A Neber approach for the synthesis of spiro-fused 2*H*-azirine-pyrazolones

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Supporting Information

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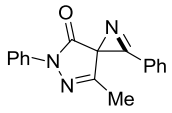
1. General Methods

Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by thinlayer chromatography (TLC), and column chromatography purifications were performed using 300-400 mesh silica gel.

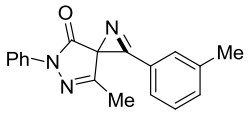
^{1}H NMR and ^{13}C NMR spectra (300 and 75 MHz, respectively) were recorded in $CDCl_3$. ^{1}H NMR chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ($CDCl_3$ at 7.26 ppm). Data are reported as follows: chemical shift, multiplicity (s=singlet, br s=broad singlet, d=doublet, t=triplet, q=quartet, m=multiplet), coupling constants (Hz) and integration. ^{13}C NMR chemical shifts are reported in parts per million (ppm) from tetramethylsilane (TMS) with the solvent resonance as the internal standard ($CDCl_3$ at 77.20 ppm).

2. General procedure for the synthesis of compounds 3

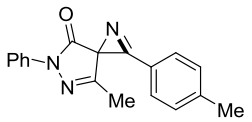
In an ordinary vial equipped with a magnetic stirring bar, compounds **1** (0.2 mmol, 1.0 equiv), compounds **2** (0.24 mmol, 1.2 equiv) and sodium carbonate (26 mg, 1.2 equiv) were dissolved in 4 mL of acetonitrile, and then the mixture was stirred at 25 ℃ for the indicated time. After completion of the reaction, as indicated by TLC, the products **3** were isolated by flash chromatography on silica gel (petroleum ether/ethyl acetate = 8/1).



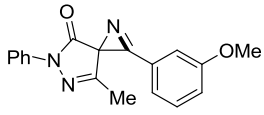
7-methyl-2,5-diphenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3a). White solid; 48.8 mg, 88% yield; m.p. 129.7-131.1 ℃; HPLC (AD-H, *i*-propanol/*n*-hexane = 10/90, flow rate = 1.0 mL/min, λ = 254 nm) t_R = 16.4 min (major), 20.4 min (minor); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 3H), 7.18-7.23 (m, 1H), 7.40-7.46 (m, 2H), 7.59-7.64 (m, 2H), 7.69-7.75 (m, 1H), 7.85-7.88 (m, 2H), 8.00 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 46.1, 118.4, 119.9, 125.0, 128.9, 129.8, 131.1, 135.2, 138.7, 157.5, 157.6, 168.9; HRMS (ESI-TOF) calcd. for $C_{17}H_{14}N_3O$ $[M + H]^+$ 276.1131; found: 276.1123.



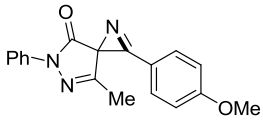
7-methyl-5-phenyl-2-(m-tolyl)-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3b). White solid; 49.1 mg, 84% yield; m.p. 116.2-117.9 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 3H), 2.45 (s, 3H), 7.17-7.23 (m, 1H), 7.40-7.46 (m, 2H), 7.49-7.52 (m, 2H), 7.65-7.71 (m, 2H), 8.00 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 21.1, 46.1, 118.4, 119.7, 125.0, 128.3, 128.9, 129.6, 131.6, 136.1, 138.7, 139.9, 157.5, 157.7, 169.0; HRMS (ESI-TOF) calcd. for $C_{18}H_{16}N_3O$ $[M + H]^+$ 290.1288; found: 290.1284.



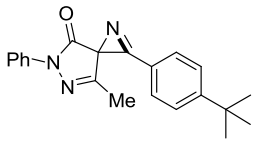
7-methyl-5-phenyl-2-(p-tolyl)-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3c). Yellow solid; 47.8 mg, 82% yield; m.p. 102.8-104.2 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.93 (s, 3H), 2.48 (s, 3H), 7.17-7.22 (m, 1H), 7.40-7.45 (m, 4H), 7.75 (d, *J* = 8.1 Hz, 2H), 7.98-8.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 22.1, 46.0, 117.0, 118.4, 124.9, 128.8, 130.5, 131.2, 138.7, 146.7, 157.0, 157.8, 169.1; HRMS (ESI-TOF) calcd. for $C_{18}H_{16}N_3O$ $[M + H]^+$ 290.1288; found: 290.1277.



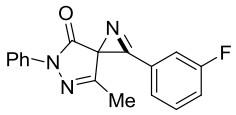
2-(3-methoxyphenyl)-7-methyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3d). Yellow solid; 57.4 mg, 94% yield; m.p. 80.4-81.0 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 3H), 3.88 (s, 3H), 7.20-7.24 (m, 2H), 7.37-7.54 (m, 5H), 7.98-8.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 46.3, 55.7, 114.8, 118.4, 121.0, 121.9, 123.8, 125.0, 128.9, 130.8, 138.7, 157.6, 157.7, 160.3, 168.9; HRMS (ESI-TOF) calcd. for $C_{18}H_{16}N_3O_2$ $[M + H]^+$ 306.1237; found: 306.1237.



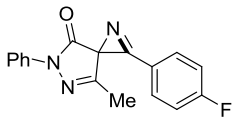
2-(4-methoxyphenyl)-7-methyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3e). Yellow solid; 48.5 mg, 79% yield; m.p. 135.1-136.3 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.93 (s, 3H), 3.90 (s, 3H), 7.08 (d, *J* = 8.7 Hz, 2H), 7.17-7.22 (m, 1H), 7.39-7.45 (m, 2H), 7.80 (d, *J* = 8.7 Hz, 2H), 7.98-8.01 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 46.0, 55.8, 111.8, 115.4, 118.4, 124.9, 128.8, 133.4, 138.8, 156.0, 158.0, 165.1, 169.3; HRMS (ESI-TOF) calcd. for $C_{18}H_{16}N_3O_2$ $[M + H]^+$ 306.1237; found: 306.1231.



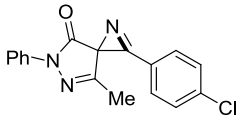
2-(4-(tert-butyl)phenyl)-7-methyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3f). White solid; 51.6 mg, 77% yield; m.p. 126.5-127.7 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.36 (s, 9H), 1.94 (s, 3H), 7.20-7.25 (m, 1H), 7.40-7.46 (m, 2H), 7.61-7.64 (m, 2H), 7.78-7.81 (m, 2H), 7.98-8.02 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 30.9, 35.6, 46.0, 117.0, 118.4, 124.9, 126.9, 128.9, 131.1, 138.8, 157.0, 157.8, 159.6, 169.1; HRMS (ESI-TOF) calcd. for $C_{21}H_{22}N_3O$ $[M + H]^+$ 332.1757; found: 332.1766.



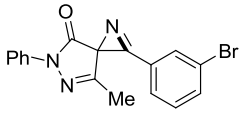
2-(3-fluorophenyl)-7-methyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3g). Yellow solid; 51.0 mg, 87% yield; m.p. 132.7-134.5 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 3H), 7.20-7.23 (m, 1H), 7.40-7.46 (m, 3H), 7.57-7.69 (m, 3H), 7.98 (d, *J* = 7.8 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 46.3, 117.5 (d, *J* = 23.1 Hz, 1C), 118.4, 121. 8 (d, *J* = 8.2 Hz, 1C), 122.4 (d, *J* = 21.1 Hz, 1C), 125.0, 126.9 (d, *J* = 3.3 Hz, 1C), 126.9, 128.8, 131.7 (d, *J* = 8.0 Hz, 1C), 138.5, 157.0, 157.3 (d, *J* = 3.3 Hz, 1C), 162.8 (d, *J* = 250.0 Hz, 1C), 168.4; HRMS (ESI-TOF) calcd. for $C_{17}H_{13}FN_3O$ $[M + H]^+$ 294.1037; found: 294.1032.



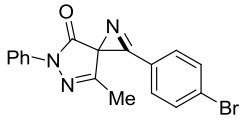
2-(4-fluorophenyl)-7-methyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3h). White solid; 41.3 mg, 70% yield; m.p. 123.3-125.2 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 3H), 7.18-7.23 (m, 1H), 7.29-7.35 (m, 2H), 7.40-7.46 (m, 2H), 7.88-7.93 (m, 2H), 7.96-8.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 46.1, 116.3 (d, *J* = 3.1 Hz, 1C), 117.5 (d, *J* = 22.7 Hz, 1C), 118.4, 125.1, 128.9, 133.7 (d, *J* = 9.8 Hz, 1C), 138.6, 156.6, 157.4, 166.7 (d, *J* = 258.1 Hz, 1C), 168.8; HRMS (ESI-TOF) calcd. for $C_{17}H_{13}FN_3O$ $[M + H]^+$ 294.1037; found: 294.1029.



2-(4-chlorophenyl)-7-methyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3i). White solid; 34.5 mg, 55% yield; m.p. 124.9-126.5 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 3H), 7.18-7.23 (m, 1H), 7.40-7.46 (m, 2H), 7.60 (d, *J* = 8.1 Hz, 2H), 7.82 (d, *J* = 8.1 Hz, 2H), 7.96-8.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2, 46.1, 118.4, 125.1, 128.9, 130.3, 132.2, 138.6, 142.0, 157.0, 157.3, 168.6; HRMS (ESI-TOF) calcd. for $C_{17}H_{13}ClN_3O$ $[M + H]^+$ 310.0742; found: 310.0730.

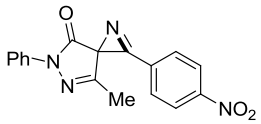


2-(3-bromophenyl)-7-methyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3j). White solid; 42.3 mg, 59% yield; m.p. 108.4-109.9 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 3H), 7.20-7.25 (m, 1H), 7.40-7.46 (m, 2H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.81-7.85 (m, 2H), 7.97-8.01 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2, 46.3, 118.5, 121.9, 123.8, 125.1, 128.9, 129.5, 131.2, 133.6, 138.1, 138.6, 157.1, 157.2, 168.5; HRMS (ESI-TOF) calcd. for $C_{17}H_{13}BrN_3O$ $[M + H]^+$ 354.0237; found: 354.0227.

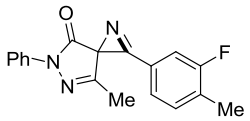


2-(4-bromophenyl)-7-methyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3k). White solid; 55.9 mg, 78% yield; m.p. 142.9-144.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.93 (s, 3H), 7.17-7.23 (m, 1H), 7.40-7.46

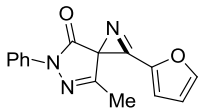
(m, 2H), 7.71-7.80 (m, 4H), 7.96-8.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2, 46.1, 118.4, 118.8, 125.1, 128.9, 130.7, 132.2, 133.3, 138.6, 157.1, 157.2, 168.6; HRMS (ESI-TOF) calcd. for $C_{17}H_{13}BrN_3O$ $[M + H]^+$ 354.0237; found: 354.0230.



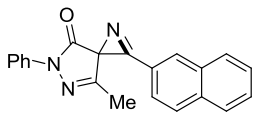
7-methyl-2-(4-nitrophenyl)-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3l). Yellow solid; 49.6 mg, 77% yield; m.p. 141.5-142.3 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 3H), 7.19-7.24 (m, 1H), 7.40-7.46 (m, 2H), 7.94-7.98 (m, 2H), 8.09 (d, *J* = 8.7 Hz, 2H), 8.45 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2, 46.5, 118.4, 124.8, 125.3, 125.5, 128.9, 131.9, 138.4, 151.4, 156.5, 157.6, 168.0; HRMS (ESI-TOF) calcd. for $C_{17}H_{13}N_4O_3$ $[M + H]^+$ 321.0982; found: 321.0972.



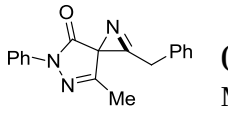
2-(3-fluoro-4-methylphenyl)-7-methyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3m). White solid; 46.8 mg, 76% yield; m.p. 128.8-130.4 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 3H), 2.40 (d, *J* = 9.2 Hz, 3H), 7.18-7.23 (m, 1H), 7.40-7.47 (m, 3H), 7.52-7.57 (m, 2H), 7.97-8.00 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 15.2 (d, *J* = 3.5 Hz, 1C), 46.2, 117.1 (d, *J* = 24.1 Hz, 1C), 118.4, 119.0 (d, *J* = 8.3 Hz, 1C), 125.0, 126.8 (d, *J* = 3.2 Hz, 1C), 128.8, 132.9 (d, *J* = 5.2 Hz, 1C), 133.8 (d, *J* = 17.1 Hz, 1C), 138.6, 156.8 (d, *J* = 3.1 Hz, 1C), 157.3, 161.4 (d, *J* = 248.2 Hz, 1C), 168.6; HRMS (ESI-TOF) calcd. for $C_{18}H_{15}FN_3O$ $[M + H]^+$ 308.1194; found: 308.1191.



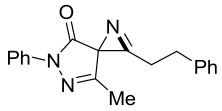
2-(furan-2-yl)-7-methyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3n). Yellow solid; 46.9 mg, 78% yield; m.p. 139.2-140.6 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.95 (s, 3H), 6.74 (dd, *J* = 1.7 Hz, 3.6 Hz, 1H), 7.17-7.23 (m, 1H), 7.36-7.37 (m, 1H), 7.39-7.45 (m, 2H), 7.90-7.91 (m, 1H), 7.95-7.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 45.5, 113.6, 118.5, 124.1, 125.1, 128.9, 136.5, 138.6, 147.2, 150.6, 157.2, 168.3; HRMS (ESI-TOF) calcd. for $C_{15}H_{12}N_3O_2$ $[M + H]^+$ 266.0924; found: 266.0924.



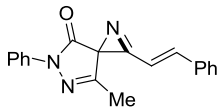
7-methyl-2-(naphthalen-2-yl)-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3o). White solid; 47.4 mg, 72% yield; m.p. 143.4-144.2 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98 (s, 3H), 7.19-7.25 (m, 1H), 7.42-7.48 (m, 2H), 7.60-7.65 (m, 1H), 7.67-7.73 (m, 1H), 7.93-8.00 (m, 3H), 8.03-8.08 (m, 3H), 8.25 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2, 46.3, 117.1, 118.4, 124.8, 125.0, 127.8, 128.2, 128.9, 129.3, 129.9, 130.0, 132.5, 134.2, 136.2, 138.8, 157.6, 157.8, 169.0; HRMS (ESI-TOF) calcd. for $C_{21}H_{16}N_3O$ $[M + H]^+$ 326.1288; found: 326.1275.



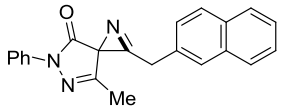
2-benzyl-7-methyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3p). Yellow solid; 53.6 mg, 92% yield; m.p. 79.8-81.4 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56 (s, 3H), 4.20 (d, *J* = 16.6 Hz, 1H), 4.40 (d, *J* = 16.6 Hz, 1H), 7.16-7.22 (m, 1H), 7.31-7.44 (m, 7H), 7.91-7.94 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.7, 33.1, 45.8, 118.4, 125.0, 128.5, 128.8, 129.1, 129.4, 130.0, 138.6, 157.3, 160.6, 169.0; HRMS (ESI-TOF) calcd. for $C_{18}H_{16}N_3O$ $[M + H]^+$ 290.1288; found: 290.1277.



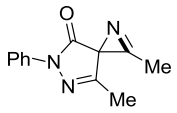
7-methyl-2-phenethyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3q). White solid; 56.8 mg, 93% yield; m.p. 104.9-106.2 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.68 (s, 3H), 3.07-3.22 (m, 2H), 3.28-3.34 (m, 2H), 7.16-7.30 (m, 6H), 7.38-7.44 (m, 2H), 7.89-7.93 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.9, 28.2, 30.2, 45.6, 118.5, 125.0, 127.1, 128.2, 128.8, 128.9, 138.1, 138.6, 157.4, 161.3, 169.2; HRMS (ESI-TOF) calcd. for $C_{19}H_{18}N_3O$ $[M + H]^+$ 304.1444; found: 304.1437.



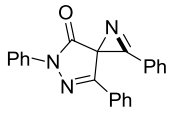
(E)-7-methyl-5-phenyl-2-styryl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3r). Yellow solid; 54.3 mg, 90% yield; m.p. 79.7-81.6 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.57 (s, 3H), 4.20 (d, *J* = 16.5 Hz, 1H), 4.39 (d, *J* = 16.5 Hz, 1H), 7.18-7.26 (m, 1H), 7.31-7.43 (m, 7H), 7.91-7.94 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.7, 33.1, 45.8, 118.4, 125.0, 128.5, 128.8, 129.1, 129.4, 130.0, 138.6, 157.3, 160.6, 169.0; HRMS (ESI-TOF) calcd. for $C_{19}H_{16}N_3O$ $[M + H]^+$ 301.1215; found: 301.1384.



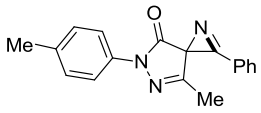
7-methyl-2-(naphthalen-2-ylmethyl)-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3s). Yellow solid; 51.4 mg, 75% yield; m.p. 124.3-126.1 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.56 (s, 3H), 4.37 (d, *J* = 16.8 Hz, 1H), 4.55 (d, *J* = 16.8 Hz, 1H), 7.16-7.22 (m, 1H), 7.38-7.44 (m, 3H), 7.51-7.56 (m, 2H), 7.81-7.90 (m, 4H), 7.91-7.95 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.8, 33.3, 45.9, 118.4, 125.0, 126.3, 126.7, 126.9, 127.3, 127.7, 127.8, 128.4, 128.8, 129.4, 132.8, 133.4, 138.6, 157.3, 160.7, 169.1; HRMS (ESI-TOF) calcd. for $C_{22}H_{18}N_3O$ $[M + H]^+$ 340.1444; found: 340.1434.



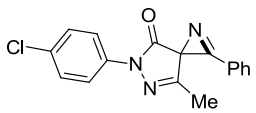
2,7-dimethyl-5-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3t). Yellow oil; 38.7 mg, 90% yield; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.88 (s, 3H), 2.63 (s, 3H), 7.13-7.18 (m, 1H), 7.34-7.40 (m, 2H), 7.87-7.91 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 12.4, 13.1, 45.3, 118.4, 124.9, 128.8, 138.5, 157.4, 158.6, 169.2; HRMS (ESI-TOF) calcd. for $C_{12}H_{12}N_3O$ $[M + H]^+$ 214.0975; found: 214.0968.



2,5,7-triphenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3u). Yellow solid; 43.5 mg, 64% yield; m.p. 155.4-157.2 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.22-7.28 (m, 1H), 7.29-7.38 (m, 3H), 7.45-7.51 (m, 2H), 7.59-7.64 (m, 4H), 7.69-7.75 (m, 1H), 7.91-7.94 (m, 2H), 8.11-8.15 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 45.1, 118.7, 120.0, 125.3, 126.2, 128.8, 128.9, 129.7, 129.8, 130.3, 131.3, 135.2, 138.7, 154.9, 158.0, 169.3; HRMS (ESI-TOF) calcd. for $C_{22}H_{16}N_3O$ $[M + H]^+$ 338.1288; found: 338.1301.



