Supporting information

Iridium(III)-catalysed annulation of pyrazolidinones with propiolates: a facile route to pyrazolo [1,2-a] indazoles.

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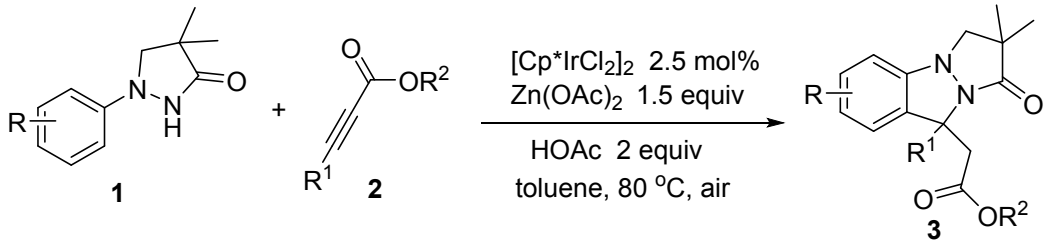
1. General Information

All chemicals were analytically pure and used directly after purchased. All solvents were used without any particular precautions to extrude moisture. ^{1}H NMR spectra were recorded on 400 MHz spectrometer, and ^{13}C NMR spectra were recorded on a 100 MHz spectrometer. All spectra were referenced to the solvent peaks (^{1}H: residual $CDCl_3$ = 7.26 ppm, ^{13}C: $CDCl_3$ = 77.00 ppm). High-resolution mass spectra (HRMS) were equipped with an ESI source and a TOF detector. Column chromatography was performed on silica gel (70-230 mesh ASTM) using the reported eluents. Thin-layer chromatography (TLC) was carried out on 4×15 cm plates with a layer thickness of 0.2 mm (silica gel 60 F254). Pyrazolidiones[1] and aryl but-2-ynoates [2] were synthesized according to the previously reported procedure.

2. General procedure for synthesis of 3



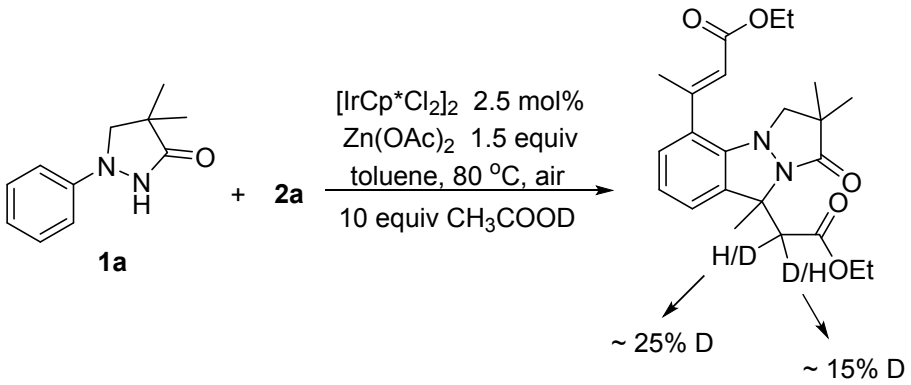
To a tube equipped with magnetic stir bar, pyrazolidiones (**1**, 0.20 mmol), propiolates (**2**, 0.50 mmol), $[IrCp^*Cl_2]_2$ (0.005 mmol, 2.5 mmol %), $Zn(OAc)_2$ (0.30 mmol, 1.5 equiv) and HOAc (0.40 mmol, 2.0 equiv) in toluene (2.0 mL) was stirred at 80 °C for appropriate time under air atmosphere. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 10:1 to 4:1) as eluent to afford corresponding products.

3. Procedure for the synthesis of 3aa on lage scale:

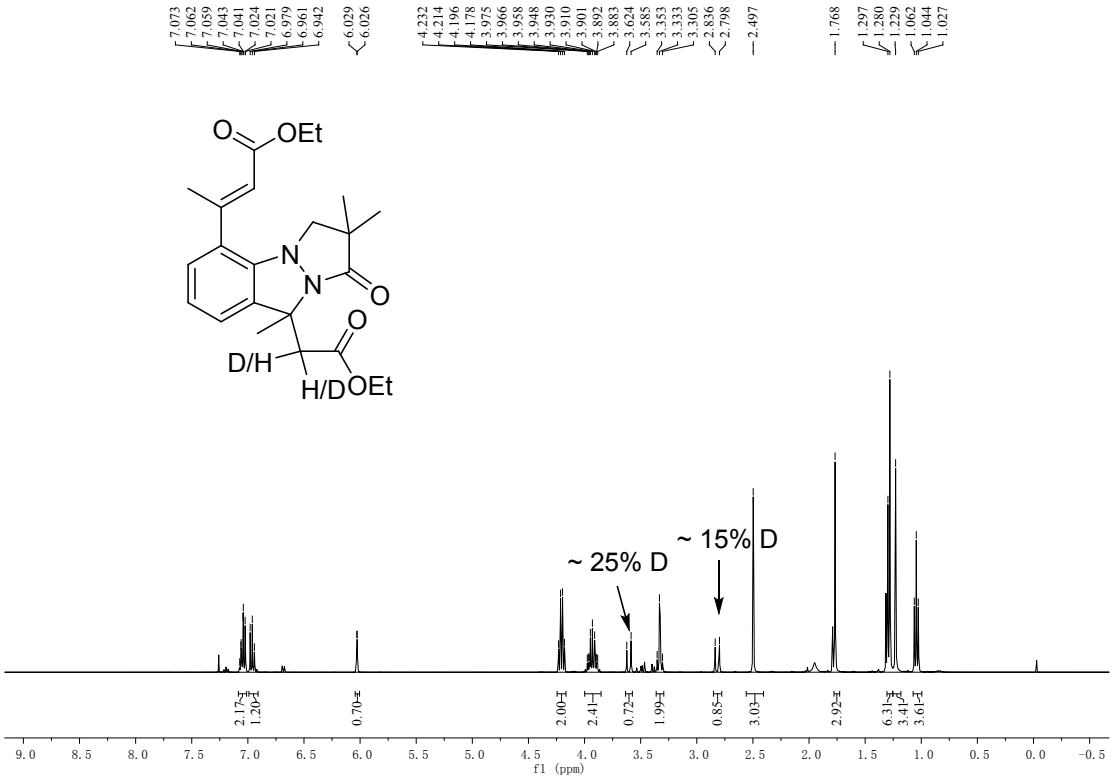
The mixture of pyrazolidione **1a** (1.0 mmol, 1.0 equiv), ethyl but-2-ynoates **2a** (5.0 mmol, 5.0 equiv), $[IrCp^*Cl_2]_2$ (0.025 mmol, 0.025 equiv), $Zn(OAc)_2$ (1.5 mmol, 1.5 equiv), HOAc (2.0 mmol, 2.0 equiv) and toluene (6 mL) was stirred at 80 °C for 1 h. Afterwards, the solvent was removed under reduce pressure, and the resulted mixture was purified by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 10:1 to 4:1) as eluent to furnish the desired compound **3aa** (352 mg) in 85% yield.

4. Mechanism Experiments

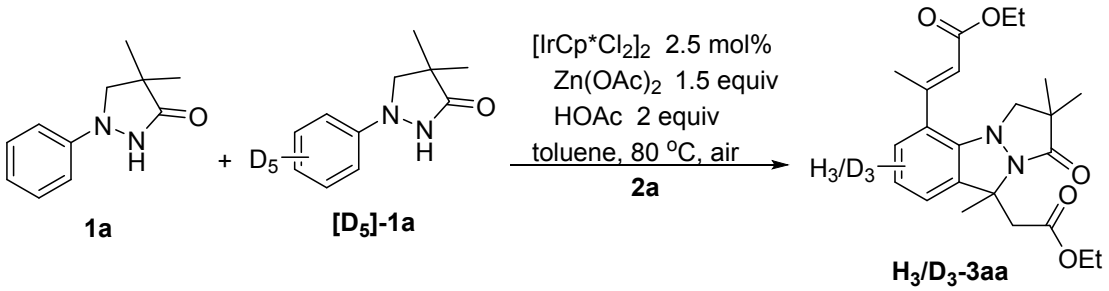
(1) H/D exchange



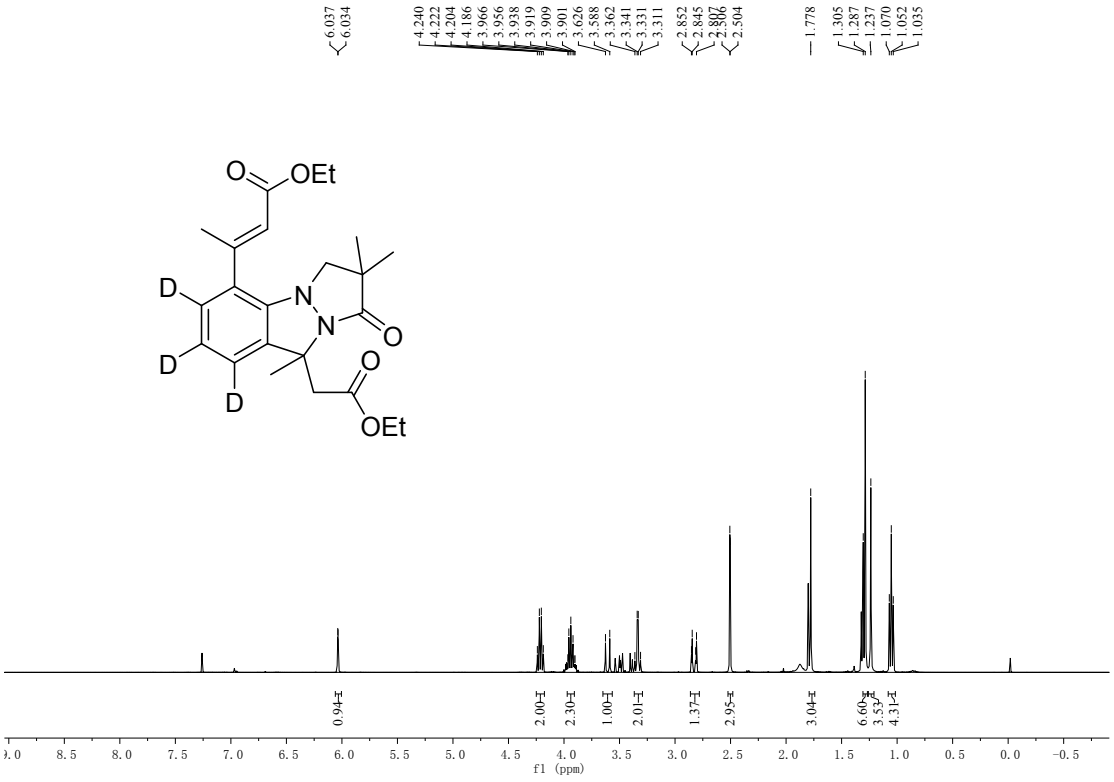
To a tube equipped with magnetic stir bar, pyrazolidiones (**1a**, 0.20 mmol), ethyl but-2-ynoates (**2a**, 0.50 mmol), $[IrCp^*Cl_2]_2$ (0.005 mmol, 2.5 mmol %), $Zn(OAc)_2$ (0.30 mmol, 1.5 equiv) and CH_3COOD (2.0 mmol, 10.0 equiv) in toluene (2.0 mL) was stirred at 80 °C for 30 min under air atmosphere. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 10:1 to 4:1) as eluent to afford the corresponding products.



(2) General procedure for estimation of the KIE:

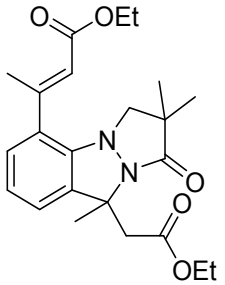


A two separated tube containing pyrazolidiones (**1a**, 0.20 mmol) or **D_5-1a** (0.20 mmol), ethyl but-2-ynoates (**2a**, 0.50 mmol), $[IrCp^*Cl_2]_2$ (0.005 mmol, 2.5 mmol %), $Zn(OAc)_2$ (0.30 mmol, 1.5 equiv), HOAc (0.4 mmol, 2.0 equiv) in toluene (2.0 mL) was stirred at 80 °C for 15 min under air atmosphere. After removal of the solvent under reduced pressure, purification was performed by flash column chromatography on silica gel with petroleum ether/ethyl acetate (gradient mixture ratio from 10:1 to 4:1) as eluent to afford the corresponding products.



