Supporting Information

Convenient synthesis of spiro-pyrazolone-pyrrolidinones via *ipso*-cyclization of arylidene pyrazolones with 2-chloro-*N*-phenylacetamides

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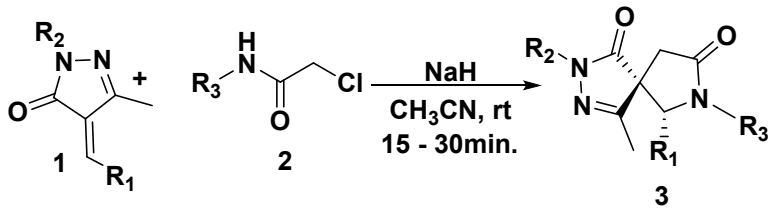
Material and Methods General Information

All reactions were carried out in oven-dried glassware and the compounds synthesized were fully characterized by spectroscopic data. The NMR spectra were recorded on JEOL - 400 spectrometers, (^{1}H-NMR 400 MHz, ^{13}C-NMR 100 MHz) and were referenced to the residual peaks of $CDCl_3$ at 7.26 ppm (^{1}H-NMR) and $CDCl_3$ at 77.23 ppm (^{13}C-NMR). Chemical shifts (δ) are expressed in ppm, and *J* values are given in Hz. Data are reported as follows: Chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (Hz), and integration. The reactions were monitored by thin layer chromatography (TLC) using silica gel GF254. The melting points (m.p.) were determined on the digital melting point apparatus and are uncorrected. Micromass Q-TOF mass spectrometer was used to record high-resolution mass spectra 60-70 eV in ESI mode. Materials unless otherwise indicated, all reagents were obtained from commercial suppliers used without further purification.

All the Arylidene pyrazolone and 2-chloro-*N*-phenylacetamide was synthesized using the procedure given in the literature.[1&2]

General Procedure for the preparation of spiro-pyrazolone-pyrrolidinones



To a solution of arylidene pyrazolone **1** (100 mg, 1 equiv., 0.381 mmol) in acetonitrile (3 mL), was added 2-chloro-*N*-phenylacetamide **2** (1 equiv., 0.342 mmol) and NaH (2.0 equiv. 0.684 mmol). The reaction mixture was stirred at room temperature for 15 minutes. The progress of the reaction was monitored by TLC. After the completion of the reaction, the mixture was quenched with water and the product was extracted with ethyl acetate. The combined organic layers were dried over sodium sulfate, concentrated under reduced pressure, and purified by column chromatography to afford the pure product **3** as a white solid.

References

1. R. Maity, C. Gharui, AK Sil, S.C. Pan*, Org. Lett.*, 2017, **19**, 3, 665.

2. S. C. Kim, B.M. Kwon, Synthesis, 1982, **9**, 795.

Table 1: Crystal data and structure refinement of 3j.

Identification code	KG -384
Empirical formula	$C_{25}H_{19}Cl_2N_3O_2$
CCDC Number	2361417
Formula weight	464.33
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P21/c
a/Å	13.15780(10)
b/Å	7.97410(10)
c/Å	20.9819(2)
α/°	90
β/°	91.0860(10)
γ/°	90
Volume/Å3	2201.06(4)
Z	4
ρcalcg/cm3	1.401
μ/mm 1	2.884
F(000)	960.0
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.72 to 144.092
Index ranges	-16 ≤ h ≤ 16, -7 ≤ k ≤ 9, -25 ≤ l ≤ 25
Reflections collected	24013
Independent reflections	4321 [Rint = 0.0306,
Data/restraints/parameters	4321/0/290
Goodness-of-fit on F2	1.068
Final R indexes [I>=2σ (I)]	R1 = 0.0358,

Sample preparation for crystal growth: Compound **3j** was dissolved in ethanol, while slow evaporation of solvent at room temperature needle-type crystals were grown.

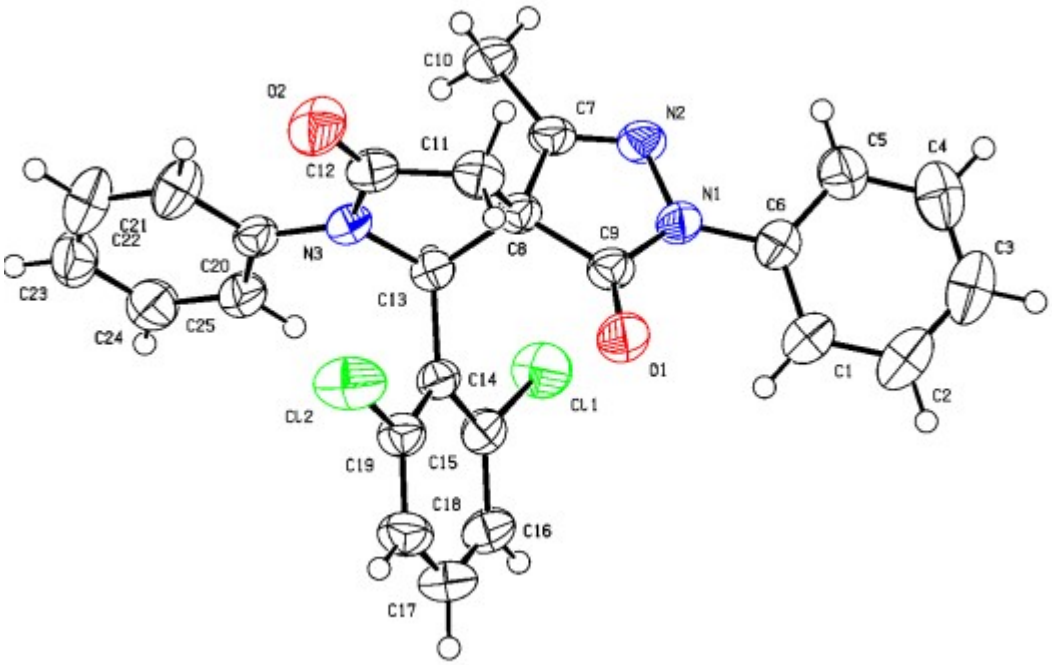
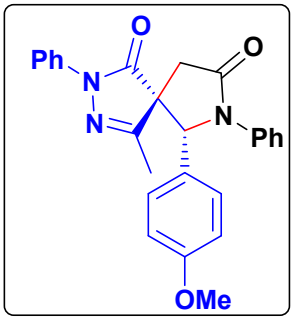


Figure 1: ORTEP diagram of compound of **3j** with 50% ellipsoid probability.

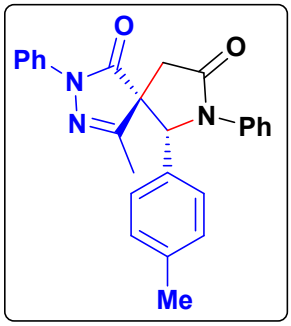
Analytical Data

(5*R*,6*S*)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-7-oxa-2,3-diazaspiro[4.4]non-3-en-1-one (3a) :



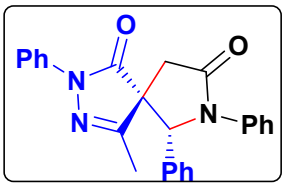
White solid; m.p. 168 - 170 °C; Yield – 76% (110 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.52 (s, 3H), 3.81 (s, 3H), 4.52 – 4.57 (m, 1H), 4.77 – 4.82 (m, 1H), 5.86 (s, 1H), 6.89 – 6.93 (m, 2H), 7.23 – 7.27 (m, 1H), 7.28 – 7.36 (m, 3H), 7.40 – 7.49 (m, 6H), 7.72 – 7.76 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 12.63, 55.37, 59.83, 71.86, 100.18, 114.43, 121.48, 125.77, 126.43, 127.27, 127.42, 128.98, 129.48, 134.46, 143.89, 146.19, 150.88, 159.29, 166.33; HRMS (ESI): m/z calcd for $C_{26}H_{23}N_3O_3$ [M+1] 426.1809 found 426.1812.

(5*R*,6*S*)-4-methyl-2,7-diphenyl-6-(p-tolyl)-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3b) :



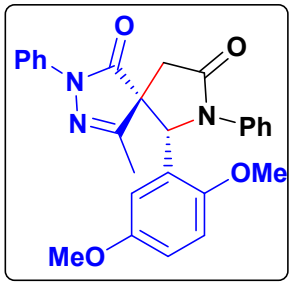
White solid; m.p. 198 - 200 °C; Yield – 71% (105 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1.82 (s, 3H), 2.24 (s, 3H), 2.86 – 2.92 (m, 1H), 3.10 – 3.16 (m, 1H), 5.65 (s, 1H), 6.91 – 7.03 (m, 4H), 7.11 – 7.25 (m, 2H), 7.27 – 7.44 (m, 6H), 7.81 – 7.85 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 15.26, 21.10, 37.21, 58.45, 68.57, 119.00, 122.95, 125.59, 125.86, 125.98, 128.86, 128.95, 129.60, 130.90, 137.26, 137.55, 138.68, 159.53, 170.67, 173.01; HRMS (ESI): m/z calcd for $C_{26}H_{23}N_3O_2$ [M+1] 410.1845 found 410.1849.

(5*R*,6*S*)-4-methyl-2,6,7-triphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3c) :



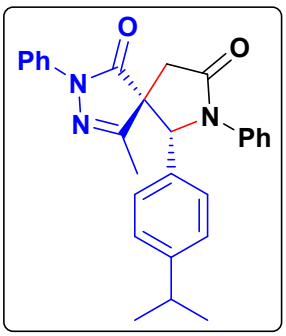
White solid; m.p. 162 - 164 °C; Yield – 64% (96 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.36 (s, 3H), 2.78 – 2.81 (m, 1H), 3.17 – 3.23 (m, 1H), 5.33 (s, 1H), 7.08 – 7.15 (m, 5H), 7.21 – 7.24 (m, 5H), 7.25 – 7.30 (m, 1H), 7.37 – 7.42 (m, 2H), 7.47 – 7.52 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 13.89, 29.68, 57.35, 67.38, 118.91, 122.36, 125.33, 125.80, 127.02, 128.68, 128.74, 128.96, 129.13, 137.12, 137.17, 139.61, 170.71, 188.87; HRMS (ESI): m/z calcd for $C_{25}H_{21}N_3O_2$ [M+1] 396.0976 found 396.0977.

(5*R*,6*S*)-6-(2,5-dimethoxyphenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3d) :



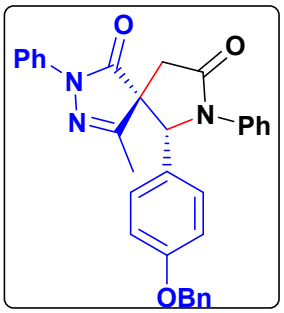
White solid; m.p. 153 - 155 °C; Yield – 65% (91 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1.59 (s, 3H), 2.90 – 2.96 (m, 1H), 3.04 – 3.11 (m, 1H), 3.48 (s, 3H), 3.55 (s, 3H), 6.02 (s, 1H), 6.62 – 6.64 (m, 1H), 6.66 – 6.74 (m, 2H), 7.11 – 7.22 (m, 2H), 7.29 – 7.35 (m, 2H), 7.38 – 7.44 (m, 2H), 7.46 – 7.50 (m, 2H), 7.92 – 7.96 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 14.84, 37.83, 55.35, 55.61, 56.23, 110.99, 113.88, 114.03, 118.27, 122.60, 124.01, 125.00, 125.78, 128.92, 128.95, 137.57, 137.95, 151.08, 153.13, 159.49, 170.65, 174.65; HRMS (ESI): m/z calcd for $C_{27}H_{25}N_3O_4$ [M+1] 456.1918 found 456.1923.

(5*R*,6*S*)-6-(4-isopropylphenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3e) :



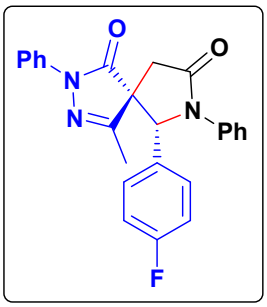
White solid; m.p. 168 - 170 °C; Yield – 64% (92 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1.14 – 1.16 (m, 6H), 1.71(s, 3H), 2.76 – 2.91 (m, 2H), 3.02 – 3.08 (m, 1H), 3.74 (s, 3H), 5.54 (s, 1H), 6.80 – 6.84 (m, 2H), 6.95 – 6.99 (m, 1H), 7.05 – 7.09 (m, 2H), 7.18 – 7.23 (m, 1H), 7.25 – 7.30 (m, 2H), 7.37 – 7.42 (m, 2H), 7.79 – 7.84 (m, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 15.07, 23.71, 33.65, 36.91, 55.37, 58.56, 68.90, 114.42, 119.03, 124.78, 125.55, 126.20, 126.97, 128.94, 130.20, 131.44, 137.52, 149.73, 157.47, 159.66, 170.79, 173.35; HRMS (ESI): m/z calcd for $C_{28}H_{27}N_3O_2$ [M+1] 438.1821 found 438.1822.

(5*R*,6*S*)-6-(4-(benzyloxy)phenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3f) :



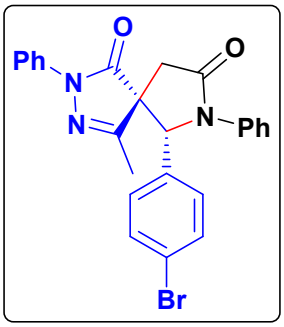
White solid; m.p. 213 - 215 °C; Yield – 67% (94 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.25 (s, 3H), 4.52 – 4.58 (m, 1H), 4.77 – 4.82 (m, 1H), 5.07 (s, 2H), 5.85 (s, 1H), 6.96 – 7.00 (m, 2H), 7.23 – 7.49 (m, 15H), 7.72 – 7.76 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 12.95, 29.39, 59.83, 70.13, 72.28, 76.68, 100.00, 105.98, 115.38, 121.50, 125.76, 127.27, 127.44, 128.11, 128.64, 128.98, 129.48, 134.73, 136.52, 138.17, 143.84, 146.24, 150.80, 158.49, 166.33; HRMS (ESI): m/z calcd for $C_{32}H_{27}N_3O_3$ [M+1] 502.0114 found 502.0116.

(5*R*,6*S*)-6-(4-fluorophenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3g) :



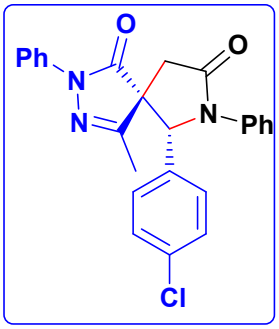
White solid; m.p. 183 - 185 °C; Yield – 56% (82 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.19 (s, 3H), 4.48 – 4.53 (m, 1H), 4.63 –4.68 (m, 1H), 5.13 (s, 1H), 6.98 – 7.06 (m, 2H), 7.18 – 7.28 (m, 4H), 7.32 – 7.44 (m, 6H), 7.64 – 7.69 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 17.42, 34.46, 64.46, 104.45, 120.78, 121.00, 126.30, 130.47, 131.33, 132.20, 132.70, 132.78, 133.79, 134.36, 148.53, 150.92, 170.91; HRMS (ESI): m/z calcd for $C_{25}H_{20}FN_3O_2$ [M+1] 414.1567 found 414.1569.

(5*R*,6*S*)-6-(4-bromophenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3h) :



White solid; m.p. 142 - 144 °C; Yield – 52% (72 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1.83 (s, 3H), 2.77 – 2.83 (m, 1H), 3.08 – 3.13 (m, 1H), 5.59 (s, 1H), 6.82 – 6.86 (m, 2H), 7.07 – 7.18 (m, 2H), 7.25 – 7.29 (m, 6H), 7.32 – 7.38 (m, 2H), 7.45 – 7.77 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 15.39, 29.57, 37.20, 58.52, 68.15, 118.92, 122.89, 125.57, 125.79, 126.12, 127.73, 129.02, 131.61, 131.78, 132.12, 159.19, 161.39, 170.60, 172.60; HRMS (ESI): m/z calcd for $C_{25}H_{20}BrN_3O_2$ [M+1] 474.0776 found 474.0778.

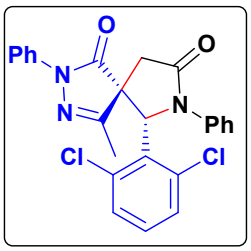
(5*R*,6*S*)-6-(4-chlorophenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3i) :



White solid; m.p. 205 - 207 °C; Yield – 51% (73 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.34 (s, 3H), 2.79 – 2.82 (m, 1H), 3.14 – 3.21 (m, 1H), 5.30 (s, 1H), 7.04 – 7.15 (m, 4H), 7.20 – 7.27 (m, 1H), 7.28 – 7.37 (m, 7H), 7.50 – 7.54 (m, 2H);

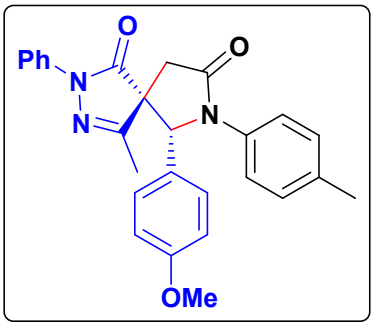
^{13}C-NMR (100 MHz, $CDCl_3$); δ = 14.11, 29.72, 36.39, 57.17, 66.62, 118.89, 122.38, 125.50, 126.01, 128.45, 128.84, 128.98, 129.07, 131.90, 135.03, 136.99, 137.75, 159.30, 170.56, ; HRMS (ESI): m/z calcd for $C_{25}H_{20}ClN_3O_2$ [M+1] 430.1276 found 430.1278.

