Supporting Information

Phosphine-mediated [2+3]/[2+3] domino annulation reaction: Access to cyclopentane[3,4]pyrrolo[1,2-a]indoles

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1. General information

All the solvents were used without further purification. ^{1}H NMR (400 MHz) and ^{13}C NMR (101 MHz) were recorded on a Bruker AV 400 (400 MHz) spectrometer with $CDCl_3$ as solvent. Chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane as an internal reference. All shifts are reported in ppm as downfield from TMS as standard. Multiplicity is indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), dd (doublet of doublet), m (multiplet). Coupling constants J are reported in Hz. HRMS were obtained on an VG ZAB-HS mass spectrometer with ESI resource. Melting points were measured on a RY-I apparatus and are reported uncorrected. Column chromatography was performed on silica gel 200-300 mesh. The starting materials indole-derived enones **2**[1] were prepared according to the known methods.

2. References

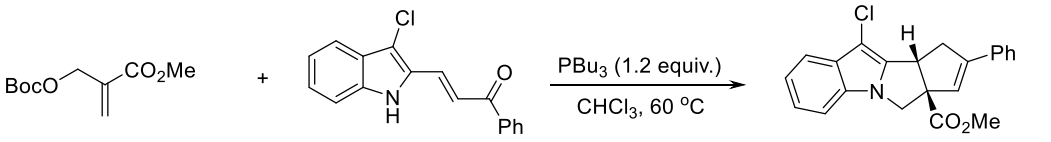
1. (a) C. Zhao, F. D. Toste and R. G. Bergman, *J. Am. Chem. Soc.,* 2011, **133**, 10787–10789; (b) T. Su, X. Han and X. Lu, *Tetrahedron Lett.,* 2014, **55**, 27–30; (c) Y. Chen, R. Yang, F. Xiao, T. Xu, G. Mao and G.-J. Deng, *Org. Lett.,* 2023, **25**, 3702–3707.

3. General procedures

3.1 General procedure for the synthesis of cyclopentane[3,4]pyrrolo[1,2-a]indoles 3:

The indole-derived enones **2** (0.20 mmol), PBu_3 (0.24 mmol, 1.2 equiv.) and $CHCl_3$ (2.0 mL) were added to a 15 mL dry sealed tube at 60 ℃ in water bath. Then MBH carbonates **1** (0.24 mmol, 1.2 equiv.) were added in one portion. This solution was stirred at 60 ºC for 6 hours until the complete consumption of indole-derived enones **2** monitored by TLC. The reaction mixture was concentrated and the residue was purified by flash column chromatography (petroleum ether: EtOAc = 20:1) on silica gel to afford corresponding products **3**.

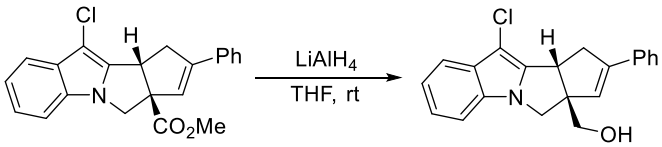
3.2 Procedure for the gram-scale synthesis of 3z:



1b (4.8 mmol) **2a** (4.0 mmol) **3z**, 1.18 g, 81% yield, >20:1 dr

The indole-derived enone **2a** (4.0 mmol, 1.13 g), PBu_3 (4.8 mmol, 1.2 equiv., 971 mg) and $CHCl_3$ (40 mL) were added to a 250 mL dry round bottom flask at 60 ℃ in water bath. Then MBH carbonate **1b** (4.8 mmol, 1.2 equiv., 1.04 g) was added in one portion. This solution was stirred at 60 ºC for 6 hours until the complete consumption of indole-derived enone **2a** monitored by TLC. The reaction mixture was concentrated and the residue was purified by flash column chromatography (petroleum ether: EtOAc = 20:1) on silica gel to afford product **3z** as white solid (1.18 g, 81% yield, >20:1 dr).

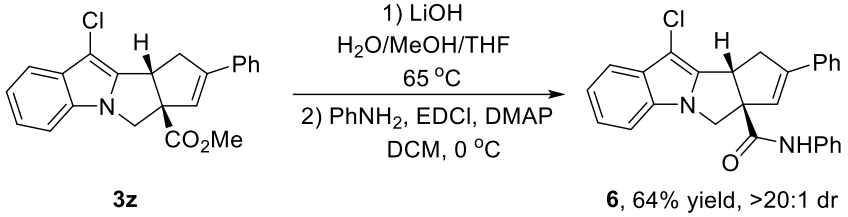
3.3 Procedure for the derivatizations of 3z:



3z **5**, 88% yield, >20:1 dr

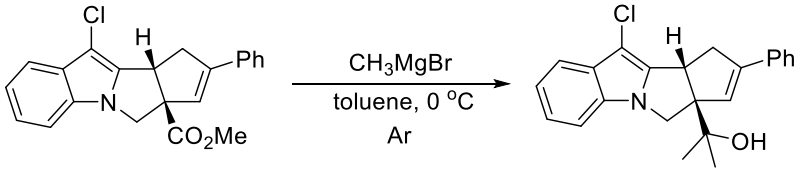
To a suspension of lithium aluminium tetrahydride (0.60 mmol, 3.0 equiv., 22.8 mg) in THF (6 mL) was

added **3z** (0.20 mmol, 72.8 mg) in one portion, mixture was stirred 30 min at 25 °C. NH_4Cl (aq) was added in small portions. Then, extracted with EtOAc, dried with Na_2SO_4 and concentrated in vacuo. The residue was purified by column chromatography (petroleum ether: EtOAc = 4:1) on silica gel to afford product **5** (59.0 mg, 88% yield, > 20:1 dr).



3z **6**, 64% yield, >20:1 dr

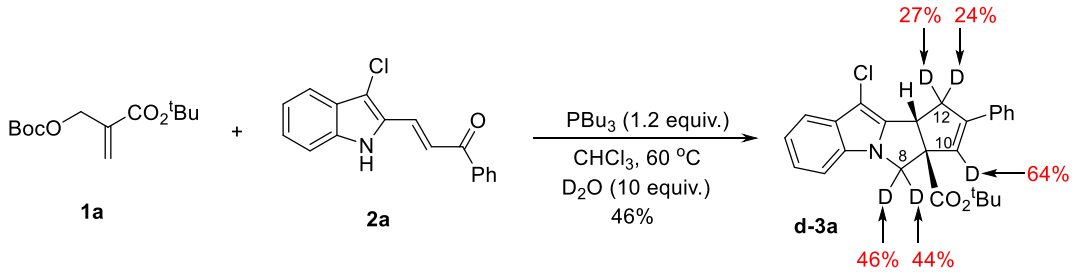
To a stirred solution of **3z** (0.20 mmol, 72.8 mg) in THF (2.0 mL), H_2O (1.0 mL) and MeOH (0.5 mL) at room temperature was added LiOH•H_2O (0.60 mmol, 3.0 equiv., 25.2 mg), and the resulting mixture was stirred at 65 °C in an oil bath for 8 h. Acidify the solution with the 1M HCl, followed by adding 10 mL of water and 10 mL EtOAc. The aqueous phase was separated and extracted three times with 10 mL EtOAc. The combined organic phases were dried over Na_2SO_4 and the solvents were removed in vacuo. Add 1-ethyl-3-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDCl) (0.2 mmol, 1.0 equiv., 38.3 mg), above residue and 4-dimethyl-aminopyridine (DMAP) (0.02 mmol, 0.1 equiv., 2.4 mg) to a stirred solution of aniline (0.2 mmol, 1.0 equiv., 18.6 mg) in CH_2Cl_2 at 0 °C in an ice-water bath. Stir the reaction mixture at this temperature for 2 hours. After completion (TLC control using petroleum ether: EtOAc = 10:1 as eluent), wash the reaction mixture with water and brine. Dry the organic layer with Na_2SO_4. The crude residue was purified by column chromatography on silica gel (petroleum ether: EtOAc = 10:1) to afford the product **6** (54.5 mg, 64% yield (for two steps), > 20:1 dr).



3z **7**, 74% yield, >20:1 dr

A solution of **3z** (0.20 mmol, 72.8 mg) in anhydrous toluene (4.0 mL) was added CH_3MgBr (1.0 mmol, 1.0 M in THF) dropwise at 0 °C in an ice-water bath under argon atmosphere. After addition, the mixture was stirred at 40 °C in an oil bath for 5 h. The mixture was quenched by adding saturated NH_4Cl (4.0 mL) and extracted with EtOAc (2 ×6.0 mL). The organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. The product was purified by column chromatography on silica gel (petroleum ether: EtOAc = 5:1) to afford the product **7** (53.6 mg, 74% yield, > 20:1 dr).

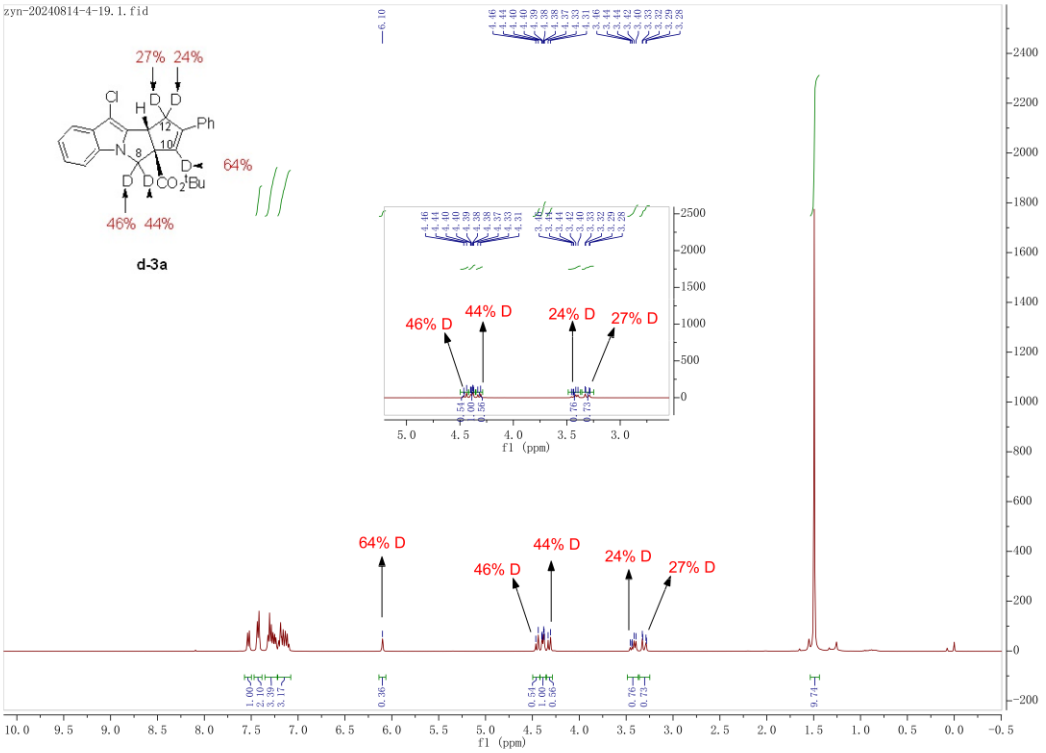
3.4 Procedure for the deuterium labeling experiment:



1a **2a** **d-3a**

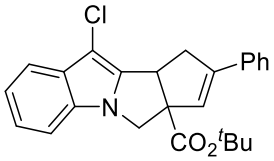
The indole-derived enone **2a** (0.20 mmol, 56.3 mg), PBu_3 (0.24 mmol, 1.2 equiv., 48.6 mg), $CHCl_3$ (2.0 mL) and D_2O (2.0 mmol, 10 equiv., 40 μL) were added to a 15 mL dry sealed tube at 60 °C in water bath.

Then MBH carbonate **1a** (0.24 mmol, 1.2 equiv., 62.0 mg) was added in one portion. This solution was stirred at 60 ºC for 6 hours until the complete consumption of indole-derived enone **2a** monitored by TLC. The reaction mixture was concentrated and the residue was purified by flash column chromatography (petroleum ether: EtOAc = 20:1) on silica gel to afford corresponding product **d-3a**.



4. Characterization data

tert-butyl 10-chloro-2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3a)



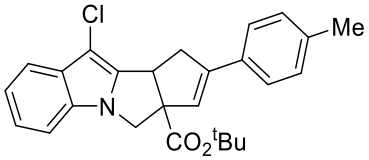
63.7 mg, 78% yield.; white solid; mp 133-135°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.41 – 7.30 (m, 3H), 7.29 – 7.15 (m, 3H), 6.17 (d, *J* = 2.5 Hz, 1H), 4.53 (dd, *J* = 10.4, 1.8 Hz, 1H), 4.49 – 4.44 (m, 1H), 4.40 (dd, *J* = 10.4, 1.8 Hz, 1H), 3.50 (ddt, *J* = 16.3, 8.1, 2.1 Hz, 1H), 3.38 (dd, *J* = 16.2, 1.9 Hz, 1H), 1.57 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 145.3, 141.9, 134.8, 131.2, 129.9, 128.5, 128.4, 126.3, 125.3, 121.7, 120.0, 117.9, 109.8, 96.3, 82.2, 71.7, 52.1, 43.6, 37.4, 28.1.

HRMS (ESI): m/z calcd for $C_{25}H_{25}ClNO_2$ ($[M+H]^+$): 406.1568; found: 406.1564.

tert-butyl 10-chloro-2-(p-tolyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3b)



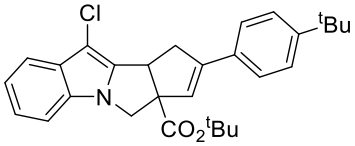
63.1 mg, 75% yield.; white solid; mp 120-122°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dt, *J* = 7.3, 1.7 Hz, 1H), 7.31 (dd, *J* = 8.2, 1.5 Hz, 2H), 7.17 (ddt, *J* = 8.3, 6.6, 1.5 Hz, 2H), 7.11 (td, *J* = 8.5, 7.7, 1.9 Hz, 3H), 6.07 – 5.99 (m, 1H), 4.43 (dd, *J* = 10.3, 1.1 Hz, 1H), 4.37 (dt, *J* = 8.1, 1.7 Hz, 1H), 4.30 (dd, *J* = 10.3, 1.3 Hz, 1H), 3.40 (ddt, *J* = 16.2, 8.1, 2.1 Hz, 1H), 3.28 (dq, *J* = 16.1, 1.8 Hz, 1H), 2.30 (s, 3H), 1.48 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 145.2, 142.0, 138.3, 132.0, 131.2, 129.9, 129.2, 126.2, 124.3, 121.7, 119.9, 117.9, 109.8, 96.2, 82.1, 71.6, 52.1, 43.6, 37.4, 28.1, 21.3.

HRMS (ESI): m/z calcd for $C_{26}H_{27}ClNO_2$ ($[M+H]^+$): 420.1725; found: 420.1717.

tert-butyl 2-(4-(tert-butyl)phenyl)-10-chloro-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3c)



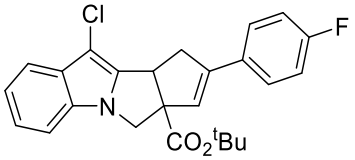
59.8 mg, 65% yield.; white solid; mp 145-147°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dq, *J* = 7.2, 1.4 Hz, 1H), 7.42 – 7.29 (m, 4H), 7.23 – 7.06 (m, 3H), 6.06 (dd, *J* = 2.6, 1.3 Hz, 1H), 4.46 – 4.41 (m, 1H), 4.38 (dq, *J* = 8.0, 1.6 Hz, 1H), 4.31 (dt, *J* = 10.4, 1.2 Hz, 1H), 3.47 – 3.37 (m, 1H), 3.31 (dq, *J* = 16.1, 1.6 Hz, 1H), 1.55 – 1.46 (s, 9H), 1.30 – 1.27 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 151.6, 145.2, 141.9, 132.0, 131.2, 129.9, 126.0, 125.4, 124.6, 121.7, 119.9, 117.9, 109.8, 96.3, 82.1, 71.6, 52.0, 43.6, 37.4, 34.7, 31.3, 28.1.

HRMS (ESI): m/z calcd for $C_{29}H_{33}ClNO_2$ ($[M+H]^+$): 462.2194; found: 462.2186.

tert-butyl 10-chloro-2-(4-fluorophenyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3d)



64.9 mg, 77% yield.; white solid; mp 162-164°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 1H), 7.42 – 7.35 (m, 2H), 7.22 – 7.08 (m, 3H), 7.02 – 6.94 (m, 2H), 6.03 (dd, *J* = 2.4, 1.4 Hz, 1H), 4.44 (d, *J* = 10.4 Hz, 1H), 4.38 (dd, *J* = 8.1, 1.6 Hz, 1H), 4.31 (d, *J* = 10.4 Hz, 1H), 3.39 (ddd, *J* = 16.2, 8.1, 2.4 Hz, 1H), 3.26 (dt, *J* = 16.2, 1.6 Hz, 1H), 1.50 (s, 9H).

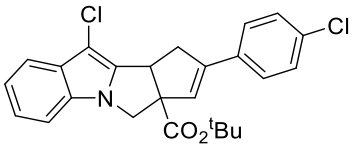
^{13}C NMR (101 MHz, $CDCl_3$) δ 171.7, 162.7 (d, *J* = 248.2 Hz), 143.0 (d, *J* = 247.0 Hz), 131.1, 131.0 (d, *J* = 3.4 Hz), 129.9, 128.0 (d, *J* = 8.1 Hz), 125.0 (d, *J* = 1.9 Hz), 121.8, 120.0, 117.9, 115.4 (d, *J* = 21.6 Hz), 109.8, 96.3, 82.3, 71.7, 52.0, 43.6, 37.5, 28.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -112.97 (s, 1F).

HRMS (ESI): m/z calcd for $C_{25}H_{24}ClFNO_2$ ($[M+H]^+$): 424.1474; found: 424.1467.

tert-butyl 10-chloro-2-(4-chlorophenyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-

3a(4H)-carboxylate (3e)



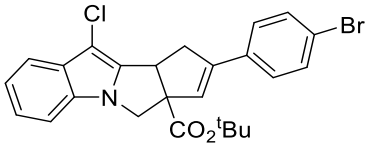
70.8 mg, 80% yield.; white solid; mp 139-142°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.2, 1.4 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.28 – 7.23 (m, 2H), 7.22 – 7.10 (m, 3H), 6.09 (dd, *J* = 2.4, 1.4 Hz, 1H), 4.45 (d, *J* = 10.4 Hz, 1H), 4.39 (dd, *J* = 8.1, 1.7 Hz, 1H), 4.32 (d, *J* = 10.4 Hz, 1H), 3.39 (ddd, *J* = 16.2, 8.1, 2.4 Hz, 1H), 3.26 (dt, *J* = 16.2, 1.6 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 144.2, 141.6, 134.1, 133.2, 131.1, 129.9, 128.6, 127.5, 125.9, 121.8, 120.0, 117.9, 109.8, 96.3, 82.3, 71.7, 52.0, 43.6, 37.4, 28.1.

HRMS (ESI): m/z calcd for $C_{25}H_{24}Cl_2NO_2$ ($[M+H]^+$): 440.1179; found: 440.1171.

tert-butyl 2-(4-bromophenyl)-10-chloro-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3f)



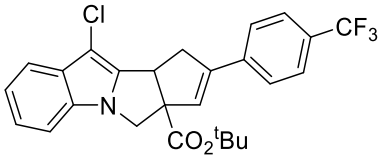
70.5 mg, 73% yield.; light yellow solid; mp 144-146°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.51 (m, 1H), 7.45 – 7.40 (m, 2H), 7.31 – 7.26 (m, 2H), 7.23 – 7.10 (m, 3H), 6.10 (dd, *J* = 2.4, 1.4 Hz, 1H), 4.45 (d, *J* = 10.4 Hz, 1H), 4.39 (dd, *J* = 8.1, 1.7 Hz, 1H), 4.32 (d, *J* = 10.4 Hz, 1H), 3.40 (ddd, *J* = 16.2, 8.1, 2.4 Hz, 1H), 3.26 (dt, *J* = 16.1, 1.6 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 144.2, 141.6, 133.6, 131.6, 131.1, 129.9, 127.8, 126.0, 122.3, 121.8, 120.0, 117.9, 109.8, 96.3, 82.4, 71.7, 51.9, 43.6, 37.3, 28.1.

HRMS (ESI): m/z calcd for $C_{25}H_{24}BrClNO_2$ ($[M+H]^+$): 484.0673; found: 484.0667.

tert-butyl 10-chloro-2-(4-(trifluoromethyl)phenyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3g)



54.1 mg, 57% yield.; white solid; mp 110-112°C.

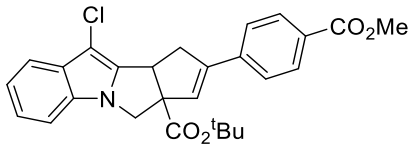
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.48 (m, 5H), 7.23 – 7.10 (m, 3H), 6.21 (dd, *J* = 2.4, 1.4 Hz, 1H), 4.47 (d, *J* = 10.4 Hz, 1H), 4.41 (dd, *J* = 8.1, 1.6 Hz, 1H), 4.35 (d, *J* = 10.5 Hz, 1H), 3.44 (ddd, *J* = 16.2, 8.1, 2.4 Hz, 1H), 3.30 (dt, *J* = 16.2, 1.6 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 144.1, 141.4, 138.1 (d, *J* = 1.5 Hz), 131.1, 130.1 (q, *J* = 32.6 Hz), 129.9, 127.8, 126.5, 125.4 (q, *J* = 3.8 Hz), 121.8, 120.1, 118.0, 109.8, 96.4, 82.5, 71.7, 51.9, 43.6, 37.3, 28.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -62.60 (s, 3F).

HRMS (ESI): m/z calcd for $C_{26}H_{24}ClF_3NO_2$ ($[M+H]^+$): 474.1442; found: 474.1433.

tert-butyl 10-chloro-2-(4-(methoxycarbonyl)phenyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3h)



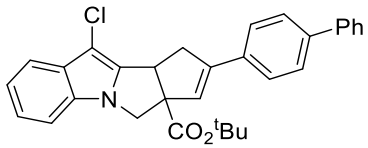
72.7 mg, 78% yield.; white solid; mp 115-117°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 – 7.94 (m, 2H), 7.56 – 7.51 (m, 1H), 7.51 – 7.44 (m, 2H), 7.23 – 7.09 (m, 3H), 6.23 (dd, *J* = 2.4, 1.4 Hz, 1H), 4.47 (d, *J* = 10.4 Hz, 1H), 4.41 (dd, *J* = 8.1, 1.7 Hz, 1H), 4.35 (d, *J* = 10.4 Hz, 1H), 3.90 (s, 3H), 3.45 (ddd, *J* = 16.3, 8.1, 2.5 Hz, 1H), 3.31 (dt, *J* = 16.2, 1.6 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 166.7, 144.5, 141.5, 139.0, 131.1, 129.9, 129.8, 129.7, 127.8, 126.2, 121.8, 120.0, 117.9, 109.8, 82.5, 71.7, 52.2, 52.0, 43.6, 37.3, 28.1.

HRMS (ESI): m/z calcd for $C_{27}H_{27}ClNO_4$ ($[M+H]^+$): 464.1623; found: 464.1619.

tert-butyl 2-([1,1'-biphenyl]-4-yl)-10-chloro-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3i)



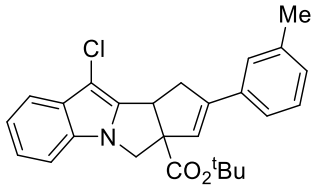
71.9 mg, 75% yield.; white solid; mp 182-185°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.47 (m, 7H), 7.42 (t, *J* = 7.6 Hz, 2H), 7.36 – 7.30 (m, 1H), 7.22 – 7.09 (m, 3H), 6.14 (t, *J* = 1.8 Hz, 1H), 4.46 (d, *J* = 10.4 Hz, 1H), 4.41 (dd, *J* = 8.0, 1.7 Hz, 1H), 4.34 (d, *J* = 10.4 Hz, 1H), 3.46 (ddd, *J* = 16.2, 8.0, 2.4 Hz, 1H), 3.34 (dt, *J* = 16.1, 1.6 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 144.9, 141.8, 141.1, 140.5, 133.7, 131.2, 129.9, 128.9, 127.5, 127.1, 127.0, 126.7, 125.4, 121.7, 120.0, 117.9, 109.8, 96.3, 82.2, 71.7, 52.0, 43.6, 37.4, 28.1.

HRMS (ESI): m/z calcd for $C_{31}H_{29}ClNO_2$ ($[M+H]^+$): 482.1881; found: 482.1875.

tert-butyl 10-chloro-2-(m-tolyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3j)



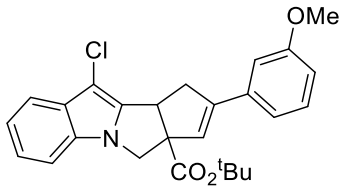
56.3 mg, 67% yield.; white solid; mp 153-155°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 7.7 Hz, 1H), 7.27 – 7.10 (m, 6H), 7.09 – 7.04 (m, 1H), 6.08 (s, 1H), 4.44 (d, *J* = 10.4 Hz, 1H), 4.38 (d, *J* = 7.9 Hz, 1H), 4.32 (d, *J* = 10.4 Hz, 1H), 3.42 (ddd, *J* = 16.2, 8.1, 2.4 Hz, 1H), 3.29 (d, *J* = 16.1 Hz, 1H), 2.32 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 145.4, 141.9, 138.0, 134.7, 131.1, 129.1, 128.4, 127.0, 125.1, 123.4, 121.7, 119.9, 117.9, 109.8, 96.3, 82.2, 71.6, 52.0, 43.5, 37.4, 28.1, 21.5.

HRMS (ESI): m/z calcd for $C_{26}H_{27}ClNO_2$ ($[M+H]^+$): 420.1725; found: 420.1715.

tert-butyl 10-chloro-2-(3-methoxyphenyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3k)



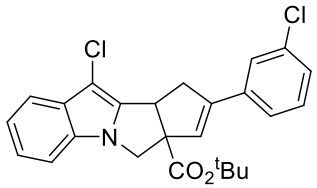
49.1 mg, 56% yield.; light yellow solid; mp 170-172°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.24 – 7.08 (m, 4H), 7.02 (dq, *J* = 7.7, 1.2 Hz, 1H), 6.94 (dt, *J* = 2.9, 1.4 Hz, 1H), 6.80 (ddd, *J* = 8.3, 2.6, 1.0 Hz, 1H), 6.09 (dt, *J* = 2.8, 1.4 Hz, 1H), 4.44 (d, *J* = 10.5 Hz, 1H), 4.37 (dt, *J* = 8.1, 1.5 Hz, 1H), 4.31 (dd, *J* = 10.4, 1.0 Hz, 1H), 3.78 (s, 3H), 3.41 (ddt, *J* = 16.2, 8.1, 1.9 Hz, 1H), 3.28 (dt, *J* = 16.1, 1.6 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.8, 159.6, 145.2, 141.8, 136.2, 131.1, 129.5, 125.7, 121.7, 120.0, 118.8, 117.9, 113.7, 112.0, 109.8, 96.3, 82.2, 71.6, 55.3, 52.0, 43.5, 37.5, 28.1.

