Electronic Supplementary Material (ESI) for RSC Advances.

Asymmetric Synthesis of Spiro[chroman-3,3'-pyrazol] Scaffolds with an All-carbon Quaternary Stereocenter *via* a *oxa*-Michael-Michael Cascade Strategy with Bifunctional Amine-thiourea Organocatalysts

Weiping Zheng, Jiarong Zhang, Shuang Liu, and Zhiwei Miao*,[a]

State Key Laboratory and Institute of Elemento-Organic Chemistry, Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Nankai University, Weijin Road 94, Tianjin 300071 (P. R. China) *Fax: (+86)-22-2350-2351; e-mail: miaozhiwei@nankai.edu.cn*

Supporting Information

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General Comments:

Solvents were dried and distilled prior to use according to the standard methods. Unless otherwise indicated, all materials were obtained from commercial sources, and used as purchased without dehydration. Nitrogen gas (99.999%) was purchased from Boc Gas Inc. Flash column chromatography was performed on silica gel (particle size 10-40 μm, Ocean Chemical Factory of Qingdao, China). ^{1}H NMR, ^{13}C NMR spectra were recorded in DMSO at Bruker AV 400 MHz spectrometers, TMS served as internal standard (δ = 0 ppm). Data are presented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, cm = complex multiplet) and coupling constant in Hertz (Hz). The crystal structure was determined on a Bruker SMART 1000 CCD diffractometer. The SHELXTL was used for structure solution and refinement**.** Mass spectra were recorded on a LCQ advantage spectrometer with ESI resource. HR-MS were recorded on APEXII and ZAB-HS spectrometer. Melting points were determined on a T-4 melting point apparatus (uncorrected). Optical rotations were recorded on a Perkin Elemer 241 Polarimeter.

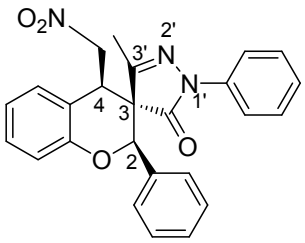
Typical reaction procedure for the synthesis of spiro[chroman-3,3'-pyrazol] derivatives 11:

(*E*)-2-(2-nitrovinyl)phenol **9** (0.5 mmol), catalyst **3** (15 mol%), additive BSA (15 mol%) and 4 Å MS (50 mg) in an oven-dried Schlenk tube were dissolved in 1 mL of anhydrous CH_3CN under nitrogen at 0 °C. Then 4-benzylidene-5-methyl-2-phenyl-pyrazolone **10** (0.6 mmol) was diluted with 1 mL of anhydrous CH_3CN and was added to the mixture by using a syringe. The mixture was stirred for the

corresponding time at 0 ˚C. The solvent was then removed under reduced pressure and the crude residue was purified by silica gel chromatography [petroleum ether/ethyl acetate 20:1 (v/v)] to give the corresponding products **11**.

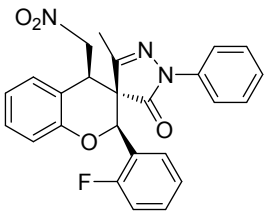
Characterizations of products 11a-t:

(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1',2-diphenyl spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11a):



Light yellow solid; m.p. 154-155 °C. $[\alpha]_D^{25}$ = +68 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.0 Hz, 2H), 7.24-7.38 (m, 7H), 7.18 (t, *J* = 7.1 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 2H), 5.44 (s, 1H), 4.83 (dd, *J* = 7.7, 3.4 Hz, 1H), 4.68 (dd, *J* = 14.3, 7.7 Hz, 1H), 4.19 (dd, *J* = 14.2, 3.4 Hz, 1H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.82, 157.34, 153.76, 136.65, 133.87, 130.00, 129.57, 129.40, 129.37,128.80, 128.40, 127.06, 126.49, 126.44, 126.00, 122.89, 120.15, 119.59, 117.75, 117.62, 81.29, 75.97, 60.00, 38.64, 17.83. HRMS (ESI): calcd for $C_{25}H_{21}N_3O_4$ $[M+H]^+$: 428.1610, found: 428.1604. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH /EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 42 bar, 23°C, UV 254 nm): tr (minor) = 10.49 min, tr (major) = 11.76 min.

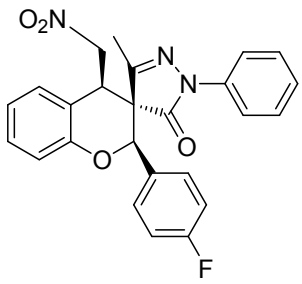
(2R,3R,4R)-2-(2-Fluorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11b):



Yellow solid; m.p. 162-163°C. $[\alpha]_D^{25}$ = +60 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 8.6, 1.0 Hz, 1H), 7.38-7.42 (m, 1H), 7.33-7.37 (m, 2H), 7.26-7.33 (m, 3H), 7.16-7.21 (m, 2H), 7.13 (dd, *J* = 7.5, 3.9 Hz, 2H), 7.04-7.07 (m, 2H), 5.79 (s, 1H), 4.87 (dd, *J* = 7.9, 3.4 Hz, 1H), 4.69 (dd, *J* = 14.2, 7.9 Hz, 1H), 4.17-4.22 (dd, *J* = 14.2, 3.4 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.03, 157.15, 153.95, 136.73, 131.39, 130.89, 129.97, 129.57, 128.83, 128.40, 126.60, 125.89, 124.12, 123.04, 119.87, 119.37, 117.76, 117.56, 116.13, 115.91, 76.01, 75.91, 59.26, 38.94, 18.04. HRMS(ESI): calcd for $C_{25}H_{20}FN_3O_4$ $[M+ H]^+$: 446.1516, found: 446.1514. HPLC (Daicel Chiralpak AD-H: *n*-

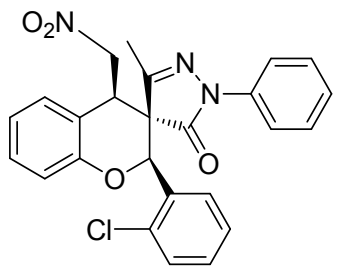
Hexane/*i*-PrOH, 95:5 v/v, flow rate = 1.0 mL/min, column pressure = 37 bar, 23°C, UV 254 nm): tr (minor) = 16.40 min, tr (major) = 25.43 min.

(2R,3R,4R)-2-(4-Fluorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11c):



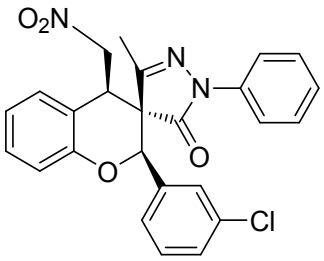
Yellow solid; m.p. 157-158 °C. $[\alpha]_D^{25}$ = +30 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (d, *J* = 7.7 Hz, 1H), 7.38-7.42 (m, 1H), 7.33-7.37 (m, 2H), 7.26-7.34 (m, 3H), 7.16-7.21 (m, 2H), 7.13 (dd, *J* = 7.5, 3.8 Hz, 2H), 7.05 (t, *J* = 9.0 Hz, 2H), 5.79 (s, 1H), 4.87 (dd, *J* = 7.8, 3.3 Hz, 1H), 4.69 (dd, *J* = 14.2, 7.9 Hz, 1H), 4.20 (dd, *J* = 14.2, 3.5 Hz, 1H), 2.16 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.03, 157.16, 153.93, 136.71, 131.40, 129.97, 129.58, 128.83, 128.39, 126.61, 125.89, 124.13, 123.04, 119.87, 119.51, 119.37, 117.76, 117.56, 116.13, 115.90, 75.98, 75.91, 59.26, 38.93, 18.06. HRMS (ESI): calcd for $C_{25}H_{20}FN_3O_4$ $[M+H]^+$: 446.1516, found: 446.1514. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH/EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 44 bar, 23°C, UV 254 nm): tr (minor) = 12.13 min, tr (major) = 10.58 min.

(2R,3R,4R)-2-(2-Chlorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11d):



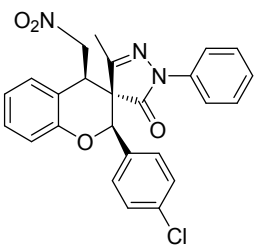
Light yellow solid; m.p. 173-174°C. $[\alpha]_D^{25}$ = +30 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49-7.74 (m, 3H), 7.28-7.43 (m, 5H), 7.13-7.26 (m, 3H), 7.10 (t, *J* = 7.8 Hz, 2H), 5.32 (s, 1H), 4.81 (dd, *J* = 7.8, 3.4 Hz, 1H), 4.68 (dd, *J* = 14.3, 7.7 Hz, 1H), 4.19 (dd, *J* = 14.2, 3.4 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.66, 157.13, 153.39, 136.54, 136.22, 132.46, 130.90, 130.12, 129.94, 129.68, 129.33, 128.91, 128.79, 126.50, 126.17, 125.16, 123.13, 122.47, 119.59, 117.63, 80.23, 75.85, 60.42, 38.52, 17.73. HRMS (ESI): calcd for $C_{25}H_{20}ClN_3O_4$ $[M+H]^+$: 462.1221, found: 462.1212. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH/EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 44 bar , 23°C, UV 254nm): tr (minor) = 8.89 min, tr (major) = 9.82 min.

(2R,3R,4R)-2-(3-Chlorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11e):



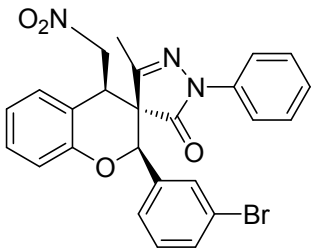
Light yellow solid; m.p. 172-173 °C. $[\alpha]_D^{25}$ = +68 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (d, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 7.0 Hz, 2H), 7.28-7.36 (m, 6H), 7.18 (t, *J* = 7.1 Hz, 2H), 7.12 (t, *J* = 7.5 Hz, 2H), 5.42 (s, 1H), 4.81 (dd, *J* =7.9, 3,3 Hz, 1H), 4.67 (dd, *J* = 14.2, 7.9 Hz, 1H), 4.18 (dd, *J* = 14.2, 3.3 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.66, 157.13, 153.41, 136.57, 136.00, 134.43, 130.11, 129.68, 129.53, 129.35, 128.89, 126.50, 126.43, 126.14, 124.74, 123.12, 120.06, 119.55, 117.74, 117.62, 80.34, 75.85, 59.84,38.56, 17.74. HRMS (ESI): calcd for $C_{25}H_{20}ClN_3O_4$ $[M+H]^+$: 462.1221, found: 462.1212. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH/EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 44 bar, 23°C, UV 254 nm): tr (minor) = 14.21 min, tr (major) = 11.53 min.

(2R,3R,4R)-2-(4-Chlorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11f):



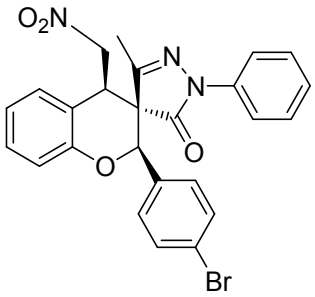
Light yellow solid; m.p. 175-176 °C. [α]D25 = +80 (c = 1.0, CH2Cl2). 1H NMR (400 MHz, CDCl3): δ 7.45-7.79 (m, 2H), 7.24-7.49 (m, 7H), 7.15-7.27 (m, 2H), 7.01-7.16 (m, 2H), 5.32 (s, 1H), 4.81 (dd, J = 7.7, 3.5 Hz, 1H), 4.67 (dd, J = 14.2, 7.7 Hz, 1H), 4.18 (dd, J = 14.2, 3.6 Hz, 1H), 2.08 (s, 3H). ^{13}C NMR (101 MHz, CDCl3): δ 169.68, 156.15, 152.49, 135.57, 134.24, 131.51, 129.87, 129.05, 128.62, 127.88, 127.61, 127.44, 126.83, 125.48, 125.12, 122.04, 118.98, 118.45, 116.68, 116.56, 79.49, 74.84, 58.88, 37.64, 16.73. HRMS (ESI): calcd for $C_{25}H_{20}ClN_3O_4$ $[M+H]^+$: 462.1221, found: 462.1212. HPLC (Daicel Chiralpak ID-H: n-Hexane/i-PrOH, 93:7 v/v, flow rate = 1.0 mL/min, column pressure = 39 bar, 23°C, UV 254 nm): tr (minor) = 22.84 min, tr (major) = 24.70 min.

(2R,3R,4R)-2-(3-Bromophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11g):



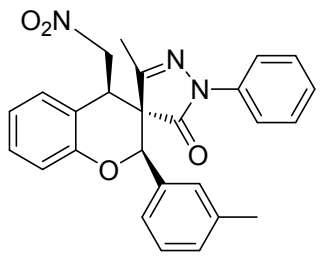
Light yellow solid; m.p. 103-104 °C. $[\alpha]_D^{25}$ = +40 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.40-7.67 (m, 4H), 7.29-7.40 (m, 4H), 7.14-7.29 (m, 3H), 7.12 (dd, *J* = 7.9, 6.4 Hz, 2H), 5.76 (dd, *J* = 15.7, 8.9 Hz, 1H), 5.39 (s, 1H), 4.80 (dd, *J* = 7.7, 3.4 Hz, 1H), 4.68 (dd, *J* = 14.2, 7.7 Hz, 1H), 4.19 (dd, *J* = 14.2, 3.5 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.67, 157.13, 153.39, 136.56, 136.23, 132.46, 130.11, 129.94, 129.67, 129.34, 128.90, 126.52, 126.16, 125.17, 123.13, 122.46, 120.10, 119.60, 117.74, 117.63, 80.24, 75.85, 59.86, 38.53, 17.72. HRMS (ESI): calcd for $C_{25}H_{20}BrN_3O_4$ $[M+H]^+$: 506.0715, found: 506.0702. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH/EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 44 bar, 23°C, UV 254 nm): tr (minor) = 13.44 min, tr (major) = 11.71 min.

(2R,3R,4R)-2-(4-Bromophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11h) :



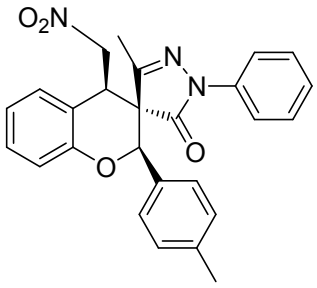
Light yellow solid; m.p. 132-133 °C. $[\alpha]_D^{25}$ = +28 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.53 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.41-7.48 (m, 2H), 7.29-7.41 (m, 5H), 7.16-7.25 (m, 2H), 7.06-7.16 (m, 2H), 5.40 (s, 1H), 4.81 (dd, *J* = 7.7, 3.5 Hz, 1H), 4.67 (dd, *J* = 14.2, 7.7 Hz, 1H), 4.18 (dd, *J* = 14.2, 3.6 Hz, 1H), 2.07 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.70, 157.15, 153.50, 136.59, 133.06, 131.60, 130.92, 130.09, 129.65, 128.92, 128.73, 128.12, 126.51, 126.18, 123.51, 123.08, 120.05, 119.51, 117.72, 117.60, 80.55, 75.86, 59.83, 38.68, 17.76. HRMS (ESI): calcd for $C_{25}H_{20}BrN_3O_4$ $[M+H]^+$: 506.0715, found: 506.0702. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH, 90:10 v/v, flow rate = 1.0 mL/min, column pressure = 40 bar, 23°C, UV 254 nm): tr (minor) = 19.88 min, tr (major) = 21.78 min.

(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1'-phenyl-2-(m-tolyl)spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11i):



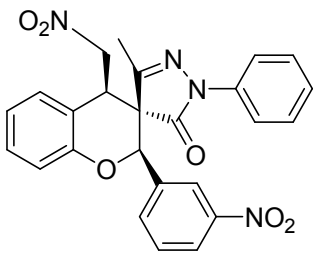
Light yellow solid; m.p.135-136 °C. $[\alpha]_D^{25}$ = +80 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.28-7.53 (m, 5H), 7.15-7.28 (m, 5H), 7.02-7.15 (m, 3H), 5.40 (s, 1H), 4.82 (dd, *J* = 8,7, 3,3 Hz, 1H), 4.67 (dd, *J* = 14.1,8.7 Hz, 1H), 4.19 (dd, *J* = 14.2, 3.3 Hz, 1H), 2.27 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.90, 156.43, 152.72, 137.05, 135.70, 132.81, 129.03, 128.49, 127.75, 127.24, 125.96, 125.44, 124.90, 122.89, 122.28, 121.79, 119.07, 118.51, 116.71, 116.57, 80.16, 74.93, 58.95, 37.49, 20.32, 16.74. HRMS (ESI): calcd for $C_{26}H_{23}N_3O_4$ $[M+H]^+$: 442.1767, found: 442.1759. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH/EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 44 bar, 23°C, UV 254 nm): tr (minor) = 11.79 min, tr (major) = 9.86 min.

(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1'-phenyl-2-(p-tolyl)spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11j) :



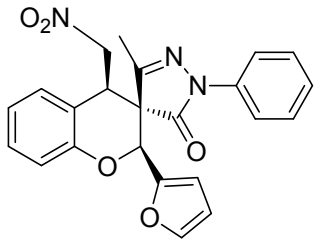
Light yellow solid; m.p. 154-155 °C. $[\alpha]_D^{25}$ = +60 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.25-7.61 (m, 7H), 7.15-7.22 (m, 2H), 7.02-7.14 (m, 4H), 5.41 (s, 1H), 4.81 (dd, *J* = 7.8, 3.4 Hz, 1H), 4.67 (dd, *J* = 14.2, 7.9 Hz, 1H), 4.18 (dd, *J* = 14.2, 3.4 Hz, 1H), 2.29 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.90, 156.43, 152.72, 137.05, 135.70, 132.81, 129.03, 128.49, 127.75, 127.24, 125.96, 125.44, 124.90, 122.89, 122.28, 121.79, 119.07, 118.51, 116.71, 116.57, 80.16, 74.93, 58.95, 37.49, 20.32, 16.74. HRMS (ESI): calcd for $C_{26}H_{23}N_3O_4$ $[M+H]^+$: 442.1767, found: 442.1759. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH/EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 44 bar , 23 °C, UV 254 nm): tr (minor) =14.65 min, tr (major) = 12.09 min.

(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-2-(3-nitrophenyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11k):



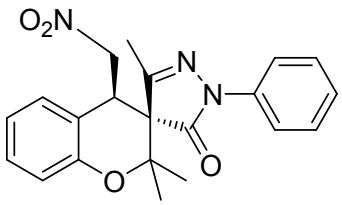
Light yellow solid; m.p. 168-169 °C. $[\alpha]_D^{25}$ = +60 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 11.7 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 7.44-7.95 (m, 4H), 7.24-7.44 (m, 4H), 7.10-7.21 (m, 3H), 5.54 (s, 1H), 4.85 (dd, *J* = 7.2, 3.2 Hz, 1H), 4.70 (dd, *J* = 14.2, 7.2 Hz, 1H), 4.20 (dd, *J* = 14.2, 3.2 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.46, 157.00, 153.09, 148.12, 136.22, 132.85, 130.28, 129.86, 129.49, 129.42, 128.98, 126.57, 126.25, 124.30, 123.44, 121.31, 119.63, 119.16, 117.80, 117.71, 79.86, 75.78, 59.88, 38.51, 17.76. HRMS (ESI): calcd for $C_{25}H_{20}N_3O_5$ $[M+H]^+$: 473.1461, found: 473.1454. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH/EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 45 bar , 23 °C, UV 254 nm): tr (minor) = 36.77 min, tr (major) = 31.81 min.

(2R,3R,4R)-2-(Furan-3-yl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11l):



Yellow solid; m.p. 125-126 °C. $[\alpha]_D^{25}$ = +17 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.70 (dd, *J* = 5.6, 3.4 Hz, 1H), 7.59 (dd, *J* = 5.6, 3.4 Hz, 1H), 7.37 (qd, *J* = 11.6, 7.2 Hz, 4H), 7.05-7.25 (m, 4H), 6.48 (dd, *J* = 7.6, 3.3 Hz, 1H), 6.27-6.36 (m, 1H), 5.45 (s, 1H), 4.72 (dd, *J* = 8.7, 2.9 Hz, 1H), 4.63 (dd, *J* = 14.0, 8.7 Hz, 1H), 4.18 (dd, *J* = 14.0, 3.0 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.43, 159.24, 152.27, 146.17, 142.70, 135.92, 129.05, 128.59, 127.82, 125.35, 124.95, 121.91, 118.85, 117.98, 116.62, 115.85, 109.56, 109.27, 74.56, 69.62, 56.78, 37.79, 16.21. HRMS (ESI): calcd for $C_{23}H_{19}N_3O_5$ $[M+Na]^+$: 440.1217, found: 440.1214. HPLC (Daicel Chiralpak AD-H: *n*-Hexane/*i*-PrOH, 95:5 v/v, flow rate = 1.0 mL/min , column pressure = 37 bar, 23°C, UV 254 nm): tr (minor) = 44.67 min, tr (major) = 27.80 min.

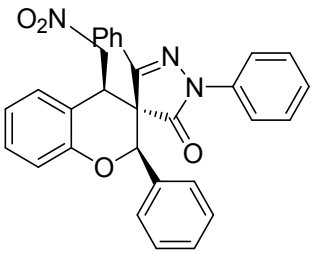
(3R,4R)-2,2,3'-Trimethyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11m):



Yellow solid; m.p. 97-98 °C. $[\alpha]_D^{25}$ = -144 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.93 (d, *J* = 8.1 Hz, 2H), 7.46 (t, *J* = 7.9 Hz, 2H),

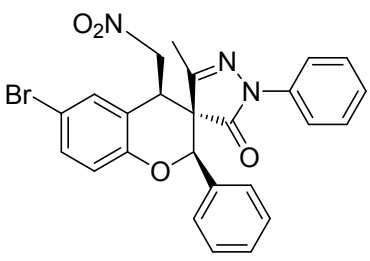
7.22-7.34 (m, 4H), 7.11 (d, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 7.2 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 4.60 (dd, *J* = 14.1, 7.7 Hz, 1H), 4.49 (dd, *J* = 7.3, 2.2 Hz, 1H), 4.05 (dd, *J* = 14.1, 2.9 Hz, 1H), 2.00 (s, 3H), 1.61 (s, 3H), 1.58 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 169.88, 158.76, 151.31, 136.28, 128.58, 128.01, 125.39, 124.83, 121.23, 118.28, 118.09, 117.11, 76.19, 75.84, 75.39, 35.22, 23.24, 21.68, 16.31. HRMS (ESI): calcd for $C_{21}H_{21}N_3O_4$ $[M+Na]^+$: 402.1424, found: 402.1422. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH/EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 40 bar, 23 °C, UV 254 nm): tr (major) = 5.42 min.

(2R,3R,4R)-4-(Nitromethyl)-1',2,3'-triphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11n):



Light yellow solid; m.p. 139-140 °C. $[\alpha]_D^{25}$ = -32 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (dd, *J* = 5.3, 3.6 Hz, 2H), 7.65 (d, *J* = 7.7 Hz, 1H), 7.57 (dd, *J* = 12.3, 7.8 Hz, 4H), 7.31-7.46 (m, 7H), 7.21 (t, *J* = 9.9 Hz, 4H), 7.06 (dd, *J* = 30.0, 8.2 Hz, 1H), 5.36 (s, 1H), 4.95 (dd, *J* = 5.8, 6.4 Hz, 1H), 4.76 (dd, *J* = 19.6, 5.8 Hz, 1H), 4.08 (dd, *J* = 19.6, 6.4 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.67, 166.75, 132.64, 131.44, 129.86, 129.54, 129.15,128.62, 128.42, 128.33, 128.25, 127.79, 127.70, 127.28, 127.13, 126.99, 126.65, 126.60, 125.95, 125.27, 122.27, 121.98, 119.58, 119.27, 117.35, 117.09, 81.74, 78.49, 67.15, 37.72. HRMS (ESI): calcd for $C_{30}H_{23}N_3O_5$ $[M+Na]^+$: 512.1586, found: 512.1585. HPLC (Daicel Chiralpak AD-H: *n*-Hexane/*i*-PrOH, 95:5 v/v, flow rate = 1.0 mL/min, column pressure = 37bar, 23 °C, UV 254 nm): tr (minor) = 32.44 min, tr (major) = 26.48 min.

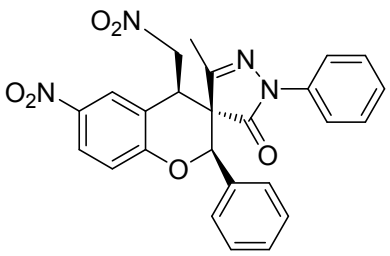
(2R,3R,4R)-6-Bromo-3'-methyl-4-(nitromethyl)-1',2-diphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11o):



Light yellow solid; m.p. 170-171 °C. $[\alpha]_D^{25}$ = +48 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.34-7.53 (m, 5H), 7.26-7.34 (m, 6H), 7.13-7.22 (m, 1H), 7.00 (d, *J* = 8.7 Hz, 1H), 5.40 (s, 1H), 4.78 (dd, *J* = 7.5, 3.5 Hz, 1H), 4.66 (dd, *J* = 14.5, 7.6 Hz, 1H), 4.19 (dd, *J* = 14.4, 3.6 Hz, 1H), 2.11 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.50, 156.85, 152.95, 136.57, 133.43, 133.13, 132.70, 131.84, 129.55, 129.39, 128.83, 128.45, 127.04, 126.39, 126.12, 121.58, 120.18, 119.62,

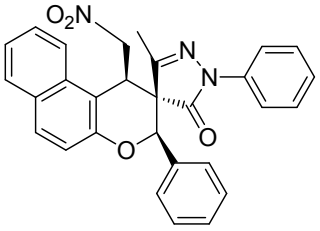
119.41, 115.08, 81.50, 75.62, 59.68, 38.44, 17.81. HRMS (ESI): calcd for $C_{25}H_{20}BrN_3O_4$ $[M+H]^+$: 506.0715, found: 506.0702. HPLC (Daicel Chiralpak AD-H: *n*-Hexane/*i*-PrOH , 95:5 v/v, flow rate = 1.0 mL/min, column pressure = 37 bar, 23 °C, UV 254 nm): tr (minor) = 31.89 min, tr (major) = 25.96 min.

(2R,3R,4R)-3'-Methyl-6-nitro-4-(nitromethyl)-1',2-diphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11p):



Yellow solid; m.p. 209-210 °C. $[\alpha]_D^{25}$ = +53 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, DMSO): δ 8.70 (s, 1H), 8.22 (d, *J* = 9.4 Hz, 1H), 7.70 (d, *J* = 13.3 Hz, 1H), 7.24-7.36 (m, 9H), 7.15 (t, *J* = 7.6 Hz, 1H), 5.85 (dd, *J* = 15.2, 9.2 Hz,1H), 5.81 (s, 1H), 5.13 (dd, *J* = 17.4, 15.2 Hz, 1H), 4.41 (dd, *J* = 17.4, 9.2 Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (101 MHz, DMSO): δ 170.84, 159.64, 142.33, 136.92, 133.99, 132.18, 132.00, 129.77, 129.31, 129.14, 128.66, 128.19, 127.82, 126.16, 125.35, 119.64, 119.48, 118.49, 77.47, 75.27, 56.58, 36.00, 17.13. HRMS (ESI): calcd for $C_{25}H_{20}N_4O_6$ $[M+Na]^+$: 495.1281, found:496.1275. HPLC (Daicel Chiralpak AD-H: *n*-Hexane/*i*-PrOH, 95:5 v/v, flow rate = 1.0 mL/min, column pressure = 37bar, 23 °C, UV 254 nm): tr (minor) = 69.38 min, tr (major) = 49.21 min.

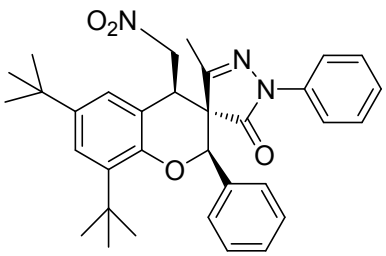
(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1',2-diphenyl-2,4-dihydrospiro[benzo[g]chromene-3,4'-pyrazol]-5'(1'H)-one (11q):



Yellow solid; m.p. 176-177 °C. $[\alpha]_D^{25}$ = +68 (c = 1.0, CH_2Cl_2). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 9.0 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.47-7.52 (m, 1H), 7.44 (d, *J* = 4.1 Hz, 2H), 7.37 (d, *J* = 7.9 Hz, 2H), 7.22-7.34 (m, 6H), 7.14 (t, *J* = 7.4 Hz, 1H), 5.77 (dd, *J* = 17.0, 9.8 Hz, 1H), 5.44 (s, 1H), 4.74 (t, *J* = 12.2 Hz, 2H), 1.93 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.08, 158.91, 152.38, 136.68, 133.79, 130.99, 130.80, 130.23, 129.72, 129.41, 128.71, 128.46, 128.41, 127.08, 125.93, 124.79, 120.57, 120.16, 118.39, 108.23, 77.23, 73.74, 55.57, 33.64, 17.07. HRMS (ESI): calcd for $C_{29}H_{23}N_3O_6$ $[M+Na]^+$: 500.1586, found: 500.1583. HPLC (Daicel

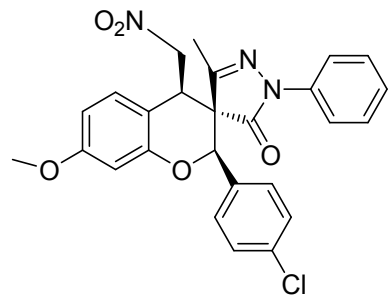
Chiralpak AD-H: *n*-Hexane/*i*-PrOH, 95:5 v/v, flow rate = 1.0 mL/min, column pressure = 37 bar, 23 °C, UV 254 nm): tr (minor) = 36.82 min, tr (major) = 29.99 min.

(2R,3R,4R)-6,8-Di-*tert*-butyl-3'-methyl-4-(nitromethyl)-1',2-diphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11r):



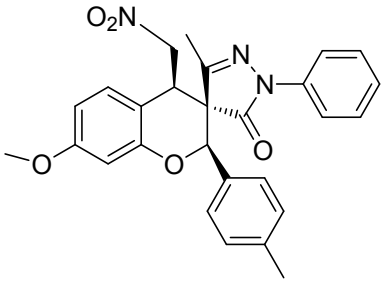
Yellow solid; m.p. 136-137 °C. $[\alpha]_D^{25}$ = +20 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.59 (d, *J* = 8.0 Hz, 1H), 7.41-7.44 (m, 1H), 7.37-7.40 (m, 1H), 7.32-7.36 (m, 3H), 7.26-7.32 (m, 4H), 7.12-7.21 (m, 1H), 7.07 (s, 1H), 5.03 (s, 1H), 4.82 (dd, *J* = 14.0, 9.0 Hz, 1H), 4.45 (dd, *J* = 9.0, 3.7 Hz, 1H), 4.34 (dd, *J* = 14.0, 3.7 Hz, 1H), 2.04 (s, 3H), 1.42 (s, 3H), 1.38 (s, 6H), 1.35 (s, 3H), 1.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.03, 158.16, 149.68, 143.85, 137.05, 135.66, 133.04, 128.18, 127.61, 127.23, 126.24, 124.83, 123.26, 122.57, 119.20, 115.67, 76.62, 75.52, 55.72, 36.28, 34.14, 33.52, 30.46, 28.79, 15.88. HRMS (ESI): calcd for $C_{33}H_{37}N_3O_6$ $[M+Na]^+$: 562.282, found: 562.2680. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH/EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 44 bar , 23°C, UV 254 nm) : tr (minor) = 3.77 min, tr (major) = 5.01 min.

(2R,3R,4R)-2-(4-Chlorophenyl)-7-methoxy-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11s):



Light yellow solid; m.p. 135-136 °C. $[\alpha]_D^{25}$ = +9 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.46-7.58 (m, 2H), 7.23-7.40 (m, 7H), 7.07 (d, *J* = 8.2 Hz, 1H), 6.55-6.76 (m, 2H), 5.40 (s, 1H), 4.72 (dd, *J* = 7.8, 4.2 Hz, 1H) 4.64 (dd, *J* = 14.4, 4.2 Hz, 1H), 4.16 (d, *J* = 14.4,7.8 Hz, 1H), 3.84 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.74, 160.54, 157.17, 154.51, 136.61, 135.28, 132.53, 130.92, 130.03, 128.91, 128.79, 128.64, 128.47, 127.87, 127.24, 126.13, 119.48, 111.14, 110.01, 102.20, 80.70, 76.00, 59.95, 55.49, 38.44, 17.80. HRMS (ESI): calcd for $C_{26}H_{22}ClN_3O_5$ $[M+ H]^+$: 492.1326, found: 492.1315. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH/EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 44 bar, 23 °C, UV 254 nm): tr (minor) = 13.71 min, tr (major) = 9.94 min.