(5*R*,6*R*)-6-(2,5-dichlorophenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3j) :



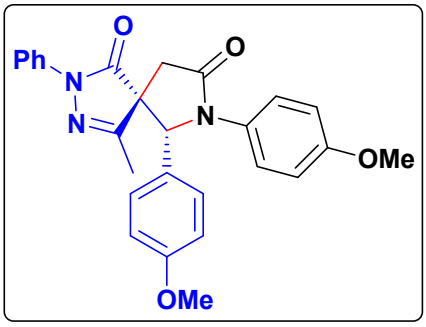
White solid; m.p. 236 - 238 °C; Yield – 61% (85 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.32 (s, 3H), 2.71 – 2.78 (m, 1H), 3.51 – 3.57 (m, 1H), 6.19 (s, 1H), 7.12 – 7.19 (m, 3H), 7.24 – 7.37 (m, 6H), 7.49 – 7.56 (m, 2H), 7.64 – 7.69 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 13.37, 39.71, 54.83, 62.72, 119.03, 120.61, 125.42, 125.80, 128.53, 128.82, 129.02, 129.14, 130.29, 130.84, 135.04, 135.60, 137.07, 137.46, 160.67, 169.41, 170.96; HRMS (ESI): m/z calcd for $C_{25}H_{19}Cl_2N_3O_2$ [M+1] 464.0918 found 464.0920.

(5*R*,6*S*)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-7-(p-tolyl)-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3m) :



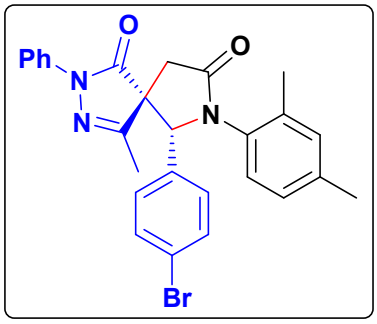
White solid; m.p. 198 - 200 °C; Yield – 68% (102 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1.85 (s, 3H), 2.27(s, 3H), 2.84 – 2.90 (m, 1H), 3.08 – 3.14 (m, 1H), 3.71 (s, 3H), 5.60 (s, 1H), 6.70 – 6.75 (m, 2H), 6.94 – 7.00 (m, 2H), 7.08 – 7.12 (m, 2H), 7.20 – 7.24 (m, 3H), 7.38 – 7.43 (m, 2H), 7.81 – 7.85(m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 12.61, 21.08, 29.68, 55.35, 59.90, 72.22, 99.95, 114.38, 121.45, 125.56, 126.39, 127.44, 128.97, 130.07, 134.48, 137.20, 138.07, 141.40, 150.88, 159.25, 166.36; HRMS (ESI): m/z calcd for $C_{27}H_{25}N_3O_3$ [M+1] 440.1921 found 440.1922.

(5*R*,6*S*)-6,7-bis(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3n) :



White solid; m.p. 176 - 178 °C; Yield – 71% (110 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.23 (s, 3H), 3.80 – 3.84 (m, 6H), 4.52 – 4.87 (m, 1H), 4.76 – 4.81 (m, 1H), 5.79 (s, 1H), 6.90 – 6.99 (m, 4H), 7.23 – 7.26 (m, 1H), 7.26 – 7.35 (m, 4H), 7.40 – 7.46 (m, 2H), 7.72 – 7.76 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 17.43, 60.16, 60.32, 64.92, 77.00, 104.80, 119.20, 119.46, 126.26, 131.20, 131.78, 132.25, 133.78, 139.23, 141.69, 142.89, 151.06, 155.68, 163.18, 164.07, 171.27; HRMS (ESI): m/z calcd for $C_{27}H_{25}N_3O_4$ [M+1] 455.1852 found 455.1856.

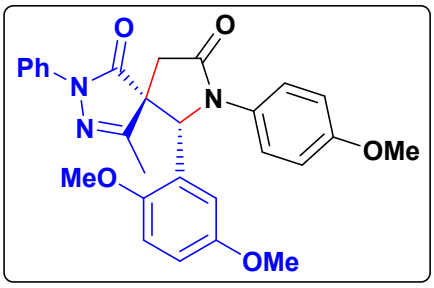
(5*R*,6*S*)-6-(4-bromophenyl)-7-(2,5-dimethylphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3o) :



White solid; m.p. 137 - 139 °C; Yield – 59% (86 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1.84 (s, 3H), 2.24(s, 3H), 2.27 (s, 2H), 2.84 – 2.90 (m, 1H), 3.08 – 3.15 (m, 1H), 5.62 (s, 1H), 6.91 – 6.95 (m, 2H), 6.98 – 7.02 (m, 2H), 7.08 – 7.12 (m, 2H), 7.20 – 7.25 (m, 2H), 7.38 – 7.44 (m, 2H), 7.80 – 7.85 (m, 2H) ; ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 15.25, 20.85, 29.66, 37.19, 58.73, 68064, 119.01, 122.92, 125.56, 126.04, 128.94, 129.48, 129.56, 130.90, 134.36, 134.46, 134.57, 135.72, 137.48,

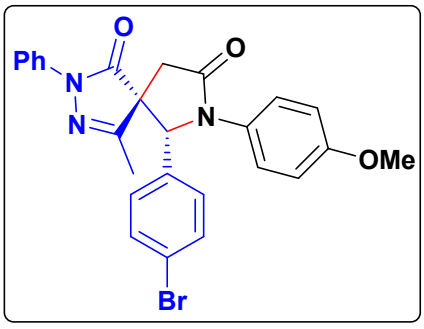
138.69, 159.75, 170.72, 173.10; HRMS (ESI): m/z calcd for $C_{27}H_{24}BrN_3O_2$ [M+1] 503.1021 found 503.1022.

(5*R*,6*S*)-6-(2,5-dimethoxyphenyl)-7-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3p) :



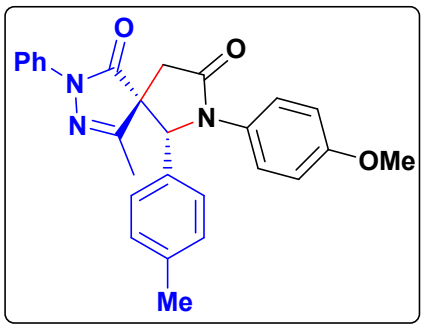
White solid; m.p. 189- 191 °C; Yield – 68% (102 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.81 – 2.87 (m, 1H), 2.94 – 3.01 (m, 1H), 3.41 (s, 3H), 3.53 (s, 3H), 3.69 (s, 3H), 5.87 (s, 1H), 6.60 – 6.68 (m, 2H), 6.77 – 6.80 (m, 2H), 7.00 – 7.20 (m, 1H), 7.31 – 7.37 (m, 5H), 7.85 – 7.89 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 14.83, 29.67, 37.60, 55.34, 55.38, 55.64, 56.32, 110.96, 113.75, 114.24, 118.32, 124.11, 124.16, 124.41, 125.13, 128.93, 130.51, 137.83, 151.18, 153.23, 157.62, 159.65, 170.80, 174.75; HRMS (ESI): m/z calcd for $C_{27}H_{25}N_3O_4$ [M+1] 456.1918 found 456.1923.

(5*R*,6*S*)-6-(4-bromophenyl)-7-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3q) :



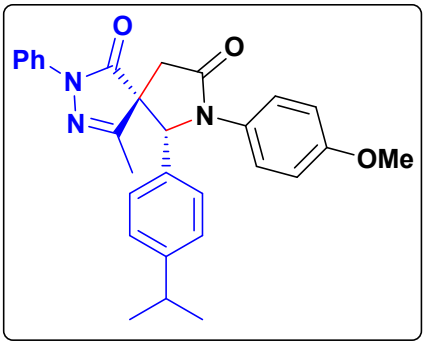
White solid; m.p. 196 - 198 °C; Yield – 64% (110 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.30 (s, 3H), 2.71 – 2.77 (m, 1H), 3.08 – 3.14 (m, 1H), 3.69 (s, 3H), 5.15 (s, 1H), 6.73 – 6.77 (m, 2H), 6.92 – 6.97 (m, 2H), 7.05 – 7.11 (m, 1H), 7.21 – 7.35 (m, 6H), 7.44 – 7.48 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 14.07, 29.68, 36.36, 56.38, 67.03, 114.43, 118.91, 123.23, 124.25, 125.50, 128.88, 131.85, 132.49, 133.57, 134.59, 135.60, 137.08, 157.38, 159.54; HRMS (ESI): m/z calcd for $C_{26}H_{22}BrN_3O_3$ [M+1] 504.0356 found 504.0359.

(5*R*,6*S*)-7-(4-methoxyphenyl)-4-methyl-2-phenyl-6-(p-tolyl)-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3r) :



White solid; m.p. 133 - 135 °C; Yield – 78% (124 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 2.22 (s, 3H), 2.83 – 2.89 (m, 1H), 3.04 – 3.09 (m, 1H), 3.71 (s, 3H), 5.55 (s, 1H), 6.80 – 6.82 (m, 2H), 6.90 – 7.01 (m, 4H), 7.16 – 7.27 (m, 3H), 7.35 – 7.41 (m, 2H), 7.80 – 7.84 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 15.18, 21.05, 36.93, 55.29, 58.65, 68.80, 114.12, 118.93, 124.61, 125.49, 126.09, 128.89, 129.53, 130.02, 130.88, 137.42, 138.69, 157.40, 159.65, 170.74, 173.12; HRMS (ESI): m/z calcd for $C_{27}H_{25}N_3O_3$ [M+1] 440.1986 found 440.1989.

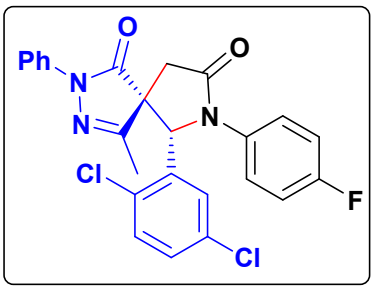
(5*R*,6*S*)-6-(4-isopropylphenyl)-7-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3s) :



White solid; m.p. 216 - 218 °C; Yield – 71% (109 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1.15 – 1.16 (m, 6H), 2.76 – 2.87 (m, 1H), 2.87 – 2.94 (m, 1H), 3.07 – 3.13 (m, 1H), 5.63 (s, 1H), 6.95 – 6.99 (m, 2H), 7.05 – 7.09 (m, 2H), 7.12 – 7.25 (m, 2H), 7.28 – 7.44 (m, 6H), 7.80 – 7.84 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 15.11, 23.75, 29.68, 33.62, 37.22, 58.57, 68.62, 119.02, 123.00, 125.58,

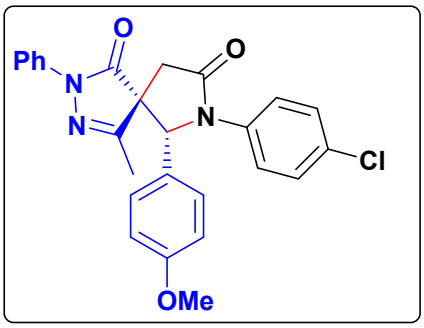
125.87, 126.03, 126.99, 128.88, 128.95, 131.22, 131.86, 137.21, 137.46, 149.70, 170.75, 173.18 HRMS (ESI): m/z calcd for $C_{29}H_{29}N_3O_3$ [M+1] 468.2209 found 468.2212.

(5*R*,6*R*)-6-(2,5-dichlorophenyl)-7-(4-fluorophenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3t) :



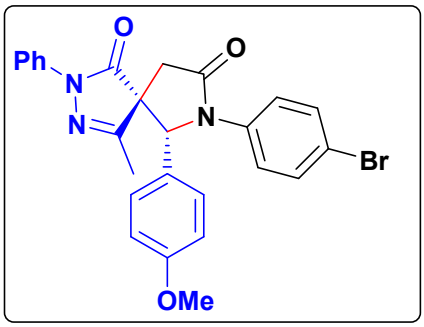
White solid; m.p. 133 - 135 °C; Yield – 48% (70 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1.59 (s, 3H), 2.84 – 2.91 (m, 1H), 3.24 – 3.30 (m, 1H), .31 (s, 1H), 6.96 – 7.02 (m, 2H), 7.20 – 7.27 (m, 5H), 7.27 – 7.32 (m, 1H), 7.34 – 7.38 (m, 1H), 7.40 – 7.46 (m, 2H), 7.49 – 7.54 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 13.34, 39.49, 54.68, 62.85, 115.88, 116.10, 119.02, 122.53, 122.61, 125.47, 128.60, 128.83, 130.44, 130.48, 135.07, 135.55, 137.38, 160.41, 161.30, 169.33, 170.89; HRMS (ESI): m/z calcd for $C_{25}H_{18}Cl_2FN_3O_2$ [M+1] 482.0833 found 482.0836.

(5*R*,6*S*)-7-(4-chlorophenyl)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3u) :



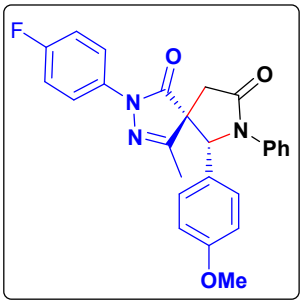
White solid; m.p. 240 - 242 °C; Yield- 4 6 % (72 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1.81 (s, 3H), 2.85 – 2.91 (m, 1H), 3.07 – 3.13 (m, 1H), 3.72 (s, 3H), 5056 (s, 1H), 6.71 – 6.75 (m, 2H), 6.91 – 6.95(m, 2H), 7.18 – 7.24 (m, 2H), 7.25 – 7.32 (m, 4H), 7.37 – 7.43 (m, 2H), 7.79 – 7.84 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 15.28, 29.68, 37.06, 55.20, 68.26, 114.44, 118.95, 124.31, 125.10, 125.64, 127.30, 128.97, 131.52, 131.92, 136.02, 137.52, 159.44, 159.88, 170.64, 172.90; HRMS (ESI): m/z calcd for $C_{26}H_{22}ClN_3O_3$ [M+1] 460.1463 found 460.1464.

(5*R*,6*S*)-7-(4-bromophenyl)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3v) :



White solid; m.p. 163 - 165 °C; Yield – 51% (87 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 1.76 (s, 3H), 2.79 – 2.85 (m, 1H), 3.01 – 3.08 (m, 1H), 3.66 (s, 1H), 6.85 – 6.89 (m, 2H), 7.12 – 7.18 (m, 5H), 7.31 – 7.37 (m, 4H), 7.74 – 7.78 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 15.28, 29.68, 37.06, 55.20, 68.26, 114.44, 118.95, 124.31, 125.10, 125.64, 127.30, 128.97, 131.52, 131.92, 136.02, 137.52, 159.44, 159.88, 170.64, 172.90; HRMS (ESI): m/z calcd for $C_{26}H_{22}BrN_3O_3$ [M+1] 504.1632 found 504.1635.

(5*R*,6*S*)-2-(4-fluorophenyl)-6-(4-methoxyphenyl)-4-methyl-7-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3w):



White solid; m.p. 227 - 229 °C; Yield – 64% (91 mg); ^{1}H-NMR (400 MHz, $CDCl_3$); δ = 3.81 (s, 3H), 4.52 – 4.57 (m, 1H), 4.77 – 4.83 (m, 1H), 5.85 (s, 3H), 6.90 – 6.94 (m, 2H), 7.10 – 7.15 (m, 2H), 7.23 – 7.25 (m, 2H), 7.31 – 7.36 (m, 1H), 7.40 – 7.49 (m, 4H), 7.67 – 7.74 (m, 2H); ^{13}C-NMR (100 MHz, $CDCl_3$); δ = 17.34, 34.41, 60.10, 64.50, 77.00, 104.76, 119.16, 120.41, 120.64, 128.05, 130.46, 132.11, 134.23, 139.07, 148.55, 151.03, 155.43, 164.02, 164.41, 166.86, 170.95; HRMS (ESI): m/z calcd for $C_{26}H_{22}FN_3O_3$ [M+1] 444.1718 found 444.1720.

