

Desymmetrisation of Prochiral *N*-Pyrazolyl Maleimides via Organocatalyzed Asymmetric Michael Addition with Pyrazolones: Construction of Tri-*N*-heterocyclic Scaffolds Bearing both Central and Axial Chirality

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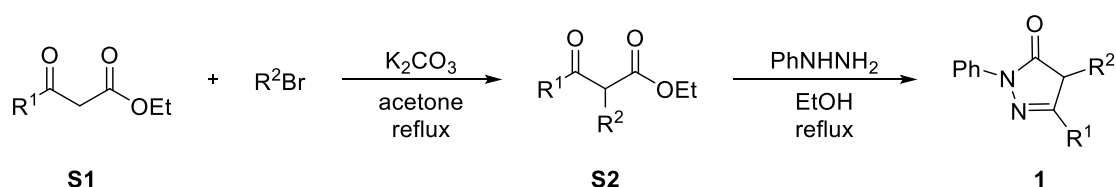
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1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (200–300 mesh). Enantiomeric excesses (ee) were determined by HPLC (Agilent, Palo Alto, CA, USA) using corresponding commercial chiral columns as stated at 25 °C with UV detector at 254 nm. Optical rotations (JiaHang Instruments, Shanghai, China) were reported as follows: $[\alpha]_D^{25}$ (*c* g/100 mL, solvent). All ^1H NMR and ^{19}F NMR spectra were recorded on a Bruker Avance II 400 MHz (Bruker, Karlsruhe, Germany) and Bruker Avance III 600 MHz (Bruker, Karlsruhe, Germany), respectively, ^{13}C NMR spectra were recorded on a Bruker Avance II 101 MHz or Bruker Avance III 151 MHz with chemical shifts reported as ppm (in CDCl_3 , TMS as an internal standard). Data for ^1H NMR are recorded as follows: chemical shift (δ , ppm), multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet, br = broad singlet, dd = double doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XL TM, Agilent, Palo Alto, CA, USA). The absolute configuration of **4** was assigned by the X-ray analysis.

2. General procedures for preparation of pyrazol-5-ones **1**

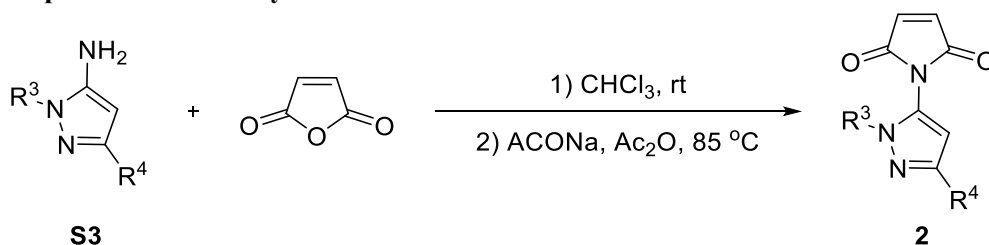


A mixture of β -keto ester **S1** (10 mmol) and anhydrous K_2CO_3 (13 mmol) in dry acetone was stirred under argon atmosphere for five minutes. Then, alkyl bromide or corresponding benzyl bromide (13 mmol) was added carefully. Then reaction was refluxed overnight. After filtration, the solvent was evaporated. The crude mixture purified by flash chromatography on silica gel with mixture of hexane/ethyl acetate (20:1) affording corresponding pure compound **S2**,

A mixture of **S2** (1.0 eq) and phenylhydrazine (1.0 eq) was refluxed in EtOH until full conversion. The solvent was removed and a residue was crystallized from Et_2O . Solid material was filtered affording corresponding pyrazol-5-ones **1**. NMR data fit with data published in the literature.

3. General procedures for preparation of pyrazol-maleimide **2**

Typical procedure for the synthesis of substrates **2a–2k**

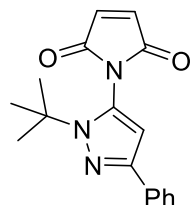


5-Aminopyrazole **S3** were prepared according to the literature. 1) The maleic anhydride (7.5 mmol) and 5-aminopyrazole **S3** (5 mmol) were dissolved in 10 mL CHCl_3 , stirred for 10 hours, and the solid (maleimide acid) precipitated from the reaction mixture was filtered. 2) Maleimide acid was dissolved in 20 mL acetic anhydride and 200 mg sodium acetate was added. Heat the mixture at 85 °C and stir for 4 hours. The reaction is cooled and quenched with water, mixture was filtered, quenched with water and extracted with ethyl acetate. The organic phase was separated, washed

with water and dried over Na₂SO₄. The product was purified by silica gel column chromatography with a mixture of petroleum ether and ethyl acetate (10:1) as eluent. The target compound **2** (0.96 g, 65 %) was obtained as a solid.

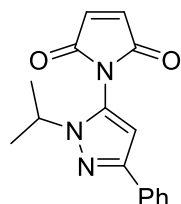
Characterization of substrates 2a–2k

1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)-1H-pyrrole-2,5-dione (2a)



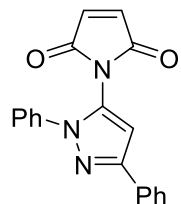
White solid (960 mg, 65% yield, Petroleum ether/EtOAc = 10/1 as the eluent), mp 154.1 - 154.9 °C. ¹H NMR (600 MHz, Chloroform-d) δ 7.80 – 7.75 (m, 2H), 7.38 (dd, J = 7.5 Hz, 2H), 7.31 – 7.27 (m, 1H), 6.92 (d, J = 3.4 Hz, 2H), 6.47 (s, 1H), 1.59 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 169.10, 148.85, 135.29, 133.38, 128.54, 127.99, 127.71, 125.45, 104.50, 61.24, 29.90. HRMS (m/z): Calcd for C₁₇H₁₈N₃O₂, [M+H]⁺, 296.1394, found: 296.1392.

1-(1-isopropyl-3-phenyl-1H-pyrazol-5-yl)-1H-pyrrole-2,5-dione (2b)



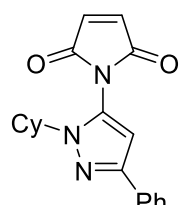
White solid (300 mg, 60% yield, Petroleum ether/EtOAc = 10/1 as the eluent), mp 115.1 - 115.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.76 (m, 2H), 7.38 (dd, J = 7.5 Hz, 2H), 7.33 – 7.26 (m, 1H), 6.90 (d, J = 1.8 Hz, 2H), 6.48 (s, 1H), 4.14 (h, J = 6.6 Hz, 1H), 1.50 (d, J = 6.6 Hz, 6H). ¹³C NMR (101 MHz, CDCl₃) δ 168.48, 150.58, 135.04, 133.47, 128.57, 127.78, 125.56, 101.61, 50.35, 22.63. HRMS (m/z): Calcd for C₁₆H₁₆N₃O₂, [M+H]⁺, 282.1237, found: 282.1240.

1-(1,3-diphenyl-1H-pyrazol-5-yl)-1H-pyrrole-2,5-dione (2c)



White solid (200 mg, 40% yield, Petroleum ether/EtOAc = 10/1 as the eluent), mp 108.1 - 108.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.90 – 7.83 (m, 2H), 7.46 – 7.34 (m, 8H), 6.81 (s, 2H), 6.76 (s, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 168.11, 152.02, 138.22, 134.94, 132.60, 129.54, 129.38, 128.69, 128.65, 128.36, 125.76, 124.51, 104.10. HRMS (m/z): Calcd for C₁₉H₁₄N₃O₂, [M+H]⁺, 316.1081, found: 316.1080.

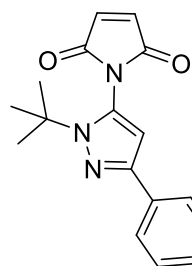
1-(1-cyclohexyl-3-phenyl-1H-pyrazol-5-yl)-1H-pyrrole-2,5-dione (2d)



White solid (400 mg, 50% yield, Petroleum ether/EtOAc = 10/1 as the eluent), mp 105.1 - 105.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.79 (d, J = 7.6 Hz, 2H), 7.38 (t, J = 7.5 Hz, 2H), 7.30 (d, J = 7.3 Hz, 1H), 6.93 (s, 2H), 6.47 (s, 1H), 3.67 (tt, J = 10.9, 4.5 Hz, 1H), 2.16 – 1.79 (m, 7H), 1.74 – 1.62 (m, 1H), 1.31 (d, J = 11.7 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 168.51, 150.45, 135.05, 133.48, 128.54, 127.97, 127.72, 125.57, 101.51, 58.04, 32.91, 25.65, 25.12. HRMS (m/z):

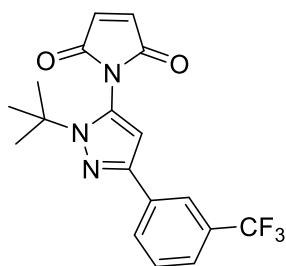
Calcd for C₁₉H₂₀N₃O₂, [M+H]⁺, 322.1550, found: 322.1551.

1-(1-(tert-butyl)-3-(3-chlorophenyl)-1H-pyrazol-5-yl)-1H-pyrrole-2,5-dione (2e)



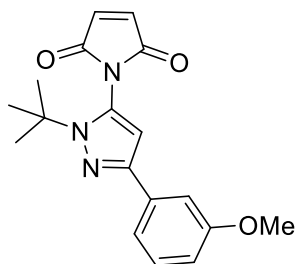
Orange solid (600 mg, 52% yield, Petroleum ether/EtOAc = 10/1 as the eluent), mp 140.1 - 140.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.79 (s, 1H), 7.63 (dt, J = 7.5, 1.5 Hz, 1H), 7.33 – 7.25 (m, 2H), 6.94 (d, J = 0.9 Hz, 2H), 6.46 (s, 1H), 1.58 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 168.99, 147.50, 135.32, 135.17, 134.51, 129.81, 128.25, 127.66, 125.46, 123.55, 104.70, 61.52, 29.87. HRMS (m/z): Calcd for C₁₇H₁₇ClN₃O₂, [M+H]⁺, 330.1004, found: 330.0999.

1-(1-(tert-butyl)-3-(3-(trifluoromethyl)phenyl)-1H-pyrazol-5-yl)-1H-pyrrole-2,5-dione (2f)



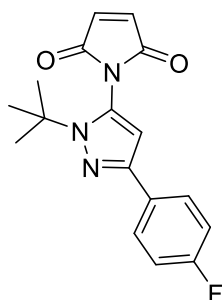
White solid (400 mg, 53% yield, Petroleum ether/EtOAc = 10/1 as the eluent), mp 146.1 - 146.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 8.03 (d, J = 2.2 Hz, 1H), 7.97 – 7.93 (m, 1H), 7.56 – 7.47 (m, 2H), 6.95 (s, 2H), 6.52 (s, 1H), 1.60 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 168.98, 147.46, 135.34, 134.15, 131.08, 130.76, 128.99, 128.57, 128.41, 125.60, 124.25 (d, J = 4.04 Hz), 122.89, 122.21 (d, J = 4.04 Hz), 104.73, 61.62, 29.87. ¹⁹F NMR (565 MHz, CDCl₃) δ -62.66. HRMS (m/z): Calcd for C₁₈H₁₇F₃N₃O₂, [M+H]⁺, 364.1267, found: 364.1267.

1-(1-(tert-butyl)-3-(3-methoxyphenyl)-1H-pyrazol-5-yl)-1H-pyrrole-2,5-dione (2g)



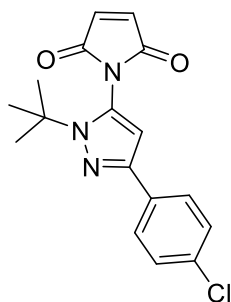
White solid (300 mg, 50% yield, Petroleum ether/EtOAc = 10/1 as the eluent), mp 103.1 - 103.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.35 (s, 2H), 7.31 (s, 1H), 6.91 (s, 2H), 6.84 (s, 1H), 6.45 (s, 1H), 3.85 (s, 3H), 1.58 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 169.10, 159.84, 135.29, 134.77, 129.58, 127.99, 118.11, 113.44, 110.83, 104.69, 61.28, 55.65, 29.89. HRMS (m/z): Calcd for C₁₈H₂₀N₃O₃, [M+H]⁺, 326.1499, found: 326.1498.

1-(1-(tert-butyl)-3-(4-fluorophenyl)-1H-pyrazol-5-yl)-1H-pyrrole-2,5-dione (2h)



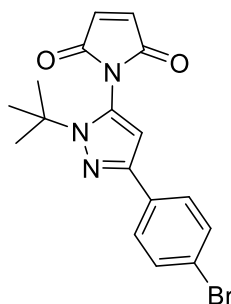
White solid (500 mg, 55% yield, Petroleum ether/EtOAc = 10/1 as the eluent), mp 166.1 - 166.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.77 – 7.72 (m, 2H), 7.09 – 7.04 (m, 2H), 6.94 (s, 2H), 6.42 (s, 1H), 1.58 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 169.06, 162.6 (d, J = 246.4 Hz), 148.01, 135.31, 129.63, 129.60, 128.10, 127.15, 127.07, 115.53, 115.32, 104.27, 61.29, 29.88. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.71. HRMS (m/z): Calcd for C₁₇H₁₇FN₃O₂, [M+H]⁺, 314.1299, found: 314.1298.

1-(1-(tert-butyl)-3-(4-chlorophenyl)-1H-pyrazol-5-yl)-1H-pyrrole-2,5-dione (2i)



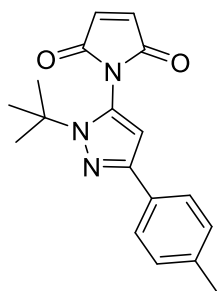
Orange solid (500 mg, 55% yield, Petroleum ether/EtOAc = 10/1 as the eluent), mp 155.1 - 155.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.72 (s, 2H), 7.35 (s, 2H), 6.93 (s, 2H), 6.44 (s, 1H), 1.58 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 169.04, 147.76, 135.32, 133.39, 131.91, 128.71, 128.20, 126.70, 104.48, 61.43, 29.87. HRMS (m/z): Calcd for C₁₇H₁₇ClN₃O₂, [M+H]⁺, 330.1004, found: 330.1003.

1-(3-(4-bromophenyl)-1-(tert-butyl)-1H-pyrazol-5-yl)-1H-pyrrole-2,5-dione (2j)



White solid (400 mg, 58% yield, Petroleum ether/EtOAc = 10/1 as the eluent), mp 164.1 - 164.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.67 (d, J = 8.6 Hz, 2H), 7.52 (d, J = 8.6 Hz, 2H), 6.97 (s, 2H), 6.47 (s, 1H), 1.60 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 169.02, 147.77, 135.32, 132.35, 131.64, 128.20, 127.00, 121.59, 104.47, 61.45, 29.87. HRMS (m/z): Calcd for C₁₇H₁₇BrN₃O₂, [M+H]⁺, 374.0499, found: 374.0496.

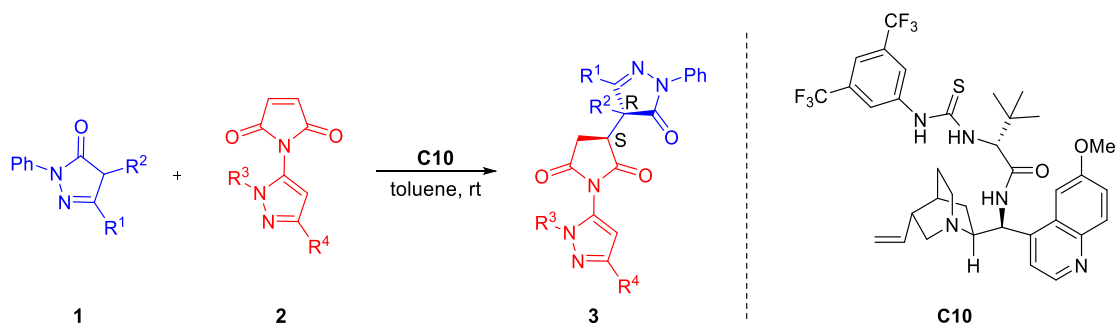
1-(1-(tert-butyl)-3-(p-tolyl)-1H-pyrazol-5-yl)-1H-pyrrole-2,5-dione (2k)



White solid (400 mg, 48% yield, Petroleum ether/EtOAc = 10/1 as the eluent), mp 176.1 - 176.9 °C. ¹H NMR (400 MHz, Chloroform-d) δ 7.65 (s, 2H), 7.17 (s, 2H), 6.91 (s, 2H), 6.42 (s, 1H), 2.36 (s, 3H), 1.55 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 169.14, 148.95, 137.38, 135.28, 130.63, 129.22, 127.85, 125.36, 104.27, 61.12, 29.90. HRMS (m/z): Calcd for C₁₈H₂₀N₃O₂, [M+H]⁺, 310.1550, found: 310.1551.

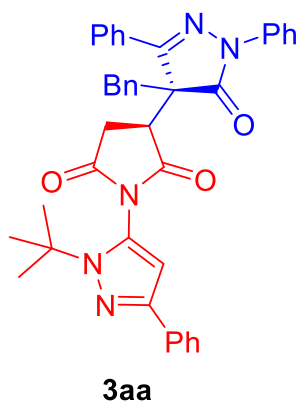
Catalyst **C1-C10** were synthesized according to the literature procedure. The racemic products were synthesized using quinine/quinidine = 1:1 as the catalyst.

4. Experimental procedures and characterization of products 3 and 4



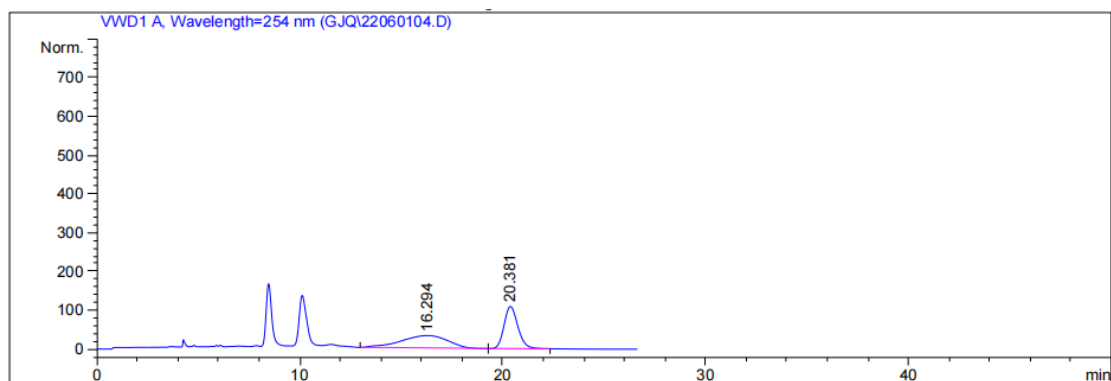
In a reaction tube, pyrazol-5-ones **1** (0.24 mmol), pyrazol-maleimide **2** (0.20 mmol), catalyst **C10** (0.02 mmol) were added into toluene (4 mL). The reaction solution was stirred at 25 °C. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10 to 1/3) on silica gel to give the product **3**.

(S)-3-((R)-4-benzyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3aa)



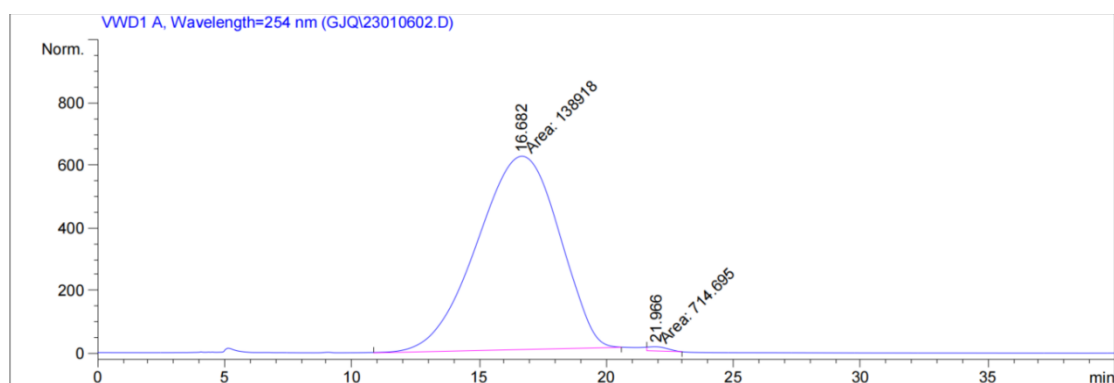
Prepared according to the procedure within 1 h as white solid (121.8 mg, 98% yield, dr = 1:1). mp 127.1 – 127.9 °C; [α]_D¹⁷ = -33.206 (c 0.52, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 8.00 (dq, J = 6.7, 2.6, 1.6 Hz, 4H), 7.69 – 7.48 (m, 15H), 7.40 – 7.28 (m, 9H), 7.23 – 7.16 (m, 2H), 7.12 – 7.01 (m, 10H), 6.29 (s, 1H), 5.50 (s, 1H), 4.22 (dd, J = 17.6, 7.4 Hz, 2H), 3.99 (dd, J = 9.3, 7.4 Hz, 1H), 3.76 (dd, J = 9.4, 5.5 Hz, 1H), 3.61 (dd, J = 19.5, 13.5 Hz, 2H), 3.50 (d, J = 13.2 Hz, 1H), 3.18 (dd, J = 17.8, 9.4 Hz, 1H), 3.01 (dd, J = 18.6, 9.7 Hz, 1H), 2.78 (s, 1H), 1.53 (s, 9H), 1.38 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 174.89, 173.87, 173.72, 173.43, 173.07, 158.07, 157.37, 148.93, 148.66, 137.00, 136.82, 133.31, 133.24, 132.50, 131.10, 131.02,

130.99, 130.71, 129.42, 129.36, 129.35, 129.17, 128.99, 128.79, 128.71, 128.49, 128.47, 128.44, 128.39, 127.95, 127.79, 127.69, 127.61, 127.00, 126.29, 126.05, 125.40, 125.34, 120.04, 119.89, 103.68, 61.50, 57.13, 44.93, 43.58, 41.24, 40.02, 31.06, 30.04, 29.81, 29.69. HRMS (ESI) m/z Calcd. for C₃₉H₃₆N₅O₃, [M+H]⁺, 622.2813, Found: 622.2806. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral IB-H column, hexane/2-propanol = 7/3, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 21.9 min, t_{minor} = 16.6 min).



Signal 1: VWD1 A, Wavelength=254 nm

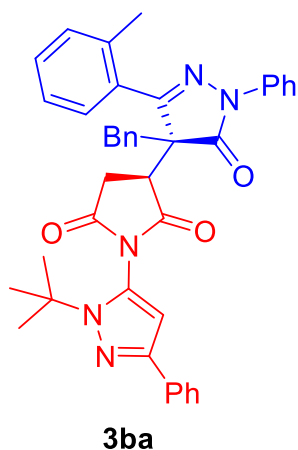
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.294	BP	2.2224	5175.55811	32.16374	50.0676
2	20.381	VB	0.7344	5161.57666	108.73219	49.9324



Signal 1: VWD1 A, Wavelength=254 nm

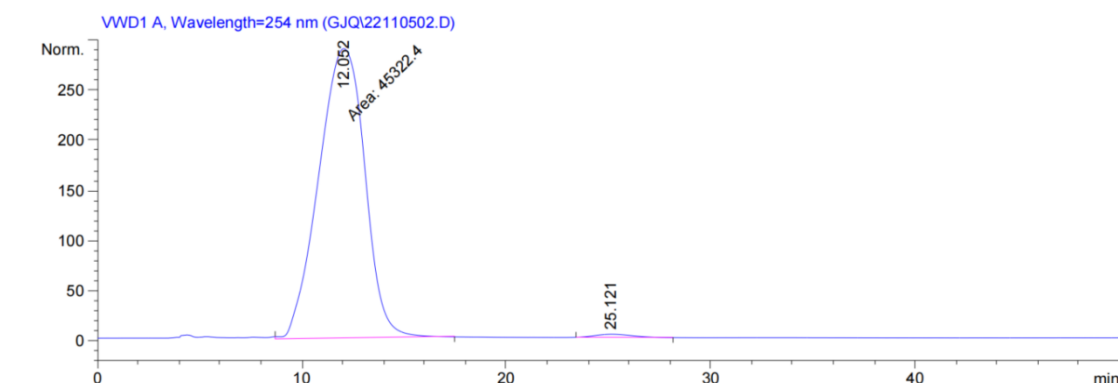
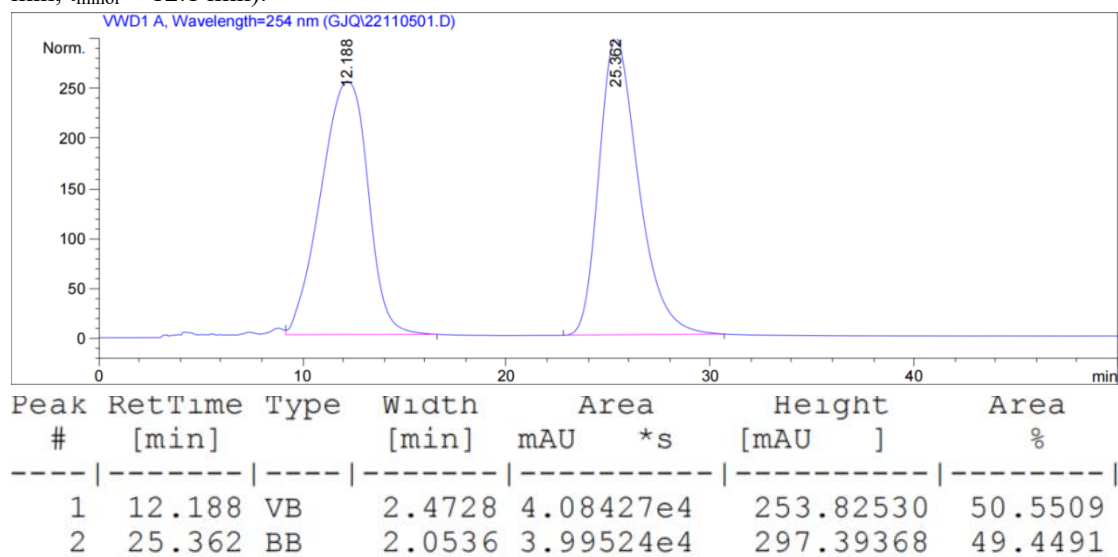
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.682	MM	3.7494	1.38918e5	617.51477	99.4882
2	21.966	MM	0.8841	714.69501	13.47279	0.5118

(S)-3-((R)-4-benzyl-5-oxo-1-phenyl-3-(o-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ba)



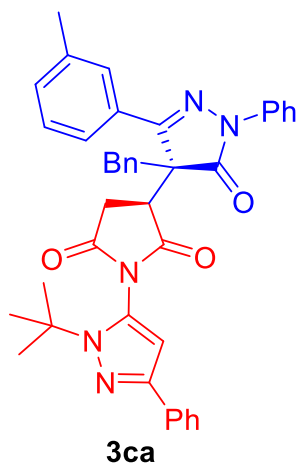
Prepared according to the procedure within 1.2 h as white solid (125.8 mg, 99% yield, dr = 1:1). mp 108.1 – 108.9 °C; $[\alpha]_D^{17} = -35.030$ (c 0.33, CH_2Cl_2); ^1H NMR (400 MHz, CHloroform-d) δ 7.83 (d, $J = 11.5$ Hz, 2H), 7.77 (q, $J = 3.5$ Hz, 2H), 7.69 – 7.61 (m, 6H), 7.58 (d, $J = 8.0$ Hz, 2H), 7.46 – 7.41 (m, 2H), 7.41 – 7.26 (m, 12H), 7.22 – 7.15 (m, 2H), 7.08 (d, $J = 6.9$ Hz, 8H), 7.03 (dd, $J = 7.8, 1.8$ Hz, 2H), 6.29 (s, 1H), 5.51 (s, 1H), 4.31 – 4.13 (m, 2H), 3.98 (dd, $J = 9.3, 7.4$ Hz, 1H), 3.75 (dd, $J = 9.4, 5.4$ Hz, 1H), 3.60 (dd, $J = 26.7, 13.5$ Hz, 2H), 3.48 (d, $J = 13.2$ Hz, 1H), 3.18 (dd, $J = 17.8, 9.4$ Hz, 1H), 2.99 (dd, $J = 18.6, 9.7$ Hz, 1H), 2.66 (d, $J = 58.4$ Hz, 1H), 2.43 (s, 6H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 173.89, 173.75, 173.46, 173.08, 158.23, 157.50, 148.90, 148.64, 139.37, 139.09, 137.00, 136.83, 133.39, 133.33,

133.27, 132.55, 131.90, 131.63, 130.98, 130.89, 129.39, 129.26, 128.97, 128.88, 128.81, 128.70, 128.50, 128.46, 128.41, 128.37, 128.17, 127.93, 127.75, 127.68, 127.60, 126.27, 126.03, 125.39, 125.26, 124.66, 123.88, 120.09, 119.94, 103.70, 103.63, 61.50, 57.14, 44.95, 43.55, 41.28, 40.04, 31.10, 30.07, 29.81, 29.70, 21.68, 21.65. HRMS (ESI) m/z Calcd. for $\text{C}_{40}\text{H}_{38}\text{N}_5\text{O}_3$, $[\text{M}+\text{H}]^+$, 636.2969, Found: 636.2972. Enantiomeric excess was determined to be 98% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, $\lambda = 254$ nm, 25 °C, 0.8 mL/min, $t_{\text{major}} = 25.1$ min, $t_{\text{minor}} = 12.1$ min).



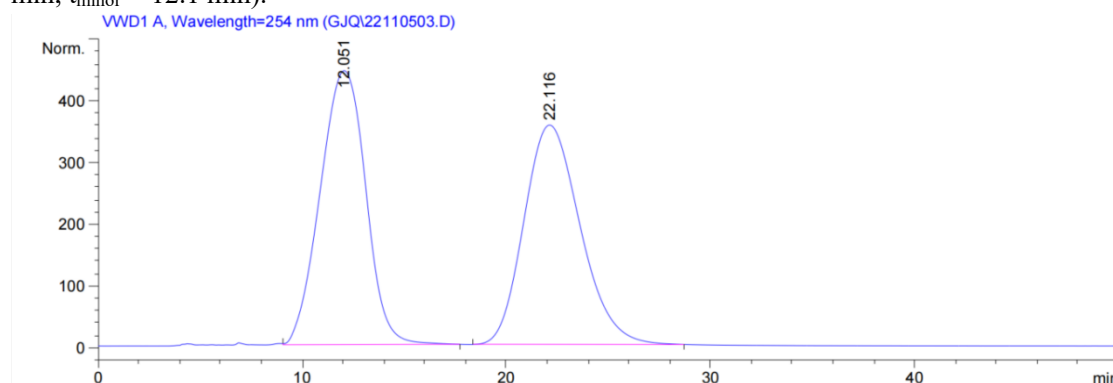
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.052	MM	2.6128	4.53224e4	289.10687	99.1233
2	25.121	BB	1.4906	400.85406	3.16214	0.8767

(S)-3-((R)-4-benzyl-5-oxo-1-phenyl-3-(m-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ca)

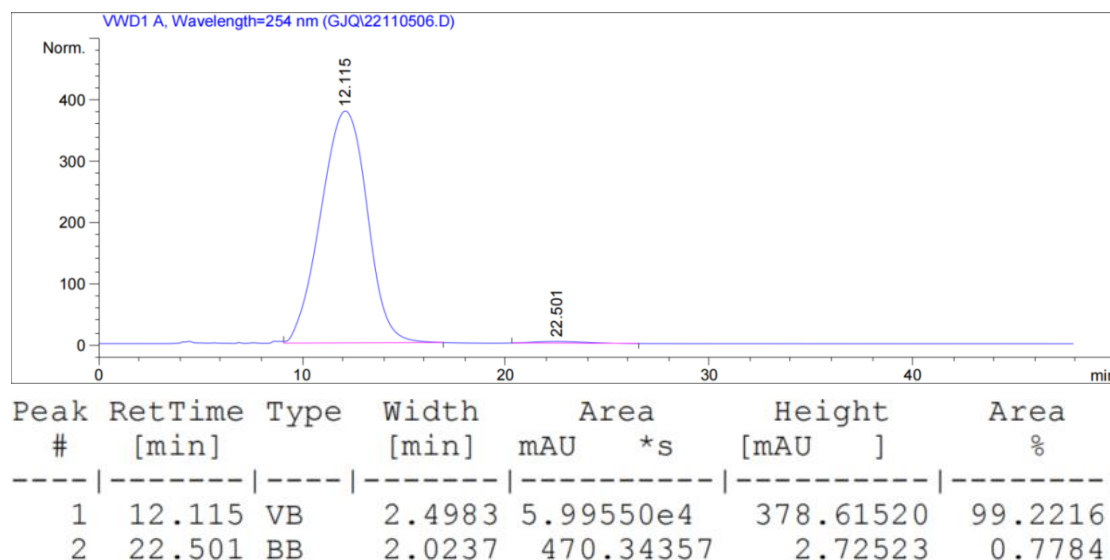


Prepared according to the procedure within 1.2 h as white solid (125.8 mg, 99% yield, dr = 1:1). mp 109.1 – 109.9 °C; $[\alpha]_D^{17} = -33.491$ (*c* 0.42, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 7.85 (s, 1H), 7.82 (s, 1H), 7.78 (d, *J* = 7.2 Hz, 2H), 7.68 (d, *J* = 1.5 Hz, 1H), 7.67 – 7.61 (m, 5H), 7.60 – 7.55 (m, 2H), 7.43 (dd, *J* = 12.2, 6.9 Hz, 3H), 7.40 – 7.27 (m, 11H), 7.23 – 7.16 (m, 2H), 7.09 (d, *J* = 5.6 Hz, 8H), 7.04 (dd, *J* = 7.7, 1.9 Hz, 2H), 6.29 (d, *J* = 1.0 Hz, 1H), 5.50 (s, 1H), 4.31 – 4.15 (m, 2H), 3.99 (dd, *J* = 9.3, 7.5 Hz, 1H), 3.75 (dd, *J* = 9.5, 5.4 Hz, 1H), 3.65 (d, *J* = 13.2 Hz, 1H), 3.57 (d, *J* = 13.8 Hz, 1H), 3.49 (d, *J* = 13.2 Hz, 1H), 3.19 (dd, *J* = 17.8, 9.4 Hz, 1H), 3.00 (dd, *J* = 18.6, 9.7 Hz, 1H), 2.66 (d, *J* = 49.9 Hz, 1H), 2.44 (s, 6H), 1.54 (s, 9H), 1.38 (d, *J* = 1.0 Hz, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 174.94, 173.90, 173.76,

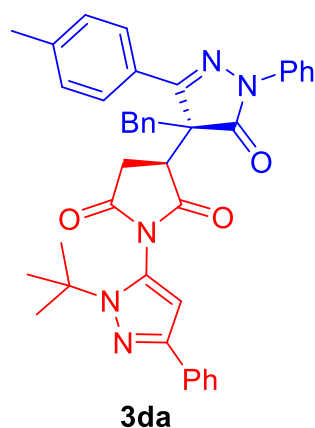
173.46, 173.11, 173.08, 158.23, 157.51, 148.90, 148.65, 139.37, 139.09, 137.00, 136.82, 133.39, 133.33, 133.26, 132.55, 131.90, 131.63, 130.98, 130.89, 129.39, 129.26, 128.97, 128.88, 128.81, 128.70, 128.50, 128.47, 128.41, 128.37, 128.17, 127.93, 127.75, 127.69, 127.61, 126.28, 126.04, 125.40, 125.27, 124.66, 123.88, 120.09, 119.94, 103.70, 103.63, 61.50, 57.14, 44.95, 43.55, 41.28, 40.04, 31.10, 30.07, 29.81, 29.70, 21.65. HRMS (ESI) *m/z* Calcd. for C₄₀H₃₈N₅O₃, [M+H]⁺, 636.2969, Found: 636.2974. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 25 °C, 0.8 mL/min, *t*_{major} = 22.5 min, *t*_{minor} = 12.1 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.051	VB	2.4691	6.89116e4	444.30835	50.2770
2	22.116	BB	2.9303	6.81522e4	355.85284	49.7230

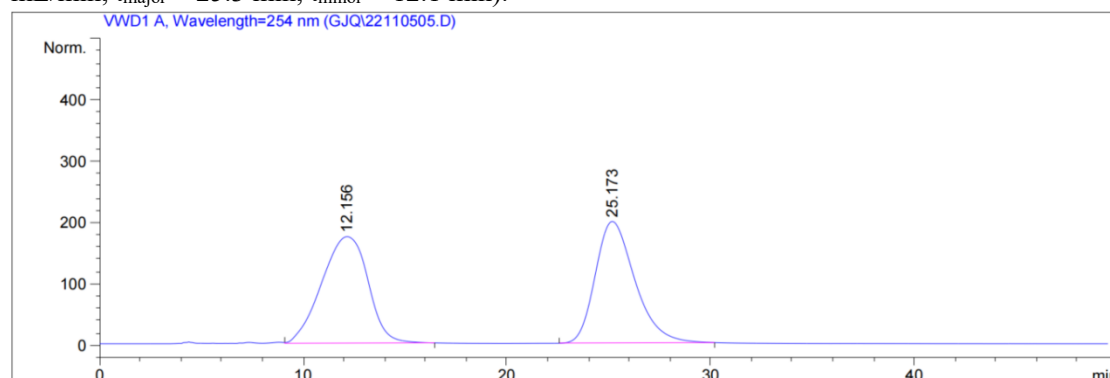


(S)-3-((R)-4-benzyl-5-oxo-1-phenyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3da)

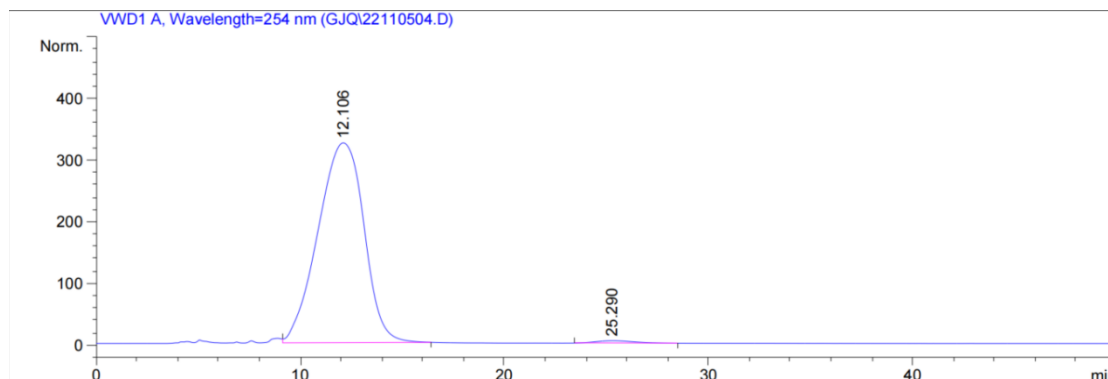


Prepared according to the procedure within 1.2 h as white solid (125.8 mg, 99% yield, dr = 1:1). mp 127.1 – 127.9 °C; $[\alpha]_D^{17} = -61.572$ (c 0.23, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 7.89 (dd, J = 8.0 Hz, 4H), 7.68 – 7.56 (m, 9H), 7.39 – 7.28 (m, 14H), 7.19 (dd, J = 16.7, 8.2 Hz, 2H), 7.09 (d, J = 6.7 Hz, 8H), 7.06 – 7.01 (m, 2H), 6.28 (s, 1H), 5.48 (s, 1H), 4.20 (d, J = 26.5 Hz, 2H), 3.97 (dd, J = 9.3, 7.4 Hz, 1H), 3.74 (dd, J = 9.7, 5.2 Hz, 1H), 3.61 (dd, J = 27.2, 13.5 Hz, 2H), 3.49 (d, J = 13.2 Hz, 1H), 3.17 (dd, J = 17.8, 9.4 Hz, 1H), 2.99 (dd, J = 18.6, 9.7 Hz, 1H), 2.63 (d, J = 27.3 Hz, 1H), 2.50 (s, 3H), 2.44 (s, 3H), 1.38 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 174.98, 173.84, 173.76, 173.38, 173.08, 173.01, 158.07, 157.37, 148.92,

148.63, 141.58, 141.11, 137.03, 136.86, 133.46, 133.33, 133.26, 132.59, 130.09, 129.89, 129.37, 128.95, 128.80, 128.67, 128.48, 128.45, 128.40, 128.35, 128.32, 128.20, 127.89, 127.71, 127.58, 126.90, 126.21, 125.96, 125.38, 125.36, 120.04, 119.87, 103.68, 103.66, 61.51, 61.48, 57.15, 44.97, 43.50, 41.21, 39.88, 31.12, 30.07, 29.80, 29.67, 21.62, 21.55. HRMS (ESI) m/z Calcd. for C₄₀H₃₈N₅O₃, [M+H]⁺, 636.2969, Found: 636.2979. Enantiomeric excess was determined to be 98% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 25.3 min, t_{minor} = 12.1 min).

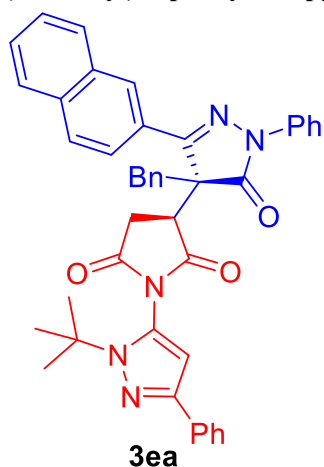


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.156	VB	2.4071	2.74575e4	173.61469	50.5762
2	25.173	BB	2.0362	2.68319e4	198.25240	49.4238



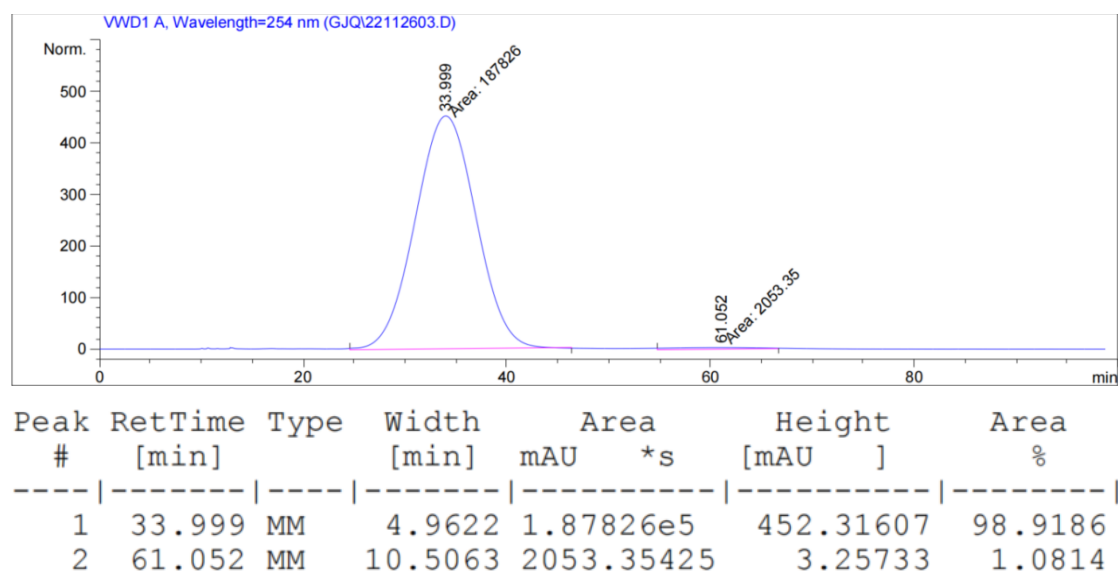
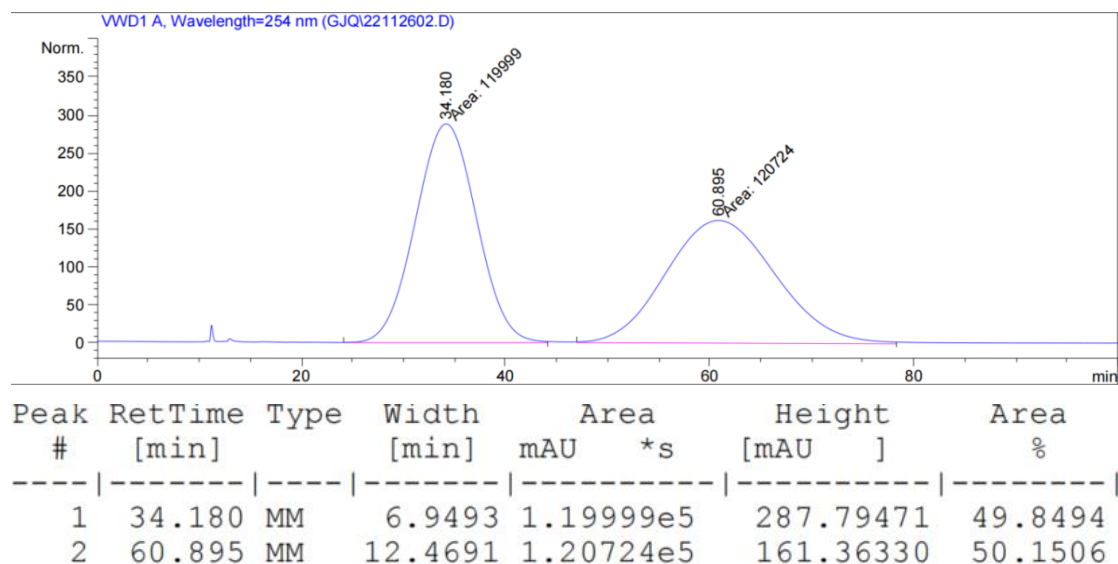
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	12.106	VB	2.4667	5.06706e4	324.25516	99.0246
2	25.290	BB	1.5296	499.11697	3.85080	0.9754

(S)-3-((R)-4-benzyl-3-(naphthalen-2-yl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ea)

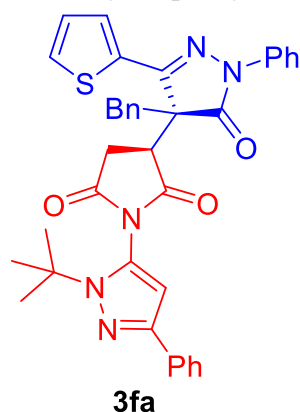


Prepared according to the procedure within 2.5 h as white solid (106.1mg, 79% yield, dr = 1:1). mp 110.1 – 110.9 °C; $[\alpha]_D^{17} = -46.491$ (c 0.79, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 8.42 (d, J = 2.3 Hz, 1H), 8.39 (s, 1H), 8.20 – 8.12 (m, 3H), 8.00 – 7.92 (m, 7H), 7.91 – 7.85 (m, 1H), 7.72 – 7.61 (m, 9H), 7.61 – 7.51 (m, 4H), 7.37 (dt, J = 15.5, 7.6 Hz, 5H), 7.32 – 7.17 (m, 15H), 7.15 – 7.01 (m, 13H), 6.26 (d, J = 2.0 Hz, 1H), 4.95 (s, 1H), 4.47 (s, 1H), 4.20 (dd, J = 10.1, 5.1 Hz, 1H), 4.11 (t, J = 8.2 Hz, 1H), 3.81 (q, J = 6.2, 5.6 Hz, 2H), 3.66 (dd, J = 13.9, 1.6 Hz, 1H), 3.56 (d, J = 13.2 Hz, 1H), 3.22 (dd, J = 17.6, 9.1 Hz, 1H), 3.00 (dd, J = 18.7, 9.8 Hz, 1H), 2.47 (s, 1H), 1.52 (d, J = 1.2 Hz, 9H), 1.35 (d, J = 2.1 Hz, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 175.41, 173.92, 173.74, 173.51, 173.14,

173.03, 157.91, 157.12, 148.68, 137.00, 136.82, 134.37, 134.28, 133.50, 133.29, 132.95, 132.92, 132.85, 132.56, 129.43, 129.39, 129.29, 129.23, 129.04, 128.77, 128.71, 128.46, 128.43, 128.40, 128.23, 128.15, 128.04, 128.00, 127.97, 127.76, 127.67, 127.60, 127.48, 127.05, 126.56, 126.40, 126.16, 125.38, 125.28, 124.13, 124.04, 120.13, 119.97, 103.66, 103.58, 61.49, 57.31, 45.19, 43.54, 41.45, 40.11, 31.21, 30.12, 29.82, 29.65. HRMS (ESI) m/z Calcd. for C₄₃H₃₈N₅O₃, [M+H]⁺, 672.2969, Found: 672.2976. Enantiomeric excess was determined to be 98% (determined by HPLC using chiral OD-H-AD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 25 °C, 0.6 mL/min, t_{major} = 61.0 min, t_{minor} = 34.0 min).



