Supporting Information

Asymmetric Synthesis of Atropisomeric Pyrazole via an Enantioselective Reaction of Azonaphthalene with Pyrazolone

Huijun Yuan, Yao Li, Hanhui Zhao, Zhihong Yang, Xin Li,* and Wenjun Li*

Department of Medicinal Chemistry, School of Pharmacy, Qingdao University, Qingdao, 266021, China.
State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin, 300071, China.
Email: liwj@qdu.edu.cn; xin_li@nankai.edu.cn

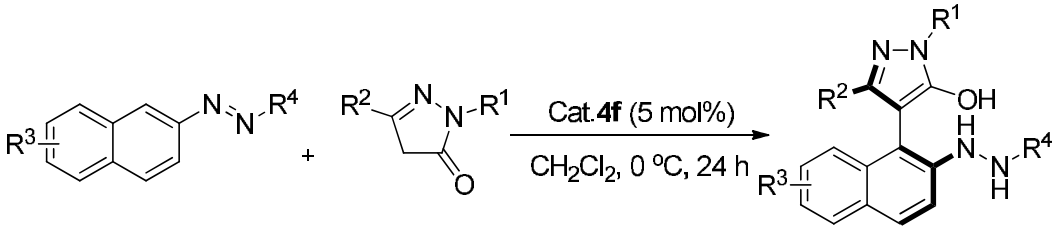
Contents

1. General Information and Starting Materials

General Information. Proton nuclear magnetic resonance (^{1}H NMR) spectra and carbon nuclear magnetic resonance (^{13}C NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz and 125 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent (DMSO-d_6: δ 2.50; $CDCl_3$: δ 7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent (DMSO-d_6: δ 39.50; $CDCl_3$: δ 77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

Starting Materials. All solvents, inorganic reagents were from commercial sources and used without purification unless otherwise noted. The azonaphthalenes and pyrazolones derivatives were prepared following the literature procedures.[1-2]

2. General Procedure for Reactions between Azonaphthalenes and Pyrazolones.

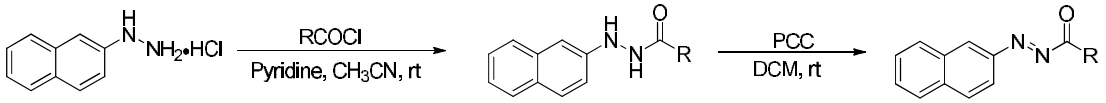


1 **2** **3**

To a solution of CH_2Cl_2 (0.3 mL) were added azonaphthalenes derivatives **1** (0.05 mmol), pyrazolones derivatives **2** (0.06 mmol), and catalyst **4f** (0.0025 mmol). The reaction mixture was stirred at 0 °C for 24 h and then the solvent was removed under vacuum to give a residue, which was purified by silica gel chromatography to yield the desired product **3**.

3. General Procedure for Synthesis of Azonaphthalenes and Pyrazolones.

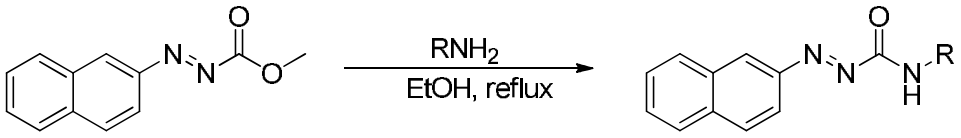
Procedures for Preparation of Substrates 1.



The corresponding hydrazine hydrochloride (10 mmol) was dissolved in CH_3CN (20 mL). Pyridine (1.71 mL, 21.2 mmol) was added. The solution was cooled to 0 ^oC and chloroformate (1.04 mL, 11 mmol) was added dropwise under stirring. The reaction mixture was stirred for 15 min at 0 ^oC and then for 1 h at room temperature. Water (20 mL) was added and the resulting mixture was acidified with HCl (6 M) to pH 4-6. The product was extracted with CH_2Cl_2 (5 x 10 mL). The combined organic layers were washed with saturated aq. $NaHCO_3$ (50 mL), brine (50 mL), dried over Na_2SO_4, and the solvent was evaporated to dryness. The crude products were purified by flash chromatography on silica gel eluted with PE/EA to afford the corresponding products in 70-97% yield.

PCC (1.078g, 6 mmol) was added to a solution of corresponding hydrazinecarboxylate (5 mmol) in 30 mL DCM. The mixture was stirred until hydrazinecarboxylate completely consumed (monitored by TLC). The reaction mixture was filtered. The filtrate was concentrated under reduced pressure and purified by chromatography on silica gel eluted with PE/EA (100/1-20/1) to afford the corresponding product **1a-1f** in 38-80% yield.

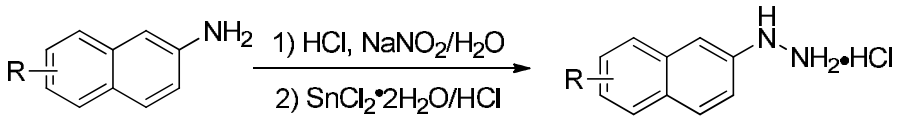
1g, 1h were synthesis from **1a.**



Propylamine (180 μL, 2.2 mmol) was added to a solution of **1a** (0.456 g, 2.0 mmol) in 10 mL EtOH. The reaction mixture was stirred and heated to 80 ^oC for 1 h. The

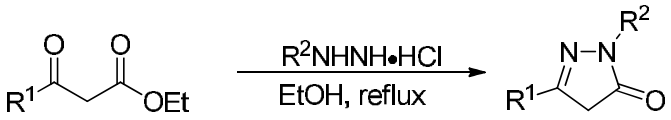
reaction mixture was concentrated under reduced pressure and purified by chromatography on silica gel eluted with PE/EA (100/1-5/1) to afford the desired product **1g**, **1h** in 94-97% yield.

1i-l was synthesized from naphthalen-2-amine derivatives.



$NaNO_2$ (513 mg, 5.76 mmol) in H_2O (1 mL) was slowly added over a suspension of naphthalen-2-amine derivatives (4.5 mmol) in con. HCl (5 mL) cooled in a H_2O-ice bath. The resulting solution was stirred in H_2O-ice bath for 1 h and $SnCl_2$•$2H_2O$ (3.556 g, 15.76 mol) was added slowly. The resulting suspension was stirred in H_2O-ice bath for 3.5 h and then filtered. The solid was successively washed with H_2O (4 x 8 mL) at 0 °C, with H_2O (1 x 8 mL) at room temperature, with Et_2O/hexane (1:1, 2 x 4 mL). The solid was dried to afford the desired product in 80-85% yield. The next procedures were similar to substrate **1a**.

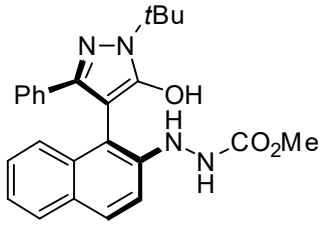
Procedures for Preparation of Substrates 2



To a solution of β-ketoester (15 mmol) in ethanol (10 ml) or acetic acid (10 ml) at room temperature was added corresponding hydrazine hydrochloride (1.0 equiv., 15 mmol). The mixture was then brought to reflux utill TLC indicated the completion of the reaction (3-24 h). The solvent was removed and the residue was recystallized from ethanol or purified by column chromatography on silica gel to give the desired products **2a-2t** in 56-91% yield.

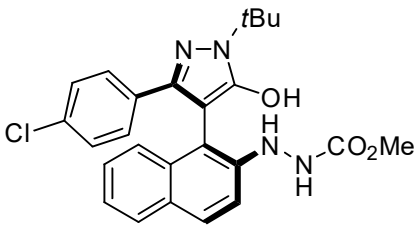
4. Characterization Data of Products

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3aa)



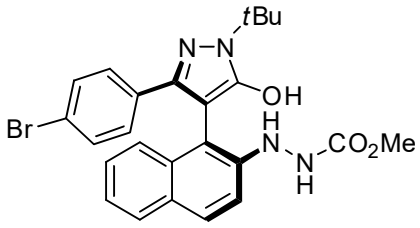
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 18.9 mg, 88% yield. mp 191.5-192.7 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.38 (br, 1H), 7.80 (d, *J* = 10.0 Hz, 1H), 7.74-7.72 (m, 1H), 7.47-7.43 (m, 3H), 7.25-7.21 (m, 2H), 7.08-7.07 (m, 4H), 6.01 (s, 1H), 3.68 (s, 3H), 1.79 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.5, 149.6, 146.9, 143.9, 134.3, 133.9, 129.8, 129.7, 128.1, 127.9, 127.0, 126.9, 125.8, 125.2, 123.8, 114.9, 112.9, 94.1, 59.3, 53.3, 29.0. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{25}H_{27}N_4O_3$) requires m/z 431.2083, found m/z 431.2075. The enantiomeric excess was determined to be 90% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 4.0 min (minor), 5.8 min (major). $[\alpha]^{22}_D$ = -44.00 (c = 1.00, CH_2Cl_2).

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(4-chlorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ab)



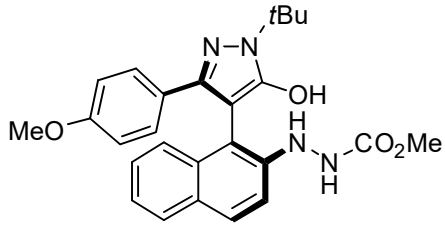
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 19.3 mg, 83% yield. mp 184.6-185.6 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.38 (br, 1H), 7.82 (d, *J* = 10.0 Hz, 1H), 7.75-7.73 (m, 1H), 7.38-7.36 (m, 3H), 7.29-7.27 (m, 1H), 7.26-7.24 (m, 1H), 7.04-7.02 (m, 3H), 6.03 (s, 1H), 3.72 (s, 3H), 1.76 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.4, 149.6, 145.8, 143.9, 133.7, 132.8, 132.7, 129.9, 129.8, 128.3, 127.9, 127.0, 124.9, 123.9, 114.9, 112.6, 94.0, 59.5, 53.4, 28.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{25}H_{26}ClN_4O_3$) requires m/z 465.1693, found m/z 465.1691. The enantiomeric excess was determined to be 90% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.4 min (minor), 6.9 min (major). $[\alpha]^{22}_D$ = -54.40 (c = 1.00, CH_2Cl_2).

(*S*)-methyl 2-(1-(3-(4-bromophenyl)-1-(*tert*-butyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ac)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 22.4 mg, 88% yield. mp 181.3-182.0 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.37 (br, 1H), 7.83-7.82 (m, 1H), 7.75-7.73 (m, 1H), 7.38-7.36 (m, 1H), 7.31-7.29 (m, 3H), 7.26-7.25 (m, 1H), 7.18-7.17 (m, 2H), 7.01 (s, 1H), 6.03 (s, 1H), 3.72 (s, 3H), 1.76 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.4, 149.6, 145.8, 143.9, 133.7, 133.3, 131.2, 129.9, 129.8, 127.9, 127.3, 127.0, 124.9, 123.9, 120.9, 114.9, 112.6, 94.0, 59.5, 53.4, 28.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{25}H_{26}BrN_4O_3$) requires m/z 509.1188, found m/z 509.1187. The enantiomeric excess was determined to be 89% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.5 min (minor), 7.5 min (major). $[\alpha]^{22}_{D}$ = -43.00 (c = 1.00, CH_2Cl_2).

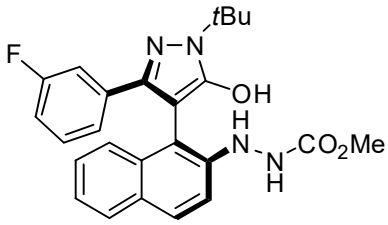
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-(4-methoxyphenyl)-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ad)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 17.5 mg, 76% yield. mp 94.7-95.6 ^{o}C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.20 (br, 1H), 7.81 (d, *J* = 10.0 Hz, 1H), 7.73-7.72 (m, 1H), 7.44-7.42 (m, 1H), 7.37-7.35 (m, 2H), 7.27-7.26 (m, 2H), 7.01 (s, 1H), 6.61-6.59 (m, 2H), 6.06 (s, 1H), 3.72 (s, 3H), 3.65 (s, 3H), 1.76 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.6, 149.6, 146.9, 143.9, 133.9, 129.8, 129.6, 127.9, 127.1, 127.0, 126.9, 125.2, 123.8, 123.4, 114.9, 113.6, 113.1, 93.6, 59.2, 55.0, 53.3, 29.0. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{26}H_{29}N_4O_4$) requires m/z 461.2189, found m/z 461.2185. The enantiomeric excess was determined to be 87% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 4.6 min (minor), 7.7 min (major). $[\alpha]^{22}_{D}$ = -51.20 (c = 1.00,

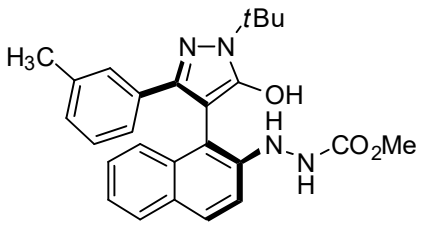
CH_2Cl_2).

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(3-fluorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ae)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 20.3 mg, 91% yield. mp 202.6-203.3 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.39 (br, 1H), 7.83 (d, *J* = 5.0 Hz, 1H), 7.75-7.73 (m, 1H), 7.40-7.38 (m, 1H), 7.29-7.27 (m, 2H), 7.25-7.24 (m, 1H), 7.13-7.11 (m, 1H), 7.05 (s, 1H), 7.00-6.97 (m, 1H), 6.76-6.73 (m, 1H), 6.04 (s, 1H), 3.72 (s, 3H), 1.77 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 162.8 (d, *J* = 970.0 Hz), 158.5, 149.6, 145.8, 143.9, 136.6 (d, *J* = 25.0 Hz), 133.8, 129.9, 129.8, 129.6 (d, *J* = 35.0 Hz), 127.9, 126.9, 124.9, 123.9, 121.4, 115.0, 113.8 (d, *J* = 85.0 Hz), 112.5 (d, *J* = 85.0 Hz), 109.9, 94.3, 59.5, 53.4, 28.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{25}H_{26}FN_4O_3$) requires m/z 449.1989, found m/z 449.1986. The enantiomeric excess was determined to be 92% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.3 min (minor), 9.6 min (major). $[\alpha]^{22}_D$ = -58.00 (c = 1.00, CH_2Cl_2).

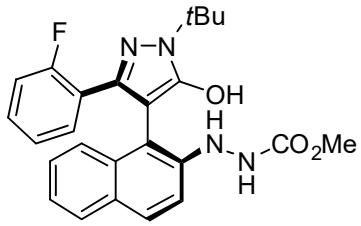
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-(*m*-tolyl)-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3af)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 18.9 mg, 85% yield. mp 182.2-183.2 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 9.79 (s, 1H), 9.40 (s, 1H), 7.83-7.81 (m, 1H), 7.74-7.73 (m, 1H), 7.35 (s, 1H), 7.25-7.14 (m, 4H), 7.04 (s, 1H), 6.88-6.83 (m, 2H), 6.72 (s, 1H), 3.61 (s, 3H), 2.09 (s, 3H), 1.68 (s, 9H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ (ppm) 158.4, 151.2, 146.1, 145.4, 136.9, 135.3, 134.6, 129.1, 128.8, 128.2, 128.1, 127.6, 126.9, 126.5, 124.6, 123.5, 122.6, 114.7, 110.5,

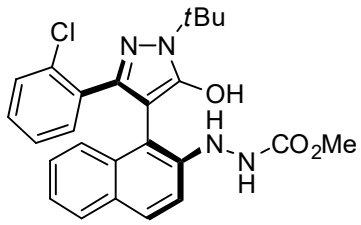
94.3, 58.6, 52.4, 29.3, 21.5. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{26}H_{29}N_4O_3$) requires m/z 445.2240, found m/z 445.2235. The enantiomeric excess was determined to be 91% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 70:30, 1.0 mL/min]: 3.6 min (minor), 6.1 min (major). $[\alpha]^{22}_D$ = -9.00 (c = 1.00, CH_2Cl_2).

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(2-fluorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ag)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 21.4 mg, 96% yield. mp 215.0-216.6 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.68 (s, 1H), 7.76-7.74 (m, 1H), 7.67-7.65 (m, 1H), 7.56-7.53 (m, 1H), 7.34-7.33 (m, 1H), 7.25-7.19 (m, 3H), 7.05-7.03 (m, 1H), 6.98-6.95 (m, 1H), 6.77-6.74 (m, 1H), 6.11 (s, 1H), 3.71 (s, 3H), 1.79 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 159.9 (d, *J* = 990.0 Hz), 158.6, 149.1, 144.2, 143.8, 133.7, 130.5 (d, *J* = 15.0 Hz), 129.7, 129.5, 128.9 (d, *J* = 30.0 Hz), 127.8, 126.4, 124.9, 123.9 (d, *J* = 10.0 Hz), 123.5, 122.4 (d, *J* = 55.0 Hz), 115.5 (d, *J* = 85.0 Hz), 114.9, 113.1, 95.9, 59.4, 53.4, 29.0. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{25}H_{26}FN_4O_3$) requires m/z 449.1983, found m/z 449.1976. The enantiomeric excess was determined to be 83% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.1 min (minor), 6.4 min (major). $[\alpha]^{22}_D$ = -93.00 (c = 1.00, CH_2Cl_2).

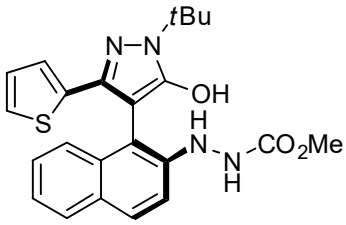
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(2-chlorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ah)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 18.6 mg, 80% yield. mp 188.4-189.8 °C. ^{1}H NMR (DMSO-*d*$_6$, 500 MHz): δ (ppm) 9.89 (s, 1H), 9.44 (s, 1H), 7.70 (d, *J* = 10.0 Hz, 1H), 7.64-7.62 (m, 1H), 7.35-7.33 (m, 2H),

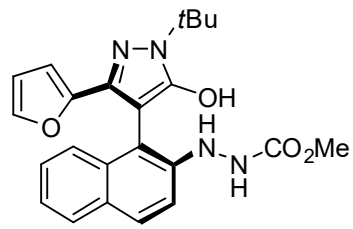
7.26-7.25 (m, 1H), 7.16-7.15 (m, 2H), 7.11-7.07 (m, 2H), 6.99-6.96 (m, 1H), 6.77 (s, 1H), 3.62 (s, 3H), 1.65 (s, 9H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ (ppm) 158.5, 150.5, 145.7, 145.0, 134.3, 132.9, 132.4, 130.1, 129.7, 128.9, 128.8, 128.6, 128.1, 126.7, 126.1, 124.7, 122.5, 114.6, 110.0, 95.9, 58.8, 52.5, 29.3. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{25}H_{26}ClN_4O_3$) requires m/z 465.1693, found m/z 465.1691. The enantiomeric excess was determined to be 87% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.0 min (minor), 8.0 min (major). $[\alpha]^{22}_D$ = -6.00 (c = 1.00, CH_2Cl_2).

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-(thiophen-2-yl)-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ai)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 21.4 mg, 98% yield. mp 193.7-195.4 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.43 (br, 1H), 7.84 (d, *J* = 10.0 Hz, 1H), 7.77-7.76 (m, 1H), 7.50-7.48 (m, 1H), 7.32-7.30 (m, 2H), 7.27-7.25 (m, 1H), 7.00-6.98 (m, 1H), 6.67-6.65 (m, 1H), 6.55-6.54 (m, 1H), 5.98 (s, 1H), 3.71 (s, 3H), 1.76 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.4, 149.5, 144.2, 142.9, 137.0, 133.9, 130.0, 129.8, 127.9, 127.1, 127.0, 125.2, 123.9, 123.8, 123.5, 115.2, 112.3, 93.6, 59.5, 53.4, 28.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{23}H_{25}N_4O_3S$) requires m/z 437.1647, found m/z 437.1643. The enantiomeric excess was determined to be 91% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 70:30, 1.0 mL/min]: 3.8 min (minor), 6.3 min (major). $[\alpha]^{22}_D$ = -11.80 (c = 1.00, CH_2Cl_2).

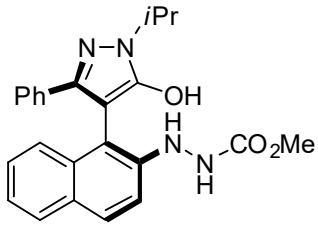
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(furan-2-yl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3aj)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 15.6 mg, 74% yield. mp 114.2-116.2 °C. ^{1}H NMR ($CDCl_3$, 500 MHz):

δ (ppm) 8.53 (s, 1H), 7.82 (d, *J* = 10.0 Hz, 1H), 7.77-7.75 (m, 1H), 7.47-7.45 (m, 1H), 7.31-7.27 (m, 3H), 7.08 (s, 1H), 6.05 (s, 1H), 5.90 (s, 1H), 5.53 (s, 1H), 3.70 (s, 3H), 1.77 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.5, 149.5, 148.2, 143.9, 141.3, 140.2, 133.8, 129.9, 129.8, 127.9, 126.9, 125.2, 123.9, 115.1, 112.0, 110.8, 106.8, 93.5, 59.6, 53.4, 28.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{23}H_{25}N_4O_4$) requires m/z 421.1870, found m/z 421.1865. The enantiomeric excess was determined to be 90% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 4.0 min (minor), 5.2 min (major). $[\alpha]^{22}_D$ = 10.00 (c = 1.00, CH_2Cl_2).

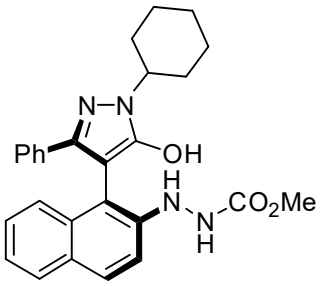
(*S*)-methyl 2-(1-(5-hydroxy-1-isopropyl-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ak)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 17.5 mg, 84% yield. mp 104.3-105.7 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 10.07 (s, 1H), 9.41 (s, 1H), 7.85-7.84 (m, 1H), 7.76-7.75 (m, 1H), 7.44-7.43 (m, 2H), 7.29-7.27 (m, 2H), 7.21-7.16 (m, 2H), 7.07-7.06 (m, 3H), 6.77 (s, 1H), 4.71-4.63 (m, 1H), 3.62 (s, 3H), 1.53 (d, *J* = 5.0 Hz, 6H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ (ppm) 158.4, 149.9, 146.9, 146.2, 135.4, 134.6, 129.1, 128.8, 128.3, 127.0, 126.6, 126.3, 124.6, 122.7, 114.7, 110.4, 92.8, 52.5, 47.8, 22.6, 22.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{24}H_{25}N_4O_3$) requires m/z 417.1927, found m/z 417.1921. The enantiomeric excess was determined to be 84% by HPLC. [IC column, 254 nm, *n*-hexane:IPA = 80:20, 1.0 mL/min]: 4.8 min (minor), 8.1 min (major). $[\alpha]^{22}_D$ = -38.00 (c = 1.00, CH_2Cl_2).

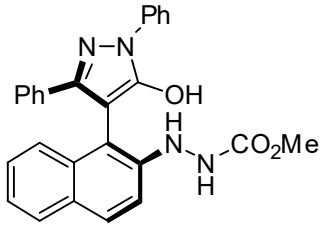
(*S*)-methyl 2-(1-(1-cyclohexyl-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3al)

Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 18.9 mg, 83% yield. mp 196.6-198.0 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 9.98 (s, 1H), 9.35 (s, 1H), 7.82-7.80 (m, 1H), 7.73-7.72 (m, 1H), 7.37-7.36 (m,



2H), 7.23-7.20 (m, 2H), 7.18-7.13 (m, 2H), 7.03-7.02 (m, 3H), 6.70 (s, 1H), 4.24-4.19 (m, 1H), 3.59 (s, 3H), 2.04-1.86 (m, 7H), 1.70-1.68 (m, 1H), 1.42-1.40 (m, 1H), 1.30-1.28 (m, 1H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.6, 148.7, 148.1, 143.8, 134.2, 133.9, 129.8, 129.7, 128.1, 127.8, 127.0, 126.8, 126.0, 125.2, 123.8, 114.9, 113.0, 92.4, 56.3, 53.4, 32.4, 32.0, 25.8, 25.7, 25.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{29}N_4O_3$) requires m/z 457.2240, found m/z 457.2233. The enantiomeric excess was determined to be 89% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 4.4 min (minor), 7.5 min (major). $[\alpha]^{22}_D$ = -21.70 (c = 1.00, CH_2Cl_2).

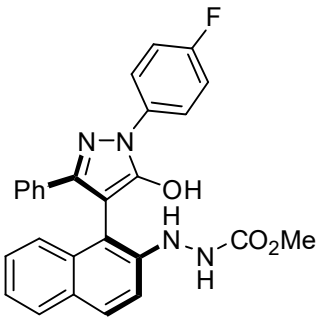
(*S*)-methyl 2-(1-(5-hydroxy-1,3-diphenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3am)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 22.3 mg, 99% yield. mp 145.0-146.3 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 9.15 (br, 1H), 8.05-8.03 (m, 2H), 7.83-7.81 (m, 1H), 7.75-7.73 (m, 1H), 7.54-7.48 (m, 5H), 7.33-7.30 (m, 1H), 7.27-7.26 (m, 1H), 7.25-7.24 (m, 1H), 7.20 (s, 1H), 7.13-7.09 (m, 3H), 6.04 (s, 1H), 3.68 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.6, 150.7, 149.4, 144.0, 138.9, 133.7, 133.4, 130.1, 129.8, 128.9, 128.2, 127.9, 127.8, 127.1, 126.3, 125.1, 123.9, 121.9, 115.1, 112.1, 94.4, 53.5. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{23}N_4O_3$) requires m/z 451.1770, found m/z 451.1764. The enantiomeric excess was determined to be 93% by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 6.2 min (minor), 8.5 min (major). $[\alpha]^{22}_D$ = -158.00 (c = 1.00, CH_2Cl_2).

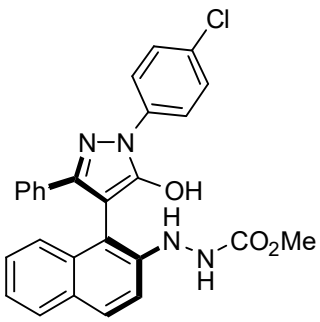
(*S*)-methyl 2-(1-(1-(4-fluorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3an)

Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White



solid, 22.1 mg, 94% yield. mp 139.1-141.1 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 10.74 (br, 1H), 9.37 (s, 1H), 7.95-7.94 (m, 2H), 7.85-7.83 (m, 1H), 7.75-7.73 (m, 1H), 7.48 (s, 2H), 7.38-7.35 (m, 2H), 7.32-7.24 (m, 3H), 7.20-7.10 (m, 5H), 3.61 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 160.9 (d, J = 980.0 Hz), 158.7, 150.7, 149.3, 144.0, 135.0, 133.7, 133.2, 130.2, 129.8, 128.3, 128.0, 127.9, 127.1, 126.3, 125.0, 124.0, 123.7 (d, J =35.0 Hz), 115.8, 115.7 (d, J = 90.0 Hz), 111.9, 94.3, 53.5. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{22}FN_4O_3$) requires m/z 469.1676, found m/z 469.1672. The enantiomeric excess was determined to be 92% by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.3 min (minor), 7.3 min (major). $[\alpha]^{22}_D$ = -140.70 (c = 1.00, CH_2Cl_2).

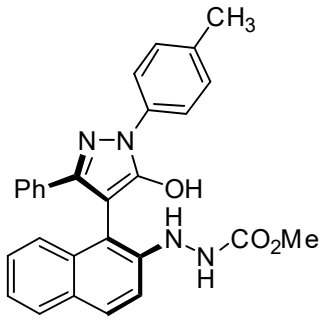
(*S*)-methyl 2-(1-(1-(4-chlorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ao)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 23.6 mg, 98% yield. mp 133.5-134.8 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 10.98 (br, 1H), 9.43 (s, 1H), 8.07-8.05 (m, 2H), 7.89-7.87 (m, 1H), 7.78-7.76 (m, 1H), 7.63-7.61 (m, 2H), 7.56 (s, 2H), 7.38-7.31 (m, 3H), 7.21-7.15 (m, 5H), 3.64 (s, 3H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ (ppm) 158.5, 151.9, 149.8, 146.7, 138.4, 134.5, 134.3, 130.1, 129.6, 129.3, 128.6, 128.5, 128.4, 128.0, 126.8, 126.7, 124.4, 123.3, 122.6, 114.8, 108.7, 95.2, 52.5. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{22}ClN_4O_3$) requires m/z 485.1380, found m/z 485.1377. The enantiomeric excess was determined to be 98% by HPLC. [IA column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 6.4 min (minor), 9.9 min (major). $[\alpha]^{22}_D$ = -171.00 (c = 1.00, CH_2Cl_2).

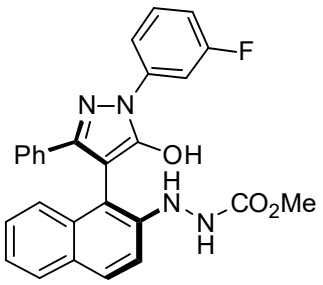
(*S*)-methyl 2-(1-(5-hydroxy-3-phenyl-1-(*p*-tolyl)-1*H*-pyrazol-4-yl)naphthalen-2-y

l)hydrazinecarboxylate (3ap)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 21.5 mg, 93% yield. mp 144.3-145.1 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 9.07 (br, 1H), 7.91-7.89 (m, 2H), 7.81-7.80 (m, 1H), 7.74-7.72 (m, 1H), 7.53-7.49 (m, 3H), 7.30-7.29 (m, 2H), 7.25-7.22 (m, 3H), 7.11-7.08 (m, 3H), 6.04 (s, 1H), 3.66 (s, 3H), 2.41 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.7, 150.6, 149.3, 144.1, 136.4, 136.1, 133.7, 133.5, 130.0, 129.8, 129.5, 128.2, 127.9, 127.8, 127.0, 126.4, 125.1, 123.9, 122.0, 115.1, 111.9, 94.3, 53.3, 21.1. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{28}H_{25}N_4O_3$) requires m/z 465.1927, found m/z 465.1921. The enantiomeric excess was determined to be 90% by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 6.9 min (minor), 11.7 min (major). $[\alpha]^{22}_D$ = -147.20 (c = 1.00, CH_2Cl_2).

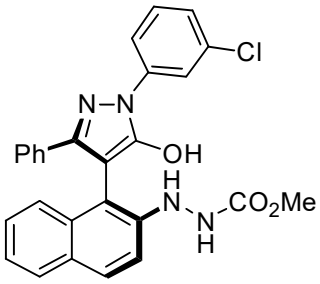
(*S*)-methyl 2-(1-(1-(3-fluorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3aq)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 22.7 mg, 97% yield. mp 185.6-186.9 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 11.03 (br, 1H), 9.38 (s, 1H), 7.88-7.81 (m, 3H), 7.76-7.74 (m, 1H), 7.59-7.52 (m, 3H), 7.33-7.26 (m, 3H), 7.21-7.12 (m, 6H), 3.62 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 162.9 (d, J = 975.0 Hz), 158.7, 151.1, 149.6, 143.9, 140.3 (d, J = 40.0 Hz), 133.6, 133.1, 130.3, 130.1 (d, J = 40.0 Hz), 129.9, 128.3, 128.0, 127.9, 127.1, 126.3, 124.9, 124.1, 116.9, 115.2, 112.8 (d, J = 85.0 Hz), 111.8, 108.9 (d, J = 105.0 Hz), 94.9, 53.5. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{22}FN_4O_3$) requires m/z 469.1676, found m/z 469.1670. The enantiomeric excess was determined to be 94% by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.2 min (minor), 5.8 min (major).

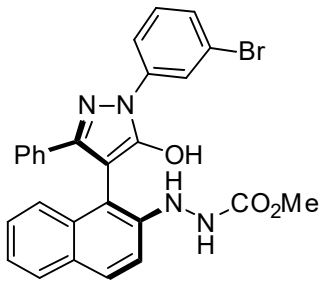
$[\alpha]^{22}_D$ = -134.00 (c = 1.00, CH_2Cl_2).

(*S*)-methyl 2-(1-(1-(3-chlorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ar)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 22.1 mg, 91% yield. mp 142.5-143.2 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 11.01 (br, 1H), 9.36 (s, 1H), 8.03 (s, 1H), 7.97-7.95 (m, 1H), 7.85-7.83 (m, 1H), 7.75-7.73 (m, 1H), 7.56-7.49 (m, 3H), 7.37-7.24 (m, 4H), 7.20-7.11 (m, 5H), 3.61 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.7, 151.2, 149.6, 143.9, 139.9, 134.6, 133.6, 133.1, 130.3, 129.9, 129.8, 128.3, 128.0, 127.9, 127.1, 126.3, 126.1, 124.9, 124.1, 121.7, 119.6, 115.0, 111.8, 94.7, 53.6. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{22}ClN_4O_3$) requires m/z 485.1380, found m/z 485.1379. The enantiomeric excess was determined to be 95% by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.3 min (minor), 6.1 min (major). $[\alpha]^{22}_D$ = -147.20 (c = 1.00, CH_2Cl_2).

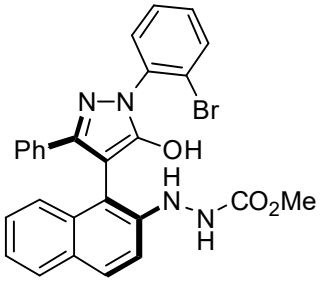
(*S*)-methyl 2-(1-(1-(3-bromophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3as)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 26.3 mg, 99% yield. mp 135.4-136.3 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 11.11 (br, 1H), 9.44 (s, 1H), 8.27 (s, 1H), 8.09-8.07 (m, 1H), 7.90-7.88 (m, 1H), 7.79-7.77 (m, 1H), 7.58 (s, 2H), 7.52-7.49 (m, 2H), 7.41-7.32 (m, 3H), 7.24-7.17 (m, 5H), 3.65 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.7, 151.3, 149.6, 144.0, 140.0, 133.6, 133.0, 130.3, 130.2, 129.8, 129.0, 128.3, 128.1, 128.0, 127.1, 126.3, 124.9, 124.6, 124.1, 122.6, 120.1, 115.1, 111.7, 94.8, 53.6. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{22}BrN_4O_3$) requires m/z 529.0875, found m/z 529.0873. The enantiomeric

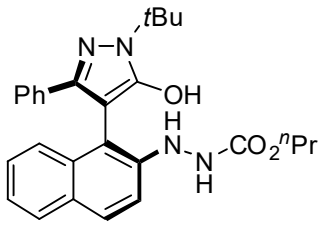
excess was determined to be 98% by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.6 min (minor), 8.1 min (major). $[\alpha]^{22}_{D}$ = -32.00 (c = 0.50, CH_2Cl_2).

(*S*)-methyl 2-(1-(1-(2-bromophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3at)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 17.9 mg, 68% yield. mp 79.9-81.5 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 10.54 (br, 1H), 9.36 (br, 1H), 7.85-7.83 (m, 2H), 7.77-7.74 (m, 2H), 7.60-7.56 (m, 1H), 7.48-7.40 (m, 4H), 7.25-7.21 (m, 2H), 7.18-7.15 (m, 1H), 7.07-7.06 (s, 3H), 6.91 (s, 1H), 3.60 (s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.6, 151.4, 150.1, 143.9, 137.6, 133.7, 133.4, 133.3, 130.5, 130.1, 130.0, 129.9, 128.3, 128.2, 127.9, 127.7, 127.0, 126.3, 125.2, 123.9, 122.6, 115.1, 112.3, 93.4, 53.5. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{22}BrN_4O_3$) requires m/z 529.0875, found m/z 529.0874. The enantiomeric excess was determined to be 91% by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 80:20, 1.0 mL/min]: 5.6 min (minor), 13.1 min (major). $[\alpha]^{22}_{D}$ = -106.00 (c = 0.50, CH_2Cl_2).

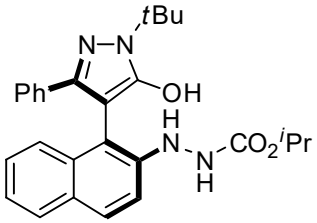
(*S*)-propyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ba)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 19.1 mg, 83% yield. mp 176.8-178.1 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.39 (br, 1H), 7.82 (d, *J* = 10.0 Hz, 1H), 7.74-7.72 (m, 1H), 7.46-7.42 (m, 3H), 7.28-7.27 (m, 1H), 7.25-7.23 (m, 1H), 7.09-7.06 (m, 3H), 6.98 (s, 1H), 6.07 (s, 1H), 4.06 (t, *J* = 10.0 Hz, 2H), 1.77 (s, 9H), 1.67-1.63 (m, 2H), 0.93 (t, *J* = 10.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 153.4, 144.8, 142.1, 139.2,

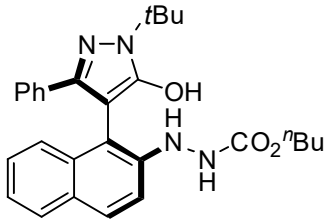
129.6, 129.2, 125.0, 124.9, 123.4, 123.1, 122.2, 122.1, 121.0, 120.5, 119.0, 110.2, 108.3, 89.3, 63.4, 54.5, 24.2, 17.4, 5.4. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{31}N_4O_3$) requires m/z 459.2396, found m/z 459.2390. The enantiomeric excess was determined to be 92% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 4.3 min (minor), 5.4 min (major). $[\alpha]^{22}_D$ = -103.60 (c = 1.00, CH_2Cl_2).

(*S*)-isopropyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ca)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 18.5 mg, 81% yield. mp 169.9-171.3 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.45 (br, 1H), 7.82 (d, *J* = 10.0 Hz, 1H), 7.74-7.72 (m, 1H), 7.46-7.42 (m, 3H), 7.29-7.27 (m, 1H), 7.25-7.23 (m, 1H), 7.07-7.06 (m, 3H), 6.92 (s, 1H), 6.08 (s, 1H), 4.96-4.88 (m, 1H), 1.77 (s, 9H), 1.25-1.23 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 152.9, 144.8, 142.1, 139.3, 129.6, 129.2, 125.0, 124.9, 123.4, 123.1, 122.2, 122.1, 121.0, 120.5, 119.0, 110.2, 108.3, 89.4, 65.9, 54.5, 24.2, 17.2. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{31}N_4O_3$) requires m/z 459.2396, found m/z 459.2390. The enantiomeric excess was determined to be 95% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 4.1 min (minor), 4.9 min (major). $[\alpha]^{22}_D$ = -84.00 (c = 1.00, CH_2Cl_2).

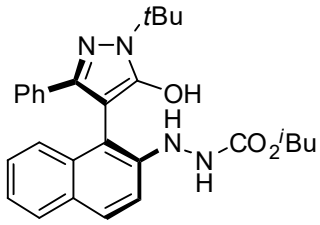
(*S*)-butyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3da)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 19.7 mg, 83% yield. mp 145.9-147.0 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.81 (d, *J* = 10.0 Hz, 1H), 7.74-7.72 (m, 1H), 7.46-7.42 (m, 3H), 7.27-7.26 (m, 1H), 7.25-7.23 (m, 1H), 7.09-7.06 (m, 3H), 7.01 (s, 1H), 6.07 (s,

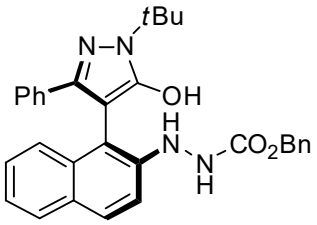
1H), 4.10 (t, J = 10.0 Hz, 2H), 1.77 (s, 9H), 1.63-1.58 (m, 2H), 1.41-1.33 (m, 2H), 0.93 (t, J = 10.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.2, 149.5, 146.9, 143.9, 134.3, 133.9, 129.8, 129.7, 128.1, 127.8, 126.9, 126.8, 125.8, 125.2, 123.8, 114.9, 113.1, 94.1, 66.5, 59.3, 30.8, 28.9, 18.9, 13.7. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{28}H_{33}N_4O_3$) requires m/z 473.2553, found m/z 473.2549. The enantiomeric excess was determined to be 94% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 4.2 min (minor), 5.5 min (major). $[\alpha]^{22}_D$ = -99.70 (c = 1.00, CH_2Cl_2).

(*S*)-isobutyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ea)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 21.5 mg, 91% yield. mp 197.9-199.1 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 7.81 (d, J = 10.0 Hz, 1H), 7.74-7.72 (m, 1H), 7.47-7.42 (m, 3H), 7.25-7.23 (m, 2H), 7.09-7.06 (m, 3H), 7.03 (s, 1H), 6.06 (s, 1H), 3.90-3.88 (m, 2H), 1.78 (s, 9H), 1.27-1.26 (m, 1H), 0.94-0.92 (m, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.2, 149.5, 146.9, 143.9, 134.3, 133.9, 129.8, 129.7, 128.1, 127.9, 126.9, 126.8, 125.8, 125.2, 123.8, 114.9, 113.0, 94.1, 72.6, 59.3, 29.0, 27.9, 18.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{28}H_{33}N_4O_3$) requires m/z 473.2553, found m/z 473.2548. The enantiomeric excess was determined to be 92% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 4.0 min (minor), 4.6 min (major). $[\alpha]^{22}_D$ = -88.00 (c = 1.00, CH_2Cl_2).

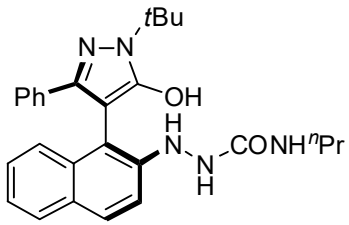
(*S*)-benzyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3fa)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 7:1. White solid, 22.5 mg, 89% yield. mp 155.3-156.7 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm)

8.27 (br, 1H), 7.80 (d, J = 10.0 Hz, 1H), 7.75-7.73 (m, 1H), 7.47-7.44 (m, 3H), 7.37-7.35 (m, 4H), 7.29-7.27 (m, 2H), 7.26-7.24 (m, 1H), 7.06-7.05 (m, 4H), 6.06 (s, 1H), 5.15-5.09 (m, 2H), 1.79 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 153.1, 144.8, 142.1, 139.1, 130.4, 129.5, 129.2, 125.1, 125.0, 124.0, 123.9, 123.7, 123.4, 123.1, 122.2, 122.2, 121.0, 120.5, 119.1, 110.2, 108.3, 89.3, 63.5, 54.6, 24.3. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{31}H_{31}N_4O_3$) requires m/z 507.2396, found m/z 507.2395. The enantiomeric excess was determined to be 93% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 6.5 min (minor), 15.1 min (major). $[\alpha]^{22}_D$ = -112.00 (c = 1.00, CH_2Cl_2).

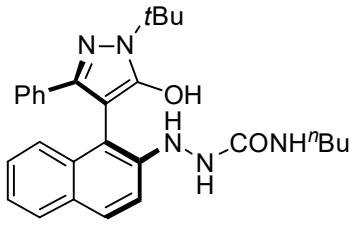
(*S*)-2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)-*N*-propylhydrazinecarboxamide (3ga)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. White solid, 21.6 mg, 95% yield. mp 111.9-112.8 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 10.17 (s, 1H), 7.99 (s, 1H), 7.83-7.82 (m, 1H), 7.75-7.73 (m, 1H), 7.28-7.15 (m, 6H), 7.04-7.03 (m, 2H), 6.75 (s, 1H), 6.04 (br, 1H), 2.91-2.84 (m, 2H), 1.66 (s, 9H), 1.28-1.22 (m, 2H), 0.76 (t, J = 5.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 159.5, 150.9, 145.6, 143.3, 134.8, 133.6, 129.3, 129.0, 128.2, 127.8, 127.1, 127.0, 125.7, 124.8, 123.4, 113.6, 111.0, 93.2, 59.4, 41.1, 29.1, 22.9, 11.1. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{27}H_{32}N_5O_2$) requires m/z 458.2556, found m/z 458.2550. The enantiomeric excess was determined to be 95% by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 95:5, 1.0 mL/min]: 7.6 min (major), 8.5 min (minor). $[\alpha]^{22}_D$ = -169.00 (c = 1.00, CH_2Cl_2).

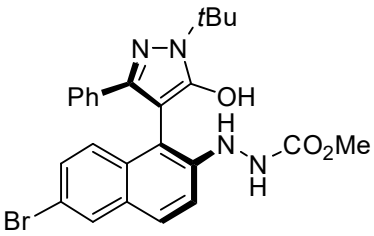
(*S*)-*N*-butyl-2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxamide (3ha)

Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. White



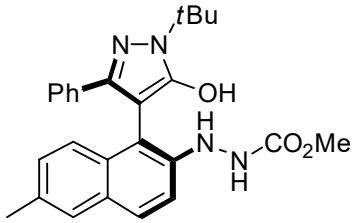
solid, 22.1 mg, 94% yield. mp 87.9-89.7 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 10.16 (s, 1H), 7.98 (s, 1H), 7.83-7.82 (m, 1H), 7.75-7.74 (m, 1H), 7.28-7.15 (m, 6H), 7.04-7.03 (m, 2H), 6.75 (s, 1H), 6.04 (br, 1H), 2.94-2.88 (m, 2H), 1.67 (s, 9H), 1.24-1.17 (m, 4H), 0.82 (t, J = 10.0 Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 159.4, 150.9, 145.6, 143.4, 134.7, 133.6, 129.3, 129.1, 128.2, 127.9, 127.2, 127.0, 125.7, 124.7, 123.4, 113.7, 111.1, 93.2, 59.4, 39.2, 31.8, 29.0, 19.8, 13.8. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{28}H_{34}N_5O_2$) requires m/z 472.2713, found m/z 472.2707. The enantiomeric excess was determined to be 96% by HPLC. [IC column, 254 nm, *n*-hexane:EtOH = 95:5, 1.0 mL/min]: 7.1 min (major), 7.8 min (minor). $[\alpha]^{22}_D$ = -38.30 (c = 1.00, CH_2Cl_2).

(*S*)-methyl 2-(6-bromo-1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ia)



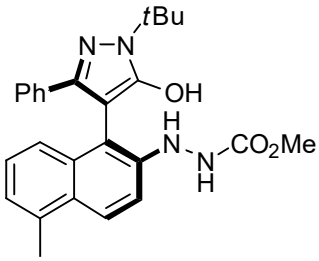
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. White solid, 25.1 mg, 99% yield. mp 193.0-194.2 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.31 (br, 1H), 7.87 (s, 1H), 7.71 (d, J = 5.0 Hz, 1H), 7.42-7.40 (m, 2H), 7.29-7.27 (m, 2H), 7.08-7.04 (m, 4H), 6.06 (s, 1H), 3.73 (s, 3H), 1.76 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.4, 149.4, 146.9, 144.2, 134.0, 132.4, 130.9, 130.1, 129.8, 128.8, 128.2, 127.1, 125.8, 117.7, 116.1, 113.3, 93.6, 59.4, 53.5, 28.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{25}H_{26}BrN_4O_3$) requires m/z 510.1261, found m/z 510.1215. The enantiomeric excess was determined to be 92% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.6 min (minor), 9.6 min (major). $[\alpha]^{22}_D$ = -19.50 (c = 1.00, CH_2Cl_2).

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)-6-methylnaphthalen-2-yl)hydrazinecarboxylate (3ja)



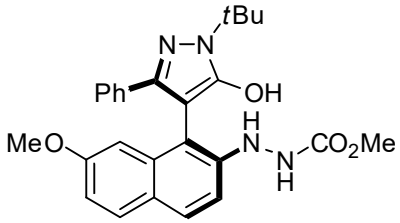
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. White solid, 19.3 mg, 88% yield. mp 171.0-171.7 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.36 (br, 1H), 7.73 (d, *J* = 10.0 Hz, 1H), 7.51 (s, 1H), 7.45-7.44 (m, 2H), 7.33 (d, *J* = 10.0 Hz, 1H), 7.22 (d, *J* = 10.0 Hz, 1H), 7.10-7.06 (m, 4H), 6.98 (s, 1H), 6.02 (s, 1H), 3.71 (s, 3H), 2.40 (s, 3H), 1.77 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.4, 149.6, 146.8, 143.2, 134.3, 133.3, 132.1, 130.0, 129.2, 129.0, 128.1, 126.9, 125.8, 125.0, 114.9, 113.0, 94.1, 59.3, 53.3, 29.0, 21.3. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{26}H_{29}N_4O_3$) requires m/z 445.2234, found m/z 445.2237. The enantiomeric excess was determined to be 98% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.2 min (minor), 9.1 min (major). $[\alpha]^{22}_D$ = -53.00 (c = 1.00, CH_2Cl_2).

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)-5-methylnaphthalen-2-yl)hydrazinecarboxylate (3ka)



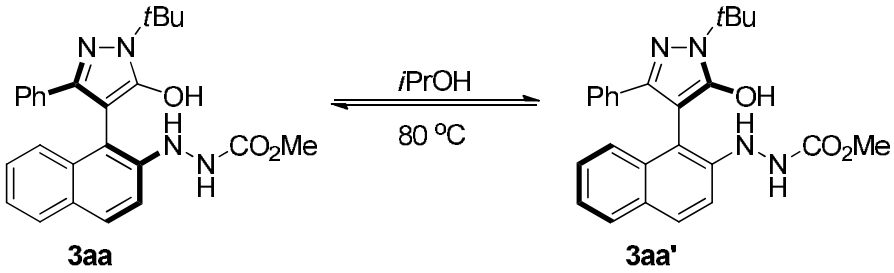
Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. White solid, 18.5 mg, 83% yield. mp 182.9-183.9 °C. ^{1}H NMR (DMSO-d_6, 500 MHz): δ (ppm) 9.75 (br, 1H), 9.37 (br, 1H), 7.94 (d, *J* = 10.0 Hz, 1H), 7.36-7.34 (m, 2H), 7.24 (d, *J* = 10.0 Hz, 1H), 7.09-6.99 (m, 6H), 6.65 (br, 1H), 3.59 (s, 3H), 2.58 (s, 3H), 1.66 (s, 9H). ^{13}C NMR (DMSO-d_6, 125 MHz): δ (ppm) 158.4, 151.2, 145.9, 145.1, 135.4, 134.2, 128.2, 127.7, 126.9, 126.2, 126.1, 125.4, 123.6, 123.2, 114.3, 111.0, 94.5, 58.6, 52.4, 29.2, 19.6. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{26}H_{29}N_4O_3$) requires m/z 445.2234, found m/z 445.2237. The enantiomeric excess was determined to be 91% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.3 min (minor), 9.4 min (major). $[\alpha]^{22}_D$ = -31.00 (c = 1.00, CH_2Cl_2).

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)-7-methoxynaphthalen-2-yl)hydrazinecarboxylate (3la)



Eluent for flash column chromatography: petroleum ether/ethyl acetate = 5:1. Yellow solid, 19.7 mg, 85% yield. mp 168.8-169.8 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ (ppm) 8.35 (br, 1H), 7.72 (d, *J* = 10.0 Hz, 1H), 7.61 (d, *J* = 10.0 Hz, 1H), 7.46-7.45 (m, 2H), 7.11-7.08 (m, 4H), 6.99 (s, 1H), 6.91 (d, *J* = 10.0 Hz, 1H), 6.71 (s, 1H), 6.05 (s, 1H), 3.72 (s, 3H), 3.56 (s, 3H), 1.77 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm) 158.4, 149.5, 147.0, 144.3, 135.2, 134.4, 129.4, 129.3, 128.2, 127.0, 125.9, 125.1, 116.2, 112.3, 111.9, 103.9, 94.2, 59.3, 55.0, 53.4, 28.9. HRMS (ESI): exact mass calculated for $[M+H]^+$ ($C_{26}H_{29}N_4O_4$) requires m/z 461.2183, found m/z 461.2185. The enantiomeric excess was determined to be 92% by HPLC. [OD-H column, 254 nm, *n*-hexane:EtOH = 90:10, 1.0 mL/min]: 5.8 min (minor), 10.5 min (major). $[\alpha]^{22}_D$ = -25.00 (c = 1.00, CH_2Cl_2).

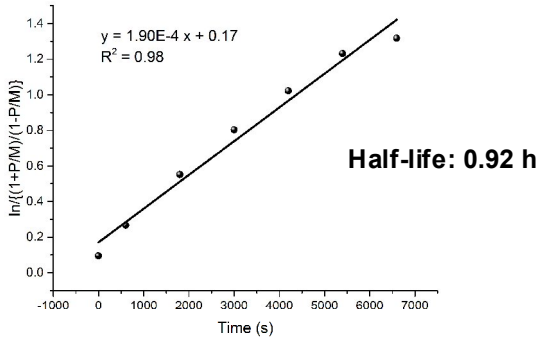
5. The Racemization Experiments[3-6]

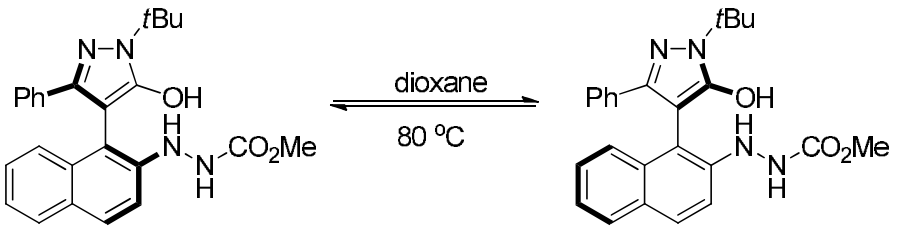


3aa **3aa'**

Compound **3aa** (0.04 mmol) was dissolved in isopropanol (1.0 mL) in a sealed tude. The tube was immersed in a pre-heated oil bath at 80 °C. At given interval of time, small samples (5.0 μL) was removed via syringe and injected into the HPLC to measure the enantiomeric excess. (HPLC conditions: OD-H column, *n*-hexane:EtOH = 80:20, flow rate = 1.0 mL/min, UV = 254 nm)

Time (s)	er
0	4.5:95.5
600s	11.7:88.3
1800s	21.2:78.8
3000s	27.6:72.4
4200s	32.0:68.0
5400s	35.4:64.6
6600s	36.6:63.4

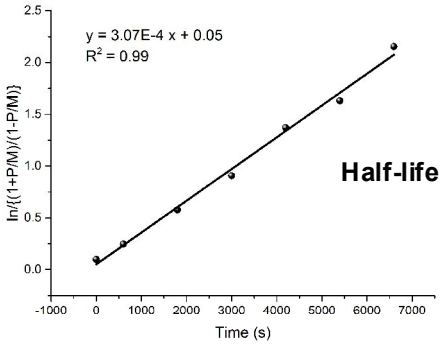




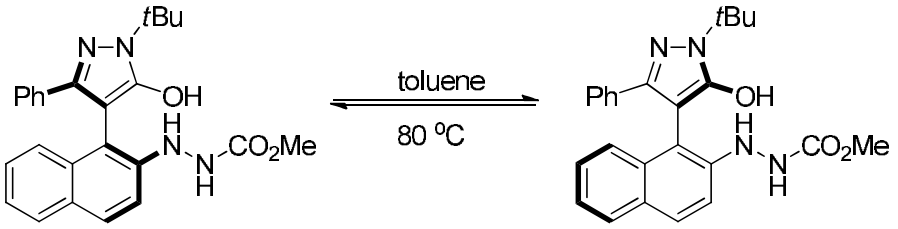
3aa **3aa'**

Compound **3aa** (0.04 mmol) was dissolved in dioxane (1.0 mL) in a sealed tude. The tube was immersed in a pre-heated oil bath at 80 °C. At given interval of time, small samples (5.0 μL) was removed via syringe and injected into the HPLC to measure the enantiomeric excess. (HPLC conditions: OD-H column, *n*-hexane:EtOH = 80:20, flow rate = 1.0 mL/min, UV = 254 nm)

Time (s)	er
0	4.7:95.3
600s	10.9:89.1
1800s	21.9:78.1
3000s	29.8:70.2
4200s	37.3:62.7
5400s	40.2:59.8
6600s	44.2:55.8



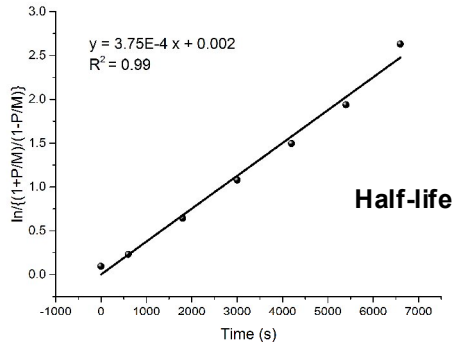
Half-life: 0.67 h



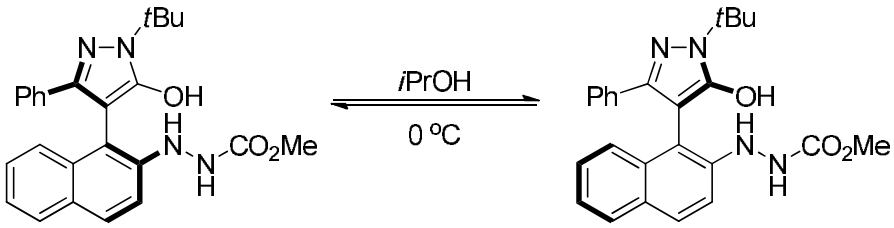
3aa **3aa'**

Compound **3aa** (0.04 mmol) was dissolved in toluene (1.0 mL) in a sealed tude. The tube was immersed in a pre-heated oil bath at 80 °C. At given interval of time, small samples (5.0 μL) was removed via syringe and injected into the HPLC to measure the enantiomeric excess. (HPLC conditions: OD-H column, *n*-hexane:EtOH = 80:20, flow rate = 1.0 mL/min, UV = 254 nm)

Time (s)	er
0	4.5:95.5
600s	10.3:89.7
1800s	23.7:76.3
3000s	33.0:67.0
4200s	38.8:61.2
5400s	42.8:57.2
6600s	46.4:53.6



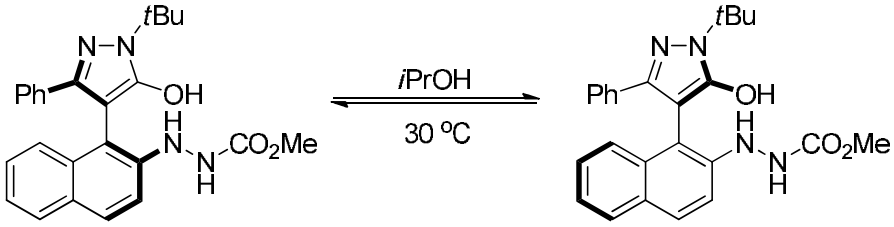
Half-life: 0.59 h



3aa **3aa'**

Compound **3aa** (0.04 mmol) was dissolved in isopropanol (1 mL) in a sealed tude. The tube was immersed in a pre-heated oil bath at 0 °C. At given interval of time, small samples (5μL) was removed via syringe and injected into the HPLC to measure the enantiomeric excess. (HPLC conditions: OD-H column, n-hexane:EtOH = 80:20, flow rate = 1.0 mL/min, UV = 254 nm).

