Electronic Supplementary Material (ESI) for RSC Advances.

Stoichiometry-controlled cycloaddition of nitrilimines with unsymmetrical exocyclic dienones: Microwave-assisted synthesis of novel mono and dispiropyrazoline derivatives

Houda Gazzeh,[a] Sarra Boudriga,[a] Moheddine Askri,[a,*] Abderrahim Khatyr,[b] Michael Knorr,[b] Carsten Strohmann,[c] Christopher Golz, [c]Yoann Rousselin,[d] Marek M. Kubicki[d]

[a]*Laboratory of Heterocyclic Chemistry Natural product and Reactivity/CHPNR, Department of Chemistry, Faculty of Science of Monastir, 5000 Monastir, Tunisia.* *E-mail: moheddine.askri@fsm.rnu.tn;Tel: +216 98676187.*
[b]*Institut UTINAM - UMR CNRS 6213, Université de Franche-Comté, 16 Route de Gray, 25030 Besançon, France*
[c]*Technische Universität Dortmund, Anorganische Chemie Otto-Hahn-Strasse 6, 44221 Dortmund (Germany)*
[d]*Institute of Molecular Chemistry - UMR CNRS 6302 , University of Bourgogne, 9 Avenue A. Savary, F-21078 Dijon, France*

Supporting information

Table of contents **Page**

1. Spectroscopic data of synthesized compounds 3 and 4

Spiro[(4R*, 5R*)-4-hydro-1,3,4-triphenyl-Δ²-pyrazoline-5:3'-1'-(benzylidene)]tetral-2'-one (3a)

Orange crystals (0.43g, 85%); mp 104°C ±2;^{1}H NMR: δ 2.79 (d,1H, *J* = 15 MHz, H-4'), 3.96 (d, 1H, *J* = 15 MHz, H-4'), 4.5 (s, 1H, H-4), 6.2-7.59 (m, 22H, H_{arom}), 7.96 (s, 1H, $H_{ethylenic}$);^{13}C NMR: δ 33.1, 61.1, 75.3, 117.9, 121.1, 126.1, 126.9, 127.7, 127.9, 128.0, 128.2, 128.4, 128.6, 129.2, 129.5, 130.2, 131.0, 132.0, 132.2, 134.0, 135.0, 135.3, 139.0, 143.2, 147.6, 195.7; IR (ν_{max}, cm^{-1}): 1369, 1485, 1691 cm^{-1}; Anal Calcd for $C_{37}H_{28}N_2O$: C, 86.02; H, 5.46; N, 5.42; Found: C, 85.90; H, 5.40; N, 5.35.

Spiro[(4R*, 5R*)--4-hydro-1,3-diphenyl-4-*p*-tolyl-Δ²-pyrazoline-5:3'-1'-(*p*-tolylidene)] tetral-2'-one (3b)

Orange crystals(0.4 g, 73%); mp 248°C ±2; ^{1}H NMR: δ 2.28 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.76 (d, 1H, *J*=15 MHz, H-4'), 3.93 (d, 1H, *J*=15MHz, H-4'), 4.47 (s, 1H, H-4), 6.22-7.25 (m, 22H, H_{arom}), 7.91 (s,1H, $H_{ethylenic}$);^{13}C NMR δ = 21.1, 21.5, 32.8, 60.6, 75.2, 117.6, 120.9, 126.2, 127.5, 128.0, 128.1, 128.7, 129.2, 129.8, 129.9, 130.8, 131.2, 131.2, 131.9, 132.1, 134.9, 137.4, 139.2, 139.8, 143.1, 147.7, 195.9; IR (ν_{max}, cm^{-1}):1367, 1486, 1689cm^{-1}; Anal Calcd for $C_{39}H_{32}N_2O$: C, 86.00; H, 5.92; N, 5.14; Found: C, 85.97; H, 5.87; N, 4.91.

Spiro[(4R*, 5R*)-4-*p*-anis-4-hydro-1,3-diphenyl-Δ²-pyrazoline-5:3'-1'-(*p*-anisylidene)] tetral-2'-one (3c)

Orange crystals (0.47 g, 82%); mp 196°C±2; ^{1}H NMR : δ 2.73 (d, 1H, *J* = 15MHz, H-4'), 3.75 (s, 3H, OCH_3), 3.84 (s, 3H, OCH_3), 3.93 (d, 1H, *J*=15MHz, H-4'), 4.43 (s, 1H, H-4), 6.29-7.57 (m, 22H, H_{arom}), 7.88 (s,1H, $H_{ethylenic}$);^{13}C NMR: δ 32.9, 55.2, 55.3, 60.2, 75.3, 113.9, 117.6, 120.8, 126, 126.1, 126.2, 127.3, 127.4, 127.8, 127.9, 128.0, 129.9, 129.9, 131.4, 131.7, 131.9, 134.9, 139, 143.1, 147.8, 159.1, 160.7, 195.7; IR (ν_{max}, cm^{-1}): 1370, 1485, 1690 cm^{-1}; Anal Calcd for $C_{39}H_{32}N_2O_3$: C, 81.23; H, 5.59; N, 4.86; Found: C, 81.10; H, 5.50; N, 4.68.

Spiro[(4R*, 5R*)-4-hydro-4-*p*-chlorophenyl-1,3-diphenyl-Δ²-pyrazoline-5:3'-1'-(*p*-chlorobenzylidene)]tetral-2'-one (3d)

Orange crystals (0.45g, 77%); mp 260°C ±2; ^{1}H NMR: δ 2.73 (d, 1H, *J*=15MHz , H-4'), 3.95 (d,1H, *J*=15MHz, H-4'), 4.47 (s, 1H, H-4), 6.92-7.29 (m, 22H, H_{arom}), 7.88 (s, 1H, $H_{ethylenic}$);^{13}C NMR : δ 32.9, 60.2, 75.2, 117.9, 121.4, 126.2, 126.4, 128.1, 128.2, 128.2, 128.8, 128.8, 129.9, 130.7, 130.9, 131.5, 132.2, 132.4, 133.4, 133.8, 134.9, 135.3, 137.8, 142.8, 147.1, 195.3; IR (ν_{max}, cm^{-1}): 1371, 1485, 1690 cm^{-1}; Anal Calcd for $C_{37}H_{26}N_2Cl_2O$: C, 75.91; H, 4.48; N, 4.78; Found: C, 75.82; H, 4.39; N, 4,65.

Spiro[(4R*, 5R*)-4-hydro-4-*p*-cyanophenyl-1,3-diphenyl-Δ^2-pyrazoline-5:3'-1'-(*p*-cyanobenzylidene)]tetral-2'- one (3e)

Orange crystals (0.47g, 83%); mp 260°C ±2; ^{1}H NMR : δ 2.69 (d, 1H, *J*=15MHz , H-4'), 3.97 (d,1H, *J*=15MHz, H-4'), 4.51 (s, 1H, H-4), 6.23-7.60 (m, 22H, H_{arom}), 7.87 (s, 1H, $H_{ethylenic}$);^{13}C NMR: δ : 33.0, 60.3, 75.3, 111.9, 112.6, 118.3, 122.0, 126.0, 126.8, 128.3, 128.4, 128.5, 128.7, 129.4, 129.9, 130.2, 131.0, 131.7, 131.8, 132.3, 132.5, 134.8, 136.9, 139.2, 139.8, 142.5, 146.5, 194.5; IR: (ν_{max}, cm^{-1}): 1371, 1486, 1691, 2240 cm^{-1}; Anal Calcd for$C_{39}H_{26}N_4O$: C, 82.66; H, 4.62; N, 9.89; Found: C, 82.53; H, 4.51; N, 9.78

.

Spiro[(4R*, 5R*)-4-hydro-1,4-diphenyl-3-p-tolyl-Δ^2-pyrazoline-5:3'-1'-(benzylidene)] tetral-2'-one (3f)

Orange crystals (0.38g, 73%); mp 112°C ±2; ^{1}H NMR: δ 2.25 (s, 3H, CH_3); 2.77 (d,1H, *J*=15MHz, H-4'), 3.96 (d, 1H, *J*=15MHz, H-4'), 4.49 (s, 1H, H-4), 6.19-7.49 (m, 21H, H_{arom}), 7.95 (s,1H, $H_{ethylenic}$); ^{13}C NMR : δ 21.2, 33.0, 61.0, 75.0, 117.6, 120.9, 126.1, 126.2, 127.7, 127.7, 128.1, 128.5, 128.7, 128.8, 129.1, 129.3, 129.6, 129.8, 131.0, 132.1, 134.0, 135.0, 135.2, 138.0, 139.0, 143.2, 147.8, 195.8; IR (ν_{max}, cm^{-1}): 1366, 1488, 1690 cm^{-1}; Anal Calcd for $C_{38}H_{30}N_2O$: C, 86.01; H, 5.70; N, 5.28; Found: C, 85.92; H, 5.59; N, 5.13.

Spiro[(4R*, 5R*)-4-hydro-1-phenyl-3,4-*p*-tolyl-Δ^2-pyrazoline-5:3'-1'-(*p*-tolylidene)] tetral-2'-one (3g)

Orange crystals (0.40g, 70%); mp 198°C ±2; ^{1}H NMR : δ 2.26 (s, 3H, CH_3), 2.28 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.77 (d, 1H, *J*=15MHz, H-4'), 3.93 (d, 1H, *J*=15MHz, H-4'), 4.47 (s, 1H, H-4), 6.25-7.50 (m, 21H, H_{arom}), 7.91 (s, 1H, $H_{ethylenic}$);^{13}C NMR : δ 20.6, 20.7, 21.0, 32.4, 60.3, 74.6, 117.0, 120.2, 125.5, 125.7, 127.0, 127.5, 128.2, 128.3, 128.7, 129.3, 130.5, 130.7, 130.9, 131.7, 134.5, 136.8, 137.4, 138.6, 139.3, 142.8, 147.4, 195.5;

IR (ν_{max}, cm^{-1}):1365, 1489, 1689 cm^{-1}; Anal Calcd for $C_{40}H_{34}N_2O$: C, 85.99; H, 6.13; N, 5.01; Found: C, 85.57; H, 5.98; N, 4.98.

Spiro[(4R*, 5R*)-4-*p*-anisyl-4-hydro-1-phenyl-3-*p*-tolyl-Δ²-pyrazoline-5:3'-1'-(*p*-anisylidene)]tetral-2'-one (3h)

Orange crystals (0.45g, 77%); mp 146°C ±2; ^{1}H NMR : δ 2.25 (s, 3H, CH_3), 2.75 (d, 1H, *J*=15MHz, H-4'), 3.76 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 3.94 (d, 1H, *J*=15MHz, H4'), 4.43 (s, 1H, H-4), 6.26-7.57 (m, 21H, H_{arom}), 7.88 (s, 1H, $H_{ethylenic}$);^{13}C NMR : δ 21.2, 32.9, 55.2, 55.3, 60.3, 75.1, 113.9, 117.4, 120.6, 126.0, 126.2, 126.25, 127.3, 127.4, 127.8, 128.7, 128.8, 129.1, 129.9, 130.0, 131.4, 131.7, 135.0, 137.9, 138.9, 143.2, 147.9, 159.0, 160.7, 195.8; IR (ν_{max}, cm^{-1}): 1368, 1487, 1692cm^{-1}; Anal Calcd for $C_{40}H_{34}N_2O_3$: C, 81.33; H, 5.8; N, 4.74;found: C, 81.23; H, 5.74; N, 4.41.

Spiro [(4R*, 5R*)-4-*p*-chlorophenyl-4-hydro-1-phenyl-3-*p*-tolyl-Δ²-pyrazoline-5:3'-1'-(*p*-chlorobenzylidéne)] tetral-2'-one (3i)

Orange crystals (0.44 g, 75%); mp 258°C ±2; ^{1}H NMR : δ 2.26 (s, 3H, CH_3), 2.73 (d, 1H, *J*=15MHz , H-4'), 3.95 (d, 1H, *J*=15MHz , H-4'), 4.46 (s,1H, H-4), 6.29-7.41 (m, 21H, H_{arom}), 7.86 (s,1H, $H_{ethylenic}$);^{13}C NMR : δ 20.7, 32.5, 59.8, 74.5, 117.3, 120.7, 125.6, 125.9, 127.6, 128.2, 128.2, 128.3, 128.4, 129.4, 130.2, 130.4, 131.8, 132.0, 132.9, 133.3, 134.4, 134.7, 137.8, 142.5, 146.7, 194.9; IR (ν_{max}, cm^{-1}): 1370, 1488, 1691 cm^{-1}; Anal Calcd for $C_{38}H_{28}N_2Cl_2O$: C, 76.13; H, 4.71; N, 4.67; Found: C, 75.99; H, 4.52; N, 4.57.

Spiro [(4R*, 5R*)-4-*p*-cyanophenyl-4-hydro-1-phenyl-3-*p*-tolyl-Δ²-pyrazoline-5:3'-1'-(*p*-cyanobenzylidene)]tetral-2'-one (3j)

Orange crystals (0.42g, 72%); mp 176°C ±2; ^{1}H NMR : δ 2.25 (s, 3H, CH_3), 2.69 (d, 1H, *J*=15MHz, H-4'), 3.97 (d,1H, *J*=15MHz, H-4'), 4.51 (s, 1H, H-4), 6.23-7.59 (m, 21H, Harom), 7.87 (s,1H, $H_{ethylenic}$);^{13}C NMR : δ 20.7, 32.5, 60.0, 74.6, 117.5, 117.8, 119.6, 121.3, 124.4, 125.5, 125.9, 126.3, 128.2, 128.3, 128.6, 128.8, 129.0, 129.5, 129.7, 131.8, 133.4, 136.3, 138.2, 142.2, 146.2, 194.1; IR (ν_{max}, cm^{-1}):1370, 1487, 1692, 2239cm^{-1}; Anal Calcd for $C_{40}H_{28}N_4O$: C, 82.74; H, 4.86; N, 9.65; Found: C, 82.62; H, 4.72; N, 9.54.

Spiro [(4S*, 5S*, 4'R*, 5'R*)-4-hydro-1,3,4-triphenyl-Δ²-pyrazoline-5:1''.3'':5']tetral-2''-one (4a)

Yellow crystals (0.59 g, 84%); mp > 260 °C;^{1}H NMR : δ 3.39 (q, 2H, *J* = 15MHz, CH_2), 4.9 (s, 1H, H-4), 5.08 (s, 1H, H-4'), 6.33-7.7 (m, 32H, H_{arom});^{13}C NMR : δ 39.9, 59.0, 66.4, 74.5, 83.8, 116.3, 119.7, 124.6, 124.7, 126.1, 126.2, 126.6, 127.8, 127.9, 128.1, 128.4, 128.9, 129.3, 129.9, 131.5, 131.9, 133.5, 135.4, 143.3, 144.0, 146.1, 149.8, 200.8; IR (ν_{max}, cm^{-1}): 1367, 1485, 1691 cm^{-1};Anal Calcd for $C_{50}H_{38}N_4O$: C, 84.48; H, 5.39; N, 7.88; Found: C, 84.31; H, 5.28; N, 7.65.

Spiro [(4S*, 5S*, 4'R*, 5'R*)-4-hydro-1,3-diphenyl-4-*p*-tolyl-Δ^2-pyrazoline-5:1''.3'':5'] tetral-2''-one (4b)

Yellow crystals (0.62g, 85%); mp > 260 °C;^{1}H NMR : δ 1.99 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.15 (d, 1H, *J*=18MHz, H-4''), 3.34 (d, 1H, *J*=18MHz, H-4''), 4.78 (s, 1H, H-4), 4.93 (s, 1H, H-4'), 6.22-7.6 (m, 32H, H_{arom});^{13}C NMR : δ 20.9, 21.3, 39.4, 58.8, 66.2, 74.4, 83.8, 116.3, 119.5, 124.5, 124.6, 126.1, 126.2, 126.6, 127.7, 128.0, 128.3, 128.4, 128.4,129.0, 129.3, 130.1, 130.4, 131.6, 132.1, 132.3, 133.5, 137.5, 138.7, 143.4, 144.1, 146.2, 149.9, 200.9; IR (ν_{max}, cm^{-1}):1368, 1486, 1691 cm^{-1}; Anal Calcd for $C_{52}H_{42}N_4O$: C, 84.52; H, 5.73; N, 7.58; found: C, 84.32; H, 5.59; N, 7.43.

Spiro [(4S*, 5S*, 4'R*, 5'R*)-4-*p*-anisyl-4-hydro-1,3-diphenyl-Δ^2-pyrazoline-5:1''.3'':5'] tetral-2''-one (4c)

Yellow crystals (0.63 g, 83%); mp >260 °C;^{1}H NMR : δ 3.25 (d, 1H, *J*=15MHz, H-4''), 3.43 (d, 1H, *J*=15MHz, H-4''); 3.60 (s, 3H, OCH_3); 3.91 (s, 3H, OCH_3); 4.86 (s,1H, H-4); 5.01 (s,1H, H-4'); 6.29-7.7 (m, 32H, H_{arom});^{13}C NMR : δ 38.9, 54.5, 54.9, 57.9, 65.3, 66.4, 73.9, 83.3, 113.3, 113.9, 115.1, 115.7, 119.0, 124.0, 124.1, 125.0, 125.6, 125.8, 126.1, 126.8, 127.4, 127.6, 127.8, 128.0, 128.7, 129.6, 130.3, 131.0, 131.5, 132.9, 142.8, 143.6, 145.7, 149.6, 158.5, 159.3, 200.5; IR (ν_{max}, cm^{-1}): 1368, 1485, 1690 cm^{-1}; Anal Calcd for $C_{52}H_{42}N_4O_3$: C, 81.02; H, 5.49; N, 7.27; Found: C, 80.89; H, 5.34; N, 6.97.

Spiro [(4S*, 5S*, 4'R*, 5'R*)-4-*p*-chlorophenyl-4-hydro-1,3-diphenyl-Δ^2-pyrazoline-5:1''.3'':5')] tetral-2''-one (4d)

Yellow crystals(0.63 g, 81%); mp > 260 °C;^{1}H NMR : δ 3.25 (d, 1H, *J*=18 MHz, H-4''), 3.34 (d, 1H, *J*=18 MHz, H-4''), 4.77 (s, 1H, H-4), 4.99 (s, 1H, H-4'), 6.26-7.63 (m, 32H, H_{arom});^{13}C NMR : δ 39.3, 58.3, 65.6, 74.2, , 83.7, 116.3, 119.9, 124.7, 125.0, 126.5, 126.7, 128.1, 128.2, 128.4, 128.6, 128.7, 129.2, 129.7, 130.8, 131.1, 131.6, 131.9, 133.0, 133.8,

133.9, 134.9, 143.1, 143.7, 145.6, 149.5, 200.4; IR (ν_{max}, cm^{-1}):1369, 1487, 1692cm^{-1}; Anal Calcd for: $C_{50}H_{36}Cl_2N_4O$: C, 77.02; H, 4.65; N, 7.19; Found: C, 76.95; H, 4.55; N, 7.04.