5. Characterization of products 3

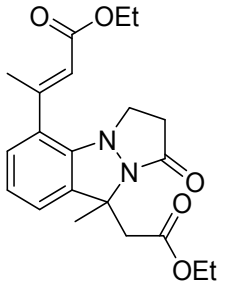
Ethyl (E)-3-(9-(2-ethoxy-2-oxoethyl)-2,2,9-trimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo [1,2-a]indazol-5-yl)but-2-enoate (3aa)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 71.2 mg, 86% yield, yellow oil. Reaction time is 30 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.04 (td, *J* = 7.5, 1.2 Hz, 2H), 6.96 (t, *J* = 7.6 Hz, 1H), 6.03 (d, *J* = 1.4 Hz, 1H), 4.21 (q, *J* = 7.1 Hz, 2H), 3.93 (qd, *J* = 7.2, 3.5 Hz, 2H), 3.60 (d, *J* = 15.4 Hz, 1H), 3.36 – 3.28 (m, 2H), 2.82 (d, *J* = 15.4 Hz, 1H), 2.50 (d, *J* = 1.3 Hz, 3H), 1.77 (s,3H), 1.29 (d, *J* = 8.7 Hz, 6H), 1.23 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.29, 169.27, 166.51, 153.52, 143.29, 135.19, 127.99, 126.79, 122.65, 121.56, 120.15, 63.90, 62.65, 60.27, 59.92, 45.30, 41.47, 26.56, 22.68, 22.19, 18.51, 14.24, 13.89. **HRMS (ESI)**: Calcd for $C_{23}H_{30}N_2O_5$ $[M+H]^+$: 415.2227; found: 415.2232

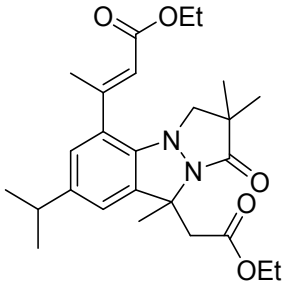
Ethyl (E)-3-(9-(2-ethoxy-2-oxoethyl)-9-methyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo [1,2-a]indazol-5-yl)but-2-enoate (3ba)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 67.9 mg, 88% yield, yellow oil. Reaction time is 10 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (ddd, *J* = 11.2, 7.5, 1.4 Hz, 2H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.01 (d, *J* = 1.4 Hz, 1H), 4.19 (q, *J* = 7.1 Hz, 2H), 3.94 (ddq, *J* = 10.8, 7.2, 3.7 Hz, 2H), 3.67 – 3.59 (m, 2H), 3.55 (q, *J* = 8.7 Hz, 1H), 2.89 – 2.78 (m, 2H), 2.71 (ddd, *J* = 16.1, 8.5, 5.8 Hz, 1H), 2.50 (d, *J* = 1.3 Hz, 3H), 1.77 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 169.32, 166.42, 166.18, 153.32, 143.32, 135.18, 128.02, 126.84, 122.85, 121.53, 120.17, 62.74, 60.31, 59.96, 51.04, 41.15, 34.90, 26.56, 18.81, 14.23, 13.88. **HRMS (ESI)**: Calcd for $C_{21}H_{26}N_2O_5$ $[M+H]^+$: 387.1914; found: 387.1901

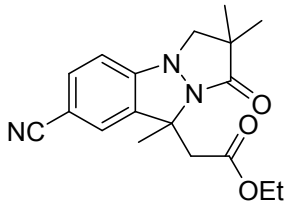
Ethyl (E)-3-(9-(2-ethoxy-2-oxoethyl)-7-isopropyl-2,2,9-trimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-5-yl)but-2-enoate (3ca)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 80.4 mg, 88% yield, yellow solid. Reaction time is 15 min. mp 128-130 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, *J* = 3.5 Hz, 2H), 6.03 (d, *J* = 1.3 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 4.02 – 3.87 (m, 2H), 3.58 (d, *J* = 15.2 Hz, 1H), 3.30 (dd, *J* = 18.7, 8.2 Hz, 2H), 2.91 – 2.79 (m, 2H), 2.51 (d, *J* = 1.2 Hz, 3H), 1.80 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.28 (s, 3H), 1.25 (s, 3H), 1.21 (d, *J* = 6.9 Hz, 6H), 1.05 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.28, 169.34, 166.63, 154.07, 143.75, 141.47, 135.33, 126.64, 126.04, 119.98, 119.63, 64.17, 62.81, 60.27, 59.94, 45.36, 41.64, 33.70, 26.45, 24.16, 24.03, 22.67, 22.27, 18.58, 14.30, 13.96. **HRMS (ESI)**: Calcd for $C_{26}H_{36}N_2O_5$ $[M+H]^+$: 457.2697; found: 457.2697

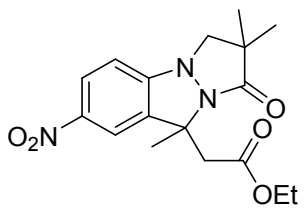
Ethyl 2-(7-cyano-2,2,9-trimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3da)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 52.3 mg, 80% yield, white solid. Reaction time is 2 h. mp 122-124 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (dd, *J* = 8.2, 1.5 Hz, 1H), 7.30 (d, *J* = 1.3 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 3.95 (dtt, *J* = 10.8, 7.3, 3.7 Hz, 2H), 3.68 (d, *J* = 16.2 Hz, 1H), 3.54 (q, *J* = 8.1 Hz, 2H), 2.82 (d, *J* = 16.2 Hz, 1H), 1.75 (s, 3H), 1.34 (s, 3H), 1.27 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.87, 169.06, 150.00, 135.29, 133.86, 125.43, 119.13, 109.15, 104.50, 63.10, 62.37, 60.52, 45.84, 40.94, 26.51, 23.36, 22.44, 13.92. **HRMS (ESI)**: Calcd for $C_{18}H_{21}N_3O_3$ $[M+H]^+$: 328.1656; found: 328.1660

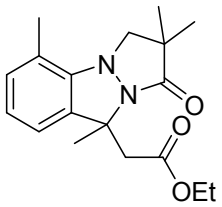
Ethyl 2-(2,2,9-trimethyl-7-nitro-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3ea)



silica gel column chromatography (petroleum ether/ethyl acetate = 2:1), 49.3 mg,71% yield, yellow solid. Reaction time is 75 min. mp 151-154 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.92 (d, *J* = 2.1 Hz, 1H), 6.65 (d, *J* = 8.7 Hz, 1H), 4.00 – 3.87 (m, 2H), 3.75 (d, *J* = 16.5 Hz, 1H), 3.62 (dd, *J* = 18.9, 8.2 Hz, 2H), 2.86 (d, *J* = 16.5 Hz, 1H), 1.77 (s, 3H), 1.36 (s, 3H), 1.28 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.05, 169.11, 151.34, 142.34, 135.10, 126.37, 117.94, 107.63, 63.17, 61.93, 60.57, 45.91, 40.94, 26.75, 23.62, 22.47, 13.92. **HRMS (ESI)**: Calcd for $C_{17}H_{21}N_3O_5$ $[M+H]^+$: 348.1554; found: 348.1559

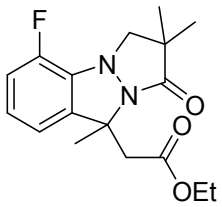
Ethyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fa)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 56.2 mg, 89% yield, colorless oil. Reaction time is 10 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (dd, *J* = 6.3, 1.8 Hz, 1H), 6.92 – 6.85 (m, 2H), 3.99 – 3.87 (m, 2H), 3.64 – 3.50 (m, 3H), 2.80 (d, *J* = 15.4 Hz, 1H), 2.27 (s, 3H), 1.75 (s, 3H), 1.34 (s, 3H), 1.28 (s, 3H), 1.05 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.17, 169.41, 144.78, 134.12, 130.57, 122.67, 120.71, 119.06, 64.82, 62.95, 60.19, 45.58, 41.44, 26.64, 22.82, 22.32, 17.63, 13.89. **HRMS (ESI)**: Calcd for $C_{18}H_{24}N_2O_3$ $[M+H]^+$: 317.1860; found: 317.1859

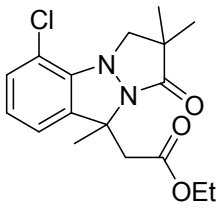
Ethyl 2-(5-fluoro-2,2,9-trimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3ga)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 63.3 mg, 99% yield, yellow oil. Reaction time is 15 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 – 6.87 (m, 2H), 6.85 (dd, *J* = 7.0, 1.6 Hz, 1H), 4.01 – 3.87 (m, 2H), 3.65 – 3.54 (m, 3H), 2.82 (d, *J* = 15.6 Hz, 1H), 1.76 (s, 3H), 1.32 (s, 3H), 1.26 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.36, 169.18, 148.72 (d, J_{C-F} = 245.1 Hz), 137.56 (d, J_{C-F} = 3.8 Hz), 134.00 (d, J_{C-F} = 13.0 Hz), 123.47 (d, J_{C-F} = 5.9 Hz), 117.18 (d, J_{C-F} = 3.4 Hz), 115.63 (d, J_{C-F} = 17.3 Hz), 64.33 (d, J_{C-F} = 1.8 Hz), 63.73 (d, J_{C-F} = 1.4 Hz), 60.33, 45.83, 41.22, 26.47, 22.74, 22.21, 13.90. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -133.46. **HRMS (ESI)**: Calcd for $C_{17}H_{21}N_2O_3$ $[M+H]^+$: 321.1609; found: 321.1609

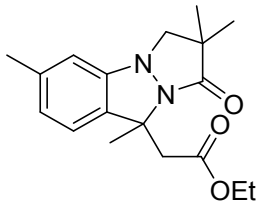
Ethyl 2-(5-chloro-2,2,9-trimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3ha)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 49.0 mg, 73% yield, yellow oil. Reaction time is 30 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (dd, *J* = 7.8, 1.1 Hz, 1H), 6.96 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.90 (t, *J* = 7.7 Hz, 1H), 4.01 – 3.89 (m, 2H), 3.78 (d, *J* = 8.3 Hz, 1H), 3.67 (dd, *J* = 12.0, 9.1 Hz, 2H), 2.81 (d, *J* = 15.7 Hz, 1H), 1.74 (s, 3H), 1.34 (s, 3H), 1.27 (s, 3H), 1.06 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.29, 169.22, 143.27, 136.59, 129.49, 123.46, 119.91, 116.44, 64.30, 63.34, 60.34, 45.45, 41.24, 26.71, 22.90, 22.27, 13.91. **HRMS (ESI)**: Calcd for $C_{17}H_{21}ClN_2O_3$ $[M+H]^+$: 337.1313; found: 337.1313

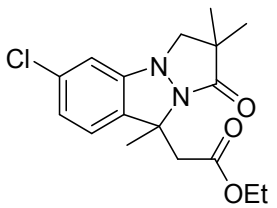
Ethyl 2-(2,2,6,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3ia)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 46.7 mg, 74% yield, yellow oil. Reaction time is 2 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.95 (d, *J* = 7.7 Hz, 1H), 6.76 (d, *J* = 7.7 Hz, 1H), 6.51 (s, 1H), 3.96 (tt, *J* = 8.9, 4.5 Hz, 2H), 3.49 (d, *J* = 5.5 Hz, 1H), 3.46 (d, *J* = 1.7 Hz, 1H), 3.36 (d, *J* = 7.9 Hz, 1H), 2.82 (d, *J* = 15.2 Hz, 1H), 2.31 (s, 3H), 1.78 (s, 3H), 1.30 (s, 3H), 1.28 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.64, 169.41, 147.13, 138.94, 131.58, 123.08, 121.36, 110.19, 63.79, 63.04, 60.27, 45.78, 41.70, 25.99, 22.85, 22.52, 21.47, 13.91. **HRMS (ESI)**: Calcd for $C_{18}H_{24}N_2O_3$ $[M+H]^+$: 317.1860; found: 317.1862

Ethyl 2-(6-chloro-2,2,9-trimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3ja)

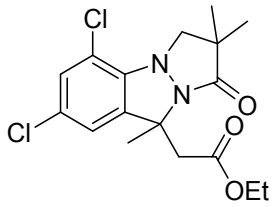


silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 50.4 mg, 75% yield, yellow oil. Reaction time is 2 h.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.98 (d, *J* = 8.1 Hz, 1H), 6.91 (dd, *J* = 8.1, 1.7 Hz, 1H), 6.67 (d, *J* = 1.7 Hz, 1H), 4.02 – 3.86 (m, 2H), 3.56 (d, *J* = 15.6 Hz, 1H), 3.47 (d, *J* = 7.9 Hz, 1H), 3.41 (d, *J* = 7.9 Hz, 1H), 2.81 (d, *J* = 15.6 Hz, 1H), 1.76 (s, 3H), 1.31 (s,

3H), 1.27 (s, 3H), 1.08 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 170.81, 169.22, 148.13, 134.58, 132.89, 122.58, 122.19, 109.93, 63.43, 63.05, 60.40, 45.80, 41.27, 26.17, 23.00, 22.47, 13.95. **HRMS (ESI)**: Calcd for $C_{17}H_{21}ClN_2O_3$ $[M+H]^+$: 337.1313; found: 337.1312

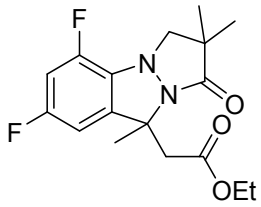
Ethyl 2-(5,7-dichloro-2,2,9-trimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3ka)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 46.6 mg, 63% yield, pale yellow solid. Reaction time is 35 min. mp 103-105 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (d, J = 1.8 Hz, 1H), 6.94 (d, J = 1.8 Hz, 1H), 4.04 – 3.93 (m, 2H), 3.79 (d, J = 8.3 Hz, 1H), 3.71 (d, J = 16.1 Hz, 1H), 3.66 (d, J = 8.3 Hz, 1H), 2.79 (d, J = 16.1 Hz, 1H), 1.72 (s, 3H), 1.35 (s, 3H), 1.26 (s, 3H), 1.11 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.51, 169.10, 142.30, 137.85, 129.20, 127.81, 120.45, 116.93, 64.28, 63.50, 60.52, 45.45, 40.93, 26.88, 23.02, 22.25, 13.97. **HRMS (ESI)**: Calcd for $C_{17}H_{20}Cl2N_2O_3$ $[M+H]^+$: 371.0924; found: 371.0923

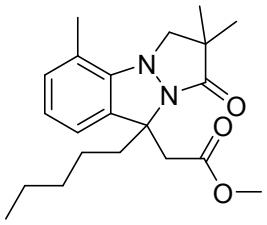
Ethyl 2-(5,7-difluoro-2,2,9-trimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3la)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 61.5 mg, 91% yield, yellow solid. Reaction time is 35 min. mp 111-113 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.73 (ddd, J = 10.3, 9.0, 2.2 Hz, 1H), 6.66 – 6.61 (m, 1H), 3.97 (dtt, J = 10.8, 7.3, 3.7 Hz, 2H), 3.65 (d, J = 16.0 Hz, 1H), 3.56 (d, J = 1.2 Hz, 2H), 2.81 (d, J = 16.0 Hz, 1H), 1.74 (s, 3H), 1.32 (s, 3H), 1.25 (s, 3H), 1.10 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.66, 169.06, 158.64 (dd, $J_{C\text{-}F}$ = 243.8, 9.3 Hz), 148.10 (dd, $J_{C\text{-}F}$ = 248.3, 12.5 Hz), 138.08 (dd, $J_{C\text{-}F}$ = 5.1, 3.7 Hz), 130.59 (dd, $J_{C\text{-}F}$ = 13.1, 2.8 Hz), 104.94 (dd, $J_{C\text{-}F}$ = 24.8, 3.8 Hz), 104.13 (dd, $J_{C\text{-}F}$ = 21.6, 6.1Hz), 64.64, 64.0 (dd, $J_{C\text{-}F}$ = 2.5, 2.4 Hz), 60.47, 45.73, 40.84, 26.47, 22.74, 22.17, 13.93. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.01, -129.38. **HRMS (ESI)**: Calcd for $C_{17}H_{20}F_2N_2O_3$ $[M+H]^+$: 339.1515; found: 339.1514

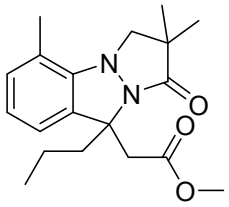
Methyl 2-(2,2,5-trimethyl-1-oxo-9-pentyl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate （3fb）