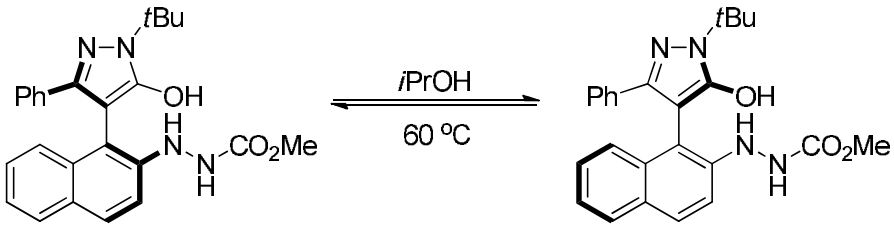
Time (s)	er	Time (s)	er
0	4.3:95.7	5400s	6.2:93.8
600s	6.0:94.0	6600s	6.2:93.8
1800s	6.4:93.6	14400	6.3:93.7
3000s	6.3:93.7	28800	6.1:93.9
4200s	5.9:94.1		



3aa **3aa'**

Compound **3aa** (0.04 mmol) was dissolved in isopropanol (1 mL) in a sealed tude. The tube was immersed in a pre-heated oil bath at 30 °C. At given interval of time, small samples (5μL) was removed via syringe and injected into the HPLC to measure the enantiomeric excess. (HPLC conditions: OD-H column, *n*-hexane:EtOH = 80:20, flow rate = 1.0 mL/min, UV = 254 nm)

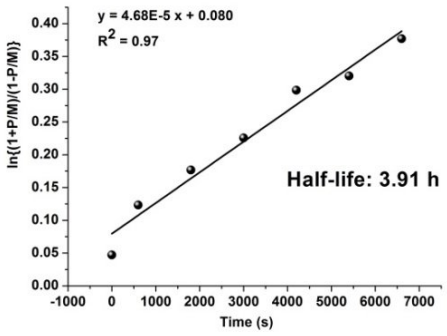
Time (s)	er	Time (s)	er
0	4.9:95.1	5400s	5.8:94.2
600s	6.3:93.7	6600s	6.1:93.9
1800s	5.5:94.5	14400	5.9:94.1
3000s	5.7:94.3	28800	6.4:93.6
4200s	5.9:94.1		



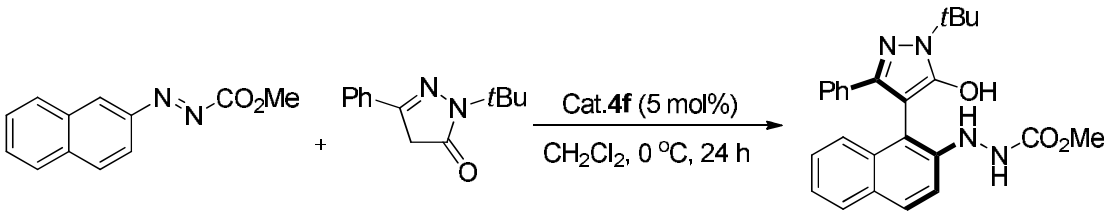
3aa **3aa'**

Compound **3aa** (0.04 mmol) was dissolved in isopropanol (1 mL) in a sealed tude. The tube was immersed in a pre-heated oil bath at 60 °C. At given interval of time, small samples (5μL) was removed via syringe and injected into the HPLC to measure the enantiomeric excess. (HPLC conditions: OD-H column, *n*-hexane:EtOH = 80:20, flow rate = 1.0 mL/min, UV = 254 nm)

Time (s)	er
0	2.3:97.7
600s	5.8:94.2
1800s	8.1:91.9
3000s	10.1:89.9
4200s	12.9:87.1
5400s	13.7:86.3
6600s	15.7:84.3



6. Large Scale Reaction

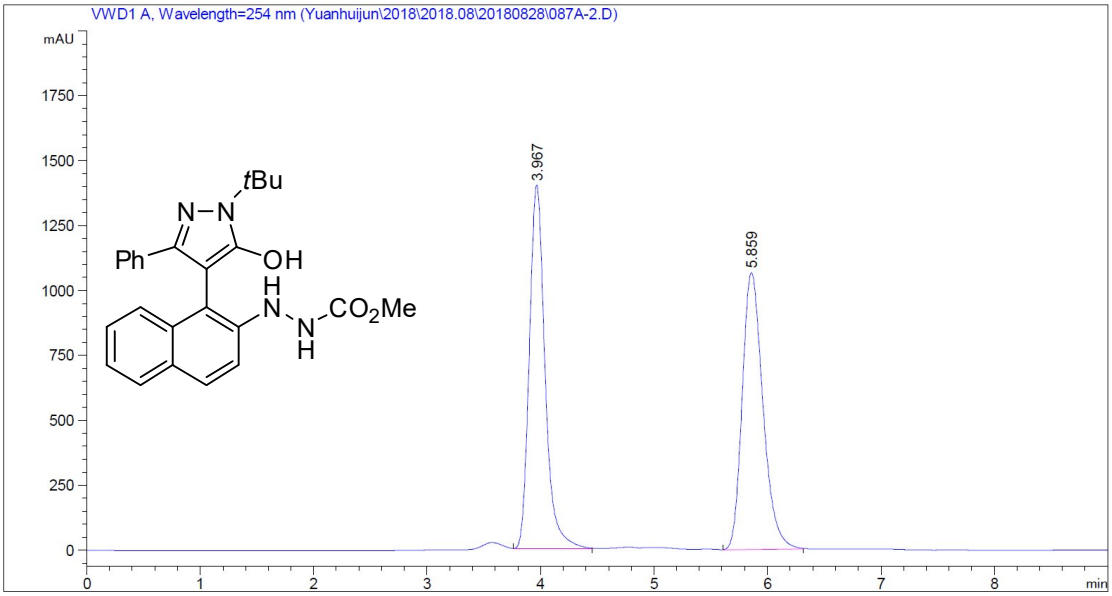


1a 267.5 mg (1.25 mmol) + **2a** 324.0 mg (1.5 mmol) → **3aa** 450.1 mg, 84% yield 86% ee

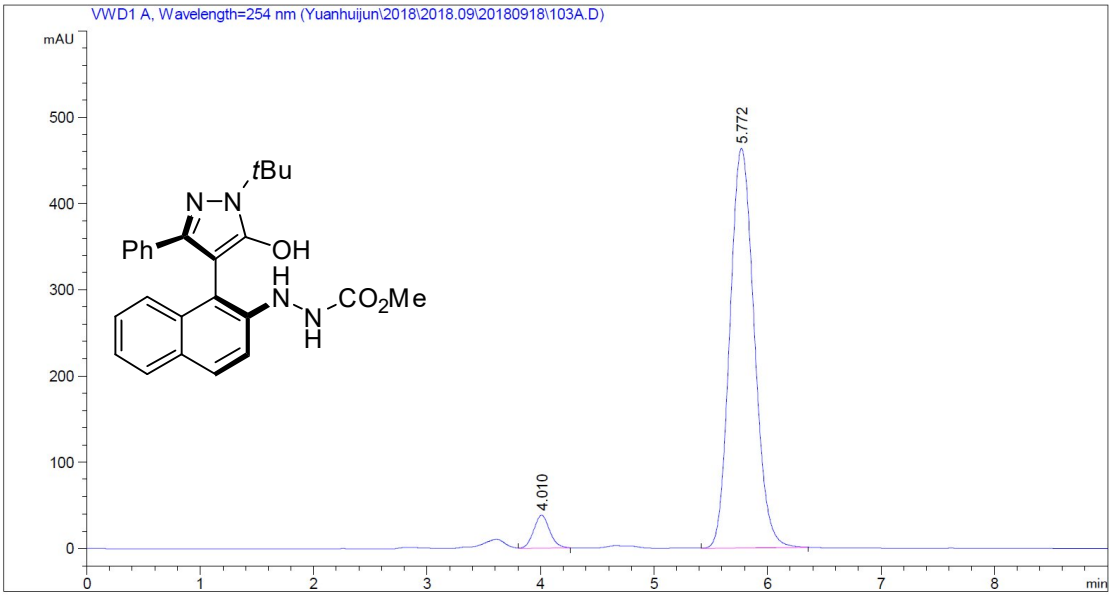
To a solution of CH_2Cl_2 (7.5 mL) were added azonaphthalene **1a** (267.5 mg, 1.25 mmol), pyrazolone **2a** (324.0 mg, 1.5 mmol) and catalyst **4f** (44.9 mg, 0.0625 mmol). The reaction mixture was stirred at 0 °C for 24 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **3aa** as a white solid (450.1 mg, 84% yield, 86% ee).

7. HPLC Spectra

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3aa)

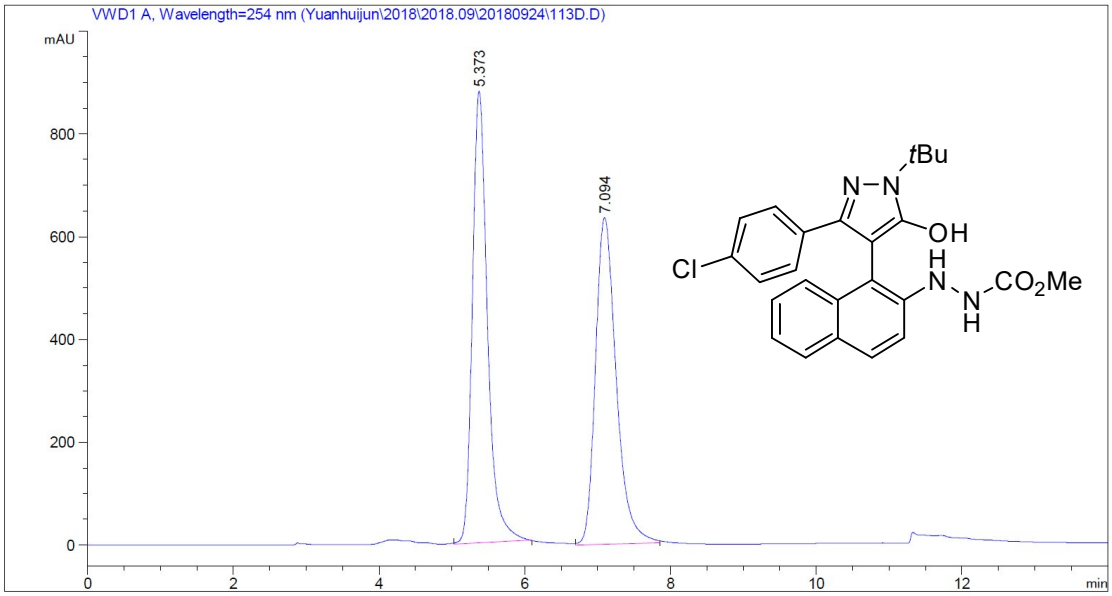


#	Time	Area	Height	Width	Symmetry	Area %
1	3.967	13491.9	1400.2	0.1606	0.831	49.897
2	5.859	13547.4	1066.7	0.2117	0.764	50.103

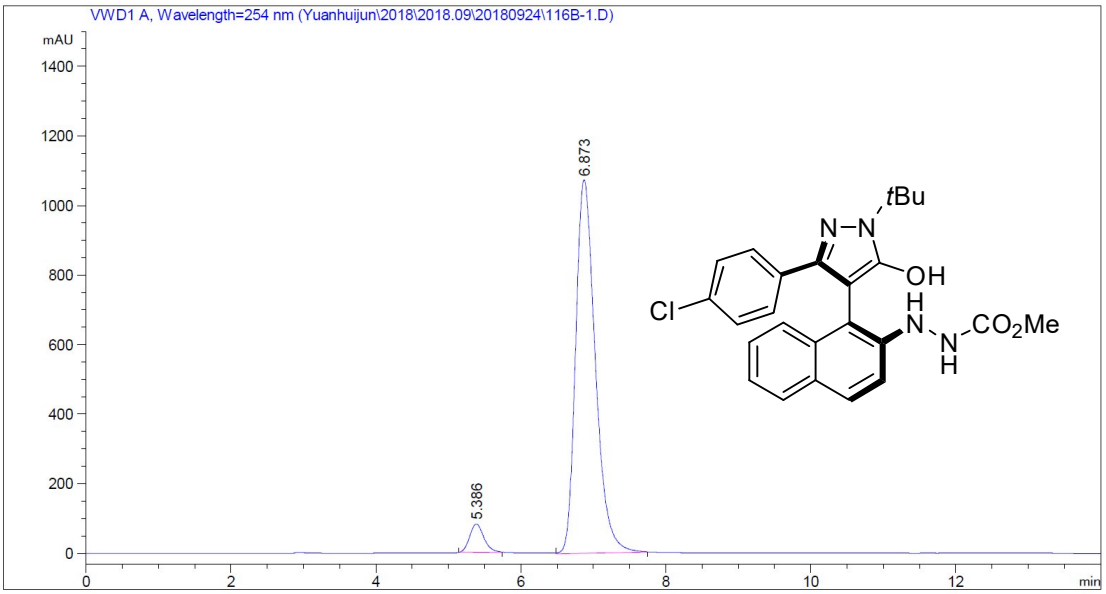


#	Time	Area	Height	Width	Symmetry	Area %
1	4.01	376	38.3	0.1636	0.94	5.171
2	5.772	6896.9	463.3	0.2481	0.865	94.829

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(4-chlorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ab)

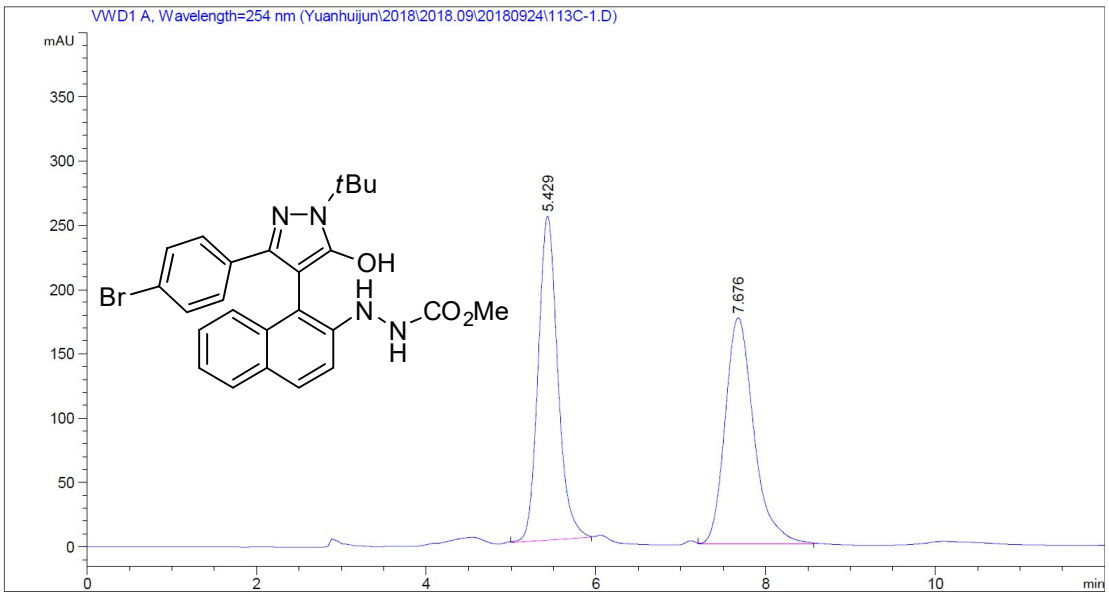


#	Time	Area	Height	Width	Symmetry	Area %
1	5.373	12625.1	878.8	0.2394	0.758	50.160
2	7.094	12544.3	635.5	0.329	0.739	49.840

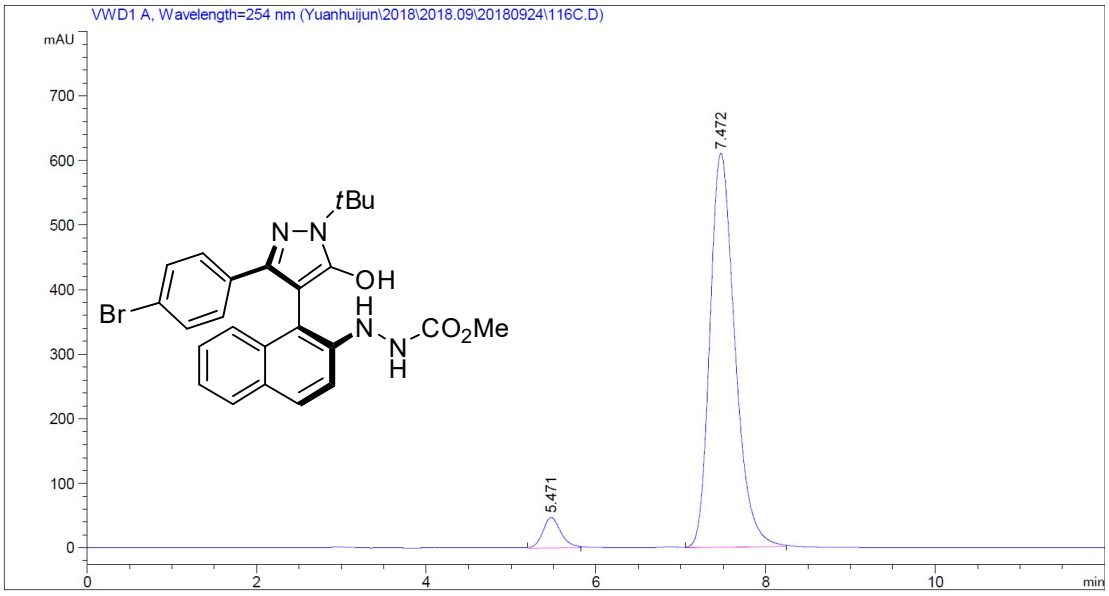


#	Time	Area	Height	Width	Symmetry	Area %
1	5.386	1115.6	82	0.2267	0.821	5.243
2	6.873	20163.4	1073.6	0.313	0.723	94.757

(*S*)-methyl 2-(1-(3-(4-bromophenyl)-1-(*tert*-butyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ac)

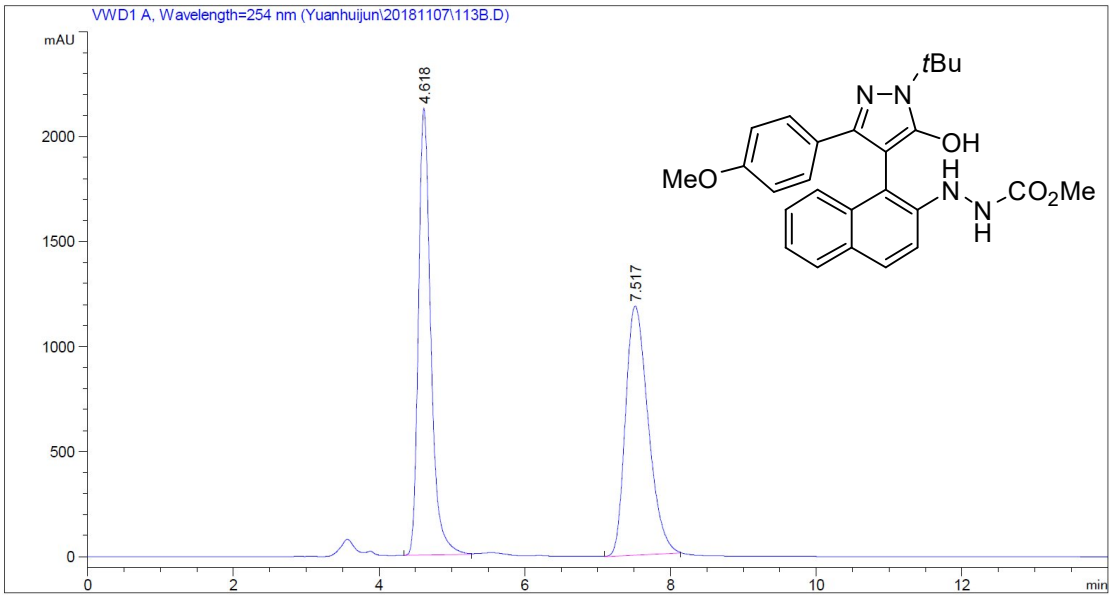


#	Time	Area	Height	Width	Symmetry	Area %
1	5.429	4058.3	252.2	0.2681	0.879	49.630
2	7.676	4118.9	175.8	0.3906	0.793	50.370

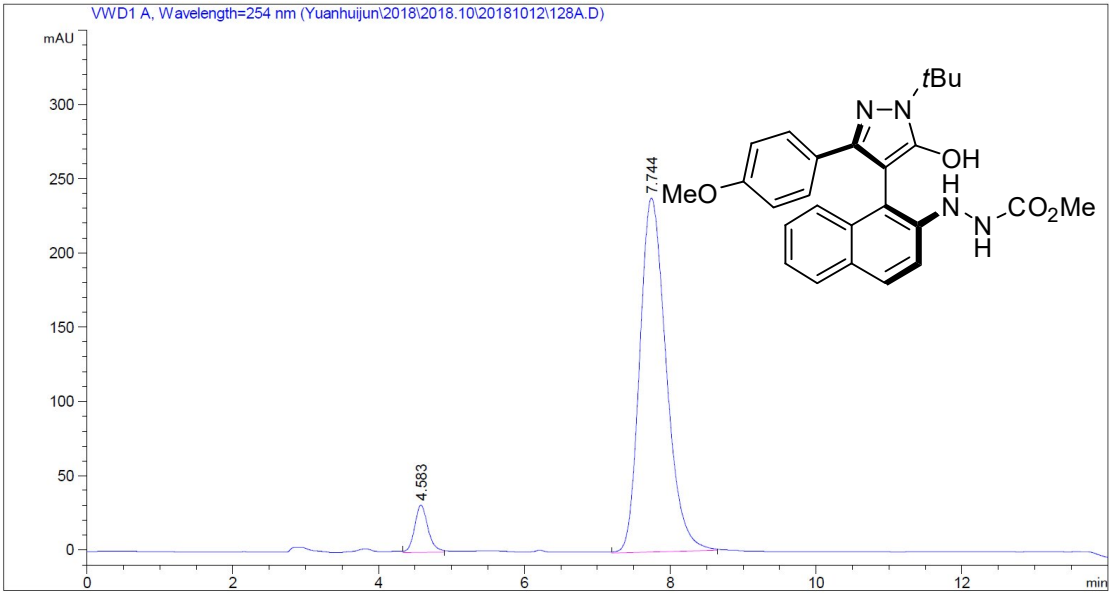


#	Time	Area	Height	Width	Symmetry	Area %
1	5.471	704.4	47.4	0.2479	0.841	5.351
2	7.472	12460.5	610.2	0.3403	0.748	94.649

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-(4-methoxyphenyl)-1*H*-pyrazol-4-yl) naphthalen-2-yl)hydrazinecarboxylate (3ad)

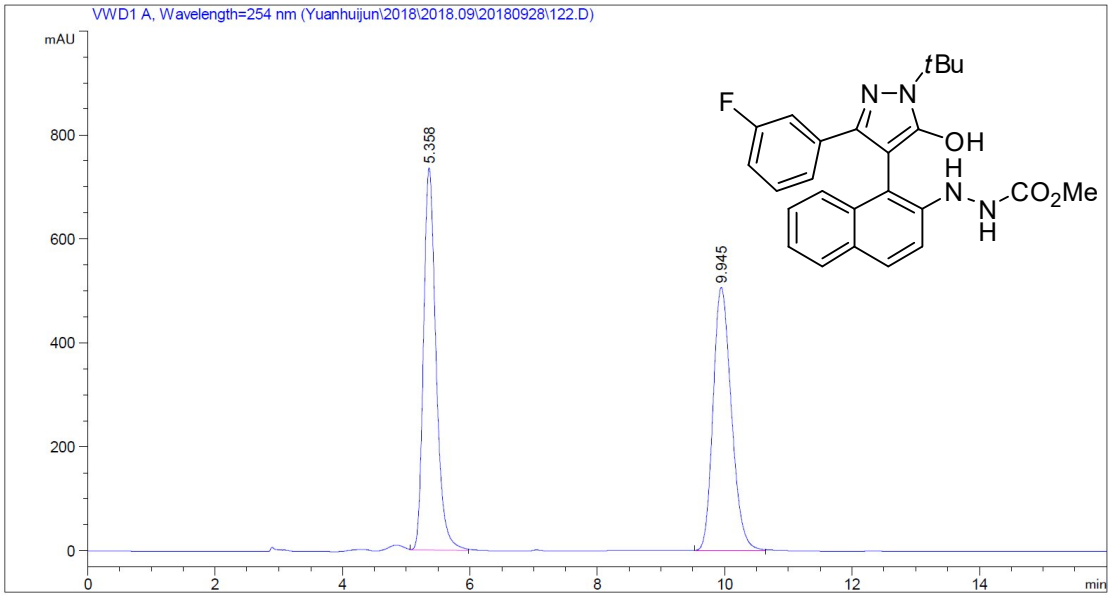


#	Time	Area	Height	Width	Symmetry	Area %
1	4.618	25087.8	2128.7	0.1964	0.744	49.388
2	7.517	25710.1	1187.7	0.3608	0.717	50.612

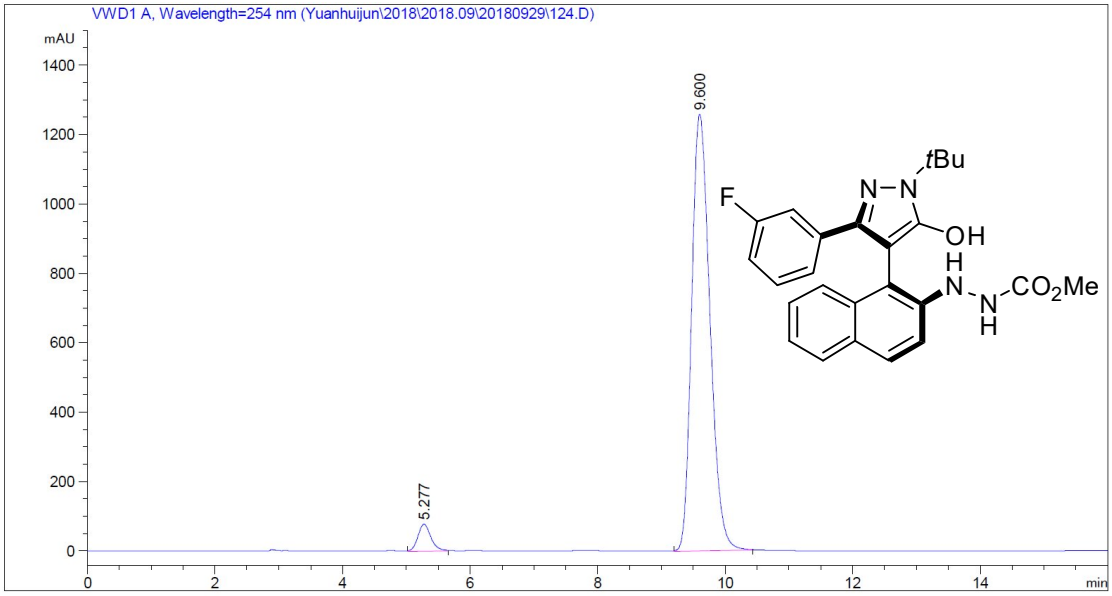


#	Time	Area	Height	Width	Symmetry	Area %
1	4.583	405.9	31.8	0.213	0.863	6.322
2	7.744	6014.7	238.3	0.4207	0.766	93.678

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(3-fluorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ae)

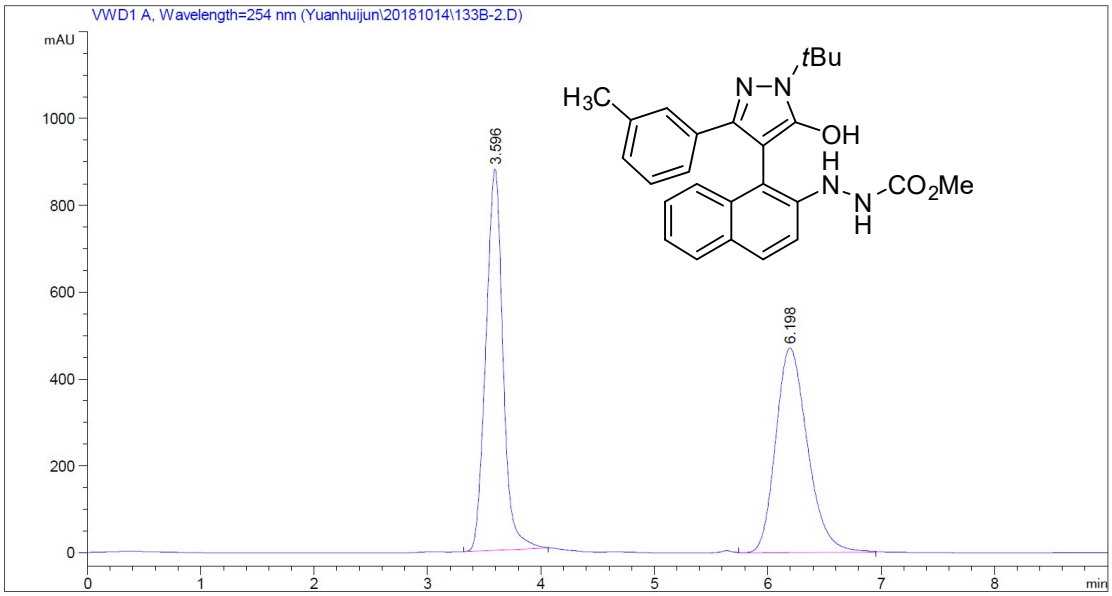


#	Time	Area	Height	Width	Symmetry	Area %
1	5.358	9999.6	735.1	0.2267	0.757	49.624
2	9.945	10151.1	507	0.3337	0.772	50.376

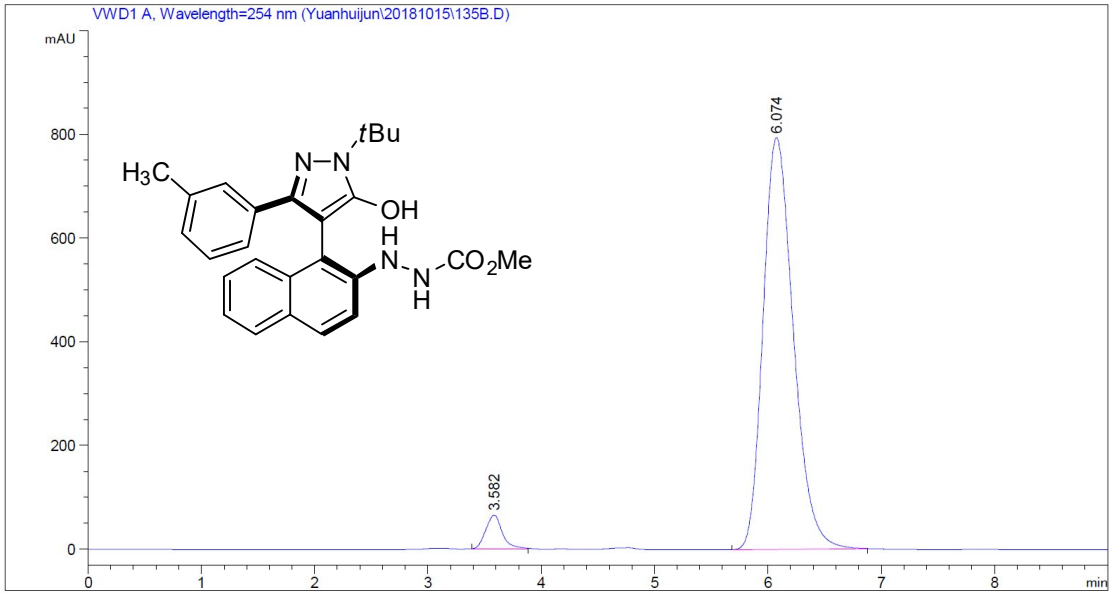


#	Time	Area	Height	Width	Symmetry	Area %
1	5.277	1103.4	77.7	0.2367	0.855	4.221
2	9.6	25038.6	1257.1	0.332	0.748	95.779

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-(*m*-tolyl)-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3af)

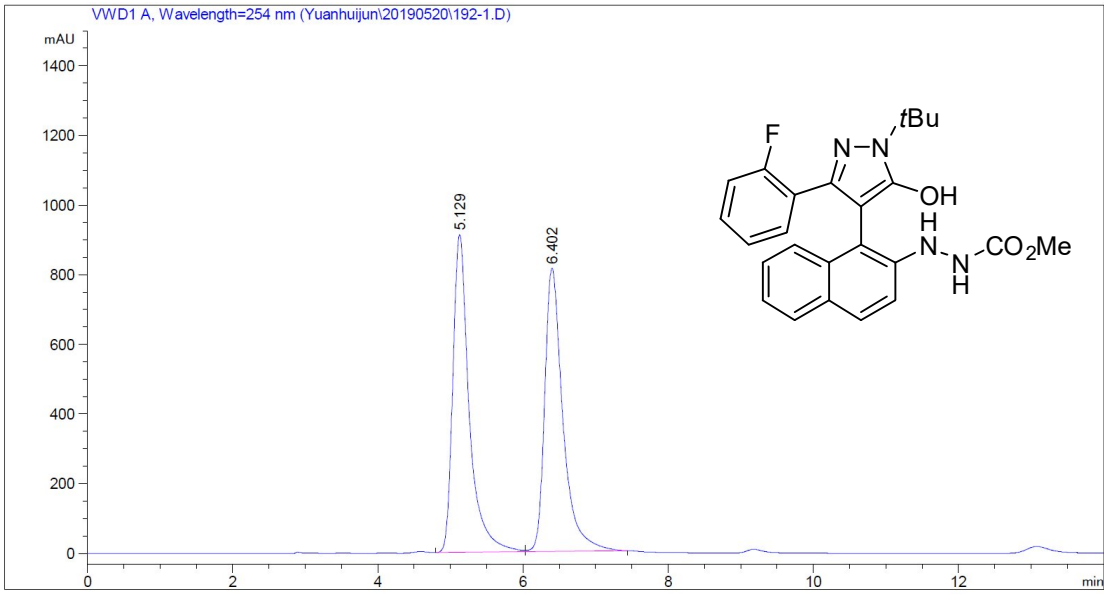


#	Time	Area	Height	Width	Symmetry	Area %
1	3.596	9193.8	877.8	0.1746	1.058	49.962
2	6.198	9207.8	471.2	0.3257	0.783	50.038

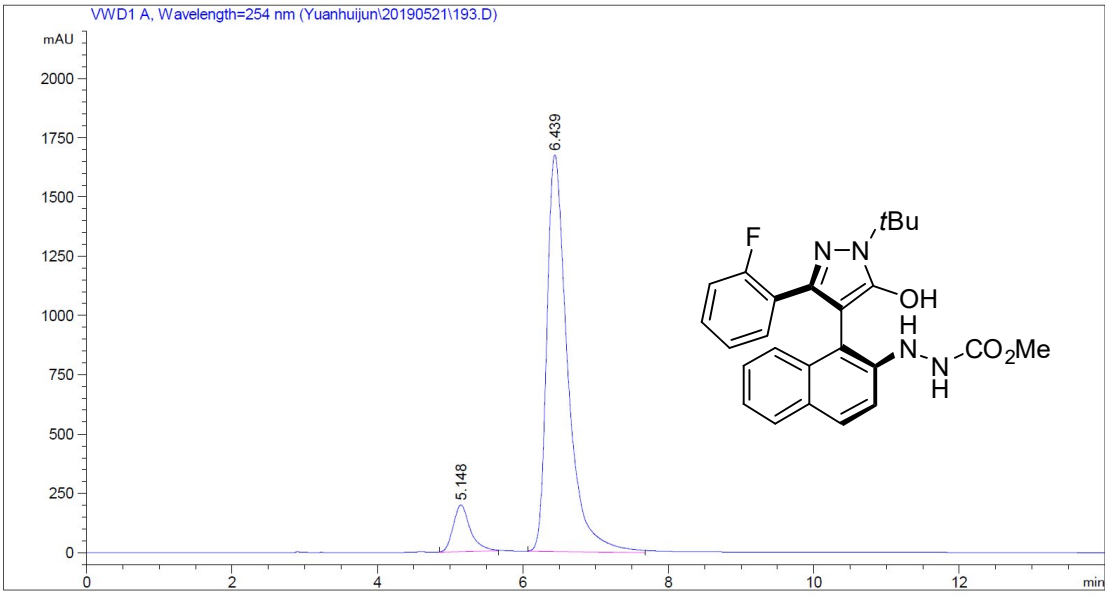


#	Time	Area	Height	Width	Symmetry	Area %
1	3.582	671.7	65.5	0.1708	0.964	4.347
2	6.074	14778.6	794.6	0.31	0.762	95.653

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(2-fluorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ag)

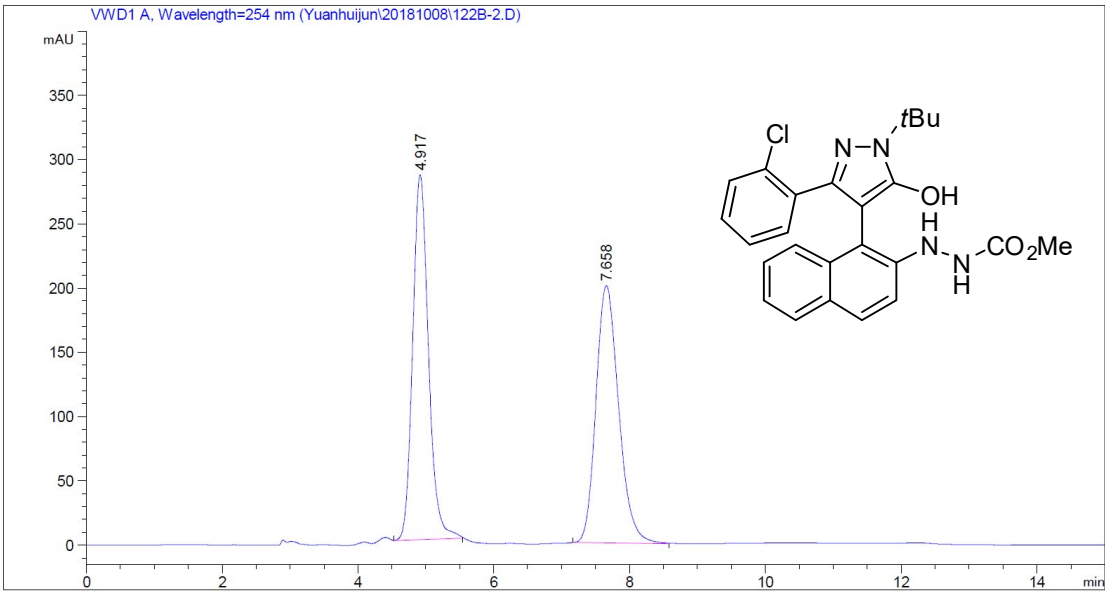


#	Time	Area	Height	Width	Symmetry	Area %
1	5.129	14325.7	912.7	0.2341	0.636	50.229
2	6.402	14195.3	814	0.2615	0.617	49.771

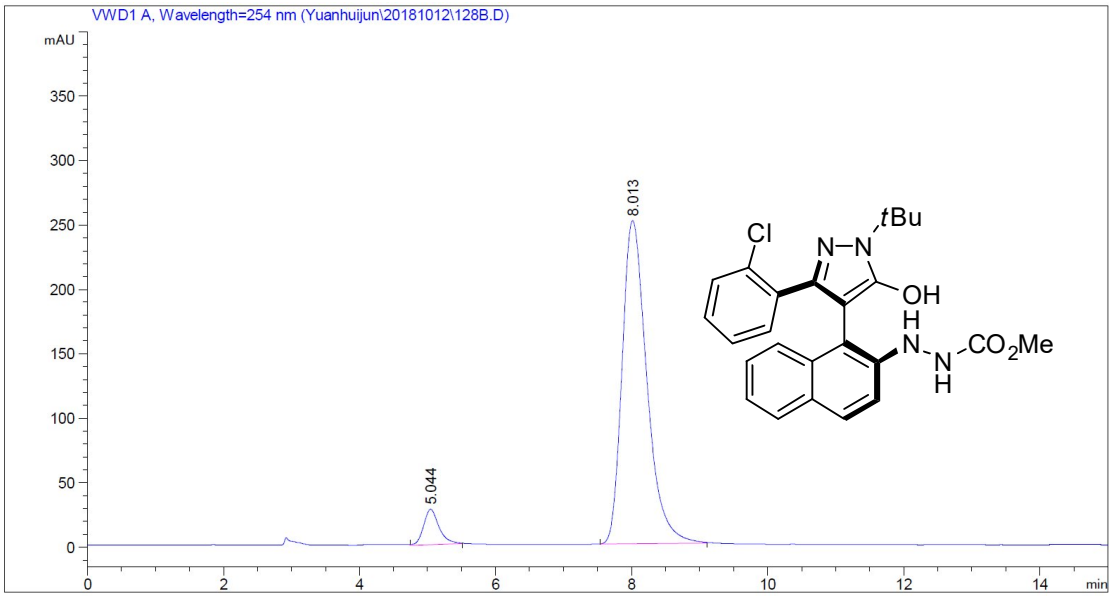


#	Time	Area	Height	Width	Symmetry	Area %
1	5.148	3202	196.9	0.2711	0.783	8.745
2	6.439	33413.2	1674.7	0.3325	0.587	91.255

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(2-chlorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ah)

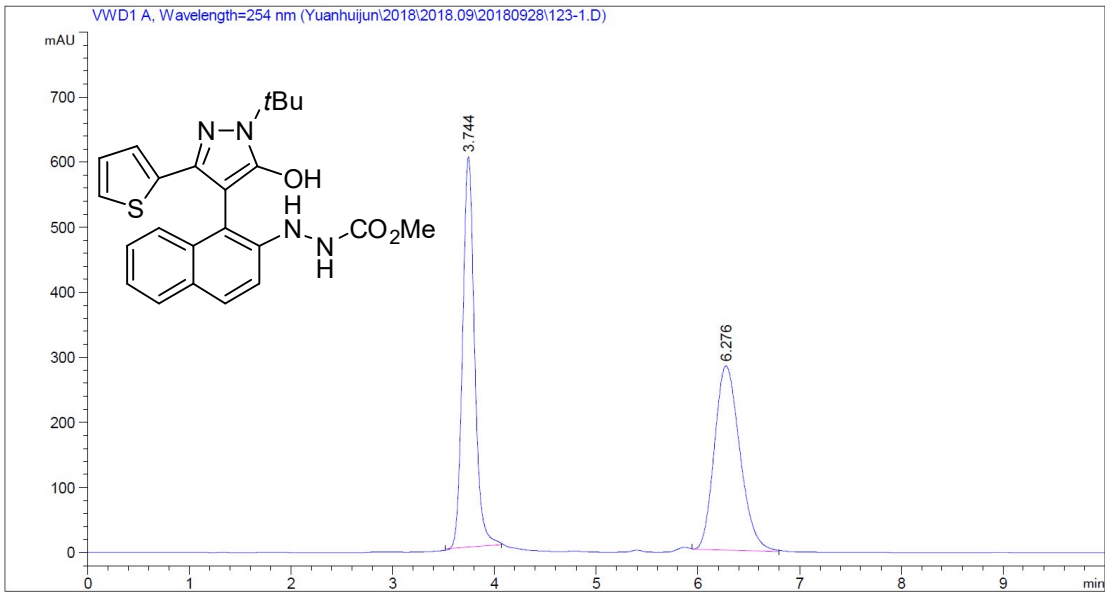


#	Time	Area	Height	Width	Symmetry	Area %
1	4.917	4577.7	284.1	0.2685	0.859	49.569
2	7.658	4657.3	200.4	0.3874	0.801	50.431

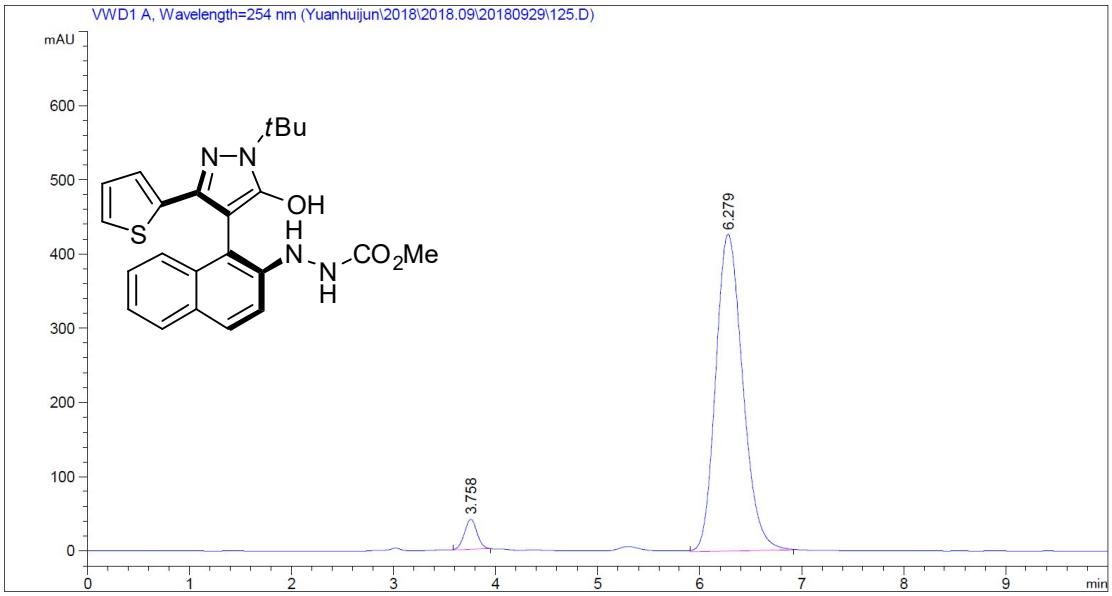


#	Time	Area	Height	Width	Symmetry	Area %
1	5.044	434	27.5	0.2626	0.793	6.396
2	8.013	6351.3	250.9	0.4219	0.702	93.604

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-(thiophen-2-yl)-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ai)

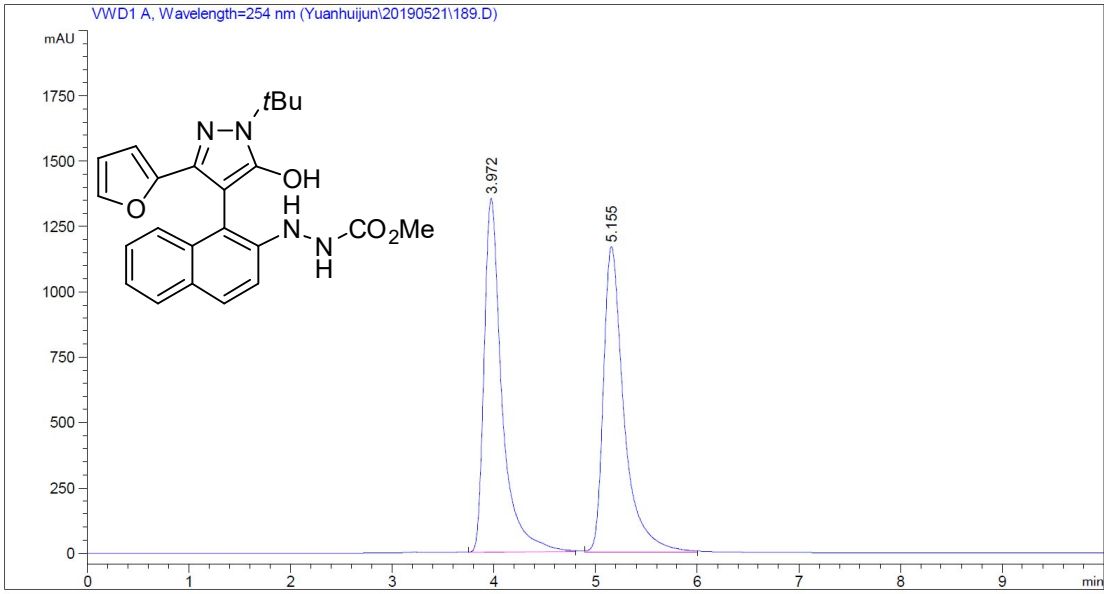


#	Time	Area	Height	Width	Symmetry	Area %
1	3.744	4880.3	600	0.1356	0.891	49.728
2	6.276	4933.7	283.3	0.2902	0.799	50.272

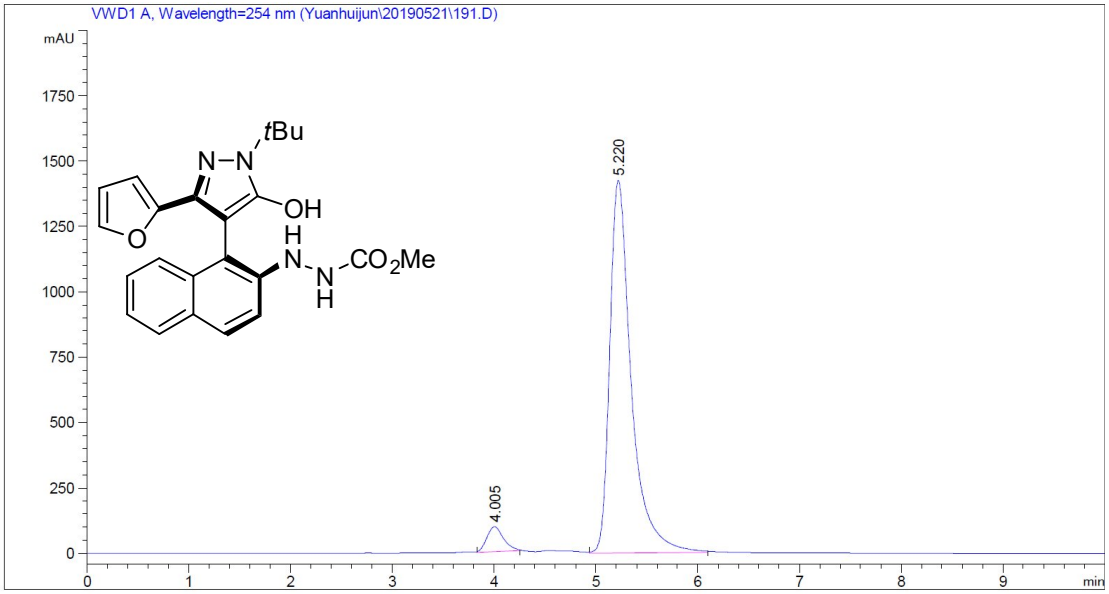


#	Time	Area	Height	Width	Symmetry	Area %
1	3.758	352.1	40.7	0.1443	1.004	4.279
2	6.279	7876	427	0.3074	0.811	95.721

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(furan-2-yl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3aj)

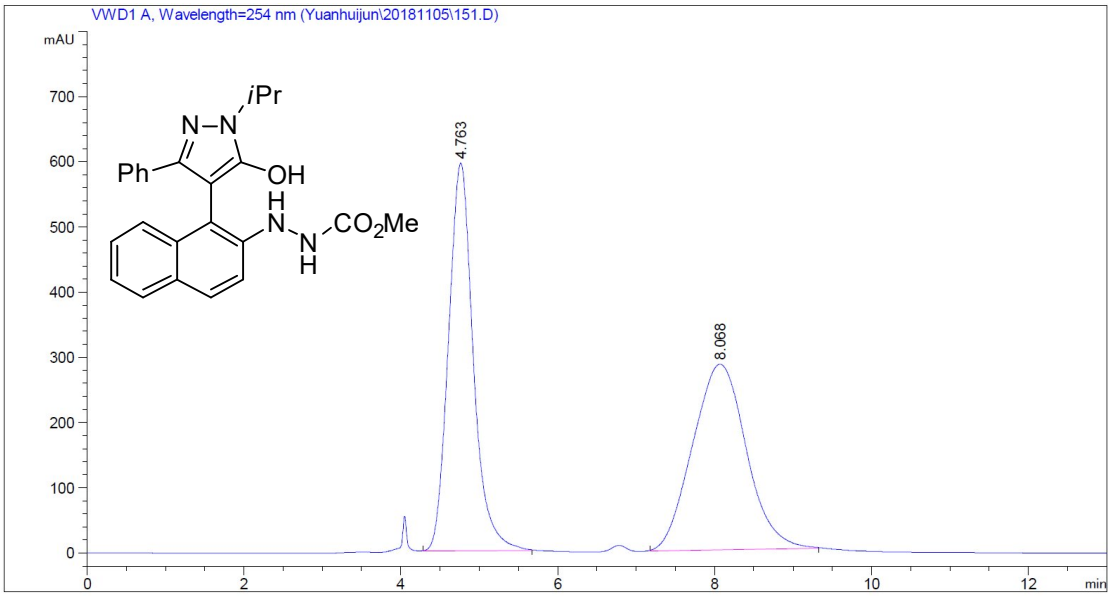


#	Time	Area	Height	Width	Symmetry	Area %
1	3.972	16514.6	1353.9	0.2033	0.611	50.173
2	5.155	16400.8	1167.6	0.2341	0.602	49.827

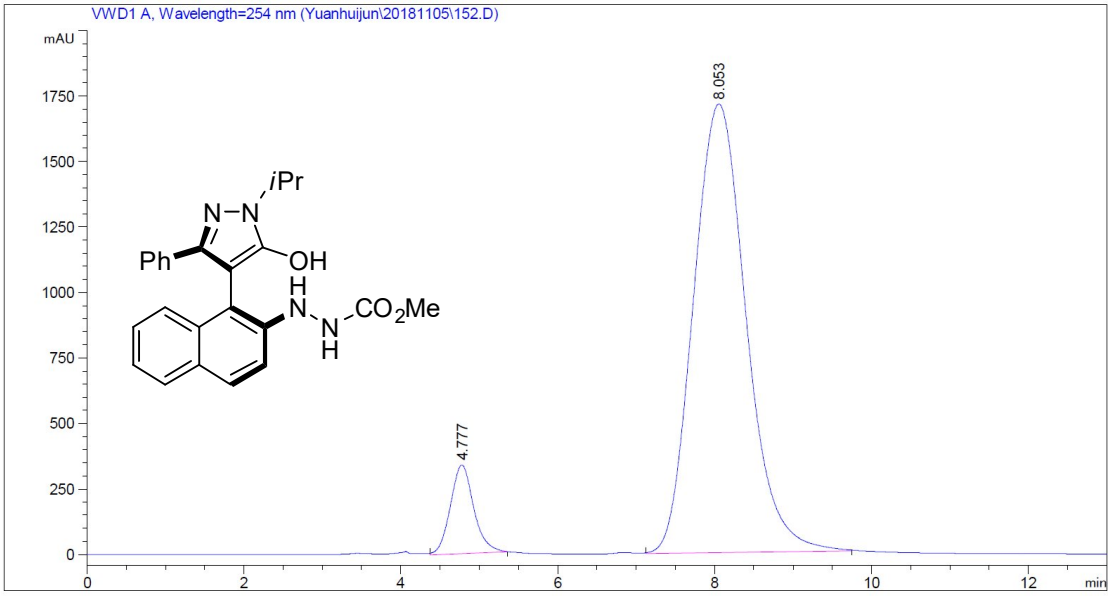


#	Time	Area	Height	Width	Symmetry	Area %
1	4.005	1085.1	95.7	0.1889	0.83	4.936
2	5.22	20900.1	1426.3	0.2442	0.621	95.064

(*S*)-methyl 2-(1-(5-hydroxy-1-isopropyl-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ak)

