Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Chiral Iminophosphorane Catalyzed Asymmetric Sulfenylation of 4-Substituted Pyrazolones

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Ⅰ. General Information

NMR spectra were recorded on a Bruker or Agilent 400 MHz, ^{1}H NMR , ^{13}C NMR, ^{19}F NMR spectra were respectively recorded at 400 MHz, 100 MHz, 376 MHz. Chemical shifts (δ) and coupling constants (J) were expressed in parts per million and hertz, respectively. The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. High-resolution mass spectra (HRMS) were equipped with an ESI source. Melting point were measured with SWG X-4. Optical rotations were reported as $[\alpha]^{T}_{D}$ (solvent, concentration in grams/100 mL). Enantiomeric excesses (*ee*) were determined by HPLC using corresponding commercial chiral columns.

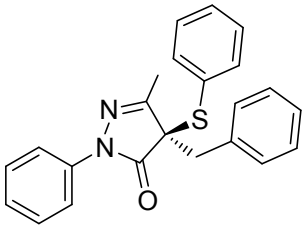
Ⅱ. Materials

The catalysts were prepared according to the literature.[1] All 4-substituted pyrazolones were prepared according to the literature and references therein.[2] All substituted *N*-(phenylthio)-phthalimides were prepared according to the literature.[3] All solvents were dried and/or distilled by standard methods**.** Unless otherwise mentioned, substrates were purchased from commercial suppliers.

Ⅲ. General Procedure for the Synthesis of products

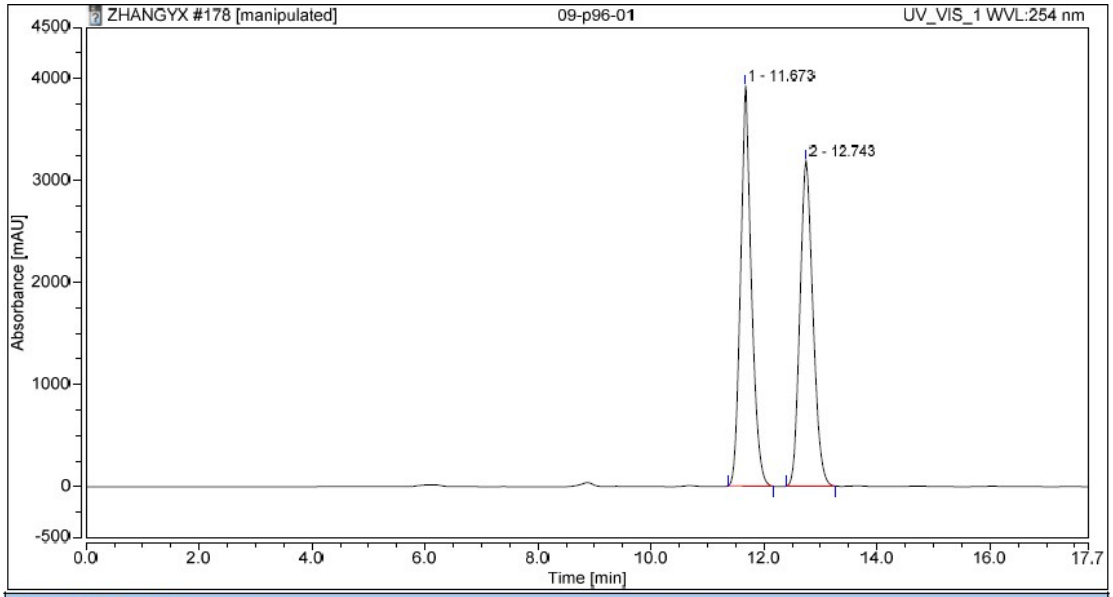
4-Substituted pyrazolones (0.1 mmol, 1.0 eq), *N*-(phenylthio)phthalimides (0.15 mmol, 1.5 eq) and catalyst (0.001 mmol, 1.0 mol%) were added to a Schlenk tube. Then 2 ml *n*-pentane was added using a syringe. The reaction was stirred at room temperature until started materials of pyrazolone derivative were disappeared in argon. After the solvent was removed in vacuo and the residue was purified by silica gel using eluent.

(*R*)-4-Benzyl-3-methyl-1-phenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (3a)



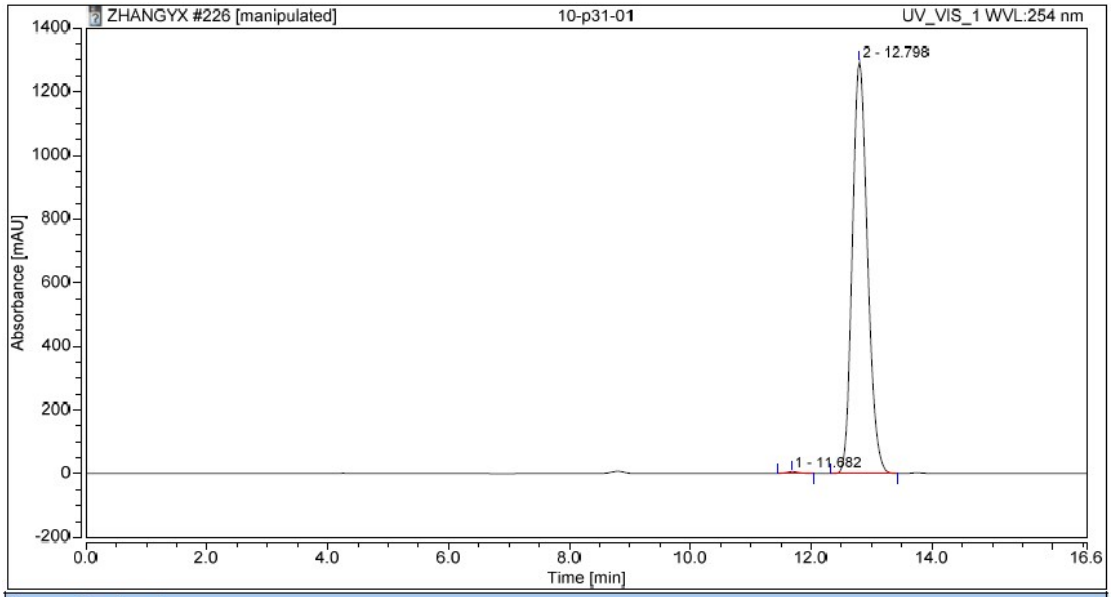
The crude product was purified by flash chromatography to obtain **3a** (white solid, 99% yield). M. p.: 70-74 ℃. $[\alpha]^{29}_{D}$ = -197.3° (c = 0.98, DCM). *Ee* = 99%; HPLC condition：CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 11.7 (minor) and 12.8 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.2 Hz,

2H), 7.32-7.12 (m, 12H), 7.08 (t, J = 7.6 Hz, 1H), 3.56 (d, J = 14.0 Hz, 1H), 3.06 (d, J = 14.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 159.0, 137.1, 135.9, 134.3, 130.3, 129.19, 129.15, 128.8, 128.6, 128.1, 127.7, 125.5, 119.7, 64.8, 38.3, 14.5. IR ν_{max} (film) cm^{-1} 3061， 3031, 2921， 2852， 1706， 1595， 1497， 1118， 1025， 749， 723， 689. HRMS (ESI) for $C_{23}H_{20}N_2OS$: calculated $[M+H]^+$, 373.1374. Found, 373.1360.



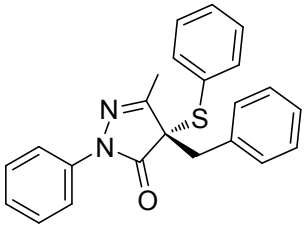
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		11.673	872.079	3929.780	50.66	55.16	n.a.
2		12.743	849.421	3194.222	49.34	44.84	n.a.
Total:			**1721.500**	**7124.002**	**100.00**	**100.00**	

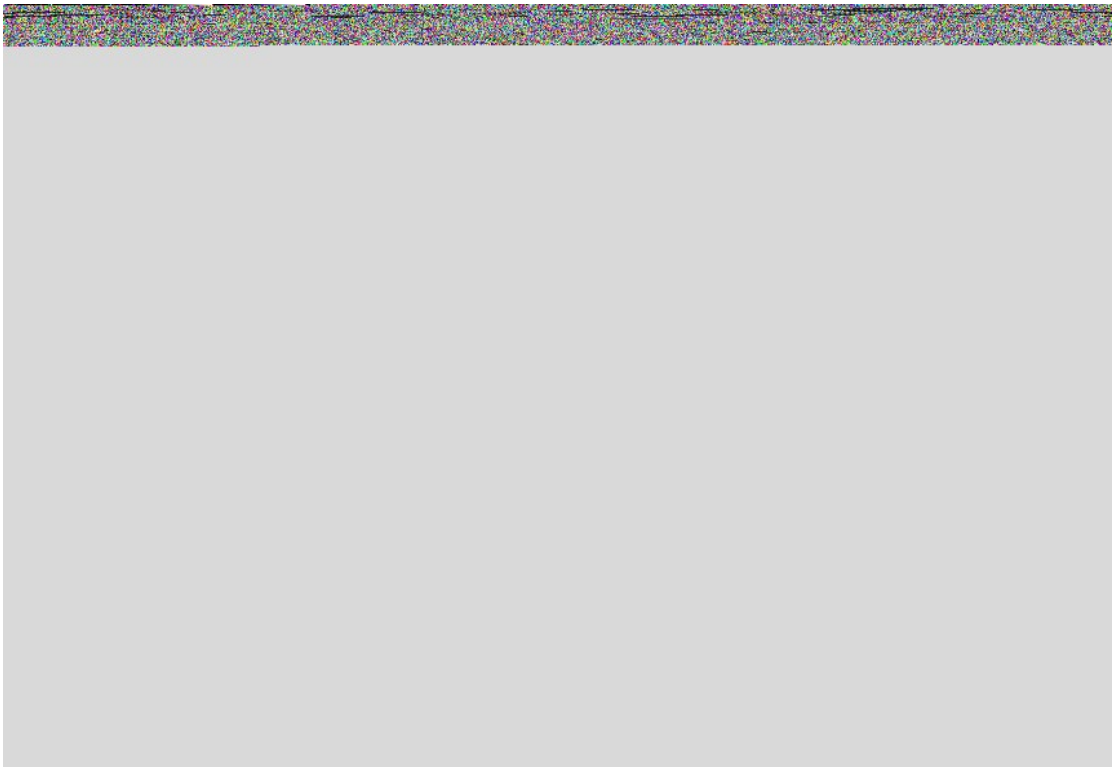


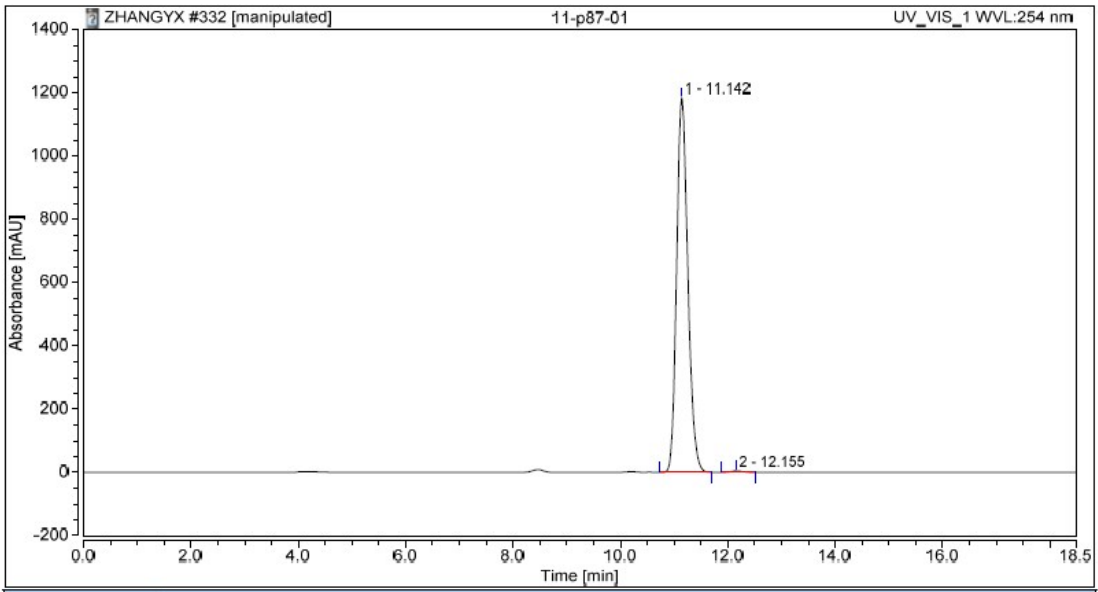
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		11.682	1.529	6.123	0.41	0.47	n.a.
2		12.798	375.070	1295.188	99.59	99.53	n.a.
Total:			**376.599**	**1301.311**	**100.00**	**100.00**	

(*S*)-4-Benzyl-3-methyl-1-phenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (3a')



The crude product was purified by flash chromatography to obtain **3a'** (91% yield). $[\alpha]^{30}_{D} = 177.6^{o}$ (c=1.00, DCM). *Ee* = -99%; HPLC condition：CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 11.1 (major) and 12.2 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.2 Hz, 2H), 7.32-7.12 (m, 12H), 7.08 (t, J = 7.2 Hz, 1H), 3.56 (d, J = 13.6 Hz, 1H), 3.07 (d, J = 13.6 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 159.0, 137.2, 136.0, 134.3, 130.3, 129.22, 129.18, 128.8, 128.7, 128.2, 127.7, 125.5, 119.8, 64.8, 38.3, 14.5.

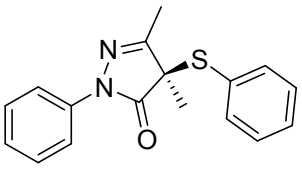




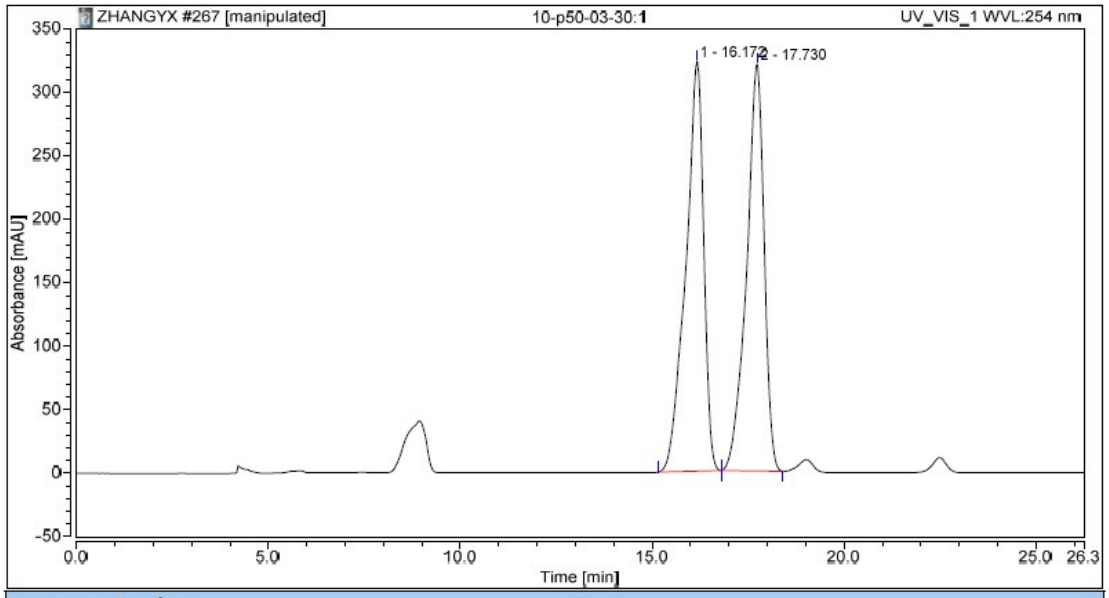
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		11.142	286.244	1183.713	99.59	99.60	n.a.
2		12.155	1.173	4.731	0.41	0.40	n.a.
Total:			**287.417**	**1188.444**	**100.00**	**100.00**	

(*R*)-3,4-Dimethyl-1-phenyl-4-(phenylthio)-1*H*-pyrazol-5(4*H*)-one (3b)

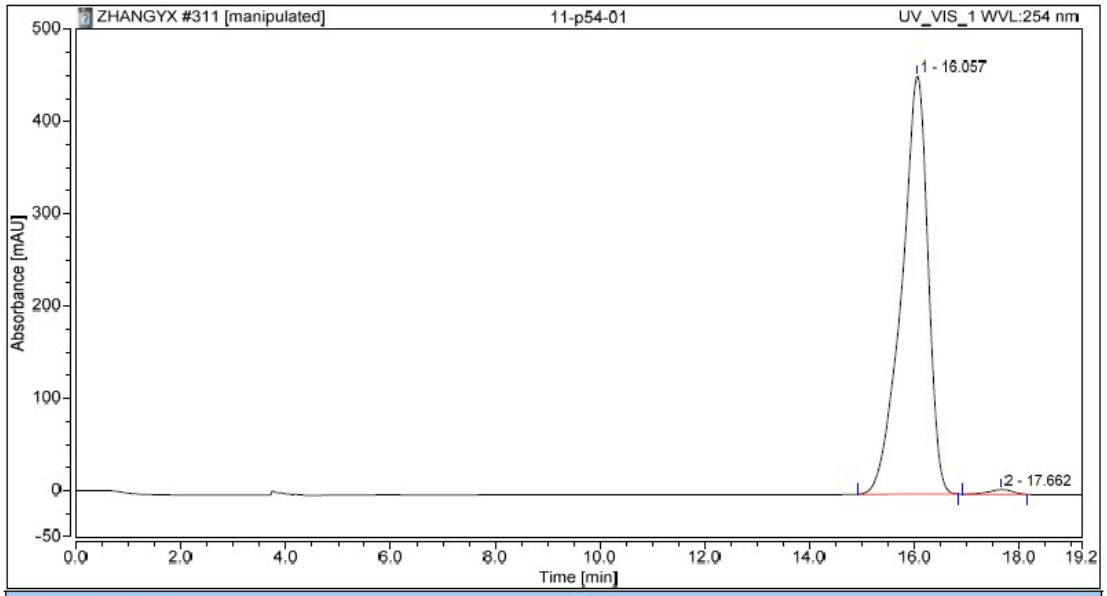


The crude product was purified by flash chromatography to obtain **3b** (white solid, 94% yield). M. p.: 64-68 ˚C. $[\alpha]^{28}_{D}$ = -546.3° (c=1.01, DCM). *Ee* = 98%; HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (30:1 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 16.1 (major) and 17.7 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 6.8 Hz, 2H), 7.28 (t, J = 8.0 Hz, 3H), 7.19 (t, J = 7.6 Hz, 2H), 7.11 (t, J = 7.2 Hz, 1H), 2.27 (s, 3H), 1.58(s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.7, 160.7, 137.4, 135.8, 130.3, 129.1, 128.7, 128.6, 125.3, 119.3, 59.3, 17.8, 13.5. IR ν_{max} (film) cm^{-1} 3060, 2924, 2852, 1710，1595, 1497, 1125, 1023, 750, 689. HRMS (ESI) for $C_{17}H_{16}N_2OS$: calculated $[M+H]^+$, 297.1061. Found, 297.1054.



Integration Results

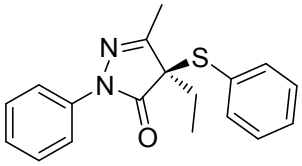
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		16.172	174.269	322.972	50.66	50.19	n.a.
2		17.730	169.753	320.574	49.34	49.81	n.a.
Total:			**344.021**	**643.546**	**100.00**	**100.00**	



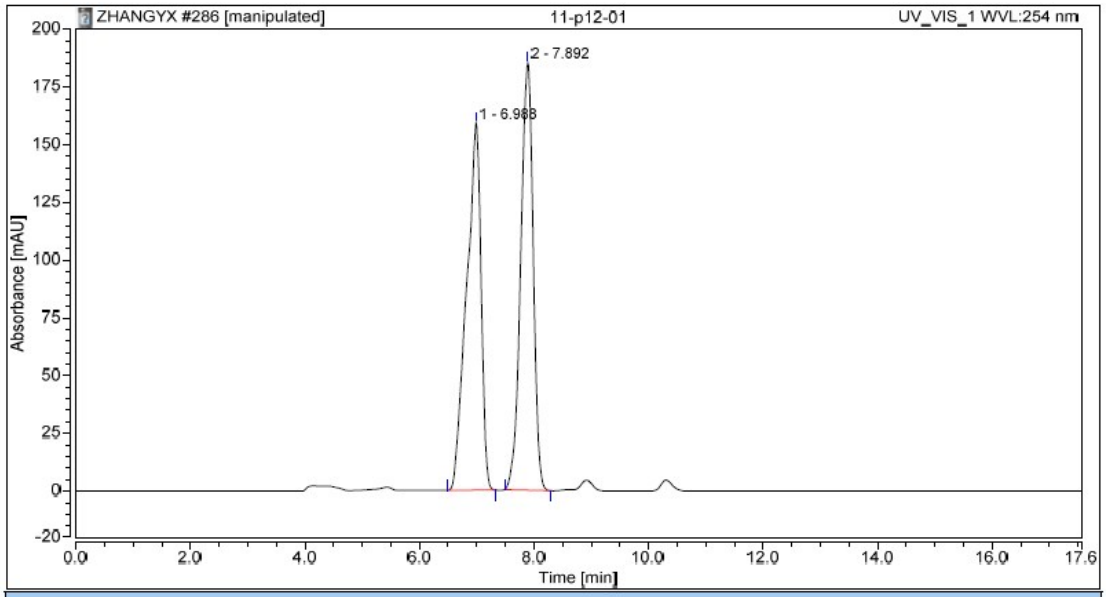
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		16.057	264.008	453.315	98.97	98.85	n.a.
2		17.662	2.757	5.257	1.03	1.15	n.a.
Total:			**266.765**	**458.571**	**100.00**	**100.00**	

(*R*)-4-Ethyl-3-methyl-1-phenyl-4-(phenylthio)-1*H*-pyrazol-5(4*H*)-one (3c)

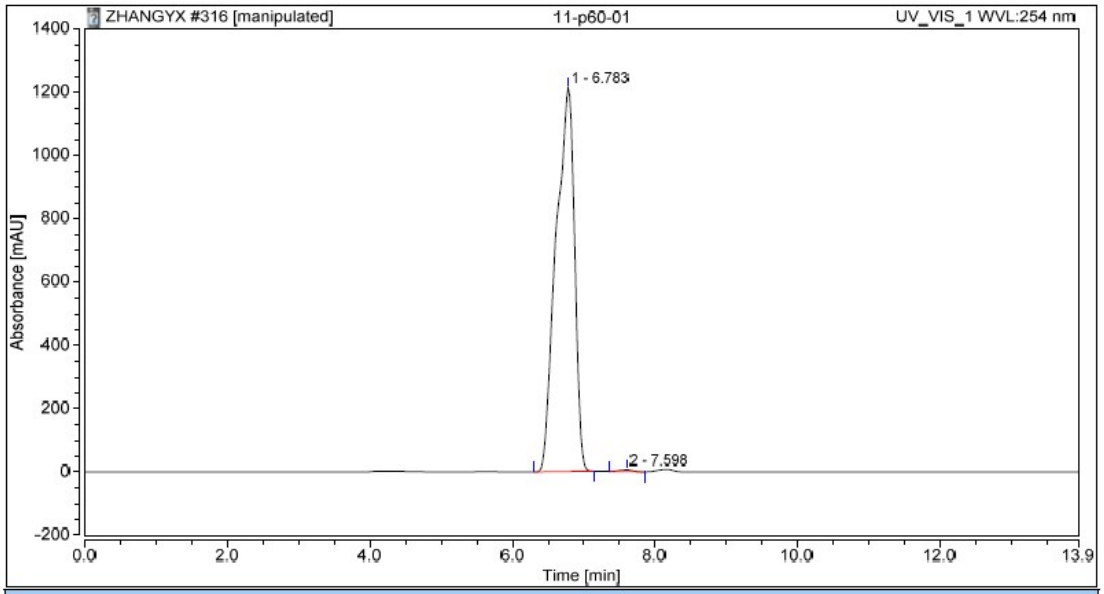


The crude product was purified by flash chromatography to obtain **3c** (colorless oil, 97% yield). $[\alpha]^{28}_{D}$ = -502.3° (c = 1.00, DCM). *Ee* = 99% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 6.8 (major) and 7.6 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (d, J = 8.4 Hz, 2H), 7.45-7.40 (m, 2H), 7.29 (t, J = 8.0 Hz, 2H), 7.24 (d, J = 7.2 Hz, 1H), 7.18 (t, J = 7.6 Hz, 2H), 7.12 (t, J = 7.6 Hz, 1H), 2.25 (s, 3H), 2.18 (td, J = 14.8 Hz, 7.6 Hz, 1H), 1.88 (td, J = 14.8 Hz, 7.2 Hz, 1H), 0.86 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 159.6, 137.4, 135.8, 130.2, 129.1, 128.7, 128.4, 125.3, 119.3, 64.5, 25.8, 13.8, 9.5. IR ν_{max} (film) cm^{-1} 3061, 2969， 2922， 2876， 2854， 1709， 1595， 1497， 1127， 1025， 749， 689. HRMS (ESI) for $C_{18}H_{18}N_2OS$: calculated $[M+H]^+$, 311.1218. Found, 311.1215.



Integration Results

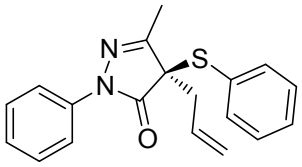
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		6.988	46.656	159.020	50.07	46.21	n.a.
2		7.892	46.517	185.077	49.93	53.79	n.a.
Total:			**93.173**	**344.097**	**100.00**	**100.00**	



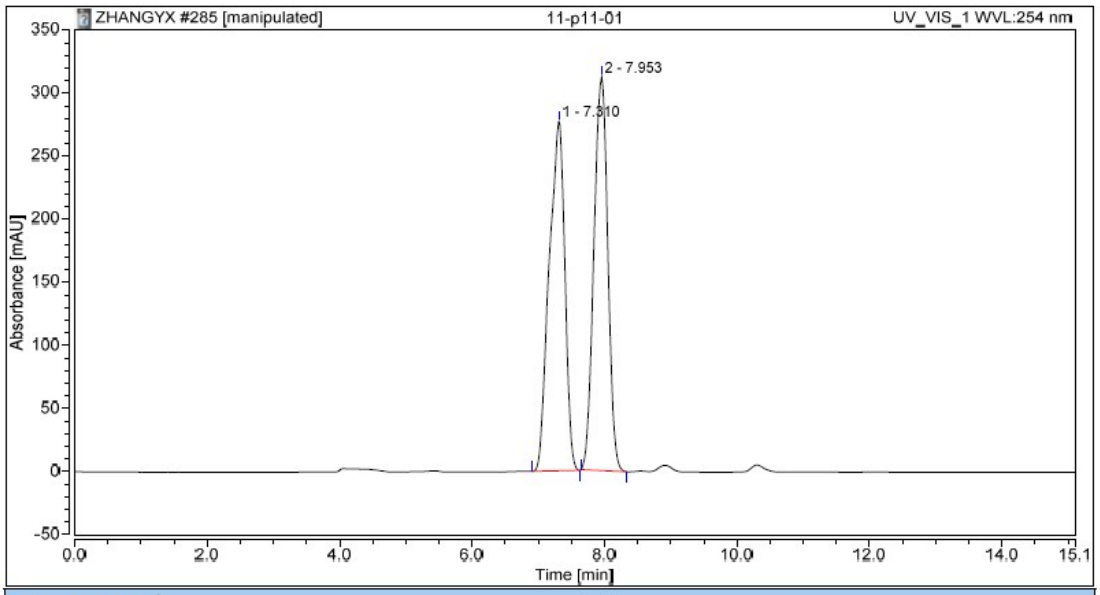
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		6.783	364.496	1213.442	99.67	99.53	n.a.
2		7.598	1.199	5.687	0.33	0.47	n.a.
Total:			**365.695**	**1219.129**	**100.00**	**100.00**	

(*R*)-4-Allyl-3-methyl-1-phenyl-4-(phenylthio)-1*H*-pyrazol-5(4*H*)-one (3d)

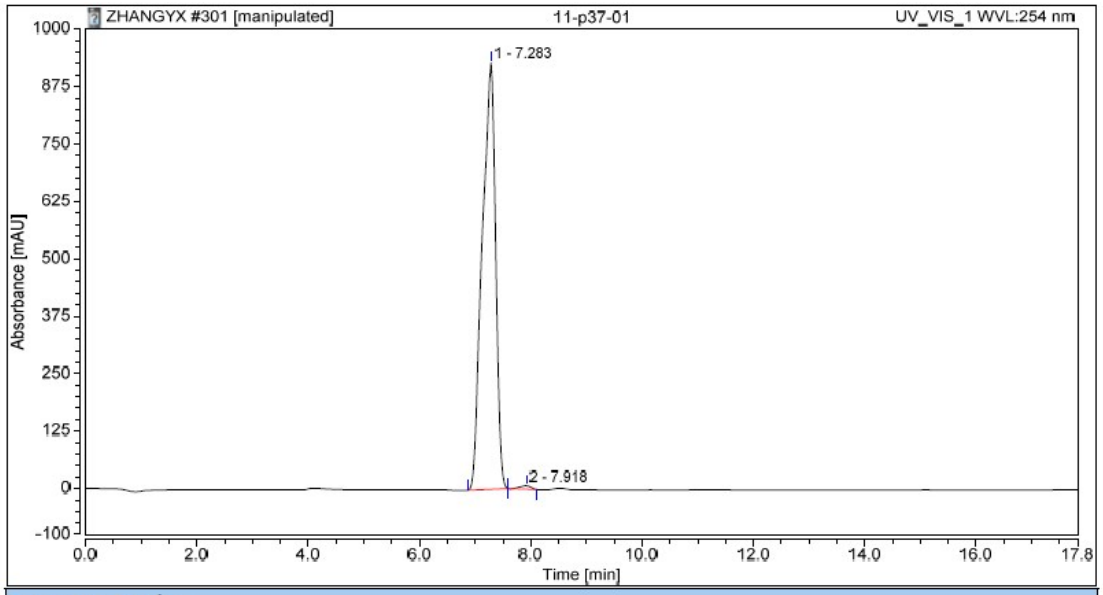


The crude product was purified by flash chromatography to obtain **3d** (colorless oil, 94% yield). $[\alpha]^{28}_{D}$ = -274.2° (c = 1.00, DCM). *Ee* = 99% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio， 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time=7.3（major）and 7.9（minor）. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.31-7.22 (m, 3H), 7.18 (t, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 1H), 5.60-5.47 (m, 1H), 5.20 (dd, *J* = 16.8 Hz, 1.2 Hz, 1H), 5.11 (d, *J* = 10.0 Hz, 1H), 2.89 (dd, *J* = 14.0 Hz, 6.8 Hz, 1H), 2.58 (dd, *J* = 14.0 Hz, 8.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 159.3, 137.4, 135.9, 130.3, 130.2, 129.1, 128.7, 128.1, 125.3, 120.5, 119.3, 63.1, 36.6, 14.1. IR ν_{max} (film) cm^{-1} 3076， 2917， 1595， 1498， 1395， 1116， 1025， 926， 748， 689. HRMS (ESI) for $C_{19}H_{18}N_2OS$: calculated $[M+H]^+$, 323.1218. Found, 323.1216.



Integration Results

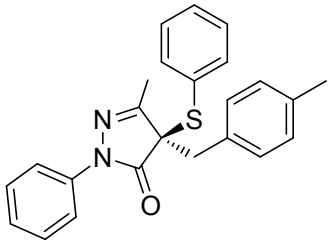
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		7.310	75.732	276.993	49.96	47.01	n.a.
2		7.953	75.854	312.192	50.04	52.99	n.a.
Total:			**151.586**	**589.185**	**100.00**	**100.00**	



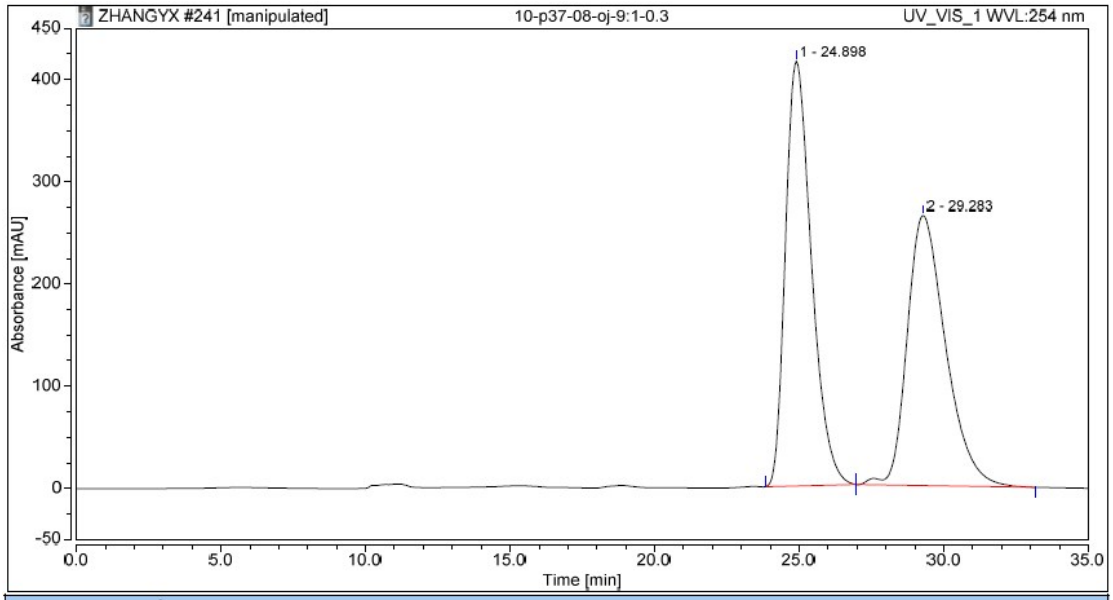
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		7.283	257.980	928.926	99.33	99.20	n.a.
2		7.918	1.732	7.473	0.67	0.80	n.a.
Total:			259.712	936.400	100.00	100.00	

(*R*)-3-Methyl- 4-(4-methylbenzyl)-1-phenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (3e)

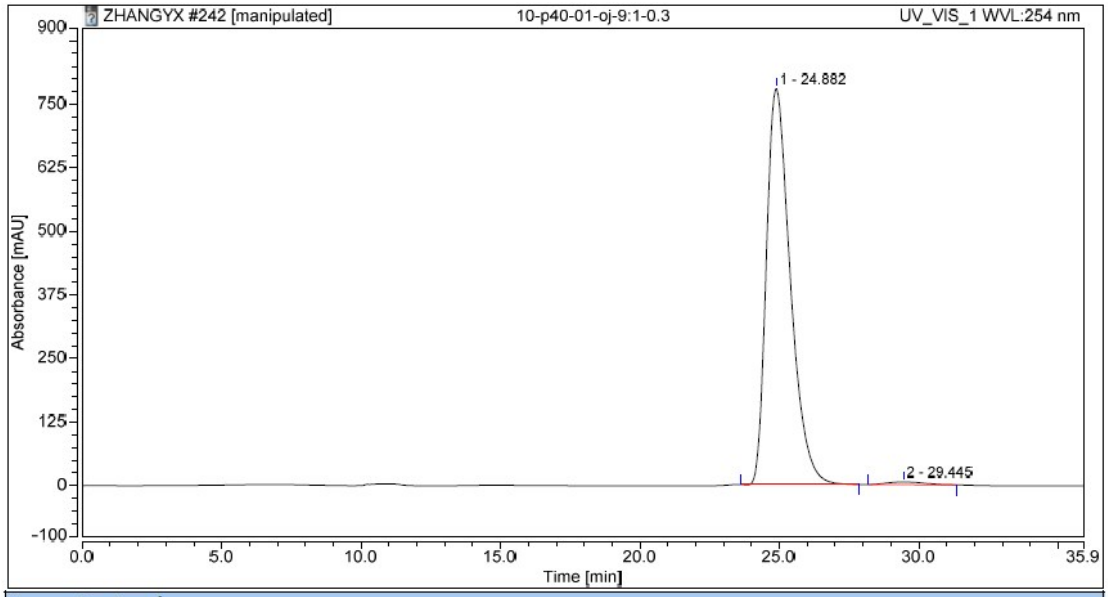


The crude product was purified by flash chromatography to obtain **3e** (white solid, 99% yield). M. p.: 42-47 ℃. $[\alpha]^{29}_{D}$ = -144.8° (c=1.01, DCM). *Ee* = 98% HPLC condition: CHIRALPAK OJ-H. Hexane/*i*-PrOH eluent (90:10 ratio， 0.3 mL/min flow rate) with 254nm wave length UV. Retention time (min) = 24.9 (major) and 29.4 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 7.2 Hz, 2H), 7.31 (d, J = 7.6 Hz, 2H), 7.26-7.15 (m, 5H), 7.12-6.96 (m, 5H), 3.52(d, J = 14.0 Hz, 1H), 3.02 (d, J = 14.0 Hz, 1H), 2.25 (s, 3H), 2.22 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 159.0, 137.2, 137.1, 135.8, 131.1, 130.2, 129.3, 129.0, 128.9, 128.5, 128.1, 125.3, 119.6, 64.7, 37.8, 21.0, 14.4. IR ν_{max} (film) cm^{-1} 3064, 3029, 2916, 2848, 1710, 1593, 1498, 1119, 1023, 744, 687. HRMS (ESI) for $C_{24}H_{22}N_2OS$: calculated $[M+H]^+$, 387.1531. Found, 387.1521.



Integration Results

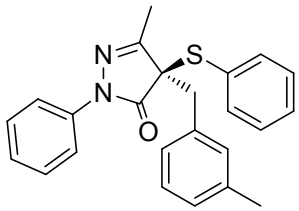
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		24.898	433.013	415.682	51.48	61.13	n.a.
2		29.283	408.135	264.271	48.52	38.87	n.a.
Total:			**841.148**	**679.953**	**100.00**	**100.00**	



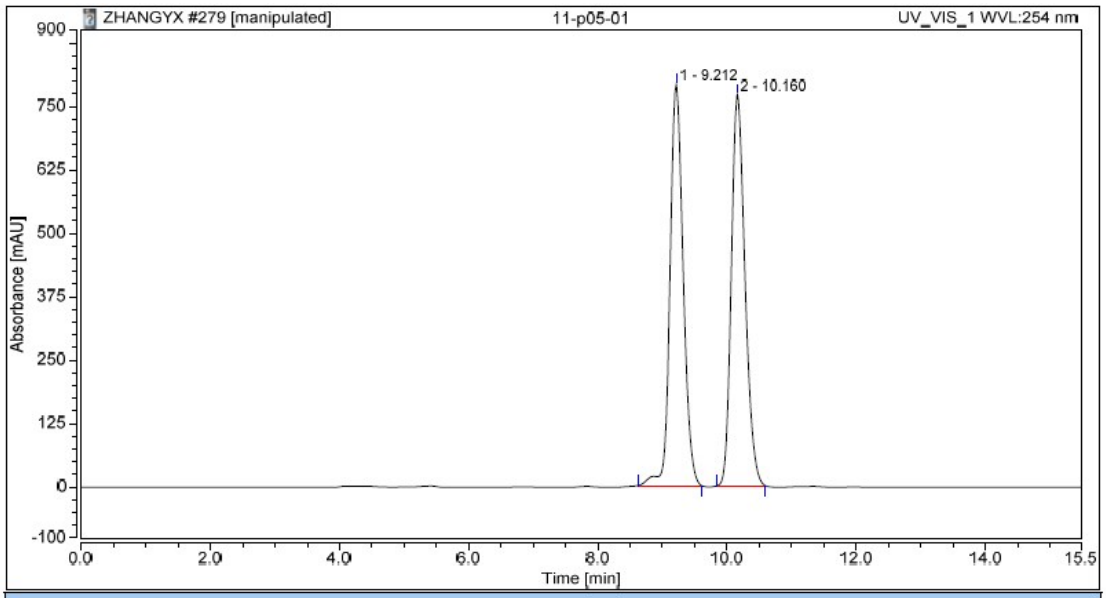
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		24.882	775.016	779.655	98.92	99.29	n.a.
2		29.445	8.440	5.591	1.08	0.71	n.a.
Total:			**783.455**	**785.246**	**100.00**	**100.00**	

(*R*)-3-Methyl-4-(3-methylbenzyl)-1-phenyl-4-(phenylthio)-1*H*-pyrazol-5(4*H*)-one (3f)

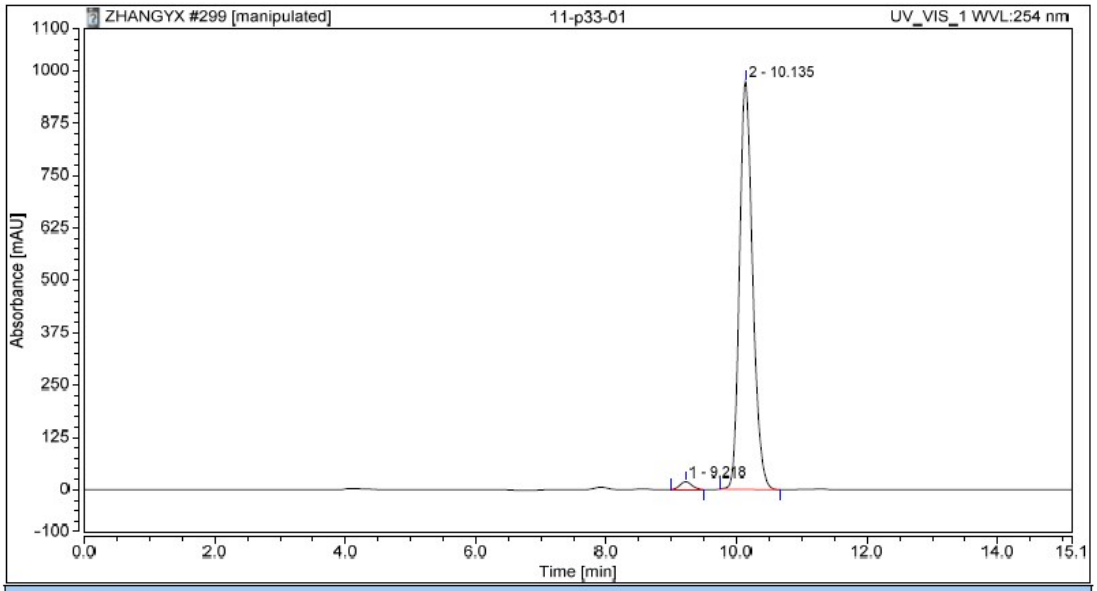


The crude product was purified by flash chromatography to obtain **3f** (colorless oil, 95% yield). $[\alpha]^{28}_{D}$ = -202.9° (c = 1.00, DCM). *Ee* = 97% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 9.2 (minor) and 10.1 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.44 (m, 2H), 7.32-7.16 (m, 7H), 7.12-7.05 (m, 2H), 7.00-6.92 (m, 3H), 3.54 (d, J = 13.6 Hz, 1H), 3.02 (d, J = 13.6 Hz, 1H), 2.24 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 159.1, 138.4, 137.2, 136.0, 134.3, 130.3, 129.9, 129.2, 128.7, 128.5, 128.3, 126.2, 125.5, 119.8, 64.8, 38.3, 21.5, 14.5. IR ν_{max} (film) cm^{-1} 3059， 2918， 2848， 1707， 1595， 1497， 1118， 1025， 788， 750， 689. HRMS (ESI) for $C_{24}H_{22}N_2OS$: calculated $[M+H]^+$, 387.1531. Found, 387.1524.



Integration Results

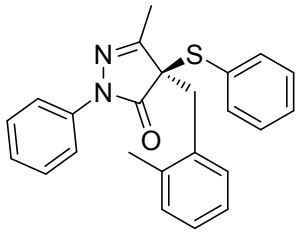
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		9.212	187.297	790.430	49.95	50.65	n.a.
2		10.160	187.635	770.034	50.05	49.35	n.a.
Total:			**374.932**	**1560.464**	**100.00**	**100.00**	



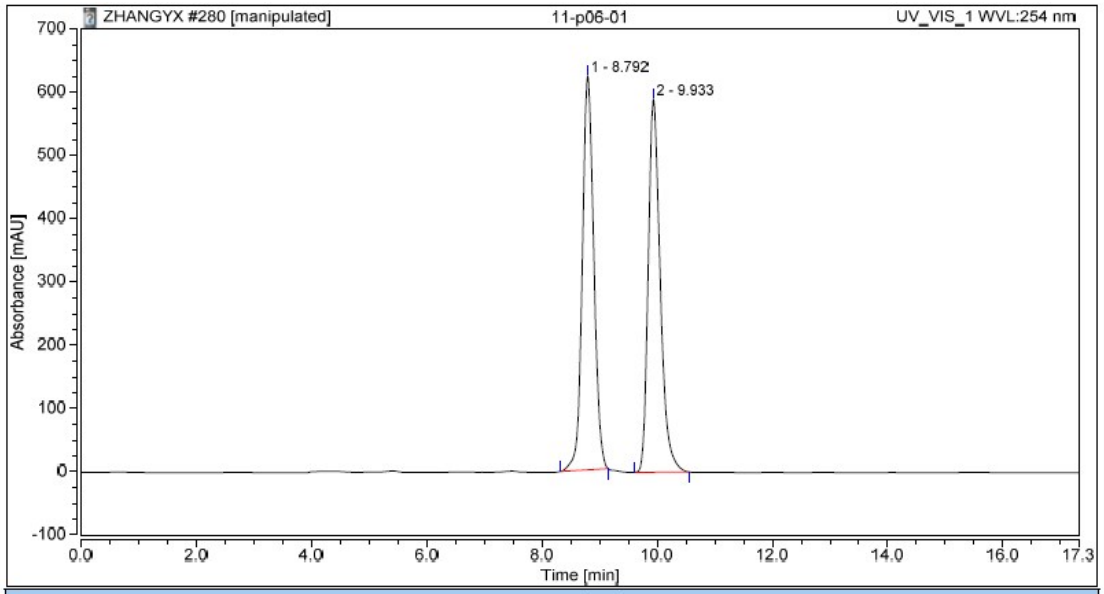
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		9.218	3.863	18.586	1.67	1.87	n.a.
2		10.135	227.136	974.157	98.33	98.13	n.a.
Total:			**230.998**	**992.742**	**100.00**	**100.00**	

(*R*)-3-Methyl-4-(2-methylbenzyl)-1-phenyl-4-(phenylthio)-1*H*-pyrazol-5(4*H*)-one (3g)

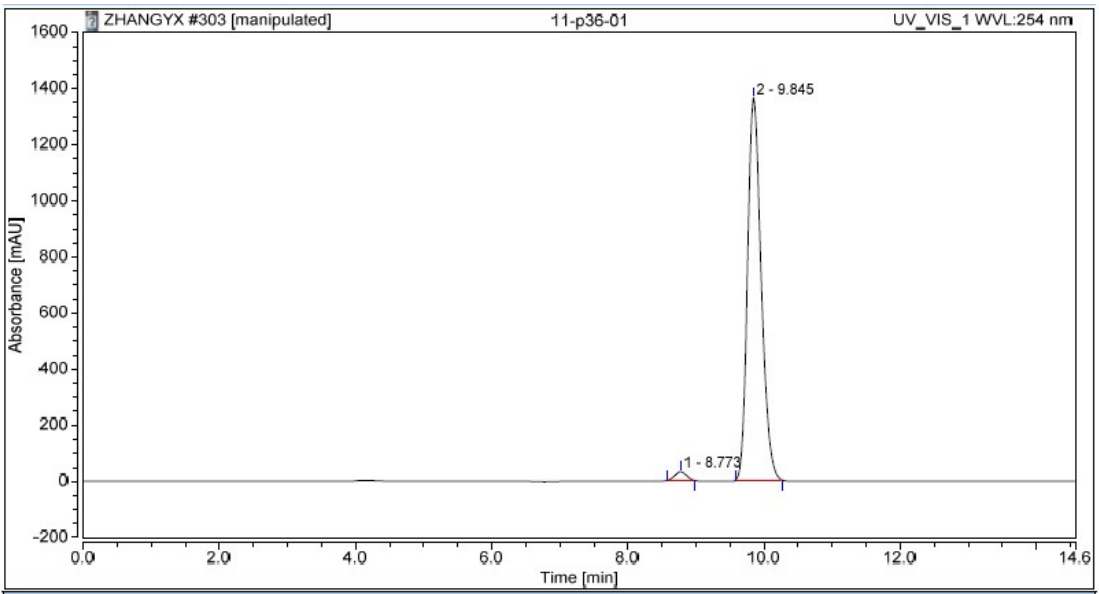


The crude product was purified by flash chromatography to obtain **3g** (white solid, 95% yield). M. p.: 99-104 ℃. $[\alpha]^{29}_{D}$ = -295.0° (c = 1.01, DCM). *Ee* = 96% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 8.8 (minor) and 9.8 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 7.2 Hz, 2H), 7.34 (d, J = 8.4 Hz, 2H), 7.27-7.16 (m, 5H), 7.15-7.07 (m, 3H), 7.01 (t, J = 7.2 Hz, 1H), 6.94 (d, J = 7.2 Hz, 1H), 3.55 (d, J = 14.8 Hz, 1H), 3.18 (d, J = 15.2 Hz, 1H), 2.40 (s, 3H), 2.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.0, 159.2, 137.3, 136.5, 136.1, 133.3, 130.9, 130.4, 129.1, 128.6, 128.2, 128.1, 127.5, 126.4, 125.4, 119.5, 64.2, 34.0, 20.3, 14.4. IR ν_{max} (film) cm^{-1} 3060， 3023， 2920， 1709， 1595， 1497， 1179， 1145， 1117， 1025， 738， 688. HRMS (ESI) for $C_{24}H_{22}N_2OS$: calculated $[M+H]^+$, 387.1531. Found, 387.1524.



Integration Results

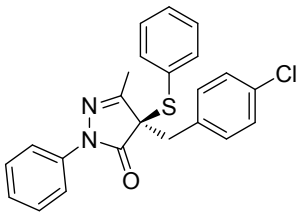
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		8.792	143.779	622.411	50.16	51.37	n.a.
2		9.933	142.836	589.129	49.84	48.63	n.a.
Total:			**286.616**	**1211.540**	**100.00**	**100.00**	



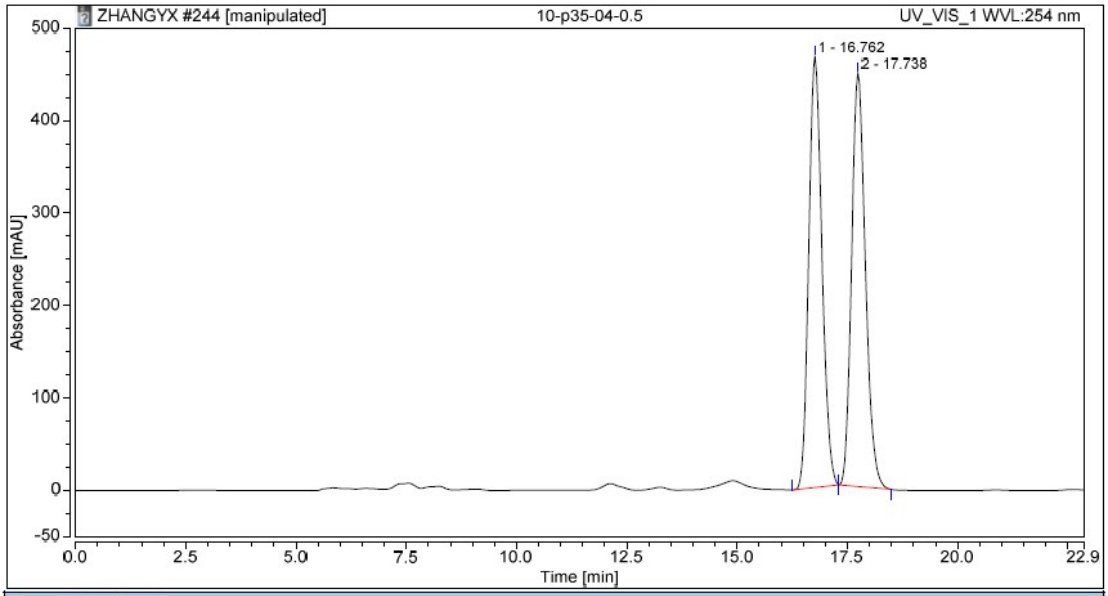
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		8.773	5.998	31.061	1.86	2.23	n.a.
2		9.845	316.078	1362.827	98.14	97.77	n.a.
Total:			**322.076**	**1393.888**	**100.00**	**100.00**	

(*R*)-4-(4-Chlorobenzyl)-3-methyl-1-phenyl-4-(phenylthio)-1*H*-pyrazol-5(4*H*)-one (3h)

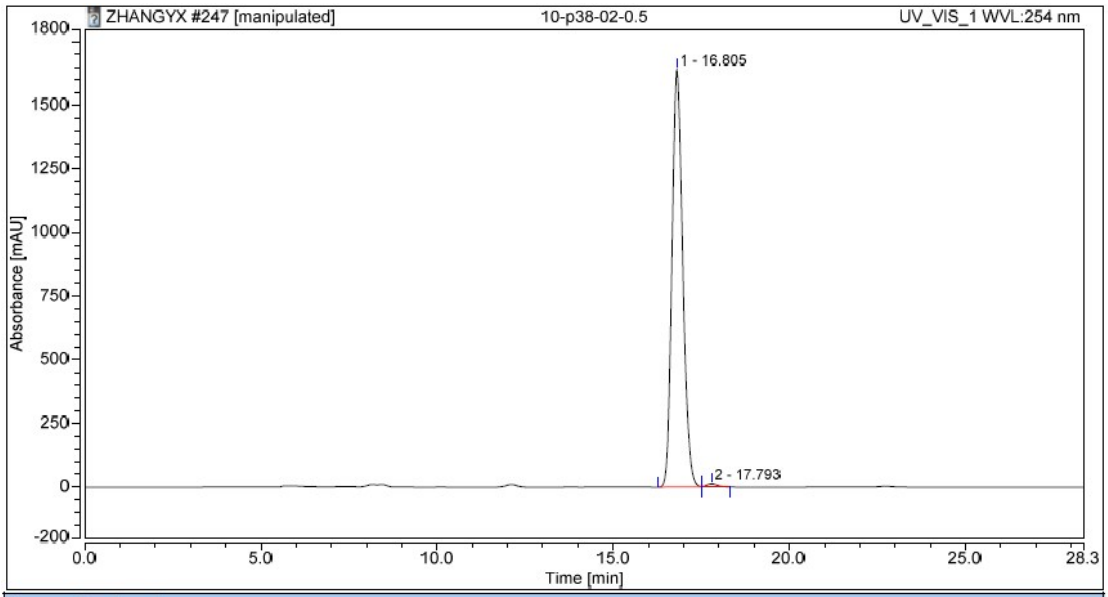


The crude product was purified by flash chromatography to obtain **3h** (white solid, 99% yield). M. p.: 59-62 ℃. $[\alpha]^{29}_{D} = -131.4°$ (c=0.99, DCM). ee=99% HPLC condition： CHIRALPAK AD-H. Hexane/i-PrOH eluent （80：20 ratio， 0.5 mL/min flow rate） 254nm wave length UV. Retention time=16.8（major）and 17.8（minor）. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.43 (m, 2H), 7.34-7.27 (m, 2H), 7.27-7.15 (m, 7H), 7.13-7.06 (m, 3H), 3.51(d, J = 14.0 Hz, 1H), 3.04 (d, J = 14.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 158.7, 137.1, 136.0, 133.7, 132.8, 130.6, 130.5, 129.2, 129.0, 128.7, 127.9, 125.6, 119.6, 64.6, 37.5, 14.5. IR ν_{max} (film) cm^{-1} 3065, 2917, 2848, 1709, 1594, 1494, 1121, 1099, 1066, 1021, 1016, 835, 742, 687, 650. HRMS (ESI) for $C_{23}H_{19}ClN_2OS$: calculated $[M+H]^+$, 407.0985. Found, 407.0972.



