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New spiro-fused 2-nitrocyclopropanecarboxylates: synthesis and structure

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Experimental

Physicochemical studies were performed using the equipment of the Center for Collective Use "Physicochemical methods for the study of nitro compounds, coordination, biologically active substances and nanostructured materials" of the Interdisciplinary Resource Center for collective use "Modern physicochemical methods for the formation and study of materials for the needs of industry, science and education" Herzen State Pedagogical University of Russia. The ^{1}H, $^{13}C\{^{1}H\}$, $^{1}H—^{1}H$ dqf-COSY, $^{1}H—^{13}C$ HMQC, $^{1}H—^{13}C$ HMBC and $^{1}H—^{15}N$ HMBC NMR spectra were recorded on a JEOL ECX400A spectrometer operating at 399.78 MHz (^{1}H), 100.53 MHz (^{13}C) and 40.52 (^{15}N) MHz in $CDCl_3$ using residual signals of the nondeuterated solvent (δ_H 7.26, δ_C 77.16) as the references. The chemical shifts of ^{15}N NMR nuclei were determined relative to MeNO2. The vibrational spectra were measured on a Shimadzu IR-Prestige-21 Fourier-transform IR spectrometer in chloroform (*c* 40 mg mL^{-1}) or KBr pellets (resolution was 2 cm^{-1}). Elemental analysis was performed on a Euro Vector EA 3000 analyzer (CHN Dual). Isolation of individual diastereomers was carried out by column chromatography on silica gel MN Kieselgel 60 Mecherey-Negel 140-270, eluent was a mixture of solvents hexane–EtOAc, 3:1. The reaction progress and purity of the obtained compounds were controlled by TLC on Silufol UV-254 plates with 3:1 hexane–EtOAc mobile phase. Visualization under UV light (λ 254 nm).

The starting alkyl 3-bromo-3-nitroacrylates **1a,b** were synthesized according to a procedure described previously.[29]

Methyl *rac*-(1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate (2a). To a solution of 2,2-dimethyl-1,3-dioxane-4,6-dione (206 mg, 1.43 mmol) and freshly fused of AcOK (210 mg, 2.14 mmol) in anhydrous MeOH (10 ml), a solution of methyl 3-bromo-3-nitroacrylate (**1a**) (300 mg, 1.43 mmol) in anhydrous MeOH (5 ml) was added dropwise. The resulted mixture was stirred for 3 h at 18-20 °C and then poured on crushed ice. The product was extracted with $CHCl_3$ (3×20 ml). The combined extracts were dried over $MgSO_4$, filtered and evaporated to dryness to give **2a** as crystalline solids. The yield was 220 mg (56%), colorless crystals, mp 144-146°C (MeOH). IR (KBr), (ν/см$^{-1}$): 1205 (s), 1263 (s), 1327 (s, ν, C-O), 1364 (s, ν_s, NO_2), 1387 (m, δ, CH_3), 1563 (s, ν_{as}, NO_2), 1755 (s), 1784 (s, ν, C=O), 3036 (m, ν, C-H). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.88 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 4.04 (d, 1H, 1-CH, ^{3}J = 6.9 Hz), 5.37 (d, 1H, 2-CH, ^{3}J = 6.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 27.74 (CH_3), 27.96 (CH_3), 34.73 (C^3), 37.47 (C^1), 53.89 (OCH_3), 68.11 (C^2), 107.45 (C^6), 161.07, 161.76 (C^4/C^8), 162.32 (C=O). ^{15}N NMR ($CDCl_3$), δ: -15.2 (NO_2). Found (%): C 43.61, H 3.89, N 4.98. Calculated $C_{10}H_{11}NO_8$ (%): C 43.96, H 4.06, N 5.13.

Ethyl *rac*-(1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate (2b) was synthesized as described for compound **2a** starting from 2,2-dimethyl-1,3-dioxane-4,6-dione(193 mg, 1.34 mmol), freshly fused of AcOK (197 mg, 2.01 mmol) and ethyl 3-bromo-3-nitroacrylate (**1b**) (300 mg, 1.34 mmol). After removal of the solvent, diethyl ether was added to the oily residue, the resulting crystals were separated and dried. The yield was 75 mg (20%), colorless crystals, mp 108-111°C (EtOH). IR (KBr), (ν/см$^{-1}$): 1204 (m), 1281 (m), 1326 (s, ν, C-O), 1372 (m, ν_s, NO_2), 1385 (m, δ, CH_3), 1570 (s, ν_{as}, NO_2), 1744 (s), 1781 (m, ν, C=O), 2998 (w), 3036 (w), 3077 (w, ν, C-H). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.29 (t, 3H, $OCH_2C\underline{H}_3$, ^{3}J = 7.2 Hz), 1.89 (s, 3H, CH_3), 1.91 (s, 3H, CH_3), 4.03 (d, 1H, 1-CH, ^{3}J = 6.9 Hz), 4.26 (q, 2H, $OC\underline{H}_2CH_3$, ^{3}J = 7.2 Hz), 5.38

(d, 1H, 2-CH, ^3J = 6.9 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.00 ($OCH_2\underline{C}H_3$), 27.81 (CH_3), 27.92 (CH_3), 34.75 (C^3), 37.76 (C^1), 63.42 ($O\underline{C}H_2CH_3$), 68.09 (C^2), 107.39 (C^6), 161.19, 161.70 (C^4/C^8), 161.78 (C=O). Found (%): C 45.98, H 4.14, N 4.71. Calculated $C_{11}H_{13}NO_8$ (%): C 46.00, H 4.56, N 4.88.

Methyl (*rel*-1*R*,2*S*,3*S*)- & (*rel*-1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate (3'a, 3"a), racemates**.** To a solution of 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (249 mg, 1.43 mmol) and freshly fused of AcOK (210 mg, 2.14 mmol) in anhydrous MeOH (10 ml), a solution of methyl 3-bromo-3-nitroacrylate (**1a**) (300 mg, 1.43 mmol) in anhydrous MeOH (5 ml) was added dropwise. The resulted mixture was stirred for 3 h at 18-20 °C and then poured on crushed ice. The product was extracted with $CHCl_3$ (3×20 ml). The combined extracts were dried over $MgSO_4$, filtered and evaporated to dryness to give 330 mg (77%) of the residue of a mixture of diastereomers (NMR: **3'a**/**3"a** = 2:1), which was separated by column chromatography on silica gel (eluent C_6H_{14}–EtOAc = 3:1). After the second chromatography, 200 mg (47%) of diastereomer **3'a** and 50 mg (12%) of diastereomer **3"a** were obtained.

Diastereomer *rac*-***rel*-1*R*,2*S*,3*S* (3'a)**: colorless crystals, R_f 0.42 (C_6H_{14}–EtOAc, 3:1), mp 119-121 (MeOH). IR ($CHCl_3$), ν/см$^{-1}$: 1277 (m), 1287 (m, ν, C-O), 1321 (s, ν, C-N), 1366 (s, ν_s, NO_2), 1374 (s, δ, CH_3), 1501 (s, ν, N-C=O, arC-C), 1562 (s, ν_{as}, NO_2), 1597 (m, ν, C=N, arC-C), 1717 (s), 1751 (s, ν, C=O), 2957 (w), 3029 (w, ν, C-H). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 2.11 (s, 3H, CH_3), 3.80 (s, 3H, OCH_3), 3.96 (d, 1H, 1-CH, ^3J = 6.3 Hz), 5.26 (d, 1H, 2-CH, ^3J = 6.3 Hz), 7.22 (t, 1H, H^p Ph, ^3J = 7.5 Hz), 7.41 (dd, 2H, H^m Ph, ^3J = 7.5, 8.5 Hz), 7.84 (d, 2H, H^o Ph, ^3J = 8.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.85 (CH_3), 34.39 (C^1), 43.56 (C^3), 53.63 (OCH_3), 68.34 (C^2), 118.88 (C^o Ph), 125.99 (C^p Ph), 129.12 (C^m Ph), 137.47 (C^i Ph), 152.05 (C^4), 162.40 (C=O), 165.26 (C^7). ЯМР ^{15}N, δ: -45.9 (N^5), -12.1 (NO_2).Found (%): C 55.02, H 4.13, N 14.07. Calculated $C_{14}H_{13}N_3O_5$ (%): C 55.45, H 4.32, N 13.86.

***Diastereomer rac*-*rel*-1*R*,2*S*,3*R* (3"a)**: yellow crystals, R_f 0.26 (C_6H_{14}–EtOAc, 3:1), mp 97-100°C (MeOH). IR ($CHCl_3$), ν/см$^{-1}$: 1261 (m), 1288 (m, ν, C-O), 1327 (s, ν, C-N), 1360 (m, ν_s, NO_2), 1374 (m, δ, CH_3), 1501 (s, ν, N-C=O, arC-C), 1565 (s, ν_{as}, NO_2), 1597 (m, ν, C=N, arC-C), 1722 (s), 1742 (s, ν, C=O), 2958 (w), 3033 (w, ν, C-H). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 2.13 (s, 3H, CH_3), 3.75 (d, 1H, 1-CH, ^3J = 6.4 Hz), 3.84 (s, 3H, OCH_3), 5.37 (d, 1H, 2-CH, ^3J = 6.4 Hz), 7.21 (t, 1H, H^p Ph, ^3J = 7.5 Hz), 7.40 (dd, 2H, H^m Ph, ^3J = 7.5, 8.7 Hz), 7.84 (d, 2H, H^o Ph, ^3J = 8.7 Hz). ^{13}C NMR ($CDCl_3$), δ: 15.25 (CH_3), 36.66 (C^1), 42.85 (C^3), 53.70 (OCH_3), 66.66 (C^2), 118.89 (C^o Ph), 125.93 (C^p Ph), 129.09 (C^m Ph), 137.54 (C^i Ph), 152.86 (C^4), 164.39 (C=O), 164.83 (C^7). Found (%): C 55.10, H 4.16, N 14.05. Calculated $C_{14}H_{13}N_3O_5$ (%): C 55.45, H 4.32, N 13.86.

Ethyl (*rel*-1*R*,2*S*,3*S*)- & (*rel*-1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate (3'b, 3"b), racemates, were synthesized as described for compound **3'a, 3"a** starting from 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (233 mg, 1.34 mmol), freshly fused of AcOK (300 mg, 1.34 mmol) and ethyl 3-bromo-3-nitroacrylate (**1b**) (300 mg, 1.34 mmol). The resulted mixture was stirred for 3 h at 18-20 °C and then poured on crushed ice. The precipitate was filtered off. The yield was 280 mg (67%) a mixture of diastereomers (NMR: **3'b**/**3"b** = 2:1), which was separated by column chromatography on silica gel (eluent C_6H_{14}–EtOAc = 3 : 1). After the second chromatography, 80 mg (19%) of diastereomer **3'b** and 40 mg (10%) of diastereomer **3"b** were obtained.

Diastereomer *rac*-***rel*-1*R*,2*S*,3*S* (3'b)**: colorless crystals, R_f 0.6 (C_6H_{14}–EtOAc, 3:1), mp 143-145°C (EtOH). IR ($CHCl_3$), ν/см$^{-1}$: 1272 (m), 1283 (m, ν, C-O), 1321 (s, ν, C-N), 1363 (s, ν_s, NO_2), 1374 (s, δ, CH_3), 1501 (m, ν, N-C=O, arC-C), 1561 (s, ν_{as}, NO_2), 1597 (m, ν, C=N, arC-C), 1717 (s), 1747 (s, ν, C=O), 3029 (w, ν, C-H). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.29 (t, 3H, $OCH_2C\underline{H}_3$, ^3J = 7.2 Hz), 2.11 (s,

CH_3), 3.95 (d, 1H, 1-CH, ^3J = 6.3 Hz), 4.26 (q, 2H, OC$\underline{H}_2$CH$_3$, ^3J = 7.2 Hz), 5.25 (d, 1H, 2-CH,^3J = 6.3 Hz), 7.22 (t, 1H, H^p Ph, ^3J = 7.5 Hz), 7.41 (dd, 2H, H^m Ph, ^3J = 7.5, 8.5 Hz), 7.84 (d, 2H, H^o Ph, ^3J = 8.5 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.14 (OCH$_2\underline{C}$H$_3$), 14.85 (CH_3), 34.61 (C^1), 43.63 (C^3), 63.11 (O$\underline{C}$H$_2$CH$_3$), 68.42 (C^2), 118.86 (C^o Ph), 125.94 (C^p Ph), 129.12 (C^m Ph), 137.51 (C^i Ph), 152.10 (C^4), 161.89 (C=O), 165.23 (C^7). ^{15}N NMR ($CDCl_3$), δ: -46.4 (N^5), -14.3 (NO_2). Found (%): C 56.41, H 4.49, N 13.31. Calculated $C_{15}H_{15}N_3O_5$ (%): C 56.78, H 4.77, N 13.24.

***Diastereomer rac-rel*-1*R*,2*S*,3*R* (3b′′)**: yellow oil, R_f 0.51 (C_6H_{14}–EtOAc, 3:1). IR ($CHCl_3$), ν/см$^{-1}$: 1287 (m), 1295 (m, ν, C-O), 1327 (s, ν, C-N), 1370 (s, ν_s, NO_2), 1373 (s, δ, CH_3), 1501 (s, ν, N-C=O, arC-C), 1564 (s, ν_{as}, NO_2), 1597 (m, ν, C=N, arC-C), 1723 (s), 1743 (shoulder, ν, C=O). ^{1}H NMR ($CDCl_3$), δ, (*J*, Hz): 1.33 (t, 3H, OCH$_2$C$\underline{H}_3$, ^3J = 7.2 Hz), 2.13 (s, CH_3), 3.73 (d, 1H, 1-CH, ^3J = 6.4 Hz), 4.26 (dq, 1H, OC$\underline{H}_2$CH$_3$, ^3J = 7.2, ^2J 10.8 Hz), 4.30 (dq, 1H, OC$\underline{H}_2$CH$_3$, ^3J = 7.2, ^2J = 10.8 Hz), 5.37 (d, 1H, 2-CH, ^3J = 6.4 Hz), 7.21 (t, 1H, H^p Ph, ^3J = 7.5 Hz), 7.39 (dd, 2H, H^m Ph, ^3J = 7.5, 8.6 Hz), 7.85 (d, 2H, H^o Ph, ^3J = 8.6 Hz). ^{13}C NMR ($CDCl_3$), δ: 14.10 (OCH$_2\underline{C}$H$_3$), 15.27 (CH_3), 36.91 (C^1), 42.87 (C^3), 63.28 (O$\underline{C}$H$_2$CH$_3$), 66.70 (C^2), 118.85 (C^o Ph), 125.89 (C^p Ph), 129.08 (C^m Ph), 137.59 (C^i Ph), 152.98 (C^4), 164.31 (C=O), 164.47 (C^7). Found (%): C 56.30, H 4.51, N 13.00. Calculated $C_{15}H_{15}N_3O_5$ (%): C 56.78, H 4.77, N 13.24.

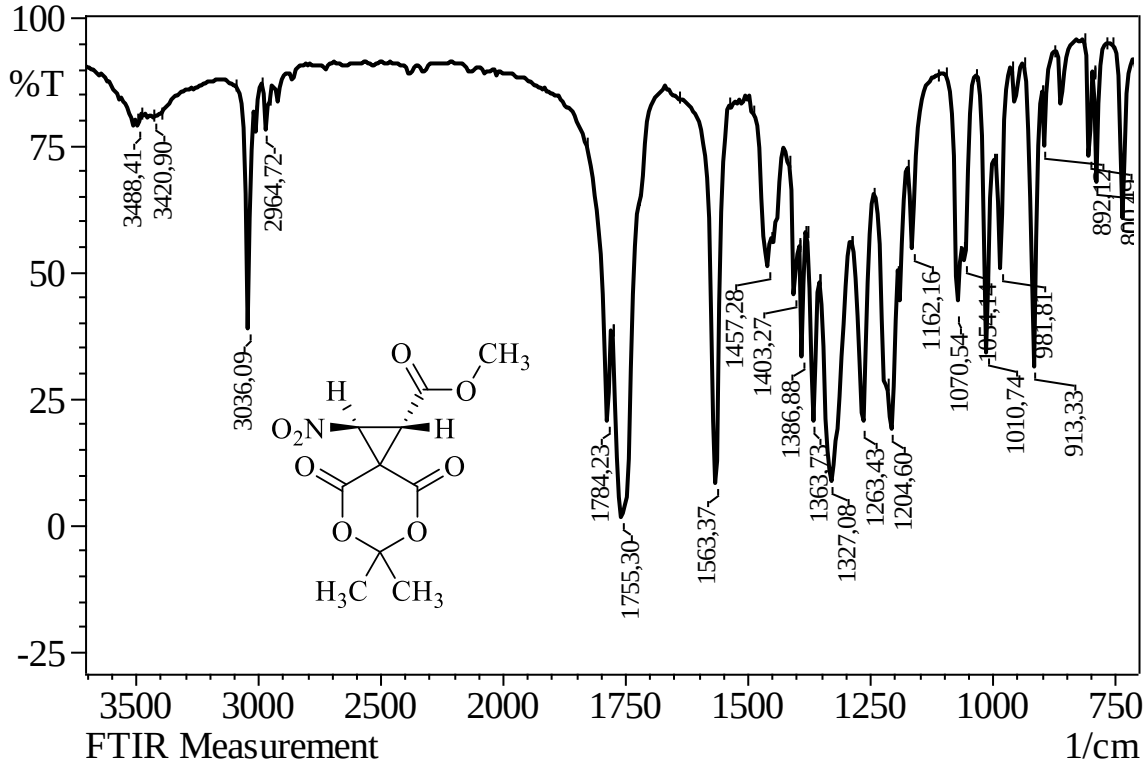


Figure S1. IR spectrum of methyl (1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate **2a** in KBr.

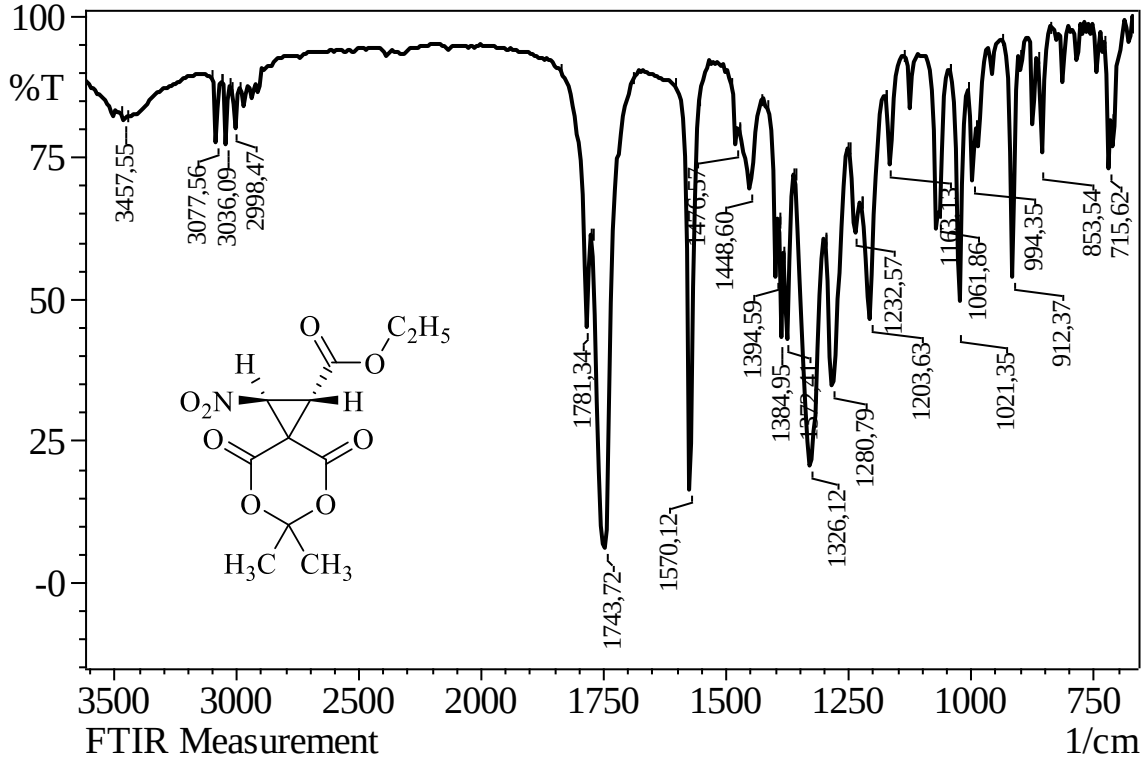


Figure S2. IR spectrum of ethyl (1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate **2b** in KBr.

