

Supplementary Material

Synthesis of novel C-2 substituted imidazoline derivatives having the norbornene/dibenzobarrelene skeletons

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The synthesis of Bicyclo [2.2.1] hepta-5-ene-2,3-dicarbonitrile (1)

The dicyclopentadiene was converted into cyclopentadiene by heating in an oil bath at 180 °C. 240 mmol cyclopentadiene (15.86 g) was dissolved in methanol (100 mL) and the solution was cooled to 0 °C. To this solution, 120 mmol fumaronitrile (9.37 g) was added and stirred at 0 °C for 1 hour. After stirring for 24 hours at 25 °C, the solvent was removed under reduced pressure. The resulting solid was crystallized with ethanol.²⁴ Colorless powder; yield: 17.10 g, 118 mmol (99%); mp: 90-91 °C, (Ref [24]: 94-95 °C) 17.10 g. IR (KBr) (ν_{\max} , cm^{-1}): 3073, 2999, 2960, 2886, 2241, 1461, 1332, 729; ^1H NMR (400 MHz, CDCl_3): δ_{H} = 6.39 (2H, s), 3.46 (2H, d, J = 12.8 Hz), 3.19 (1H, m), 2.52 (1H, m), 1.79 (1H, dd, A part of AB system, J = 2.0 Hz), 1.96 (1H, dd, B part of AB system, J = 5.9, 3.4 Hz); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} = 137.7, 137.2 (=CH), 119.9, 119.5 (CN), 48.4, 46.3 (CH), 47.3 (CH_2), 34.8, 34.6 (CH); Anal. calc. for $\text{C}_9\text{H}_8\text{N}_2$ (144,18): C, 74.98; H, 5.59; N, 19.43; found C, 75.04; H, 5.73; N, 19.61 %.

The synthesis of 9,10-Dihydro-9,10-ethanoanthracene-11,12-dicarbonitrile (2)

The mixture of anthracene (1.00 g, 5.61 mmol) and of fumaronitrile (0.44 g, 5.61 mmol) in benzene (30 mL) was refluxed for 24 hours. After the removal of the solvent in vacuo, the residue was crystallized from benzene.²⁶ Colorless powder; yield: 1.29 g, 5.03 mmol (90%); mp: 269-270 °C {Ref [24]: 259 °C}; IR (KBr) (ν_{\max} , cm^{-1}): 3082, 3046, 3026, 2943, 2241, 1460, 1201, 1171, 760, 747; ^1H NMR (400 MHz, CDCl_3): δ_{H} = 7.52-7.49 (2H, dd, J = 6.4, 2.2 Hz), 7.42-7.40 (2H, m), 7.33-7.29 (4H, m), 4.69 (2H, s), 3.18 (2H, s); ^{13}C NMR (100 MHz, CDCl_3): δ_{C} = 139.3, 137.4 (Ar- C_{ipso}), 128.0, 127.9, 125.8, 124.3 (Ar. CH), 118.6 (CN), 46.4 ($\text{CH}_{\text{bridgehead}}$), 35.5 (CH); Anal. calc. for $\text{C}_{18}\text{H}_{12}\text{N}_2$ (256,31): C, 84.35; H, 4.72; N, 10.93; found C, 84.52; H, 4.87; N, 11.13 %.

The synthesis of Bicyclo [2.2.1] hept-5-ene-2,3 dicarboxylic acid (13)

This compound was prepared according a reported procedure²⁵. 15.1 mmol cyclopentadiene, which was obtained by cleavage of dicyclopentadiene at 180 °C, and 12.6 mmol fumaric acid were dissolved in the mixture of acetone-water (50 mL, 10 :1) and stirred at 50 °C for 24 hours. The solvent was removed under reduced pressure. The resulting solid was crystallized from the mixture of acetone-water (10: 1). Compound 13 was obtained with quantitative yields as colorless powder 2.30 grams. Its melting point corresponds well with the reported one. Colorless powder; yield: 2.30 g, 12.63 mmol (100%); mp: 174 °C {Ref [25]: 167-173 °C}; IR (KBr) (ν_{\max} , cm^{-1}): 3078, 2997, 2984, 2876, 1682, 1422, 1275, 1216, 925, 729, 687; ^1H NMR (400 MHz, CDCl_3): δ_{H} = 12.32 (2H, s), 6.30 (1H, dd, J = 5.6, 3.1 Hz), 6.07 (1H, dd, J = 5.6, 2.5 Hz), 3.19-3.17 (2H, m), 3.04 (1H, s), 2.43 (1H, dd, J = 4.1, 1.3 Hz), 1.51 (1H, d, A part of AB system, J = 8.5 Hz), 1.34 (1H, dd, B part of AB system, J = 8.5, 1.5 Hz). ^{13}C NMR (100 MHz, CDCl_3): δ_{C} = 175.8, 174.6 (C=O), 138.0, 135.4 (C=C), 47.5 (CH_2), 47.9, 47.4 (CH), 47.2, 45.4 ($\text{CH}_{\text{bridgehead}}$); Anal. calc. for $\text{C}_9\text{H}_{10}\text{O}_4$ (182,18): C, 59.34; H, 5.53; found C, 59.56; H, 5.70 %.

General synthesis of C-2 aromatic-heteroaromatic substituted imidazolines 6-10

To a solution of the requisite aldehyde (0.87 mmol) in CH₂Cl₂ (30 mL), ethylenediamine (1.05 mmol) was added and stirred at 0 °C in an argon atmosphere for 2 hours. *N*-bromosuccinimide (NBS, 1.05 mmol) was slowly added to the mixture. After stirring at room temperature overnight, % NaOH solution was added until pH 8-10. The mixture was extracted with CH₂Cl₂. The organic phase was dried with Na₂SO₄ and the solvent was removed under reduced pressure. The crude products were crystallized from methanol-ethyl acetate 1:1 solvent mixture.

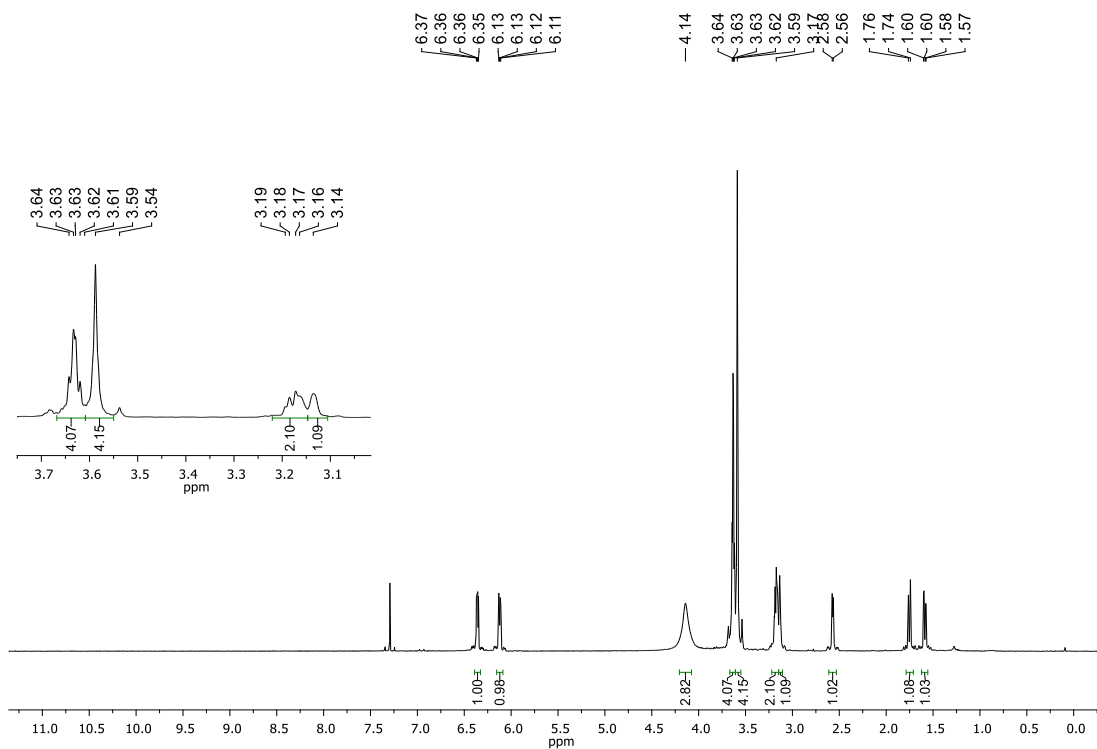
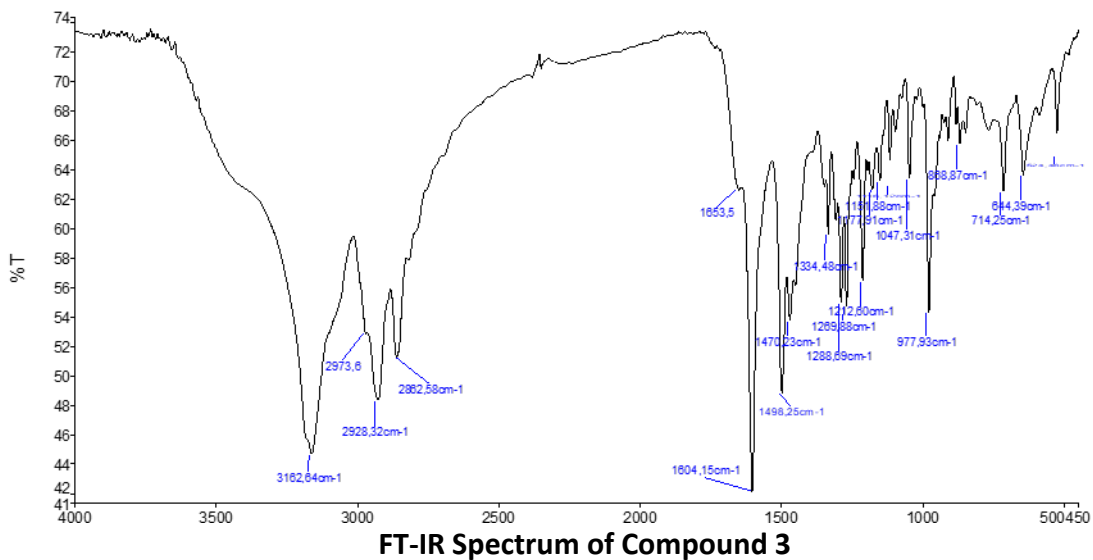
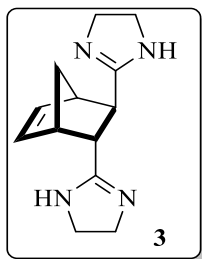
2-Phenyl-4,5-dihydro-1H-imidazole (6) Yield 96% (1.32 g, 9.03 mmol), m.p.: 98-100 °C, [Ref. 35: 100-101 °C]; IR (ATR) (ν_{\max} , cm⁻¹): 3197, 3064, 2970, 2929, 2868, 1636, 1610, 1598, 1573, 1508, 1468, 1269, 981. ¹H NMR (400 MHz, CDCl₃) δ_{H} : 7.80-7.78 (2H, m), 7.45-7.38 (3H, m), 4.82 (1H, br), 3.77 (4H, s). ¹³C NMR (100 MHz, CDCl₃) δ_{C} : 164.9 (C=N), 130.7, 128.5, 127.0 (CH_{Ar}), 130.3 (C_{Ar-ipso}), 50.3 (CH₂). Anal. calc. for C₉H₁₀N₂ (146,19): C, 73.94; H, 6.89; N, 19.16; found C, 74.06; H, 7.11; N, 19.48.

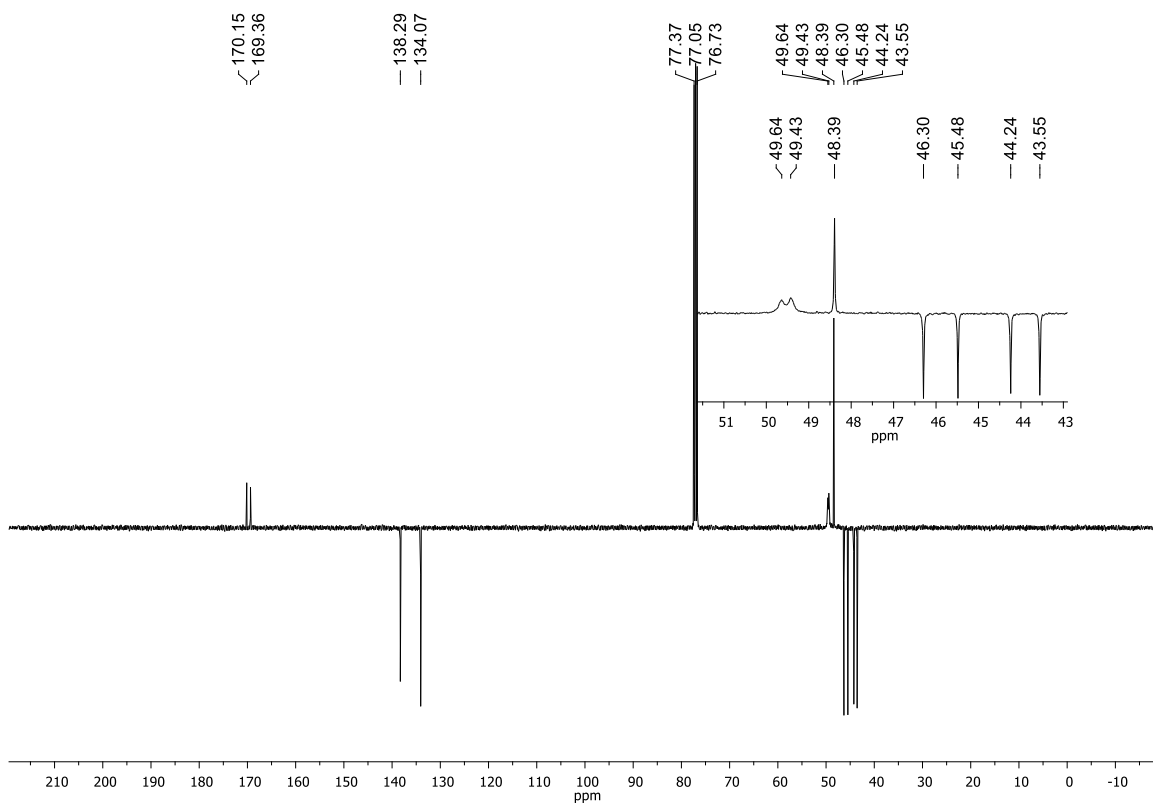
2-(3-Chlorophenyl)-4,5-dihydro-1H-imidazole (7) Yield 94% (1.26 g, 6.98 mmol), m. p.: 137-138 °C, [Ref. 35: 138-139 °C]; IR (KBr) (ν_{\max} , cm⁻¹): 3145, 3075, 2964, 2924, 2857, 1608, 1597, 1563, 1271, 757. ¹H NMR (400 MHz, CDCl₃) δ_{H} : 7.86 (1H, d, J = 1.2), 7.81 (1H, dd, J = 7.6, 1.2), 7.55-7.53 (1H, m), 7.08 (1H, br), 3.63 (4H, s). ¹³C NMR (100 MHz, CDCl₃) δ_{C} : 162.8 (C=N), 133.5, 133.1 (C_{Ar-ipso}), 130.7, 130.5, 127.3, 126.2 (CH_{Ar}), 50.2 (CH₂). Anal. calc. for C₉H₉ClN₂ (180,64): C, 59.84; H, 5.02; Cl, 19.63; N, 15.51; found C, 59.75; H, 5.26; N, 15.86.

2-(4-Methoxyphenyl)-4,5-dihydro-1H-imidazole (8) Yields 90% (1.16 g, 6.58 mmol), m. p.: 138-139 °C, [Ref. 35: 138-139 °C]; IR (KBr) (ν_{\max} , cm⁻¹): 3111, 3011, 2929, 2870, 2835, 1602, 1523, 1491, 1252, 1172, 1032, 841. ¹H NMR (400 MHz, CDCl₃) δ_{H} : 7.73-7.70 (2H, m), 6.89-6.88 (2H, m), 4.91 (1H, br), 3.82-3.80 (3H, d, J = 5.2), 3.73 (4H, s). ¹³C NMR (100 MHz, CDCl₃) δ_{C} : 161.5 (C=N), 161.4, 123.0 (C_{Ar-ipso}), 128.5, 113.7 (CH_{Ar}), 55.3 (CH₃). Anal. calc. for C₁₀H₁₂N₂O (176,22): C, 68.16; H, 6.86; N, 15.90; found C, 68.41; H, 7.13; N, 16.07.

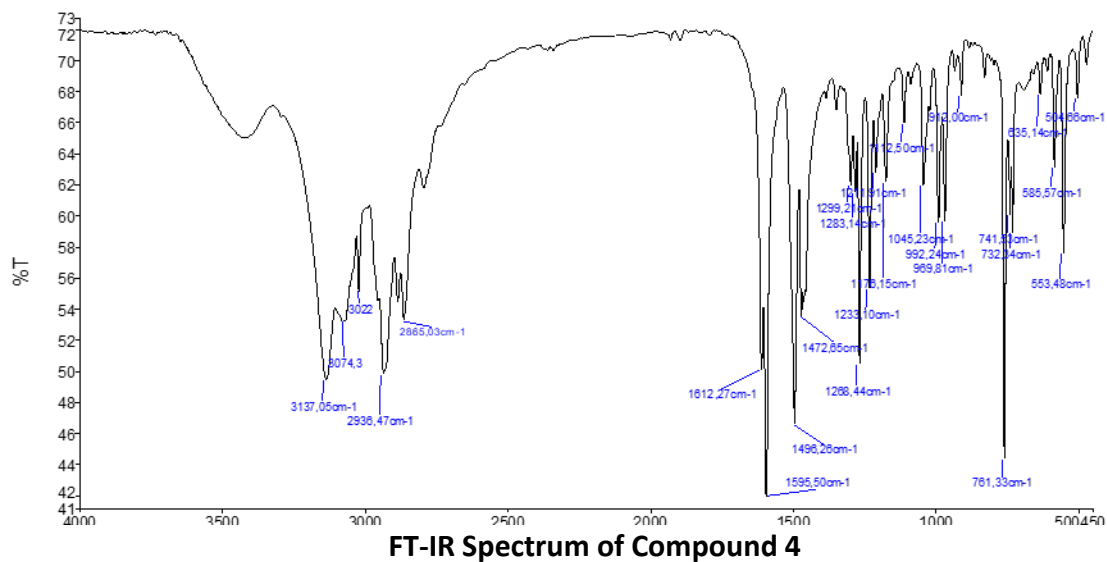
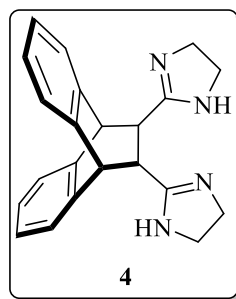
2-(Thiophen-2-yl)-4,5-dihydro-1H-imidazole (9) Yield 92% (1.24 g, 8.15 mmol), m. p.: 179-181 °C, [Ref. 35: 180-181 °C]; IR (ATR) (ν_{\max} , cm⁻¹): 3146, 3084, 2931, 2856, 1596, 1529, 1495, 1101, 707. ¹H NMR (400 MHz, DMSO-d₆) δ_{H} : 7.64-7.63 (1H, d, J = 4 Hz), 7.50-7.49 (1H, d, J = 4 Hz), 7.13-7.11 (1H, dd, J = 4, 0.8 Hz), 6.99 (1H, br), 3.58 (4H, s). ¹³C NMR (100 MHz, DMSO-d₆) δ_{C} : 159.5 (C=N), 134.9 (C_{Ar-ipso}), 129.4, 128.3, 127.9 (CH_{Ar}), 60.9 (CH₂). Anal. calc. for C₇H₈N₂S (152,22): C, 55.24; H, 5.30; N, 18.40; S, 21.06; found C, 55.52; H, 5.63; N, 18.56; S, 21.25.

Spectra of Compound 3

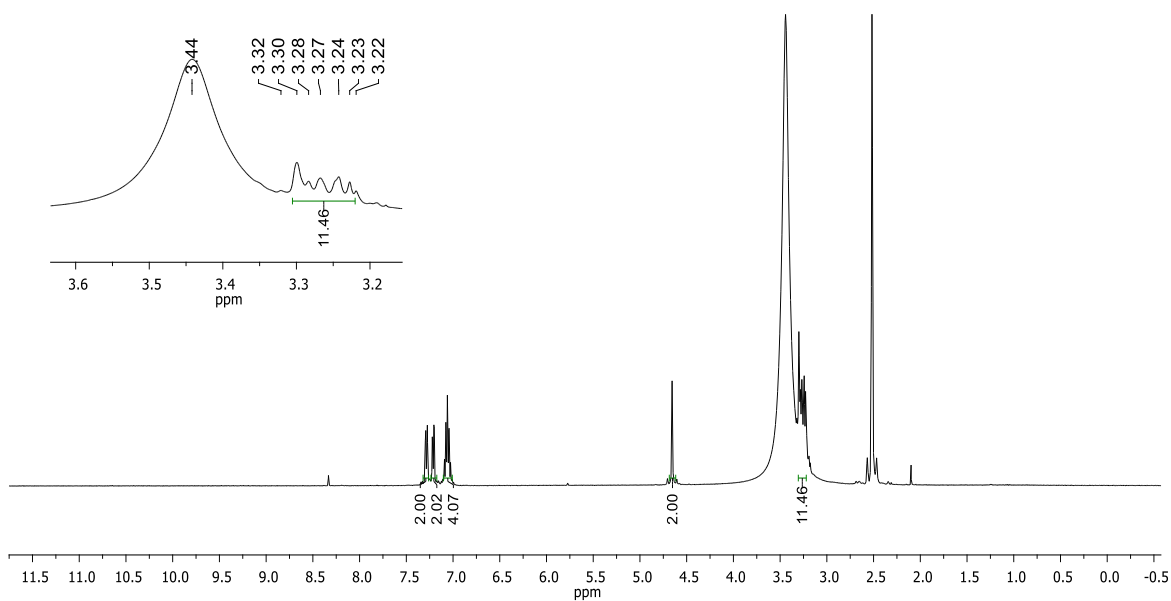


 $^{13}\text{C}_{\text{APT}}$ -NMR Spectrum of Compound 3

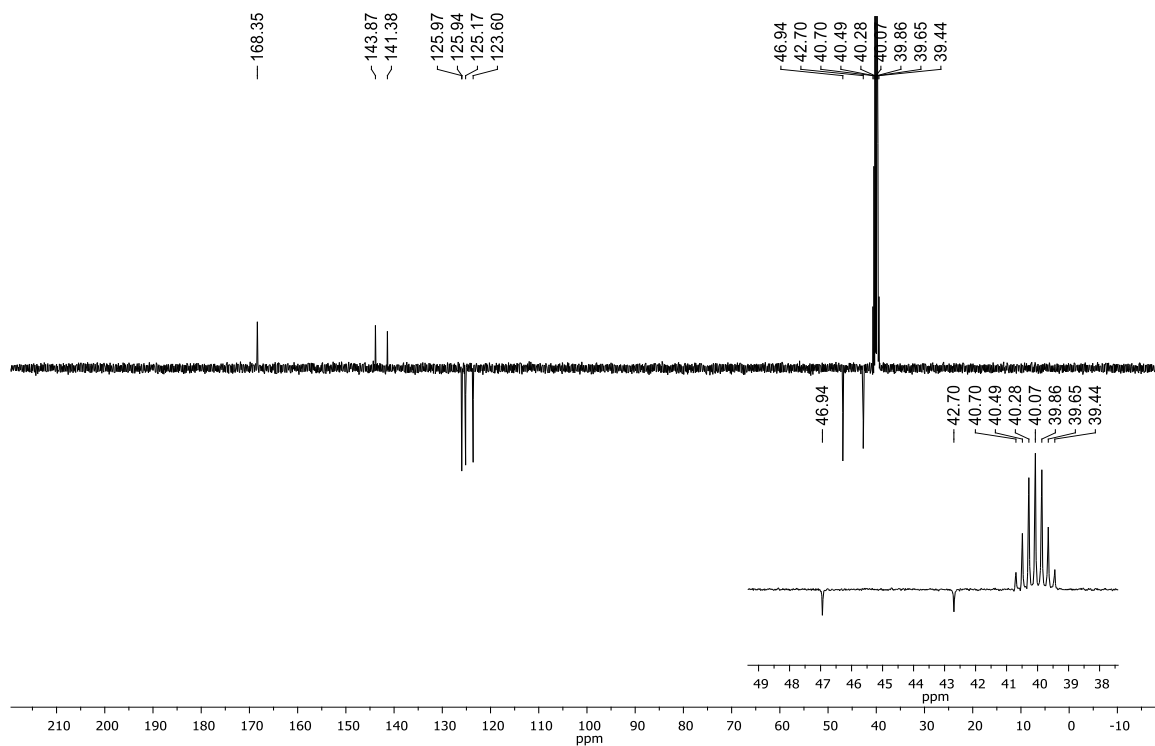
Spectra of Compound 4



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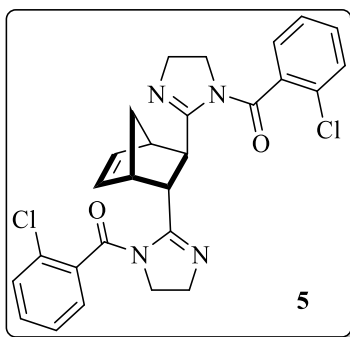


¹H-¹H-NMR Spectrum of Compound 4

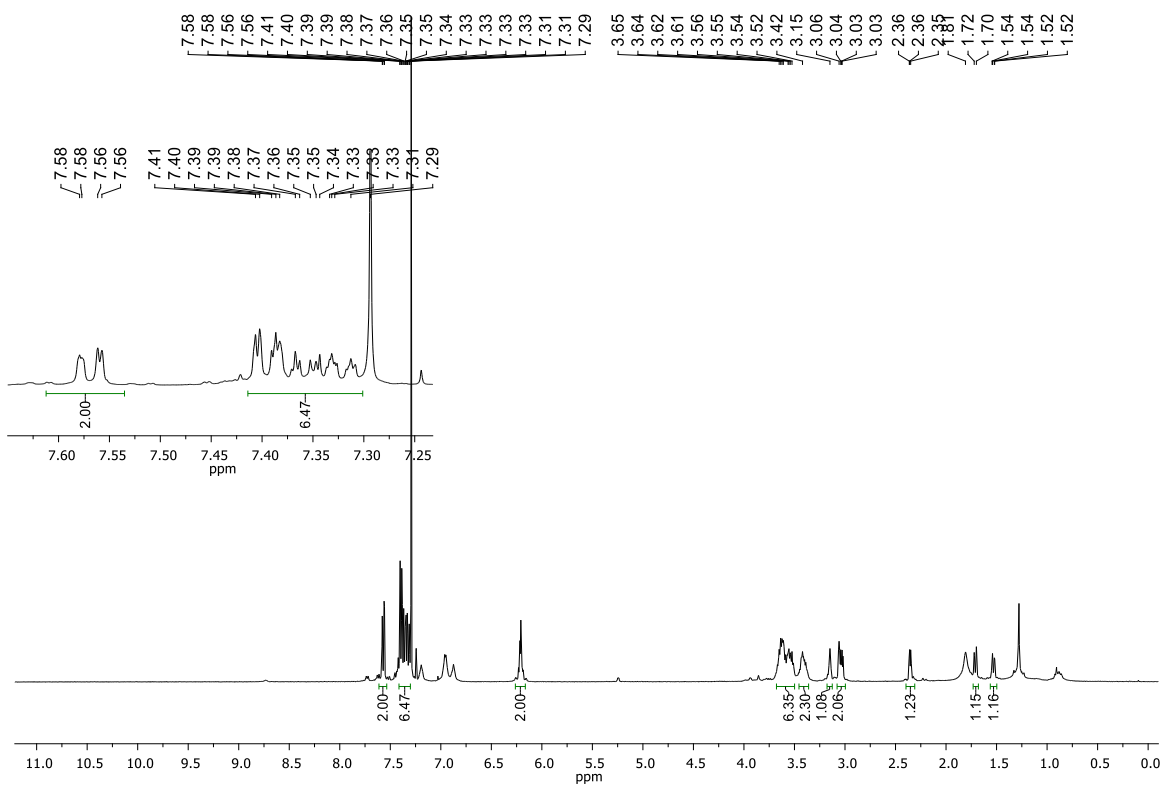
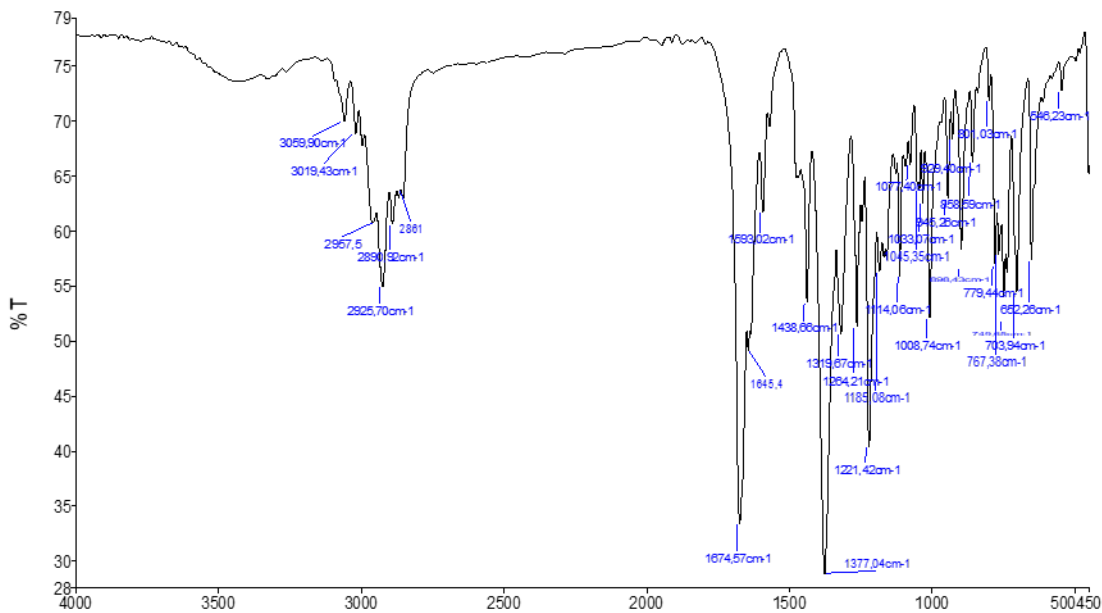