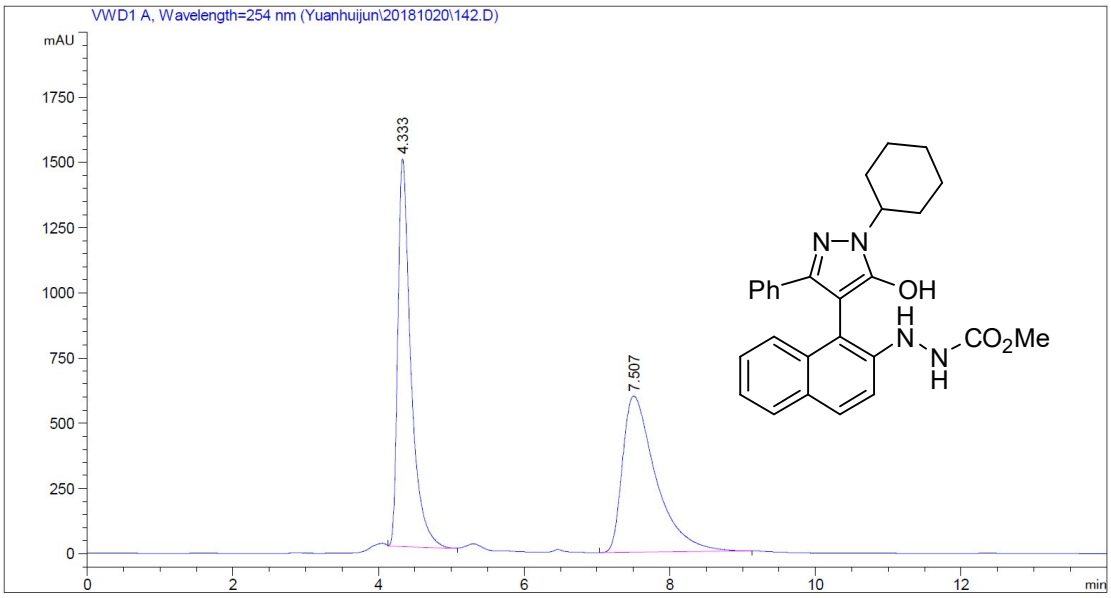


#	Time	Area	Height	Width	Symmetry	Area %
1	4.763	13038.4	594.4	0.3656	0.919	49.091
2	8.068	13521.4	284.6	0.7919	1.007	50.909

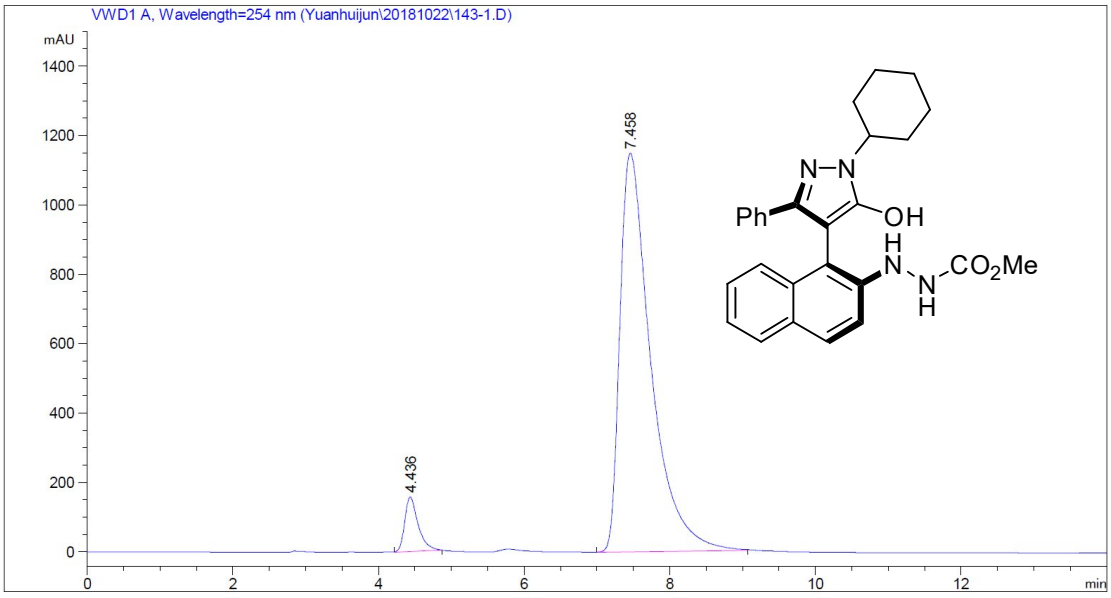


#	Time	Area	Height	Width	Symmetry	Area %
1	4.777	7028.6	339	0.3455	0.927	8.103
2	8.053	79715.3	1712.6	0.7758	0.891	91.897

(*S*)-methyl 2-(1-(1-cyclohexyl-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3al)

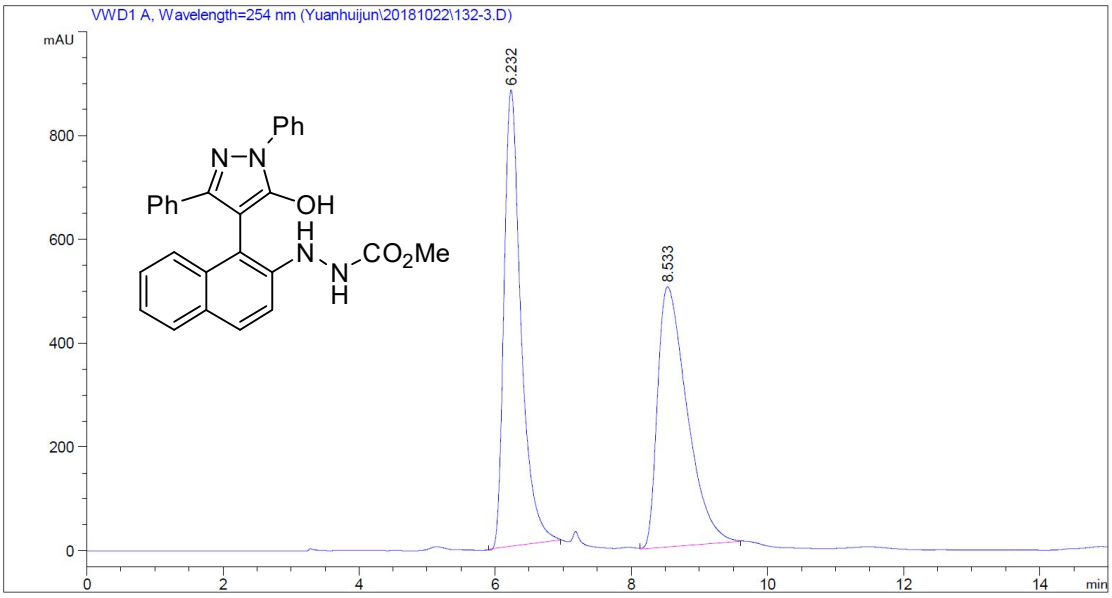


#	Time	Area	Height	Width	Symmetry	Area %
1	4.333	18483.9	1486.9	0.2072	0.553	49.144
2	7.507	19127.8	599.6	0.5316	0.492	50.856

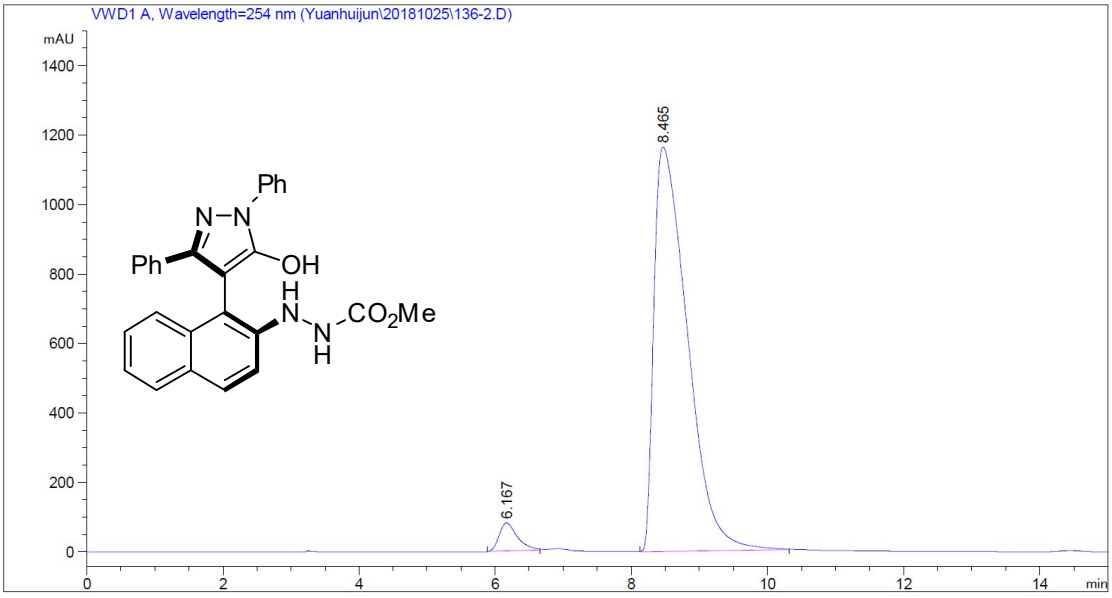


#	Time	Area	Height	Width	Symmetry	Area %
1	4.436	2016.8	157.6	0.2133	0.676	5.608
2	7.458	33945.7	1149.2	0.4923	0.485	94.392

(*S*)-methyl 2-(1-(5-hydroxy-1,3-diphenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3am)

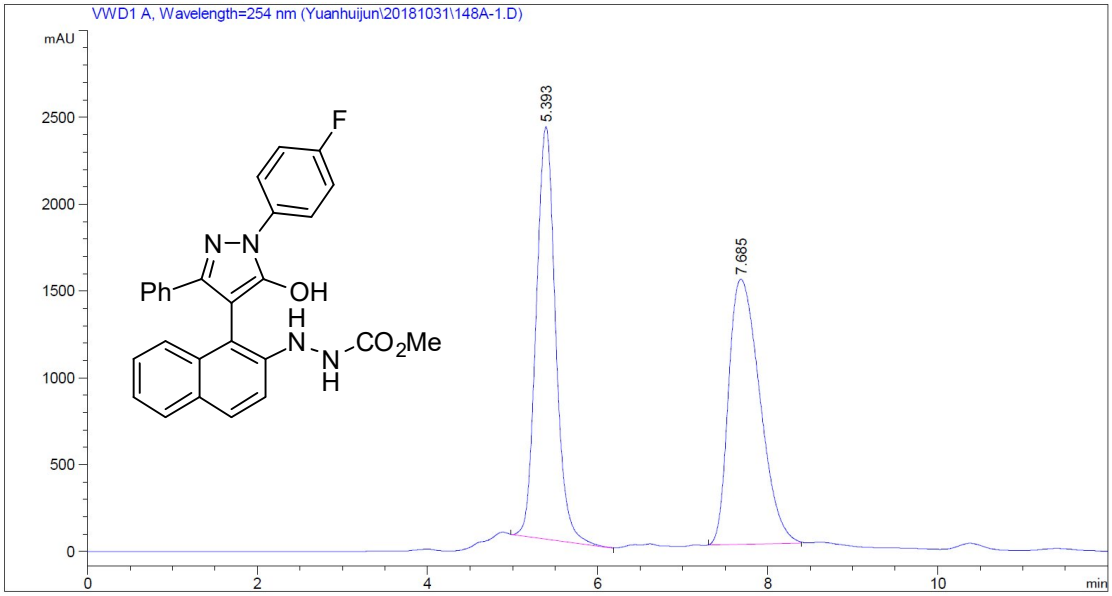


#	Time	Area	Height	Width	Symmetry	Area %
1	6.232	15198.8	879.4	0.2881	0.656	50.250
2	8.533	15047.6	501.1	0.5005	0.5	49.750

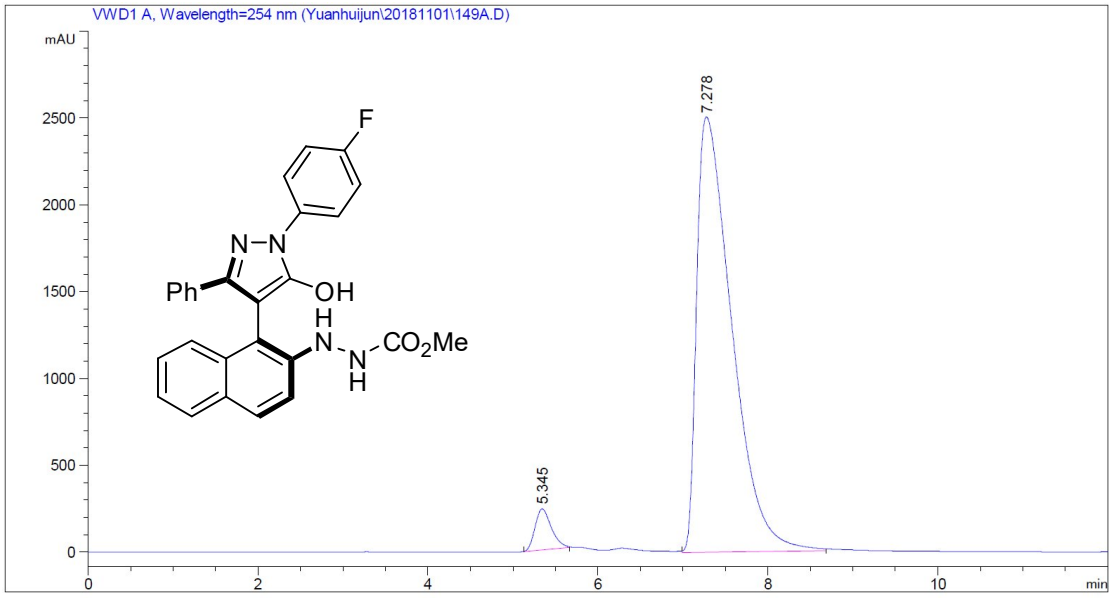


#	Time	Area	Height	Width	Symmetry	Area %
1	6.167	1489.9	80.3	0.3093	0.653	3.625
2	8.465	39607.5	1163.7	0.5673	0.363	96.375

(*S*)-methyl 2-(1-(1-(4-fluorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3an)

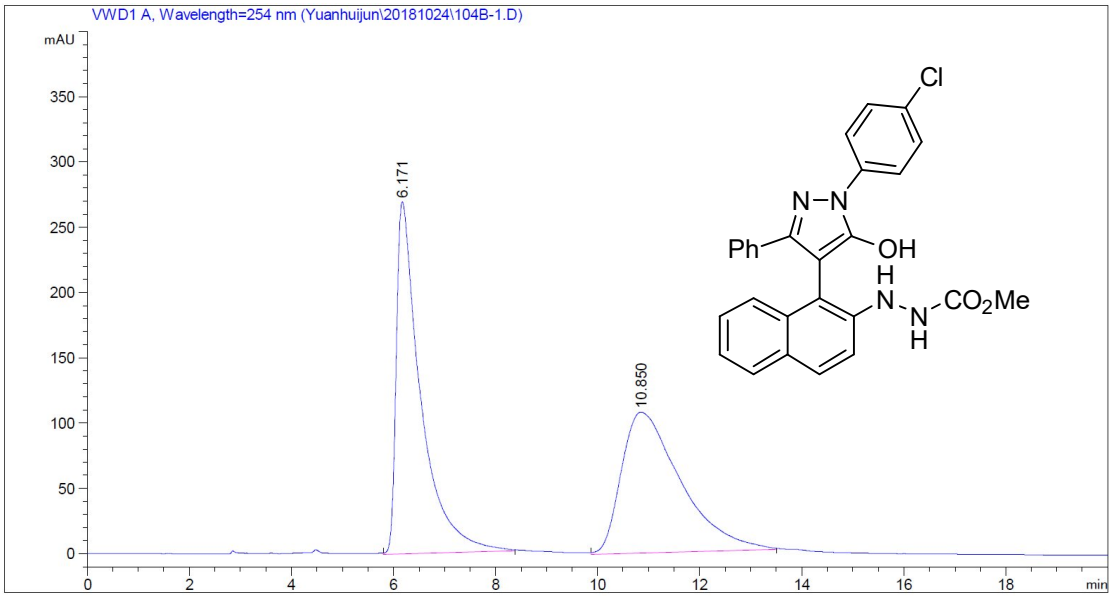


#	Time	Area	Height	Width	Symmetry	Area %
1	5.393	37546.6	2374.6	0.2635	0.954	49.010
2	7.685	39063.5	1526.7	0.4265	0.624	50.990

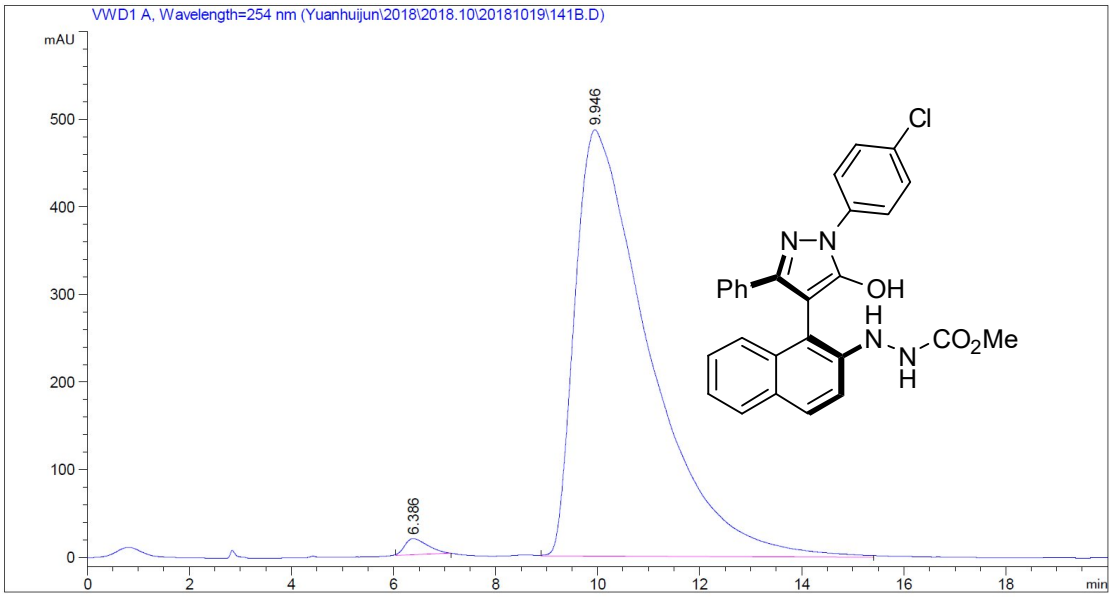


#	Time	Area	Height	Width	Symmetry	Area %
1	5.345	3132.5	236.2	0.221	0.758	4.180
2	7.278	71814.3	2505.5	0.4777	0.37	95.820

(*S*)-methyl 2-(1-(1-(4-chlorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ao)

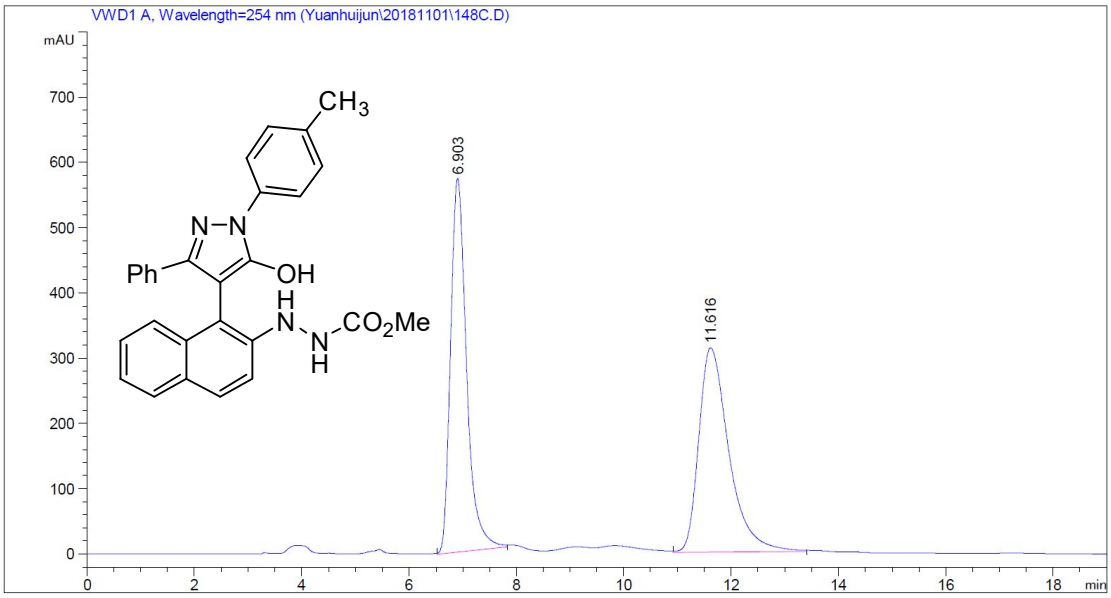


#	Time	Area	Height	Width	Symmetry	Area %
1	6.171	8912.8	269.6	0.551	0.315	50.549
2	10.85	8719.1	107.9	1.3466	0.485	49.451

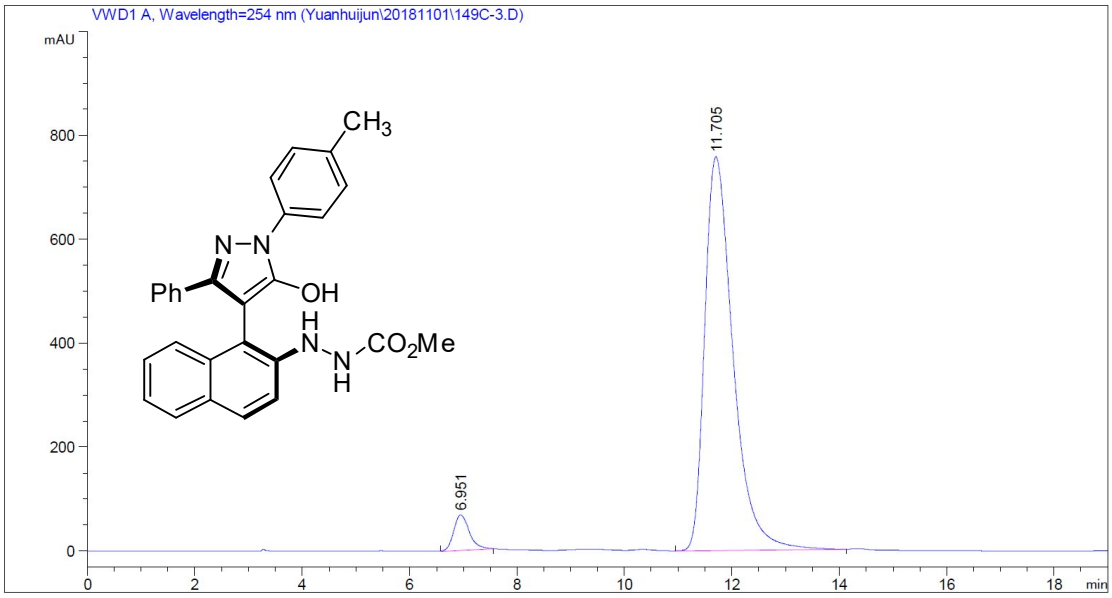


#	Time	Area	Height	Width	Symmetry	Area %
1	6.386	575	18.5	0.5184	0.585	1.156
2	9.946	49157.6	486.2	1.6851	0.356	98.844

(*S*)-methyl 2-(1-(5-hydroxy-3-phenyl-1-(*p*-tolyl)-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ap)

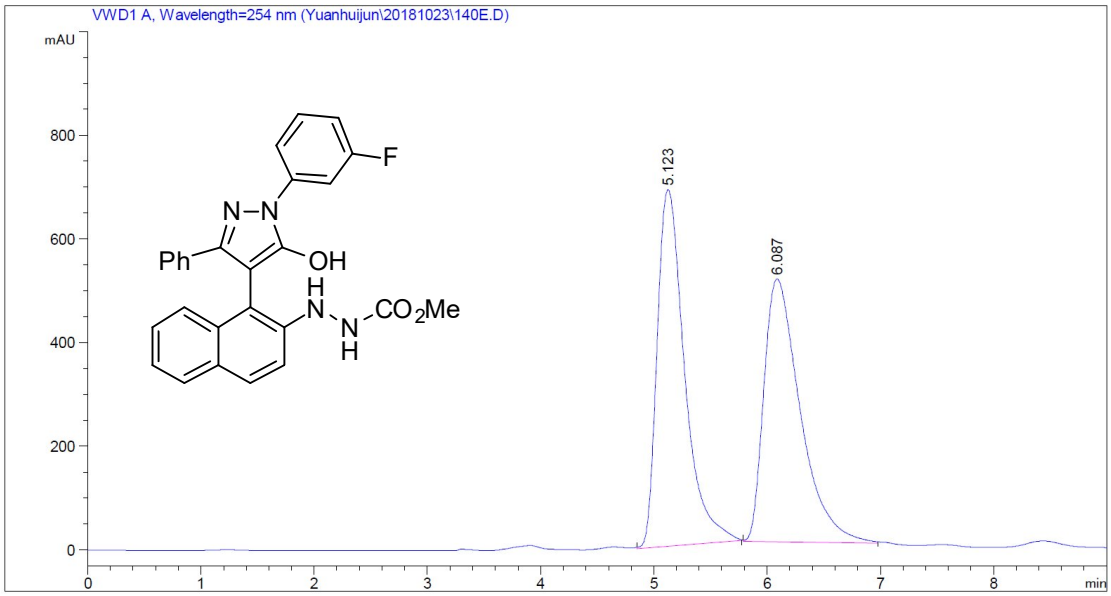


#	Time	Area	Height	Width	Symmetry	Area %
1	6.903	11836.5	572.9	0.3443	0.75	49.134
2	11.616	12253.7	313.2	0.6522	0.617	50.866

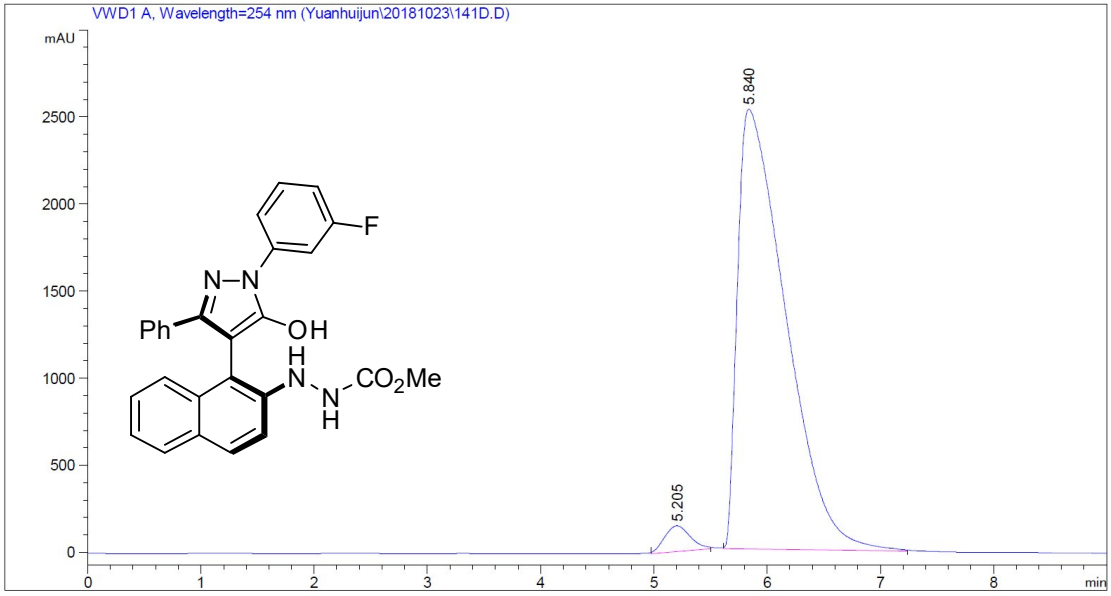


#	Time	Area	Height	Width	Symmetry	Area %
1	6.951	1414.6	69	0.3417	0.778	4.827
2	11.705	27891.8	758.3	0.613	0.622	95.173

(*S*)-methyl 2-(1-(1-(3-fluorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3aq)

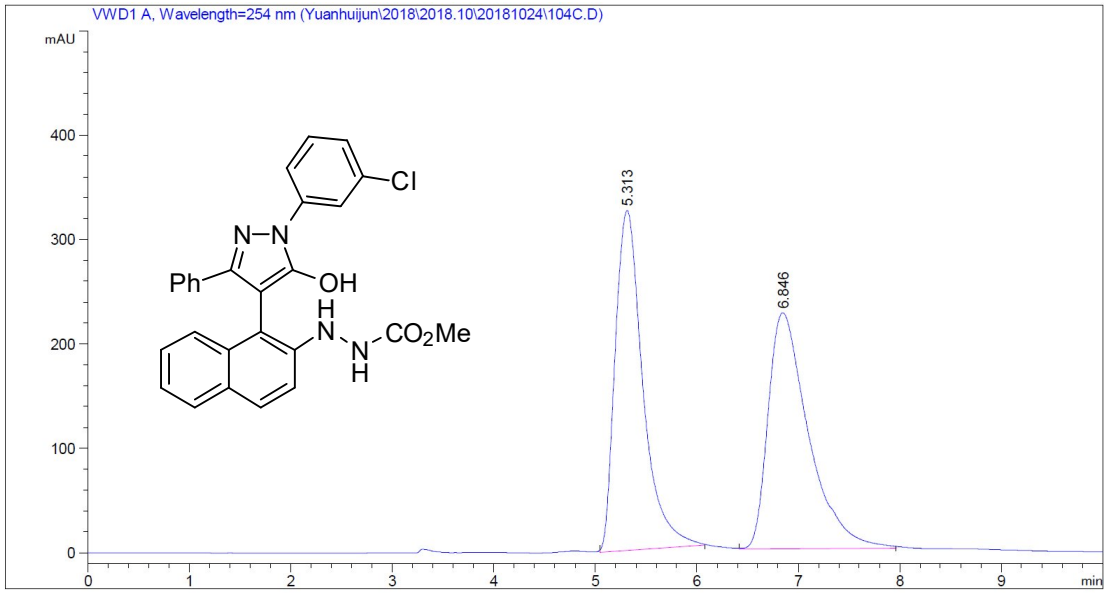


#	Time	Area	Height	Width	Symmetry	Area %
1	5.123	11570.9	687.4	0.2805	0.625	50.593
2	6.087	11299.6	506.9	0.3715	0.547	49.407

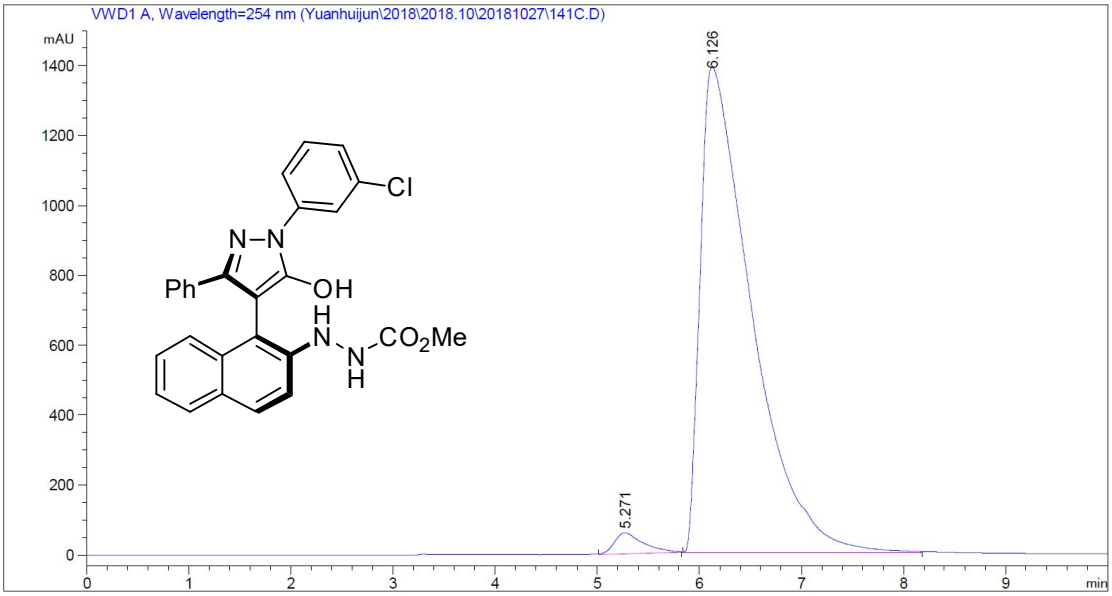


#	Time	Area	Height	Width	Symmetry	Area %
1	5.205	2325.5	148	0.262	0.928	3.025
2	5.84	74545.5	2525.4	0.492	0.3	96.975

(*S*)-methyl 2-(1-(1-(3-chlorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ar)

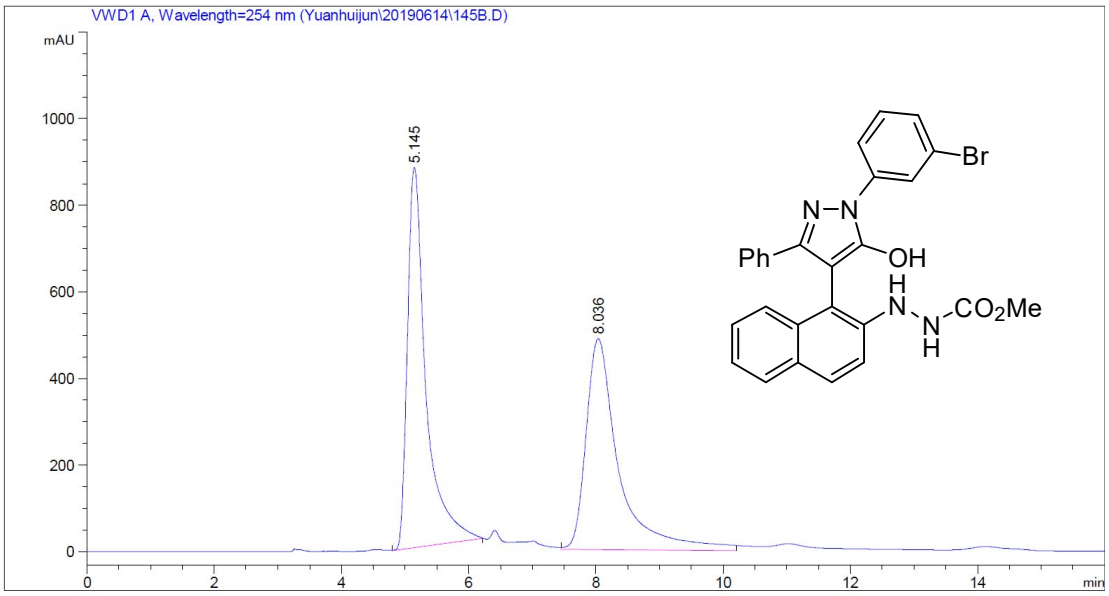


#	Time	Area	Height	Width	Symmetry	Area %
1	5.313	6182	325.9	0.3161	0.713	49.645
2	6.846	6270.4	226.5	0.4613	0.549	50.355

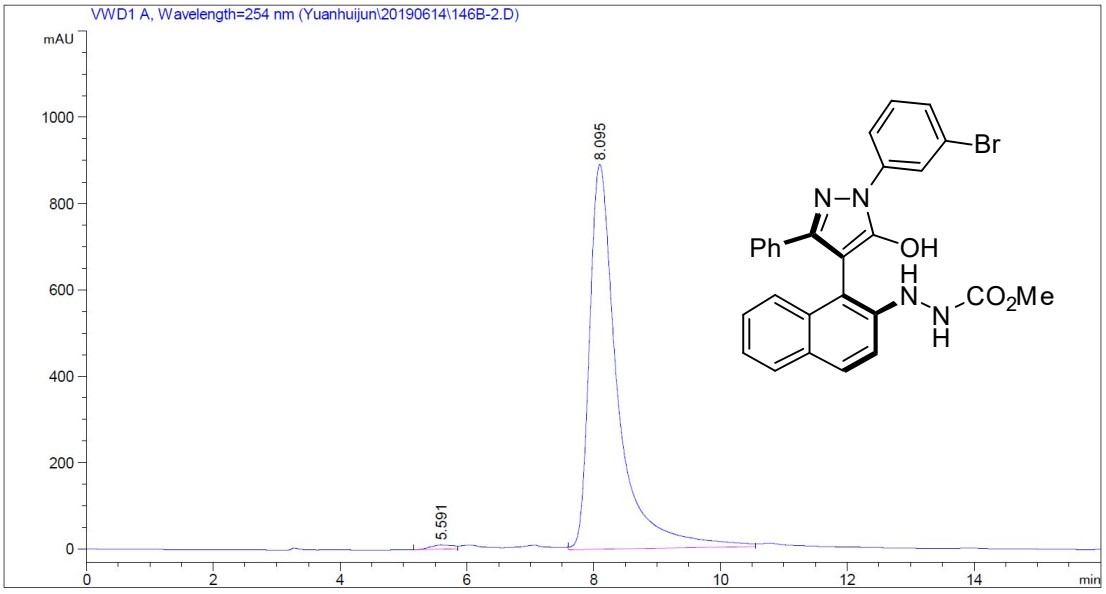


#	Time	Area	Height	Width	Symmetry	Area %
1	5.271	1185.7	60.5	0.3266	0.575	2.386
2	6.126	48510.2	1390.6	0.5814	0.296	97.614

(*S*)-methyl 2-(1-(1-(3-bromophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3as)

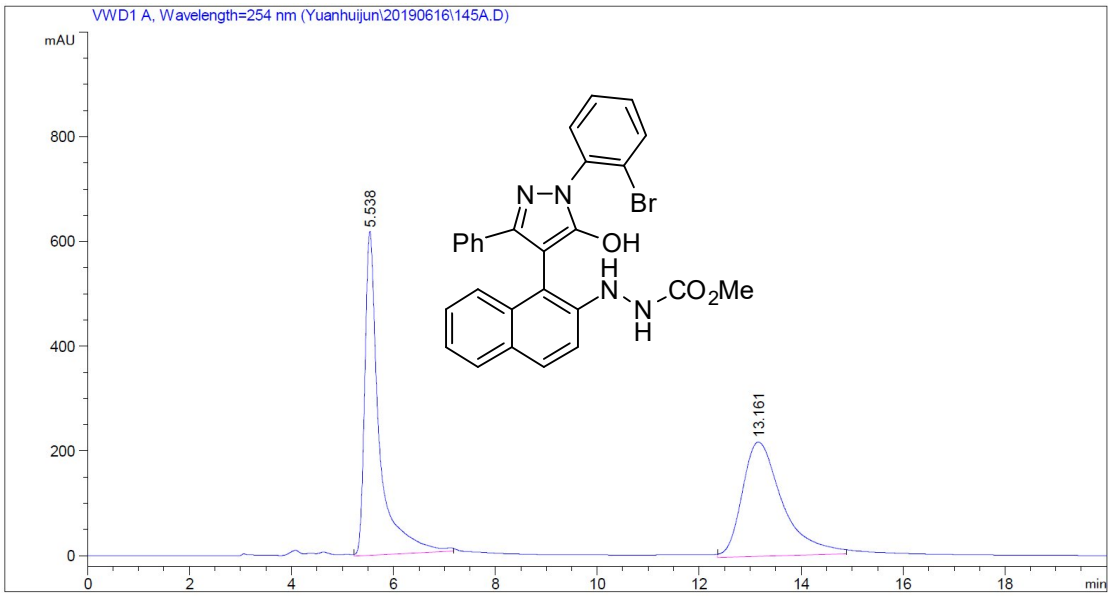


#	Time	Area	Height	Width	Symmetry	Area %
1	5.145	17731.7	878.3	0.3365	0.556	50.366
2	8.036	17473.8	486.9	0.5981	0.558	49.634

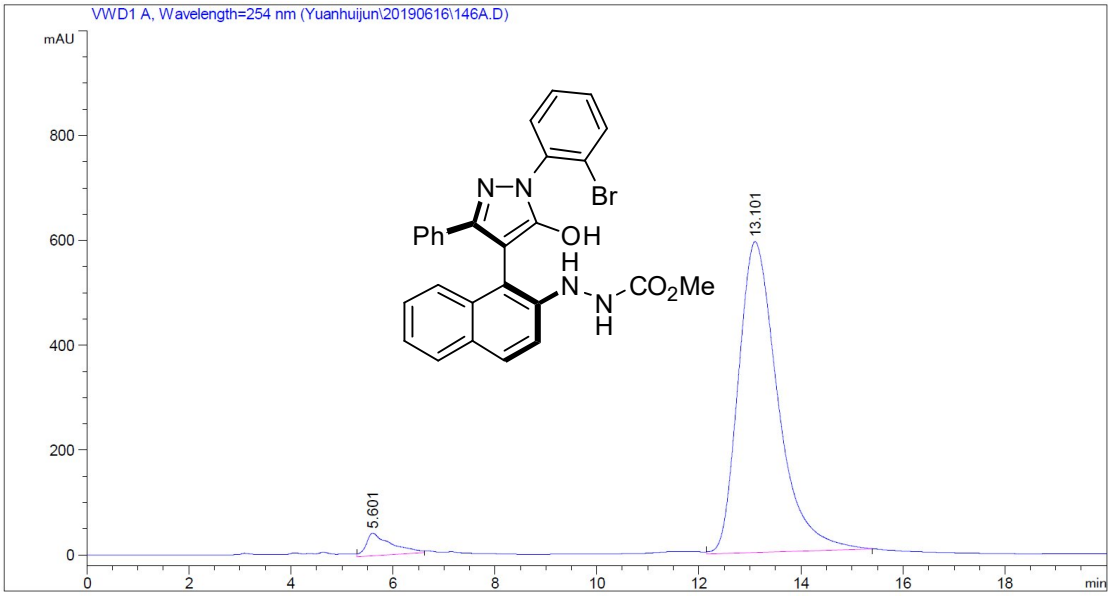


#	Time	Area	Height	Width	Symmetry	Area %
1	5.591	240.3	9.7	0.3348	0.839	0.865
2	8.095	27535.8	891.2	0.5149	0.542	99.135

(*S*)-methyl 2-(1-(1-(2-bromophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3at)

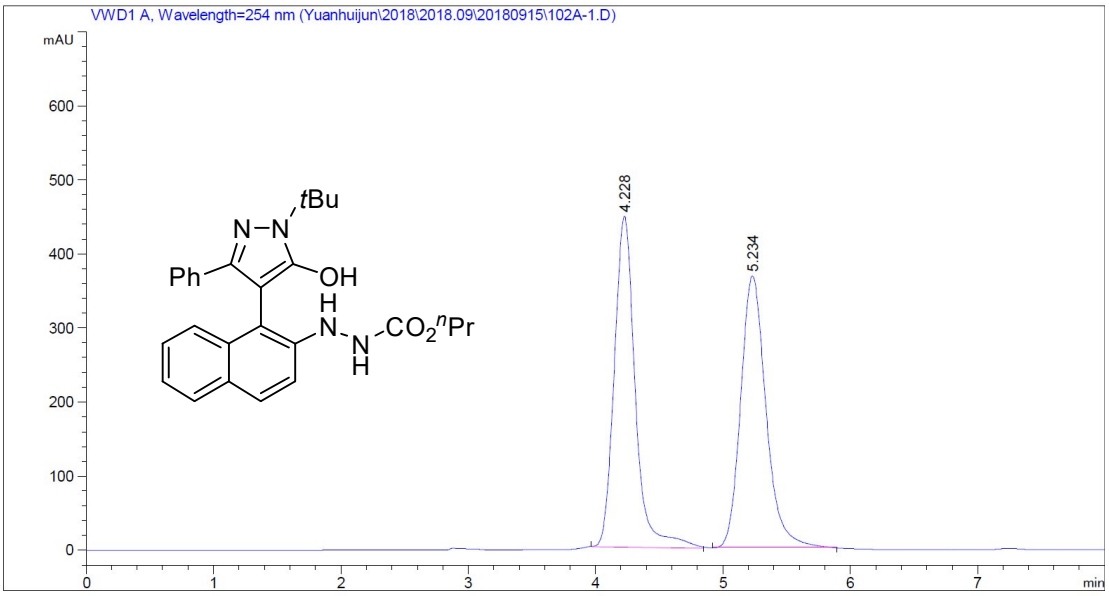


#	Time	Area	Height	Width	Symmetry	Area %
1	5.538	12212.3	618.6	0.329	0.506	50.451
2	13.161	11994	218.3	0.9156	0.645	49.549

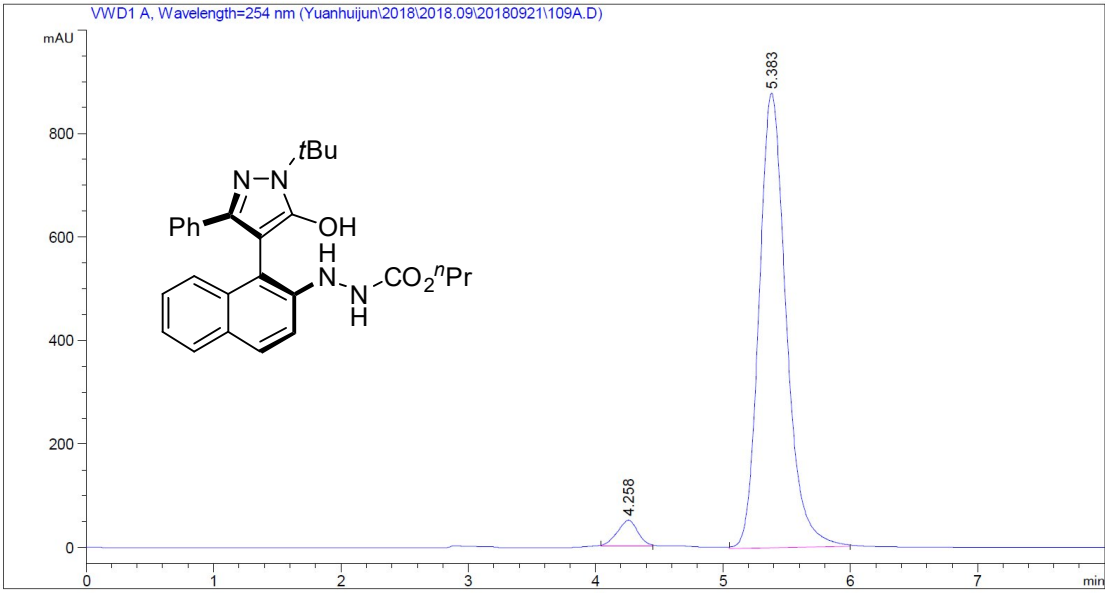


#	Time	Area	Height	Width	Symmetry	Area %
1	5.601	1473.4	43.2	0.5678	0.353	4.415
2	13.101	31896.1	593.3	0.896	0.705	95.585

(*S*)-propyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ba)

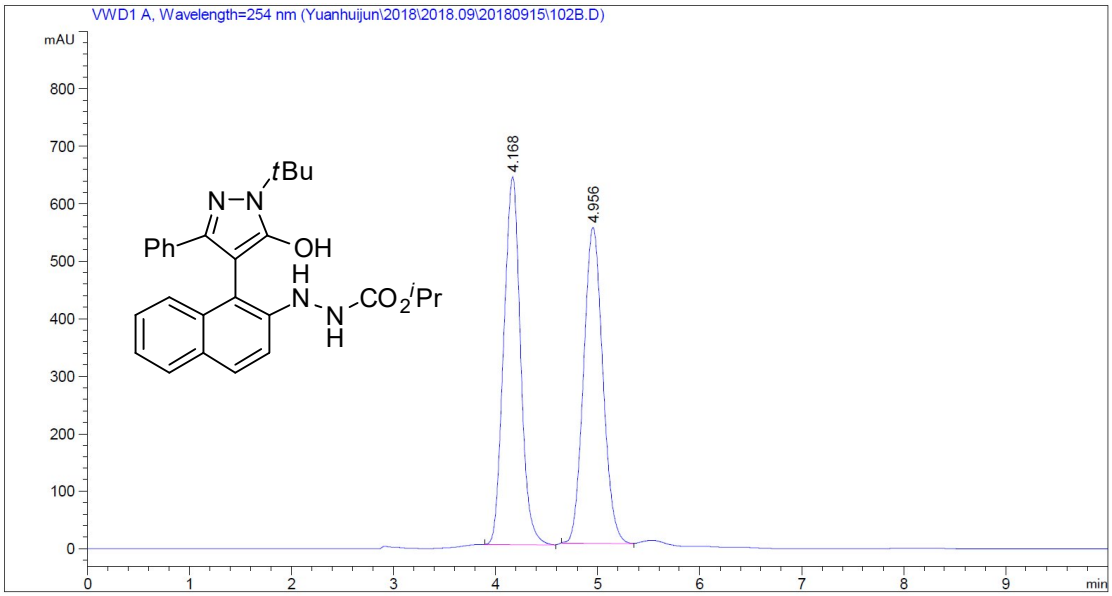


#	Time	Area	Height	Width	Symmetry	Area %
1	4.228	5111.2	446.7	0.1907	0.878	50.259
2	5.234	5058.5	366.6	0.23	0.824	49.741

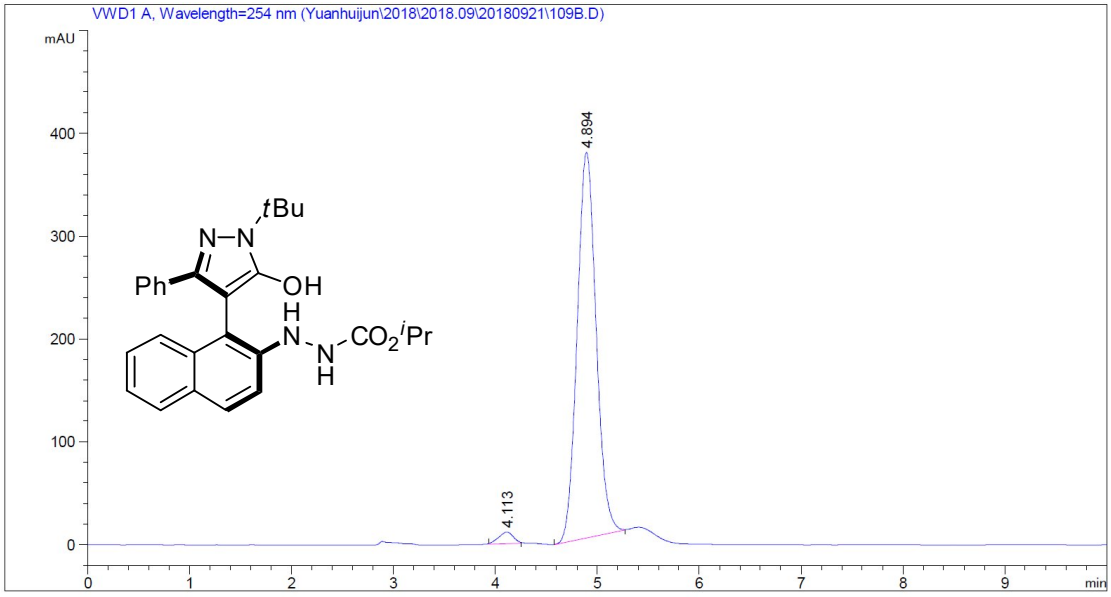


#	Time	Area	Height	Width	Symmetry	Area %
1	4.258	565.2	50	0.1883	1.155	4.183
2	5.383	12945.5	878.4	0.2456	0.816	95.817

(*S*)-isopropyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ca)

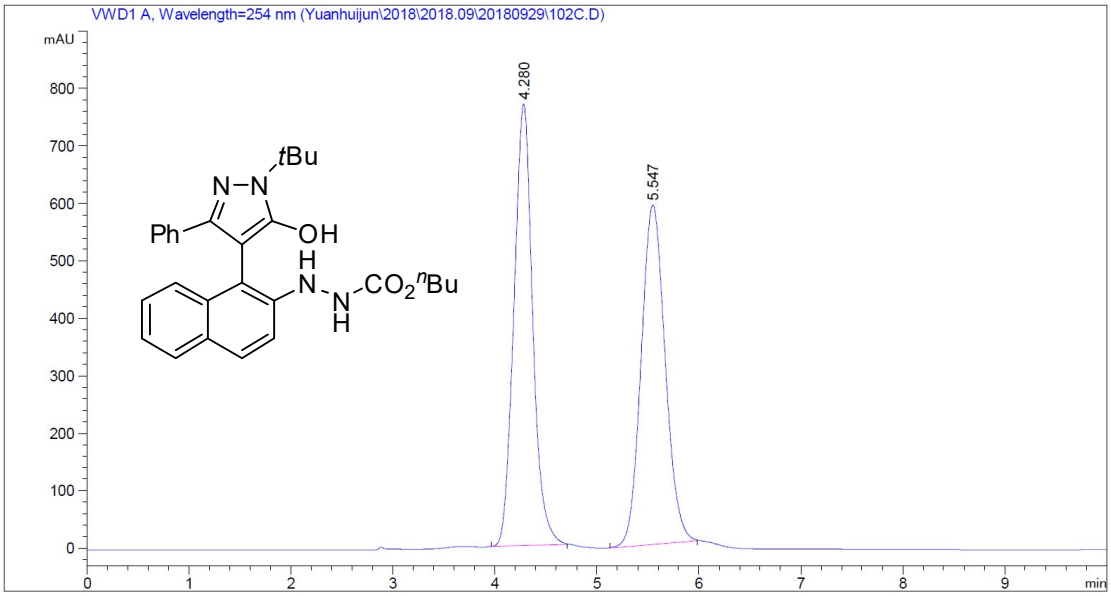


#	Time	Area	Height	Width	Symmetry	Area %
1	4.168	7315.4	639.8	0.1906	1.06	50.411
2	4.956	7196.1	549.6	0.2182	0.92	49.589

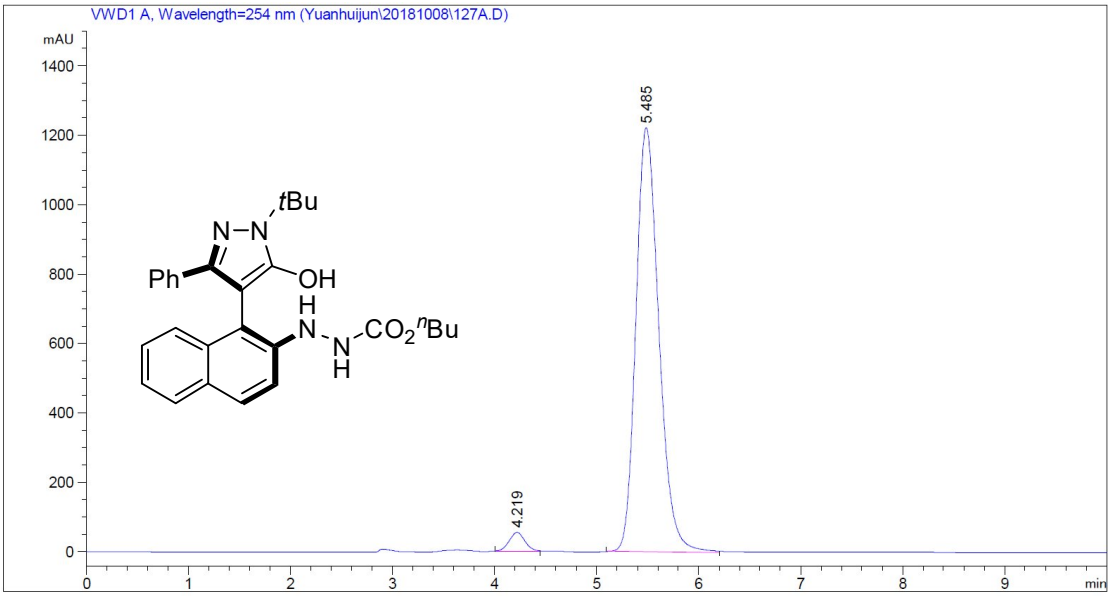


#	Time	Area	Height	Width	Symmetry	Area %
1	4.113	111.6	11.2	0.1653	1.239	2.251
2	4.894	4844.3	375	0.2153	0.931	97.749

(*S*)-butyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3da)