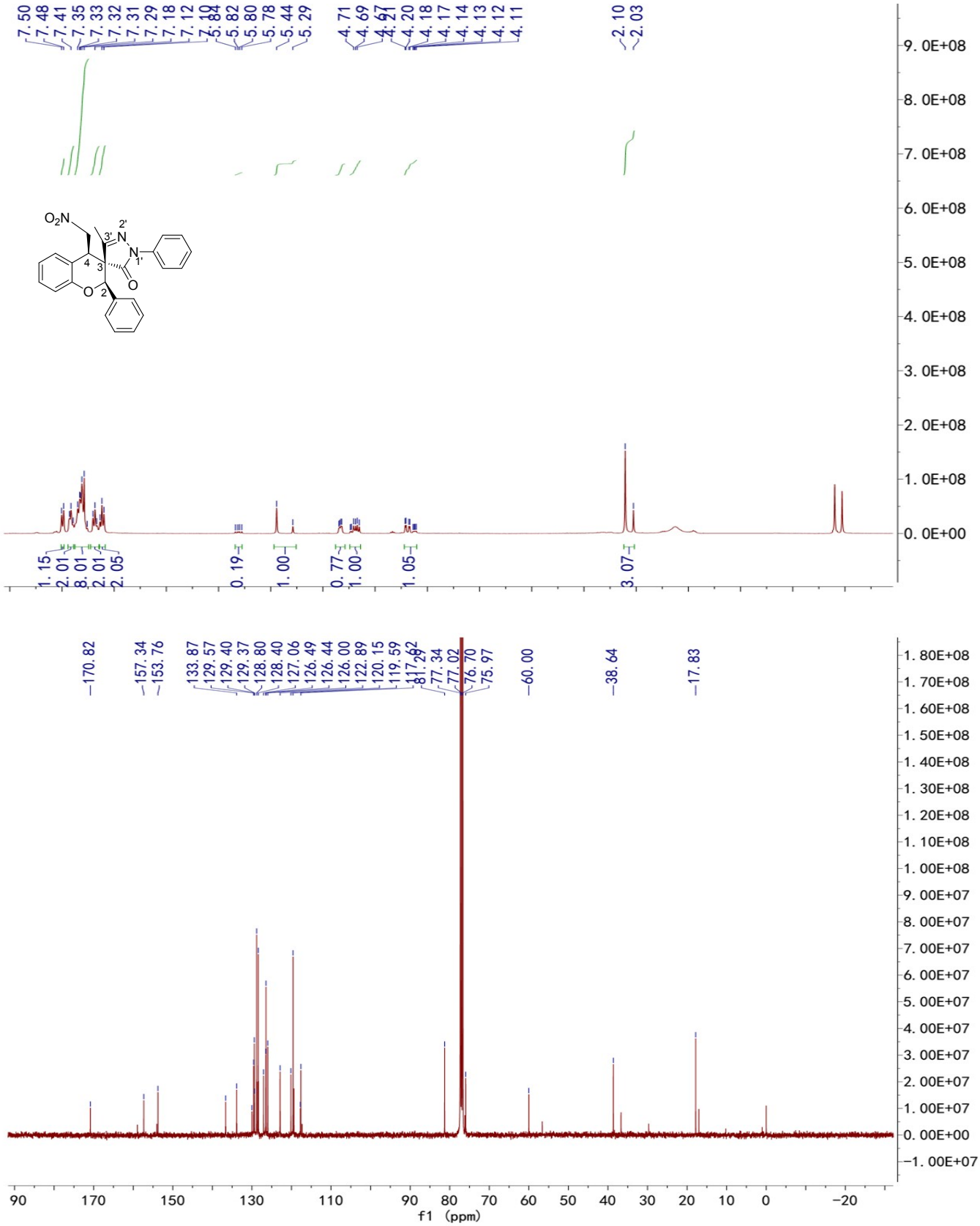
(2R,3R,4R)-7-Methoxy-3'-methyl-4-(nitromethyl)-1'-phenyl-2-(p-tolyl)spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11t):



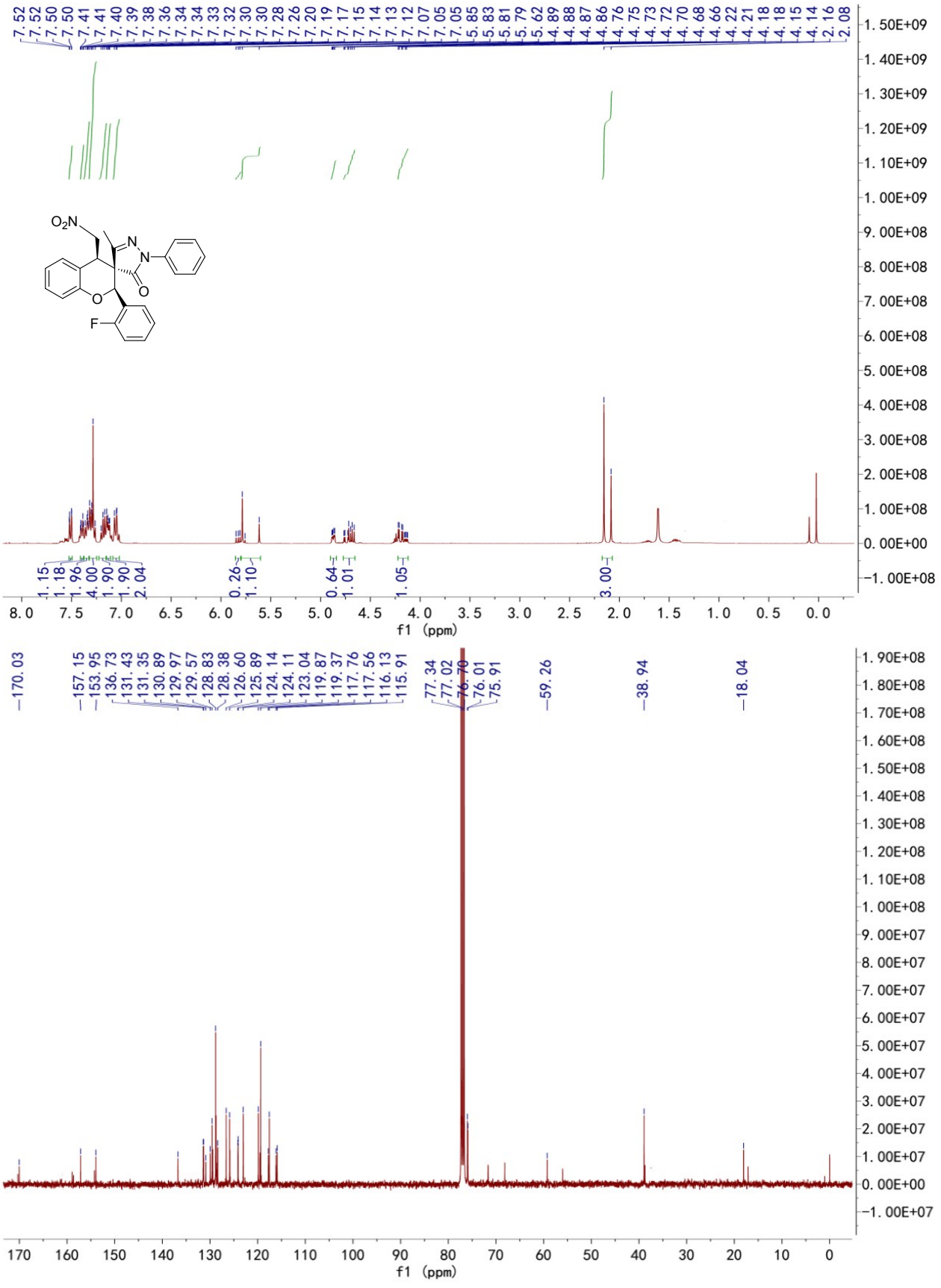
Light yellow solid; m.p. 145-146 °C. $[\alpha]_D^{25}$ = +40 (c = 1.0, CH_2Cl_2). ^1H NMR (400 MHz, $CDCl_3$): δ 7.51 (dd, *J* = 5.6, 3.3 Hz, 2H), 7.23-7.43 (m, 6H), 7.18 (t, *J* = 7.4 Hz, 1H), 7.01-7.15 (m, 3H), 5.39 (s, 1H), 4.73 (dd, *J* = 7.6, 3.4 Hz, 1H), 4.62 (dd, *J* = 14.0, 7.6 Hz, 1H), 4.15 (dd, *J* = 14.0, 3.4 Hz, 1H), 3.84 (s, 3H), 2.28 (s, 3H), 2.20 (s, 3H), 2.10 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.96, 160.46, 157.51, 154.85, 139.24, 136.78, 130.93, 129.99, 129.07, 128.77, 127.19, 126.95, 126.35, 125.91, 120.09, 119.61, 111.31, 110.32, 109.77, 102.18, 81.40, 76.10, 60.07, 55.46, 38.48, 21.16, 17.83. HRMS (ESI): calcd for $C_{27}H_{25}N_3O_5$ $[M+H]^+$:472.1872, found: 472.1865. HPLC (Daicel Chiralpak ID-H: *n*-Hexane/*i*-PrOH/EtOH, 85:10:5 v/v, flow rate = 1.0 mL/min, column pressure = 44 bar, 23 °C, UV 254 nm): tr (minor) = 13.93 min, tr (major) = 9.41 min.

^{1}H-NMR and ^{13}C-NMR Spectra

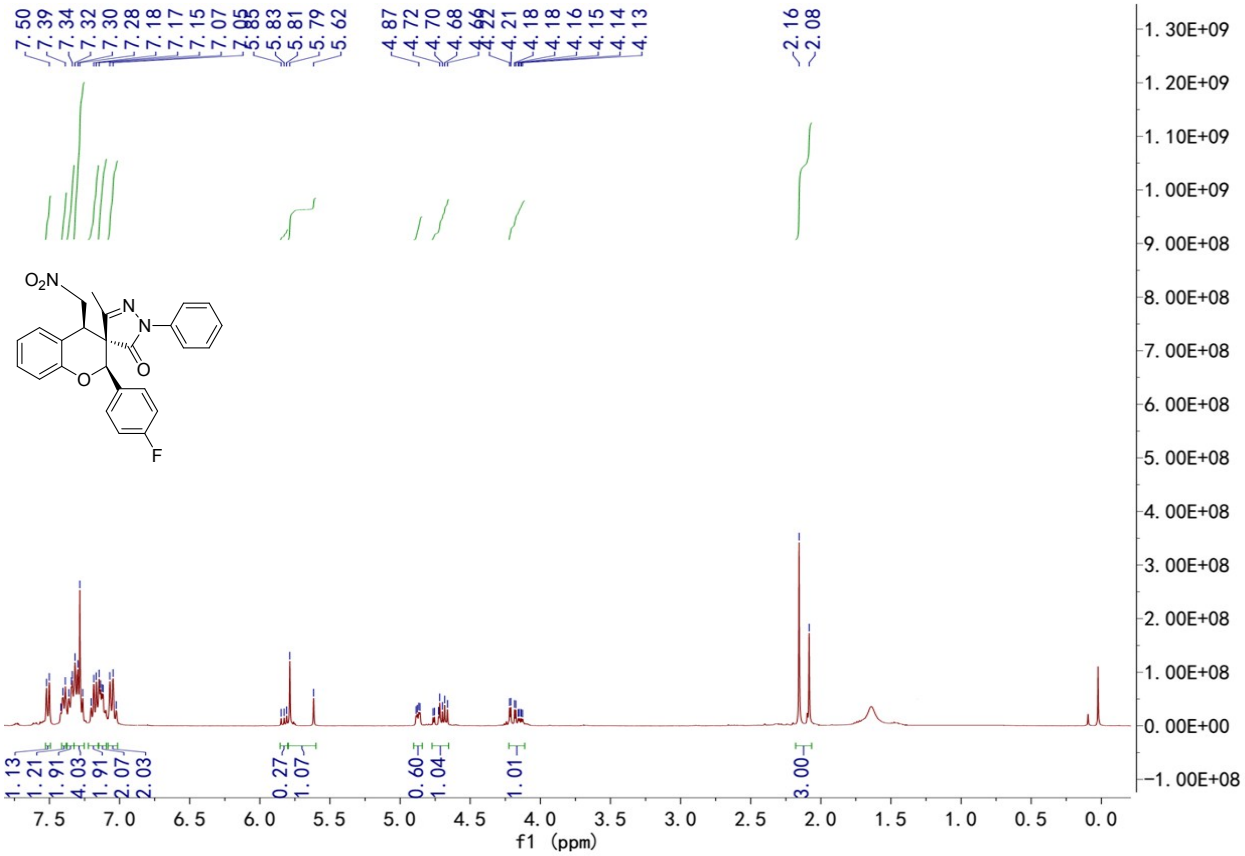
(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1',2-diphenyl spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11a):

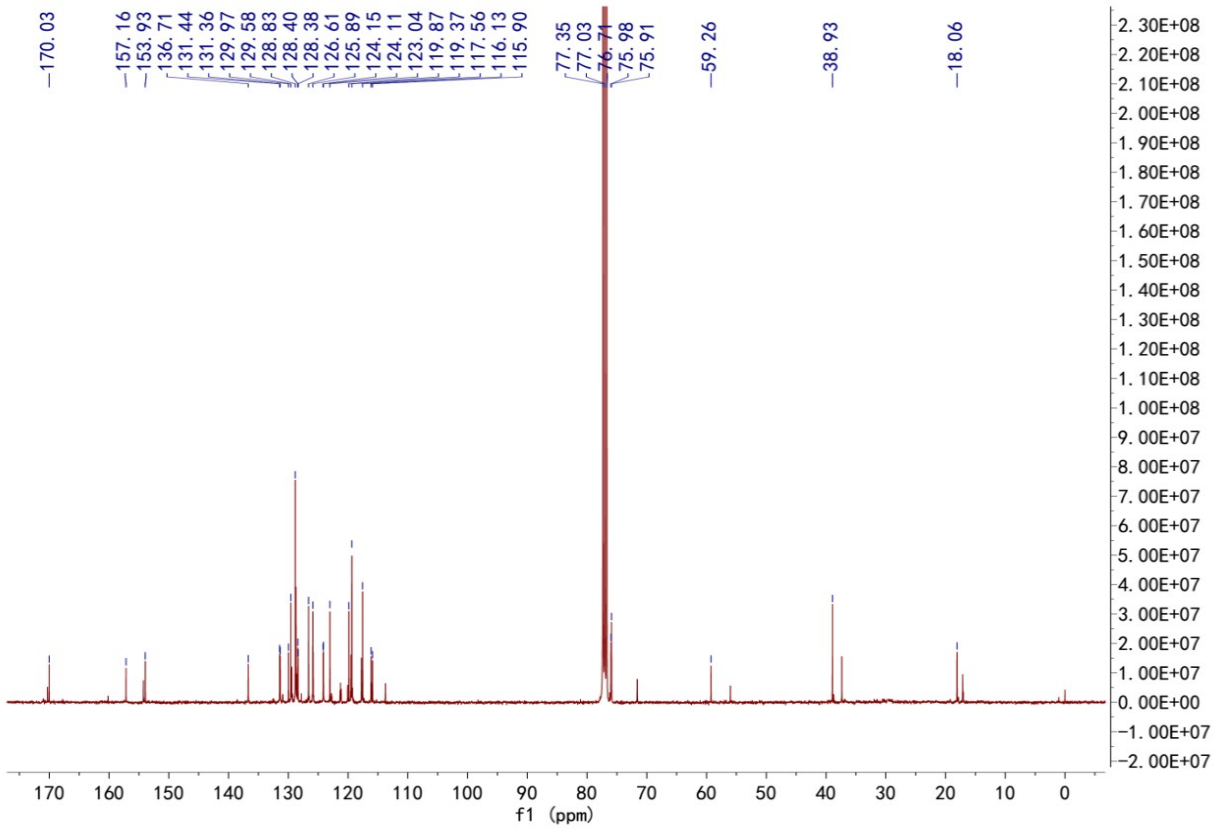


(2R,3R,4R)-2-(2-Fluorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11b)：

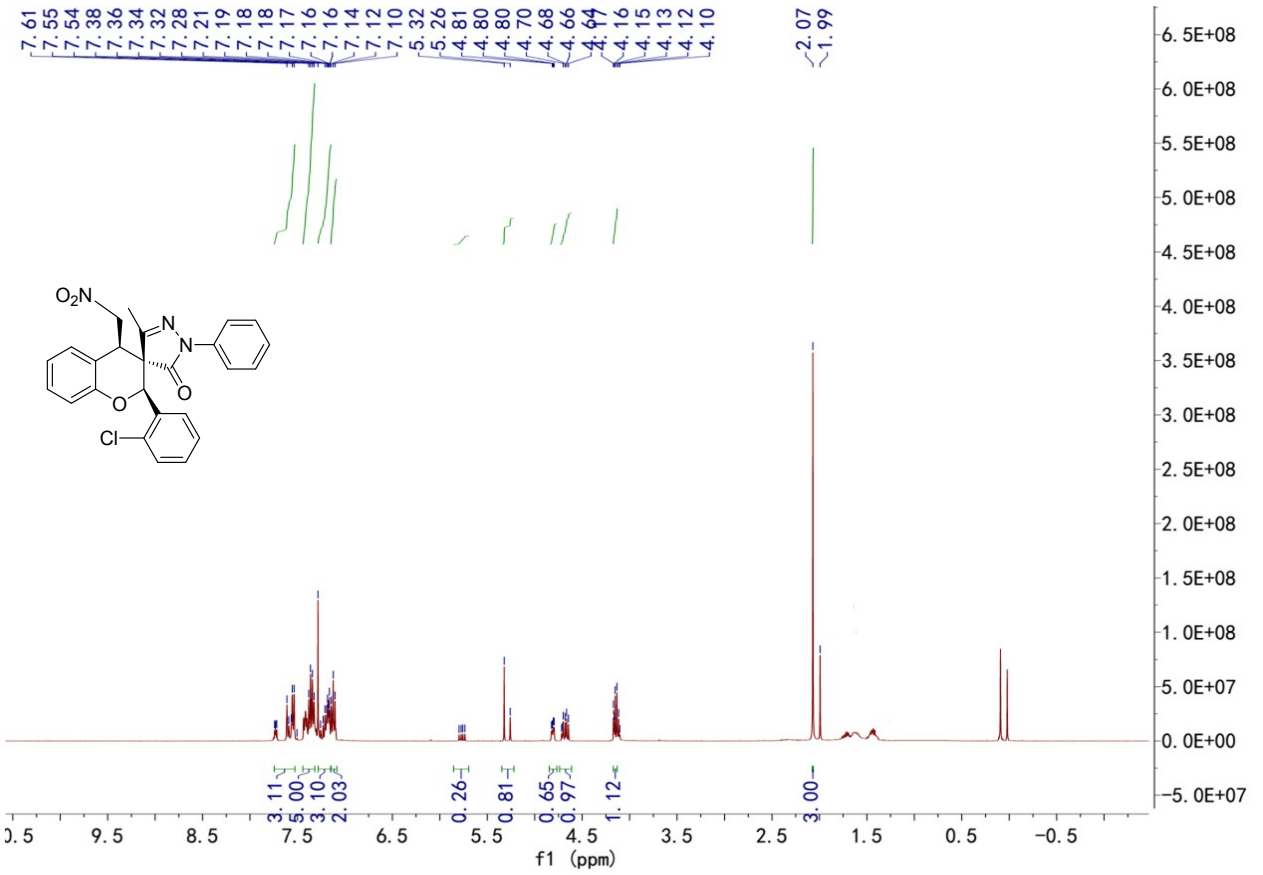


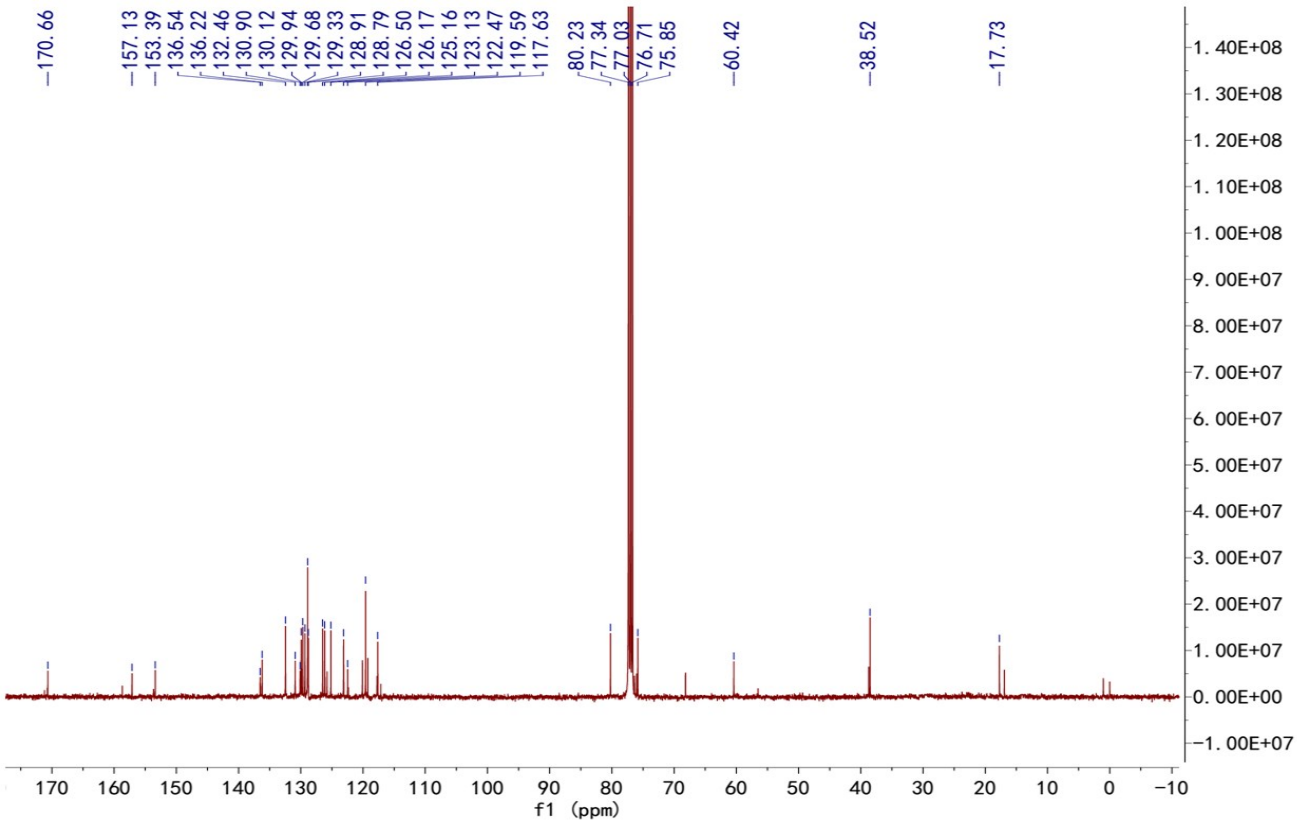
(2R,3R,4R)-2-(4-Fluorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11c):



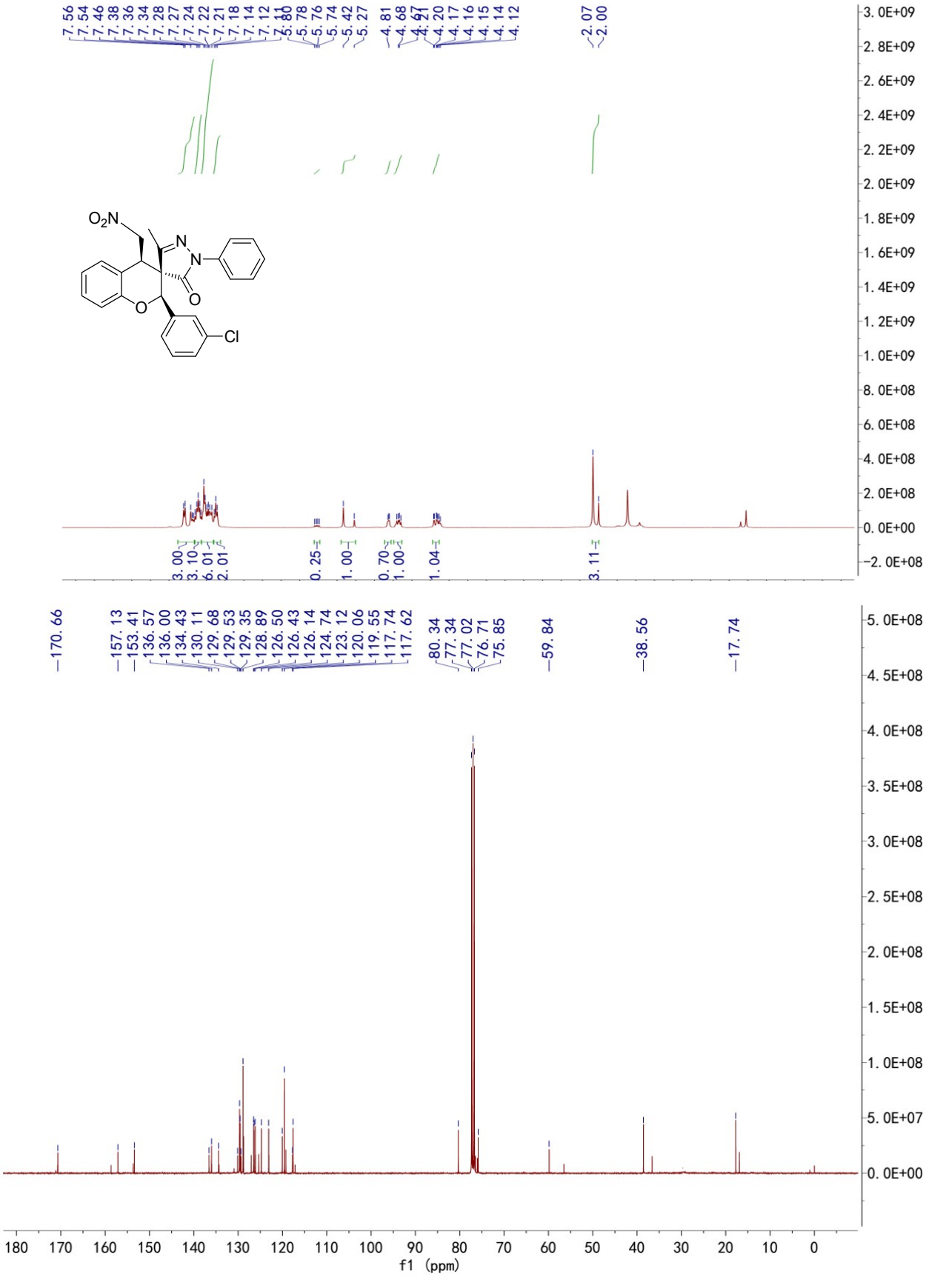


(2R,3R,4R)-2-(2-Chlorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11d):

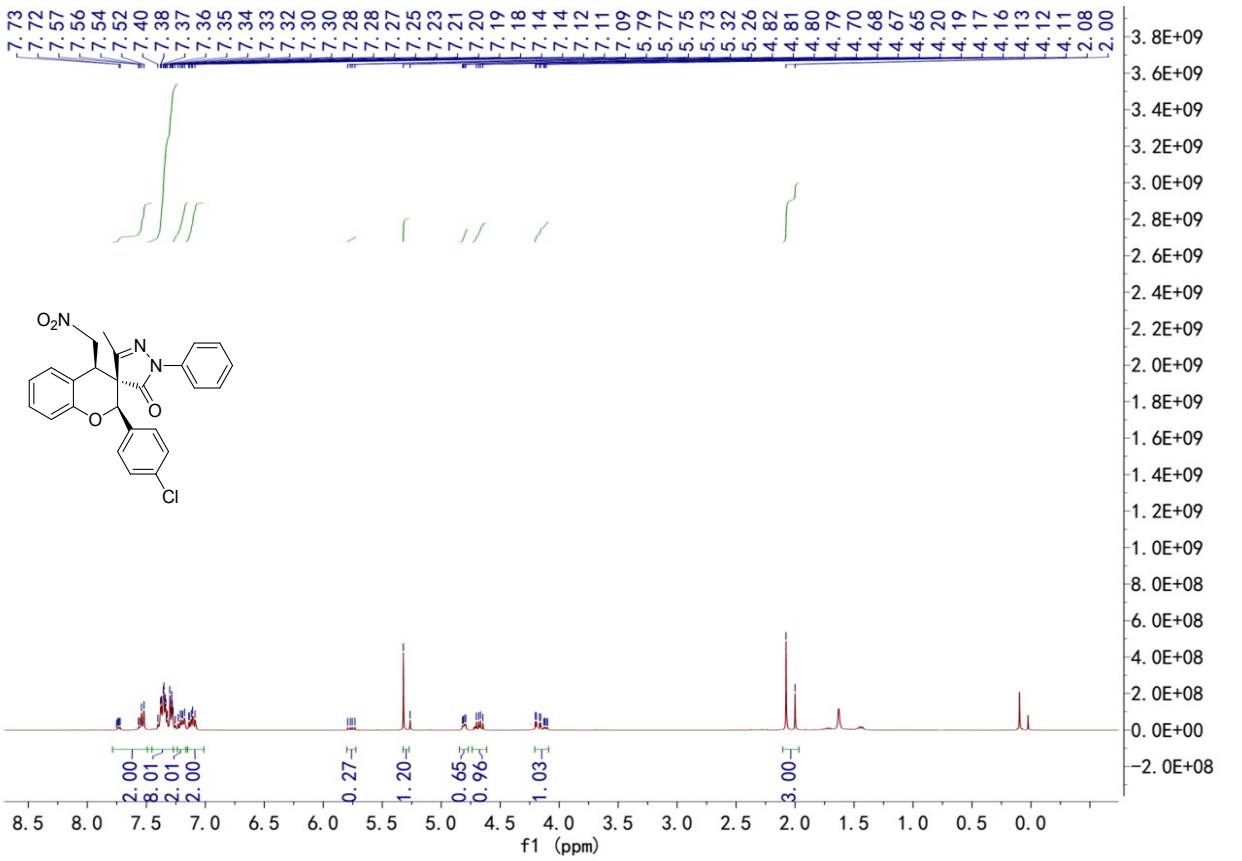


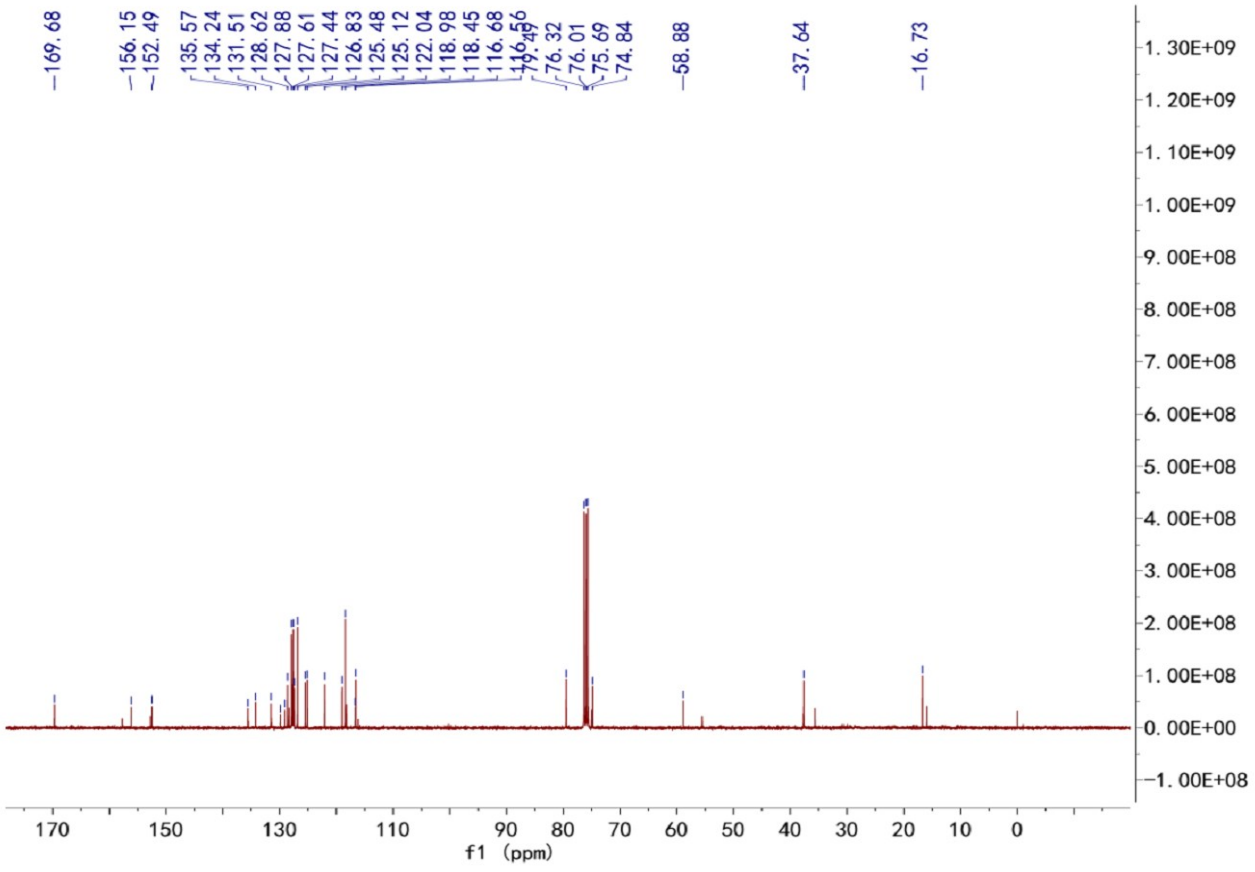


(2R,3R,4R)-2-(3-Chlorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11e):