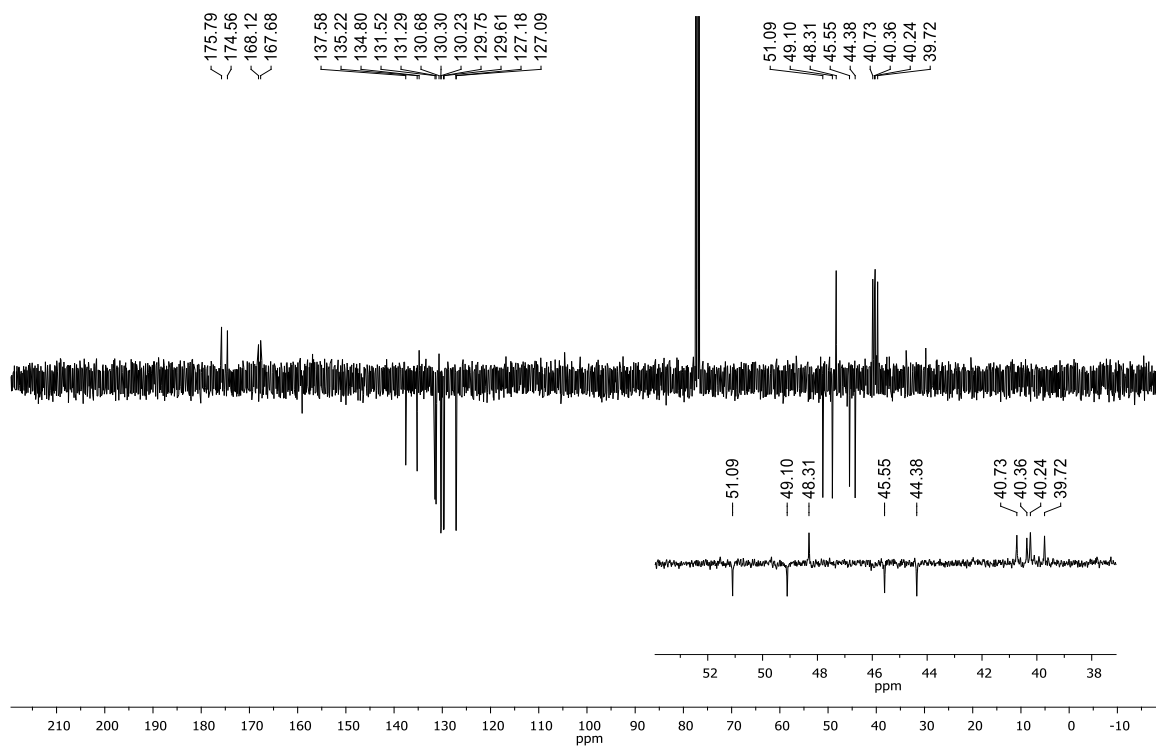
$^{13}\text{C}_{\text{APT}}$ -NMR Spectrum of Compound 4

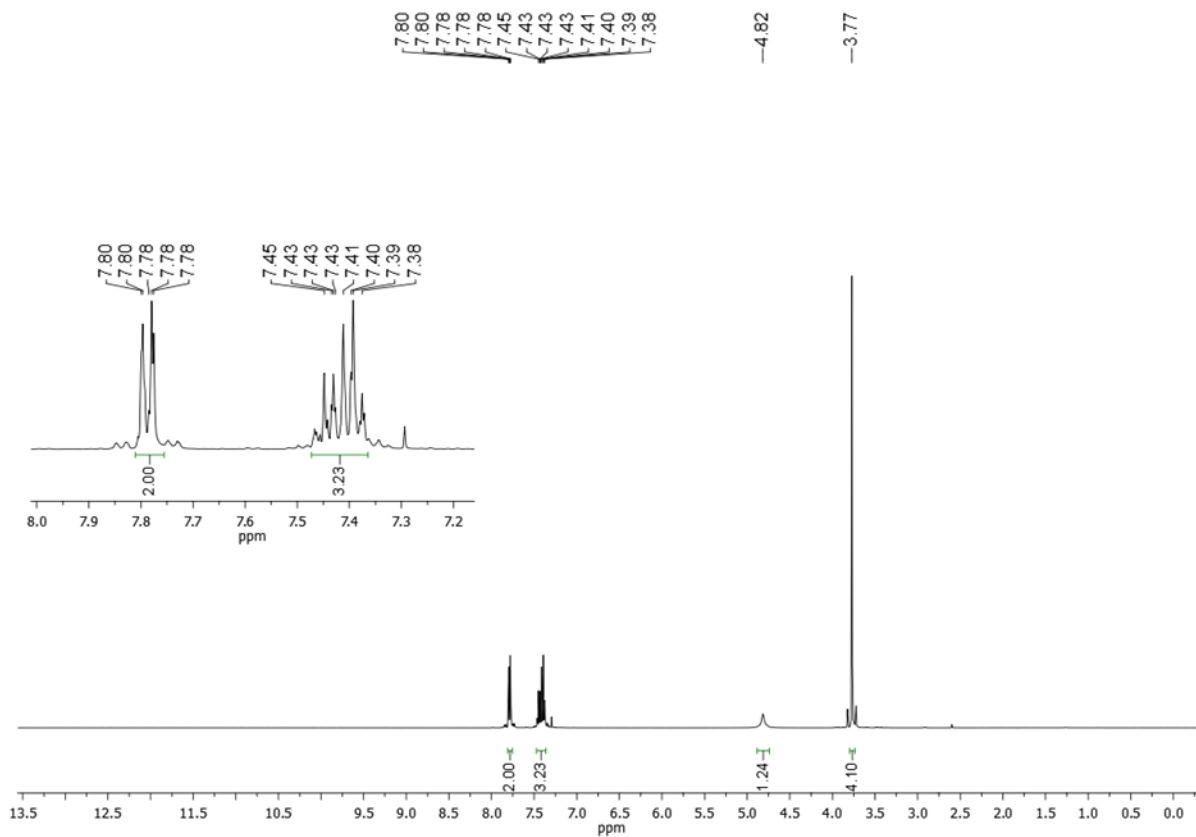
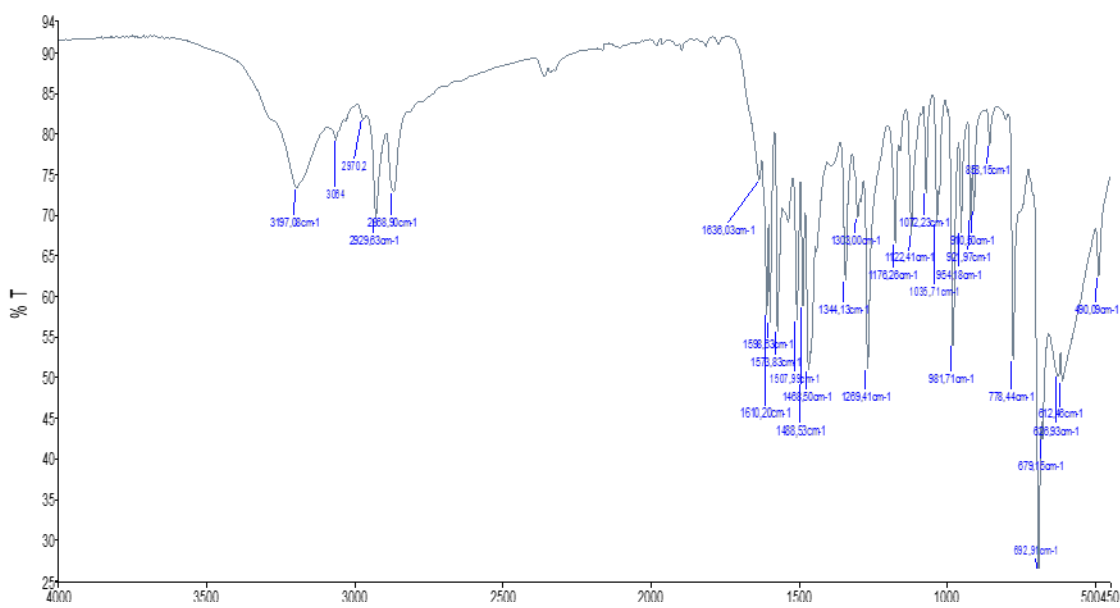
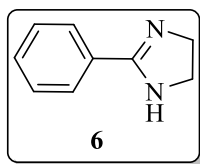
Spectra of Compound 5

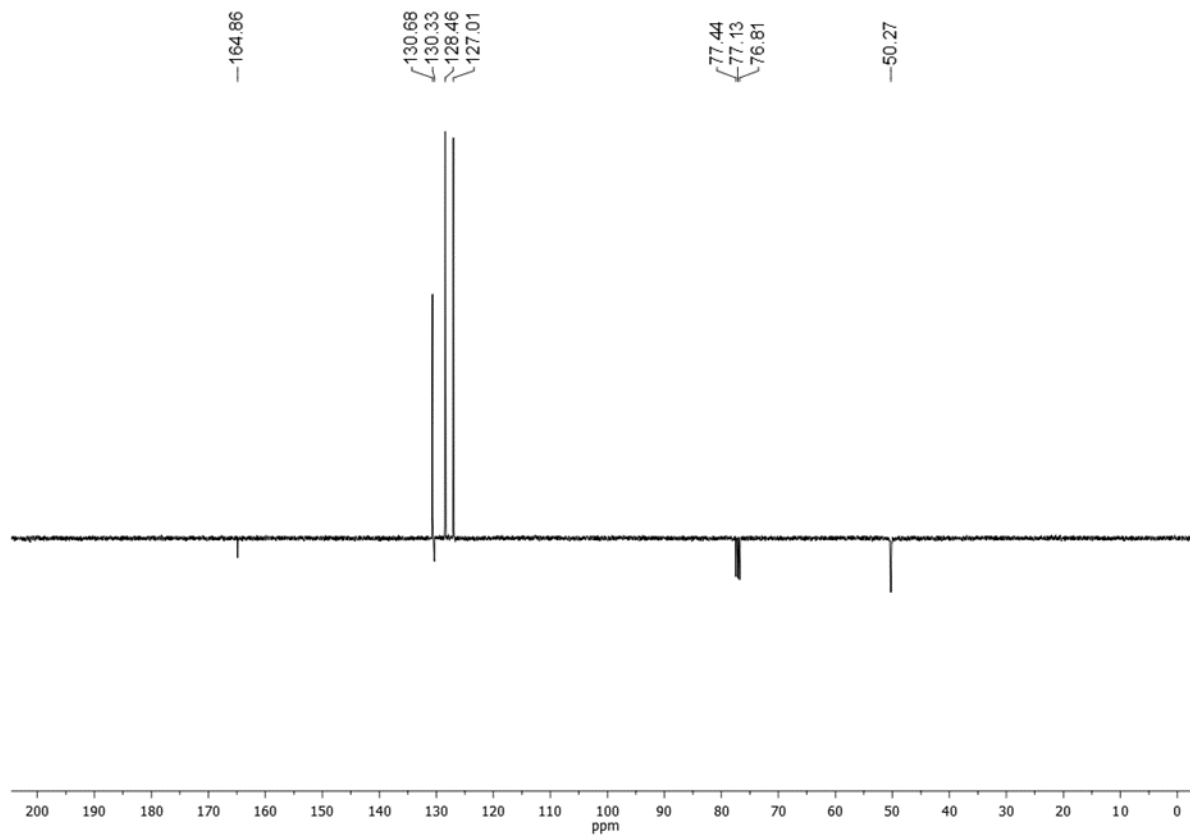


FT-IR Spectrum of Compound 5

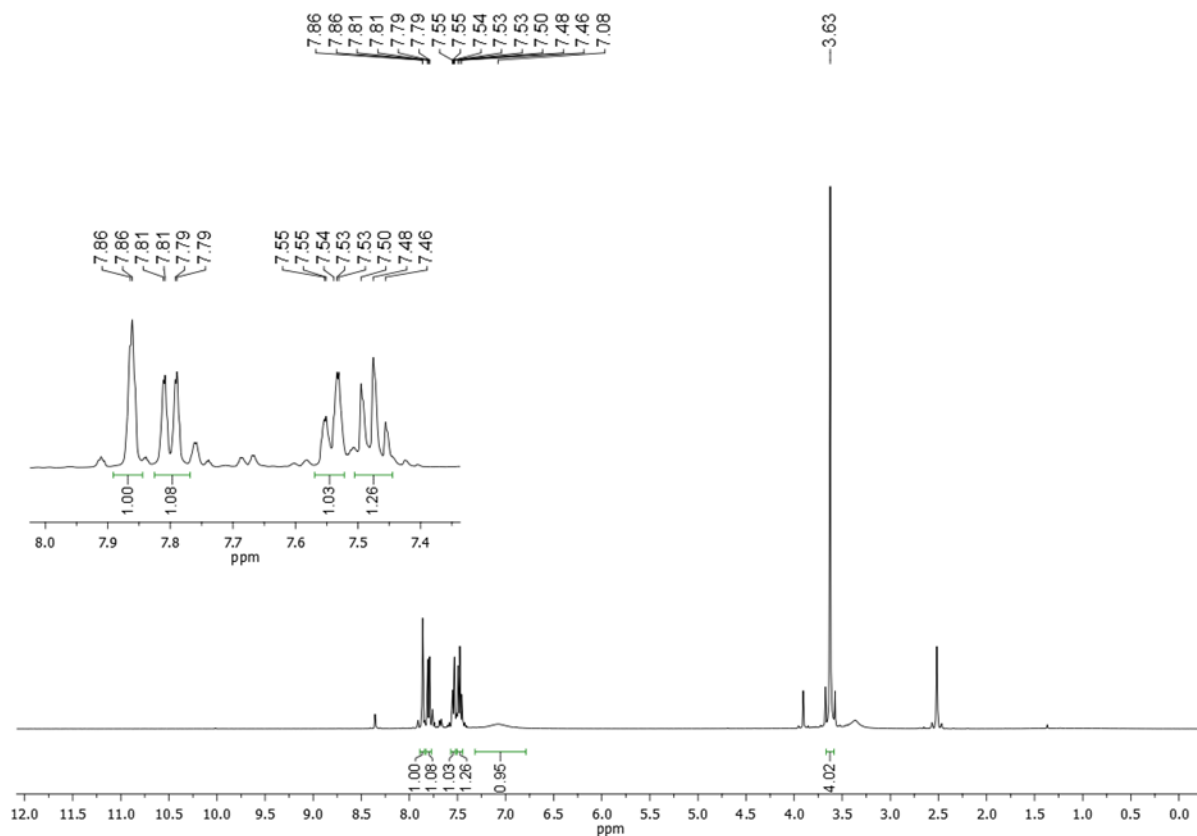
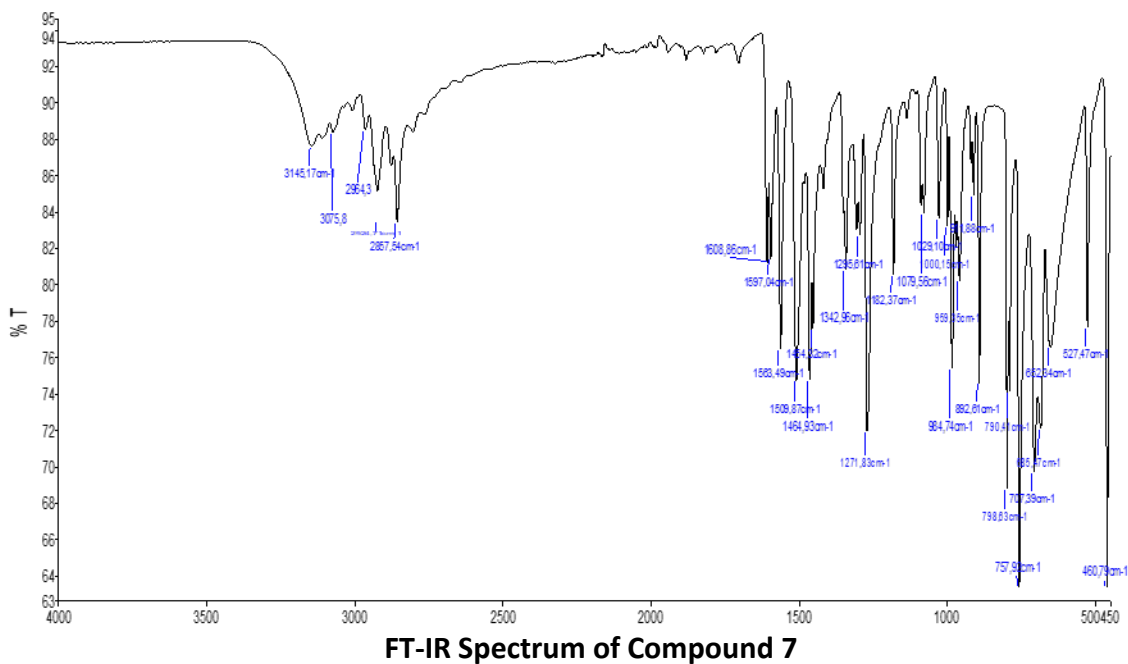
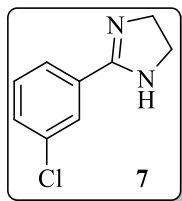
¹H-NMR Spectrum of Compound 5

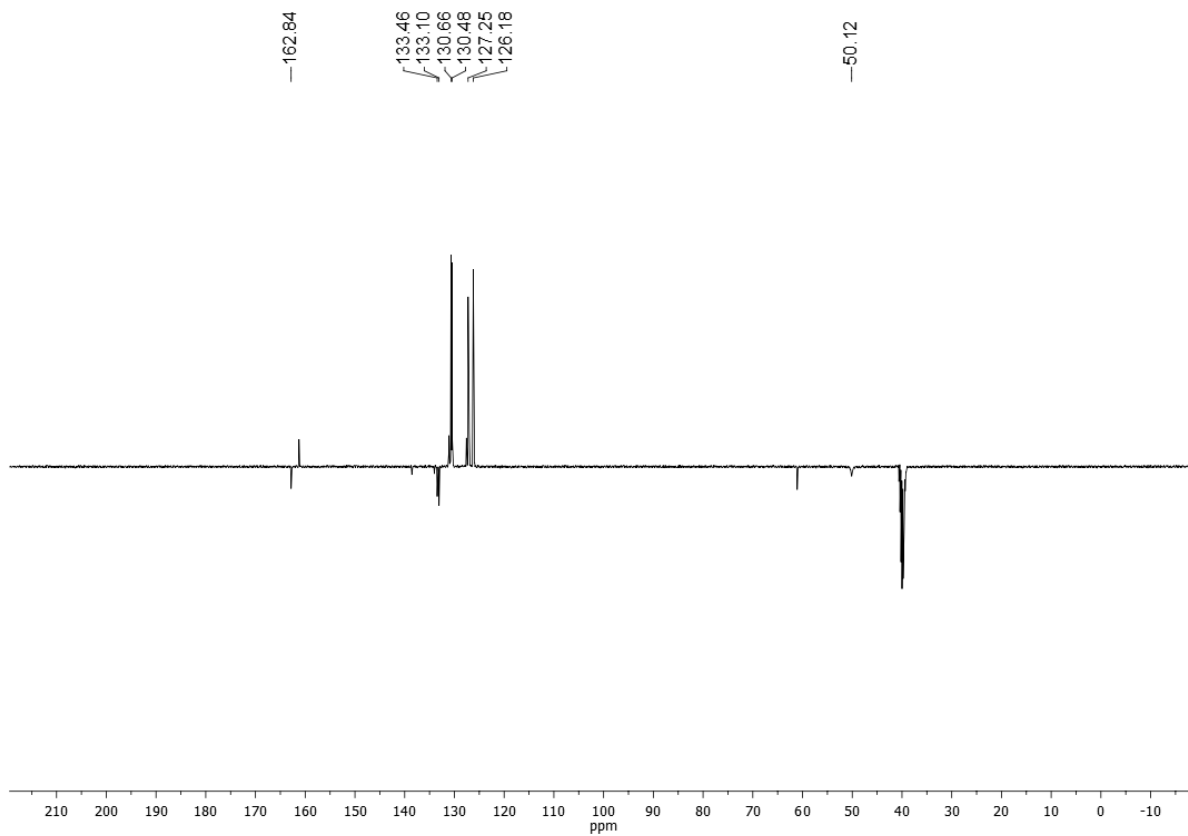
 $^{13}\text{C}_{\text{APT}}$ -NMR Spectrum of Compound 5





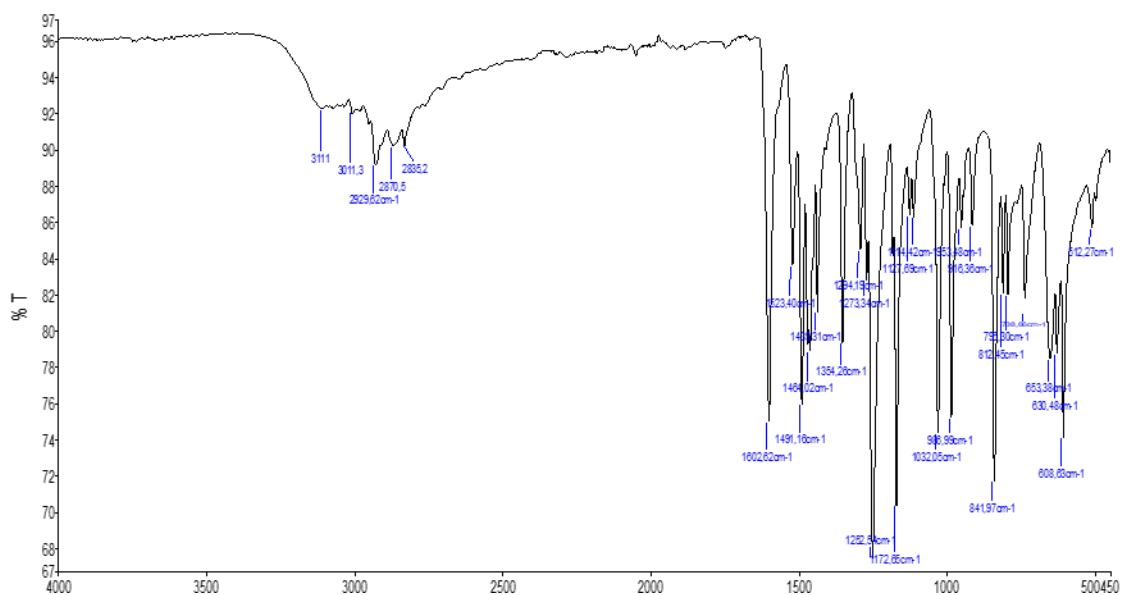
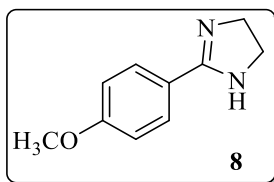
$^{13}\text{C}_{\text{APT}}$ -NMR Spectrum of Compound 6



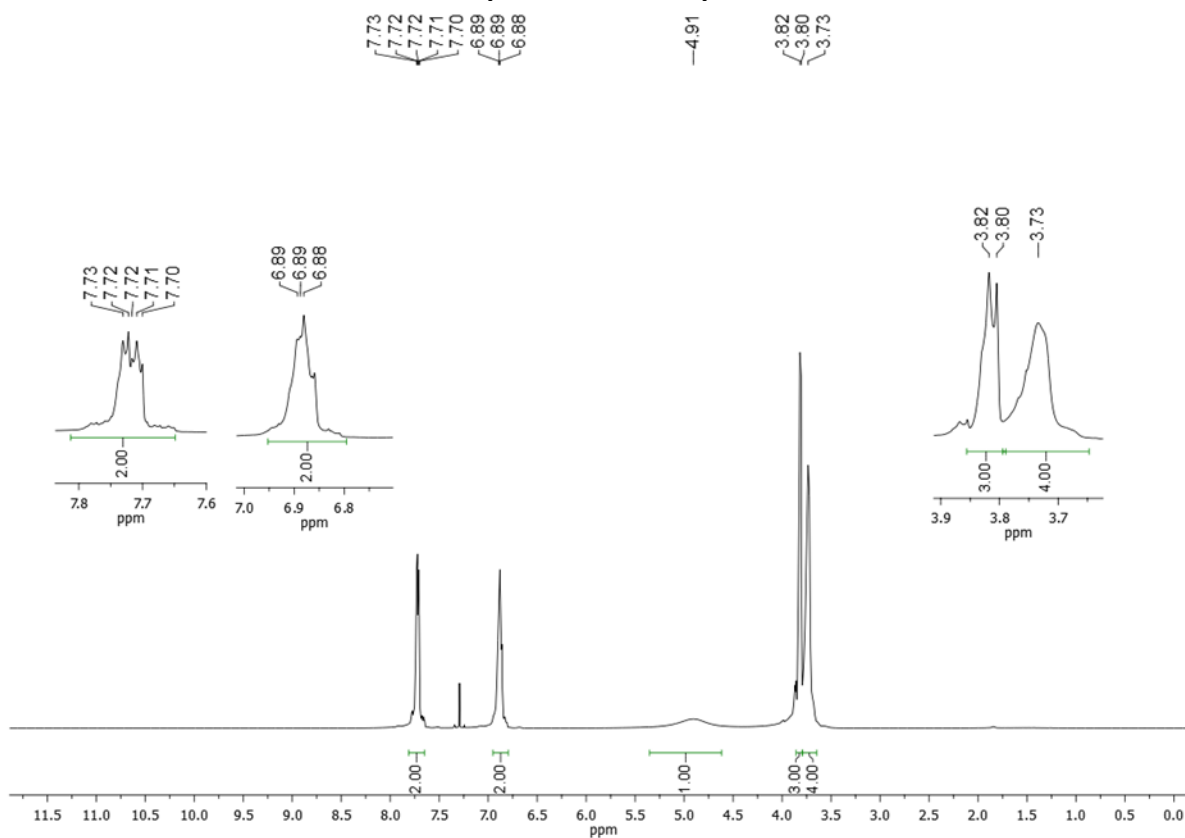


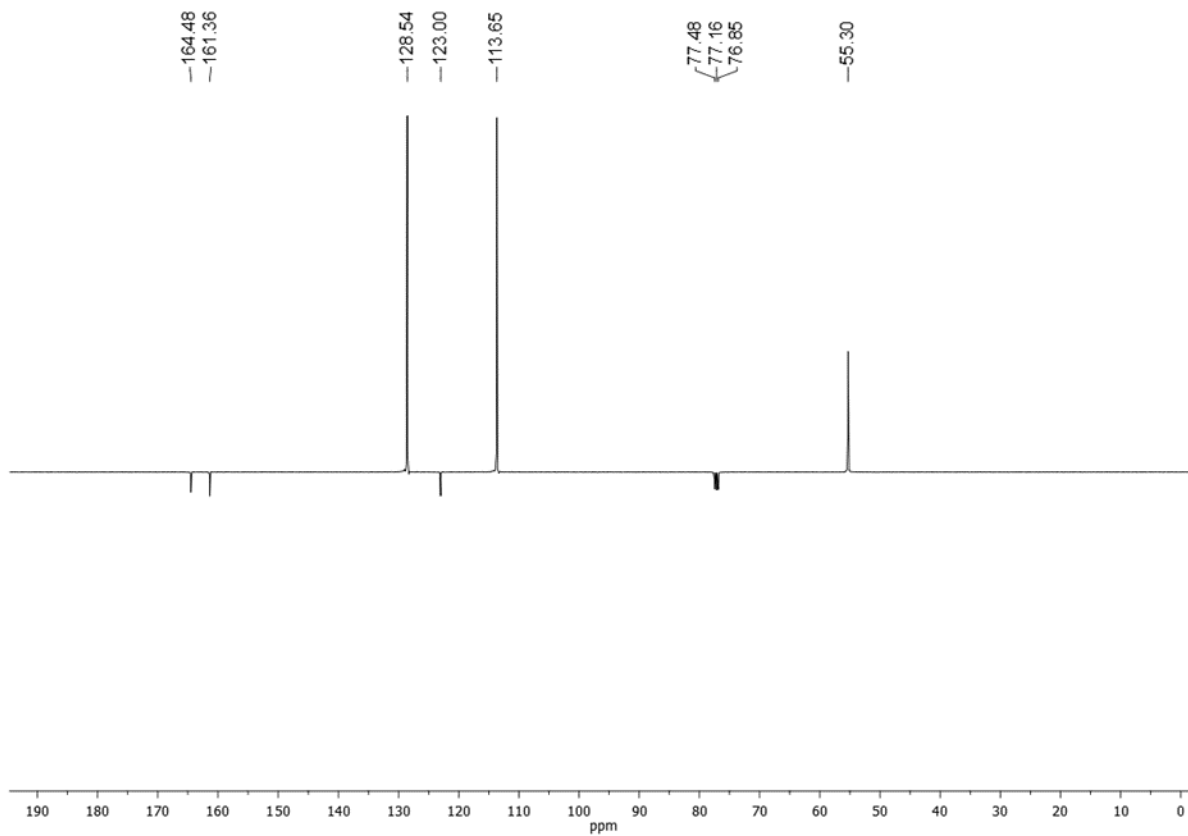
$^{13}\text{C}_{\text{APT}}$ -NMR Spectrum of Compound 7