Spiro [(4S*, 5S*, 4'R*, 5'R*)-4-*p*-cyanophenyl-4-hydro-1,3-diphenyl-Δ^2-pyrazoline-5:1''.3'':5'] tetral-2''-one (4e)

Yellow crystals (0.63g, 83%); mp > 260°C;^{1}H NMR : δ 3.29 (s, 2H, CH_2), 4.79 (s, 1H, H-4), 5.04 (s, 1H, H-4'), 6.21-7.59 (m, 32H, H_{arom}), ^{13}C NMR : δ 38.1, 58.6, 65.8, 74.0, 83.7,112.1, 113.4, 116.3, 117.9, 120.3, 124.9, 125.3, 125.8, 126.4, 127.0, 128.2, 128.3, 128.4, 128.6, 129.1, 129.2, 129.3, 130.6, 130.9, 131.2, 132.3, 132.6, 140.6, 143.4, 144.9, 200.1; IR (ν_{max}, cm^{-1}): 1370, 1487, 1692, 2240 cm^{-1};Anal Calcd for: $C_{52}H_{36}N_6O$: C, 82.08; H, 4.77; N, 11.05; Found: C, 81.98; H, 4.68; N, 10.86.

Spiro [(4S*, 5S*, 4'R*, 5'R*)-4-hydro-1,4-diphenyl-3-*p*-tolyl-Δ^2-pyrazoline-5:1''.3'':5'] tetral-2''-one (4f)

Yellow crystals (0.62g, 85%); mp > 260 °C;^{1}H NMR: δ 2.17(s, 3H, CH_3), 2.29 (s, 3H, CH_3), 3.23 (d, 1H, *J*=18 MHz , H-4''), 3.3 (d, 1H, *J*=18 MHz , H-4''), 4.79 (s, 1H, H-4), 4.97 (s,1H, H-4'), 6.25-7.51 (m, 30H, H_{arom});^{13}C NMR : δ 21.3, 21.4, 39.4, 59.0, 66.5, 74.4, 83.7, 116.3, 119.5, 124.6, 124.6, 125.2, 126.1, 126.17, 126.6, 127.7, 127.8, 128.1, 128.2, 128.3, 128.7, 128.8, 128.8, 129.0, 129.2, 129.3, 129.9, 130.1, 133.5, 133.6, 135.5, 138.3, 138.6, 143.5, 144.1, 146.3, 149.9, 201.0; IR (ν_{max}, cm^{-1}) :1368, 1485, 1690 cm^{-1}; Anal Calcd for $C_{52}H_{42}N_4O$: C, 84.52; H, 5.73; N, 7.58; Found: C, 84.40; H, 5.65; N, 7.46.

Spiro [(9S*, 10R*, 7R*, 10R*)-4-hydro-1-phenyl-3,4-*p*-tolyl-Δ^2-pyrazoline-5:1''.3'':5'] tetral-2''-one (4g)

Yellow crystals(0.68 g, 89%); mp>260 °C;^{1}H NMR : δ 2.09(s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.48 (s, 3H, CH_3), 3.25 (d, 1H, *J* =18 MHz , H-4''), 3.43 (d, 1H, *J*=18 MHz , H-4''), 4.88 (s, 1H, H-4), 5.03 (s, 1H, H-4'), 6.33-7.61 (m, 30H, H_{arom});^{13}C NMR : δ 20.4, 20.7, 20.8, 20.9, 38.9, 58.3, 65.8, 73.8, 83.2, 115.7, 118.9, 124.0, 124.8, 125.6, 126.1, 127.2, 127.5, 127.7, 128.3, 128.5, 128.7, 128.8, 129.7, 130.1, 131.9, 136.9, 137.7, 138.1, 143.1, 143.7, 145.9, 200.5; IR (ν_{max}, cm^{-1}) :1366, 1486, 1689cm^{-1}; Anal Calcd for $C_{54}H_{46}N_4O$: C, 84.56; H, 6.05; N, 7.30; Found: C, 84.49; H, 5.94; N, 6.93

Spiro [(4S*, 5S*, 4'R*, 5'R*)-4-*p*-anisyl-4-hydro-1-phenyl-3-*p*-tolyl-Δ^2-pyrazoline-5:1''.3'':5'] tetral-2''-one (4h)

Yellow crystals(0.68 g, 86%); mp > 260 °C;^{1}H NMR : δ 2.26 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 3.39 (d, 1H, *J*=15 MHz , H-4''), 3.47 (d, 1H, *J*=15 MHz , H-4''), 3.60 (s,3H, OCH_3), 3.91 (s, 3H, OCH_3), 4.85 (s, 1H, H-4); 5.00 (s, 1H, H-4'), 6.32-7.6 (m, 30H, Harom), ^{13}C NMR : δ 21.2, 21.3, 39.4, 55.0, 55.3, 58.5, 65.9, 74.3, 83.8, 113.8, 114.4, 115.5, 116.2, 119.4, 124.4, 124.5, 125.7, 126.0, 126.2, 126.6, 127.4, 127.8, 128.0, 128.4, 128.8, 129.2, 129.2, 129.3, 130.3, 130.8,133.5, 138.3, 138.5, 143.5, 144.28, 146.4, 150.1, 159.0, 159.8, 201.1; IR (ν_{max}, cm^{-1}):1368, 1486, 1690 cm^{-1}; Anal Calcd for $C_{54}H_{46}N_4O_3$: C, 81.18; H, 5.80; N, 7.01; Found: : C, 81.12; H, 5.75; N, 6.93.

Spiro [(4S*, 5S*, 4'R*, 5'R*)-4-*p*-chlorophenyl-4-hydro-1-diphenyl-3-*p*-tolyl-Δ^2-pyrazoline-5:1''.3'':5')] tetral-2''-one (4i)

Yellow crystals(0.71g, 88%); mp > 260 °C; ^{1}H NMR : δ 2.27 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.30 (d, 1H, *J*=18MHz , H-4''), 3.32 (d, 1H, *J*=18MHz , H-4''), 4.78 (s,1H, H-4), 5.01 (s,1H, H-4'), 6.28-7.58 (m, 32H, H_{arom});^{13}C NMR :δ 20.8, 20.9, 38.9, 57.8, 65.2, 73.6, 83.1, 115.7, 119.2, 124.2, 124.4, 125.4, 126.0, 126.1, 127.6, 127.7, 127.8, 127.9, 128.2, 128.3, 128.5, 128.6, 128.9, 129.2, 130.3, 131.5, 132.5, 133.3, 133.5,134.3, 138.2, 138.4, 142.7, 143.4, 145.3, 149.5, 200.4;IR (ν_{max}, cm^{-1}):1389, 1492, 1693cm^{-1};Anal Calcd for $C_{52}H_{40}Cl_2N_4O$: C,77.32; H, 4.99; N, 6.94; Found: C,77.27; H, 4.94; N, 6.89

Spiro [(4S*, 5S*, 4'R*, 5'R*)-4-*p*-cyanophenyl-4-hydro-1-diphenyl-3-*p*-tolyl-Δ^2-pyrazoline-5:1''.3'':5'] tetral-2''-one (4j)

Yellow crystals(0.67g, 85%); mp > 260 °C; ^{1}H NMR : δ 2.27 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 3.29 (s, 2H, CH_2), 4.79 (s,1H, H-4), 5.05 (s,1H, H-4'), 6.29-7.86 (m, 32H, H_{arom});^{13}C NMR : δ 21.3, 21.3, 39.4, 58.6, 65.9, 73.9, 83.6, 112.0, 113.1, 116.2,118.0, 120.1, 124.9, 125.3, 125.7, 126.4, 127.0, 127.8, 128.2, 128.3, 128.4, 128.5, 128.6, 129.1, 129.3, 129.5, , 132.3, 132.6, 138.7, 139.1, 139.4, 140.8, 142.8, 143.5, 145.1, 149.3, 199.8;IR (ν_{max}, cm^{-1}):1370, 1488, 1692, 2238 cm^{-1}; Anal Calcd for $C_{54}H_{40}N_6O$: C, 82.21; H, 5.11; N, 10.65; Found: C, 82.09; H,5.02; N, 10.52.