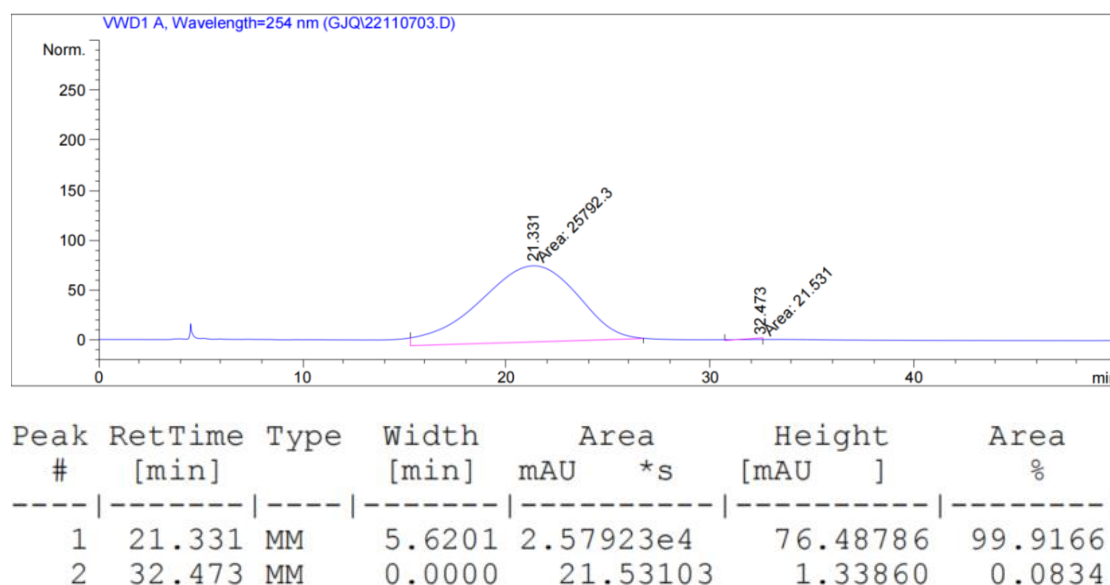
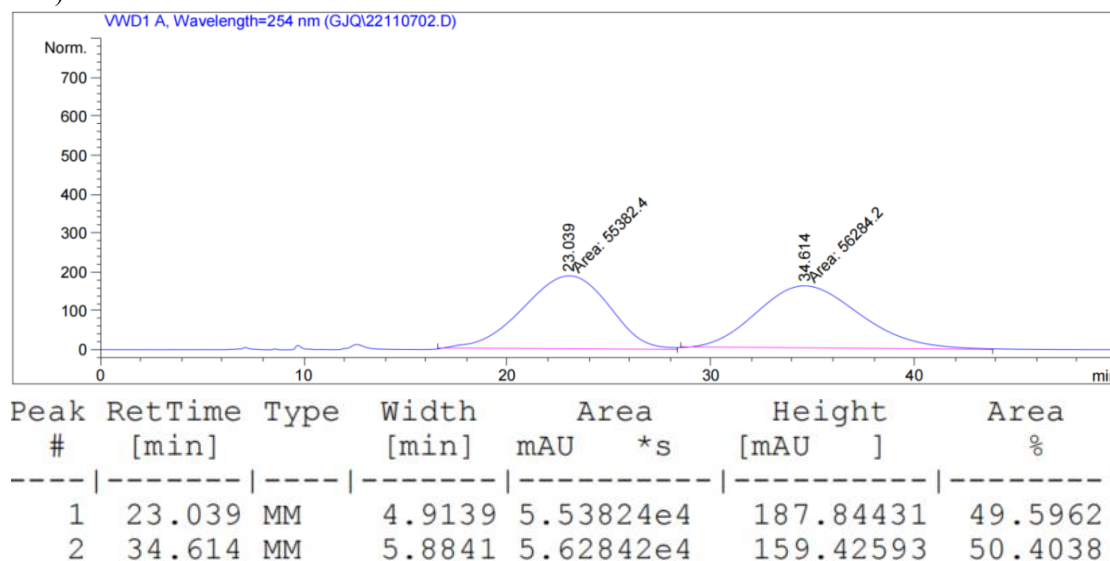
(S)-3-((R)-4-benzyl-5-oxo-1-phenyl-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3fa)



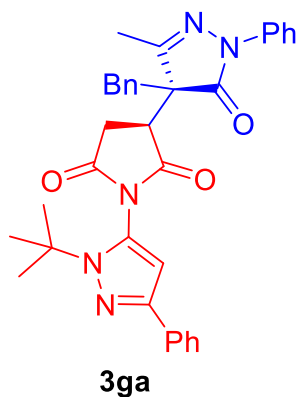
Prepared according to the procedure within 1.1 h as white solid (124.2 mg, 99% yield, dr = 1:1). mp 120.1 – 120.9 °C; $[\alpha]_D^{17} = -35.474$ (c 0.65, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 7.64 (ddd, J = 19.8, 10.9, 7.0 Hz, 9H), 7.53 (dd, J = 10.3, 6.5 Hz, 3H), 7.39 – 7.28 (m, 9H), 7.25 – 7.17 (m, 4H), 7.16 – 7.00 (m, 11H), 6.33 (s, 1H), 5.80 (s, 1H), 4.09 (d, J = 28.1 Hz, 2H), 4.00 – 3.94 (m, 1H), 3.77 (dd, J = 9.4, 5.6 Hz, 1H), 3.59 – 3.51 (m, 2H), 3.47 (d, J = 13.1 Hz, 1H), 3.19 (dd, J = 17.8, 9.3 Hz, 1H), 3.03 (dd, J = 18.5, 9.6 Hz, 1H), 2.79 (s, 1H), 1.57 (s, 9H), 1.38 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 173.69, 173.56, 172.98, 172.69, 172.39, 154.24, 149.01, 148.68, 136.79, 136.61, 134.42, 134.31, 133.30, 133.21, 132.36, 129.63, 129.46, 129.40,

128.96, 128.92, 128.70, 128.50, 128.46, 128.44, 128.24, 127.97, 127.91, 127.78, 127.72, 127.61, 127.39, 126.33, 126.10, 125.39, 125.35, 120.08, 119.96, 103.67, 61.59, 61.51, 45.35, 41.07, 39.72, 31.05, 30.11, 29.83, 29.65. HRMS (ESI) m/z Calcd. for C₃₇H₃₄N₅O₃S, [M+H]⁺, 628.2377, Found:

628.2387. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 32.4 min, t_{minor} = 21.3 min).

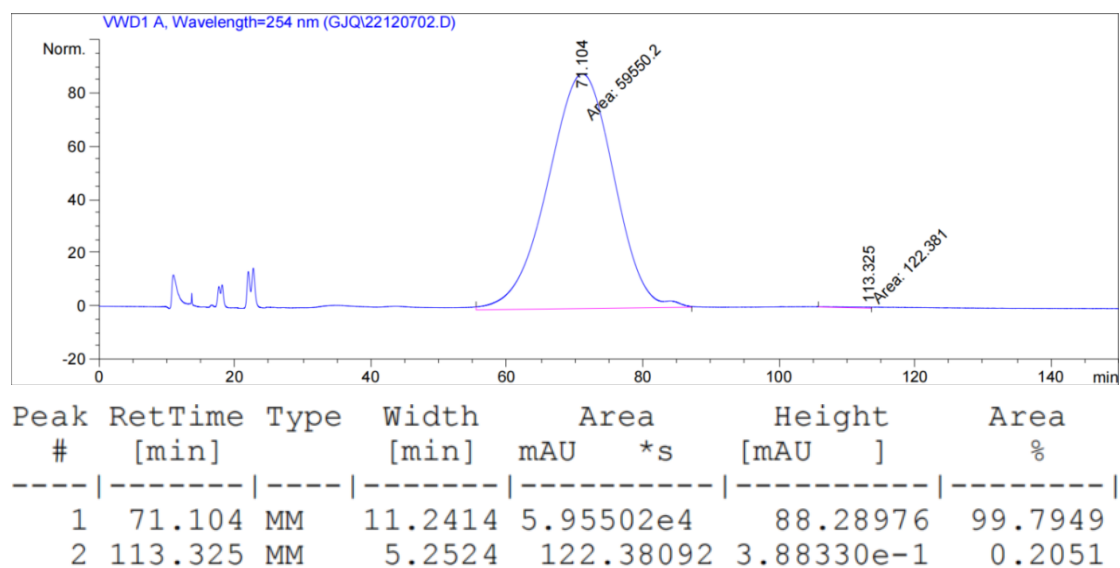
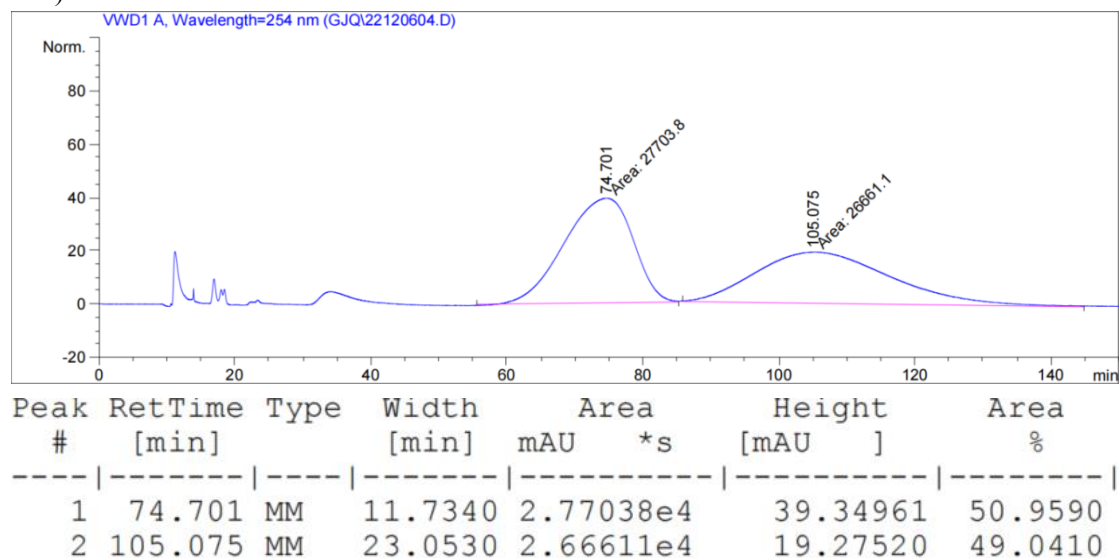


(S)-3-((R)-4-benzyl-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ga)

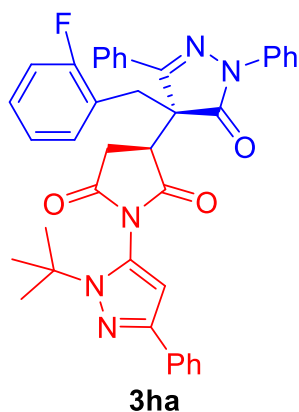


Prepared according to the procedure within 1.1 h as white solid (108.5mg, 97% yield, dr = 1:1). mp 124.1 – 124.9 °C; $[\alpha]_{\text{D}}^{17} = 80.357$ (c 0.45, CH_2Cl_2); ^1H NMR (400 MHz, CHloroform-d) δ 7.75 – 7.70 (m, 2H), 7.66 – 7.61 (m, 2H), 7.61 – 7.56 (m, 2H), 7.53 – 7.48 (m, 2H), 7.38 – 7.26 (m, 10H), 7.21 – 7.08 (m, 12H), 6.38 (s, 1H), 6.18 (s, 1H), 4.17 (dd, J = 18.1, 6.8 Hz, 1H), 3.56 – 3.35 (m, 4H), 3.28 (t, J = 14.2 Hz, 2H), 3.13 – 3.03 (m, 2H), 3.02 – 2.96 (m, 1H), 2.28 (s, 3H), 2.26 (s, 3H), 1.58 (s, 7H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 174.51, 174.00, 173.76, 173.29, 172.63, 172.49, 160.48, 159.29, 149.12, 148.67, 137.04, 136.92, 133.30, 133.14, 133.09, 132.60,

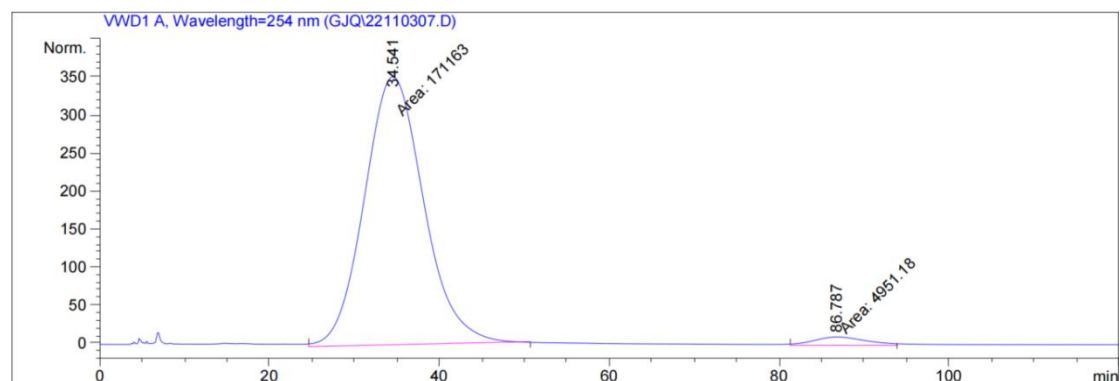
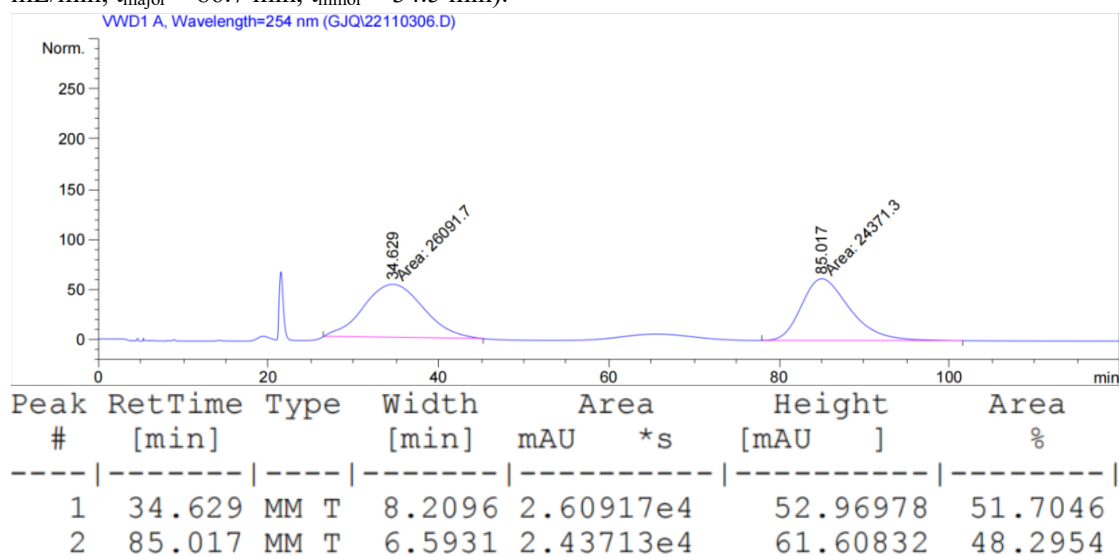
129.20, 129.13, 128.93, 128.91, 128.85, 128.74, 128.70, 128.66, 128.61, 128.53, 128.47, 128.02, 127.92, 127.75, 127.69, 127.25, 125.91, 125.70, 125.43, 125.41, 125.12, 119.63, 119.07, 103.61, 103.51, 61.59, 61.52, 59.86, 57.34, 53.71, 44.04, 43.24, 40.46, 39.44, 33.77, 30.78, 29.87, 29.68, 29.61, 15.32, 14.71. HRMS (ESI) m/z Calcd. for $C_{34}H_{34}N_5O_3$, $[M+H]^+$, 560.2656, Found: 560.2659. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral IA-H-OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 25 °C, 0.6 mL/min, t_{major} = 113.3 min, t_{minor} = 71.1 min).



(S)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)-3-((R)-4-(2-fluorobenzyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)pyrrolidine-2,5-dione (3ha)

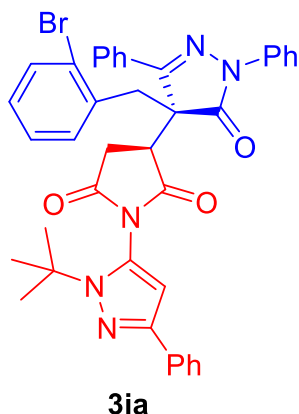


Prepared according to the procedure within 1.5 h as white solid (126.6 mg, 99% yield, dr = 1:1). mp 113.1 – 113.9 °C; $[\alpha]_D^{17} = -42.005$ (c 0.89, CH_2Cl_2); ^1H NMR (400 MHz, CHloroform-d) δ 7.99 – 7.93 (m, 4H), 7.76 – 7.71 (m, 2H), 7.67 (ddd, $J = 8.1, 3.3, 1.2$ Hz, 4H), 7.64 – 7.55 (m, 4H), 7.55 – 7.44 (m, 5H), 7.42 – 7.28 (m, 9H), 7.23 – 7.03 (m, 6H), 6.92 – 6.81 (m, 4H), 6.28 (s, 1H), 5.54 (s, 1H), 4.36 – 4.14 (m, 2H), 4.02 (dd, $J = 9.3, 7.4$ Hz, 1H), 3.81 – 3.71 (m, 2H), 3.66 (d, $J = 14.2$ Hz, 1H), 3.52 (d, $J = 13.7$ Hz, 1H), 3.18 (dd, $J = 17.8, 9.4$ Hz, 1H), 2.99 (dd, $J = 18.5, 9.7$ Hz, 1H), 2.82 (s, 1H), 1.52 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 174.85, 173.83, 173.72, 173.42, 173.01, 172.89, 161.74 (d, $J = 8.08$ Hz), 160.14, 160.06, 158.39, 157.77, 148.94, 148.63, 137.06, 136.88, 133.29, 133.23, 131.29, 131.26, 131.20, 131.18, 131.02, 130.71, 130.64, 129.88, 129.83, 129.73, 129.67, 129.54, 129.28, 129.22, 129.08, 129.05, 128.93, 128.79, 128.50, 128.47, 128.40, 127.74, 127.69, 127.62, 127.09, 126.89, 126.27, 126.04, 125.39, 125.35, 124.15, 124.12, 124.08, 120.70, 120.60, 120.03, 119.93, 119.84, 119.78, 119.70, 115.69, 115.67, 115.53, 103.71, 61.50, 56.25, 49.45, 45.07, 44.90, 43.50, 33.77, 32.63, 31.04, 30.09, 29.81, 29.75, 29.69, 29.67, 17.67. ^{19}F NMR (376 MHz, CDCl_3) δ -113.91, -114.43. HRMS (ESI) m/z Calcd. for $\text{C}_{39}\text{H}_{35}\text{FN}_5\text{O}_3$, $[\text{M}+\text{H}]^+$, 640.2718, Found: 640.2726. Enantiomeric excess was determined to be 94% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 9/1, $\lambda = 254$ nm, 25 °C, 0.8 mL/min, $t_{\text{major}} = 86.7$ min, $t_{\text{minor}} = 34.5$ min).



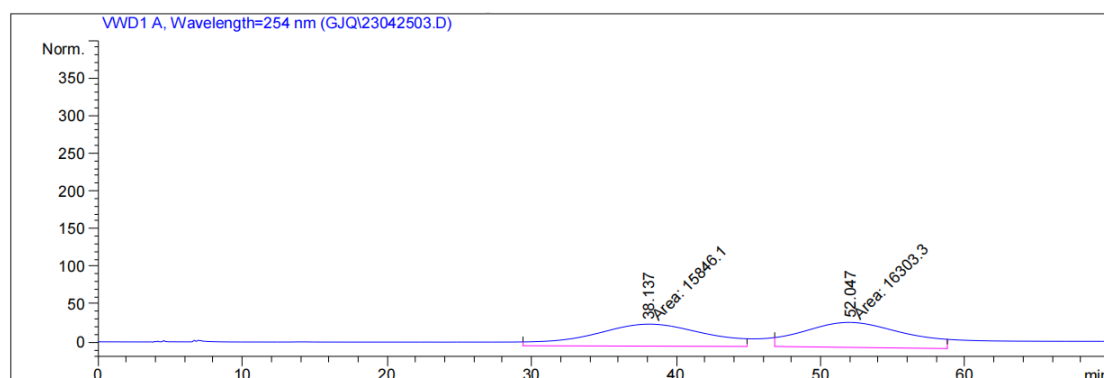
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	34.541	MM	8.0945	1.71163e5	352.42606	97.1887
2	86.787	MM T	7.3152	4951.17969	11.28065	2.8113

(S)-3-((R)-4-(2-bromobenzyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ia)

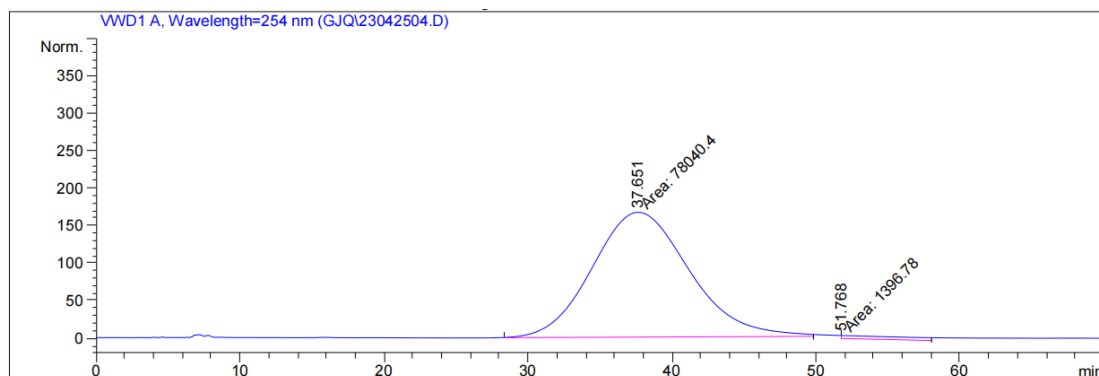


Prepared according to the procedure within 2 h as white solid (137.1 mg, 98% yield, dr = 1:1). mp 125.1 – 125.9 °C; $[\alpha]_D^{17} = -7.206$ (c 0.68, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 7.99 – 7.95 (m, 2H), 7.93 – 7.89 (m, 2H), 7.87 – 7.82 (m, 2H), 7.78 – 7.73 (m, 2H), 7.69 – 7.65 (m, 2H), 7.63 – 7.58 (m, 3H), 7.55 – 7.41 (m, 10H), 7.40 – 7.35 (m, 3H), 7.34 – 7.30 (m, 2H), 7.29 – 7.26 (m, 2H), 7.23 – 7.19 (m, 2H), 7.07 (ddtd, J = 28.0, 14.7, 7.3, 1.8 Hz, 6H), 6.29 (d, J = 2.9 Hz, 1H), 5.37 (s, 1H), 4.26 (d, J = 7.9 Hz, 1H), 4.21 – 4.03 (m, 3H), 3.89 (d, J = 14.4 Hz, 1H), 3.77 (q, J = 7.1 Hz, 2H), 3.17 (dd, J = 17.5, 9.0 Hz, 1H), 2.97 (dd, J = 18.6, 9.6 Hz, 1H), 2.72 (s, 1H), 1.53 (s, 9H), 1.33 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 173.73, 173.70, 172.98,

172.93, 172.27, 158.50, 157.85, 148.93, 148.65, 137.16, 137.05, 133.55, 133.37, 133.29, 133.23, 132.93, 131.10, 130.80, 130.74, 130.71, 130.33, 129.95, 129.49, 129.37, 129.25, 129.13, 129.07, 128.92, 128.84, 128.76, 128.69, 128.46, 128.30, 127.76, 127.67, 127.60, 127.56, 127.24, 126.23, 126.04, 125.77, 125.40, 125.33, 119.77, 119.54, 103.65, 103.63, 61.49, 61.47, 56.05, 45.22, 39.18, 37.65, 30.88, 30.09, 29.82, 29.65. HRMS (ESI) m/z Calcd. for C₃₉H₃₅BrN₅O₃, [M+H]⁺, 700.1918, Found: 700.1926. Enantiomeric excess was determined to be 96% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 9/1, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 51.7 min, t_{minor} = 37.6 min).

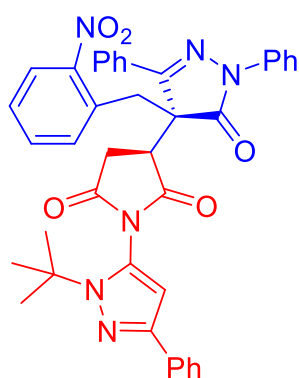


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	38.137	MM	9.0624	1.58461e4	29.14249	49.2889
2	52.047	MM	8.2131	1.63033e4	33.08375	50.7111



Peak #	RetTime [min]	Type	Width [min]	Area mAU*s	Height [mAU]	Area %
1	37.651	MM T	7.8287	7.80404e4	166.14117	98.2417
2	51.768	MM	5.9877	1396.77734	3.88789	1.7583

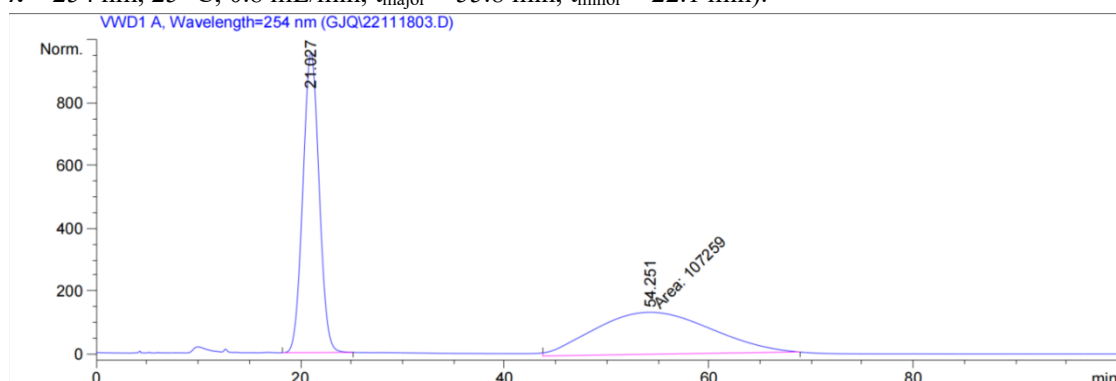
(S)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)-3-((R)-4-(2-nitrobenzyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)pyrrolidine-2,5-dione (3ja)



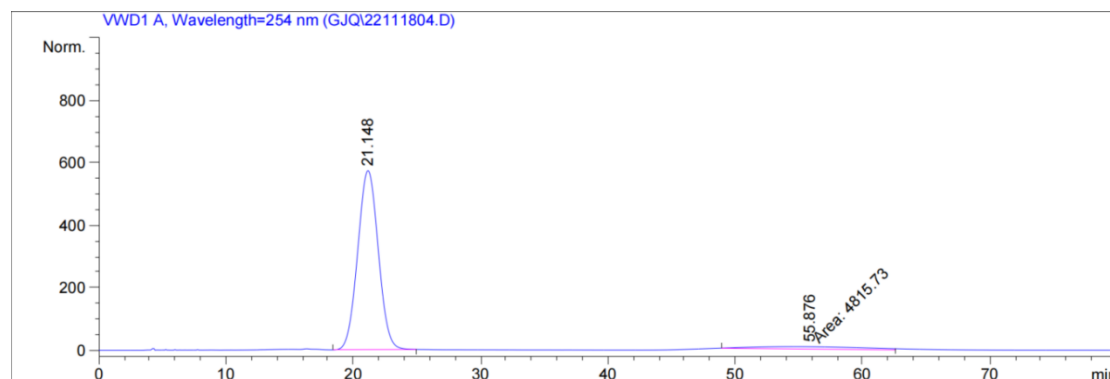
3ja

Prepared according to the procedure within 1.2 h as white solid (129.3 mg, 97% yield, dr = 1:1). mp 120.1 – 120.9 °C; $[\alpha]_D^{17} = -42.404$ (c 0.44, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 7.97 – 7.89 (m, 5H), 7.78 – 7.72 (m, 3H), 7.68 – 7.64 (m, 4H), 7.63 – 7.59 (m, 3H), 7.55 (t, J = 7.6 Hz, 3H), 7.50 (dd, J = 5.2, 2.0 Hz, 4H), 7.47 – 7.41 (m, 2H), 7.40 (s, 1H), 7.39 – 7.33 (m, 6H), 7.32 (s, 1H), 7.31 – 7.26 (m, 4H), 7.22 (dd, J = 5.6, 3.2 Hz, 3H), 6.27 (s, 1H), 5.37 (s, 1H), 4.43 (q, J = 14.2 Hz, 2H), 4.18 (d, J = 14.1 Hz, 1H), 4.09 (q, J = 4.4, 3.8 Hz, 2H), 4.06 (s, 1H), 3.73 (s, 1H), 3.24 – 3.12 (m, 1H), 2.93 (dd, J = 18.6, 9.6 Hz, 1H), 2.61 (s, 1H), 1.52 (s, 9H), 1.31 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 174.87, 173.65, 173.42, 172.82, 172.12, 157.74, 157.28,

149.97, 148.93, 148.64, 136.88, 136.81, 133.27, 133.20, 133.03, 132.65, 132.32, 132.01, 131.27, 131.08, 130.42, 130.20, 129.54, 129.27, 129.09, 128.99, 128.91, 128.81, 128.72, 128.48, 128.44, 128.26, 127.78, 127.69, 127.60, 127.43, 126.69, 126.32, 126.13, 125.46, 125.37, 125.32, 119.61, 119.55, 103.61, 61.52, 61.47, 56.51, 45.05, 35.22, 34.06, 30.89, 30.03, 29.80, 29.62. HRMS (ESI) m/z Calcd. for C₃₉H₃₅N₆O₅, [M+H]⁺, 667.2663, Found: 667.2673. Enantiomeric excess was determined to be 86% (determined by HPLC using chiral IG-H column, hexane/2-propanol = 7/3, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 55.8 min, t_{minor} = 22.1 min).

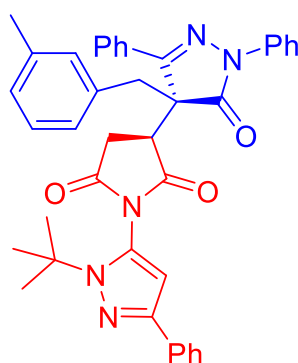


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.027	BB	1.7308	1.05528e5	953.61609	49.5933
2	54.251	MM	9.3342	1.07259e5	134.28444	50.4067



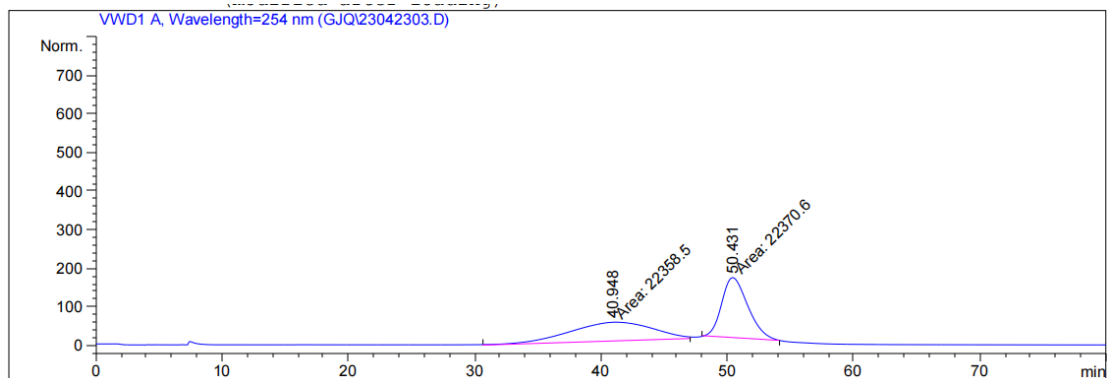
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	21.148	PB	1.7549	6.43660e4	572.88092	93.0390
2	55.876	MM	10.1646	4815.73242	7.89623	6.9610

(S)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)-3-((R)-4-(3-methylbenzyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)pyrrolidine-2,5-dione (3ka)

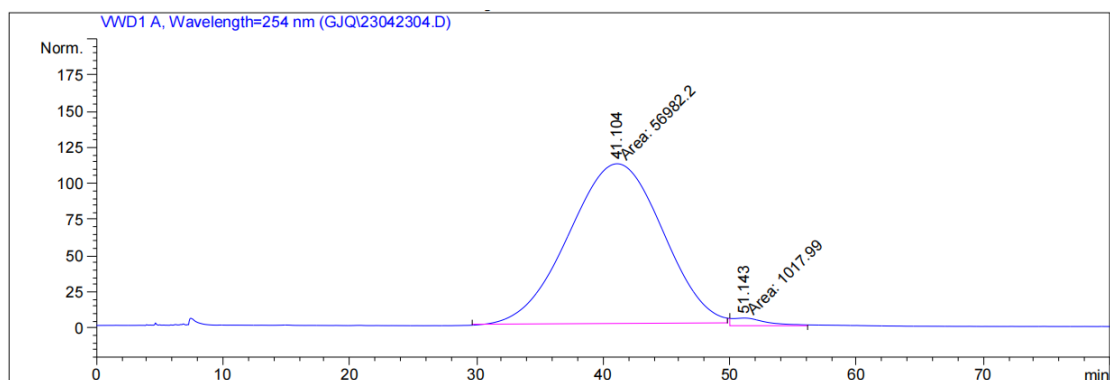


3ka

Prepared according to the procedure within 1 h as white solid (120.7 mg, 95% yield, dr = 1:1). mp 109.1 – 109.9 °C; $[\alpha]_D^{17} = -40.141$ (*c* 0.14, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 8.04 – 7.97 (m, 4H), 7.71 (d, *J* = 7.8 Hz, 4H), 7.66 – 7.52 (m, 10H), 7.38 (ddt, *J* = 16.5, 12.1, 7.9 Hz, 9H), 7.26 – 7.20 (m, 2H), 7.03 – 6.80 (m, 9H), 6.33 (s, 1H), 5.55 (s, 1H), 4.32 – 4.12 (m, 2H), 4.02 (dd, *J* = 9.4, 7.3 Hz, 1H), 3.85 – 3.75 (m, 1H), 3.60 (dd, *J* = 13.5, 4.0 Hz, 2H), 3.51 (d, *J* = 13.2 Hz, 1H), 3.22 (dd, *J* = 17.8, 9.4 Hz, 1H), 3.05 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.10 (d, *J* = 8.6 Hz, 6H), 1.56 (s, 9H), 1.42 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 173.90, 173.75, 173.62, 173.24, 158.24, 148.92, 148.64, 138.00, 137.01, 136.87, 133.17, 132.35, 131.15, 130.94, 130.65, 130.10, 129.32, 129.08, 128.95, 128.78, 128.69, 128.62, 128.46, 128.25, 128.20, 127.66, 127.59, 127.02, 126.27, 126.24, 126.02, 120.05, 119.87, 103.67, 61.48, 57.11, 44.90, 41.26, 31.07, 30.04, 29.80, 29.67, 21.16, 21.10. HRMS (ESI) *m/z* Calcd. for C₄₀H₃₈N₅O₃, [M+H]⁺, 636.2969, Found: 636.2976. Enantiomeric excess was determined to be 96% (determined by HPLC using chiral IB-H column, hexane/2-propanol = 4/1, λ = 254 nm, 25 °C, 0.6 mL/min, *t*_{major} = 51.1 min, *t*_{minor} = 41.1 min).

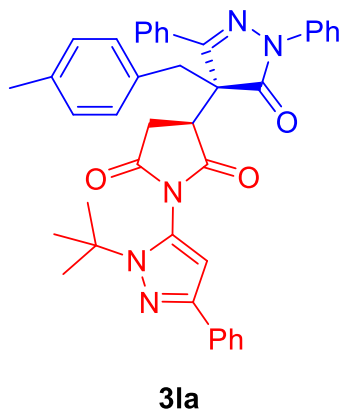


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	40.948	MM T	8.4498	2.23585e4		48.63107	49.9864
2	50.431	MM T	2.4018	2.23706e4		155.23814	50.0136



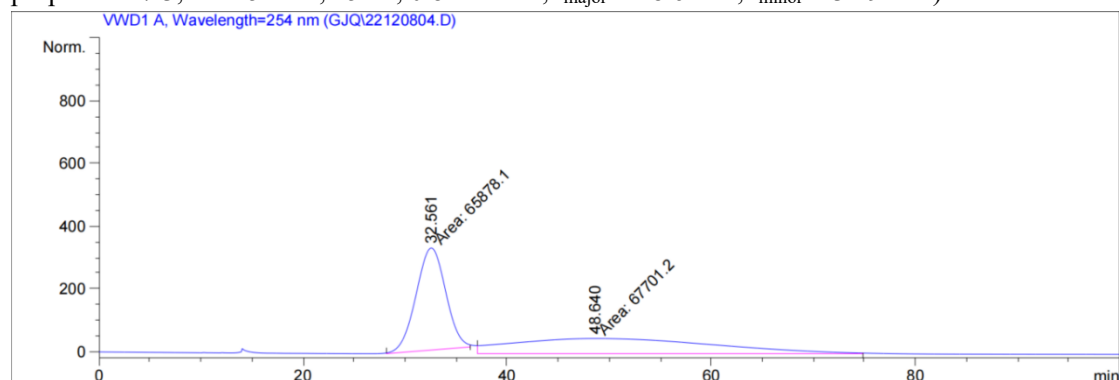
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	41.104	MM	8.5845	5.69822e4		110.63047	98.2448
2	51.143	MM	3.1904	1017.99371		5.31807	1.7552

(S)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)-3-((R)-4-(4-methylbenzyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)pyrrolidine-2,5-dione (3la)

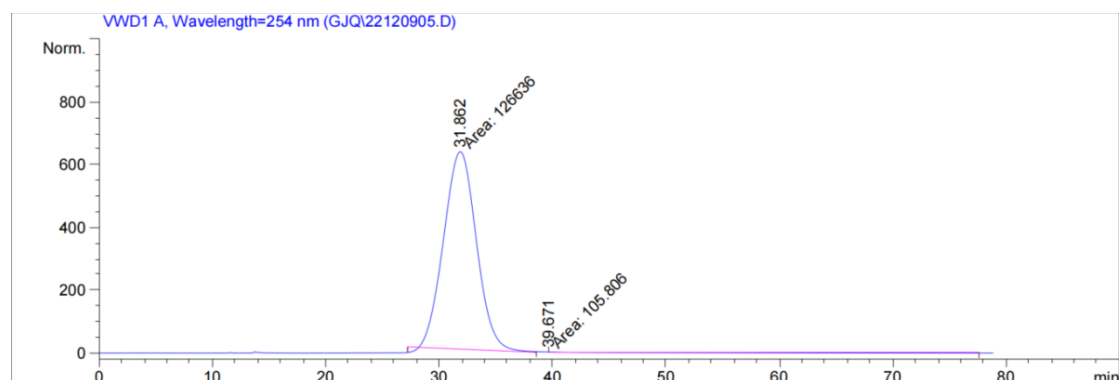


Prepared according to the procedure within 1.5 h as white solid (124.5 mg, 98% yield, dr = 1:1). mp 112.1 – 112.9 °C; $[\alpha]_D^{17} = -30.363$ (*c* 0.85, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 8.04 – 7.95 (m, 4H), 7.67 (ddd, *J* = 8.1, 5.5, 1.2 Hz, 4H), 7.65 – 7.58 (m, 5H), 7.58 – 7.47 (m, 5H), 7.41 – 7.25 (m, 10H), 7.24 – 7.16 (m, 2H), 6.97 (d, *J* = 7.8 Hz, 2H), 6.93 – 6.84 (m, 6H), 6.29 (s, 1H), 5.50 (s, 1H), 4.20 (dd, *J* = 18.6, 6.7 Hz, 2H), 3.96 (dd, *J* = 9.3, 7.3 Hz, 1H), 3.74 (dd, *J* = 9.3, 5.5 Hz, 1H), 3.57 (dd, *J* = 13.6, 10.3 Hz, 2H), 3.46 (d, *J* = 13.3 Hz, 1H), 3.16 (dd, *J* = 17.9, 9.4 Hz, 1H), 2.99 (dd, *J* = 18.5, 9.7 Hz, 1H), 2.83 (s, 1H), 2.16 (d, *J* = 2.5 Hz, 6H), 1.37 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 174.84, 173.87, 173.72, 173.55, 173.19, 173.09, 158.20, 157.51, 148.93, 148.65, 137.58, 137.39, 137.09,

136.93, 133.34, 133.27, 131.15, 131.04, 130.94, 130.65, 130.19, 129.40, 129.35, 129.19, 129.12, 129.07, 128.96, 128.82, 128.67, 128.46, 127.66, 127.60, 127.02, 126.23, 125.99, 125.39, 125.34, 120.07, 119.91, 103.67, 61.48, 57.20, 44.95, 43.63, 40.90, 39.63, 31.04, 30.02, 29.80, 29.67, 20.99. HRMS (ESI) m/z Calcd. for $C_{40}H_{38}N_5O_3$, $[M+H]^+$, 636.2969, found: 636.2976. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral ID-H-OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 48.6 min, t_{minor} = 31.9 min).