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 64.5 mg, 90% yield, colorless oil. Reaction time is 20 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 7.3 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 3.89 (d, *J* = 15.9 Hz, 1H), 3.67 (d, *J* = 7.7 Hz, 1H), 3.48 (d, *J* = 7.7 Hz, 1H), 3.43 (s, 3H), 2.79 (d, *J* = 15.9 Hz, 1H), 2.26 (s, 3H), 2.19 – 2.08 (m, 1H), 1.76 – 1.64 (m, 1H), 1.38 (s, 3H), 1.36 – 1.27 (m, 1H), 1.24 (s, 3H), 1.22 – 1.12 (m, 4H), 1.10 – 0.97 (m, 1H), 0.79 (t, *J* = 6.7 Hz, 3H). **^{13}C NMR** (100MHz, $CDCl_3$) δ 171.89, 170.00, 145.28, 132.41, 130.56, 122.55, 120.55, 118.95, 66.62, 64.81, 51.18, 45.60, 39.99, 39.73, 31.51, 23.36, 23.15, 22.30, 22.05, 17.66, 13.88. **HRMS (ESI)**: Calcd for $C_{21}H_{20}N_2O_3$ $[M+H]^+$: 359.2329; found: 359.2330

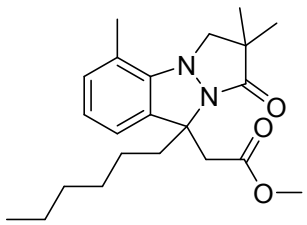
Methyl 2-(2,2,5-trimethyl-1-oxo-9-propyl-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fc)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 60.1 mg, 91% yield, yellow oil. Reaction time is 60 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 7.3 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.82 (d, *J* = 7.3 Hz, 1H), 3.91 (d, *J* = 15.9 Hz, 1H), 3.68 (d, *J* = 7.7 Hz, 1H), 3.48 (d, *J* = 7.7 Hz, 1H), 3.43 (s, 3H), 2.79 (d, *J* = 15.9 Hz, 1H), 2.26 (s, 3H), 2.19 – 2.08 (m, 1H), 1.73 – 1.61 (m, 1H), 1.39 (s, 3H), 1.38 – 1.31 (m, 1H), 1.24 (s, 3H), 1.12 – 0.98 (m, 1H), 0.83 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.94, 169.97, 145.28, 132.42, 130.56, 122.57, 120.56, 118.94, 66.60, 64.83, 51.17, 45.59, 42.43, 39.60, 23.17, 22.05, 17.65, 17.23, 13.85. **HRMS (ESI)**: Calcd for $C_{19}H_{26}N_2O_3$ $[M+H]^+$: 331.2016; found: 330.2015

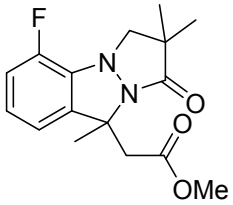
Methyl 2-(9-hexyl-2,2,5-trimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fd)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 66.6 mg, 90% yield, yellow oil. Reaction time is 15 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 (d, *J* = 7.3 Hz, 1H), 6.87 (t, *J* = 7.4 Hz, 1H), 6.81 (d, *J* = 7.2 Hz, 1H), 3.88 (d, *J* = 15.9 Hz, 1H), 3.67 (d, *J* = 7.7 Hz, 1H), 3.48 (d, *J* = 7.7 Hz, 1H), 3.43 (s, 3H), 2.79 (d, *J* = 15.9 Hz, 1H), 2.26 (s, 3H), 2.20 – 2.08 (m, 1H), 1.76 – 1.65 (m, 1H), 1.38 (s, 3H), 1.36 – 1.29 (m, 1H), 1.24 (s, 3H), 1.23 – 1.11 (m, 6H), 1.10 – 0.93 (m, 1H), 0.81 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.87, 169.98, 145.27, 132.41, 130.54, 122.53, 120.53, 118.94, 66.61, 64.80, 51.16, 45.58, 40.08, 39.70, 31.50, 29.02, 23.68, 23.15, 22.46, 22.03, 17.65, 13.92. **HRMS (ESI)**: Calcd for $C_{22}H_{32}N_2O_3$ $[M+H]^+$: 373.2486; found: 373.2486

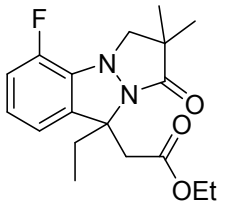
Methyl 2-(5-fluoro-2,2,9-trimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3gb)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 59.9mg, 98% yield, yellow oil. Reaction time is 15 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 – 6.89 (m, 2H), 6.84 (dd, *J* = 6.9, 1.7 Hz, 1H), 3.63 (d, *J* = 15.8 Hz, 1H), 3.59 (s, 2H), 3.49 (s, 3H), 2.84 (d, *J* = 15.8 Hz, 1H), 1.75 (s, 3H), 1.33 (s, 3H), 1.26 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.41, 169.65, 148.73 (d, $J_{C\text{-}F}$ = 245.2 Hz), 137.51 (d, $J_{C\text{-}F}$ = 3.8 Hz), 133.99 (d, $J_{C\text{-}F}$ = 13.0 Hz), 123.55 (d, $J_{C\text{-}F}$ = 5.9 Hz), 117.08 (d, $J_{C\text{-}F}$ = 3.4 Hz), 115.70 (d, $J_{C\text{-}F}$ = 17.3 Hz), 64.34 (d, $J_{C\text{-}F}$ = 1.8 Hz), 63.62 (d, $J_{C\text{-}F}$ = 1.5 Hz), 51.44, 45.83, 40.94, 26.41, 22.72, 22.18. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -133.34. **HRMS (ESI)**: Calcd for $C_{16}H_{19}FN_2O_3$ $[M+H]^+$: 307.1452; found: 307.1452

Ethyl 2-(9-ethyl-5-fluoro-2,2-dimethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3gc)

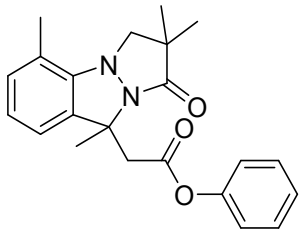


silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 62.1 mg, 93% yield, yellow oil. Reaction time is 25 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.97 – 6.86 (m, 2H), 6.78 (dd, *J* = 7.1, 1.4 Hz, 1H), 3.97 – 3.83 (m, 3H), 3.69 (dd, *J* = 8.1, 2.0 Hz, 1H), 3.54 (d, *J* = 8.1 Hz, 1H), 2.78 (d, *J* = 15.9 Hz, 1H), 2.22 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.79 (dq, *J* = 14.6, 7.3 Hz, 1H), 1.37 (s, 3H), 1.25 (s, 3H), 1.02 (t, *J* = 7.1 Hz, 3H), 0.81 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 172.13, 169.34, 148.76 (d, $J_{C\text{-}F}$ = 245.0 Hz), 135.63 (d, $J_{C\text{-}F}$ = 4.0 Hz), 134.54 (d, $J_{C\text{-}F}$ = 12.9 Hz), 123.31 (d, $J_{C\text{-}F}$ = 5.9 Hz), 117.25 (d, $J_{C\text{-}F}$ = 3.4 Hz), 115.64

(d, $J_{C\text{-}F}$ = 17.3 Hz), 68.11 (d, $J_{C\text{-}F}$ = 1.3 Hz), 64.33 (d, $J_{C\text{-}F}$ = 1.8 Hz), 60.18, 45.93, 39.71, 32.84, 23.11, 21.95, 13.89, 8.24. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -133.61. **HRMS (ESI)**: Calcd for $C_{18}H_{23}FN_2O_3$ $[M+H]^+$: 335.1765; found: 335.1765

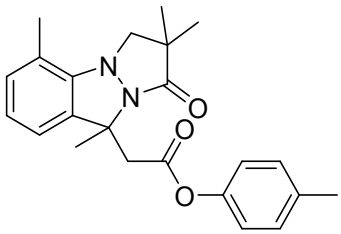
Phenyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fg)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 41.6 mg, 55% yield, yellow oil. Reaction time is 10 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (dd, *J* = 10.7, 5.0 Hz, 2H), 7.18 – 7.11 (m, 1H), 7.03 (t, *J* = 6.9 Hz, 2H), 6.98 – 6.93 (m, 1H), 6.74 (dd, *J* = 8.4, 0.9 Hz, 2H), 4.04 (d, *J* = 15.4 Hz, 1H), 3.57 (d, *J* = 7.8 Hz, 1H), 3.48 (d, *J* = 7.8 Hz, 1H), 3.05 (d, *J* = 15.4 Hz, 1H), 2.27 (s, 3H), 1.82 (s, 3H), 1.37 (s, 3H), 1.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.49, 168.07, 150.24, 144.85, 133.69, 130.78, 129.25, 129.25, 125.72, 122.87, 121.47, 121.47, 120.96, 119.21, 64.76, 63.06, 45.62, 41.31, 27.03, 22.92, 22.23, 17.62. **HRMS (ESI)**: Calcd for $C_{22}H_{24}N_2O_3$ $[M+H]^+$: 365.1860; found: 365.1860

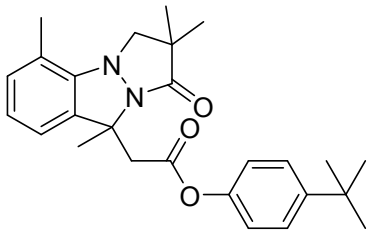
***p*-Tolyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fh)**



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 68.0 mg, 90% yield, white solid. Reaction time is 15 min. mp 131-134 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.03 (dd, *J* = 15.7, 7.3 Hz, 4H), 6.98 – 6.92 (m, 1H), 6.60 (d, *J* = 8.4 Hz, 2H), 4.05 (d, *J* = 15.4 Hz, 1H), 3.57 (d, *J* = 7.8 Hz, 1H), 3.48 (d, *J* = 7.8 Hz, 1H), 3.03 (d, *J* = 15.4 Hz, 1H), 2.27 (s, 3H), 1.82 (s, 3H), 1.38 (s, 3H), 1.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.45, 168.24, 147.94, 144.82, 135.30, 133.65, 130.71, 129.75, 129.75 122.80, 121.10, 121.10, 120.89, 119.20, 64.69, 63.04, 45.59, 41.19, 27.04, 22.90, 22.19, 20.73, 17.59. **HRMS (ESI)**: Calcd for $C_{23}H_{26}N_2O_3$ $[M+H]^+$: 379.2016; found: 379.2013

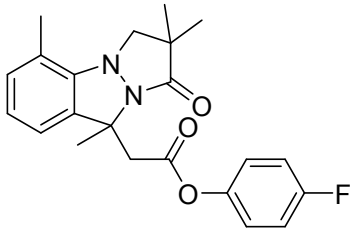
4-(Tert-butyl)phenyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fi)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 73.9 mg, 88% yield, white solid. Reaction time is 10 min. mp 175-177 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (d, *J* = 8.7 Hz, 2H), 7.05 (t, *J* = 6.8 Hz, 2H), 6.97 (t, *J* = 7.4 Hz, 1H), 6.68 (d, *J* = 8.7 Hz, 2H), 4.06 (d, *J* = 15.4 Hz, 1H), 3.60 (d, *J* = 7.8 Hz, 1H), 3.53 (d, *J* = 7.8 Hz, 1H), 3.07 (d, *J* = 15.4 Hz, 1H), 2.30 (s, 3H), 1.85 (s, 3H), 1.40 (s, 3H), 1.29 (s, 9H), 1.27 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.39, 168.21, 148.40, 147.84, 144.83, 133.70, 130.72, 126.12, 126.12, 122.81, 120.87, 120.71, 120.71, 119.21, 64.72, 63.01, 45.60, 41.26, 34.32, 31.29, 31.29, 31.29, 26.99, 22.88, 22.25, 17.61. **HRMS (ESI)**: Calcd for $C_{26}H_{32}N_2O_3$ $[M+H]^+$: 421.2486; found: 421.2487

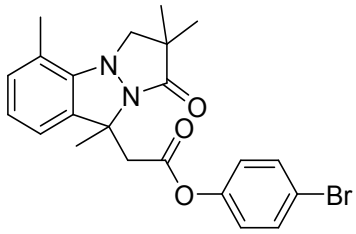
4-Fluorophenyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fj)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 72.5mg, 95% yield, white solid. Reaction time is 10 min. mp 139-140 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.02 (dd, *J* = 12.7, 7.0 Hz, 2H), 6.98 – 6.90 (m, 3H), 6.74 – 6.66 (m, 2H), 3.98 (d, *J* = 15.3 Hz, 1H), 3.56 (d, *J* = 7.8 Hz, 1H), 3.47 (d, *J* = 7.8 Hz, 1H), 3.02 (d, *J* = 15.3 Hz, 1H), 2.27 (s, 3H), 1.82 (s, 3H), 1.37 (s, 3H), 1.22 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.52, 168.21, 160.21 (d, J_{C-F} = 244.1 Hz), 146.12 (d, J_{C-F} = 2.8 Hz), 144.93, 133.74, 130.89, 122.99, 122.94, 122.90, 121.08, 119.20, 116.08, 115.85, 64.85, 63.07, 45.65, 41.44, 26.96, 22.94, 22.30, 17.68. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -117.10. **HRMS (ESI)**: Calcd for $C_{22}H_{23}FN_2O_3$ $[M+H]^+$: 383.1765; found: 383.1755

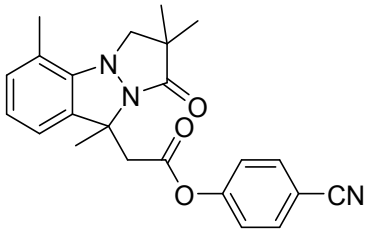
4-Bromophenyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fk)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 68.9mg, 78% yield, white solid. Reaction time is 10 min. mp 145-147 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.07 – 6.90 (m, 3H), 6.67 – 6.59 (m, 2H), 3.98 (d, *J* = 15.3 Hz, 1H), 3.56 (d, *J* = 7.8 Hz, 1H), 3.46 (d, *J* = 7.8 Hz, 1H), 3.02 (d, *J* = 15.2 Hz, 1H), 2.27 (s, 3H), 1.82 (s, 3H), 1.36 (s, 3H), 1.22 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.45, 167.79, 149.25, 144.83, 133.58, 132.30, 132.30, 130.83, 123.31, 123.31, 122.87, 121.01, 119.12, 118.88, 64.77, 62.99, 45.58, 41.38, 26.90, 22.86, 22.23, 17.61. **HRMS (ESI)**: Calcd for $C_{22}H_{23}BrN_2O_3$ $[M+H]^+$: 443.0965; found:443.0962