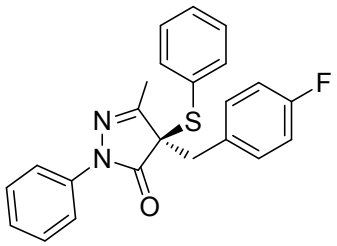
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		16.762	161.054	466.147	49.86	51.03	n.a.
2		17.738	161.977	447.246	50.14	48.97	n.a.
Total:			**323.031**	**913.394**	**100.00**	**100.00**	

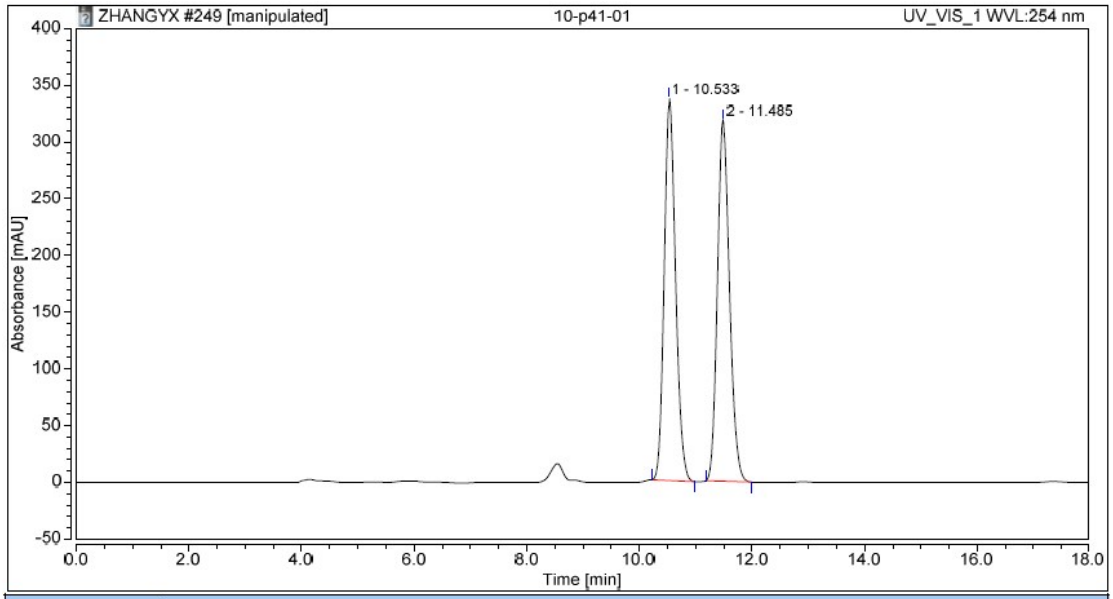


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		16.805	581.646	1640.647	99.26	99.27	n.a.
2		17.793	4.358	12.127	0.74	0.73	n.a.
Total:			**586.004**	**1652.774**	**100.00**	**100.00**	

(*R*)-4-(4-Fluorobenzyl)-3-methyl-1-phenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (3i)

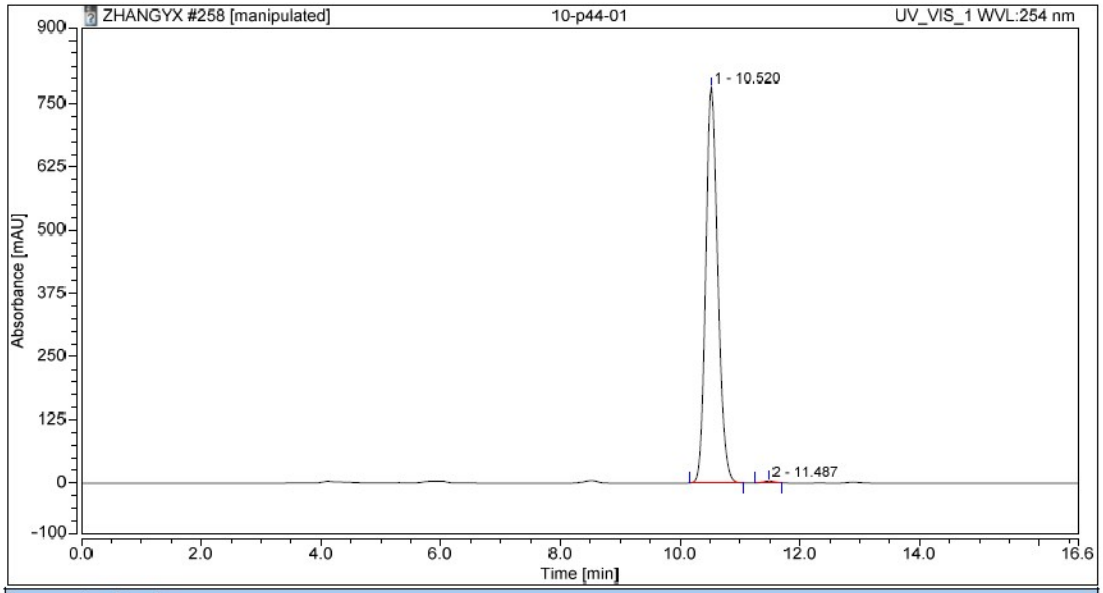


The crude product was purified by flash chromatography to obtain **3i** (colorless oil, 97% yield). $[\alpha]^{29}_{D}$ = -179.8° (c = 1.01, DCM). *Ee* = 99% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 10.5 (major) and 11.5 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 7.2 Hz, 2H), 7.32-7.16 (m, 7H), 7.16-7.06 (m, 3H), 6.89 (t, J = 8.8 Hz, 2H), 3.51(d, J = 13.6 Hz, 1H), 3.06 (d, J = 14.0 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 162.1 (d. J = 245.1 Hz), 158.7, 136.9, 135.8, 130.8 (d. J = 8.0 Hz), 130.3, 130.0 (d, J = 3.3 Hz), 129.1, 128.6, 127.9, 125.5, 119.5, 115.6 (d, J = 21.3 Hz), 64.6, 37.3, 14.3. IR ν_{max} (film) cm^{-1} 3061, 2921, 2849, 1706, 1596, 1499, 1222, 1098, 1067, 1024, 992, 879, 749, 689. HRMS (ESI) for $C_{23}H_{19}FN_2OS$: calculated $[M+H]^+$,391.1280. Found, 391.1271.



Integration Results

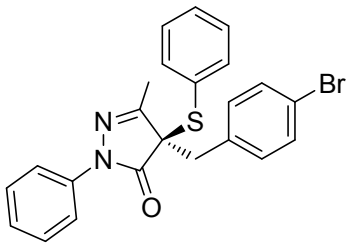
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.533	78.880	336.852	49.84	51.43	n.a.
2		11.485	79.394	318.137	50.16	48.57	n.a.
Total:			**158.273**	**654.988**	**100.00**	**100.00**	



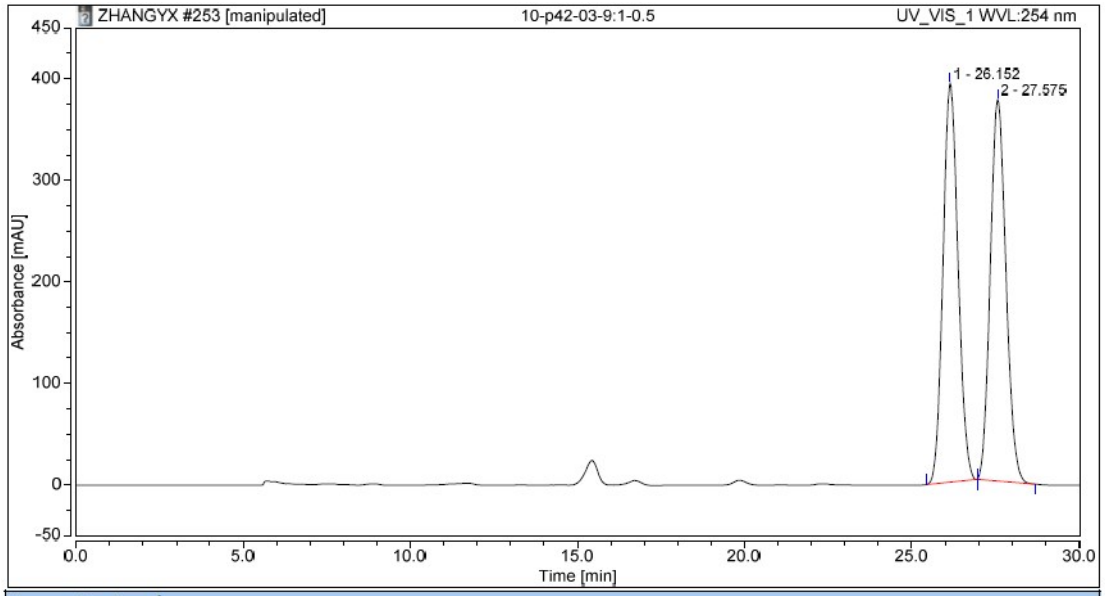
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.520	183.566	781.712	99.62	99.58	n.a.
2		11.487	0.703	3.301	0.38	0.42	n.a.
Total:			**184.269**	**785.013**	**100.00**	**100.00**	

(*R*)-4-(4-Bromobenzyl)-3-methyl-1-phenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (3j)

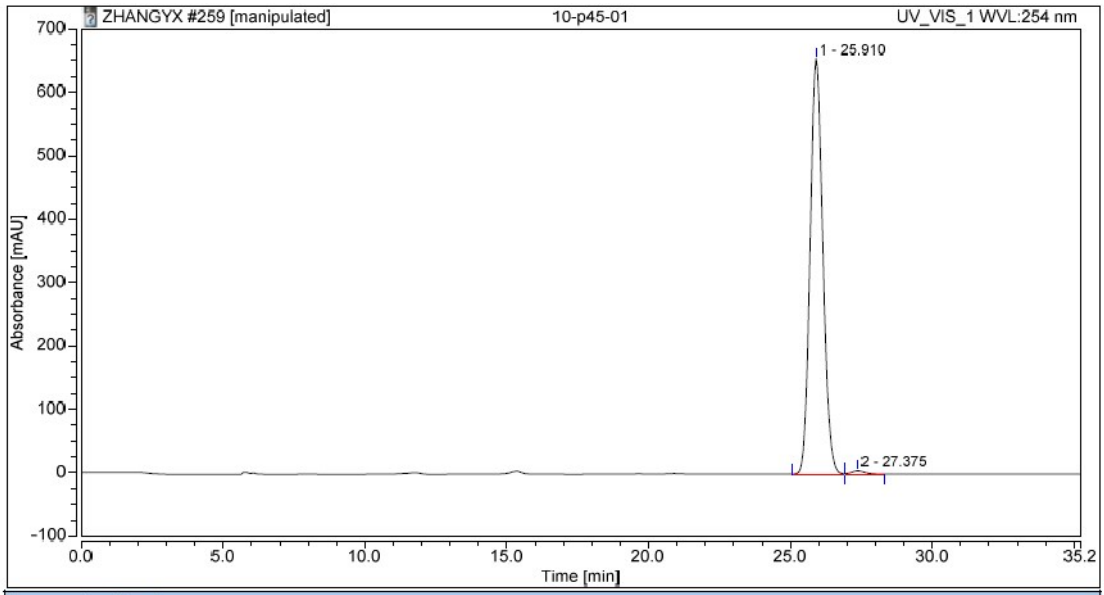


The crude product was purified by flash chromatography to obtain **3j** (colorless oil, 98% yield). $[\alpha]^{28}_{D}$ = -117.6° (c = 1.02, DCM). *Ee* = 98% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (90:10 ratio, 0.5 mL/min flow rate) with 254 nm wave length UV. Retention time = 25.9 (major) and 27.4 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 7.2 Hz, 2H), 7.32 (t, J = 8.8 Hz, 4H), 7.28-7.16 (m, 5H), 7.10 (t, J = 7.2 Hz, 1H), 7.03 (d, J = 8.4 Hz, 2H), 3.50(d, J = 14.0 Hz, 1H), 3.02 (d, J = 14.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 158.7, 137.1, 136.0, 133.4, 131.9, 130.9, 130.5, 129.2, 128.7, 127.9, 125.6, 121.9, 119.7, 64.5, 37.6, 14.5. IR ν_{max} (film) cm^{-1} 3060, 2920, 2849, 1706, 1594, 1488, 1362, 1144, 1071, 1011, 992, 832, 798, 746, 689, 613. HRMS (ESI) for $C_{23}H_{19}BrN_2OS$: calculated $[M+H]^+$, 451.0480. Found, 451.0467.



Integration Results

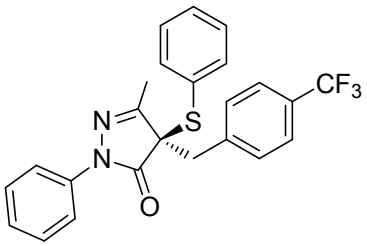
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		26.152	204.829	392.745	50.12	51.11	n.a.
2		27.575	203.834	375.682	49.88	48.89	n.a.
Total:			**408.663**	**768.427**	**100.00**	**100.00**	



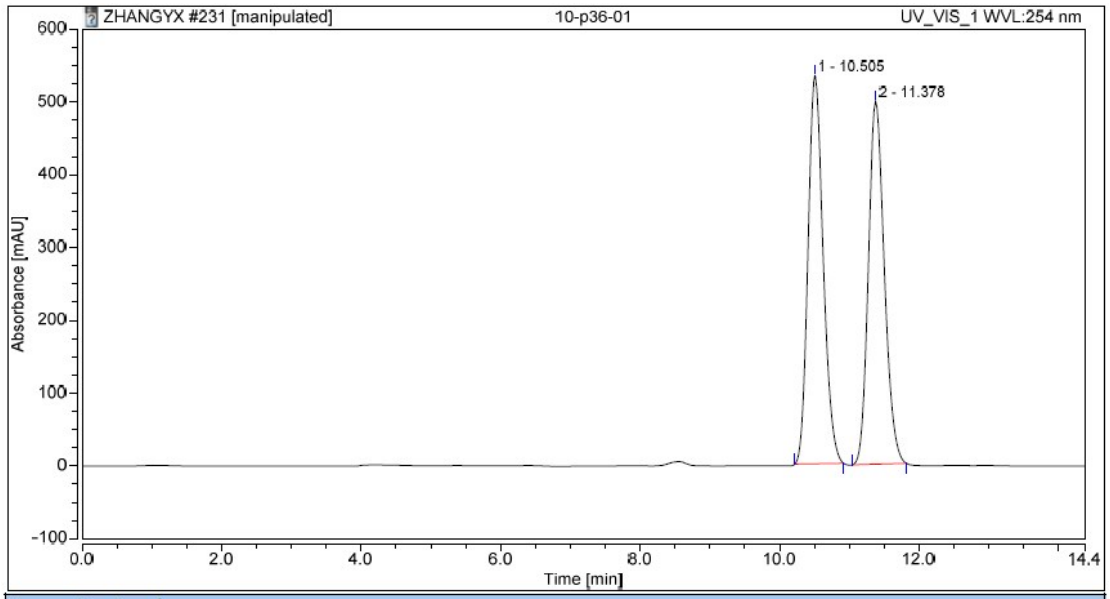
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		25.910	340.625	654.561	99.20	99.22	n.a.
2		27.375	2.749	5.129	0.80	0.78	n.a.
Total:			**343.374**	**659.690**	**100.00**	**100.00**	

(*R*)-3-Methyl-1-phenyl-4-(phenylthio)- 4-(4-(trifluoromethyl) benzyl)-1*H*-pyrazol-5(4*H*)-one (3k)

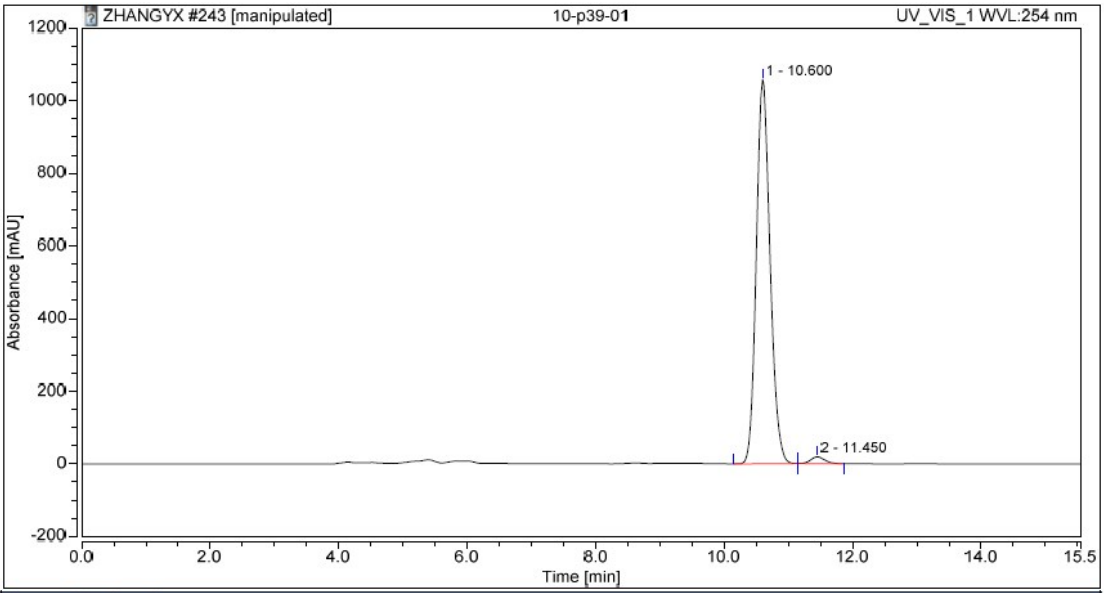


The crude product was purified by flash chromatography to obtain **3k** (colorless oil, 99% yield). $[\alpha]^{28}_{D}$ = -46.8° (c = 1.00, DCM). *Ee* = 96% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) =10.6 (major) and 11.5 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.43 (m, 4H), 7.30-7.16 (m, 9H), 7.09 (tt, *J* = 7.2 Hz,1.6 Hz, 1H), 3.59(d, *J* = 13.6 Hz, 1H), 3.12(d, *J* = 13.6 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.3, 158.4, 137.6 (d, *J* = 146.1 Hz), 135.9, 130.4, 130.0 (d, *J* = 32.2 Hz), 129.5, 129.1, 128.6, 127.6, 125.69, 125.6 (d, *J* = 3.8 Hz), 125.56, 125.2 (q, *J* = 270.5 Hz), 119.5, 64.3, 37.7, 14.3; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.7 (m). IR ν_{max} (film) cm^{-1} 3062, 2922, 2850, 1707, 1595, 1499, 1321, 1164, 1110, 1067, 1018, 846, 747, 689. HRMS (ESI) for $C_{24}H_{19}F_3N_2OS$: calculated $[M+H]^+$, 441.1248. Found, 441.1239.



Integration Results

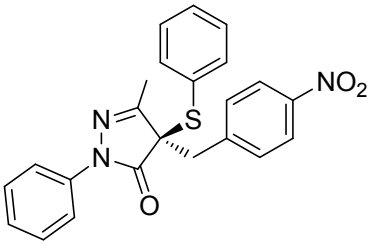
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.505	134.907	533.361	50.39	51.68	n.a.
2		11.378	132.798	498.738	49.61	48.32	n.a.
Total:			**267.705**	**1032.099**	**100.00**	**100.00**	



Integration Results

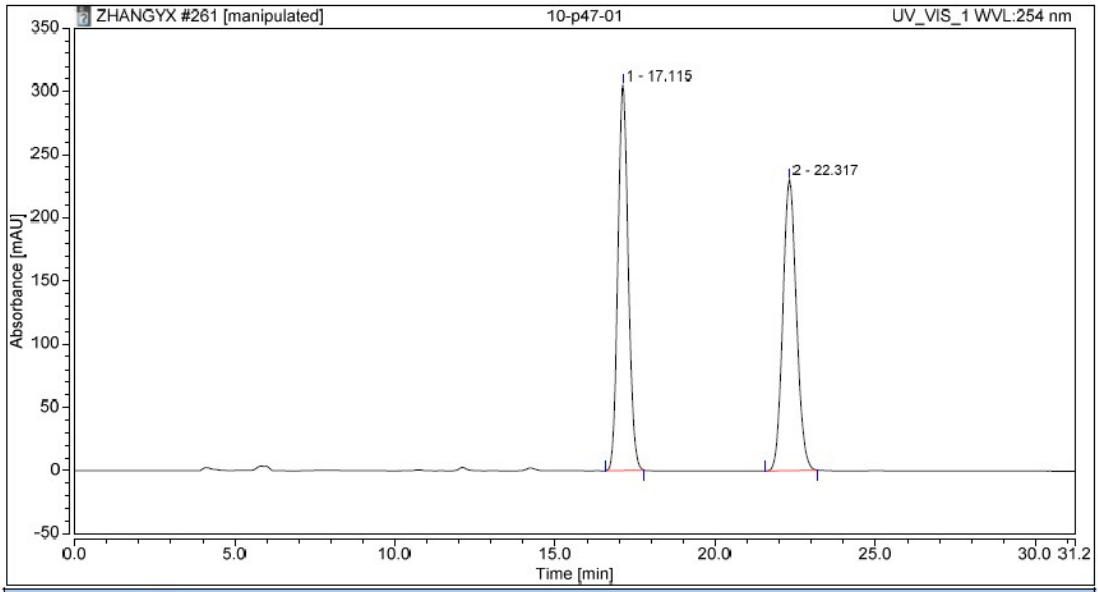
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.600	262.749	1057.412	98.22	98.26	n.a.
2		11.450	4.775	18.689	1.78	1.74	n.a.
Total:			**267.524**	**1076.101**	**100.00**	**100.00**	

(*R*)-3-Methyl-4-(4-nitrobenzyl)-1-phenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (3l)



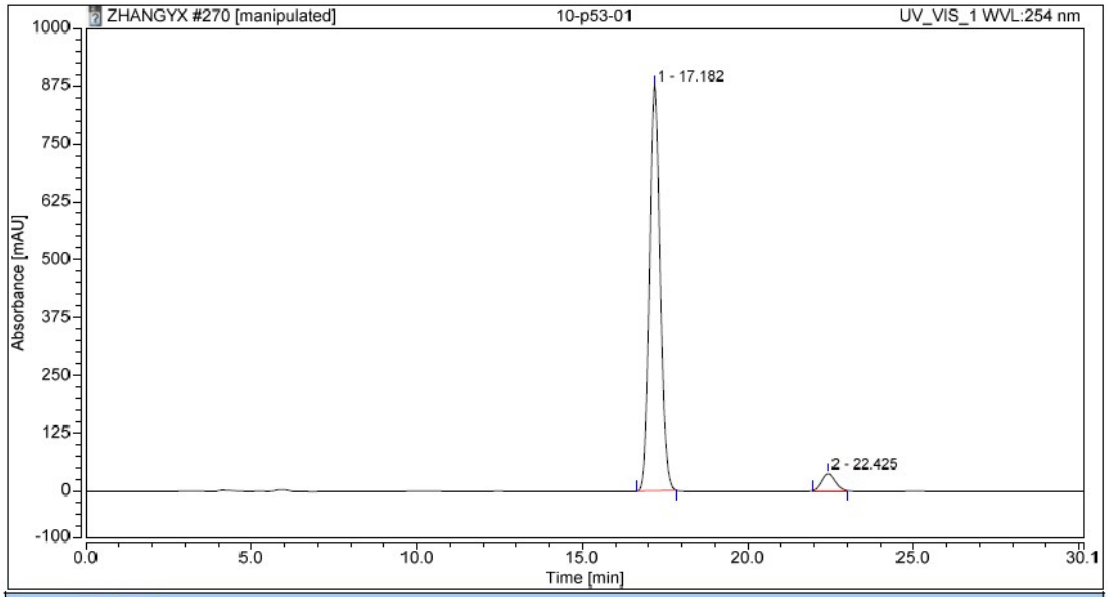
The crude product was purified by flash chromatography to obtain **3l** (white solid, 99% yield).

M. p.: 120-122 ˚C. $[\alpha]^{29}_{D}$ = -120.9° (c = 1.01, DCM). *Ee* = 90% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254nm wave length UV. Retention time (min) = 17.2 (major) and 22.4 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.4 Hz, 2H), 7.45 (d, J = 7.6 Hz, 2H), 7.39-7.16 (m, 9H), 7.10 (t, J = 6.8 Hz, 1H), 3.61 (d, J = 14.0 Hz, 1H), 3.18 (d, J = 14.0 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.1, 158.2, 147.4, 141.7, 136.7, 135.9, 130.5, 130.2, 129.2, 128.7, 127.4, 125.7, 123.9, 119.3, 64.1, 37.6, 14.3. IR ν_{max} (film) cm^{-1} 3185, 3074, 2920, 2849, 1707, 1597, 1515, 1499, 1343, 1118, 1106, 1067, 753, 729, 692. HRMS (ESI) for $C_{23}H_{19}N_3O_3S$: calculated $[M+H]^+$, 418.1225. Found, 418.1215.



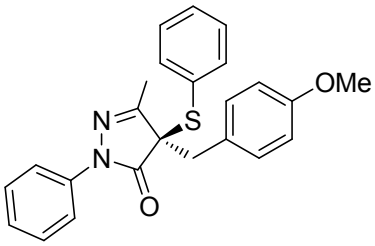
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		17.115	113.705	305.012	50.02	56.97	n.a.
2		22.317	113.614	230.397	49.98	43.03	n.a.
Total:			**227.319**	**535.409**	**100.00**	**100.00**	



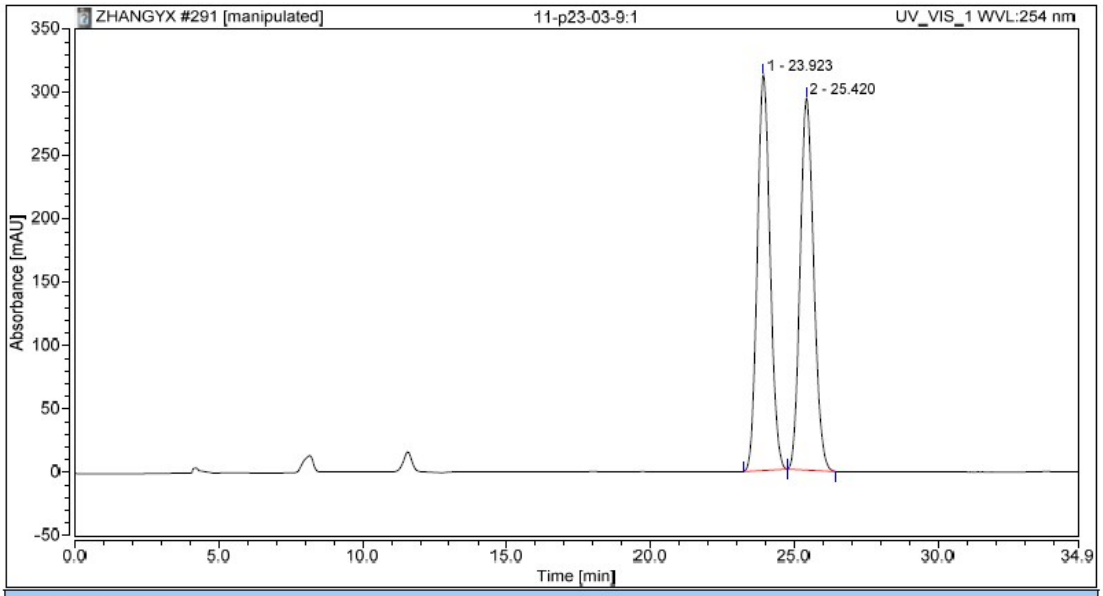
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		17.182	326.827	874.684	94.99	96.00	n.a.
2		22.425	17.220	36.492	5.01	4.00	n.a.
Total:			**344.047**	**911.176**	**100.00**	**100.00**	

(*R*)-4-(4-Methoxybenzyl)-3-methyl-1-phenyl-4-(phenylthio)-1*H*-pyrazol-5(4*H*)-one (3m)



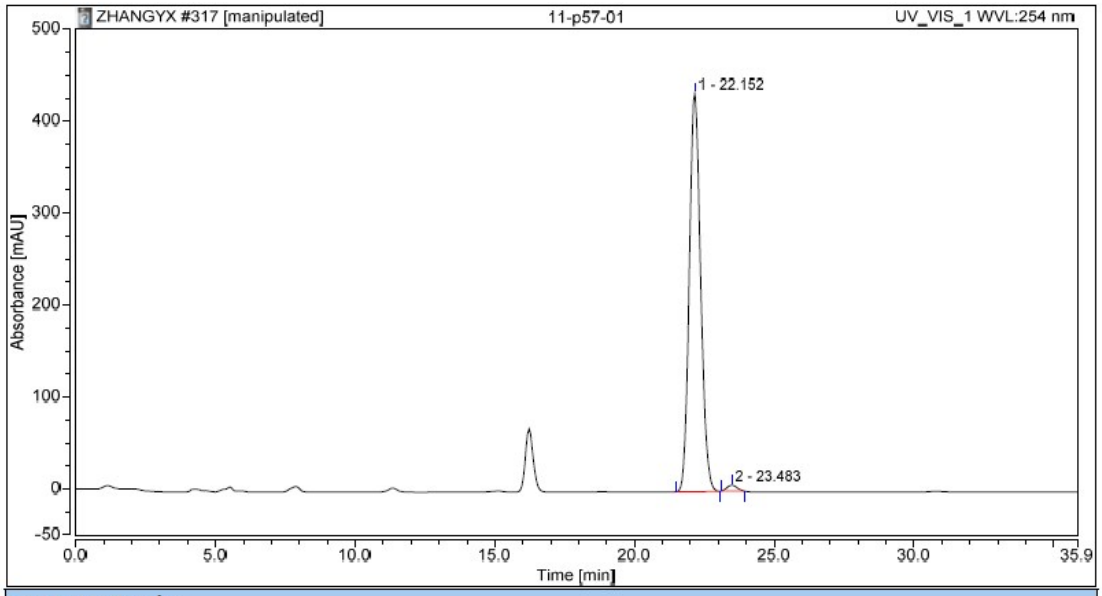
The crude product was purified by flash chromatography to obtain **3m** (pale yellow solid, 99% yield).

M. p.: 78-82 ˚C. $[\alpha]^{28}_{D}$ = -148.6° (c=1.01, DCM). *Ee* = 98% HPLC condition： CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (90:10 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 22.2 (major) and 23.5 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, J = 7.2 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 7.28-7.14 (m, 5H), 7.12-7.03 (m, 3H), 6.72 (d, J = 7.6 Hz, 2H), 3.70 (s, 3H), 3.50 (d, J = 13.6 Hz, 1H), 3.02 (d, J = 13.6 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 159.1, 159.0, 137.2, 135.9, 130.33, 130.26, 129.1, 128.6, 128.3, 126.3, 125.4, 119.7, 114.1, 64.9, 55.2, 37.5, 14.5. IR ν_{max} (film) cm^{-1} 2961， 2920， 2836， 1707， 1595， 1511， 1253， 1085， 1068， 1027， 799， 750， 689. HRMS (ESI) for $C_{24}H_{22}N_2O_2S$: calculated $[M+H]^+$, 403.1480. Found, 403.1472.



Integration Results

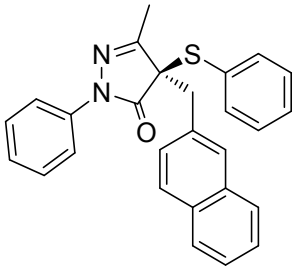
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		23.923	160.874	312.417	50.06	51.56	n.a.
2		25.420	160.465	293.481	49.94	48.44	n.a.
Total:			**321.339**	**605.898**	**100.00**	**100.00**	



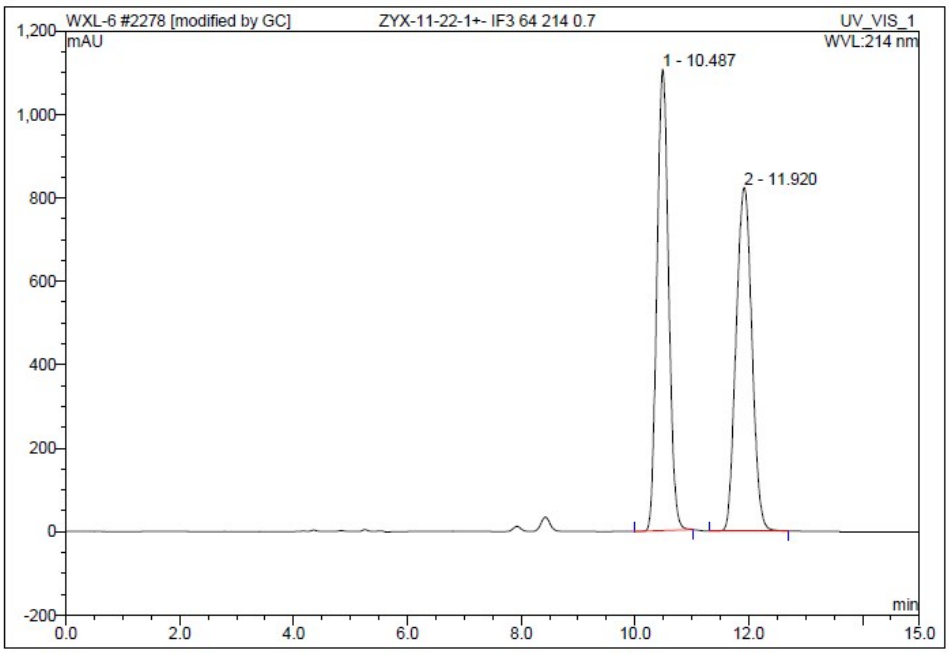
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		22.152	203.643	433.015	98.75	98.59	n.a.
2		23.483	2.587	6.186	1.25	1.41	n.a.
Total:			**206.230**	**439.201**	**100.00**	**100.00**	

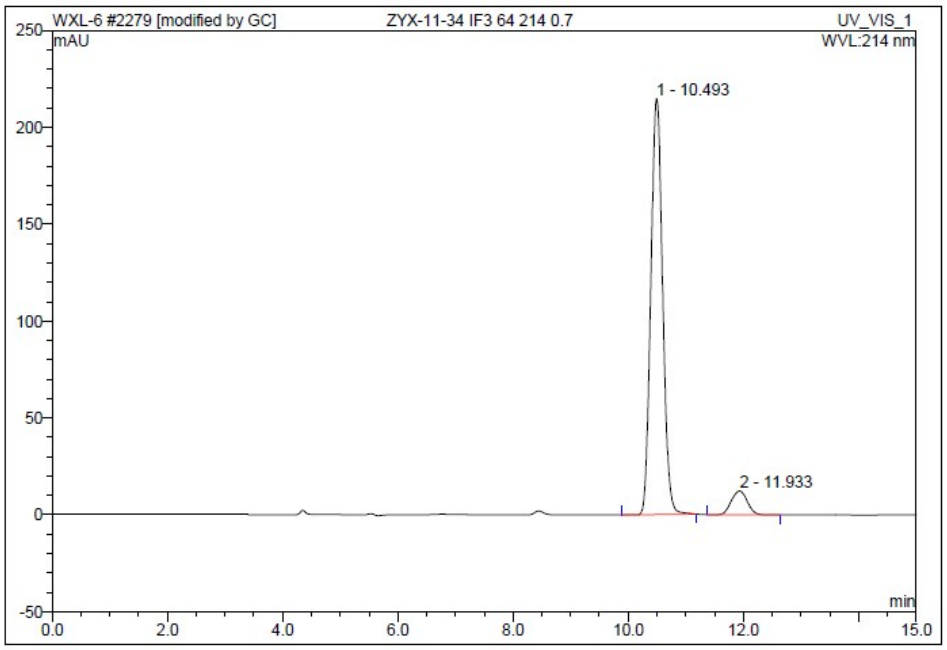
(*R*)-3-Methyl-4-(naphthalen-2-ylmethyl) -1-phenyl-4-(phenylthio)-1*H*-pyrazol-5(4*H*)-one (3n)



The crude product was purified by flash chromatography to obtain **3n** (white solid, 98% yield). M. p.: 148-153 ℃. $[\alpha]^{28}_{D}$ = -36.8° (c = 0.98, DCM). *Ee* = 86% HPLC condition: CHIRALPAK IF-3. Hexane/*i*-PrOH eluent (60:40 ratio, 0.7 mL/min flow rate) with 214 nm wave length UV. Retention time (min) =10.5 (major) and 11.9 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77-7.65 (m, 3H), 7.63 (s, 1H), 7.48 (d, J = 7.2 Hz, 2H), 7.44-7.38 (m, 2H), 7.31-7.24 (m, 4H), 7.24-7.17 (m, 4H), 7.07 (t, J = 7.2 Hz, 1H), 3.75 (d, J = 14.0 Hz, 1H), 3.23 (d, J = 13.6 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 159.1, 137.2, 136.1, 133.4, 132.7, 132.0, 130.4, 129.2, 128.7, 128.6, 128.2, 128.1, 127.8, 127.7, 127.0, 126.4, 126.2, 125.5, 119.8, 64.7, 38.5, 14.6. IR ν_{max} (film) cm^{-1} 3056， 3028， 3011， 2920， 1701， 1592， 1488， 1118， 1087， 1064， 1025， 858， 816， 747， 687. HRMS (ESI) for $C_{27}H_{22}N_2OS$: calculated $[M+H]^+$, 423.1531. Found, 423.1524.

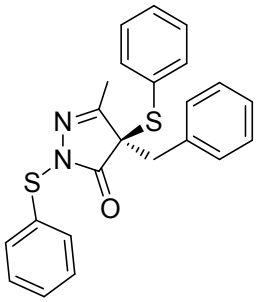


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.49	n.a.	1105.891	262.070	49.71	n.a.	BMB*
2	11.92	n.a.	823.241	265.116	50.29	n.a.	BMB*
Total:			1929.132	527.186	100.00	0.000	



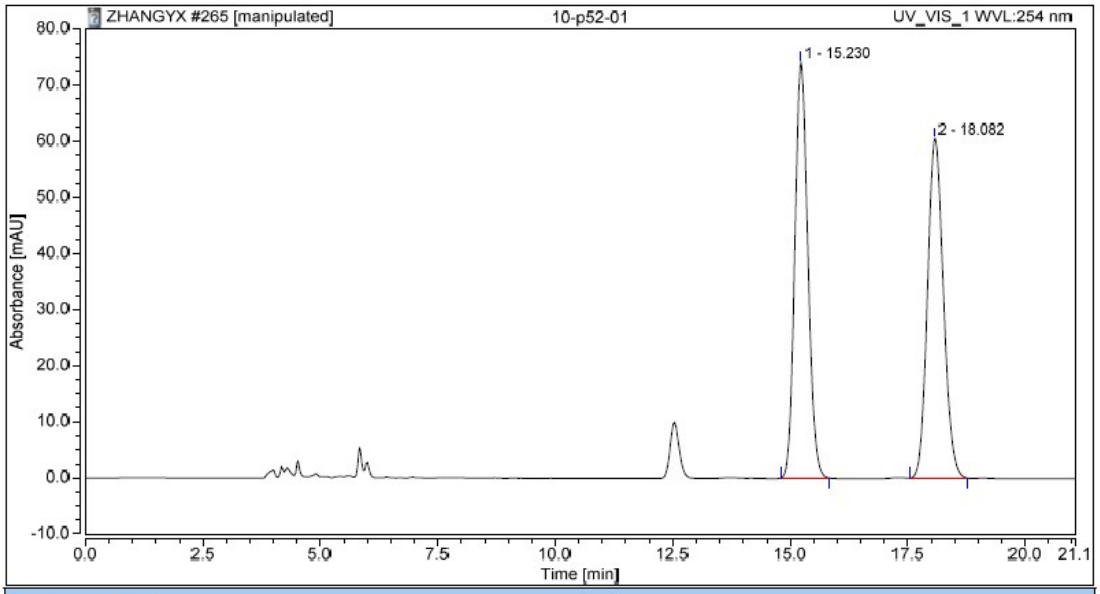
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	10.49	n.a.	214.861	50.871	92.82	n.a.	BMB*
2	11.93	n.a.	12.377	3.933	7.18	n.a.	BMB*
Total:			227.238	54.803	100.00	0.000	

(*R*)-4-Benzyl-3-methyl-1,4-bis(phenylthio)- 1*H*-pyrazol-5(4*H*)-one (3o)



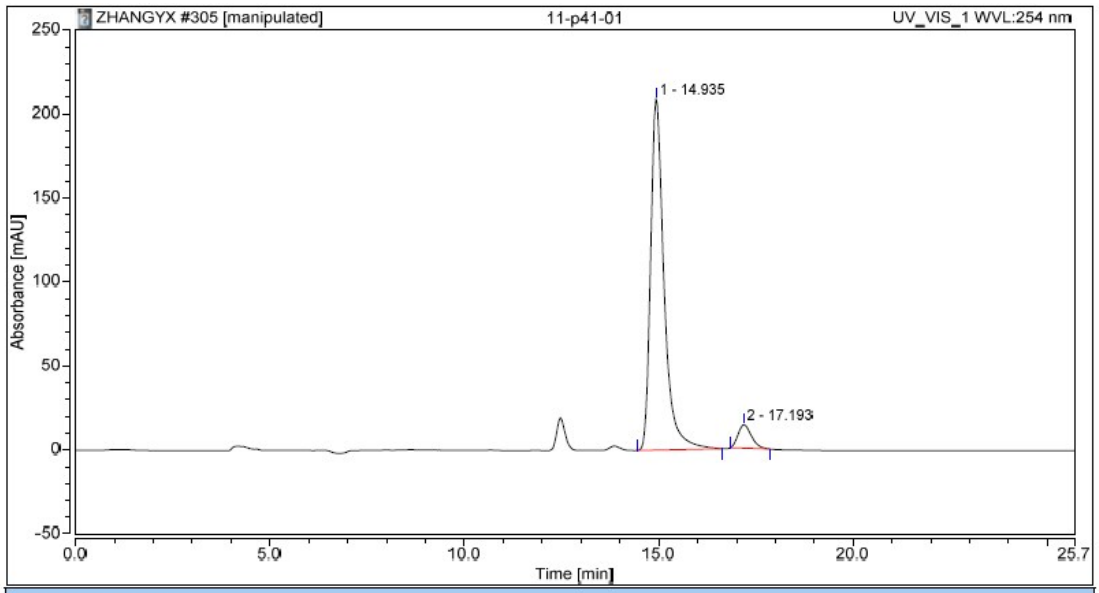
The crude product was purified by flash chromatography to obtain **3o** (white solid, 84% yield).

M. p.: 174-178 ℃. $[\alpha]^{29}_{D}$ = -244.0° (c = 0.99, DCM). *Ee* = 88% HPLC condition： CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) =14.9 (major) and 17.2 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (d, J = 7.2 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 7.29 (d, J = 7.6 Hz, 2H), 7.24-7.05 (m, 8H), 6.81 (dd, J = 8.0 Hz, 1.2 Hz, 2H), 3.47 (d, J = 13.6 Hz, 1H), 3.09 (d, J = 13.6 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.9, 160.3, 136.1, 136.0, 133.9, 130.7, 129.4, 129.1, 128.9, 127.83, 127.80, 127.7, 127.2, 62.9, 38.3, 14.6. IR ν_{max} (film) cm^{-1} 2919， 2849， 1719， 1597， 1438， 1244， 1220， 1052， 756， 721， 692. HRMS (ESI) for $C_{23}H_{20}N_2OS_2$: calculated $[M+H]^+$, 405.1095. Found, 405.1084.



Integration Results

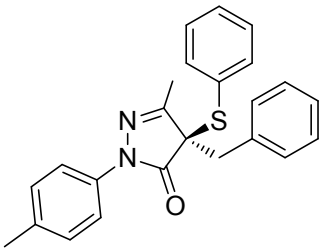
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		15.230	23.820	74.089	50.07	55.05	n.a.
2		18.082	23.757	60.505	49.93	44.95	n.a.
Total:			**47.578**	**134.594**	**100.00**	**100.00**	



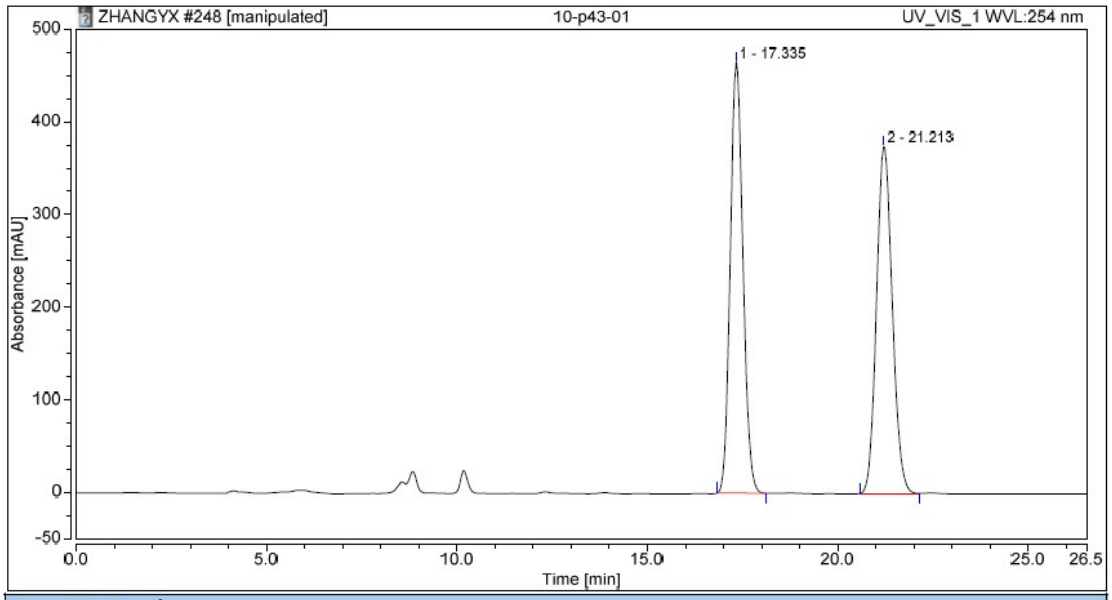
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		14.935	83.991	209.189	93.77	93.73	n.a.
2		17.193	5.577	13.994	6.23	6.27	n.a.
Total:			**89.568**	**223.183**	**100.00**	**100.00**	

(*R*)-4-Benzyl-3-methyl-4-(phenylthio) -1-(*p*-tolyl)-1*H*-pyrazol-5(4*H*)-one (3p)

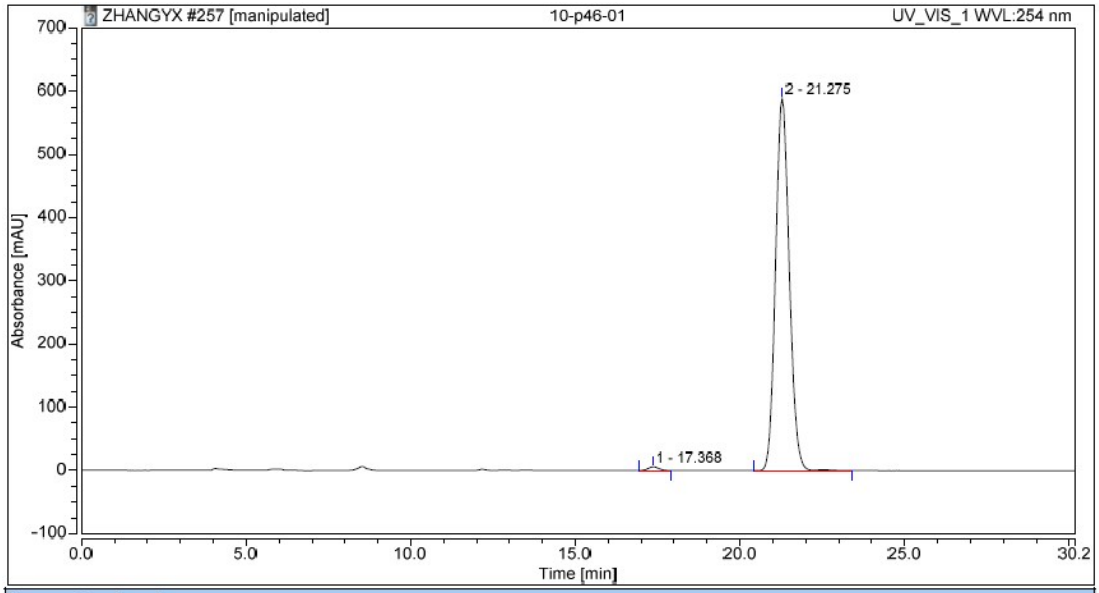


The crude product was purified by flash chromatography to obtain **3p** (white solid, 97% yield). M. p.: 87-92 ˚C. $[\alpha]^{29}_{D}$ = -175.2° (c = 0.98, DCM). *Ee* = 98% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254nm wave length UV. Retention time (min) = 17.4 (minor) and 21.3 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (d, J = 7.6 Hz, 2H), 7.28-7.10 (m, 10H), 7.03 (d, J = 8.4 Hz, 2H), 3.56 (d, J = 14.0 Hz, 1H), 3.06 (d, J = 14.4 Hz, 1H), 2.26 (s, 3H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 158.8, 135.9, 135.3, 134.7, 134.4, 130.3, 129.23, 129.20, 129.17, 128.8, 128.3, 127.7, 119.9, 64.7, 38.3, 21.1, 14.5. IR ν_{max} (film) cm^{-1} 3057, 2920, 2849, 1700, 1613, 1508, 1127, 1079, 1026, 822, 751, 723, 691. HRMS (ESI) for $C_{24}H_{22}N_2OS$: calculated $[M+H]^+$, 387.1531. Found, 387.1522.



Integration Results

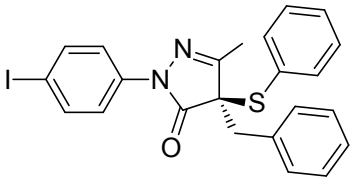
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		17.335	178.526	464.534	49.93	55.37	n.a.
2		21.213	179.055	374.500	50.07	44.63	n.a.
Total:			**357.581**	**839.034**	**100.00**	**100.00**	



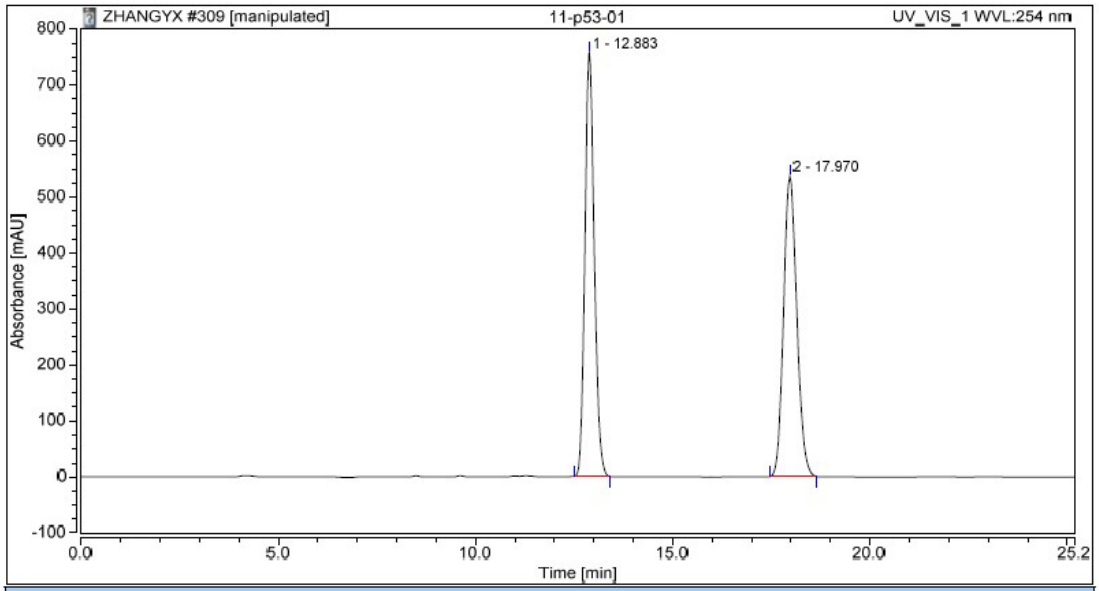
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		17.368	2.186	5.791	0.76	0.97	n.a.
2		21.275	284.837	589.022	99.24	99.03	n.a.
Total:			**287.023**	**594.813**	**100.00**	**100.00**	

(*R*)-4-Benzyl-1-(4-iodophenyl)-3-methyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (3q)

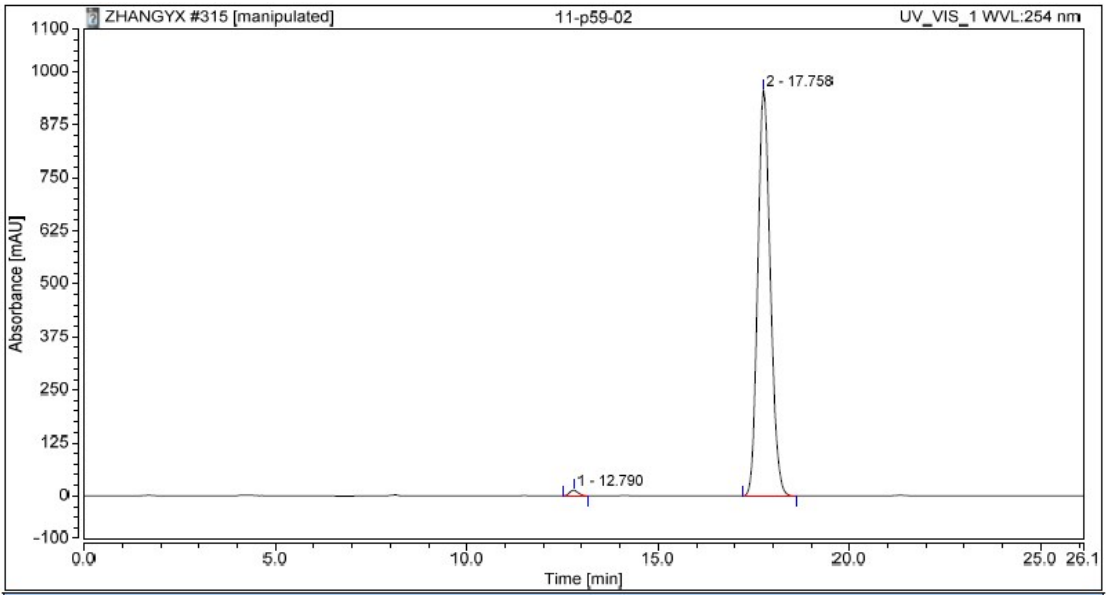


The crude product was purified by flash chromatography to obtain **3q** (pale yellow solid, 99% yield). M. p.: 75-79 ℃. $[\alpha]^{29}_{D}$ = -144.5° (c=1.00, DCM). *Ee* = 98% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 12.8 (minor) and 17.8 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (d, J = 7.6 Hz, 2H), 7.42 (d, J = 7.6 Hz, 2H), 7.24 (d, J = 8.0 Hz, 1H), 7.22-7.07 (m, 9H), 3.54 (d, J = 14.0 Hz, 1H), 3.06 (d, J = 13.6 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.7, 159.4, 137.6, 137.0, 135.9, 134.2, 130.4, 129.2, 129.1, 128.8, 128.0, 127.8, 121.0, 89.2, 64.9, 38.2, 14.5. IR ν_{max} (film) cm^{-1} 3058， 3029， 2919， 2849， 1709， 1582， 1486， 1218， 1125， 1025， 1002， 747， 725， 692. HRMS (ESI) for $C_{23}H_{19}IN_2OS$: calculated $[M+H]^+$, 499.0341. Found, 499.0335.



Integration Results

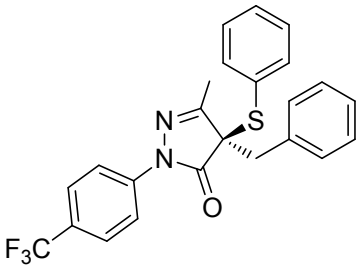
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		12.883	208.201	756.786	50.01	58.52	n.a.
2		17.970	208.117	536.445	49.99	41.48	n.a.
Total:			**416.318**	**1293.231**	**100.00**	**100.00**	



Integration Results

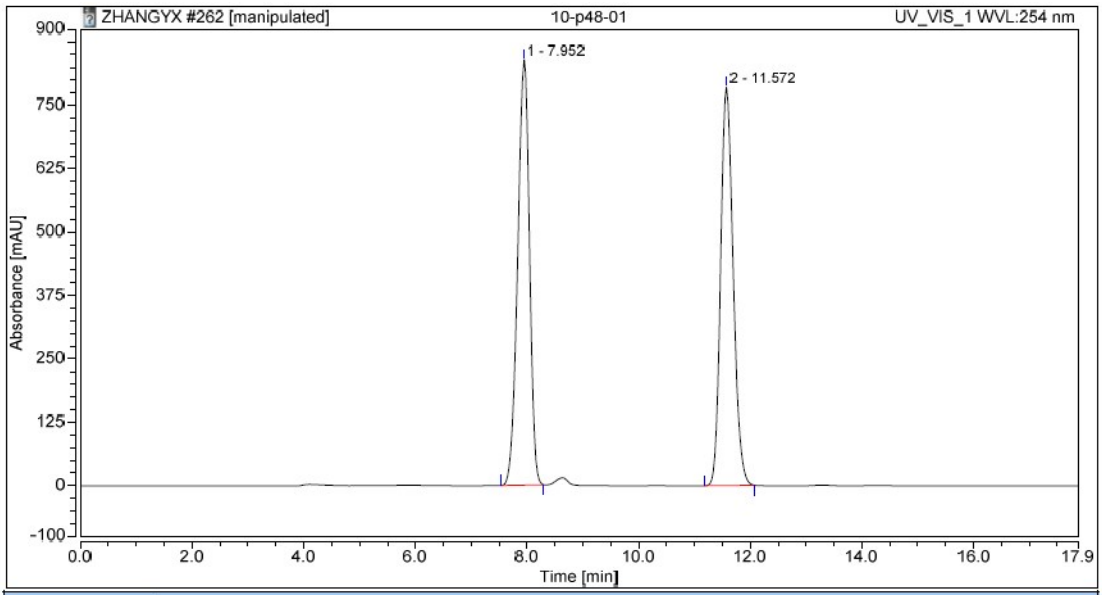
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		12.790	3.555	13.467	0.96	1.39	n.a.
2		17.758	367.063	955.610	99.04	98.61	n.a.
Total:			**370.619**	**969.077**	**100.00**	**100.00**	

(*R*)-4-Benzyl-3-methyl-4-(phenylthio)-1-(4-(trifluoromethyl)phenyl)-1*H*-pyrazol-5(4*H*)-one (3r)



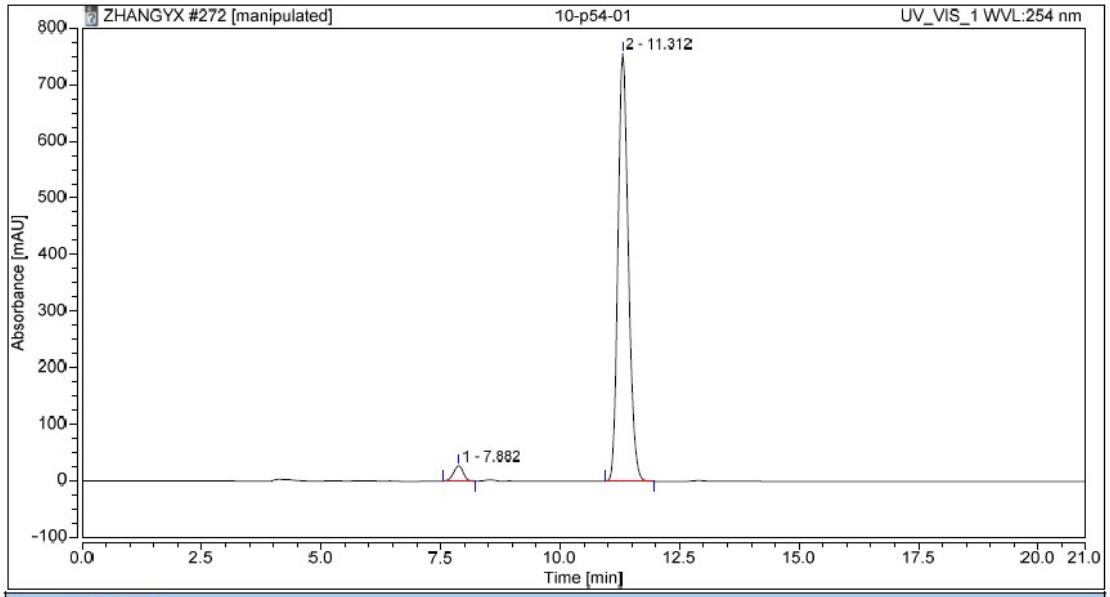
The crude product was purified by flash chromatography to obtain **3r** (white solid, 88% yield).