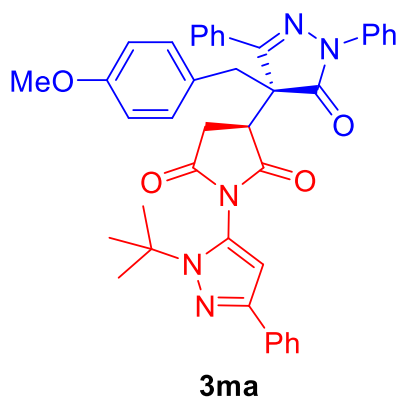


Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	32.561	MM	3.3724	6.58781e4		325.57639	49.3176
2	48.640	MM T	23.1456	6.77012e4		48.75010	50.6824

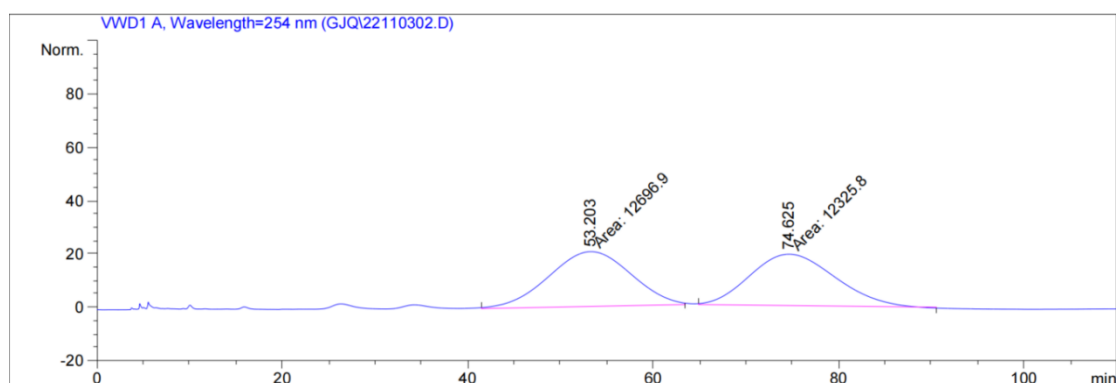


Peak #	RetTime [min]	Type	Width [min]	Area mAU	*s	Height [mAU]	Area %
1	31.862	MM	3.3545	1.26636e5		629.17596	99.9165
2	39.671	MM	0.8980	105.80643		1.38719	0.0835

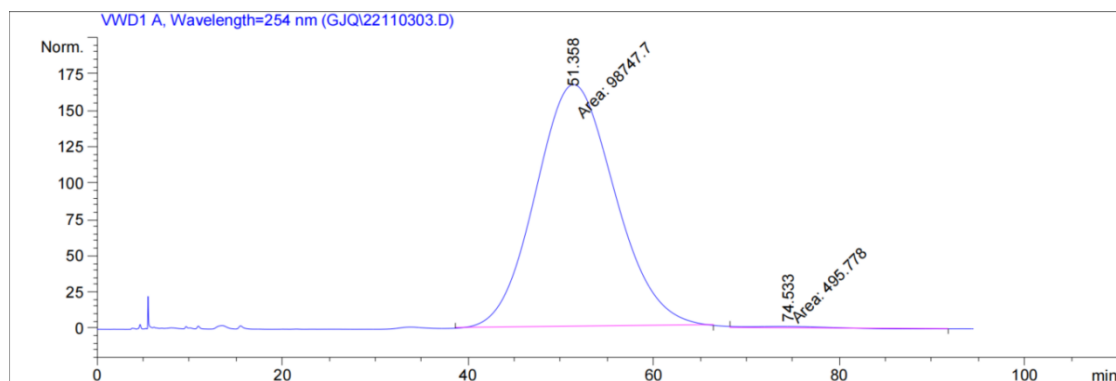
(S)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)-3-((R)-4-(4-methoxybenzyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)pyrrolidine-2,5-dione (3ma)



Prepared according to the procedure within 1.5 h as white solid (129.0 mg, 99% yield, dr = 1:1). mp 112.1 – 112.9 °C; $[\alpha]_D^{17} = -29.344$ (c 0.78, CH_2Cl_2); ^1H NMR (400 MHz, Chloroform- d) δ 8.04 – 7.96 (m, 4H), 7.71 – 7.65 (m, 4H), 7.64 – 7.58 (m, 5H), 7.58 – 7.48 (m, 5H), 7.41 – 7.27 (m, 9H), 7.24 – 7.17 (m, 2H), 7.04 – 6.98 (m, 2H), 6.96 – 6.91 (m, 2H), 6.64 – 6.57 (m, 4H), 6.29 (s, 1H), 5.51 (s, 1H), 4.20 (dd, J = 18.1, 7.4 Hz, 2H), 3.96 (dd, J = 9.3, 7.3 Hz, 1H), 3.74 (dd, J = 9.0, 5.8 Hz, 1H), 3.63 (d, J = 2.0 Hz, 6H), 3.56 (dd, J = 18.2, 13.7 Hz, 2H), 3.44 (d, J = 13.3 Hz, 1H), 3.16 (dd, J = 17.8, 9.4 Hz, 1H), 3.00 (dd, J = 18.5, 9.6 Hz, 1H), 2.83 (s, 1H), 1.52 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 174.85, 173.91, 173.75, 173.57, 173.22, 173.11, 159.15, 159.02, 158.20, 157.51, 148.92, 148.65, 137.08, 136.91, 133.33, 133.25, 131.15, 131.04, 130.97, 130.67, 130.45, 129.39, 129.15, 128.98, 128.83, 128.70, 128.46, 127.67, 127.60, 127.56, 126.99, 126.24, 126.00, 125.39, 125.34, 125.23, 124.45, 120.02, 119.88, 113.81, 113.76, 103.67, 61.49, 57.30, 55.11, 44.88, 43.59, 40.52, 39.26, 31.04, 30.00, 29.80, 29.68. HRMS (ESI) m/z Calcd. for $\text{C}_{40}\text{H}_{38}\text{N}_5\text{O}_4$, $[\text{M}+\text{H}]^+$, 652.2918, found: 652.2922. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 9/1, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 74.5 min, t_{minor} = 51.3 min).

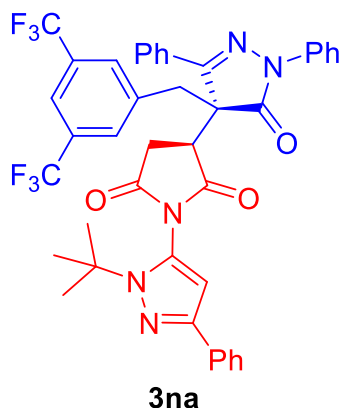


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Height [mAU]	Area %
1	53.203	MM	10.2805	1.26969e4	20.58406	50.7415
2	74.625	MM	10.6463	1.23258e4	19.29592	49.2585

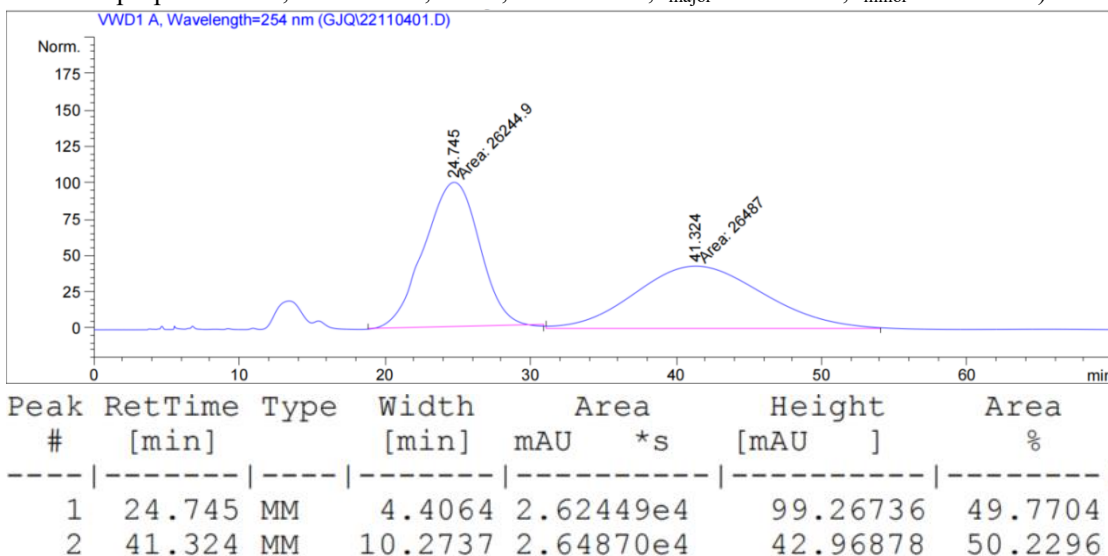


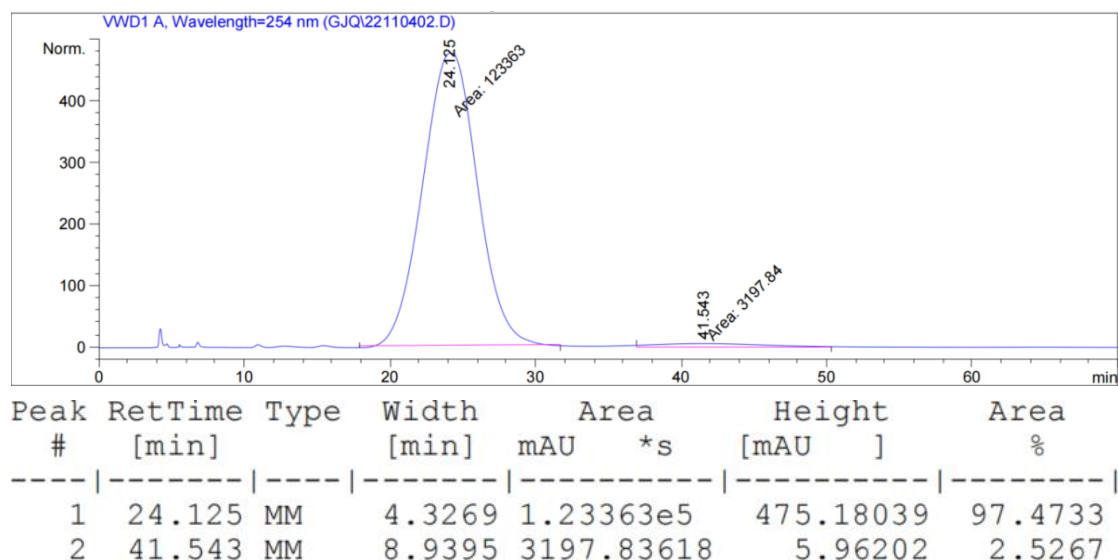
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	51.358	MM	9.8925	9.87477e4		166.36861	99.5004
2	74.533	MM	9.0046	495.77789		9.17636e-1	0.4996

(S)-3-((R)-4-(3,5-bis(trifluoromethyl)benzyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3na)

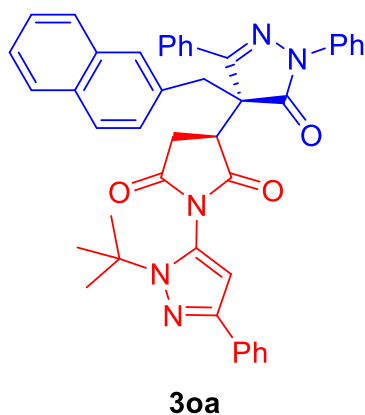


Prepared according to the procedure within 2.5 h as white solid (146.9 mg, 97% yield, dr = 1:1). mp 112.1 – 112.9 °C; $[\alpha]_D^{17} = 1.1617$ (c 0.80, CH_2Cl_2); ^1H NMR (400 MHz, CHCl_3 -d) δ 7.94 (d, $J = 7.4$ Hz, 4H), 7.72 – 7.47 (m, 20H), 7.41 – 7.30 (m, 10H), 7.23 (d, $J = 8.7$ Hz, 2H), 6.32 (s, 1H), 5.58 (s, 1H), 4.23 (s, 2H), 4.11 (t, $J = 8.2$ Hz, 1H), 3.81 (t, $J = 7.3$ Hz, 1H), 3.70 (dd, $J = 22.0, 13.6$ Hz, 2H), 3.60 (d, $J = 13.1$ Hz, 1H), 3.21 (dd, $J = 17.6, 9.1$ Hz, 1H), 3.03 (dd, $J = 18.6, 9.7$ Hz, 1H), 2.78 (s, 1H), 1.56 (s, 9H), 1.35 (s, 9H). ^{13}C NMR (151 MHz, CDCl_3) δ 173.53, 173.32, 172.71, 172.68, 172.32, 157.34, 156.70, 148.97, 148.70, 136.49, 136.38, 135.93, 135.13, 133.21, 133.09, 131.96, 131.79, 131.74, 131.57, 131.52, 131.35, 131.29, 130.36 (d, $J = 14.14$ Hz), 129.75, 129.62, 129.42, 129.10, 128.84, 128.63, 128.53, 128.50, 128.29, 127.78, 127.70, 127.13, 126.63, 126.60, 126.44, 125.51, 125.37, 125.30, 123.74, 123.69, 121.93, 121.89, 121.83, 119.66, 119.48, 103.64, 103.59, 61.58, 61.53, 56.82, 44.86, 43.37, 40.35, 39.14, 30.90, 29.81, 29.77, 29.62. ^{19}F NMR (376 MHz, CDCl_3) δ -63.14, -63.17. HRMS (ESI) m/z Calcd. for $\text{C}_{41}\text{H}_{34}\text{F}_6\text{N}_5\text{O}_3$, $[\text{M}+\text{H}]^+$, 758.2560, Found: 758.2570. Enantiomeric excess was determined to be 95% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 9/1, $\lambda = 254$ nm, 25 °C, 0.8 mL/min, $t_{\text{major}} = 41.5$ min, $t_{\text{minor}} = 24.1$ min).



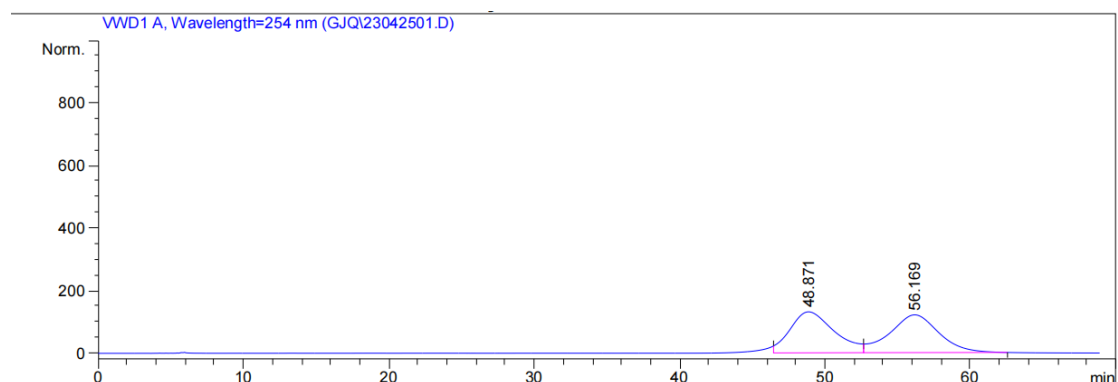


(S)-1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)-3-((R)-4-(naphthalen-2-ylmethyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)pyrrolidine-2,5-dione (3oa)

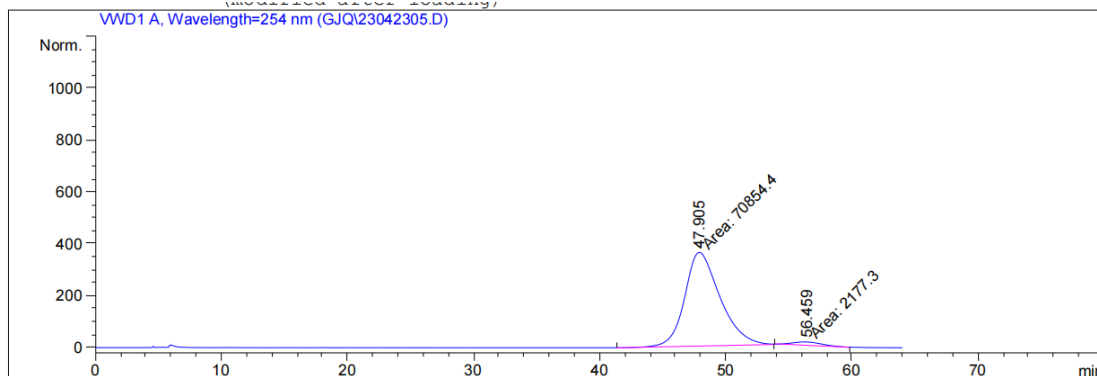


Prepared according to the procedure within 4 h as white solid (99.4 mg, 74% yield, dr = 1:1). mp 116.1 – 116.9 °C; $[\alpha]_D^{17} = -66.632$ (c 0.96, CH₂Cl₂); ¹H NMR (600 MHz, Chloroform-d) δ 8.19 (d, J = 8.3 Hz, 1H), 8.08 – 8.03 (m, 1H), 7.96 – 7.93 (m, 2H), 7.92 – 7.89 (m, 2H), 7.76 – 7.71 (m, 2H), 7.69 – 7.56 (m, 8H), 7.52 – 7.38 (m, 13H), 7.37 – 7.26 (m, 11H), 7.24 – 7.14 (m, 9H), 7.13 – 7.09 (m, 1H), 6.32 (s, 1H), 5.49 (s, 1H), 4.60 (s, 1H), 4.40 (s, 1H), 4.29 (d, J = 15.0 Hz, 1H), 4.17 (dd, J = 15.4, 6.8 Hz, 2H), 4.00 – 3.86 (m, 2H), 3.29 (dd, J = 17.9, 9.4 Hz, 1H), 3.04 (dd, J = 18.9, 9.9 Hz, 1H), 2.88 (s, 1H), 1.56 (d, J = 2.0 Hz, 9H), 1.34 (s, 9H). ¹³C NMR (101 MHz, Chloroform-d) δ 173.91,

173.71, 173.46, 173.02, 158.36, 148.97, 148.62, 136.74, 136.68, 133.82, 133.75, 133.33, 133.25, 131.82, 131.68, 131.31, 131.06, 130.97, 130.60, 129.91, 129.35, 129.06, 128.98, 128.88, 128.79, 128.73, 128.69, 128.54, 128.51, 128.45, 127.90, 127.66, 127.58, 127.04, 126.74, 126.17, 126.04, 125.97, 125.75, 125.70, 125.39, 125.34, 124.92, 124.76, 123.67, 123.50, 120.06, 119.71, 103.67, 103.63, 61.51, 61.47, 56.60, 45.40, 43.90, 36.34, 34.65, 31.09, 30.26, 29.84, 29.65. HRMS (ESI) m/z Calcd. for C₄₃H₃₈N₅O₃, [M+H]⁺, 672.2969, Found: 672.2981. Enantiomeric excess was determined to be 94% (determined by HPLC using chiral IB-H column, hexane/2-propanol = 4/1, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 56.4 min, t_{minor} = 47.9 min).

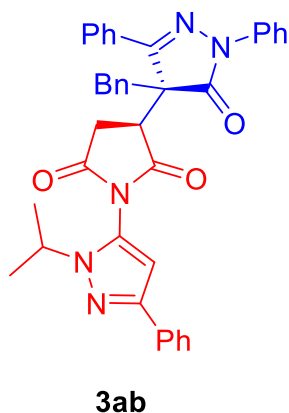


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	48.871	BV	2.9766	2.77069e4	131.02893	49.4175
2	56.169	VB	3.2680	2.83601e4	120.77757	50.5825



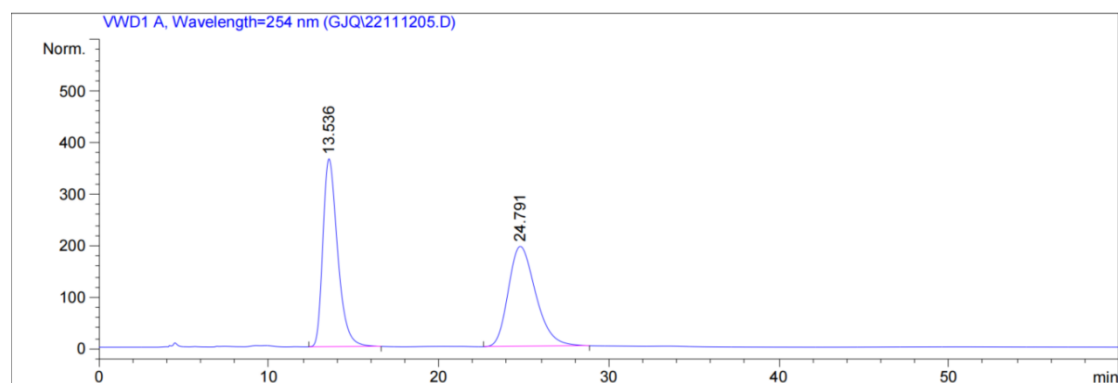
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	47.905	MM	3.2651	7.08544e4	361.67343	97.0187
2	56.459	MM T	2.7281	2177.30493	13.30177	2.9813

(S)-3-((R)-4-benzyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-isopropyl-3-phenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ab)

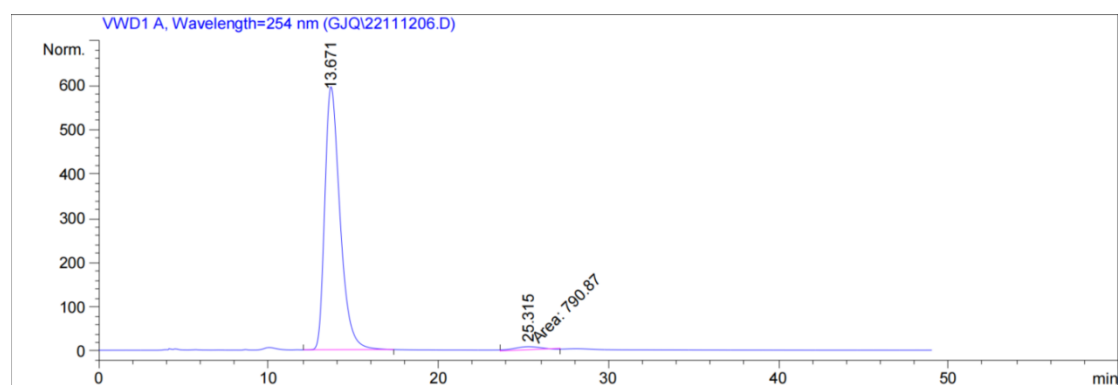


Prepared according to the procedure within 1 h as white solid (120.2 mg, 99% yield, dr > 20:1). mp 105.1 – 105.9 °C; $[\alpha]_D^{17} = 9.067$ (*c* 1.15, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.04 – 7.95 (m, 2H), 7.76 – 7.62 (m, 4H), 7.53 (dt, *J* = 5.3, 2.7 Hz, 3H), 7.34 (q, *J* = 7.4 Hz, 4H), 7.27 (d, *J* = 1.4 Hz, 1H), 7.20 (dd, *J* = 7.4 Hz, 1H), 7.15 – 7.01 (m, 5H), 6.17 (s, 1H), 3.94 (dd, *J* = 9.4, 5.7 Hz, 1H), 3.82 (s, 2H), 3.56 (d, *J* = 13.4 Hz, 1H), 3.16 (dd, *J* = 18.3, 9.7 Hz, 1H), 1.58 (s, 1H), 1.35 (d, *J* = 6.6 Hz, 3H), 1.10 (s, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 173.72, 173.51, 172.82, 150.49, 136.88, 133.39, 132.76, 130.98, 130.85, 129.31, 129.21, 128.83, 128.49, 128.40, 128.12, 127.91, 127.68, 127.17, 126.14, 125.51, 119.77, 100.97, 50.25, 44.09, 40.68, 30.51, 22.49, 22.11.

HRMS (ESI) *m/z* Calcd. for C₃₈H₃₄N₅O₃, [M+H]⁺, 608.2656, Found: 608.2666. Enantiomeric excess was determined to be 96% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 25 °C, 0.8 mL/min, *t*_{major} = 25.3 min, *t*_{minor} = 13.6 min).

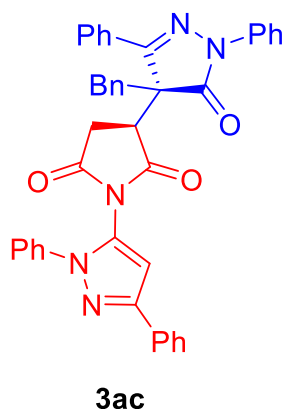


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.536	BB	0.9235	2.19903e4	364.61627	50.2205
2	24.791	BB	1.7339	2.17972e4	194.08760	49.7795



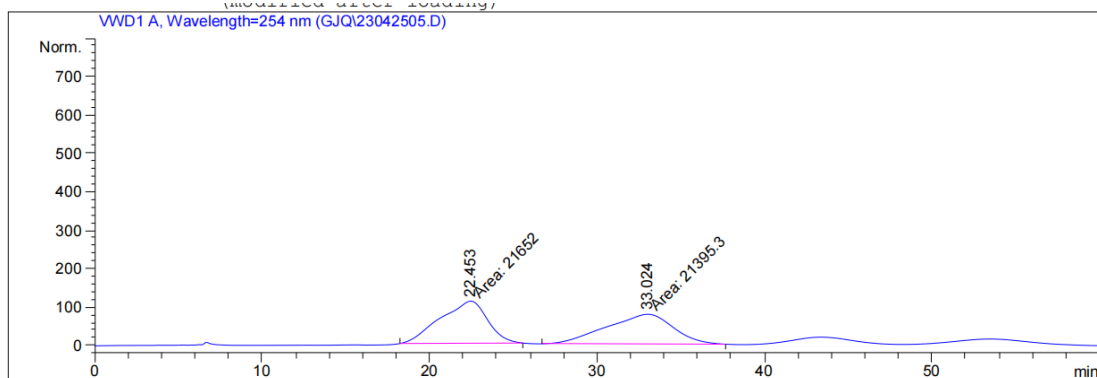
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.671	VB	0.9557	3.69886e4	592.29419	97.9066
2	25.315	MM	1.3057	790.86957	7.24189	2.0934

(S)-3-((R)-4-benzyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1,3-diphenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ac)

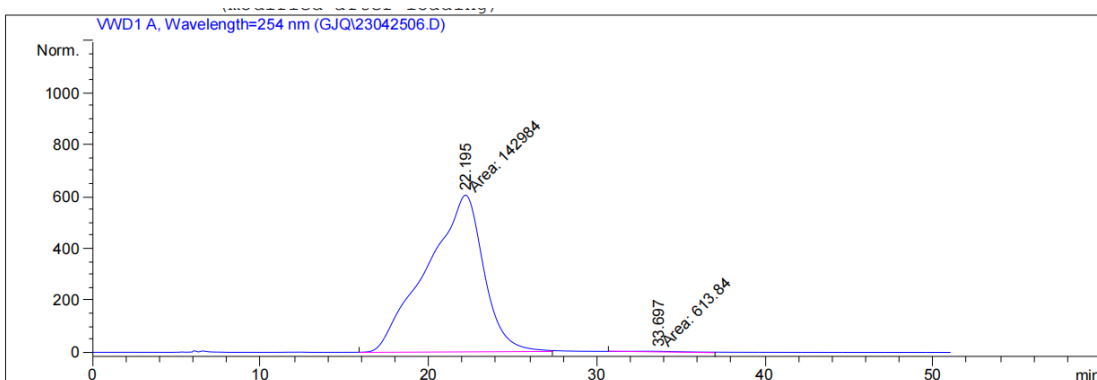


Prepared according to the procedure within 1 h as white solid (123.1 mg, 96% yield, dr > 20:1). mp 108.1 – 108.9 °C; $[\alpha]_D^{17} = 11.915$ (c 1.13, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 7.98 – 7.91 (m, 2H), 7.78 – 7.72 (m, 2H), 7.59 – 7.48 (m, 5H), 7.43 – 7.26 (m, 9H), 7.22 (d, J = 11.9 Hz, 2H), 7.12 – 6.99 (m, 5H), 6.28 (s, 1H), 4.02 – 3.09 (m, 4H), 2.95 (dd, J = 18.1, 9.4 Hz, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 173.51, 173.01, 172.25, 157.43, 151.85, 137.82, 136.86, 132.51, 131.02, 130.82, 129.78, 129.42, 129.32, 129.25, 128.82, 128.64, 128.35, 128.32, 127.84, 127.19, 126.19, 125.68, 124.19, 120.15, 103.42, 44.16, 40.63, 30.50. HRMS (ESI) m/z Calcd. for C₄₁H₃₂N₅O₃, [M+H]⁺, 642.2500, Found: 642.2507. Enantiomeric excess was determined to be 99% (determined

by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 33.7 min, t_{minor} = 22.2 min).

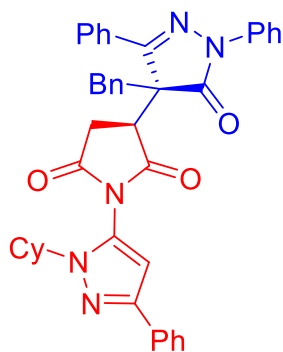


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	22.453	MM T	3.2914	2.16520e4		109.63880	50.2982
2	33.024	MM T	4.6189	2.13953e4		77.20210	49.7018



Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	22.195	MM T	3.9314	1.42984e5		606.15686	99.5725
2	33.697	MM T	4.1505	613.84021		2.46493	0.4275

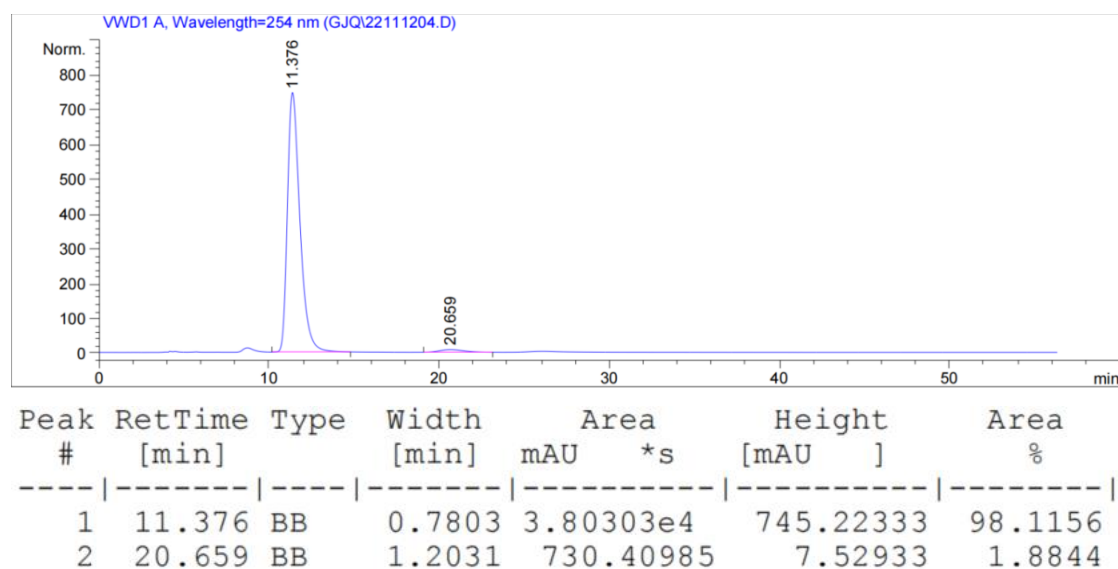
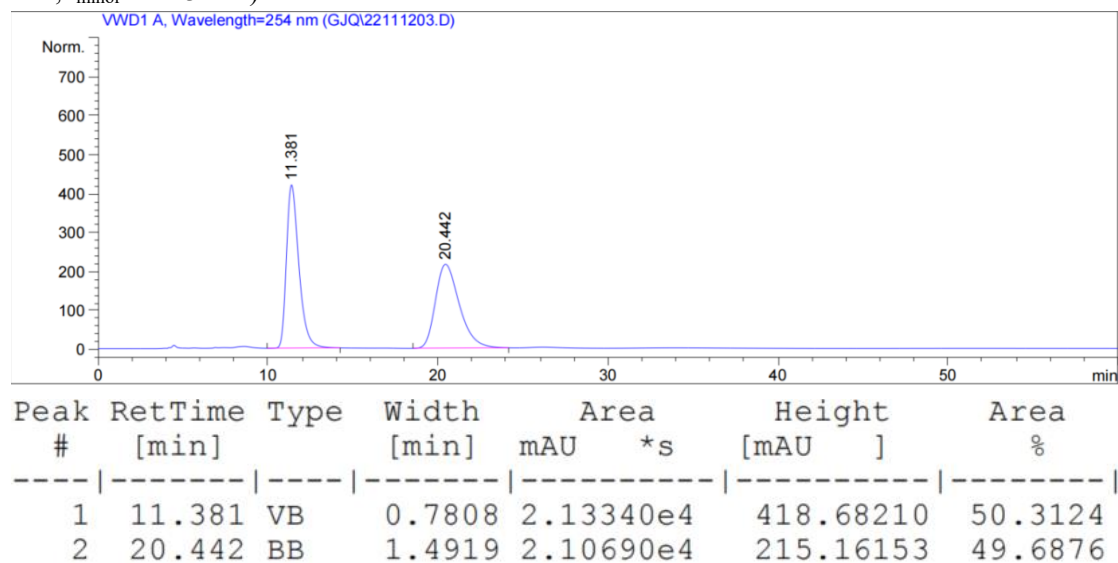
(S)-3-((R)-4-benzyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-cyclohexyl-3-phenyl-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ad)



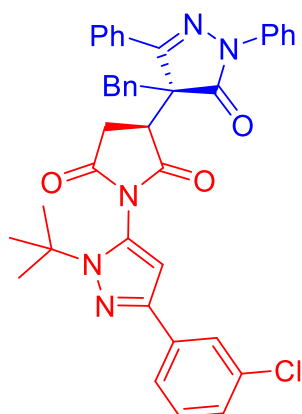
3ad

Prepared according to the procedure within 1 h as white solid (124.3 mg, 96% yield, dr > 20:1). mp 112.1 – 112.9 °C; $[\alpha]_D^{17} = 10.511$ (*c* 1.05, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 7.99 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.71 – 7.65 (m, 2H), 7.63 – 7.57 (m, 2H), 7.56 – 7.49 (m, 3H), 7.33 (t, *J* = 7.4 Hz, 4H), 7.27 (d, *J* = 1.4 Hz, 1H), 7.18 (dd, *J* = 7.4 Hz, 1H), 7.09 (q, *J* = 5.0, 3.3 Hz, 5H), 6.16 (s, 1H), 3.96 (t, *J* = 7.9 Hz, 1H), 3.78 (s, 1H), 3.55 (d, *J* = 13.3 Hz, 1H), 3.47 (dt, *J* = 11.3, 6.7 Hz, 1H), 3.17 (dd, *J* = 18.2, 9.6 Hz, 1H), 1.87 (q, *J* = 6.6 Hz, 4H), 1.56 – 0.76 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 173.86, 172.95, 157.77, 150.33, 136.82, 133.41, 130.97, 130.82, 129.36, 129.25, 128.81, 128.51, 128.39, 128.25, 127.95, 127.67, 127.10, 126.24, 125.52, 120.25, 100.94, 57.88, 44.11, 40.89, 32.82, 32.72, 30.52, 25.39, 25.07. HRMS (ESI) *m/z* Calcd. for C₄₁H₃₈N₅O₃, [M+H]⁺,

648.2969, Found: 648.2978. Enantiomeric excess was determined to be 96% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 7/3, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 20.6 min, t_{minor} = 11.3 min).

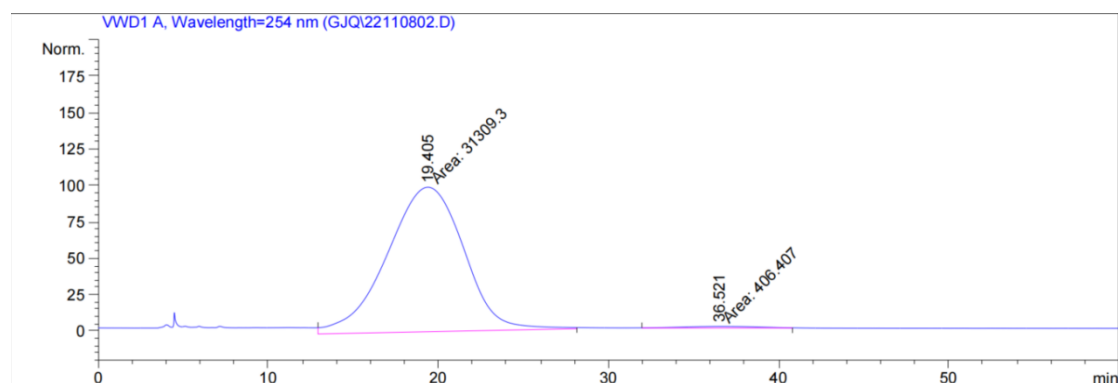
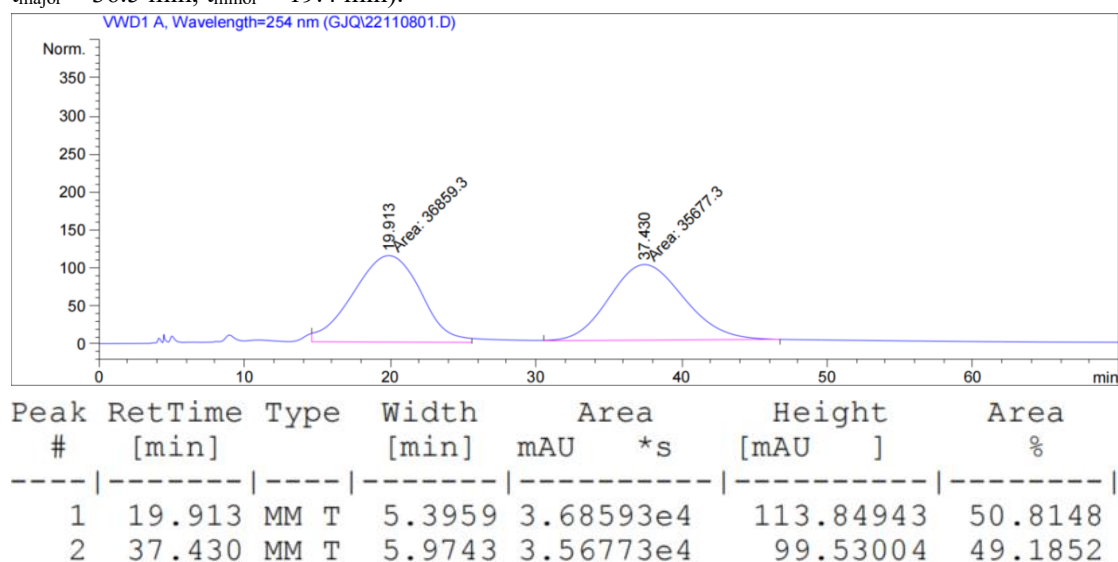


(S)-3-((R)-4-benzyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-(3-chlorophenyl)-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ae)



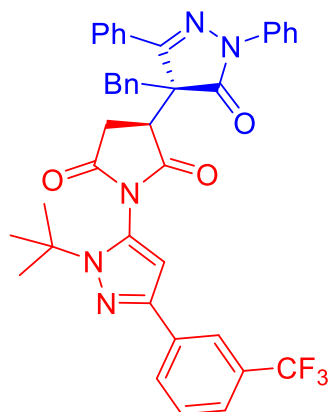
3ae

Prepared according to the procedure within 1.1 h as white solid (123.2 mg, 94% yield, dr = 1:1). mp 120.1 – 120.9 °C; $[\alpha]_D^{17} = -17.123$ (c 0.22, CH_2Cl_2); ^1H NMR (400 MHz, CHCl_3 -d) δ 8.03 – 7.97 (m, 4H), 7.71 – 7.45 (m, 15H), 7.42 – 7.27 (m, 5H), 7.24 – 7.16 (m, 4H), 7.13 – 7.05 (m, 8H), 7.04 – 7.00 (m, 2H), 6.28 (s, 1H), 5.45 (s, 1H), 4.23 (d, $J = 26.3$ Hz, 2H), 4.00 (dd, $J = 9.4, 7.4$ Hz, 1H), 3.80 – 3.74 (m, 1H), 3.61 (dd, $J = 18.0, 13.5$ Hz, 2H), 3.50 (d, $J = 13.2$ Hz, 1H), 3.19 (dd, $J = 17.8, 9.4$ Hz, 1H), 3.02 (dd, $J = 18.4, 9.7$ Hz, 1H), 2.83 (s, 1H), 1.52 (s, 9H), 1.38 (s, 9H). ^{13}C NMR (101 MHz, CDCl_3) δ 174.73, 173.82, 173.63, 173.42, 173.01, 158.05, 157.35, 147.57, 147.29, 136.97, 136.79, 135.09, 134.99, 134.44, 133.23, 132.45, 131.07, 131.03, 131.00, 130.73, 129.75, 129.42, 129.34, 129.17, 129.04, 128.99, 128.72, 128.45, 128.39, 127.96, 127.81, 127.62, 127.58, 126.98, 126.39, 126.06, 125.39, 123.47, 123.36, 120.01, 119.87, 103.89, 103.86, 61.78, 61.75, 57.11, 44.94, 43.72, 41.24, 40.01, 31.03, 30.04, 29.78, 29.65. HRMS (ESI) m/z Calcd. for $\text{C}_{39}\text{H}_{35}\text{ClN}_5\text{O}_3$, $[\text{M}+\text{H}]^+$, 656.2423, Found: 656.2434. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, $\lambda = 254$ nm, 25 °C, 0.8 mL/min, $t_{\text{major}} = 36.5$ min, $t_{\text{minor}} = 19.4$ min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.405	MM	3.7002	3.13093e4	99.38270	98.7186
2	36.521	MM T	5.5009	406.40714	1.23134	1.2814

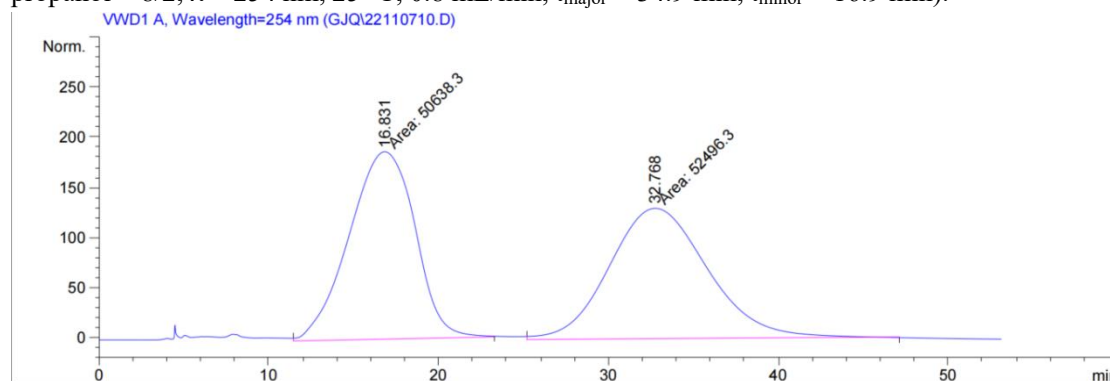
(S)-3-((R)-4-benzyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-(3-(trifluoromethyl)phenyl)-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3af)



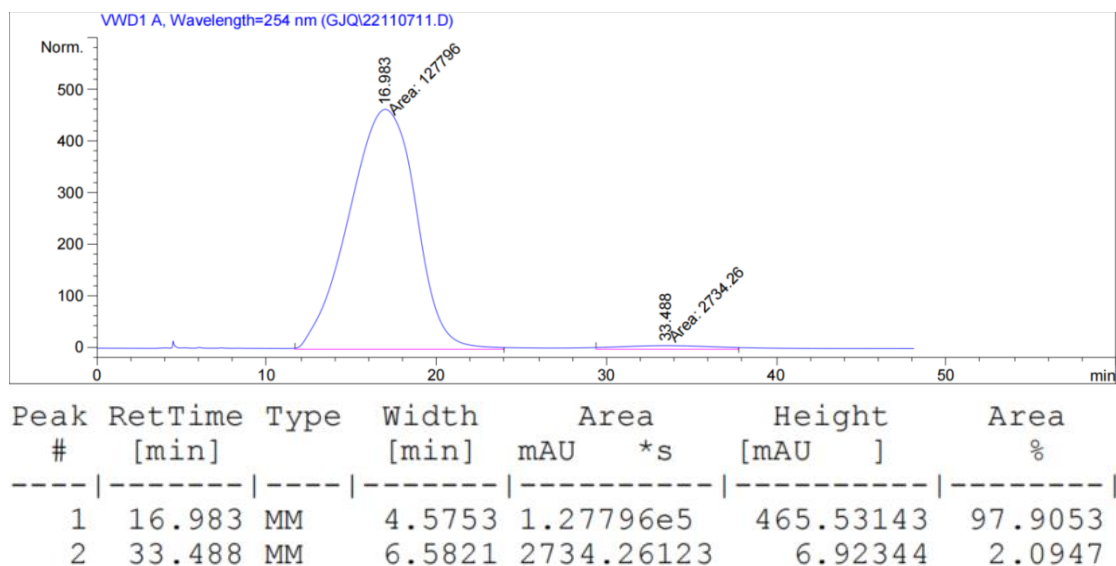
3af

Prepared according to the procedure within 1 h as white solid (128.2 mg, 93% yield, dr = 1:1). mp 118.1 – 118.9 °C; $[\alpha]_D^{17} = -24.115$ (c 0.68, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 8.03 – 7.97 (m, 4H), 7.92 (s, 1H), 7.86 – 7.79 (m, 3H), 7.66 (d, J = 8.1 Hz, 2H), 7.62 (d, J = 7.0 Hz, 1H), 7.58 (dd, J = 8.3, 3.0 Hz, 4H), 7.51 (dtd, J = 11.6, 8.9, 7.8, 3.9 Hz, 6H), 7.44 (d, J = 8.1 Hz, 1H), 7.36 (dt, J = 16.5, 7.8 Hz, 4H), 7.24 – 7.17 (m, 2H), 7.13 – 7.06 (m, 8H), 7.03 (d, J = 7.0 Hz, 2H), 6.35 (s, 1H), 5.46 (s, 1H), 4.31 – 4.15 (m, 2H), 4.00 (dd, J = 9.4, 7.4 Hz, 1H), 3.78 (dd, J = 9.3, 5.4 Hz, 1H), 3.62 (dd, J = 18.9, 13.5 Hz, 2H), 3.51 (d, J = 13.2 Hz, 1H), 3.20 (dd, J = 17.9, 9.4 Hz, 1H), 3.03 (dd, J = 18.5, 9.7 Hz, 1H), 2.83 (s, 1H), 1.54 (s, 10H), 1.39 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 174.72, 173.81, 173.62, 173.43, 173.01, 158.05, 157.32, 147.51, 147.25,

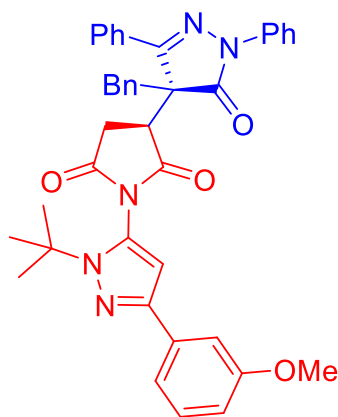
136.97, 136.78, 134.05, 133.97, 133.24, 132.43, 131.06, 131.00, 130.95, 130.74, 130.67, 129.44, 129.33, 129.20, 129.17, 128.98, 128.93, 128.87, 128.72, 128.46, 128.39, 127.97, 127.81, 127.64, 126.97, 126.37, 126.07, 124.19, 122.14, 120.02, 119.85, 103.92, 103.89, 61.88, 61.85, 57.10, 44.96, 43.68, 41.25, 40.00, 31.07, 30.05, 29.78, 29.65. ¹⁹F NMR (376 MHz, CDCl₃) δ -62.62, -62.70. HRMS (ESI) m/z Calcd. for C₄₀H₃₅F₃N₅O₃, [M+H]⁺, 690.2687, Found: 690.2694. Enantiomeric excess was determined to be 96% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 34.9 min, t_{minor} = 16.9 min).