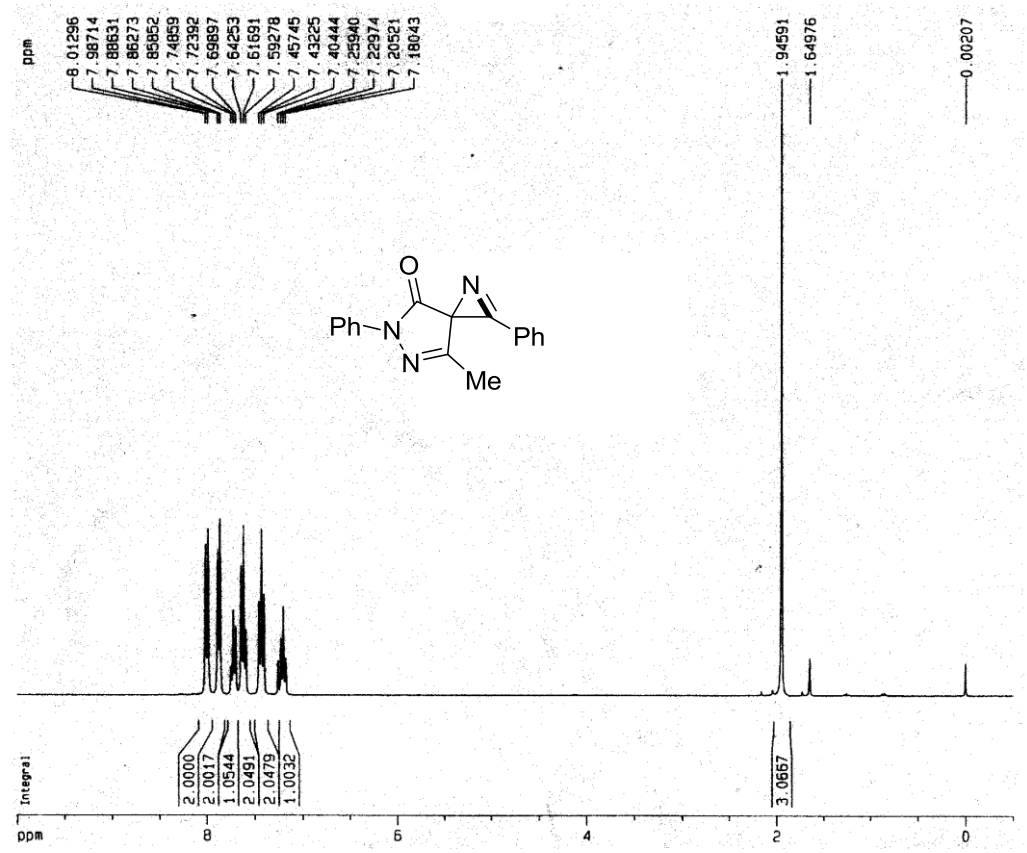
7-methyl-2-phenyl-5-(p-tolyl)-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3v). Yellow solid; 46.4 mg, 80% yield; m.p. 157.1-158.9 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 3H), 2.36 (s, 3H), 7.21-7.26 (m, 2H), 7.58-7.64 (m, 2H), 7.69-7.72 (m, 1H), 7.84-7.89 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.1, 20.9, 46.1, 118.5, 120.0, 129.4, 129.7, 131.1, 134.6, 135.1, 136.3, 157.4, 157.7, 168.7; HRMS (ESI-TOF) calcd. for $C_{18}H_{16}N_3O$ $[M + H]^+$ 290.1288; found: 290.1285.

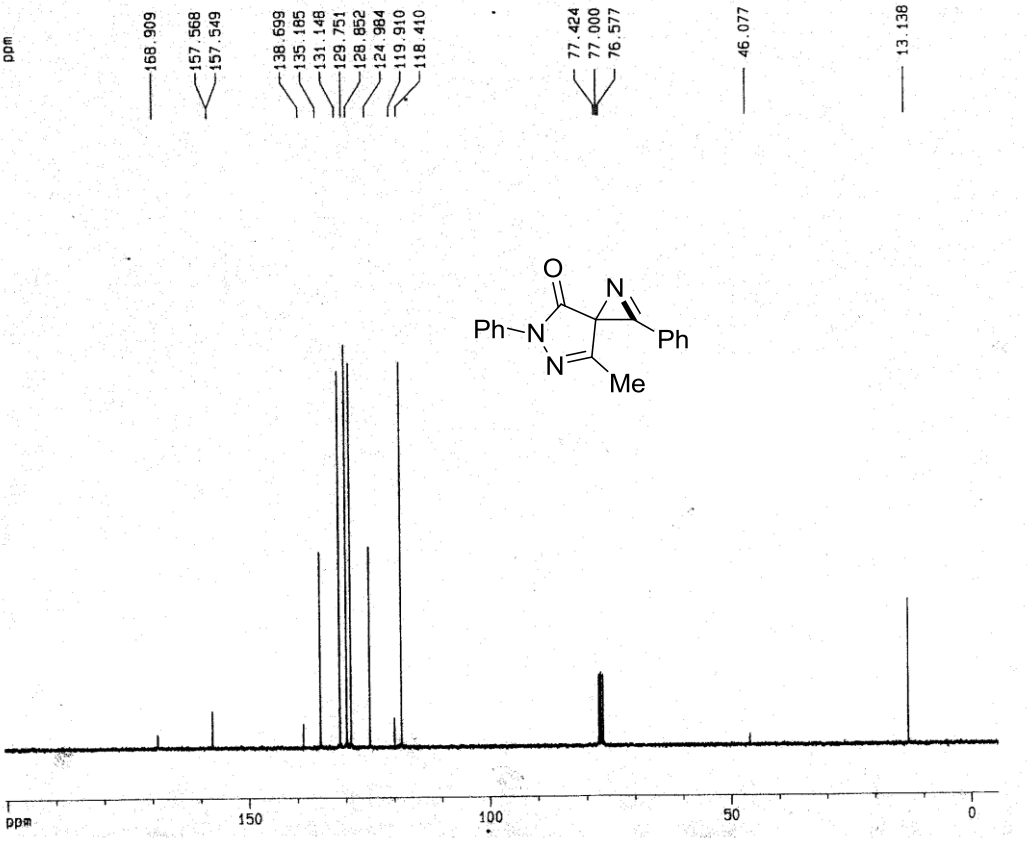


5-(4-chlorophenyl)-7-methyl-2-phenyl-1,5,6-triazaspiro[2.4]hepta-1,6-dien-4-one (3w). Yellow solid; 48.9 mg, 79% yield; m.p. 166.7-168.6 ℃; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.94 (s, 3H), 7.36-7.40 (m, 2H), 7.59-7.65 (m, 2H), 7.70-7.73 (m, 1H), 7.85-7.89 (m, 2H), 7.95-7.99 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.2, 46.1, 119.5, 119.8, 128.9, 129.8, 130.0, 131.2, 135.3, 137.3, 157.4, 157.9, 168.9; HRMS (ESI-TOF) calcd. for $C_{17}H_{13}ClN_3O$ $[M + H]^+$ 310.0742; found: 310.0730.

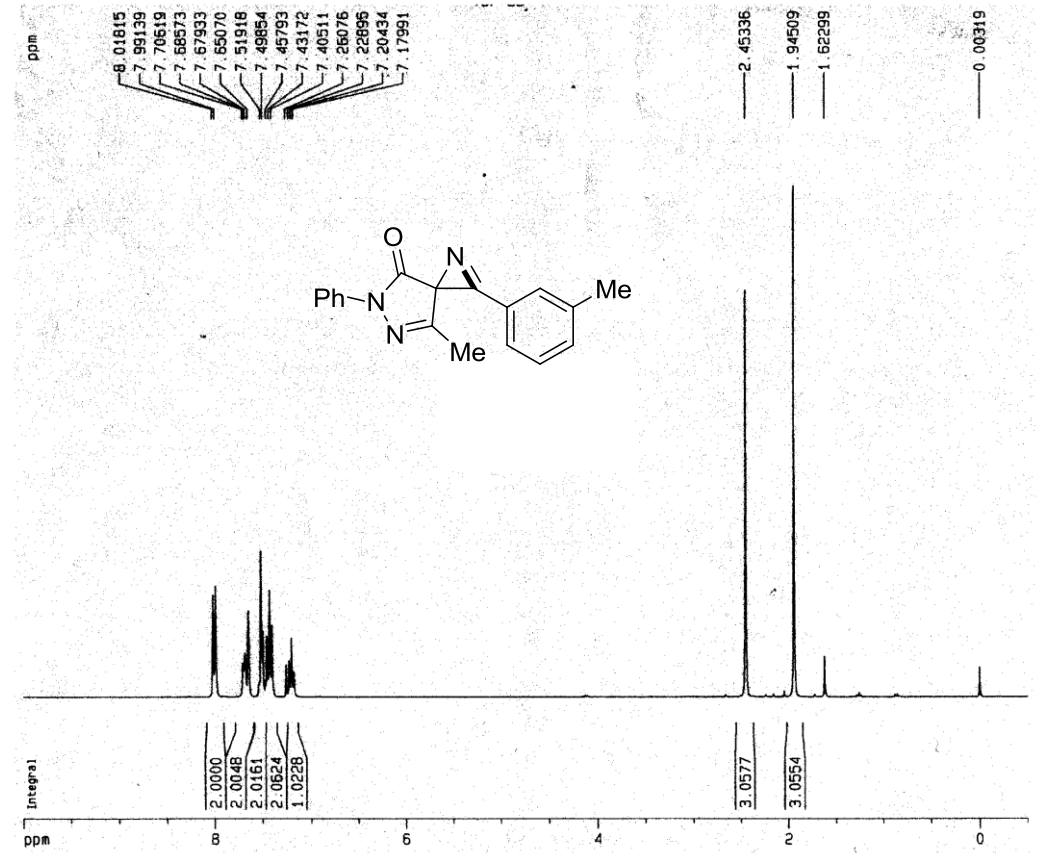
3. The copies of ^{1}H NMR, ^{13}C NMR spectra for compounds 3