M. p.: 116-120 ℃. $[\alpha]^{29}_{D}$ = -134.5° (c = 0.99, DCM). *Ee* = 93% HPLC condition： CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 7.9 (minor) and 11.3 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 8.4 Hz, 2H), 7.48 (d, J = 8.8 Hz, 2H), 7.44 (d, J = 8.0 Hz, 2H),7.27-7.10 (m, 8H), 3.57 (d, J = 14.0 Hz, 1H), 3.09 (d, J = 13.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 159.7, 140.0, 136.0, 134.2, 130.5, 129.2 (d, J = 6.7 Hz), 128.9, 127.89, 127.86, 126.7 (d, J = 32.7 Hz), 125.9 (d, J = 3.8 Hz), 125.89 (d, J = 11.2 Hz), 125.5 (q, J = 270.0 Hz), 118.6, 65.0, 38.2, 14.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -62.2 (s). IR ν_{max} (film) cm^{-1} 3058, 3031, 2921, 2848, 1713, 1610, 1584, 1316, 1120, 1062, 1012, 849, 748, 695, 664. HRMS (ESI) for $C_{24}H_{19}F_3N_2OS$: calculated $[M+H]^+$, 441.1248. Found, 441.1232.



Integration Results

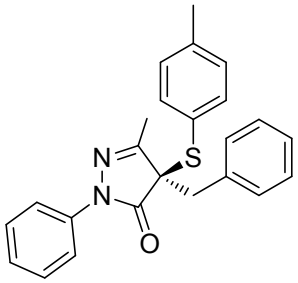
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		7.952	204.243	838.798	49.99	51.65	n.a.
2		11.572	204.297	785.167	50.01	48.35	n.a.
Total:			**408.540**	**1623.965**	**100.00**	**100.00**	



Integration Results

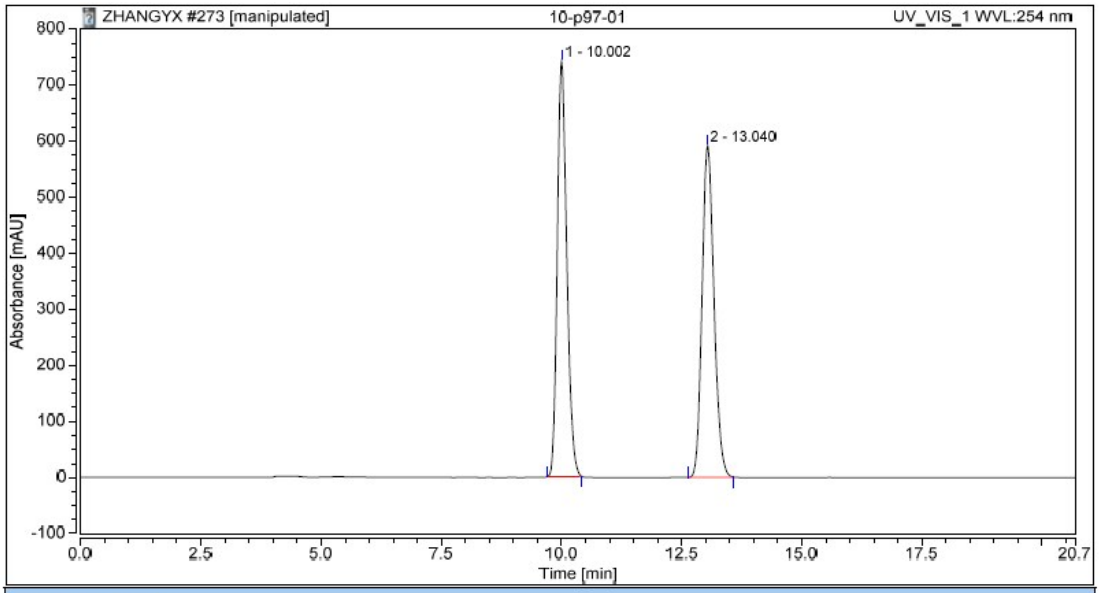
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		7.882	6.460	27.349	3.28	3.49	n.a.
2		11.312	190.374	756.794	96.72	96.51	n.a.
Total:			**196.834**	**784.143**	**100.00**	**100.00**	

(*R*)-4-Benzyl-3-methyl-1-phenyl-4-(*p*-tolylthio) -1*H*-pyrazol-5(4*H*)-one (3s)



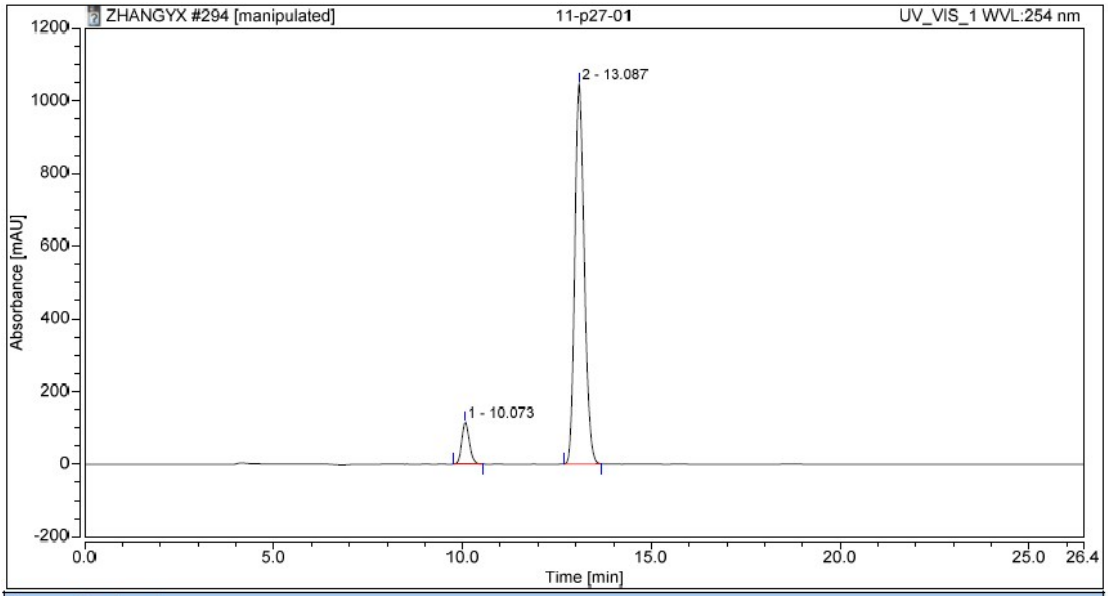
The crude product was purified by flash chromatography to obtain **3s** (white solid, 80% yield).

M. p.: 69-73 ℃. $[\alpha]^{27}_{D}$ = -167.4° (c = 1.02, DCM). *Ee* = 84% HPLC condition： CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) =10.1 (minor) and 13.1 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 8.0 Hz, 2H), 7.30 (dd, J = 8.8 Hz, 1.2 Hz, 2H), 7.23 (t, J = 8.0 Hz, 2H), 7.20-7.12 (m, 5H), 7.08 (t, J = 7.2 Hz, 1H), 6.99 (d, J = 8.0 Hz, 2H), 3.55 (d, J = 14.0 Hz, 1H), 3.05 (d, J = 14.0 Hz, 1H), 2.24 (s, 3H), 2.21 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 159.0, 140.7, 137.3, 135.9, 134.5, 129.9, 129.2, 128.8, 128.6, 127.7, 125.4, 124.7, 119.8, 64.8, 38.2, 21.3, 14.5. IR ν_{max} (film) cm^{-1} 3062， 3031， 2920， 2851， 1707， 1595， 1496， 1454， 1119， 1030， 811， 754， 723， 692. HRMS (ESI) for $C_{24}H_{22}N_2OS$: calculated $[M+H]^+$, 387.1531. Found, 387.1523.



Integration Results

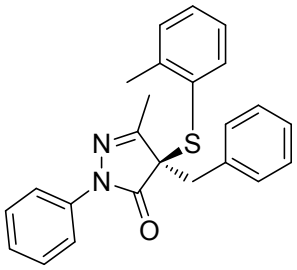
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.002	169.407	741.624	49.86	55.63	n.a.
2		13.040	170.381	591.559	50.14	44.37	n.a.
Total:			**339.788**	**1333.183**	**100.00**	**100.00**	



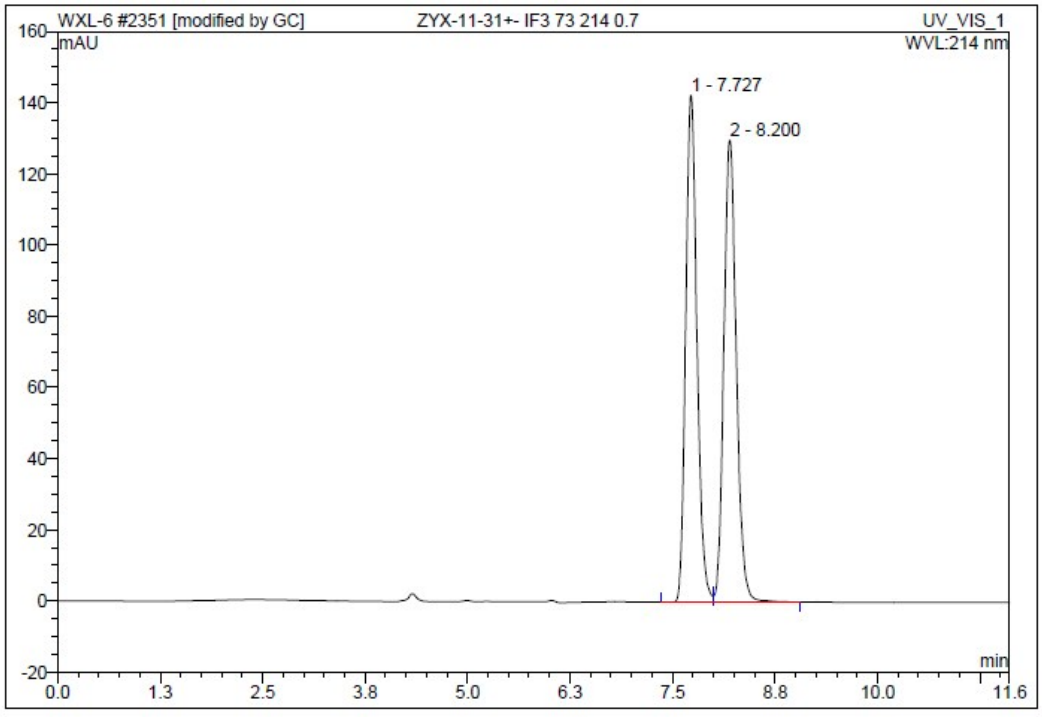
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.073	26.895	116.148	8.12	9.99	n.a.
2		13.087	304.204	1046.214	91.88	90.01	n.a.
Total:			**331.099**	**1162.362**	**100.00**	**100.00**	

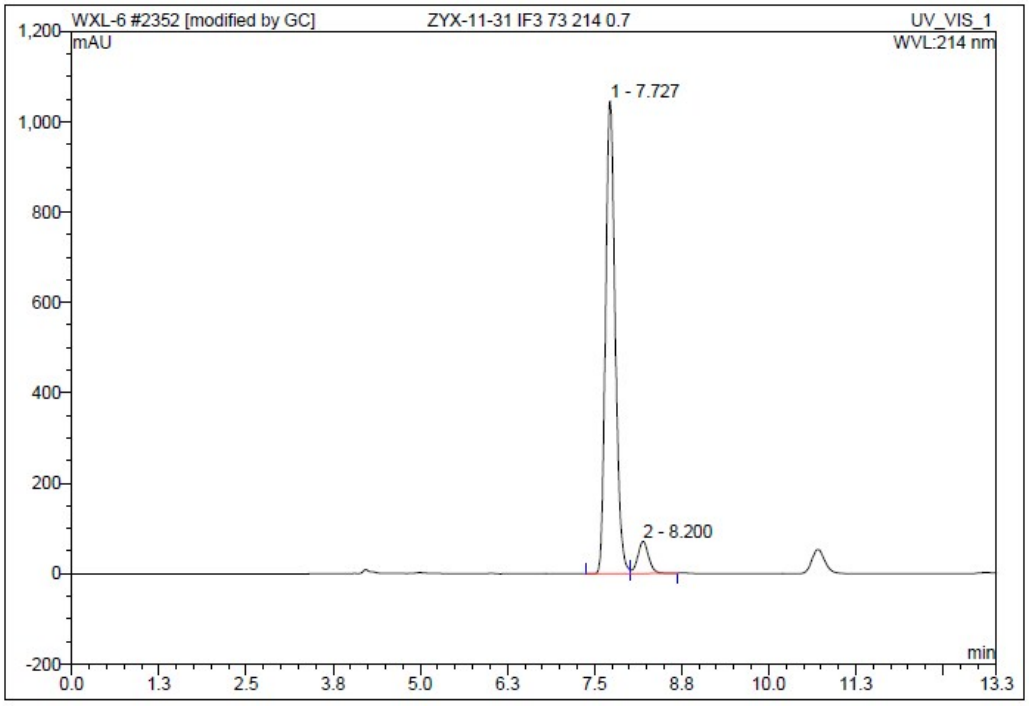
(*R*)-4-Benzyl-3-methyl-1-phenyl-4-(*o*-tolylthio)-1*H*-pyrazol-5(4*H*)-one (3t)



The crude product was purified by flash chromatography to obtain **3t** (white solid, 93% yield). M. p.: 60-64 ˚C. $[\alpha]^{28}_{D}$ = -123.9° (c = 1.00, DCM). *Ee* = 86% HPLC condition: CHIRALPAK IF-3. Hexane/*i*-PrOH eluent (70:30 ratio, 0.7 mL/min flow rate) with 214 nm wave length UV. Retention time (min) = 7.7 (major) and 8.2 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (d, J = 7.6 Hz, 1H), 7.31 (d, J = 8.4 Hz, 2H), 7.26-7.11 (m, 9H), 7.08 (t, J = 7.6 Hz, 1H), 6.98 (d, J = 7.2 Hz, 1H), 3.60 (d, J = 13.6 Hz, 1H), 3.09 (d, J = 13.6 Hz, 1H), 2.55 (s, 3H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 159.2, 143.3, 137.3, 136.7, 134.4, 130.8, 130.2, 129.2, 128.8, 128.7, 128.0, 127.7, 126.4, 125.4, 119.7, 64.3, 38.8, 21.4, 14.7. IR ν_{max} (film) cm^{-1} 3059， 3031， 2920， 2850， 1704， 1594， 1492， 1081， 1060， 1030， 757， 725， 692. HRMS (ESI) for $C_{24}H_{22}N_2OS$: calculated $[M+H]^+$, 387.1531. Found, 387.1523.

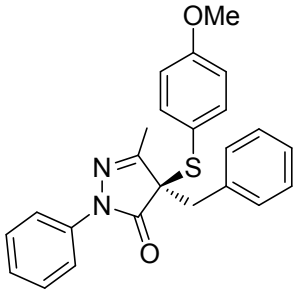


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.73	n.a.	142.460	22.578	49.71	n.a.	BM *
2	8.20	n.a.	129.792	22.845	50.29	n.a.	MB*
Total:			272.252	45.423	100.00	0.000	



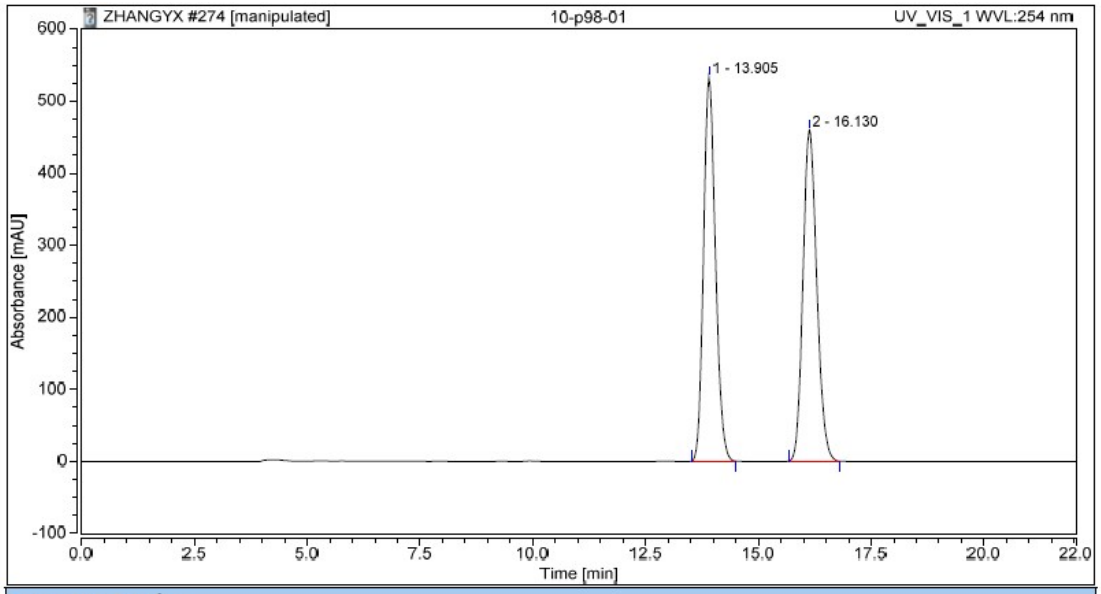
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.73	n.a.	1046.248	167.809	92.87	n.a.	BM *
2	8.20	n.a.	70.840	12.877	7.13	n.a.	MB*
Total:			1117.089	180.686	100.00	0.000	

(*R*)-4-Benzyl-4-((4-methoxyphenyl)thio)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (3u)



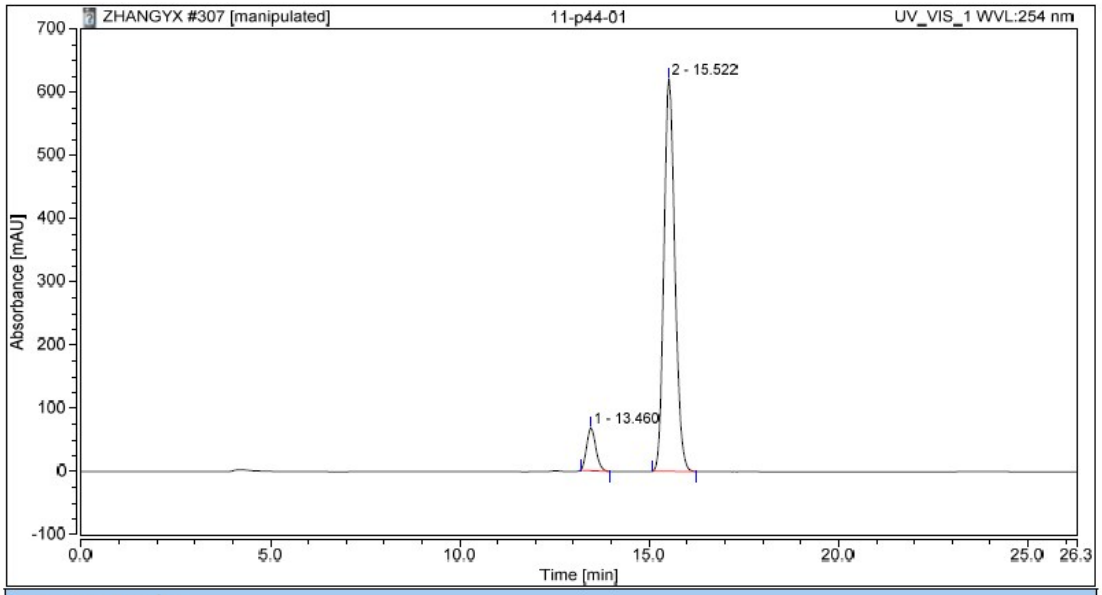
The crude product was purified by flash chromatography to obtain **3u** (colorless oil, 97% yield). $[\alpha]^{28}_{D}$ = -177.5° (c = 1.00, DCM). *Ee* = 83% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 13.5 (minor) and 15.5 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (d, J = 8.4 Hz, 2H), 7.33 (d, J = 7.6 Hz, 2H), 7.27-7.10 (m, 7H), 7.08 (t, J = 7.2 Hz, 1H), 6.69 (d, J = 8.8 Hz, 2H), 3.65 (s, 3H),3.54 (d, J = 14.0 Hz, 1H), 3.03 (d, J = 14.0 Hz, 1H), 2.25 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 161.4, 159.1, 137.7, 137.3, 134.6, 129.2, 128.8, 128.6, 127.6, 125.4, 119.7, 118.7, 114.7, 65.0, 55.4, 37.9, 14.5. IR ν_{max} (film) cm^{-1} 3062， 3031， 3007， 2920， 2837， 1706， 1590，

1492， 1248， 1120， 1105， 1093， 1081， 1027， 829, 755， 723， 692. HRMS (ESI) for $C_{24}H_{22}N_2O_2S$: calculated $[M+H]^+$, 403.1480. Found, 403.1471.



Integration Results

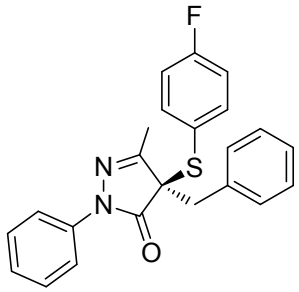
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		13.905	162.967	533.151	50.01	53.72	n.a.
2		16.130	162.921	459.265	49.99	46.28	n.a.
Total:			**325.888**	**992.415**	**100.00**	**100.00**	



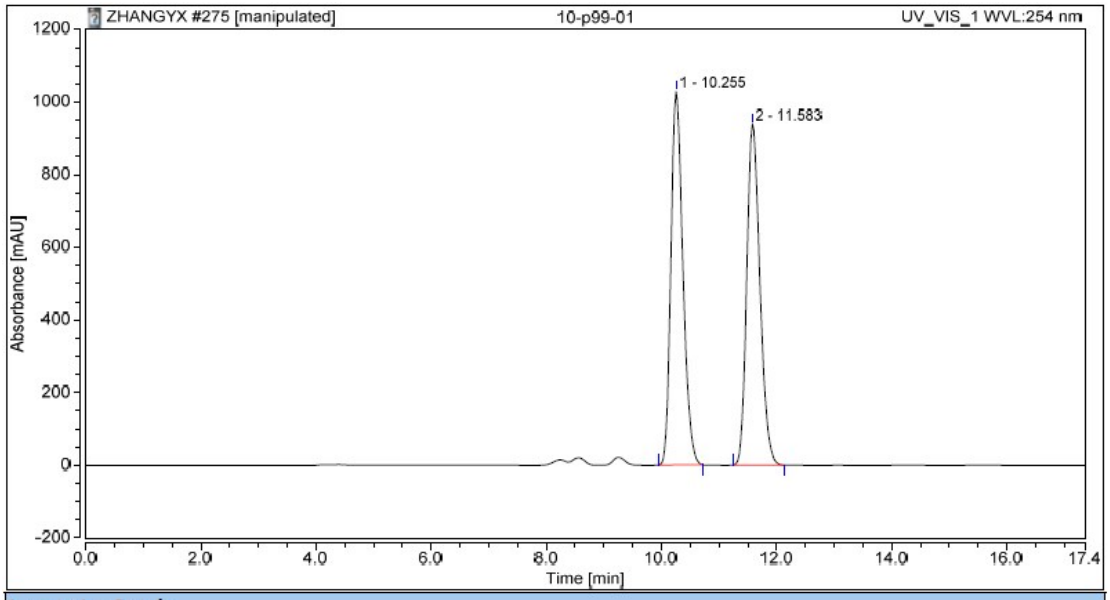
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		13.460	19.068	67.989	8.41	9.86	n.a.
2		15.522	207.792	621.206	91.59	90.14	n.a.
Total:			**226.860**	**689.195**	**100.00**	**100.00**	

(*R*)-4-Benzyl-4-((4-fluorophenyl)thio)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (3v)

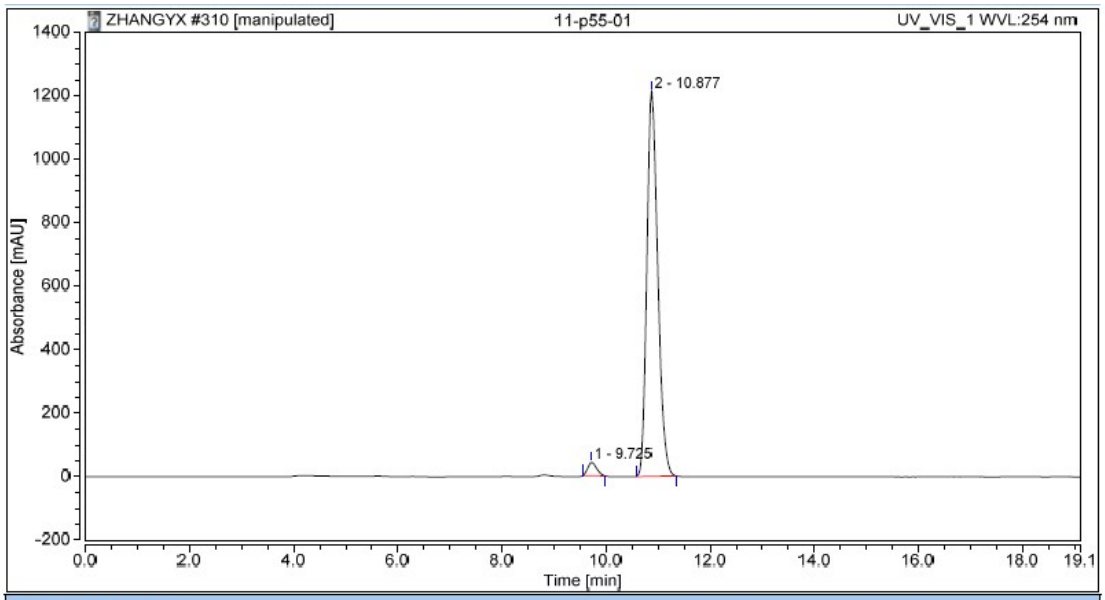


The crude product was purified by flash chromatography to obtain **3v** (white solid, 99% yield). M. p.: 107-111 ℃. $[\alpha]^{28}_{D}$ = -160.4° (c = 1.00, DCM). *Ee* = 95% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 9.7 (minor) and 10.9 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.42 (m, 2H), 7.34-7.29 (m, 2H), 7.28-7.22 (m, 2H), 7.21-7.12 (m, 5H),7.10 (t, J = 7.6 Hz, 1H), 6.89 (t, J = 8.4 Hz, 2H), 3.55 (d, J = 14.0 Hz, 1H), 3.05 (d, J = 14.0 Hz, 1H), 2.26 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.6, 164.1 (d, J = 250.4 Hz), 158.8, 138.2 (d, J = 8.8 Hz), 137.1, 134.2, 129.2, 128.8, 128.7, 127.8, 125.6, 123.5 (d, J = 3.3 Hz), 119.5, 116.4 (d, J = 21.8 Hz), 64.9, 38.1, 14.4; ^{19}F NMR (376 MHz, $CDCl_3$): δ -109.5(m). IR ν_{max} (film) cm^{-1} 3060， 3035， 3012， 2919， 1700， 1589， 1489， 1227， 1118， 1081， 1030， 835， 759， 725， 691. HRMS (ESI) for $C_{23}H_{19}FN_2OS$: calculated $[M+H]^+$,391.1280. Found, 391.1272.



Integration Results

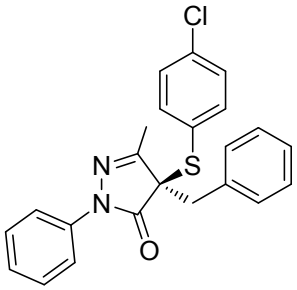
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.255	248.072	1028.131	49.90	52.29	n.a.
2		11.583	249.114	937.958	50.10	47.71	n.a.
Total:			**497.185**	**1966.090**	**100.00**	**100.00**	



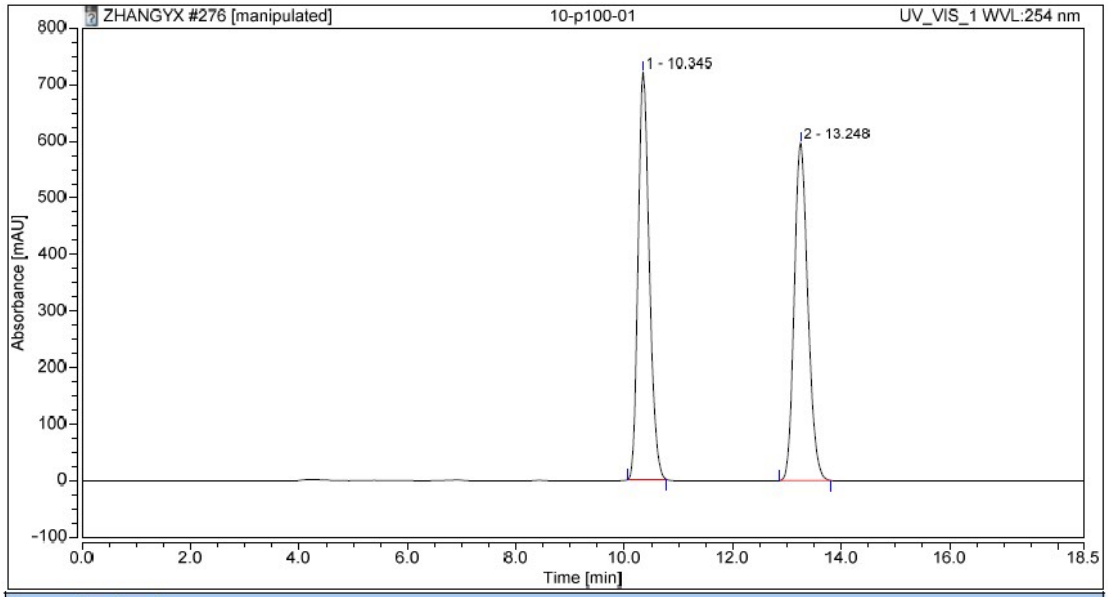
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		9.725	8.237	42.051	2.72	3.35	n.a.
2		10.877	294.399	1212.498	97.28	96.65	n.a.
Total:			**302.636**	**1254.549**	**100.00**	**100.00**	

(*R*)-4-Benzyl-4-((4-chlorophenyl)thio)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (3w)

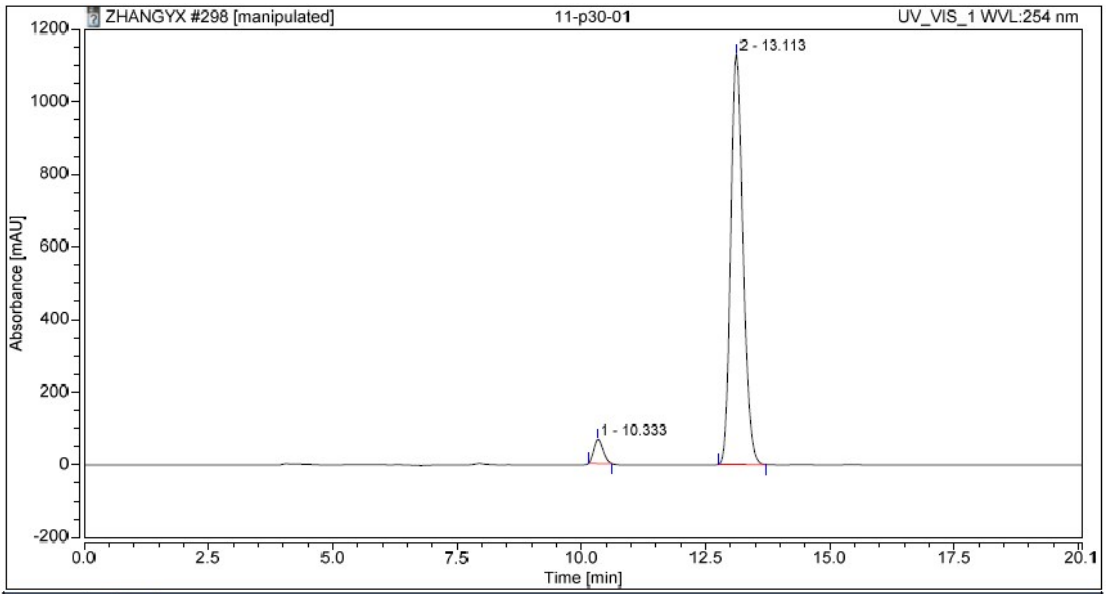


The crude product was purified by flash chromatography to obtain **3w** (colorless oil, 95% yield). $[\alpha]^{28}_{D}$ = -165.6° (c = 1.01, DCM). *Ee* = 92% HPLC condition： CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 10.3 (minor) and 13.1 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40-7.35 (m, 2H), 7.30-7.22 (m, 4H), 7.22-7.08 (m, 8H), 3.54 (d, J = 13.6 Hz, 1H), 3.05 (d, J = 14.0 Hz, 1H), 2.24 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 158.8, 137.2, 137.04, 136.97, 134.1, 129.4, 129.2, 128.8, 128.7, 127.8, 126.6, 125.7, 119.6, 64.8, 38.2, 14.5. IR ν_{max} (film) cm^{-1} 3062，3031， 2920， 2849， 1706， 1594， 1497， 1093， 1030， 1013， 823， 754，722， 692. HRMS (ESI) for $C_{23}H_{19}ClN_2OS$: calculated $[M+H]^+$, 407.0985. Found, 407.0976.



Integration Results

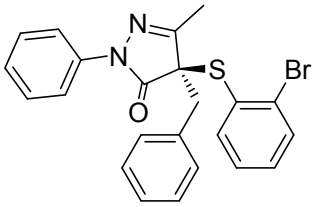
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.345	171.833	719.403	49.76	54.67	n.a.
2		13.248	173.486	596.392	50.24	45.33	n.a.
Total:			**345.319**	**1315.795**	**100.00**	**100.00**	



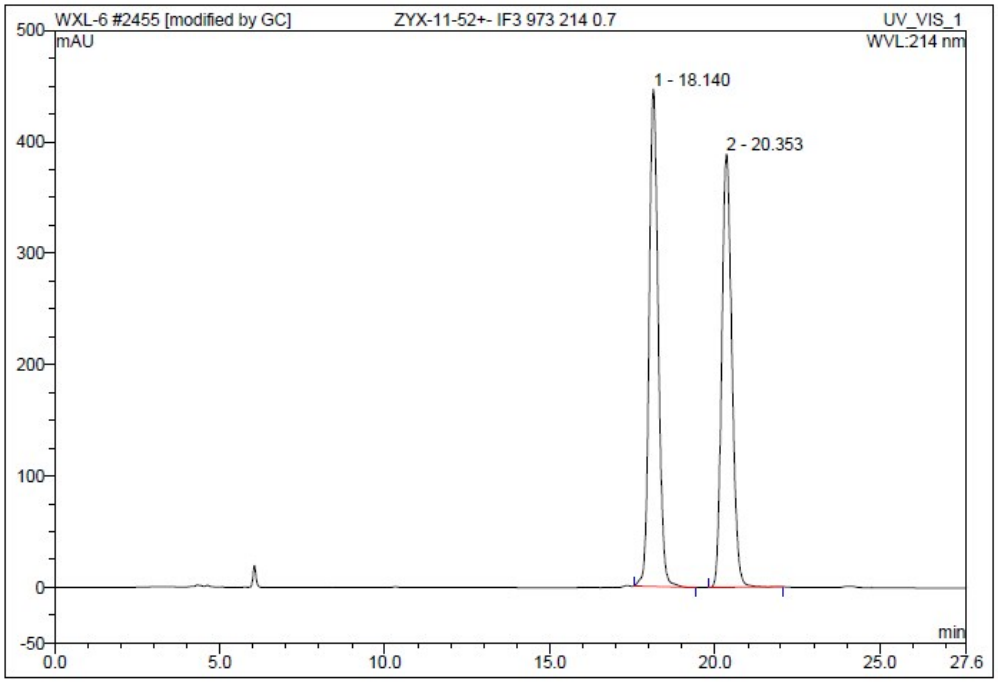
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.333	14.312	66.560	4.22	5.57	n.a.
2		13.113	324.626	1128.677	95.78	94.43	n.a.
Total:			**338.938**	**1195.237**	**100.00**	**100.00**	

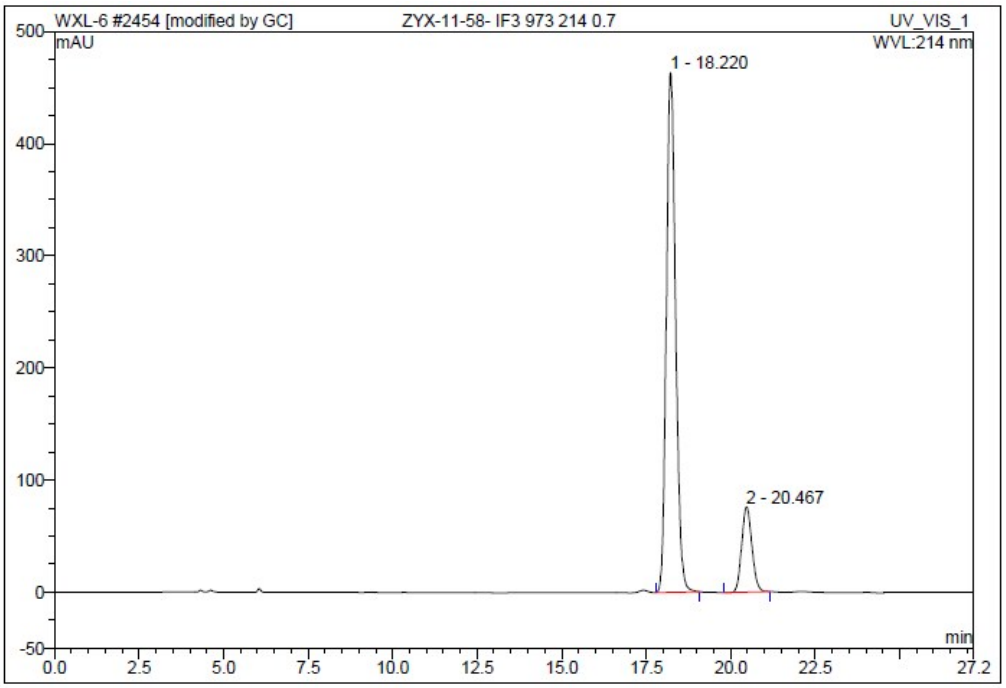
(*R*)-4-Benzyl-4-((2-bromophenyl)thio)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (3x)



The crude product was purified by flash chromatography to obtain **3x** (colorless oil, 92% yield). $[\alpha]^{28}_{D}$ = -149.3° (c = 1.01, DCM). *Ee* = 69% HPLC condition： CHIRALPAK IF-3. Hexane/*i*-PrOH eluent (97:3 ratio, 0.7 mL/min flow rate) with 214 nm wave length UV. Retention time (min) = 18.2 (major) and 20.5 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.57 (m, 1H), 7.53-7.48 (m, 1H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.23-7.05 (m, 8H), 3.57 (d, *J* = 13.6 Hz, 1H), 3.16 (d, *J* = 13.6 Hz, 1H), 2.27 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.5, 159.2, 141.6, 137.3, 137.1, 133.9, 133.7, 131.2, 130.4, 129.9, 129.3, 128.8, 128.0, 127.9, 125.6, 119.6, 64.3, 39.0, 15.0. IR ν_{max} (film) cm^{-1} 3061， 3032， 2920， 2850， 1706， 1595， 1498， 1362， 1159， 1117， 1019， 991， 752， 722， 692. HRMS (ESI) for $C_{23}H_{19}BrN_2OS$: calculated $[M+H]^+$, 451.0479. Found, 451.0474.

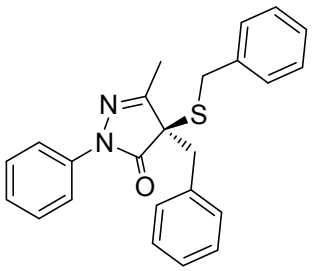


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.14	n.a.	446.365	142.484	50.59	n.a.	BMB*
2	20.35	n.a.	389.054	139.154	49.41	n.a.	BMB*
Total:			835.419	281.638	100.00	0.000	

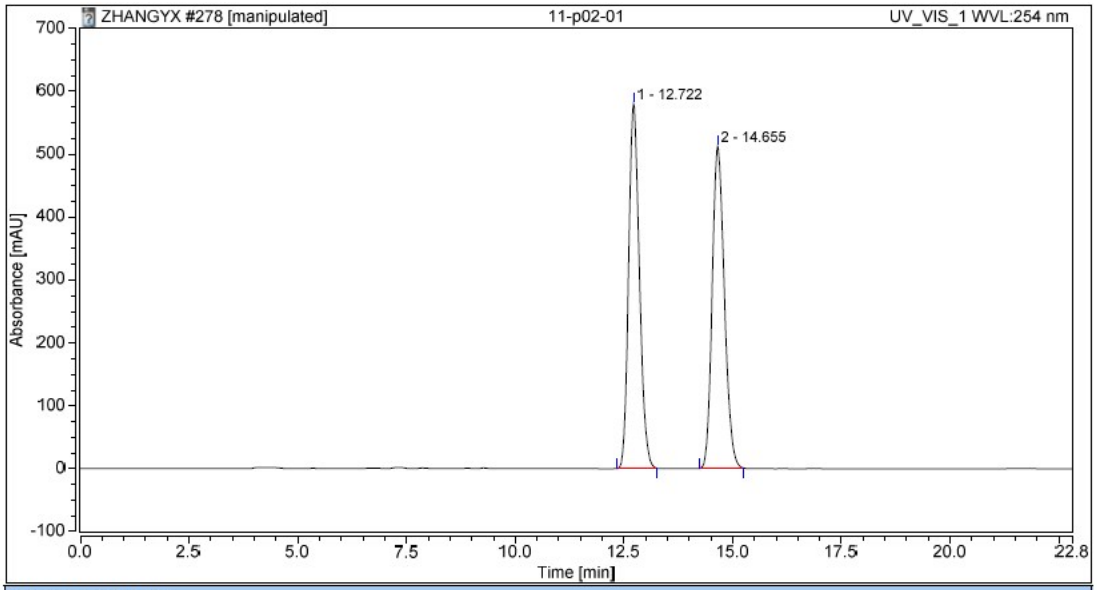


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.22	n.a.	463.290	146.829	84.66	n.a.	BMB*
2	20.47	n.a.	75.926	26.612	15.34	n.a.	BMB*
Total:			539.217	173.441	100.00	0.000	

(*R*)-4-benzyl-4-(benzylthio)-3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one (3y)

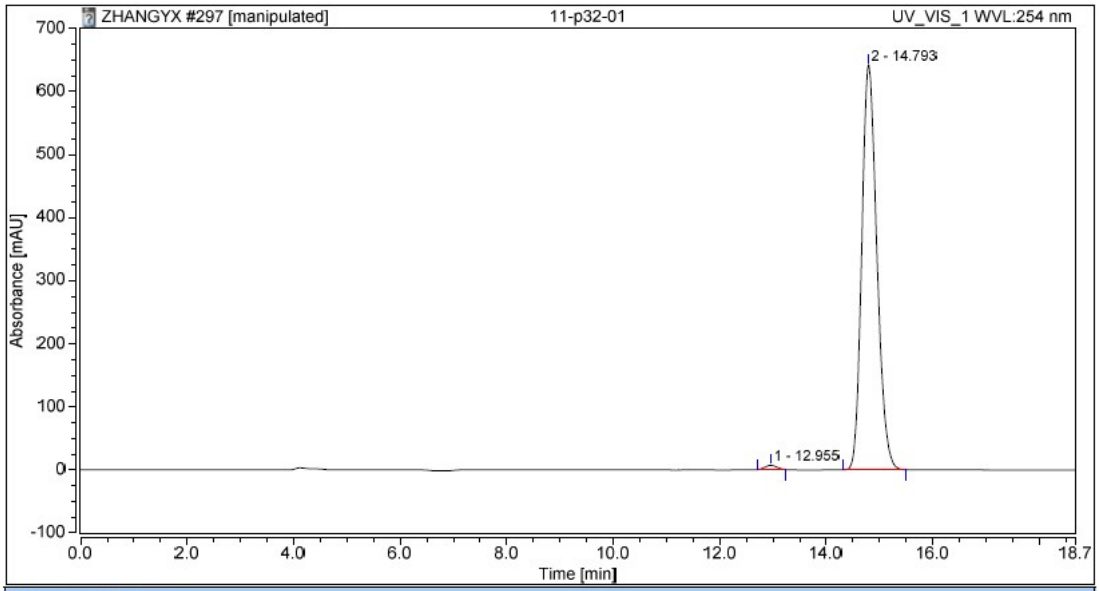


The crude product was purified by flash chromatography to obtain **3y** (colorless oil, 96% yield). $[\alpha]^{27}_{D}$ = -84.2° (c = 0.98, DCM). *Ee* = 98% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) =13.0 (minor) and 14.8 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (dd, J = 8.8 Hz, 1.2 Hz, 2H), 7.37-7.30 (m, 2H), 7.24-7.07 (m, 11H), 3.71 (d, J = 12.4 Hz, 1H), 3.58 (d, J = 12.4 Hz, 1H), 3.46 (d, J = 14.0 Hz, 1H), 2.99 (d, J = 13.6 Hz, 1H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.8, 159.3, 137.5, 135.7, 134.0, 129.3, 129.2, 128.9, 128.7, 128.6, 127.8, 127.7, 125.4, 119.3, 61.3, 39.5, 34.3, 14.2. IR ν_{max} (film) cm^{-1} 3061， 3030， 2912， 2848， 1705， 1594， 1495， 1081， 1030， 755， 722， 692. HRMS (ESI) for $C_{24}H_{22}N_2OS$: calculated $[M+H]^+$, 387.1531. Found, 387.1522.



Integration Results

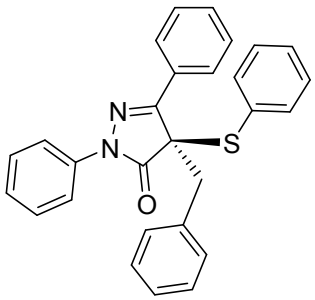
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		12.722	165.729	579.499	49.89	53.09	n.a.
2		14.655	166.449	511.948	50.11	46.91	n.a.
Total:			**332.178**	**1091.447**	**100.00**	**100.00**	



Integration Results

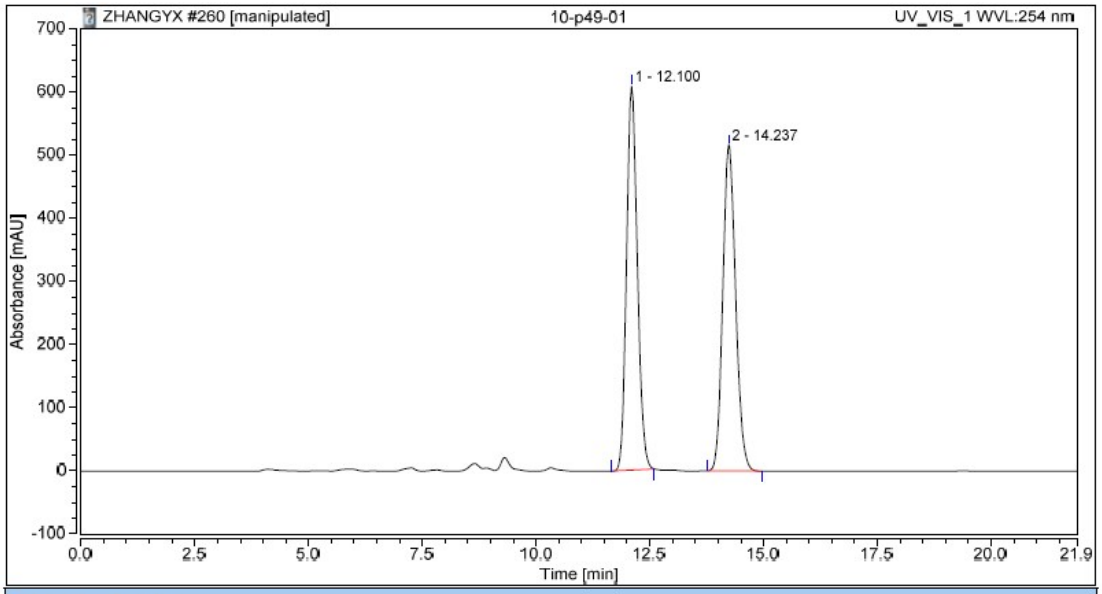
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		12.955	1.770	6.882	0.83	1.06	n.a.
2		14.793	210.677	641.931	99.17	98.94	n.a.
Total:			**212.448**	**648.813**	**100.00**	**100.00**	

(*R*)-4-Benzyl-1,3-diphenyl-4-(phenylthio)-1*H*-pyrazol-5(4*H*)-one (5a)



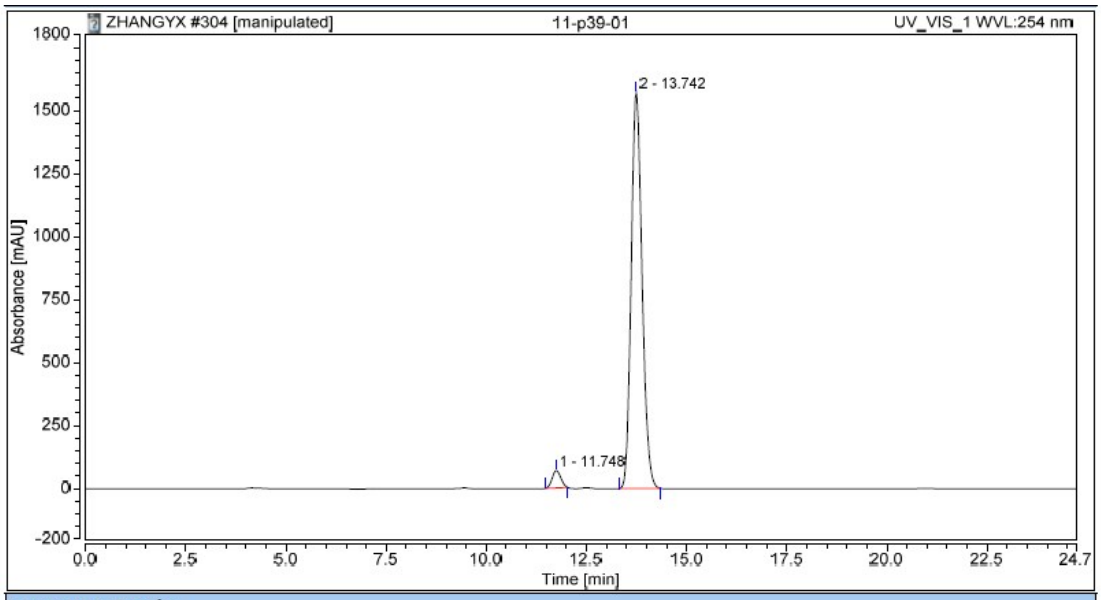
The crude product was purified by flash chromatography to obtain **5a** (white solid, 98% yield).

M. p.: 106-110 ˚C. $[\alpha]^{28}_{D} = 10.8°$ (c = 1.00, DCM). *Ee* = 93% HPLC condition： CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80: 20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) =11.7 (minor) and 13.7 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.25-8.20 (m, 2H), 7.54-7.48 (m, 3H), 7.39-7.30 (m, 4H), 7.27-7.16 (m, 3H), 7.13-6.97 (m, 6H), 6.85 (d, J = 7.2 Hz, 2H), 3.65 (d, J = 13.2 Hz, 1H), 3.50 (d, J = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 156.2, 137.2, 136.2, 134.0, 131.2, 130.7, 130.4, 129.6, 129.0, 128.9, 128.7, 128.4, 128.1, 127.5, 127.1, 125.8, 120.1, 63.8, 39.6. IR ν_{max} (film) cm^{-1} 3060, 3028, 2918, 2849, 1711, 1593, 1491, 1182, 1136, 1022, 751, 689, 645. HRMS (ESI) for $C_{28}H_{22}N_2OS$: calculated $[M+H]^+$, 435.1531. Found, 435.1527.



Integration Results

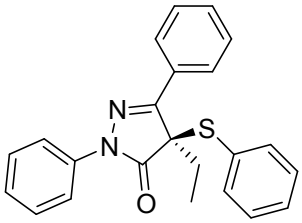
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		12.100	167.603	608.957	49.81	54.12	n.a.
2		14.237	168.900	516.303	50.19	45.88	n.a.
Total:			**336.503**	**1125.260**	**100.00**	**100.00**	



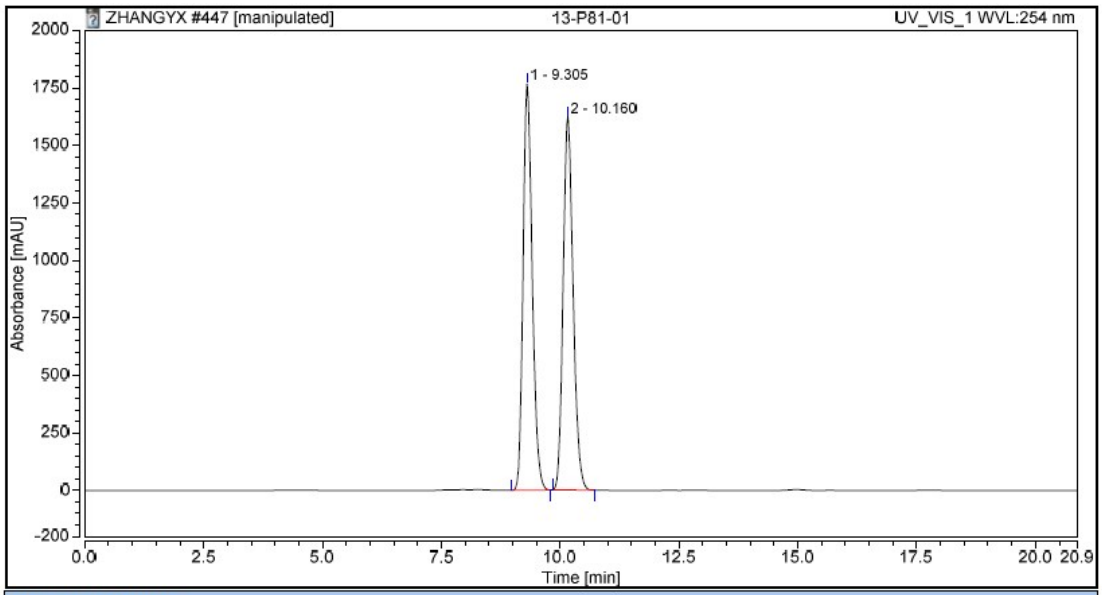
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		11.748	16.998	68.841	3.33	4.20	n.a.
2		13.742	493.916	1568.778	96.67	95.80	n.a.
Total:			510.914	1637.619	100.00	100.00	

(*R*)-4-Ethyl-1, 3-diphenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (5b)

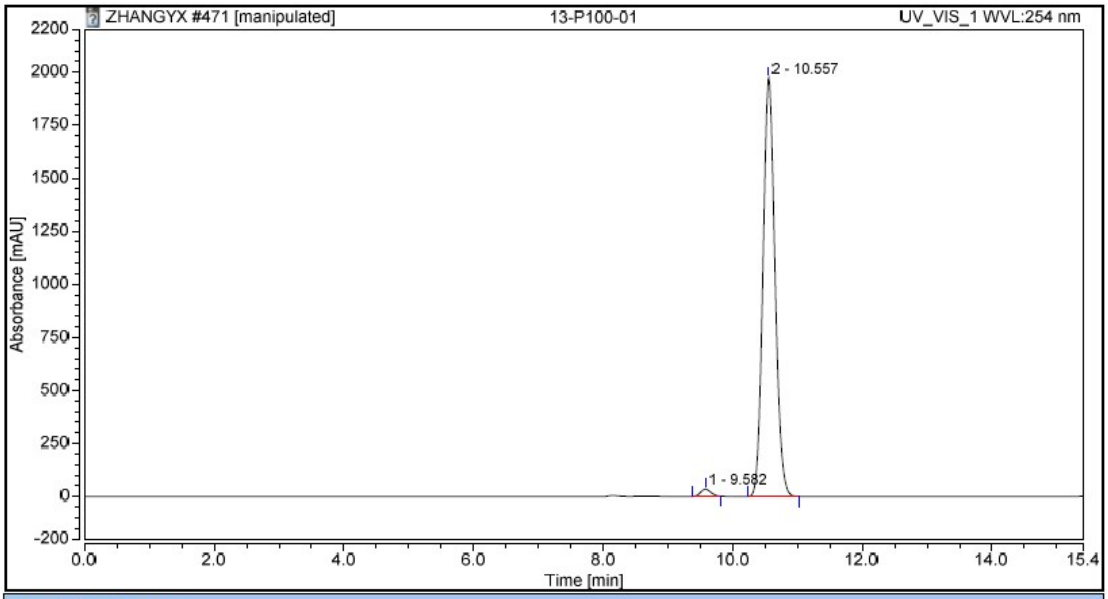


The crude product was purified by flash chromatography to obtain **5b** (colorless oil, 96% yield). $[\alpha]^{28}_{D}$ = -53.7° (c=0.99, DCM). *Ee* = 97% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 9.6 (minor) and 10.6 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (td, J = 3.6 Hz, 1.2 Hz, 2H), 7.60 (dd, J = 8.4 Hz, 1.2 Hz, 2H), 7.54-7.47 (m, 3H), 7.36-7.28 (m, 4H), 7.22-7.12 (m, 2H), 7.08 (t, J = 7.6 Hz, 2H), 2.44-2.21 (m, 2H), 0.78 (t, J = 7.6 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.8, 156.6, 137.4, 136.1, 130.7, 130.6, 130.3, 128.94, 128.93, 128.8, 128.2, 126.9, 125.6, 119.5, 63.7, 27.6, 9.8. IR ν_{max} (film) cm^{-1} 3059, 2967, 2932, 1712, 1594, 1492, 1384, 1152, 748, 688. HRMS (ESI) for $C_{23}H_{20}N_2OS$: calculated $[M+H]^+$, 373.1375. Found, 373.1368.