Spectra of Compound 8



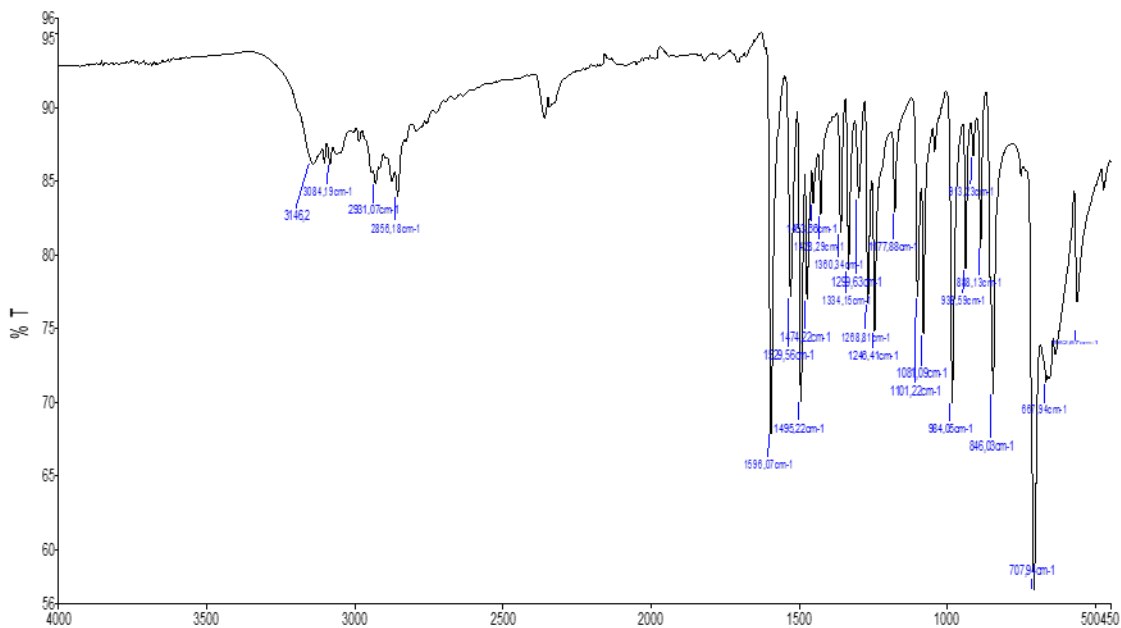
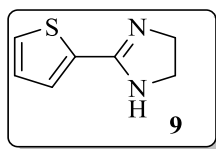
FT-IR Spectrum of Compound 8

 $^1\text{H-NMR}$ Spectrum of Compound 8

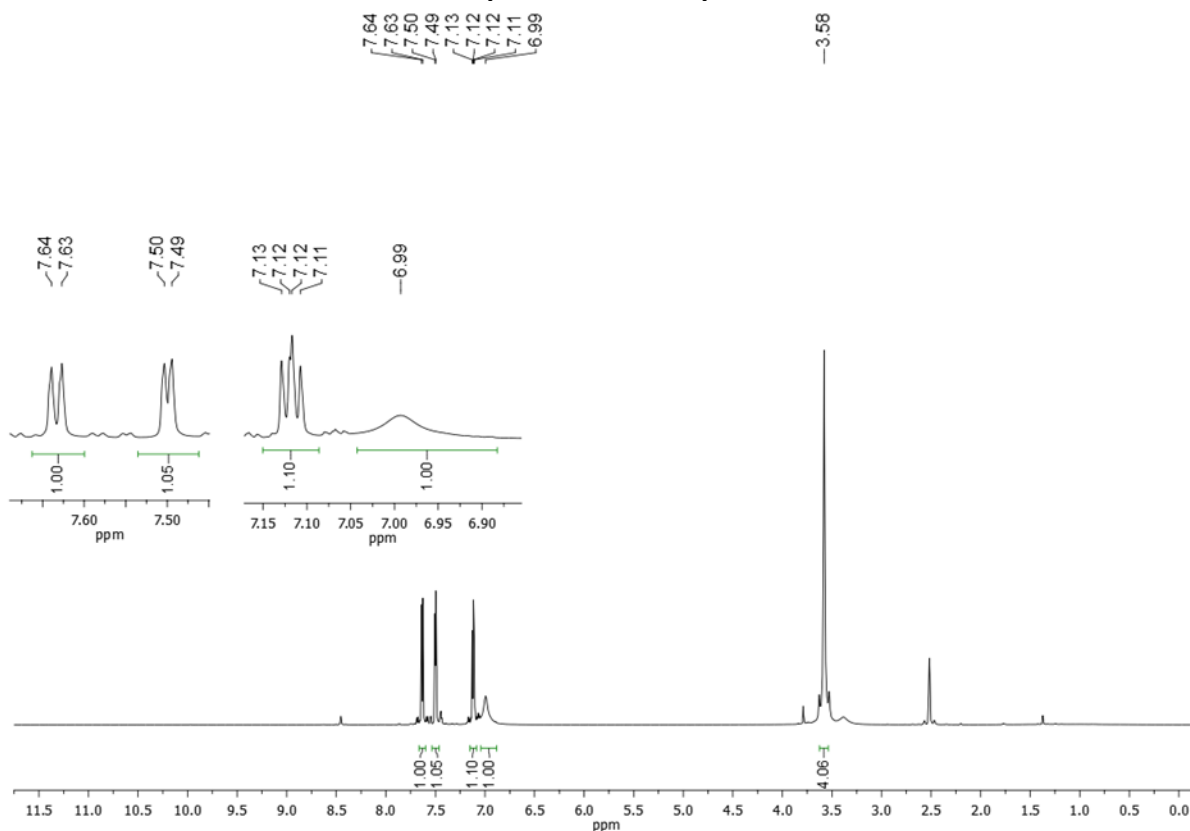


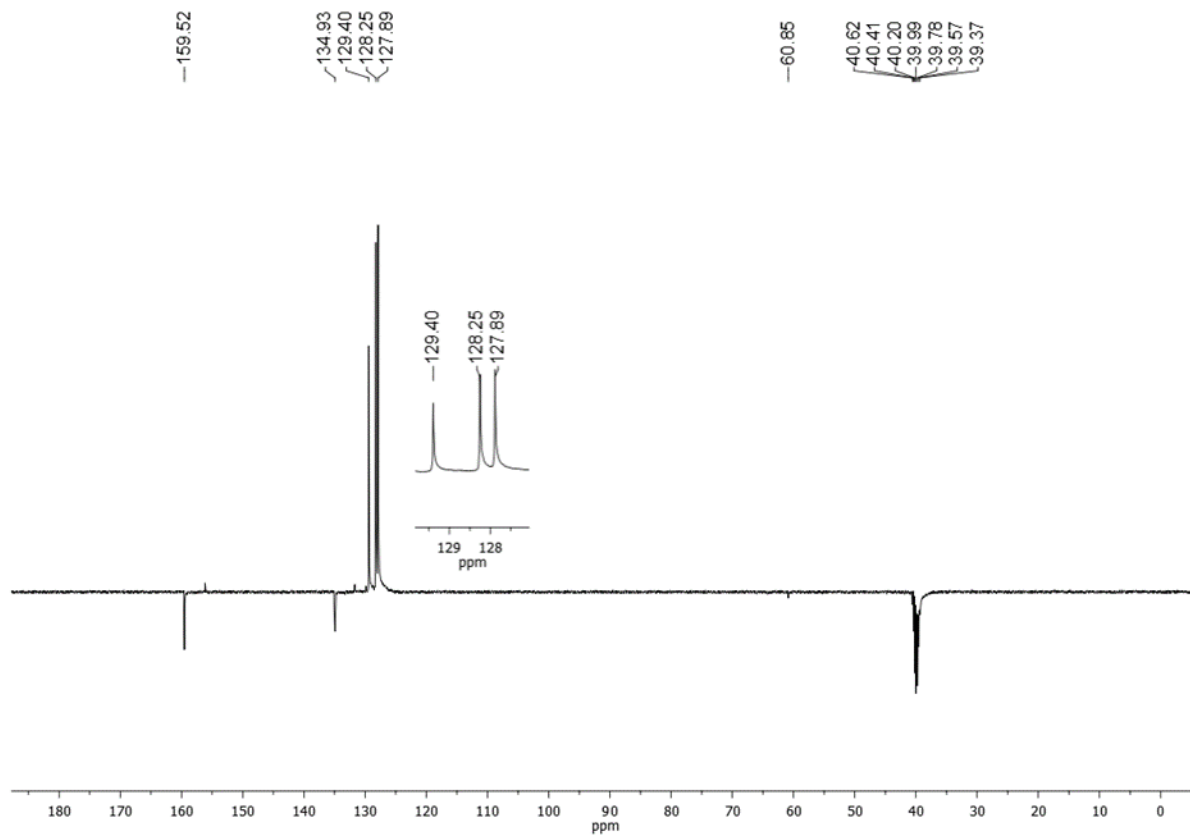
$^{13}\text{C}_{\text{APT}}$ -NMR Spectrum of Compound 8

Spectra of Compound 9



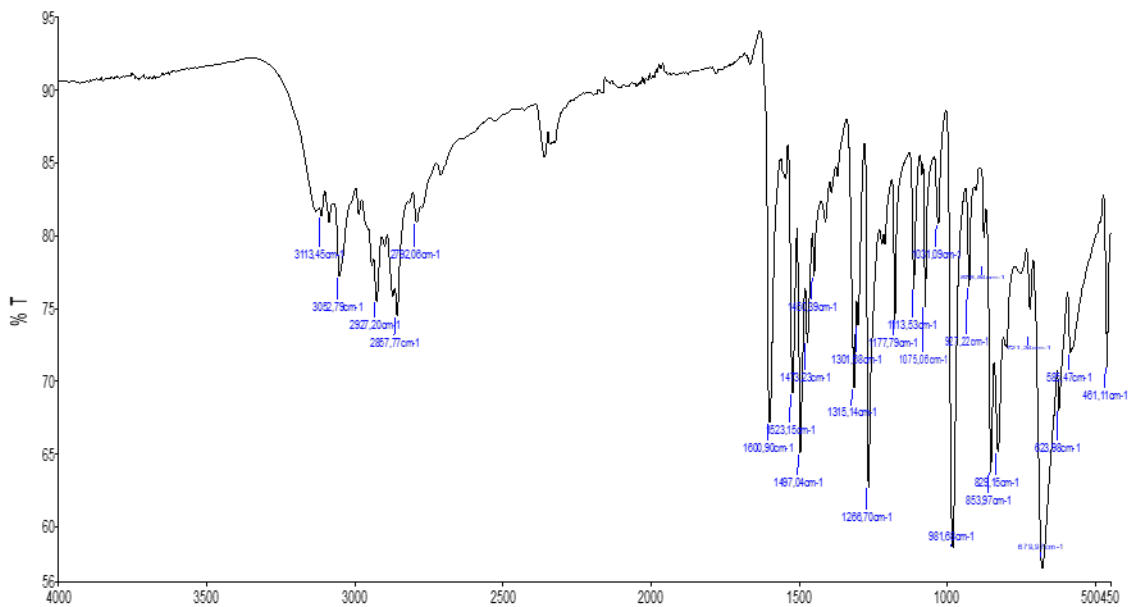
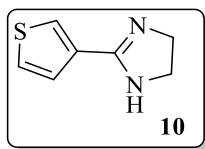
FT-IR Spectrum of Compound 9

¹H-NMR Spectrum of Compound 9

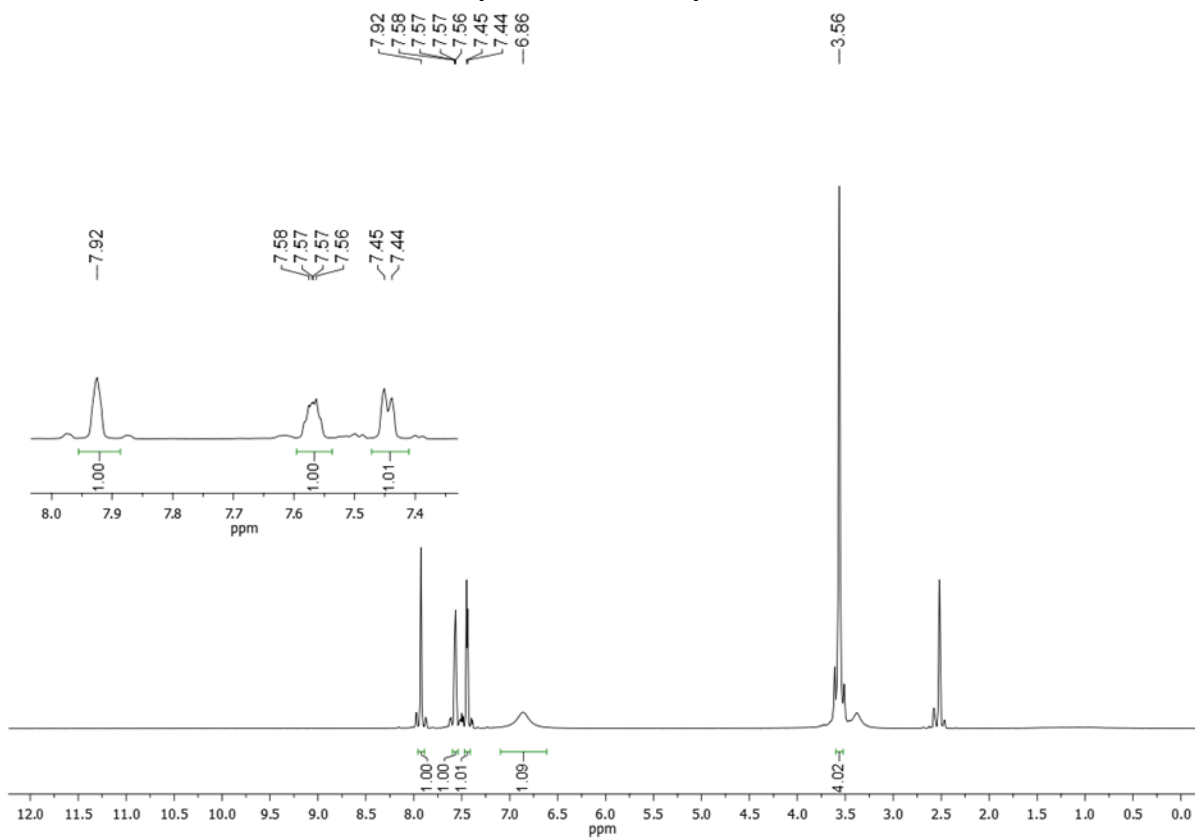


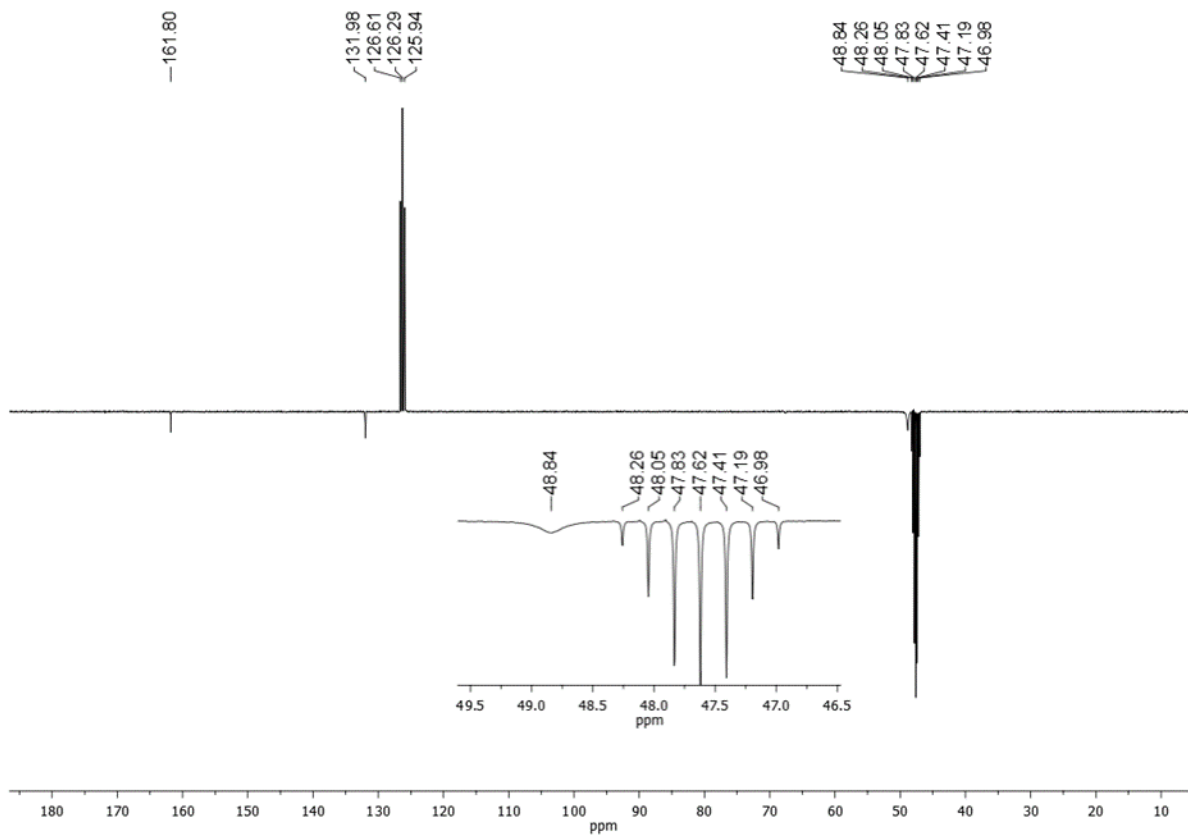
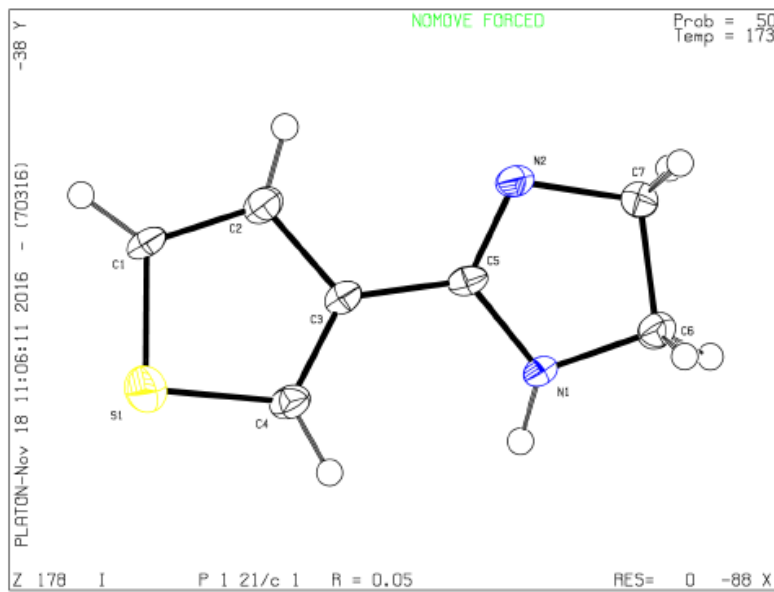
$^{13}\text{C}_{\text{APT}}$ -NMR Spectrum of Compound 9

Spectra of Compound 10



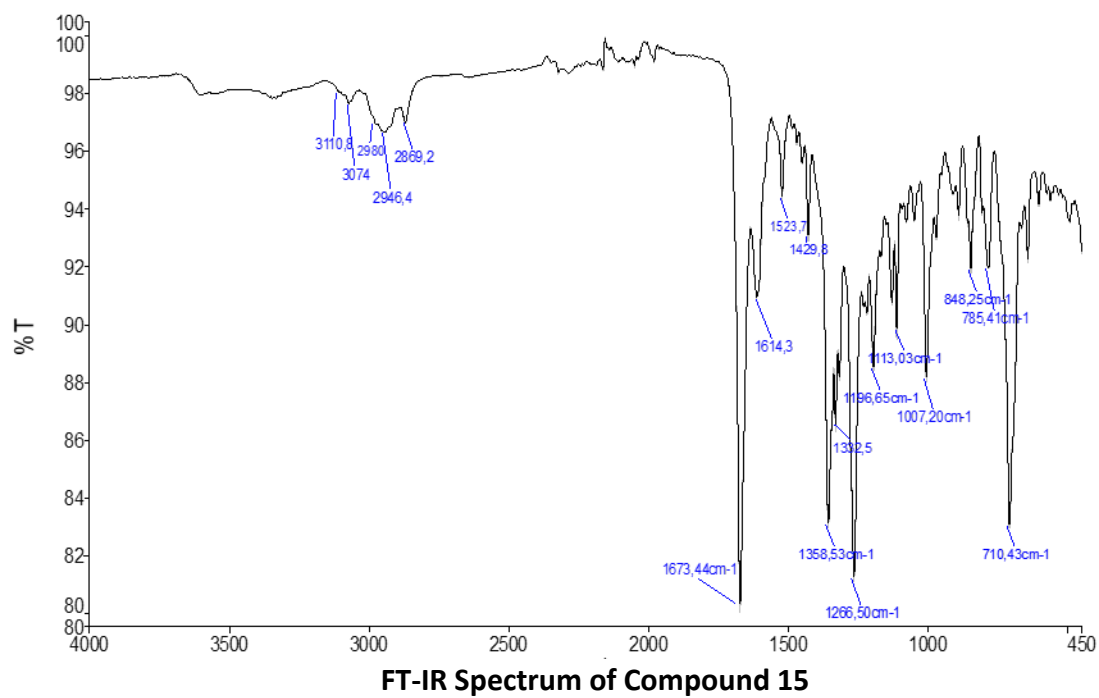
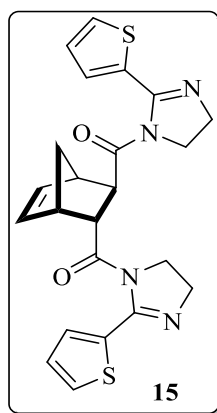
FT-IR Spectrum of Compound 10

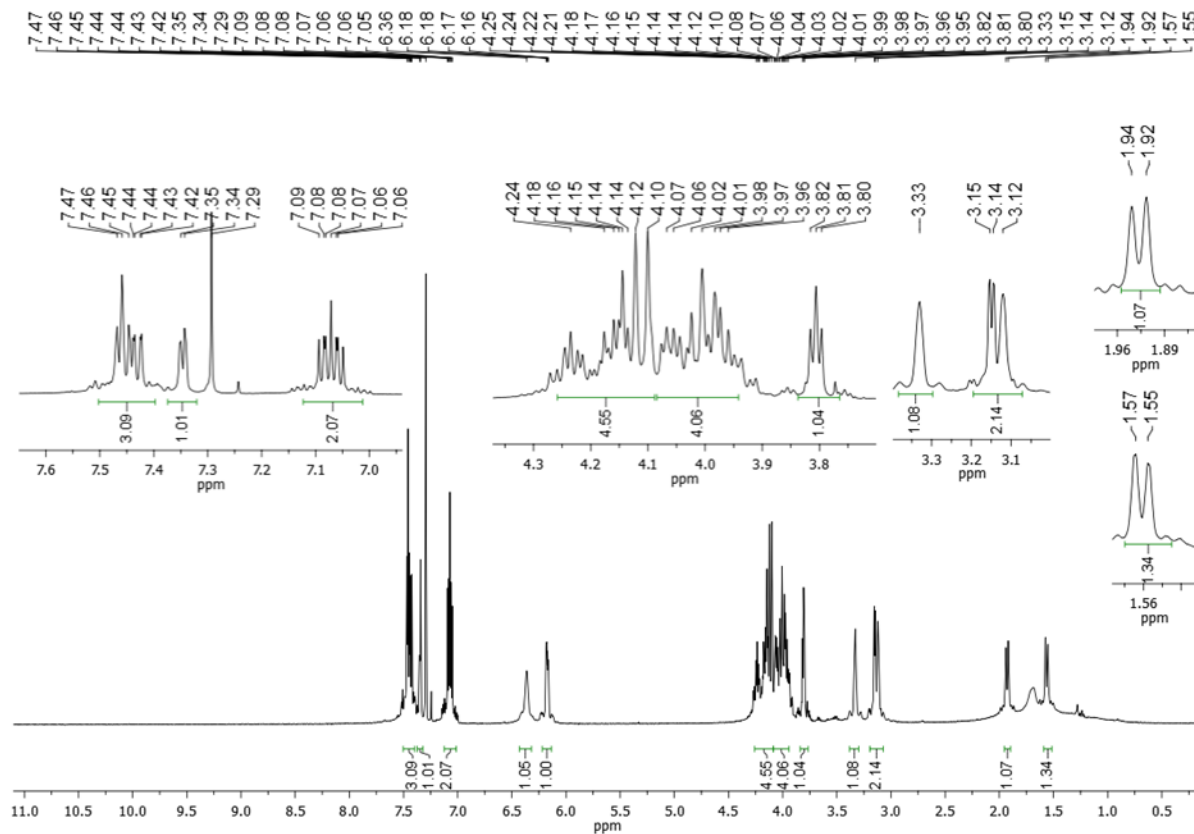
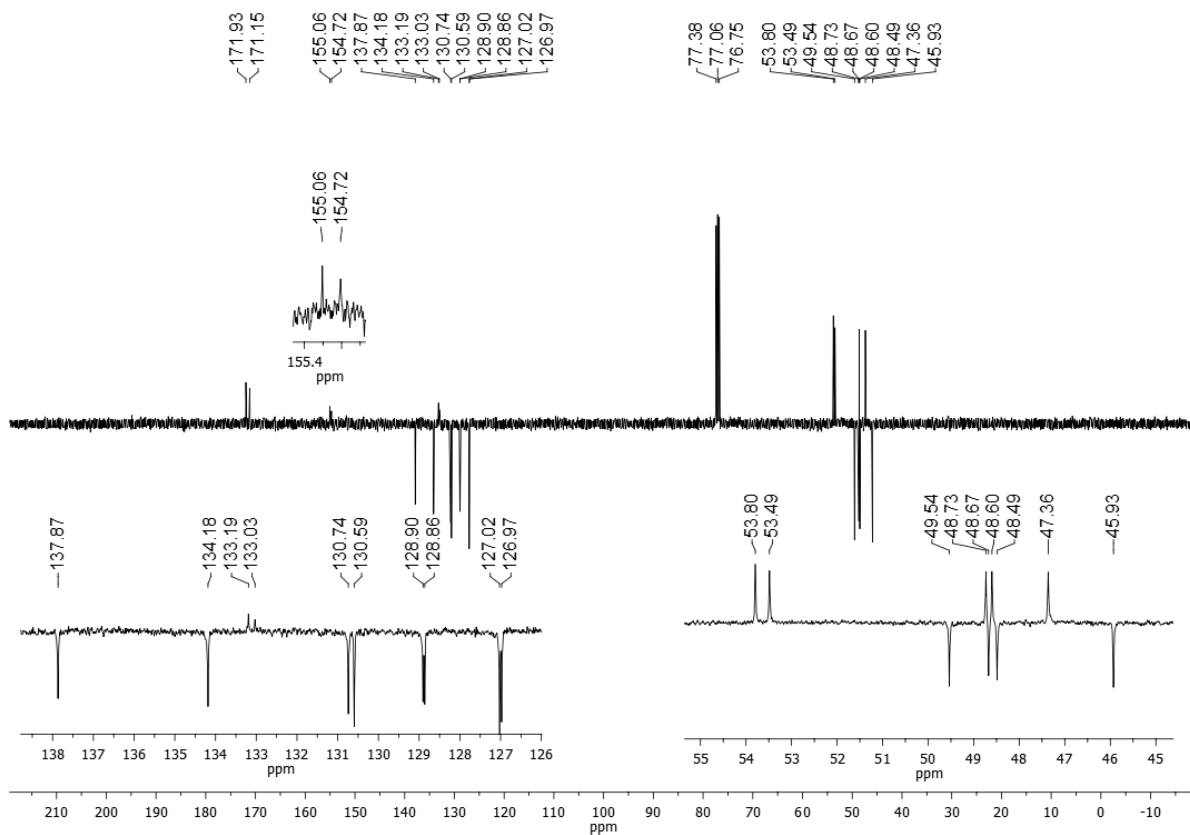
¹H-NMR Spectrum of Compound 10

