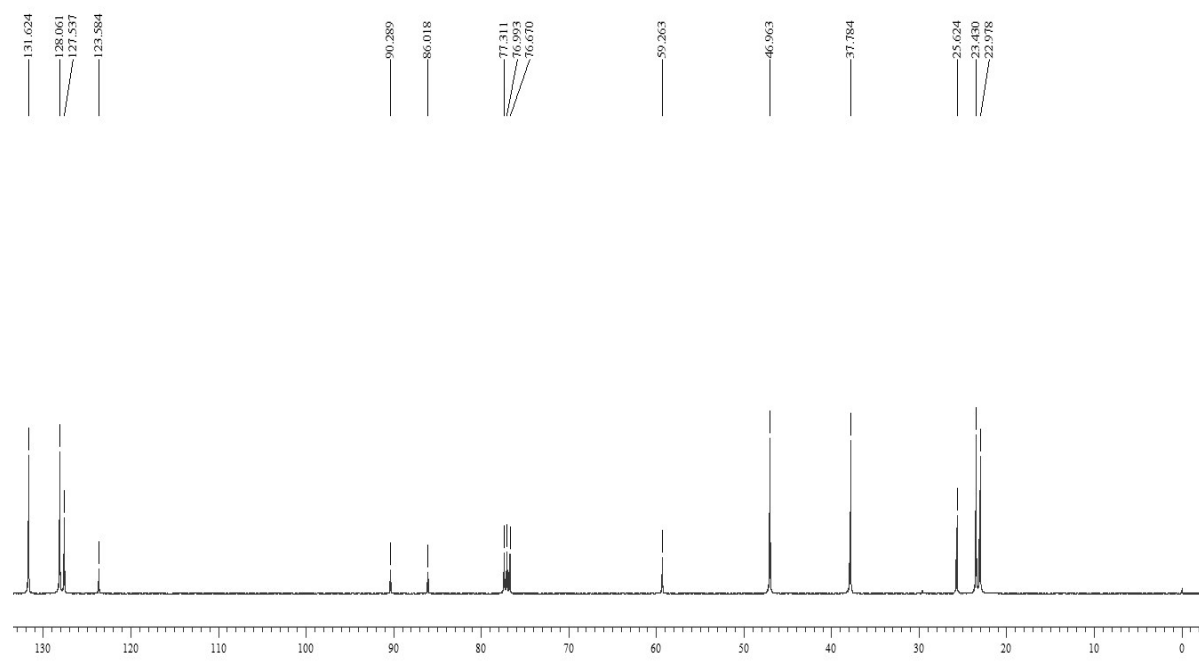
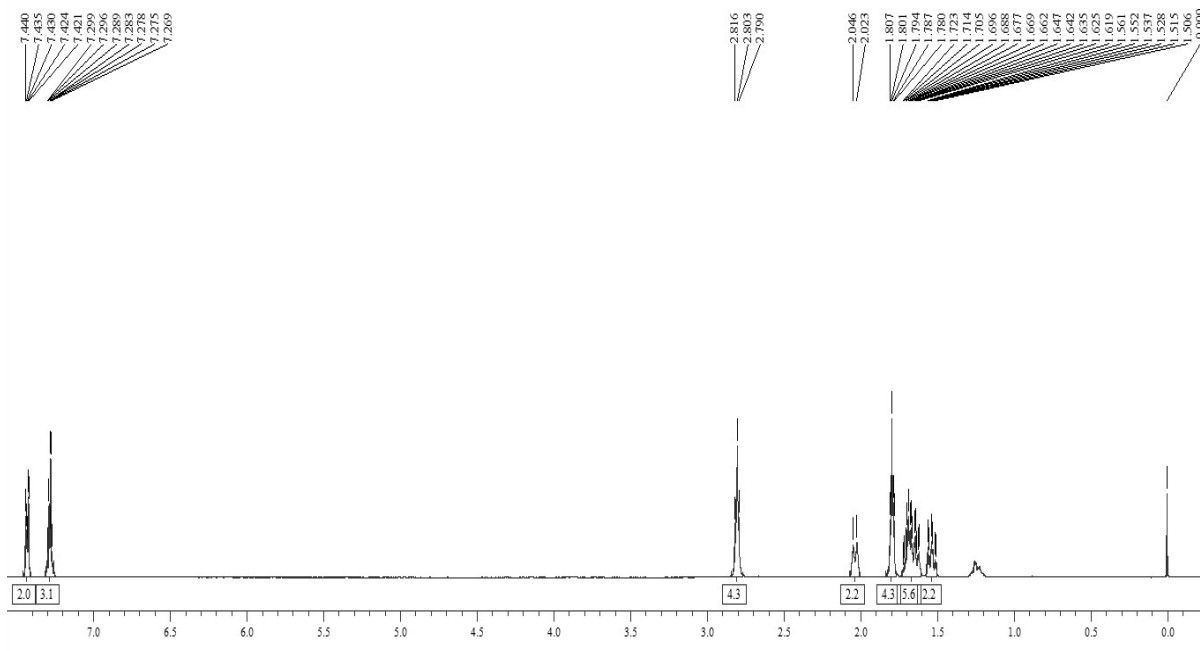
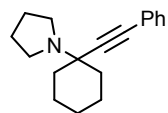
^1H & ^{13}C NMR spectrum of 8d



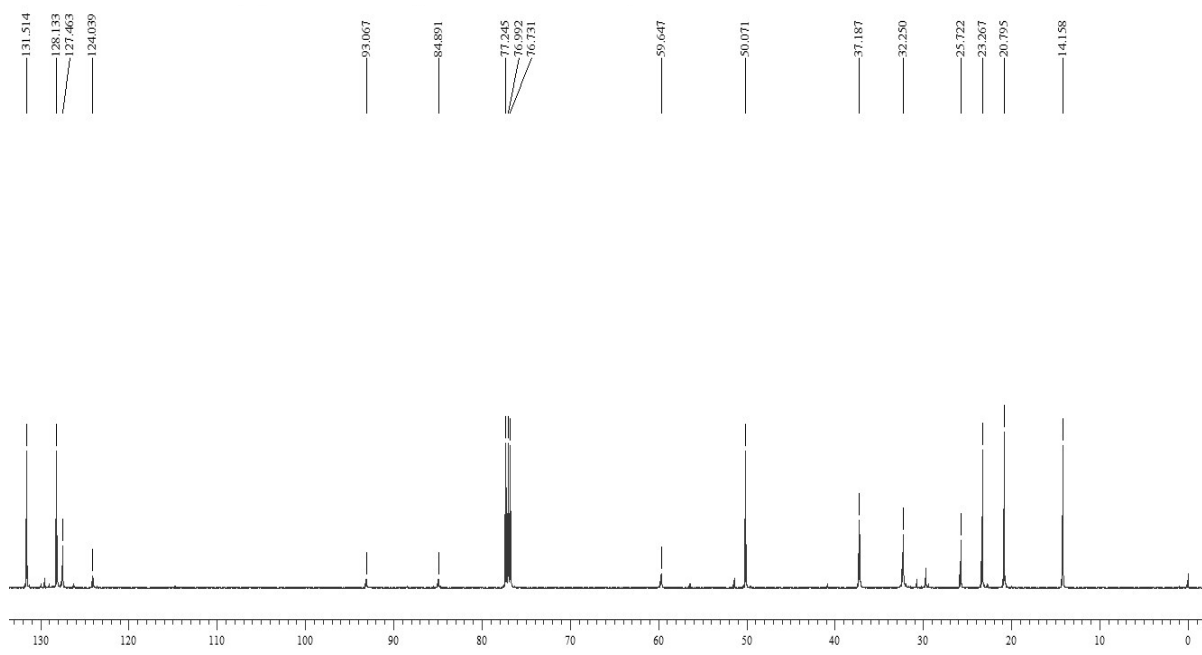
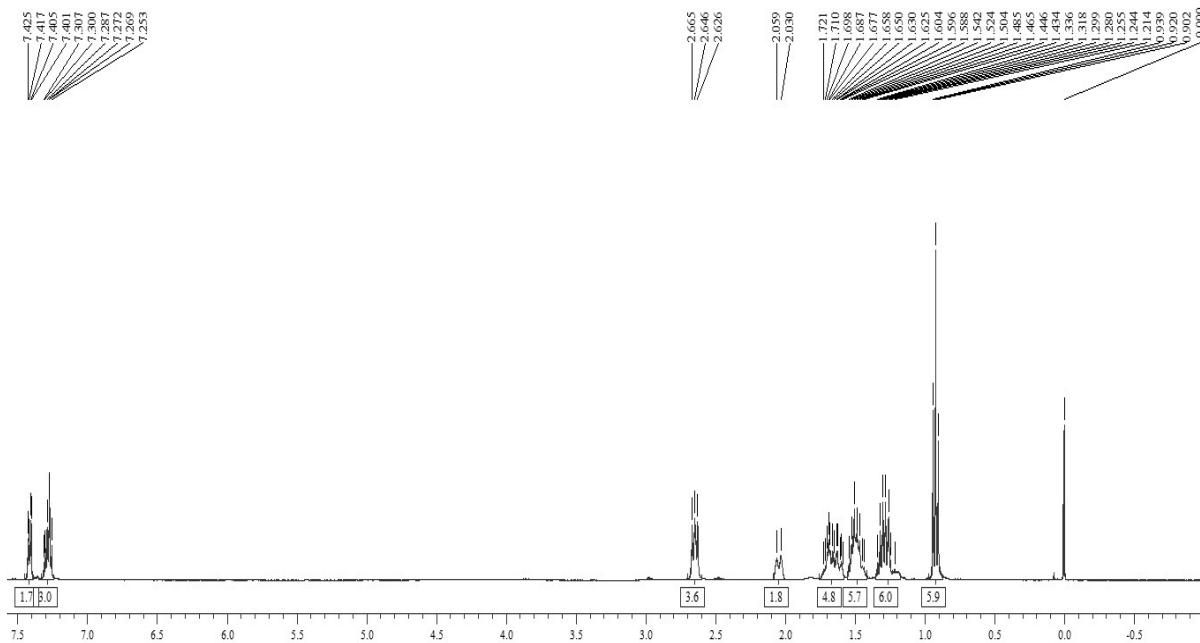
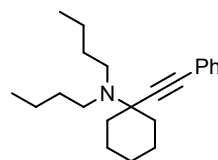
¹H & ¹³C NMR spectrum of 8e