HRMS (ESI): m/z calcd for $C_{26}H_{27}ClNO_3$ ($[M+H]^+$): 436.1674; found: 436.1667.

tert-butyl 10-chloro-2-(3-chlorophenyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3l)



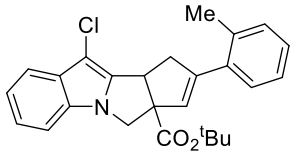
65.5 mg, 74% yield.; white solid; mp 124-126°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.3, 1.5 Hz, 1H), 7.40 (t, *J* = 1.4 Hz, 1H), 7.27 (qd, *J* = 4.4, 1.7 Hz, 1H), 7.25 – 7.08 (m, 5H), 6.12 (t, *J* = 1.8 Hz, 1H), 4.44 (d, *J* = 10.4 Hz, 1H), 4.39 (dd, *J* = 8.1, 1.6 Hz, 1H), 4.32 (d, *J* = 10.4 Hz, 1H), 3.40 (ddd, *J* = 16.2, 8.1, 2.4 Hz, 1H), 3.26 (dt, *J* = 16.3, 1.6 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 144.1, 141.6, 136.6, 134.5, 131.1, 129.9, 129.7, 128.3, 126.7, 126.3, 124.4, 121.8, 120.0, 118.0, 109.8, 96.4, 82.4, 71.6, 52.0, 43.5, 37.4, 28.1.

HRMS (ESI): m/z calcd for $C_{25}H_{24}Cl_2NO_2$ ($[M+H]^+$): 440.1179; found: 440.1172.

tert-butyl 10-chloro-2-(o-tolyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3m)



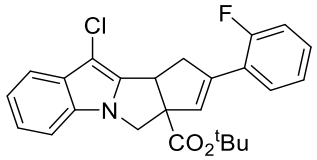
49.0 mg, 58% yield.; white solid; mp 138-140°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.53 (m, 1H), 7.24 – 7.17 (m, 2H), 7.16 – 7.06 (m, 5H), 5.71 – 5.67 (m, 1H), 4.49 (d, *J* = 10.4 Hz, 1H), 4.33 – 4.27 (m, 2H), 3.39 (ddd, *J* = 16.5, 7.9, 2.4 Hz, 1H), 3.25 (dd, *J* = 16.6, 1.7 Hz, 1H), 2.25 (s, 3H), 1.52 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 146.8, 141.7, 135.9, 135.7, 131.2, 130.6, 129.9, 129.2, 128.3, 127.8, 125.8, 121.7, 119.9, 118.0, 109.9, 96.3, 82.1, 71.8, 51.7, 44.1, 40.6, 28.1, 20.8.

HRMS (ESI): m/z calcd for $C_{26}H_{27}ClNO_2$ ([M+H]$^+$): 420.1725; found: 420.1716.

tert-butyl 10-chloro-2-(2-fluorophenyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3n)



56.2 mg, 66% yield.; white solid; mp 117-119°C.

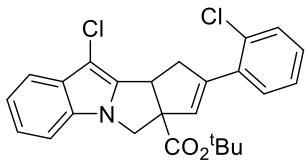
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 1H), 7.32 (td, *J* = 7.8, 1.8 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.14 (ddd, *J* = 10.7, 7.7, 1.3 Hz, 1H), 7.11 – 7.06 (m, 1H), 7.02 (ddd, *J* = 11.8, 8.2, 1.2 Hz, 1H), 6.32 (q, *J* = 1.7 Hz, 1H), 4.47 (d, *J* = 10.4 Hz, 1H), 4.38 – 4.32 (m, 2H), 3.48 (ddd, *J* = 16.2, 8.1, 2.5 Hz, 1H), 3.33 (dt, *J* = 16.1, 1.6 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 160.9 (d, *J* = 252.0 Hz), 141.7, 139.4 (d, *J* = 3.0 Hz), 131.1, 130.4 (d, *J* = 11.7 Hz), 129.9, 129.5 (d, *J* = 8.8 Hz), 129.1 (d, *J* = 3.9 Hz), 124.1 (d, *J* = 3.5 Hz), 122.8 (d, *J* = 12.3 Hz), 121.7, 120.0, 117.9, 116.0 (d, *J* = 22.9 Hz), 109.8, 96.3, 82.3, 72.1 (d, *J* = 1.2 Hz), 52.0, 42.8, 38.6 (d, *J* = 1.5 Hz), 28.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -110.55 (s, 1F).

HRMS (ESI): m/z calcd for $C_{25}H_{24}ClFNO_2$ ([M+H]$^+$): 424.1474; found: 424.1466.

tert-butyl 10-chloro-2-(2-chlorophenyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3o)



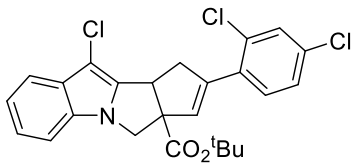
67.1 mg, 76% yield.; white solid; mp 128-130°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dq, *J* = 7.5, 1.0 Hz, 1H), 7.37 – 7.30 (m, 1H), 7.24 – 7.19 (m, 2H), 7.19 – 7.14 (m, 3H), 7.14 – 7.10 (m, 1H), 6.04 (p, *J* = 1.1 Hz, 1H), 4.49 (d, *J* = 10.4 Hz, 1H), 4.37 – 4.29 (m, 2H), 3.52 (dddd, *J* = 16.4, 8.1, 2.5, 1.0 Hz, 1H), 3.30 (dq, *J* = 16.3, 1.4 Hz, 1H), 1.52 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 144.1, 141.6, 134.8, 132.6, 131.2, 131.0, 130.2, 130.0, 129.9, 128.9, 126.7, 121.7, 119.9, 118.0, 109.9, 82.2, 71.8, 51.7, 43.8, 39.9, 28.1.

HRMS (ESI): m/z calcd for $C_{25}H_{24}Cl_2NO_2$ ([M+H]$^+$): 440.1179; found: 440.1170.

tert-butyl 10-chloro-2-(2,4-dichlorophenyl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3p)



72.9 mg, 77% yield.; white solid; mp 150-152°C.

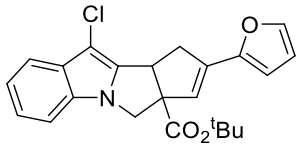
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.36 (d, *J* = 2.0 Hz, 1H), 7.24 – 7.17 (m, 2H), 7.17 – 7.13 (m, 2H), 7.12 (s, 1H), 6.05 (t, *J* = 1.5 Hz, 1H), 4.49 (d, *J* = 10.5 Hz, 1H), 4.35 – 4.28

(m, 2H), 3.49 (ddd, *J* = 16.3, 8.1, 2.5 Hz, 1H), 3.26 (dt, *J* = 16.5, 1.8 Hz, 1H), 1.51 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.4, 143.0, 141.4, 134.0, 133.3, 131.6, 131.2, 130.8, 130.0, 129.9, 127.0, 121.8, 120.0, 118.0, 109.9, 96.4, 82.4, 71.8, 51.6, 43.8, 39.8, 28.1.

HRMS (ESI): m/z calcd for $C_{25}H_{23}Cl_3NO_2$ ($[M+H]^+$): 474.0789; found: 474.0782.

tert-butyl 10-chloro-2-(furan-2-yl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3q)



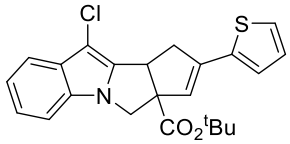
54.6 mg, 69% yield.; white solid; mp 140-142°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 1H), 7.35 (d, *J* = 1.8 Hz, 1H), 7.21 – 7.09 (m, 3H), 6.36 (dd, *J* = 3.4, 1.8 Hz, 1H), 6.32 (d, *J* = 3.4 Hz, 1H), 6.01 (d, *J* = 2.0 Hz, 1H), 4.43 (d, *J* = 10.4 Hz, 1H), 4.36 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.31 (d, *J* = 10.4 Hz, 1H), 3.32 (ddd, *J* = 16.0, 8.0, 2.4 Hz, 1H), 3.19 (dt, *J* = 16.0, 1.6 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 150.4, 142.8, 141.5, 135.1, 131.1, 129.8, 123.7, 121.7, 120.0, 117.9, 111.3, 109.8, 108.9, 96.3, 82.3, 71.7, 52.0, 43.6, 36.4, 28.1.

HRMS (ESI): m/z calcd for $C_{23}H_{23}ClNO_3$ ($[M+H]^+$): 396.1361; found: 396.1353.

tert-butyl 10-chloro-2-(thiophen-2-yl)-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3r)



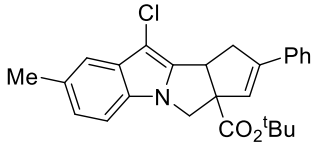
49.7 mg, 60% yield.; light yellow oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (t, *J* = 7.8 Hz, 2H), 7.29 – 7.06 (m, 3H), 7.05 – 6.90 (m, 2H), 5.93 (d, *J* = 6.9 Hz, 1H), 4.49 – 4.17 (m, 3H), 3.47 – 3.34 (m, 1H), 3.28 (dd, *J* = 16.5, 7.0 Hz, 1H), 1.58 – 1.23 (m, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 141.5, 139.3, 138.7, 131.1, 129.9, 127.4, 125.8, 125.7, 124.4, 121.8, 120.0, 117.9, 109.8, 82.3, 71.7, 51.9, 43.7, 38.2, 28.1.

HRMS (ESI): m/z calcd for $C_{23}H_{23}ClNO_2S$ ($[M+H]^+$): 412.1133; found: 412.1125.

tert-butyl 10-chloro-8-methyl-2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3s)



70.6 mg, 84% yield.; white solid; mp 133-136°C.

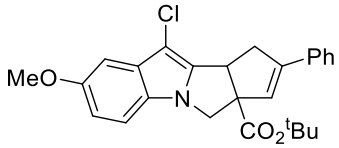
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.33 – 7.29 (m, 2H), 7.29 – 7.20 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.97 (dd, *J* = 8.4, 1.6 Hz, 1H), 6.09 (dt, *J* = 2.3, 1.0 Hz, 1H), 4.42 (d, *J* = 10.4 Hz, 1H), 4.37 (dt, *J* = 7.9, 1.4 Hz, 1H), 4.29 (d, *J* = 10.3 Hz, 1H), 3.41 (ddd, *J* = 16.3, 8.0, 2.4 Hz, 1H), 3.29 (dq,

J = 16.3, 1.3 Hz, 1H), 2.43 (s, 3H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.9, 145.3, 141.9, 134.8, 130.1, 129.5, 129.4, 128.5, 128.3, 126.3, 125.3, 123.3, 117.5, 109.5, 95.6, 82.1, 71.7, 52.1, 43.6, 37.4, 28.1, 21.6.

HRMS (ESI): m/z calcd for $C_{26}H_{27}ClNO_2$ ($[M+H]^+$): 420.1725; found: 420.1719.

tert-butyl 10-chloro-8-methoxy-2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3t)



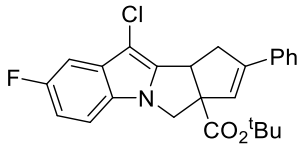
61.0 mg, 70% yield.; white solid; mp 166-168°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 – 7.40 (m, 2H), 7.33 – 7.28 (m, 2H), 7.27 – 7.22 (m, 1H), 7.08 (d, *J* = 8.8 Hz, 1H), 6.96 (d, *J* = 2.4 Hz, 1H), 6.81 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.10 (t, *J* = 2.0 Hz, 1H), 4.42 (d, *J* = 10.3 Hz, 1H), 4.37 (dd, *J* = 8.1, 1.7 Hz, 1H), 4.29 (d, *J* = 10.3 Hz, 1H), 3.84 (s, 3H), 3.41 (ddd, *J* = 16.2, 8.1, 2.4 Hz, 1H), 3.29 (dt, *J* = 16.2, 1.7 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 171.8, 154.6, 145.2, 142.4, 134.8, 130.2, 128.5, 128.4, 126.3, 126.3, 125.3, 112.1, 110.7, 99.5, 82.2, 71.7, 55.9, 52.2, 43.8, 37.4, 28.1.

HRMS (ESI): m/z calcd for $C_{26}H_{27}ClNO_3$ ($[M+H]^+$): 436.1674; found: 436.1667.

tert-butyl 10-chloro-8-fluoro-2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3u)



68.5 mg, 81% yield.; white solid; mp 168-170°C.

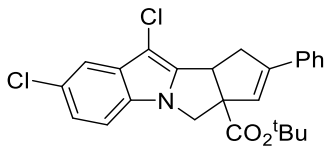
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.39 (m, 2H), 7.33 – 7.22 (m, 3H), 7.17 (dd, *J* = 9.4, 2.5 Hz, 1H), 7.08 (dd, *J* = 8.8, 4.2 Hz, 1H), 6.88 (td, *J* = 9.1, 2.5 Hz, 1H), 6.10 (dt, *J* = 2.3, 1.2 Hz, 1H), 4.43 (d, *J* = 10.3 Hz, 1H), 4.40 – 4.36 (m, 1H), 4.30 (d, *J* = 10.4 Hz, 1H), 3.42 (ddd, *J* = 16.2, 8.1, 2.4 Hz, 1H), 3.29 (dq, *J* = 16.1, 1.4 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 158.2 (d, *J* = 235.6 Hz), 145.3, 143.7, 134.6, 130.2 (d, *J* = 10.4 Hz), 128.5, 128.5, 127.8, 126.3, 125.1, 110.6 (d, *J* = 9.8 Hz), 110.1 (d, *J* = 26.6 Hz), 103.1 (d, *J* = 24.8 Hz), 96.3 (d, *J* = 4.8 Hz), 82.3, 71.7, 52.3, 43.8, 37.3, 28.1.

^{19}F NMR (376 MHz, $CDCl_3$) δ -123.45 (s, 1F).

HRMS (ESI): m/z calcd for $C_{25}H_{24}ClFNO_2$ ($[M+H]^+$): 424.1474; found: 424.1467.

tert-butyl 8,10-dichloro-2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3v)



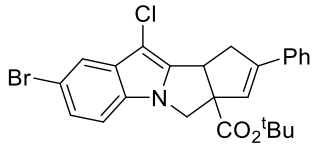
64.9 mg, 74% yield.; white solid; mp 151-153°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (t, *J* = 1.3 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.26 – 7.15 (m, 3H), 7.00 (d, *J* = 1.3 Hz, 2H), 6.02 (t, *J* = 1.9 Hz, 1H), 4.35 (d, *J* = 10.5 Hz, 1H), 4.29 (dd, *J* = 8.2, 1.6 Hz, 1H), 4.21 (d, *J* = 10.5 Hz, 1H), 3.34 (ddd, *J* = 16.2, 8.1, 2.4 Hz, 1H), 3.21 (dt, *J* = 16.1, 1.6 Hz, 1H), 1.41 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.5, 144.3, 142.3, 133.5, 129.7, 128.5, 127.4, 127.4, 125.2, 124.8, 124.0, 120.9, 116.4, 109.7, 94.9, 81.3, 70.6, 51.1, 42.6, 36.2, 27.0.

HRMS (ESI): m/z calcd for $C_{25}H_{24}Cl_2NO_2$ ($[M+H]^+$): 440.1179; found: 440.1171.

tert-butyl 8-bromo-10-chloro-2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3w)



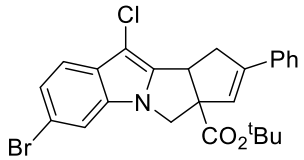
84.2 mg, 87% yield.; light yellow solid; mp 130-132°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 1.8 Hz, 1H), 7.45 – 7.40 (m, 2H), 7.34 – 7.28 (m, 2H), 7.28 – 7.24 (m, 1H), 7.21 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.03 (d, *J* = 8.6 Hz, 1H), 6.10 (p, *J* = 1.1 Hz, 1H), 4.42 (d, *J* = 10.4 Hz, 1H), 4.37 (dd, *J* = 8.2, 1.6 Hz, 1H), 4.29 (d, *J* = 10.5 Hz, 1H), 3.42 (ddd, *J* = 16.2, 8.1, 2.4 Hz, 1H), 3.28 (dt, *J* = 16.1, 1.6 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.6, 145.4, 143.2, 134.6, 131.4, 129.8, 128.5, 128.5, 126.3, 125.1, 124.6, 120.5, 113.3, 111.2, 95.8, 82.4, 71.6, 52.1, 43.7, 37.3, 28.1.

HRMS (ESI): m/z calcd for $C_{25}H_{24}BrClNO_2$ ($[M+H]^+$): 484.0673; found: 484.0666.

tert-butyl 7-bromo-10-chloro-2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3x)



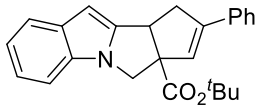
75.9 mg, 78% yield.; white solid; mp 117-119°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.39 (m, 2H), 7.37 – 7.27 (m, 4H), 7.27 – 7.21 (m, 1H), 7.18 (dd, *J* = 8.5, 1.7 Hz, 1H), 6.26 – 6.02 (m, 1H), 4.39 (d, *J* = 10.5 Hz, 1H), 4.35 (d, *J* = 1.6 Hz, 1H), 4.26 (d, *J* = 10.5 Hz, 1H), 3.42 (ddd, *J* = 16.2, 8.1, 2.4 Hz, 1H), 3.28 (dt, *J* = 16.1, 1.5 Hz, 1H), 1.49 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 171.5, 145.4, 142.5, 134.6, 131.8, 128.8, 128.5, 128.5, 126.3, 125.1, 123.2, 119.2, 115.1, 112.8, 96.7, 82.3, 71.6, 52.0, 43.5, 37.3, 28.1.

HRMS (ESI): m/z calcd for $C_{25}H_{24}BrClNO_2$ ($[M+H]^+$): 484.0673; found: 484.0666.

tert-butyl 2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3y)



38.8 mg, 52% yield.; white solid; mp 128-130°C.

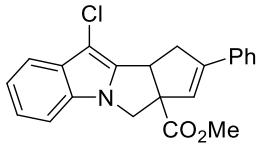
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.51 (m, 1H), 7.41 (dq, *J* = 6.2, 1.3 Hz, 2H), 7.29 (td, *J* = 7.3, 1.3 Hz, 2H), 7.27 – 7.20 (m, 2H), 7.11 (tt, *J* = 8.1, 1.2 Hz, 1H), 7.08 – 7.01 (m, 1H), 6.22 (d, *J* = 1.2 Hz, 1H),

6.11 (p, *J* = 1.3 Hz, 1H), 4.47 (dd, *J* = 10.5, 1.1 Hz, 1H), 4.36 – 4.29 (m, 2H), 3.51 – 3.42 (m, 1H), 3.08 (dq, *J* = 15.8, 1.4 Hz, 1H), 1.50 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.1, 148.1, 145.0, 135.0, 132.9, 132.2, 128.4, 128.2, 126.2, 125.6, 120.5, 120.5, 119.4, 109.4, 92.3, 81.9, 71.6, 51.3, 43.9, 39.9, 28.1.

HRMS (ESI): m/z calcd for $C_{25}H_{26}NO_2$ ($[M+H]^+$): 372.1958; found: 372.1956.

methyl 10-chloro-2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3z)



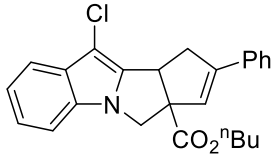
61.9 mg, 85% yield.; white solid; mp 161-163°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.24 – 7.13 (m, 3H), 7.12 – 7.00 (m, 3H), 6.02 (s, 1H), 4.40 (d, *J* = 10.3 Hz, 1H), 4.36 – 4.31 (m, 1H), 4.27 (d, *J* = 10.4 Hz, 1H), 3.70 (s, 3H), 3.36 (ddd, *J* = 16.3, 8.1, 2.4 Hz, 1H), 3.24 (d, *J* = 16.2 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.2, 145.7, 141.6, 134.5, 131.2, 130.0, 128.5, 126.3, 124.6, 121.8, 120.0, 118.0, 109.8, 96.4, 70.6, 52.8, 52.1, 43.8, 37.4.

HRMS (ESI): m/z calcd for $C_{22}H_{19}ClNO_2$ ($[M+H]^+$): 364.1099; found: 364.1092.

butyl 10-chloro-2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3aa)



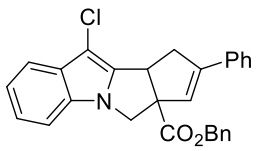
65.8 mg, 81% yield.; white solid; mp 154-156°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (ddd, *J* = 6.3, 3.3, 1.7 Hz, 1H), 7.40 (dt, *J* = 7.9, 1.5 Hz, 2H), 7.31 – 7.20 (m, 3H), 7.19 – 7.08 (m, 3H), 6.09 (q, *J* = 2.0 Hz, 1H), 4.45 (d, *J* = 10.4 Hz, 1H), 4.41 (dq, *J* = 8.0, 1.6 Hz, 1H), 4.34 (dd, *J* = 10.4, 1.4 Hz, 1H), 4.18 (ttd, *J* = 6.1, 4.1, 2.3 Hz, 2H), 3.42 (ddq, *J* = 16.3, 8.0, 1.9, 1.4 Hz, 1H), 3.32 (dp, *J* = 16.2, 1.8 Hz, 1H), 1.70 – 1.57 (m, 2H), 1.38 (dqd, *J* = 9.5, 7.4, 5.5 Hz, 2H), 0.93 (tt, *J* = 7.4, 2.0 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.8, 145.6, 141.6, 134.6, 131.2, 129.9, 128.5, 128.5, 126.3, 124.9, 121.8, 120.0, 118.0, 109.8, 96.4, 70.8, 65.6, 52.0, 43.7, 37.4, 30.7, 19.2, 13.8.

HRMS (ESI): m/z calcd for $C_{25}H_{25}ClNO_2$ ($[M+H]^+$): 406.1568; found: 406.1561.

benzyl 10-chloro-2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxylate (3ab)



73.2 mg, 83% yield.; white solid; mp 142-144°C.

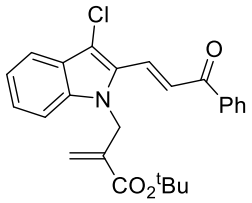
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.43 – 7.37 (m, 2H), 7.37 – 7.30 (m, 5H),

7.30 – 7.21 (m, 3H), 7.19 – 7.08 (m, 3H), 6.11 (t, *J* = 1.8 Hz, 1H), 5.21 (s, 2H), 4.48 – 4.41 (m, 2H), 4.35 (d, *J* = 10.4 Hz, 1H), 3.44 (ddd, *J* = 16.3, 8.0, 2.4 Hz, 1H), 3.32 (dt, *J* = 16.3, 1.7 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 172.5, 145.9, 141.5, 135.5, 134.5, 131.1, 129.9, 128.8, 128.6, 128.5, 128.1, 128.1, 126.3, 124.6, 121.8, 120.0, 118.0, 109.8, 96.5, 70.7, 67.4, 52.0, 43.7, 37.4.

HRMS (ESI): m/z calcd for $C_{28}H_{23}ClNO_2$ ($[M+H]^+$): 440.1412; found: 440.1405.

tert-butyl (E)-2-((3-chloro-2-(3-oxo-3-phenylprop-1-en-1-yl)-1H-indol-1-yl)methyl)acrylate (4a)

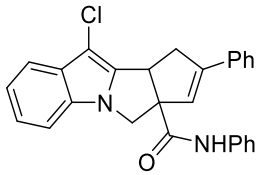


^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 – 7.97 (m, 3H), 7.84 (d, *J* = 15.7 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.62 – 7.55 (m, 1H), 7.50 (dd, *J* = 8.2, 6.8 Hz, 2H), 7.32 (ddd, *J* = 8.2, 6.9, 1.2 Hz, 1H), 7.28 – 7.17 (m, 2H), 6.16 (d, *J* = 1.9 Hz, 1H), 5.10 (t, *J* = 2.0 Hz, 2H), 4.91 (d, *J* = 2.0 Hz, 1H), 1.56 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 164.5, 138.1, 137.2, 137.1, 133.0, 129.7, 129.4, 128.8, 128.5, 126.0, 125.6, 124.8, 123.5, 121.5, 119.3, 110.5, 110.1, 82.1, 44.5, 28.2.

HRMS (ESI): m/z calcd for $C_{25}H_{24}ClNO_3$ ($[M+H]^+$): 422.1517; found: 422.1515.

10-chloro-N,2-diphenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indole-3a(4H)-carboxamide (5)



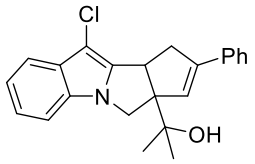
54.2 mg, 64% yield.; white solid; mp 167-169°C.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 2.7 Hz, 1H), 7.51 (dtdd, *J* = 10.5, 6.3, 4.7, 2.2 Hz, 5H), 7.40 – 7.29 (m, 5H), 7.26 – 7.10 (m, 4H), 6.26 (t, *J* = 1.8 Hz, 1H), 5.01 (d, *J* = 10.1 Hz, 1H), 4.32 (dd, *J* = 7.2, 2.6 Hz, 1H), 4.25 (d, *J* = 10.1 Hz, 1H), 3.52 – 3.36 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 170.1, 148.9, 140.9, 137.2, 133.9, 131.2, 130.1, 129.2, 129.2, 128.8, 126.4, 125.1, 123.9, 121.8, 120.3, 120.0, 118.0, 110.0, 96.1, 72.0, 52.0, 46.8, 36.9.

HRMS (ESI): m/z calcd for $C_{27}H_{22}ClN_2O$ ($[M+H]^+$): 425.1415; found: 425.1407.

2-(10-chloro-2-phenyl-1,10b-dihydrocyclopenta[3,4]pyrrolo[1,2-a]indol-3a(4H)-yl)propan-2-ol (6)



53.7 mg, 74% yield.; white solid; mp 181-183°C.