Integration Results

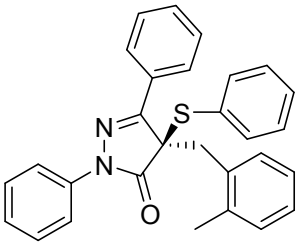
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		9.305	395.453	1768.223	50.02	52.20	n.a.
2		10.160	395.119	1619.444	49.98	47.80	n.a.
Total:			**790.572**	**3387.667**	**100.00**	**100.00**	



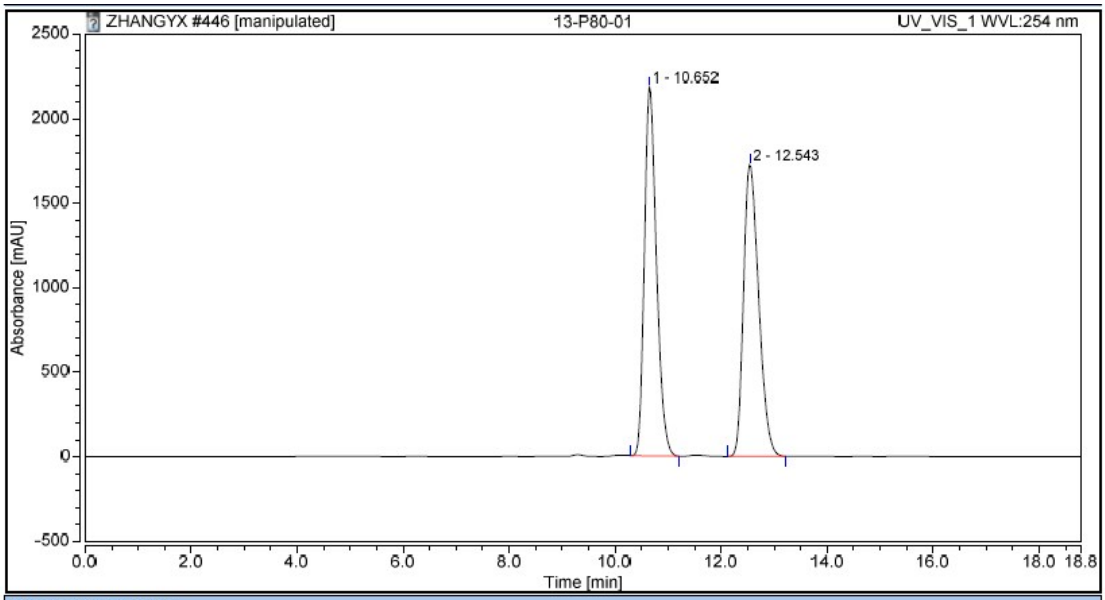
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		9.582	6.129	33.489	1.43	1.67	n.a.
2		10.557	421.564	1973.124	98.57	98.33	n.a.
Total:			**427.693**	**2006.613**	**100.00**	**100.00**	

(*R*)-4-(2-Methylbenzyl)-1, 3-diphenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (5c)

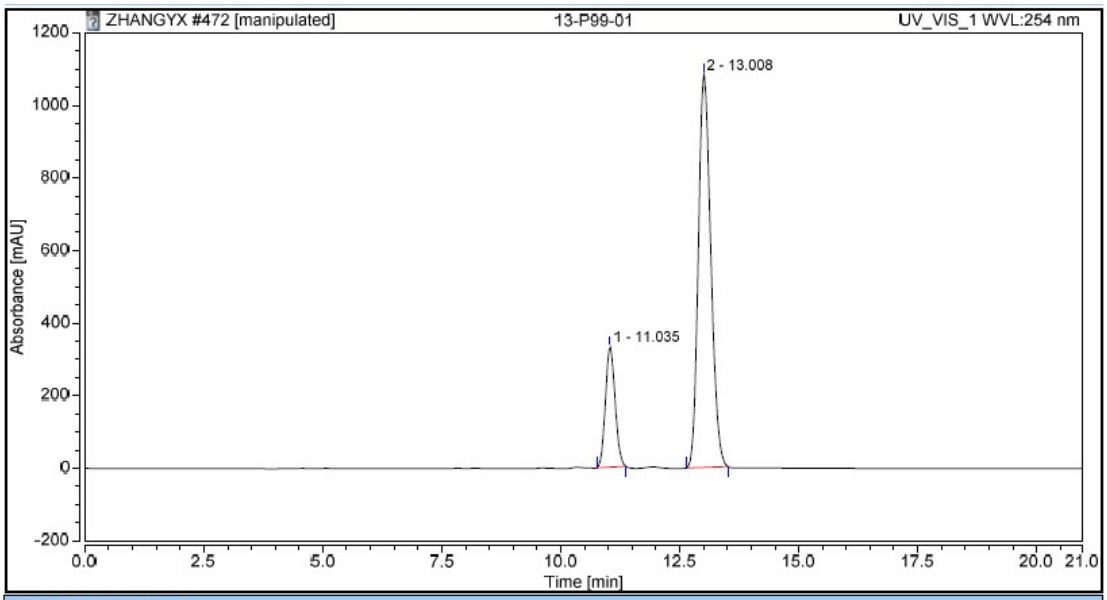


The crude product was purified by flash chromatography to obtain **5c** (colorless oil, 97% yield). $[\alpha]^{28}_{D}$ = -7.9° (c = 1.01, DCM). *Ee* = 62% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 11.0 (minor) and 13.0 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.21 (dd, *J* = 7.6 Hz, 2.0 Hz, 2H), 7.51-7.42 (m, 3H), 7.37 (d, *J* = 8.0 Hz, 4H), 7.29-7.16 (m,3H), 7.10 (q, *J* = 8.0 Hz, 3H), 7.01-6.92 (m, 2H), 6.86 (d, *J* = 2.8 Hz, 2H), 3.70 (d, *J* = 14.4 Hz, 1H), 3.53 (d, *J* = 14.4 Hz, 1H), 2.10 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 156.6, 137.2, 137.0, 136.2, 132.9, 131.2, 130.67, 130.65, 130.4, 129.01, 128.96, 128.9, 128.7, 128.0, 127.4, 127.3, 125.9, 125.7, 119.9, 63.7, 35.2, 19.9. IR ν_{max} (film) cm^{-1} 3062, 2917, 1708, 1593, 1489, 1129, 747, 690. HRMS (ESI) for $C_{29}H_{24}N_2OS$: calculated $[M+H]^+$, 449.1688. Found, 449.1680.



Integration Results

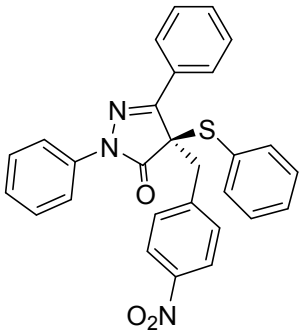
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.652	575.730	2181.938	50.13	55.80	n.a.
2		12.543	572.820	1728.482	49.87	44.20	n.a.
Total:			**1148.550**	**3910.419**	**100.00**	**100.00**	



Integration Results

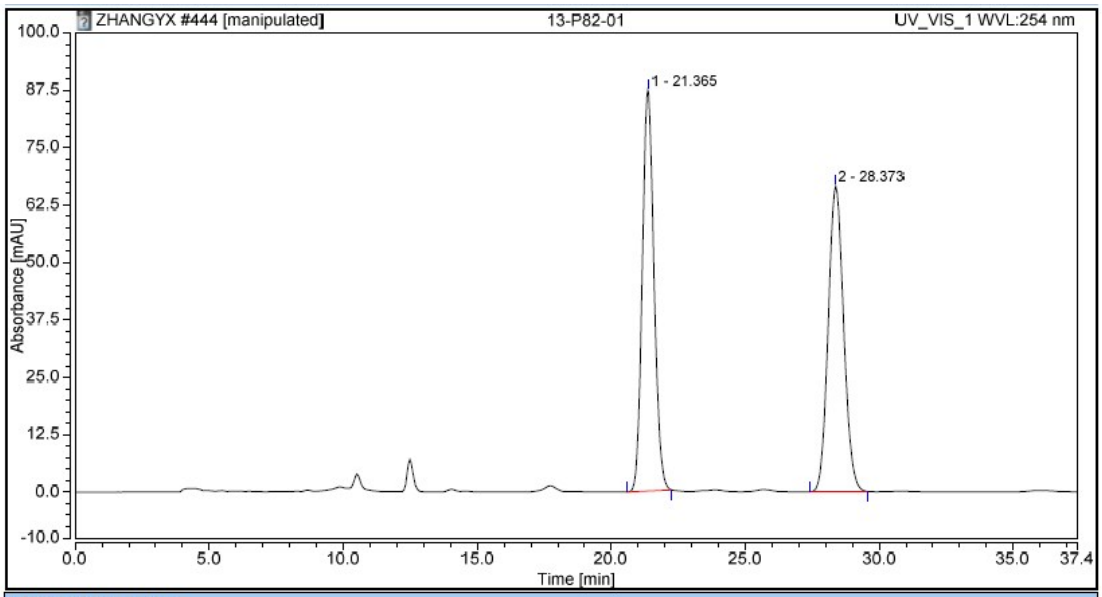
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		11.035	77.730	331.841	19.19	23.47	n.a.
2		13.008	327.425	1082.188	80.81	76.53	n.a.
Total:			**405.155**	**1414.030**	**100.00**	**100.00**	

(*R*)-4-(4-Nitrobenzyl)-1, 3-diphenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (5d)



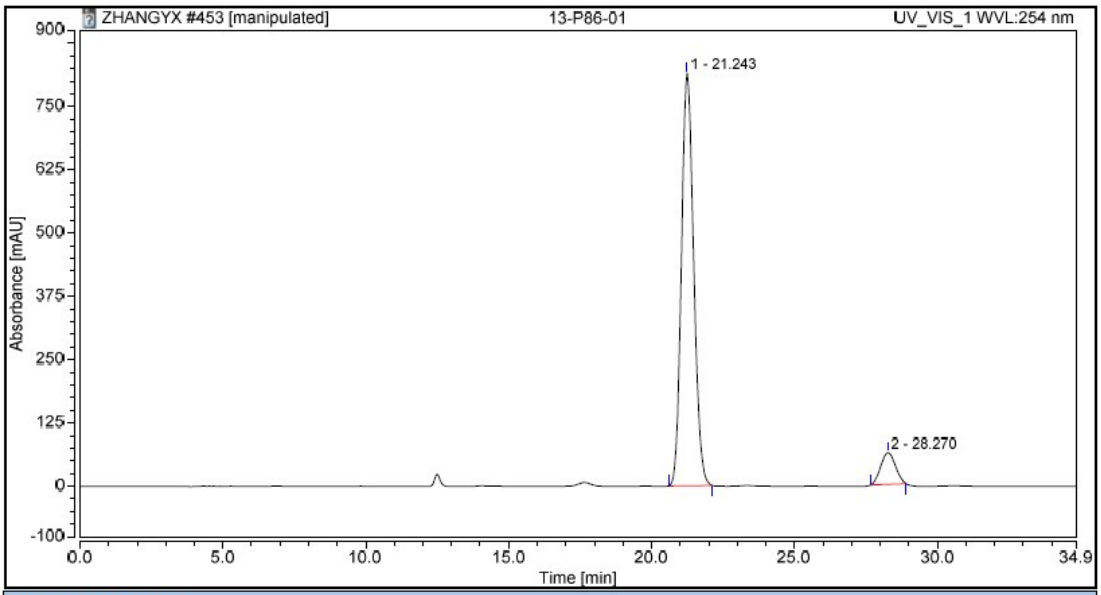
The crude product was purified by flash chromatography to obtain **5d** (white solid, 96% yield). M. p.: 48-52 ˚C. $[\alpha]^{28}_{D} = 2.0^{\circ}$ (c = 1.00, DCM). *Ee* = 83% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 21.2 (major) and 28.3 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (dd, *J* = 7.6 Hz, 2.0 Hz, 2H), 7.89 (d, *J* = 8.8 Hz, 2H), 7.61-7.51 (m, 3H), 7.37 (dd, *J* = 8.8 Hz, 8.0 Hz, 4H), 7.30-7.20 (m,3H), 7.13 (q, *J* = 7.6 Hz, 3H), 7.00 (d, *J* = 8.4 Hz, 2H), 3.73 (d, *J* = 13.2 Hz, 1H), 3.59 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.9, 155.6, 147.3, 141.6, 136.8, 136.3, 131.1, 130.73, 130.71, 130.6, 129.20, 129.17, 128.8, 127.4, 127.0, 126.0, 123.6, 119.7, 63.2, 38.9. IR ν_{max} (film) cm^{-1} 3060, 2925, 1710, 1597, 1520, 1492, 1386, 1131, 1025, 855, 750, 726,

689. HRMS (ESI) for $C_{28}H_{21}N_3O_3S$: calculated $[M+H]^+$, 480.1382. Found, 480.1374.



Integration Results

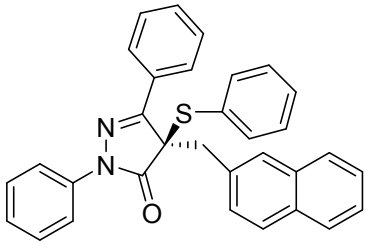
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		21.365	44.156	87.252	49.89	56.74	n.a.
2		28.373	44.353	66.518	50.11	43.26	n.a.
Total:			**88.509**	**153.770**	**100.00**	**100.00**	



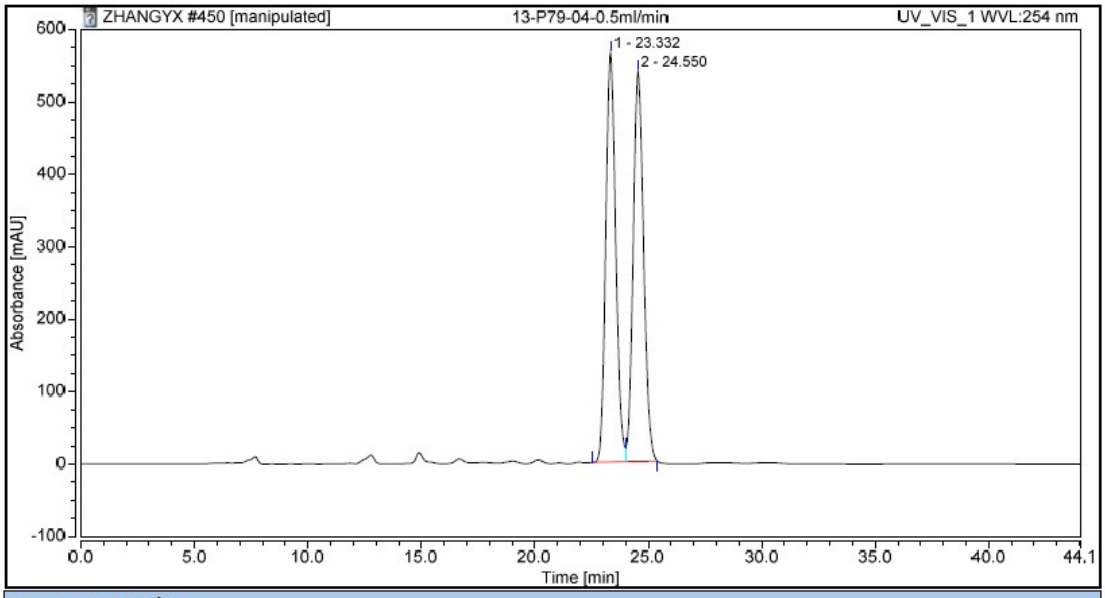
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		21.243	404.152	814.788	91.51	92.86	n.a.
2		28.270	37.484	62.629	8.49	7.14	n.a.
Total:			**441.635**	**877.417**	**100.00**	**100.00**	

(*R*)-4-(Naphthalen-2-ylmethyl)-1, 3-diphenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (5e)

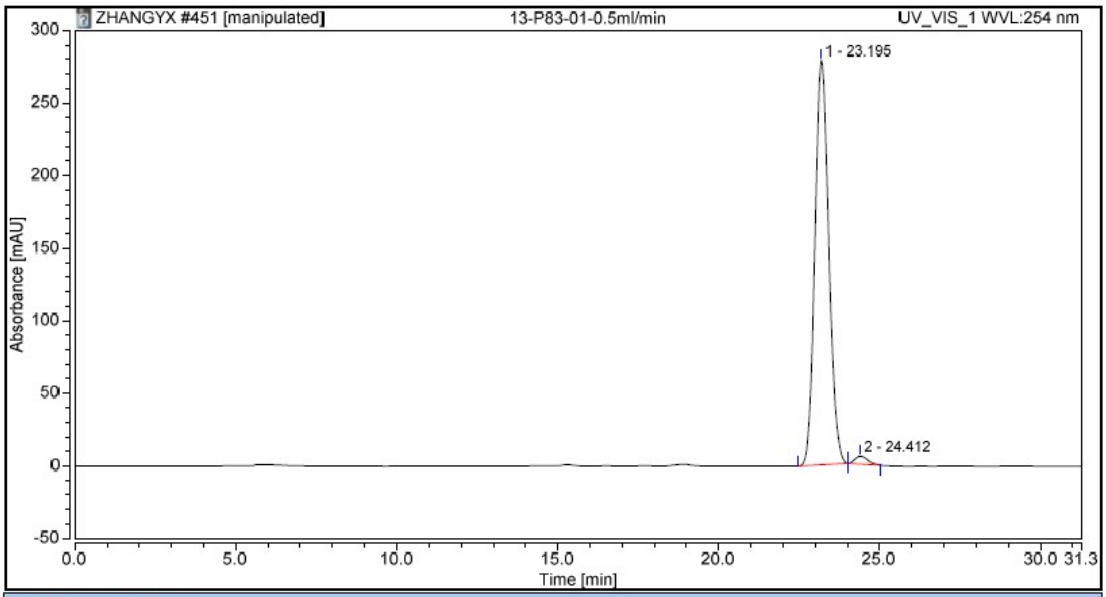


The crude product was purified by flash chromatography to obtain **5e** (colorless oil, 99% yield). $[\alpha]^{28}_{D}$=36.0° (c=1.01, DCM). *Ee* = 97% HPLC condition: CHIRALPAK AD-H. Hexane/i-PrOH eluent (80:20 ratio, 0.5 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 23.2 (major) and 24.4 (minor). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (d, J = 8.0 Hz, 2H), 7.69-7.61 (m, 1H), 7.60-7.26 (m, 11H), 7.24-7.17 (m, 4H), 7.16-7.04 (m, 3H), 6.99 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 3.81 (d, J = 13.6 Hz, 1H), 3.64 (d, J = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 156.3, 137.1, 136.3, 133.1, 132.5, 131.6, 131.3, 130.7, 130.4, 129.1, 128.9, 128.8, 128.6, 128.0, 127.8, 127.6, 127.4, 127.3, 126.0, 125.9, 125.7, 120.0, 108.7, 63.8, 39.5. IR ν_{max} (film) cm^{-1} 3056, 2921, 1710, 1594, 1492, 1126, 734, 690. HRMS (ESI) for $C_{32}H_{24}N_2OS$: calculated $[M+H]^+$, 485.1688. Found, 485.1679.



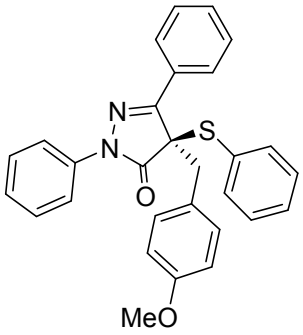
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		23.332	285.841	565.775	49.96	51.23	n.a.
2		24.550	286.339	538.661	50.04	48.77	n.a.
Total:			**572.181**	**1104.436**	**100.00**	**100.00**	

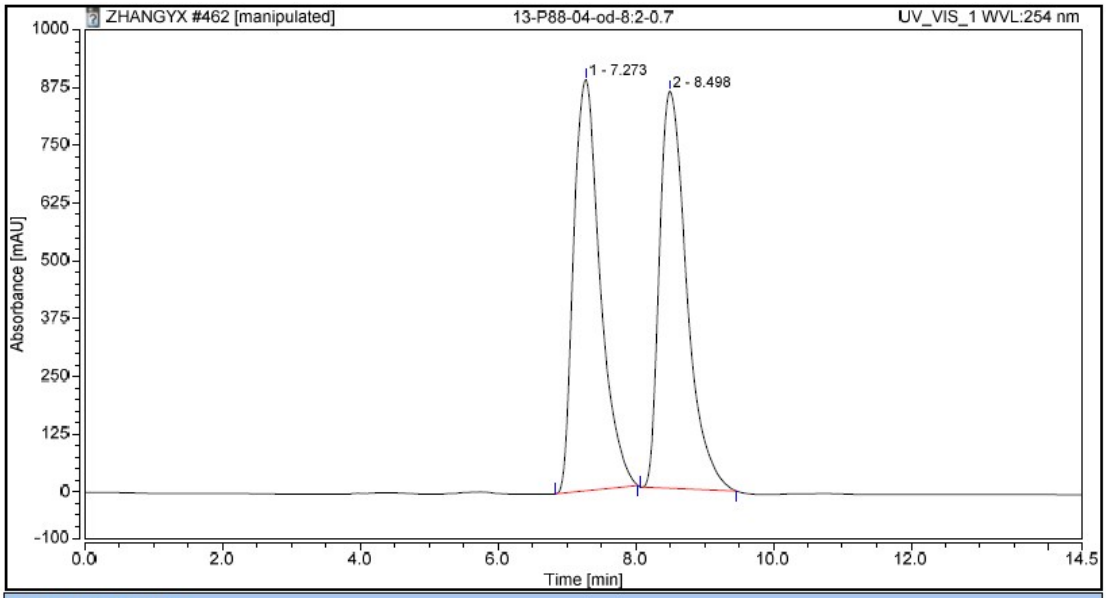


Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		23.195	138.725	278.560	98.30	98.12	n.a.
2		24.412	2.395	5.344	1.70	1.88	n.a.
Total:			**141.120**	**283.904**	**100.00**	**100.00**	

(*R*)-4-(4-Methoxybenzyl)-1, 3-diphenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (5f)

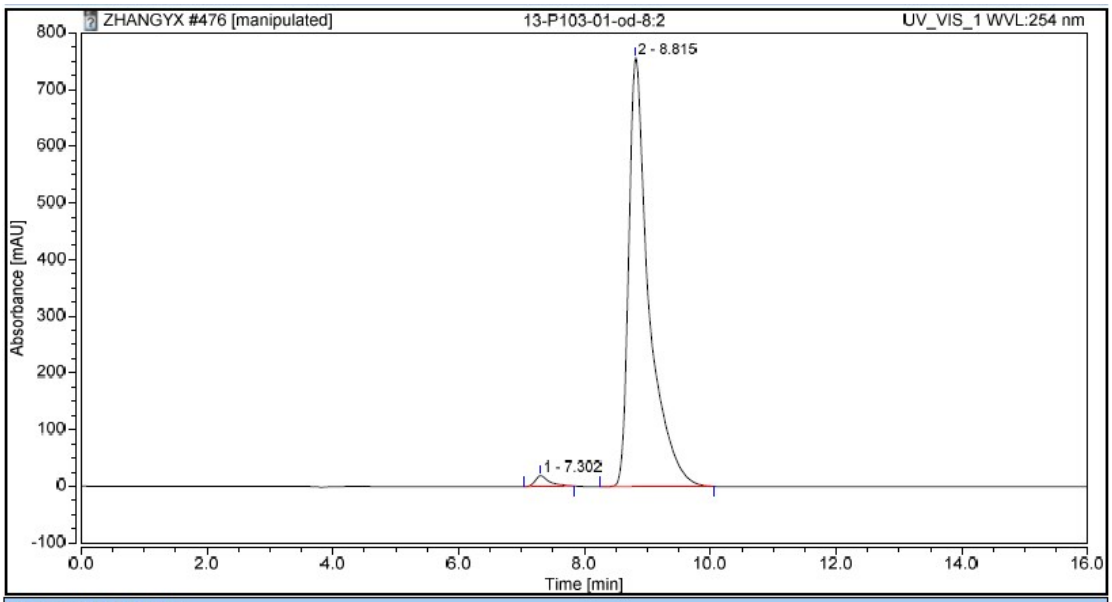


The crude product was purified by flash chromatography to obtain **5f** (colorless oil, 99% yield). $[\alpha]^{27}_{D}$ = 6.9° (c = 0.99, DCM). *Ee* = 97% HPLC condition: CHIRALPAK OD. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 7.3 (minor) and 8.8 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24 (q, J = 3.2 Hz, 2H), 7.56-7.48 (m, 3H), 7.39-7.32 (m, 4H), 7.29-7.17 (m, 3H), 7.11 (q, J = 8.0 Hz, 3H), 6.76 (d, J = 8.8 Hz, 2H), 6.54 (d, J = 8.8 Hz, 2H), 3.64 (s, 3H), 3.59 (d, J = 13.6 Hz, 1H), 3.46 (d, J = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.5, 158.8, 156.3, 137.2, 136.2, 131.2, 130.69, 130.64, 130.3, 129.0, 128.9, 128.7, 128.1, 127.1, 126.0, 125.7, 120.0, 113.7, 63.9, 55.1, 38.7. IR ν_{max} (film) cm^{-1} 3059, 2960, 1711, 1595, 1510, 1492, 1250, 1026, 749, 688. HRMS (ESI) for $C_{29}H_{24}N_2O_2S$: calculated $[M+H]^+$, 465.1637. Found, 465.1629.



Integration Results

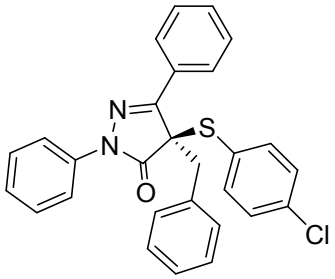
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		7.273	396.868	889.821	50.17	50.88	n.a.
2		8.498	394.228	859.001	49.83	49.12	n.a.
Total:			**791.096**	**1748.822**	**100.00**	**100.00**	



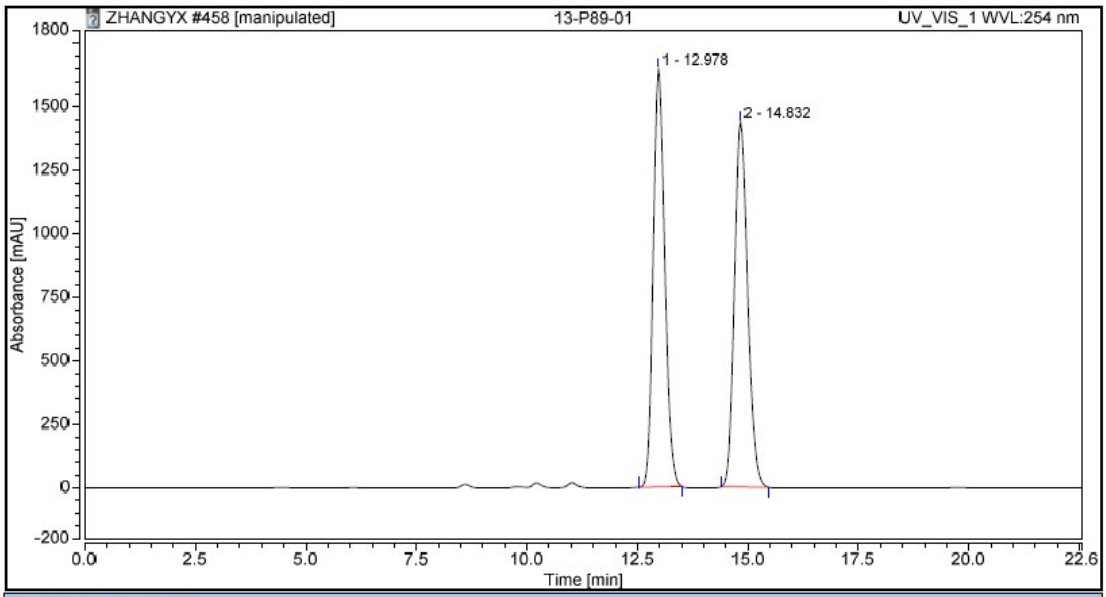
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		7.302	4.903	18.907	1.72	2.44	n.a.
2		8.815	280.599	756.682	98.28	97.56	n.a.
Total:			**285.502**	**775.589**	**100.00**	**100.00**	

(*R*)-4-benzyl-1, 3-diphenyl-4-((4-chlorophenyl)thio) -1*H*-pyrazol-5(4*H*)-one (5g)

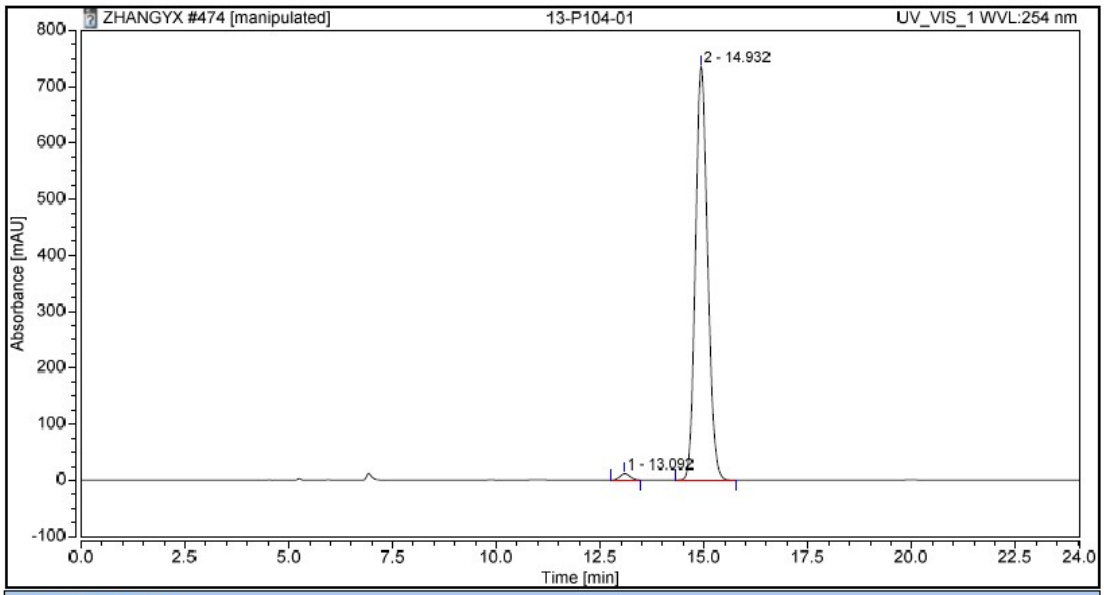


The crude product was purified by flash chromatography to obtain **5g** (colorless oil, 94% yield). $[\alpha]^{27}_{D}$=25.6° (c=1.00, DCM). *Ee* = 97% HPLC condition： CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 13.1 (minor) and 14.9 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.24-8.17 (m, 2H), 7.58-7.48 (m, 3H), 7.35 (dd, *J* = 8.4 Hz, 1.2 Hz, 2H), 7.29 (t, *J* = 8.4 Hz, 4H), 7.15 (t, *J* = 7.2 Hz, 1H), 7.07 (d, *J* = 8.4 Hz, 3H), 7.02 (t, *J* = 7.2 Hz, 2H), 6.84 (d, *J* = 7.2 Hz, 2H), 3.63 (d, *J* = 13.2 Hz, 1H), 3.50 (d, *J* = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 155.9, 137.4, 136.99, 136.97, 133.8, 130.93, 130.81, 129.5, 129.3, 129.0, 128.8, 128.4, 127.6, 127.0, 126.5, 125.9, 119.9, 63.8, 39.4. IR ν_{max} (film) cm^{-1} 3061, 2921, 1711, 1595, 1493, 1131, 1013, 822, 756, 723, 689. HRMS (ESI) for $C_{28}H_{21}ClN_2OS$: calculated $[M+H]^+$, 469.1141. Found, 469.1134.



Integration Results

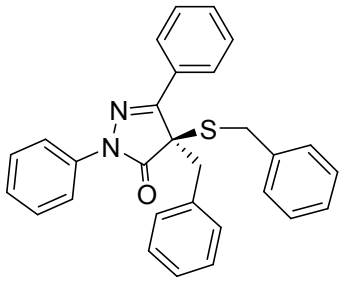
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		12.978	497.053	1644.420	49.98	53.37	n.a.
2		14.832	497.434	1436.730	50.02	46.63	n.a.
Total:			**994.487**	**3081.149**	**100.00**	**100.00**	



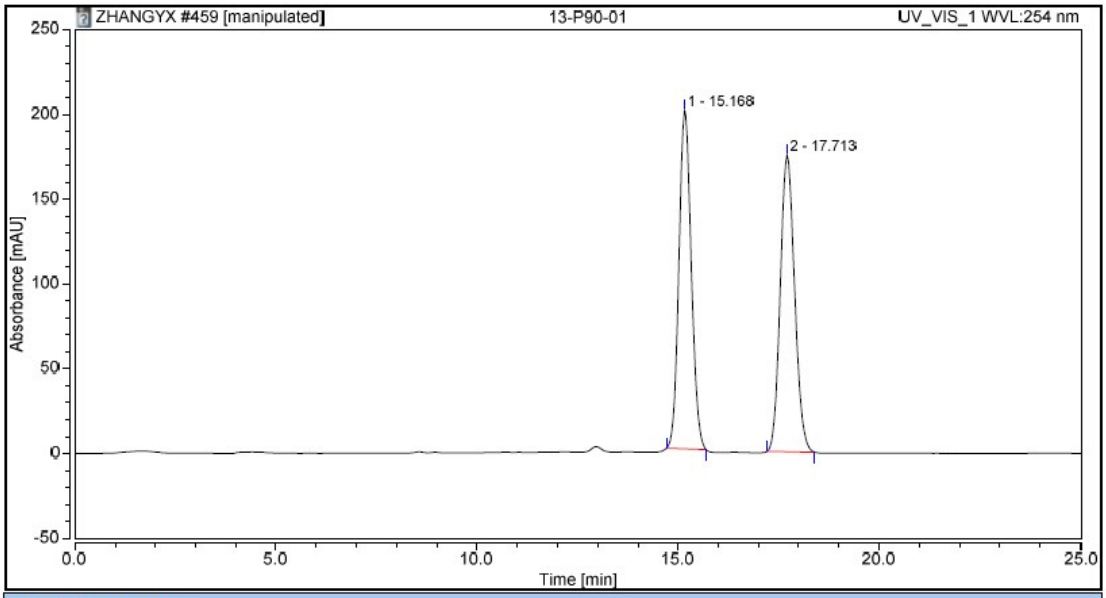
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		13.092	3.255	11.529	1.28	1.54	n.a.
2		14.932	250.084	735.212	98.72	98.46	n.a.
Total:			**253.339**	**746.741**	**100.00**	**100.00**	

(*R*)-4-Benzyl-1, 3-diphenyl-4-(benzylthio) -1*H*-pyrazol-5(4*H*)-one (5h)

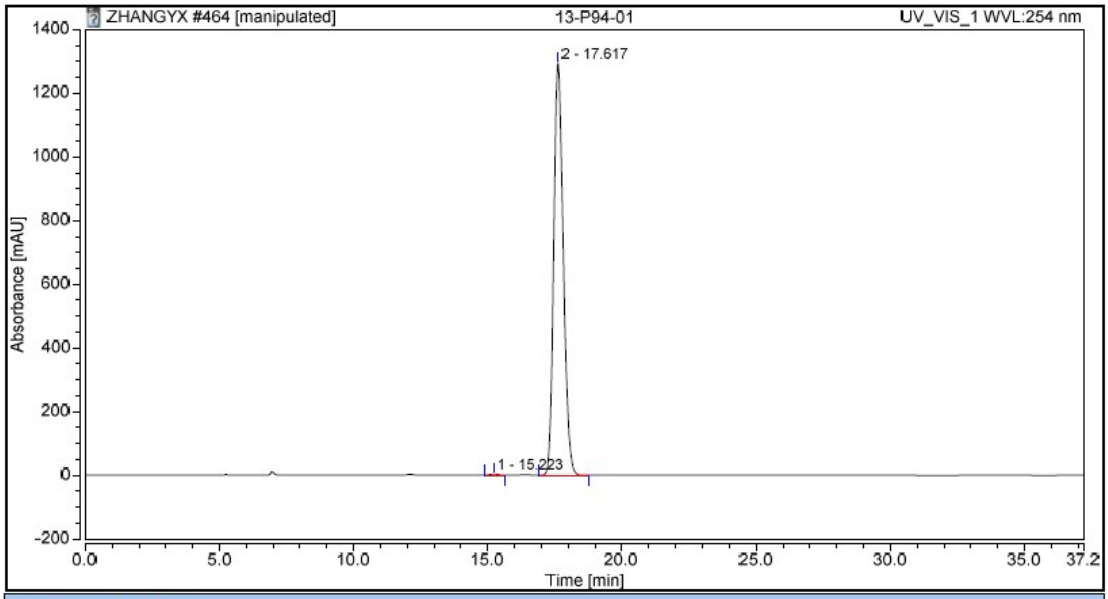


The crude product was purified by flash chromatography to obtain **5h** (colorless oil, 91% yield). $[\alpha]^{27}_{D}$ =48.2° (c=0.99, DCM). *Ee* = 99% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 15.2 (minor) and 17.6 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (dd, J = 8.0 Hz, 1.6 Hz, 2H), 7.70 (d, J = 8.0 Hz, 2H), 7.55-7.45 (m, 3H), 7.36 (t, J = 8.0 Hz, 2H), 7.22-6.97 (m, 9H), 6.82 (d, J = 6.8 Hz, 2H), 3.76 (q, J = 12.4 Hz, 2H), 3.54 (d, J = 13.6 Hz, 1H), 3.43 (d, J = 13.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.6, 155.9, 137.5, 135.4, 133.7, 130.9, 130.8, 129.5, 129.3, 128.9, 128.8, 128.6, 128.3, 127.59, 127.56, 126.9, 125.6, 119.5, 60.2, 40.8, 34.6. IR ν_{max} (film) cm^{-1} 3060, 3029, 2962, 1709, 1595, 1492, 1383, 1127, 1025, 755, 689. HRMS (ESI) for $C_{29}H_{24}N_2OS$: calculated $[M+H]^+$, 449.1688. Found, 449.1680.



Integration Results

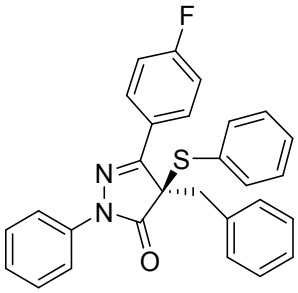
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		15.168	70.816	199.563	49.51	53.30	n.a.
2		17.713	72.224	174.869	50.49	46.70	n.a.
Total:			**143.040**	**374.433**	**100.00**	**100.00**	



Integration Results

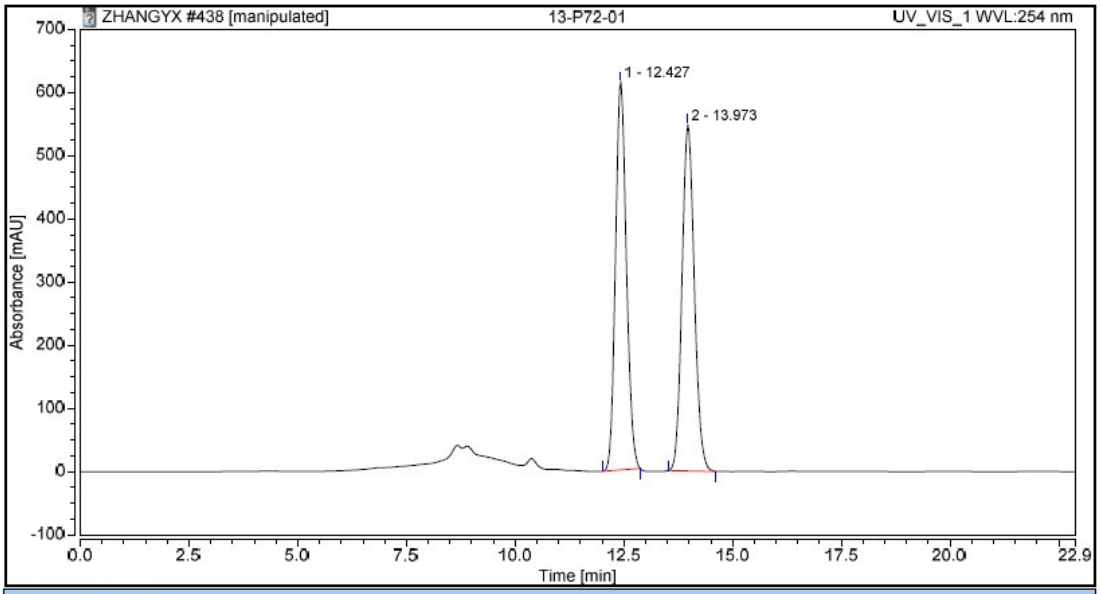
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		15.223	1.310	3.936	0.24	0.30	n.a.
2		17.617	535.145	1293.792	99.76	99.70	n.a.
Total:			**536.455**	**1297.728**	**100.00**	**100.00**	

(*R*)-4-Benzyl-3-(4-fluorophenyl)-1-phenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (5i)



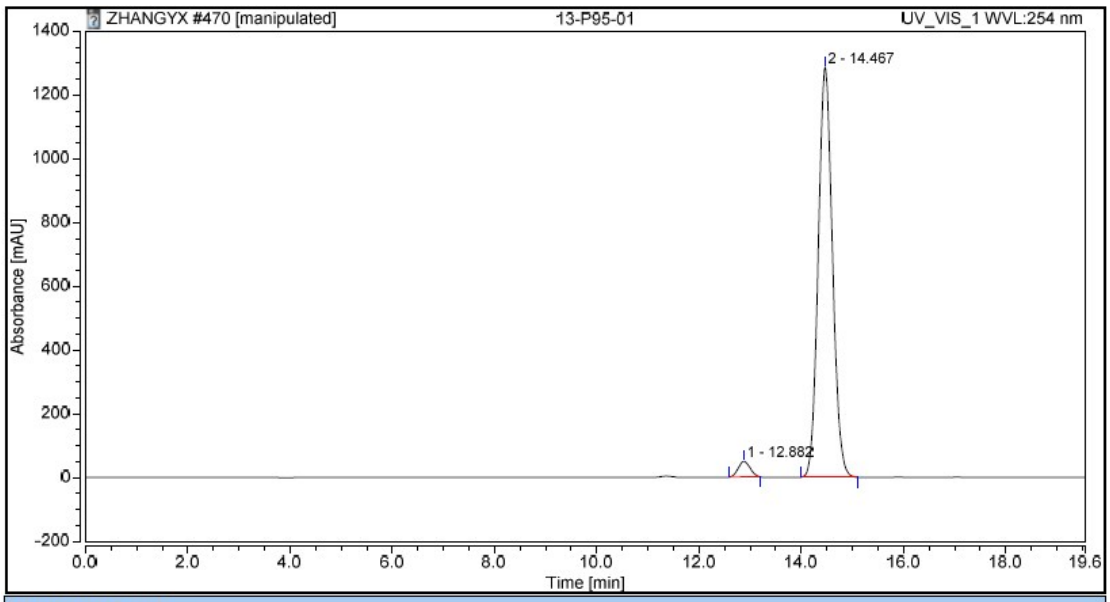
The crude product was purified by flash chromatography to obtain **5i** (white solid, 88% yield).

M. p.: 118-123 ˚C. $[\alpha]^{28}_{D}$ = 17.2° (c = 0.99, DCM). *Ee* = 94% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 12.9 (minor) and 14.5 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (dd, J = 8.8 Hz,5.6 Hz, 2H), 7.38-7.29 (m, 4H), 7.29-7.17 (m, 5H), 7.16-7.00 (m, 6H), 6.84 (d, J = 7.2 Hz, 2H), 3.66 (d, J = 13.2 Hz, 1H), 3.44 (d, J = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 165.3, 162.8, 155.2, 137.0, 136.1, 133.9, 130.5, 129.5, 129.2(J = 8.3 Hz), 129.1, 128.7, 128.4, 127.9, 127.4 (J = 3.4 Hz), 126.7 (J = 176 Hz), 120.0, 116.1 (J = 21.6 Hz), 63.7, 39.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -108.8 (m). IR ν_{max} (film) cm^{-1} 3068, 3030, 2922, 1704, 1595, 1494, 1226, 1099, 1067, 1027, 1007, 879, 749, 687. HRMS (ESI) for $C_{28}H_{21}FN_2OS$: calculated $[M+H]^+$, 453.1437. Found, 453.1434.



Integration Results

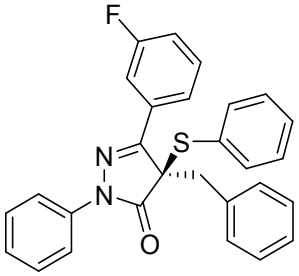
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		12.427	177.976	614.031	49.75	52.81	n.a.
2		13.973	179.783	548.709	50.25	47.19	n.a.
Total:			**357.759**	**1162.740**	**100.00**	**100.00**	



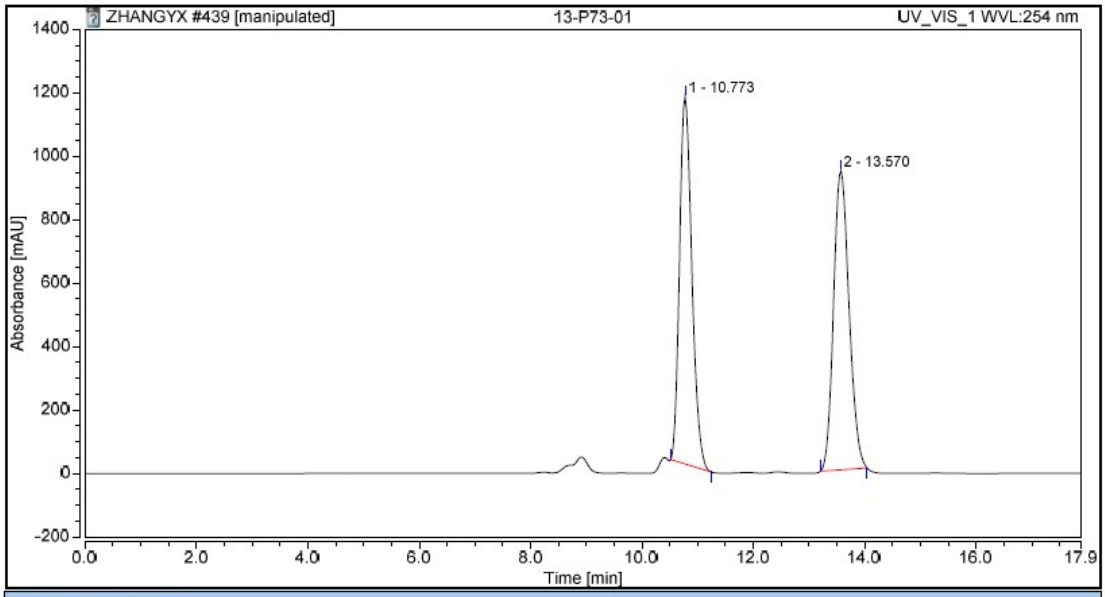
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		12.882	13.044	48.957	3.05	3.67	n.a.
2		14.467	414.037	1285.231	96.95	96.33	n.a.
Total:			**427.081**	**1334.188**	**100.00**	**100.00**	

(*R*)-4-Benzyl-3-(3-fluorophenyl)-1-phenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (5j)

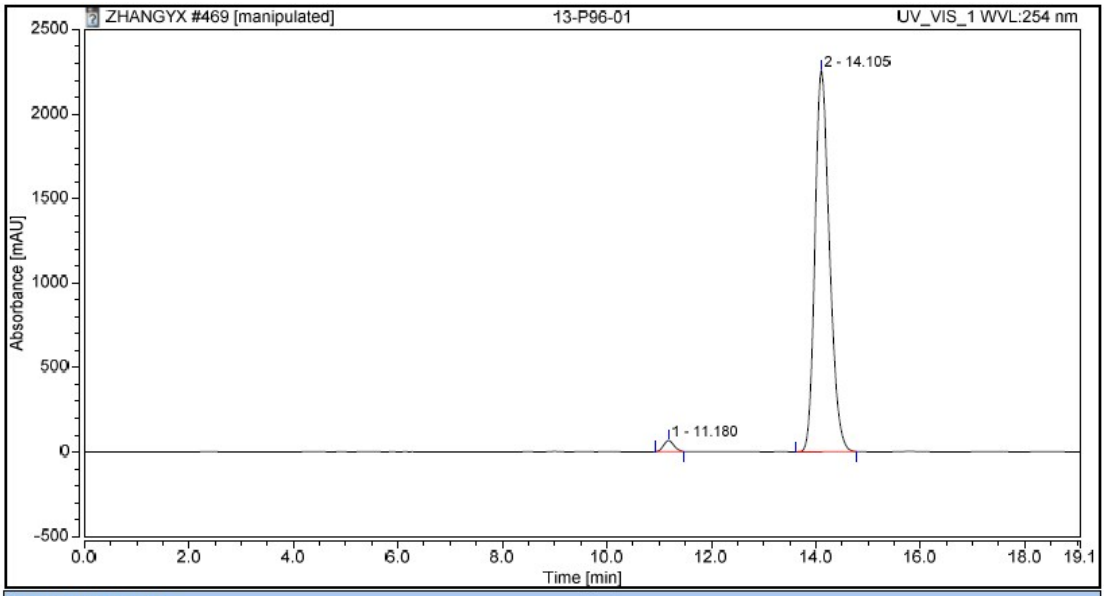


The crude product was purified by flash chromatography to obtain **5j** (colorless oil, 95% yield). $[\alpha]^{28}_{D}$=16.5° (c = 1.00, DCM). *Ee* = 96% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 11.2 (minor) and 14.1 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, J = 8.0 Hz, 1H), 7.89 (d, J = 10.0 Hz, 1H), 7.51 (q, J = 8.0 Hz, 1H), 7.38-7.18 (m, 8H), 7.16-7.00 (m, 6H), 6.85 (d, J = 7.2 Hz, 2H), 3.66 (d, J = 13.6 Hz, 1H), 3.47 (d, J = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.4, 164.2, 161.8, 155.1 (J = 3.0 Hz), 137.0, 136.2, 133.8, 133.2 (J = 8.0 Hz), 130.52 (J = 8.0 Hz), 130.51, 129.5, 129.1, 128.7, 128.5, 127.9, 126.8 (J = 169.2 Hz), 122.9 (J = 2.9 Hz), 120.1, 117.7 (J = 21.3 Hz), 113.8 (J = 23.5 Hz), 63.7, 39.5; ^{19}F NMR (376 MHz, $CDCl_3$): δ -111.4 (m). IR ν_{max} (film) cm^{-1} 3062, 2916, 1714, 1589, 1487, 1228, 1083, 1069, 1025, 976, 875, 752, 690. HRMS (ESI) for $C_{28}H_{21}FN_2OS$: calculated $[M+H]^+$, 453.1437. Found, 453.1428.



Integration Results

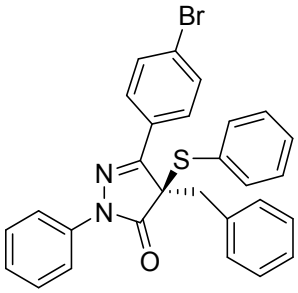
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		10.773	296.332	1158.741	49.46	55.13	n.a.
2		13.570	302.773	943.095	50.54	44.87	n.a.
Total:			**599.105**	**2101.836**	**100.00**	**100.00**	



Integration Results

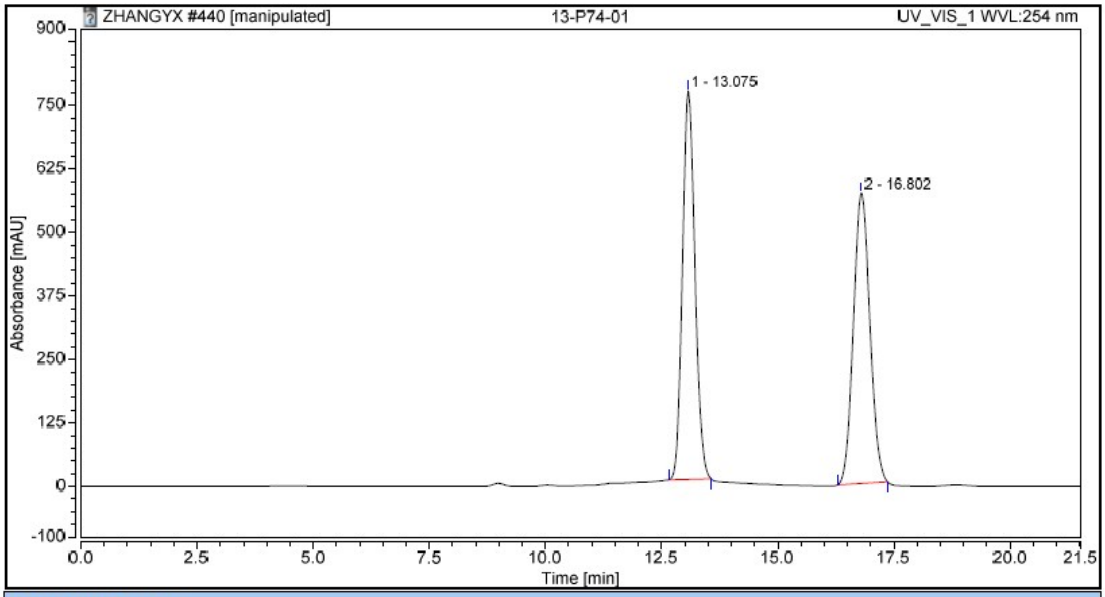
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		11.180	14.723	64.748	1.98	2.79	n.a.
2		14.105	728.816	2256.295	98.02	97.21	n.a.
Total:			**743.539**	**2321.043**	**100.00**	**100.00**	

(*R*)-4-Benzyl-3-(4-bromophenyl)-1-phenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (5k)



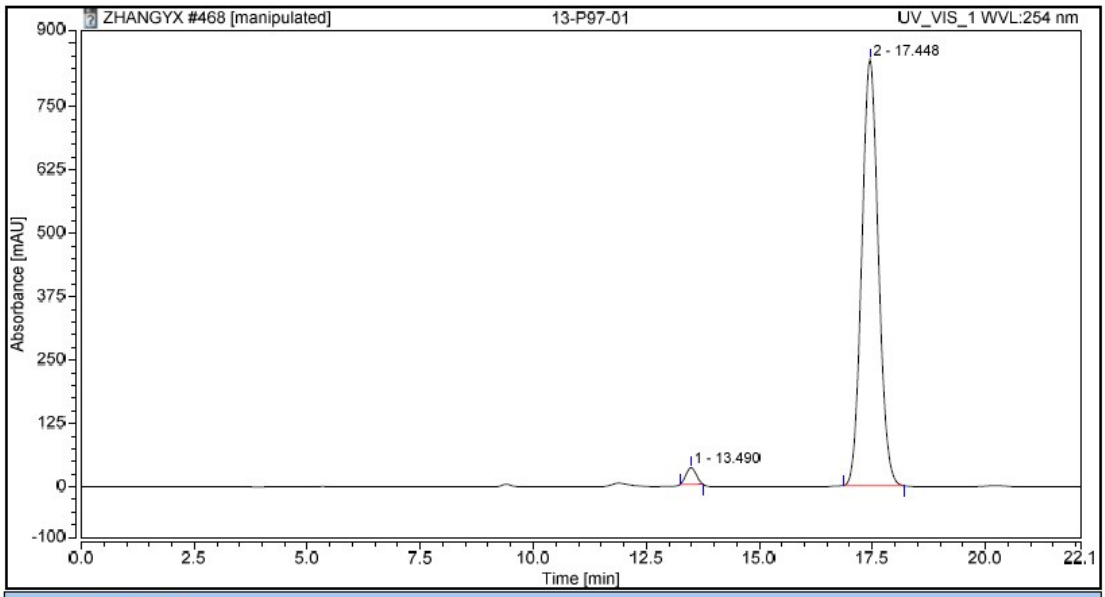
The crude product was purified by flash chromatography to obtain **5k** (white solid, 95% yield).