Spectral data:

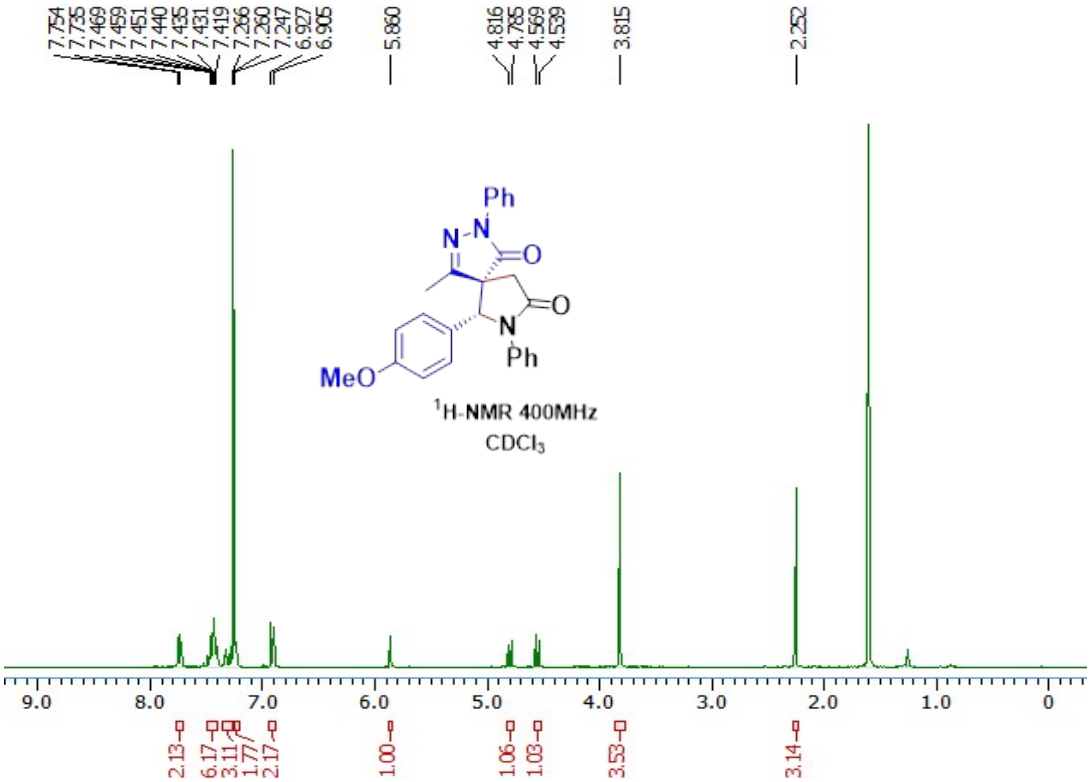


Fig. 2: ^{1}H-NMR spectrum of (5*R*,6*R*)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-7-oxa-2,3-diazaspiro[4.4]non-3-en-1-one (3a)

Fig. 3: ^{13}C-NMR spectrum of (5*R*,6*R*)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-7-oxa-2,3-diazaspiro[4.4]non-3-en-1-one (3a)

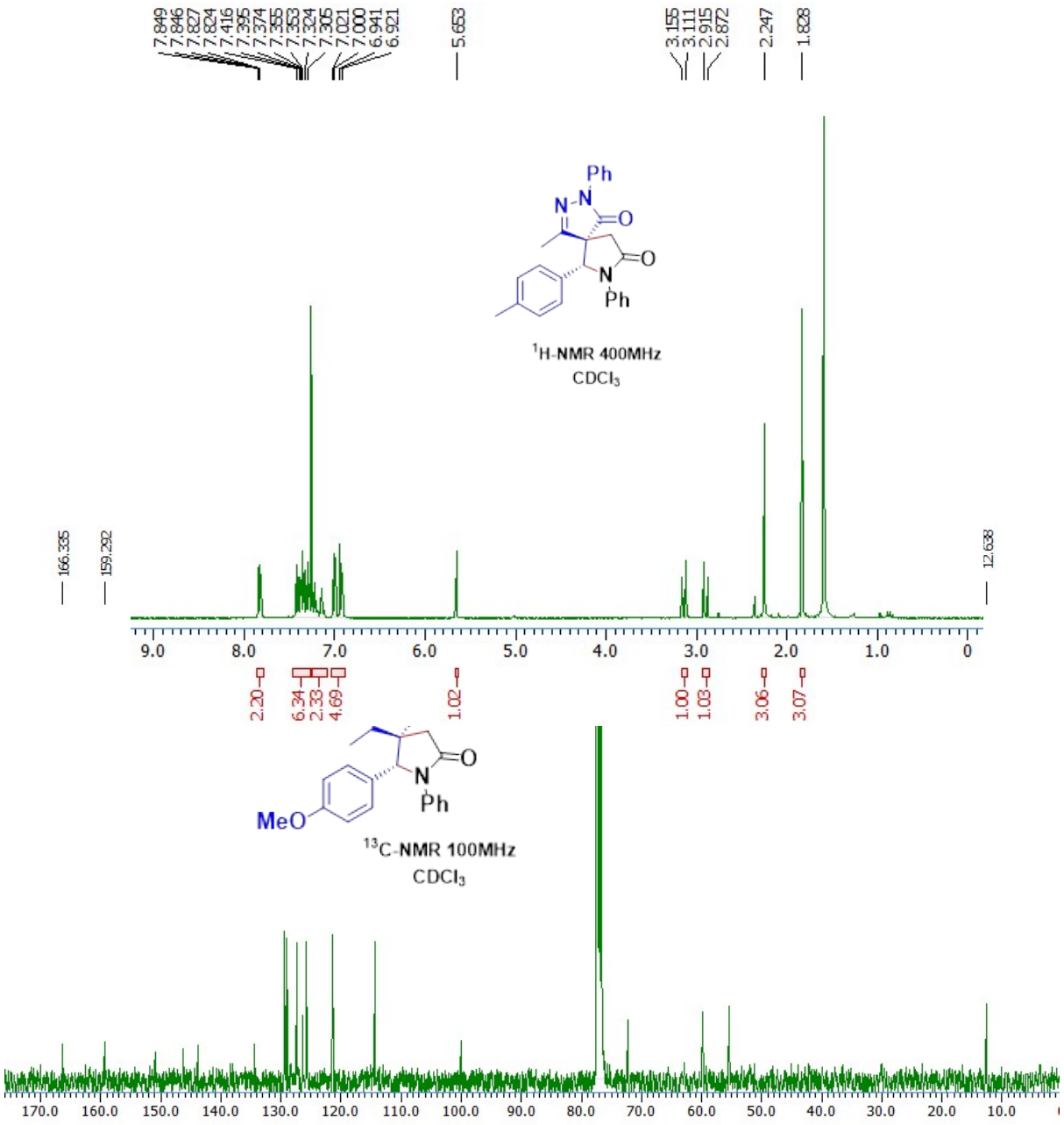


Fig. 4: ^{1}H-NMR spectrum of (5*R*,6*R*)-4-methyl-2,7-diphenyl-6-(p-tolyl)-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3b)

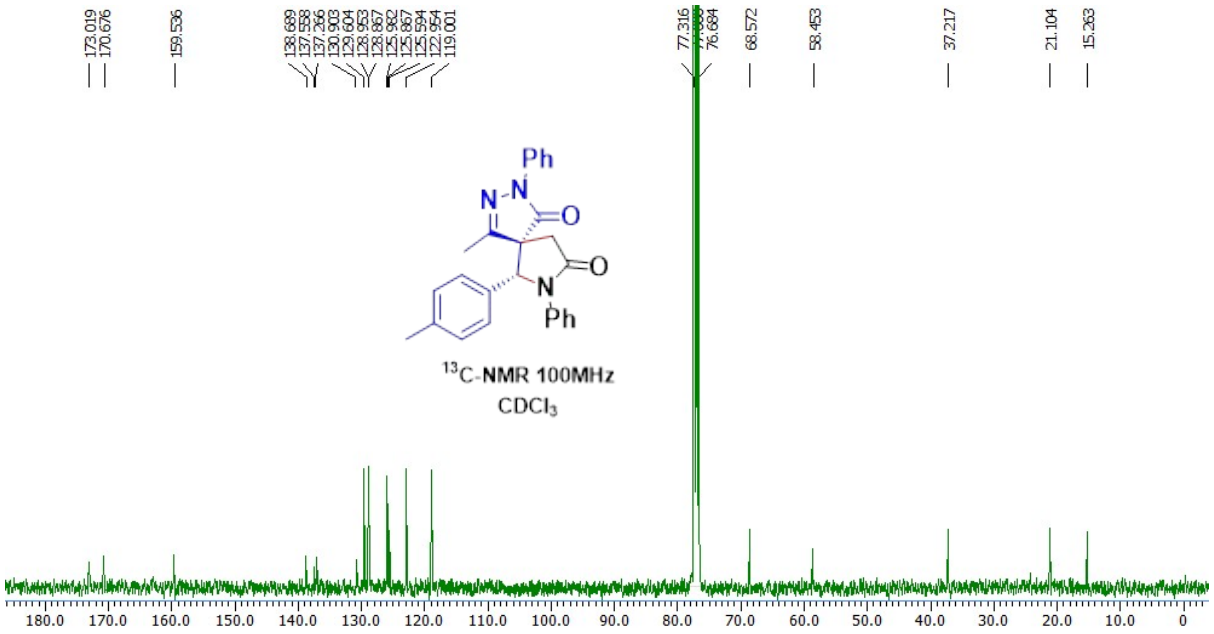


Fig. 5: ^{1}H-NMR spectrum of (5*R*,6*R*)-4-methyl-2,7-diphenyl-6-(p-tolyl)-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3b)

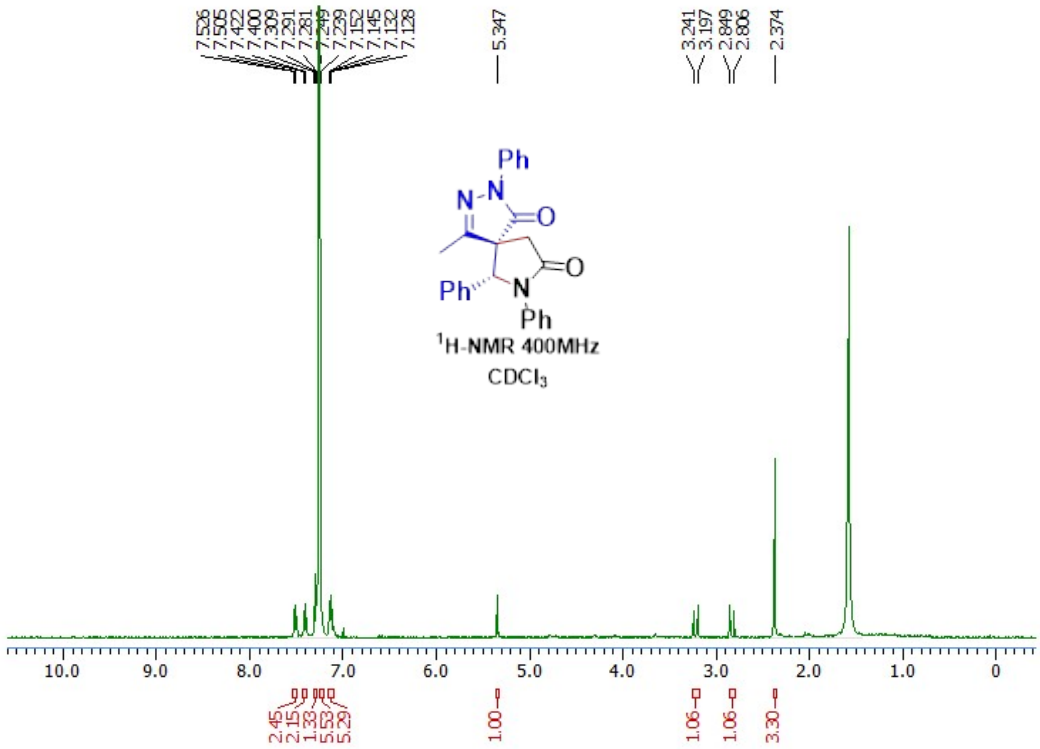

7.526
7.505
7.422
7.400
7.309
7.291
7.281
7.249
7.239
7.152
7.145
7.132
7.128
5.347
3.241
3.197
2.849
2.806
2.374
Ph
N
N
O
O
Ph
N
Ph
1H-NMR 400MHz
CDCl3
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.45
2.15
1.33
5.53
5.29
1.00
1.06
1.06
3.30

Fig. 6: ^{1}H-NMR spectrum of (5*R*,6*R*)-4-methyl-2,6,7-triphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3c)

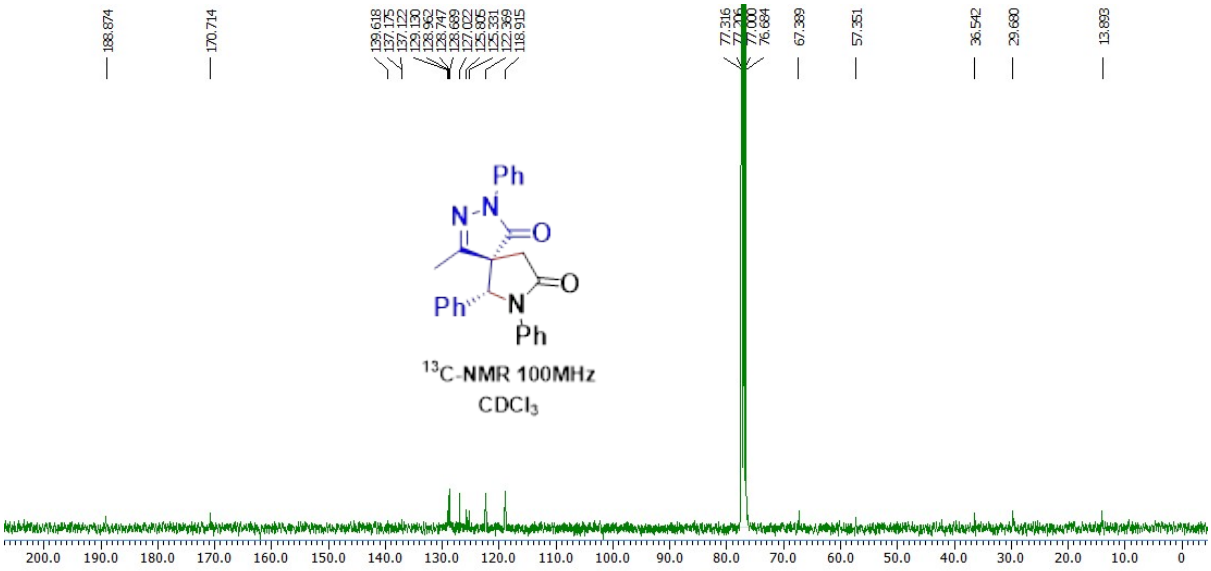


Fig. 7: ^{13}C-NMR spectrum of (5*R*,6*R*)-4-methyl-2,6,7-triphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3c)

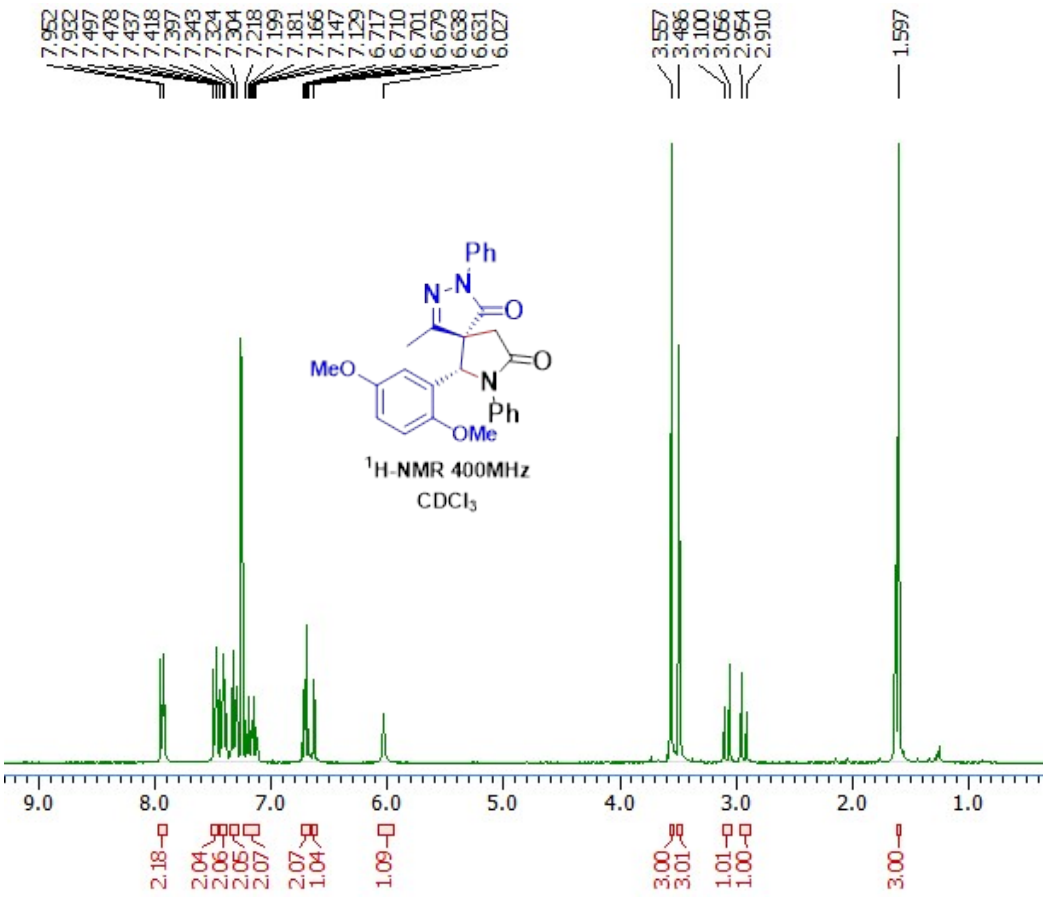


Fig. 8: ^{1}H-NMR spectrum of (5*R*,6*R*)-6-(2,5-dimethoxyphenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3d)