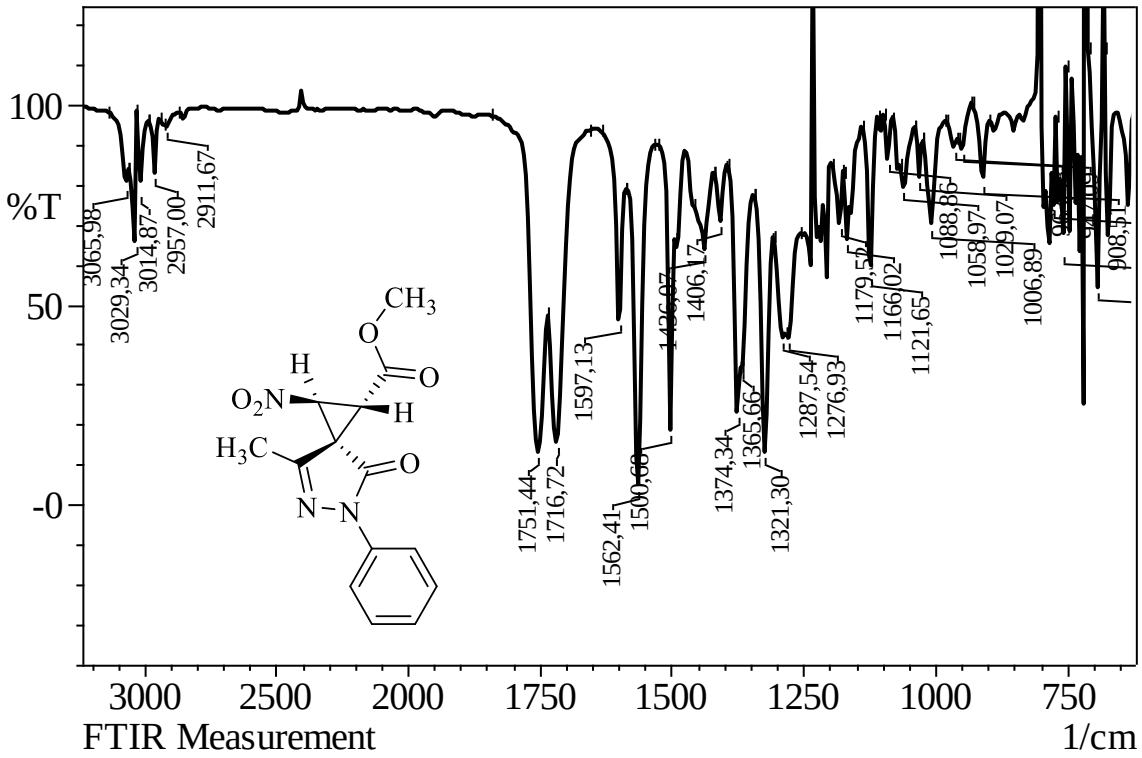


Figure S3. IR spectrum of methyl (*1R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'a** in $CHCl_3$.

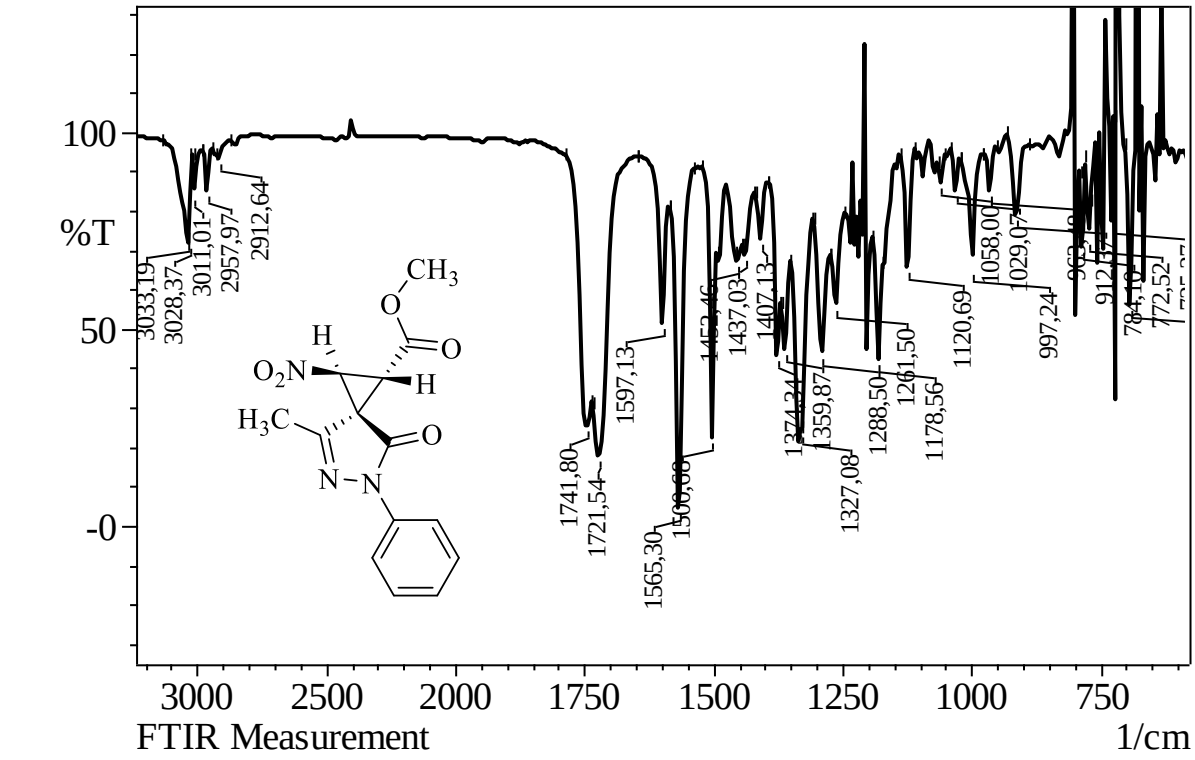


Figure S4. IR spectrum of methyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"a** in $CHCl_3$.

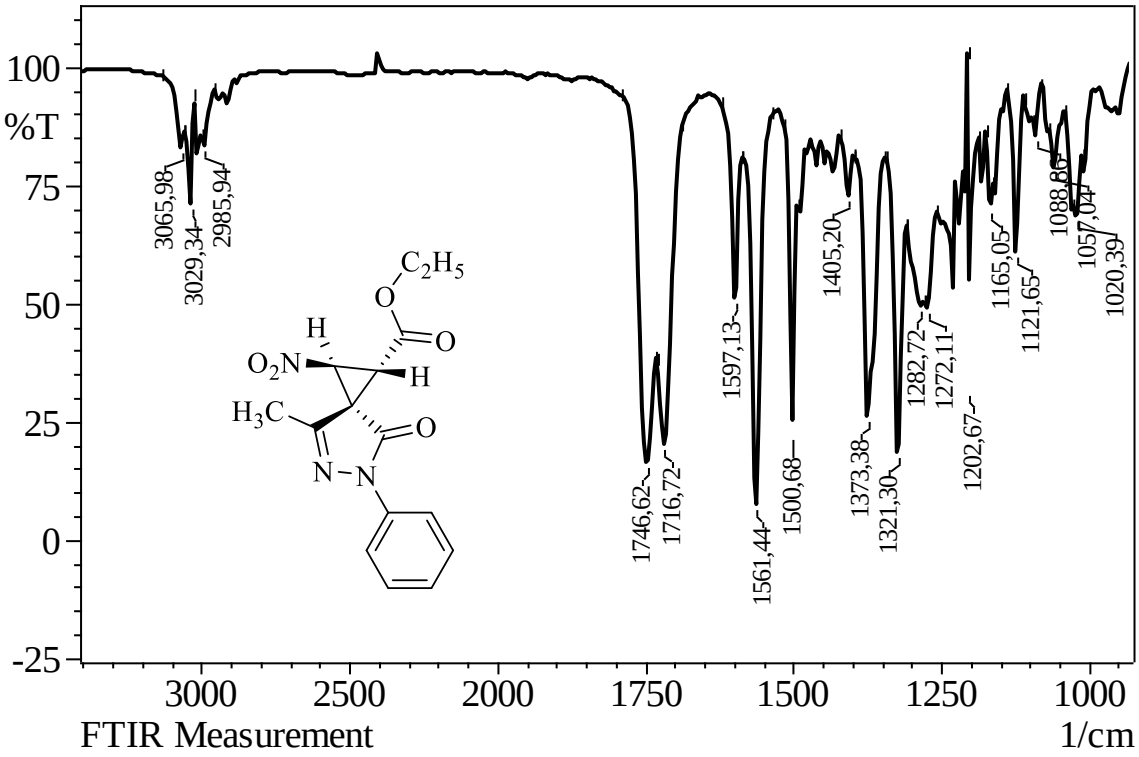


Figure S5. IR spectrum of ethyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'b** in $CHCl_3$.

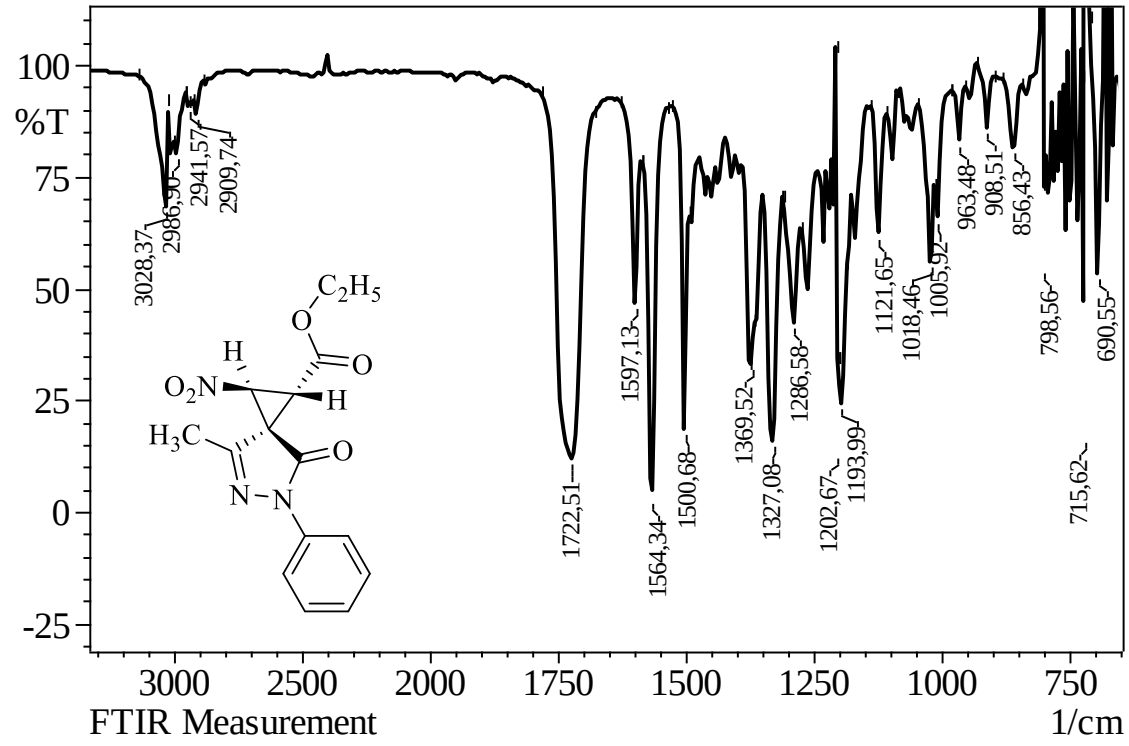


Figure S6. IR spectrum of ethyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"b** in $CHCl_3$.

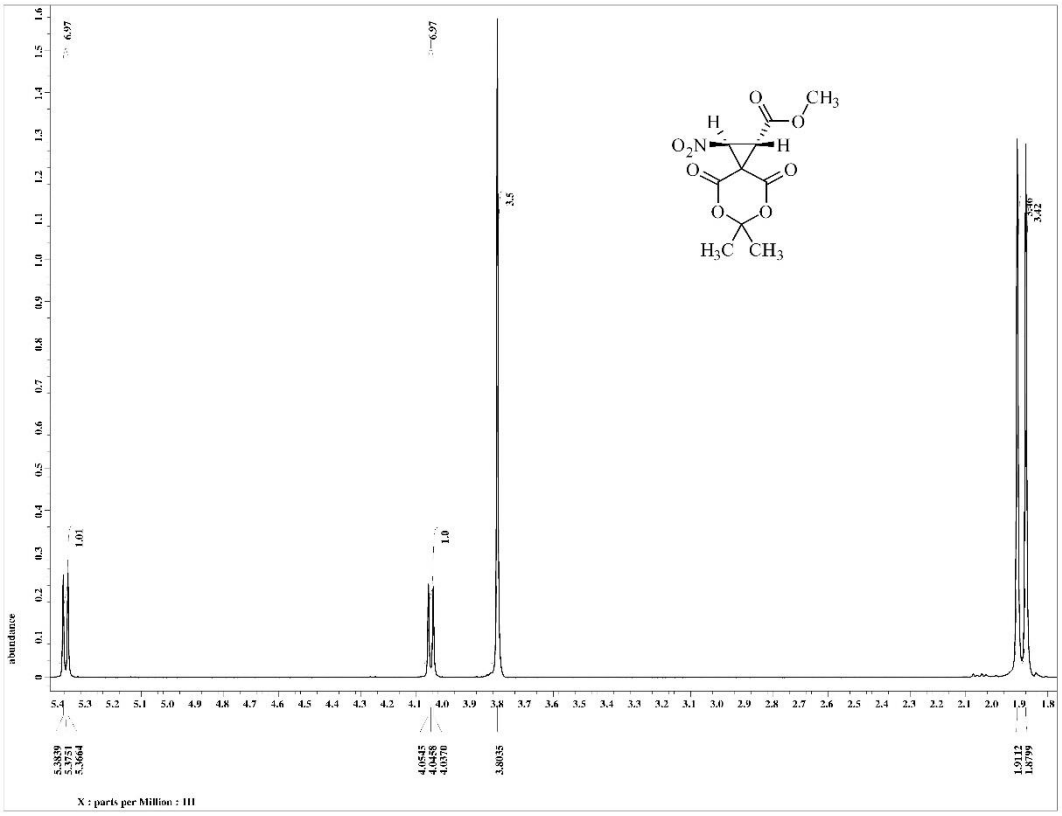


Figure S7. ^{1}H NMR spectrum of methyl (1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate **2a** in $CDCl_3$.

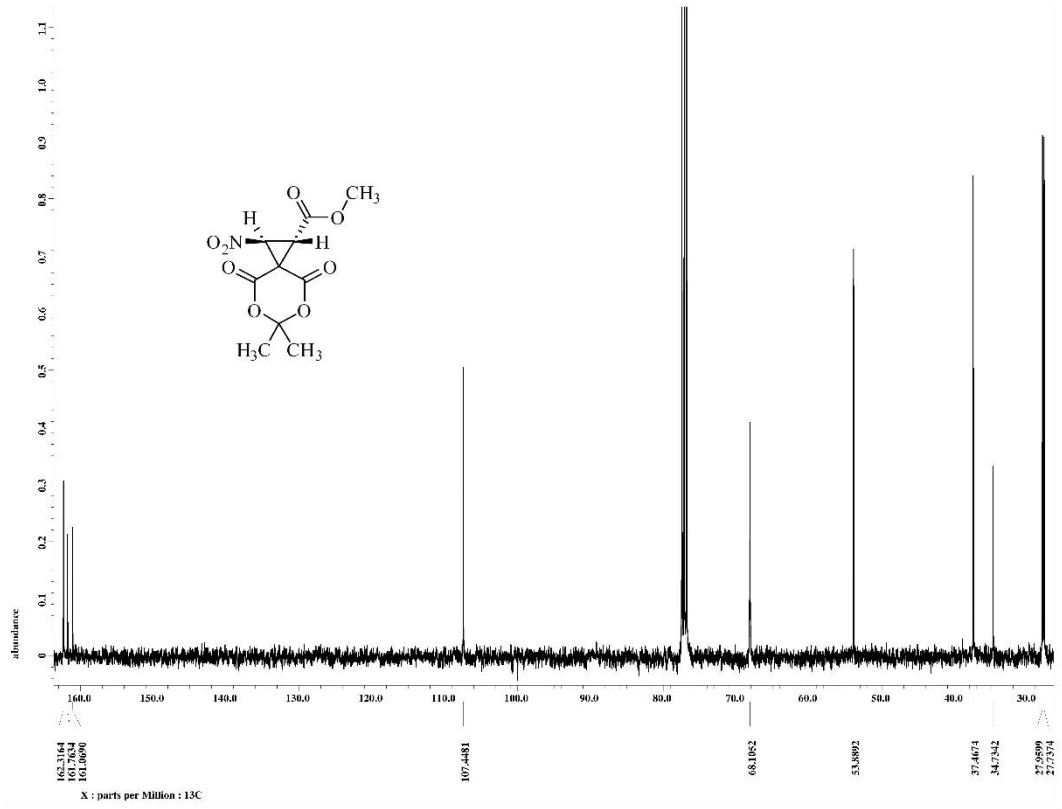


Figure S8. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate **2a** in $CDCl_3$.

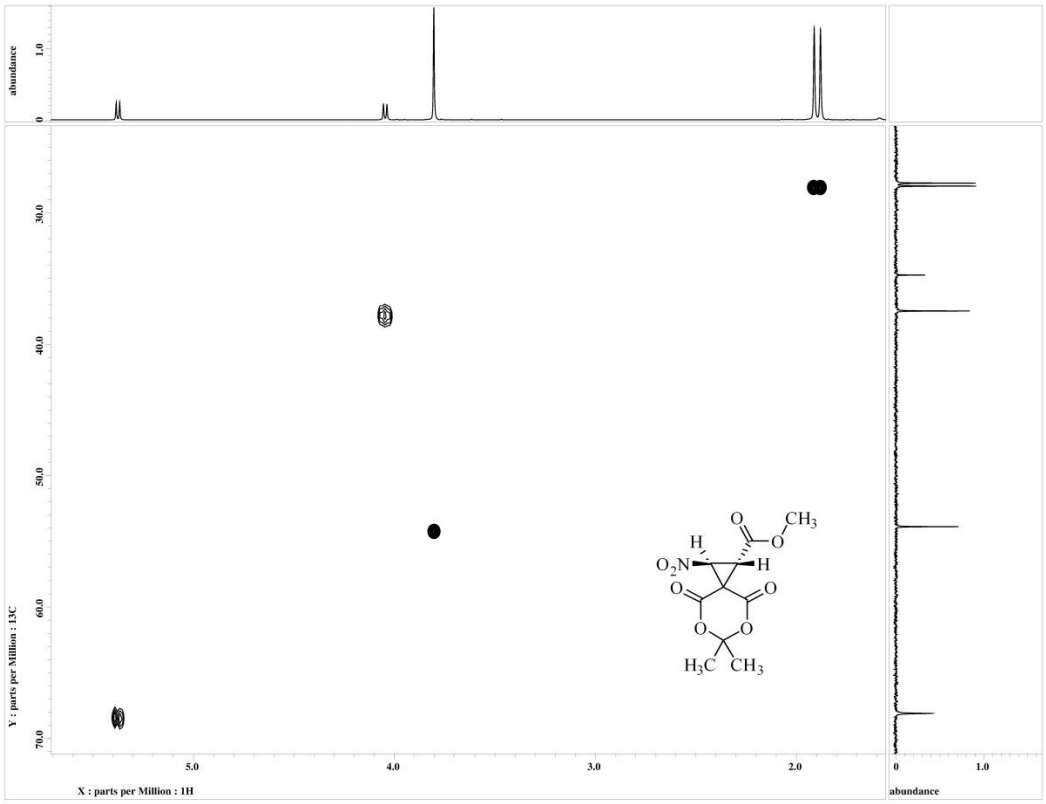


Figure S9. ^{1}H-^{13}C HMQC spectrum of methyl (1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate **2a** in $CDCl_3$.

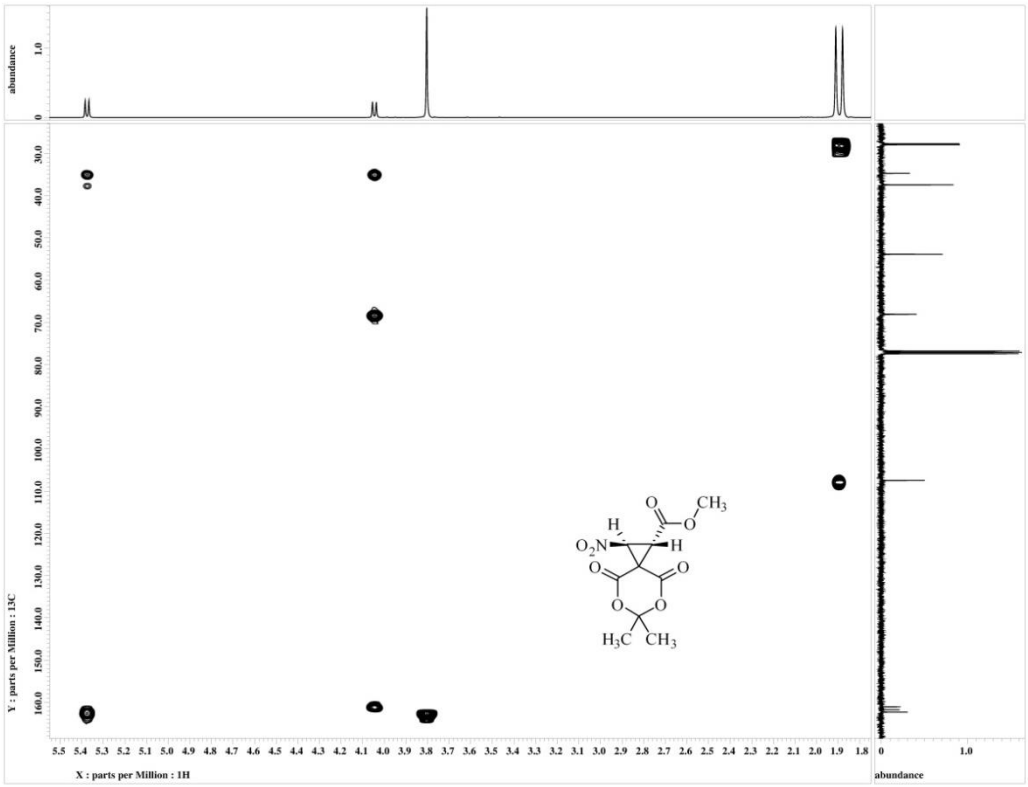


Figure S10. ^{1}H-^{13}C HMBC spectrum of methyl (1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate **2a** in $CDCl_3$.