M. p.: 147-151 ℃. $[\alpha]^{28}_{D} = 41.6^{\circ}$ (c = 1.01, DCM). *Ee* = 95% HPLC condition： CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) = 13.5 (minor) and 17.5 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.8 Hz, 2H), 7.66 (d, J = 8.8 Hz, 2H), 7.36-7.19 (m, 7H), 7.16-7.00 (m, 6H), 6.85 (d, J = 6.8 Hz, 2H), 3.66 (d, J = 13.2 Hz, 1H), 3.45 (d, J = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.3, 155.2, 136.9, 136.1, 133.8, 132.2, 130.5, 130.0, 129.5, 129.1, 128.7, 128.48, 128.46, 127.8, 127.6, 125.9, 125.1, 120.1, 63.6, 39.5. IR ν_{max} (film) cm^{-1} 3060, 2921, 2850, 1706, 1589, 1491, 1378, 1181, 1127, 1023, 955, 748, 727, 687. HRMS (ESI) for $C_{28}H_{21}BrN_2OS$: calculated $[M+H]^+$, 513.0636. Found, 513.0630.



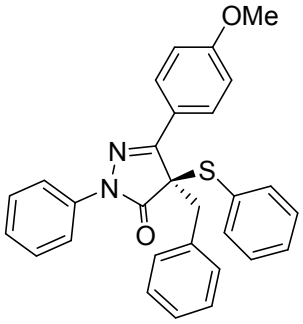
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		13.075	237.644	764.386	50.37	57.22	n.a.
2		16.802	234.159	571.533	49.63	42.78	n.a.
Total:			**471.804**	**1335.919**	**100.00**	**100.00**	



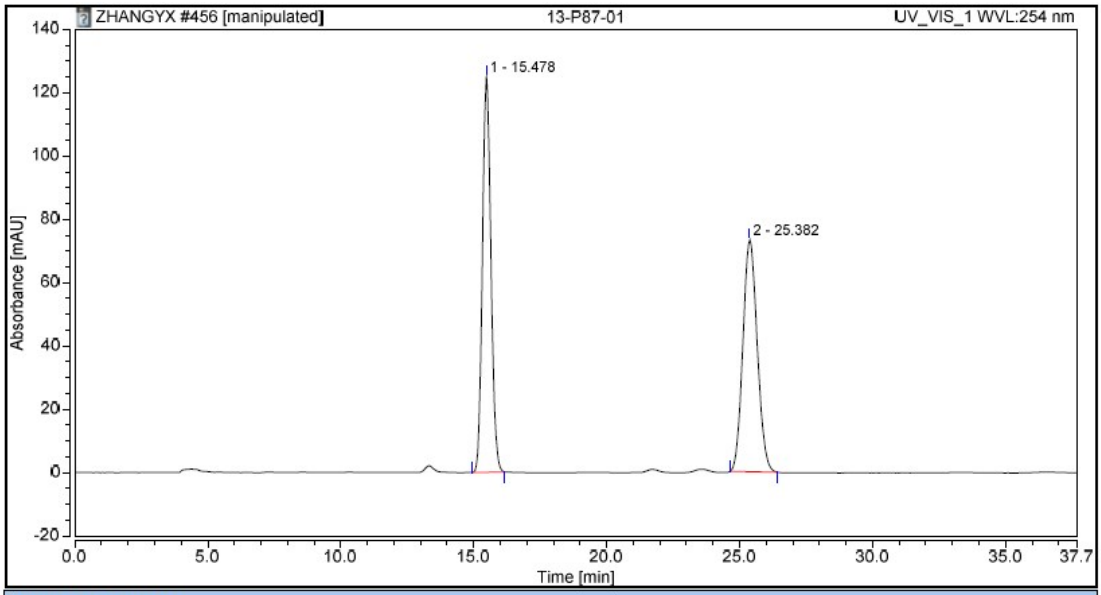
Integration Results							
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		13.490	8.571	32.992	2.34	3.78	n.a.
2		17.448	357.980	840.906	97.66	96.22	n.a.
Total:			366.551	873.898	100.00	100.00	

(*R*)-4-Benzyl-3-(4-methoxyphenyl)-1-phenyl-4-(phenylthio) -1*H*-pyrazol-5(4*H*)-one (5l)



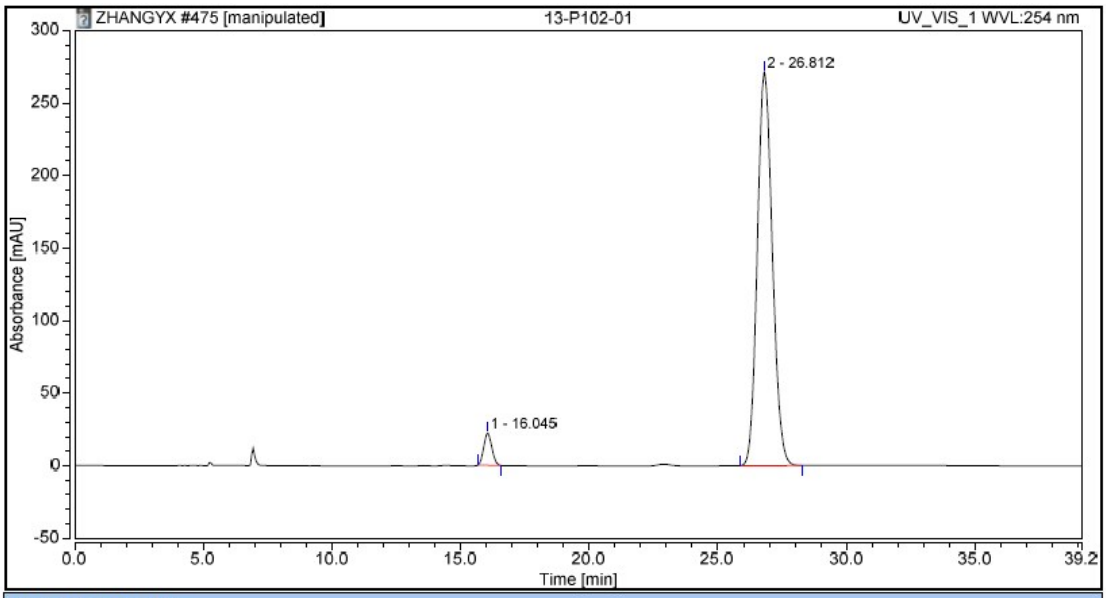
The crude product was purified by flash chromatography to obtain **5l** (white solid, 99% yield).

M. p.: 148-152 ℃. $[\alpha]^{26}_{D}$=54.2° (c = 1.00, DCM). *Ee* = 92% HPLC condition: CHIRALPAK AD-H. Hexane/*i*-PrOH eluent (80:20 ratio, 0.7 mL/min flow rate) with 254 nm wave length UV. Retention time (min) =16.0 (minor) and 26.8 (major). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.18 (d, J = 8.8 Hz, 2H), 7.39-7.30 (m, 4H), 7.25-7.17 (m, 3H), 7.14-6.99 (m, 8H), 6.87 (d, J = 6.8 Hz, 2H), 3.94 (s, 3H), 3.63 (d, J = 13.2 Hz, 1H), 3.48 (d, J = 13.6 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 172.2, 161.4, 155.9, 137.2, 136.2, 134.1, 130.3, 129.6, 129.0, 128.7, 128.6, 128.3, 128.2, 127.5, 125.6, 123.8, 120.0, 114.2, 63.8, 55.5, 39.7. IR ν_{max} (film) cm^{-1} 3061, 2963, 2927, 1703, 1598, 1254, 1126, 1025, 837, 748, 689. HRMS (ESI) for $C_{29}H_{24}N_2O_2S$: calculated $[M+H]^+$, 465.1637. Found, 465.1634.



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		15.478	46.158	125.062	50.20	63.06	n.a.
2		25.382	45.787	73.275	49.80	36.94	n.a.
Total:			**91.945**	**198.337**	**100.00**	**100.00**	



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount mg/l
n.a.	PhMe	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
1		16.045	8.010	22.136	4.18	7.55	n.a.
2		26.812	183.765	271.124	95.82	92.45	n.a.
Total:			**191.774**	**293.260**	**100.00**	**100.00**	

Ⅳ. Crystallographic information

Structure Refinement and Crystal Data for **3g**

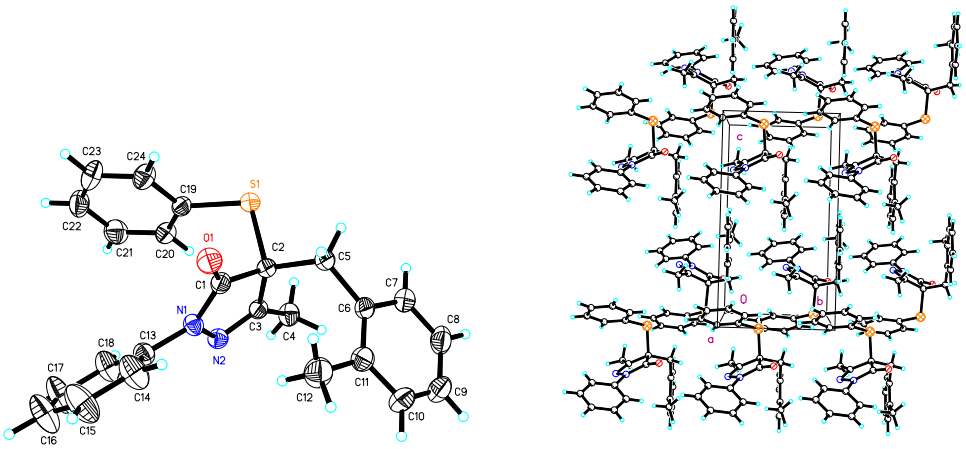


Figure S1. (a) Crystal structure of **3g** (left); (b) Packing model (right). (carbon atoms in this view are depicted with ellipsoids at the 30% probability level)

Table 1. Crystal data and structure refinement for mo_d8v17287_0m.

Identification code	mo_d8v17287_0m	
Empirical formula	C24 H22 N2 O S	
Formula weight	386.49	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 11.4030(5) Å	α= 90°.
	b = 7.0095(3) Å	β= 91.0273(13)°.
	c = 12.9123(6) Å	γ = 90°.
Volume	1031.91(8) $Å^3$	
Z	2	
Density (calculated)	1.244 Mg/m^3	
Absorption coefficient	0.173 mm^{-1}	
F(000)	408	
Crystal size	0.200 x 0.170 x 0.130 mm^3	
Theta range for data collection	3.156 to 25.492°.	
Index ranges	-13<=h<=13, -8<=k<=8, -15<=l<=15	
Reflections collected	19690	
Independent reflections	3804 [R(int) = 0.0312]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.6543	
Refinement method	Full-matrix least-squares on F^2	

Data / restraints / parameters	3804 / 1 / 256
Goodness-of-fit on F^2	1.021
Final R indices [I>2sigma(I)]	R1 = 0.0307, wR2 = 0.0882
R indices (all data)	R1 = 0.0355, wR2 = 0.0945
Absolute structure parameter	0.00(2)
Extinction coefficient	0.022(7)
Largest diff. peak and hole	0.128 and -0.123 e.Å^{-3}

Crystal Data and Structure Refinement for **5l**

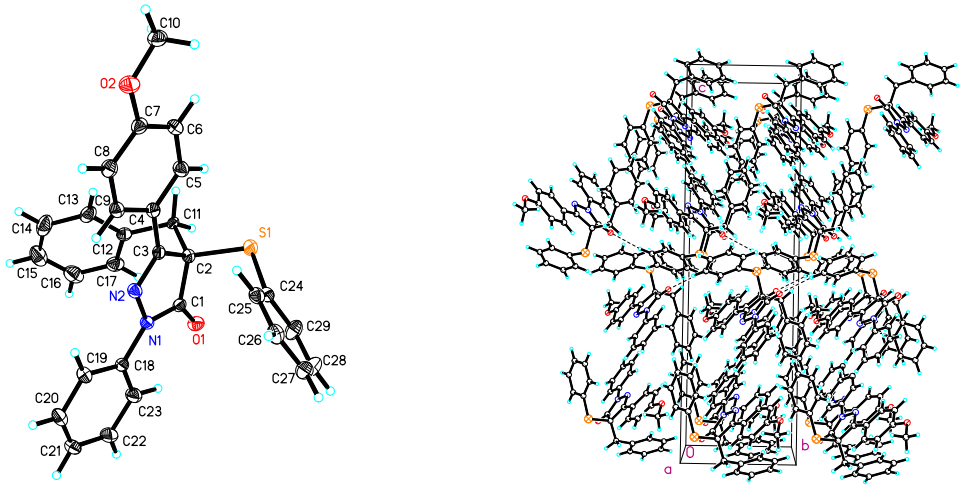


Figure S2. (a) Crystal structure of **5l** (left); (b) Packing model (right). (carbon atoms in this view are depicted with ellipsoids at the 30% probability level)

Table 2. Crystal data and structure refinement for mo_d8v17770_0m.

Identification code	mo_d8v17770_0m	
Empirical formula	C29 H24 N2 O2 S	
Formula weight	464.56	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21	
Unit cell dimensions	a = 10.2478(2) Å	α= 90°.
	b = 8.1523(2) Å	β= 93.4810(10)°.
	c = 28.2987(6) Å	γ = 90°.
Volume	2359.80(9) Å^3	
Z	4	
Density (calculated)	1.308 Mg/m^3	
Absorption coefficient	0.167 mm^{-1}	
F(000)	976	

Crystal size	0.200 x 0.170 x 0.130 mm^3
Theta range for data collection	1.991 to 25.999°.
Index ranges	-12<=h<=12, -9<=k<=10, -34<=l<=34
Reflections collected	38624
Independent reflections	9155 [R(int) = 0.0559]
Completeness to theta = 25.242°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7456 and 0.5383
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	9155 / 1 / 615
Goodness-of-fit on F^2	1.037
Final R indices [I>2sigma(I)]	R1 = 0.0370, wR2 = 0.0945
R indices (all data)	R1 = 0.0415, wR2 = 0.0986
Absolute structure parameter	0.05(3)
Extinction coefficient	n/a
Largest diff. peak and hole	0.271 and -0.304 $e.Å^{-3}$

Ⅴ. References

1 X. Gao, J. Han, L. Wang. *Organic. Letters.* 2015, **17**, 4596.

2 (a) L. A. Carpino, *J. Am. Chem. Soc.* 1958, **80**, 599. (b) S. A. Shiba, N. M. S. Harb, M. A. El-kassaby, M. A. Hassan, Mohsen Abou El-Regal, *Phosphorus, Sulfur, and Silicon and the Related Elements*, 1995, **104**, 15. (c) J. Sun, C. –G.. Yan, Y. Han, *Synthetic Communications*, 2001, **31**, 151. (d) R. V. Hangarge, D. V. Jarikote, M. S. Shingare, *Green Chemistry*, 2002, **4**, 266.

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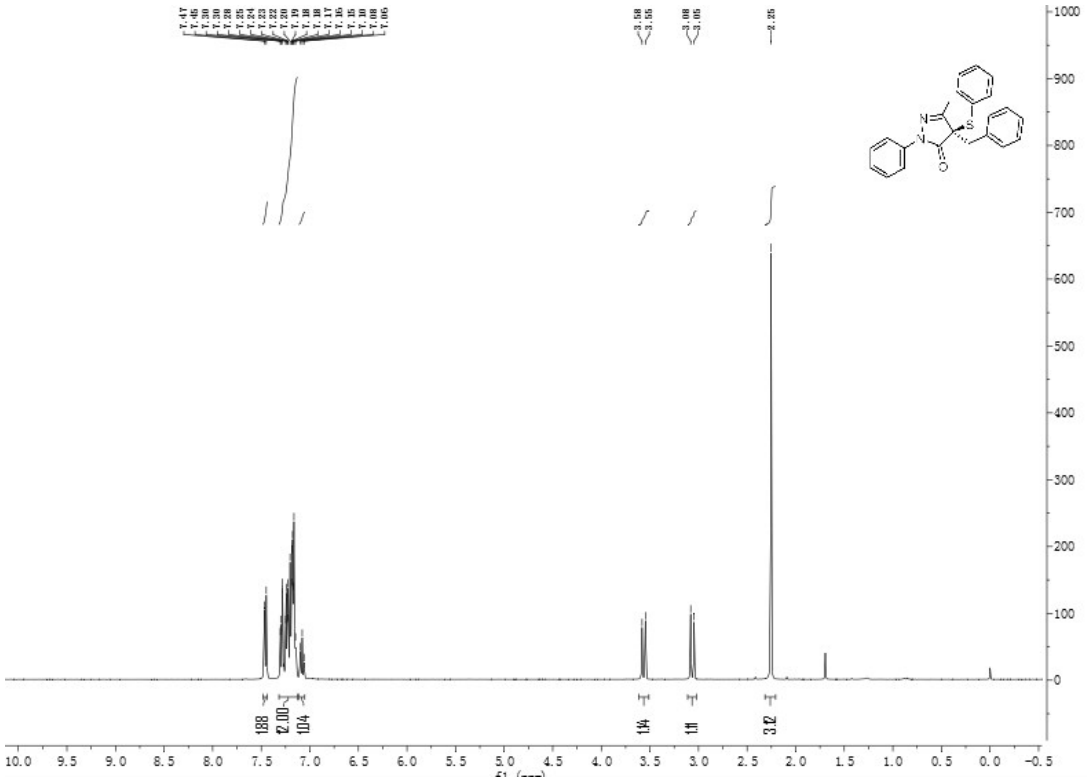
Ⅵ. NMR spectra

^{1}H NMR ($CDCl_3$)



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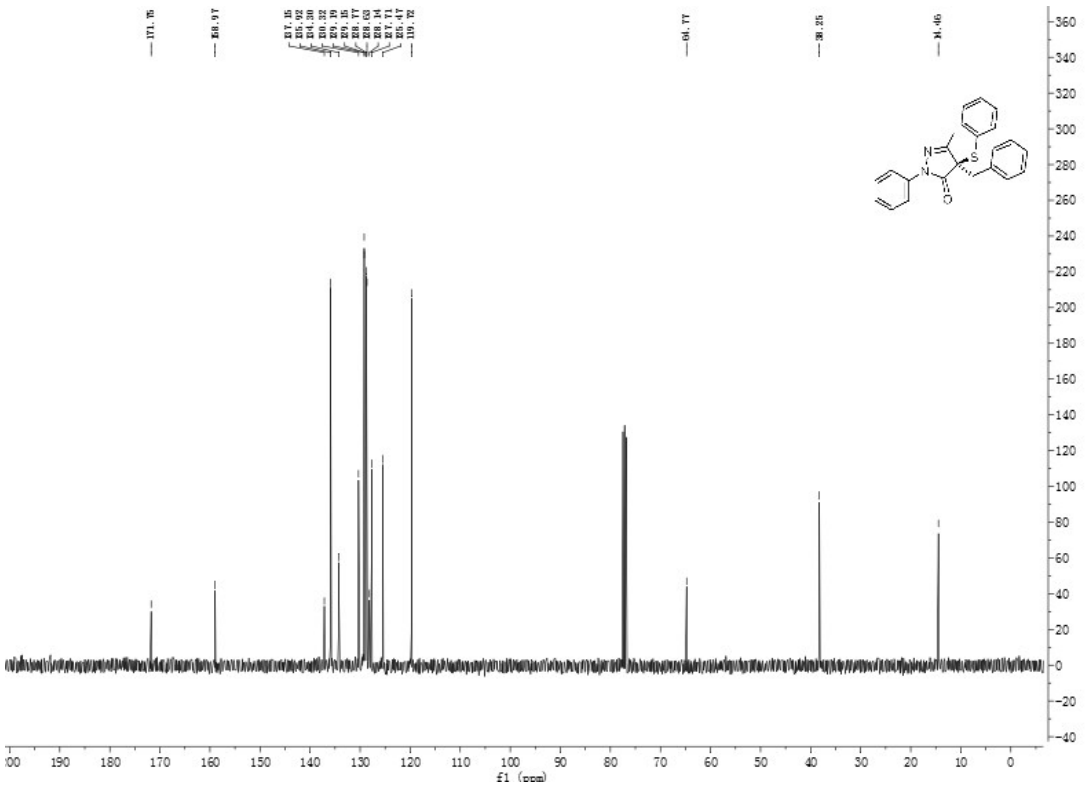

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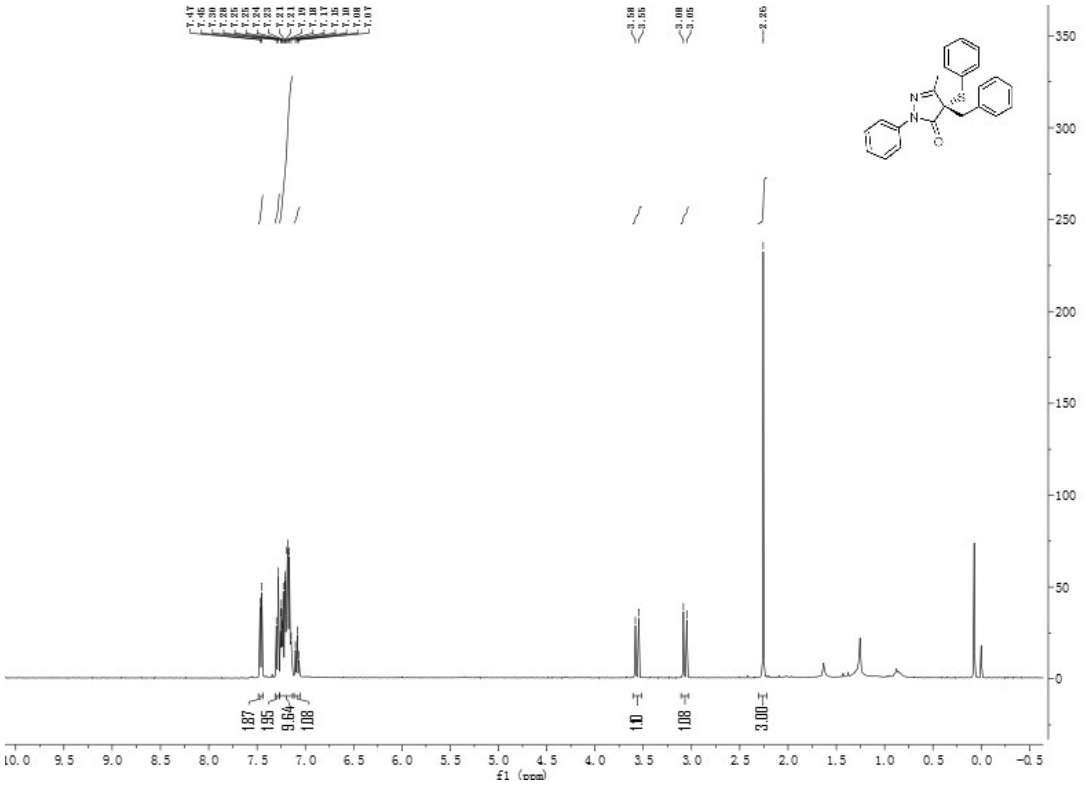

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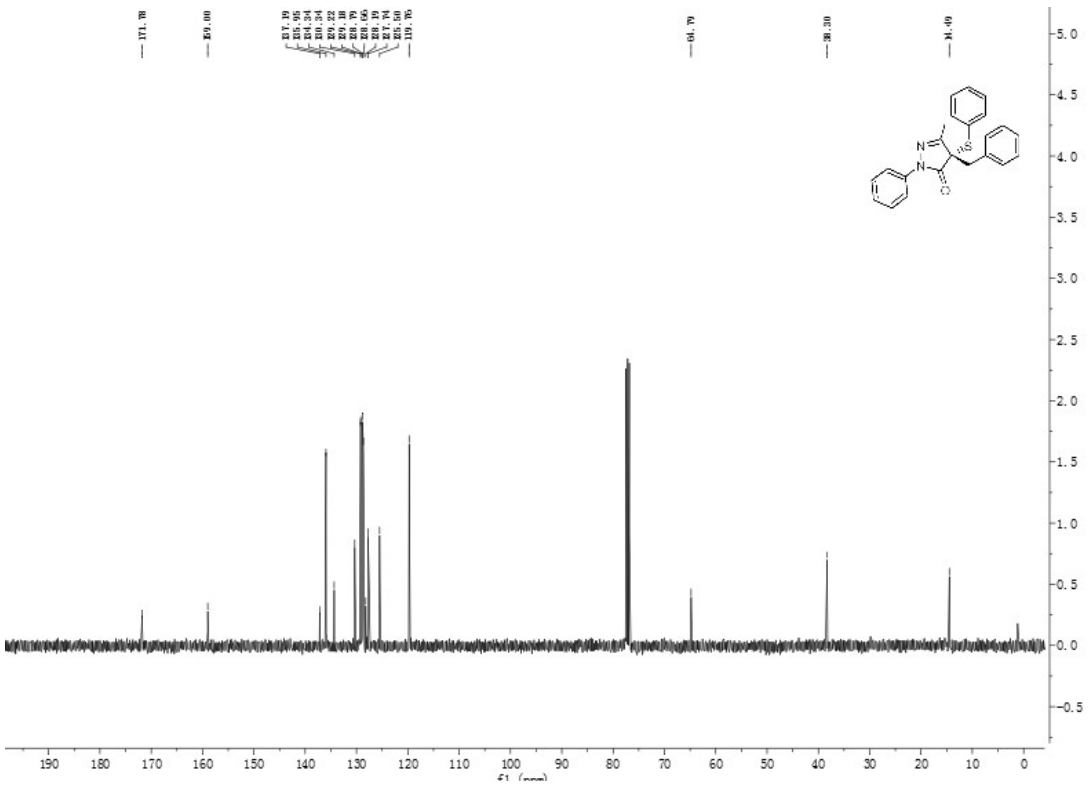

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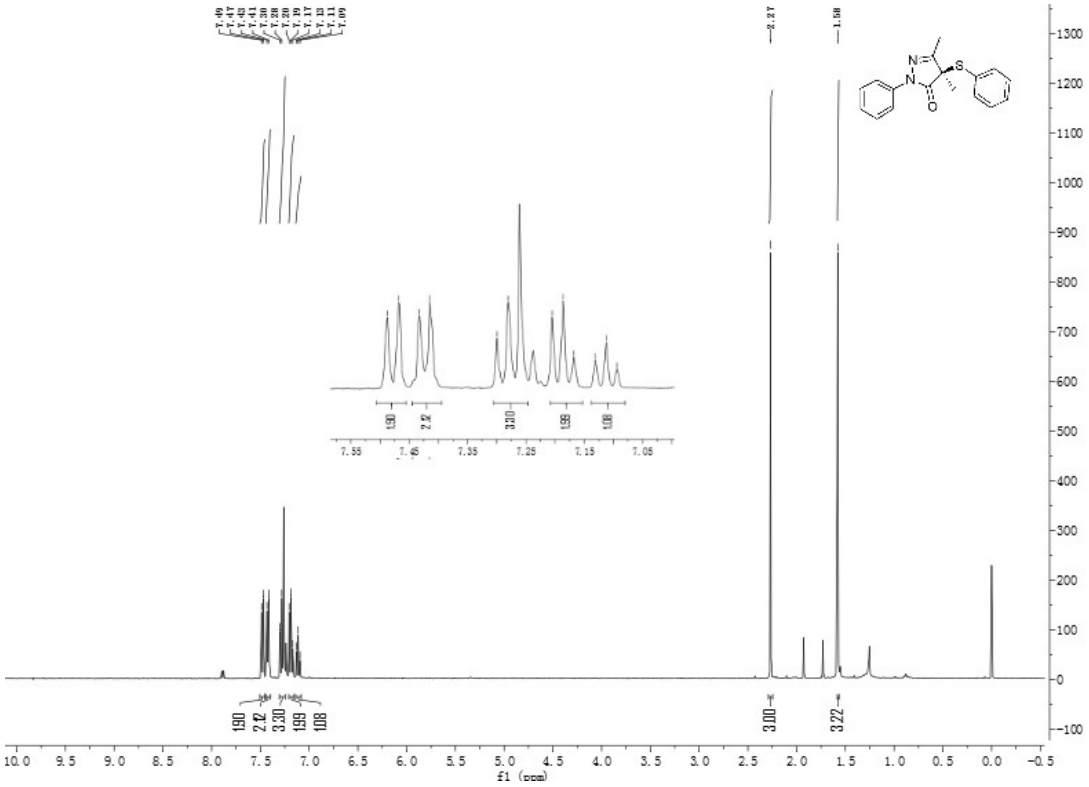

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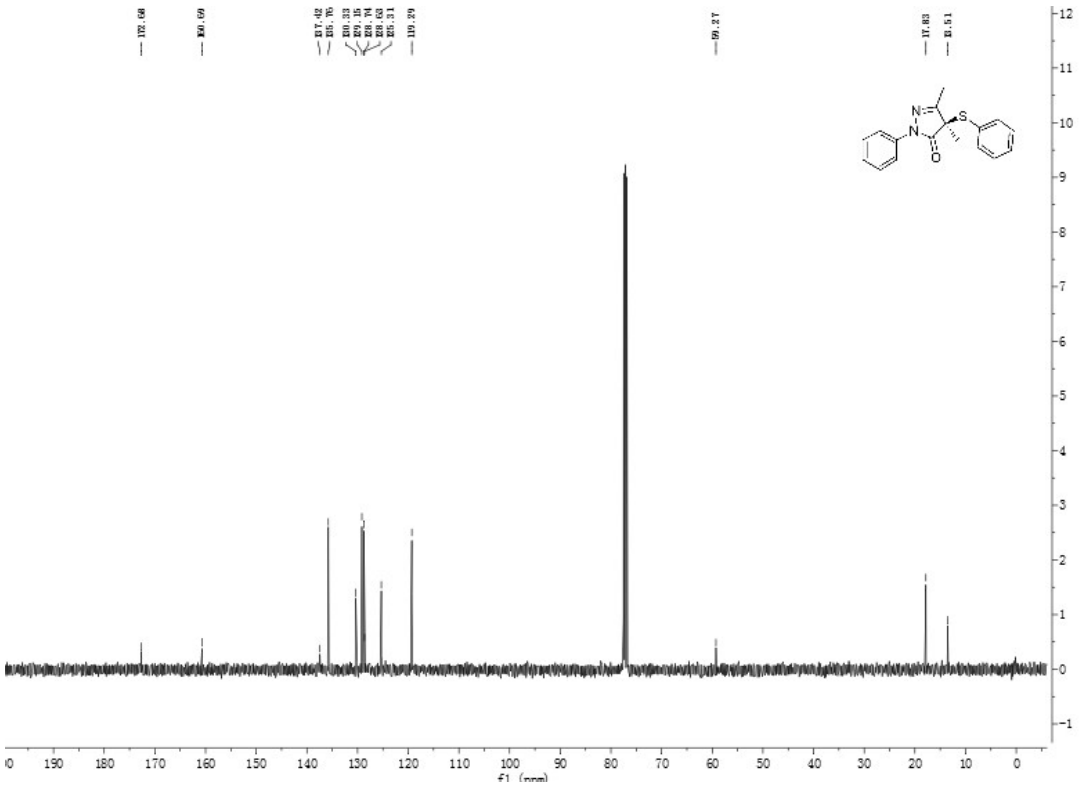

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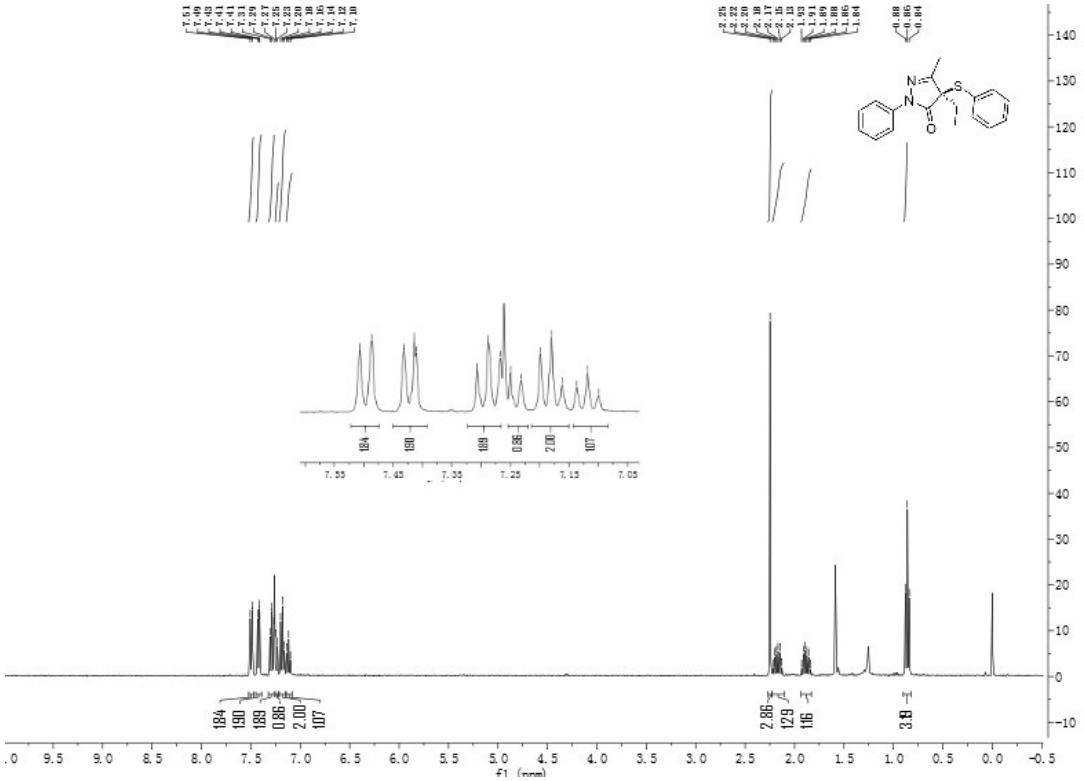

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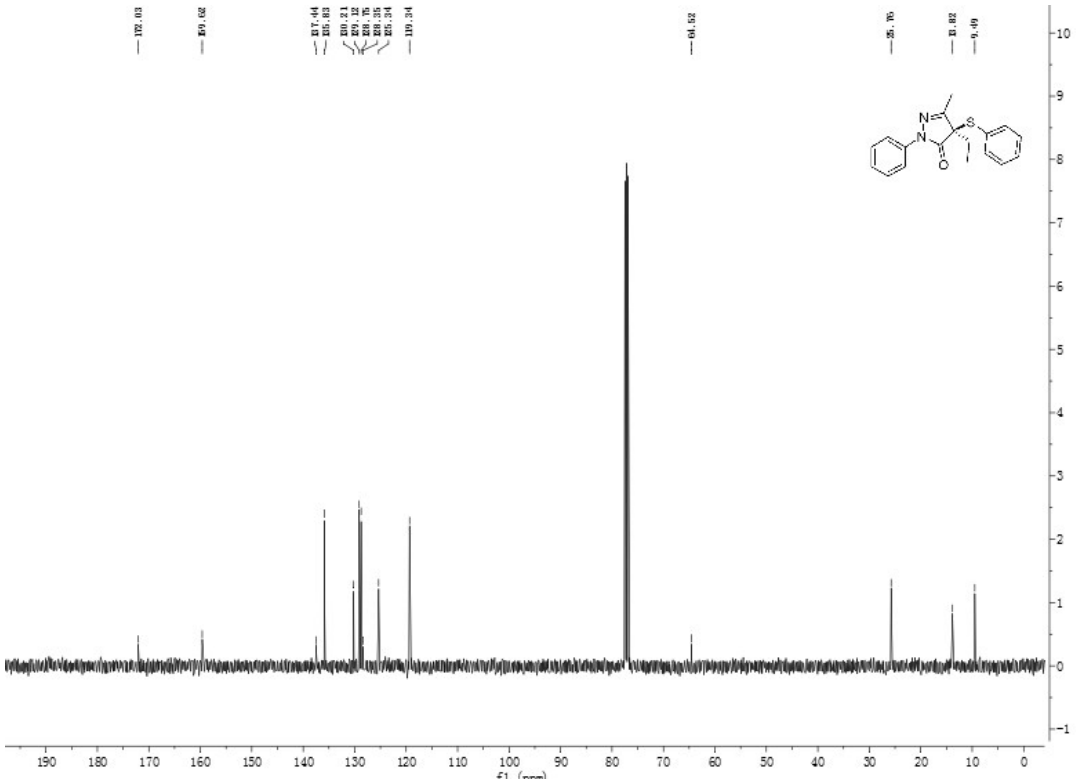

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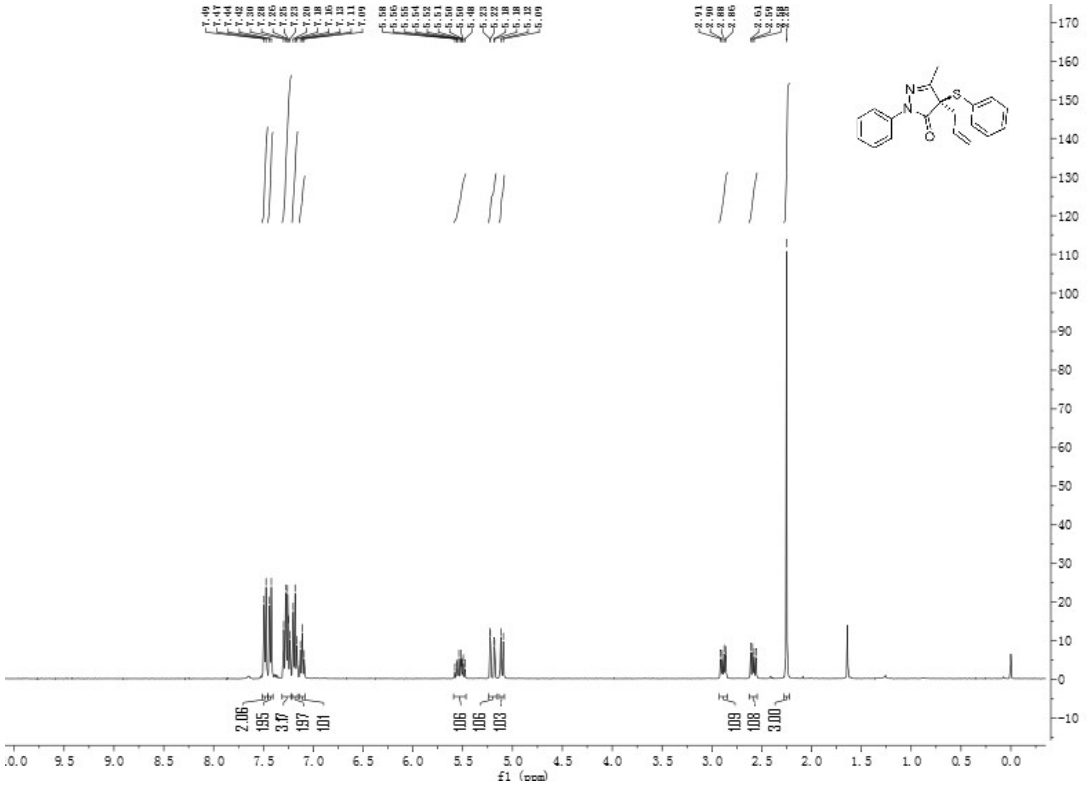

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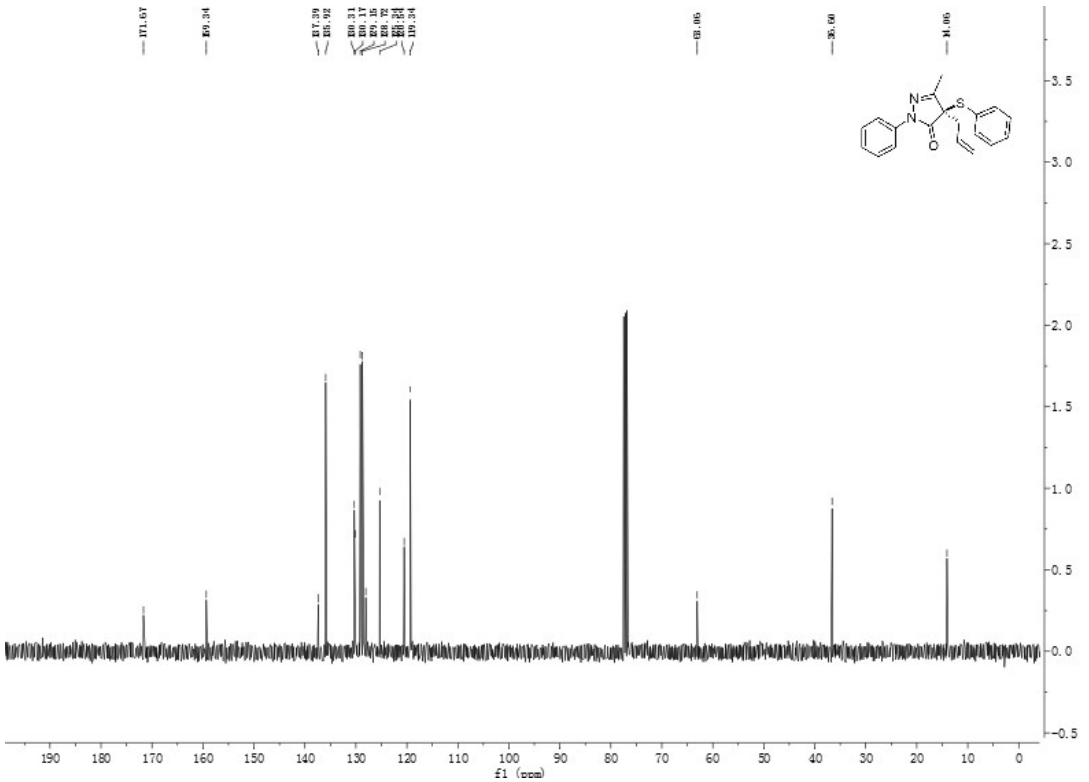

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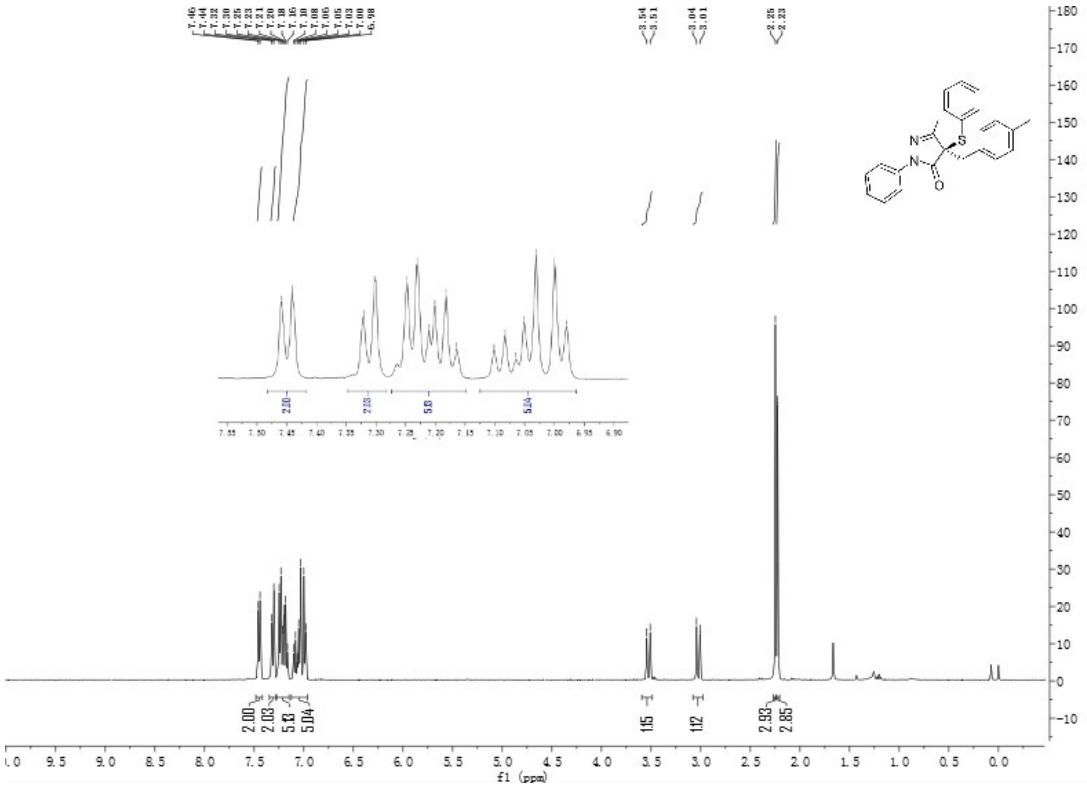

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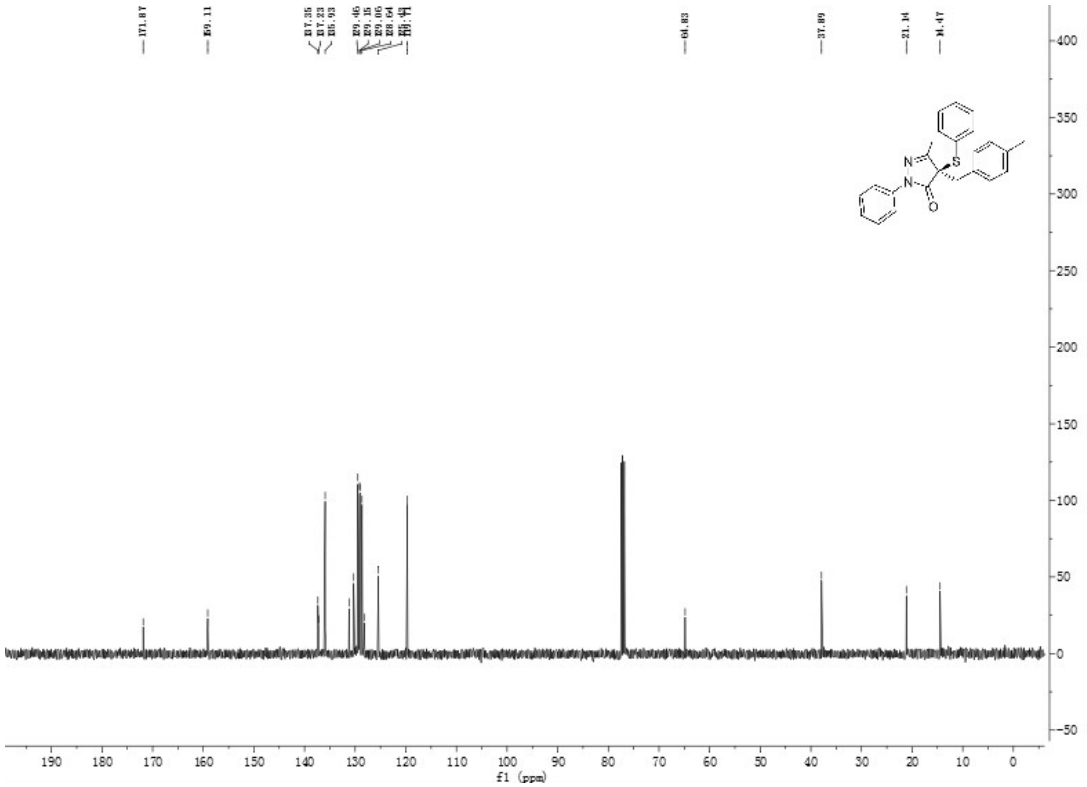

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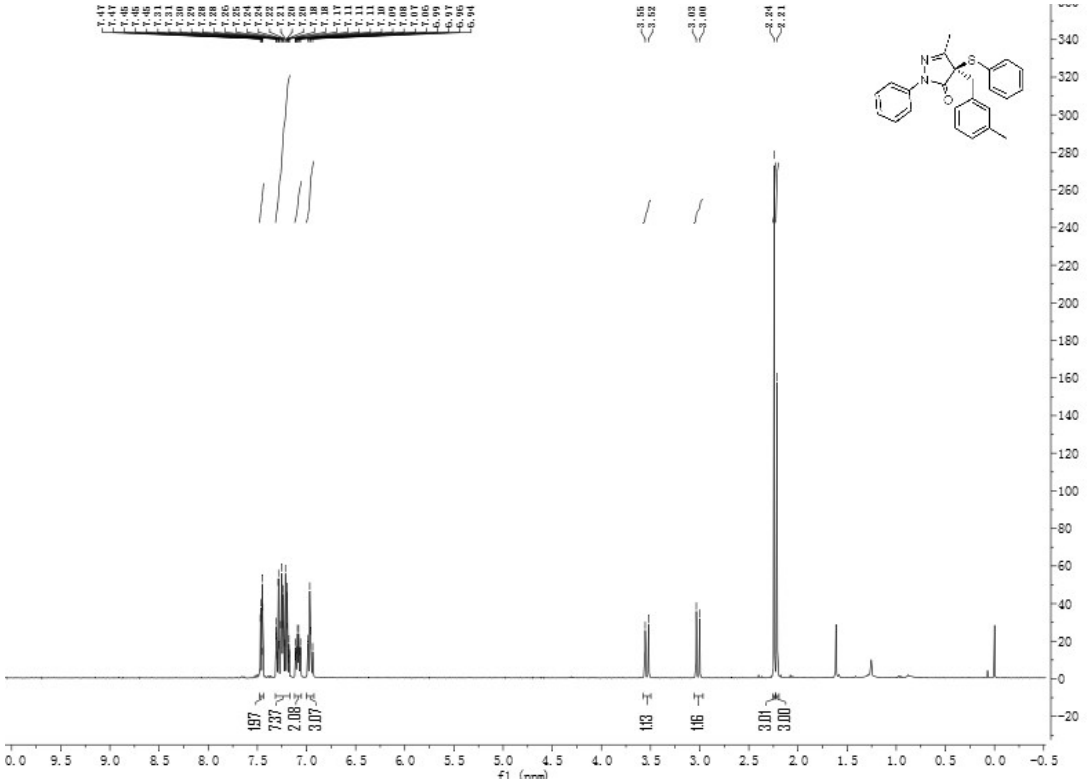

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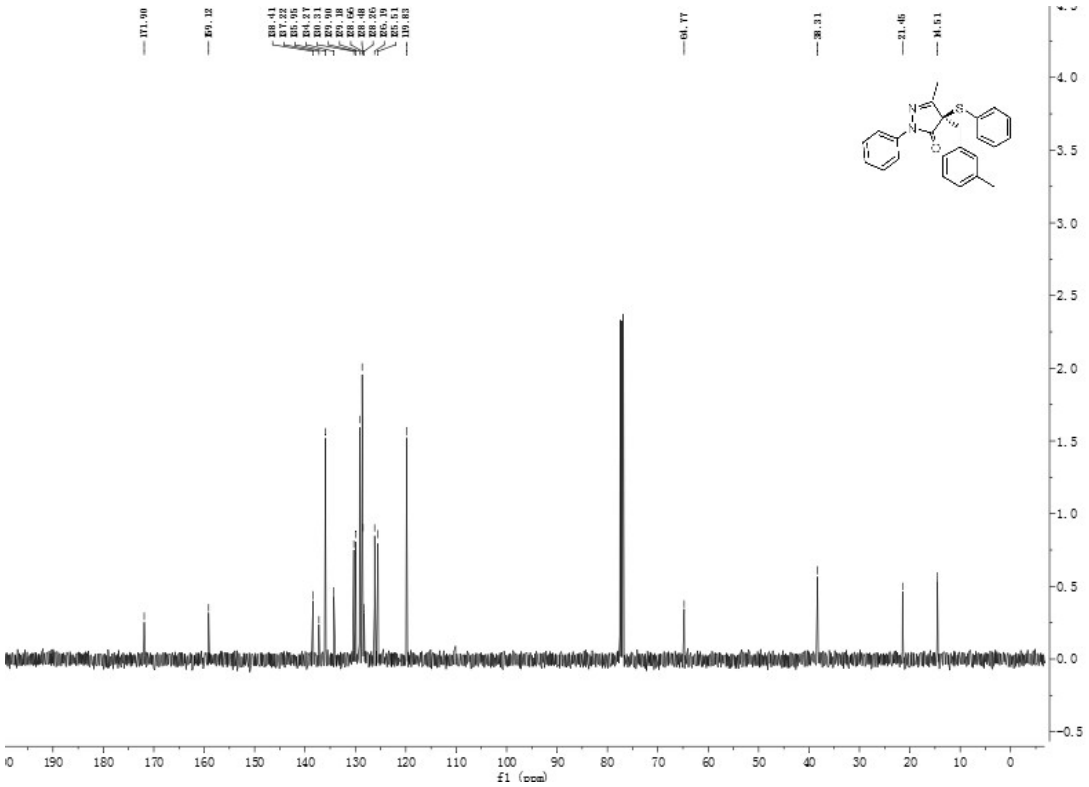

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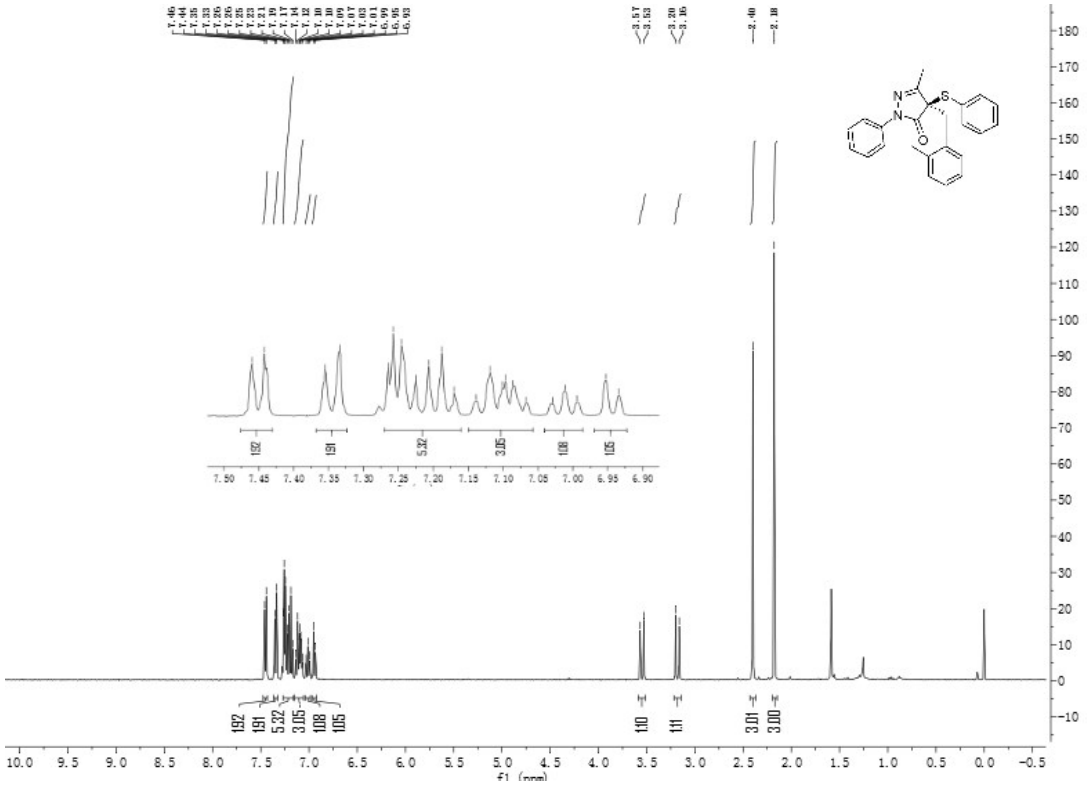

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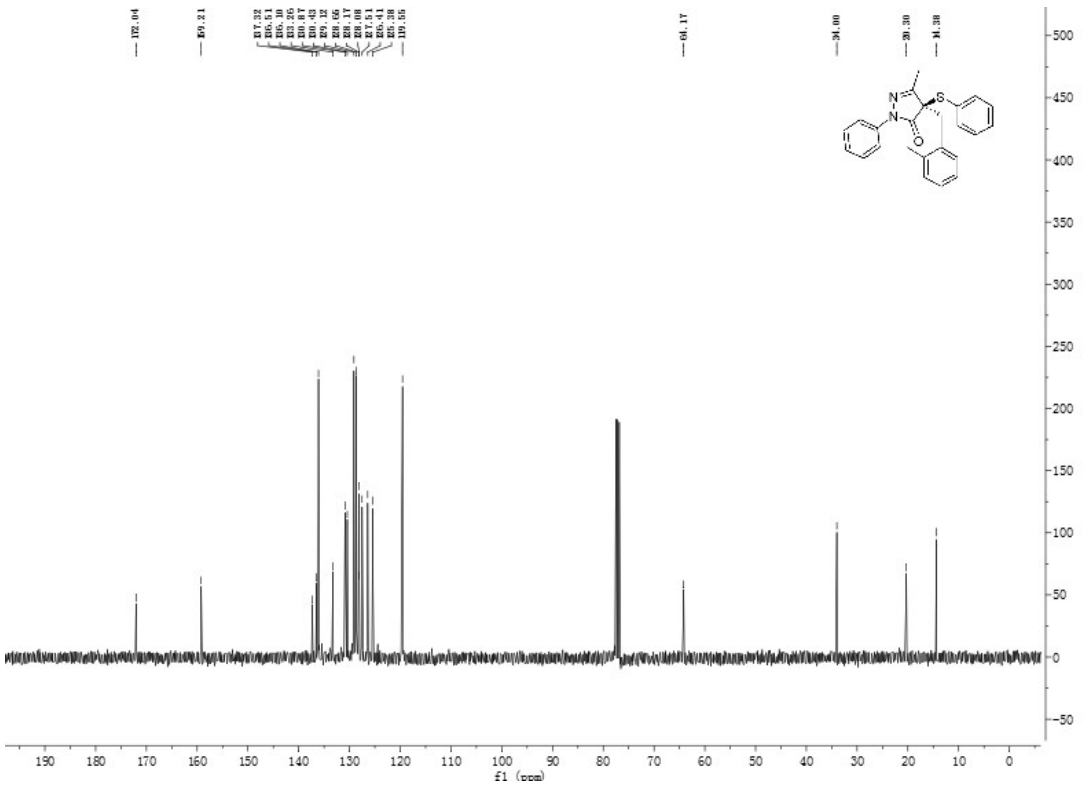