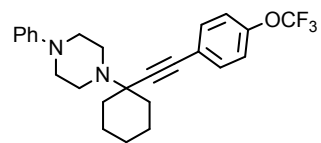


^1H & ^{13}C NMR spectrum of 8f

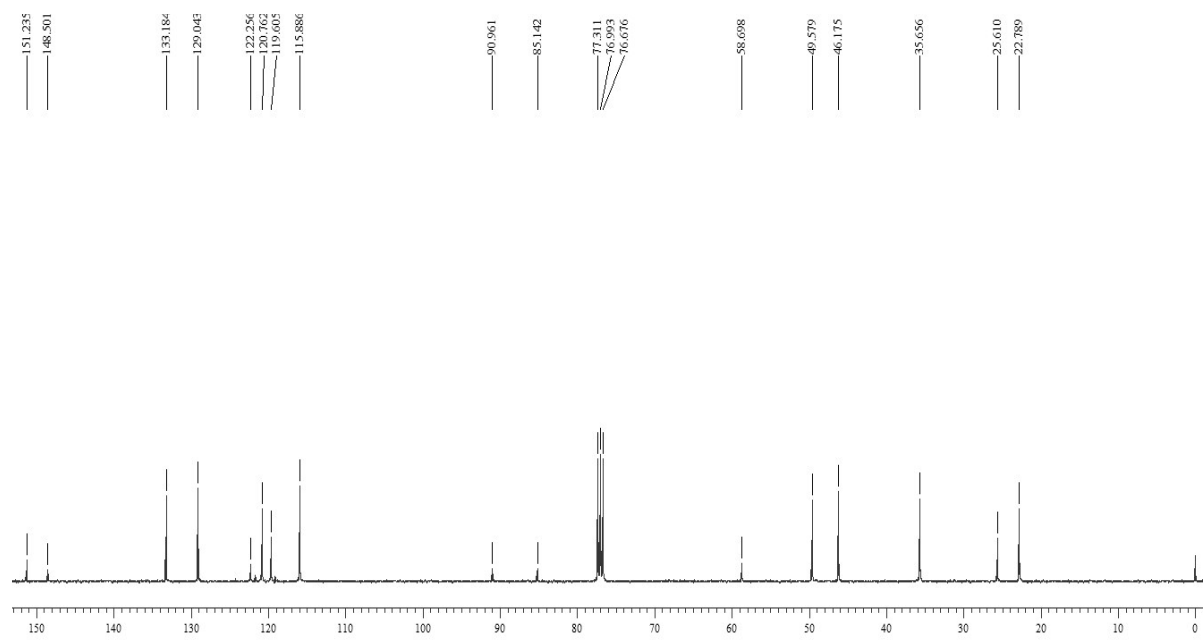
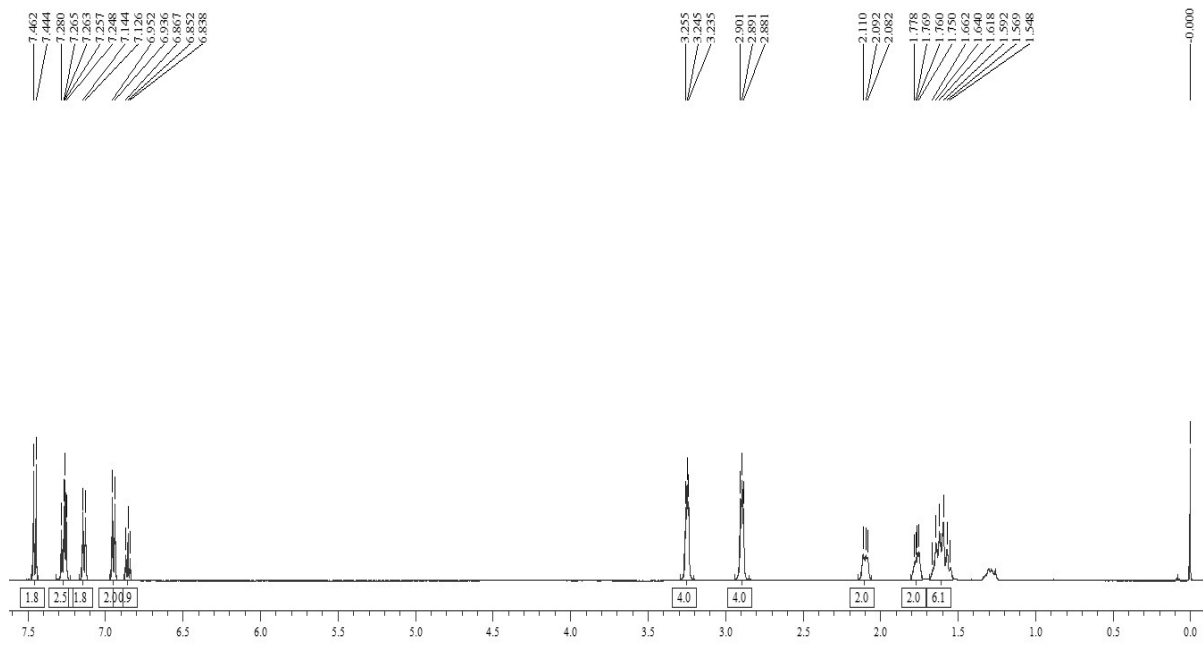


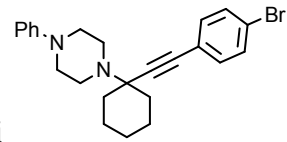
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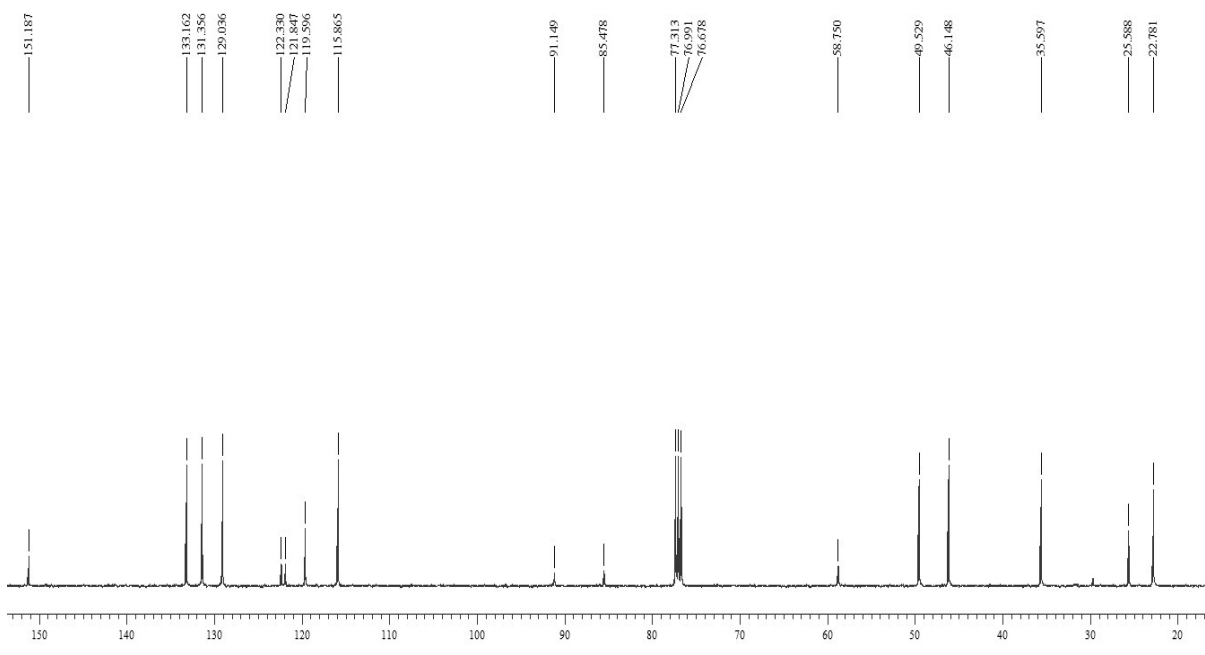
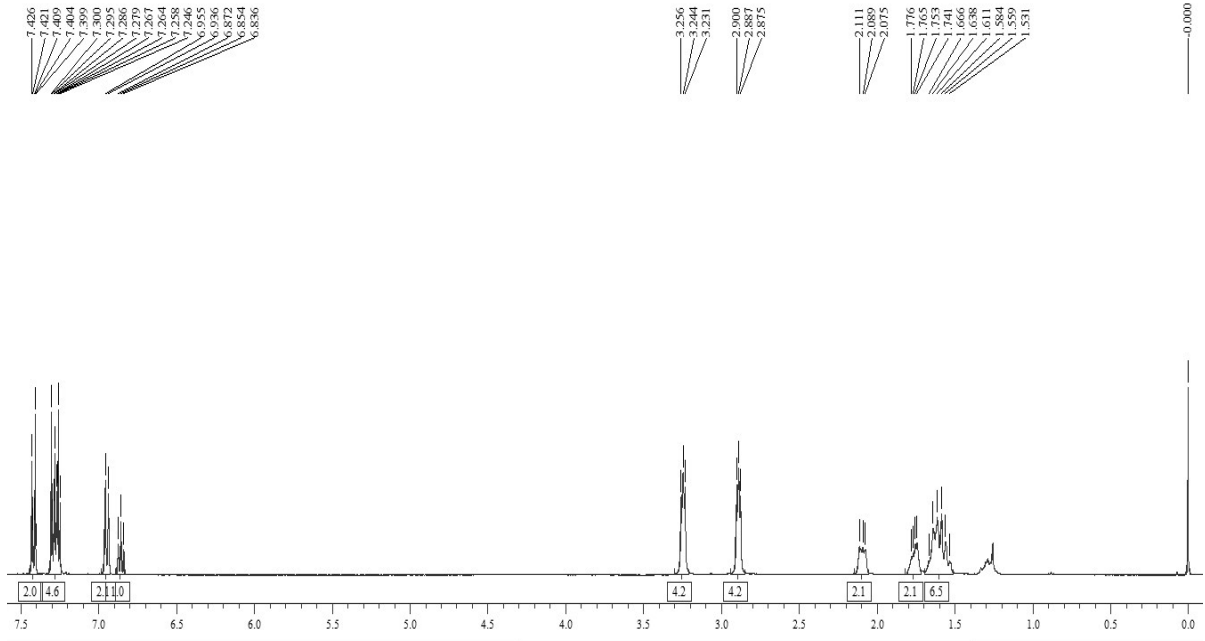


