

Enantioselective and Diastereodivergent Construction of Oxindole-pyrazolone Conjugates Bearing an Alkenyl Substituted Quaternary Chlorinated Stereogenic Centre

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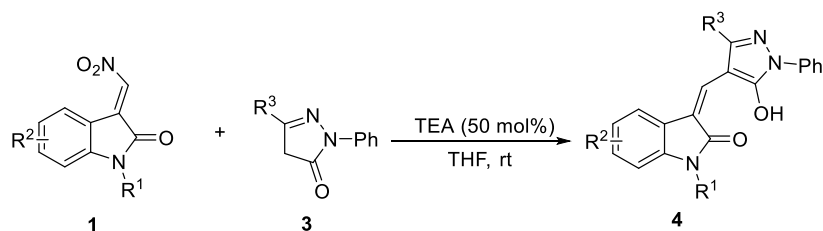
1. General information

Unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (200~300 mesh). Cis-trans isomerism ratio (*Z/E*) were determined by ^1H NMR (500 MHz). Enantiomeric excesses (ee) were determined by HPLC using corresponding commercial chiral columns as stated at 25 °C with UV detector at 254 nm. Optical rotations were reported as follows: $[\alpha]_{\text{TD}}$ (c g/100 mL, solvent). All ^1H NMR and ^{19}F NMR spectra were recorded on a Bruker AvanceII 500 MHz and Bruker Avance III 376 MHz respectively, ^{13}C NMR spectra were recorded on a Bruker Avance III 126 MHz with chemical shifts reported as ppm (in CDCl_3 , TMS as 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 = doublet doublet, coupling constants in Hz, integration). HRMS (ESI) was obtained with a HRMS/MS instrument (LTQ Orbitrap XL TM). The absolute configuration of **5oe** was assigned by the X-ray analysis. DMEM cell culture medium, penicillin/streptomycin stock solutions, fetal bovine serum (FBS) and trypsin were all purchased from Gibco BRL (Gaithersburg, MD, USA). A549, HepG2, U87, SW-620, HCT-116 and Hela cells were all obtained from the China Center for Type Culture Collection (Wuhan, China). All of the cells were cultured in DMEM containing 10% FBS and 1% antibiotics (Penicillin/Streptomycin).

Indole nitroalkene series **1** were prepared from isatin according to the literature¹. Pyrazolone series **3** were obtained according to the literature^{2,3}. Intermediate product series **4** were synthesized according to literature procedures⁴. And the racemic products were synthesized using triethylamine as catalyst.

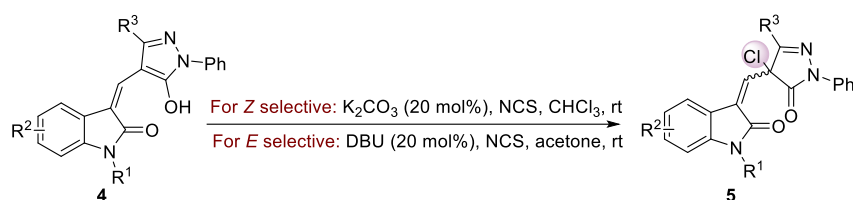
2. Experimental procedures and characterization of products 4 and 5.

General procedure A: Synthesis of Substrates.



Nitroalkenes **1** (1.0 mmol, 1.0 equiv.), TEA (50 mol%), and THF (20 mL) were added to a 100 mL flask. Then pyrazolone **3** (1.5 mmol, 1.5 equiv.) was added and the mixture was stirred at room temperature until completion (indicated by TLC). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel using (PE:EA = 20:1) as eluent to afford **4**.

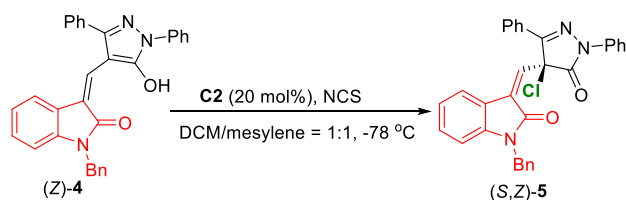
General procedure B: Synthesis of cis-trans isomeric products.



The first part, in order to obtain the *E* configuration products. Nitroalkenes **4** (0.1 mmol, 1.0 equiv.), DBU (20 mol%), and acetone (2 mL) were added to a reaction tube. Then *N*-chlorosuccinimide (NCS, 0.2 mmol, 2.0 equiv.) was added and the mixture was stirred at room temperature until completion (indicated by TLC). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel using (PE:EA = 20:1 to 10:1) as eluent to afford **4** (simultaneously containing *Z/E* configuration products). After determining the *Z/E* ratio through nuclear magnetic resonance (^1H NMR), **5** (only *E* configuration) was purified by recrystallization and used for NMR identification.

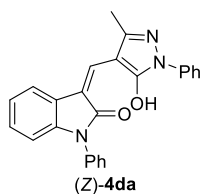
The second part, in order to obtain the *Z* configuration products. Nitroalkenes **4** (0.1 mmol, 1.0 equiv.), K_2CO_3 (20 mol%), and CHCl_3 (2 mL) were added to a reaction tube. Then *N*-chlorosuccinimide (NCS, 0.2 mmol, 2.0 equiv.) was added and the mixture was stirred at room temperature until completion (indicated by TLC). The filtrate was concentrated, and the residue was purified by column chromatography on silica gel using (PE:EA = 20:1 to 10:1) as eluent to afford **5** (simultaneously containing *Z/E* configuration products). After determining the *Z/E* ratio through nuclear magnetic resonance (^1H NMR), **5** (only *Z* configuration) was purified by recrystallization and used for NMR identification.

General procedure C: Synthesis of chiral products.



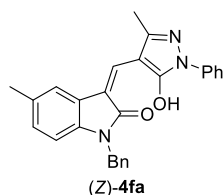
Nitroalkenes (Z)-**4** (0.2 mmol, 1.0 equiv.), **C2** (20 mol%), and DCM/Mes. = 1:1 (4 mL) were added to a reaction tube. The solution was stirred at $-78\text{ }^\circ\text{C}$ for 10 minutes. Then *N*-chlorosuccinimide (NCS, 0.4 mmol, 2.0 equiv.) was added and the mixture was stirred for 24 h. The filtrate was concentrated, and the residue was purified by column chromatography on silica gel using (PE:EA = 20:1 to 10:1) as eluent to afford (*S,Z*)-**5** (simultaneously containing *Z/E* configuration products). After determining the *Z/E* ratio through nuclear magnetic resonance (^1H NMR), (*S,Z*)-**5** was purified by recrystallization and used for NMR identification.

(Z)-3-((5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methylene)-1-phenylindolin-2-one ((Z)-4da)



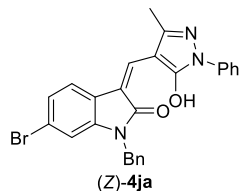
Yellow solid; **m.p.** 173-175 °C; **Yield:** 153 mg, 39%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 15.66 (s, 1H), 7.89-7.84 (m, 2H), 7.64-7.60 (m, 1H), 7.62-7.56 (m, 3H), 7.51-7.46 (m, 3H), 7.41-7.45 (m, 2H), 7.28 (dd, *J* = 9.2, 2.0 Hz, 1H), 7.23-7.17 (m, 2H), 6.94-6.89 (m, 1H), 2.46 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.8, 156.5, 152.1, 139.4, 138.4, 134.4, 130.6, 130.0, 129.2, 129.0, 127.2, 126.9, 126.8, 126.2, 123.6, 122.1, 118.0, 113.0, 110.4, 102.9, 13.5; **HRMS (ESI)** calcd for C₂₅H₂₀N₃O₂⁺ [M+H]⁺: 394.1550, found: 394.1558.

(Z)-1-benzyl-3-((5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methylene)-5-methylindolin-2-one ((Z)-4fa)



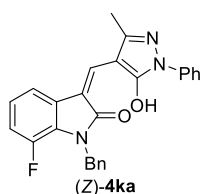
Yellow solid; **m.p.** 190-193 °C; **Yield:** 126 mg, 30%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 16.09 (s, 1H), 7.92-7.85 (m, 2H), 7.47-7.42 (m, 3H), 7.33 (s, 1H), 7.31-7.29 (m, 4H), 7.28-7.24 (m, 2H), 6.96 (dd, *J* = 8.1, 1.6 Hz, 1H), 6.76 (d, *J* = 5.0 Hz, 1H), 5.05 (s, 2H), 2.44 (s, 3H), 2.39 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.9, 156.4, 152.0, 138.5, 136.3, 135.9, 132.8, 129.7, 129.2, 128.1, 127.7, 127.3, 126.8, 126.2, 122.2, 118.6, 113.1, 109.7, 102.6, 44.7, 21.7, 13.5; **HRMS (ESI)** calcd for C₂₇H₂₄N₃O₂⁺ [M+H]⁺: 422.1863, found: 422.1867.

(Z)-1-benzyl-6-bromo-3-((5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ja)



Yellow solid; **m.p.** 193-195 °C; **Yield:** 310 mg, 64%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 15.87 (s, 1H), 7.88-7.84 (m, 2H), 7.48-7.42 (m, 3H), 7.39-7.37 (m, 1H), 7.35-7.32 (m, 2H), 7.31-7.27 (m, 4H), 7.26-7.22 (m, 1H), 7.03-7.01 (m, 1H), 5.05 (s, 2H), 2.42 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.0, 156.6, 152.2, 139.3, 138.3, 135.4, 130.8, 129.4, 129.3, 128.4, 127.7, 127.0, 126.1, 125.2, 122.3, 119.7, 119.1, 113.1, 111.8, 103.0, 44.9, 13.5; **HRMS (ESI)** calcd for C₂₆H₂₁BrN₃O₂⁺ [M+H]⁺: 486.0812, found: 486.0820.

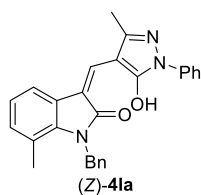
(Z)-1-benzyl-7-fluoro-3-((5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ka)



Yellow solid; **m.p.** 203-205 °C; **Yield:** 216 mg, 51%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 16.07 (s, 1H), 7.90-7.85 (m, 2H), 7.48-7.43 (m, 3H), 7.38 (dd, *J* = 8.0, 1.5 Hz, 2H), 7.34-7.29 (m, 4H), 7.29-7.26 (m, 1H), 7.03-6.98 (m, 1H), 6.95-6.91 (m, 1H), 5.23 (s, 2H), 2.42 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.8, 156.8, 152.2, 148.11 (d, *J*_{C-F} = 244.4 Hz), 138.3, 136.9, 131.5, 129.3 (d, *J*_{C-F} = 3.7 Hz), 129.3, 129.1, 128.2, 128.1, 127.0, 123.6 (d, *J*_{C-F} = 7.5 Hz), 122.3, 114.3, 114.1, 113.7 (d, *J*_{C-F} = 3.8 Hz), 112.2, 103.2, 46.6 (d, *J*_{C-F} = 5 Hz), 13.4; **¹⁹F NMR** (376 MHz, Chloroform-*d*) δ -134.34; **HRMS (ESI)** calcd for C₂₆H₂₁FN₃O₂⁺

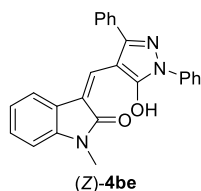
[M+H]⁺: 426.1613, found: 426.1617.

(Z)-1-benzyl-3-((5-hydroxy-3-methyl-1-phenyl-1H-pyrazol-4-yl)methylene)-7-methylindolin-2-one ((Z)-4la)



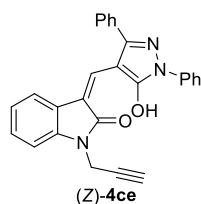
Yellow solid; **m.p.** 188-190 °C; **Yield:** 197 mg, 47%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 16.05 (s, 1H), 7.90-7.86 (m, 2H), 7.51 (s, 1H), 7.46-7.42 (m, 3H), 7.34-7.29 (m, 2H), 7.29-7.24 (m, 2H), 7.15-7.13 (m, 2H), 7.07-7.04 (m, 1H), 6.94-6.92 (m, 1H), 5.37 (s, 2H), 2.44 (s, 3H), 2.35 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.6, 156.6, 152.1, 138.5, 137.5, 136.6, 130.7, 130.0, 129.3, 129.2, 127.7, 126.8, 126.0, 123.2, 122.2, 120.9, 115.9, 112.6, 102.9, 46.1, 19.1, 13.4; **HRMS (ESI)** calcd for C₂₇H₂₄N₃O₂⁺ [M+H]⁺: 422.1863, found: 422.1868.

(Z)-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)-1-methylindolin-2-one ((Z)-4be)



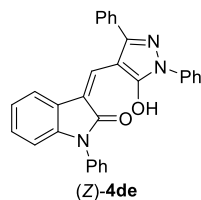
Orange solid; **m.p.** 212-214 °C; **Yield:** 267 mg, 68%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 15.61 (s, 1H), 8.02-7.98 (m, 2H), 7.68-7.64 (m, 2H), 7.59 (s, 1H), 7.55-7.53 (m, 1H), 7.52-7.50 (m, 2H), 7.49-7.46 (m, 2H), 7.34-7.31 (m, 2H), 7.24 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.11-7.08 (m, 1H), 6.96 (dd, *J* = 7.8, 0.9 Hz, 1H), 3.43 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.0, 156.7, 154.7, 139.4, 138.6, 132.8, 131.0, 129.7, 129.3, 129.2, 129.1, 127.1, 127.0, 126.0, 123.3, 122.6, 118.3, 114.6, 109.1, 101.7, 27.2; **HRMS (ESI)** calcd for C₂₅H₂₀N₃O₂⁺ [M+H]⁺: 394.1550, found: 394.1558.

(Z)-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)-1-(prop-2-yn-1-yl)indolin-2-one ((Z)-4ce)



Yellow solid; **m.p.** 196-198 °C; **Yield:** 166 mg, 40%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 15.09 (s, 1H), 7.98 (dd, *J* = 8.6, 1.2 Hz, 2H), 7.66 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.63 (s, 1H), 7.55-7.52 (m, 1H), 7.52-7.49 (m, 2H), 7.49-7.45 (m, 2H), 7.36-7.31 (m, 2H), 7.30-7.27 (m, 1H), 7.19-7.10 (m, 2H), 4.72 (d, *J* = 2.6 Hz, 2H), 2.29 (s, 1H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.4, 156.4, 154.9, 138.5, 137.7, 132.7, 131.7, 129.7, 129.4, 129.3, 129.2, 127.2, 127.1, 126.0, 123.6, 122.7, 118.5, 114.4, 109.9, 101.8, 73.1, 30.3; **HRMS (ESI)** calcd for C₂₇H₂₀N₃O₂⁺ [M+H]⁺: 418.1550, found: 418.1555.

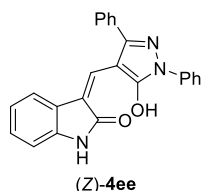
(Z)-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)-1-phenylindolin-2-one ((Z)-4de)



Yellow solid; **m.p.** 231-233 °C; **Yield:** 168 mg, 37%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 15.13 (s, 1H), 7.97 (dd, *J* = 8.6, 1.3 Hz, 2H), 7.73-7.67 (m, 3H), 7.61-7.58 (m, 1H), 7.57-7.56 (m, 1H), 7.55-7.52 (m, 2H), 7.51-7.49 (m, 3H), 7.49-7.42 (m, 3H), 7.41 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.33-7.29 (m, 1H), 7.21-

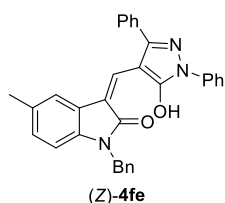
7.17 (m, 1H), 7.15-7.12 (m, 1H), 6.92 (d, $J = 5.0$ Hz, 1H); ^{13}C NMR (126 MHz, Chloroform- d) δ 168.9, 156.6, 154.9, 139.6, 138.5, 134.4, 132.7, 131.9, 130.1, 129.8, 129.5, 129.2, 129.2, 129.0, 127.2, 127.1, 127.0, 126.0, 123.7, 122.5, 118.5, 114.6, 110.4, 102.1; **HRMS (ESI)** calcd for $\text{C}_{30}\text{H}_{22}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 456.1707, found: 456.1713.

(Z)-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ee)



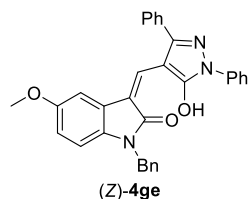
Yellow solid; **m.p.** 150-153 °C; **Yield:** 159 mg, 42%; petroleum ether/EtOAc = 10:1; ^1H NMR (500 MHz, Chloroform- d) δ 15.21 (s, 1H), 8.32 (s, 1H), 7.99-7.96 (m, 2H), 7.68-7.65 (m, 2H), 7.63 (s, 1H), 7.55-7.47 (m, 1H), 7.51 (dd, $J = 4.3, 2.2$ Hz, 2H), 7.50-7.47 (m, 2H), 7.36-7.30 (m, 2H), 7.21-7.16 (m, 1H), 7.08-7.05 (m, 1H), 6.99-6.97 (m, 1H); ^{13}C NMR (126 MHz, Chloroform- d) δ 170.7, 156.6, 154.9, 138.5, 136.5, 132.6, 131.9, 129.7, 129.5, 129.3, 129.2, 127.3, 127.1, 126.8, 123.2, 122.7, 118.7, 114.6, 110.5, 102.0; **HRMS (ESI)** calcd for $\text{C}_{24}\text{H}_{18}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 380.1394, found: 380.1396.

(Z)-1-benzyl-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)-5-methylindolin-2-one ((Z)-4fe)



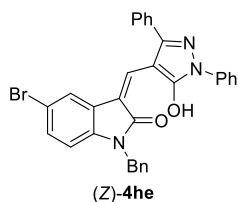
Yellow solid; **m.p.** 219-220 °C; **Yield:** 130 mg, 27%; petroleum ether/EtOAc = 20:1; ^1H NMR (500 MHz, Chloroform- d) δ 15.44 (s, 1H), 8.03-7.95 (m, 2H), 7.73-7.66 (m, 2H), 7.62 (s, 1H), 7.57-7.54 (m, 2H), 7.53-7.52 (m, 1H), 7.51-7.47 (m, 2H), 7.34-7.32 (m, 4H), 7.32-7.26 (m, 2H), 7.17-7.12 (m, 1H), 7.01-6.92 (m, 1H), 6.79-6.77 (m, 1H), 5.11 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (126 MHz, Chloroform- d) δ 169.1, 156.6, 154.7, 138.6, 136.5, 135.9, 133.0, 132.9, 131.1, 129.7, 129.4, 129.3, 129.2, 128.2, 127.8, 127.7, 127.1, 126.1, 122.6, 119.1, 114.8, 109.7, 101.8, 44.9, 21.7; **HRMS (ESI)** calcd for $\text{C}_{32}\text{H}_{26}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 484.2020, found: 484.2026.

(Z)-1-benzyl-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)-5-methoxyindolin-2-one ((Z)-4ge)



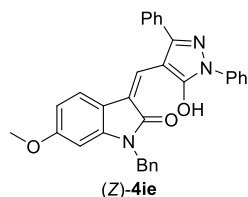
Orange solid; **m.p.** 225-227 °C; **Yield:** 154 mg, 31%; petroleum ether/EtOAc = 20:1; ^1H NMR (500 MHz, Chloroform- d) δ 15.65 (s, 1H), 8.03-7.97 (m, 2H), 7.70-7.66 (m, 2H), 7.60 (s, 1H), 7.55-7.52 (m, 1H), 7.51-7.49 (m, 2H), 7.48-7.47 (m, 2H), 7.46-7.32 (m, 4H), 7.31-7.26 (m, 2H), 6.91-6.89 (m, 1H), 6.79-6.77 (m, 1H), 6.70 (dd, $J = 8.5, 2.4$ Hz, 1H), 5.09 (s, 2H), 3.76 (s, 3H); ^{13}C NMR (126 MHz, Chloroform- d) δ 168.7, 156.5, 154.5, 138.4, 135.6, 132.5, 132.4, 131.3, 129.4, 129.2, 129.0, 128.9, 128.0, 127.5, 127.0, 126.9, 122.3, 114.4, 111.7, 110.2, 104.9, 101.5, 56.0, 44.7; **HRMS (ESI)** calcd for $\text{C}_{32}\text{H}_{26}\text{N}_3\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 500.1969, found: 500.1975.

(Z)-1-benzyl-5-bromo-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4he)



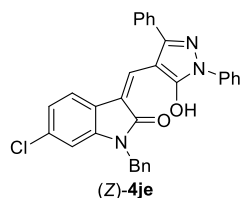
Yellow solid; **m.p.** 224-226 °C; **Yield:** 246 mg, 45%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 15.48 (s, 1H), 8.03-7.93 (m, 2H), 7.68-7.65 (m, 2H), 7.60 (s, 1H), 7.58-7.52 (m, 3H), 7.51-7.47 (m, 2H), 7.43-7.41 (m, 1H), 7.35-7.32 (m, 3H), 7.31-7.29 (m, 3H), 7.26-7.23 (m, 1H), 6.75 (d, *J* = 10 Hz, 1H), 5.11 (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.9, 156.9, 155.1, 138.4, 137.3, 135.4, 132.7, 132.5, 129.7, 129.6, 129.5, 129.4, 129.3, 128.4, 128.0, 127.7, 127.3, 122.7, 121.3, 116.4, 113.0, 111.4, 102.2, 44.9; **HRMS (ESI)** calcd for C₃₁H₂₃BrN₃O₂⁺ [M+H]⁺: 548.0968, found: 548.0973.

(Z)-1-benzyl-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)-6-methoxyindolin-2-one ((Z)-4ie)



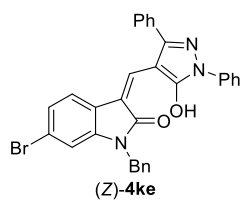
Yellow solid; **m.p.** 208-210 °C; **Yield:** 119 mg, 24%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 14.93 (s, 1H), 8.01-7.95 (m, 2H), 7.71-7.65 (m, 2H), 7.54-7.51 (m, 1H), 7.51-7.48 (m, 3H), 7.48-7.44 (m, 2H), 7.36-7.34 (m, 3H), 7.33-7.30 (m, 2H), 7.26 (s, 1H), 7.25 (s, 1H), 6.60 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.47 (d, *J* = 2.5 Hz, 1H), 5.09 (s, 2H), 3.77 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.9, 159.9, 155.9, 154.5, 140.1, 138.7, 135.8, 132.9, 129.7, 129.3, 129.3, 129.2, 129.1, 128.3, 127.8, 127.1, 122.7, 119.4, 118.9, 115.1, 108.0, 101.5, 97.6, 56.0, 44.9; **HRMS (ESI)** calcd for C₃₂H₂₆N₃O₃⁺ [M+H]⁺: 500.1969, found: 500.1978.

(Z)-1-benzyl-6-chloro-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4je)



Yellow solid; **m.p.** 255-257 °C; **Yield:** 246 mg, 49%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 15.33 (s, 1H), 8.00-7.95 (m, 2H), 7.69-7.64 (m, 2H), 7.60 (s, 1H), 7.55-7.53 (m, 1H), 7.53-7.50 (m, 2H), 7.49-7.46 (m, 2H), 7.38-7.33 (m, 4H), 7.33-7.29 (m, 2H), 7.24-7.22 (m, 1H), 7.03 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.90-6.88 (m, 1H), 5.09 (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.3, 156.6, 155.0, 139.4, 138.5, 135.4, 132.6, 132.5, 132.0, 129.7, 129.5, 129.4, 129.3, 129.2, 128.5, 127.8, 127.3, 124.6, 123.4, 122.7, 119.2, 113.5, 110.4, 102.1, 45.0; **HRMS (ESI)** calcd for C₃₁H₂₃ClN₃O₂⁺ [M+H]⁺: 504.1474, found: 504.1476.

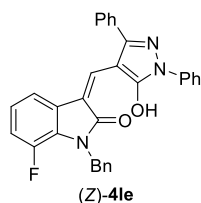
(Z)-1-benzyl-6-bromo-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ke)



Yellow solid; **m.p.** 256-258 °C; **Yield:** 268 mg, 49%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 15.36 (s, 1H), 8.00-7.94 (m, 2H), 7.68-7.64 (m, 2H), 7.61 (s, 1H), 7.55-7.53 (m, 1H), 7.53-7.50 (m, 2H), 7.49-7.46 (m, 2H), 7.38-7.33 (m, 4H), 7.33-7.29 (m, 2H), 7.20-7.16 (m, 2H), 7.04 (dd, *J* = 1.5, 0.7 Hz, 1H), 5.09 (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.2, 156.7, 139.5, 138.5, 135.4, 132.6, 132.1, 129.7, 129.5, 129.4, 129.3, 129.2, 128.5, 127.7, 127.3, 126.2, 125.1, 122.7, 120.1, 119.5, 113.4, 113.1, 102.1, 45.0; **HRMS (ESI)** calcd for C₃₁H₂₃BrN₃O₂⁺

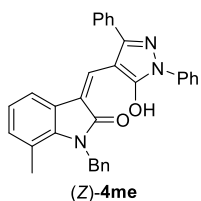
[M+H]⁺: 548.0968, found: 548.0976.

(Z)-1-benzyl-7-fluoro-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4le)



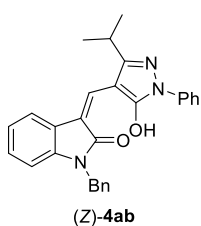
Yellow solid; **m.p.** 218-220 °C; **Yield:** 214 mg, 44%; petroleum ether/EtOAc = 20:1; ¹H NMR (500 MHz, Chloroform-*d*) δ 15.57 (s, 1H), 8.03-7.95 (m, 2H), 7.70-7.64 (m, 3H), 7.57-7.54 (m, 1H), 7.53-7.50 (m, 2H), 7.49-7.46 (m, 2H), 7.43-7.40 (m, 2H), 7.37-7.32 (m, 3H), 7.31-7.28 (m, 1H), 7.12 (dd, *J* = 7.6, 1.0 Hz, 1H), 7.03-6.98 (m, 1H), 6.95-6.91 (m, 1H), 5.29 (s, 2H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 169.0, 156.9, 155.0, 148.1 (d, *J*_{C-F} = 244.4 Hz), 138.5, 136.9, 132.9, 132.5, 129.7, 129.5, 129.4, 129.3, 129.2, 129.1, 128.2, 128.1, 127.3, 125.0, 125.0, 123.8, 123.7, 122.7, 114.6, 114.4, 114.1, 114.0, 113.8, 113.7, 102.3, 46.7; ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -134.34; **HRMS (ESI)** calcd for C₃₁H₂₃FN₃O₂⁺ [M+H]⁺: 488.1769, found: 488.1777.

(Z)-1-benzyl-3-((5-hydroxy-1,3-diphenyl-1H-pyrazol-4-yl)methylene)-7-methylindolin-2-one ((Z)-4me)



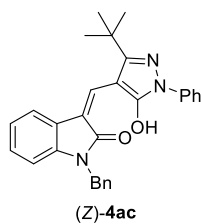
Yellow solid; **m.p.** 200-201 °C; **Yield:** 188 mg, 39%; petroleum ether/EtOAc = 20:1; ¹H NMR (500 MHz, Chloroform-*d*) δ 15.52 (s, 1H), 8.00-7.94 (m, 2H), 7.70-7.68 (m, 3H), 7.55-7.53 (m, 1H), 7.53-7.50 (m, 2H), 7.49-7.46 (m, 2H), 7.36-7.26 (m, 4H), 7.24 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.18-7.15 (m, 2H), 7.00-6.97 (m, 1H), 6.92 (s, 1H), 5.41 (s, 2H), 2.35 (s, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 169.8, 156.8, 154.8, 138.6, 137.4, 136.9, 132.8, 131.3, 131.0, 129.7, 129.4, 129.3, 129.2, 129.1, 127.8, 127.1, 126.7, 126.0, 123.3, 122.6, 120.9, 116.4, 114.2, 102.1, 46.1, 19.1; **HRMS (ESI)** calcd for C₃₂H₂₆N₃O₂⁺ [M+H]⁺: 484.2020, found: 484.2022.

(Z)-1-benzyl-3-((5-hydroxy-3-isopropyl-1-phenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ab)



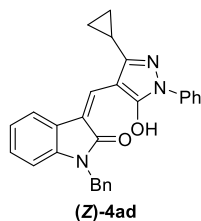
Yellow solid; **m.p.** 186-187 °C; **Yield:** 139 mg, 32%; petroleum ether/EtOAc = 20:1; ¹H NMR (500 MHz, Chloroform-*d*) δ 15.77 (s, 1H), 7.97-7.87 (m, 2H), 7.60 (s, 1H), 7.56-7.51 (m, 1H), 7.48-7.43 (m, 2H), 7.34-7.31 (m, 4H), 7.30-7.26 (m, 2H), 7.19-7.11 (m, 2H), 6.90 (dd, *J* = 7.2, 1.5 Hz, 1H), 5.11 (s, 2H), 3.30-3.17 (m, 1H), 1.43 (s, 3H), 1.42 (s, 3H); ¹³C NMR (126 MHz, Chloroform-*d*) δ 169.1, 160.1, 156.7, 138.7, 138.4, 135.9, 129.9, 129.3, 129.2, 128.2, 127.8, 126.8, 126.7, 126.4, 123.2, 122.4, 117.9, 112.6, 109.9, 101.4, 44.8, 27.4, 22.4; **HRMS (ESI)** calcd for C₂₉H₂₅N₃O₂⁺ [M+H]⁺: 436.2020, found: 436.2024.

(Z)-1-benzyl-3-((3-(tert-butyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ac)



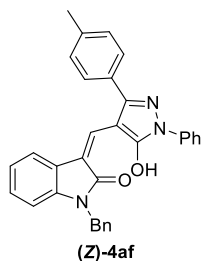
Yellow solid; **m.p.** 184-186 °C; **Yield:** 31 mg, 7%; petroleum ether/EtOAc = 20:1; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 15.24 (s, 1H), 8.08 (s, 1H), 7.97-7.92 (m, 2H), 7.51 (dd, J = 7.0, 1.7 Hz, 1H), 7.47-7.42 (m, 2H), 7.36-7.31 (m, 4H), 7.31-7.26 (m, 2H), 7.20-7.14 (m, 2H), 6.92 (dd, J = 7.1, 1.6 Hz, 1H), 5.12 (s, 2H), 1.54 (s, 9H); $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 169.1, 161.0, 157.3, 138.8, 138.3, 135.9, 131.6, 129.3, 129.2, 128.2, 127.8, 126.7, 126.7, 126.5, 123.3, 122.2, 117.8, 112.2, 110.0, 101.9, 44.9, 34.7, 30.8; **HRMS (ESI)** calcd for $\text{C}_{32}\text{H}_{26}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 450.2176, found: 450.2186.

(Z)-1-benzyl-3-((3-cyclopropyl-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ad)



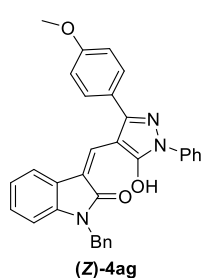
Yellow solid; **m.p.** 148-149 °C; **Yield:** 155 mg, 36%; petroleum ether/EtOAc = 20:1; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 15.96 (s, 1H), 7.89-7.85 (m, 2H), 7.80 (s, 1H), 7.58-7.54 (m, 1H), 7.45-7.41 (m, 2H), 7.35-7.31 (m, 4H), 7.29-7.26 (m, 2H), 7.19-7.11 (m, 2H), 6.90 (dd, J = 7.1, 1.4 Hz, 1H), 5.10 (s, 2H), 2.01-1.96 (m, 1H), 1.09-1.07 (m, 2H), 1.05-1.00 (m, 2H); $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 169.1, 156.5, 156.3, 138.6, 138.4, 135.9, 130.3, 129.3, 129.2, 128.2, 127.8, 126.8, 126.7, 126.3, 123.2, 122.3, 118.0, 112.9, 109.9, 103.2, 44.8, 7.9, 7.1; **HRMS (ESI)** calcd for $\text{C}_{28}\text{H}_{24}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 434.1863, found: 434.1867.

(Z)-1-benzyl-3-((5-hydroxy-1-phenyl-3-(p-tolyl)-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4af)



Yellow solid; **m.p.** 158-161 °C; **Yield:** 183 mg, 38%; petroleum ether/EtOAc = 20:1; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 16.07 (s, 1H), 8.03-7.97 (m, 2H), 7.48 (dd, J = 8.6, 7.4 Hz, 2H), 7.44-7.36 (m, 3H), 7.35-7.33 (m, 4H), 7.33-7.30 (m, 2H), 7.30-7.27 (m, 1H), 7.24 (s, 1H), 7.18 (dd, J = 7.6, 1.1 Hz, 1H), 7.14-7.11 (m, 1H), 7.03-7.00 (m, 1H), 6.88-6.86 (m, 1H), 5.11 (s, 2H), 2.40 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 169.0, 156.2, 155.5, 138.6, 138.5, 138.2, 135.8, 131.8, 131.4, 131.0, 129.5, 129.3, 129.2, 128.2, 127.8, 127.0, 126.9, 126.1, 126.0, 123.2, 122.4, 118.1, 113.8, 109.9, 102.8, 44.8, 20.7; **HRMS (ESI)** calcd for $\text{C}_{32}\text{H}_{26}\text{N}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 484.2020, found: 484.2023.

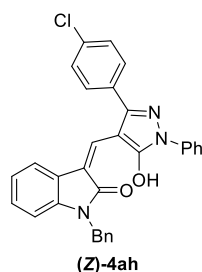
(Z)-1-benzyl-3-((5-hydroxy-3-(4-methoxyphenyl)-1-phenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ag)



Yellow solid; **m.p.** 213-215 °C; **Yield:** 169 mg, 34%; petroleum ether/EtOAc = 20:1; $^1\text{H NMR}$ (500 MHz, Chloroform-*d*) δ 15.49 (s, 1H), 8.00-7.96 (m, 2H), 7.65-7.59 (m, 3H), 7.48 (dd, J = 8.5, 7.4 Hz, 2H), 7.38-7.33 (m, 4H), 7.32 (dd, J = 7.4, 1.4 Hz, 2H), 7.31-7.27 (m, 1H), 7.17-7.15 (m, 1H), 7.10-7.03 (m, 3H), 6.91-6.89 (m, 1H), 5.13 (s, 2H), 3.90 (s, 3H); $^{13}\text{C NMR}$ (126 MHz, Chloroform-*d*) δ 169.2, 160.8, 156.6, 154.7, 138.6, 138.5, 135.9, 131.7, 131.0, 129.3, 129.2,

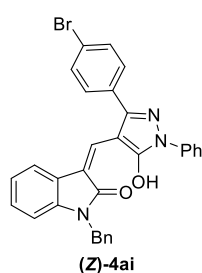
128.2, 127.8, 127.1, 126.9, 126.2, 125.2, 123.3, 122.6, 118.4, 114.6, 114.2, 109.9, 101.9, 55.8, 44.8; **HRMS (ESI)** calcd for $C_{32}H_{26}N_3O_3^+$ $[M+H]^+$: 500.1969, found: 500.1971.

(Z)-1-benzyl-3-((3-(4-chlorophenyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ah)



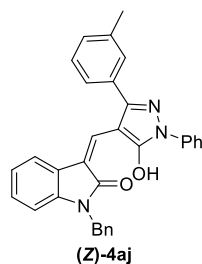
Yellow solid; **m.p.** 200-201 °C; **Yield:** 226 mg, 45%; petroleum ether/EtOAc = 20:1; **1H NMR** (500 MHz, Chloroform-*d*) δ 15.42 (s, 1H), 8.01-7.93 (m, 2H), 7.63-7.60 (m, 2H), 7.56 (s, 1H), 7.51-7.49 (m, 2H), 7.48-7.46 (m, 2H), 7.37-7.34 (m, 3H), 7.34-7.31 (m, 3H), 7.30-7.27 (m, 1H), 7.19-7.16 (m, 1H), 7.11-7.07 (m, 1H), 6.92-6.90 (m, 1H), 5.12 (s, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.2, 156.6, 153.6, 138.7, 138.5, 135.8, 135.6, 131.3, 130.9, 130.7, 129.4, 129.3, 128.3, 127.8, 127.3, 127.2, 125.9, 123.4, 122.7, 118.4, 115.0, 110.0, 101.7, 44.9; **HRMS (ESI)** calcd for $C_{31}H_{23}ClN_3O_2^+$ $[M+H]^+$: 504.1474, found: 504.1479.

(Z)-1-benzyl-3-((3-(4-bromophenyl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ai)



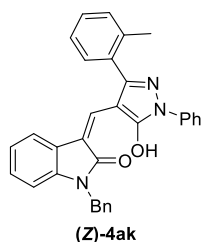
Yellow solid; **m.p.** 210-211 °C; **Yield:** 207 mg, 38%; petroleum ether/EtOAc = 20:1; **1H NMR** (500 MHz, Chloroform-*d*) δ 15.42 (s, 1H), 8.00-7.94 (m, 2H), 7.70-7.62 (m, 2H), 7.56-7.54 (m, 3H), 7.51-7.46 (m, 2H), 7.37-7.36 (m, 1H), 7.35-7.34 (m, 2H), 7.34-7.33 (m, 2H), 7.33-7.31 (m, 1H), 7.30-7.27 (m, 1H), 7.19-7.16 (m, 1H), 7.11-7.08 (m, 1H), 6.92-6.90 (m, 1H), 5.12 (s, 2H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.2, 156.6, 153.5, 138.7, 138.5, 135.8, 132.4, 131.7, 131.2, 130.7, 129.4, 129.3, 128.3, 127.8, 127.3, 127.2, 125.9, 123.8, 123.4, 122.6, 118.5, 115.0, 110.0, 101.7, 44.9; **HRMS (ESI)** calcd for $C_{31}H_{23}BrN_3O_2^+$ $[M+H]^+$: 548.0968, found: 548.0973.

(Z)-1-benzyl-3-((5-hydroxy-1-phenyl-3-(m-tolyl)-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4aj)



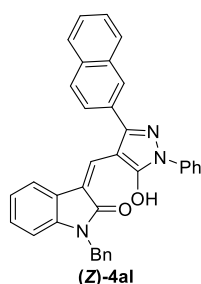
Yellow solid; **m.p.** 185-187 °C; **Yield:** 188 mg, 39%; petroleum ether/EtOAc = 20:1; **1H NMR** (500 MHz, Chloroform-*d*) δ 15.52 (s, 1H), 8.02-7.95 (m, 2H), 7.66 (s, 1H), 7.54 (s, 1H), 7.49 (dd, J = 8.6, 7.3 Hz, 2H), 7.45-7.39 (m, 2H), 7.36-7.34 (m, 3H), 7.34-7.32 (m, 3H), 7.32-7.27 (m, 2H), 7.17-7.15 (m, 1H), 7.09-7.06 (m, 1H), 6.92-6.90 (m, 1H), 5.13 (s, 2H), 2.46 (s, 3H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 169.2, 156.6, 155.0, 139.0, 138.6, 135.9, 132.6, 131.6, 130.2, 130.1, 129.3, 129.3, 128.9, 128.3, 127.8, 127.2, 127.0, 127.0, 126.2, 123.3, 122.7, 118.3, 114.4, 109.9, 101.9, 44.8, 21.9; **HRMS (ESI)** calcd for $C_{32}H_{26}N_3O_2^+$ $[M+H]^+$: 484.2020, found: 484.2024.

(Z)-1-benzyl-3-((5-hydroxy-1-phenyl-3-(o-tolyl)-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ak)



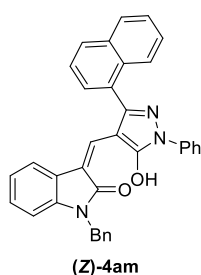
Yellow solid; **m.p.** 167-168 °C; **Yield:** 125 mg, 26%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 16.05 (s, 1H), 8.01-7.96 (m, 2H), 7.47 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.43-7.37 (m, 3H), 7.36-7.33 (m, 4H), 7.32-7.31 (m, 2H), 7.30-7.27 (m, 1H), 7.22 (s, 1H), 7.18 (dd, *J* = 7.5, 1.1 Hz, 1H), 7.13-7.10 (m, 1H), 7.03-7.01 (m, 1H), 6.88-6.86 (m, 1H), 5.10 (s, 2H), 2.39 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.1, 156.2, 155.5, 138.7, 138.5, 138.3, 135.8, 131.8, 131.4, 131.0, 129.5, 129.3, 129.2, 128.2, 127.8, 127.0, 126.9, 126.1, 126.0, 123.3, 122.4, 118.1, 113.8, 109.9, 102.8, 44.8, 20.7; **HRMS (ESI)** calcd for C₃₂H₂₆N₃O₂⁺ [M+H]⁺: 484.2020, found: 484.2026.

(Z)-1-benzyl-3-((5-hydroxy-3-(naphthalen-2-yl)-1-phenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4al)



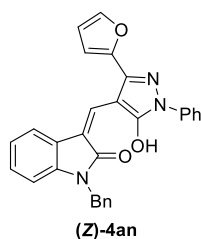
Orange solid; **m.p.** 169-171 °C; **Yield:** 186 mg, 36%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 15.50 (s, 1H), 8.12 (s, 1H), 8.05-7.98 (m, 3H), 7.96-7.91 (m, 2H), 7.84 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.74 (s, 1H), 7.60-7.53 (m, 2H), 7.53-7.48 (m, 2H), 7.38-7.32 (m, 5H), 7.31-7.27 (m, 2H), 7.17-7.14 (m, 1H), 7.05-7.03 (m, 1H), 6.92-6.90 (m, 1H), 5.14 (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.2, 156.7, 154.7, 138.7, 138.6, 135.8, 133.9, 133.7, 131.4, 130.2, 129.4, 129.3, 128.9, 128.8, 128.3, 128.2, 127.8, 127.3, 127.2, 127.1, 127.0, 126.9, 126.1, 123.4, 122.7, 118.4, 114.7, 110.0, 102.1, 44.9; **HRMS (ESI)** calcd for C₃₅H₂₆N₃O₂⁺ [M+H]⁺: 520.2020, found: 520.2021.

(Z)-1-benzyl-3-((5-hydroxy-3-(naphthalen-1-yl)-1-phenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4am)



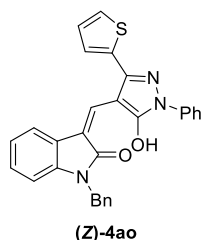
Orange solid; **m.p.** 183-184 °C; **Yield:** 159 mg, 31%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 16.06 (s, 1H), 8.18 (dd, *J* = 8.5, 1.4 Hz, 1H), 8.06-8.03 (m, 2H), 8.01 (dd, *J* = 7.7, 1.9 Hz, 1H), 7.96 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.65-7.59 (m, 2H), 7.56-7.48 (m, 4H), 7.36-7.33 (m, 4H), 7.32-7.29 (m, 1H), 7.29-7.26 (m, 2H), 7.09-7.06 (m, 1H), 6.93-6.88 (m, 2H), 6.85-6.83 (m, 1H), 5.10 (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.1, 156.4, 154.4, 138.7, 138.5, 135.8, 134.3, 132.9, 131.4, 130.0, 129.9, 129.5, 129.3, 128.7, 128.3, 127.8, 127.2, 127.1, 126.9, 126.6, 126.5, 126.0, 125.6, 123.2, 122.5, 118.2, 114.1, 109.8, 103.6, 44.8; **HRMS (ESI)** calcd for C₃₅H₂₆N₃O₂⁺ [M+H]⁺: 520.2020, found: 520.2023.

(Z)-1-benzyl-3-((3-(furan-2-yl)-5-hydroxy-1-phenyl-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4an)



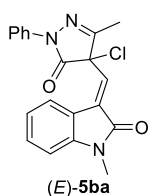
Orange solid; **m.p.** 197-198 °C; **Yield:** 58 mg, 13%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 15.61 (s, 1H), 8.13 (s, 1H), 7.98-7.93 (m, 2H), 7.65 (s, 1H), 7.54-7.52 (m, 1H), 7.50-7.47 (m, 2H), 7.35-7.31 (m, 5H), 7.31-7.26 (m, 1H), 7.20-7.12 (m, 2H), 6.92-6.86 (m, 2H), 6.60 (dd, *J* = 3.4, 1.8 Hz, 1H), 5.11 (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.9, 156.1, 147.9, 144.6, 143.5, 138.4, 138.1, 135.5, 130.5, 129.1, 129.0, 128.0, 127.5, 127.1, 126.9, 125.9, 123.2, 122.5, 118.3, 114.8, 111.7, 110.1, 109.7, 101.2, 44.6; **HRMS (ESI)** calcd for C₂₉H₂₂N₃O₃⁺ [M+H]⁺: 460.1656, found: 460.1660.

(Z)-1-benzyl-3-((5-hydroxy-1-phenyl-3-(thiophen-2-yl)-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-4ao)



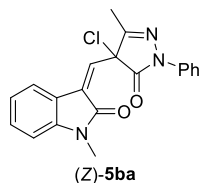
Orange solid; **m.p.** 217-218 °C; **Yield:** 71 mg, 15%; petroleum ether/EtOAc = 20:1; **¹H NMR** (500 MHz, Chloroform-*d*) δ 15.52 (s, 1H), 8.01-7.95 (m, 2H), 7.86 (s, 1H), 7.51-7.48 (m, 2H), 7.48-7.45 (m, 2H), 7.37 (dd, *J* = 3.6, 1.2 Hz, 1H), 7.36-7.33 (m, 4H), 7.32-7.28 (m, 2H), 7.22 (dd, *J* = 5.1, 3.6 Hz, 1H), 7.20-7.16 (m, 1H), 7.13-7.10 (m, 1H), 6.92-6.90 (m, 1H), 5.12 (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 169.1, 156.6, 148.5, 138.7, 138.4, 135.8, 134.6, 130.6, 129.4, 129.3, 128.3, 128.1, 128.0, 127.8, 127.5, 127.3, 127.2, 126.0, 123.4, 122.6, 118.5, 115.0, 110.0, 101.8, 44.9; **HRMS (ESI)** calcd for C₂₉H₂₂N₃O₂S⁺ [M+H]⁺: 476.1427, found: 476.1430.

(E)-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-1-methylindolin-2-one ((E)-5ba)



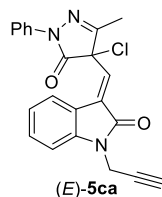
Yellow solid; **m.p.** 115-116 °C; **Yield:** 58 mg, 79%; *Z/E* = 12:88; **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.90-7.84 (m, 2H), 7.79 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.47-7.40 (m, 2H), 7.33-7.31 (m, 1H), 7.26-7.23 (m, 1H), 6.99-6.95 (m, 1H), 6.89 (s, 1H), 6.80-6.78 (m, 1H), 3.23 (s, 3H), 2.30 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 167.5, 167.3, 158.1, 145.8, 137.5, 134.3, 132.1, 129.5, 127.5, 126.9, 126.4, 123.0, 119.5, 119.3, 108.8, 64.0, 26.8, 13.9; **HRMS (ESI)** calcd for C₂₀H₁₇ClN₃O₂ [M+H]⁺: 366.1004, found: 366.0999.

(Z)-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-1-methylindolin-2-one ((Z)-5ba)



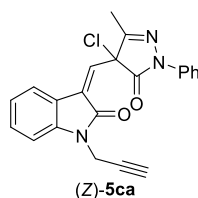
Yellow solid; **m.p.** 173-175 °C; **Yield:** 56 mg, 77%; *Z/E* = 89:11; **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.95-7.91 (m, 2H), 7.49-7.47 (m, 1H), 7.46-7.41 (m, 2H), 7.36-7.33 (m, 1H), 7.24-7.20 (m, 1H), 7.09-7.05 (m, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.74 (s, 1H), 3.10 (s, 3H), 2.16 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.4, 165.0, 153.4, 144.7, 138.2, 132.4, 131.6, 129.2, 128.7, 125.7, 122.9, 121.3, 119.9, 109.0, 65.8, 26.5, 14.0; **HRMS (ESI)** calcd for C₂₀H₁₆ClN₃O₂Na⁺ [M+Na]⁺: 388.0824, found: 388.0831.

(E)-3-((4-chloro-1-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-1-(prop-2-yn-1-yl)indolin-2-one ((E)-5ca)



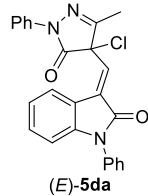
Yellow solid; **m.p.** 117-118 °C; **Yield:** 61 mg, 79%; **Z/E** = 11:89; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.92-7.87 (m, 2H), 7.87-7.85 (m, 1H), 7.46 (dd, J = 8.7, 7.3 Hz, 2H), 7.39-7.36 (m, 1H), 7.30-7.27 (m, 1H), 7.06-7.00 (m, 2H), 6.93 (s, 1H), 4.55 (d, J = 2.6 Hz, 2H), 2.33 (s, 3H), 2.27 (t, J = 2.5 Hz, 1H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 167.4, 166.4, 158.0, 143.9, 137.5, 133.9, 132.1, 129.5, 127.7, 127.5, 126.4, 123.4, 119.5, 119.3, 109.8, 73.0, 63.9, 29.8, 13.9; **HRMS (ESI)** calcd for $\text{C}_{22}\text{H}_{16}\text{ClN}_3\text{O}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 412.0824, found: 412.0836.

(Z)-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-1-(prop-2-yn-1-yl)indolin-2-one ((Z)-5ca)



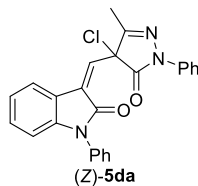
Yellow solid; **m.p.** 104-105 °C; **Yield:** 46 mg, 59%; **Z/E** = 84:16; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.95-7.89 (m, 2H), 7.51 (dd, J = 7.7, 1.2 Hz, 1H), 7.47-7.41 (m, 2H), 7.39-7.37 (m, 1H), 7.25-7.20 (m, 1H), 7.13-7.09 (m, 1H), 7.05-7.03 (m, 1H), 6.77 (s, 1H), 4.51 (dd, J = 17.8, 2.6 Hz, 1H), 4.29 (dd, J = 17.8, 2.5 Hz, 1H), 2.21 (t, J = 2.5 Hz, 1H), 2.17 (s, 3H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 168.3, 163.9, 153.4, 142.8, 138.1, 132.0, 131.6, 129.5, 129.3, 125.8, 123.3, 121.4, 121.3, 120.0, 110.2, 73.2, 65.7, 29.6, 14.0; **HRMS (ESI)** calcd for $\text{C}_{22}\text{H}_{16}\text{ClN}_3\text{O}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 412.0824, found: 412.0836.

(E)-3-((4-chloro-1-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-1-phenylindolin-2-one ((E)-5da)



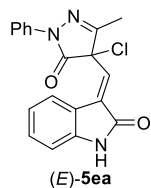
Yellow solid; **m.p.** 83-85 °C; **Yield:** 45 mg, 53%; **Z/E** = 12:88; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.93-7.89 (m, 3H), 7.54 (dd, J = 8.5, 7.0 Hz, 2H), 7.48-7.43 (m, 3H), 7.41-7.38 (m, 2H), 7.27 (dd, J = 7.6, 1.3 Hz, 1H), 7.26-7.23 (m, 1H), 7.03-6.99 (m, 1H), 6.98 (s, 1H), 6.78-6.76 (m, 1H), 2.36 (s, 3H). ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 167.5, 166.7, 158.1, 145.8, 137.5, 134.4, 134.3, 132.0, 130.1, 129.5, 128.8, 127.8, 127.4, 127.1, 126.4, 123.5, 119.5, 119.2, 110.1, 64.0, 14.0; **HRMS (ESI)** calcd for $\text{C}_{25}\text{H}_{19}\text{ClN}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 428.1161, found: 428.1171.

(Z)-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-1-phenylindolin-2-one ((Z)-5da)



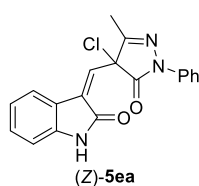
Yellow solid; **m.p.** 145-147 °C; **Yield:** 24 mg, 28%; **Z/E** = 67:33; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.88-7.86 (m, 2H), 7.57-7.55 (m, 1H), 7.47-7.42 (m, 3H), 7.40-7.36 (m, 2H), 7.36-7.32 (m, 3H), 7.21-7.16 (m, 1H), 7.13-7.10 (m, 1H), 6.85-6.80 (m, 2H), 2.18 (s, 3H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 168.1, 164.2, 153.3, 144.6, 138.2, 134.0, 132.3, 131.5, 129.9, 129.1, 128.5, 126.7, 125.7, 123.4, 121.5, 121.3, 120.0, 119.5, 110.4, 66.0, 14.0; **HRMS (ESI)** calcd for $\text{C}_{25}\text{H}_{18}\text{ClN}_3\text{O}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 450.0981, found: 450.0987.

(E)-3-((4-chloro-1-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((E)-5ea)



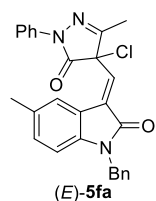
Yellow solid; **m.p.** 175-177 °C; **Yield:** 55 mg, 79%; **Z/E** = 33:67; **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.28 (s, 1H), 7.97-7.89 (m, 2H), 7.46-7.40 (m, 3H), 7.24-7.20 (m, 1H), 7.18 (td, *J* = 7.7, 1.2 Hz, 1H), 7.04-7.00 (m, 1H), 6.73 (s, 1H), 6.42 (s, 1H), 2.16 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.3, 167.3, 153.2, 142.0, 138.3, 132.9, 131.7, 129.4, 129.3, 125.7, 122.8, 121.7, 121.4, 119.5, 111.1, 65.8, 13.9; **HRMS (ESI)** calcd for C₁₉H₁₄ClN₃O₂Na⁺ [*M*+Na]⁺: 374.0668, found: 374.0678.

(Z)-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-5ea)



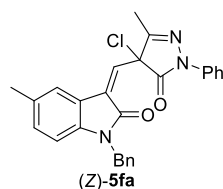
Yellow solid; **m.p.** 125-126 °C; **Yield:** 22 mg, 32%; **Z/E** = 81:19; **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.96 (s, 1H), 7.90-7.86 (m, 2H), 7.80-7.78 (m, 1H), 7.44 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.28-7.26 (m, 1H), 7.24 (dd, *J* = 3.8, 1.1 Hz, 1H), 6.97-6.94 (m, 1H), 6.85 (s, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 2.32 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.0, 167.0, 157.6, 142.5, 137.1, 134.0, 131.8, 129.1, 129.0, 127.4, 126.8, 126.0, 122.7, 119.1, 110.2, 63.5, 13.6; **HRMS (ESI)** calcd for C₁₉H₁₄ClN₃O₂Na⁺ [*M*+Na]⁺: 374.0668, found: 374.0671.

(E)-1-benzyl-3-((4-chloro-1-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-5-methylindolin-2-one ((E)-5fa)



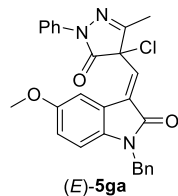
Yellow solid; **m.p.** 83-84 °C; **Yield:** 70 mg, 77%; **Z/E** = 12:88; **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.96-7.89 (m, 2H), 7.48-7.41 (m, 2H), 7.32-7.31 (m, 1H), 7.30-7.29 (m, 2H), 7.28-7.26 (m, 3H), 7.23-7.18 (m, 1H), 6.98-6.96 (m, 2H), 6.56 (d, *J* = 10.0 Hz, 1H), 4.91 (q, *J* = 15.8 Hz, 2H), 2.31 (s, 3H), 2.01 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 167.5, 167.3, 157.7, 142.6, 137.5, 135.8, 133.6, 132.5, 132.3, 129.5, 129.2, 128.1, 127.8, 127.7, 127.6, 126.4, 119.4, 119.3, 109.6, 64.3, 44.4, 21.2, 14.1; **HRMS (ESI)** calcd for C₂₇H₂₂ClN₃O₂Na⁺ [*M*+Na]⁺: 478.1294, found: 478.1305.

(Z)-1-benzyl-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-5-methylindolin-2-one ((Z)-5fa)



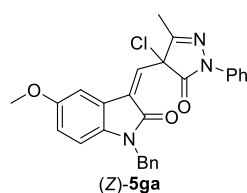
Yellow solid; **m.p.** 155-156 °C; **Yield:** 61 mg, 67%; **Z/E** = 86:14; **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.91 (dd, *J* = 8.7, 1.3 Hz, 2H), 7.42 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.34-7.30 (m, 1H), 7.27 (dd, *J* = 7.8, 6.1 Hz, 2H), 7.25-7.19 (m, 2H), 7.18-7.15 (m, 2H), 7.01-6.99 (m, 1H), 6.75 (s, 1H), 6.51 (d, *J* = 8.0 Hz, 1H), 4.79 (q, *J* = 15.8 Hz, 2H), 2.31 (s, 3H), 2.19 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.4, 165.1, 153.5, 141.6, 138.2, 135.8, 132.6, 132.5, 131.9, 129.2, 129.1, 128.7, 128.0, 127.6, 125.8, 122.0, 121.4, 120.1, 109.9, 65.9, 44.0, 21.4, 14.0; **HRMS (ESI)** calcd for C₂₇H₂₂ClN₃O₂Na⁺ [*M*+Na]⁺: 478.1294, found: 478.1301.

(E)-1-benzyl-3-((4-chloro-1-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-5-methoxyindolin-2-one ((E)-5ga)



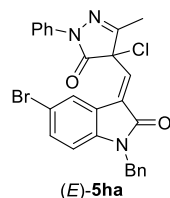
Yellow solid; **m.p.** 83-85 °C; **Yield:** 31 mg, 33%; *Z/E* = 6:94; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.92-7.90 (m, 2H), 7.46-7.40 (m, 3H), 7.34-7.31 (m, 1H), 7.30-7.28 (m, 3H), 7.27-7.26 (m, 1H), 7.25-7.22 (m, 1H), 6.96 (s, 1H), 6.76 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.58-6.56 (m, 1H), 4.97-4.84 (m, 2H), 3.54 (s, 3H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.4, 167.3, 158.2, 156.1, 138.7, 137.6, 135.8, 134.6, 129.4, 129.2, 128.1, 127.7, 127.4, 126.4, 120.0, 119.3, 118.2, 113.3, 110.3, 64.0, 56.1, 44.5, 14.0; **HRMS (ESI)** calcd for $\text{C}_{27}\text{H}_{23}\text{ClN}_3\text{O}_3^+$ [$\text{M}+\text{H}$] $^+$: 472.1423, found: 472.1426.

(Z)-1-benzyl-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-5-methoxyindolin-2-one ((Z)-5ga)



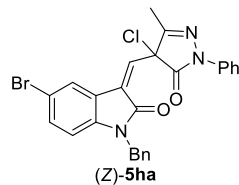
Yellow solid; **m.p.** 173-175 °C; **Yield:** 45 mg, 48%; *Z/E* = 81:19; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.97-7.88 (m, 2H), 7.42 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.32-7.26 (m, 2H), 7.25-7.19 (m, 2H), 7.18-7.14 (m, 2H), 7.06-7.05 (m, 1H), 6.77 (s, 1H), 6.74 (s, 1H), 6.50 (d, *J* = 8.5 Hz, 1H), 4.88-4.67 (m, 2H), 3.77 (s, 3H), 2.20 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.4, 165.0, 156.2, 153.4, 138.2, 137.6, 135.7, 132.8, 129.2, 129.1, 128.0, 127.7, 127.6, 125.8, 122.2, 120.1, 117.0, 110.7, 107.6, 65.9, 56.3, 44.0, 14.0; **HRMS (ESI)** calcd for $\text{C}_{27}\text{H}_{22}\text{ClN}_3\text{O}_2\text{Na}^+$ [$\text{M}+\text{Na}$] $^+$: 494.1243, found: 494.1251.

(E)-1-benzyl-5-bromo-3-((4-chloro-1-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((E)-5ha)



Yellow solid; **m.p.** 173-176 °C; **Yield:** 53 mg, 51%; *Z/E* = 10:90; ^1H NMR (500 MHz, Chloroform-*d*) δ 8.02-8.00 (m, 1H), 7.93-7.88 (m, 2H), 7.44 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.34-7.32 (m, 2H), 7.31-7.30 (m, 2H), 7.29-7.27 (m, 2H), 7.24 (s, 1H), 7.00 (s, 1H), 6.56 (d, *J* = 8.3 Hz, 1H), 4.97-4.85 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 168.1, 164.5, 153.1, 142.6, 138.1, 135.1, 134.0, 131.3, 130.9, 129.3, 128.3, 127.6, 125.9, 124.4, 123.1, 120.1, 115.7, 111.6, 58.9, 44.1, 14.0; **HRMS (ESI)** calcd for $\text{C}_{26}\text{H}_{20}\text{BrClN}_3\text{O}_2^+$ [$\text{M}+\text{H}$] $^+$: 520.0422, found: 520.0441.

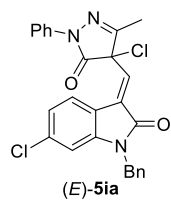
(Z)-1-benzyl-5-bromo-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-5ha)



Yellow solid; **m.p.** 113-114 °C; **Yield:** 81 mg, 78%; *Z/E* = 81:19; ^1H NMR (500 MHz, Chloroform-*d*) δ 7.92-7.88 (m, 2H), 7.62-7.61 (m, 1H), 7.42 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.32 (dd, *J* = 8.4, 1.9 Hz, 1H), 7.28-7.27 (m, 2H), 7.24-7.20 (m, 2H), 7.16-7.13 (m, 2H), 6.80 (s, 1H), 6.50 (d, *J* = 8.4 Hz, 1H), 4.86-4.72 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 166.9, 157.9, 143.8, 135.3, 134.6, 130.7, 129.5, 129.3, 128.9, 128.4, 127.6, 126.6, 119.7, 115.8, 111.1, 63.8, 53.8, 44.5, 14.0;

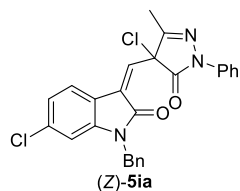
HRMS (ESI) calcd for $C_{26}H_{19}BrClN_3O_2Na^+$ $[M+Na]^+$: 542.0242, found: 542.0257.

(E)-1-benzyl-6-chloro-3-((4-chloro-1-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((E)-5ia)



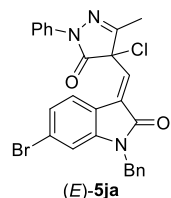
Orange solid; **m.p.** 97-99 °C; **Yield:** 64 mg, 67%; $Z/E < 5:95$; 1H NMR (500 MHz, Chloroform- d) δ 7.97-7.96 (m, 1H), 7.87-7.85 (m, 2H), 7.43 (dd, J = 8.7, 7.4 Hz, 2H), 7.36-7.33 (m, 2H), 7.31-7.26 (m, 3H), 7.26-7.21 (m, 1H), 6.96-6.91 (m, 2H), 6.69 (d, J = 1.9 Hz, 1H), 4.97-4.85 (m, 2H), 2.35 (s, 3H); ^{13}C NMR (126 MHz, Chloroform- d) δ 167.6, 167.3, 158.2, 138.2, 137.4, 135.2, 133.7, 129.5, 129.4, 129.0, 128.4, 127.6, 127.0, 126.5, 123.1, 120.2, 119.5, 117.9, 110.3, 63.7, 44.5, 13.9; **HRMS (ESI)** calcd for $C_{26}H_{20}Cl_2N_3O_2^+$ $[M+H]^+$: 476.0927, found: 476.0941.

(Z)-1-benzyl-6-chloro-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-5ia)



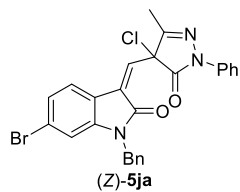
Yellow solid; **m.p.** 173-175 °C; **Yield:** 60 mg, 62%; $Z/E > 95:5$; 1H NMR (500 MHz, Chloroform- d) δ 7.94-7.88 (m, 2H), 7.46-7.38 (m, 3H), 7.35-7.27 (m, 3H), 7.25-7.20 (m, 1H), 7.19-7.14 (m, 2H), 7.01 (dd, J = 8.1, 1.8 Hz, 1H), 6.78 (s, 1H), 6.63 (d, J = 1.8 Hz, 1H), 4.85-4.70 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (126 MHz, Chloroform- d) δ 168.2, 165.0, 153.2, 144.7, 138.1, 137.3, 135.1, 131.3, 129.9, 129.3, 129.2, 128.3, 127.6, 125.9, 123.0, 122.2, 120.1, 119.8, 110.7, 65.7, 44.1, 14.0; **HRMS (ESI)** calcd for $C_{26}H_{19}Cl_2N_3O_2Na^+$ $[M+Na]^+$: 498.0747, found: 498.0758.

(E)-1-benzyl-6-bromo-3-((4-chloro-1-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((E)-5ja)



Yellow solid; **m.p.** 181-182 °C; **Yield:** 74 mg, 71%; Z/E = 11:89; 1H NMR (500 MHz, Chloroform- d) δ 7.91-7.84 (m, 3H), 7.43 (dd, J = 8.7, 7.4 Hz, 2H), 7.37-7.32 (m, 2H), 7.31-7.27 (m, 3H), 7.26-7.23 (m, 1H), 7.11 (dd, J = 8.3, 1.8 Hz, 1H), 6.95 (s, 1H), 6.85 (d, J = 1.8 Hz, 1H), 5.00-4.78 (m, 2H), 2.34 (s, 3H); ^{13}C NMR (126 MHz, Chloroform- d) δ 167.4, 167.3, 158.2, 146.0, 137.4, 135.2, 133.8, 129.5, 129.4, 129.1, 128.4, 127.6, 127.3, 126.5, 126.4, 126.1, 119.4, 118.3, 113.1, 63.8, 44.5, 13.9; **HRMS (ESI)** calcd for $C_{26}H_{20}BrClN_3O_2^+$ $[M+H]^+$: 520.0422, found: 520.0438.

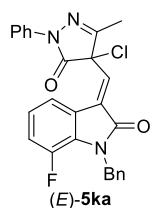
(Z)-1-benzyl-6-bromo-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((Z)-5ja)



Yellow solid; **m.p.** 142-144 °C; **Yield:** 62 mg, 60%; Z/E = 50:50; 1H NMR (500 MHz, Chloroform- d) δ 7.91-7.87 (m, 2H), 7.42 (dd, J = 8.6, 7.4 Hz, 2H), 7.34 (m, 1H), 7.32-7.27 (m, 3H), 7.24-7.20 (m, 1H), 7.19-6.15 (m, 3H), 6.80 (s, 1H), 6.79 (d, J = 1.6 Hz, 1H), 4.84-4.72 (m, 2H), 2.19 (s, 3H); ^{13}C NMR (126 MHz, Chloroform- d) δ 168.1, 164.8, 153.1, 144.8, 138.1, 135.1, 131.4, 130.0, 129.3, 129.2, 128.3, 127.6, 125.9, 125.3, 122.4, 120.3, 120.1, 113.4, 65.8, 44.1, 14.0; **HRMS (ESI)** calcd for

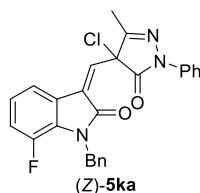
$\text{C}_{26}\text{H}_{19}\text{BrClN}_3\text{O}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 542.0242, found: 542.0249.

(E)-1-benzyl-3-((4-chloro-1-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-7-fluoroindolin-2-one ((E)-5ka)



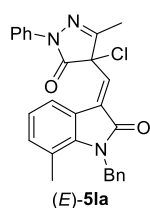
Yellow solid; **m.p.** 135-136 °C; **Yield:** 73 mg, 80%; **Z/E** = 19:81; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.89-7.84 (m, 2H), 7.71 (dd, J = 7.7, 0.9 Hz, 1H), 7.43 (dd, J = 8.7, 7.4 Hz, 2H), 7.36-7.29 (m, 4H), 7.28-7.26 (m, 1H), 7.26-7.23 (m, 1H), 7.01-7.00 (m, 1H), 6.98 (s, 1H), 6.91-6.85 (m, 1H), 5.09 (s, 2H), 2.33 (s, 3H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 167.3, 158.0, 147.9 (d, $J_{\text{C-F}}$ = 244.4 Hz), 137.4, 137.0, 133.8 (d, $J_{\text{C-F}}$ = 2.5 Hz), 131.6, 129.5, 129.0, 128.6, 128.1, 127.9, 126.5, 123.8 (d, $J_{\text{C-F}}$ = 2.5 Hz), 123.6 (d, $J_{\text{C-F}}$ = 7.5 Hz), 122.2 (d, $J_{\text{C-F}}$ = 2.5 Hz), 120.2, 120.1, 119.5, 63.7, 46.2, 46.1, 13.9; ^{19}F **NMR** (377 MHz, Chloroform-*d*) δ -133.38; **HRMS (ESI)** calcd for $\text{C}_{26}\text{H}_{19}\text{ClFN}_3\text{O}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 482.1043, found: 482.1055.

(Z)-1-benzyl-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-7-fluoroindolin-2-one ((Z)-5ka)



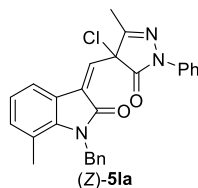
Yellow solid; **m.p.** 162-163 °C; **Yield:** 55 mg, 60%; **Z/E** = 67:33; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.91-7.89 (m, 2H), 7.43 (dd, J = 8.7, 7.4 Hz, 2H), 7.30-7.26 (m, 2H), 7.26-7.24 (m, 2H), 7.23-7.19 (m, 3H), 7.06-6.93 (m, 2H), 6.81 (s, 1H), 4.99-4.88 (m, 2H), 2.18 (s, 3H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 168.1, 164.8, 153.1, 147.9 (d, $J_{\text{C-F}}$ = 245.7 Hz), 138.1, 136.9, 131.9 (d, $J_{\text{C-F}}$ = 3.7 Hz), 130.8, 130.3 (d, $J_{\text{C-F}}$ = 8.8 Hz), 129.2, 128.9, 128.0, 127.8, 126.0, 124.1 (d, $J_{\text{C-F}}$ = 3.7 Hz), 123.5 (d, $J_{\text{C-F}}$ = 6.3 Hz), 120.2, 119.5, 119.3, 117.4 (d, $J_{\text{C-F}}$ = 3.7 Hz), 65.7, 45.6, 45.5, 14.0; ^{19}F **NMR** (377 MHz, Chloroform-*d*) δ -133.38; **HRMS (ESI)** calcd for $\text{C}_{26}\text{H}_{19}\text{ClFN}_3\text{O}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 482.1043, found: 482.1055.

(E)-1-benzyl-3-((4-chloro-1-methyl-5-oxo-3-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-7-methylindolin-2-one ((E)-5la)



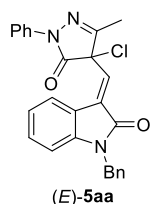
Orange solid; **m.p.** 174-175 °C; **Yield:** 75 mg, 84%; **Z/E** = 14:86; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.90-7.88 (m, 2H), 7.67-7.61 (m, 1H), 7.44 (dd, J = 8.7, 7.4 Hz, 2H), 7.32 (dd, J = 8.1, 6.7 Hz, 2H), 7.28-7.26 (m, 1H), 7.25-7.23 (m, 1H), 7.18-7.13 (m, 2H), 6.98 (d, J = 7.7 Hz, 1H), 6.96 (s, 1H), 6.84 (m, 1H), 5.28-5.17 (m, 2H), 2.33 (s, 3H), 2.24 (s, 3H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 168.6, 167.5, 158.0, 143.0, 137.6, 137.5, 136.2, 133.7, 129.5, 129.3, 127.7, 127.1, 126.4, 126.0, 125.5, 123.1, 120.5, 120.2, 119.6, 64.1, 45.9, 19.3, 14.0; **HRMS (ESI)** calcd for $\text{C}_{27}\text{H}_{22}\text{ClN}_3\text{O}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 478.1294, found: 478.1315.

(Z)-1-benzyl-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-7-methylindolin-2-one ((Z)-5la)



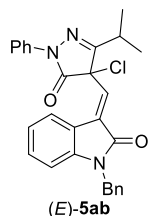
Yellow solid; **m.p.** 186-187 °C; **Yield:** 57 mg, 63%; *Z/E* = 86:14; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.89-7.85 (m, 2H), 7.41-7.35 (m, 3H), 7.29-7.26 (m, 1H), 7.25 (s, 1H), 7.24-7.17 (m, 2H), 7.04-7.01 (m, 2H), 7.00-6.95 (m, 2H), 6.78 (s, 1H), 5.14-4.99 (m, 2H), 2.18 (d, *J* = 1.1 Hz, 6H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 168.3, 166.0, 153.4, 141.9, 138.2, 137.6, 135.4, 132.2, 129.3, 129.2, 128.7, 127.6, 126.0, 125.7, 123.0, 122.0, 121.0, 120.1, 119.3, 66.0, 45.1, 18.9, 14.0; **HRMS (ESI)** calcd for $\text{C}_{27}\text{H}_{22}\text{ClN}_3\text{O}_2\text{Na}^+$ [*M*+*Na*] $^+$: 478.1294, found: 478.1303.

(E)-1-benzyl-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((E)-5aa)



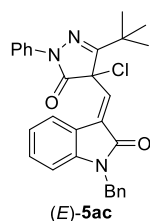
Yellow solid; **m.p.** 121-123 °C; **Yield:** 89 mg, 96%; *Z/E* < 5:95; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.91-7.86 (m, 2H), 7.84 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.46-7.41 (m, 2H), 7.34-7.29 (m, 4H), 7.28-7.26 (m, 1H), 7.26-7.21 (m, 1H), 7.20-7.19 (m, 1H), 6.96-6.95 (m, 1H), 6.94-6.90 (m, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 4.98-4.89 (m, 2H), 2.34 (s, 3H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 167.0, 166.9, 157.6, 144.4, 137.0, 135.2, 133.7, 131.5, 129.0, 128.7, 127.7, 127.2, 127.1, 126.7, 125.9, 122.6, 119.0, 118.9, 109.3, 63.5, 43.9, 13.5; **HRMS (ESI)** calcd for $\text{C}_{26}\text{H}_{21}\text{ClN}_3\text{O}_2$ [*M*+*H*] $^+$: 464.1137, found: 464.1134.

(E)-1-benzyl-3-((4-chloro-3-isopropyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((E)-5ab)



Yellow solid; **m.p.** 161-162 °C; **Yield:** 87 mg, 93%; *Z/E* = 8:92; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.94-7.89 (m, 2H), 7.52-7.42 (m, 3H), 7.36-7.33 (m, 1H), 7.33-7.31 (m, 2H), 7.31-7.26 (m, 3H), 7.21-7.17 (m, 1H), 7.09 (s, 1H), 6.89-6.86 (m, 1H), 6.70 (d, *J* = 10.0 Hz, 1H), 5.00 (d, *J* = 15.7 Hz, 1H), 4.90 (d, *J* = 15.7 Hz, 1H), 3.02-2.94 (m, 1H), 1.47 (d, *J* = 6.8 Hz, 3H), 1.32 (d, *J* = 6.9 Hz, 3H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 167.4, 165.0, 144.9, 137.6, 135.7, 133.2, 131.8, 129.5, 129.2, 128.8, 128.2, 127.7, 127.0, 126.4, 123.1, 119.5, 119.4, 109.8, 64.4, 44.4, 29.7, 21.7, 21.4; **HRMS (ESI)** calcd for $\text{C}_{28}\text{H}_{24}\text{ClN}_3\text{O}_2\text{Na}^+$ [*M*+*Na*] $^+$: 492.1450, found: 492.1457.

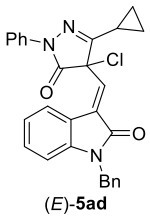
(E)-1-benzyl-3-((3-(tert-butyl)-4-chloro-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((E)-5ac)



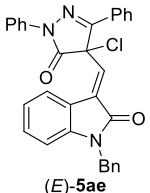
Yellow solid; **m.p.** 140-142 °C; **Yield:** 93 mg, 97%; *Z/E* = 33:67; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.97-7.85 (m, 2H), 7.52-7.42 (m, 2H), 7.34 (s, 1H), 7.32-7.30 (m, 2H), 7.30-7.26 (m, 3H), 7.19 (s, 1H), 7.18-7.12 (m, 2H), 6.82-6.79 (m, 1H), 6.68 (d, *J* = 10.0 Hz, 1H), 5.02 (d, *J* = 15.8 Hz, 1H), 4.86 (d, *J* = 15.8 Hz, 1H), 1.43 (s, 9H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 167.4, 167.3, 166.4, 144.8, 137.5, 135.8, 131.9, 131.6, 130.7, 129.5, 129.2, 128.1, 127.7, 126.4, 126.3, 123.1, 119.6, 109.9, 64.4, 44.4, 37.0,

30.1; **HRMS (ESI)** calcd for $C_{29}H_{27}ClN_3O_2^+$ $[M+H]^+$: 484.1787, found: 484.1802.

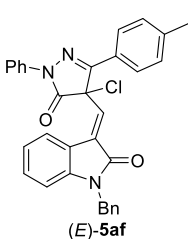
(E)-1-benzyl-3-((4-chloro-3-cyclopropyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((E)-5ad)

 Yellow solid; **m.p.** 166-168 °C; **Yield:** 87 mg, 93%; *Z/E* < 5:95; 1H NMR (500 MHz, Chloroform-*d*) δ 7.92-7.82 (m, 3H), 7.45-7.38 (m, 2H), 7.35-7.29 (m, 4H), 7.29-7.26 (m, 1H), 7.24-7.18 (m, 2H), 7.09 (s, 1H), 6.95-6.92 (m, 1H), 6.70 (d, *J* = 7.9 Hz, 1H), 4.94 (q, *J* = 15.8 Hz, 2H), 1.84 (m, 1H), 1.30-1.25 (m, 1H), 1.19-1.11 (m, 2H), 1.09-1.05 (m, 1H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.6, 167.4, 163.5, 144.9, 137.6, 135.8, 134.3, 131.9, 129.4, 129.2, 128.1, 127.9, 127.7, 127.6, 126.2, 123.0, 119.5, 119.4, 109.7, 64.1, 44.4, 9.9, 9.8, 9.5; **HRMS (ESI)** calcd for $C_{28}H_{22}ClN_3O_2Na^+$ $[M+Na]^+$: 490.1294, found: 490.1307.

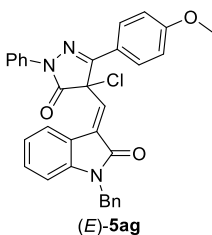
(E)-1-benzyl-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((E)-5ae)

 Orange solid; **m.p.** 195-196 °C; **Yield:** 84 mg, 84%; *Z/E* = 7:93; 1H NMR (500 MHz, Chloroform-*d*) δ 8.04 (dd, *J* = 7.9, 1.9 Hz, 2H), 8.02-7.98 (m, 2H), 7.95-7.93 (m, 1H), 7.52-7.46 (m, 5H), 7.34-7.32 (m, 1H), 7.31-7.30 (m, 3H), 7.29-7.26 (m, 2H), 7.26-7.24 (m, 1H), 7.21-7.17 (m, 1H), 6.94-6.92 (m, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 4.93 (q, *J* = 15.8 Hz, 2H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.6, 167.5, 156.6, 145.0, 137.5, 135.7, 133.8, 131.9, 129.5, 129.4, 129.2, 128.8, 128.1, 127.9, 127.8, 127.7, 127.6, 126.7, 123.0, 119.8, 119.5, 109.8, 62.6, 44.4; **HRMS (ESI)** calcd for $C_{31}H_{22}ClN_3O_2Na^+$ $[M+Na]^+$: 526.1294, found: 526.1300.

(E)-1-benzyl-3-((4-chloro-5-oxo-1-phenyl-3-(p-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((E)-5af)

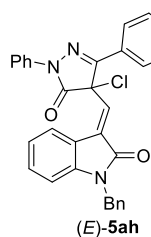
 Orange solid; **m.p.** 187-188 °C; **Yield:** 99 mg, 96%; *Z/E* < 5:95; 1H NMR (500 MHz, Chloroform-*d*) δ 8.02-7.98 (m, 2H), 7.93-7.90 (m, 3H), 7.50-7.44 (m, 2H), 7.34-7.30 (m, 1H), 7.29 (dd, *J* = 4.3, 2.3 Hz, 4H), 7.28-7.26 (m, 3H), 7.25-7.23 (m, 1H), 7.18-7.15 (m, 1H), 6.92-6.89 (m, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 4.91 (q, *J* = 15.8 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (126 MHz, Chloroform-*d*) δ 167.6, 167.5, 156.7, 144.9, 142.6, 137.6, 135.7, 133.6, 131.9, 130.2, 129.5, 129.2, 129.1, 128.1, 127.7, 127.6, 127.5, 126.6, 125.1, 123.0, 119.8, 119.5, 109.7, 62.7, 44.4, 22.0; **HRMS (ESI)** calcd for $C_{32}H_{25}ClN_3O_2^+$ $[M+H]^+$: 518.1630, found: 518.1635.