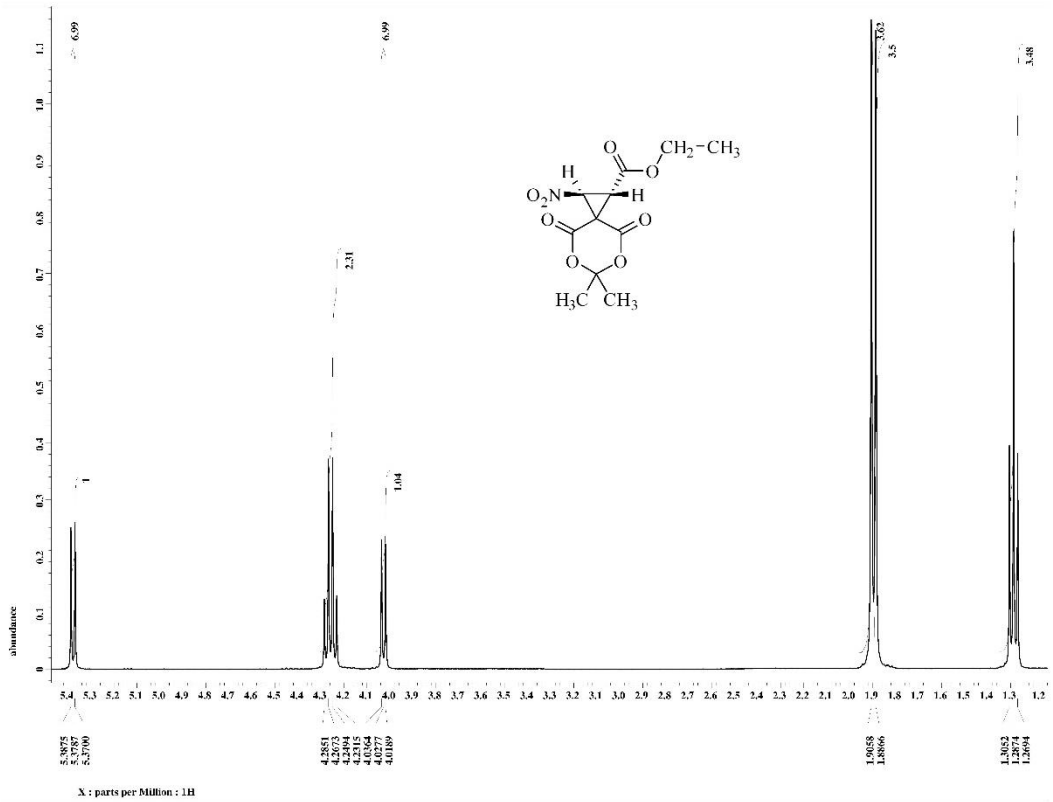


Figure S11. ^{1}H NMR spectrum of ethyl (1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate **2b** in $CDCl_3$.

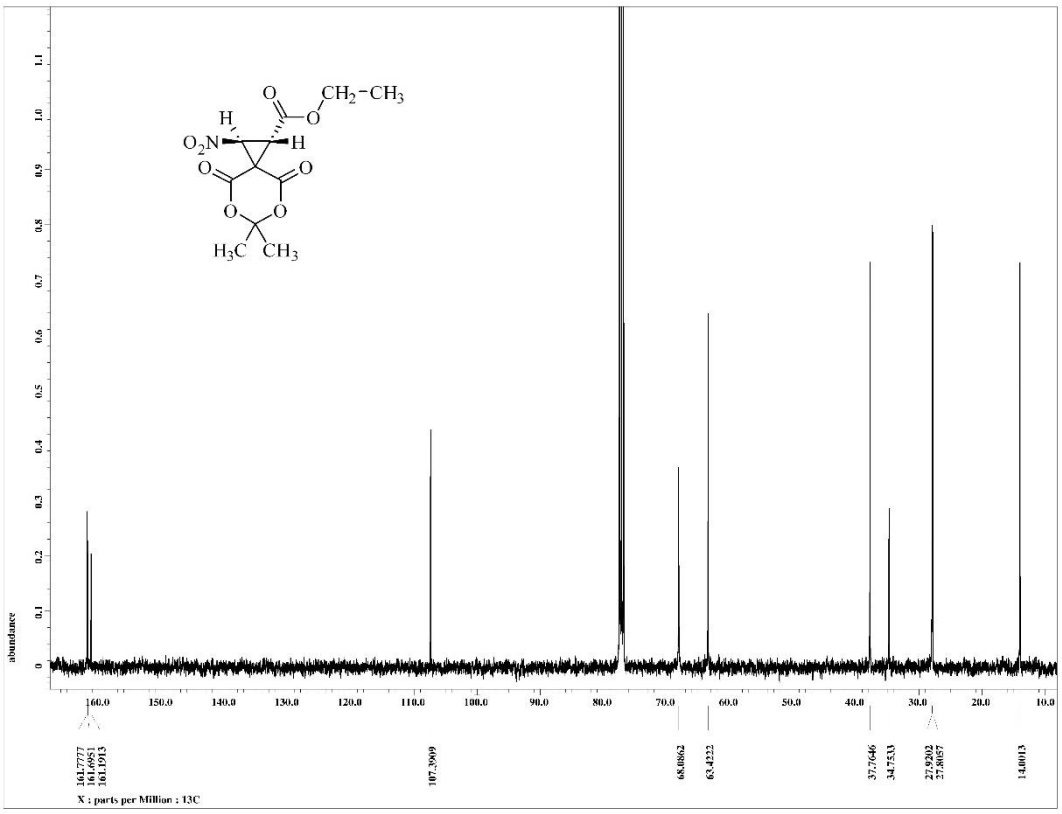


Figure S12. ^{13}C{^{1}H} NMR spectrum of ethyl (1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate **2b** in $CDCl_3$.

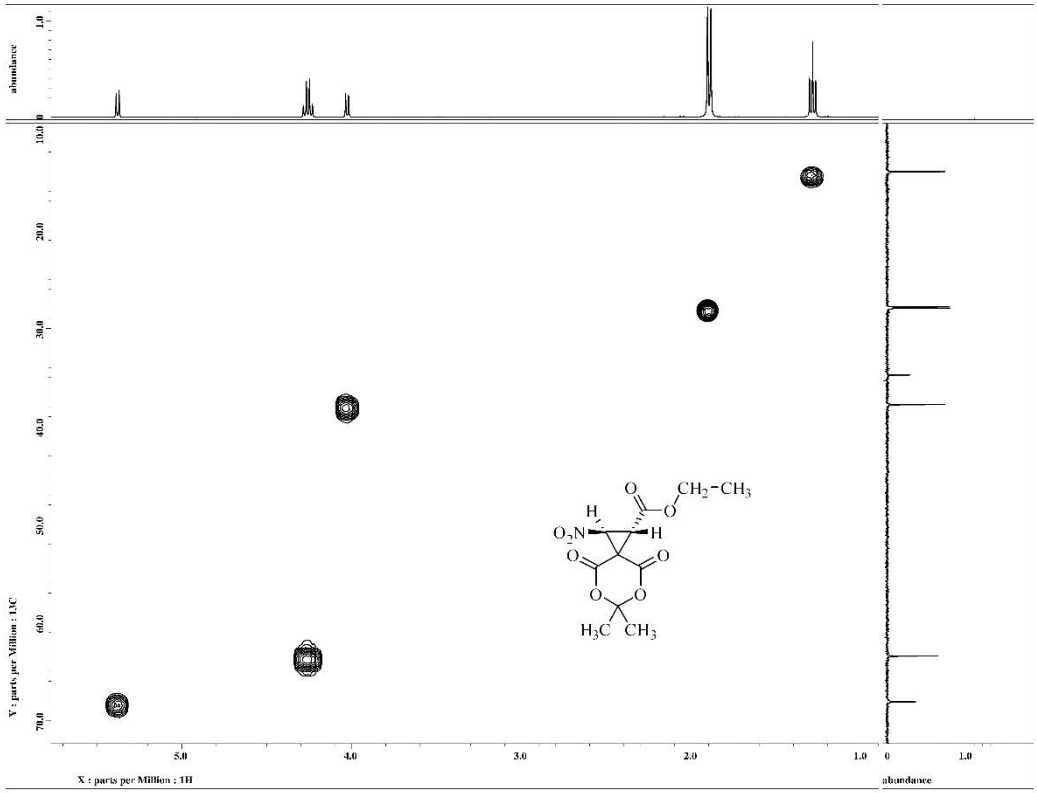


Figure S13. ^{1}H-^{13}C HMQC spectrum of ethyl (1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate **2b** in $CDCl_3$.

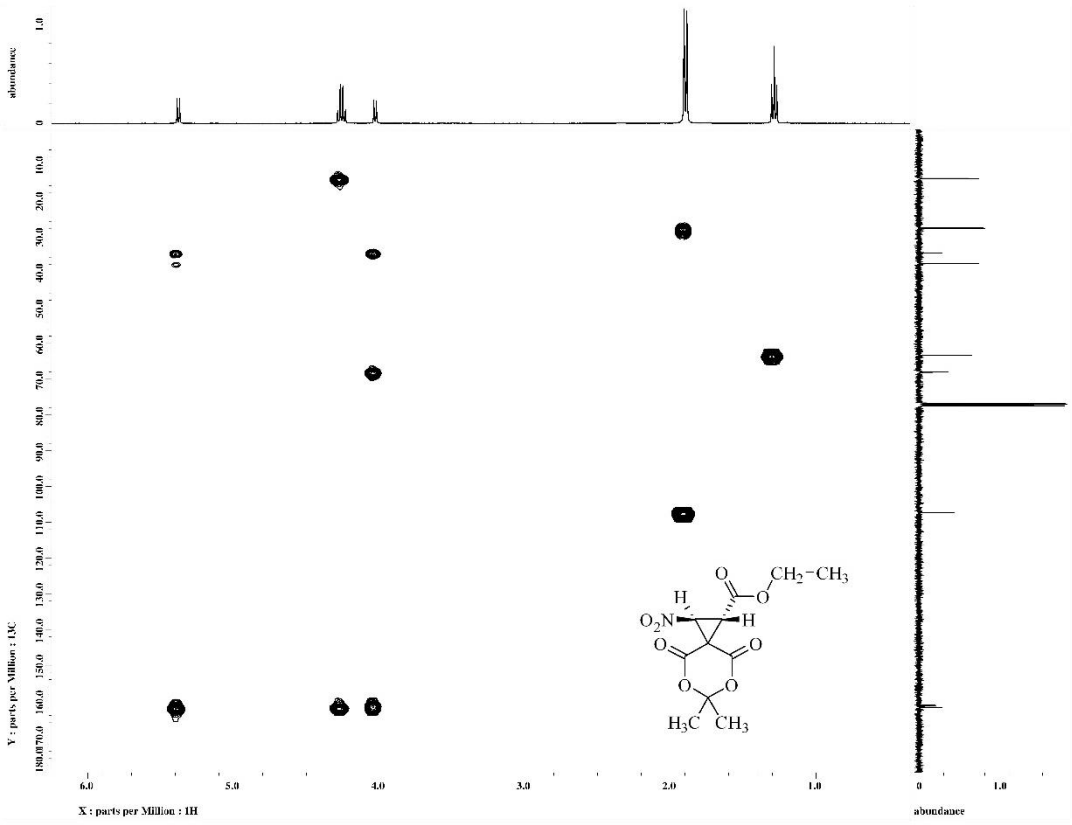


Figure S14. ^{1}H-^{13}C HMBC spectrum of ethyl (1*R*,2*S*)-6,6-dimethyl-2-nitro-4,8-dioxo-5,7-dioxaspiro[2.5]octane-1-carboxylate **2b** in $CDCl_3$.

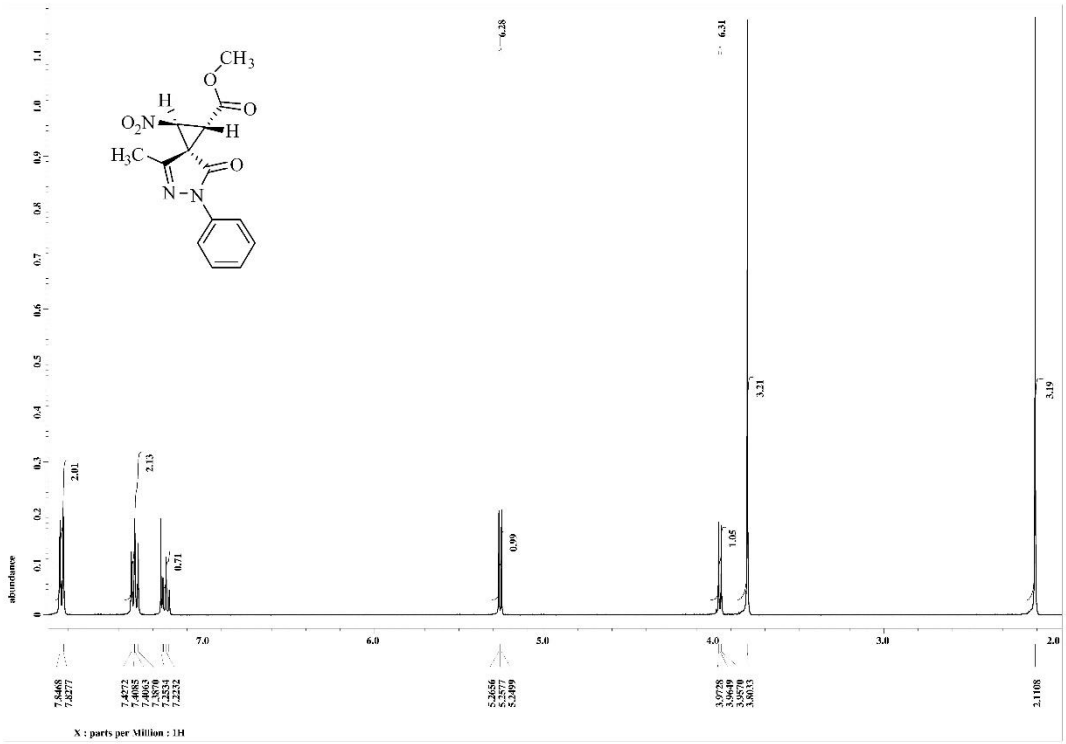


Figure S15. ^{1}H NMR spectrum of methyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'a** in $CDCl_3$.

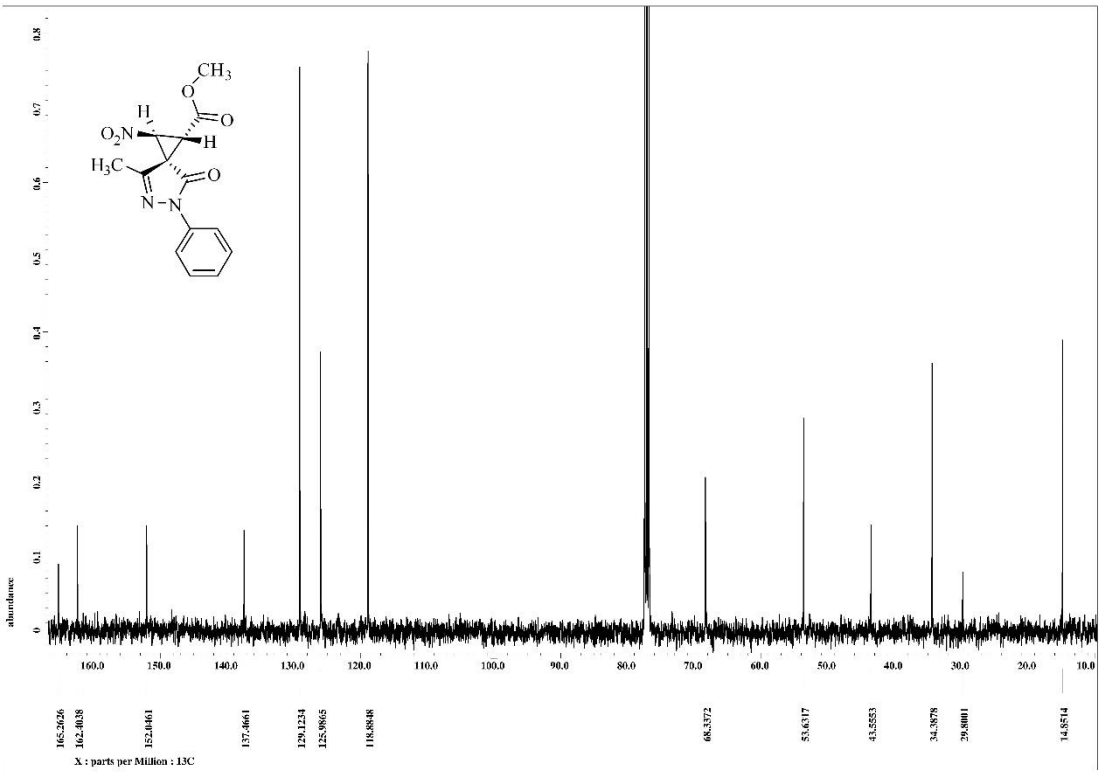


Figure S16. ^{13}C{^{1}H} NMR spectrum of methyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'a** in $CDCl_3$.

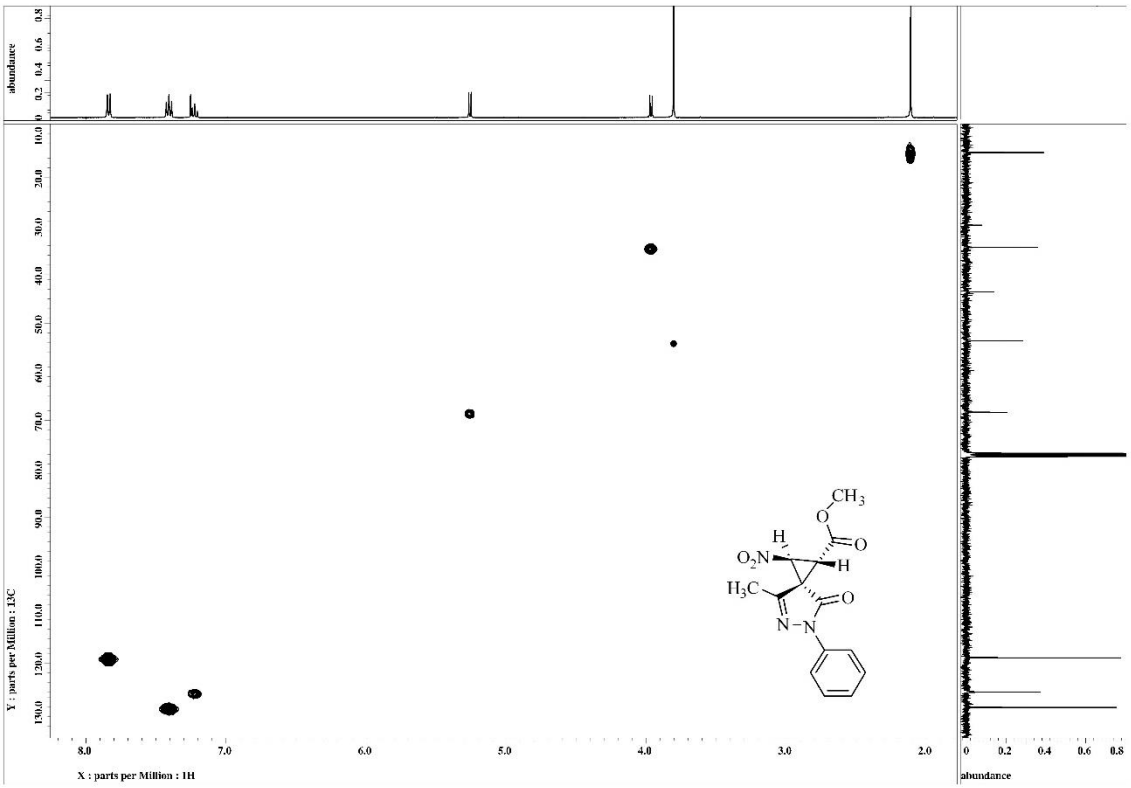


Figure S17. ^{1}H-^{13}C HMQC spectrum of methyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'a** in $CDCl_3$.