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.831	MM	4.5051	5.06383e4	187.33504	49.0993
2	32.768	MM	6.7110	5.24963e4	130.37428	50.9007



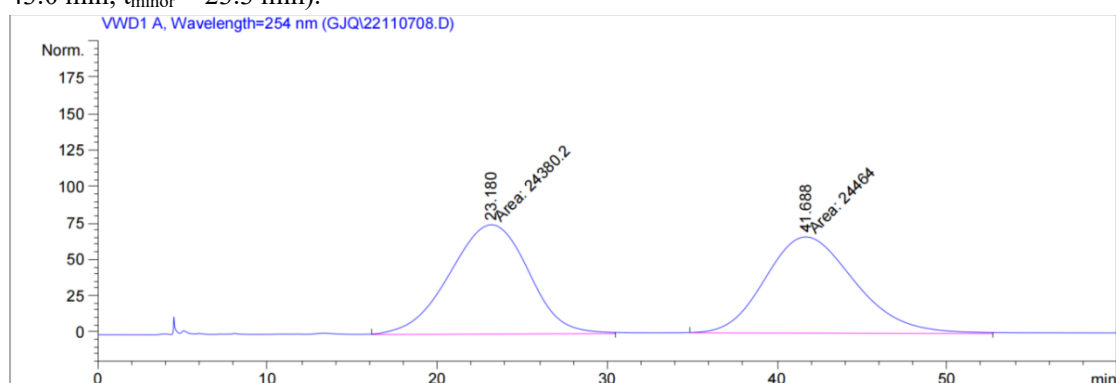
(S)-3-((R)-4-benzyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-(3-methoxyphenyl)-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ag)



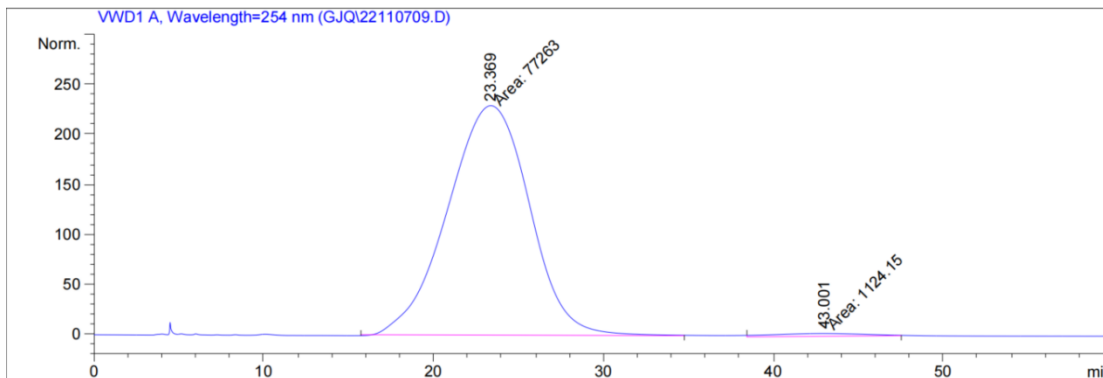
3ag

Prepared according to the procedure within 1 h as white solid (125.0 mg, 96% yield, dr = 1:1). mp 114.1 – 114.9 °C; $[\alpha]_D^{17} = -37.751$ (c 0.25, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 7.98 (d, J = 7.6 Hz, 4H), 7.67 – 7.46 (m, 10H), 7.34 (dt, J = 15.4, 7.7 Hz, 4H), 7.26 – 7.15 (m, 8H), 7.07 (d, J = 9.5 Hz, 8H), 7.00 (d, J = 7.5 Hz, 2H), 6.85 – 6.75 (m, 2H), 6.29 (s, 1H), 5.50 (s, 1H), 4.21 (q, J = 7.8, 7.3 Hz, 2H), 3.97 (t, J = 8.3 Hz, 1H), 3.80 (d, J = 21.3 Hz, 7H), 3.58 (dd, J = 13.6, 6.5 Hz, 2H), 3.47 (d, J = 13.2 Hz, 1H), 3.15 (dd, J = 17.8, 9.4 Hz, 1H), 3.00 (dd, J = 18.5, 9.6 Hz, 1H), 1.52 (s, 9H), 1.35 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 174.88, 173.92, 173.79, 173.47, 173.10, 159.83, 159.78, 158.11, 157.40, 148.78, 148.50, 137.01, 136.82, 134.73, 134.63, 133.31, 132.53, 131.09, 131.04, 131.00, 130.73, 129.54, 129.44, 129.37,

129.19, 129.00, 128.85, 128.73, 128.45, 128.38, 127.94, 127.81, 127.60, 126.99, 126.34, 126.07, 120.04, 119.91, 118.07, 118.01, 113.42, 110.77, 103.90, 103.88, 61.55, 57.12, 55.29, 55.25, 44.94, 43.60, 41.23, 40.04, 31.05, 30.03, 29.82, 29.70. HRMS (ESI) m/z Calcd. for C₄₀H₃₈N₅O₄ [M+H]⁺ 652.2918, Found: 652.2926. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral, [M+H]⁺, column, hexane/2-propanol = 8/2, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 43.0 min, t_{minor} = 23.3 min).

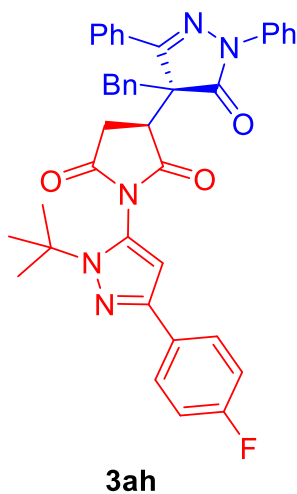


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.180	MM	5.4062	2.43802e4	75.16162	49.9141
2	41.688	MM	6.1597	2.44640e4	66.19364	50.0859



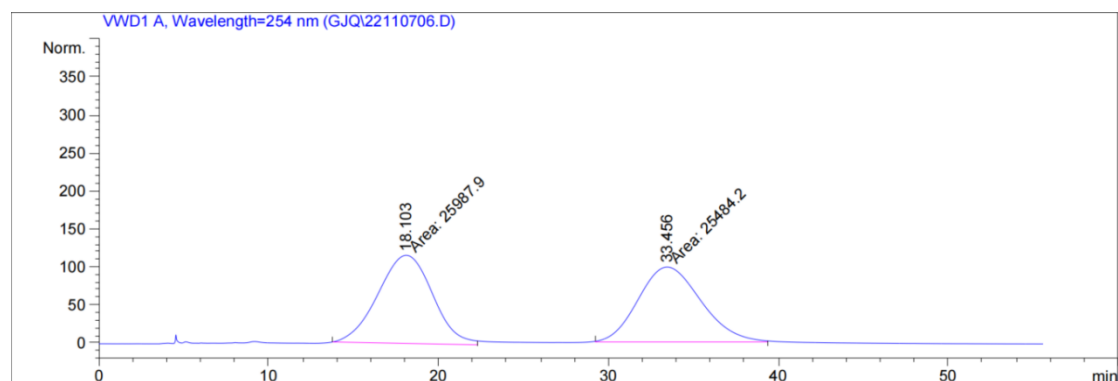
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	23.369	MM	5.5949	7.72630e4	230.15930	98.5659
2	43.001	MM	6.4655	1124.15320	2.89782	1.4341

(S)-3-((R)-4-benzyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-(4-fluorophenyl)-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ah)

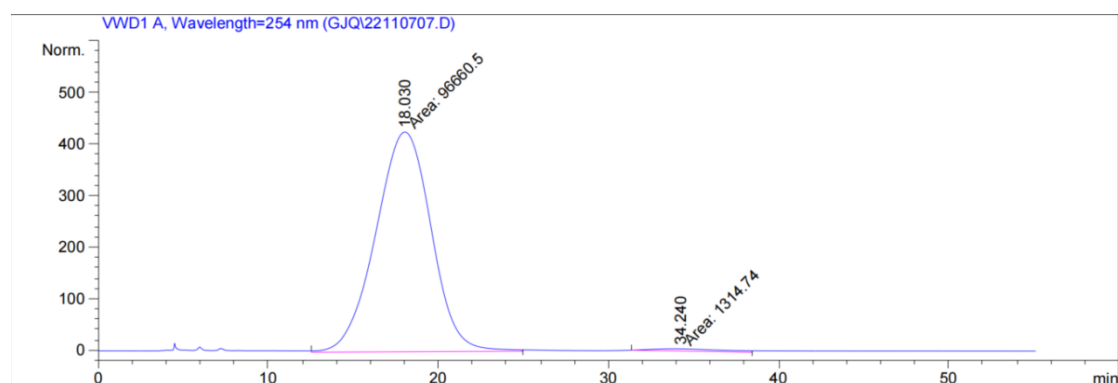


Prepared according to the procedure within 1 h as white solid (120.2 mg, 94% yield, dr = 1:1). mp 104.1 – 104.9 °C; $[\alpha]_D^{17} = -24.525$ (c 0.58, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 7.99 (ddt, J = 6.7, 4.2, 1.9 Hz, 4H), 7.67 – 7.48 (m, 14H), 7.41 – 7.30 (m, 4H), 7.23 – 7.16 (m, 2H), 7.13 – 6.96 (m, 14H), 6.24 (s, 1H), 5.47 (s, 1H), 4.22 (dd, J = 17.9, 7.2 Hz, 2H), 3.99 (dd, J = 9.3, 7.4 Hz, 1H), 3.81 – 3.72 (m, 1H), 3.61 (dd, J = 18.5, 13.5 Hz, 2H), 3.49 (d, J = 13.2 Hz, 1H), 3.18 (dd, J = 17.8, 9.4 Hz, 1H), 3.02 (dd, J = 18.4, 9.6 Hz, 1H), 1.52 (s, 9H), 1.37 (s, 9H). ¹³C NMR (151 MHz, CDCl₃) δ 173.86, 173.71, 173.42, 173.09, 173.04, 163.36, 163.32, 161.72, 161.69, 158.05, 157.35, 148.07, 147.79, 136.97, 136.82, 133.22, 132.45, 131.08, 131.01, 130.95, 130.72, 129.55, 129.48, 129.39, 129.34, 129.17, 128.98, 128.89, 128.71, 128.57, 128.44, 128.39, 127.96, 127.81, 127.56, 127.07,

127.01, 126.99, 126.96, 126.28, 126.06, 120.02, 119.88, 115.37 (d, J = 15.15 Hz), 103.47, 103.43, 61.55, 57.11, 44.93, 41.24, 40.04, 31.03, 30.04, 29.79, 29.66. ¹⁹F NMR (376 MHz, CDCl₃) δ -114.70, -114.83. HRMS (ESI) m/z Calcd. for C₃₉H₃₅FN₅O₃, [M+H]⁺, 640.2718, Found: 640.2731. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 34.2 min, t_{minor} = 18.0 min).

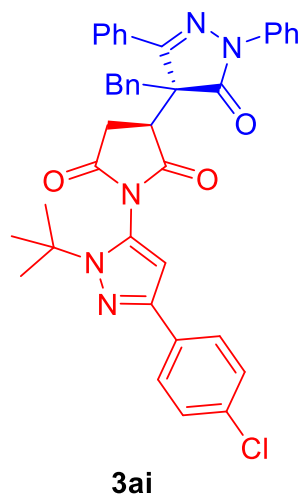


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.103	MM	3.7317	2.59879e4	116.06711	50.4893
2	33.456	MM	4.2994	2.54842e4	98.78864	49.5107



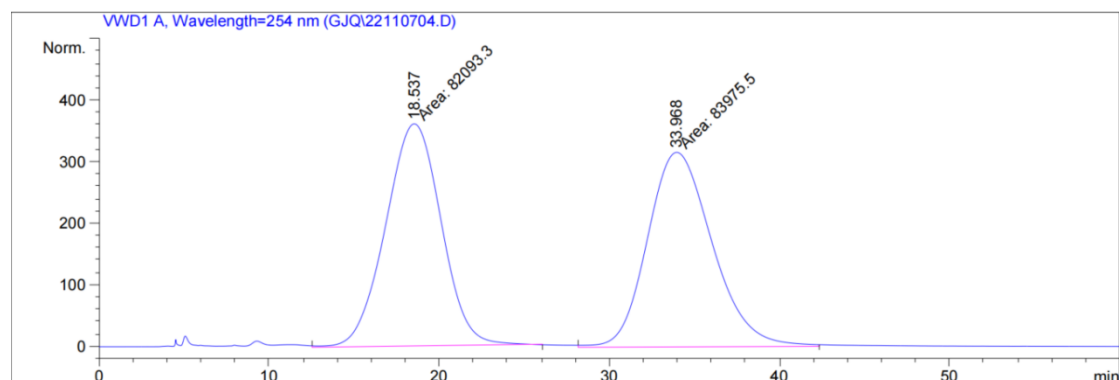
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.030	MM	3.7800	9.66605e4	426.18832	98.6581
2	34.240	MM	5.0129	1314.73633	4.37118	1.3419

(S)-3-((R)-4-benzyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-(4-chlorophenyl)-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ai)

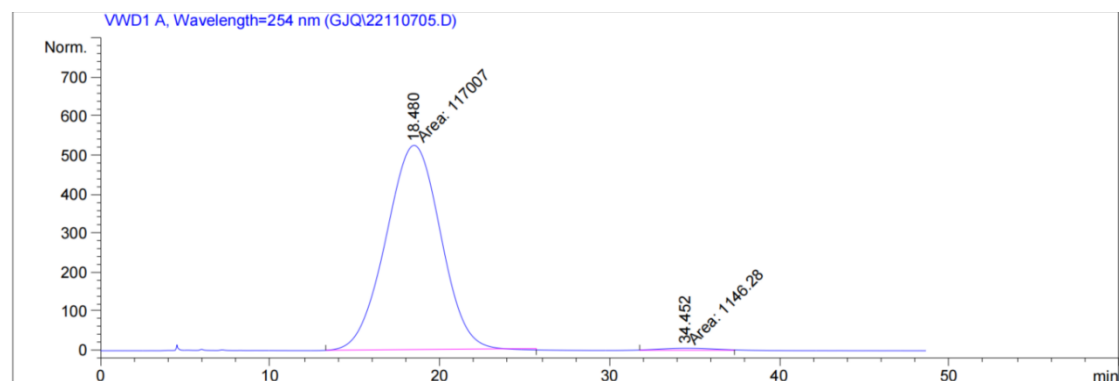


Prepared according to the procedure within 1 h as white solid (125.8 mg, 96% yield, dr = 1:1). mp 101.1 – 101.9 °C; $[\alpha]_D^{17} = -29.557$ (c 0.77, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 8.07 – 8.00 (m, 4H), 7.71 – 7.66 (m, 2H), 7.65 – 7.52 (m, 12H), 7.43 – 7.29 (m, 8H), 7.27 – 7.18 (m, 2H), 7.11 (q, J = 6.8, 5.1 Hz, 8H), 7.09 – 7.02 (m, 2H), 6.30 (s, 1H), 5.51 (s, 1H), 4.26 (d, J = 25.9 Hz, 2H), 4.02 (dd, J = 9.3, 7.4 Hz, 1H), 3.83 – 3.75 (m, 1H), 3.65 (dd, J = 21.6, 13.5 Hz, 2H), 3.53 (d, J = 13.2 Hz, 1H), 3.22 (dd, J = 17.8, 9.4 Hz, 1H), 3.05 (dd, J = 18.4, 9.6 Hz, 1H), 2.87 (s, 1H), 1.55 (s, 9H), 1.40 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 174.77, 173.84, 173.66, 173.41, 173.06, 173.03, 158.04, 157.34, 147.84, 147.55, 136.97, 136.82, 133.36, 133.30, 133.21, 132.44, 131.83, 131.76, 131.08, 131.02, 130.94, 130.72, 129.38, 129.33, 129.17, 128.98, 128.71, 128.64, 128.44, 128.39, 127.96, 127.81, 127.55, 126.98, 126.62, 126.57, 126.28, 126.06, 103.66, 103.63, 61.68, 57.10, 44.93,

43.70, 41.24, 40.04, 31.02, 30.04, 29.78, 29.65. HRMS (ESI) m/z Calcd. for $C_{39}H_{35}ClN_5O_3$, $[M+H]^+$, 656.2423, Found: 656.2433. Enantiomeric excess was determined to be 98% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 25 °C, 0.8 mL/min, t_{major} = 34.4 min, t_{minor} = 18.5 min).

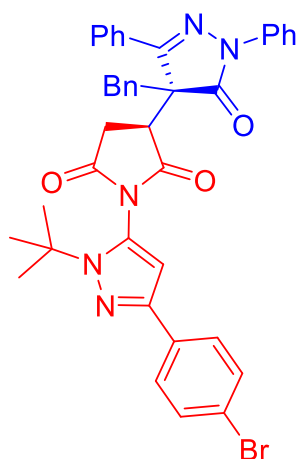


Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	18.537	MM	3.7862	8.20933e4		361.36658	49.4333
2	33.968	MM	4.4218	8.39755e4		316.52121	50.5667



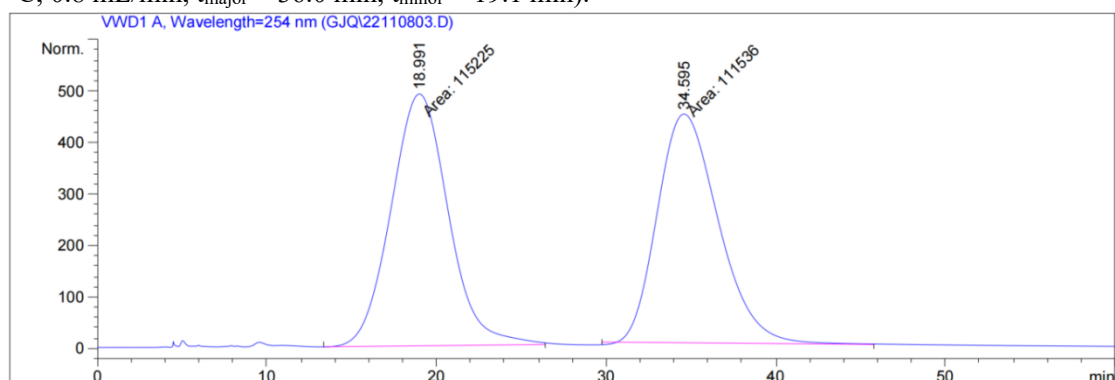
Peak #	RetTime [min]	Type	Width [min]	Area mAU	Area *s	Height [mAU]	Area %
1	18.480	MM	3.7272	1.17007e5		523.21790	99.0298
2	34.452	MM	3.6800	1146.27747		5.19148	0.9702

(S)-3-((R)-4-benzyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(3-(4-bromophenyl)-1-(tert-butyl)-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3aj)

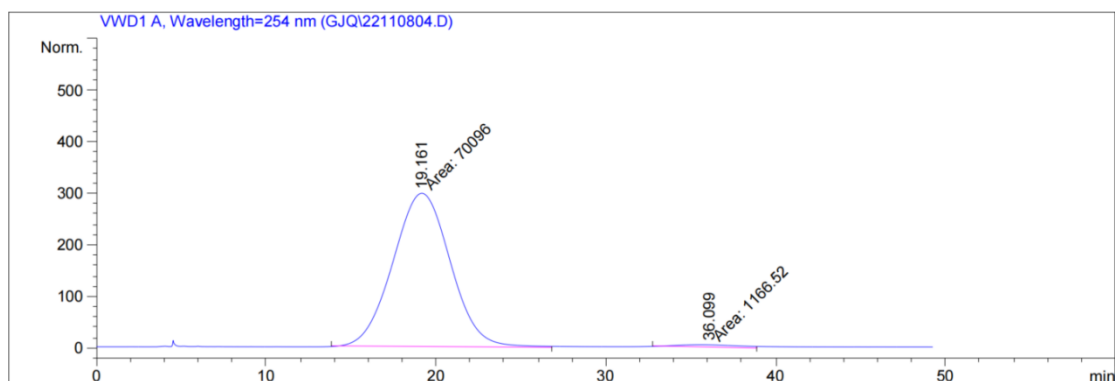


3aj

Prepared according to the procedure within 1 h as white solid (130.0 mg, 93% yield, dr = 1:1). mp 126.1 – 126.9 °C; $[\alpha]_D^{17} = -27.602$ (*c* 0.22, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.99 (ddt, *J* = 6.9, 5.4, 2.5 Hz, 4H), 7.68 – 7.62 (m, 2H), 7.61 – 7.49 (m, 10H), 7.48 – 7.30 (m, 10H), 7.24 – 7.16 (m, 2H), 7.14 – 6.99 (m, 10H), 6.27 (s, 1H), 5.49 (s, 1H), 4.23 (dd, *J* = 18.1, 7.4 Hz, 2H), 3.99 (dd, *J* = 9.4, 7.4 Hz, 1H), 3.82 – 3.75 (m, 1H), 3.61 (dd, *J* = 20.1, 13.5 Hz, 2H), 3.50 (d, *J* = 13.2 Hz, 1H), 3.19 (dd, *J* = 17.9, 9.4 Hz, 1H), 3.02 (dd, *J* = 18.3, 9.6 Hz, 1H), 2.84 (s, 1H), 1.52 (s, 9H), 1.37 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 173.83, 173.65, 173.41, 173.05, 173.02, 158.03, 157.33, 147.85, 147.55, 136.96, 136.81, 133.20, 132.43, 132.27, 132.20, 131.58, 131.07, 131.02, 130.94, 130.72, 129.38, 129.33, 129.17, 128.98, 128.71, 128.68, 128.44, 128.39, 127.96, 127.81, 127.54, 126.97, 126.93, 126.89, 126.28, 126.06, 121.55, 121.49, 120.02, 119.87, 103.66, 103.63, 61.70, 57.10, 44.93, 43.69, 41.24, 40.04, 31.02, 30.04, 29.78, 29.65. HRMS (ESI) *m/z* Calcd. for C₃₉H₃₅BrN₅O₃, [M+H]⁺, 700.1918, Found: 700.1924. Enantiomeric excess was determined to be 97% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 25 °C, 0.8 mL/min, *t*_{major} = 36.0 min, *t*_{minor} = 19.1 min).

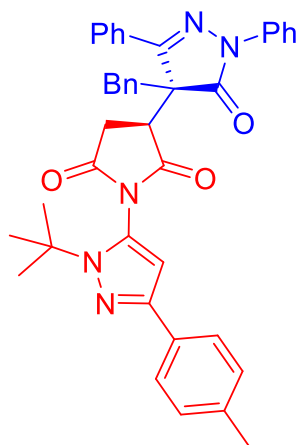


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	18.991	MM	3.9216	1.15225e5	489.70486	50.8132
2	34.595	MM	4.1777	1.11536e5	444.97040	49.1868



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	19.161	MM	3.9293	7.00960e4	297.32370	98.3631
2	36.099	MM	4.2089	1166.51892	4.61926	1.6369

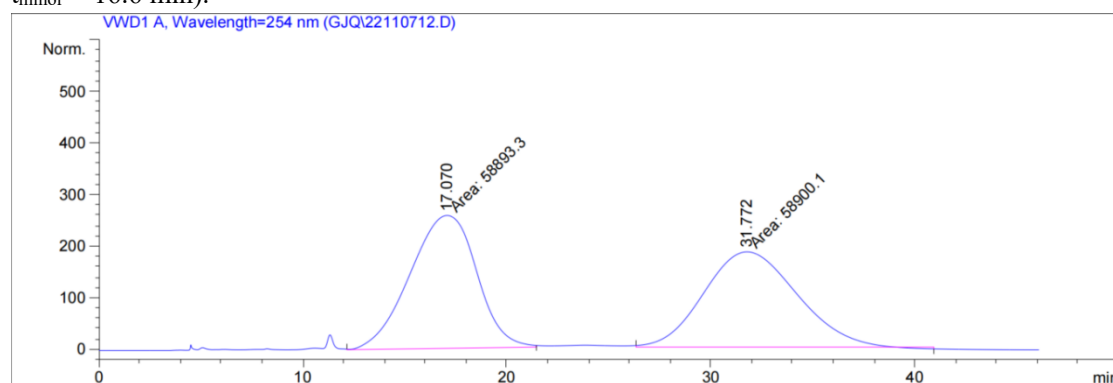
(S)-3-((R)-4-benzyl-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)-1-(1-(tert-butyl)-3-(p-tolyl)-1H-pyrazol-5-yl)pyrrolidine-2,5-dione (3ak)



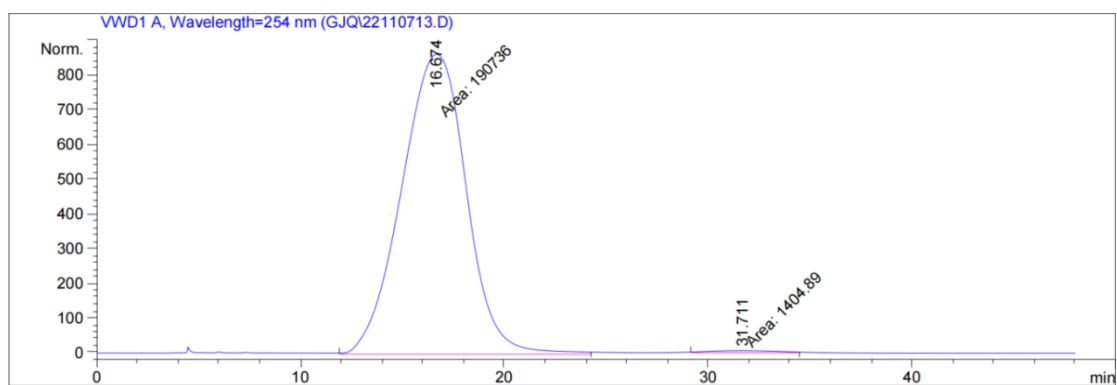
3ak

Prepared according to the procedure within 1 h as white solid (120.7 mg, 95% yield, dr = 1:1). mp 125.1 – 125.9 °C; $[\alpha]_D^{17} = -39.223$ (*c* 0.28, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 8.01 – 7.92 (m, 4H), 7.67 – 7.62 (m, 2H), 7.62 – 7.45 (m, 12H), 7.33 (dt, *J* = 16.2, 7.9 Hz, 4H), 7.23 – 7.17 (m, 2H), 7.17 – 7.09 (m, 5H), 7.06 (d, *J* = 11.2 Hz, 7H), 6.99 (dd, *J* = 7.9, 1.8 Hz, 2H), 6.26 (s, 1H), 5.49 (s, 1H), 4.24 – 4.12 (m, 2H), 3.94 (dd, *J* = 9.3, 7.3 Hz, 1H), 3.75 (dd, *J* = 8.9, 5.8 Hz, 1H), 3.57 (d, *J* = 14.2 Hz, 2H), 3.45 (d, *J* = 13.2 Hz, 1H), 3.12 (dd, *J* = 17.8, 9.4 Hz, 1H), 2.98 (dd, *J* = 18.4, 9.6 Hz, 1H), 2.33 (s, 3H), 2.29 (s, 3H), 1.51 (s, 9H), 1.37 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 174.89, 173.95, 173.82, 173.48, 173.17, 173.12, 158.13, 157.45, 149.05, 148.77, 137.39, 137.32, 137.05, 136.88, 133.35, 132.58, 131.14, 131.03, 130.71, 130.61, 130.53, 129.42, 129.39, 129.21,

129.18, 129.01, 128.78, 128.73, 128.45, 128.42, 128.38, 127.93, 127.81, 127.59, 127.02, 126.31, 126.06, 125.34, 125.29, 120.06, 119.92, 103.47, 61.41, 57.15, 44.95, 43.67, 41.23, 40.06, 31.04, 30.03, 29.83, 29.73, 21.34, 21.30. HRMS (ESI) *m/z* Calcd. for C₄₀H₃₈N₅O₃, [M+H]⁺, 636.2969, Found: 636.2976. Enantiomeric excess was determined to be 99% (determined by HPLC using chiral OD-H column, hexane/2-propanol = 8/2, λ = 254 nm, 25 °C, 0.8 mL/min, *t*_{major} = 31.7 min, *t*_{minor} = 16.6 min).

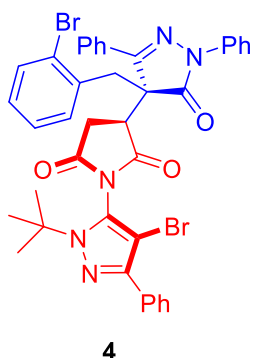


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	17.070	MM	3.8044	5.88933e4	258.00790	49.9971
2	31.772	MM	5.3084	5.89001e4	184.92781	50.0029



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	16.674	MM	3.6831	1.90736e5	863.11517	99.2688
2	31.711	MM	3.9622	1404.89136	5.90956	0.7312

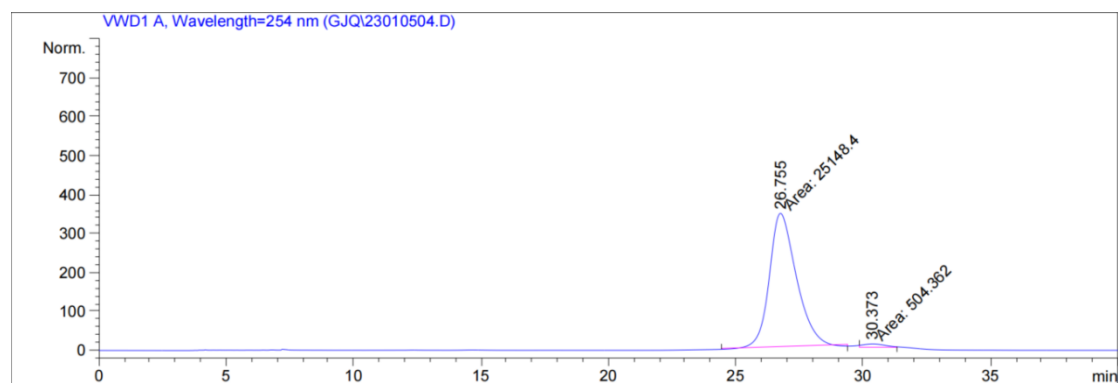
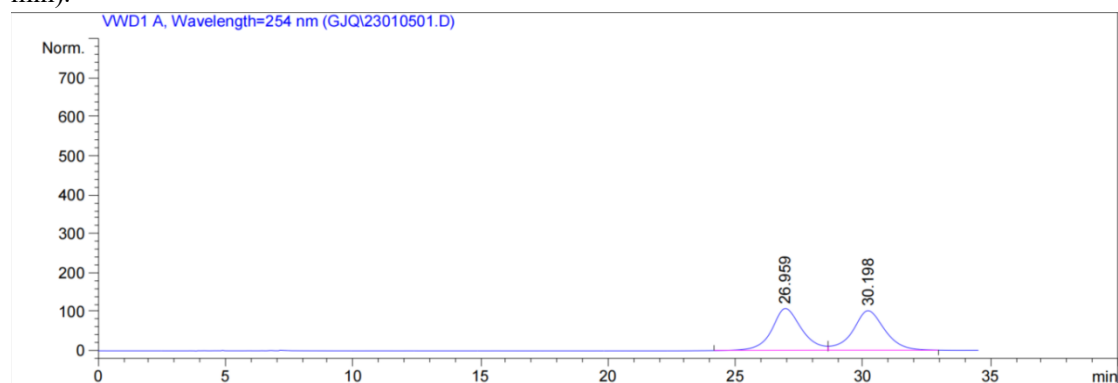
(S)-1-(4-bromo-1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)-3-((R)-4-(2-bromobenzyl)-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)pyrrolidine-2,5-dione (4)



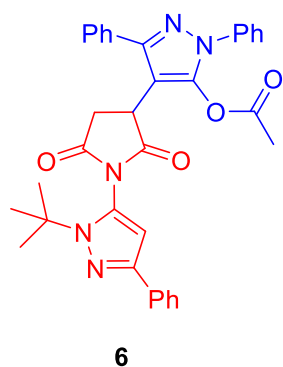
4

Prepared according to the procedure within 96 h as white solid (106.1mg, 58% yield, dr > 20:1). mp 126.1–126.9 °C; $[\alpha]_D^{17} = -22.000$ (*c* 0.50, CH₂Cl₂); ¹H NMR (400 MHz, Chloroform-d) δ 7.95 (dd, *J* = 6.8, 2.9 Hz, 2H), 7.79 (dd, *J* = 11.0, 7.5 Hz, 4H), 7.49 (dd, *J* = 6.4, 3.6 Hz, 4H), 7.38 (q, *J* = 7.6 Hz, 4H), 7.31 (dd, *J* = 7.3 Hz, 1H), 7.21 (s, 1H), 7.14–6.99 (m, 3H), 4.19–4.02 (m, 2H), 3.92 (d, *J* = 14.4 Hz, 1H), 3.82 (d, *J* = 14.6 Hz, 1H), 3.24 (dd, *J* = 17.2, 8.7 Hz, 1H), 1.30 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 172.93, 172.85, 172.68, 158.49, 145.99, 137.17, 133.37, 132.98, 132.06, 130.84, 130.68, 130.20, 129.46, 129.10, 128.85, 128.38, 128.29, 128.17, 127.58, 127.30, 126.03, 125.46, 119.70, 93.34, 62.45, 56.44, 45.18,

39.06, 30.28, 29.33. HRMS (ESI) *m/z* Calcd. for C₃₉H₃₄Br₂N₅O₃, [M+H]⁺, 778.1023, Found: 778.1022. Enantiomeric excess was determined to be 96% (determined by HPLC using chiral IB-H column, hexane/2-propanol = 9/1, λ = 254 nm, 25 °C, 0.8 mL/min, *t*_{major} = 30.3 min, *t*_{minor} = 26.8 min).



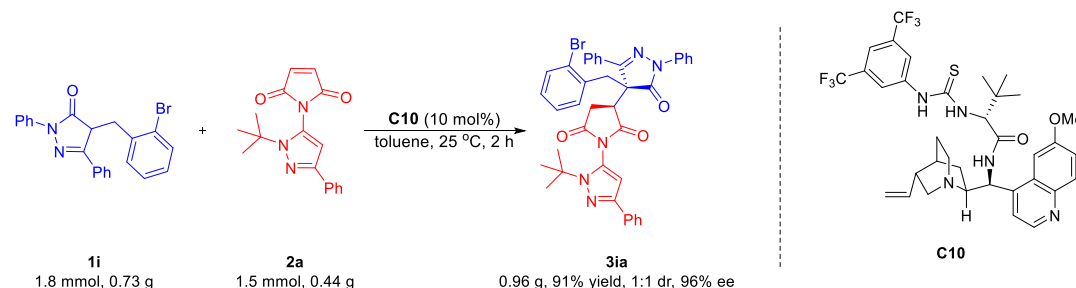
4-(1-(1-(tert-butyl)-3-phenyl-1H-pyrazol-5-yl)-2,5-dioxopyrrolidin-3-yl)-1,3-diphenyl-1H-pyrazol-5-yl acetate (**6**)



Prepared according to the procedure within 18 h as white solid (68.8 mg, 60% yield, dr = 6:1). mp 126.1–126.9 °C; ¹H NMR (600 MHz, Chloroform-d) δ 7.77 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 7.3 Hz, 2H), 7.59 (d, J = 7.9 Hz, 2H), 7.50 (q, J = 8.1 Hz, 5H), 7.39 (dd, J = 7.5 Hz, 4H), 6.33 (s, 1H), 4.21 (dd, J = 10.2, 5.2 Hz, 1H), 3.25 (dd, J = 18.8, 10.1 Hz, 1H), 3.04 (dd, J = 18.7, 5.3 Hz, 1H), 2.26 (s, 3H), 1.60 (s, 9H). ¹³C NMR (101 MHz, CDCl₃) δ 175.53, 174.64, 167.28, 151.32, 149.07, 141.74, 137.56, 133.39, 132.65, 129.39, 128.96, 128.94, 128.79, 128.55, 128.22, 127.74, 125.47, 123.50, 104.06, 103.44, 61.51, 36.50, 29.92, 20.56. HRMS (ESI) m/z Calcd. for C₃₄H₃₂N₅O₄, [M+H]⁺, 574.2449, Found:

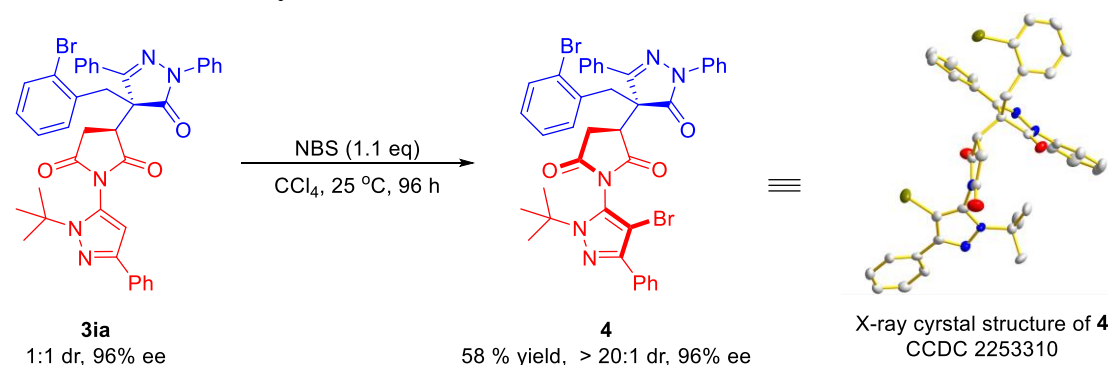
574.2455.

Gram-scale reaction



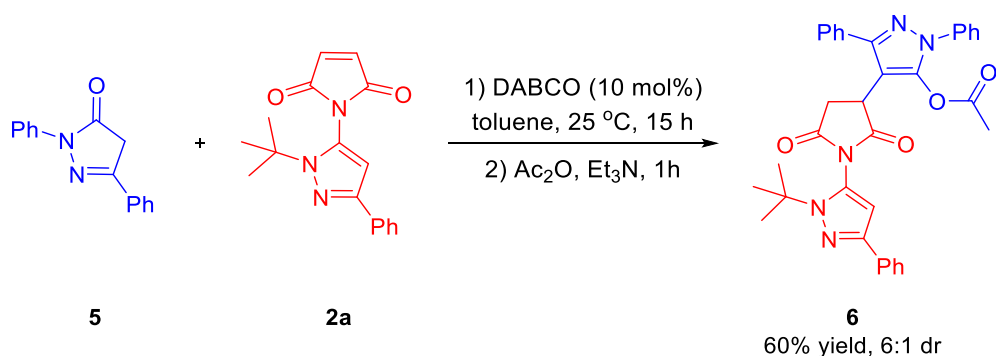
In a reaction tube, 4-(2-bromobenzyl)-2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one **1i** (1.8 mmol), **2a** (1.5 mmol) were added into toluene (30 mL). The reaction solution was stirred at 25 °C. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10 to 1/3) on silica gel to give the product **3ia** with 91% yield with 1:1 dr and 96% ee.

Procedure for the Synthesis of **4**



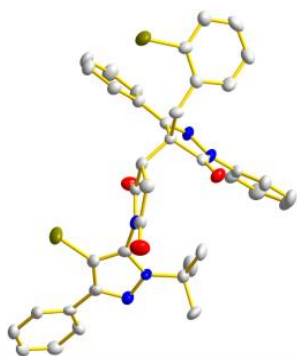
A solution of **3ia** (70 mg, 0.1 mmol) in CCl₄ was stirred at 0 °C, and NBS (20 mg, 0.11 mmol) was added. The reaction was stirred at 25 °C until it was complete (monitored by TLC), then the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/10) on silica gel to give the product **4** as a white solid.

Procedure for the Synthesis of **6**



In a reaction tube, 2,5-diphenyl-2,4-dihydro-3H-pyrazol-3-one **5** (0.24 mmol), **2a** (0.2 mmol) were added into toluene (4 mL). The reaction solution was stirred for 15 hours at 25 °C. Subsequently, the Ac₂O (0.3 mmol) and Et₃N (0.04 mmol) were added into the reaction solution. After the reaction was complete (monitored by TLC), the crude product was purified by column chromatography (ethyl acetate/petroleum ether = 1/8 to 1/3) on silica gel to give the product **6** with 60% yield and 6:1 dr.