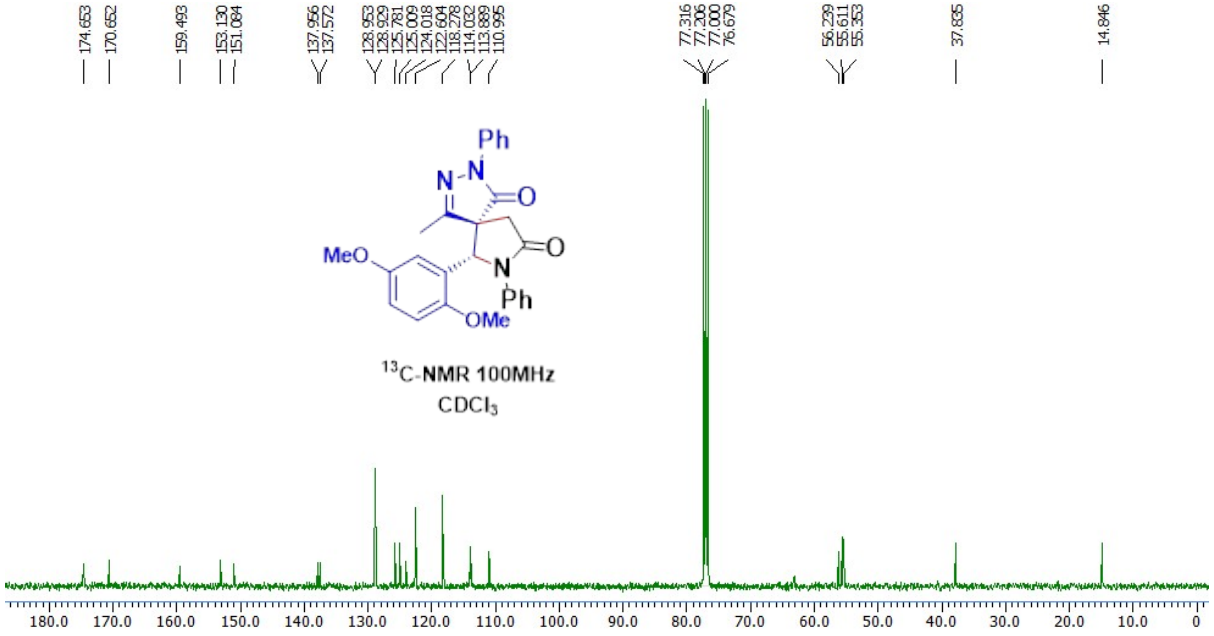


Fig. 9: ^{13}C-NMR spectrum of (5*R*,6*R*)-6-(2,5-dimethoxyphenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3d)

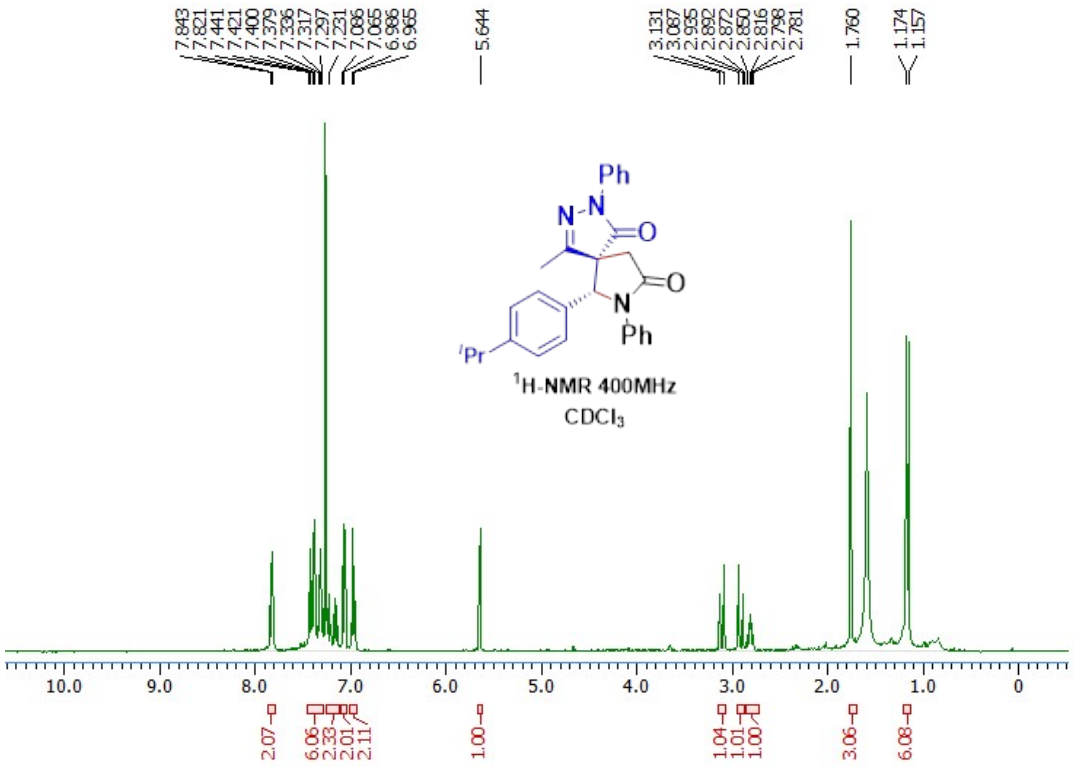
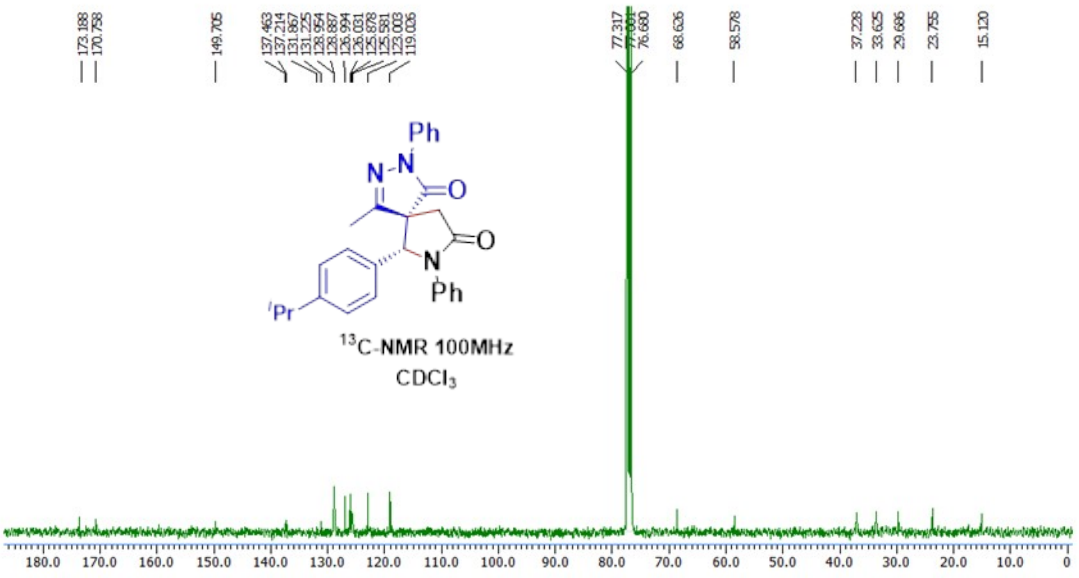


Fig. 10:



^{1}H-NMR spectrum of (5*R*,6*R*)-6-(4-isopropylphenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3e)

Fig. 11: ^{13}C-NMR spectrum of (5*R*,6*R*)-6-(4-isopropylphenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3e)

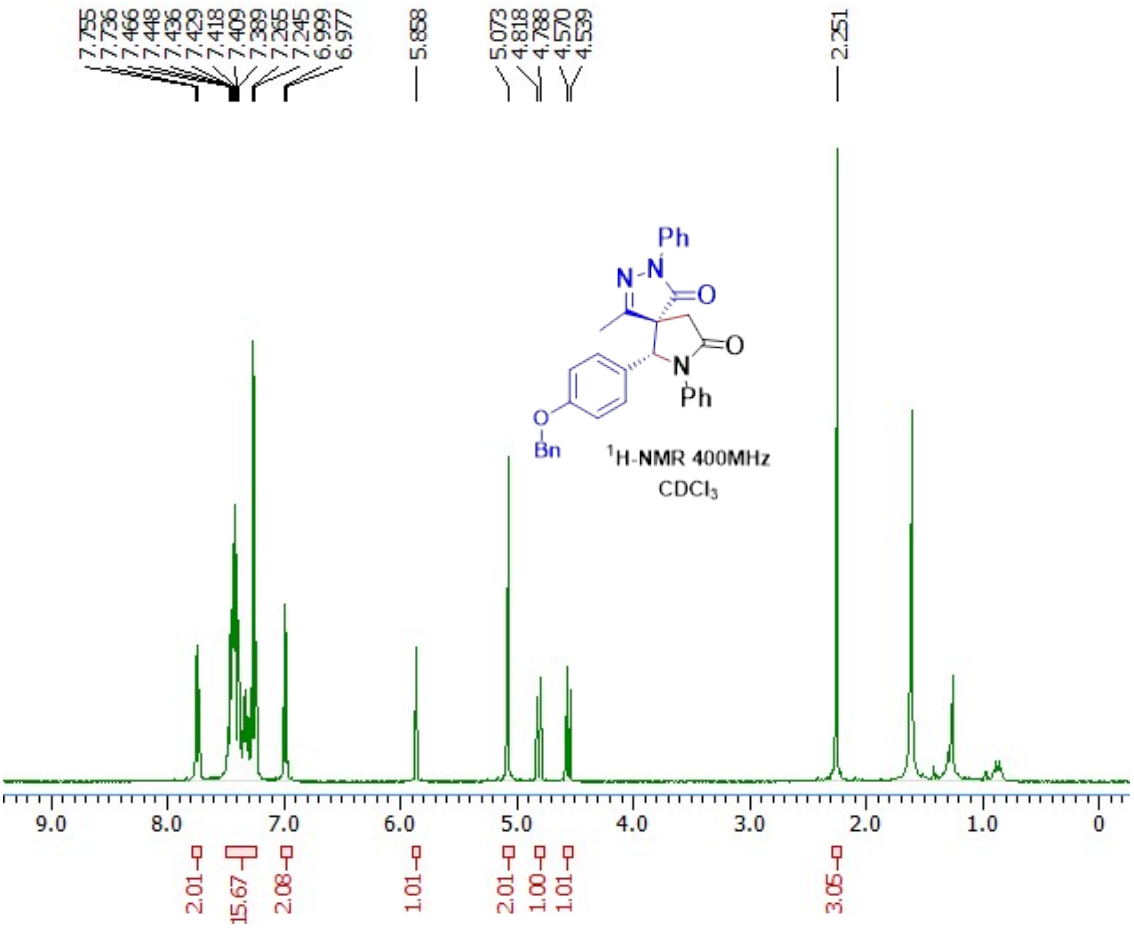
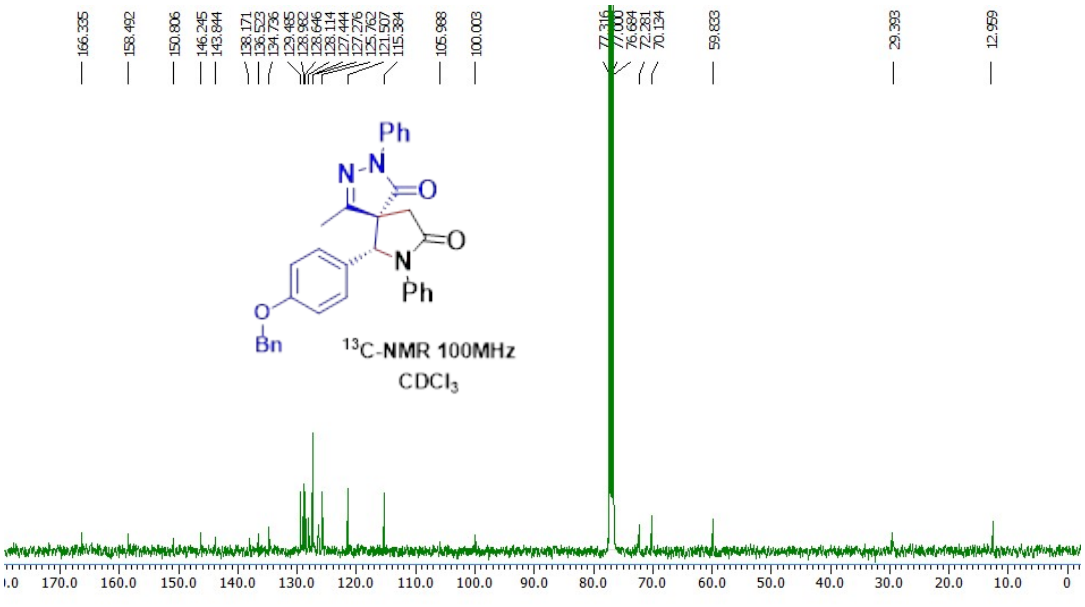
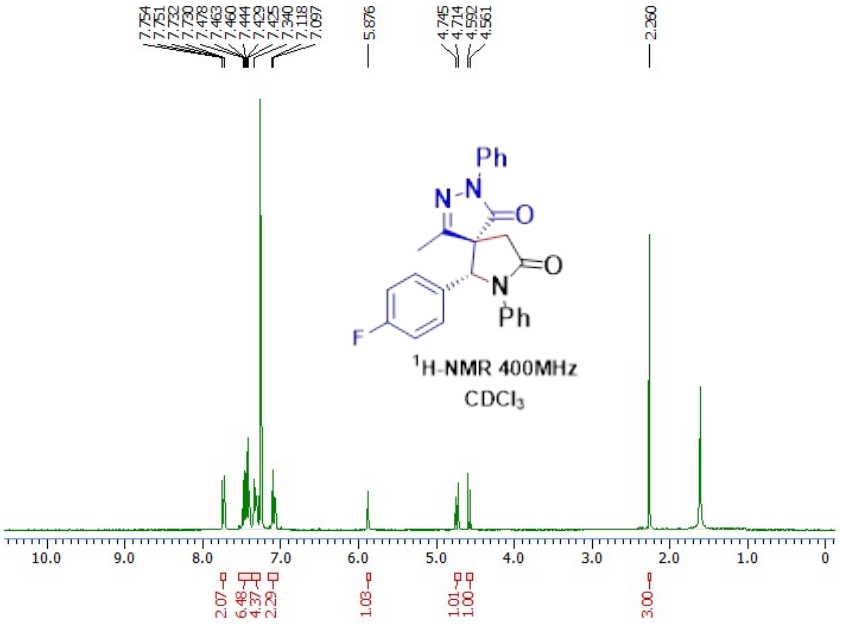


Fig. 12:



^{1}H-NMR spectrum of (5*R*,6*R*)-6-(4-(benzyloxy)phenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3f)

Fig. 13: ^{1}H-NMR spectrum of (5*R*,6*R*)-6-(4-(benzyloxy)phenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3f)


7.754
7.751
7.732
7.730
7.478
7.463
7.460
7.444
7.429
7.425
7.340
7.118
7.097
5.876
4.745
4.714
4.592
4.561
2.260
Ph
N
N
O
O
N
Ph
F
^{1}H-NMR 400MHz
$CDCl_3$
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.07
6.48
4.37
2.29
1.03
1.01
1.00
3.00

triazaspiro[4.4]non-3-ene-1,8-dione (3g)

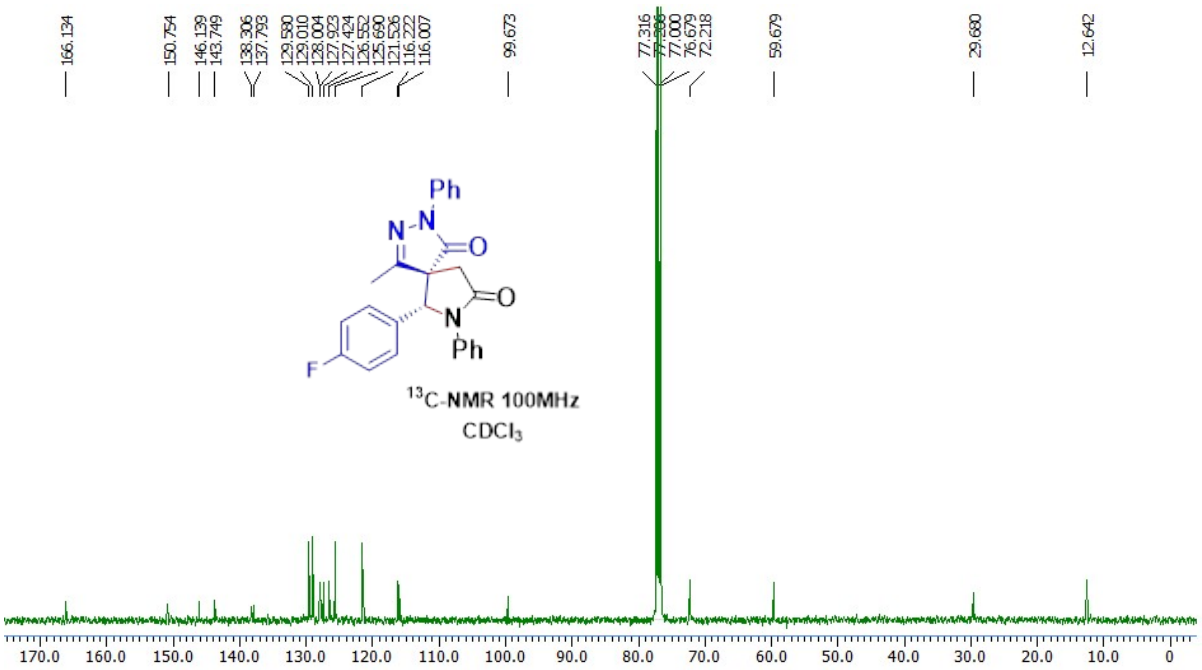


Fig. 15: ^{13}C-NMR spectrum of (5*R*,6*R*)-6-(4-fluorophenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3g)