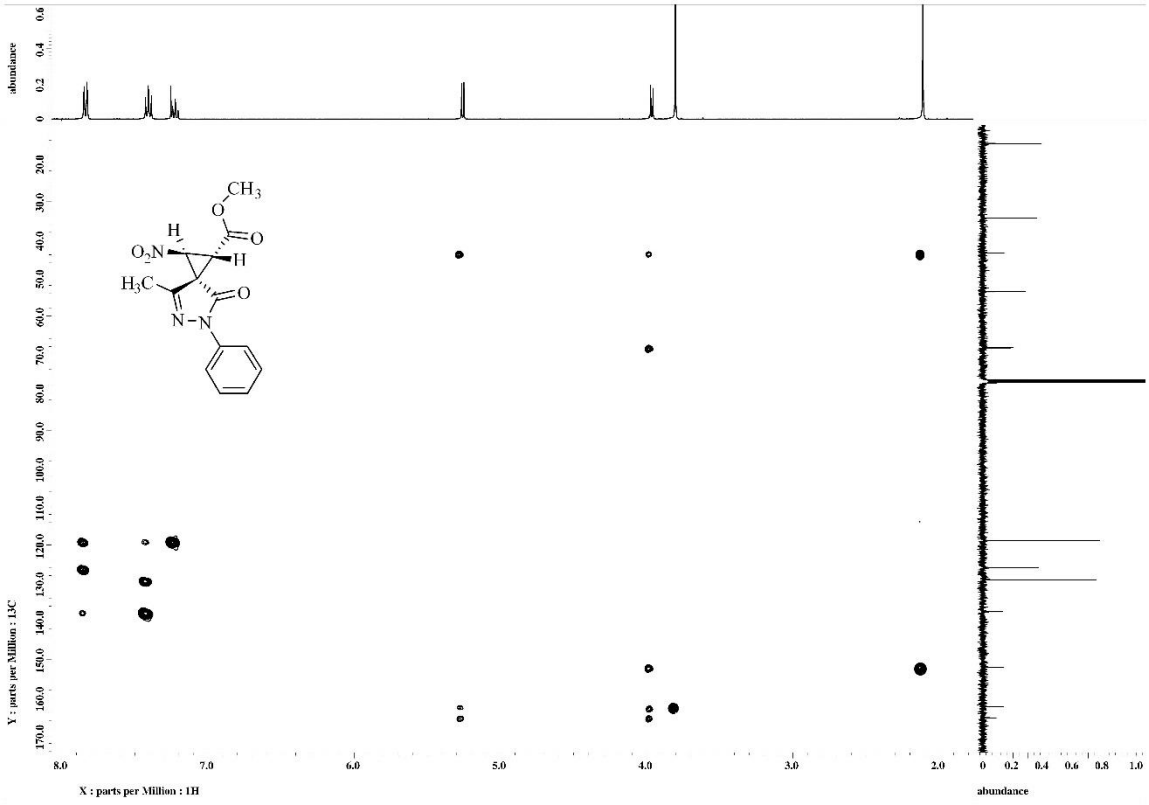


Figure S18. ^{1}H-^{13}C HMBC spectrum of methyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'a** in $CDCl_3$.

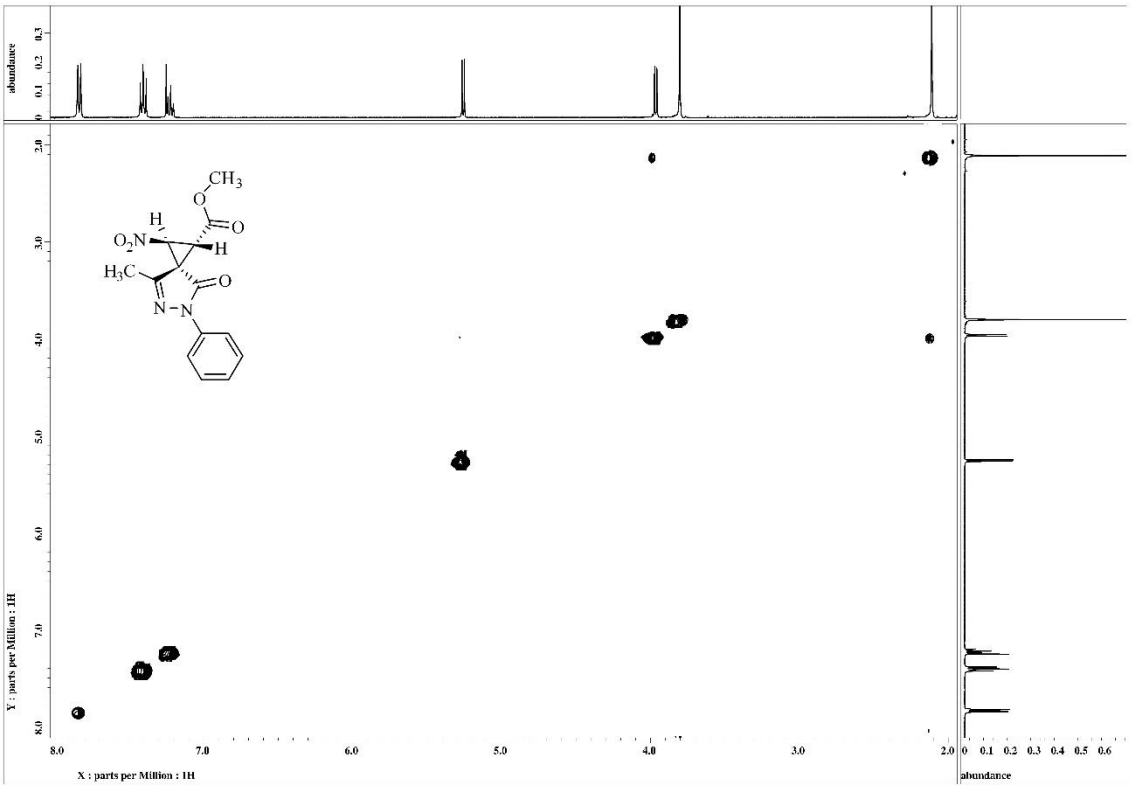


Figure S19. ^{1}H-^{1}H NOESY spectrum of methyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'a** in $CDCl_3$.

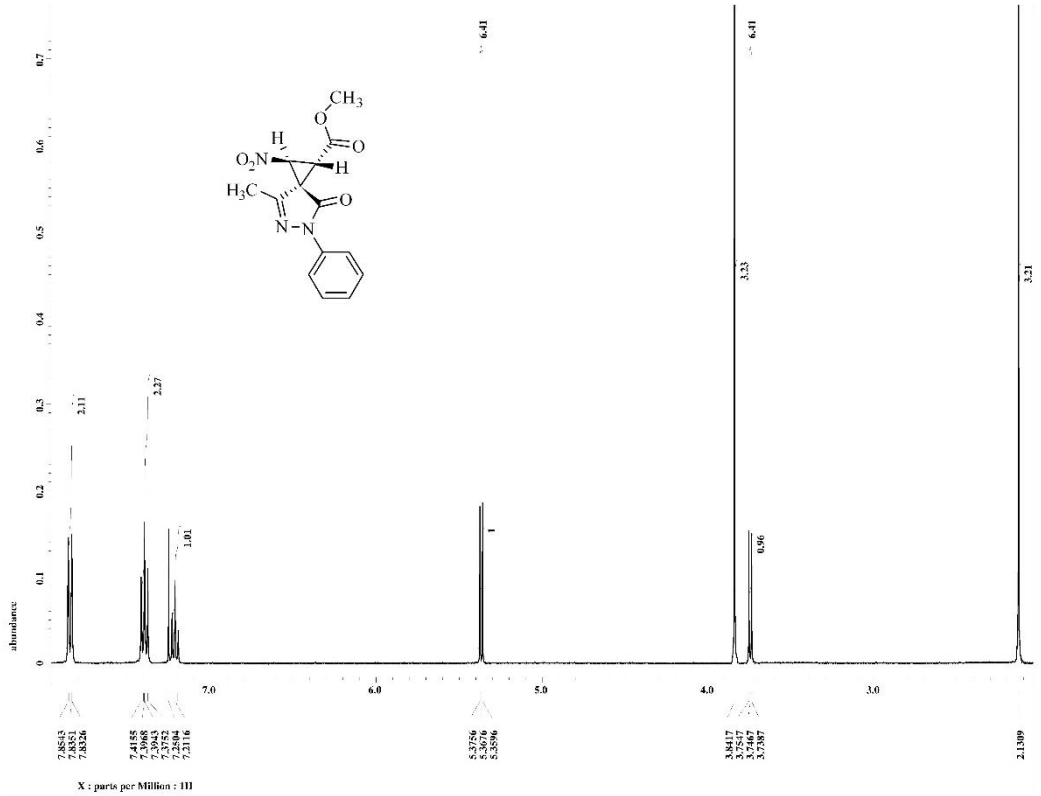


Figure S20. ^{1}H NMR spectrum of methyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"a** in $CDCl_3$.

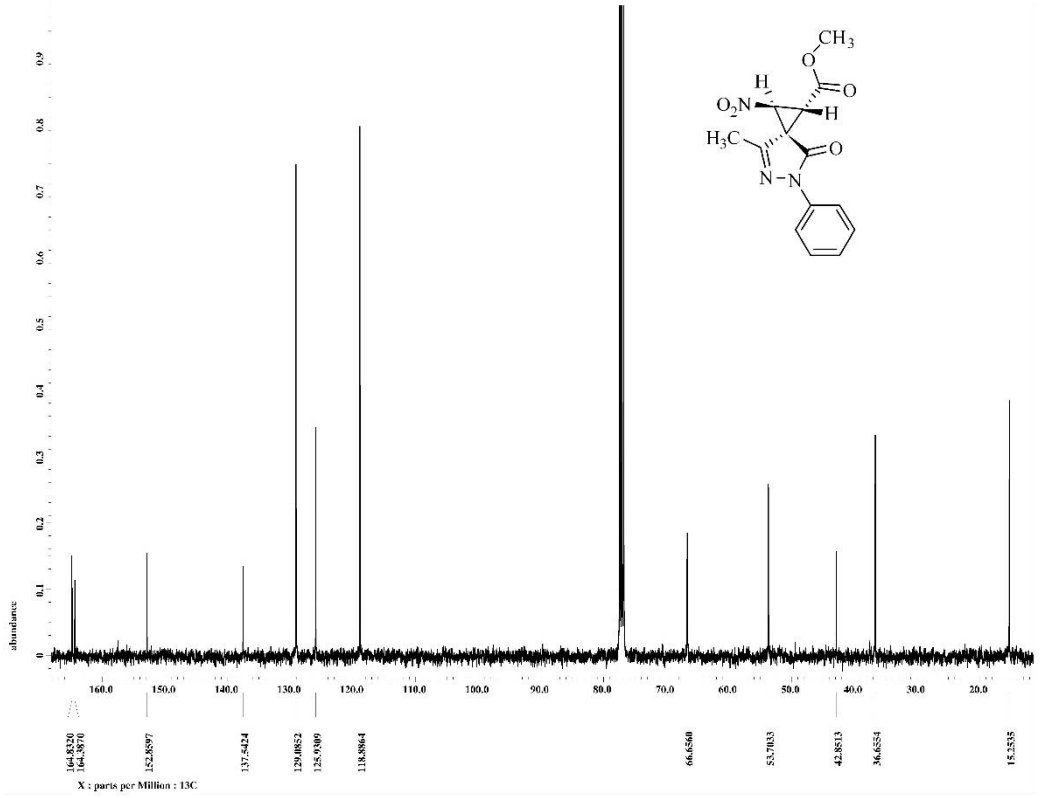


Figure S21. $^{13}C\{^{1}H\}$ NMR spectrum of methyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"a** in $CDCl_3$.

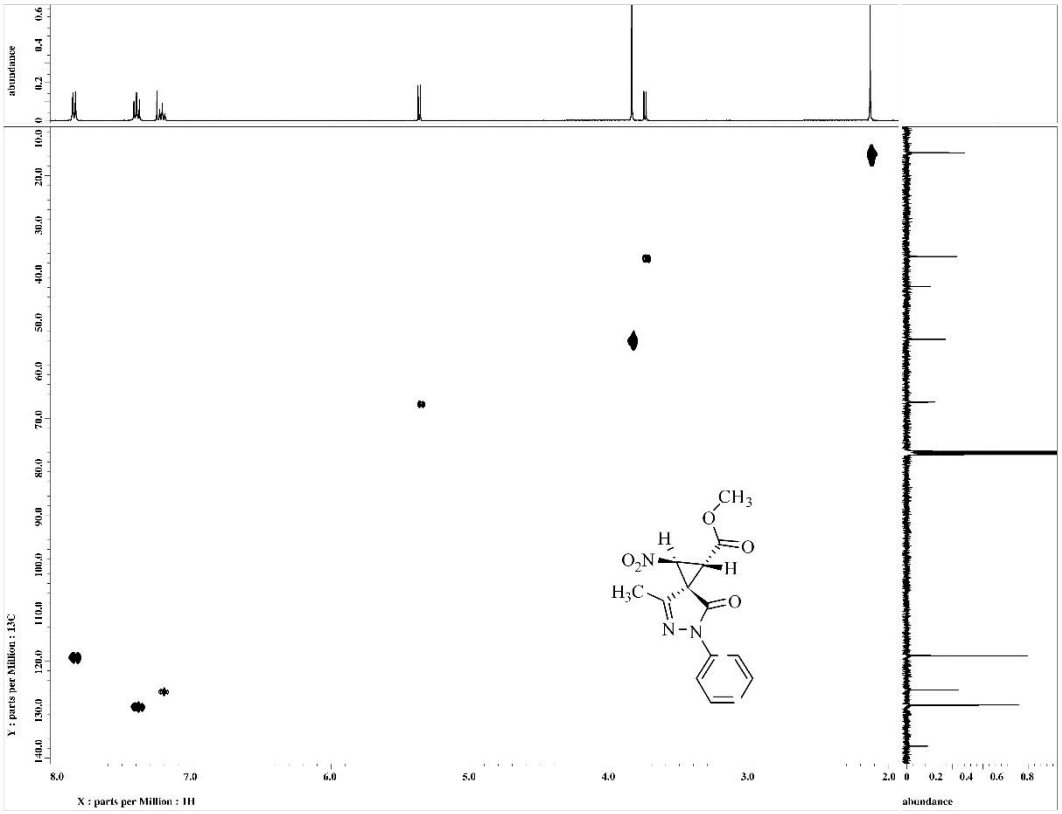


Figure S22. ^{1}H-^{13}C HMQC spectrum of methyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"a** in $CDCl_3$.

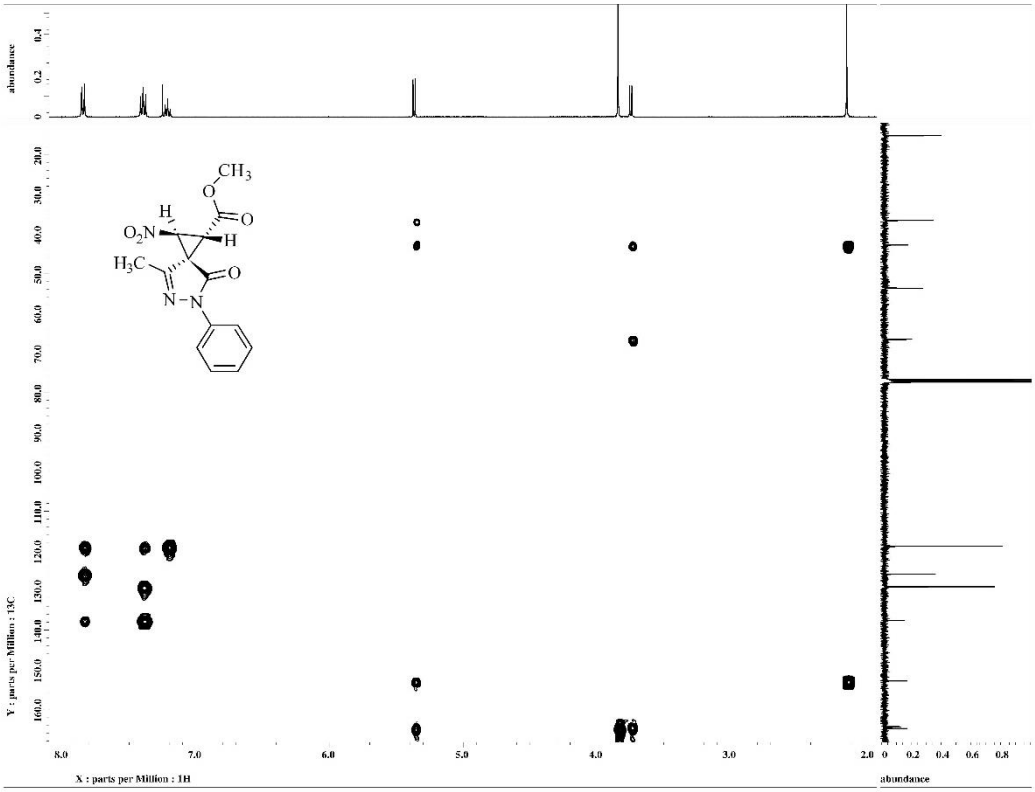


Figure S23. ^{1}H-^{13}C HMBC spectrum of methyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"a** in $CDCl_3$.

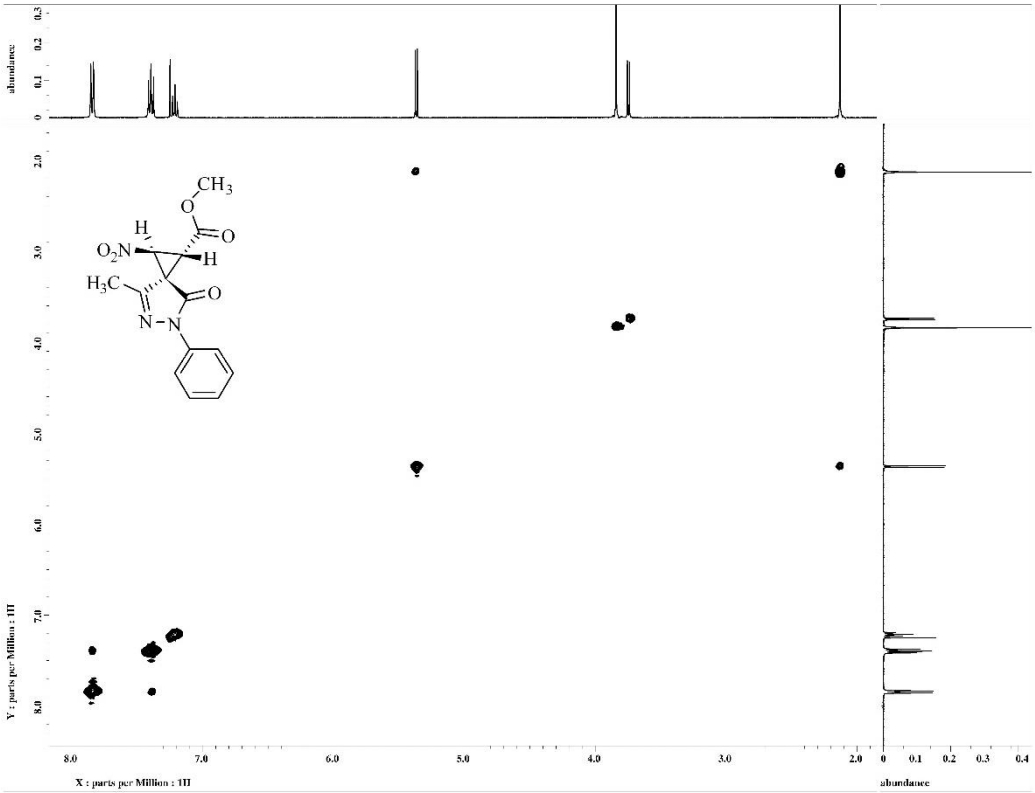


Figure S24. ^{1}H-^{1}H NOESY spectrum of methyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"a** in $CDCl_3$.

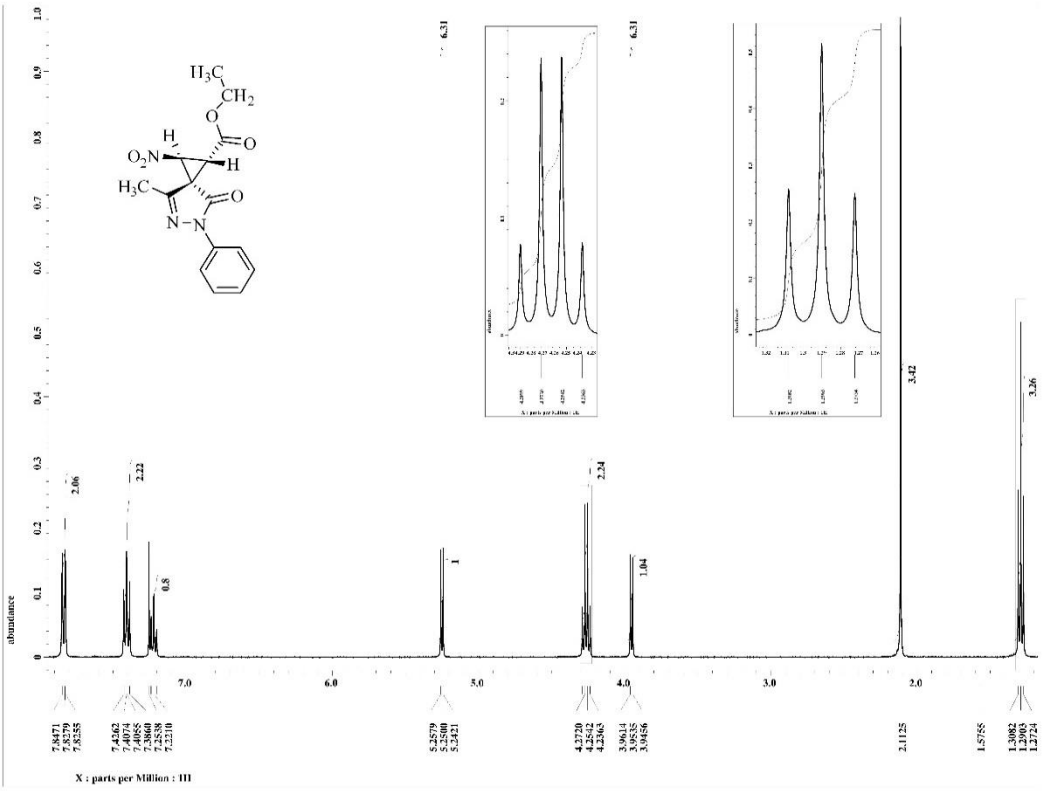


Figure S25. ^{1}H NMR spectrum of ethyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'b** in $CDCl_3$.