^1H & ^{13}C NMR spectrum of 8h

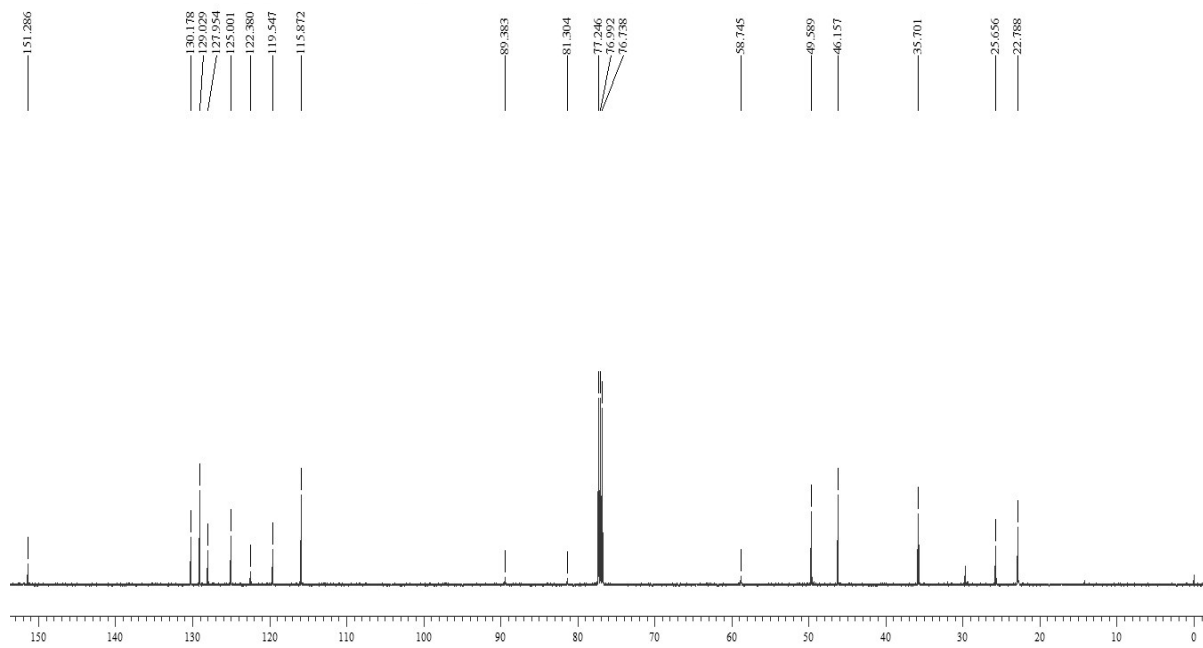
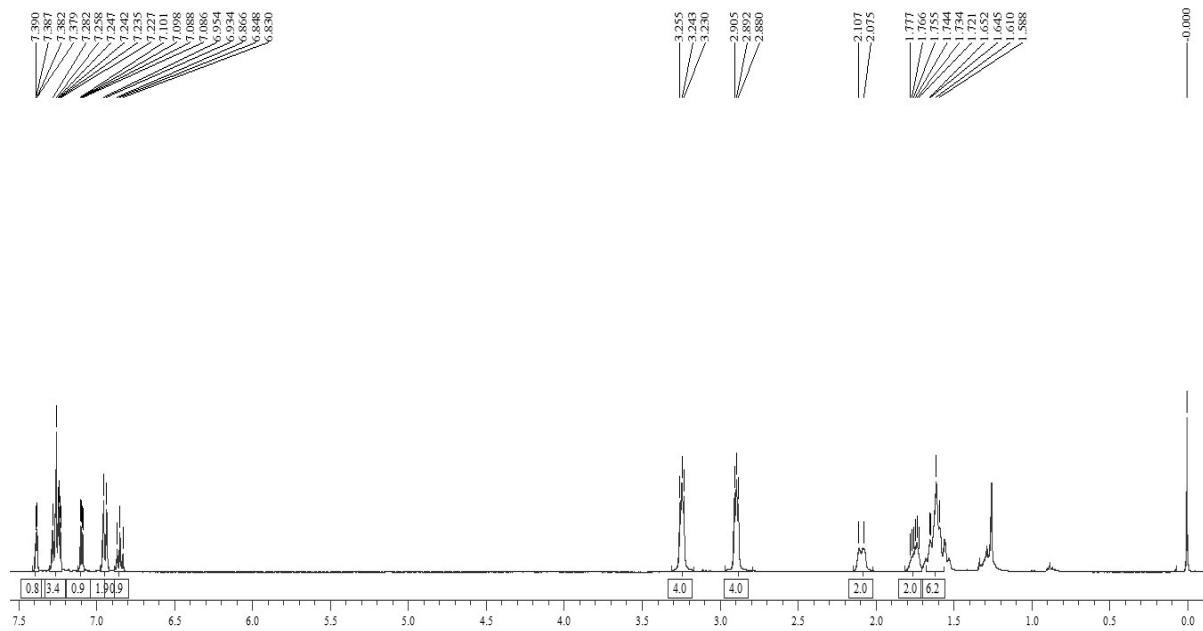
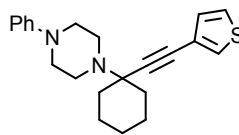




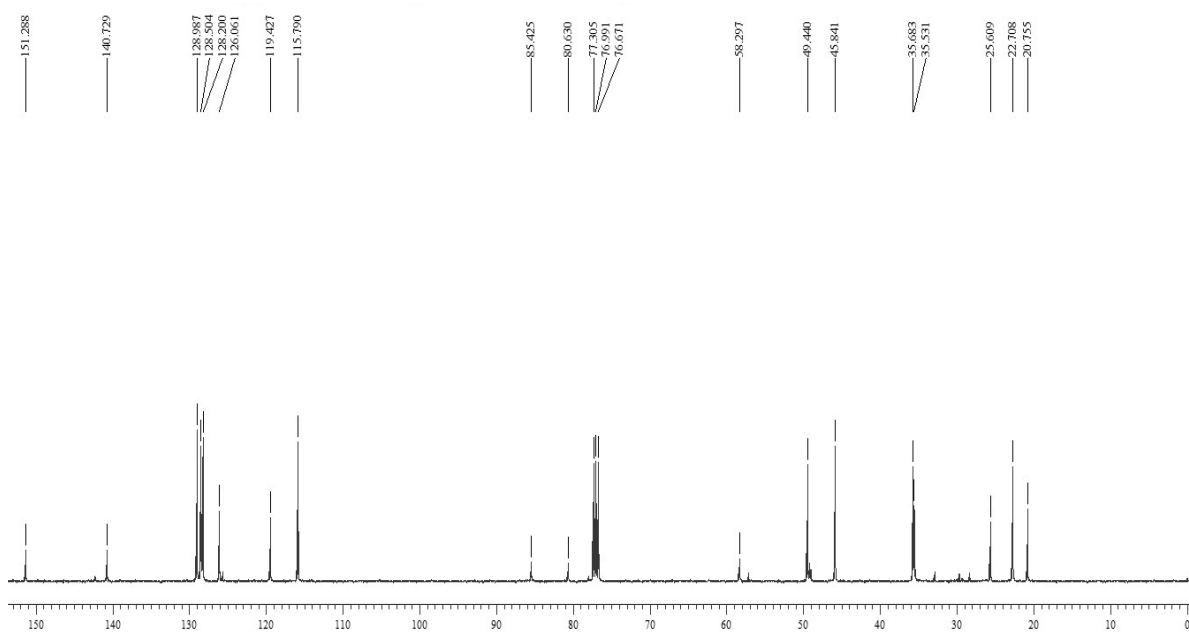
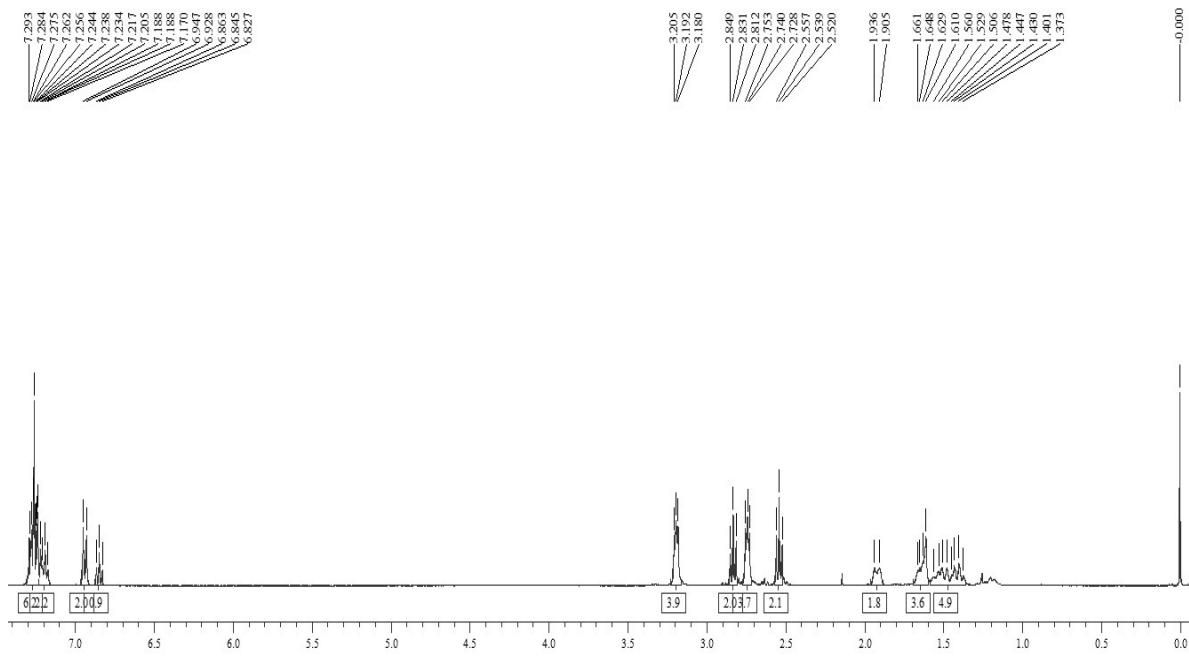
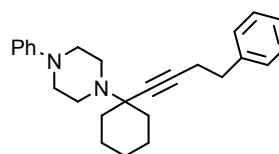
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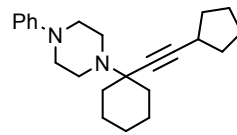