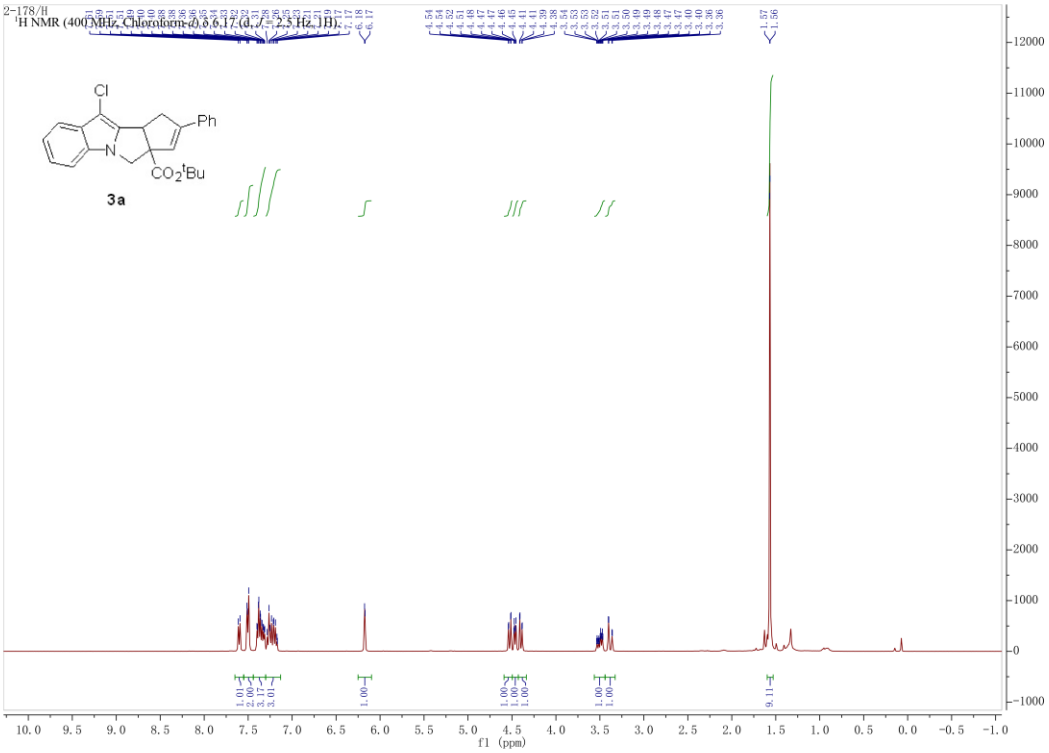
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.44 – 7.39 (m, 2H), 7.29 (t, *J* = 7.3 Hz, 2H), 7.27 – 7.23 (m, 1H), 7.22 (s, 1H), 7.19 (td, *J* = 7.1, 1.5 Hz, 1H), 7.12 (ddd, *J* = 14.3, 7.7, 1.4 Hz, 2H), 6.10 (t, *J* = 1.9 Hz, 1H), 4.40 (d, *J* = 9.9 Hz, 1H), 4.06 (d, *J* = 10.0 Hz, 1H), 4.03 (dd, *J* = 7.3, 2.7 Hz, 1H), 3.32 – 3.16 (m, 2H), 1.33 (s, 3H), 1.30 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 144.3, 143.4, 135.0, 131.2, 129.9, 128.5, 128.2, 127.3, 126.1, 121.4,

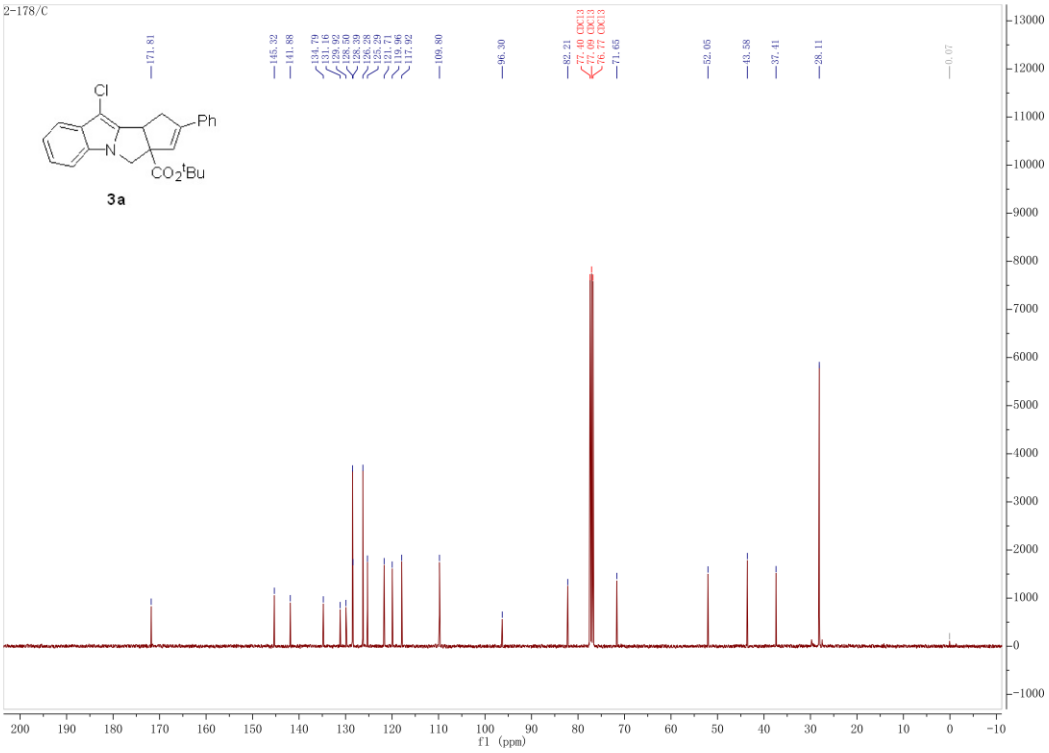
119.8, 117.8, 109.9, 95.5, 74.9, 74.1, 51.2, 41.4, 38.1, 26.8, 26.4.

HRMS (ESI): m/z calcd for $C_{27}H_{22}ClN_2O$ ([M+H]$^+$): 364.1463; found: 364.1456.

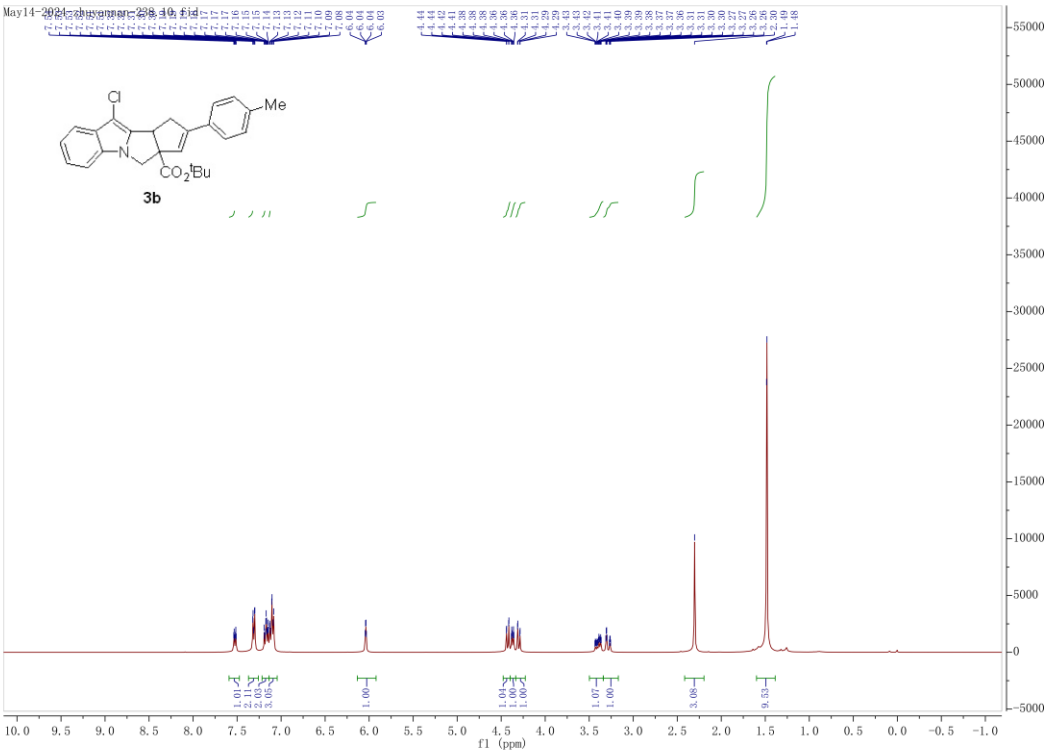
5. NMR data



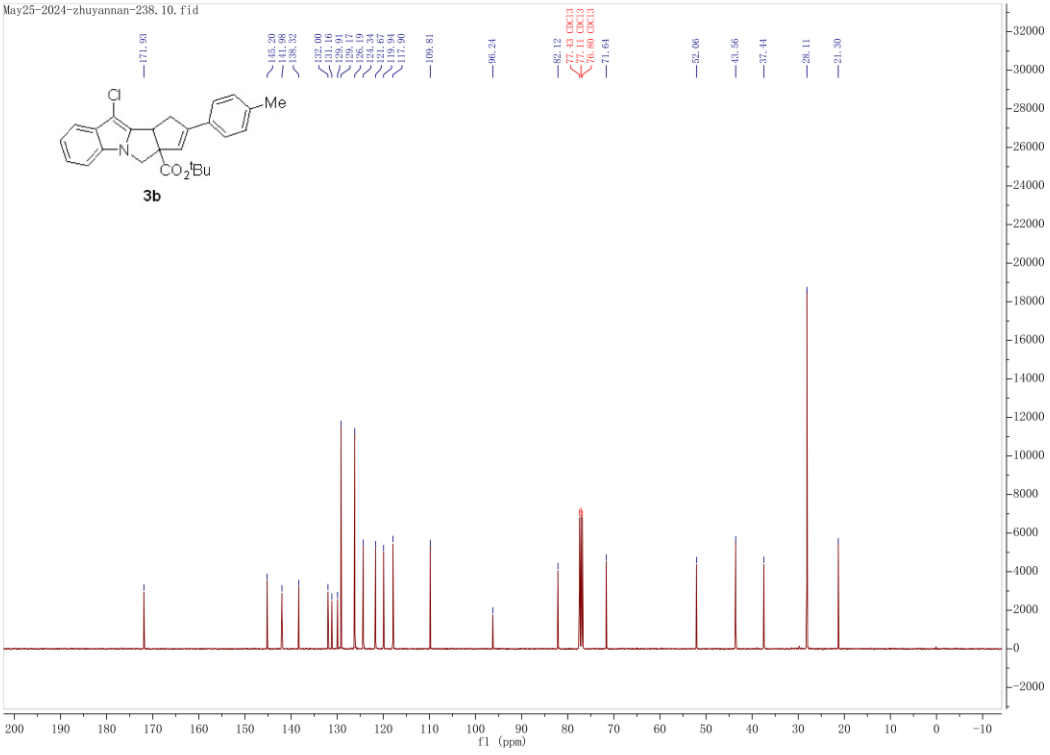
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3a**



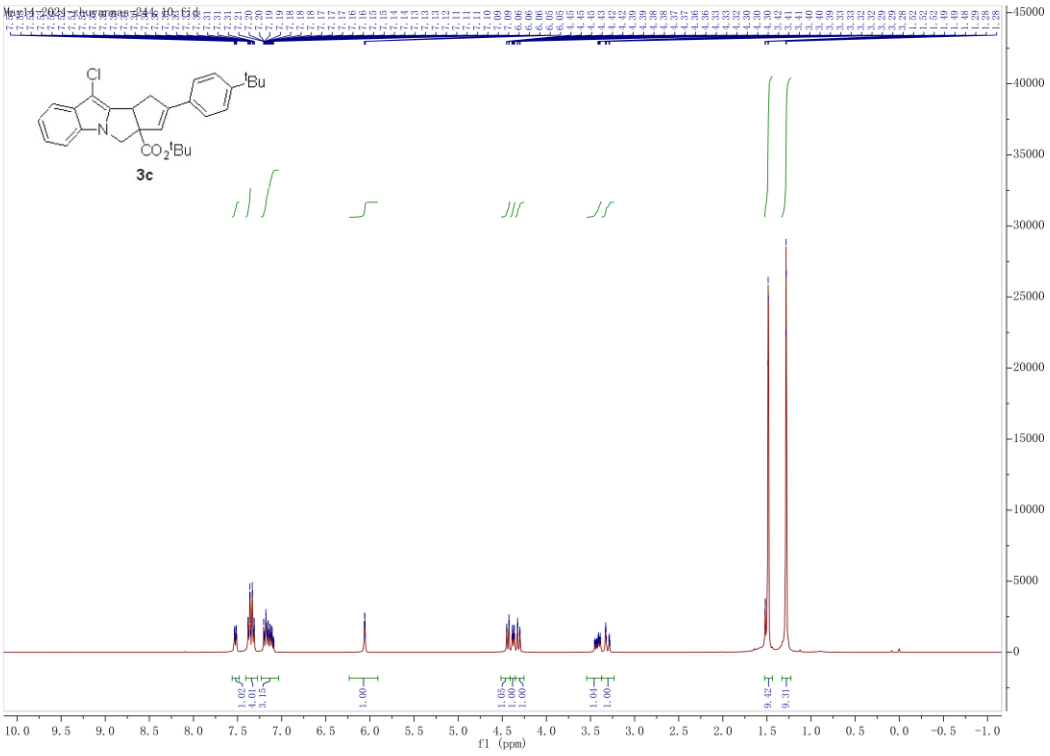
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3a**



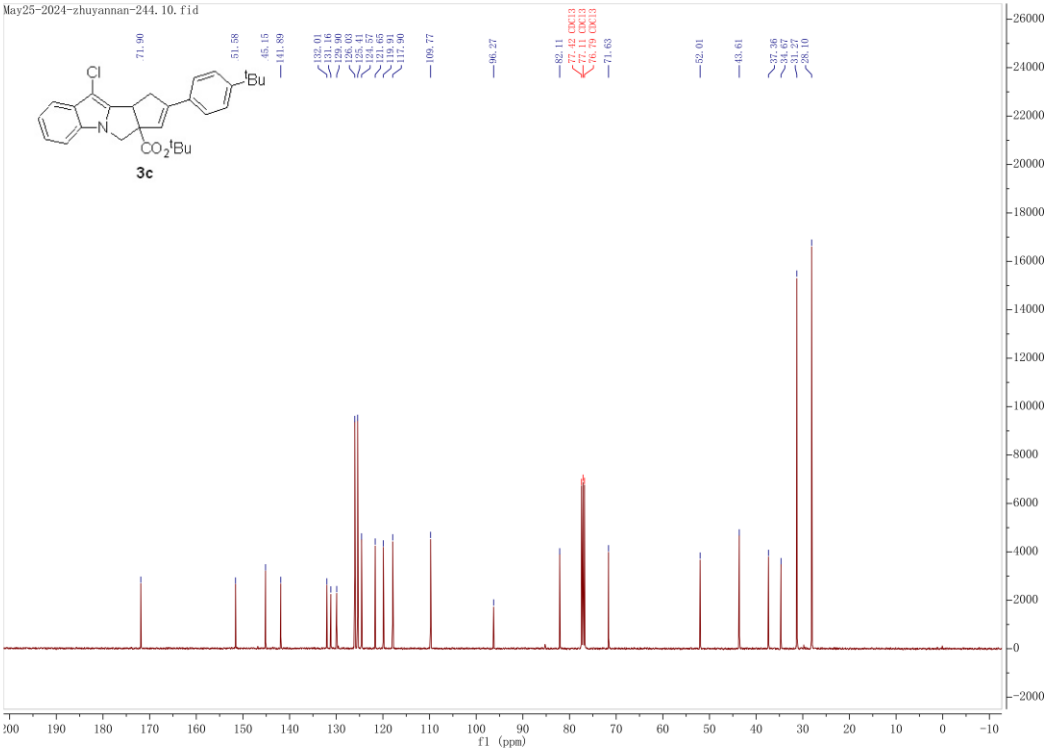
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3b**



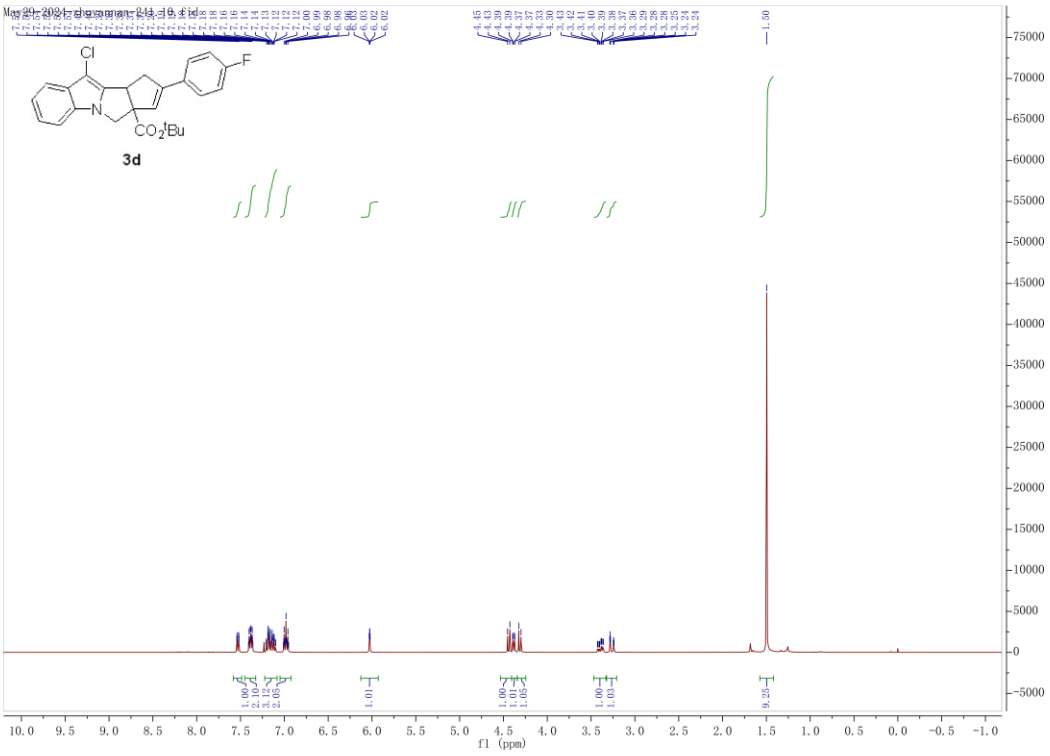
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3b**



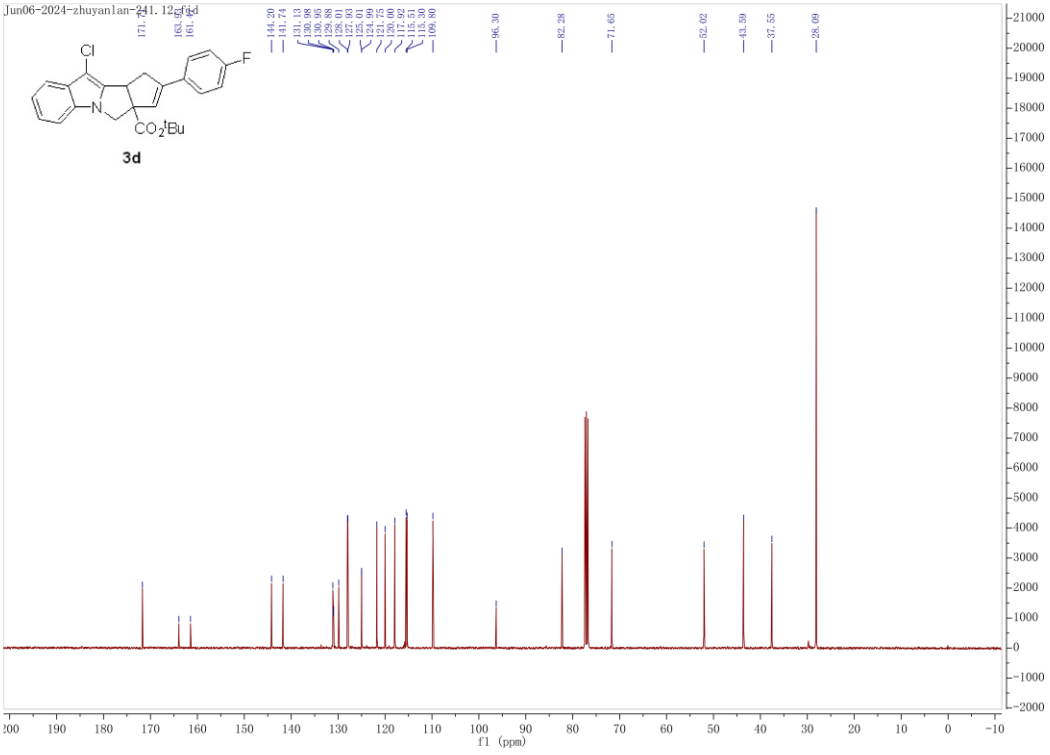
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3c**



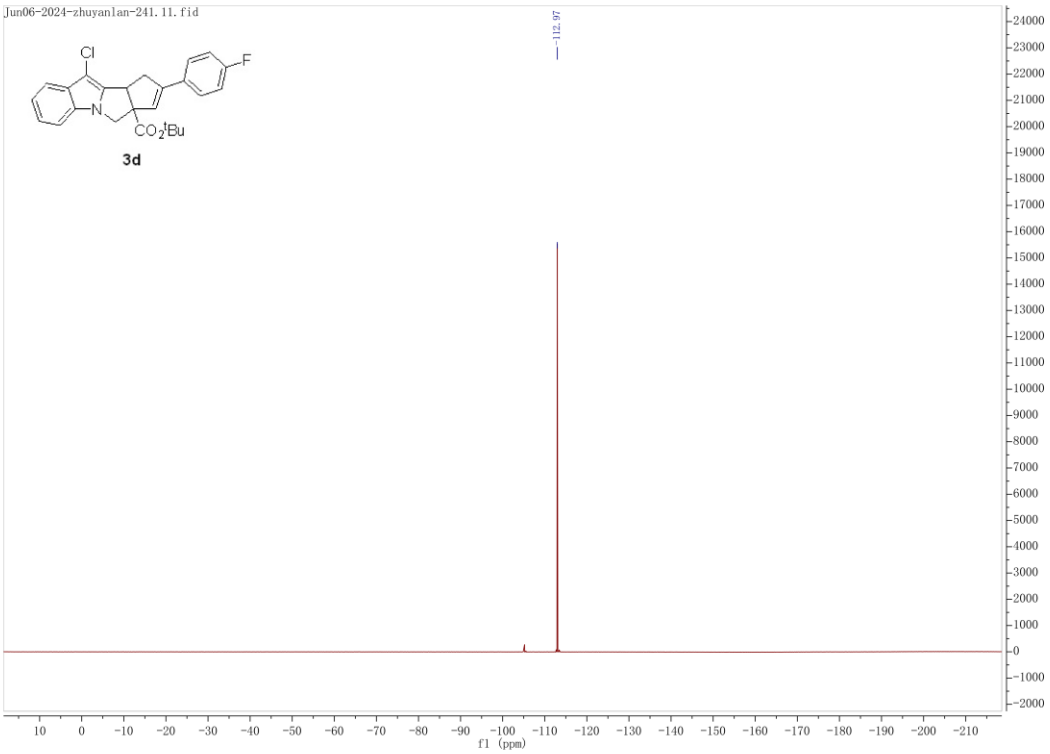
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3c**



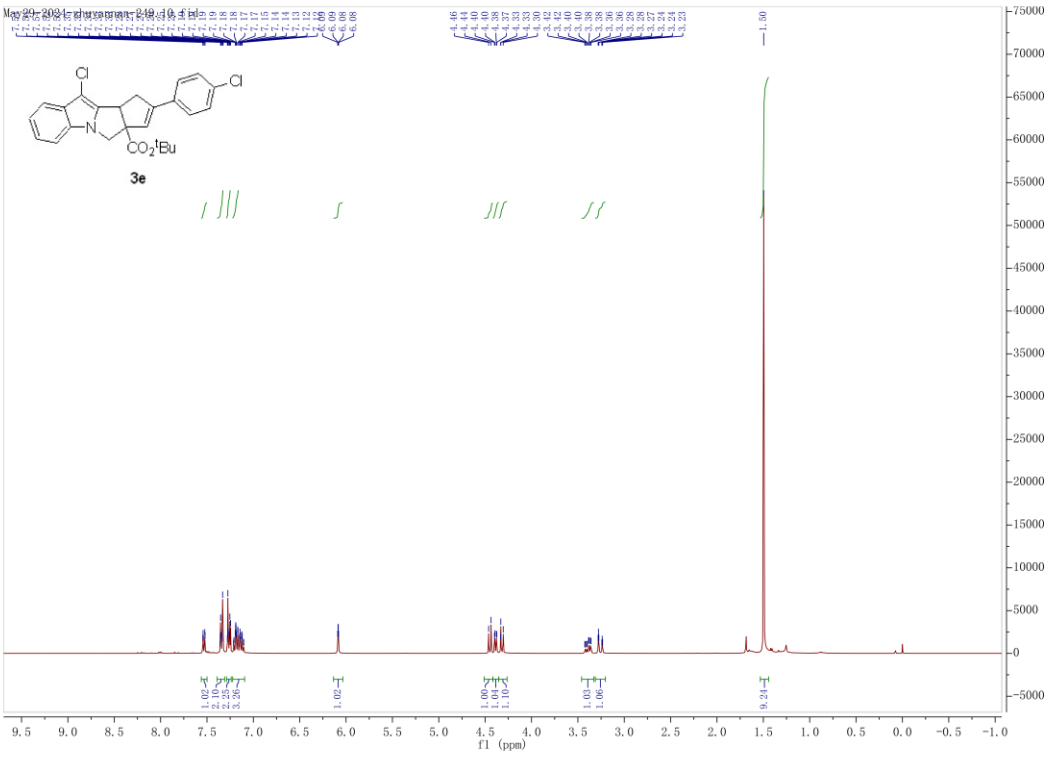
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3d**



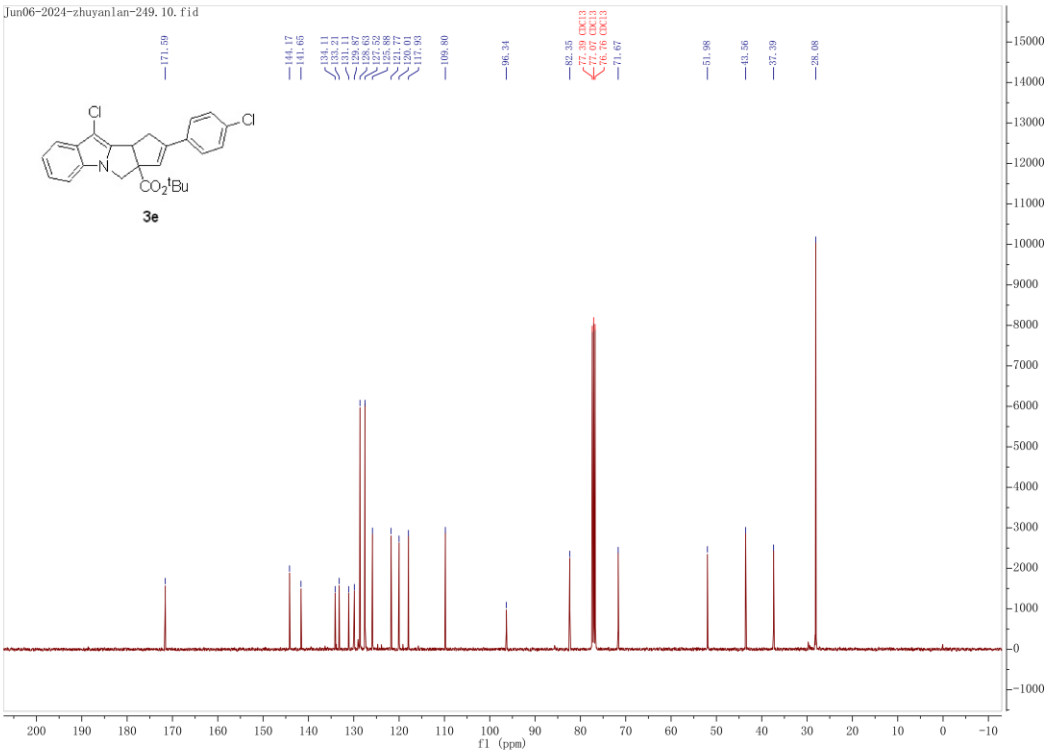
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3d**