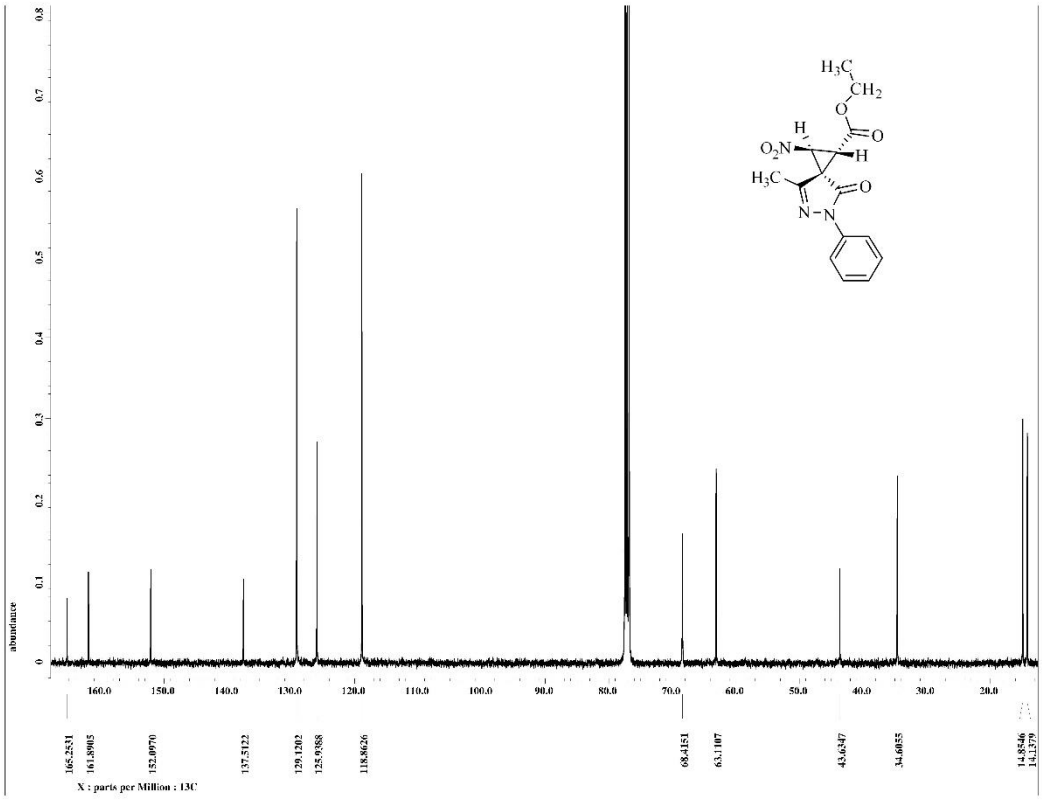


Figure S26. $^{13}C\{^{1}H\}$ NMR spectrum of ethyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'b** in $CDCl_3$.

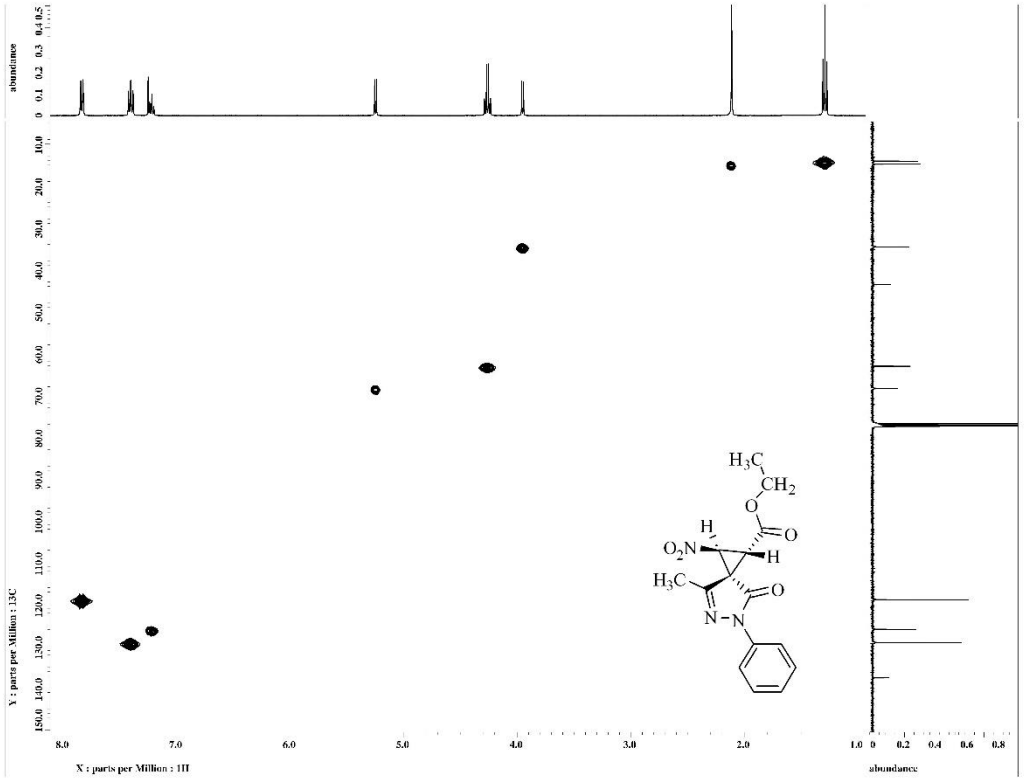


Figure S27. ^{1}H-^{13}C HMQC spectrum of ethyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'b** in $CDCl_3$.

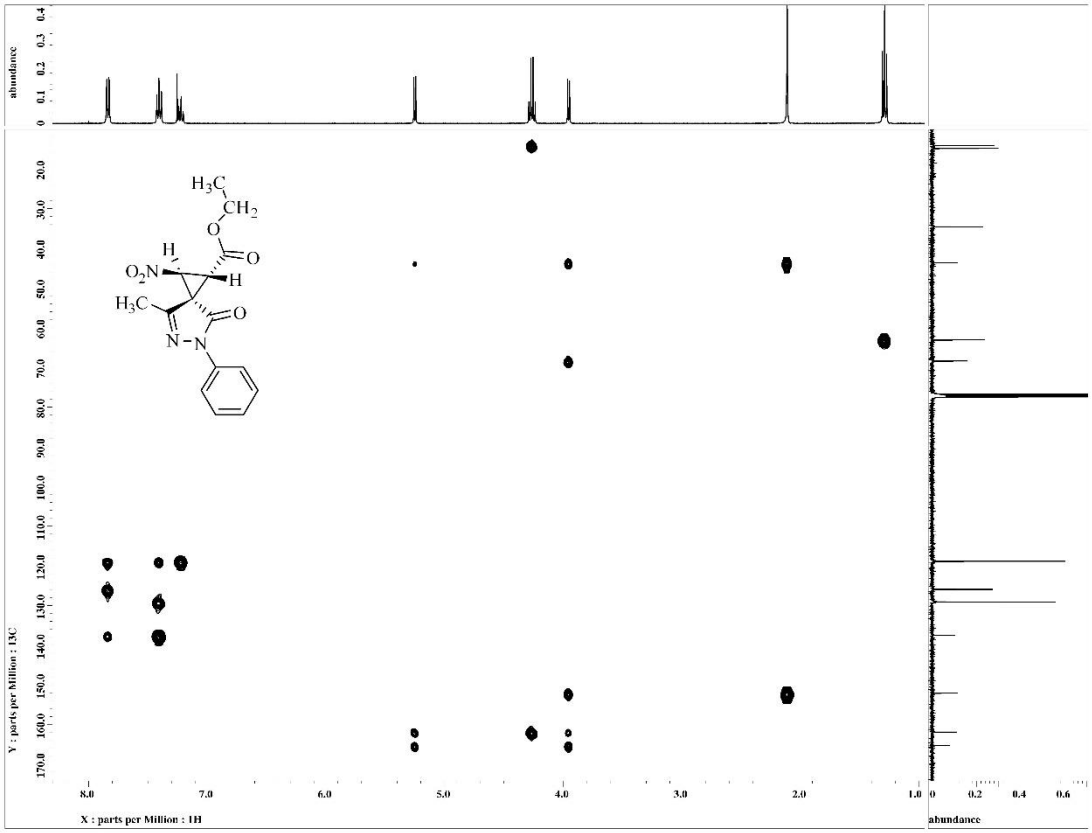


Figure S28. ^{1}H-^{13}C HMBC spectrum of ethyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'b** in $CDCl_3$.

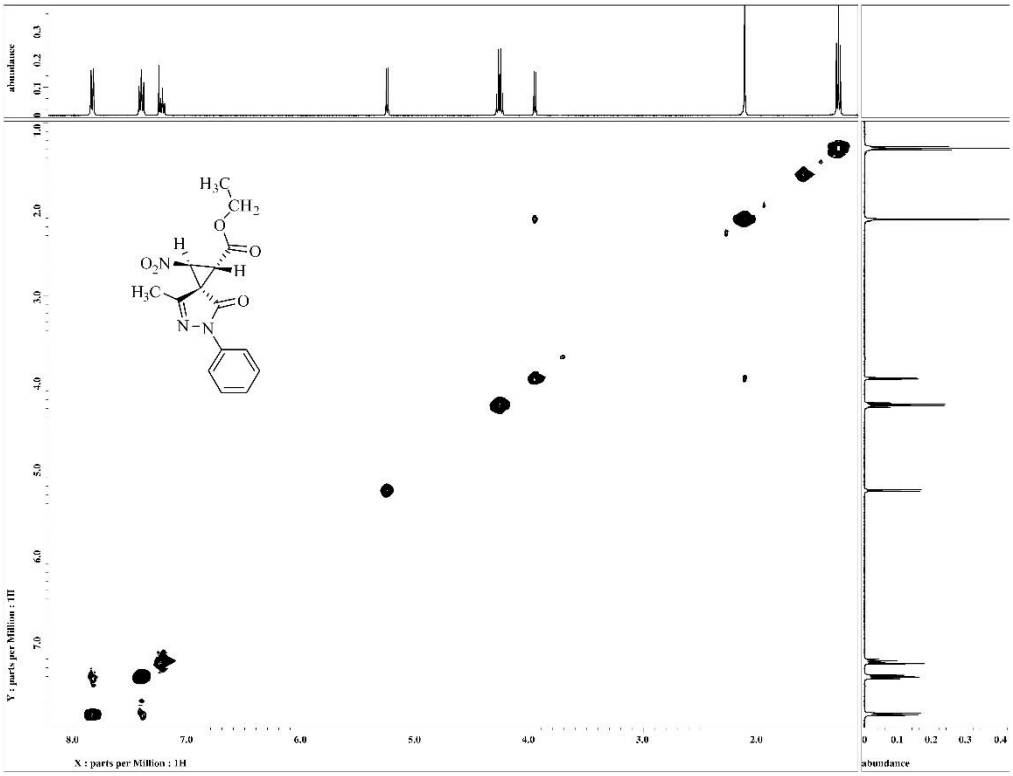


Figure S29. ^{1}H-^{1}H NOESY spectrum of ethyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'b** in $CDCl_3$.

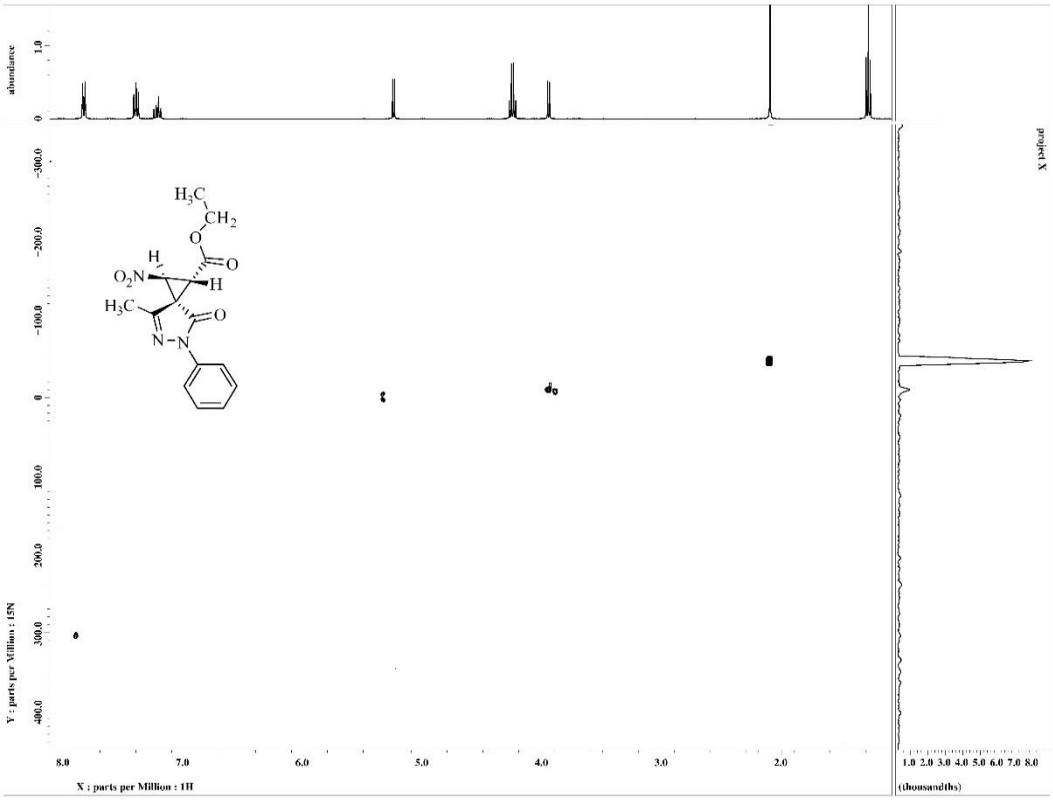


Figure S30. ^{1}H-^{15}N HMBC spectrum of ethyl (1*R*,2*S*,3*S*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3'b** in $CDCl_3$.

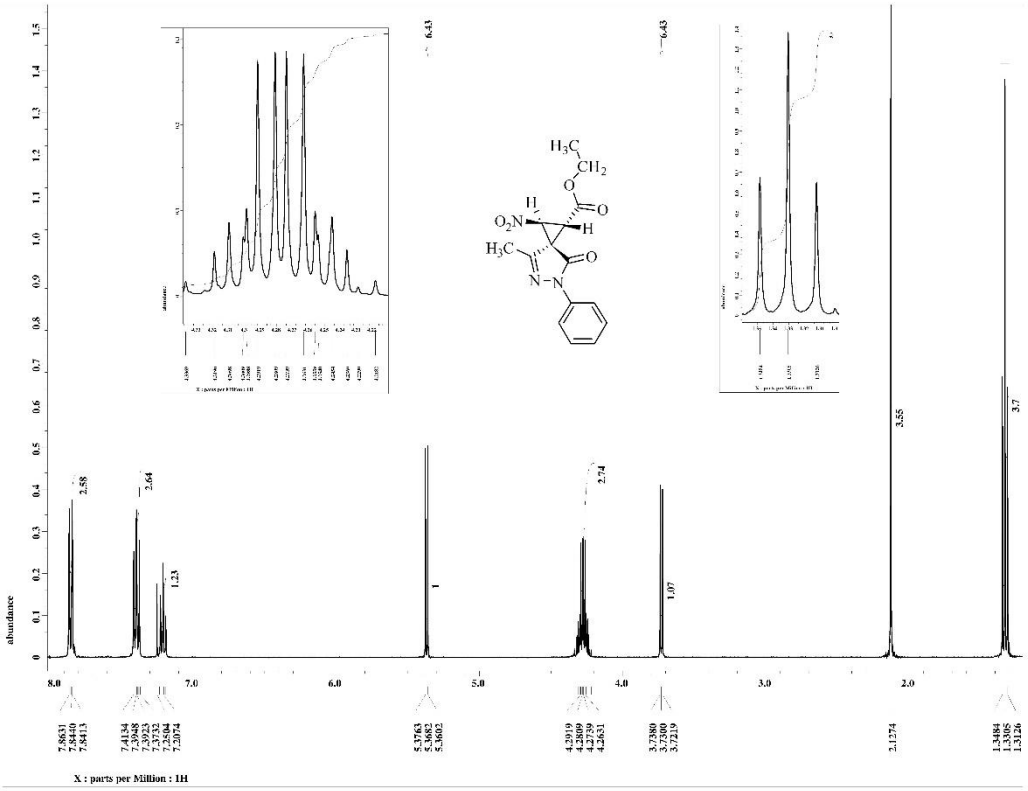


Figure S31. ^{1}H NMR spectrum of ethyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"b** in $CDCl_3$.

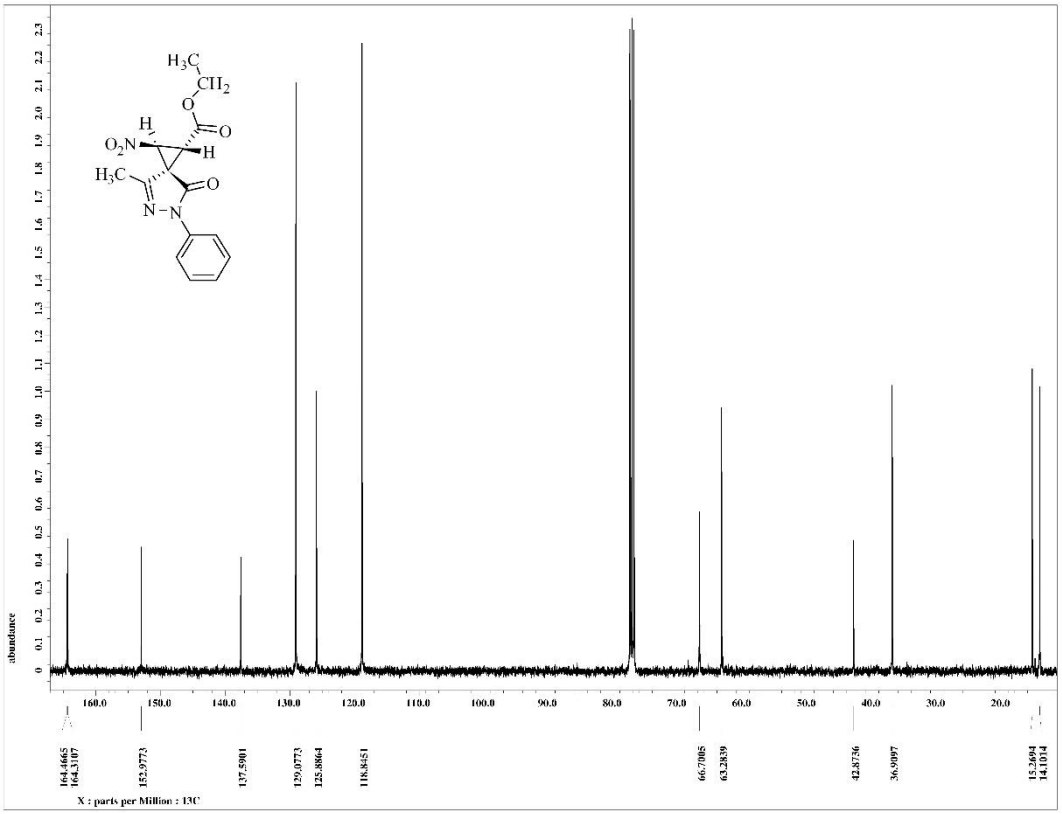


Figure S32. ^{13}C{^{1}H} NMR spectrum of ethyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"b** in $CDCl_3$.