(E)-1-benzyl-3-((4-chloro-3-(4-methoxyphenyl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((E)-5ag)

 Yellow solid; **m.p.** 197-198 °C; **Yield:** 103 mg, 97%; *Z/E* < 5:95; 1H NMR (500 MHz, Chloroform-*d*) δ 8.02-7.99 (m, 2H), 7.99-7.95 (m, 2H), 7.93-7.91 (m, 1H), 7.48 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.33 (m, 1.4 Hz, 1H), 7.31-7.28 (m, 4H), 7.28-7.26 (m, 2H), 7.20-7.17 (m,

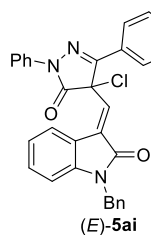
1H), 7.01-6.96 (m, 2H), 6.92-6.90 (m, 1H), 6.67 (d, $J = 7.9$ Hz, 1H), 4.93 (q, $J = 15.8$ Hz, 2H), 3.87 (s, 3H); ^{13}C NMR (126 MHz, Chloroform- d) δ 167.5, 167.4, 162.6, 156.5, 144.9, 137.6, 135.8, 133.6, 131.9, 129.5, 129.4, 129.3, 129.2, 128.1, 127.8, 127.7, 126.5, 123.0, 120.5, 119.8, 119.6, 115.0, 109.7, 62.8, 55.9, 44.4; **HRMS (ESI)** calcd for $\text{C}_{32}\text{H}_{25}\text{ClN}_3\text{O}_3^+$ $[\text{M}+\text{H}]^+$: 534.1579, found: 534.1584.

(*E*)-1-benzyl-3-((4-chloro-3-(4-chlorophenyl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*E*)-5ah)



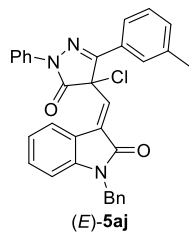
Orange solid; **m.p.** 183-185 °C; **Yield:** 103 mg, 96%; $Z/E = 6:94$; ^1H NMR (500 MHz, Chloroform- d) δ 8.00-7.98 (m, 2H), 7.97-7.94 (m, 2H), 7.94-7.90 (m, 1H), 7.52-7.40 (m, 4H), 7.32 (s, 1H), 7.31-7.29 (m, 3H), 7.28-7.26 (m, 2H), 7.23-7.15 (m, 2H), 6.94-6.91 (m, 1H), 6.67 (d, $J = 7.8$ Hz, 1H), 4.92 (q, $J = 15.8$ Hz, 2H); ^{13}C NMR (126 MHz, Chloroform- d) δ 167.4, 167.3, 155.6, 145.0, 138.2, 137.4, 135.7, 134.1, 132.1, 129.9, 129.6, 129.2, 128.8, 128.2, 127.8, 127.7, 126.8, 126.3, 123.0, 119.8, 119.4, 109.8, 62.3, 44.4; **HRMS (ESI)** calcd for $\text{C}_{31}\text{H}_{21}\text{Cl}_2\text{N}_3\text{O}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 560.0904, found: 560.0905.

(*E*)-1-benzyl-3-((3-(4-bromophenyl)-4-chloro-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*E*)-5ai)



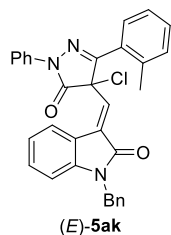
Yellow solid; **m.p.** 162-163 °C; **Yield:** 106 mg, 91%; $Z/E = 8:92$; ^1H NMR (500 MHz, Chloroform- d) δ 7.99-7.94 (m, 2H), 7.90 (dd, $J = 12.4, 8.2$ Hz, 3H), 7.64-7.57 (m, 2H), 7.48 (dd, $J = 8.6, 7.4$ Hz, 2H), 7.34-7.29 (m, 4H), 7.28-7.27 (m, 2H), 7.20 (dd, $J = 7.8, 1.1$ Hz, 1H), 7.18 (s, 1H), 6.92 (m, 1H), 6.67 (d, $J = 7.9$ Hz, 1H), 4.92 (q, $J = 15.8$ Hz, 2H); ^{13}C NMR (126 MHz, Chloroform- d) δ 167.4, 155.8, 145.1, 137.4, 135.7, 134.1, 132.8, 132.1, 129.6, 129.2, 128.9, 128.2, 127.8, 127.7, 126.8, 126.7, 126.6, 123.1, 119.8, 119.4, 109.8, 62.3, 44.4; **HRMS (ESI)** calcd for $\text{C}_{31}\text{H}_{21}\text{BrClN}_3\text{O}_2\text{Na}^+$ $[\text{M}+\text{Na}]^+$: 604.0399, found: 604.0417.

(*E*)-1-benzyl-3-((4-chloro-5-oxo-1-phenyl-3-(*m*-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*E*)-5aj)



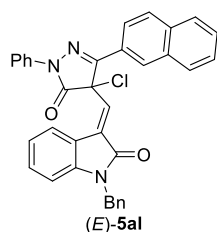
Yellow solid; **m.p.** 173-175 °C; **Yield:** 101 mg, 98%; ^1H NMR (500 MHz, Chloroform- d) δ 8.04-7.98 (m, 2H), 7.94-7.92 (m, 1H), 7.87 (s, 1H), 7.81-7.79 (m, 1H), 7.49 (dd, $J = 8.7, 7.4$ Hz, 2H), 7.39-7.35 (m, 1H), 7.34-7.32 (m, 2H), 7.31-7.28 (m, 4H), 7.27 (s, 2H), 7.21-7.18 (m, 1H), 6.94-6.92 (m, 1H), 6.67 (d, $J = 7.9$ Hz, 1H), 5.00-4.85 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (126 MHz, Chloroform- d) δ 167.6, 167.5, 156.8, 145.0, 139.3, 137.6, 135.7, 133.7, 132.9, 131.9, 129.5, 129.3, 129.2, 129.0, 128.1, 127.9, 127.8, 127.8, 127.7, 126.7, 125.0, 123.0, 119.8, 119.6, 109.7, 62.7, 44.4, 21.9; **HRMS (ESI)** calcd for $\text{C}_{32}\text{H}_{25}\text{ClN}_3\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 518.1630, found: 518.1627.

(*E*)-1-benzyl-3-((4-chloro-5-oxo-1-phenyl-3-(*o*-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*E*)-5ak)



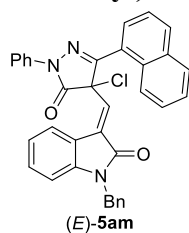
Yellow solid; **m.p.** 165-166 °C; **Yield:** 97 mg, 94%; *Z/E* < 5:95; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 7.99 (dd, *J* = 8.7, 1.2 Hz, 2H), 7.82-7.80 (m, 2H), 7.49 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.40-7.34 (m, 2H), 7.34-7.30 (m, 2H), 7.30 (dd, *J* = 4.2, 1.6 Hz, 3H), 7.29-7.27 (m, 2H), 7.24 (s, 1H), 7.19-7.16 (m, 1H), 6.91-6.88 (m, 1H), 6.66 (d, *J* = 10.0 Hz, 1H), 5.00-4.84 (m, 2H), 2.76 (s, 3H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 167.5, 167.2, 157.4, 144.9, 140.0, 137.7, 135.7, 133.3, 133.0, 131.9, 131.0, 130.0, 129.6, 129.5, 129.2, 128.1, 127.7, 127.5, 126.6, 126.5, 123.0, 119.6, 119.5, 109.8, 64.1, 44.4, 24.4; **HRMS (ESI)** calcd for $\text{C}_{32}\text{H}_{25}\text{ClN}_3\text{O}_2^+$ [*M*+*H*] $^+$: 518.1630, found: 518.1634.

(*E*)-1-benzyl-3-((4-chloro-3-(naphthalen-2-yl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*E*)-5al)



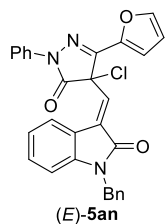
Orange solid; **m.p.** 177-179 °C; **Yield:** 108 mg, 98%; *Z/E* = 5:95; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 8.20 (dd, *J* = 8.7, 1.8 Hz, 1H), 8.06-8.03 (m, 2H), 7.98-7.91 (m, 3H), 7.86 (dd, *J* = 7.4, 1.7 Hz, 1H), 7.58-7.54 (m, 2H), 7.52-7.48 (m, 2H), 7.37 (s, 1H), 7.34-7.29 (m, 2H), 7.29-7.28 (m, 2H), 7.28-7.25 (m, 2H), 7.19-7.16 (m, 1H), 6.95-6.91 (m, 1H), 6.66 (d, *J* = 7.8 Hz, 1H), 4.92 (q, *J* = 15.8 Hz, 2H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 167.7, 167.5, 156.8, 145.0, 137.6, 135.7, 135.0, 133.8, 133.2, 132.0, 129.7, 129.6, 129.5, 129.2, 129.1, 128.7, 128.4, 128.2, 128.1, 127.7, 127.6, 127.3, 126.7, 125.2, 123.4, 123.0, 119.9, 119.5, 109.8, 62.6, 44.4; **HRMS (ESI)** calcd for $\text{C}_{35}\text{H}_{24}\text{ClN}_3\text{O}_2\text{Na}^+$ [*M*+*Na*] $^+$: 576.1450, found: 576.1459.

(*E*)-1-benzyl-3-((4-chloro-3-(naphthalen-1-yl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*E*)-5am)



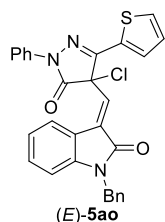
Yellow solid; **m.p.** 164-167 °C; **Yield:** 28 mg, 25%; *Z/E* < 5:95; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 9.20 (dd, *J* = 8.7, 1.1 Hz, 1H), 8.09-8.04 (m, 3H), 7.99-7.97 (m, 1H), 7.92 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.84 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.70-7.67 (m, 1H), 7.60-7.58 (m, 1H), 7.55-7.51 (m, 3H), 7.36-7.34 (m, 1H), 7.33-7.31 (m, 2H), 7.29 (dd, *J* = 7.4, 2.2 Hz, 2H), 7.27 (s, 2H), 7.17-7.14 (m, 1H), 6.89-6.86 (m, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 5.00-4.82 (m, 2H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 167.5, 167.3, 157.2, 144.9, 137.6, 135.7, 134.8, 133.5, 132.9, 131.9, 131.6, 130.0, 129.6, 129.5, 129.2, 128.6, 128.1, 127.6, 127.5, 126.9, 126.8, 126.5, 125.2, 124.3, 123.0, 119.8, 119.5, 109.8, 64.6, 44.4; **HRMS (ESI)** calcd for $\text{C}_{35}\text{H}_{24}\text{ClN}_3\text{O}_2\text{Na}^+$ [*M*+*Na*] $^+$: 576.1450, found: 576.1460.

(*E*)-1-benzyl-3-((4-chloro-3-(furan-2-yl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*E*)-5an)



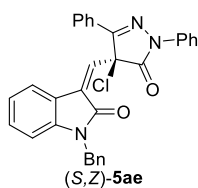
Orange solid; **m.p.** 147-148 °C; **Yield:** 88 mg, 89%; *Z/E* < 5:95; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.96 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.66-7.64 (m, 1H), 7.46 (dd, *J* = 8.7, 7.4 Hz, 2H), 7.35-7.31 (m, 1H), 7.31-7.28 (m, 4H), 7.27-7.24 (m, 1H), 7.21-7.19 (m, 1H), 7.17 (s, 1H), 7.08-7.07 (m, 1H), 6.96-6.92 (m, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 6.58 (dd, *J* = 3.6, 1.8 Hz, 1H), 4.93 (q, *J* = 15.8 Hz, 2H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 167.5, 166.7, 149.3, 146.3, 145.0, 143.8, 137.4, 135.7, 134.1, 132.0, 129.5, 129.2, 128.2, 128.1, 128.0, 127.6, 126.8, 123.0, 119.9, 119.4, 115.7, 112.8, 109.7, 62.0, 44.4; **HRMS (ESI)** calcd for $\text{C}_{29}\text{H}_{20}\text{ClN}_3\text{O}_3\text{Na}^+$ [*M*+*Na*] $^+$: 516.1086, found: 516.1099.

(*E*)-1-benzyl-3-((4-chloro-5-oxo-1-phenyl-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*E*)-5ao)

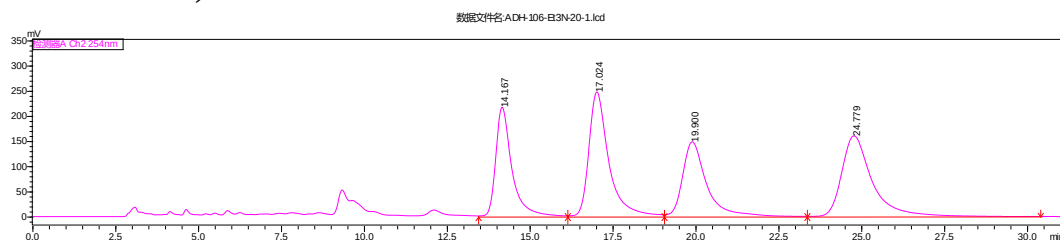


Orange solid; **m.p.** 167-168 °C; **Yield:** 100 mg, 89%; *Z/E* = 6:94; ^1H **NMR** (500 MHz, Chloroform-*d*) δ 8.04-8.03 (m, 1H), 7.98-7.94 (m, 2H), 7.64 (dd, *J* = 3.8, 1.0 Hz, 1H), 7.52 (dd, *J* = 5.1, 1.0 Hz, 1H), 7.49-7.44 (m, 2H), 7.33-7.32 (m, 1H), 7.31-7.27 (m, 5H), 7.23-7.18 (m, 2H), 7.13 (dd, *J* = 5.0, 3.8 Hz, 1H), 6.96-6.93 (m, 1H), 6.68 (d, *J* = 7.9 Hz, 1H), 5.02-4.83 (m, 2H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 167.5, 167.0, 153.3, 145.0, 137.4, 135.7, 134.3, 132.1, 131.4, 130.8, 130.5, 129.5, 129.2, 128.5, 128.2, 128.1, 128.0, 127.6, 126.7, 123.0, 119.8, 119.4, 109.7, 62.7, 44.4; **HRMS (ESI)** calcd for $\text{C}_{29}\text{H}_{20}\text{ClN}_3\text{O}_2\text{SNa}^+$ [*M*+*Na*] $^+$: 532.0858, found: 532.0871.

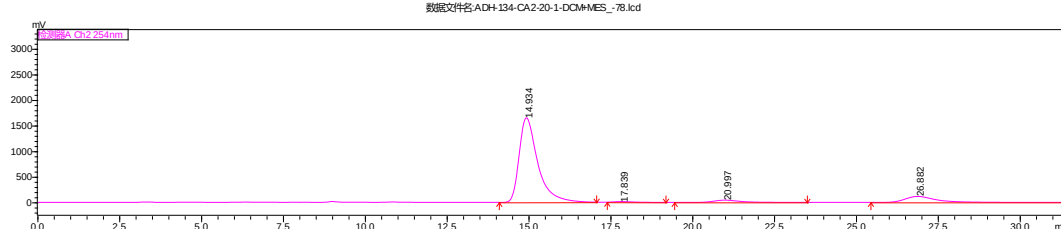
(*S,Z*)-1-benzyl-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5ae)



Yellow solid; **m.p.** 129-132 °C; **Yield:** 89 mg, 96%; *Z/E* > 95:5; petroleum ether/EtOAc = 20:1; $[\alpha]_{\text{D}}^{25} = -214.11$ (c 0.13, CHCl_3); ^1H **NMR** (500 MHz, Chloroform-*d*) δ 8.06-7.98 (m, 2H), 7.96-7.91 (m, 2H), 7.53 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.49-7.45 (m, 2H), 7.44-7.39 (m, 3H), 7.26 (s, 1H), 7.24-7.19 (m, 3H), 7.18-7.16 (m, 1H), 7.10 (s, 1H), 7.09-7.05 (m, 2H), 7.04-7.00 (m, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 4.74 (q, *J* = 15.8 Hz, 2H); ^{13}C **NMR** (126 MHz, Chloroform-*d*) δ 168.7, 165.1, 152.4, 143.7, 138.2, 135.6, 132.0, 131.3, 130.9, 130.4, 129.3, 129.2, 129.1, 129.0, 128.0, 127.7, 127.5, 126.1, 122.8, 121.5, 121.3, 120.5, 110.0, 64.4, 43.9; **HRMS (ESI)** calcd for $\text{C}_{31}\text{H}_{22}\text{ClN}_3\text{O}_2\text{Na}^+$ [*M*+*Na*] $^+$: 526.1294, found: 526.1300. **HPLC Data** 93% ee (Daicel Chiralpak ADH column, hexane/Isopropanol = 80/20, λ = 254 nm, 30 °C, 1 mL/min, t_{major} = 14.9 min, t_{minor} = 21.0 min).

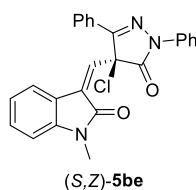


Peak	RetTime	Area	Heigh	Area%
1	14.167	7379090	217355	20.796
2	17.024	10364928	247585	29.211
3	19.900	7504044	148613	21.148
4	24.779	10234993	160405	28.845

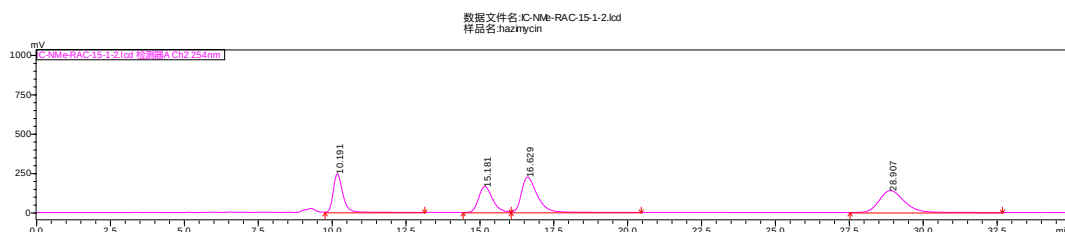


Peak	RetTime	Area	Heigh	Area%
1	14.934	65300077	1651887	86.001
2	17.839	447903	12447	0.590
3	20.997	2440092	43917	3.214
4	26.882	7741148	117059	10.195

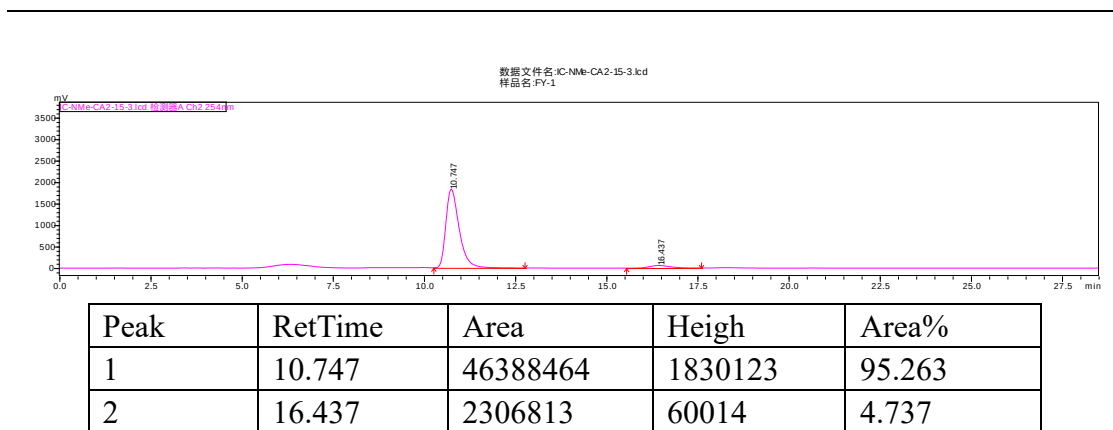
(*S,Z*)-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-1-methylindolin-2-one ((*S,Z*)-5be)



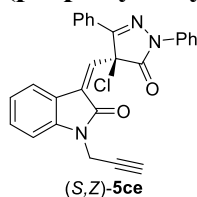
Yellow solid; **m.p.** 151-153 °C; **Yield:** 82 mg, 96%; *Z/E* > 95:5; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -216.66$ (c 0.13, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.07-8.02 (m, 2H), 7.95-7.90 (m, 2H), 7.55-7.51 (m, 1H), 7.50-7.45 (m, 2H), 7.41 (dd, *J* = 5.2, 2.0 Hz, 3H), 7.32-7.26 (m, 2H), 7.09-7.03 (m, 2H), 6.71 (d, *J* = 7.8 Hz, 1H), 3.03 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.7, 165.0, 152.3, 144.7, 138.2, 132.0, 131.4, 130.9, 129.9, 129.3, 129.2, 129.1, 129.0, 127.6, 126.1, 122.7, 121.2, 120.3, 108.9, 64.3, 26.4; **HRMS (ESI)** calcd for C₂₅H₁₉ClN₃O₂⁺ [M+H]⁺: 428.1161, found: 428.1174; **HPLC Data** 90% ee (Daicel Chiralpak ADH column, hexane/Isopropanol = 85/15, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 10.7 min, *t*_{minor} = 16.4 min).



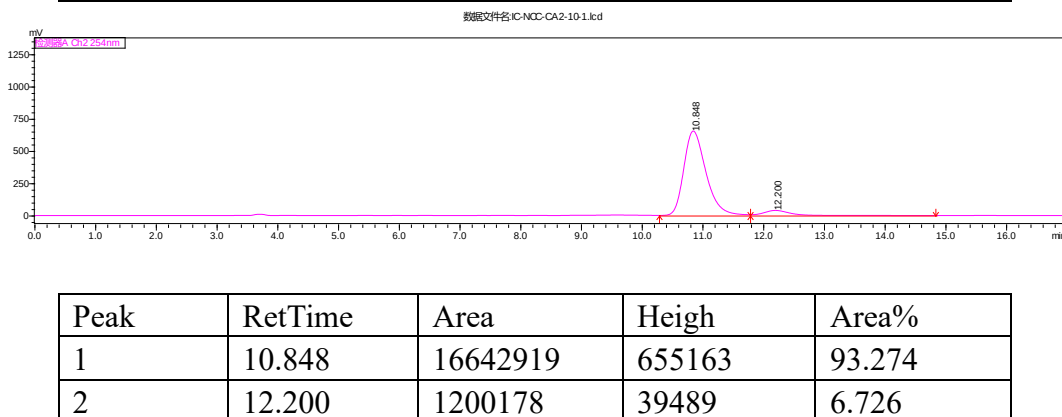
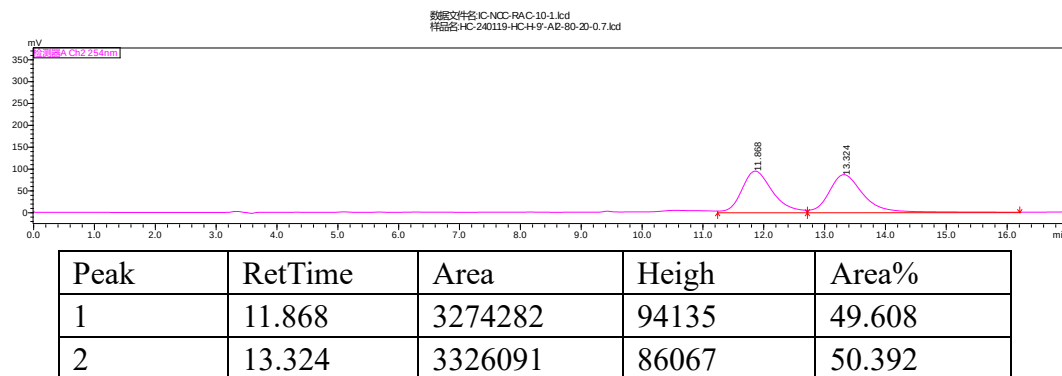
Peak	RetTime	Area	Heigh	Area%
1	10.191	5538791	244969	20.272
2	15.181	5383692	164536	19.704
3	16.629	8267932	223533	30.260
4	28.907	8132241	139372	29.764



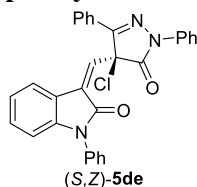
(*S,Z*)-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-1-(prop-2-yn-1-yl)indolin-2-one ((*S,Z*)-5ce)



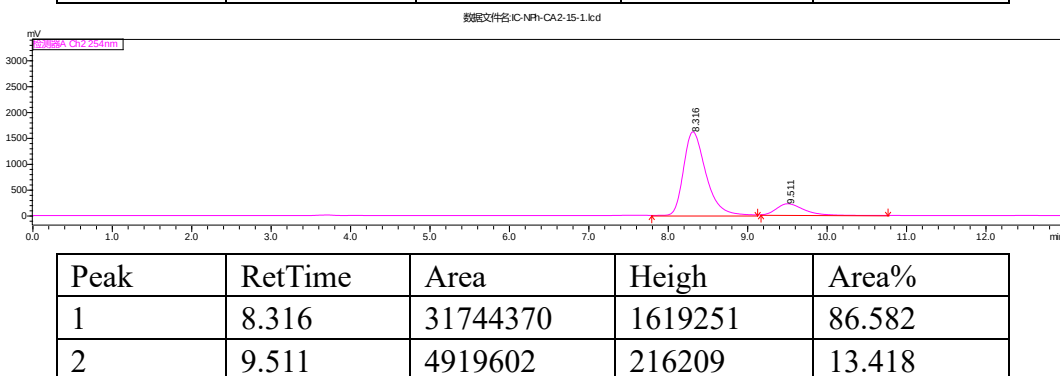
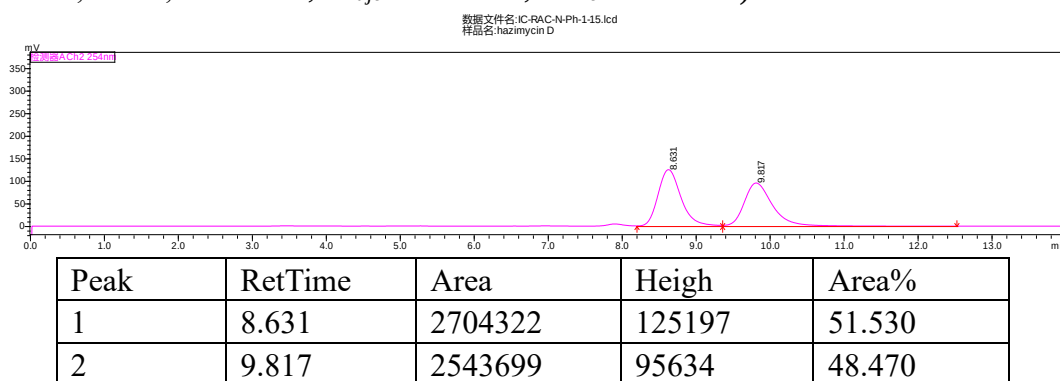
Yellow solid; **m.p.** 196-199 °C; **Yield:** 80 mg, 92%; *Z/E* = 87:13; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -252.00$ (c 0.10, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.04-8.03 (m, 2H), 7.93-7.92 (m, 2H), 7.56-7.55 (m, 1H), 7.50-7.47 (m, 2H), 7.42-7.41 (m, 3H), 7.35-7.32 (m, 1H), 7.29-7.27 (m, 1H), 7.11-7.08 (m, 2H), 6.98 (d, *J* = 7.9 Hz, 1H), 4.46-4.37 (m, 1H), 4.30-4.22 (m, 1H), 2.16 (s, 1H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.6, 163.9, 152.2, 142.7, 138.1, 131.5, 131.4, 131.0, 130.7, 129.3, 129.2, 128.9, 127.6, 126.1, 123.2, 121.3, 121.2, 120.3, 110.1, 73.2, 64.2, 29.5; **HRMS (ESI)** calcd for C₂₇H₁₉ClN₃O₂⁺ [M+H]⁺: 452.1161, found: 452.1175; **HPLC Data** 86% ee (Daicel Chiralpak IC column, hexane/Isopropanol = 90/10, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 10.8 min, *t*_{minor} = 12.2 min).



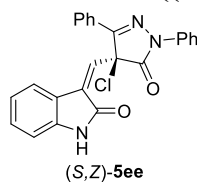
(*S,Z*)-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-1-phenylindolin-2-one ((*S,Z*)-5de)



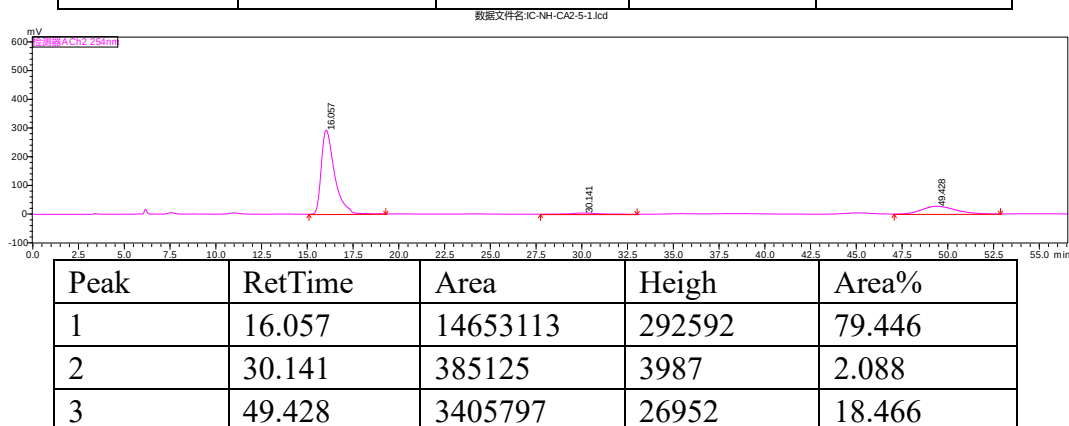
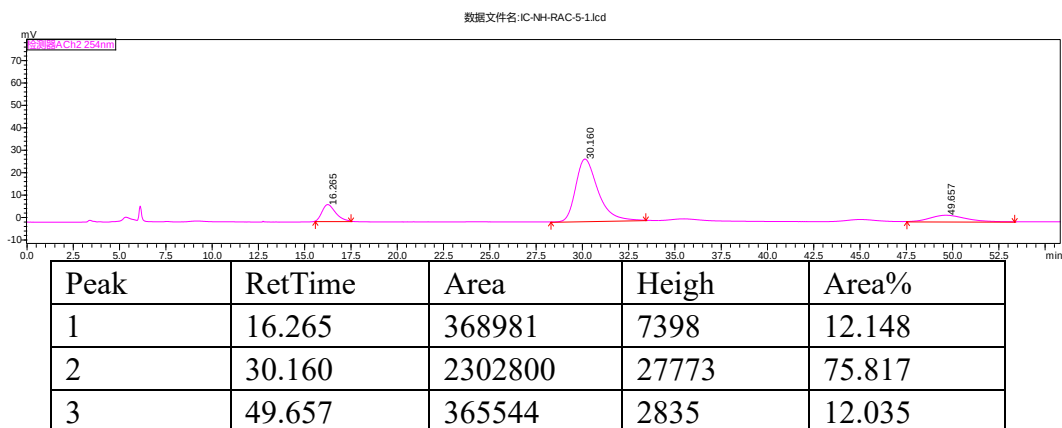
Yellow solid; **m.p.** 150-152 °C; **Yield:** 96 mg, 98%; *Z/E* = 86:14; petroleum ether/EtOAc = 20:1; $[\alpha]_{\text{D}}^{25} = -89.02$ (c 0.14, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.00-7.98 (m, 2H), 7.94-7.93 (m, 2H), 7.61 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.46-7.43 (m, 2H), 7.43-7.41 (m, 3H), 7.40-7.38 (m, 2H), 7.33-7.27 (m, 1H), 7.26-7.23 (m, 3H), 7.23-7.21 (m, 1H), 7.16 (s, 1H), 7.12-7.09 (m, 1H), 6.77 (d, *J* = 7.9 Hz, 1H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.4, 164.2, 152.1, 144.6, 138.2, 134.0, 131.9, 131.3, 130.9, 130.6, 129.8, 129.2, 129.0, 128.4, 127.7, 126.6, 126.0, 123.3, 121.5, 121.4, 120.4, 110.3, 64.5; **HRMS (ESI)** calcd for C₃₀H₂₁ClN₃O₂⁺ [*M*+*H*]⁺: 490.1317, found: 490.1333; **HPLC Data** 74% ee (Daicel Chiralpak IC column, hexane/isopropanol = 85/15, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 8.3 min, *t*_{minor} = 9.5 min).



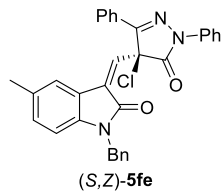
(*S,Z*)-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5ee)



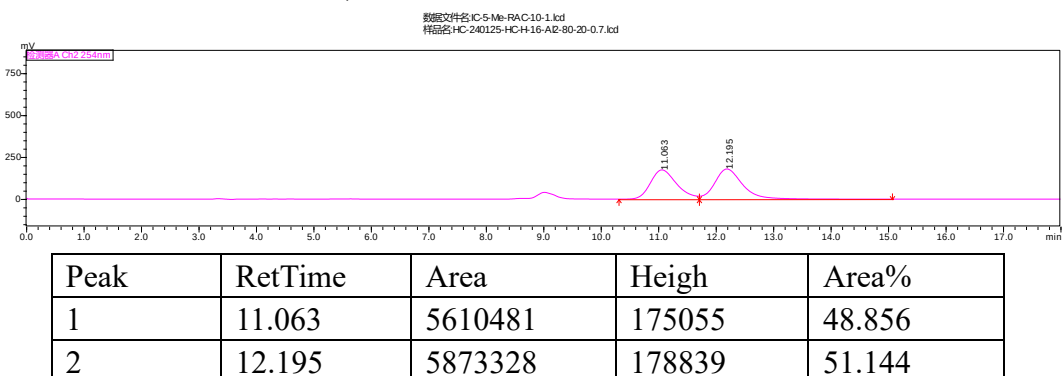
Yellow solid; **m.p.** 173-174 °C; **Yield:** 36 mg, 44%; *Z/E* > 95:5; petroleum ether/EtOAc = 20:1; $[\alpha]_{\text{D}}^{25} = -123.94$ (c 0.11, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.43 (s, 1H), 8.08-8.00 (m, 2H), 7.91-7.84 (m, 2H), 7.50-7.43 (m, 3H), 7.41-7.37 (m, 3H), 7.28-7.27 (m, 1H), 7.13-7.09 (m, 1H), 7.04 (s, 1H), 6.01-6.98 (m, 1H), 6.23 (d, *J* = 7.8 Hz, 1H). **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.6, 167.0, 152.0, 141.9, 138.3, 132.3, 131.5, 131.0, 130.6, 129.5, 129.2, 128.9, 127.6, 126.0, 122.8, 121.9, 121.5, 119.9, 110.9, 64.2; **HRMS (ESI)** calcd for C₂₄H₁₇ClN₃O₂⁺ [*M*+*H*]⁺: 414.1004, found: 414.1015; **HPLC Data** 62% ee (Daicel Chiralpak IC column, hexane/Isopropanol = 95/5, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 16.1 min, *t*_{minor} = 49.4 min).

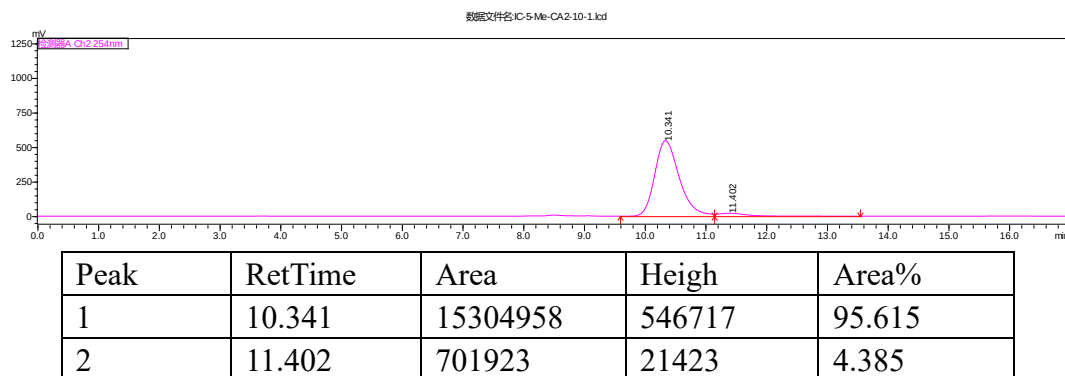


(*S,Z*)-1-benzyl-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-5-methylindolin-2-one ((*S,Z*)-5fe)

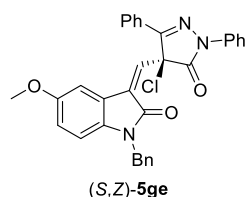


Yellow solid; **m.p.** 204-206 °C; **Yield:** 102 mg, 99%; *Z/E* = 95:5; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -235.21$ (c 0.11, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.12-8.03 (m, 2H), 8.01-7.94 (m, 2H), 7.51-7.47 (m, 2H), 7.44 (dd, *J* = 5.3, 1.9 Hz, 3H), 7.38 (s, 1H), 7.30-7.26 (m, 1H), 7.24-7.19 (m, 3H), 7.11 (s, 1H), 7.08-7.05 (m, 2H), 6.98-6.96 (m, 1H), 6.45 (d, *J* = 8.0 Hz, 1H), 4.76 (d, *J* = 15.8 Hz, 1H), 4.66 (d, *J* = 15.8 Hz, 1H), 2.32 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.7, 165.1, 152.4, 141.4, 138.2, 135.7, 132.3, 132.2, 131.7, 130.8, 129.9, 129.2, 129.1, 129.1, 128.9, 127.8, 127.6, 127.4, 126.1, 121.9, 121.4, 120.4, 109.7, 64.5, 43.8, 21.3; **HRMS (ESI)** calcd for C₃₂H₂₅ClN₃O₂⁺ [*M*+*H*]⁺: 518.1630, found: 518.1642; **HPLC Data** 92% ee (Daicel Chiralpak IC column, hexane/isopropanol = 90/10, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 10.3 min, *t*_{minor} = 11.4 min).

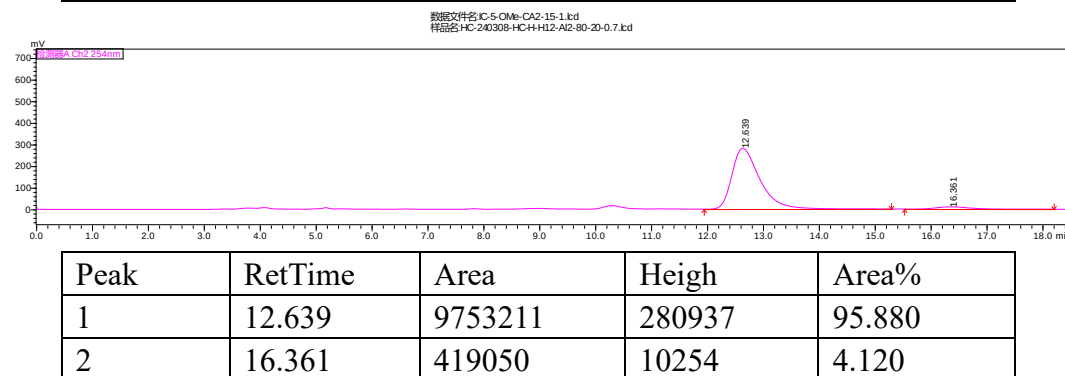
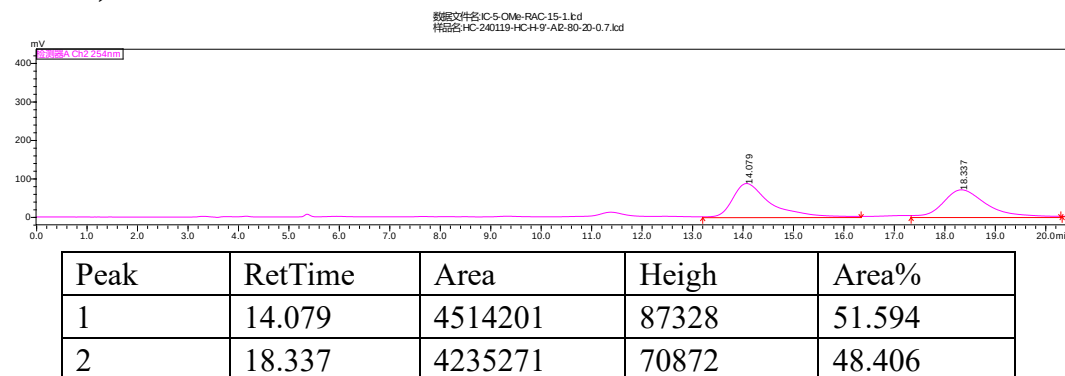




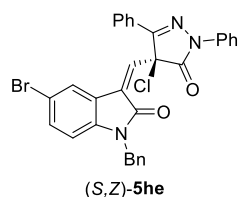
(*S,Z*)-1-benzyl-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-5-methoxyindolin-2-one ((*S,Z*)-5ge)



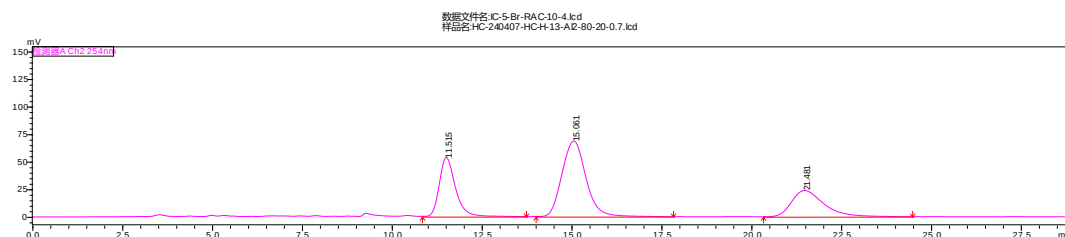
Red solid; **m.p.** 145-147 °C; **Yield:** 74 mg, 70%; *Z/E* > 95:5; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -186.00$ (c 0.11, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.09-7.99 (m, 2H), 7.98-7.89 (m, 2H), 7.47 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.43 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.28-7.27 (m, 1H), 7.22-7.18 (m, 3H), 7.11-7.10 (m, 2H), 7.04 (dd, *J* = 7.3, 2.3 Hz, 2H), 6.70 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.42 (d, *J* = 8.5 Hz, 1H), 4.75 (d, *J* = 15.8 Hz, 1H), 4.62 (d, *J* = 15.8 Hz, 1H), 3.77 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.3, 164.7, 155.8, 152.0, 137.8, 137.1, 135.3, 132.0, 130.5, 130.1, 128.9, 128.8, 128.7, 128.6, 127.5, 127.3, 127.1, 125.7, 121.9, 120.1, 116.3, 110.2, 107.3, 64.0, 55.9, 43.6; **HRMS (ESI)** calcd for C₃₂H₂₅ClN₃O₃⁺ [M+H]⁺: 534.1579, found: 534.1594; **HPLC** **Date** 92% ee (Daicel Chiralpak IC column, hexane/isopropanol = 85/15, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 12.6 min, *t*_{minor} = 16.4 min).



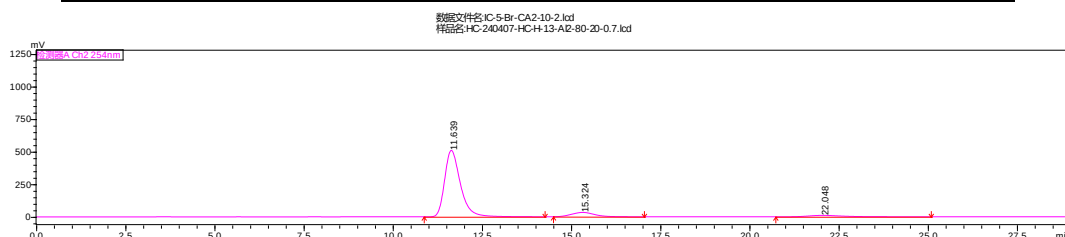
(*S,Z*)-1-benzyl-5-bromo-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5he)



Yellow solid; **m.p.** 184-186 °C; **Yield:** 116 mg, 98%; *Z/E* = 88:12; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -201.67$ (c 0.12, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.05-8.03 (m, 2H), 7.96-7.92 (m, 2H), 7.67-7.66 (m, 1H), 7.53-7.48 (m, 2H), 7.46-7.44 (m, 3H), 7.31-7.26 (m, 2H), 7.22 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.14 (s, 1H), 7.06-7.02 (m, 2H), 6.43 (d, *J* = 8.4 Hz, 1H), 4.75 (d, *J* = 15.8 Hz, 1H), 4.66 (d, *J* = 15.8 Hz, 1H) **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.4, 164.6, 152.1, 142.4, 138.1, 135.1, 133.8, 132.2, 131.0, 130.9, 129.3, 129.2, 129.1, 128.9, 128.1, 127.6, 127.5, 126.2, 124.4, 123.1, 120.4, 115.6, 111.5, 64.2, 44.0; **HRMS (ESI)** calcd for C₃₁H₂₂BrClN₃O₂⁺ [M+H]⁺: 582.0579, found: 582.0592; **HPLC Data** 92% ee (Daicel Chiralpak IC column, hexane/isopropanol = 90/10, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 11.6 min, *t*_{minor} = 22.0 min).

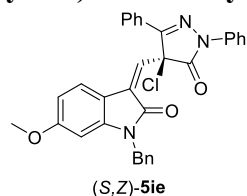


Peak	RetTime	Area	Heigh	Area%
1	11.515	1533777	52233	24.727
2	15.061	3177458	68600	51.226
3	21.481	1491560	23789	24.047



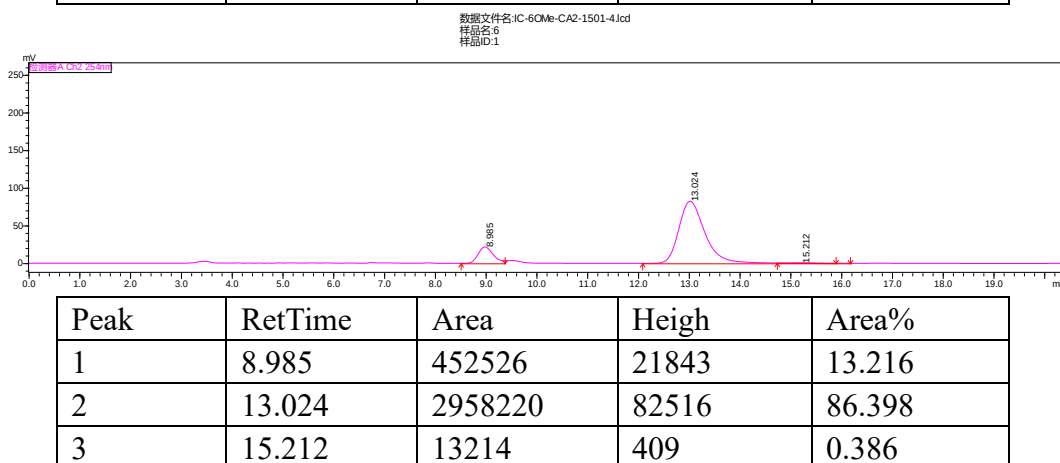
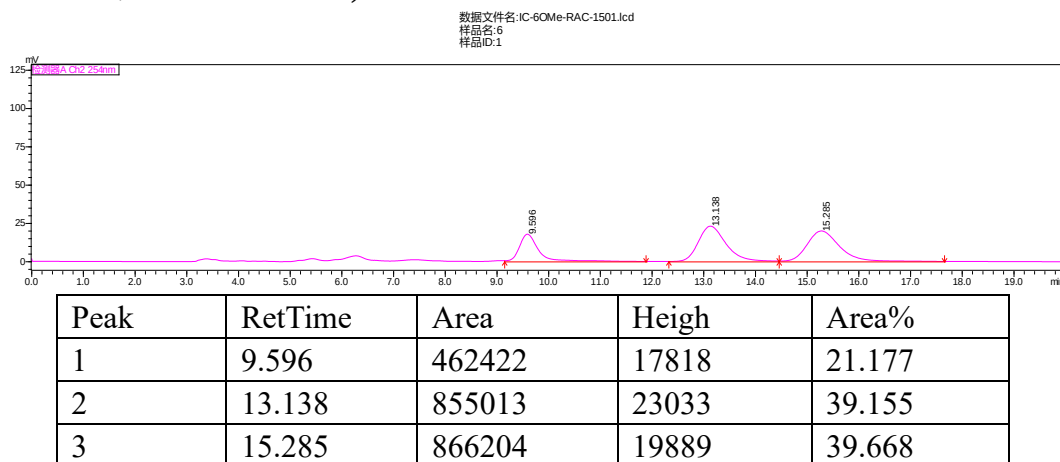
Peak	RetTime	Area	Heigh	Area%
1	11.639	15755247	510023	87.823
2	15.324	1474614	33053	8.220
3	22.048	709880	10591	3.957

(*S,Z*)-1-benzyl-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-6-methoxyindolin-2-one ((*S,Z*)-5ie)

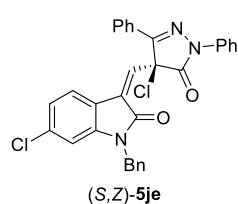


Yellow solid; **m.p.** 147-149 °C; **Yield:** 38 mg, 36%; *Z/E* > 95:5; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -197.09$ (c 0.16, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.03-8.01 (m, 2H), 7.97-7.91 (m, 2H), 7.46 (dd, *J* = 8.8, 7.6 Hz, 3H), 7.43-7.39 (m, 3H), 7.28-7.22 (m, 2H), 7.21-7.20 (m, 2H), 7.08-7.03 (m, 2H), 6.91 (s, 1H), 6.51-6.49 (m, 1H), 6.12 (d, *J* = 2.2 Hz, 1H), 4.78-4.61 (m, 2H), 3.70 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.9, 165.8, 162.7, 152.6, 145.3, 138.3, 135.6, 131.5, 130.8, 129.3, 129.2, 129.1, 129.0, 128.0, 127.7, 127.5, 127.4,

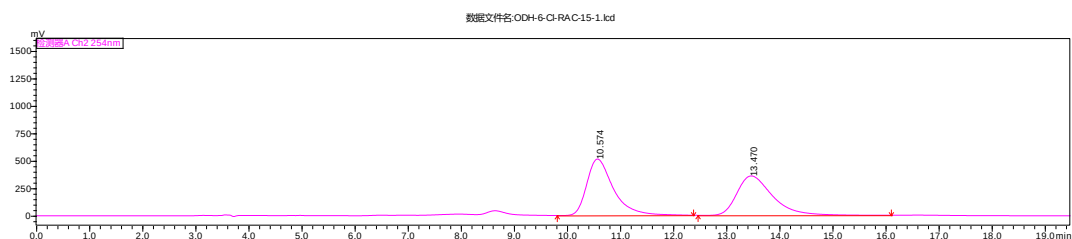
126.1, 122.6, 120.4, 114.4, 107.1, 97.6, 64.5, 55.9, 43.9; **HRMS (ESI)** calcd for $C_{32}H_{25}ClN_3O_3^+$ $[M+H]^+$: 534.1579, found: 534.1596; **HPLC Date** 99% ee (Daicel Chiralpak IC column, hexane/isopropanol = 85/15, λ = 254 nm, 30 °C, 1 mL/min, t_{major} = 13.0 min, t_{minor} = 15.2 min).



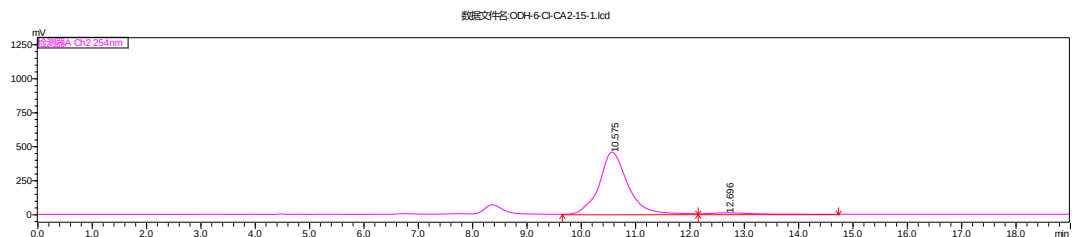
(*S,Z*)-1-benzyl-6-chloro-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5je)



Yellow solid; **m.p.** 184-185 °C; **Yield:** 106 mg, 99%; *Z/E* = 89:11; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25}$ = -130.51 (c 0.13, $CHCl_3$); **1H NMR** (500 MHz, Chloroform-*d*) δ 8.08-7.99 (m, 2H), 7.93 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.50-7.46 (m, 2H), 7.46-7.39 (m, 4H), 7.29-7.26 (m, 1H), 7.23 (dd, *J* = 5.1, 1.9 Hz, 3H), 7.11 (s, 1H), 7.05 (dd, *J* = 6.7, 2.8 Hz, 2H), 6.99 (dd, *J* = 8.1, 1.8 Hz, 1H), 6.56 (d, *J* = 1.8 Hz, 1H), 4.75 (d, *J* = 15.8 Hz, 1H), 4.65 (d, *J* = 15.8 Hz, 1H); **^{13}C NMR** (126 MHz, Chloroform-*d*) δ 168.5, 165.1, 152.2, 144.6, 138.1, 137.1, 135.1, 131.1, 131.0, 130.9, 129.3, 129.2, 129.0, 128.2, 127.6, 127.5, 126.2, 122.9, 122.2, 120.5, 119.9, 110.5, 64.3, 44.0; **HRMS (ESI)** calcd for $C_{31}H_{21}Cl_2N_3O_2Na^+$ $[M+Na]^+$: 560.0904, found: 560.0908; **HPLC Date** 94% ee (Daicel Chiralpak ODH column, hexane/isopropanol = 85/15, λ = 254 nm, 30 °C, 1 mL/min, t_{major} = 10.6 min, t_{minor} = 12.7 min).

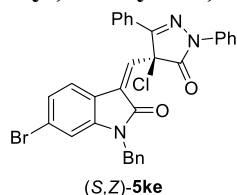


Peak	RetTime	Area	Heigh	Area%
1	10.574	17867672	513045	51.806
2	13.470	16621599	358341	48.194

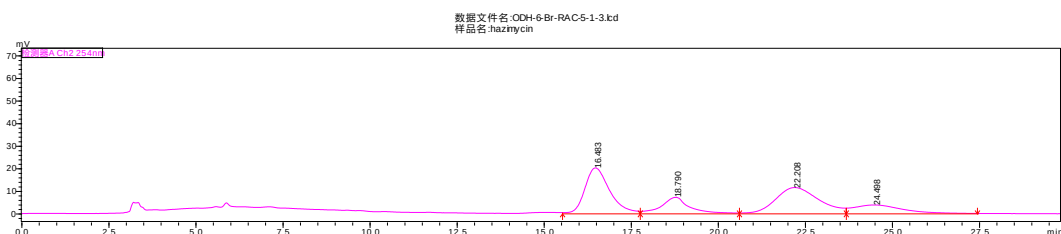


Peak	RetTime	Area	Heigh	Area%
1	10.575	16634437	456769	96.606
2	12.696	584452	11037	3.394

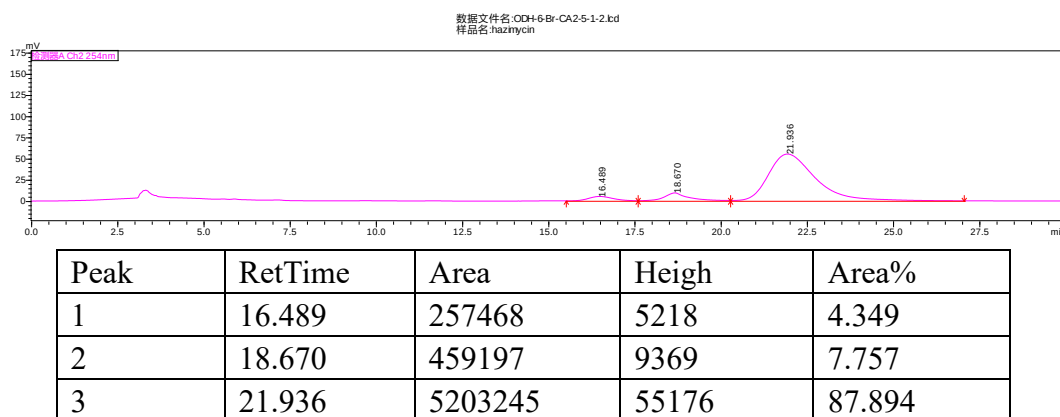
(*S,Z*)-1-benzyl-6-bromo-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5ke)



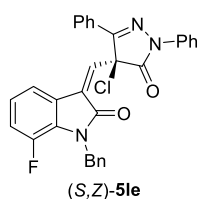
Yellow solid; **m.p.** 185-187 °C; **Yield:** 116 mg, 99%; *Z/E* = 92:8; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -150.01$ (c 0.12, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.07-8.01 (m, 2H), 7.93 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.48 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.45-7.41 (m, 3H), 7.38-7.37 (m, 1H), 7.30-7.26 (m, 1H), 7.23 (dd, *J* = 5.0, 1.9 Hz, 3H), 7.15 (s, 1H), 7.13-7.11 (m, 1H), 7.08-6.99 (m, 2H), 6.71 (d, *J* = 1.6 Hz, 1H), 4.75 (d, *J* = 15.8 Hz, 1H), 4.63 (d, *J* = 15.8 Hz, 1H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.0, 164.4, 151.7, 144.1, 137.6, 134.5, 130.8, 130.5, 128.8, 128.7, 128.6, 128.5, 127.7, 127.1, 126.9, 125.7, 125.3, 124.6, 121.9, 119.9, 119.8, 112.7, 63.8, 43.5; **HRMS (ESI)** calcd for C₃₁H₂₂BrClN₃O₂⁺ [M+H]⁺: 582.0579, found: 582.0586; **HPLC Data** 90% ee (Daicel Chiralpak ODH column, hexane/isopropanol = 95/5, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 21.9 min, *t*_{minor} = 16.5 min).



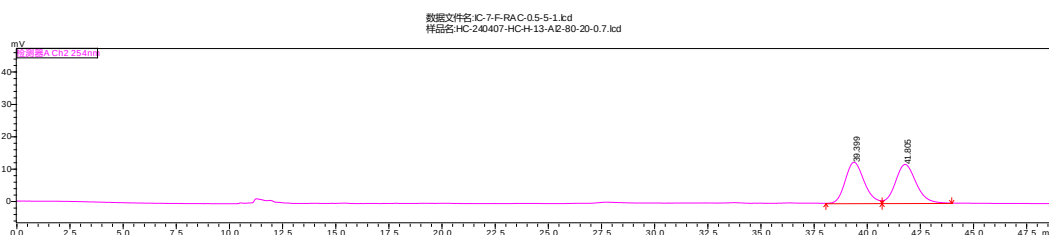
Peak	RetTime	Area	Heigh	Area%
1	16.483	994042	20147	36.436
2	18.790	389578	7101	14.280
3	22.208	983820	11469	36.061
4	24.498	360765	3758	13.224



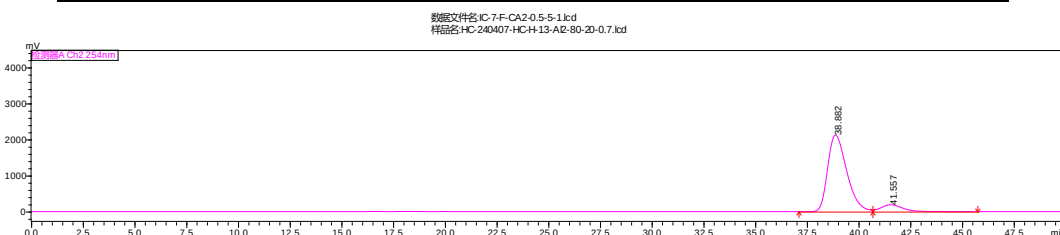
(*S,Z*)-1-benzyl-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-7-fluoroindolin-2-one ((*S,Z*)-5le)



Yellow solid; **m.p.** 161-163 °C; **Yield:** 102 mg, 96%; **Z/E** = 95:5; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -334.00$ (c 0.10, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.05-7.98 (m, 2H), 7.94-7.89 (m, 2H), 7.48 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.45-7.41 (m, 3H), 7.35-7.31 (m, 1H), 7.28 (m, 1H), 7.22-7.16 (m, 3H), 7.12 (s, 1H), 7.11-7.07 (m, 2H), 6.98-6.93 (m, 2H), 4.94-4.79 (m, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.5, 164.9, 147.9 (d, *J*_{C-F} = 245.7 Hz), 152.2, 138.2, 136.9, 132.1, 131.5, 131.0, 130.3, 130.2, 129.3, 129.2, 129.0, 128.9, 127.9, 127.8, 127.6, 126.2, 124.3 (d, *J*_{C-F} = 3.7 Hz), 123.4 (d, *J*_{C-F} = 6.3 Hz), 120.5, 119.3, 119.2, 117.3 (d, *J*_{C-F} = 3.7 Hz), 64.3, 45.5; **¹⁹F NMR** (377 MHz, Chloroform-*d*) δ -133.61; **HRMS (ESI)** calcd for C₃₁H₂₁ClFN₃O₂Na⁺ [M+Na]⁺: 544.1199, found: 544.1206; **HPLC** **Date** 82% ee (Daicel Chiralpak IC column, hexane/isopropanol = 95/5, λ = 254 nm, 30 °C, 0.5 mL/min, *t*_{major} = 41.6 min, *t*_{minor} = 38.9 min).

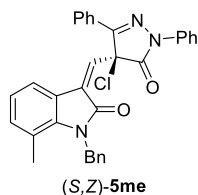


Peak	RetTime	Area	Heigh	Area%
1	39.399	780580	12664	49.261
2	41.805	803995	11967	50.739

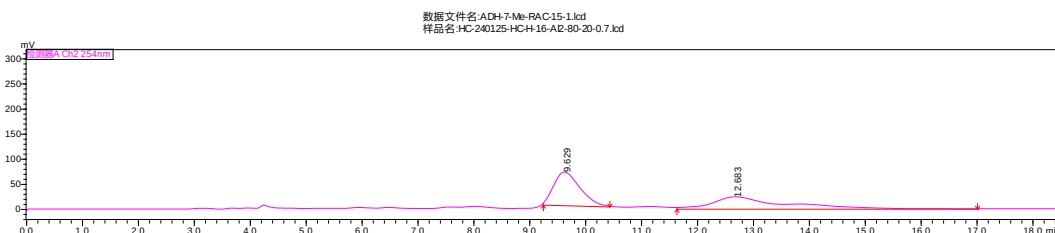


Peak	RetTime	Area	Heigh	Area%
1	38.882	135803144	2124244	90.737
2	41.557	13864017	191230	9.263

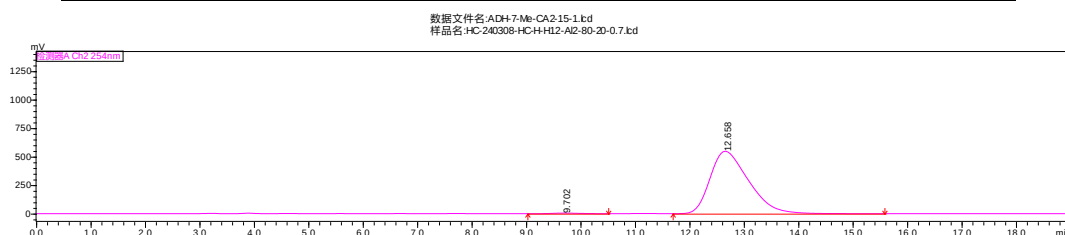
(S,Z)-1-benzyl-3-((4-chloro-5-oxo-1,3-diphenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)-7-methylindolin-2-one ((S,Z)-5me)



Yellow solid; **m.p.** 201-203 °C; **Yield:** 102 mg, 98%; **Z/E** = 89:11; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -140.00$ (c 0.13, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.01-7.99 (m, 2H), 7.93 (dd, *J* = 6.6, 3.1 Hz, 2H), 7.44 (dd, *J* = 7.0, 2.0 Hz, 3H), 7.45-7.42 (m, 3H), 7.24 (s, 1H), 7.21-7.12 (m, 3H), 7.11 (s, 1H), 6.95-6.94 (m, 2H), 6.92-6.88 (m, 2H), 5.11-4.88 (m, 2H), 2.14 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.6, 166.1, 152.3, 141.8, 138.2, 137.5, 135.2, 131.8, 130.8, 130.0, 129.2, 129.1, 129.0, 127.7, 127.5, 126.1, 126.0, 122.9, 122.1, 120.9, 120.4, 119.2, 64.6, 45.1, 18.9; **HRMS (ESI)** calcd for C₃₂H₂₅ClN₃O₂⁺ [M+H]⁺: 518.1630, found: 518.1646; **HPLC** **Date** 98% ee (Daicel Chiralpak ADH column, hexane/isopropanol = 85/15, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 12.7 min, *t*_{minor} = 9.7 min).

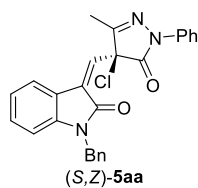


Peak	RetTime	Area	Heigh	Area%
1	9.629	2153623	66270	50.806
2	12.683	2085329	23814	49.194



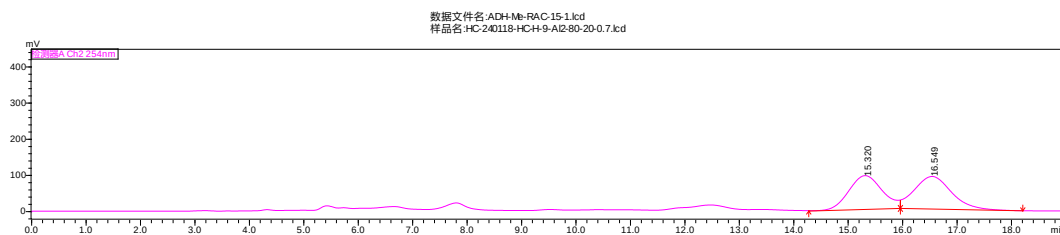
Peak	RetTime	Area	Heigh	Area%
1	9.702	176333	5511	0.650
2	12.658	26939156	547628	99.350

(S,Z)-1-benzyl-3-((4-chloro-3-methyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((S,Z)-5aa)

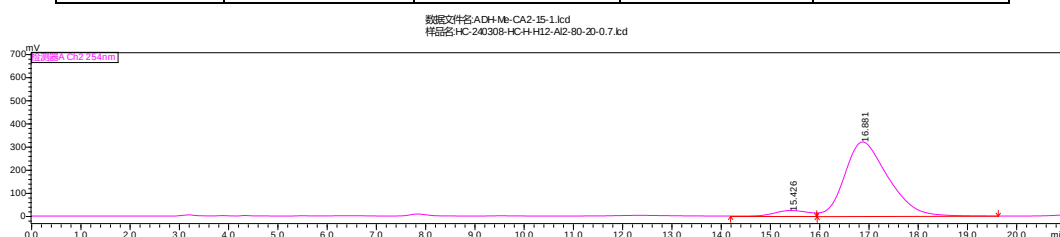


Yellow solid; **m.p.** 135-136 °C; **Yield:** 80 mg, 91%; **Z/E** = 88:12; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -100.00$ (c 0.12, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.98-7.84 (m, 2H), 7.51-7.47 (m, 1H), 7.45-7.39 (m, 2H), 7.31-7.26 (m, 2H), 7.26-7.21 (m, 2H), 7.20-7.17 (m, 3H), 7.05-7.02 (m, 1H), 6.78 (s, 1H), 6.63 (d, *J* = 7.9 Hz, 1H), 4.81 (q, *J* = 15.8 Hz, 2H), 2.20 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.3, 165.1, 153.4, 143.8, 138.2, 135.6, 132.4, 131.5, 129.3, 129.2, 129.1, 128.1, 127.6,

125.8, 122.9, 121.4, 121.3, 120.1, 110.1, 65.9, 44.0, 14.0; **HRMS (ESI)** calcd for $C_{26}H_{20}ClN_3O_2Na^+$ $[M+Na]^+$: 464.1137, found: 464.1148; **HPLC Date** 90% ee (Daicel Chiralpak ADH column, hexane/isopropanol = 85/15, λ = 254 nm, 30 °C, 1 mL/min, t_{major} = 16.9 min, t_{minor} = 15.4 min).

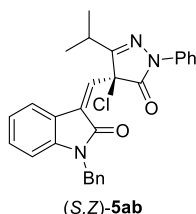


Peak	RetTime	Area	Heigh	Area%
1	15.320	3887639	92109	48.500
2	16.549	4128159	88634	51.500

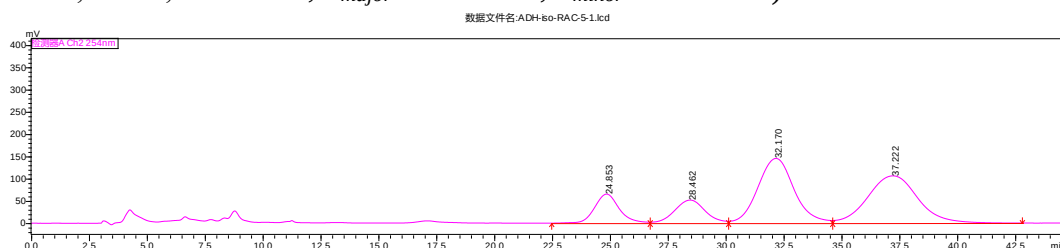


Peak	RetTime	Area	Heigh	Area%
1	15.426	1136532	24064	5.538
2	16.881	19387122	320028	94.462

(*S,Z*)-1-benzyl-3-((4-chloro-3-isopropyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5ab)

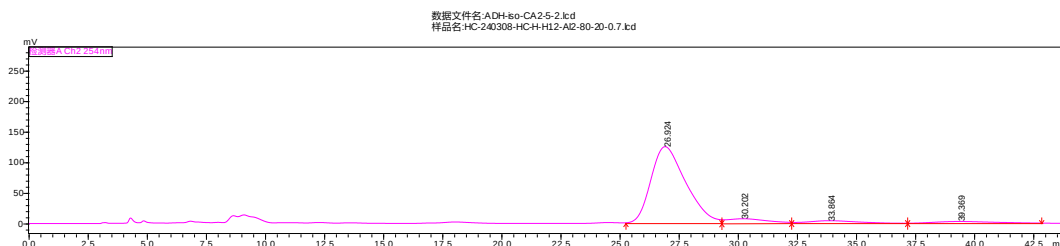


Yellow solid; **m.p.** 149-150 °C; **Yield:** 78 mg, 83%; *Z/E* = 93:7; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25}$ = -143.61 (c 0.12, $CHCl_3$); **¹H NMR** (500 MHz, $CHCl_3-d$) δ 7.98-7.94 (m, 2H), 7.53-7.51 (m, 1H), 7.46-7.42 (m, 2H), 7.35-7.25 (m, 3H), 7.25-7.20 (m, 2H), 7.20-7.16 (m, 2H), 7.06-7.04 (m, 1H), 6.88 (s, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 4.95 (d, *J* = 15.8 Hz, 1H), 4.70 (d, *J* = 15.8 Hz, 1H), 2.89-2.81 (m, 1H), 1.43 (d, *J* = 6.9 Hz, 3H), 1.26 (d, *J* = 6.9 Hz, 3H); **¹³C NMR** (126 MHz, $CHCl_3-d$) δ 168.4, 165.1, 160.1, 143.7, 138.3, 135.7, 132.3, 131.4, 129.7, 129.2, 129.1, 128.0, 127.5, 125.7, 122.8, 121.4, 121.3, 120.2, 110.0, 65.9, 43.9, 29.8, 21.5, 21.2; **HRMS (ESI)** calcd for $C_{28}H_{24}ClN_3O_2Na^+$ $[M+Na]^+$: 492.1450, found: 492.1457; **HPLC Date** 88% ee (Daicel Chiralpak ADH column, hexane/isopropanol = 95/5, λ = 254 nm, 30 °C, 1 mL/min, t_{major} = 26.9 min, t_{minor} = 30.2 min).



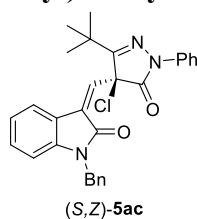
Peak	RetTime	Area	Heigh	Area%
1	24.853			
2	29.462			
3	32.170			
4	37.222			

1	24.853	4807977	65231	11.660
2	28.462	4721596	51767	11.450
3	32.170	15765243	145280	38.231
4	37.222	15941748	106095	38.659

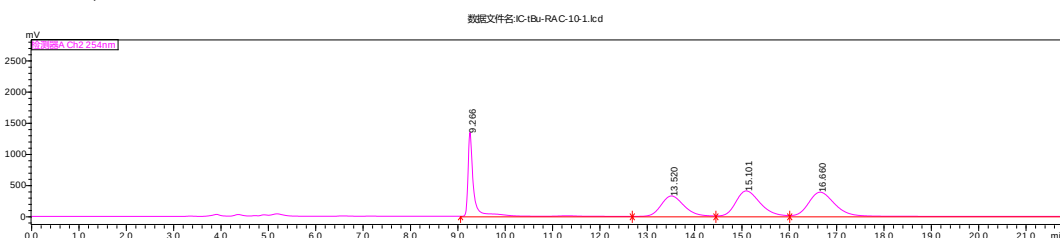


Peak	RetTime	Area	Height	Area%
1	26.924	12793730	125074	87.159
2	30.202	884795	7514	6.028
3	33.864	540231	3997	3.680
4	39.369	459773	2717	3.132

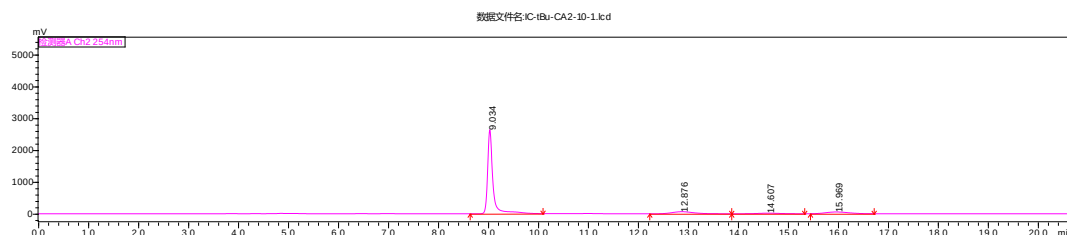
(*S,Z*)-1-benzyl-3-((3-(tert-butyl)-4-chloro-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5ac)



Yellow solid; **m.p.** 142-143 °C; **Yield:** 94 mg, 98%; *Z/E* = 90:10; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -246.03$ (c 0.11, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.97-7.89 (m, 2H), 7.53-7.51 (m, 1H), 7.44-7.38 (m, 2H), 7.28-7.27 (m, 1H), 7.26-7.23 (m, 2H), 7.22-7.19 (m, 2H), 7.17-7.13 (m, 2H), 7.05-7.02 (m, 1H), 6.91 (s, 1H), 6.63 (d, *J* = 7.8 Hz, 1H), 4.97 (d, *J* = 15.8 Hz, 1H), 4.65 (d, *J* = 15.8 Hz, 1H), 1.36 (s, 9H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.6, 165.3, 161.6, 143.7, 138.4, 135.8, 131.8, 131.3, 130.5, 129.2, 129.1, 128.0, 127.5, 125.7, 122.8, 121.3, 120.1, 110.0, 65.7, 43.9, 36.8, 29.9; **HRMS (ESI)** calcd for C₂₉H₂₆ClN₃O₂Na⁺ [M+Na]⁺: 506.1607, found: 506.1616; **HPLC Data** 82% ee (Daicel Chiralpak IC column, hexane/isopropanol = 90/10, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 9.0 min, *t*_{minor} = 12.9 min).

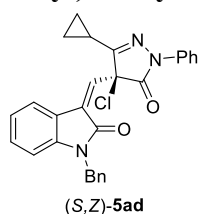


Peak	RetTime	Area	Height	Area%
1	9.266	11442503	1346770	21.951
2	13.520	11046235	327213	21.191
3	15.101	14669105	408410	28.141
4	16.660	14968702	387640	28.716

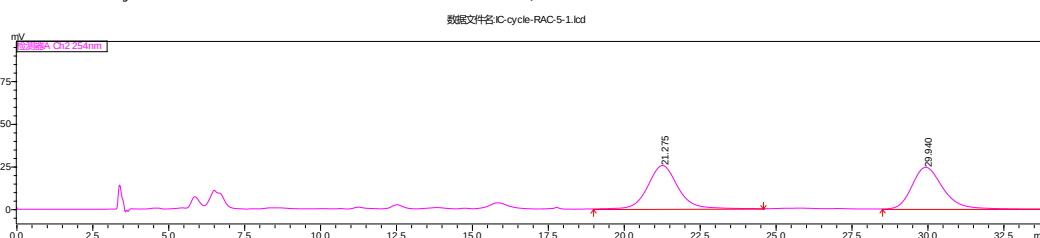


Peak	RetTime	Area	Heigh	Area%
1	9.034	19621131	2639314	82.242
2	12.876	1912760	64833	8.017
3	14.607	588419	17651	2.466
4	15.969	1735607	54614	7.275

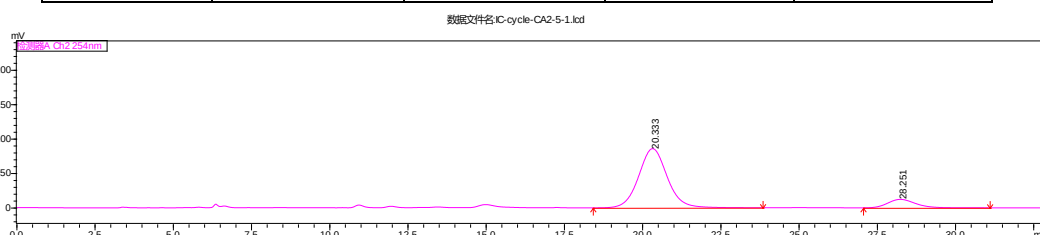
(*S,Z*)-1-benzyl-3-((4-chloro-3-cyclopropyl-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5ad)



Yellow solid; **m.p.** 148-149 °C; **Yield:** 86 mg, 91%; **Z/E** = 88:12; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = +5.60$ (c 0.12, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.90-7.89 (m, 2H), 7.52-7.50 (m, 1H), 7.42-7.39 (m, 2H), 7.29 (dd, *J* = 14.5, 7.3 Hz, 2H), 7.26-7.21 (m, 2H), 7.21-7.15 (m, 3H), 7.05-7.02 (m, 1H), 6.88 (s, 1H), 6.64 (d, *J* = 7.9 Hz, 1H), 4.92 (d, *J* = 15.8 Hz, 1H), 4.71 (d, *J* = 15.8 Hz, 1H), 1.69-1.64 (m, 1H), 1.32-1.27 (m, 1H), 1.03-0.82 (m, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.3, 165.1, 158.1, 143.8, 138.3, 135.8, 132.3, 131.4, 129.6, 129.2, 129.1, 128.0, 127.5, 125.7, 122.8, 121.5, 121.3, 120.1, 110.1, 65.9, 43.9, 9.7, 9.0, 7.4; **HRMS (ESI)** calcd for C₂₈H₂₂ClN₃O₂Na⁺ [M+Na]⁺: 490.1294, found: 490.1308; **HPLC** **Date** 76% ee (Daicel Chiralpak IC column, hexane/isopropanol = 95/5, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 20.3 min, *t*_{minor} = 28.3 min).



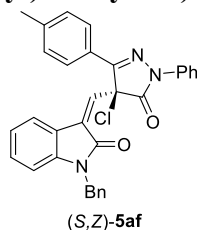
Peak	RetTime	Area	Heigh	Area%
1	21.275	1764745	25451	50.597
2	29.940	1723086	24430	49.403



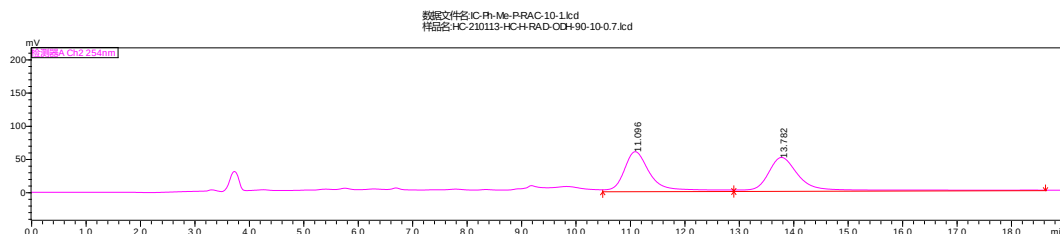
Peak	RetTime	Area	Heigh	Area%
1	20.333	5458496	85931	87.808

2	28.251	757913	12268	12.192
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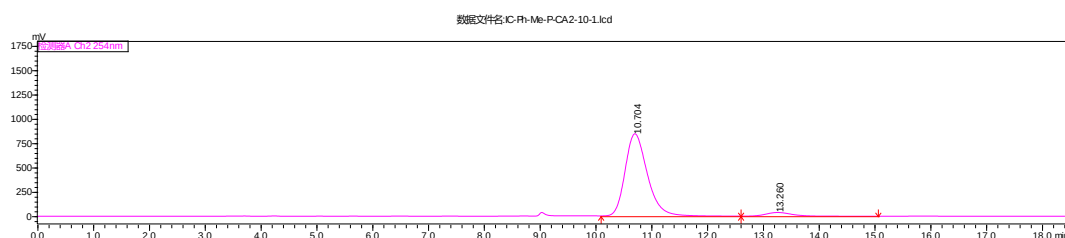
(*S,Z*)-1-benzyl-3-((4-chloro-5-oxo-1-phenyl-3-(*p*-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5af)



Yellow solid; **m.p.** 111-112 °C; **Yield:** 100 mg, 97%; *Z/E* = 88:12; petroleum ether/EtOAc = 20:1; $[\alpha]_{\text{D}}^{25} = -290.22$ (c 0.15, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.09-8.01 (m, 2H), 7.85-7.82 (m, 2H), 7.54-7.51 (m, 1H), 7.49-7.44 (m, 2H), 7.33-7.27 (m, 1H), 7.25 (s, 2H), 7.23-7.20 (m, 3H), 7.18-7.16 (m, 1H), 7.11 (s, 1H), 7.08 (dd, *J* = 7.1, 2.4 Hz, 2H), 7.03-7.00 (m, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 4.80-4.66 (m, 2H), 2.38 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.6, 165.1, 152.5, 143.7, 141.3, 138.3, 135.6, 131.8, 131.3, 130.5, 129.9, 129.2, 129.0, 127.9, 127.6, 127.5, 126.3, 126.0, 122.7, 121.5, 121.2, 120.4, 109.9, 64.5, 43.9, 21.9; **HRMS (ESI)** calcd for C₃₂H₂₄ClN₃O₂Na⁺ [*M*+Na]⁺: 540.1450, found: 540.1469; **HPLC** **Date** 90% ee (Daicel Chiralpak IC column, hexane/isopropanol = 90/10, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 10.7 min, *t*_{minor} = 13.3 min).