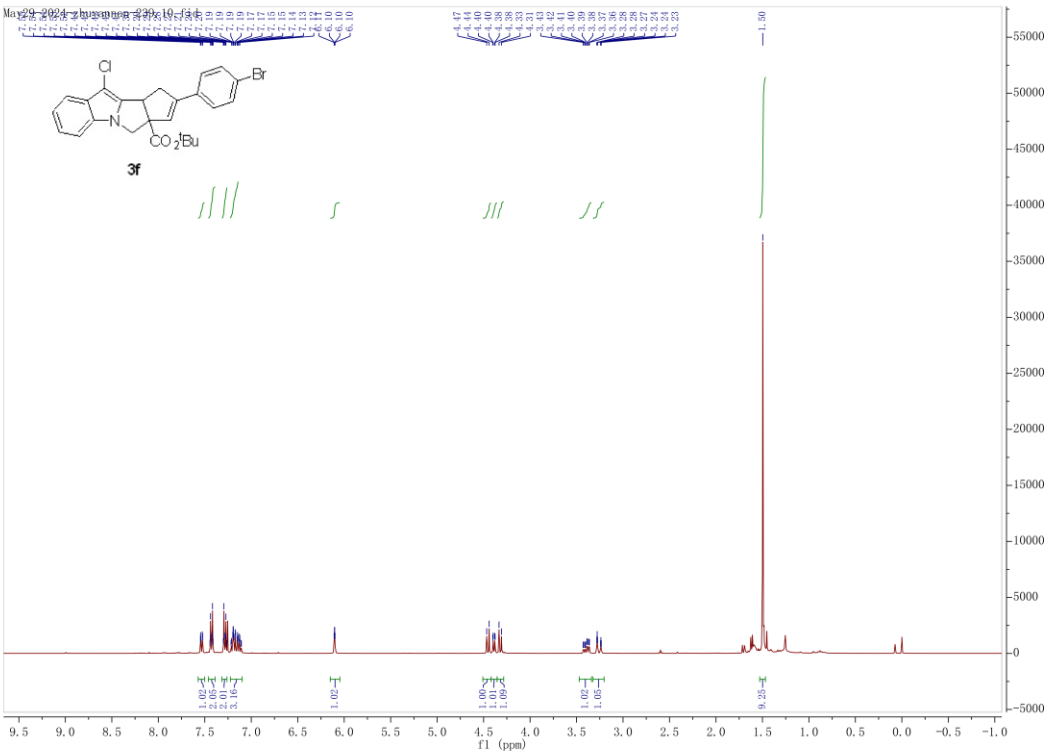
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **3d**



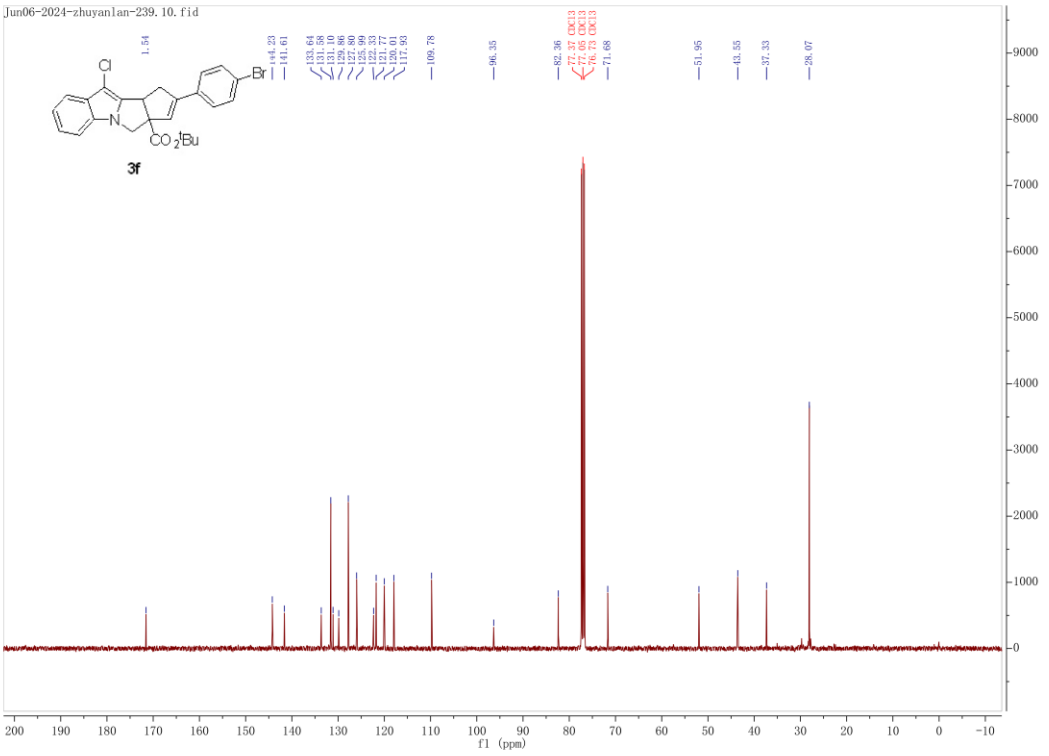
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3e**



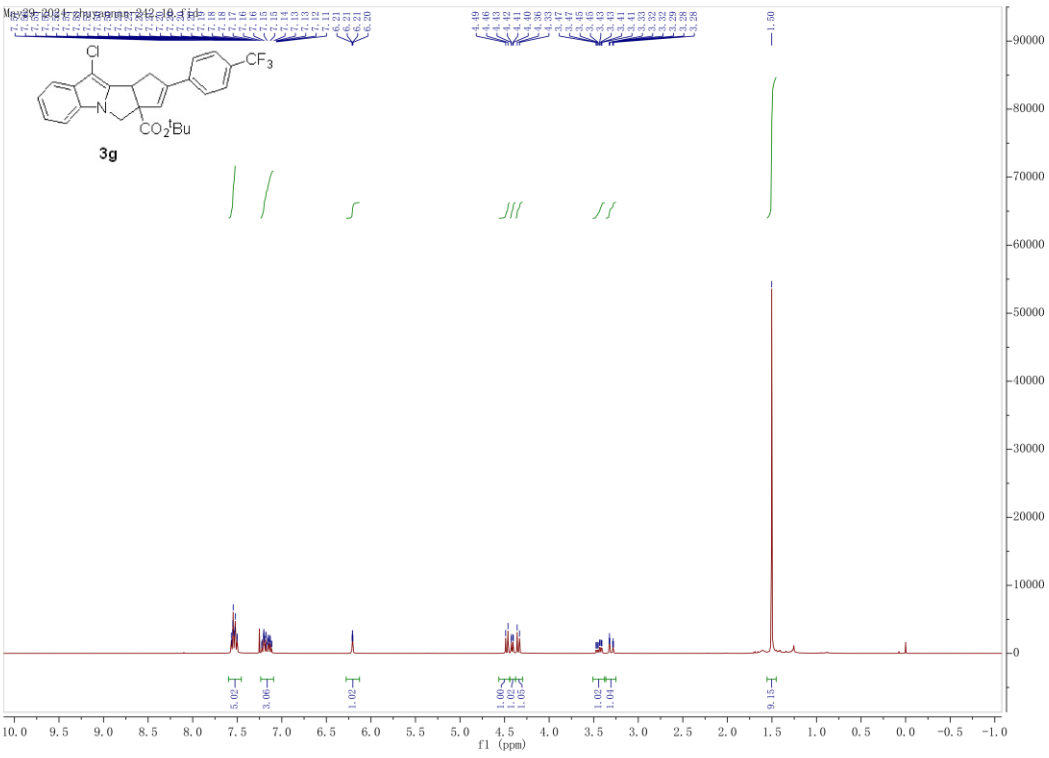
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3e**



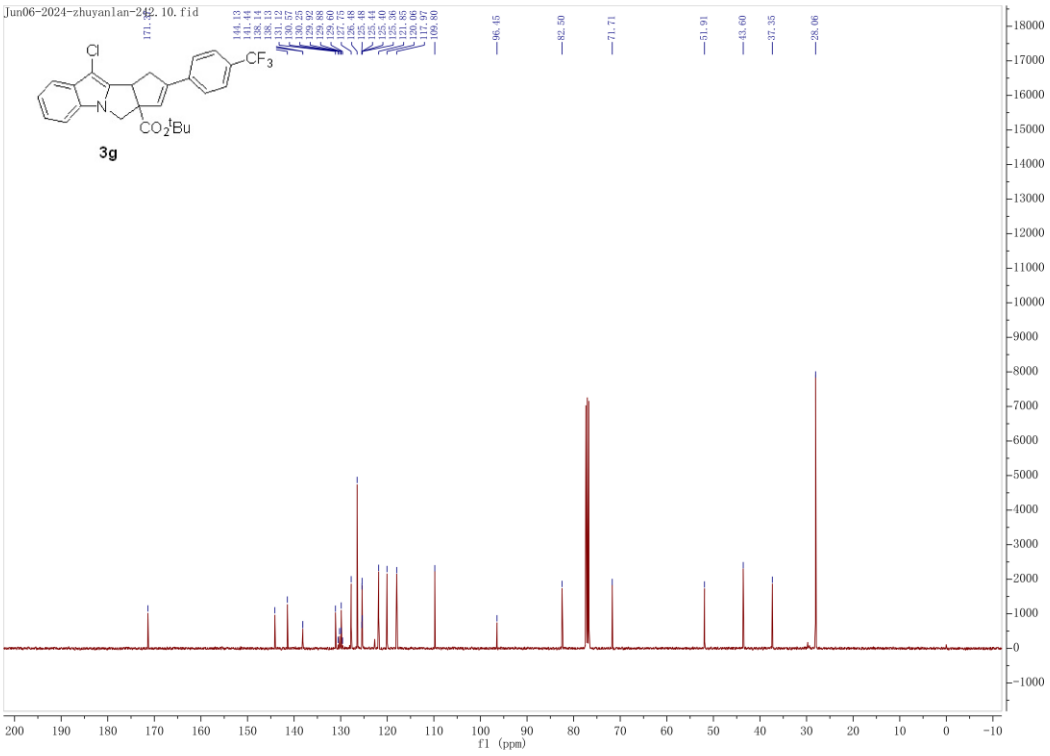
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3f**



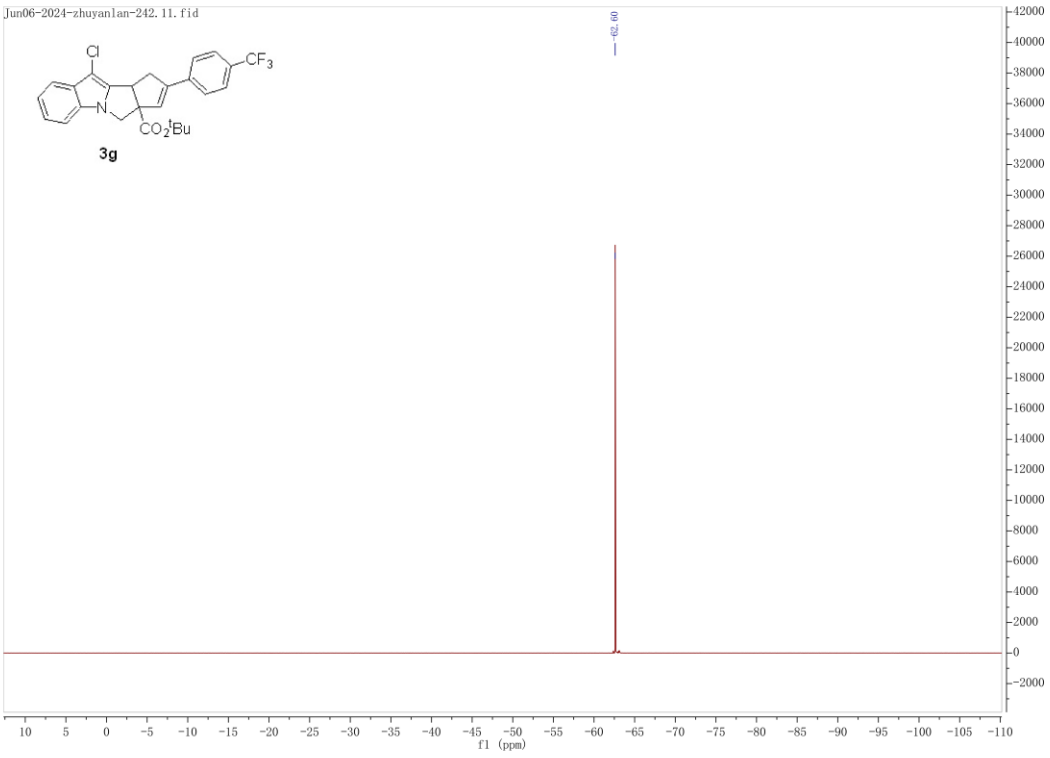
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3f**



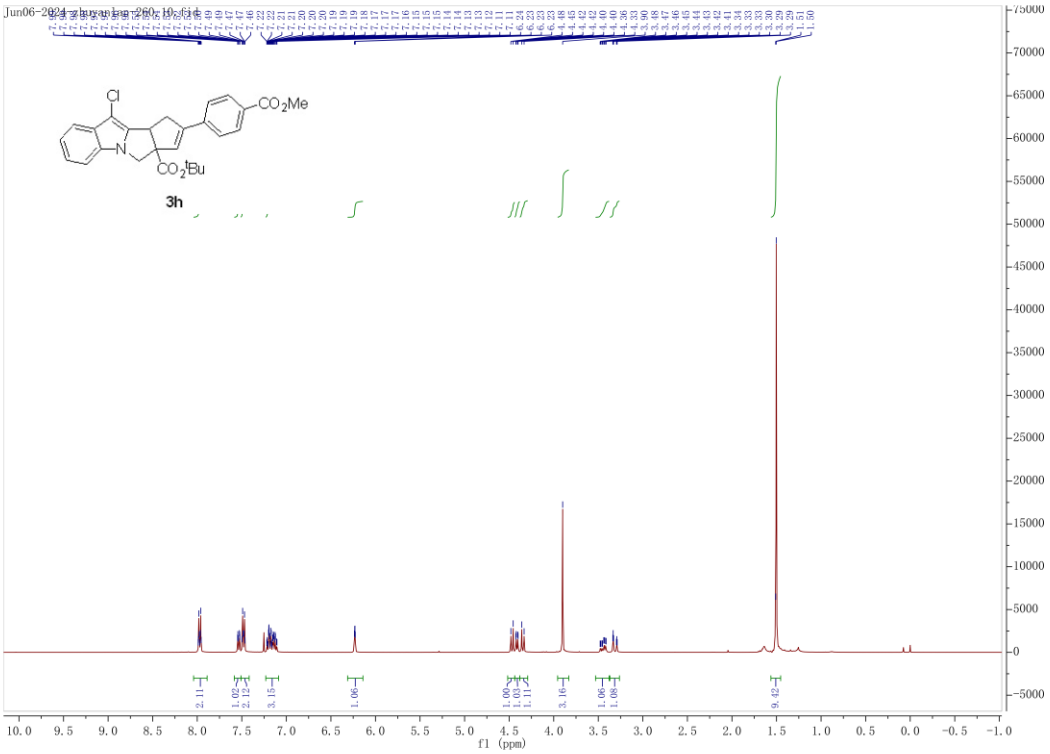
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3g**



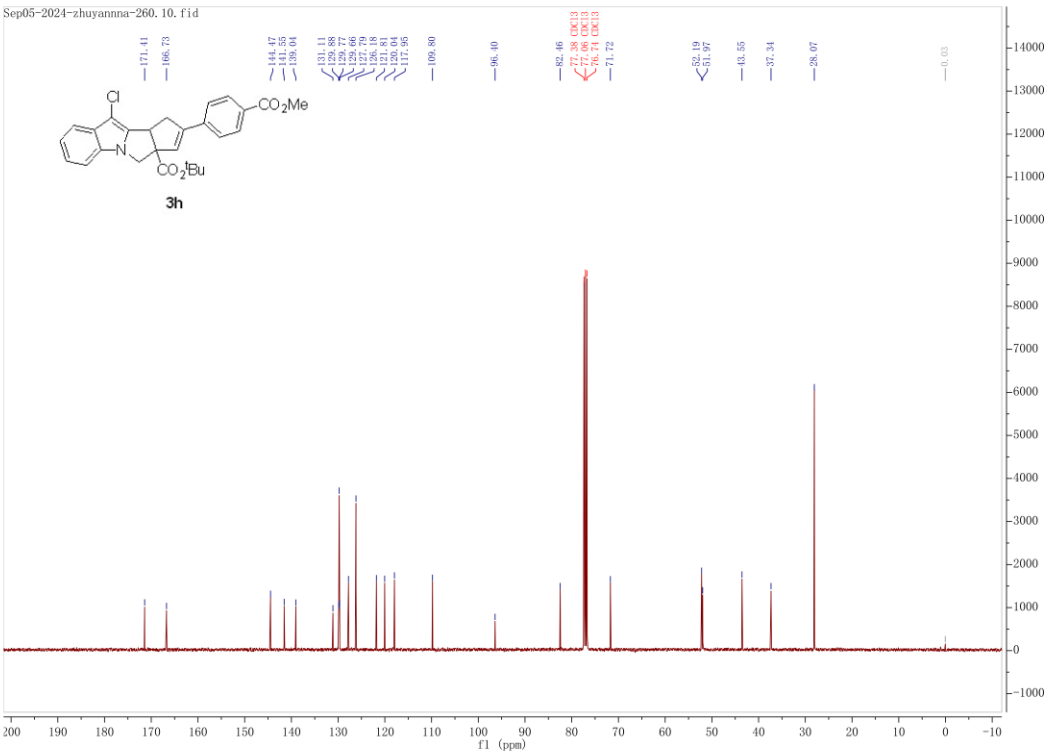
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3g**



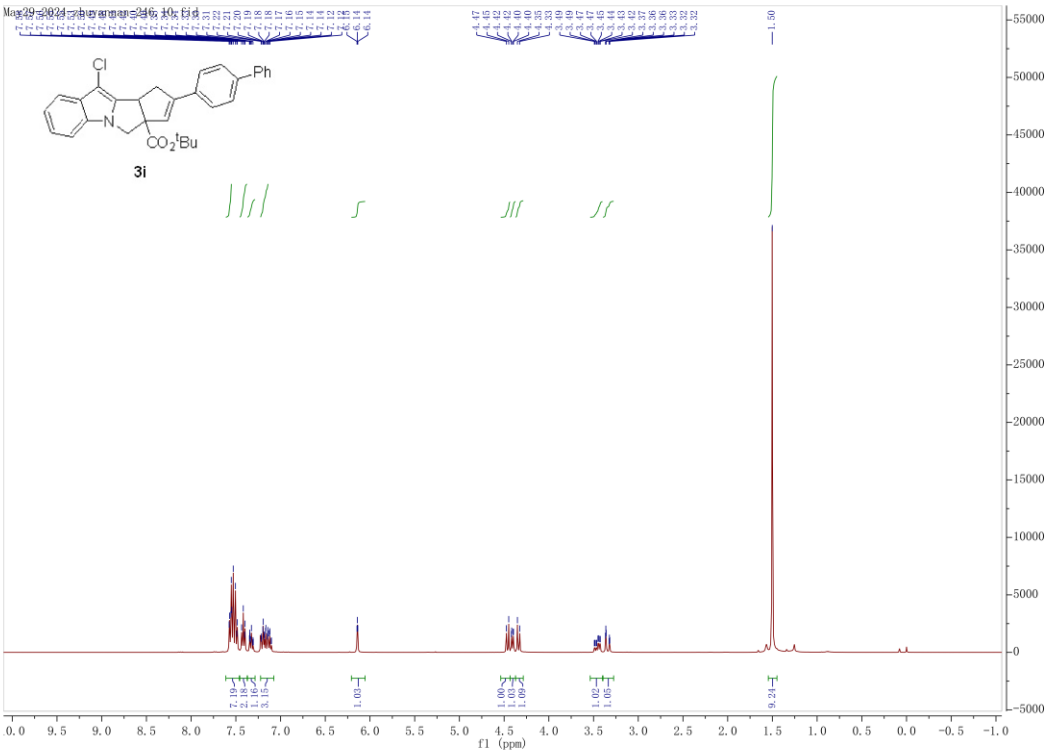
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **3g**



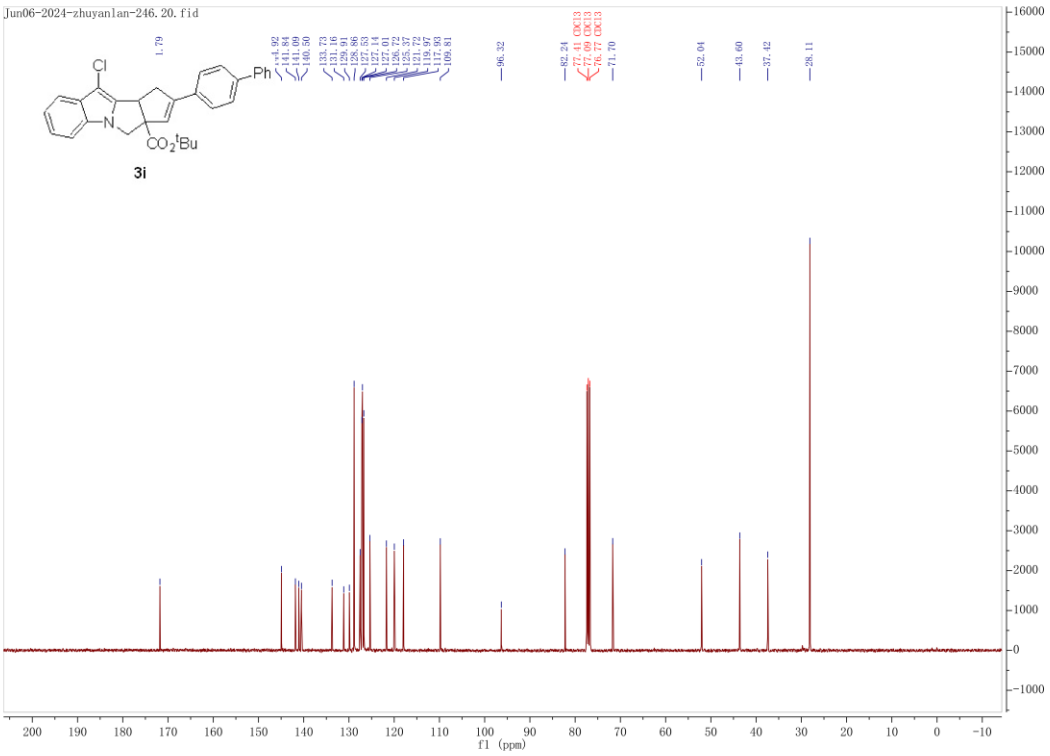
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3h**



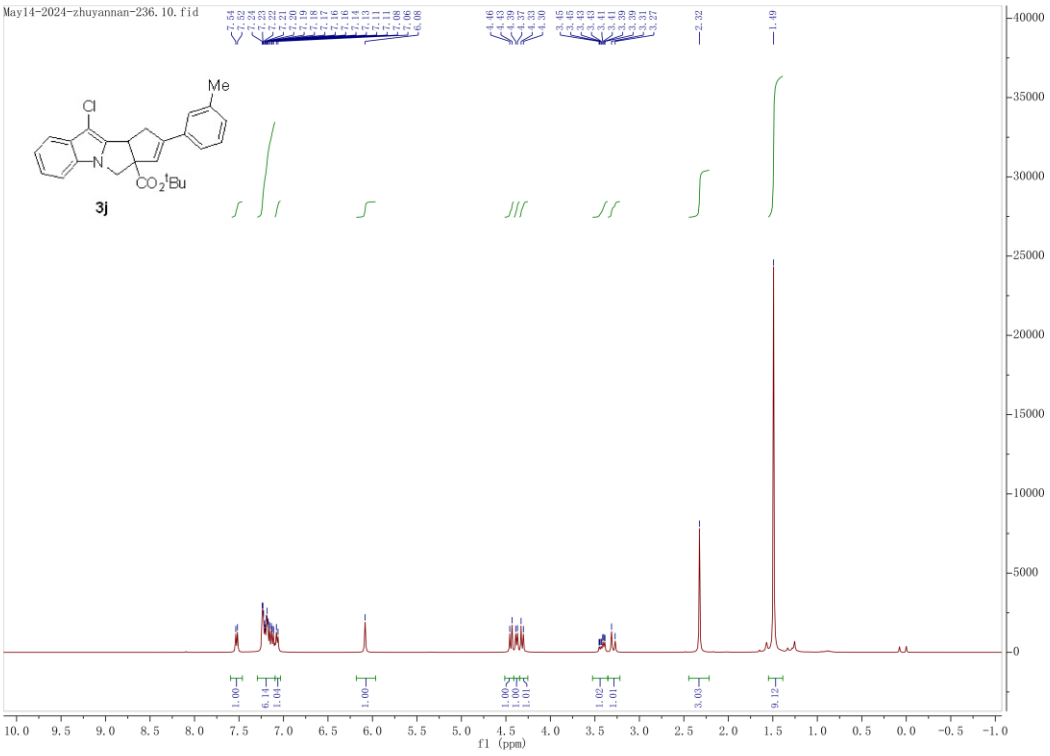
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3h**



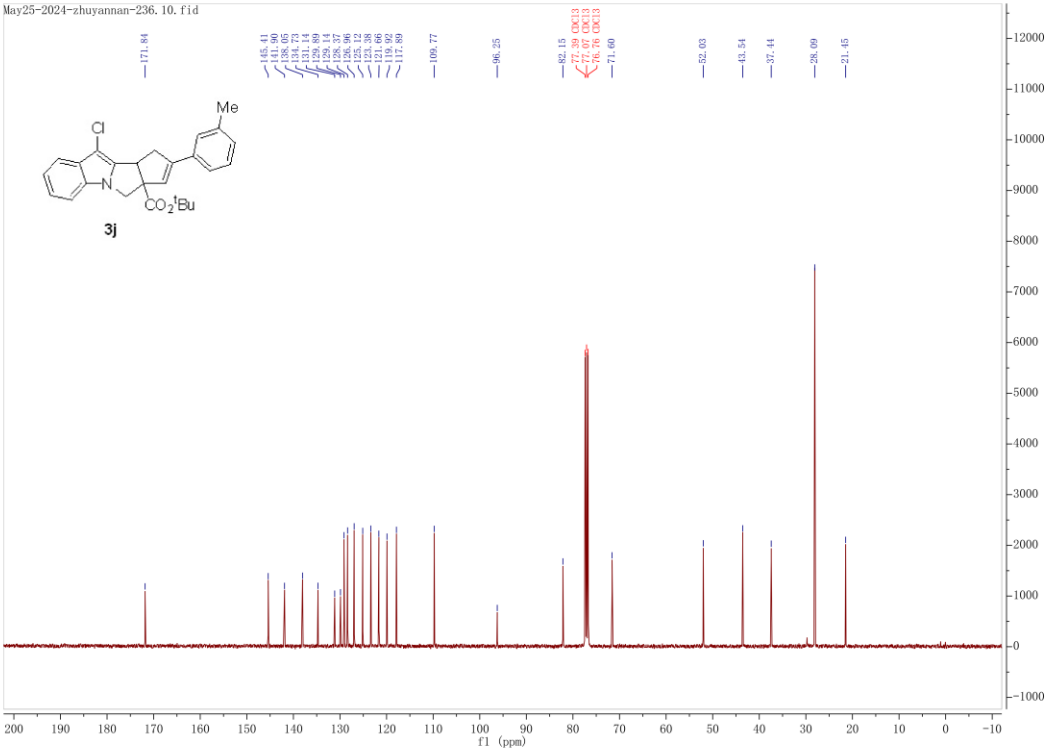
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3i**