¹H & ¹³C NMR spectrum of 8j

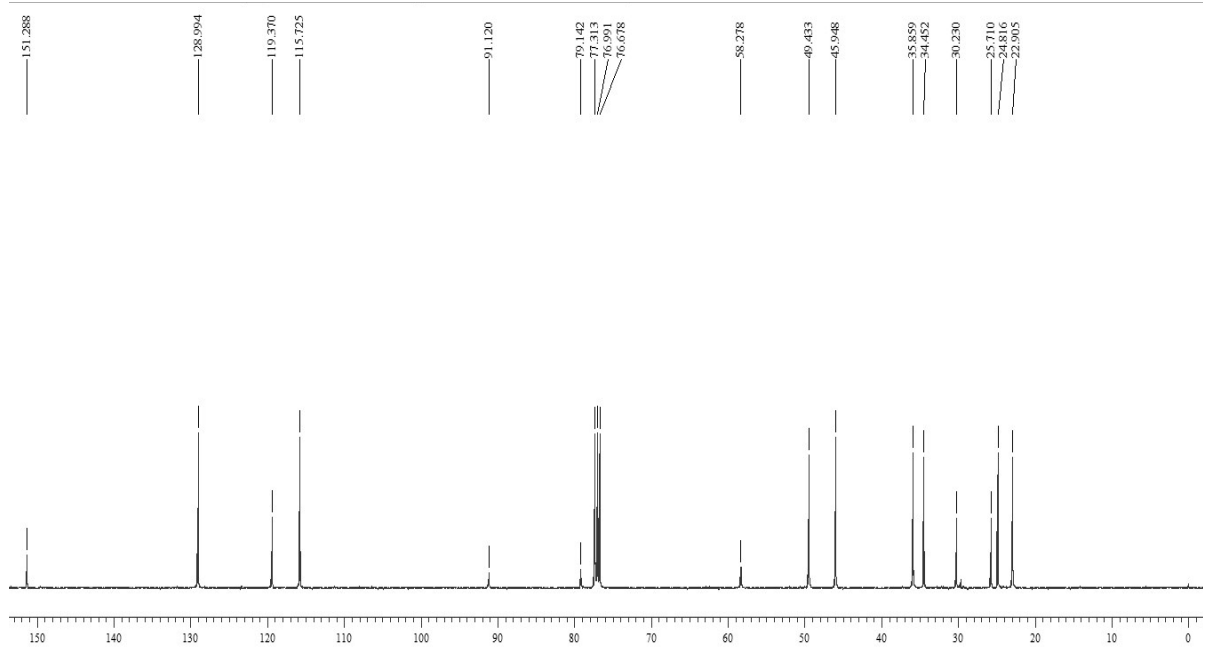
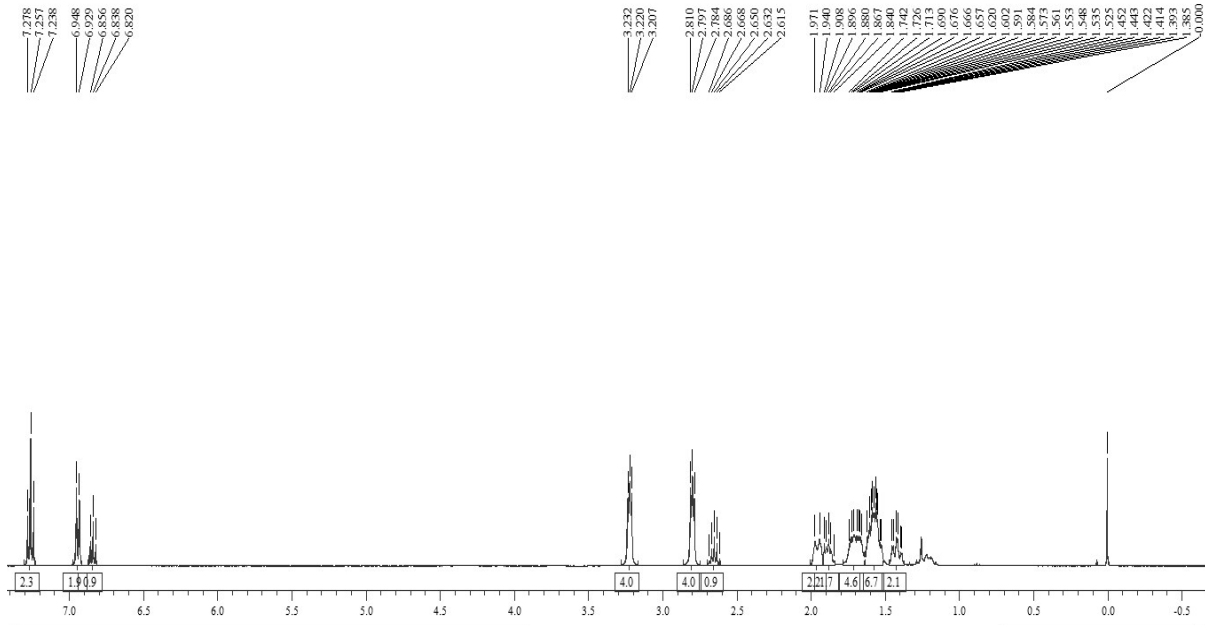


^1H & ^{13}C NMR spectrum of 8k

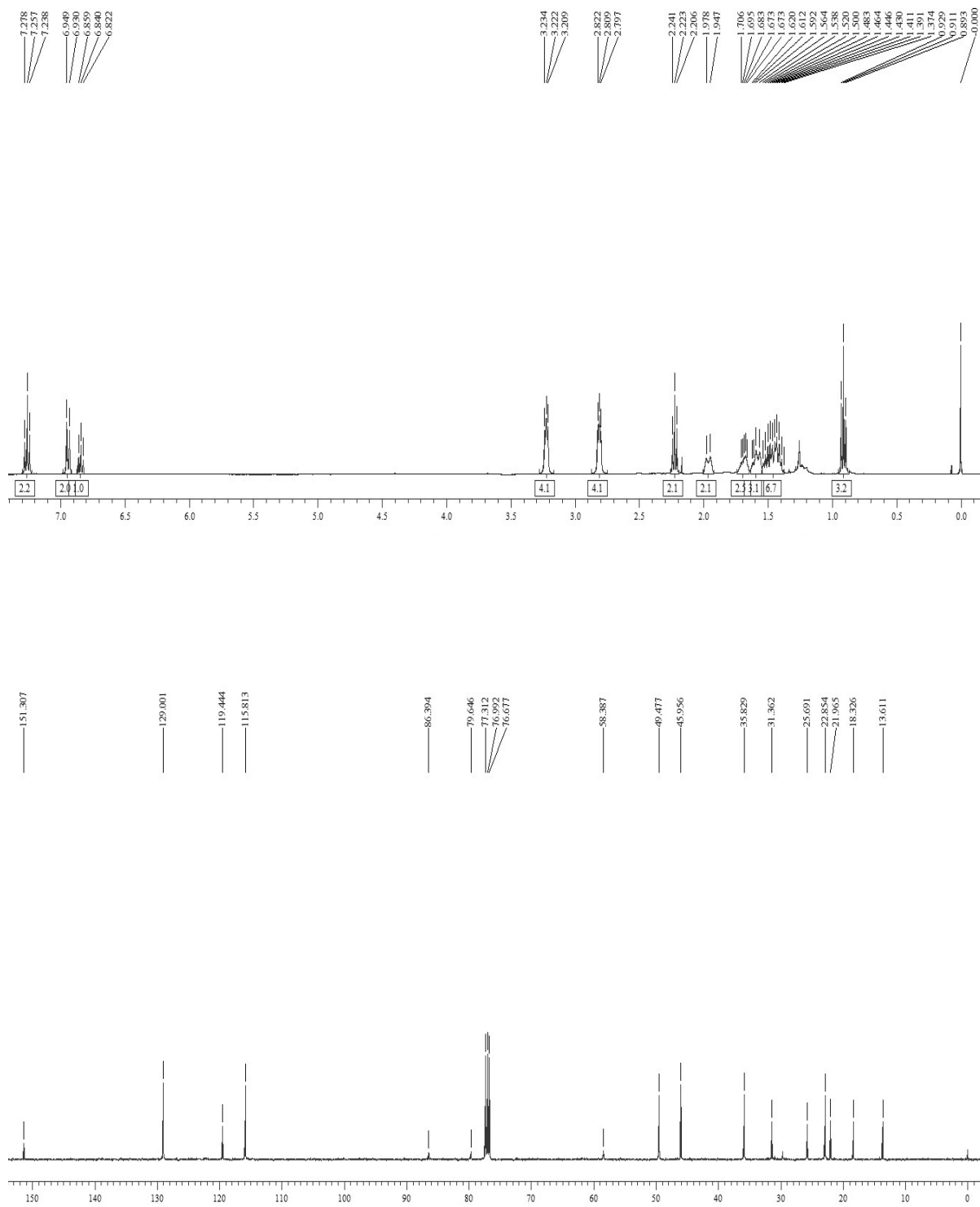
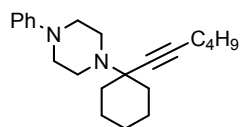