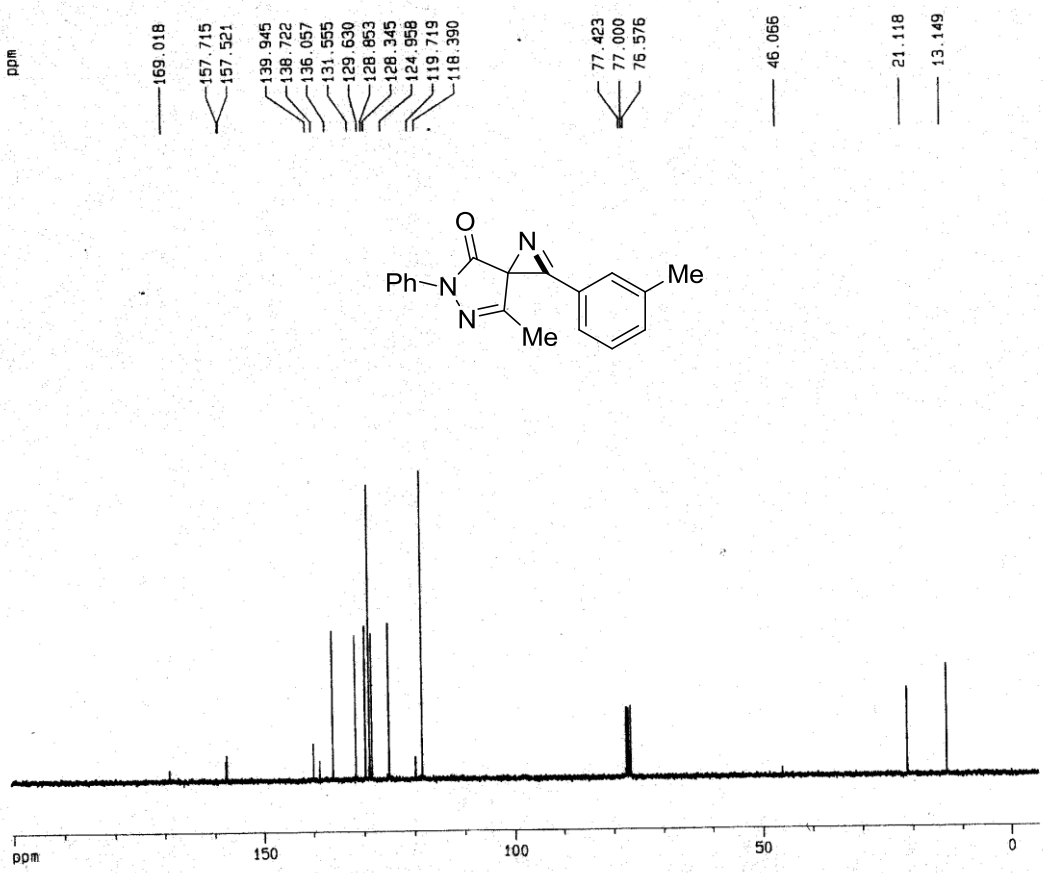
^{1}H NMR, ^{13}C NMR spectra of 3a



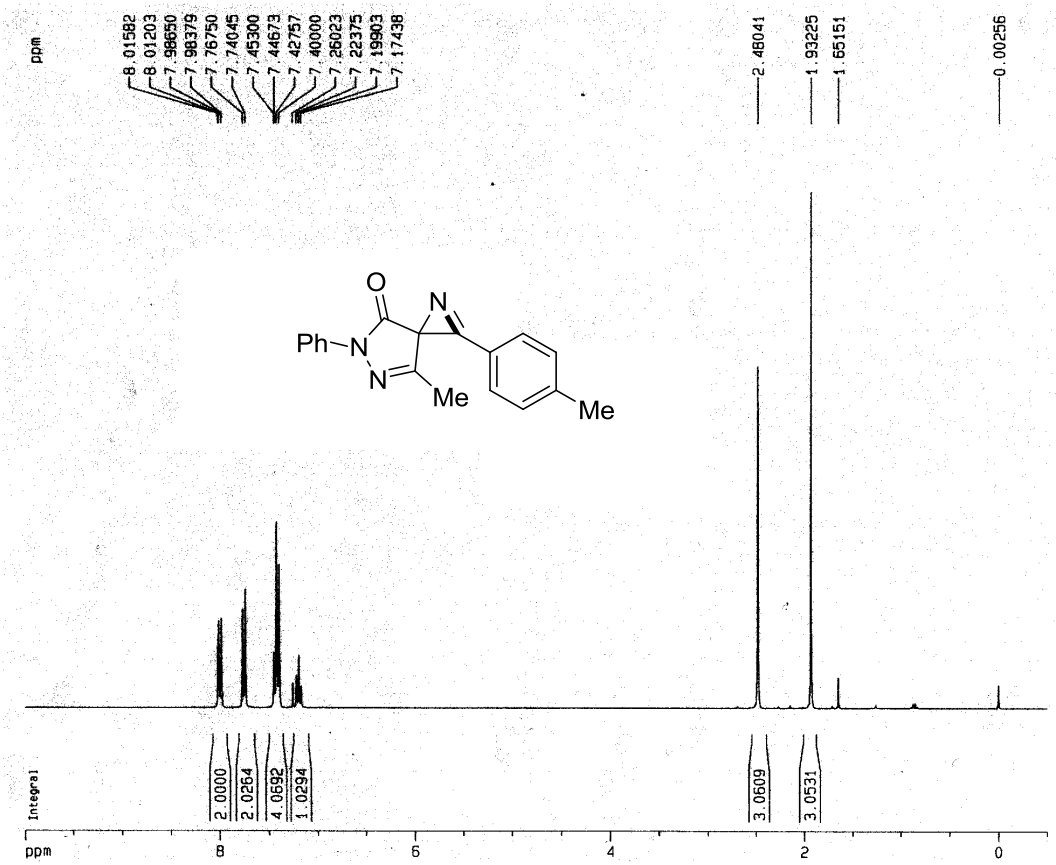


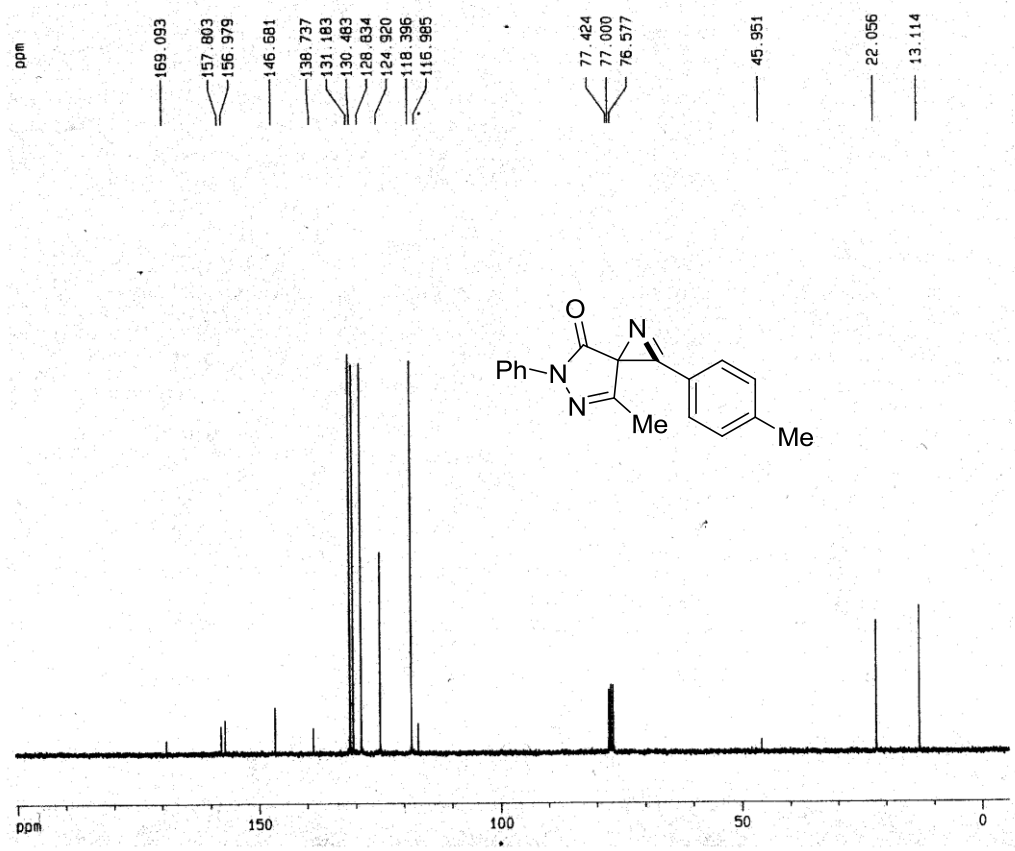
^{1}H NMR, ^{13}C NMR spectra of 3b



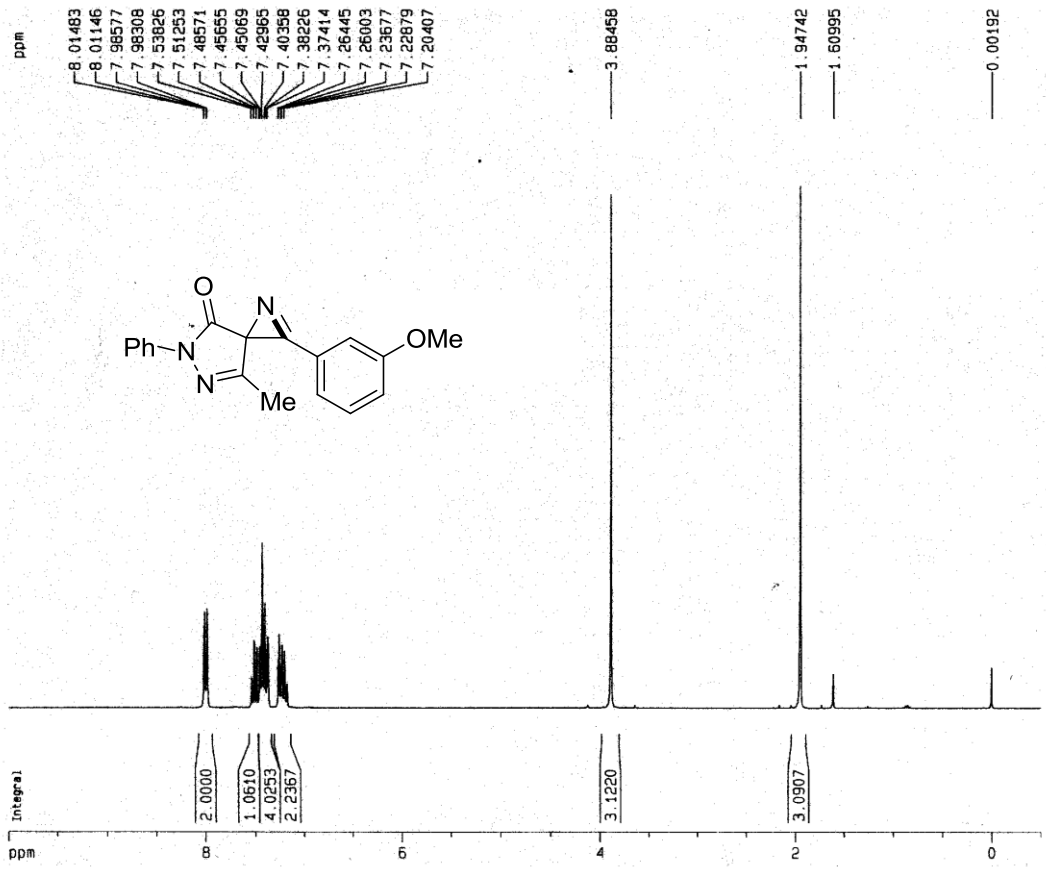


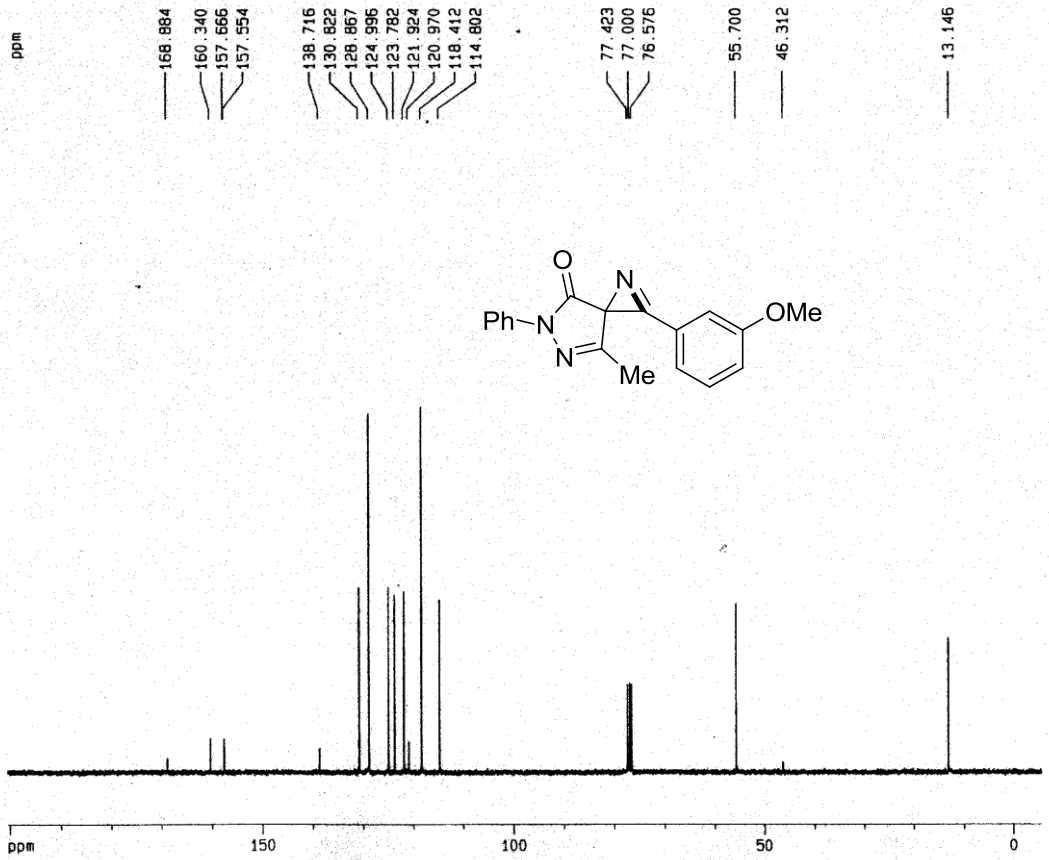
^{1}H NMR, ^{13}C NMR spectra of 3c



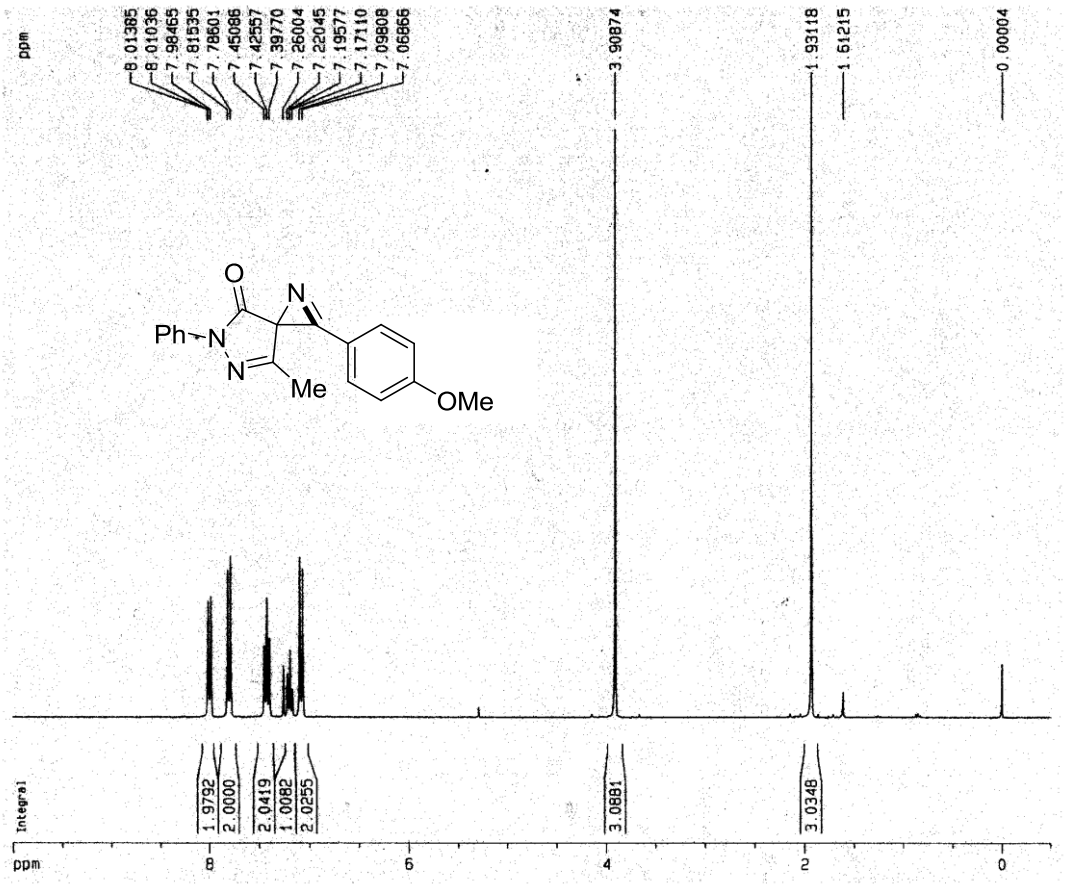


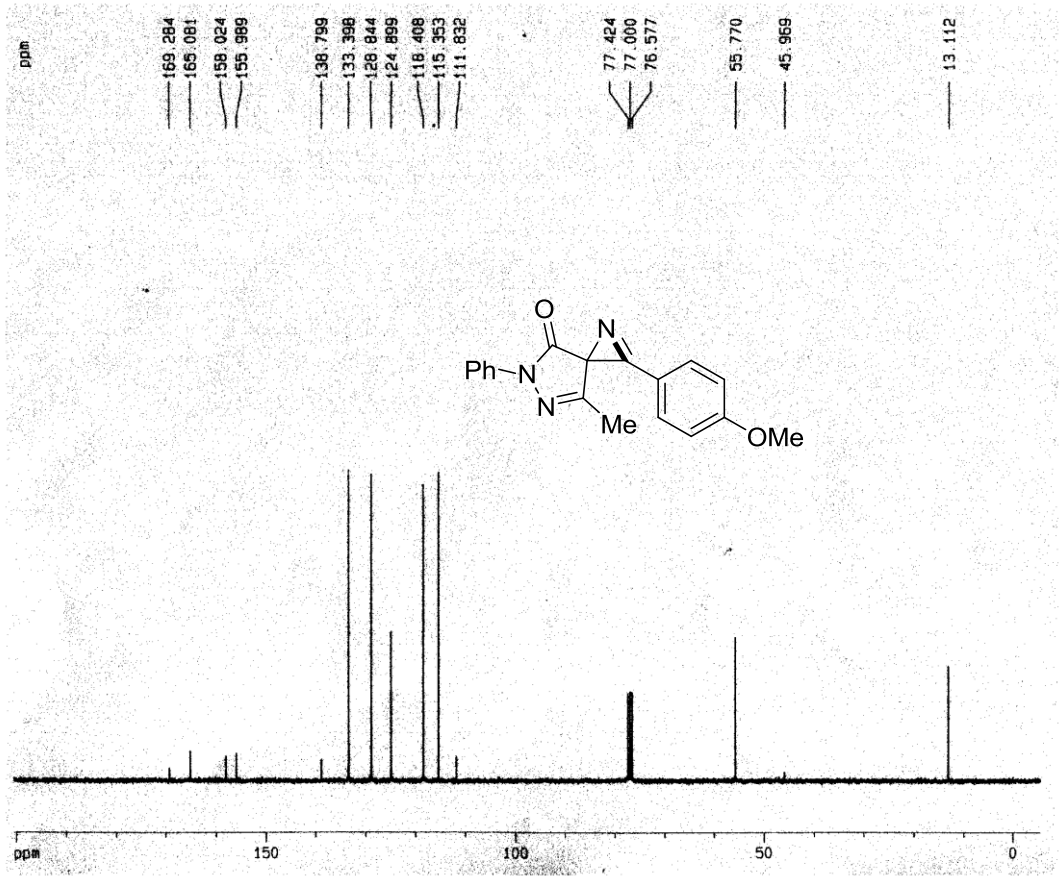
^{1}H NMR, ^{13}C NMR spectra of 3d



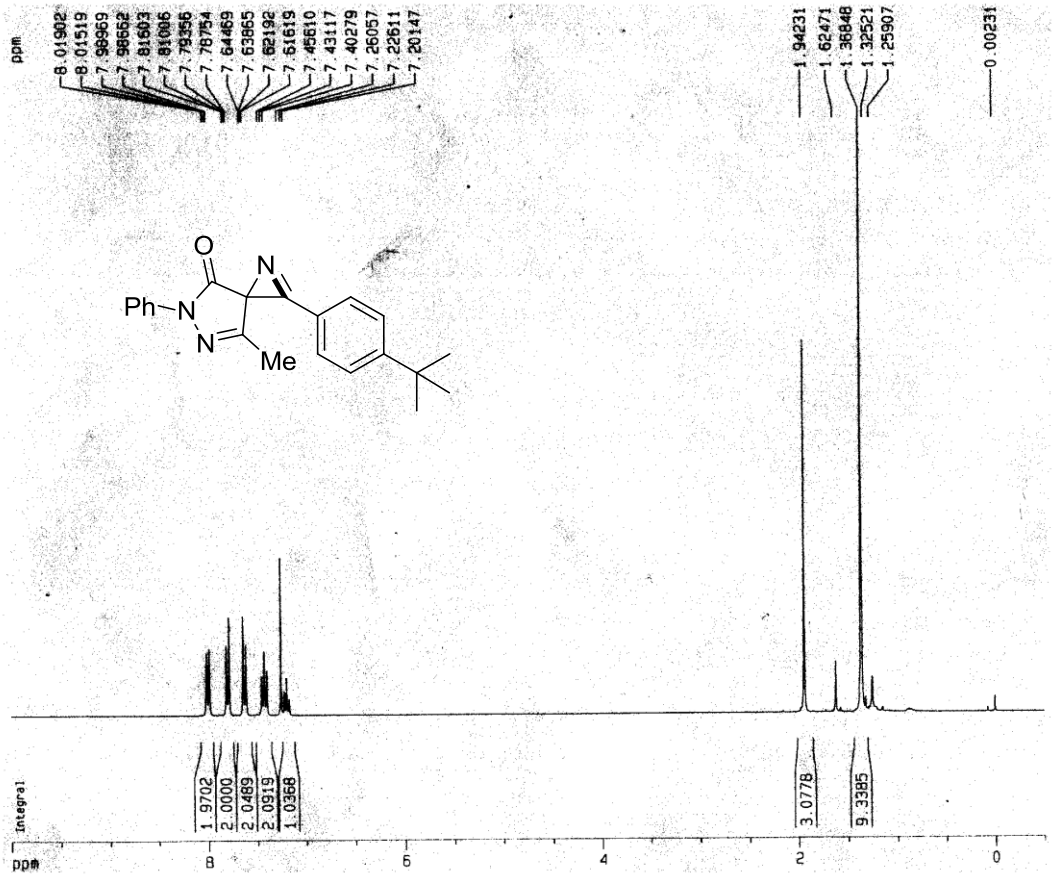


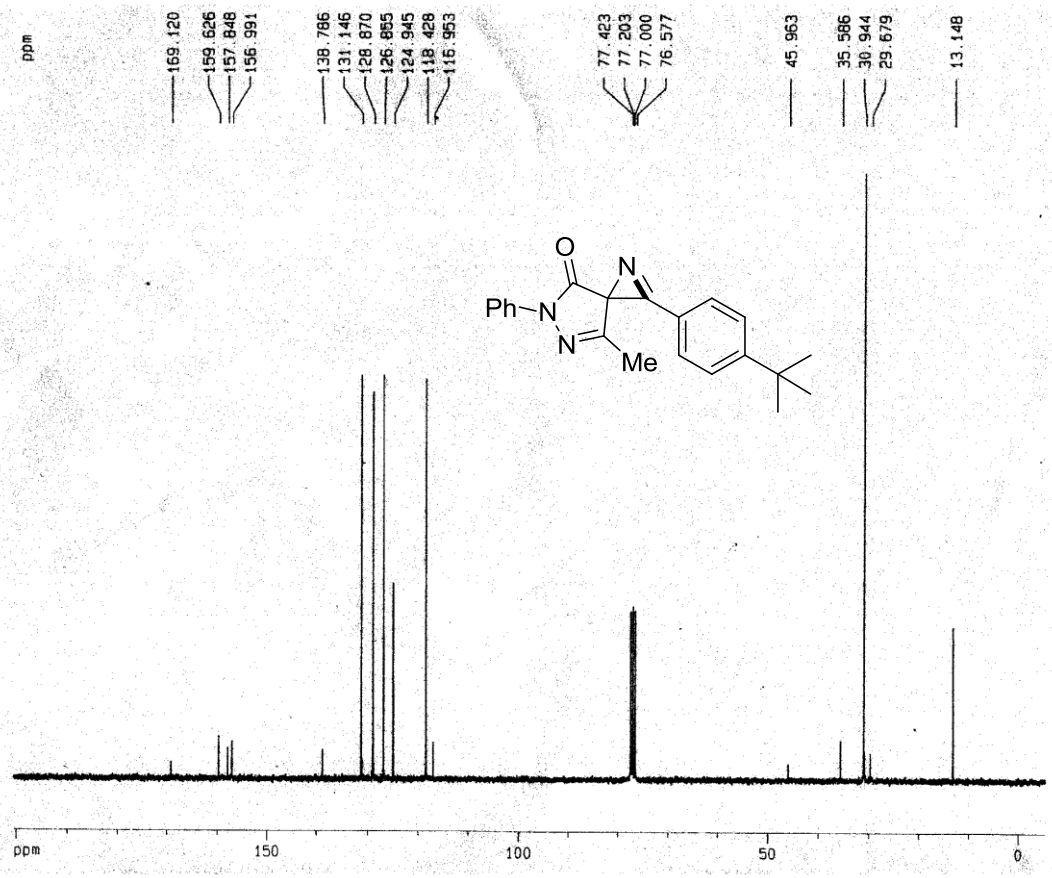