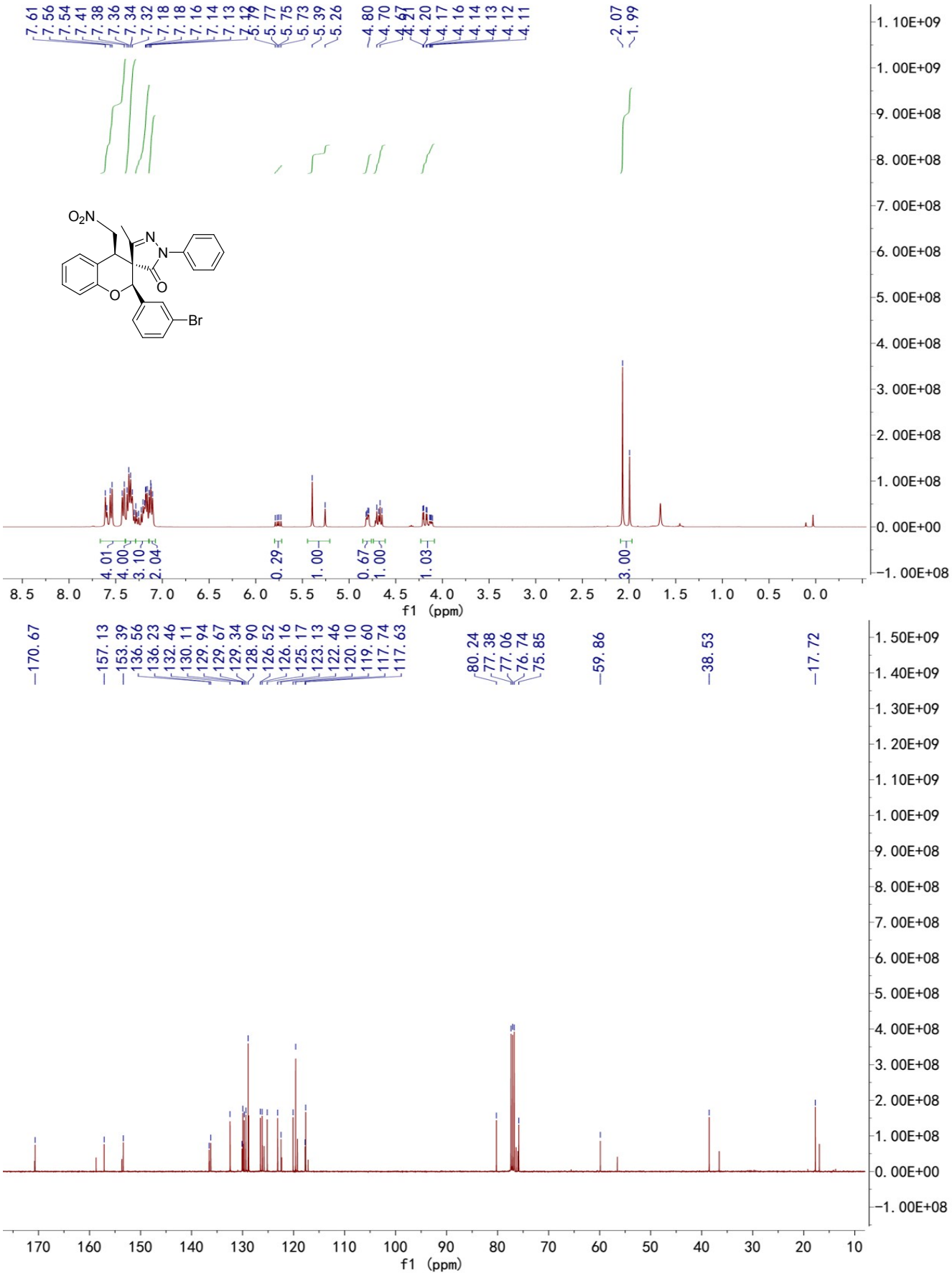


(2R,3R,4R)-2-(4-Chlorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11f):

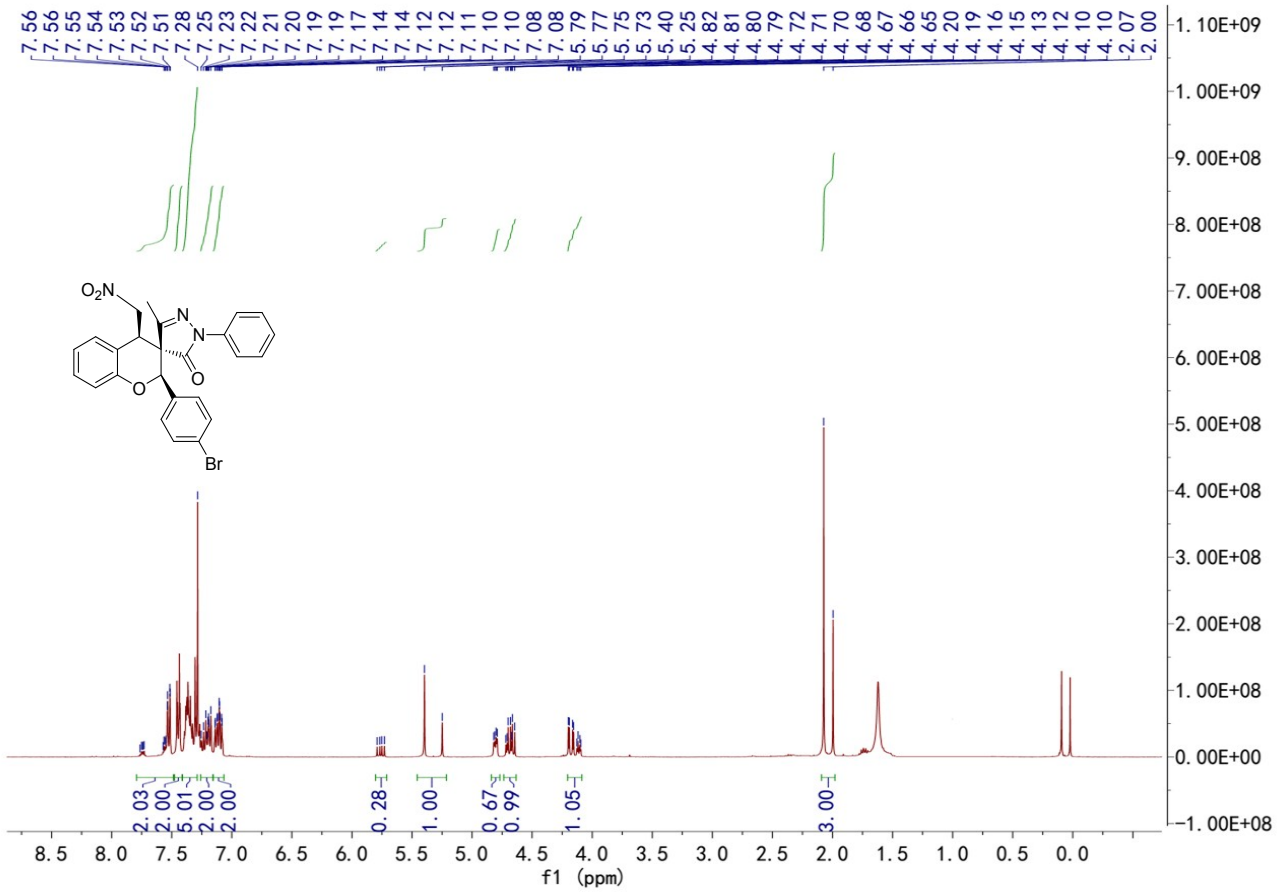


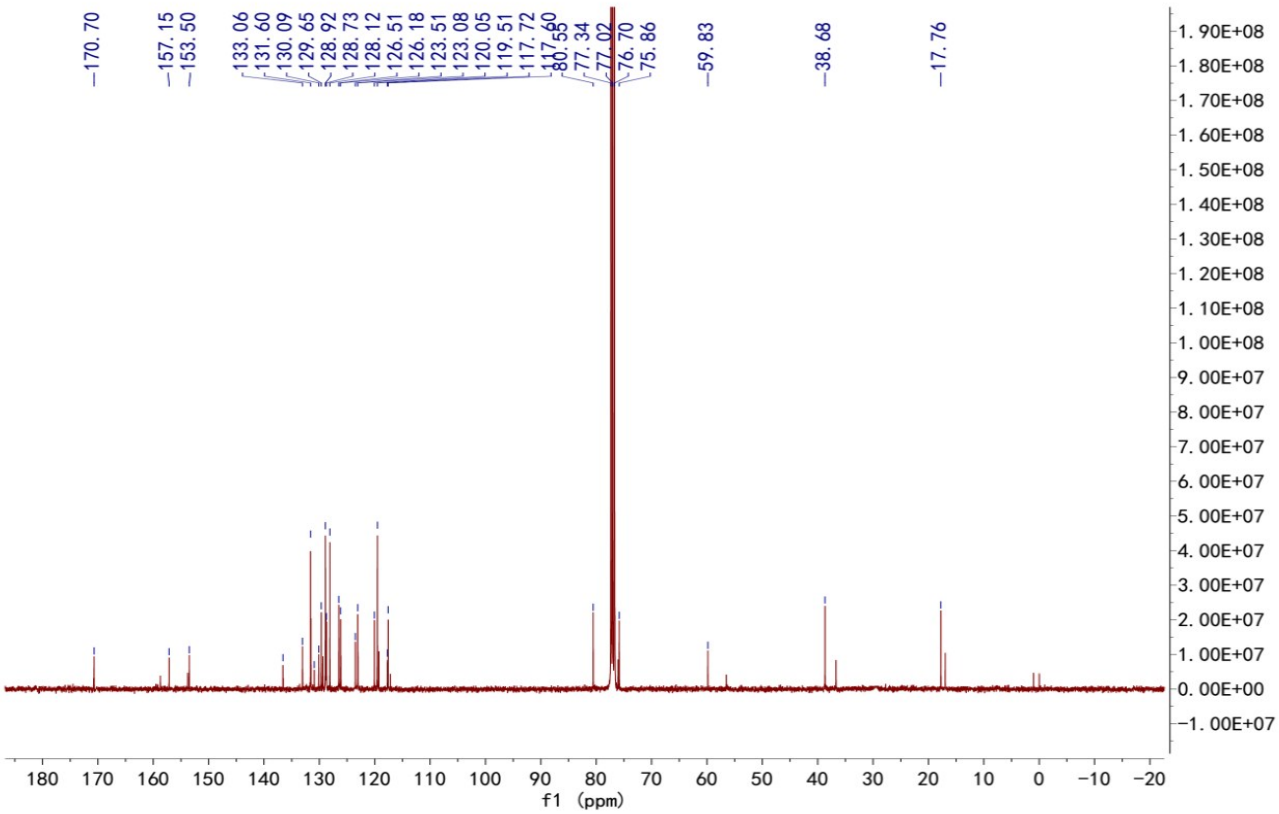


(2R,3R,4R)-2-(3-Bromophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11g):

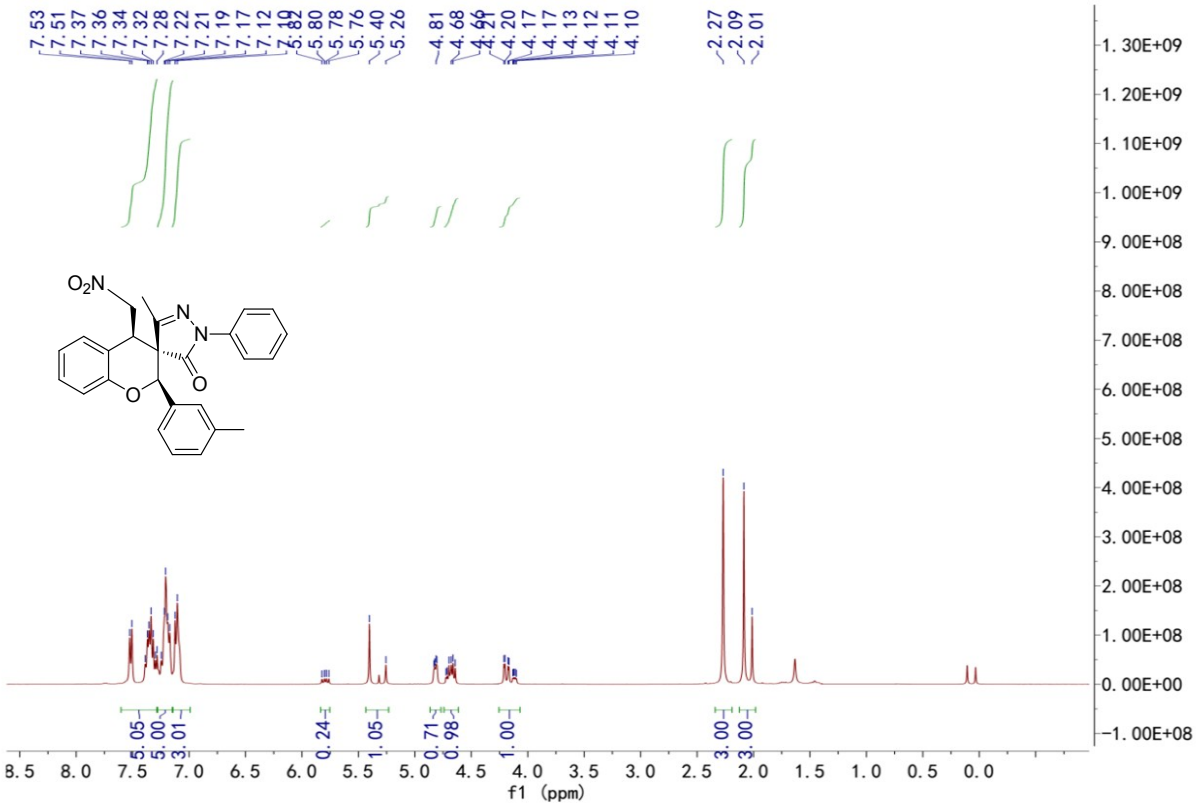


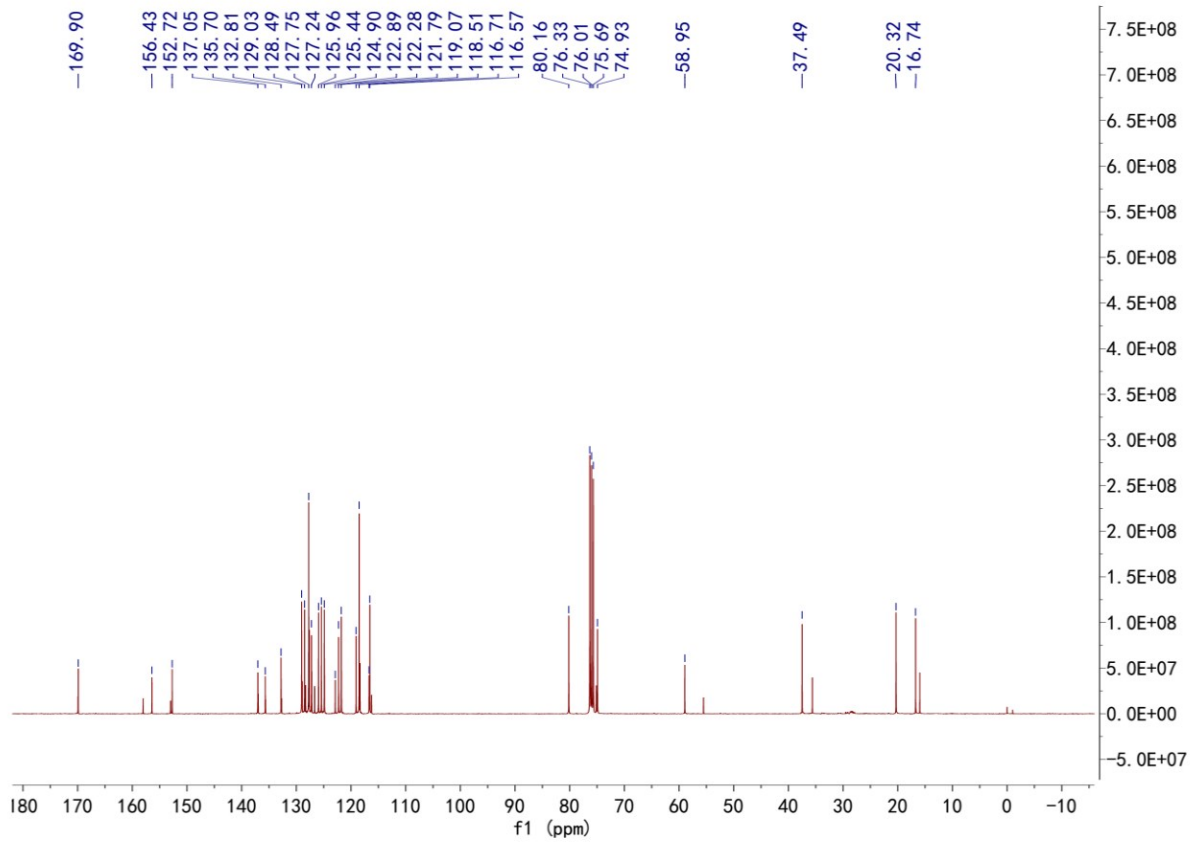
(2R,3R,4R)-2-(4-Bromophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11h):



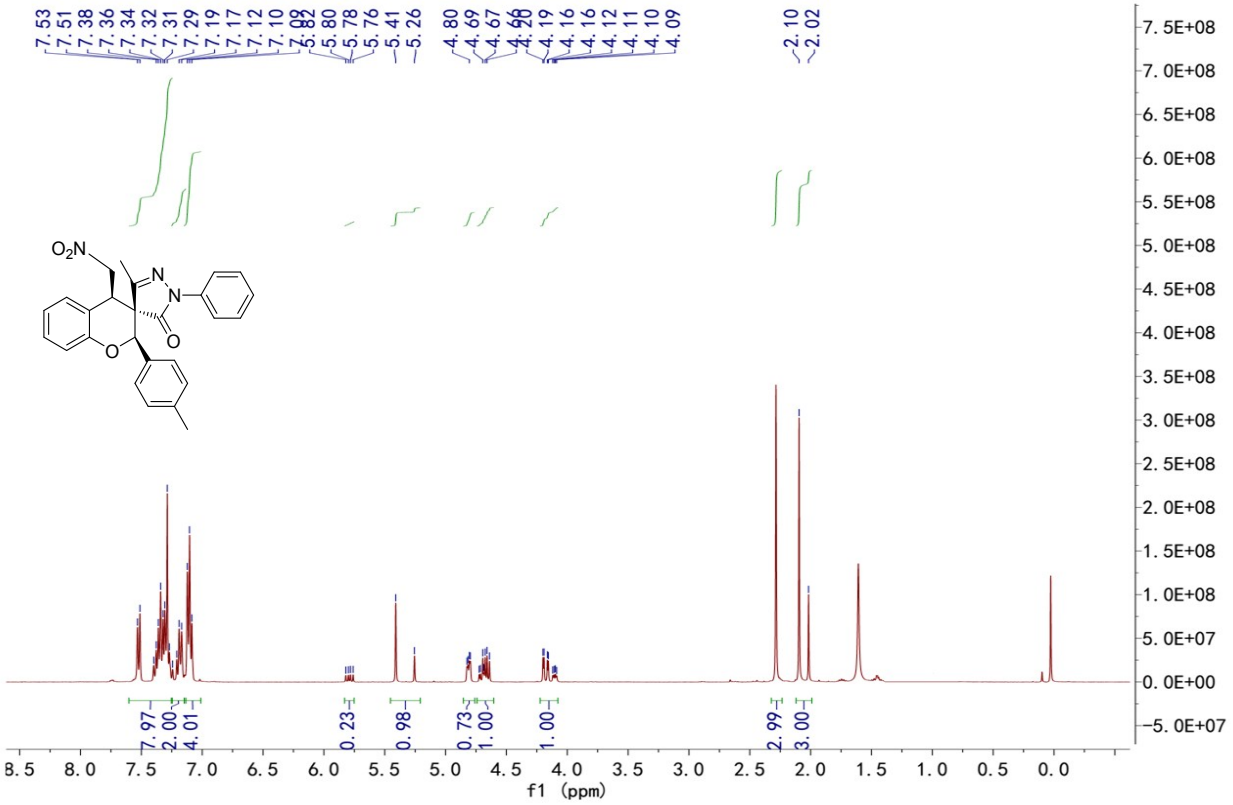


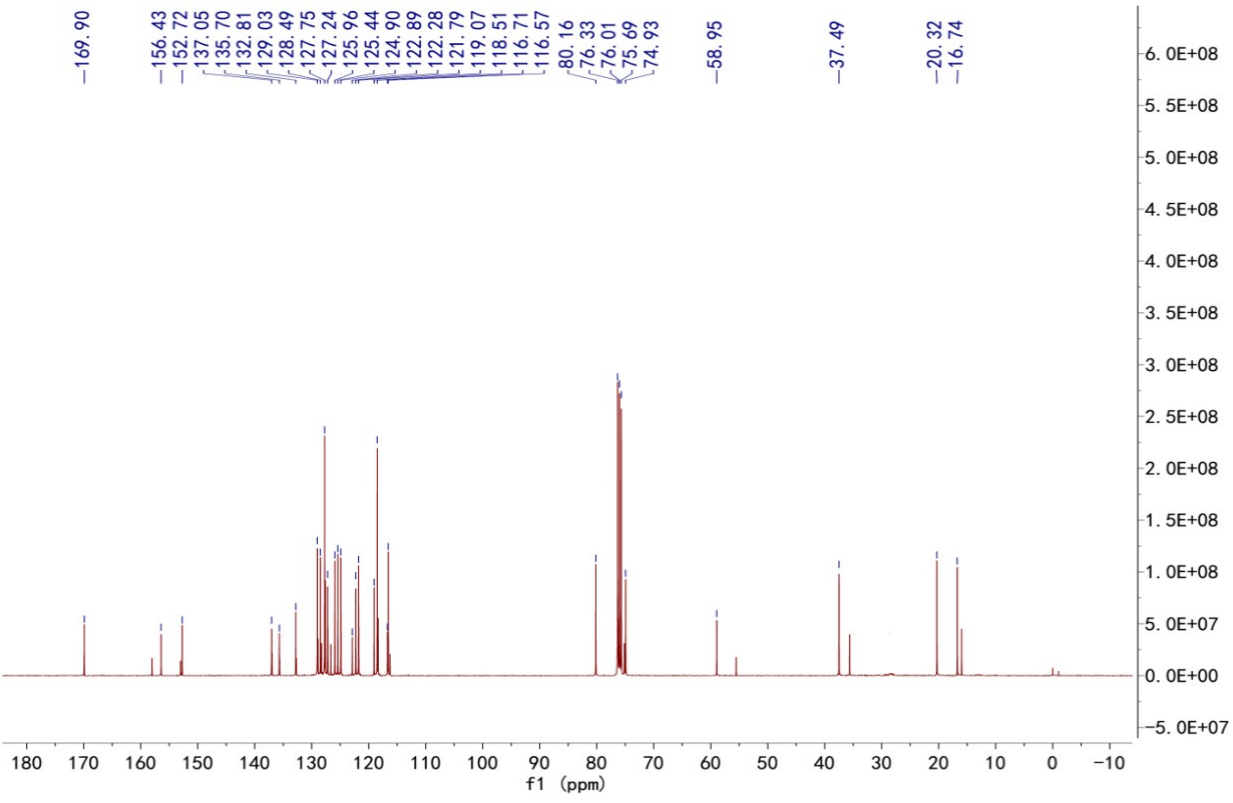
(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1'-phenyl-2-(m-tolyl)spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11i):



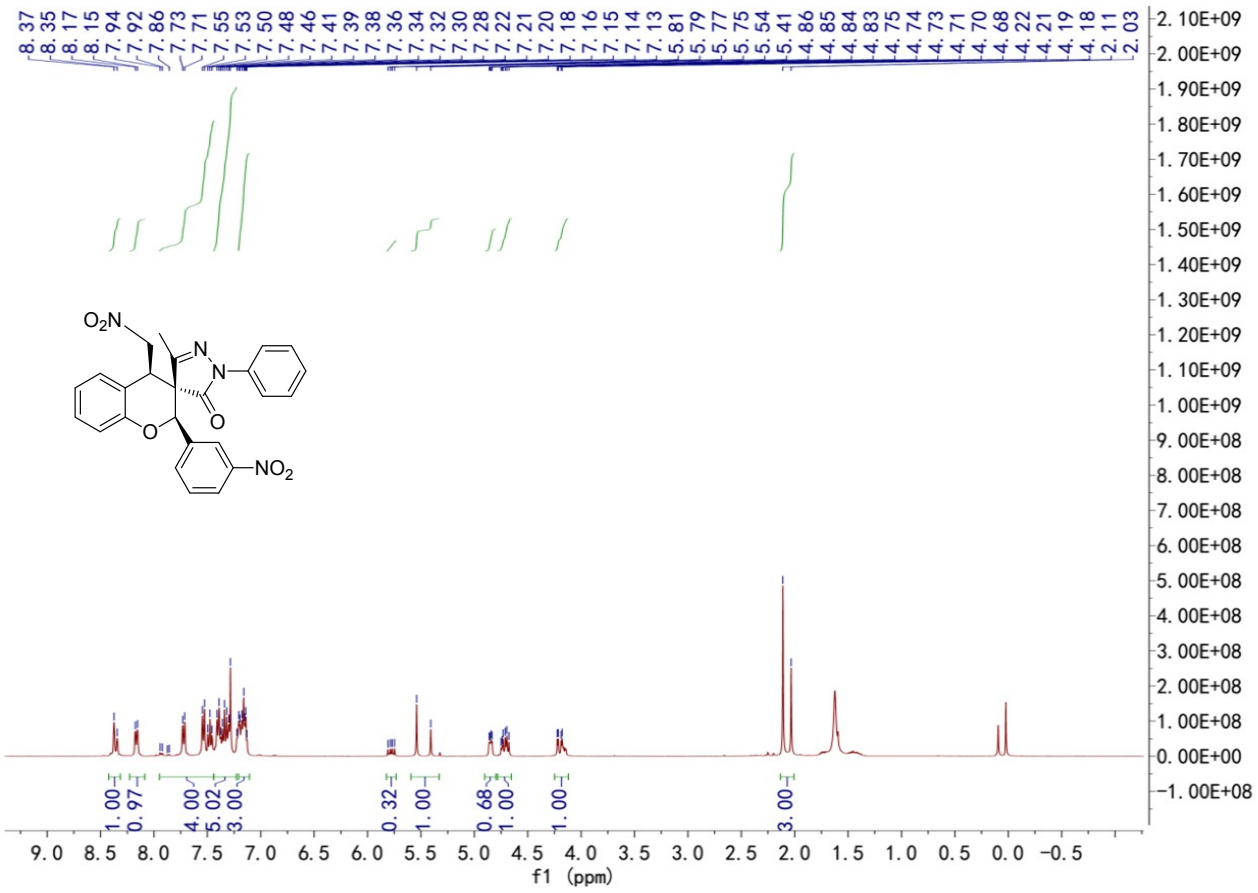


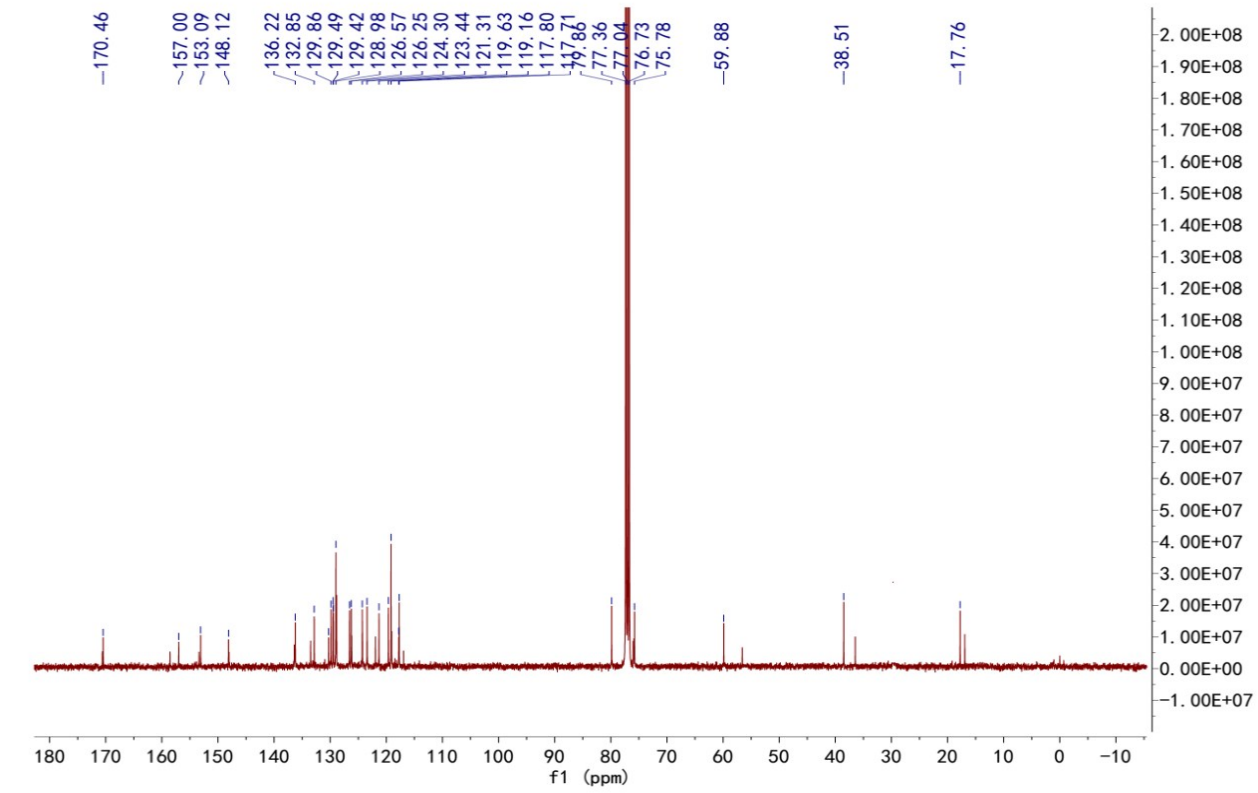
(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1'-phenyl-2-(p-tolyl)spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11j):