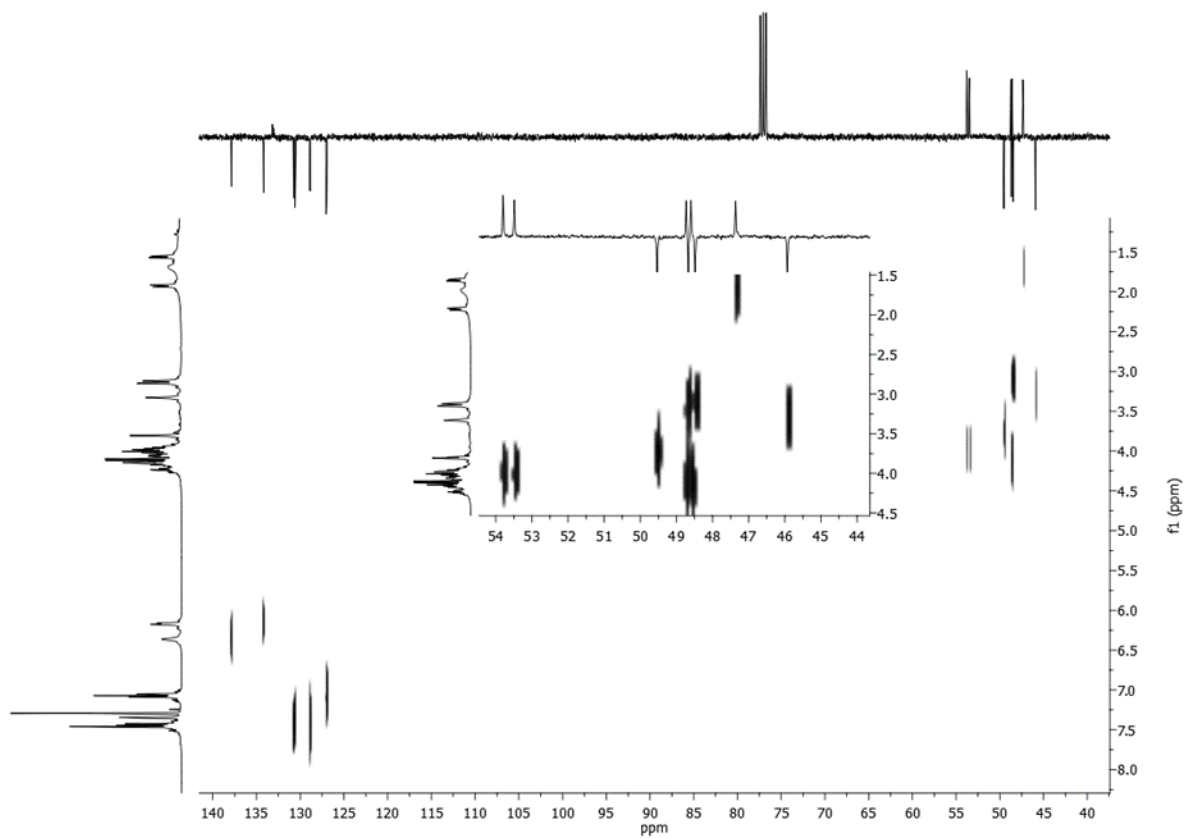
 $^{13}\text{C}_{\text{APT}}$ -NMR Spectrum of Compound 10

X-ray ORTEP diagram of Compound 10

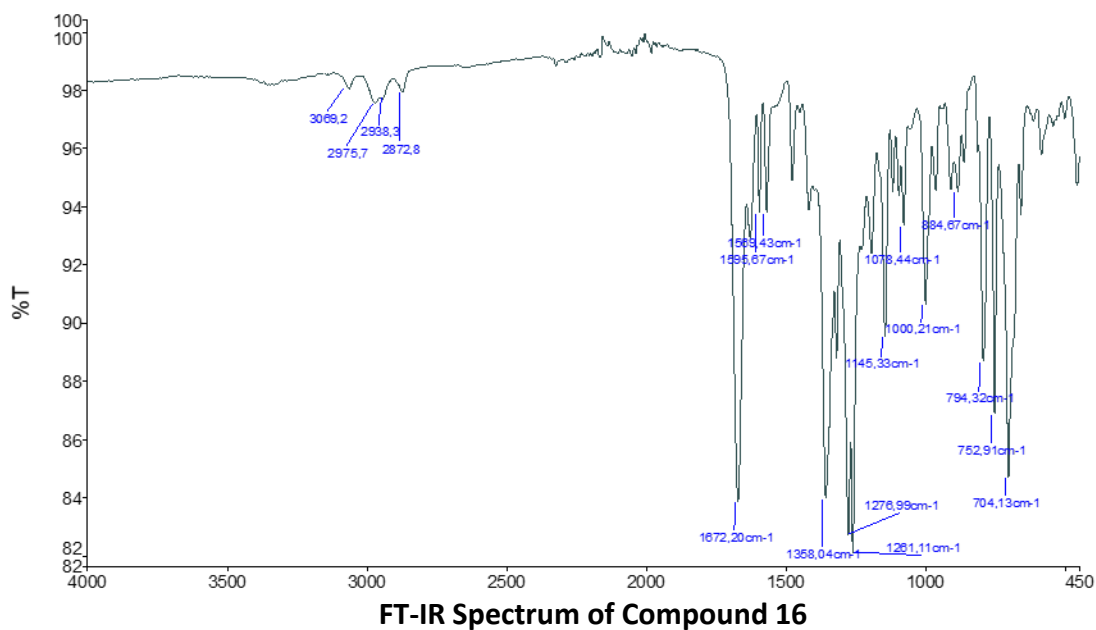
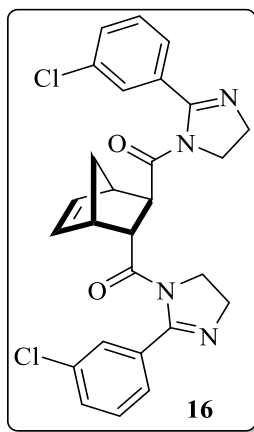
Spectra of Compound 15

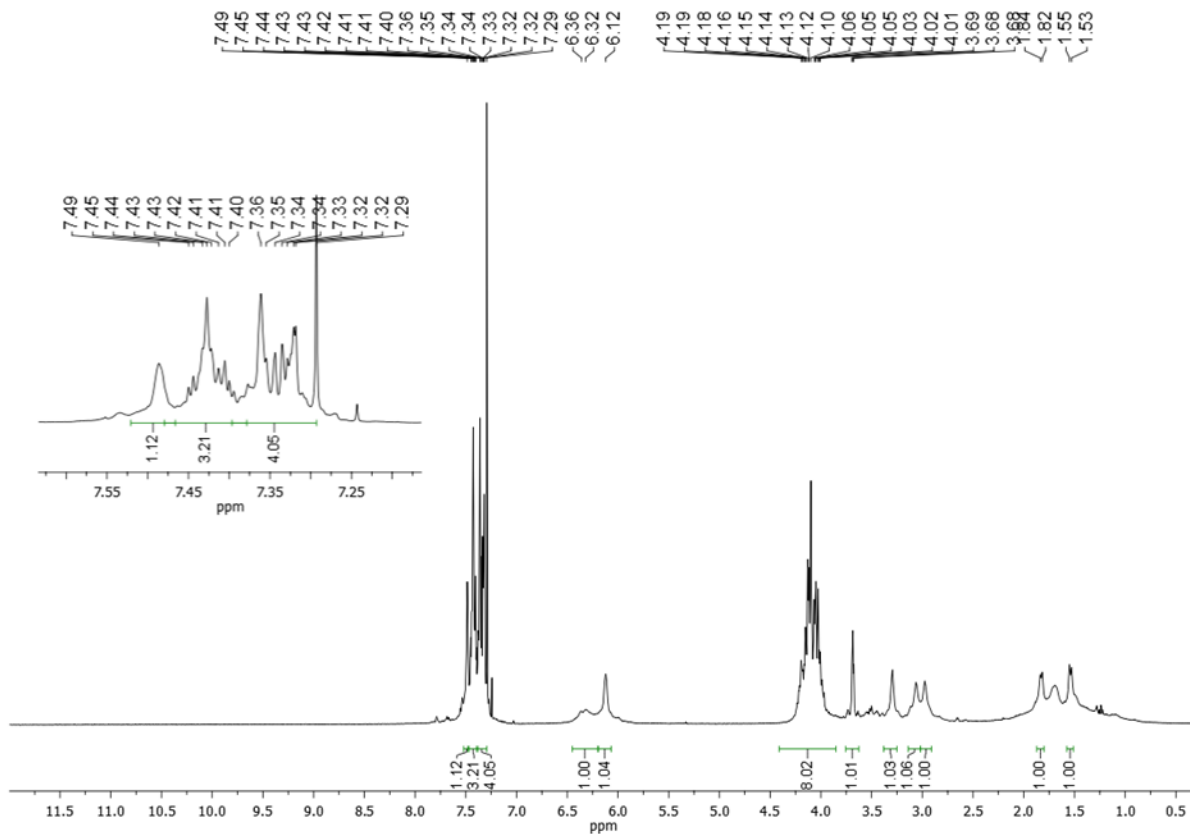


**¹H-NMR Spectrum of Compound 15****¹³C_{CAPT}-NMR Spectrum of Compound 15**

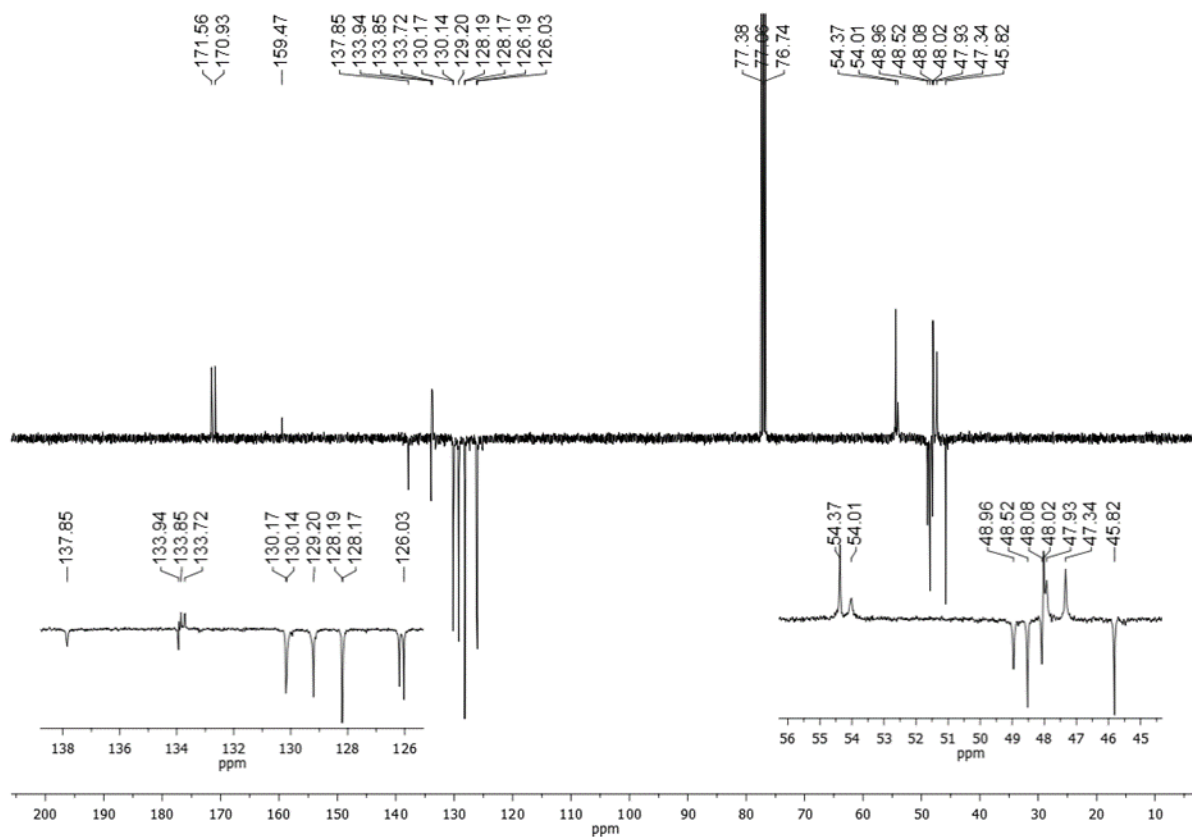
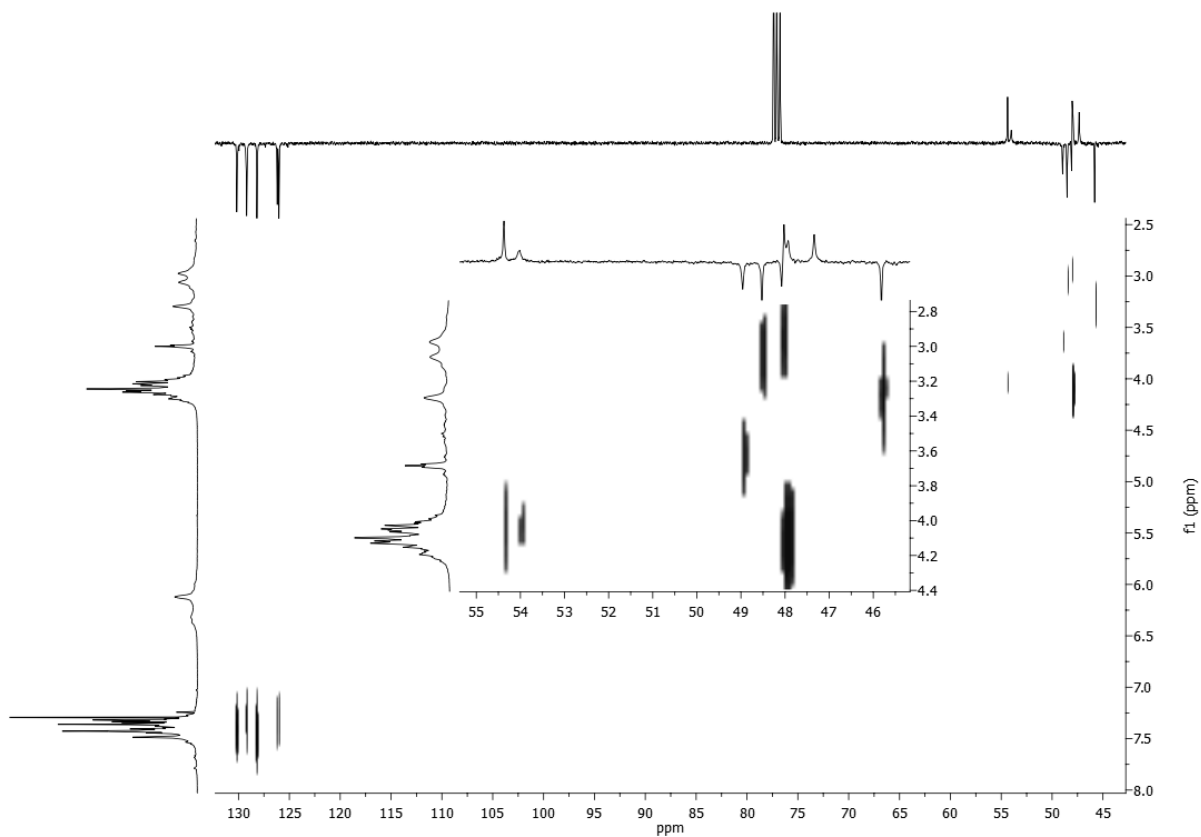
**HETCOR-NMR Spectrum of Compound 15**

Spectra of Compound 16

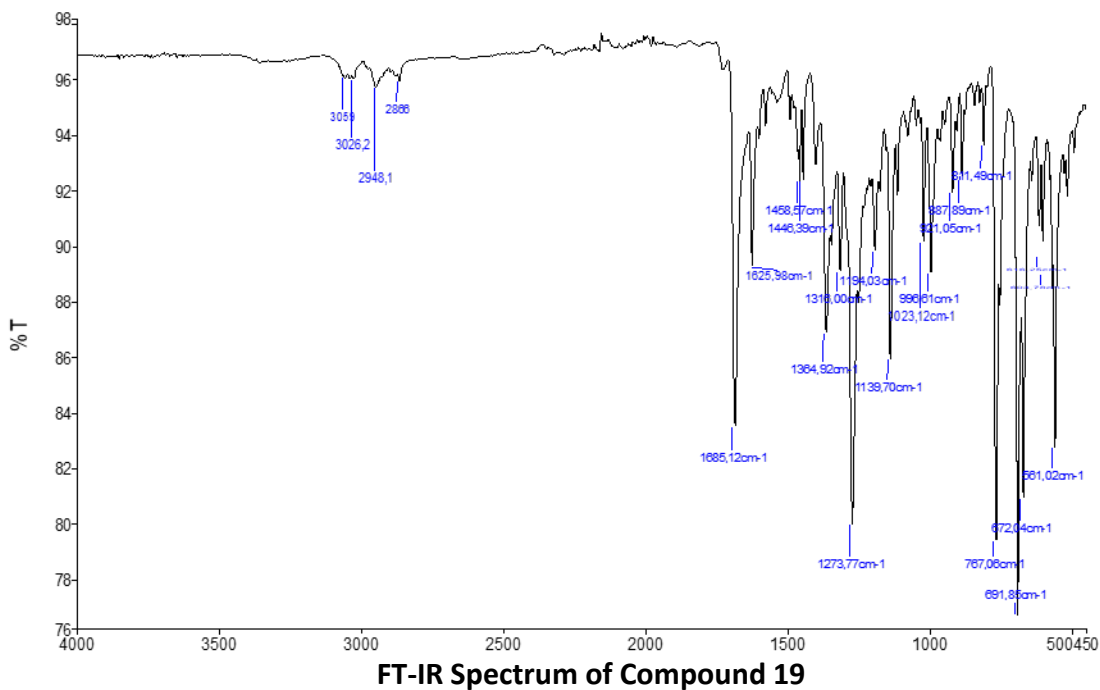
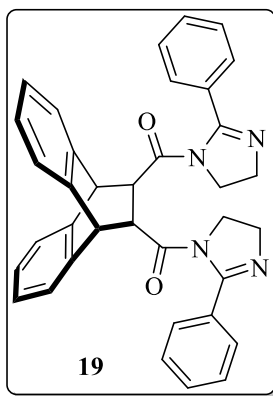


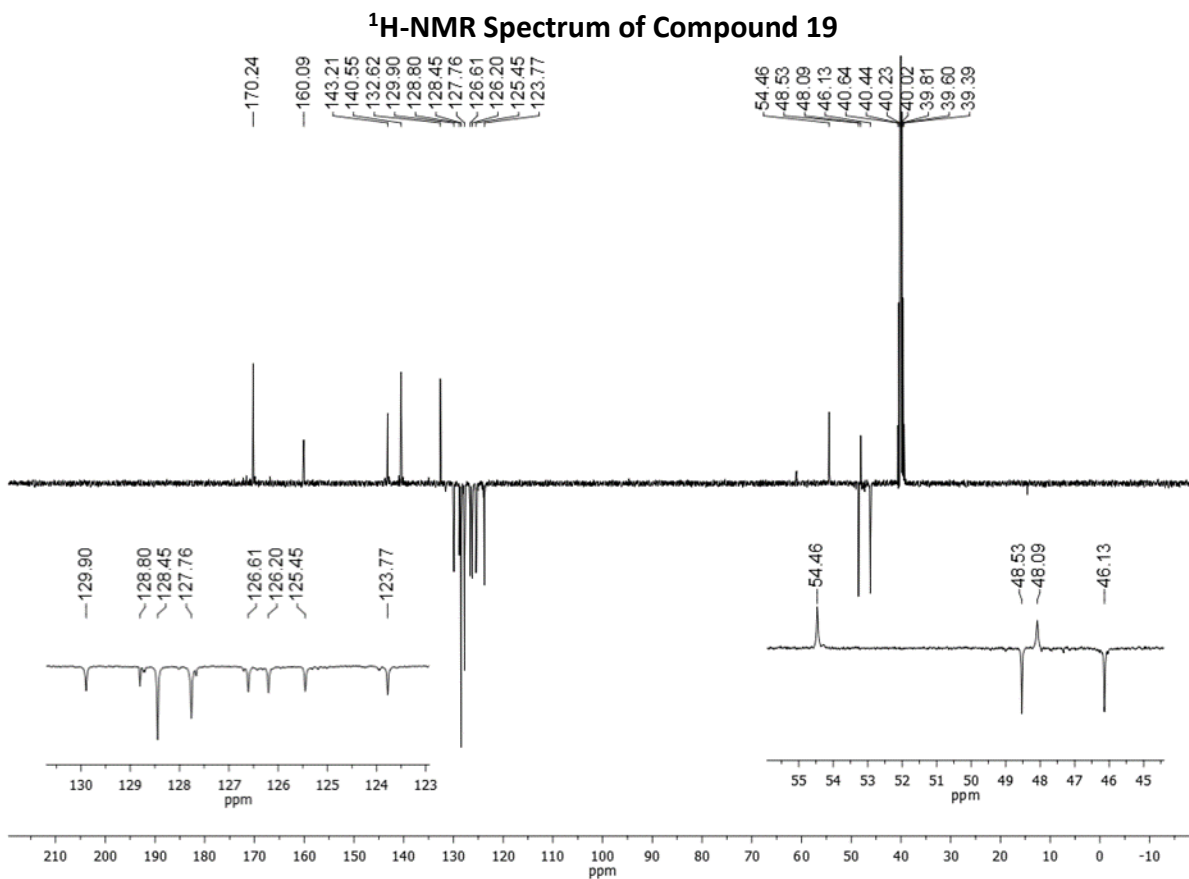
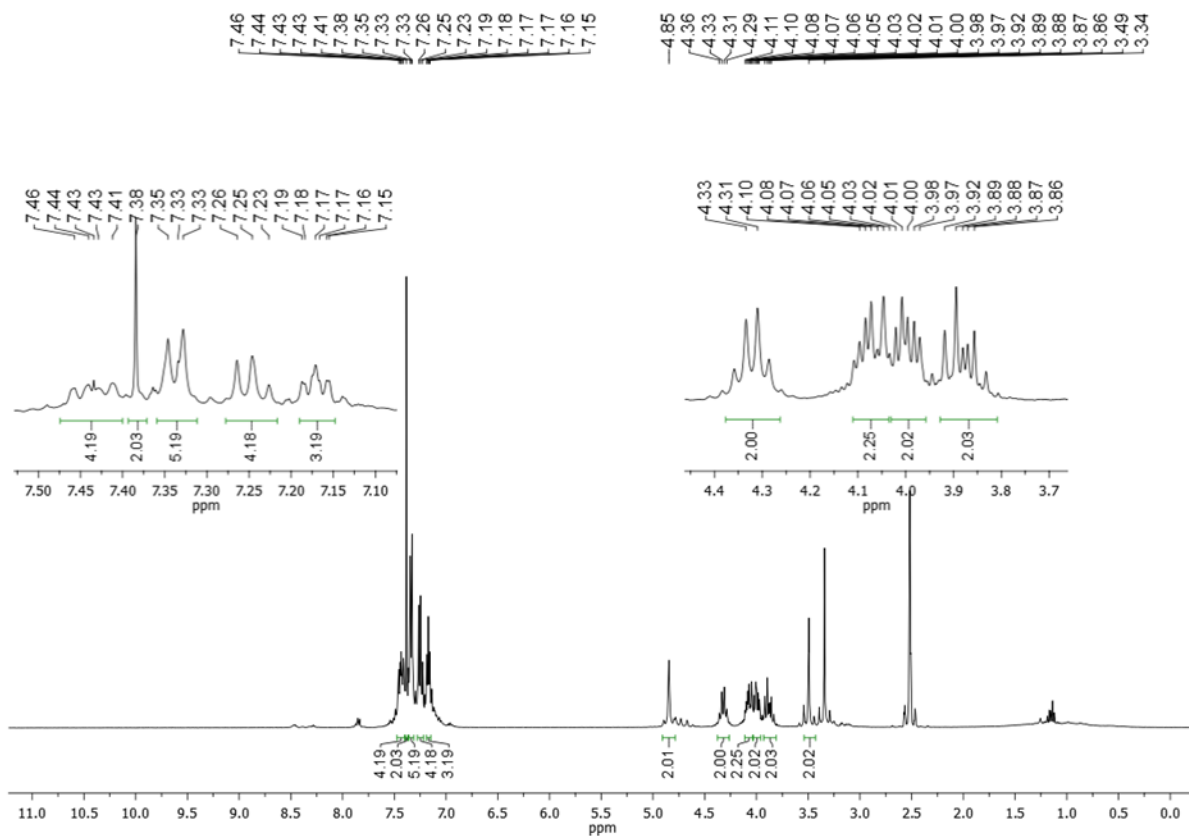