^{1}H NMR, ^{13}C NMR spectra of 3e



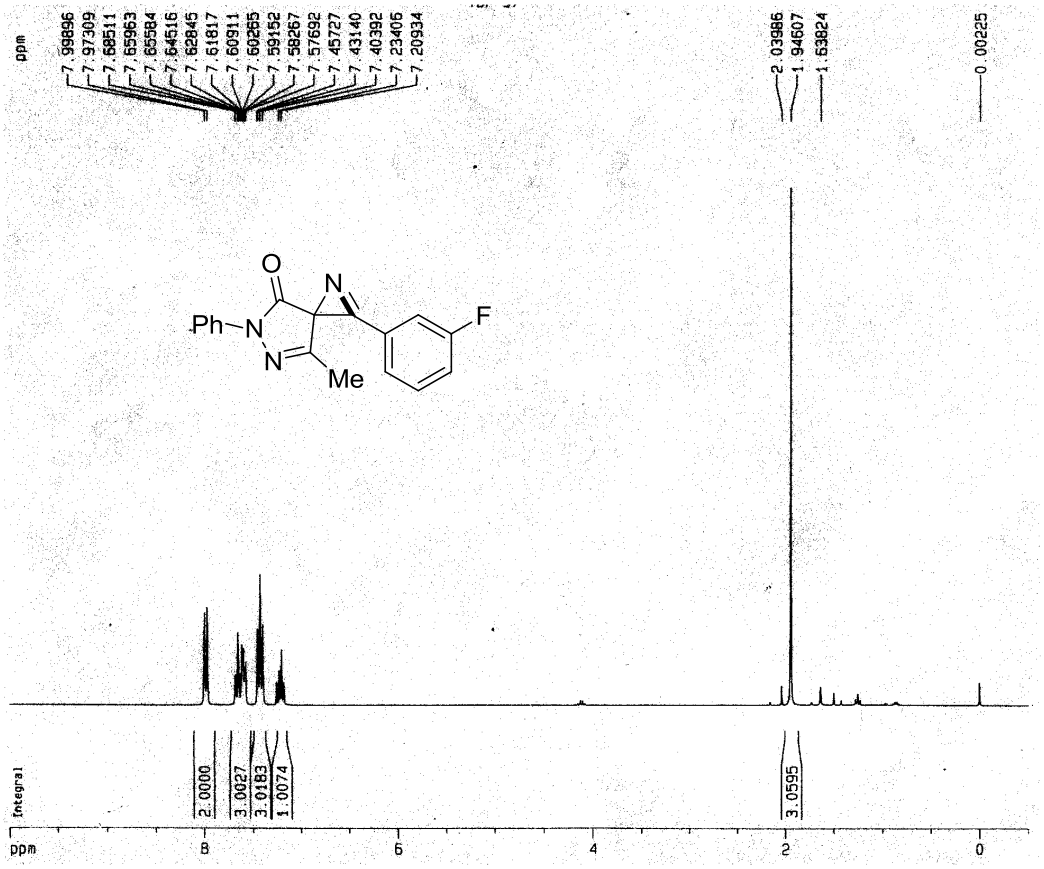


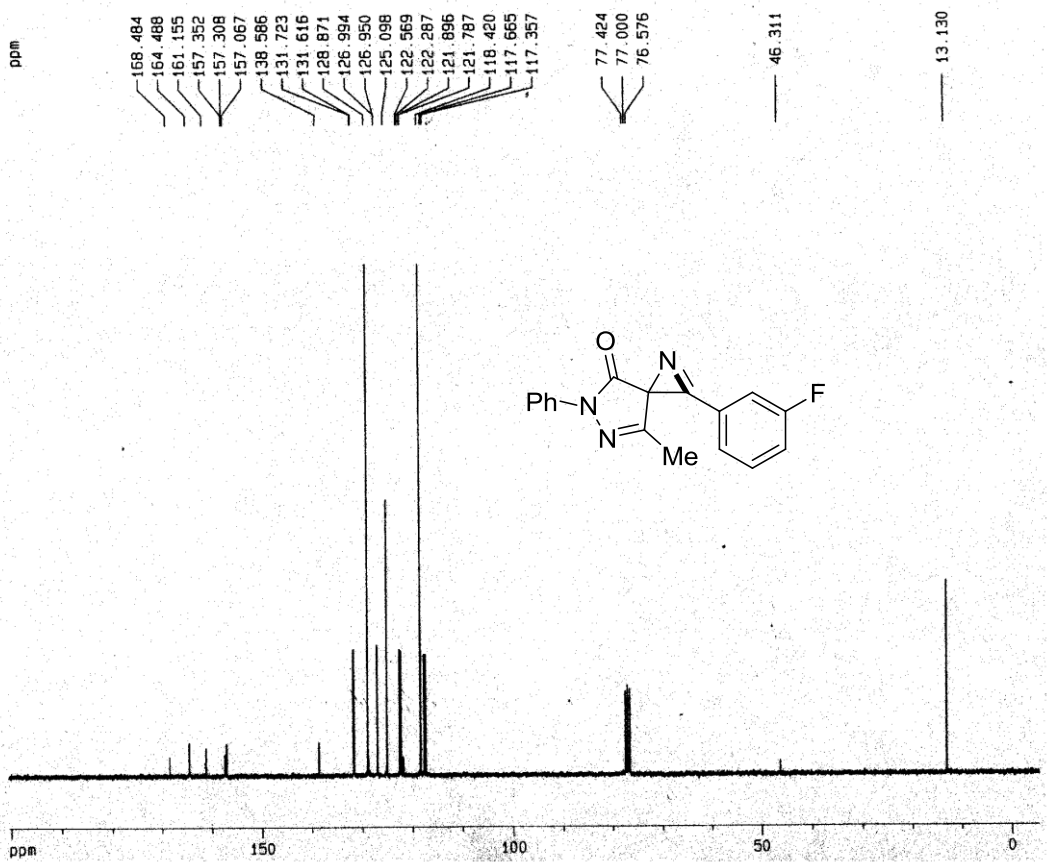
^{1}H NMR, ^{13}C NMR spectra of 3f



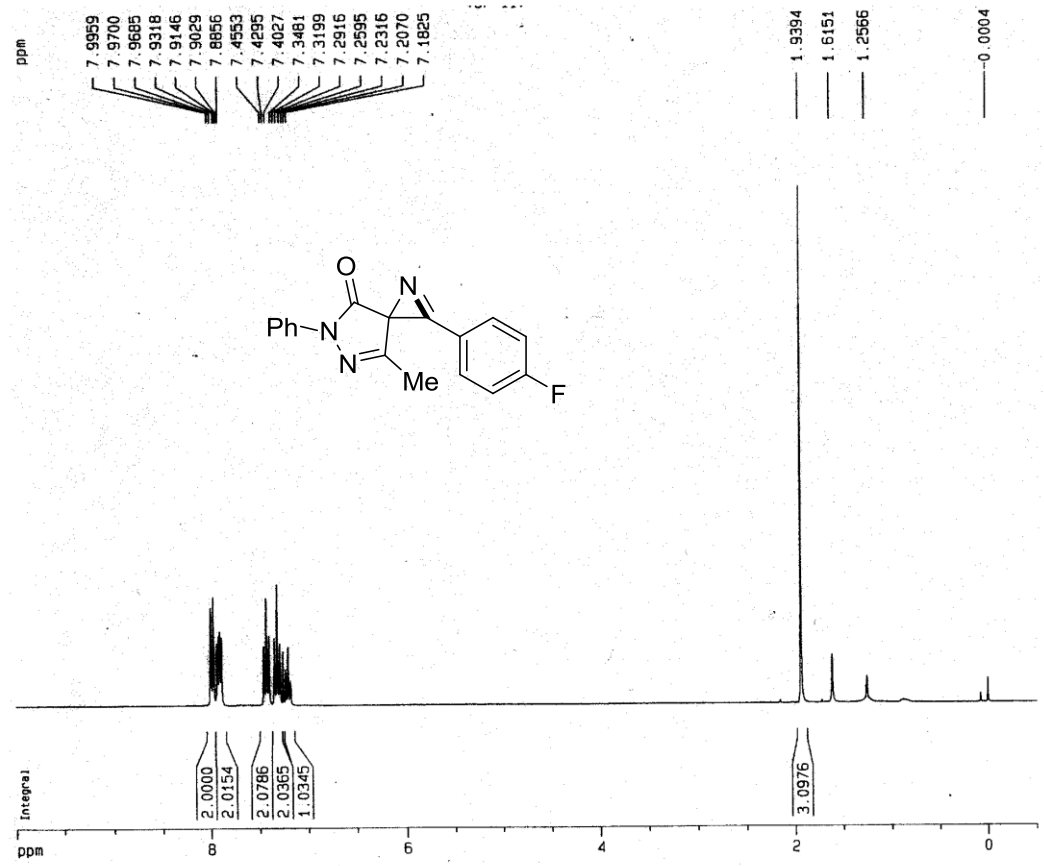


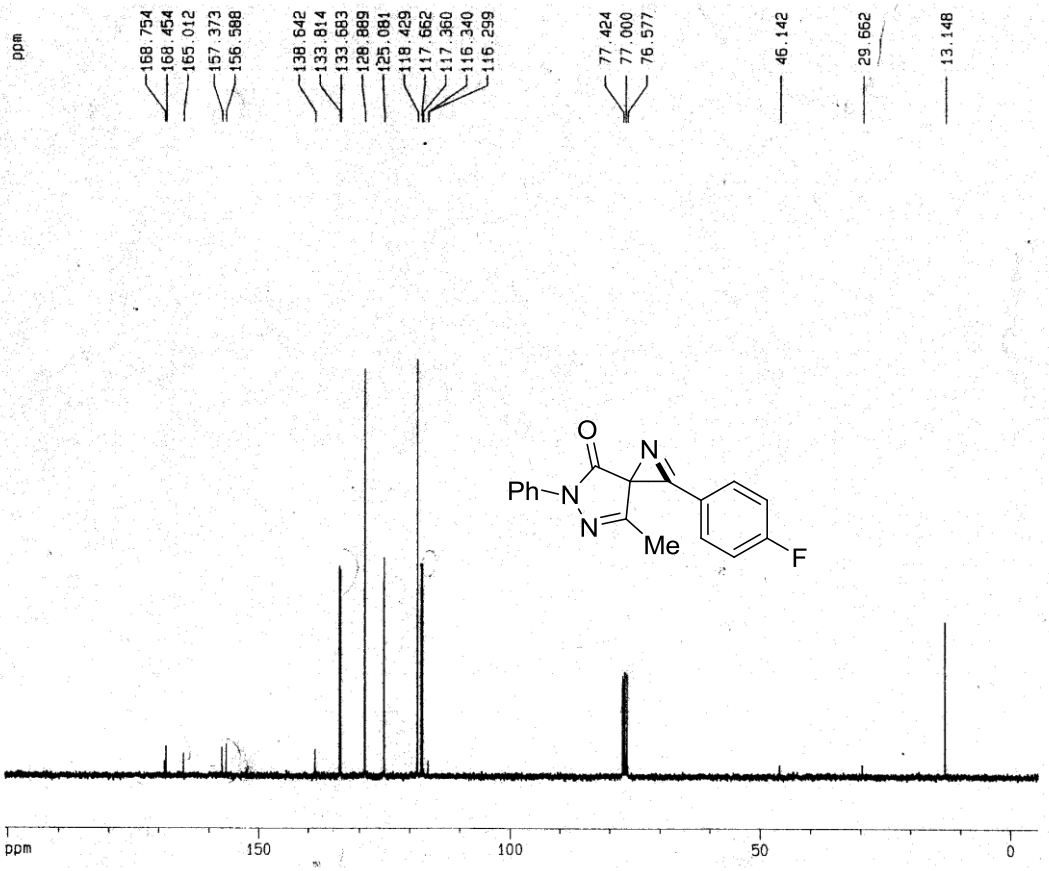
^{1}H NMR, ^{13}C NMR spectra of 3g



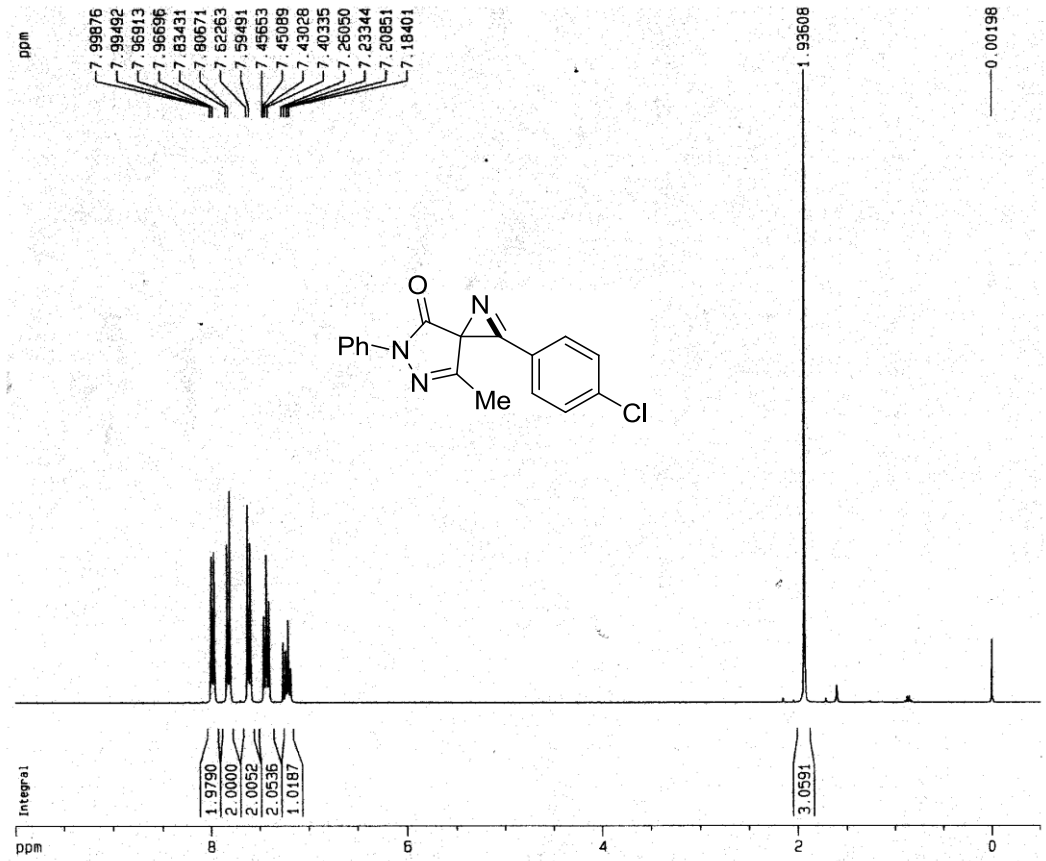


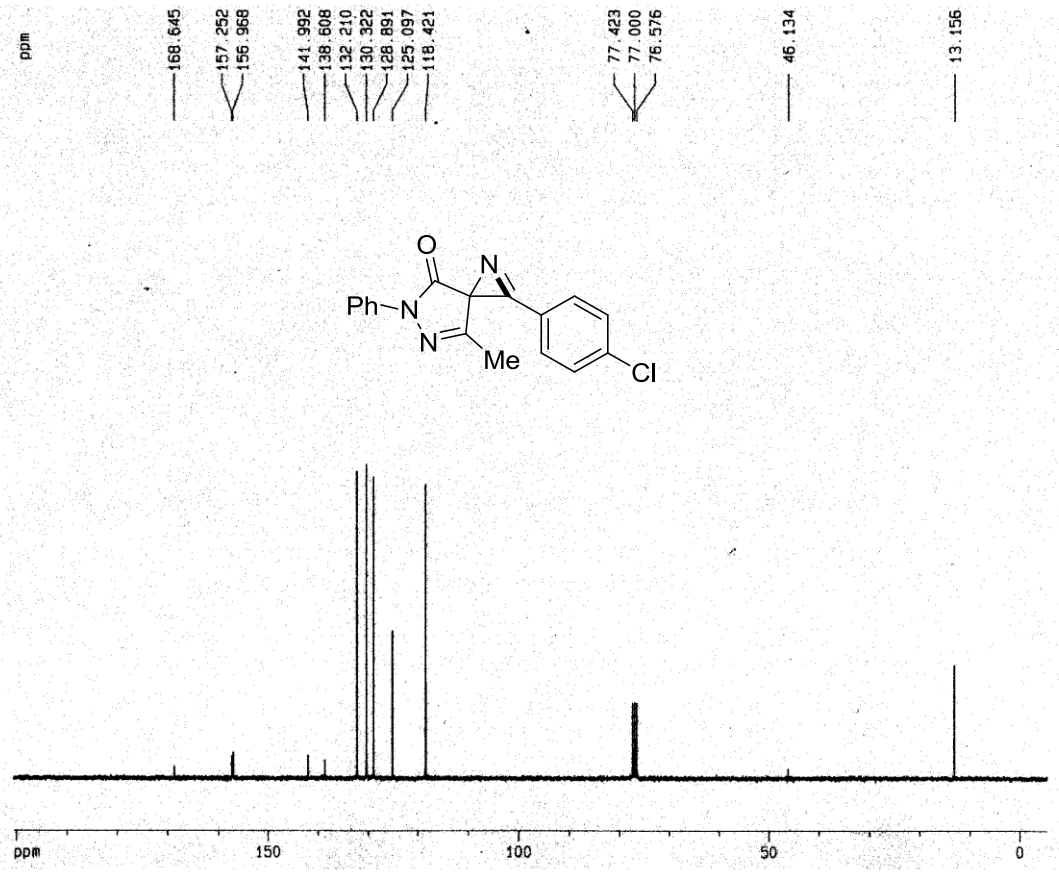
^{1}H NMR, ^{13}C NMR spectra of 3h



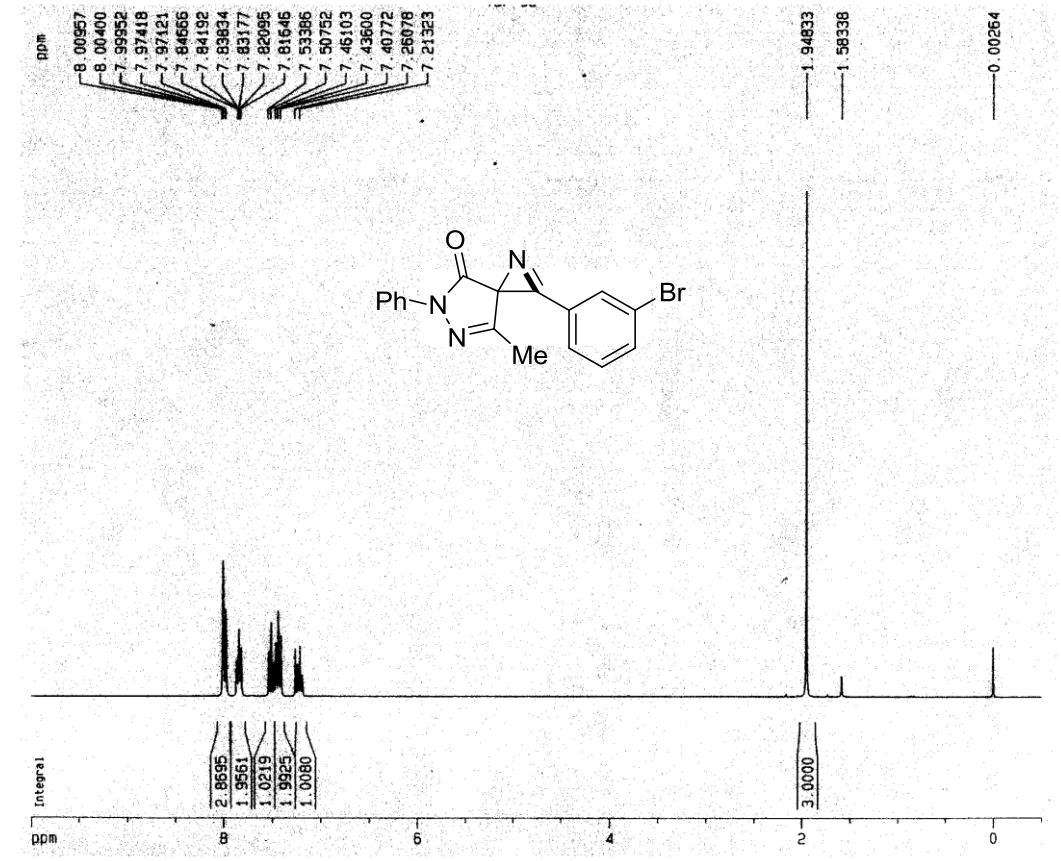


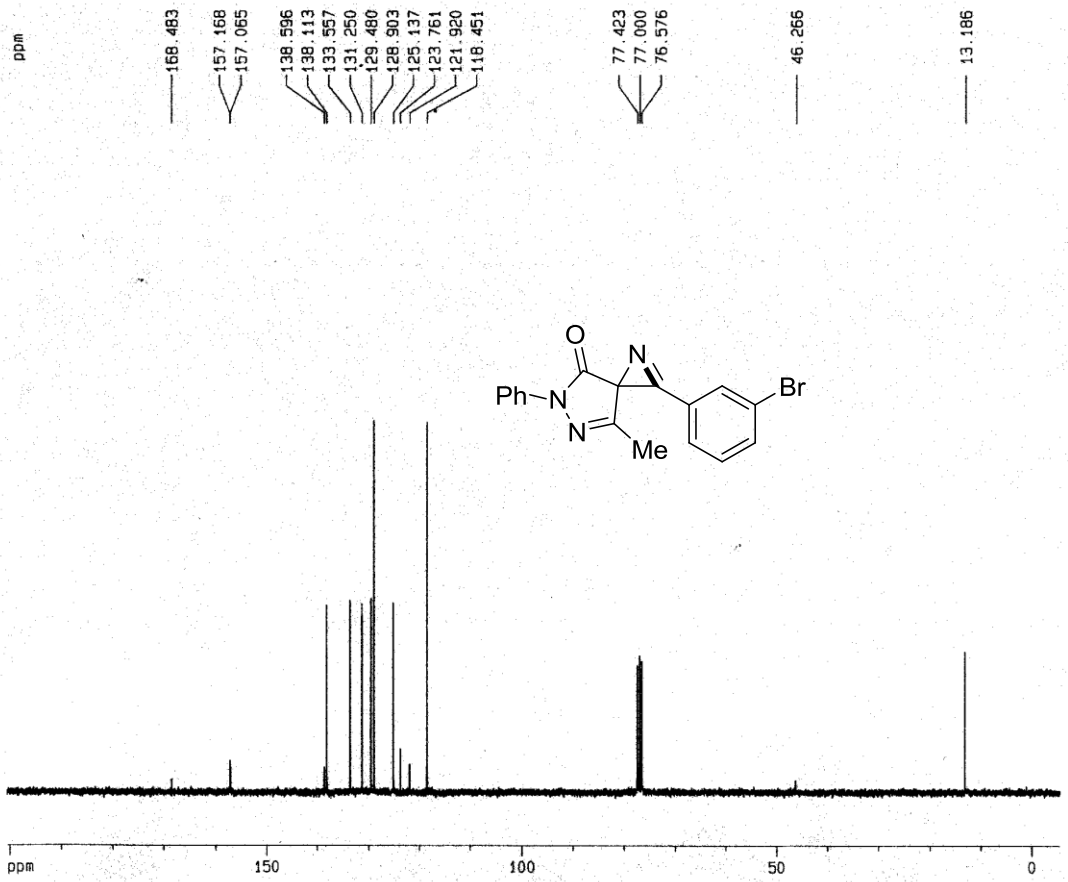
^{1}H NMR, ^{13}C NMR spectra of 3i