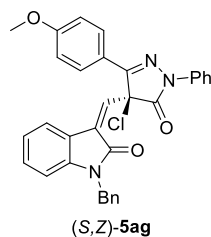


Peak	RetTime	Area	Heigh	Area%
1	11.096	1715262	57351	49.840
2	13.782	1726279	48858	50.160

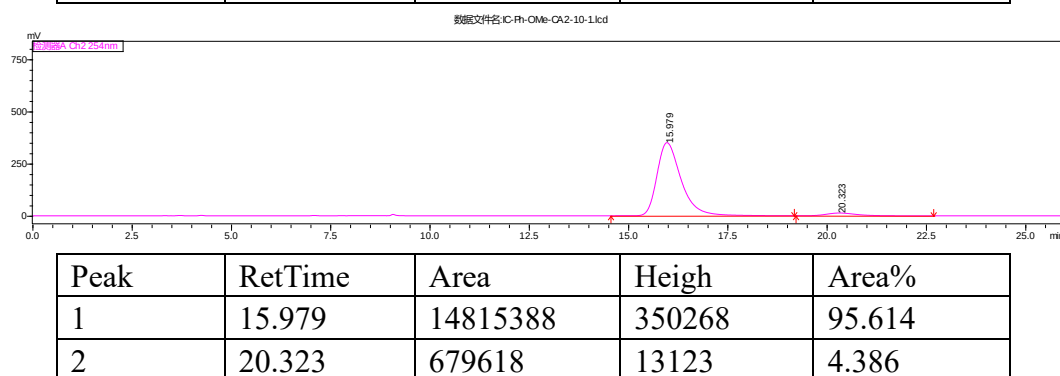
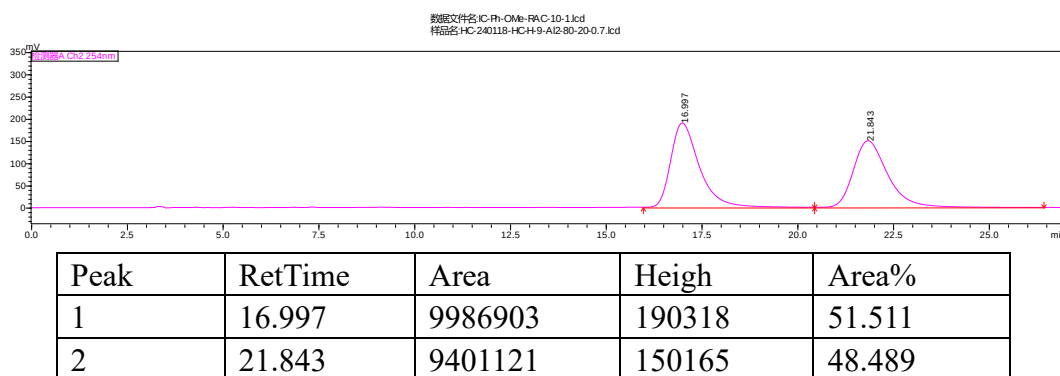


Peak	RetTime	Area	Heigh	Area%
1	10.704	23686741	847319	94.714
2	13.260	1321910	38653	5.286

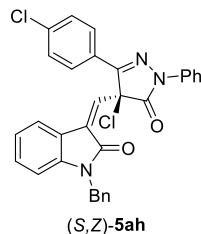
(*S,Z*)-1-benzyl-3-((4-chloro-3-(4-methoxyphenyl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5ag)



Yellow solid; **m.p.** 112-114 °C; **Yield:** 92 mg, 86%; **Z/E** = 93:7; petroleum ether/EtOAc = 20:1; $[\alpha]_{\text{D}}^{25} = -259.00$ (c 0.20, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.08-8.03 (m, 2H), 7.91-7.90 (m, 2H), 7.54-7.53 (m, 1H), 7.47 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.28-7.27 (m, 1H), 7.25-7.20 (m, 3H), 7.18-7.16 (m, 1H), 7.11 (s, 1H), 7.09-7.05 (m, 2H), 7.04-7.00 (m, 1H), 6.96-6.94 (m, 2H), 6.57 (d, *J* = 7.8 Hz, 1H), 4.74 (q, *J* = 15.8 Hz, 2H), 3.83 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.5, 165.1, 161.8, 152.3, 143.7, 138.3, 135.6, 131.9, 131.3, 130.6, 129.3, 129.2, 129.0, 127.9, 127.5, 125.9, 122.7, 121.7, 121.5, 121.2, 120.4, 114.7, 110.0, 64.6, 55.8, 43.9; **HRMS (ESI)** calcd for C₃₂H₂₄ClN₃O₃Na⁺ [M+Na]⁺: 556.1399, found: 556.1408; **HPLC** **Date** 92% ee (Daicel Chiralpak IC column, hexane/isopropanol = 90/10, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 16.0 min, *t*_{minor} = 20.3 min).

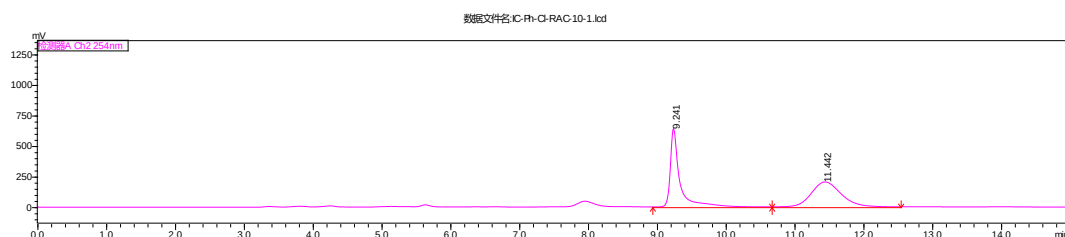


(S,Z)-1-benzyl-3-((4-chloro-3-(4-chlorophenyl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((S,Z)-5ah)

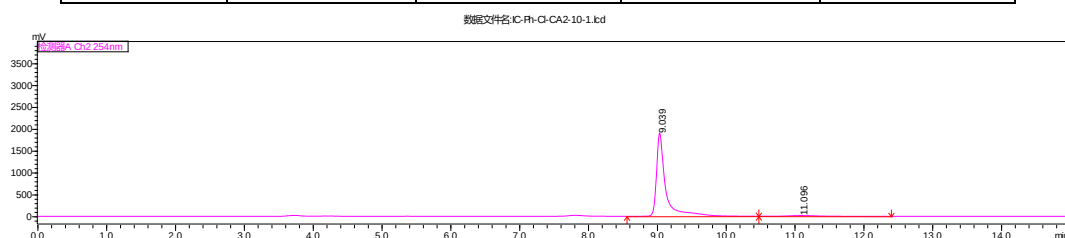


Yellow solid; **m.p.** 108-110 °C; **Yield:** 98 mg, 91%; **Z/E** = 86:14; petroleum ether/EtOAc = 20:1; $[\alpha]_{\text{D}}^{25} = -149.17$ (c 0.12, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.05-7.97 (m, 2H), 7.91-7.84 (m, 2H), 7.54-7.52 (m, 1H), 7.50-7.44 (m, 2H), 7.42-7.39 (m, 2H), 7.29-7.27 (m, 1H), 7.25-7.20 (m, 3H), 7.19-7.16 (m, 1H), 7.07-7.04 (m, 3H), 7.04-7.01 (m, 1H), 6.58 (d, *J* = 7.8 Hz, 1H), 4.82-4.65 (m, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.5, 165.1, 151.4, 143.7, 138.1, 136.9, 135.5, 132.3, 131.5, 129.9, 129.5, 129.3, 129.1, 128.8, 128.0, 127.6, 127.5, 126.3, 122.9, 121.3, 121.2, 120.5, 110.1, 64.1, 43.9; **HRMS (ESI)** calcd for C₃₁H₂₁Cl₂N₃O₂Na⁺ [M+Na]⁺: 560.0904, found: 560.0905; **HPLC** **Date** 96% ee (Daicel Chiralpak IC column,

hexane/isopropanol = 90/10, λ = 254 nm, 30 °C, 1 mL/min, t_{major} = 9.0 min, t_{minor} = 11.1 min).

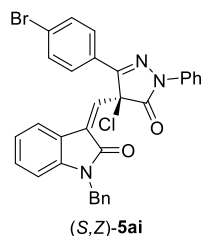


Peak	RetTime	Area	Heigh	Area%
1	9.241	6333191	643269	49.717
2	11.442	6405377	206134	50.283

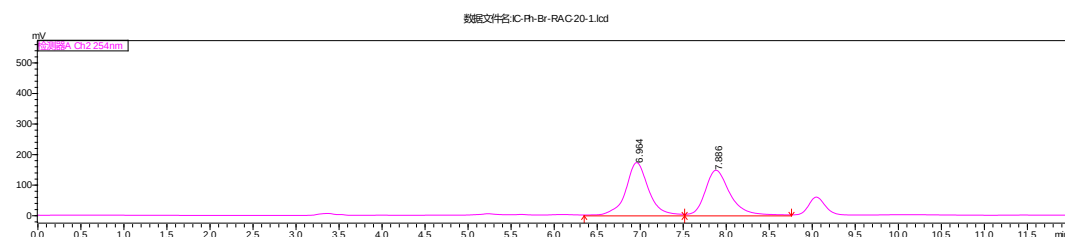


Peak	RetTime	Area	Heigh	Area%
1	9.039	17450054	1900675	97.677
2	11.096	414999	15923	2.323

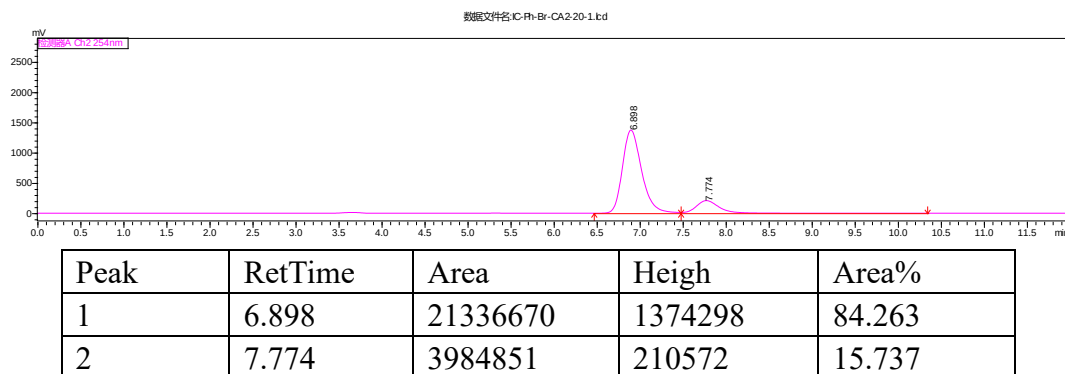
(*S,Z*)-1-benzyl-3-((3-(4-bromophenyl)-4-chloro-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5ai)



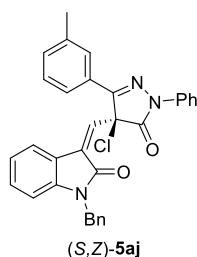
Yellow solid; **m.p.** 124-125 °C; **Yield:** 106 mg, 92%; *Z/E* = 89:11; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25}$ = -1.54 (c 0.13, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.03-7.96 (m, 2H), 7.83-7.77 (m, 2H), 7.60-7.50 (m, 3H), 7.47 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.30-7.26 (m, 1H), 7.26-7.20 (m, 3H), 7.20-7.16 (m, 1H), 7.09-7.04 (m, 3H), 7.04-7.01 (m, 1H), 6.57 (d, *J* = 7.9 Hz, 1H), 4.80-4.67 (m, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.5, 165.1, 151.5, 143.7, 138.1, 135.5, 132.5, 132.3, 131.5, 129.9, 129.3, 129.1, 129.0, 128.1, 128.0, 127.5, 126.3, 125.3, 122.9, 121.3, 121.2, 120.5, 110.1, 64.1, 43.9; **HRMS (ESI)** calcd for C₃₁H₂₁BrClN₃O₂Na⁺ [M+Na]⁺: 604.0399, found: 604.0417; **HPLC Date** 68% ee (Daicel Chiralpak IC column, hexane/isopropanol = 80/20, λ = 254 nm, 30 °C, 1 mL/min, t_{major} = 6.9 min, t_{minor} = 7.8 min).



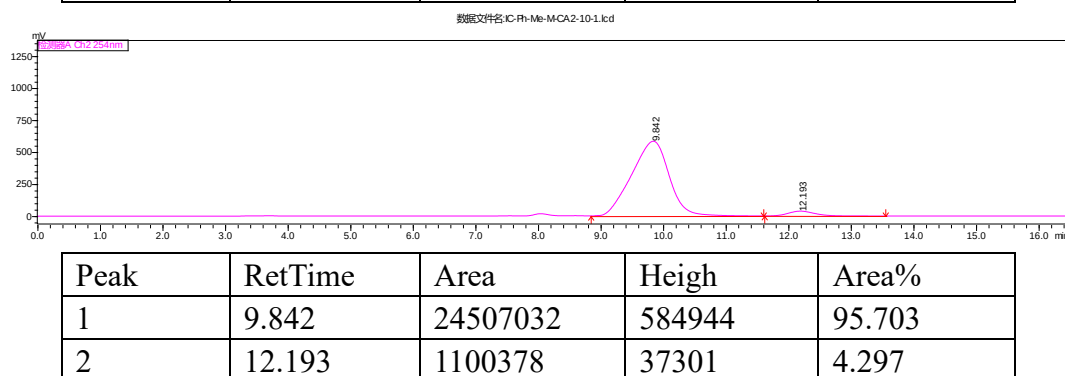
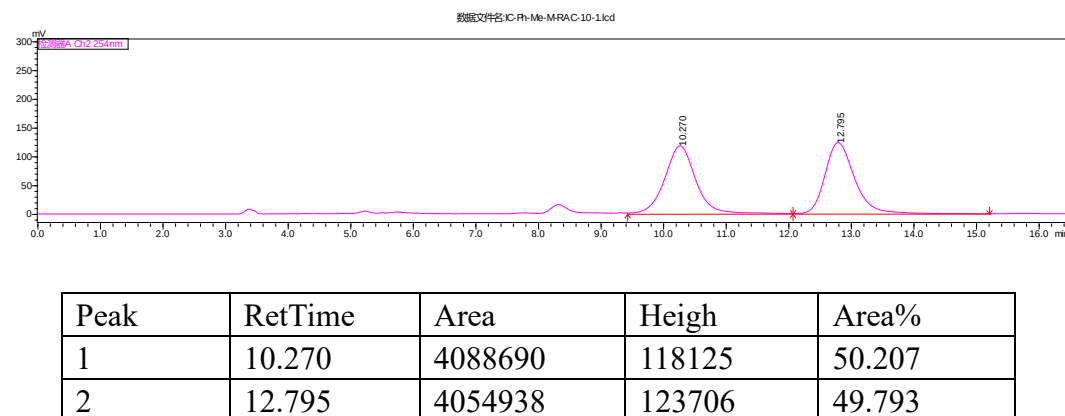
Peak	RetTime	Area	Heigh	Area%
1	6.964	3180409	172707	51.768
2	7.886	2963149	147664	48.232



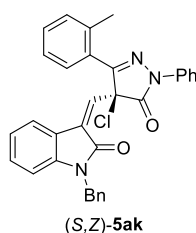
(*S,Z*)-1-benzyl-3-((4-chloro-5-oxo-1-phenyl-3-(*m*-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5aj)



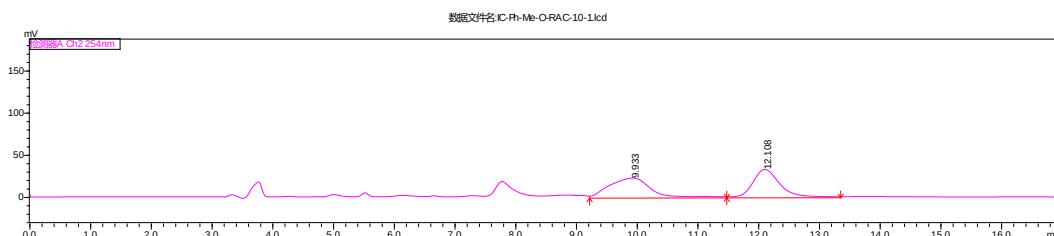
Yellow solid; **m.p.** 105-107 °C; **Yield:** 96 mg, 94%; *Z/E* = 88:12; petroleum ether/EtOAc = 20:1; $[\alpha]_D^{25} = -176.70$ (c 0.11, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.08-8.01 (m, 2H), 7.85-7.81 (m, 1H), 7.70-7.69 (m, 1H), 7.53 (dd, *J* = 7.6, 1.1 Hz, 1H), 7.50-7.45 (m, 2H), 7.33-7.28 (m, 2H), 7.26-7.24 (m, 1H), 7.23-7.20 (m, 3H), 7.19-7.17 (m, 1H), 7.12-7.07 (m, 3H), 7.04-6.99 (m, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 4.79-4.68 (m, 2H), 2.40 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.4, 164.9, 152.3, 143.4, 138.7, 138.0, 135.4, 131.6, 131.5, 131.0, 130.2, 129.0, 128.8, 128.7, 127.8, 127.7, 127.3, 125.8, 124.7, 122.5, 121.3, 121.0, 120.2, 109.7, 64.2, 43.6, 21.6; **HRMS (ESI)** calcd for C₃₂H₂₄ClN₃O₂Na⁺ [*M*+Na]⁺: 540.1450, found: 540.1462; **HPLC Date** 92% ee (Daicel Chiralpak IC column, hexane/isopropanol = 90/10, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 9.8 min, *t*_{minor} = 12.2 min).



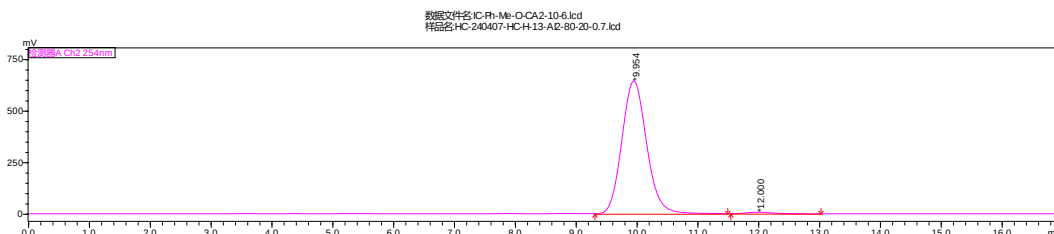
(*S,Z*)-1-benzyl-3-((4-chloro-5-oxo-1-phenyl-3-(*o*-tolyl)-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5ak)



Yellow solid; **m.p.** 104-105 °C; **Yield:** 98 mg, 95%; *Z/E* = 94:6; petroleum ether/EtOAc = 20:1; $[\alpha]_{\text{D}}^{25} = -15.42$ (c 0.08, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.00 (dd, *J* = 8.7, 1.1 Hz, 2H), 7.75 (dd, *J* = 7.6, 1.2 Hz, 1H), 7.50-7.44 (m, 3H), 7.33-7.28 (m, 2H), 7.28-7.26 (m, 1H), 7.25 (s, 1H), 7.24-7.22 (m, 3H), 7.17-7.15 (m, 1H), 7.08 (dd, *J* = 7.6, 1.9 Hz, 2H), 7.02-6.94 (m, 2H), 6.59 (d, *J* = 7.9 Hz, 1H), 4.88 (d, *J* = 15.7 Hz, 1H), 4.62 (d, *J* = 15.8 Hz, 1H), 2.68 (s, 3H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.4, 165.2, 152.6, 143.7, 140.0, 138.4, 135.7, 132.6, 131.8, 131.3, 130.5, 130.1, 129.3, 129.1, 129.0, 128.4, 128.0, 127.6, 126.1, 125.9, 122.8, 121.5, 121.4, 120.1, 109.9, 66.0, 43.9, 23.0; **HRMS (ESI)** calcd for C₃₂H₂₄ClN₃O₂Na⁺ [M+Na]⁺: 540.1450, found: 540.1454; **HPLC** **Date** 98% ee (Daicel Chiralpak IC column, hexane/isopropanol = 90/10, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 10.0 min, *t*_{minor} = 12.0 min).

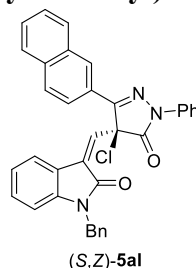


Peak	RetTime	Area	Heigh	Area%
1	9.933	1096207	23337	51.687
2	12.108	1024650	33201	48.313



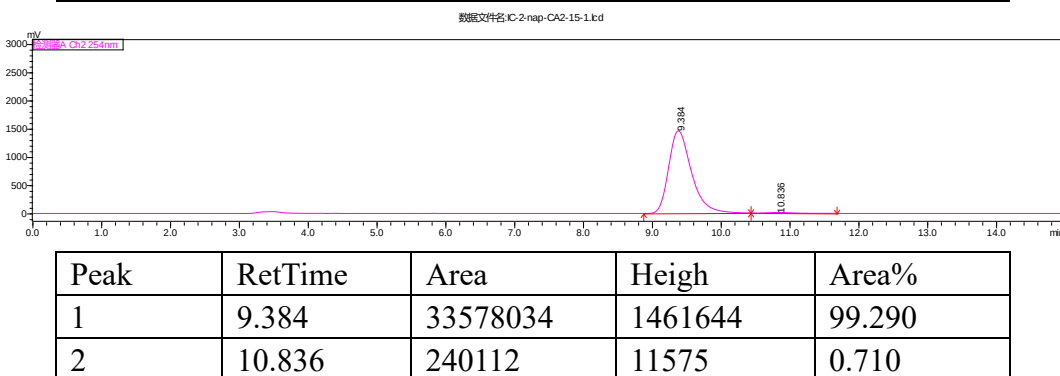
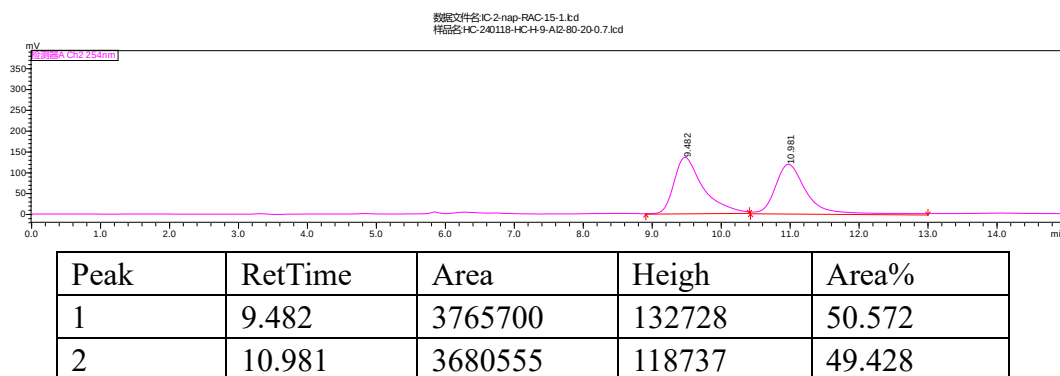
Peak	RetTime	Area	Heigh	Area%
1	9.954	18261088	644382	98.970
2	12.000	190054	6724	1.030

(*S,Z*)-1-benzyl-3-((4-chloro-3-(naphthalen-2-yl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5al)

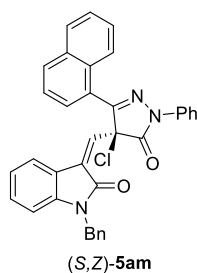


Yellow solid; **m.p.** 122-124 °C; **Yield:** 108 mg, 98%; *Z/E* = 87:13; petroleum ether/EtOAc = 20:1; $[\alpha]_{\text{D}}^{25} = -37.33$ (c 0.15, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.27 (s, 1H), 8.15 (dd, *J* = 8.7, 1.8 Hz, 1H), 8.10-8.05 (m, 2H), 7.92-7.86 (m, 2H), 7.85-7.82 (m, 1H), 7.58-7.54 (m, 1H), 7.54-7.51 (m, 2H), 7.51-7.42 (m, 2H), 7.32-7.26 (m, 1H), 7.21 (s, 1H), 7.18-7.15 (m, 2H), 7.14-7.10 (m, 2H), 7.05-

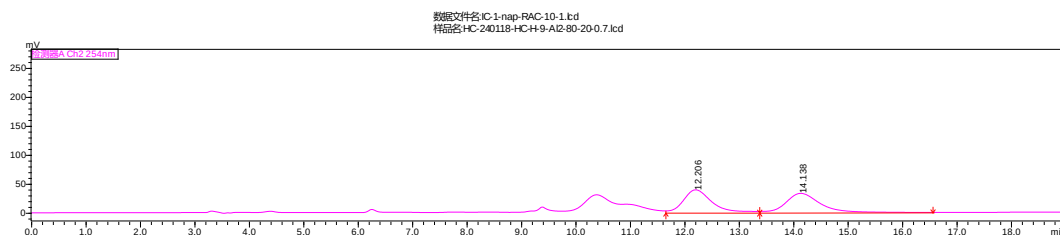
6.98 (m, 3H), 6.53 (d, $J = 7.8$ Hz, 1H), 4.72 (q, $J = 15.8$ Hz, 2H); ^{13}C NMR (126 MHz, Chloroform- d) δ 168.2, 164.6, 152.1, 143.2, 137.8, 135.0, 134.1, 132.7, 131.6, 130.8, 129.9, 128.8, 128.7, 128.6, 128.5, 127.7, 127.6, 127.4, 127.3, 127.0, 126.6, 126.1, 125.7, 123.7, 122.3, 121.0, 120.7, 120.0, 109.5, 64.0, 43.4; **HRMS (ESI)** calcd for $\text{C}_{35}\text{H}_{24}\text{ClN}_3\text{O}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 576.1450, found: 576.1459; **HPLC Data** 98% ee (Daicel Chiralpak IC column, hexane/isopropanol = 85/15, $\lambda = 254$ nm, 30 °C, 1 mL/min, $t_{\text{major}} = 9.4$ min, $t_{\text{minor}} = 10.8$ min).



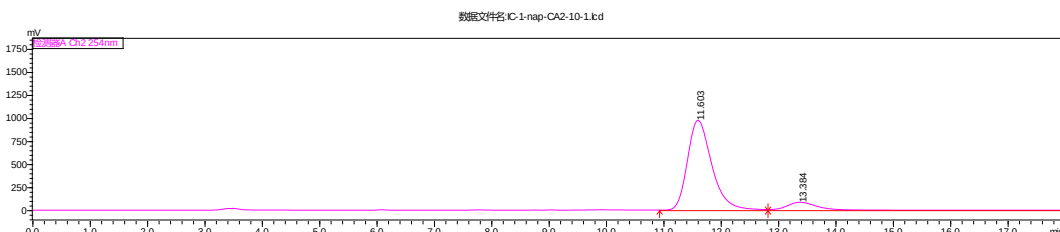
(*S,Z*)-1-benzyl-3-((4-chloro-3-(naphthalen-1-yl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5am)



Yellow solid; **m.p.** 112-114 °C; **Yield:** 90 mg, 83%; $Z/E > 95:5$; petroleum ether/EtOAc = 20:1; $[\alpha]_{\text{D}}^{25} = -201.43$ (c 0.14, CHCl_3); ^1H NMR (500 MHz, Chloroform- d) δ 9.06-8.91 (m, 1H), 8.11-8.02 (m, 3H), 7.92-7.89 (m, 1H), 7.88-7.85 (m, 1H), 7.55-7.53 (m, 2H), 7.51-7.46 (m, 3H), 7.42-7.40 (m, 1H), 7.30-7.28 (m, 1H), 7.19-7.14 (m, 1H), 7.14-7.06 (m, 3H), 7.02-6.94 (m, 3H), 6.93 (s, 1H), 6.57-6.50 (m, 1H), 4.96 (d, $J = 15.6$ Hz, 1H), 4.52 (d, $J = 15.6$ Hz, 1H); ^{13}C NMR (126 MHz, Chloroform- d) δ 168.6, 165.3, 152.1, 143.6, 138.4, 135.6, 134.6, 132.1, 131.9, 131.5, 131.3, 130.3, 129.4, 129.0, 128.8, 128.0, 127.9, 127.7, 127.6, 126.9, 126.8, 126.7, 126.1, 125.0, 122.8, 121.4, 120.4, 109.8, 66.4, 43.9; **HRMS (ESI)** calcd for $\text{C}_{35}\text{H}_{24}\text{ClN}_3\text{O}_2\text{Na}^+ [\text{M}+\text{Na}]^+$: 576.1450, found: 576.1460; **HPLC Data** 84% ee (Daicel Chiralpak IC column, hexane/isopropanol = 90/10, $\lambda = 254$ nm, 30 °C, 1 mL/min, $t_{\text{major}} = 11.6$ min, $t_{\text{minor}} = 13.4$ min).

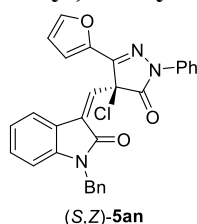


Peak	RetTime	Area	Heigh	Area%
1	12.206	1445933	39500	49.811
2	14.138	1456882	33240	50.189

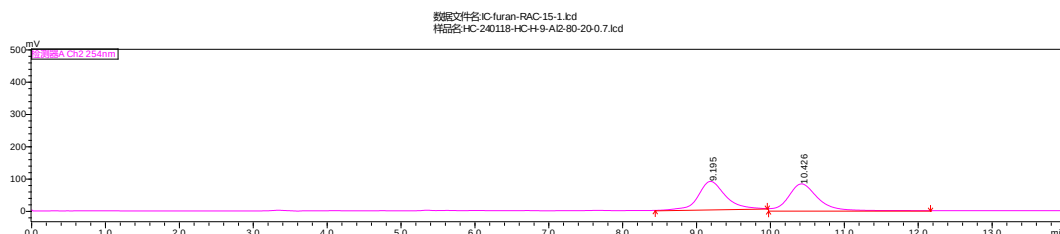


Peak	RetTime	Area	Heigh	Area%
1	11.603	28864575	976710	91.611
2	13.384	2643350	80764	8.389

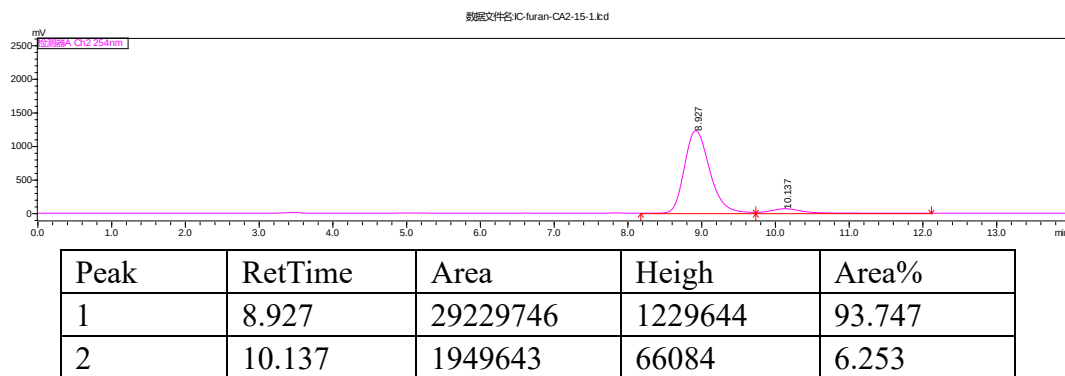
(*S,Z*)-1-benzyl-3-((4-chloro-3-(furan-2-yl)-5-oxo-1-phenyl-4,5-dihydro-1H-pyrazol-1-yl)methylene)indolin-2-one ((*S,Z*)-5an)



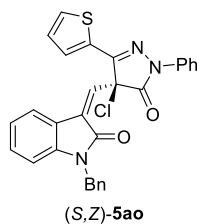
Yellow solid; **m.p.** 166-167 °C; **Yield:** 70 mg, 72%; **Z/E** = 82:18; petroleum ether/EtOAc = 20:1; $[\alpha]_{\text{D}}^{25} = -176.19$ (c 0.11, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 7.98 (dd, *J* = 8.8, 1.2 Hz, 2H), 7.57-7.52 (m, 2H), 7.45 (dd, *J* = 8.6, 7.4 Hz, 2H), 7.33-7.27 (m, 1H), 7.26-7.22 (m, 3H), 7.21-7.17 (m, 1H), 7.15-7.10 (m, 2H), 7.06-7.01 (m, 2H), 6.93-6.92 (m, 1H), 6.59 (d, *J* = 7.9 Hz, 1H), 6.51 (dd, *J* = 3.5, 1.7 Hz, 1H), 4.77 (s, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 167.7, 165.2, 145.3, 145.1, 145.0, 143.8, 138.1, 135.6, 131.8, 131.4, 129.9, 129.3, 129.1, 128.0, 127.6, 126.2, 122.8, 121.5, 121.3, 120.7, 119.9, 113.5, 112.4, 110.1, 63.8, 44.0; **HRMS (ESI)** calcd for C₂₉H₂₀ClN₃O₃Na⁺ [M+Na]⁺: 516.1086, found: 516.1099; **HPLC Data** 88% ee (Daicel Chiralpak IC column, hexane/isopropanol = 85/15, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 8.9 min, *t*_{minor} = 10.1 min).



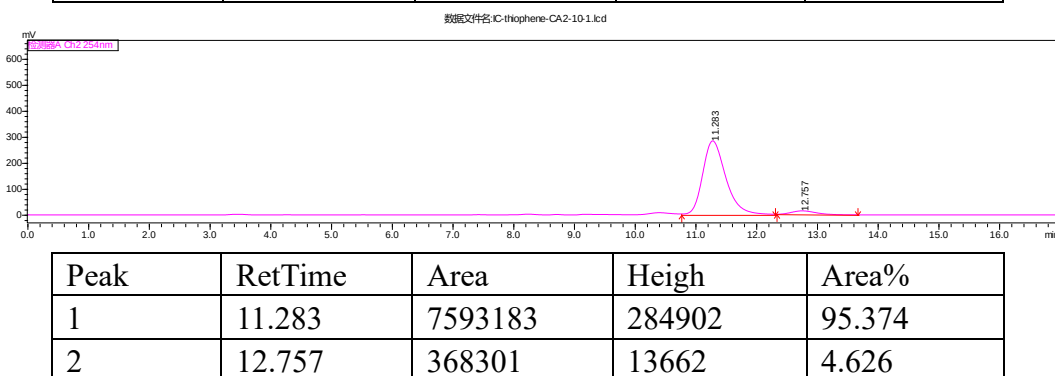
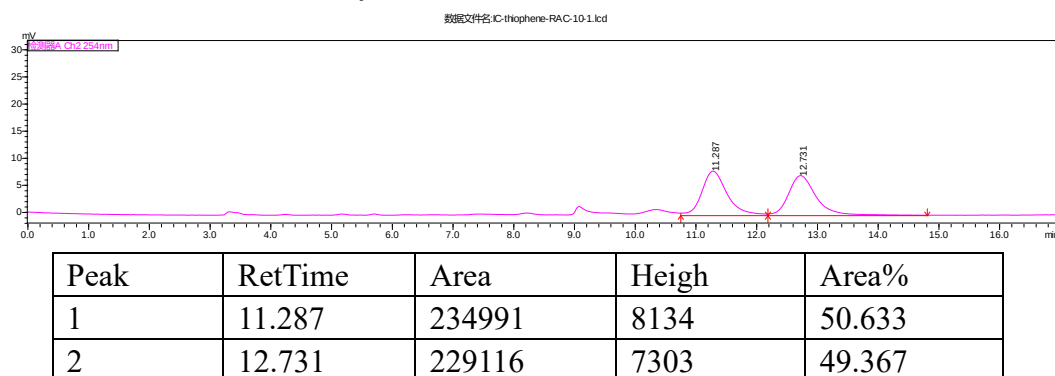
Peak	RetTime	Area	Heigh	Area%
1	9.195	2185509	87055	49.306
2	10.426	2247023	82882	50.694



(*S,Z*)-1-benzyl-3-((4-chloro-5-oxo-1-phenyl-3-(thiophen-2-yl)-4,5-dihydro-1H-pyrazol-4-yl)methylene)indolin-2-one ((*S,Z*)-5ao)



Yellow solid; **m.p.** 179-180 °C; **Yield:** 84 mg, 84%; *Z/E* = 85:13; petroleum ether/EtOAc = 20:1; $[\alpha]_{\text{D}}^{25} = -247.69$ (c 0.13, CHCl₃); **¹H NMR** (500 MHz, Chloroform-*d*) δ 8.02-7.95 (m, 2H), 7.55-7.53 (m, 1H), 7.49-7.45 (m, 2H), 7.45-7.40 (m, 2H), 7.27-7.24 (m, 2H), 7.24-7.22 (m, 1H), 7.22-7.20 (m, 2H), 7.18 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.10 (dd, *J* = 7.7, 1.8 Hz, 2H), 7.07 (dd, *J* = 5.0, 3.7 Hz, 1H), 7.05-7.00 (m, 2H), 6.59 (d, *J* = 7.8 Hz, 1H), 4.81-4.70 (m, 2H); **¹³C NMR** (126 MHz, Chloroform-*d*) δ 168.1, 165.1, 148.6, 143.8, 138.1, 135.6, 132.5, 132.3, 131.5, 129.8, 129.3, 129.2, 129.1, 129.0, 128.1, 128.0, 127.6, 126.2, 122.9, 121.4, 121.3, 120.5, 110.1, 64.5, 44.0; **HRMS (ESI)** calcd for C₂₉H₂₀ClN₃O₂SN⁺ [M+Na]⁺: 532.0858, found: 532.0871; **HPLC Date** 90% ee (Daicel Chiralpak IC column, hexane/isopropanol = 90/10, λ = 254 nm, 30 °C, 1 mL/min, *t*_{major} = 11.3 min, *t*_{minor} = 12.8 min).



3. Additional Experimental Data of Table S1-S5

Table S1. Solvents screening for the product 5aa^a

Reaction scheme: (Z)-4aa $\xrightarrow[\text{NCS, solvent, rt}]{\text{No base}}$ (Z)-5aa + (E)-5aa + 6

Entry ^a	Sol.	Yield (%) ^b	ee (%) ^c	Z/E ^d
1	CH ₂ Cl ₂	51	--	67:33
2	Toluene	52	--	87:13
3	CHCl₃	34	--	92:8
4	Ether	46	--	67:33
5	EtOH	46	--	67:33
6	Acetone	66	--	9:91

^a Reaction conditions: **4aa** (0.05 mmol), NCS (0.1 mmol) in 1.0 mL of solvent at room temperature. In all the cases, no product **6** was observed. ^b Isolated yield. ^c Determined by chiral HPLC analysis. ^d Determined by ¹H NMR of the crude reaction mixture.

Table S2. Optimization of reaction conditions for the *E/Z* ratio of 5aa

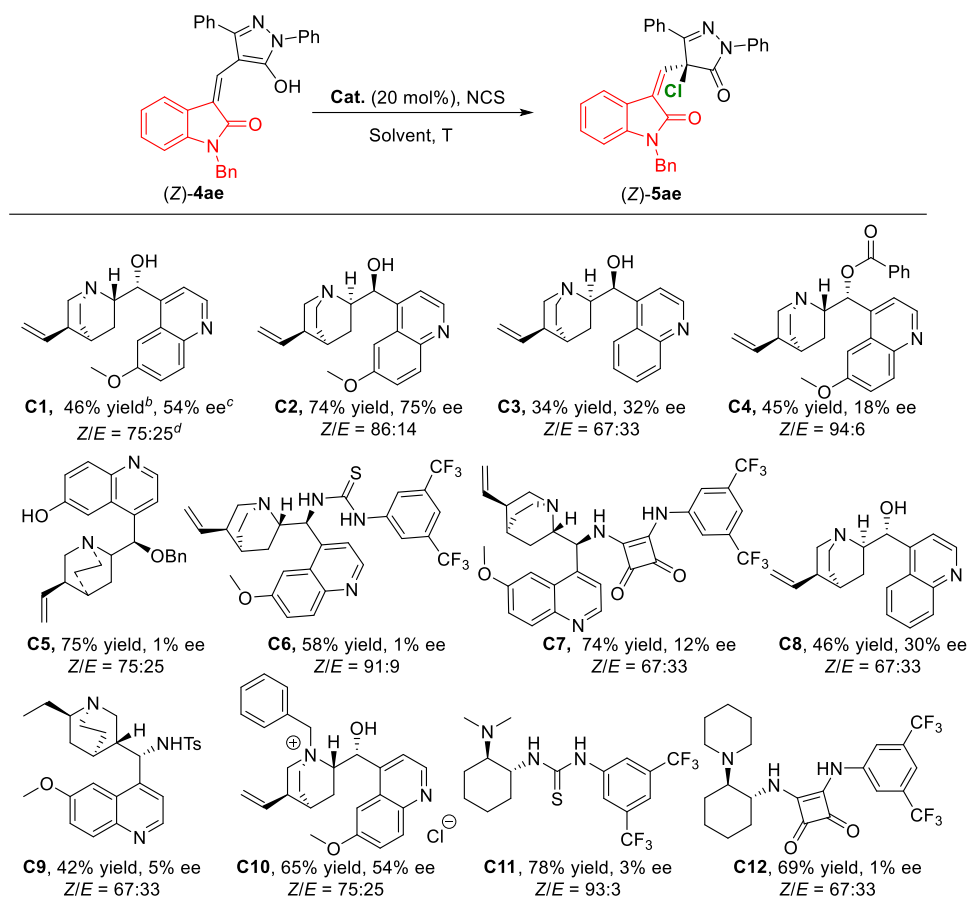
Reaction scheme: (Z)-4aa $\xrightarrow[\text{NCS, solvent, rt}]{\text{DBU or K}_2\text{CO}_3}$ (Z)-5aa + (E)-5aa + 6

Solvent ^a	Entry	Base	Yield (%) ^b	<i>Z/E</i> ^c
CHCl ₃	1	TEA	95	67:33
	2	DIPEA	87	67:33
	3	DABCO	87	75:25
	4	DBU	95	16:84
	5	TMG	93	25:75
	6	K₂CO₃	85	>95:5
	7	Na ₂ CO ₃	64	75:25
	8	K ₃ PO ₄	58	80:20
	9 ^d	K ₂ CO ₃	82	75:25
Solvent ^a	Entry	Base	Yield (%) ^b	<i>Z/E</i> ^c
Acetone	1	TEA	88	7:93
	2	DIPEA	82	9:91
	3	DABCO	78	7:93
	4	DBU	96	<5:95
	5	TMG	82	7:93
	6	K ₂ CO ₃	59	16:84
	7	Na ₂ CO ₃	79	16:84
	8	K ₃ PO ₄	67	9:91
	9 ^d	DBU	61	14:86

^a Reaction conditions: **4aa** (0.05 mmol), **NCS** (0.1 mmol) and base (20 mol%) in 1.0 mL of solvent at room temperature. In all the cases, no product **6** was observed. ^b Isolated yield.

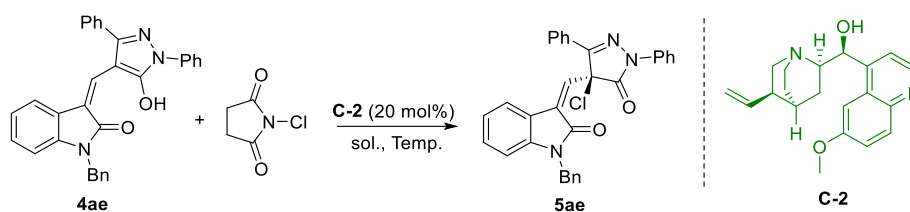
^c Determined by ¹H NMR of the crude reaction mixture. ^d **NCS** (0.075 mmol).

Table S4. Catalyst screening for the product 5ae^a



^a Reaction conditions: **4ae** (0.05 mmol), NCS (0.1 mmol) and base (20 mol%) in 1.0 mL of solvent at rt for 10 min. In all the cases, no product **6** was observed ^b Isolated yield. ^c Determined by chiral HPLC analysis ^d Determined by ¹H NMR of the crude reaction mixture.

Table S5. Optimization of reaction conditions for the 5ae



Entry ^a	Sol.	Temp. (°C)	Yield (%) ^b	ee (%) ^c	Z/E ^d
1	DCM	rt	74	87	90:10
2	DCE	rt	67	87	75:25
3	CHCl ₃	rt	74	75	86:14
4	Mesitylene (Mes.)	rt	48	75	98:2
5	Isopropyl ether (IPE)	rt	55	98	97:3
6	IPE	-30	24	41	87:13
7	DCM	-30	87	85	86:14
8	DCM + IPE (1:4)	-30	68	67	99:1
9	DCM	-78	87	95	80:20
10 ^e	DCM + 4 Å MS	-78	76	95	84:16
11	DCM + Mes. (1:3)	-78	72	93	86:14
12	DCM + Mes. (3:1)	-78	68	91	86:14
13	DCM + Mes. (1:1)	-78	85	93	89:11
14 ^f	DCM + Mes. (1:1)	-78	81	82	87:13
15	DCM + IPE (1:1)	-78	75	93	96:4
16	DCM + IPE + Mes. (1:1:1)	-78	60	88	98:2

^a Reaction conditions: **4ae** (0.05 mmol), NCS (0.1 mmol) and base (20 mol%) in 1.0 mL of solvent at rt for 10 min. In all the cases, no product **6** was observed ^b Isolated yield. ^c determined by chiral HPLC analysis ^d Determined by ¹H NMR of the crude reaction mixture. ^e 4 Å molecular sieves (100 mg) were used. ^f NCS (0.075 mmol)

4. X-ray crystallographic data

Single Crystal X-Ray Data of (E)-5aa

Single crystals of C₂₆H₂₀ClN₃O₂ ((E)-**5aa**) were obtained in a dichloromethane : hexane (1:3) solution. A suitable crystal was selected and mounted on a Bruker D8 VENTURE TXS PHOTON 100 diffractometer. The crystal was kept at 193.00 K during data collection. OLEX2 and SHELXTL were used for Data collection and integration.

Table S6 Crystal data and structure refinement for (E)-5aa.

Identification code	(E)-5aa
Empirical formula	C ₂₆ H ₂₀ ClN ₃ O ₂
Formula weight	441.90
Temperature/K	193.00
Crystal system	triclinic
Space group	P-1
a/Å	8.6024(10)
b/Å	11.4996(12)
c/Å	12.4125(14)
α/°	115.653(3)
β/°	94.820(4)
γ/°	100.152(4)
Volume/Å ³	1071.6(2)
Z	2
ρ _{calc} /cm ³	1.370
μ/mm ⁻¹	0.208
F(000)	460.0
Crystal size/mm ³	0.13 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	3.7 to 61.06
Index ranges	-8 ≤ h ≤ 12, -16 ≤ k ≤ 16, -17 ≤ l ≤ 17
Reflections collected	12707
Independent reflections	6486 [R _{int} = 0.0455, R _{sigma} = 0.0802]
Data/restraints/parameters	6486/0/290
Goodness-of-fit on F ²	1.025
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0582, wR ₂ = 0.1140
Final R indexes [all data]	R ₁ = 0.1168, wR ₂ = 0.1397
Largest diff. peak/hole / e Å ⁻³	0.34/-0.40

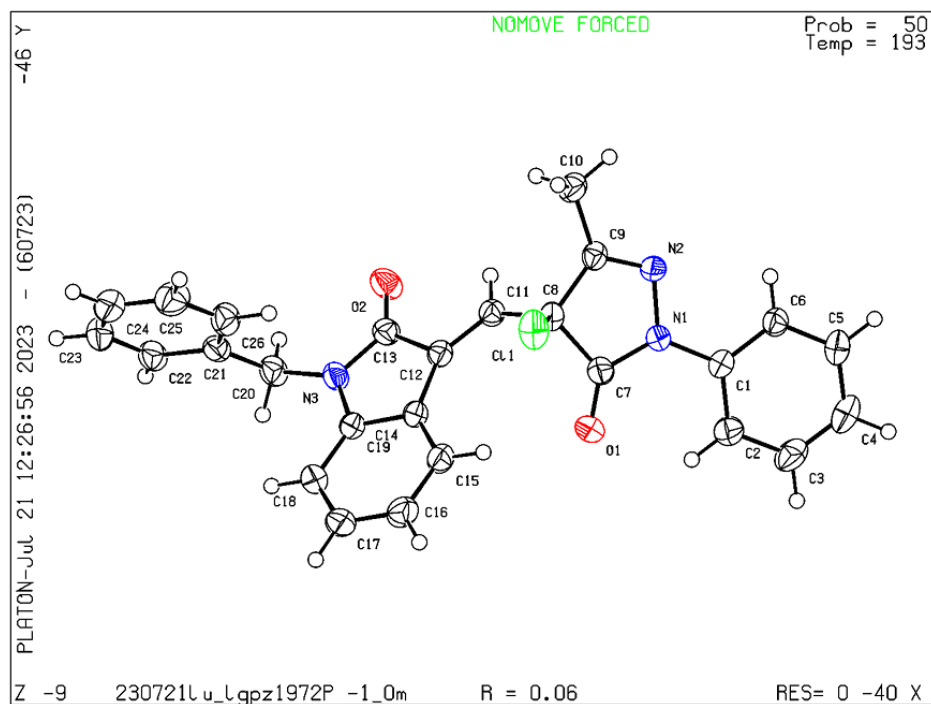


Figure S1. X-ray crystal structure of the product (*E*)-**5aa** (50% ellipsoid contour probability level, **CCDC:2363450**).

Single Crystal X-Ray Data of (Z)-5aa.

Single crystals of C₂₆H₂₀ClN₃O₂ ((Z)-**5aa**) were obtained in a dichloromethane: hexane (1:3) solution. A suitable crystal was selected and mounted on a Bruker D8 VENTURE TXS PHOTON 100 diffractometer. The crystal was kept at 193.00 K during data collection. OLEX2 and SHELXTL were used for Data collection and integration.

Table S7 Crystal data and structure refinement for (Z)-5aa.

Identification code	(Z)- 5aa
Empirical formula	C ₂₆ H ₂₀ ClN ₃ O ₂
Formula weight	441.90
Temperature/K	193.00
Crystal system	monoclinic
Space group	P2 ₁ /n
a/Å	13.5476(12)
b/Å	8.2425(7)
c/Å	19.452(2)
α/°	90
β/°	93.366(4)
γ/°	90
Volume/Å ³	2168.4(4)
Z	4
ρ _{calc} /cm ³	1.354
μ/mm ⁻¹	0.205
F(000)	920.0
Crystal size/mm ³	0.13 × 0.12 × 0.1
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	4.196 to 54.952
Index ranges	-17 ≤ h ≤ 17, -10 ≤ k ≤ 9, -23 ≤ l ≤ 25
Reflections collected	19920
Independent reflections	4952 [R _{int} = 0.0486, R _{sigma} = 0.0429]
Data/restraints/parameters	4952/0/290
Goodness-of-fit on F ²	1.025
Final R indexes [I >= 2σ (I)]	R ₁ = 0.0453, wR ₂ = 0.1015
Final R indexes [all data]	R ₁ = 0.0664, wR ₂ = 0.1138
Largest diff. peak/hole / e Å ⁻³	0.25/-0.24

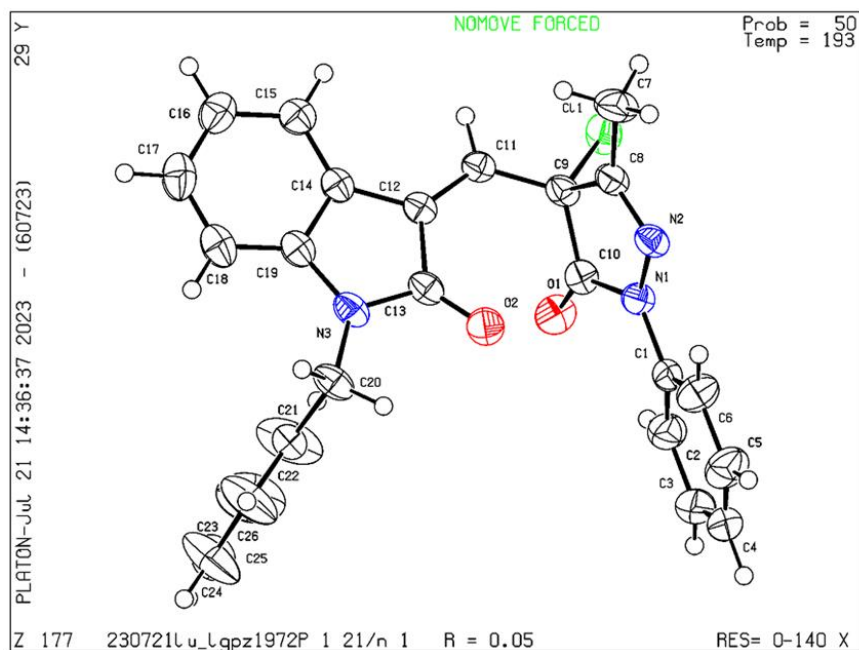


Figure S2. X-ray crystal structure of the product (Z)-5aa (50% ellipsoid contour probability level, **CCDC:2363451**).

Single Crystal X-Ray Data of (S, Z)-5ac

Single crystals of C₂₉H₂₆ClN₃O₂ ((S,Z)-5ac) were obtained in a dichloromethane : hexane (1:4) solution. A suitable crystal was selected and mounted on a Bruker D8 VENTURE dual wavelength Mo/Cu diffractometer. The crystal was kept at 301.00 K during data collection. OLEX2 and SHELXTL were used for Data collection and integration.

Table S8 Crystal data and structure refinement for (S, Z)-5ac.

Identification code	(S, Z)-5ac
Empirical formula	C ₂₉ H ₂₆ ClN ₃ O ₂
Formula weight	483.98
Temperature/K	301.00
Crystal system	monoclinic
Space group	P21
a/Å	9.0254(19)
b/Å	24.362(5)
c/Å	12.306(3)
α/°	90
β/°	110.432(13)
γ/°	90
Volume/Å ³	2535.5(10)
Z	4
ρ _{calc} /cm ³	1.268
μ/mm ⁻¹	1.576
F(000)	1016.0
Crystal size/mm ³	0.12 × 0.1 × 0.09
Radiation	CuKα (λ = 1.54178)
2θ range for data collection/°	7.258 to 178.09
Index ranges	-11 ≤ h ≤ 11, -30 ≤ k ≤ 28, -15 ≤ l ≤ 15
Reflections collected	34770
Independent reflections	9738 [R _{int} = 0.1224, R _{sigma} = 0.0953]
Data/restraints/parameters	9738/415/749
Goodness-of-fit on F ²	1.126
Final R indexes [I >= 2σ (I)]	R ₁ = 0.1082, wR ₂ = 0.2501
Final R indexes [all data]	R ₁ = 0.1631, wR ₂ = 0.2774
Largest diff. peak/hole / e Å ⁻³	0.36/-0.46

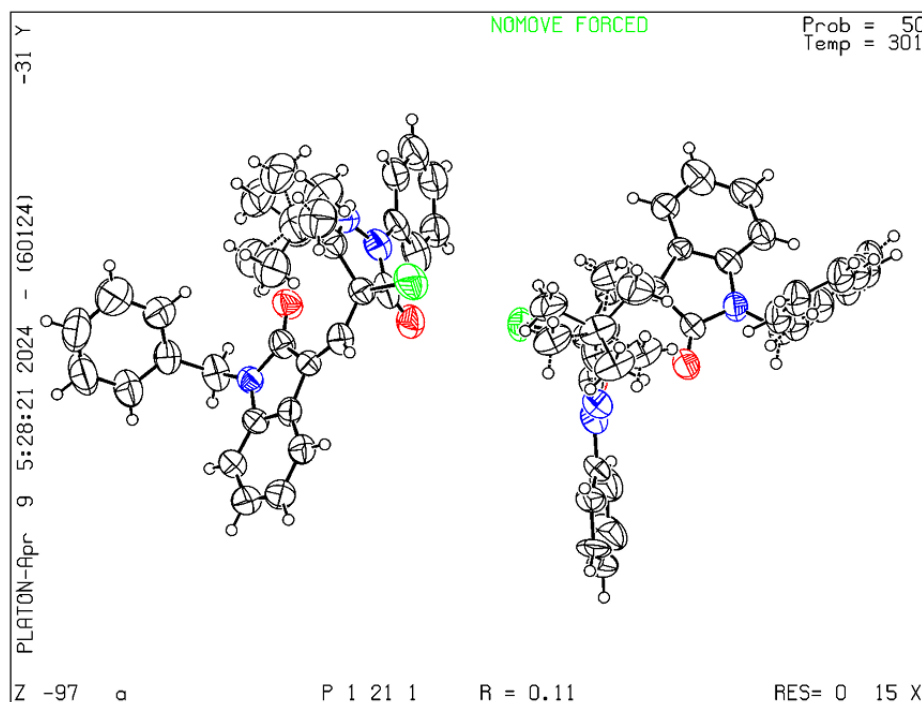


Figure S3. X-ray crystal structure of the product (*S,Z*)-**5ac** (50% ellipsoid contour probability level, **CCDC:2363453**).

5. *In vitro* anti-tumor assay

In vitro cytotoxic activity of **5** on different cancer cells.

A549, HepG2, U87, SW-620, HCT-116 and Hela cells (2.5×10^3 in 100 μL) were seeded in a 96-well plate in triplicate. Following a 24 h culture at 37 $^{\circ}\text{C}$, the suspension was replaced with fresh medium containing the different doses of compounds **5** (1, 10, 25, 50, 75 and 100 μM). The drug-free medium negative control well and the solvent control well were set with the same volume of DMSO. Cells were respectively incubated at 37 $^{\circ}\text{C}$ for 48 h. Then, added 100 μL of 0.5 mg/mL 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) (dissolved with PBS first, then diluted with fresh medium) to each well, cultured for an additional 4 h. Then removed the medium, and MTT formazan precipitates were dissolved in 100 μL of DMSO, shaken mechanically for 10 min and then read immediately at 570 nm using a plate reader (FlexStation 3, Molecular Devices).

Cell inhibition rate = $[\text{A570 (negative control well)} - \text{A570 (dosing well)}] / \text{A570 (negative control well)} \times 100\%$

Cell apoptosis study

A549 cells (5×10^4 in 1000 μL) were seeded on 12-well plates in triplicate and incubated at 37 $^{\circ}\text{C}$ for 24 h. Replaced the old medium with fresh medium containing different concentrations of (*E*)-**5ac** (10, 20 and 80 μM). The drug-free medium negative control well and the solvent control well were set with the same volume of DMSO.

Cells were cultured at 37 °C for 48 h, aspirated the medium, and 100 µL preheated 0.25% trypsin without ethylene diamine tetra-acetic acid (EDTA) was then added to each well. After trypsinization, the treated cells were stained using an Annexin V-FITC/PI apoptosis detection kit, according to the manufacturer's instructions. After incubation at room temperature for 5-15 min in the dark, the apoptotic cells were immediately analysed by CytoFLEX flow cytometry.

Cell cycle study

A549 cells (2.5×10^5 in 2500 µL) were seeded on 6-well plates in triplicate and incubated at 37 °C for 24 h. Replaced the old medium with fresh medium containing different concentrations of (*E*)-**5ac** (5, 10 and 20 µM). The drug-free medium negative control well and the solvent control well were set with the same volume of DMSO. Cells were cultured at 37 °C for 24 h, aspirated the medium, and 200 µL 0.25% trypsin was then added to each well. After trypsinization, treated cells were fixed with 70% ethanol overnight at 4 °C, and then were stained using PI cell cycle analysis kit, according to the manufacturer's instructions. After incubation at 37 °C for 30 min in the dark, the cell cycle was immediately analysed by CytoFLEX flow cytometry.

Anti-tumor data

Table S9 Effect of chlorinated products to inhibit the growth of A549 cell-lines

Entry	Compound	Inhibition rate at 50 µM (%) ^{a, b}	IC ₅₀ (µM)
1	(<i>Z</i>)- 5aa	42.6	> 50
2	(<i>E</i>)- 5aa	5.5	> 50
3	(<i>Z</i>)- 5ba	72.6	> 50
4	(<i>E</i>)- 5ba	50.0	> 50
5	(<i>Z</i>)- 5ca	-3.3	> 50
6	(<i>E</i>)- 5ca	6.1	> 50
7	(<i>Z</i>)- 5da	22.4	> 50
8	(<i>E</i>)- 5da	25.8	> 50
9	(<i>Z</i>)- 5ea	30.5	> 50
10	(<i>E</i>)- 5ea	30.7	> 50
11	(<i>Z</i>)- 5fa	45.8	> 50
12	(<i>E</i>)- 5fa	5.3	> 50
13	(<i>Z</i>)- 5ga	10.0	> 50
14	(<i>E</i>)- 5ga	47.0	> 50
15	(<i>Z</i>)- 5ha	32.5	> 50
16	(<i>E</i>)- 5ha	61.7	> 50
17	(<i>Z</i>)- 5ia	56.0	26.44±2.39
18	(<i>E</i>)- 5ia	23.8	> 50
19	(<i>Z</i>)- 5ja	61.2	> 50
20	(<i>E</i>)- 5ja	5.9	> 50
21	(<i>Z</i>)- 5ka	27.2	> 50
22	(<i>E</i>)- 5ka	58.7	> 50
23	(<i>Z</i>)- 5la	23.3	> 50

Table S9-continued

Entry	Compound	Inhibition rate (%) ^{a, b}	IC ₅₀ (μM)
24	(<i>E</i>)- 5la	8.83	> 50
25	(<i>Z</i>)- 5ab	74.291	13.89±2.44
26	(<i>E</i>)- 5ab	64.894	35.18±1.40
27	(<i>Z</i>)- 5ac	71.809	26.45±1.80
28	(<i>E</i>)- 5ac	70.390	11.64±0.38
29	(<i>Z</i>)- 5ad	75.000	28.28±2.20
30	(<i>E</i>)- 5ad	37.943	> 50
31	(<i>Z</i>)- 5ae	35.993	> 50
32	(<i>E</i>)- 5ae	39.716	> 50
33	(<i>Z</i>)- 5af	19.504	> 50
34	(<i>E</i>)- 5af	51.418	29.11±2.81
35	(<i>Z</i>)- 5ag	0.000	> 50
36	(<i>E</i>)- 5ag	28.014	> 50
37	(<i>Z</i>)- 5ah	74.113	30.36±1.85
38	(<i>E</i>)- 5ah	72.872	16.71±1.83
39	(<i>Z</i>)- 5ai	76.064	28.20±1.53
40	(<i>E</i>)- 5ai	57.624	> 50
41	(<i>Z</i>)- 5aj	12.757	> 50
42	(<i>E</i>)- 5aj	-2.311	> 50
43	(<i>Z</i>)- 5ak	4.022	> 50
44	(<i>E</i>)- 5ak	13.521	> 50
45	(<i>Z</i>)- 5al	2.305	> 50
46	(<i>E</i>)- 5al	5.319	> 50
47	(<i>Z</i>)- 5am	0.000	> 50
48	(<i>E</i>)- 5am	43.794	> 50
49	(<i>Z</i>)- 5an	29.787	> 50
50	(<i>E</i>)- 5an	15.603	> 50
51	(<i>Z</i>)- 5ao	42.730	> 50
52	(<i>E</i>)- 5ao	0.000	> 50
53	(<i>S,Z</i>)- 5ae	4.192	> 50
54	(<i>S,Z</i>)- 5be	27.632	> 50
55	(<i>S,Z</i>)- 5ce	24.509	> 50
56	(<i>S,Z</i>)- 5de	49.048	> 50
57	(<i>S,Z</i>)- 5ee	33.700	> 50
58	(<i>S,Z</i>)- 5fe	44.676	> 50
59	(<i>S,Z</i>)- 5ge	57.079	> 50
60	(<i>S,Z</i>)- 5he	60.648	42.45±2.28
61	(<i>S,Z</i>)- 5ie	40.660	> 50
62	(<i>S,Z</i>)- 5je	45.211	> 50
63	(<i>S,Z</i>)- 5ke	52.082	> 50
64	(<i>S,Z</i>)- 5le	53.867	42.15±1.34
65	(<i>S,Z</i>)- 5me	16.835	> 50

Table S9-continued

Entry	Compound	Inhibition rate (%) ^{a, b}	IC ₅₀ (μM)
66	(<i>S,Z</i>)- 5aa	9.427	> 50
67	(<i>S,Z</i>)- 5ne	35.396	> 50
68	(<i>S,Z</i>)- 5oe	79.477	35.63±0.80
69	(<i>S,Z</i>)- 5pe	30.131	> 50
70	(<i>S,Z</i>)- 5qe	15.140	> 50
71	(<i>S,Z</i>)- 5re	23.617	> 50
72	(<i>S,Z</i>)- 5se	46.728	> 50
73	(<i>S,Z</i>)- 5te	9.340	> 50
74	(<i>S,Z</i>)- 5ue	23.349	> 50
75	(<i>S,Z</i>)- 5ve	62.076	32.43±1.38
76	(<i>S,Z</i>)- 5we	11.666	> 50
77	(<i>S,Z</i>)- 5xe	30.756	> 50
78	(<i>S,Z</i>)- 5ye	7.733	> 50
79	(<i>S,Z</i>)- 5ze	14.337	> 50
80 ^c	Irinotecan	59.41	29.07±0.47

^a This antitumor activity assay was carried out at concentration of 50 μM.

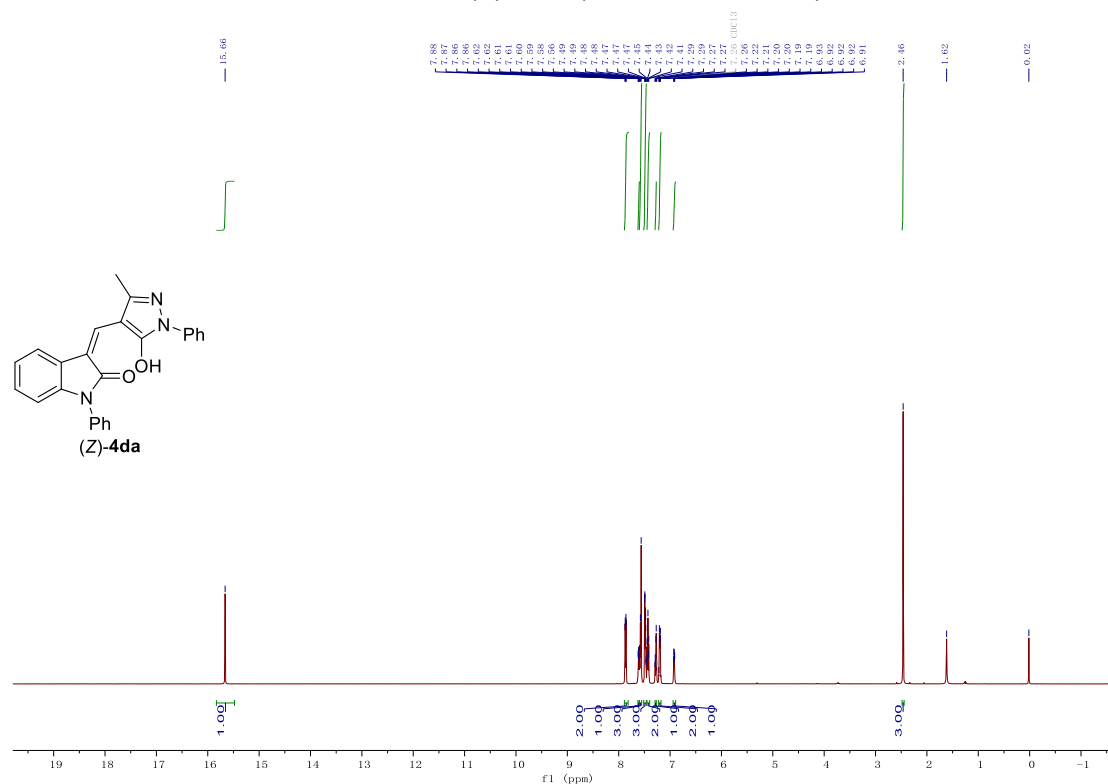
^b All experiments were conducted in three parallel groups. ^c Irinotecan was used as a positive control.

6. Reference

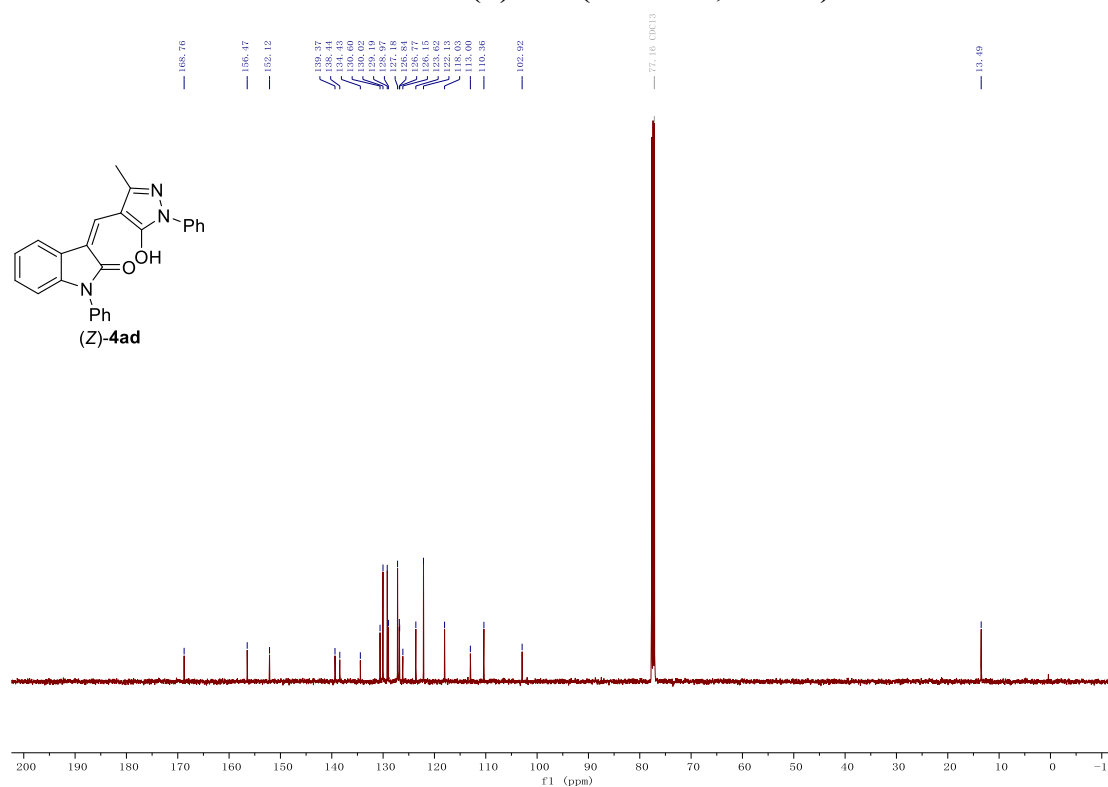
- (1) L. Satham, C. S. Sankara and I. N. N. Namboothiri, Eur. J. Org. Chem., 2020, 2020, 6903–6908.
- (2) C.-Y. Lin, W.-W. Huang, Y.-T. Huang, S. Dhole and C.-M. Sun, Eur. J. Org. Chem., 2021, 2021, 4984–4992.
- (3) X. Sheng, J. Zhang, H. Yang and G. Jiang, Org. Lett., 2017, 19, 2618–2621.
- (4) C. Vila, S. Slack, G. Blay, M. C. Muñoz and J. R. Pedro, Adv. Synth. Catal., 2019, 361, 1902–1907.