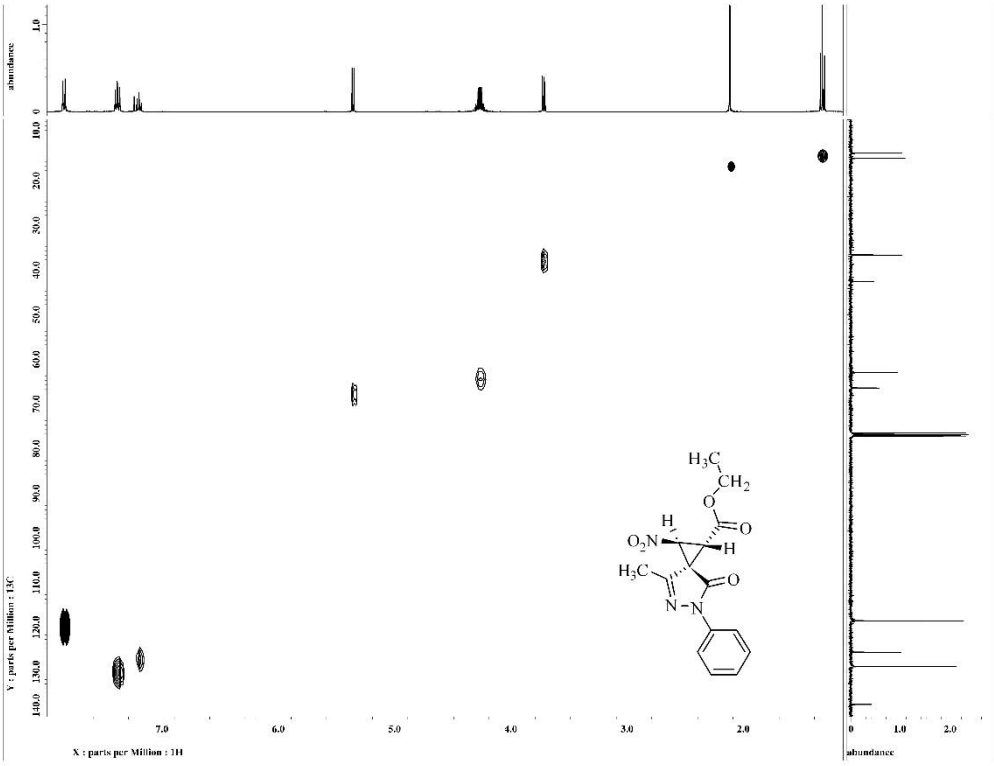


Figure S33. ^{1}H-^{13}C HMQC spectrum of ethyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"b** in $CDCl_3$.

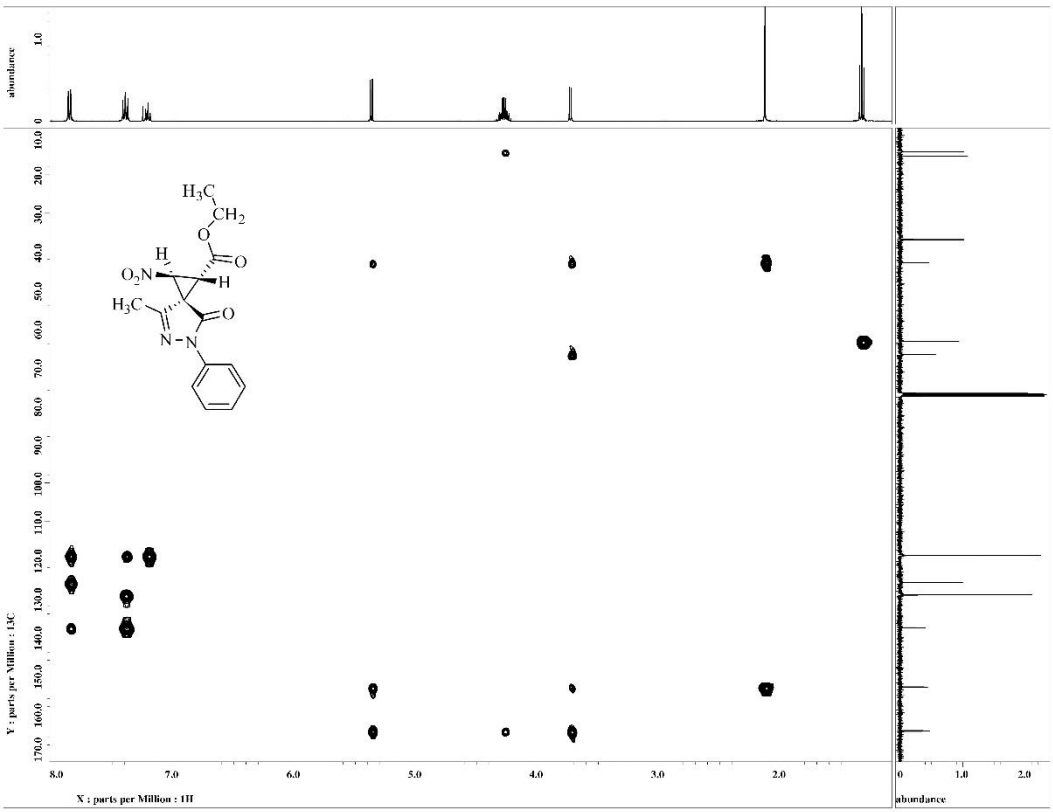


Figure S34. ^{1}H-^{13}C HMBC spectrum of ethyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"b** in $CDCl_3$.

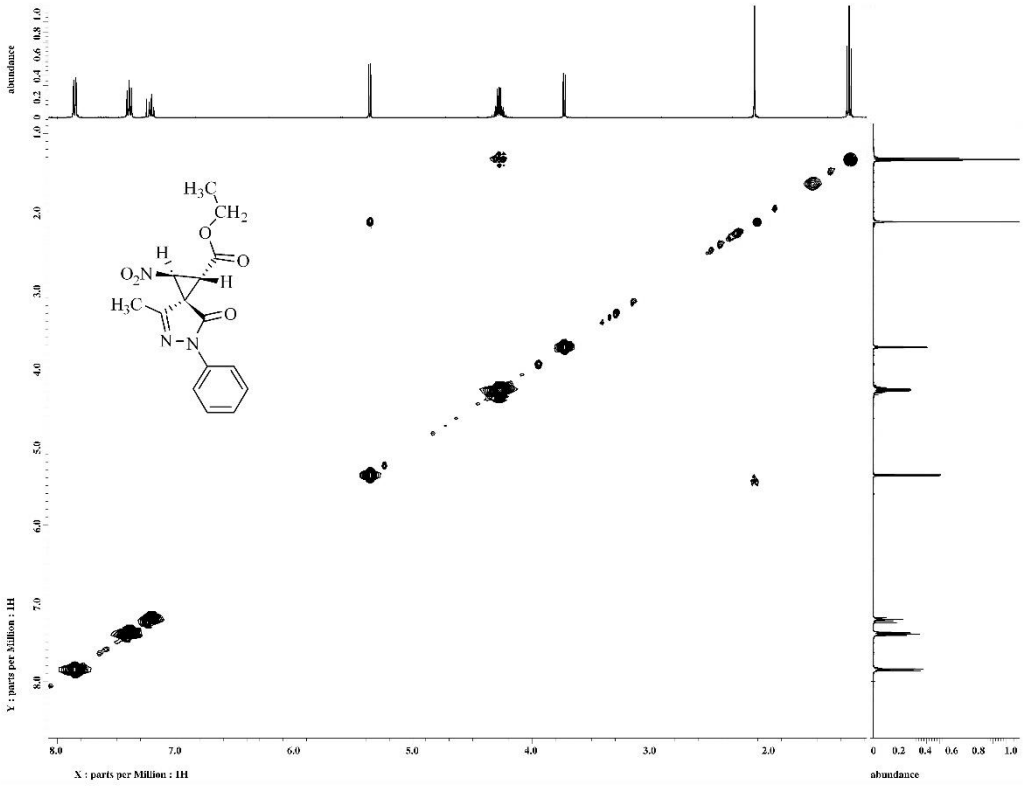


Figure S35. ^{1}H-^{1}H NOESY spectrum of ethyl (1*R*,2*S*,3*R*)-4-methyl-2-nitro-7-oxo-6-phenyl-5,6-diazaspiro[2.4]hept-4-ene-1-carboxylate **3"b** in $CDCl_3$.

X-ray diffraction study of compounds 2b, **3"a**, **3'b** was performed on a Bruker APEX II CCD area detector automatic three-circle diffractometer at 120(2) K (graphite monochromator, λMoK_α = 0.71073 Å, ω- and φ-scan with a step of 0.5°). Single crystals of a suitable size were glued to the top of a glass fiber in a random orientation. The preliminary unit cell parameters were determined using three runs at different φ angle positions with 12 frames per run (φ-scan technique). The X-ray diffraction data were collected and indexed and the unit cell parameters were determined and refined using the APEX2 software package. The empirical absorption correction based on the crystal shape and an additional spherical correction were applied and systematic errors were corrected using the SADABS software. The structures were solved by direct methods using the SHELXT-2014/5 program package and refined by the full-matrix least-squares method based on *F*2 using the SHELXL-2018/3 program package as implemented in WinGX-2020.1. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were positioned geometrically and refined using a riding model. Intermolecular interactions were analyzed and the figures were generated with the PLATON and Mercury 2020.3 programs, respectively. Crystallographic data for the structures of **3a** were deposited with the Cambridge Crystallographic Data Centre. The X-ray diffraction data collection and structure refinement statistics and the corresponding CCDC number are given in Table S1.

Table S1. Principal crystallographic parameters of compound **2b**, **3"a**, **3'b** based on X-ray diffraction data

Parameter	**2b**	**3"a**	**3'b**
Molecular formula	$C_{11}H_{13}NO_8$	$C_{14}H_{13}N_3O_5$	$C_{15}H_{15}N_3O_5$
Molecular weight	287.22	303.27	317.10
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	C_C	P-1
Z	4	4	2
Unit cell parameters			
a/Å	10.3640(4)	10.2121(14)	7.5295(3)
b/Å	10.6108(4)	18.342(3)	10.3992(4)
c/Å	11.6311(4)	8.4035(9)	11.0314(4)
β/deg	92.6370(10)	118.069(2)	70.6410(10)
V/Å^3	1277.72(8)	1388.9(3)	740.86(5)
d_{calc}/g cm^{-3}	1.493	1.450	1.422
Absorption coeffi cient, μ/mm^{-1}	0.130	0.112	0.109
F(000)	600	632	332
Θ (min, max)/deg	2.6, 29.0	2.2, 34.0	2.1, 30.0
Ranges of indices,			
h	$-14 \le h \le 14$	$-15 \le h \le 15$	$-10 \le h \le 10$
k	$-14 \le k \le 14$	$-27 \le k \le 27$	$-14 \le k \le 14$
l	$-15 \le l \le 15$	$-12 \le l \le 12$	$-15 \le l \le 15$
Number of reflections			
total	15569	10368	16670
unique	3385	4960	4338
R_{int}	0.0229	0.0264	0.0440
Number of reflections/of contraints/number of parameters	3385/0/184	4960/2/201	4338/2/219
GOOF	0.984	1.045	1.042
R [$I > 2\sigma(I)$]			
R_1	0.0334	0.0377	0.0401
wR_2	0.0915	0.0902	0.1070
R (based on all reflections)			
R_1	0.0375	0.0446	0.0465
wR_2	0.0955	0.0947	0.1120
Residual electron density (ρ_{max}/ρ_{min})/e Å^{-3}	0.40/-0.33	0.28/-0.20	0.43/-0.33
CCDC	2164322	1845522	1845521

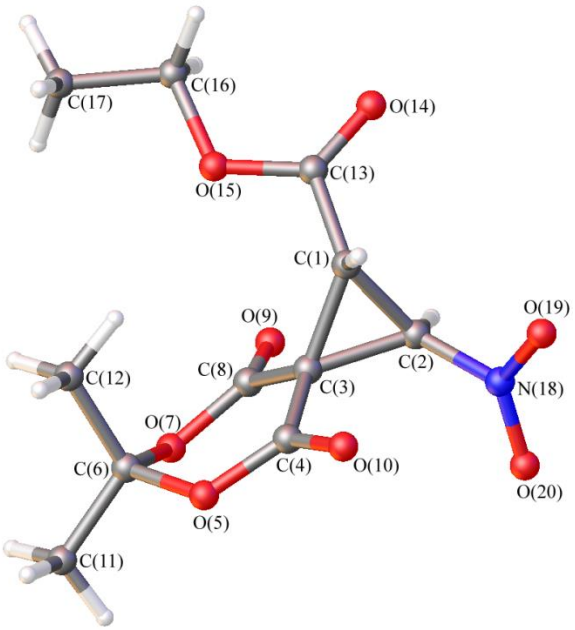


Table S2. Torsion angles (τ) in the molecule of compound **2b**

Angle	τ/deg	Angle	τ/deg
H1A–C1–C2–H2A	-148.54	C2–C3–C8–O9	-20.6(1)
H1A–C1–C2–C3	105.44	C4–C3–C8–O7	8.3(1)
H1A–C1–C2–N18	-4.1	C4–C3–C8–O9	-166.81(9)
C3–C1–C2–H2A	106.02	C3–C4–O5–C6	-17.1(1)
C3–C1–C2–N18	-109.58(9)	O10–C4–O5–C6	164.64(8)
C13–C1–C2–H2A	-6.5	C4–O5–C6–O7	48.2(1)
C13–C1–C2–C3	-112.56(9)	C4–O5–C6–C11	162.55(8)
C13–C1–C2–N18	137.86(9)	C4–O5–C6–C12	-73.6(1)
H1A–C1–C3–C2	-105.43	O5–C6–O7–C8	-52.4(1)
H1A–C1–C3–C4	4.2	C11–C6–O7–C8	-166.25(8)
H1A–C1–C3–C8	155.12	C12–C6–O7–C8	69.7(1)
C2–C1–C3–C4	109.64(8)	O5–C6–C11–H11A	-54.2
C2–C1–C3–C8	-99.45(9)	O5–C6–C11–H11B	-174.22
C13–C1–C3–C2	109.4(1)	O5–C6–C11–H11C	65.8
C13–C1–C3–C4	-140.93(8)	O7–C6–C11–H11A	62.4
C13–C1–C3–C8	10.0(1)	O7–C6–C11–H11B	-57.6
H1A–C1–C13–O14	80.9	O7–C6–C11–H11C	-177.56
H1A–C1–C13–O15	-96.2	C12–C6–C11–H11A	-175.93
C2–C1–C13–O14	-61.1(1)	C12–C6–C11–H11B	64.1
C2–C1–C13–O15	121.84(9)	C12–C6–C11–H11C	-55.9
C3–C1–C13–O14	-133.9(1)	O5–C6–C12–H12A	62.4
C3–C1–C13–O15	49.0(1)	O5–C6–C12–H12B	-57.6
C1–C2–C3–C4	-101.82(9)	O5–C6–C12–H12C	-177.64
C1–C2–C3–C8	111.98(8)	O7–C6–C12–H12A	-59.2
H2A–C2–C3–C1	-106.02	O7–C6–C12–H12B	-179.20
H2A–C2–C3–C4	152.16	O7–C6–C12–H12C	60.8
H2A–C2–C3–C8	6.0	C11–C6–C12–H12A	-178.79
N18–C2–C3–C1	111.65(9)	C11–C6–C12–H12B	61.2
N18–C2–C3–C4	9.8(1)	C11–C6–C12–H12C	-58.8
N18–C2–C3–C8	-136.37(8)	C6–O7–C8–C3	25.0(1)
C1–C2–N18–O19	-34.2(1)	C6–O7–C8–O9	-159.74(8)

C1–C2–N18–O20	149.50(9)	C1–C13–O15–C16	174.97(7)
H2A–C2–N18–O19	110.2	O14–C13–O15–C16	-2.0(1)
H2A–C2–N18–O20	-66.1	C13–O15–C16–H16A	65.2
C3–C2–N18–O19	-107.5(1)	C13–O15–C16–H16B	-55.1
C3–C2–N18–O20	76.2(1)	C13–O15–C16–C17	-174.93(8)
C1–C3–C4–O5	139.01(8)	O15–C16–C17–H17A	-178.04
C1–C3–C4–O10	-42.8(1)	O15–C16–C17–H17B	62.0
C2–C3–C4–O5	-156.64(8)	O15–C16–C17–H17C	-58.0
C2–C3–C4–O10	21.5(1)	H16A–C16–C17–H17A	-58.2
C8–C3–C4–O5	-12.3(1)	H16A–C16–C17–H17B	-178.18
C8–C3–C4–O10	165.84(9)	H16A–C16–C17–H17C	61.8
C1–C3–C8–O7	-141.32(8)	H16B–C16–C17–H17A	62.1
C1–C3–C8–O9	43.5(1)	H16B–C16–C17–H17B	-57.9
C2–C3–C8–O7	154.55(8)	H16B–C16–C17–H17C	-177.90

Table S3. Angles (τ) in the molecule of compound **2b**

Angle	**τ/deg**	**Angle**	**τ/deg**
H1A–C1–C2	114.32	C6–C11–H11B	109.47
H1A–C1–C3	114.32	C6–C11–H11C	109.47
H1A–C1–C13	114.32	H11A–C11–H11B	109.47
C2–C1–C3	60.99(6)	H11A–C11–H11C	109.47
C2–C1–C13	120.34(8)	H11B–C11–H11C	109.47
C3–C1–C13	122.31(8)	C6–C12–H12A	109.47
C1–C2–H2A	114.68	C6–C12–H12B	109.47
C1–C2–C3	61.98(6)	C6–C12–H12C	109.47
C1–C2–N18	121.05(8)	H12A–C12–H12B	109.47
H2A–C2–C3	114.68	H12A–C12–H12C	109.47
H2A–C2–N18	114.68	H12B–C12–H12C	109.47
C3–C2–N18	119.72(8)	C1–C13–O14	122.66(9)
C1–C3–C2	57.03(6)	C1–C13–O15	111.35(8)
C1–C3–C4	114.36(7)	O14–C13–O15	125.91(9)
C1–C3–C8	120.16(7)	C13–O15–C16	116.01(7)
C2–C3–C4	118.77(7)	O15–C16–H16A	110.49
C2–C3–C8	113.11(7)	O15–C16–H16B	110.49
C4–C3–C8	118.75(8)	O15–C16–C17	106.23(8)
C3–C4–O5	115.95(8)	H16A–C16–H16B	108.66
C3–C4–O10	123.04(8)	H16A–C16–C17	110.48
O5–C4–O10	120.98(8)	H16B–C16–C17	110.48
C4–O5–C6	119.64(7)	C16–C17–H17A	109.47
O5–C6–O7	109.78(7)	C16–C17–H17B	109.47
O5–C6–C11	105.59(7)	C16–C17–H17C	109.47
O5–C6–C12	110.66(7)	H17A–C17–H17B	109.5
O7–C6–C11	106.46(7)	H17A–C17–H17C	109.5
O7–C6–C12	110.12(7)	H17B–C17–H17C	109.5
C11–C6–C12	114.03(8)	C2–N18–O19	118.72(8)
C6–O7–C8	118.45(7)	C2–N18–O20	115.56(8)
C3–C8–O7	115.54(8)	O19–N18–O20	125.61(8)
C3–C8–O9	123.27(8)		
O7–C8–O9	121.01(9)		
C6–C11–H11A	109.47		

Table S4. Bond lengths (*d*) in the molecule of compound **2b**

Bond	*d*/Å	Bond	*d*/Å
C1–H1A	1.0000	C11–H11B	0.980
C1–C2	1.464(1)	C11–H11C	0.980
C1–C3	1.541(1)	C12–H12A	0.9800
C1–C13	1.507(1)	C12–H12B	0.9800
C2–H2A	1.0000	C12–H12C	0.9800
C2–C3	1.527(1)	C13–O14	1.205(1)
C2–N18	1.485(1)	C13–O15	1.322(1)
C3–C4	1.499(1)	O15–C16	1.463(1)
C3–C8	1.501(1)	C16–H16A	0.9900
C4–O5	1.343(1)	C16–H16B	0.990
C4–O10	1.202(1)	C16–C17	1.510(1)
O5–C6	1.452(1)	C17–H17A	0.980
C6–O7	1.451(1)	C17–H17B	0.980
C6–C11	1.507(1)	C17–H17C	0.980
C6–C12	1.512(1)	N18–O19	1.222(1)
O7–C8	1.347(1)	N18–O20	1.223(1)
C8–O9	1.201(1)		
C11–H11A	0.980		

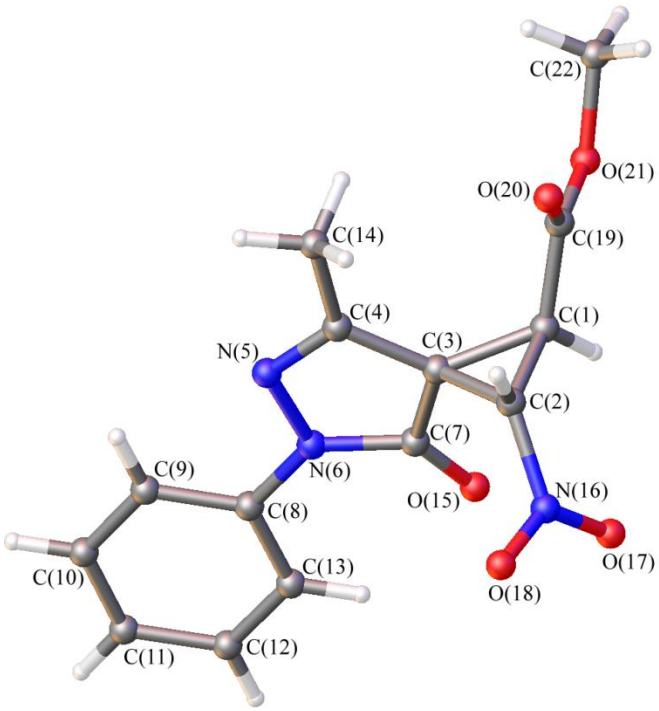


Table S5. Torsion angles (τ) in the molecule of compound **3"a**

Angle	τ/deg	Angle	τ/deg
H1A–C1–C2–H2A	146.3	C3–C4–N5–N6	-2.9(2)
H1A–C1–C2–C3	-107.2	C14–C4–N5–N6	178.0(1)
H1A–C1–C2–N16	-2.3	C3–C4–C14–H14A	-172.7
C3–C1–C2–H2A	-106.5	C3–C4–C14–H14B	67.3
C3–C1–C2–N16	104.8(2)	C3–C4–C14–H14C	-52.7