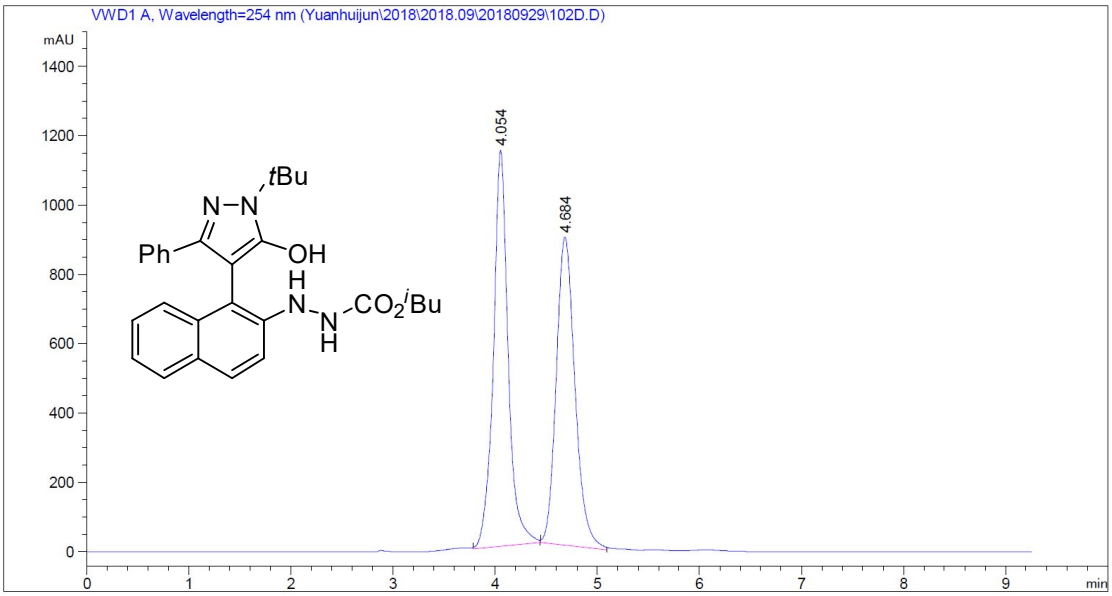


#	Time	Area	Height	Width	Symmetry	Area %
1	4.28	9813.5	768.8	0.2127	1.01	50.307
2	5.547	9693.5	591.2	0.2733	0.915	49.693

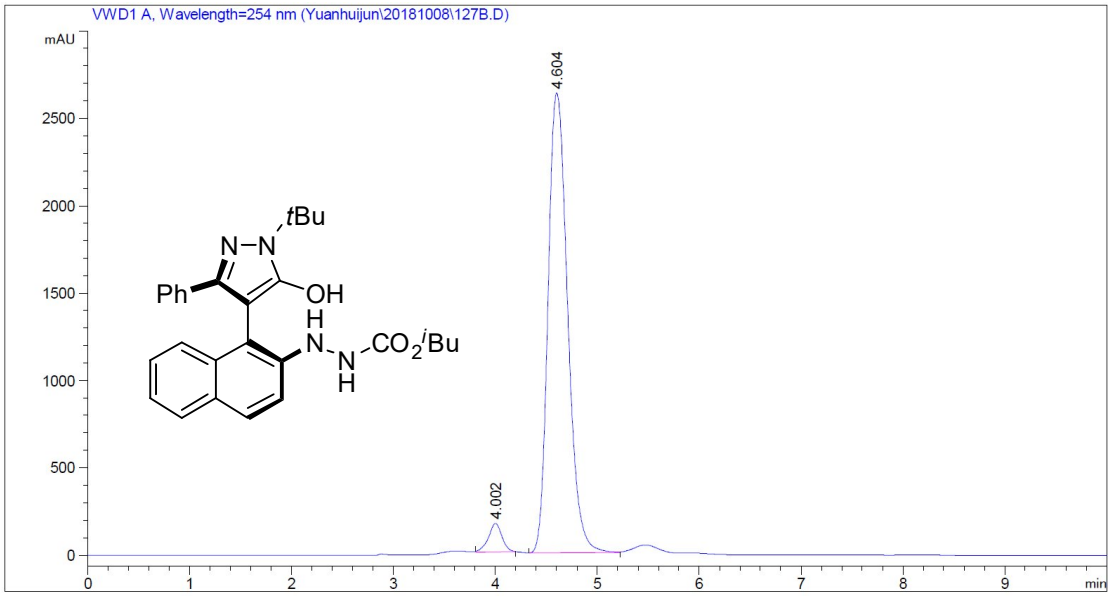


#	Time	Area	Height	Width	Symmetry	Area %
1	4.219	627.8	56.2	0.1862	0.969	3.183
2	5.485	19096.8	1221.6	0.2606	0.777	96.817

(*S*)-isobutyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ea)

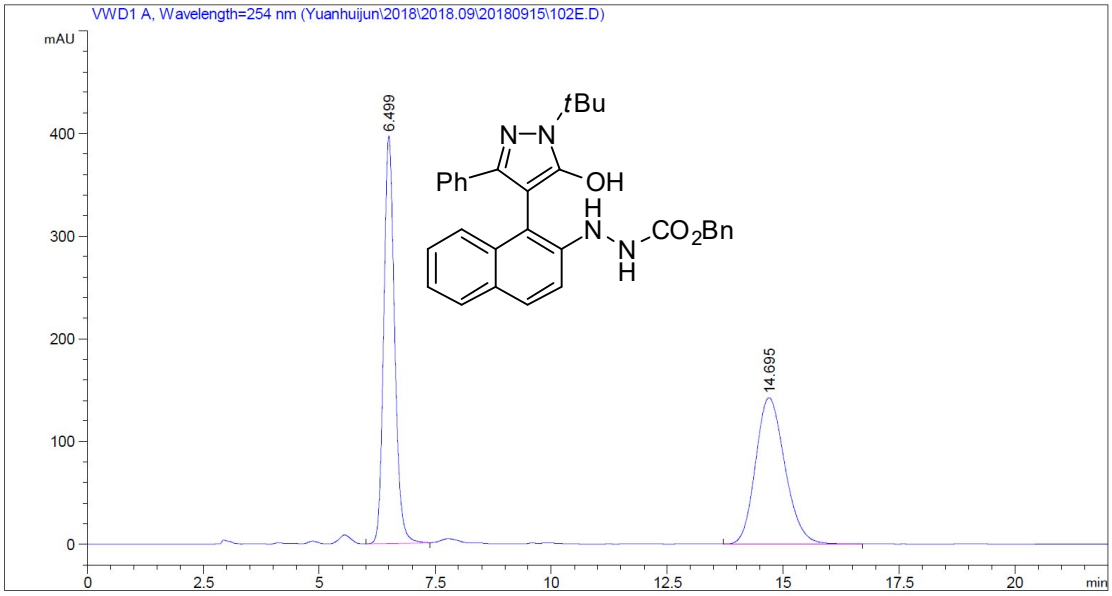


#	Time	Area	Height	Width	Symmetry	Area %
1	4.054	11480.8	1142	0.1676	0.921	50.400
2	4.684	11298.4	888.6	0.2119	0.828	49.600

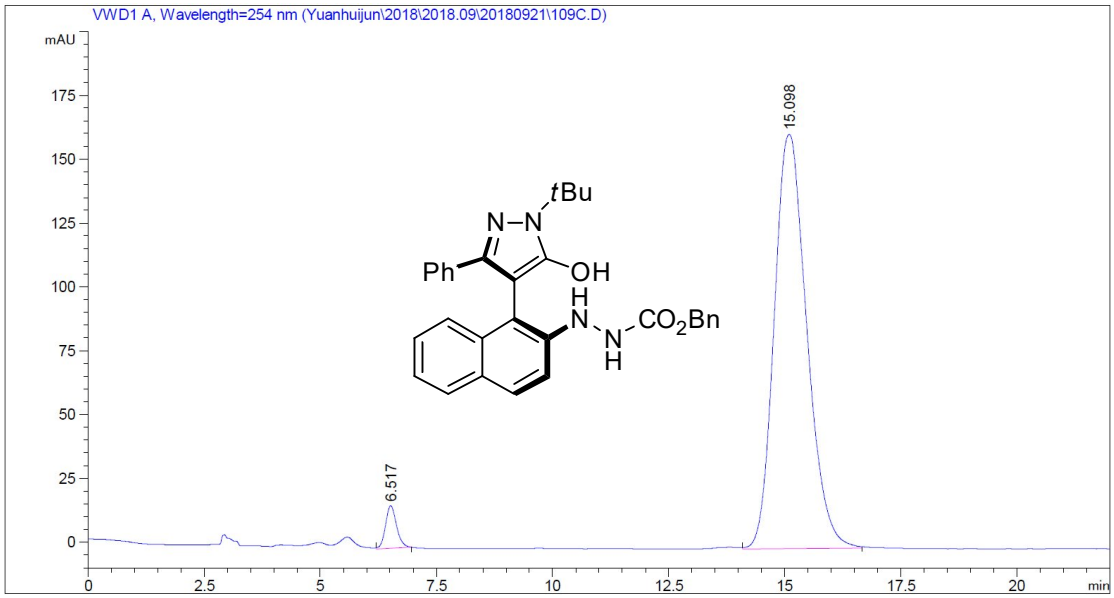


#	Time	Area	Height	Width	Symmetry	Area %
1	4.002	1509.3	164.1	0.1533	1.068	4.132
2	4.604	35020.3	2632.3	0.2217	0	95.868

(*S*)-benzyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3fa)

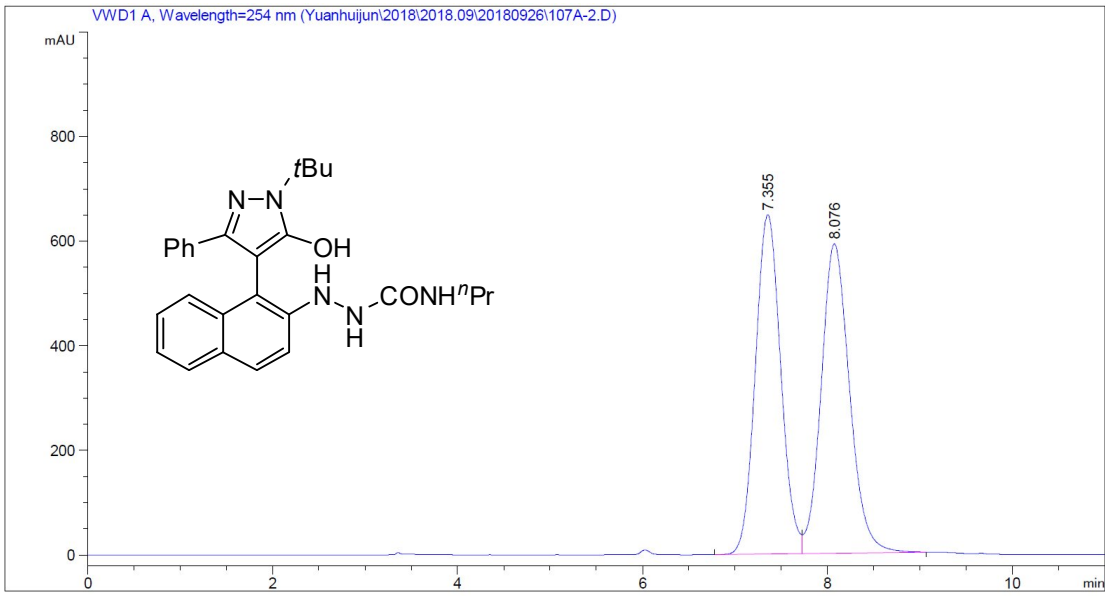


#	Time	Area	Height	Width	Symmetry	Area %
1	6.499	6492.1	396.6	0.251	0.827	50.945
2	14.695	6251.1	142.4	0.6823	0.801	49.055

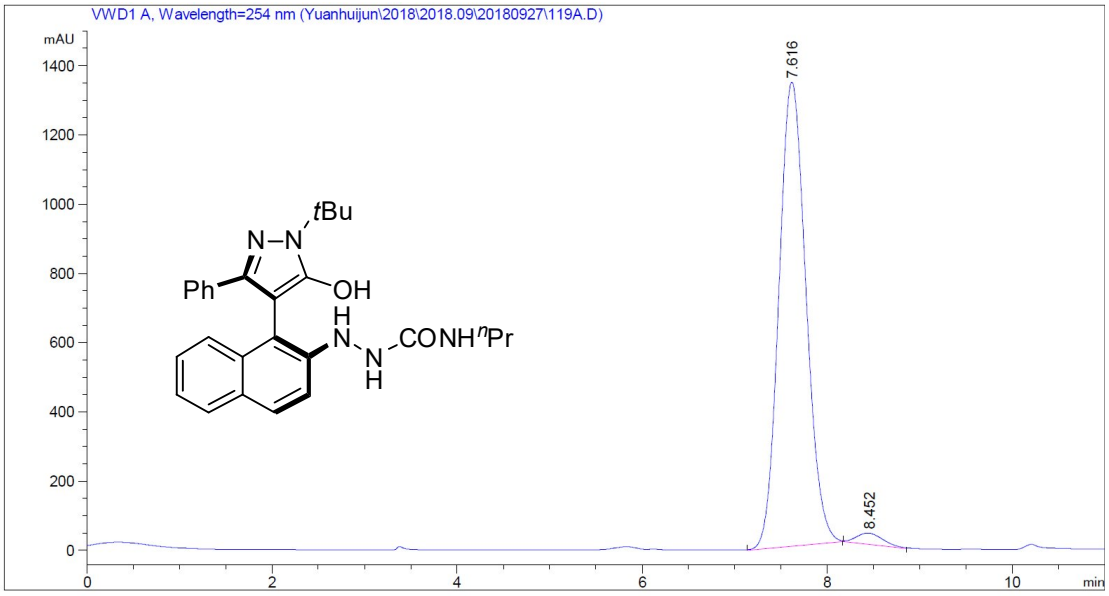


#	Time	Area	Height	Width	Symmetry	Area %
1	6.517	274.9	16.6	0.2754	0.857	3.367
2	15.098	7890.2	162.1	0.8111	0.822	96.633

(*S*)-2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)-*N*-propylhydrazinecarboxamide (3ga)

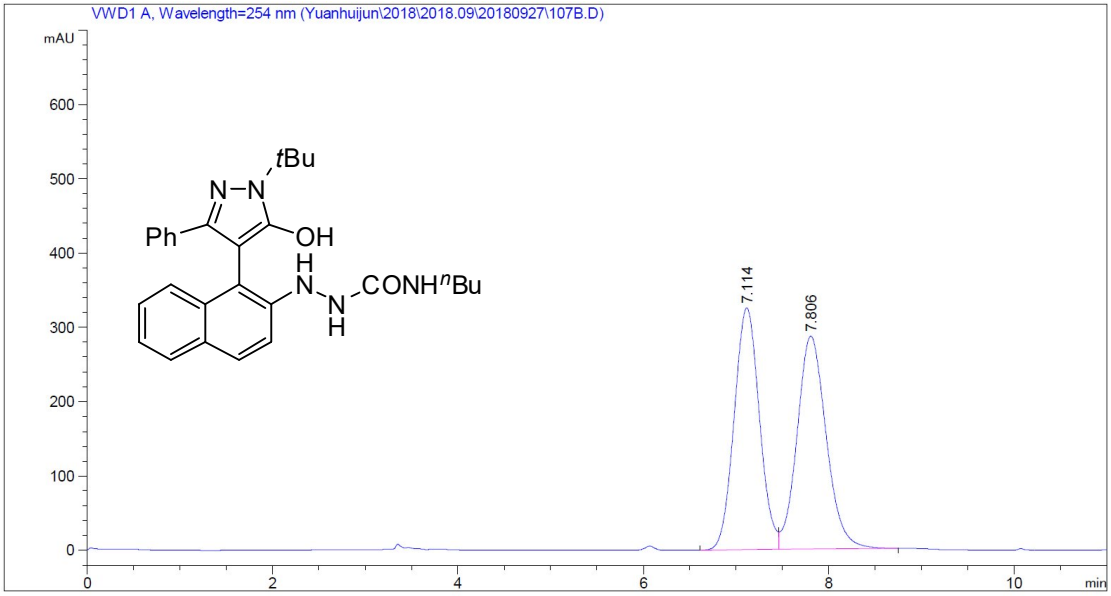


#	Time	Area	Height	Width	Symmetry	Area %
1	7.355	12340.6	649	0.2948	0.916	49.430
2	8.076	12625.2	591.6	0.327	0.823	50.570

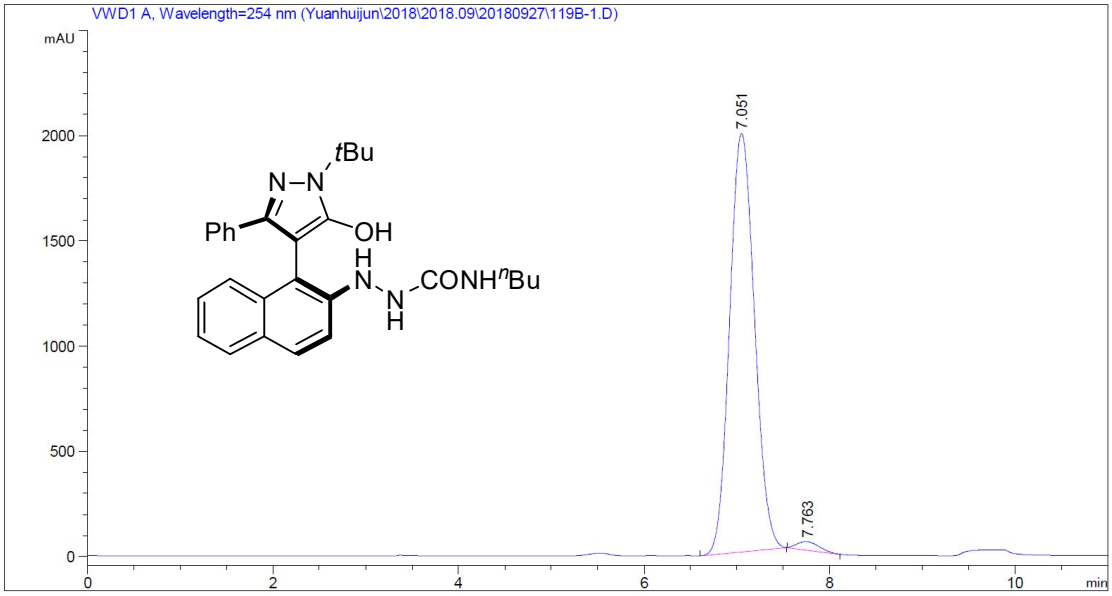


#	Time	Area	Height	Width	Symmetry	Area %
1	7.616	27165.6	1339.3	0.338	0.879	97.692
2	8.452	641.7	32.3	0.3308	0.694	2.308

(*S*)-*N*-butyl-2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxamide (3ha)

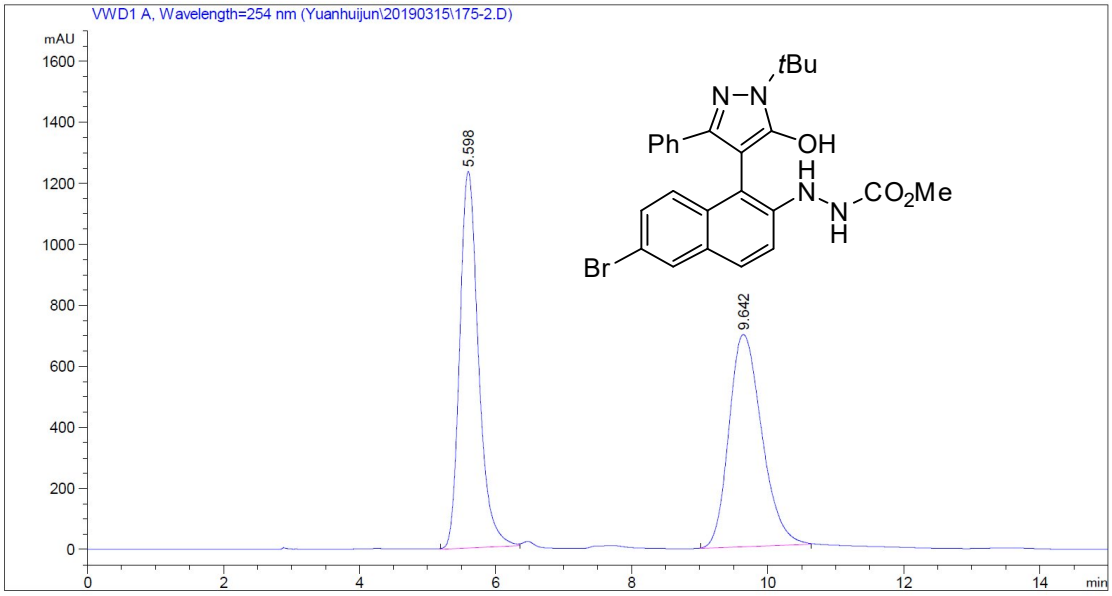


#	Time	Area	Height	Width	Symmetry	Area %
1	7.114	6153.9	325.4	0.2957	0.949	49.569
2	7.806	6261	286.6	0.3359	0.846	50.431

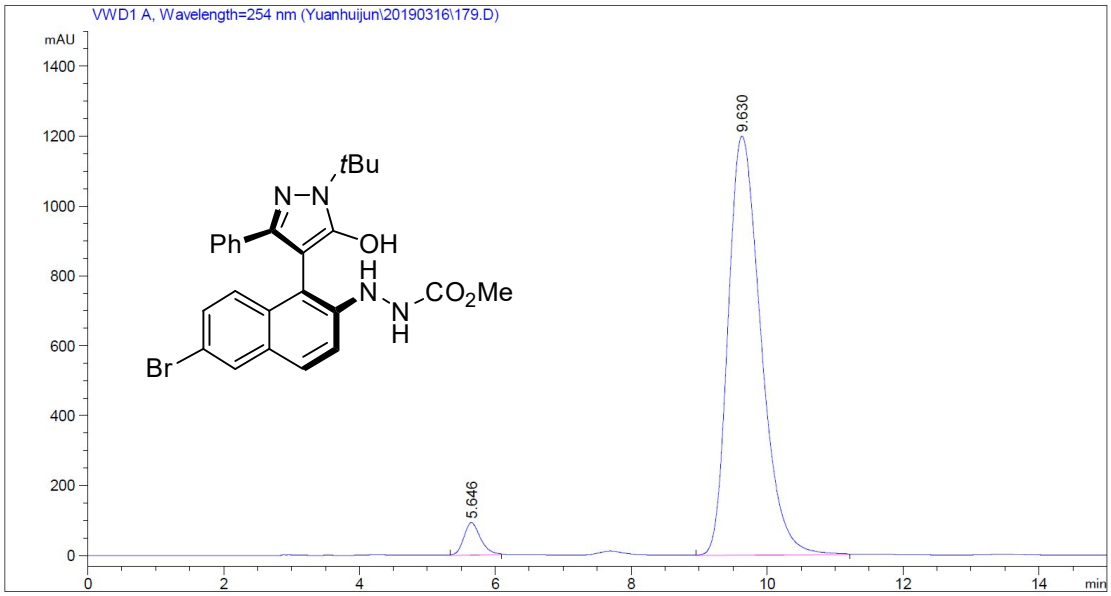


#	Time	Area	Height	Width	Symmetry	Area %
1	7.051	36982.9	1988.1	0.31	0.891	98.158
2	7.763	693.9	41.3	0.2801	0.6	1.842

(*S*)-methyl 2-(6-bromo-1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ia)

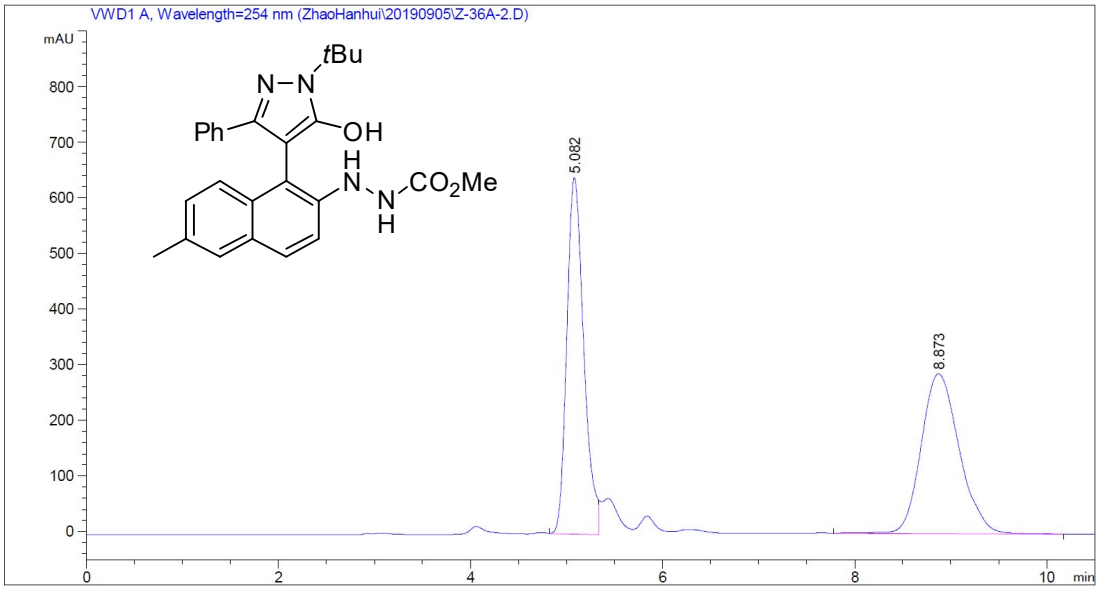


#	Time	Area	Height	Width	Symmetry	Area %
1	5.598	23628.9	1234.1	0.3191	0.792	50.230
2	9.642	23412.2	695.7	0.5609	0.759	49.770

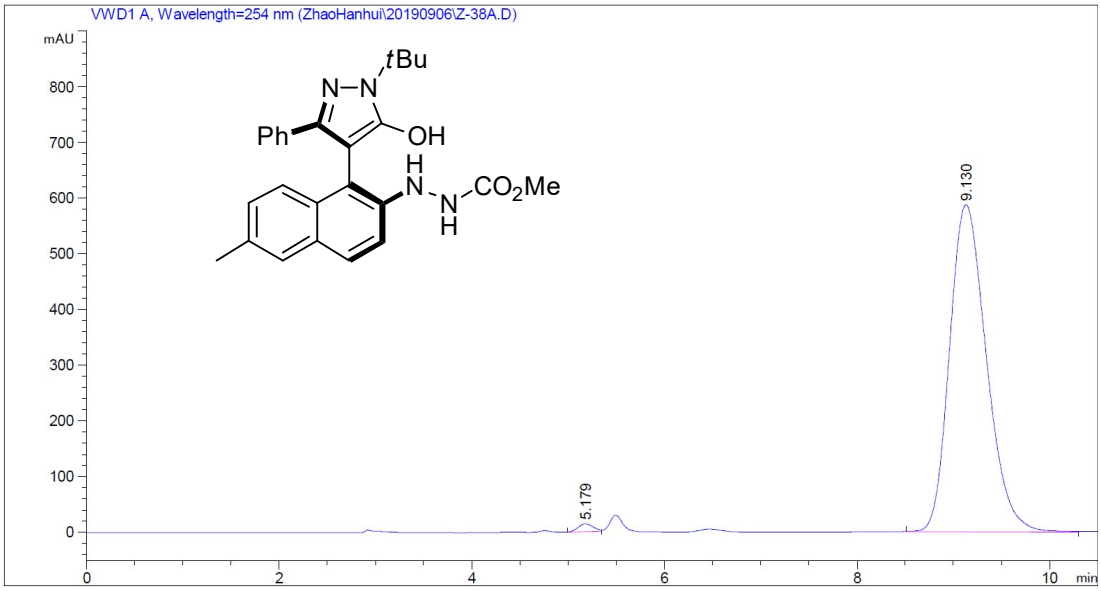


#	Time	Area	Height	Width	Symmetry	Area %
1	5.646	1587.1	92.8	0.2849	0.795	3.809
2	9.63	40077.9	1199.4	0.5569	0.705	96.191

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)-6-methylnaphthalen-2-yl)hydrazinecarboxylate (3ja)

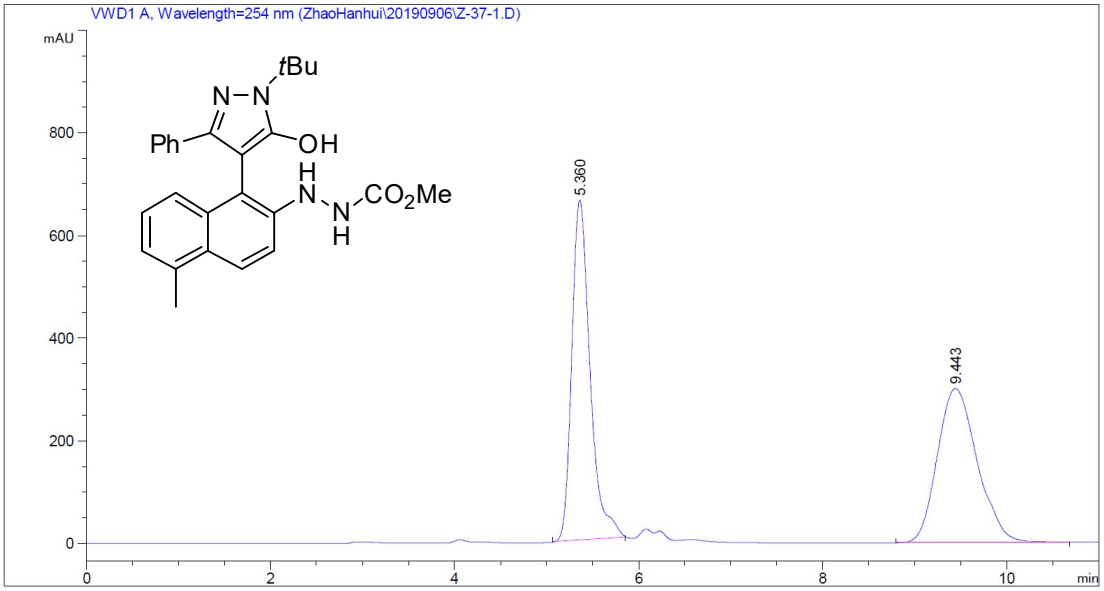


#	Time	Area	Height	Width	Symmetry	Area %
1	5.082	7846.4	640.4	0.2042	0.771	49.893
2	8.873	7880.2	287.1	0.4263	0.804	50.107

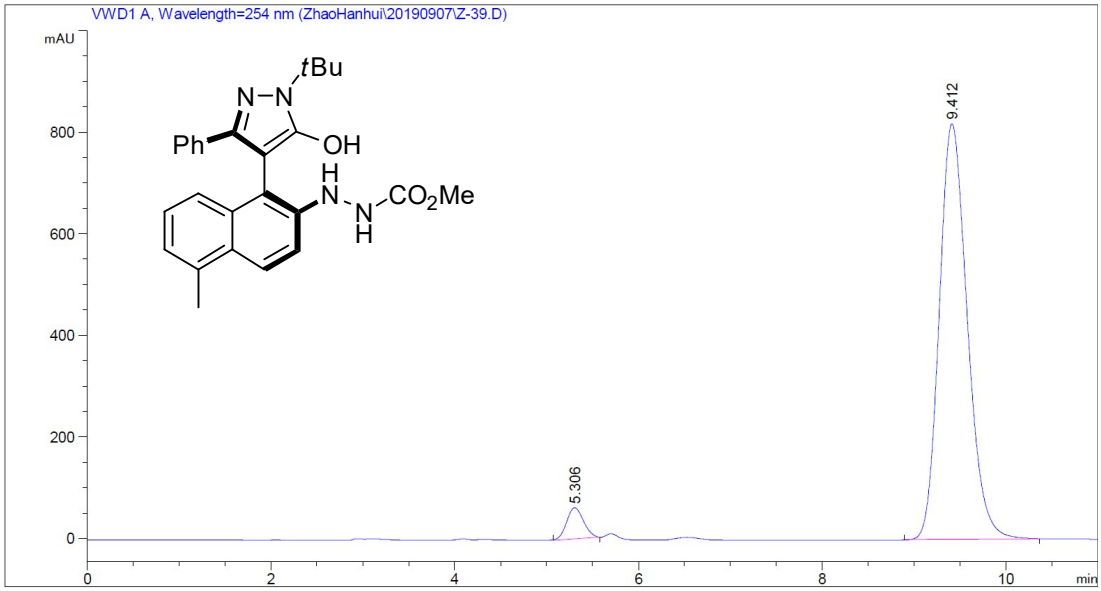


#	Time	Area	Height	Width	Symmetry	Area %
1	5.179	158.7	14.1	0.1873	0.937	1.004
2	9.13	15638.9	587.2	0.4439	0.77	98.996

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)-5-methylnaphthalen-2-yl)hydrazinecarboxylate (3ka)

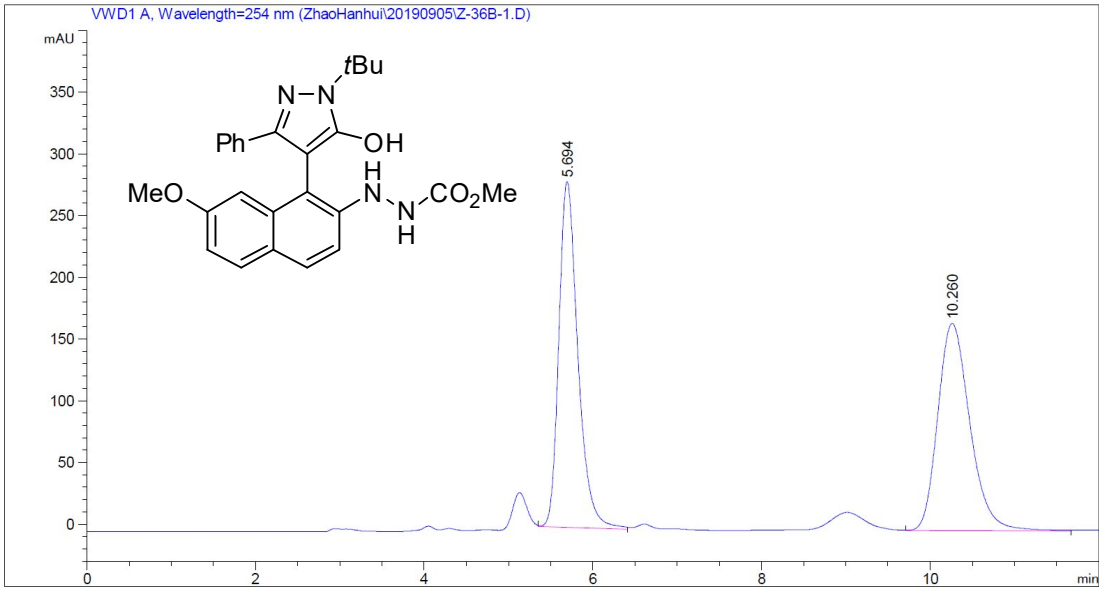


#	Time	Area	Height	Width	Symmetry	Area %
1	5.36	9101.6	662.3	0.2291	0.722	50.073
2	9.443	9075.1	300.4	0.5035	0.796	49.927

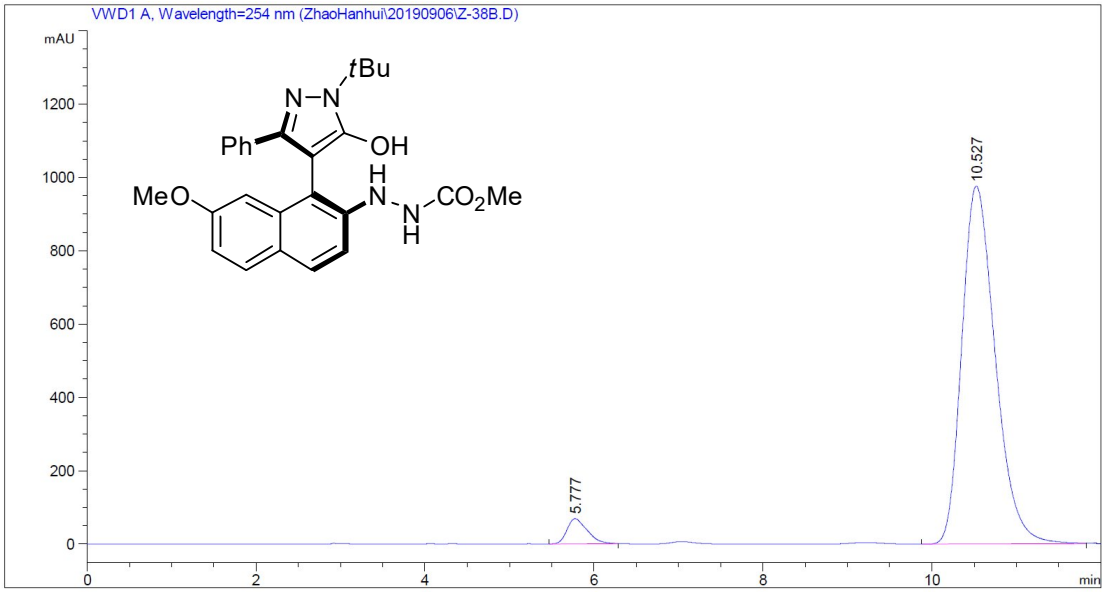


#	Time	Area	Height	Width	Symmetry	Area %
1	5.306	777.2	61.2	0.2117	0.899	4.299
2	9.412	17302.9	818.1	0.3525	0.799	95.701

(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)-7-methoxynaphthalen-2-yl)hydrazinecarboxylate (3la)



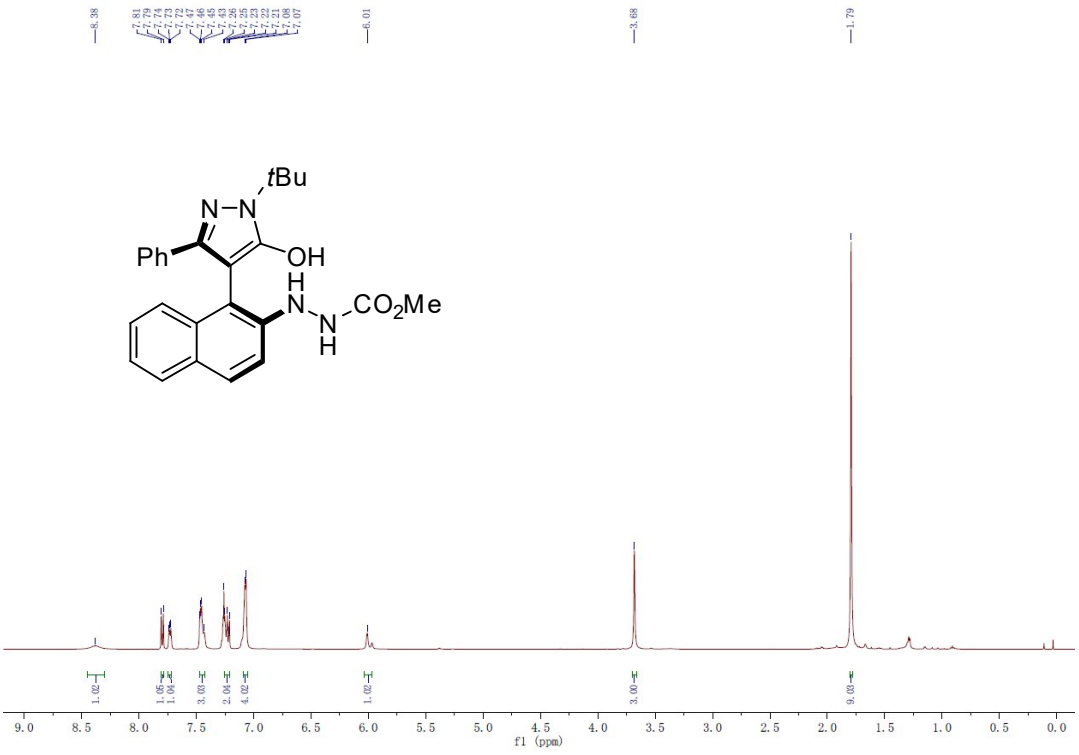
#	Time	Area	Height	Width	Symmetry	Area %
1	5.694	4396.2	280.3	0.2614	0.727	49.621
2	10.26	4463.4	167.9	0.443	0.769	50.379

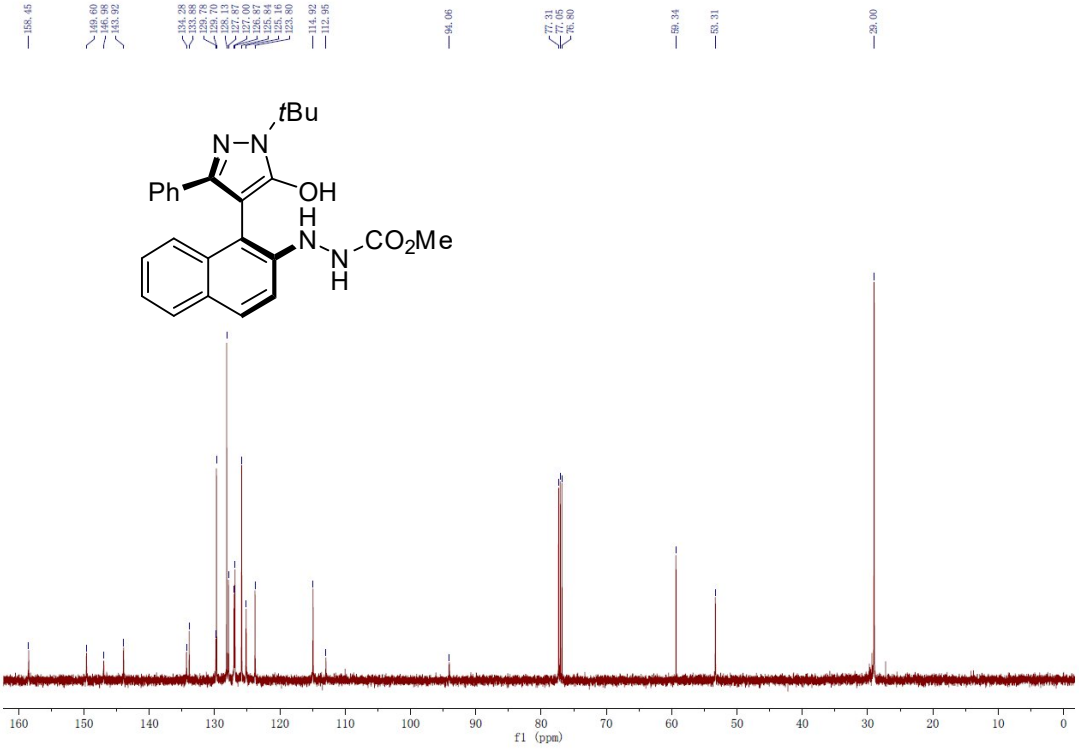


#	Time	Area	Height	Width	Symmetry	Area %
1	5.777	1131.3	68.7	0.2745	0.645	4.037
2	10.527	26888	976.4	0.459	0.733	95.963

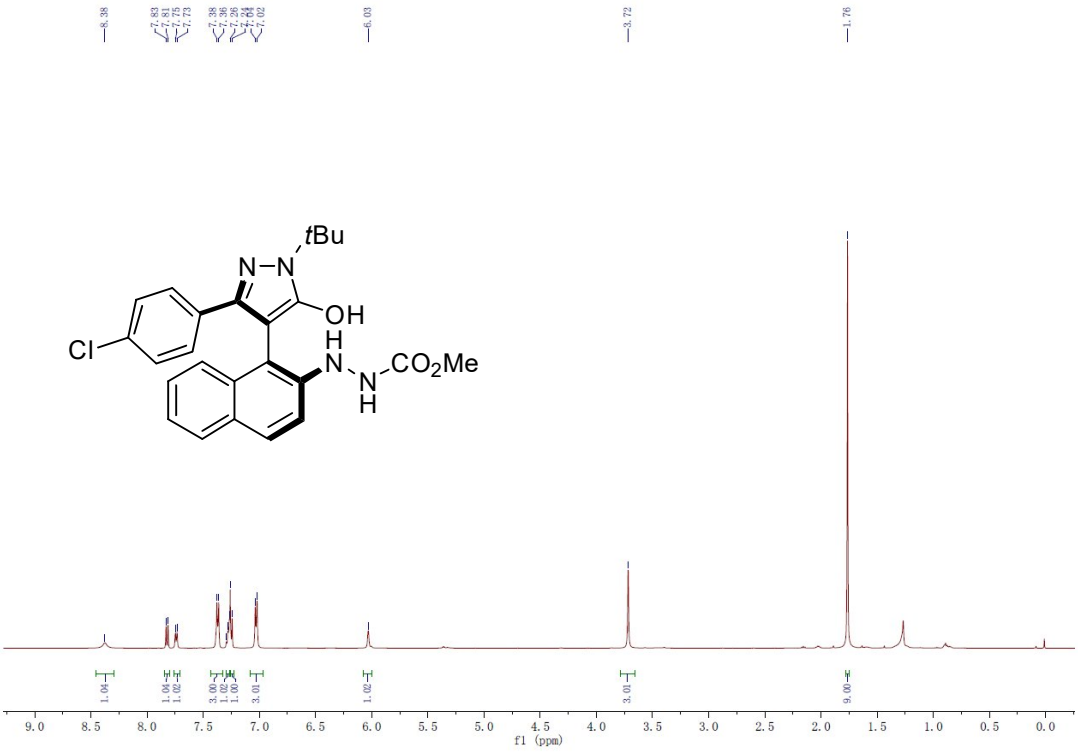
8. NMR Spectra

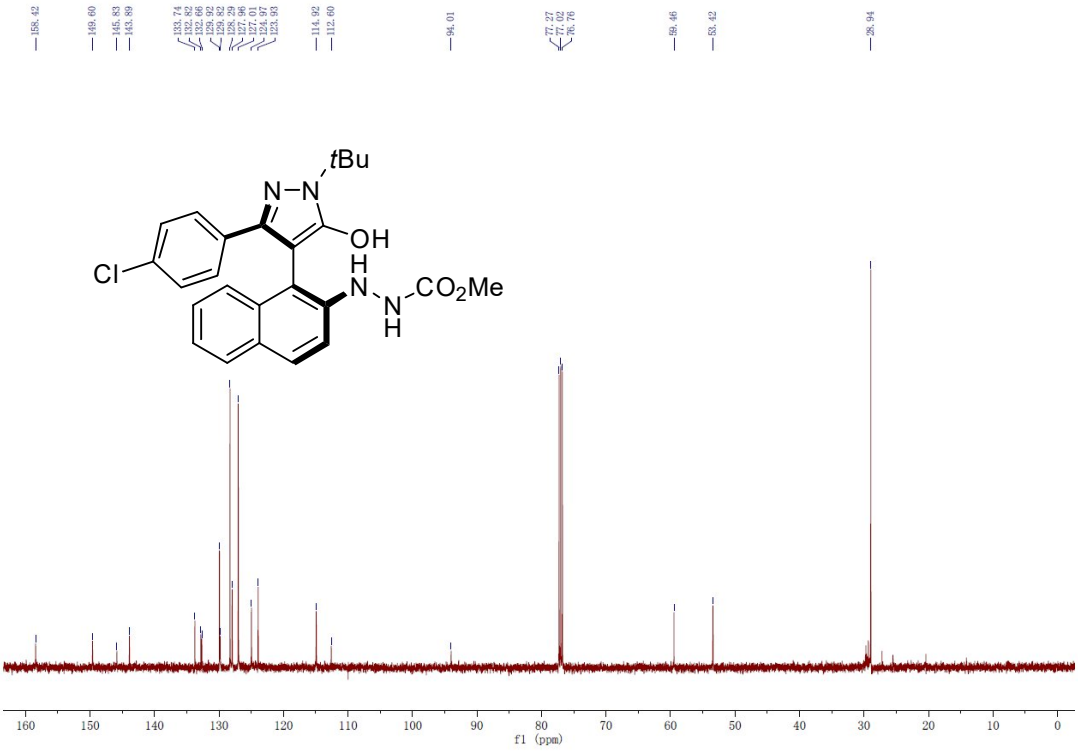
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3aa)



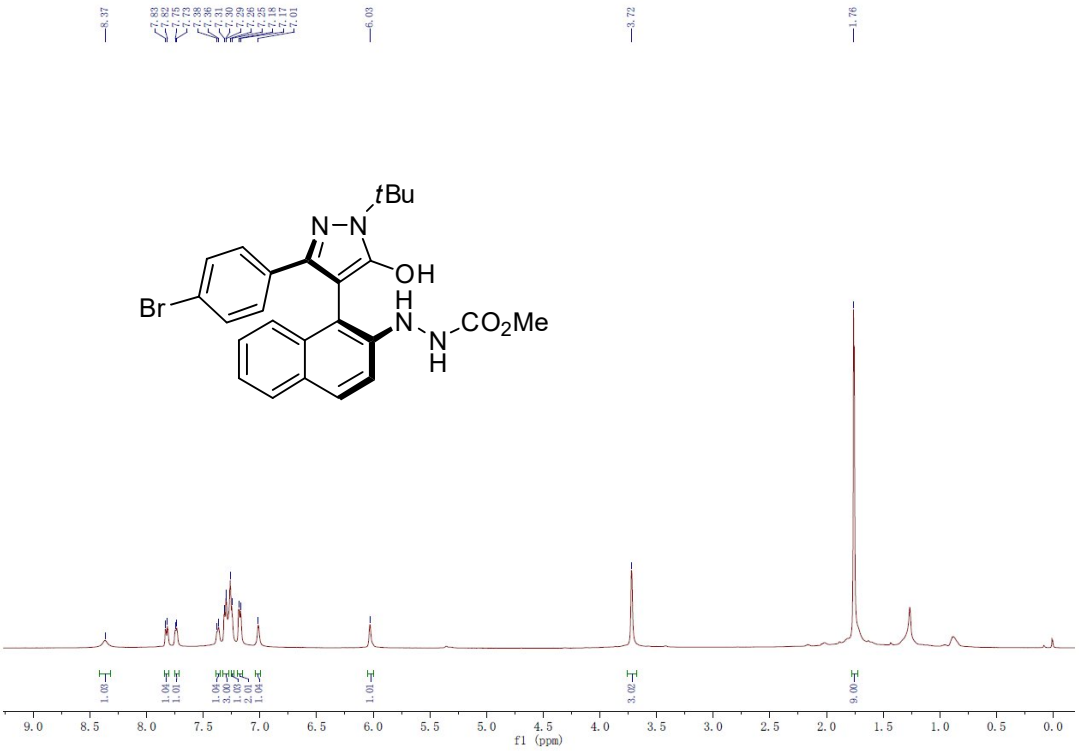


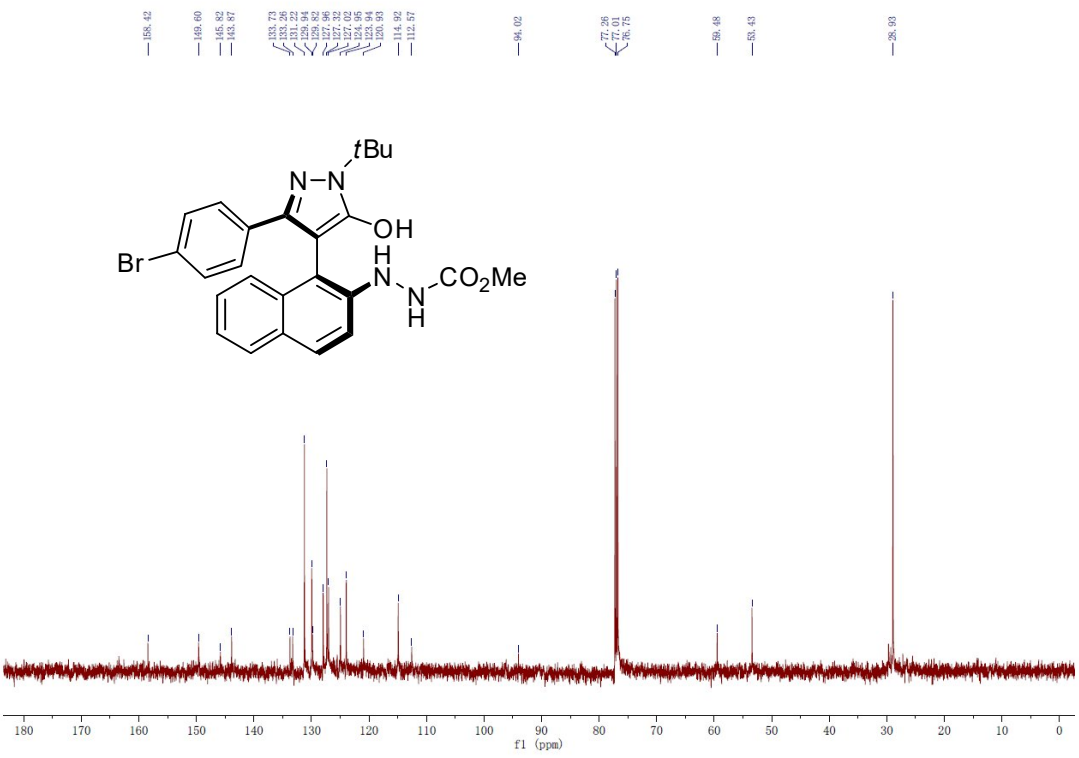
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(4-chlorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ab)



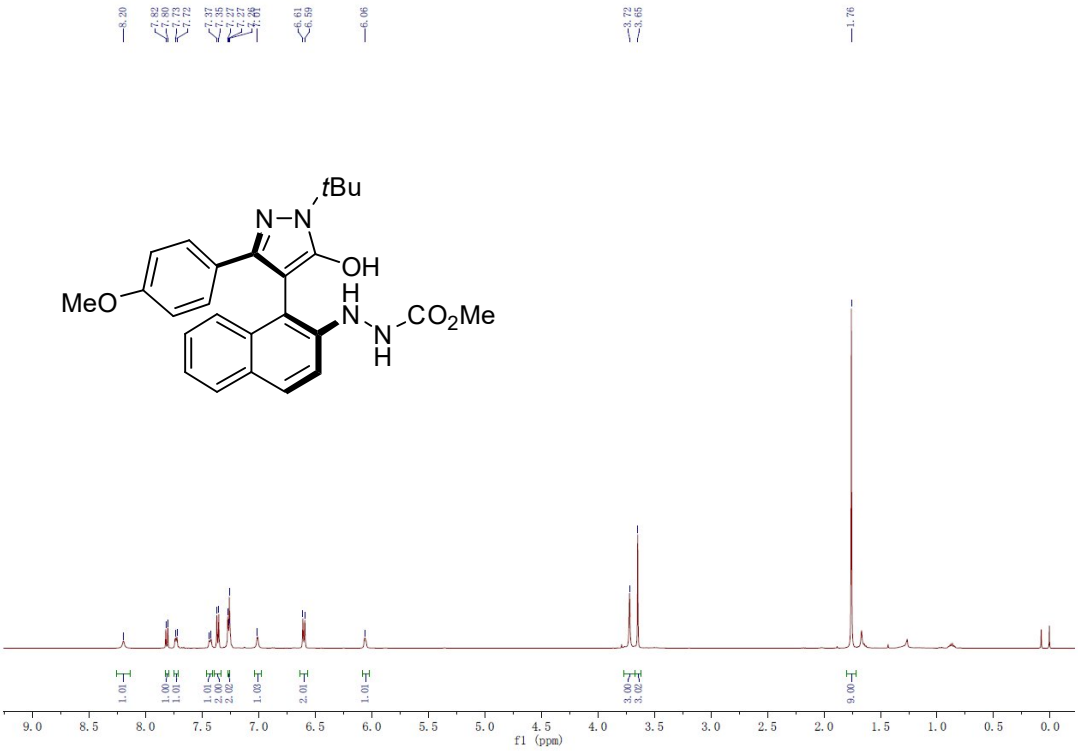


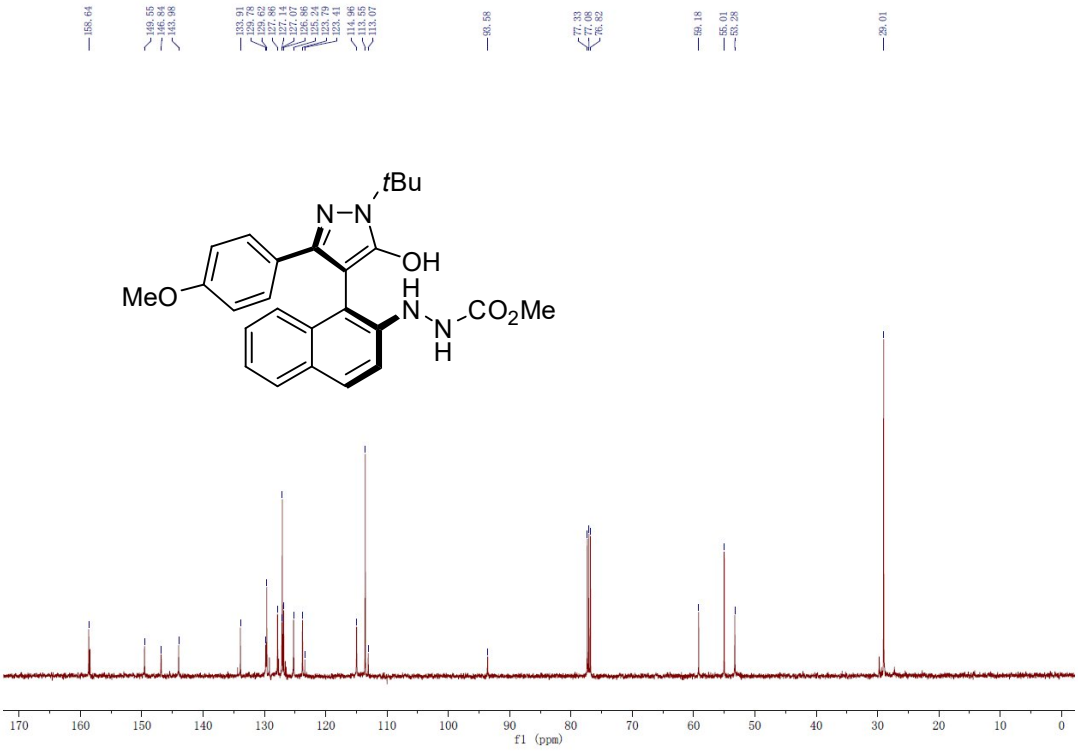
(*S*)-methyl 2-(1-(3-(4-bromophenyl)-1-(*tert*-butyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ac)