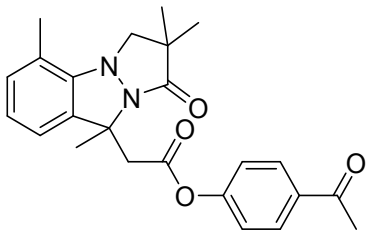
4-Cyanophenyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fl)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 63.0 mg, 81% yield, white solid. Reaction time is 30 min. mp 164-165 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 – 7.54 (m, 2H), 7.06 – 6.94 (m, 3H), 6.94 – 6.87 (m, 2H), 3.93 (d, *J* = 15.2 Hz, 1H), 3.55 (d, *J* = 7.9 Hz, 1H), 3.47 (d, *J* = 7.9 Hz, 1H), 3.04 (d, *J* = 15.2 Hz, 1H), 2.27 (s, 3H), 1.83 (s, 3H), 1.35 (s, 3H), 1.21 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.41, 167.27, 153.56, 144.84, 133.53, 133.48, 133.48, 130.93, 122.95, 122.72, 122.72, 121.11, 119.01, 118.13, 109.68, 64.83, 62.89, 45.53, 41.63, 26.68, 22.79, 22.24, 17.59. **HRMS (ESI)**: Calcd for $C_{23}H_{23}N_3O_3$ $[M+H]^+$: 390.1812; found: 390.1818

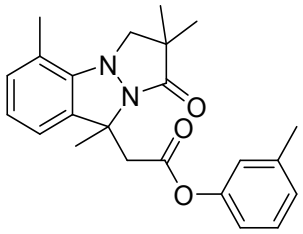
4-Acetylphenyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fm)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 79.5 mg, 98% yield, yellow oil. Reaction time is 10 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 – 7.83 (m, 2H), 7.06 – 6.90 (m, 3H), 6.87 – 6.79 (m, 2H), 3.99 (d, *J* = 15.3 Hz, 1H), 3.55 (d, *J* = 7.8 Hz, 1H), 3.45 (d, *J* = 7.9 Hz, 1H), 3.04 (d, *J* = 15.3 Hz, 1H), 2.52 (s, 3H), 2.26 (s, 3H), 1.82 (s, 3H), 1.35 (s, 3H), 1.21 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 196.73, 171.42, 167.53, 153.95, 144.81, 134.63, 133.51, 130.85, 129.74, 129.74,122.88, 121.68, 121.68, 121.01, 119.09, 64.76, 62.96, 45.55, 41.44, 26.87, 26.44, 22.81, 22.19, 17.57. **HRMS (ESI)**: Calcd for $C_{24}H_{26}N_2O_4$ $[M+H]^+$: 407.1965; found: 407.1964

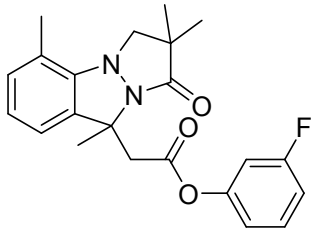
***m*-Tolyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fn)**



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 72.2 mg, 96% yield, white solid. Reaction time is 10 min. mp 136-137 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.14 (t, *J* = 7.8 Hz, 1H), 7.03 (t, *J* = 7.0 Hz, 2H), 6.95 (t, *J* = 7.3 Hz, 2H), 6.56 – 6.47 (m, 2H), 4.06 (d, *J* = 15.4 Hz, 1H), 3.58 (d, *J* = 7.8 Hz, 1H), 3.48 (d, *J* = 7.8 Hz, 1H), 3.04 (d, *J* = 15.4 Hz, 1H), 2.27 (d, *J* = 5.4 Hz, 6H), 1.82 (s, 3H), 1.38 (s, 3H), 1.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.45, 168.15, 150.13, 144.81, 139.32, 133.63, 130.69, 128.90, 126.48, 122.80, 122.03, 120.87, 119.23, 118.34, 64.68, 63.04, 45.58, 41.19, 27.09, 22.90, 22.16, 21.10, 17.57. **HRMS (ESI)**: Calcd for $C_{23}H_{26}N_2O_3$ $[M+H]^+$: 379.2016; found: 379.2013

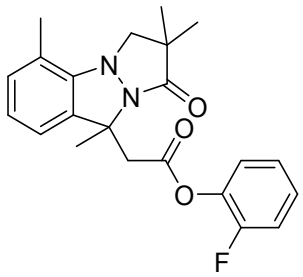
3-Fluorophenyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fo)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 74.8 mg, 98% yield, white solid. Reaction time is 10 min. mp 110-111 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.21 (td, *J* = 8.3, 6.5 Hz, 1H), 7.02 (dd, *J* = 14.8, 6.9 Hz, 2H), 6.98 – 6.92 (m, 1H), 6.86 (td, *J* = 8.7, 2.1 Hz, 1H), 6.58 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.48 (dt, *J* = 9.5, 2.3 Hz, 1H), 4.00 (d, *J* = 15.3 Hz, 1H), 3.57 (d, *J* = 7.8 Hz, 1H), 3.48 (d, *J* = 7.9 Hz, 1H), 3.03 (d, *J* = 15.3 Hz, 1H), 2.27 (s, 3H), 1.82 (s, 3H), 1.37 (s, 3H), 1.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.44, 167.67, 162.66 (d, J_{C-F} = 247.4 Hz), 151.06 (d, J_{C-F} = 10.9 Hz), 144.82, 133.54, 130.86, 129.97 (d, J_{C-F} = 9.3 Hz), 122.89, 121.01, 119.12, 117.30 (d, J_{C-F} = 3.4 Hz), 112.77 (d, J_{C-F} = 21.1 Hz), 109.58 (d, J_{C-F} = 24.4 Hz), 64.78, 62.98, 45.57, 41.38, 26.94, 22.84, 22.21, 17.57. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -111.16. **HRMS (ESI)**: Calcd for $C_{22}H_{23}FN_2O_3$ $[M+H]^+$: 383.1765; found: 383.1765

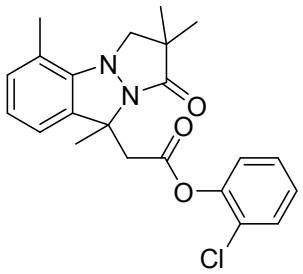
2-Fluorophenyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fp)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 71.0 mg, 93% yield, white solid. Reaction time is 10 min. mp 123-126 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.08 (m, 1H), 7.08 – 6.99 (m, 4H), 6.97 – 6.91 (m, 1H), 6.87 – 6.80 (m, 1H), 4.01 (d, *J* = 15.6 Hz, 1H), 3.56 (d, *J* = 7.8 Hz, 1H), 3.50 (d, *J* = 7.8 Hz, 1H), 3.14 (d, *J* = 15.6 Hz, 1H), 2.27 (s, 3H), 1.83 (s, 3H), 1.37 (s, 3H), 1.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.35, 166.90, 153.91 (d, J_{C-F} = 249.8 Hz), 144.79, 137.60 (d, J_{C-F} = 12.9 Hz), 133.57, 130.77, 126.92 (d, J_{C-F} = 7.0 Hz), 124.24 (d, J_{C-F} = 3.9 Hz), 123.72, 122.87, 120.90, 119.18, 116.48 (d, J_{C-F} = 18.4 Hz), 64.77, 62.84, 45.57, 40.92, 26.81, 22.83, 22.20, 17.60. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -128.30. **HRMS (ESI)**: Calcd for $C_{22}H_{23}FN_2O_3$ $[M+H]^+$: 383.1765; found: 383.1766

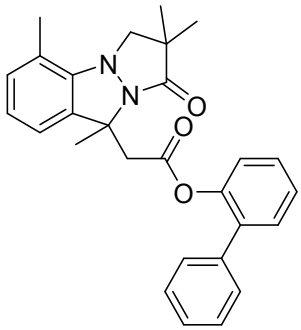
2-Chlorophenyl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fq)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 76.4 mg, 96% yield, white solid. Reaction time is 10 min. mp 143-145 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.16 (td, *J* = 7.7, 1.6 Hz, 1H), 7.09 (td, *J* = 7.7, 1.6 Hz, 1H), 7.02 (dd, *J* = 7.2, 2.5 Hz, 2H), 6.96 – 6.90 (m, 1H), 6.82 (dd, *J* = 8.0, 1.6 Hz, 1H), 4.07 (d, *J* = 15.9 Hz, 1H), 3.58 (d, *J* = 7.8 Hz, 1H), 3.51 (d, *J* = 7.8 Hz, 1H), 3.16 (d, *J* = 15.9 Hz, 1H), 2.27 (s, 3H), 1.82 (s, 3H), 1.37 (s, 3H), 1.23 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.42, 166.95, 146.58, 144.81, 133.60, 130.75, 130.04, 127.53, 126.87, 126.80, 123.60, 122.87, 120.90, 119.22, 64.73, 62.79, 45.57, 40.72, 26.97, 22.88, 22.19, 17.60. **HRMS (ESI)**: Calcd for $C_{22}H_{23}ClN_2O_3$ $[M+H]^+$: 399.1470; found: 399.1473

[1,1'-Biphenyl]-2-yl 2-(2,2,5,9-tetramethyl-1-oxo-2,3-dihydro-1H,9H-pyrazolo[1,2-a]indazol-9-yl)acetate (3fr)



silica gel column chromatography (petroleum ether/ethyl acetate = 4:1), 85.3 mg, 97% yield, white solid. Reaction time is 10 min. mp 172-173 °C

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 – 7.20 (m, 8H), 7.00 (d, *J* = 7.4 Hz, 1H), 6.87 (t, *J* = 7.5 Hz, 1H), 6.80 (dd, *J* = 7.3, 2.2 Hz, 2H), 3.84 (d, *J* = 16.1 Hz, 1H), 3.60 – 3.52 (m, 2H), 2.90 (d, *J* = 16.1 Hz, 1H), 2.28 (s, 3H), 1.74 (s, 3H), 1.38 (s, 3H), 1.24 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 171.36, 168.07, 147.24, 144.83, 137.26, 134.58, 133.71, 130.65, 130.57, 128.79, 128.79, 128.27, 128.21, 128.21, 127.36, 126.16, 122.78, 122.77, 120.76, 118.97, 64.71, 62.68, 45.49, 40.74, 26.74, 22.88, 22.22, 17.58. **HRMS (ESI)**: Calcd for $C_{28}H_{28}N_2O_3$ $[M+H]^+$: 441.2173; found: 441.2176

6. X-ray Crystallographic data of 3la

CCDC 1852306 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

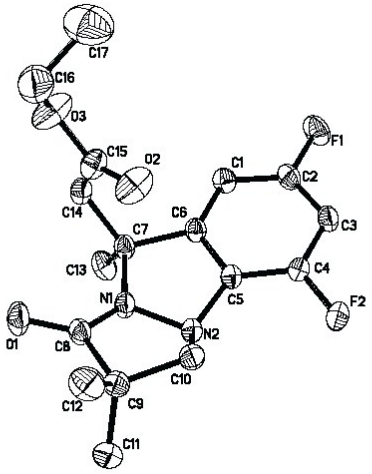


Table 1 Crystal data and structure refinement for 3la.

Identification code	exp_5657
Empirical formula	$C_{17}H_{20}F_2N_2O_3$
Formula weight	338.35
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12$
a/Å	15.6208(15)
b/Å	11.2655(7)
c/Å	9.9974(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	1759.3(2)
Z	4
ρ_{calc}g/cm^3	1.277
μ/mm^{-1}	0.102
F(000)	712.0
Crystal size/mm^3	0.15 × 0.14 × 0.12
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	7.234 to 58.852
Index ranges	-19 ≤ h ≤ 21, -14 ≤ k ≤ 15, -12 ≤ l ≤ 11
Reflections collected	15610

Independent reflections	4261 [R_{int} = 0.0369, R_{sigma} = 0.0399]
Data/restraints/parameters	4261/2/230
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0553, wR_2 = 0.1483
Final R indexes [all data]	R_1 = 0.0981, wR_2 = 0.1764
Largest diff. peak/hole / e $Å^{-3}$	0.21/-0.19
Flack parameter	0.3(5)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for 3la. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
C1	2345(3)	3305(3)	2216(4)	60.7(9)
C2	2242(3)	2661(3)	3361(4)	64.7(9)
C3	1765(2)	3020(3)	4424(4)	66.4(10)
C4	1357(2)	4096(4)	4321(4)	64.1(9)
C5	1420(2)	4781(3)	3189(3)	56.5(8)
C6	1927(2)	4380(3)	2157(3)	53.5(8)
C7	1911(2)	5269(3)	1012(3)	55.4(8)
C8	1410(2)	7392(3)	1545(4)	58.5(9)
C9	953(3)	7907(3)	2740(4)	66.3(10)
C10	1025(3)	6877(3)	3720(4)	68.5(10)
C11	30(3)	8148(4)	2340(6)	89.0(13)
C12	1393(3)	9021(4)	3226(5)	92.6(14)
C13	1445(3)	4770(4)	-193(4)	79.2(12)
C14	2806(2)	5676(3)	607(4)	61.2(9)
C15	3326(3)	6224(4)	1672(4)	71.0(11)
C16	4626(11)	7408(19)	1940(20)	136(5)
C16A	4627(18)	6920(30)	2380(30)	136(5)
C17	5130(12)	6471(15)	2573(18)	171(5)
C17A	5335(14)	7600(20)	1880(30)	171(5)
F1	2642.0(18)	1584(2)	3447(3)	93.1(8)
F2	876.5(17)	4495(2)	5353(2)	97.2(9)
N1	1404.9(19)	6218(2)	1644(3)	59.3(8)
N2	981.7(19)	5833(3)	2866(3)	61.6(8)
O1	1722(2)	7943(2)	604(3)	88.2(10)
O2	3118(2)	6438(3)	2785(3)	101.5(12)

O3	4088(2)	6512(4)	1216(4)	126.2(14)