C19–C1–C2–H2A	3.7	N5–C4–C14–H14A	6.3
C19–C1–C2–C3	110.2(2)	N5–C4–C14–H14B	-113.7
C19–C1–C2–N16	-145.0(2)	N5–C4–C14–H14C	126.3
H1A–C1–C3–C2	107.2	C4–N5–N6–C7	-3.0(2)
H1A–C1–C3–C4	-148.9	C4–N5–N6–C8	179.3(1)
H1A–C1–C3–C7	-0.5	N5–N6–C7–C3	7.2(2)
C2–C1–C3–C4	103.9(2)	N5–N6–C7–O15	-173.1(2)
C2–C1–C3–C7	-107.7(2)	C8–N6–C7–C3	-175.4(2)
C19–C1–C3–C2	-105.6(2)	C8–N6–C7–O15	4.3(3)
C19–C1–C3–C4	-1.7(3)	N5–N6–C8–C9	4.3(2)
C19–C1–C3–C7	146.8(2)	N5–N6–C8–C13	-174.2(2)
H1A–C1–C19–O20	-140.5	C7–N6–C8–C9	-173.0(2)
H1A–C1–C19–O21	40.2	C7–N6–C8–C13	8.5(3)
C2–C1–C19–O20	2.2(3)	N6–C8–C9–H9A	1.9
C2–C1–C19–O21	-177.1(1)	N6–C8–C9–C10	-178.2(2)
C3–C1–C19–O20	72.2(2)	C13–C8–C9–H9A	-179.6
C3–C1–C19–O21	-107.1(2)	C13–C8–C9–C10	0.3(3)
C1–C2–C3–C4	-123.9(2)	N6–C8–C13–C12	178.0(2)
C1–C2–C3–C7	106.0(2)	N6–C8–C13–H13A	-2.0
H2A–C2–C3–C1	106.5	C9–C8–C13–C12	-0.5(3)
H2A–C2–C3–C4	-17.4	C9–C8–C13–H13A	179.5
H2A–C2–C3–C7	-147.5	C8–C9–C10–H10A	179.9
N16–C2–C3–C1	-113.3(2)	C8–C9–C10–C11	0.0(3)
N16–C2–C3–C4	122.8(2)	H9A–C9–C10–H10A	-0.1
N16–C2–C3–C7	-7.3(2)	H9A–C9–C10–C11	179.9
C1–C2–N16–O17	7.7(3)	C9–C10–C11–H11A	179.9
C1–C2–N16–O18	-170.7(2)	C9–C10–C11–C12	-0.1(3)
H2A–C2–N16–O17	-141.0	H10A–C10–C11–H11A	-0.1
H2A–C2–N16–O18	40.6	H10A–C10–C11–C12	179.9
C3–C2–N16–O17	78.7(2)	C10–C11–C12–H12A	180.0
C3–C2–N16–O18	-99.7(2)	C10–C11–C12–C13	-0.0(3)
C1–C3–C4–N5	158.5(2)	H11A–C11–C12–H12A	-0.0
C1–C3–C4–C14	-22.5(3)	H11A–C11–C12–C13	180.0
C2–C3–C4–N5	-129.1(2)	C11–C12–C13–C8	0.4(3)
C2–C3–C4–C14	50.0(2)	C11–C12–C13–H13A	-179.6
C7–C3–C4–N5–	7.0(2)	H12A–C12–C13–C8	-179.7
C7–C3–C4–C14	-173.9(2)	H12A–C12–C13–H13A	0.3
C1–C3–C7–N6	-165.0(1)	C1–C19–O21–C22	176.1(2)
C1–C3–C7–O15	15.3(3)	O20–C19–O21–C22	-3.2(3)
C2–C3–C7–N6	129.3(2)	C19–O21–C22–H22A	174.8
C2–C3–C7–O15	-50.4(3)	C19–O21–C22–H22B	54.8
C4–C3–C7–N6	-8.2(2)	C19–O21–C22–H22C	-65.2
C4–C3–C7–O15	172.0(2)		

Table S6. Angles (τ) in the molecule of compound **3"a**

Angle	**τ/deg**	**Angle**	**τ/deg**
H1A–C1–C2	116.5	H9A–C9–C10	120.4
H1A–C1–C3	116.5	C9–C10–H10A	119.5
H1A–C1–C19	116.5	C9–C10–C11	121.1(2)
C2–C1–C3	61.4(1)	H10A–C10–C11	119.5
C2–C1–C19	115.9(1)	C10–C11–H11A	120.3

C3–C1–C19	118.8(1)	C10–C11–C12	119.4(2)
C1–C2–H2A	115.5	H11A–C11–C12	120.3
C1–C2–C3	61.3(1)	C11–C12–H12A	119.7
C1–C2–N16	121.6(2)	C11–C12–C13	120.6(2)
H2A–C2–C3	115.6	H12A–C12–C13	119.7
H2A–C2–N16	115.5	C8–C13–C12	119.4(2)
C3–C2–N16	116.3(1)	C8–C13–H13A	120.3
C1–C3–C2	57.3(1)	C12–C13–H13A	120.3
C1–C3–C4	132.9(1)	C4–C14–H14A	109.5
C1–C3–C7	117.5(1)	C4–C14–H14B	109.5
C2–C3–C4	121.1(1)	C4–C14–H14C	109.5
C2–C3–C7	118.4(1)	H14A–C14–H14B	109.5
C4–C3–C7	103.8(1)	H14A–C14–H14C	109.5
C3–C4–N5	110.6(1)	H14B–C14–H14C	109.5
C3–C4–C14	127.8(1)	C2–N16–O17	120.1(2)
N5–C4–C14	121.6(2)	C2–N16–O18	114.2(2)
C4–N5–N6	108.8(1)	O17–N16–O18	125.7(2)
N5–N6–C7	112.2(1)	C1–C19–O20	124.0(2)
N5–N6–C8	119.4(1)	C1–C19–O21	111.2(1)
C7–N6–C8	128.3(1)	O20–C19–O21	124.8(2)
C3–C7–N6	103.9(1)	C19–O21–C22	114.7(2)
C3–C7–O15	127.8(2)	O21–C22–H22A	109.5
N6–C7–O15	128.3(2)	O21–C22–H22B	109.5
N6–C8–C9	119.3(2)	O21–C22–H22C	109.5
N6–C8–C13	120.4(2)	H22A–C22–H22B	109.5
C9–C8–C13	120.3(2)	H22A–C22–H22C	109.5
C8–C9–H9A	120.4	H22B–C22–H22C	109.5
C8–C9–C10	119.2(2)		

Table S7. Bond lengths (*d*) in the molecule of compound **3"a**

Bond	***d*/Å**	**Bond**	***d*/Å**
C1–H1A	1.000	C10–H10A	0.950
C1–C2	1.467(3)	C10–C11	1.385(3)
C1–C3	1.531(2)	C11–H11A	0.950
C1–C19	1.502(2)	C11–C12	1.389(3)
C2–H2A	1.000	C12–H12A	0.950
C2–C3	1.531(3)	C12–C13	1.398(2)
C2–N16	1.484(2)	C13–H13A	0.950
C3–C4	1.482(2)	C14–H14A	0.980
C3–C7	1.504(2)	C14–H14B	0.980
C4–N5	1.290(2)	C14–H14C	0.980
C4–C14	1.491(2)	N16–O17	1.218(2)
N5–N6	1.414(2)	N16–O18	1.234(3)
N6–C7	1.374(2)	C19–O20	1.206(3)
N6–C8	1.419(2)	C19–O21	1.330(3)
C7–O15	1.214(2)	O21–C22	1.464(2)
C8–C9	1.394(2)	C22–H22A	0.980
C8–C13	1.399(2)	C22–H22B	0.980
C9–H9A	0.950	C22–H22C	0.980
C9–C10	1.396(3)		

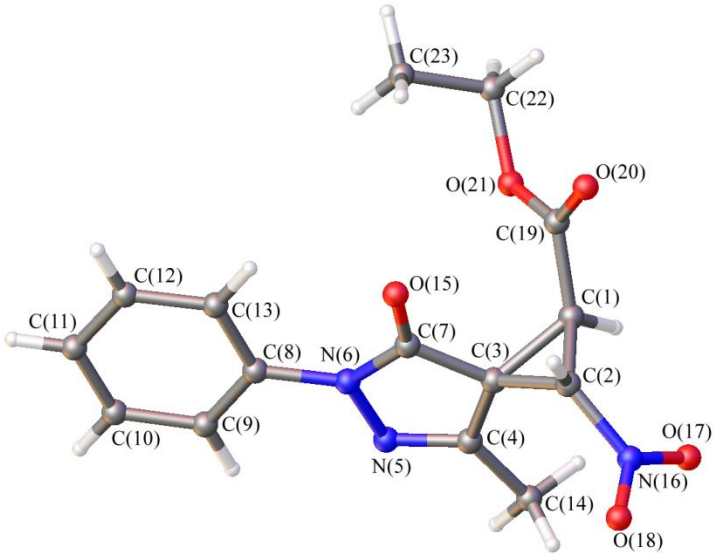


Table S8. Torsion angles (τ) in the molecule of compound **3'b**

Angle	τ/deg	Angle	τ/deg
H1A–C1–C2–H2A	147.1	C3–C4–C14–H14C	-51.4
H1A–C1–C2–C3	-106.2	N5–C4–C14–H14A	8.7
H1A–C1–C2–N16	2.1	N5–C4–C14–H14B	-111.3
C3–C1–C2–H2A	-106.7	N5–C4–C14–H14C	128.7
C3–C1–C2–N16	108.3(1)	C4–N5–N6–C7	-0.9(1)
C19–C1–C2–H2A	2.2	C4–N5–N6–C8	-178.99(9)
C19–C1–C2–C3	108.9(1)	N5–N6–C7–C3	3.1(1)
C19–C1–C2–N16	-142.7(1)	N5–N6–C7–O15	-178.4(1)
H1A–C1–C3–C2	106.2	C8–N6–C7–C3	-179.09(9)
H1A–C1–C3–C4	-14.0	C8–N6–C7–O15	-0.6(2)
H1A–C1–C3–C7	-148.07	N5–N6–C8–C9	7.5(1)
C2–C1–C3–C4	-120.1(1)	N5–N6–C8–C13	-171.08(9)
C2–C1–C3–C7	105.8(1)	C7–N6–C8–C9	-170.2(1)
C19–C1–C3–C2	-110.1(1)	C7–N6–C8–C13	11.2(2)
C19–C1–C3–C4	129.8(1)	N6–C8–C9–H9A	1.6
C19–C1–C3–C7	-4.3(1)	N6–C8–C9–C10	-178.4(1)
H1A–C1–C19–O20	-104.6	C13–C8–C9–H9A	-179.8
H1A–C1–C19–O21	73.2	C13–C8–C9–C10	0.2(2)
C2–C1–C19–O20	40.3(2)	N6–C8–C13–C12	178.5(1)
C2–C1–C19–O21	-141.9(1)	N6–C8–C13–H13A	-1.5
C3–C1–C19–O20	111.6(1)	C9–C8–C13–C12	-0.1(2)
C3–C1–C19–O21	-70.5(1)	C9–C8–C13–H13A	179.9
C1–C2–C3–C4	110.2(1)	C8–C9–C10–H10A	179.9
C1–C2–C3–C7	-106.9(1)	C8–C9–C10–C11	-0.1(2)
H2A–C2–C3–C1	106.7	H9A–C9–C10–H10A	-0.1
H2A–C2–C3–C4	-143.0	H9A–C9–C10–C11	179.9
H2A–C2–C3–C7	-0.1	C9–C10–C11–H11A	179.9
N16–C2–C3–C1	-109.1(1)	C9–C10–C11–C12	-0.1(2)
N16–C2–C3–C4	1.1(2)	H10A–C10–C11–H11A	-0.1
N16–C2–C3–C7	144.02(9)	H10A–C10–C11–C12	179.9
C1–C2–N16–O17	7.8(1)	C10–C11–C12–H12A	-179.8
C1–C2–N16–O18	-172.0(1)	C10–C11–C12–C13	0.2(2)
H2A–C2–N16–O17	-137.2	H11A–C11–C12–H12A	0.2

H2A–C2–N16–O18	43.1	H11A–C11–C12–C13	-179.8
C3–C2–N16–O17	78.7(1)	C11–C12–C13–C8	-0.1(2)
C3–C2–N16–O18	-101.1(1)	C11–C12–C13–H13A	179.9
C1–C3–C4–N5	-135.2(1)	H12A–C12–C13–C8	179.9
C1–C3–C4–C14	44.8(2)	H12A–C12–C13–H13A	-0.1
C2–C3–C4–N5	149.9(1)	C1–C19–O21–C22	-174.1(2)
C2–C3–C4–C14	-30.1(2)	O20–C19–O21–C22	3.6(3)
C7–C3–C4–N5	3.6(1)	C19–O21–C22–H22A	143.1
C7–C3–C4–C14	-176.3(1)	C19–O21–C22–H22B	23.4
C1–C3–C7–N6	138.64(9)	C19–O21–C22–C23	-96.7(3)
C1–C3–C7–O15	-39.9(2)	O21–C22–C23–H23A	-179.3
C2–C3–C7–N6	-155.76(9)	O21–C22–C23–H23B	60.7
C2–C3–C7–O15	25.7(2)	O21–C22–C23–H23C	-59.4
C4–C3–C7–N6	-3.9(1)	H22A–C22–C23–H23A	-59.1
C4–C3–C7–O15	177.6(1)	H22A–C22–C23–H23B	-179.1
C3–C4–N5–N6	-1.8(1)	H22A–C22–C23–H23C	60.8
C14–C4–N5–N6	178.13(9)	H22B–C22–C23–H23A	60.6
C3–C4–C14–H14A	-171.4	H22B–C22–C23–H23B	-59.4
C3–C4–C14–H14B	68.6	H22B–C22–C23–H23C	-179.5

Table S9. Angles (τ) in the molecule of compound **3'b**

Angle	**τ/deg**	**Angle**	**τ/deg**
H1A–C1–C2	115.31	H10A–C10–C11	119.7
H1A–C1–C3	115.32	C10–C11–H11A	120.3
H1A–C1–C19	115.31	C10–C11–C12	119.5(1)
C2–C1–C3	60.93(7)	H11A–C11–C12	120.3
C2–C1–C19	119.93(9)	C11–C12–H12A	119.5
C3–C1–C19	119.23(9)	C11–C12–C13	121.1(1)
C1–C2–H2A	115.9	H12A–C12–C13	119.5
C1–C2–C3	61.36(7)	C8–C13–C12	118.9(1)
C1–C2–N16	118.64(9)	C8–C13–H13A	120.5
H2A–C2–C3	115.90	C12–C13–H13A	120.5
H2A–C2–N16	115.9	C4–C14–H14A	109.47
C3–C2–N16	118.14(9)	C4–C14–H14B	109.47
C1–C3–C2	57.70(7)	C4–C14–H14C	109.47
C1–C3–C4	124.76(9)	H14A–C14–H14B	109.5
C1–C3–C7	117.35(9)	H14A–C14–H14C	109.5
C2–C3–C4	130.79(9)	H14B–C14–H14C	109.5
C2–C3–C7	116.72(9)	C2–N16–O17	118.93(9)
C4–C3–C7	104.23(8)	C2–N16–O18	116.43(9)
C3–C4–N5	110.87(9)	O17–N16–O18	124.6(1)
C3–C4–C14	127.65(9)	C1–C19–O20	123.9(1)
N5–C4–C14	121.48(9)	C1–C19–O21	109.52(9)
C4–N5–N6	108.20(8)	O20–C19–O21	126.5(1)
N5–N6–C7	112.85(8)	C19–O21–C22	123.3(2)
N5–N6–C8	118.24(8)	O21–C22–H22A	110.2
C7–N6–C8	128.87(9)	O21–C22–H22B	110.2
C3–C7–N6	103.69(8)	O21–C22–C23	107.6(3)
C3–C7–O15	127.1(1)	H22A–C22–H22B	108.5
N6–C7–O15	129.2(1)	H22A–C22–C23	110.2
N6–C8–C9	119.11(9)	H22B–C22–C23	110.2

N6–C8–C13	120.22(9)	C22–C23–H23A	109.5
C9–C8–C13	120.7(1)	C22–C23–H23B	109.5
C8–C9–H9A	120.4	C22–C23–H23C	109.5
C8–C9–C10	119.2(1)	H23A–C23–H23B	109.5
H9A–C9–C10	120.4	H23A–C23–H23C	109.4
C9–C10–H10A	119.7	H23B–C23–H23C	109.5
C9–C10–C11	120.6(1)		

Table S10. Bond lengths (*d*) in the molecule of compound **3'b**

Bond	***d*/Å**	**Bond**	***d*/Å**
C1–H1A	1.000	C10–C11	1.392(1)
C1–C2	1.474(2)	C11–H11A	0.950
C1–C3	1.530(1)	C11–C12	1.388(2)
C1–C19	1.507(1)	C12–H12A	0.9500
C2–H2A	1.000	C12–C13	1.393(2)
C2–C3	1.524(2)	C13–H13A	0.950
C2–N16	1.482(1)	C14–H14A	0.980
C3–C4	1.478(1)	C14–H14B	0.980
C3–C7	1.501(1)	C14–H14C	0.980
C4–N5	1.291(1)	N16–O17	1.225(1)
C4–C14	1.489(1)	N16–O18	1.221(2)
N5–N6	1.415(1)	C19–O20	1.205(1)
N6–C7	1.372(1)	C19–O21	1.328(2)
N6–C8	1.420(1)	O21–C22	1.474(3)
C7–O15	1.220(1)	C22–H22A	0.990
C8–C9	1.397(1)	C22–H22B	0.990
C8–C13	1.399(1)	C22–C23	1.512(4)
C9–H9A	0.9500	C23–H23A	0.980
C9–C10	1.395(2)	C23–H23B	0.980
C10–H10A	0.950	C23–H23C	0.980

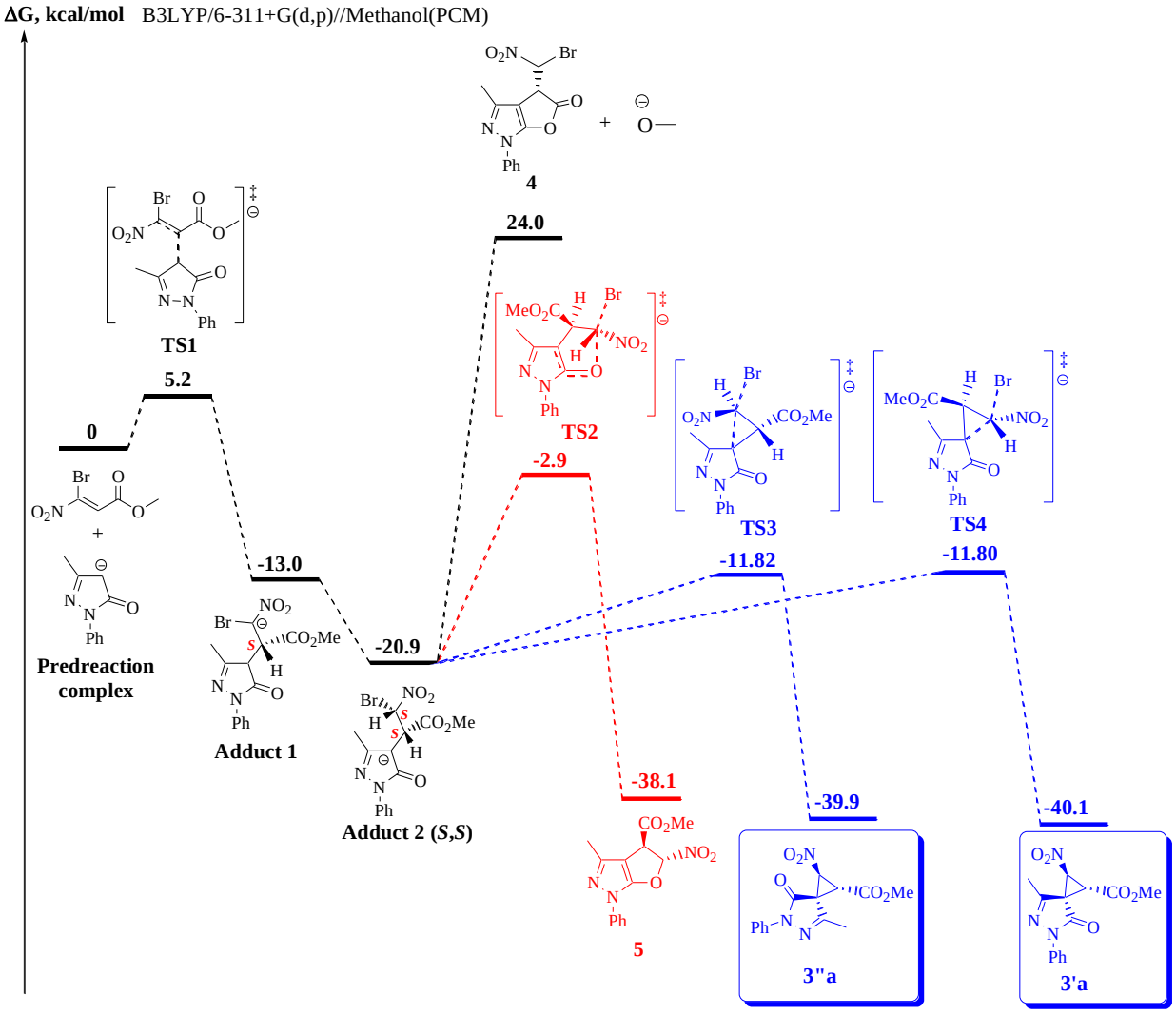


Figure S36. Diagram of free energy change in the reaction of methyl 3-bromo-3-nitroacrylate **1a** with 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one in the synthesis of trans products with the (*S,S* or *R,R*)-configuration of chiral centers using the example (*S,S*)-diastereomer according to B3LYP/6-311+G(d,p) in methanol in the approximation of the polarization continuum method (PCM).