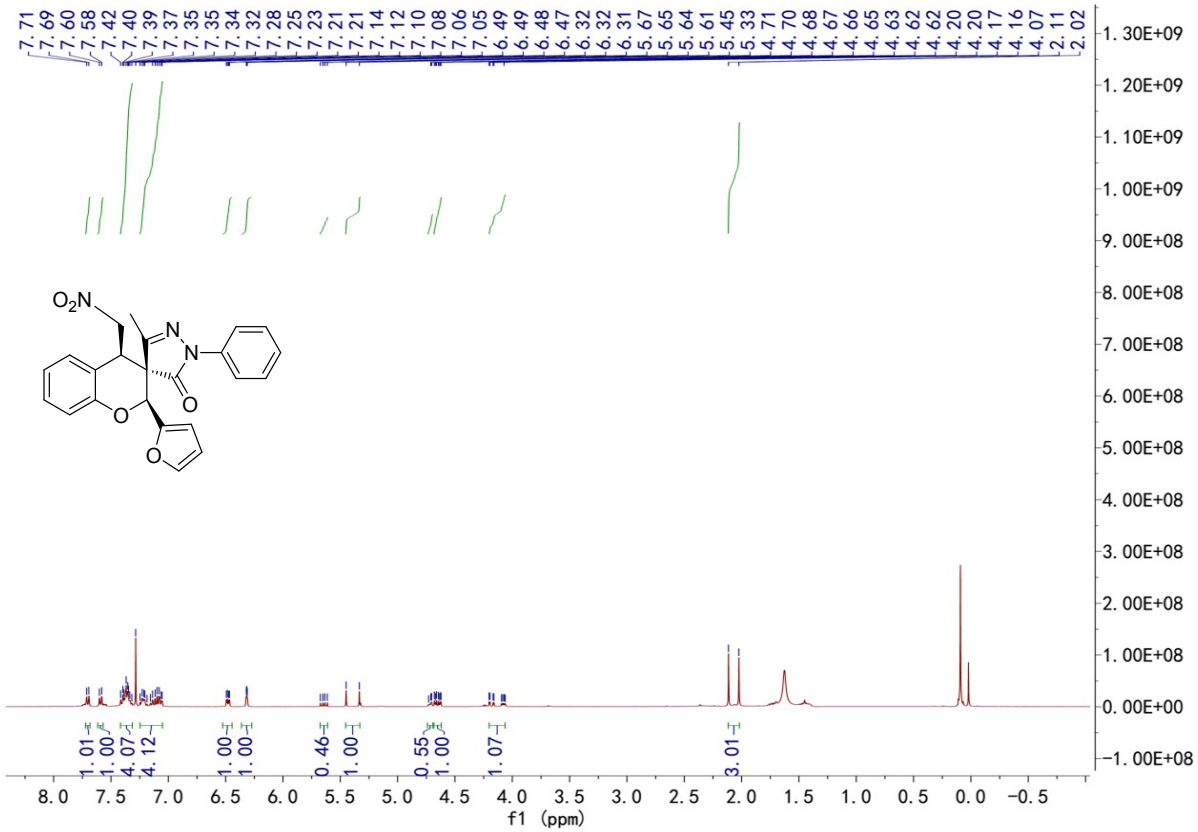


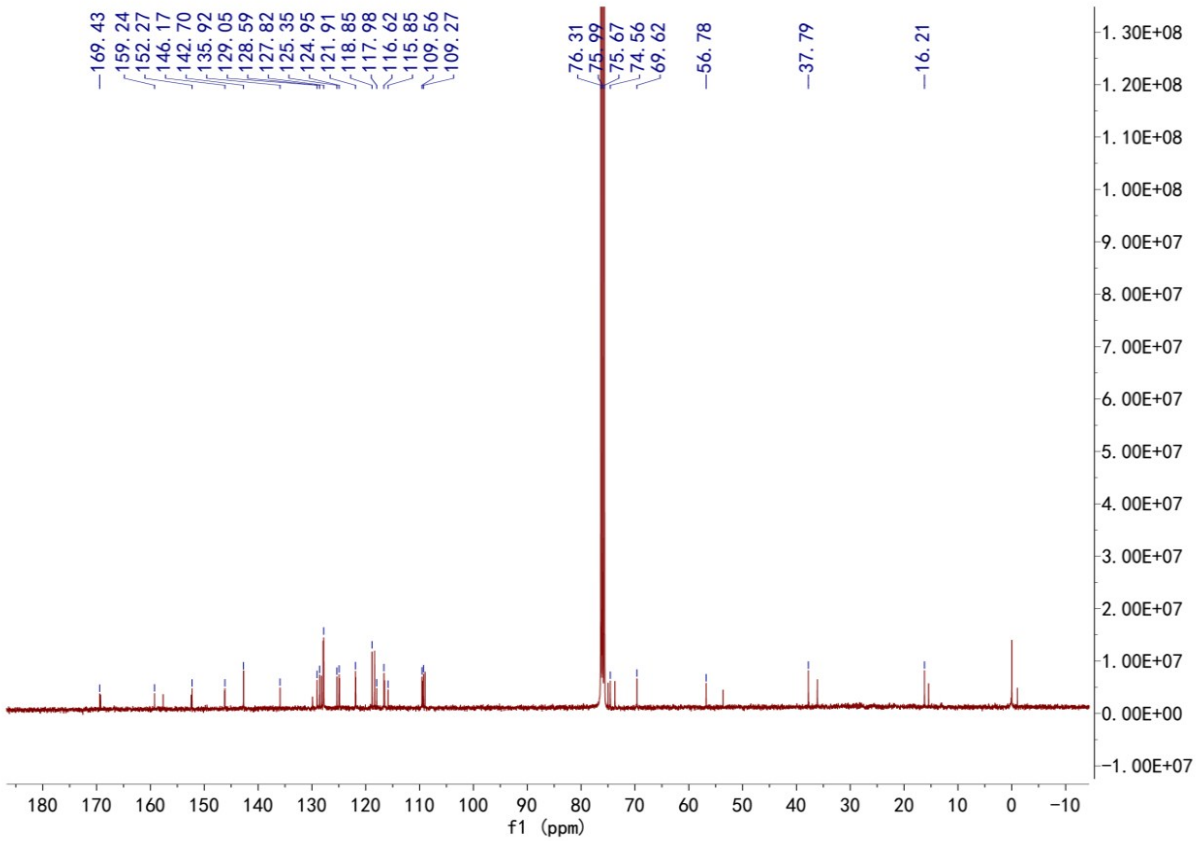
(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-2-(3-nitrophenyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11k):



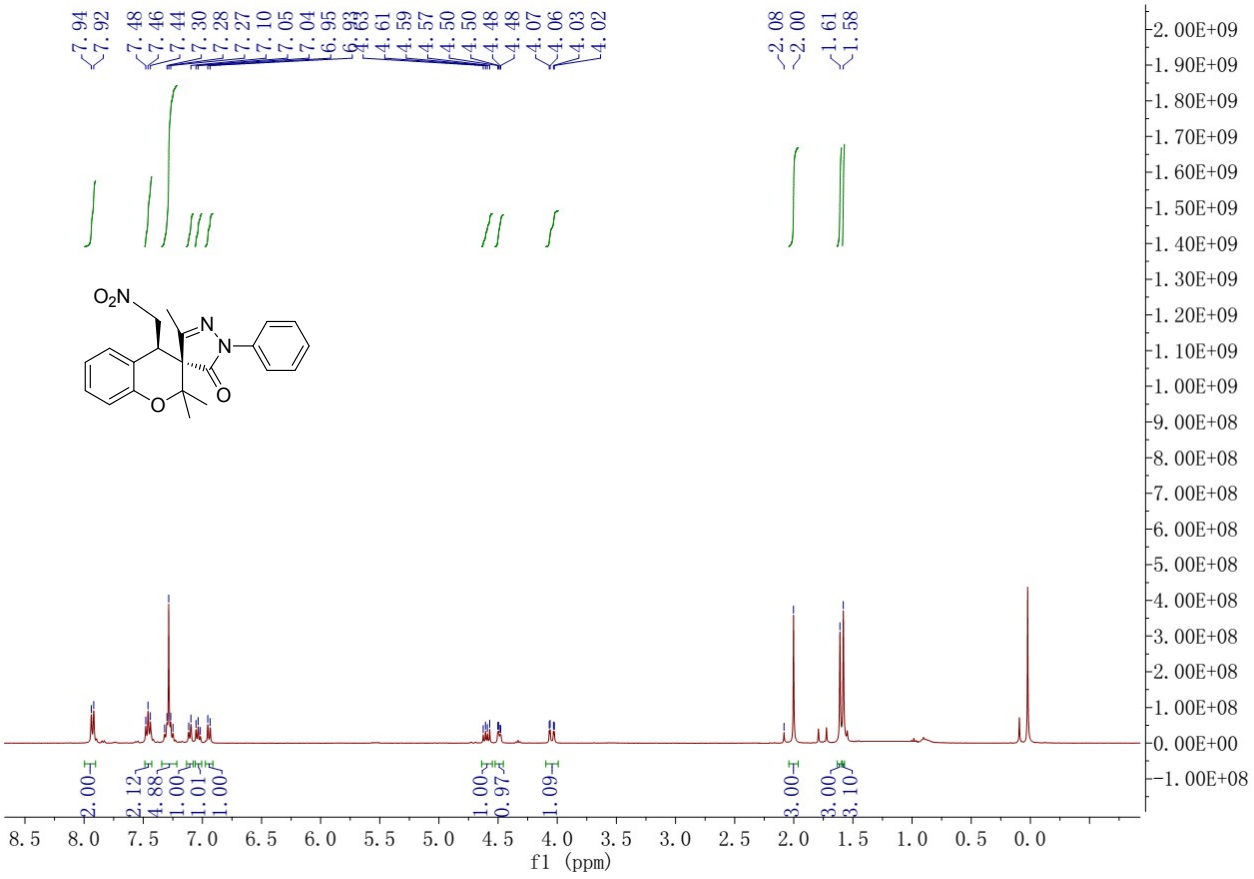


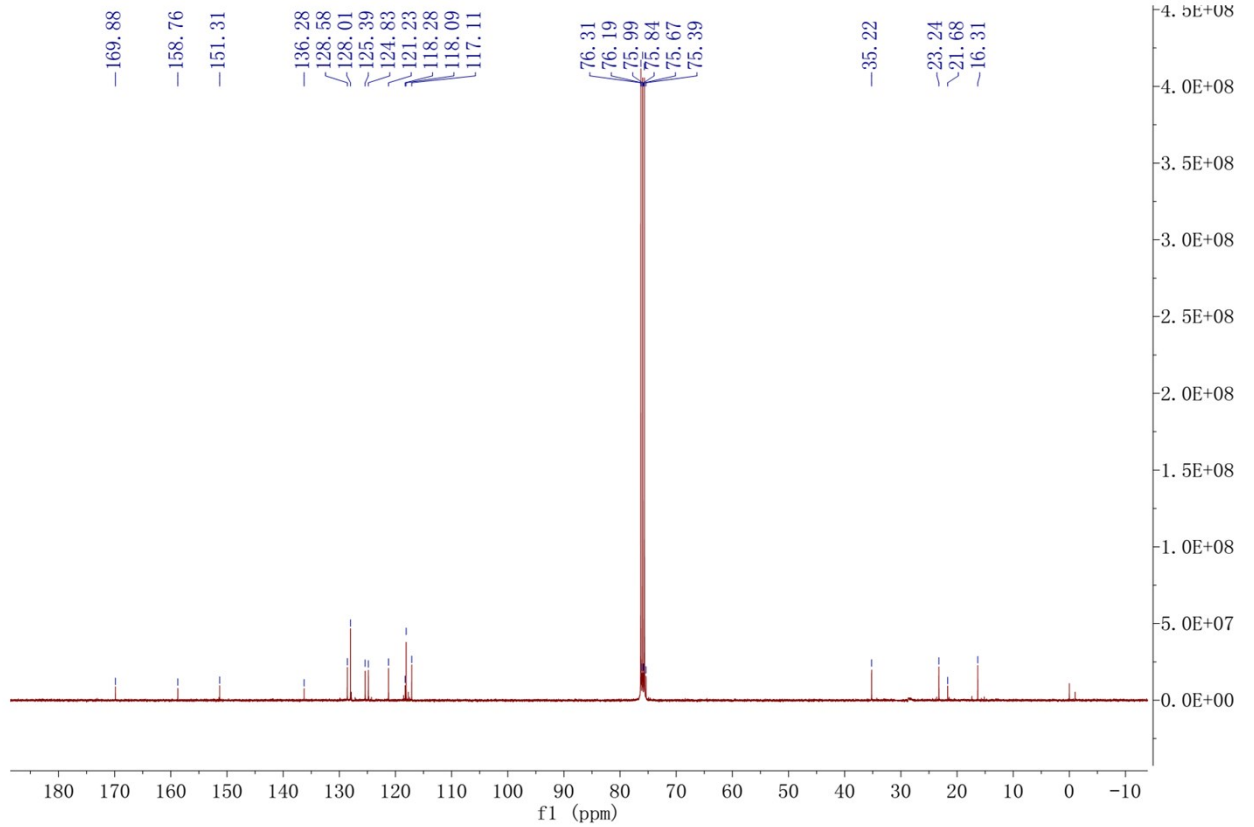
(2R,3R,4R)-2-(Furan-3-yl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11l):



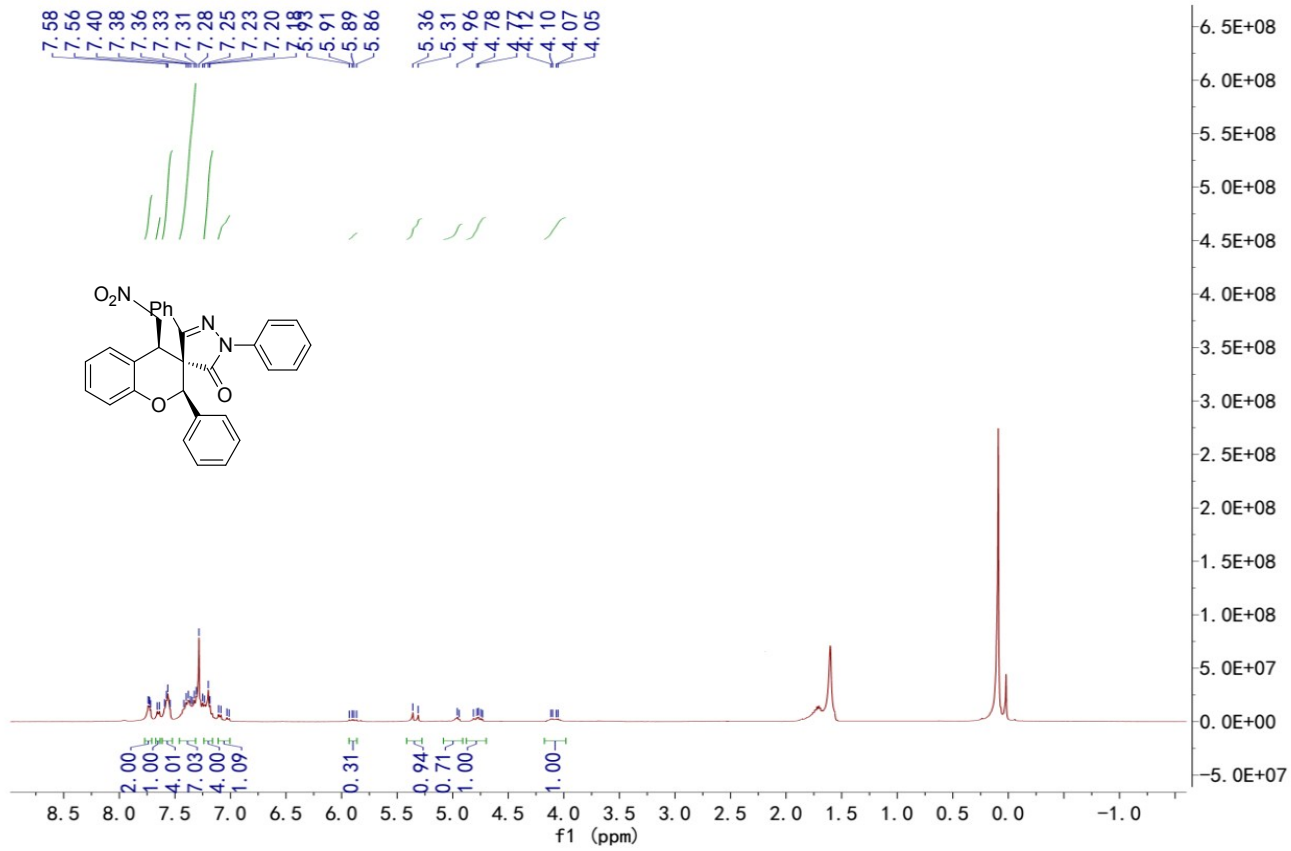


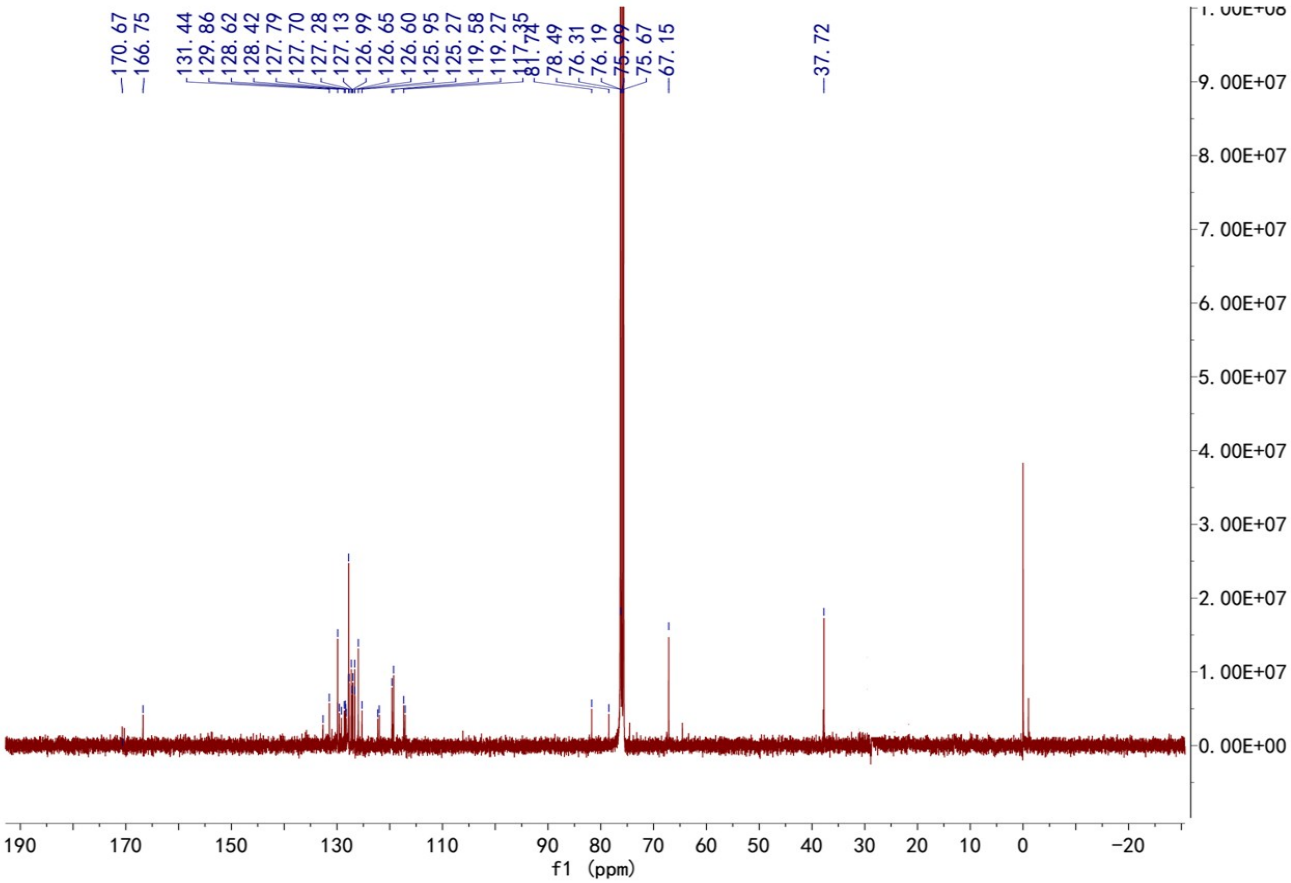
(3R,4R)-2,2,3'-Trimethyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11m):



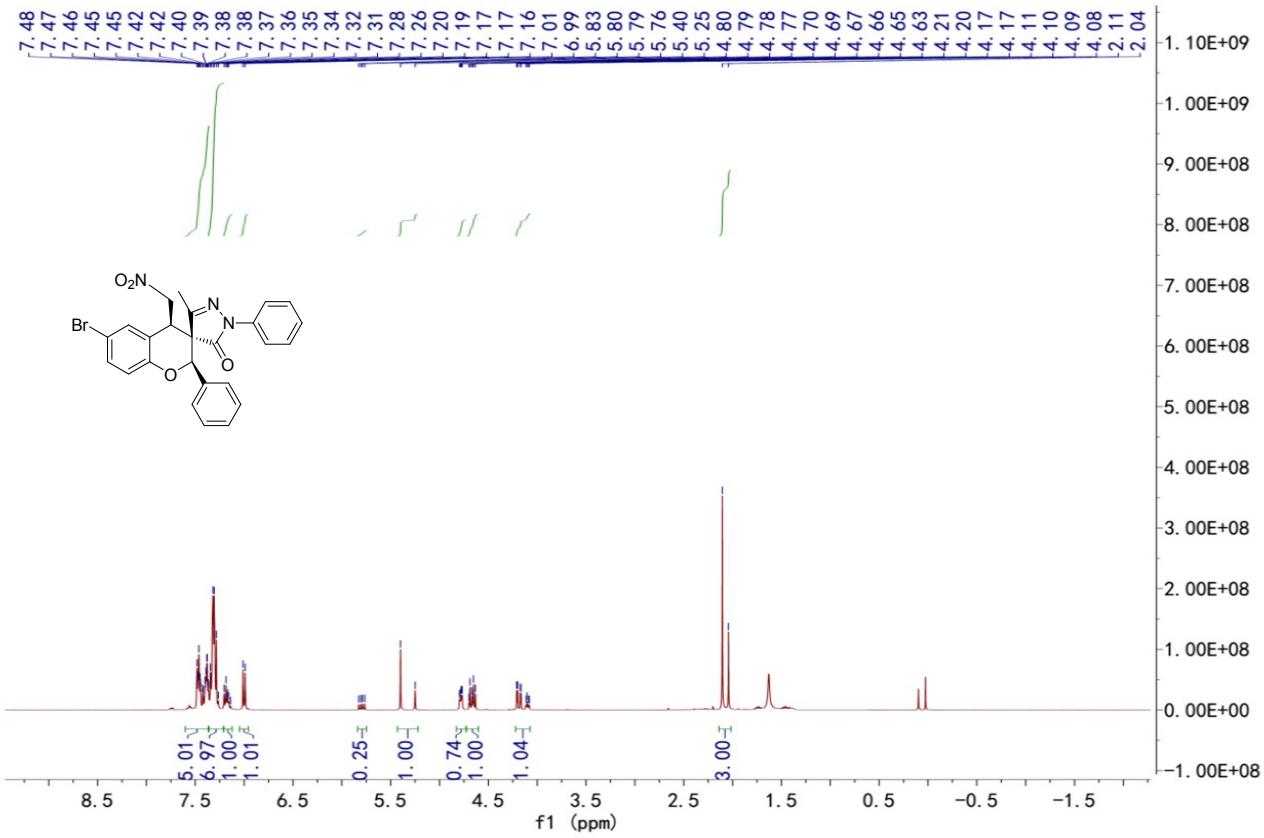


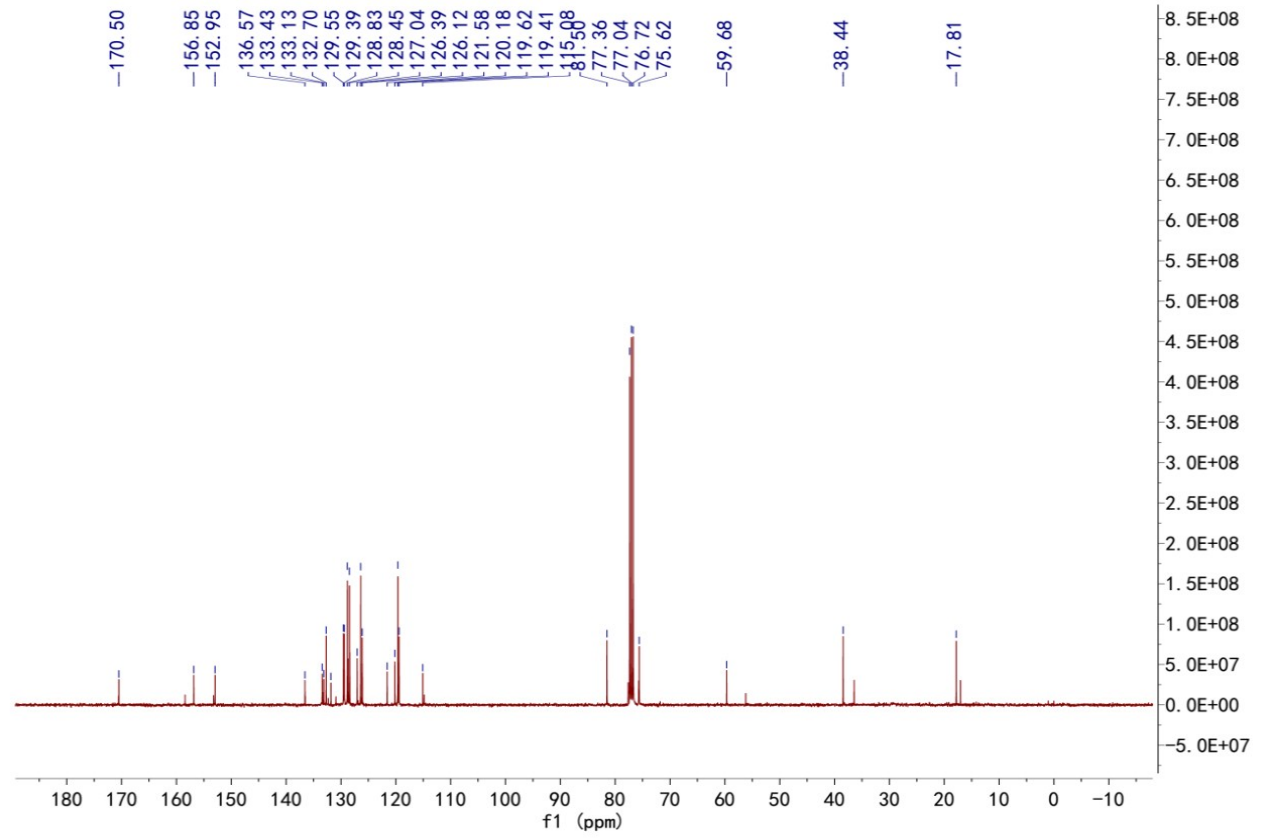
(2R,3R,4R)-4-(Nitromethyl)-1',2,3'-triphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11n):



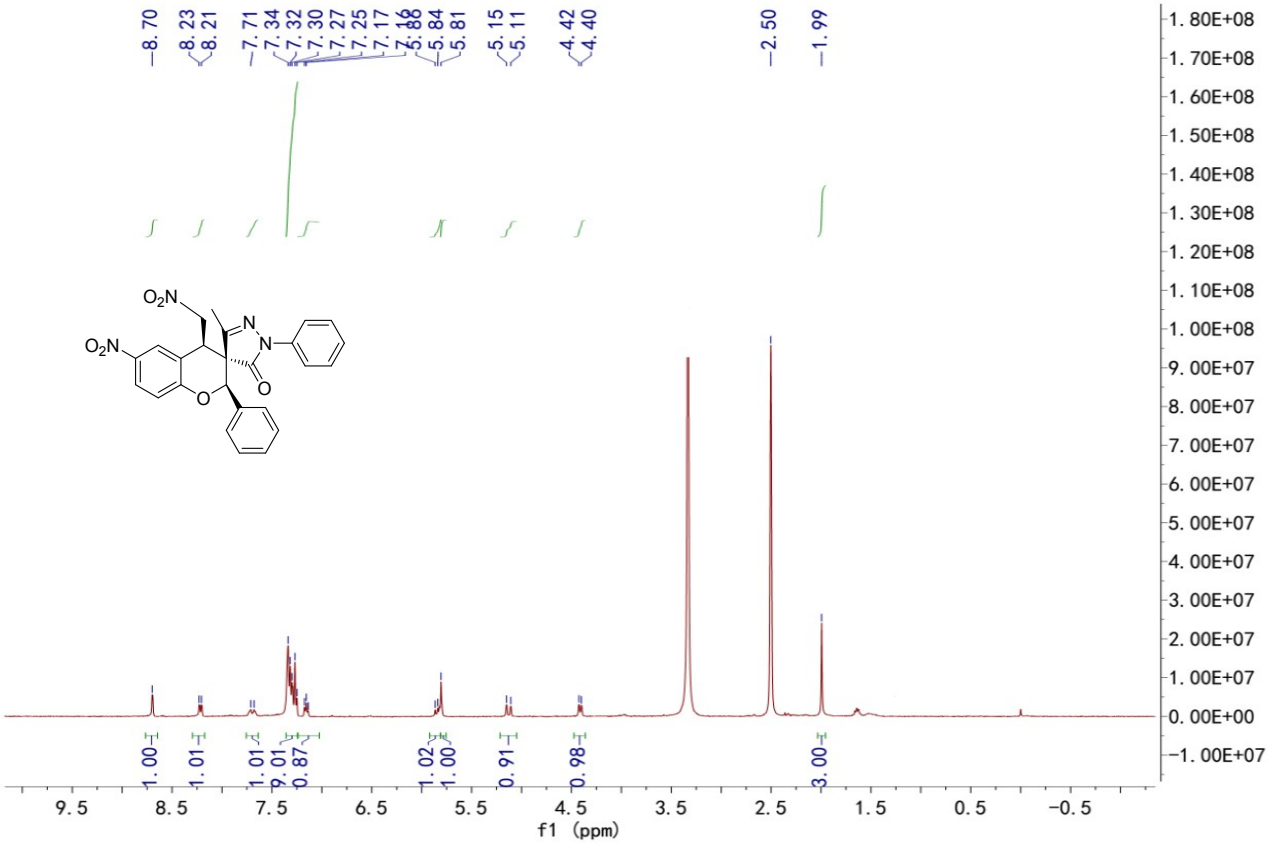


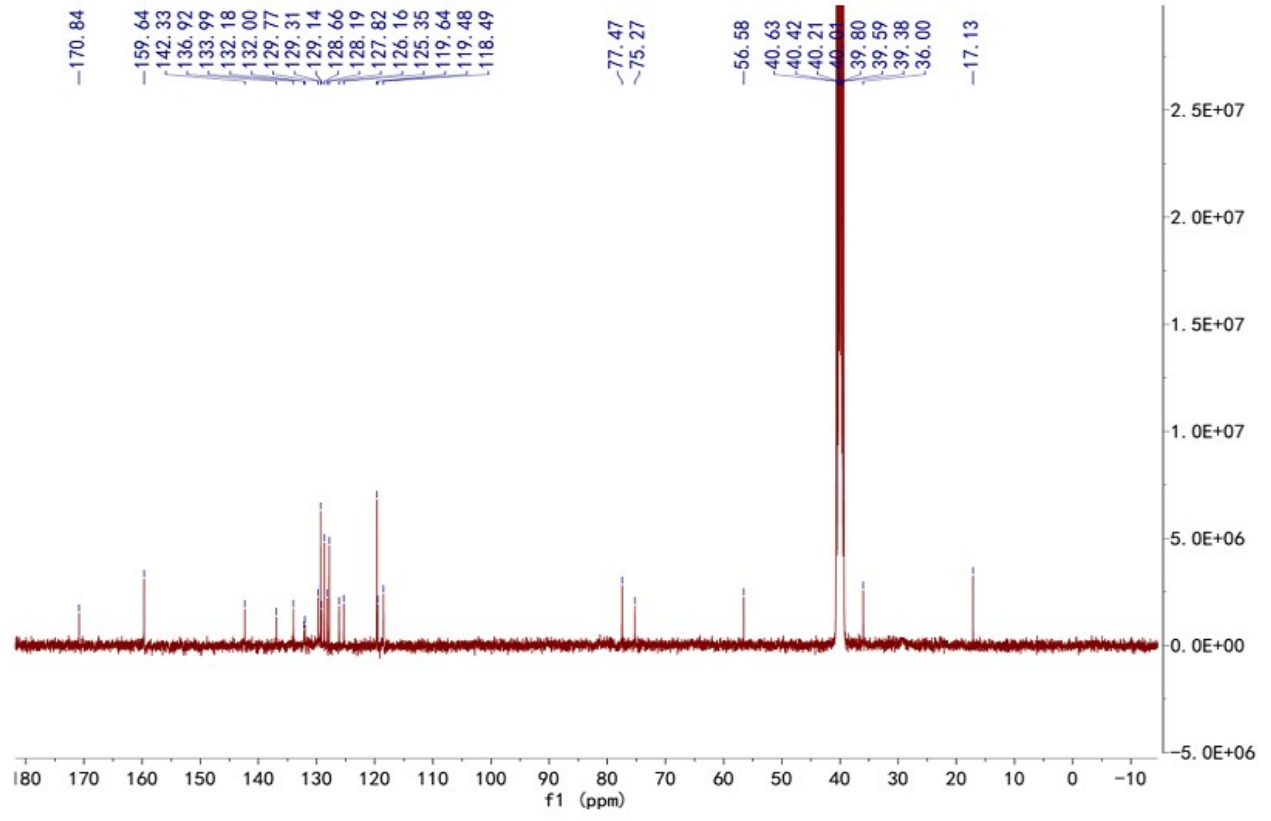
(2R,3R,4R)-6-Bromo-3'-methyl-4-(nitromethyl)-1',2-diphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11o):