2. ^{1}H and ^{13}C-NMR Spectra of compounds 3 and 4

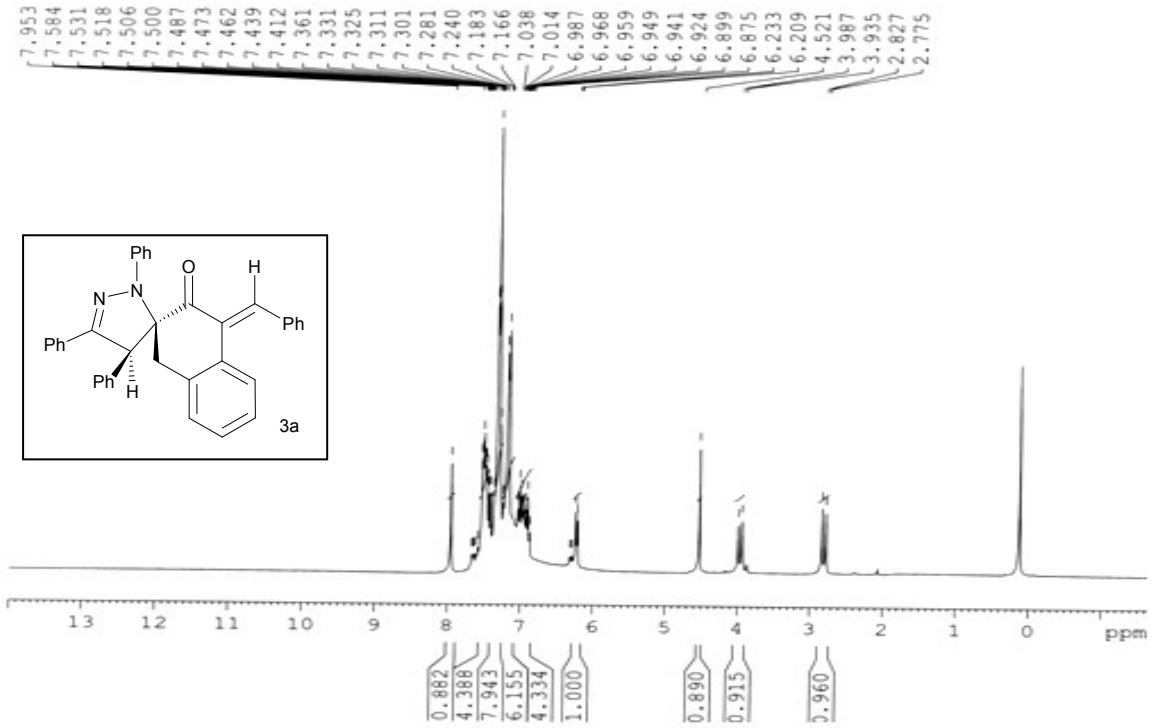

Fig 1. ^{1}H NMR Spectrum of **3a** in $CDCl_3$

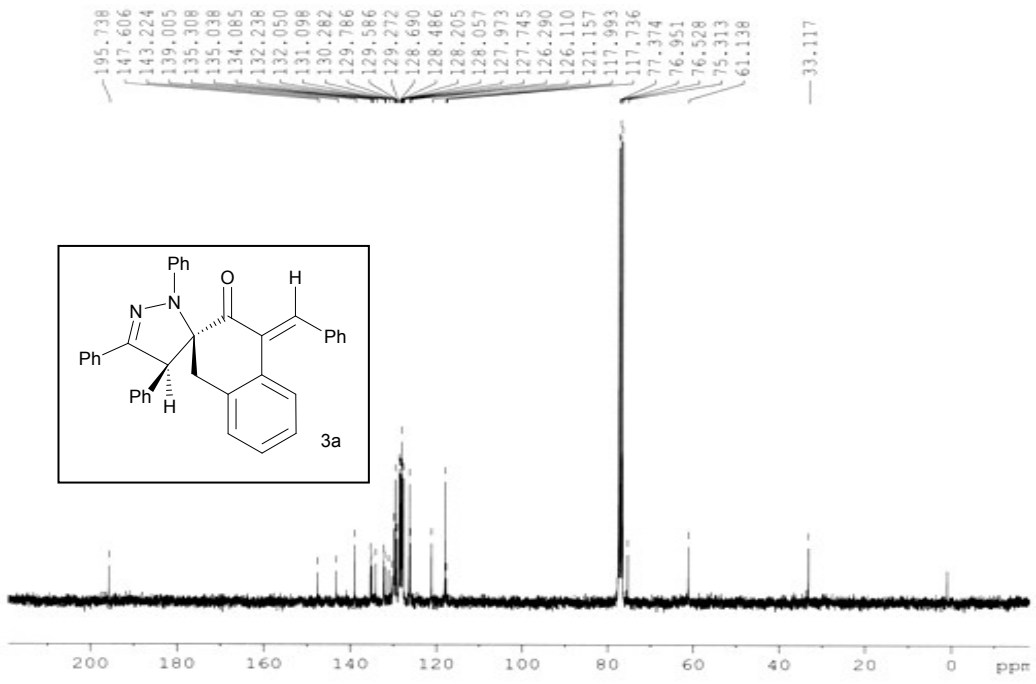

Fig 2. ^{13}C NMR Spectrum of **3a** in $CDCl_3$

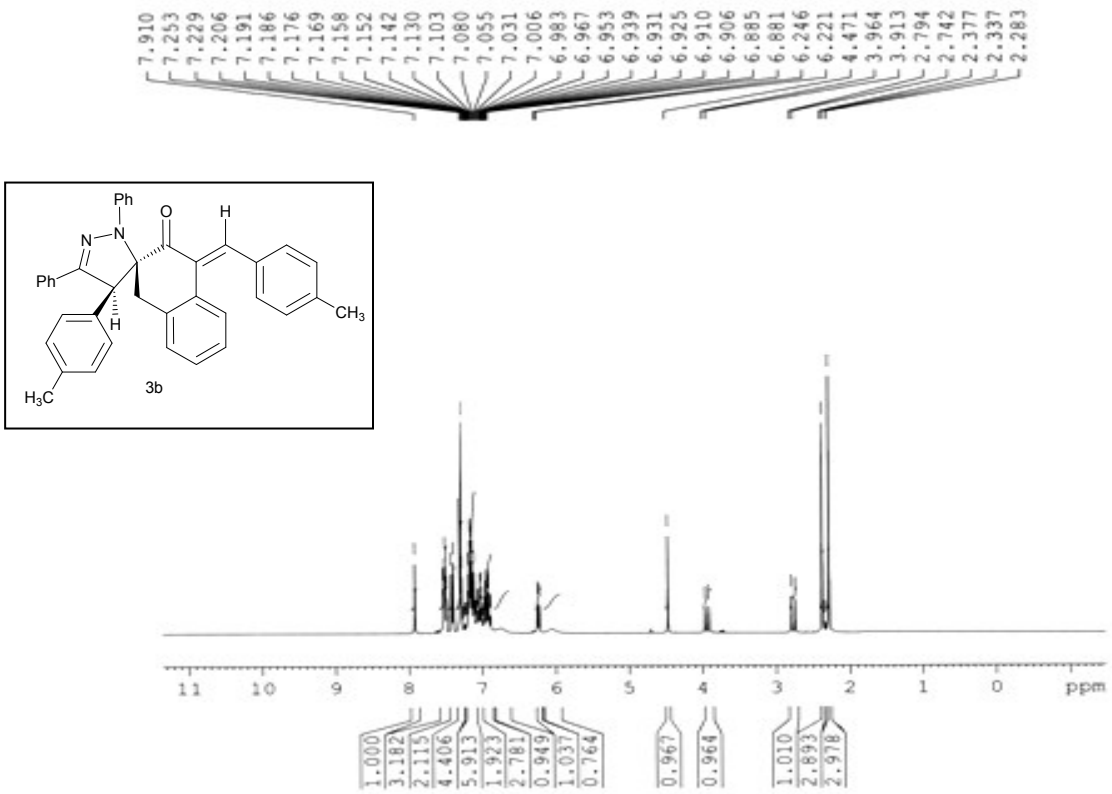

Fig 3. ^{1}H NMR Spectrum of **3b** in $CDCl_3$

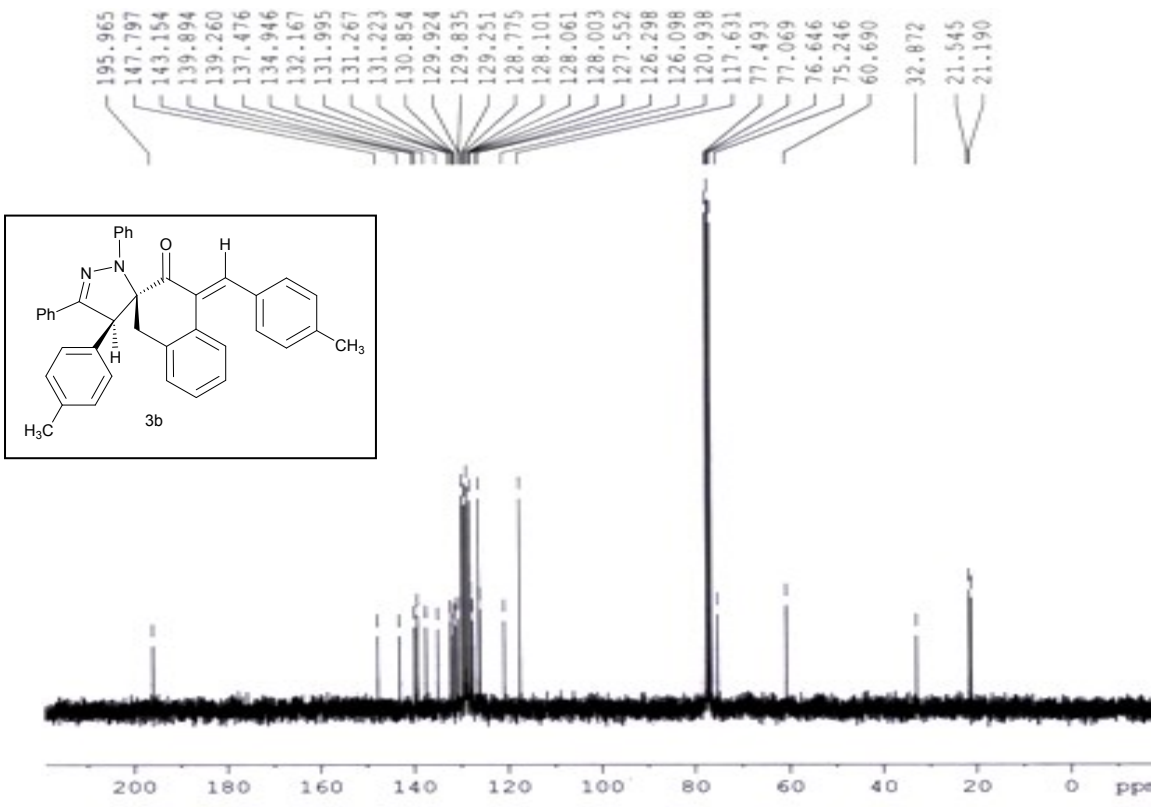

Fig 4. ^{13}C NMR Spectrum of **3b** in $CDCl_3$

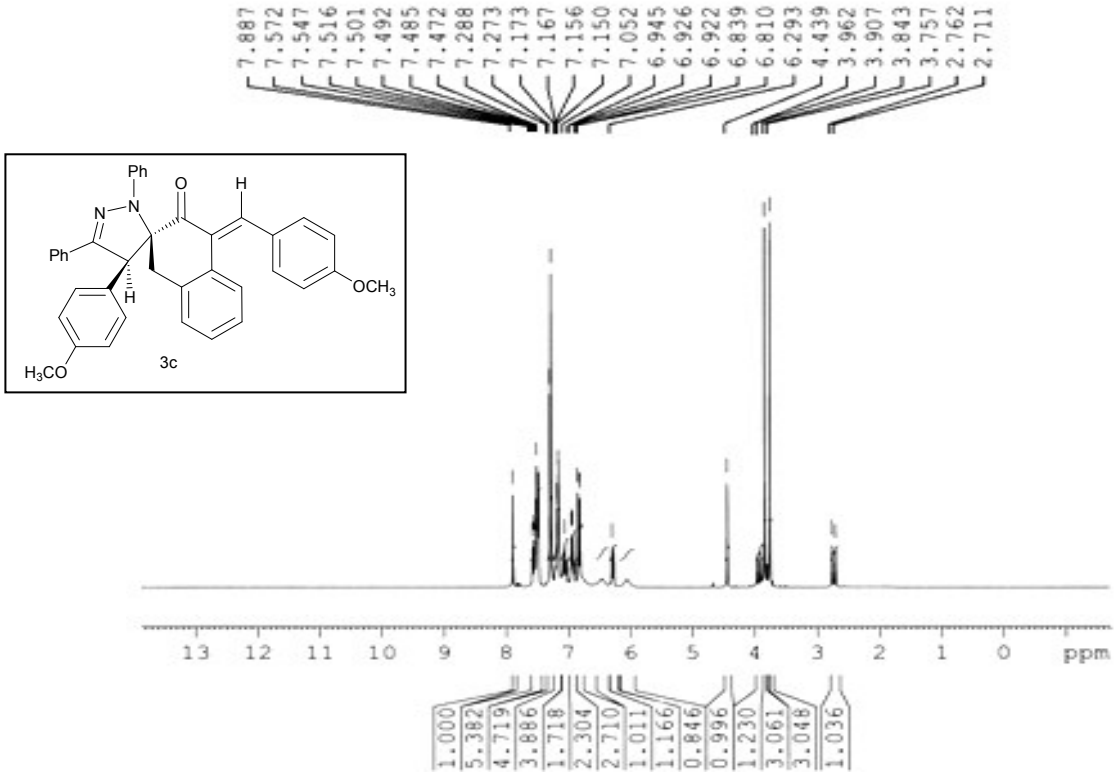

Fig 5. ^{1}H NMR Spectrum of **3c** in $CDCl_3$

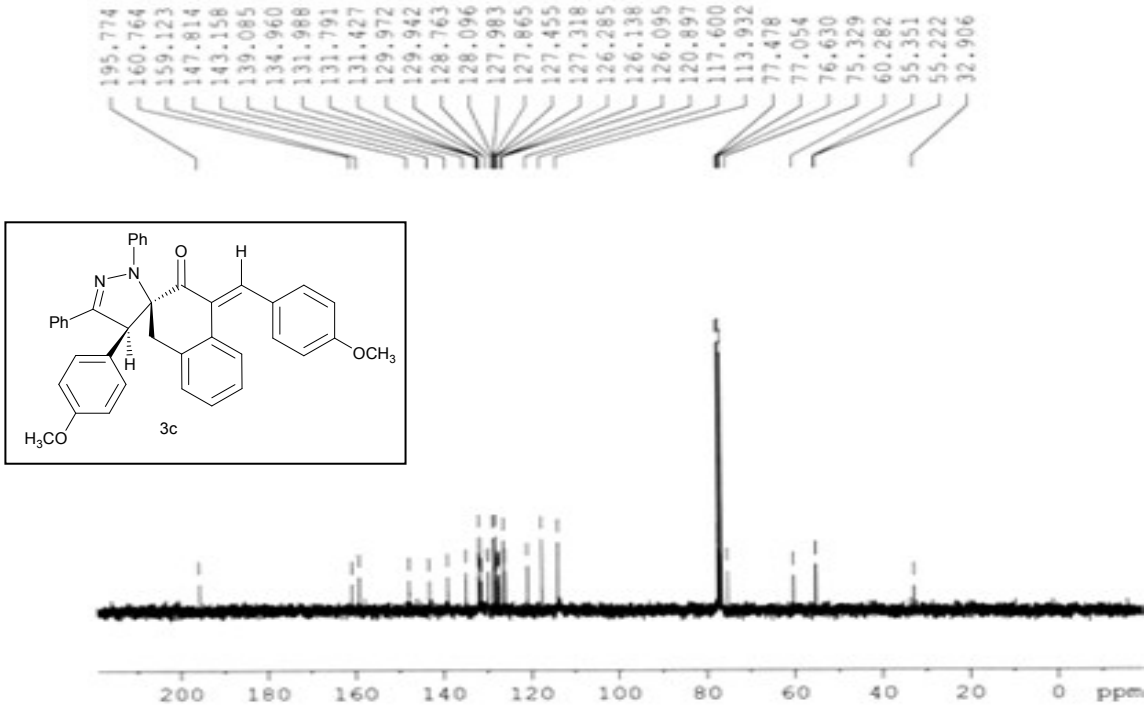

Fig 6. ^{13}C NMR Spectrum of **3c** in $CDCl_3$