7. NMR spectra for compounds

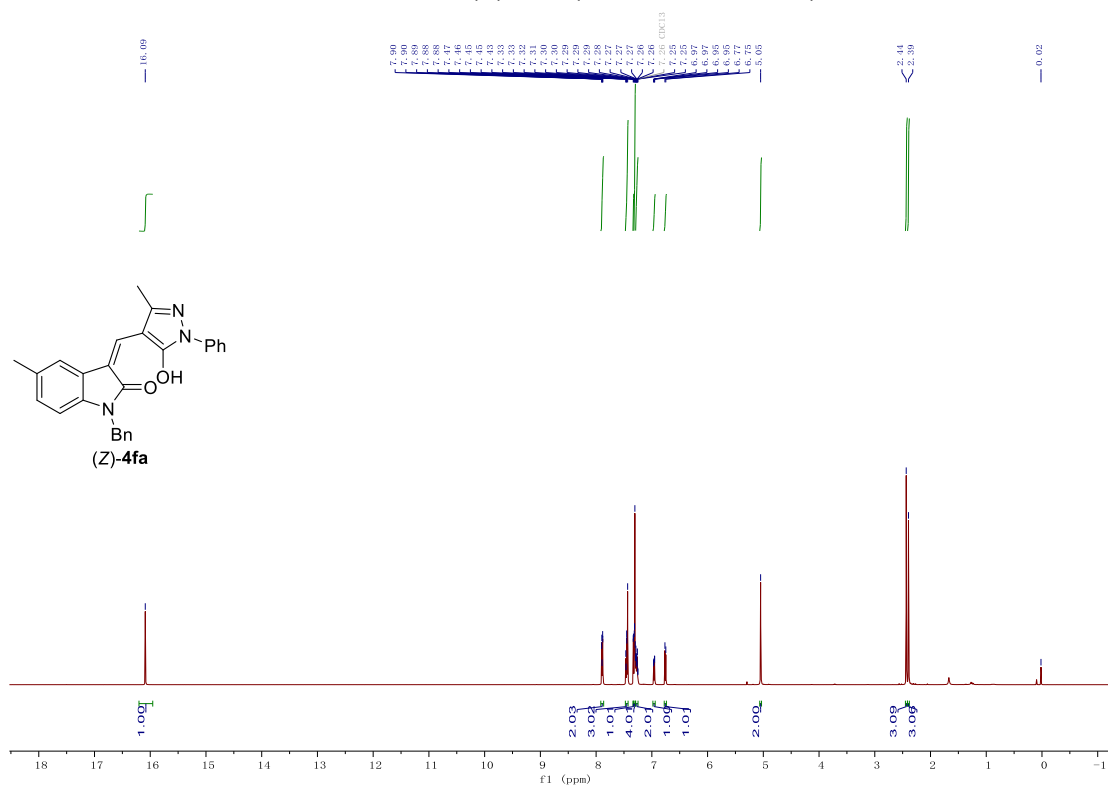
¹H NMR of (Z)-4da (500 MHz, CDCl₃)



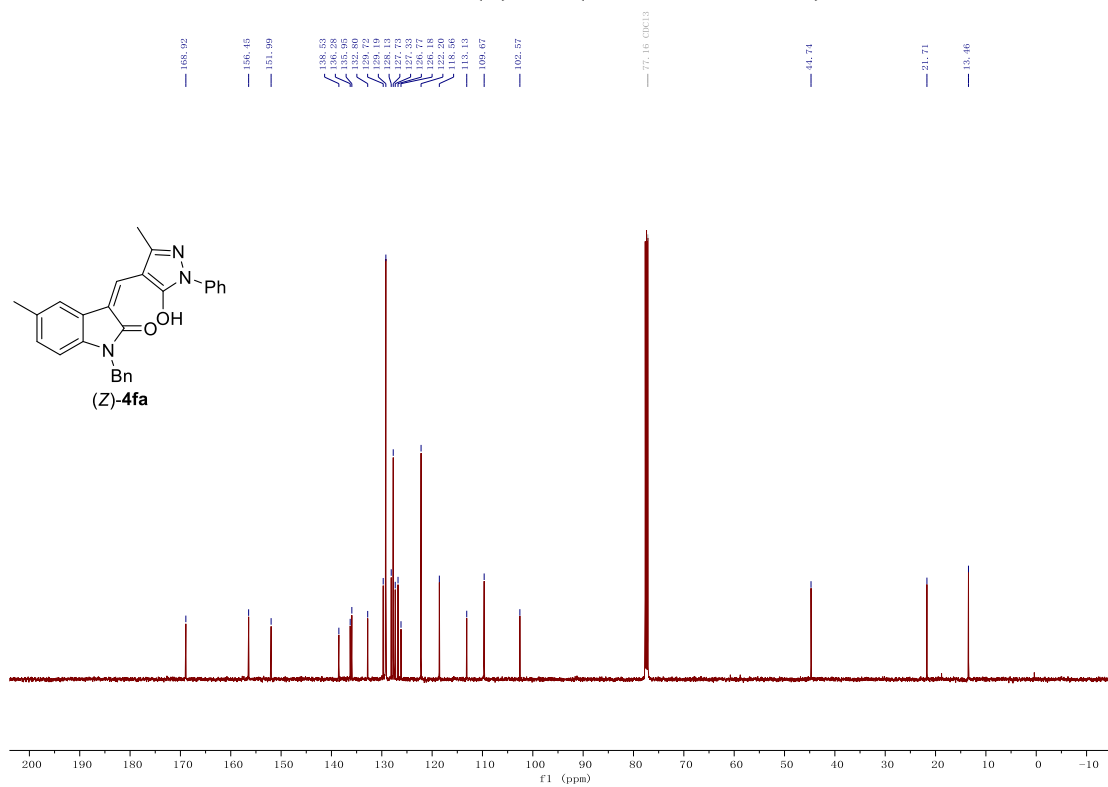
¹³C NMR of (Z)-4da (126 MHz, CDCl₃)



¹H NMR of (Z)-4fa (500 MHz, CDCl₃)



¹³C NMR of (Z)-4fa (126 MHz, CDCl₃)



Chemical structure of (Z)-4ja is shown. The ^1H NMR spectrum (CDCl₃) displays the following peaks and integrations:

Chemical Shift (ppm)	Integration
7.87	1.00
7.65 - 7.20	2.01, 3.03, 1.01, 1.86, 4.00, 1.01, 0.99
5.02	2.00
2.42	3.00
0.00	-

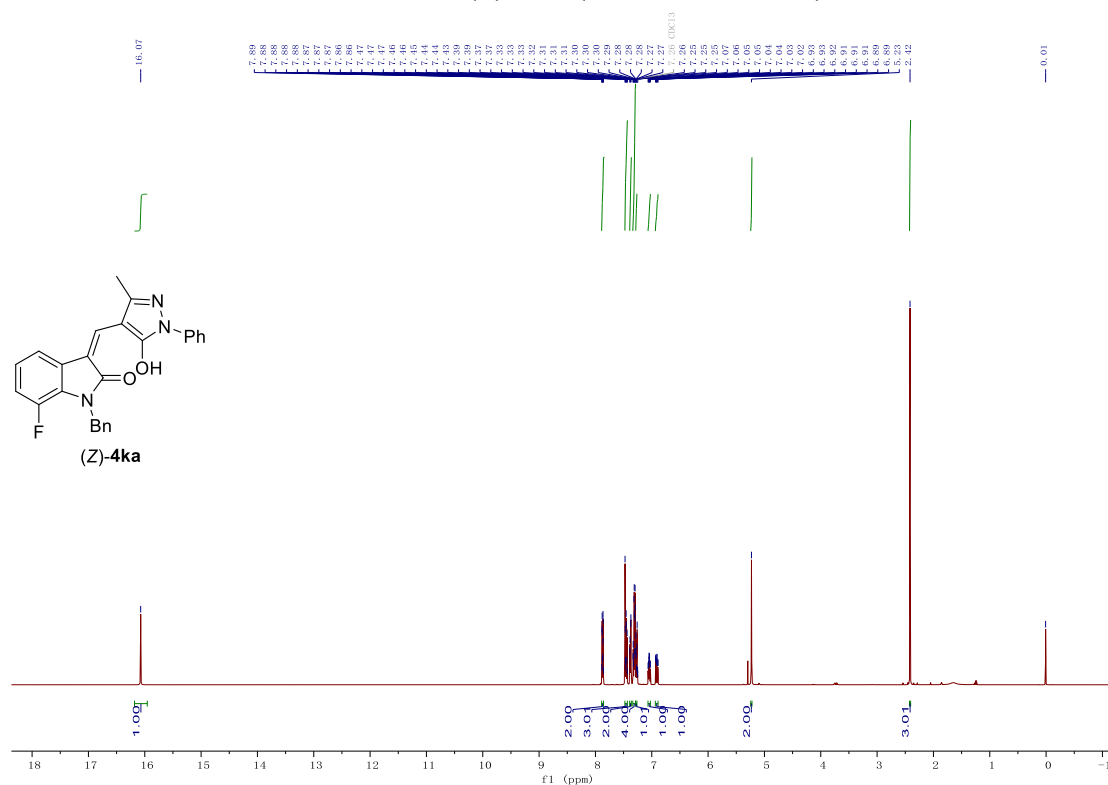
(Z)-4ja

Cc1nc(Nc2ccccc2)c(=O)c3c1c(c4ccc(Br)cc4)n(Cc5ccccc5)c3=O

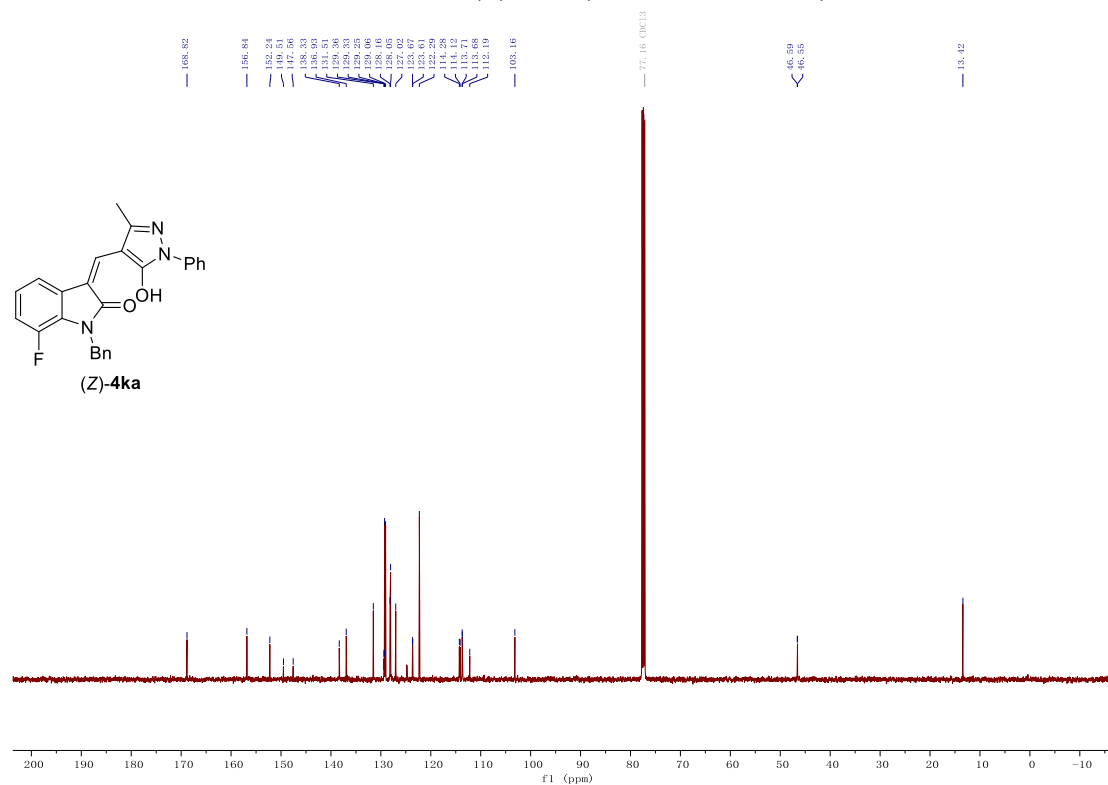
¹³C NMR (CDCl₃)

169.03, 156.55, 152.20, 139.59, 138.34, 135.42, 135.27, 134.99, 132.27, 132.22, 132.21, 132.20, 132.11, 132.04, 131.85, 131.71, 131.64, 131.41, 131.39, 131.38, 131.37, 131.36, 131.35, 131.34, 131.33, 131.32, 131.31, 131.30, 131.29, 131.28, 131.27, 131.26, 131.25, 131.24, 131.23, 131.22, 131.21, 131.20, 131.19, 131.18, 131.17, 131.16, 131.15, 131.14, 131.13, 131.12, 131.11, 131.10, 131.09, 131.08, 131.07, 131.06, 131.05, 131.04, 131.03, 131.02, 131.01, 131.00, 130.99, 130.98, 130.97, 130.96, 130.95, 130.94, 130.93, 130.92, 130.91, 130.90, 130.89, 130.88, 130.87, 130.86, 130.85, 130.84, 130.83, 130.82, 130.81, 130.80, 130.79, 130.78, 130.77, 130.76, 130.75, 130.74, 130.73, 130.72, 130.71, 130.70, 130.69, 130.68, 130.67, 130.66, 130.65, 130.64, 130.63, 130.62, 130.61, 130.60, 130.59, 130.58, 130.57, 130.56, 130.55, 130.54, 130.53, 130.52, 130.51, 130.50, 130.49, 130.48, 130.47, 130.46, 130.45, 130.44, 130.43, 130.42, 130.41, 130.40, 130.39, 130.38, 130.37, 130.36, 130.35, 130.34, 130.33, 130.32, 130.31, 130.30, 130.29, 130.28, 130.27, 130.26, 130.25, 130.24, 130.23, 130.22, 130.21, 130.20, 130.19, 130.18, 130.17, 130.16, 130.15, 130.14, 130.13, 130.12, 130.11, 130.10, 130.09, 130.08, 130.07, 130.06, 130.05, 130.04, 130.03, 130.02, 130.01, 130.00, 129.99, 129.98, 129.97, 129.96, 129.95, 129.94, 129.93, 129.92, 129.91, 129.90, 129.89, 129.88, 129.87, 129.86, 129.85, 129.84, 129.83, 129.82, 129.81, 129.80, 129.79, 129.78, 129.77, 129.76, 129.75, 129.74, 129.73, 129.72, 129.71, 129.70, 129.69, 129.68, 129.67, 129.66, 129.65, 129.64, 129.63, 129.62, 129.61, 129.60, 129.59, 129.58, 129.57, 129.56, 129.55, 129.54, 129.53, 129.52, 129.51, 129.50, 129.49, 129.48, 129.47, 129.46, 129.45, 129.44, 129.43, 129.42, 129.41, 129.40, 129.39, 129.38, 129.37, 129.36, 129.35, 129.34, 129.33, 129.32, 129.31, 129.30, 129.29, 129.28, 129.27, 129.26, 129.25, 129.24, 129.23, 129.22, 129.21, 129.20, 129.19, 129.18, 129.17, 129.16, 129.15, 129.14, 129.13, 129.12, 129.11, 129.10, 129.09, 129.08, 129.07, 129.06, 129.05, 129.04, 129.03, 129.02, 129.01, 129.00, 128.99, 128.98, 128.97, 128.96, 128.95, 128.94, 128.93, 128.92, 128.91, 128.90, 128.89, 128.88, 128.87, 128.86, 128.85, 128.84, 128.83, 128.82, 128.81, 128.80, 128.79, 128.78, 128.77, 128.76, 128.75, 128.74, 128.73, 128.72, 128.71, 128.70, 128.69, 128.68, 128.67, 128.66, 128.65, 128.64, 128.63, 128.62, 128.61, 128.60, 128.59, 128.58, 128.57, 128.56, 128.55, 128.54, 128.53, 128.52, 128.51, 128.50, 128.49, 128.48, 128.47, 128.46, 128.45, 128.44, 128.43, 128.42, 128.41, 128.40, 128.39, 128.38, 128.37, 128.36, 128.35, 128.34, 128.33, 128.32, 128.31, 128.30, 128.29, 128.28, 128.27, 128.26, 128.25, 128.24, 128.23, 128.22, 128.21, 128.20, 128.19, 128.18, 128.17, 128.16, 128.15, 128.14, 128.13, 128.12, 128.11, 128.10, 128.09, 128.08, 128.07, 128.06, 128.05, 128.04, 128.03, 128.02, 128.01, 128.00, 127.99, 127.98, 127.97, 127.96, 127.95, 127.94, 127.93, 127.92, 127.91, 127.90, 127.89, 127.88, 127.87, 127.86, 127.85, 127.84, 127.83, 127.82, 127.81, 127.80, 127.79, 127.78, 127.77, 127.76, 127.75, 127.74, 127.73, 127.72, 127.71, 127.70, 127.69, 127.68, 127.67, 127.66, 127.65, 127.64, 127.63, 127.62, 127.61, 127.60, 127.59, 127.58, 127.57, 127.56, 127.55, 127.54, 127.53, 127.52, 127.51, 127.50, 127.49, 127.48, 127.47, 127.46, 127.45, 127.44, 127.43, 127.42, 127.41, 127.40, 127.39, 127.38, 127.37, 127.36, 127.35, 127.34, 127.33, 127.32, 127.31, 127.30, 127.29, 127.28, 127.27, 127.26, 127.25, 127.24, 127.23, 127.22, 127.21, 127.20, 127.19, 127.18, 127.17, 127.16, 127.15, 127.14, 127.13, 127.12, 127.11, 127.10, 127.09, 127.08, 127.07, 127.06, 127.05, 127.04, 127.03, 127.02, 127.01, 127.00, 126.99, 126.98, 126.97, 126.96, 126.95, 126.94, 126.93, 126.92, 126.91, 126.90, 126.89, 126.88, 126.87, 126.86, 126.85, 126.84, 126.83, 126.82, 126.81, 126.80, 126.79, 126.78, 126.77, 126.76, 126.75, 126.74, 126.73, 126.72, 126.71, 126.70, 126.69, 126.68, 126.67, 126.66, 126.65, 126.64, 126.63, 126.62, 126.61, 126.60, 126.59, 126.58, 126.57, 126

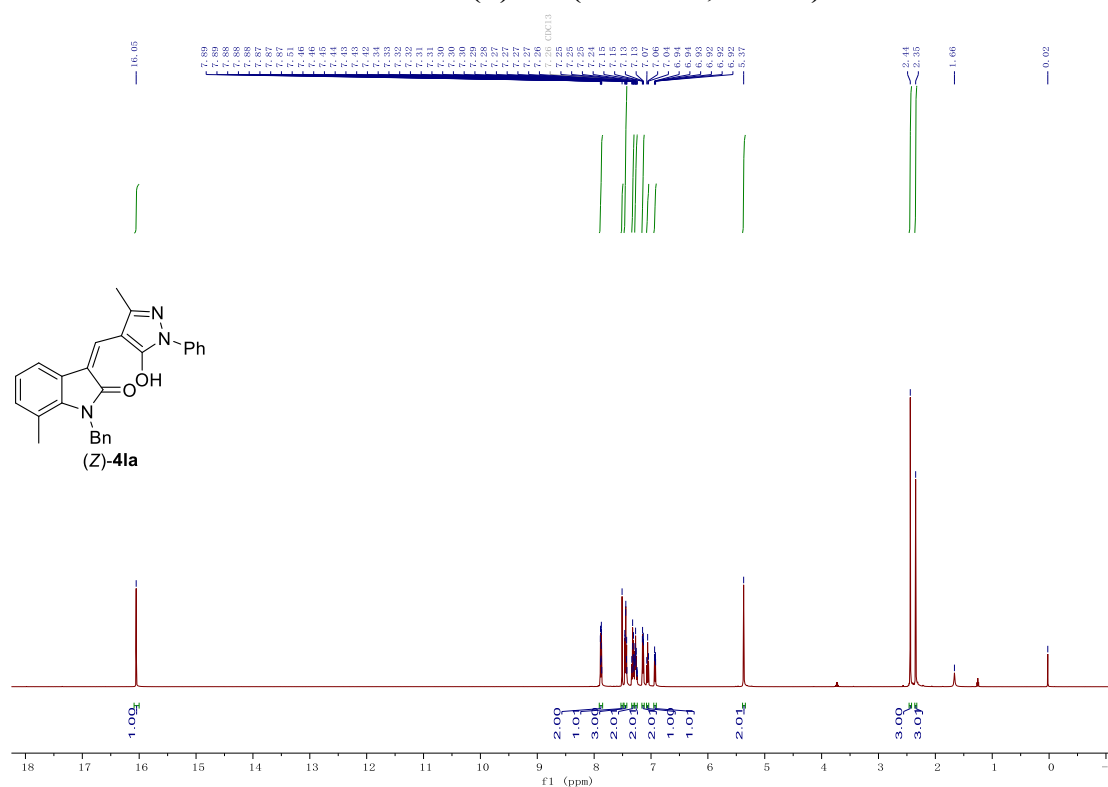
¹H NMR of (Z)-4ka (500 MHz, CDCl₃)



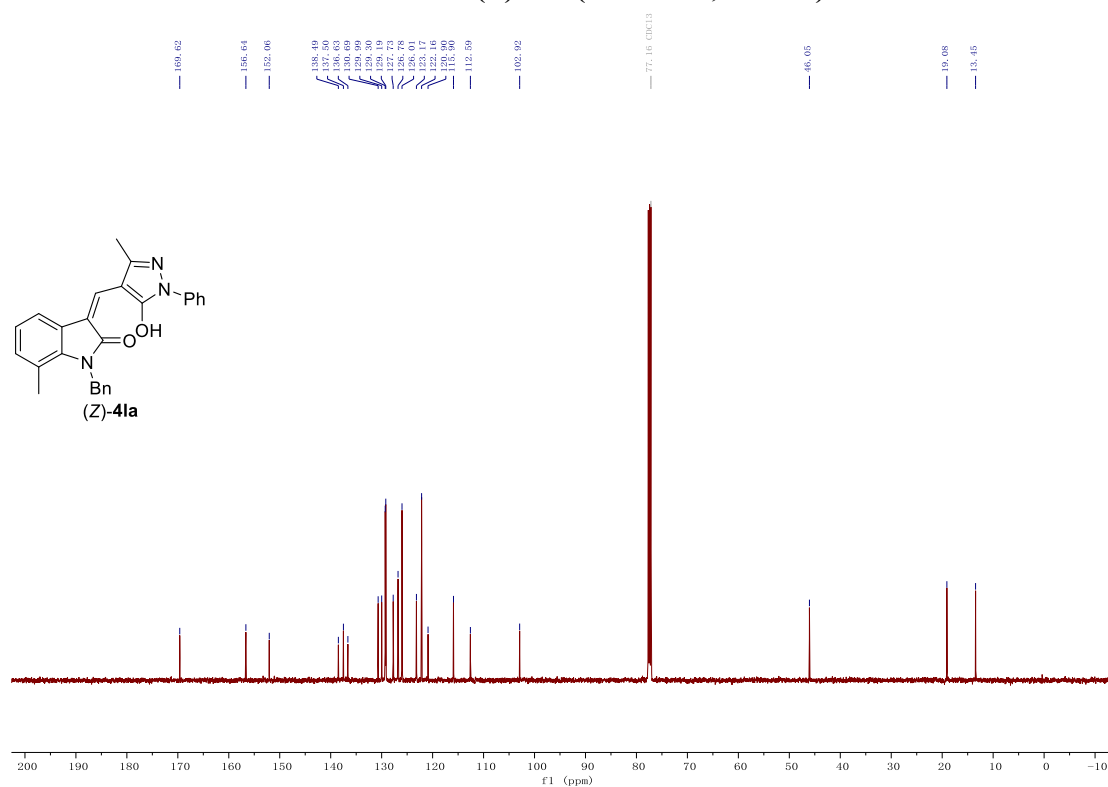
¹³C NMR of (Z)-4ka (126 MHz, CDCl₃)



¹H NMR of (Z)-4la (500 MHz, CDCl₃)



¹³C NMR of (Z)-4la (126 MHz, CDCl₃)



[illegible]

Chemical structure of (Z)-4be is shown. The ^{13}C NMR spectrum (CDCl₃) shows peaks at the following chemical shifts (ppm): 169.04, 156.67, 154.72, 138.38, 137.42, 132.77, 130.96, 130.84, 129.34, 129.23, 127.07, 127.01, 126.97, 123.31, 122.55, 118.55, 114.61, 109.00, 101.69, 77.16 (CDCl₃), and 27.19.

c1ccc2c(c1)c(c3ccccc3n2C#CC)C(=O)O/C=C/C4=CC(=C(C=C4)N(C#CC)C5=CC=CC=C5)C6=CC=CC=C6

(Z)-4ce

Chemical shifts (ppm): 7.99, 7.98, 7.97, 7.96, 7.65, 7.65, 7.63, 7.54, 7.54, 7.53, 7.53, 7.53, 7.52, 7.51, 7.51, 7.50, 7.49, 7.49, 7.49, 7.48, 7.47, 7.47, 7.46, 7.36, 7.36, 7.35, 7.34, 7.34, 7.33, 7.33, 7.32, 7.31, 7.31, 7.30, 7.28, 7.27, 7.27, 7.26, 7.17, 7.16, 7.14, 7.14, 7.13, 7.13, 7.13, 7.11, 7.11, 4.73, 4.72, 2.29, 1.58, 0.07.

Integration values: 1.00, 2.01, 2.00, 1.00, 2.03, 2.03, 2.06, 2.01, 1.00, 2.00, 2.00, 1.01, 2.29, 1.58, 0.07.

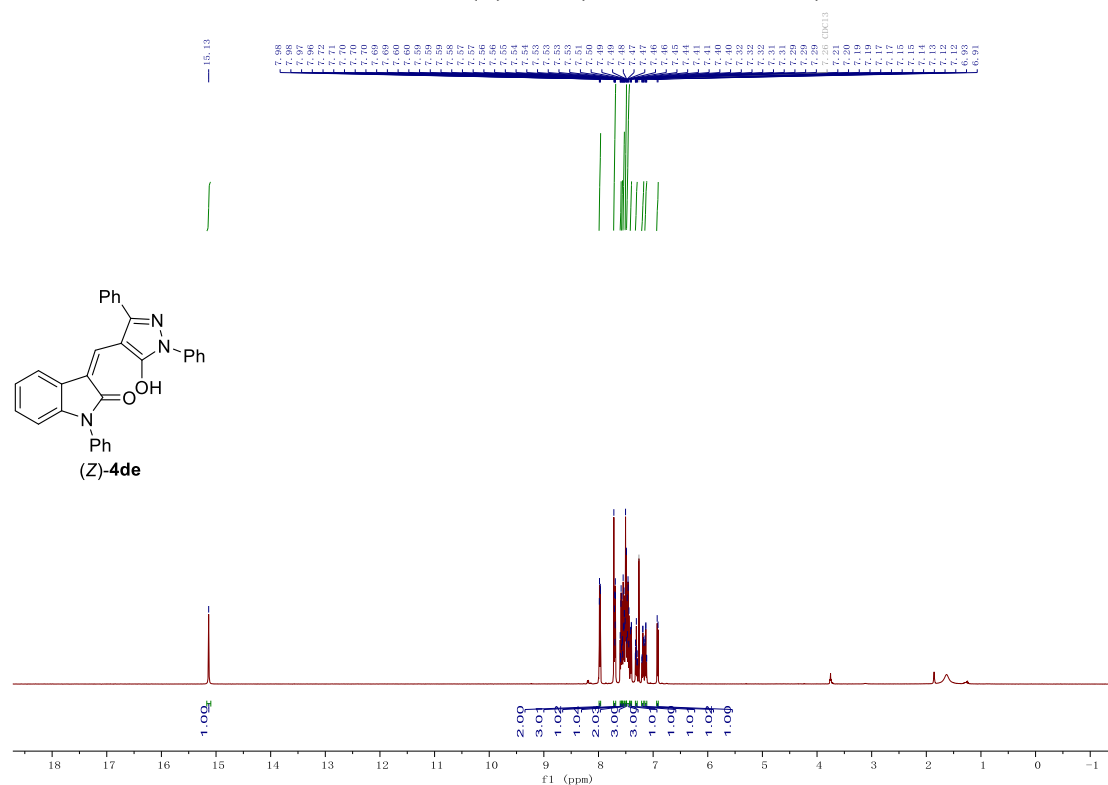
(Z)-4ce

Chemical structure of (Z)-4ce is shown above the spectrum. The structure is a benzimidazole derivative with a phenyl group on the imidazole ring, a hydroxyl group, and a prop-1-en-1-yl group on the benzimidazole ring.

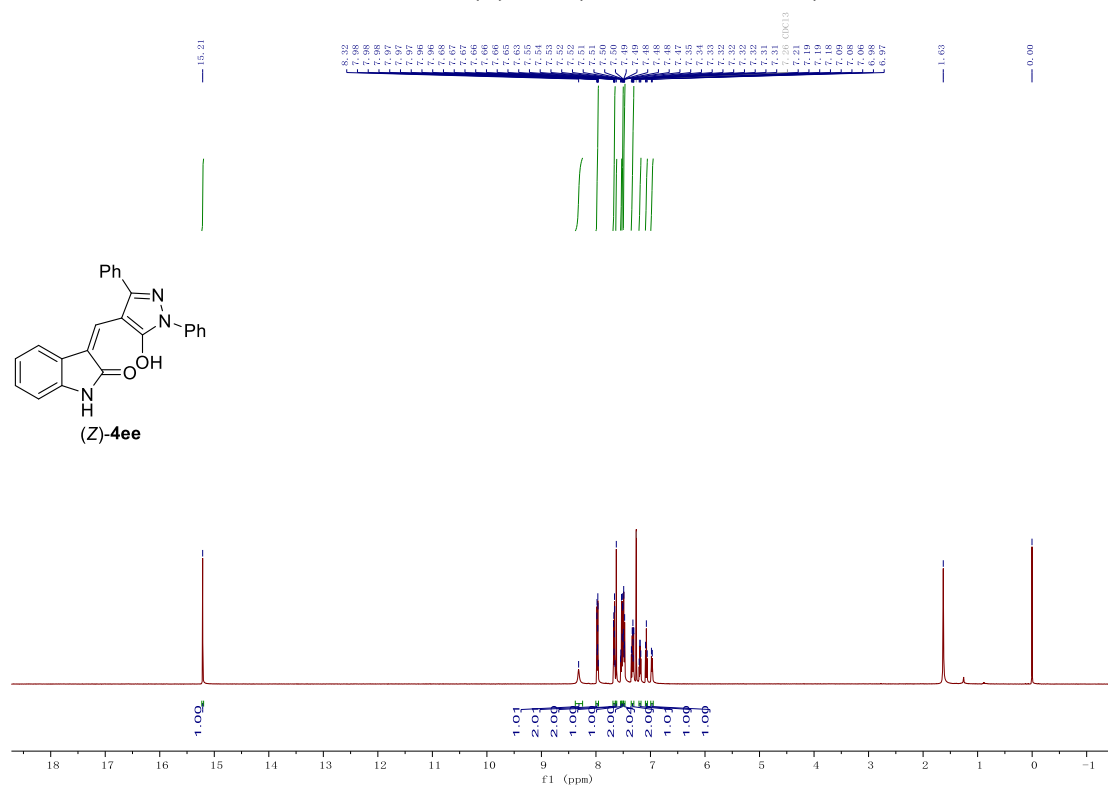
¹³C NMR spectrum (CDCl₃) of (Z)-4ce. The x-axis represents the chemical shift in ppm, ranging from 0 to 200. The spectrum shows several peaks, with the following chemical shifts (ppm) labeled above the peaks:

- 168.40
- 156.37
- 154.86
- 138.73
- 137.73
- 132.66
- 132.57
- 130.72
- 129.44
- 129.38
- 127.25
- 127.12
- 126.42
- 123.61
- 114.39
- 109.92
- 101.81
- 77.14 (triplet, solvent)
- 36.25

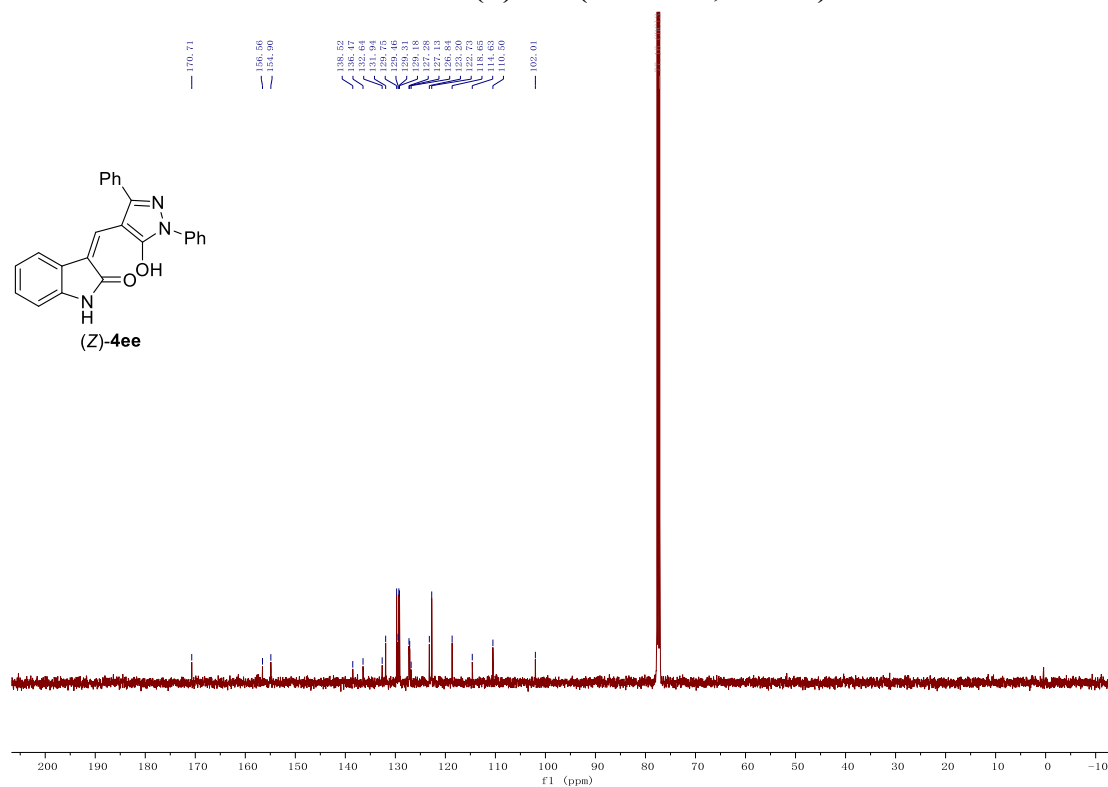
¹H NMR of (Z)-4de (500 MHz, CDCl₃)



¹H NMR of (Z)-4ee (500 MHz, CDCl₃)



^{13}C NMR of (Z)-4ee (126 MHz, CDCl_3)



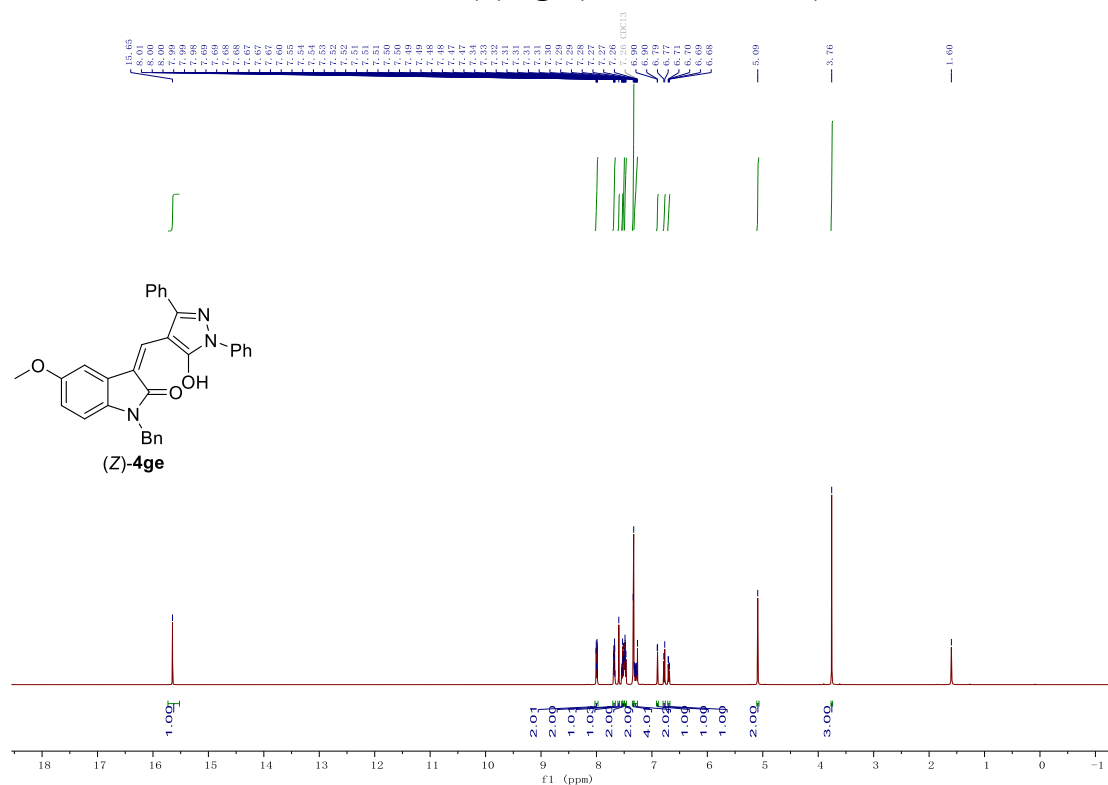
Chemical structure of (Z)-4fe is shown. The structure is a benzimidazole derivative with a phenyl group on the imidazole ring, a benzyl group on the nitrogen, and a phenyl group on the benzimidazole ring.

¹H NMR spectrum (CDCl₃) of (Z)-4fe. The spectrum shows peaks in the aromatic region (6.5-8.0 ppm) and a singlet at 2.32 ppm. Integration values are provided below the peaks.

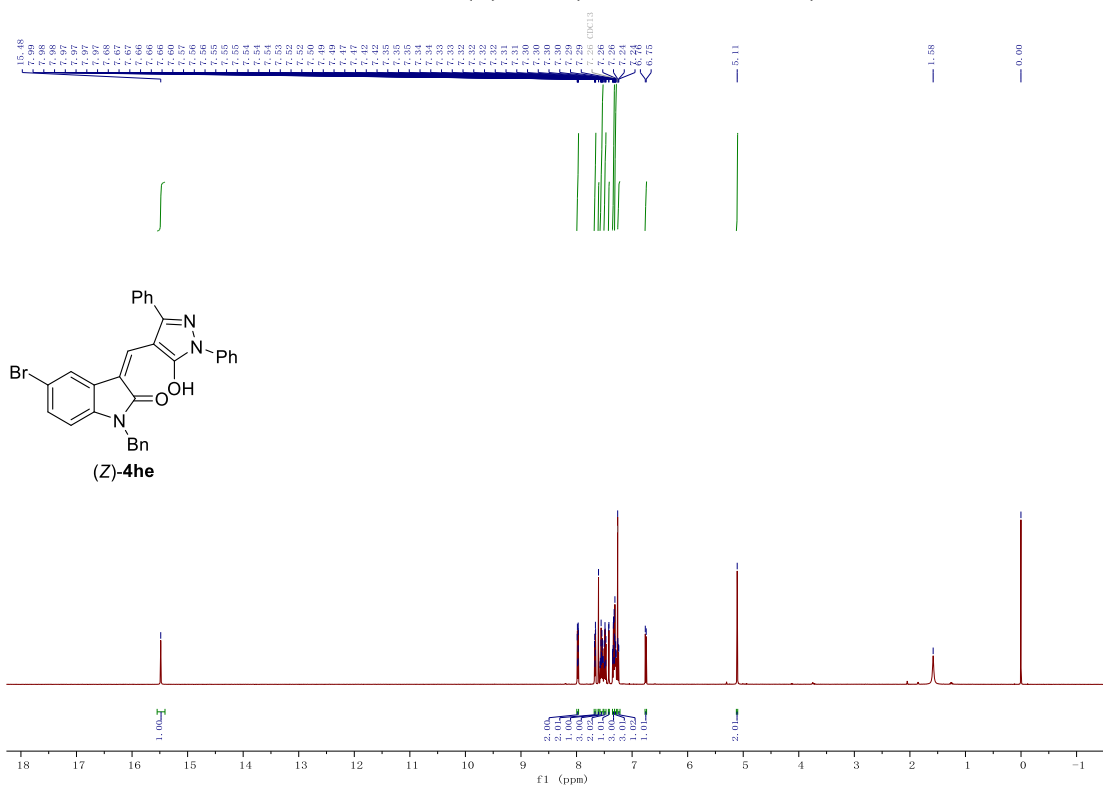
Chemical Shift (ppm)	Integration
8.00	1.00
7.99	1.00
7.98	1.00
7.97	1.00
7.96	1.00
7.95	1.00
7.94	1.00
7.93	1.00
7.92	1.00
7.91	1.00
7.90	1.00
7.89	1.00
7.88	1.00
7.87	1.00
7.86	1.00
7.85	1.00
7.84	1.00
7.83	1.00
7.82	1.00
7.81	1.00
7.80	1.00
7.79	1.00
7.78	1.00
7.77	1.00
7.76	1.00
7.75	1.00
7.74	1.00
7.73	1.00
7.72	1.00
7.71	1.00
7.70	1.00
7.69	1.00
7.68	1.00
7.67	1.00
7.66	1.00
7.65	1.00
7.64	1.00
7.63	1.00
7.62	1.00
7.61	1.00
7.60	1.00
7.59	1.00
7.58	1.00
7.57	1.00
7.56	1.00
7.55	1.00
7.54	1.00
7.53	1.00
7.52	1.00
7.51	1.00
7.50	1.00
7.49	1.00
7.48	1.00
7.47	1.00
7.46	1.00
7.45	1.00
7.44	1.00
7.43	1.00
7.42	1.00
7.41	1.00
7.40	1.00
7.39	1.00
7.38	1.00
7.37	1.00
7.36	1.00
7.35	1.00
7.34	1.00
7.33	1.00
7.32	1.00
7.31	1.00
7.30	1.00
7.29	1.00
7.28	1.00
7.27	1.00
7.26	1.00
7.25	1.00
7.24	1.00
7.23	1.00
7.22	1.00
7.21	1.00
7.20	1.00
7.19	1.00
7.18	1.00
7.17	1.00
7.16	1.00
7.15	1.00
7.14	1.00
7.13	1.00
7.12	1.00
7.11	1.00
7.10	1.00
7.09	1.00
7.08	1.00
7.07	1.00
7.06	1.00
7.05	1.00
7.04	1.00
7.03	1.00
7.02	1.00
7.01	1.00
7.00	1.00
6.99	1.00
6.98	1.00
6.97	1.00
6.96	1.00
6.95	1.00
6.94	1.00
6.93	1.00
6.92	1.00
6.91	1.00
6.90	1.00
6.89	1.00
6.88	1.00
6.87	1.00
6.86	1.00
6.85	1.00
6.84	1.00
6.83	1.00
6.82	1.00
6.81	1.00
6.80	1.00
6.79	1.00
6.78	1.00
6.77	1.00
6.76	1.00
6.75	1.00
6.74	1.00
6.73	1.00
6.72	1.00
6.71	1.00
6.70	1.00
6.69	1.00
6.68	1.00
6.67	1.00
6.66	1.00
6.65	1.00
6.64	1.00
6.63	1.00
6.62	1.00
6.61	1.00
6.60	1.00
6.59	

Chemical structure of (Z)-4fe is shown as an inset. The structure is a benzimidazole derivative with a phenyl group (Ph) attached to the imidazole ring, a benzyl group (Bn) attached to the nitrogen, and a methyl group (Me) attached to the benzene ring. The label (Z)-4fe is present below the structure.

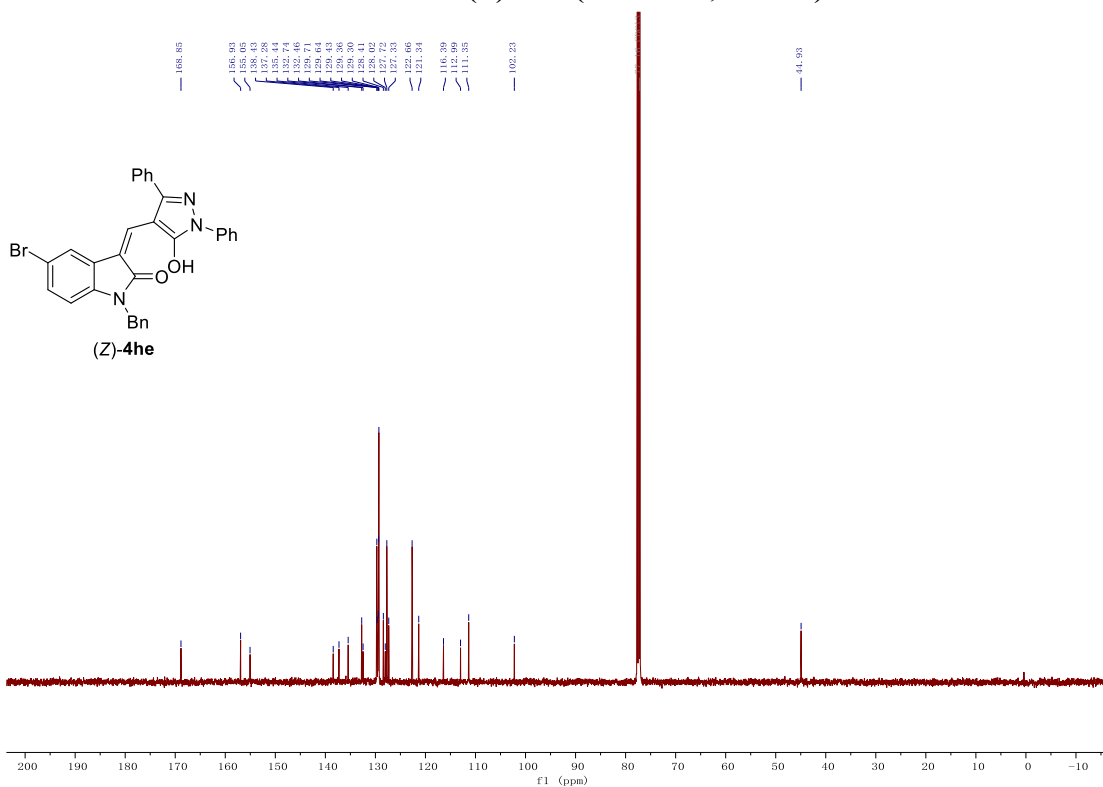
¹H NMR of (Z)-4ge (500 MHz, CDCl₃)



¹H NMR of (Z)-4he (500 MHz, CDCl₃)



¹³C NMR of (Z)-4he (126 MHz, CDCl₃)



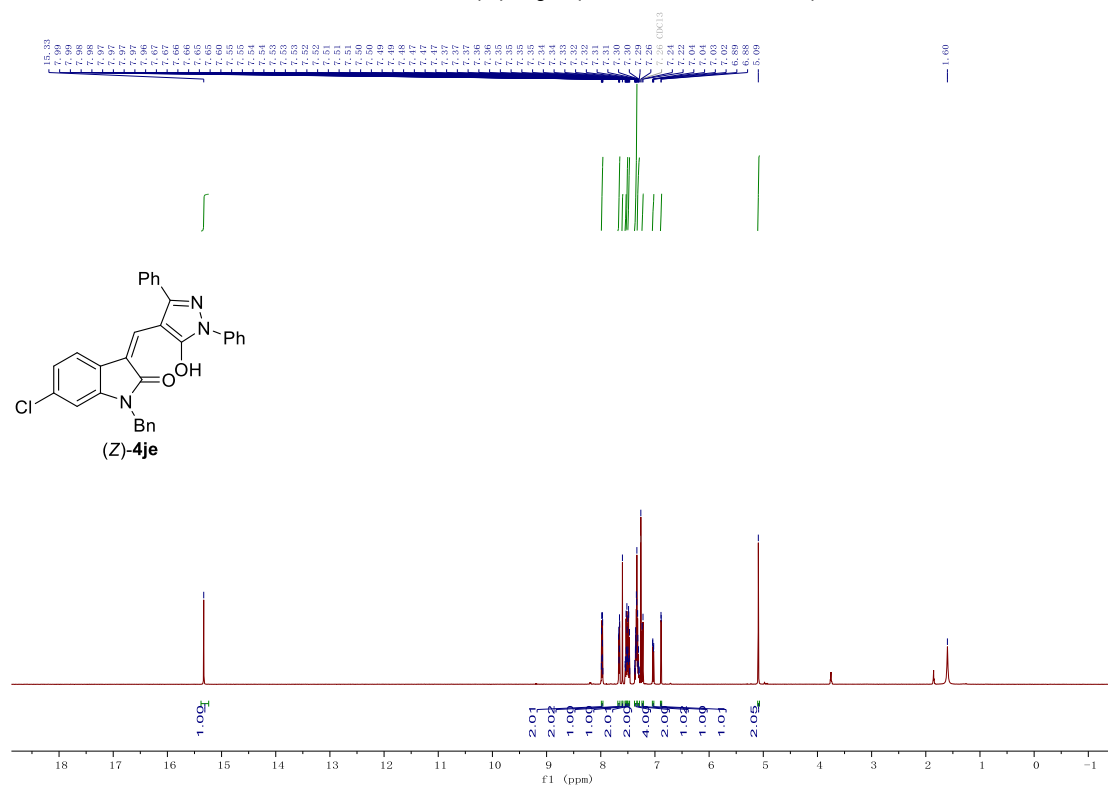
Chemical structure of (Z)-4ie is shown. The ^1H NMR spectrum (CDCl₃) displays peaks corresponding to the structure, with integration values and chemical shifts (ppm) listed below and above the spectrum, respectively.

Chemical shifts (ppm): 7.99, 7.98, 7.98, 7.97, 7.97, 7.97, 7.96, 7.68, 7.68, 7.68, 7.67, 7.67, 7.53, 7.52, 7.52, 7.51, 7.51, 7.50, 7.49, 7.49, 7.48, 7.47, 7.46, 7.35, 7.34, 7.34, 7.33, 7.32, 7.31, 7.31, 7.30, 7.29, 7.28, 7.28, 7.27, 7.27, 7.26, 7.25, 7.25, 6.61, 6.61, 6.59, 6.59, 6.47, 6.47, 5.09, 3.77, 1.58.

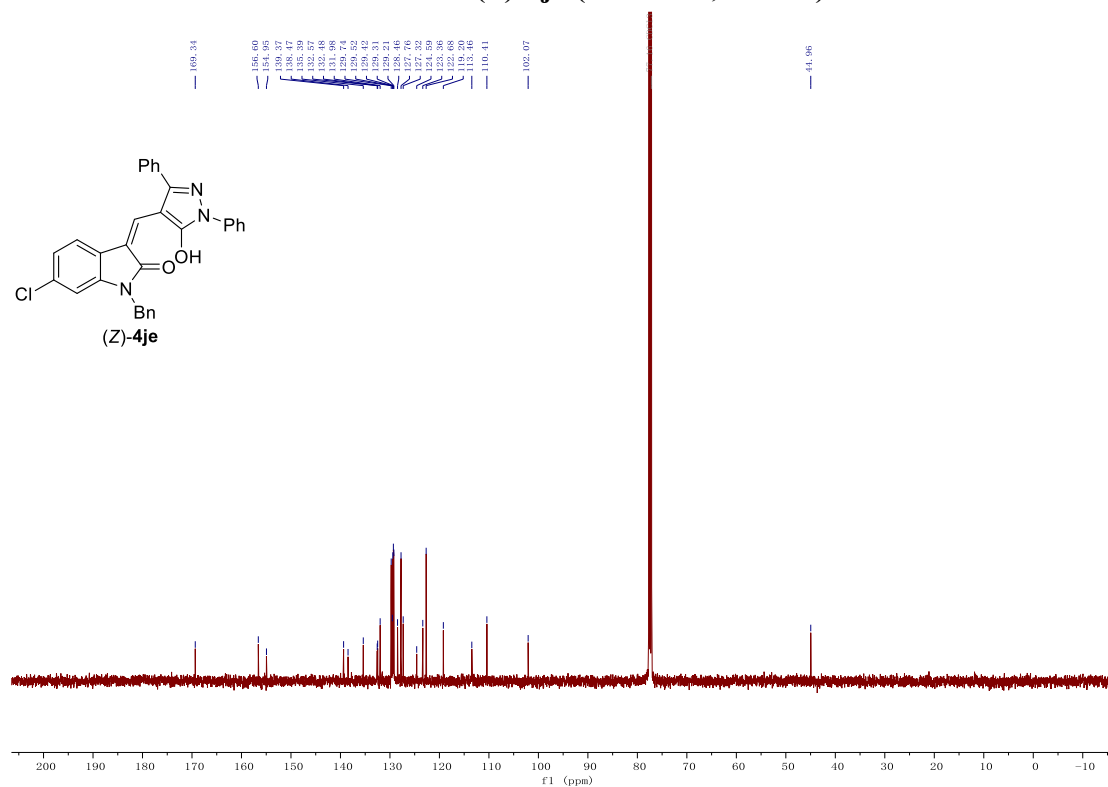
Integration values: 1.00, 2.01, 2.00, 1.02, 3.00, 2.00, 3.02, 2.01, 1.06, 1.03, 1.01, 2.01, 3.01.

[illegible]

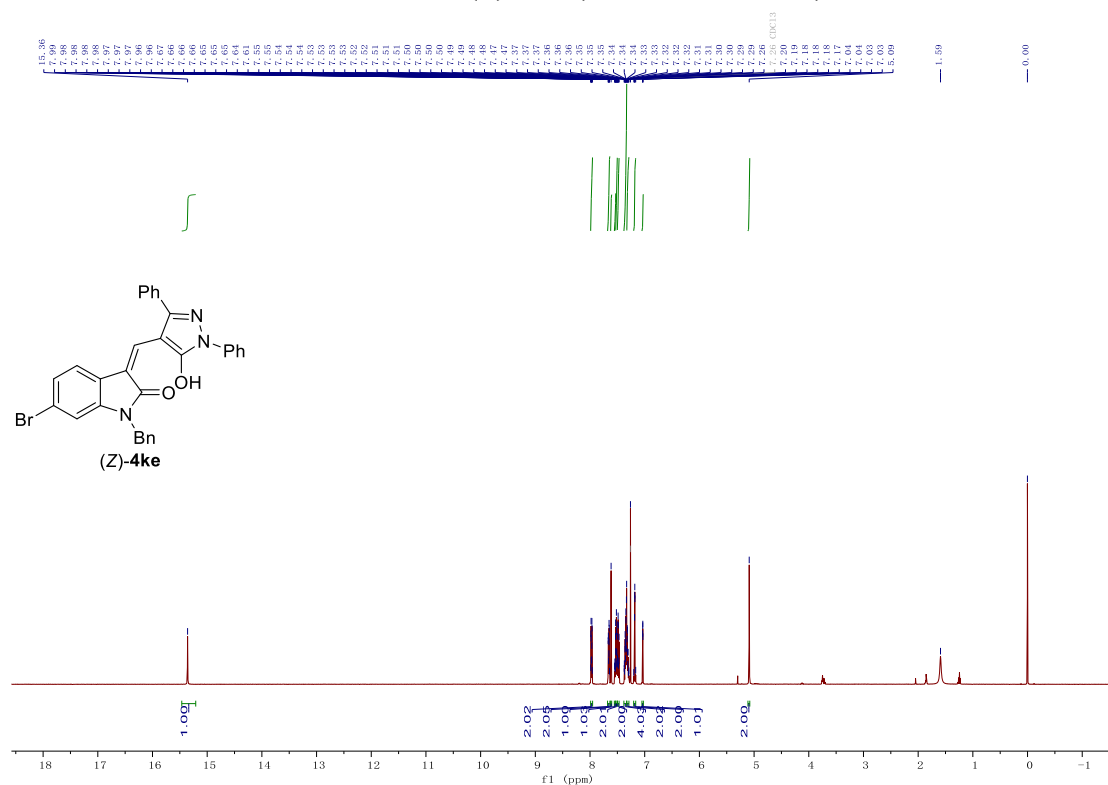
¹H NMR of (Z)-4je (500 MHz, CDCl₃)



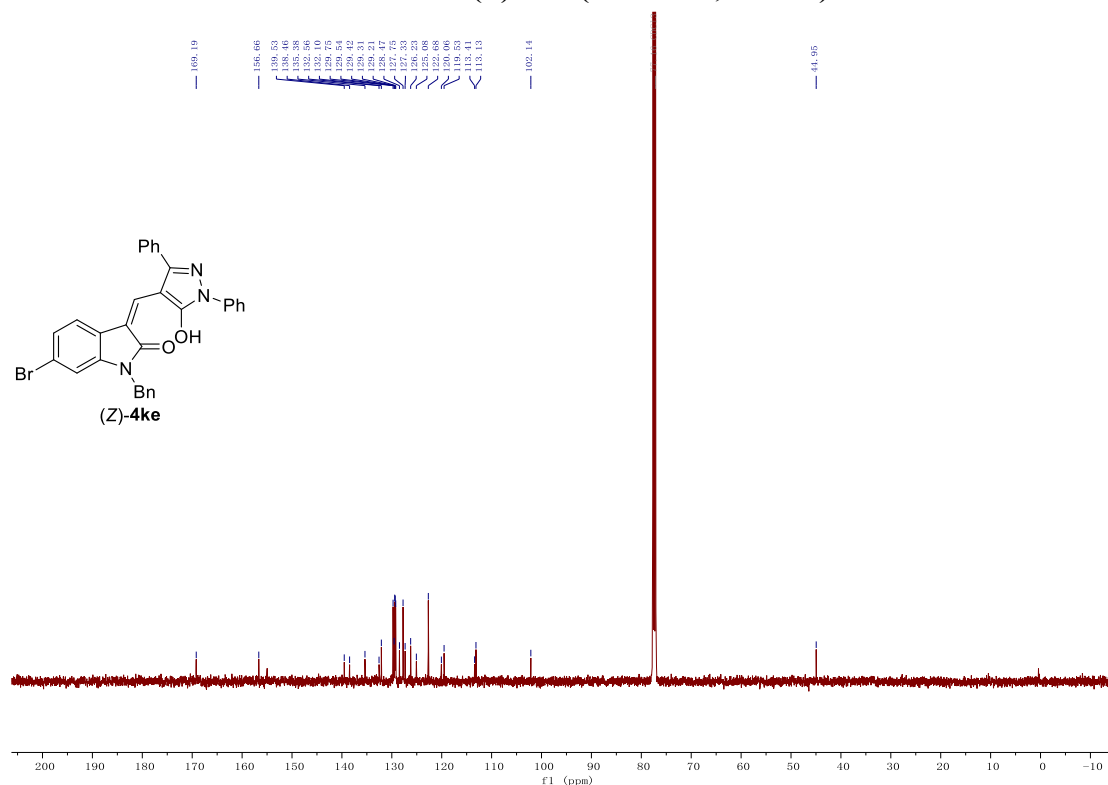
¹³C NMR of (Z)-4je (126 MHz, CDCl₃)



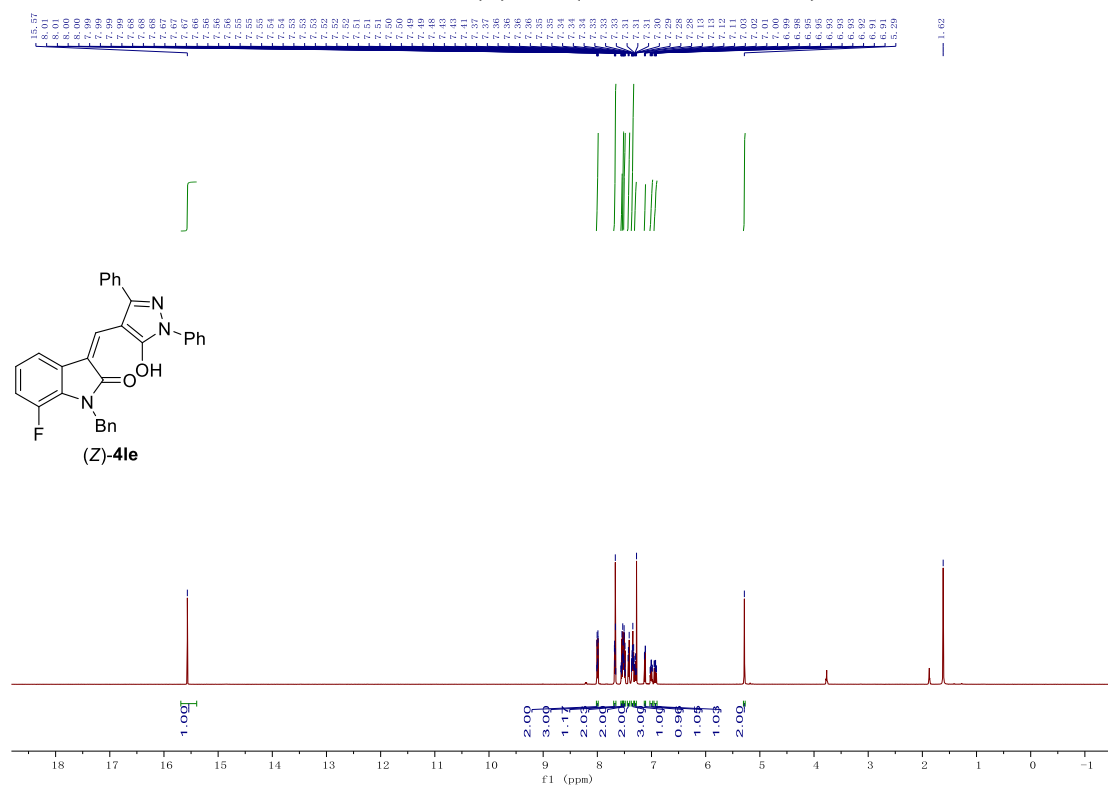
¹H NMR of (Z)-4ke (500 MHz, CDCl₃)



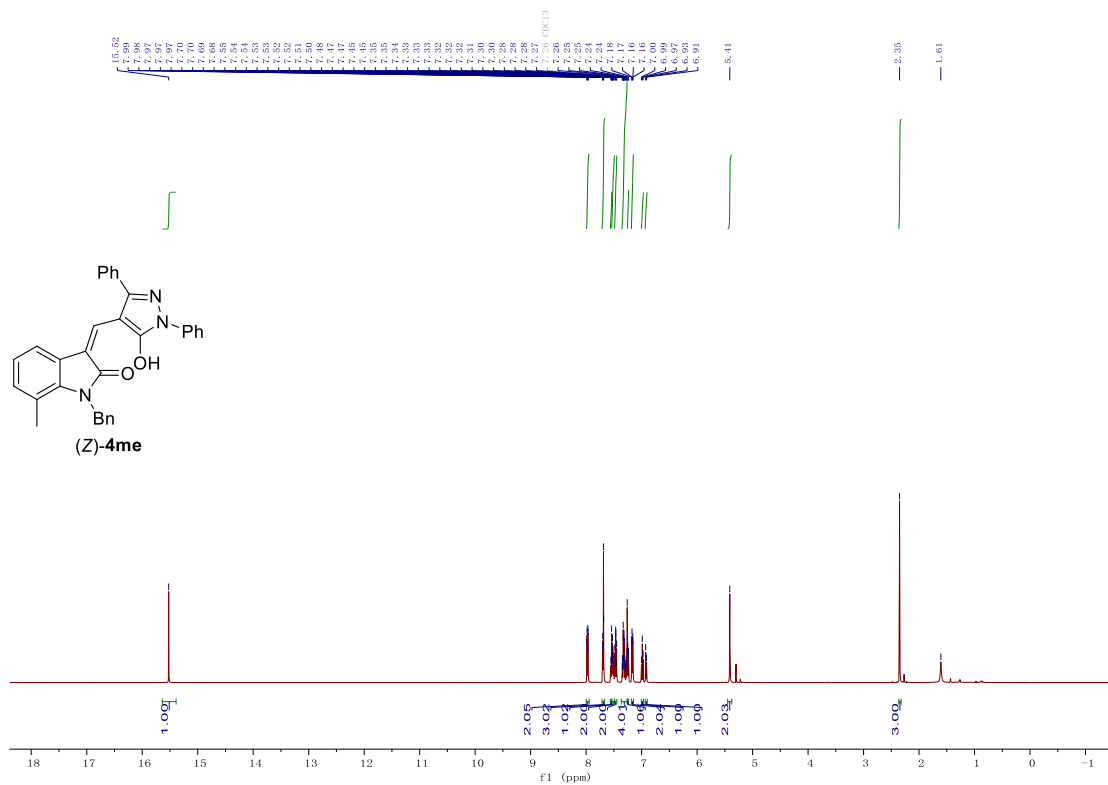
¹³C NMR of (Z)-4ke (126 MHz, CDCl₃)



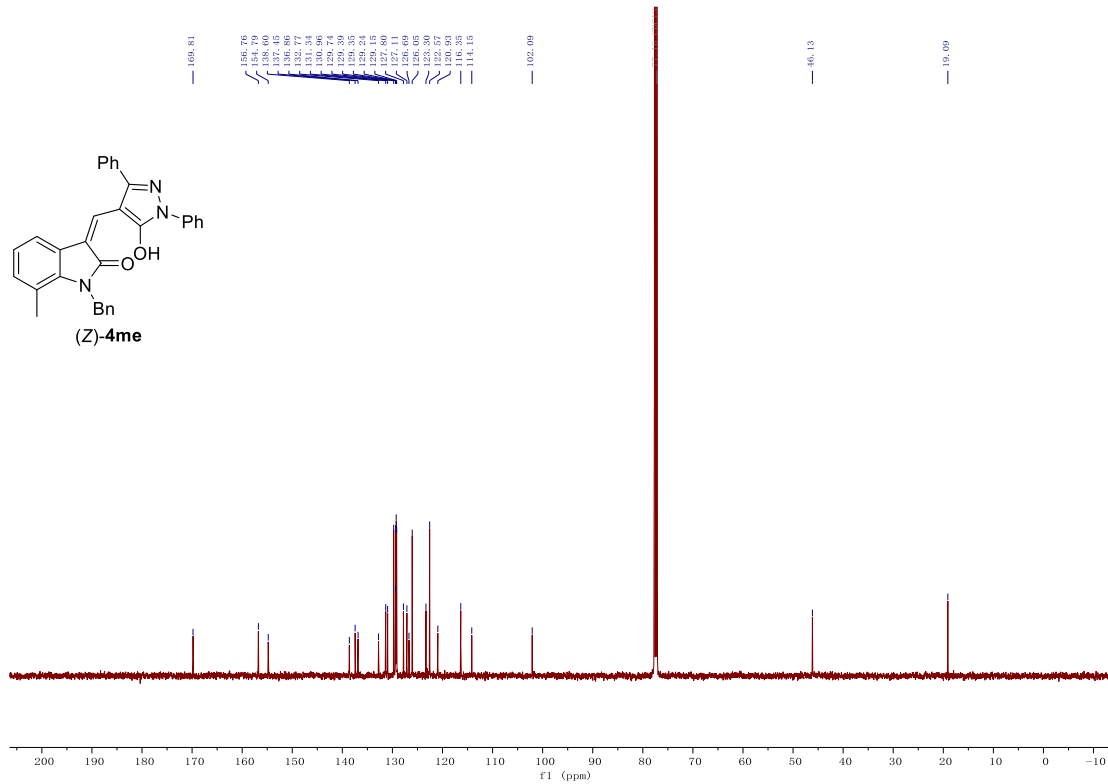
¹H NMR of (Z)-4le (500 MHz, CDCl₃)



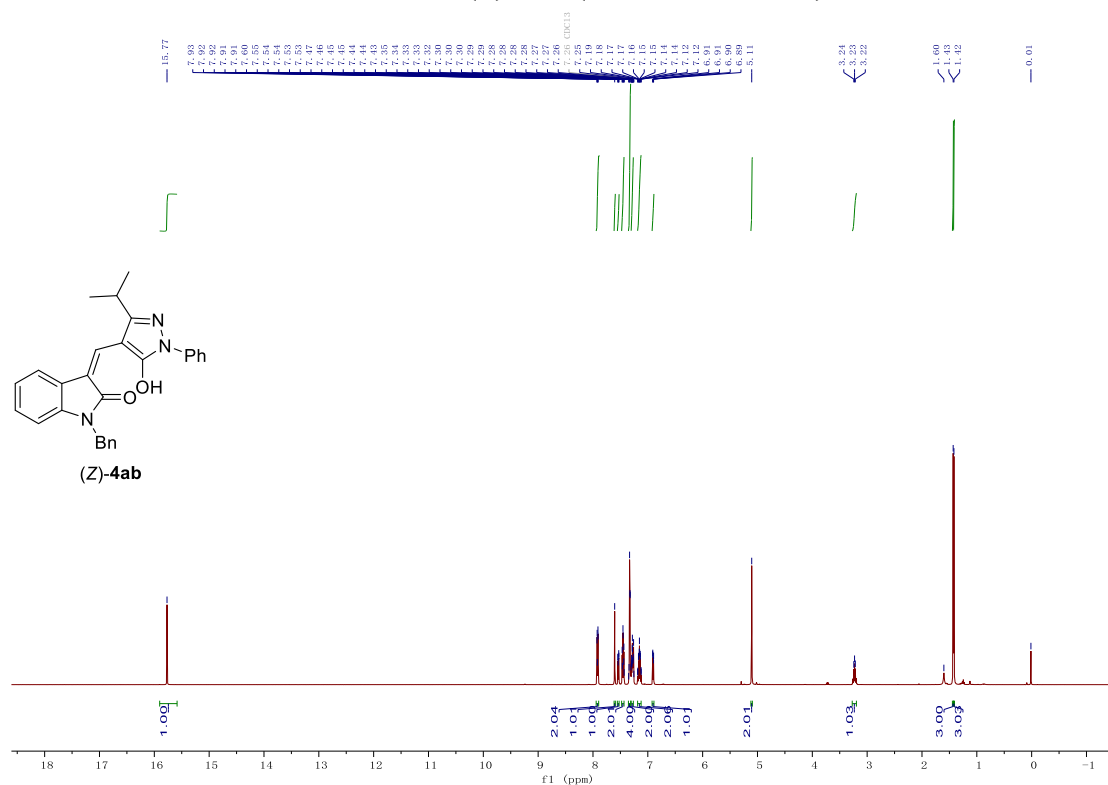
¹H NMR of (Z)-4me (500 MHz, CDCl₃)



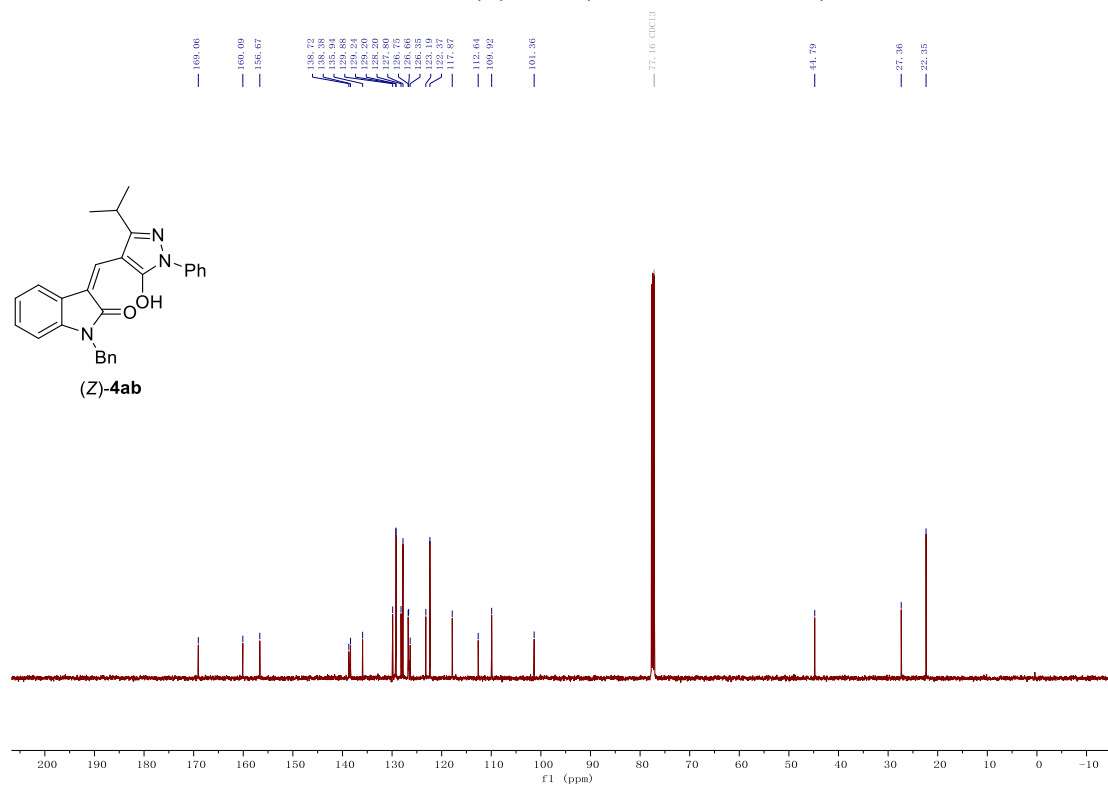
^{13}C NMR of (Z)-4me (126 MHz, CDCl_3)



¹H NMR of (Z)-4ab (500 MHz, CDCl₃)



¹³C NMR of (Z)-4ab (126 MHz, CDCl₃)



Chemical structure of (Z)-4ac is shown on the left. The structure is a benzimidazole derivative with a phenyl group on the nitrogen, a benzyl group on the nitrogen, and a (Z)-4-acetylphenyl group on the imidazole ring.

¹H NMR spectrum (CDCl₃):

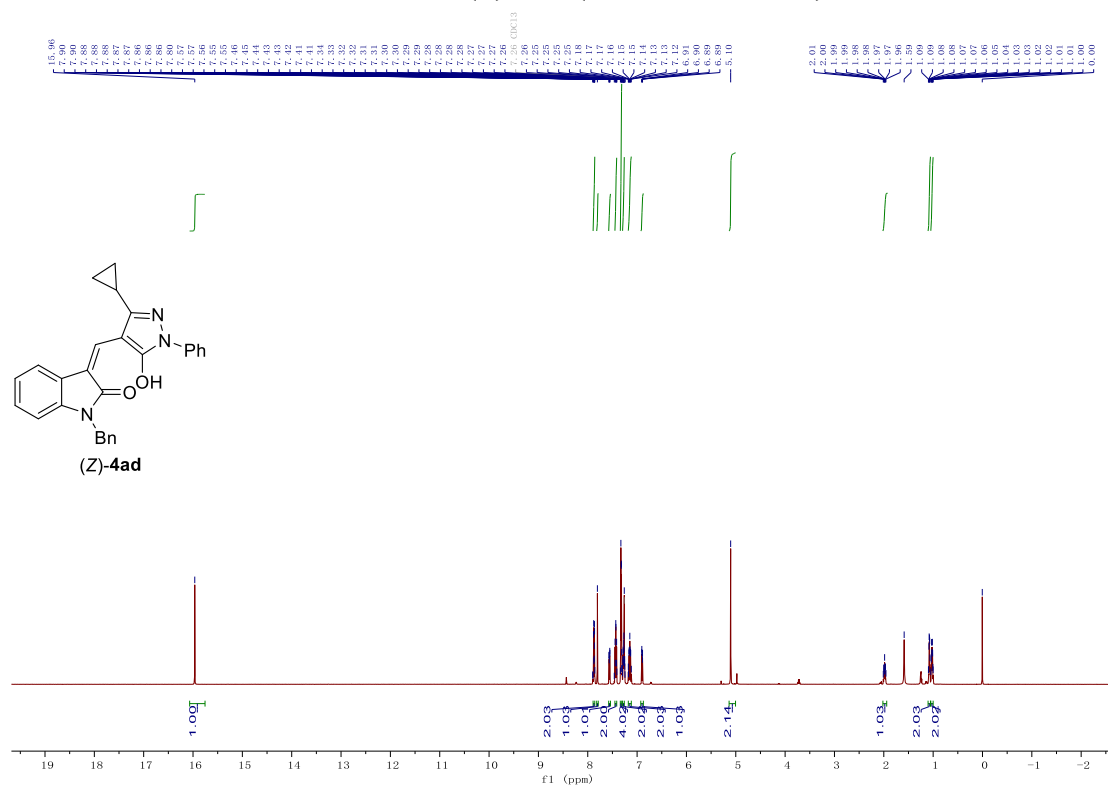
The spectrum displays peaks in the aromatic region (6.5-8.0 ppm) and a sharp singlet at 1.58 ppm corresponding to the acetyl methyl group. Integration values are provided below the peaks.

Chemical Shift (ppm)	Integration
~15.24	1.00
~7.8	1.02
~7.7	2.00
~7.6	1.04
~7.5	2.00
~7.4	4.00
~7.3	2.01
~7.2	2.01
~7.1	0.99
~6.9	2.01
1.58	9.06

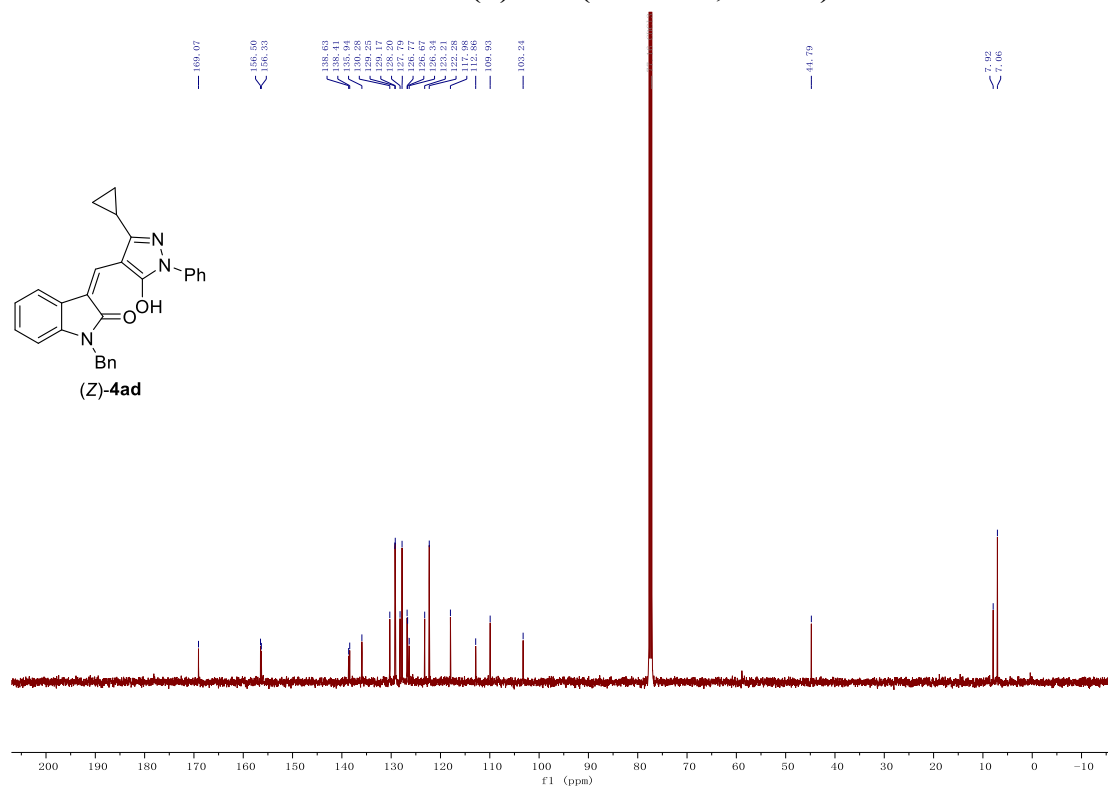
(Z)-4ac

¹³C NMR spectrum (CDCl₃) of (Z)-4ac. The x-axis represents the chemical shift in ppm, ranging from -10 to 200. The spectrum shows several peaks corresponding to the carbon atoms in the molecule. Key peaks are labeled with their chemical shifts: 169.06, 160.99, 157.26, 139.77, 138.34, 135.93, 135.50, 132.85, 129.95, 129.18, 128.18, 127.81, 127.21, 126.69, 126.51, 123.25, 122.25, 117.77, 112.21, 109.97, 101.88, 41.86, 31.69, and 30.79. A solvent triplet for CDCl₃ is visible at 77.0 ppm.

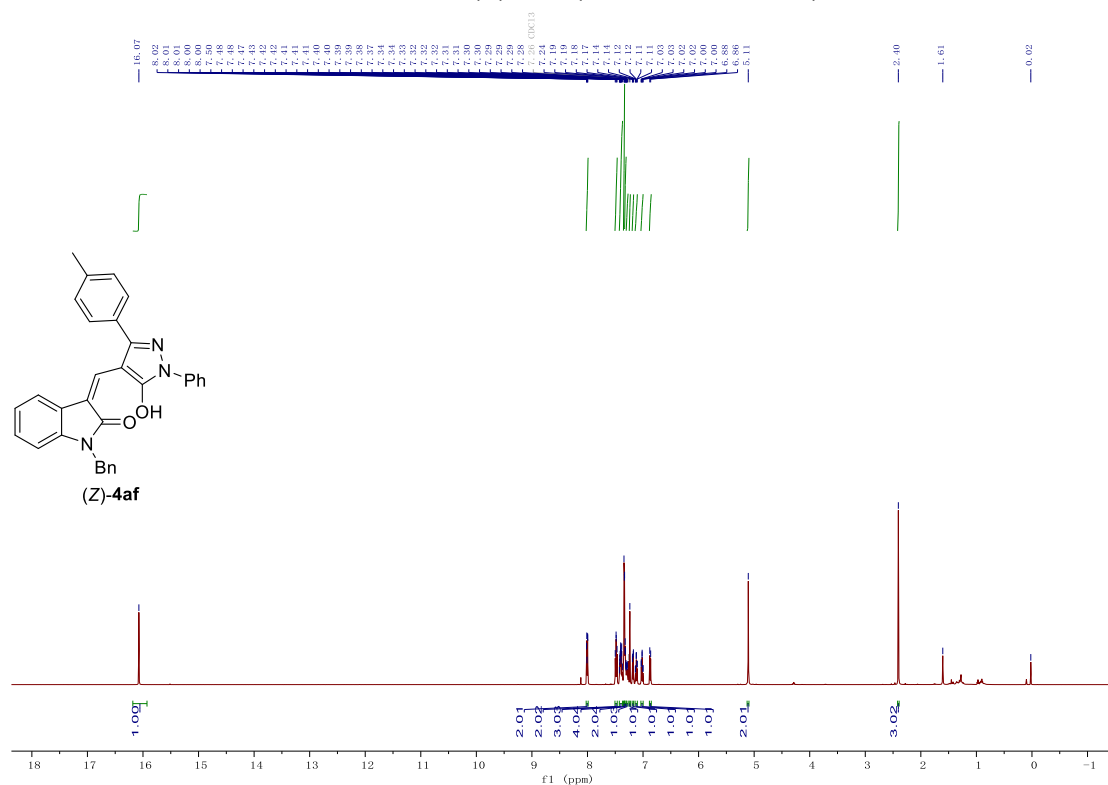
¹H NMR of (Z)-4ad (500 MHz, CDCl₃)



¹³C NMR of (Z)-4ad (126 MHz, CDCl₃)



¹H NMR of (Z)-4af (500 MHz, CDCl₃)



Chemical structure of (Z)-4ag: COc1ccc(cc1)/C=C2/C(=O)O[C@H](C2)/N(c3ccccc3)c4ccccc4

¹H NMR spectrum (CDCl₃) of (Z)-4ag. The x-axis represents the chemical shift in ppm, ranging from 0 to 18. The spectrum shows several peaks, with integration values indicated below the baseline. The chemical shifts (ppm) are listed on the right side of the spectrum.

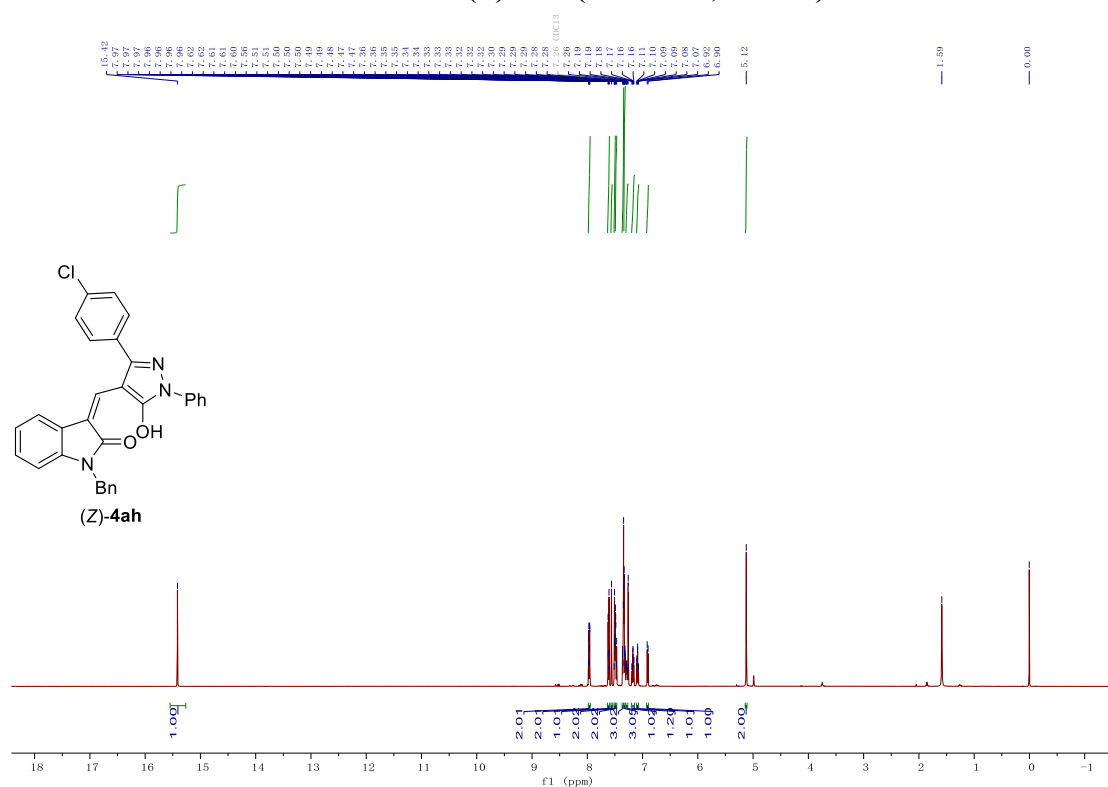
Chemical shifts (ppm): 7.99, 7.98, 7.98, 7.98, 7.98, 7.63, 7.62, 7.60, 7.60, 7.48, 7.48, 7.37, 7.36, 7.35, 7.35, 7.34, 7.34, 7.33, 7.32, 7.29, 7.29, 7.17, 7.16, 7.14, 7.14, 7.07, 7.06, 7.05, 7.05, 6.89, 6.89, 5.13, 5.13, 3.90, 1.59, 0.08.

Integration values (from left to right): 1.00, 2.00, 3.04, 2.00, 3.93, 1.93, 1.00, 1.00, 3.00, 1.02, 2.00, 3.01.