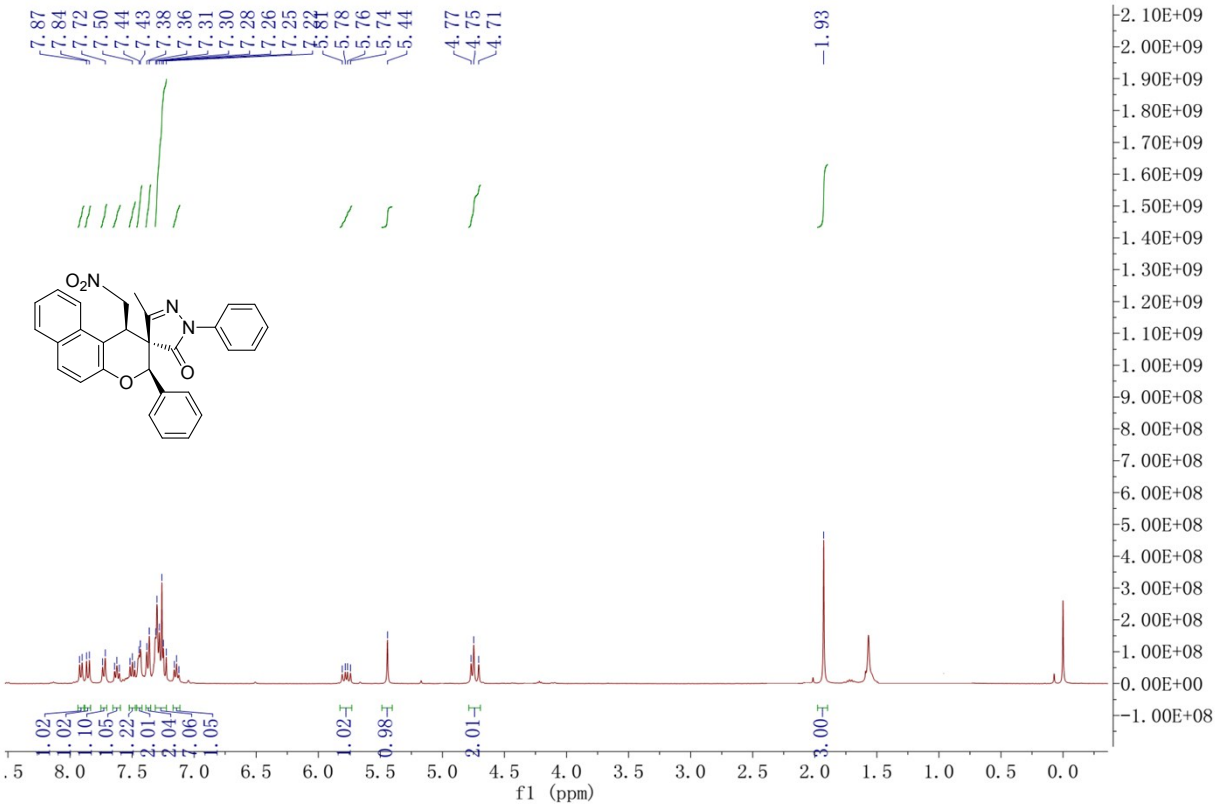


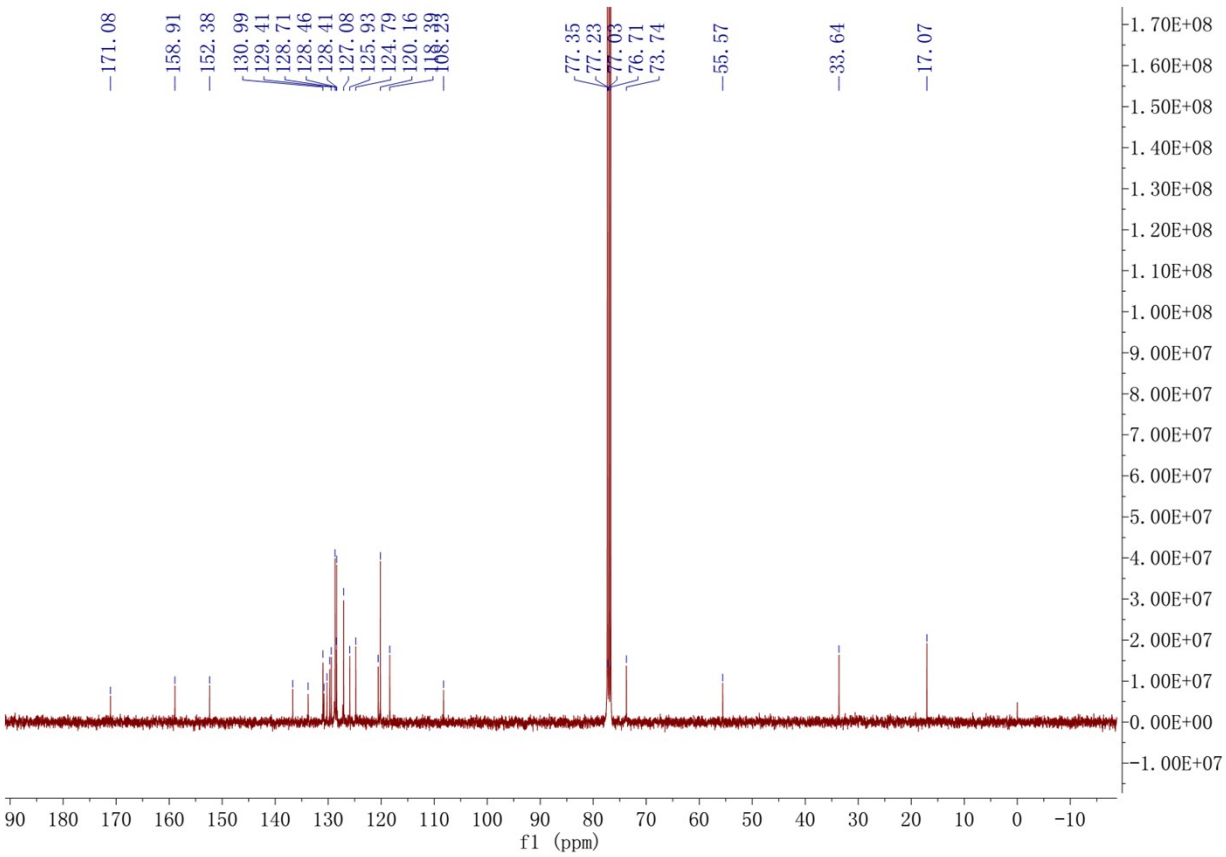
(2R,3R,4R)-3'-Methyl-6-nitro-4-(nitromethyl)-1',2-diphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11p):



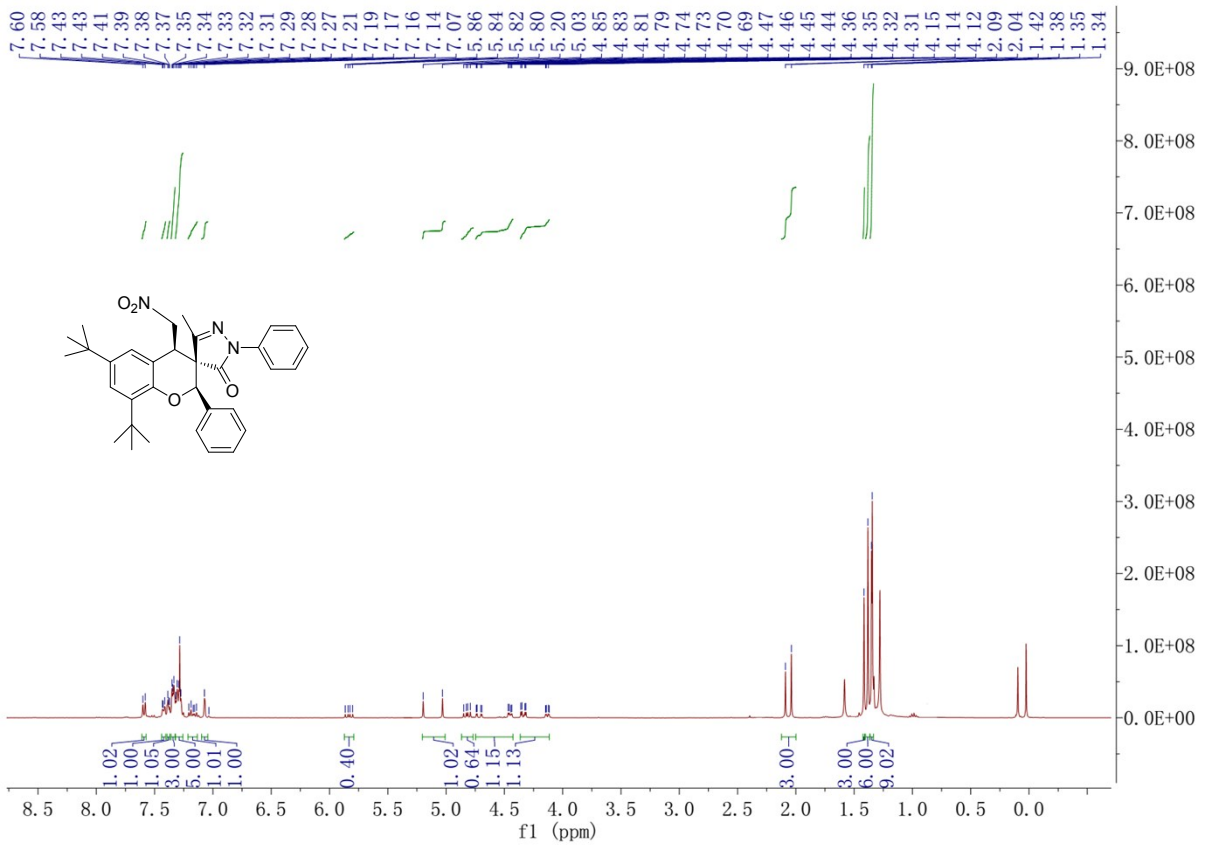


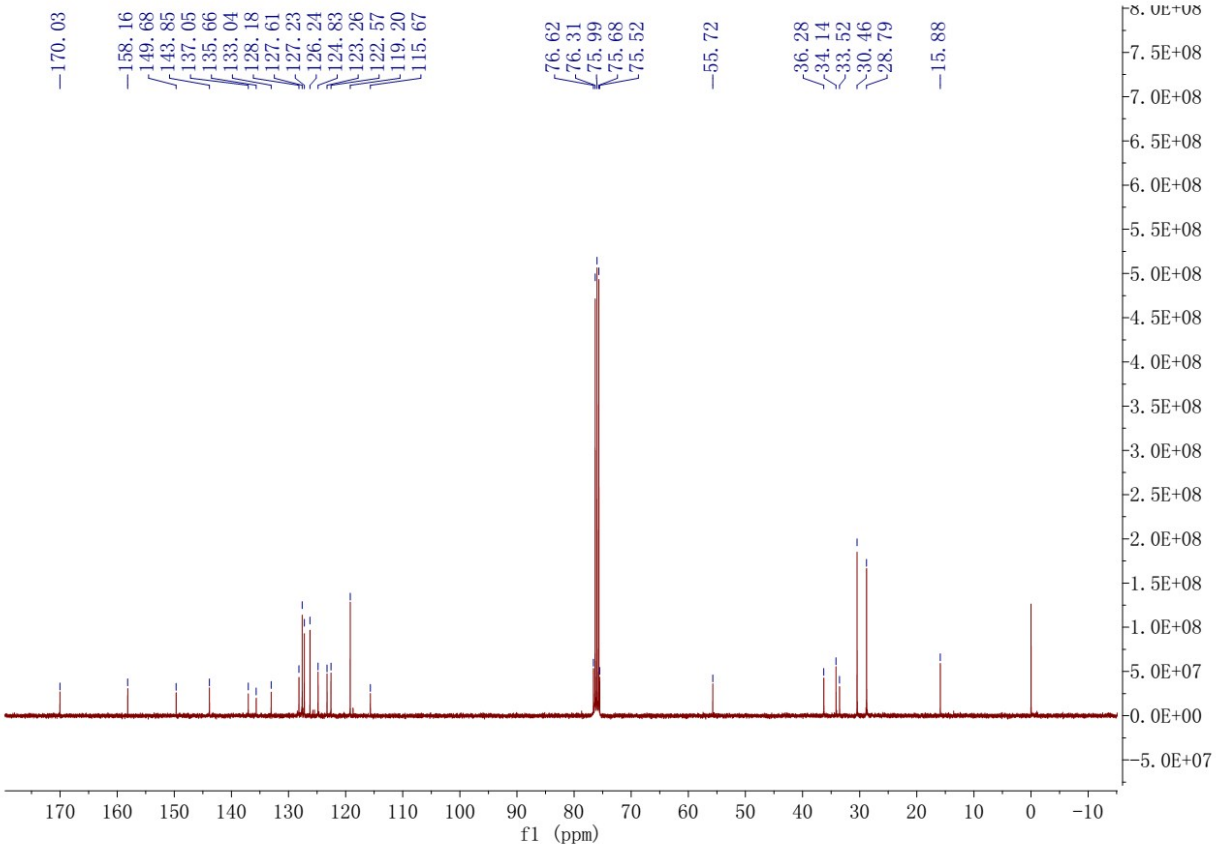
(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1',2-diphenyl-2,4-dihydrospiro[benzo[g]chromene-3,4'-pyrazol]-5'(1'H)-one (11q):



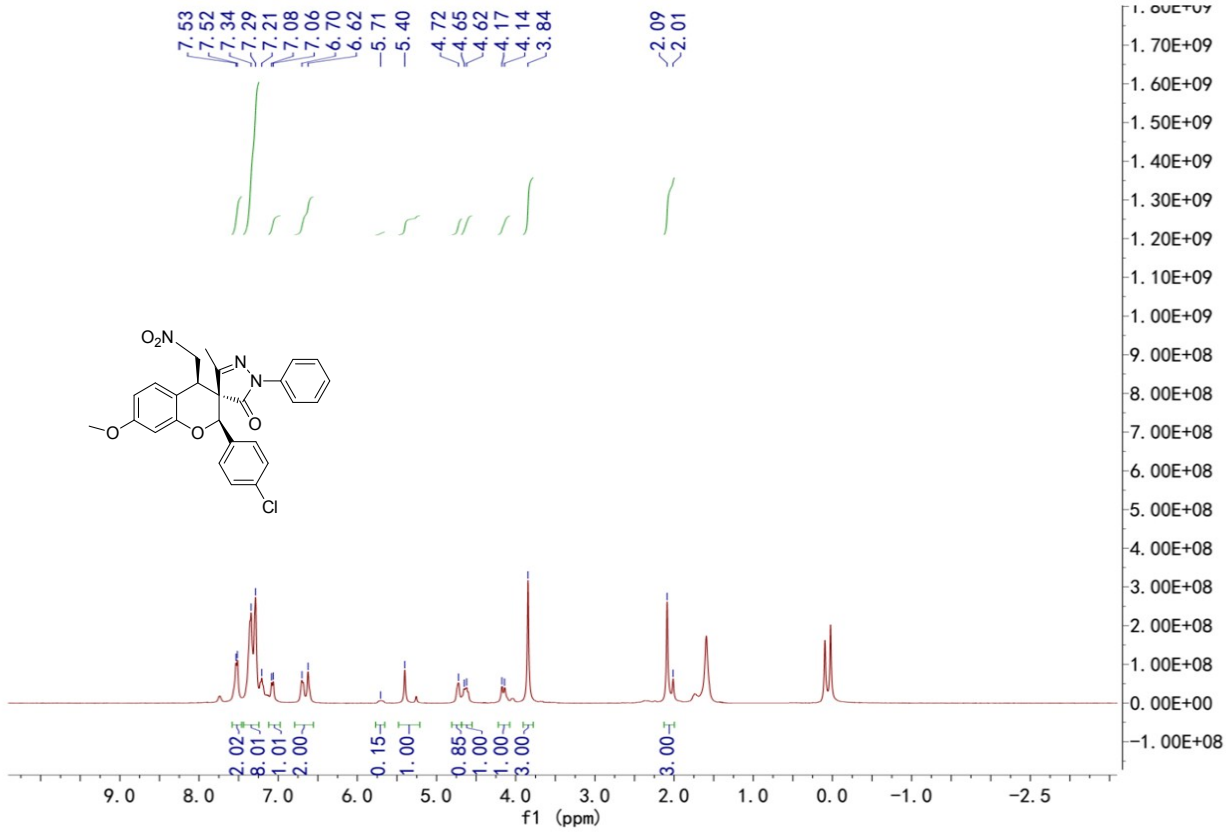


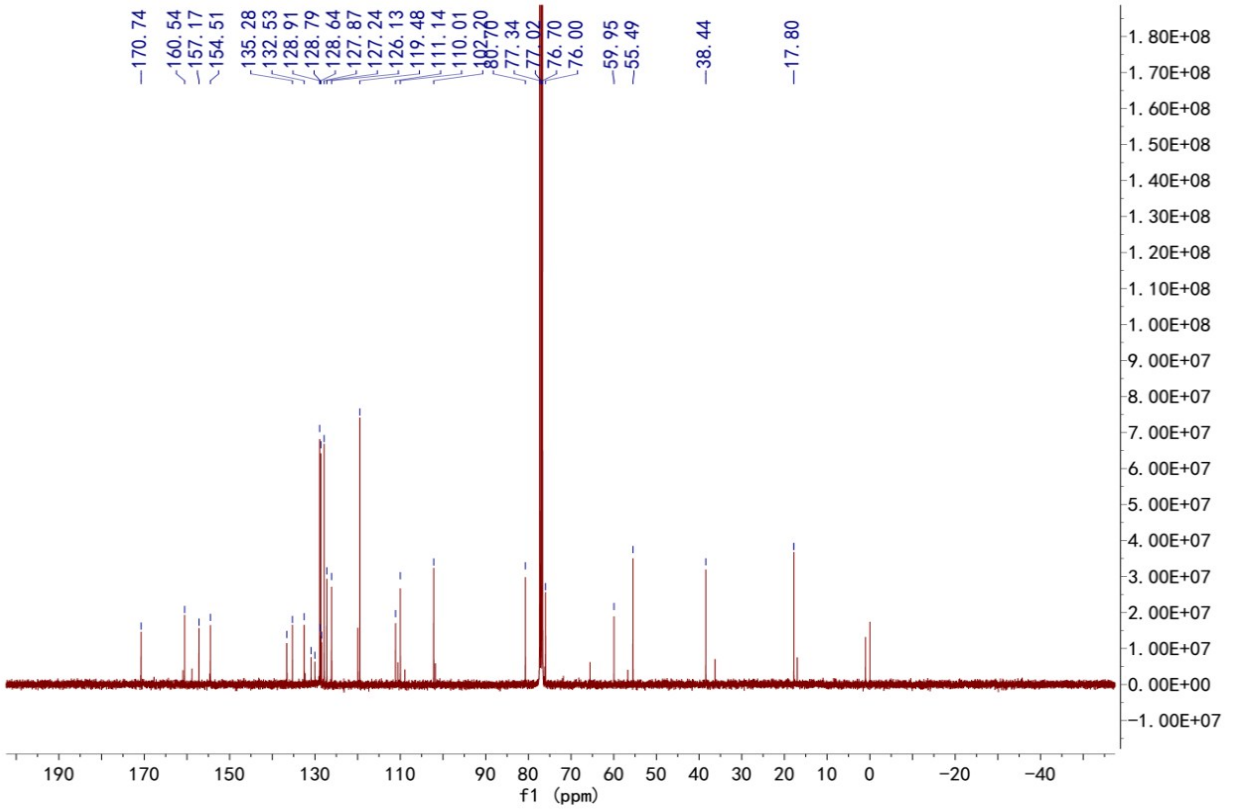
(2R,3R,4R)-6,8-Di-*tert*-butyl-3'-methyl-4-(nitromethyl)-1',2-diphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11r):



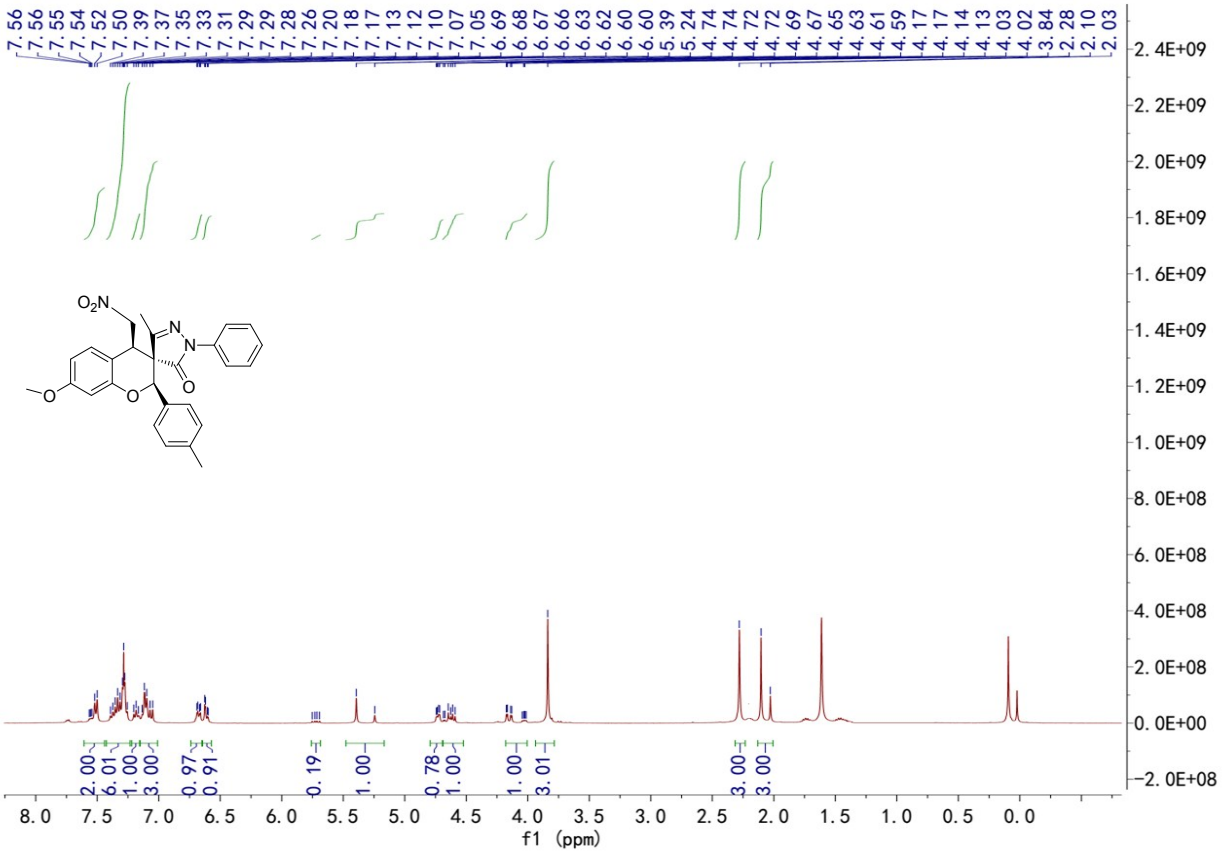


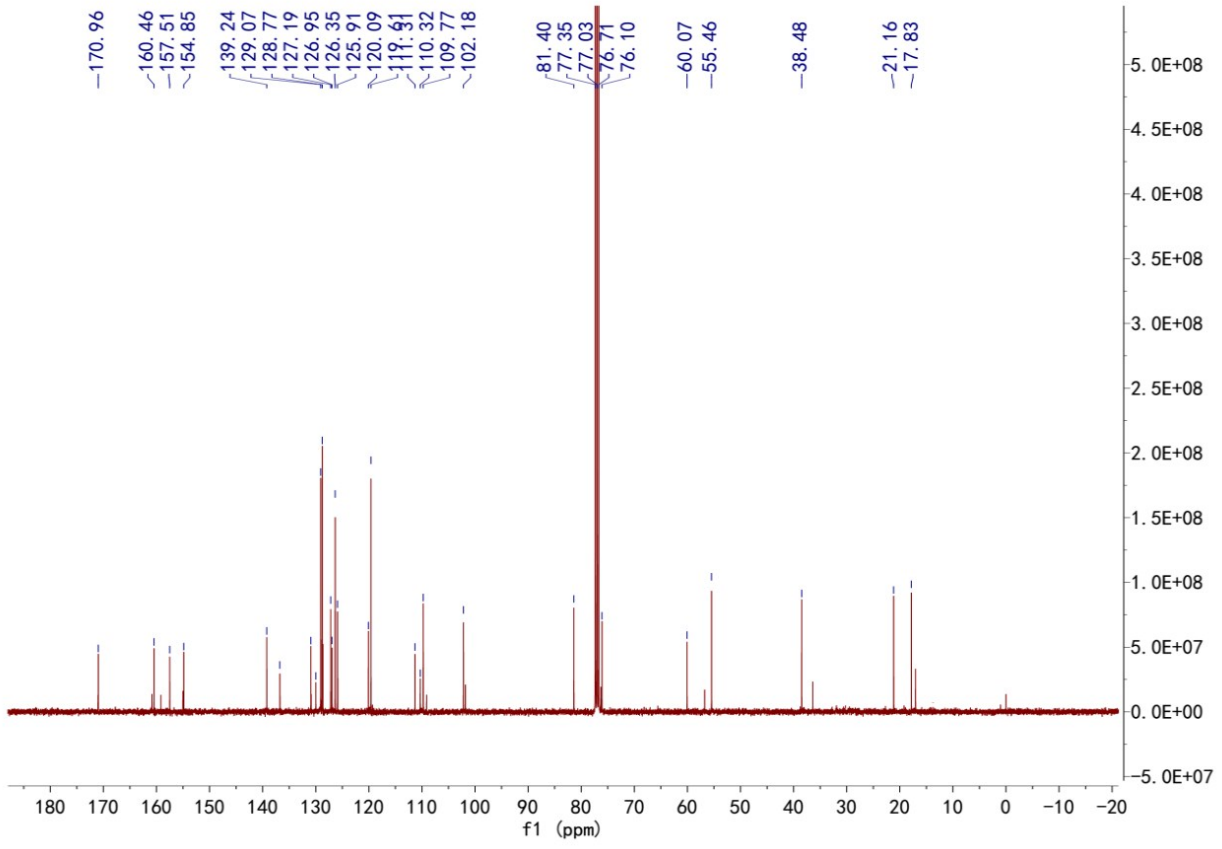
(2R,3R,4R)-2-(4-Chlorophenyl)-7-methoxy-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11s):





(2R,3R,4R)-7-Methoxy-3'-methyl-4-(nitromethyl)-1'-phenyl-2-(p-tolyl)spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11t):

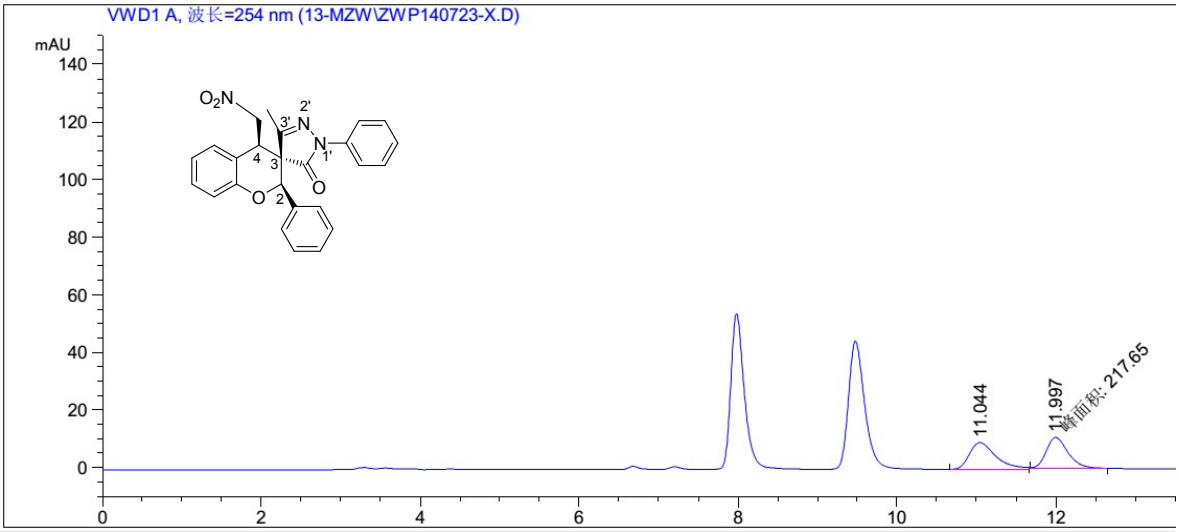




HPLC Spectra

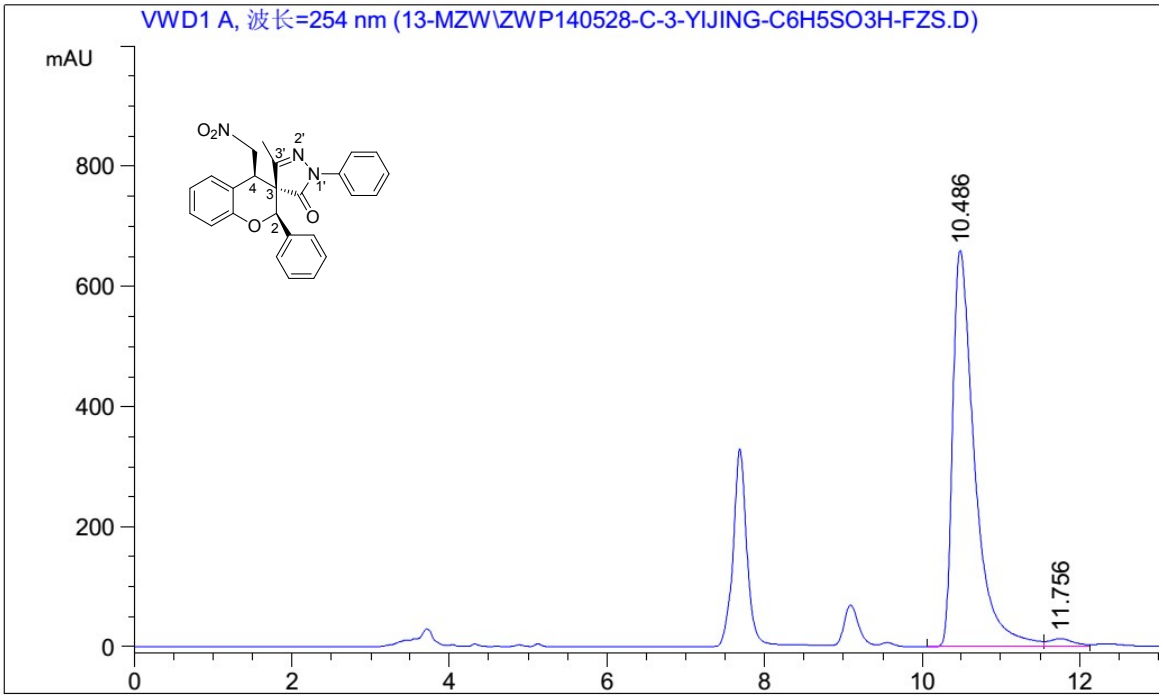
(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1',2-diphenyl spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11a):

RACEMIC 11a



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	11.044	0.3540	217.49243	9.31404	49.9819
2	11.977	0.3308	217.64986	10.96710	50.0181

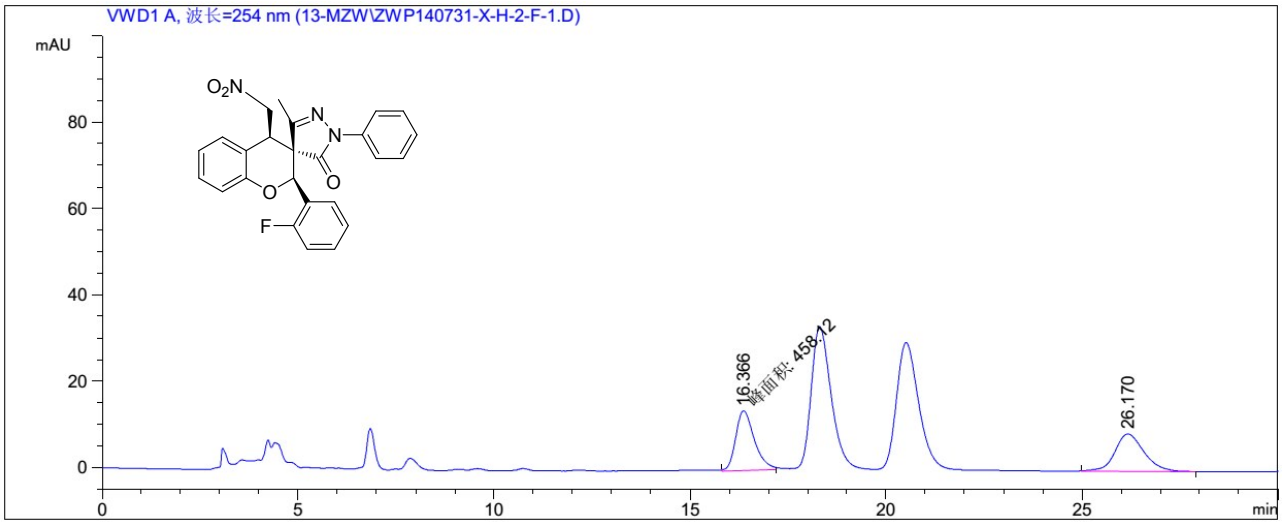
CHIRAL 11a



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	10.486	0.2914	1.28374e4	658.89728	97.5220
2	11.756	0.3350	326.18945	14.04671	2.4780