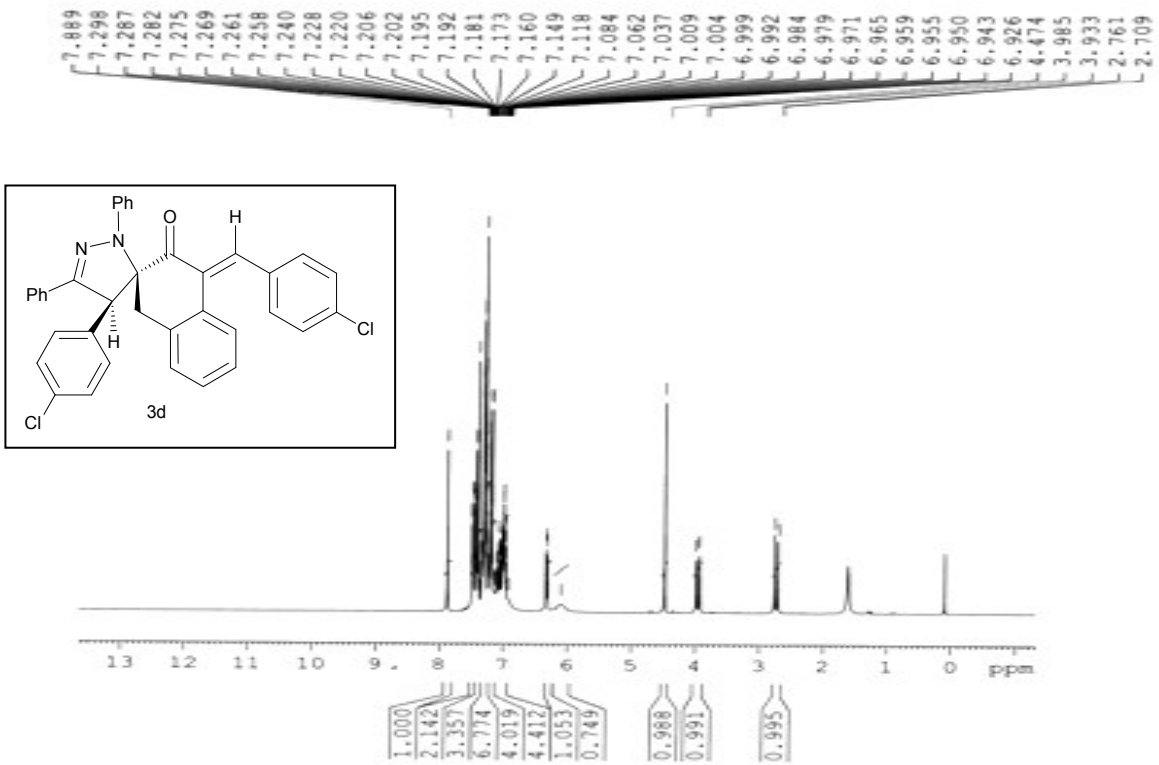

Fig 7. ^{1}H NMR Spectrum of **3d** in $CDCl_3$

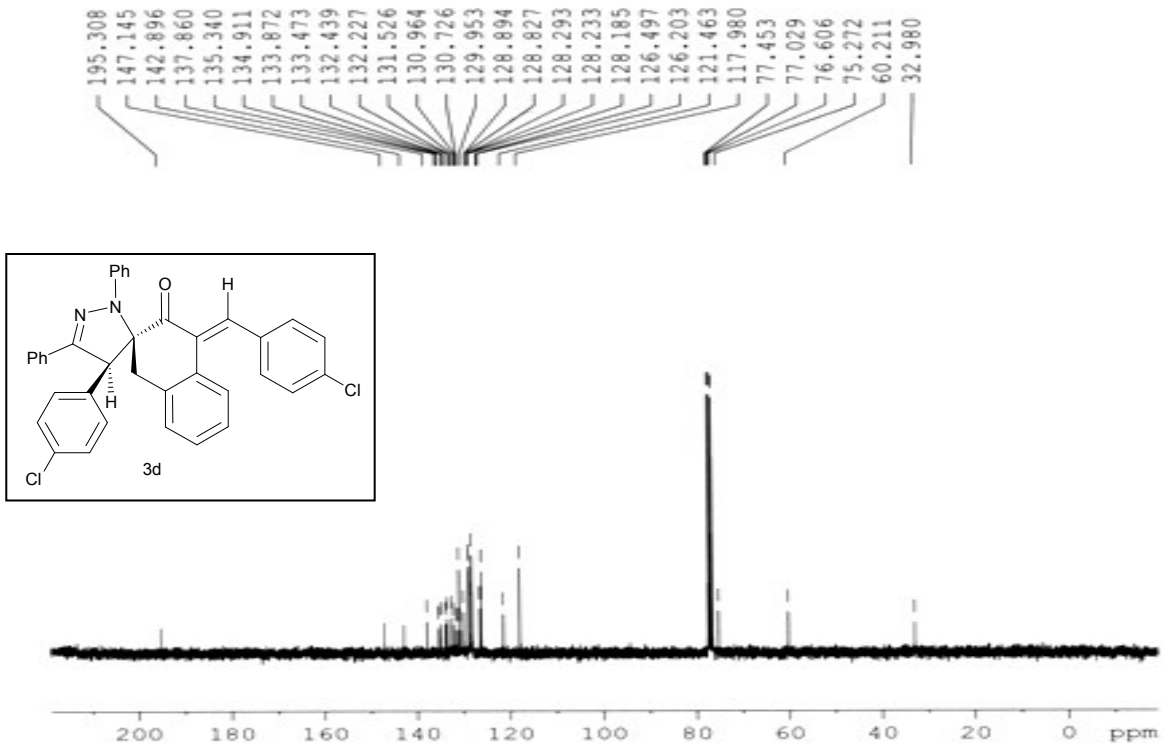

Fig 8. ^{13}C NMR Spectrum of **3d** in $CDCl_3$

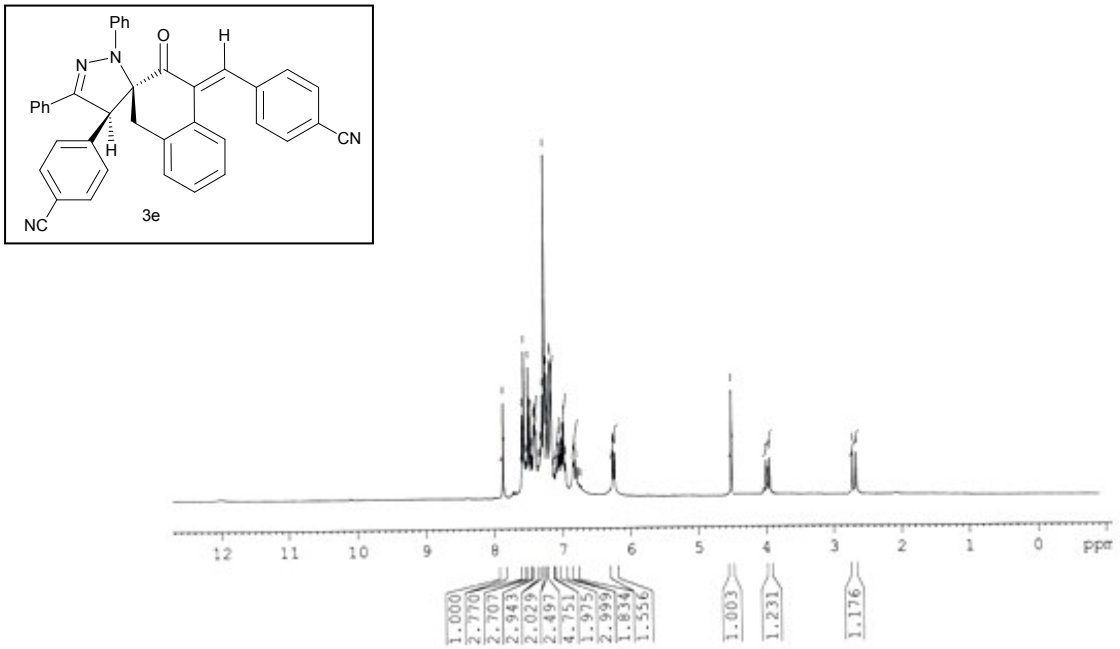

Fig 9. ^{1}H NMR Spectrum of **3e** in $CDCl_3$

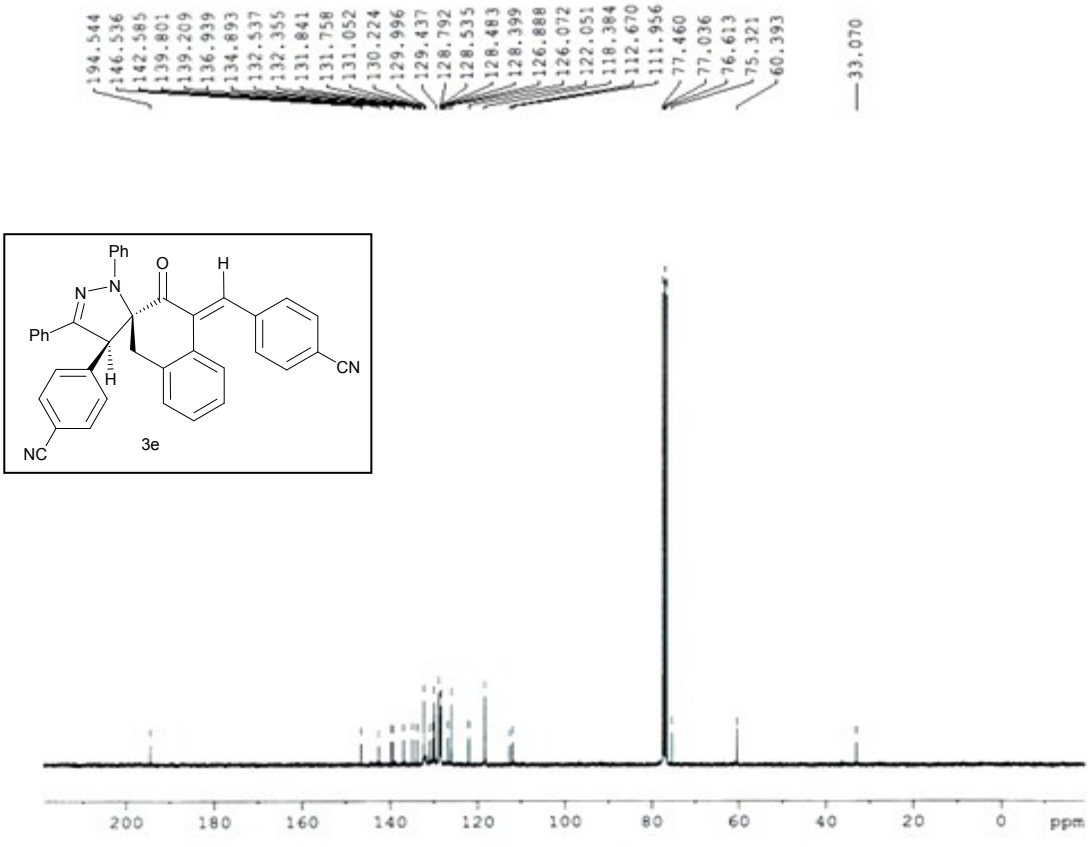

Fig 10. ^{13}C NMR Spectrum of **3e** in $CDCl_3$

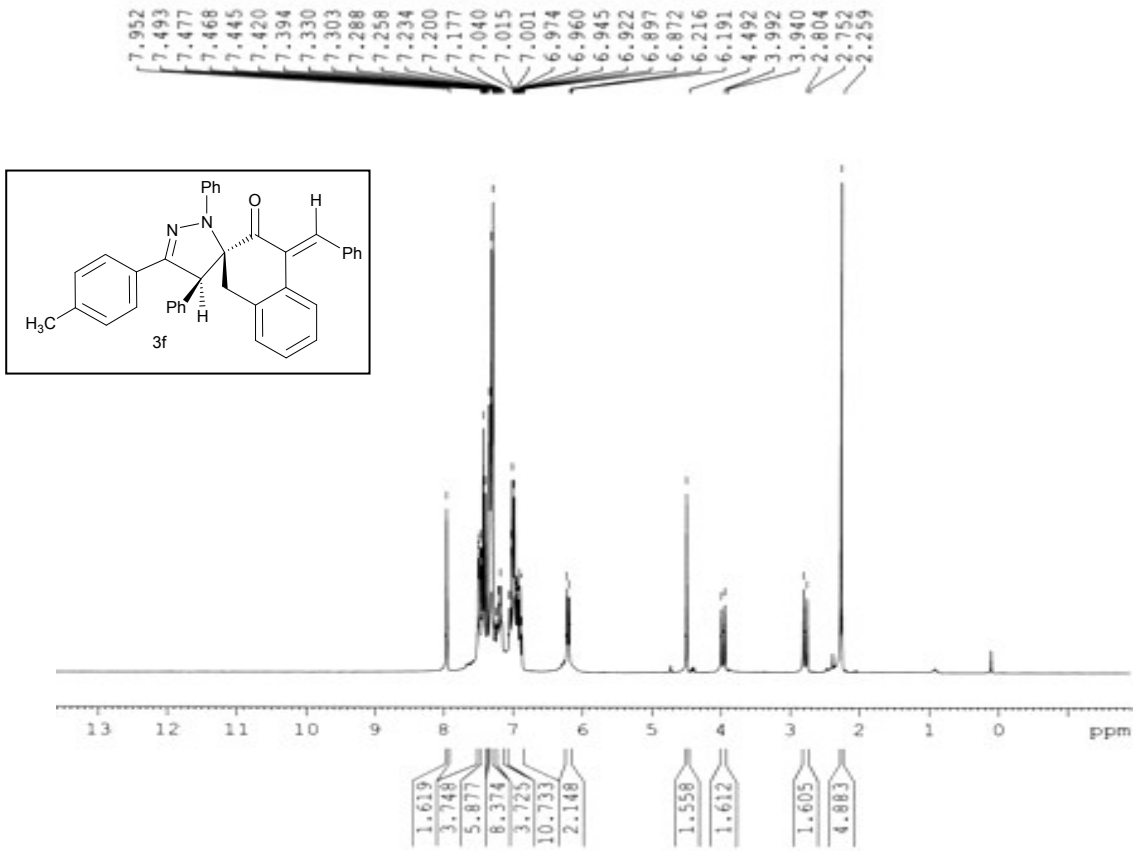

Fig 11. ^{1}H NMR Spectrum of **3f** in $CDCl_3$

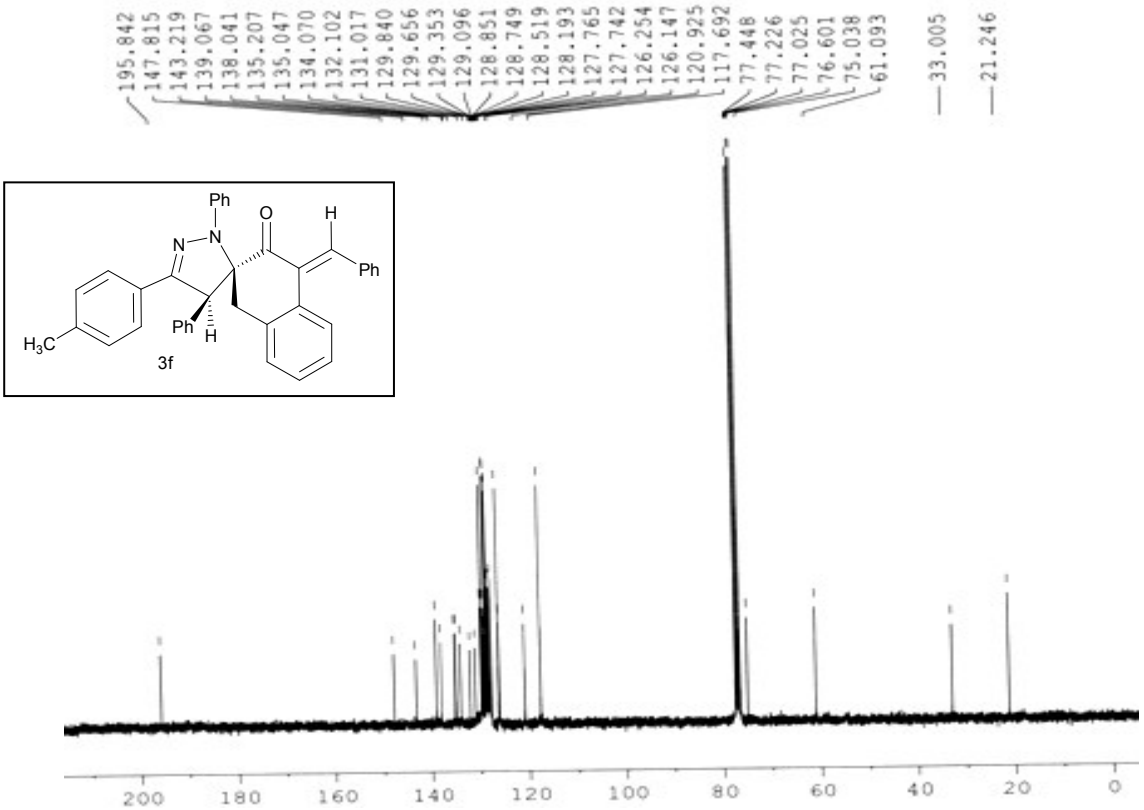

Fig 12. ^{13}C NMR Spectrum of **3f** in $CDCl_3$

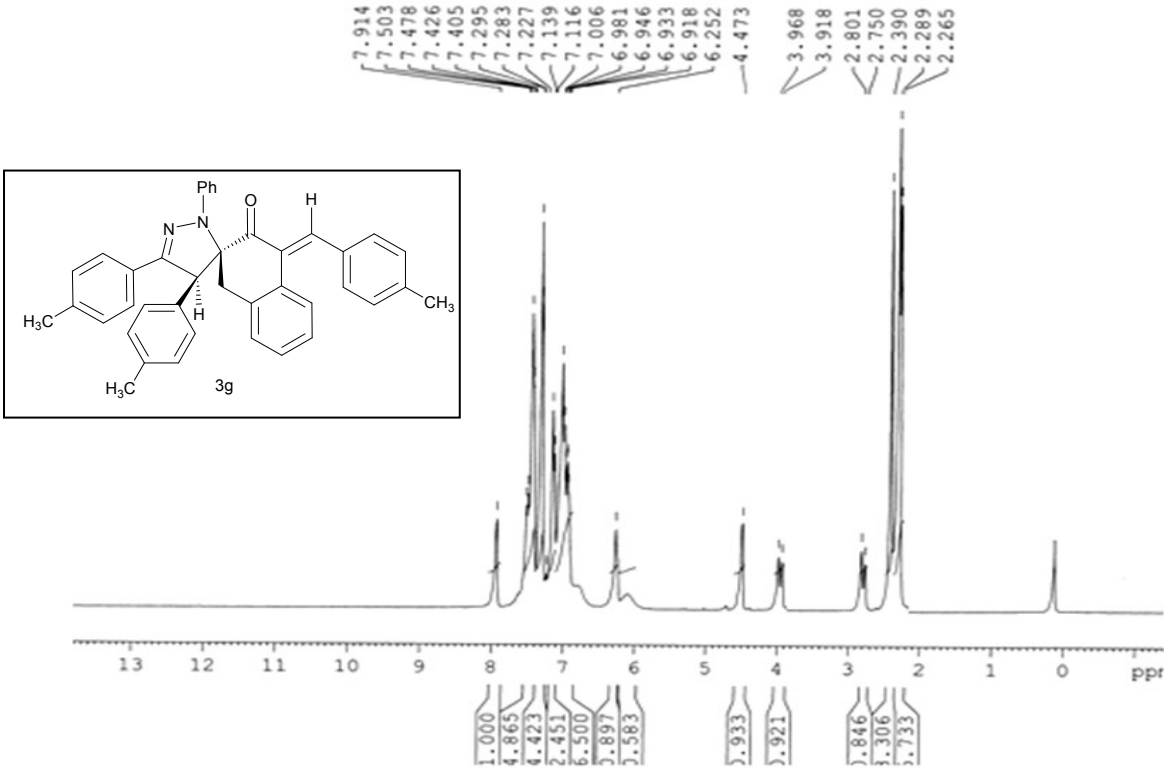

Fig 13. ^{1}H NMR Spectrum of **3g** in $CDCl_3$