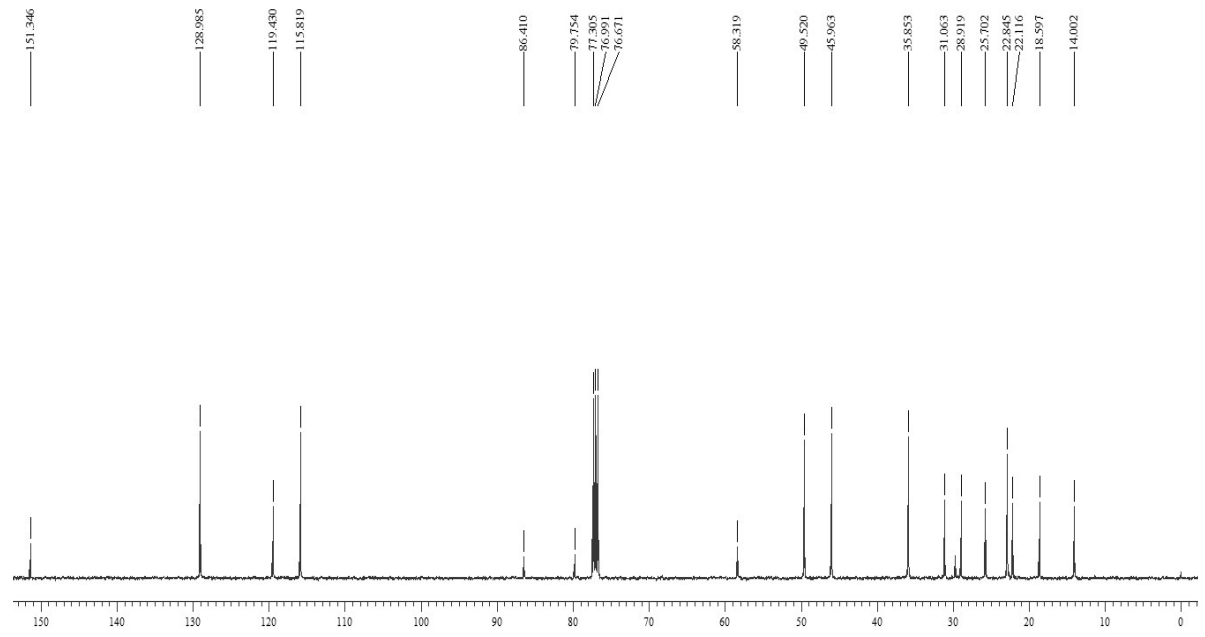
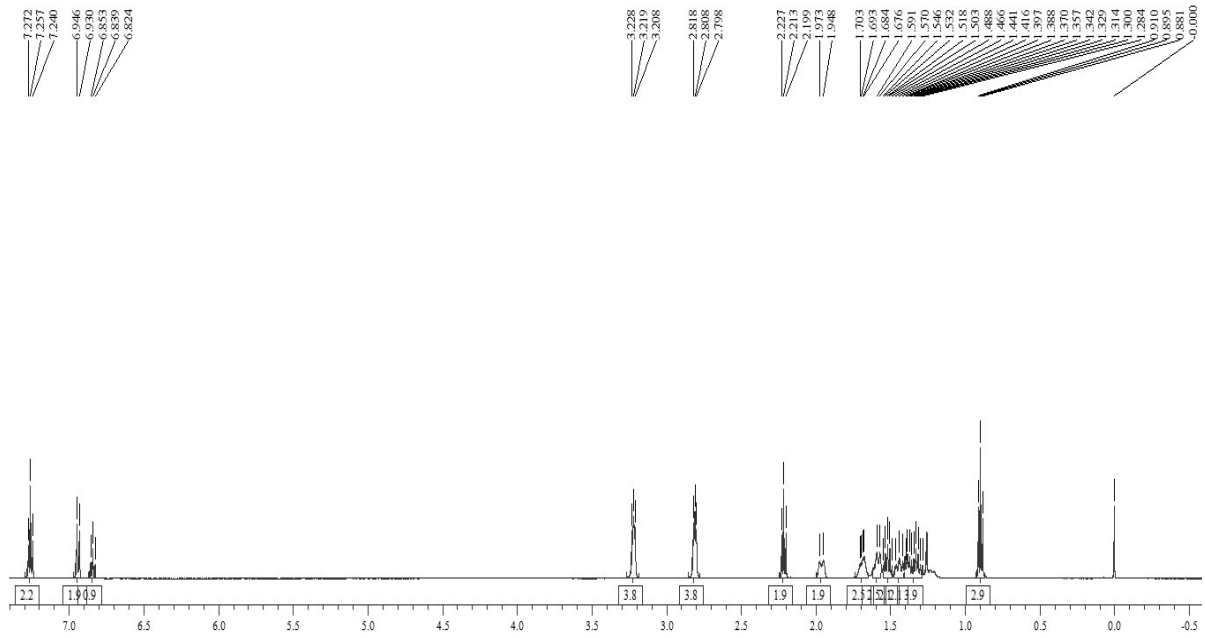
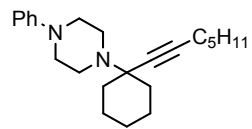
^1H & ^{13}C NMR spectrum of 8l



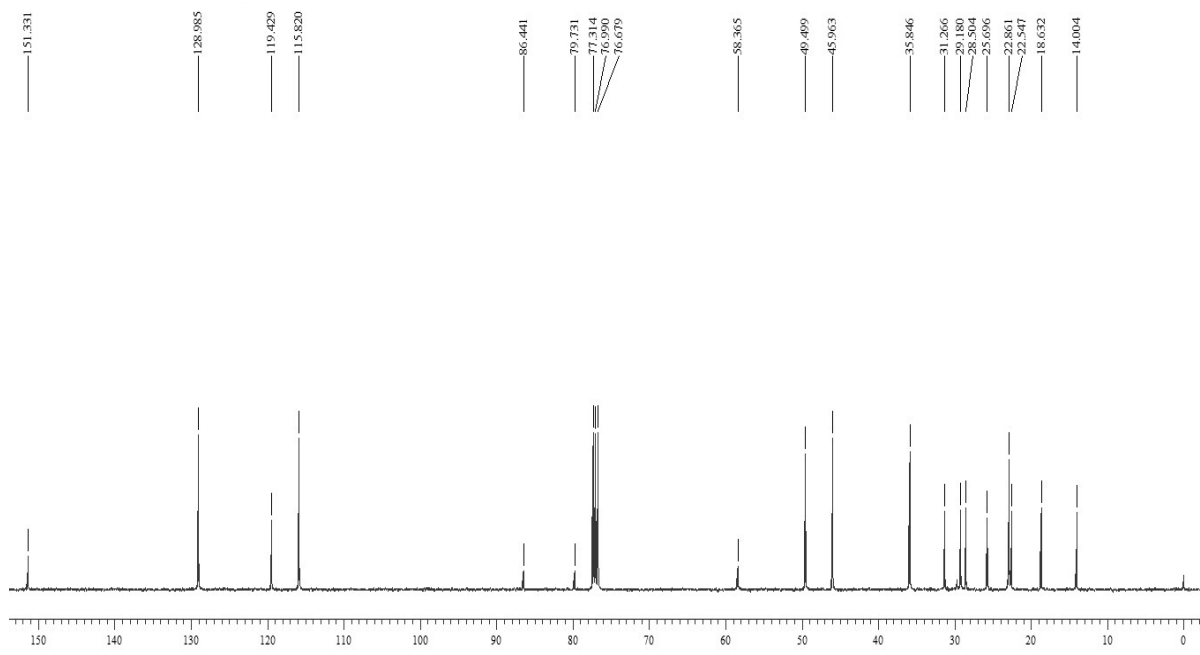
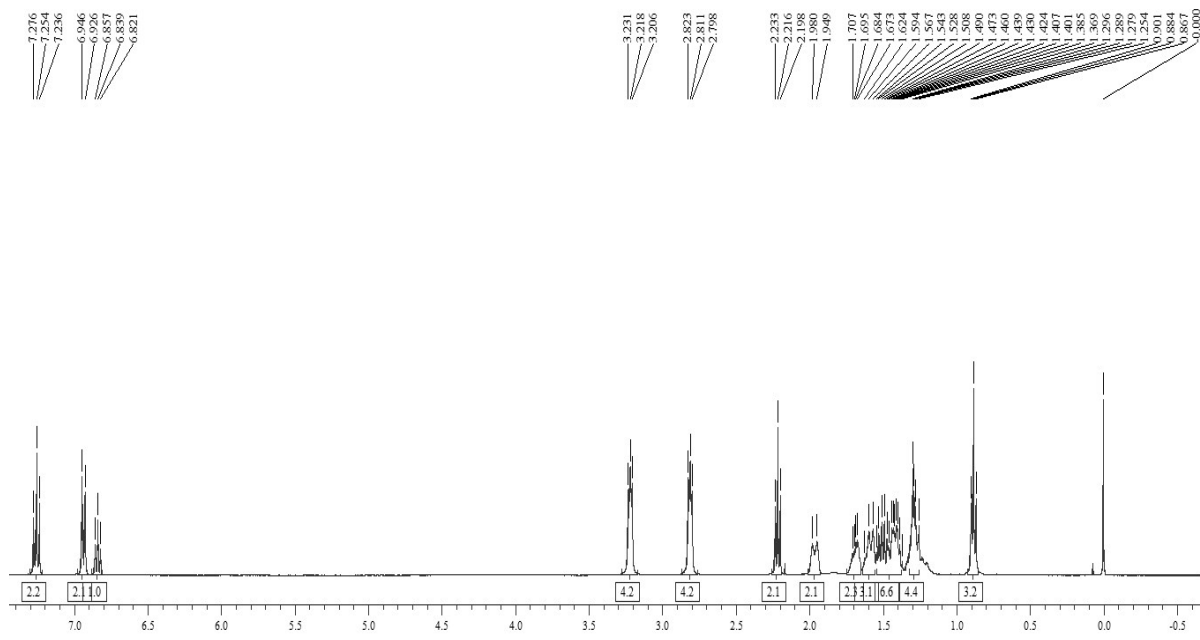
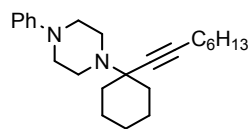
^1H & ^{13}C NMR spectrum of 8m



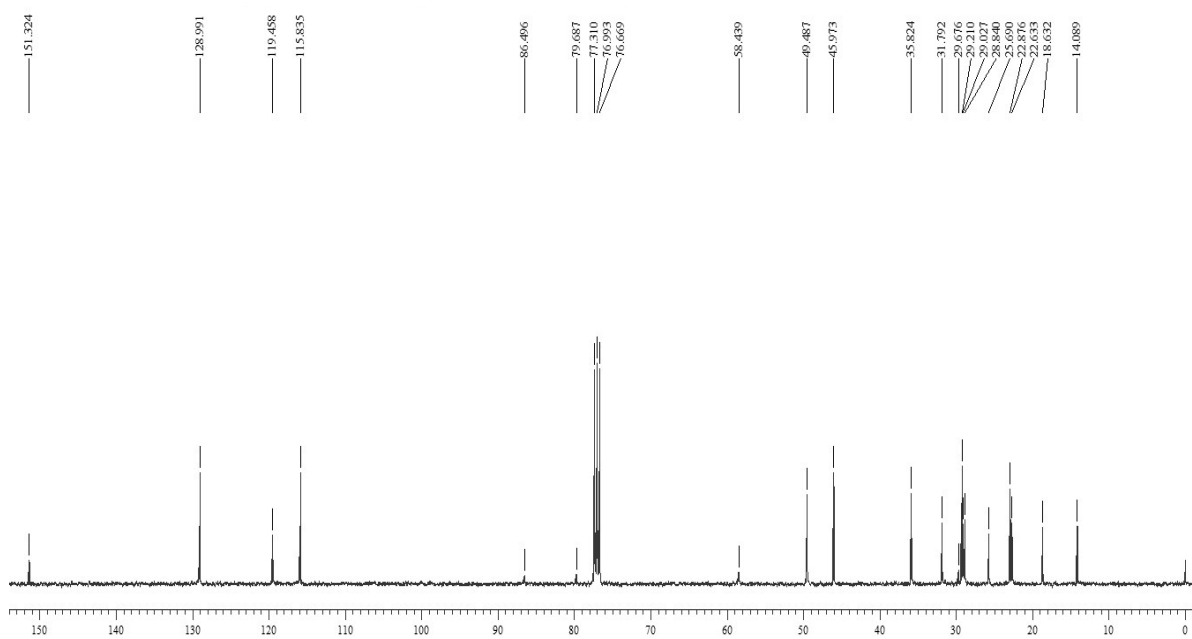
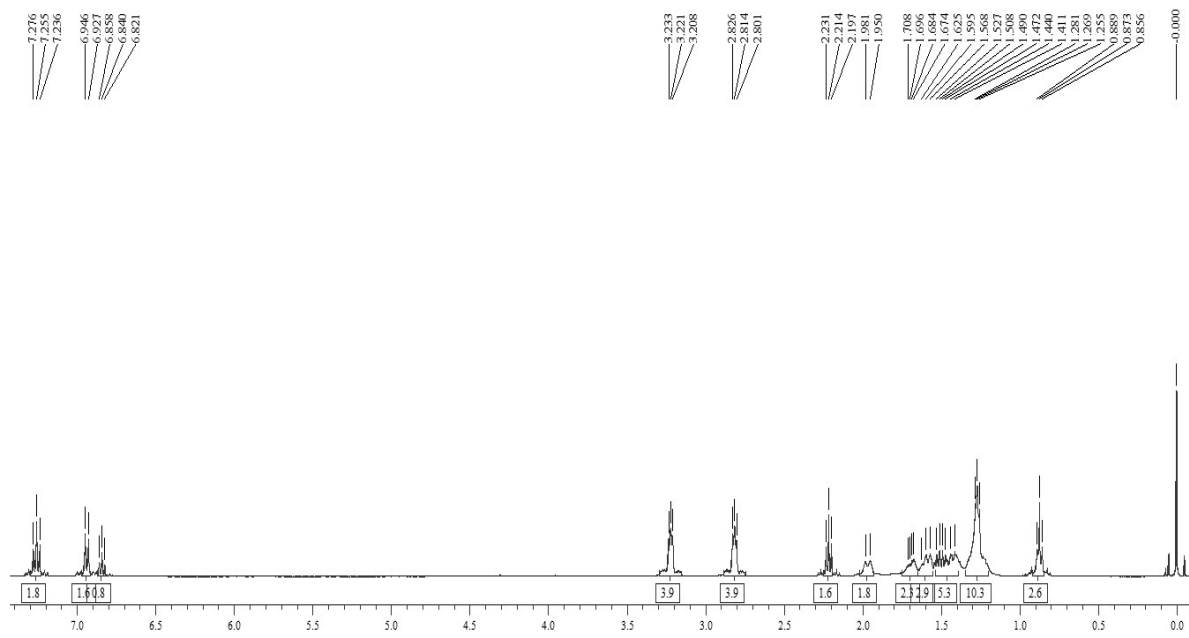
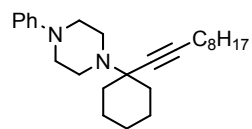
^1H & ^{13}C NMR spectrum of 8n