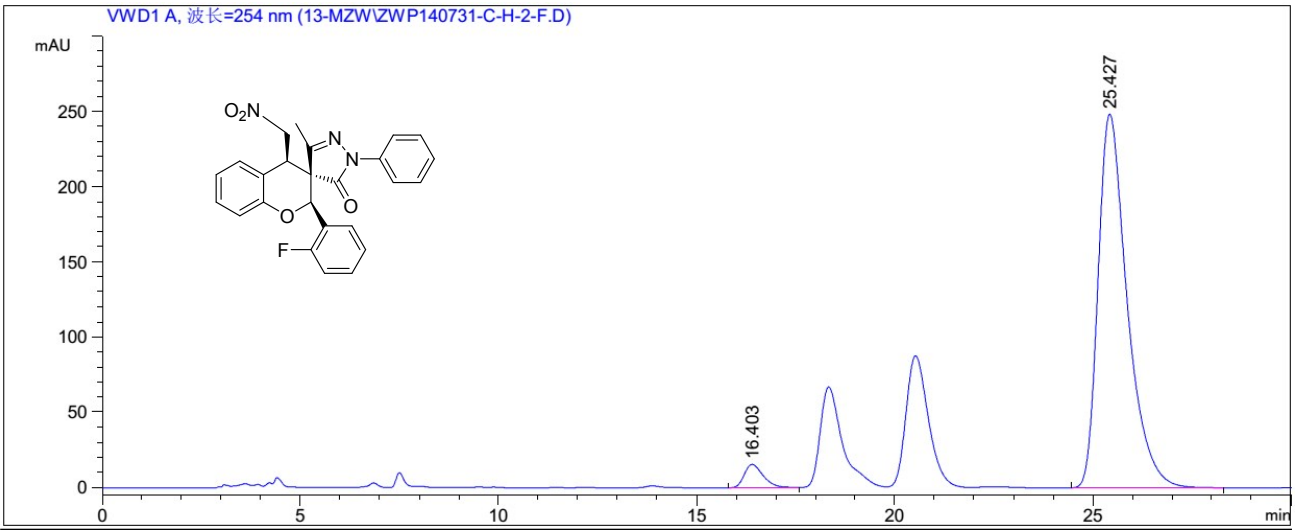
(2R,3R,4R)-2-(2-Fluorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11b):

RACEMIC 11b



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	16.366	0.5512	458.11996	13.85195	50.7513
2	26.170	0.7815	444.55719	8.63028	49.2487

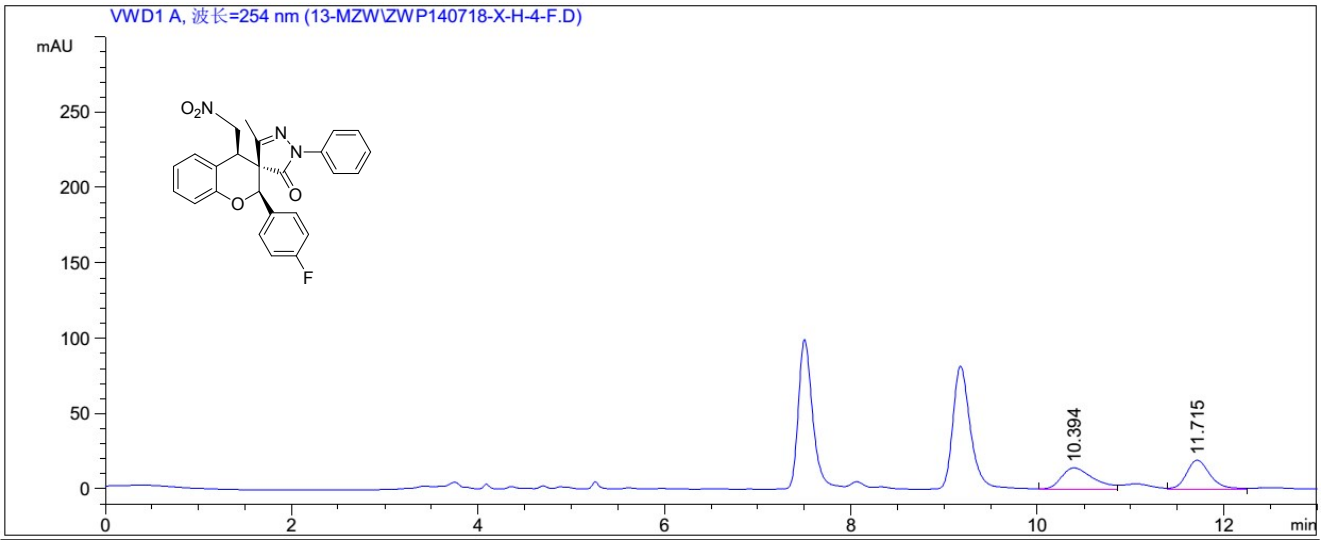
CHIRAL 11b



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	16.403	0.5140	534.94110	15.70121	4.0400
2	25.427	0.7705	1.27061e4	248.80136	95.9600

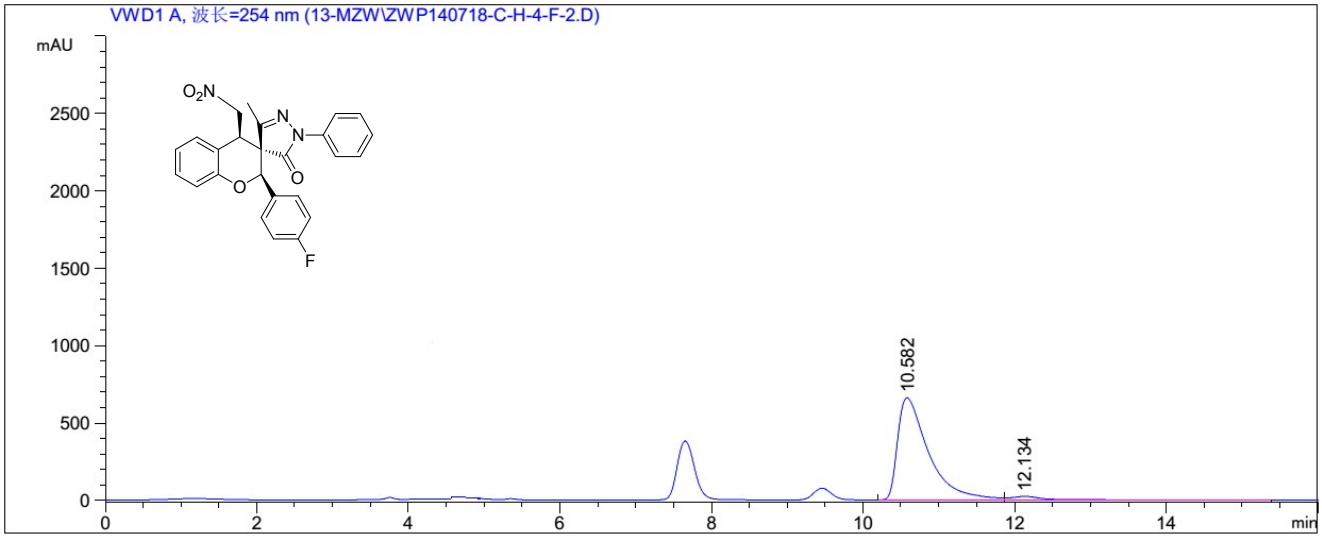
(2R,3R,4R)-2-(4-Fluorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11c):

RACEMIC 11c



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	10.394	0.3631	343.71097	14.24032	50.0627
2	11.715	0.2713	342.85056	19.29737	49.9373

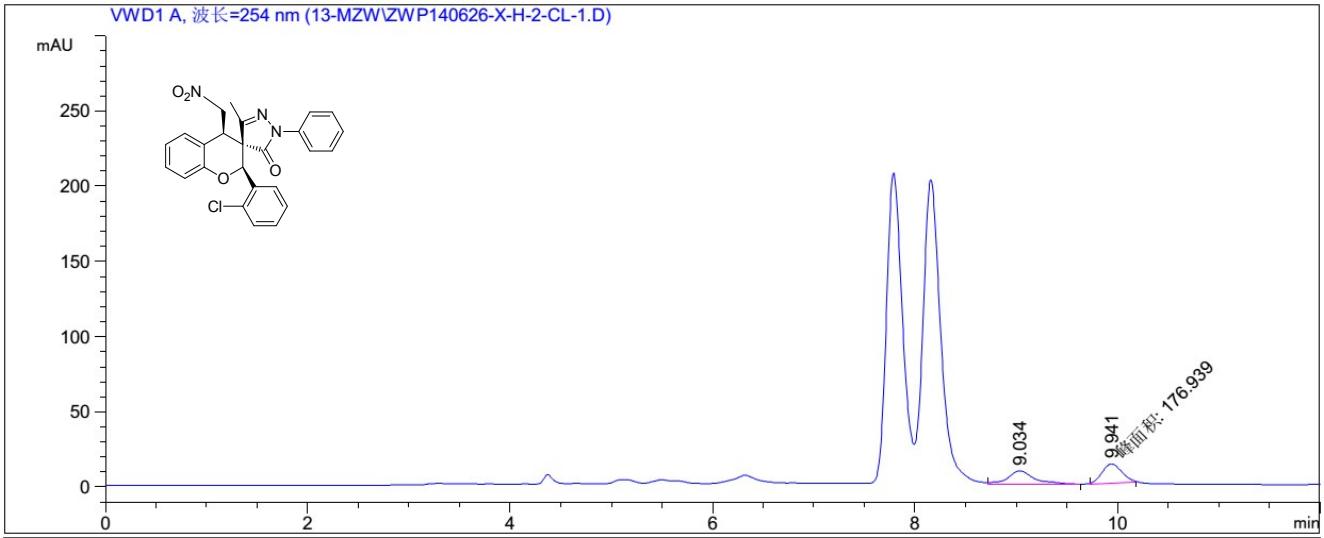
CHIRAL 11c



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	10.582	0.4202	1.88254e4	659.77625	95.5380
2	12.134	0.4836	879.21185	25.14638	4.4620

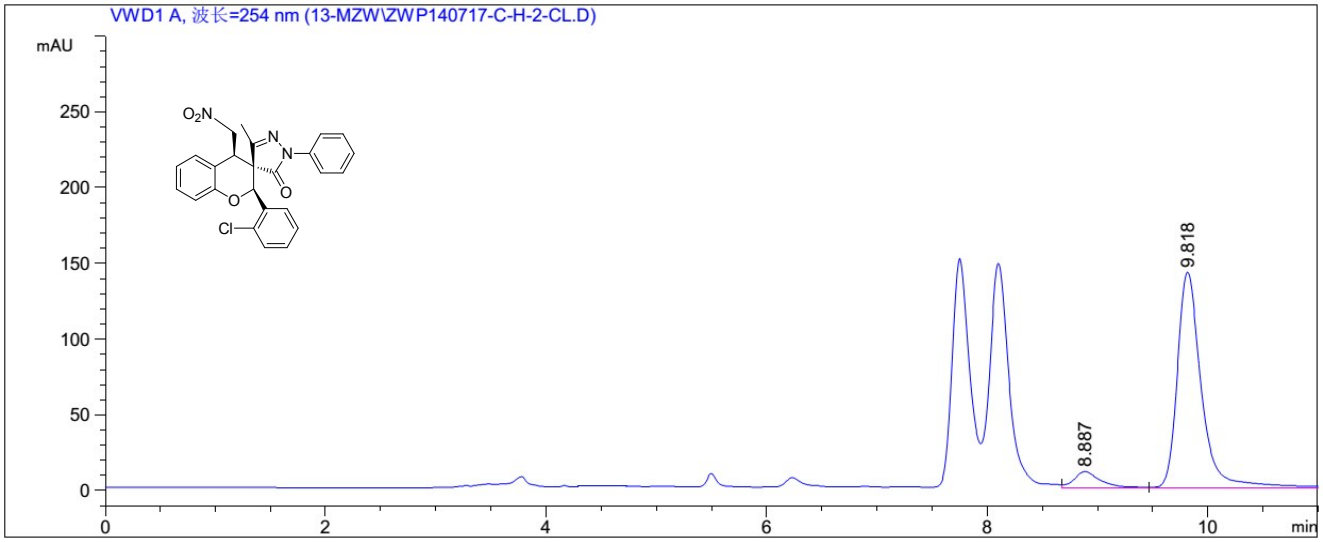
(2R,3R,4R)-2-(2-Chlorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11d):

RACEMIC 11d



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	9.034	0.2803	180.41887	9.23561	50.4870
2	9.941	0.2288	176.93855	12.89085	49.5130

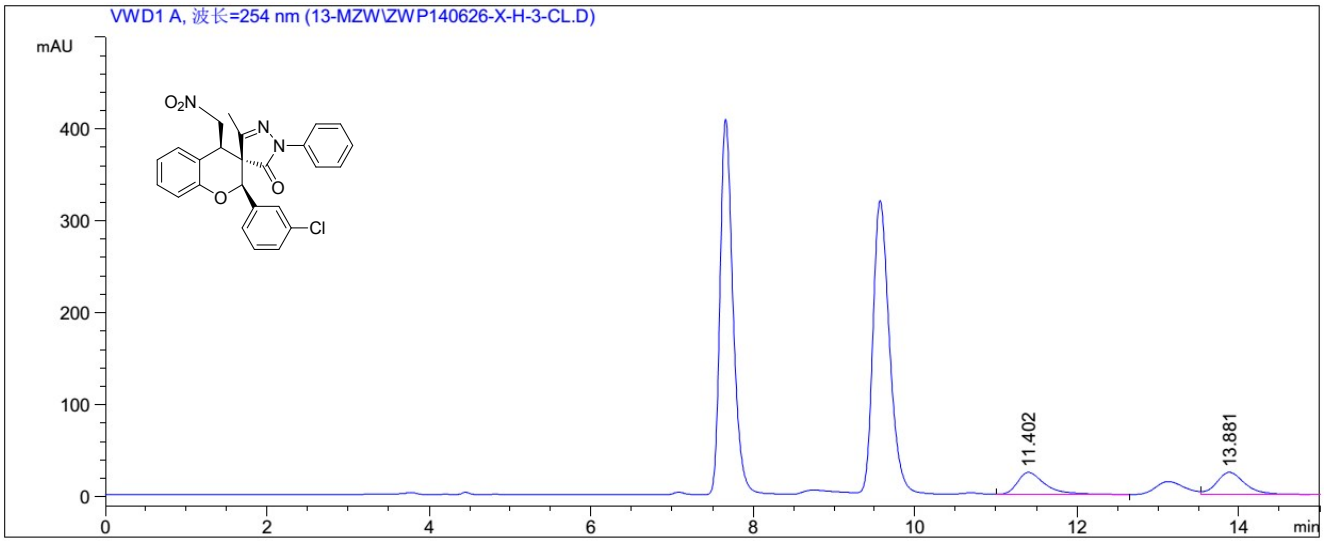
CHIRAL 11d



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	8.887	0.2415	176.07108	10.53734	7.4721
2	9.818	0.2315	2180.29517	142.02699	92.5279

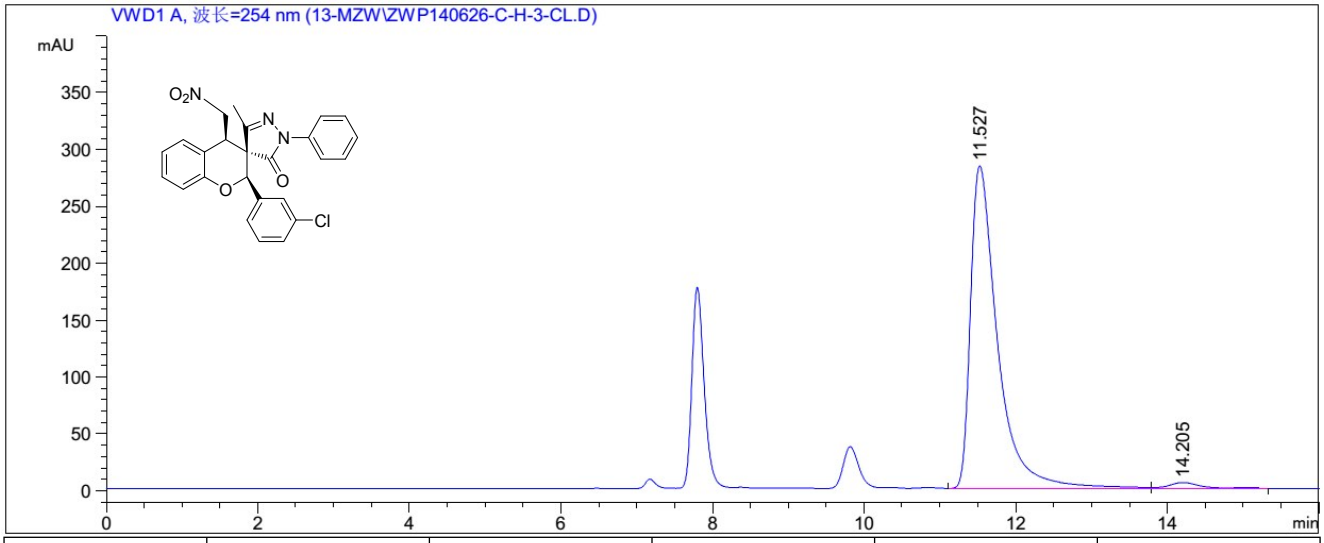
(2R,3R,4R)-2-(3-Chlorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11e):

RACEMIC 11e



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	11.402	0.3732	607.31335	24.29665	49.3482
2	13.881	0.3862	623.35724	24.33421	50.6518

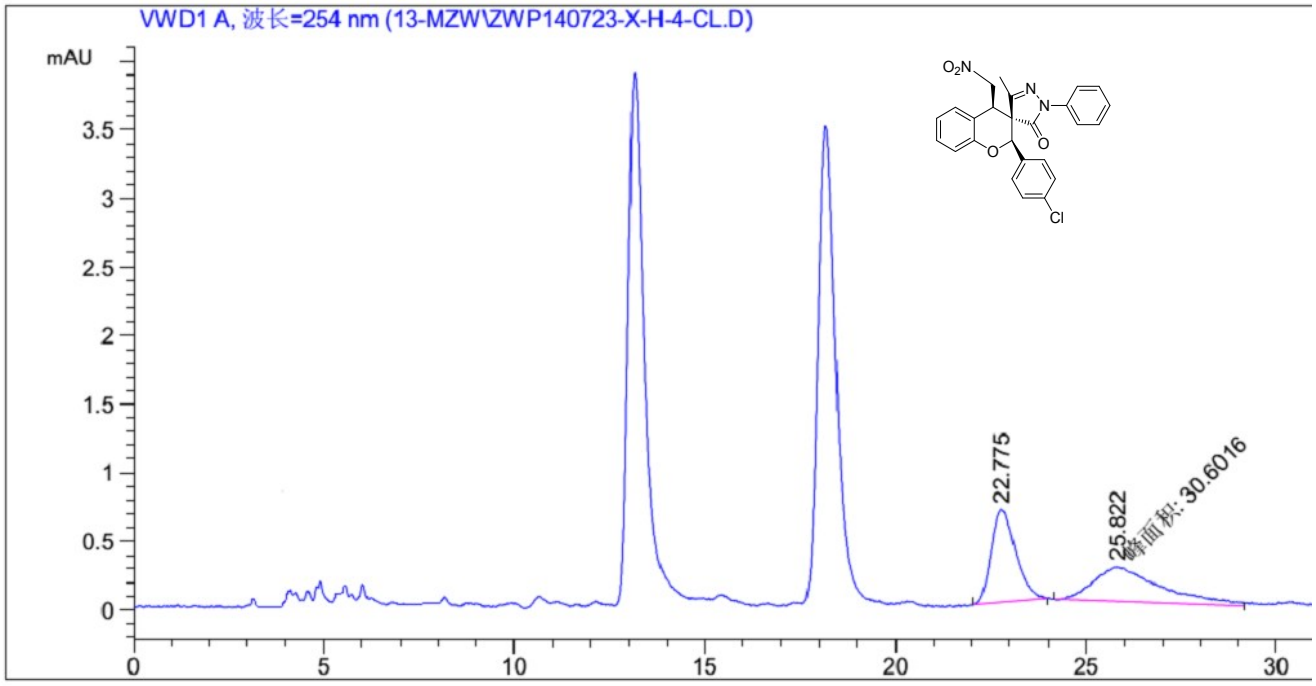
CHIRAL 11e



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	11.527	0.3723	7072.65088	283.83267	97.7785
2	14.205	0.4316	160.69164	5.54014	2.2215

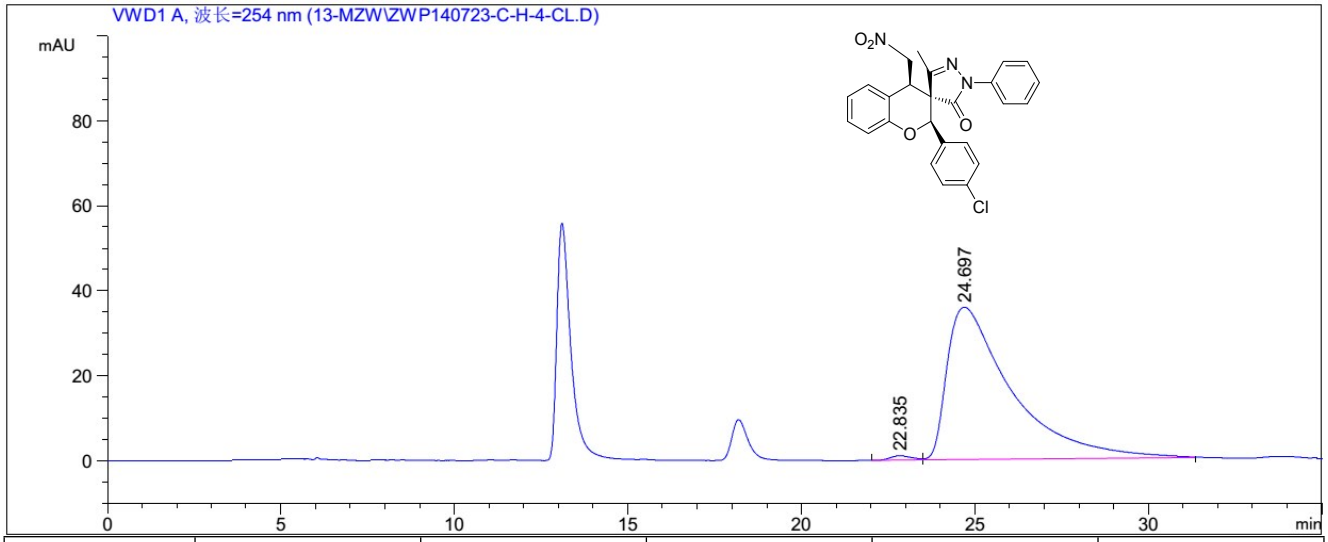
(2R,3R,4R)-2-(4-Chlorophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11f):

RACEMIC 11f



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	22.775	0.5741	30.29632	6.77539e-1	49.7493
2	25.822	2.0347	30.60162	2.50662e-1	50.2507

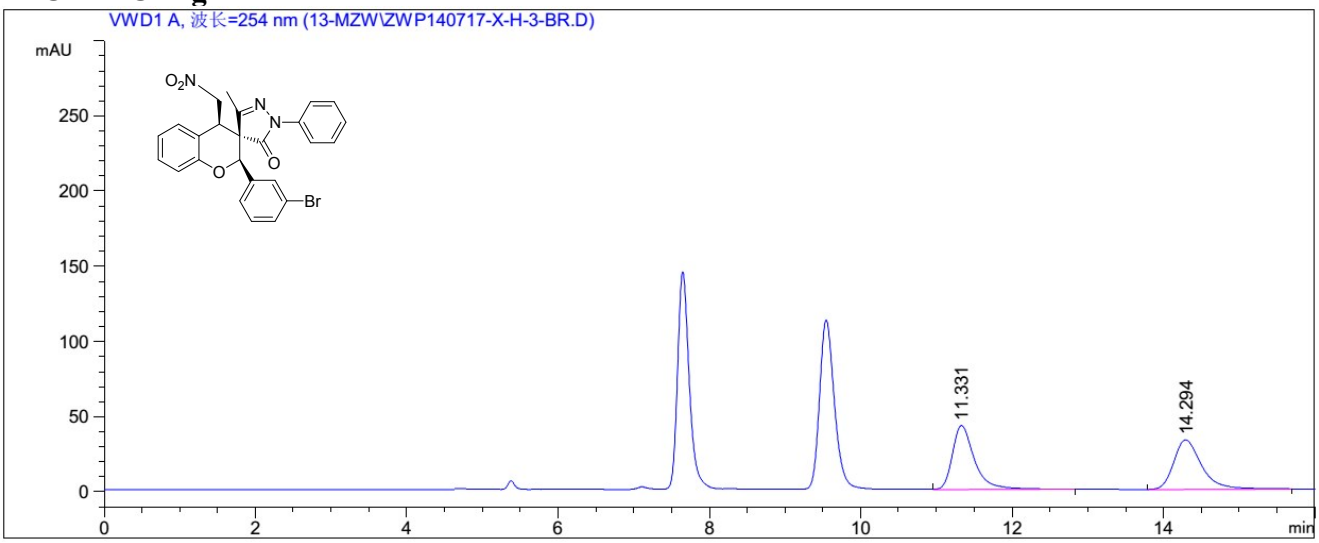
CHIRAL11f



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	22.835	0.6405	45.12573	1.02752	0.9583
2	24.697	1.8536	4664.00537	35.89781	99.0417

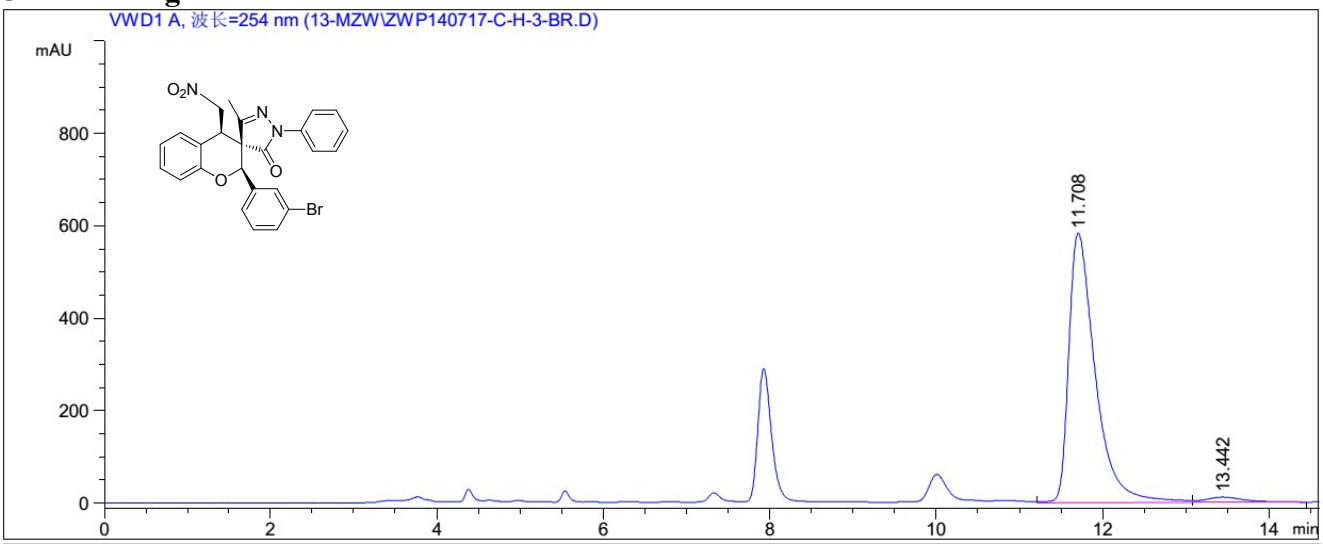
(2R,3R,4R)-2-(3-Bromophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11g):

RACEMIC 11g



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	11.331	0.3081	867.19110	42.46740	50.3827
2	14.294	0.3903	854.01752	32.89214	49.6173

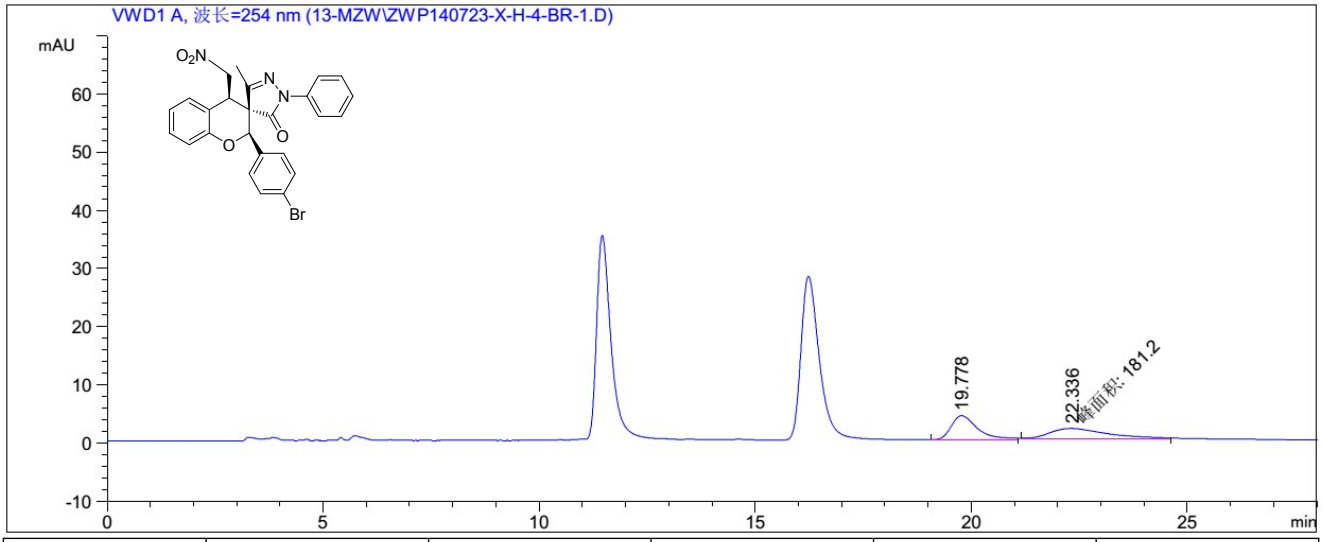
CHIRAL 11g



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	11.708	0.3346	1.29169e4	582.10260	96.8556
2	13.442	0.5009	419.34113	11.99852	3.1444