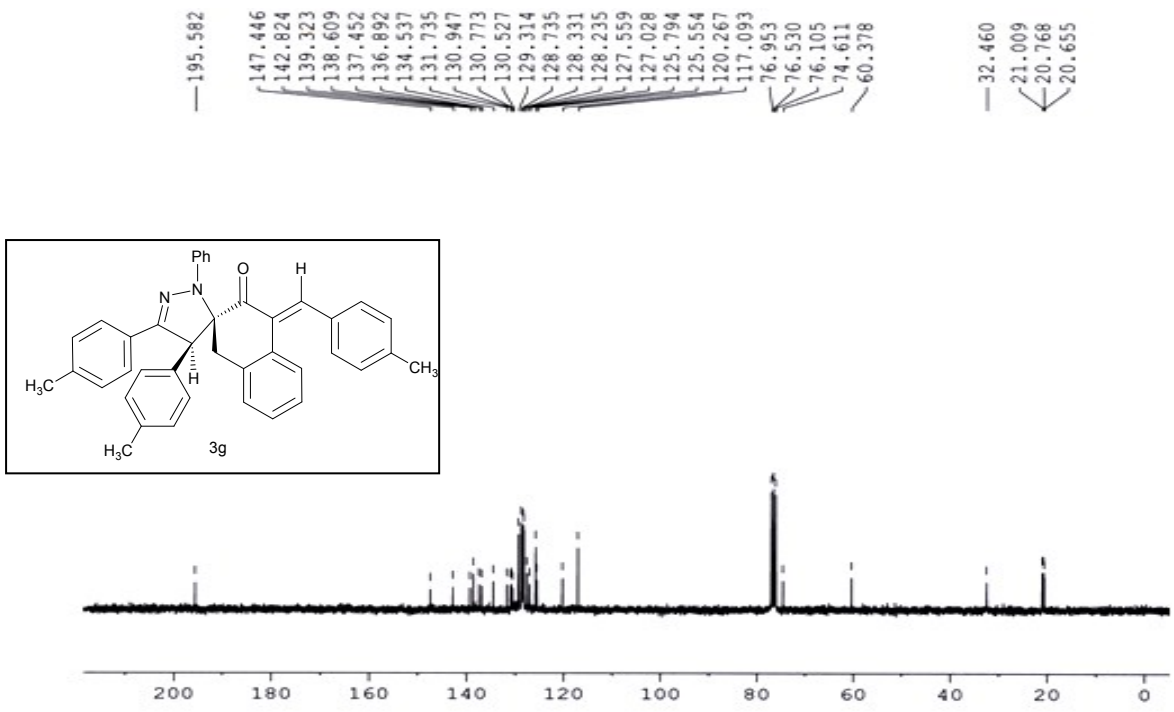

Fig 14. ^{13}C NMR Spectrum of **3g**in $CDCl_3$

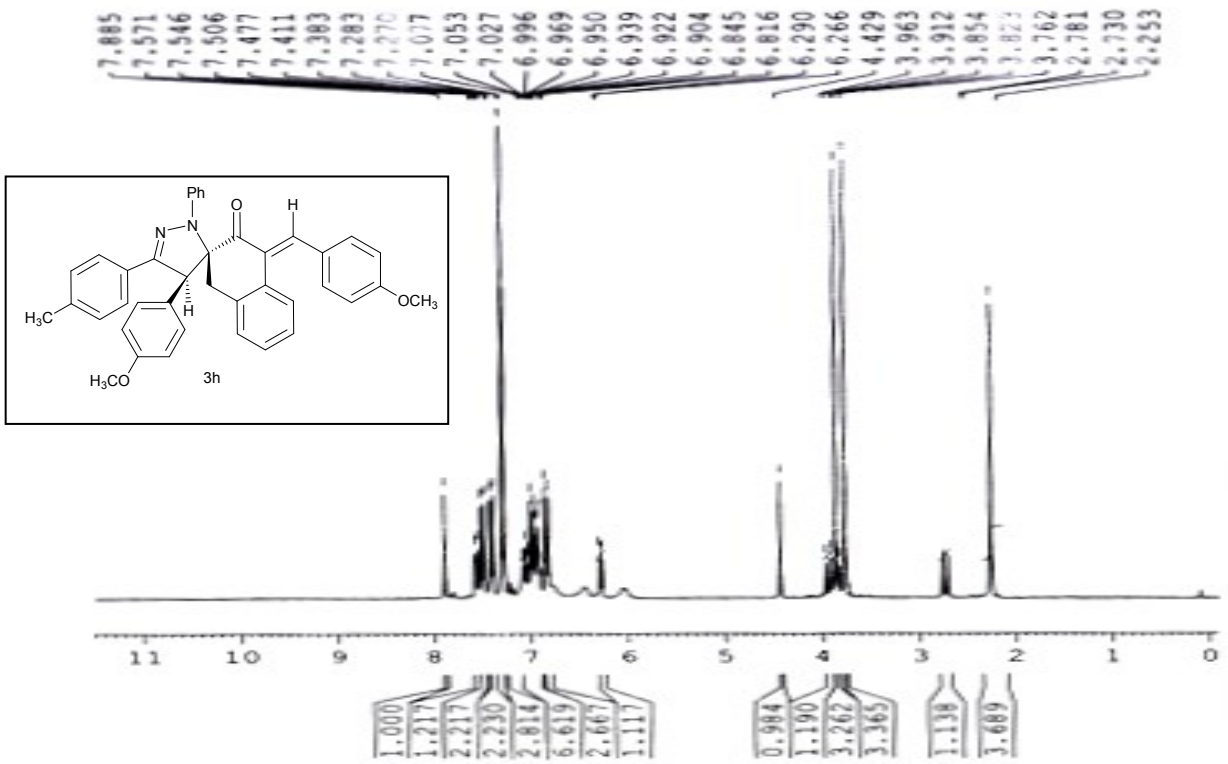

Fig 15. ^{1}H NMR Spectrum of **3h** in $CDCl_3$

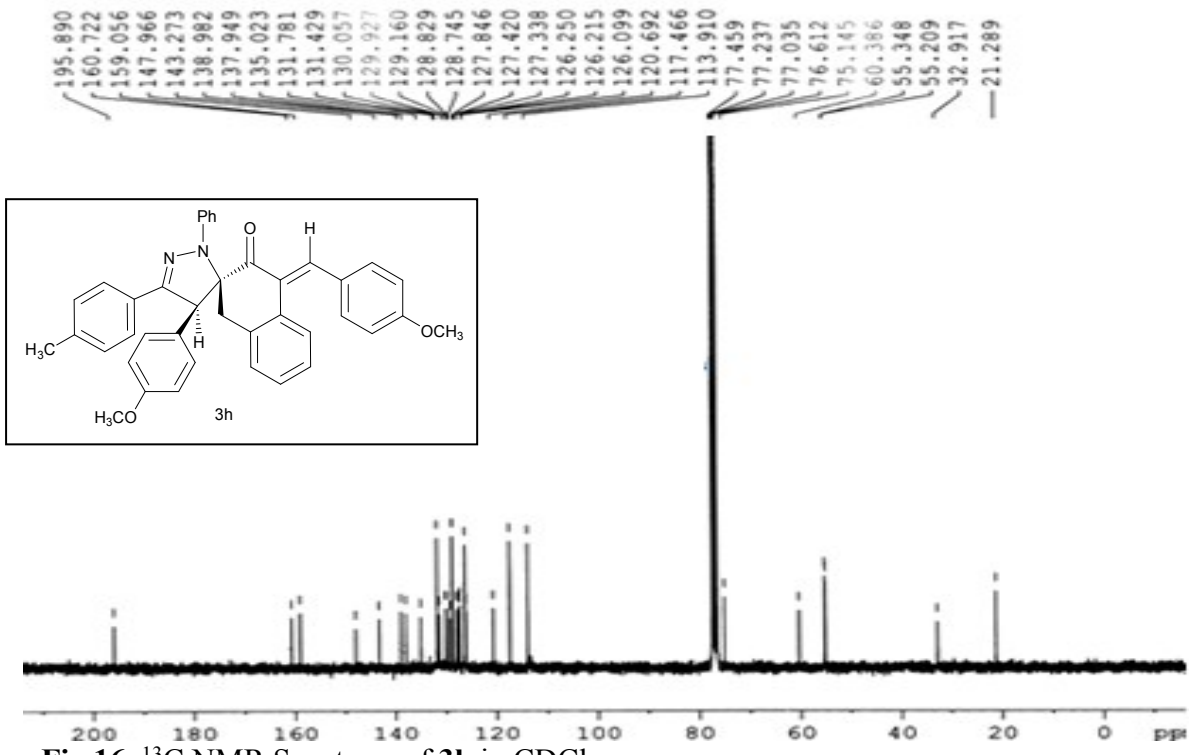

Fig 16. ^{13}C NMR Spectrum of **3h** in $CDCl_3$

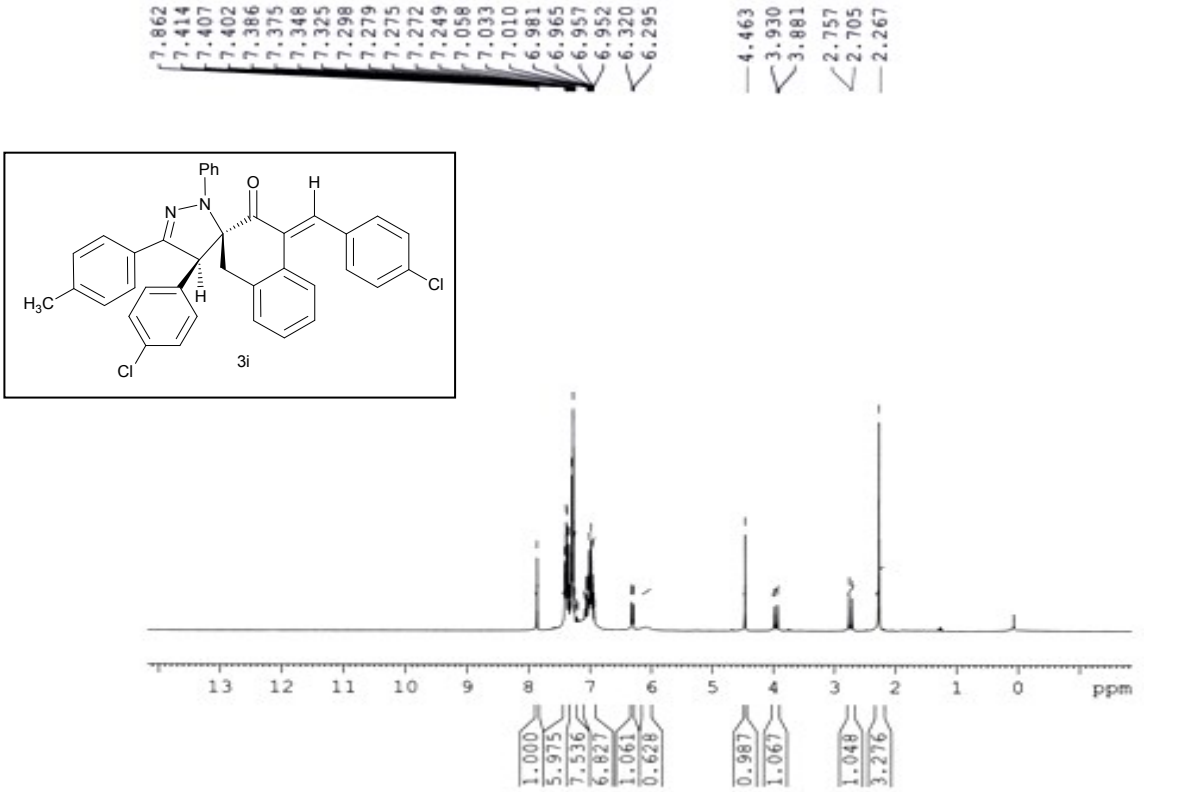

Fig 17. ^{1}H NMR Spectrum of **3i** in $CDCl_3$

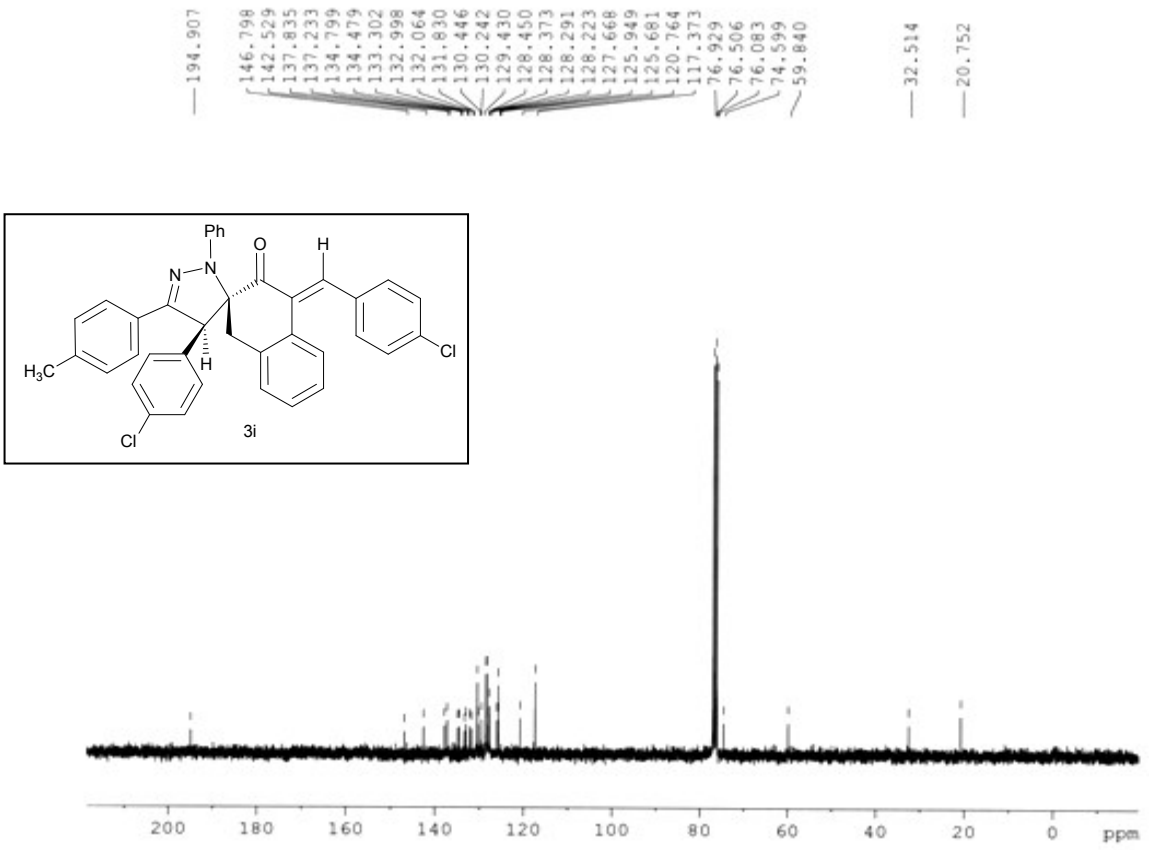

Fig 18. ^{13}C NMR Spectrum of **3i** in $CDCl_3$

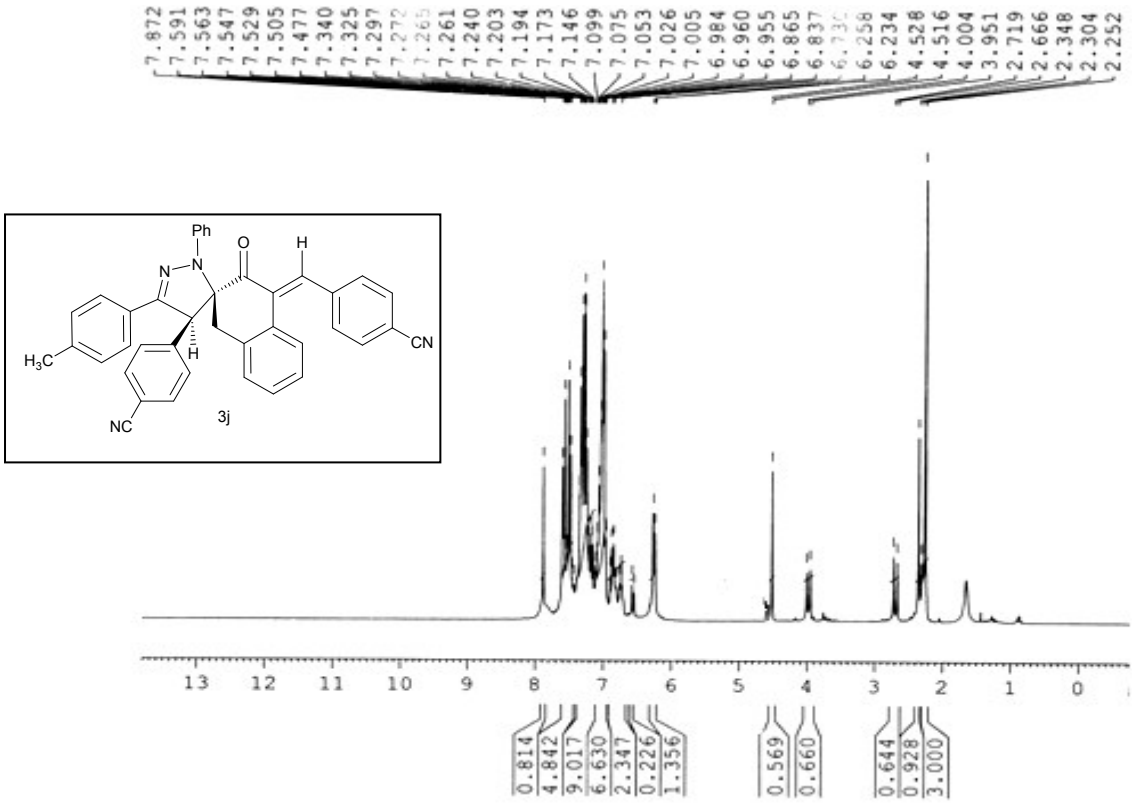

Fig 19. ^{1}H NMR Spectrum of **3j** in $CDCl_3$

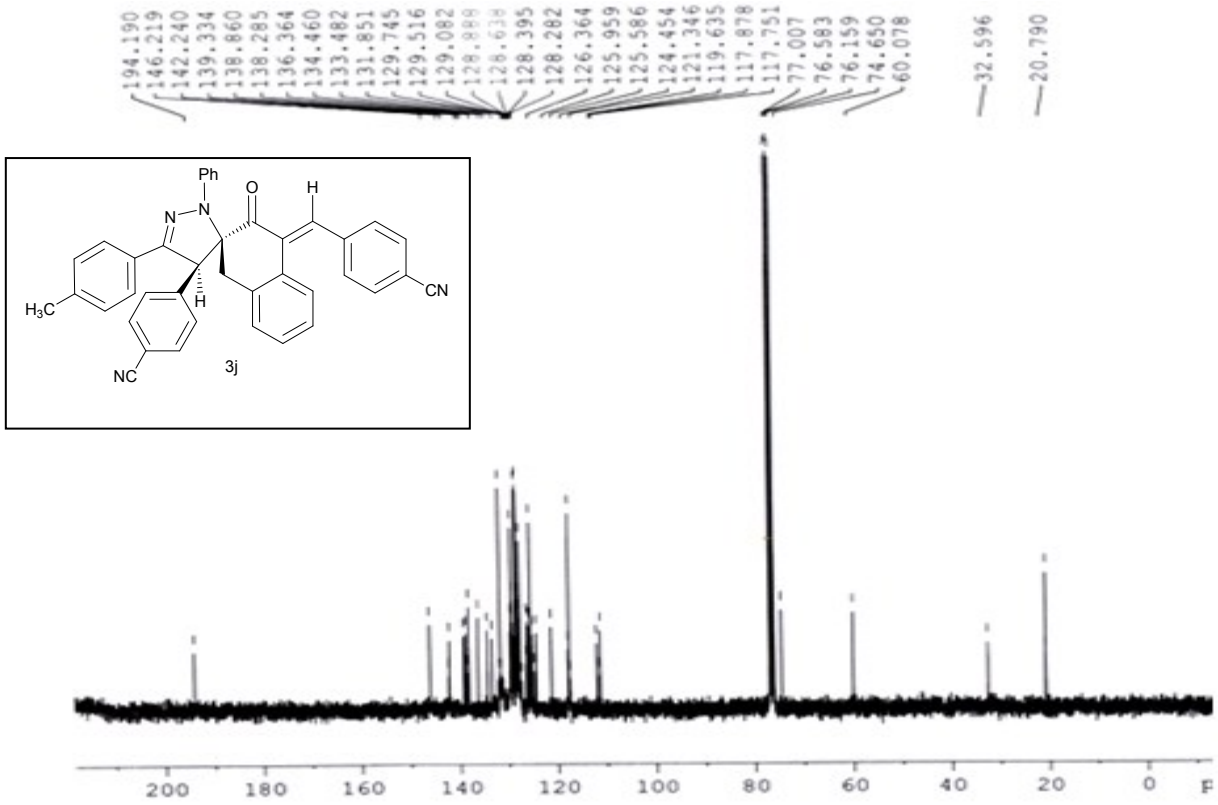

Fig 20. ^{13}C NMR Spectrum of **3j** in $CDCl_3$