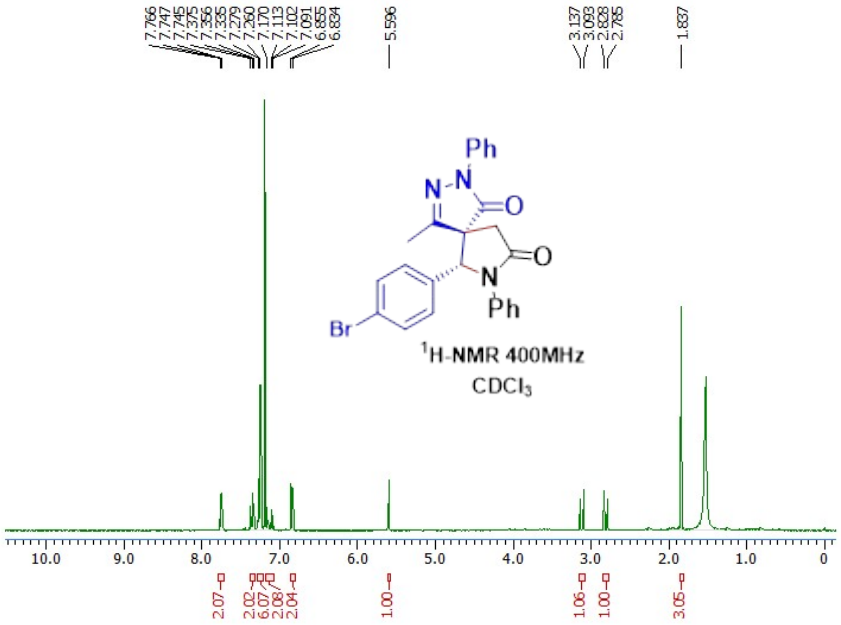
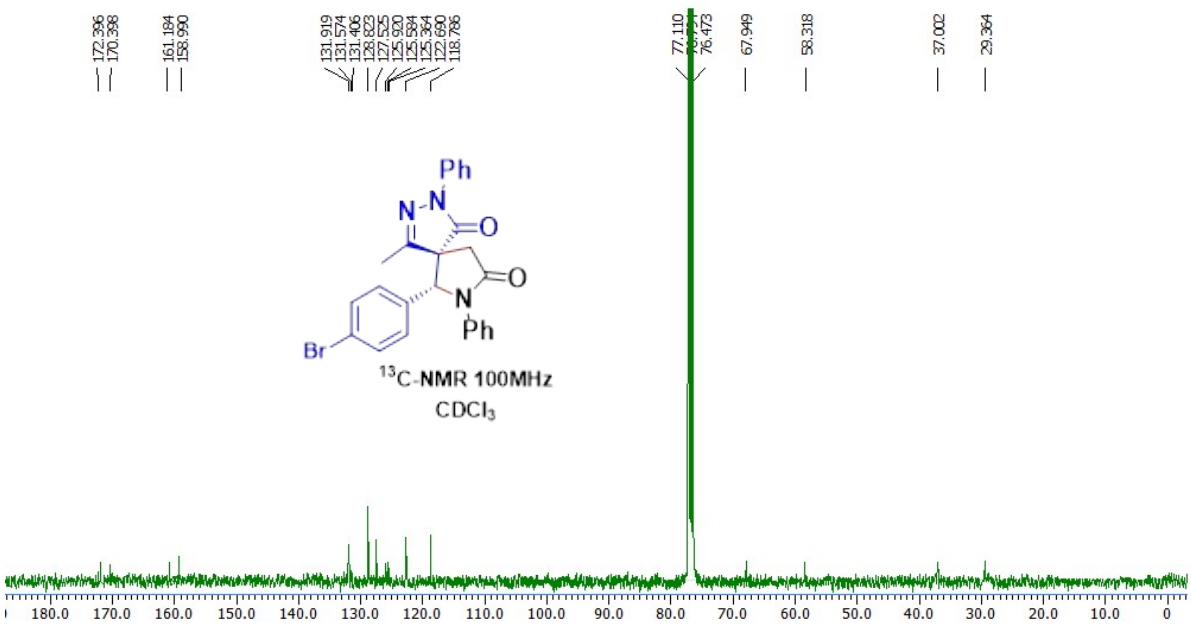
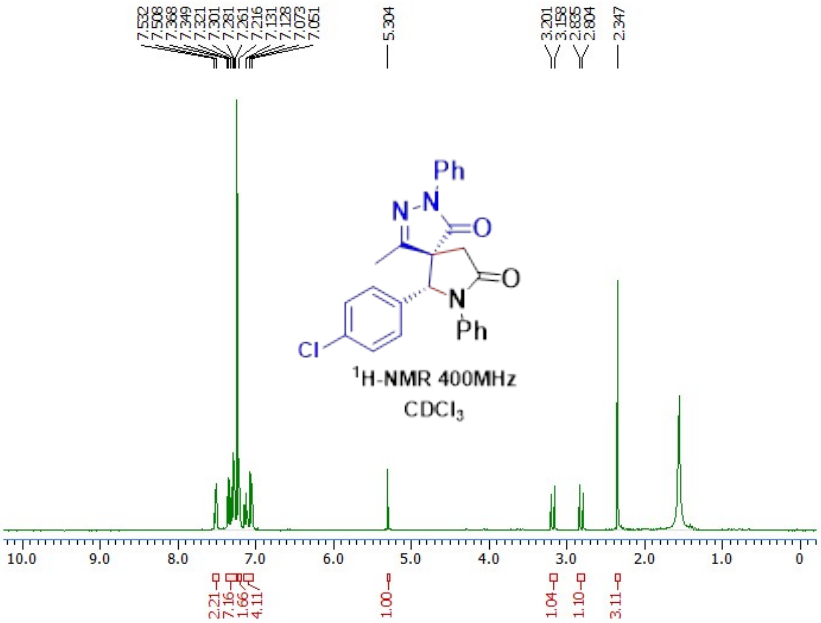


Fig. 16: ^{1}H-NMR spectrum of (5*R*,6*R*)-6-(4-bromophenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3h)

Fig. 17: ^{13}C-NMR spectrum of (5*R*,6*R*)-6-(4-bromophenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3h)




7.532
7.508
7.368
7.349
7.321
7.301
7.281
7.261
7.216
7.131
7.128
7.073
7.051
5.304
3.201
3.158
2.835
2.804
2.347
Ph
N
N
O
O
N
Ph
Cl
1H-NMR 400MHz
CDCl3
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.21
7.16
1.66
4.11
1.00
1.04
1.10
3.11

triazaspiro[4.4]non-3-ene-1,8-dione (3i)

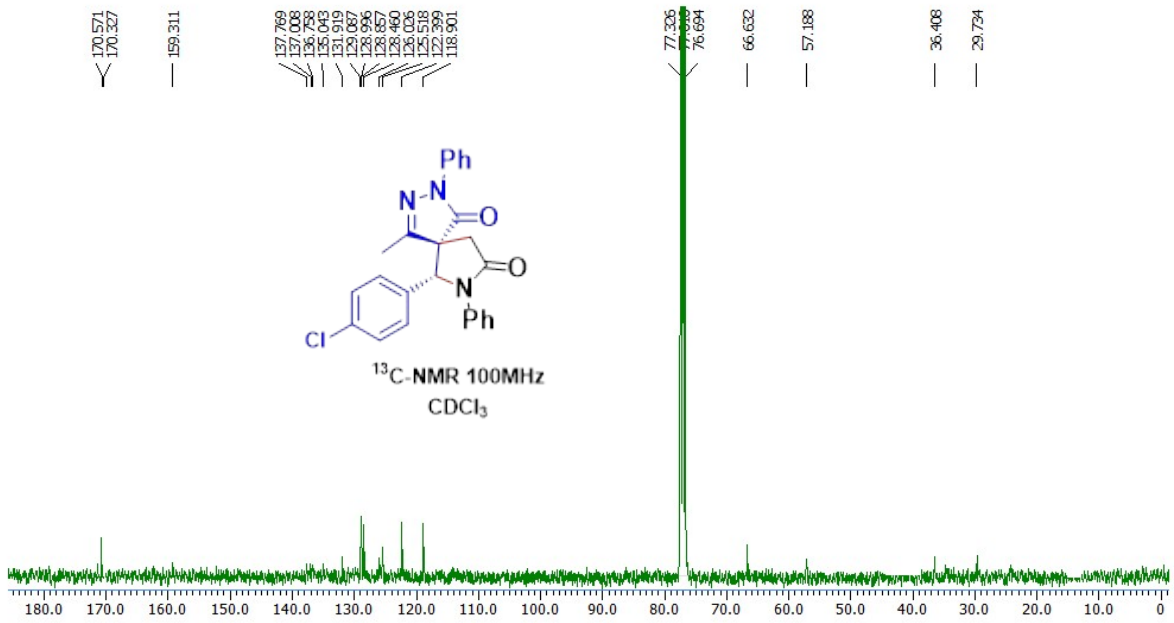


Fig. 19: ^{13}C-NMR spectrum of (5*R*,6*R*)-6-(4-chlorophenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3i)

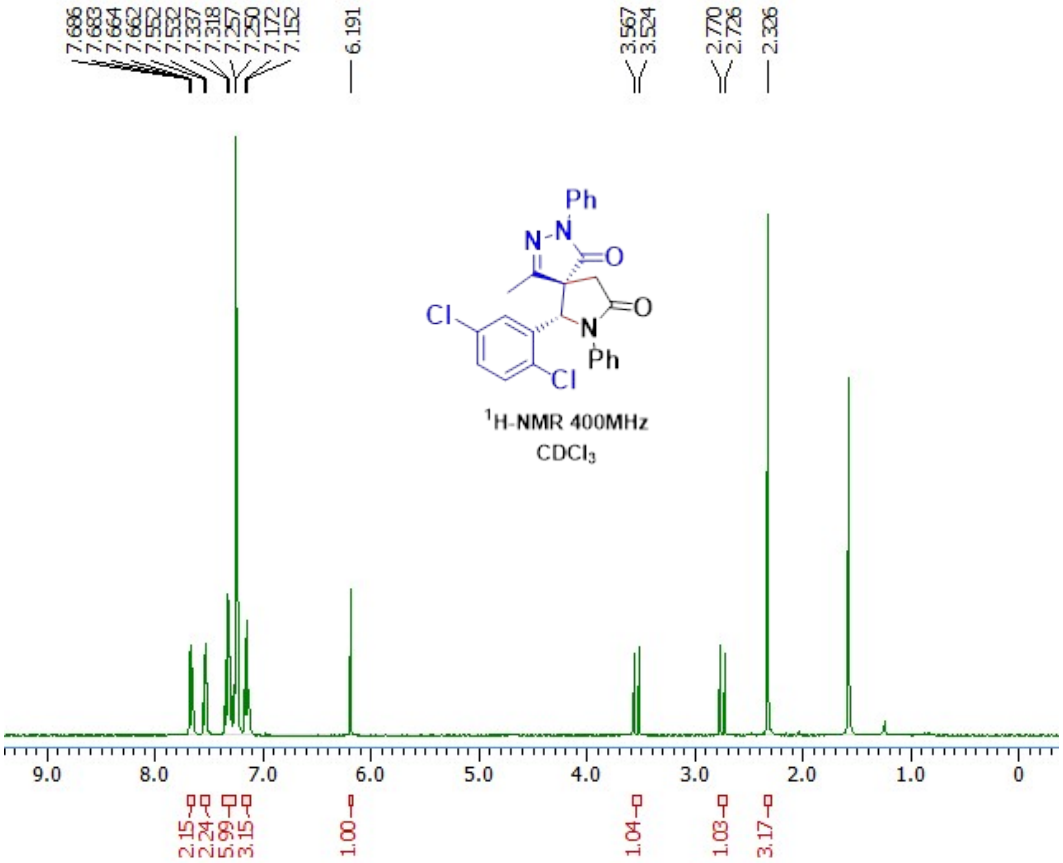


Fig. 20: ^{1}H-NMR spectrum of (5*R*,6*S*)-6-(2,5-dichlorophenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3j)

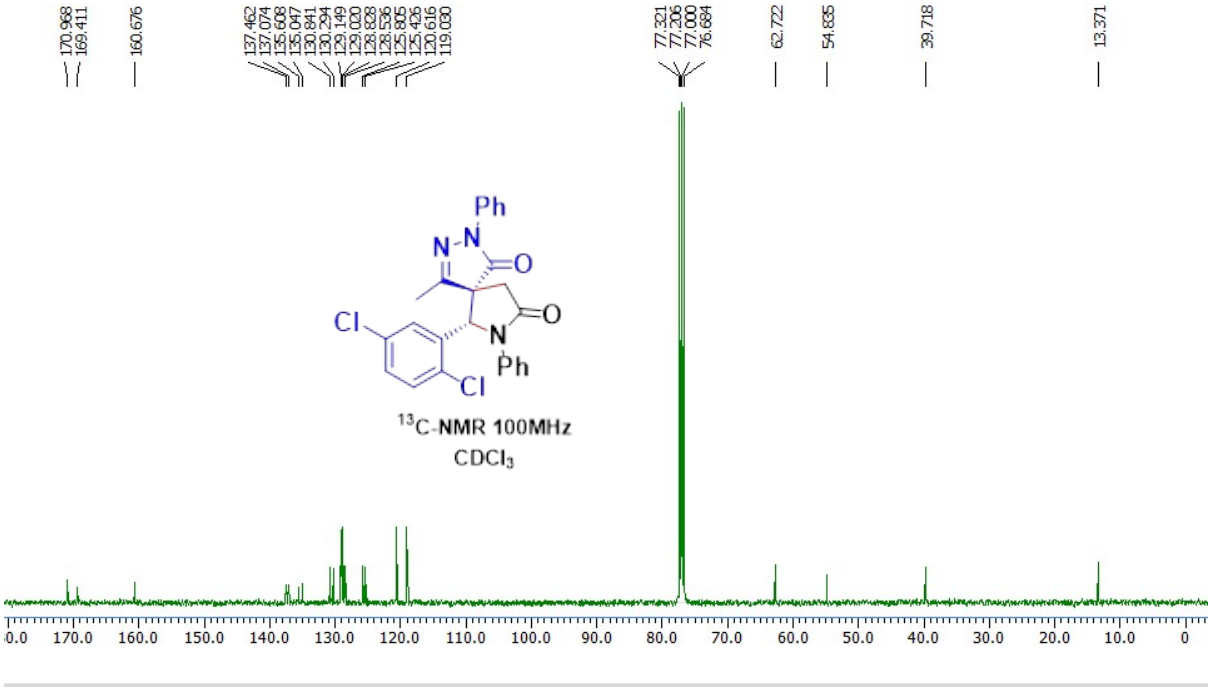


Fig. 21: ^{13}C-NMR spectrum of (5*R*,6*S*)-6-(2,5-dichlorophenyl)-4-methyl-2,7-diphenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3j)

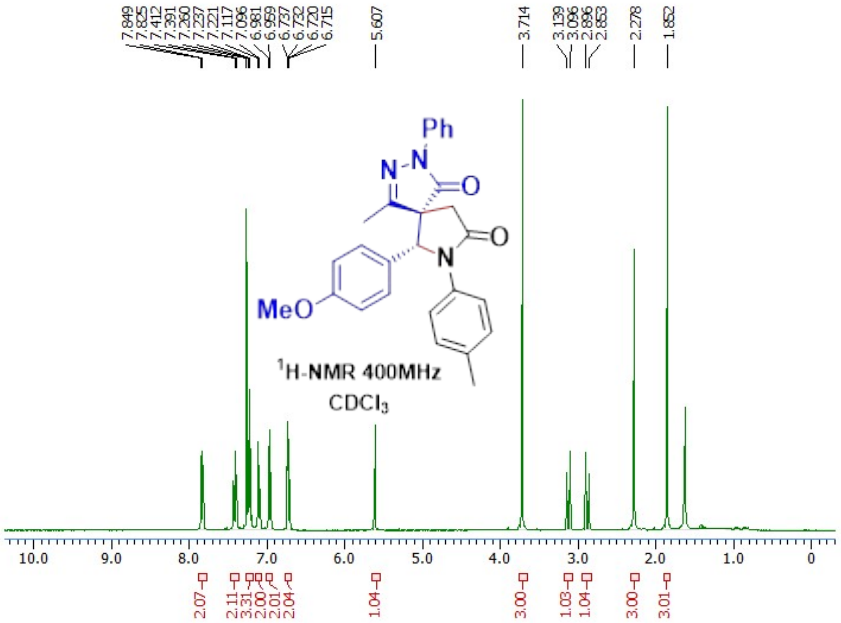


Fig. 22: ^{1}H-NMR spectrum of (5*R*,6*R*)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-7-(p-tolyl)-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3m)

Fig. 23: ^{13}C-NMR spectrum of (5*R*,6*R*)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-7-(p-tolyl)-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3m)