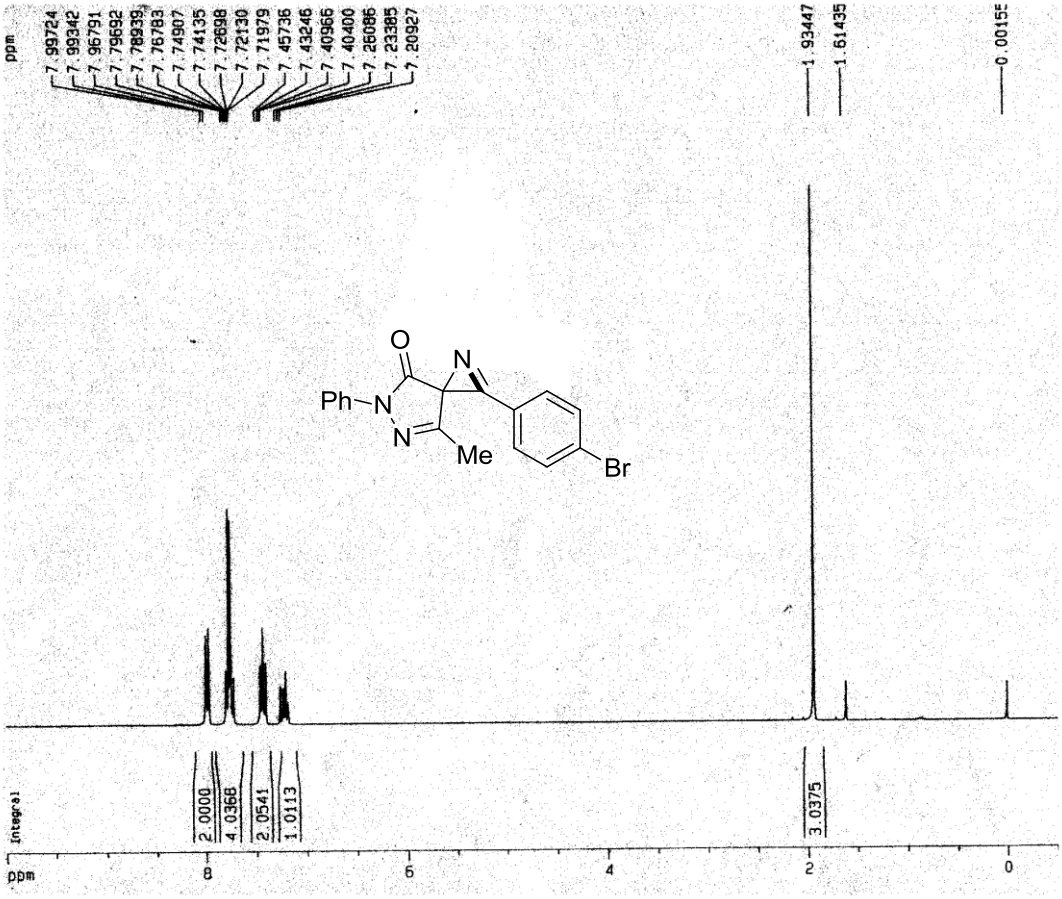


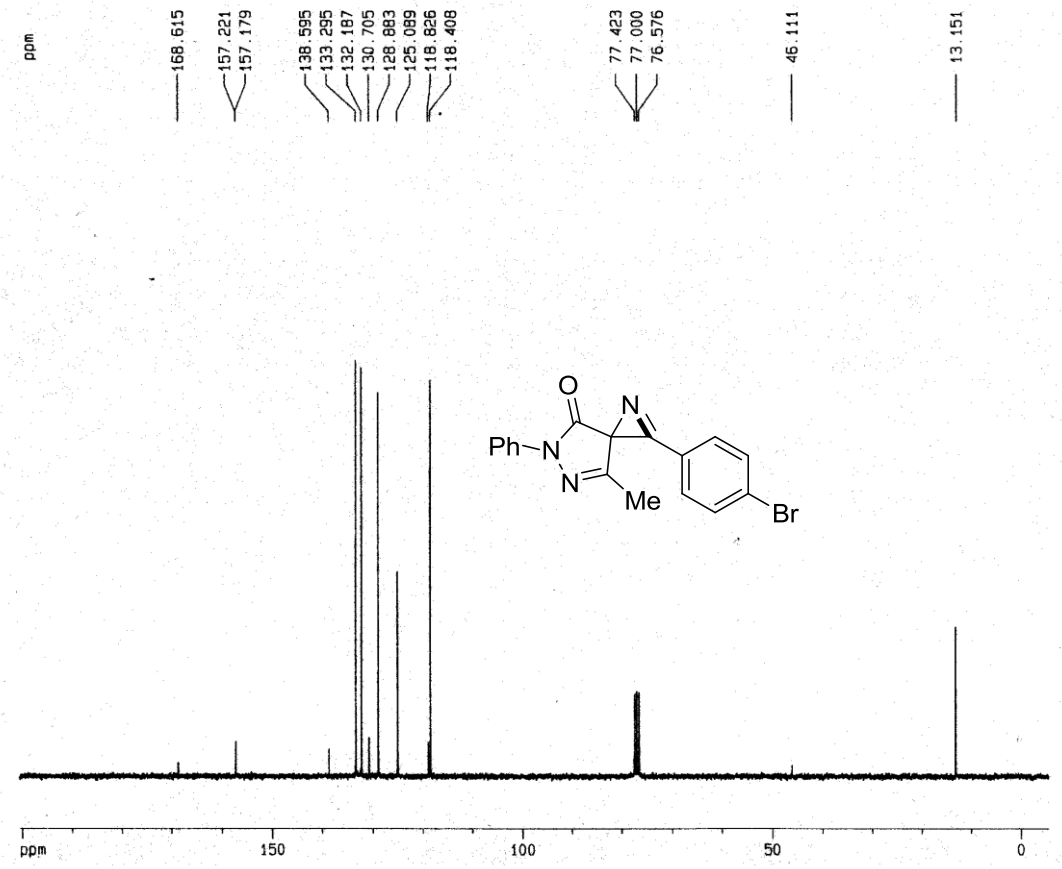
^{1}H NMR, ^{13}C NMR spectra of 3j



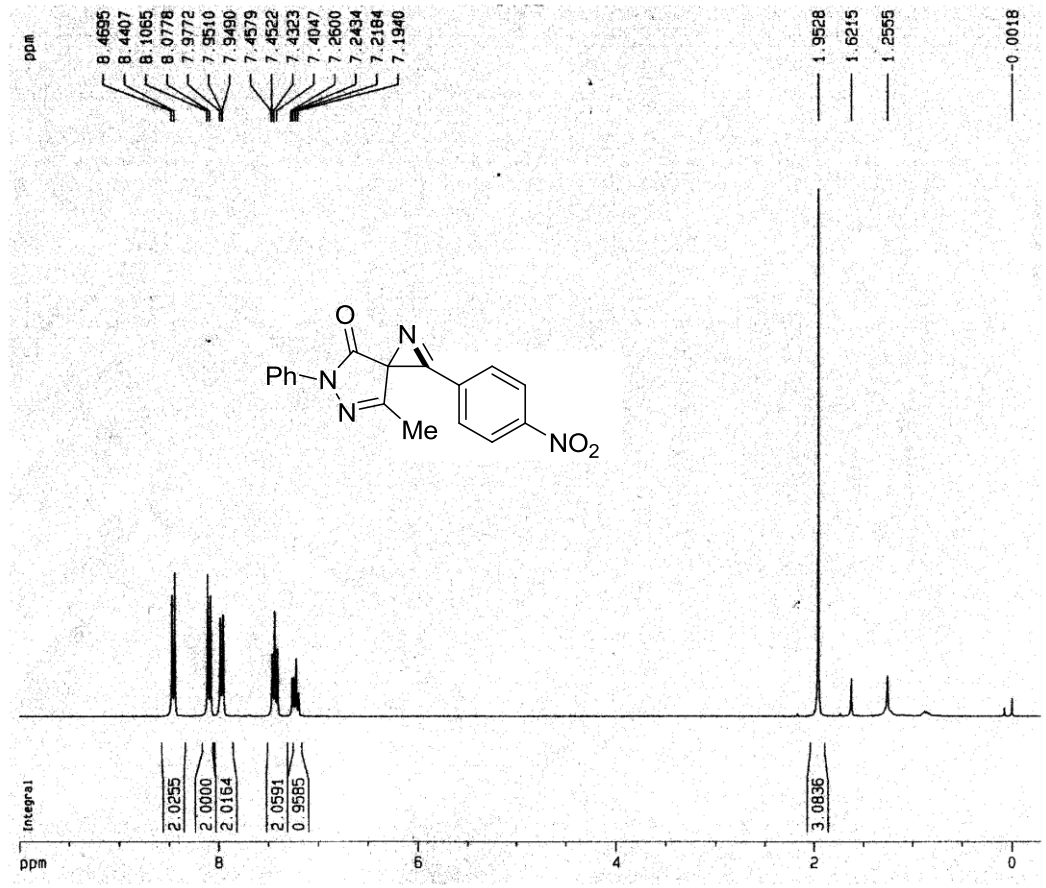


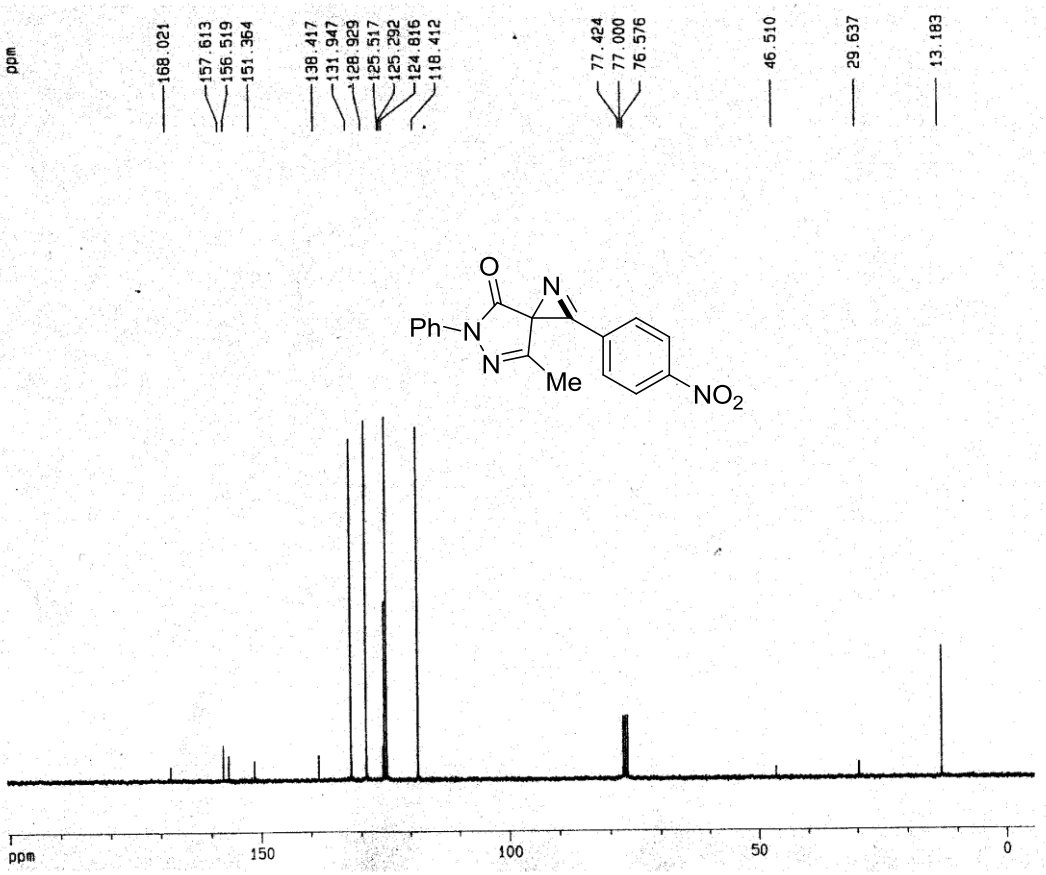
^{1}H NMR, ^{13}C NMR spectra of 3k



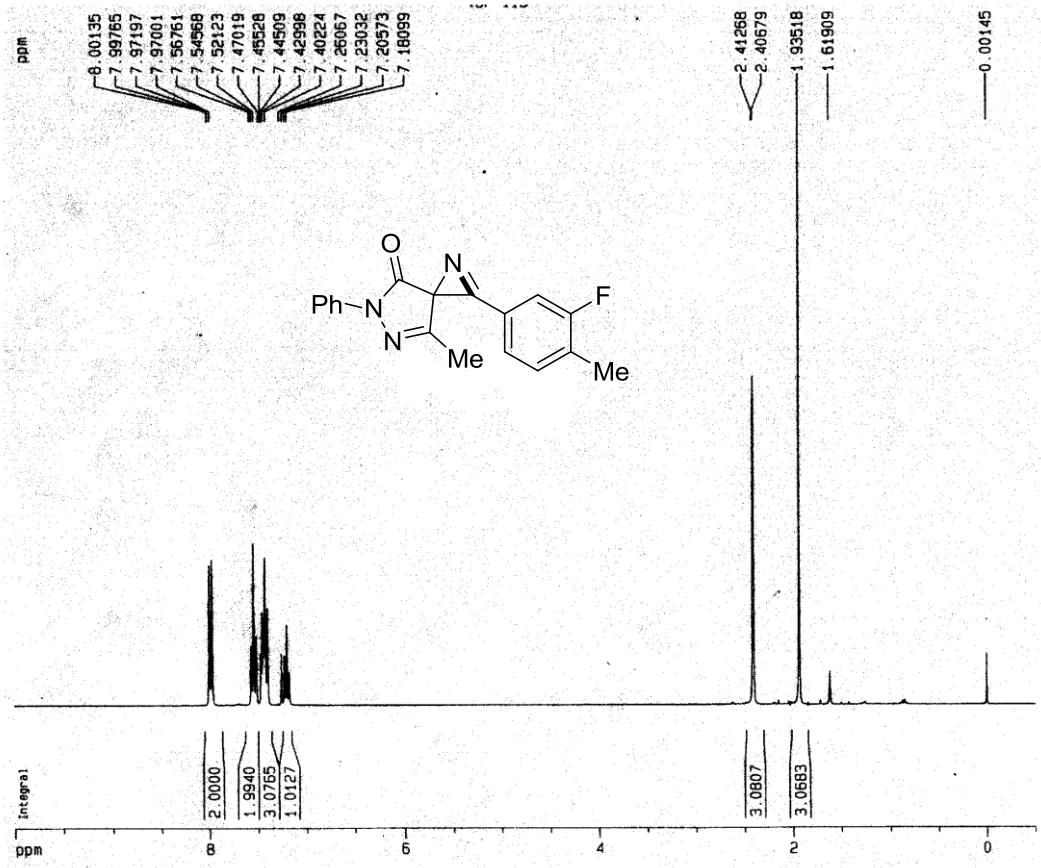


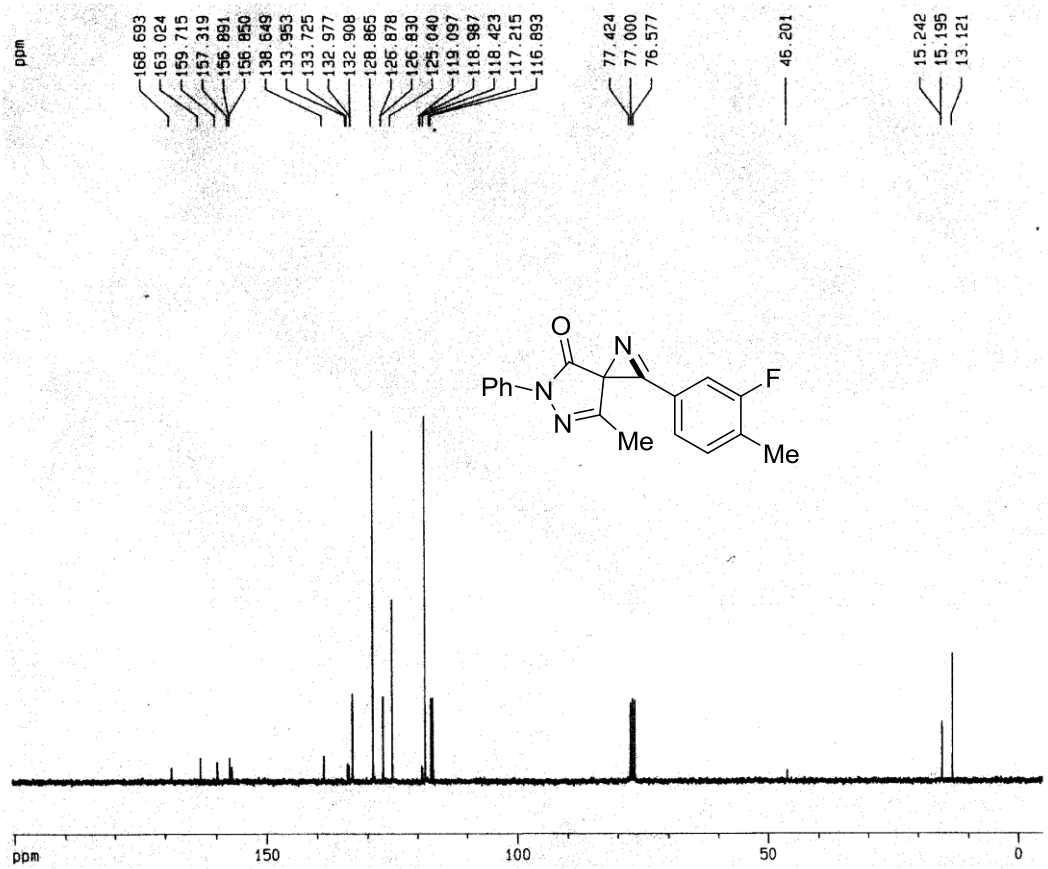
^{1}H NMR, ^{13}C NMR spectra of 3l



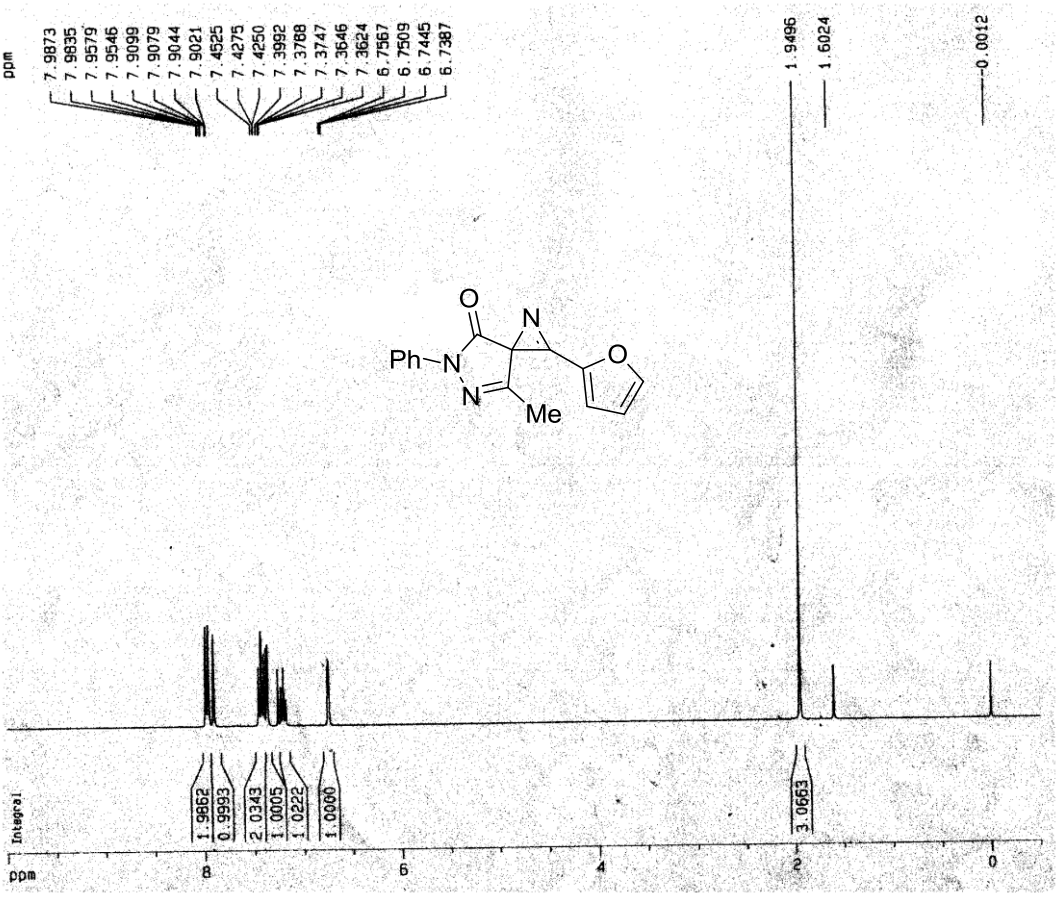


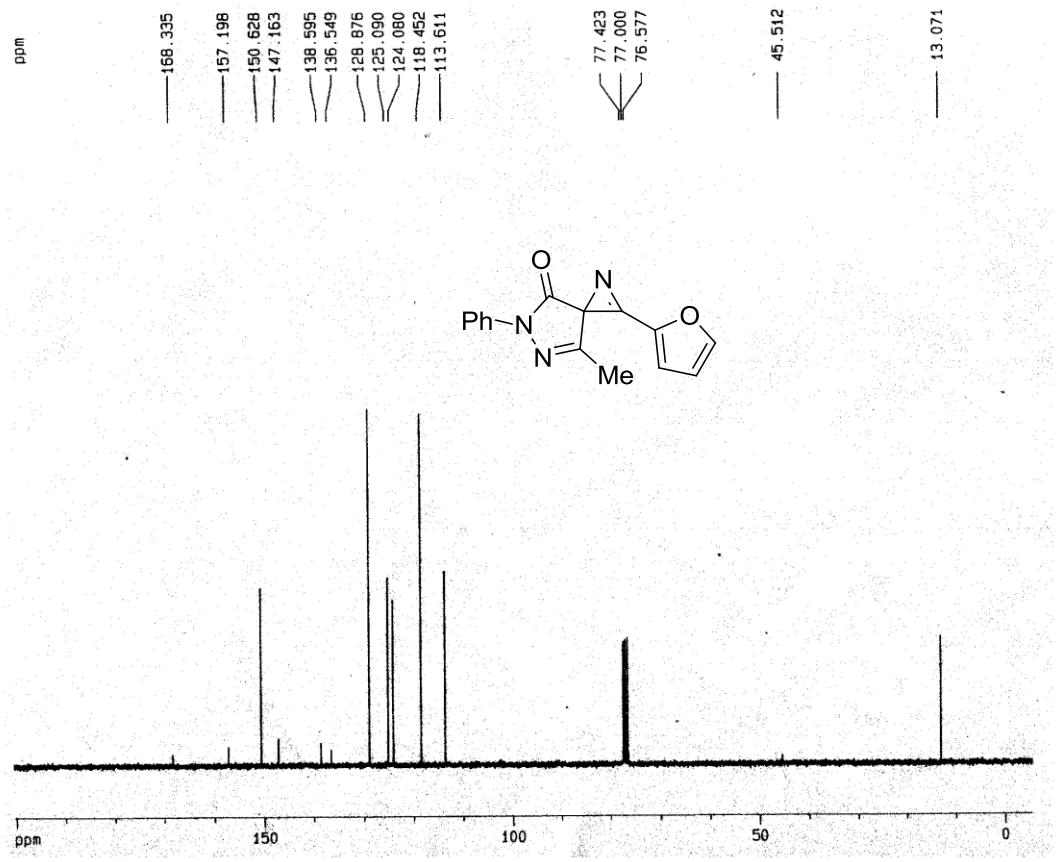
^{1}H NMR, ^{13}C NMR spectra of 3m