¹H-NMR Spectrum of Compound 16

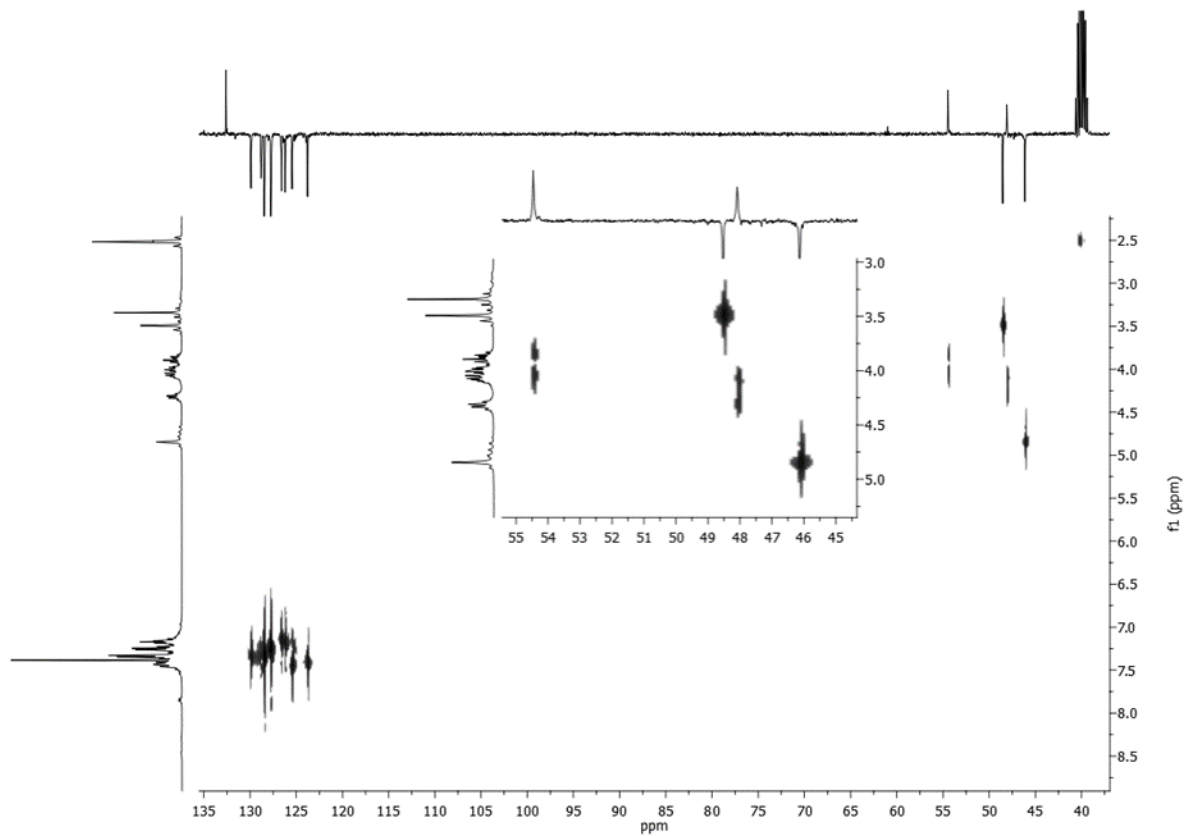
 $^{13}\text{C}_{\text{APT}}$ -NMR Spectrum of Compound 16

HETCOR-NMR Spectrum of Compound 16

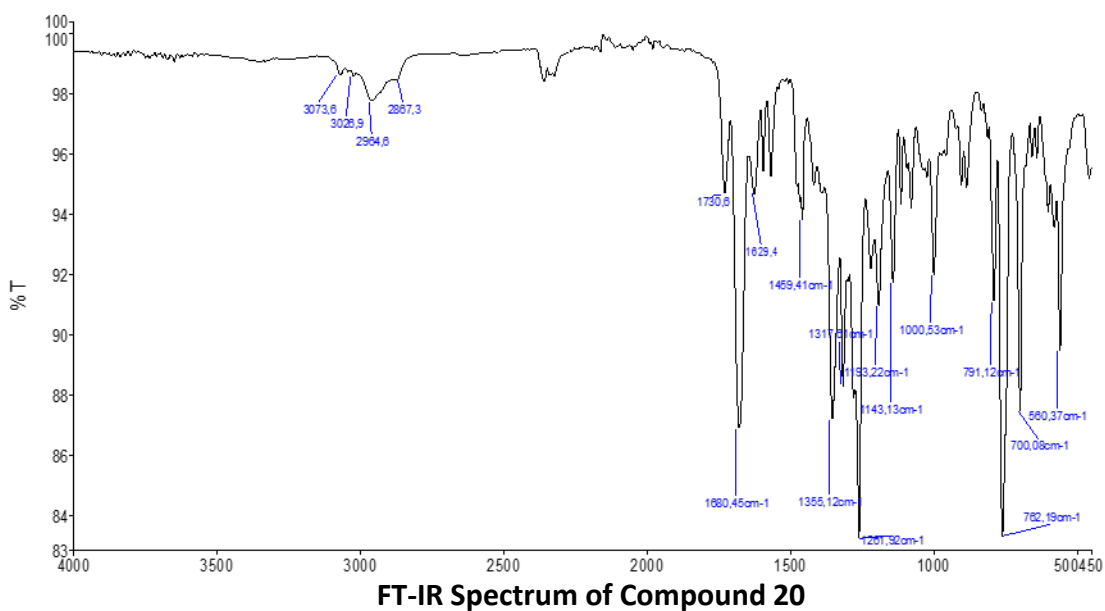
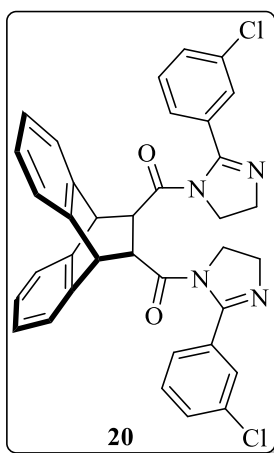


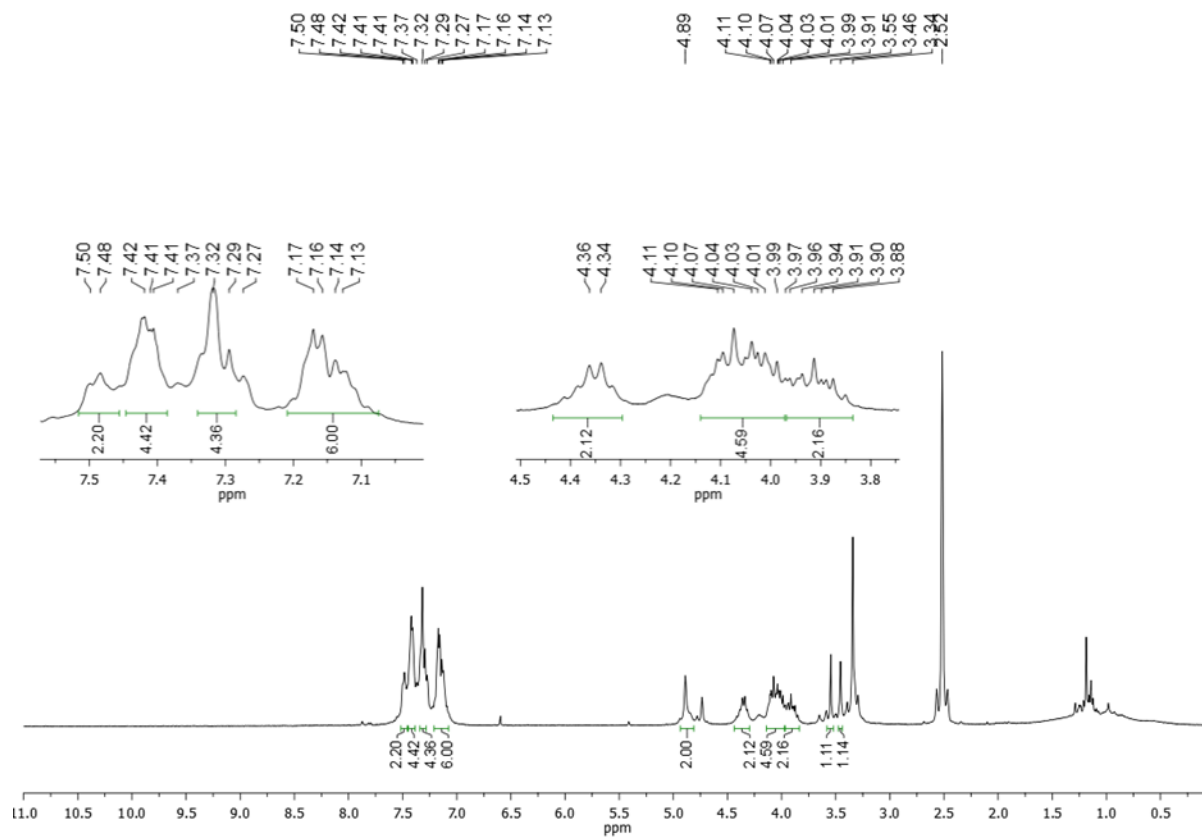


¹³C-NMR Spectrum of Compound 19

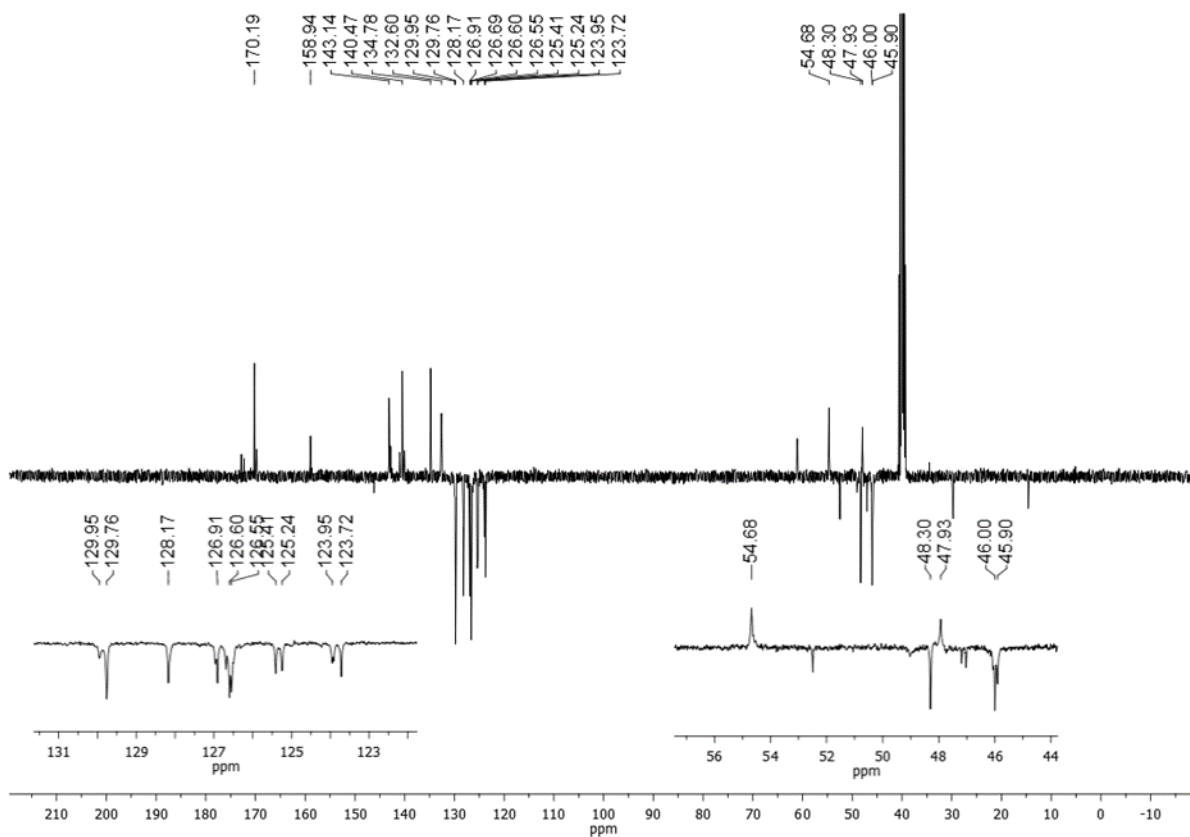
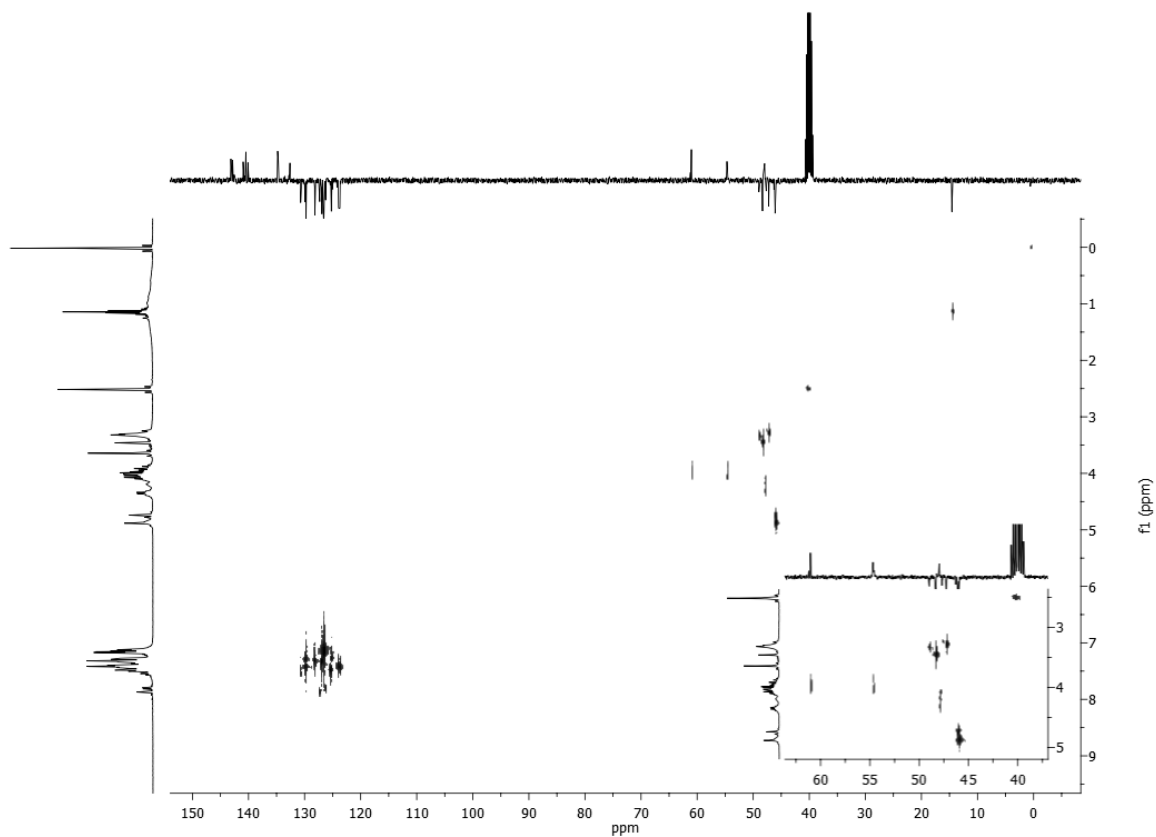
**HETCOR-NMR Spectrum of Compound 19**

Spectra of Compound 20



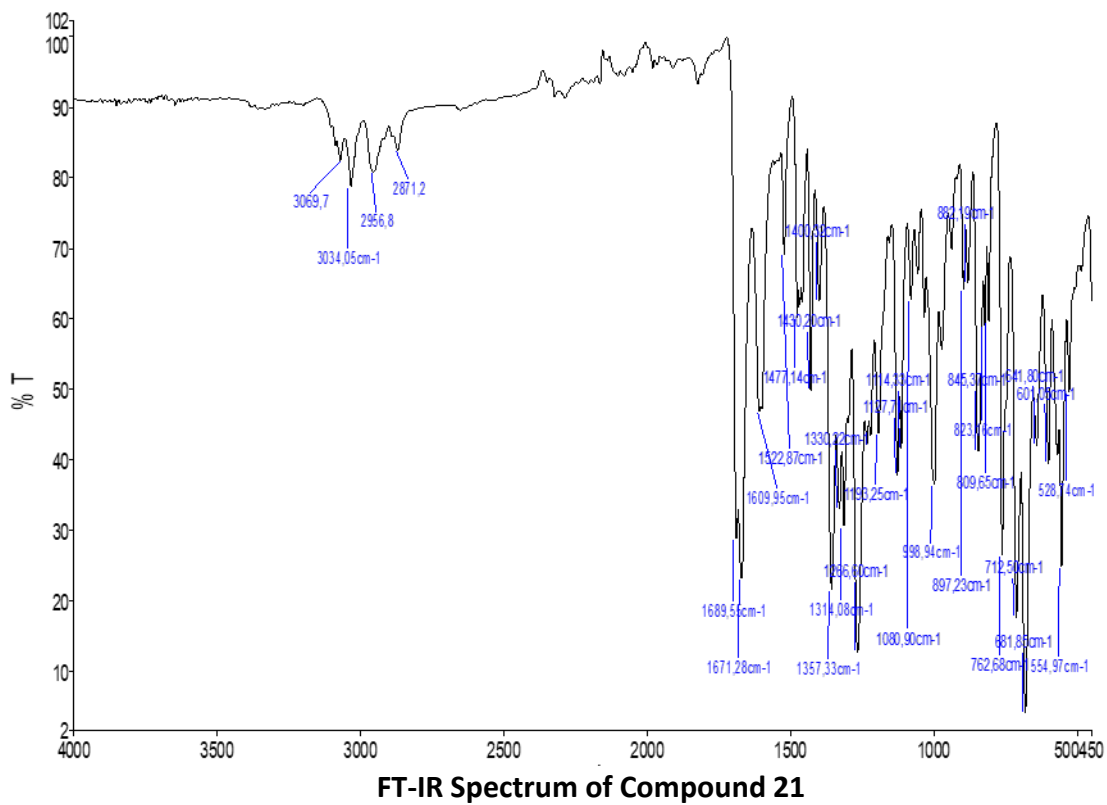
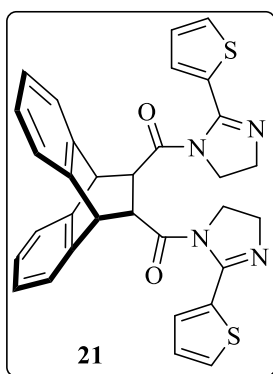


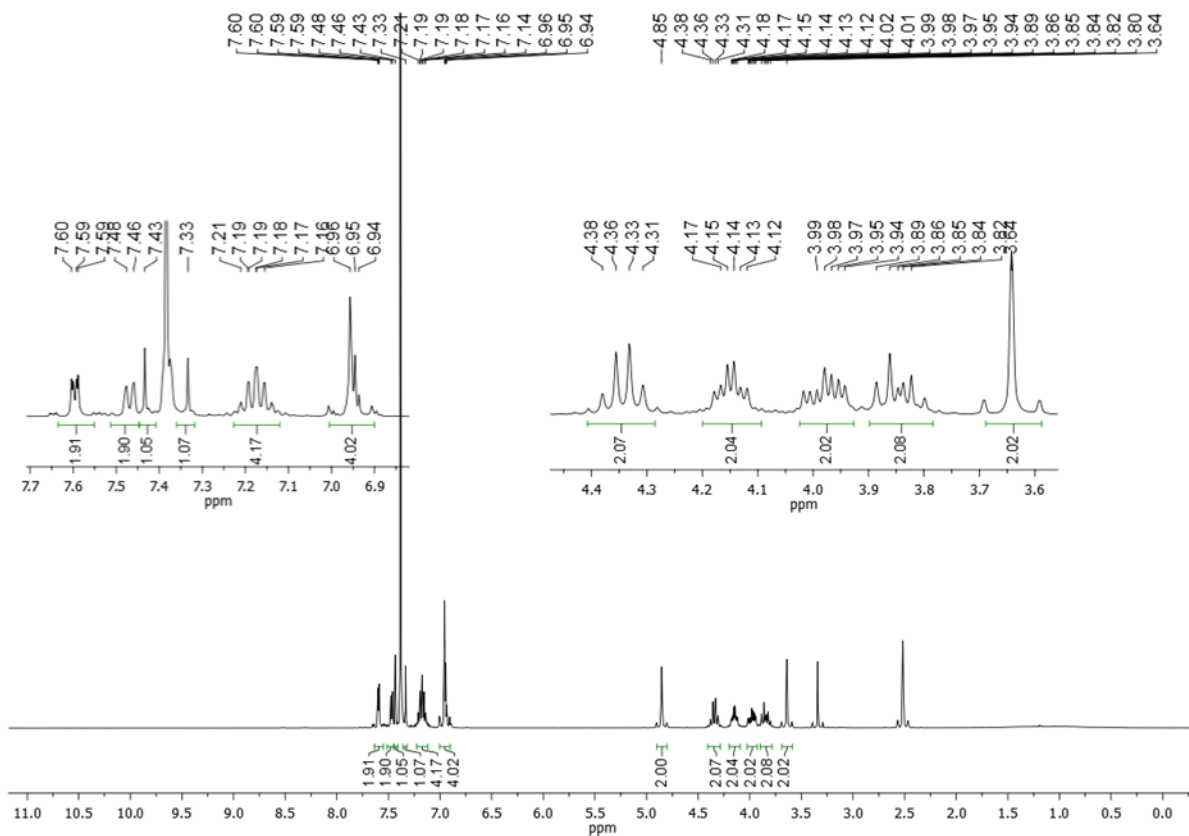
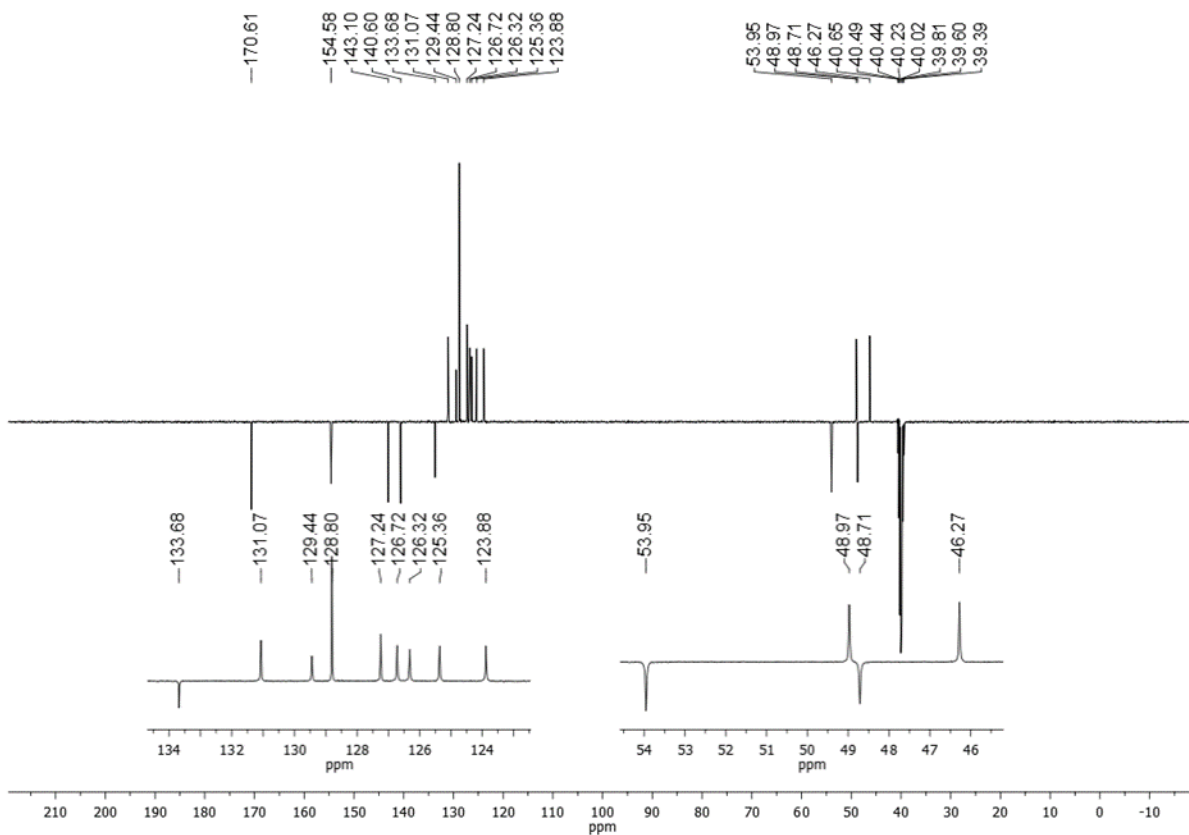
¹H-NMR Spectrum of Compound 20

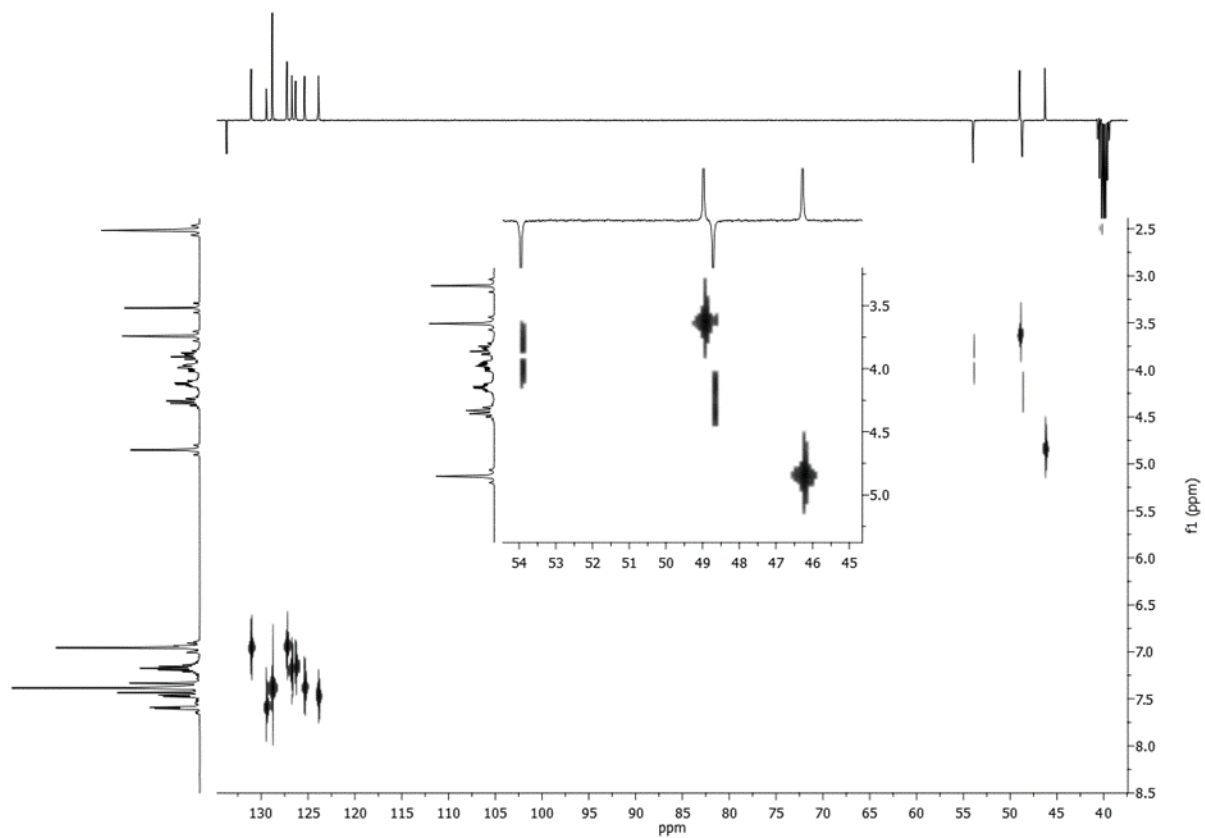
 ^{13}C APT-NMR Spectrum of Compound 20

HETCOR-NMR Spectrum of Compound 20

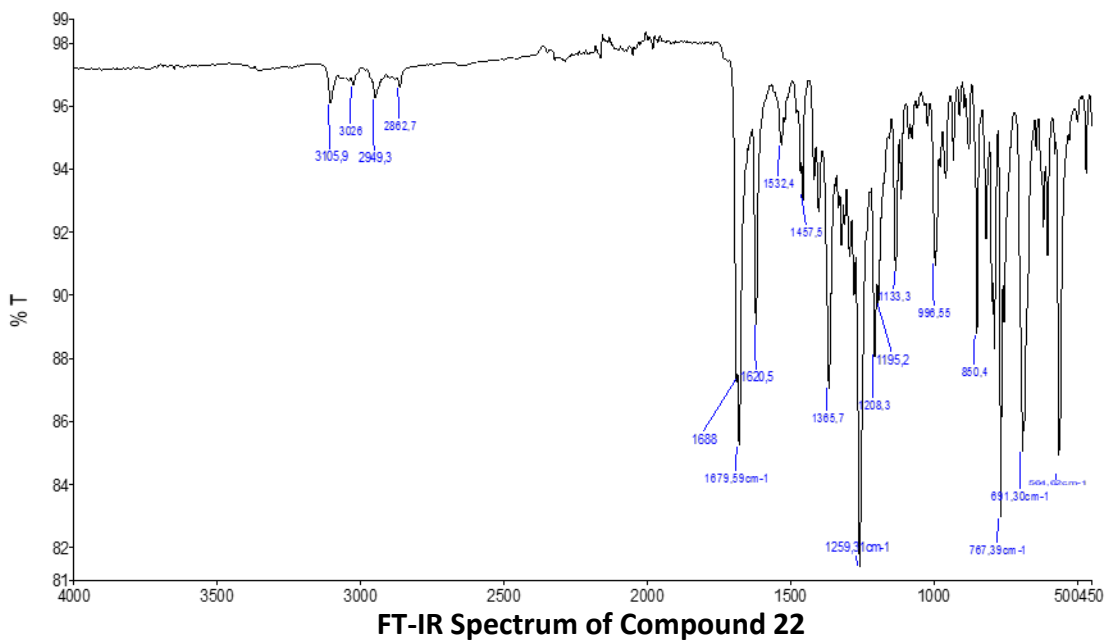
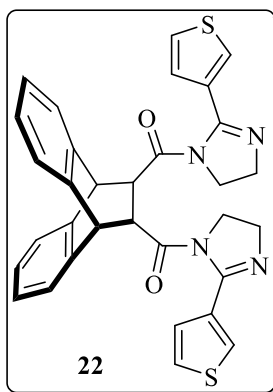
Spectra of Compound 21