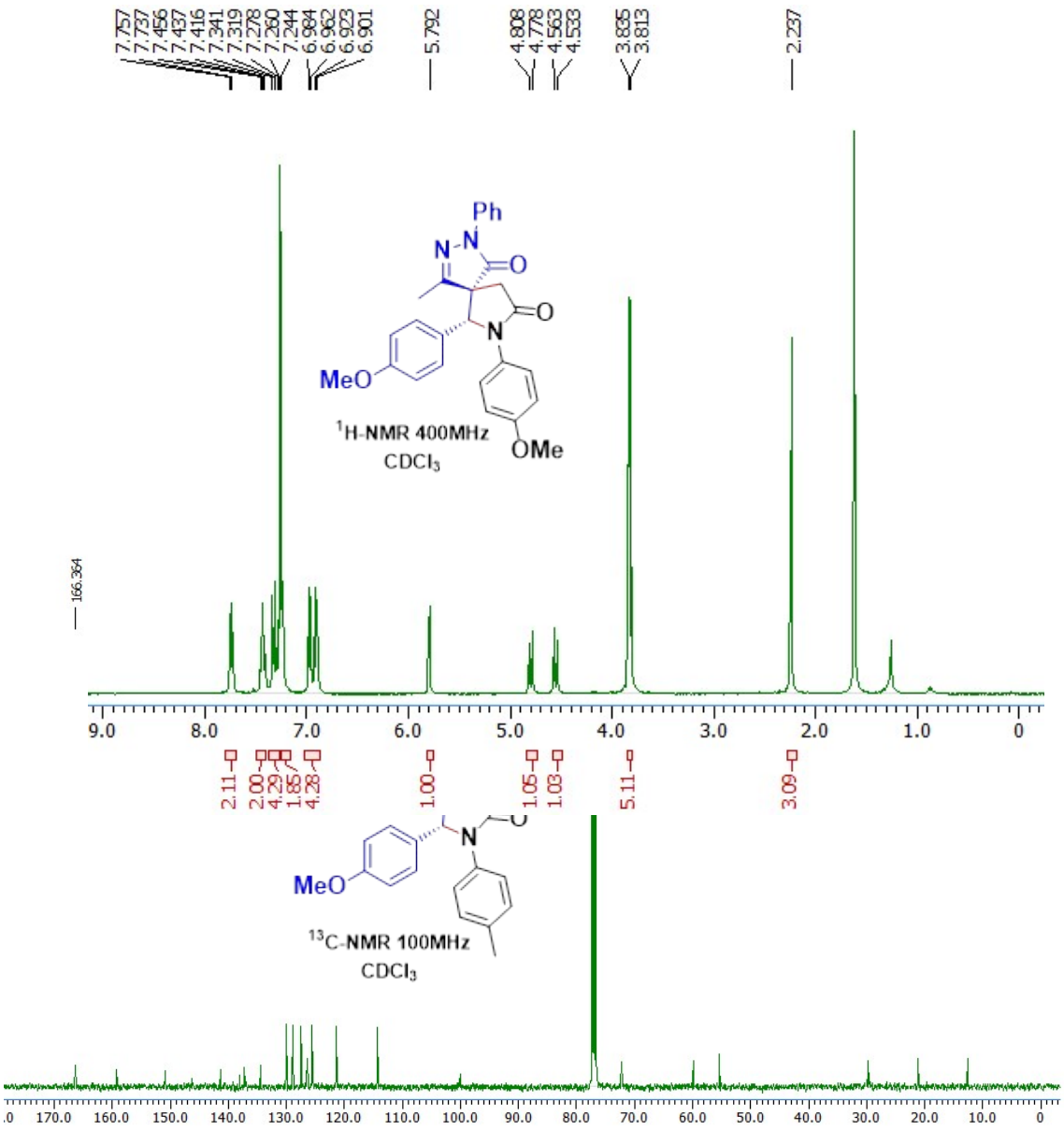


Fig. 24: ^{1}H-NMR spectrum of (5*R*,6*R*)-6,7-bis(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3n)

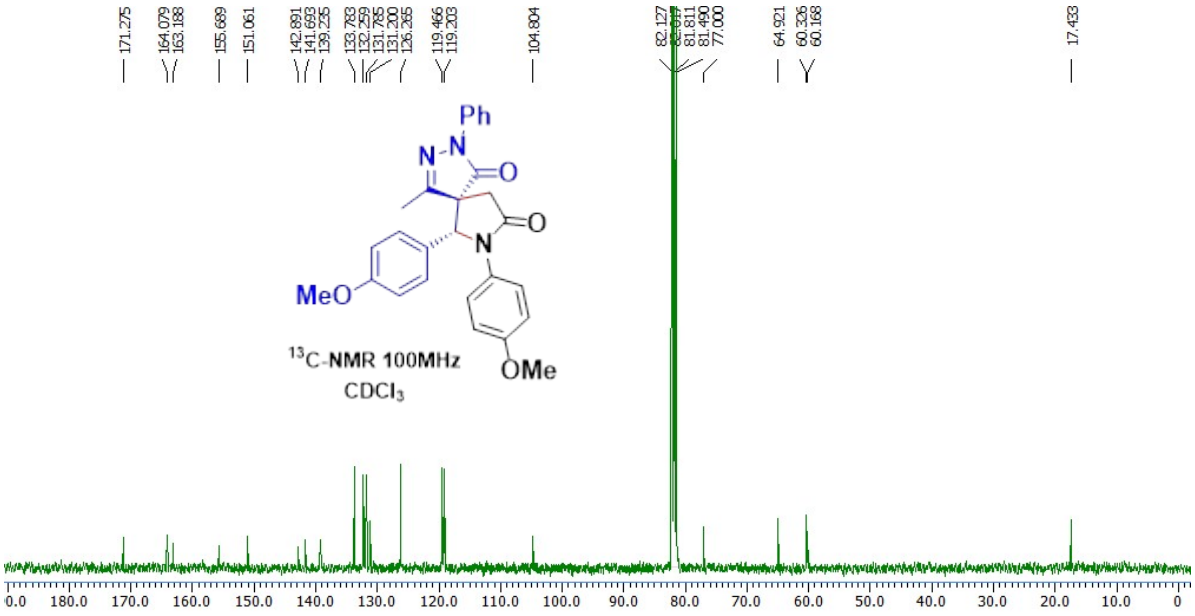


Fig. 25: ^{13}C-NMR spectrum of (5*R*,6*R*)-6,7-bis(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3n)

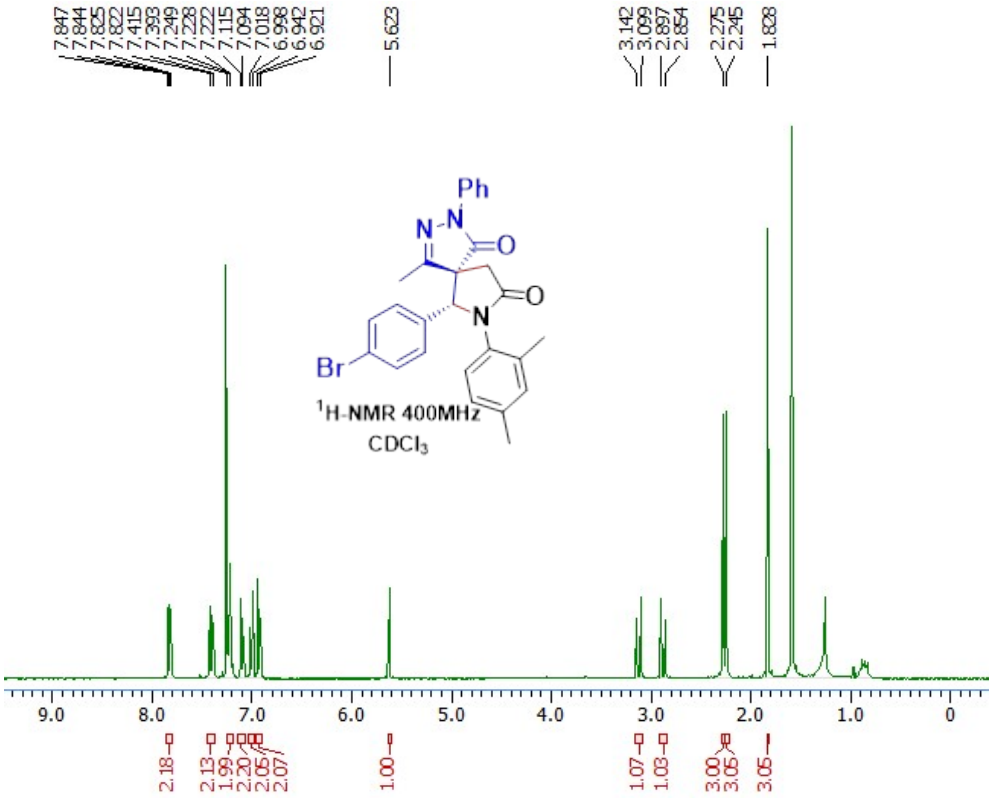


Fig. 26: ^{1}H-NMR

spectrum of (5*R*,6*R*)-6-(4-bromophenyl)-7-(2,5-dimethylphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3o)

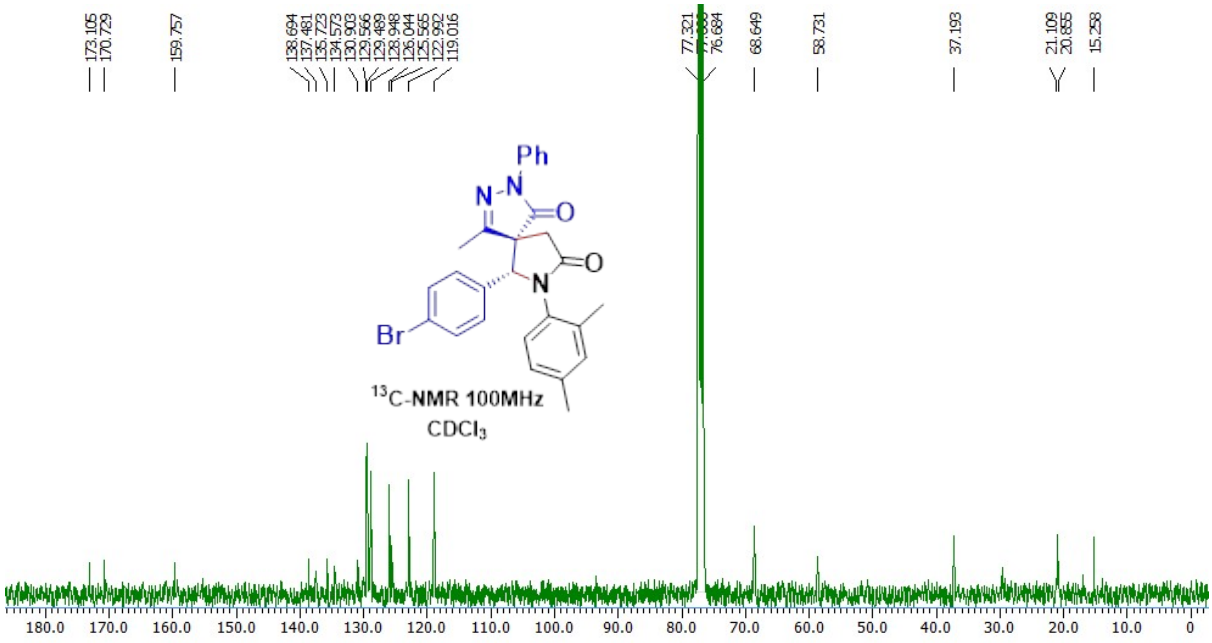


Fig. 27: ^{13}C-NMR spectrum of (5*R*,6*R*)-6-(4-bromophenyl)-7-(2,5-dimethylphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3o)

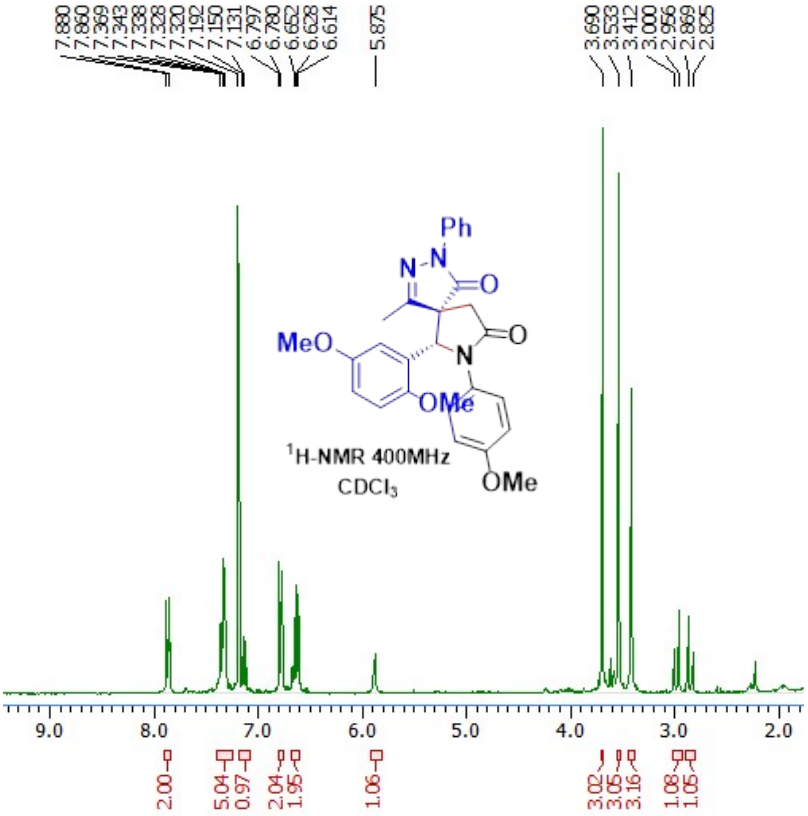
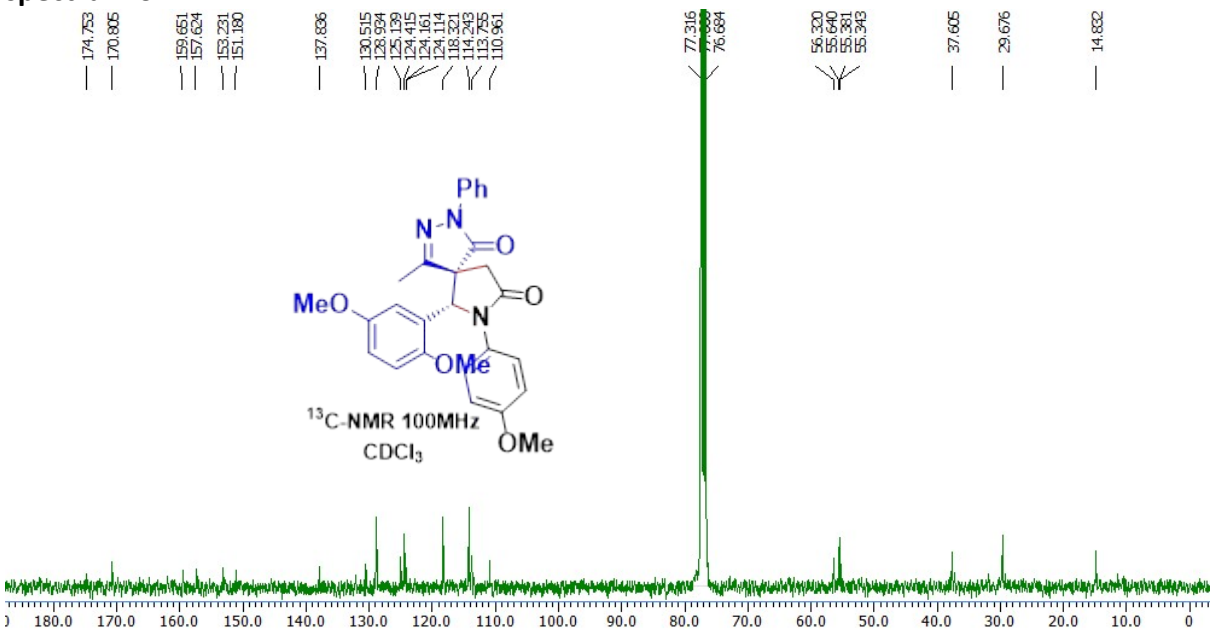


Fig. 28: ^{1}H-NMR spectrum of



(5*R*,6*R*)-6-(2,5-dimethoxyphenyl)-7-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3p)

Fig. 29: ^{13}C-NMR spectrum of (5*R*,6*R*)-6-(2,5-dimethoxyphenyl)-7-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3p)

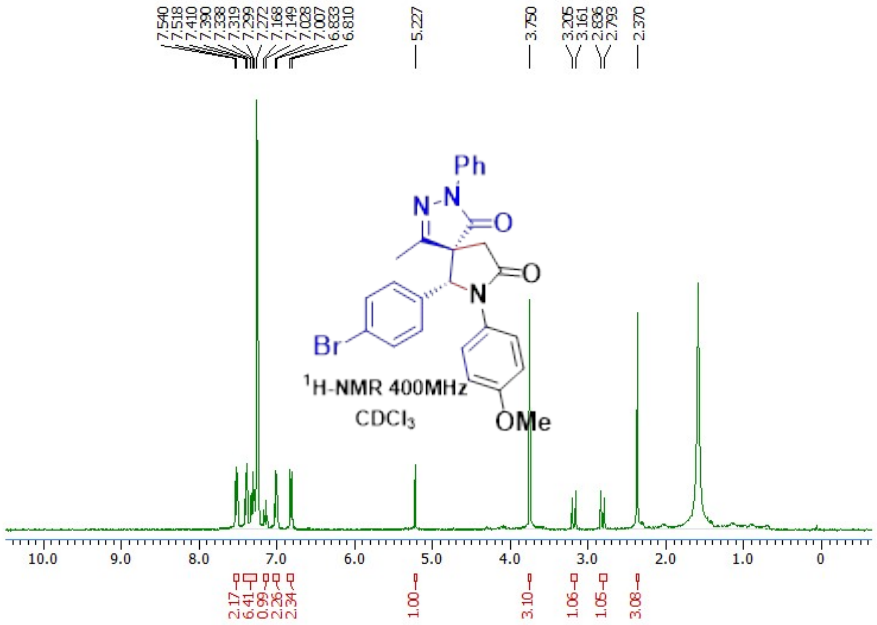

7.540
7.518
7.410
7.390
7.338
7.319
7.299
7.272
7.168
7.149
7.028
7.007
6.833
6.810
5.227
3.750
3.205
3.161
2.836
2.793
2.370
Ph
N
N
O
O
N
Br
^{1}H-NMR 400MHz
$CDCl_3$
OMe
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.17
6.41
0.99
2.26
2.34
1.00
3.10
1.06
1.05
3.08

Fig. 30: ^{1}H-NMR spectrum of (5*R*,6*R*)-6-(4-bromophenyl)-7-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3q)