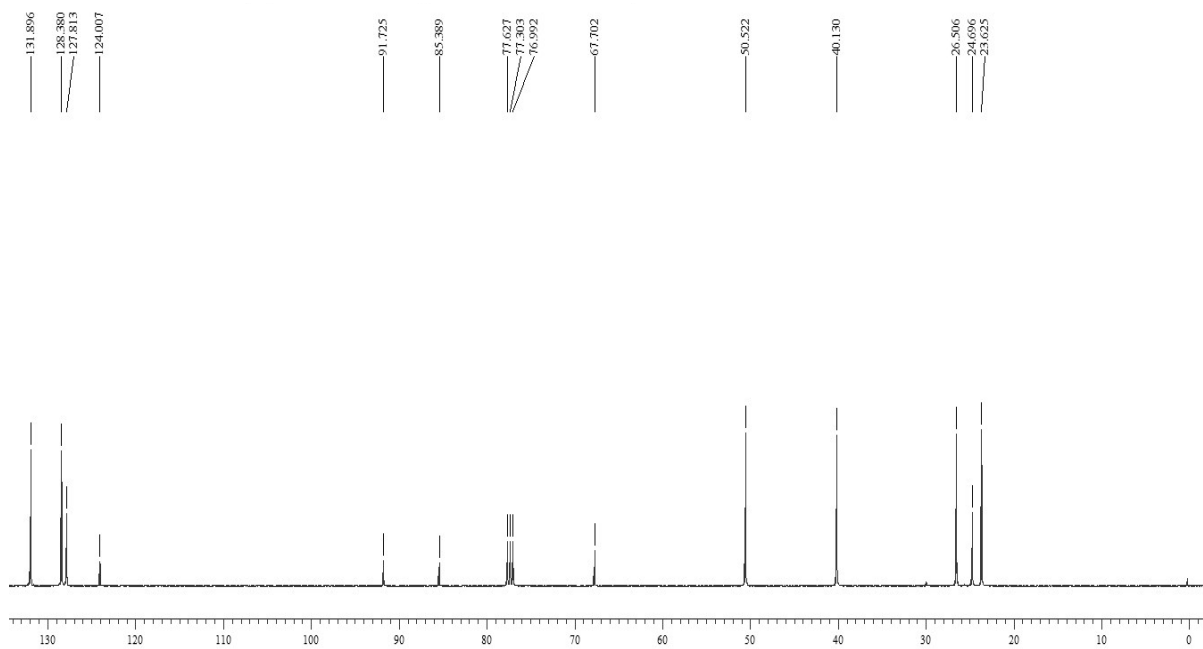
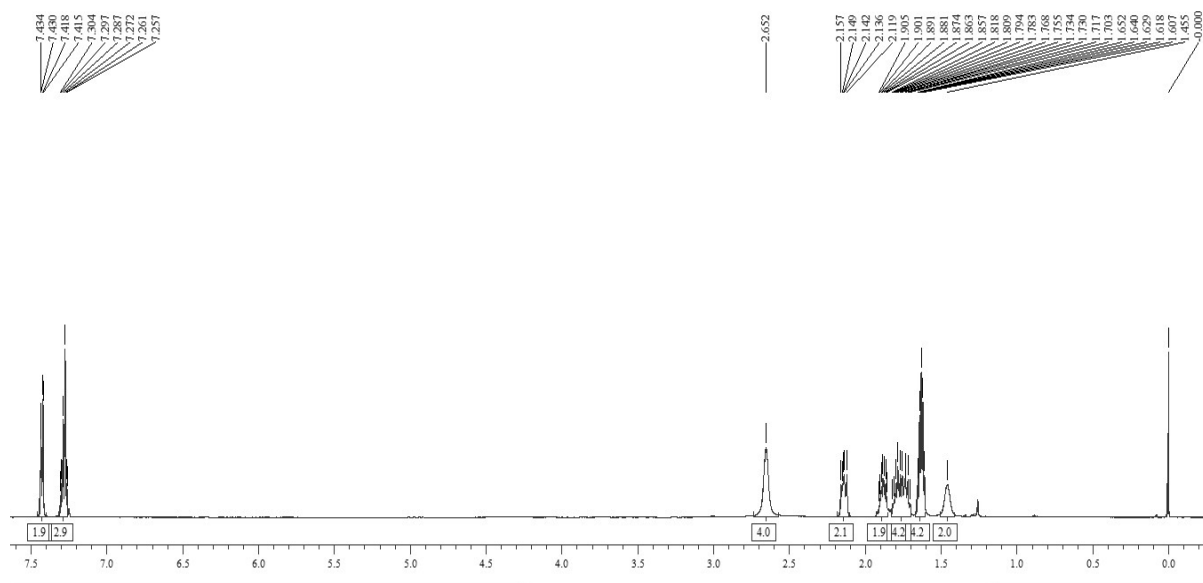
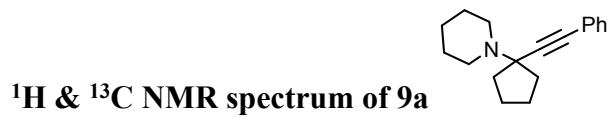


^1H & ^{13}C NMR spectrum of 8o

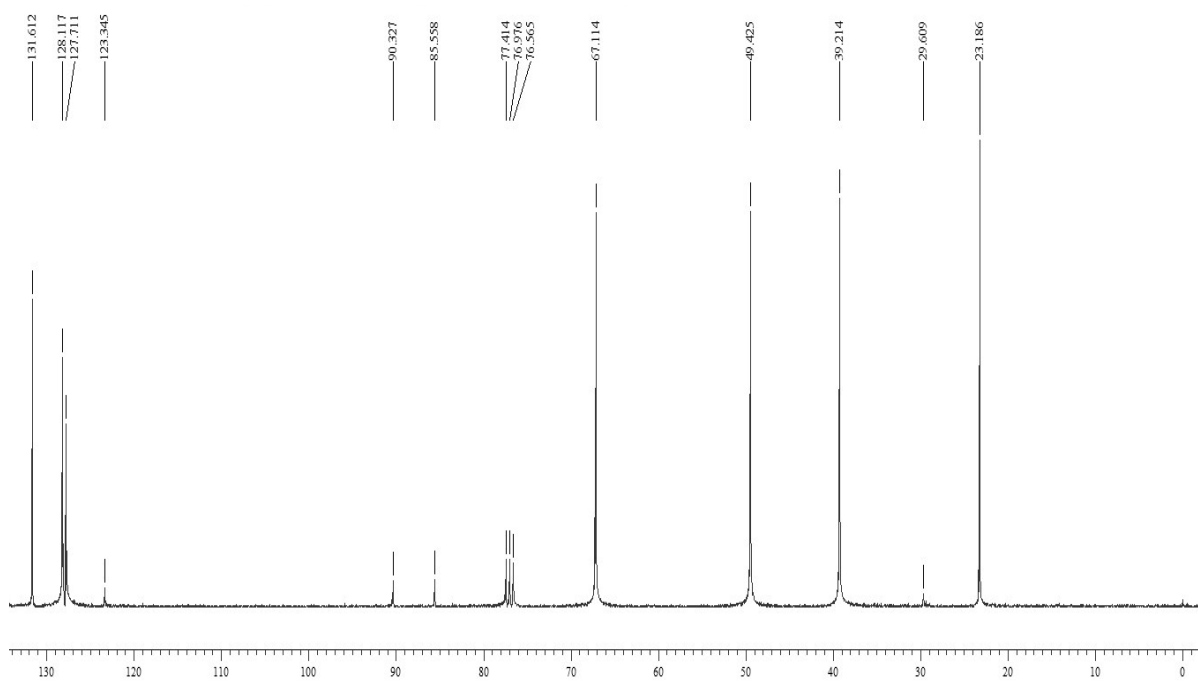
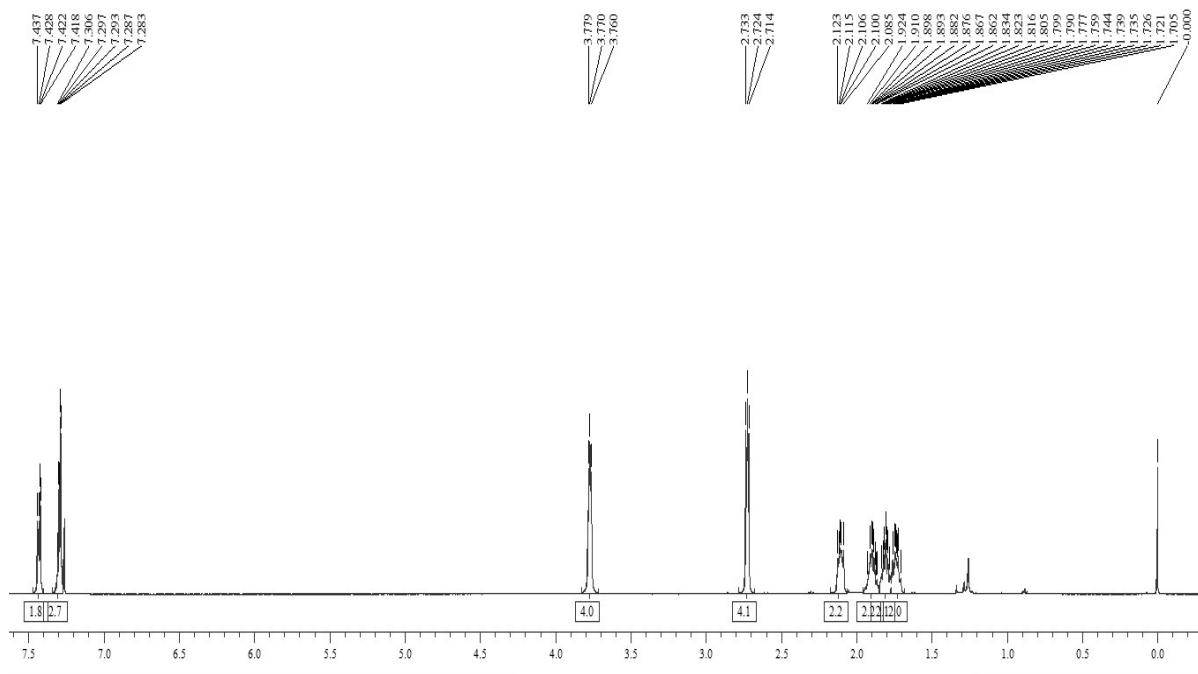
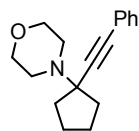