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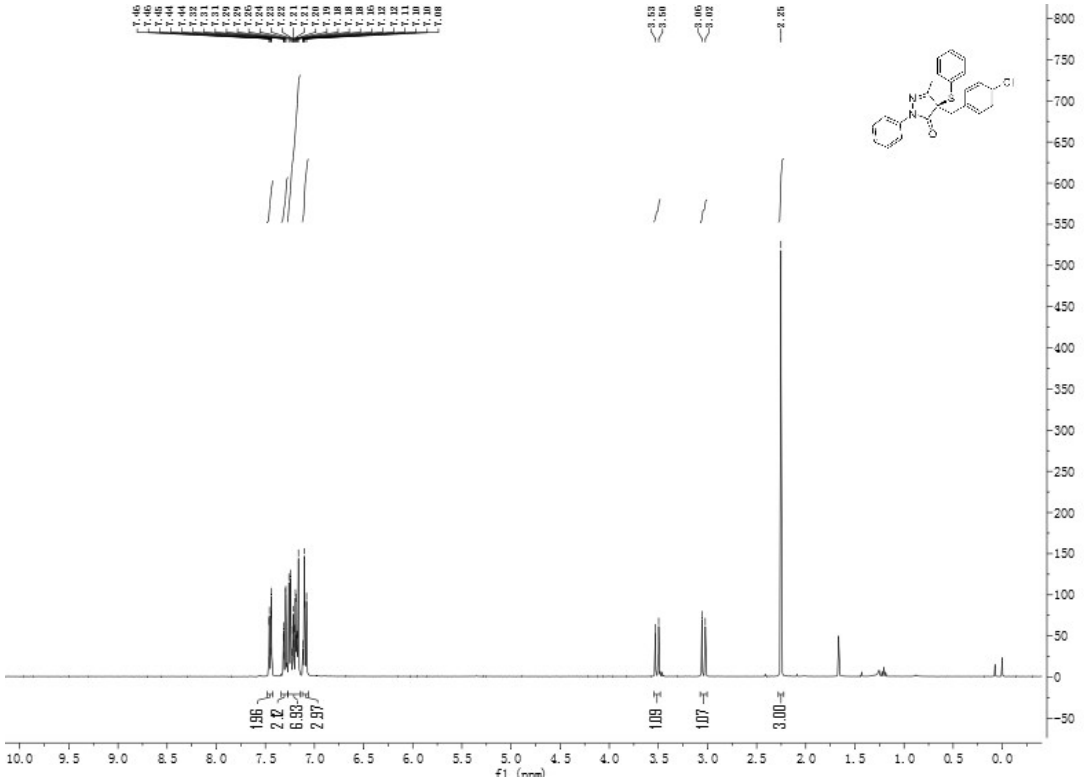

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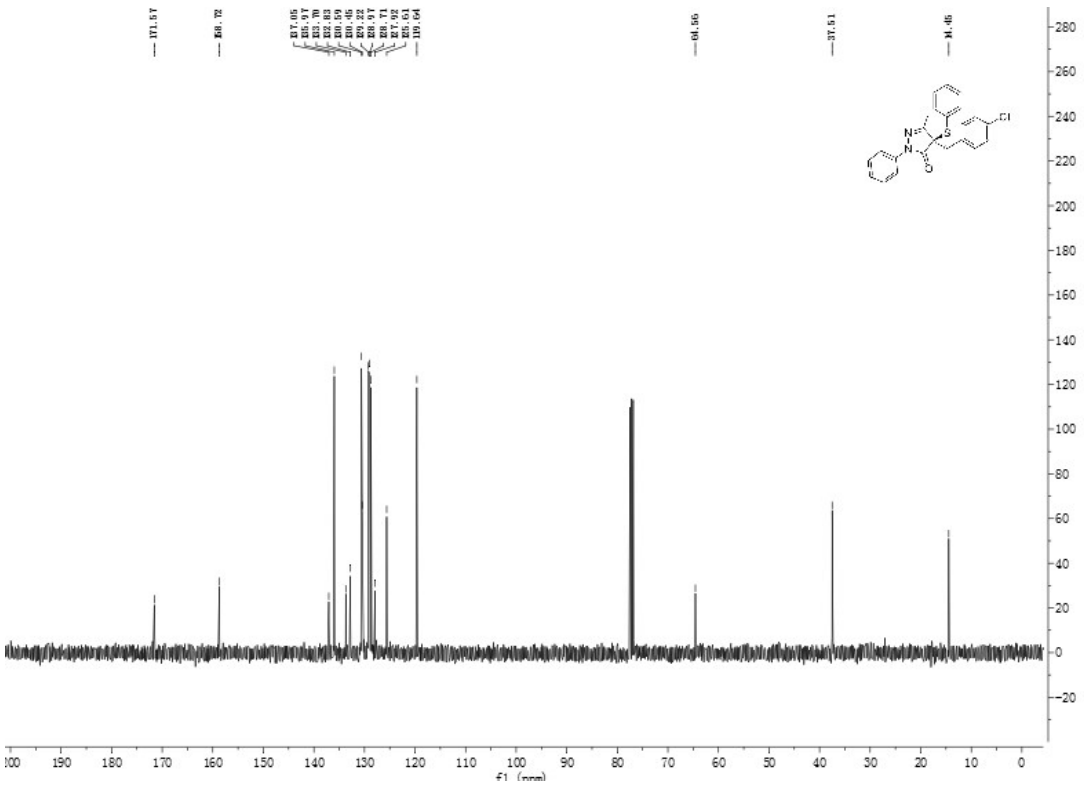

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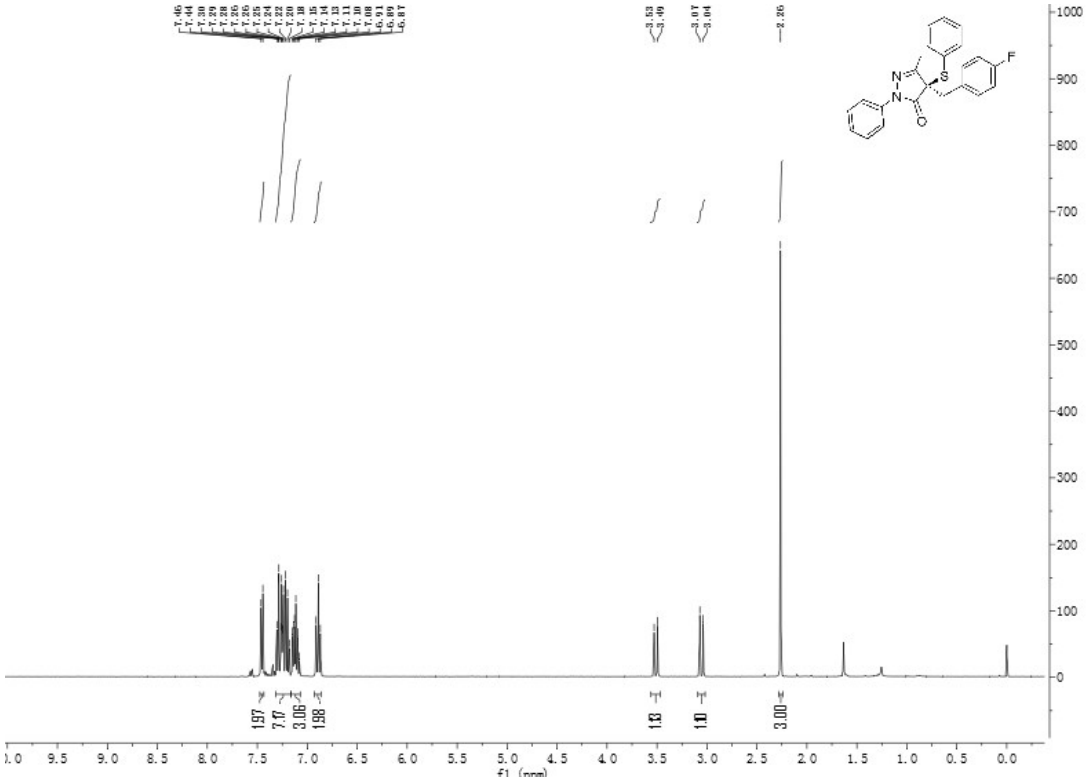

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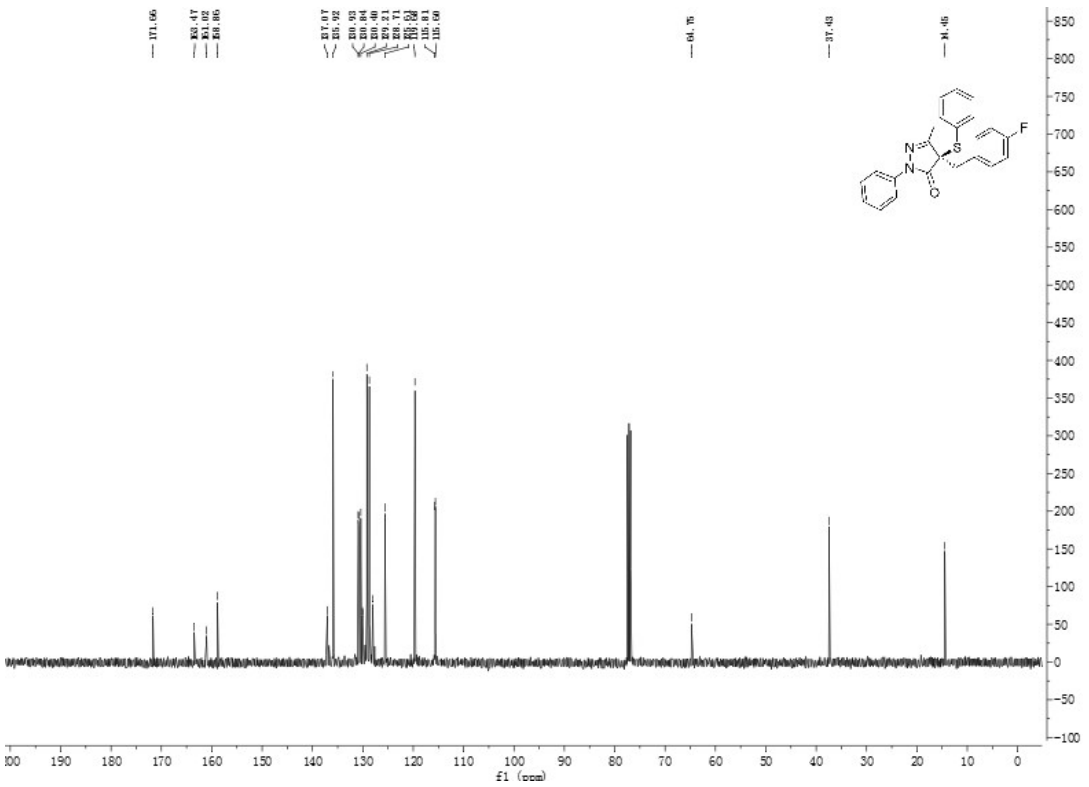

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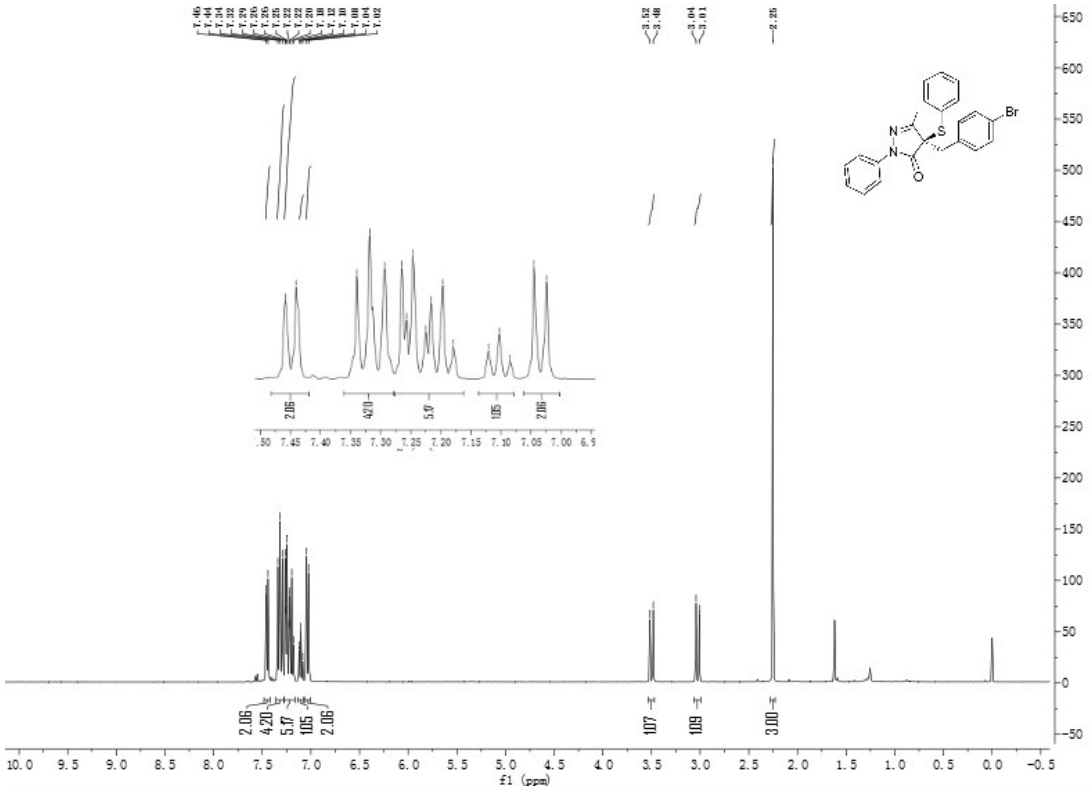

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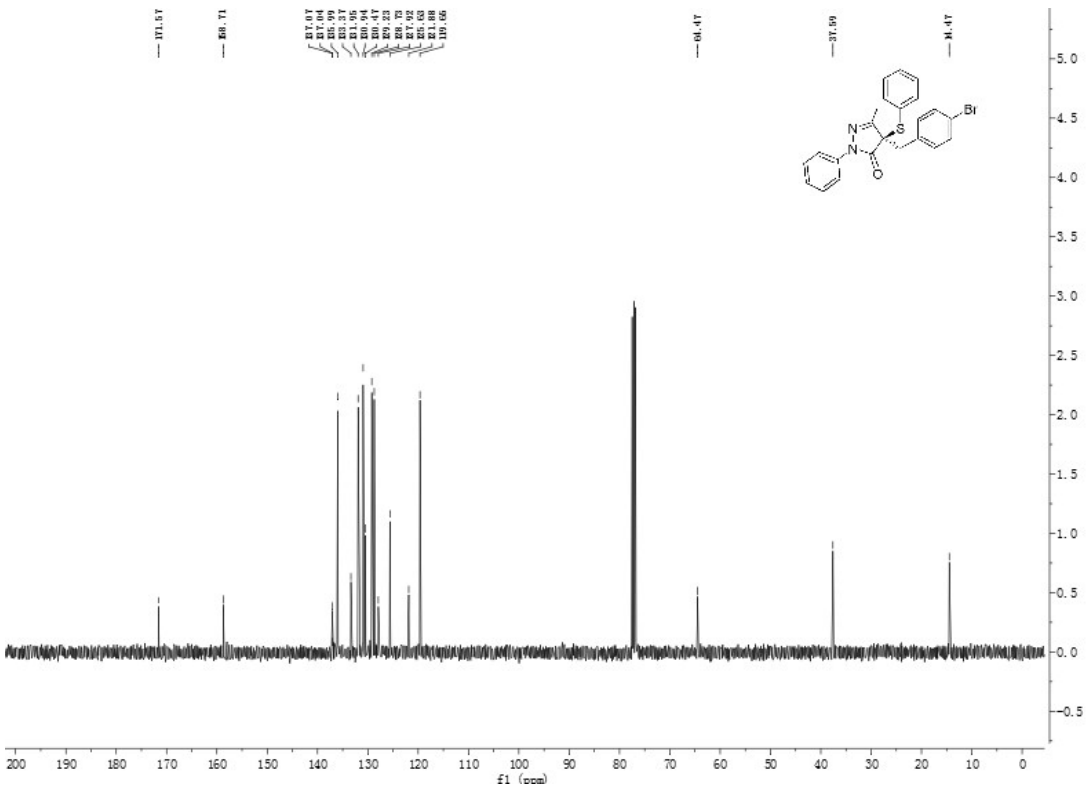

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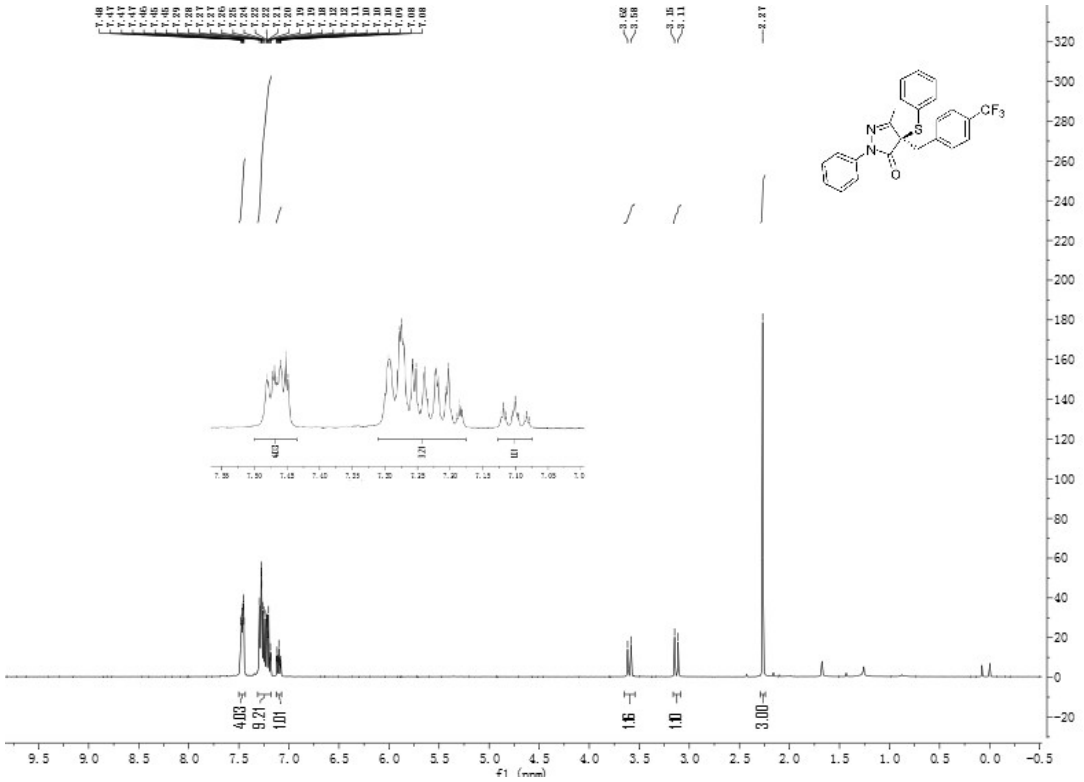

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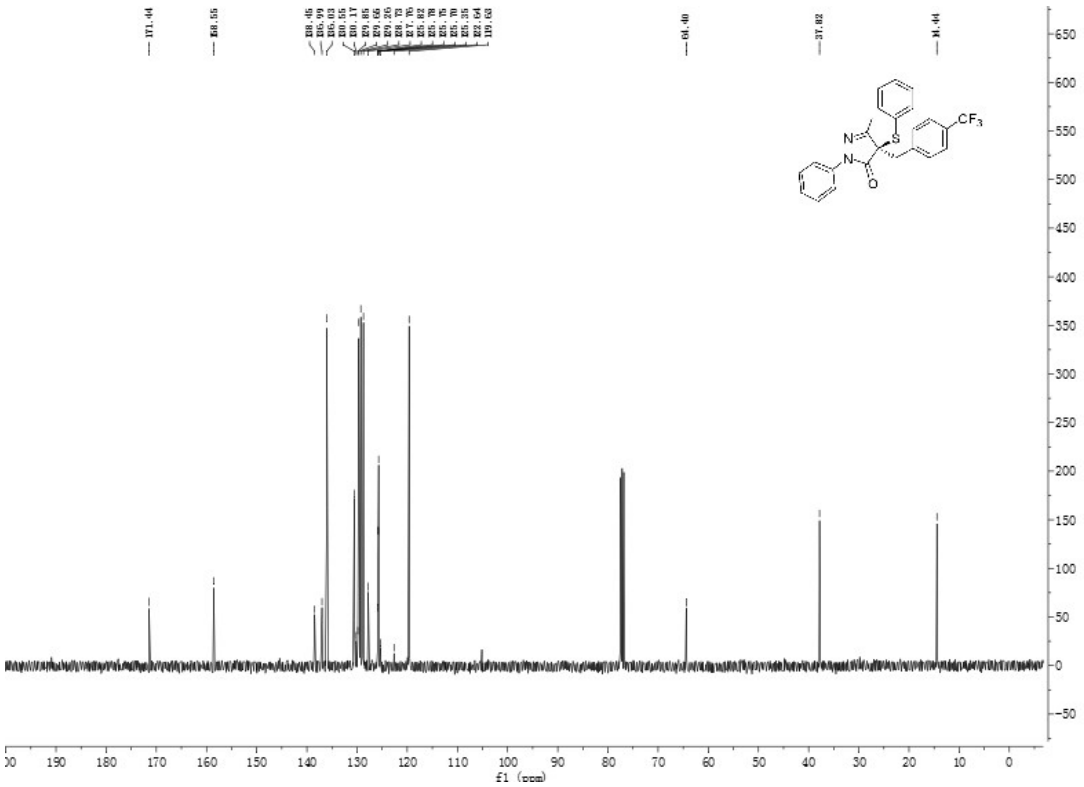

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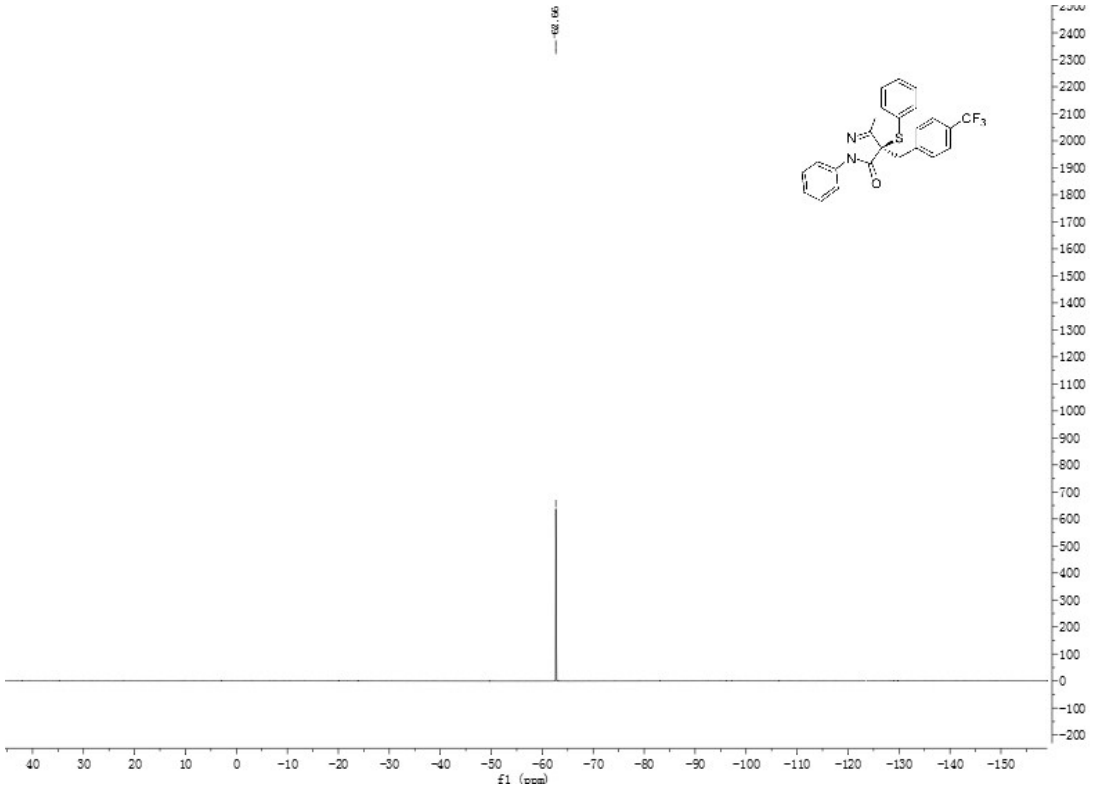

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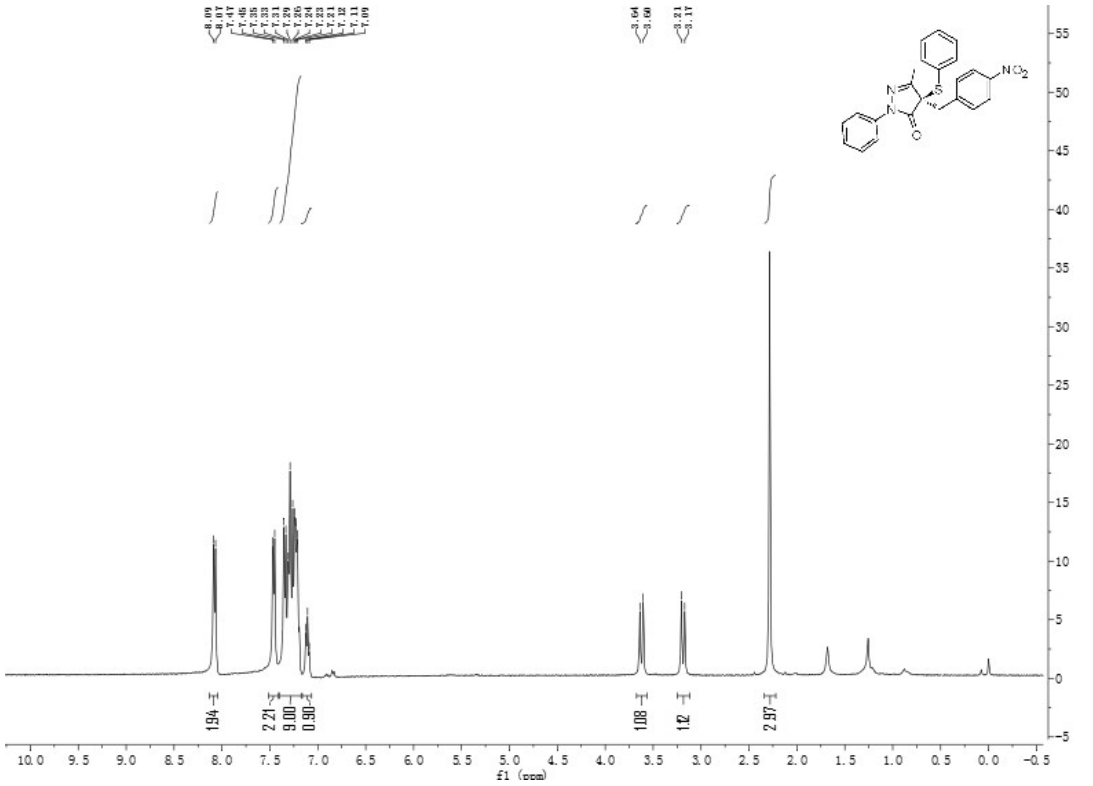

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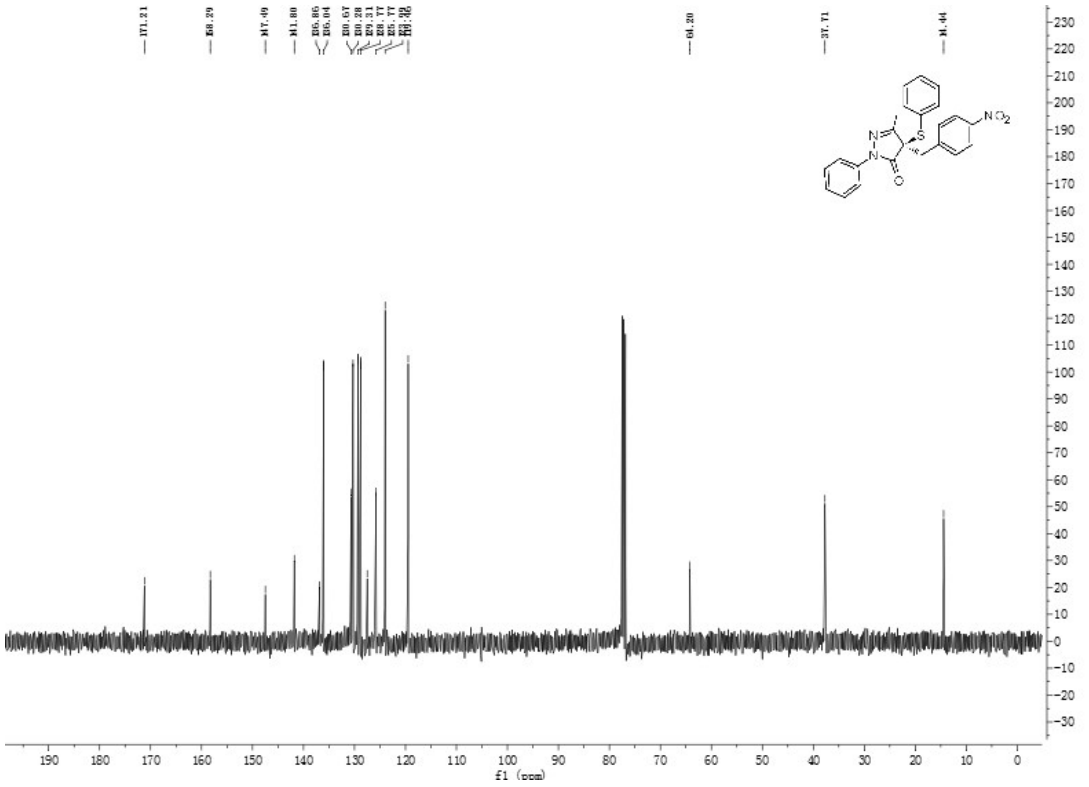

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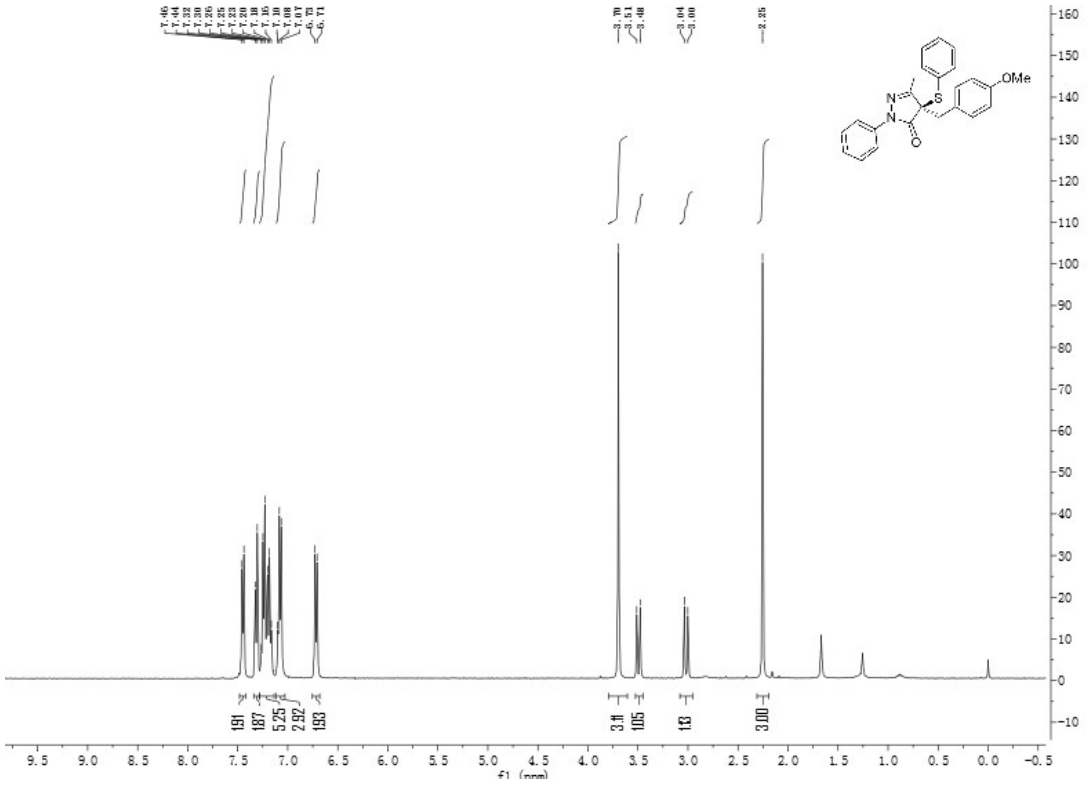

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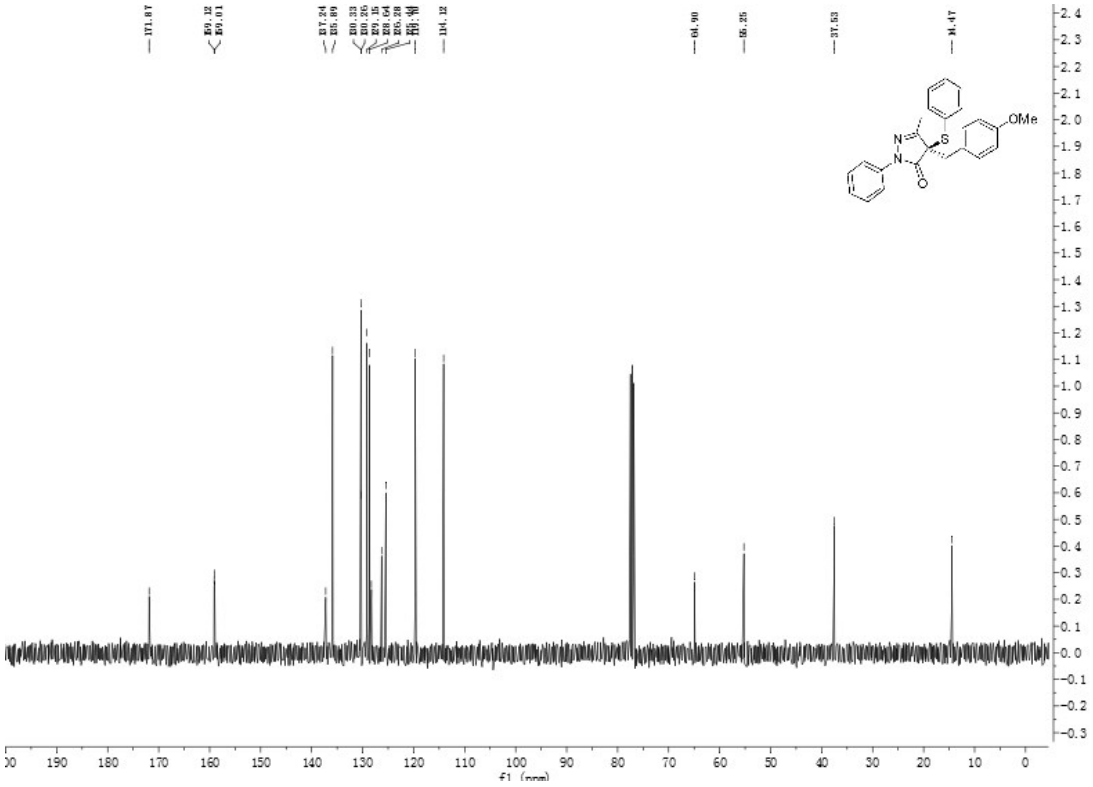

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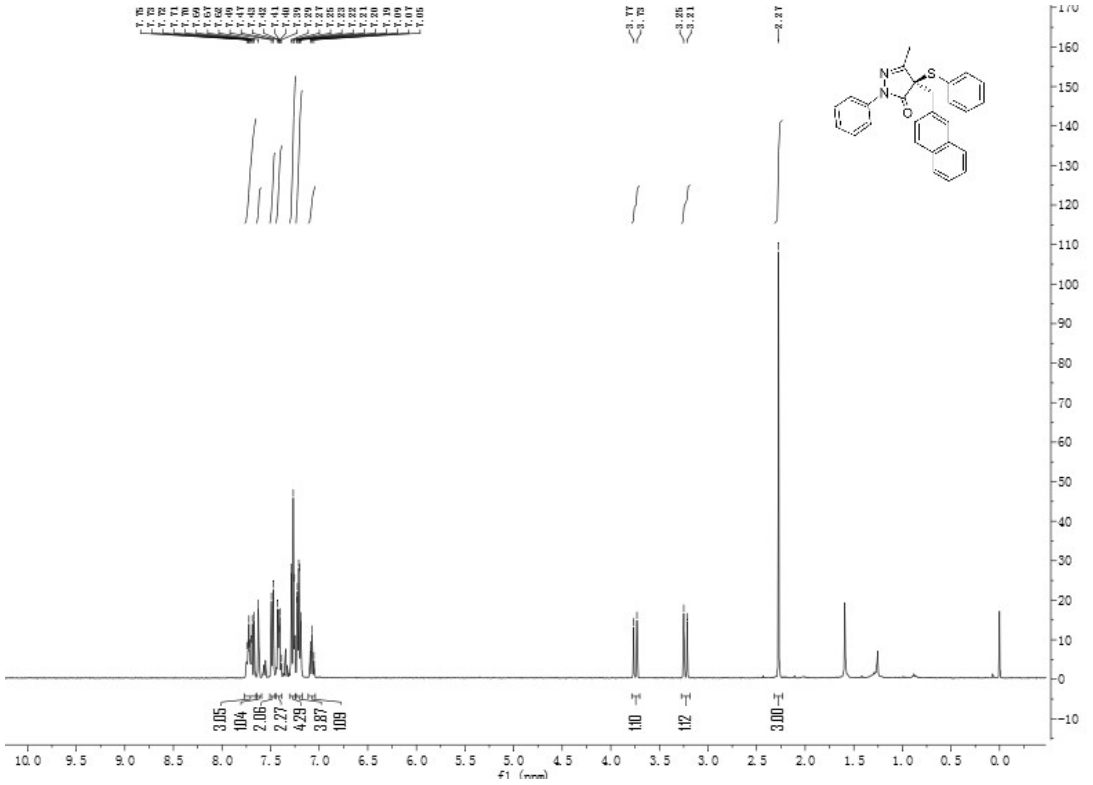

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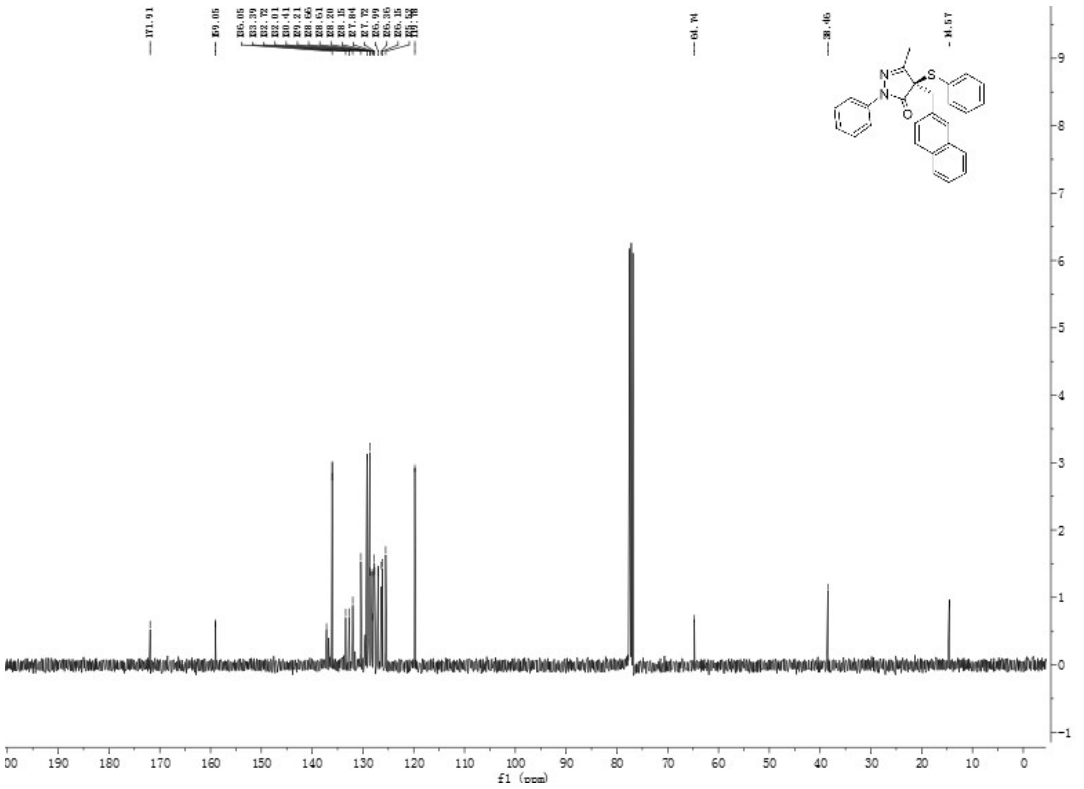

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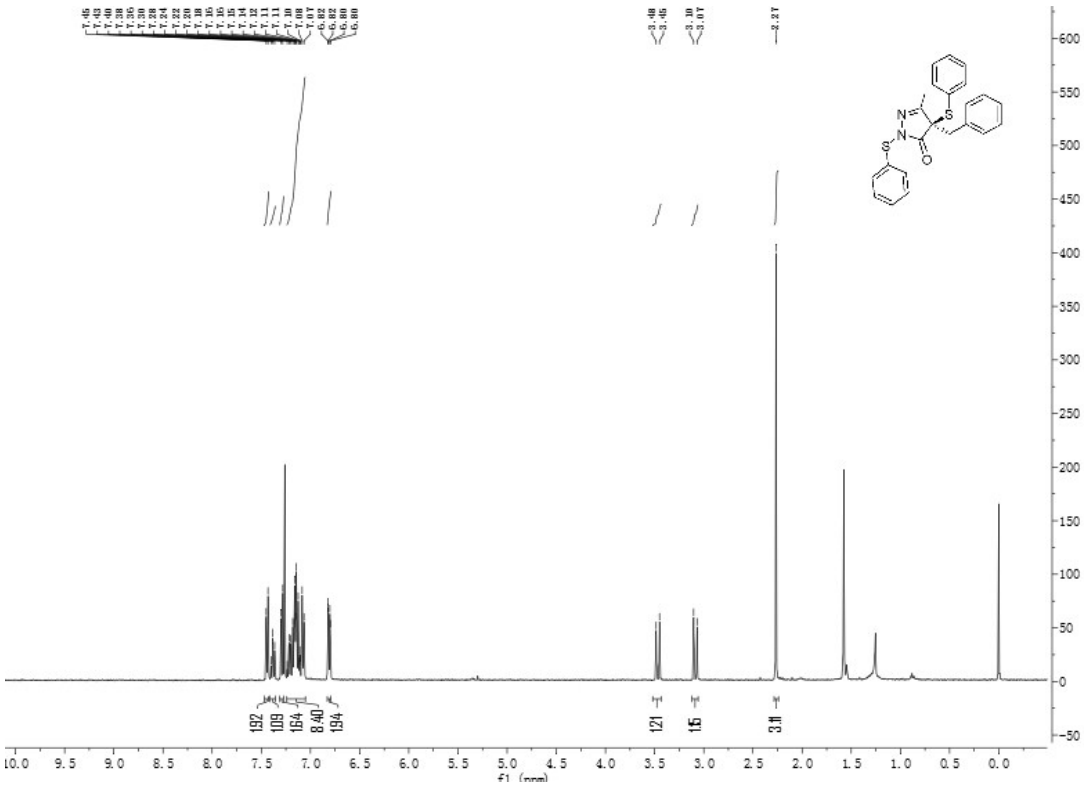

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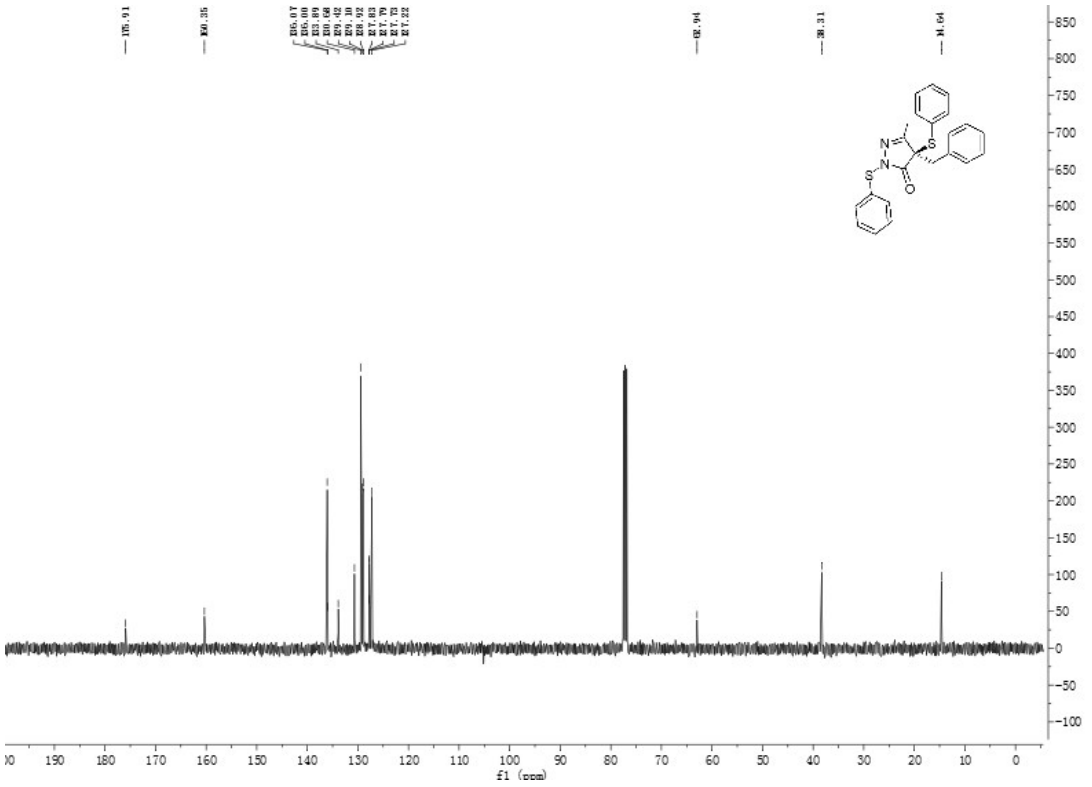

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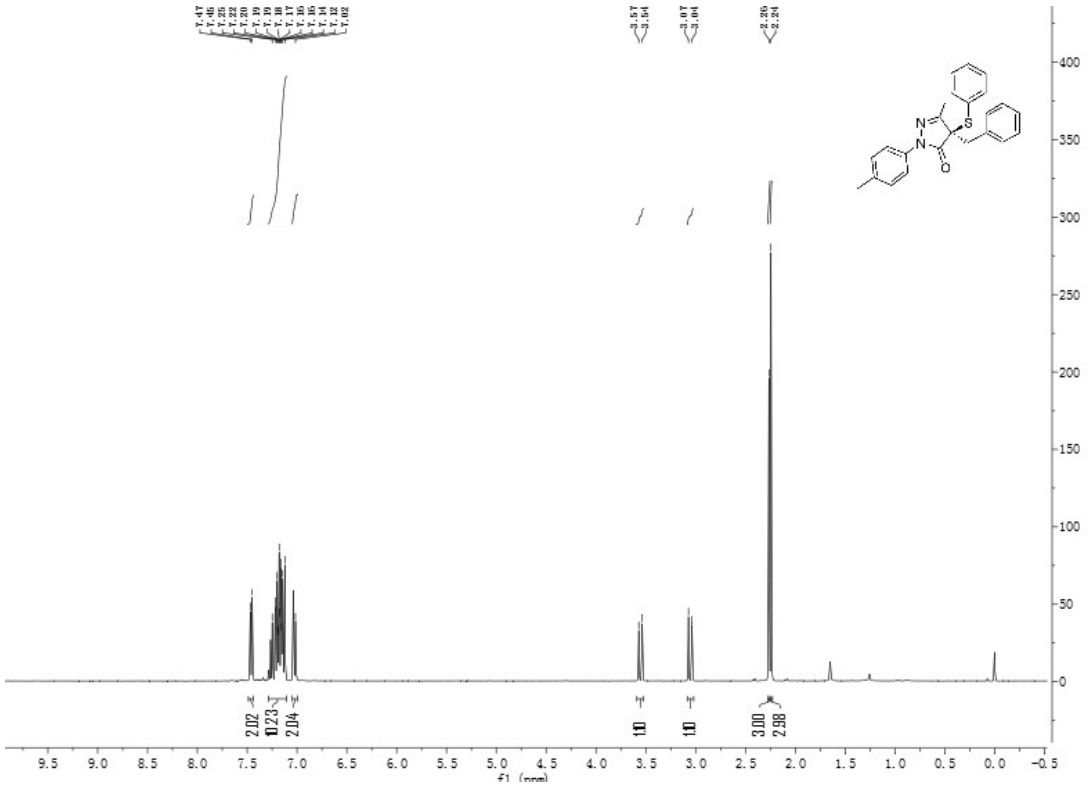

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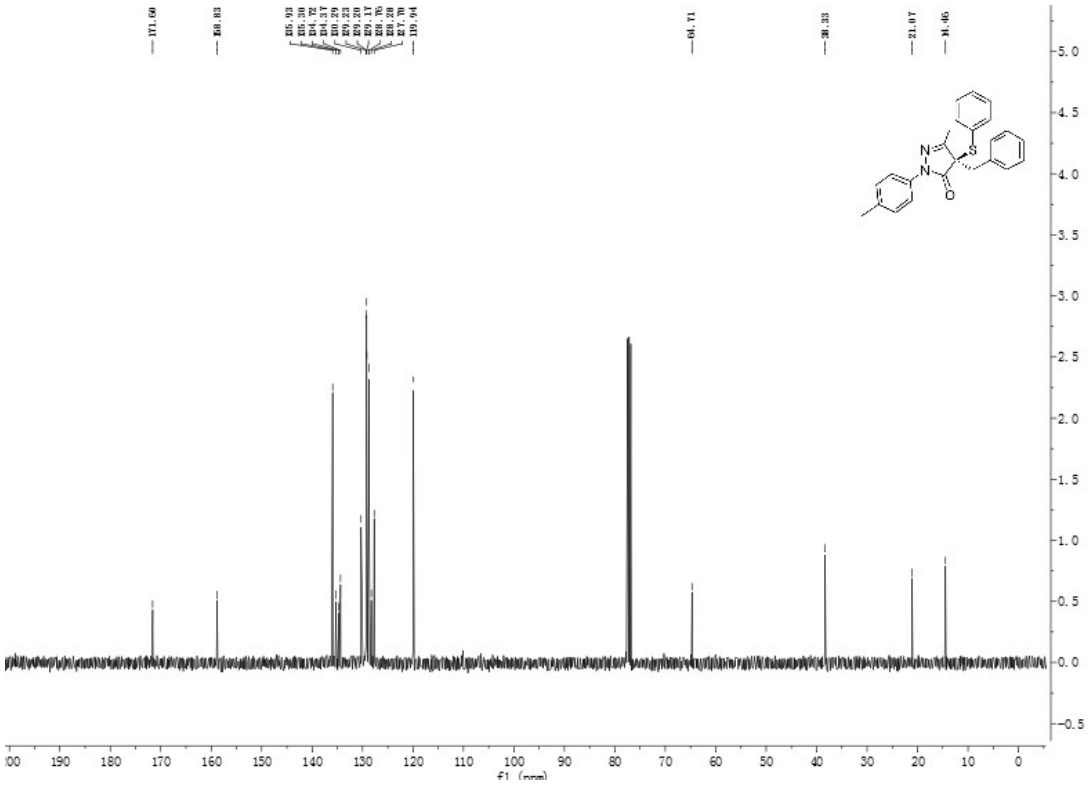

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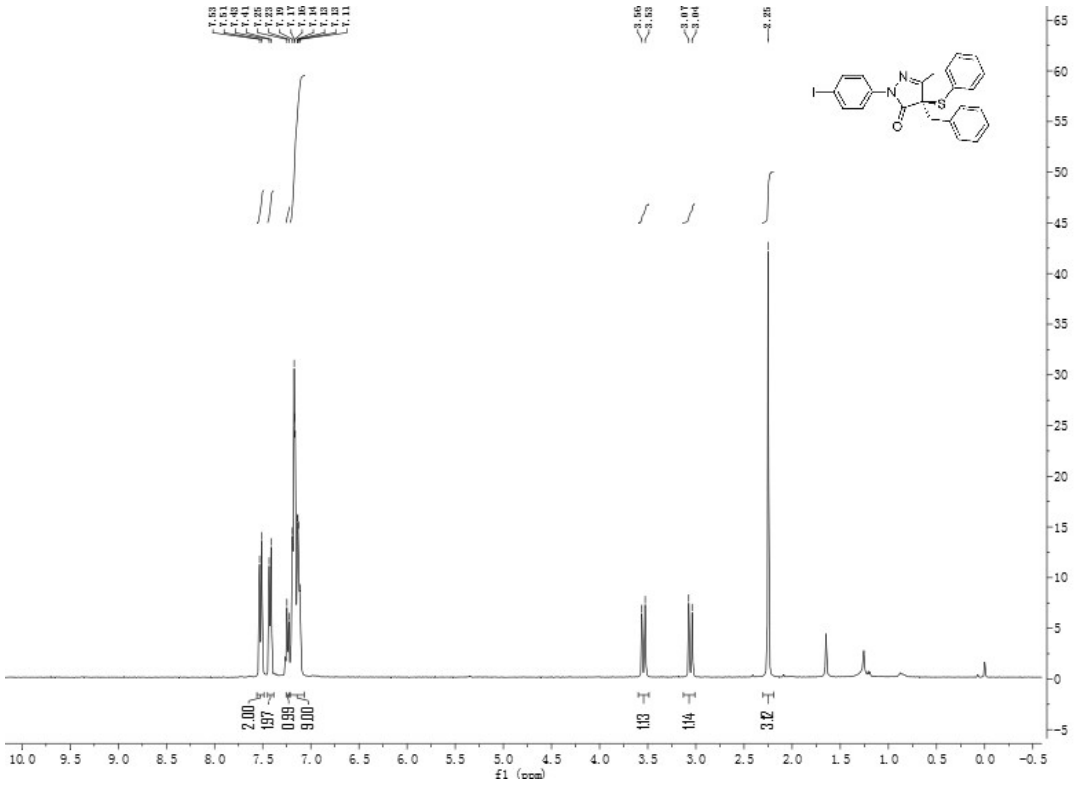

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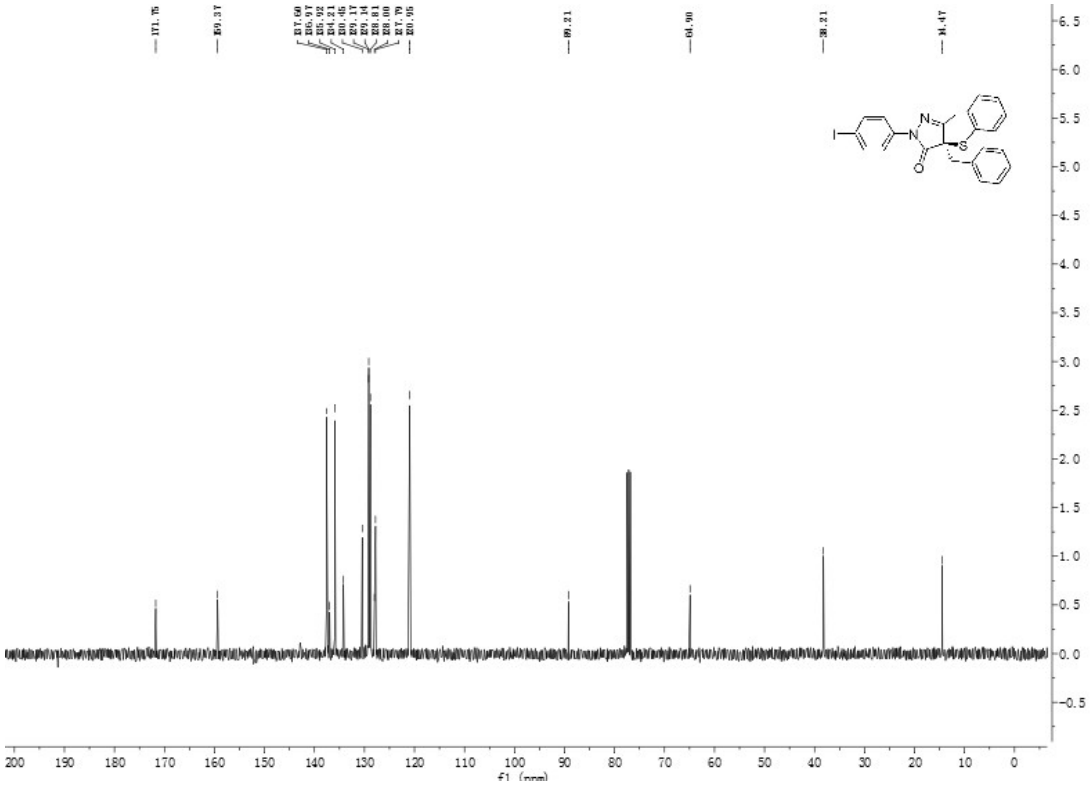