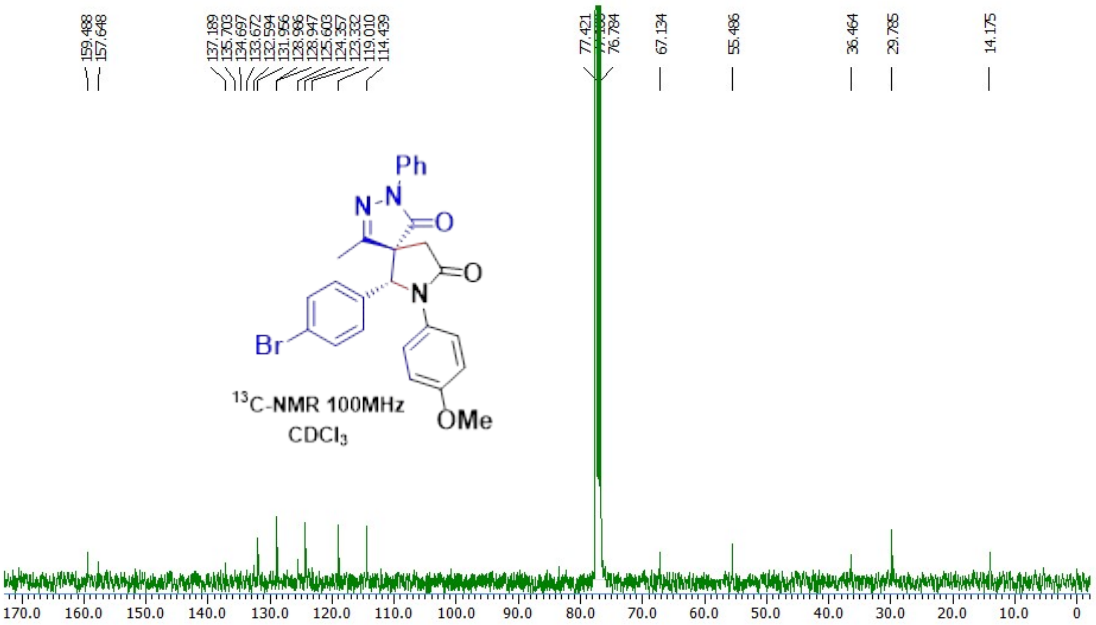
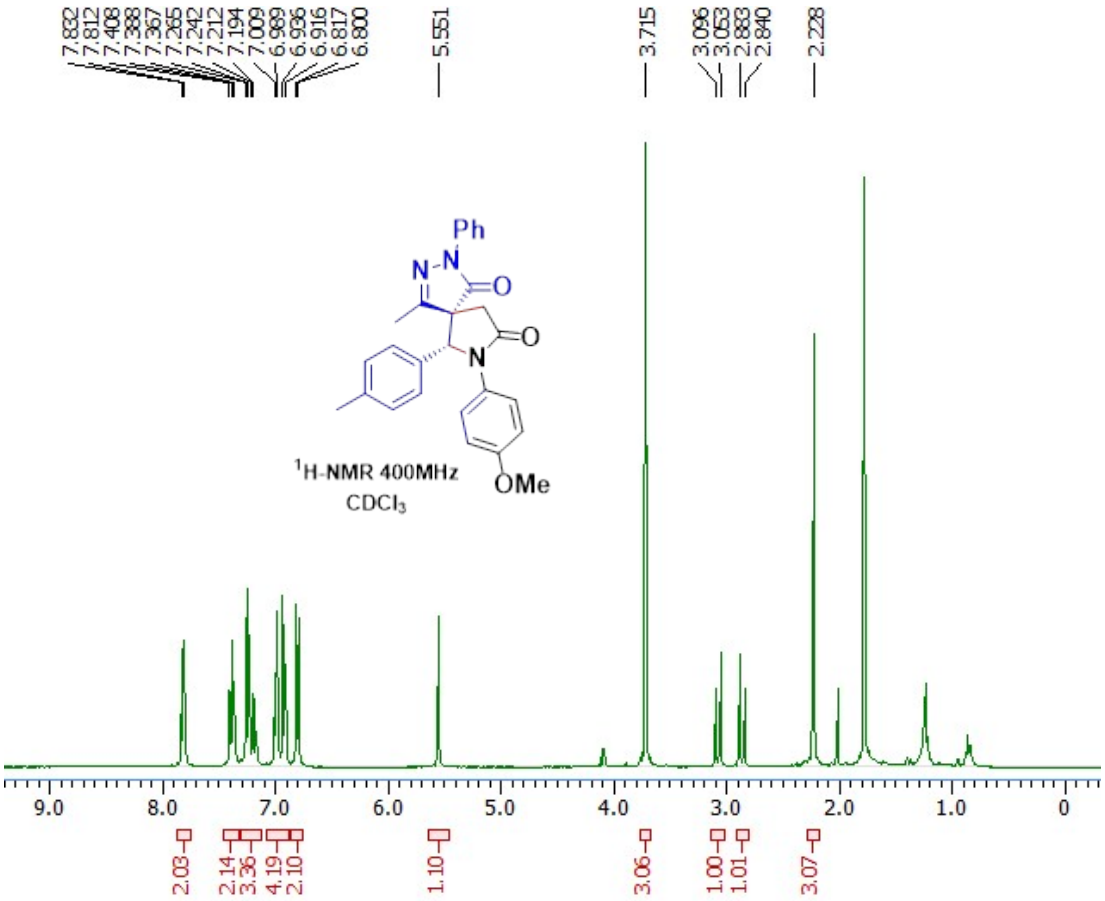


Fig. 31: ^{13}C-NMR spectrum of 5*R*,6*R*)-6-(4-bromophenyl)-7-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3q)


7.832
7.812
7.408
7.388
7.367
7.265
7.242
7.212
7.194
7.009
6.989
6.936
6.916
6.817
6.800
5.551
3.715
3.096
3.053
2.883
2.840
2.228
Ph
N
N
O
O
N
OMe
^{1}H-NMR 400MHz
$CDCl_3$
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
2.03
2.14
3.36
4.19
2.10
1.10
3.06
1.00
1.01
3.07

2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3r)

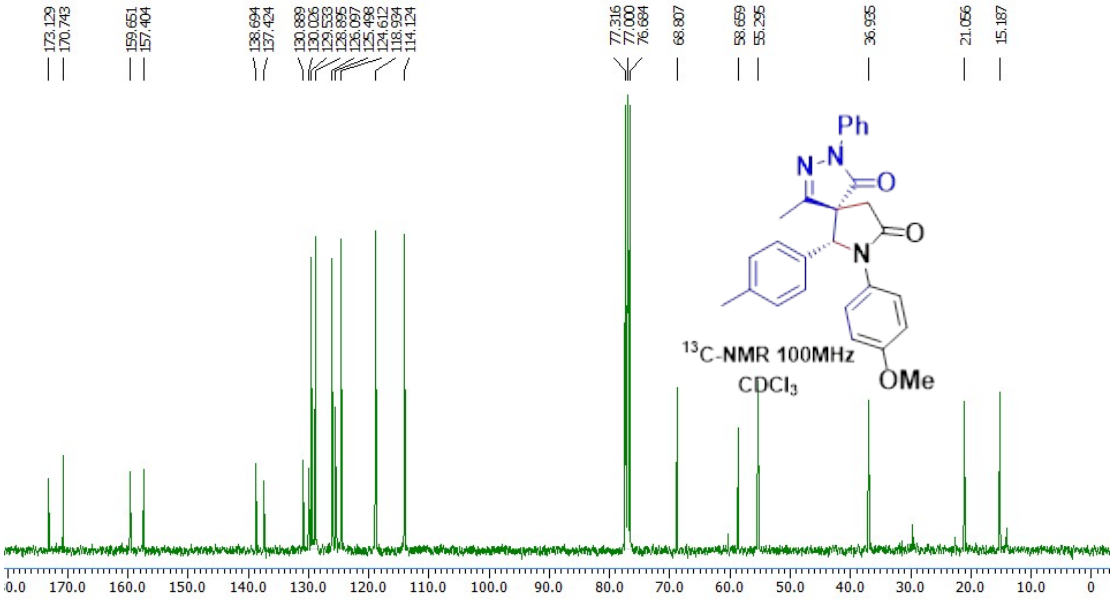


Fig. 33: ^{13}C-NMR

spectrum of (5*R*,6*R*)-7-(4-methoxyphenyl)-4-methyl-2-phenyl-6-(p-tolyl)-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3r)

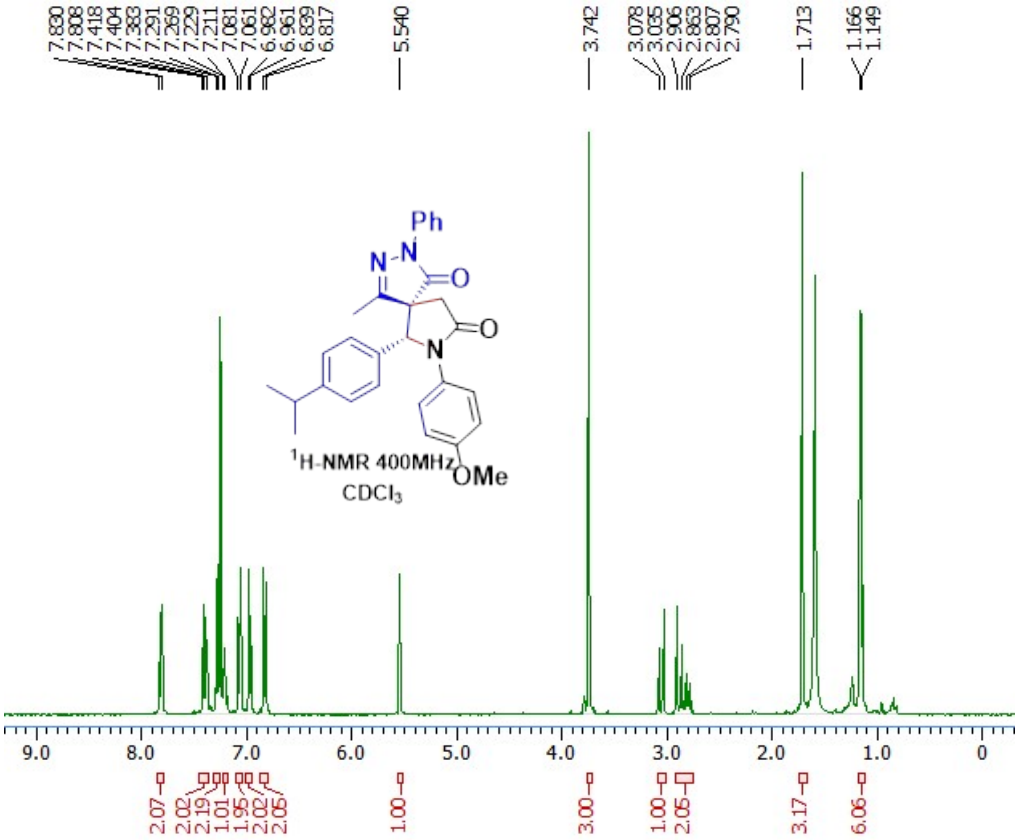
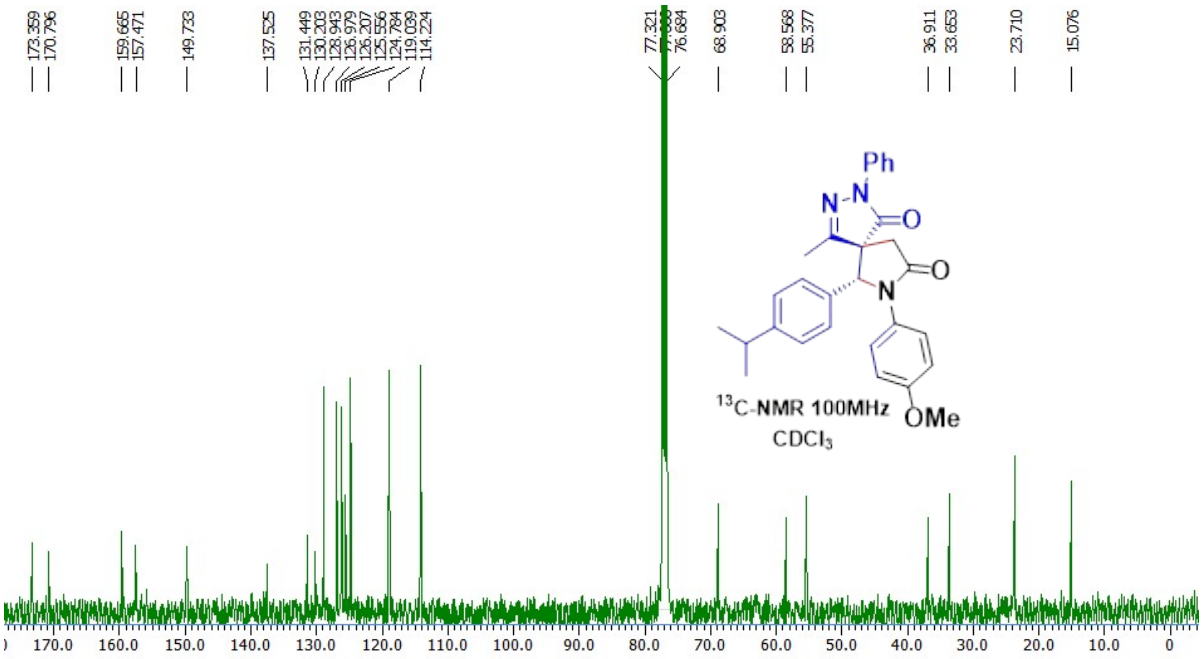


Fig. 34: ^{1}H-



NMR spectrum of (5*R*,6*R*)-6-(4-isopropylphenyl)-7-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3s)

Fig. 35: ^{13}C-NMR spectrum of (5*R*,6*R*)-6-(4-isopropylphenyl)-7-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3s)

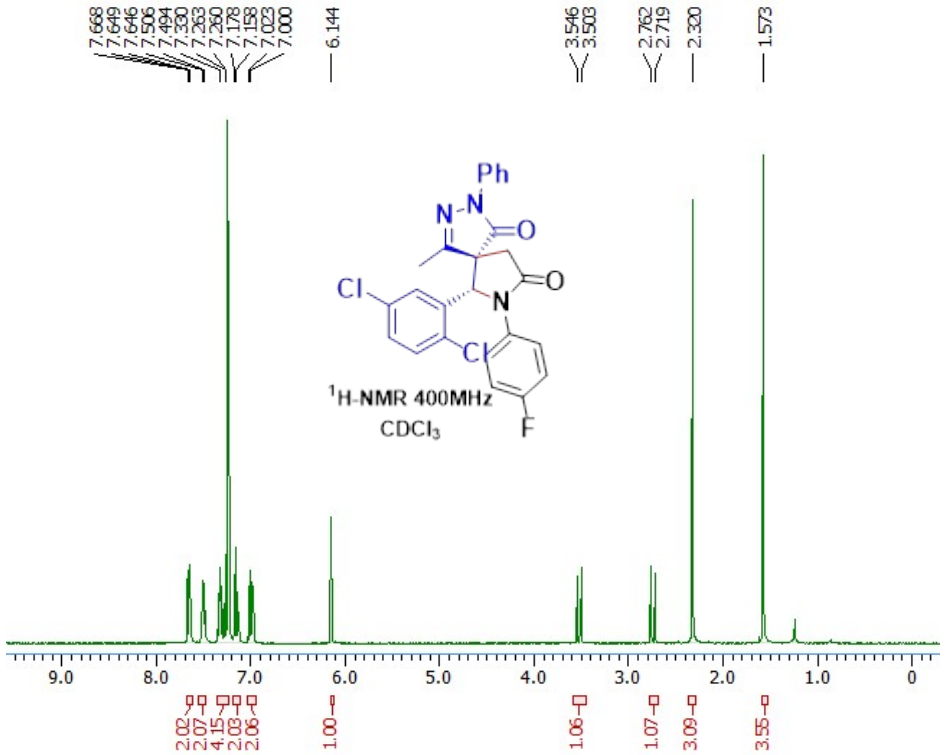
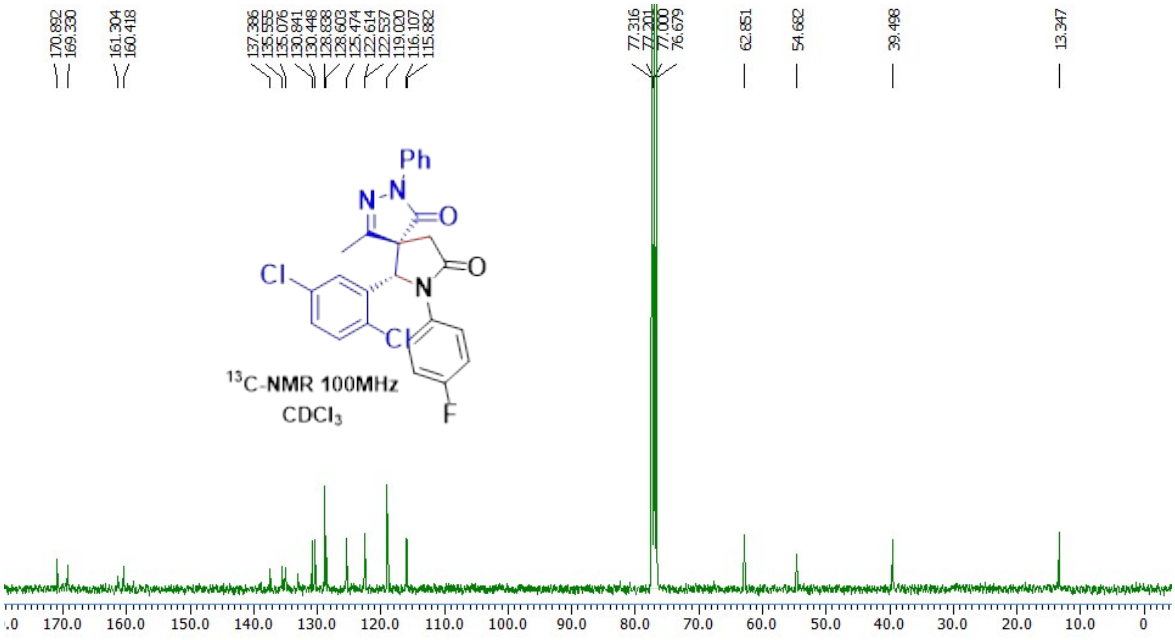