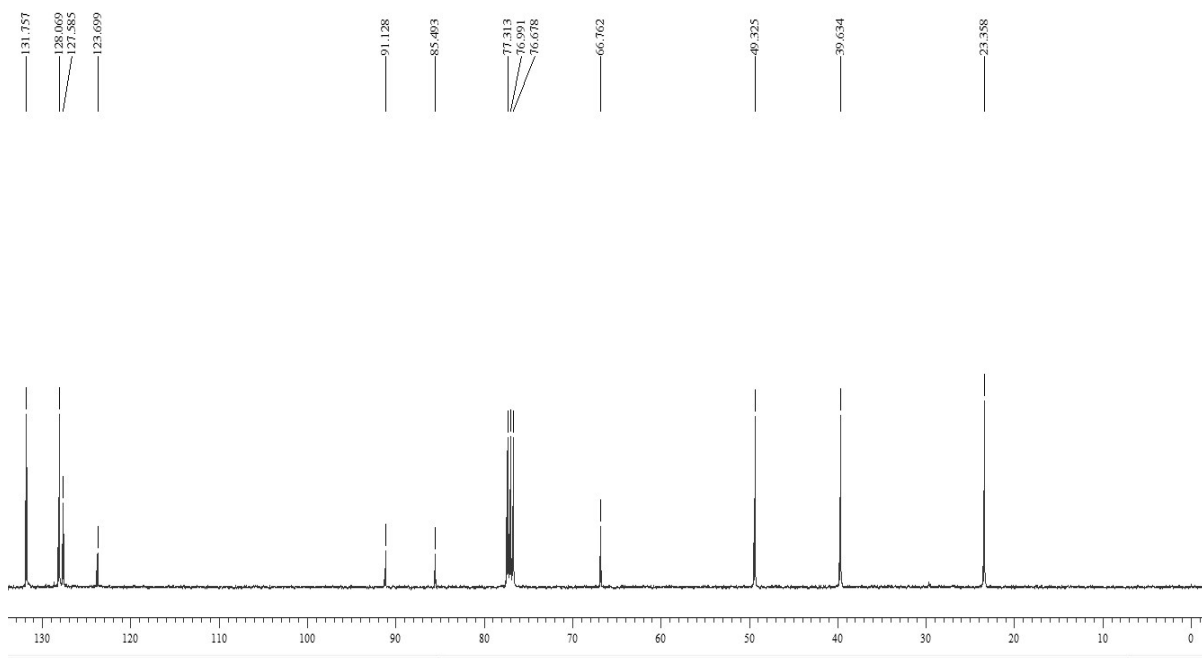
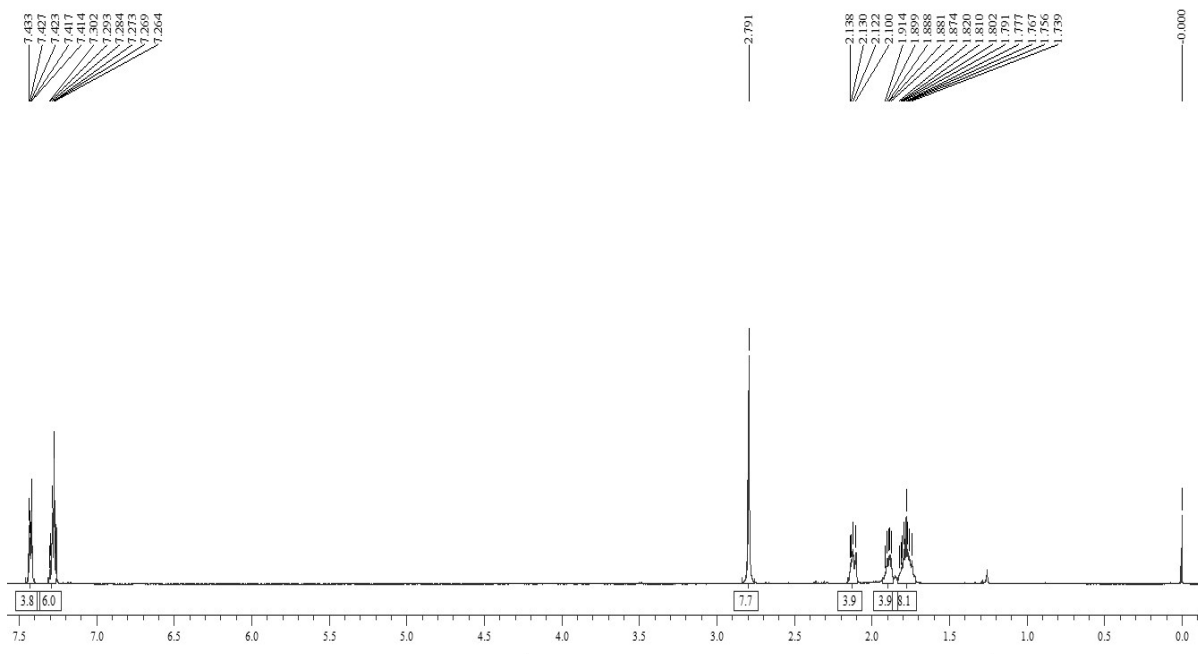
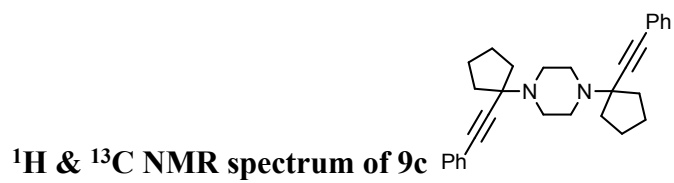
^1H & ^{13}C NMR spectrum of 8p



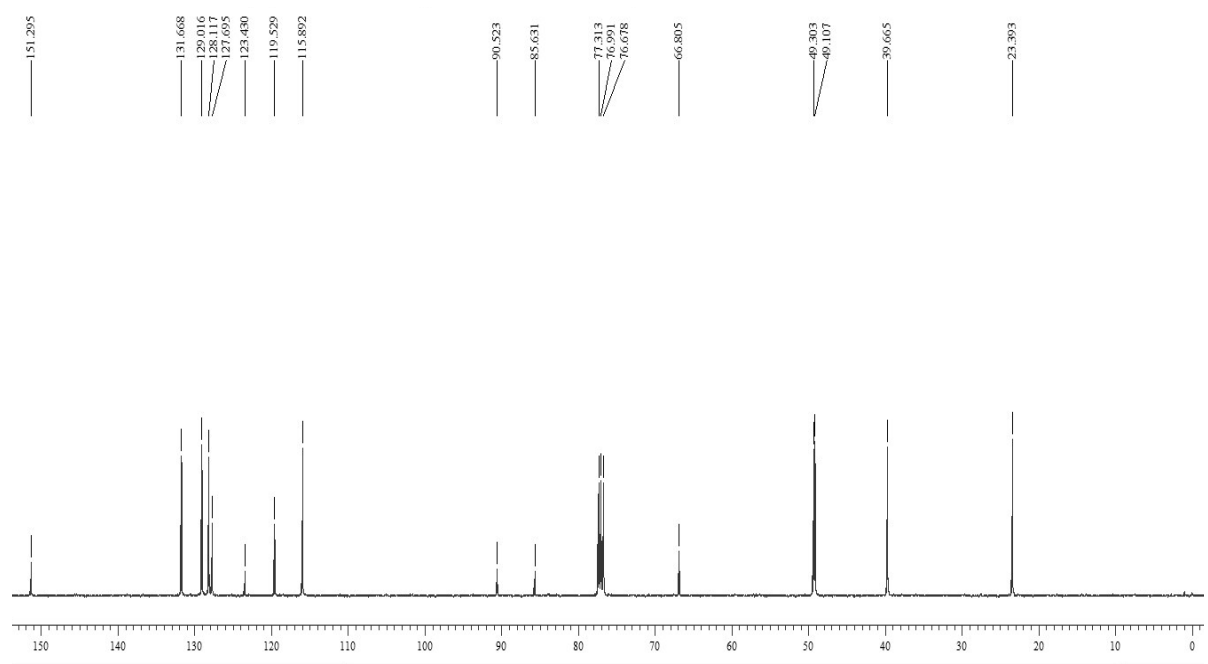
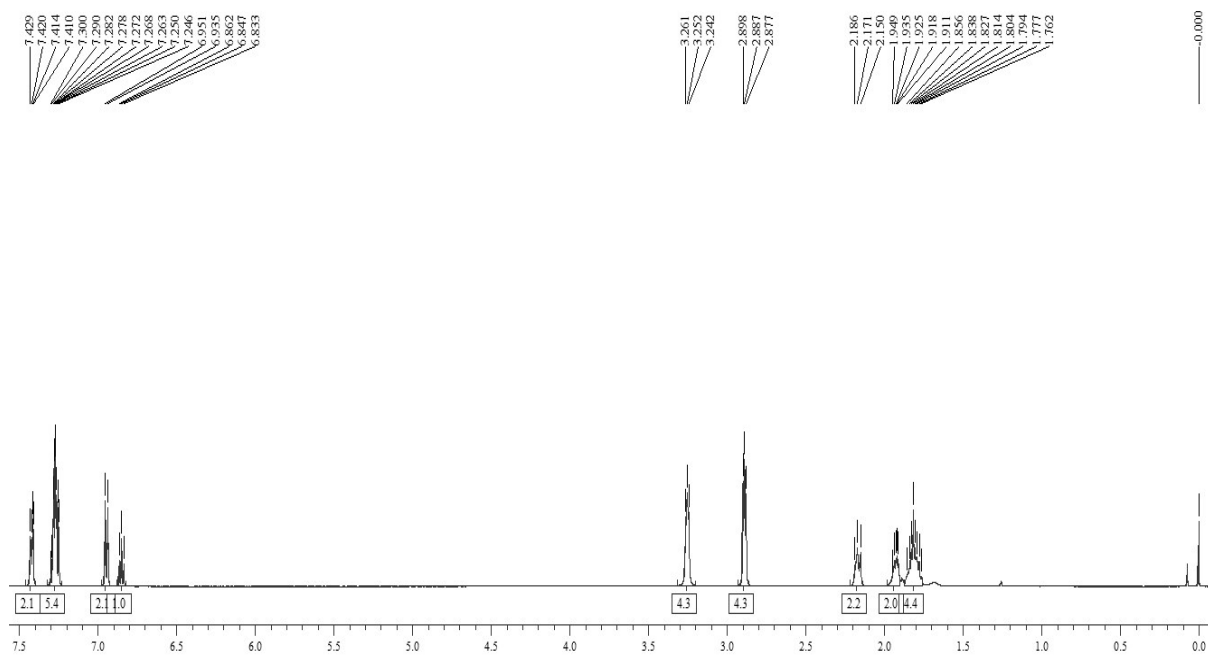
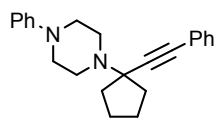