B3LYP/6-311+G(d,p)//Methanol(PCM)

	E_0	E_0+E(ZPE)	E_0+Gcorr
Predreaction complex	-3656.1516690	-3655.894770	-3655.954786
TS1	-3656.1486113	-3655.891297	-3655.946545
Adduct 1	-3656.1820708	-3655.921422	-3655.975446
Adduct 2 (*S,S*)	-3656.1940250	-3655.933066	-3655.988029
4	-3540.8417447	-3540.621969	-3540.672225
$MeO^{(-)}$	-115.2583193	-115.221916	-115.244187
Σ(I + $MeO^{(-)}$)	-3656.100064	-3655.843885	-3655.916412

TS2	-3656.1658456	-3655.905536	-3655.959345
TS3	-3656.1778934	-3655.918412	-3655.973615
TS4	-3656.1773816	-3655.918148	-3655.973589
Σ(5a+Br$^-$)	-3656.2103159	-3655.947700	-3656.015563
Σ(3"a+Br$^-$)	-3656.2113139	-3655.950582	-3656.018362
Σ(3'a+Br$^-$)	-3656.2106846	-3655.950018	-3656.018717
5	-1081.8714742	-1081.608858	-1081.660546
3"a	-1081.8724722	-1081.611740	-1081.663345
3'a	-1081.8718429	-1081.611176	-1081.663700
Anion-Br	-2574.3388417	-2574.338842	-2574.355017

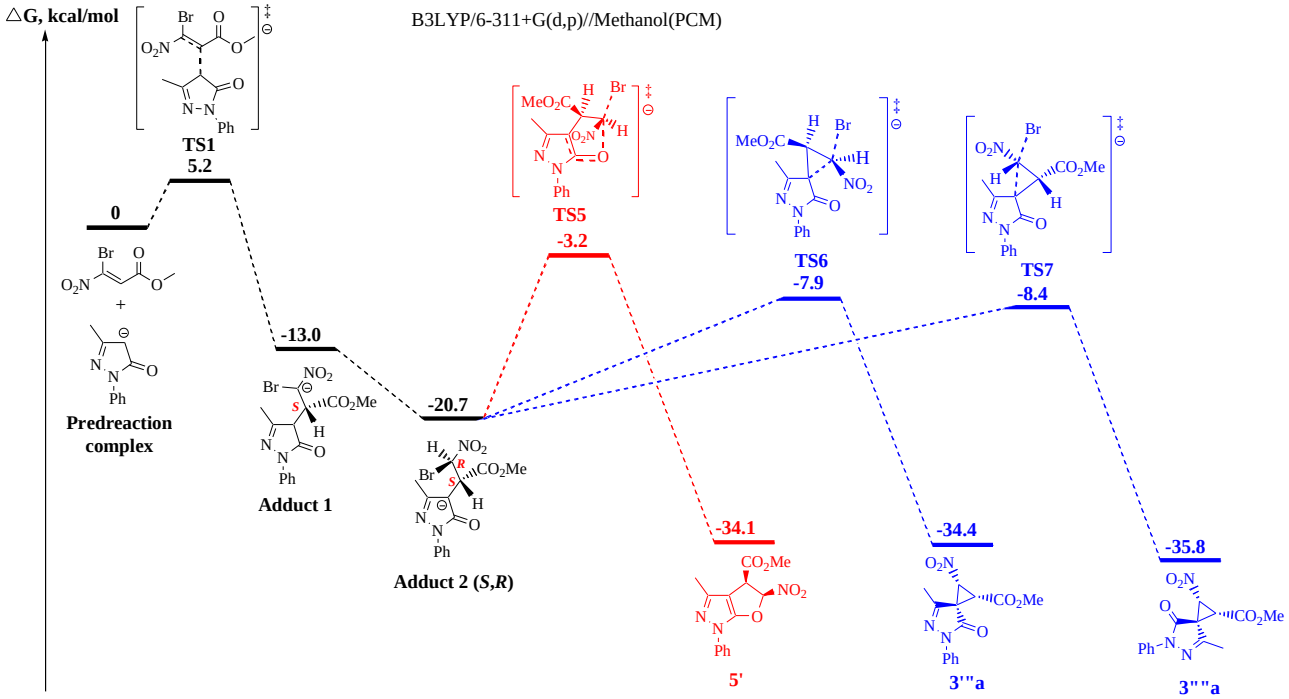


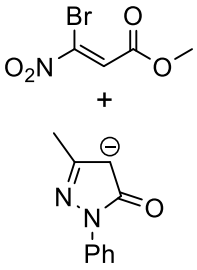
Figure S37. Diagram of the change in free energy in the reaction of methyl 3-bromo-3-nitroacrylate **1a** with 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one in the synthesis of *cis*-products with the (*S*,*R* or *R*,*S*)-configuration of chiral centers using the example (*S*,*R*)-diastereomer according to B3LYP/6-311+G(d,p) in methanol in the approximation of the polarization continuum method (PCM).

B3LYP/6-311+G(d,p)//Methanol(PCM)

	E$_0$	**E$_0$+E(ZPE)**	**E$_0$+Gcorr**
Predreaction complex	-3656.1516690	-3655.894770	-3655.954786
TS1	-3656.1486113	-3655.891297	-3655.946545
Adduct 1	-3656.1820708	-3655.921422	-3655.975446

Adduct 2(*S*,*R*)	-3656.1935613	-3655.932613	-3655.987806
TS5	-3656.1566746	-3655.896264	-3655.949708
TS6	-3656.1724536	-3655.913015	-3655.967361
TS7	-3656.1739413	-3655.914148	-3655.968234
Σ(5'+Br^-)	-3656.2051102	-3655.942232	-3656.009117
Σ(3"'a+Br)	-3656.2031908	-3655.942375	-3656.009552
Σ(3""a+Br^-)	-3656.2065752	-3655.945386	-3656.011833
5'	-1081.8662685	-1081.603390	-1081.654100
3"'a	-1081.8643491	-1081.603533	-1081.654535
3""a	-1081.8677335	-1081.606544	-1081.656816
Anion-Br	-2574.3388417	-2574.338842	-2574.355017

CARTESIAN COORDINATES FOR REACTION OF METHYL 3-BROMO-3-NITROACRYLATE WITH 5-METHYL-2-PHENYL-2,4-DIHYDRO-3*H*-PYRAZOL-3-ONE



Predreaction complex

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7	2.045996000	1.961450000	0.347749000
7	2.504216000	0.669013000	0.590324000
6	1.544634000	-0.104223000	1.305921000
6	0.448441000	0.783080000	1.460172000
1	-0.456951000	0.558862000	2.001785000
6	3.786673000	0.307456000	0.150682000
6	4.330006000	-0.965190000	0.411693000
6	4.562407000	1.234808000	-0.571660000
6	5.609442000	-1.284981000	-0.039264000
6	5.838042000	0.896367000	-1.013217000
6	6.376900000	-0.364791000	-0.753249000
1	3.740618000	-1.680903000	0.963700000
1	4.150814000	2.212295000	-0.776564000
1	6.007965000	-2.271270000	0.175212000
1	6.414823000	1.629546000	-1.567487000
1	7.371147000	-0.623221000	-1.099164000
6	0.039735000	3.280832000	0.814584000
1	-0.865311000	3.158414000	0.212477000
1	-0.273745000	3.601992000	1.812681000
1	0.640563000	4.076574000	0.369409000
8	1.720148000	-1.293783000	1.675457000
1	-0.150479000	-3.946522000	-1.173370000
6	0.555584000	-3.129036000	-1.027003000
1	0.978196000	-3.157722000	-0.024103000
1	1.340747000	-3.162950000	-1.777646000
8	-0.106770000	-1.857453000	-1.229829000
8	-1.595769000	-2.366511000	0.388694000
6	-1.159876000	-1.602768000	-0.443058000
6	-1.707501000	-0.263679000	-0.785285000
1	-1.069313000	0.376669000	-1.377577000
6	-2.939003000	0.181763000	-0.508275000
35	-4.286047000	-0.701310000	0.456350000
7	-3.316655000	1.534898000	-1.006905000
8	-2.471576000	2.159045000	-1.641484000
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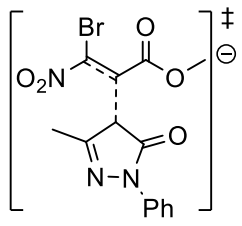

TS1

6	0.373279000	-1.590114000	-1.107071000
7	1.585264000	-1.755530000	-0.630998000
7	2.168020000	-0.486941000	-0.584928000
6	1.310538000	0.499057000	-1.114983000
6	0.071322000	-0.211686000	-1.348978000
1	-0.699930000	0.159976000	-2.005214000
6	3.502731000	-0.360939000	-0.152012000
6	4.071121000	0.898848000	0.102327000
6	4.280606000	-1.513588000	0.048812000
6	5.390966000	0.990249000	0.539809000
6	5.595907000	-1.402722000	0.490921000
6	6.164647000	-0.152928000	0.738399000
1	3.480546000	1.788854000	-0.050912000
1	3.844414000	-2.483835000	-0.139765000
1	5.813272000	1.970944000	0.730868000
1	6.179472000	-2.304700000	0.640713000
1	7.189862000	-0.072291000	1.080677000
6	-0.519220000	-2.762988000	-1.354904000
1	-1.499829000	-2.625435000	-0.893042000
1	-0.690279000	-2.894455000	-2.428360000
1	-0.069861000	-3.675705000	-0.960773000
8	1.609842000	1.688379000	-1.308260000
1	-1.091545000	4.404834000	0.887876000
6	-0.145228000	3.875114000	0.776980000
1	0.264638000	4.040778000	-0.218280000
1	0.560685000	4.192618000	1.540074000
8	-0.335872000	2.459899000	0.999117000
8	-1.799882000	2.390814000	-0.713879000
6	-1.182673000	1.833984000	0.166105000
6	-1.240173000	0.389785000	0.532866000
1	-0.478268000	0.069474000	1.228034000
6	-2.413515000	-0.332773000	0.592883000
35	-3.980308000	0.064472000	-0.397217000
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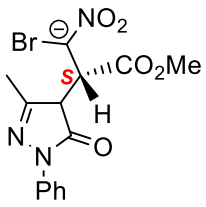
8	-3.531205000	-2.148628000	1.465091000



Adduct 1

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6	0.988428000	-0.679909000	-1.060960000
6	-0.288908000	-1.281369000	-0.480363000
1	-0.507734000	-2.192590000	-1.049739000
6	3.306480000	-0.439923000	-0.090283000
6	3.817400000	0.394546000	-1.095420000
6	4.161739000	-0.925793000	0.908805000
6	5.170830000	0.726265000	-1.092543000
6	5.510254000	-0.580251000	0.896809000
6	6.025806000	0.245084000	-0.102189000
1	3.164192000	0.772535000	-1.866627000
1	3.766108000	-1.564359000	1.685110000
1	5.554089000	1.372327000	-1.874439000
1	6.159712000	-0.963185000	1.676000000
1	7.076582000	0.510129000	-0.107570000
6	-0.632044000	-2.392471000	1.926881000
1	-1.535995000	-1.824988000	2.162057000
1	-0.954298000	-3.364484000	1.538826000
1	-0.035863000	-2.549419000	2.826500000
8	1.137314000	-0.211653000	-2.178777000
1	-5.435101000	-1.424824000	-0.601339000
6	-5.083065000	-0.905597000	-1.492893000
1	-5.009715000	-1.605835000	-2.325310000
1	-5.750654000	-0.085112000	-1.743371000
8	-3.801606000	-0.293050000	-1.236232000
8	-2.896437000	-2.322214000	-0.875049000
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6	-1.507512000	-0.327875000	-0.668067000
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6	-1.647404000	0.781677000	0.333873000
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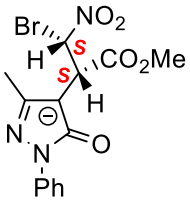

Adduct 2 (*S*,*S*)

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6	0.049473000	0.423683000	0.572692000
6	3.568990000	-0.066597000	-0.097979000
6	3.845275000	-0.489670000	-1.411399000
6	4.642664000	0.116617000	0.793020000
6	5.161669000	-0.719815000	-1.807460000
6	5.950249000	-0.118300000	0.378427000
6	6.225205000	-0.538921000	-0.923711000
1	3.025480000	-0.632007000	-2.098441000
1	4.437074000	0.443263000	1.801858000
1	5.352345000	-1.045307000	-2.824820000
1	6.760940000	0.030068000	1.084059000
1	7.245432000	-0.720649000	-1.241608000
6	0.146781000	1.241590000	3.053568000
1	-0.387808000	2.188121000	2.927083000
1	-0.567066000	0.516037000	3.455764000
1	0.937826000	1.389746000	3.790562000
8	0.934498000	-0.377541000	-1.557335000
1	-3.019828000	3.887299000	-1.321568000
6	-2.099171000	3.967273000	-0.743635000
1	-1.253933000	4.123773000	-1.414084000
1	-2.169972000	4.778434000	-0.023691000
8	-1.896761000	2.772499000	0.044635000
8	-1.871426000	1.530754000	-1.834738000
6	-1.772903000	1.620072000	-0.631521000
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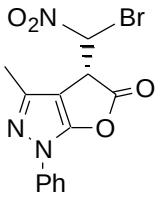

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6	0.900781000	-0.252337000	-0.419669000
6	-0.275434000	0.433905000	-0.465160000
6	3.307964000	0.301933000	0.029624000
6	3.743166000	-0.986485000	0.349242000
6	4.225007000	1.339001000	-0.153589000
6	5.108817000	-1.234409000	0.470830000
6	5.585544000	1.078174000	-0.015004000
6	6.033984000	-0.206656000	0.292772000
1	3.030199000	-1.784947000	0.508491000
1	3.868951000	2.329865000	-0.399228000
1	5.445376000	-2.234560000	0.717323000

1	6.296862000	1.883623000	-0.156060000
1	7.094444000	-0.404440000	0.394515000
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1	-1.312814000	3.160857000	-0.995575000
1	-1.480782000	2.914571000	0.741016000
1	-0.124841000	3.871471000	0.115380000
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8	-0.833310000	-2.922139000	-1.410627000
6	-0.480644000	-1.841848000	-1.063044000
6	-1.323418000	-0.534118000	-0.921608000
1	-1.702119000	-0.317768000	-1.925597000
6	-2.564873000	-0.769441000	-0.048373000
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7	-2.154153000	-0.944216000	1.428998000
8	-2.720727000	-0.330487000	2.304481000
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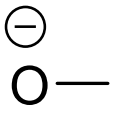

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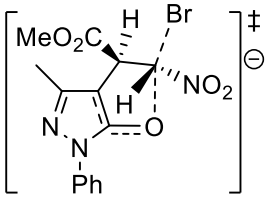
8	0.809184000	0.000043000	-0.000016000



TS2

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6	1.054711000	0.027570000	-0.054226000
6	0.127062000	0.933958000	0.419502000
6	3.574834000	0.038421000	-0.105808000
6	3.706923000	-1.141785000	-0.851516000
6	4.722217000	0.696311000	0.358548000
6	4.975632000	-1.651505000	-1.119945000
6	5.982123000	0.174654000	0.077939000
6	6.120409000	-1.001338000	-0.660211000
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1	4.614418000	1.605965000	0.931644000
1	5.064194000	-2.565020000	-1.697469000
1	6.861481000	0.693399000	0.443493000
1	7.103820000	-1.403338000	-0.874209000
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1	-0.251950000	3.857106000	0.898058000
1	-0.249672000	3.047619000	2.461555000

1	1.208366000	3.890575000	1.905513000
8	0.724694000	-1.120149000	-0.556340000
1	-4.005590000	2.850198000	-1.733598000
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1	-3.645963000	4.111141000	-0.515888000
8	-2.606468000	2.391525000	-0.251530000
8	-1.927305000	1.143662000	-2.001052000
6	-1.991643000	1.345234000	-0.809547000
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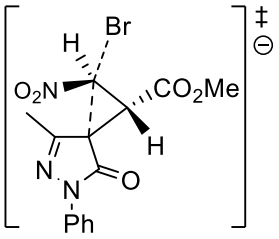

TS3

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6	-0.091130000	0.538537000	0.085145000
6	-3.694524000	0.020115000	0.021781000
6	-4.114310000	-0.971830000	-0.875929000
6	-4.649164000	0.757626000	0.735615000
6	-5.475672000	-1.208522000	-1.055602000
6	-6.005260000	0.502650000	0.549696000
6	-6.429247000	-0.477880000	-0.347580000
1	-3.381891000	-1.543049000	-1.426234000
1	-4.322061000	1.518221000	1.430561000
1	-5.788327000	-1.978350000	-1.752327000
1	-6.733261000	1.079756000	1.108950000
1	-7.486052000	-0.670575000	-0.491015000
6	0.099847000	1.836325000	2.398995000
1	0.841372000	1.195596000	2.883911000
1	0.628678000	2.717197000	2.030246000
1	-0.628346000	2.147293000	3.148698000
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1	2.673340000	4.051596000	-2.567929000
8	2.109912000	2.398334000	-1.540434000
8	2.745013000	2.059754000	0.595688000
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6	1.286141000	0.466926000	-0.507693000

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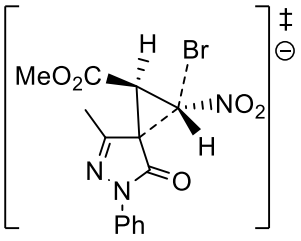

TS4

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6	5.929127000	-0.328911000	0.125376000
6	6.154183000	-0.168324000	-1.242053000
1	2.919089000	0.087041000	-2.269939000
1	4.461994000	-0.456632000	1.697127000
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1	6.766259000	-0.447752000	0.804315000
1	7.164078000	-0.162435000	-1.635273000
6	0.216597000	-0.943521000	3.207345000
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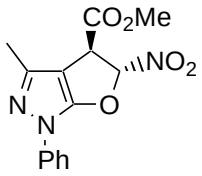

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6	-3.154676000	0.912631000	-0.303215000
6	-3.619028000	-1.464333000	-0.145618000
6	-4.485375000	1.141329000	-0.646656000
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1	-3.269649000	-2.469211000	0.046569000
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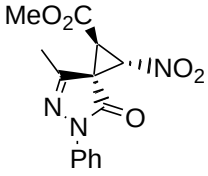

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6	2.816570000	-0.315712000	-0.025225000

6	3.483724000	0.765316000	-0.612384000
6	3.509810000	-1.494219000	0.271900000
6	4.841054000	0.652769000	-0.906934000
6	4.867662000	-1.586373000	-0.021340000
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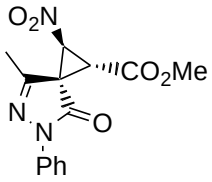

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1	-1.682713000	-3.132783000	1.402874000
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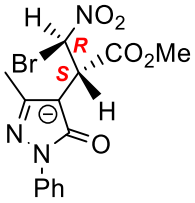

Adduct 2 (*S*,*R*)

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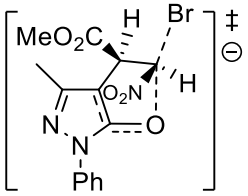

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1	-4.702848000	1.379885000	-1.025435000
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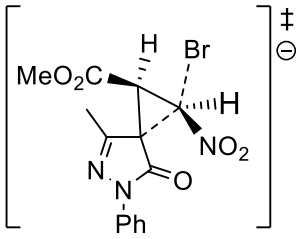

TS6

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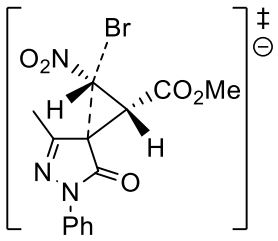

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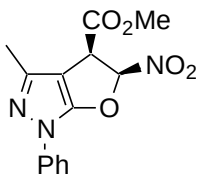

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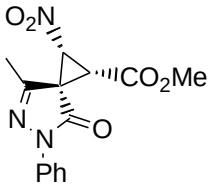

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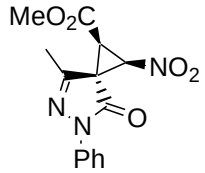

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