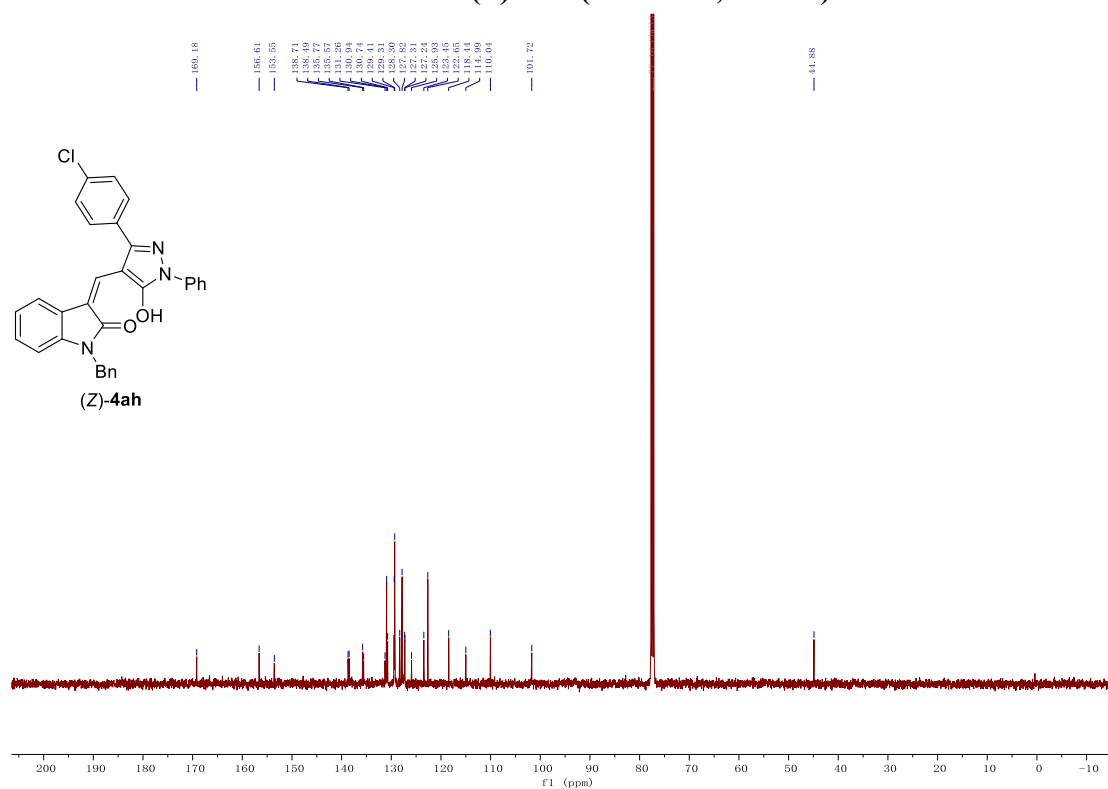
(Z)-4ag

199.16
160.77
159.42
154.67
138.62
137.85
135.88
131.68
131.67
130.70
129.28
129.26
128.23
127.10
126.92
126.42
125.16
123.29
122.52
118.35
114.64
114.23
109.94
101.92
55.81
41.85

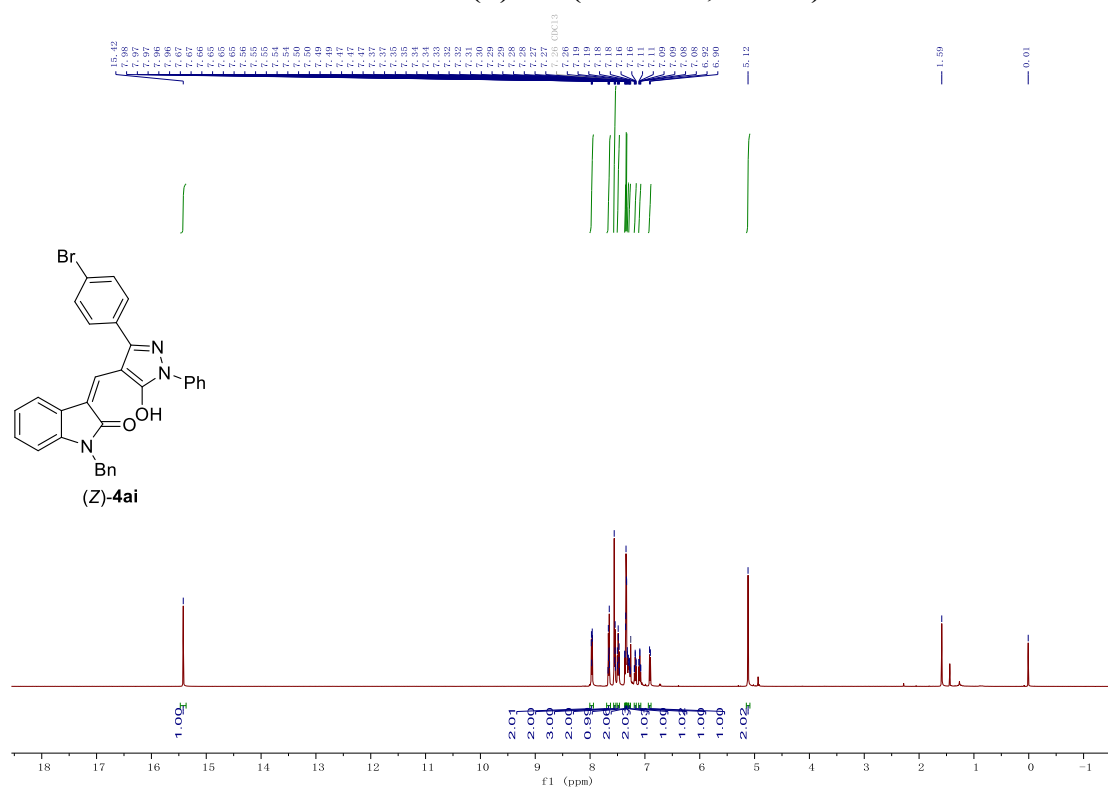
¹H NMR of (Z)-4ah (500 MHz, CDCl₃)



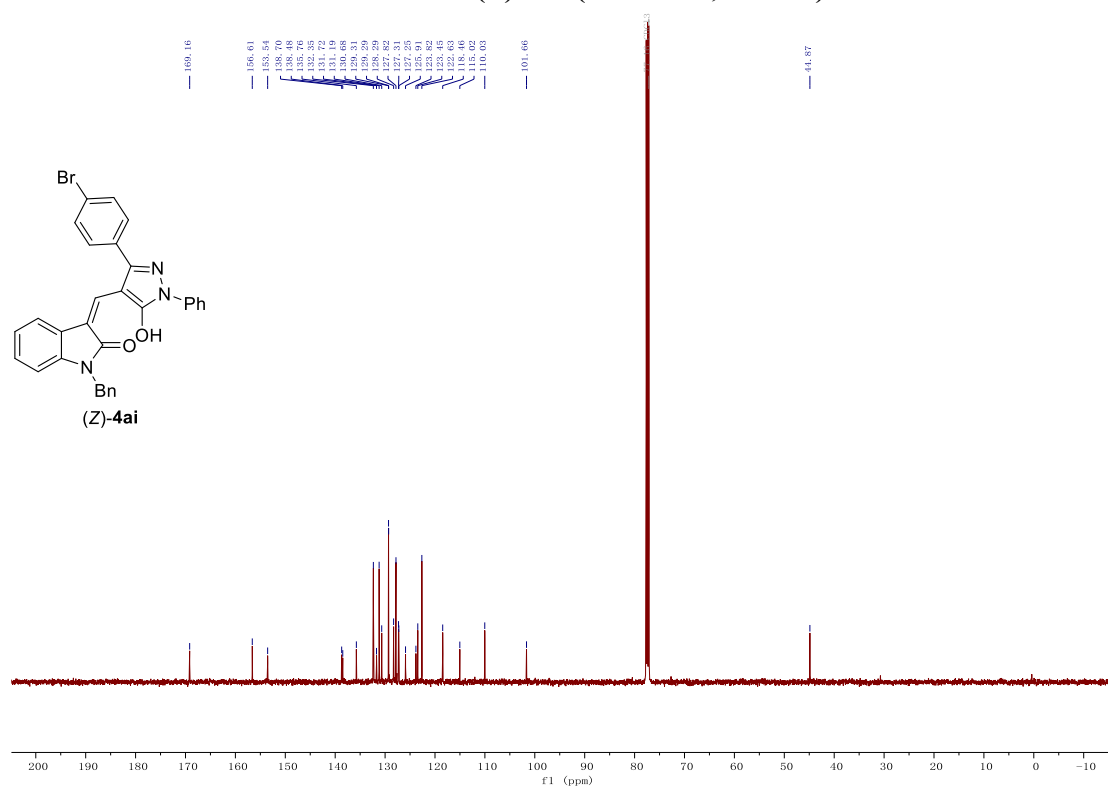
¹³C NMR of (Z)-4ah (126 MHz, CDCl₃)



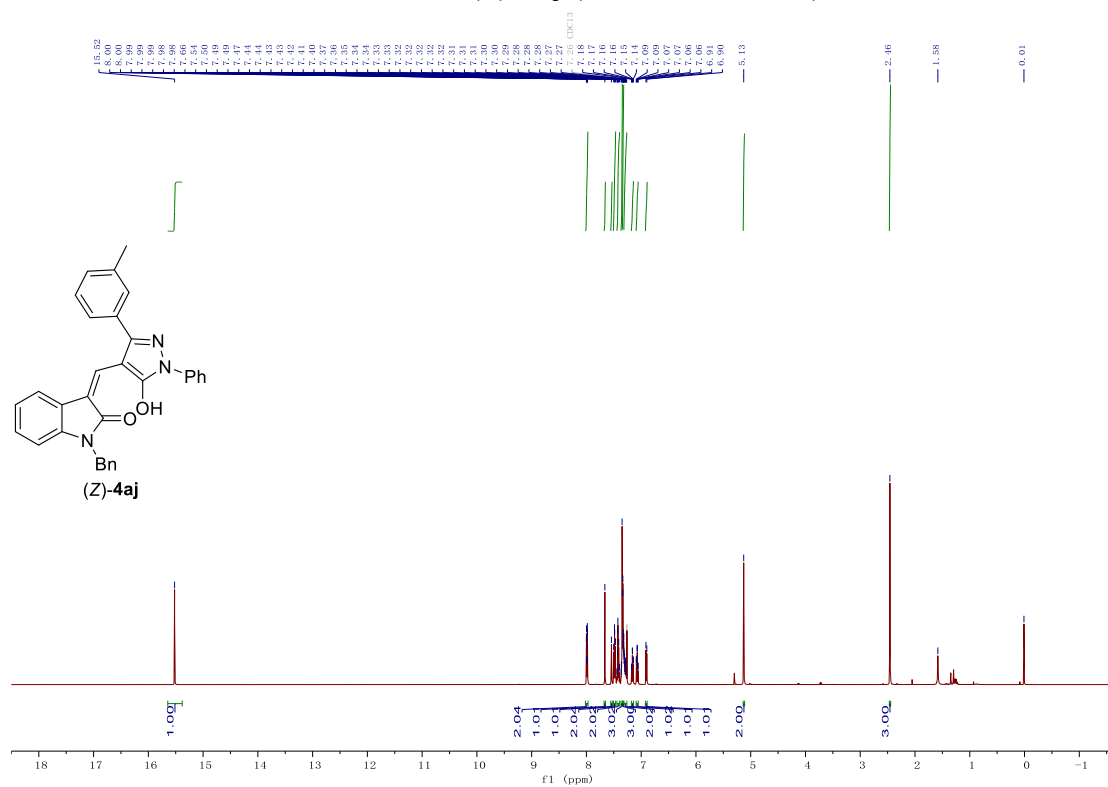
¹H NMR of (Z)-4ai (500 MHz, CDCl₃)



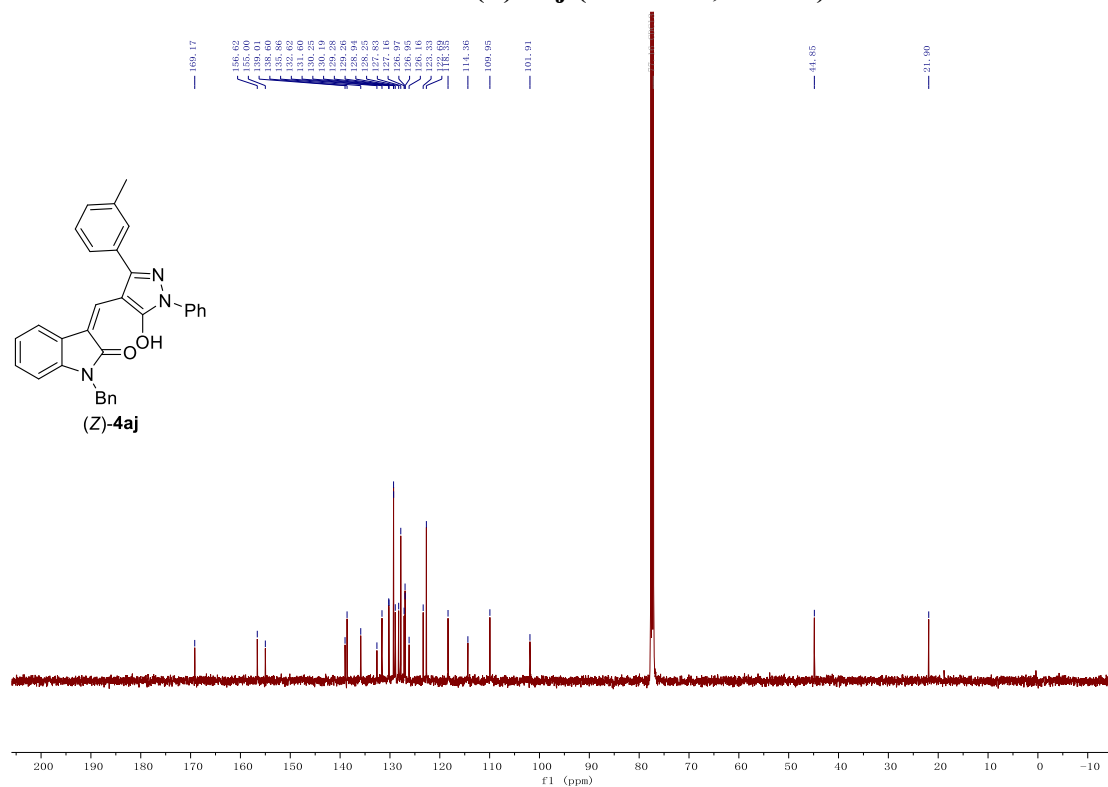
¹³C NMR of (Z)-4ai (126 MHz, CDCl₃)



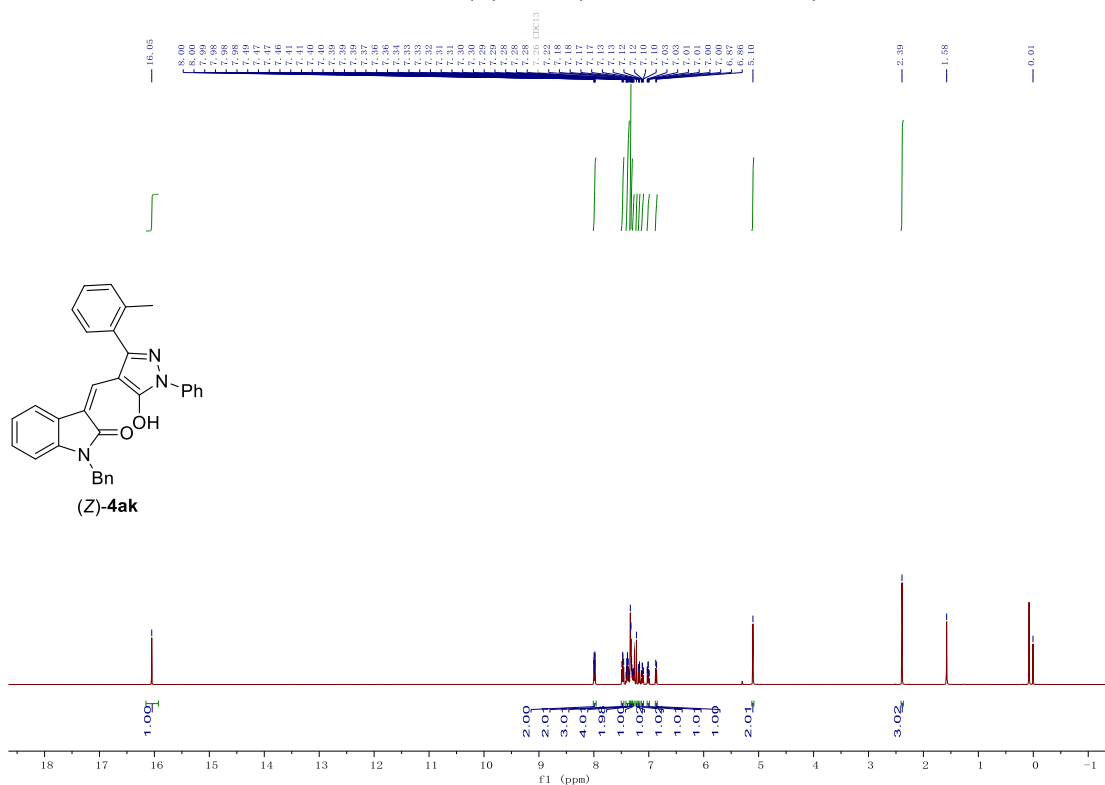
¹H NMR of (Z)-4aj (500 MHz, CDCl₃)



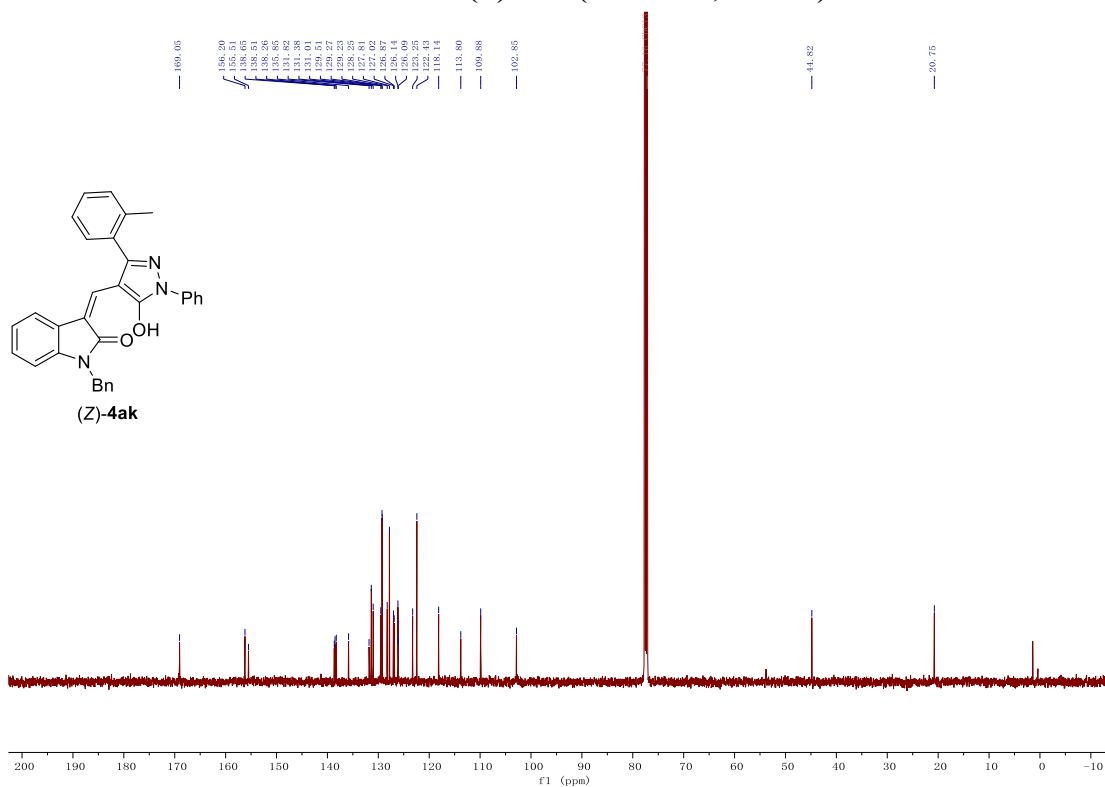
¹³C NMR of (Z)-4aj (126 MHz, CDCl₃)



¹H NMR of (Z)-4ak (500 MHz, CDCl₃)



¹³C NMR of (Z)-4ak (126 MHz, CDCl₃)

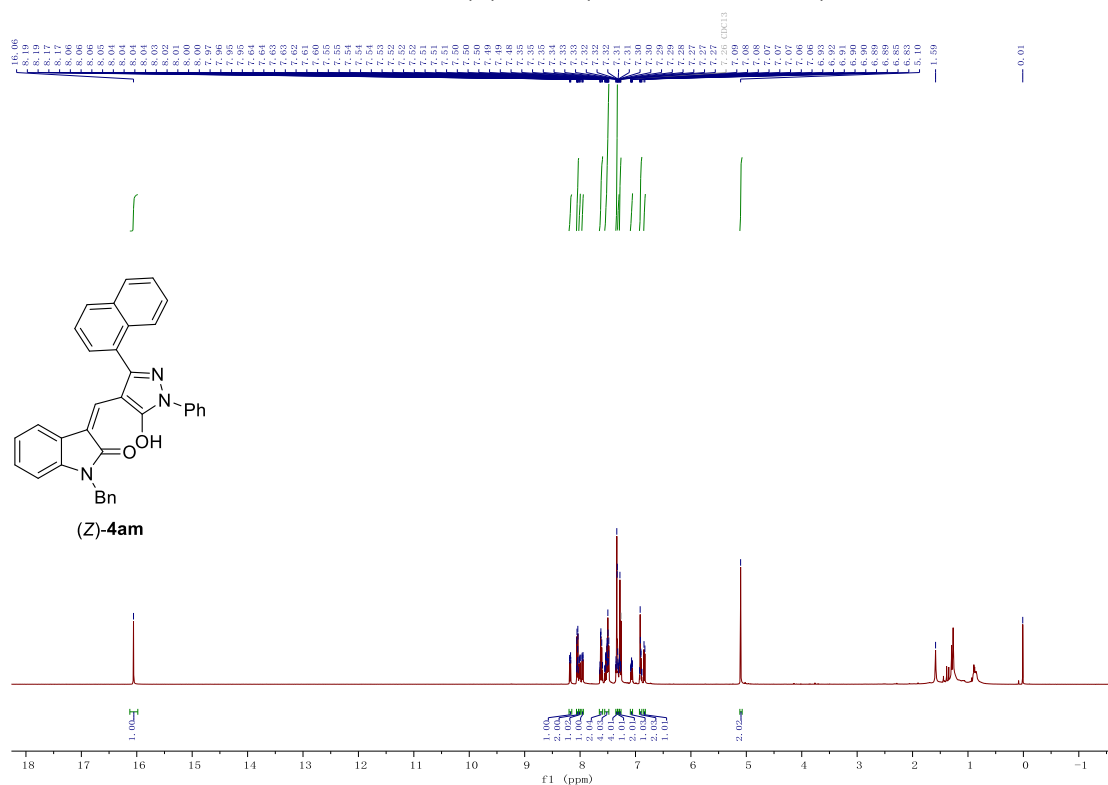


Chemical structure of (Z)-4al is shown as an inset. The structure is a benzimidazole derivative with a phenyl group on the nitrogen, a hydroxyl group, and a (Z)-2-phenyl-5-(naphthalen-1-yl)vinyl group.

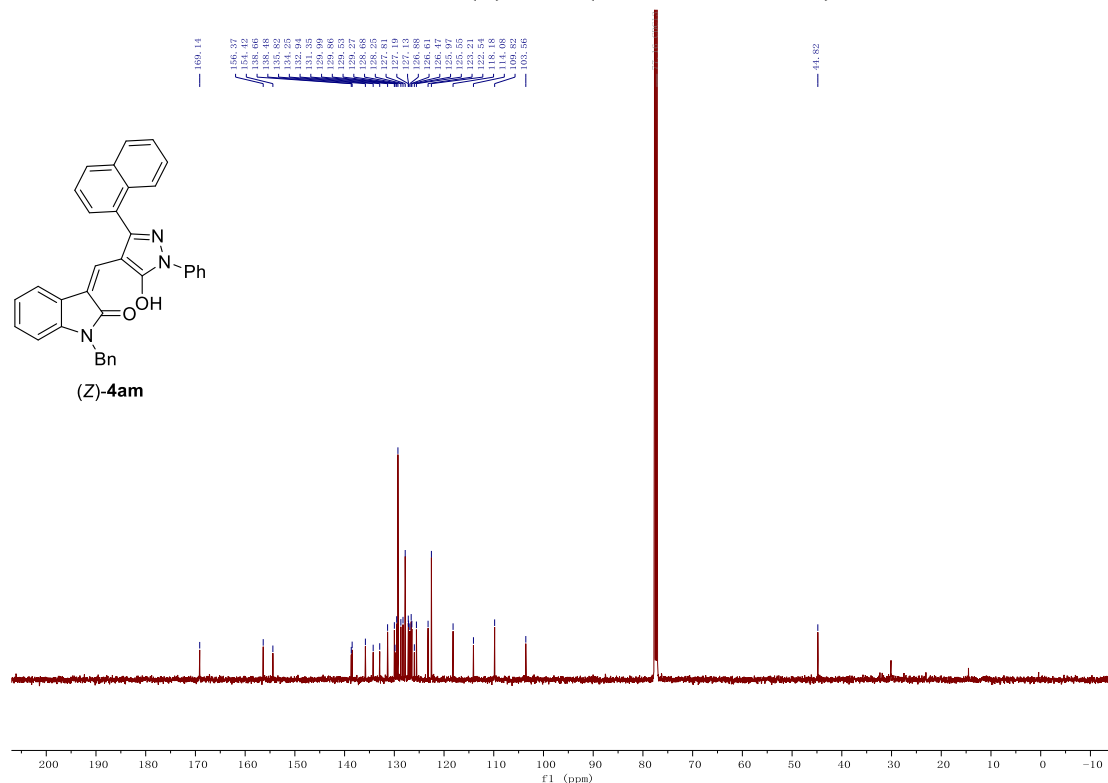
¹H NMR spectrum (CDCl₃) of (Z)-4al. The spectrum shows peaks at 15.50 (s, 1H), 7.50-7.30 (m, 10H), 5.01 (s, 1H), 1.58 (s, 3H), and 0.01 (s, 3H). The chemical structure of (Z)-4al is shown as an inset.

[illegible]

¹H NMR of (Z)-4am (500 MHz, CDCl₃)



¹³C NMR of (Z)-4am (126 MHz, CDCl₃)



Chemical structure of (Z)-4an is shown above the spectrum.

¹H NMR spectrum (CDCl₃) of (Z)-4an. The x-axis represents the chemical shift in ppm, ranging from 0 to 18. The y-axis represents the intensity. Integration values are shown below the baseline. The list of chemical shifts (δ) is provided on the right side of the spectrum.

Chemical shifts (ppm): 8.13, 7.97, 7.96, 7.95, 7.95, 7.65, 7.65, 7.54, 7.53, 7.52, 7.49, 7.48, 7.47, 7.47, 7.33, 7.33, 7.29, 7.29, 7.28, 7.28, 7.26, 7.26, 7.18, 7.18, 7.17, 7.16, 7.16, 7.14, 7.14, 7.12, 7.12, 6.91, 6.91, 6.90, 6.88, 6.87, 6.60, 6.60, 6.59, 6.59, 5.11.

Integration values (from left to right): 1.00, 1.01, 2.00, 0.98, 1.01, 2.02, 5.02, 1.04, 2.04, 2.00, 1.00, 2.02.

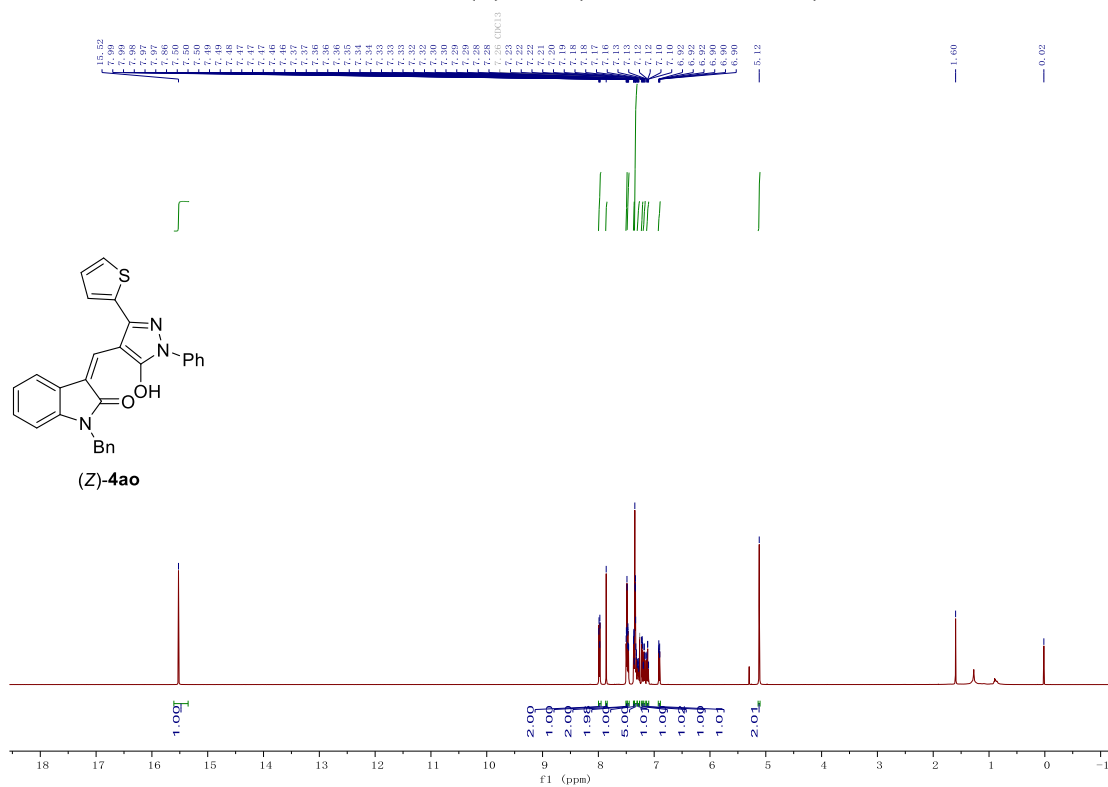
(Z)-4an

Chemical structure of (Z)-4an is shown. The structure is a benzimidazole derivative with a benzyl group on the nitrogen, a carboxylic acid group, and a (Z)-2-phenyl-5-(furan-2-yl)vinyl group.

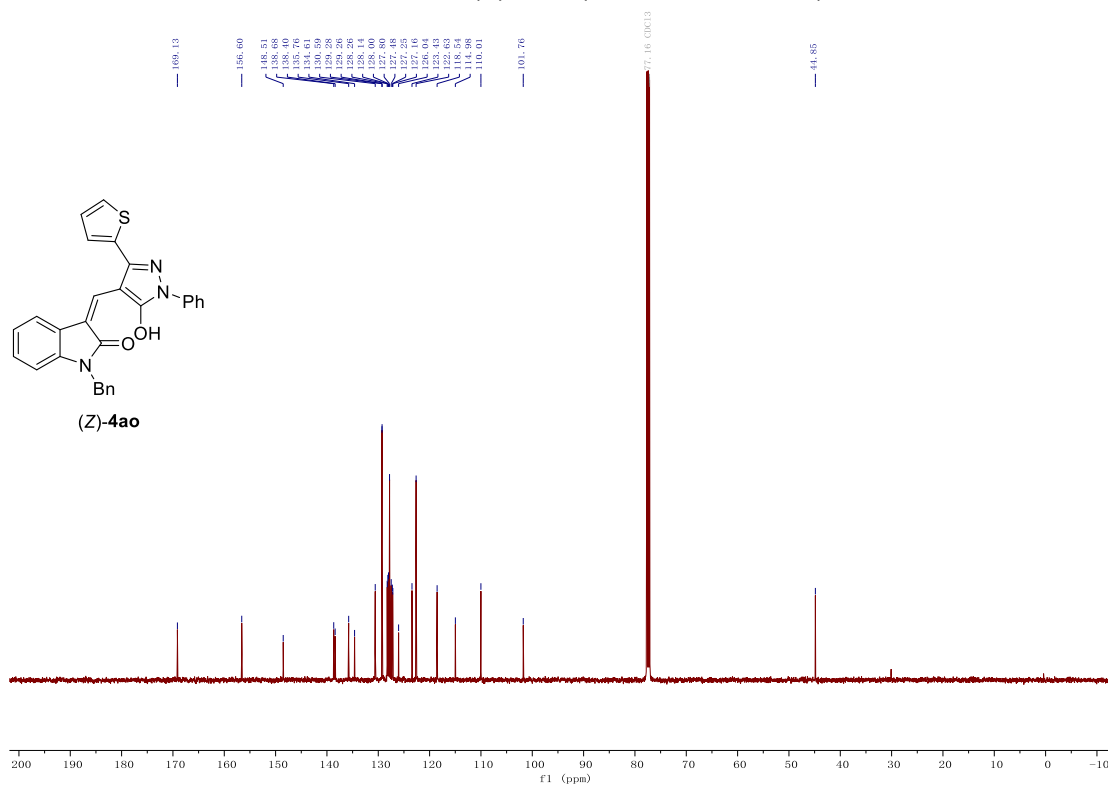
^{13}C NMR spectrum (CDCl₃) of (Z)-4an. The x-axis represents the chemical shift in ppm, ranging from -10 to 200. The spectrum shows several peaks corresponding to the carbon atoms in the molecule. The peak values are listed on the right side of the spectrum:

- 168.80
- 150.07
- 147.01
- 144.60
- 143.52
- 138.41
- 138.14
- 135.51
- 135.46
- 133.02
- 129.99
- 129.90
- 129.86
- 127.53
- 127.08
- 126.97
- 125.91
- 123.17
- 122.52
- 118.26
- 114.75
- 114.72
- 110.76
- 109.72
- 109.74
- 101.23
- 77.16 (CDCl₃)
- 44.58

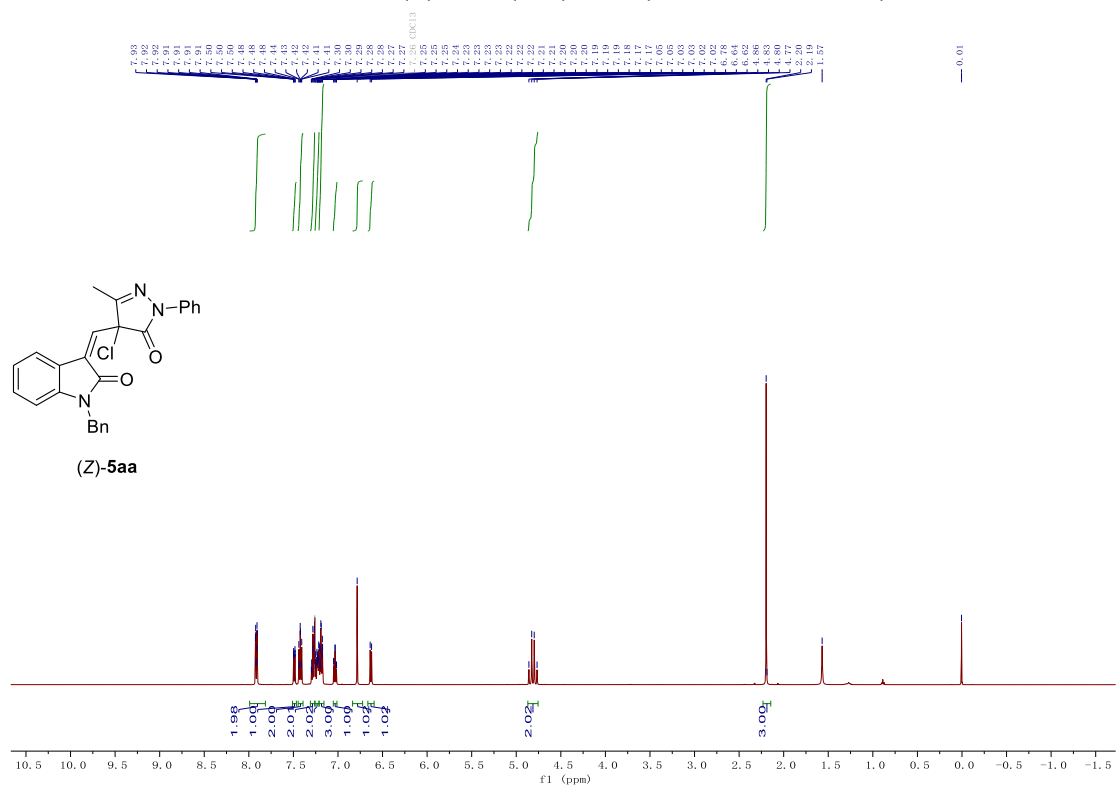
¹H NMR of (Z)-4ao (500 MHz, CDCl₃)



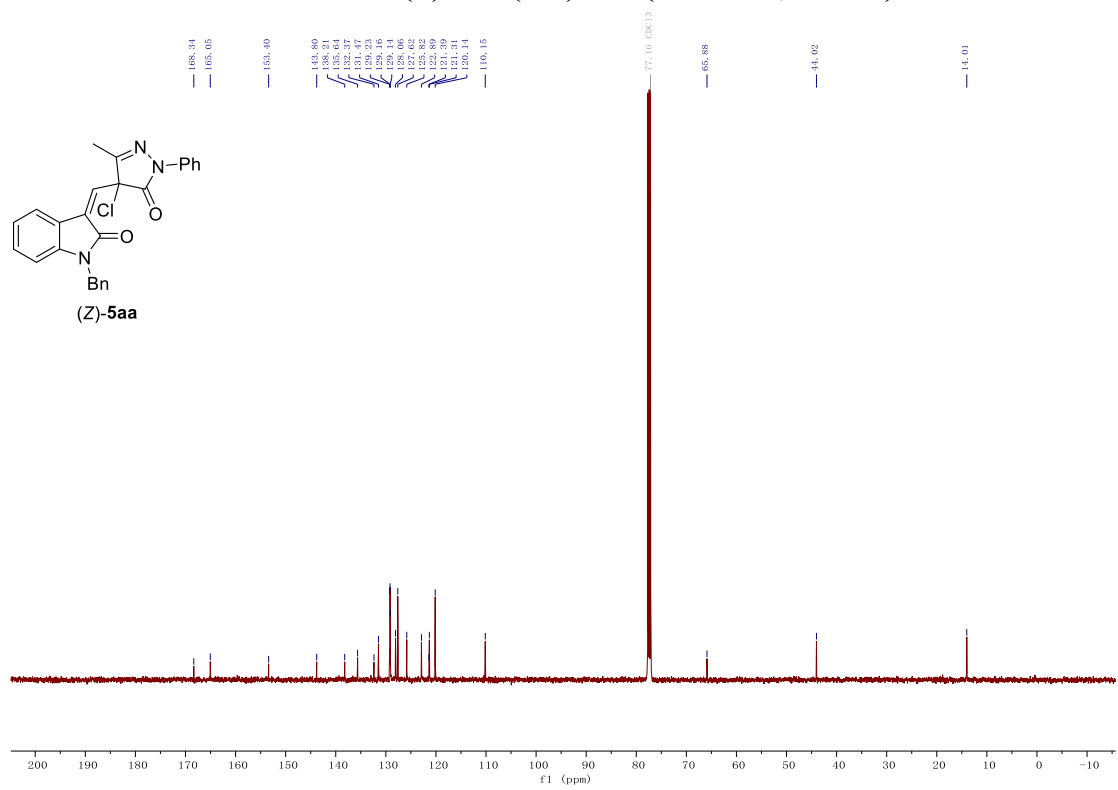
^{13}C NMR of (Z)-4ao (126 MHz, CDCl_3)



¹H NMR of (Z)-5aa/(S,Z)-5aa (500 MHz, CDCl₃)



¹³C NMR of (Z)-5aa/(S,Z)-5aa (126 MHz, CDCl₃)



Chemical structure of **(E)-5aa** is shown in the top left corner. The structure is a tricyclic compound consisting of a benzene ring fused to a five-membered ring containing a carbonyl group and a nitrogen atom substituted with a benzyl group (Bn). This five-membered ring is further fused to a six-membered ring containing a carbonyl group, a chlorine atom, and a nitrogen atom substituted with a phenyl group (Ph). The stereochemistry is (E).

The ^1H NMR spectrum (400 MHz, CDCl_3) is displayed below the structure. The x-axis represents the chemical shift in ppm, ranging from -1.5 to 10.5. The spectrum shows several peaks, with integration values indicated below the baseline. The peaks are assigned to the following protons in the molecule:

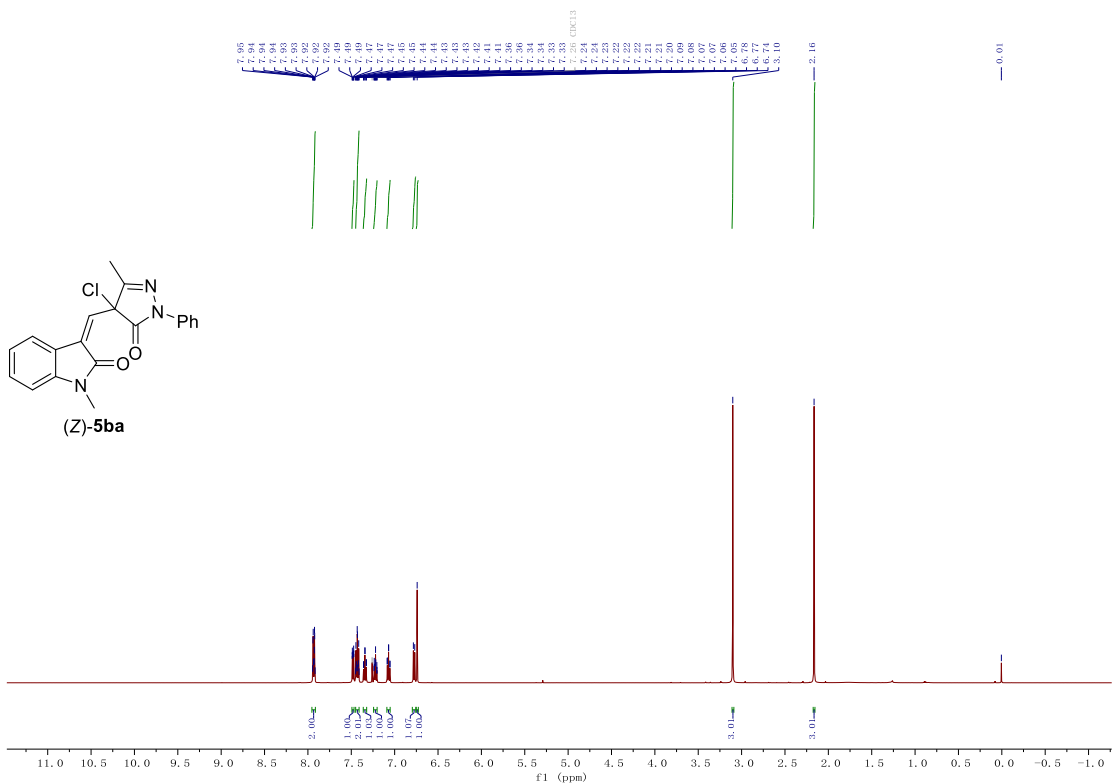
- Aromatic protons (Ph and Bn): 7.25-7.89 ppm (integration: 2.00, 1.00, 2.00, 4.00, 1.00, 1.00, 1.00, 1.00).
- Allylic protons: 6.50-7.10 ppm (integration: 1.00, 1.00, 1.00).
- Allylic protons: 4.50-4.70 ppm (integration: 2.00).
- Allylic protons: 2.50-2.70 ppm (integration: 3.00).
- Residual solvent peak: 0.00 ppm (integration: 0.00).

(E)-5aa

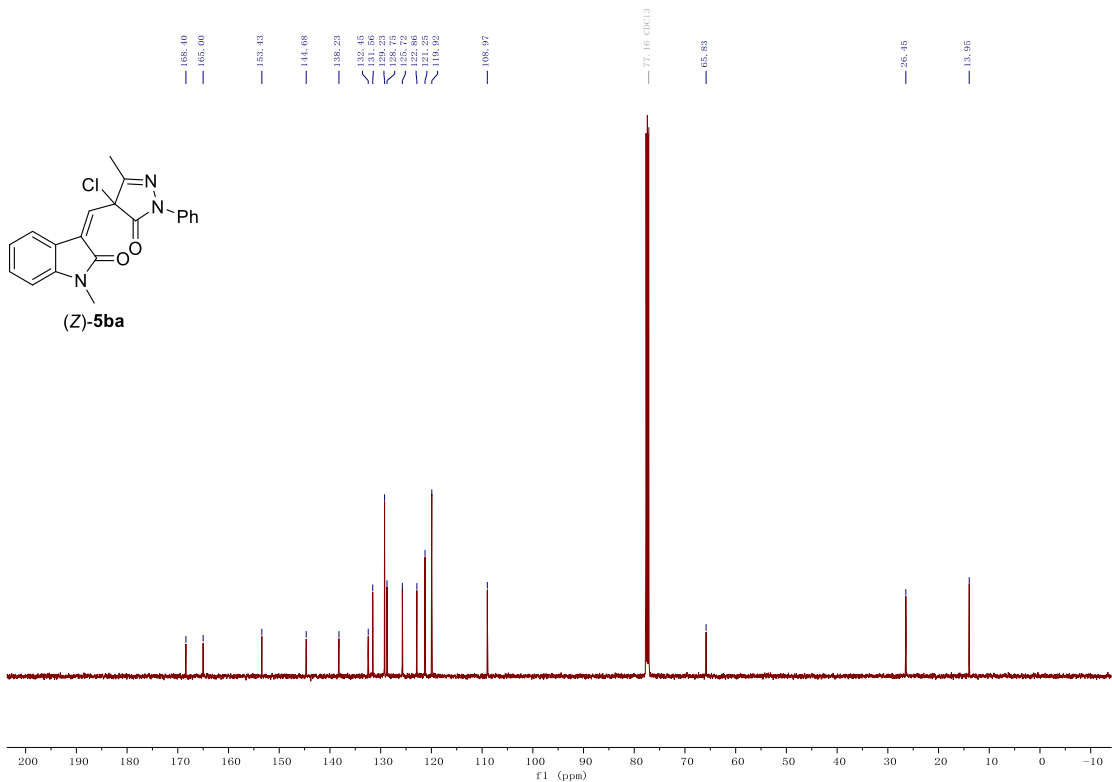
¹³C NMR spectrum (CDCl₃) of **(E)-5aa**. The x-axis represents the chemical shift in ppm, ranging from 0 to 200. The spectrum shows several peaks corresponding to the structure, including aromatic and carbonyl carbons between 120 and 167 ppm, a solvent triplet at 77.16 ppm, and alkenic/benzylic carbons at 63.45, 43.89, and 13.47 ppm.

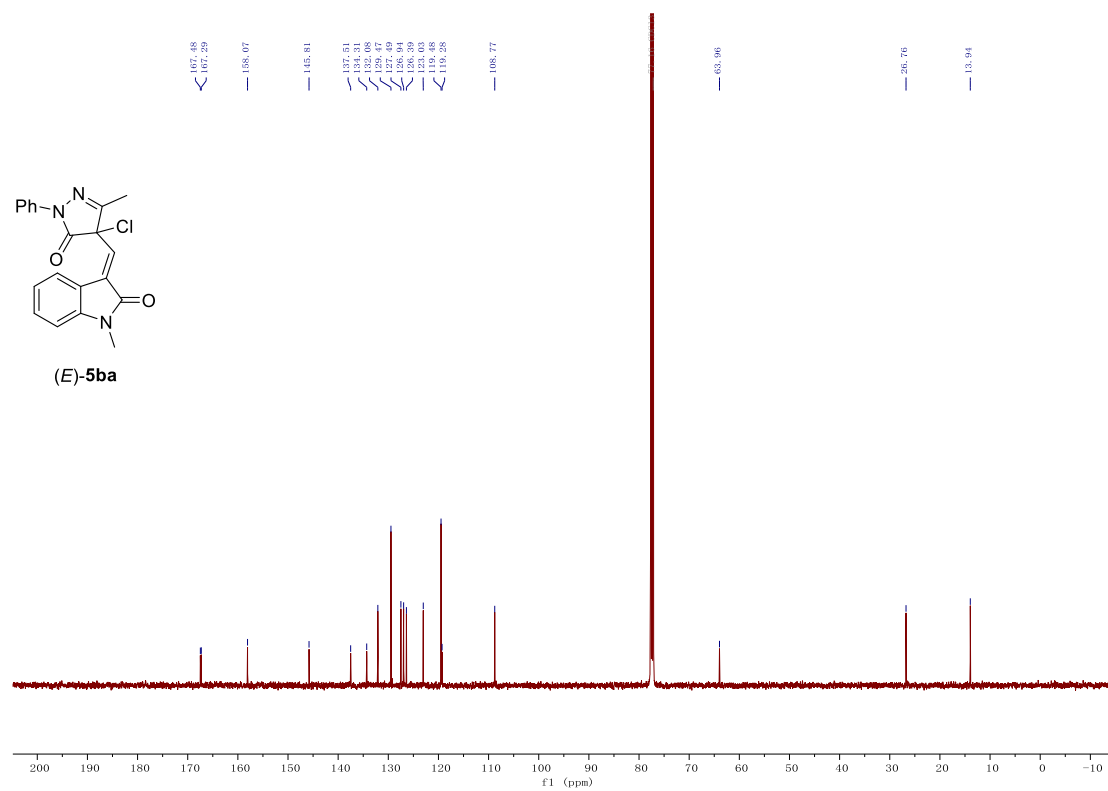
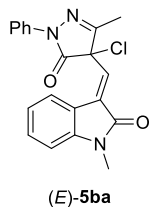
Chemical Shift (ppm)
166.96
166.93
157.42
144.44
136.98
135.41
133.70
131.62
129.85
128.73
127.66
127.14
126.66
122.90
118.88
109.28
77.16 (CDCl ₃)
63.45
43.89
13.47

¹H NMR of (Z)-5ba (500 MHz, CDCl₃)



^{13}C NMR of (Z)-5ba (126 MHz, CDCl_3)





Chemical structure of (Z)-5ca is shown above the spectrum. The structure is a benzimidazole derivative with a propargyl group on the nitrogen, a chlorine atom, and a phenyl group on the imidazole ring.

(Z)-5ca

¹H NMR spectrum (CDCl₃):

The spectrum displays the following chemical shifts (ppm) and integration values:

- 7.93, 7.93, 7.92, 7.92, 7.91, 7.91, 7.91, 7.91, 7.92, 7.92, 7.90, 7.90, 7.85, 7.85, 7.84, 7.84, 7.83, 7.83, 7.82, 7.82, 7.81, 7.81, 7.80, 7.80, 7.79, 7.79, 7.78, 7.78, 7.77, 7.77, 7.76, 7.76, 7.75, 7.75, 7.74, 7.74, 7.73, 7.73, 7.72, 7.72, 7.71, 7.71, 7.70, 7.70, 7.69, 7.69, 7.68, 7.68, 7.67, 7.67, 7.66, 7.66, 7.65, 7.65, 7.64, 7.64, 7.63, 7.63, 7.62, 7.62, 7.61, 7.61, 7.60, 7.60, 7.59, 7.59, 7.58, 7.58, 7.57, 7.57, 7.56, 7.56, 7.55, 7.55, 7.54, 7.54, 7.53, 7.53, 7.52, 7.52, 7.51, 7.51, 7.50, 7.50, 7.49, 7.49, 7.48, 7.48, 7.47, 7.47, 7.46, 7.46, 7.45, 7.45, 7.44, 7.44, 7.43, 7.43, 7.42, 7.42, 7.41, 7.41, 7.40, 7.40, 7.39, 7.39, 7.38, 7.38, 7.37, 7.37, 7.36, 7.36, 7.35, 7.35, 7.34, 7.34, 7.33, 7.33, 7.32, 7.32, 7.31, 7.31, 7.30, 7.30, 7.29, 7.29, 7.28, 7.28, 7.27, 7.27, 7.26, 7.26, 7.25, 7.25, 7.24, 7.24, 7.23, 7.23, 7.22, 7.22, 7.21, 7.21, 7.20, 7.20, 7.19, 7.19, 7.18, 7.18, 7.17, 7.17, 7.16, 7.16, 7.15, 7.15, 7.14, 7.14, 7.13, 7.13, 7.12, 7.12, 7.11, 7.11, 7.10, 7.10, 7.09, 7.09, 7.08, 7.08, 7.07, 7.07, 7.06, 7.06, 7.05, 7.05, 7.04, 7.04, 7.03, 7.03, 7.02, 7.02, 7.01, 7.01, 7.00, 7.00, 6.99, 6.99, 6.98, 6.98, 6.97, 6.97, 6.96, 6.96, 6.95, 6.95, 6.94, 6.94, 6.93, 6.93, 6.92, 6.92, 6.91, 6.91, 6.90, 6.90, 6.89, 6.89, 6.88, 6.88, 6.87, 6.87, 6.86, 6.86, 6.85, 6.85, 6.84, 6.84, 6.83, 6.83, 6.82, 6.82, 6.81, 6.81, 6.80, 6.80, 6.79, 6.79, 6.78, 6.78, 6.77, 6.77, 6.76, 6.76, 6.75, 6.75, 6.74, 6.74, 6.73, 6.73, 6.72, 6.72, 6.71, 6.71, 6.70, 6.70, 6.69, 6.69, 6.68, 6.68, 6.67, 6.67, 6.66, 6.66, 6.65, 6.65, 6.64, 6.64, 6.63, 6.63, 6.62, 6.62, 6.61, 6.61, 6.60, 6.60, 6.59, 6.59, 6.58, 6.58, 6.57, 6.57, 6.56, 6.56, 6.55, 6.55, 6.54, 6.54, 6.53, 6.53, 6.52, 6.52, 6.51, 6.51, 6.50, 6.50, 6.49, 6.49, 6.48, 6.48, 6.47, 6.47, 6.46, 6.46, 6.45, 6.45, 6.44, 6.44, 6.43, 6.43, 6.42, 6.42, 6.41, 6.41, 6.40, 6.40, 6.39, 6.39, 6.38, 6.38, 6.37, 6.37, 6.36, 6.36, 6.35, 6.35, 6.34, 6.34, 6.33, 6.33, 6.32, 6.32, 6.31, 6.31, 6.30, 6.30, 6.29, 6.29, 6.28, 6.28, 6.27, 6.27, 6.26, 6.26, 6.25, 6.25, 6.24, 6.24, 6.23, 6.23, 6.22, 6.22, 6.21, 6.21, 6.20, 6.20, 6.19, 6.19, 6.18, 6.18, 6.17, 6.17, 6.16, 6.16, 6.15, 6.15, 6.14, 6.14, 6.13, 6.13, 6.12, 6.12, 6.11, 6.11, 6.10, 6.10, 6.09, 6.09, 6.08, 6.08, 6.07, 6.07, 6.06, 6.06, 6.05, 6.05, 6.04, 6.04, 6.03, 6.03, 6.02, 6.02, 6.01, 6.01, 6.00, 6.00, 5.99, 5.99, 5.98, 5.98, 5.97, 5.97, 5.96, 5.96, 5.95, 5.95, 5.94, 5.94, 5.93, 5.93, 5.92, 5.92, 5.91, 5.91, 5.90, 5.90, 5.89, 5.89, 5.88, 5.88, 5.87, 5.87, 5.86, 5.86, 5.85, 5.85, 5.84, 5.84, 5.83, 5.83, 5.82, 5.82, 5.81, 5.81, 5.80, 5.80, 5.79, 5.79, 5.78, 5.78, 5.77, 5.77, 5.76, 5.76, 5.75, 5.75, 5.74, 5.74, 5.73, 5.73, 5.72, 5.72, 5.71, 5.71, 5.70, 5.70, 5.69, 5.69, 5.68, 5.68, 5.67, 5.67, 5.66, 5.66, 5.65, 5.65, 5.64, 5.64, 5.63, 5.63, 5.62, 5.62, 5.61, 5.61, 5.60, 5.60, 5.59, 5.59, 5.58, 5.58, 5.57, 5.57, 5.56, 5.56, 5.55, 5.55, 5.54, 5.54, 5.53, 5.53, 5.52, 5.52, 5.51, 5.51, 5.50, 5.50, 5.49, 5.49, 5.48, 5.48, 5.47, 5.47, 5.46, 5.46, 5.45, 5.45, 5.44, 5.44, 5.43, 5.43, 5.42, 5.42, 5.41, 5.41, 5.40, 5.40, 5.39, 5.39, 5.38, 5.38, 5.37, 5.37, 5.36, 5.36, 5.35, 5.35, 5.34, 5.34, 5.33, 5.33, 5.32, 5.32, 5.31, 5.31, 5.30, 5.30, 5.29, 5.29, 5.28, 5.28, 5.27, 5.27, 5.26, 5.26, 5.25, 5.25, 5.24, 5.24, 5.23, 5.23, 5.22, 5.22, 5.21, 5.21, 5.20, 5.20, 5.19, 5.19, 5.18, 5.18, 5.17, 5.17, 5.16, 5.16, 5.15, 5.15, 5.14, 5.14, 5.13, 5.13, 5.12, 5.12, 5.11, 5.11, 5.10, 5.10, 5.09, 5.09, 5.08, 5.08, 5.07, 5.07, 5.06, 5.06, 5.05, 5.05, 5.04, 5.04, 5.03, 5.03, 5.02, 5.02, 5.01, 5.01, 5.00, 5.00, 4.99, 4.99, 4.98, 4.98, 4.97, 4.97, 4.96, 4.96, 4.95, 4.95, 4.94, 4.94, 4.93, 4.93, 4.92, 4.92, 4.91, 4.91, 4.90, 4.90, 4.89, 4.89, 4.88, 4.88, 4.87, 4.87, 4.86, 4.86, 4.85, 4.85, 4.84, 4.84, 4.83, 4.83, 4.82, 4.82, 4.81, 4.81, 4.80, 4.80, 4.79, 4.79, 4.78, 4.78, 4.77, 4.77, 4.76, 4.76, 4.75, 4.75, 4.74, 4.74, 4.73, 4.73, 4.72, 4.72, 4.71, 4.71, 4.70, 4.70, 4.69, 4.69, 4.68, 4.68,

(Z)-5ca

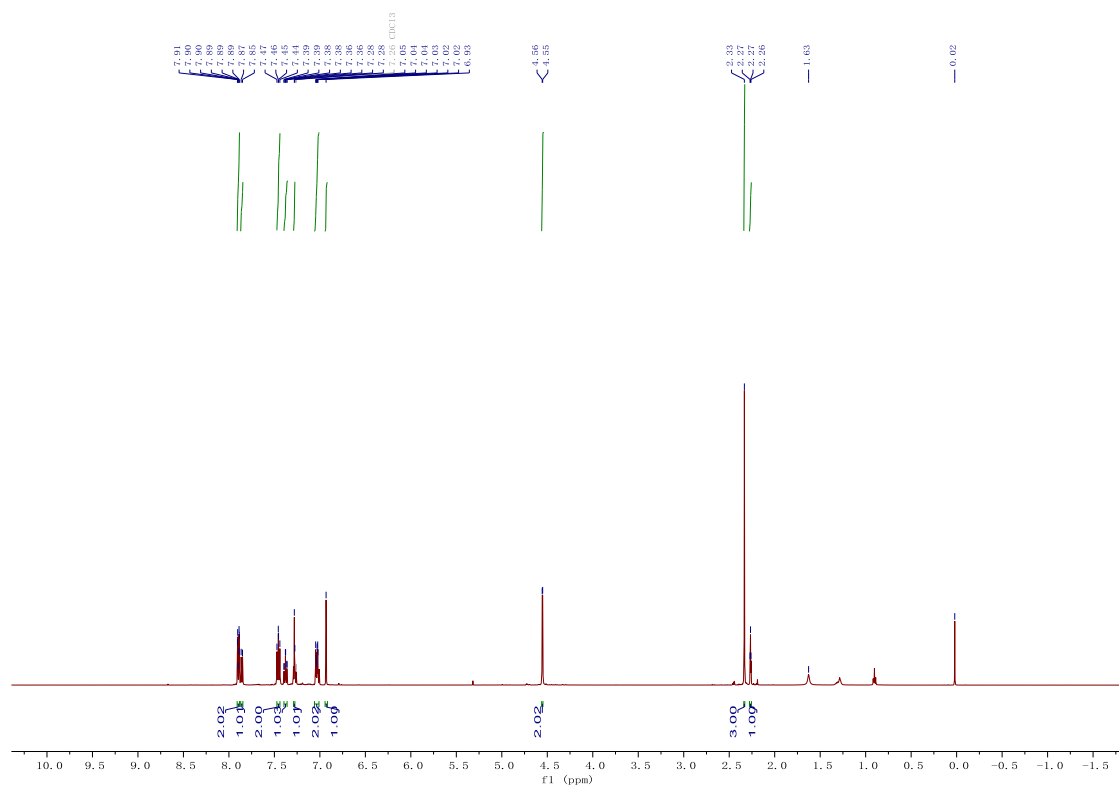
Chemical structure of (Z)-5ca is shown above the spectrum. The structure is a benzimidazole derivative with a chlorine atom and a phenyl group on the imidazole ring, and a prop-1-yn-1-yl group on the benzimidazole nitrogen.

¹³C NMR spectrum (CDCl₃) of (Z)-5ca. The x-axis represents the chemical shift in ppm, ranging from -10 to 200. The spectrum shows several peaks corresponding to the carbon atoms in the molecule.

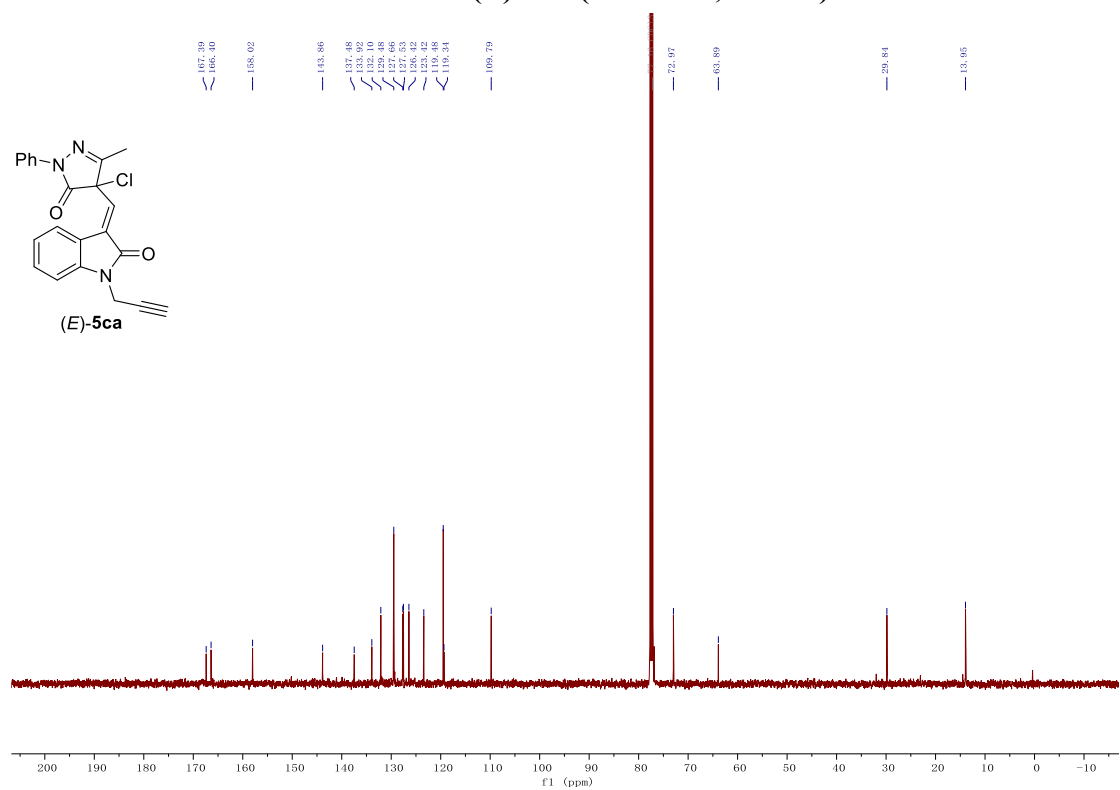
Chemical shifts (ppm) labeled above the spectrum:

- 168.27
- 163.92
- 153.37
- 142.78
- 138.14
- 131.99
- 131.58
- 131.57
- 129.38
- 125.84
- 125.83
- 121.98
- 121.30
- 118.95
- 110.23
- 77.20
- 65.72
- 25.56
- 11.00

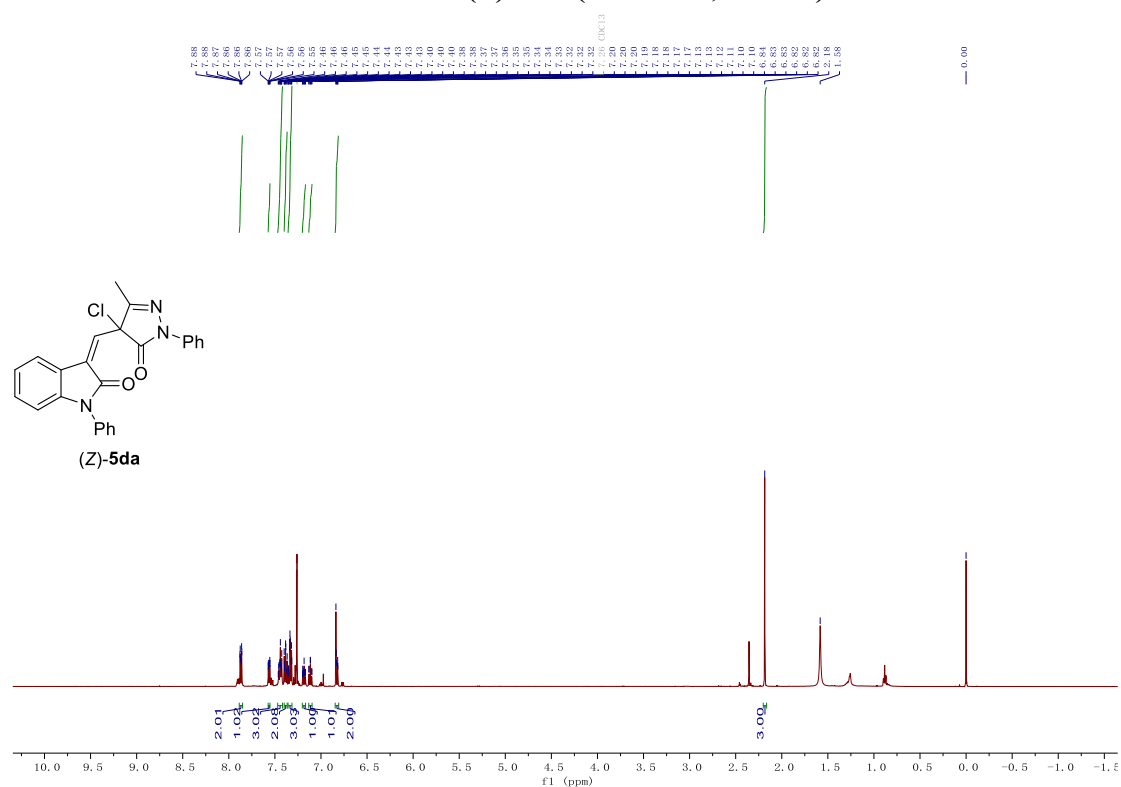
S90



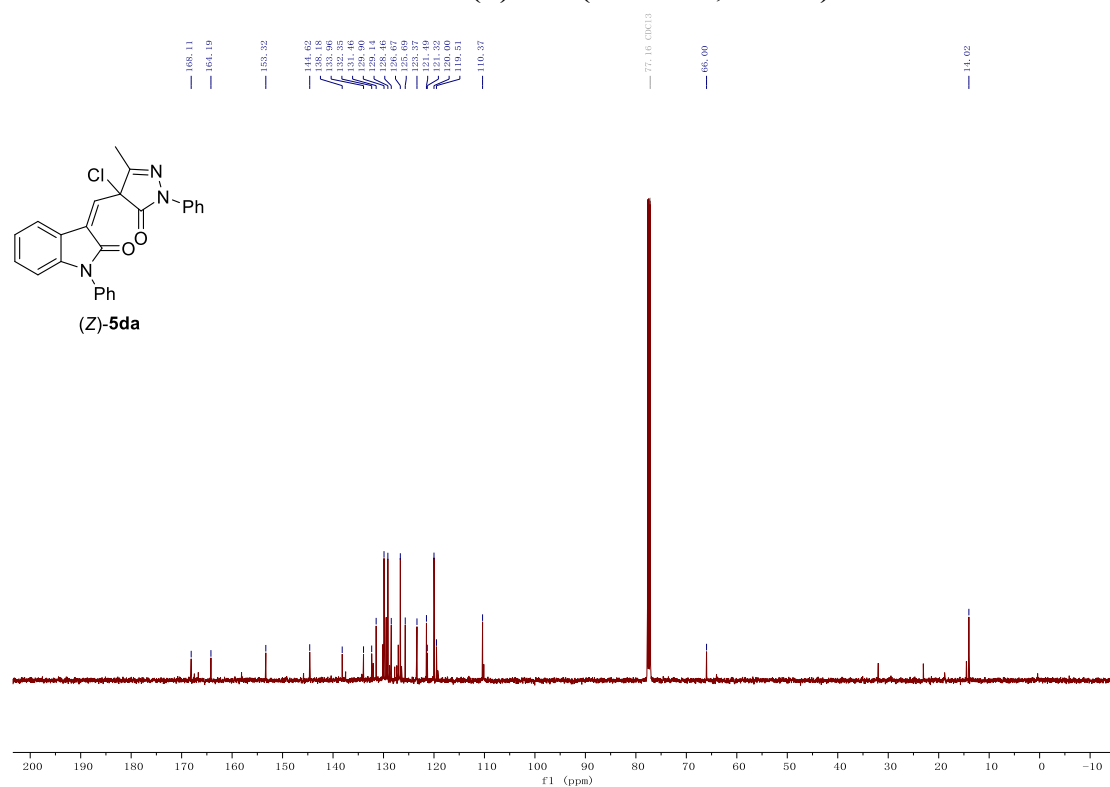
¹³C NMR of (E)-5ca (126 MHz, CDCl₃)



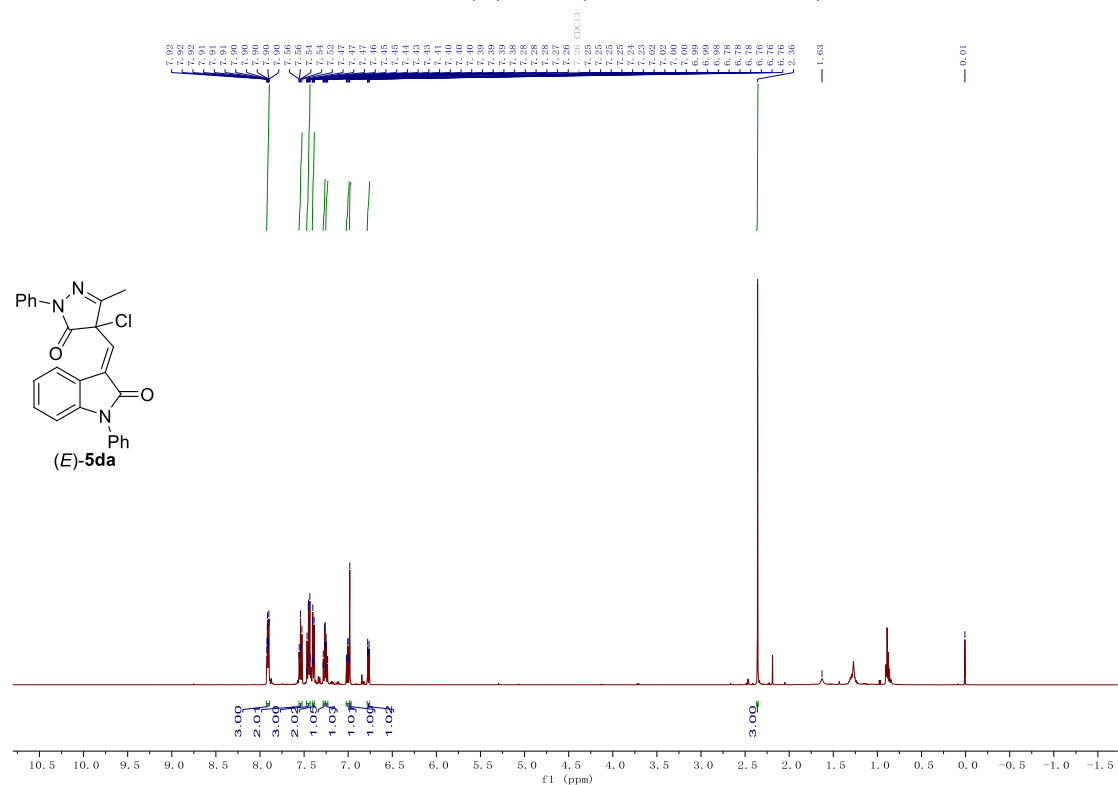
¹H NMR of (Z)-5da (500 MHz, CDCl₃)



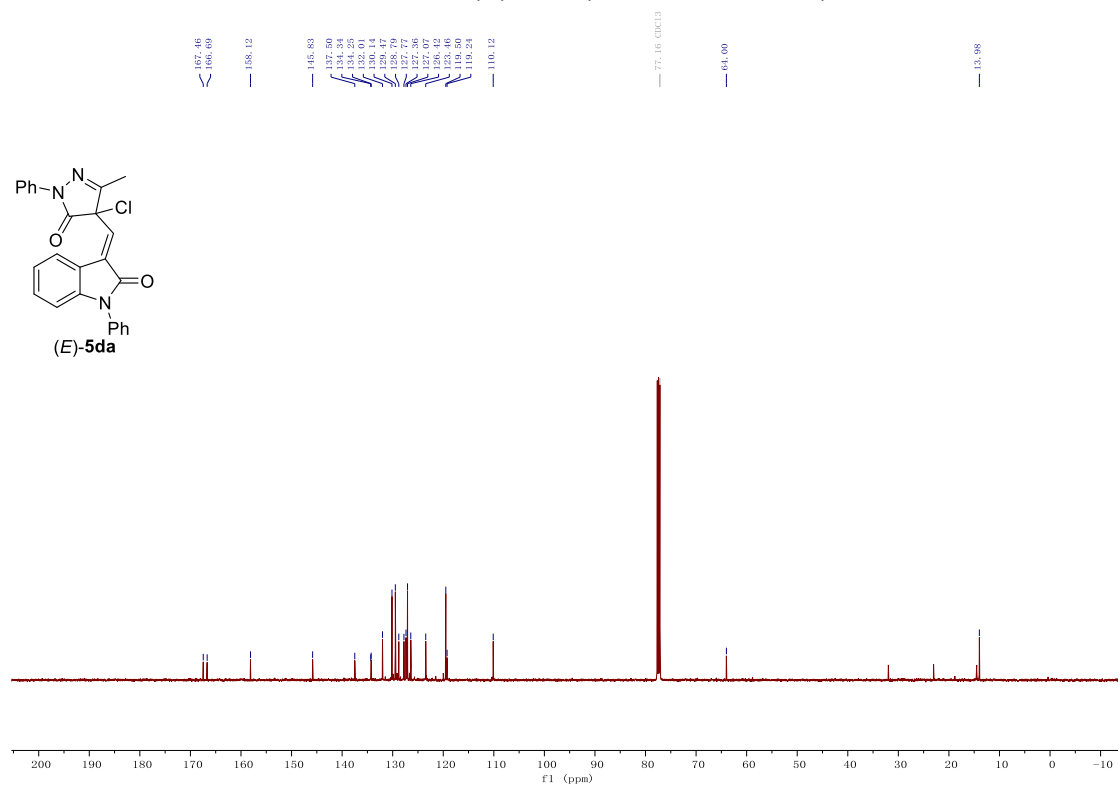
¹³C NMR of (Z)-5da (126 MHz, CDCl₃)



¹H NMR of (*E*)-5da (500 MHz, CDCl₃)



¹³C NMR of (*E*)-5da (126 MHz, CDCl₃)



(Z)-5ea

c1ccc2c(c1)c(c[nH]2)C(=O)C(Cl)C(=O)N(c3ccccc3)C=C3C(=O)N3

¹H NMR spectrum (CDCl₃) of (Z)-5ea. The x-axis represents the chemical shift in ppm (f1), ranging from -1 to 10.5. The spectrum shows several peaks corresponding to the structure, with integration values provided below the baseline.

Chemical structure of (Z)-5ea is shown above the spectrum.

Integration values (from left to right): 1.01, 2.01, 1.00, 2.01, 1.00, 1.01, 1.12, 0.89, 1.01, 3.00, 1.66, 0.00.

(Z)-5ea

Cc1nn(c2ccccc2N1C(=O)C=C3C(=O)Nc4ccccc43)C(Cl)(Cl)C1

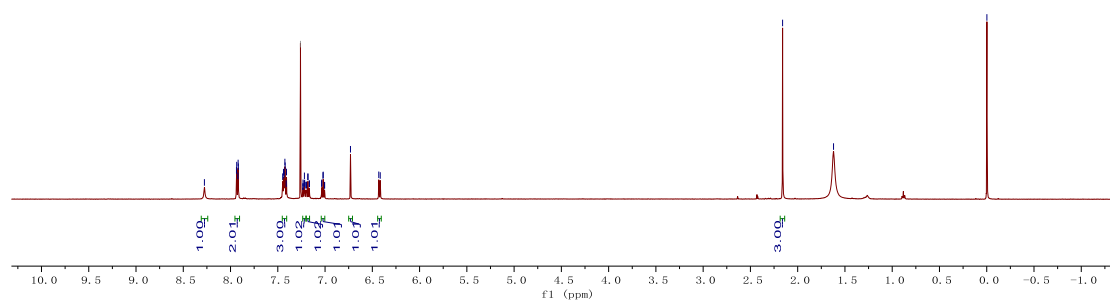
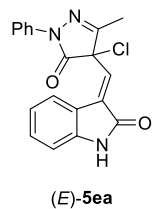
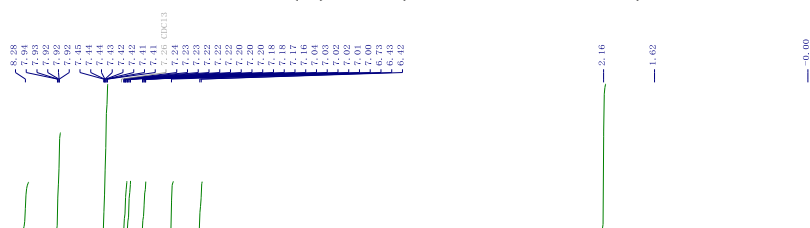
Chemical structure of (Z)-5ea is shown. The structure is a benzimidazole derivative with a chlorine atom and a phenyl group attached to the imidazole ring. The structure is labeled (Z)-5ea.

13C NMR spectrum (CDCl₃)

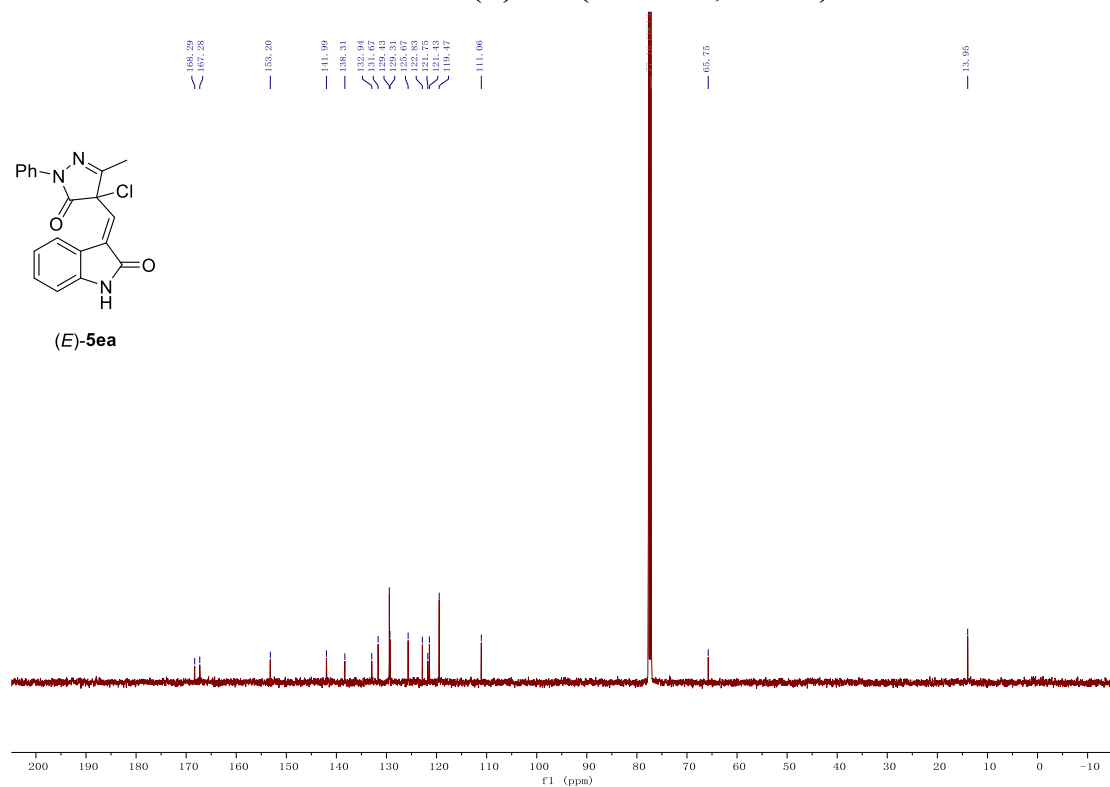
The 13C NMR spectrum shows peaks at the following chemical shifts (ppm): 169.01, 167.03, 157.62, 142.45, 137.08, 134.60, 133.62, 129.08, 128.99, 128.82, 126.83, 126.03, 125.75, 119.10, 110.21, 65.52, and 15.55.

The spectrum displays a series of peaks corresponding to the carbon atoms in the molecule. The peaks are labeled with their chemical shifts in ppm. The x-axis represents the chemical shift in ppm, ranging from 0 to 200. The y-axis represents the intensity of the signal.