¹H & ¹³C NMR spectrum of 9b

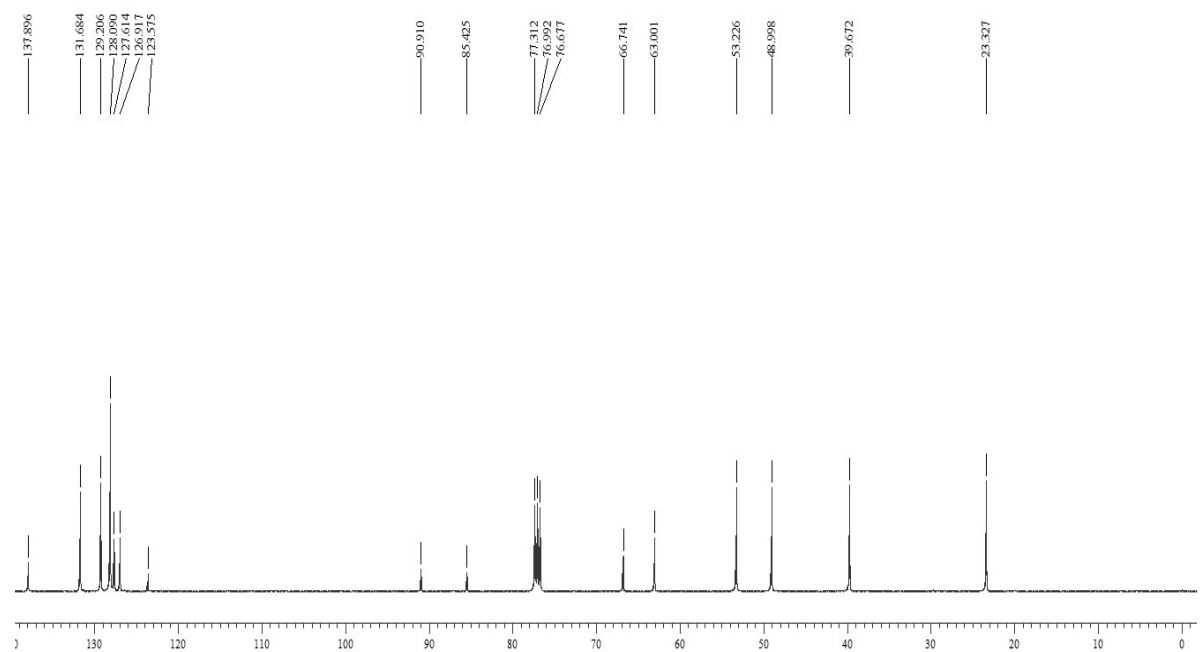
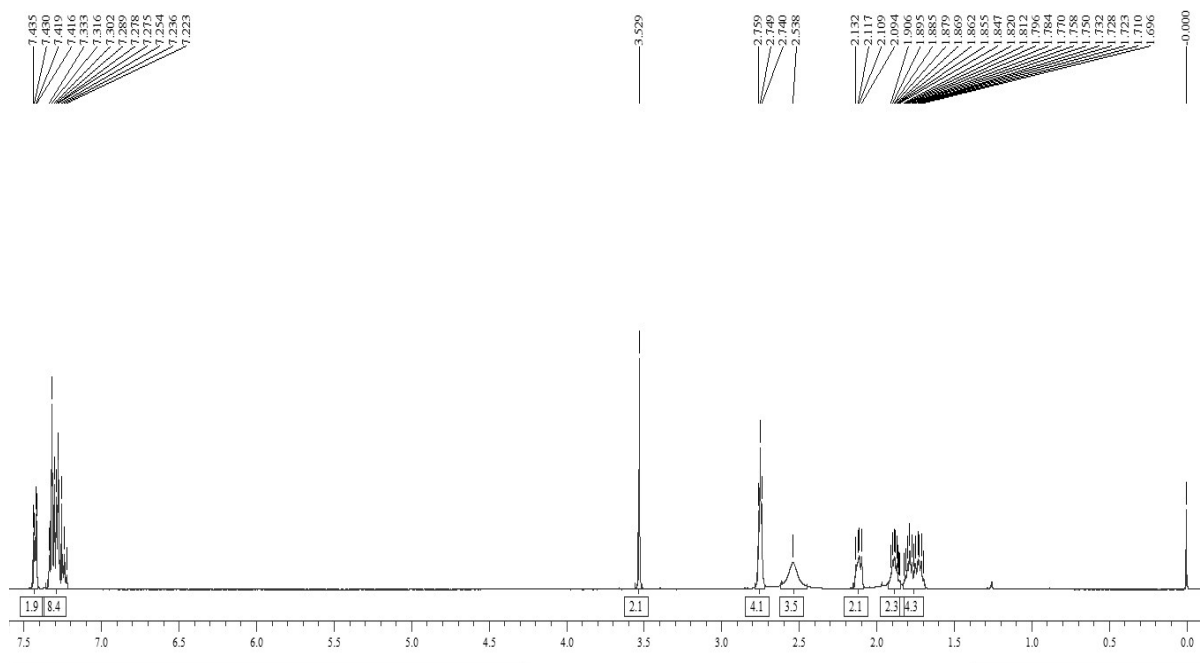
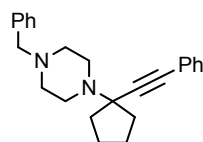




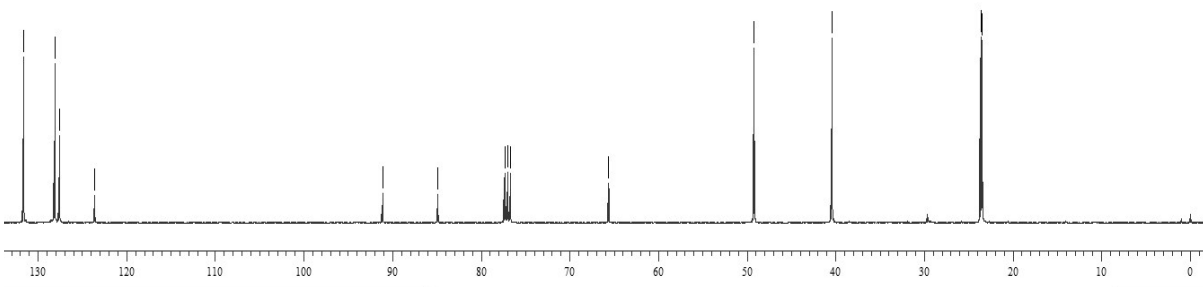
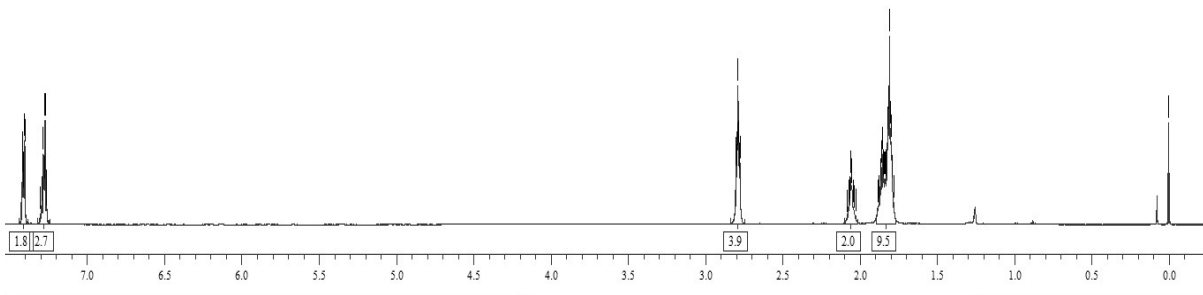
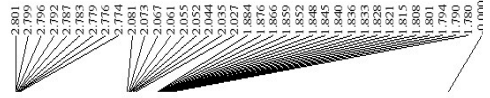
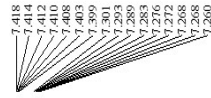
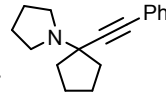
^1H & ^{13}C NMR spectrum of 9d



^1H & ^{13}C NMR spectrum of 9e



¹H & ¹³C NMR spectrum of 9f



¹H & ¹³C NMR spectrum of 9g