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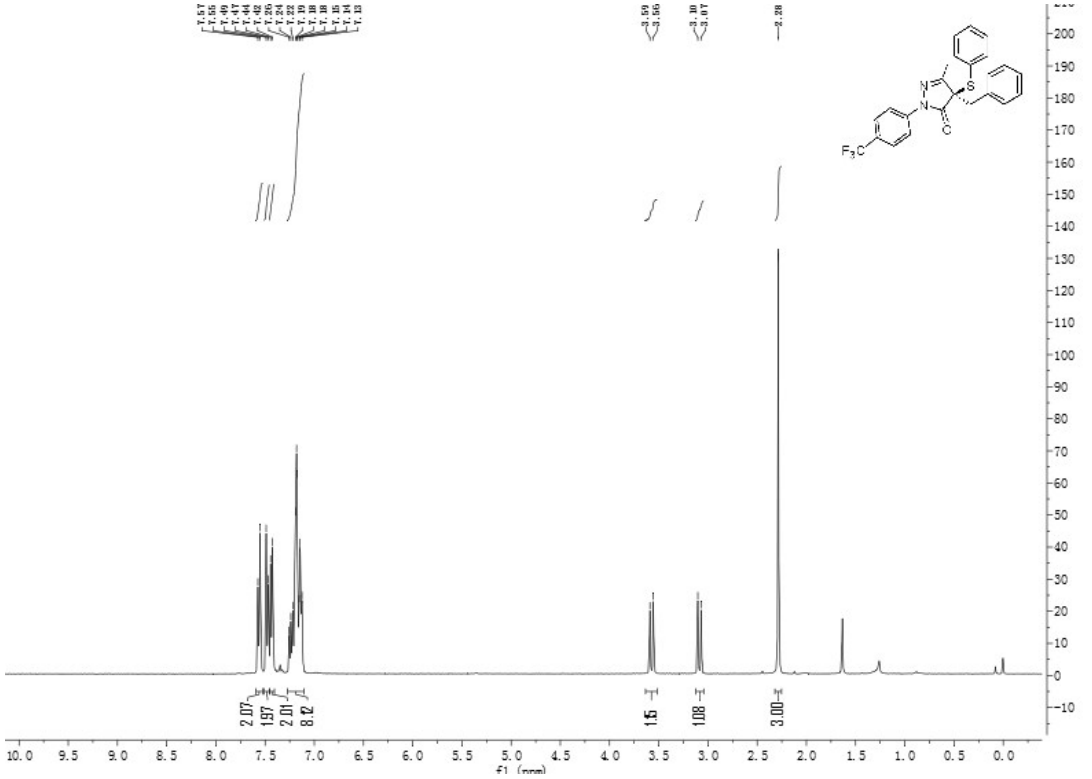

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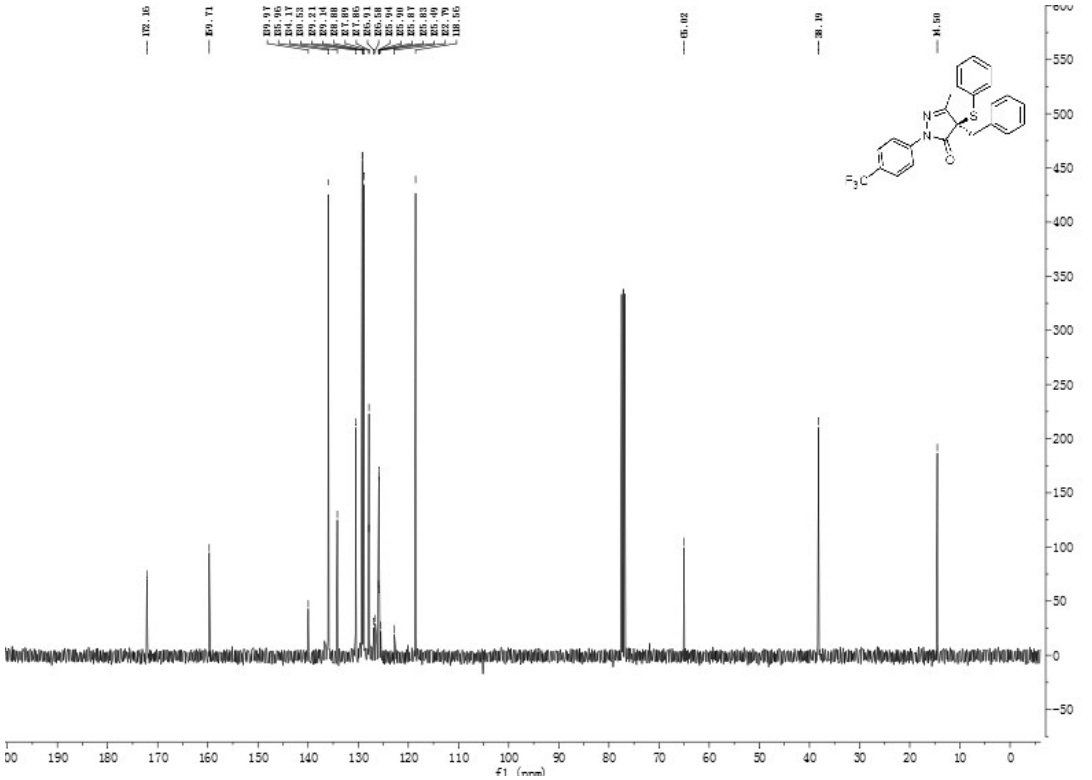

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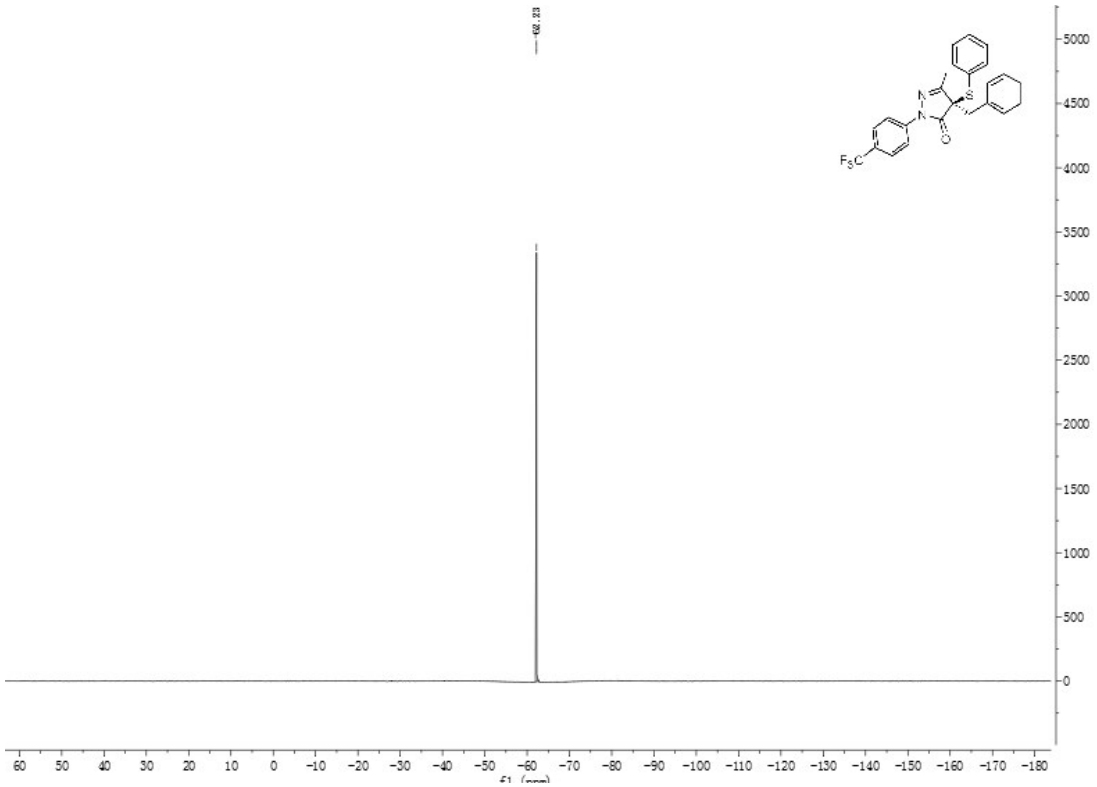

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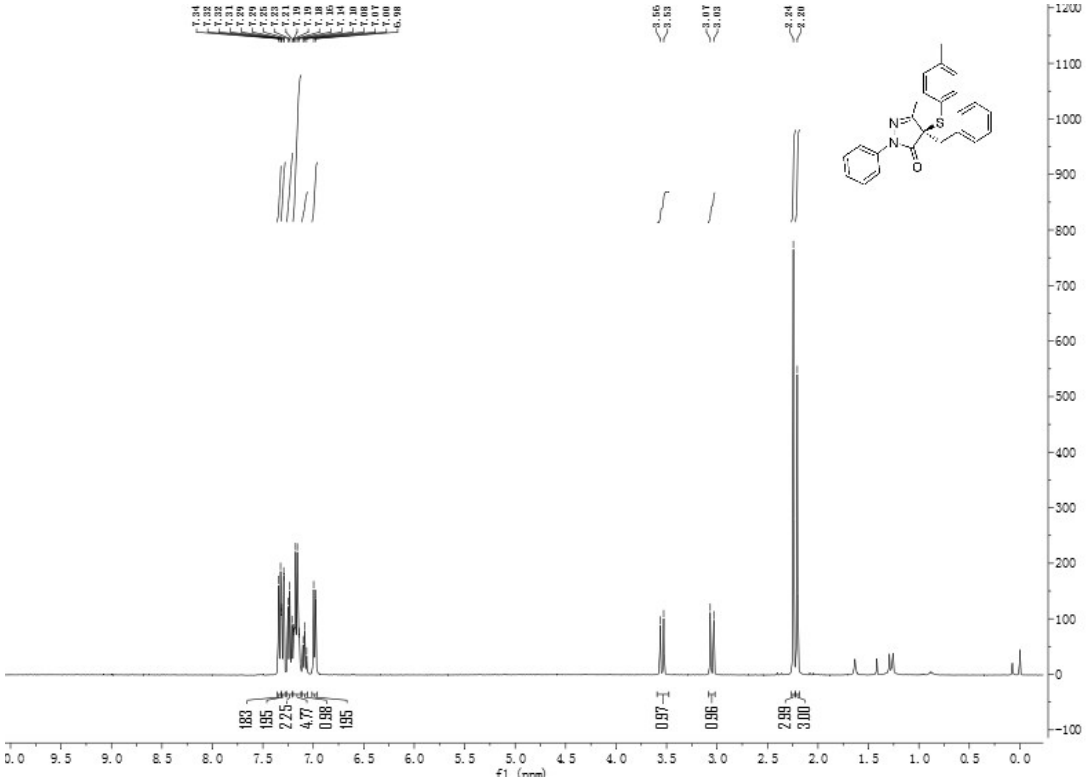

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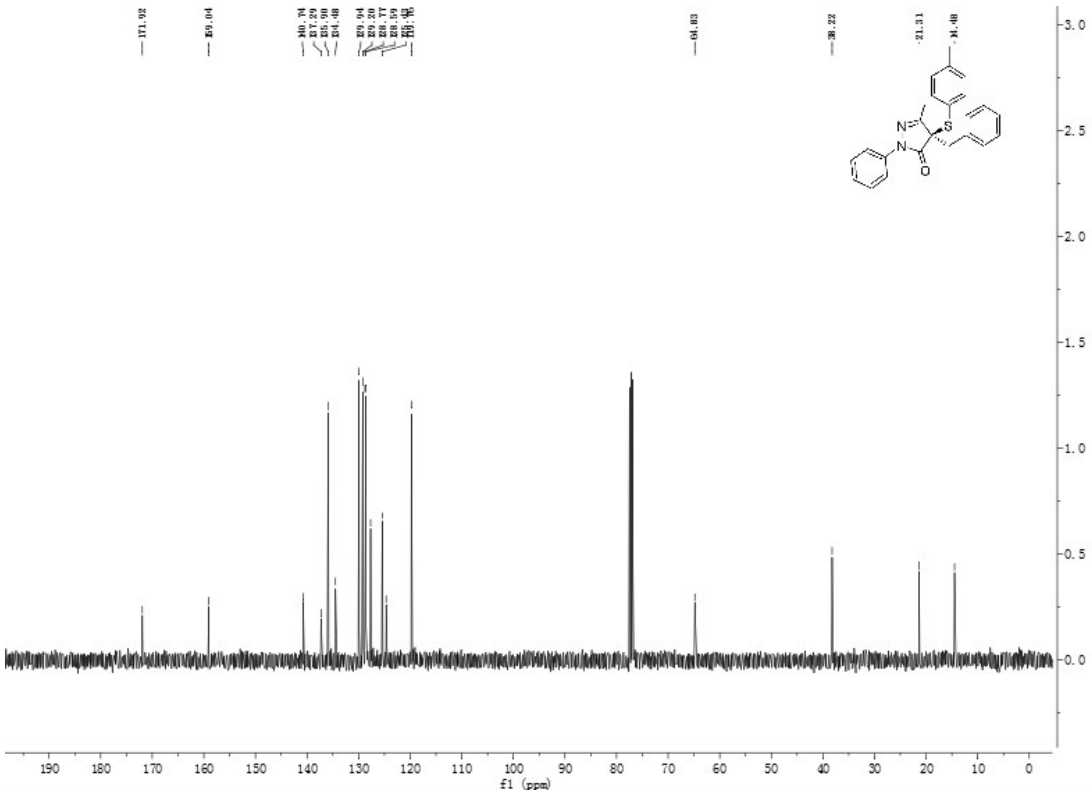

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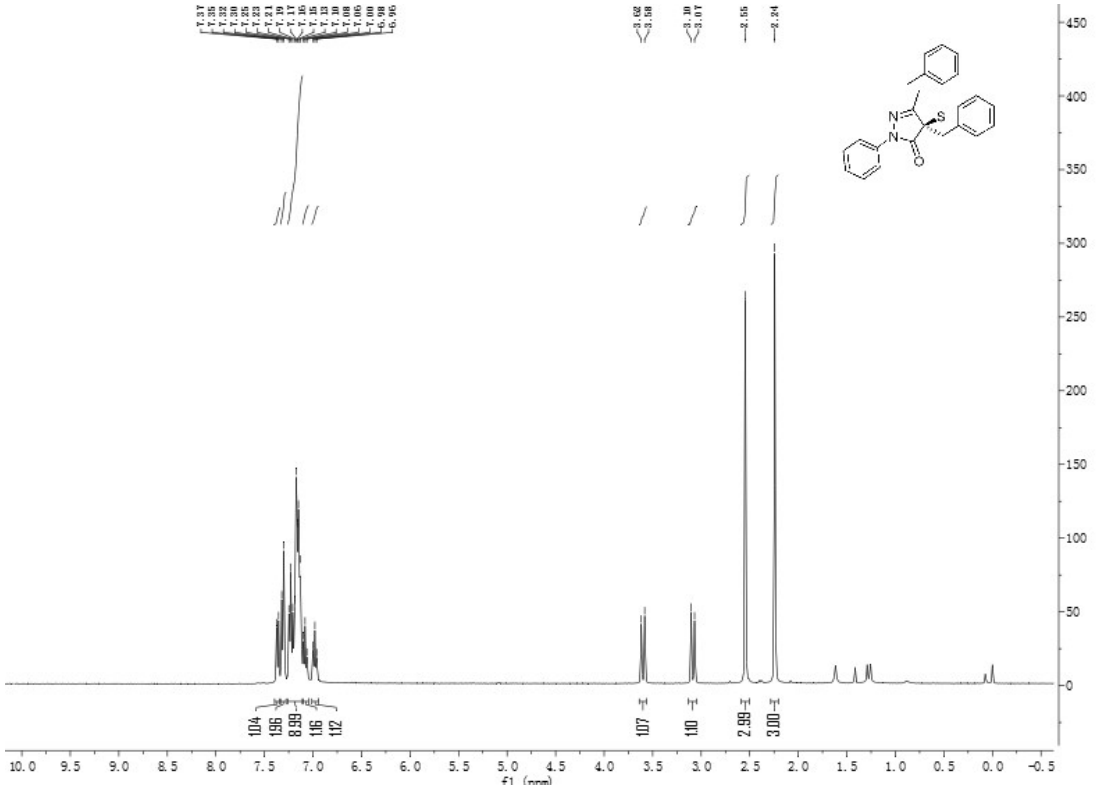

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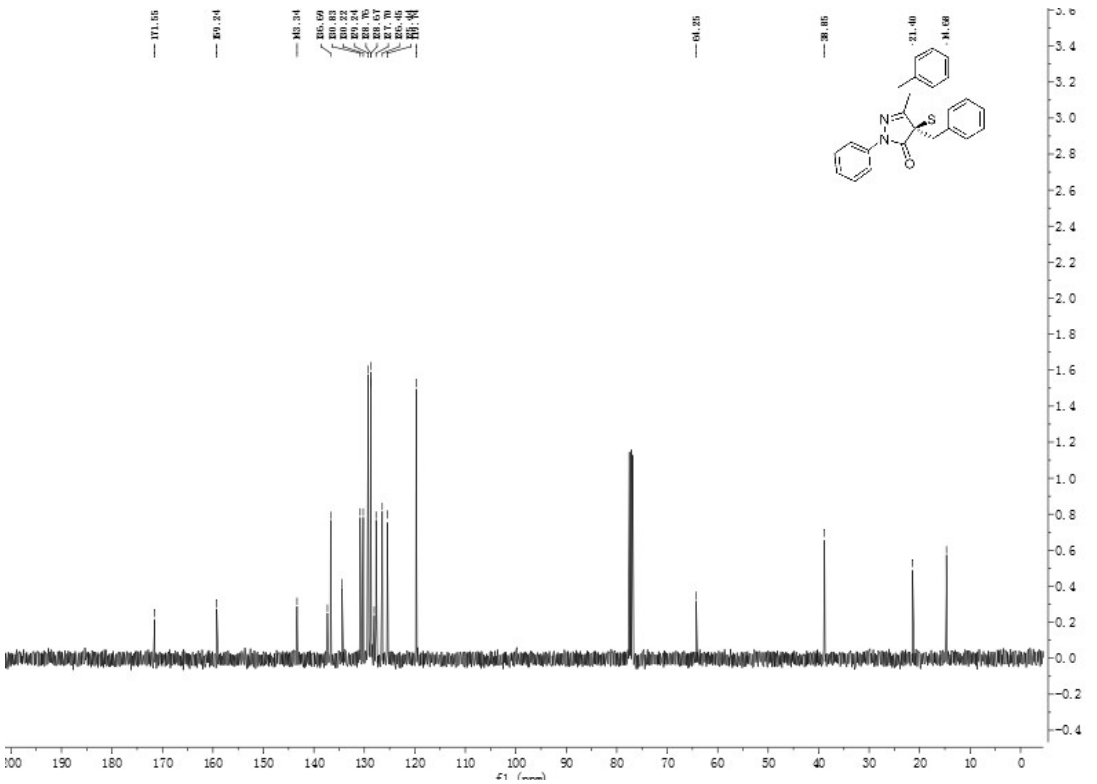

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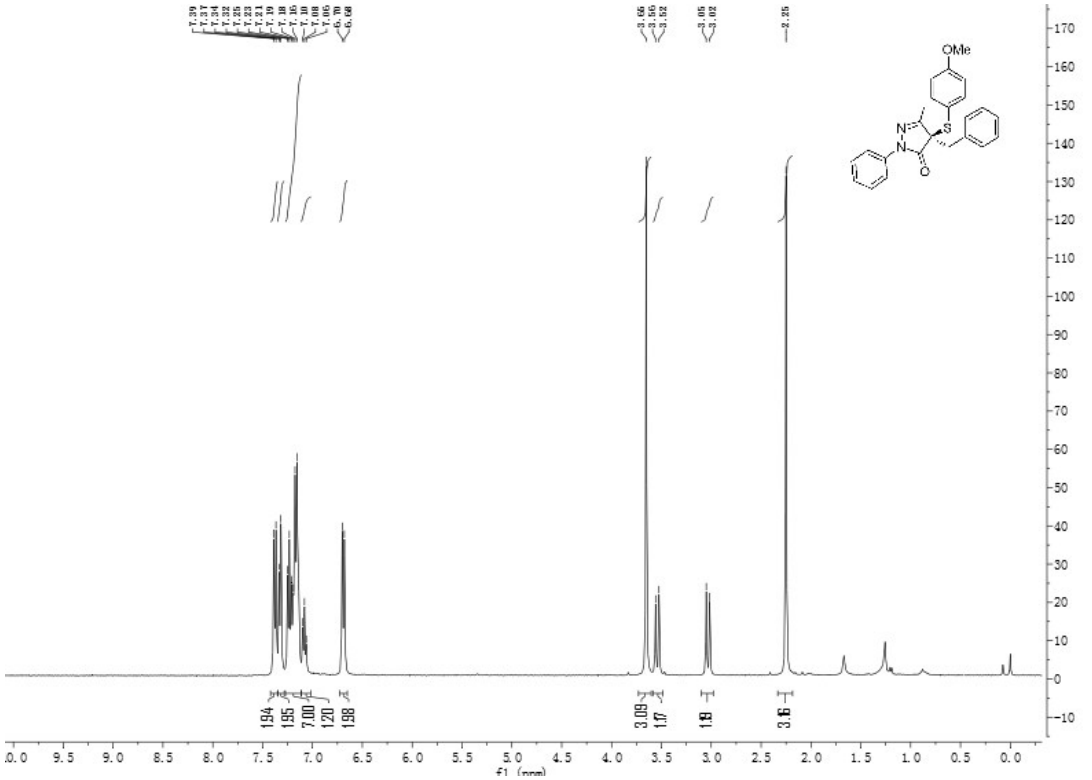

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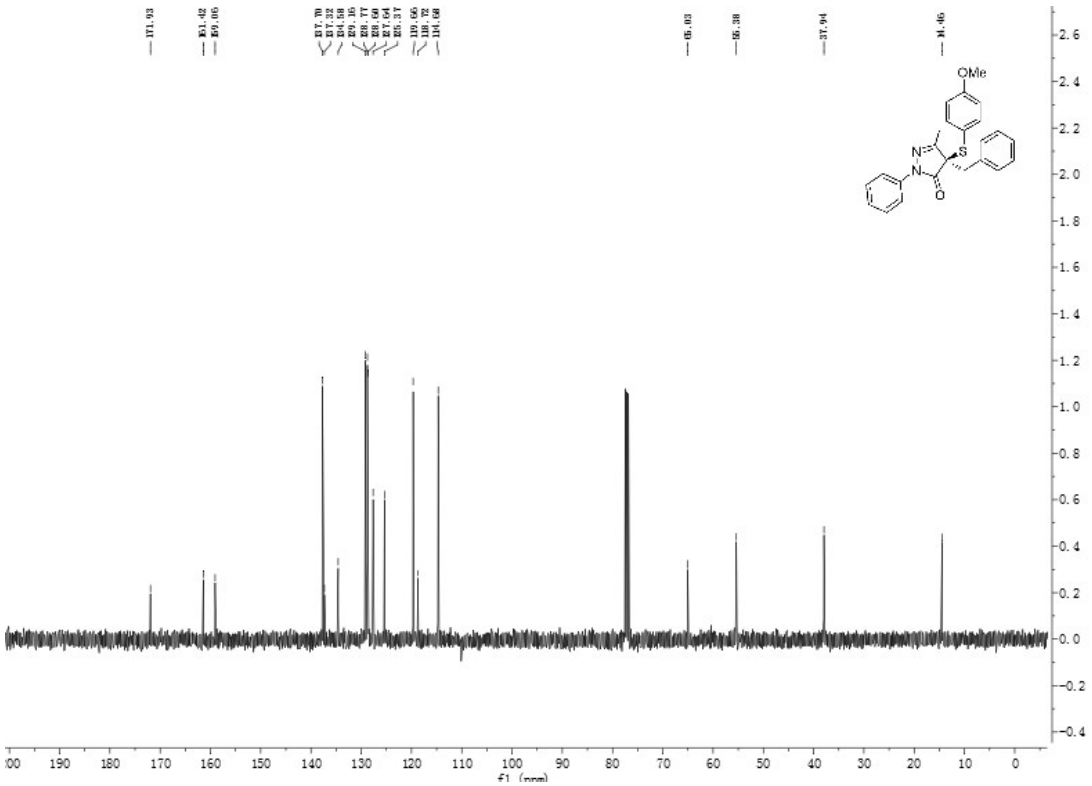

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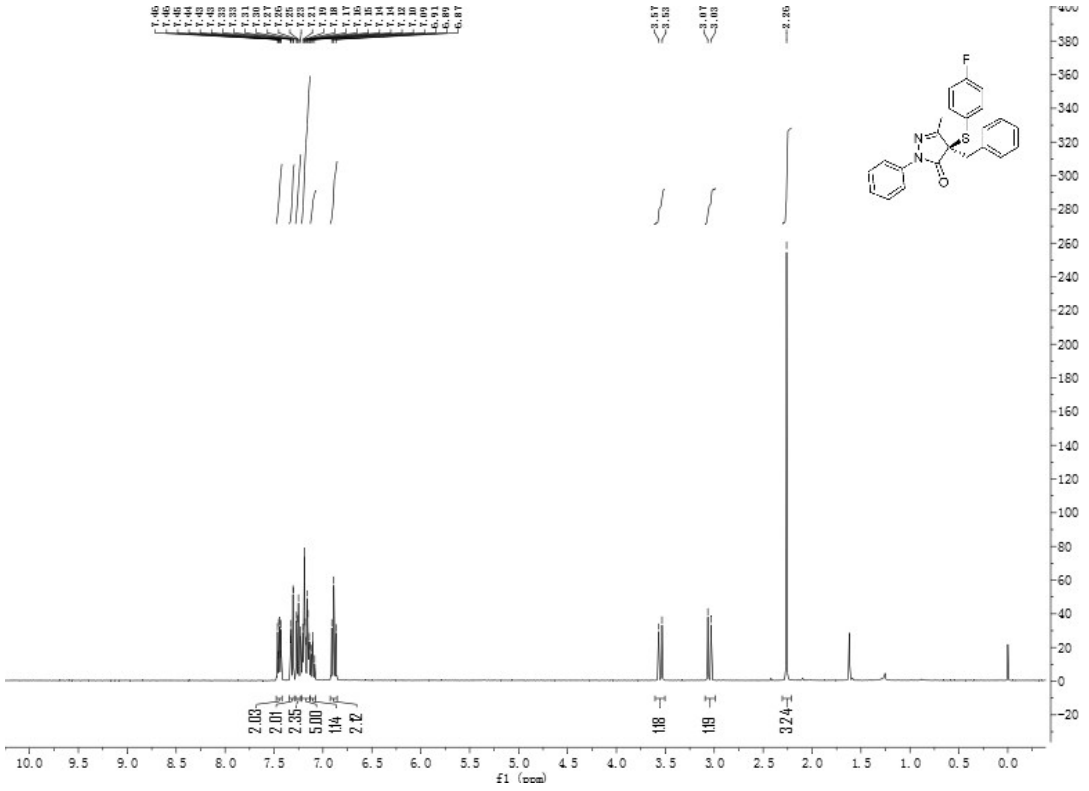

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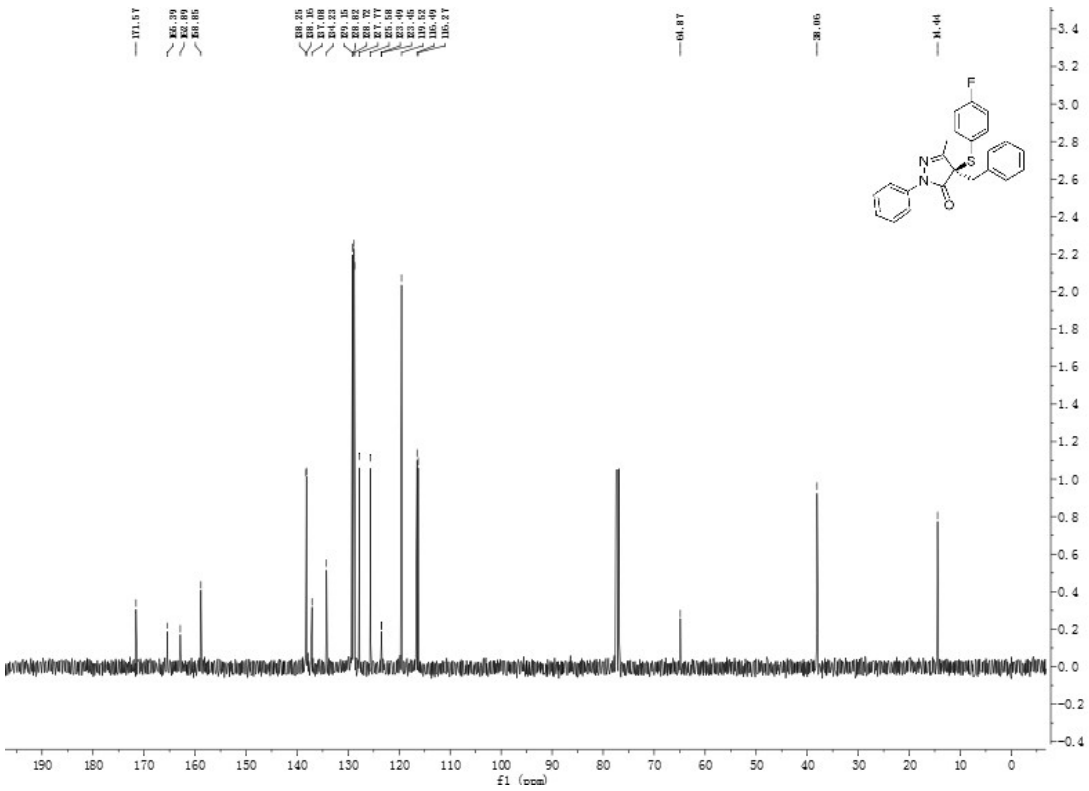

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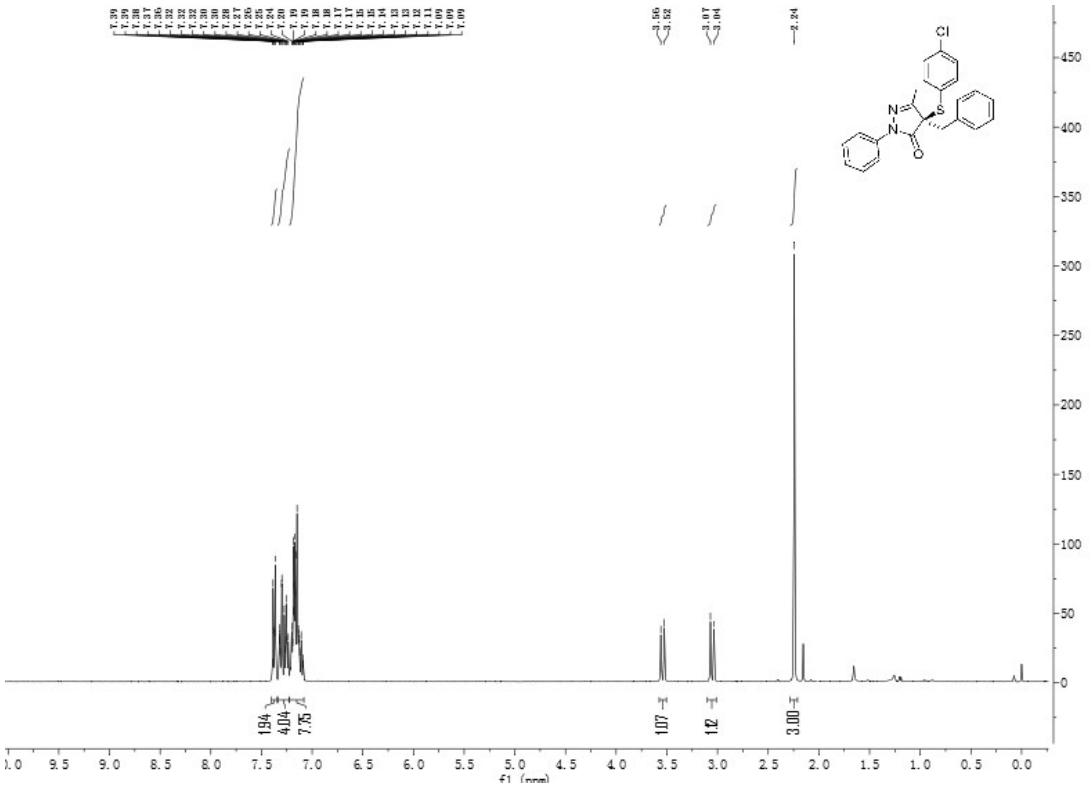

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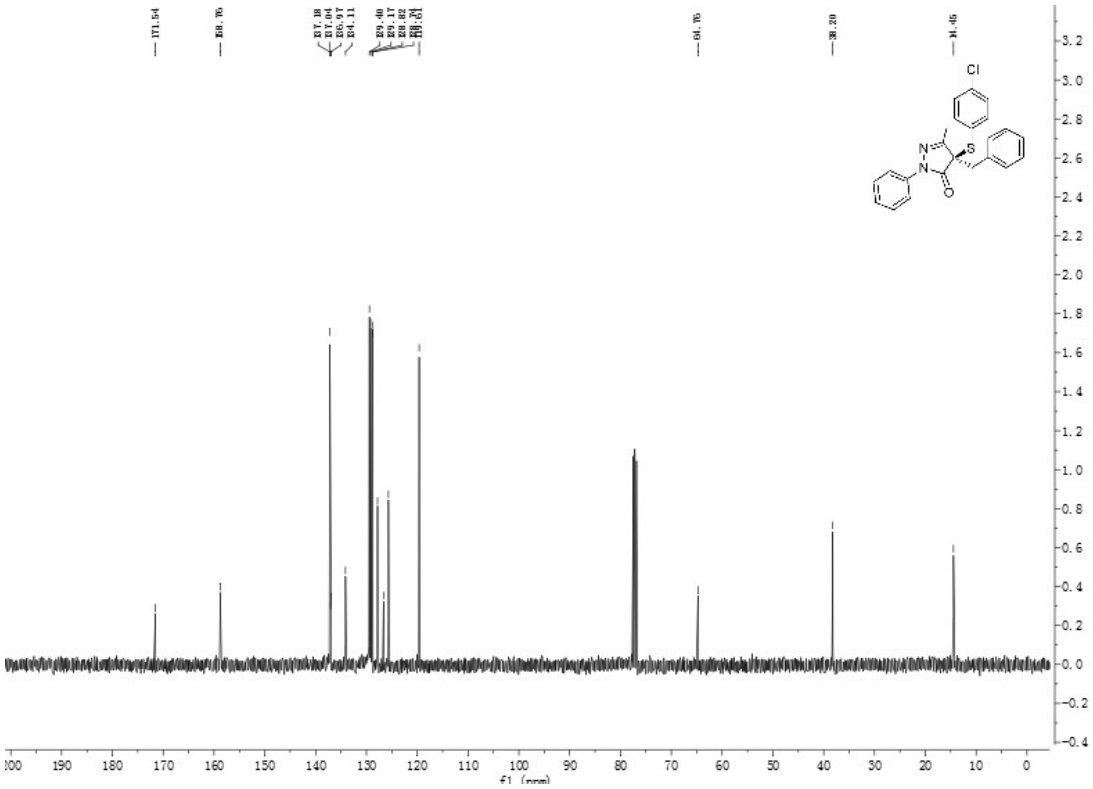

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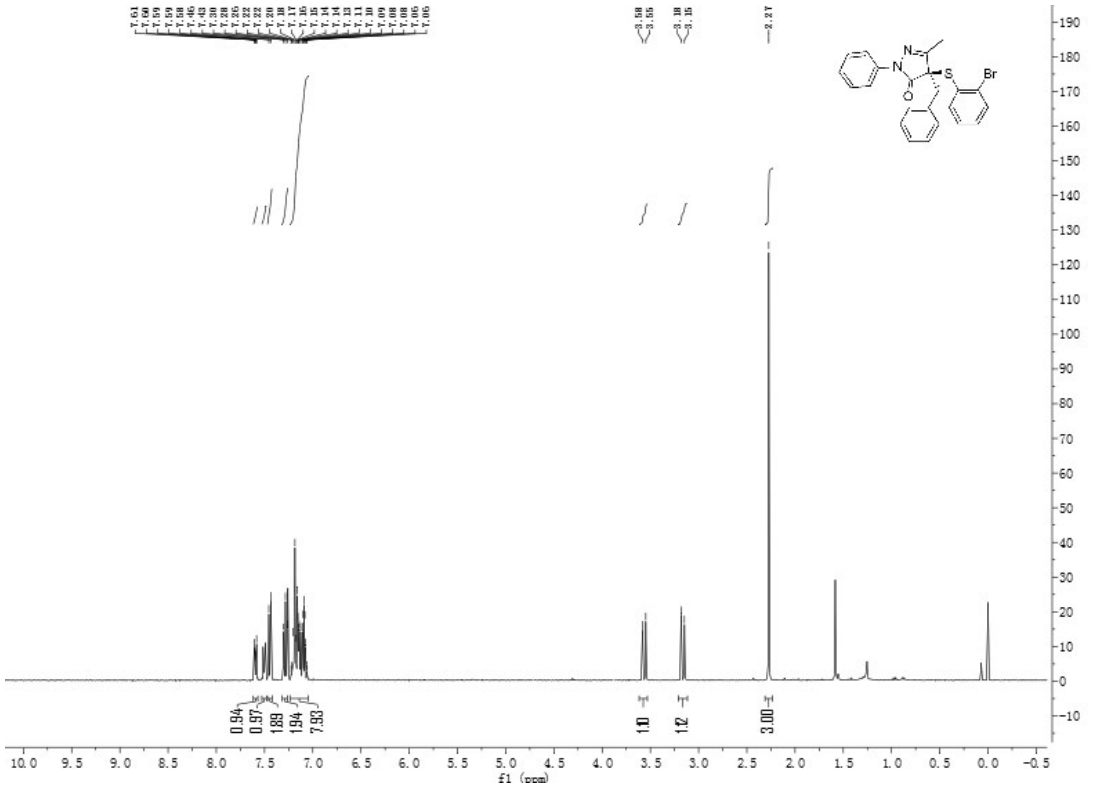

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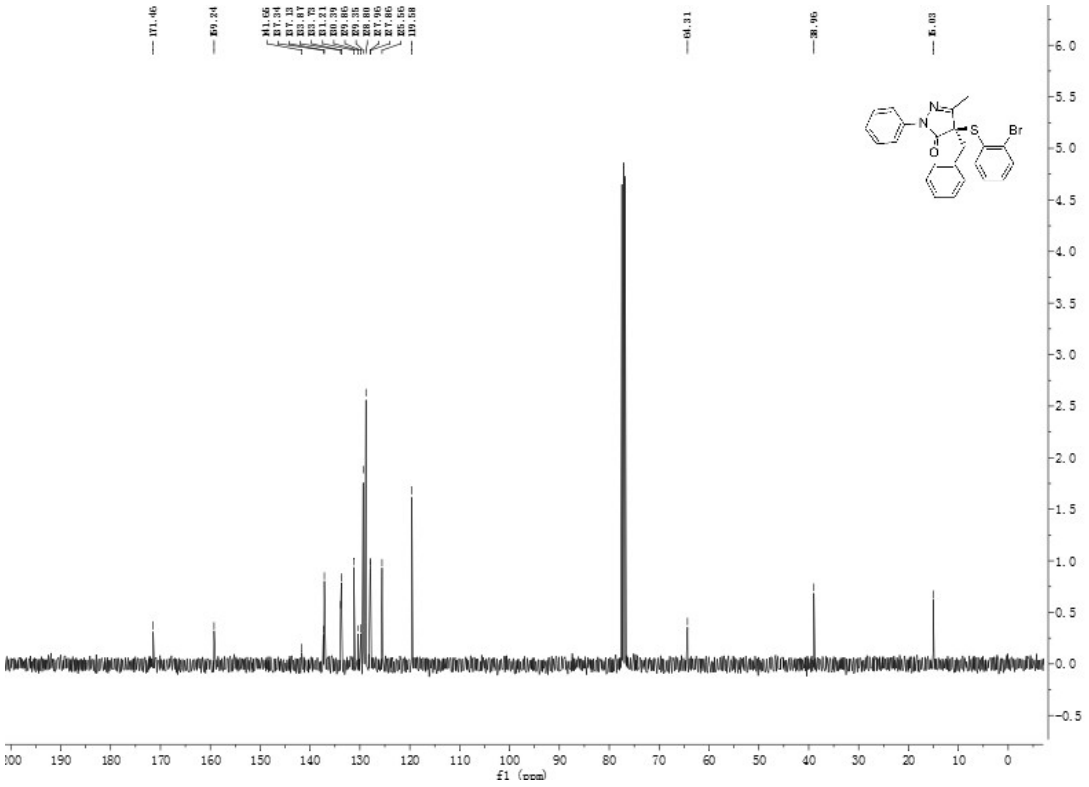

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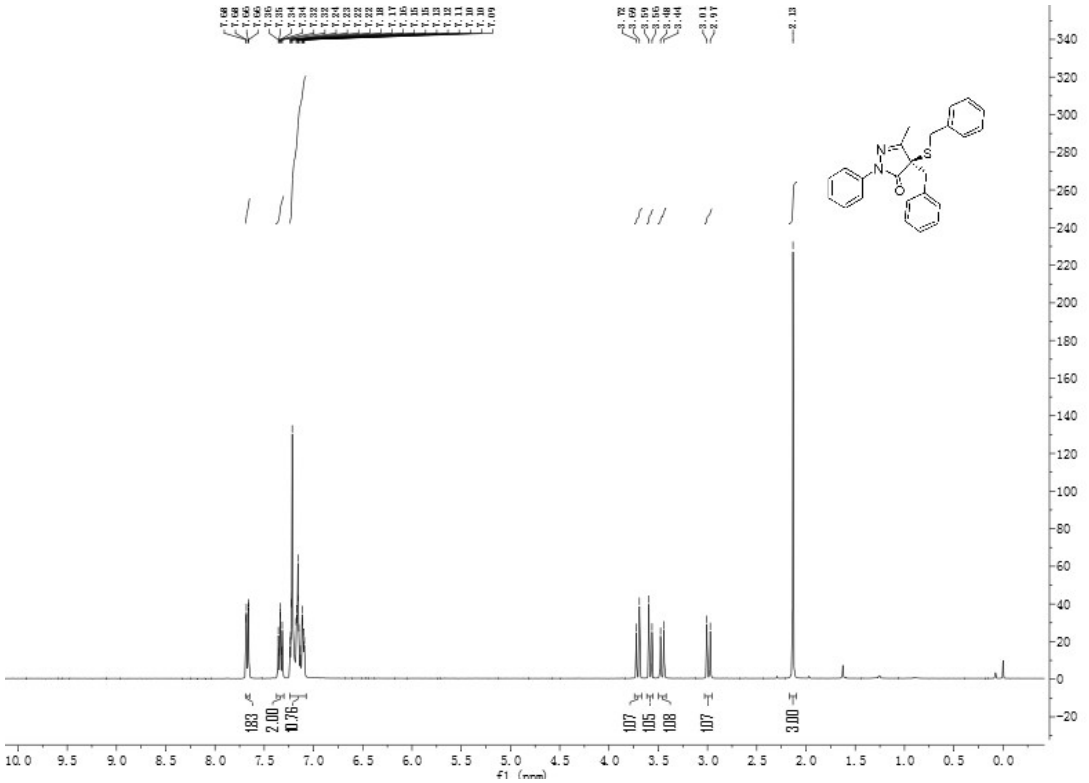

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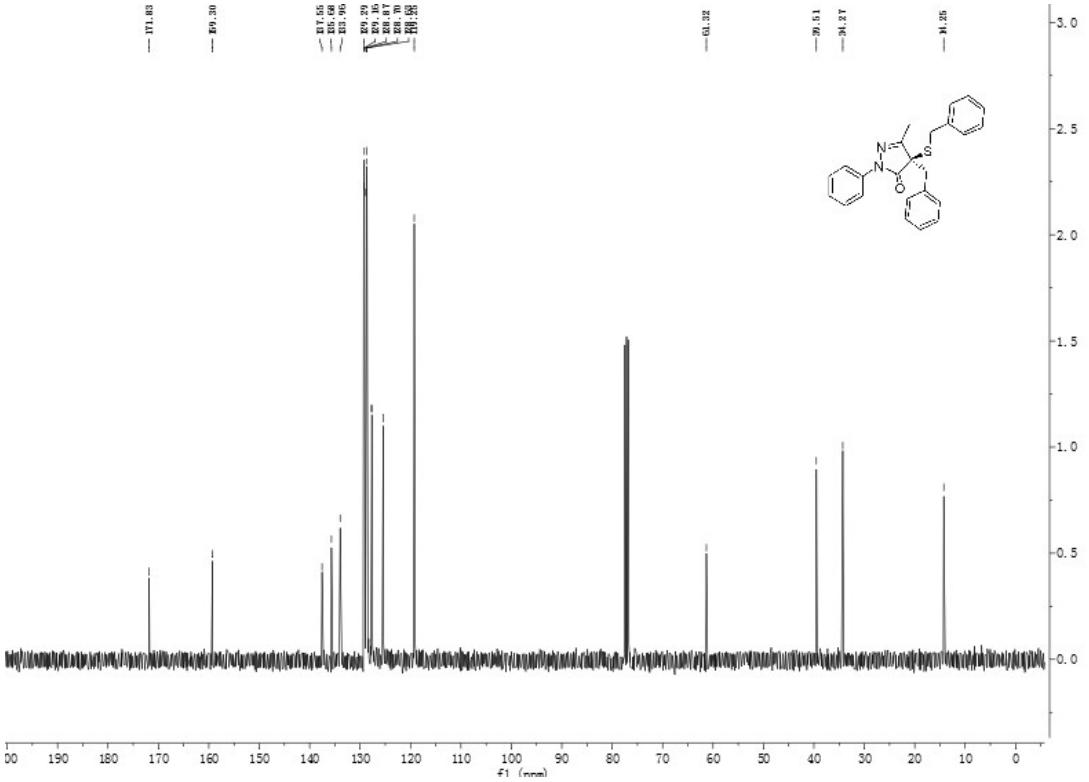

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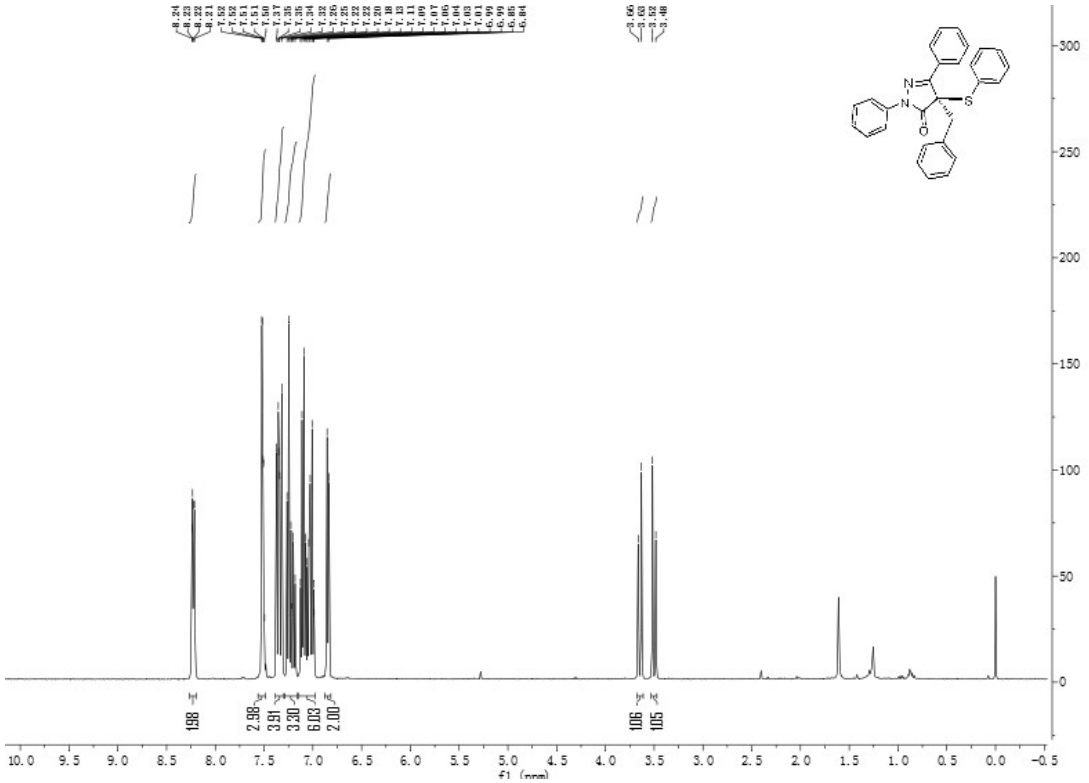

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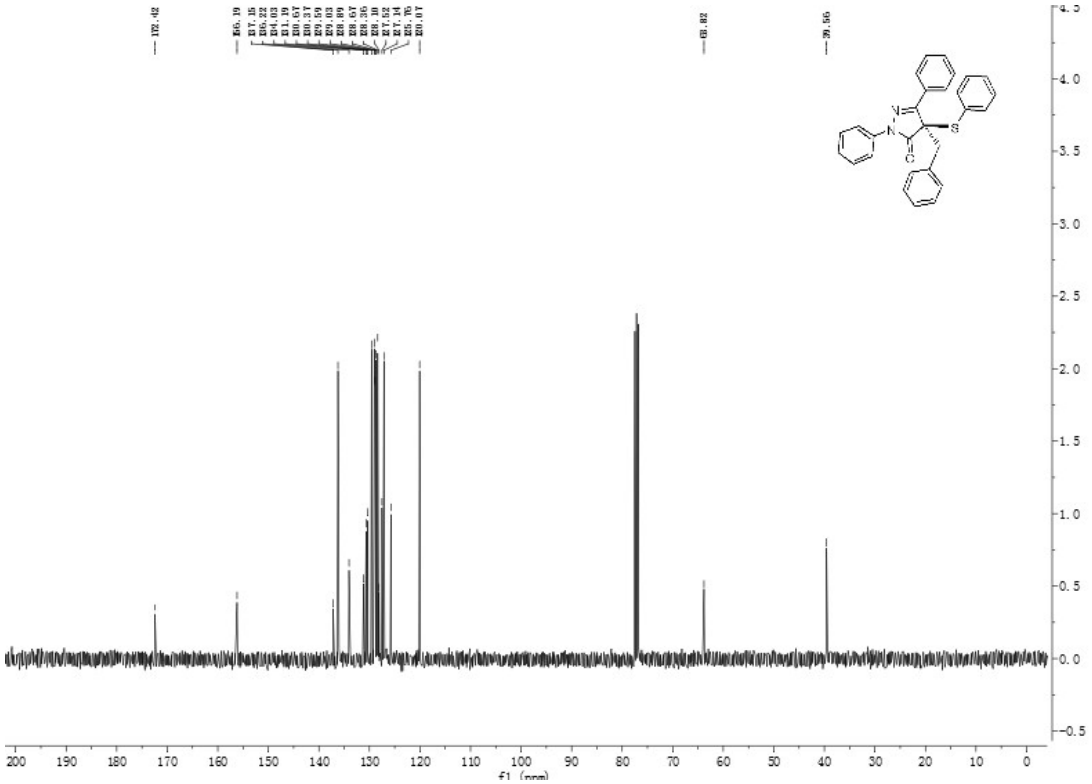

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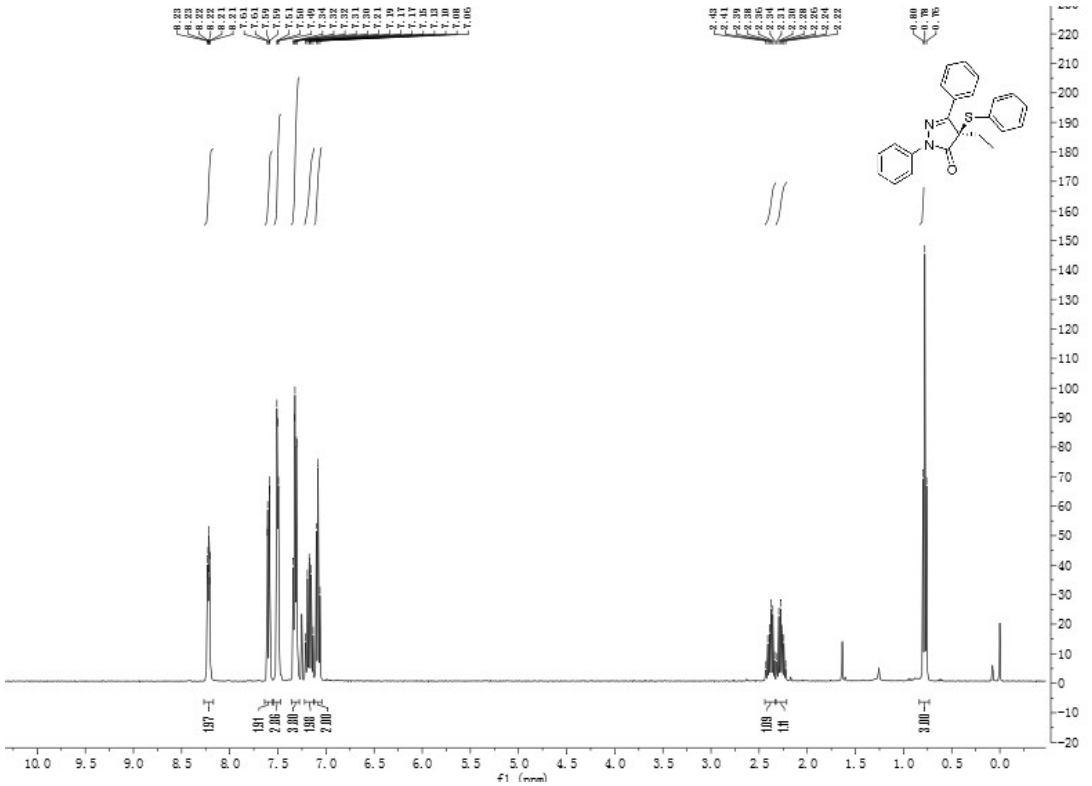
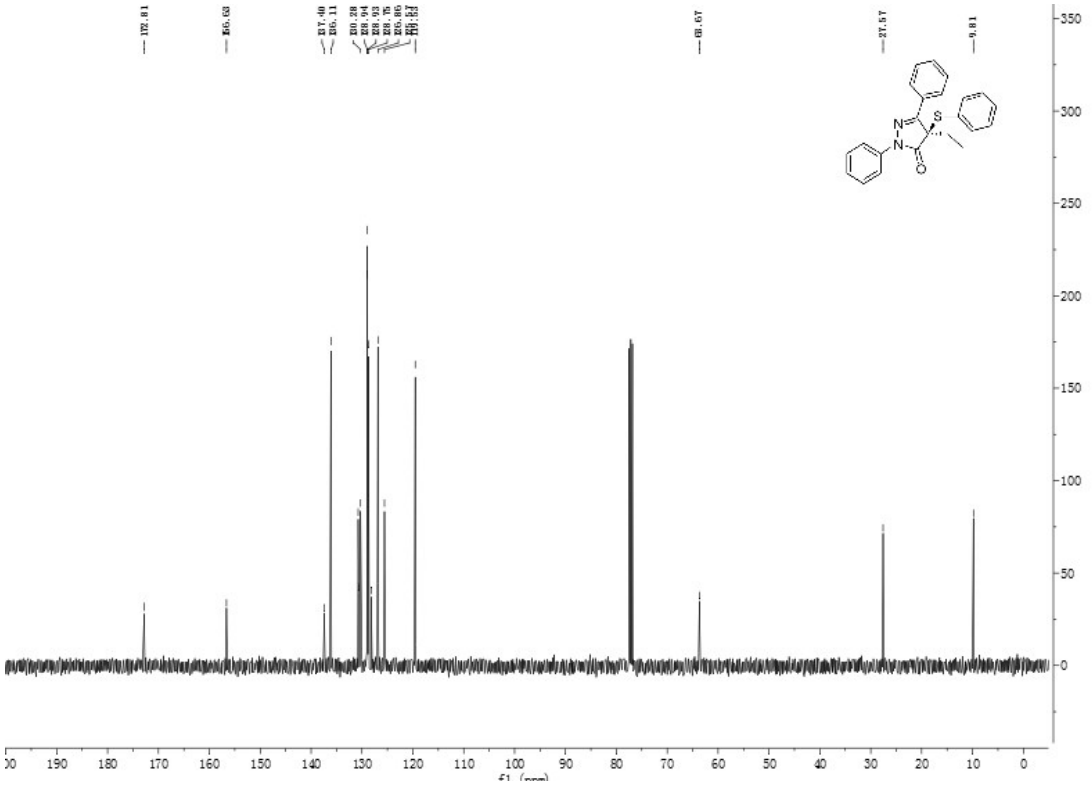
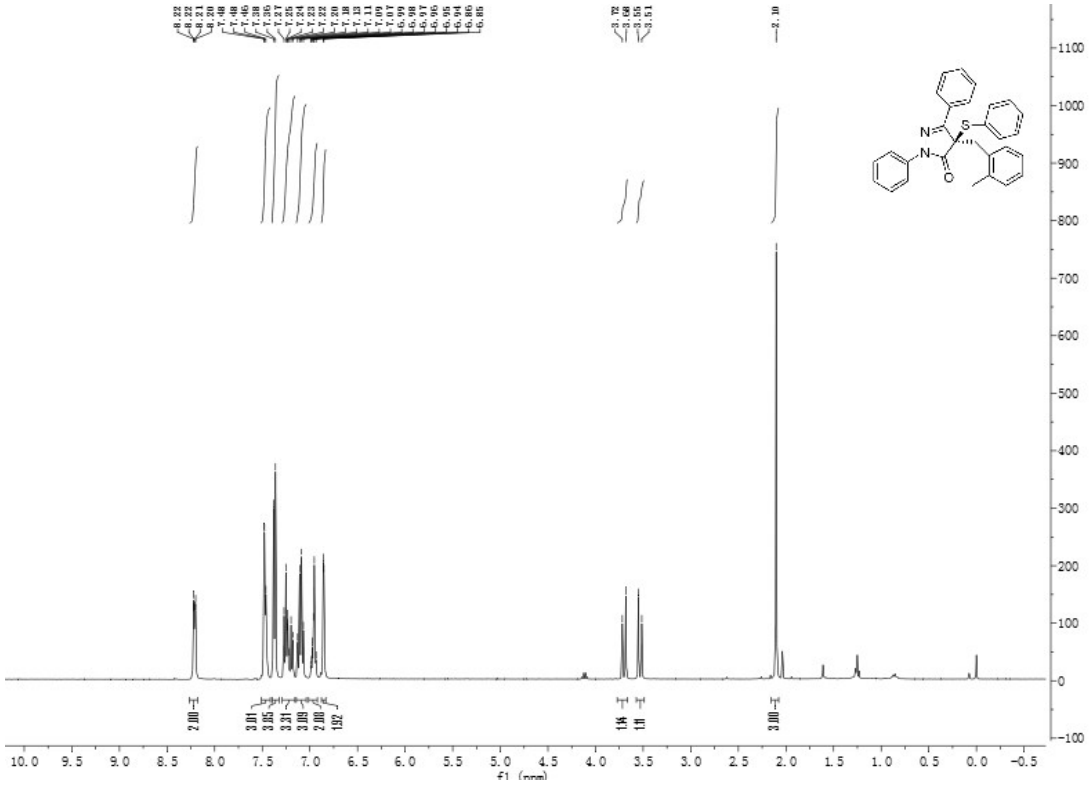