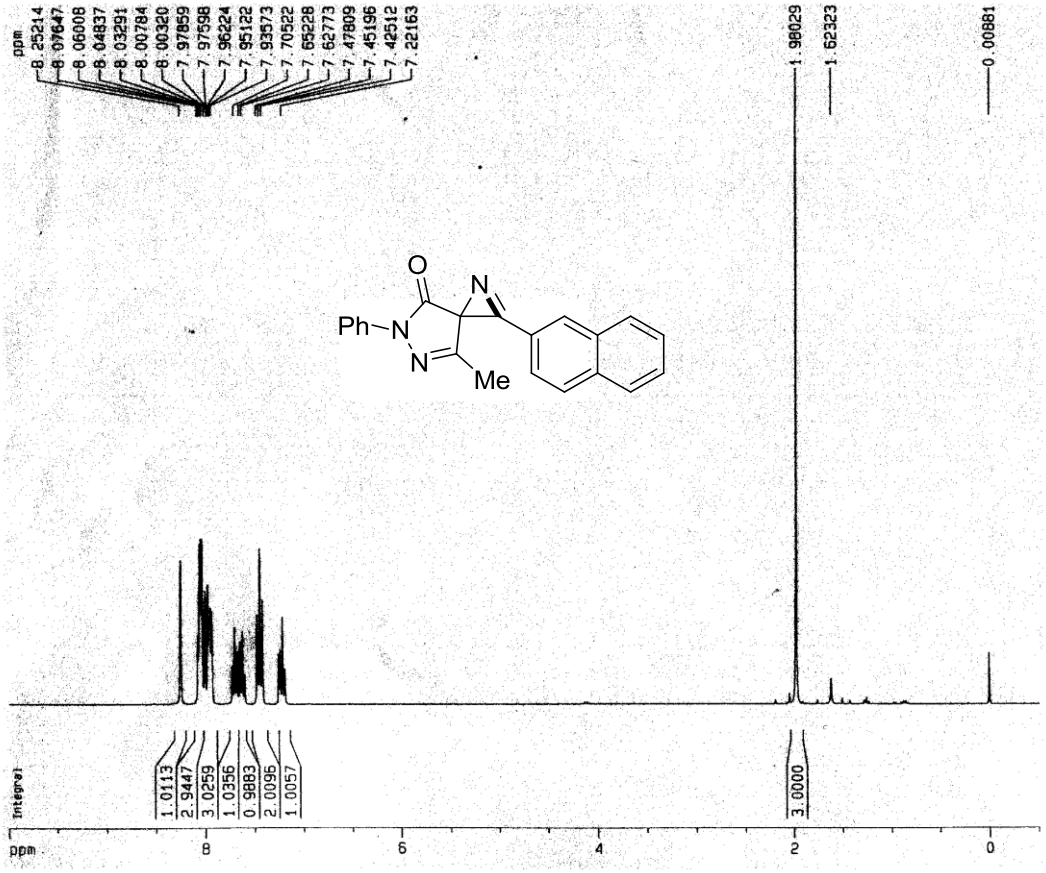


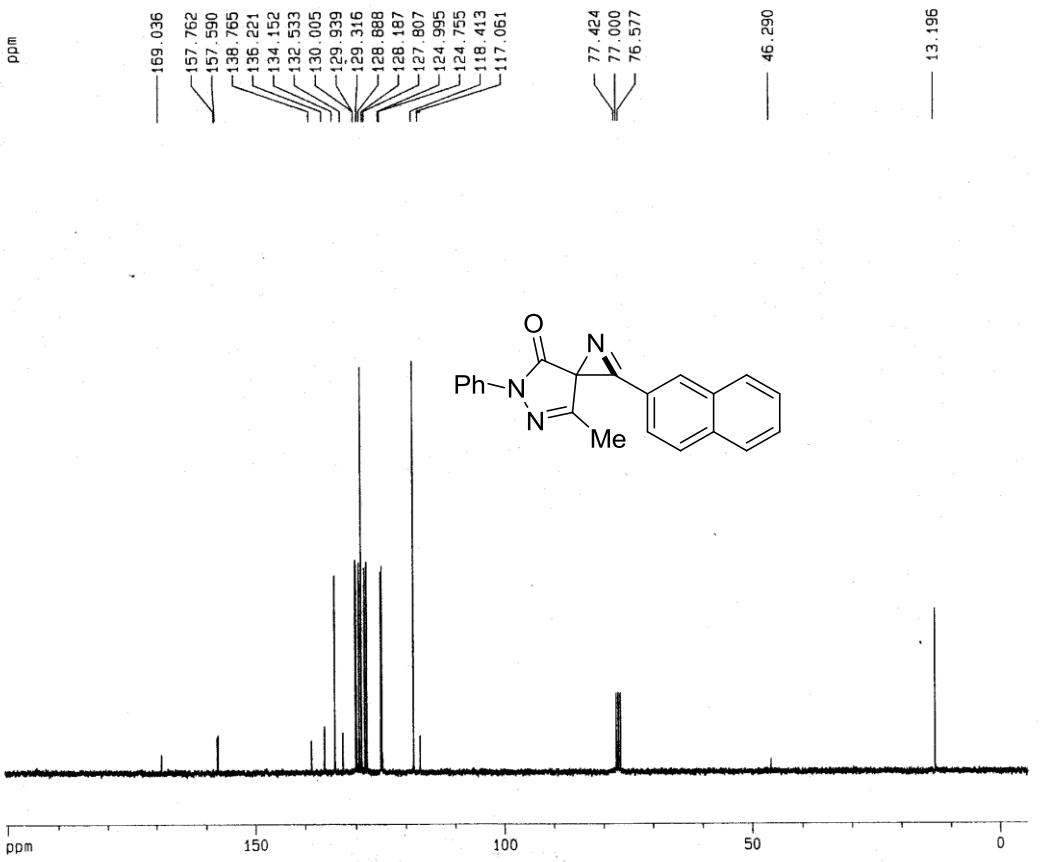
^{1}H NMR, ^{13}C NMR spectra of 3n



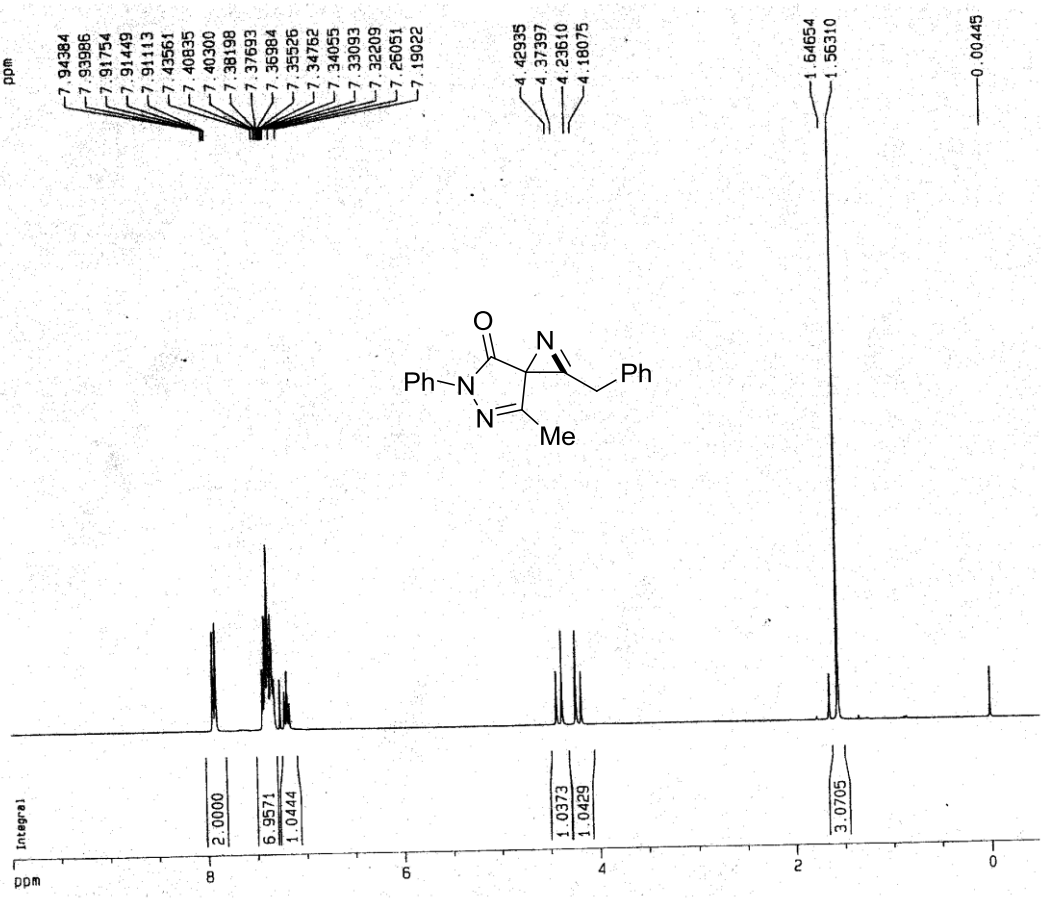


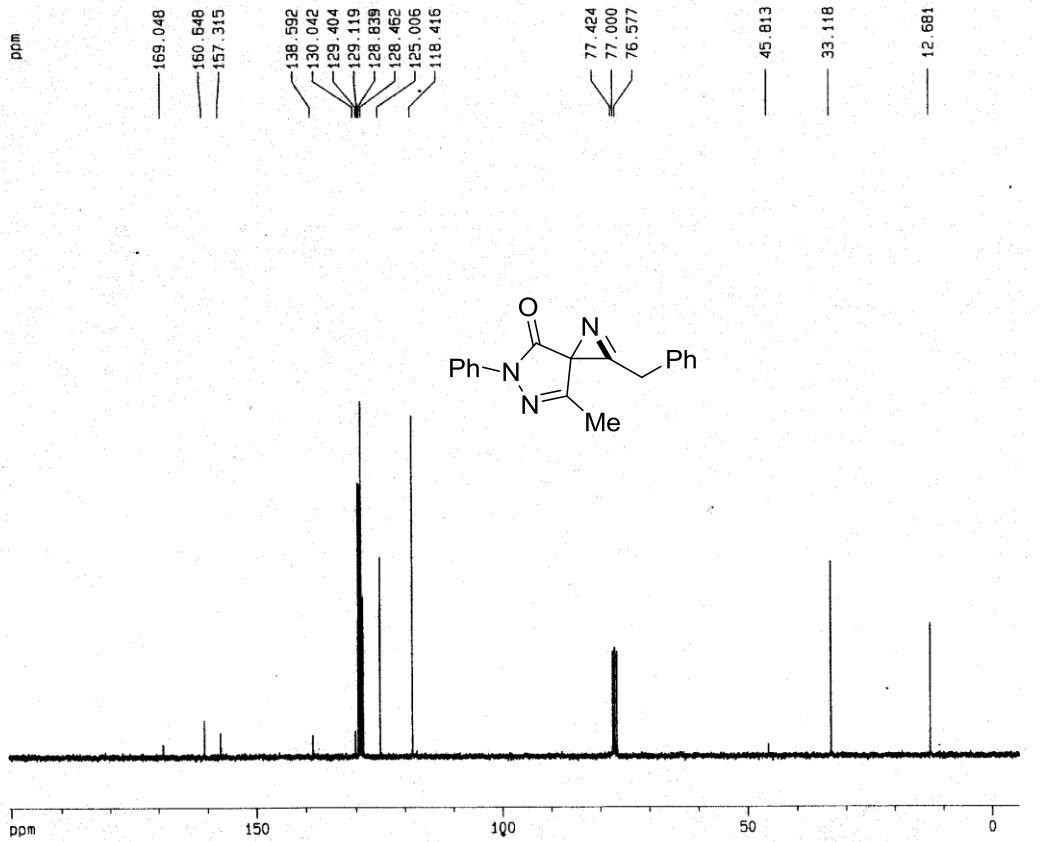
^{1}H NMR, ^{13}C NMR spectra of 3o



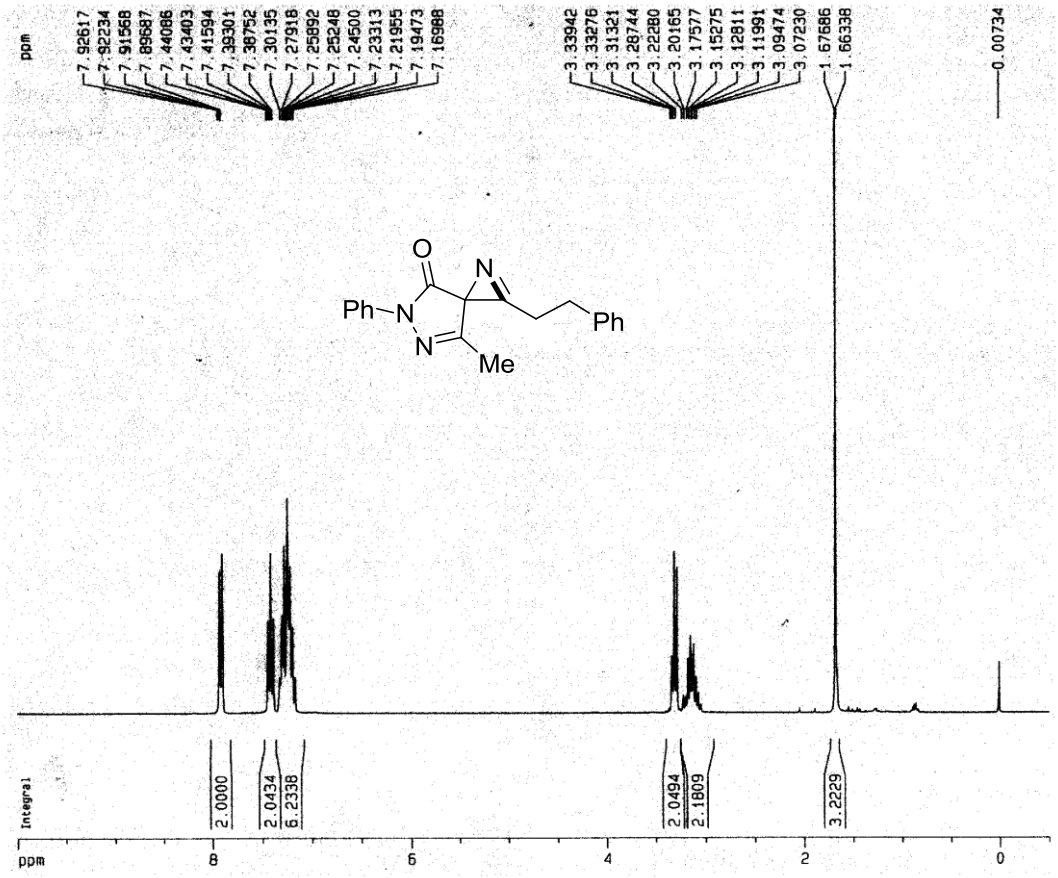


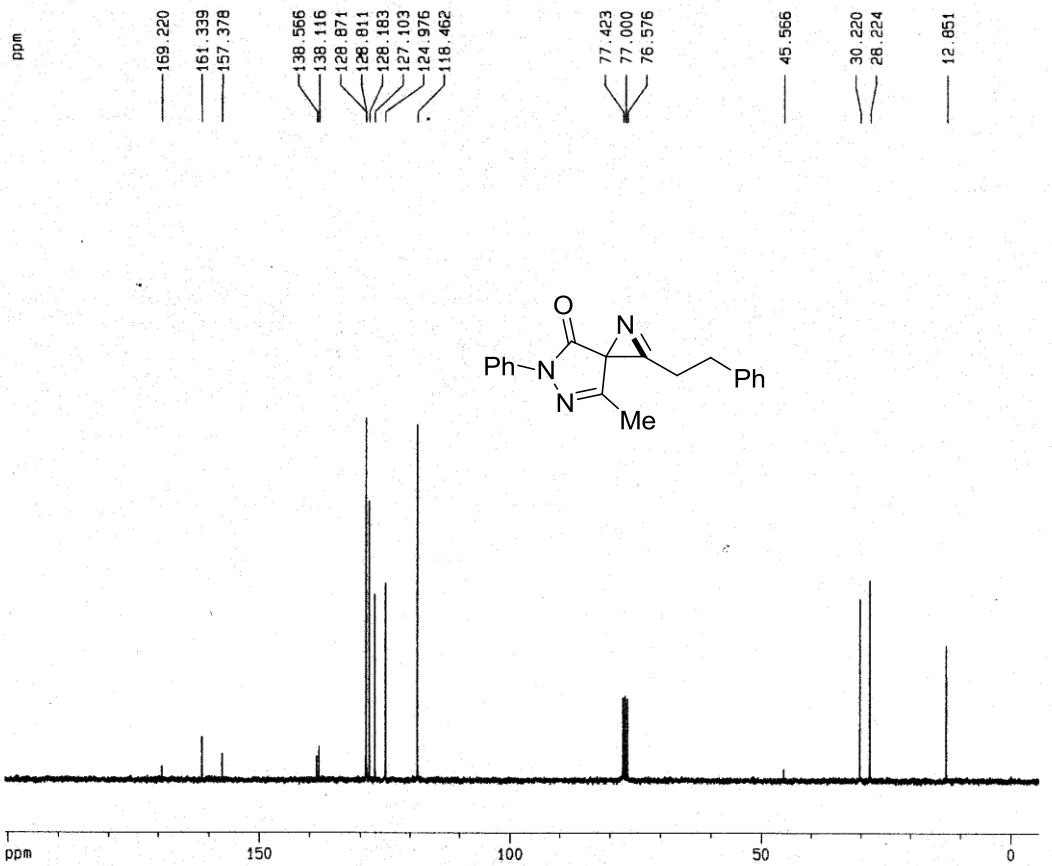
^{1}H NMR, ^{13}C NMR spectra of 3p



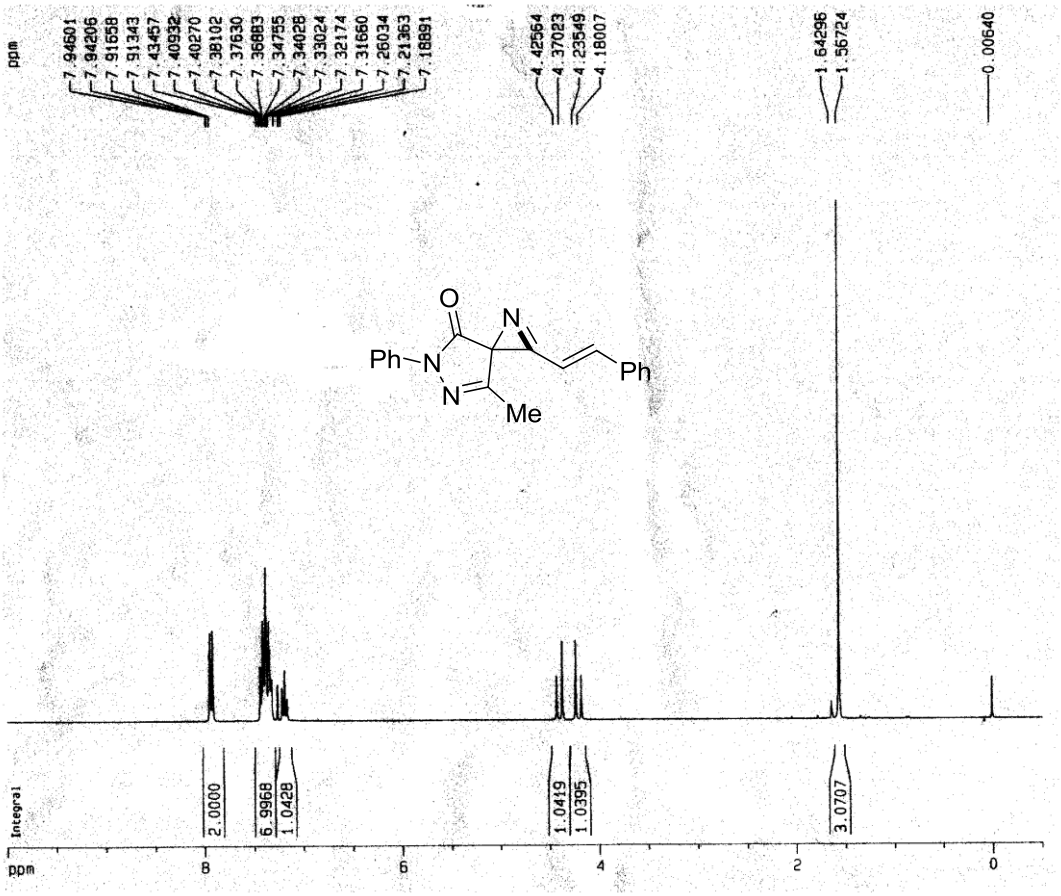


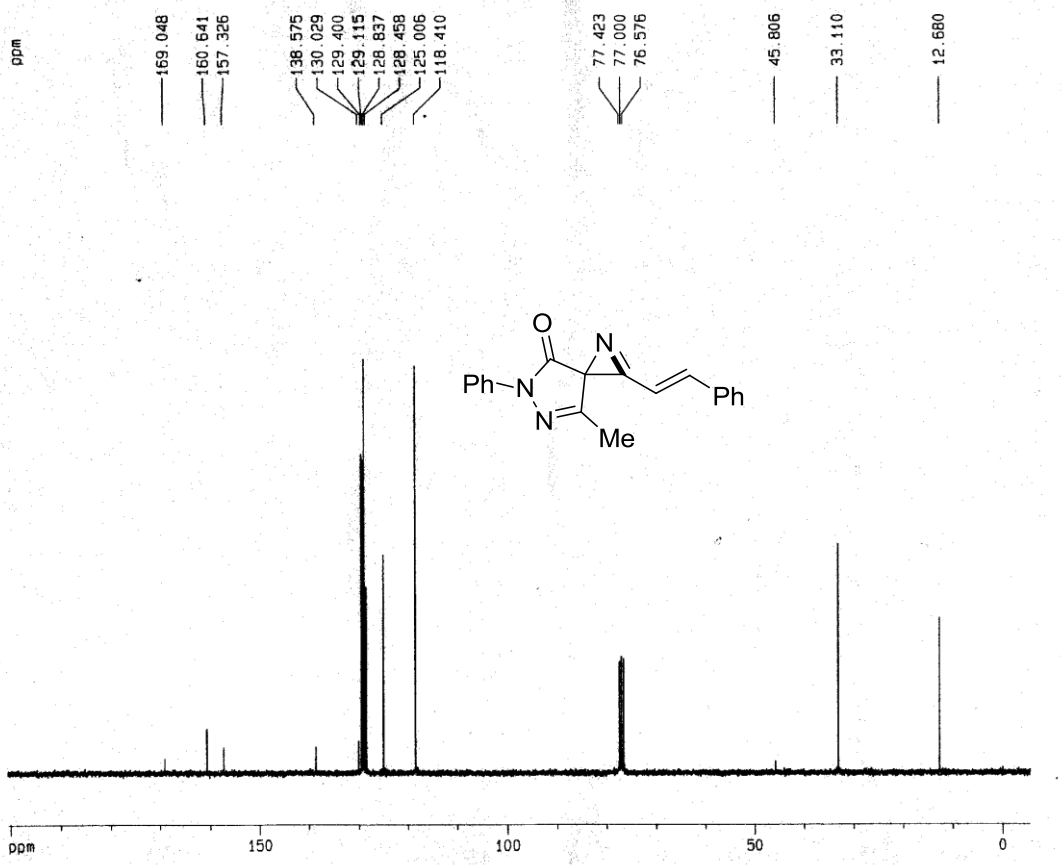
^{1}H NMR, ^{13}C NMR spectra of 3q



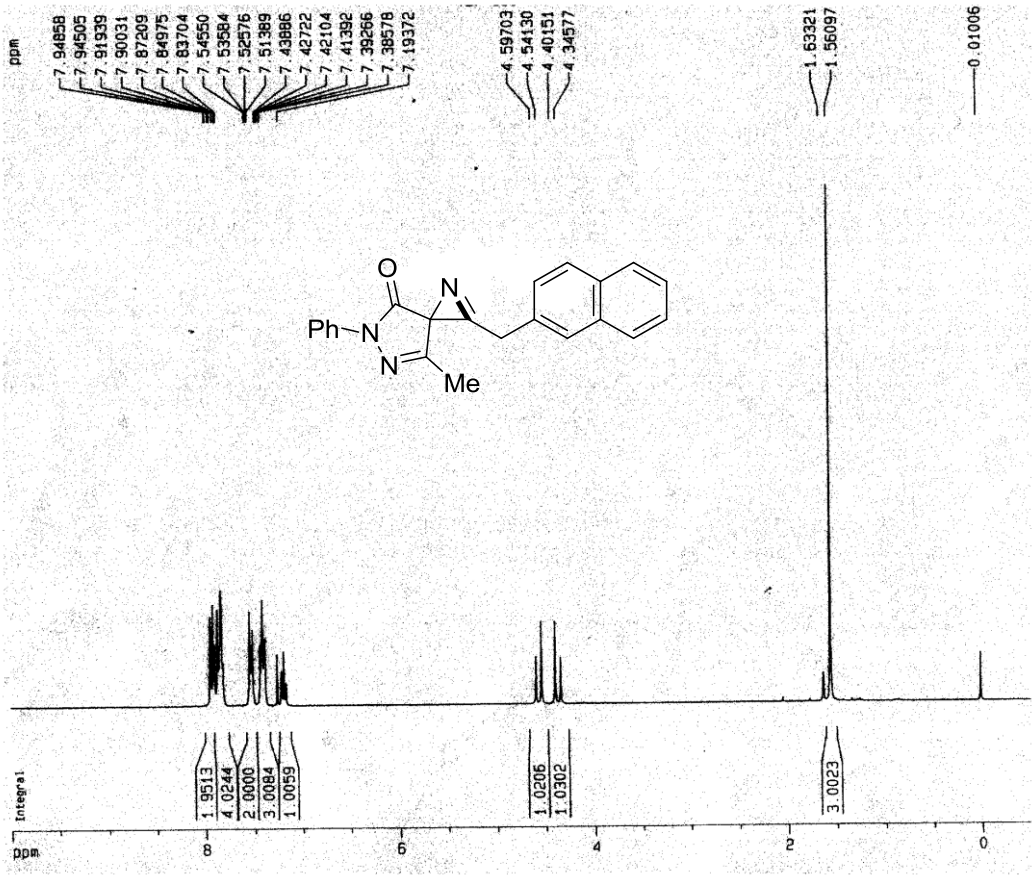