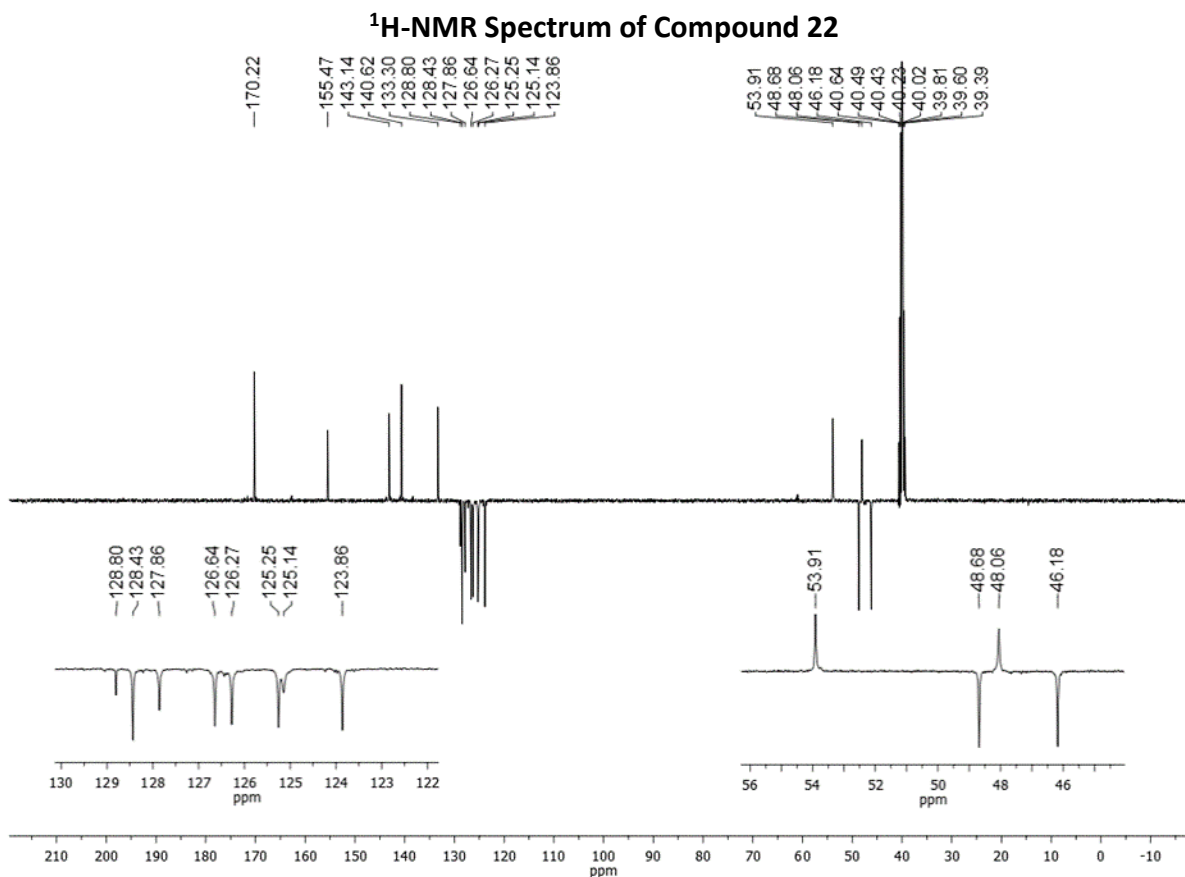
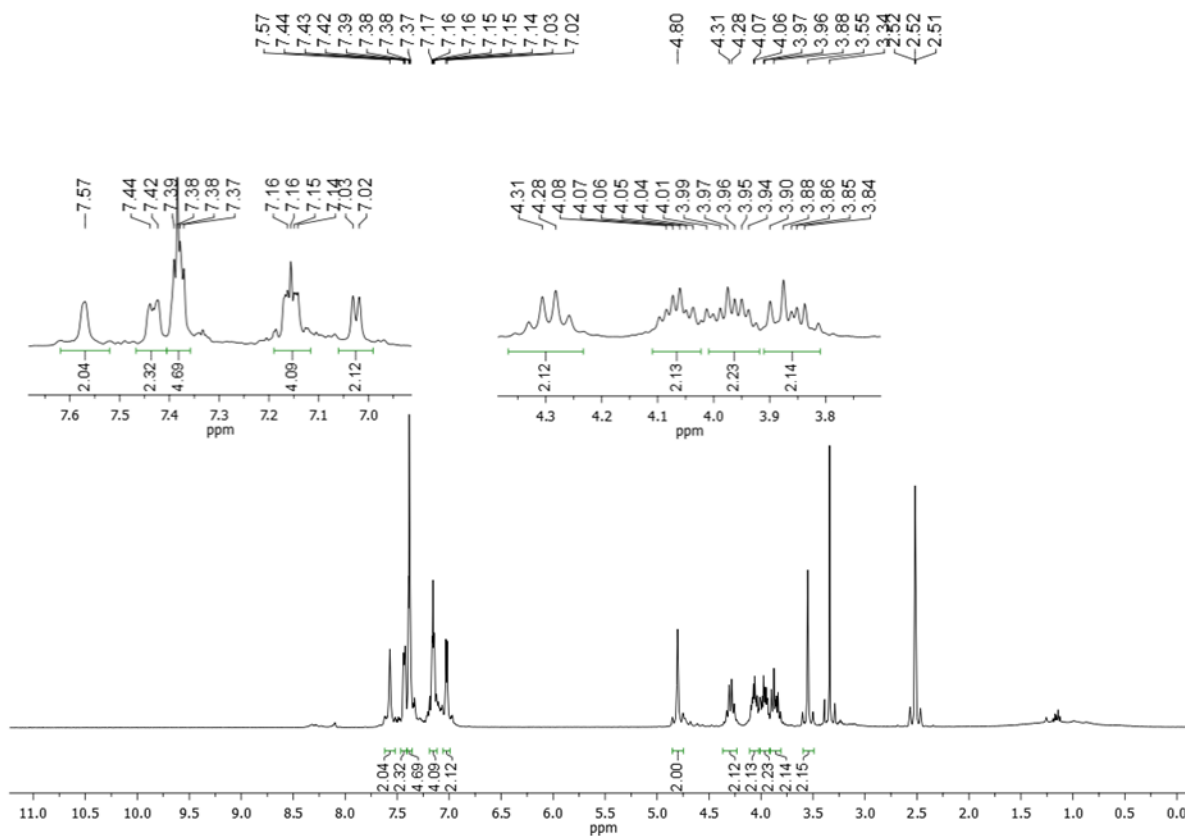


**¹H-NMR Spectrum of Compound 21****¹³C-NMR Spectrum of Compound 21**

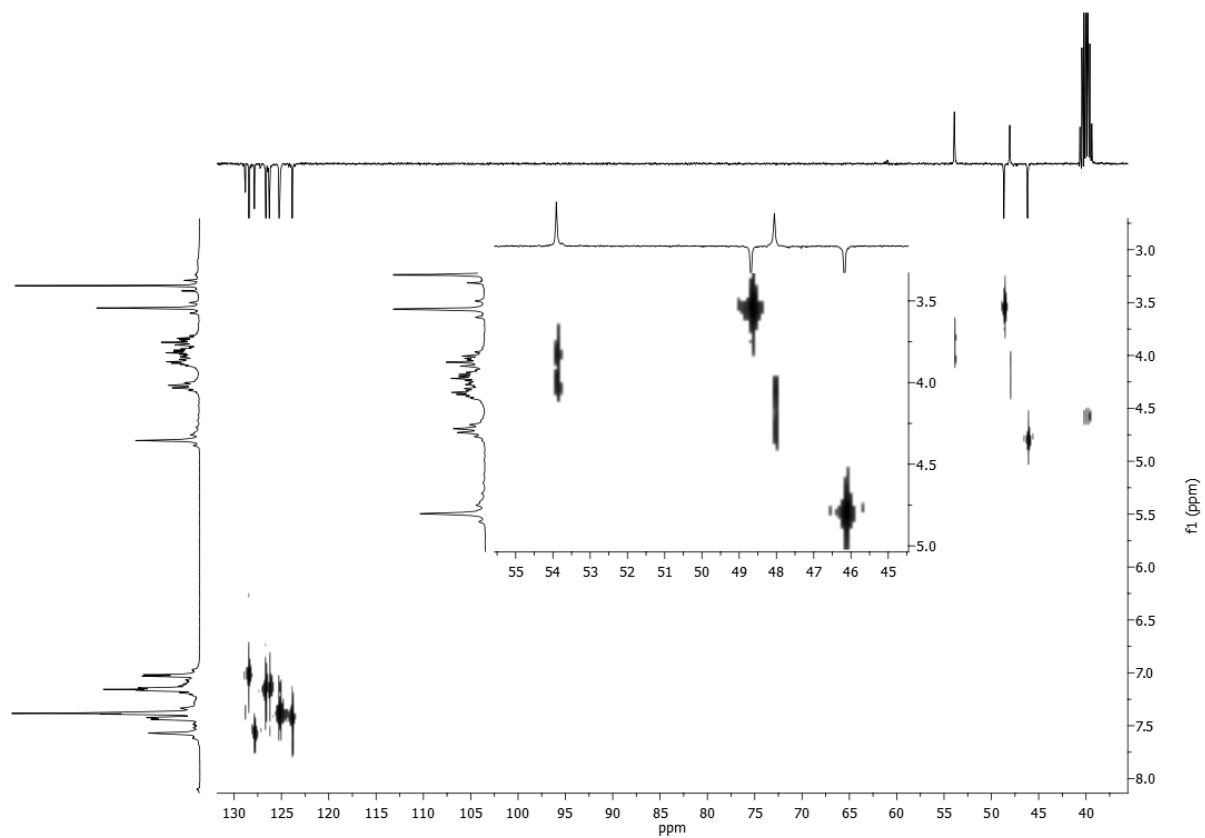


HETCOR-NMR Spectrum of Compound 21

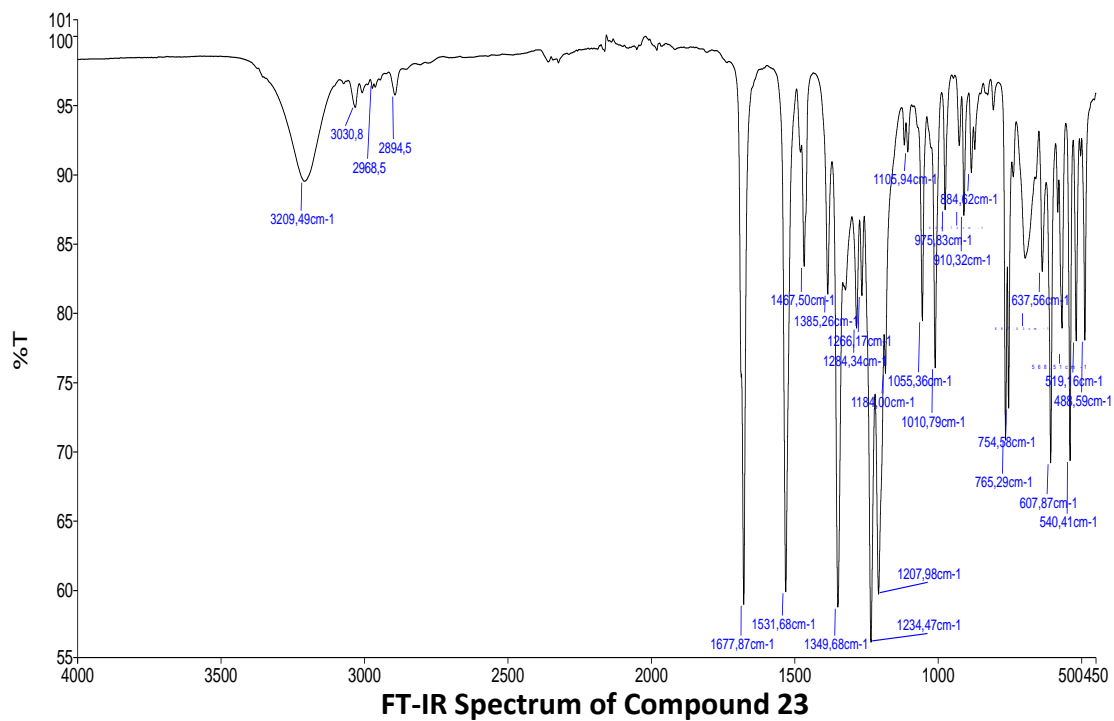
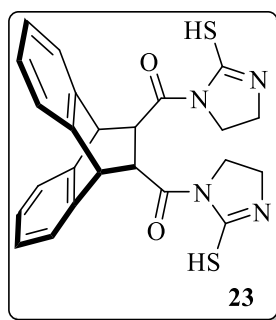


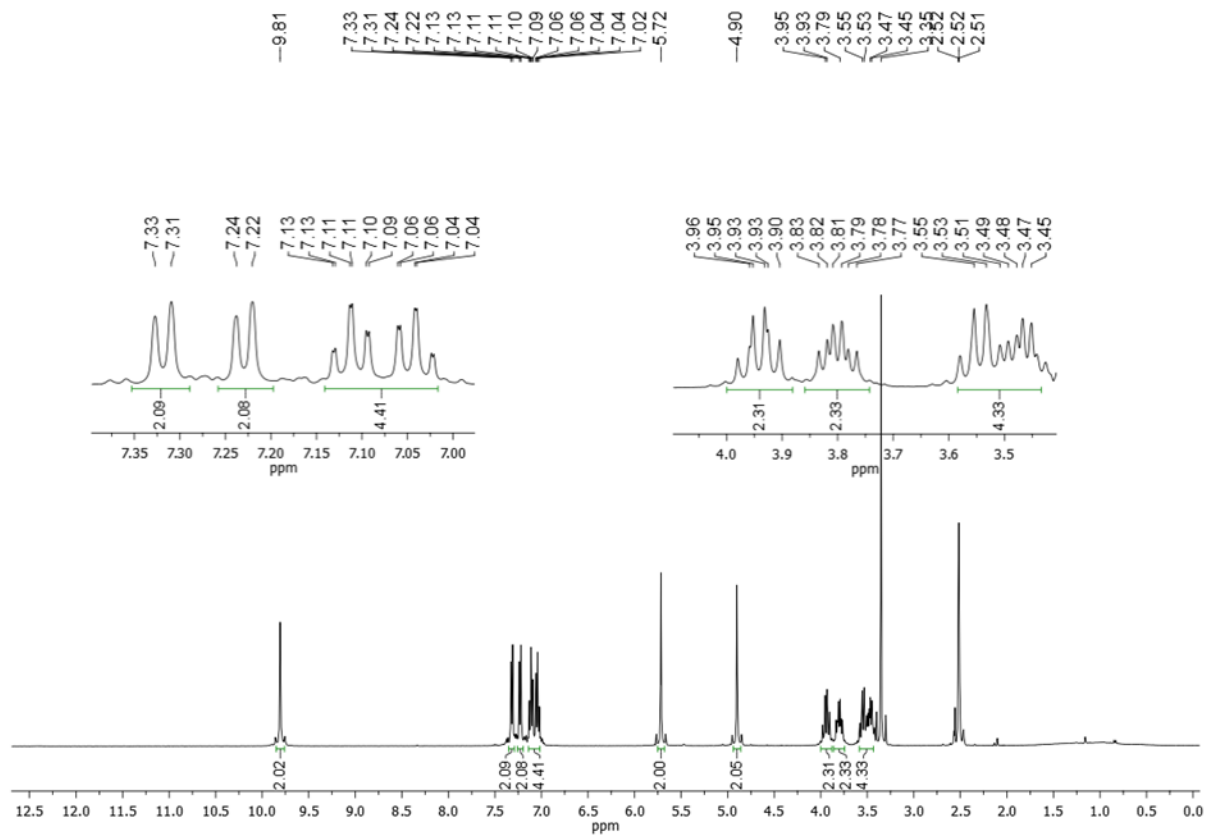


¹³C-NMR Spectrum of Compound 22

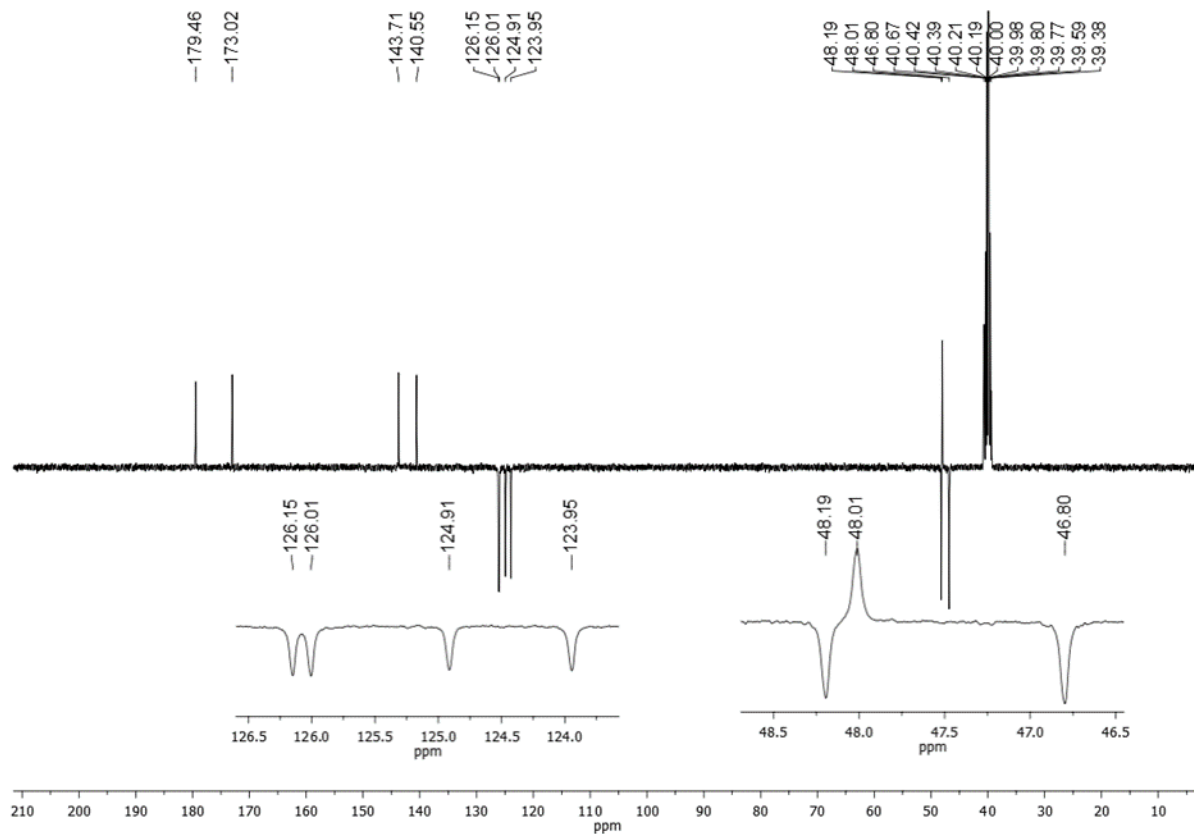
**HETCOR-NMR Spectrum of Compound 22**

Spectra of Compound 23

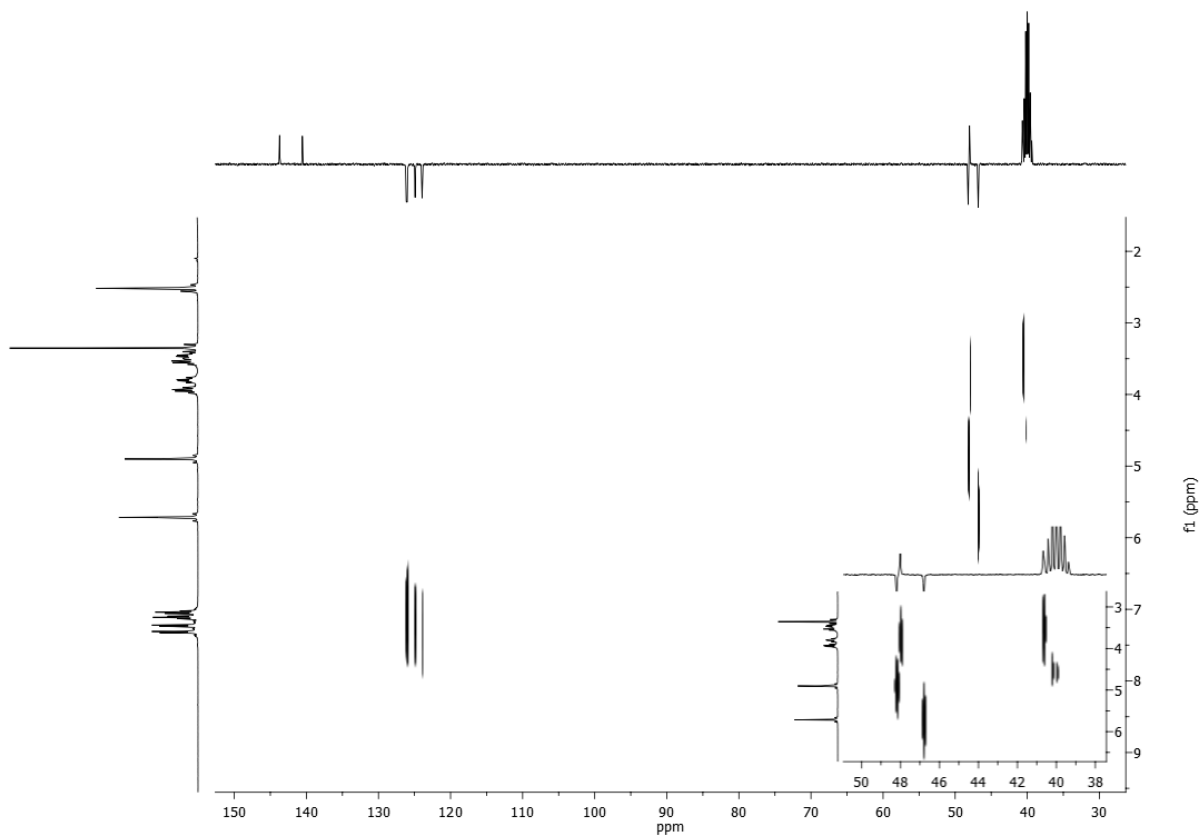




¹H-NMR Spectrum of Compound 23

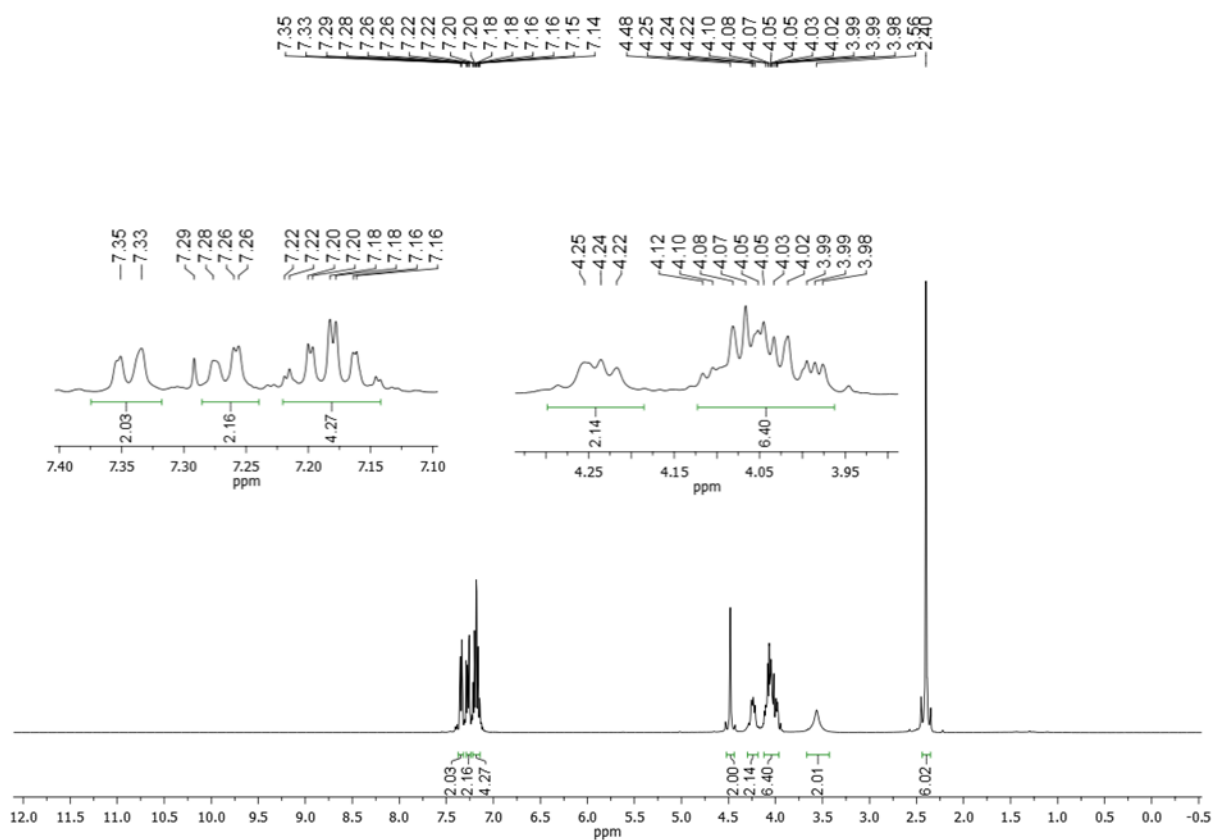
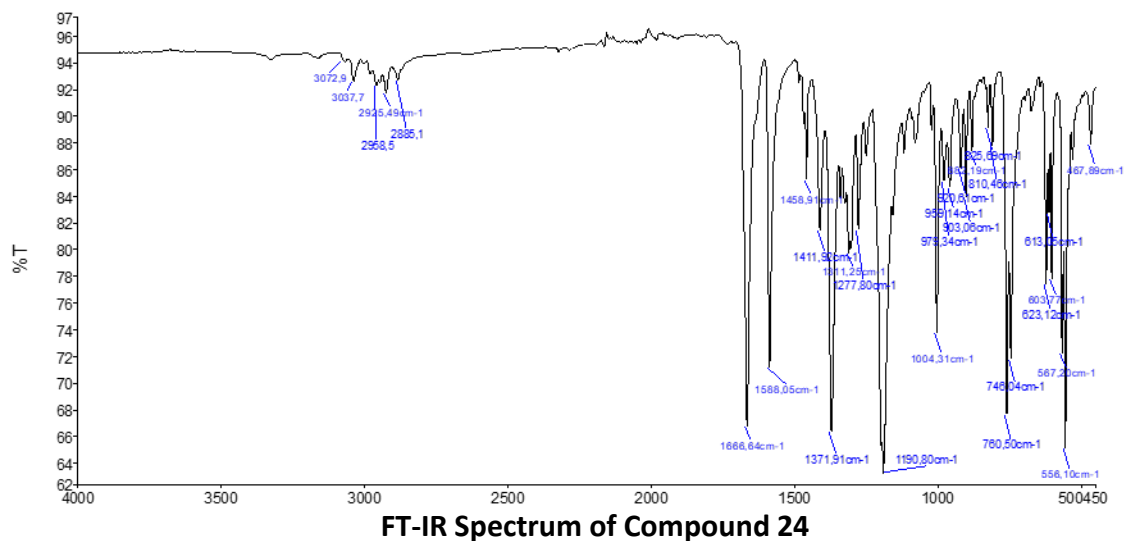
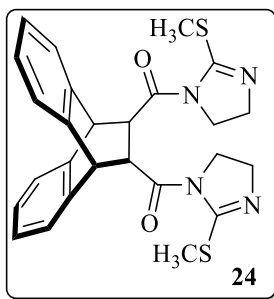