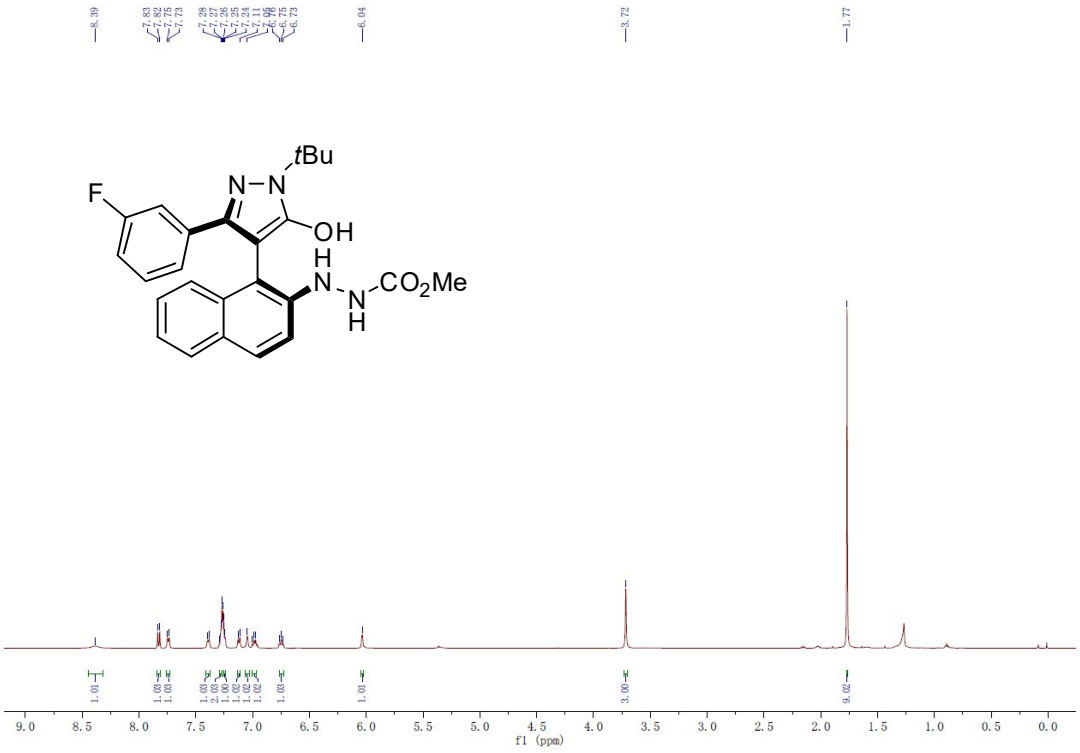


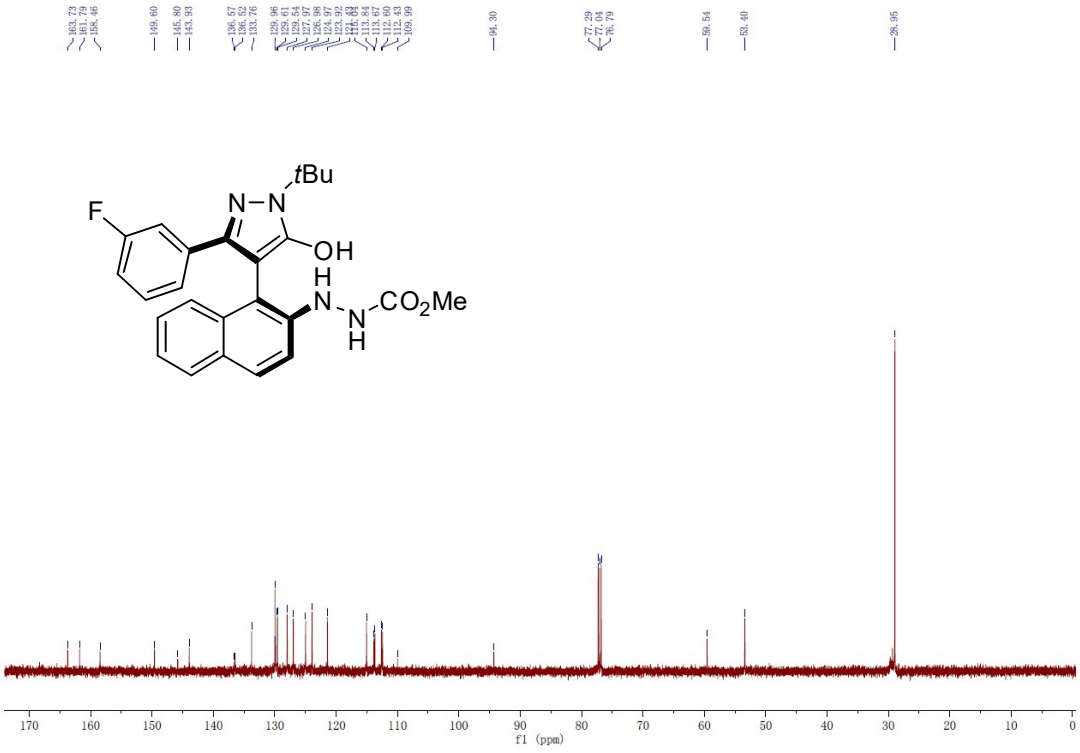
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-(4-methoxyphenyl)-1*H*-pyrazol-4-yl) naphthalen-2-yl)hydrazinecarboxylate (3ad)



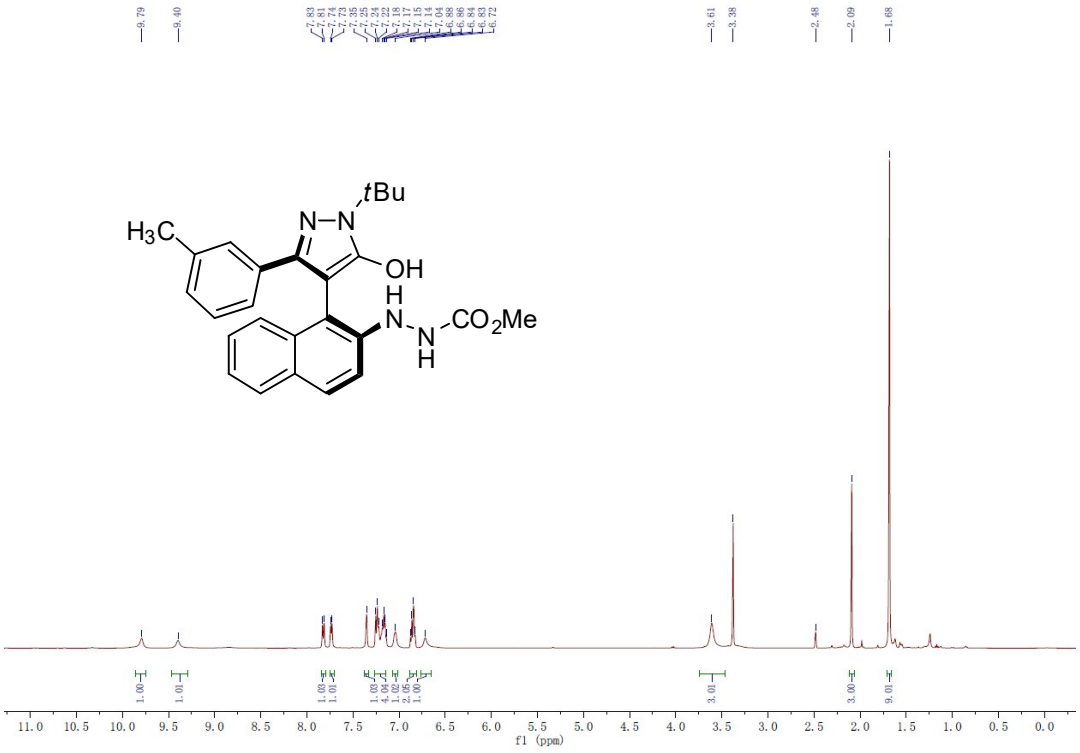


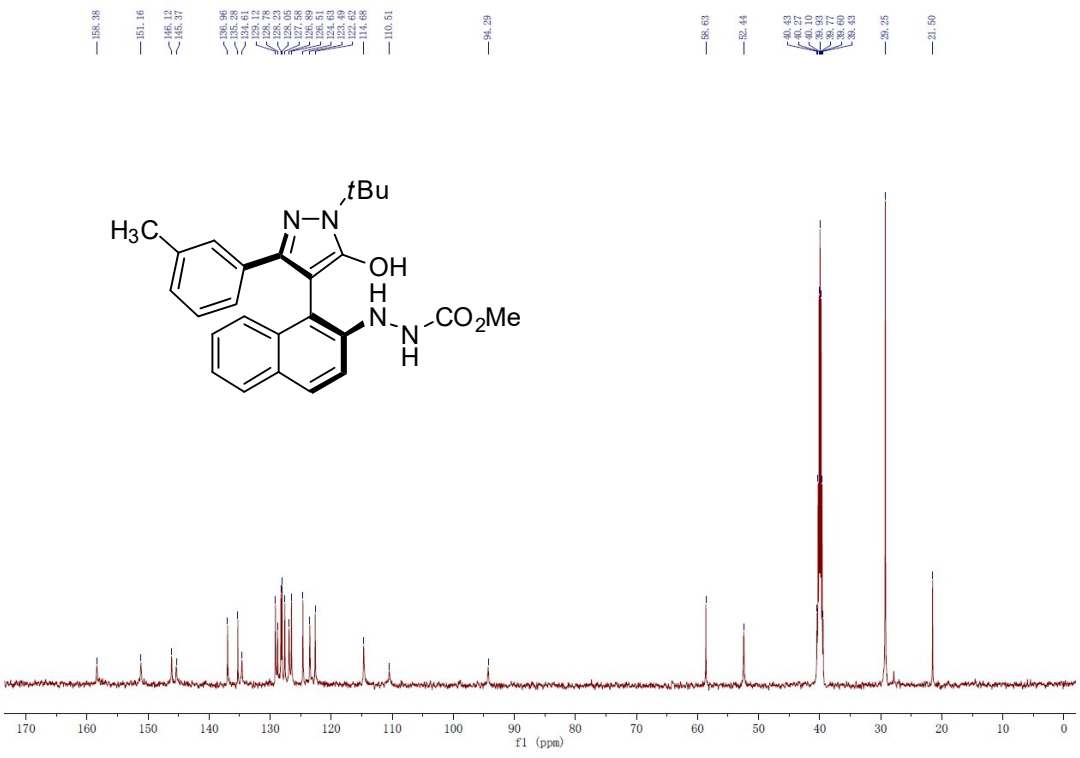
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(3-fluorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ae)



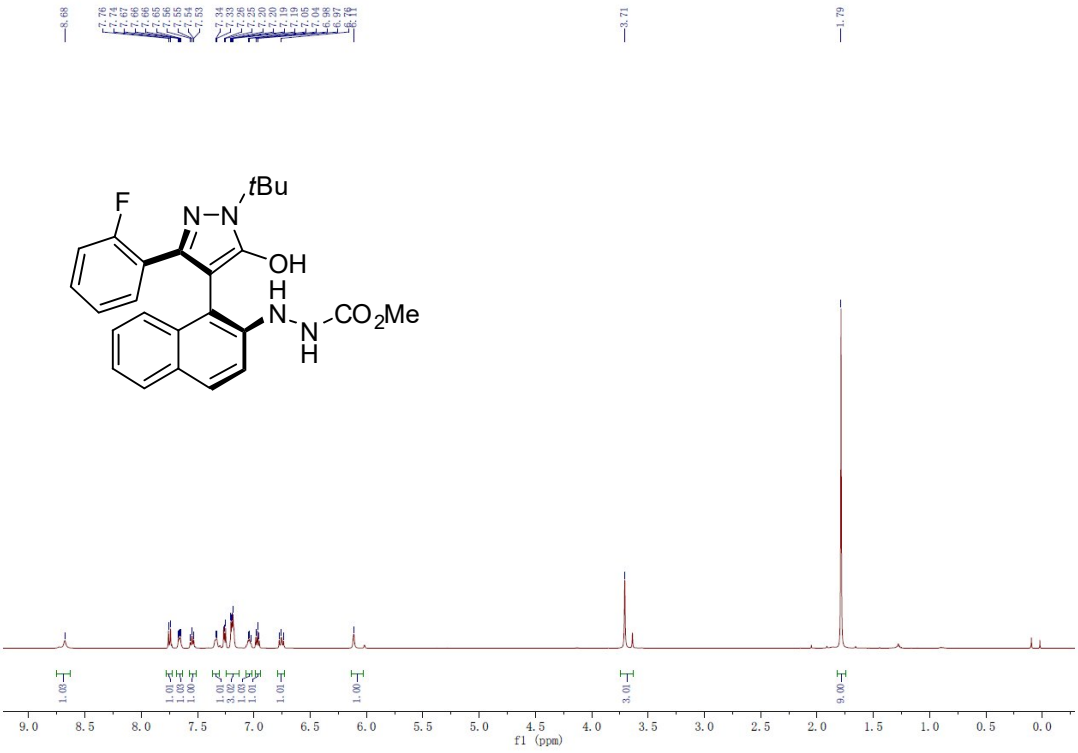


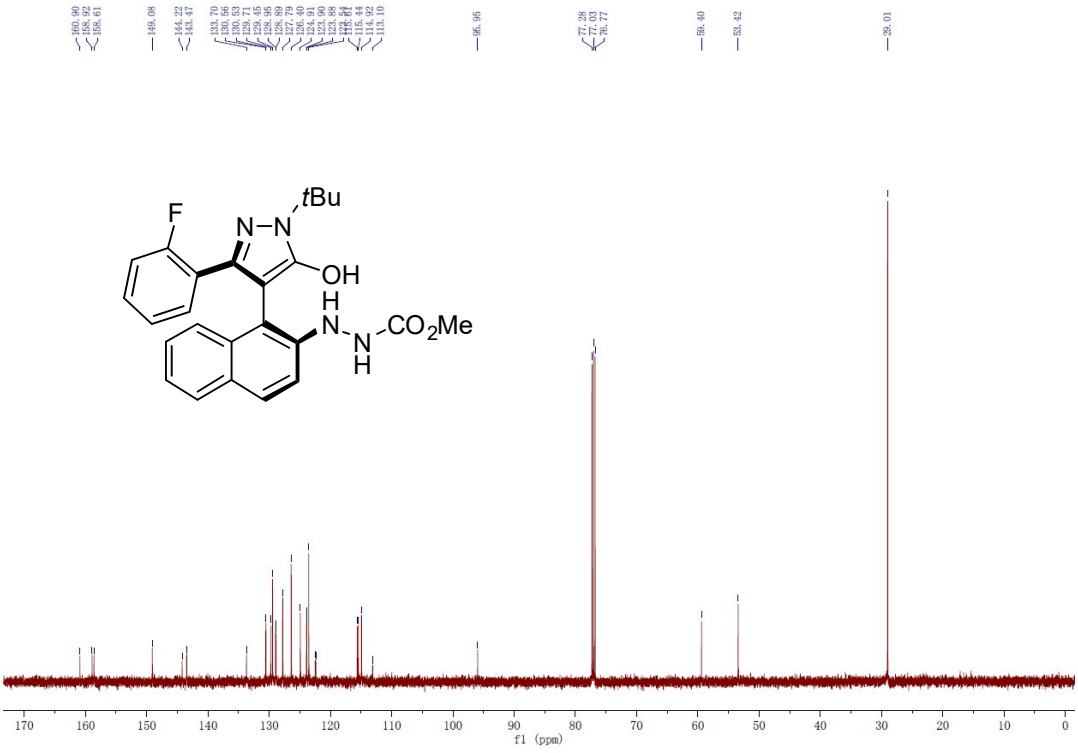
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-(*m*-tolyl)-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3af)



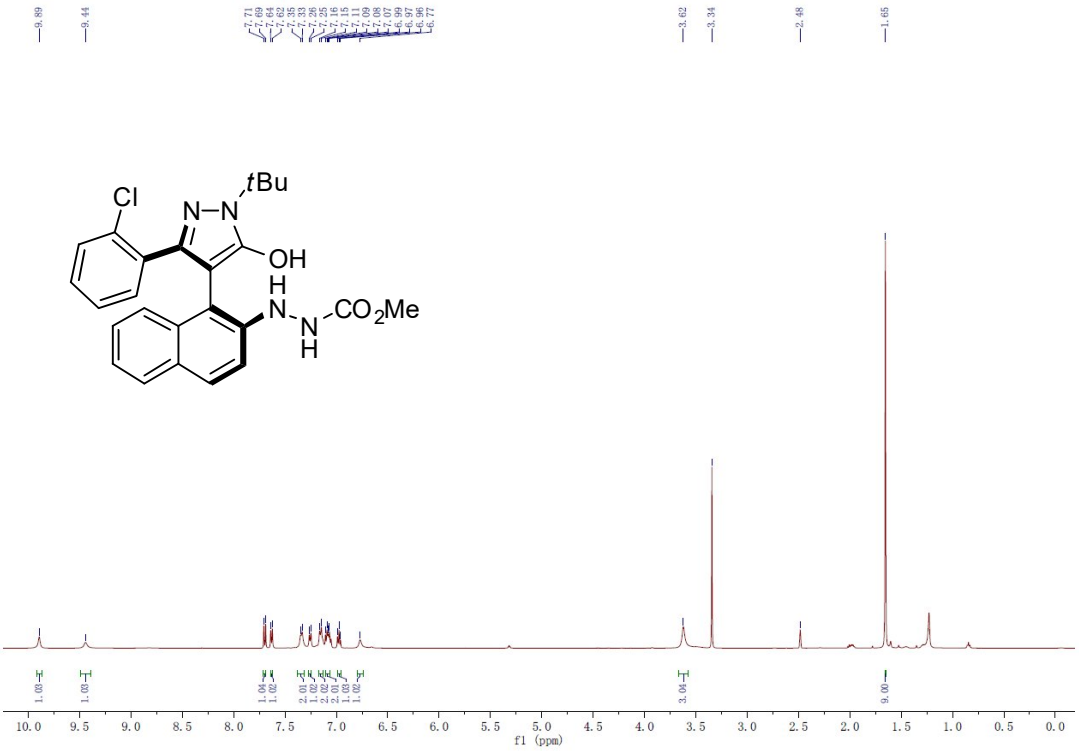


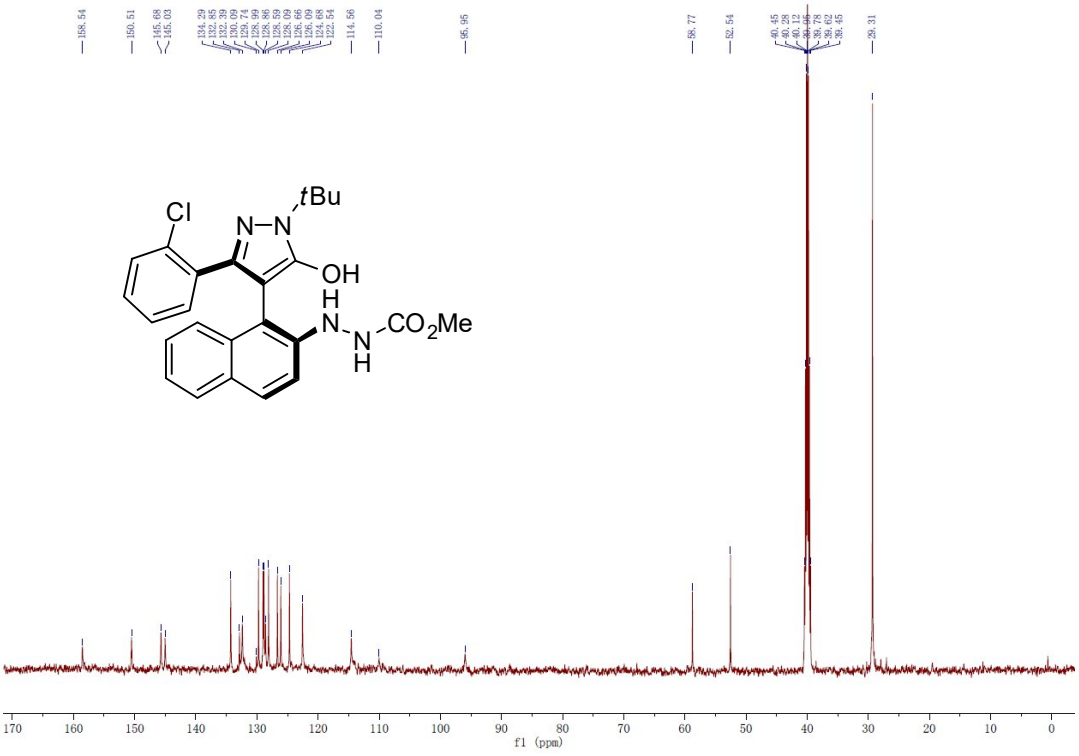
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(2-fluorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ag)



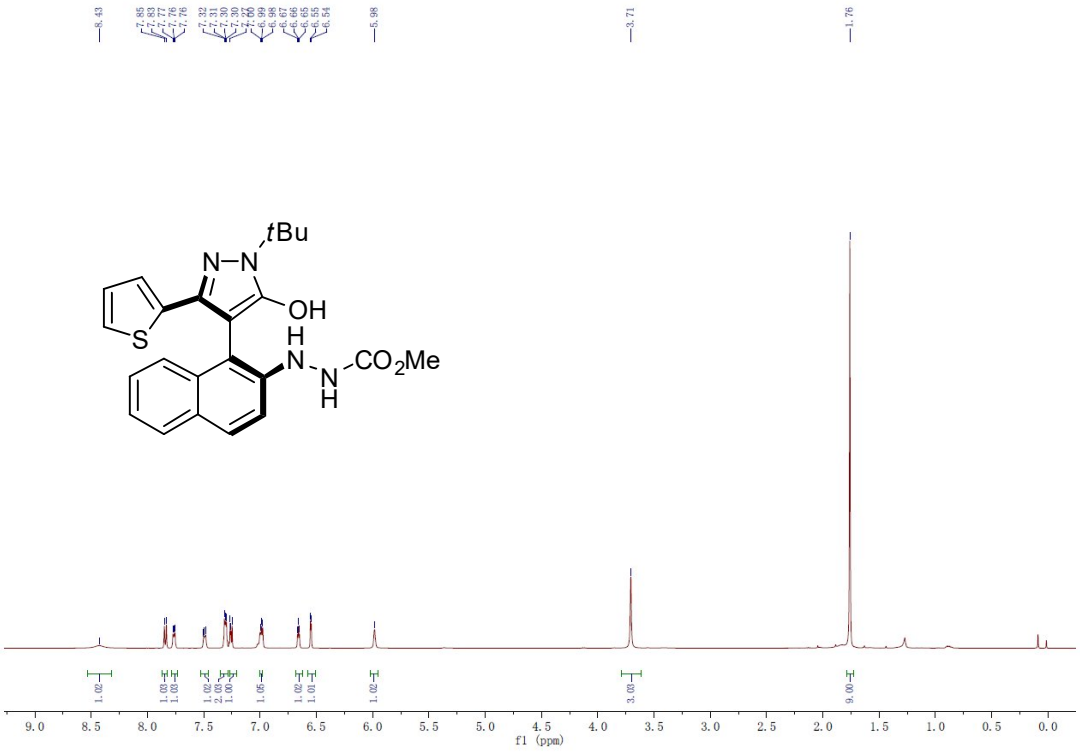


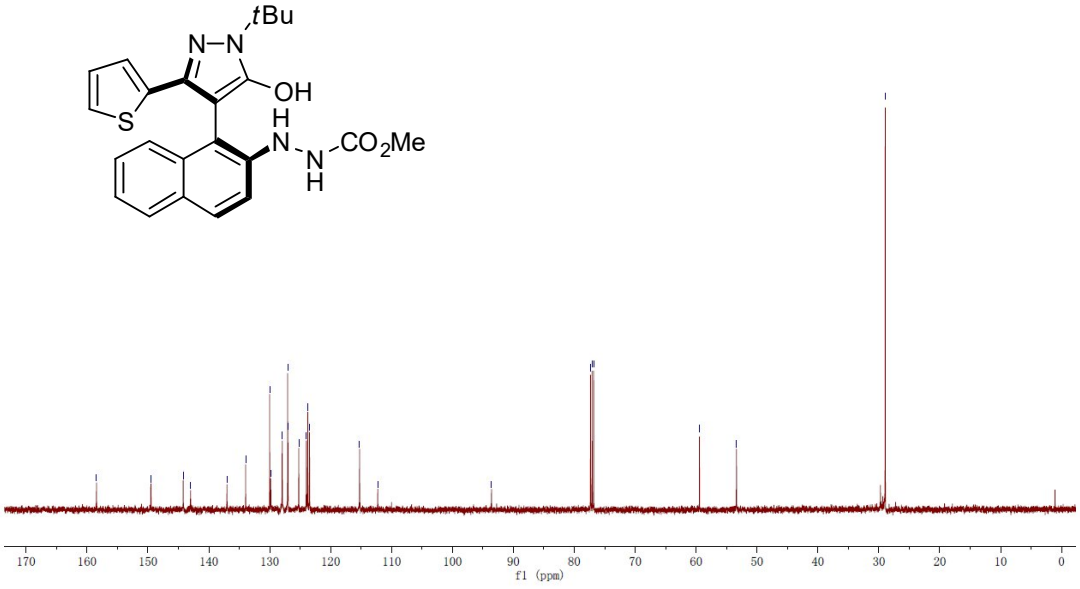
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(2-chlorophenyl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ah)



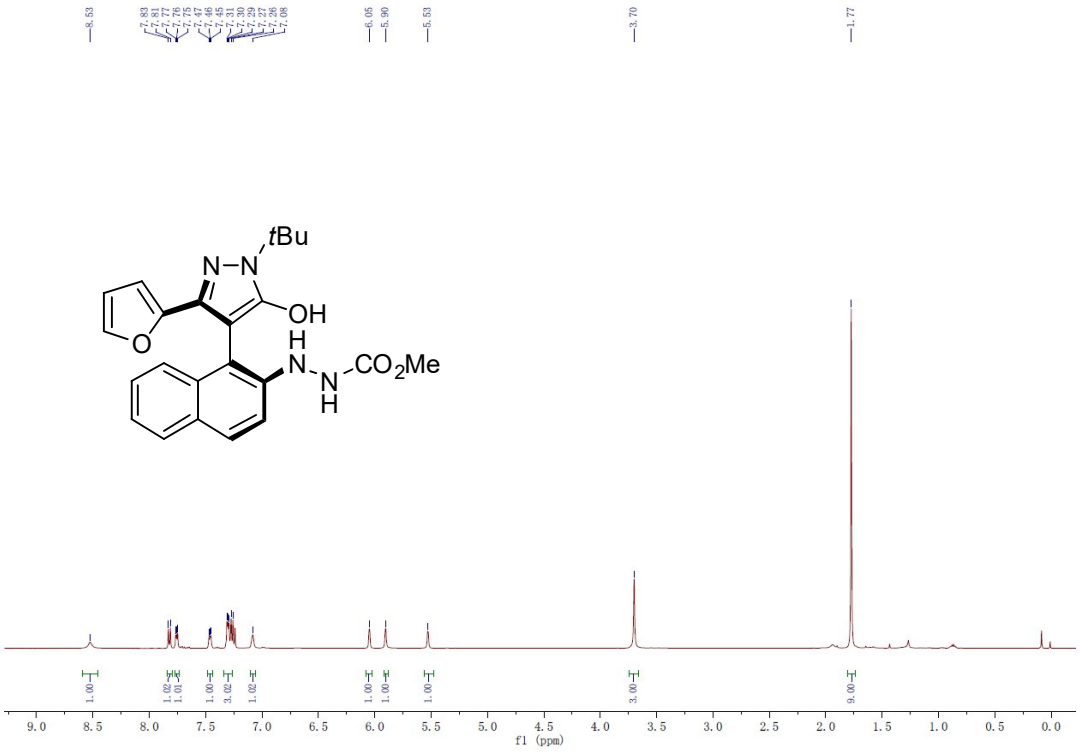


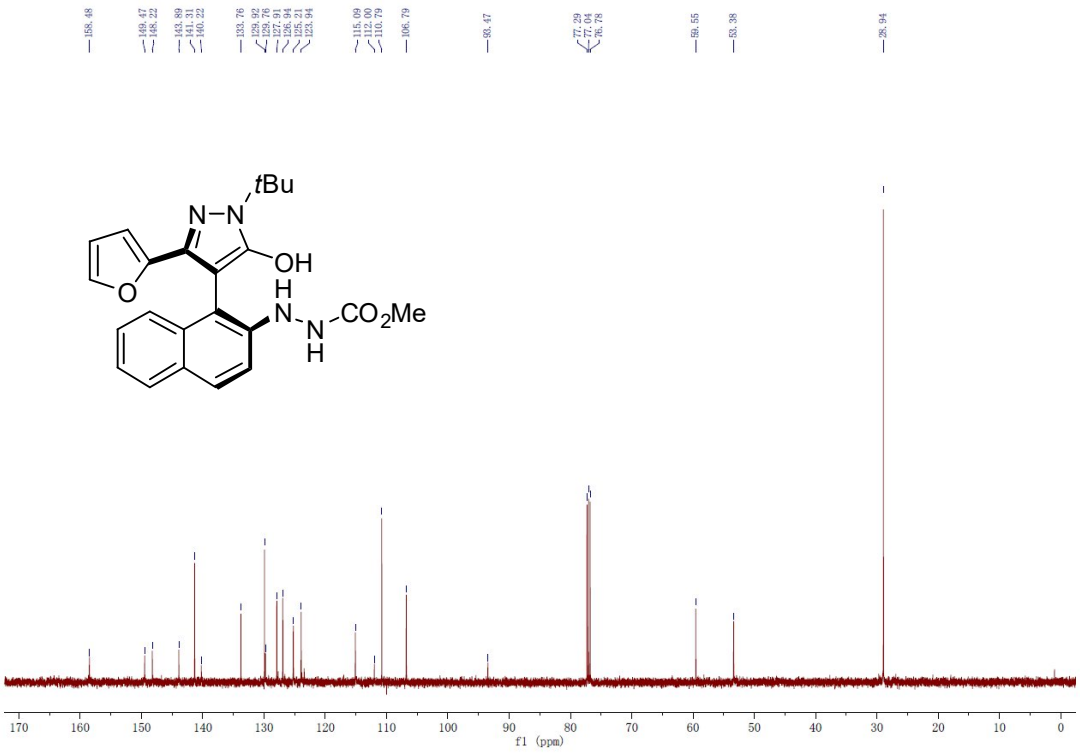
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-(thiophen-2-yl)-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ai)



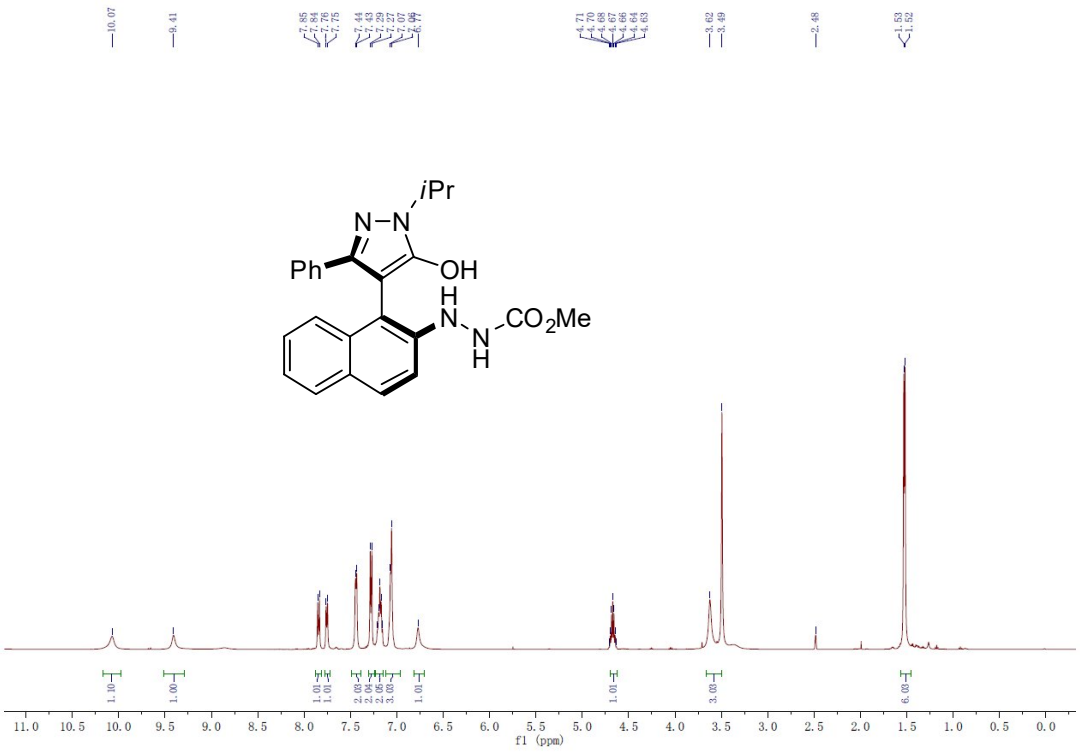


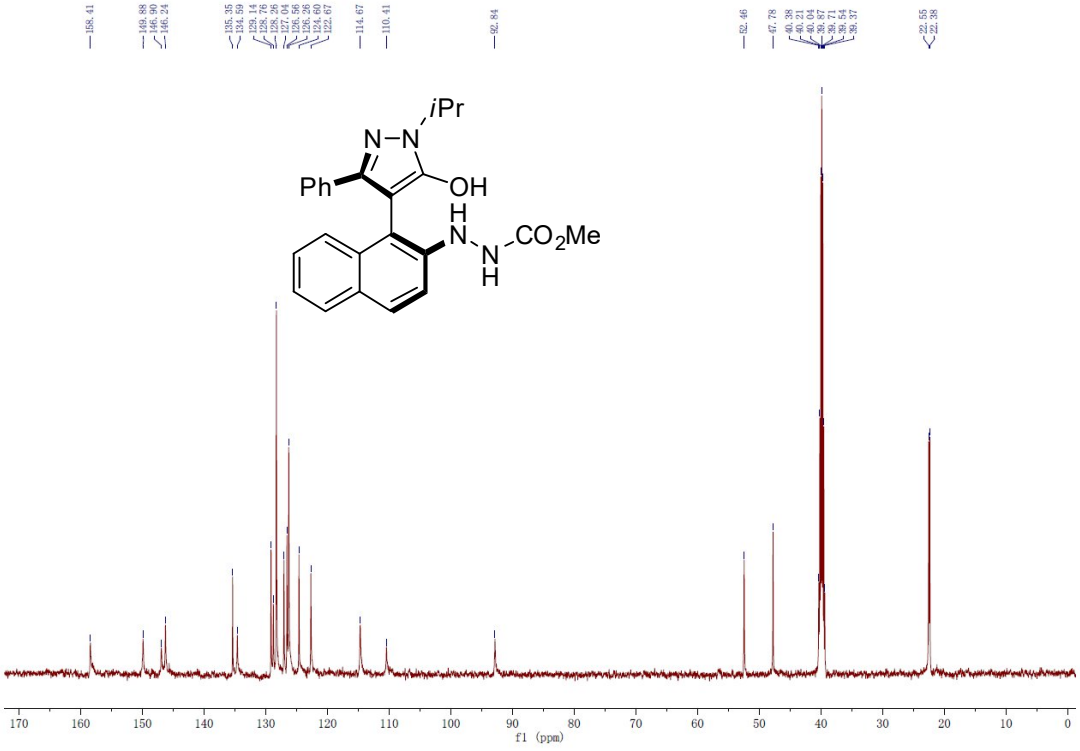
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-3-(furan-2-yl)-5-hydroxy-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3aj)



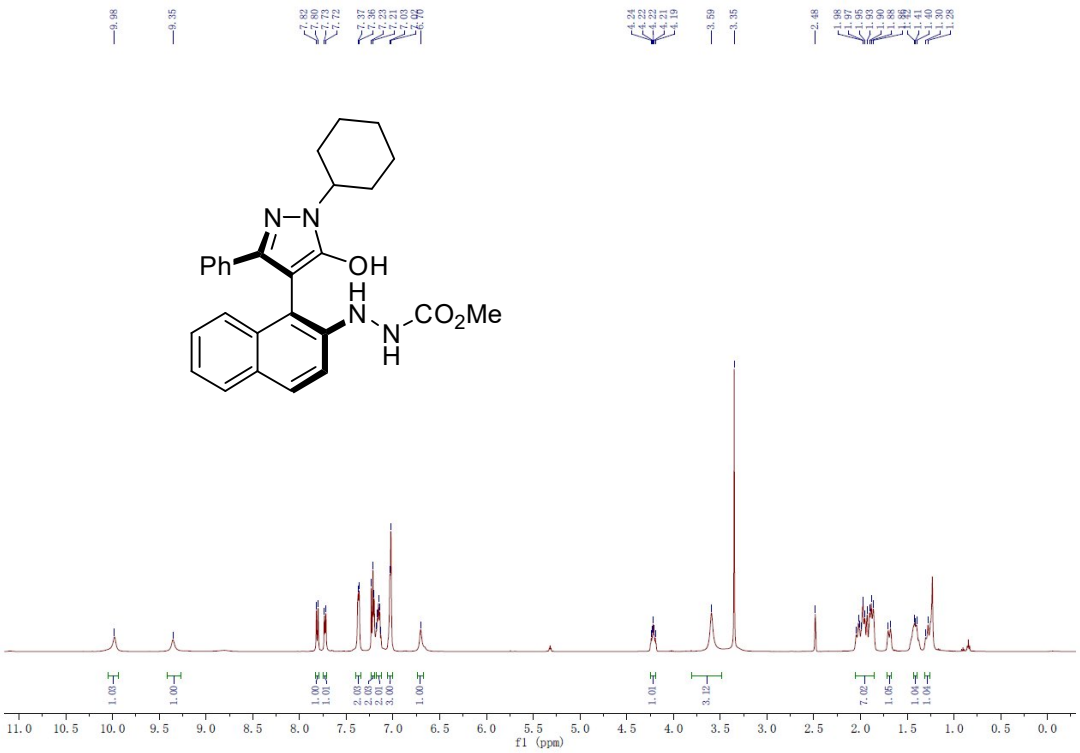


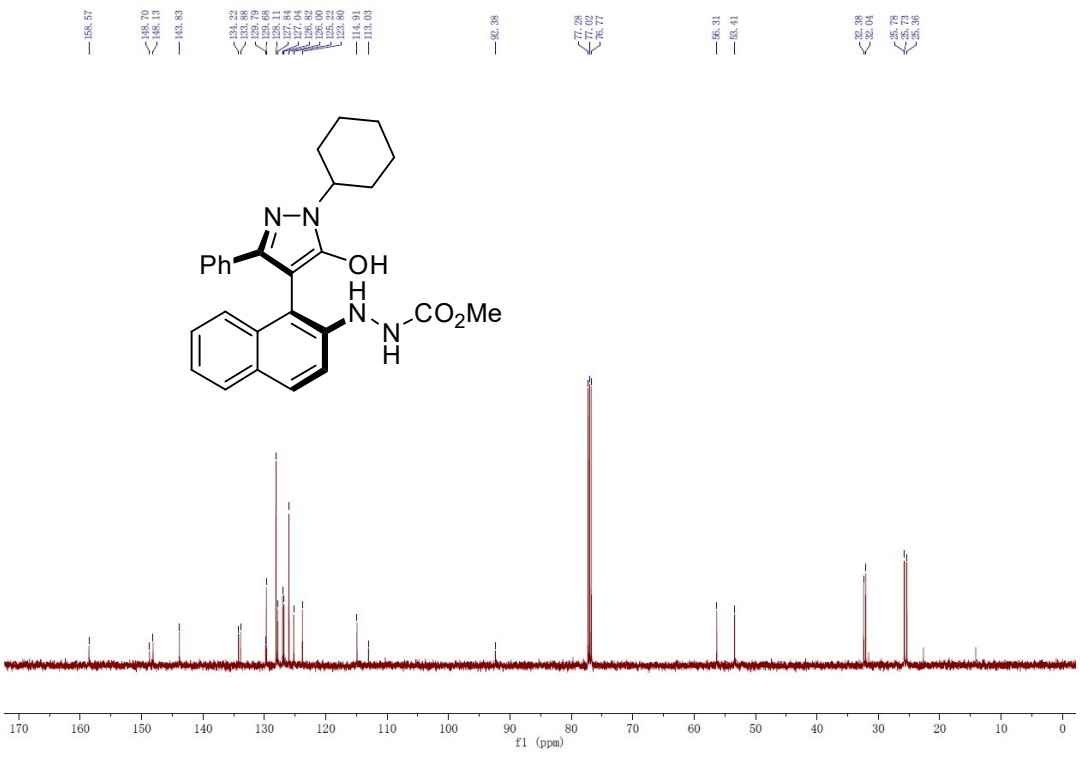
(*S*)-methyl 2-(1-(5-hydroxy-1-isopropyl-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ak)



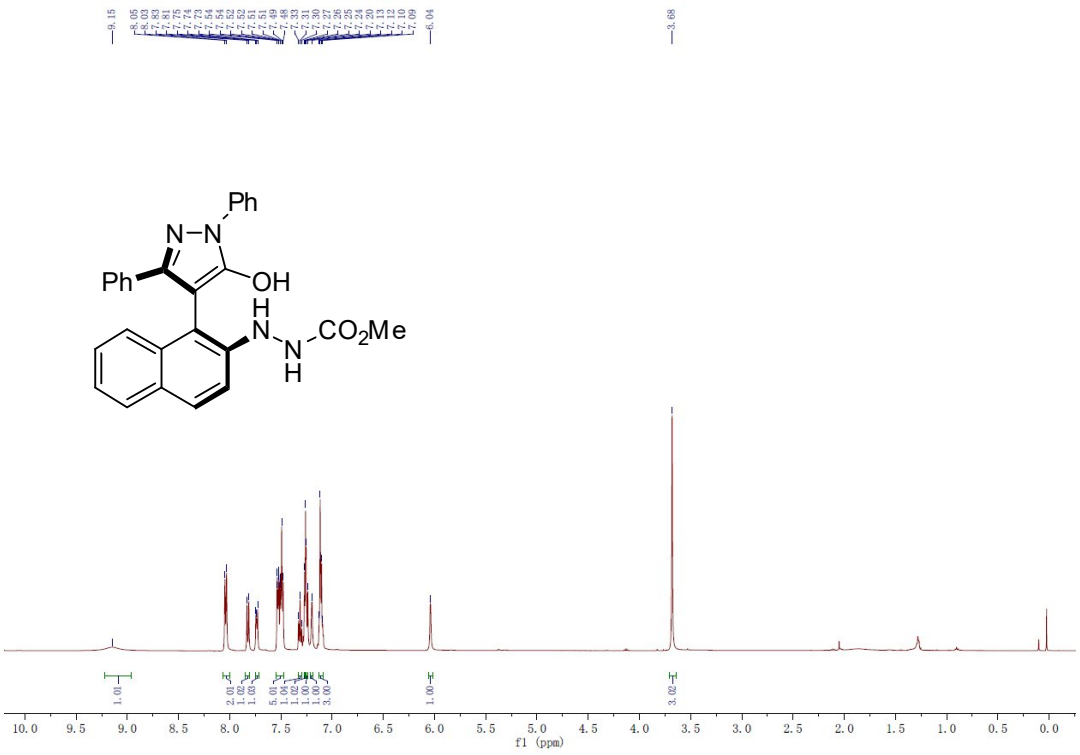


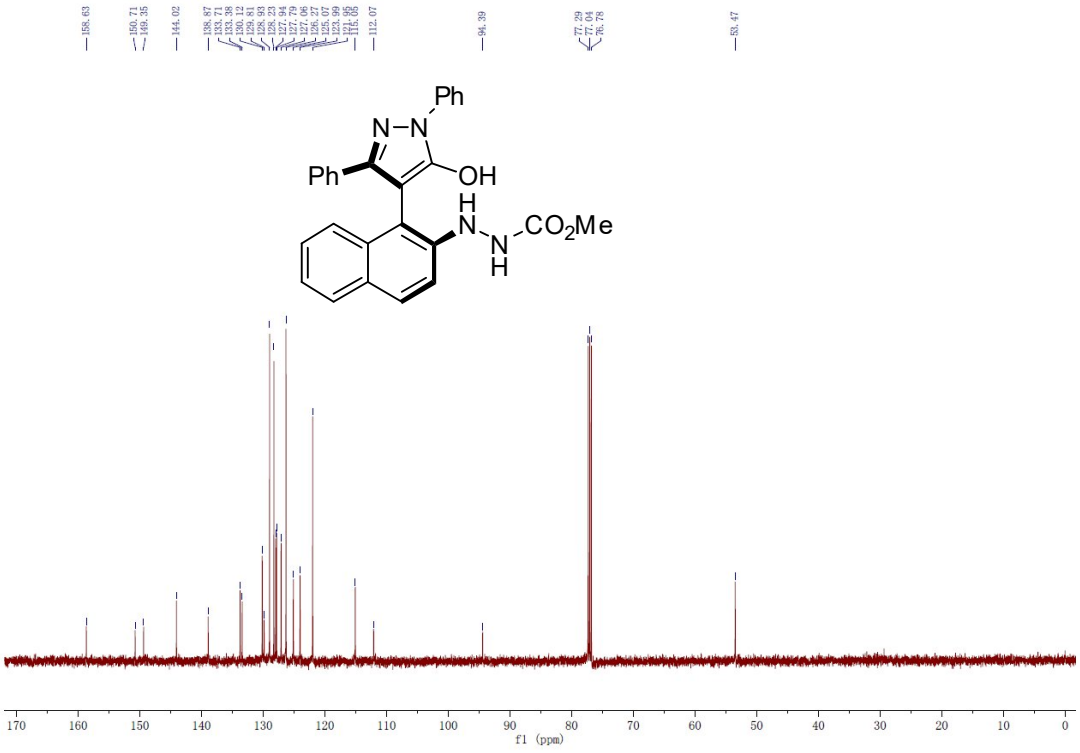
(*S*)-methyl 2-(1-(1-cyclohexyl-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3al)



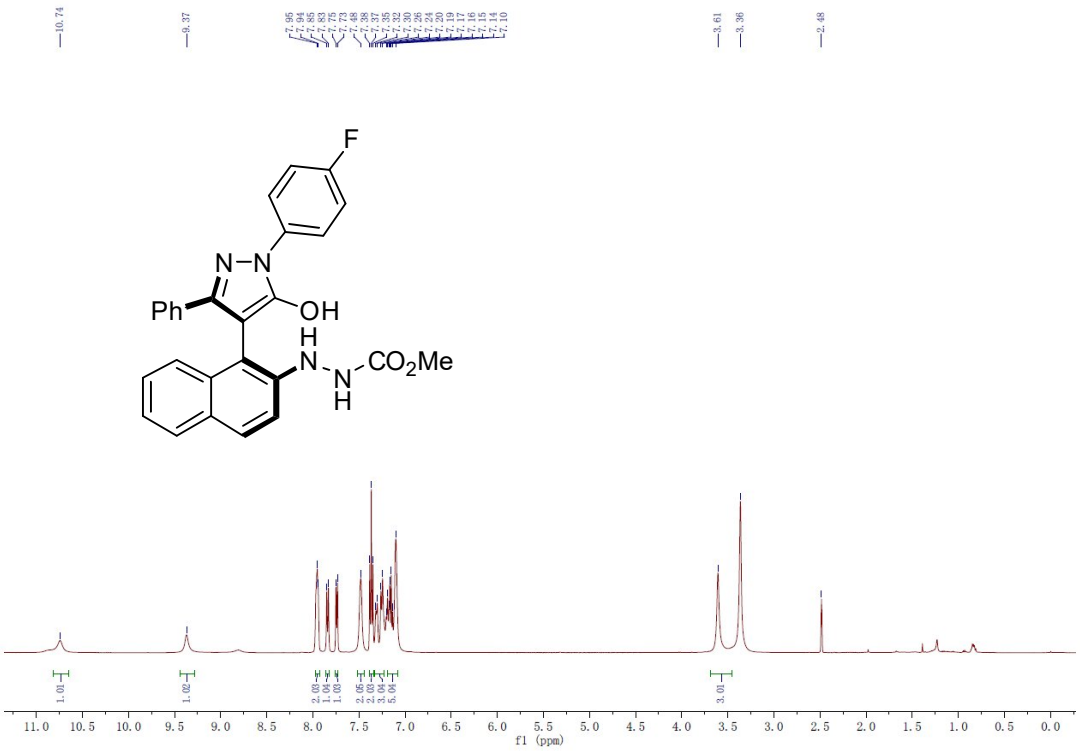


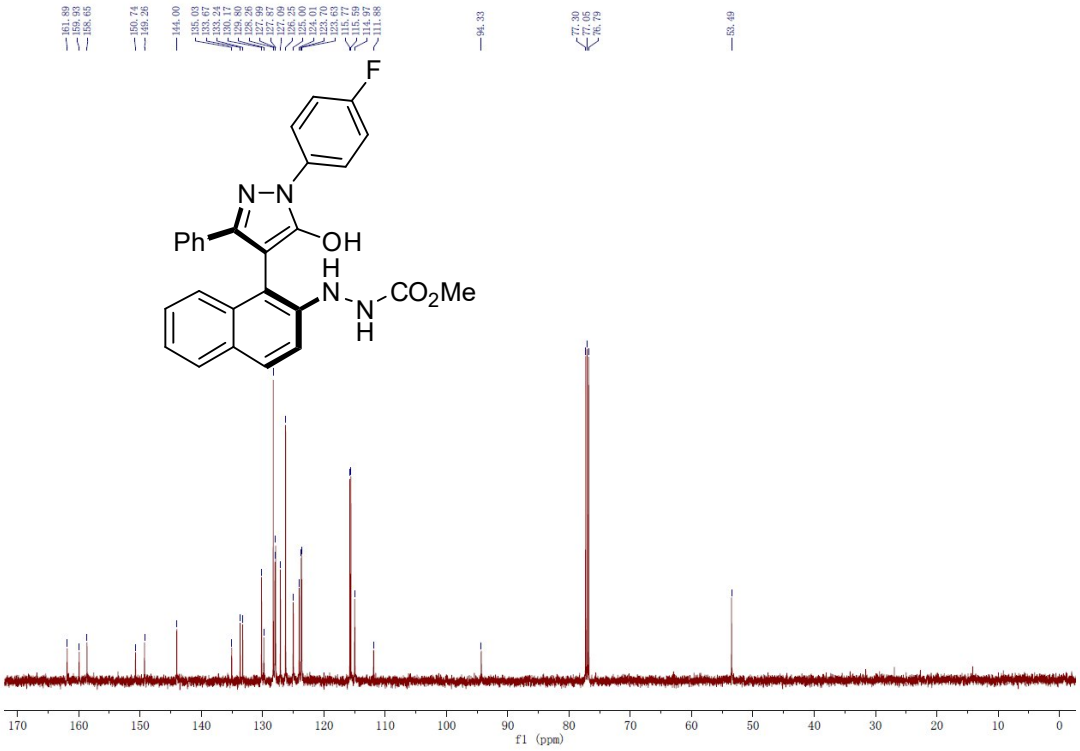
(*S*)-methyl 2-(1-(5-hydroxy-1,3-diphenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3am)



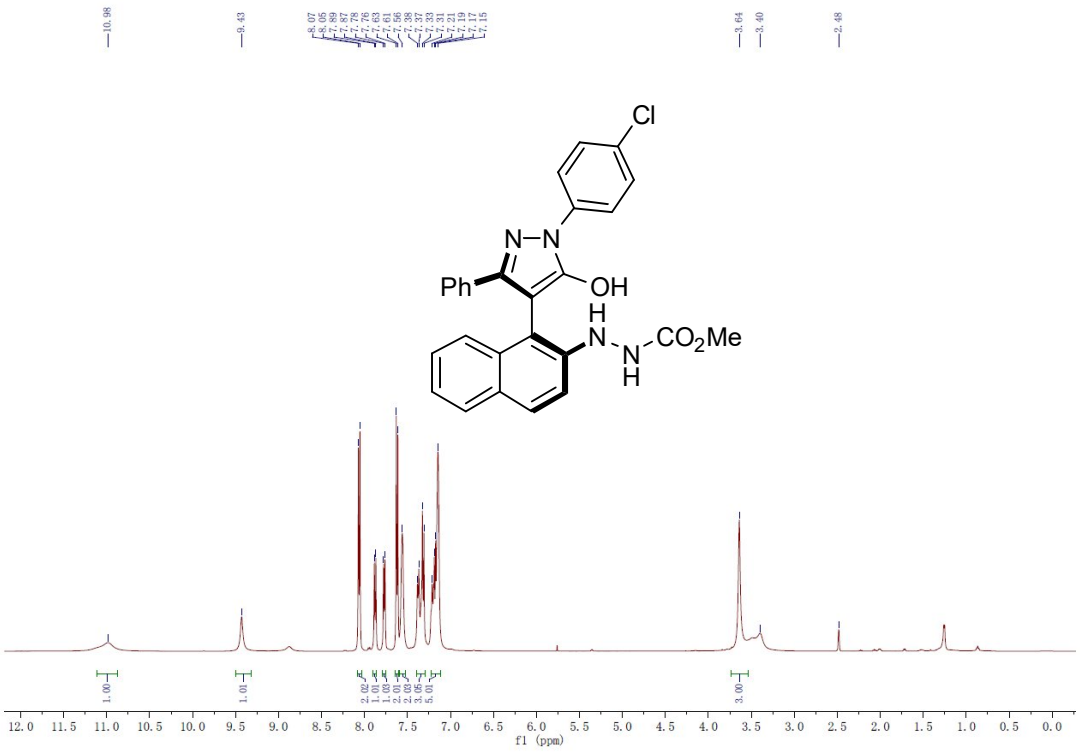


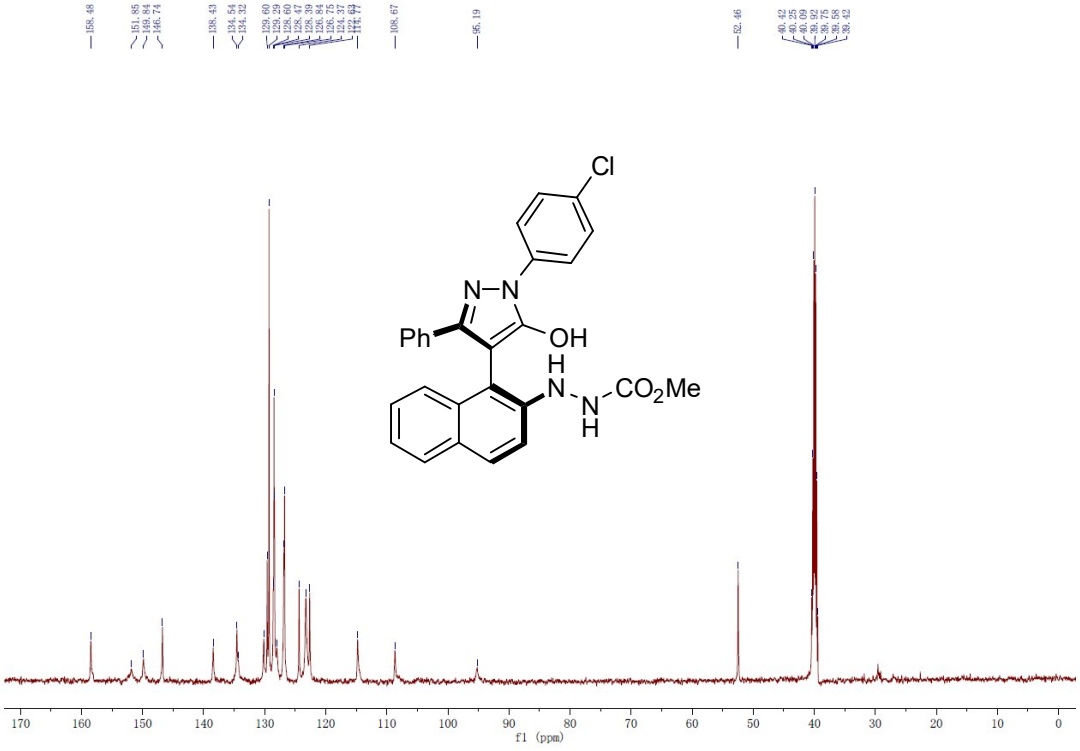
(*S*)-methyl 2-(1-(1-(4-fluorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3an)