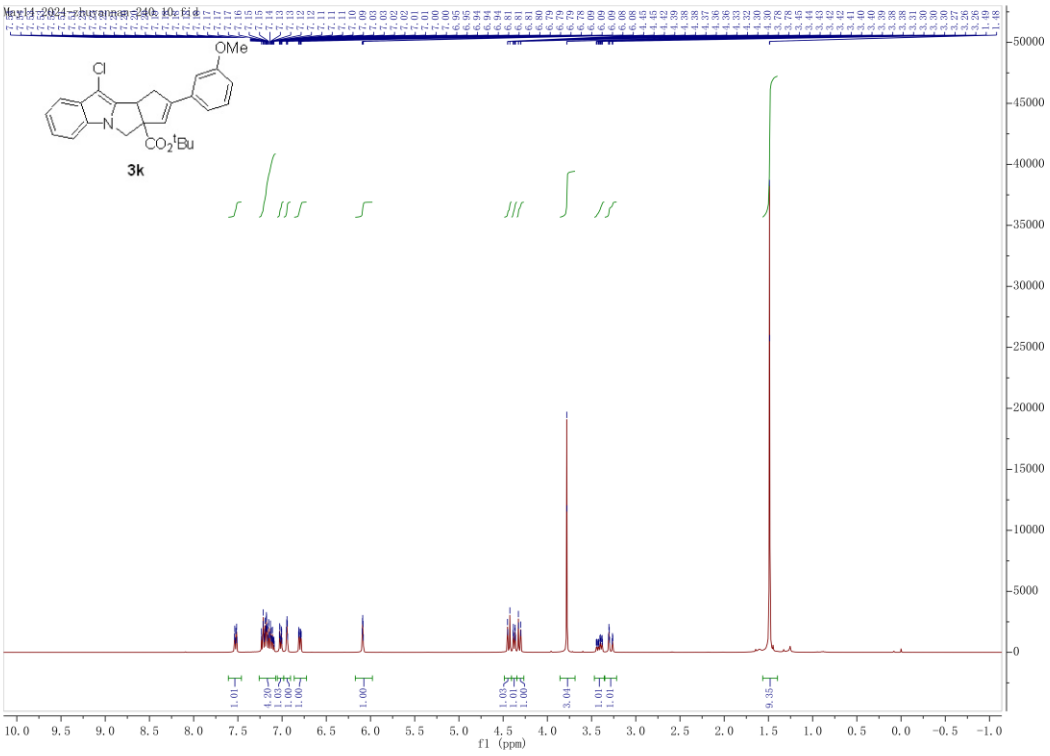
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3i**



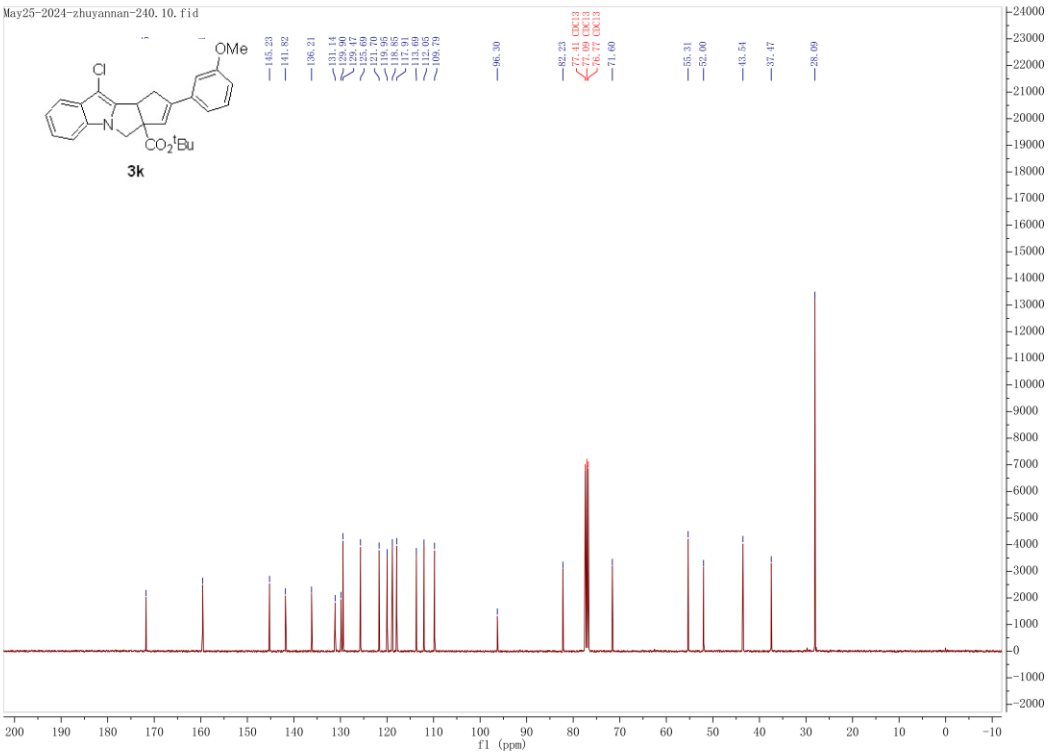
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3j**



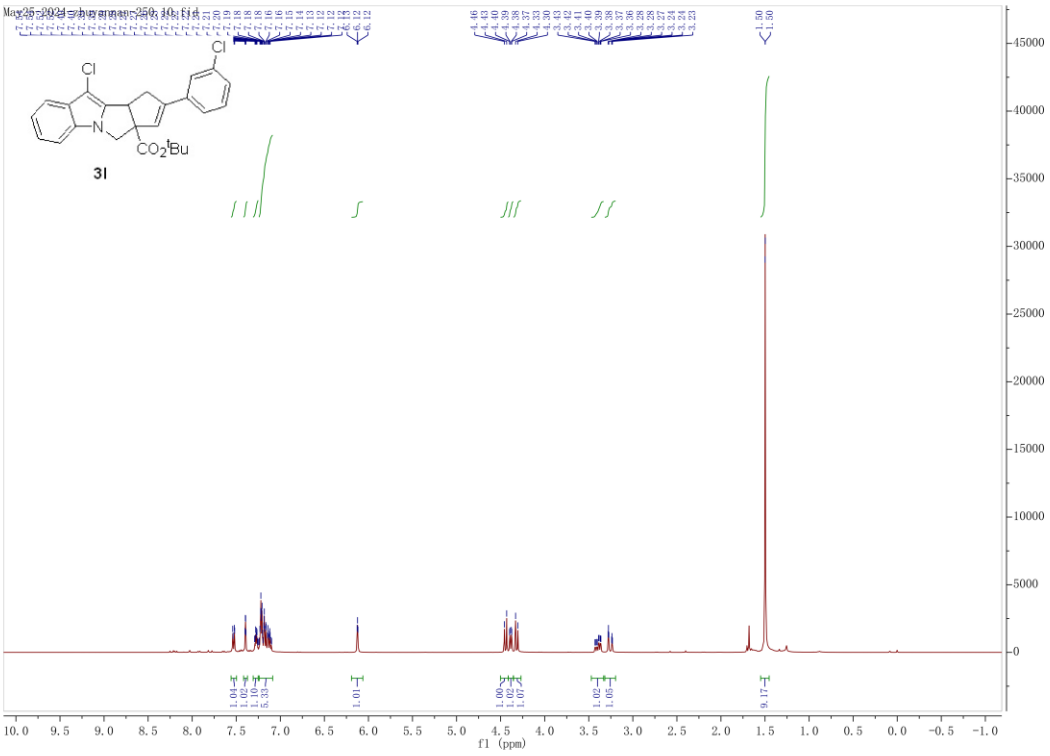
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3j**



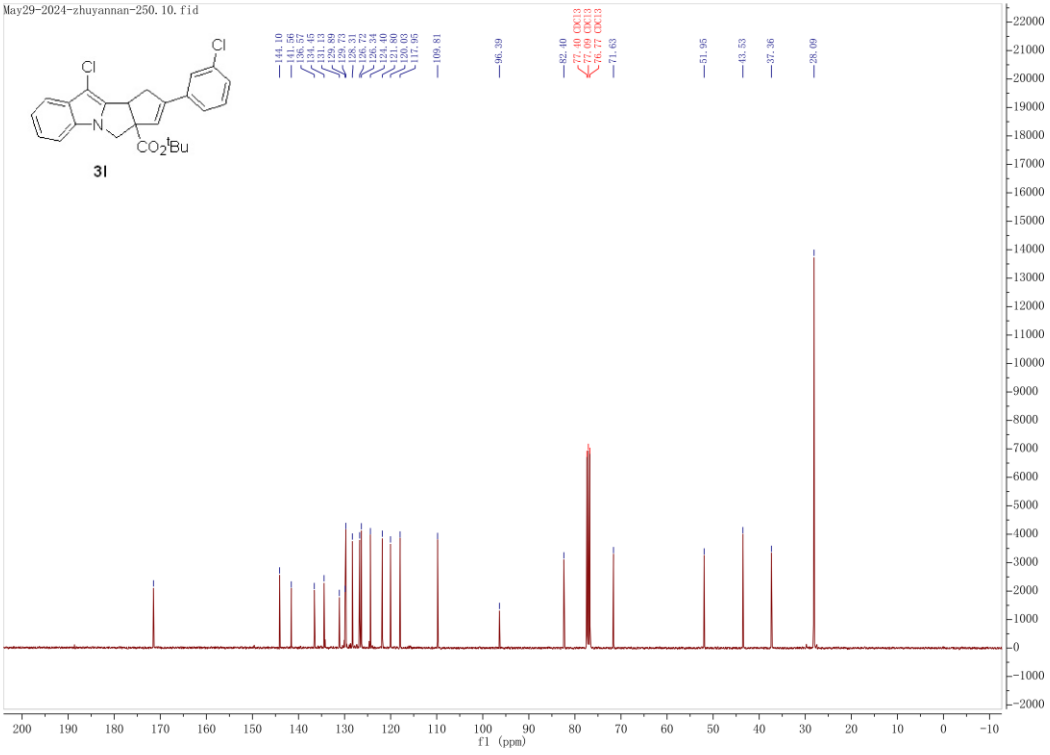
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3k**



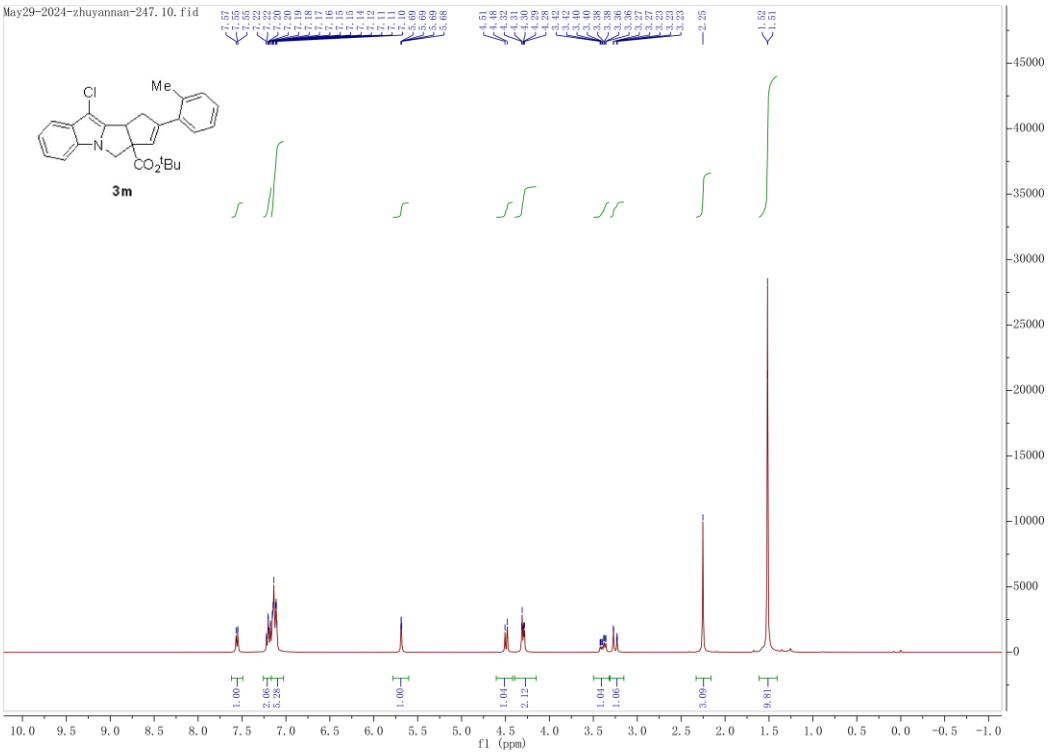
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3k**



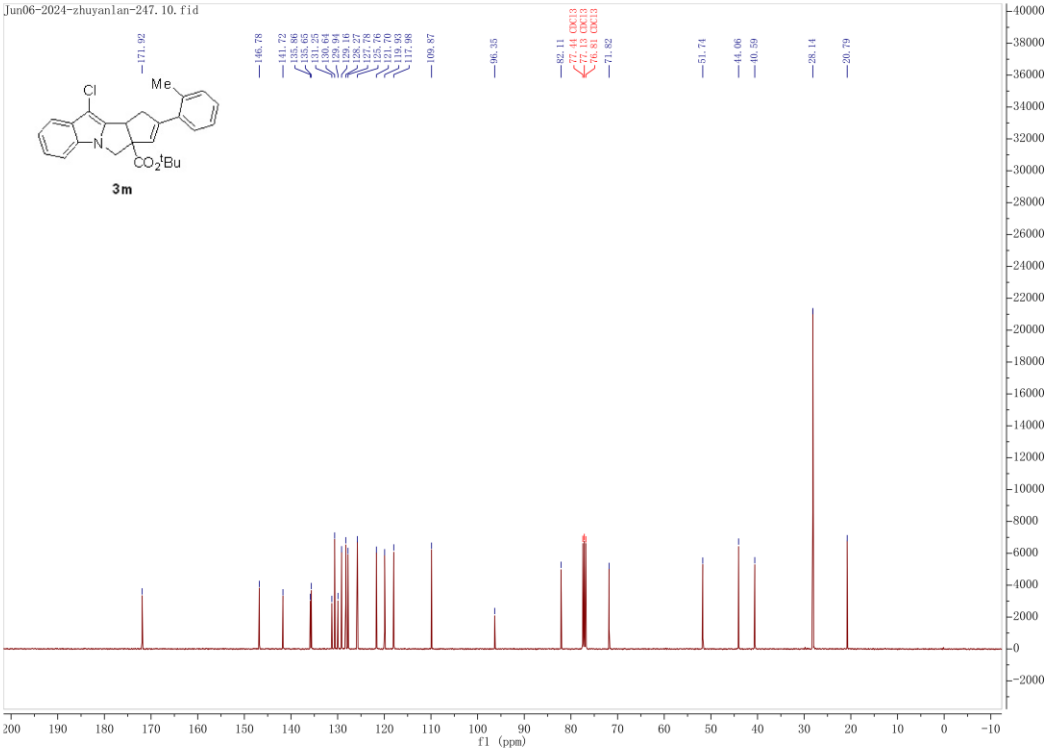
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3l**



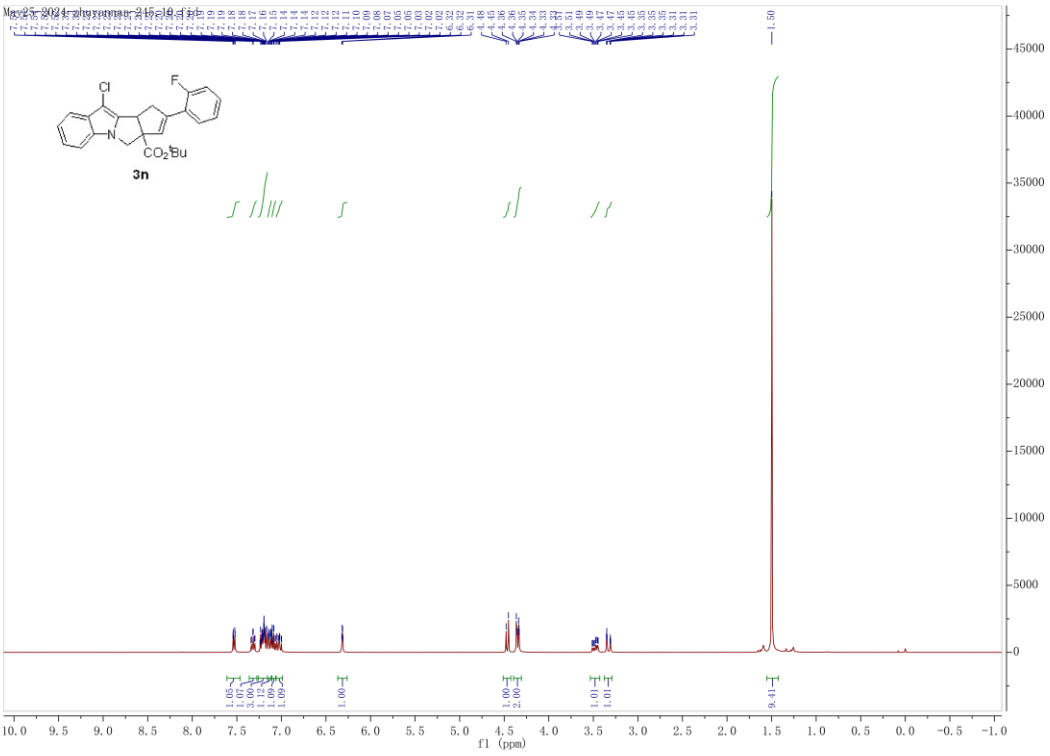
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3l**



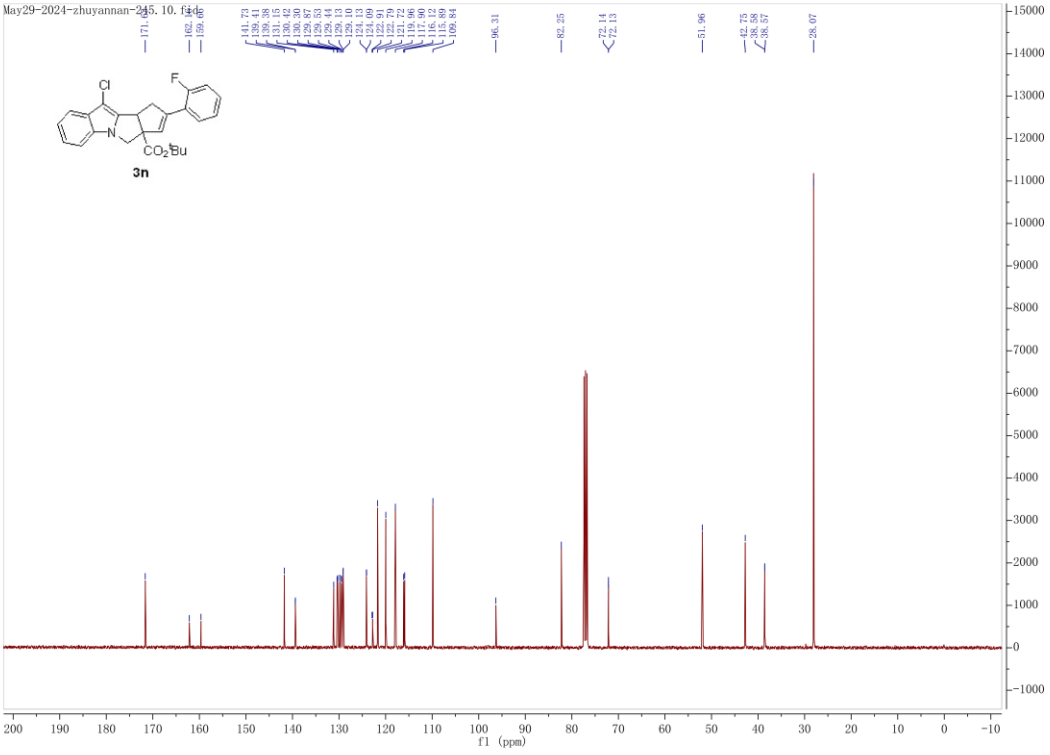
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3m**



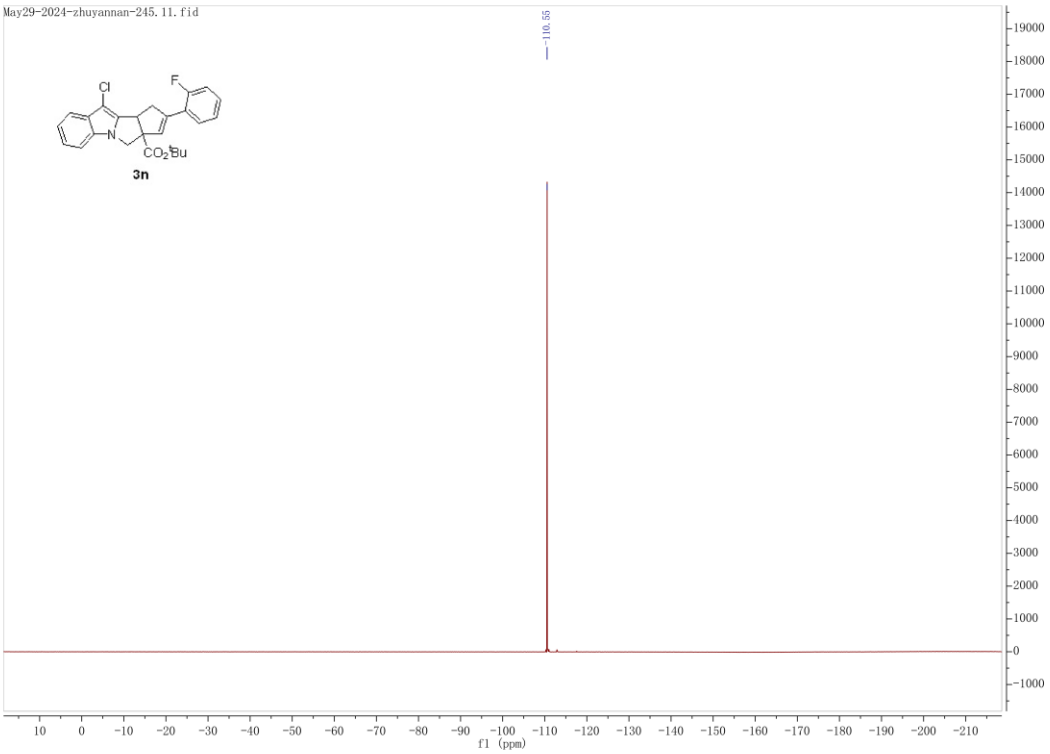
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3m**



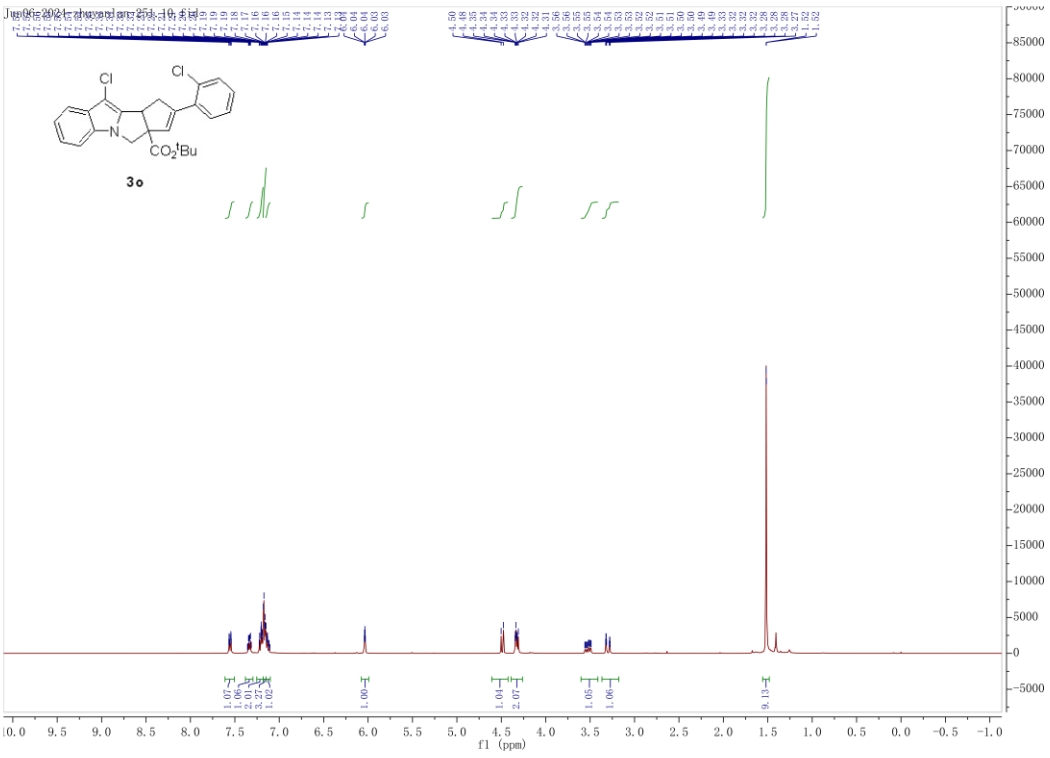
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3n**



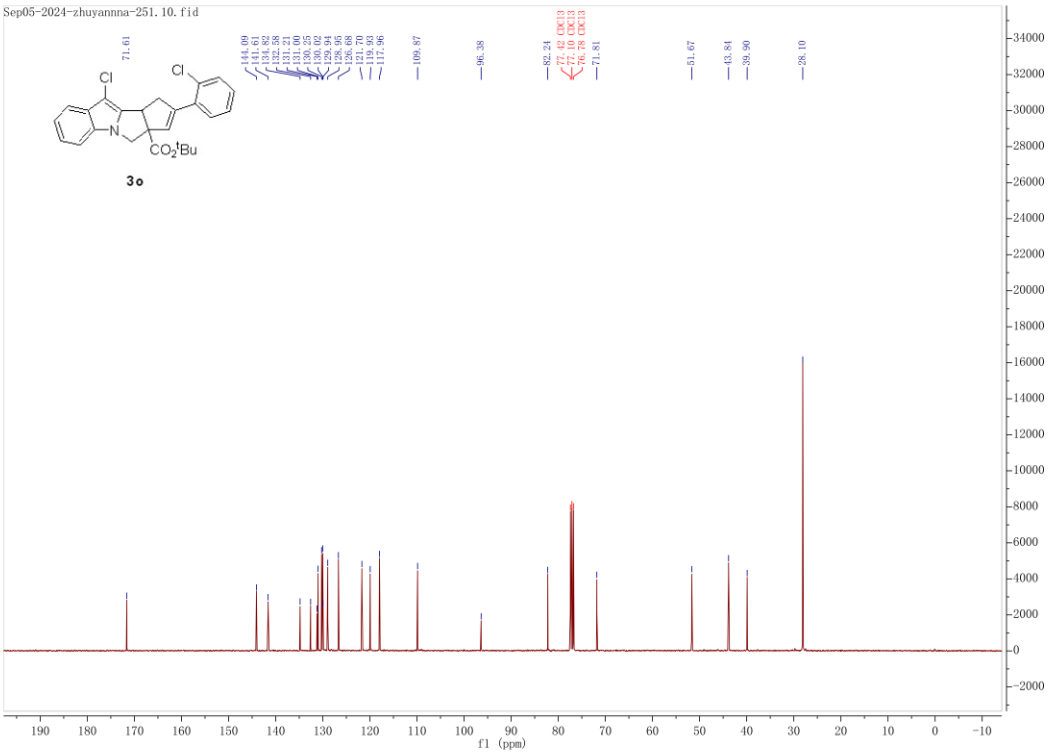
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3n**