5. X-ray crystal structure of **4**



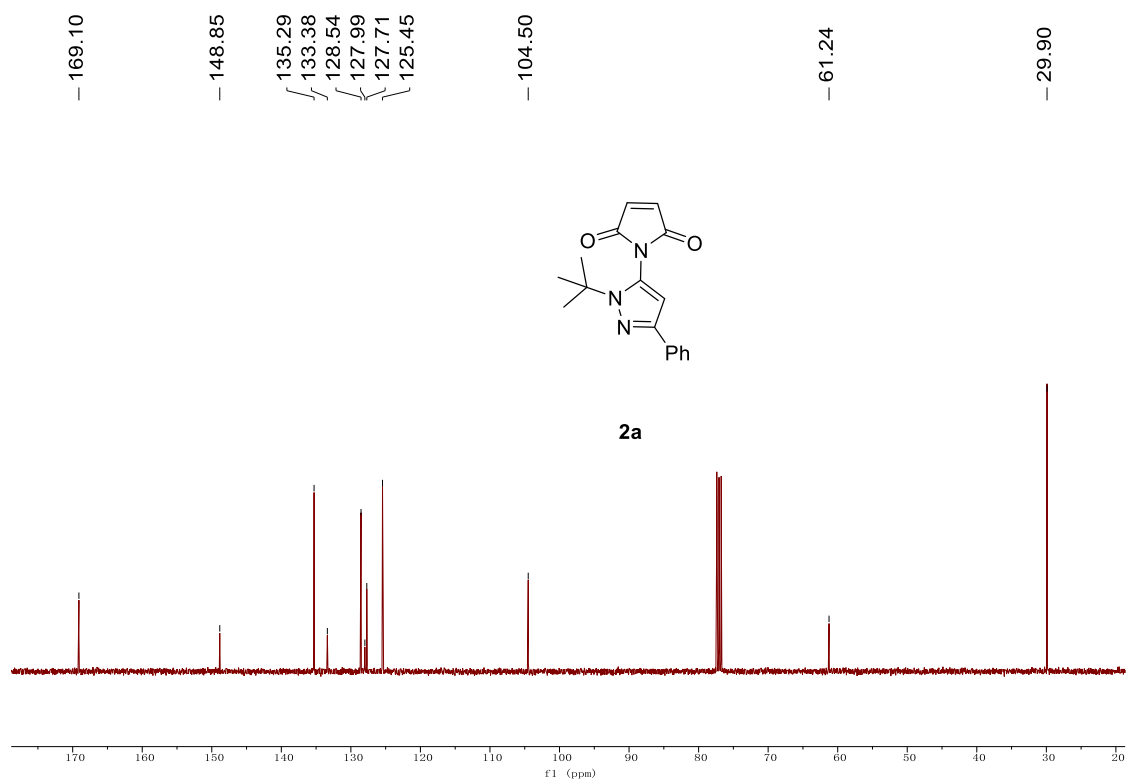
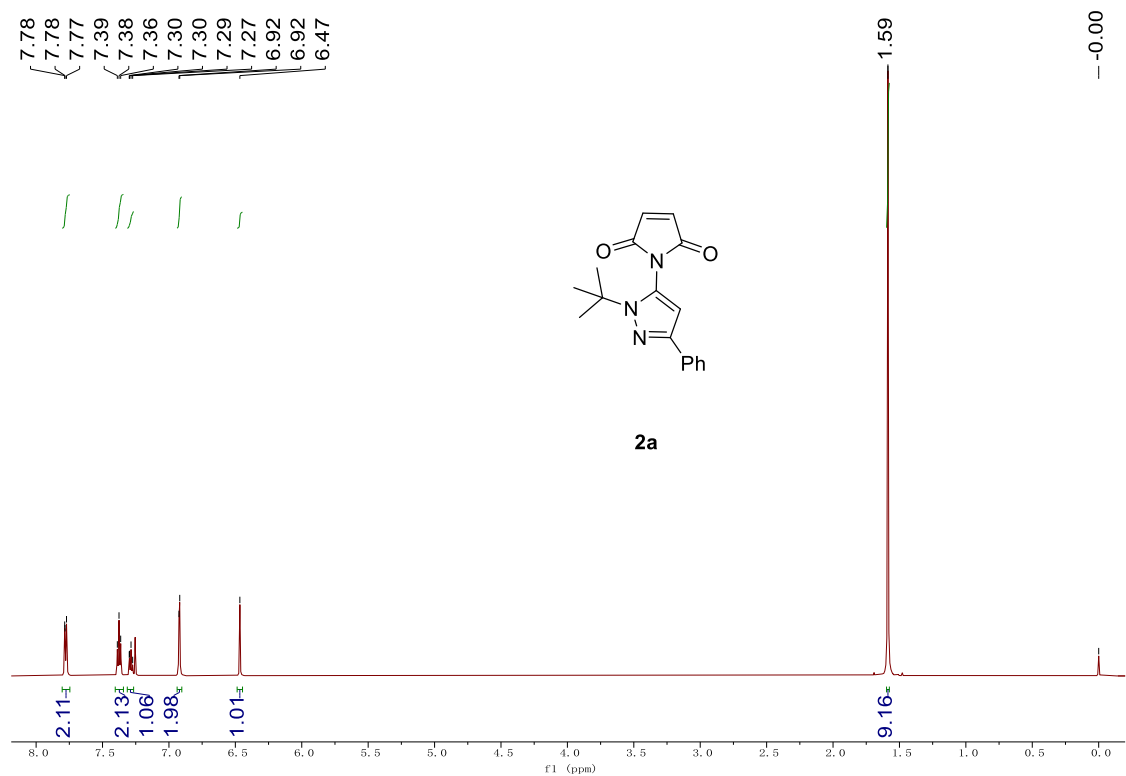
X-ray crystal structure of **4**
CCDC 2253310

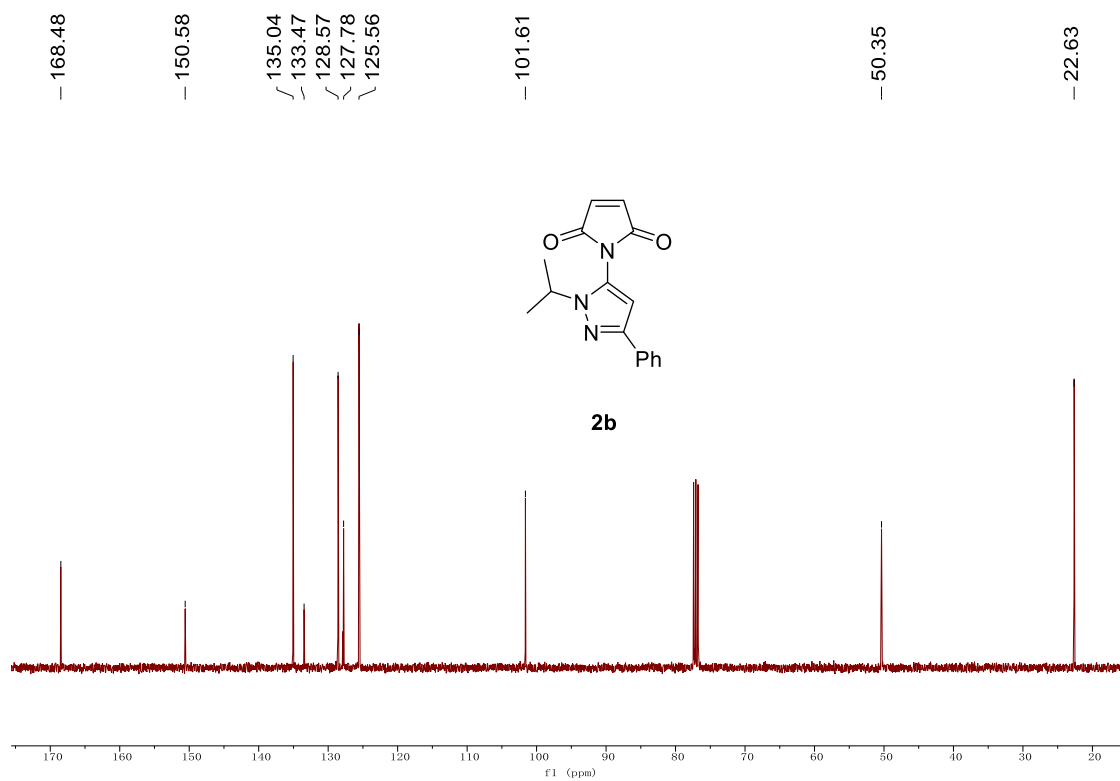
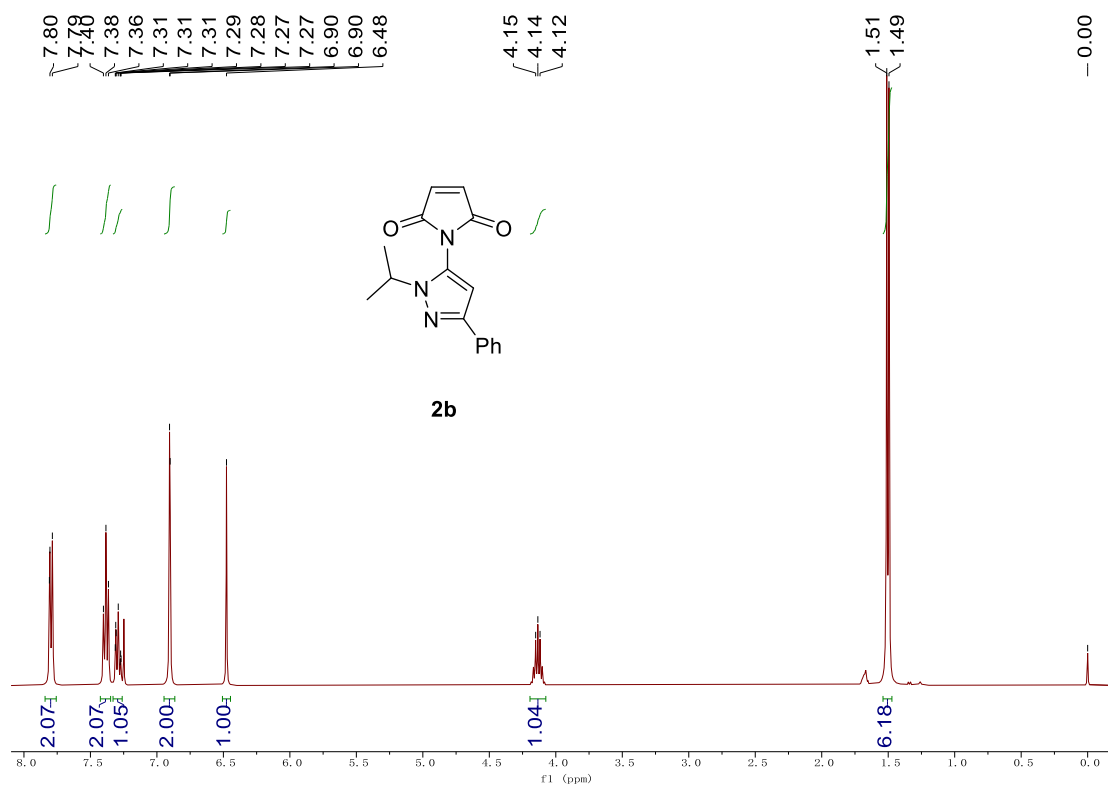
Table 1 Crystal data and structure refinement for **1**.

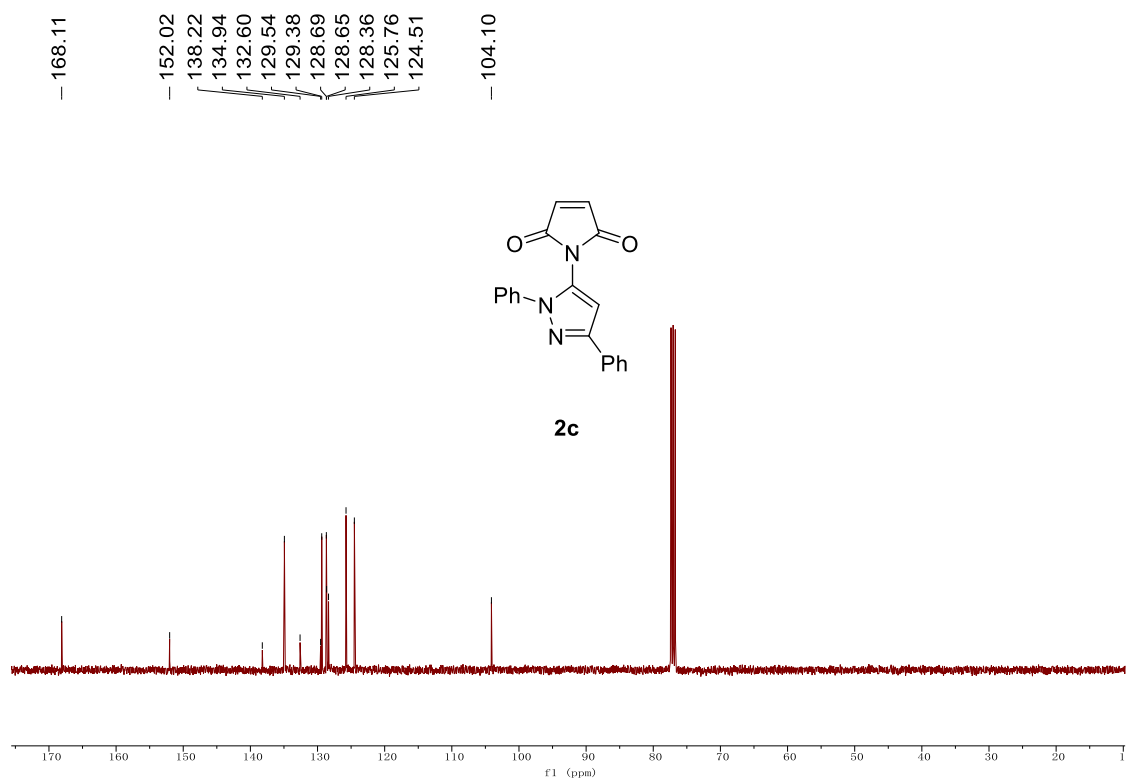
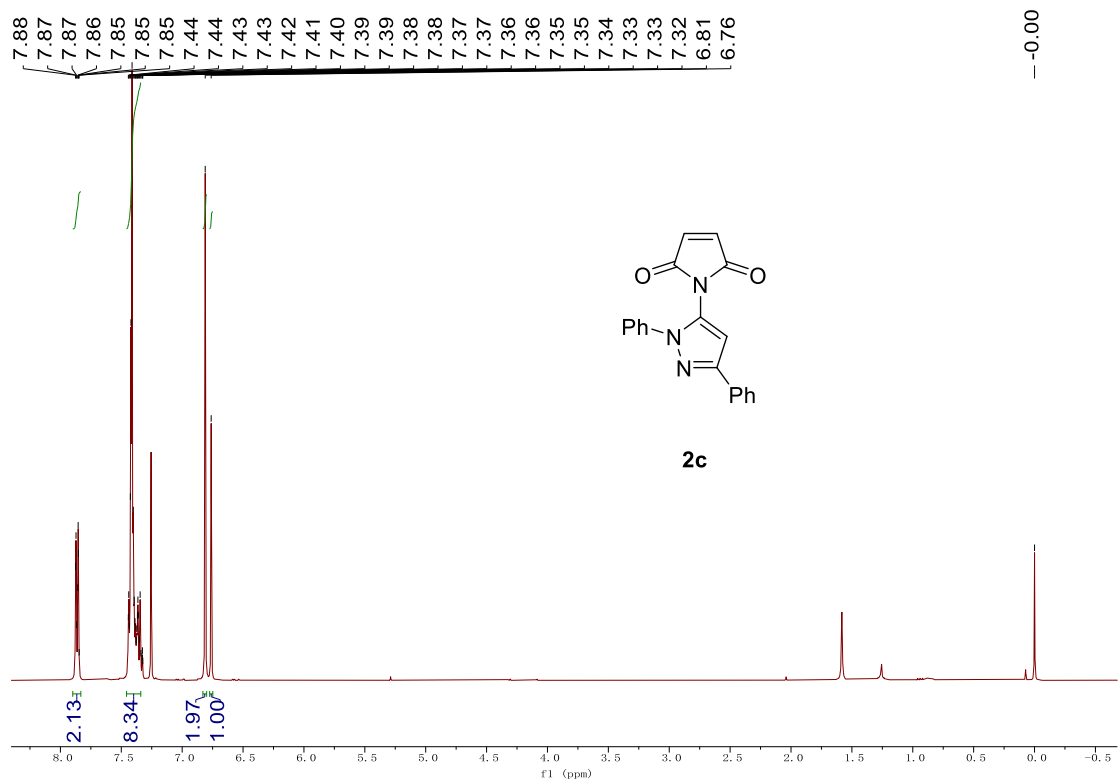
Identification code	1
Empirical formula	C ₃₉ H ₃₃ Br ₂ N ₅ O ₃
Formula weight	779.52
Temperature/K	202.00
Crystal system	orthorhombic
Space group	P2 ₁ 2 ₁ 2 ₁
a/Å	9.6462(12)
b/Å	17.850(2)
c/Å	20.055(3)
α/°	90
β/°	90
γ/°	90
Volume/Å ³	3453.1(8)

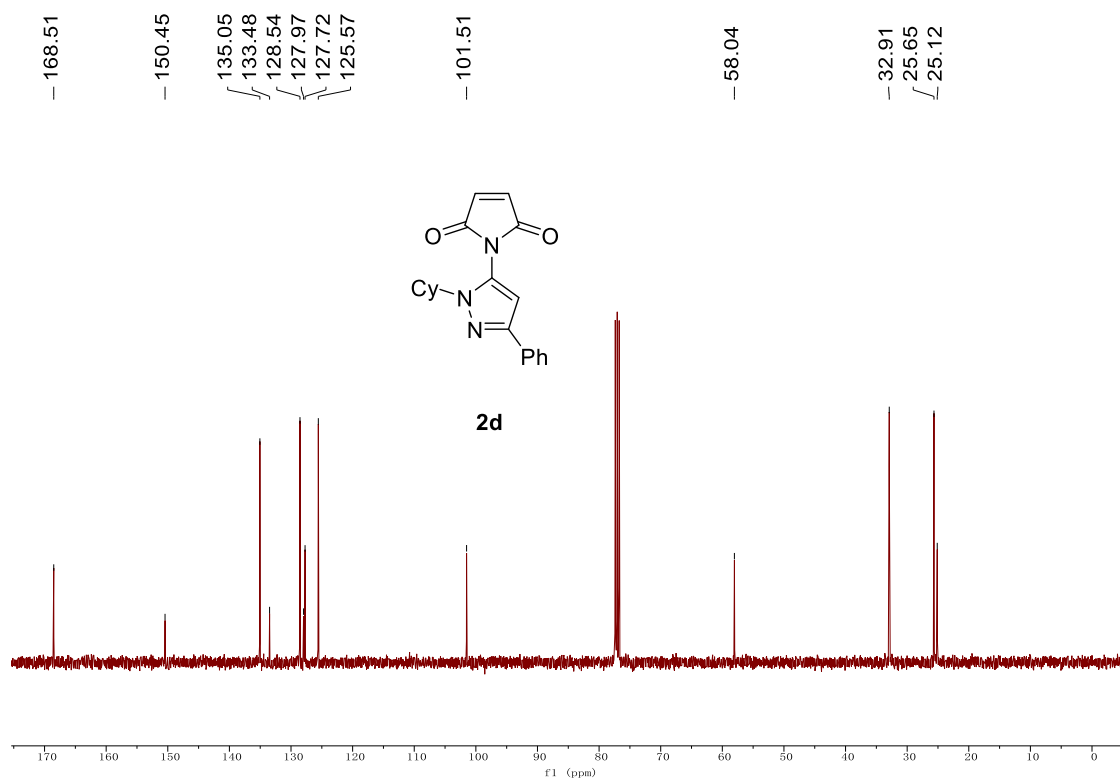
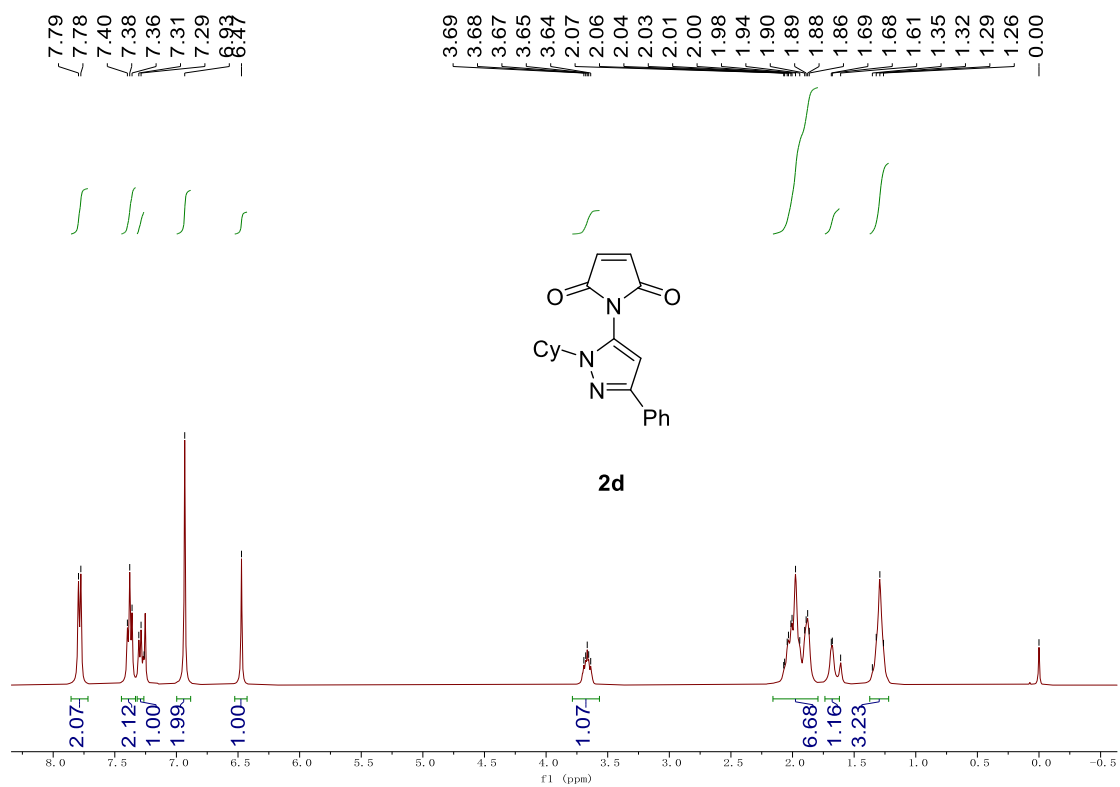
Z	4
$\rho_{\text{calc}}/\text{cm}^3$	1.499
μ/mm^{-1}	2.394
F(000)	1584.0
Crystal size/ mm^3	$0.3 \times 0.25 \times 0.22$
Radiation	MoK α ($\lambda = 0.71073$)
2 Θ range for data collection/ $^\circ$	4.564 to 50
Index ranges	$-11 \leq h \leq 11, -21 \leq k \leq 21, -23 \leq l \leq 23$
Reflections collected	41191
Independent reflections	6057 [$R_{\text{int}} = 0.0730, R_{\text{sigma}} = 0.0544$]
Data/restraints/parameters	6057/0/445
Goodness-of-fit on F^2	1.036
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0458, wR_2 = 0.1130$
Final R indexes [all data]	$R_1 = 0.0594, wR_2 = 0.1182$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.69/-0.48
Flack parameter	0.033(5)

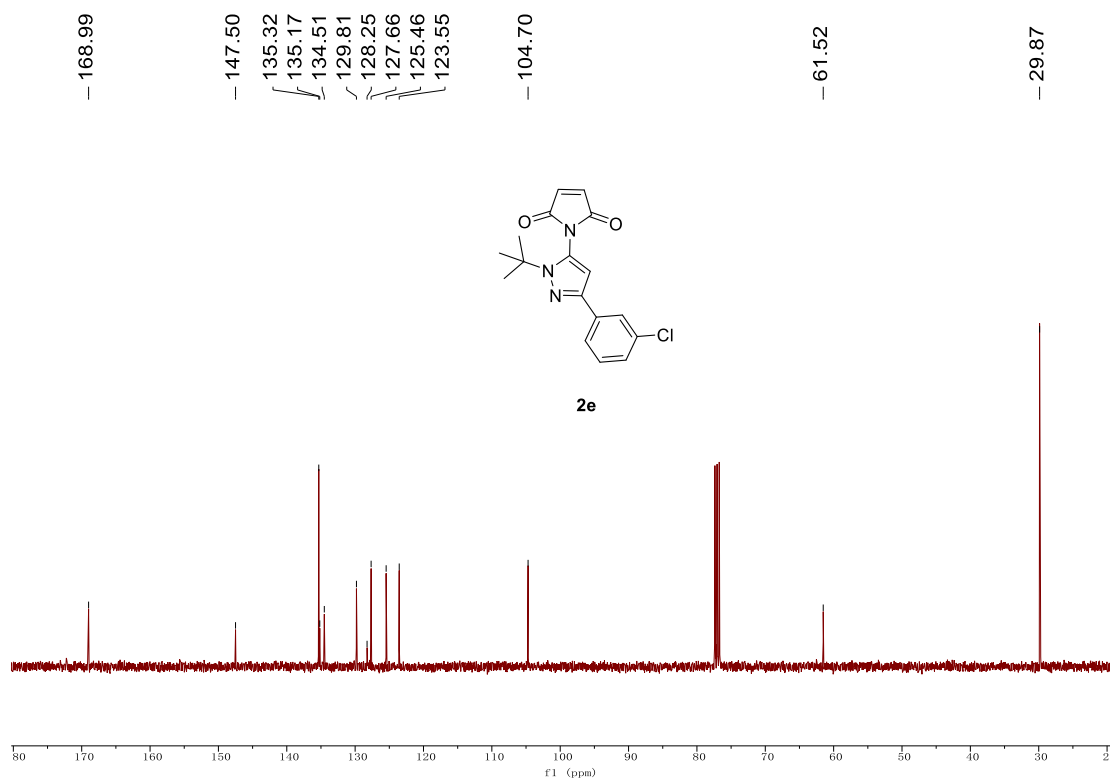
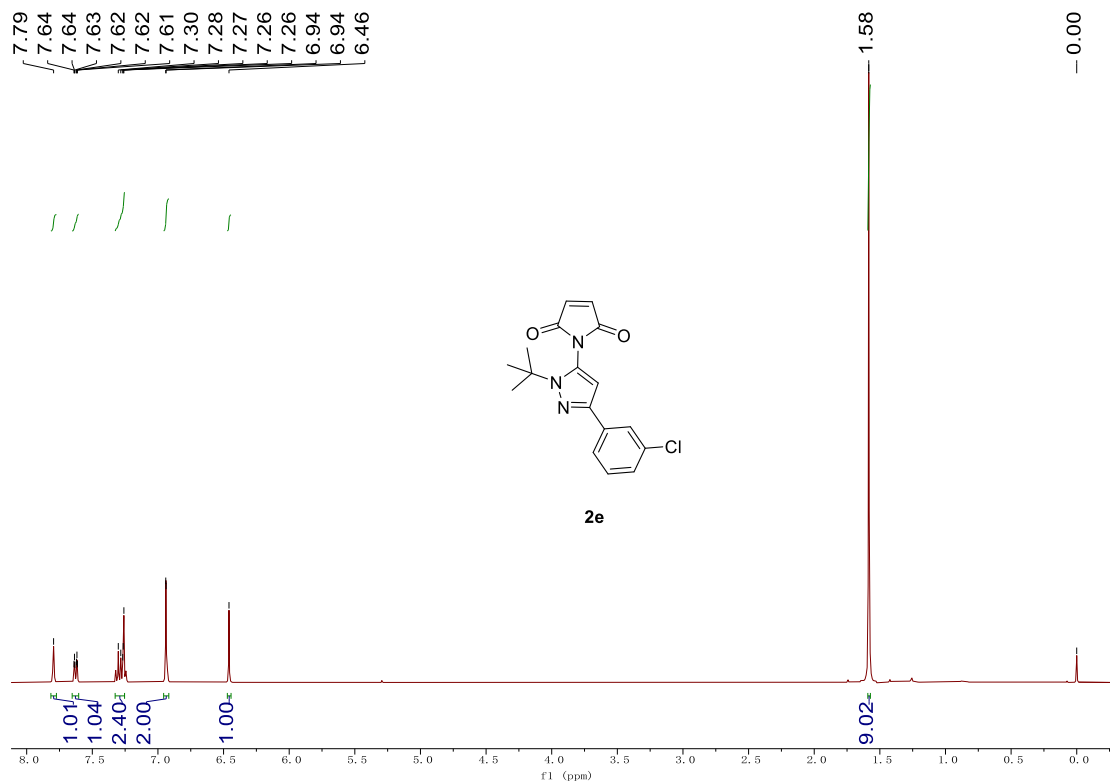
6. Copies of ^1H NMR and ^{13}C NMR spectra

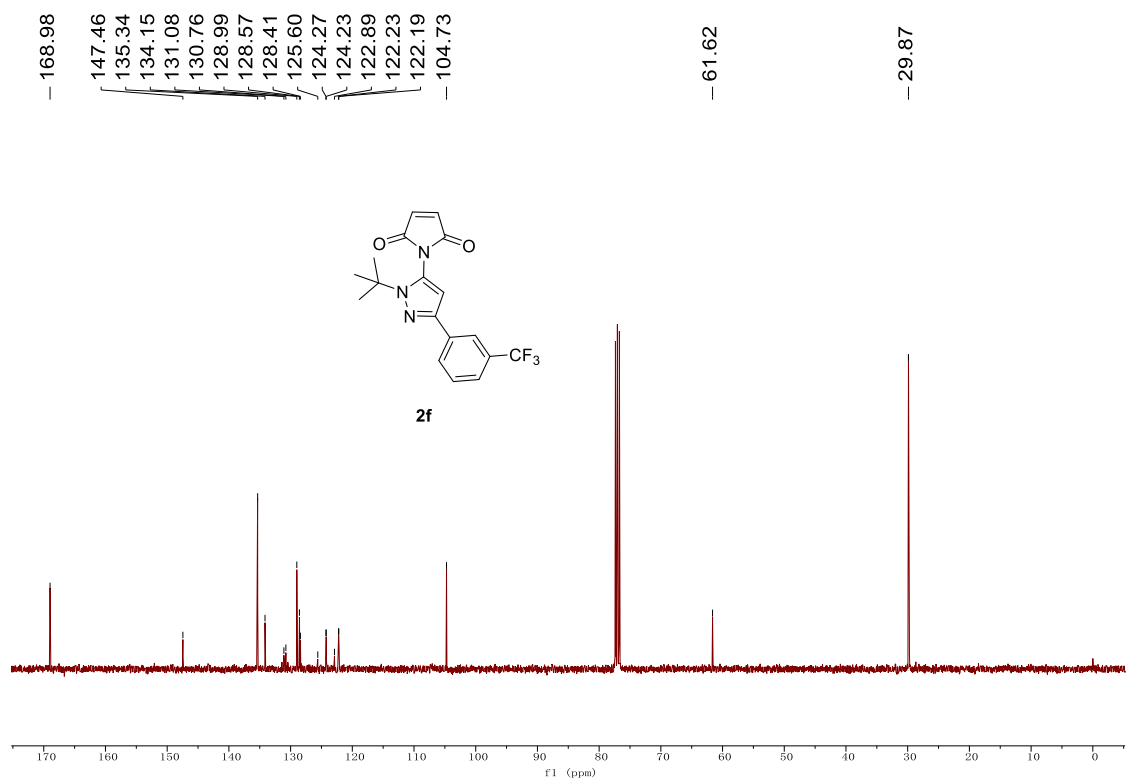
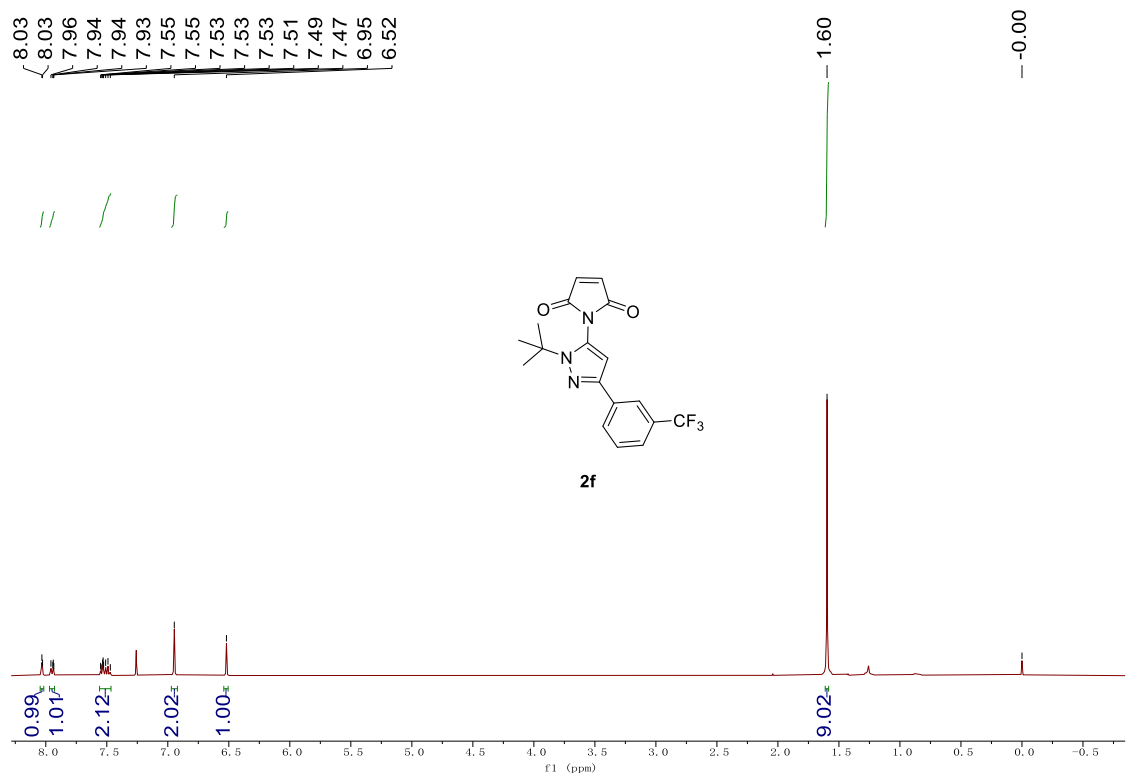


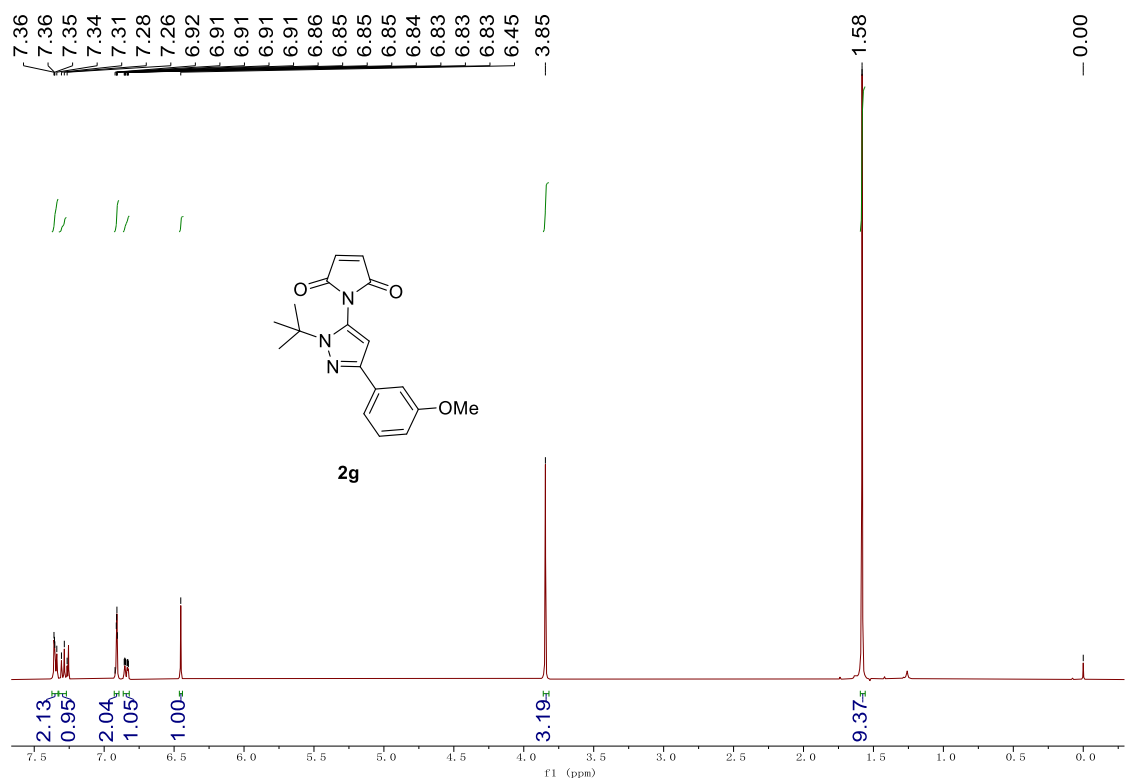
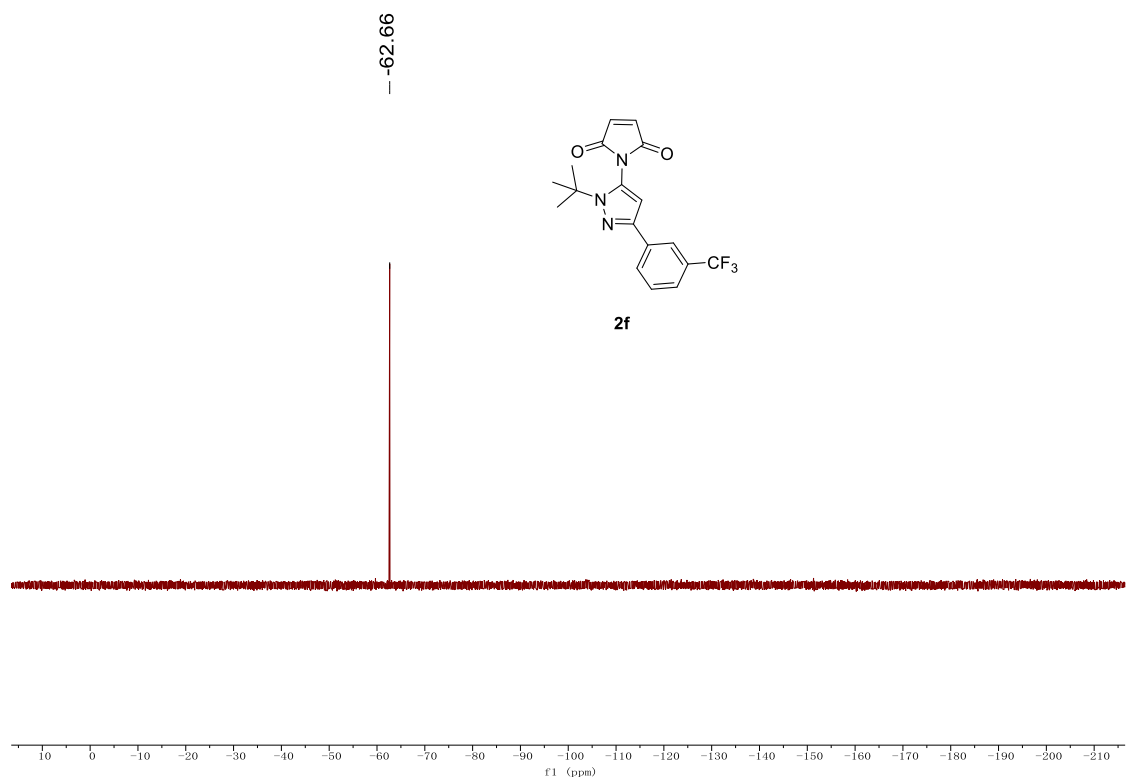


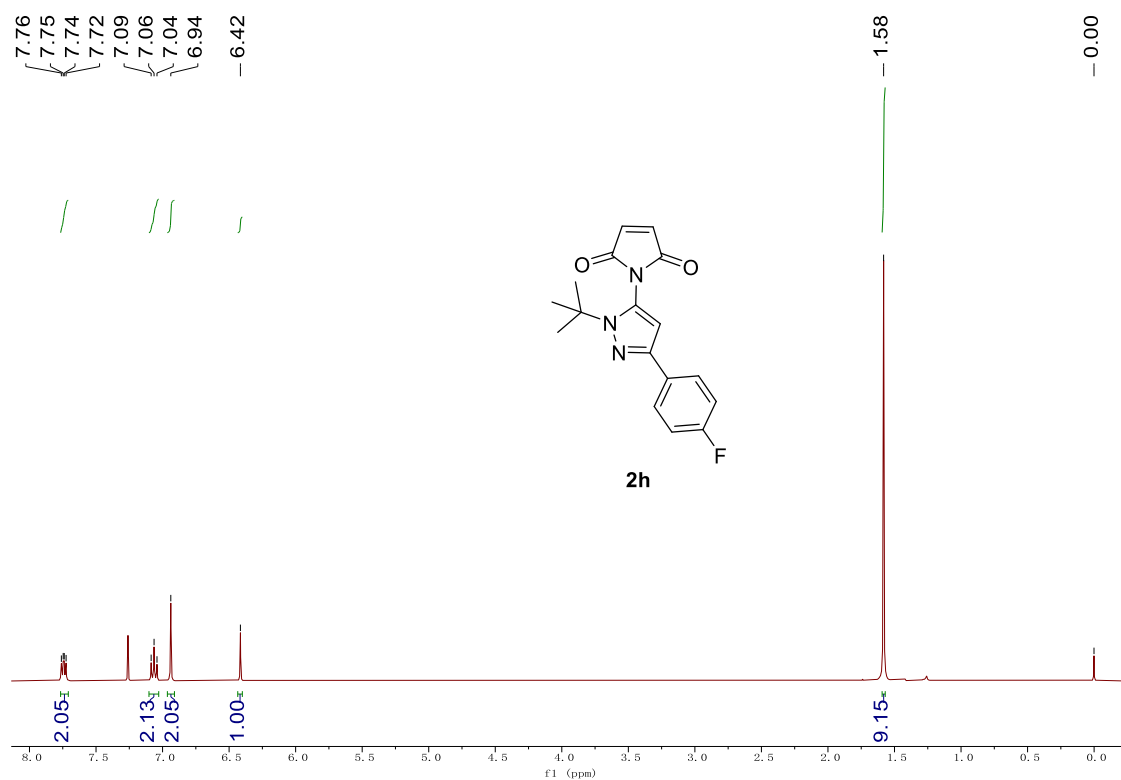
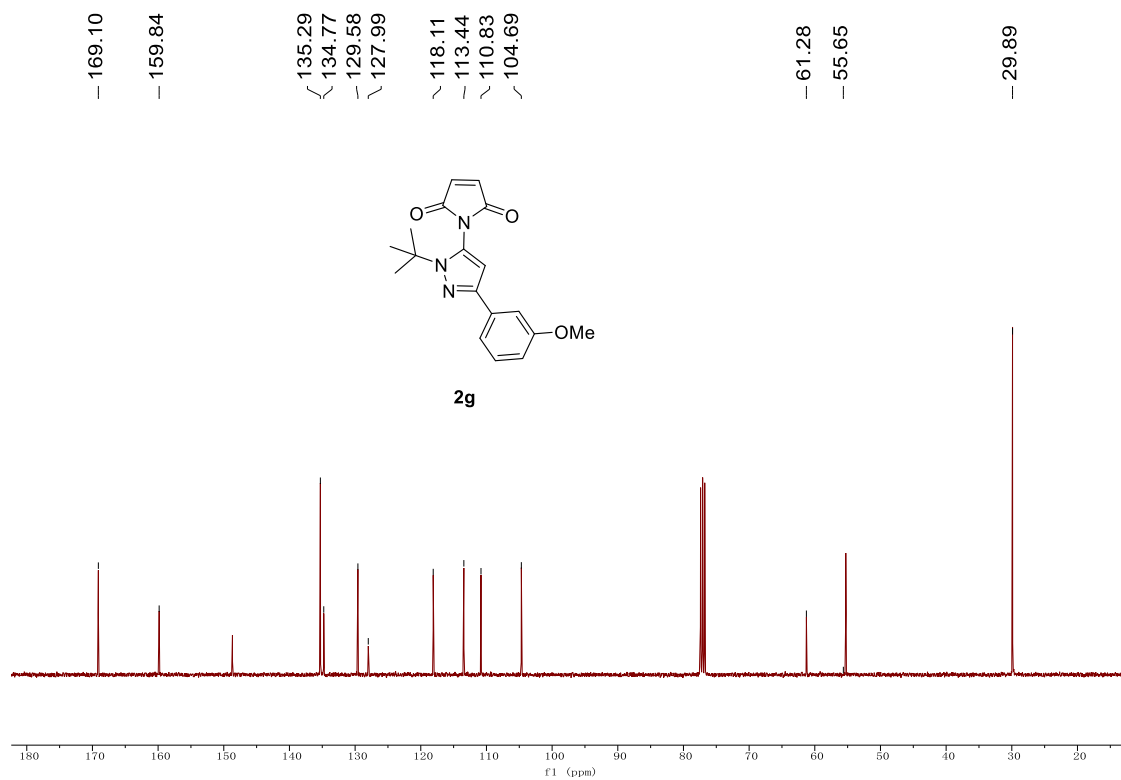


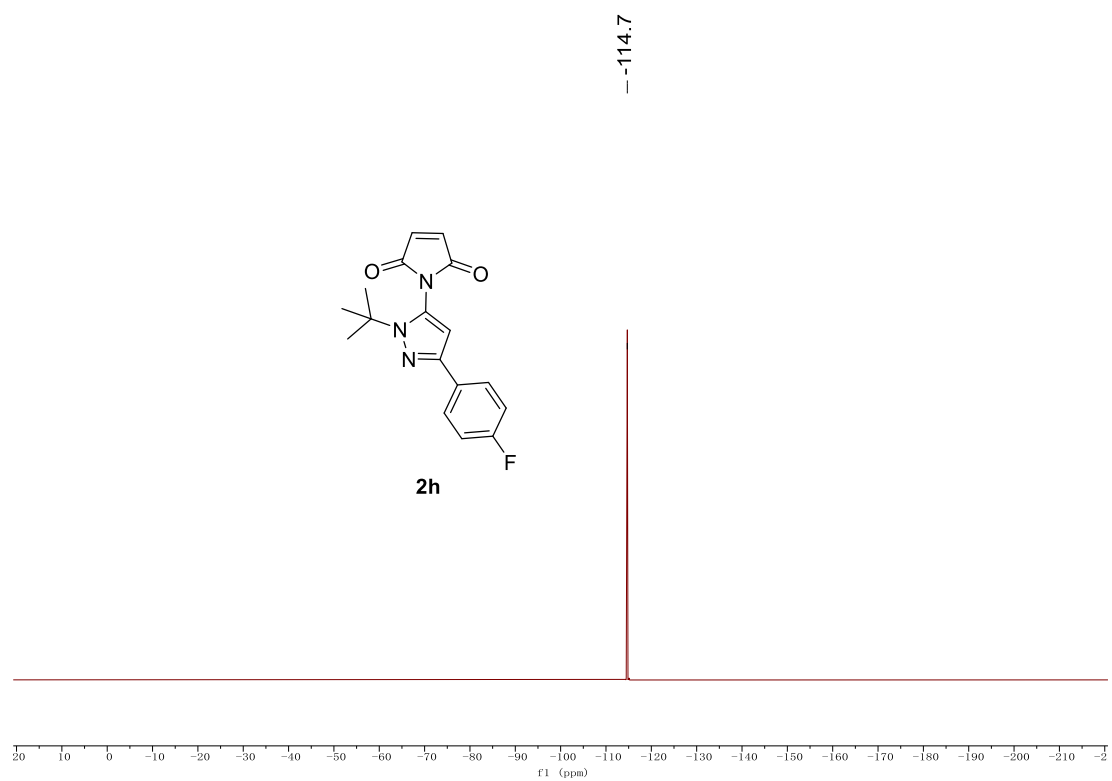
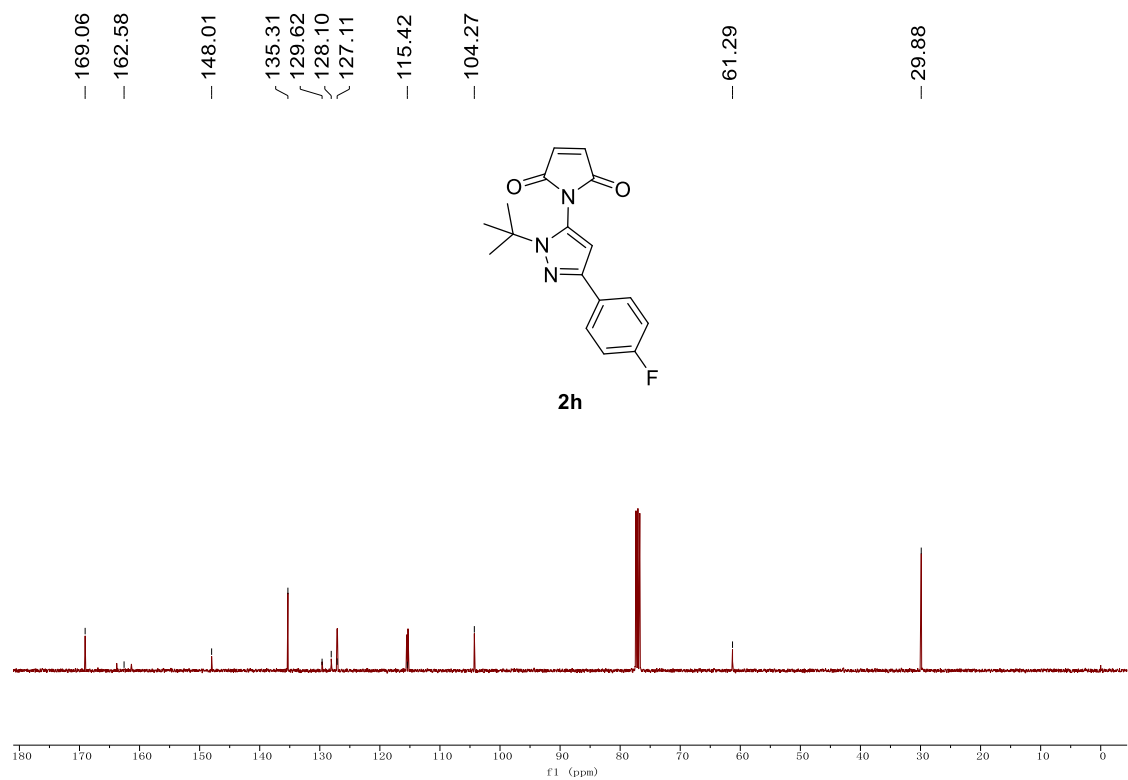