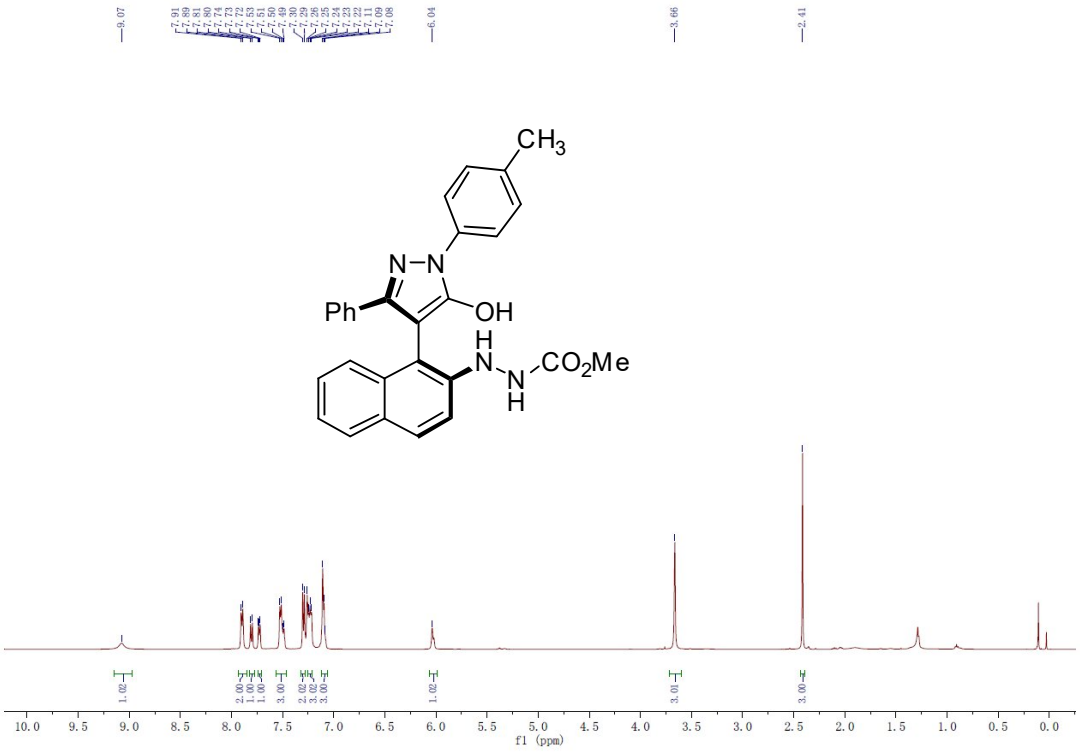


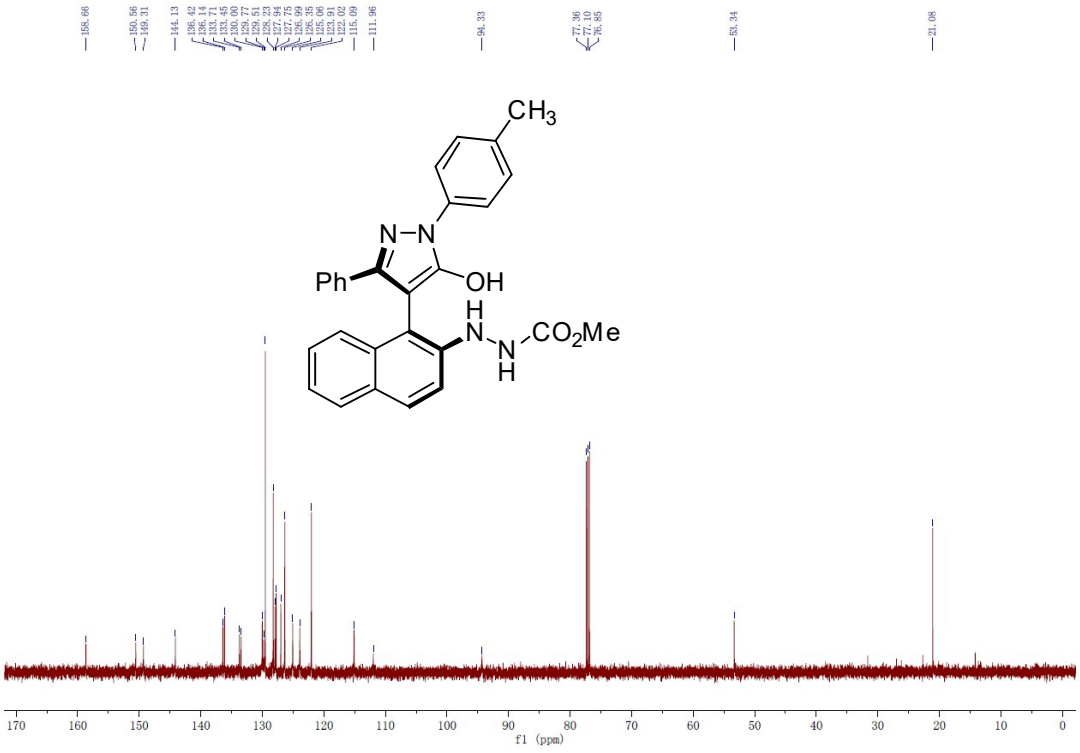
(*S*)-methyl 2-(1-(1-(4-chlorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ao)



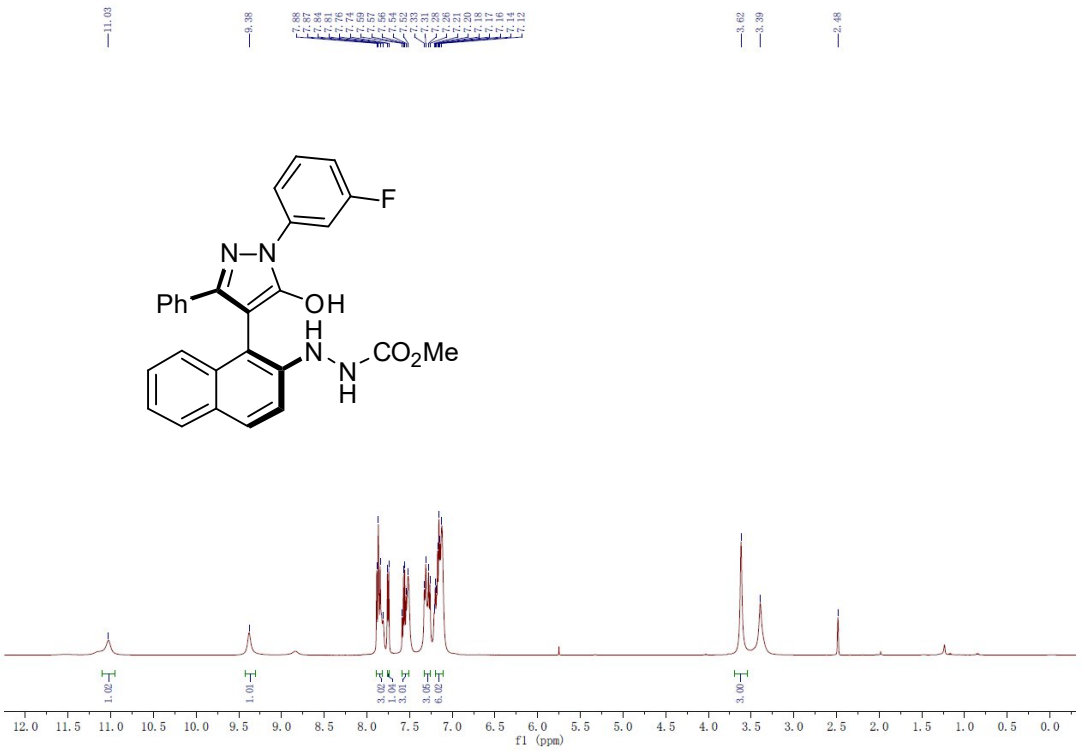


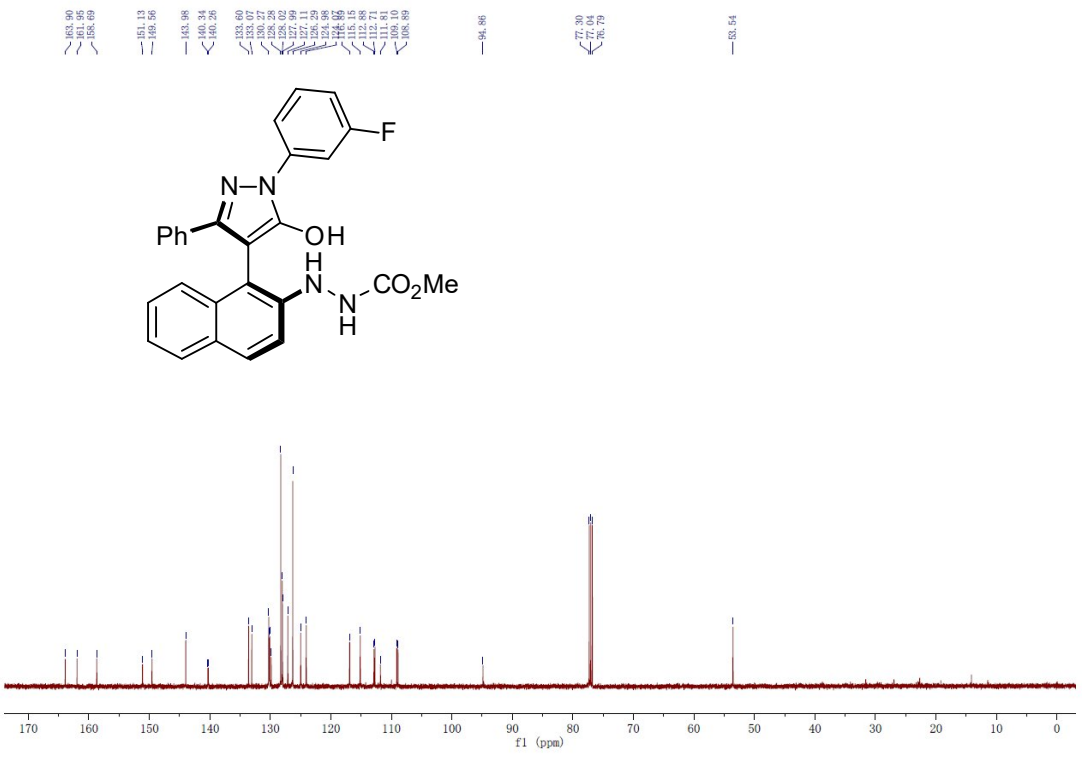
(*S*)-methyl 2-(1-(5-hydroxy-3-phenyl-1-(*p*-tolyl)-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ap)



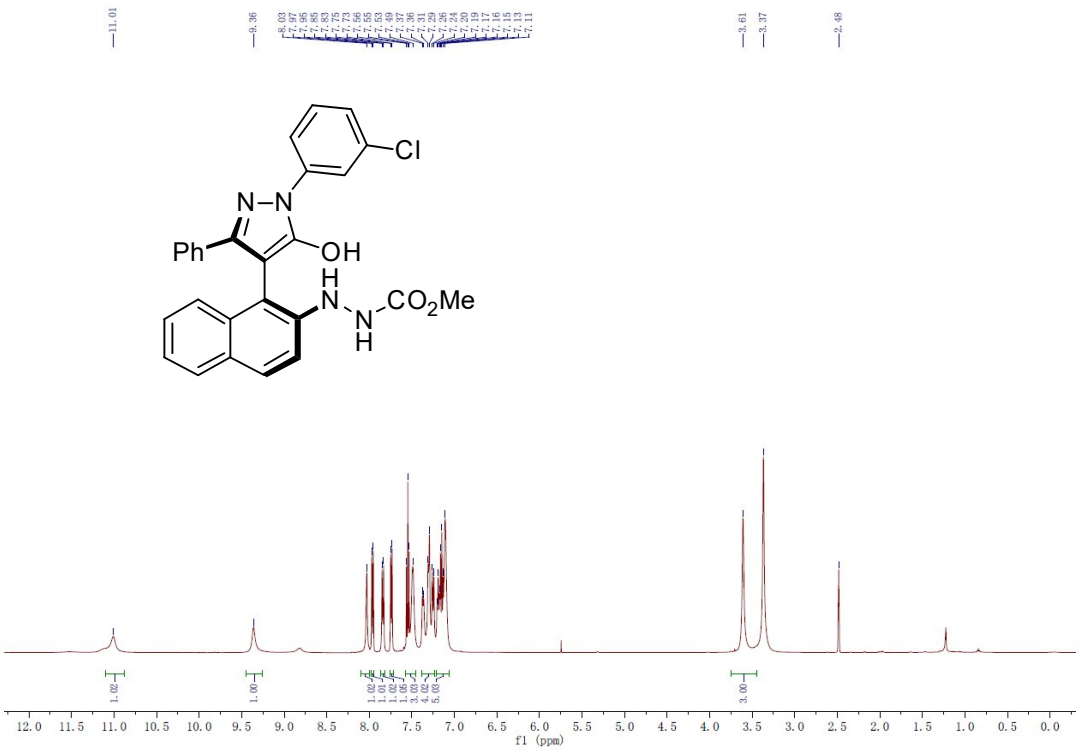


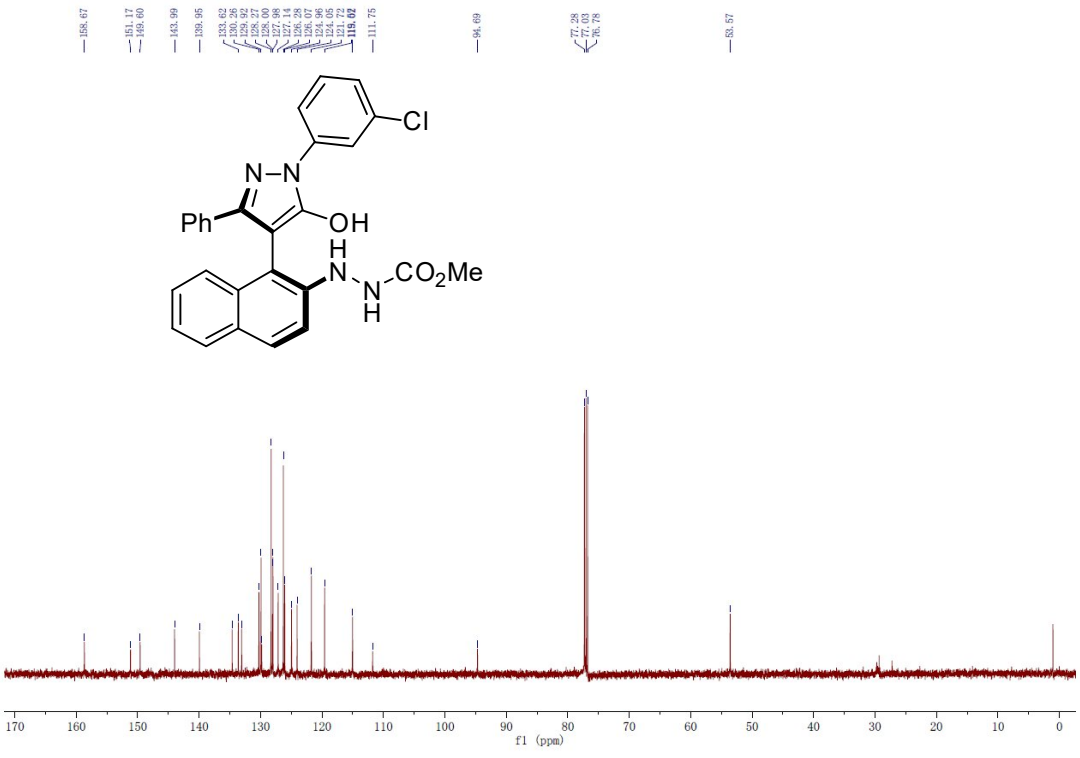
(*S*)-methyl 2-(1-(1-(3-fluorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3aq)



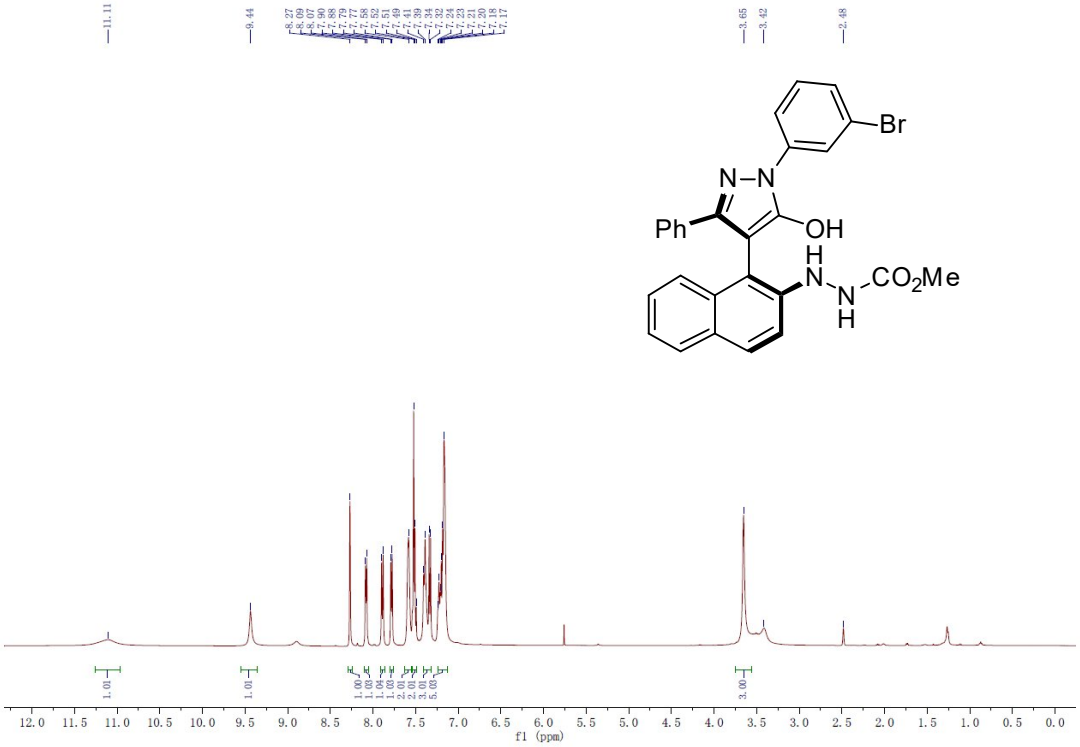


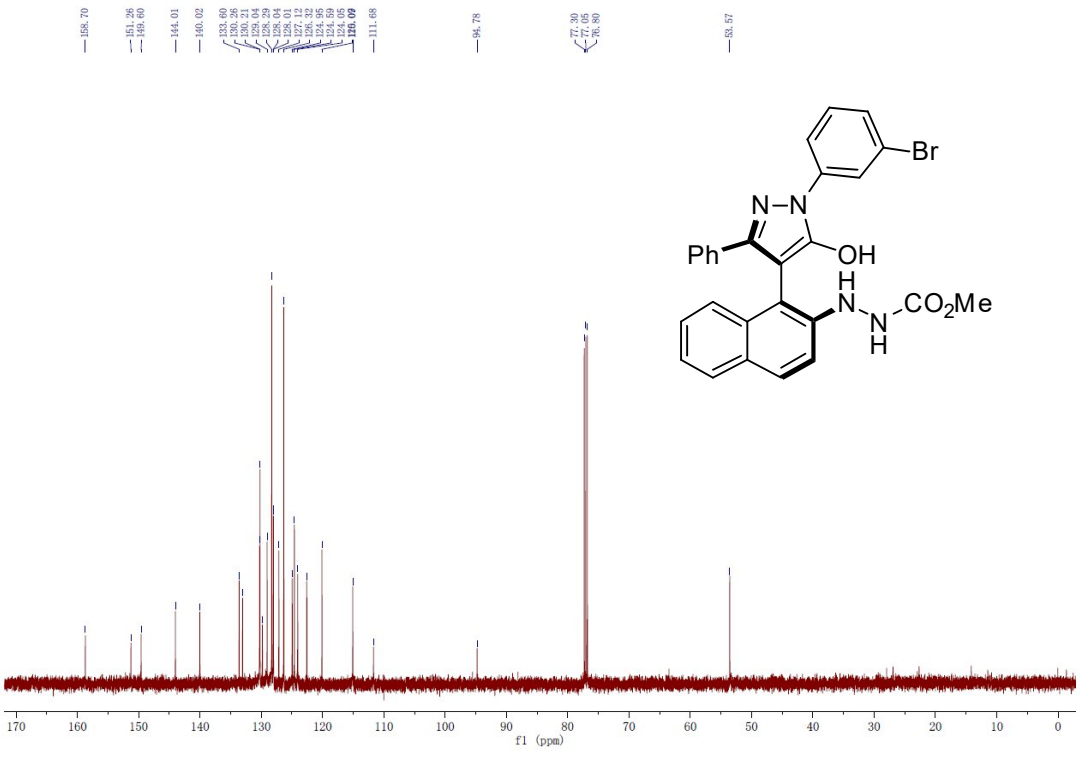
(*S*)-methyl 2-(1-(1-(3-chlorophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ar)



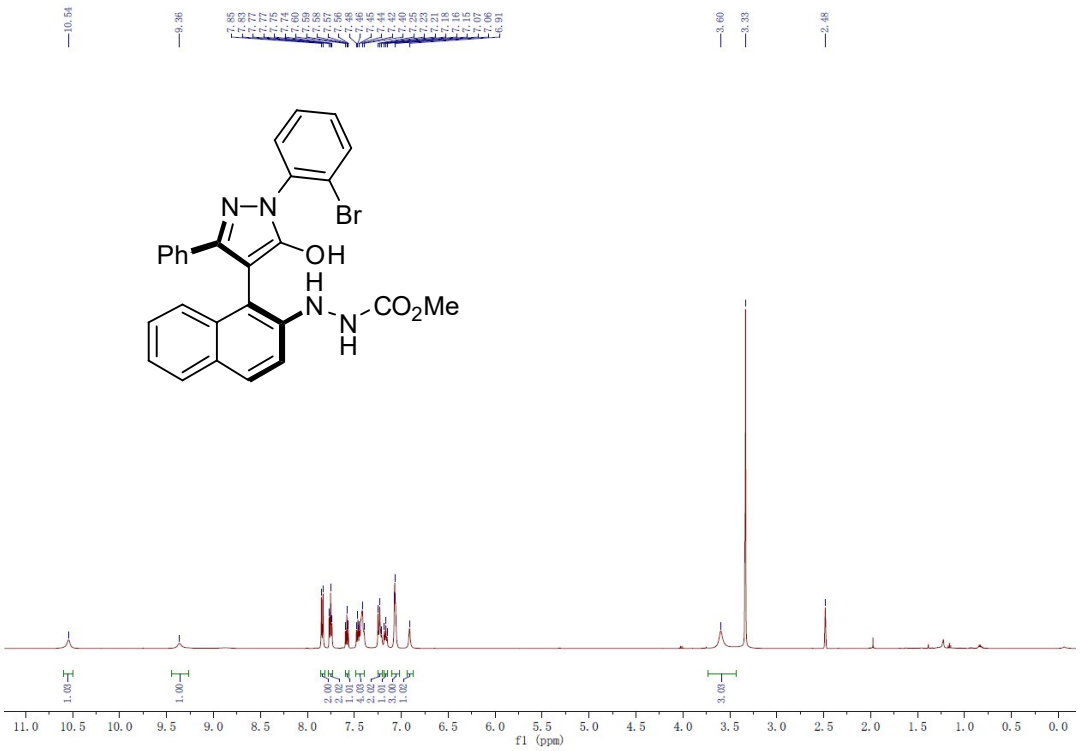


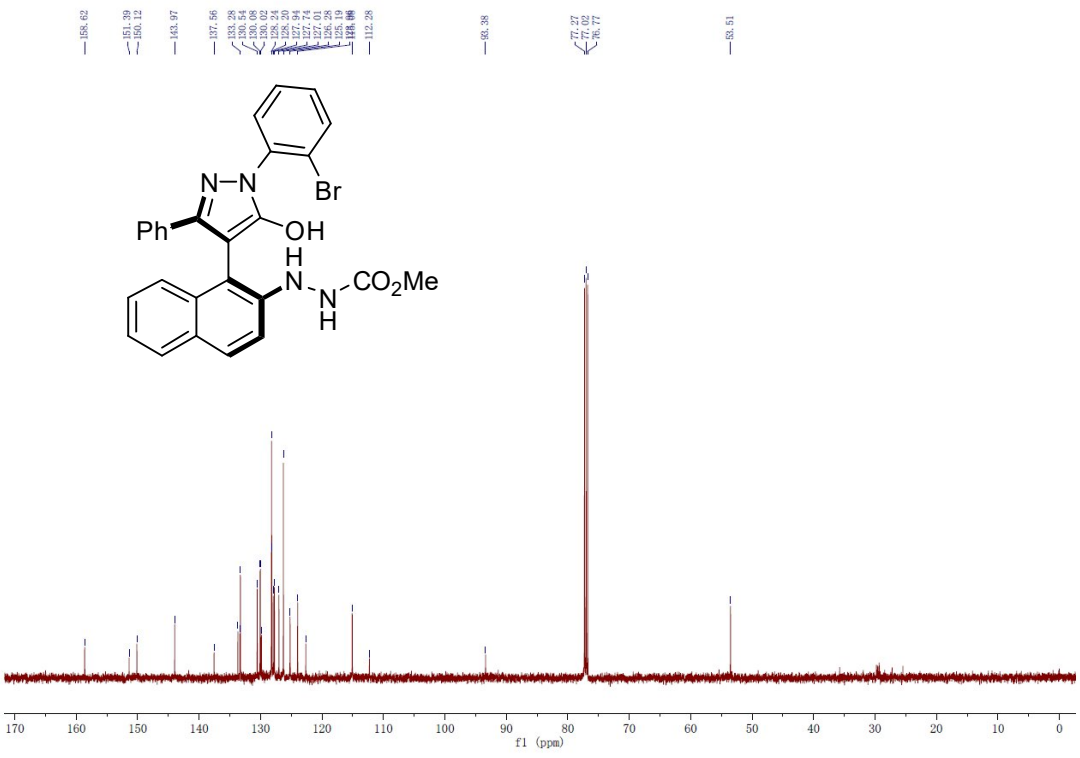
(*S*)-methyl 2-(1-(1-(3-bromophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3as)



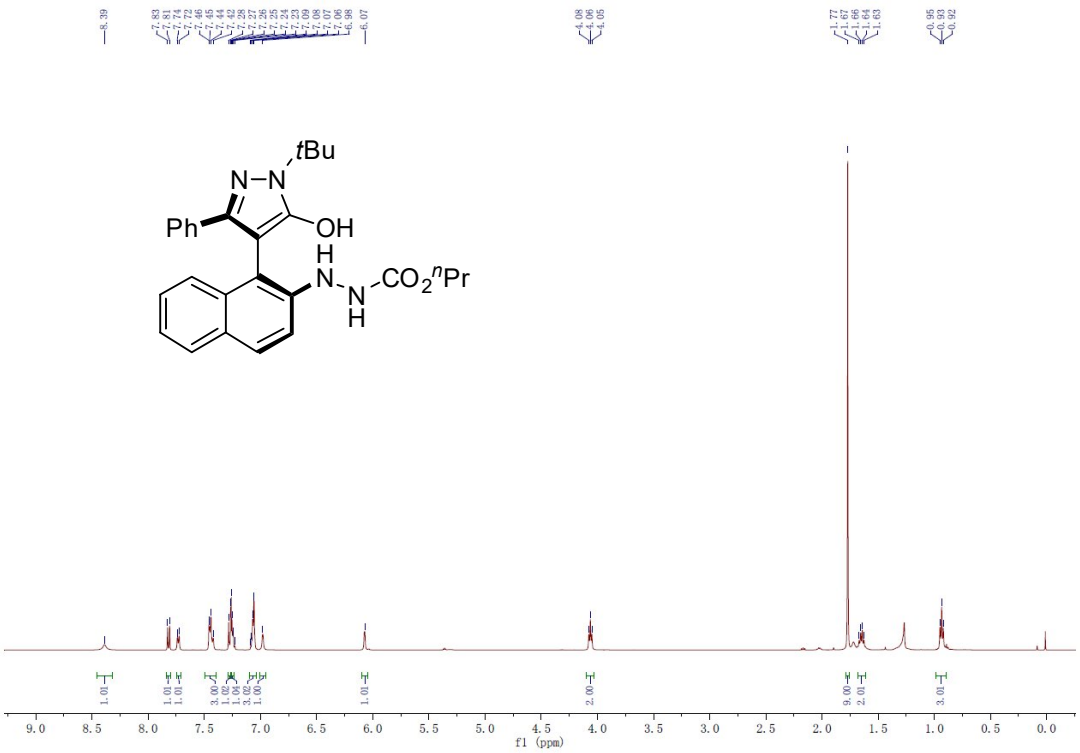


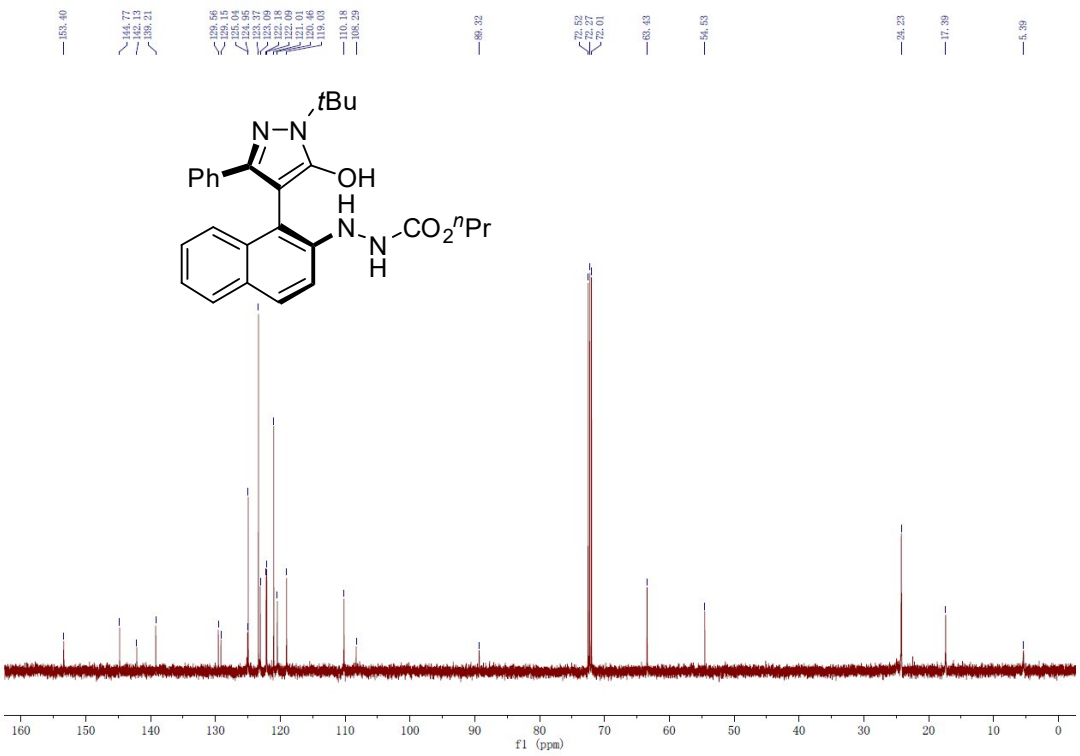
(*S*)-methyl 2-(1-(1-(2-bromophenyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3at)



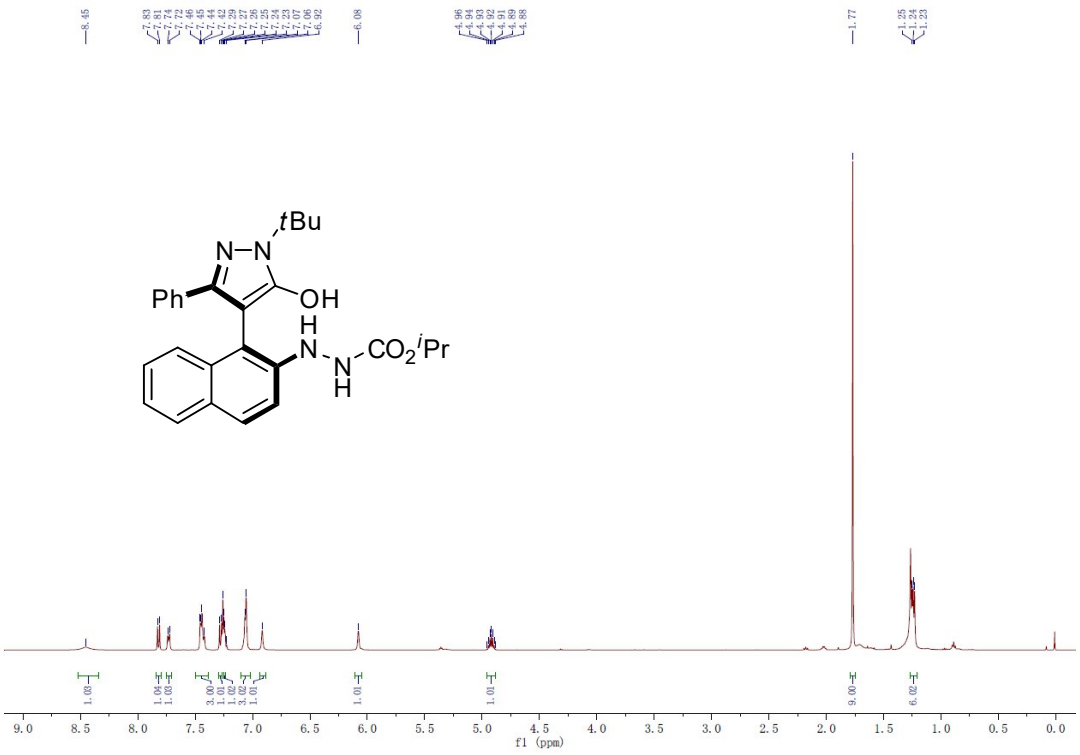


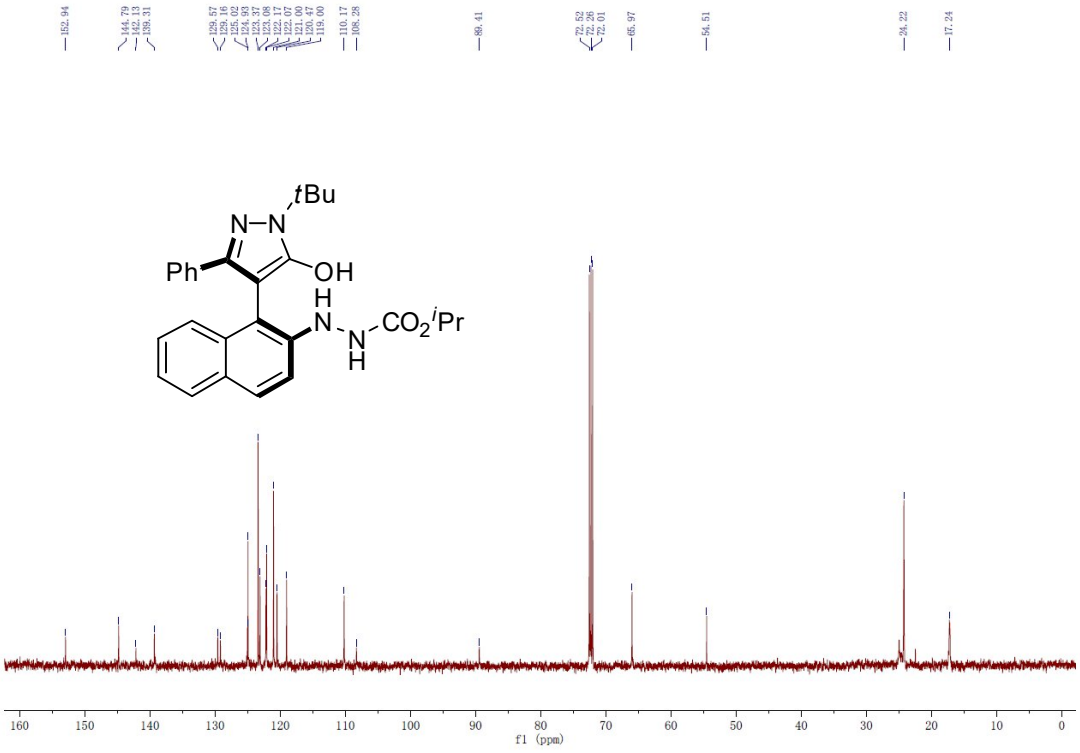
(*S*)-propyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ba)



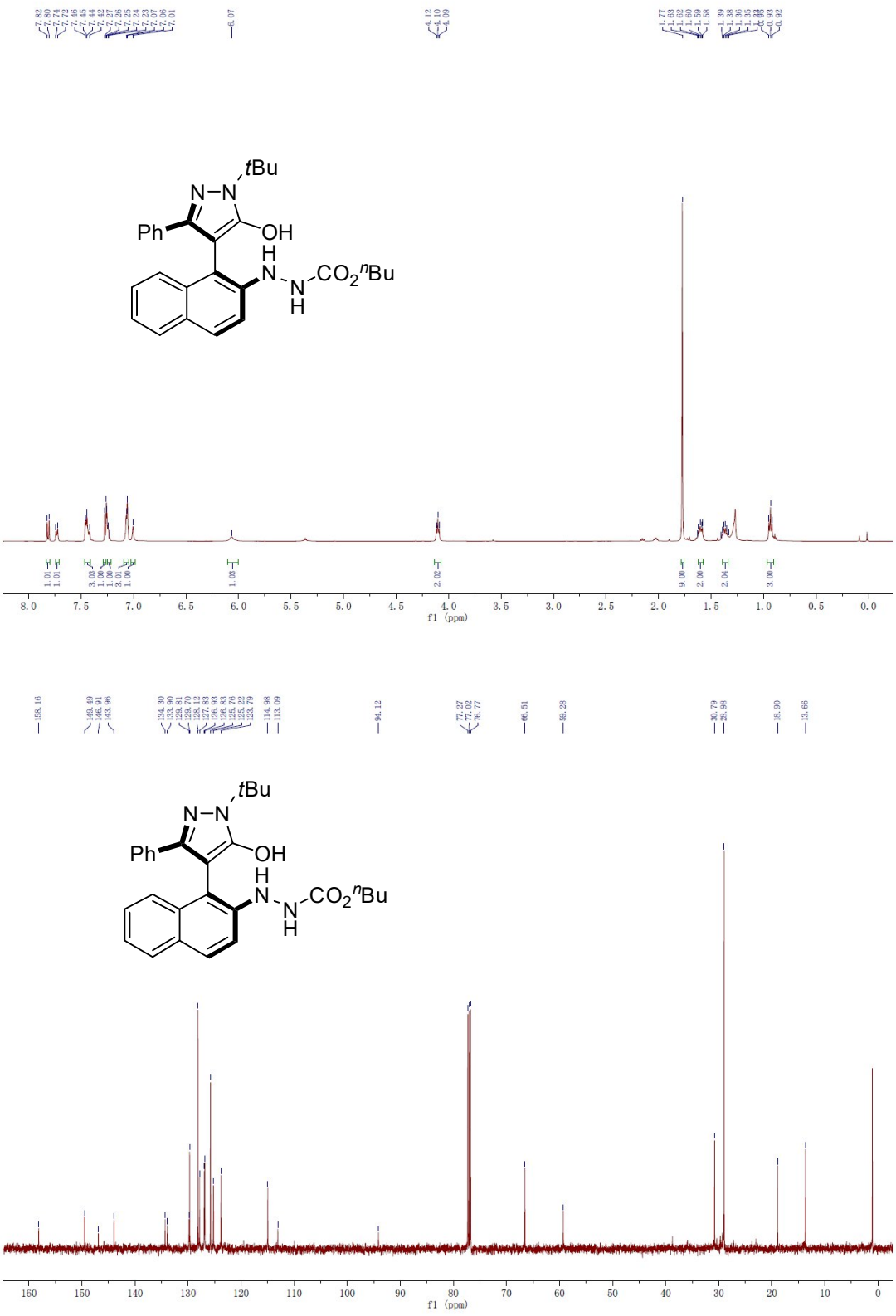


(*S*)-isopropyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ca)

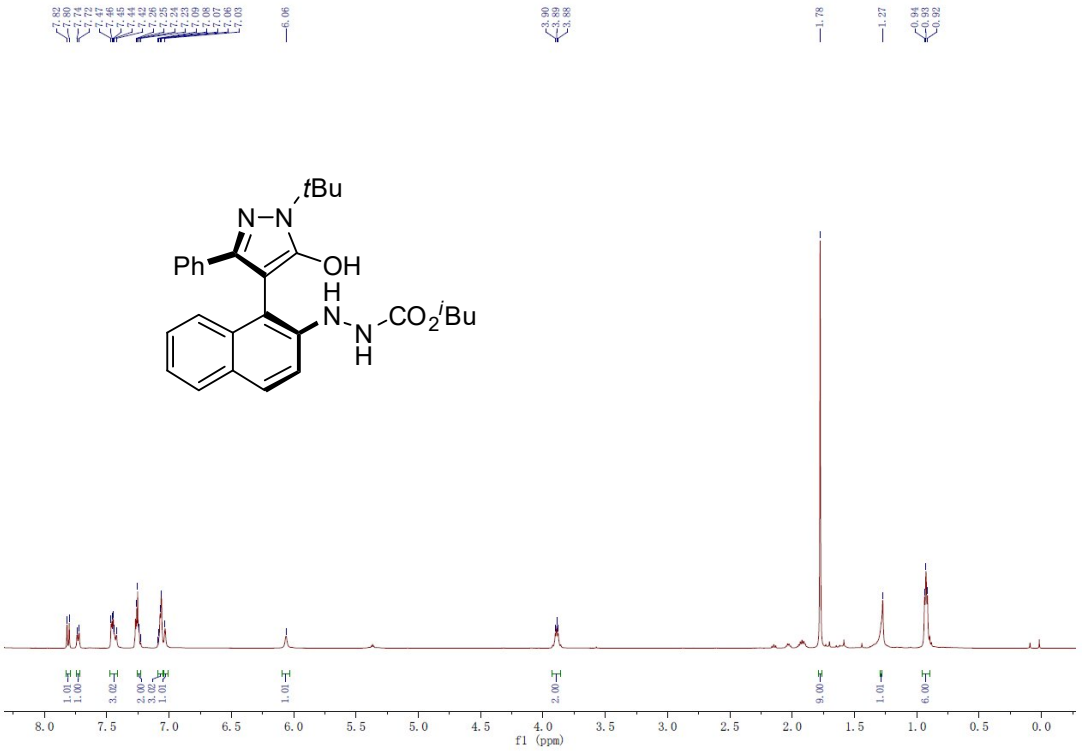


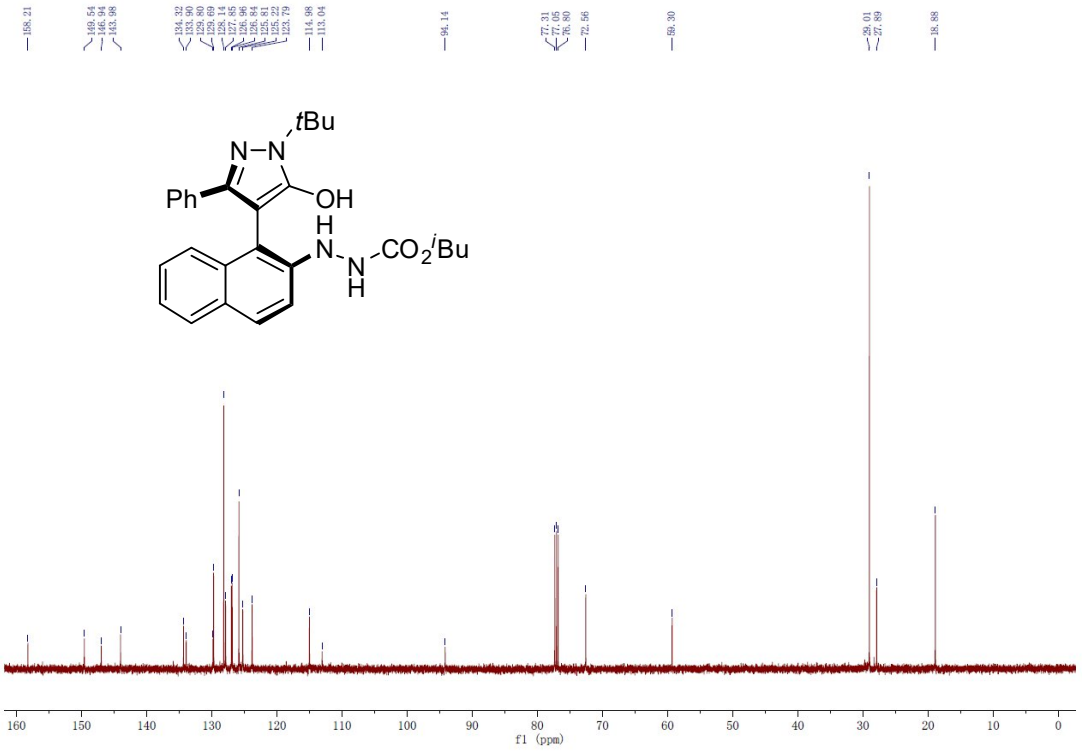


(*S*)-butyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3da)

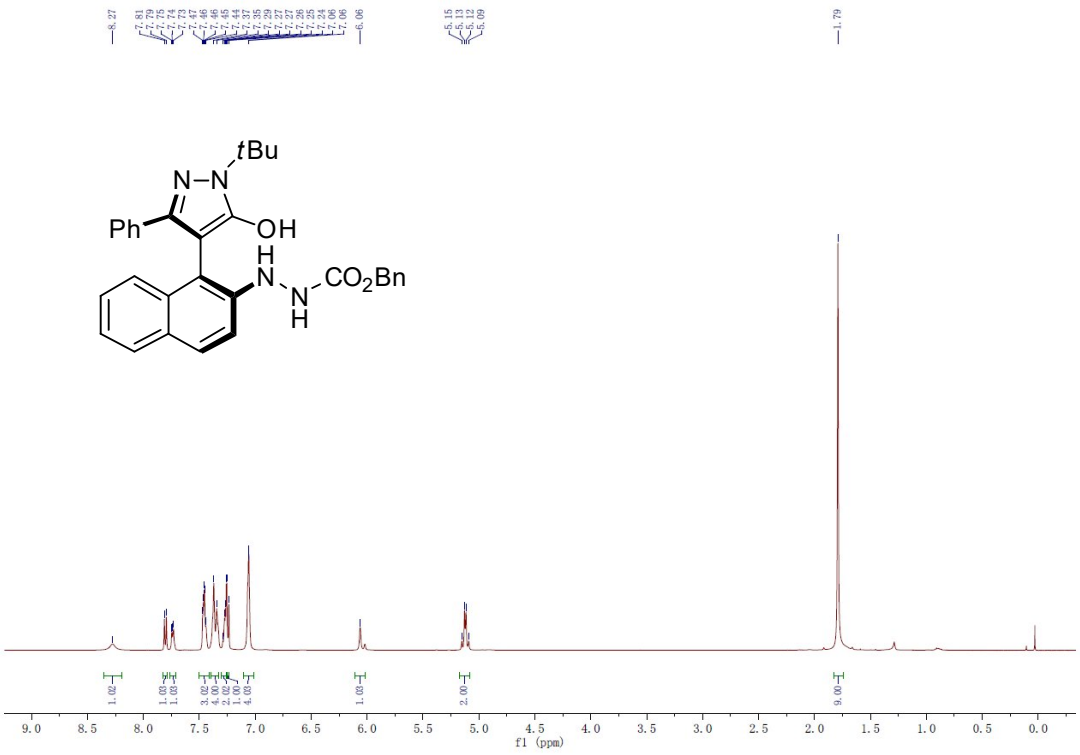


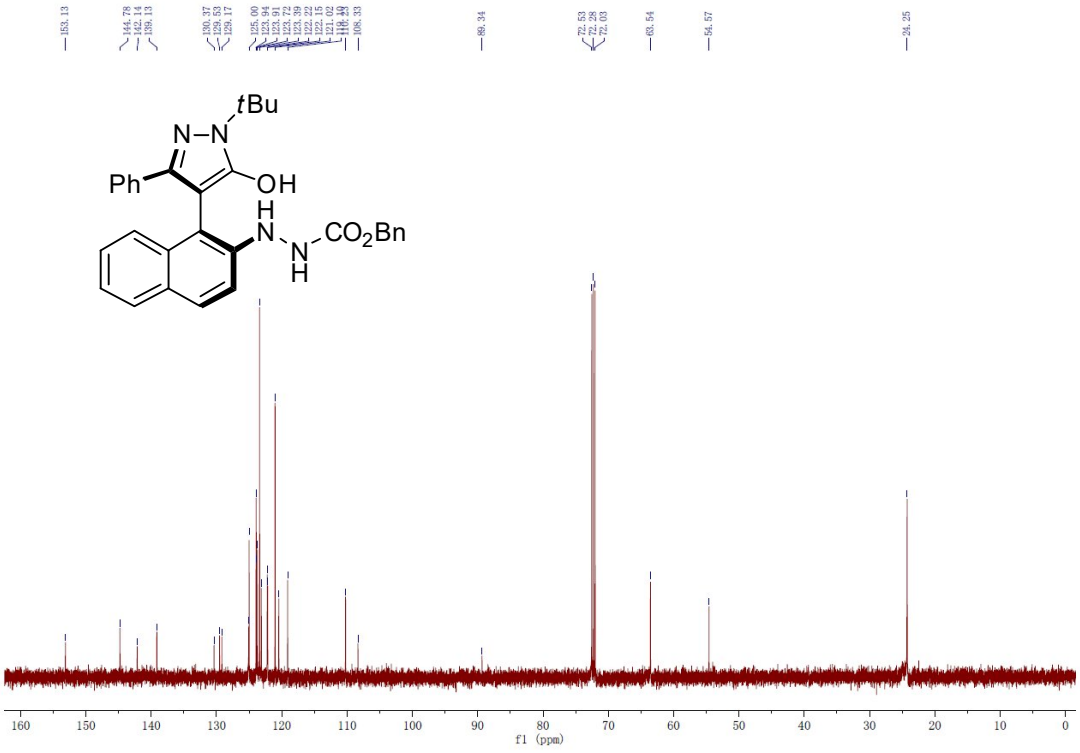
(*S*)-isobutyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ea)



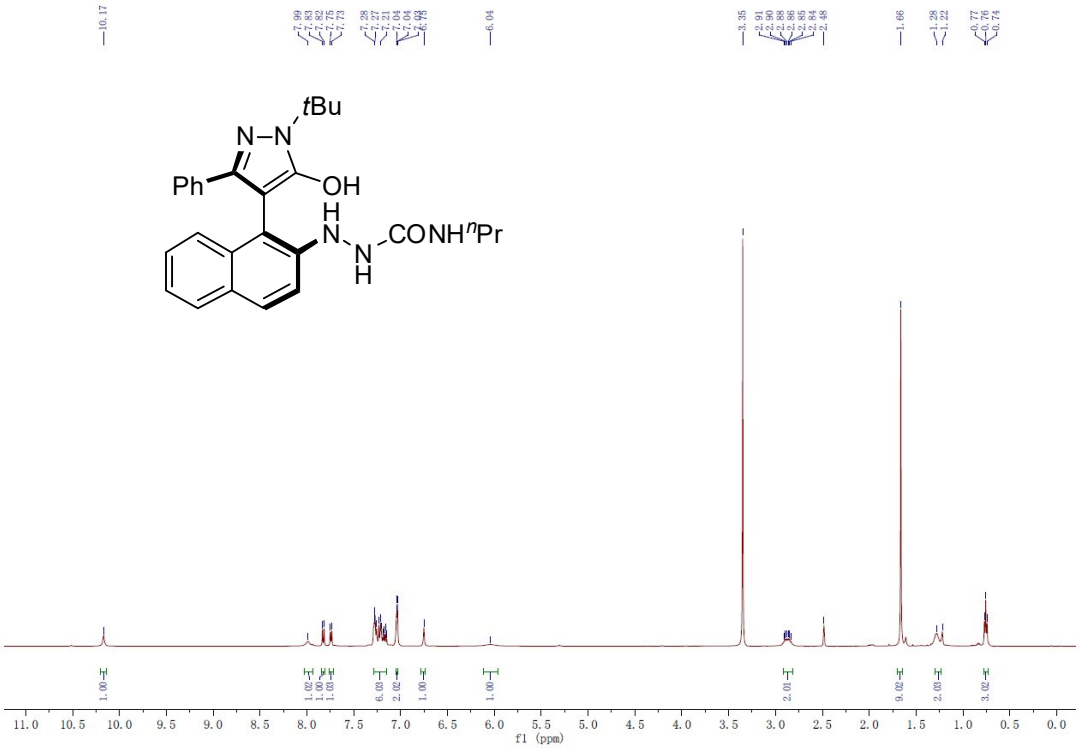


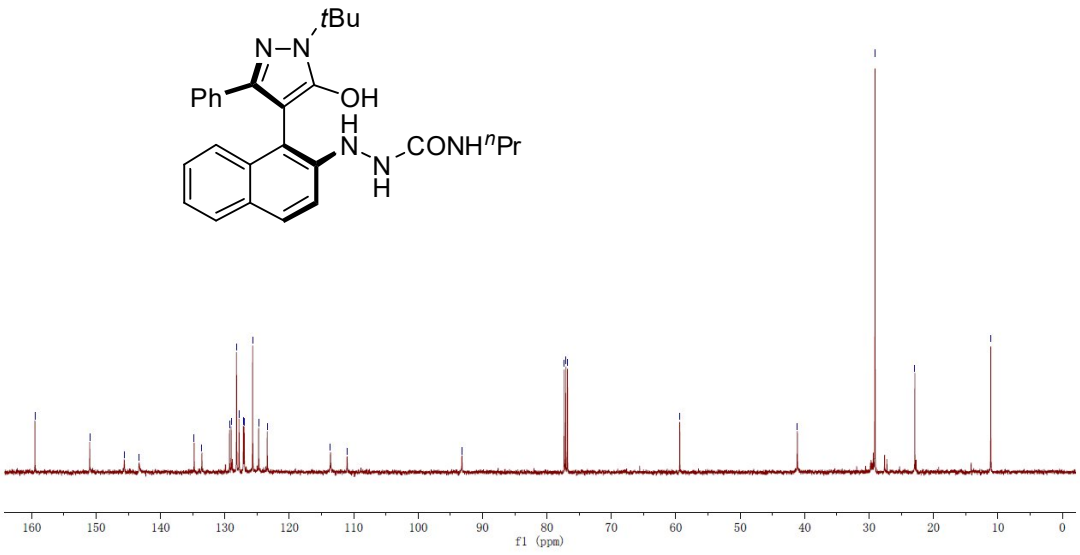
(*S*)-benzyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3fa)