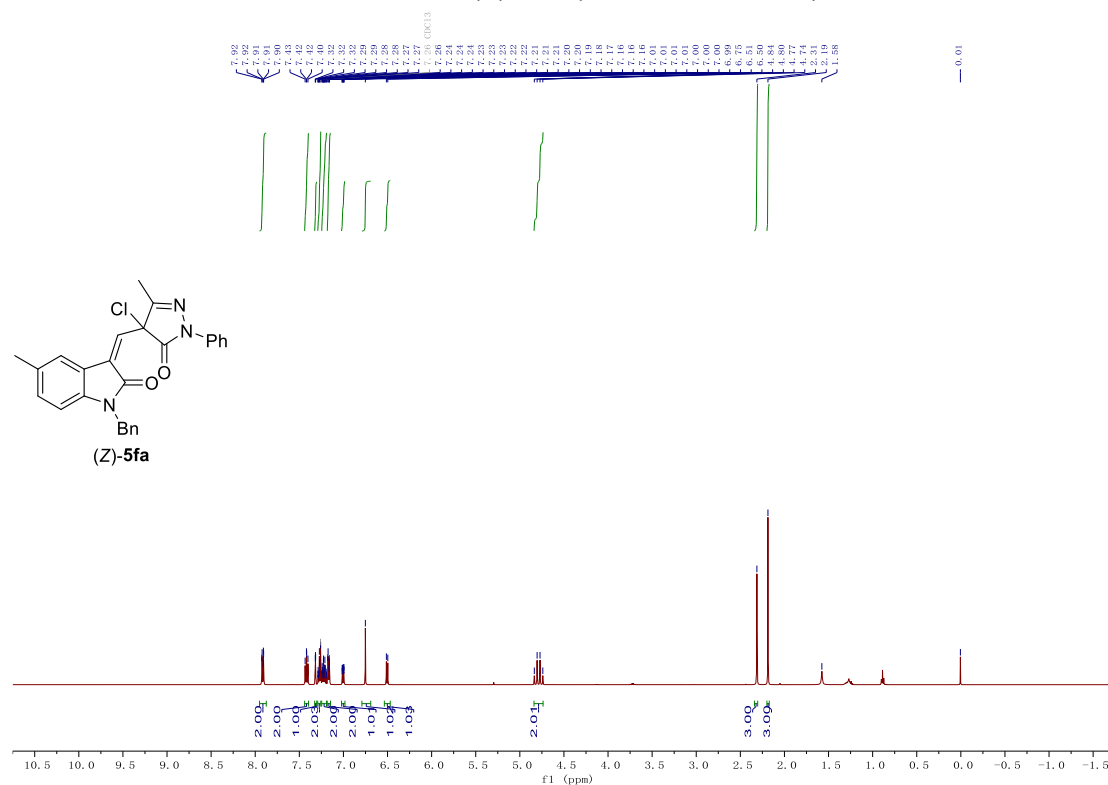
¹H NMR of (E)-5ea (500 MHz, CDCl₃)



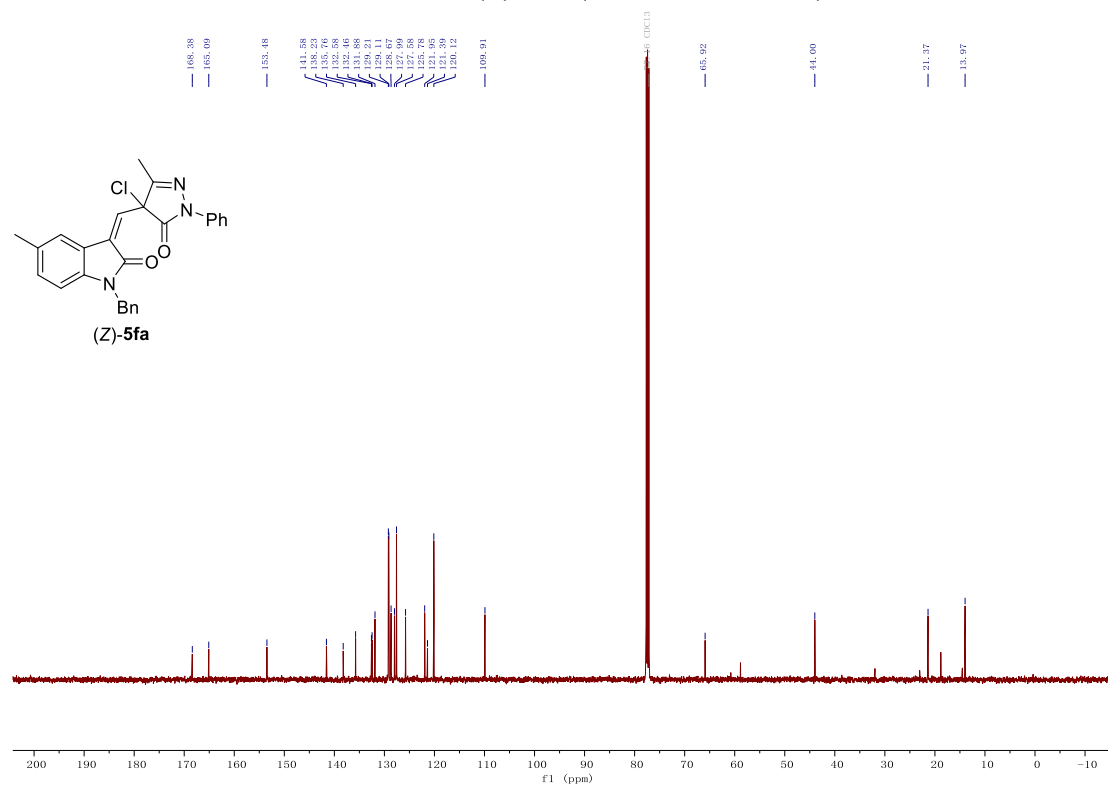
¹³C NMR of (E)-5ea (126 MHz, CDCl₃)



¹H NMR of (Z)-5fa (500 MHz, CDCl₃)



¹³C NMR of (Z)-5fa (126 MHz, CDCl₃)



[illegible]

(E)-5fa

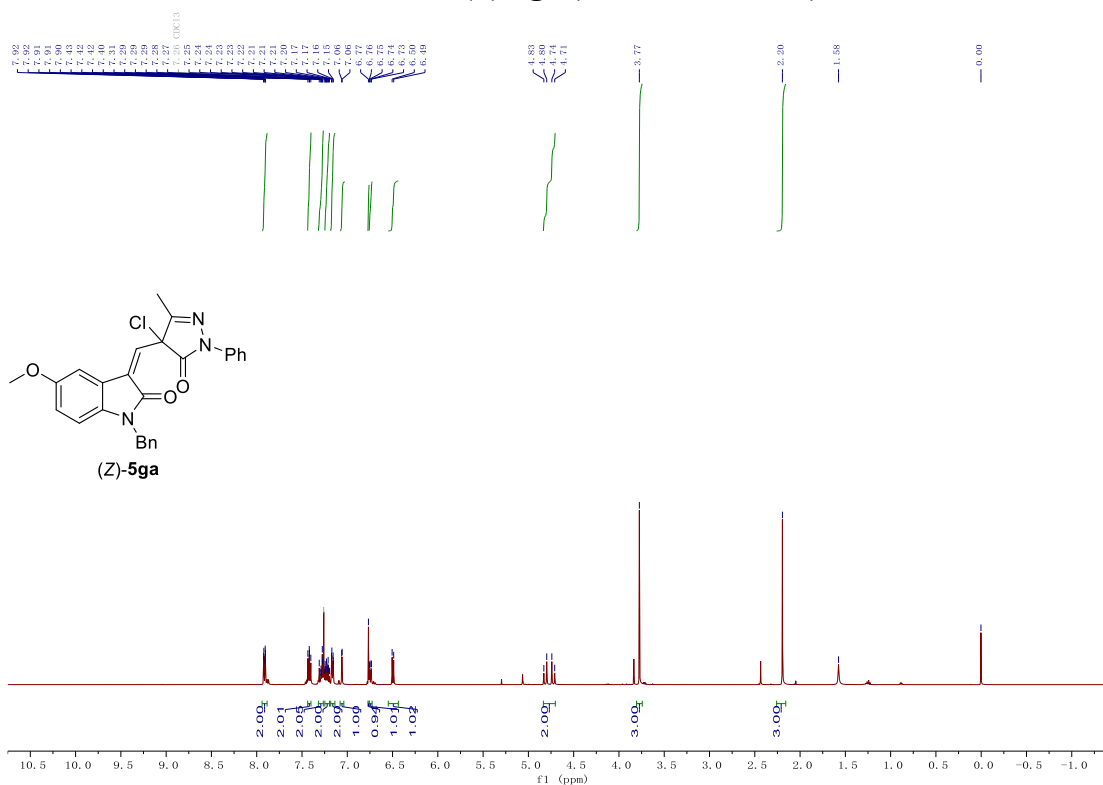
Cc1ccc2c(c1)c3c(c2)c(=O)n(c3C(=O)N(C)C4=CC=CC=C4)C(=O)C5=CC=CC=C5

Chemical structure of (E)-5fa is shown. The structure is a complex heterocyclic compound featuring a benzimidazole core. It includes a phenyl group (Ph), a benzyl group (Bn), and a chlorine atom (Cl). The structure is labeled (E)-5fa.

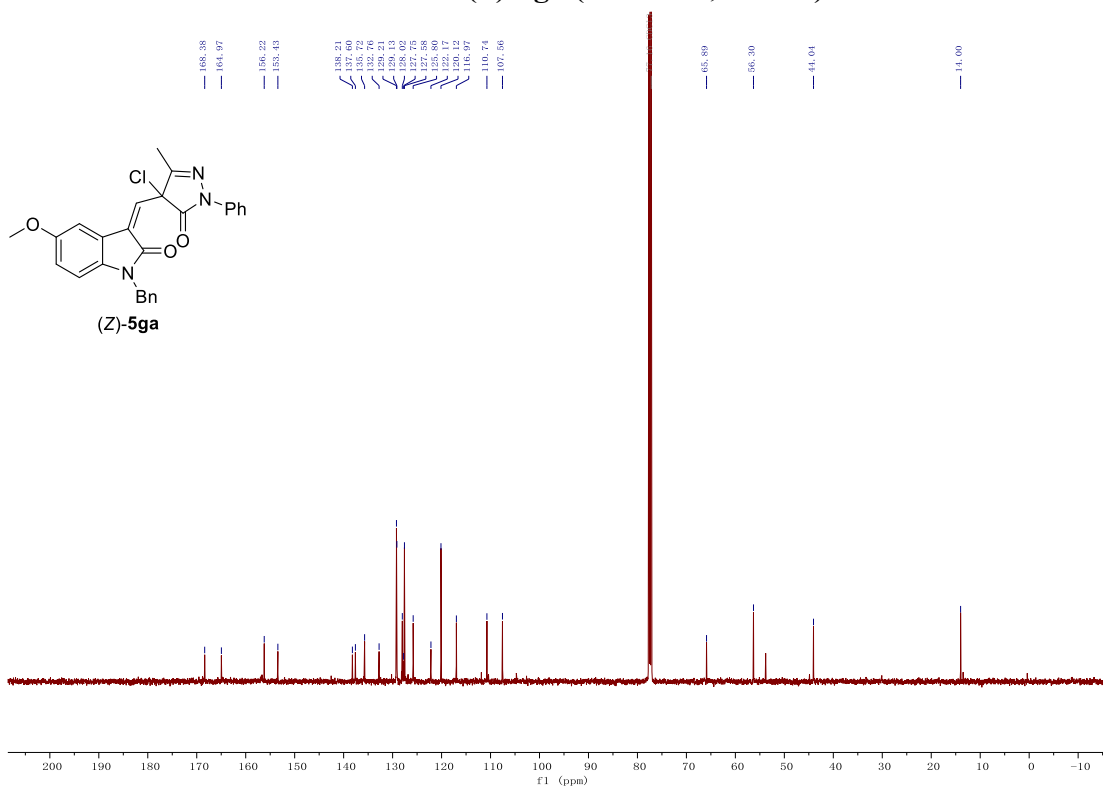
¹³C NMR spectrum (f1 (ppm)) of (E)-5fa. The spectrum shows peaks corresponding to the chemical shifts of the carbon atoms in the molecule. The peaks are labeled with their chemical shifts (ppm):

- 167.55
- 167.34
- 157.73
- 149.83
- 137.52
- 135.83
- 135.67
- 132.64
- 132.26
- 132.07
- 129.20
- 128.11
- 127.88
- 127.65
- 125.55
- 119.37
- 119.32
- 109.58
- 61.31
- 44.40
- 21.21
- 14.05

¹H NMR of (Z)-5ga (500 MHz, CDCl₃)



¹³C NMR of (Z)-5ga (126 MHz, CDCl₃)

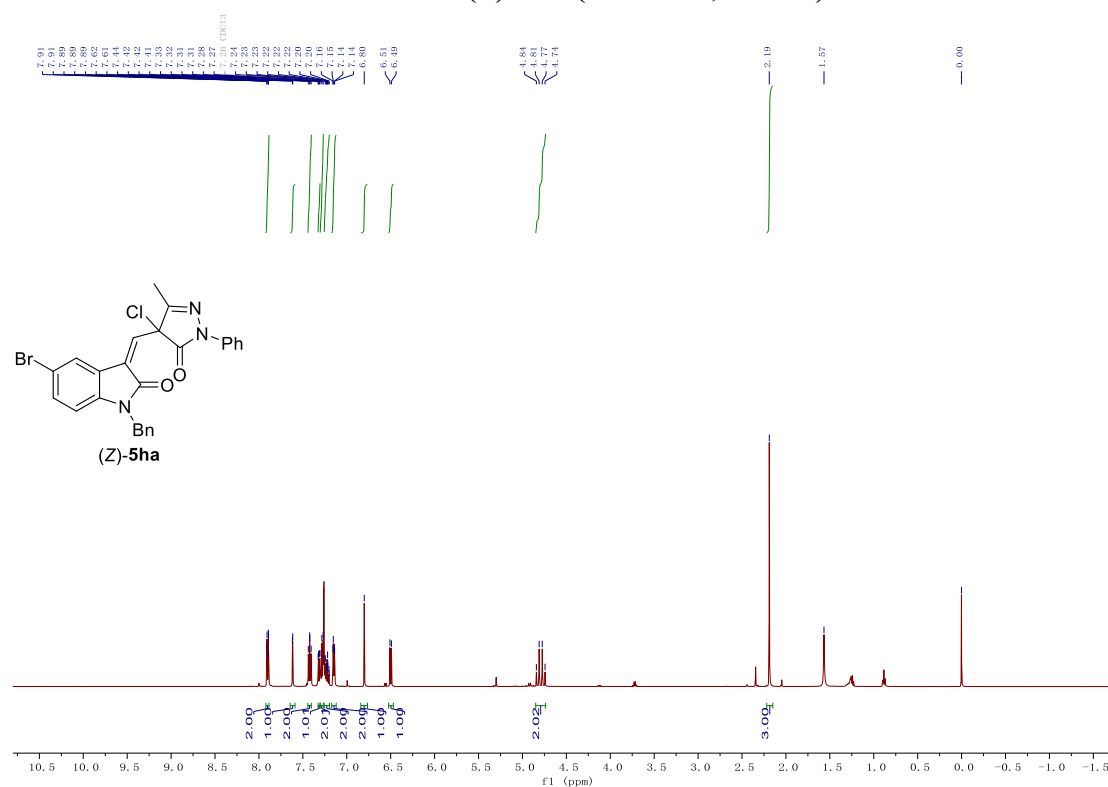


Chemical structure of (E)-5ga is shown on the left. The spectrum displays peaks from 0.00 to 7.92 ppm. Integration values are provided below the baseline for each major peak group.

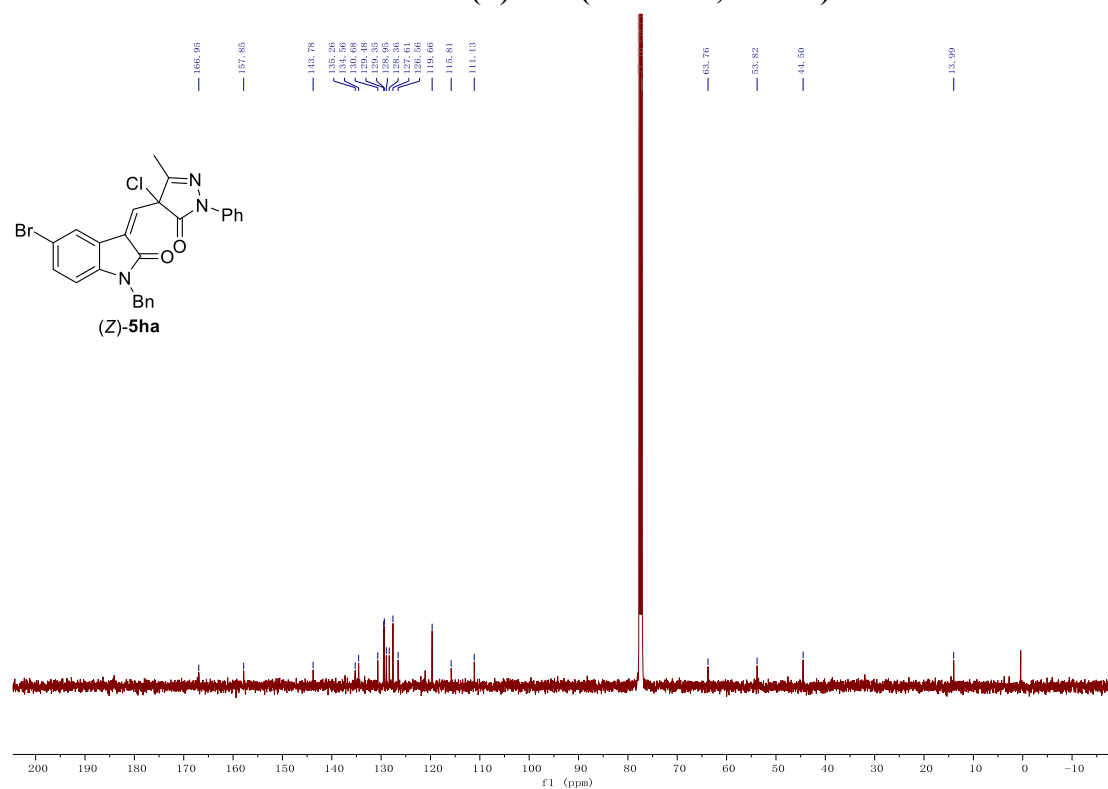
Chemical Shift (ppm)	Integration
7.92	2.00
7.90	3.00
7.89	1.00
7.88	3.00
7.87	1.00
7.86	1.00
7.85	1.00
7.84	1.00
7.83	1.00
7.82	1.00
7.81	1.00
7.80	1.00
7.79	1.00
7.78	1.00
7.77	1.00
7.76	1.00
7.75	1.00
7.74	1.00
7.73	1.00
7.72	1.00
7.71	1.00
7.70	1.00
7.69	1.00
7.68	1.00
7.67	1.00
7.66	1.00
7.65	1.00
7.64	1.00
7.63	1.00
7.62	1.00
7.61	1.00
7.60	1.00
7.59	1.00
7.58	1.00
7.57	1.00
7.56	1.00
7.55	1.00
7.54	1.00
7.53	1.00
7.52	1.00
7.51	1.00
7.50	1.00
7.49	1.00
7.48	1.00
7.47	1.00
7.46	1.00
7.45	1.00
7.44	1.00
7.43	1.00
7.42	1.00
7.41	1.00
7.40	1.00
7.39	1.00
7.38	1.00
7.37	1.00
7.36	1.00
7.35	1.00
7.34	1.00
7.33	1.00
7.32	1.00
7.31	1.00
7.30	1.00
7.29	1.00
7.28	1.00
7.27	1.00
7.26	1.00
7.25	1.00
7.24	1.00
7.23	1.00
7.22	1.00
7.21	1.00
7.20	1.00
7.19	1.00
7.18	1.00
7.17	1.00
7.16	1.00
7.15	1.00
7.14	1.00
7.13	1.00
7.12	1.00
7.11	1.00
7.10	1.00
7.09	1.00
7.08	1.00
7.07	1.00
7.06	1.00
7.05	1.00
7.04	1.00
7.03	1.00
7.02	1.00
7.01	1.00
7.00	1.00
6.99	1.00
6.98	1.00
6.97	1.00
6.96	1.00
6.95	1.00
6.94	1.00
6.93	1.00
6.92	1.00
6.91	1.00
6.90	1.00
6.89	1.00
6.88	1.00
6.87	1.00
6.86	1.00
6.85	1.00
6.84	1.00
6.83	1.00
6.82	1.00
6.81	1.00
6.80	1.00
6.79	1.00
6.78	1.00
6.77	1.00
6.76	1.00
6.75	1.00
6.74	1.00
6.73	1.00
6.72	1.00
6.71	1.00
6.70	1.00
6.69	1.00
6.68	1.00
6.67	1.00
6.66	1.00
6.65	1.00
6.64	1.00
6.63	1.00
6.62	1.00
6.61	1.00
6.60	1.00
6.59	1.00
6.58	1.00
6.57	1.00
6.56	1.00
6.55	1.00
6.54	1.00
6.53	1.00
6.52	1.00
6.51	1.00
6.50	1.00
6.49	1.00
6.48	1.00
6.47	1.00
6.46	1.00
6.45	1.00
6.44	1.00
6.43	1.00
6.42	1.00
6.41	1.00
6.40	1.00
6.39	1.00
6.38	1.00
6.37	1.00
6.36	1.00
6.35	1.00
6.34	1.00
6.33	1.00
6.32	1.00
6.31	1.00
6.30	1.00
6.29	1.00
6.28	1.00
6.27	1.00
6.26	1.00
6.25	1.00
6.24	1.00
6.23	1.00
6.22	1.00
6.21	1.00
6.20	1.00
6.19	1.00
6.18	1.00
6.17	1.00
6.16	1.00
6.15	1.00
6.14	1.00
6.13	1.00
6.12	

[illegible]

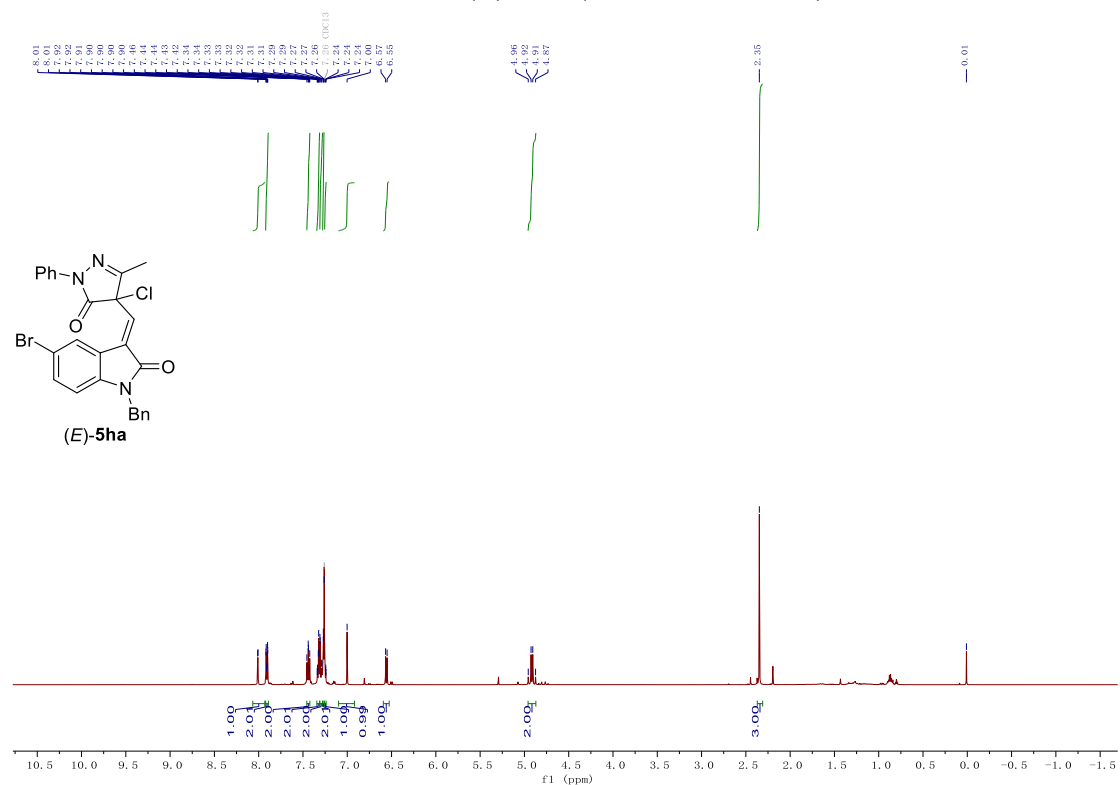
¹H NMR of (Z)-5ha (500 MHz, CDCl₃)



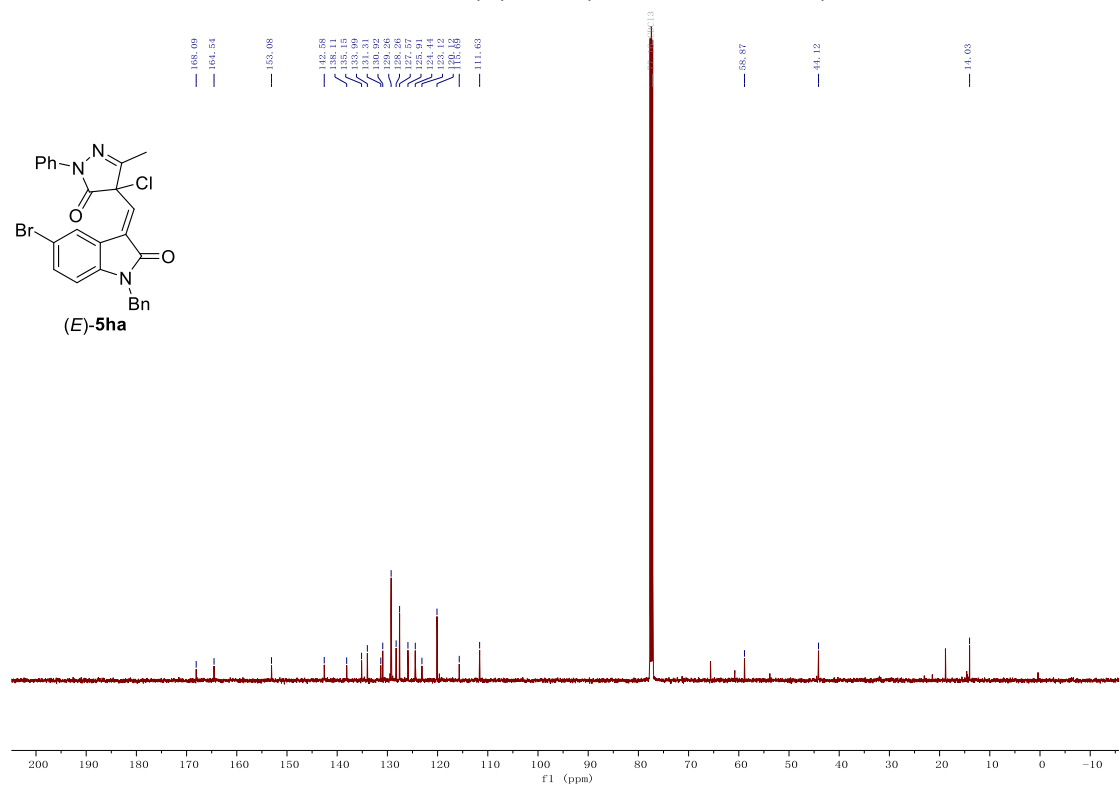
¹³C NMR of (Z)-5ha (126 MHz, CDCl₃)



¹H NMR of (*E*)-5ha (500 MHz, CDCl₃)



¹³C NMR of (*E*)-5ha (126 MHz, CDCl₃)



Chemical structure of (Z)-5ia is shown above the spectrum. The structure is a benzimidazole derivative with a 4-chlorophenyl group, a benzyl group, and a 2-phenyl-2-methyl-1H-imidazole-5-carboxamide moiety.

¹H NMR spectrum (CDCl₃):

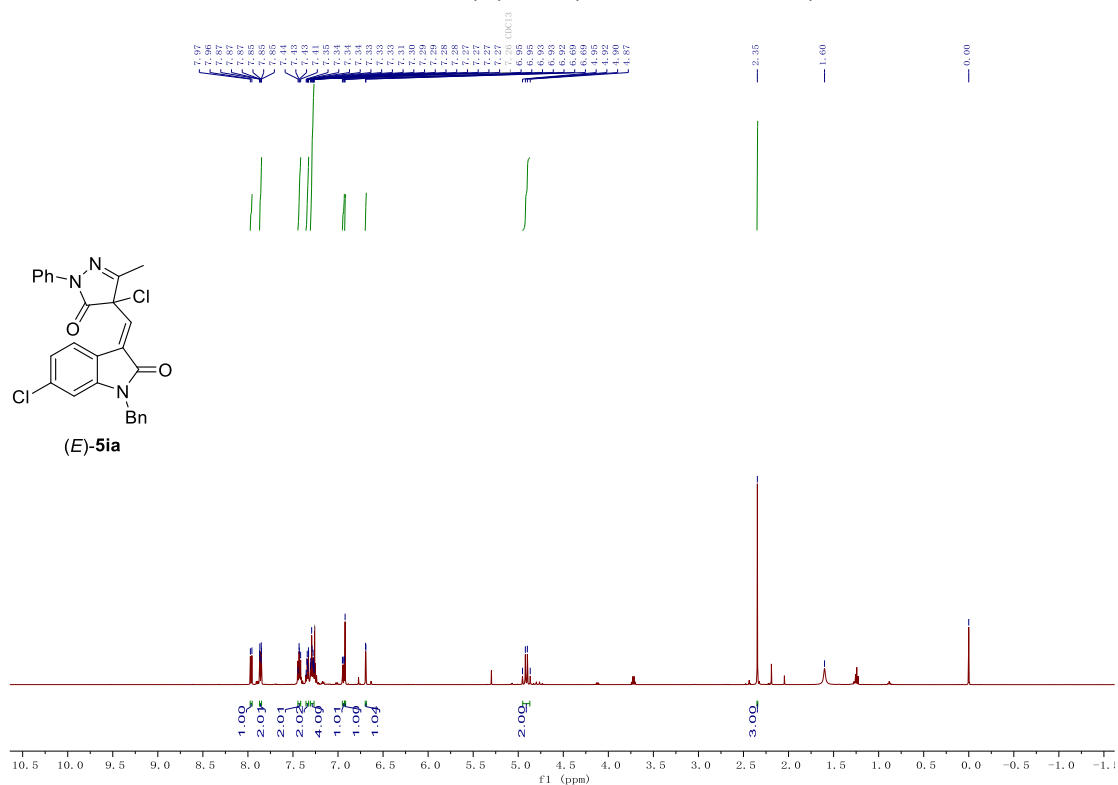
- Chemical shift range: 0.00 to 8.00 ppm.
- Integration values (from left to right): 2.00, 3.00, 1.00, 2.00, 1.00, 0.95, 1.00, 2.00, 3.00.
- Peak list (ppm): 7.92, 7.91, 7.90, 7.89, 7.88, 7.87, 7.86, 7.85, 7.84, 7.83, 7.82, 7.81, 7.80, 7.79, 7.78, 7.77, 7.76, 7.75, 7.74, 7.73, 7.72, 7.71, 7.70, 7.69, 7.68, 7.67, 7.66, 7.65, 7.64, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.5

(Z)-5ia

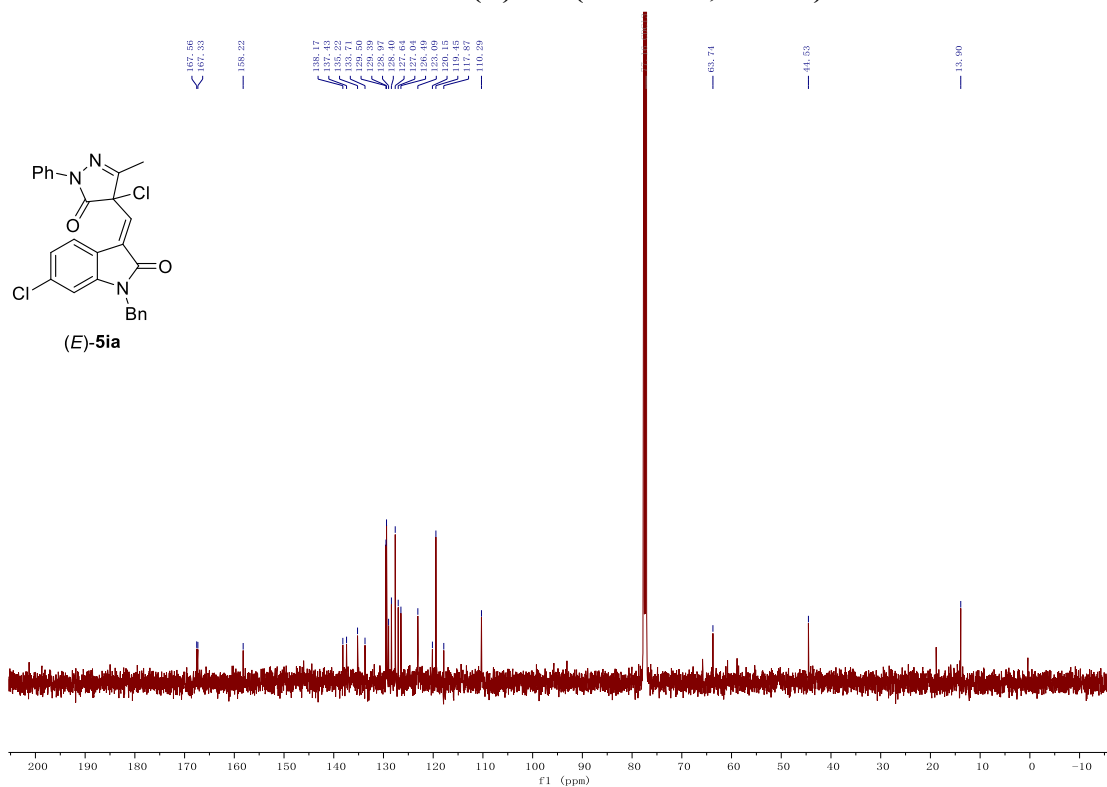
c1ccc(cc1)N2C(=O)C(Cl)=C3C(=O)N(C2)c4ccc(Cl)cc43

¹³C NMR spectrum (CDCl₃) of (Z)-5ia. The x-axis represents the chemical shift in ppm, ranging from -10 to 200. The spectrum shows several peaks corresponding to the carbon atoms in the molecule. Key peaks are labeled with their chemical shifts: 168.19, 164.98, 153.18, 144.70, 138.11, 137.27, 135.69, 134.30, 133.85, 129.30, 129.24, 128.55, 127.57, 125.91, 125.65, 122.23, 120.13, 119.81, 110.68, 77.16 (CDCl₃), 65.74, 44.12, and 14.02.

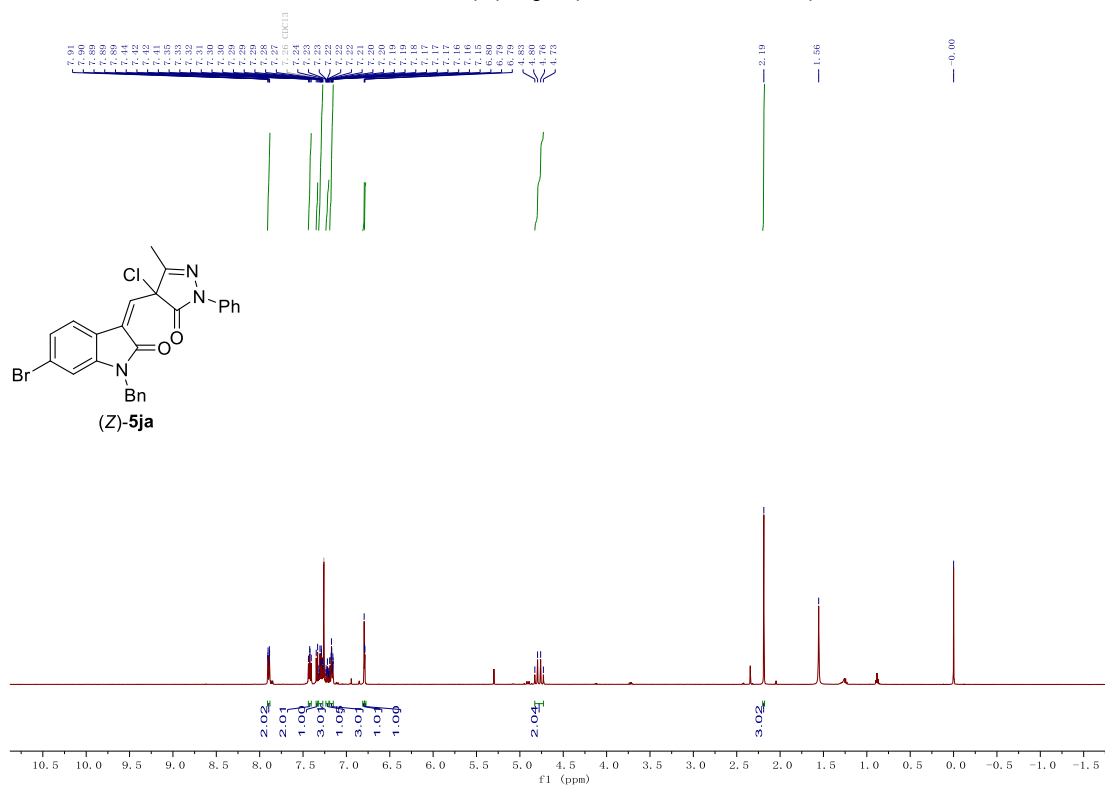
¹H NMR of (E)-5ia (500 MHz, CDCl₃)



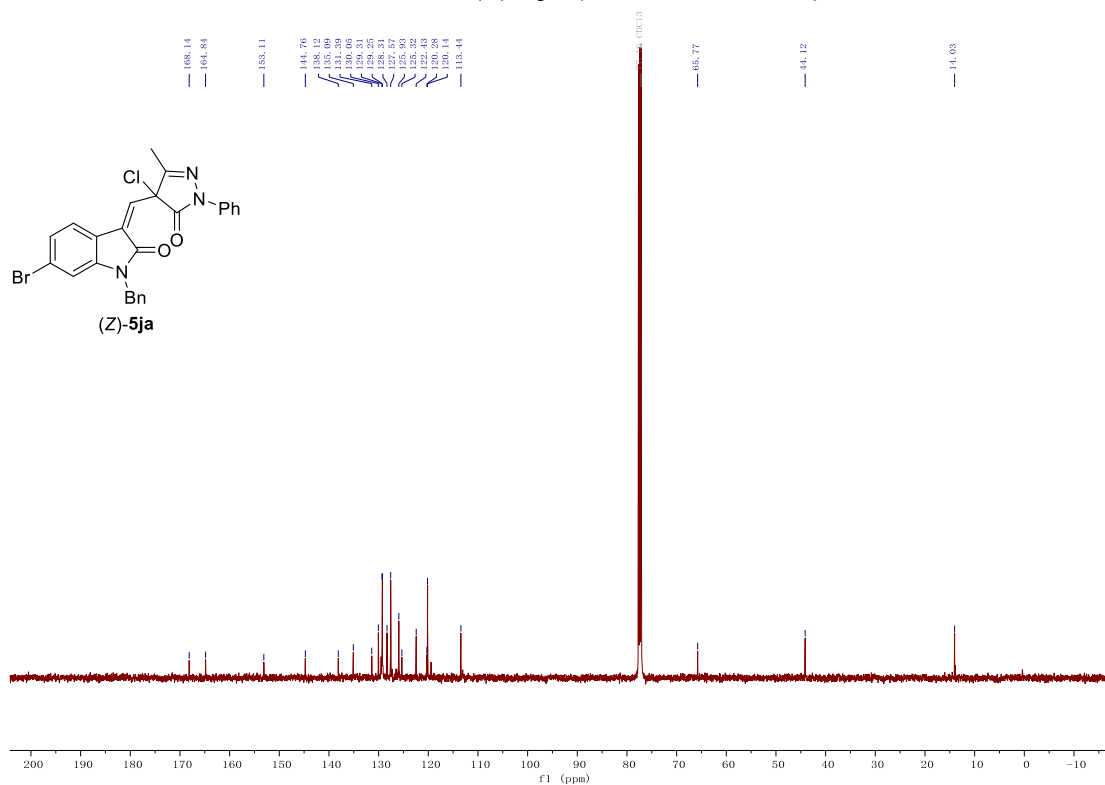
¹³C NMR of (E)-5ia (126 MHz, CDCl₃)



¹H NMR of (Z)-5ja (500 MHz, CDCl₃)



¹³C NMR of (Z)-5ja (126 MHz, CDCl₃)



(E)-5ja

Cc1nc(n1C(=O)C2=CC(=C(C=C2)N(Cc3ccccc3)C(=O)N2)C(=O)c4ccc(Br)cc4)C5=CC=CC=C5

¹H NMR spectrum (CDCl₃) of (E)-5ja. The x-axis represents the chemical shift in ppm, ranging from 10.5 to -1.5. The spectrum shows several peaks corresponding to the structure, with integration values provided below the baseline.

Chemical shift (ppm): 7.90, 7.89, 7.87, 7.85, 7.85, 7.83, 7.83, 7.82, 7.82, 7.86, 7.86, 7.83, 7.83, 7.83, 7.80, 7.80, 7.29, 7.29, 7.28, 7.27, 7.25, 7.24, 7.24, 7.12, 7.11, 7.10, 7.10, 6.85, 6.85, 6.85, 4.95, 4.89, 4.86, 2.34, 1.57, 0.00.

Integration values: 3.00, 2.01, 2.00, 3.00, 1.05, 1.00, 0.99, 0.99, 2.00, 3.00, 1.57, 0.00.

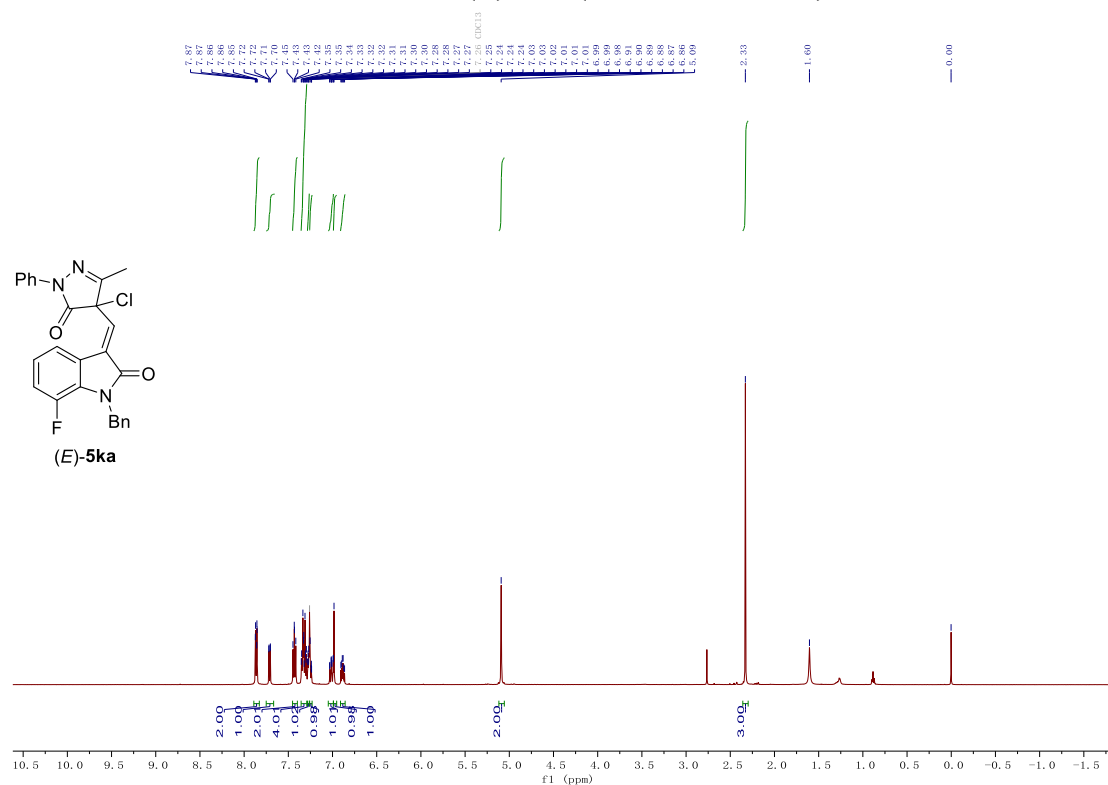
(E)-5ja

Cc1nc2c(c1)c(c3ccccc3n2C(=O)O)c4cc(Br)ccc4C(=O)Nc5ccccc5

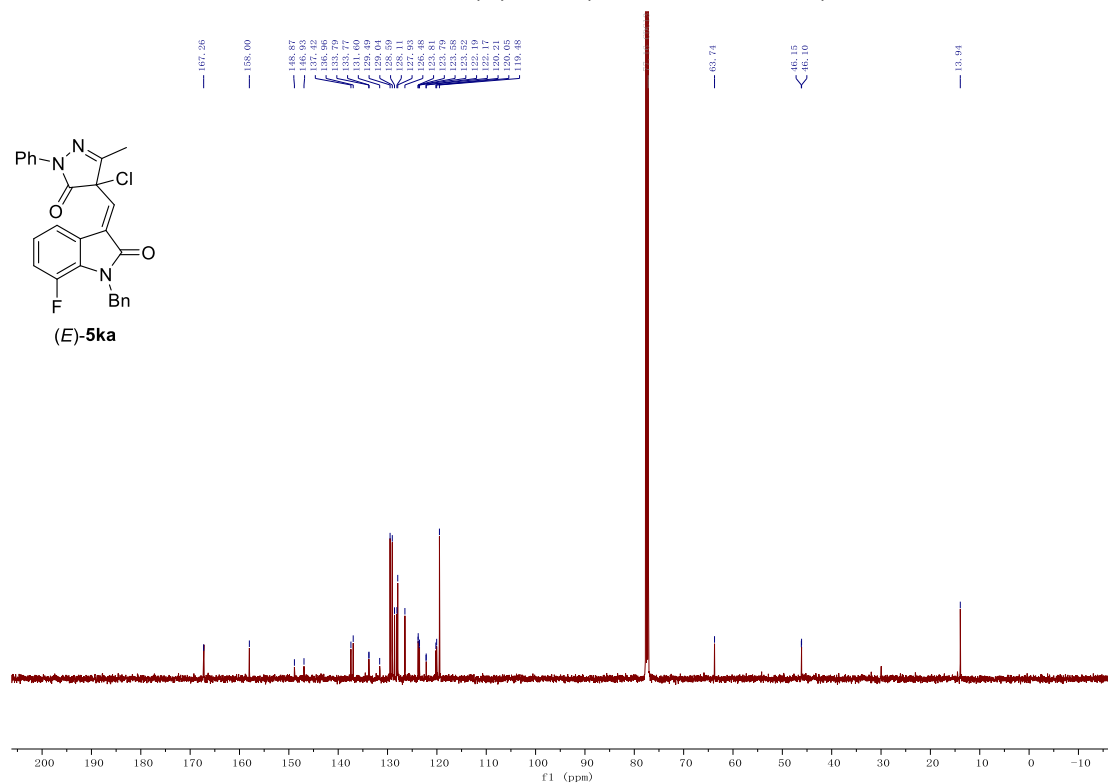
¹³C NMR spectrum (CDCl₃) of (E)-5ja. The spectrum shows peaks at the following chemical shifts (ppm): 167.27, 167.27, 158.16, 145.43, 142.92, 135.21, 133.78, 133.78, 129.89, 129.89, 129.12, 129.12, 127.63, 127.29, 127.29, 126.43, 126.06, 119.44, 118.30, 113.07, 63.76, 41.51, and 13.90.

[illegible][illegible]

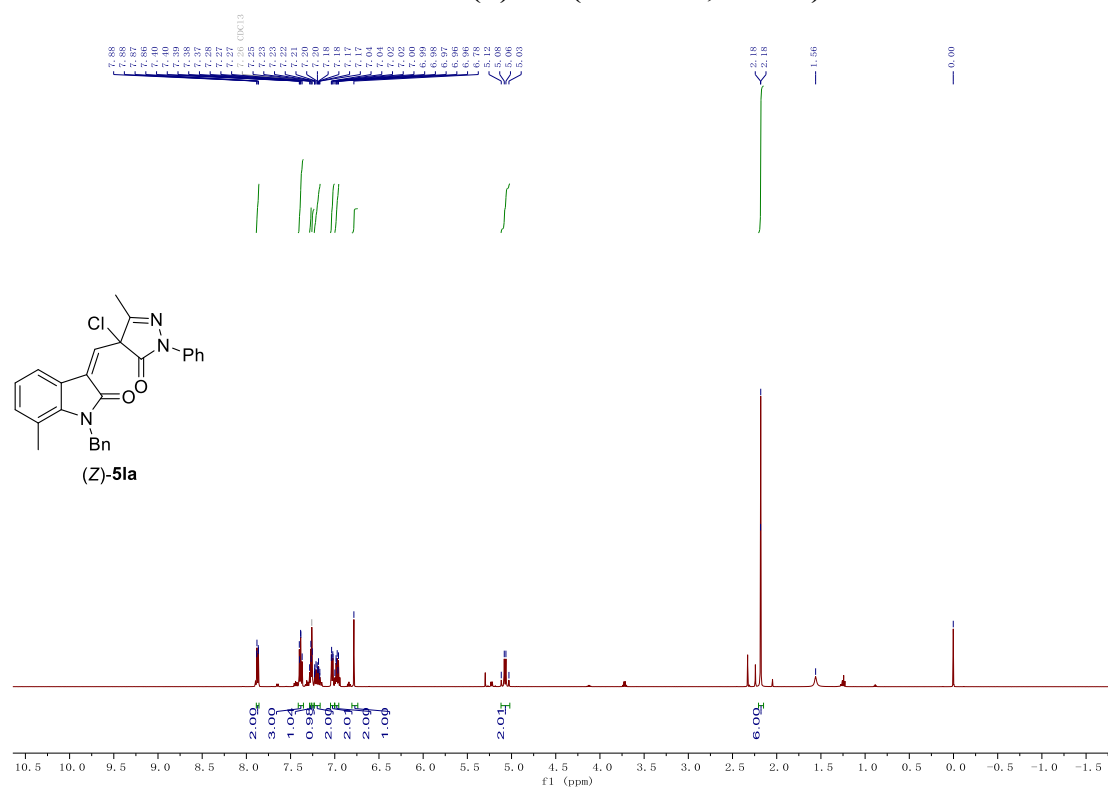
¹H NMR of (*E*)-5ka (500 MHz, CDCl₃)



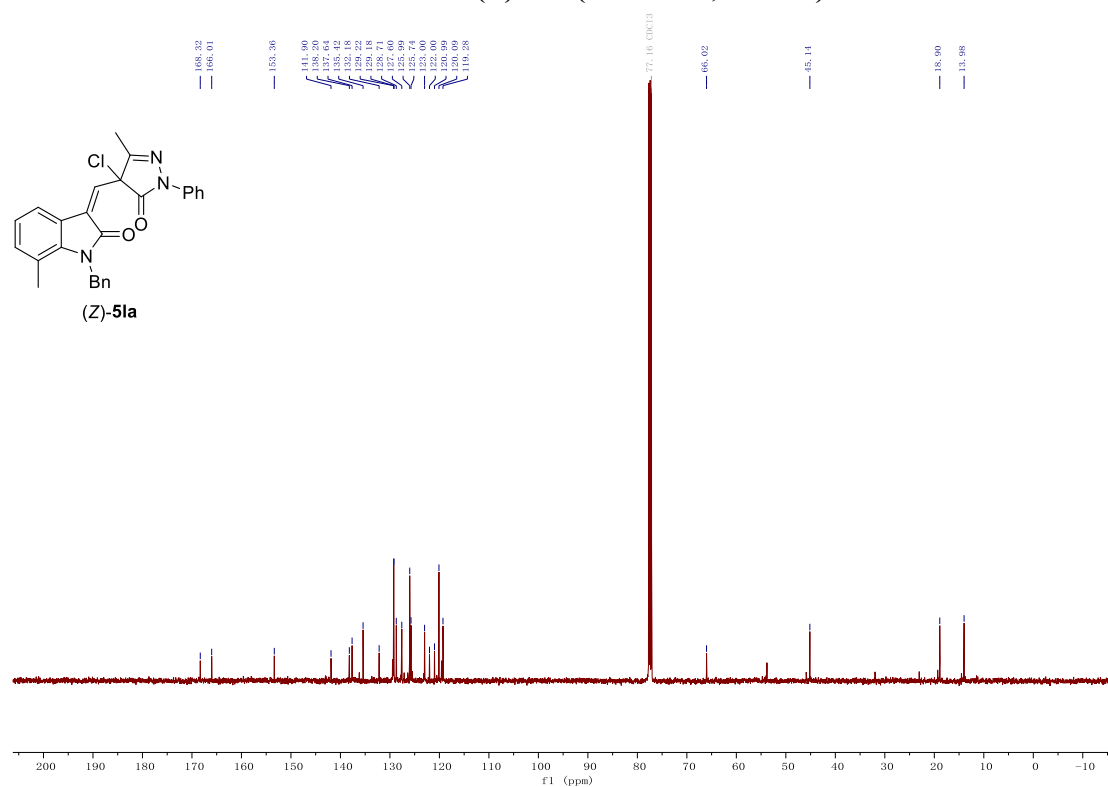
¹³C NMR of (*E*)-5ka (126 MHz, CDCl₃)



¹H NMR of (Z)-5la (500 MHz, CDCl₃)



¹³C NMR of (Z)-5la (126 MHz, CDCl₃)



Chemical structure of (E)-5Ia is shown as an inset. The structure is a tricyclic system with a benzene ring fused to a pyrrole ring, which is further fused to a pyrazole ring. The pyrazole ring has a phenyl group (Ph) and a chlorine atom (Cl) attached. The pyrrole ring has a benzyl group (Bn) attached. The pyrazole ring has a methyl group (Me) attached.

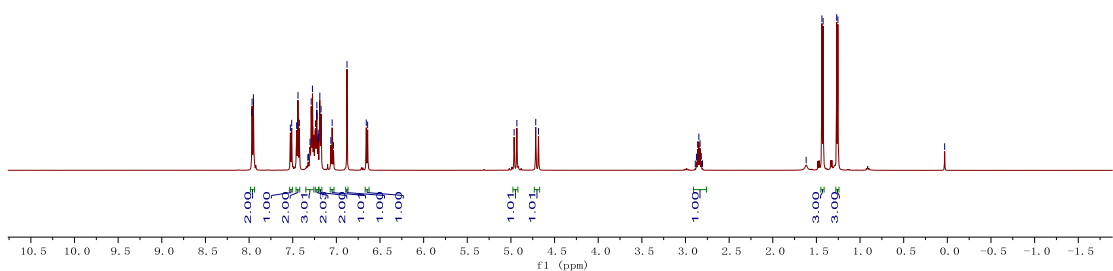
(E)-5Ia

¹H NMR spectrum (CDCl₃) showing peaks from 0.00 to 7.90 ppm. The spectrum displays a complex multiplet between 6.5 and 8.0 ppm, a doublet at 5.2 ppm, a doublet at 2.5 ppm, a singlet at 1.58 ppm, and a singlet at 0.00 ppm. Integration values are provided below the peaks.

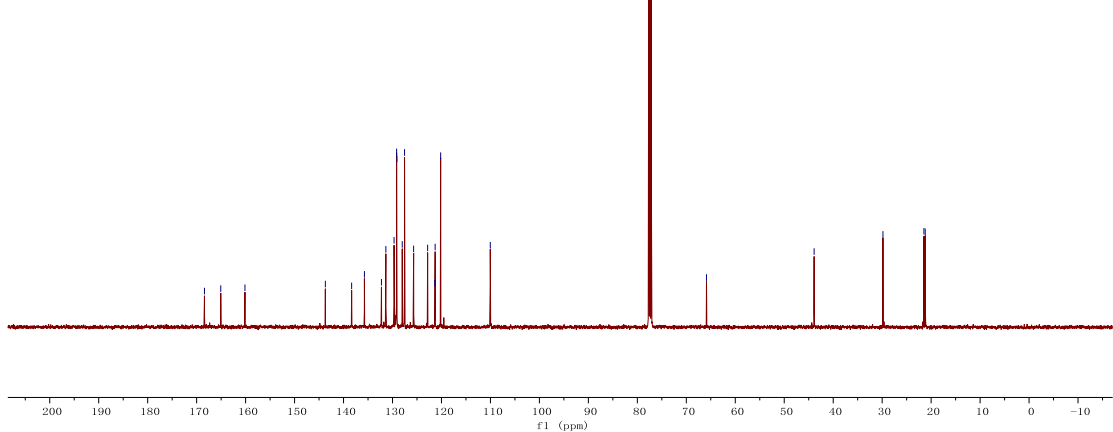
Chemical Shift (ppm)	Integration
7.90	2.02
7.89	1.01
7.88	2.00
7.87	2.00
7.86	1.00
7.85	1.00
7.84	1.00
7.83	1.00
7.82	1.00
7.81	1.00
7.80	1.00
7.79	1.00
7.78	1.00
7.77	1.00
7.76	1.00
7.75	1.00
7.74	1.00
7.73	1.00
7.72	1.00
7.71	1.00
7.70	1.00
7.69	1.00
7.68	1.00
7.67	1.00
7.66	1.00
7.65	1.00
7.64	1.00
7.63	1.00
7.62	1.00
7.61	1.00
7.60	1.00
7.59	1.00
7.58	1.00
7.57	1.00
7.56	1.00
7.55	1.00
7.54	1.00
7.53	1.00
7.52	1.00
7.51	1.00
7.50	1.00
7.49	1.00
7.48	1.00
7.47	1.00
7.46	1.00
7.45	1.00
7.44	1.00
7.43	1.00
7.42	1.00
7.41	1.00
7.40	1.00
7.39	1.00
7.38	1.00
7.37	1.00
7.36	1.00
7.35	1.00
7.34	1.00
7.33	1.00
7.32	1.00
7.31	1.00
7.30	1.00
7.29	1.00
7.28	1.00
7.27	1.00
7.26	1.00
7.25	1.00
7.24	1.00
7.23	1.00
7.22	1.00
7.21	1.00
7.20	1.00
7.19	1.00
7.18	1.00
7.17	1.00
7.16	1.00
7.15	1.00
7.14	1.00
7.13	1.00
7.12	1.00
7.11	1.00
7.10	1.00
7.09	1.00
7.08	1.00
7.07	1.00
7.06	1.00
7.05	1.00
7.04	1.00
7.03	1.00
7.02	1.00
7.01	1.00
7.00	1.00
6.99	1.00
6.98	1.00
6.97	1.00
6.96	1.00
6.95	1.00
6.94	1.00
6.93	1.00
6.92	1.00
6.91	1.00
6.90	1.00
6.89	1.00
6.88	1.00
6.87	1.00
6.86	1.00
6.85	1.00
6.84	1.00
6.83	1.00
6.82	1.00
6.81	1.00
6.80	1.00
6.79	1.00
6.78	1.00
6.77	1.00
6.76	1.00
6.75	1.00
6.74	1.00
6.73	1.00
6.72	1.00
6.71	1.00
6.70	1.00
6.69	1.00
6.68	1.00
6.67	1.00
6.66	1.00
6.65	1.00
6.64	1.00
6.63	1.00
6.62	1.00
6.61	1.00
6.60	1.00
6.59	1.00
6.58	1.00
6.57	1.00

(E)-5Ia

168.58
167.74
138.02
132.04
131.52
130.82
130.48
129.86
129.47
129.31
129.11
127.73
127.13
126.41
126.22
125.49
123.11
122.52
120.18
119.56
77.16 CDCl3
64.12
45.90
19.33
14.00



	— 165.07
	— 109.13
	— 145.71
	— 138.75
	— 135.74
	— 132.26
	— 131.36
	— 129.16
	— 128.16
	— 126.11
	— 125.11
	— 125.69
	— 125.69
	— 125.83
	— 125.83
	— 121.29
	— 120.17
	— 110.03
	— 65.88
	— 43.90
	— 29.84



[illegible]

(E)-5ab

Chemical structure of **(E)-5ab** is shown above the spectrum. The structure is a spirocyclic compound consisting of a benzimidazole core. One nitrogen of the benzimidazole is substituted with a phenyl group (Ph), and the other with a benzyl group (Bn). The spiro center is a carbon atom bonded to a chlorine atom (Cl) and a 2-isopropyl-1H-benzimidazol-5-yl group. The benzimidazole ring is in the (E) configuration.

¹H NMR spectrum (CDCl₃) of **(E)-5ab**. The x-axis represents the chemical shift in ppm, ranging from -10 to 200. The spectrum shows several peaks, with integration values indicated below the baseline.

Chemical structure of **(E)-5ab** is shown above the spectrum. The structure is a spirocyclic compound consisting of a benzimidazole core. One nitrogen of the benzimidazole is substituted with a phenyl group (Ph), and the other with a benzyl group (Bn). The spiro center is a carbon atom bonded to a chlorine atom (Cl) and a 2-isopropyl-1H-benzimidazol-5-yl group. The benzimidazole ring is in the (E) configuration.

[illegible]

(S,Z)-5ac

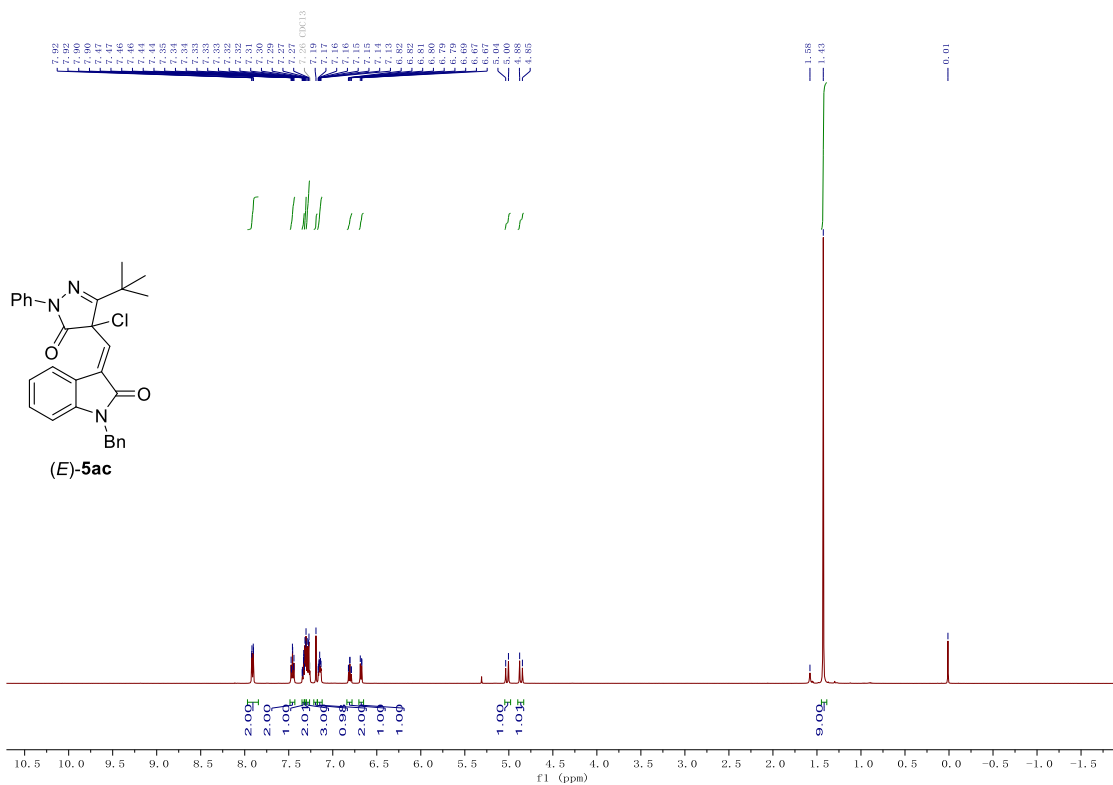
Chemical structure of (S,Z)-5ac is shown above the spectrum. The structure is a benzimidazole derivative with a benzyl group, a chlorine atom, and an isopropyl group.

¹H NMR spectrum (CDCl₃) of (S,Z)-5ac. The x-axis represents the chemical shift in ppm, ranging from -10 to 200. The spectrum shows several peaks corresponding to the protons in the molecule.

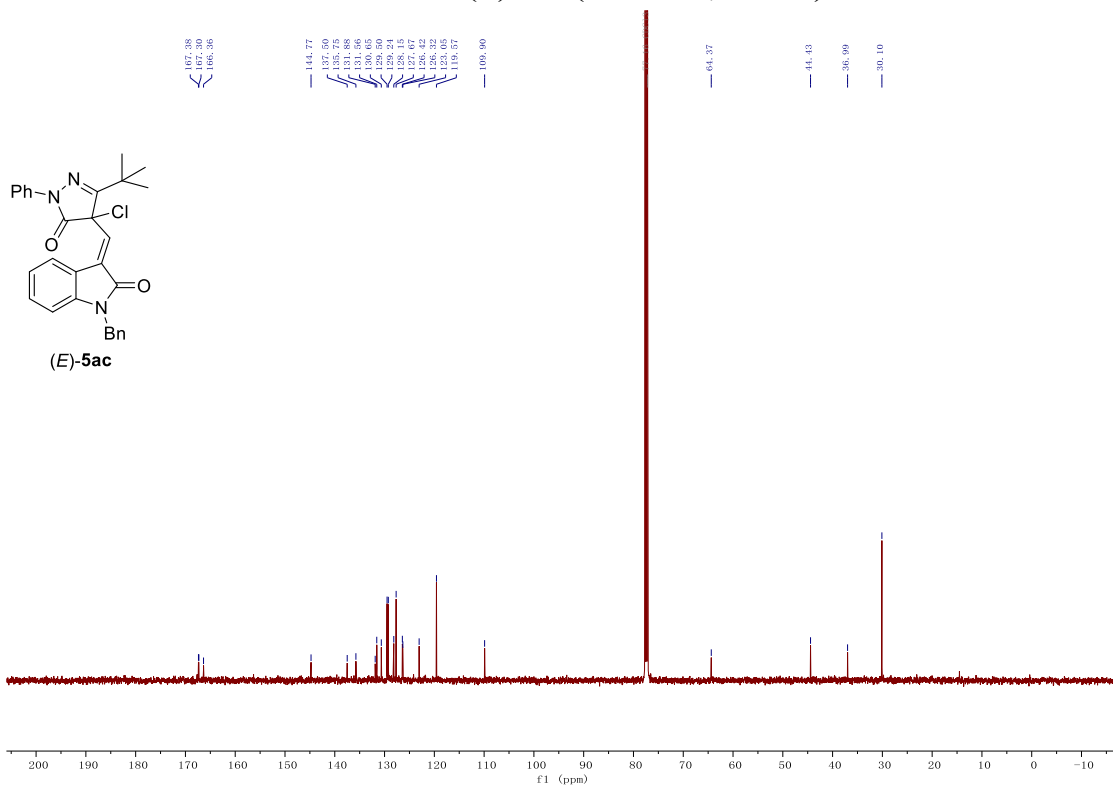
Peak list (ppm):

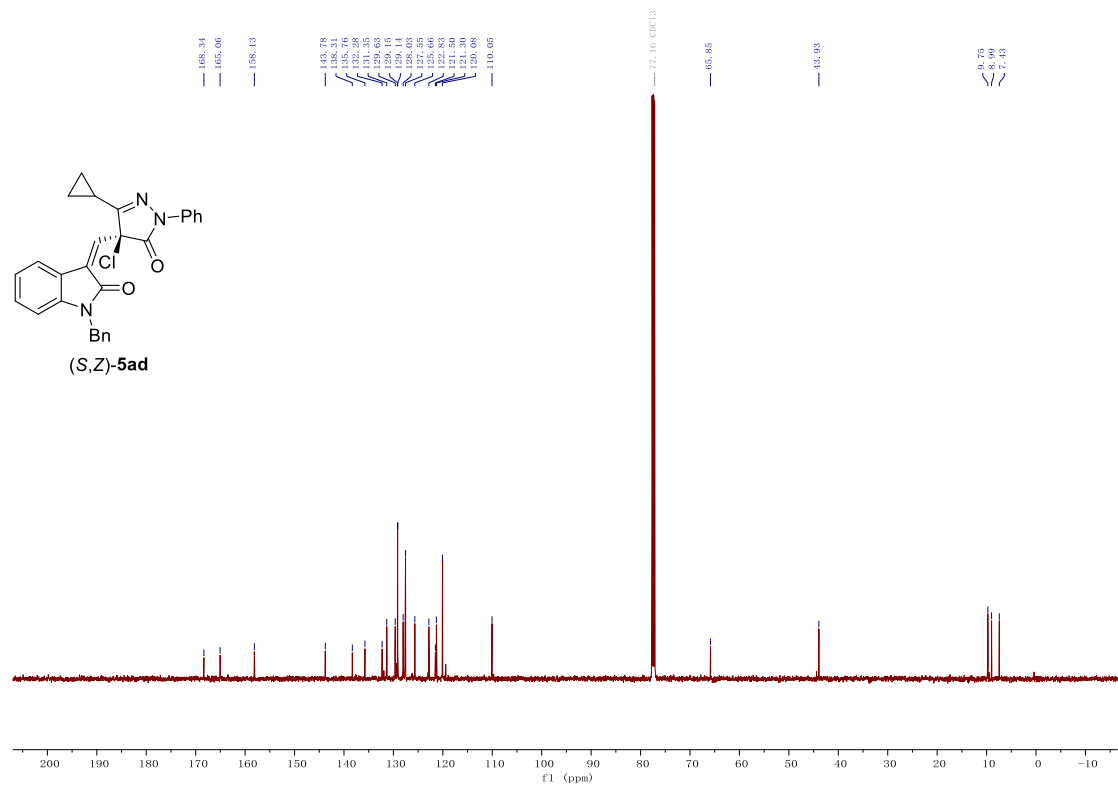
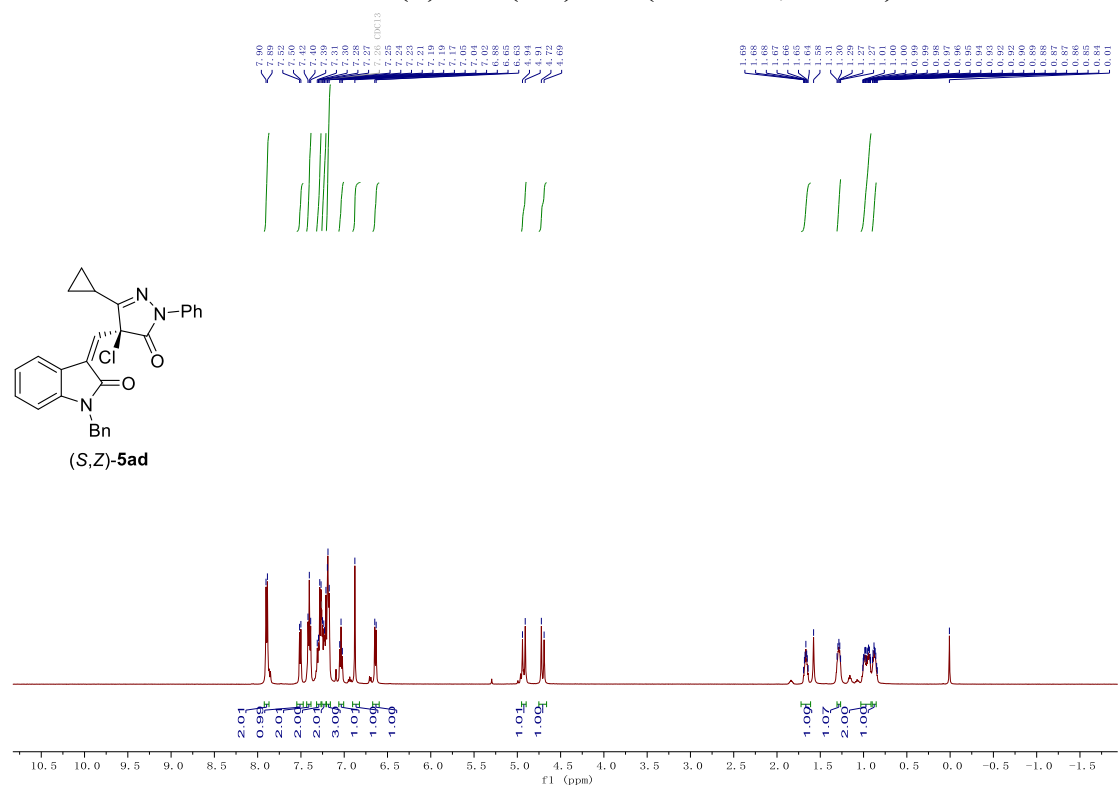
- 7.80, 7.78, 7.76, 7.74, 7.72, 7.70, 7.68, 7.66, 7.64, 7.62, 7.60, 7.58, 7.56, 7.54, 7.52, 7.50, 7.48, 7.46, 7.44, 7.42, 7.40, 7.38, 7.36, 7.34, 7.32, 7.30, 7.28, 7.26, 7.24, 7.22, 7.20, 7.18, 7.16, 7.14, 7.12, 7.10, 7.08, 7.06, 7.04, 7.02, 7.00, 6.98, 6.96, 6.94, 6.92, 6.90, 6.88, 6.86, 6.84, 6.82, 6.80, 6.78, 6.76, 6.74, 6.72, 6.70, 6.68, 6.66, 6.64, 6.62, 6.60, 6.58, 6.56, 6.54, 6.52, 6.50, 6.48, 6.46, 6.44, 6.42, 6.40, 6.38, 6.36, 6.34, 6.32, 6.30, 6.28, 6.26, 6.24, 6.22, 6.20, 6.18, 6.16, 6.14, 6.12, 6.10, 6.08, 6.06, 6.04, 6.02, 6.00, 5.98, 5.96, 5.94, 5.92, 5.90, 5.88, 5.86, 5.84, 5.82, 5.80, 5.78, 5.76, 5.74, 5.72, 5.70, 5.68, 5.66, 5.64, 5.62, 5.60, 5.58, 5.56, 5.54, 5.52, 5.50, 5.48, 5.46, 5.44, 5.42, 5.40, 5.38, 5.36, 5.34, 5.32, 5.30, 5.28, 5.26, 5.24, 5.22, 5.20, 5.18, 5.16, 5.14, 5.12, 5.10, 5.08, 5.06, 5.04, 5.02, 5.00, 4.98, 4.96, 4.94, 4.92, 4.90, 4.88, 4.86, 4.84, 4.82, 4.80, 4.78, 4.76, 4.74, 4.72, 4.70, 4.68, 4.66, 4.64, 4.62, 4.60, 4.58, 4.56, 4.54, 4.52, 4.50, 4.48, 4.46, 4.44, 4.42, 4.40, 4.38, 4.36, 4.34, 4.32, 4.30, 4.28, 4.26, 4.24, 4.22, 4.20, 4.18, 4.16, 4.14, 4.12, 4.10, 4.08, 4.06, 4.04, 4.02, 4.00, 3.98, 3.96, 3.94, 3.92, 3.90, 3.88, 3.86, 3.84, 3.82, 3.80, 3.78, 3.76, 3.74, 3.72, 3.70, 3.68, 3.66, 3.64, 3.62, 3.60, 3.58, 3.56, 3.54, 3.52, 3.50, 3.48, 3.46, 3.44, 3.42, 3.40, 3.38, 3.36, 3.34, 3.32, 3.30, 3.28, 3.26, 3.24, 3.22, 3.20, 3.18, 3.16, 3.14, 3.12, 3.10, 3.08, 3.06, 3.04, 3.02, 3.00, 2.98, 2.96, 2.94, 2.92, 2.90, 2.88, 2.86, 2.84, 2.82, 2.80, 2.78, 2.76, 2.74, 2.72, 2.70, 2.68, 2.66, 2.64, 2.62, 2.60, 2.58, 2.56, 2.54, 2.52, 2.50, 2.48, 2.46, 2.44, 2.42, 2.40, 2.38, 2.36, 2.34, 2.32, 2.30, 2.28, 2.26, 2.24, 2.22, 2.20, 2.18, 2.16, 2.14, 2.12, 2.10, 2.08, 2.06, 2.04, 2.02, 2.00, 1.98, 1.96, 1.94, 1.92, 1.90, 1.88, 1.86, 1.84, 1.82, 1.80, 1.78, 1.76, 1.74, 1.72, 1.70, 1.68, 1.66, 1.64, 1.62, 1.60, 1.58, 1.56, 1.54, 1.52, 1.50, 1.48, 1.46, 1.44, 1.42, 1.40, 1.38, 1.36, 1.34, 1.32, 1.30, 1.28, 1.26, 1.24, 1.22, 1.20, 1.18, 1.16, 1.14, 1.12, 1.10, 1.08, 1.06, 1.04, 1.02, 1.00, 0.98, 0.96, 0.94, 0.92, 0.90, 0.88, 0.86, 0.84, 0.82, 0.80, 0.78, 0.76, 0.74, 0.72, 0.70, 0.68, 0.66, 0.64, 0.62, 0.60, 0.58, 0.56, 0.54, 0.52, 0.50, 0.48, 0.46, 0.44, 0.42, 0.40, 0.38, 0.36, 0.34, 0.32, 0.30, 0.28, 0.26, 0.24, 0.22, 0.20, 0.18, 0.16, 0.14, 0.12, 0.10, 0.08, 0.06, 0.04, 0.02, 0.00, -0.02, -0.04, -0.06, -0.08, -0.10, -0.12, -0.14, -0.16, -0.18, -0.20, -0.22, -0.24, -0.26, -0.28, -0.30, -0.32, -0.34, -0.36, -0.38, -0.40, -0.42, -0.44, -0.46, -0.48, -0.50, -0.52, -0.54, -0.56, -0.58, -0.60, -0.62, -0.64, -0.66, -0.68, -0.70, -0.72, -0.74, -0.76, -0.78, -0.80, -0.82, -0.84, -0.86, -0.88, -0.90, -0.92, -0.94, -0.96, -0.98, -1.00, -1.02, -1.04, -1.06, -1.08, -1.10, -1.12, -1.14, -1.16, -1.18, -1.20, -1.22, -1.24, -1.26, -1.28, -1.30, -1.32, -1.34, -1.36, -1.38, -1.40, -1.42, -1.44, -1.46, -1.48, -1.50, -1.52, -1.54, -1.56, -1.58, -1.60, -1.62, -1.64, -1.66, -1.68, -1.70, -1.72, -1.74, -1.76, -1.78, -1.80, -1.82, -1.84, -1.86, -1.88, -1.90, -1.92, -1.94, -1.96, -1.98, -2.00, -2.02, -2.04, -2.06, -2.08, -2.10, -2.12, -2.14, -2.16, -2.18, -2.20, -2.22, -2.24, -2.26, -2.28, -2.30, -2.32, -2.34, -2.36, -2.38, -2.40, -2.42, -2.44, -2.46, -2.48, -2.50, -2.52, -2.54, -2.56, -2.58, -2.60, -2.62, -2.64, -2.66, -2.68, -2.70, -2.72, -2.74, -2.76, -2.78, -2.80, -2.82, -2.84, -2.86, -2.88, -2.90, -2.92, -2.94, -2.96, -2.98, -3.00, -3.02, -3.04, -3.06, -3.08, -3.10, -3.12, -3.14, -3.16, -3.18, -3.20, -3.22, -3.24, -3.26, -3.28, -3.30, -3.32, -3.34, -3.36, -3.38, -3.40, -3.42, -3.44, -3.46, -3.48, -3.50, -3.52, -3.54, -3.56, -3.58, -3.60, -3.62, -3.64, -3.66, -3.68, -3.70, -3.72, -3.74, -3.76, -3.78, -3.80, -3.82, -3.84, -3.86, -3.88, -3.90, -3.92, -3.94, -3.96, -3.98, -4.00, -4.02, -4.04, -4.06, -4.08, -4.10, -4.12, -4.14, -4.16, -4.18, -4.20, -4.22, -4.24, -4.26, -4.28, -4.30, -4.32, -4.34, -4.36, -4.38, -4.40, -4.42, -4.44, -4.46, -4.48, -4.50, -4.52, -4.54, -4.56, -4.58, -4.60, -4.62, -4.64, -4.66, -4.68, -4.70, -4.72, -4.74, -4.76, -4.78, -4.80, -4.82, -4.84, -4.86, -4.88, -4.90, -4.92, -4.9

¹H NMR of (*E*)-5ac (500 MHz, CDCl₃)

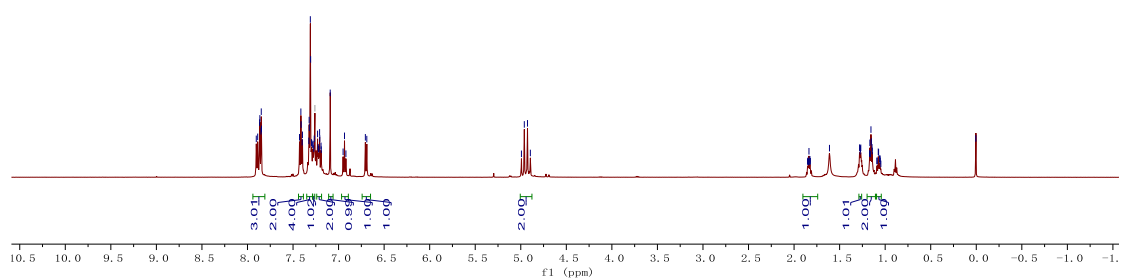
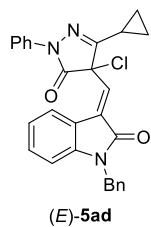
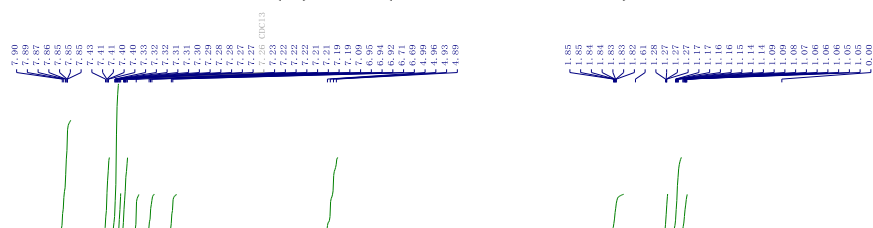


^{13}C NMR of (*E*)-5ac (126 MHz, CDCl_3)

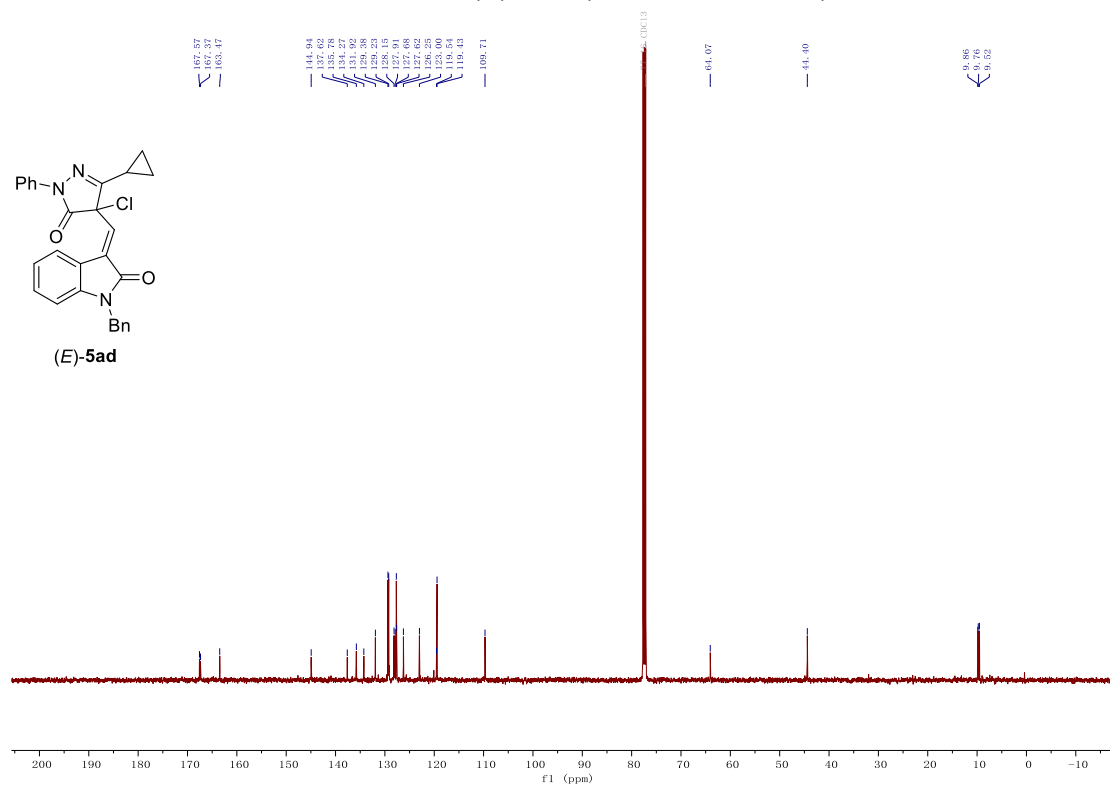




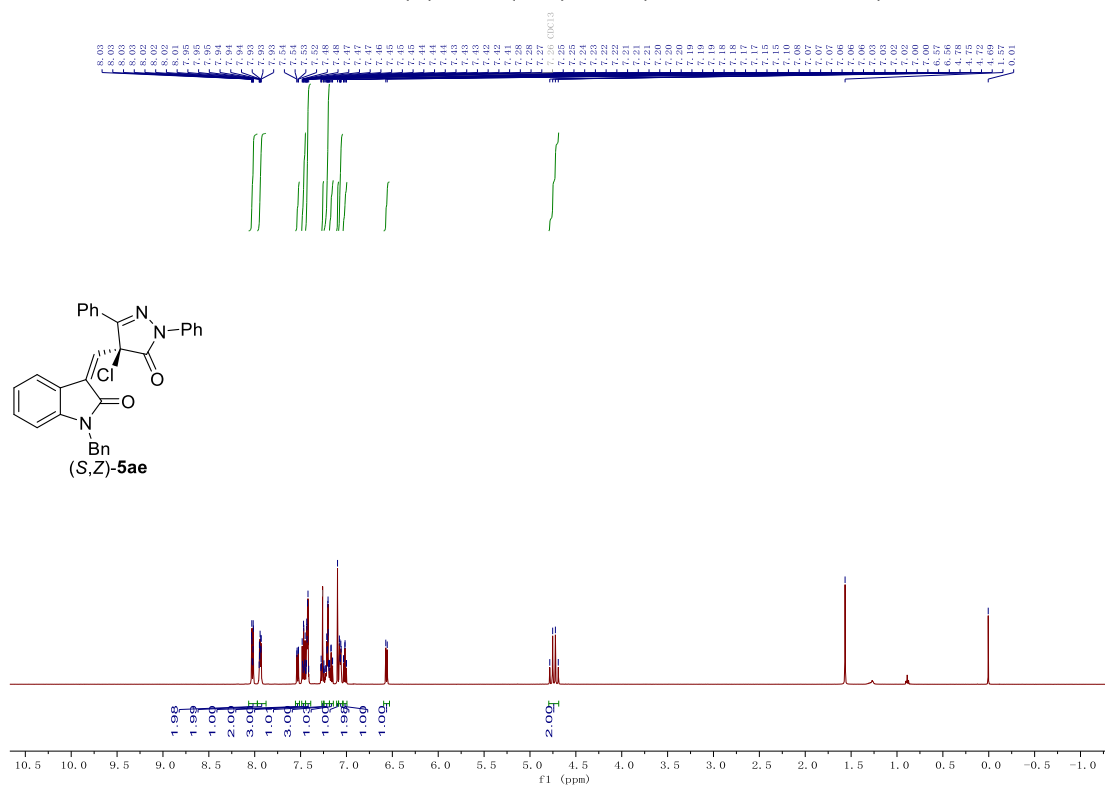
¹H NMR of (*E*)-5ad (500 MHz, CDCl₃)



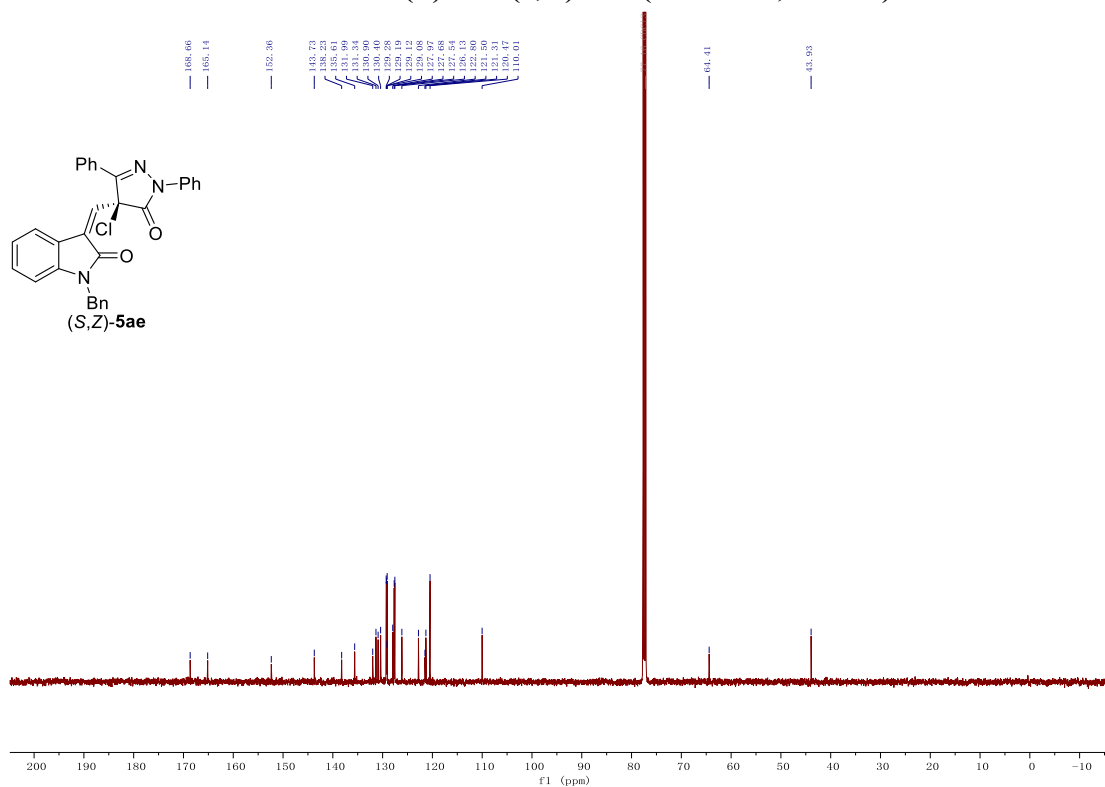
¹³C NMR of (*E*)-5ad (126 MHz, CDCl₃)



¹H NMR of (Z)-5ae/(S,Z)-5ae (500 MHz, CDCl₃)



¹³C NMR of (Z)-5ae/(S,Z)-5ae (126 MHz, CDCl₃)



Chemical structure of **(E)-5ae** is shown in the top left corner. The structure is a complex molecule featuring a benzene ring fused to a five-membered ring containing a carbonyl group and a nitrogen atom substituted with a benzyl group. A chlorine atom is attached to the five-membered ring, and a phenyl group is attached to the nitrogen atom. The molecule is labeled **(E)-5ae**.