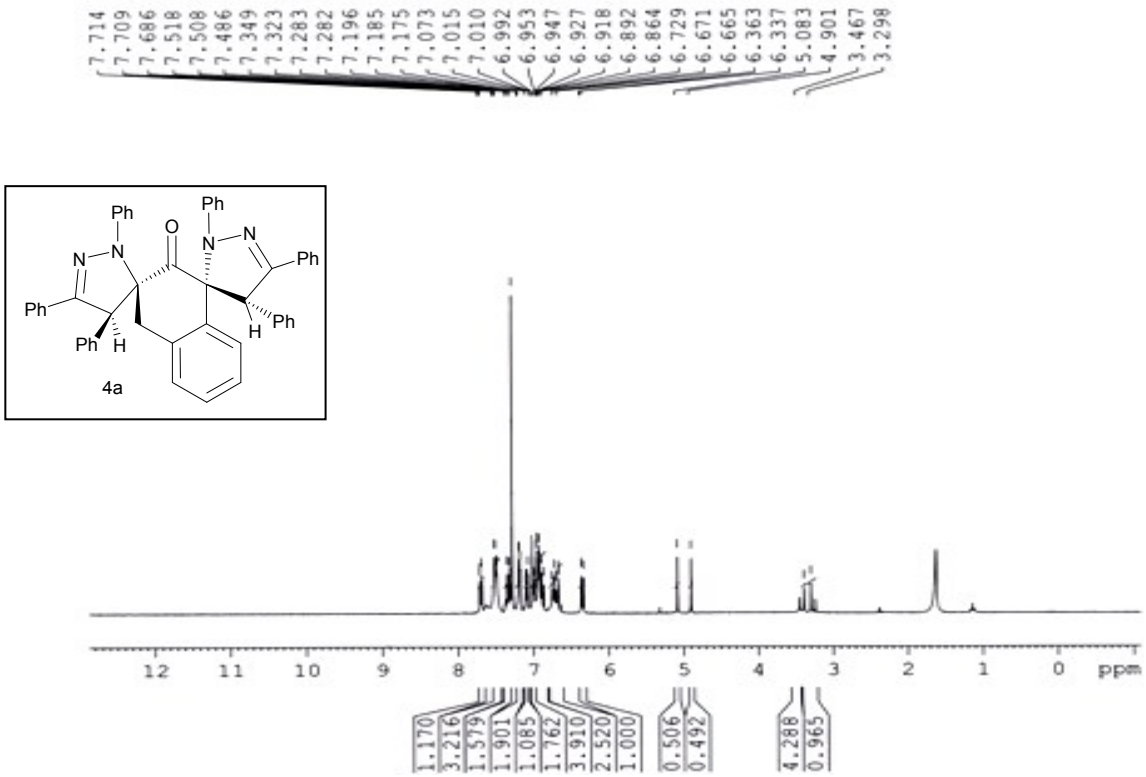

Fig 21. ^{1}H NMR Spectrum of **4a** in $CDCl_3$

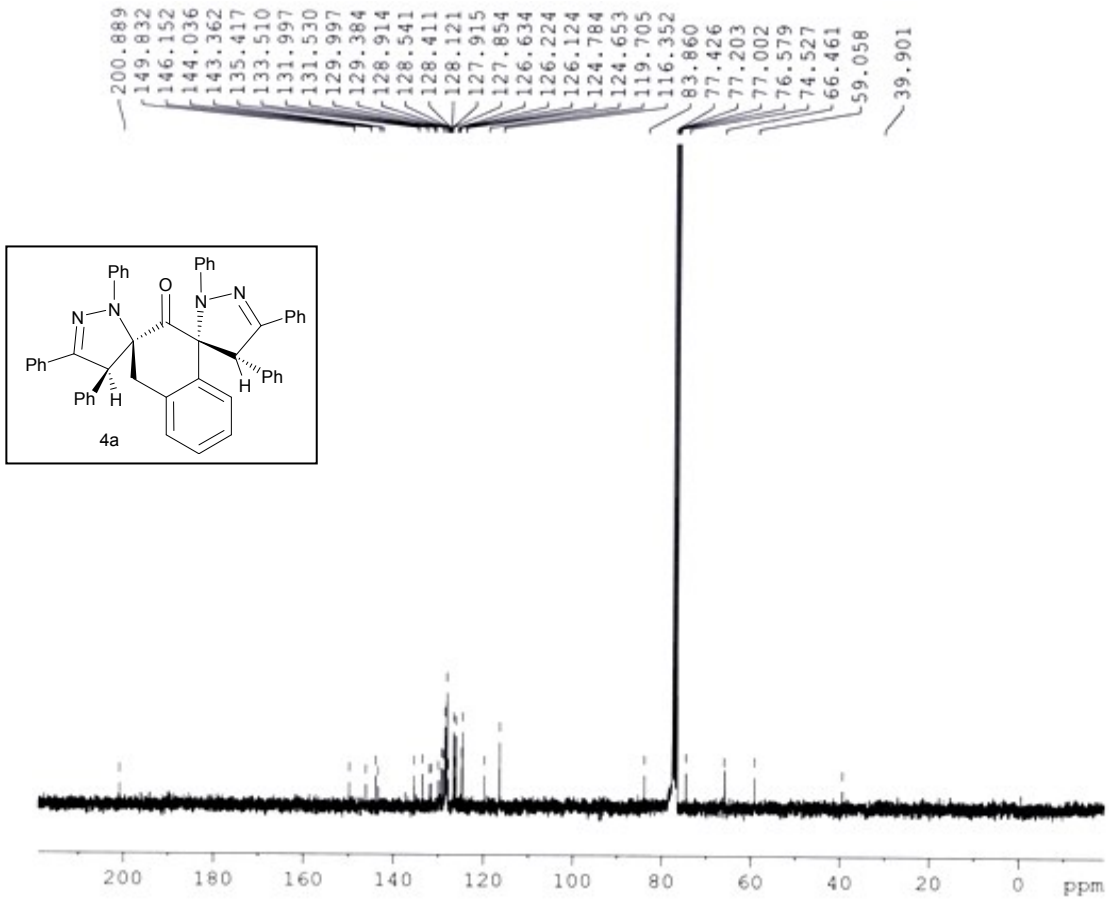

Fig 22. ^{13}C NMR Spectrum of **4a** in $CDCl_3$

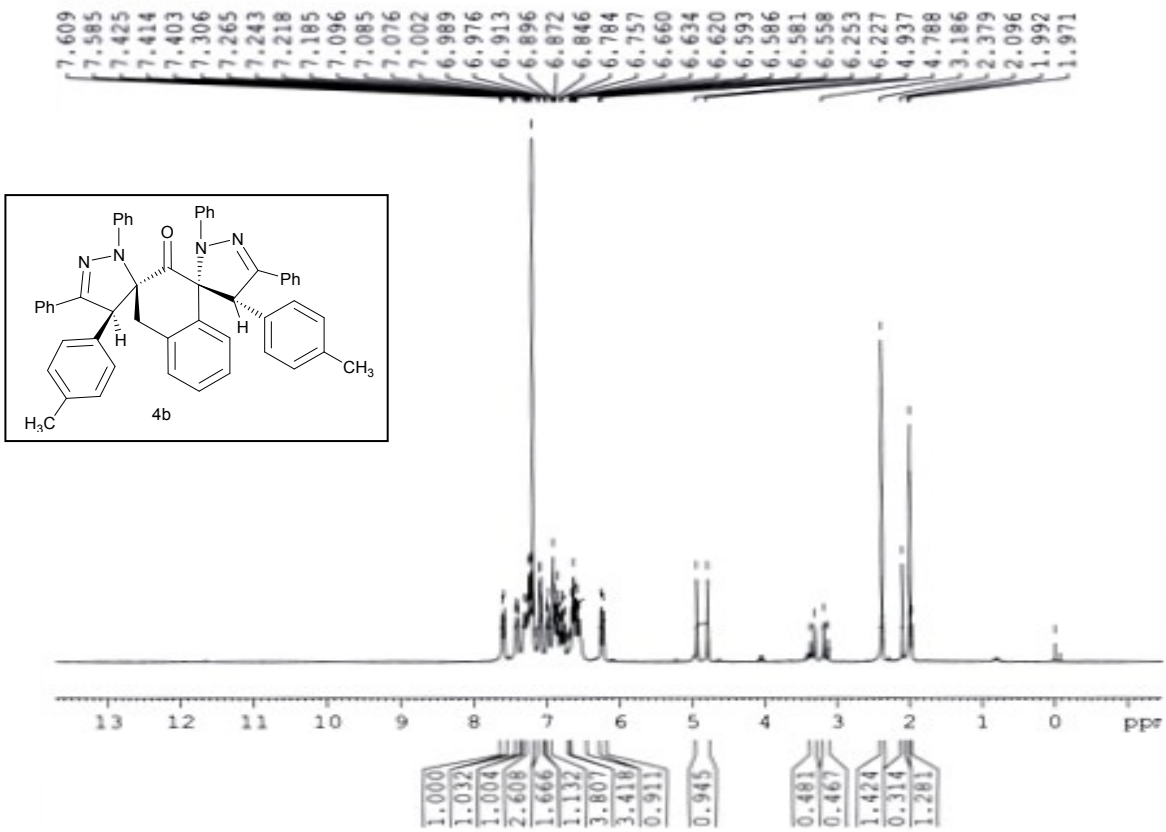

Fig 23. ^{1}H NMR Spectrum of **4b** in $CDCl_3$

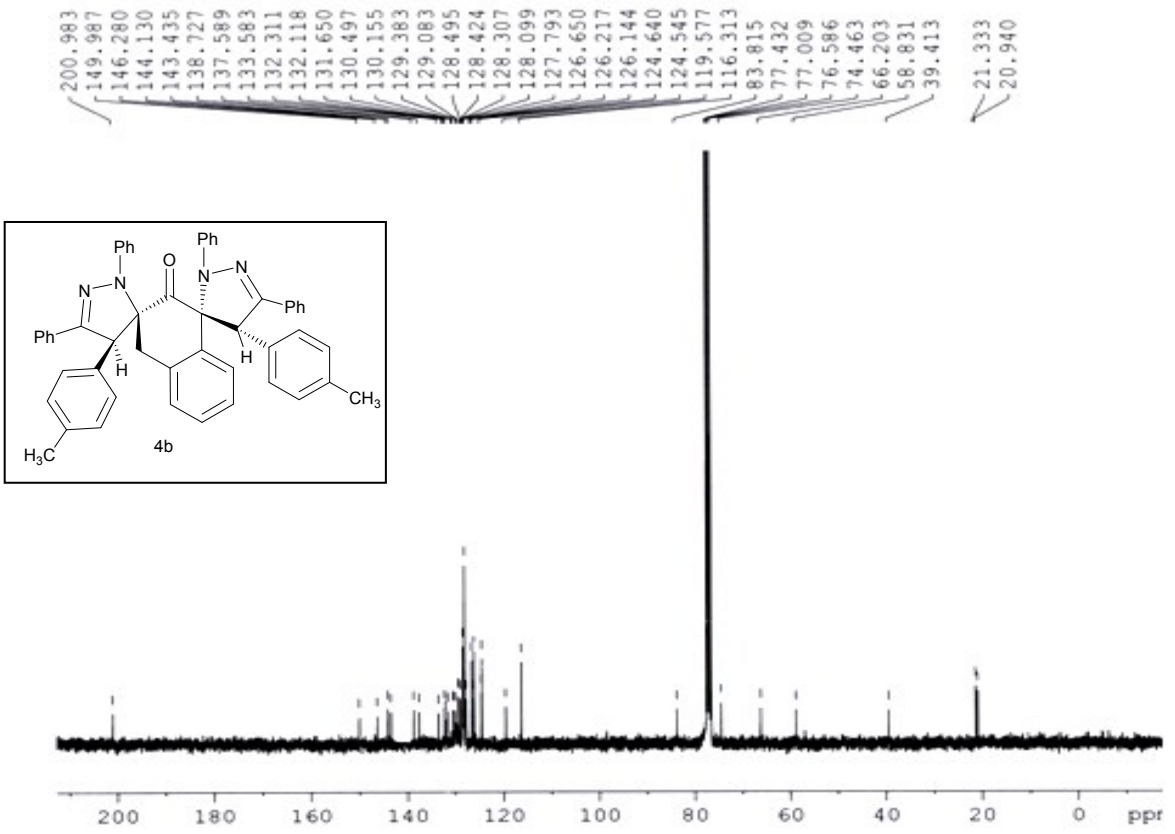

Fig 24. ^{13}C NMR Spectrum of **4b** in $CDCl_3$

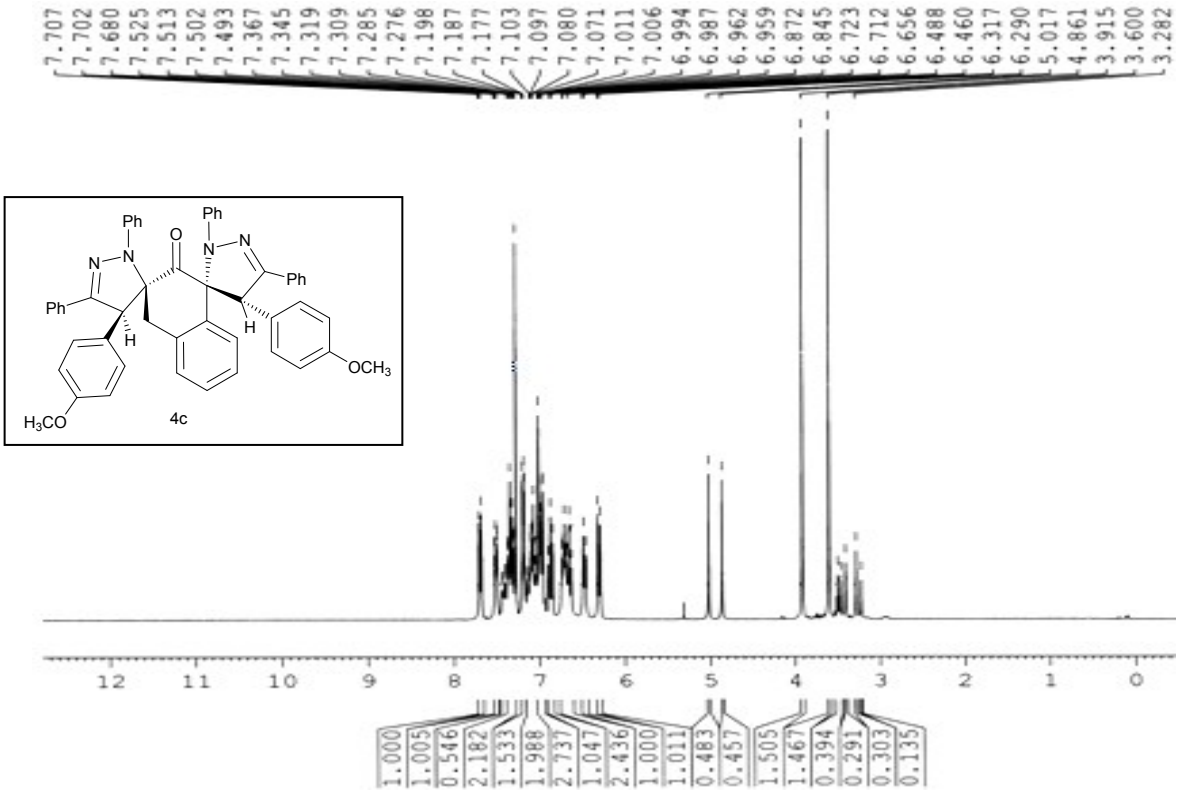

Fig 25. ^{1}H NMR Spectrum of **4c** in $CDCl_3$

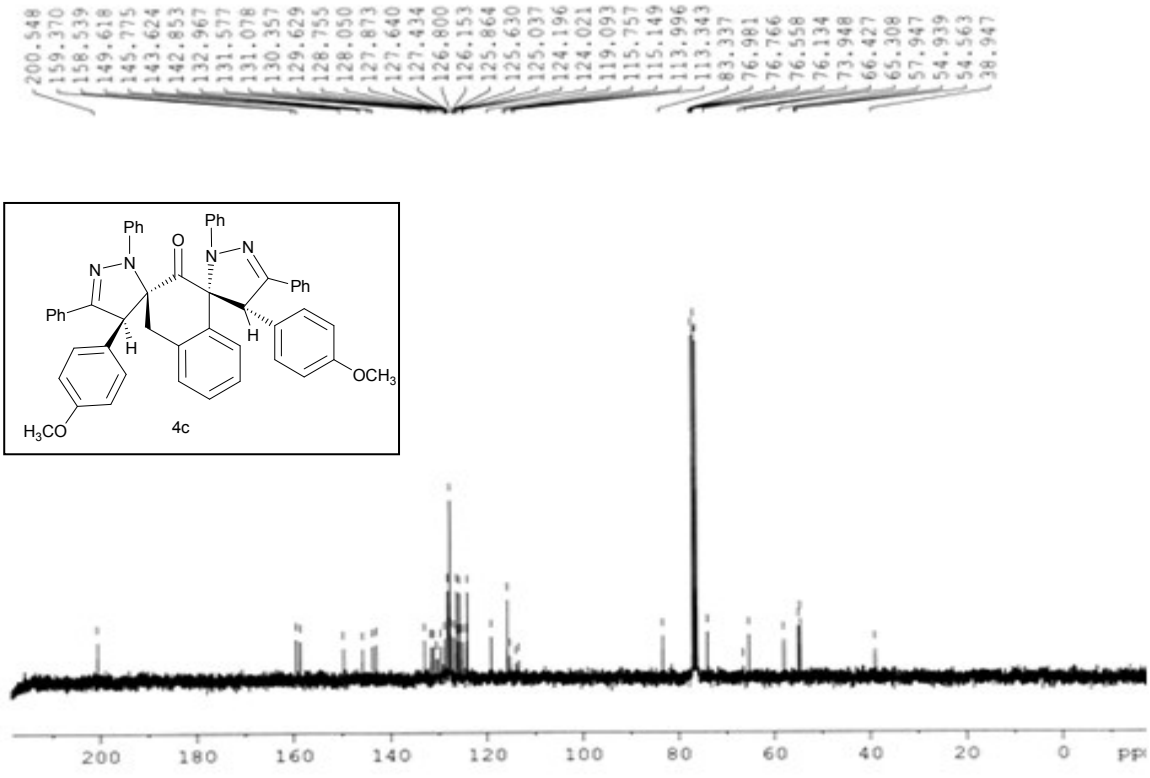

Fig 26. ^{13}C NMR Spectrum of **4c** in $CDCl_3$

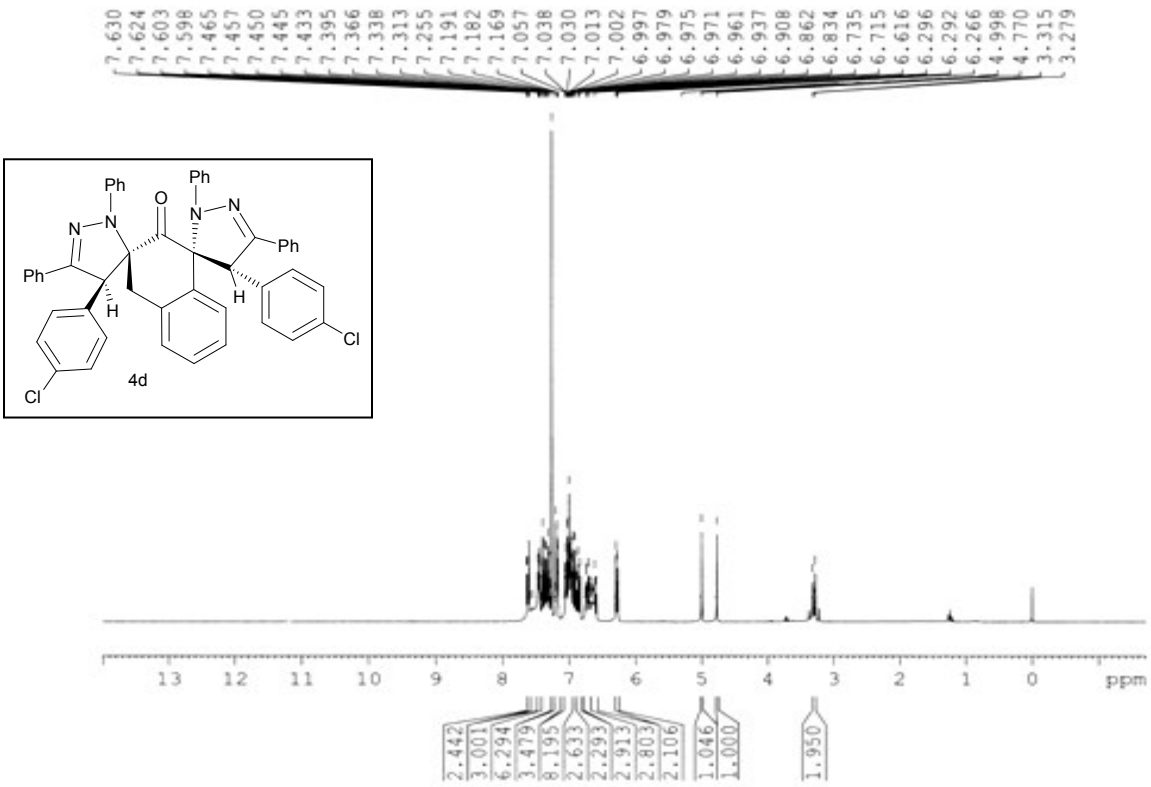