Table 3 Anisotropic Displacement Parameters ($Å^2×10^3$) for 3la. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
C1	73(2)	46.2(18)	63(2)	-3.8(17)	-0.1(18)	0.4(16)
C2	76(2)	45.6(17)	73(2)	9.7(18)	-6(2)	1.3(16)
C3	68(2)	66(2)	66(2)	23.6(19)	-2(2)	-4.3(18)
C4	56.4(19)	73(2)	63(2)	19.3(18)	10.9(18)	4.4(18)
C5	58.9(18)	51.5(18)	59.1(19)	10.5(16)	5.5(17)	-0.6(16)
C6	62.9(19)	42.0(15)	55.5(18)	4.2(15)	1.2(17)	-2.4(14)
C7	74(2)	43.1(16)	49.4(17)	1.6(14)	6.5(16)	3.1(15)
C8	73(2)	41.1(16)	61(2)	6.3(15)	9.2(19)	3.8(15)
C9	77(2)	50.7(18)	71(2)	3.7(17)	14(2)	11.5(16)
C10	80(2)	67(2)	59(2)	2.4(18)	17.3(19)	18.9(19)
C11	79(3)	80(3)	108(3)	17(3)	14(3)	21(2)
C12	108(3)	64(2)	106(3)	-15(2)	5(3)	8(2)
C13	107(3)	65(2)	65(2)	1.2(19)	-16(2)	2(2)
C14	82(2)	46.4(17)	54.7(19)	-0.7(15)	18.9(18)	4.0(17)
C15	82(3)	63(2)	68(2)	-9(2)	17(2)	-11.4(19)
C16	100(5)	170(17)	139(14)	47(9)	-20(8)	-28(10)
C16A	100(5)	170(17)	139(14)	47(9)	-20(8)	-28(10)
C17	133(9)	174(11)	206(14)	-12(11)	-46(10)	-6(9)
C17A	133(9)	174(11)	206(14)	-12(11)	-46(10)	-6(9)
F1	121(2)	56.0(13)	102.5(18)	16.5(12)	-3.8(16)	22.4(13)
F2	104.4(17)	108(2)	79.2(14)	37.7(14)	38.2(15)	27.6(15)
N1	79.1(18)	45.4(14)	53.5(15)	7.0(12)	15.4(15)	2.1(13)
N2	66.3(17)	56.3(16)	62.2(17)	15.8(13)	13.0(15)	5.8(13)
O1	132(3)	51.1(14)	81.8(17)	16.9(14)	36.2(19)	4.8(15)
O2	102(2)	122(3)	81(2)	-43(2)	12.8(18)	-27.9(19)
O3	87(2)	170(4)	122(3)	-30(3)	28(2)	-40(2)

Table 4 Bond Lengths for 3la.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
C1	C2	1.365(5)	C8	N1	1.325(4)
C1	C6	1.377(5)	C8	O1	1.228(4)
C2	C3	1.359(6)	C9	C10	1.523(5)

C2	F1	1.368(4)	C9	C11	1.521(7)
C3	C4	1.373(5)	C9	C12	1.511(6)
C4	C5	1.373(5)	C10	N2	1.455(5)
C4	F2	1.353(4)	C14	C15	1.475(6)
C5	C6	1.378(5)	C15	O2	1.184(5)
C5	N2	1.406(5)	C15	O3	1.314(5)
C6	C7	1.521(5)	C16	C17	1.459(18)
C7	C13	1.516(5)	C16	O3	1.50(2)
C7	C14	1.526(5)	C16A	C17A	1.44(2)
C7	N1	1.472(4)	C16A	O3	1.50(3)
C8	C9	1.508(5)	N1	N2	1.456(4)

Table 5 Bond Angles for 3la.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C2	C1	C6	116.6(3)	O1	C8	N1	124.3(3)
C1	C2	F1	118.0(4)	C8	C9	C10	100.5(3)
C3	C2	C1	124.2(3)	C8	C9	C11	108.0(4)
C3	C2	F1	117.7(3)	C8	C9	C12	111.1(4)
C2	C3	C4	117.3(3)	C11	C9	C10	112.0(4)
C3	C4	C5	121.6(4)	C12	C9	C10	113.1(4)
F2	C4	C3	119.6(3)	C12	C9	C11	111.5(4)
F2	C4	C5	118.8(3)	N2	C10	C9	103.6(3)
C4	C5	C6	118.3(3)	C15	C14	C7	116.0(3)
C4	C5	N2	128.9(3)	O2	C15	C14	127.8(4)
C6	C5	N2	112.6(3)	O2	C15	O3	121.6(4)
C1	C6	C5	121.9(3)	O3	C15	C14	110.6(4)
C1	C6	C7	128.3(3)	C17	C16	O3	91.4(13)
C5	C6	C7	109.8(3)	C17A	C16A	O3	109(2)
C6	C7	C14	112.5(3)	C8	N1	C7	133.6(3)
C13	C7	C6	111.2(3)	C8	N1	N2	111.3(3)
C13	C7	C14	109.9(3)	N2	N1	C7	112.8(2)
N1	C7	C6	99.5(2)	C5	N2	C10	121.6(3)
N1	C7	C13	110.6(3)	C5	N2	N1	102.9(3)
N1	C7	C14	112.8(3)	C10	N2	N1	103.3(3)
N1	C8	C9	108.8(3)	C15	O3	C16	120.3(9)
O1	C8	C9	126.9(3)	C15	O3	C16A	108.3(11)

Table 6 Torsion Angles for 3la.

A	B	C	D	Angle/°	A	B	C	D	Angle/°
C1	C2	C3	C4	0.6(6)	C9	C8	N1	C7	-161.8(3)
C1	C6	C7	C13	66.8(5)	C9	C8	N1	N2	-1.1(4)
C1	C6	C7	C14	-56.9(5)	C9	C10	N2	C5	148.0(3)
C1	C6	C7	N1	-176.6(3)	C9	C10	N2	N1	33.5(4)
C2	C1	C6	C5	-0.9(5)	C11	C9	C10	N2	81.0(4)
C2	C1	C6	C7	-178.8(3)	C12	C9	C10	N2	-151.9(4)
C2	C3	C4	C5	0.6(6)	C13	C7	C14	C15	177.9(3)
C2	C3	C4	F2	-179.8(4)	C13	C7	N1	C8	-96.0(5)
C3	C4	C5	C6	-1.8(6)	C13	C7	N1	N2	103.6(3)
C3	C4	C5	N2	172.9(4)	C14	C7	N1	C8	27.5(5)
C4	C5	C6	C1	2.0(5)	C14	C7	N1	N2	-132.9(3)
C4	C5	C6	C7	-179.7(3)	C14	C15	O3	C16	160.6(7)
C4	C5	N2	C10	57.7(5)	C14	C15	O3	C16A	-172.7(14)
C4	C5	N2	N1	172.4(4)	C17	C16	O3	C15	99.8(12)
C5	C6	C7	C13	-111.3(3)	C17A	C16A	O3	C15	-161(2)
C5	C6	C7	C14	124.9(3)	F1	C2	C3	C4	-179.2(3)
C5	C6	C7	N1	5.3(4)	F2	C4	C5	C6	178.5(3)
C6	C1	C2	C3	-0.4(6)	F2	C4	C5	N2	-6.8(6)
C6	C1	C2	F1	179.4(3)	N1	C7	C14	C15	53.9(4)
C6	C5	N2	C10	-127.4(3)	N1	C8	C9	C10	21.5(4)
C6	C5	N2	N1	-12.6(4)	N1	C8	C9	C11	-95.9(4)
C6	C7	C14	C15	-57.7(4)	N1	C8	C9	C12	141.5(4)
C6	C7	N1	C8	147.0(4)	N2	C5	C6	C1	-173.5(3)
C6	C7	N1	N2	-13.5(4)	N2	C5	C6	C7	4.7(4)
C7	C14	C15	O2	-4.0(6)	O1	C8	C9	C10	-160.1(4)
C7	C14	C15	O3	178.5(4)	O1	C8	C9	C11	82.4(5)
C7	N1	N2	C5	16.5(4)	O1	C8	C9	C12	-40.2(6)
C7	N1	N2	C10	143.9(3)	O1	C8	N1	C7	19.9(7)
C8	C9	C10	N2	-33.5(4)	O1	C8	N1	N2	-179.5(4)
C8	N1	N2	C5	-148.4(3)	O2	C15	O3	C16	-17.1(10)
C8	N1	N2	C10	-21.0(4)	O2	C15	O3	C16A	9.6(15)

Table 7 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for 3la.

Atom	*x*	*y*	*z*	U(eq)
H1	2680	3032	1512	73
H3	1716	2556	5189	80

H10A 1562	6906	4204	82
H10B 556	6886	4357	82
H11A 19	8660	1573	133
H11B -264	8525	3069	133
H11C -249	7413	2127	133
H12A 1972	8838	3477	139
H12B 1092	9331	3986	139
H12C 1396	9603	2524	139
H13A 1768	4121	-559	119
H13B 1383	5379	-858	119
H13C 890	4494	74	119
H14A 3115	4996	261	73
H14B 2750	6243	-118	73
H16A 4959	7911	1352	164
H16B 4304	7883	2577	164
H16C 4286	7397	2980	164
H16D 4836	6232	2870	164
H17A 5258	5868	1925	257
H17B 4809	6129	3296	257
H17C 5653	6799	2913	257
H17D 5384	7481	928	257
H17E 5853	7341	2305	257
H17F 5242	8422	2061	257

Table 8 Atomic Occupancy for 3la.

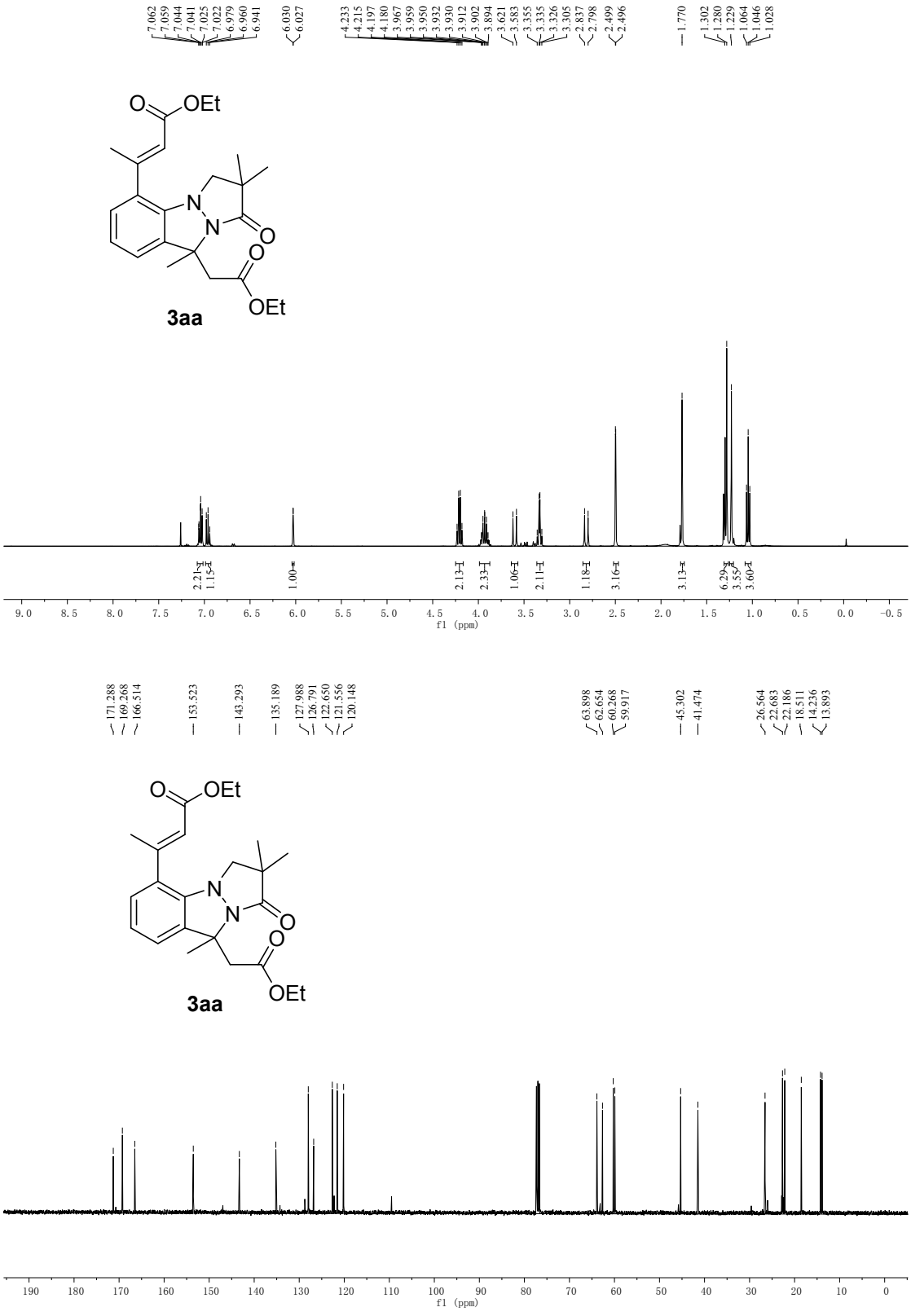
Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
C16	0.587(11)	H16A	0.587(11)	H16B	0.587(11)
C16A	0.413(11)	H16C	0.413(11)	H16D	0.413(11)
C17	0.587(11)	H17A	0.587(11)	H17B	0.587(11)
H17C	0.587(11)	C17A	0.413(11)	H17D	0.413(11)
H17E	0.413(11)	H17F	0.413(11)		

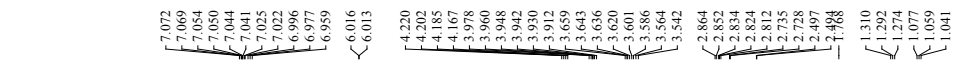
7. References:

(1) C. F. H. Allen, J. R. Jr. Byers, US2772282, 1956.