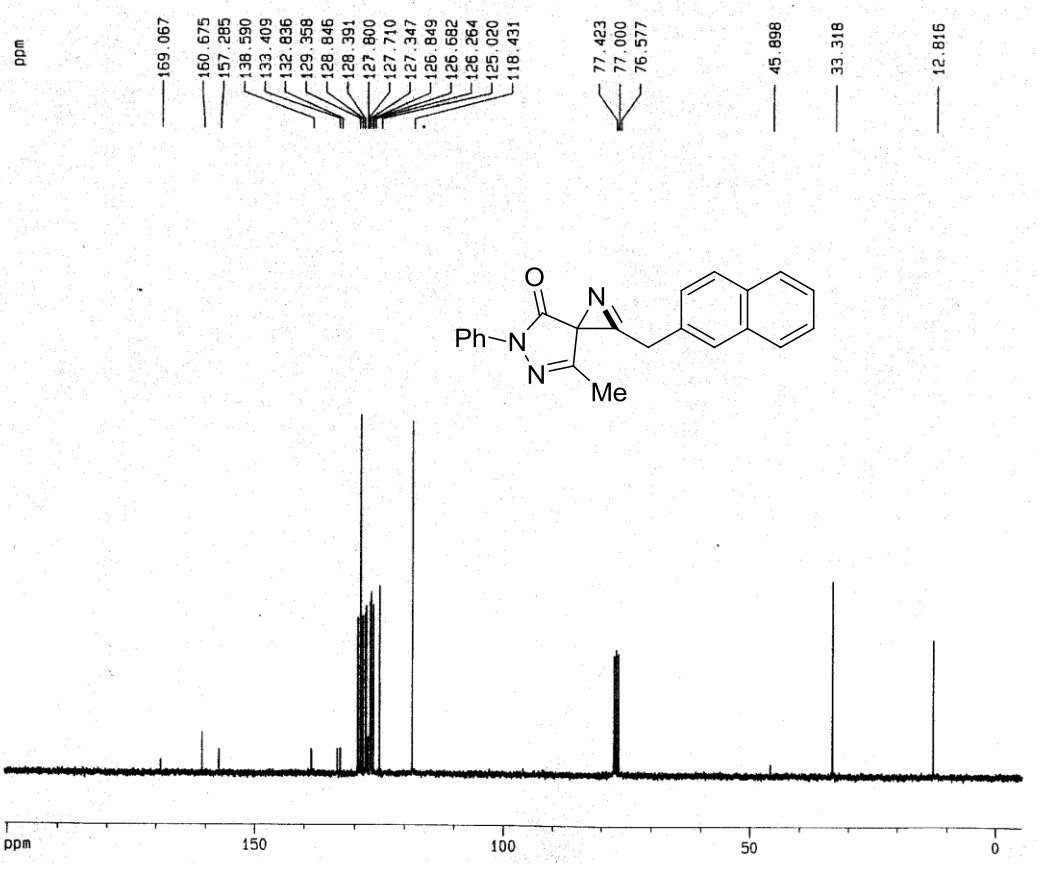
^{1}H NMR, ^{13}C NMR spectra of 3r



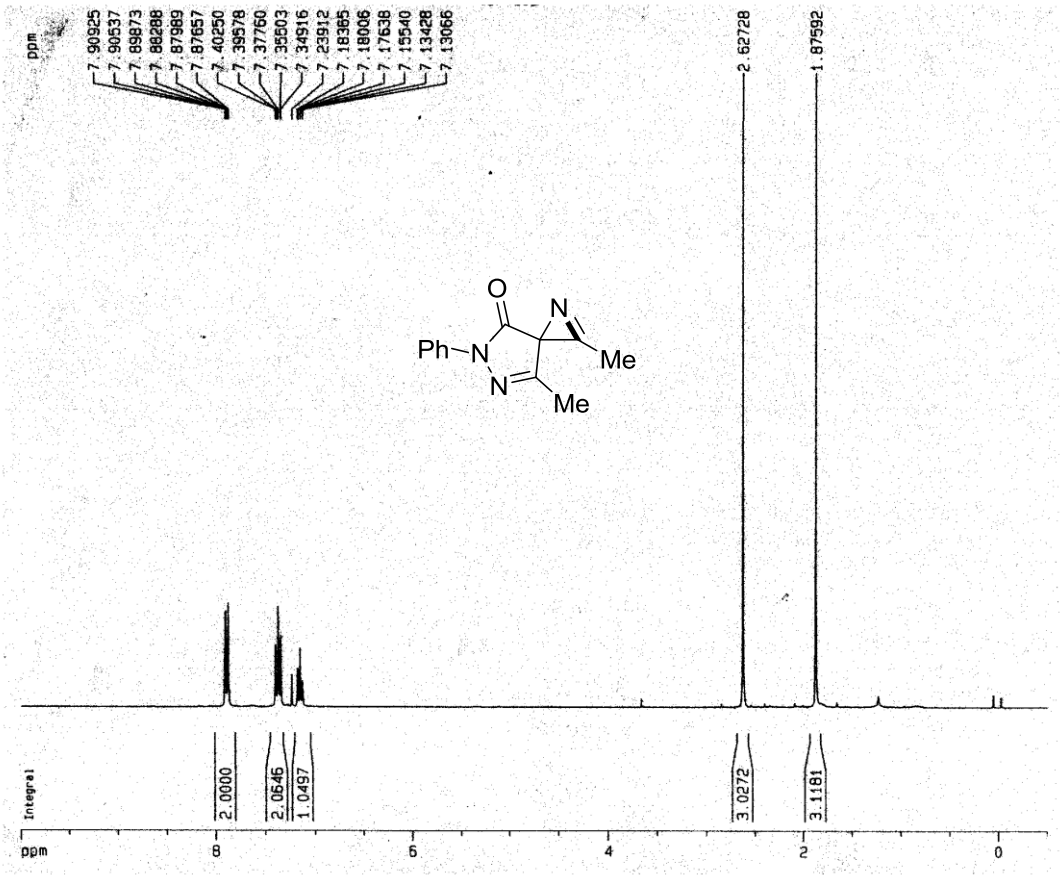


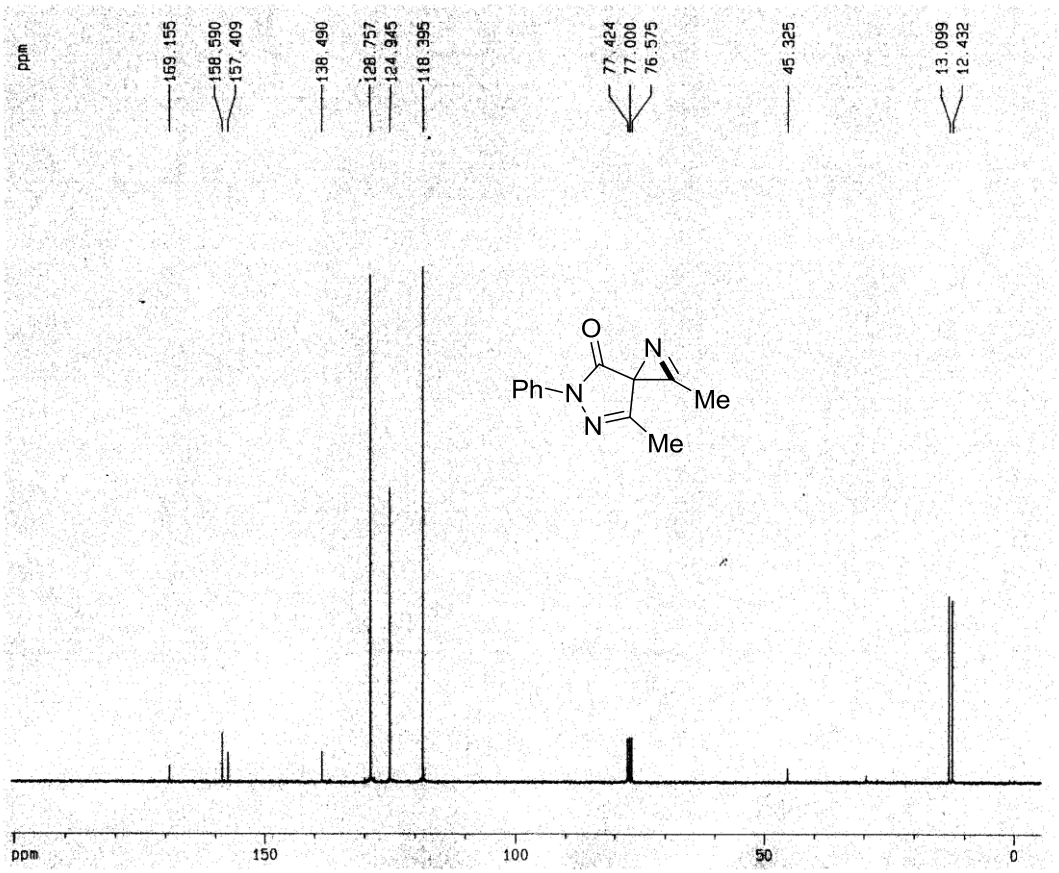
^{1}H NMR, ^{13}C NMR spectra of 3s



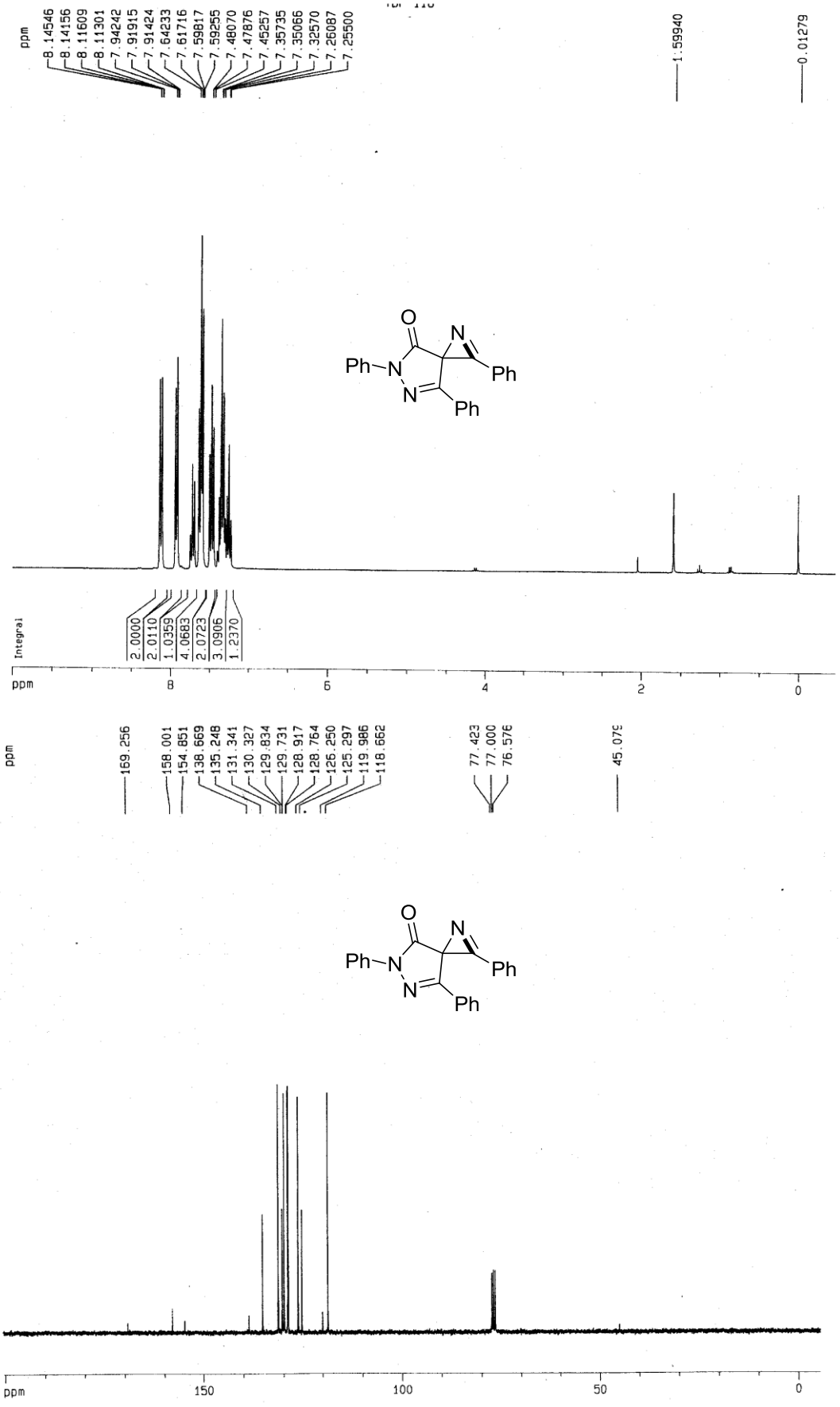


^{1}H NMR, ^{13}C NMR spectra of 3t

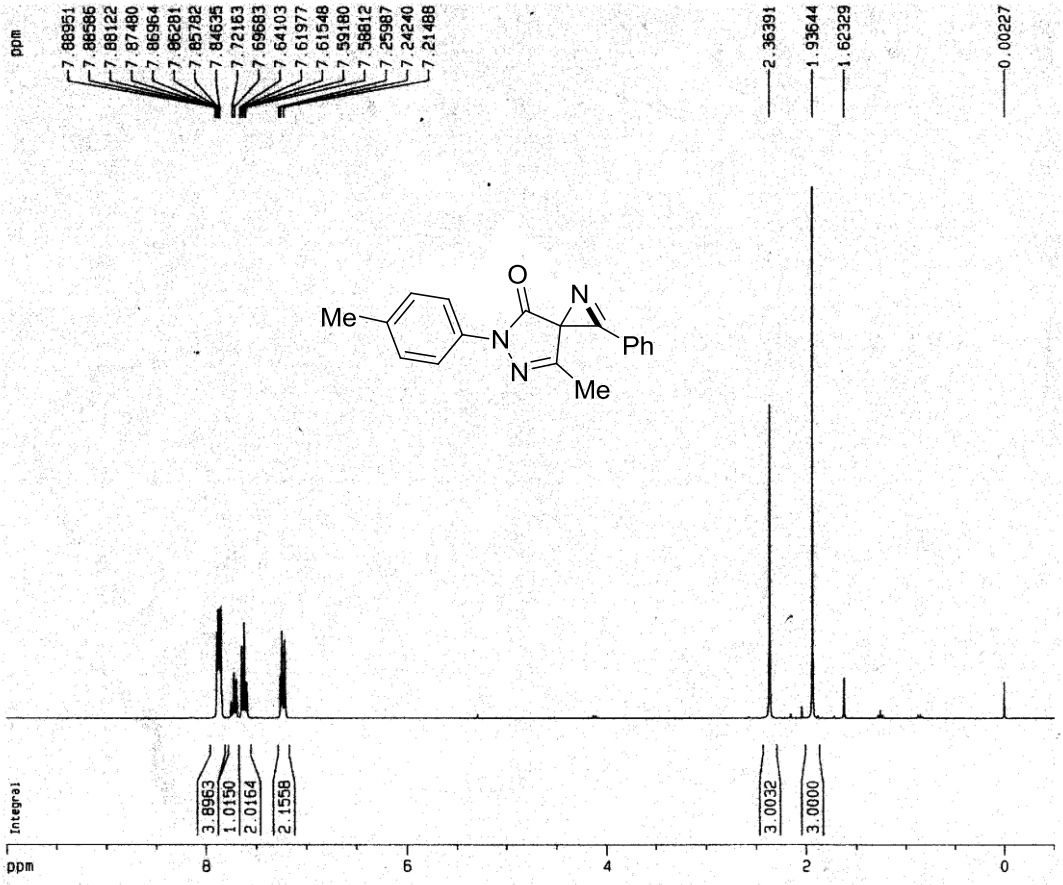


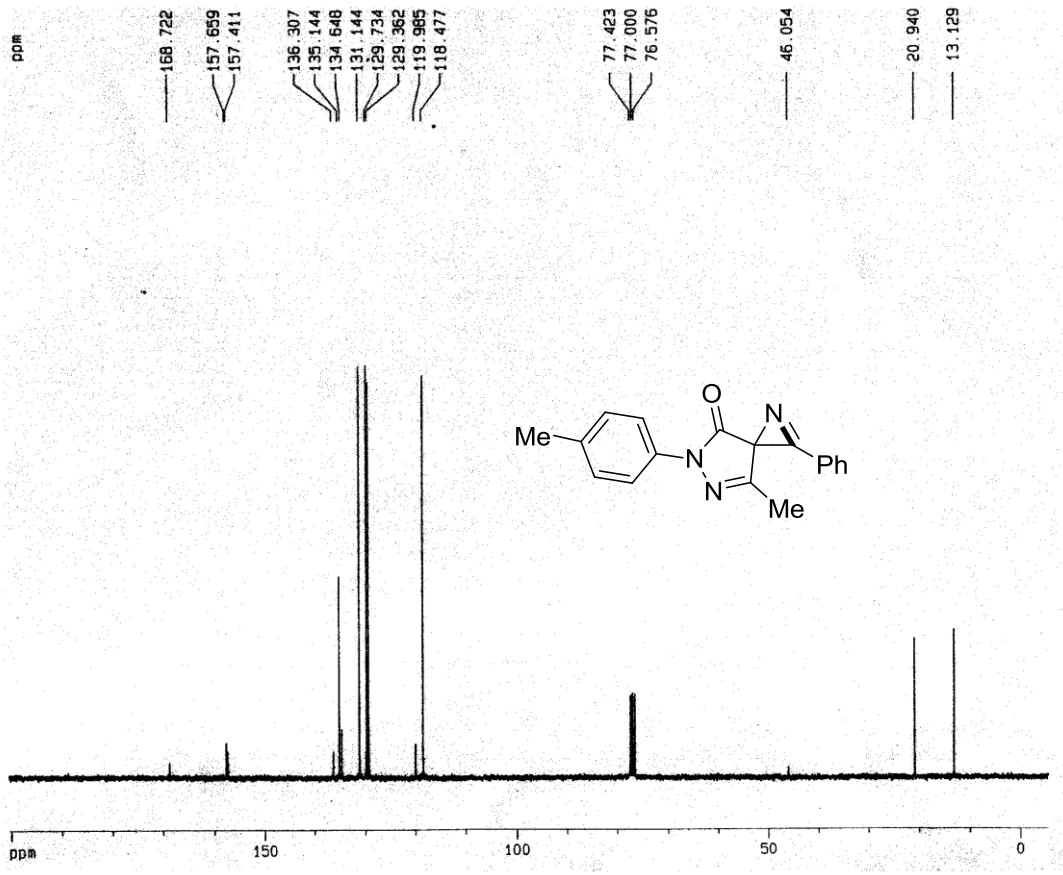


^{1}H NMR, ^{13}C NMR spectra of 3u

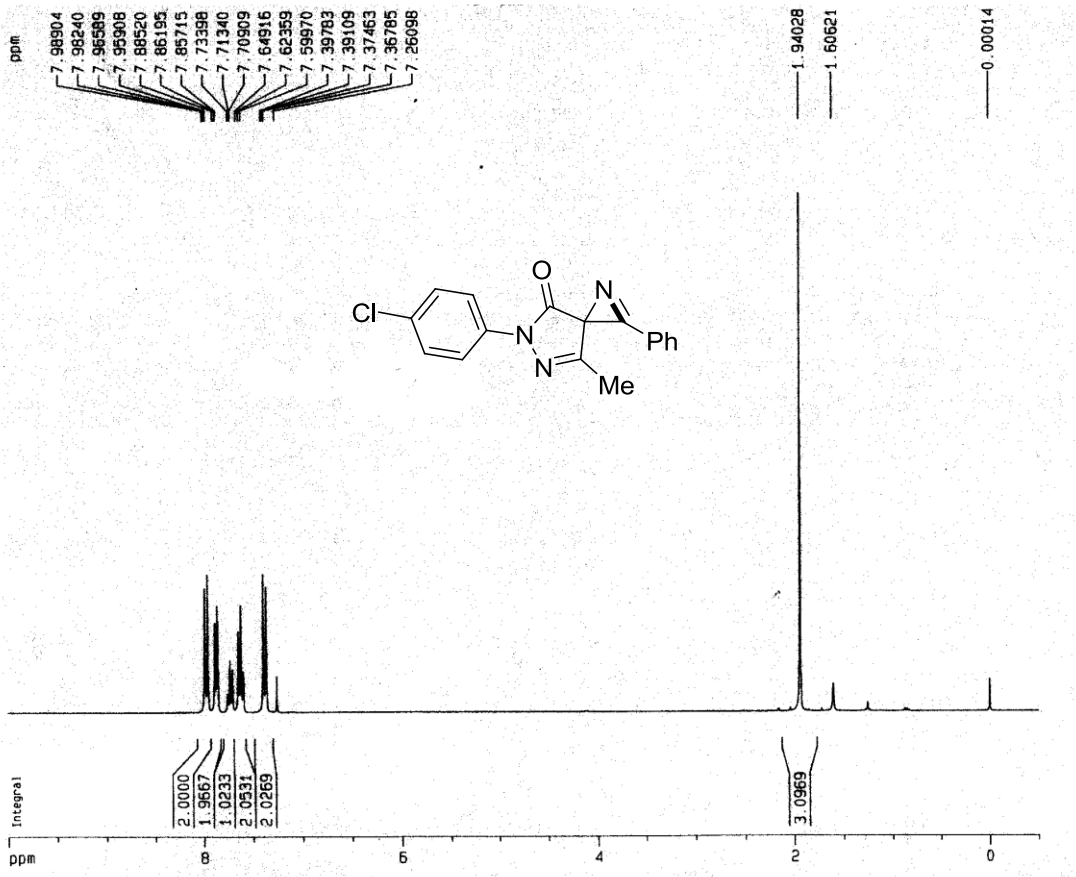


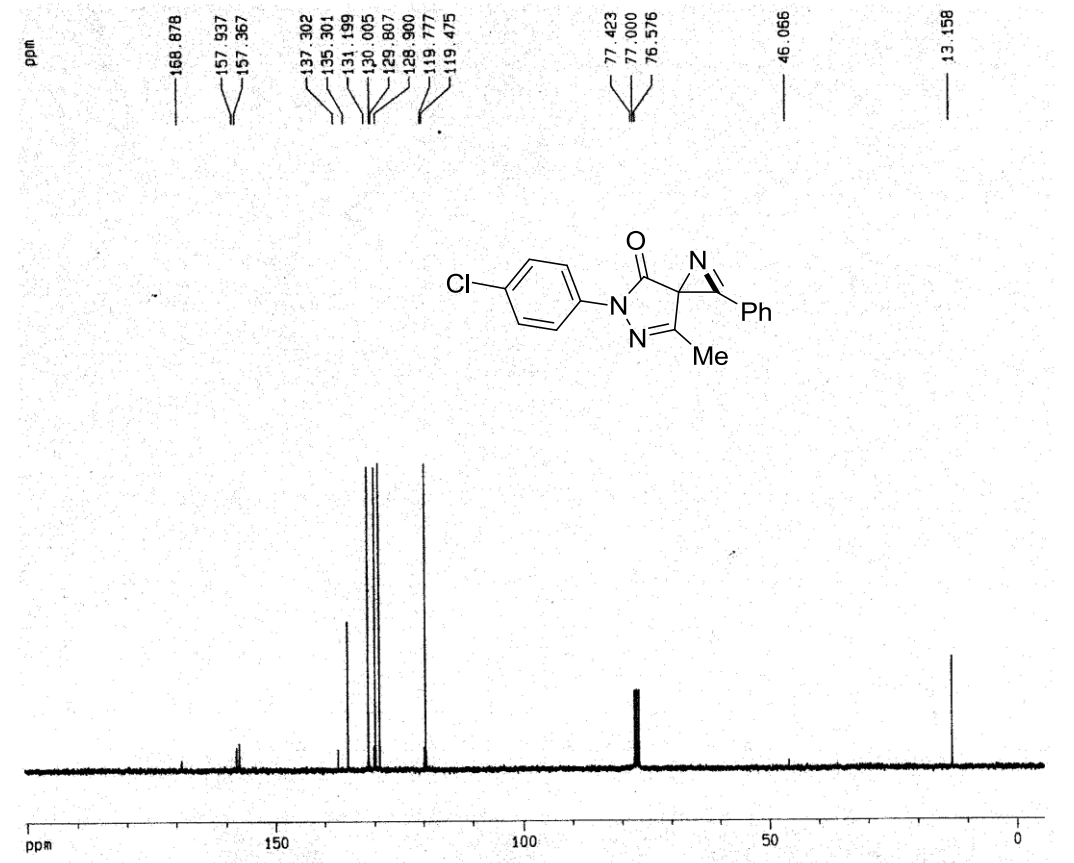
^{1}H NMR, ^{13}C NMR spectra of 3v