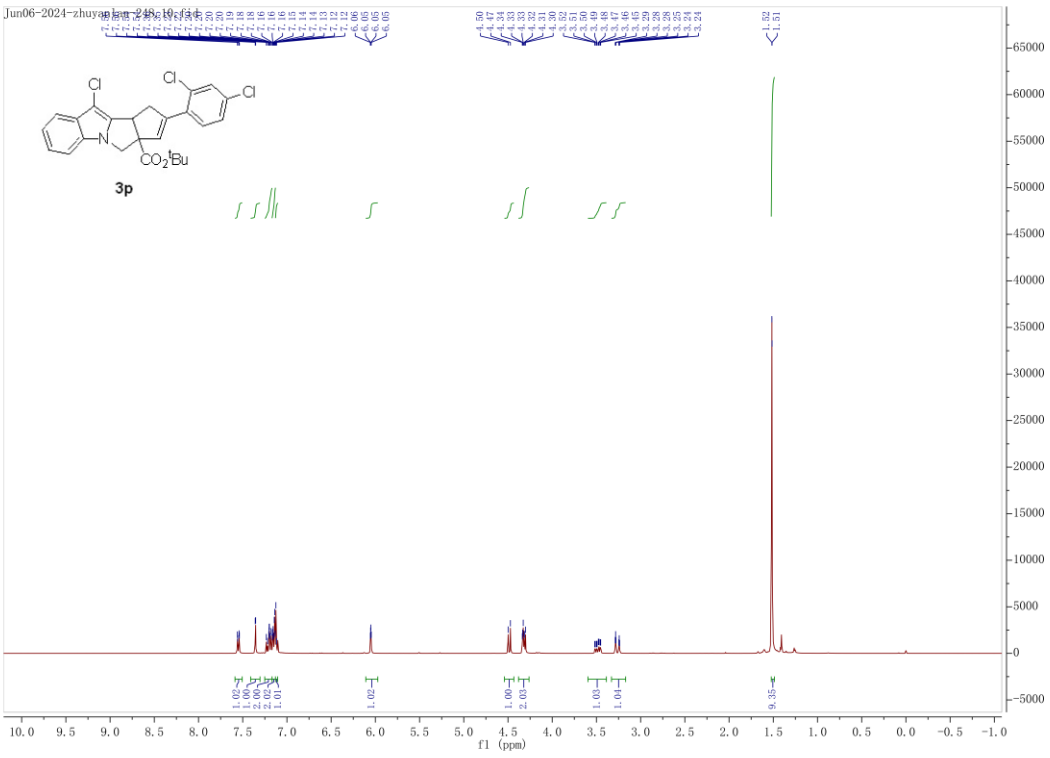
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **3n**



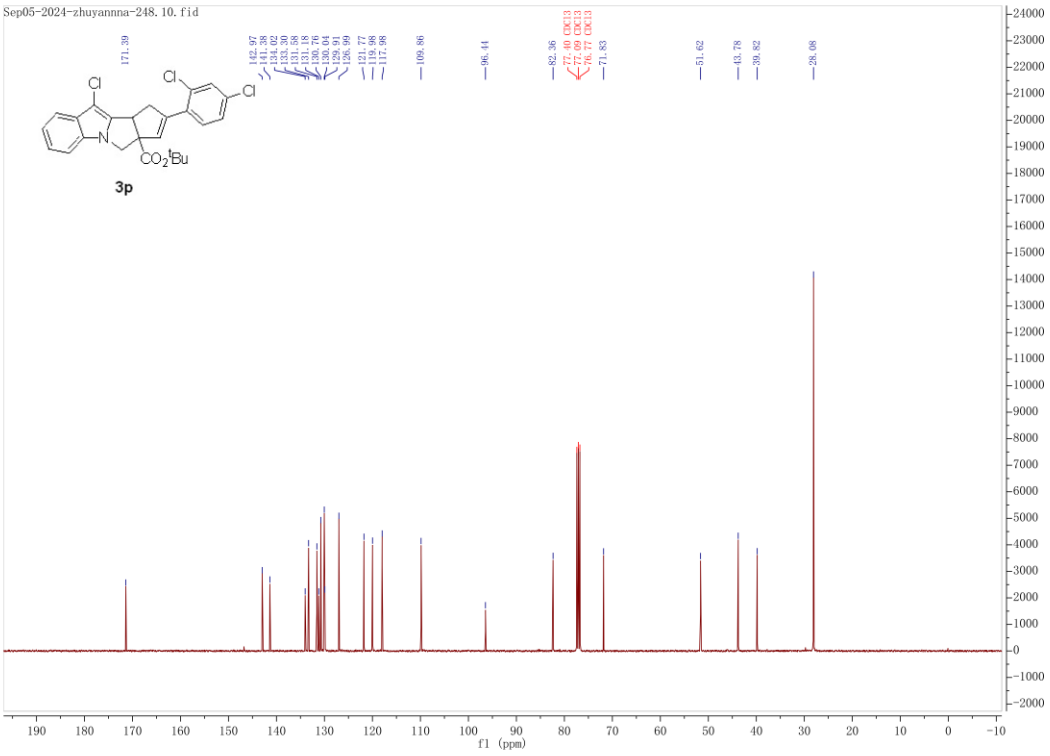
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3o**



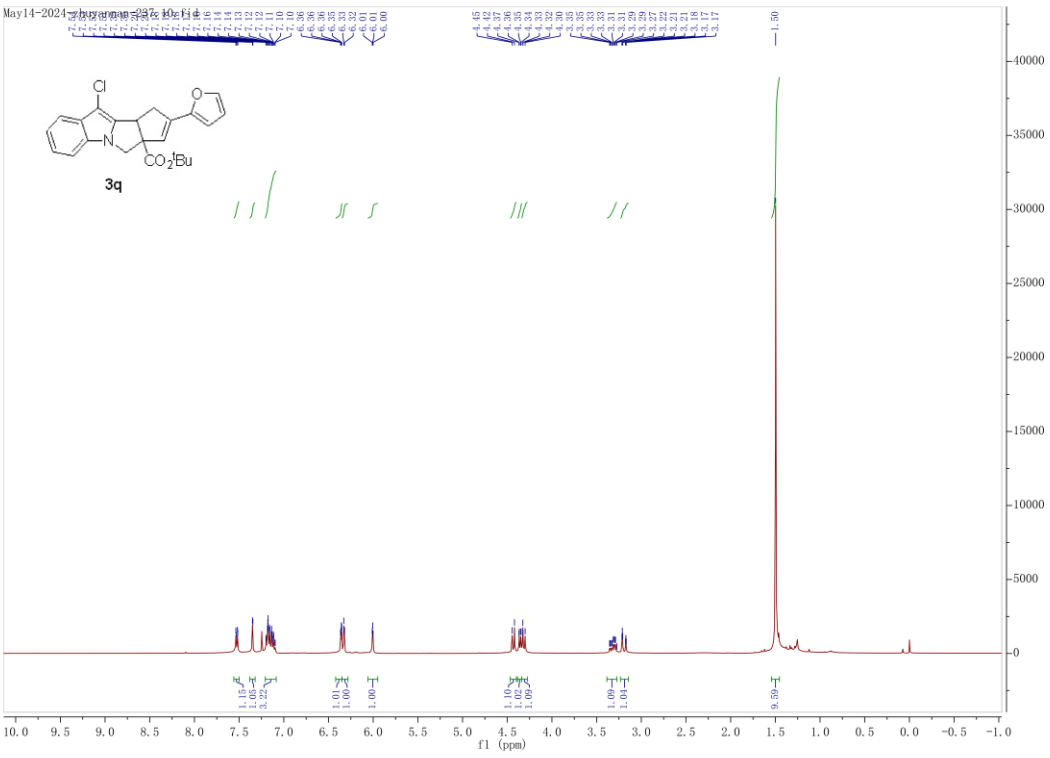
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3o**



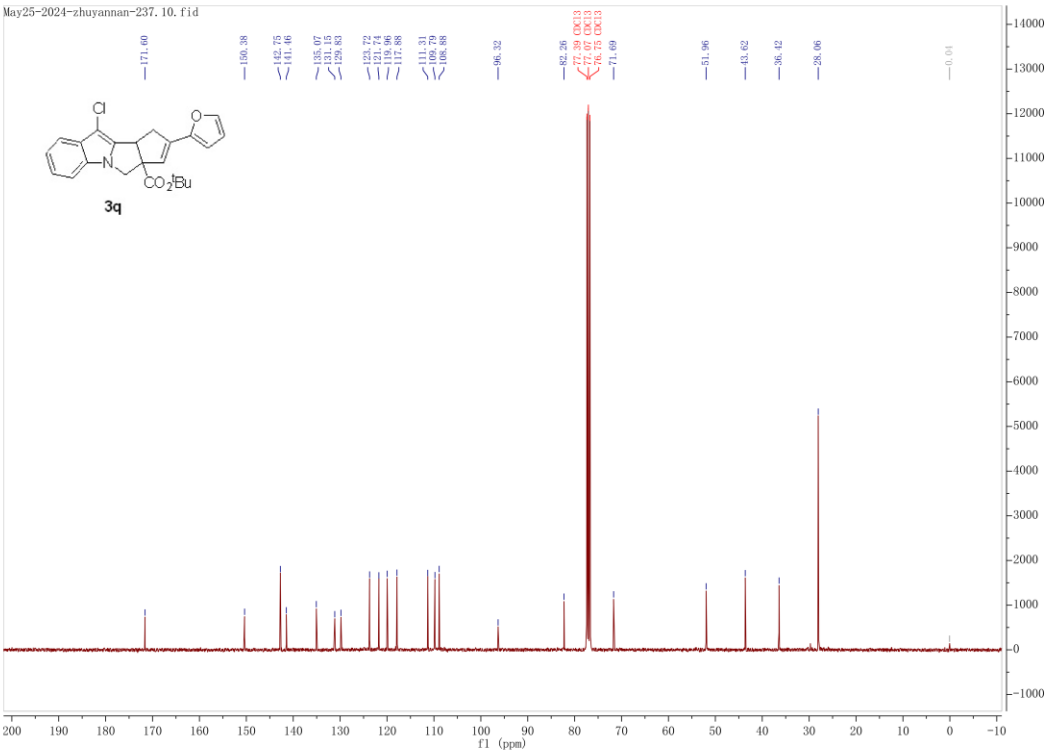
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3p**



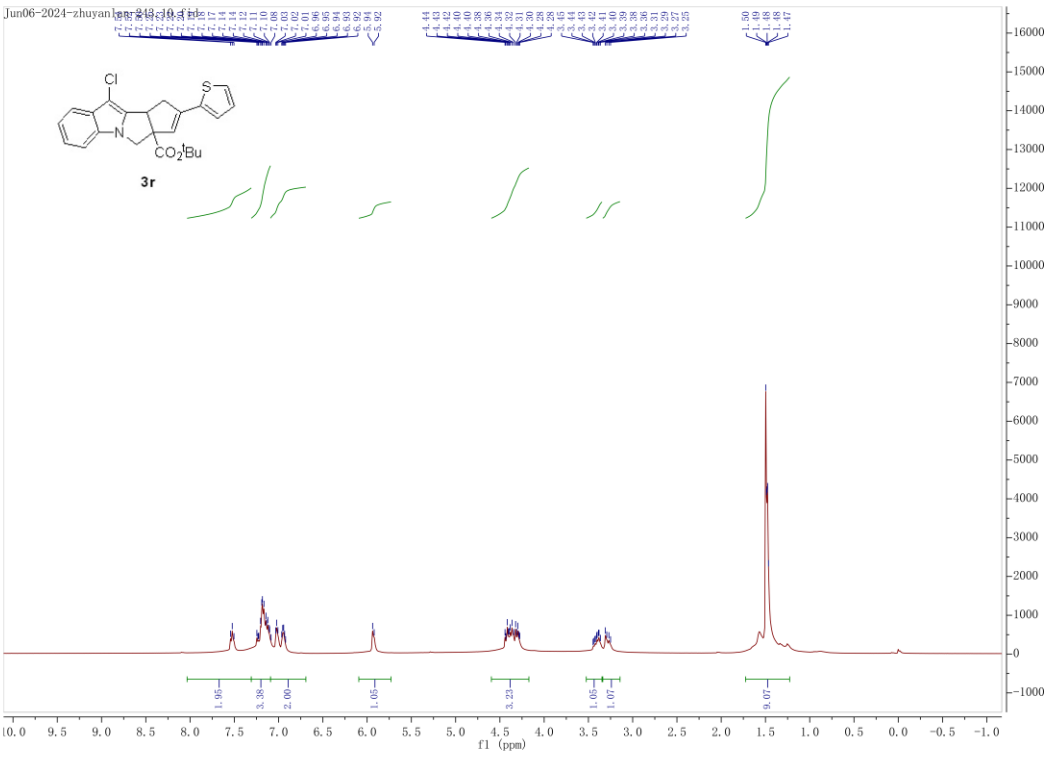
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3p**



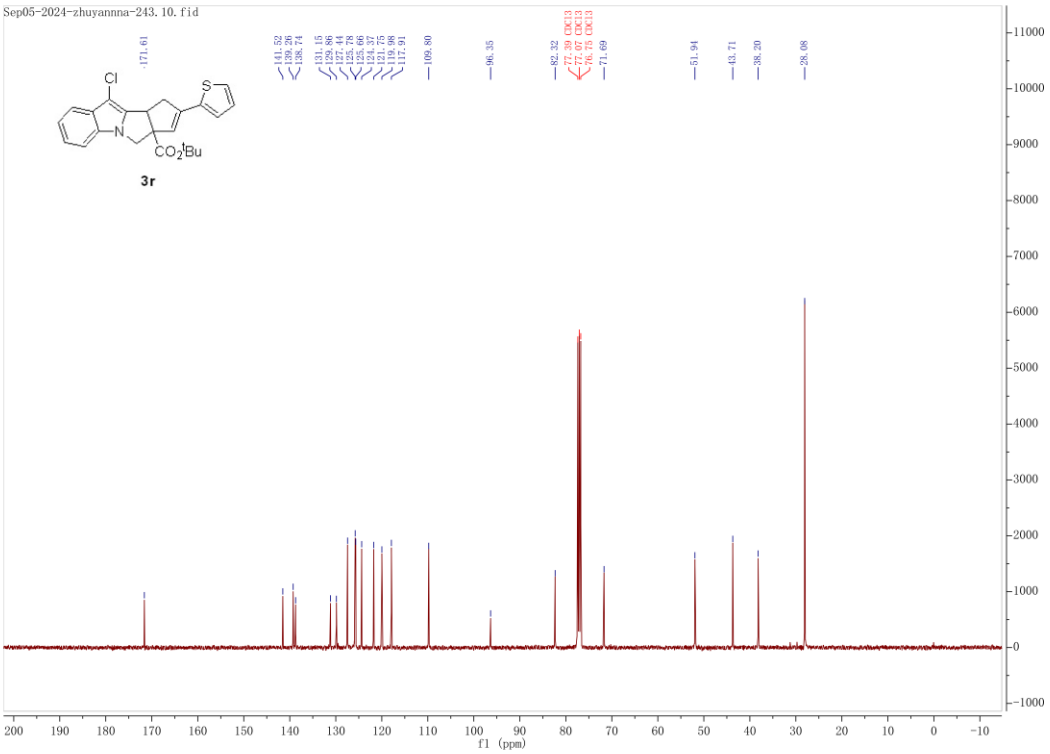
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3q**



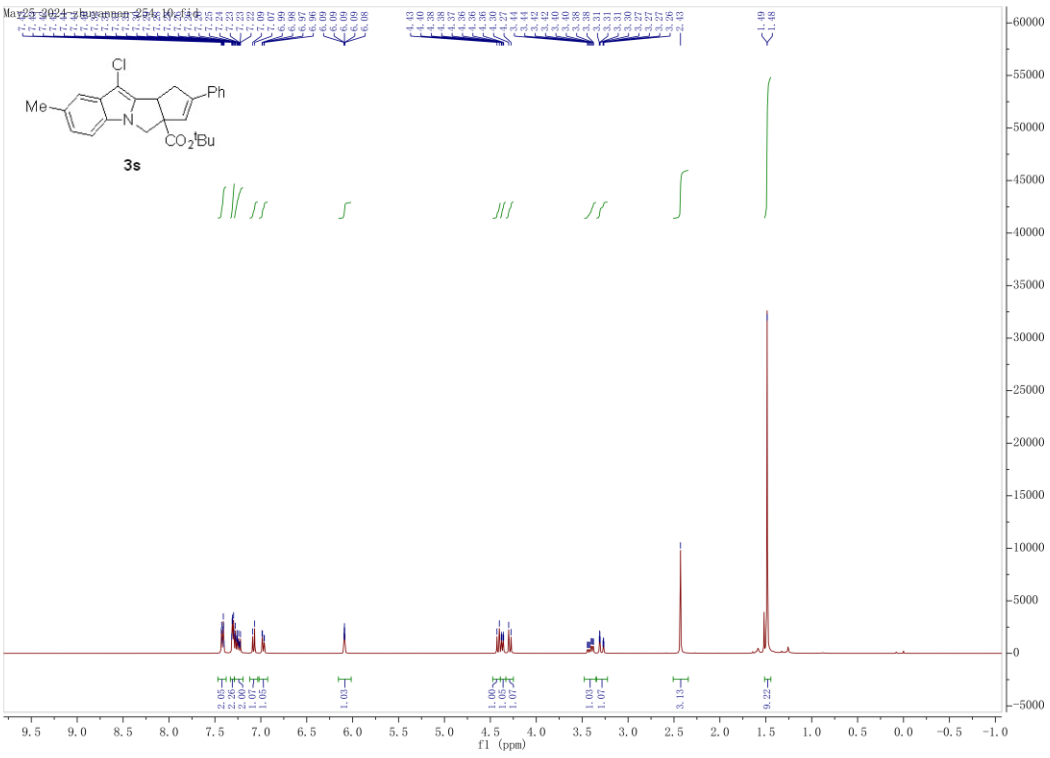
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3q**



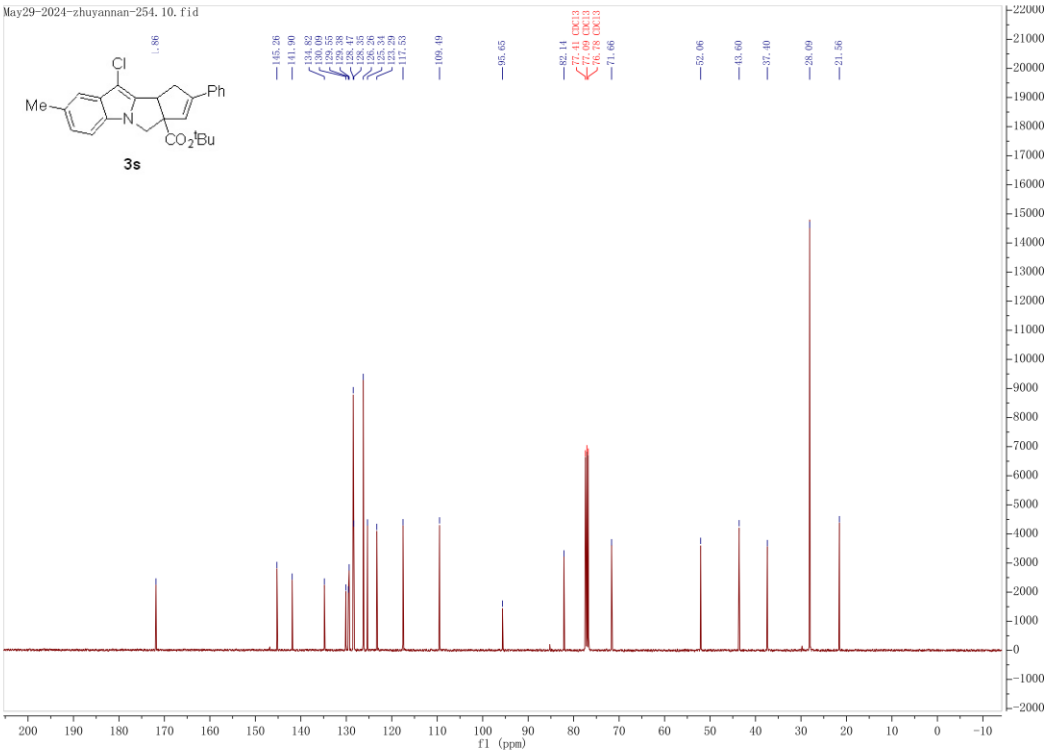
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3r**



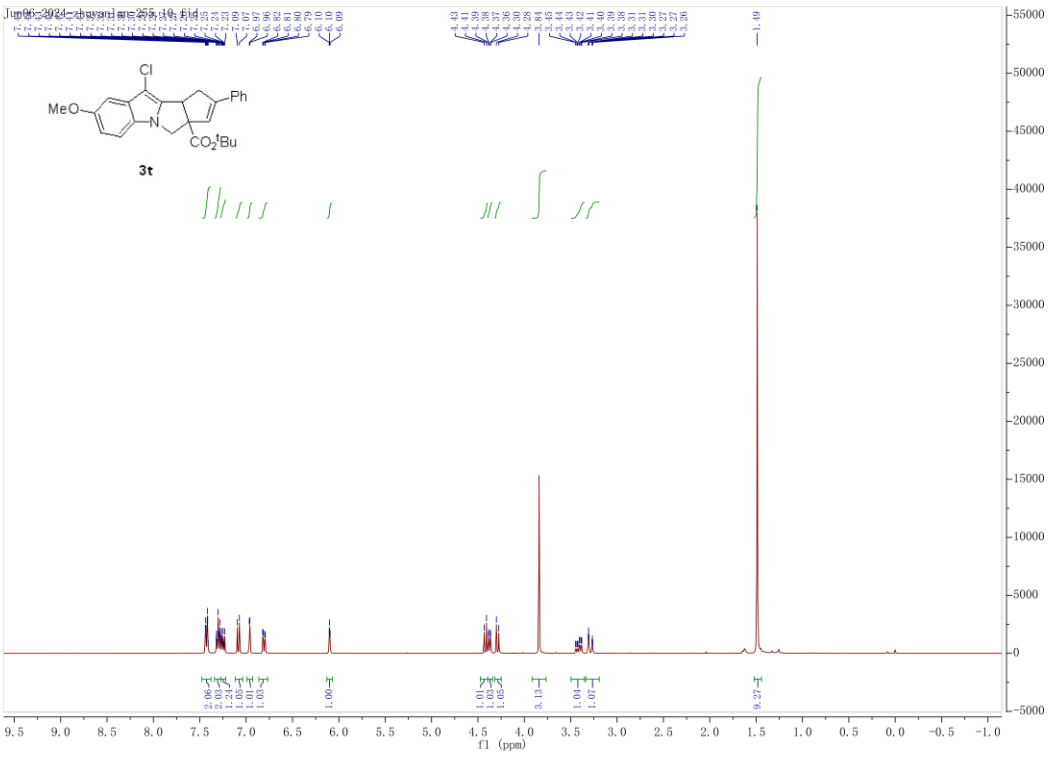
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3r**



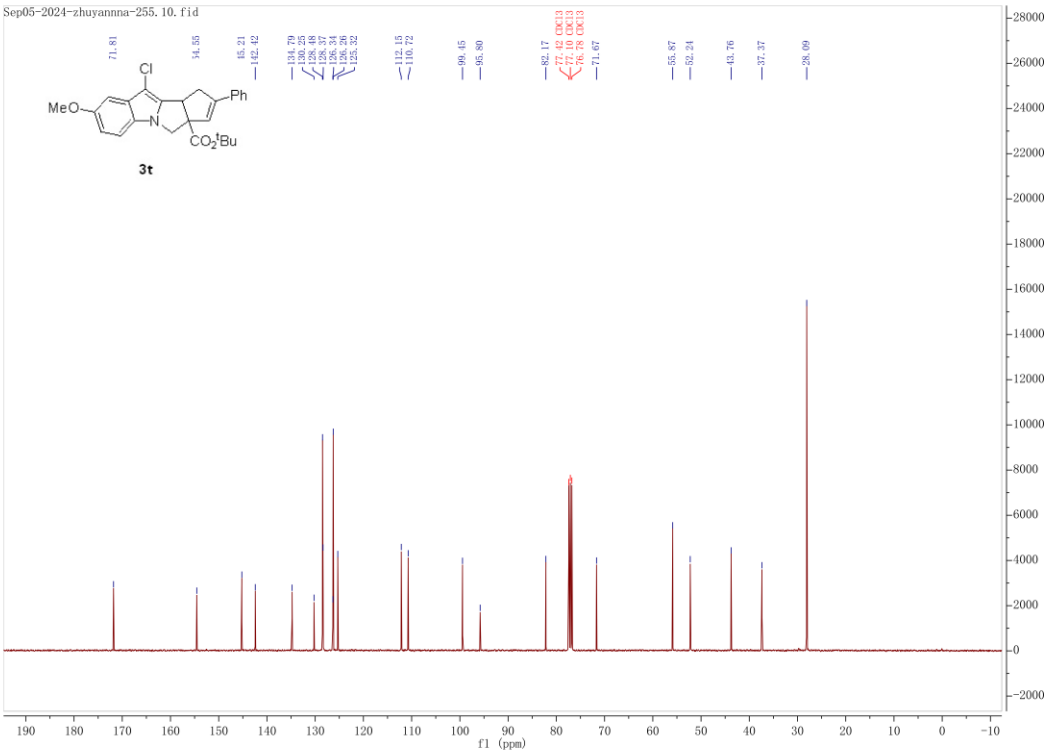
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3s**