(2) Jaimes, M. C. B.; Ahrens, A.; Rudolph, M.; Hashmi, A. S. K. *Chem. Eur. J.* 2015, 21, 427

Copies of [1] H, [13]C, and [19]F NMR of products

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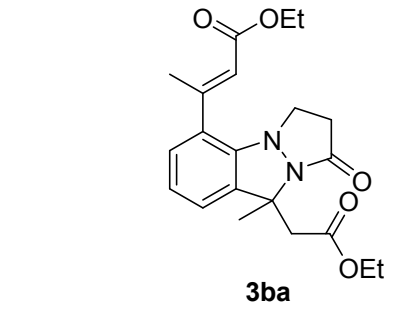
7.050
7.044
7.041
7.025
7.022
6.996
6.977
6.959
6.016
6.013
4.220
4.202
4.185
4.167
3.978
3.960
3.948
3.942
3.930
3.912
3.659
3.643
3.636
3.620
3.601
3.586
3.564
3.542
2.864
2.852
2.834
2.824
2.812
2.735
2.728
2.497
1.768
1.310
1.292
1.274
1.077
1.059
1.041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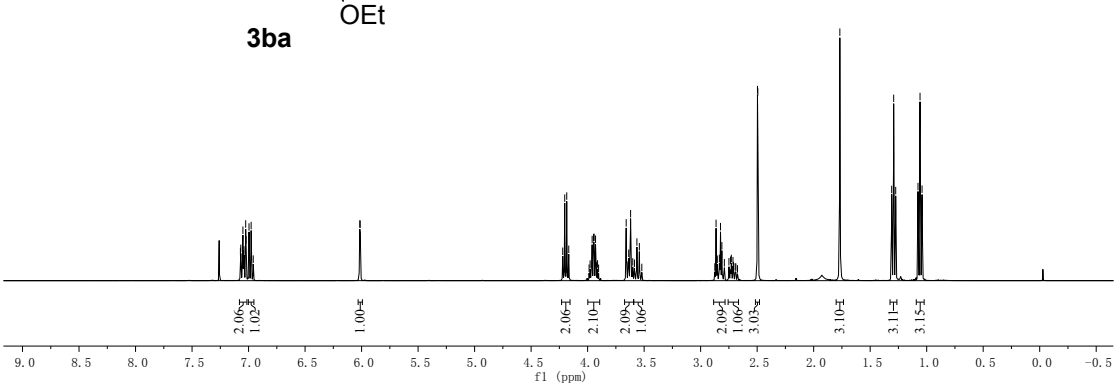
N
N
O
O
OEt

3ba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2.10
2.09
1.06
2.09
1.06
3.03
3.10
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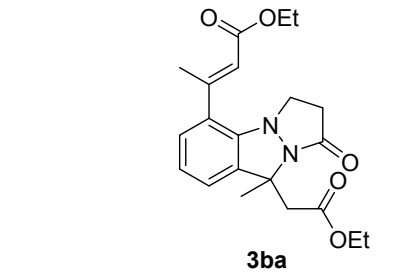
3.15
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


169.317
166.417
166.180
153.324
143.316
135.181
128.020
126.844
122.850
121.530
120.169
62.744
60.307
59.958
51.041
41.152
34.900
26.563
18.806
14.228
13.884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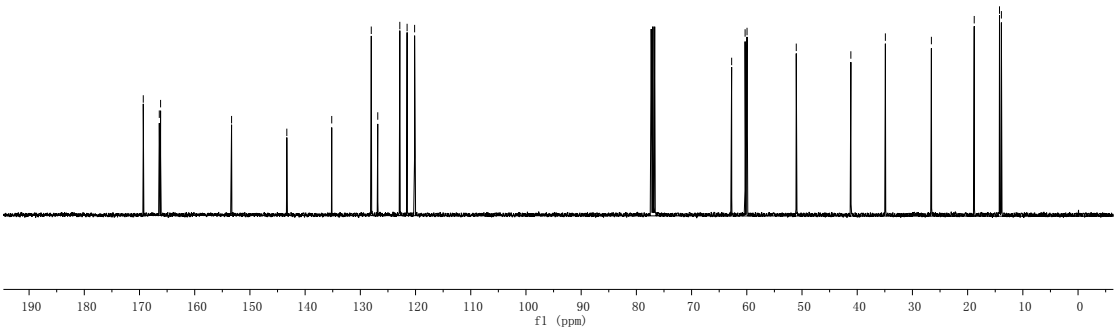
OEt
N
N
O
O
OEt

3ba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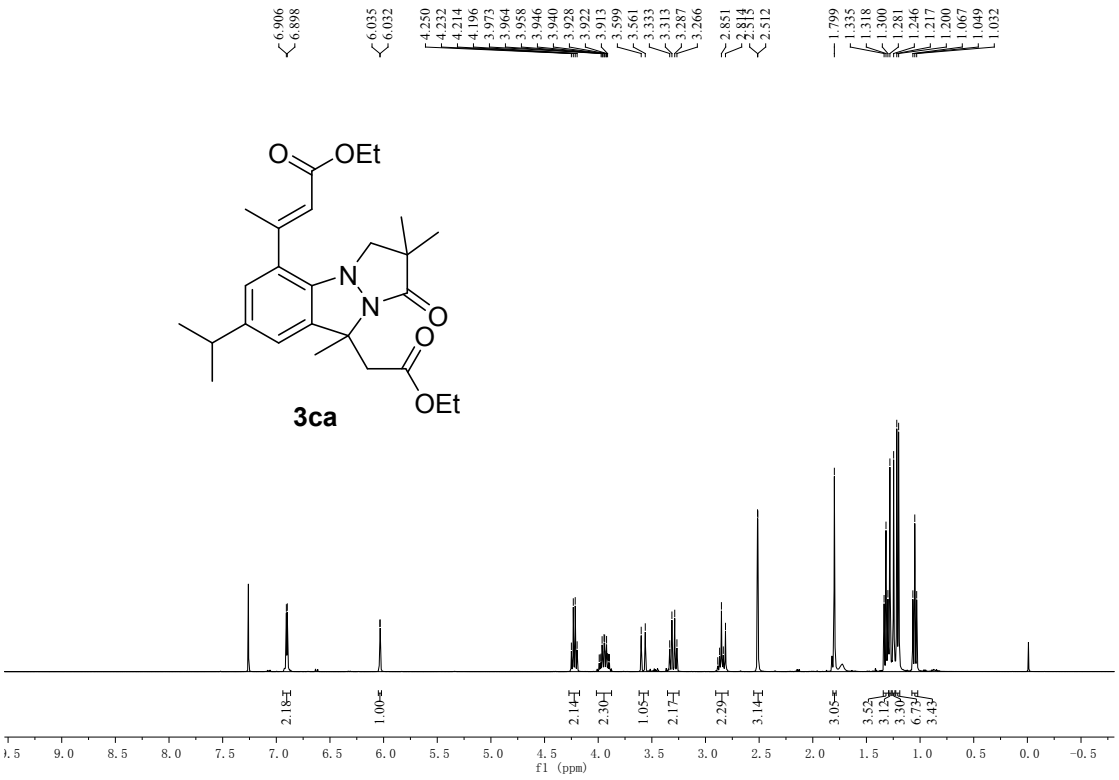
f1 (ppm)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3.940
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3.922
3.913
3.599
3.561
3.333
3.313
3.287
3.266
2.851
2.814
2.513
2.512
1.799
1.335
1.318
1.300
1.281
1.246
1.217
1.200
1.067
1.049
1.032
O
OEt
N
N
O
O
OEt
3ca
2.18
1.00
2.14
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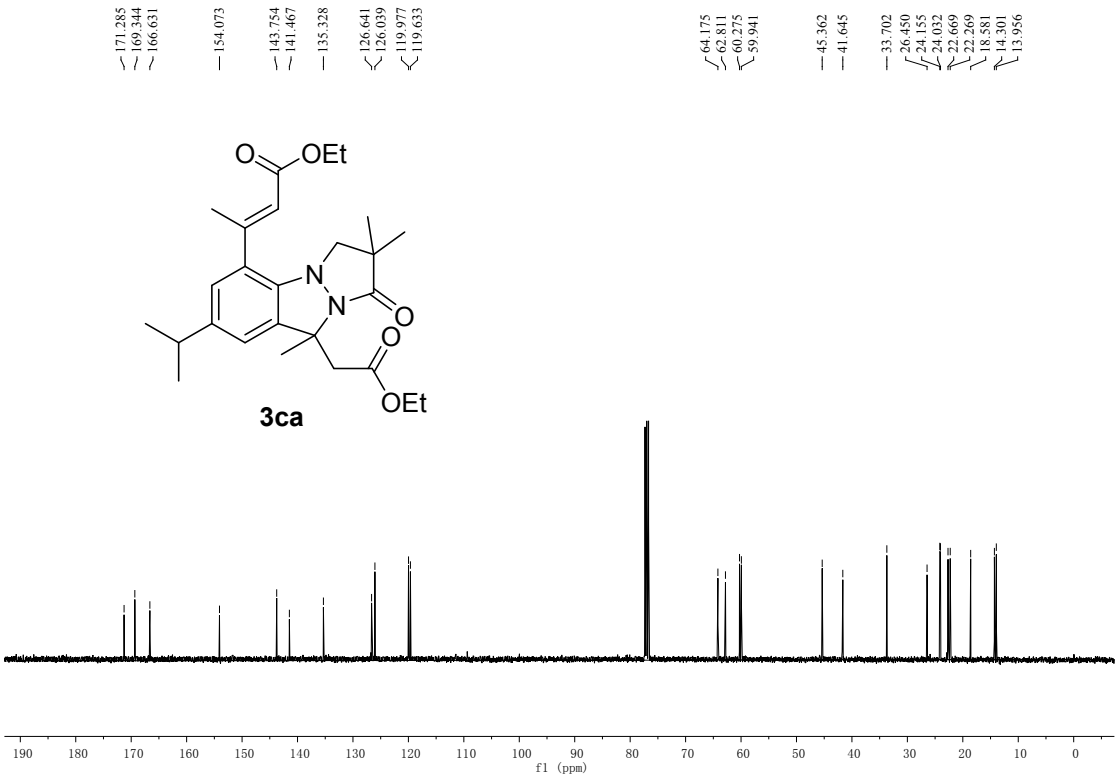
1.05
2.17
2.29
3.14
3.05
3.53
3.12
3.30
6.73
3.43
f1 (ppm)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62.811
60.275
59.941
45.362
41.645
33.702
26.450
24.155
24.032
22.669
22.269
18.581
14.301
13.956
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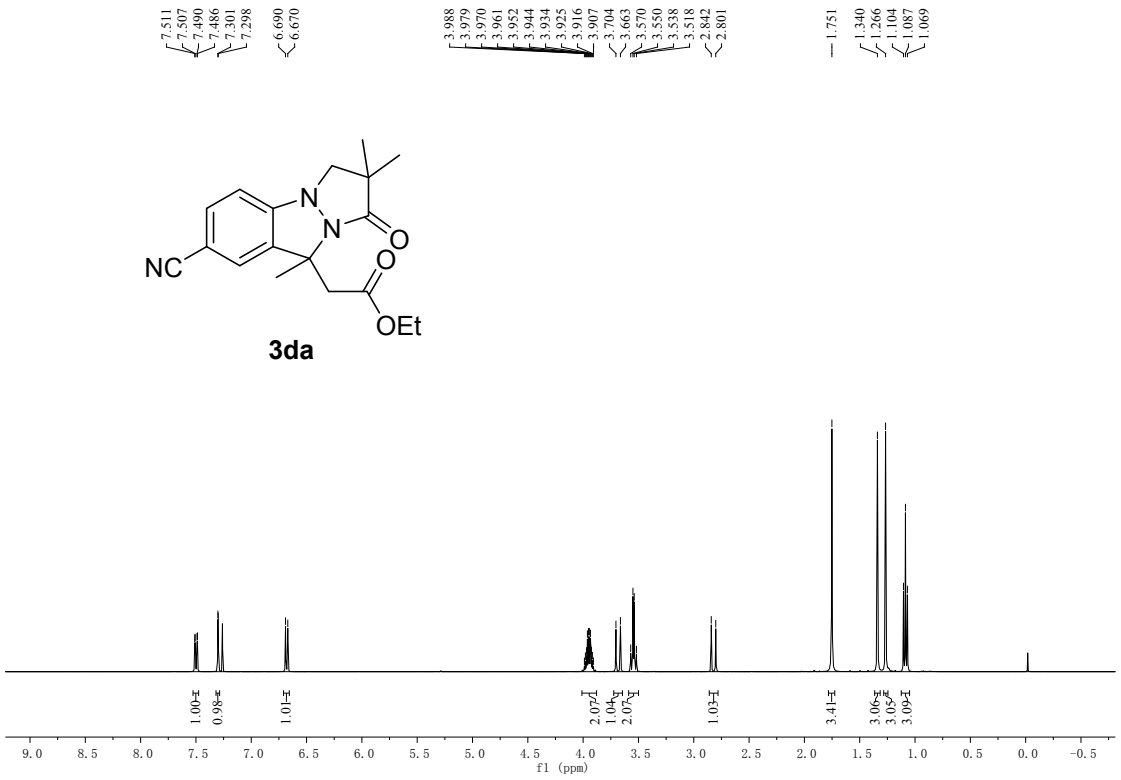
OEt
N
N
O
O
OEt
3ca
f1 (ppm)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6.670
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3.970
3.961
3.952
3.944
3.934
3.925
3.916
3.907
3.704
3.663
3.570
3.550
3.538
3.518
2.842
2.801
1.751
1.340
1.266
1.104
1.087
1.069
N
N
O
O
NC
OEt
1.00
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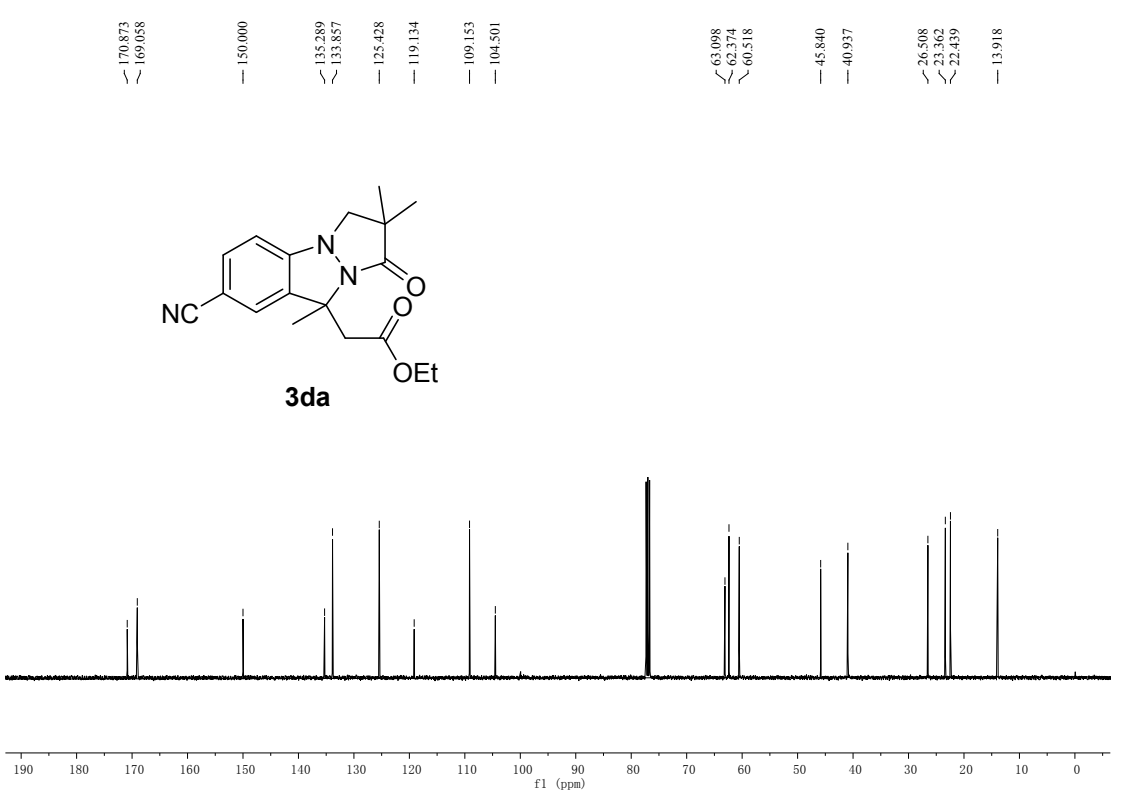
1.04
2.07
1.03
3.41
3.06
3.05
3.09
f1 (ppm)