The ^1H NMR spectrum (400 MHz, CDCl_3) is displayed below the structure. The x-axis represents the chemical shift in ppm, ranging from 0.00 to 10.5. The spectrum shows several peaks, with integration values provided below the baseline. The peaks are labeled with their corresponding chemical shifts (ppm) and integration values.

Peak list (ppm): 8.05, 8.04, 8.03, 8.02, 8.01, 8.00, 7.99, 7.98, 7.97, 7.96, 7.95, 7.94, 7.93, 7.92, 7.91, 7.90, 7.89, 7.88, 7.87, 7.86, 7.85, 7.84, 7.83, 7.82, 7.81, 7.80, 7.79, 7.78, 7.77, 7.76, 7.75, 7.74, 7.73, 7.72, 7.71, 7.70, 7.69, 7.68, 7.67, 7.66, 7.65, 7.64, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68,

(E)-5ae

c1ccc2c(c1)c3ccccc3n2C(=O)C(Cl)(C(=O)N(c4ccccc4)c5ccccc55)c6ccccc6

13C NMR (CDCl₃)

167.50, 165.60, 156.63, 144.97, 137.54, 137.22, 137.22, 133.77, 133.77, 133.14, 131.94, 129.48, 129.48, 129.21, 129.21, 128.53, 128.53, 127.88, 127.77, 127.66, 127.62, 126.68, 126.68, 125.55, 125.55, 119.80, 119.53, 109.75, 77.16 (CDCl₃), 62.57, 44.41

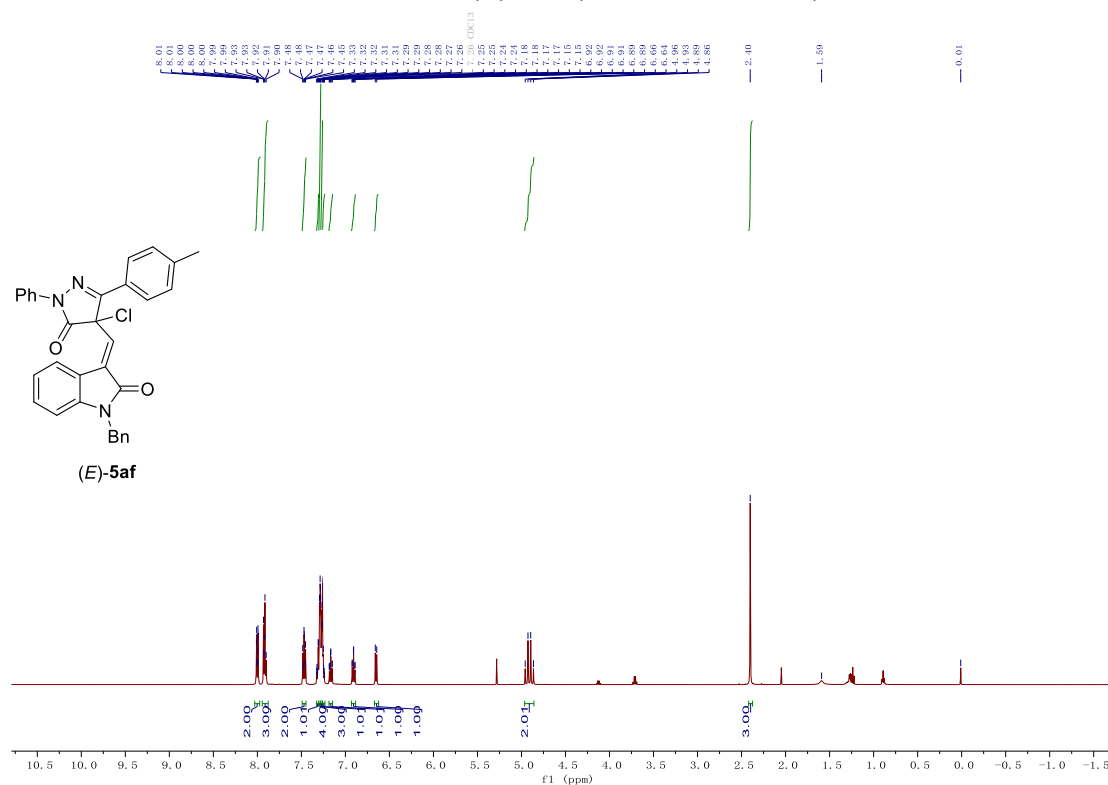
Chemical structure of (S,Z)-5af is shown. The ^1H NMR spectrum (CDCl₃) displays peaks corresponding to the structure, with integration values and chemical shifts (ppm) indicated.

Chemical Shift (ppm)	Integration
~7.8	2.01
~7.7	2.01
~7.6	1.00
~7.5	2.00
~7.4	2.00
~7.3	1.00
~7.2	3.02
~7.1	3.02
~7.0	1.00
~6.9	1.00
~6.8	2.00
~6.7	1.00
~6.6	1.01
~4.7	2.00
~2.5	3.00
~1.5	1.00
~0.0	1.00

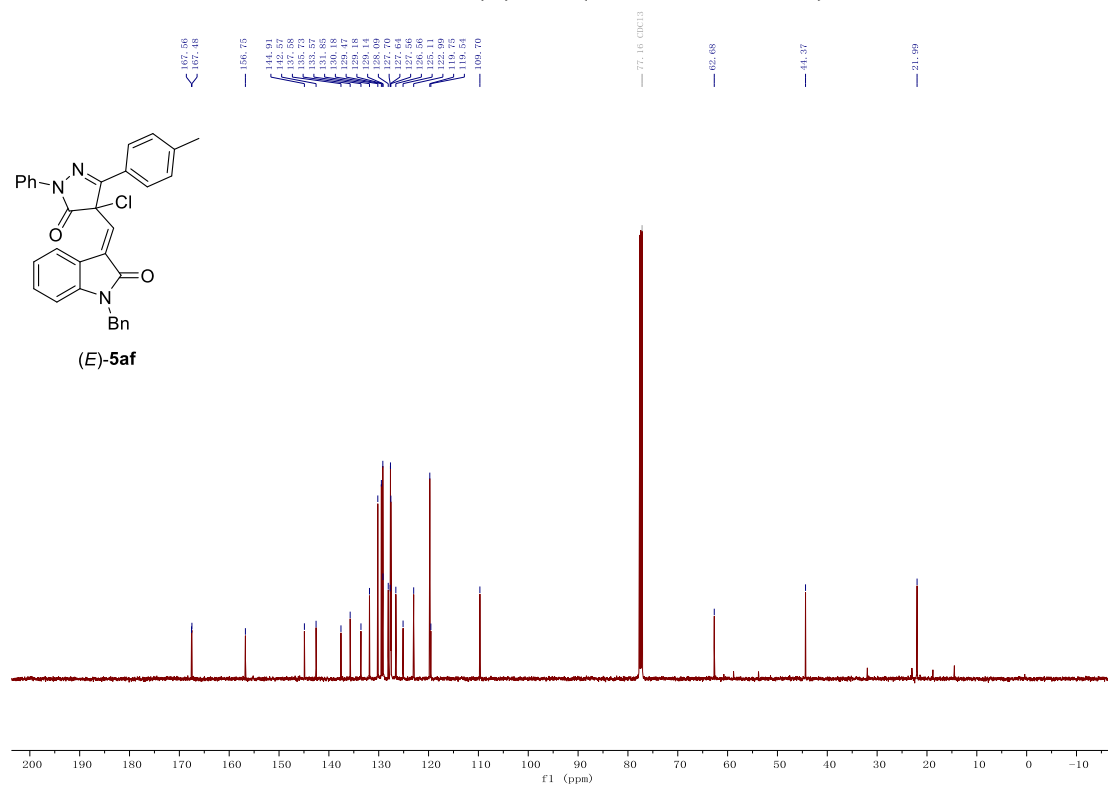
Chemical structure of (S,Z)-5af is shown as an inset. The structure is a 1-benzyl-2-chloro-3-(4-methylphenyl)-4-phenyl-5-phenyl-1H-imidazole-4-carboxamide derivative. The N-phenyl group is shown in red in the original image.

¹H NMR spectrum (CDCl₃) of (S,Z)-5af. The spectrum shows peaks from 0 to 10 ppm. Aromatic and heterocyclic protons appear between 7.0 and 8.5 ppm. A broad singlet at ~7.2 ppm is assigned to the NH proton. A sharp singlet at ~4.3 ppm is assigned to the benzylic CH₂ protons. A sharp singlet at ~2.1 ppm is assigned to the methyl protons of the N-phenyl group. The chemical structure of (S,Z)-5af is shown as an inset.

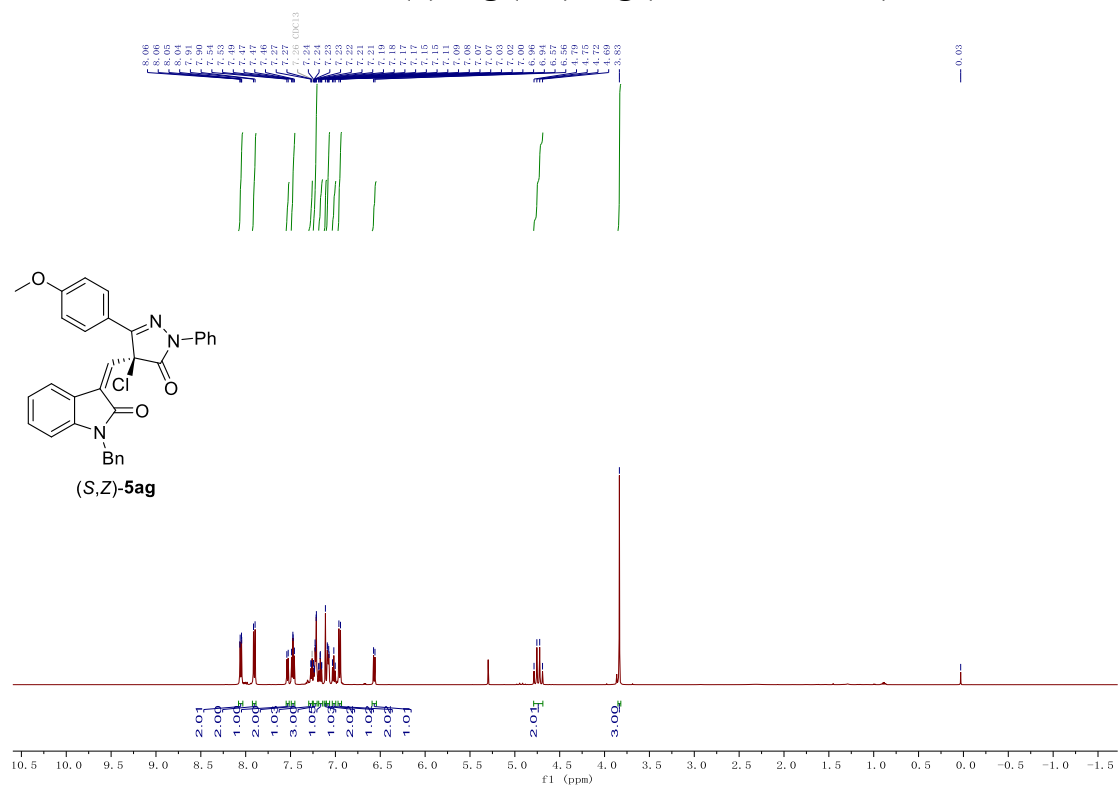
¹H NMR of (E)-5af (500 MHz, CDCl₃)



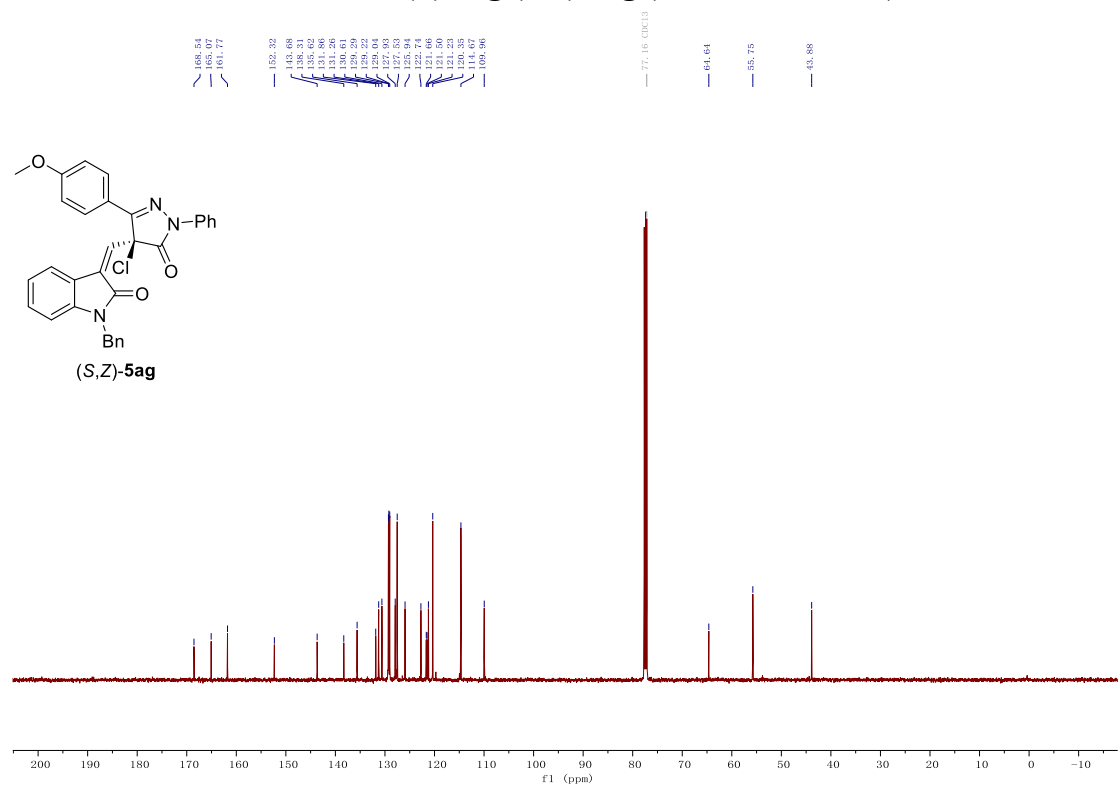
¹³C NMR of (E)-5af (126 MHz, CDCl₃)



¹H NMR of (Z)-5ag/(S,Z)-5ag (500 MHz, CDCl₃)



¹³C NMR of (Z)-5ag/(S,Z)-5ag (126 MHz, CDCl₃)



[illegible]

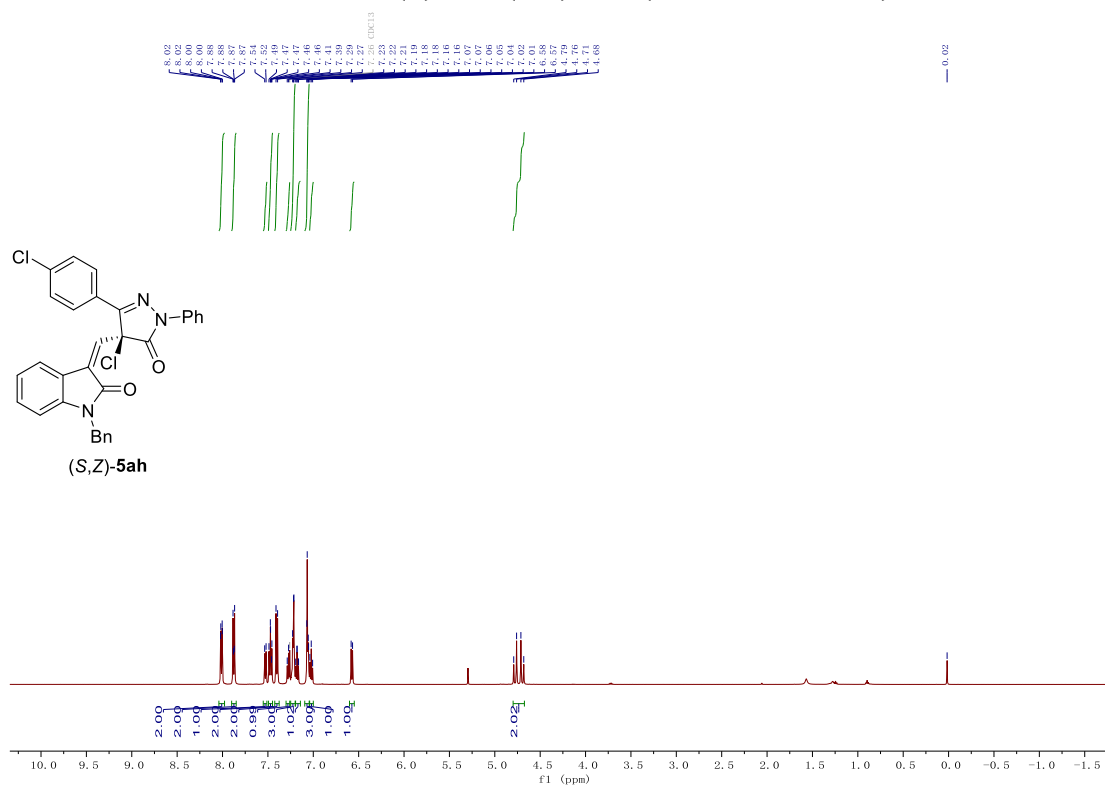
(E)-5ag

COc1ccc(cc1)C2=CC(=O)N(C2/C=C3C(=O)N(C3)Cc4ccccc4)C(=O)N2c5ccccc5

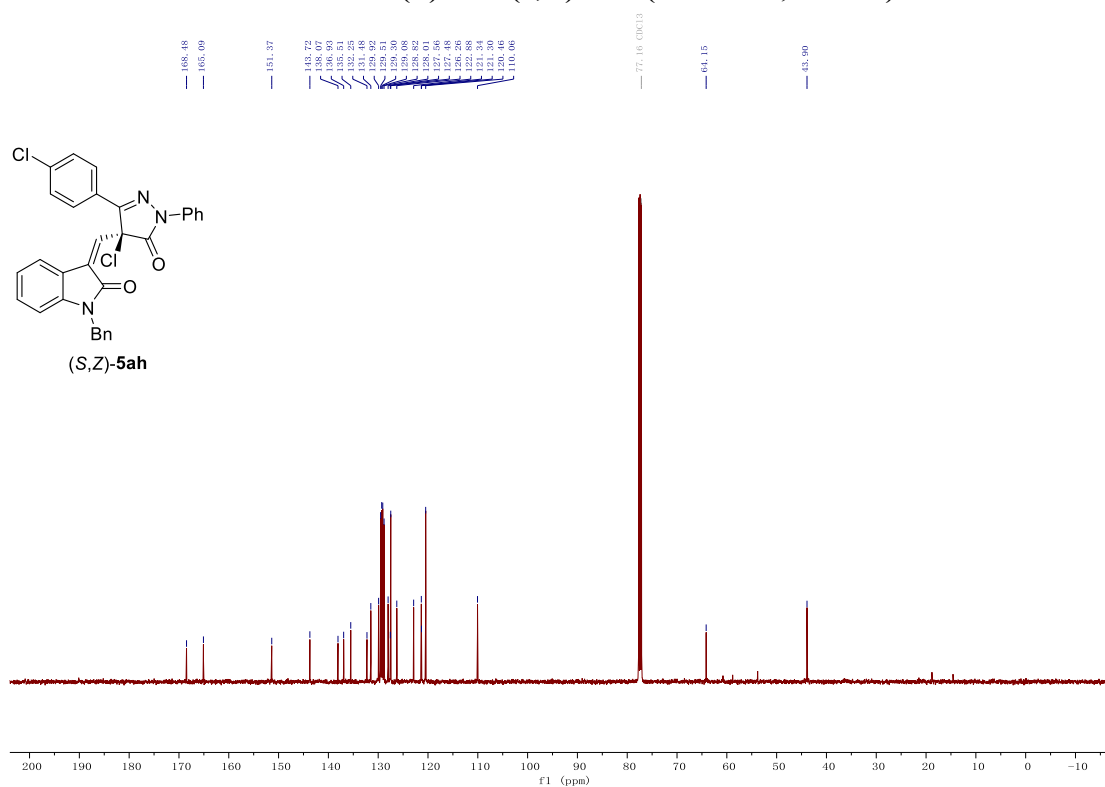
Chemical structure of (E)-5ag is shown. The structure features a benzimidazole core with a benzyl group on the nitrogen, a carbonyl group, and a 4-methoxyphenyl group. The structure is labeled (E)-5ag.

¹³C NMR spectrum (CDCl₃) of (E)-5ag. The x-axis represents the chemical shift in ppm, ranging from -10 to 200. The spectrum shows several peaks corresponding to the carbon atoms in the molecule. The peaks are labeled with their chemical shifts (ppm): 167.54, 167.50, 162.61, 156.62, 144.93, 137.65, 137.57, 133.57, 131.87, 131.87, 129.47, 129.39, 129.33, 128.72, 128.12, 127.77, 127.55, 126.93, 123.03, 122.77, 120.75, 119.57, 114.97, 109.72, 62.80, 65.87, 44.40.

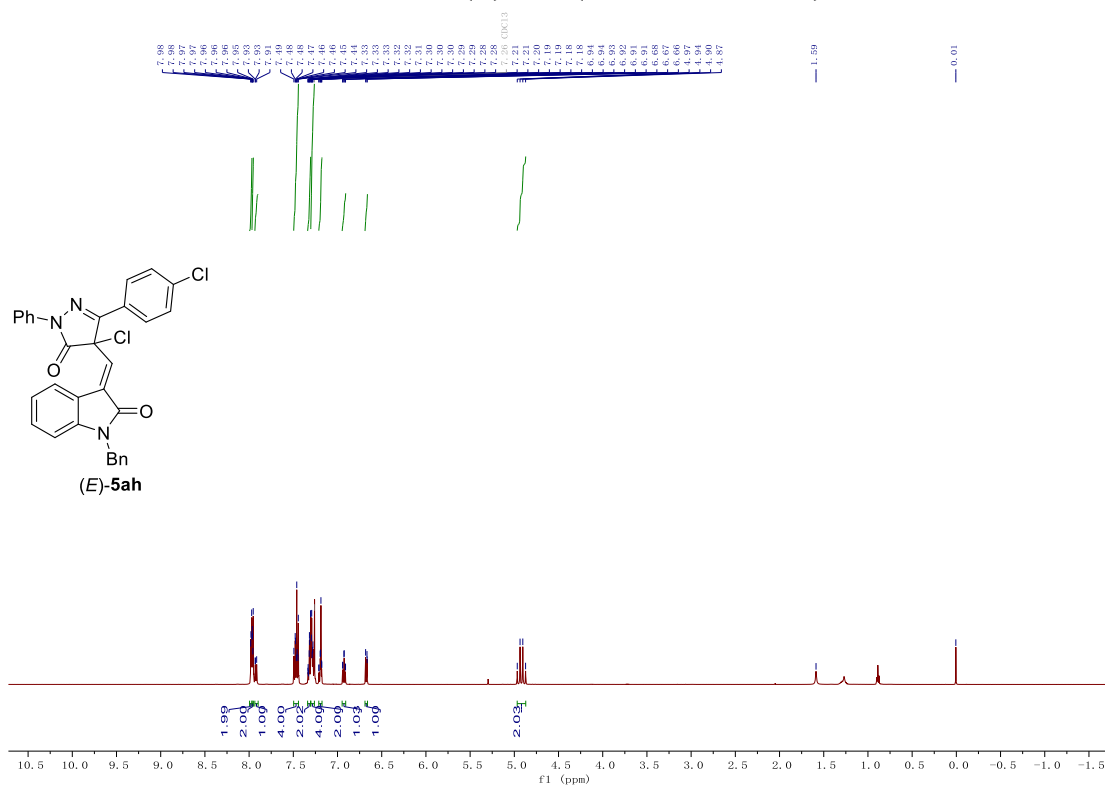
¹H NMR of (Z)-5ah/(S,Z)-5ah (500 MHz, CDCl₃)



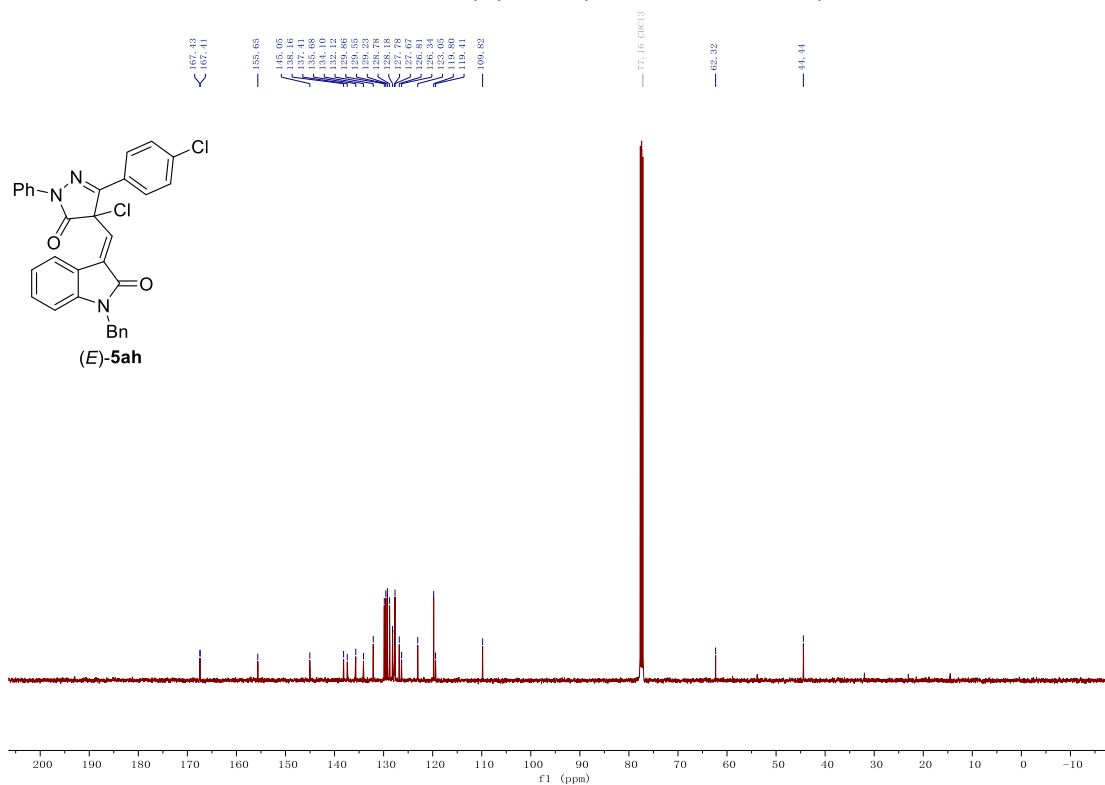
¹³C NMR of (Z)-5ah/(S,Z)-5ah (126 MHz, CDCl₃)



¹H NMR of (*E*)-5ah (500 MHz, CDCl₃)



¹³C NMR of (*E*)-5ah (126 MHz, CDCl₃)



(S,Z)-5ai

c1ccc(cc1)n2c(=O)c(c3ccccc3n2C(=O)C4=CC=CC=C4Br)C(=O)N5=CC=CC=C5

Chemical structure of (S,Z)-5ai is shown. The structure features a central five-membered ring with a carbonyl group (C=O) and a chlorine atom (Cl). The ring is substituted with a benzyl group (Bn) and a phenyl group (Ph). The stereochemistry is (S,Z).

¹H NMR spectrum (CDCl₃) of (S,Z)-5ai is displayed. The x-axis represents the chemical shift in ppm, ranging from 10.5 to -1.5. The spectrum shows several peaks, with integration values provided below the baseline. Key peaks are labeled with their chemical shifts (ppm): 8.01, 8.00, 7.99, 7.98, 7.97, 7.96, 7.95, 7.94, 7.93, 7.92, 7.91, 7.90, 7.89, 7.88, 7.87, 7.86, 7.85, 7.84, 7.83, 7.82, 7.81, 7.80, 7.79, 7.78, 7.77, 7.76, 7.75, 7.74, 7.73, 7.72, 7.71, 7.70, 7.69, 7.68, 7.67, 7.66, 7.65, 7.64, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1.65, 1.64, 1.63, 1.62, 1.61, 1.60, 1.59, 1.58, 1.57, 1.56, 1

(S,Z)-5ai

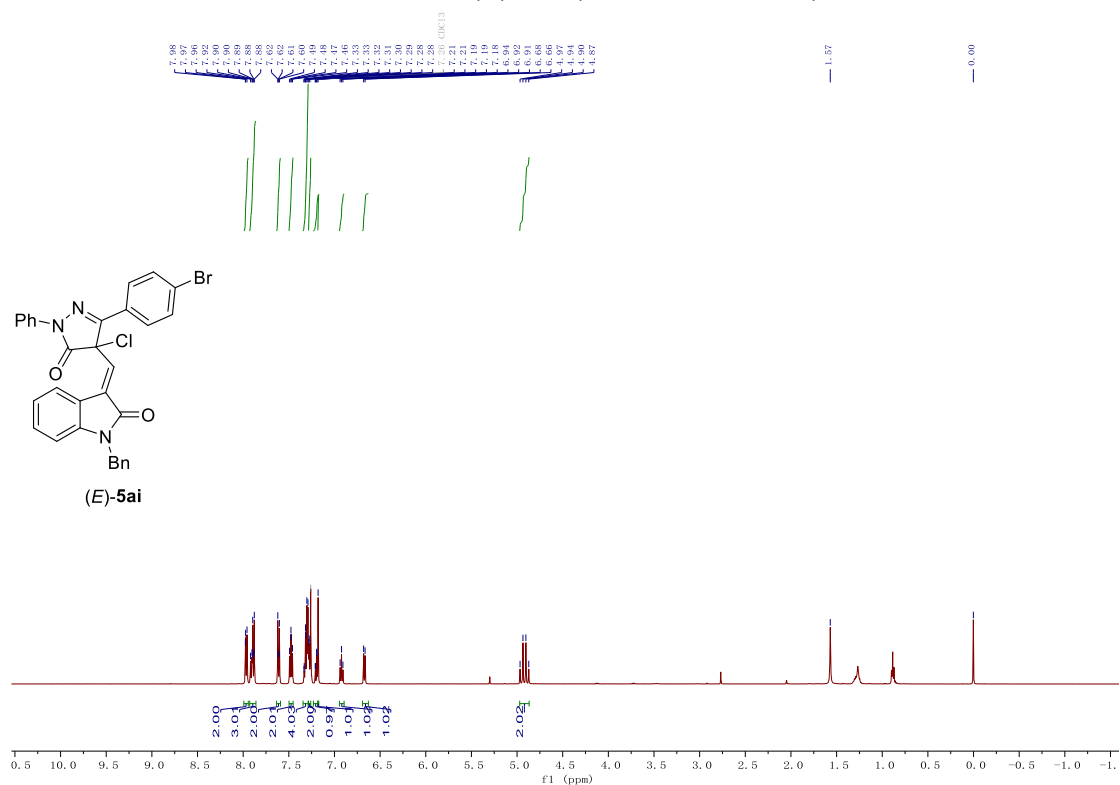
c1ccc(cc1)N2C(=O)C(Cl)C(=N2)C3=CC=C(C=C3)N4C(=O)C(=C5C(=N4)N(C5)C6=CC=CC=C6)C7=CC=C(C=C7)Br

Chemical structure of (S,Z)-5ai is shown. The structure features a benzimidazole core substituted with a benzyl group (N-Bn), a chlorine atom, and a 4-bromophenyl group. The imidazole ring is also substituted with a phenyl group (N-Ph).

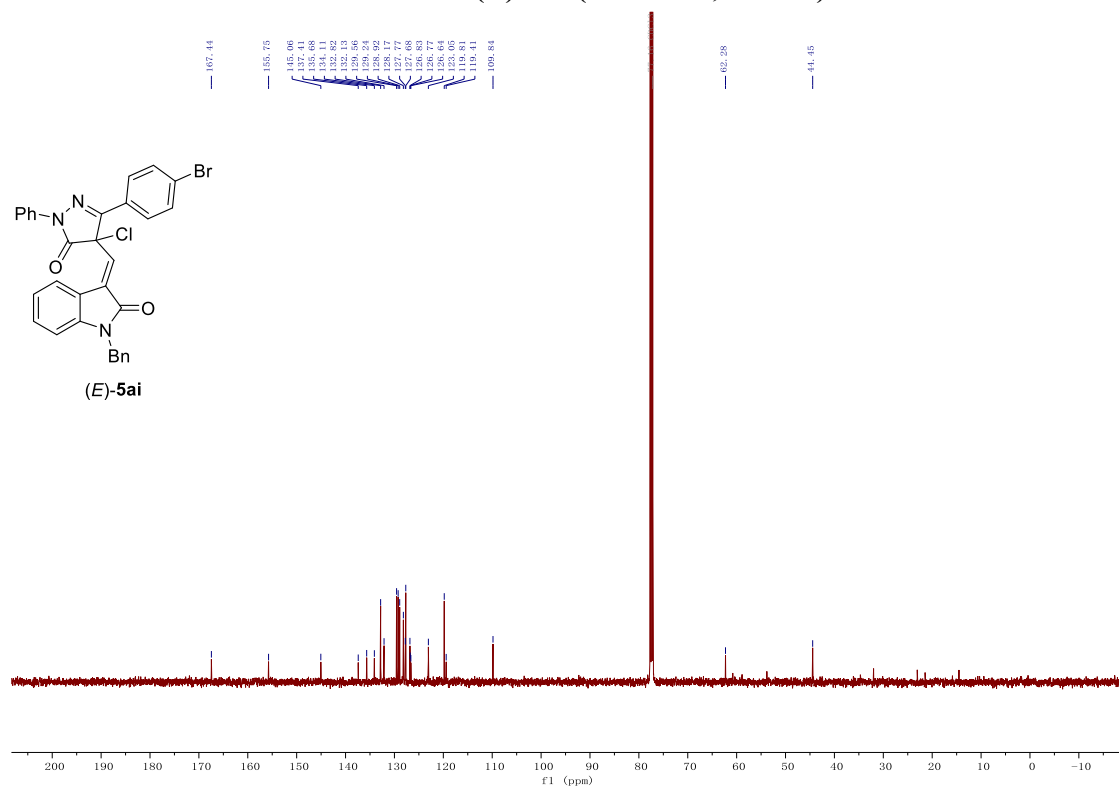
¹H NMR spectrum (CDCl₃) of (S,Z)-5ai is displayed. The x-axis represents the chemical shift in ppm, ranging from -10 to 200. The spectrum shows several peaks, with the most prominent ones in the aromatic region (6.5-7.5 ppm) and a sharp peak at approximately 7.7 ppm, likely corresponding to the solvent (CDCl₃).

¹³C NMR spectrum (CDCl₃) of (S,Z)-5ai is displayed. The x-axis represents the chemical shift in ppm, ranging from -10 to 200. The spectrum shows several peaks, with the most prominent ones in the aromatic region (120-140 ppm) and a sharp peak at approximately 77 ppm, likely corresponding to the solvent (CDCl₃).

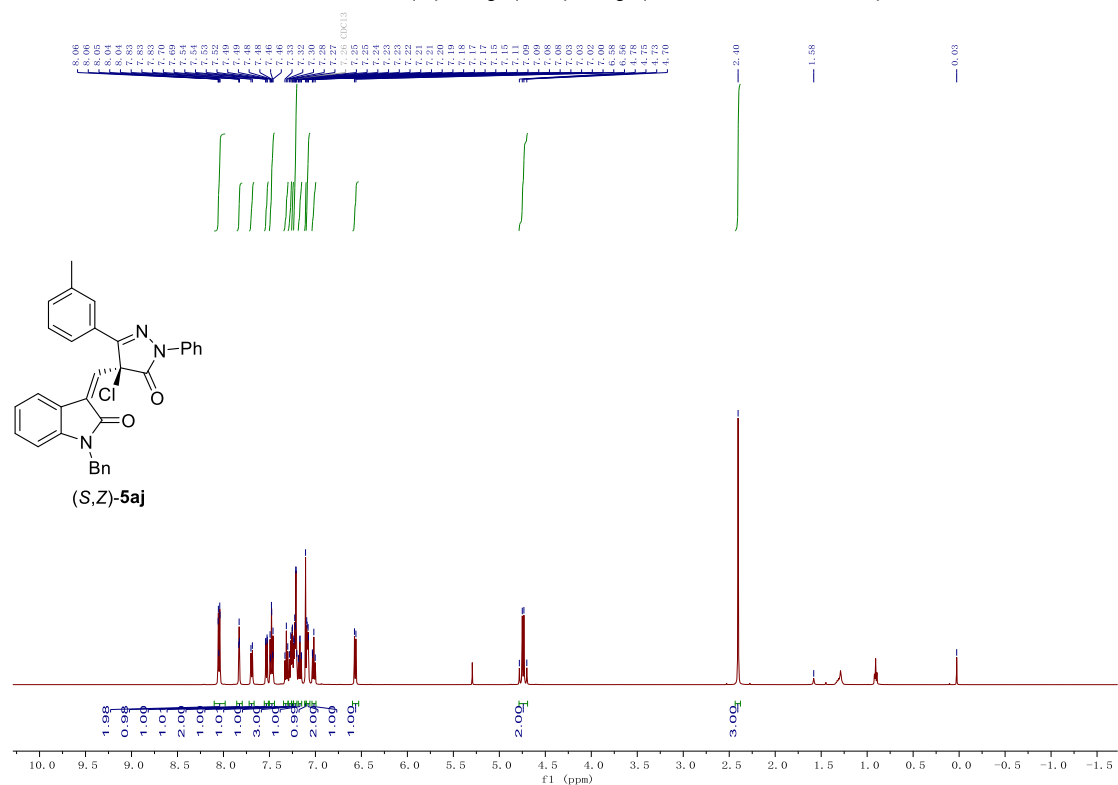
¹H NMR of (*E*)-5ai (500 MHz, CDCl₃)



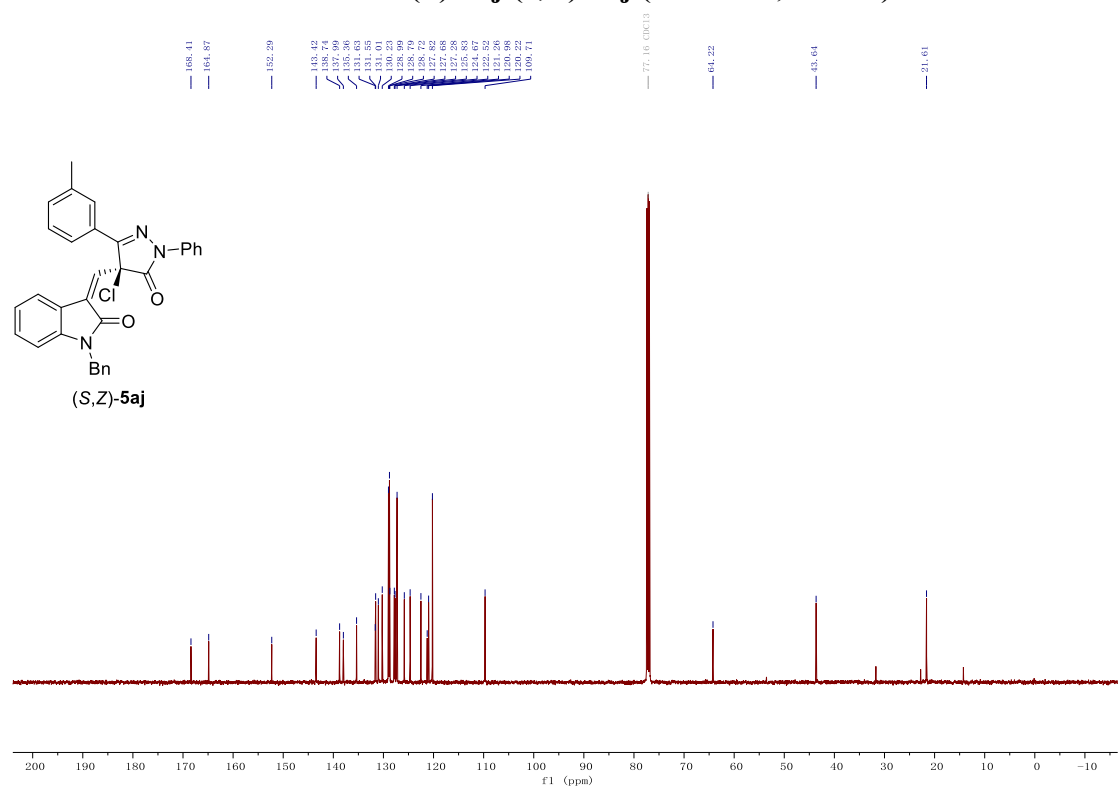
¹³C NMR of (*E*)-5ai (126 MHz, CDCl₃)



¹H NMR of (Z)-5aj/(S,Z)-5aj (500 MHz, CDCl₃)



¹³C NMR of (Z)-5aj/(S,Z)-5aj (126 MHz, CDCl₃)



(E)-5aj

Cc1ccc(cc1)C2=C(Cl)C(=O)N(C2/C(=O)c3ccccc3N(C)C)C(=O)c4ccccc4

¹H NMR (400 MHz, CDCl₃)

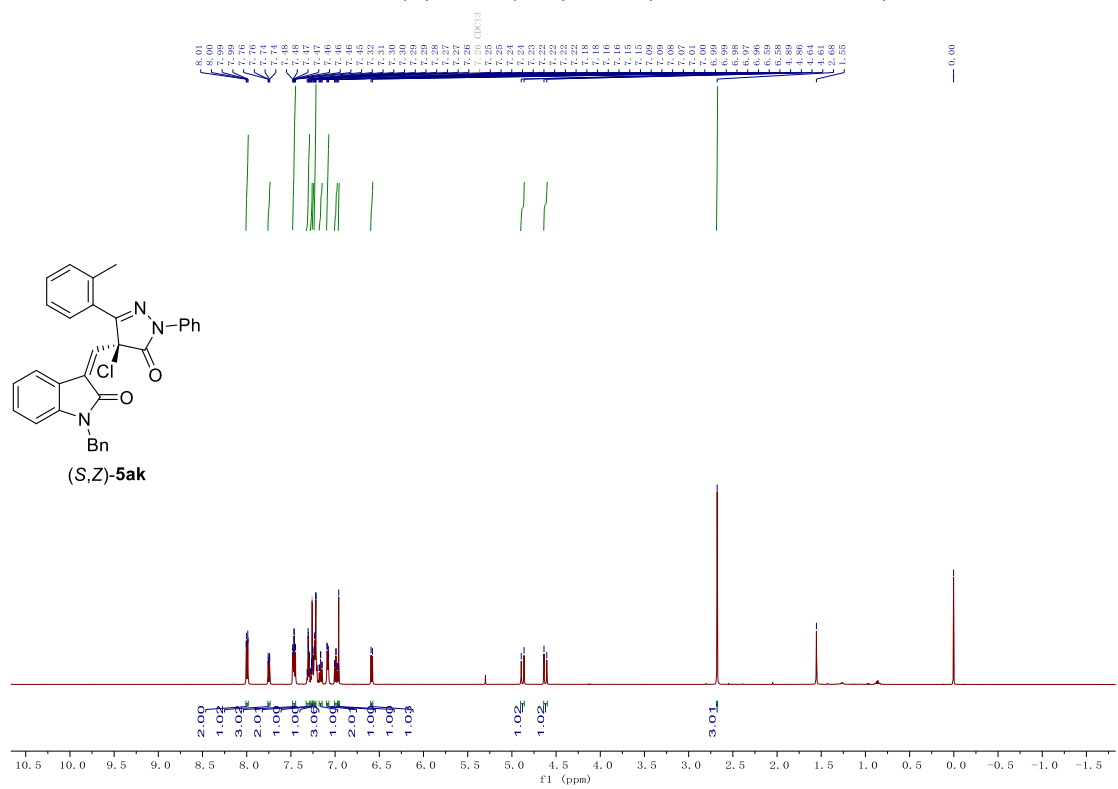
Chemical structure of (E)-5aj is shown. The structure is a complex molecule featuring a central benzene ring substituted with a phenyl group, a chlorine atom, and a carbonyl group. The carbonyl group is part of a larger system that includes a benzyl group and a phenyl ring. The structure is labeled (E)-5aj.

1H NMR (400 MHz, CDCl₃) spectrum of (E)-5aj. The spectrum shows several peaks in the aromatic region (6.5-8.5 ppm) and a broad peak in the aliphatic region (2.5-3.0 ppm). The peaks are labeled with their chemical shifts (ppm) and integration values.

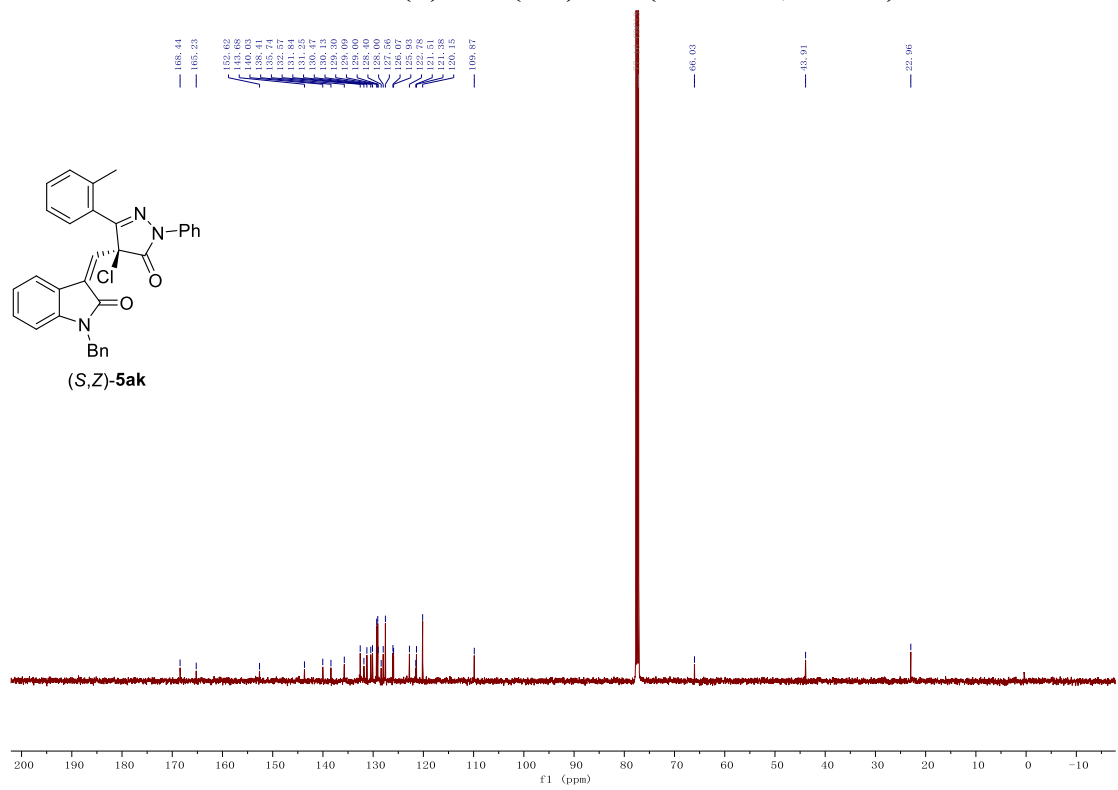
Chemical shifts (ppm): 8.02, 8.01, 8.00, 7.99, 7.98, 7.97, 7.96, 7.95, 7.94, 7.93, 7.92, 7.91, 7.90, 7.89, 7.88, 7.87, 7.86, 7.85, 7.84, 7.83, 7.82, 7.81, 7.80, 7.79, 7.78, 7.77, 7.76, 7.75, 7.74, 7.73, 7.72, 7.71, 7.70, 7.69, 7.68, 7.67, 7.66, 7.65, 7.64, 7.63, 7.62, 7.61, 7.60, 7.59, 7.58, 7.57, 7.56, 7.55, 7.54, 7.53, 7.52, 7.51, 7.50, 7.49, 7.48, 7.47, 7.46, 7.45, 7.44, 7.43, 7.42, 7.41, 7.40, 7.39, 7.38, 7.37, 7.36, 7.35, 7.34, 7.33, 7.32, 7.31, 7.30, 7.29, 7.28, 7.27, 7.26, 7.25, 7.24, 7.23, 7.22, 7.21, 7.20, 7.19, 7.18, 7.17, 7.16, 7.15, 7.14, 7.13, 7.12, 7.11, 7.10, 7.09, 7.08, 7.07, 7.06, 7.05, 7.04, 7.03, 7.02, 7.01, 7.00, 6.99, 6.98, 6.97, 6.96, 6.95, 6.94, 6.93, 6.92, 6.91, 6.90, 6.89, 6.88, 6.87, 6.86, 6.85, 6.84, 6.83, 6.82, 6.81, 6.80, 6.79, 6.78, 6.77, 6.76, 6.75, 6.74, 6.73, 6.72, 6.71, 6.70, 6.69, 6.68, 6.67, 6.66, 6.65, 6.64, 6.63, 6.62, 6.61, 6.60, 6.59, 6.58, 6.57, 6.56, 6.55, 6.54, 6.53, 6.52, 6.51, 6.50, 6.49, 6.48, 6.47, 6.46, 6.45, 6.44, 6.43, 6.42, 6.41, 6.40, 6.39, 6.38, 6.37, 6.36, 6.35, 6.34, 6.33, 6.32, 6.31, 6.30, 6.29, 6.28, 6.27, 6.26, 6.25, 6.24, 6.23, 6.22, 6.21, 6.20, 6.19, 6.18, 6.17, 6.16, 6.15, 6.14, 6.13, 6.12, 6.11, 6.10, 6.09, 6.08, 6.07, 6.06, 6.05, 6.04, 6.03, 6.02, 6.01, 6.00, 5.99, 5.98, 5.97, 5.96, 5.95, 5.94, 5.93, 5.92, 5.91, 5.90, 5.89, 5.88, 5.87, 5.86, 5.85, 5.84, 5.83, 5.82, 5.81, 5.80, 5.79, 5.78, 5.77, 5.76, 5.75, 5.74, 5.73, 5.72, 5.71, 5.70, 5.69, 5.68, 5.67, 5.66, 5.65, 5.64, 5.63, 5.62, 5.61, 5.60, 5.59, 5.58, 5.57, 5.56, 5.55, 5.54, 5.53, 5.52, 5.51, 5.50, 5.49, 5.48, 5.47, 5.46, 5.45, 5.44, 5.43, 5.42, 5.41, 5.40, 5.39, 5.38, 5.37, 5.36, 5.35, 5.34, 5.33, 5.32, 5.31, 5.30, 5.29, 5.28, 5.27, 5.26, 5.25, 5.24, 5.23, 5.22, 5.21, 5.20, 5.19, 5.18, 5.17, 5.16, 5.15, 5.14, 5.13, 5.12, 5.11, 5.10, 5.09, 5.08, 5.07, 5.06, 5.05, 5.04, 5.03, 5.02, 5.01, 5.00, 4.99, 4.98, 4.97, 4.96, 4.95, 4.94, 4.93, 4.92, 4.91, 4.90, 4.89, 4.88, 4.87, 4.86, 4.85, 4.84, 4.83, 4.82, 4.81, 4.80, 4.79, 4.78, 4.77, 4.76, 4.75, 4.74, 4.73, 4.72, 4.71, 4.70, 4.69, 4.68, 4.67, 4.66, 4.65, 4.64, 4.63, 4.62, 4.61, 4.60, 4.59, 4.58, 4.57, 4.56, 4.55, 4.54, 4.53, 4.52, 4.51, 4.50, 4.49, 4.48, 4.47, 4.46, 4.45, 4.44, 4.43, 4.42, 4.41, 4.40, 4.39, 4.38, 4.37, 4.36, 4.35, 4.34, 4.33, 4.32, 4.31, 4.30, 4.29, 4.28, 4.27, 4.26, 4.25, 4.24, 4.23, 4.22, 4.21, 4.20, 4.19, 4.18, 4.17, 4.16, 4.15, 4.14, 4.13, 4.12, 4.11, 4.10, 4.09, 4.08, 4.07, 4.06, 4.05, 4.04, 4.03, 4.02, 4.01, 4.00, 3.99, 3.98, 3.97, 3.96, 3.95, 3.94, 3.93, 3.92, 3.91, 3.90, 3.89, 3.88, 3.87, 3.86, 3.85, 3.84, 3.83, 3.82, 3.81, 3.80, 3.79, 3.78, 3.77, 3.76, 3.75, 3.74, 3.73, 3.72, 3.71, 3.70, 3.69, 3.68, 3.67, 3.66, 3.65, 3.64, 3.63, 3.62, 3.61, 3.60, 3.59, 3.58, 3.57, 3.56, 3.55, 3.54, 3.53, 3.52, 3.51, 3.50, 3.49, 3.48, 3.47, 3.46, 3.45, 3.44, 3.43, 3.42, 3.41, 3.40, 3.39, 3.38, 3.37, 3.36, 3.35, 3.34, 3.33, 3.32, 3.31, 3.30, 3.29, 3.28, 3.27, 3.26, 3.25, 3.24, 3.23, 3.22, 3.21, 3.20, 3.19, 3.18, 3.17, 3.16, 3.15, 3.14, 3.13, 3.12, 3.11, 3.10, 3.09, 3.08, 3.07, 3.06, 3.05, 3.04, 3.03, 3.02, 3.01, 3.00, 2.99, 2.98, 2.97, 2.96, 2.95, 2.94, 2.93, 2.92, 2.91, 2.90, 2.89, 2.88, 2.87, 2.86, 2.85, 2.84, 2.83, 2.82, 2.81, 2.80, 2.79, 2.78, 2.77, 2.76, 2.75, 2.74, 2.73, 2.72, 2.71, 2.70, 2.69, 2.68, 2.67, 2.66, 2.65, 2.64, 2.63, 2.62, 2.61, 2.60, 2.59, 2.58, 2.57, 2.56, 2.55, 2.54, 2.53, 2.52, 2.51, 2.50, 2.49, 2.48, 2.47, 2.46, 2.45, 2.44, 2.43, 2.42, 2.41, 2.40, 2.39, 2.38, 2.37, 2.36, 2.35, 2.34, 2.33, 2.32, 2.31, 2.30, 2.29, 2.28, 2.27, 2.26, 2.25, 2.24, 2.23, 2.22, 2.21, 2.20, 2.19, 2.18, 2.17, 2.16, 2.15, 2.14, 2.13, 2.12, 2.11, 2.10, 2.09, 2.08, 2.07, 2.06, 2.05, 2.04, 2.03, 2.02, 2.01, 2.00, 1.99, 1.98, 1.97, 1.96, 1.95, 1.94, 1.93, 1.92, 1.91, 1.90, 1.89, 1.88, 1.87, 1.86, 1.85, 1.84, 1.83, 1.82, 1.81, 1.80, 1.79, 1.78, 1.77, 1.76, 1.75, 1.74, 1.73, 1.72, 1.71, 1.70, 1.69, 1.68, 1.67, 1.66, 1

[illegible]

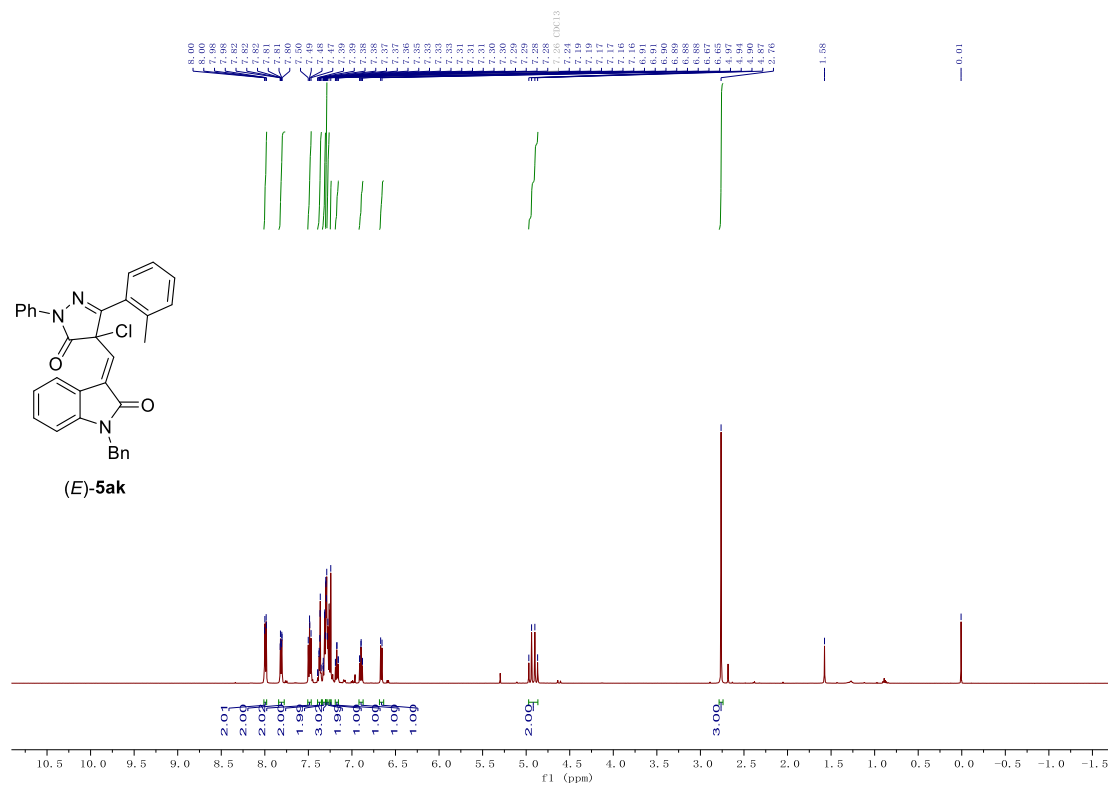
¹H NMR of (Z)-5ak/(S,Z)-5ak (500 MHz, CDCl₃)



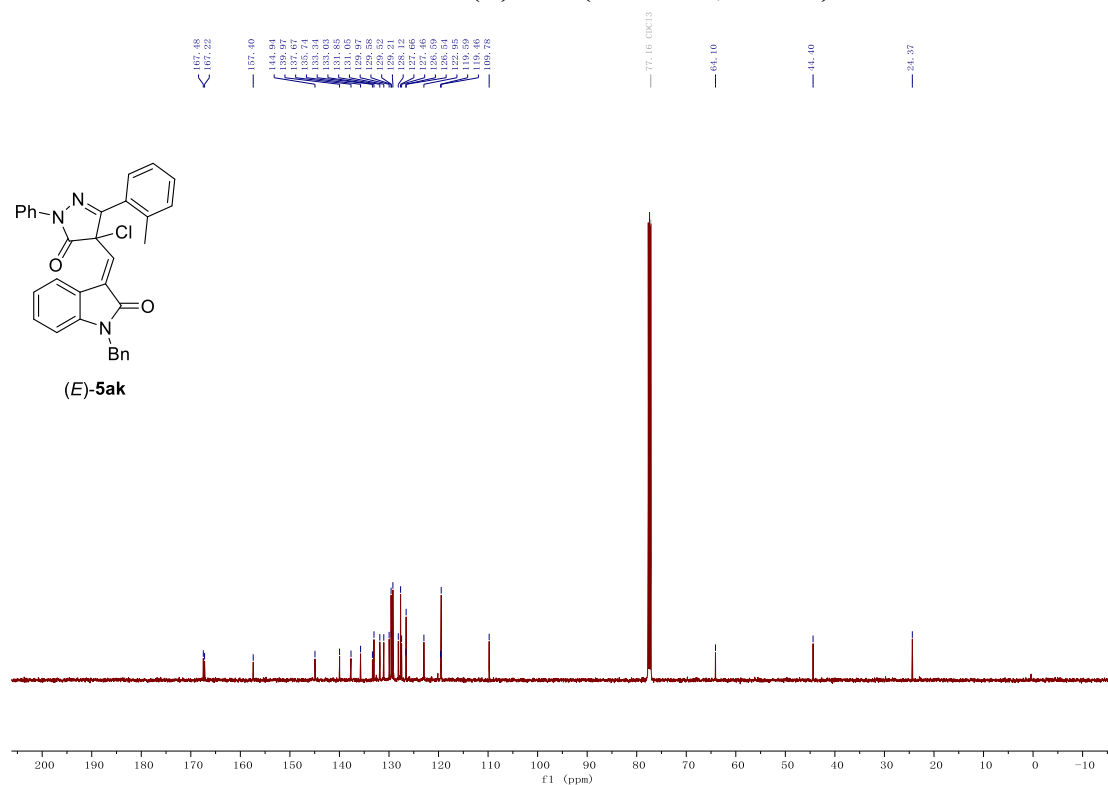
¹³C NMR of (Z)-5ak/(S,Z)-5ak (126 MHz, CDCl₃)



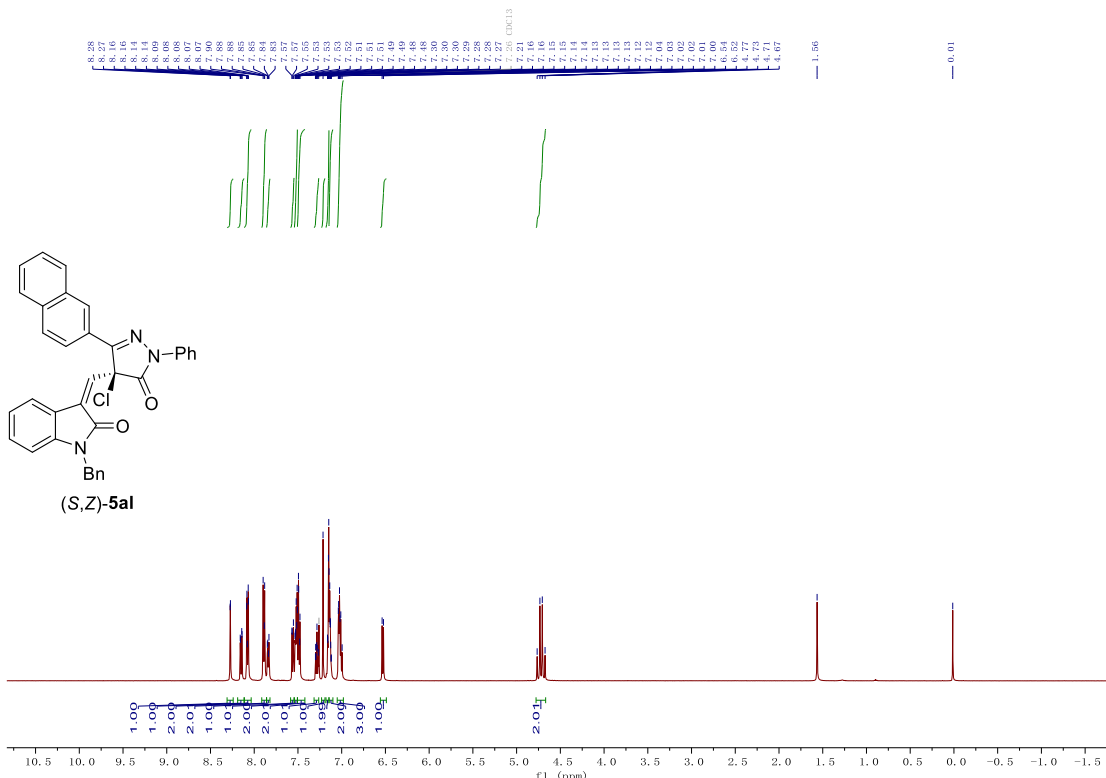
¹H NMR of (*E*)-5ak (500 MHz, CDCl₃)



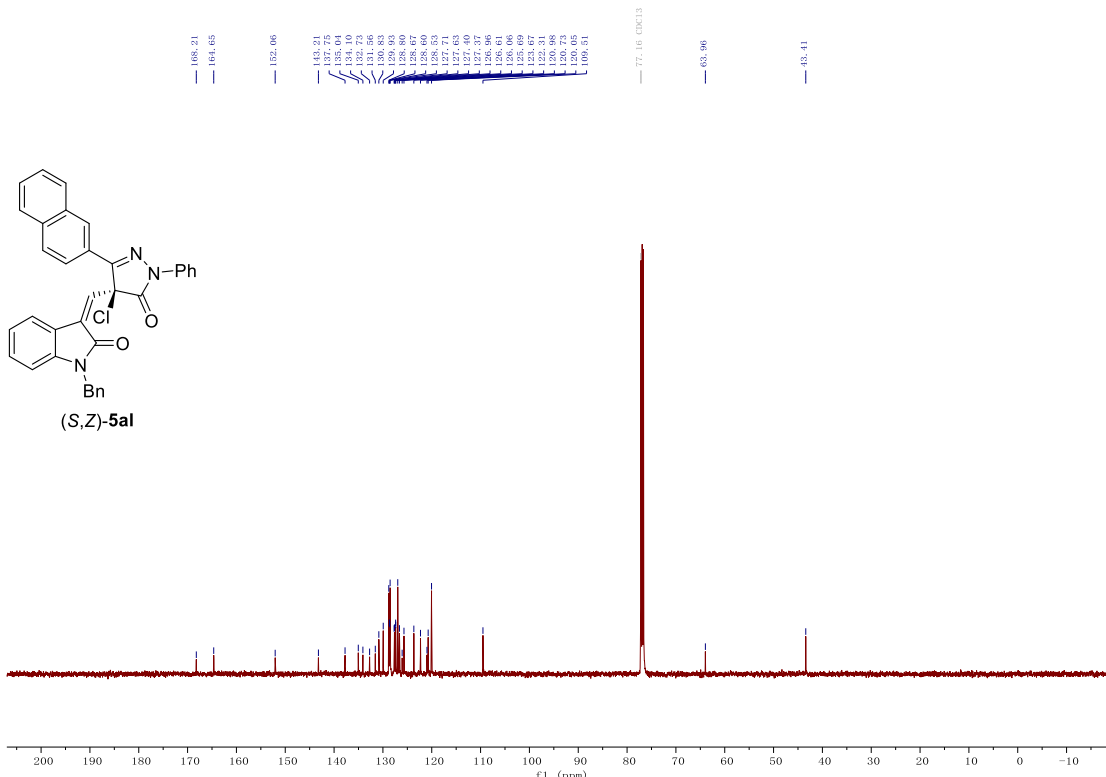
¹³C NMR of (*E*)-5ak (126 MHz, CDCl₃)



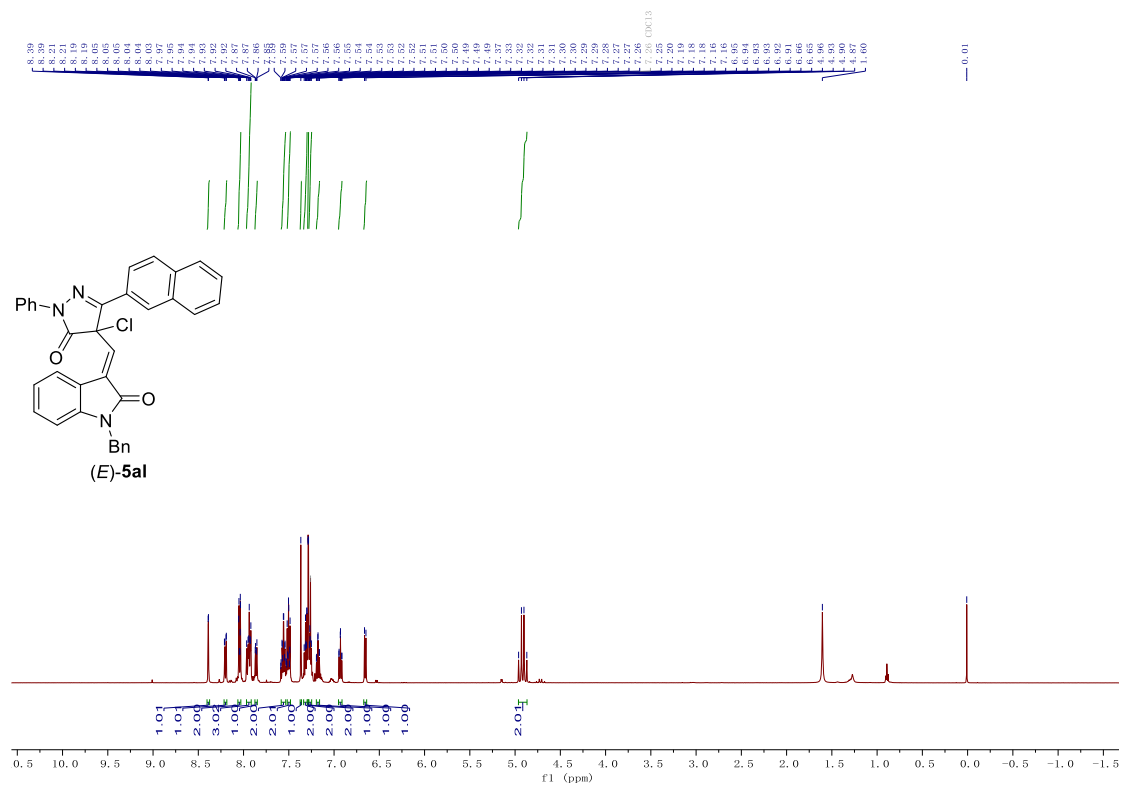
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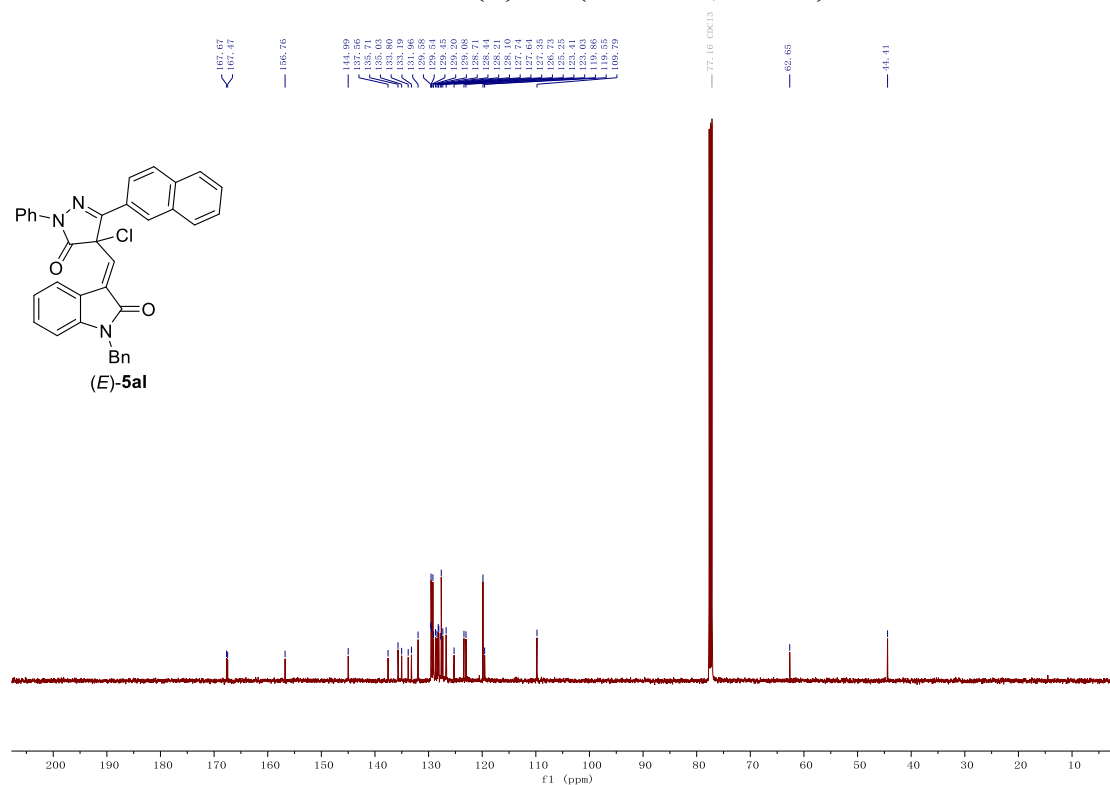
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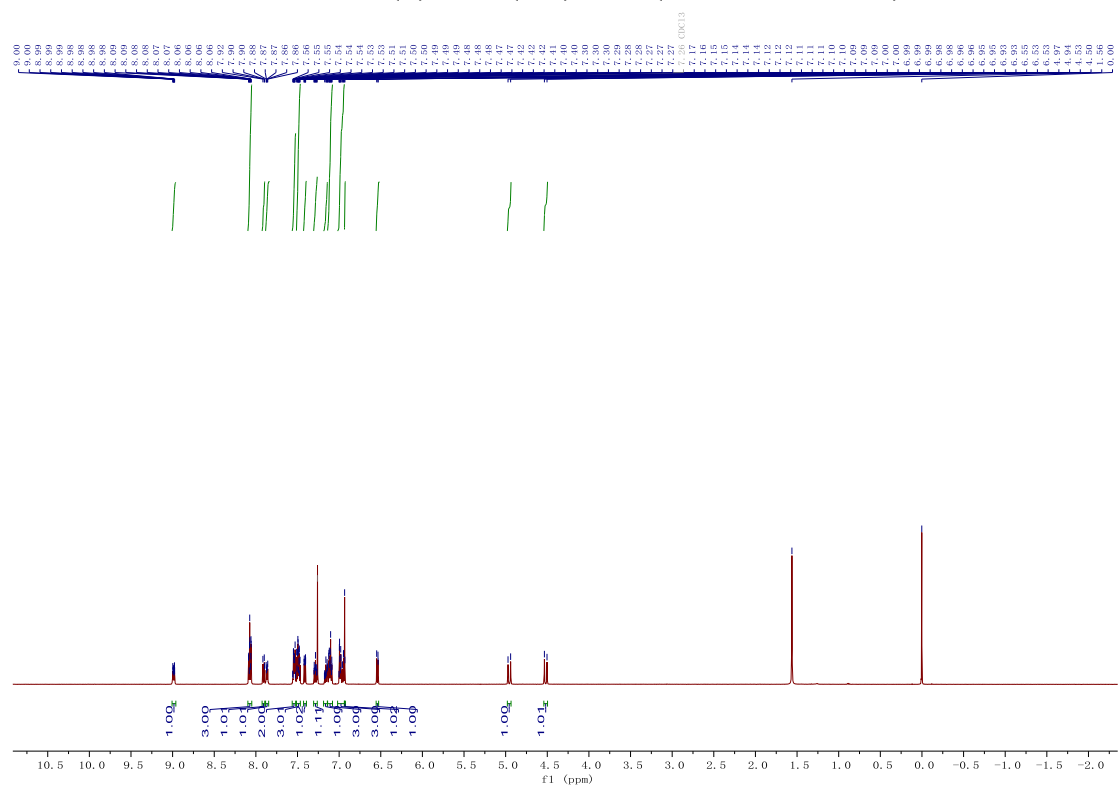
¹H NMR of (*E*)-5al (500 MHz, CDCl₃)