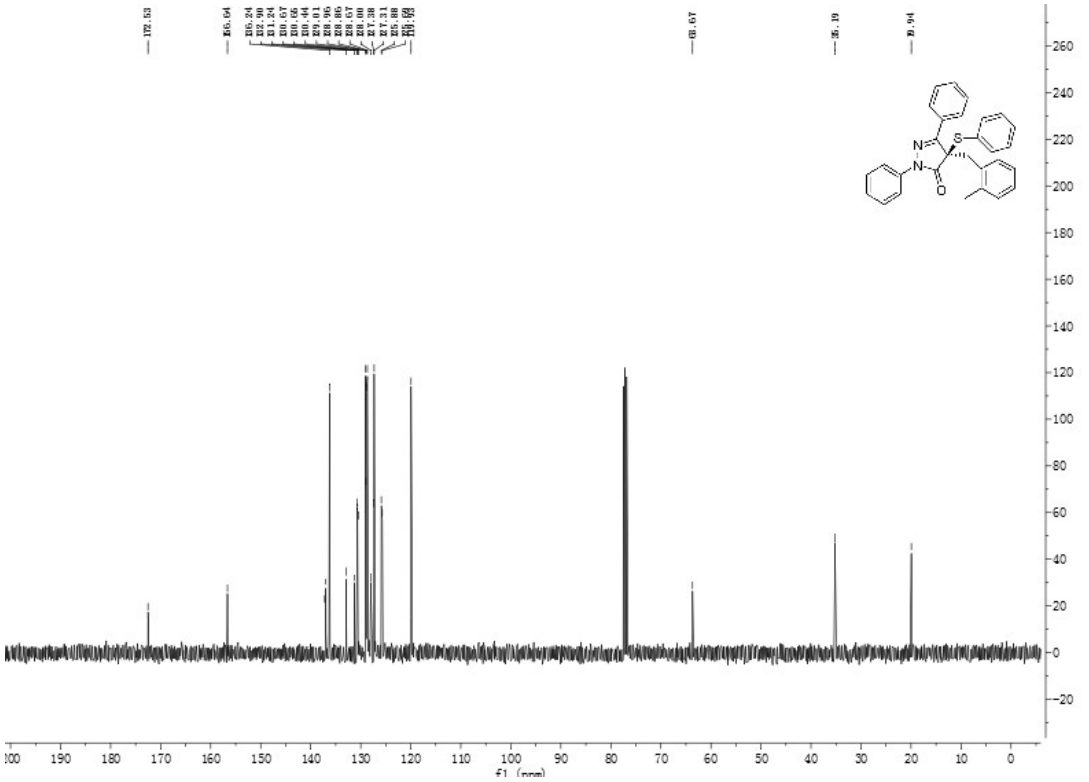
^{13}C NMR ($CDCl_3$)



^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)



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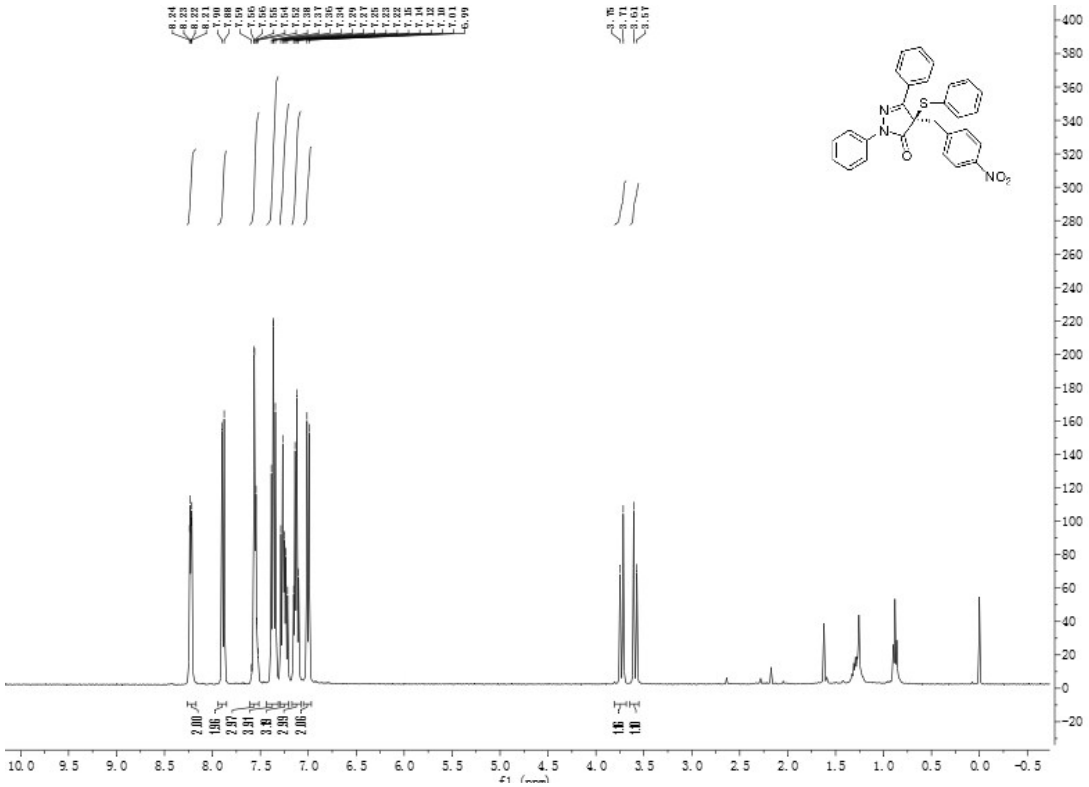

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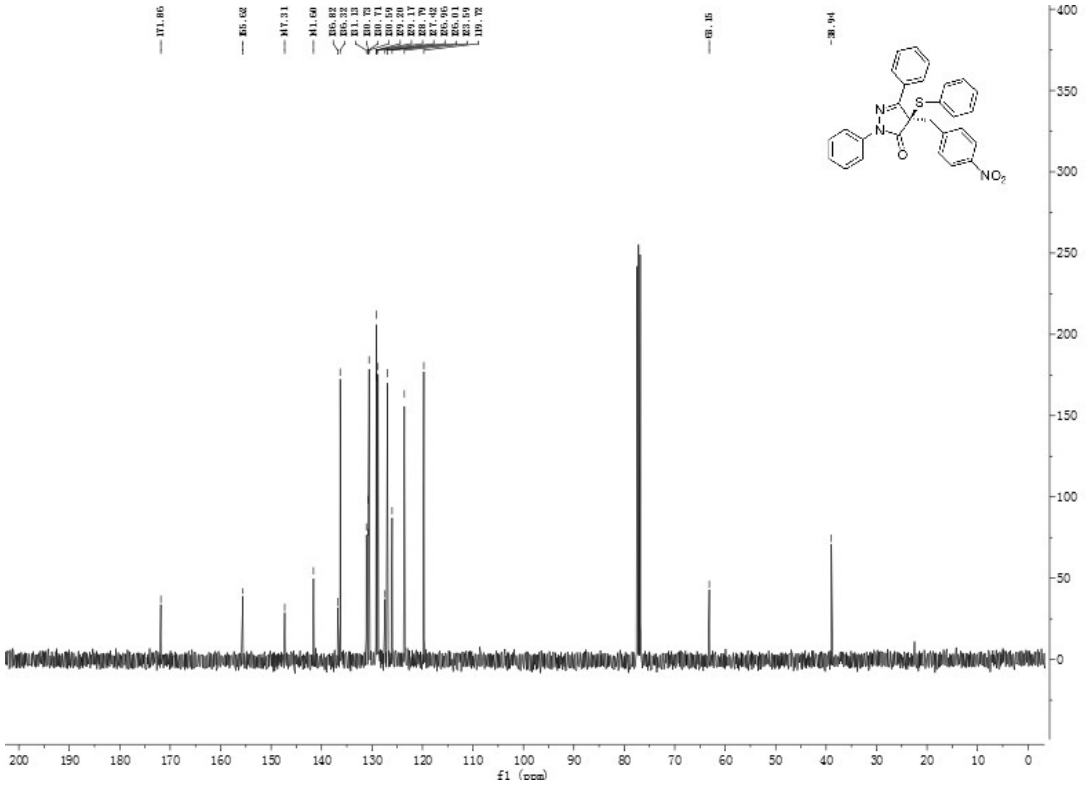

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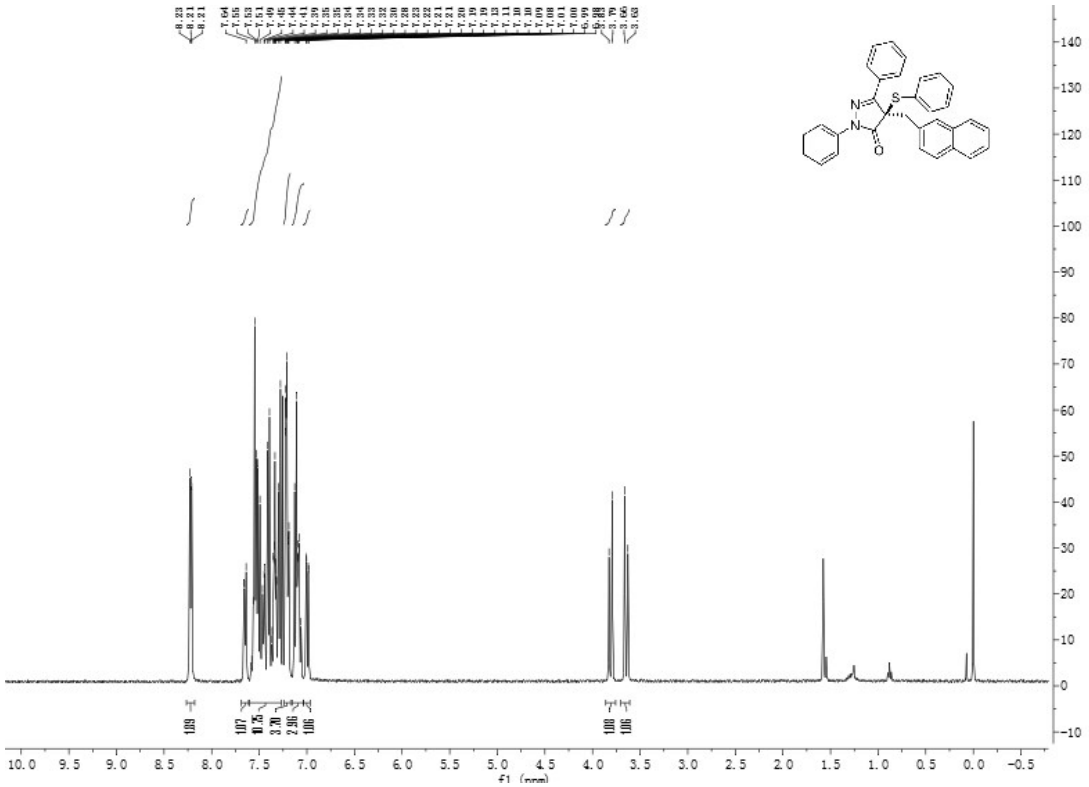
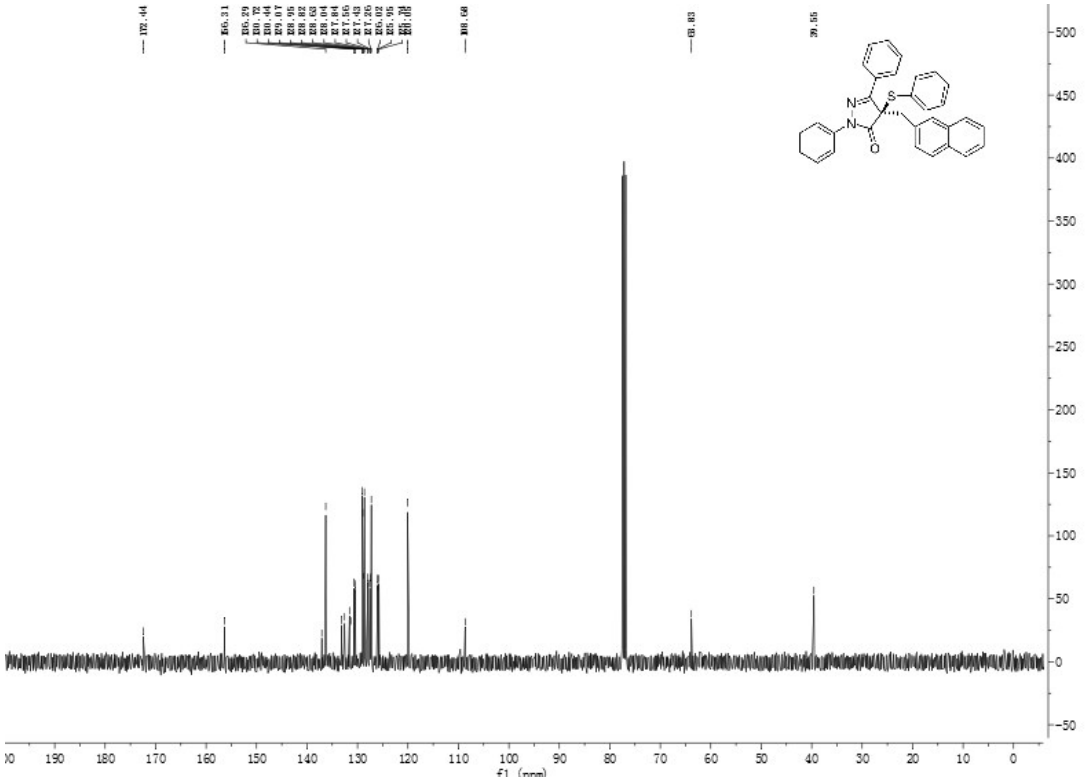
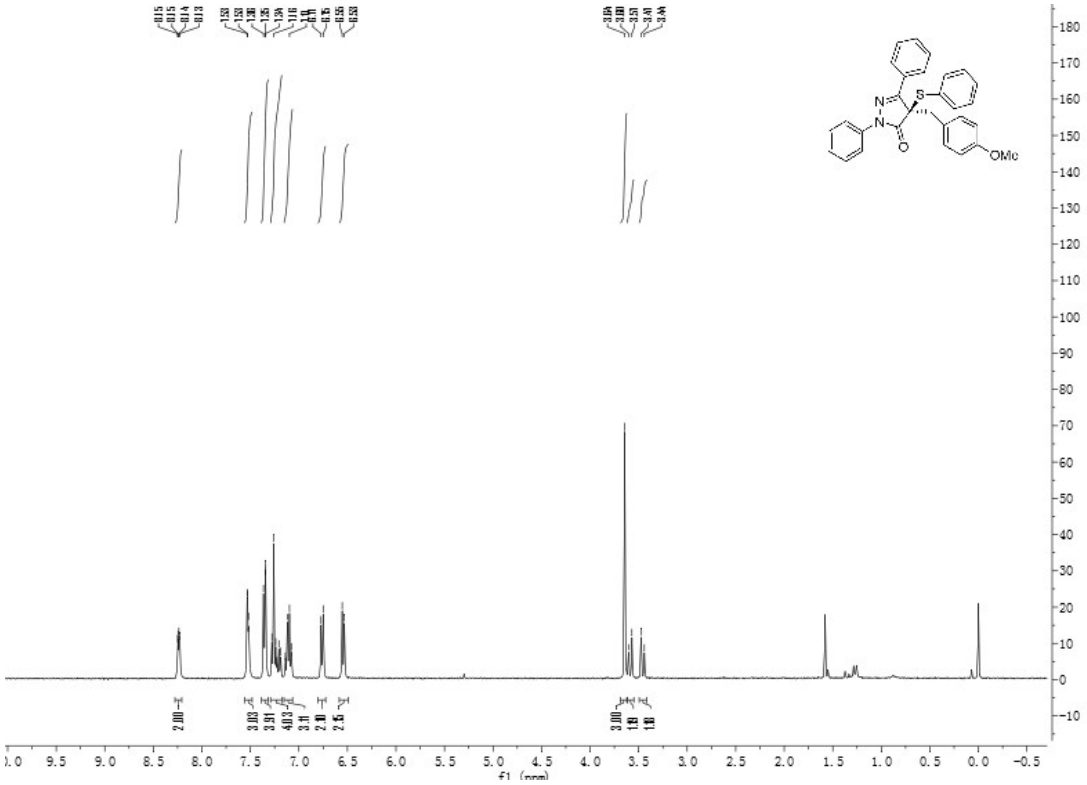


^{13}C NMR ($CDCl_3$)



^{1}H NMR ($CDCl_3$)



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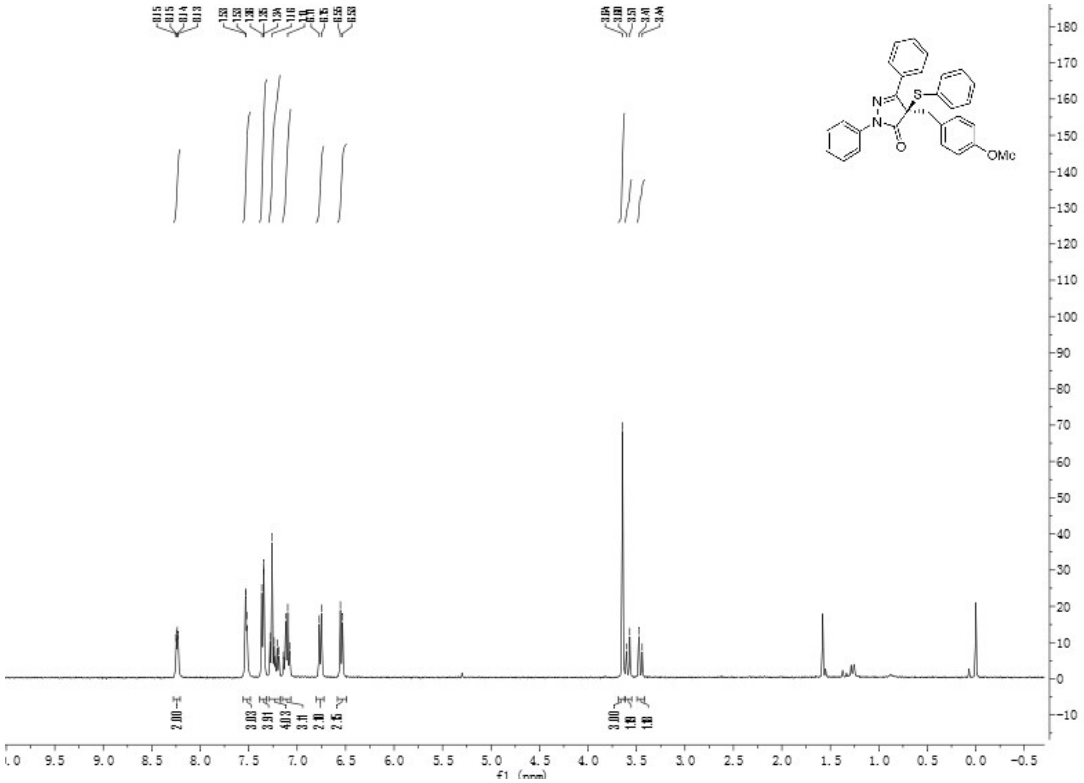

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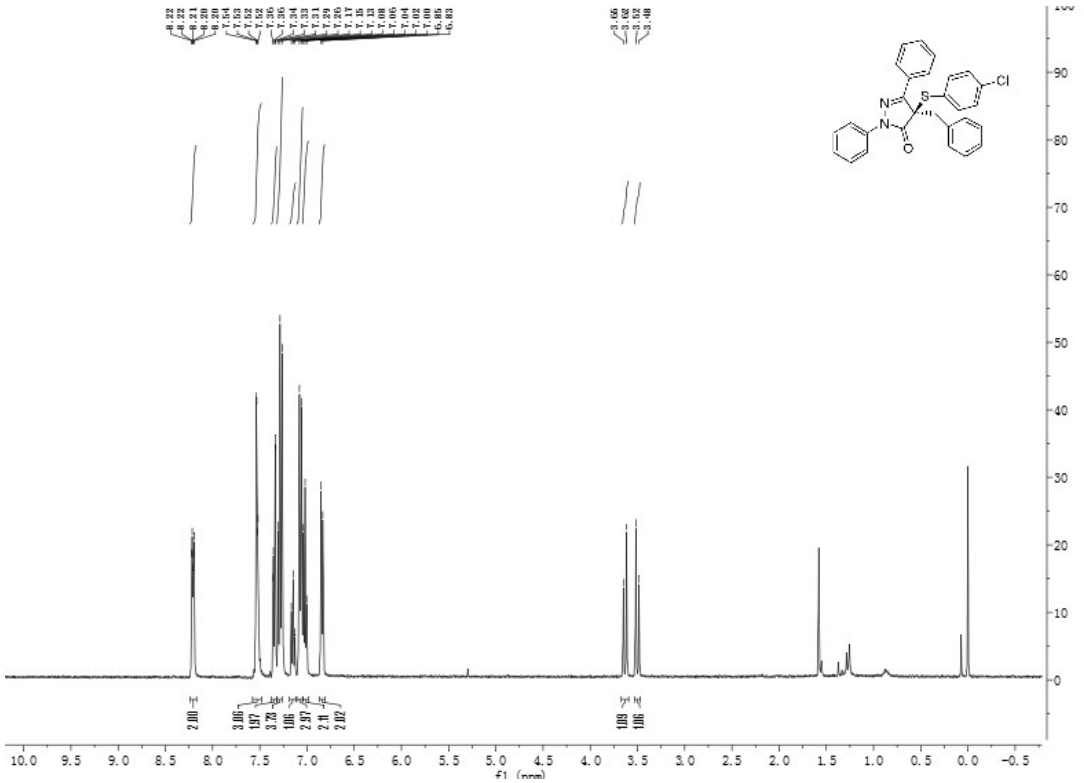
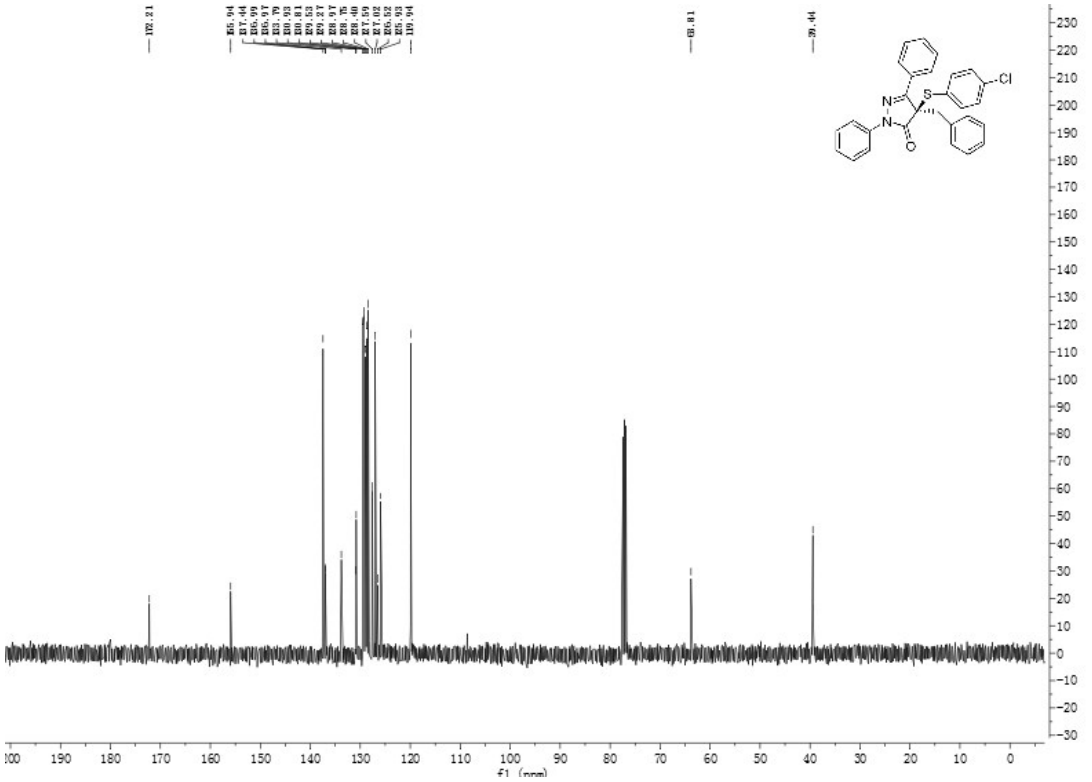


^{13}C NMR ($CDCl_3$)



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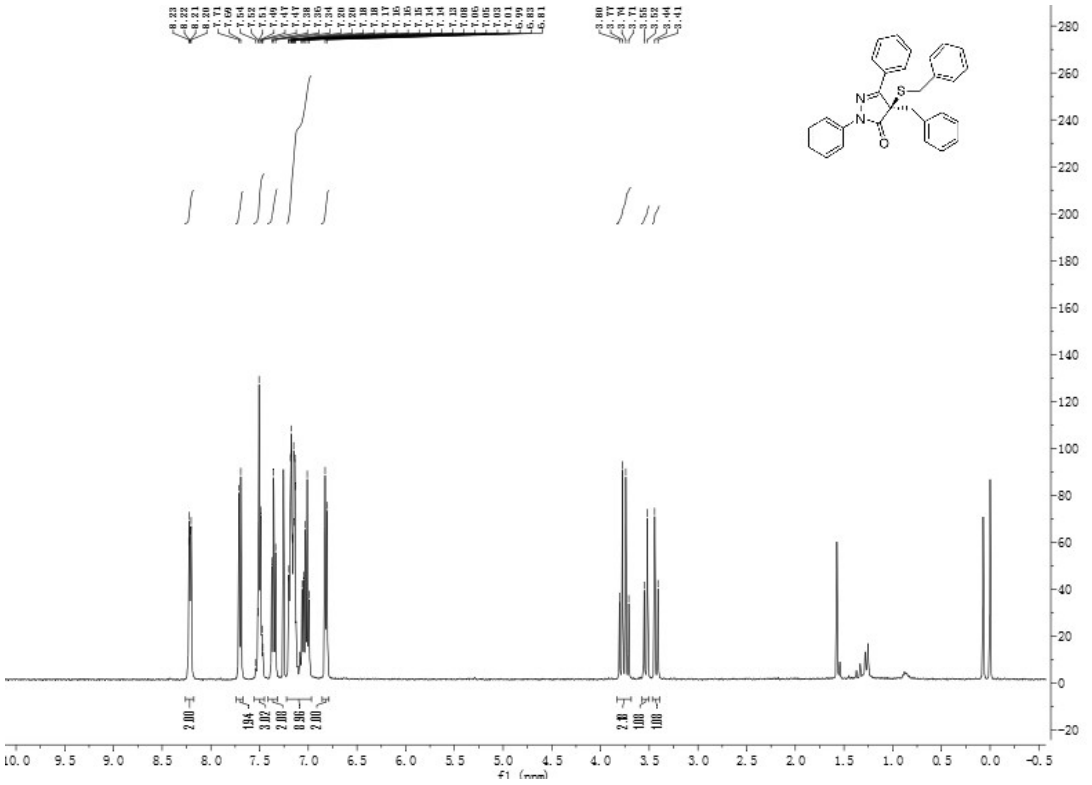

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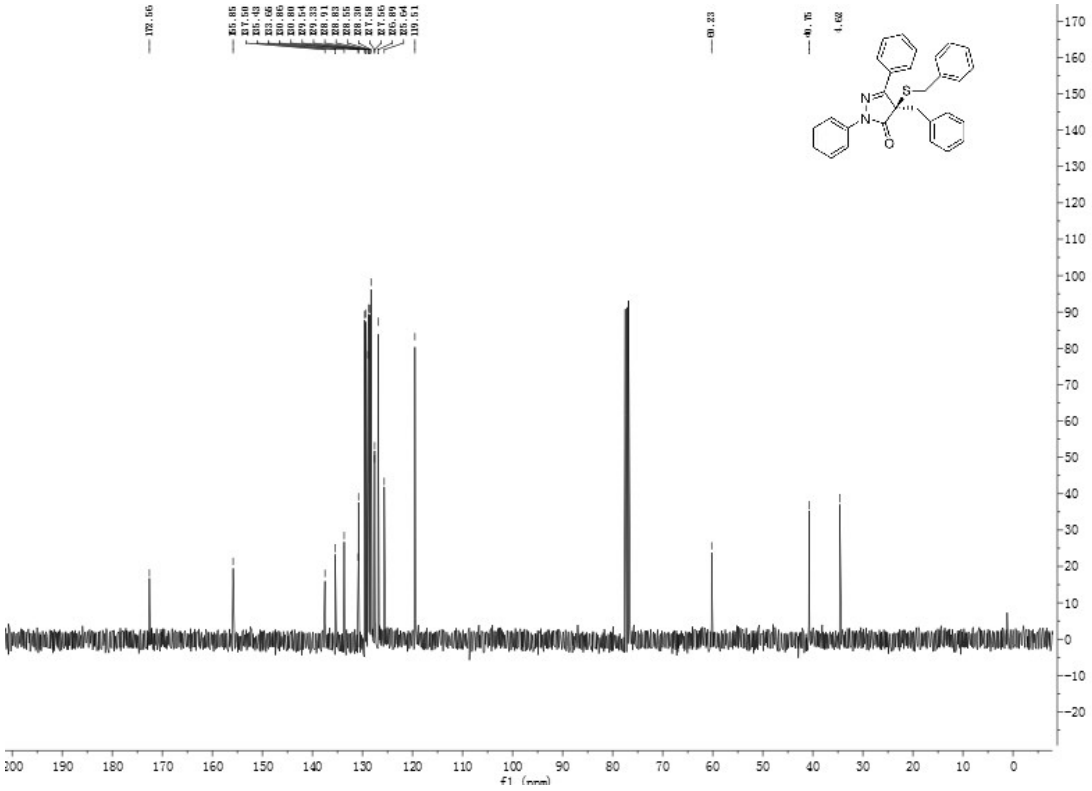

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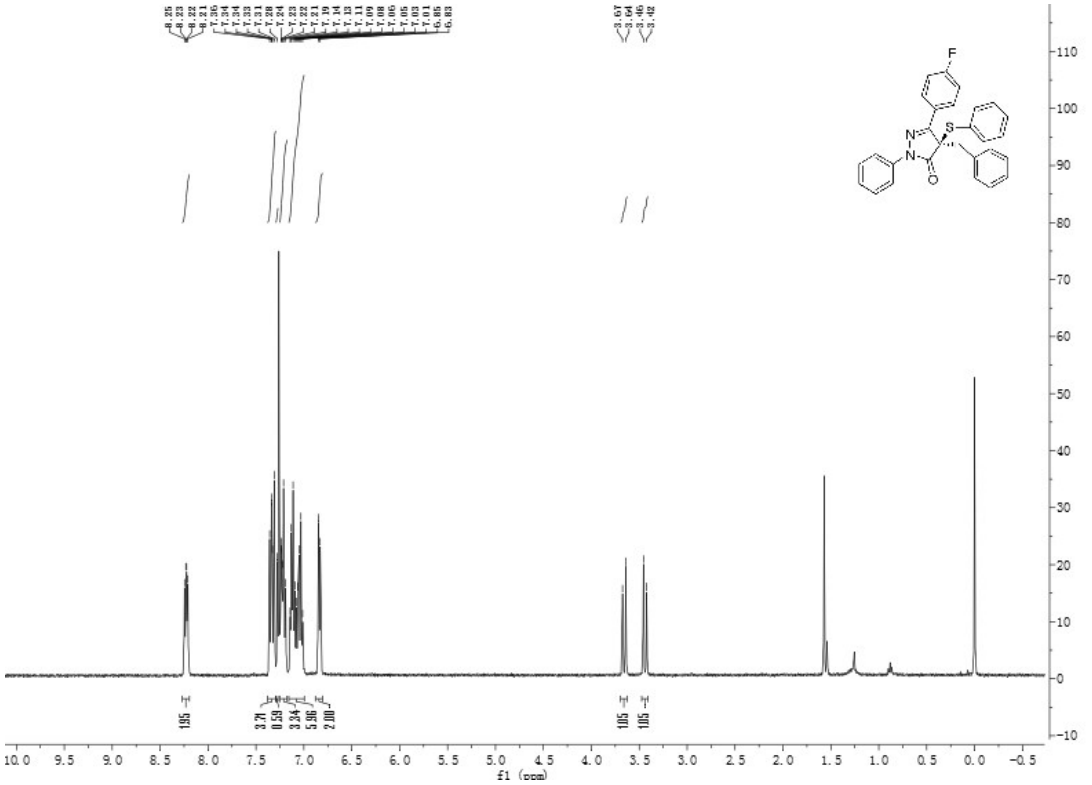

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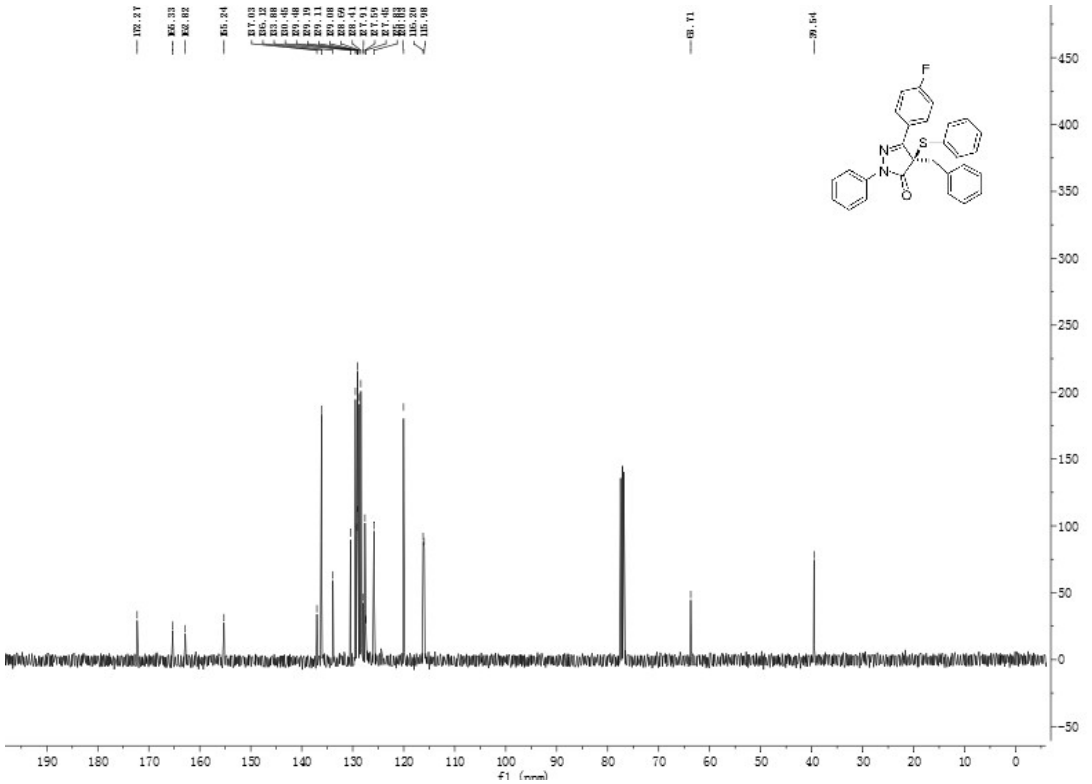
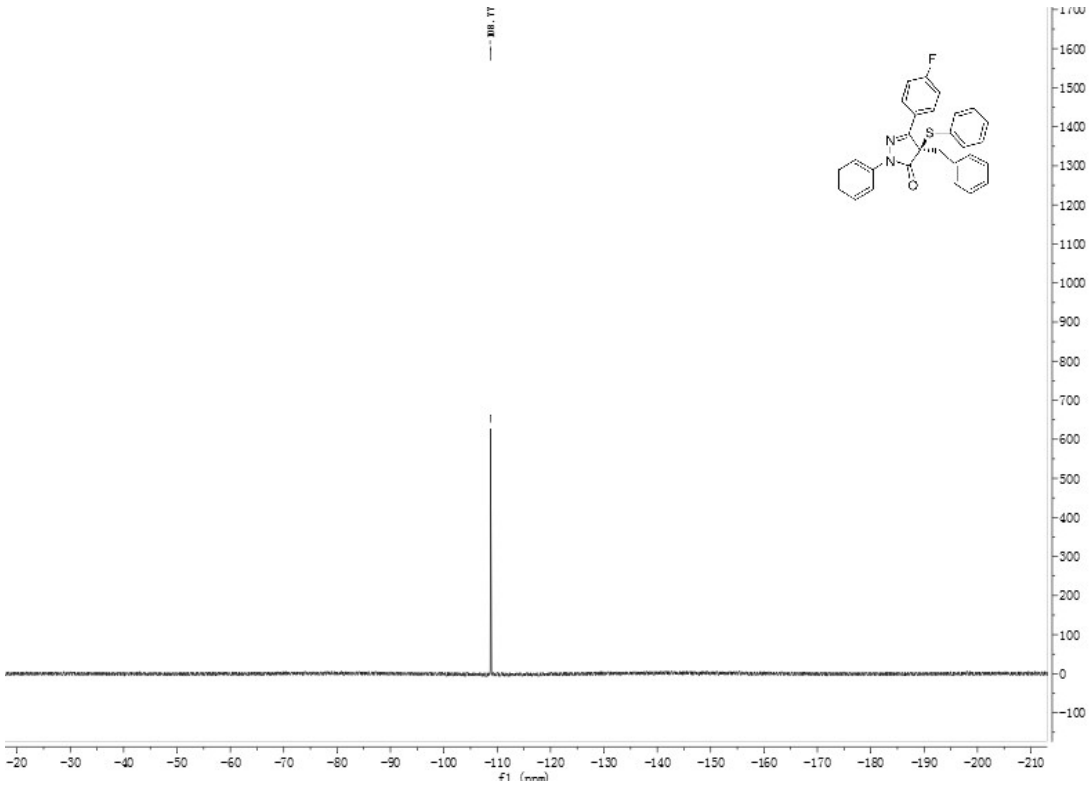
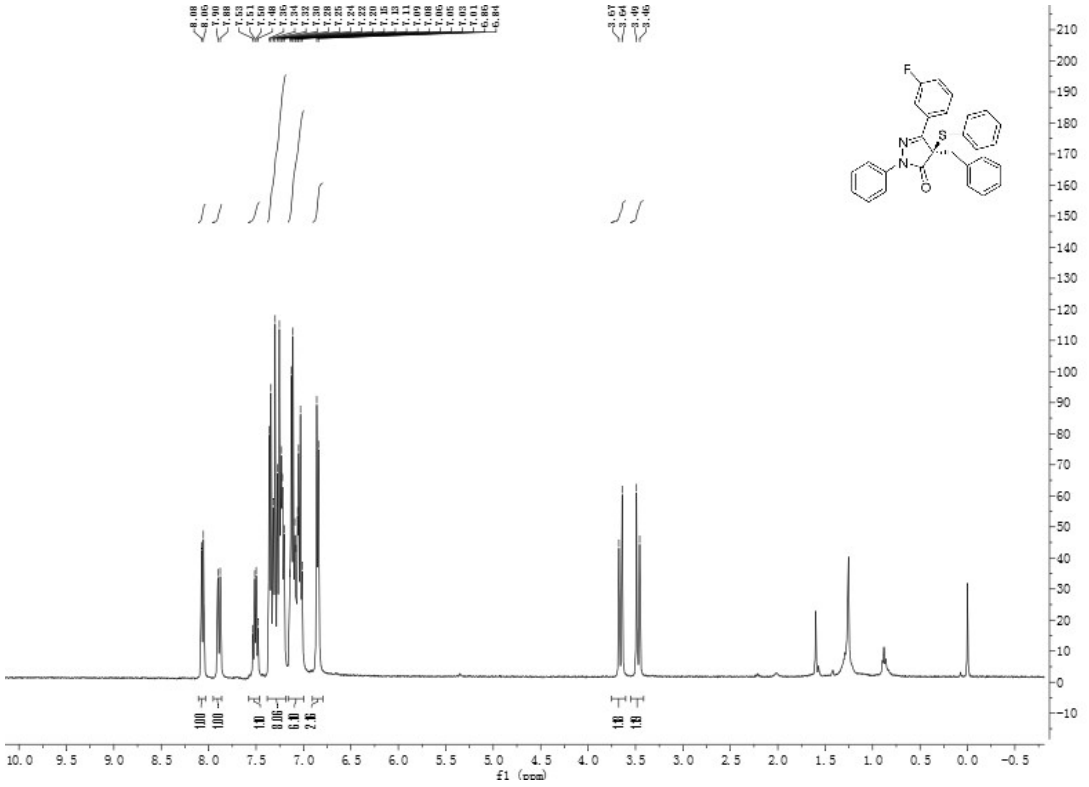


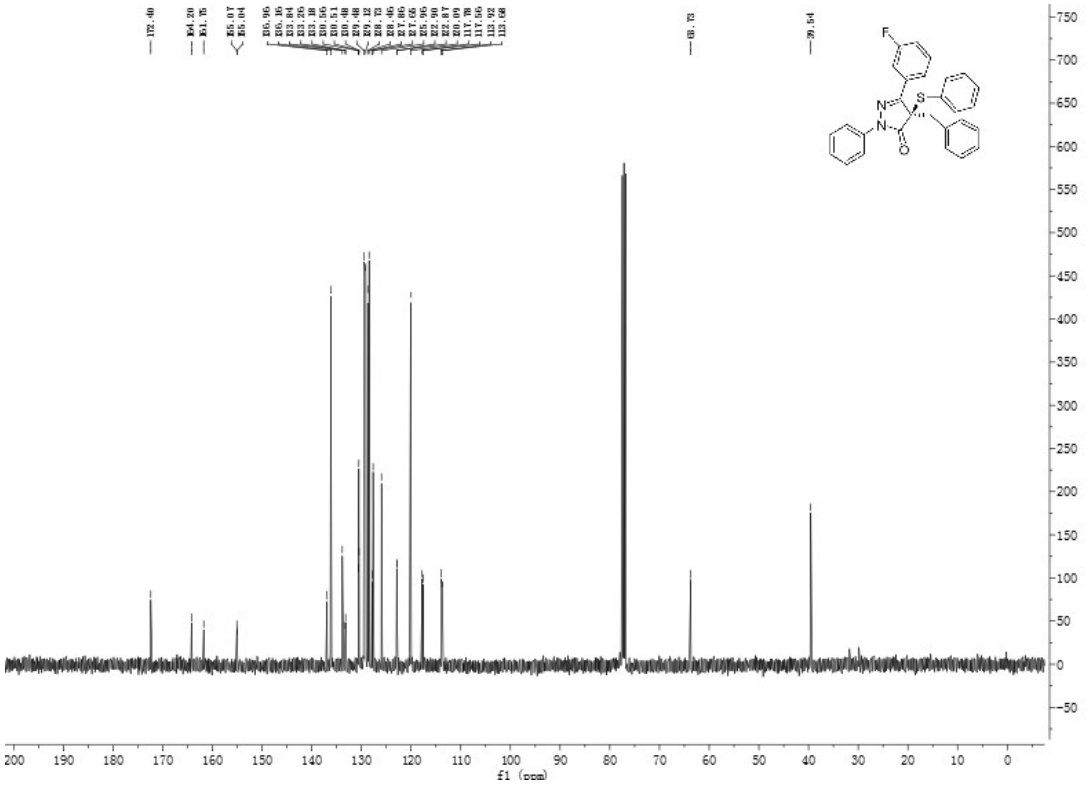
^{19}F NMR ($CDCl_3$)



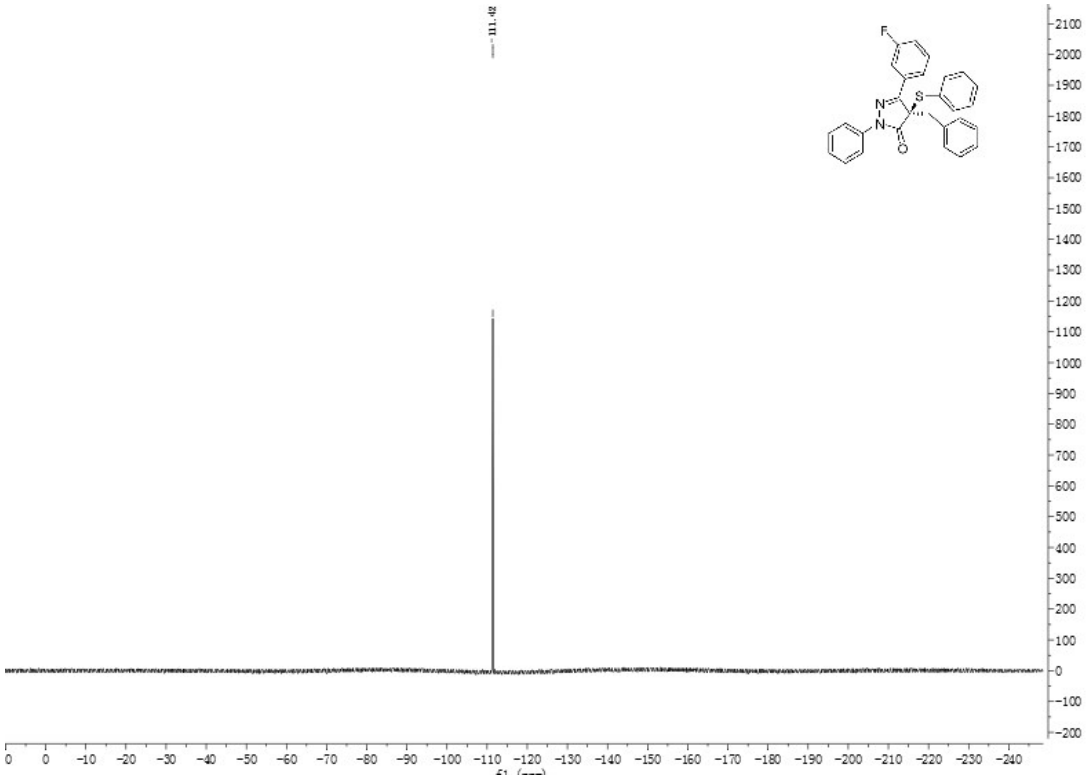
^{1}H NMR ($CDCl_3$)



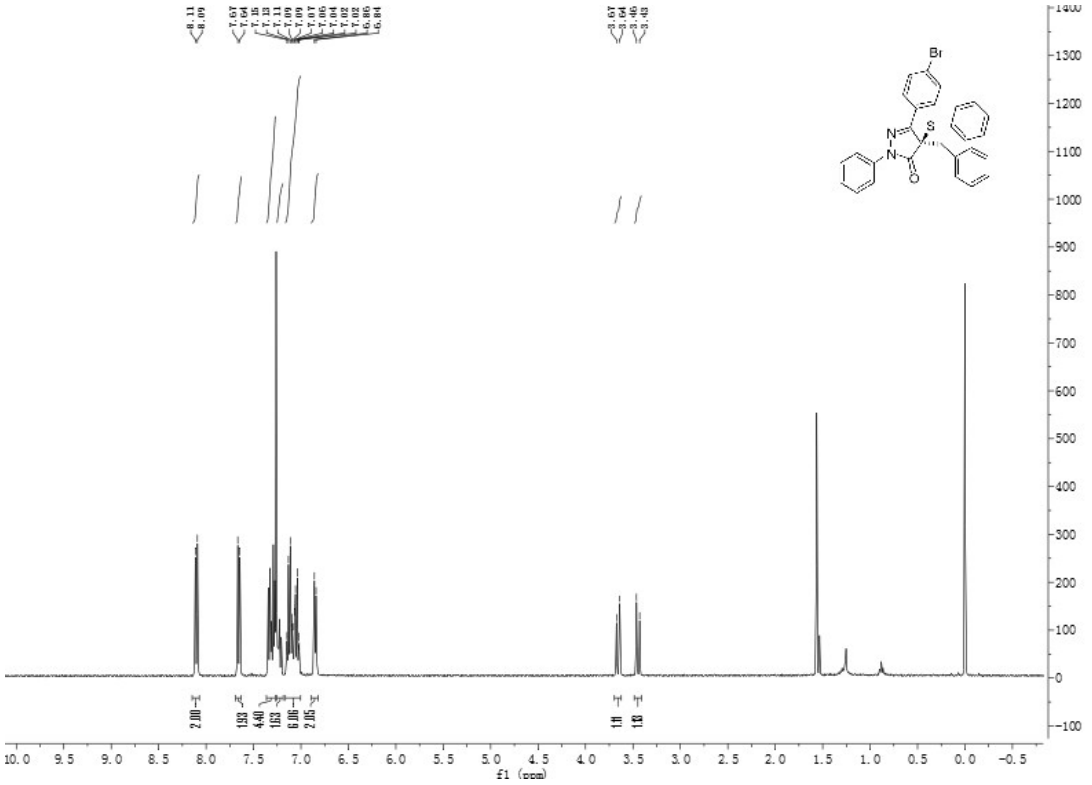
^{13}C NMR ($CDCl_3$)



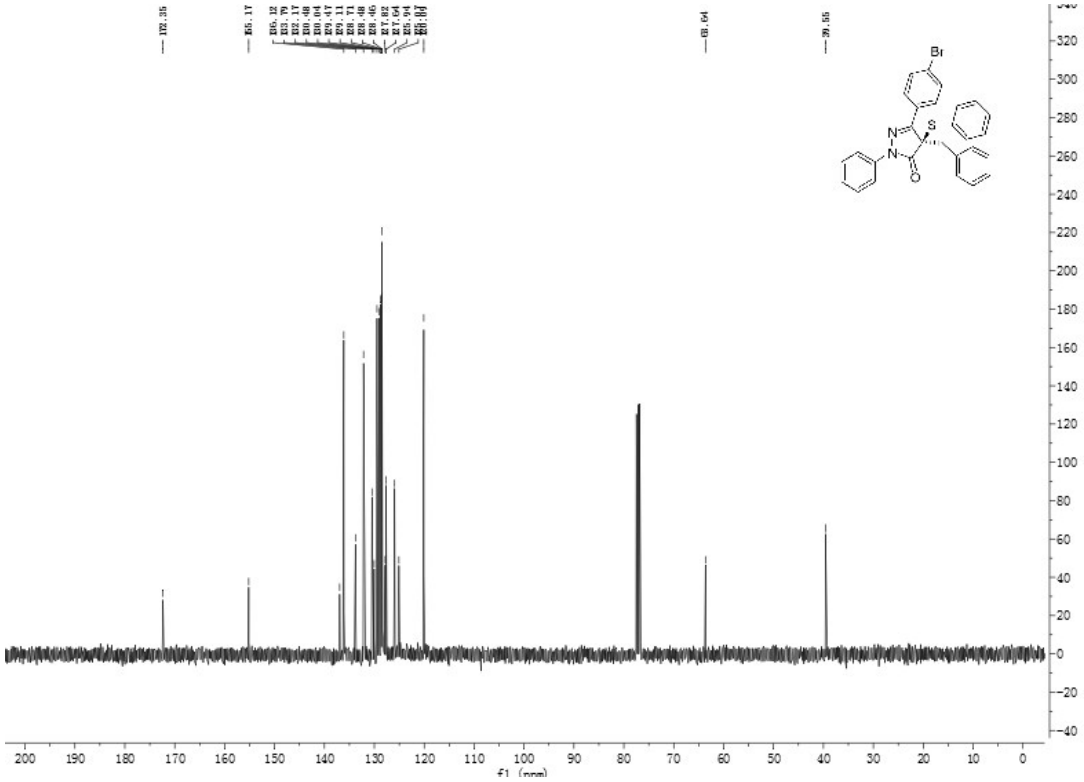
^{19}F NMR ($CDCl_3$)



^{1}H NMR ($CDCl_3$)



^{13}C NMR ($CDCl_3$)



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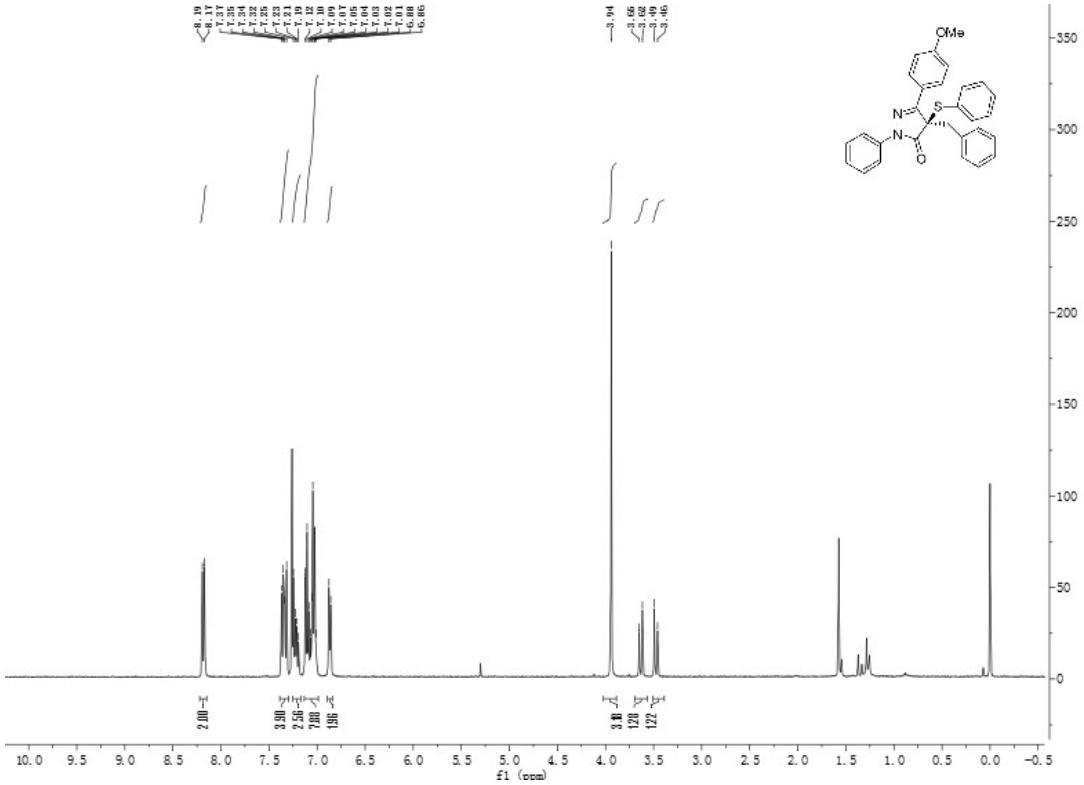

^{13}C NMR ($CDCl_3$)