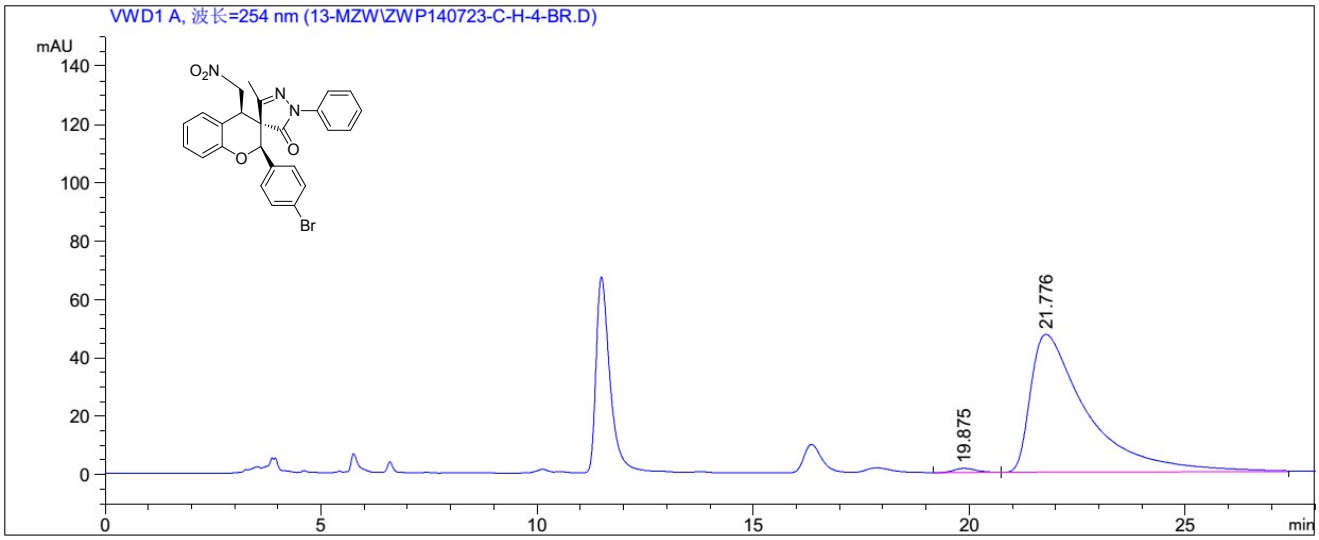
(2R,3R,4R)-2-(4-Bromophenyl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11h):

RACEMIC 11h



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	19.778	0.6340	175.65535	4.14692	49.2231
2	22.336	1.6353	181.20001	1.84678	50.7769

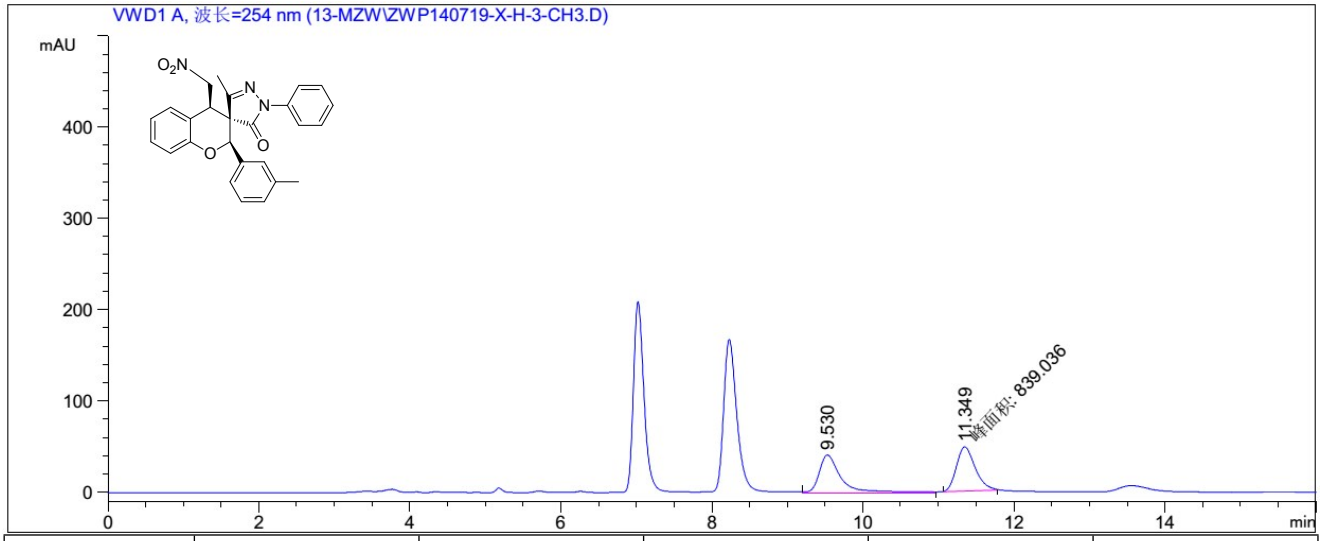
CHIRAL 11h



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	19.875	0.5524	49.95898	1.37374	1.1473
2	21.776	1.3073	4304.65381	47.25879	98.8527

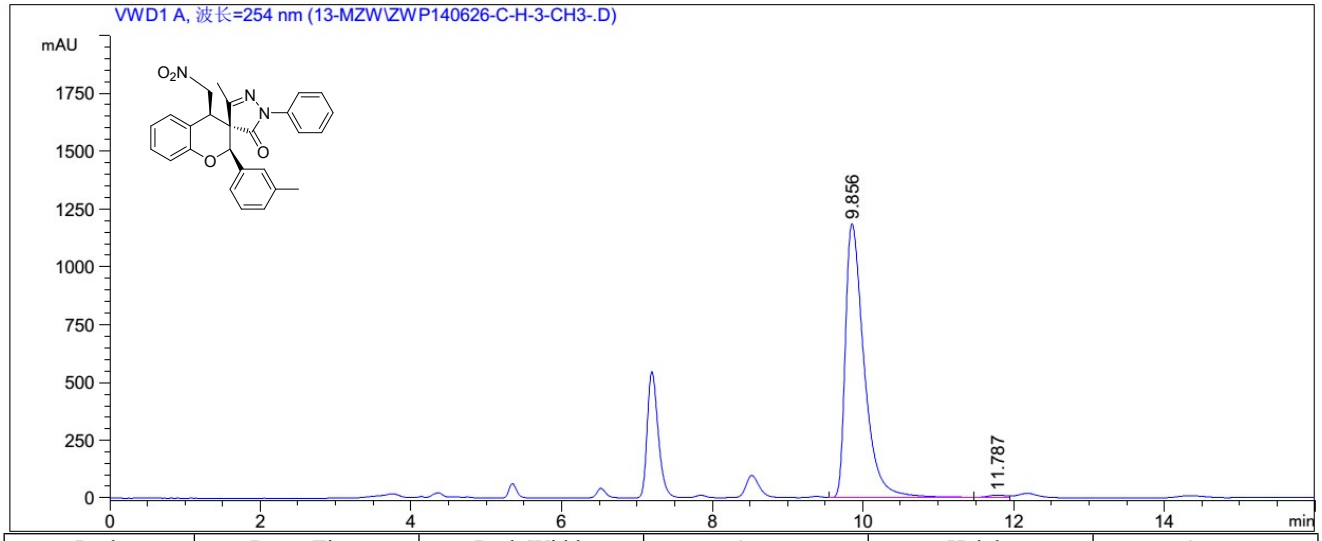
(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1'-phenyl-2-(m-tolyl)spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11i):

RACEMIC 11i



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	9.530	0.2913	823.16107	41.21480	49.5225
2	11.349	0.2893	839.03613	48.33861	50.4775

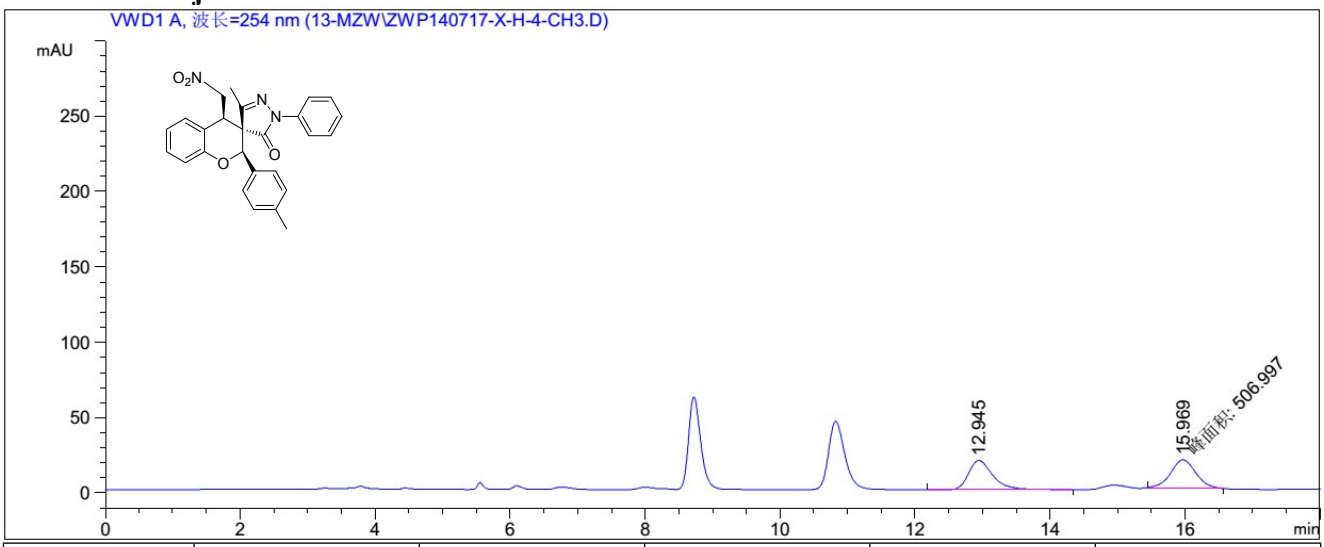
CHIRAL 11i



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	9.856	0.2635	2.08737e4	1186.67419	98.7791
2	11.787	0.2931	257.99847	13.14161	1.2209

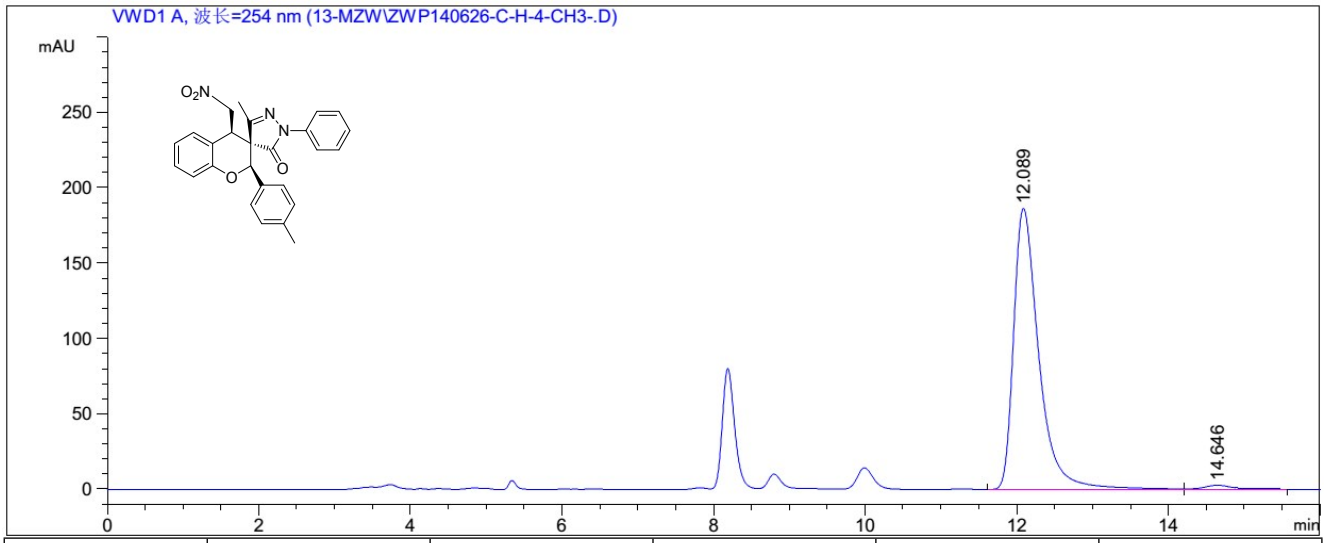
(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1'-phenyl-2-(p-tolyl)spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11j):

RACEMIC 11j



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	12.945	0.3880	500.69992	19.43040	49.6876
2	15.969	0.4426	506.99661	19.09273	50.3124

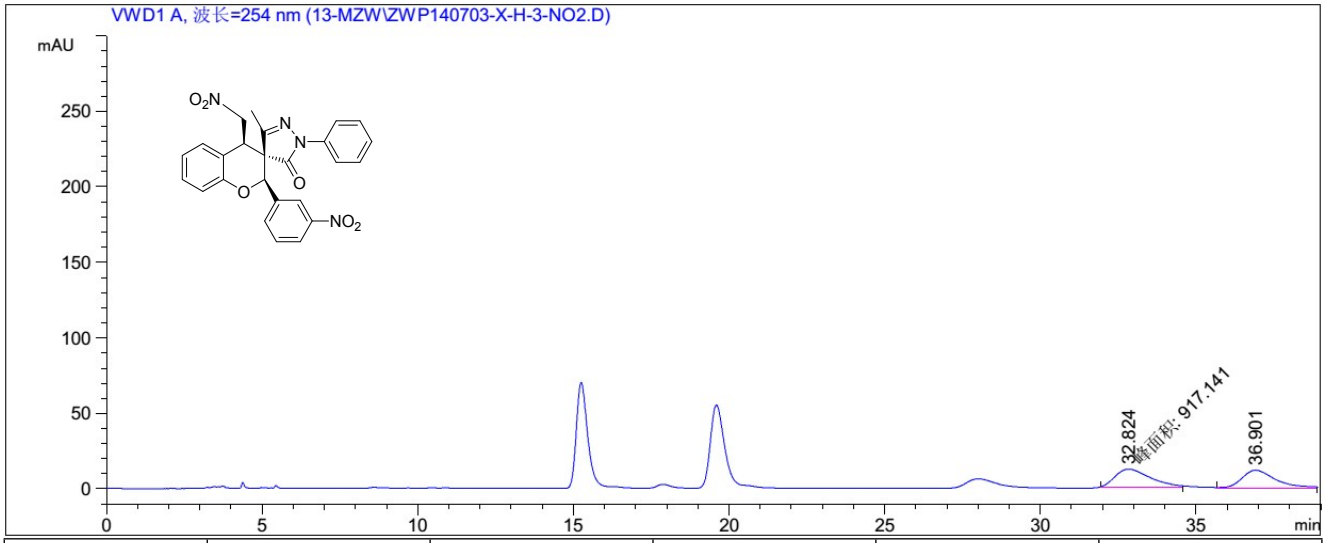
CHIRAL 11j



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	12.089	0.3521	4325.78906	186.52205	98.0854
2	14.646	0.4177	84.43727	2.98232	1.9146

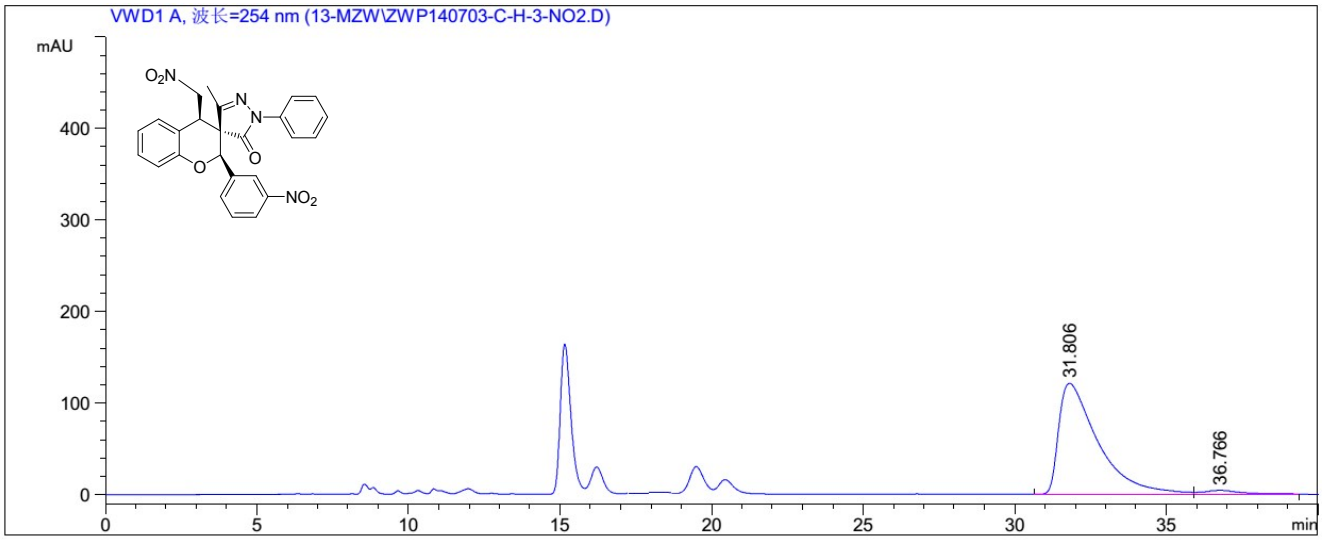
(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-2-(3-nitrophenyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11k):

RACEMIC 11k



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	32.824	1.2996	917.14111	11.76182	50.3582
2	36.901	1.1451	904.09558	11.86667	49.6418

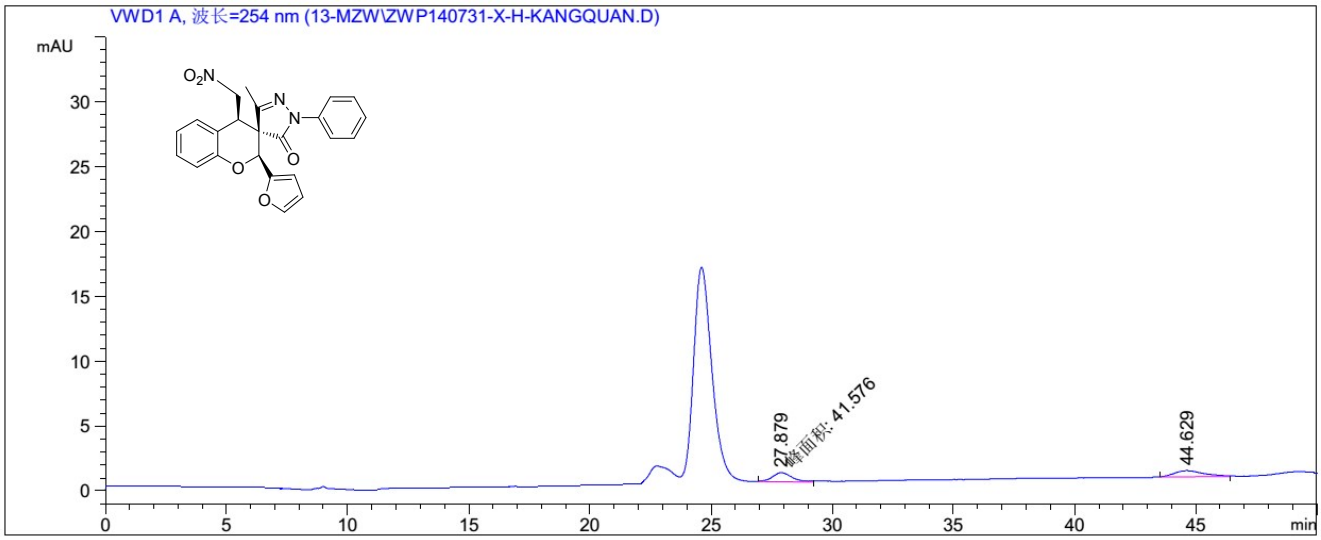
CHIRAL 11k



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	31.806	1.3423	1.09292e4	121.3065	96.8188
2	36.766	1.2968	359.10416	4.00401	3.1812

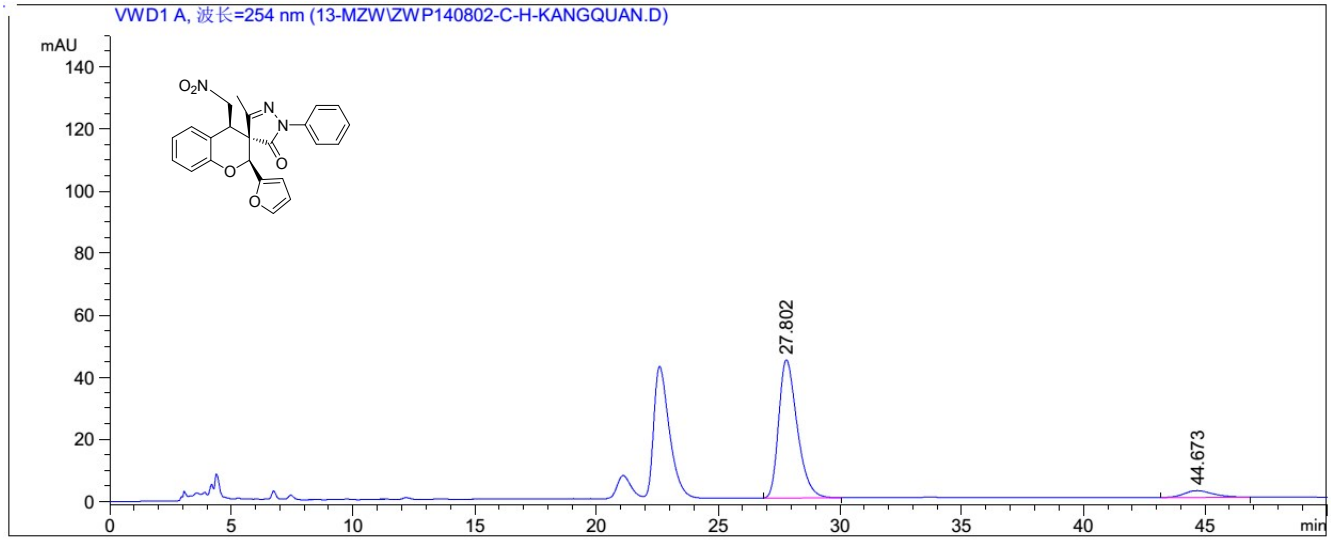
(2R,3R,4R)-2-(Furan-3-yl)-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11l):

RACEMIC 11l



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	27.879	0.9614	41.57602	7.20749e-1	50.4677
2	44.629	1.0311	40.80535	4.89328e-1	49.5323

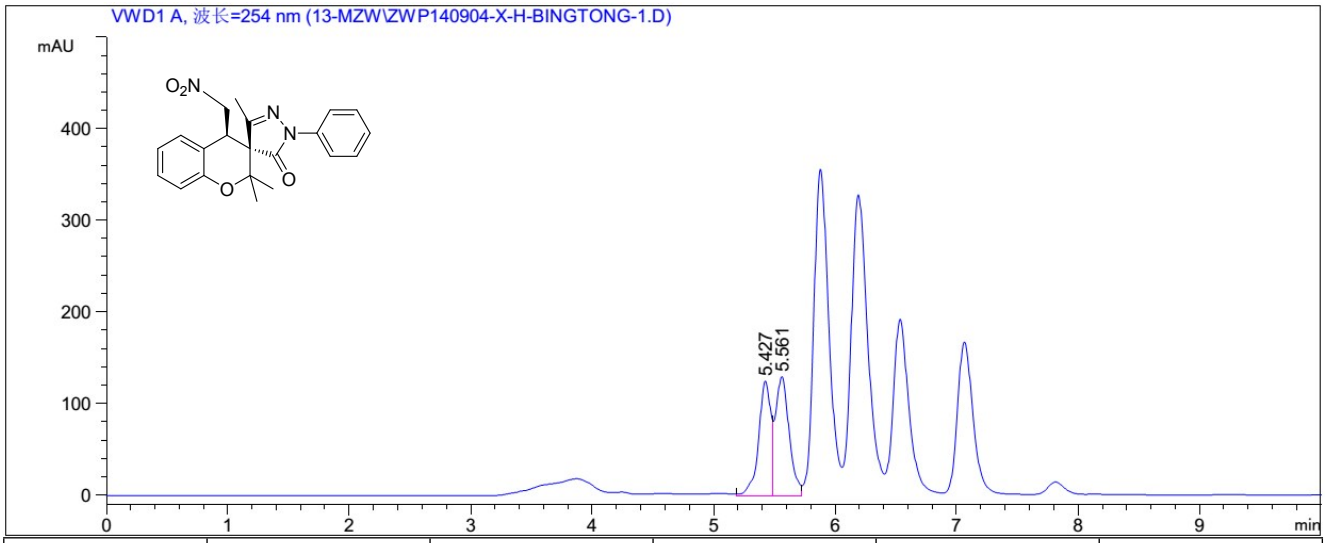
CHIRAL 11l



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	27.802	0.8107	2363.51221	44.58456	92.7051
2	44.673	1.3027	185.98387	2.18278	7.2949

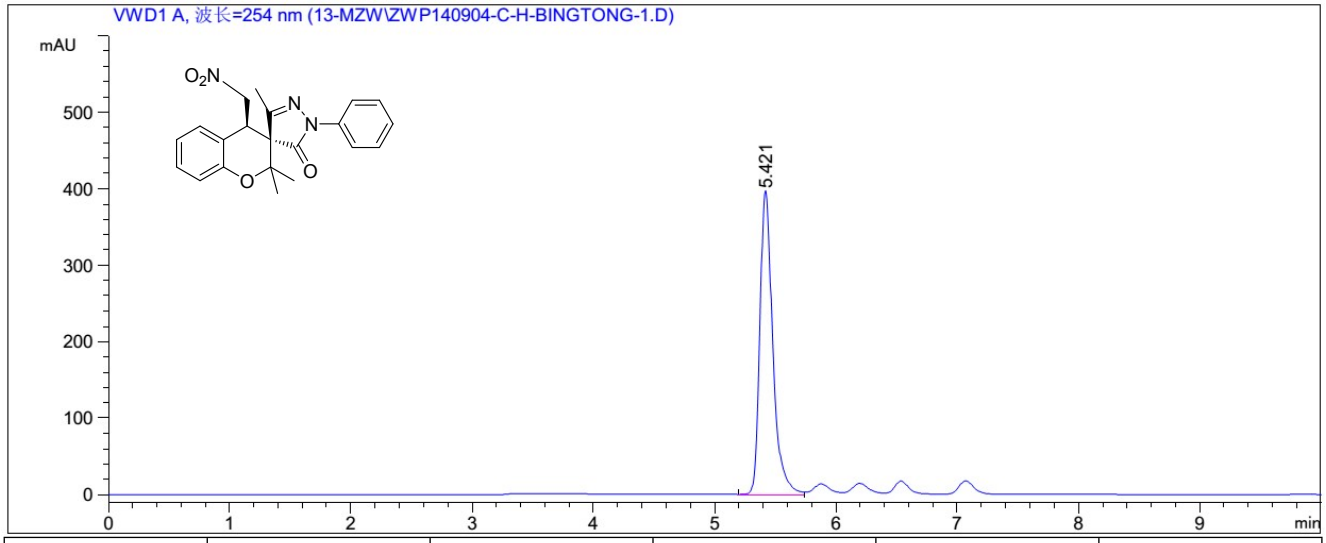
(3R,4R)-2,2,3'-Trimethyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11m):

RACEMIC 11m



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	5.427	0.1070	893.05786	124.50071	47.0919
2	5.561	0.1138	1003.35699	129.37706	52.9081

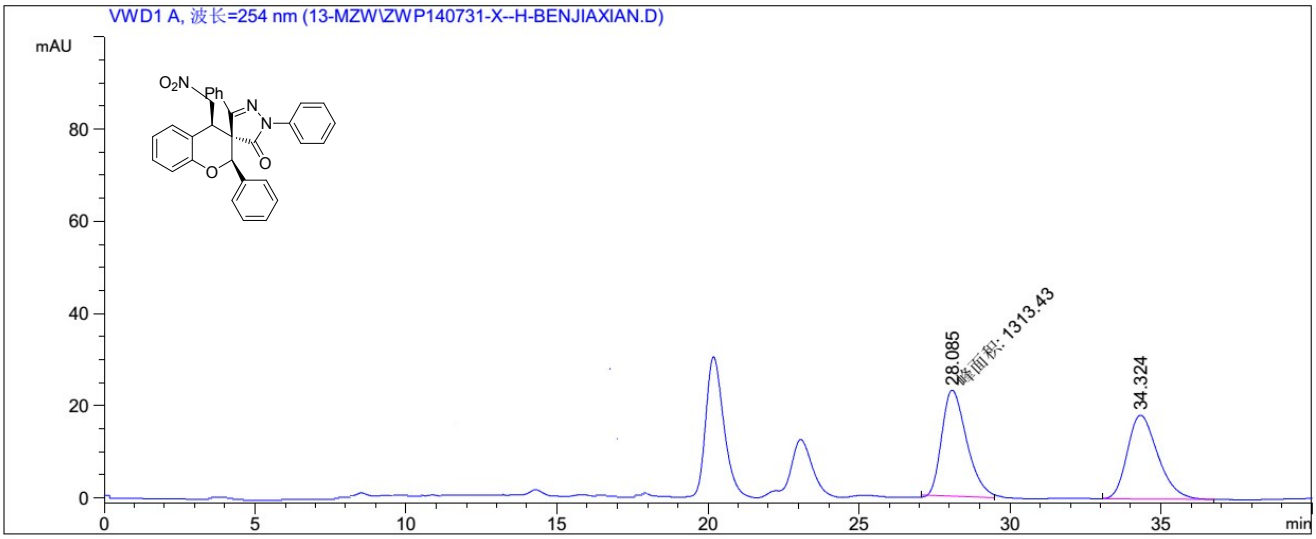
CHIRAL 11m



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	5.421	0.1166	2955.30933	394.30246	100.0000
2	-	-	-	-	-

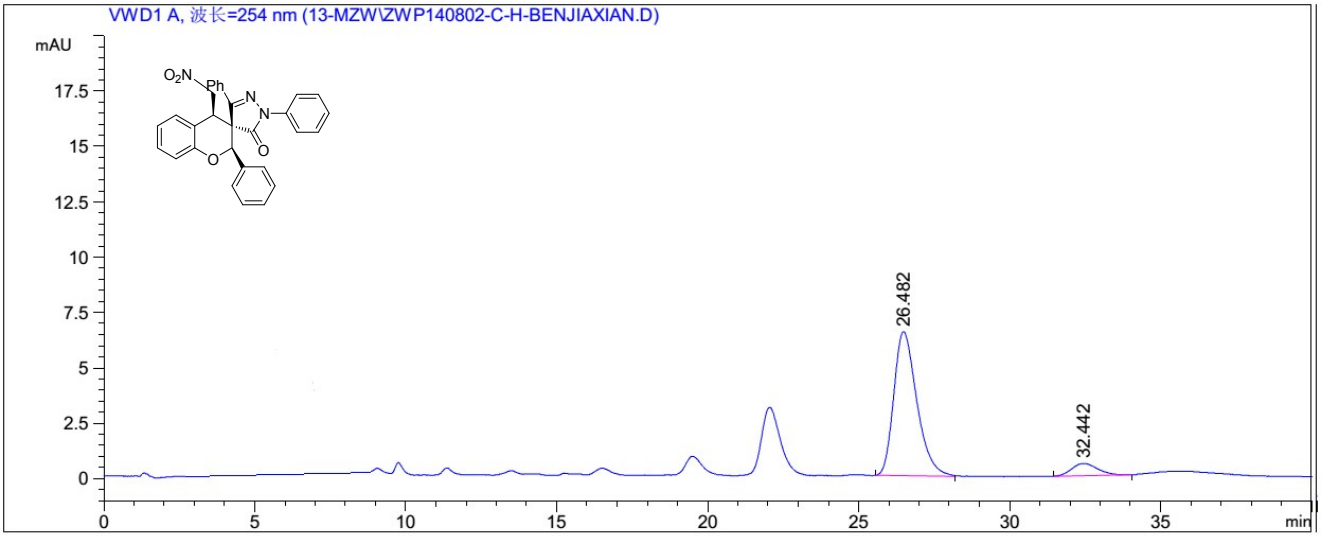
(2R,3R,4R)-4-(Nitromethyl)-1',2,3'-triphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11n):

RACEMIC 11n



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	28.085	0.9535	1313.42651	22.95694	50.7967
2	34.324	1.0803	1272.22522	18.13914	49.2033