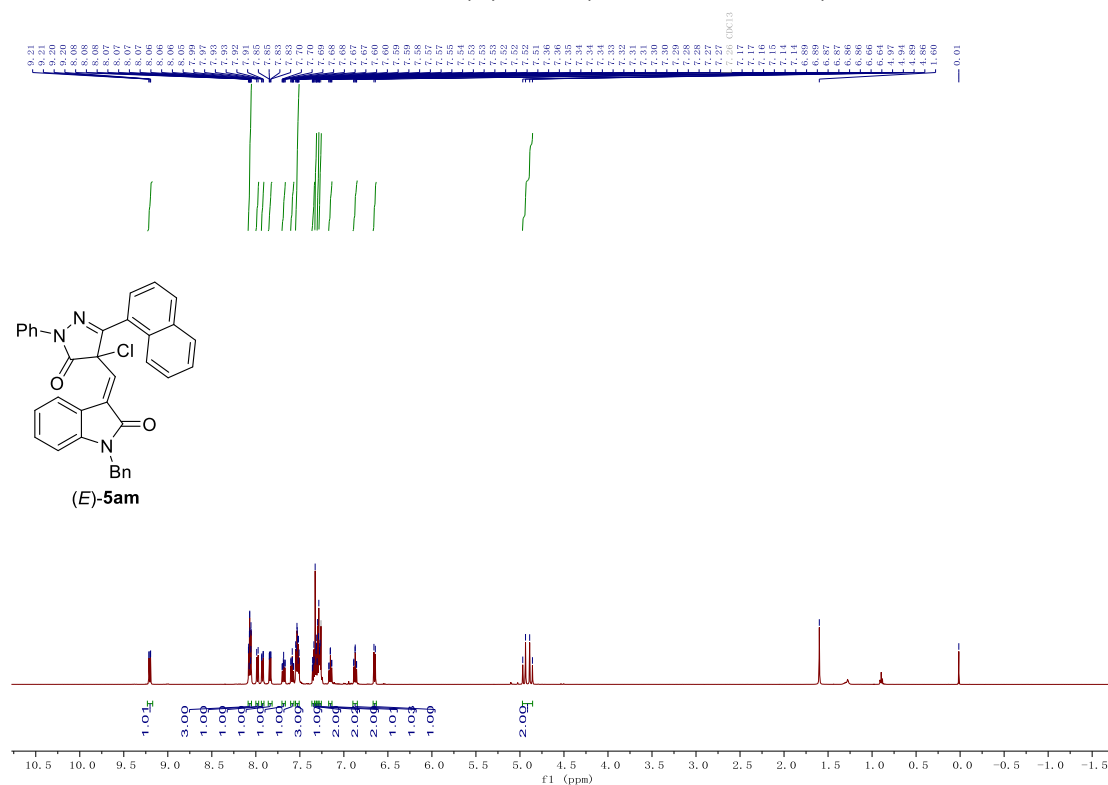
^{13}C NMR of (*E*)-5al (126 MHz, CDCl_3)



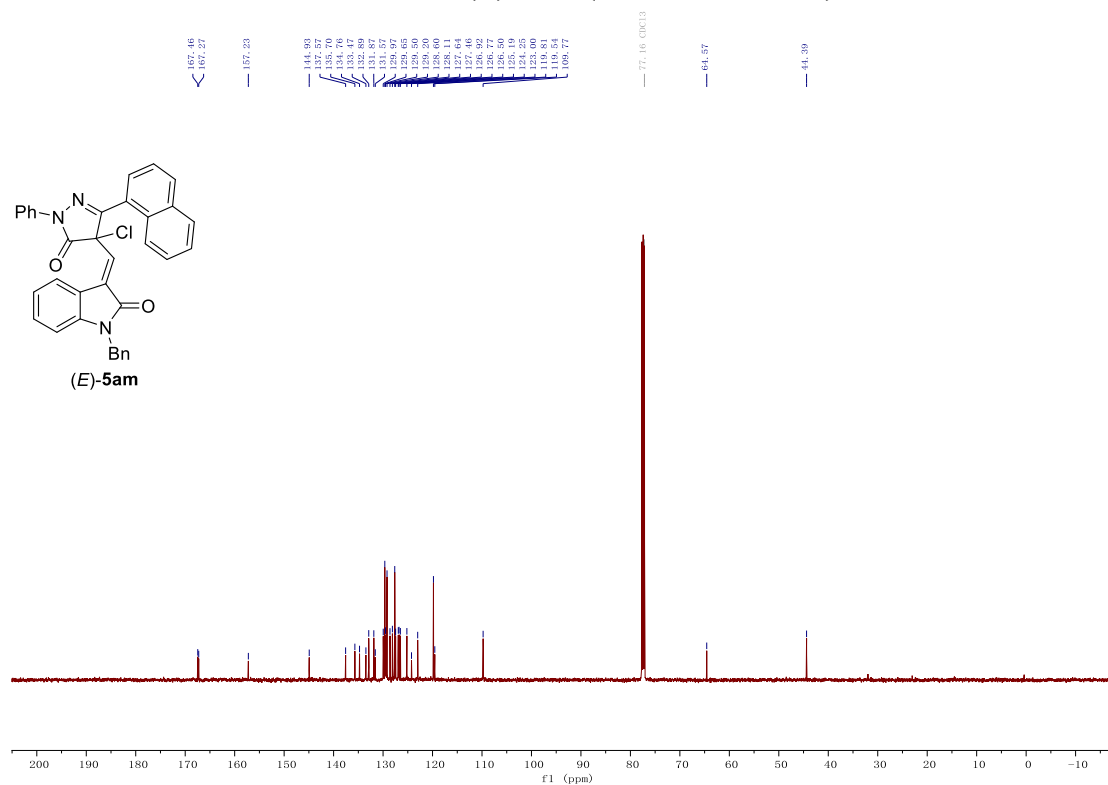
¹H NMR of (Z)-5am/(S,Z)-5am (500 MHz, CDCl₃)



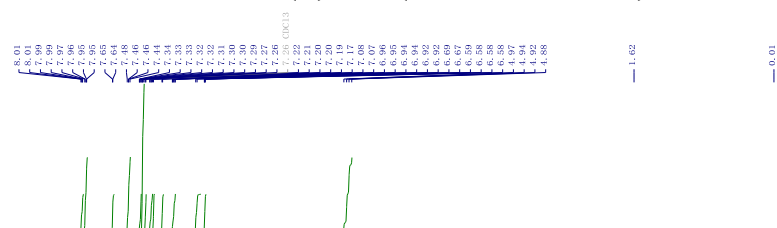
¹H NMR of (*E*)-5am (500 MHz, CDCl₃)



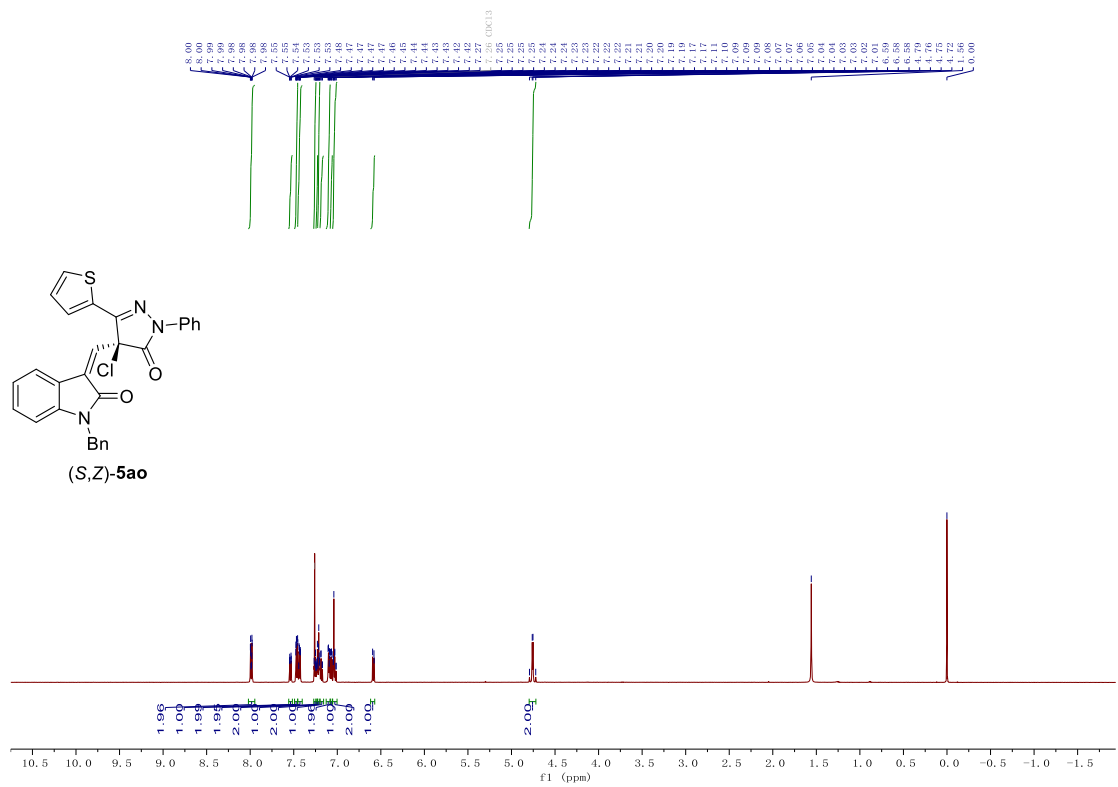
¹³C NMR of (*E*)-5am (126 MHz, CDCl₃)



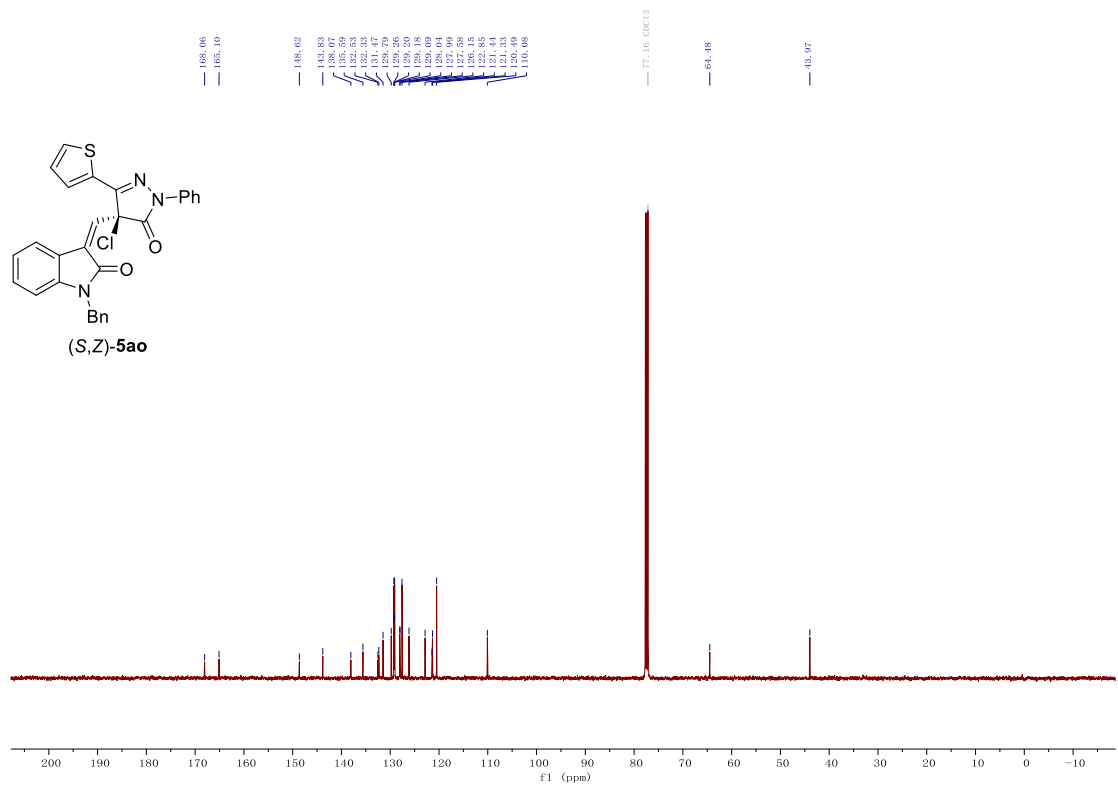
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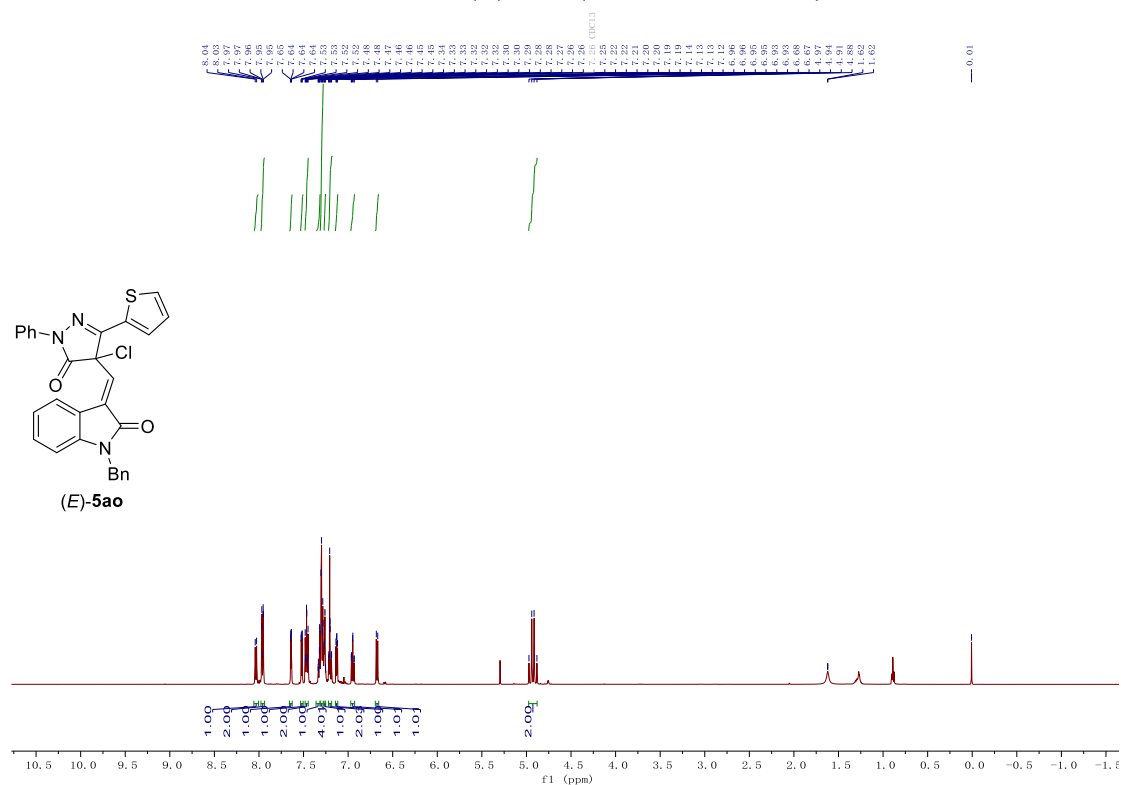
¹H NMR of (Z)-5ao/(S,Z)-5ao (500 MHz, CDCl₃)



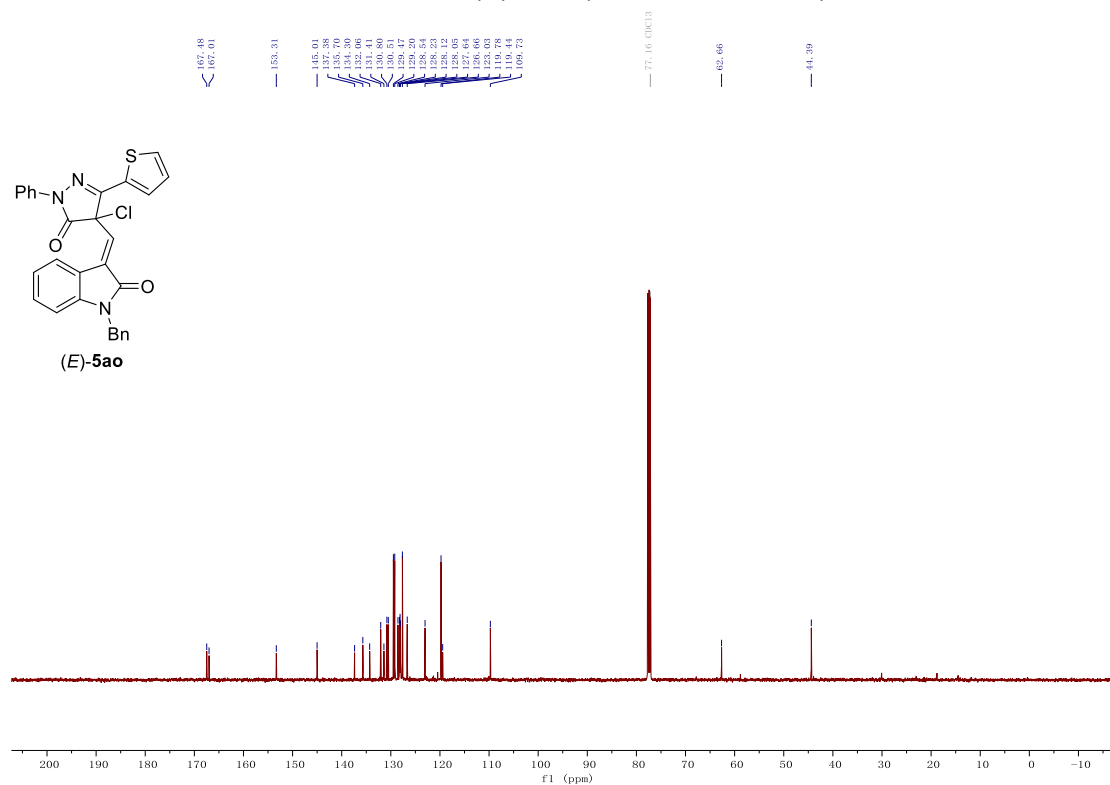
^{13}C NMR of (Z)-5ao/(S,Z)-5ao (126 MHz, CDCl_3)



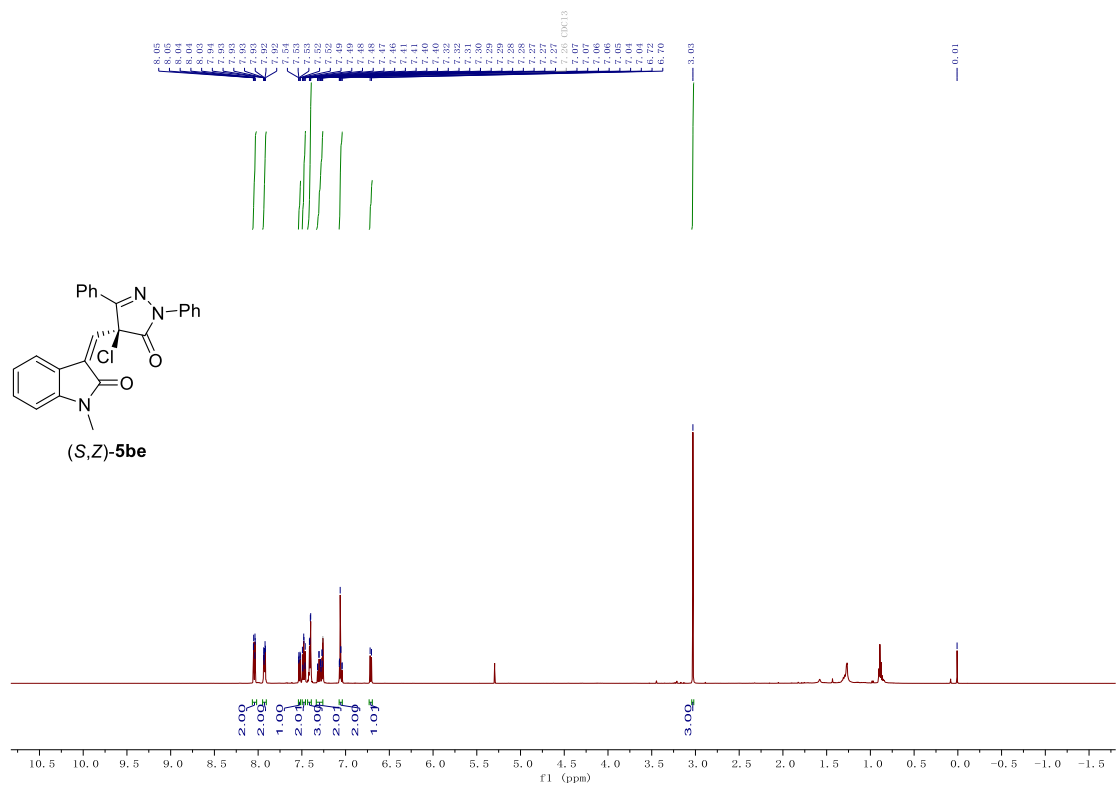
¹H NMR of (*E*)-5ao (500 MHz, CDCl₃)



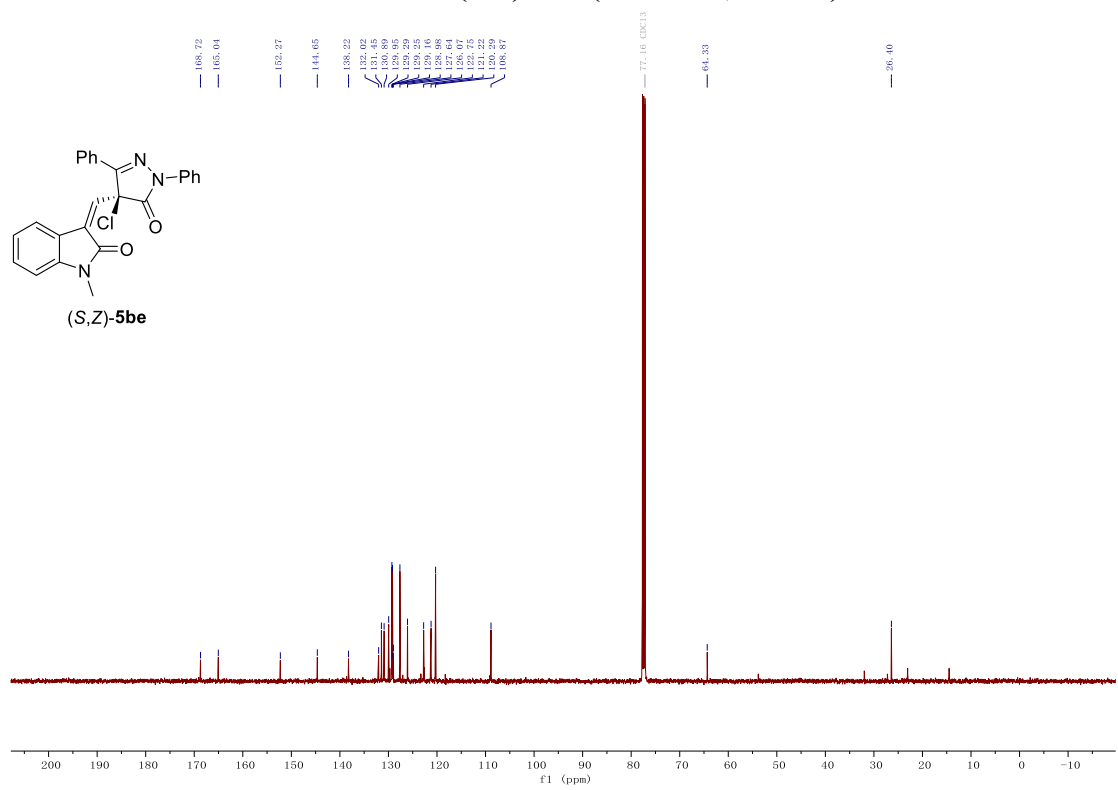
¹³C NMR of (*E*)-5ao (126 MHz, CDCl₃)



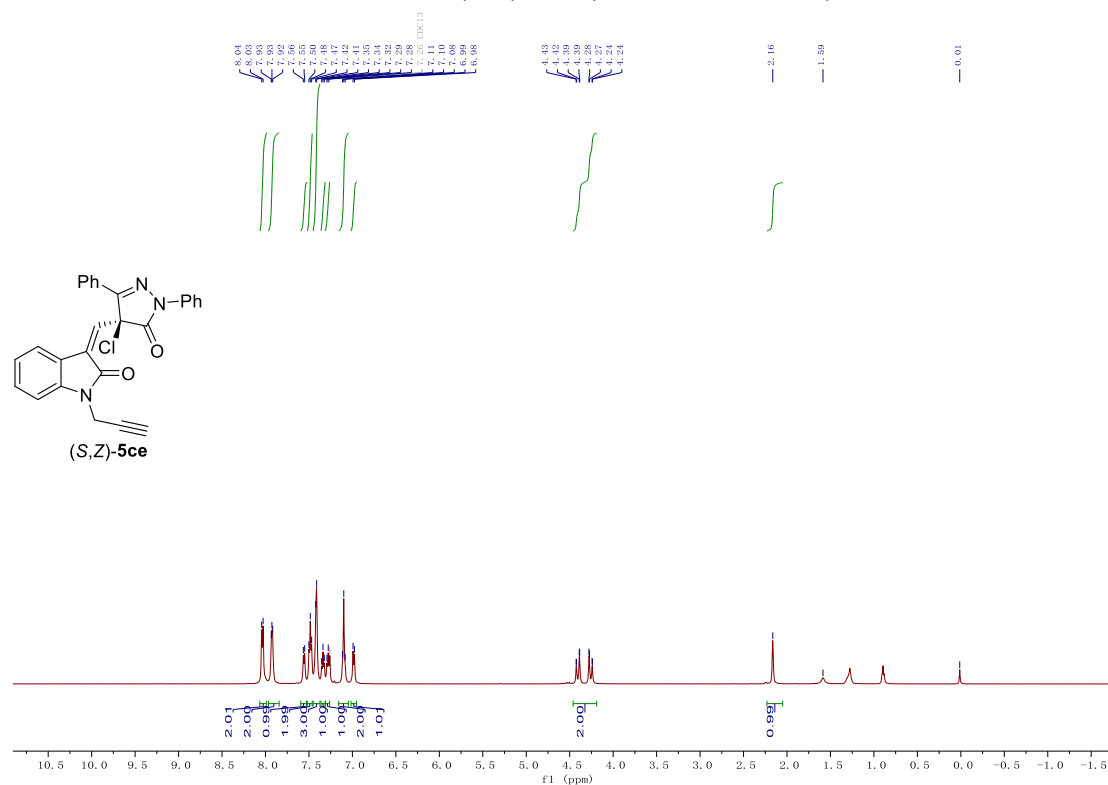
¹H NMR of (S,Z)-5be (500 MHz, CDCl₃)



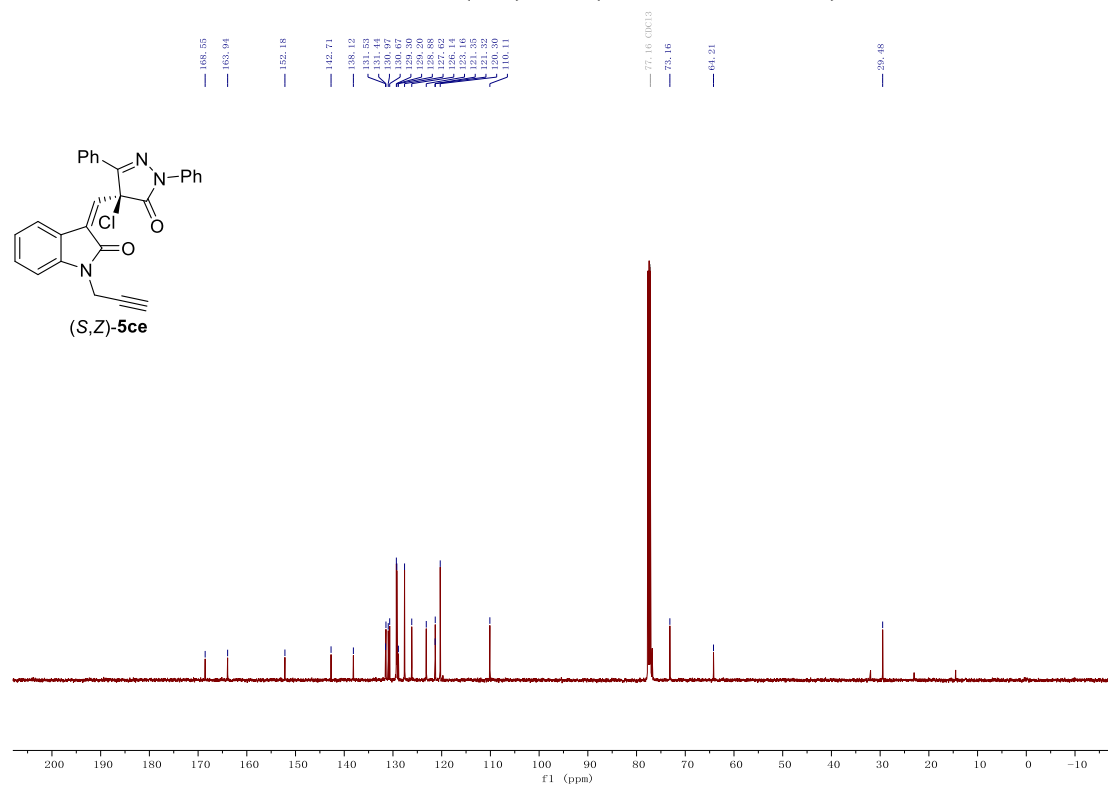
¹³C NMR of (S,Z)-5be (126 MHz, CDCl₃)



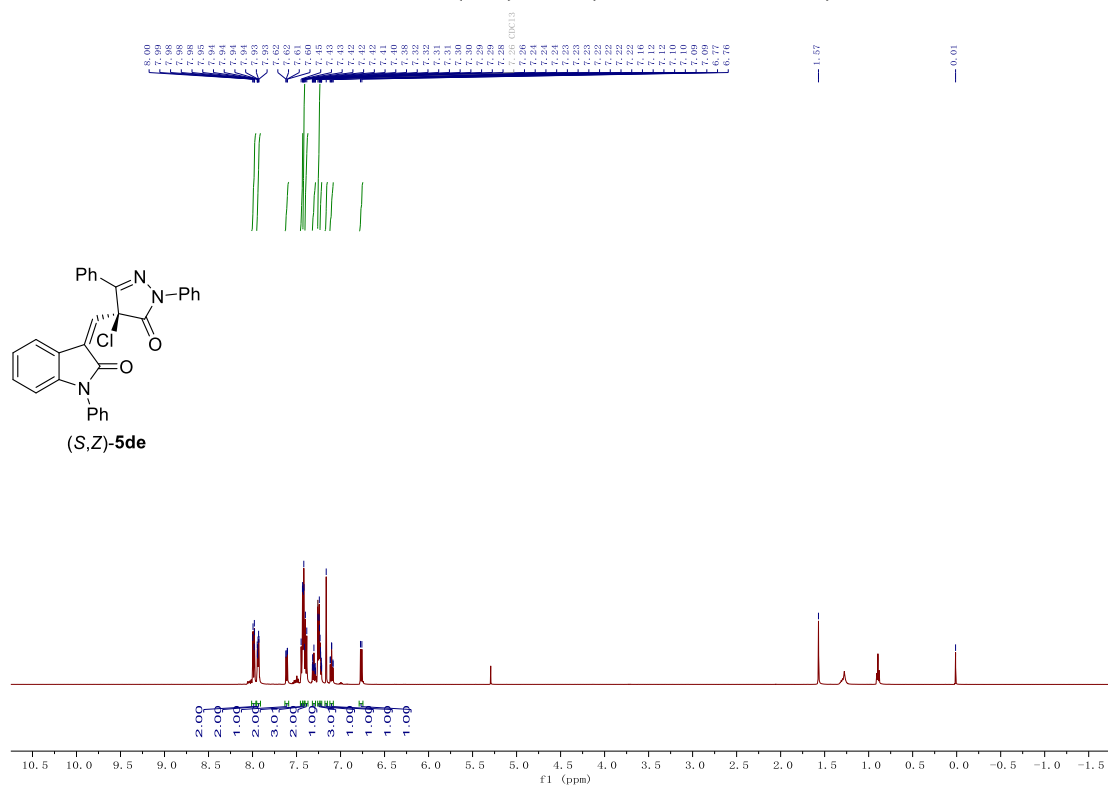
¹H NMR of (S,Z)-5ce (500 MHz, CDCl₃)



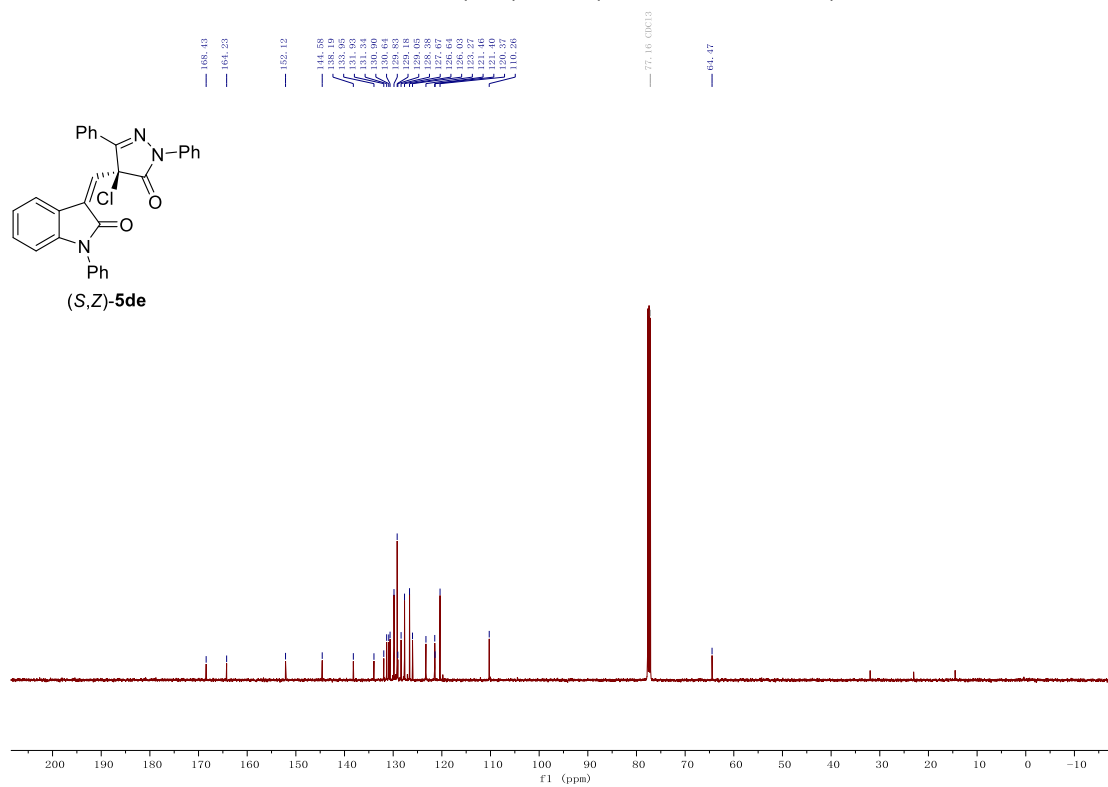
¹³C NMR of (S,Z)-5ce (126 MHz, CDCl₃)



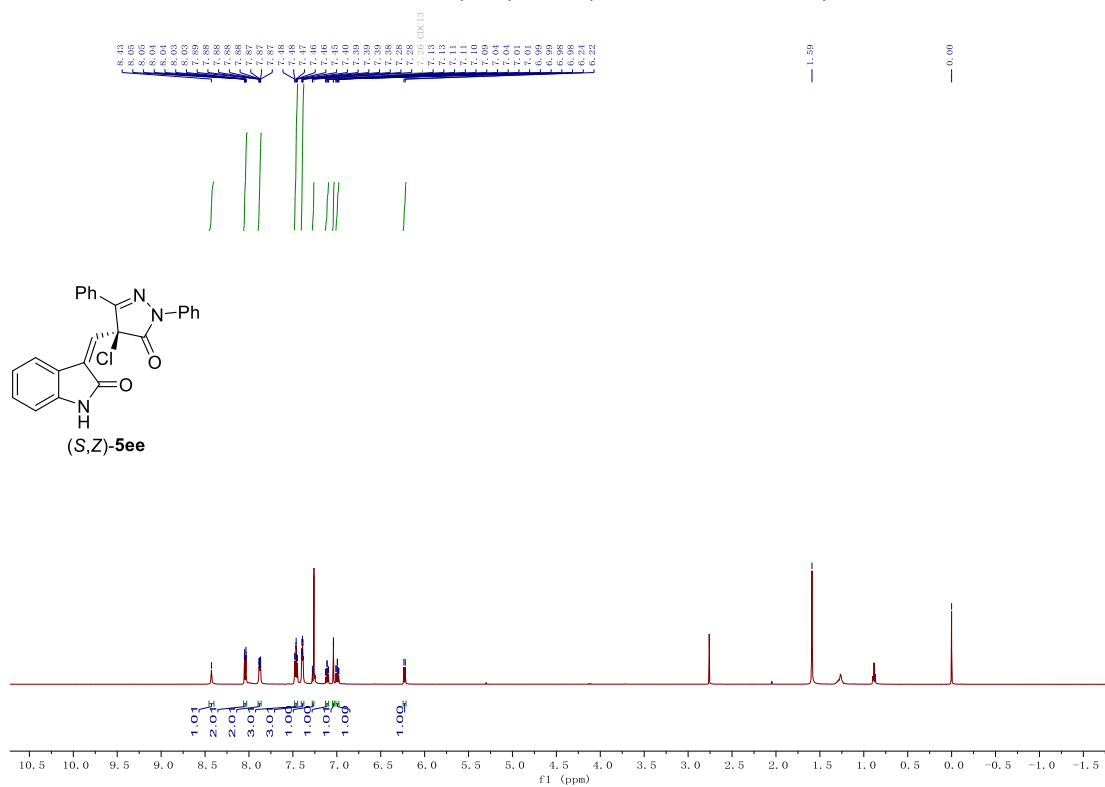
¹H NMR of (S,Z)-5de (500 MHz, CDCl₃)



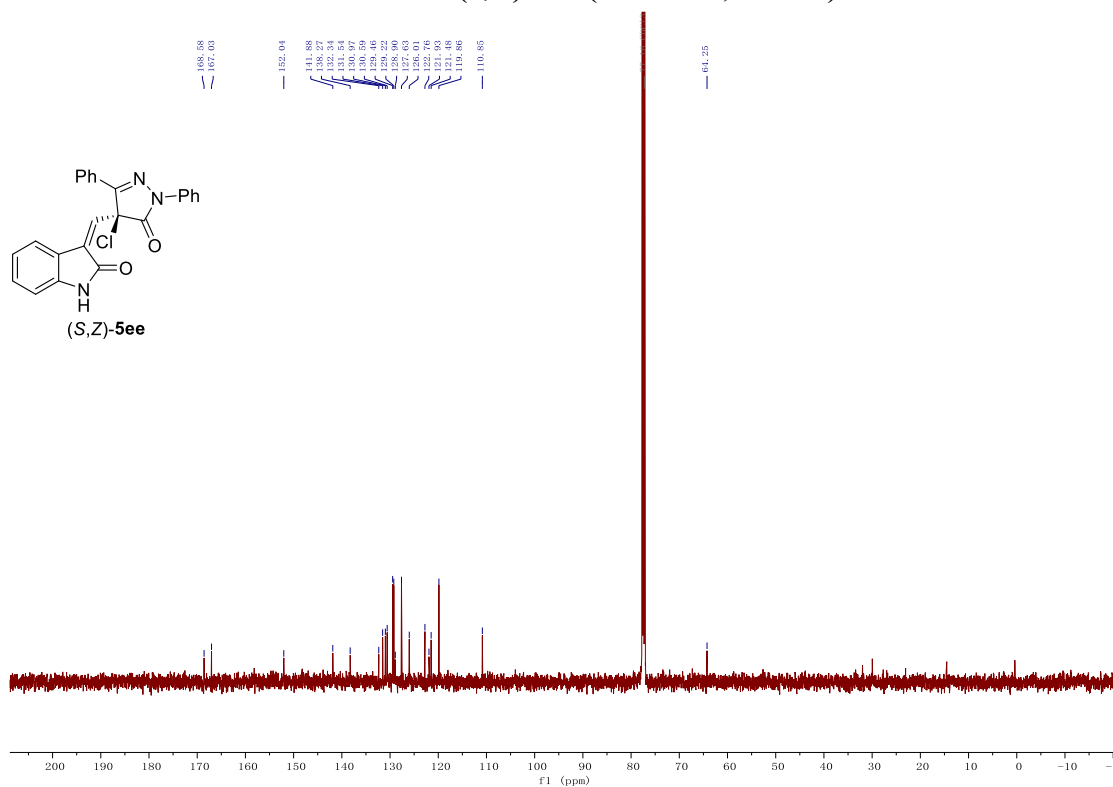
^{13}C NMR of (S,Z)-5de (126 MHz, CDCl_3)



¹H NMR of (S,Z)-5ee (500 MHz, CDCl₃)



¹³C NMR of (S,Z)-5ee (126 MHz, CDCl₃)



(S,Z)-5fe

¹H NMR spectrum (ppm): 8.08, 8.06, 8.06, 7.98, 7.97, 7.96, 7.90, 7.88, 7.48, 7.47, 7.29, 7.28, 7.28, 7.22, 7.22, 7.11, 7.11, 7.07, 7.06, 6.98, 6.96, 6.95, 6.45, 4.78, 4.75, 4.65, 4.65, 2.32, 0.04.

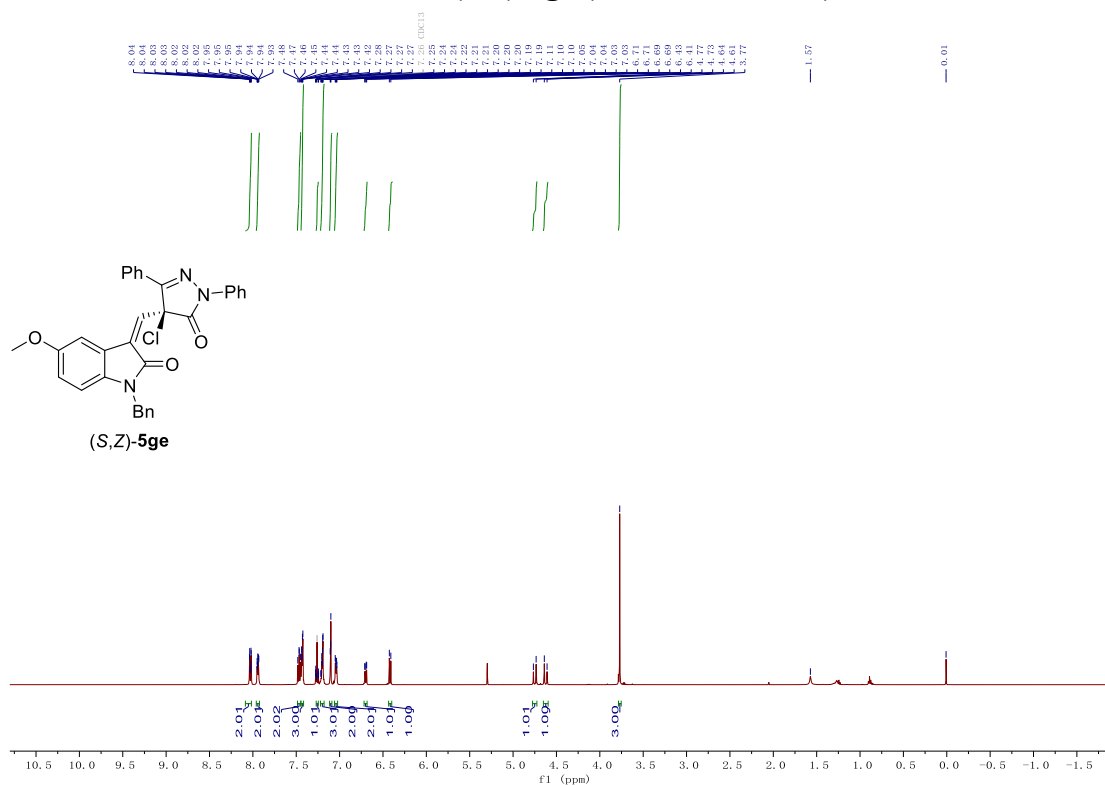
Integrations: 1.99, 1.99, 2.99, 1.00, 1.00, 3.00, 1.00, 1.00, 2.00, 1.00, 1.00, 1.00, 1.00, 1.00, 3.00, 1.00, 1.00, 3.00, 0.04.

(S,Z)-5fe

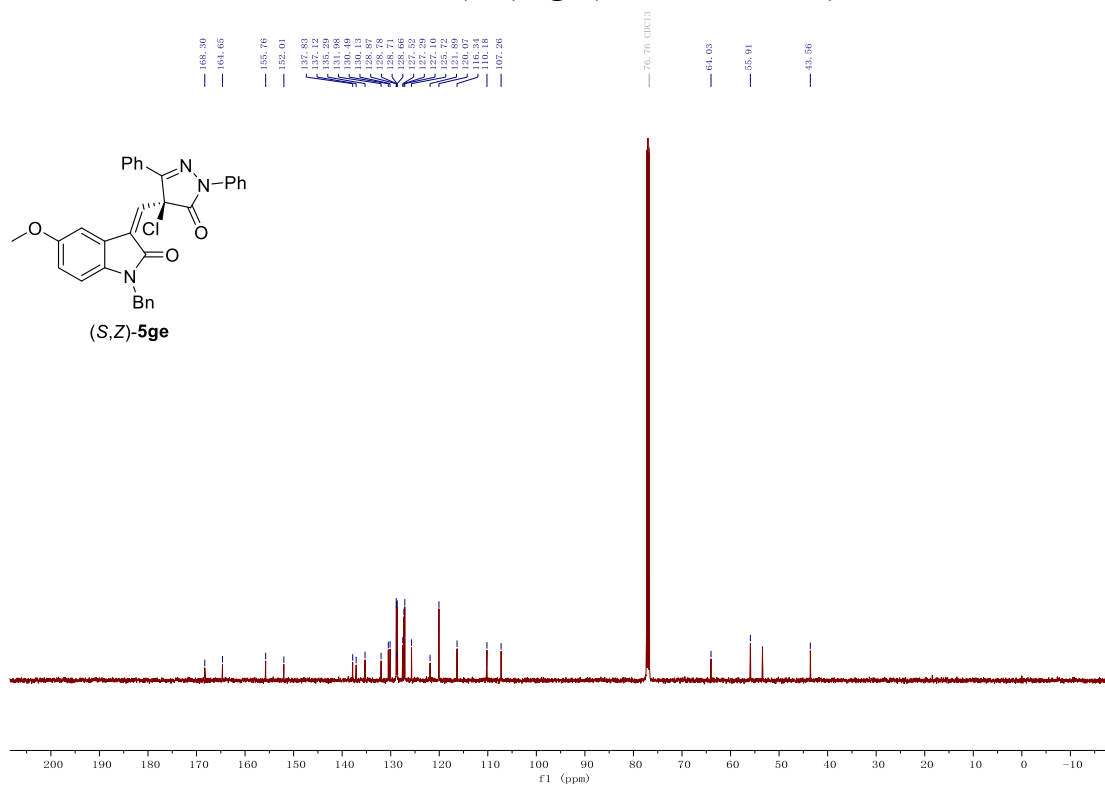
Chemical structure of (S,Z)-5fe is shown above the spectrum. The structure is a benzimidazole derivative with a phenyl group, a benzyl group, and a chlorine atom. The stereochemistry is (S,Z).

¹H NMR spectrum (CDCl₃) of (S,Z)-5fe. The spectrum shows peaks at 7.76 ppm (d, 2H), 7.71 ppm (d, 2H), 6.46 ppm (d, 2H), 4.83 ppm (d, 2H), and 2.13 ppm (d, 2H). The x-axis is labeled f1 (ppm) and ranges from 200 to -10.

¹H NMR of (S,Z)-5ge (500 MHz, CDCl₃)



¹³C NMR of (S,Z)-5ge (126 MHz, CDCl₃)



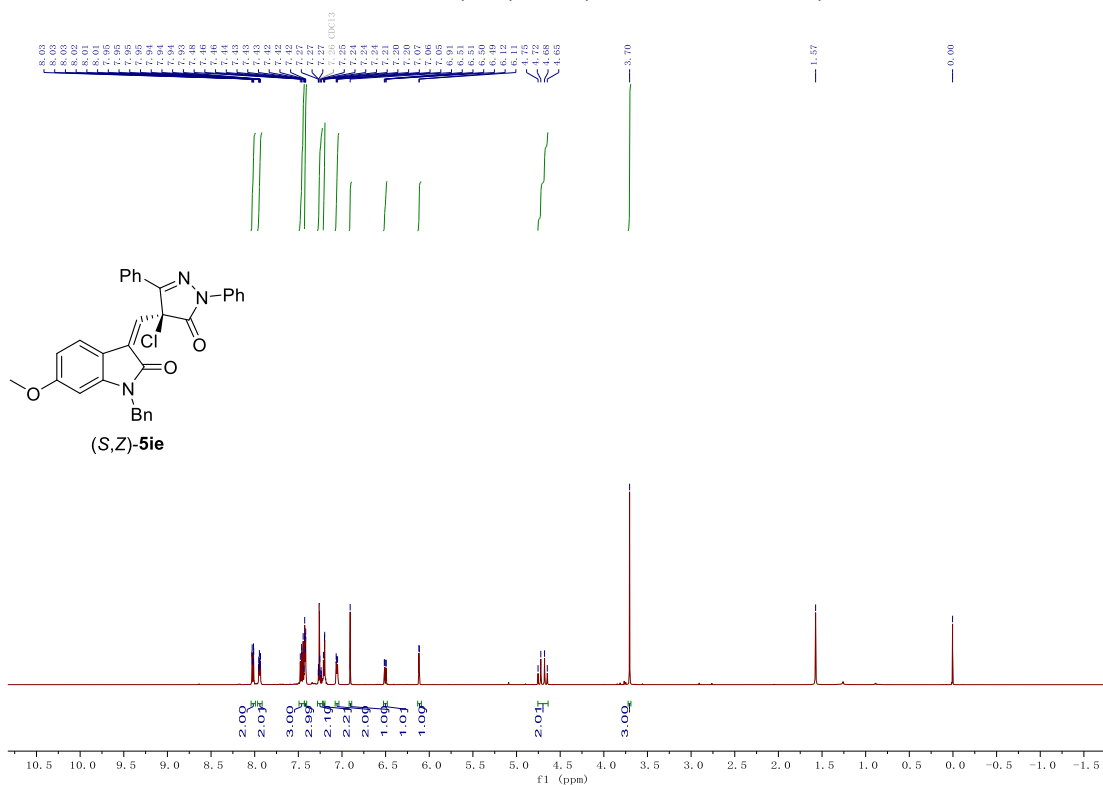
[illegible]

(S,Z)-5he

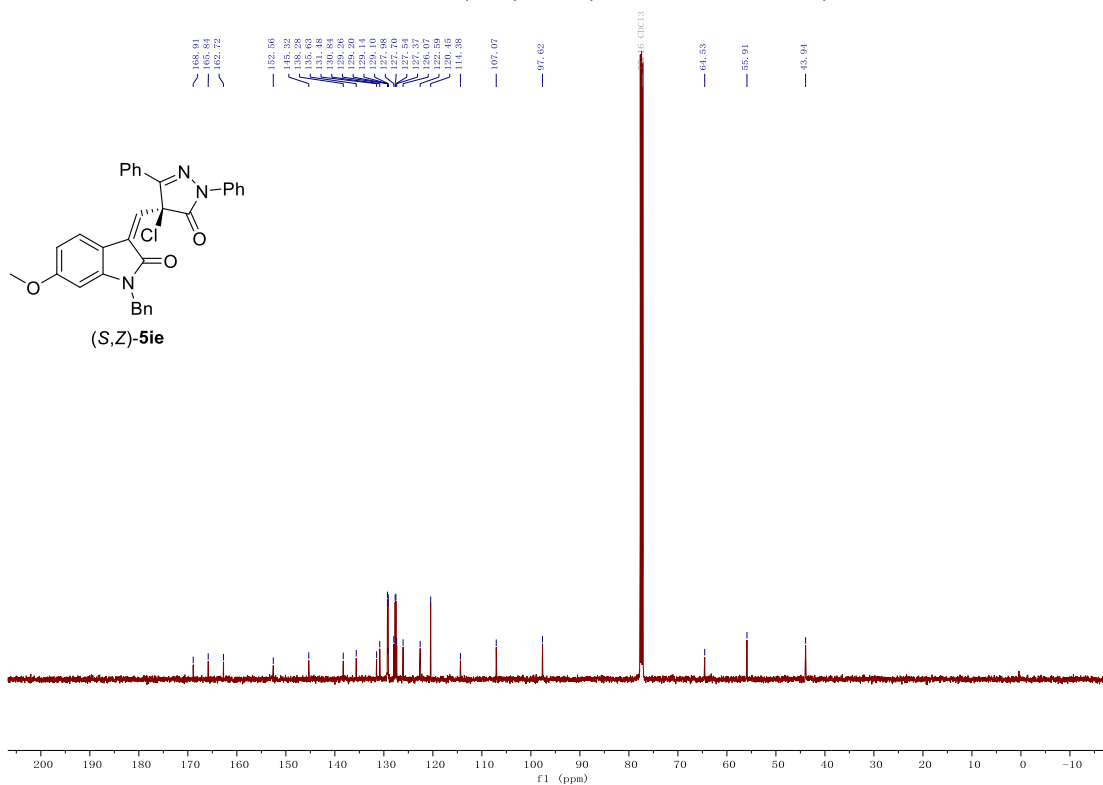
¹H NMR (CDCl₃) peaks (ppm): 7.50, 7.48, 7.46, 7.44, 7.42, 7.40, 7.38, 7.36, 7.34, 7.32, 7.30, 7.28, 7.26, 7.24, 7.22, 7.20, 7.18, 7.16, 7.14, 7.12, 7.10, 7.08, 7.06, 7.04, 7.02, 7.00, 6.98, 6.96, 6.94, 6.92, 6.90, 6.88, 6.86, 6.84, 6.82, 6.80, 6.78, 6.76, 6.74, 6.72, 6.70, 6.68, 6.66, 6.64, 6.62, 6.60, 6.58, 6.56, 6.54, 6.52, 6.50, 6.48, 6.46, 6.44, 6.42, 6.40, 6.38, 6.36, 6.34, 6.32, 6.30, 6.28, 6.26, 6.24, 6.22, 6.20, 6.18, 6.16, 6.14, 6.12, 6.10, 6.08, 6.06, 6.04, 6.02, 6.00, 5.98, 5.96, 5.94, 5.92, 5.90, 5.88, 5.86, 5.84, 5.82, 5.80, 5.78, 5.76, 5.74, 5.72, 5.70, 5.68, 5.66, 5.64, 5.62, 5.60, 5.58, 5.56, 5.54, 5.52, 5.50, 5.48, 5.46, 5.44, 5.42, 5.40, 5.38, 5.36, 5.34, 5.32, 5.30, 5.28, 5.26, 5.24, 5.22, 5.20, 5.18, 5.16, 5.14, 5.12, 5.10, 5.08, 5.06, 5.04, 5.02, 5.00, 4.98, 4.96, 4.94, 4.92, 4.90, 4.88, 4.86, 4.84, 4.82, 4.80, 4.78, 4.76, 4.74, 4.72, 4.70, 4.68, 4.66, 4.64, 4.62, 4.60, 4.58, 4.56, 4.54, 4.52, 4.50, 4.48, 4.46, 4.44, 4.42, 4.40, 4.38, 4.36, 4.34, 4.32, 4.30, 4.28, 4.26, 4.24, 4.22, 4.20, 4.18, 4.16, 4.14, 4.12, 4.10, 4.08, 4.06, 4.04, 4.02, 4.00, 3.98, 3.96, 3.94, 3.92, 3.90, 3.88, 3.86, 3.84, 3.82, 3.80, 3.78, 3.76, 3.74, 3.72, 3.70, 3.68, 3.66, 3.64, 3.62, 3.60, 3.58, 3.56, 3.54, 3.52, 3.50, 3.48, 3.46, 3.44, 3.42, 3.40, 3.38, 3.36, 3.34, 3.32, 3.30, 3.28, 3.26, 3.24, 3.22, 3.20, 3.18, 3.16, 3.14, 3.12, 3.10, 3.08, 3.06, 3.04, 3.02, 3.00, 2.98, 2.96, 2.94, 2.92, 2.90, 2.88, 2.86, 2.84, 2.82, 2.80, 2.78, 2.76, 2.74, 2.72, 2.70, 2.68, 2.66, 2.64, 2.62, 2.60, 2.58, 2.56, 2.54, 2.52, 2.50, 2.48, 2.46, 2.44, 2.42, 2.40, 2.38, 2.36, 2.34, 2.32, 2.30, 2.28, 2.26, 2.24, 2.22, 2.20, 2.18, 2.16, 2.14, 2.12, 2.10, 2.08, 2.06, 2.04, 2.02, 2.00, 1.98, 1.96, 1.94, 1.92, 1.90, 1.88, 1.86, 1.84, 1.82, 1.80, 1.78, 1.76, 1.74, 1.72, 1.70, 1.68, 1.66, 1.64, 1.62, 1.60, 1.58, 1.56, 1.54, 1.52, 1.50, 1.48, 1.46, 1.44, 1.42, 1.40, 1.38, 1.36, 1.34, 1.32, 1.30, 1.28, 1.26, 1.24, 1.22, 1.20, 1.18, 1.16, 1.14, 1.12, 1.10, 1.08, 1.06, 1.04, 1.02, 1.00, 0.98, 0.96, 0.94, 0.92, 0.90, 0.88, 0.86, 0.84, 0.82, 0.80, 0.78, 0.76, 0.74, 0.72, 0.70, 0.68, 0.66, 0.64, 0.62, 0.60, 0.58, 0.56, 0.54, 0.52, 0.50, 0.48, 0.46, 0.44, 0.42, 0.40, 0.38, 0.36, 0.34, 0.32, 0.30, 0.28, 0.26, 0.24, 0.22, 0.20, 0.18, 0.16, 0.14, 0.12, 0.10, 0.08, 0.06, 0.04, 0.02, 0.00, -0.02, -0.04, -0.06, -0.08, -0.10.

¹³C NMR (CDCl₃) peaks (ppm): 168.40, 164.58, 152.14, 142.43, 142.11, 141.80, 141.49, 141.17, 140.86, 140.54, 140.23, 139.91, 139.60, 139.28, 138.97, 138.65, 138.34, 138.02, 137.71, 137.39, 137.08, 136.76, 136.45, 136.13, 135.82, 135.50, 135.19, 134.87, 134.56, 134.24, 133.93, 133.61, 133.30, 132.98, 132.67, 132.35, 132.04, 131.72, 131.41, 131.09, 130.78, 130.46, 130.15, 129.83, 129.52, 129.20, 128.89, 128.57, 128.26, 127.94, 127.63, 127.31, 127.00, 126.68, 126.37, 126.05, 125.74, 125.42, 125.11, 124.79, 124.48, 124.16, 123.85, 123.53, 123.22, 122.90, 122.59, 122.27, 121.96, 121.64, 121.33, 121.01, 120.70, 120.38, 120.07, 119.75, 119.44, 119.12, 118.81, 118.49, 118.18, 117.86, 117.55, 117.23, 116.92, 116.60, 116.29, 115.97, 115.66, 115.34, 115.03, 114.71, 114.40, 114.08, 113.77, 113.45, 113.14, 112.82, 112.51, 112.19, 111.88, 111.56, 111.25, 110.93, 110.62, 110.30, 110.00, 109.68, 109.37, 109.05, 108.74, 108.42, 108.11, 107.79, 107.48, 107.16, 106.85, 106.53, 106.22, 105.90, 105.59, 105.27, 104.96, 104.64, 104.33, 104.01, 103.70, 103.38, 103.07, 102.75, 102.44, 102.12, 101.81, 101.49, 101.18, 100.86, 100.55, 100.23, 99.92, 99.60, 99.29, 98.97, 98.66, 98.34, 98.03, 97.71, 97.40, 97.08, 96.77, 96.45, 96.14, 95.82, 95.51, 95.19, 94.88, 94.56, 94.25, 93.93, 93.62, 93.30, 92.99, 92.67, 92.36, 92.04, 91.73, 91.41, 91.10, 90.78, 90.47, 90.15, 89.84, 89.52, 89.21, 88.89, 88.58, 88.26, 87.95, 87.63, 87.32, 87.00, 86.69, 86.37, 86.06, 85.74, 85.43, 85.11, 84.80, 84.48, 84.17, 83.85, 83.54, 83.22, 82.91, 82.59, 82.28, 81.96, 81.65, 81.33, 81.02, 80.70, 80.39, 80.07, 79.76, 79.44, 79.13, 78.81, 78.50, 78.18, 77.87, 77.55,

¹H NMR of (S,Z)-5ie (500 MHz, CDCl₃)



¹³C NMR of (S,Z)-5ie (126 MHz, CDCl₃)



(S,Z)-5je

¹H NMR spectrum (CDCl₃) of (S,Z)-5je. The x-axis represents the chemical shift in ppm, ranging from 10.5 to -1.5. The spectrum shows several multiplets in the aromatic region (6.5-8.0 ppm) and a few peaks in the aliphatic region (1.0-1.6 ppm). Integration values are provided below the baseline.

Chemical Shift (ppm)	Integration
~8.0	2.00
~7.8	2.00
~7.6	4.00
~7.4	1.00
~7.2	3.00
~7.0	1.00
~6.8	2.00
~6.6	1.00
~6.4	1.00
~1.5	1.00
~1.2	1.00

(S,Z)-5je

O=C1C(=C2C(=C(C=C2)N(C1)Cc3ccccc3)C=C3C(=O)N(C3)Cc4ccccc4)C=C5C(=O)N(C5)Cc6ccccc6

¹H NMR (400 MHz, CDCl₃) δ: 7.25 (d, 2H), 7.22 (d, 2H), 7.18 (d, 2H), 7.15 (d, 2H), 7.12 (d, 2H), 7.08 (d, 2H), 7.05 (d, 2H), 7.02 (d, 2H), 7.00 (d, 2H), 6.98 (d, 2H), 6.95 (d, 2H), 6.92 (d, 2H), 6.90 (d, 2H), 6.88 (d, 2H), 6.85 (d, 2H), 6.82 (d, 2H), 6.80 (d, 2H), 6.78 (d, 2H), 6.75 (d, 2H), 6.72 (d, 2H), 6.70 (d, 2H), 6.68 (d, 2H), 6.65 (d, 2H), 6.62 (d, 2H), 6.60 (d, 2H), 6.58 (d, 2H), 6.55 (d, 2H), 6.52 (d, 2H), 6.50 (d, 2H), 6.48 (d, 2H), 6.45 (d, 2H), 6.42 (d, 2H), 6.40 (d, 2H), 6.38 (d, 2H), 6.35 (d, 2H), 6.32 (d, 2H), 6.30 (d, 2H), 6.28 (d, 2H), 6.25 (d, 2H), 6.22 (d, 2H), 6.20 (d, 2H), 6.18 (d, 2H), 6.15 (d, 2H), 6.12 (d, 2H), 6.10 (d, 2H), 6.08 (d, 2H), 6.05 (d, 2H), 6.02 (d, 2H), 6.00 (d, 2H), 5.98 (d, 2H), 5.95 (d, 2H), 5.92 (d, 2H), 5.90 (d, 2H), 5.88 (d, 2H), 5.85 (d, 2H), 5.82 (d, 2H), 5.80 (d, 2H), 5.78 (d, 2H), 5.75 (d, 2H), 5.72 (d, 2H), 5.70 (d, 2H), 5.68 (d, 2H), 5.65 (d, 2H), 5.62 (d, 2H), 5.60 (d, 2H), 5.58 (d, 2H), 5.55 (d, 2H), 5.52 (d, 2H), 5.50 (d, 2H), 5.48 (d, 2H), 5.45 (d, 2H), 5.42 (d, 2H), 5.40 (d, 2H), 5.38 (d, 2H), 5.35 (d, 2H), 5.32 (d, 2H), 5.30 (d, 2H), 5.28 (d, 2H), 5.25 (d, 2H), 5.22 (d, 2H), 5.20 (d, 2H), 5.18 (d, 2H), 5.15 (d, 2H), 5.12 (d, 2H), 5.10 (d, 2H), 5.08 (d, 2H), 5.05 (d, 2H), 5.02 (d, 2H), 5.00 (d, 2H), 4.98 (d, 2H), 4.95 (d, 2H), 4.92 (d, 2H), 4.90 (d, 2H), 4.88 (d, 2H), 4.85 (d, 2H), 4.82 (d, 2H), 4.80 (d, 2H), 4.78 (d, 2H), 4.75 (d, 2H), 4.72 (d, 2H), 4.70 (d, 2H), 4.68 (d, 2H), 4.65 (d, 2H), 4.62 (d, 2H), 4.60 (d, 2H), 4.58 (d, 2H), 4.55 (d, 2H), 4.52 (d, 2H), 4.50 (d, 2H), 4.48 (d, 2H), 4.45 (d, 2H), 4.42 (d, 2H), 4.40 (d, 2H), 4.38 (d, 2H), 4.35 (d, 2H), 4.32 (d, 2H), 4.30 (d, 2H), 4.28 (d, 2H), 4.25 (d, 2H), 4.22 (d, 2H), 4.20 (d, 2H), 4.18 (d, 2H), 4.15 (d, 2H), 4.12 (d, 2H), 4.10 (d, 2H), 4.08 (d, 2H), 4.05 (d, 2H), 4.02 (d, 2H), 4.00 (d, 2H), 3.98 (d, 2H), 3.95 (d, 2H), 3.92 (d, 2H), 3.90 (d, 2H), 3.88 (d, 2H), 3.85 (d, 2H), 3.82 (d, 2H), 3.80 (d, 2H), 3.78 (d, 2H), 3.75 (d, 2H), 3.72 (d, 2H), 3.70 (d, 2H), 3.68 (d, 2H), 3.65 (d, 2H), 3.62 (d, 2H), 3.60 (d, 2H), 3.58 (d, 2H), 3.55 (d, 2H), 3.52 (d, 2H), 3.50 (d, 2H), 3.48 (d, 2H), 3.45 (d, 2H), 3.42 (d, 2H), 3.40 (d, 2H), 3.38 (d, 2H), 3.35 (d, 2H), 3.32 (d, 2H), 3.30 (d, 2H), 3.28 (d, 2H), 3.25 (d, 2H), 3.22 (d, 2H), 3.20 (d, 2H), 3.18 (d, 2H), 3.15 (d, 2H), 3.12 (d, 2H), 3.10 (d, 2H), 3.08 (d, 2H), 3.05 (d, 2H), 3.02 (d, 2H), 3.00 (d, 2H), 2.98 (d, 2H), 2.95 (d, 2H), 2.92 (d, 2H), 2.90 (d, 2H), 2.88 (d, 2H), 2.85 (d, 2H), 2.82 (d, 2H), 2.80 (d, 2H), 2.78 (d, 2H), 2.75 (d, 2H), 2.72 (d, 2H), 2.70 (d, 2H), 2.68 (d, 2H), 2.65 (d, 2H), 2.62 (d, 2H), 2.60 (d, 2H), 2.58 (d, 2H), 2.55 (d, 2H), 2.52 (d, 2H), 2.50 (d, 2H), 2.48 (d, 2H), 2.45 (d, 2H), 2.42 (d, 2H), 2.40 (d, 2H), 2.38 (d, 2H), 2.35 (d, 2H), 2.32 (d, 2H), 2.30 (d, 2H), 2.28 (d, 2H), 2.25 (d, 2H), 2.22 (d, 2H), 2.20 (d, 2H), 2.18 (d, 2H), 2.15 (d, 2H), 2.12 (d, 2H), 2.10 (d, 2H), 2.08 (d, 2H), 2.05 (d, 2H), 2.02 (d, 2H), 2.00 (d, 2H), 1.98 (d, 2H), 1.95 (d, 2H), 1.92 (d, 2H), 1.90 (d, 2H), 1.88 (d, 2H), 1.85 (d, 2H), 1.82 (d, 2H), 1.80 (d, 2H), 1.78 (d, 2H), 1.75 (d, 2H), 1.72 (d, 2H), 1.70 (d, 2H), 1.68 (d, 2H), 1.65 (d, 2H), 1.62 (d, 2H), 1.60 (d, 2H), 1.58 (d, 2H), 1.55 (d, 2H), 1.52 (d, 2H), 1.50 (d, 2H), 1.48 (d, 2H), 1.45 (d, 2H), 1.42 (d, 2H), 1.40 (d, 2H), 1.38 (d, 2H), 1.35 (d, 2H), 1.32 (d, 2H), 1.30 (d, 2H), 1.28 (d, 2H), 1.25 (d, 2H), 1.22 (d, 2H), 1.20 (d, 2H), 1.18 (d, 2H), 1.15 (d, 2H), 1.12 (d, 2H), 1.10 (d, 2H), 1.08 (d, 2H), 1.05 (d, 2H), 1.02 (d, 2H), 1.00 (d, 2H), 0.98 (d, 2H), 0.95 (d, 2H), 0.92 (d, 2H), 0.90 (d, 2H), 0.88 (d, 2H), 0.85 (d, 2H), 0.82 (d, 2H), 0.80 (d, 2H), 0.78 (d, 2H), 0.75 (d, 2H), 0.72 (d, 2H), 0.70 (d, 2H), 0.68 (d, 2H), 0.65 (d, 2H), 0.62 (d, 2H), 0.60 (d, 2H), 0.58 (d, 2H), 0.55 (d, 2H), 0.52 (d, 2H), 0.50 (d, 2H), 0.48 (d, 2H), 0.45 (d, 2H), 0.42 (d, 2H), 0.40 (d, 2H), 0.38 (d, 2H), 0.35 (d, 2H), 0.32 (d, 2H), 0.30 (d, 2H), 0.28 (d, 2H), 0.25 (d, 2H), 0.22 (d, 2H), 0.20 (d, 2H), 0.18 (d, 2H), 0.15 (d, 2H), 0.12 (d, 2H), 0.10 (d, 2H), 0.08 (d, 2H), 0.05 (d, 2H), 0.02 (d, 2H), 0.00 (d, 2H).

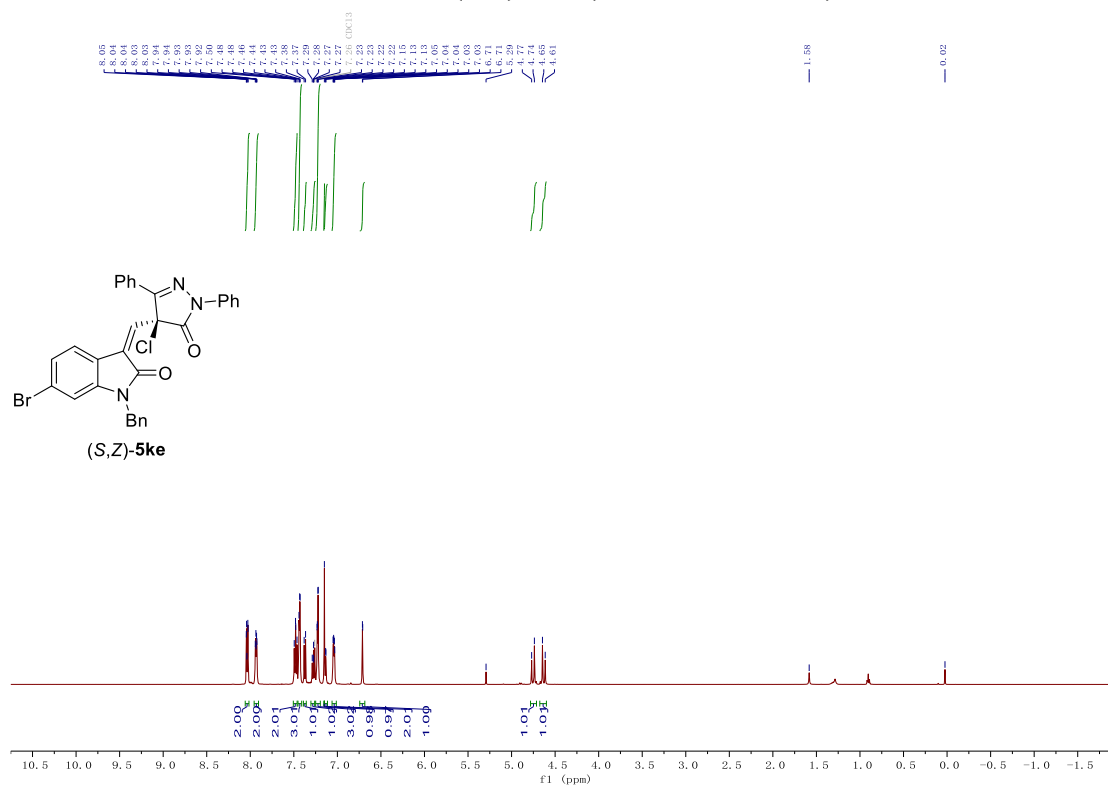
¹³C NMR (100 MHz, CDCl₃) δ: 152.23, 144.58, 142.52, 137.10, 135.05, 133.54, 130.88, 130.92, 130.88, 129.21, 128.90, 128.44, 127.63, 127.47, 126.72, 126.52, 122.89, 122.21, 119.86, 119.47, 110.51.

77.16 (CDCl₃)

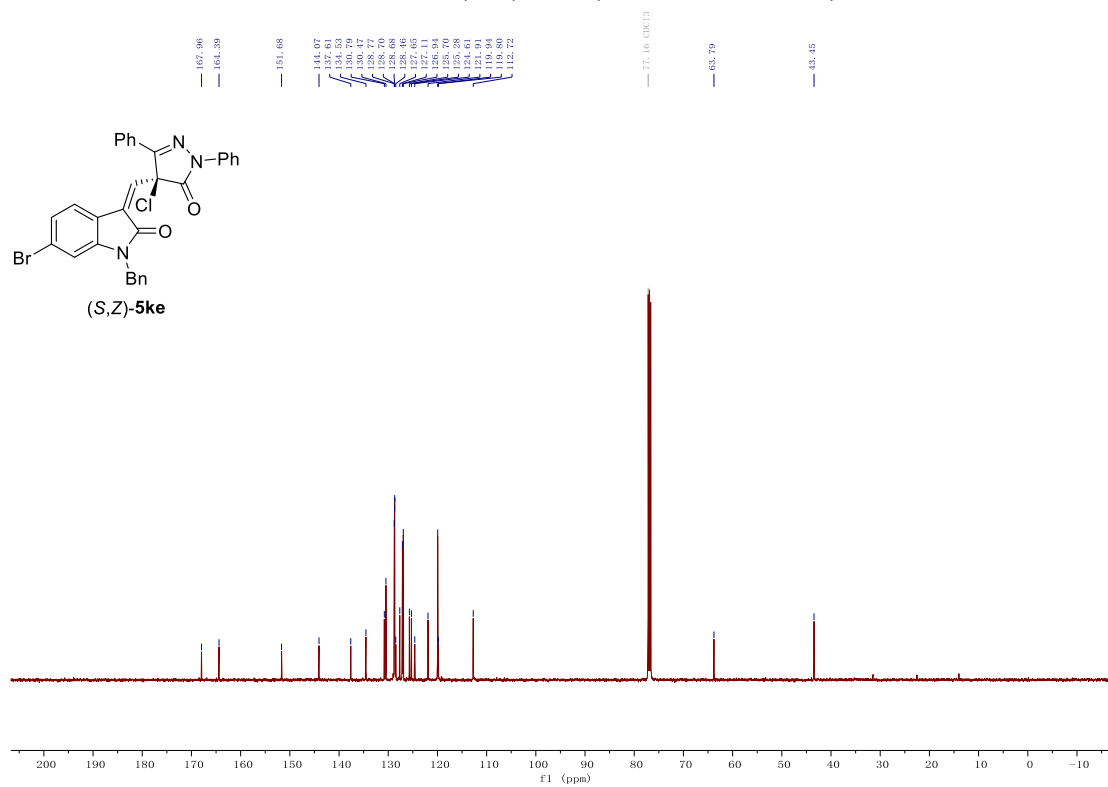
64.27

44.00

¹H NMR of (S,Z)-5ke (500 MHz, CDCl₃)



^{13}C NMR of (S,Z)-5ke (126 MHz, CDCl_3)



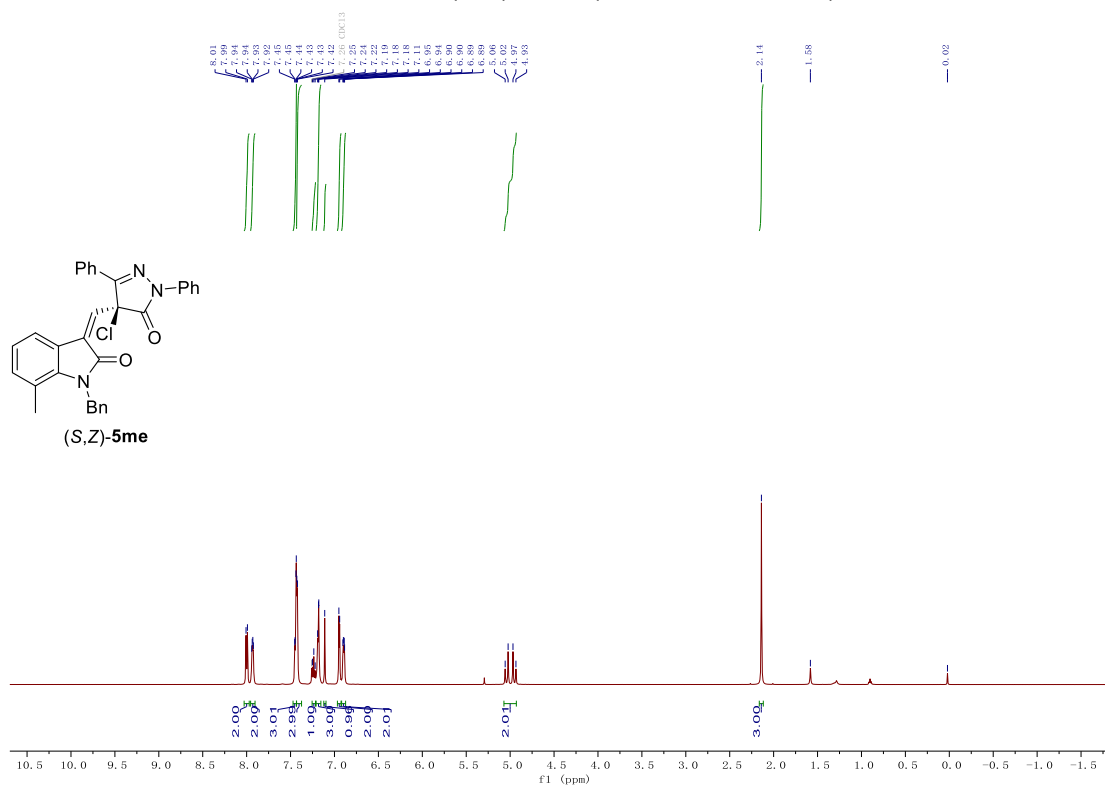
[illegible]

(S,Z)-5le

¹H NMR spectrum (CDCl₃) of (S,Z)-5le. The spectrum shows a complex aromatic region between 110 and 140 ppm, a sharp singlet at 7.71 ppm, and a broad peak at 4.5 ppm. The x-axis is labeled f1 (ppm) and ranges from -10 to 200.

Chemical Shift (ppm)
168.46
161.88
152.10
150.87
146.87
138.16
137.46
132.12
131.61
130.51
130.26
130.18
130.08
129.93
129.83
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¹H NMR of (S,Z)-5me (500 MHz, CDCl₃)



¹³C NMR of (S,Z)-5me (126 MHz, CDCl₃)