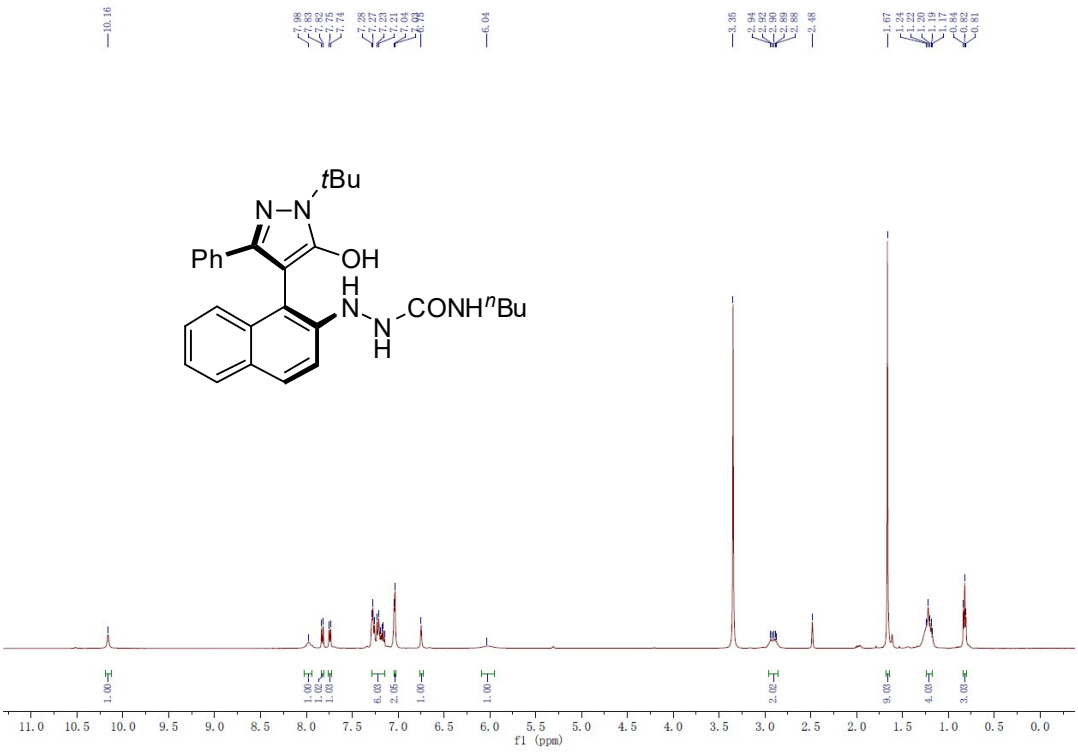


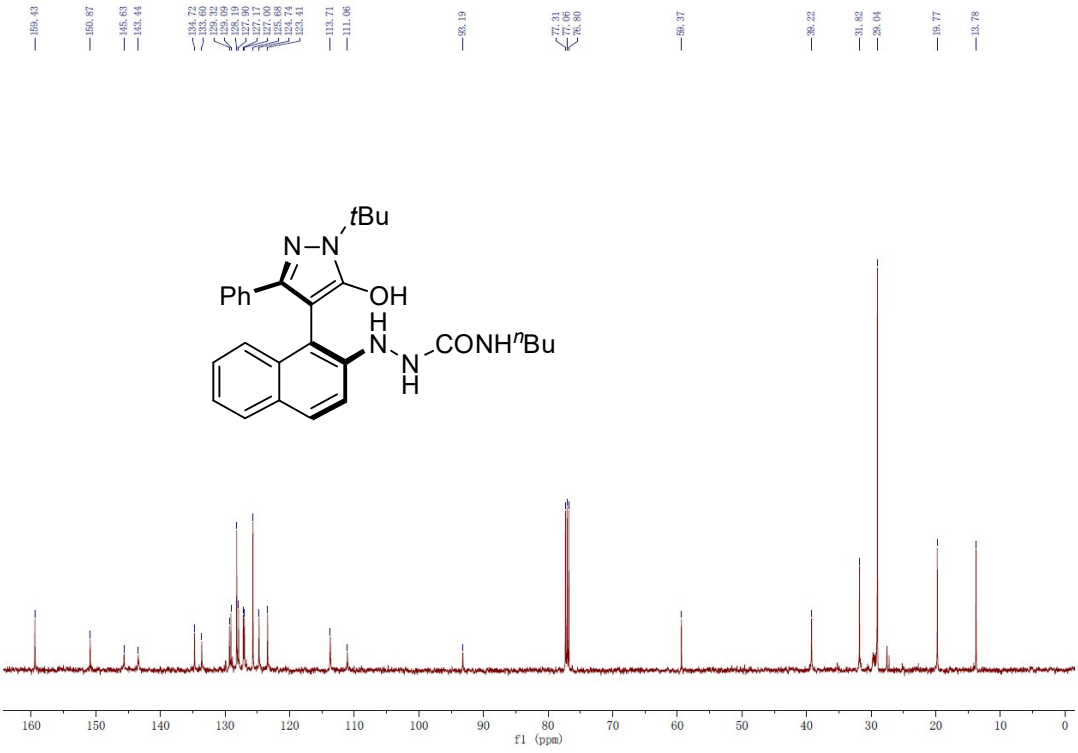
(*S*)-2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)-*N*-propylhydrazinecarboxamide (3ga)



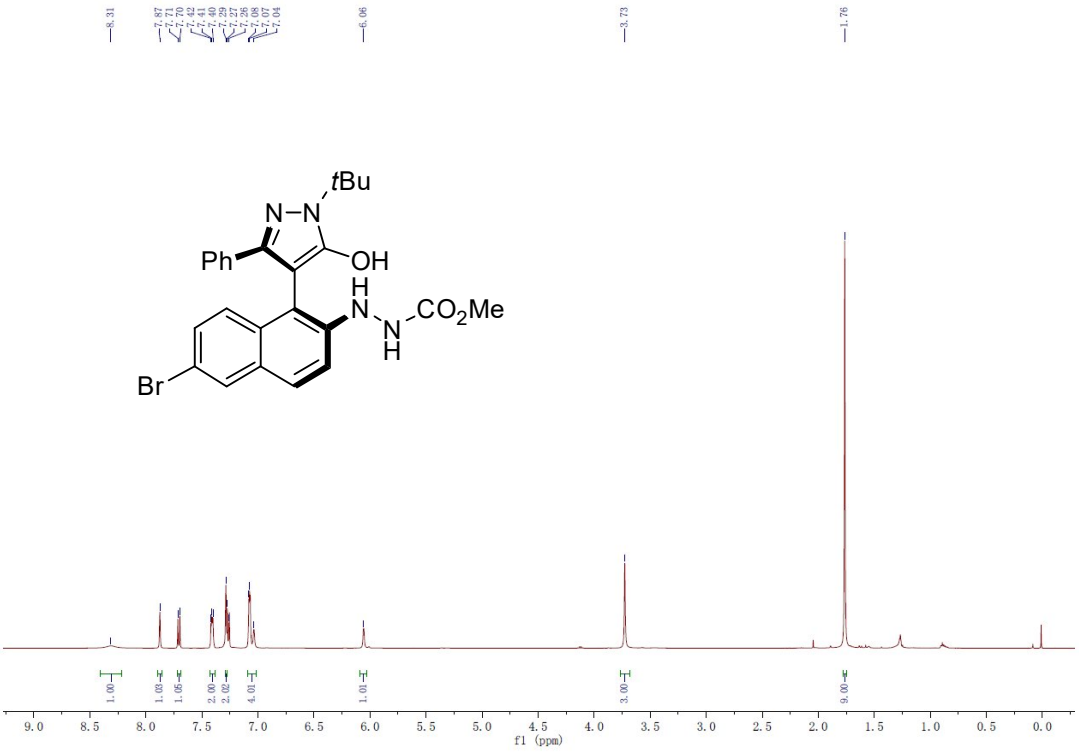


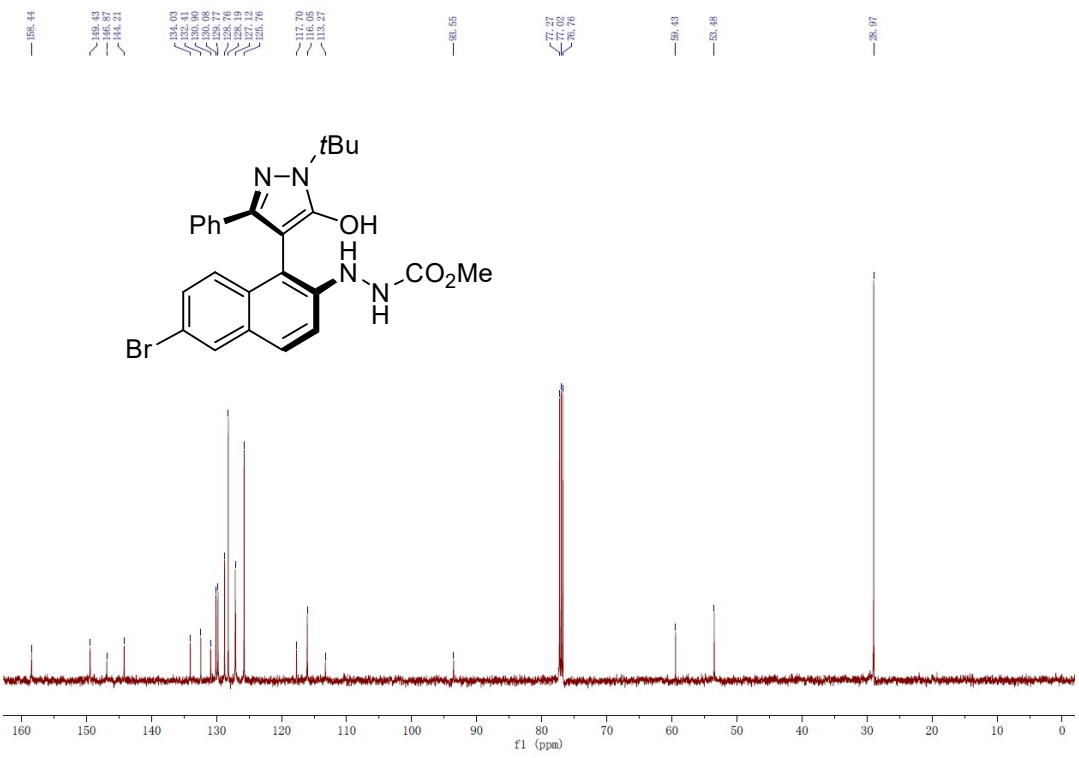
(*S*)-*N*-butyl-2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxamide (3ha)



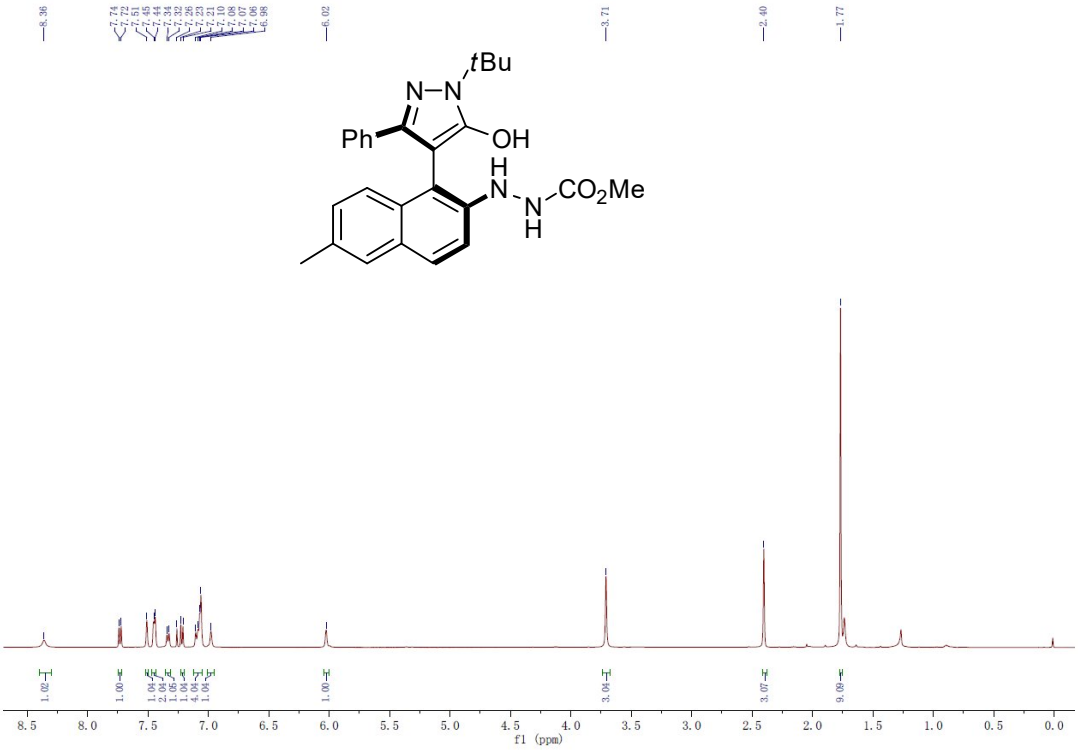


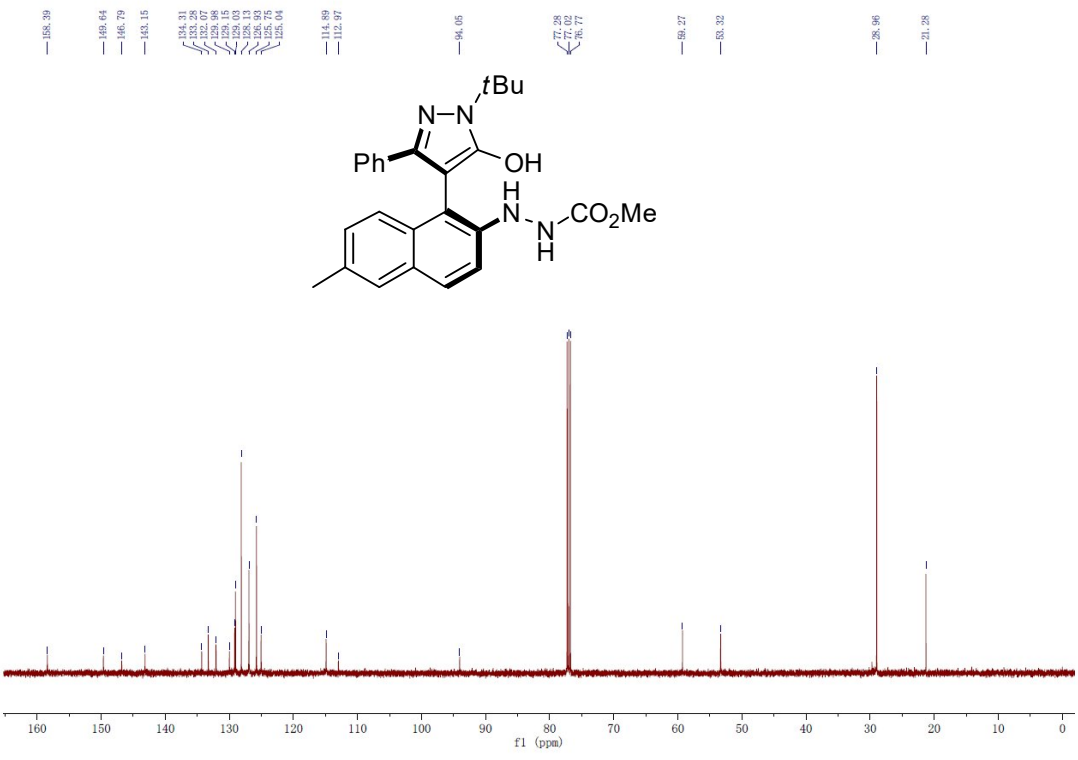
(*S*)-methyl 2-(6-bromo-1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)naphthalen-2-yl)hydrazinecarboxylate (3ia)



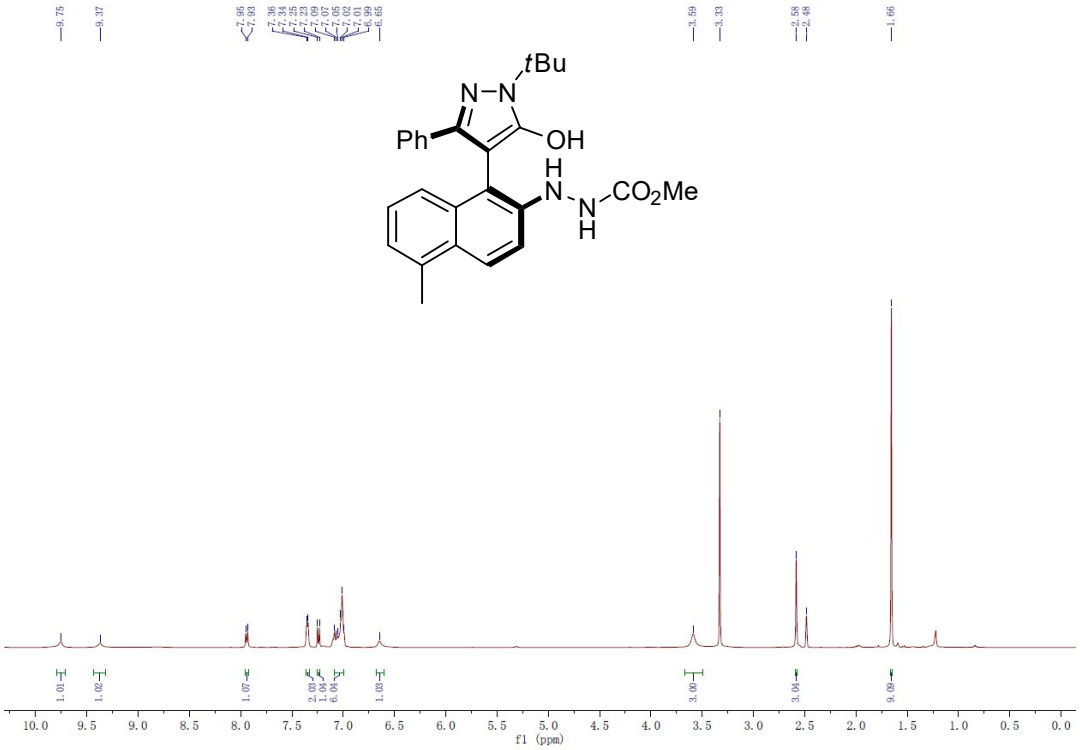


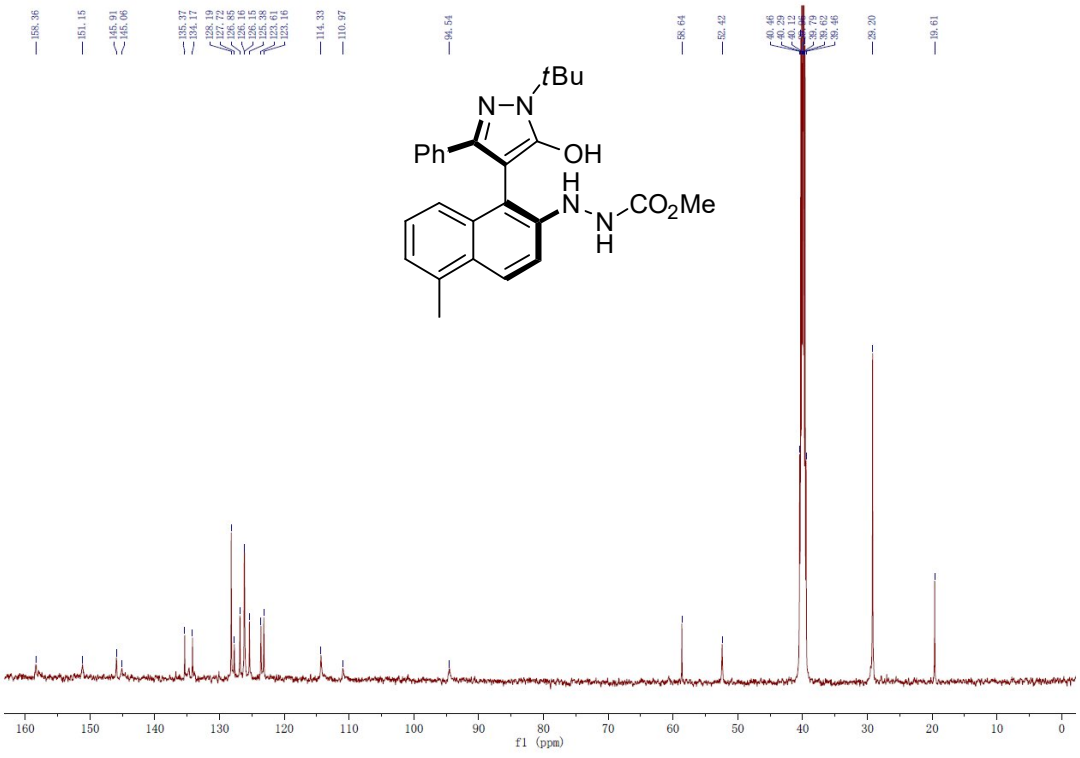
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)-6-methylnaphthalen-2-yl)hydrazinecarboxylate (3ja)



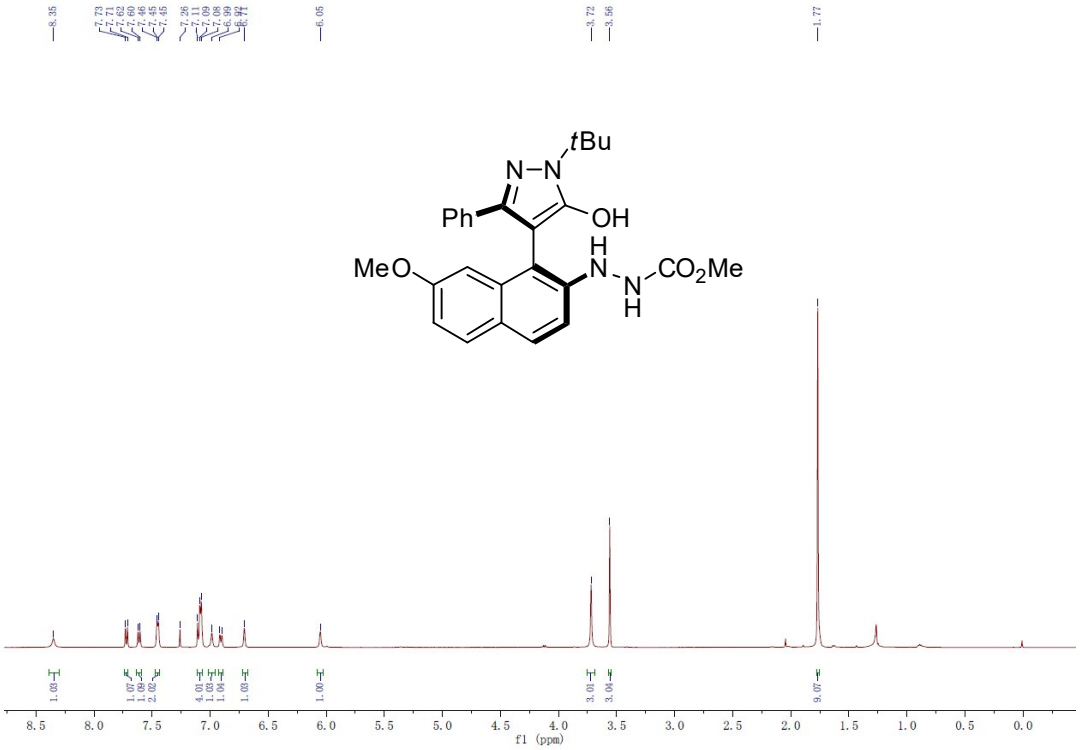


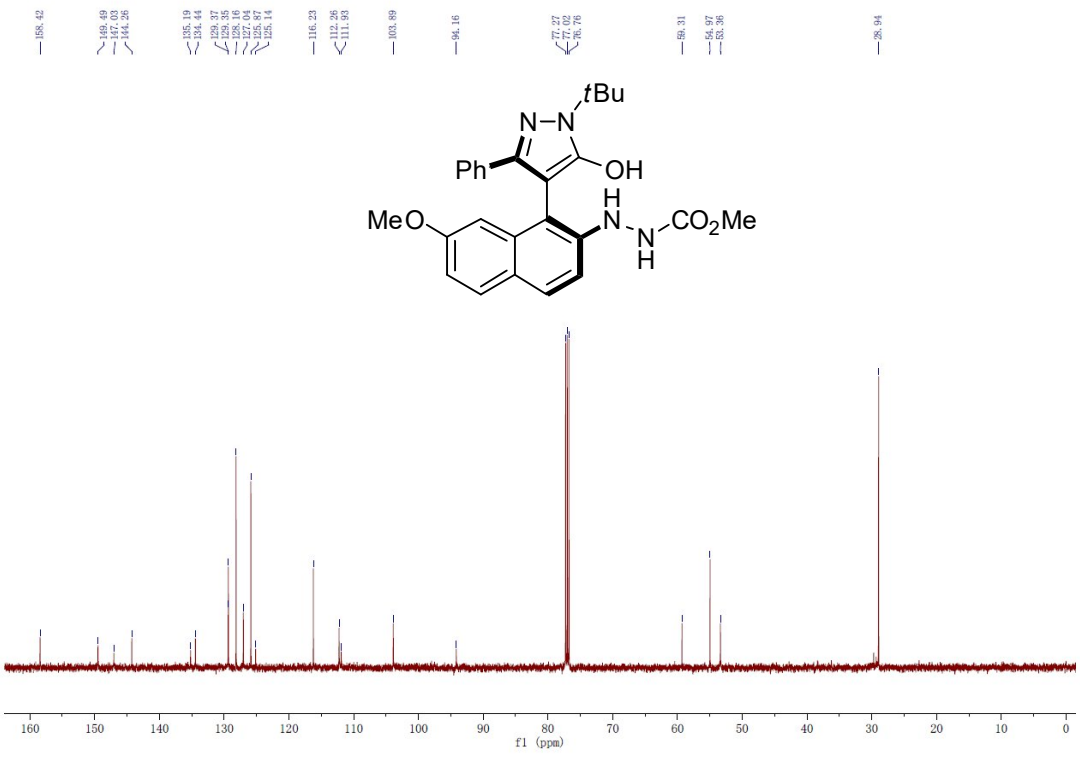
(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)-5-methylnaphthalen-2-yl)hydrazinecarboxylate (3ka)





(*S*)-methyl 2-(1-(1-(*tert*-butyl)-5-hydroxy-3-phenyl-1*H*-pyrazol-4-yl)-7-methoxynaphthalen-2-yl)hydrazinecarboxylate (3la)





9. X-ray Crystal data of 3ac

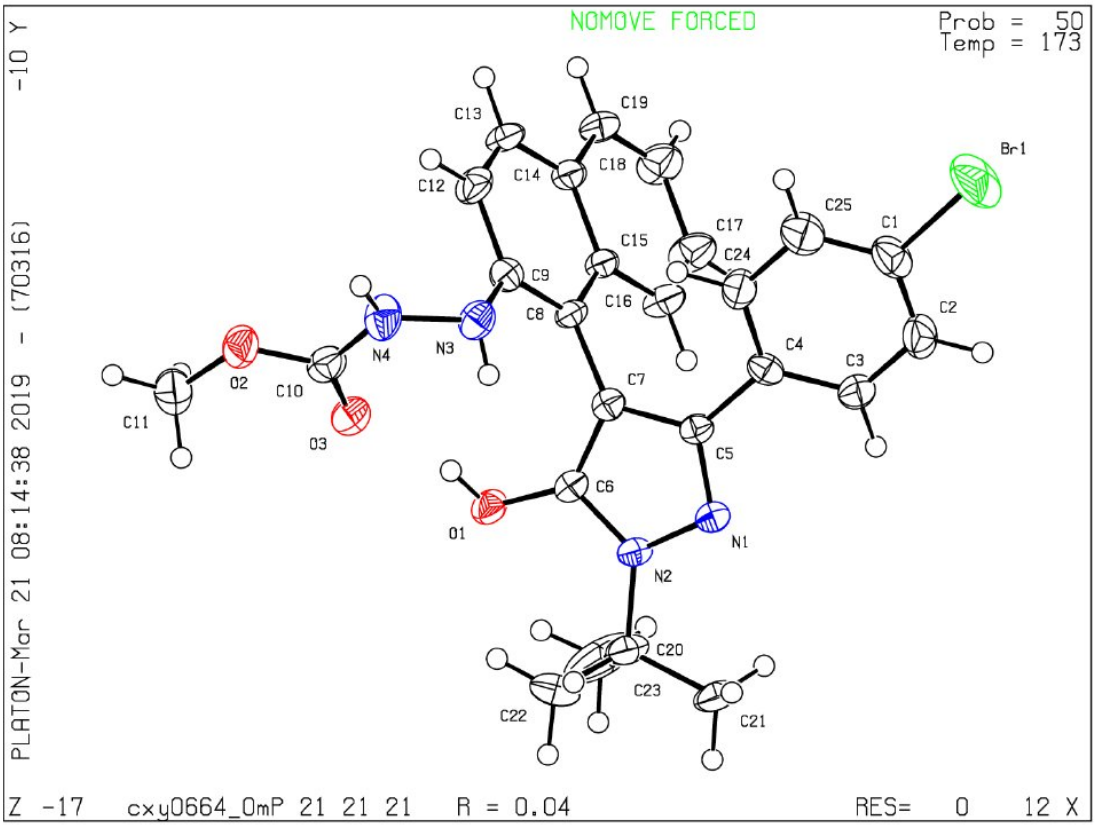


Table S1. Crystal data and structure refinement for 3ac.

Identification code	**3ac**
Empirical formula	$C_{25}H_{25}BrN_4O_3$
Formula weight	509.40
Temperature/K	173
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	10.9181(4)
b/Å	12.5117(5)
c/Å	17.7197(7)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	2420.58(16)
Z	4
ρ_{calc}g/cm^3	1.398
μ/mm^{-1}	1.732
F(000)	1048.0
Crystal size/mm^3	0.45 × 0.39 × 0.38
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.382 to 52.98
Index ranges	$-11 \leq h \leq 13$, $-15 \leq k \leq 15$, $-21 \leq l \leq 22$
Reflections collected	21960
Independent reflections	5001 [R_{int} = 0.0365, R_{sigma} = 0.0323]
Data/restraints/parameters	5001/0/303
Goodness-of-fit on F^2	1.023
Final R indexes [I>=2σ (I)]	R_1 = 0.0379, wR_2 = 0.0855
Final R indexes [all data]	R_1 = 0.0501, wR_2 = 0.0915
Largest diff. peak/hole / e Å^{-3}	0.88/-0.70
Flack parameter	-0.010(3)

10. Calculation of the Rotation Barrier of 3aa

All density functional theory (DFT) calculations were performed using Gaussian 09.[7] The geometries and frequency calculations were performed using the M06-2X[8] density functional in conjunction with the 6-31G(d,p) basis set. The SMD[9] solvation model was used to account for the solvation effects of 2-propanol, which was used for measuring the rotation barriers. Frequency calculations confirmed that optimized structures are minima (no imaginary frequency) or transition structures (one imaginary frequency). Thermal free energy corrections were obtained at 353.15 K to match measuring conditions. Low frequencies (< 100 cm^{-1}) were corrected in the vibrational component of the entropy using a free rotor approximation according to the method of Grimme *et al.*, since entropy associated with these loose vibrational modes was the most prone to computational error.[10] The quasi-harmonic oscillator corrections were obtained using the GoodVibes.[11] To obtain more accurate electronic energies, single-point energy calculations were performed at the M06-2X/def2-TZVPP-SMD(2-propanol) level of theory with the optimized structures,[12] including the D3 version of dispersion correction scheme developed by Grimme.[13] Structures were generated using CYLview.[14] Unless noted, all energetics are reported in kcal/mol, and the bond lengths are reported in angstroms (Å).

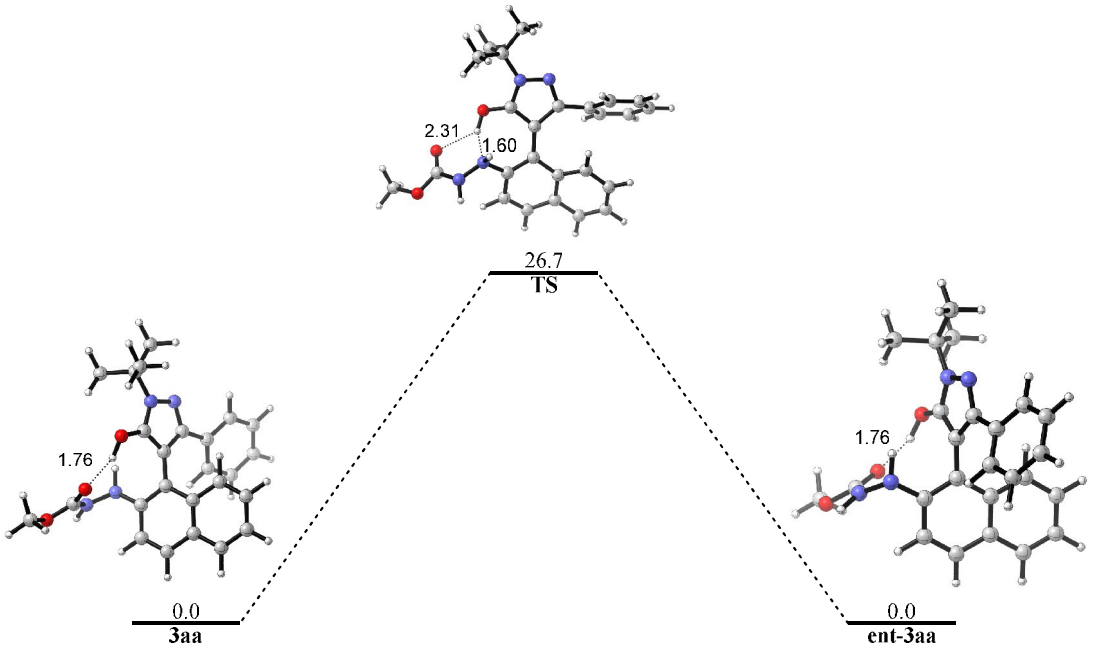


Figure S1. Free energy profile for racemization of 3aa.

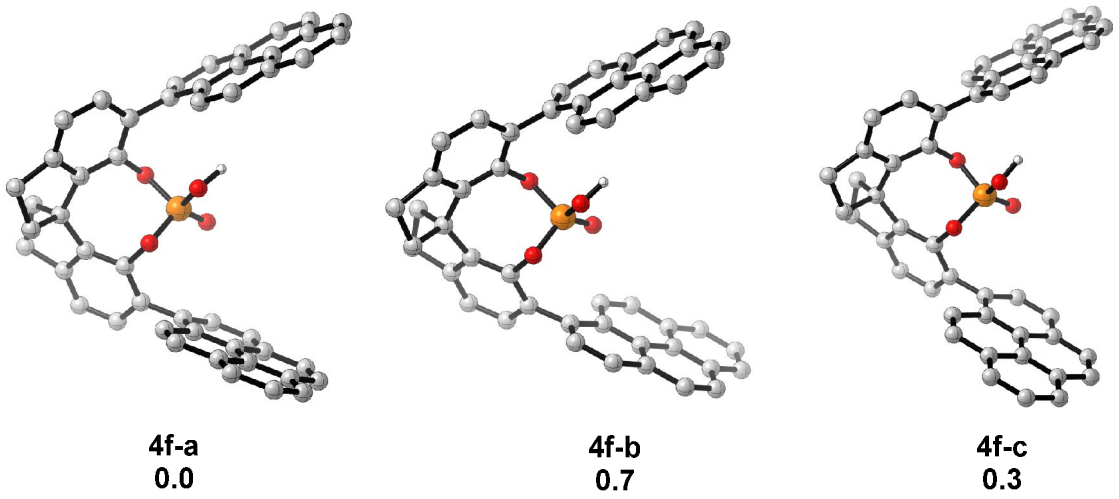
11. Calculation of the Transition States in Catalysis Process

Calculation Method

All DFT calculations were optimized using the M06-2X[8] functional with 6-31G(d) basis set as implemented in Gaussian09[7] at gas phase. The frequency calculations were conducted at the same level of theory to confirm the nature of stationary points and obtain the thermal corrections. Thermal free energy corrections were obtained at 273.15 K to match experimental conditions. Low frequencies (< 100 cm^{-1}) were corrected in the vibrational component of the entropy using a free rotor approximation according to the method of Grimme *et al.*, since entropy associated with these loose vibrational modes was the most prone to computational error.[10] The quasi-harmonic oscillator corrections were obtained using the GoodVibes.[11] The high-level solution-phase energies of the transition states were calculated at M06-2X/def2-TZVPP level,[12] including the D3 version of dispersion correction scheme developed by Grimme.[13] SMD[9] solvation model was used to account for the solvation effects in dichloromethane. Intermolecular non-covalent interactions (NCI) in transition states were analyzed by Multiwfn[15] using reduced density gradient (RDG) isosurface.[16] The corresponding NCI pictures were generated using VMD.[17] Unless noted, all energetics are reported in kcal/mol, and the bond lengths are reported in angstroms (Å). Structures were generated using CYLview.[14]

Conformers of chiral phosphoric acid 4f

Considering the rotation of 1-pyrenyl in chiral phosphoric acid **4f**, conformational searching was conducted using GFN2-xTB.[18] After optimizing using the level described above, we found three main conformers of chiral phosphoric acid **4f**. And the calculated relative free energies are within 1 kcal/mol. These three conformers were intitially considered in transition states optimization. However, we found that transition states based on **4f-c** are relative unstable than those based on **4f-a** and **4f-b**. Because the orientation of 1-pyrenyl**,** π-π interactions are weaker in transition states based on **4f-c**. Thus, the transition states based on **4f-a** and **4f-b** are reported here.



FigureS2. Conformers of chiral phosphoric acid 4f and their relative free energies.

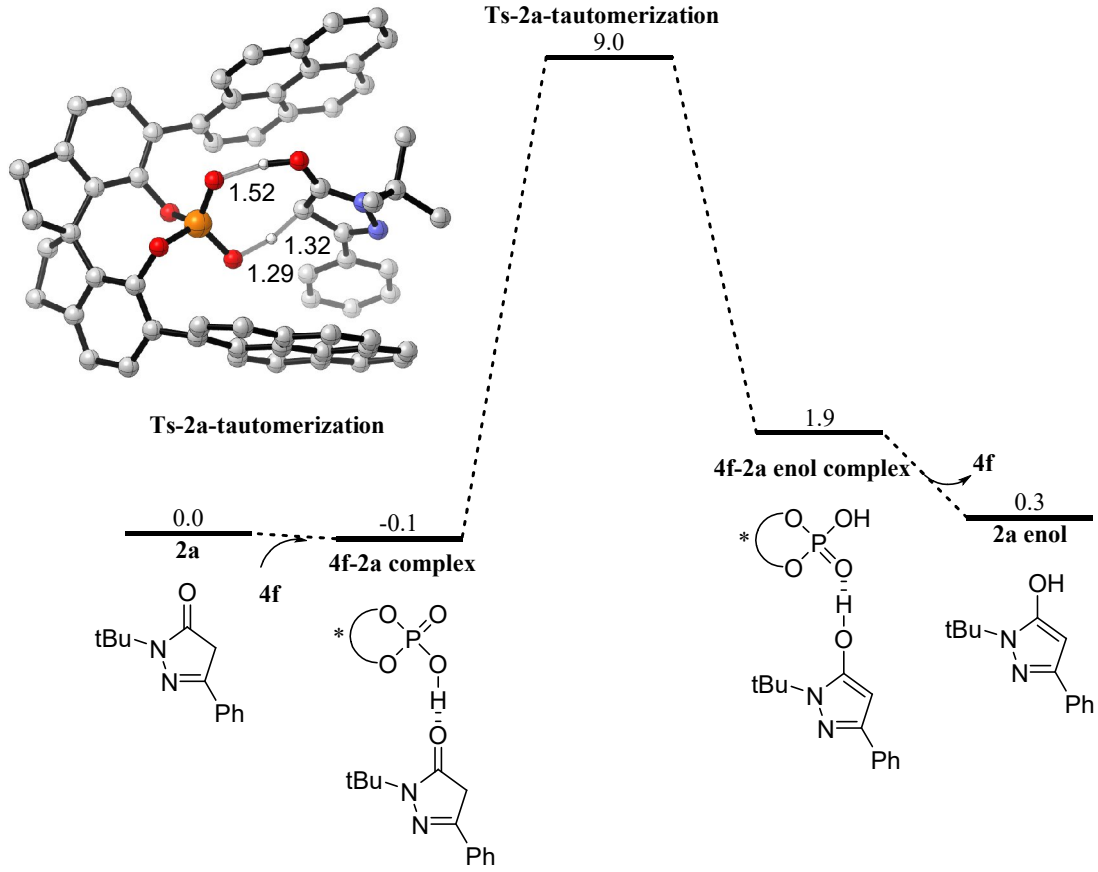


Figure S3. Free energy profile for chiral phosphoric acid 4f catalyzed tautomerization of pyrazolone.

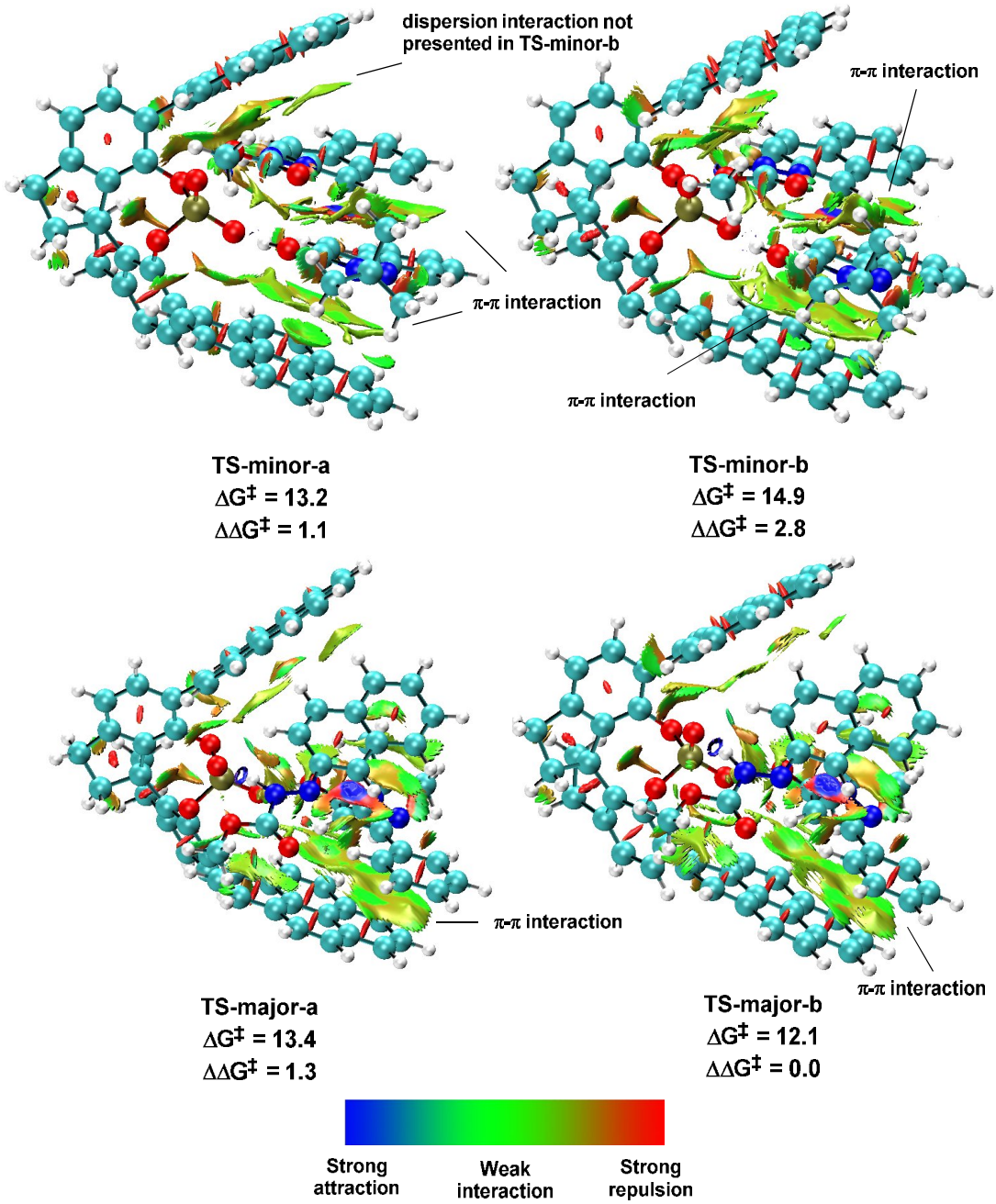


Figure S4. Non-covalent interactions (NCI) analysis of intermolecular interaction in transition states. Activation free energies are reported relative to the starting materials

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13. Calculated Cartesian Coordinates (Å) and Energies

The Cartesian coordinates (Å) and energies at 353.15 K for the rotation barrier of 3aa.

ent-3aa

Imaginary frequency: None

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(2-propanol)): -1413.016430 a.u.

Thermal correction to Free energies at 353.15 K (M06-2X/6-31G(d,p)-SMD(2-propanol)): 0.401875 a.u.

Free energies at 353.15 K (M06-2X-D3/def2-TZVPP-SMD(2-propanol)): -1412.614556 a.u.

Corrected Free energies at 353.15 K (M06-2X-D3/def2-TZVPP-SMD(2-propanol)): -1412.607149 a.u.

O	1.588628	1.594274	1.031324
O	5.214862	-0.665014	-1.219452
O	3.631848	0.001624	0.250016
N	-0.414550	2.605468	0.385405
N	-1.618438	2.295929	-0.143546
N	1.737029	-0.518602	-1.692112
H	1.426422	0.444516	-1.609143
N	3.101027	-0.608108	-1.887839
H	3.435880	-1.011309	-2.753665
C	0.365203	1.504222	0.494553
C	0.104899	-0.991933	0.042373
C	1.168520	-1.399313	-0.745957
C	-0.351043	0.414835	0.011927
C	-2.776158	0.320384	-0.950355
C	-1.592163	0.988327	-0.376555
C	-0.520570	-1.944830	0.912930
C	-4.050134	0.871309	-0.759218
H	-4.148934	1.784577	-0.180227
C	1.080487	-3.639210	0.156690
H	1.458016	-4.657007	0.205626
C	-0.031049	-3.280599	0.965577
C	-5.043621	-0.924661	-2.031076
C	-2.652283	-0.859804	-1.692609
H	-1.668973	-1.287584	-1.865346
C	-5.173768	0.254898	-1.299065
H	-6.155073	0.693186	-1.142892
C	1.664365	-2.729129	-0.677737
H	2.505753	-3.011473	-1.302234
C	3.961224	-0.392817	-0.862505
C	-3.779988	-1.478365	-2.225711
H	-3.669208	-2.393579	-2.799607
C	-2.196245	-2.533998	2.574252

H	-3.034613	-2.249370	3.202935
C	-1.248162	4.906390	0.442398
H	-1.490250	4.888423	-0.622655
H	-0.977606	5.928498	0.721282
H	-2.138003	4.615339	1.005211
C	-1.618558	-1.600712	1.748268
H	-1.997272	-0.583933	1.732537
C	-0.648192	-4.222951	1.827911
H	-0.258269	-5.237420	1.850765
C	-0.063125	3.999990	0.761812
C	-1.711473	-3.862206	2.616590
H	-2.178869	-4.588263	3.274418
C	6.205989	-0.442675	-0.205187
H	6.001437	-1.064926	0.667739
H	6.223526	0.609828	0.083246
H	7.153592	-0.727047	-0.659125
C	0.230066	4.045608	2.263590
H	-0.643205	3.711743	2.832167
H	0.460624	5.074235	2.556077
H	1.082322	3.414991	2.524937
C	1.155727	4.438997	-0.054479
H	1.399456	5.476839	0.190792
H	0.937823	4.380516	-1.125368
H	2.028107	3.820033	0.164230
H	2.171300	0.857048	0.737182
H	-5.921845	-1.408263	-2.447847

3aa

Imaginary frequency: None

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(2-propanol)): -1413.016431 a.u.

Thermal correction to Free energies at 353.15 K (M06-2X/6-31G(d,p)-SMD(2-propanol)): 0.401861 a.u.

Free energies at 353.15 K(M06-2X-D3/def2-TZVPP-SMD(2-propanol)): -1412.614570 a.u.

Corrected Free energies at 353.15 K (M06-2X-D3/def2-TZVPP-SMD(2-propanol)): -1412.607162 a.u.

O	-1.587896	1.595237	1.030764
O	-5.215196	-0.663295	-1.219136
O	-3.631773	0.003348	0.249829
N	0.415961	2.605355	0.385075
N	1.619734	2.295107	-0.143702
N	-1.737413	-0.517945	-1.692478
H	-1.426429	0.445057	-1.609653
N	-3.101522	-0.606776	-1.888081

H	-3.436584	-1.010294	-2.753679
C	-0.364462	1.504592	0.494123
C	-0.105500	-0.991738	0.042138
C	-1.169361	-1.398713	-0.746043
C	0.351200	0.414768	0.011547
C	2.776346	0.318883	-0.950423
C	1.592686	0.987504	-0.376769
C	0.519420	-1.944823	0.912948
C	2.651862	-0.861058	-1.692963
H	1.668327	-1.288220	-1.865958
C	-1.082574	-3.638482	0.157028
H	-1.460593	-4.656080	0.206200
C	0.029180	-3.280291	0.965847
C	5.043225	-0.927412	-2.031014
C	4.050666	0.868911	-0.758910
H	4.149979	1.781981	-0.179702
C	3.779272	-1.480241	-2.225997
H	3.667952	-2.395260	-2.800100
C	-1.665964	-2.728249	-0.677549
H	-2.507518	-3.010249	-1.301966
C	-3.961482	-0.391215	-0.862581
C	5.173992	0.251888	-1.298688
H	6.155553	0.689504	-1.142244
C	2.194643	-2.534535	2.574523
H	3.033120	-2.250205	3.203190
C	1.251100	4.905701	0.442347
H	2.140757	4.614110	1.005163
H	0.981217	5.928002	0.721177
H	1.493128	4.887534	-0.622707
C	1.617523	-1.601111	1.748280
H	1.996793	-0.584547	1.732371
C	0.645728	-4.222800	1.828441
H	0.255236	-5.237043	1.851476
C	0.065488	4.000070	0.761779
C	1.709146	-3.862456	2.617130
H	2.176063	-4.588599	3.275199
C	-6.206124	-0.440227	-0.204799
H	-6.222743	0.612252	0.083748
H	-6.002051	-1.062770	0.668026
H	-7.153977	-0.723734	-0.658747
C	-1.153166	4.440030	-0.054271
H	-0.935356	4.381900	-1.125191
H	-1.396436	5.477877	0.191420
H	-2.025815	3.821392	0.164249

C	-0.227437	4.045550	2.263614
H	-0.457027	5.074279	2.556498
H	0.645617	3.710706	2.831933
H	-1.080220	3.415630	2.524927
H	-2.171043	0.858440	0.736379
H	5.921214	-1.411439	-2.447779

Ts-3aa-racemization

Imaginary frequency: -22.581

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(2-propanol)): -1412.974019 a.u.

Thermal correction to Free energies at 353.15 K (M06-2X/6-31G(d,p)-SMD(2-propanol)): 0.402601 a.u.

Free energies at 353.15 K(M06-2X-D3/def2-TZVPP-SMD(2-propanol)): -1412.571418 a.u.

Corrected Free energies at 353.15 K (M06-2X-D3/def2-TZVPP-SMD(2-propanol)): -1412.564668 a.u.

O	1.818695	1.601680	0.325705
O	5.679007	-1.389739	-0.367467
O	4.409233	0.170273	0.678194
N	-0.179675	2.665134	-0.029386
N	-1.499755	2.414604	-0.121442
N	2.341017	-0.540111	-0.911798
H	1.981329	-0.168105	-1.790962
N	3.621528	-1.030376	-1.104088
H	3.742076	-1.894006	-1.625625
C	0.531342	1.519241	0.006368
C	0.041388	-1.004436	-0.221770
C	1.377827	-1.414297	-0.303057
C	-0.351361	0.426757	-0.199412
C	-3.044367	0.650610	-0.056861
C	-1.631756	1.100119	-0.196262
C	-0.898179	-2.109022	-0.132932
C	-3.458131	0.018922	1.119792
H	-2.727042	-0.197178	1.894281
C	0.902260	-3.588912	0.638473
H	1.228575	-4.527789	1.075721
C	-0.476059	-3.368296	0.388848
C	-5.724039	-0.071206	0.293256
C	-3.988215	0.946501	-1.042535
H	-3.670646	1.453153	-1.949470
C	-4.790696	-0.341543	1.293298
H	-5.101308	-0.835631	2.209100
C	1.809495	-2.666700	0.200025
H	2.871663	-2.878295	0.254815

C	4.564048	-0.681513	-0.174567
C	-5.320967	0.577299	-0.872573
H	-6.045618	0.798857	-1.650455
C	-3.076312	-3.111831	-0.592631
H	-4.055039	-3.038267	-1.057621
C	-0.833221	5.022663	-0.056563
H	-1.274830	4.907493	-1.049686
H	-0.441680	6.039513	0.035119
H	-1.616892	4.882650	0.690485
C	-2.200146	-2.056817	-0.693596
H	-2.484269	-1.194794	-1.278012
C	-1.416320	-4.419849	0.546250
H	-1.074934	-5.350271	0.992750
C	0.326685	4.051910	0.155214
C	-2.703038	-4.291573	0.086675
H	-3.410102	-5.108686	0.190220
C	6.771144	-1.049706	0.497884
H	6.507392	-1.248338	1.538431
H	7.038283	0.001747	0.376332
H	7.597418	-1.687975	0.189808
C	0.865193	4.200978	1.580347
H	0.075197	3.984488	2.306174
H	1.203293	5.229957	1.735062
H	1.705371	3.528489	1.762970
C	1.413765	4.329949	-0.886272
H	1.750755	5.365553	-0.783917
H	1.015316	4.196614	-1.896820
H	2.274721	3.673459	-0.755062
H	2.294523	0.787730	-0.027892
H	-6.762883	-0.358331	0.425391

The Cartesian coordinates (Å) and energies at 273.15 K for the catalysis process.

4f-a

Imaginary frequency: None

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -2528.395508 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 0.611192 a.u.

Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -2527.784316 a.u.

Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -2527.778074 a.u.

P	0.055170	-0.605173	-0.881113
O	0.384765	-0.098044	-2.212942

O	-0.739483	0.340176	0.124763
H	-1.452939	0.834440	-0.312749
O	-0.795325	-1.982465	-0.982802
C	-1.280251	-2.525401	0.201398
C	-0.477630	-3.379424	0.942235
C	-0.923139	-3.823236	2.191146
C	-2.181932	-3.474308	2.661394
C	-2.993017	-2.654294	1.880406
C	-2.552735	-2.149917	0.651776
C	-3.416522	-1.249662	-0.159888
C	-3.792994	-1.651147	-1.445284
C	-4.653240	-0.886527	-2.218976
C	-5.165448	0.321772	-1.735499
C	-4.768747	0.769258	-0.446985
C	-5.259083	2.018306	0.047046
C	-4.846860	2.492852	1.320026
C	-5.333924	3.719252	1.785070
C	-6.215020	4.469861	1.014602
C	-6.620757	4.014104	-0.235028
C	-6.153021	2.795281	-0.738452
C	-6.546113	2.304484	-2.033320
C	-6.072233	1.128987	-2.509238
H	-6.368010	0.768666	-3.490840
H	-7.230379	2.906418	-2.625336
H	-7.305375	4.605733	-0.836965
H	-6.585524	5.419016	1.388936
H	-5.011911	4.080615	2.758009
C	-3.920285	1.698470	2.081531
C	-3.462790	0.508131	1.624173
C	-3.884620	-0.017762	0.346415
H	-2.741910	-0.058025	2.204084
H	-3.579598	2.083055	3.039179
H	-4.940095	-1.226232	-3.210367
H	-3.405882	-2.589101	-1.831566
H	-3.981659	-2.370209	2.230551
H	-2.528032	-3.822291	3.630372
C	0.159163	-4.628107	2.873322
H	0.248978	-4.391416	3.937549
H	-0.045065	-5.703765	2.796771
C	1.411022	-4.238066	2.065676
H	2.200792	-4.995370	2.085512
H	1.825140	-3.302890	2.459046
C	0.880545	-3.977164	0.626576
C	1.911561	-3.261151	-0.225633

C	2.159640	-1.907984	-0.396698
C	3.256971	-1.451767	-1.138156
C	4.074898	-2.410538	-1.746014
C	3.804616	-3.773295	-1.643370
C	2.720610	-4.191780	-0.884422
C	2.190505	-5.590403	-0.664000
H	2.202504	-6.190802	-1.578176
H	2.791759	-6.125371	0.082323
C	0.765218	-5.321810	-0.145341
H	0.366478	-6.126779	0.479893
H	0.085875	-5.178591	-0.992764
H	4.431443	-4.495059	-2.159374
H	4.926552	-2.065993	-2.325542
C	3.531086	-0.002485	-1.330096
C	3.581313	0.494725	-2.634656
C	3.851245	1.830552	-2.888088
C	4.080239	2.722390	-1.836780
C	4.037139	2.238473	-0.501673
C	4.273628	3.141426	0.581257
C	4.243611	2.671362	1.920749
C	4.472864	3.570000	2.968215
C	4.728902	4.911742	2.708562
C	4.763640	5.380050	1.399592
C	4.540366	4.513917	0.323926
C	4.572398	4.970521	-1.041072
C	4.354298	4.116453	-2.068509
H	4.379243	4.468070	-3.096661
H	4.776777	6.021670	-1.227258
H	4.966069	6.428872	1.198616
H	4.904410	5.597812	3.531531
H	4.448776	3.204850	3.991649
C	3.986297	1.275280	2.151350
C	3.761406	0.418547	1.127435
C	3.763706	0.865451	-0.243730
H	3.580388	-0.631473	1.332094
H	3.979840	0.917643	3.177735
H	3.870858	2.197612	-3.910640
H	3.365977	-0.181735	-3.456261
O	1.257269	-0.981451	0.127172

4f-b

Imaginary frequency: None

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -2528.393964 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 0.610540 a.u.
Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -2527.783424 a.u.
Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -2527.777025 a.u.