3da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23.362
22.439
13.918
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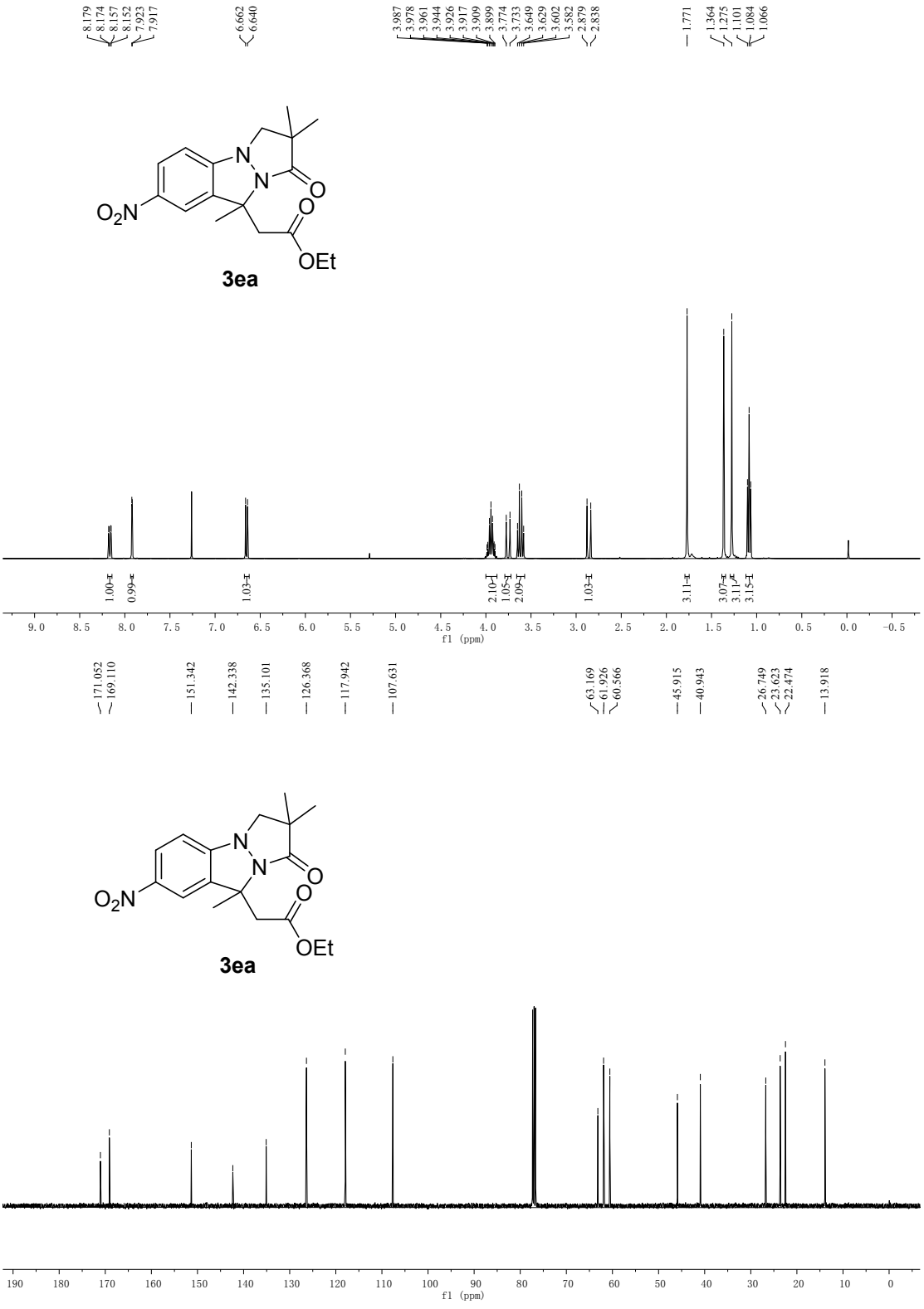
N
O
O
NC
OEt
f1 (ppm)

3da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3.926
3.917
3.909
3.899
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3.733
3.649
3.629
3.602
3.582
2.879
2.838
1.771
1.364
1.275
1.101
1.084
1.066
O2N
N
N
O
O
OEt
3ea
1.00
0.99
1.03
2.10
1.05
2.09
1.03
3.11
3.07
3.11
3.15
f1 (ppm)
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151.342
142.338
135.101
126.368
117.942
107.631
63.169
61.926
60.566
45.915
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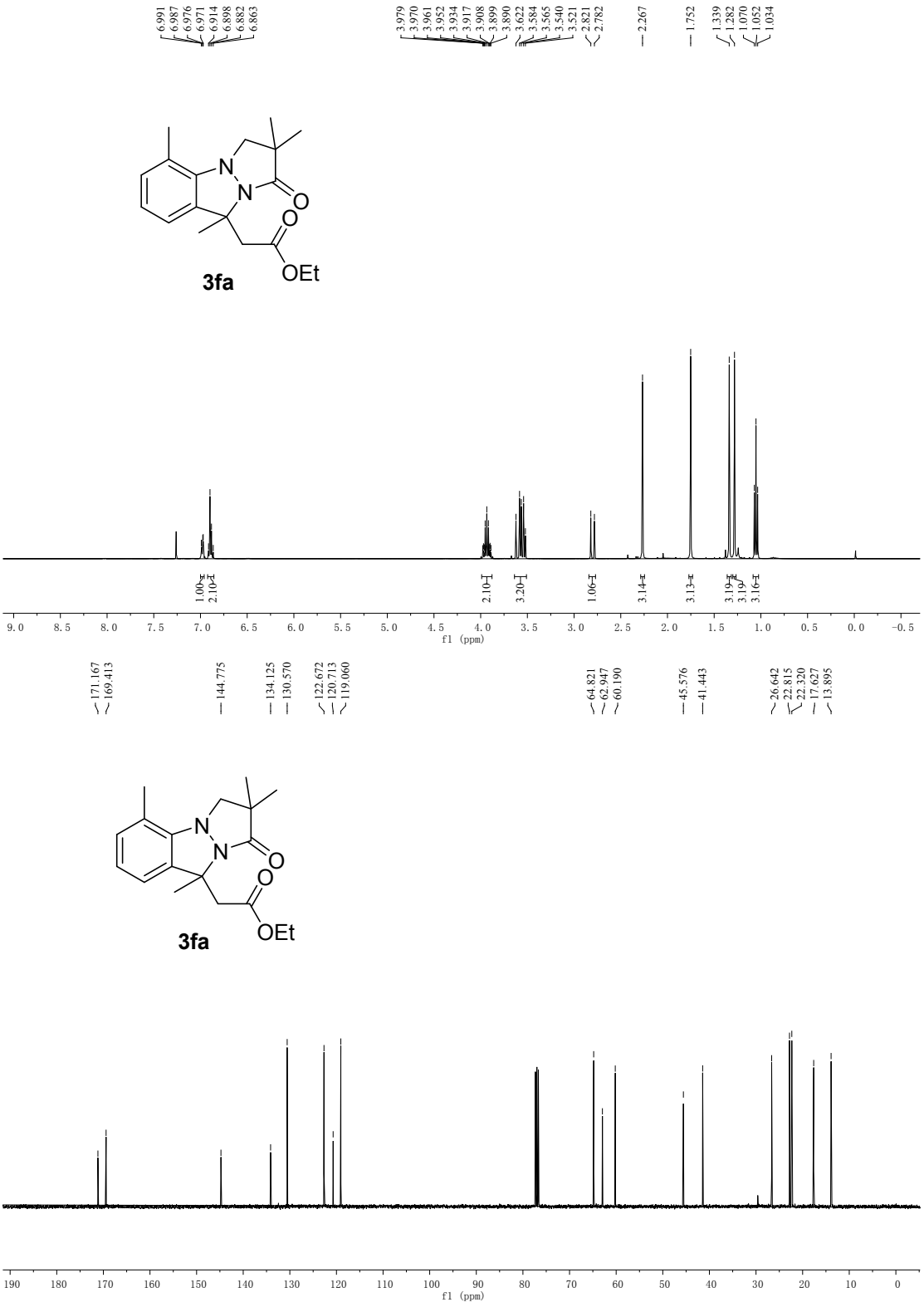
N
N
O
O
OEt
3ea
f1 (ppm)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N
N
O
O
OEt
3fa
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2.10
2.10
3.20
1.06
3.14
3.13
3.19
3.19
3.16
f1 (ppm)
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22.320
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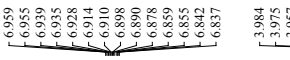
f1 (ppm)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6.842
6.837
3.984
3.975
3.957
3.943
3.939
3.925
3.907
3.898
3.880
3.637
3.613
3.610
3.597
3.592
3.590
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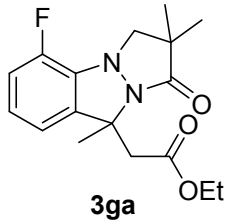
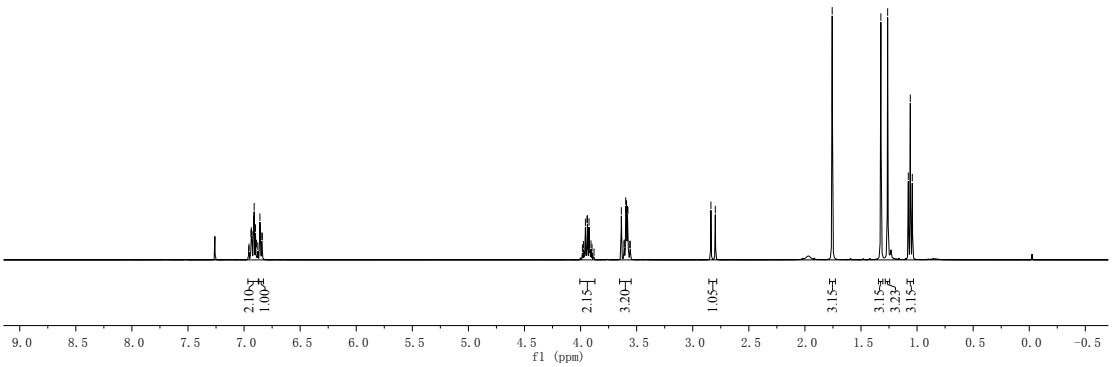

F
N
N
O
O
OEt

3ga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2.15
3.20
1.05
3.15
3.15
3.23
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f1 (ppm)


171.355
169.184
149.940
147.504
137.582
137.544
134.069
133.940
123.494
123.436
117.197
117.163
115.717
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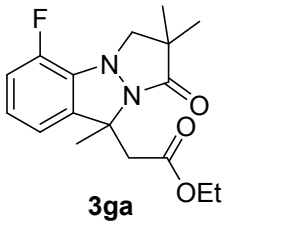
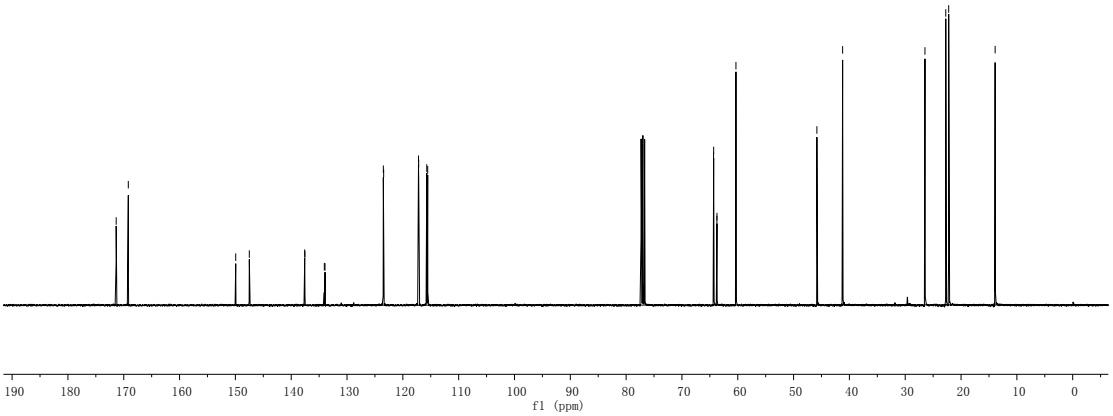