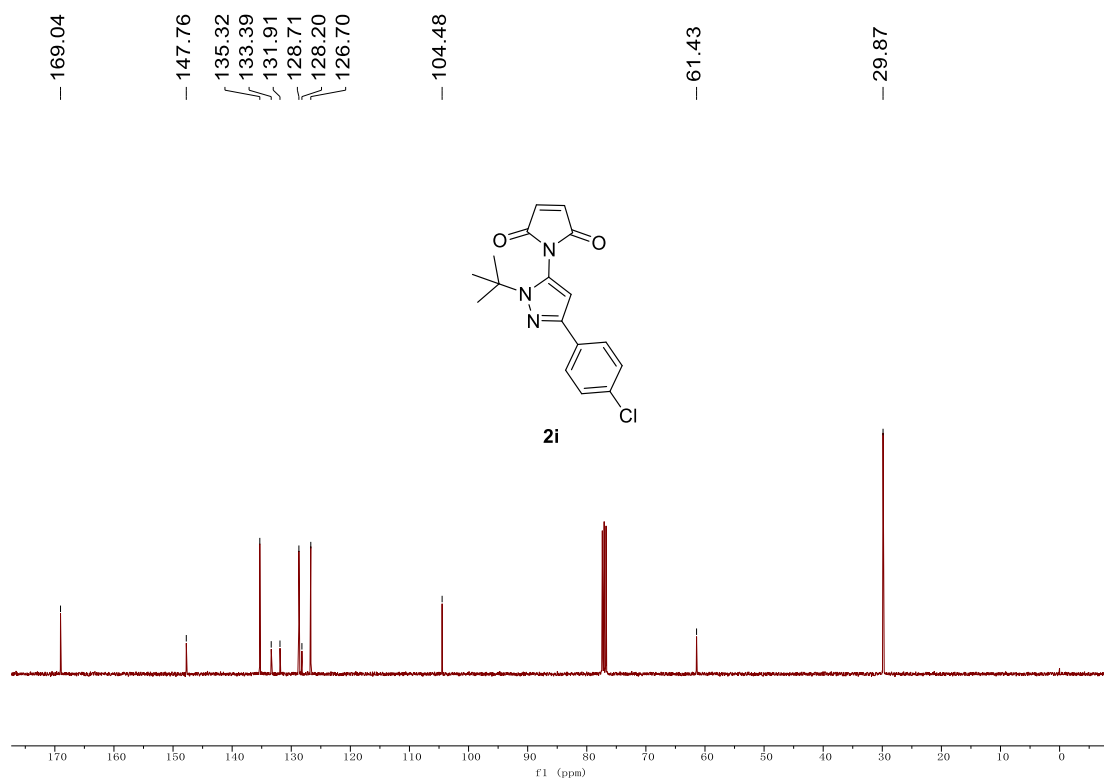
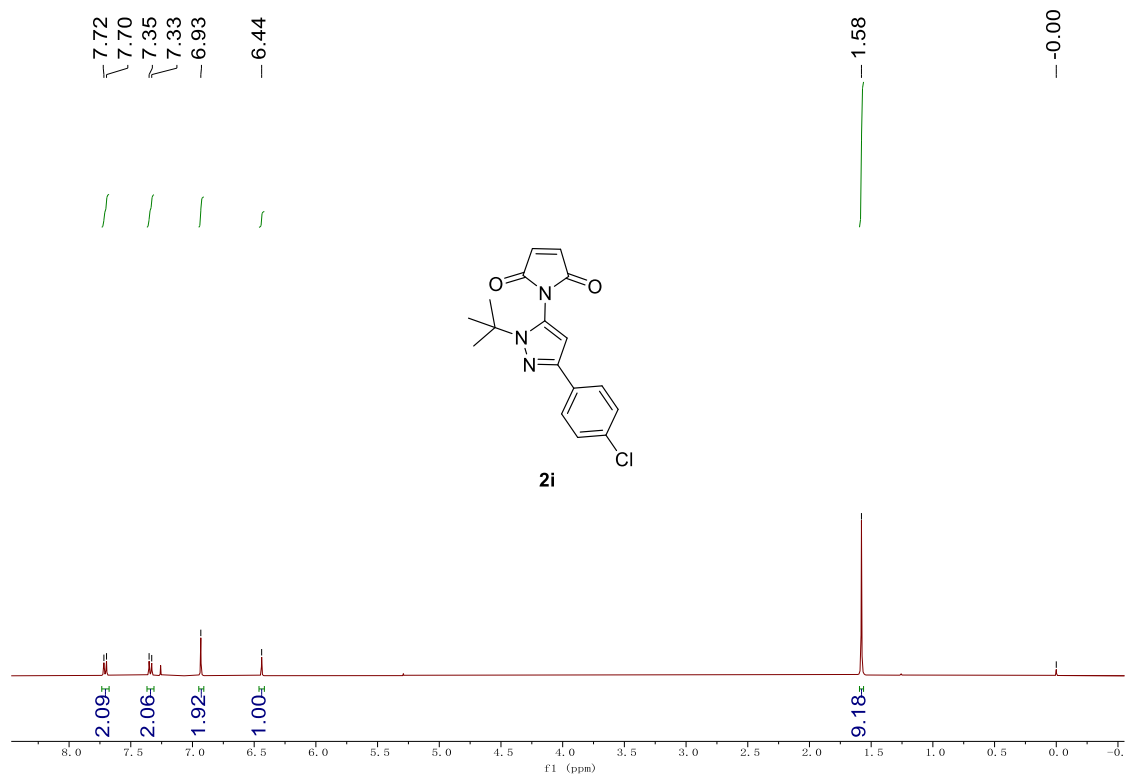


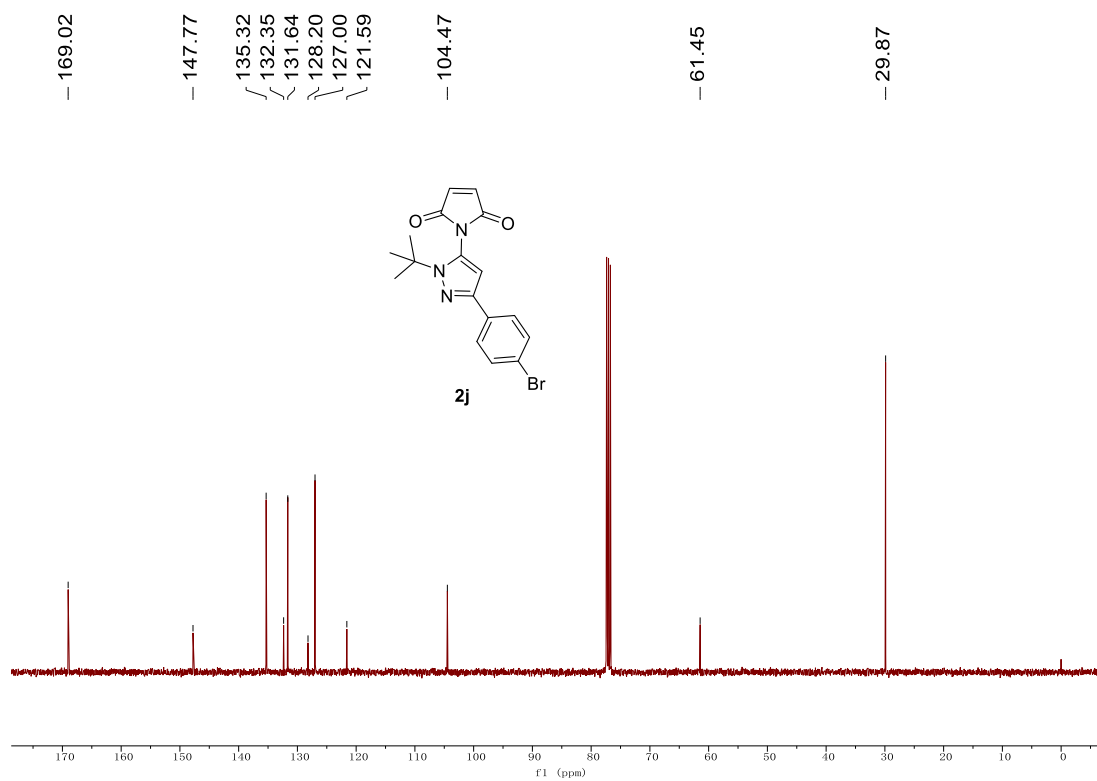
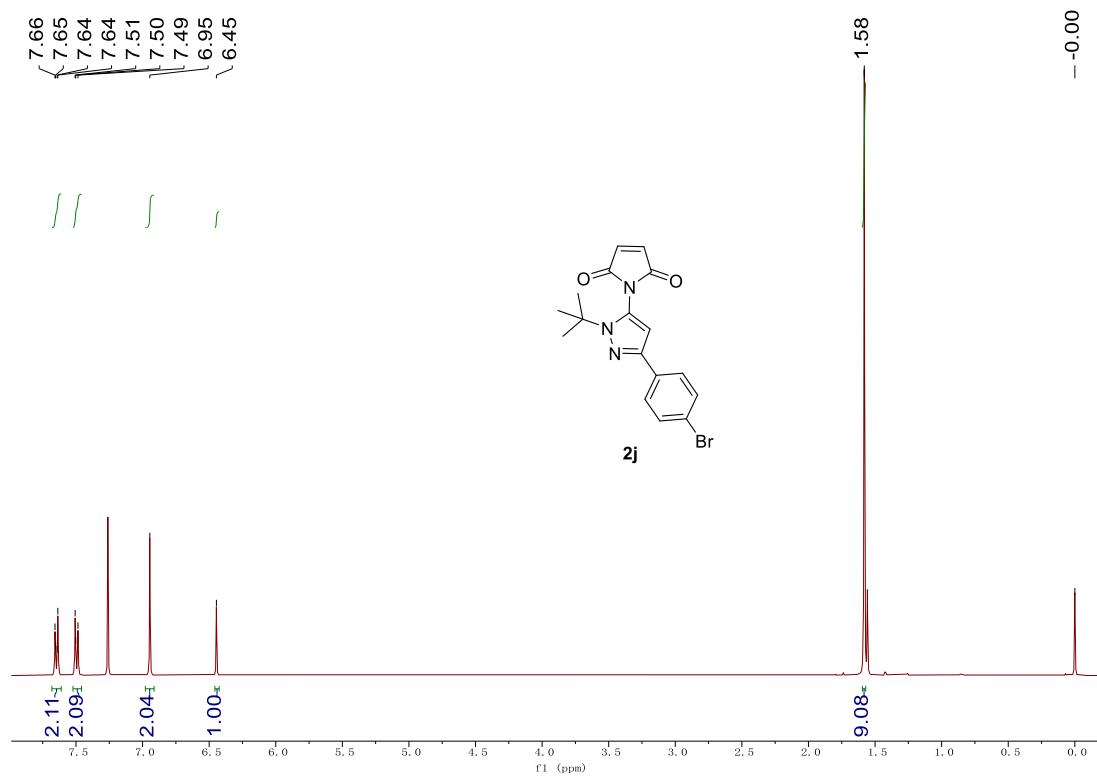


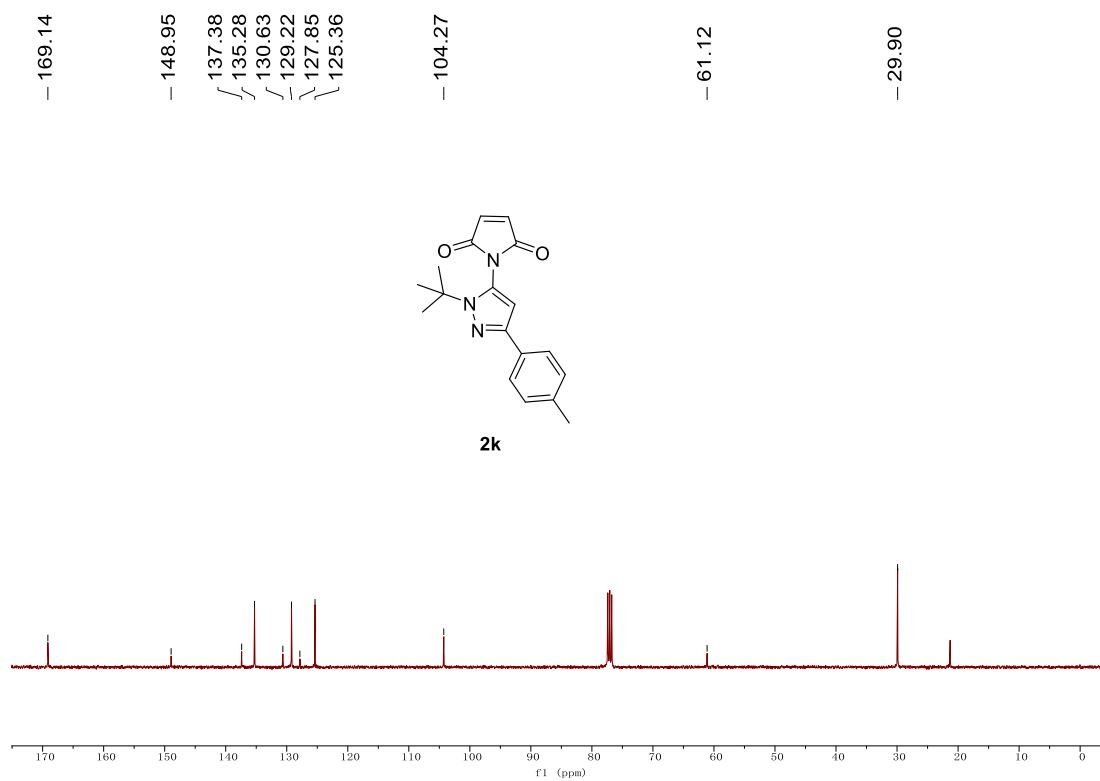
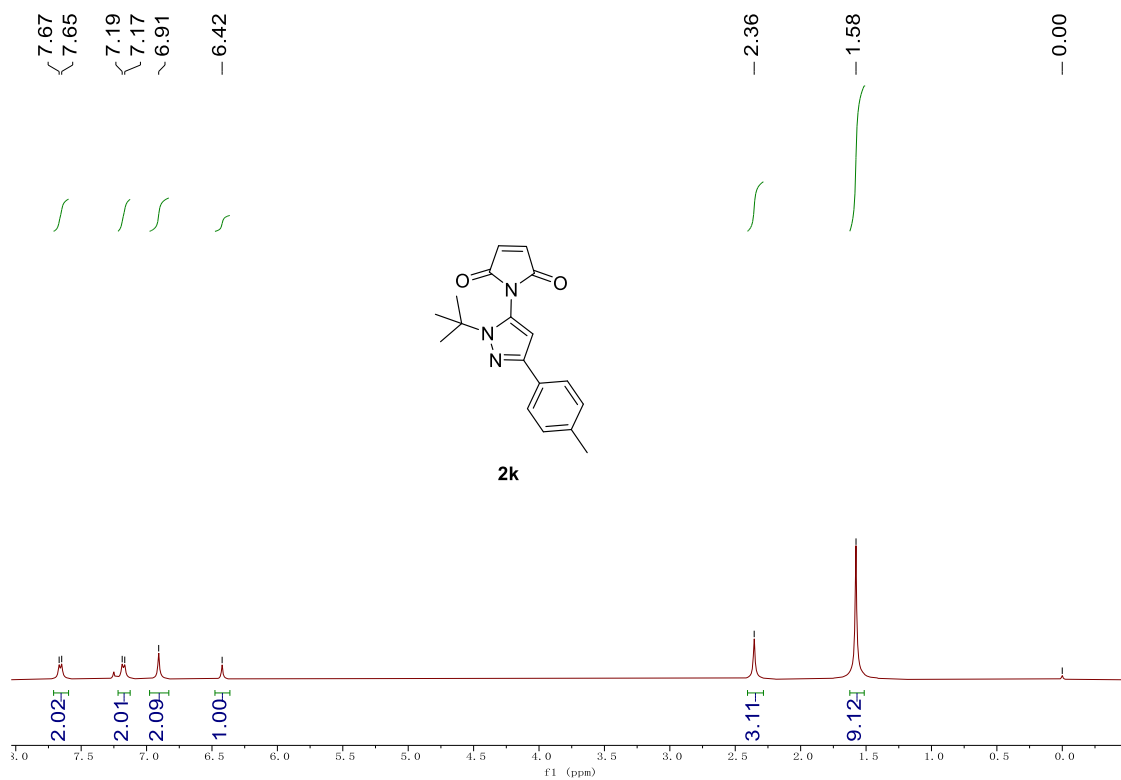


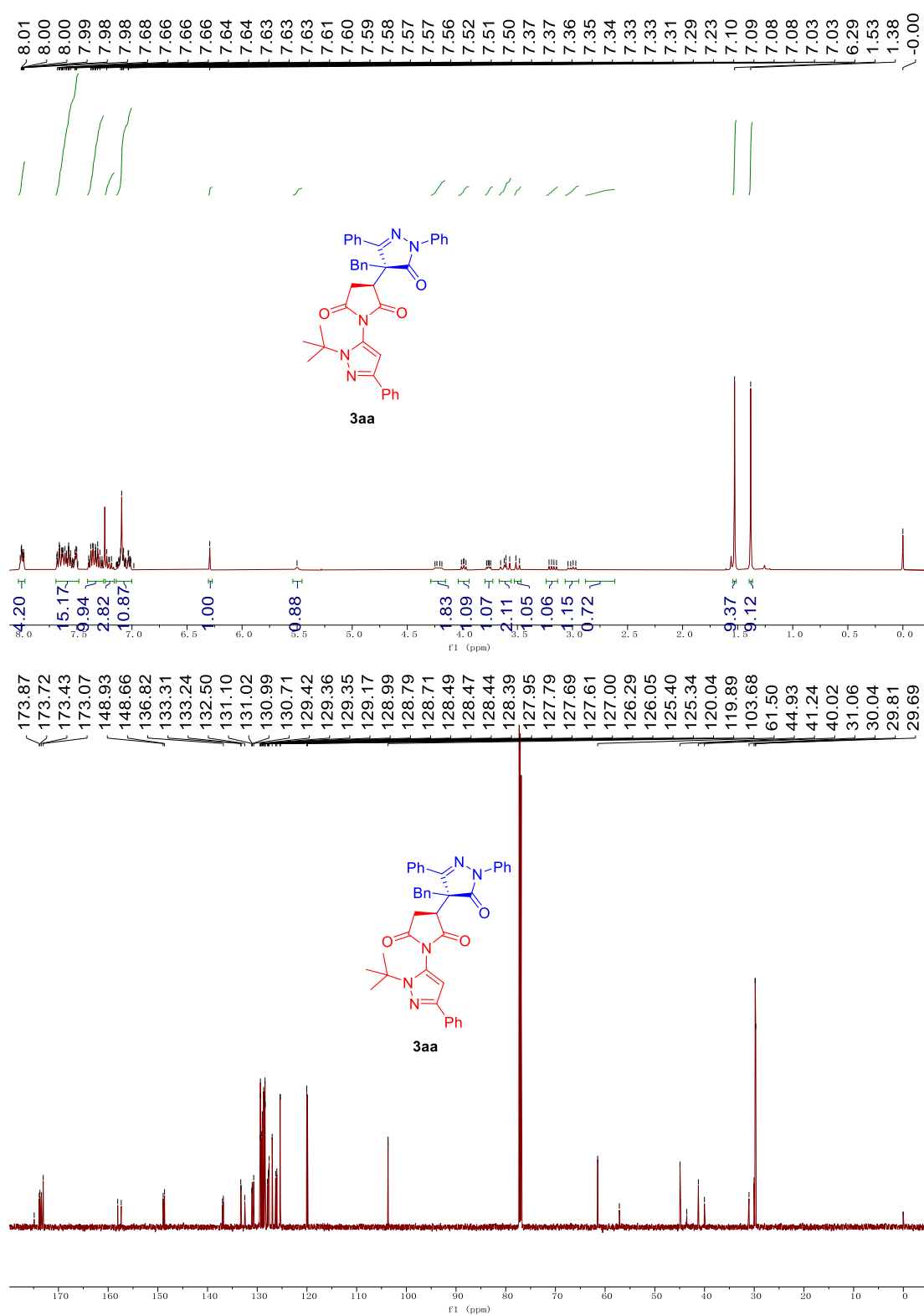


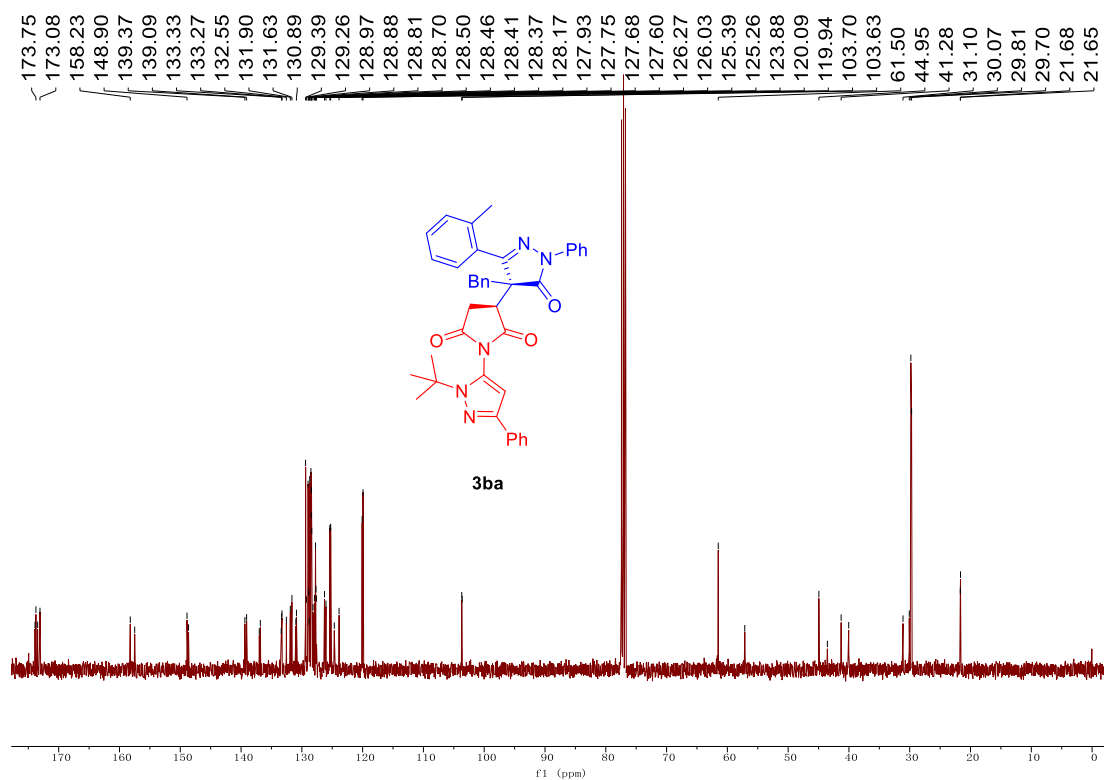
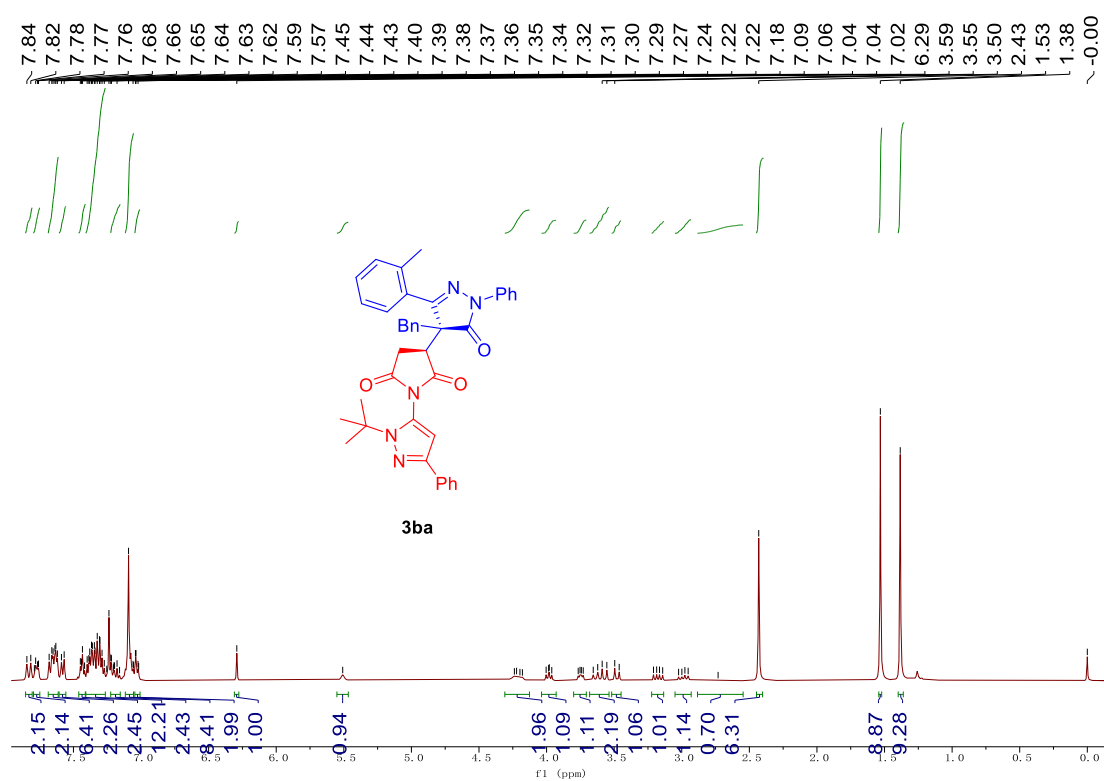


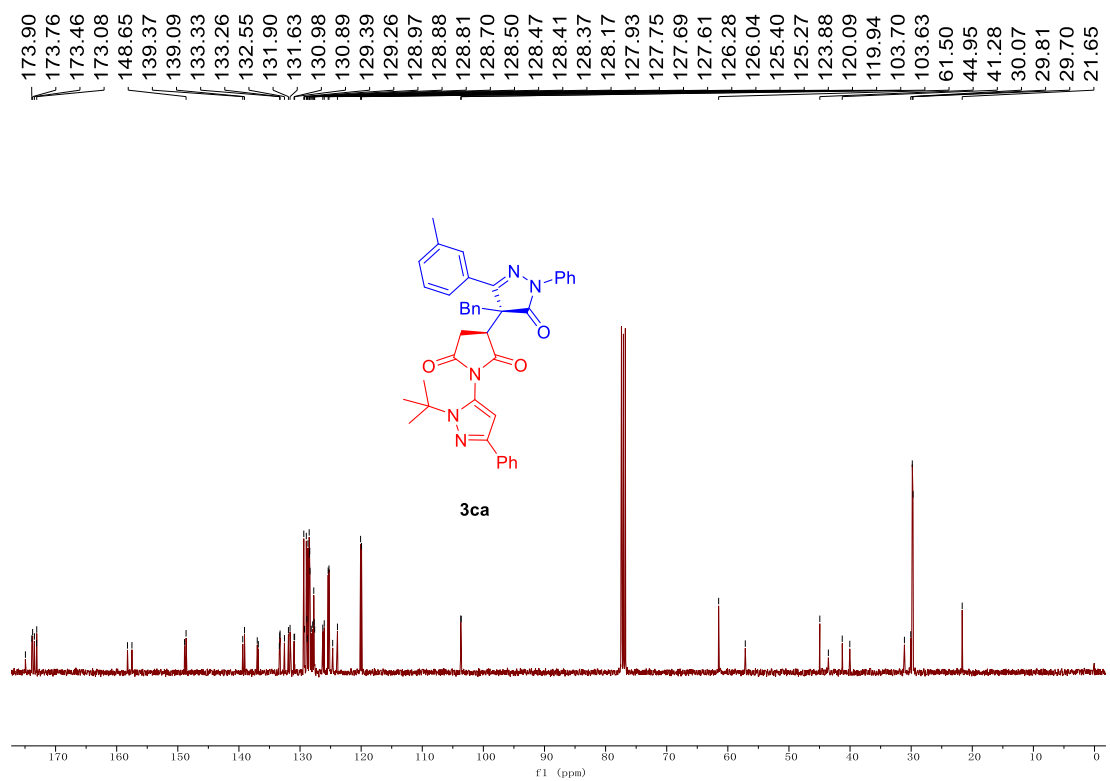
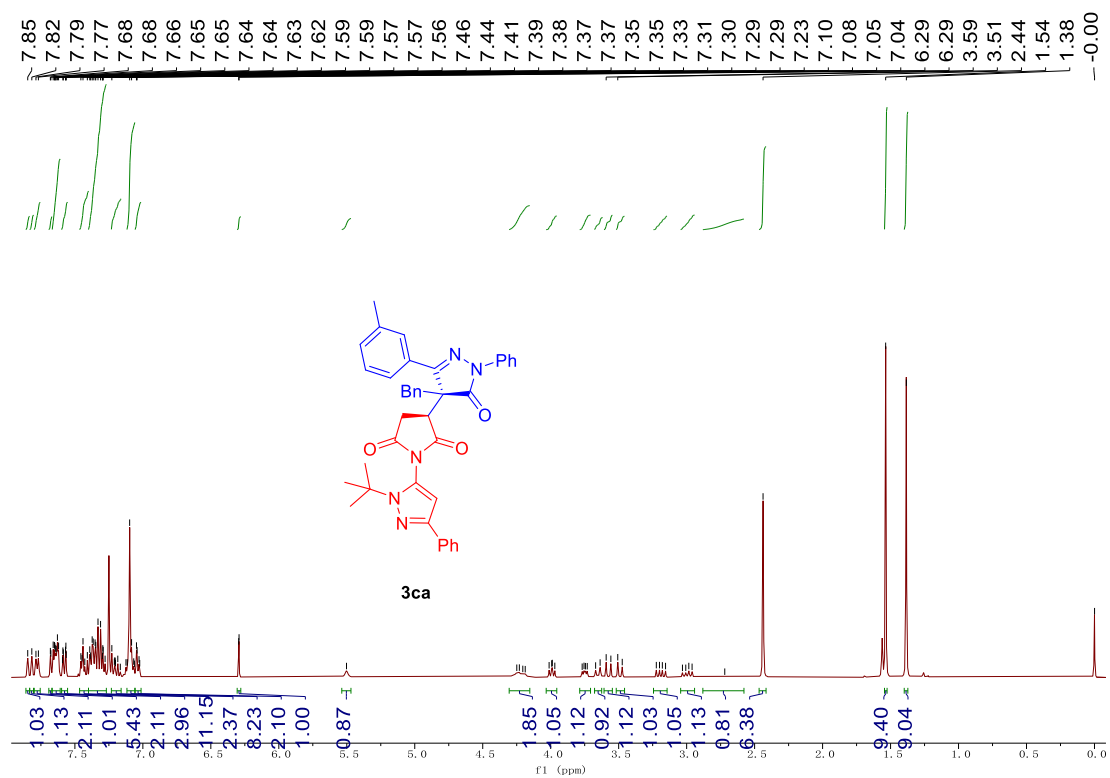


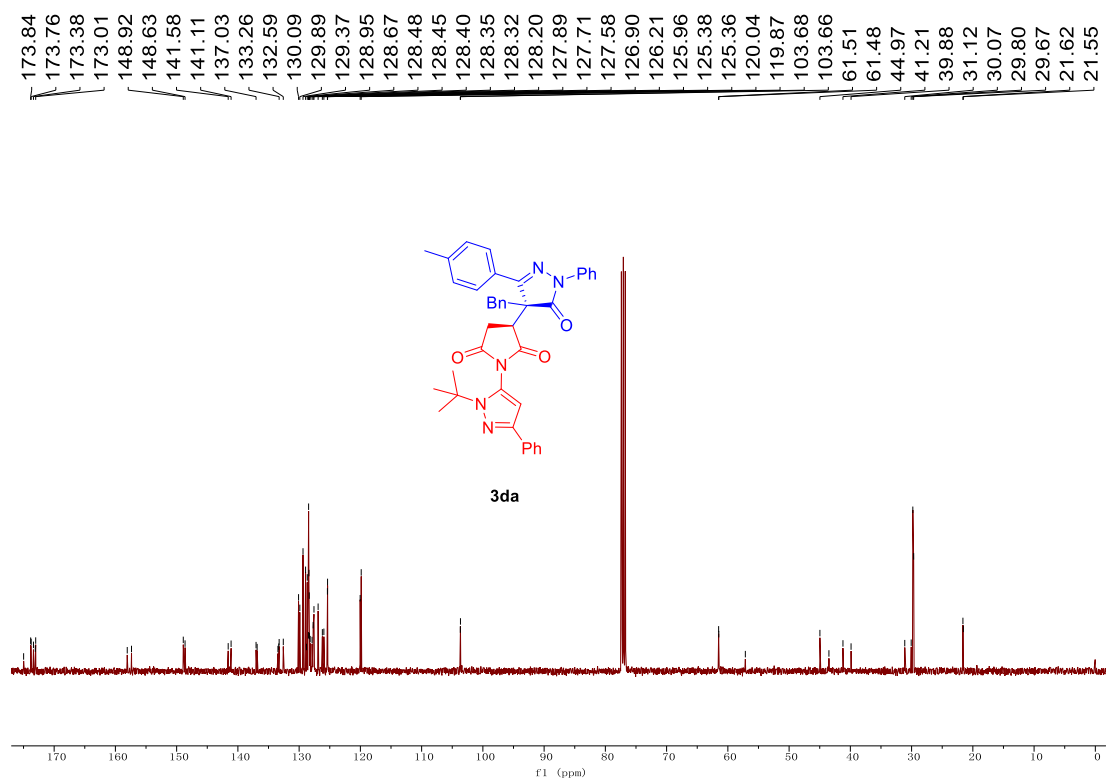
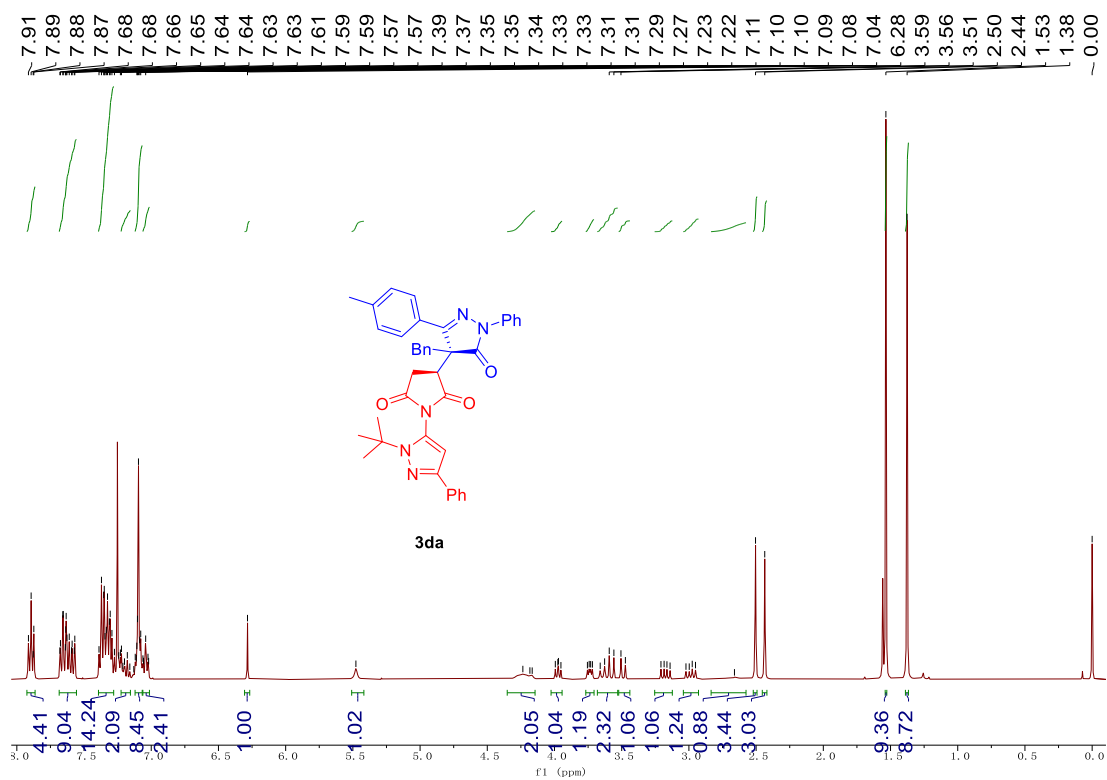


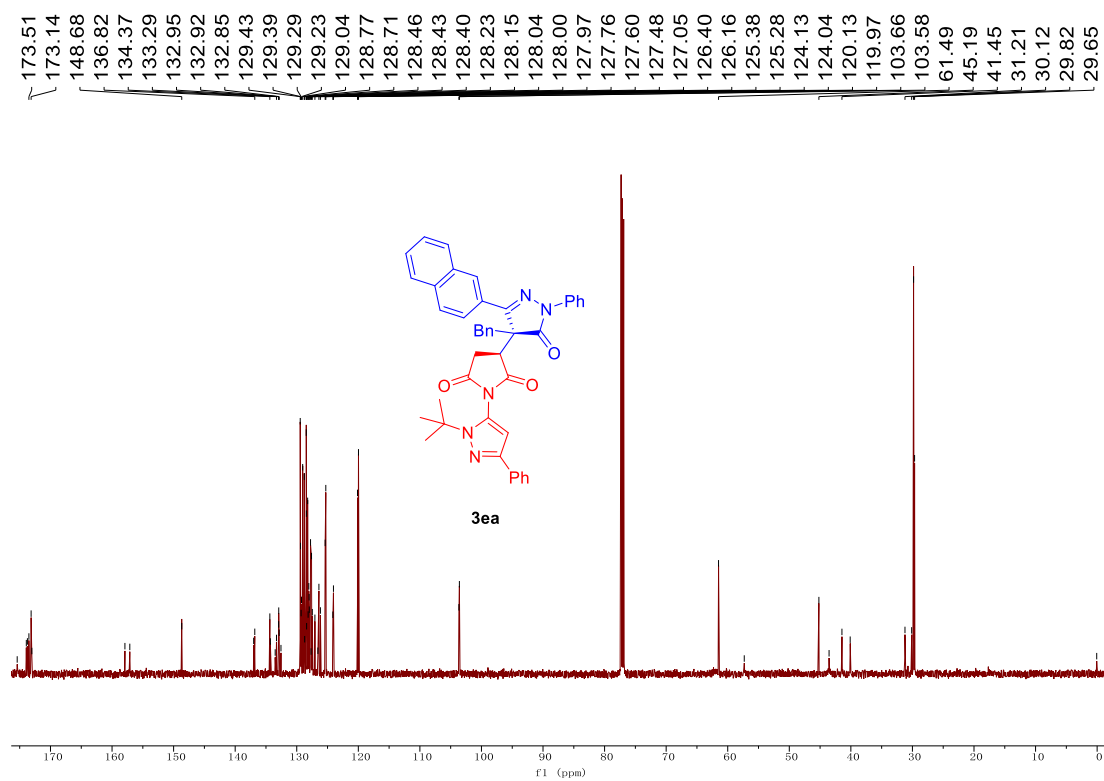
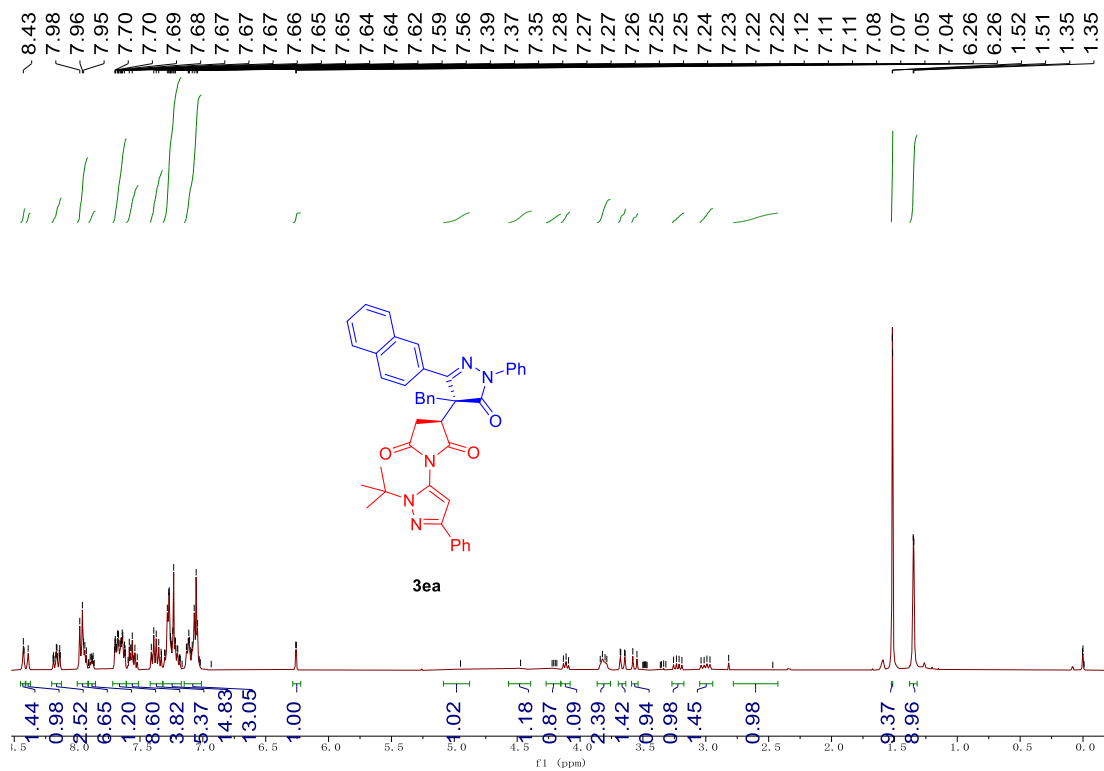


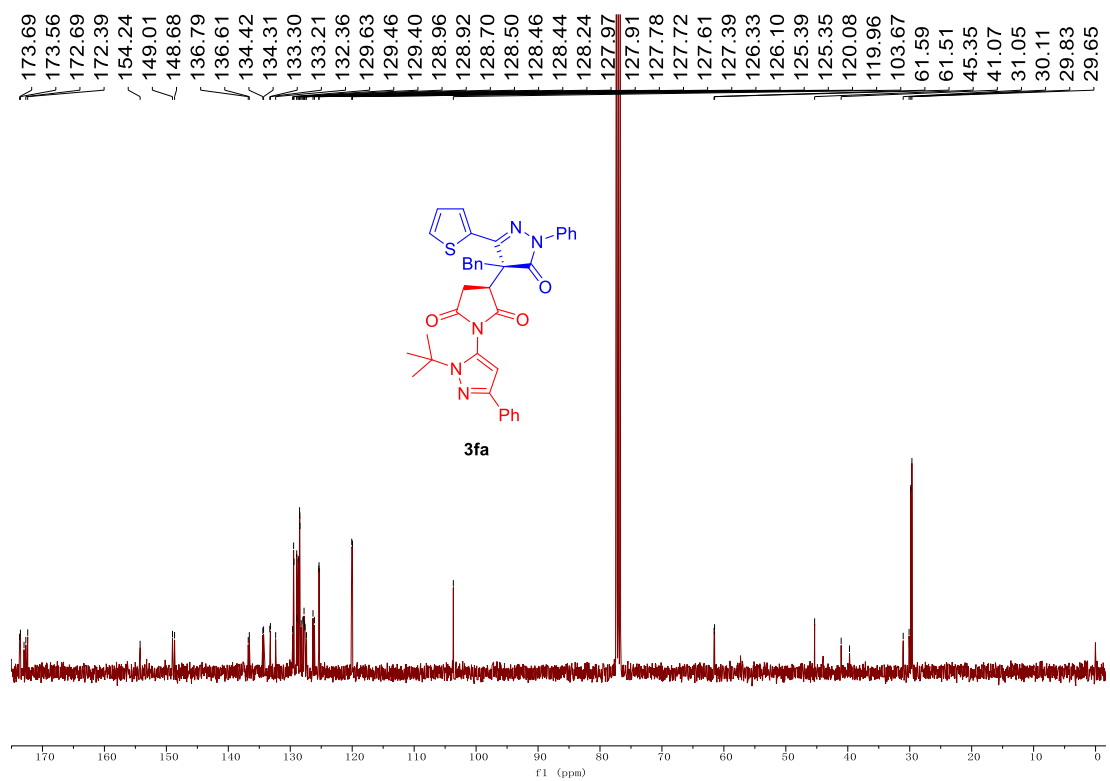
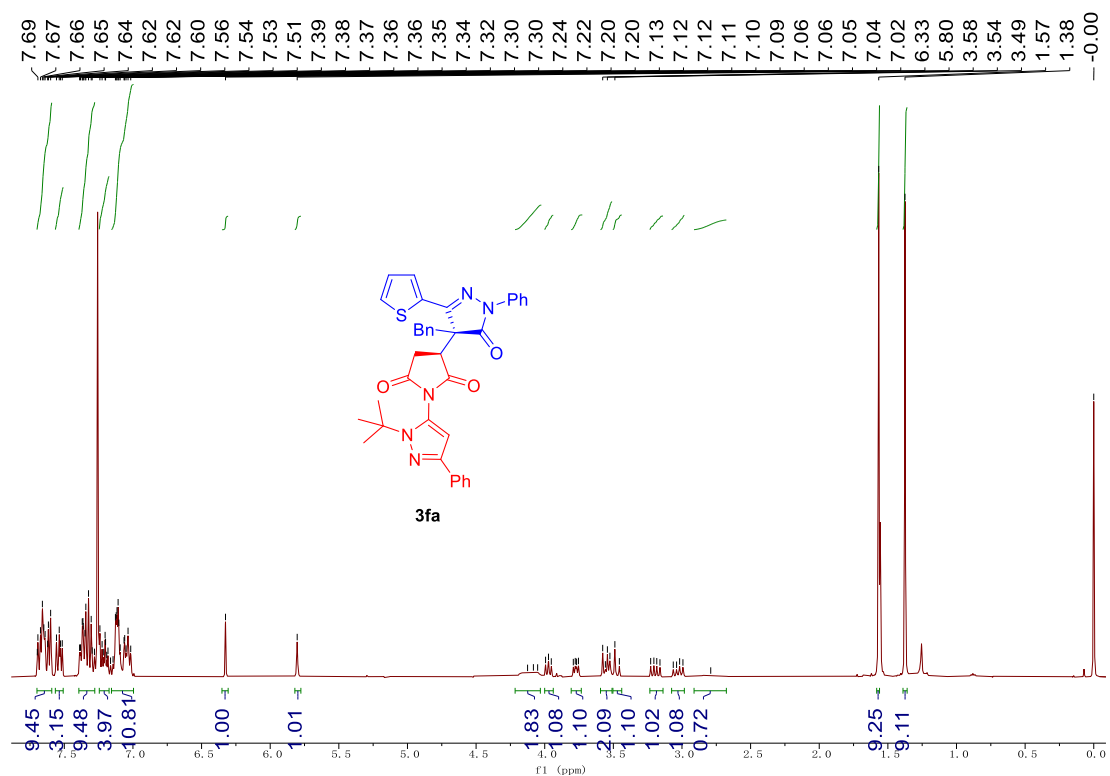