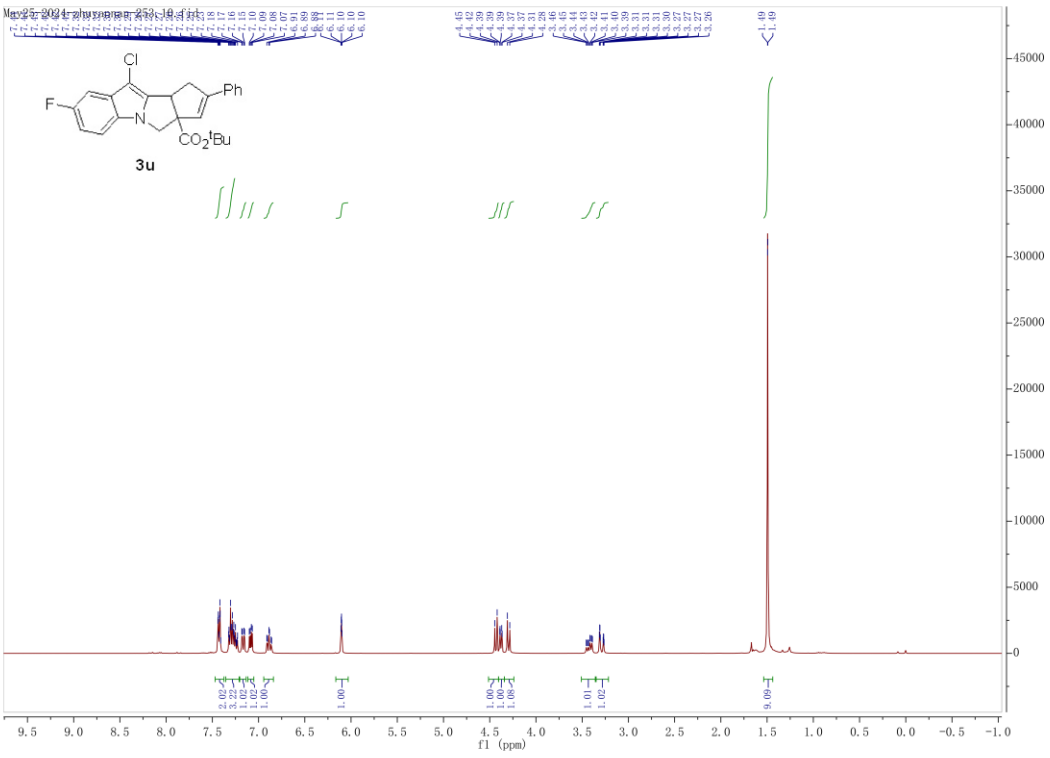
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3s**



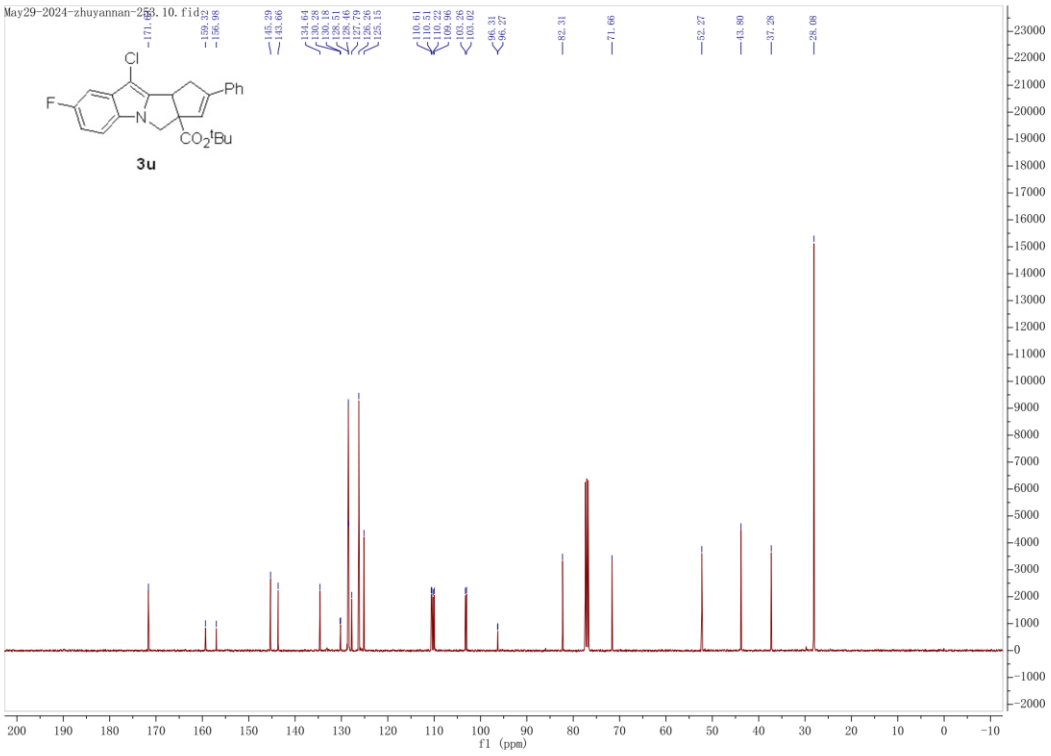
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3t**



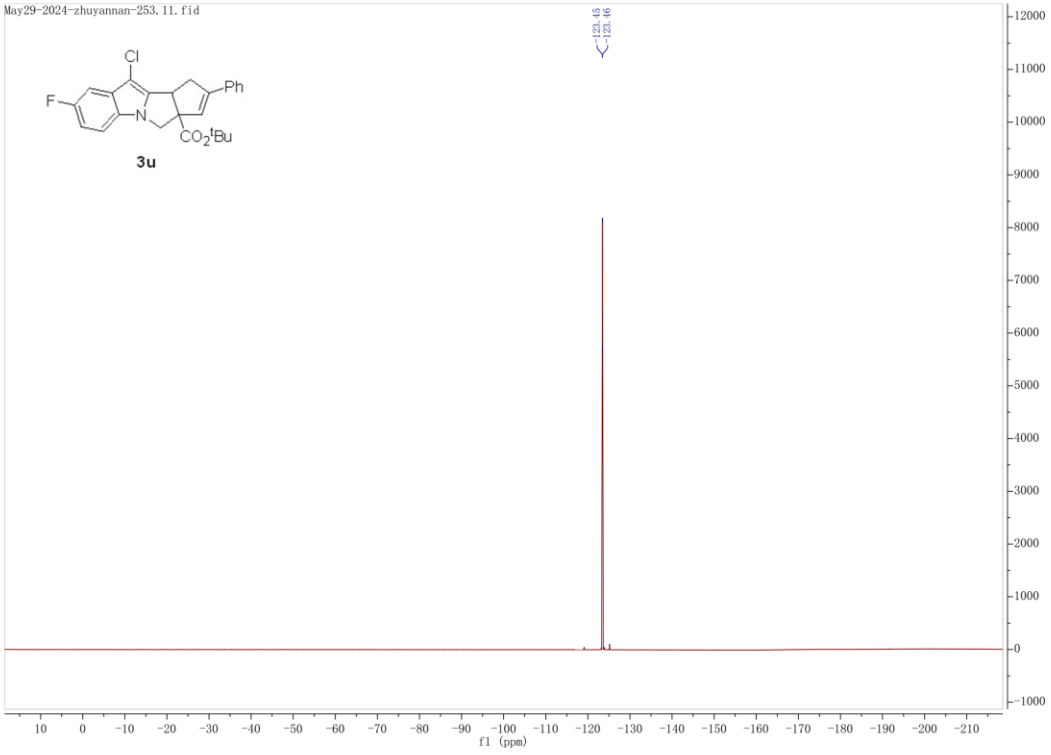
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3t**



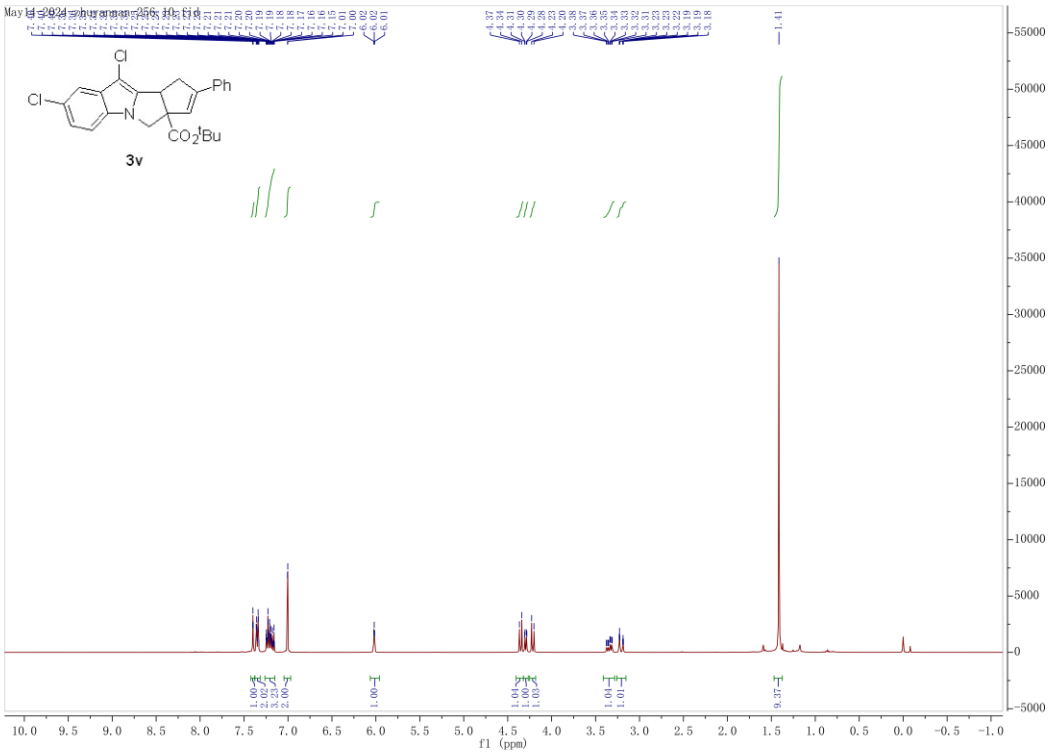
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3u**



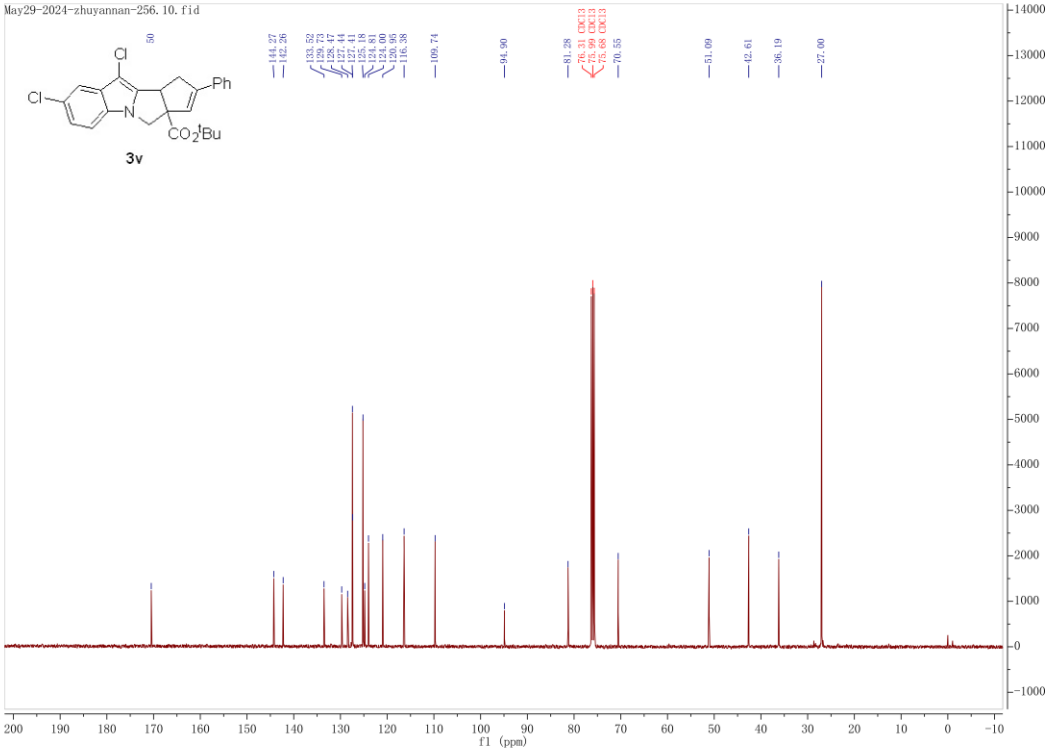
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3u**



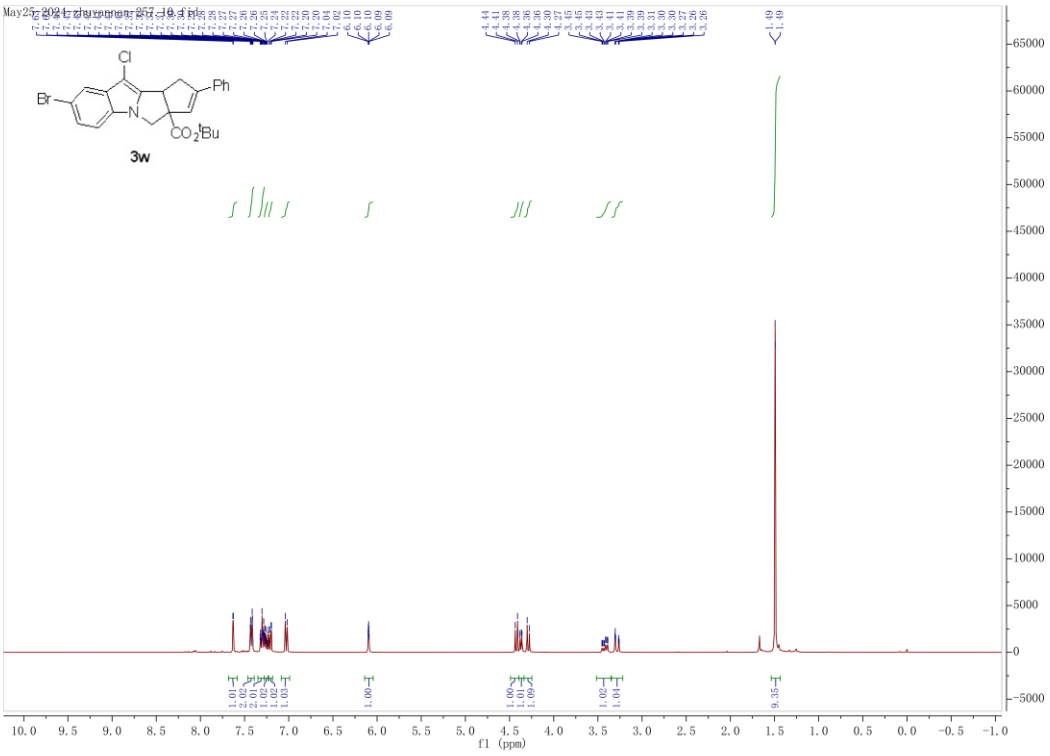
^{19}F NMR spectra (376 MHz, $CDCl_3$) of **3u**



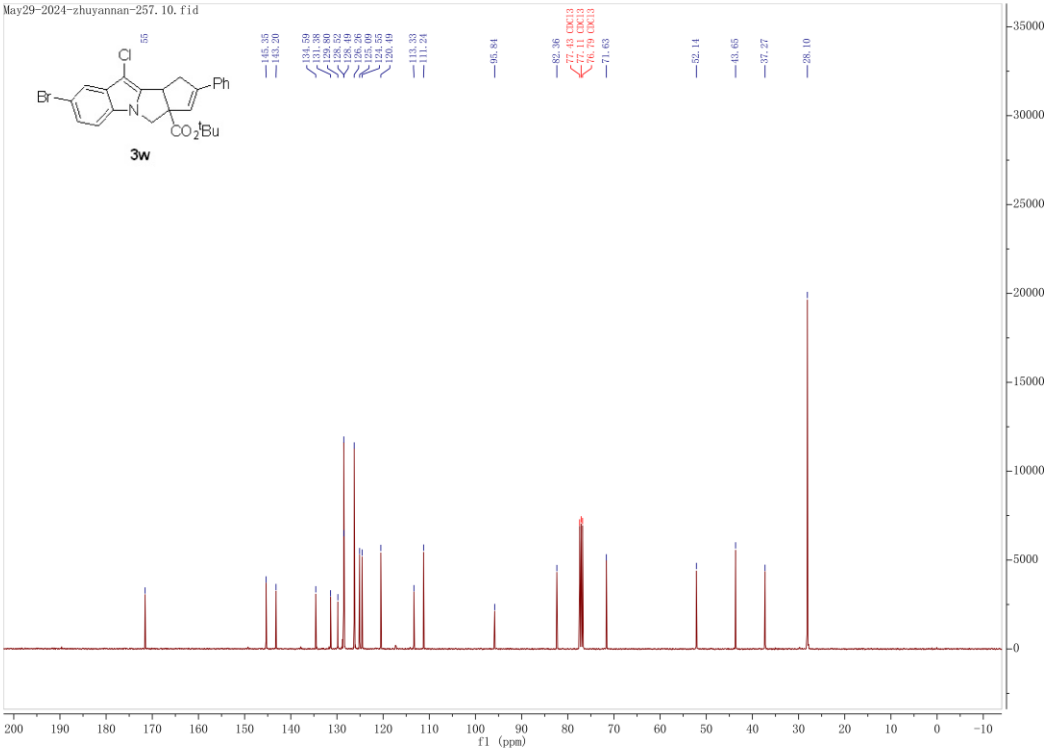
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3v**



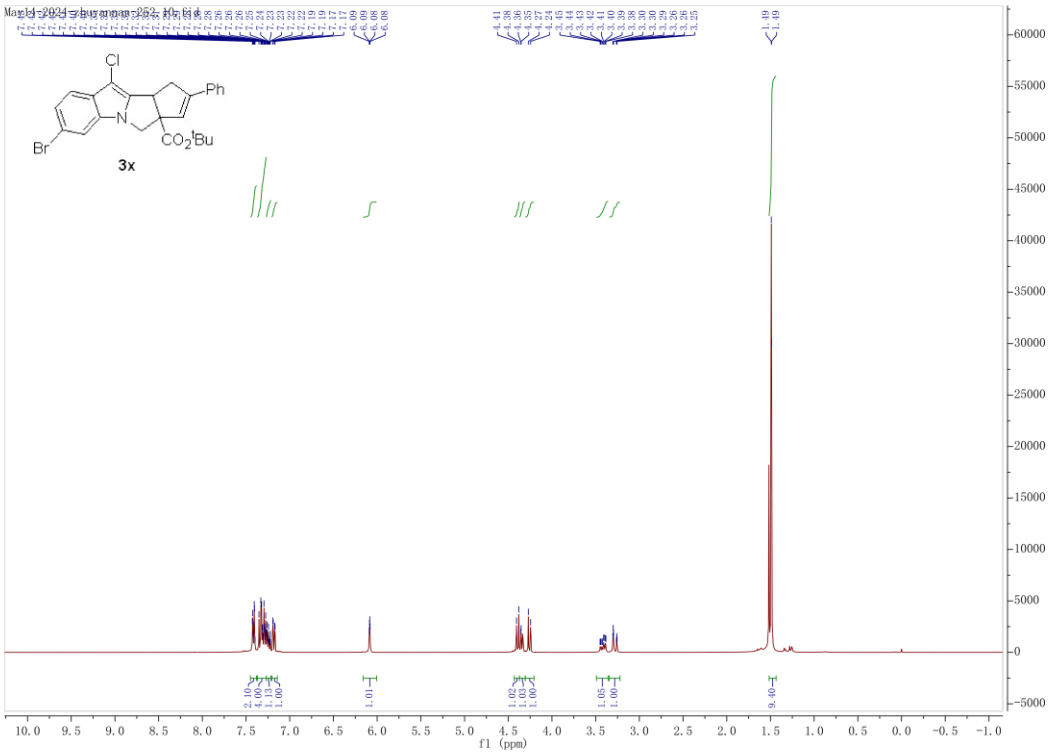
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3v**



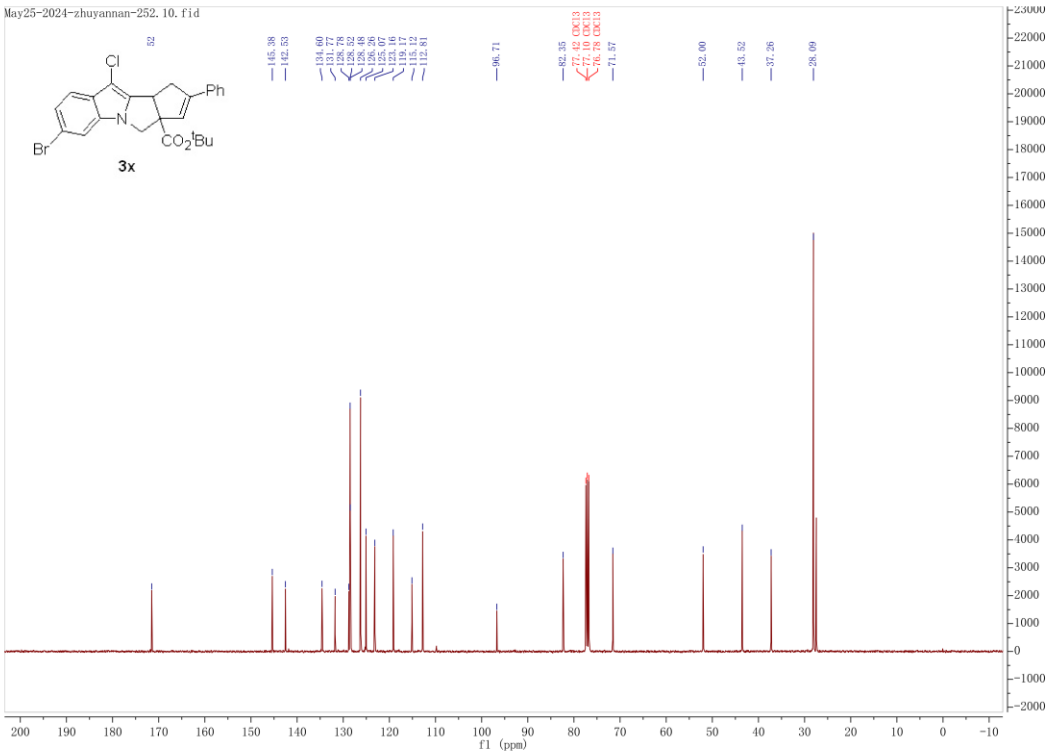
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3w**



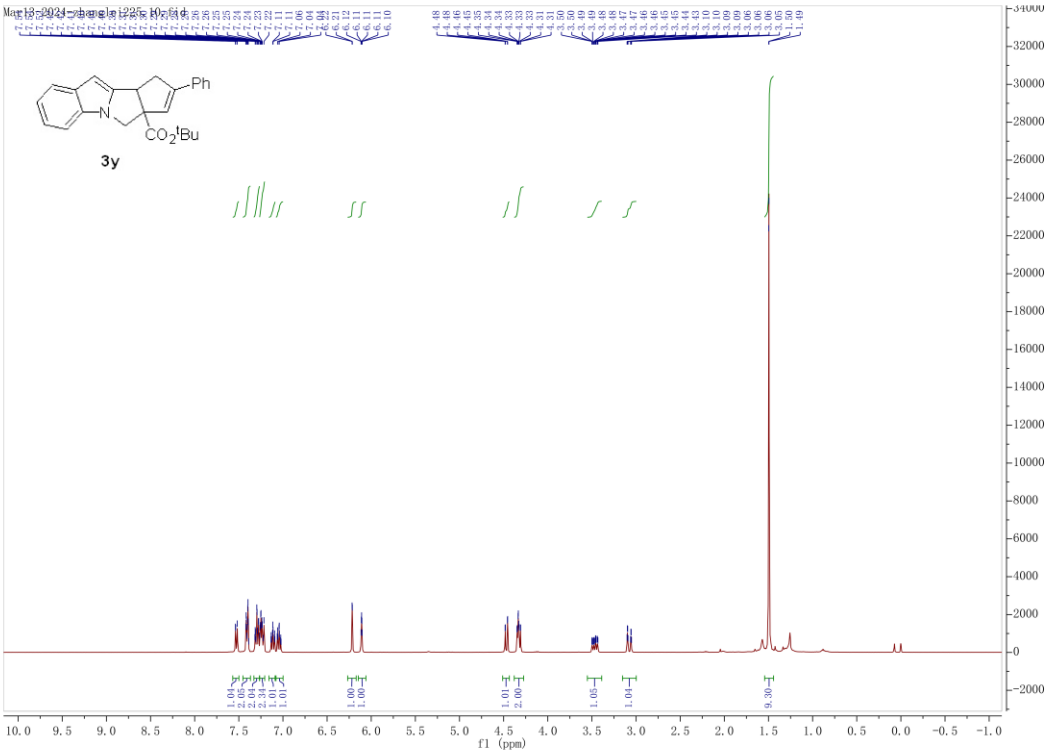
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3w**



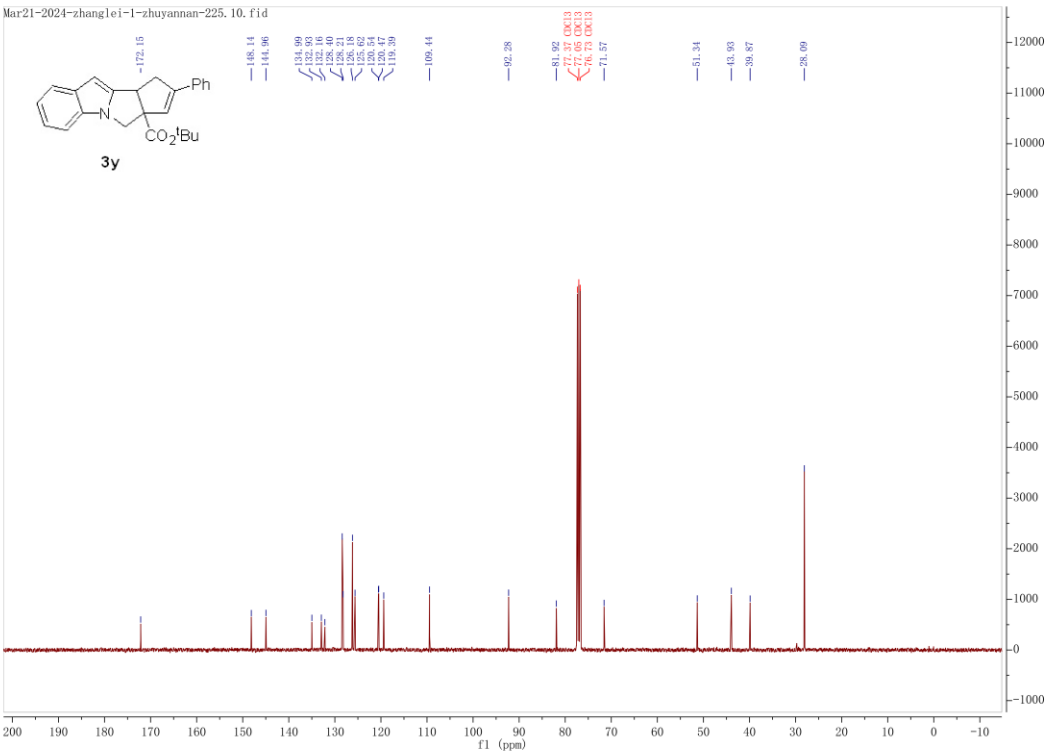
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3x**