Fig 27. ^{1}H NMR Spectrum of **4d** in $CDCl_3$

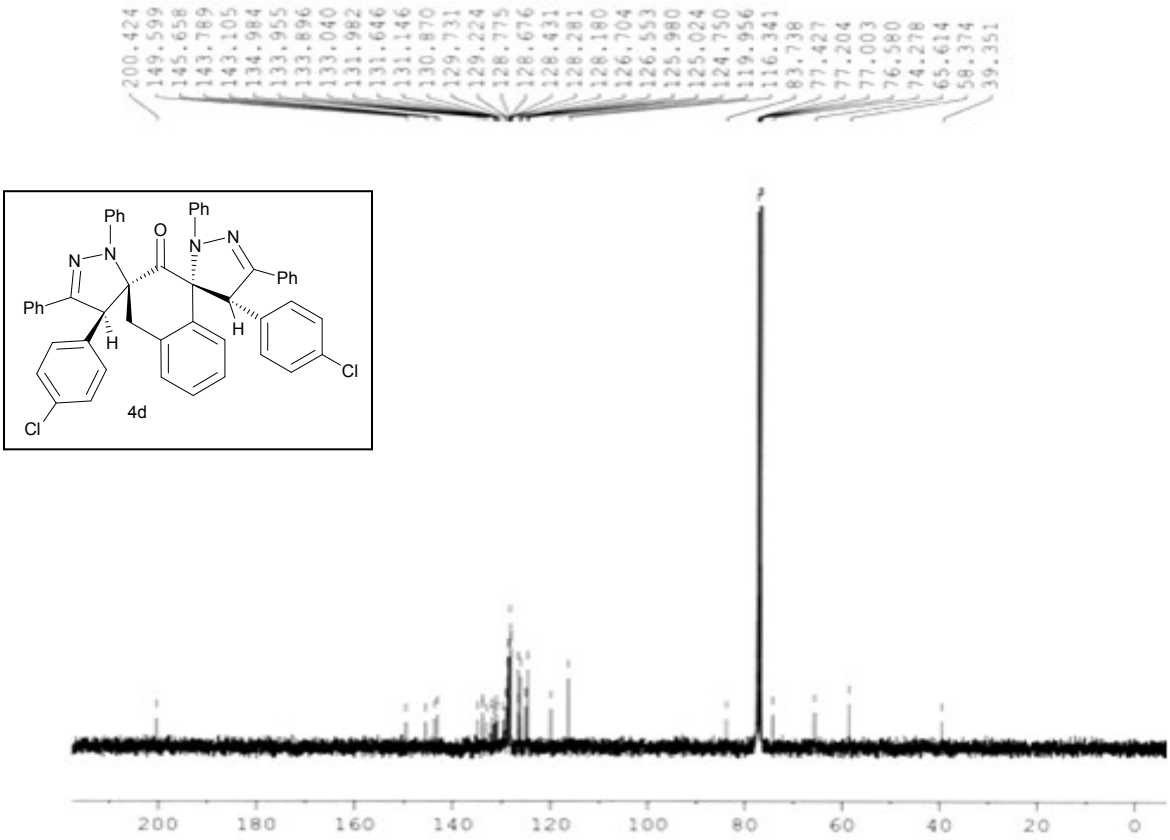

Fig 28. ^{13}C NMR Spectrum of **4d** in $CDCl_3$

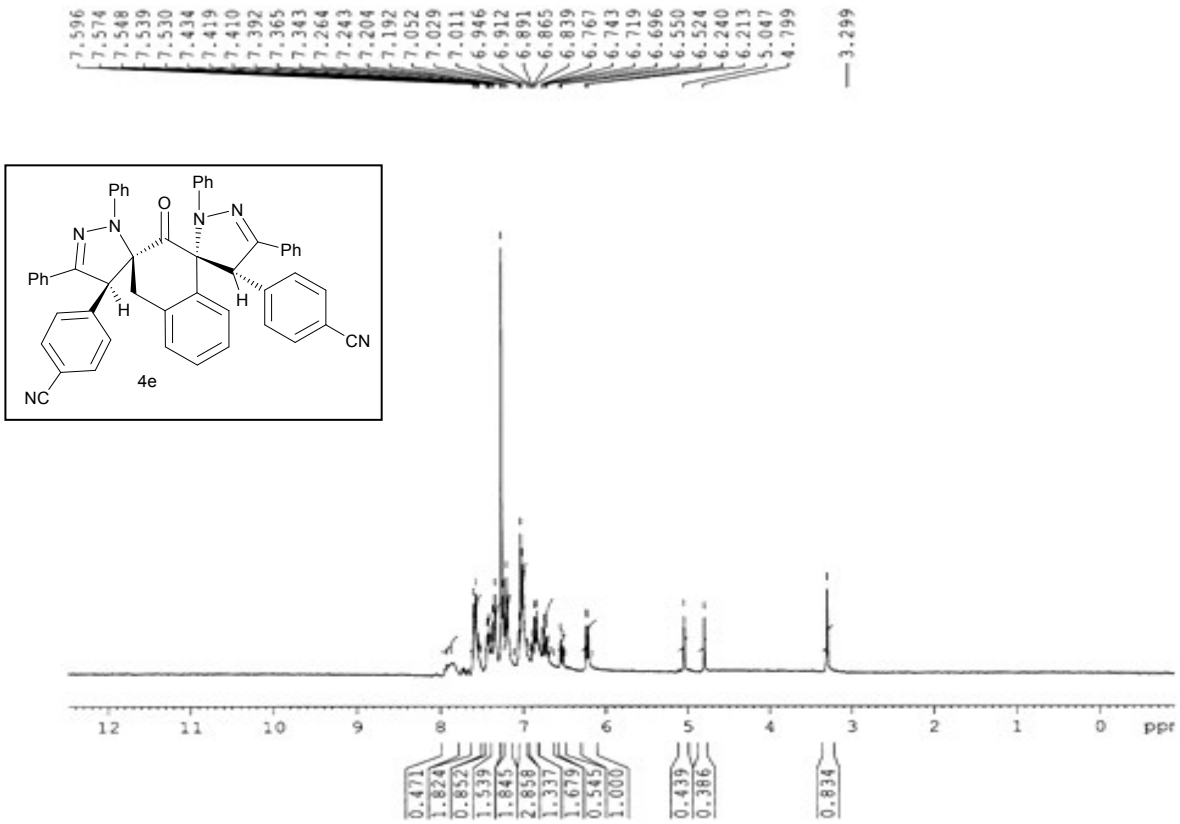

Fig 29. ^{1}H NMR Spectrum of **4e** in $CDCl_3$

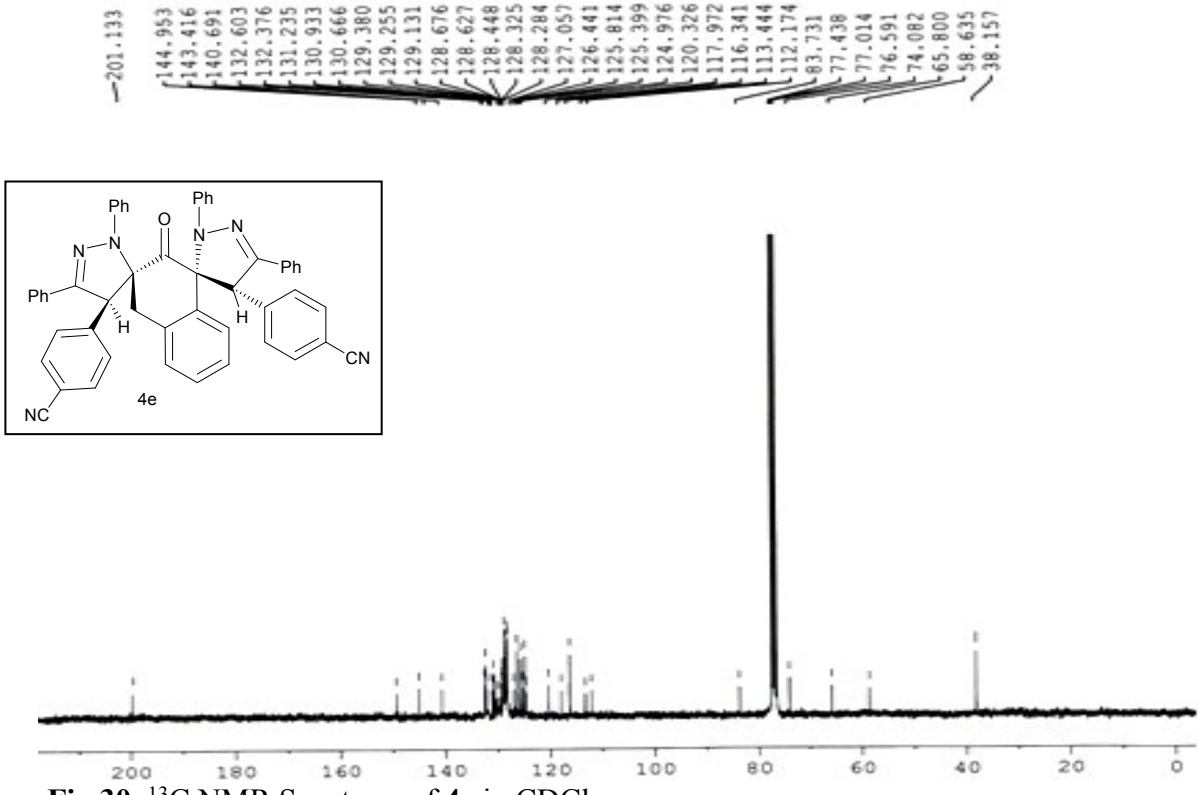

Fig 30. ^{13}C NMR Spectrum of **4e** in $CDCl_3$

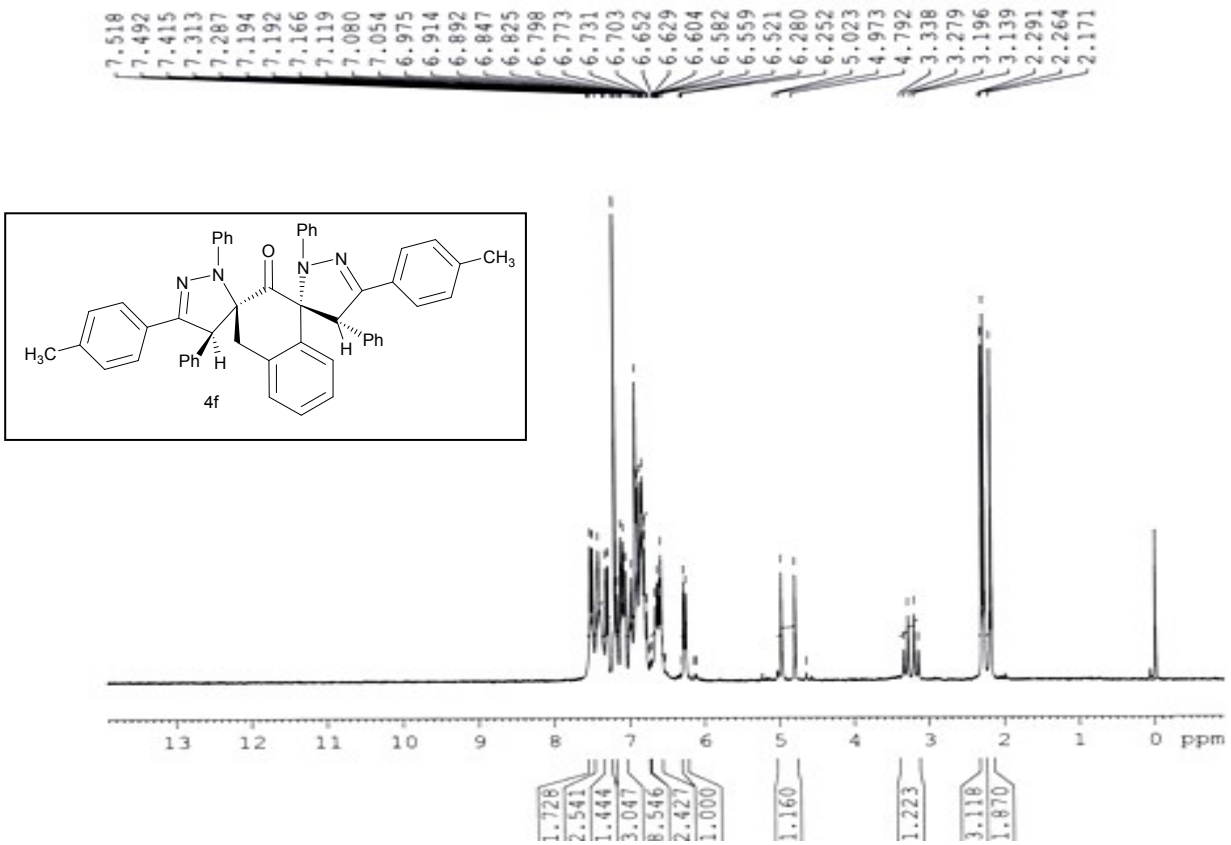

Fig 31. ^{1}H NMR Spectrum of **4f** in $CDCl_3$

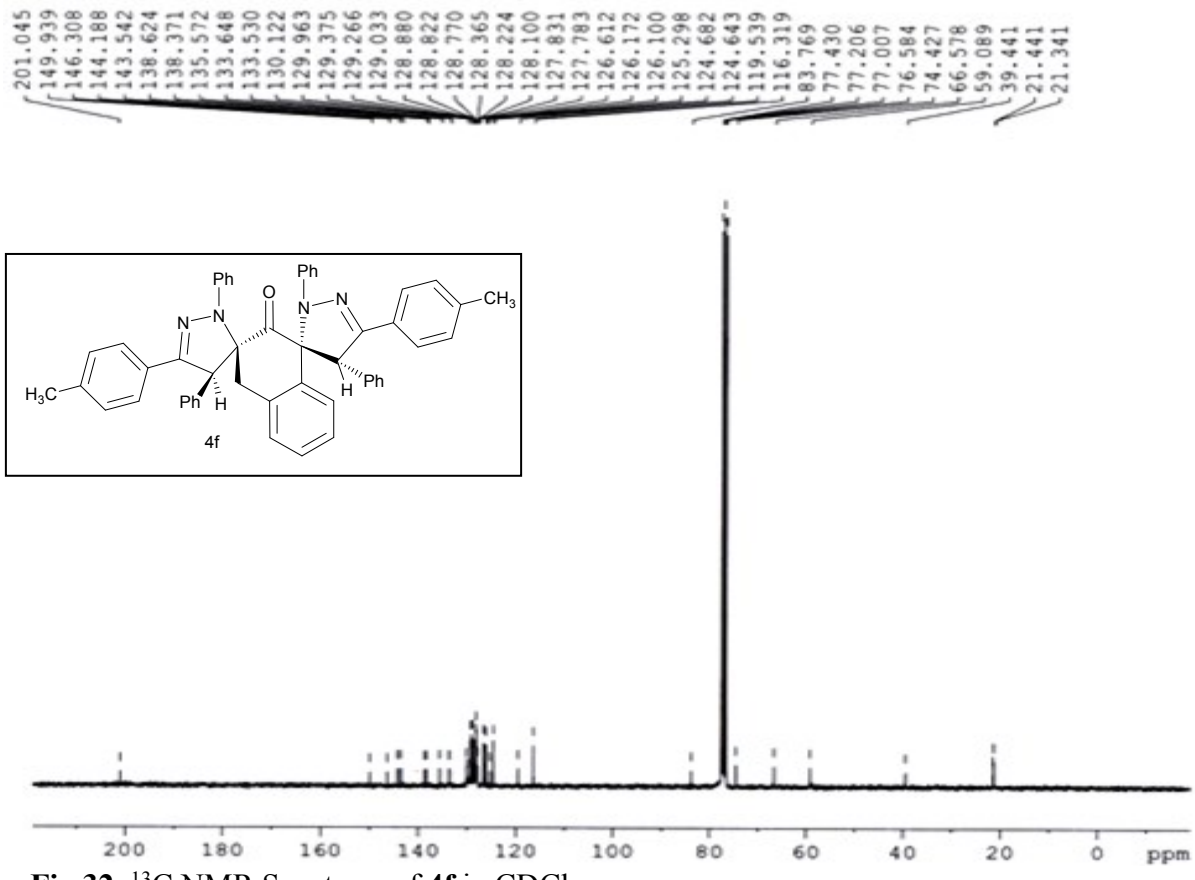

Fig 32. ^{13}C NMR Spectrum of **4f** in $CDCl_3$

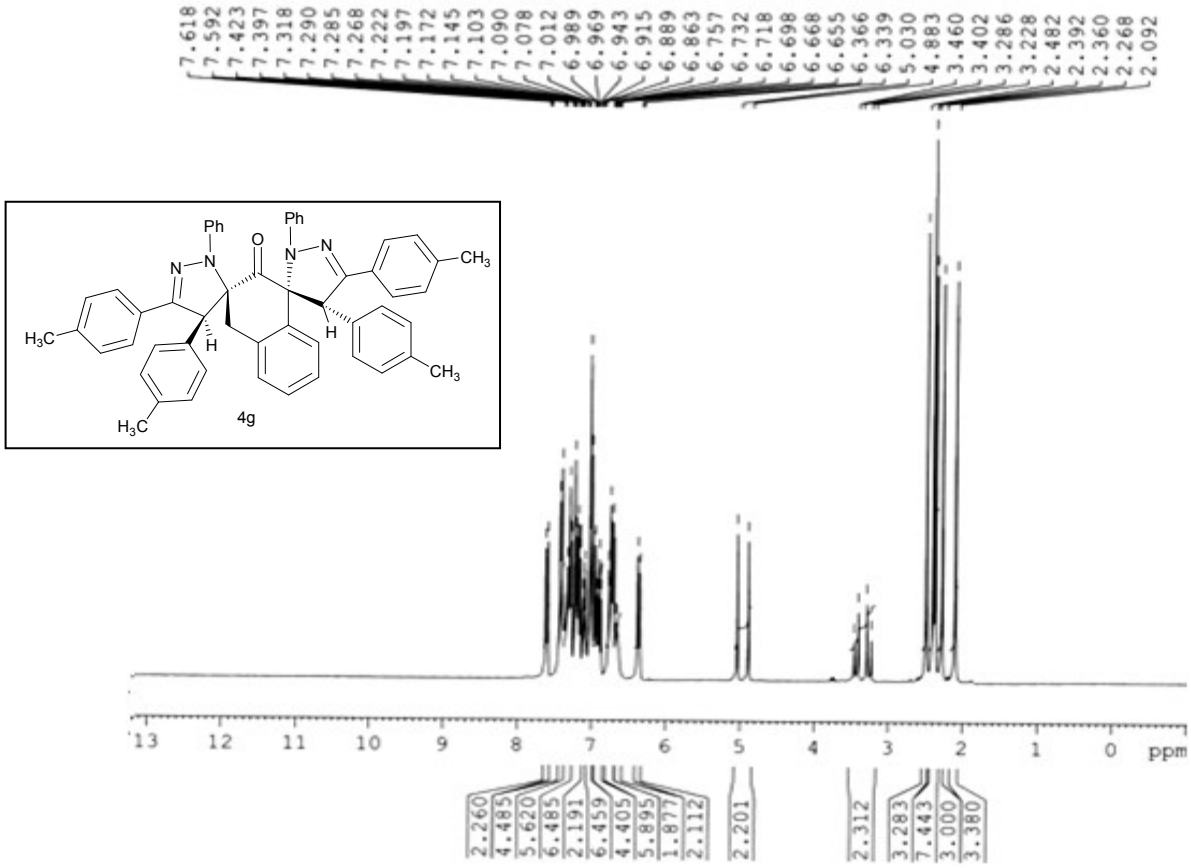

Fig 33. ^{1}H NMR Spectrum of **4g** in $CDCl_3$

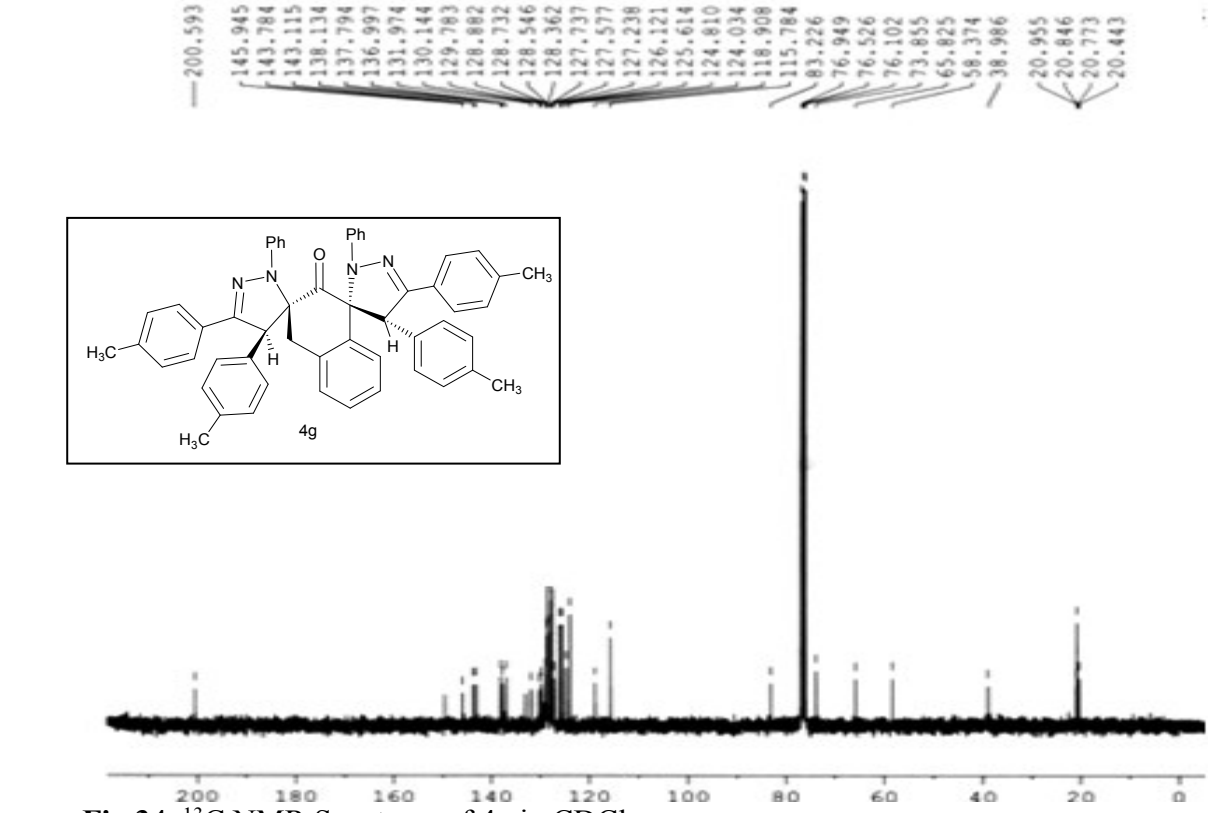