Fig. 36:

^{1}H-NMR



spectrum of (5*R*,6*S*)-6-(2,5-dichlorophenyl)-7-(4-fluorophenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3t)

Fig. 37: ^{13}C-NMR spectrum of (5*R*,6*S*)-6-(2,5-dichlorophenyl)-7-(4-fluorophenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3t)

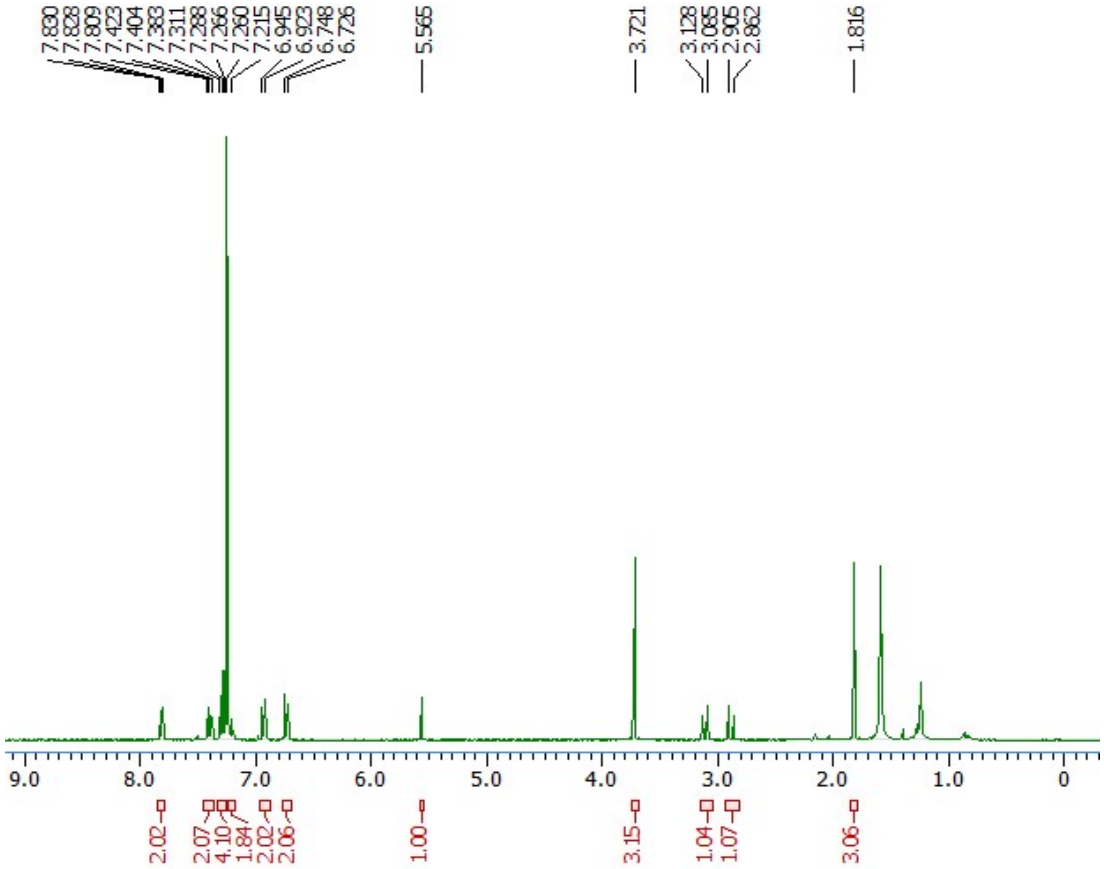


Fig. 38: ^{1}H-NMR spectrum of (5*R*,6*R*)-7-(4-chlorophenyl)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3u)

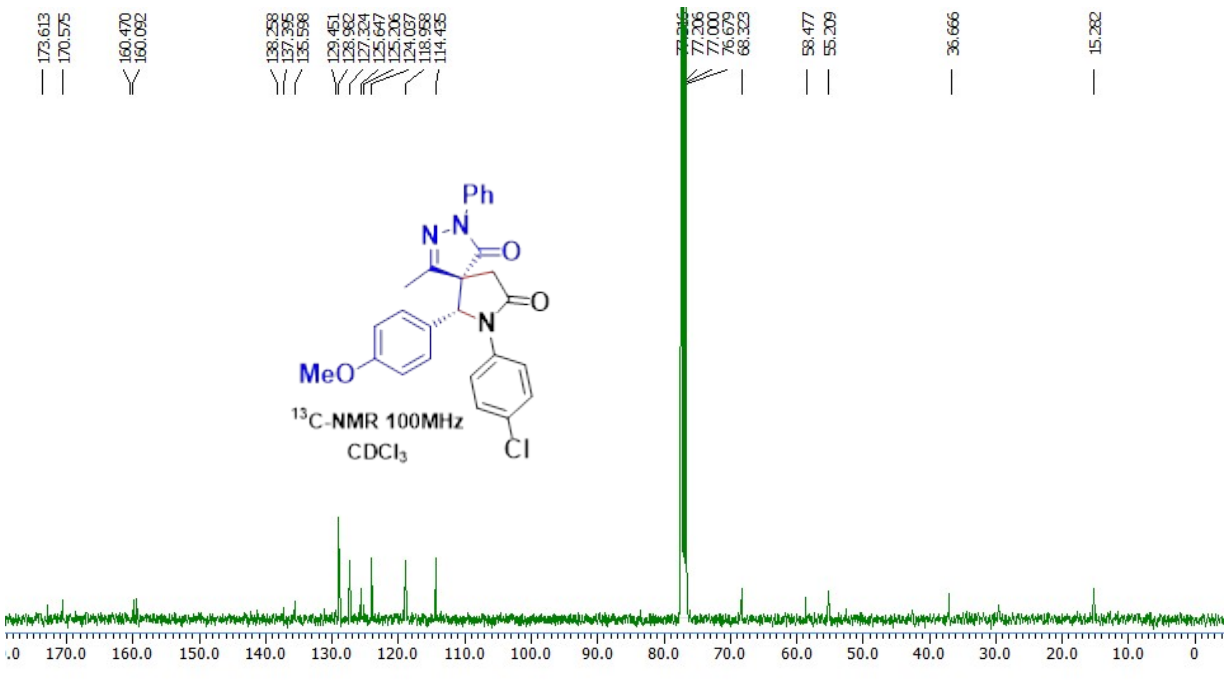


Fig. 39: ^{13}C-NMR spectrum of (5*R*,6*R*)-7-(4-chlorophenyl)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3u)

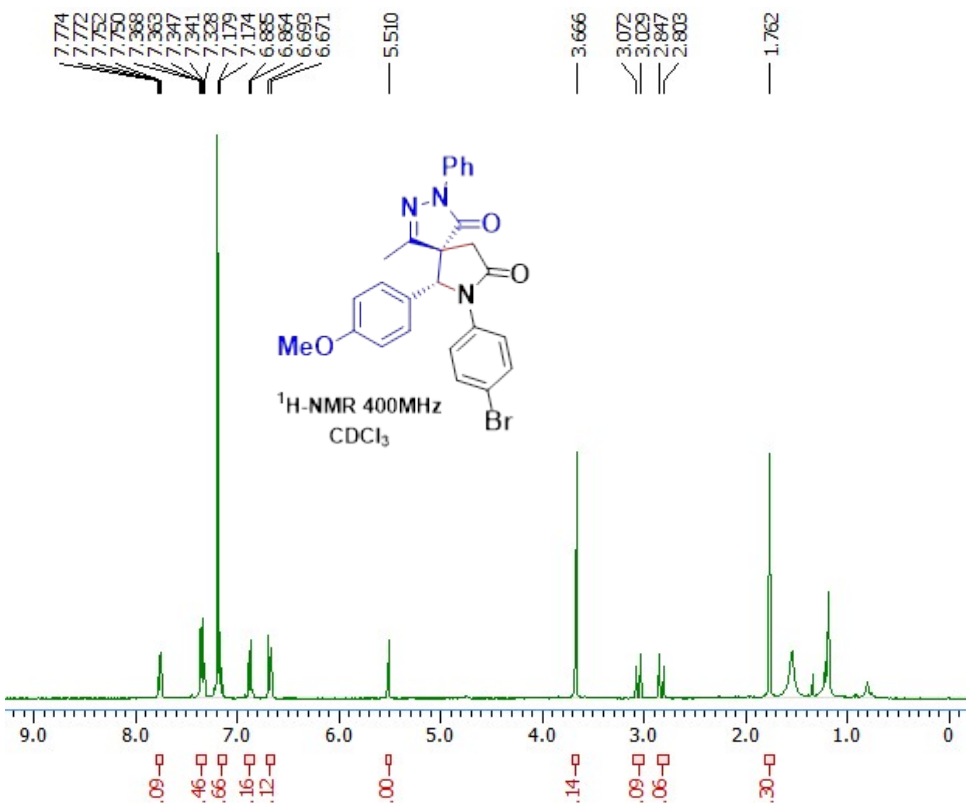
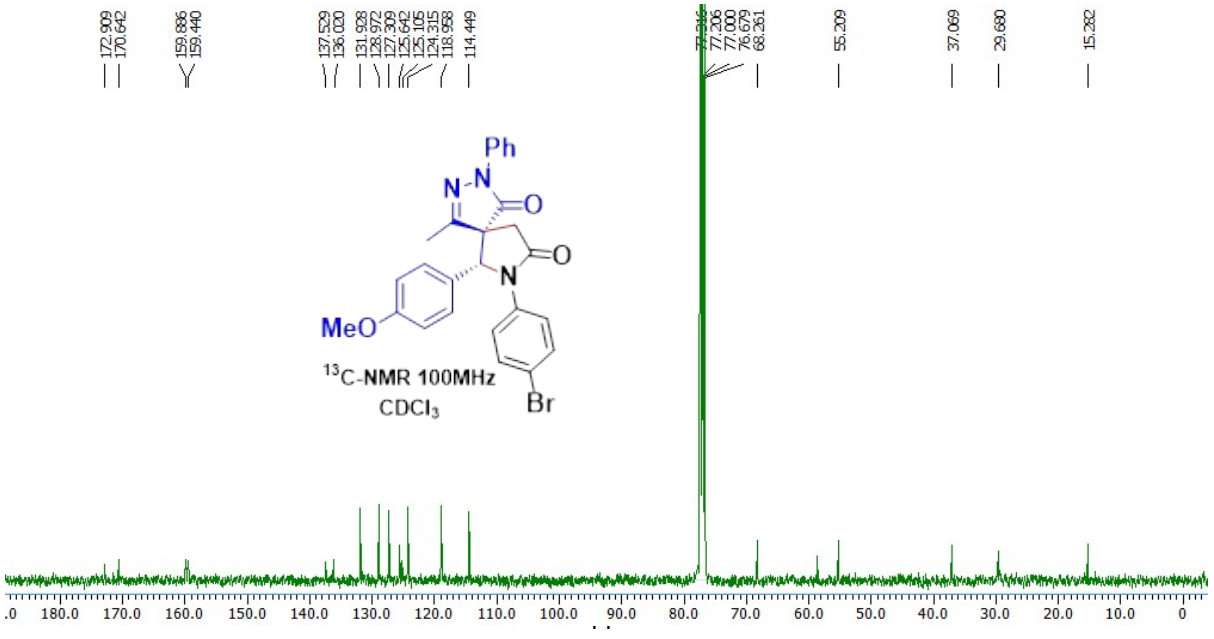


Fig. 40: ^{1}H-



NMR spectrum of (5*R*,6*R*)-7-(4-bromophenyl)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3v)

Fig. 41: ^{13}C-NMR spectrum of (5*R*,6*R*)-7-(4-bromophenyl)-6-(4-methoxyphenyl)-4-methyl-2-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3v)

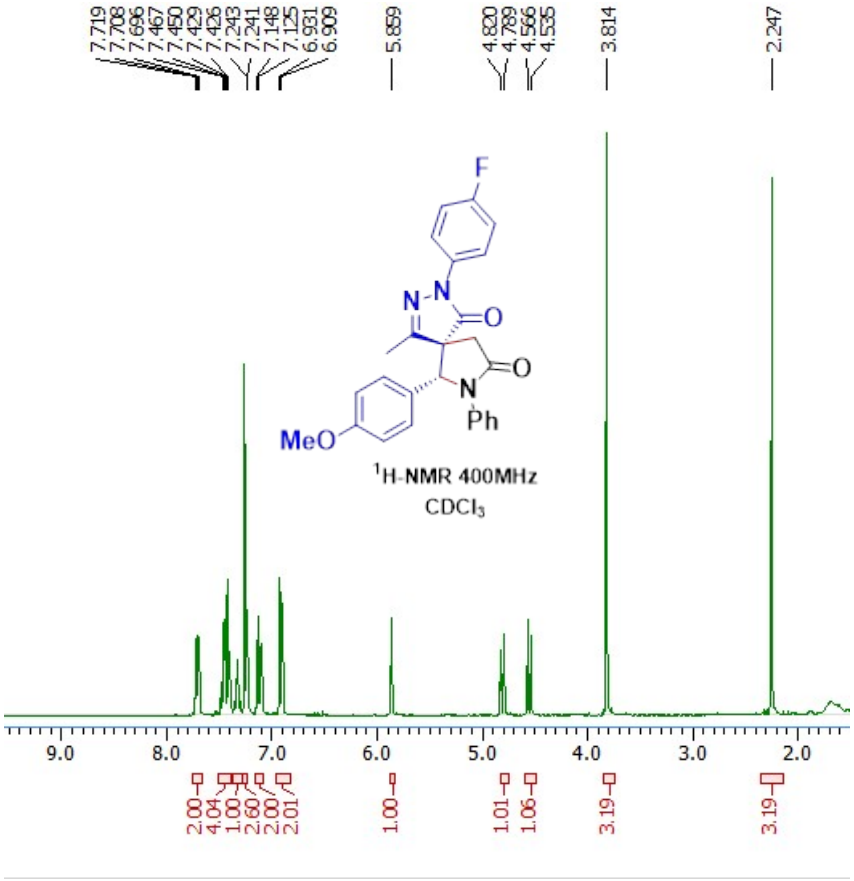
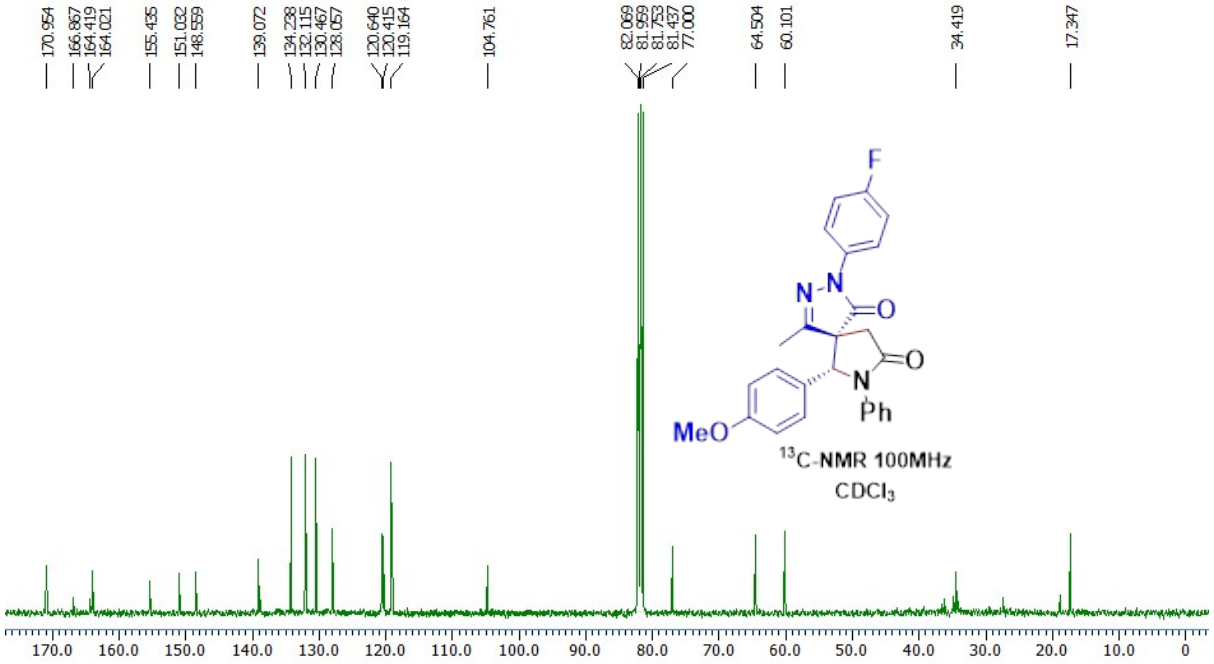


Fig. 42: ^{1}H-NMR



spectrum of (5*R*,6*R*)-2-(4-fluorophenyl)-6-(4-methoxyphenyl)-4-methyl-7-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3w)

Fig. 43: ^{1}H-NMR spectrum of (5*R*,6*R*)-2-(4-fluorophenyl)-6-(4-methoxyphenyl)-4-methyl-7-phenyl-2,3,7-triazaspiro[4.4]non-3-ene-1,8-dione (3w)