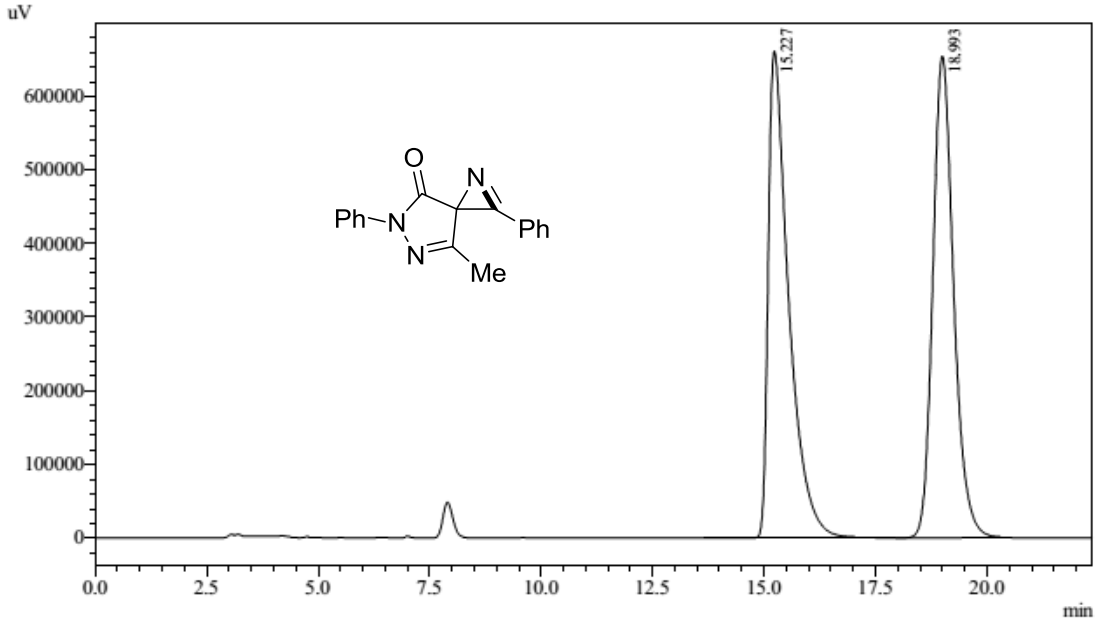


^{1}H NMR, ^{13}C NMR spectra of 3w





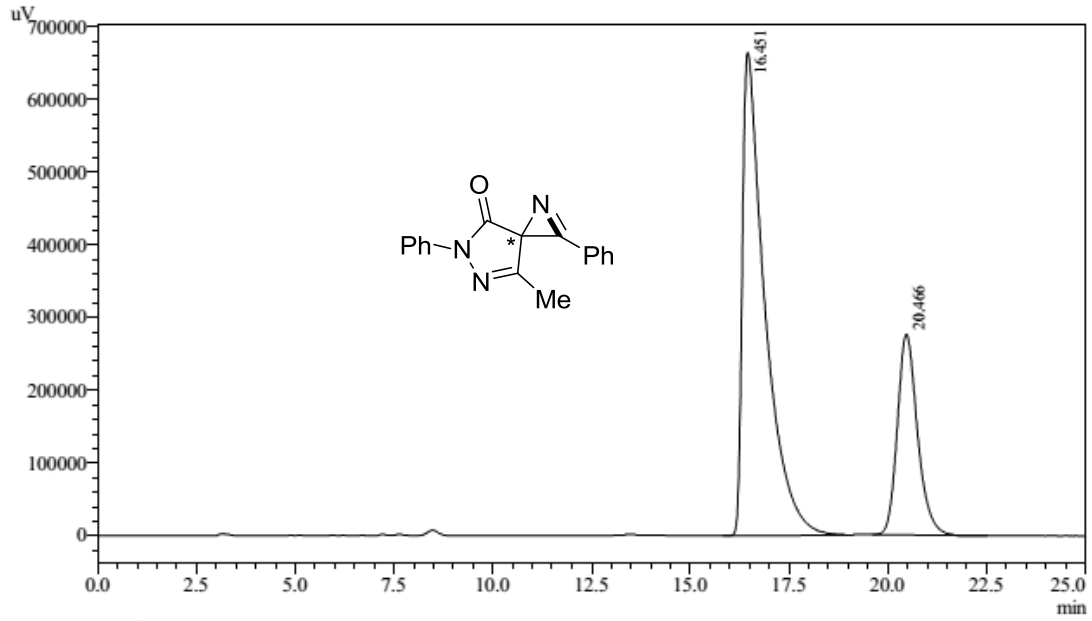
HPLC spectra for chiral compounds 3a



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.227	21156588	661181	49.927	50.260
2	18.993	21218340	654344	50.073	49.740
Total		42374928	1315525	100.000	100.000



1 Det.A Ch1 / 254nm

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	16.451	26401101	664734	72.952	70.686
2	20.466	9788475	275665	27.048	29.314
Total		36189576	940399	100.000	100.000