Fig 34. ^{13}C NMR Spectrum of **4g** in $CDCl_3$

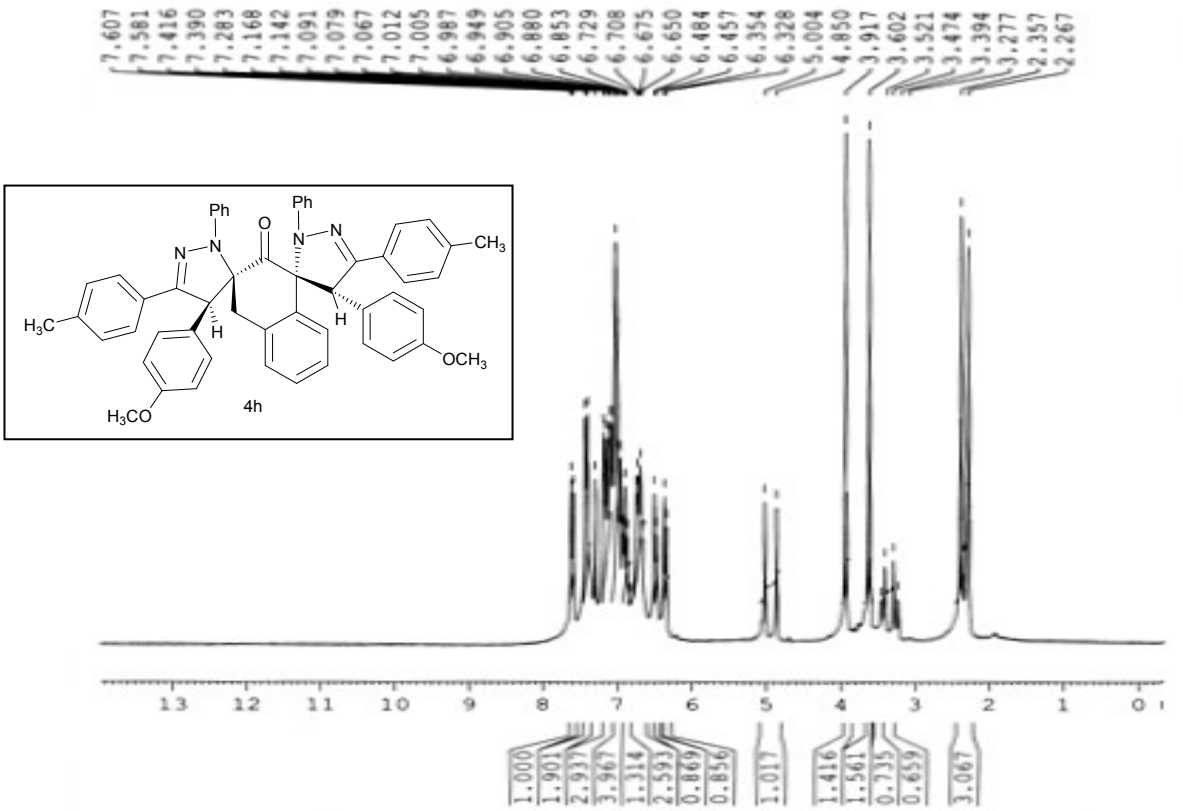

Fig 35. ^{1}H NMR Spectrum of **4h** in $CDCl_3$

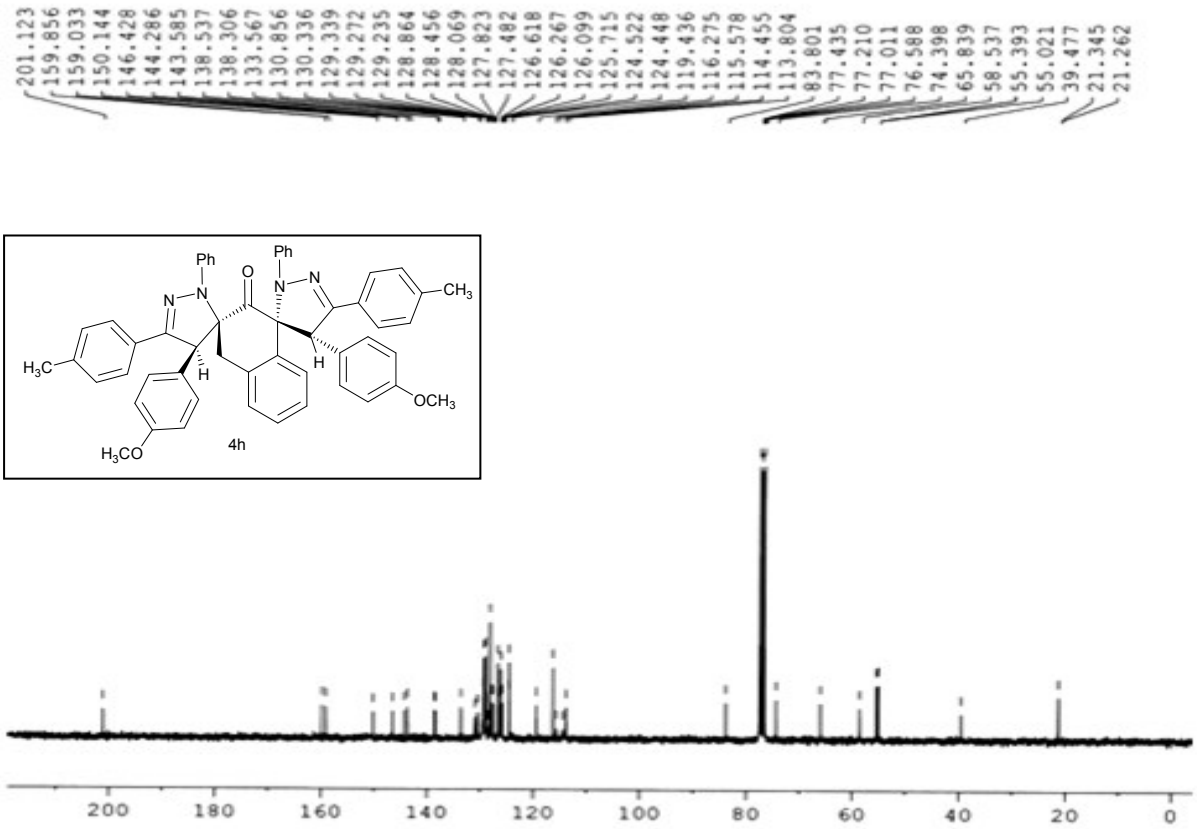

Fig 36. ^{13}C NMR Spectrum of **4h** in $CDCl_3$

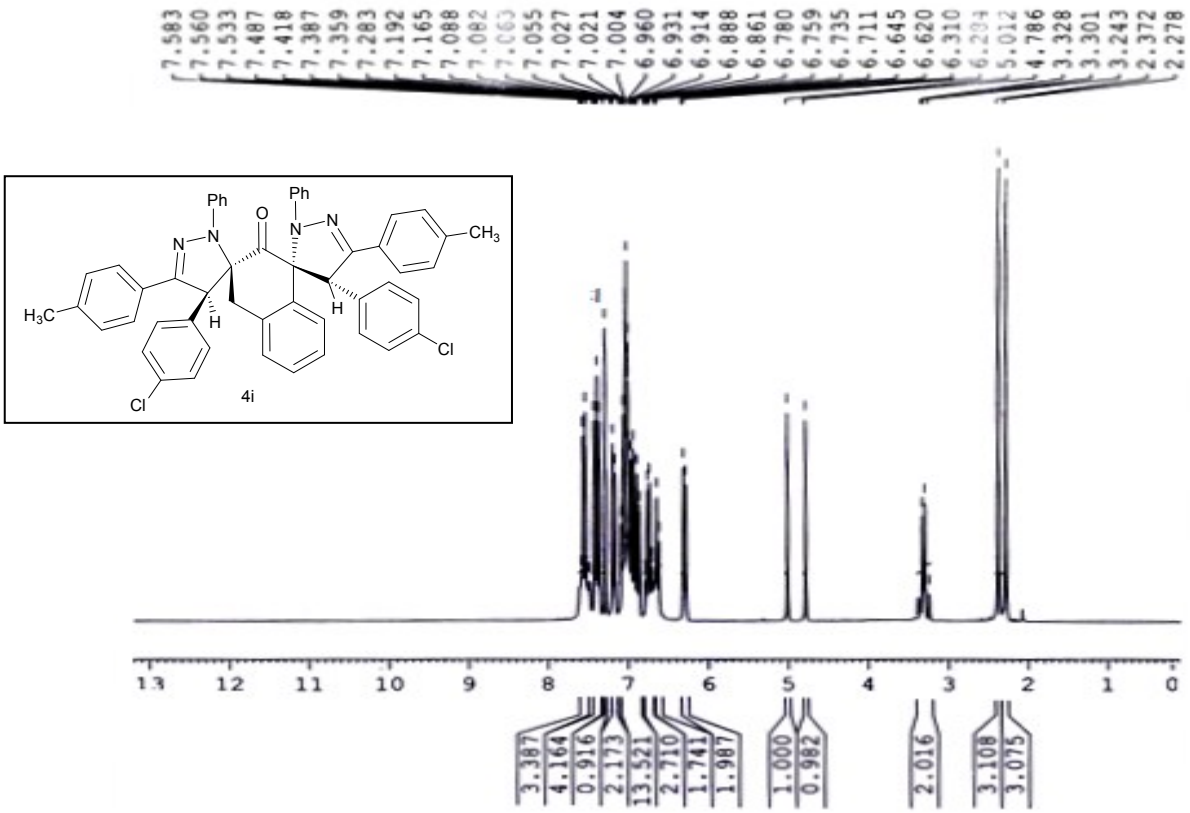

Fig 37. ^{1}H NMR Spectrum of **4i** in $CDCl_3$

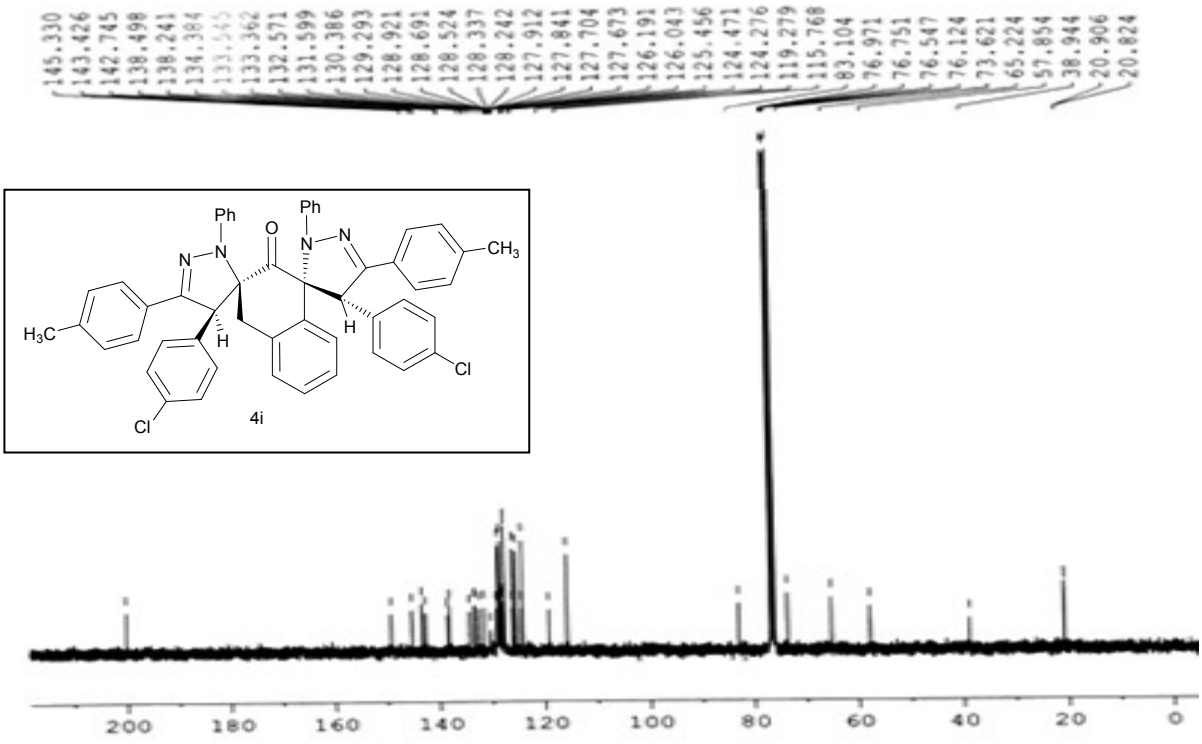

Fig 38. ^{13}C NMR Spectrum of **4i** in $CDCl_3$

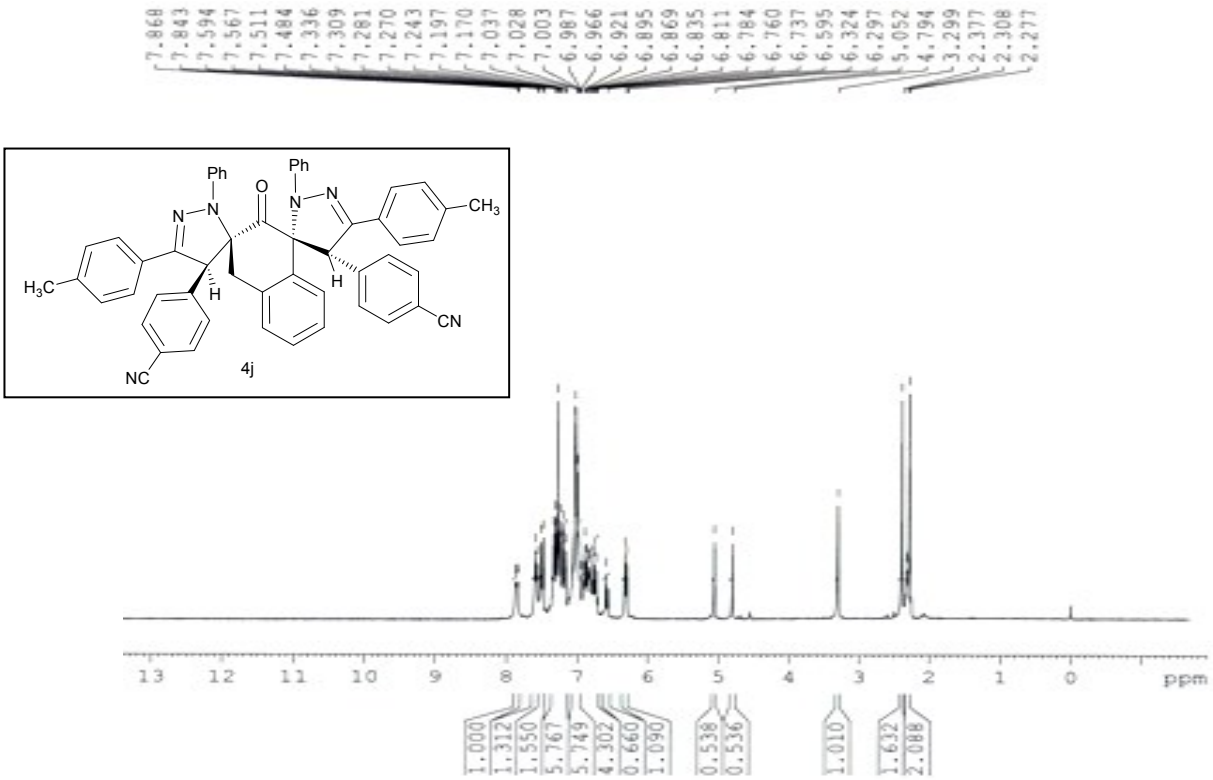

Fig 39. ^{1}H NMR Spectrum of **4j** in $CDCl_3$

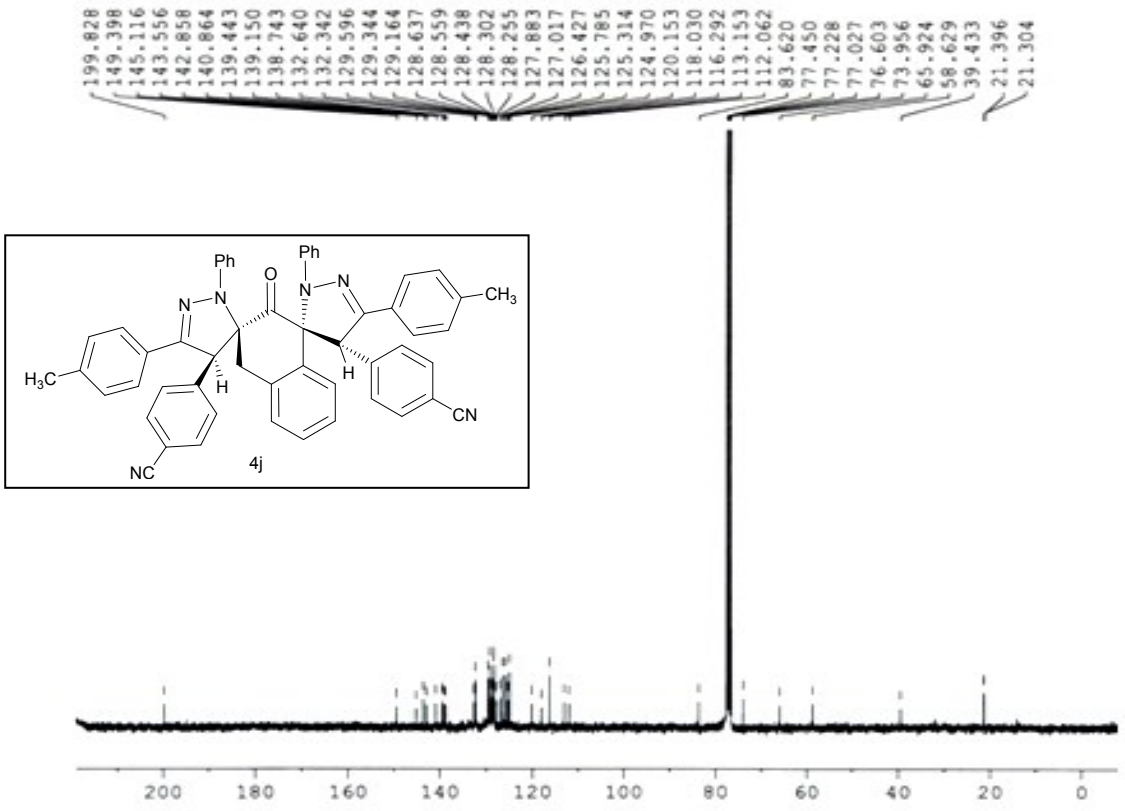

Fig 40. ^{13}C NMR Spectrum of **4j** in $CDCl_3$