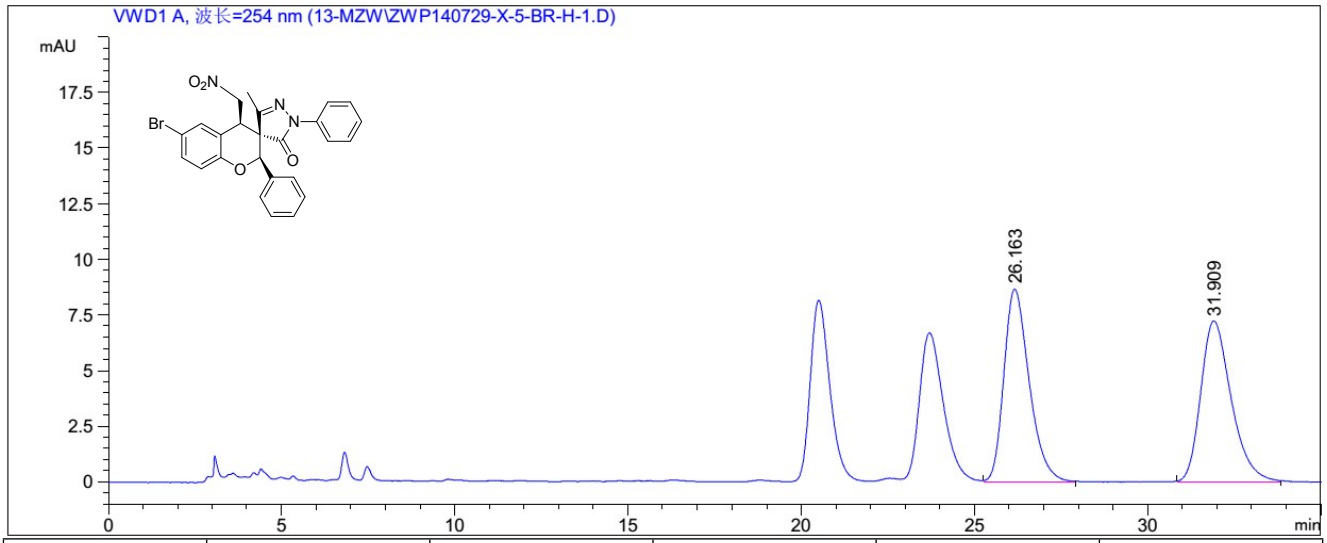
CHIRAL 11n



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	26.482	0.8173	345.13477	6.50218	91.4288
2	32.442	0.8622	32.35548	5.53772e-1	8.5712

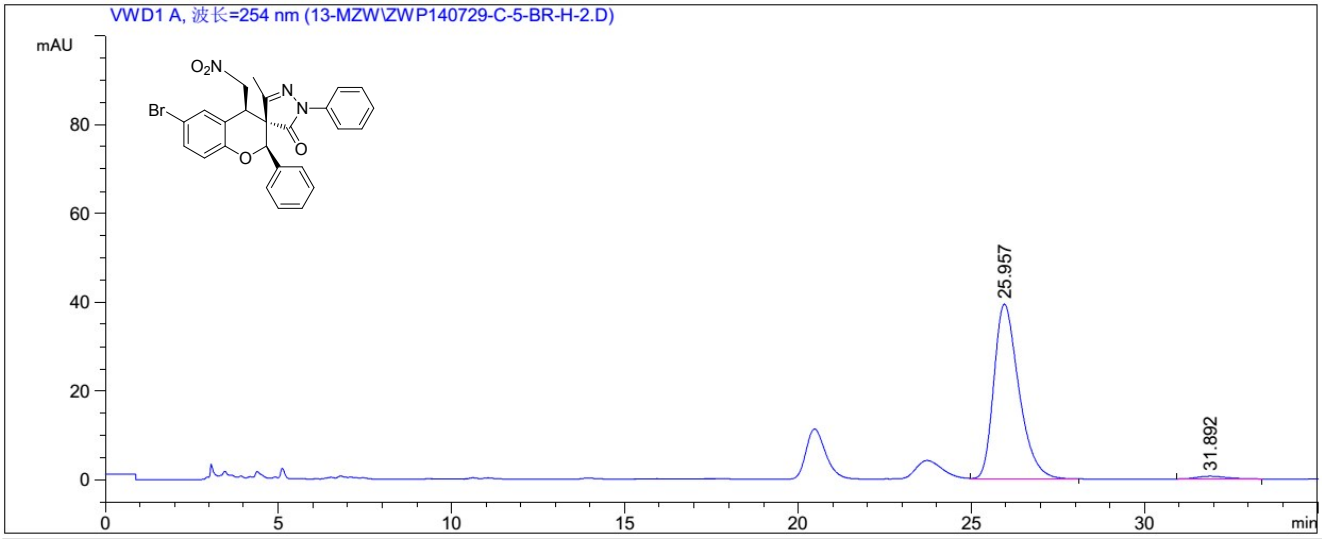
(2R,3R,4R)-6-Bromo-3'-methyl-4-(nitromethyl)-1',2-diphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11o):

RACEMIC 11o



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	26.163	0.7732	439.52283	8.65224	49.7689
2	31.909	0.9368	443.60455	7.23358	50.2311

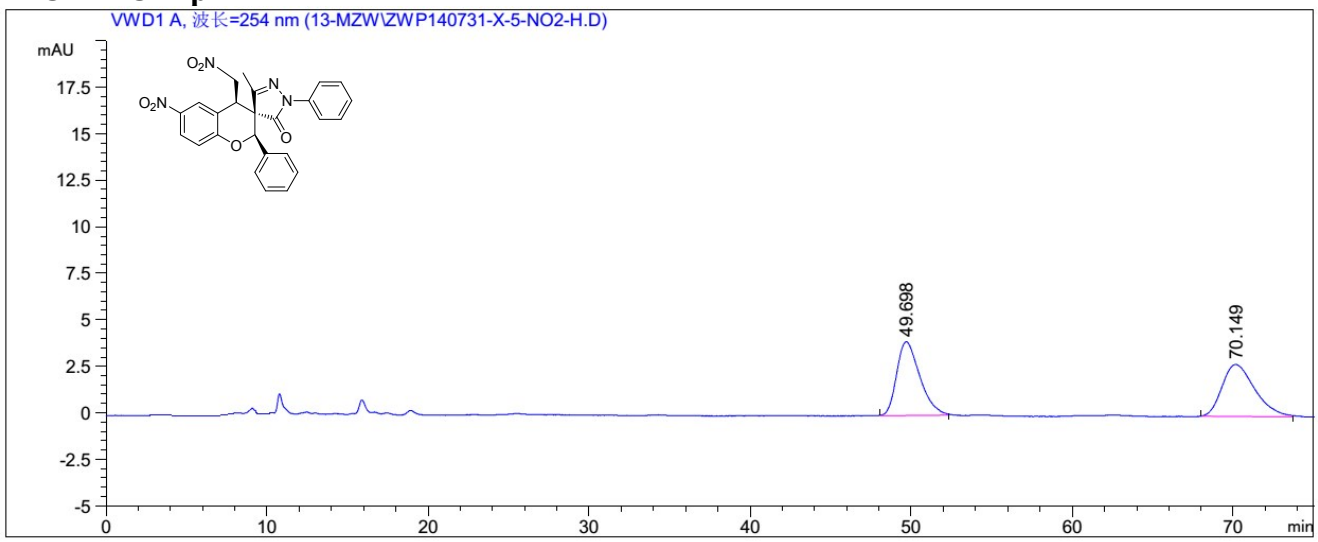
CHIRAL 11o



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	25.957	0.7623	1984.57251	39.40789	98.0704
2	31.892	0.9168	39.04733	6.44257e-1	1.9296

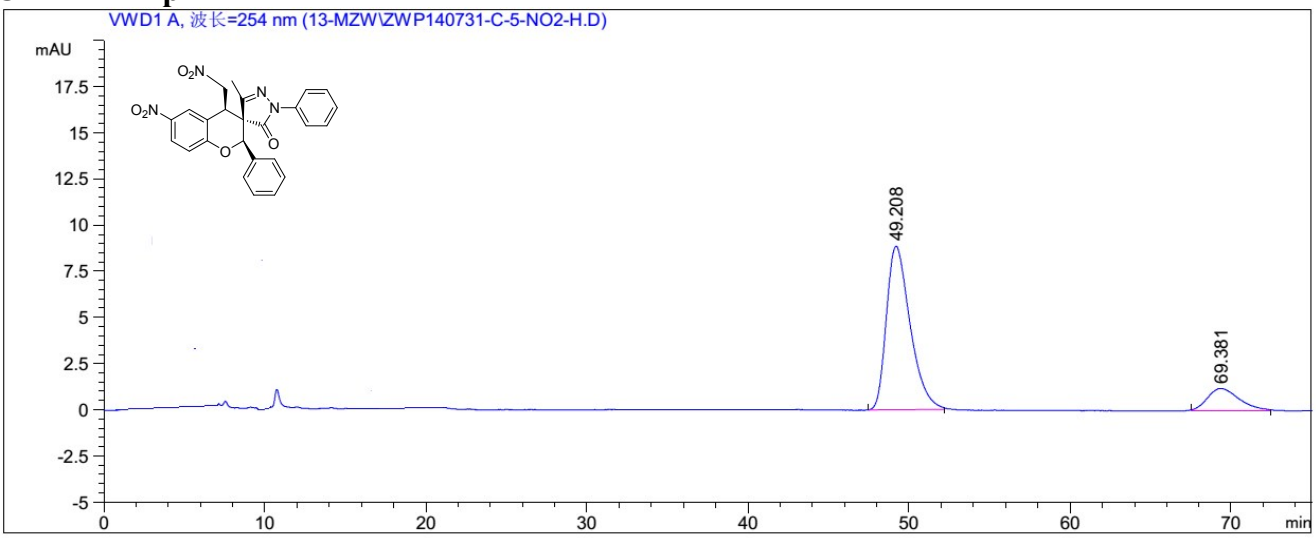
(2R,3R,4R)-3'-Methyl-6-nitro-4-(nitromethyl)-1',2-diphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11p):

RACEMIC 11p



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	49.698	1.4301	397.34888	3.96882	50.1327
2	70.149	1.7688	395.24466	2.80058	49.8673

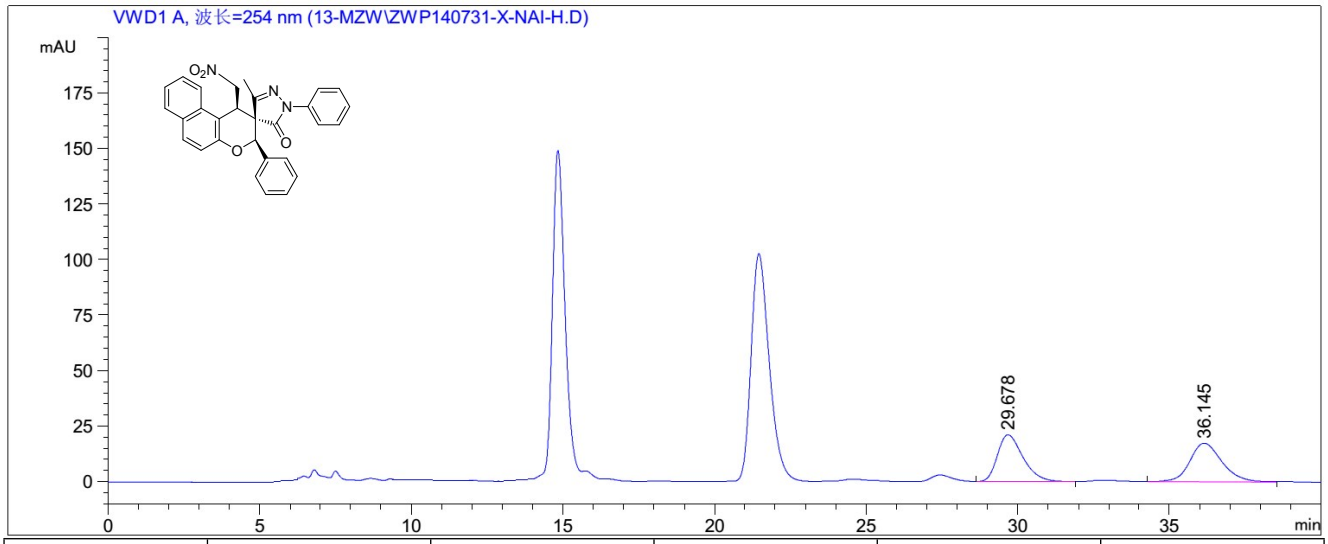
CHIRAL 11p



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	49.208	1.5144	907.44434	8.86594	84.8333
2	69.381	1.5945	162.23466	1.20018	15.1667

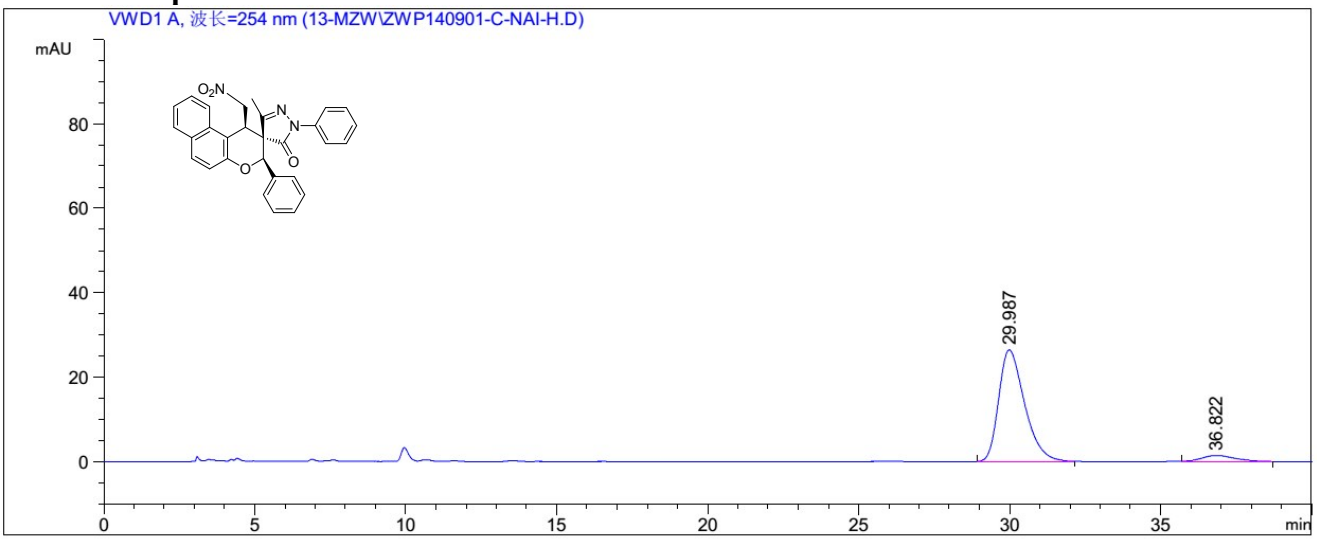
(2R,3R,4R)-3'-Methyl-4-(nitromethyl)-1',2-diphenyl-2,4-dihydrospiro[benzo[g]chromene-3,4'-pyrazol]-5'(1'H)-one (11q):

RACEMIC 11q



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	29.678	0.8976	1243.65479	21.09031	49.1743
2	36.145	1.1243	1285.41821	17.39388	50.8257

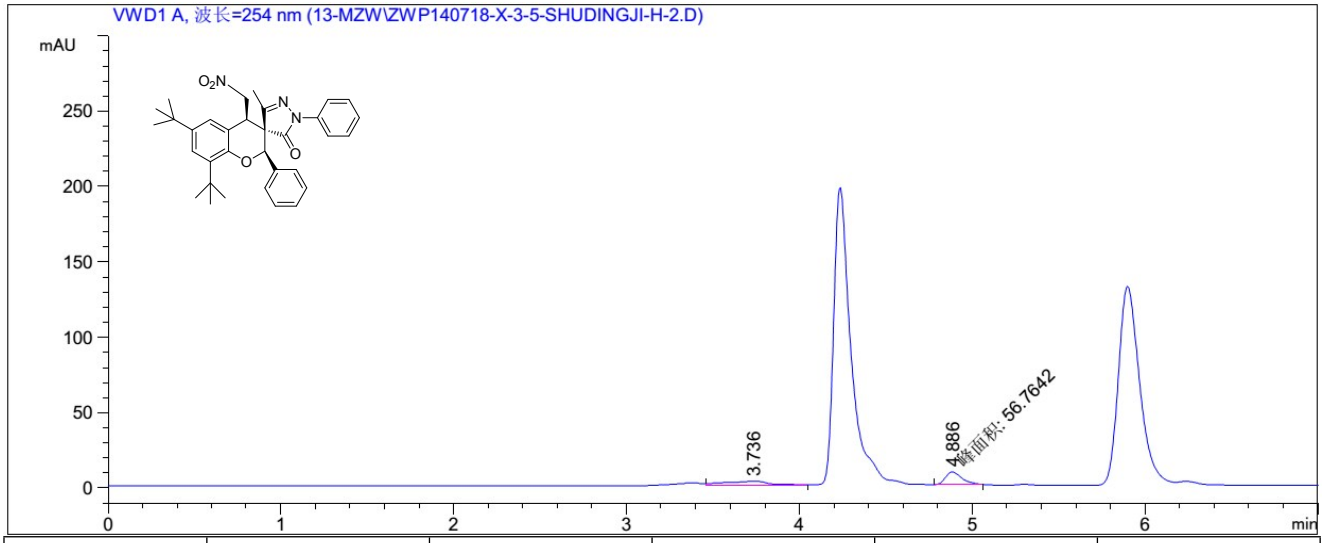
CHIRAL 11q



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	29.987	0.9065	1580.14111	26.45426	93.4063
2	36.822	0.9521	111.54506	1.44641	6.5937

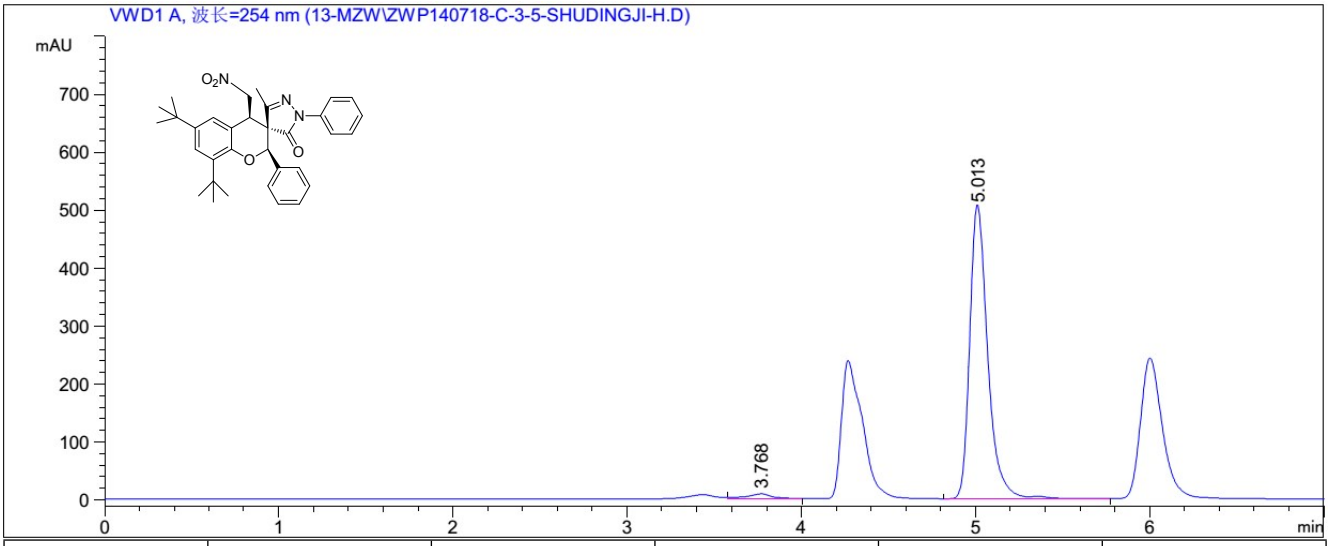
(2R,3R,4R)-6,8-Di-*tert*-butyl-3'-methyl-4-(nitromethyl)-1',2-diphenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11r):

RACEMIC 11r



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	3.736	0.2727	56.51086	2.77281	49.8882
2	4.886	0.1100	56.76424	8.60149	50.1118

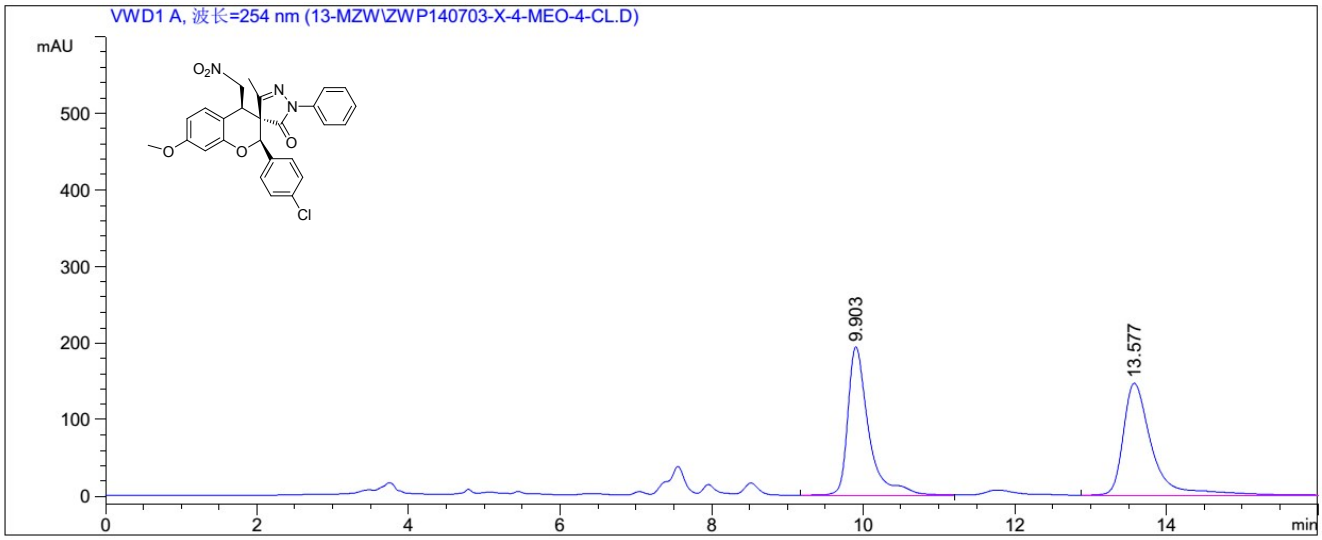
CHIRAL 11r



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	3.768	0.1676	113.96909	9.60047	2.9948
2	5.013	0.1149	3691.59229	502.01120	97.0052

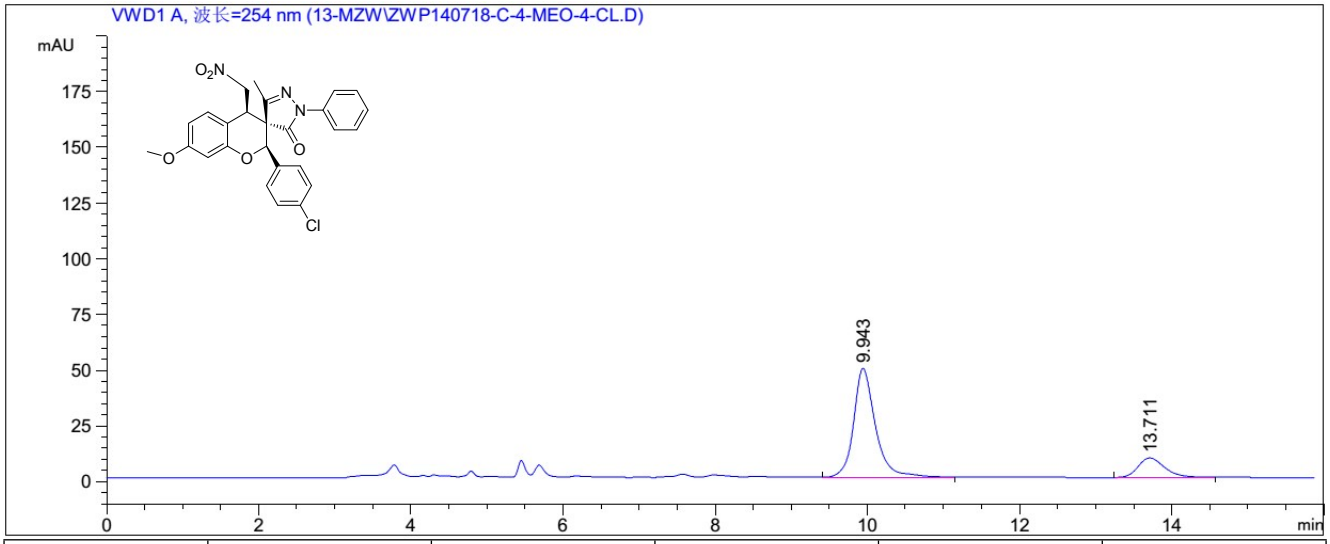
(2R,3R,4R)-2-(4-Chlorophenyl)-7-methoxy-3'-methyl-4-(nitromethyl)-1'-phenylspiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11s):

RACEMIC 11s



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	9.903	0.2924	3798.11865	194.04611	49.1643
2	13.577	0.3994	3927.23901	146.84163	50.8357

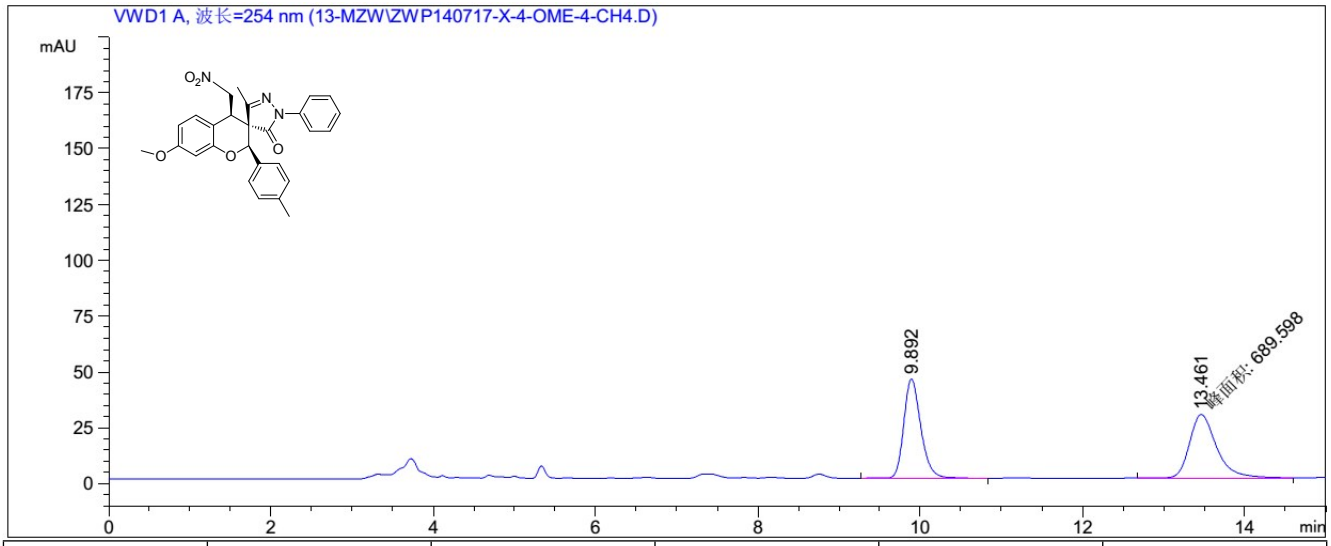
CHIRAL 11s



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	9.943	0.3009	996.71765	49.09279	82.1712
2	13.711	0.3737	216.25900	8.81174	17.8288

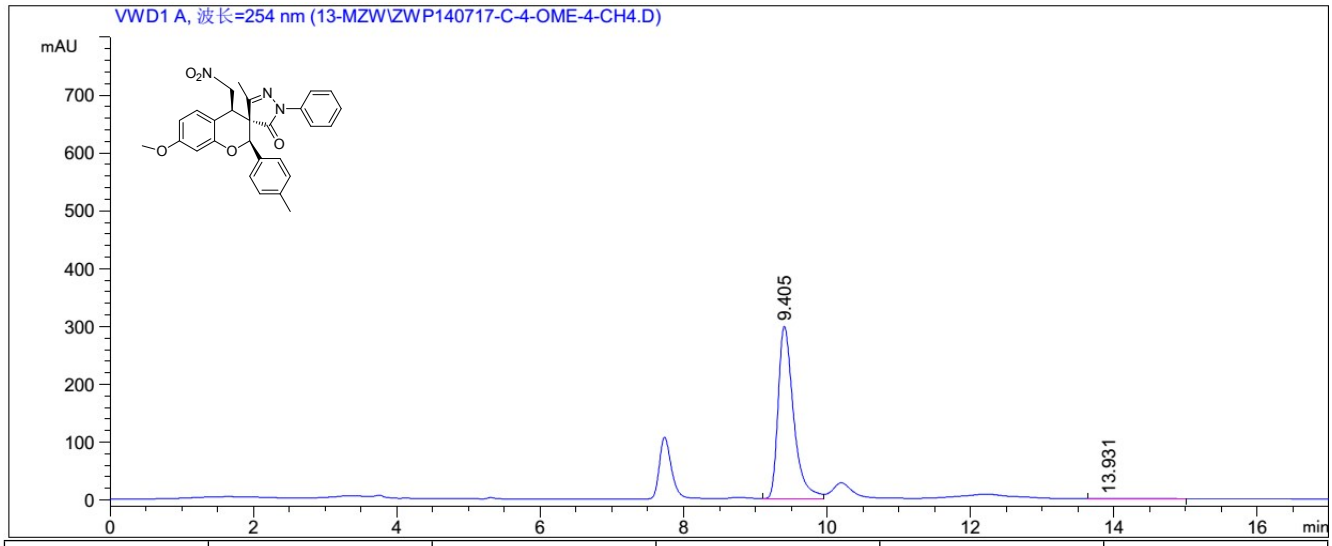
(2R,3R,4R)-7-Methoxy-3'-methyl-4-(nitromethyl)-1'-phenyl-2-(p-tolyl)spiro[chroman-3,4'-pyrazol]-5'(1'H)-one (11t):

RACEMIC 11t



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	9.892	0.2288	676.18842	44.73312	49.5091
2	13.461	0.4000	689.59766	28.73280	50.4909

CHIRAL 11t



Peak	Reten.Time [min]	Peak.Width [min]	Area [mAU]	Height [mAU]	Area [%]
1	9.405	0.2282	4492.71875	298.14685	99.3500
2	13.931	0.7344	29.39480	4.86228e-1	0.6500

X-ray crystal structure of 11a;

Crystallographic data for the structural analysis of compound **11a** has been deposited at the Cambridge Crystallographic Data Centre as No. CCDC 1428773. These data can be obtained free of charge by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk.

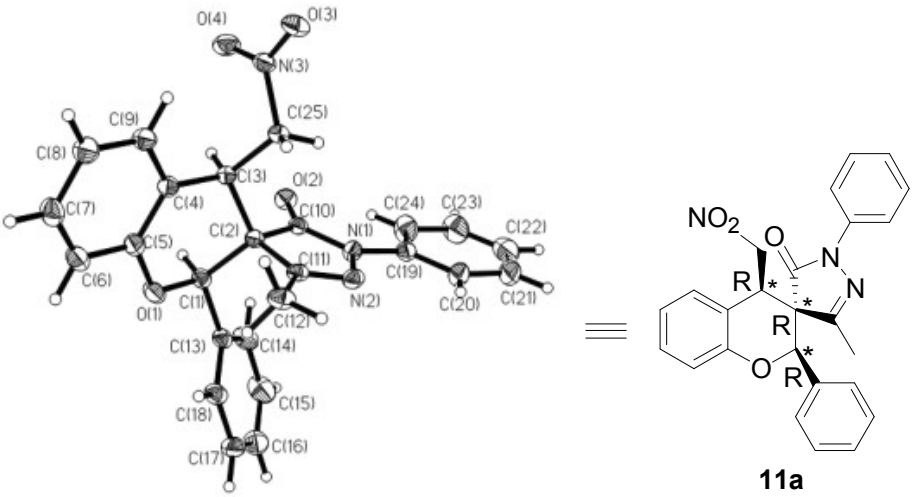


Table 1. Crystal data and structure refinement for shelxl.

Identification code	shelxl
Empirical formula	C25 H21 N3 O4
Formula weight	427.45
Temperature	173(2) K
Wavelength	1.54187 A
Crystal system, space group	Monoclinic, P2(1)
Unit cell dimensions	a = 9.007(4) A alpha = 90 deg.
	b = 13.691(4) A beta = 112.6366(10) deg.
	c = 11.577(4) A gamma = 90 deg.
Volume	1317.6(8) A^3
Z, Calculated density	2, 1.264 Mg/m^3
Absorption coefficient	0.708 mm^-1

F(000)	532
Crystal size	0.260 x 0.200 x 0.160 mm
Theta range for data collection	6.228 to 77.702 deg.
Limiting indices	-11<=h<=11, -17<=k<=14, -14<=l<=14
Reflections collected / unique	22397 / 4797 [R(int) = 0.0235]
Completeness to theta = 67.687	99.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.893 and 0.778
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4797 / 1 / 338
Goodness-of-fit on F^2	1.051
Final R indices [I>2sigma(I)]	R1 = 0.0309, wR2 = 0.0837
R indices (all data)	R1 = 0.0312, wR2 = 0.0840
Absolute structure parameter	0.00(4)
Extinction coefficient	0.0184(11)
Largest diff. peak and hole	0.208 and -0.175 e.A^-3