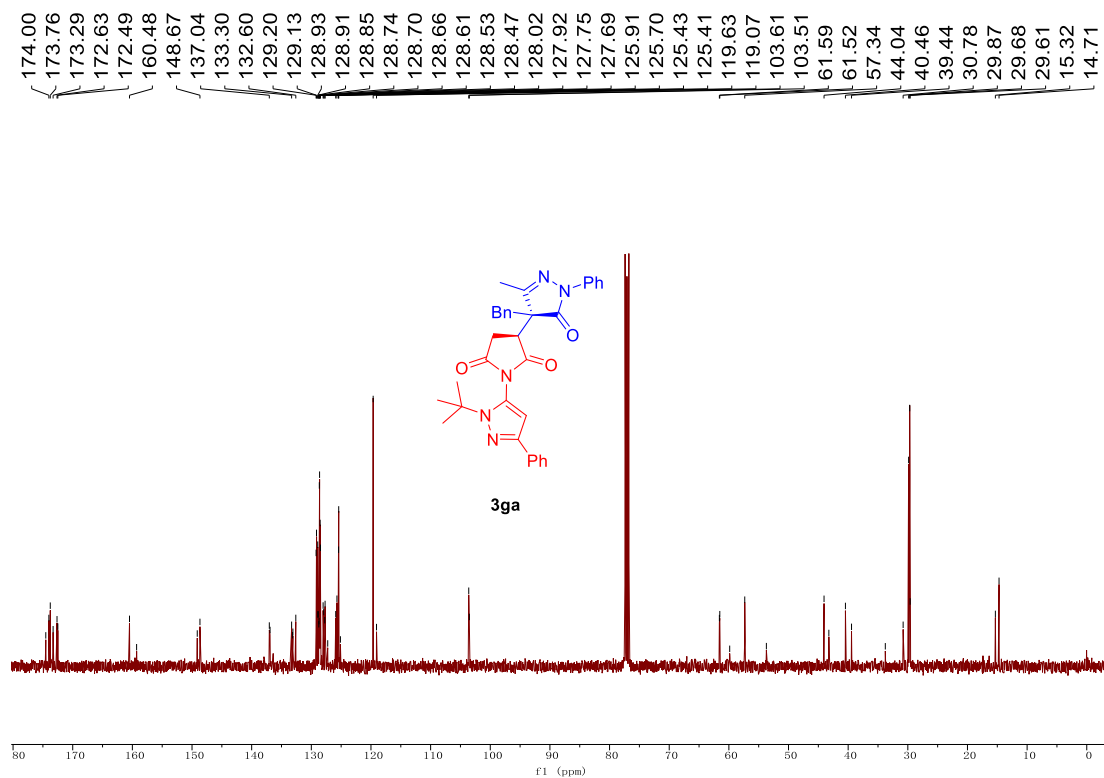
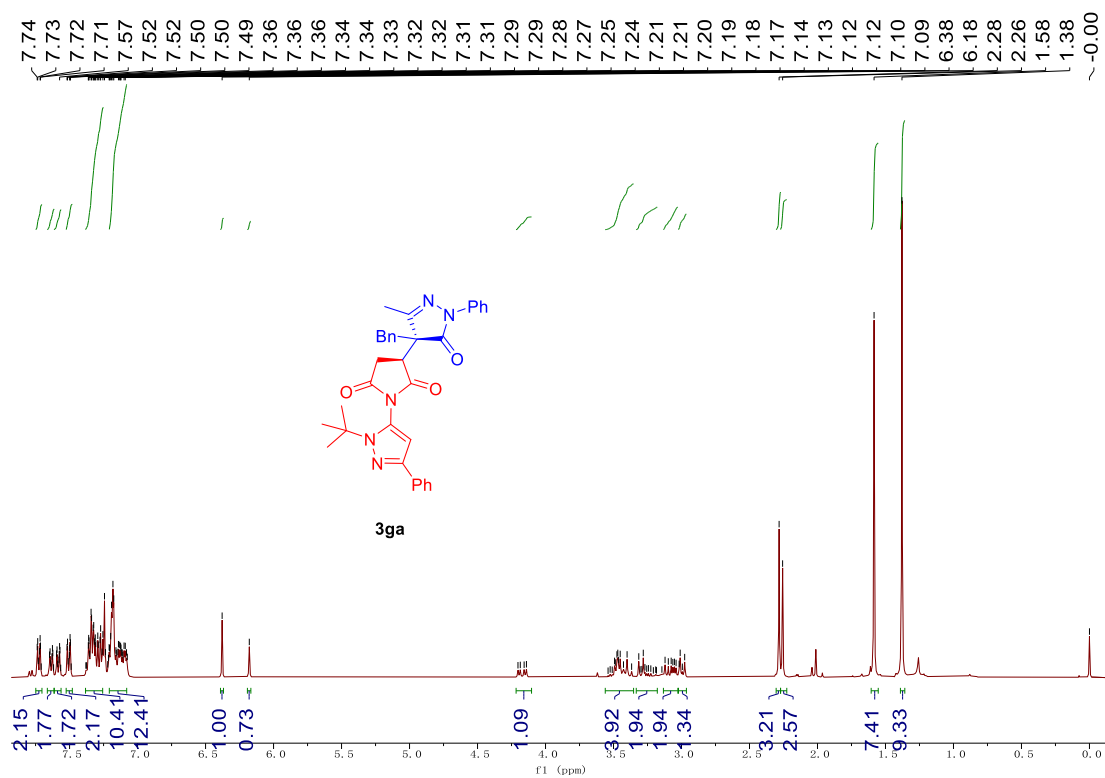


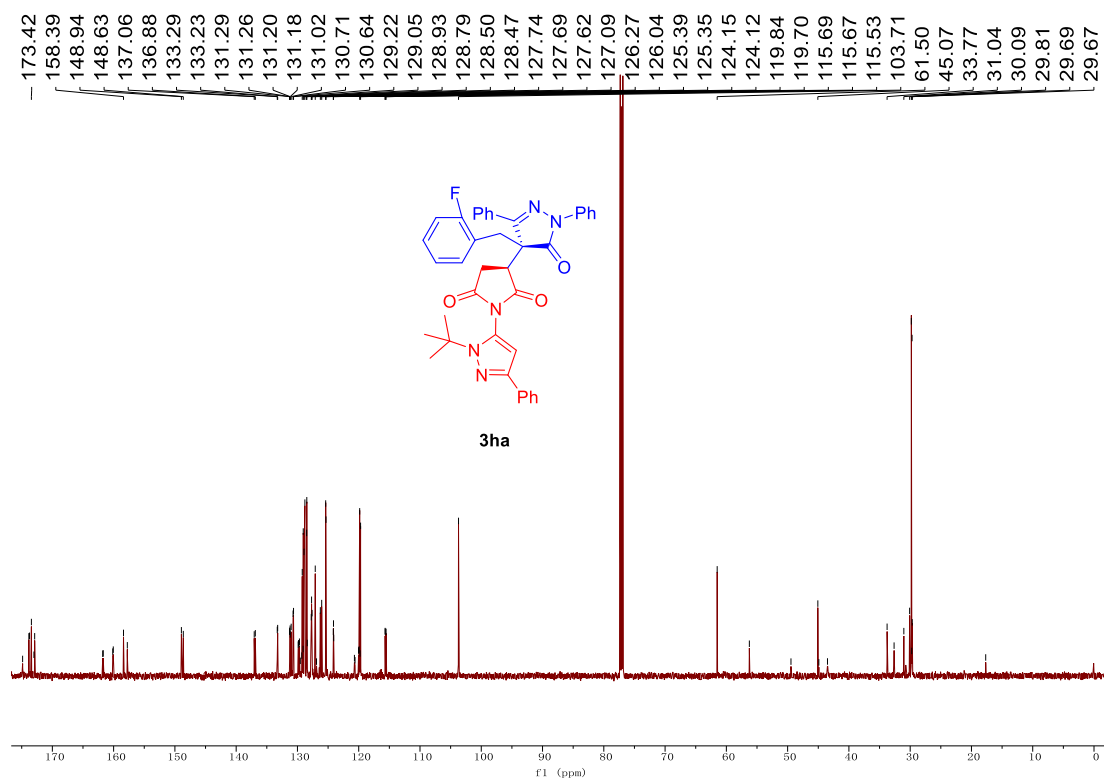
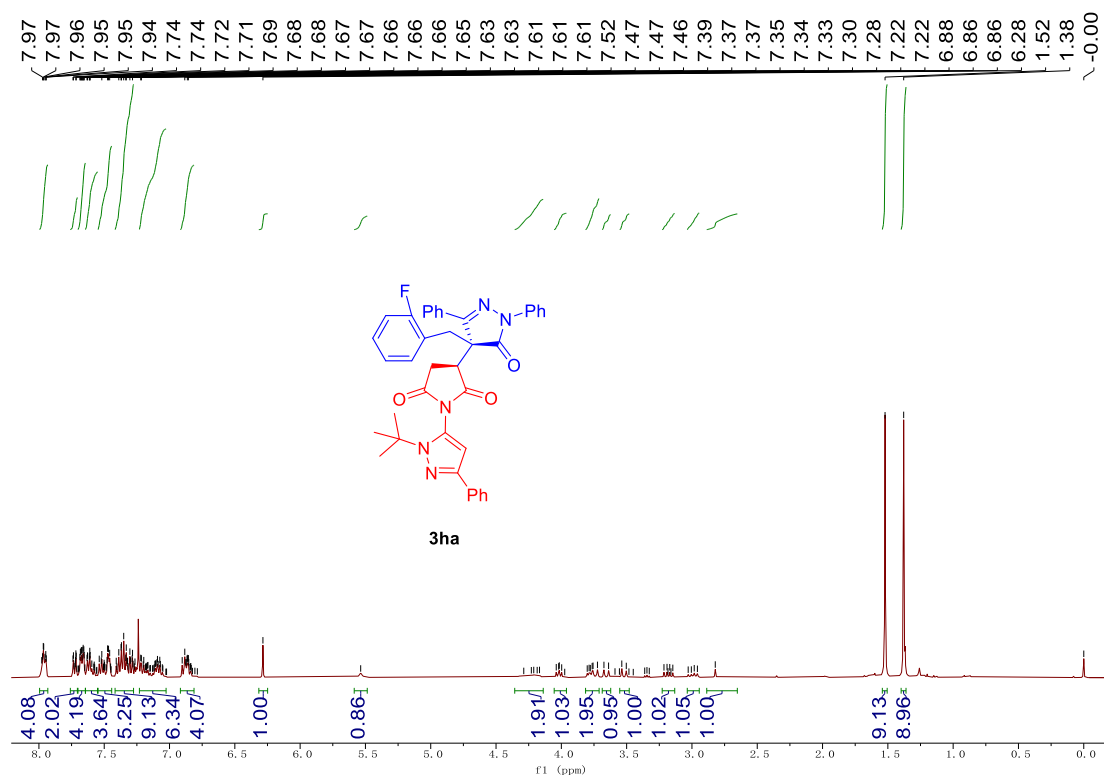


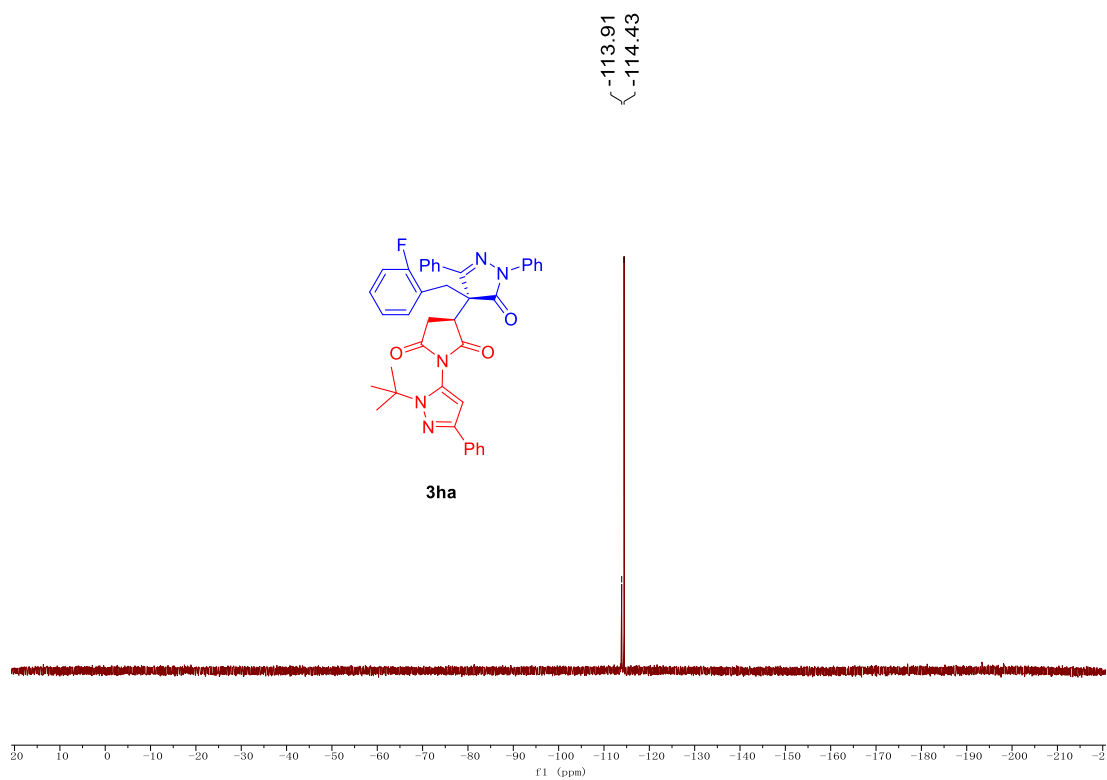


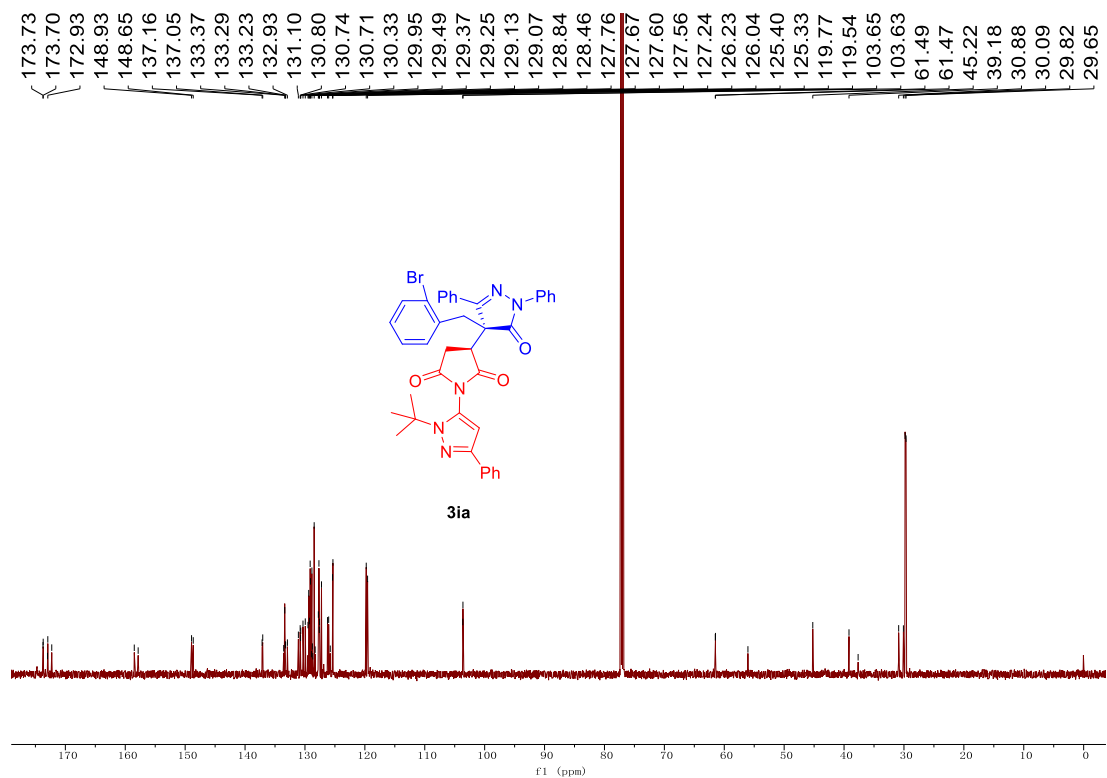
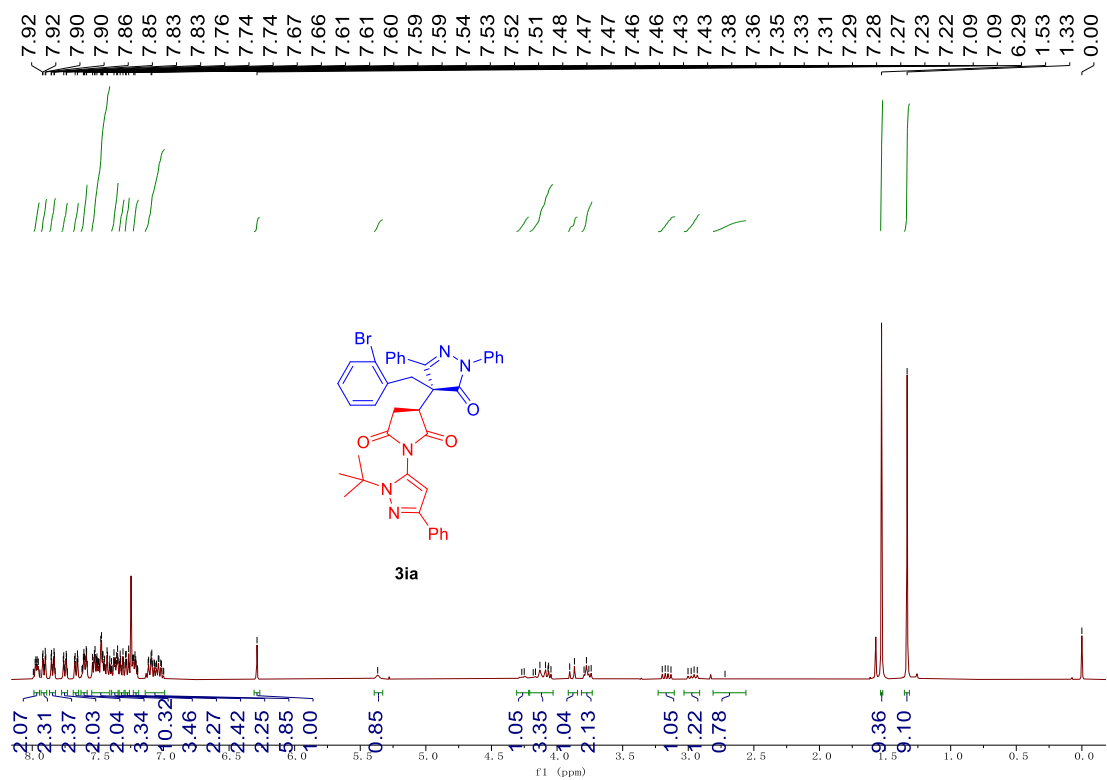


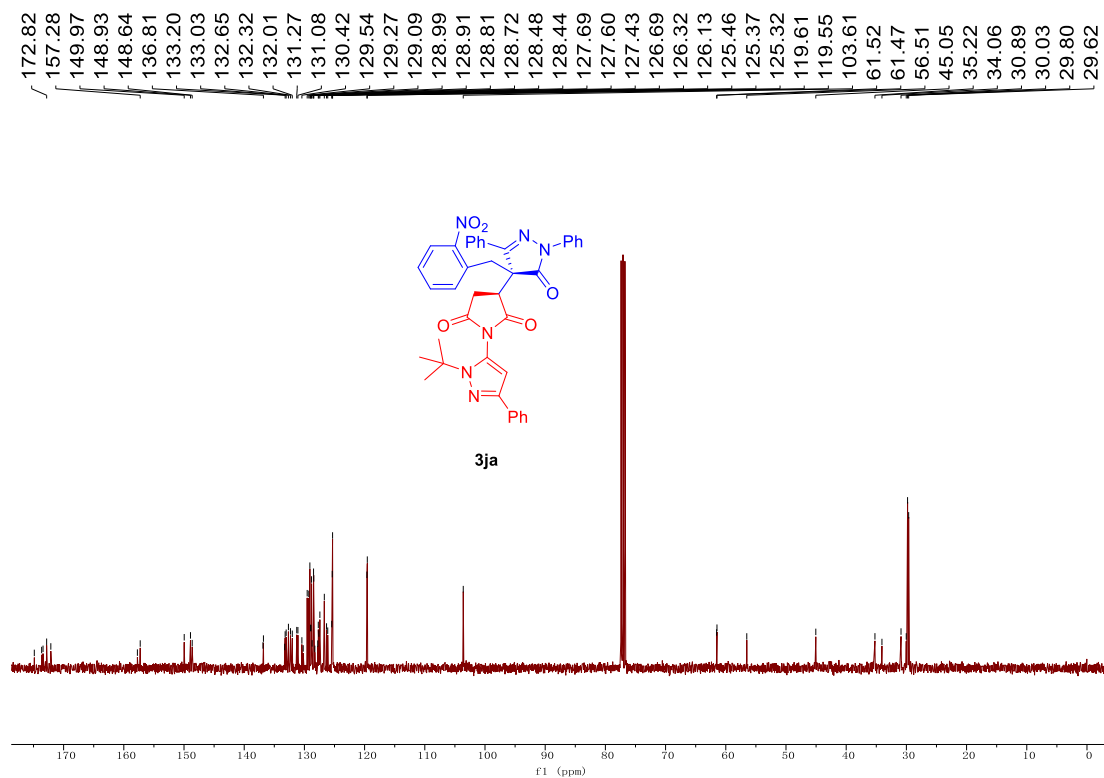
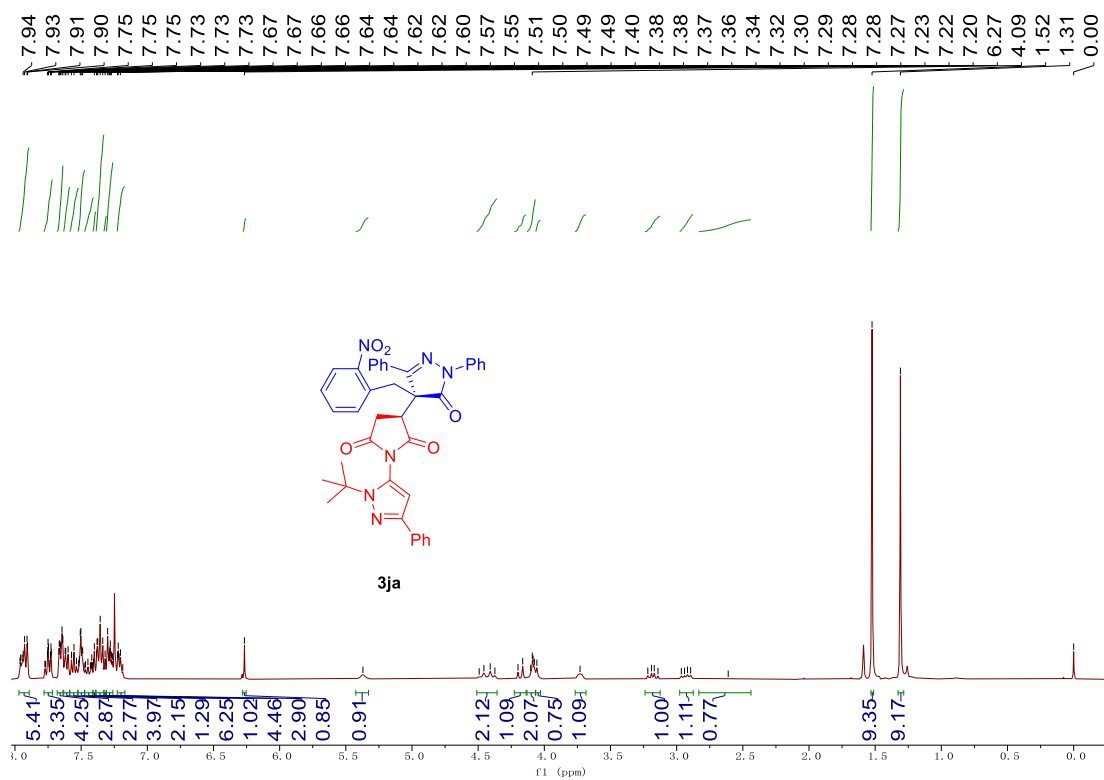


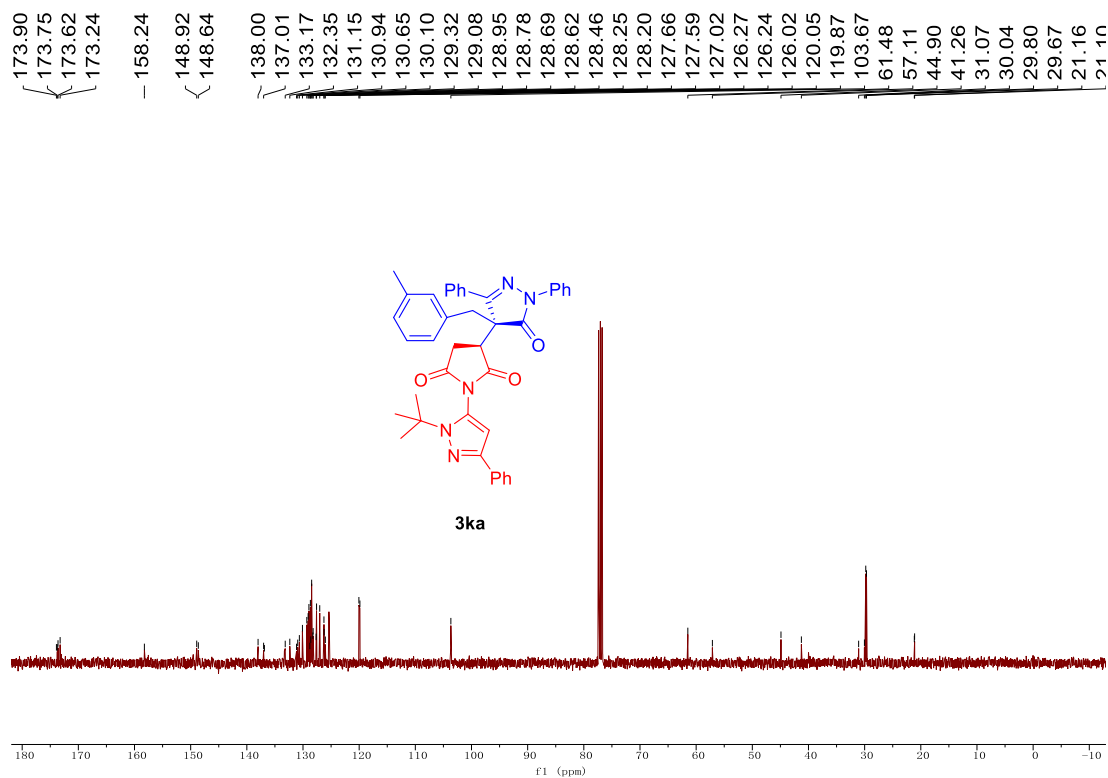
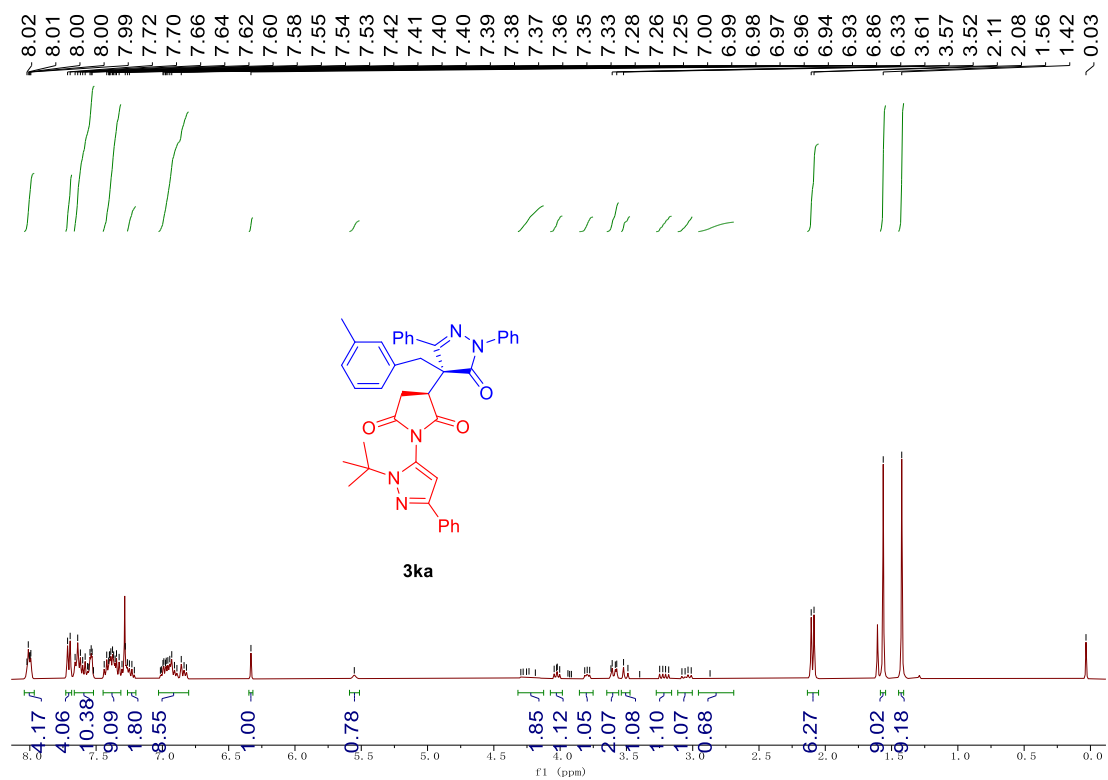


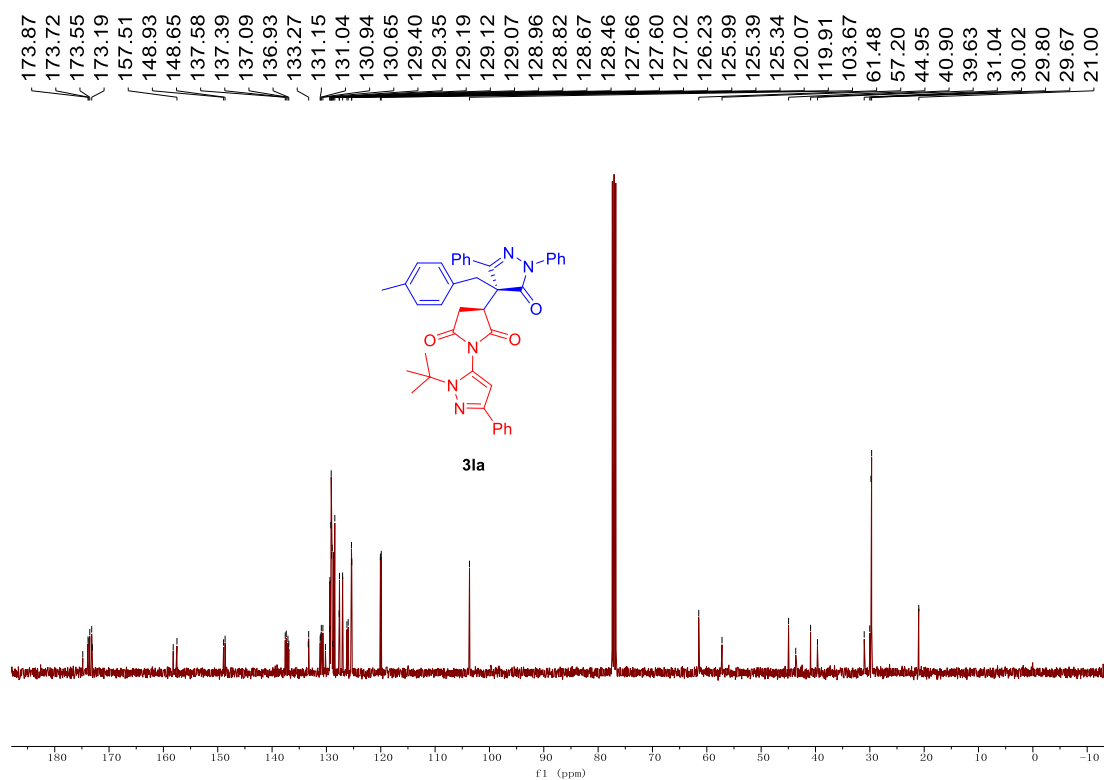
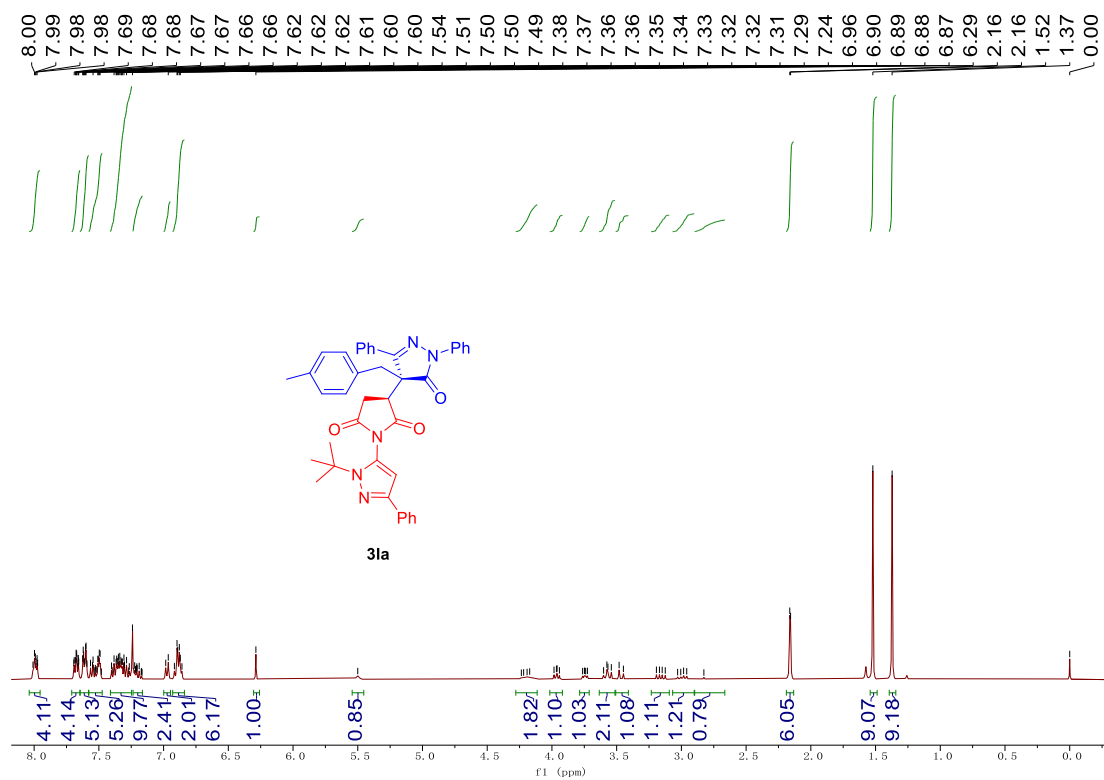


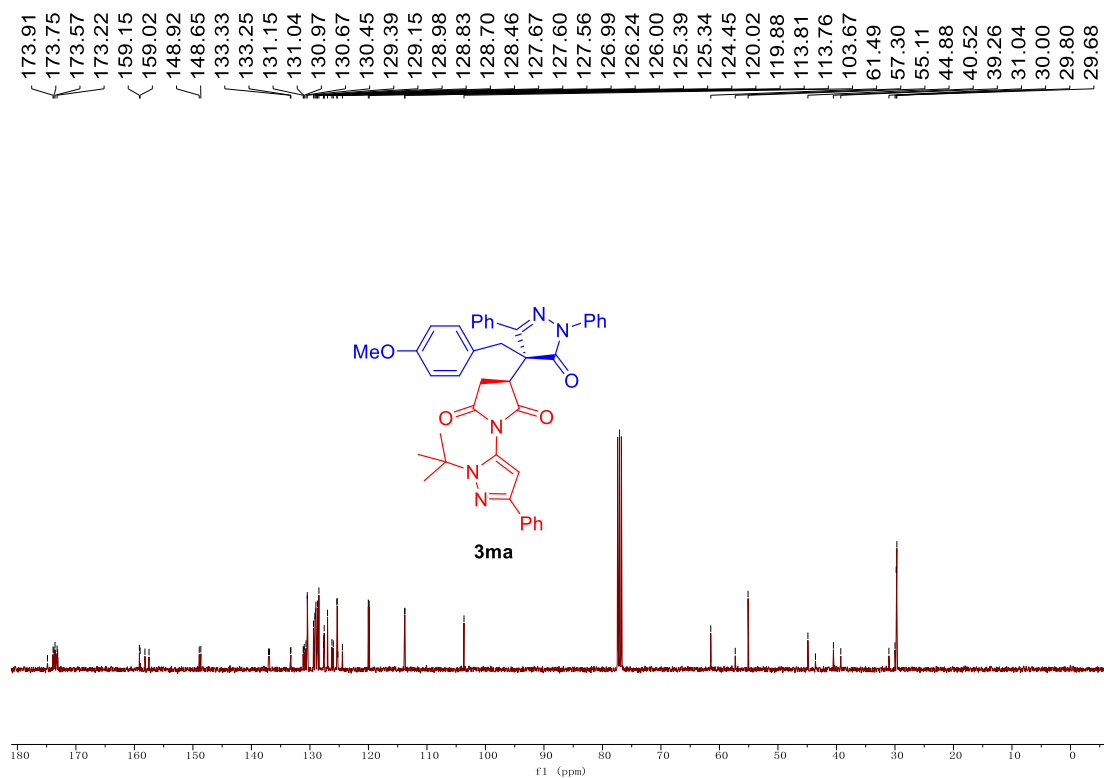
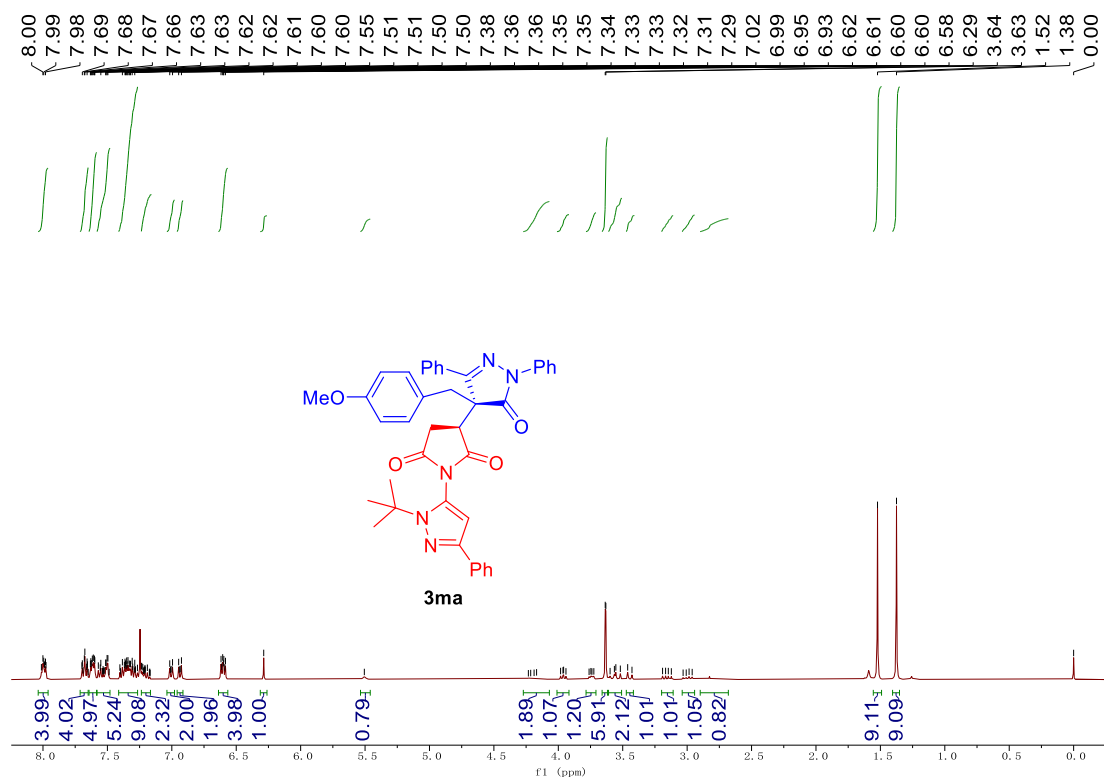