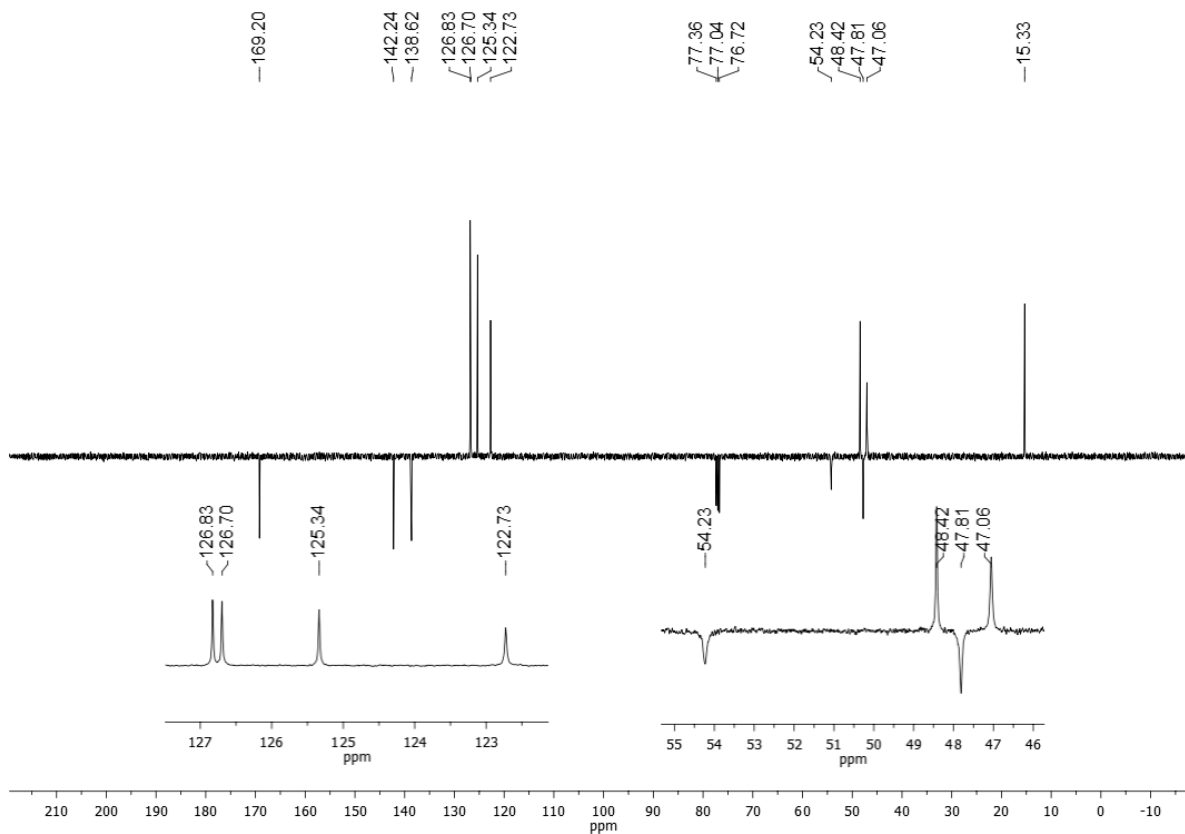
^{13}C -CAPT-NMR Spectrum of Compound 23



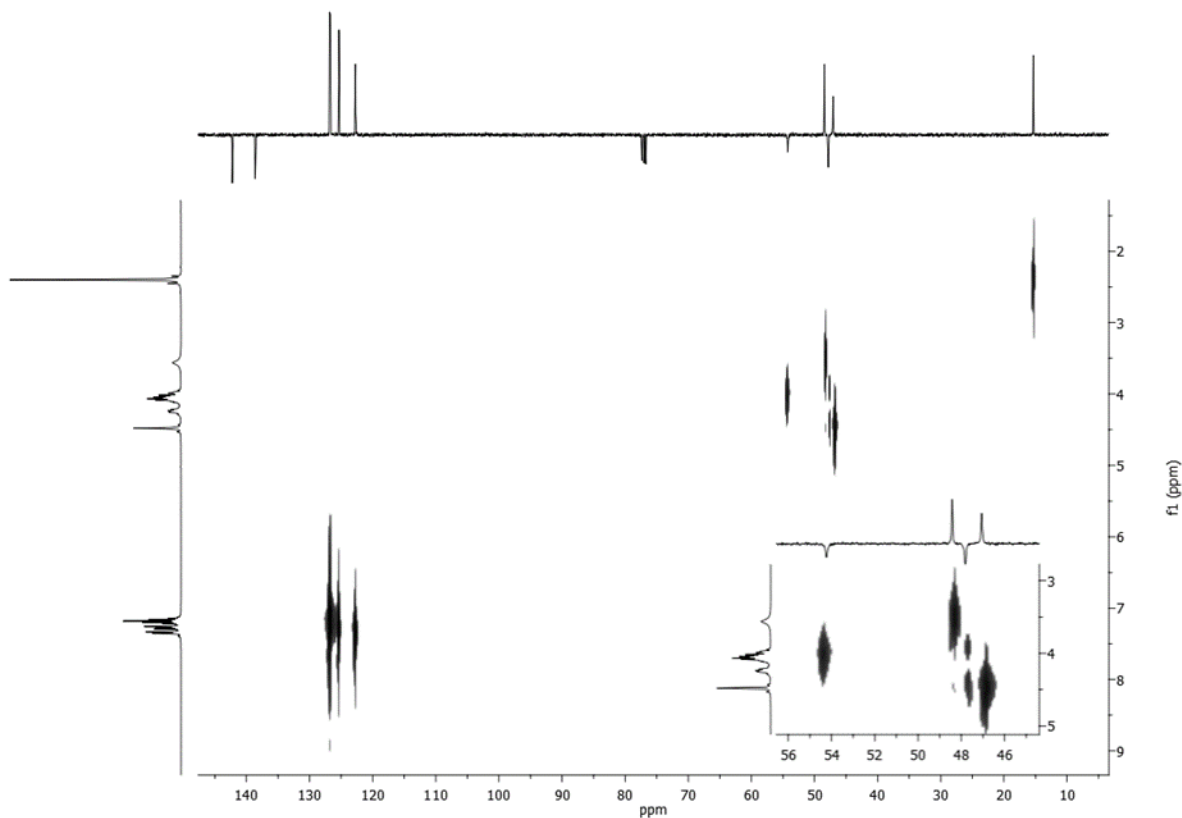
HETCOR-NMR Spectrum of Compound 23

Spectra of Compound 24

¹H-NMR Spectrum of Compound 24

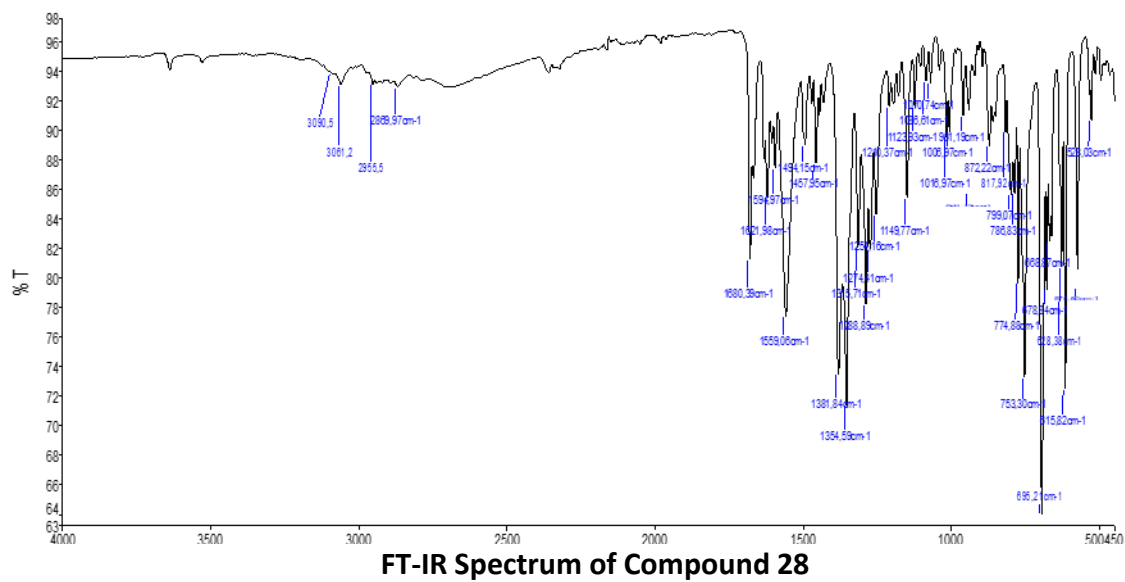
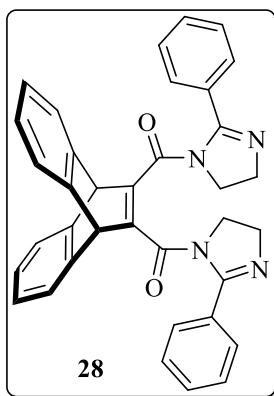


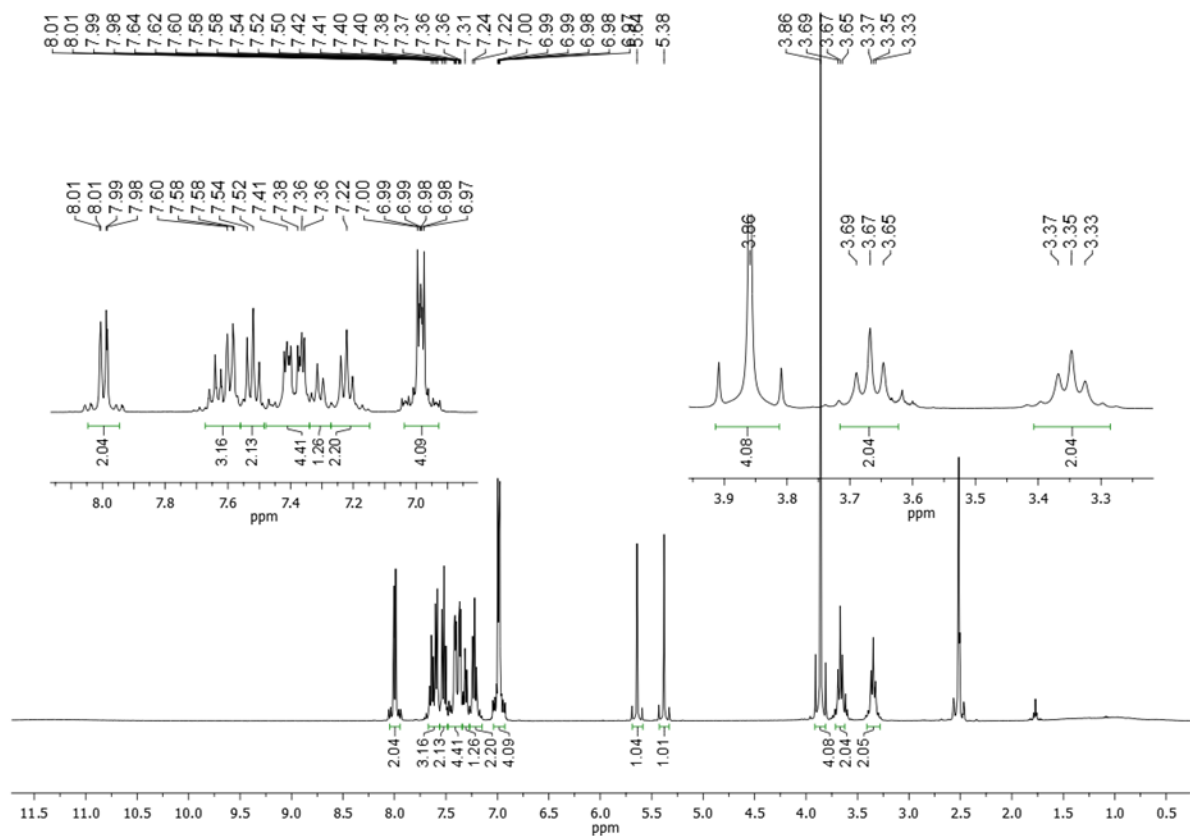
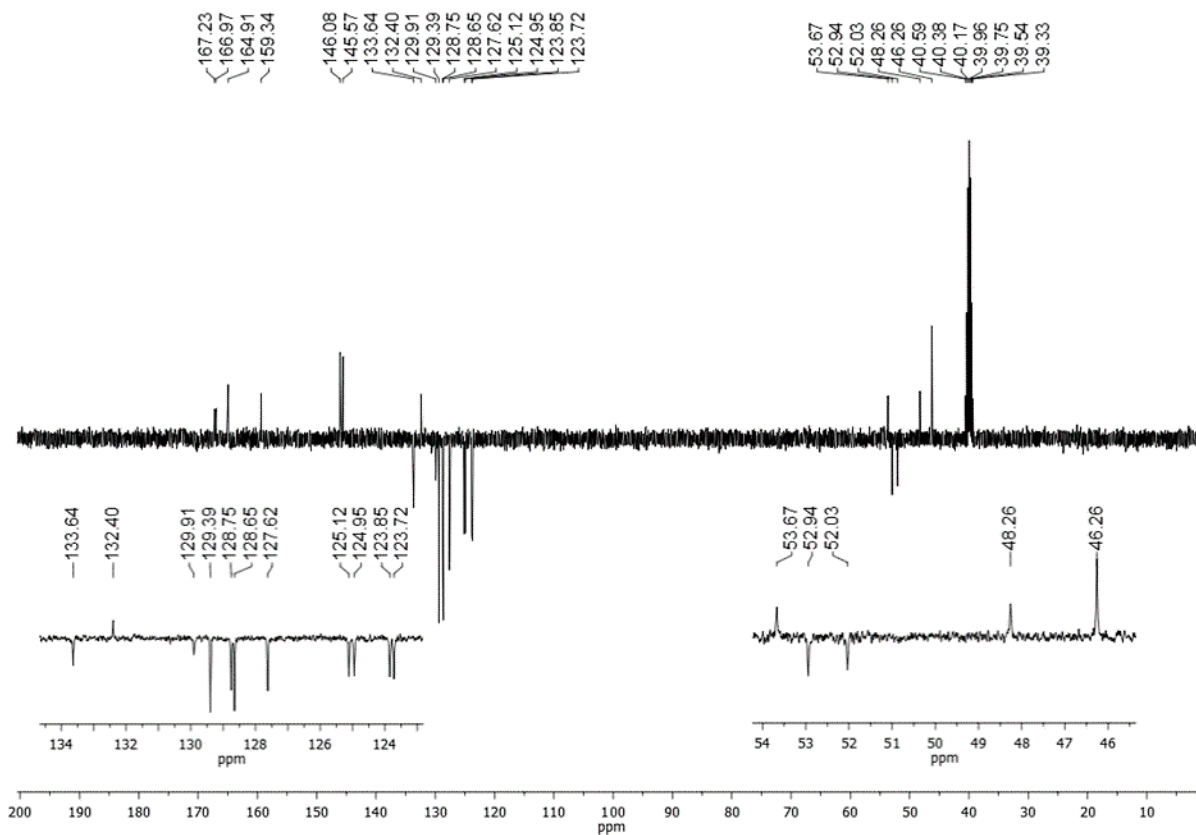
¹³C_{CAPT}-NMR Spectrum of Compound 24

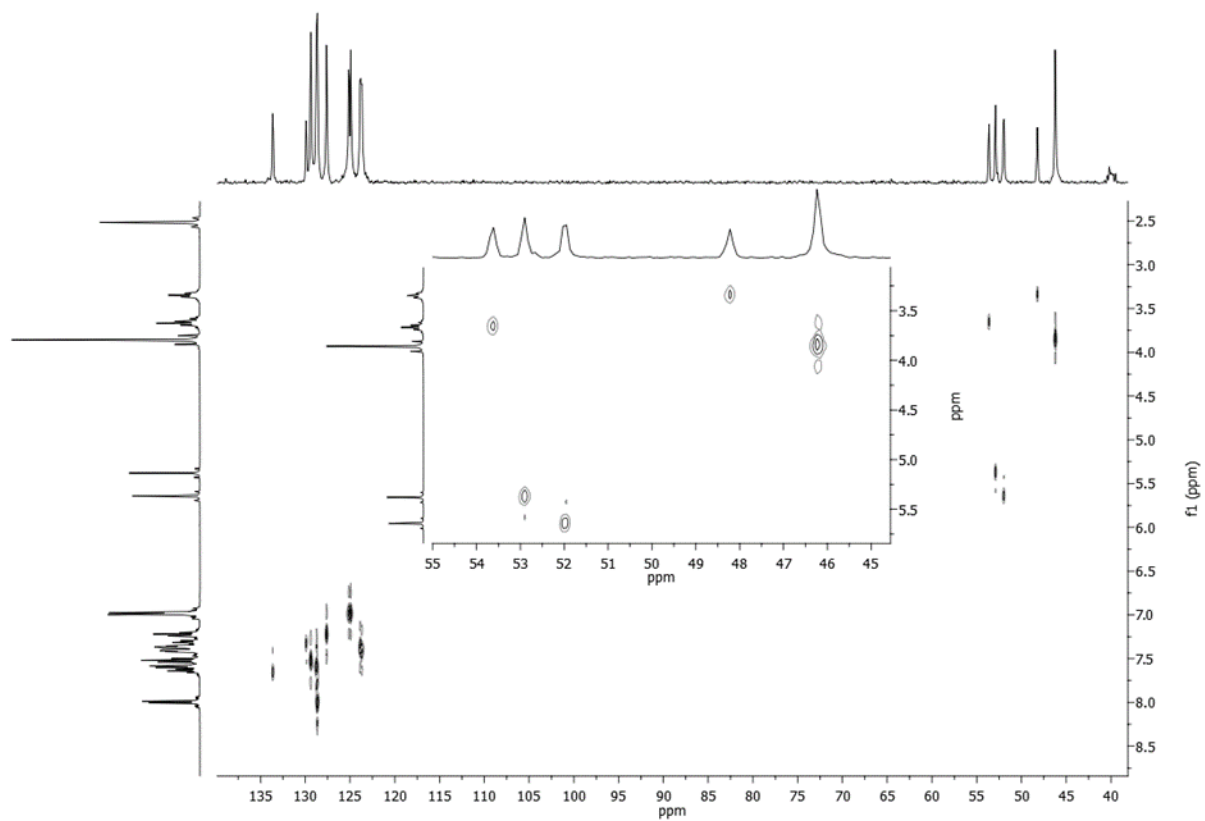


HETCOR-NMR Spectrum of Compound 24

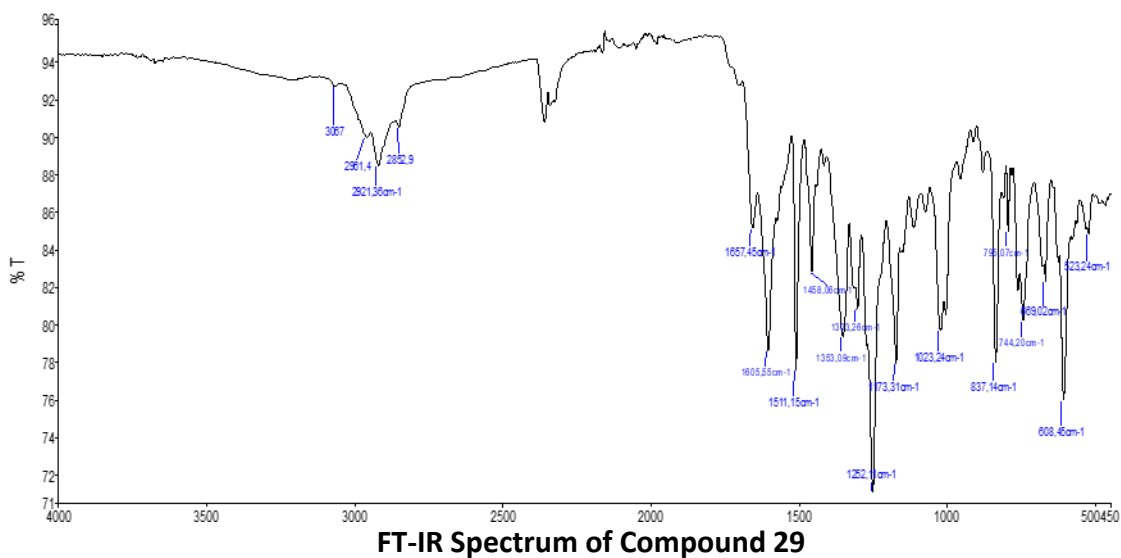
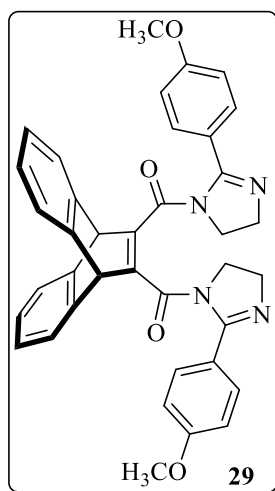
Spectra of Compound 28