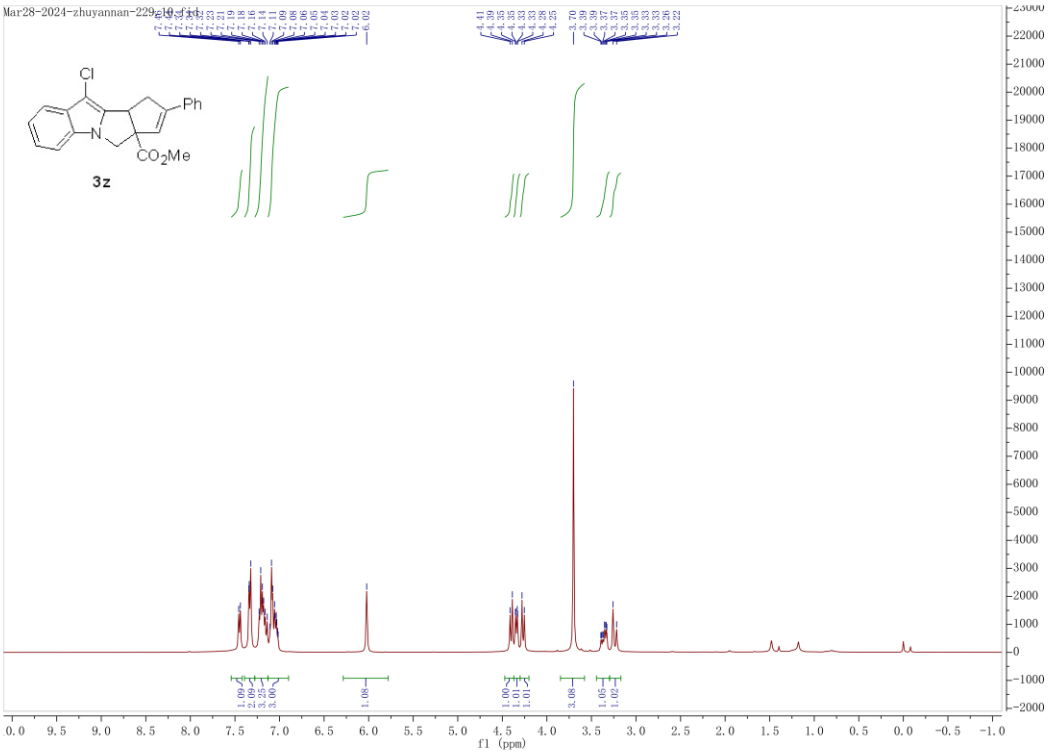
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3x**



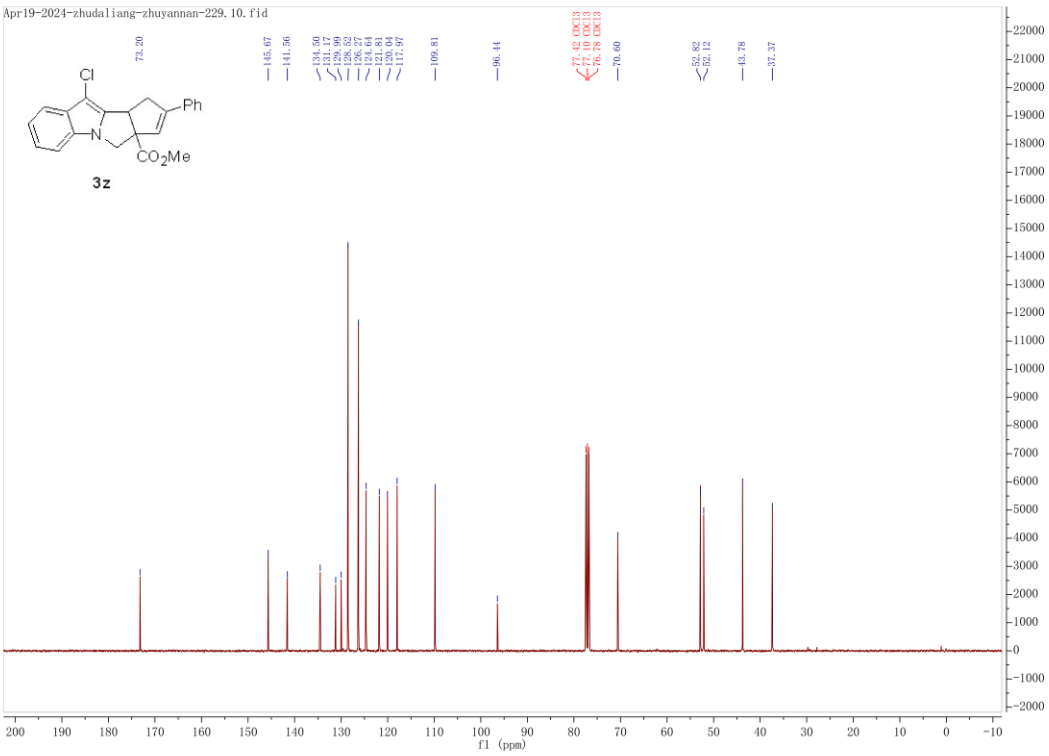
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3y**



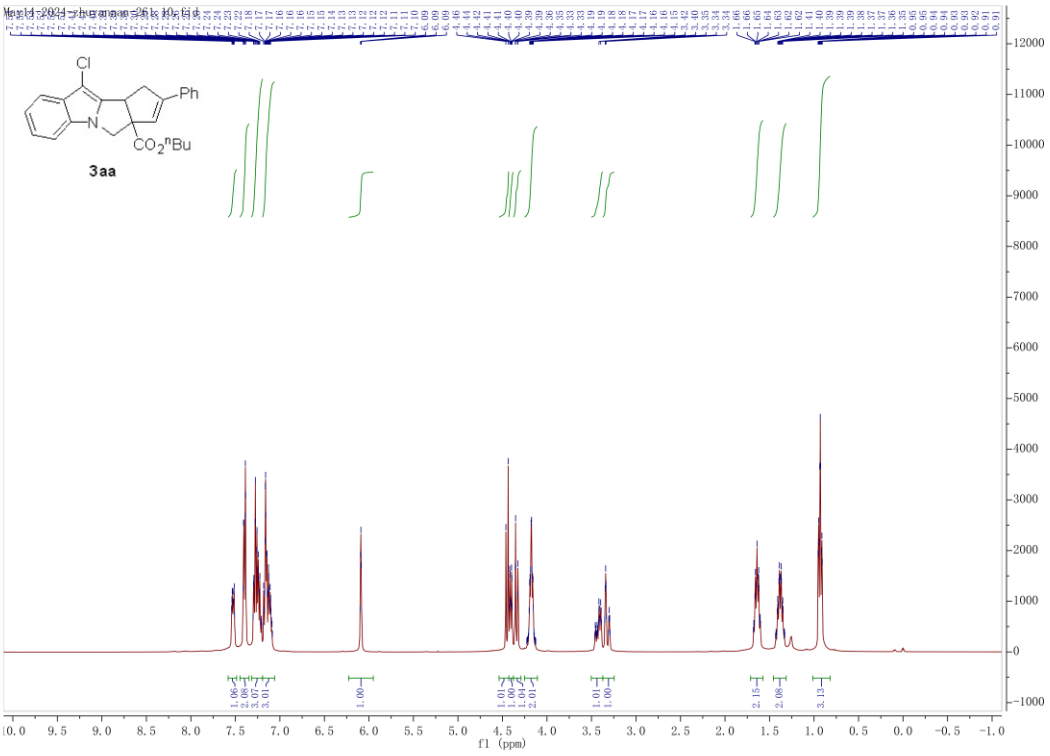
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3y**



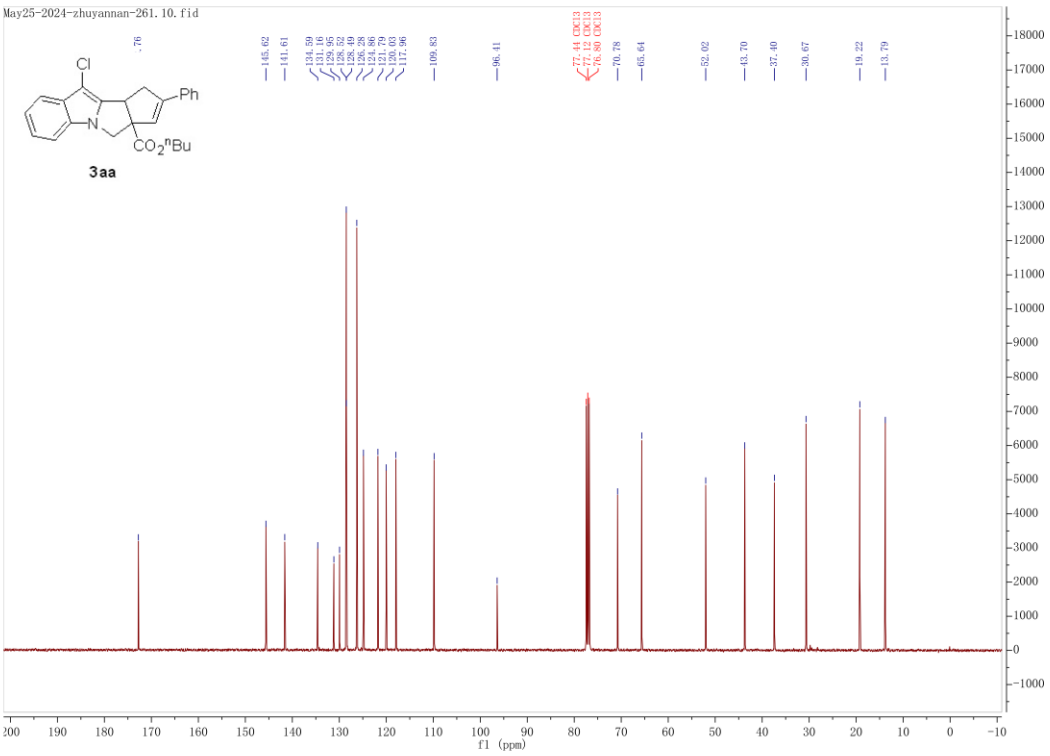
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3z**



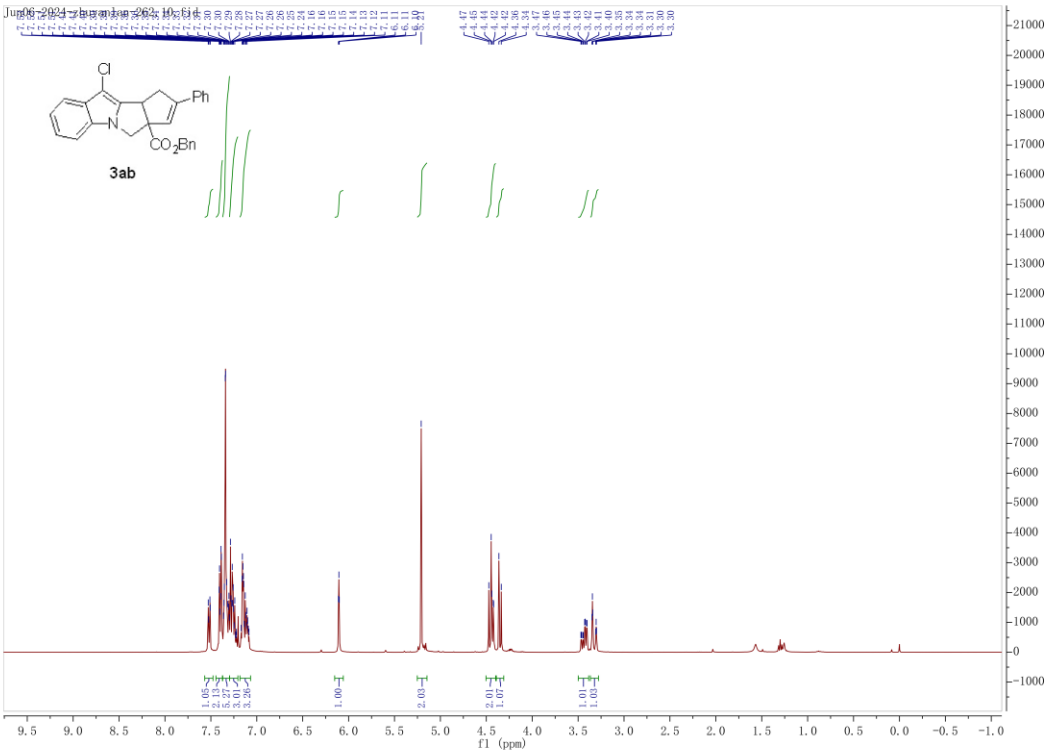
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3z**



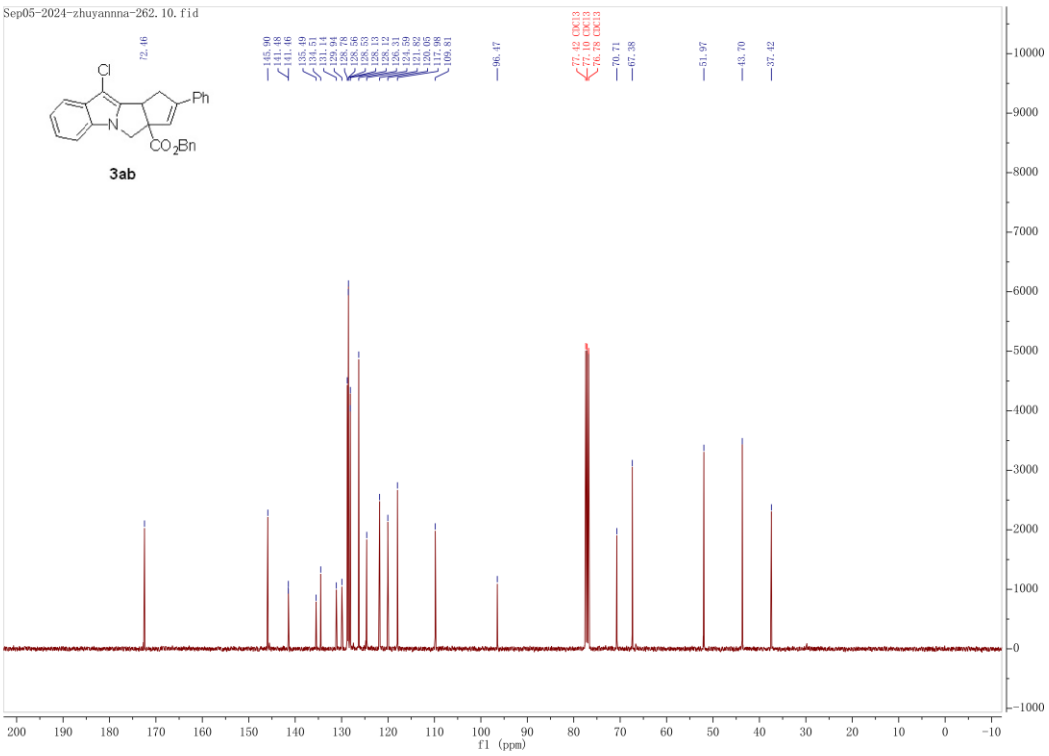
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3aa**



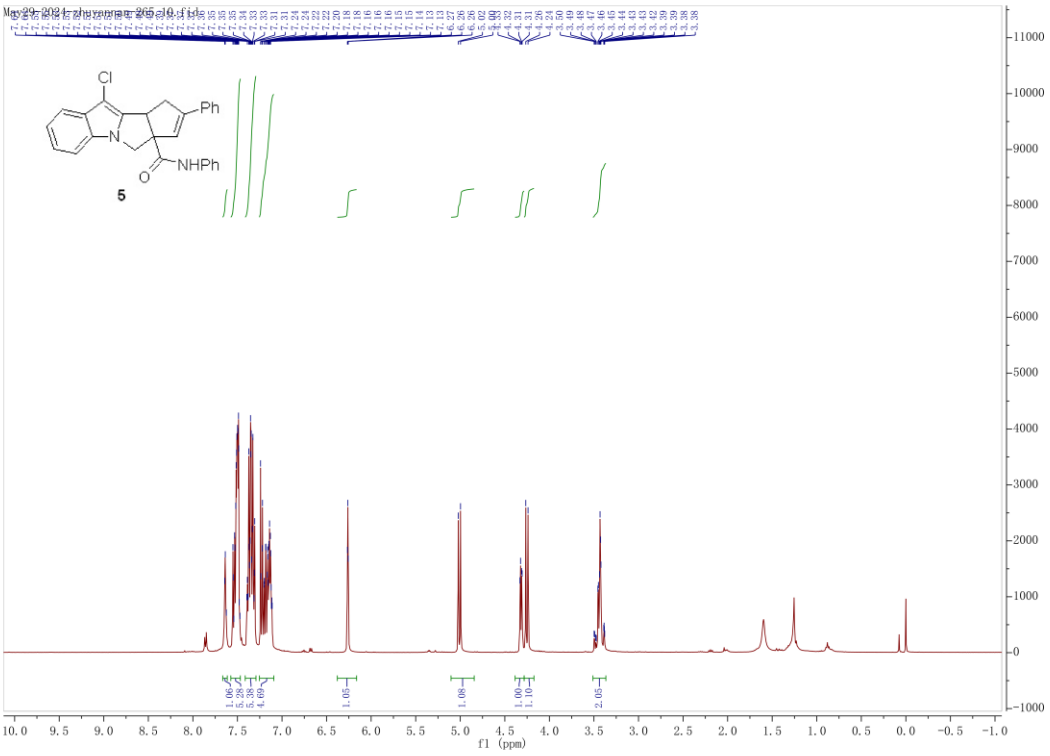
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3aa**



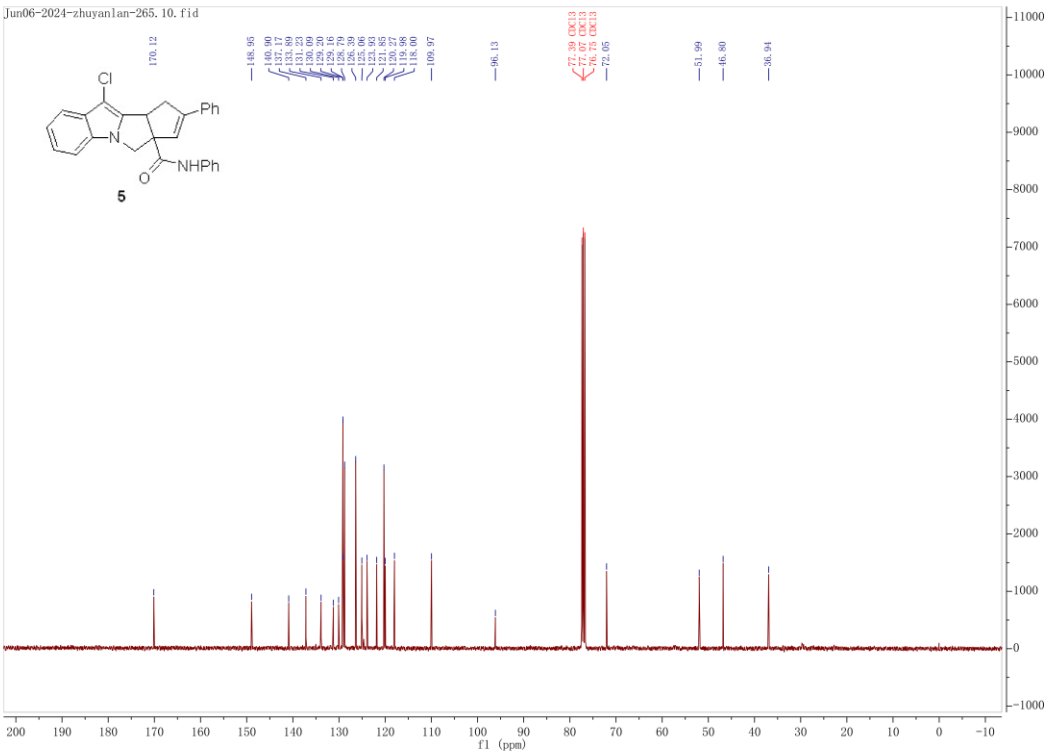
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **3ab**



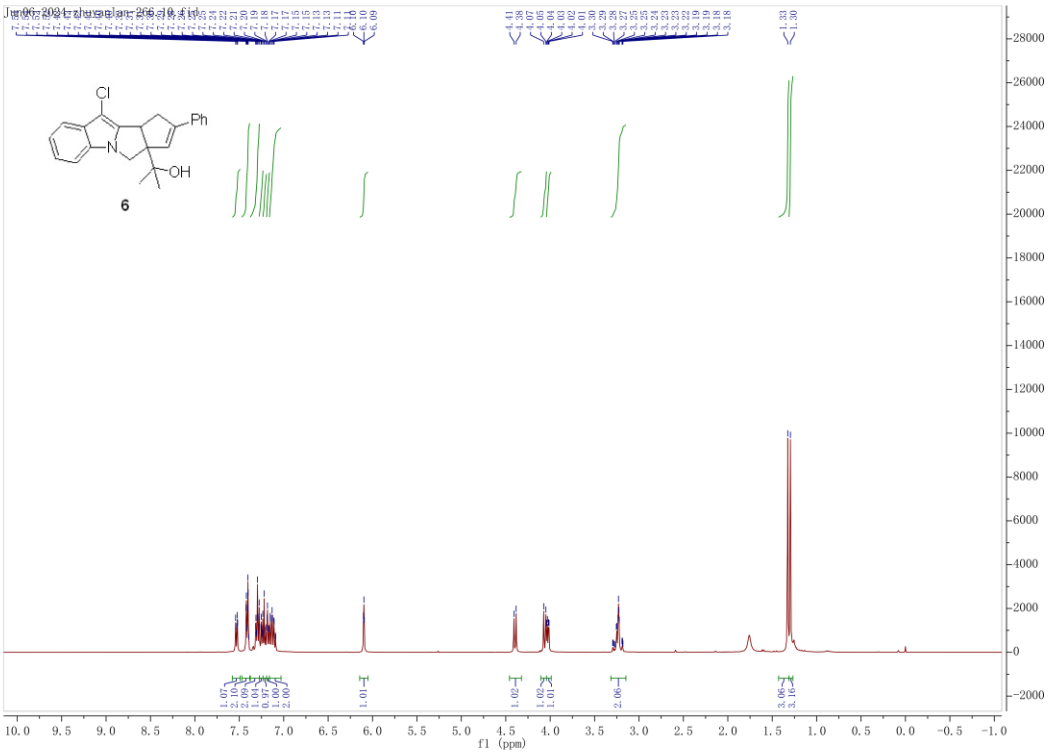
^{13}C NMR spectra (101 MHz, $CDCl_3$) of **3ab**



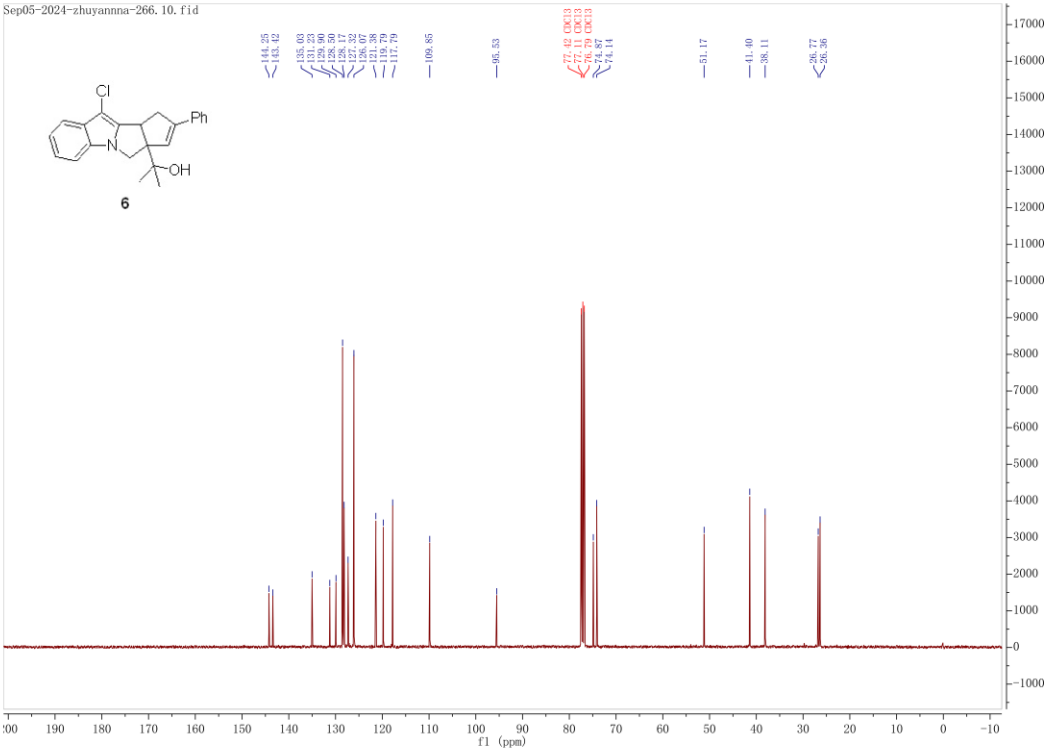
^{1}H NMR spectra (400 MHz, $CDCl_3$) of **5**



^{13}C NMR spectra (101 MHz, $CDCl_3$) of **5**

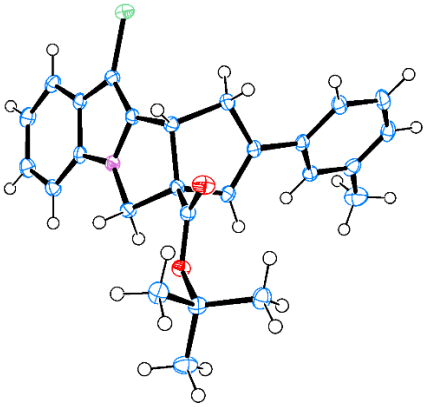


^{1}H NMR spectra (400 MHz, $CDCl_3$) of **6**



^{13}C NMR spectra (101 MHz, $CDCl_3$) of **6**

6. X-ray crystallography data



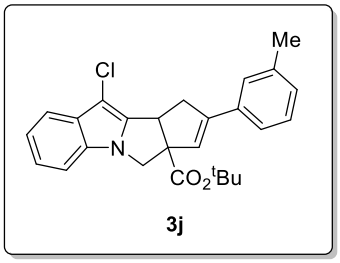


Figure S1. ORTEP diagram of **3j** (CCDC: 2371644). Thermal ellipsoids are shown at the 50% probability level.

Method of crystallization: A solution of **3j** in n-hexane/CH_2Cl_2 (2:1) was added to a 10 mL vial. The vial was closed with parafilm and poked a few of holes with a needle on the parafilm to slowly evaporation of solvent.

The X-ray intensity data was measured on a Rigaku 007 Saturn 70 single crystal diffractometer.

Table S1. Crystal data and structure refinement for **3j**.

Identification code	**3j**
Empirical formula	$C_{26}H_{26}ClNO_2$
Formula weight	419.93
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	18.6824(8)
b/Å	6.6263(2)
c/Å	19.1143(9)
α/°	90
β/°	116.330(5)
γ/°	90
Volume/Å^3	2120.77(17)

Z	4
ρcalcg/cm^3	1.315
μ/mm-1	0.203
F(000)	888.0
Crystal size/mm^3	0.25 × 0.23 × 0.1
Radiation	Mo Kα (λ = 0.71073)
2Θ range for data collection/°	4.274 to 58.098
Index ranges	-22 ≤ h ≤ 17, -8 ≤ k ≤ 5, -24 ≤ l ≤ 23
Reflections collected	12291
Independent reflections	4548 [R_{int} = 0.0245, R_{sigma} = 0.0319]
Data/restraints/parameters	4548/0/275
Goodness-of-fit on F^2	1.026
Final R indexes [I>=2σ (I)]	R_1 = 0.0360, wR_2 = 0.0855
Final R indexes [all data]	R_1 = 0.0467, wR_2 = 0.0923
Largest diff. peak/hole / e Å^{-3}	0.35/-0.27