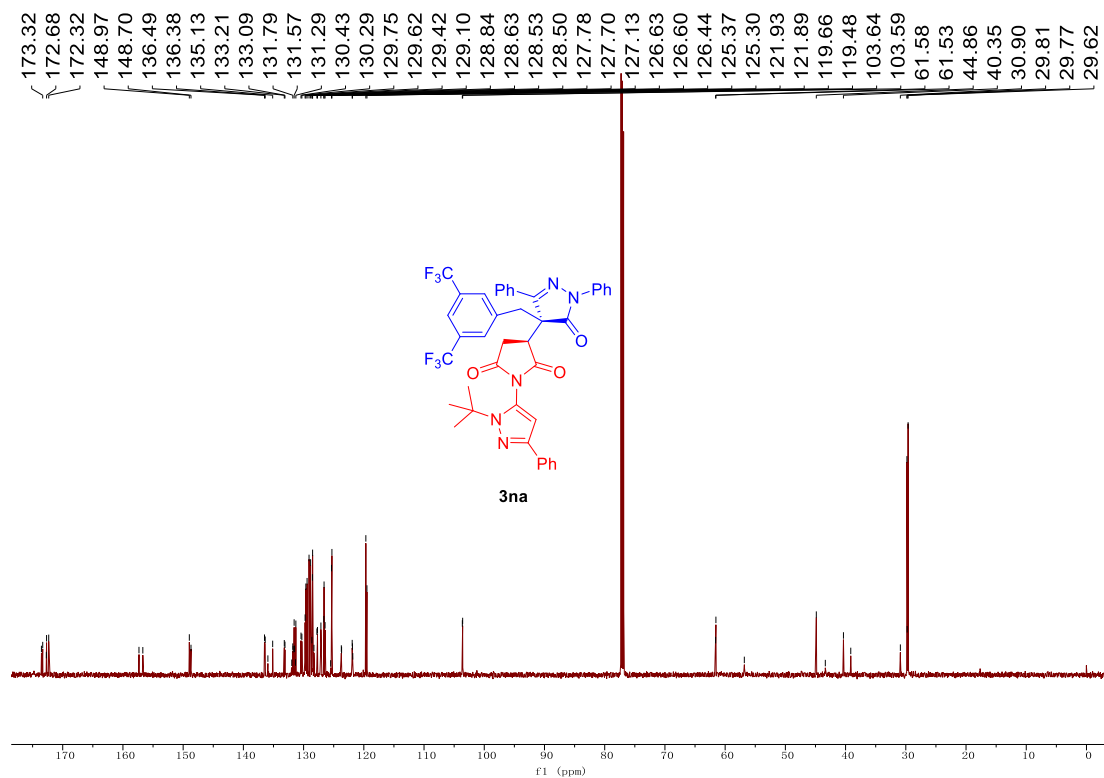
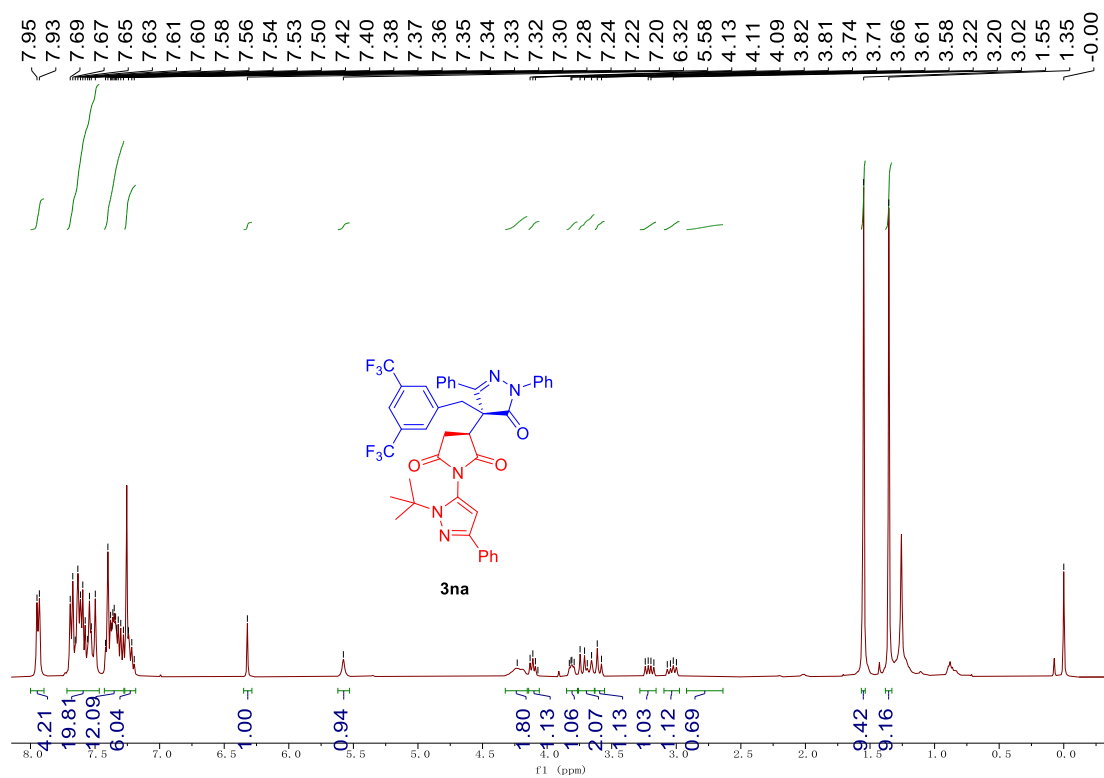


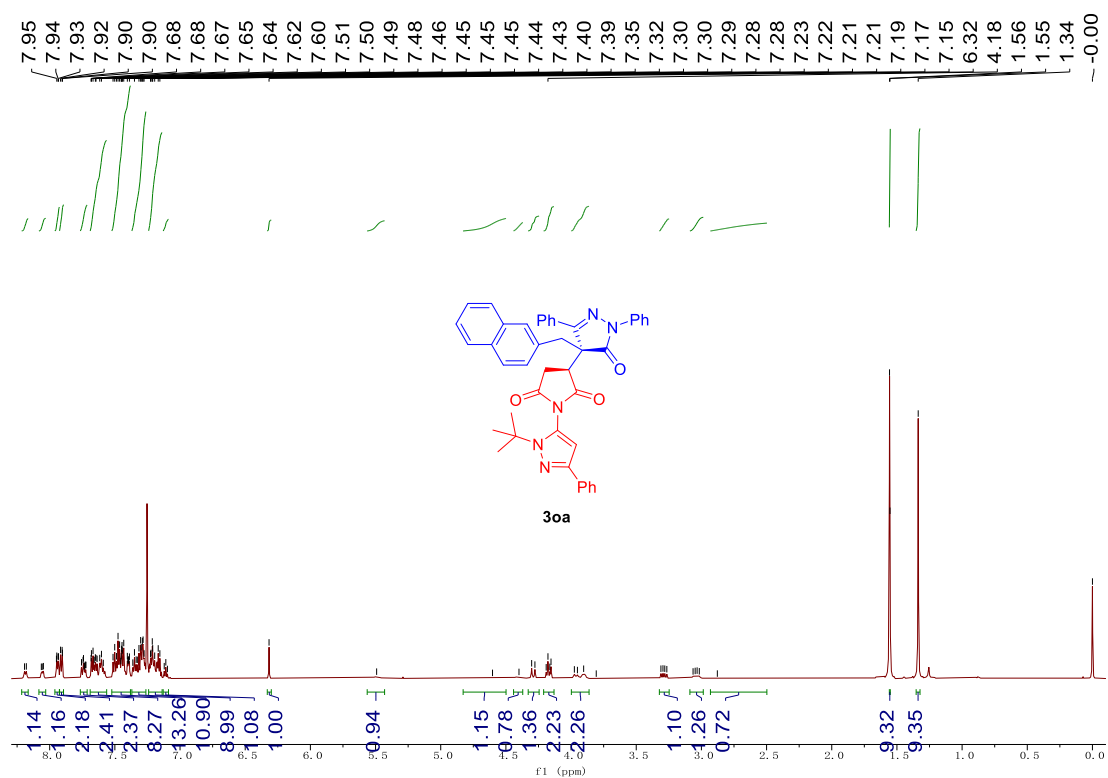
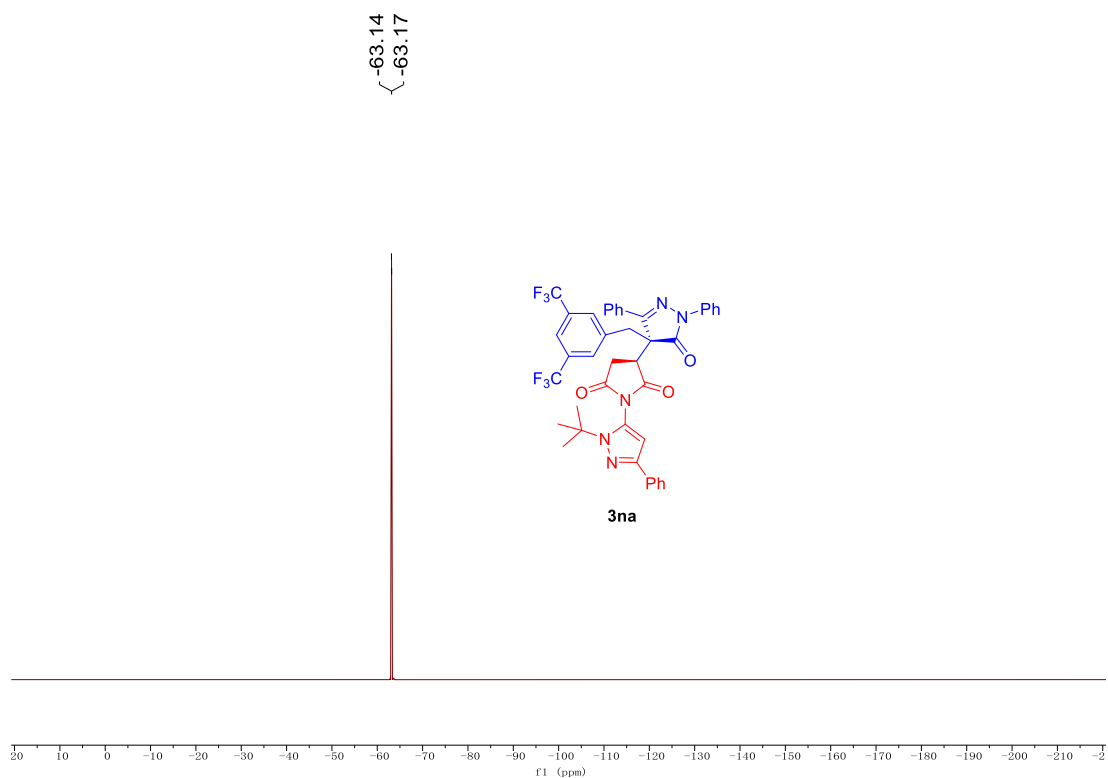


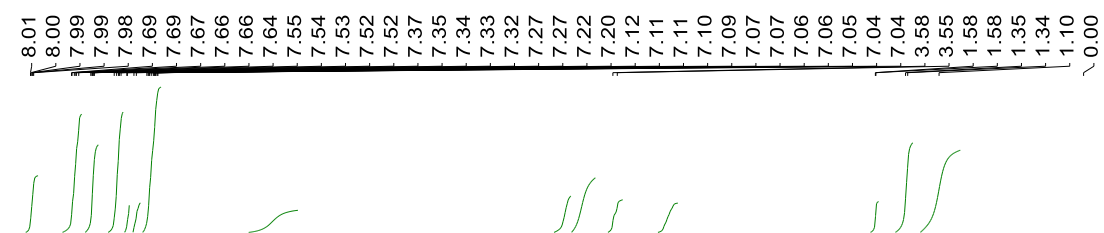


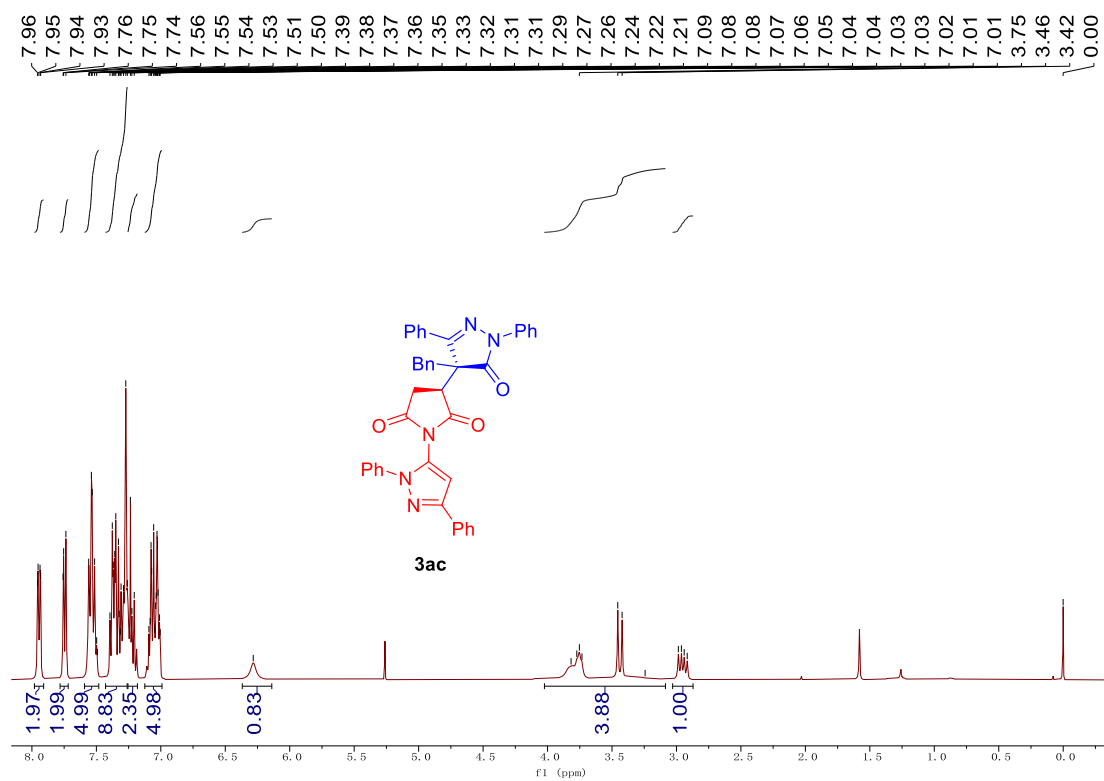
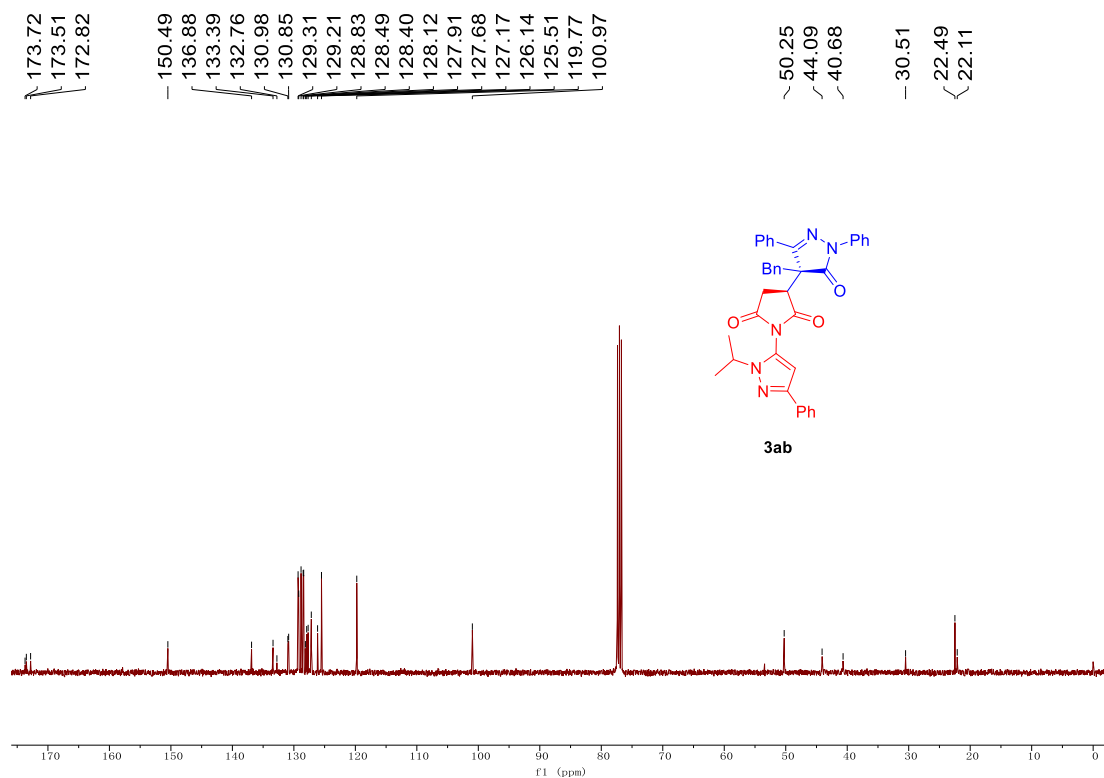


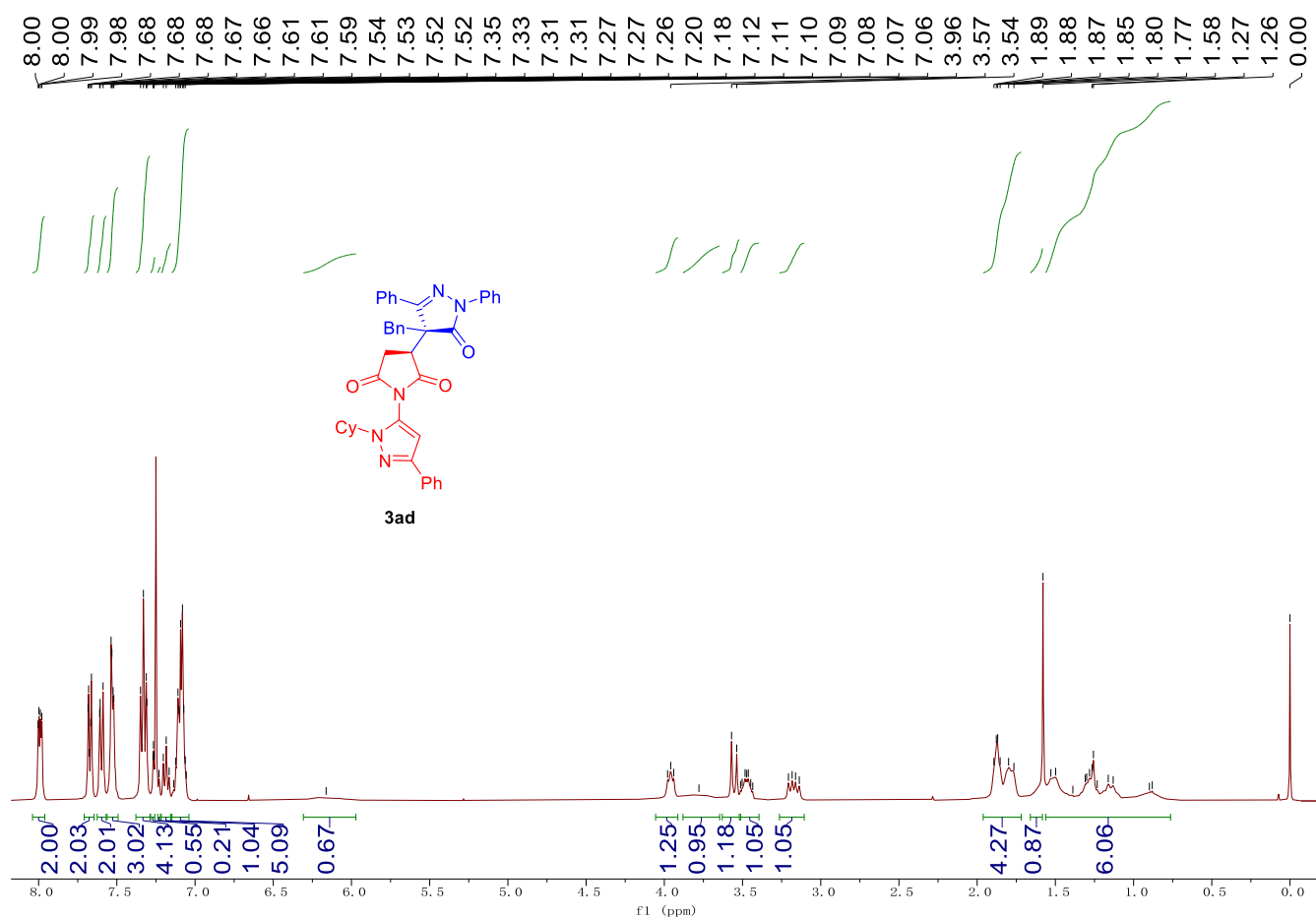
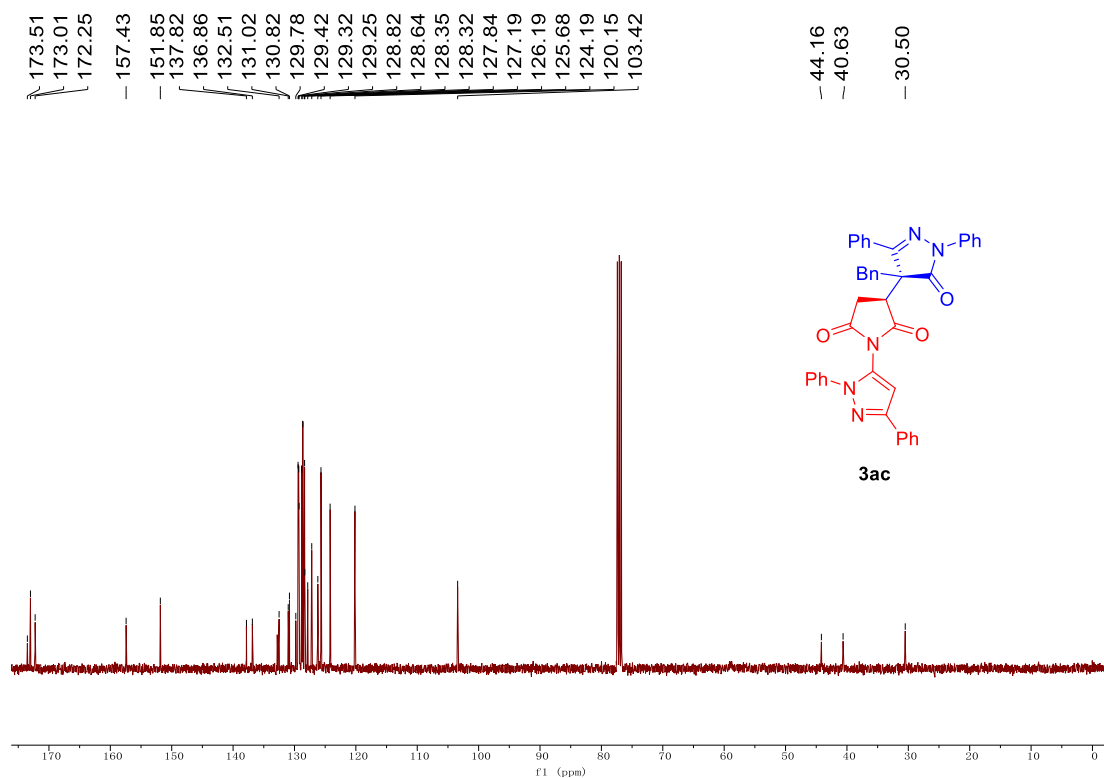


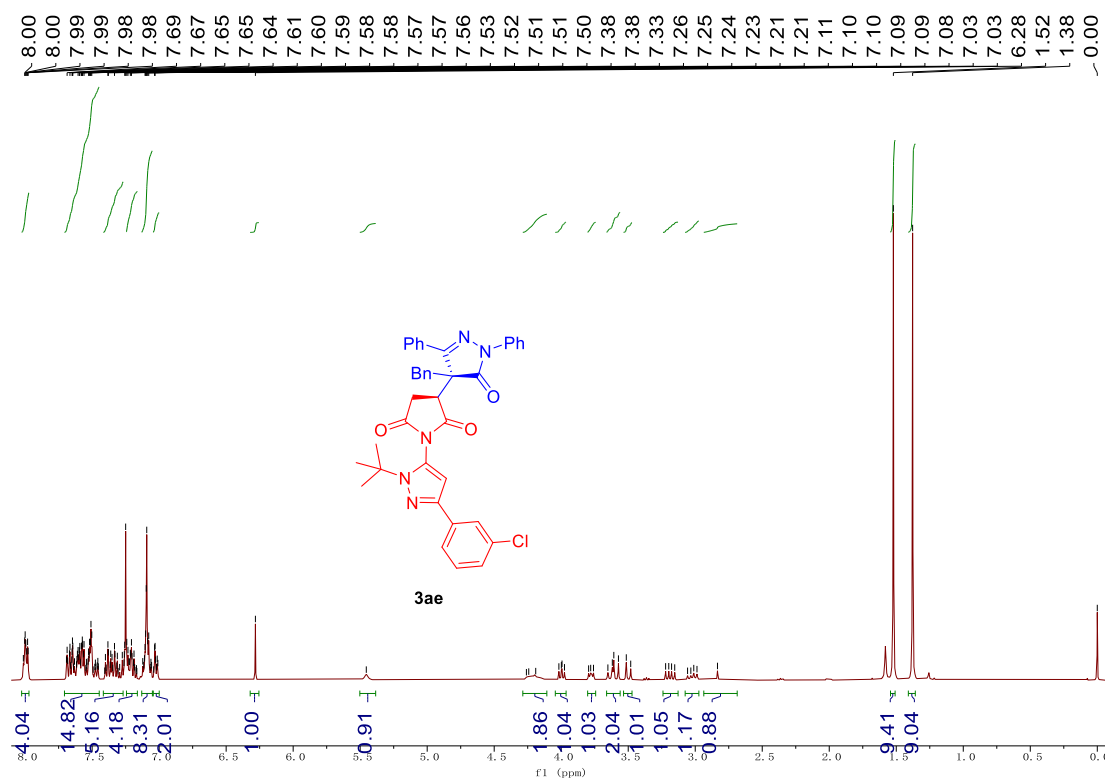
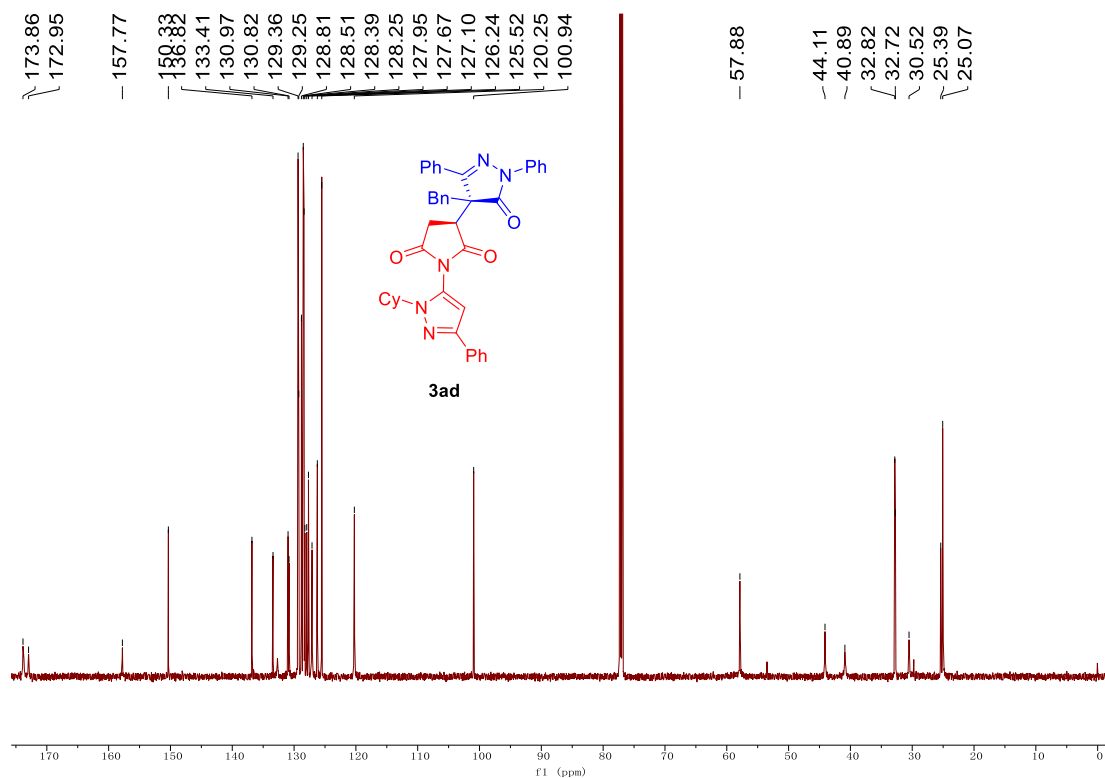


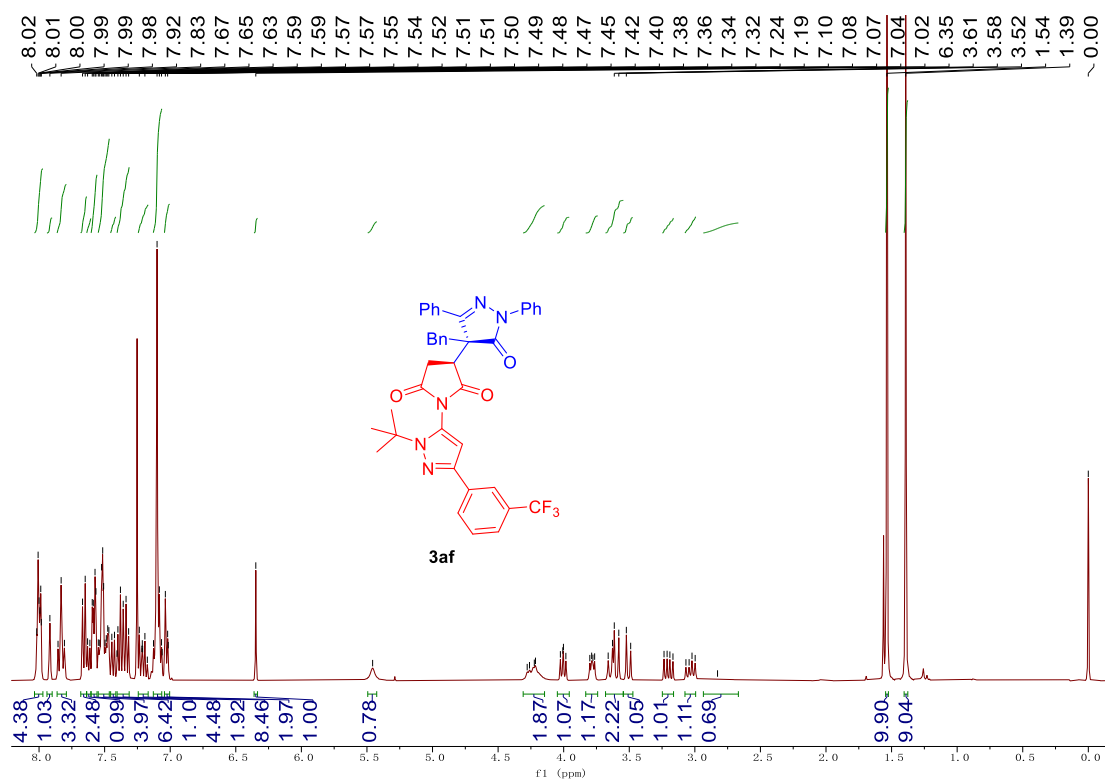
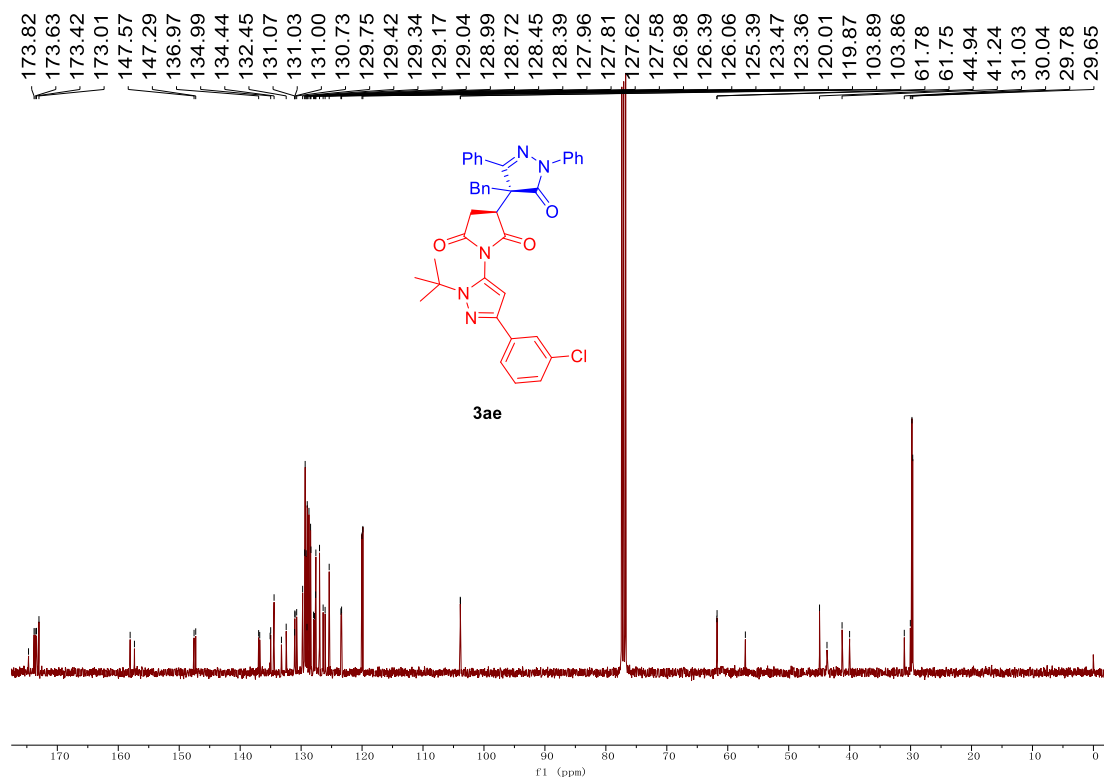


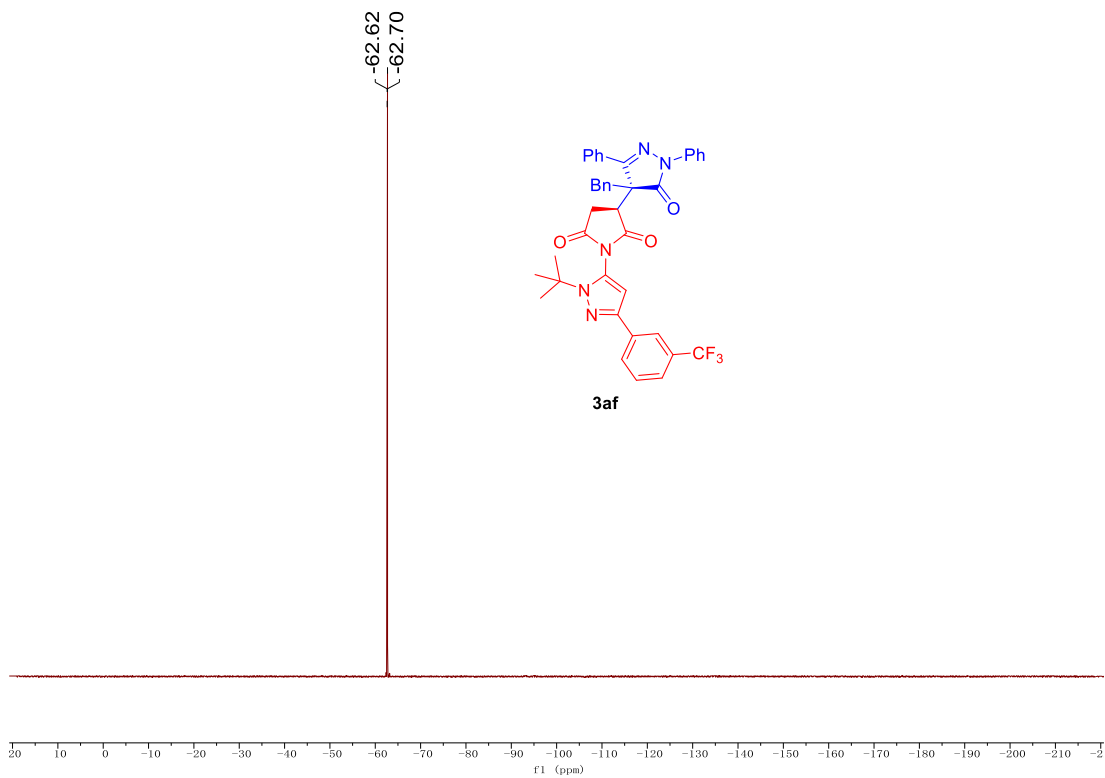


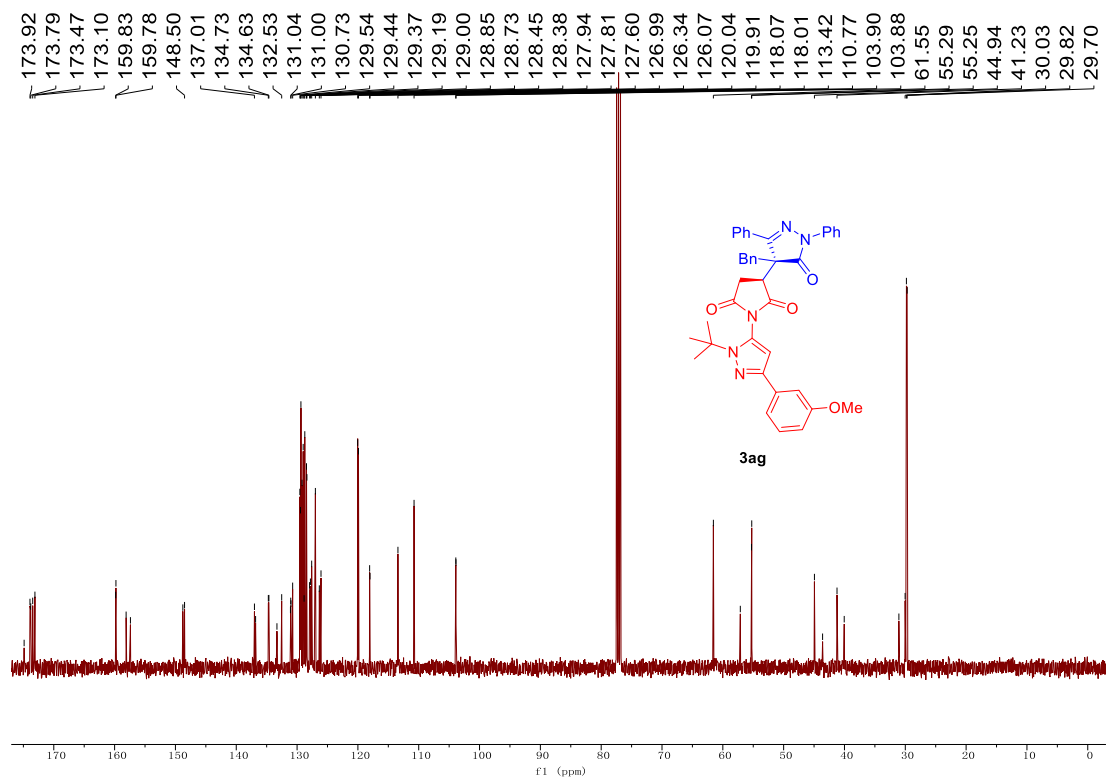
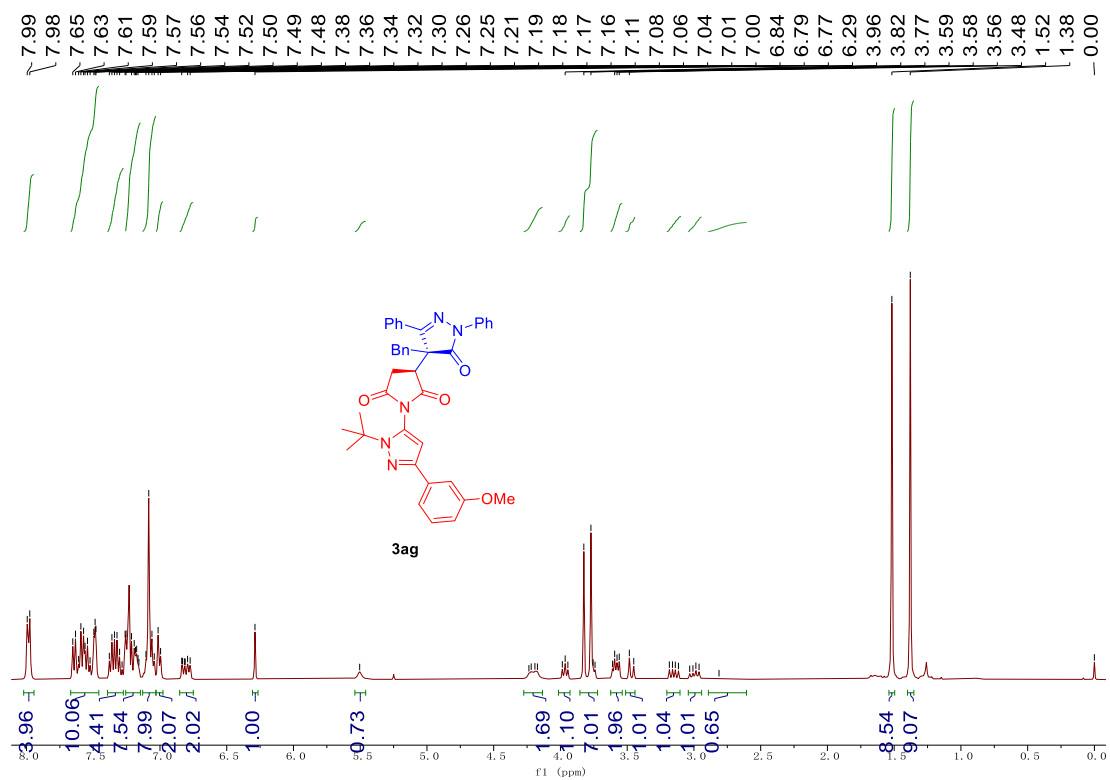


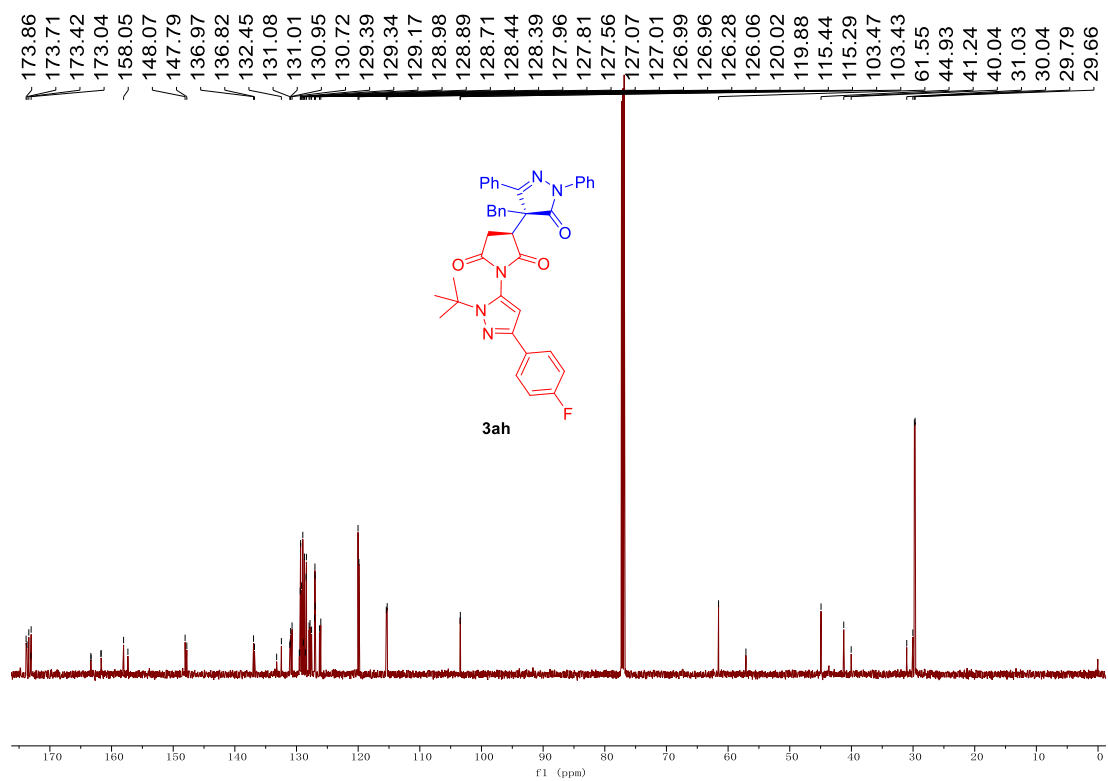
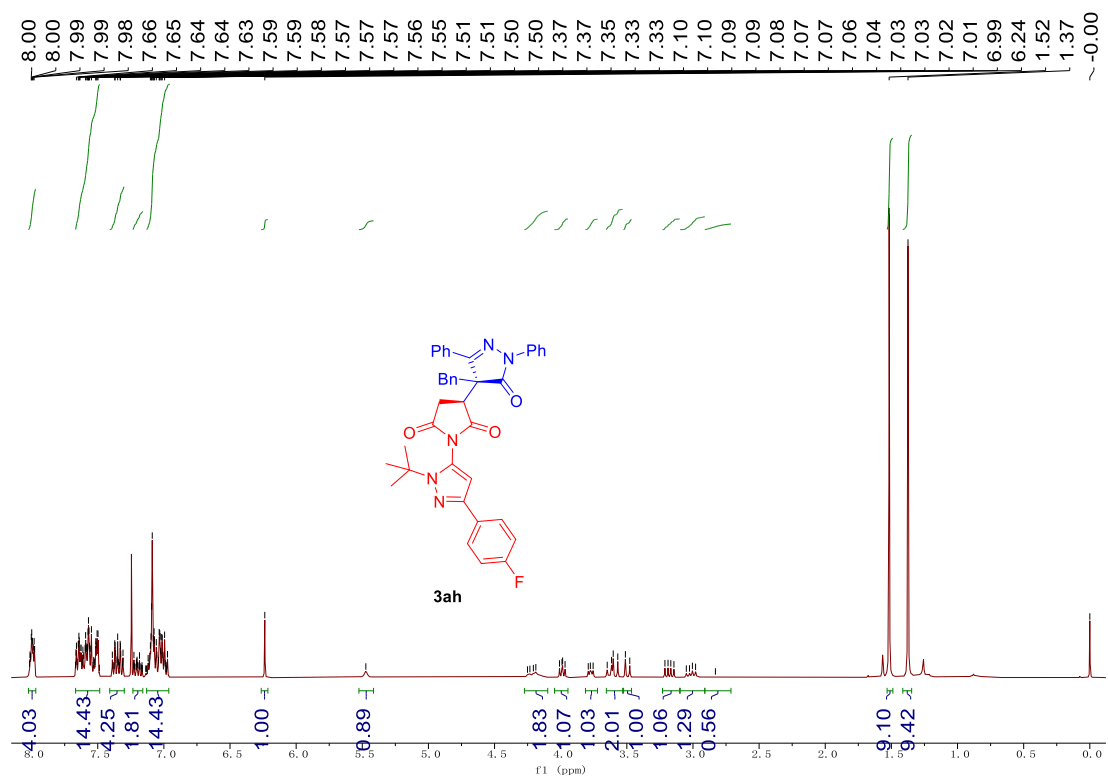



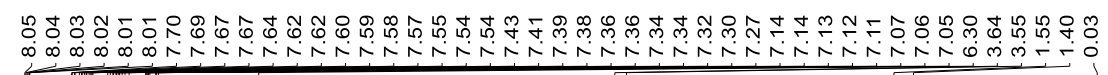












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