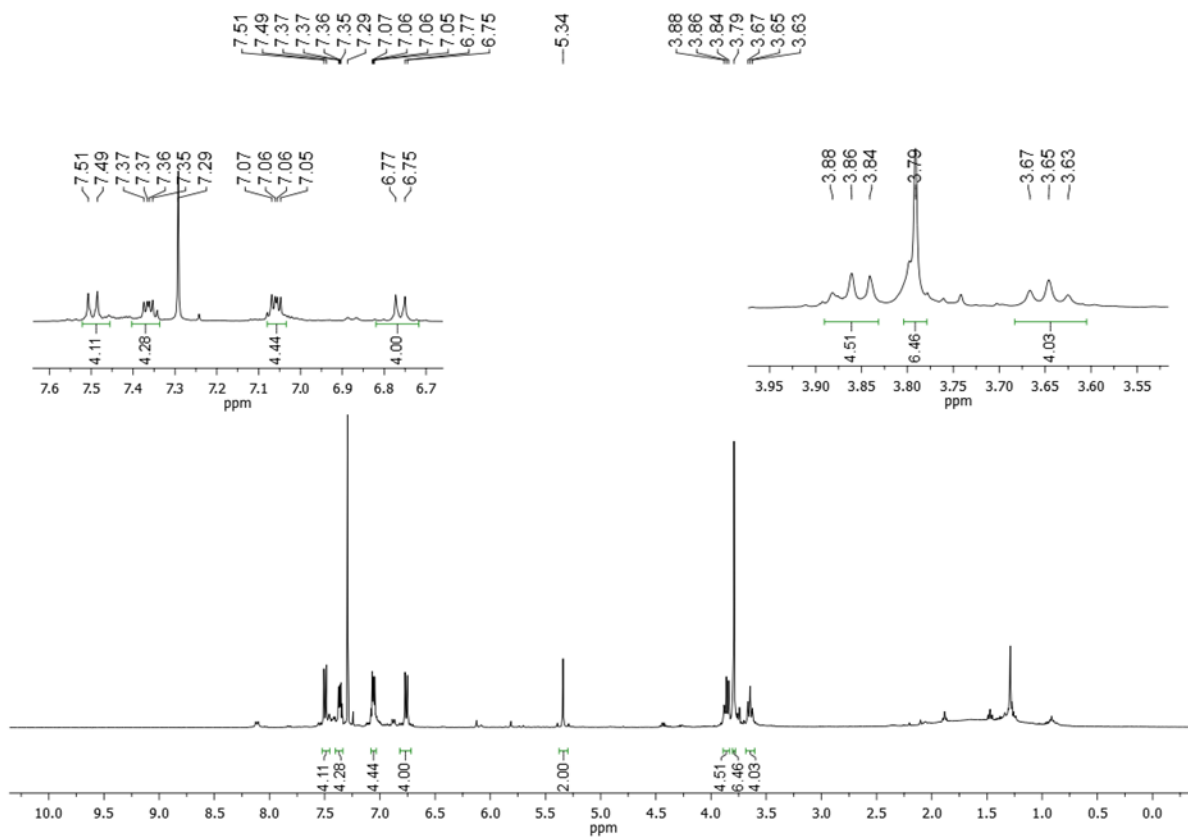


 **$^1\text{H-NMR}$ Spectrum of Compound 28** **$^{13}\text{C}_{\text{APT}}$ Spectrum of Compound 28**

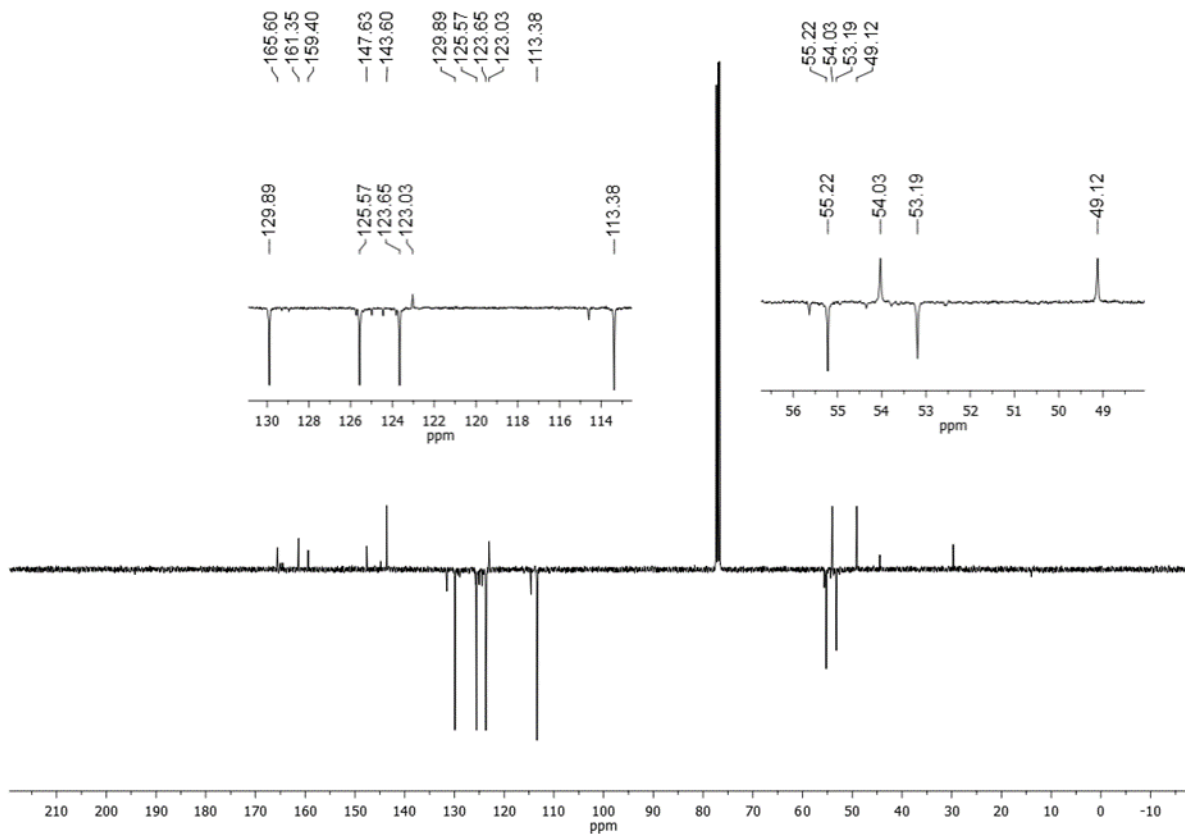
**HETCOR-NMR Spectrum of Compound 28**

Spectra of Compound 29

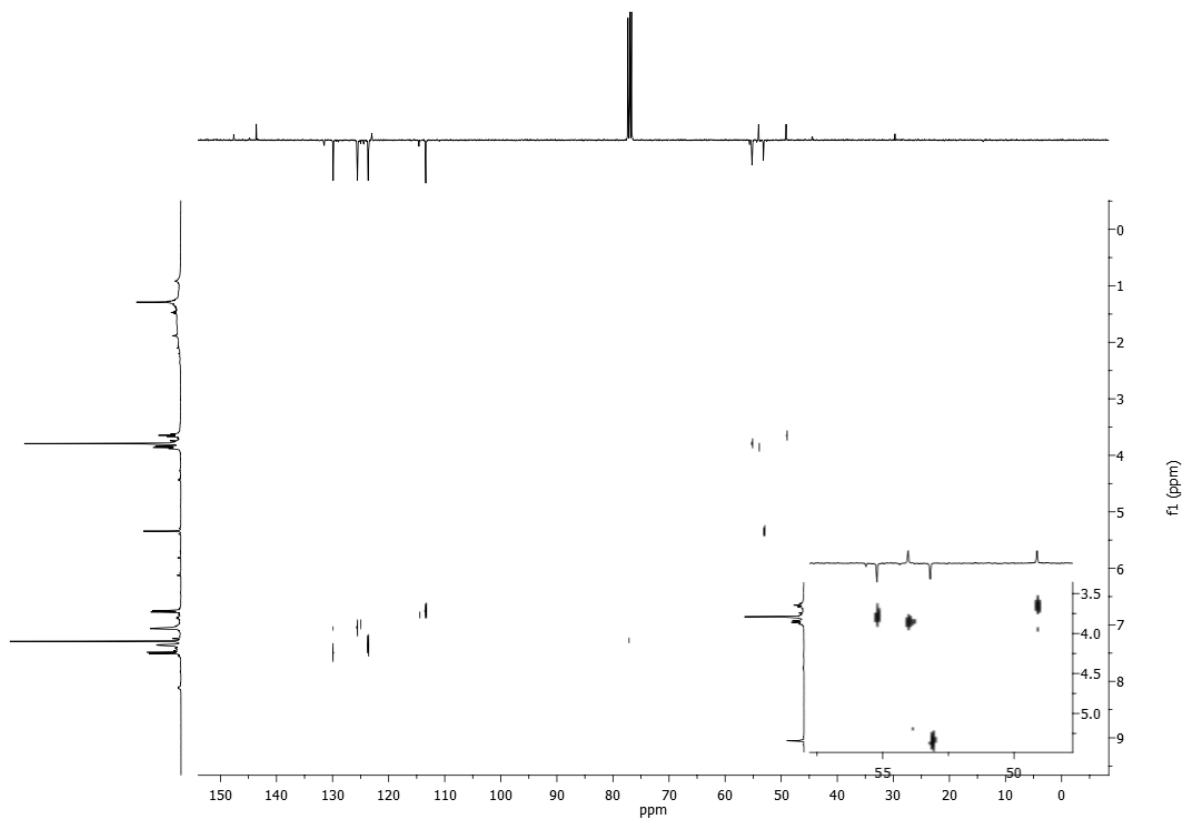




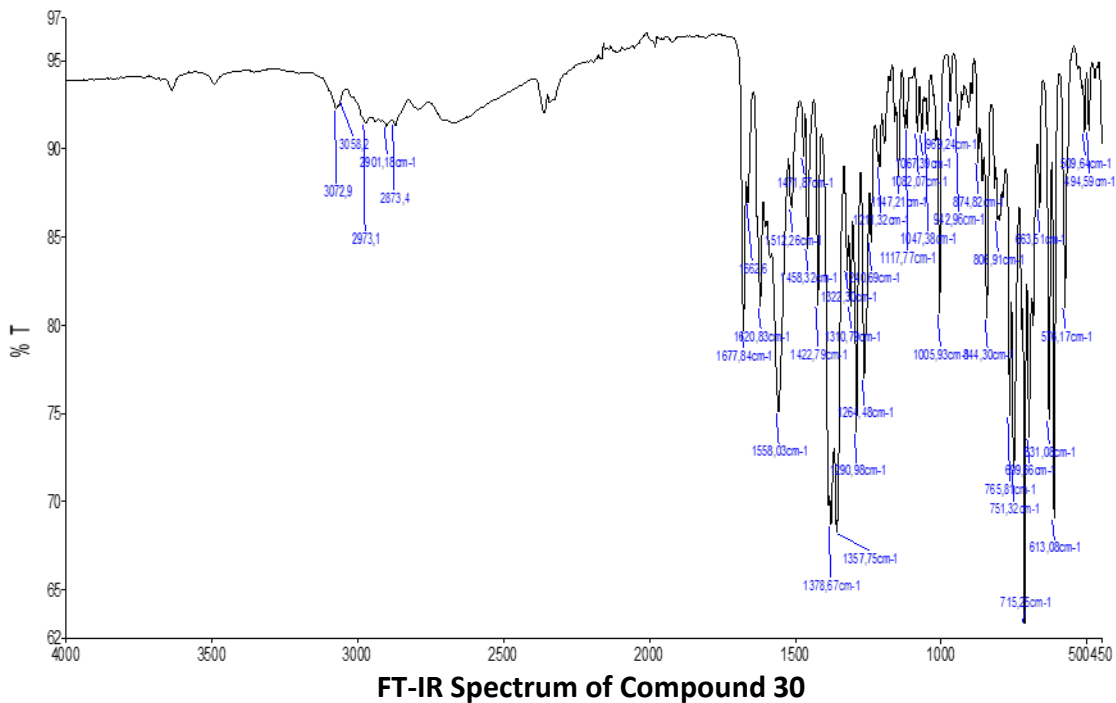
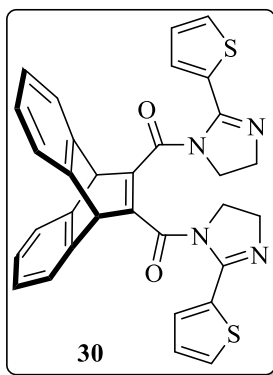
¹H-NMR Spectrum of Compound 29

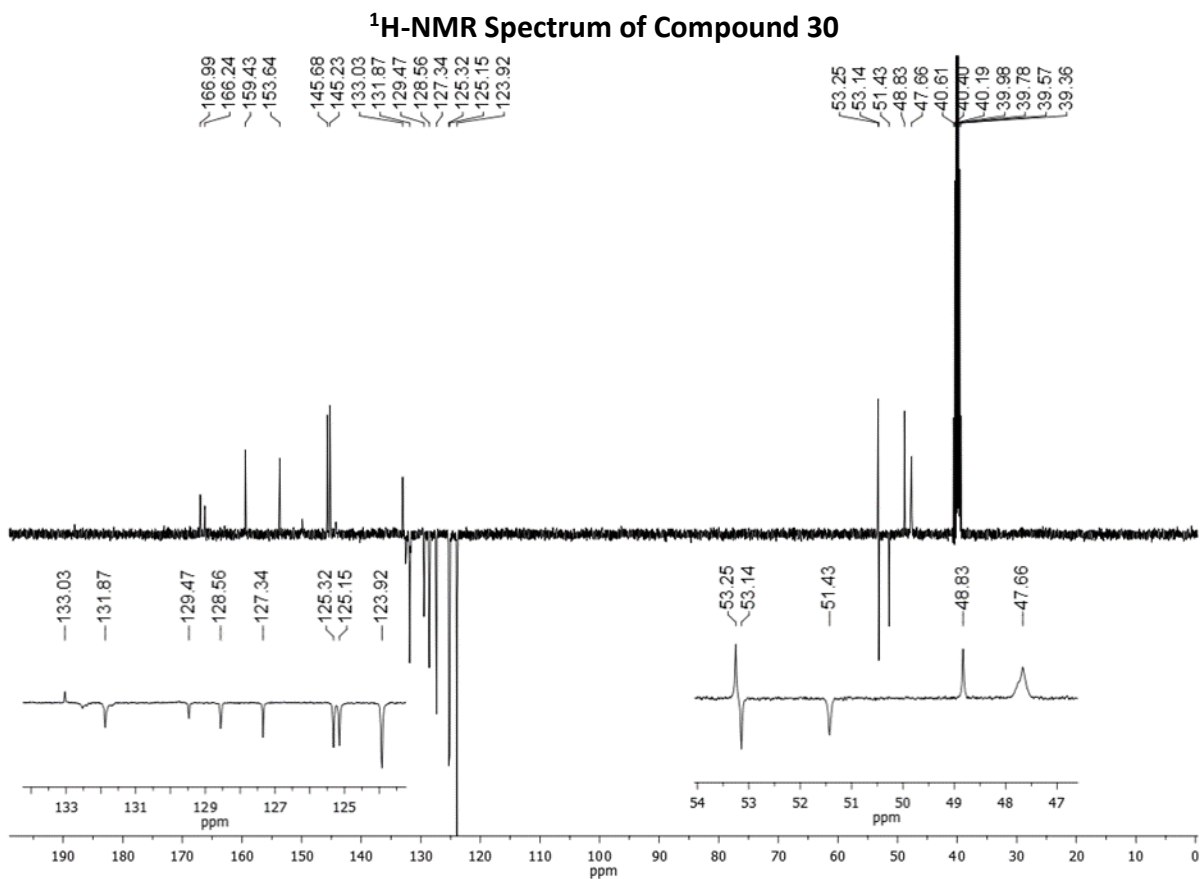
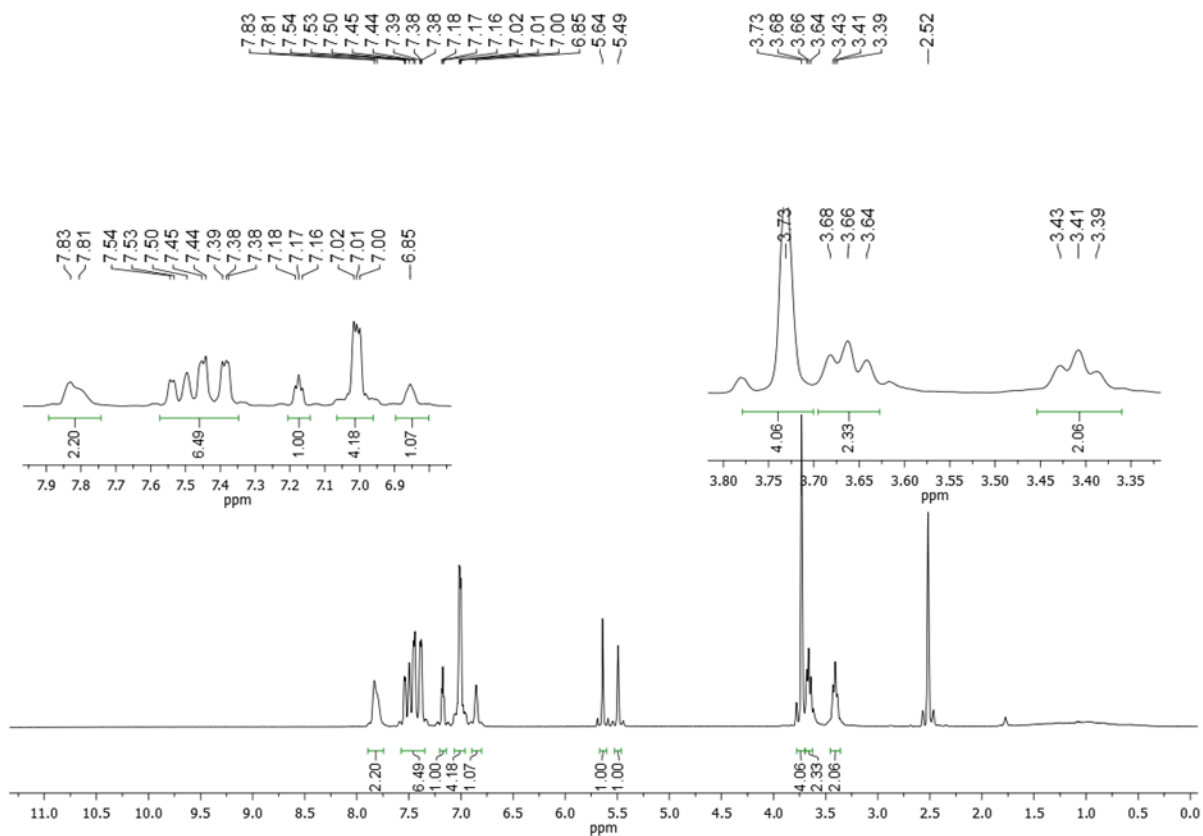


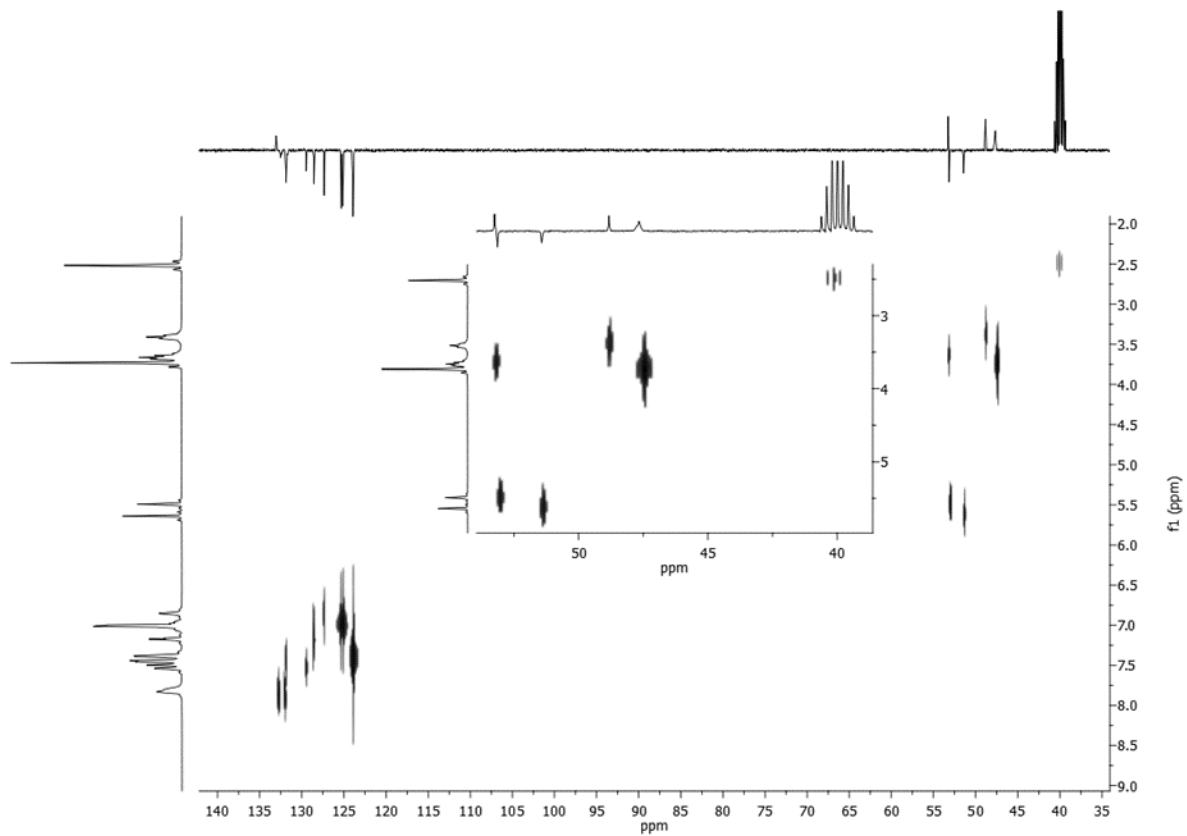
¹³C_{APT}-NMR Spectrum of Compound 29



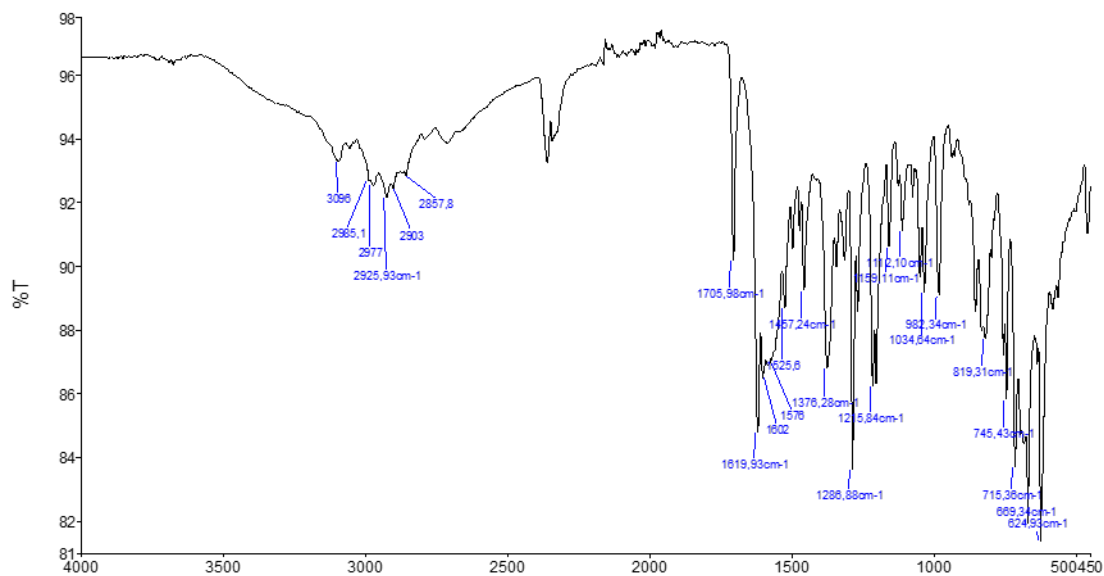
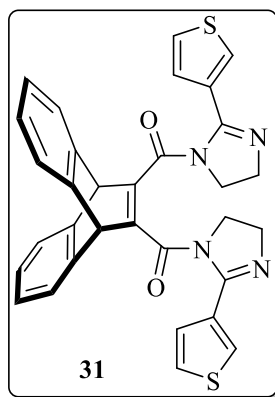
HETCOR-NMR Spectrum of Compound 29



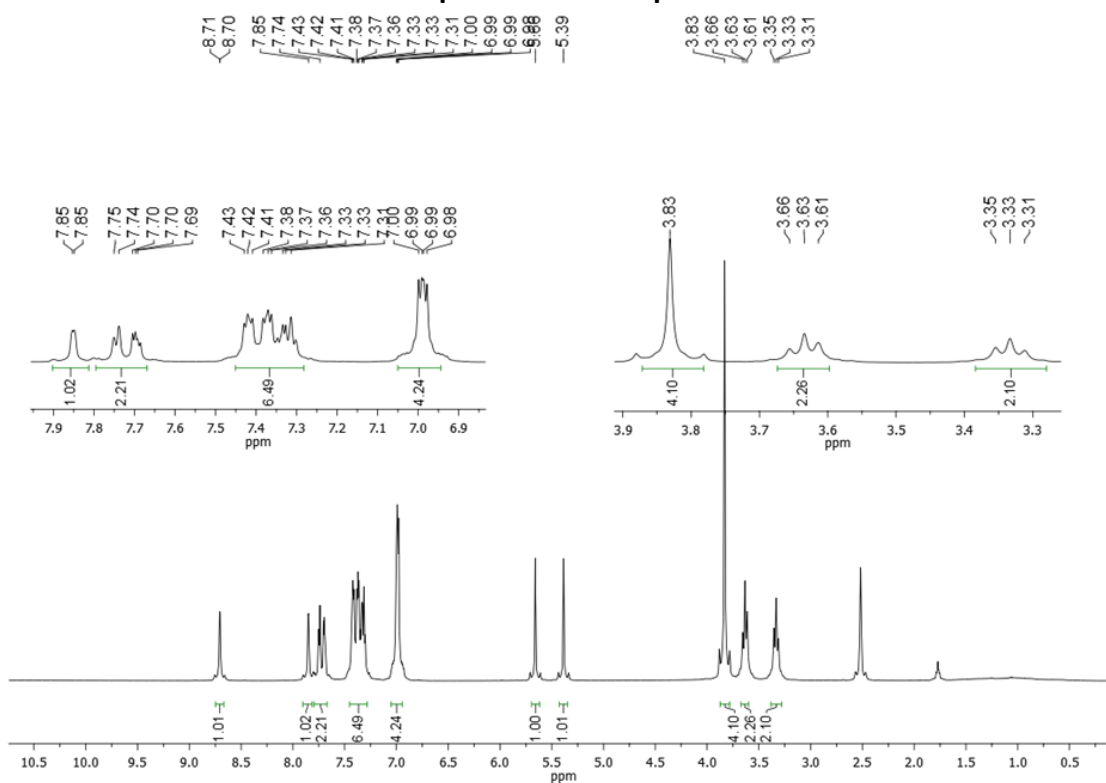


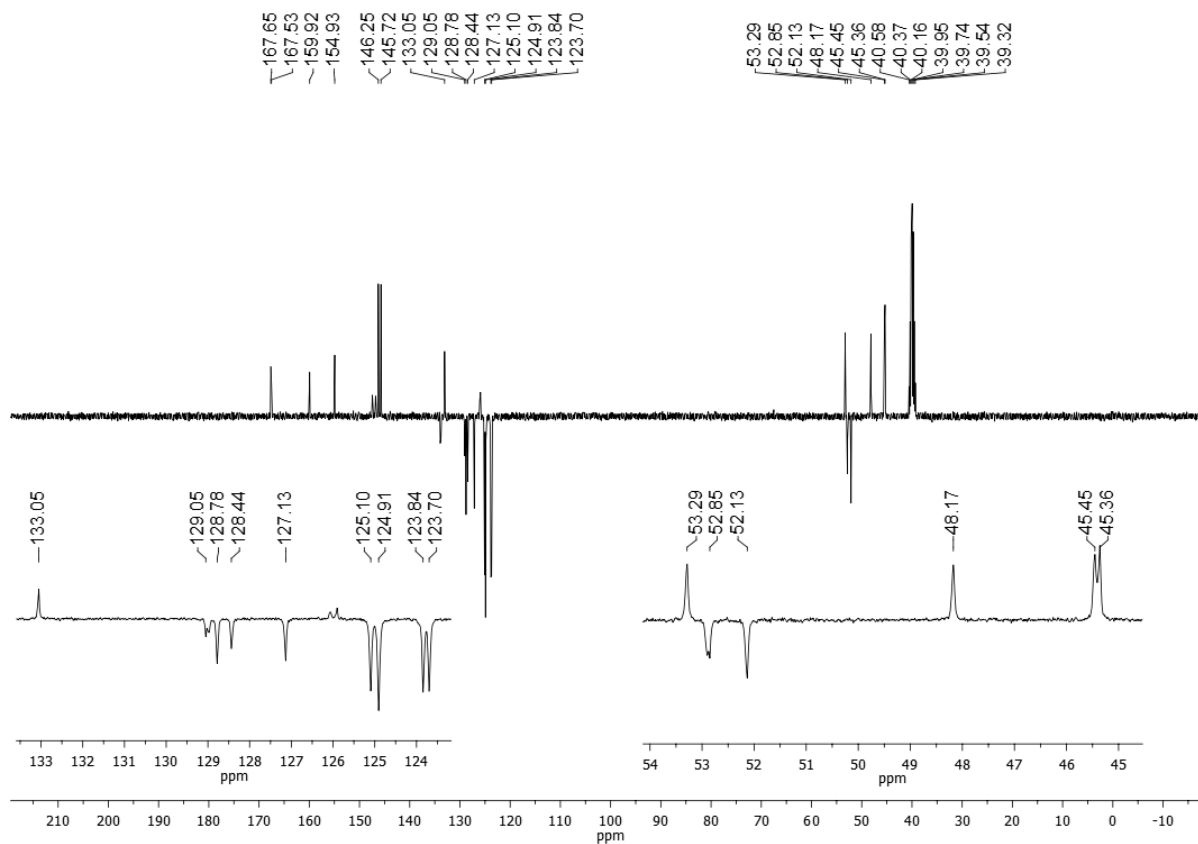
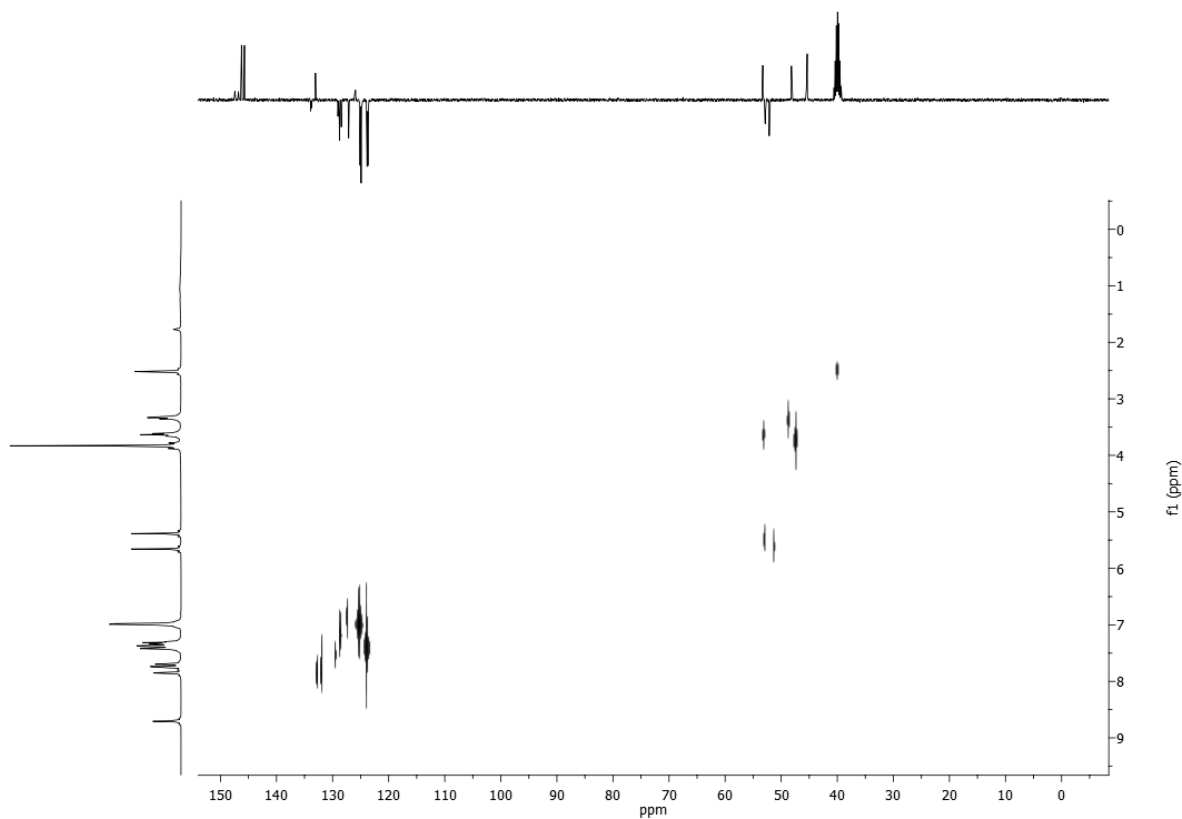
**HETCOR-NMR Spectrum of Compound 30**

Spectra of Compound 31



FT-IR Spectrum of Compound 31

¹H-NMR Spectrum of Compound 31

 $^{13}\text{C}_{\text{APT}}$ -NMR Spectrum of Compound 31

HETCOR-NMR Spectrum of Compound 31