P	-0.026131	0.487227	-0.130521
O	-0.893418	-0.360458	-0.948942
O	1.018501	-0.200481	0.856905
H	1.490372	-0.943126	0.443352
O	0.823482	1.506136	-1.062313
C	1.768396	2.312457	-0.439253
C	1.383120	3.534650	0.090099
C	2.312701	4.287519	0.813965
C	3.627578	3.860177	0.942579
C	4.005832	2.650851	0.364846
C	3.083270	1.845048	-0.311503
C	3.483469	0.529501	-0.880344
C	3.311412	0.299857	-2.249212
C	3.724950	-0.883495	-2.841975
C	4.329785	-1.889590	-2.082252
C	4.486455	-1.694335	-0.683684
C	5.082176	-2.724383	0.109105
C	5.219344	-2.555809	1.512316
C	5.809050	-3.572423	2.270925
C	6.258926	-4.739420	1.663514
C	6.121994	-4.915843	0.290987
C	5.534631	-3.924842	-0.502851
C	5.369191	-4.085127	-1.924045
C	4.790703	-3.118077	-2.674401
H	4.662461	-3.249271	-3.745547
H	5.716964	-5.008059	-2.380546
H	6.469856	-5.831673	-0.179572
H	6.715934	-5.519470	2.264494
H	5.909848	-3.439292	3.344821
C	4.720510	-1.345716	2.109011
C	4.163848	-0.362463	1.361575
C	4.050218	-0.482101	-0.073929
H	3.764663	0.525980	1.838812
H	4.787525	-1.240074	3.188705
H	3.586935	-1.033974	-3.909164
H	2.850763	1.075577	-2.853158
H	5.029376	2.297846	0.456448
H	4.350176	4.450014	1.499272
C	1.644952	5.505855	1.409211
H	1.961325	5.694328	2.439302

H	1.882171	6.406275	0.828356
C	0.152343	5.143939	1.298912
H	-0.508690	6.014885	1.256679
H	-0.142052	4.533410	2.159459
C	0.057486	4.269414	0.015864
C	-1.273763	3.546304	-0.075761
C	-1.668427	2.310714	0.416201
C	-2.990242	1.864115	0.301723
C	-3.908409	2.703990	-0.340037
C	-3.521475	3.922791	-0.891099
C	-2.201205	4.333621	-0.763640
C	-1.525126	5.562148	-1.328511
H	-1.844970	5.781529	-2.351369
H	-1.749965	6.449050	-0.722376
C	-0.034670	5.184318	-1.238094
H	0.634390	6.047734	-1.171041
H	0.250266	4.598632	-2.118855
H	-4.243163	4.535131	-1.424312
H	-4.937654	2.367191	-0.426598
C	-3.417082	0.556179	0.866923
C	-3.240510	0.324731	2.233942
C	-3.703927	-0.835522	2.835086
C	-4.369247	-1.809068	2.083945
C	-4.530877	-1.608540	0.687005
C	-5.197246	-2.602661	-0.094472
C	-5.346301	-2.425239	-1.495362
C	-6.009950	-3.404146	-2.242510
C	-6.520028	-4.542199	-1.627509
C	-6.371917	-4.727233	-0.257353
C	-5.712656	-3.773226	0.525320
C	-5.536662	-3.941304	1.944333
C	-4.892864	-3.007983	2.684463
H	-4.759416	-3.144579	3.754592
H	-5.931923	-4.841558	2.407751
H	-6.767785	-5.619901	0.219965
H	-7.033553	-5.292826	-2.220526
H	-6.119528	-3.265098	-3.314928
C	-4.783540	-1.248399	-2.101515
C	-4.155902	-0.302755	-1.363470
C	-4.034427	-0.427042	0.068350
H	-3.698444	0.552646	-1.847979
H	-4.854434	-1.143663	-3.181063
H	-3.565389	-0.989495	3.901963
H	-2.742991	1.082975	2.831674

O	-0.704368	1.460433	0.962434

4f-c

Imaginary frequency: None

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -2528.395714 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 0.611938 a.u.

Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -2527.783776 a.u.

Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -2527.777612 a.u.

P	0.102134	-0.122055	-0.171747
O	0.059556	-0.945562	-1.379885
O	0.192963	-0.832341	1.250762
H	0.956239	-1.432757	1.316176
O	1.345171	0.920098	-0.234484
C	1.559848	1.737612	0.867785
C	0.883506	2.942650	0.966084
C	1.012545	3.706194	2.130630
C	1.853660	3.298843	3.156743
C	2.567108	2.110350	3.015703
C	2.431018	1.307709	1.878928
C	3.148352	0.007619	1.780780
C	2.939069	-0.952789	2.778308
C	3.573192	-2.188238	2.740010
C	4.454353	-2.504152	1.700430
C	4.692934	-1.539075	0.684891
C	5.598589	-1.845884	-0.378005
C	5.853978	-0.888626	-1.394003
C	6.740574	-1.206952	-2.427910
C	7.370132	-2.445901	-2.466154
C	7.127999	-3.388441	-1.472838
C	6.247820	-3.108931	-0.421854
C	5.979044	-4.064376	0.620736
C	5.125302	-3.776226	1.631442
H	4.929102	-4.502582	2.415625
H	6.480880	-5.027431	0.576923
H	7.622151	-4.355902	-1.504970
H	8.054653	-2.678901	-3.275800
H	6.931088	-0.470974	-3.204426
C	5.195204	0.387279	-1.317726
C	4.336135	0.681003	-0.314055
C	4.039289	-0.274912	0.723724
H	3.859257	1.654237	-0.275278
H	5.404774	1.120859	-2.091630

H	3.387733	-2.920504	3.521316
H	2.245207	-0.721940	3.582893
H	3.238035	1.779038	3.803330
H	1.948709	3.889696	4.063303
C	0.102193	4.911116	2.064313
H	-0.407388	5.104400	3.012682
H	0.670294	5.815368	1.811113
C	-0.866459	4.524834	0.931888
H	-1.314332	5.383961	0.423143
H	-1.676642	3.908016	1.336947
C	-0.014842	3.648383	-0.030882
C	-0.888617	2.893935	-1.014456
C	-1.505610	1.657543	-0.907799
C	-2.402978	1.202563	-1.881262
C	-2.609728	2.007612	-3.005391
C	-1.938302	3.217986	-3.170661
C	-1.081966	3.656528	-2.170495
C	-0.213641	4.894226	-2.126592
H	0.274714	5.095578	-3.084478
H	-0.807398	5.781644	-1.872956
C	0.787819	4.553762	-1.006510
H	1.205277	5.434194	-0.507887
H	1.617557	3.969275	-1.419884
H	-2.083336	3.804144	-4.073778
H	-3.300391	1.656836	-3.766809
C	-3.112326	-0.098079	-1.745798
C	-2.912282	-1.082515	-2.715643
C	-3.589808	-2.291941	-2.662846
C	-4.496109	-2.557653	-1.632200
C	-4.710383	-1.571168	-0.632559
C	-5.638362	-1.828307	0.424085
C	-5.867823	-0.848305	1.425441
C	-6.779422	-1.117045	2.452154
C	-7.459856	-2.328575	2.497216
C	-7.243165	-3.293130	1.518893
C	-6.338712	-3.063962	0.476356
C	-6.095281	-4.043007	-0.550702
C	-5.217938	-3.801106	-1.553352
H	-5.040062	-4.545756	-2.324807
H	-6.635578	-4.984848	-0.501454
H	-7.777943	-4.238680	1.555487
H	-8.165798	-2.522109	3.299040
H	-6.950816	-0.363251	3.216154
C	-5.157929	0.399242	1.339425

C	-4.282337	0.646844	0.336819
C	-4.013575	-0.331931	-0.687415
H	-3.772958	1.603710	0.290233
H	-5.344987	1.150537	2.102284
H	-3.411969	-3.048716	-3.422085
H	-2.185597	-0.898185	-3.500891
O	-1.169661	0.817333	0.156437

1a

Imaginary frequency: None

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -723.218641 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 0.165461 a.u.

Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -723.053180 a.u.

Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -723.051417 a.u.

C	-4.917694	-0.050713	-0.105727
C	-4.009556	0.970824	-0.234228
C	-2.619404	0.718356	-0.131016
C	-2.178652	-0.613651	0.108600
C	-3.139334	-1.649660	0.237729
C	-4.479103	-1.374696	0.132876
H	-5.209268	-2.171377	0.233507
H	-2.792938	-2.663303	0.420925
C	-0.787307	-0.862012	0.212375
C	0.117019	0.163240	0.080729
C	-0.315392	1.497136	-0.156247
C	-1.652000	1.757365	-0.258353
H	-2.001549	2.770708	-0.437968
H	0.429157	2.279421	-0.248310
N	1.483727	-0.216278	0.194572
N	2.286695	0.724076	0.056977
C	3.653178	0.300017	0.207553
O	4.415927	0.872689	0.935862
O	3.956358	-0.715391	-0.598775
C	5.324134	-1.124518	-0.534318
H	5.980415	-0.282940	-0.765890
H	5.559370	-1.496829	0.464949
H	5.430117	-1.914420	-1.275580
H	-0.416851	-1.866989	0.395066
H	-4.344314	1.988461	-0.417176
H	-5.980696	0.154168	-0.186926

2a

Imaginary frequency: None

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -689.7340317 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 0.234977 a.u.

Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -689.499055 a.u.

Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -689.497475 a.u.

C	0.596802	0.400623	-0.000292
C	0.000789	1.778449	-0.000310
C	-1.488789	1.457545	-0.000405
N	-1.550872	0.080680	-0.000650
N	-0.308947	-0.515634	-0.000437
C	-2.794616	-0.718735	0.000173
C	-3.597156	-0.372859	-1.259213
H	-4.526017	-0.951780	-1.272624
H	-3.021028	-0.622203	-2.155755
H	-3.844813	0.690627	-1.277904
C	-2.434135	-2.202253	-0.000540
H	-1.851847	-2.471405	0.884133
H	-1.853021	-2.470824	-0.886171
H	-3.363282	-2.779773	-0.000121
C	-3.595218	-0.373546	1.260978
H	-3.842883	0.689927	1.280573
H	-3.017702	-0.623321	2.156508
H	-4.524048	-0.952490	1.275546
O	-2.428394	2.226363	-0.000038
H	0.263856	2.367376	-0.884872
H	0.263807	2.367483	0.884188
C	2.028449	0.079023	-0.000117
C	2.455865	-1.255286	-0.000360
C	3.810541	-1.553993	-0.000190
C	4.757803	-0.529152	0.000212
C	4.340072	0.797644	0.000443
C	2.981308	1.101095	0.000279
H	2.661234	2.139773	0.000458
H	5.070994	1.600368	0.000759
H	5.817103	-0.766525	0.000335
H	4.132972	-2.590717	-0.000383
H	1.710275	-2.044090	-0.000697

2a-enol

Imaginary frequency: None

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -689.7331938 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 0.234061 a.u.
Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -689.499132 a.u.
Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -689.497009 a.u.

C	0.599080	0.422235	-0.000210
C	-0.025637	1.693230	-0.000798
C	-1.368915	1.393580	-0.000539
N	-1.505045	0.047292	-0.000016
N	-0.297638	-0.555699	0.000117
C	-2.762260	-0.734987	0.000358
C	-3.558209	-0.390647	1.263891
H	-4.477762	-0.983755	1.287473
H	-3.827416	0.667667	1.287534
H	-2.969699	-0.627439	2.155309
C	-3.558471	-0.391455	-1.263230
H	-2.970103	-0.628703	-2.154621
H	-3.827796	0.666815	-1.287436
H	-4.477965	-0.984674	-1.286297
C	-2.408705	-2.220593	0.000793
H	-1.825679	-2.487477	0.884604
H	-1.825961	-2.488053	-0.883032
H	-3.341345	-2.792722	0.001120
O	-2.473659	2.177917	-0.000753
C	2.039257	0.111136	-0.000088
C	2.468840	-1.220789	-0.001108
C	3.824508	-1.523138	-0.000964
C	4.774098	-0.502626	0.000158
C	4.354603	0.824325	0.001166
C	2.996643	1.128502	0.001053
H	2.680211	2.167833	0.001944
H	5.085492	1.627599	0.002101
H	5.833390	-0.740671	0.000254
H	4.143435	-2.561292	-0.001753
H	1.722731	-2.008835	-0.002024
H	-2.184339	3.100918	-0.001370
H	0.421874	2.675661	-0.001382

Ts-2a-tautomerization

Imaginary frequency: -1023.8832
Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3218.137797 a.u.
Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 0.868059 a.u.
Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3217.269738 a.u.
Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)):

-3217.261155 a.u.

P	1.610670	0.148844	-0.420646
O	0.953945	1.226298	-1.222459
O	0.754265	-0.967802	0.152658
H	-0.448039	-0.530898	0.348013
O	2.820326	-0.446858	-1.316769
C	3.673753	-1.364010	-0.718403
C	4.792695	-0.899265	-0.039568
C	5.610127	-1.818480	0.625376
C	5.351048	-3.181313	0.561824
C	4.237993	-3.628417	-0.147167
C	3.369710	-2.733099	-0.778368
C	2.113692	-3.177093	-1.450005
C	1.990510	-3.031188	-2.832889
C	0.795659	-3.302187	-3.484609
C	-0.339378	-3.674505	-2.758105
C	-0.237420	-3.819698	-1.348377
C	-1.413006	-4.097341	-0.582396
C	-1.333959	-4.198014	0.831302
C	-2.501436	-4.407220	1.571863
C	-3.732562	-4.521782	0.936184
C	-3.818140	-4.446964	-0.449727
C	-2.673164	-4.234314	-1.226258
C	-2.730403	-4.135215	-2.661629
C	-1.618069	-3.873079	-3.390427
H	-1.673397	-3.784674	-4.472736
H	-3.694468	-4.265000	-3.148364
H	-4.781235	-4.546662	-0.944807
H	-4.632295	-4.666548	1.526915
H	-2.437142	-4.447502	2.657367
C	-0.048998	-4.048736	1.460390
C	1.061036	-3.768838	0.739335
C	1.009327	-3.618895	-0.694468
H	2.008567	-3.608150	1.241903
H	0.001354	-4.134148	2.543113
H	0.723614	-3.186611	-4.562879
H	2.847630	-2.677322	-3.398718
H	4.006740	-4.689274	-0.190700
H	5.991927	-3.890292	1.078507
C	6.686939	-1.094428	1.400155
H	6.858307	-1.531300	2.388345
H	7.643704	-1.121707	0.862794
C	6.125904	0.336507	1.466545
H	6.894239	1.104431	1.598197

H	5.419056	0.415027	2.299913
C	5.338260	0.511337	0.135192
C	4.448241	1.742386	0.184044
C	3.136237	1.889581	0.604341
C	2.518575	3.147326	0.658068
C	3.267013	4.260950	0.265219
C	4.569990	4.126329	-0.215605
C	5.148855	2.864774	-0.266024
C	6.493180	2.446395	-0.819204
H	6.736765	2.958941	-1.754485
H	7.299381	2.670315	-0.108959
C	6.314651	0.925472	-1.001124
H	7.255332	0.367152	-0.964252
H	5.834211	0.723203	-1.964572
H	5.115477	4.999828	-0.561580
H	2.801360	5.241922	0.309784
C	1.104891	3.251733	1.120843
C	0.794697	2.822342	2.415437
C	-0.502362	2.867711	2.907099
C	-1.550664	3.331102	2.104586
C	-1.263740	3.759516	0.780466
C	-2.332412	4.201409	-0.062361
C	-2.063946	4.623075	-1.391141
C	-3.119008	5.068656	-2.194642
C	-4.421840	5.095248	-1.706218
C	-4.695622	4.668186	-0.411911
C	-3.667952	4.214811	0.423871
C	-3.922884	3.758506	1.765297
C	-2.914164	3.339254	2.565600
H	-3.114837	2.991764	3.575709
H	-4.949430	3.759529	2.122394
H	-5.715138	4.681751	-0.034961
H	-5.229766	5.444853	-2.341763
H	-2.908105	5.392132	-3.210639
C	-0.708978	4.557628	-1.871144
C	0.302998	4.125098	-1.082287
C	0.071818	3.725578	0.285257
H	1.307380	4.035365	-1.480303
H	-0.515389	4.844565	-2.901465
H	-0.715850	2.525907	3.916581
H	1.596147	2.440612	3.041255
O	2.388054	0.756105	0.879119
C	-2.595512	-0.595182	1.149277
C	-1.513166	0.210854	0.602856

C	-2.054958	0.595185	-0.672421
N	-3.226623	-0.022459	-0.822537
N	-3.569933	-0.754498	0.299160
C	-4.139506	0.059733	-1.993049
C	-4.646516	1.501867	-2.082074
H	-5.320106	1.603862	-2.939181
H	-3.817441	2.205473	-2.206435
H	-5.194602	1.769199	-1.173250
C	-3.373583	-0.343795	-3.256694
H	-2.955808	-1.348683	-3.141520
H	-2.566369	0.355508	-3.478520
H	-4.070071	-0.351210	-4.101093
C	-5.296477	-0.910666	-1.766278
H	-5.958554	-0.859314	-2.635893
H	-5.865383	-0.654618	-0.870277
H	-4.927073	-1.934438	-1.656215
O	-1.548304	1.357297	-1.597960
C	-2.613752	-1.230977	2.472151
C	-3.819064	-1.664310	3.033743
C	-3.823786	-2.293044	4.272045
C	-2.625986	-2.494699	4.959445
C	-1.424408	-2.063410	4.402036
C	-1.415217	-1.429775	3.162112
H	-0.474877	-1.123217	2.708088
H	-0.489283	-2.224812	4.930125
H	-2.630935	-2.986478	5.927666
H	-4.761819	-2.627431	4.705148
H	-4.740483	-1.506639	2.481550
H	-0.535163	1.435168	-1.451337
H	-1.003164	0.964506	1.203825

4f-2a-enol complex

Imaginary frequency: None

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3218.153380 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 0.872249 a.u.

Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3217.281131 a.u.

Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3217.272078 a.u.

P	1.625886	0.242091	-0.512936
O	0.878163	1.209796	-1.337962
O	0.854539	-0.981145	0.093264
H	-0.121388	-0.821450	0.173789
O	2.852603	-0.375204	-1.339223

C	3.748663	-1.232408	-0.699506
C	4.825966	-0.686728	-0.015029
C	5.685399	-1.544046	0.679799
C	5.508919	-2.920614	0.636214
C	4.437452	-3.445896	-0.082448
C	3.525754	-2.616971	-0.742923
C	2.307325	-3.153721	-1.415897
C	2.186407	-3.053202	-2.802828
C	1.010699	-3.404377	-3.451758
C	-0.110067	-3.808670	-2.719904
C	-0.009634	-3.908064	-1.305660
C	-1.178023	-4.205173	-0.535680
C	-1.105971	-4.243826	0.881154
C	-2.269082	-4.464081	1.624541
C	-3.489514	-4.653818	0.986830
C	-3.567497	-4.640515	-0.401314
C	-2.427248	-4.413381	-1.180243
C	-2.480148	-4.363504	-2.618161
C	-1.376370	-4.078466	-3.350937
H	-1.430399	-4.022512	-4.435229
H	-3.436422	-4.542512	-3.104242
H	-4.523270	-4.793054	-0.896741
H	-4.387873	-4.805036	1.577721
H	-2.210637	-4.452866	2.710854
C	0.167324	-4.021518	1.511753
C	1.272866	-3.733468	0.786440
C	1.223834	-3.633396	-0.652507
H	2.210218	-3.522150	1.289558
H	0.211406	-4.059452	2.597308
H	0.939238	-3.322649	-4.533037
H	3.027051	-2.670427	-3.374735
H	4.270912	-4.519138	-0.111005
H	6.182286	-3.580748	1.175685
C	6.707485	-0.744702	1.453807
H	6.885879	-1.149811	2.454085
H	7.672882	-0.732122	0.931782
C	6.068960	0.654263	1.479071
H	6.792897	1.465619	1.600797
H	5.348593	0.714528	2.302248
C	5.291565	0.754945	0.133729
C	4.339636	1.938927	0.145493
C	3.018750	2.036645	0.550340
C	2.341839	3.262519	0.590486
C	3.043390	4.403021	0.187211

C	4.353179	4.320203	-0.286324
C	4.991465	3.087005	-0.313940
C	6.360530	2.725686	-0.845880
H	6.587199	3.231154	-1.789121
H	7.146876	3.004574	-0.132985
C	6.261170	1.194460	-0.999063
H	7.227936	0.685212	-0.937577
H	5.805640	0.948739	-1.964596
H	4.860128	5.212697	-0.642196
H	2.533728	5.362160	0.218313
C	0.928947	3.312057	1.064221
C	0.656511	2.893572	2.371218
C	-0.633343	2.897458	2.881527
C	-1.709562	3.305383	2.086773
C	-1.459782	3.726695	0.753299
C	-2.556967	4.112031	-0.078969
C	-2.325651	4.533479	-1.414469
C	-3.410096	4.912966	-2.211765
C	-4.707677	4.873117	-1.710330
C	-4.944003	4.448999	-0.407928
C	-3.885119	4.063403	0.422926
C	-4.101714	3.617588	1.774261
C	-3.064769	3.260473	2.567728
H	-3.235743	2.917217	3.584549
H	-5.122918	3.572355	2.143458
H	-5.958883	4.410632	-0.020407
H	-5.540527	5.167869	-2.341359
H	-3.227266	5.234130	-3.233924
C	-0.975208	4.527669	-1.911122
C	0.064762	4.138608	-1.135660
C	-0.131629	3.736442	0.236857
H	1.066636	4.091074	-1.548221
H	-0.807429	4.819619	-2.944683
H	-0.819828	2.560447	3.897771
H	1.482373	2.558871	2.992640
O	2.308773	0.864105	0.813627
C	-2.552330	-0.615417	1.159952
C	-1.650954	0.340543	0.619475
C	-2.168891	0.604236	-0.643466
N	-3.268803	-0.168393	-0.799802
N	-3.516688	-0.912704	0.302491
C	-4.173165	-0.196240	-1.972758
C	-4.800935	1.194310	-2.120037
H	-5.490301	1.199663	-2.971040

H	-4.036116	1.958601	-2.284645
H	-5.360020	1.454207	-1.215229
C	-3.366343	-0.578756	-3.218002
H	-2.895282	-1.556707	-3.075705
H	-2.593726	0.161570	-3.431458
H	-4.041401	-0.639594	-4.078028
C	-5.254456	-1.245140	-1.723304
H	-5.915966	-1.266728	-2.594894
H	-5.842026	-1.007019	-0.834272
H	-4.810381	-2.234489	-1.582977
O	-1.783724	1.438268	-1.610941
C	-2.508817	-1.249983	2.486448
C	-3.676528	-1.773168	3.052705
C	-3.637268	-2.403680	4.290088
C	-2.430441	-2.520525	4.980701
C	-1.265333	-1.998222	4.423358
C	-1.302861	-1.364799	3.183503
H	-0.385208	-0.984072	2.739291
H	-0.320650	-2.088318	4.952214
H	-2.399119	-3.012882	5.948109
H	-4.550531	-2.804753	4.720231
H	-4.606492	-1.683313	2.499822
H	-0.808132	1.568683	-1.537485
H	-0.875075	0.900587	1.126087

4f-2a complex

Imaginary frequency: None

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3218.155259 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 0.869888 a.u.

Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3217.285371 a.u.

Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3217.275687 a.u.

P	1.707428	-0.287867	-0.162085
O	1.478455	0.954435	-1.085283
O	0.539605	-0.988903	0.389709
H	-1.118098	-0.228036	1.284786
O	2.696980	-1.141394	-1.114158
C	3.174031	-2.305360	-0.519373
C	4.360145	-2.251921	0.197047
C	4.770456	-3.382591	0.908961
C	4.035967	-4.560645	0.855051
C	2.866350	-4.602150	0.096736
C	2.402923	-3.475000	-0.588079

C	1.136289	-3.477544	-1.377208
C	1.222097	-3.304235	-2.760757
C	0.087089	-3.234411	-3.554440
C	-1.185217	-3.302014	-2.979604
C	-1.296799	-3.463107	-1.572084
C	-2.592399	-3.469739	-0.966218
C	-2.720246	-3.609450	0.441233
C	-3.993759	-3.599085	1.018841
C	-5.128270	-3.437941	0.230906
C	-5.014025	-3.300568	-1.147503
C	-3.757989	-3.319353	-1.765855
C	-3.609175	-3.187444	-3.191730
C	-2.383587	-3.184560	-3.769505
H	-2.278087	-3.075897	-4.846040
H	-4.507963	-3.085138	-3.795228
H	-5.902857	-3.178715	-1.762082
H	-6.107504	-3.411973	0.700077
H	-4.087179	-3.689303	2.099385
C	-1.523230	-3.732595	1.230977
C	-0.295321	-3.711156	0.660947
C	-0.129405	-3.576883	-0.765691
H	0.594478	-3.754020	1.279630
H	-1.631338	-3.819393	2.309685
H	0.180012	-3.104873	-4.629480
H	2.204875	-3.211327	-3.214067
H	2.276789	-5.513706	0.051211
H	4.354757	-5.436360	1.413412
C	6.007340	-3.063705	1.717853
H	5.975346	-3.497087	2.721800
H	6.908991	-3.451264	1.226274
C	5.997566	-1.523274	1.732021
H	6.987902	-1.079739	1.874531
H	5.346083	-1.168680	2.538341
C	5.361599	-1.120515	0.369940
C	4.950906	0.342924	0.350643
C	3.764578	0.949658	0.728609
C	3.608404	2.343573	0.715334
C	4.693166	3.116396	0.290807
C	5.878633	2.523438	-0.145184
C	5.997043	1.139190	-0.122875
C	7.131731	0.263938	-0.606467
H	7.561092	0.617643	-1.548340
H	7.945575	0.233592	0.129407
C	6.449878	-1.112601	-0.741035

H	7.143953	-1.954030	-0.649660
H	5.953853	-1.183653	-1.715252
H	6.693351	3.141813	-0.511236
H	4.587995	4.197896	0.280369
C	2.306647	2.925692	1.150805
C	1.861933	2.641236	2.445982
C	0.631931	3.084234	2.905187
C	-0.215281	3.820688	2.070330
C	0.210841	4.119349	0.749531
C	-0.669118	4.826637	-0.127907
C	-0.274985	5.099349	-1.463954
C	-1.148192	5.792456	-2.309224
C	-2.396525	6.206730	-1.856127
C	-2.797611	5.928583	-0.554376
C	-1.952647	5.238026	0.322147
C	-2.348849	4.924589	1.670165
C	-1.519315	4.251768	2.502910
H	-1.824764	4.017371	3.519869
H	-3.332689	5.242597	2.005187
H	-3.777164	6.243983	-0.204398
H	-3.063331	6.743340	-2.524179
H	-0.840790	5.999287	-3.331059
C	1.007988	4.625737	-1.910505
C	1.839698	3.946644	-1.085552
C	1.482821	3.675918	0.286347
H	2.781533	3.559765	-1.458898
H	1.290470	4.809006	-2.943999
H	0.311332	2.849996	3.917253
H	2.497537	2.045164	3.093990
O	2.677115	0.155832	1.060205
C	-3.285813	0.023422	1.313994
C	-1.888832	0.552593	1.234255
C	-1.888478	1.144378	-0.153330
N	-3.124548	0.898916	-0.659031
N	-3.949832	0.228279	0.229145
C	-3.579270	1.242485	-2.026625
C	-3.565567	2.768547	-2.164616
H	-3.881778	3.050989	-3.174286
H	-2.561949	3.166981	-1.989645
H	-4.253940	3.223693	-1.444945
C	-2.627600	0.589778	-3.035826
H	-2.595931	-0.493321	-2.880980
H	-1.617838	0.993694	-2.942681
H	-2.991339	0.783743	-4.050305

C	-4.990644	0.694446	-2.224208
H	-5.316876	0.951010	-3.236718
H	-5.692290	1.126286	-1.506492
H	-5.007694	-0.393434	-2.108368
O	-0.986858	1.740353	-0.748167
C	-3.872857	-0.686031	2.455773
C	-5.253569	-0.908540	2.521587
C	-5.793659	-1.634356	3.574058
C	-4.964684	-2.144634	4.575026
C	-3.592382	-1.916935	4.519666
C	-3.047879	-1.186597	3.466128
H	-1.974063	-1.027053	3.414857
H	-2.942114	-2.309266	5.295615
H	-5.390230	-2.712843	5.396613
H	-6.865259	-1.804809	3.618208
H	-5.884254	-0.518710	1.728602
H	0.565007	1.346423	-0.934894
H	-1.655970	1.318654	1.982514

Ts-major-a

Imaginary frequency: -229.4137

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3941.384023 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 1.067715 a.u.

Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3940.316308 a.u.

Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3940.305548 a.u.

P	-1.509274	-1.574608	0.542799
O	-0.281716	-0.979704	-0.084740
O	-1.840080	-1.274403	1.972148
H	-0.566402	-0.551096	2.725161
O	-2.777337	-1.185795	-0.433734
C	-3.996854	-1.717846	-0.047397
C	-4.376265	-2.977995	-0.498762
C	-5.546937	-3.563875	-0.003935
C	-6.368173	-2.882641	0.881709
C	-6.001723	-1.602097	1.284155
C	-4.817030	-1.005645	0.840958
C	-4.475460	0.345979	1.365843
C	-4.264975	0.492604	2.740167
C	-4.047365	1.738607	3.309711
C	-4.047313	2.894250	2.521499
C	-4.263958	2.770035	1.124421
C	-4.237527	3.939607	0.300560

C	-4.410945	3.824597	-1.105288
C	-4.360869	4.977365	-1.898933
C	-4.136371	6.224632	-1.324563
C	-3.951035	6.343609	0.049133
C	-3.995379	5.216240	0.877706
C	-3.790413	5.306337	2.300173
C	-3.816001	4.200393	3.080540
H	-3.655016	4.276324	4.152785
H	-3.610130	6.286793	2.732885
H	-3.769599	7.318215	0.494550
H	-4.104064	7.110077	-1.952185
H	-4.498478	4.884730	-2.973117
C	-4.613872	2.515157	-1.667954
C	-4.639670	1.406714	-0.889720
C	-4.459901	1.486286	0.539008
H	-4.789655	0.429949	-1.337750
H	-4.742859	2.433488	-2.744034
H	-3.871542	1.825619	4.378782
H	-4.245564	-0.401402	3.354996
H	-6.629933	-1.045015	1.973551
H	-7.273323	-3.342663	1.267918
C	-5.691372	-4.974969	-0.524591
H	-6.036582	-5.671417	0.245317
H	-6.415815	-5.017988	-1.348306
C	-4.267271	-5.281338	-1.016605
H	-4.224189	-6.046682	-1.797747
H	-3.652252	-5.617645	-0.174683
C	-3.721692	-3.909361	-1.505726
C	-2.222917	-3.965475	-1.724280
C	-1.184146	-3.708596	-0.842611
C	0.152613	-3.914500	-1.221570
C	0.392579	-4.434683	-2.501053
C	-0.637377	-4.648883	-3.413737
C	-1.944146	-4.384171	-3.026988
C	-3.219330	-4.445431	-3.837896
H	-3.098188	-4.016893	-4.837303
H	-3.556284	-5.481566	-3.970188
C	-4.202072	-3.645057	-2.960335
H	-5.250314	-3.922098	-3.110768
H	-4.097224	-2.574846	-3.171415
H	-0.413944	-5.003987	-4.415910
H	1.418800	-4.645016	-2.788103
C	1.268759	-3.593305	-0.294757
C	1.199801	-4.032726	1.031688

C	2.225347	-3.786445	1.930529
C	3.385629	-3.117231	1.531040
C	3.483836	-2.664788	0.188115
C	4.679443	-2.005086	-0.241201
C	4.782707	-1.507200	-1.566130
C	5.953241	-0.853866	-1.966001
C	7.015277	-0.701440	-1.081928
C	6.925863	-1.190513	0.216462
C	5.768040	-1.839088	0.657056
C	5.627085	-2.301801	2.012677
C	4.485362	-2.895571	2.433092
H	4.372625	-3.219330	3.464420
H	6.455570	-2.141673	2.698081
H	7.745536	-1.043921	0.914918
H	7.912933	-0.179566	-1.399863
H	6.015729	-0.452204	-2.974296
C	3.648263	-1.649651	-2.436972
C	2.518074	-2.282362	-2.036587
C	2.404073	-2.866952	-0.721227
H	1.661943	-2.322237	-2.700530
H	3.707576	-1.214306	-3.430951
H	2.152091	-4.156024	2.949894
H	0.321483	-4.580430	1.355523
O	-1.488974	-3.205217	0.407081
C	0.371031	5.651328	-1.289277
C	-0.561919	4.699411	-0.908746
C	-0.160019	3.584608	-0.158169
C	1.201087	3.465408	0.221039
C	2.145117	4.420006	-0.211103
C	1.727982	5.507362	-0.957472
H	2.446633	6.254198	-1.279358
H	3.188571	4.294925	0.065271
C	1.565061	2.384795	1.078038
C	0.563852	1.554759	1.674268
C	-0.802282	1.646105	1.198945
C	-1.115433	2.598423	0.292861
H	-2.120107	2.665407	-0.103738
H	-1.564553	0.968839	1.573450
N	1.089444	0.708488	2.544799
N	0.392679	-0.254264	3.060081
C	1.084244	-1.125328	3.927367
O	2.236714	-1.021992	4.249087
O	0.225923	-2.058752	4.338977
C	0.750570	-2.959370	5.311234

H	1.684931	-3.400817	4.960185
H	0.939075	-2.430635	6.249042
H	-0.013525	-3.722163	5.447118
H	2.546080	2.373787	1.542795
H	-1.610733	4.809659	-1.177193
H	0.049423	6.516939	-1.861274
C	3.634046	1.417621	-0.576782
N	3.620841	2.098166	-1.705800
N	2.426082	1.800519	-2.309233
C	1.702543	0.932018	-1.576372
O	0.555260	0.459524	-2.007884
H	0.140693	-0.135948	-1.293414
C	2.415705	0.700938	-0.385433
H	2.184306	-0.082405	0.321325
C	2.143355	2.272523	-3.685884
C	3.150917	3.364921	-4.038143
H	2.923553	3.729935	-5.044415
H	4.174872	2.988323	-4.016442
H	3.076520	4.197371	-3.332643
C	0.728437	2.851651	-3.751766
H	-0.030026	2.101044	-3.525715
H	0.553221	3.236954	-4.761538
H	0.631412	3.678982	-3.044323
C	2.293100	1.081405	-4.636980
H	1.620550	0.268334	-4.346874
H	2.049699	1.388914	-5.659019
H	3.325261	0.717010	-4.621916
C	4.744519	1.534065	0.380979
C	5.891333	2.268701	0.052925
C	6.926532	2.396553	0.969196
C	6.828993	1.800849	2.228162
C	5.688963	1.076721	2.562695
C	4.651209	0.940310	1.644386
H	3.772781	0.359321	1.921962
H	5.596608	0.605633	3.536823
H	7.638268	1.906580	2.944681
H	7.813990	2.963578	0.703626
H	5.957543	2.722902	-0.931225

Ts-major-b

Imaginary frequency: -220.7203

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3941.383819 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 1.064769 a.u.

Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3940.319050 a.u.
Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3940.307633 a.u.

P	-1.808530	-1.213629	0.125144
O	-0.438236	-0.930446	-0.419741
O	-2.368827	-0.386933	1.242864
H	-1.150541	0.086059	2.238117
O	-2.854870	-1.237019	-1.141601
C	-4.174117	-1.445359	-0.767430
C	-4.654885	-2.739372	-0.623385
C	-5.916753	-2.948805	-0.058680
C	-6.727206	-1.876199	0.286976
C	-6.265446	-0.582048	0.055901
C	-4.988151	-0.346391	-0.461595
C	-4.534177	1.040487	-0.751198
C	-4.330410	1.396798	-2.087439
C	-4.011123	2.695803	-2.450397
C	-3.871109	3.690067	-1.477365
C	-4.031113	3.341194	-0.108688
C	-3.816621	4.330939	0.901140
C	-3.944240	3.985623	2.272843
C	-3.723957	4.966445	3.245936
C	-3.377991	6.263793	2.883106
C	-3.240822	6.607278	1.543103
C	-3.453781	5.656792	0.538404
C	-3.314436	5.979909	-0.858150
C	-3.517229	5.043872	-1.817702
H	-3.409436	5.295296	-2.870095
H	-3.045485	6.998977	-1.125352
H	-2.965989	7.620694	1.262592
H	-3.210951	7.012303	3.651477
H	-3.822515	4.699956	4.294996
C	-4.275314	2.626648	2.613460
C	-4.473812	1.684468	1.661092
C	-4.365319	2.006883	0.258650
H	-4.669574	0.653450	1.932997
H	-4.344231	2.365341	3.666255
H	-3.868616	2.951111	-3.497204
H	-4.443200	0.632666	-2.850684
H	-6.890822	0.273531	0.296508
H	-7.705125	-2.038165	0.731560
C	-6.165238	-4.429611	0.125071
H	-6.613082	-4.659446	1.096639
H	-6.849169	-4.812421	-0.643355

C	-4.752305	-5.022974	-0.037091
H	-4.748862	-6.061028	-0.384506
H	-4.222642	-4.980111	0.920906
C	-4.043581	-4.064509	-1.033118
C	-2.544550	-4.279691	-1.085180
C	-1.541598	-3.731187	-0.296748
C	-0.204842	-4.112722	-0.473417
C	0.085382	-5.060919	-1.464635
C	-0.904503	-5.589855	-2.286565
C	-2.219033	-5.186373	-2.095943
C	-3.454952	-5.557723	-2.882662
H	-3.269546	-5.607669	-3.959739
H	-3.834922	-6.540076	-2.573119
C	-4.432206	-4.434177	-2.494216
H	-5.486220	-4.714773	-2.585461
H	-4.255378	-3.559745	-3.130306
H	-0.647079	-6.298035	-3.069208
H	1.118912	-5.370758	-1.592043
C	0.892037	-3.600840	0.388033
C	0.794448	-3.737128	1.776565
C	1.877529	-3.473951	2.603656
C	3.107685	-3.081750	2.067797
C	3.209493	-2.873483	0.666860
C	4.456821	-2.456295	0.104691
C	4.555047	-2.184329	-1.284963
C	5.777331	-1.749250	-1.810578
C	6.889844	-1.605093	-0.989617
C	6.806992	-1.891378	0.369450
C	5.600919	-2.312592	0.936466
C	5.470084	-2.568595	2.347729
C	4.277484	-2.910668	2.889819
H	4.177755	-3.074791	3.959619
H	6.350940	-2.445389	2.973043
H	7.675799	-1.764767	1.010333
H	7.829158	-1.257592	-1.409444
H	5.843122	-1.516794	-2.870583
C	3.376770	-2.333994	-2.097995
C	2.204549	-2.770384	-1.574943
C	2.083339	-3.096193	-0.174529
H	1.319863	-2.845411	-2.198981
H	3.442634	-2.075486	-3.152068
H	1.797079	-3.603229	3.679621
H	-0.140612	-4.097770	2.196858
O	-1.878031	-2.769691	0.637376

C	1.757448	5.707700	-1.621150
C	0.579127	5.037918	-1.330751
C	0.598265	3.891926	-0.522512
C	1.836564	3.450115	0.009649
C	3.029642	4.130288	-0.312066
C	2.987205	5.250038	-1.122800
H	3.901937	5.781408	-1.364054
H	3.970507	3.772767	0.096857
C	1.826520	2.340963	0.908480
C	0.590696	1.777097	1.353531
C	-0.645934	2.173057	0.707372
C	-0.618846	3.188163	-0.185360
H	-1.534344	3.522001	-0.660897
H	-1.582150	1.679201	0.953284
N	0.768882	0.885961	2.317571
N	-0.221333	0.164998	2.736729
C	0.061191	-0.796704	3.728583
O	1.098646	-0.910904	4.320959
O	-1.039847	-1.529657	3.894635
C	-0.946819	-2.535036	4.899367
H	-0.232894	-3.304781	4.597944
H	-0.626248	-2.097737	5.847412
H	-1.946262	-2.957423	4.983202
H	2.703679	2.137716	1.513821
H	-0.373694	5.391397	-1.716618
H	1.730939	6.596394	-2.244919
C	3.881947	0.976994	-0.492809
N	4.064085	1.572020	-1.654647
N	2.893857	1.413101	-2.345710
C	1.984626	0.717182	-1.634467
O	0.821037	0.403773	-2.150852
H	0.254958	-0.118329	-1.478880
C	2.555172	0.466154	-0.369742
H	2.151909	-0.221547	0.360289
C	2.789829	1.828681	-3.764515
C	4.022132	2.658735	-4.117710
H	3.927768	2.984703	-5.158052
H	4.941096	2.080034	-4.006361
H	4.091135	3.539588	-3.473130
C	1.532995	2.681480	-3.953645
H	1.596204	3.580304	-3.334027
H	0.628537	2.130768	-3.690435
H	1.466379	2.987951	-5.002696
C	2.735384	0.562341	-4.625164

H	1.877296	-0.056891	-4.349209
H	2.647443	0.835264	-5.681613
H	3.654684	-0.017340	-4.491490
C	4.922757	1.017814	0.545236
C	6.195058	1.520776	0.242065
C	7.174369	1.586198	1.223314
C	6.897021	1.157013	2.522444
C	5.634194	0.662056	2.830690
C	4.650296	0.588017	1.847650
H	3.674865	0.173049	2.100527
H	5.408674	0.315619	3.834730
H	7.663673	1.213237	3.289670
H	8.159834	1.970906	0.977072
H	6.398748	1.841911	-0.774951

Ts-minor-a

Imaginary frequency: -214.7423

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3941.383316 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 1.0660223 a.u.

Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3940.317293 a.u.

Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3940.305964 a.u.

P	-1.170237	-1.873693	0.430860
O	-0.014111	-1.115861	-0.170532
O	-1.514906	-1.717187	1.875874
H	-1.076234	-0.236190	2.629461
O	-2.484133	-1.491163	-0.497865
C	-3.657978	-2.142019	-0.152235
C	-3.933305	-3.392803	-0.691498
C	-5.039224	-4.117964	-0.235812
C	-5.912285	-3.576029	0.695605
C	-5.670488	-2.289211	1.170362
C	-4.548488	-1.561281	0.766033
C	-4.328791	-0.189436	1.304240
C	-3.882464	-0.024047	2.617447
C	-3.636913	1.241042	3.137621
C	-3.830181	2.386217	2.357928
C	-4.320551	2.240869	1.032888
C	-4.472150	3.395564	0.204733
C	-4.935140	3.258985	-1.131770
C	-5.056799	4.399624	-1.934999
C	-4.707900	5.652772	-1.443075
C	-4.235163	5.791737	-0.141939

C	-4.112778	4.679480	0.697406
C	-3.618267	4.792007	2.045341
C	-3.492433	3.701273	2.837709
H	-3.113908	3.794350	3.852254
H	-3.344748	5.777965	2.411462
H	-3.952984	6.771052	0.235365
H	-4.800915	6.527930	-2.079139
H	-5.421986	4.291963	-2.953281
C	-5.236205	1.940063	-1.623298
C	-5.055020	0.839981	-0.851916
C	-4.577218	0.944841	0.505133
H	-5.269441	-0.147881	-1.247417
H	-5.600904	1.842329	-2.642631
H	-3.255609	1.344819	4.150679
H	-3.664742	-0.909639	3.206393
H	-6.349715	-1.833750	1.885566
H	-6.767952	-4.142704	1.051888
C	-5.064697	-5.490128	-0.869396
H	-5.307409	-6.277726	-0.149692
H	-5.816274	-5.539615	-1.668072
C	-3.638633	-5.615667	-1.434774
H	-3.563854	-6.294238	-2.290405
H	-2.961847	-5.976428	-0.652508
C	-3.235779	-4.159096	-1.799015
C	-1.750691	-4.034759	-2.065176
C	-0.707595	-3.795106	-1.182173
C	0.622392	-3.814155	-1.625075
C	0.862493	-4.072628	-2.981302
C	-0.176978	-4.261587	-3.887467
C	-1.484219	-4.232637	-3.422014
C	-2.777273	-4.349872	-4.196051
H	-2.753306	-3.795934	-5.139331
H	-2.994703	-5.397230	-4.442070
C	-3.805317	-3.785966	-3.197555
H	-4.819967	-4.168111	-3.348304
H	-3.835322	-2.693496	-3.278754
H	0.036031	-4.421842	-4.940627
H	1.893329	-4.102642	-3.323400
C	1.769102	-3.630235	-0.697601
C	1.887359	-4.473827	0.410877
C	3.031588	-4.479567	1.195371
C	4.111584	-3.645565	0.889254
C	3.984941	-2.730110	-0.189337
C	5.071612	-1.855977	-0.503864

C	4.938050	-0.899220	-1.545556
C	6.010855	-0.049277	-1.837900
C	7.215090	-0.168649	-1.153030
C	7.361399	-1.116160	-0.144079
C	6.297406	-1.953044	0.211273
C	6.399829	-2.907723	1.284303
C	5.352389	-3.700096	1.617504
H	5.433604	-4.408578	2.437884
H	7.337402	-2.968449	1.830954
H	8.302471	-1.201769	0.393571
H	8.044330	0.486824	-1.400887
H	5.891302	0.702050	-2.614219
C	3.696739	-0.844085	-2.270656
C	2.684905	-1.708078	-2.009056
C	2.796505	-2.703421	-0.972238
H	1.745034	-1.631894	-2.546183
H	3.581804	-0.075959	-3.032448
H	3.110765	-5.164601	2.035441
H	1.074488	-5.158430	0.633487
O	-1.003240	-3.475727	0.132197
C	-0.548615	5.349714	-2.233317
C	-1.271665	4.210117	-1.924173
C	-0.830612	3.344975	-0.909977
C	0.364796	3.661502	-0.216821
C	1.095449	4.819142	-0.555176
C	0.639258	5.659415	-1.549889
H	1.204078	6.547023	-1.814666
H	2.018945	5.033216	-0.023339
C	0.796626	2.783130	0.820492
C	-0.108559	1.821032	1.358433
C	-1.270673	1.459317	0.580003
C	-1.580953	2.171765	-0.526529
H	-2.452951	1.899569	-1.115650
H	-1.911175	0.645938	0.899727
N	0.274145	1.338922	2.531248
N	-0.411251	0.407329	3.122301
C	0.107347	-0.062485	4.342871
O	1.113077	0.327027	4.872387
O	-0.725177	-0.992006	4.809899
C	-0.293004	-1.618754	6.017045
H	0.675261	-2.099864	5.864809
H	-0.206341	-0.880154	6.816891
H	-1.056812	-2.357767	6.250862
H	1.673043	3.037523	1.413303

H	-2.200432	3.985305	-2.442123
H	-0.905346	6.014704	-3.014458
C	3.073580	2.148658	-0.868197
N	4.002223	2.165751	0.069196
N	3.660944	1.189309	0.964376
C	2.514080	0.575178	0.598908
O	1.945495	-0.376285	1.295001
H	1.167990	-0.753624	0.741720
C	2.038822	1.222624	-0.552719
H	1.197775	0.876884	-1.138221
C	4.387250	1.124975	2.260432
C	5.854131	1.452615	1.987057
H	6.278080	0.736499	1.278635
H	6.405868	1.389243	2.929894
H	5.966513	2.456592	1.574679
C	4.268694	-0.275316	2.865853
H	3.269023	-0.460678	3.260255
H	4.986284	-0.349111	3.689171
H	4.509698	-1.044551	2.127550
C	3.763415	2.163361	3.197794
H	2.717469	1.915437	3.408654
H	4.307820	2.175845	4.147826
H	3.828583	3.162040	2.750486
C	3.105679	3.045578	-2.029612
C	4.054954	4.070929	-2.126570
C	4.013942	4.962185	-3.191477
C	3.030785	4.840682	-4.174791
C	2.097862	3.810438	-4.094505
C	2.137664	2.915652	-3.031367
H	1.395067	2.125420	-2.965306
H	1.331156	3.705947	-4.856244
H	2.998986	5.542391	-5.002849
H	4.749477	5.758652	-3.256229
H	4.806902	4.162414	-1.348483

Ts-minor-b

Imaginary frequency: -238.0828

Electronic energies (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3941.381192 a.u.

Thermal correction to Free energies at 273.15 K (M06-2X/6-31G(d)): 1.067596 a.u.

Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3940.313596 a.u.

Corrected Free energies at 273.15 K (M06-2X-D3/def2-TZVPP-SMD(dichloromethane)): -3940.303286 a.u.

P	-1.657926	1.343438	-0.345639

O	-0.221690	1.119112	0.056363
O	-2.372934	0.323526	-1.169370
H	-1.820292	-1.311895	-1.155808
O	-2.502288	1.627178	1.046604
C	-3.859954	1.858099	0.863751
C	-4.312559	3.142216	0.574076
C	-5.650274	3.344252	0.218255
C	-6.560980	2.298418	0.238137
C	-6.116541	1.035165	0.615045
C	-4.772066	0.791967	0.914231
C	-4.354129	-0.582132	1.307292
C	-4.023263	-0.830906	2.642564
C	-3.666733	-2.100924	3.074617
C	-3.593275	-3.165595	2.171696
C	-3.934146	-2.936561	0.811756
C	-3.847344	-4.010037	-0.128158
C	-4.210163	-3.796969	-1.484690
C	-4.087252	-4.850174	-2.397171
C	-3.618309	-6.094675	-1.987759
C	-3.275485	-6.314062	-0.658507
C	-3.385955	-5.287801	0.286781
C	-3.043482	-5.484170	1.671783
C	-3.150066	-4.475961	2.569643
H	-2.888310	-4.633313	3.612815
H	-2.695191	-6.466165	1.980993
H	-2.914274	-7.288220	-0.339926
H	-3.521823	-6.899336	-2.709924
H	-4.371652	-4.684920	-3.433764
C	-4.667549	-2.491074	-1.878389
C	-4.708042	-1.460236	-1.003396
C	-4.343282	-1.642808	0.380300
H	-4.983058	-0.466298	-1.336001
H	-4.936839	-2.335276	-2.919834
H	-3.412555	-2.272639	4.117870
H	-4.053344	-0.003925	3.346965
H	-6.810151	0.199458	0.654445
H	-7.599238	2.458482	-0.038610
C	-5.876269	4.780608	-0.196242
H	-6.487569	4.859499	-1.100319
H	-6.393189	5.342104	0.592461
C	-4.438787	5.291332	-0.399591
H	-4.330881	6.371728	-0.261166
H	-4.096092	5.039076	-1.409008
C	-3.597026	4.479475	0.622395

C	-2.110077	4.623398	0.378828
C	-1.270350	3.882685	-0.441913
C	0.086056	4.221653	-0.560376
C	0.547893	5.347674	0.135874
C	-0.277156	6.080110	0.982706
C	-1.604011	5.696708	1.115622
C	-2.674106	6.262010	2.020701
H	-2.294848	6.502187	3.018589
H	-3.094828	7.186355	1.604245
C	-3.714856	5.128992	2.031681
H	-4.732752	5.466643	2.249911
H	-3.435417	4.381076	2.782104
H	0.118706	6.925008	1.539346
H	1.591095	5.628462	0.020588
C	1.034416	3.451726	-1.405597
C	0.739736	3.237137	-2.754509
C	1.665835	2.659769	-3.611080
C	2.927920	2.279074	-3.147207
C	3.226151	2.426916	-1.766039
C	4.495487	1.993661	-1.268320
C	4.805311	2.124721	0.111092
C	6.045186	1.679386	0.582862
C	6.967081	1.105143	-0.284378
C	6.679959	0.988856	-1.640348
C	5.458334	1.437490	-2.153613
C	5.143826	1.356511	-3.556343
C	3.936853	1.751034	-4.027478
H	3.704081	1.676369	-5.087121
H	5.900733	0.964919	-4.231956
H	7.406873	0.549503	-2.319105
H	7.915907	0.744066	0.100775
H	6.265791	1.757383	1.645166
C	3.805377	2.673781	0.986624
C	2.598393	3.077076	0.518879
C	2.268076	3.001446	-0.884599
H	1.844394	3.444073	1.206356
H	4.033869	2.733479	2.048130
H	1.424662	2.525451	-4.662450
H	-0.225329	3.557721	-3.134161
O	-1.793291	2.788302	-1.108462
C	2.053424	-2.312463	5.185183
C	0.932596	-1.687595	4.662605
C	0.674500	-1.721554	3.282959
C	1.605399	-2.374048	2.439176

C	2.735631	-3.009494	2.985253
C	2.952704	-2.990946	4.349564
H	3.829738	-3.472658	4.768827
H	3.437582	-3.501116	2.316376
C	1.361067	-2.364062	1.025733
C	0.049338	-2.053682	0.537960
C	-0.864692	-1.352701	1.413715
C	-0.534391	-1.167925	2.711027
H	-1.222039	-0.643777	3.368061
H	-1.823341	-1.011302	1.037480
N	-0.138004	-2.443385	-0.710334
N	-1.214586	-2.139985	-1.378018
C	-1.231407	-2.612597	-2.704014
O	-0.477355	-3.433806	-3.155552
O	-2.210421	-2.001710	-3.366115
C	-2.359243	-2.428141	-4.717279
H	-1.462016	-2.186745	-5.291549
H	-2.530809	-3.506935	-4.756282
H	-3.219177	-1.881941	-5.102376
H	2.003801	-2.951085	0.372653
H	0.231145	-1.179564	5.318929
H	2.235179	-2.281026	6.255374
C	3.788222	-0.892526	0.682723
N	4.231051	-1.502863	-0.395513
N	3.278451	-1.320986	-1.367307
C	2.239868	-0.600218	-0.891710
O	1.184850	-0.273046	-1.588103
H	0.600481	0.340344	-1.004492
C	2.466725	-0.383785	0.482454
H	1.877024	0.294386	1.084626
C	3.383731	-2.159256	-2.593870
C	4.846887	-2.164779	-3.036895
H	4.937558	-2.795244	-3.926696
H	5.496025	-2.558207	-2.253013
H	5.172961	-1.152865	-3.286874
C	2.498233	-1.597142	-3.705551
H	1.440516	-1.737467	-3.482169
H	2.728978	-2.144715	-4.624727
H	2.694462	-0.534584	-3.868534
C	2.930946	-3.576961	-2.228312
H	1.872694	-3.583311	-1.947166
H	3.054453	-4.235966	-3.093937
H	3.541816	-3.967417	-1.406588
C	4.577918	-0.812449	1.916371

C	5.820744	-1.449665	2.010345
C	6.556873	-1.374226	3.185504
C	6.065696	-0.658201	4.278726
C	4.832893	-0.017070	4.187574
C	4.092185	-0.093802	3.012388
H	3.123667	0.395547	2.950783
H	4.441396	0.537151	5.035561
H	6.644508	-0.600636	5.195689
H	7.519932	-1.871808	3.252109
H	6.195037	-1.992305	1.147501