F
N
N
O
O
OEt

3ga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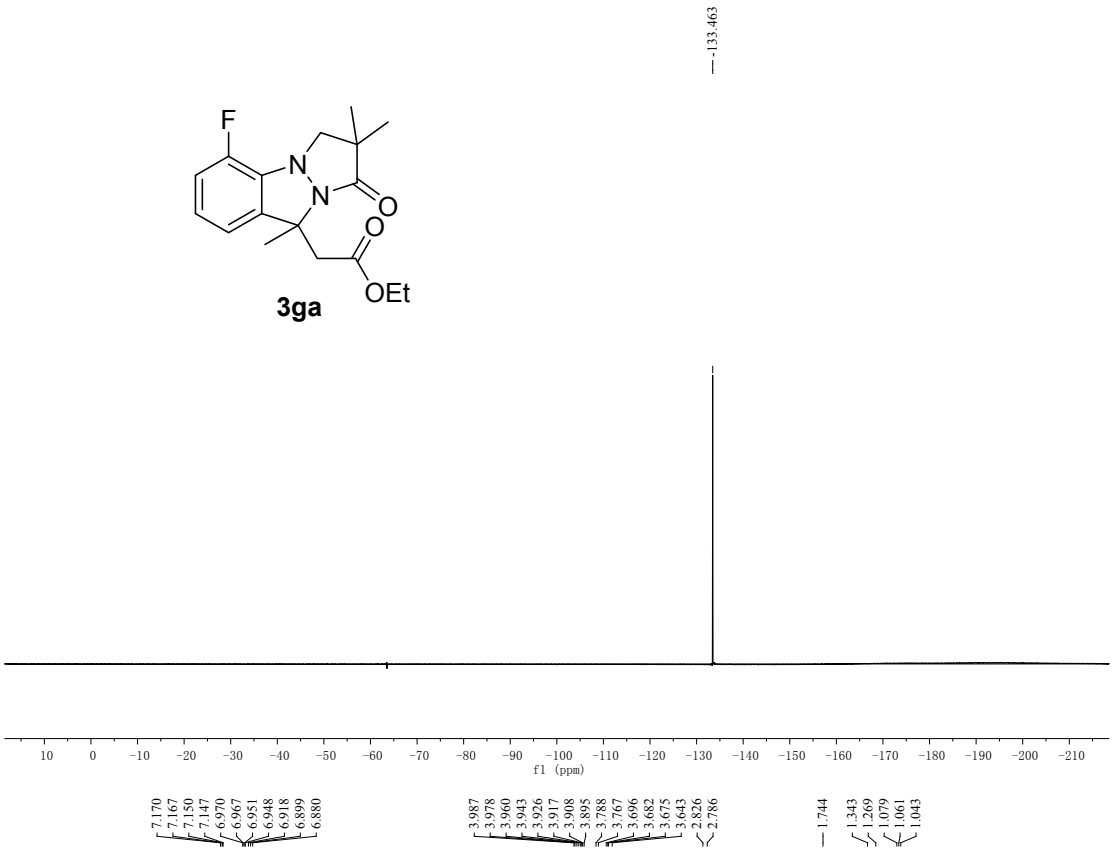
f1 (ppm)

F
N
N
O
O
OEt

3ga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10 0 −10 −20 −30 −40 −50 −60 −70 −80 −90 −100 −110 −120 −130 −140 −150 −160 −170 −180 −190 −200 −210
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7.150
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6.951
6.948
6.918
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6.880
3.987
3.978
3.960
3.943
3.926
3.917
3.908
3.895
3.788
3.767
3.696
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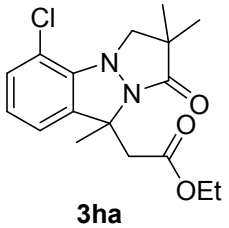
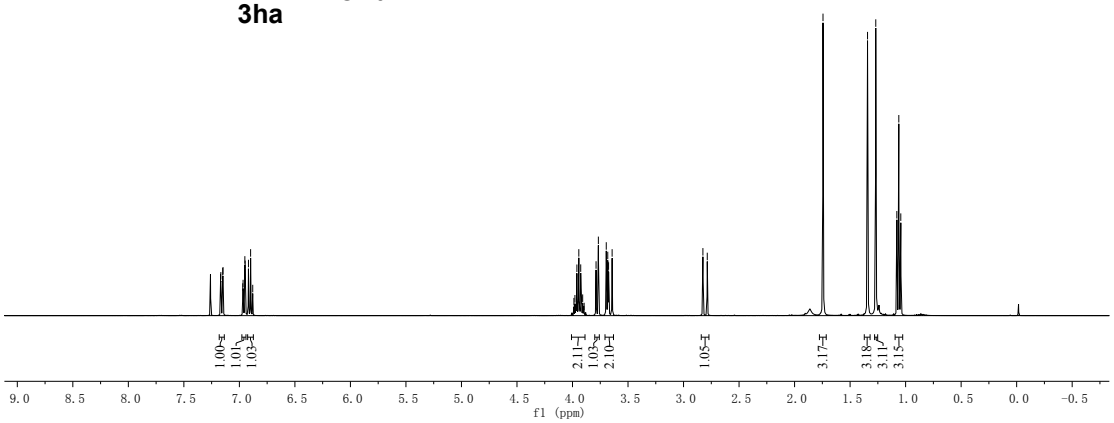
1.079
1.061
1.043


Cl
N
N
O
O
OEt

3ha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1.03
2.10
1.05
3.17
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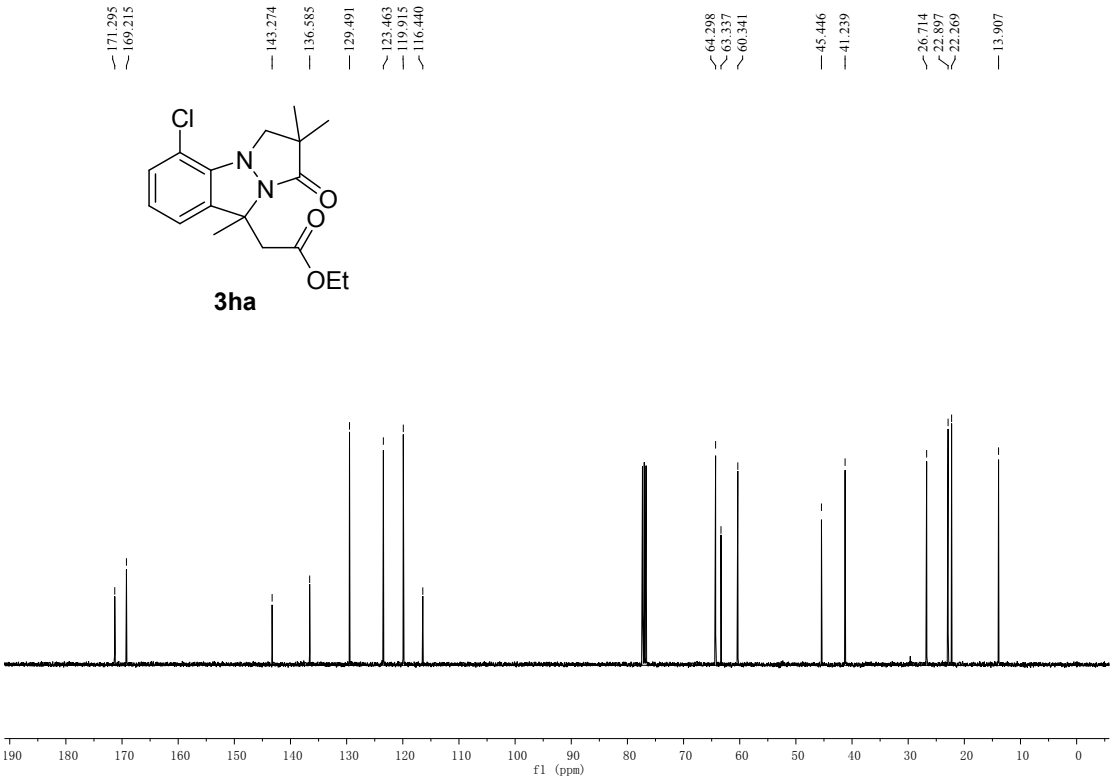
3.11
3.15
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)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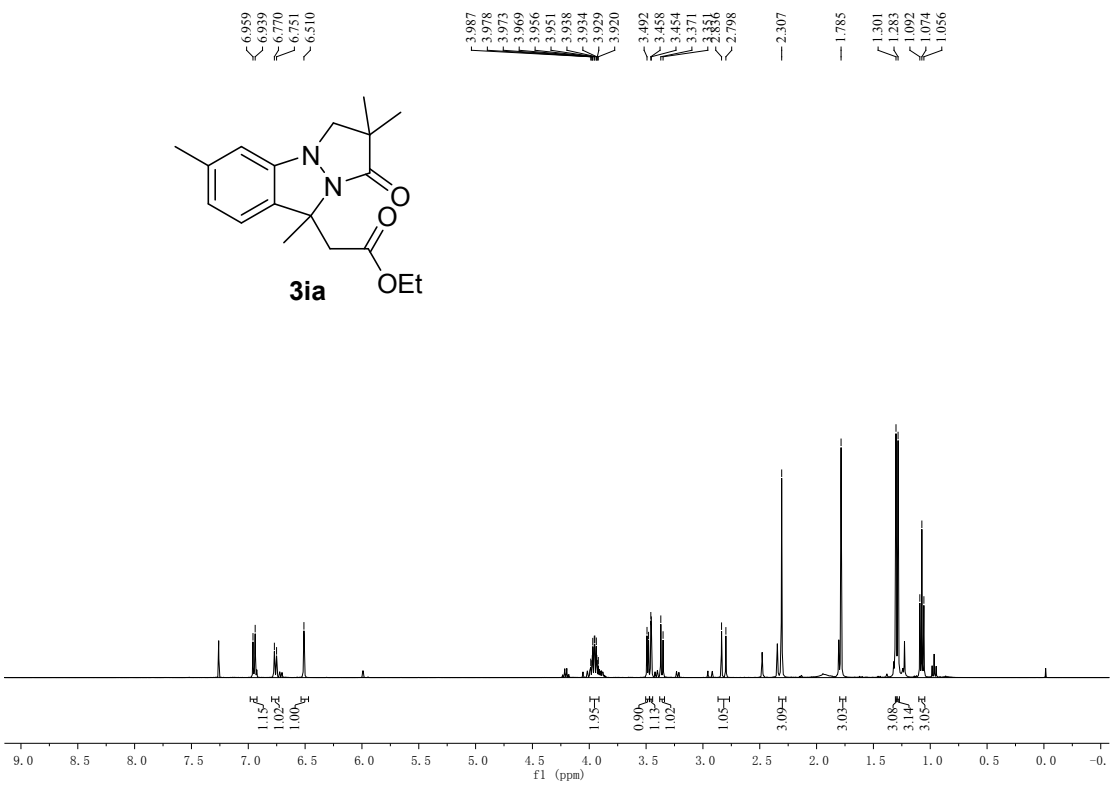
Cl
N
N
O
O
OEt
3ha
f1 (ppm)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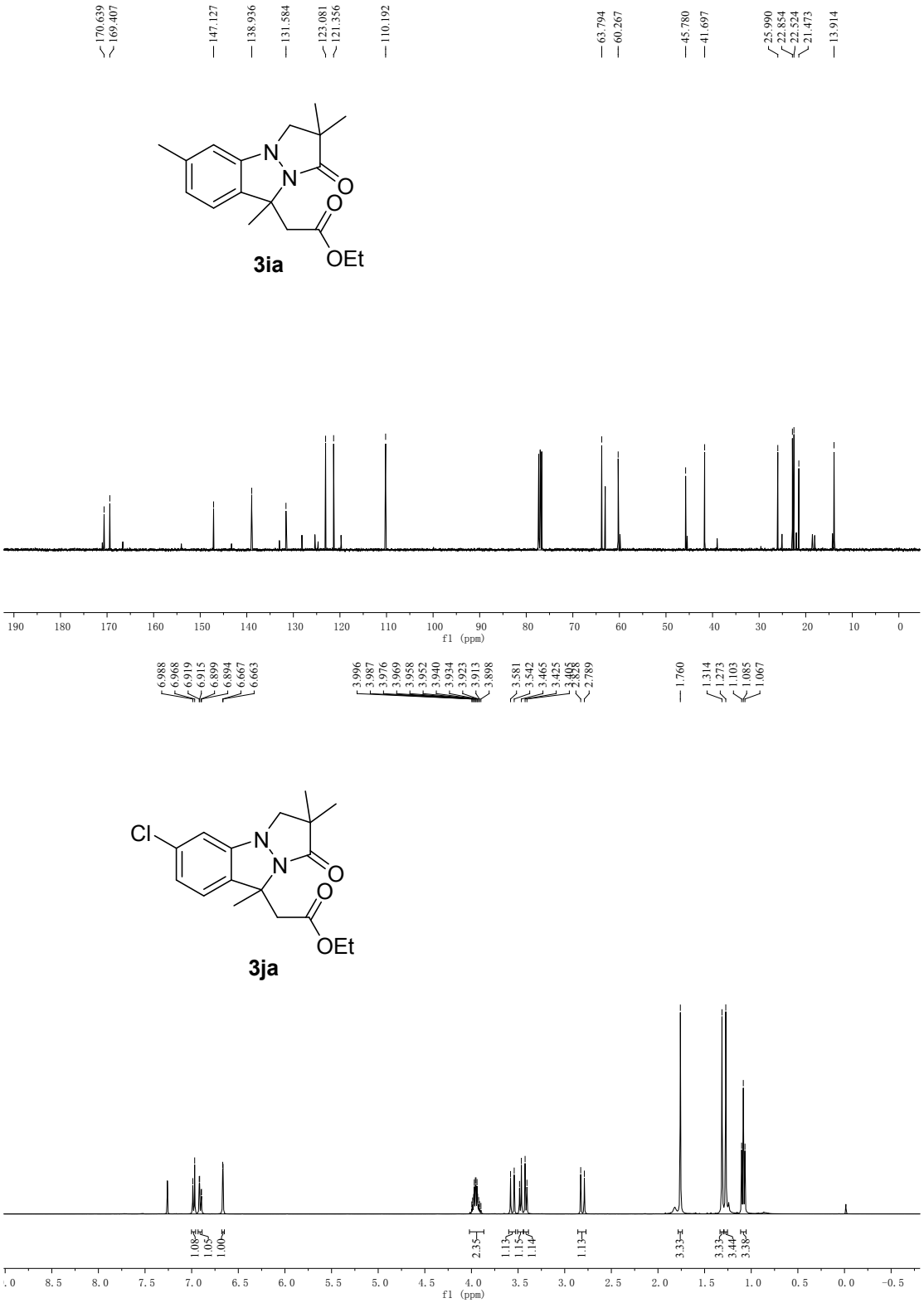
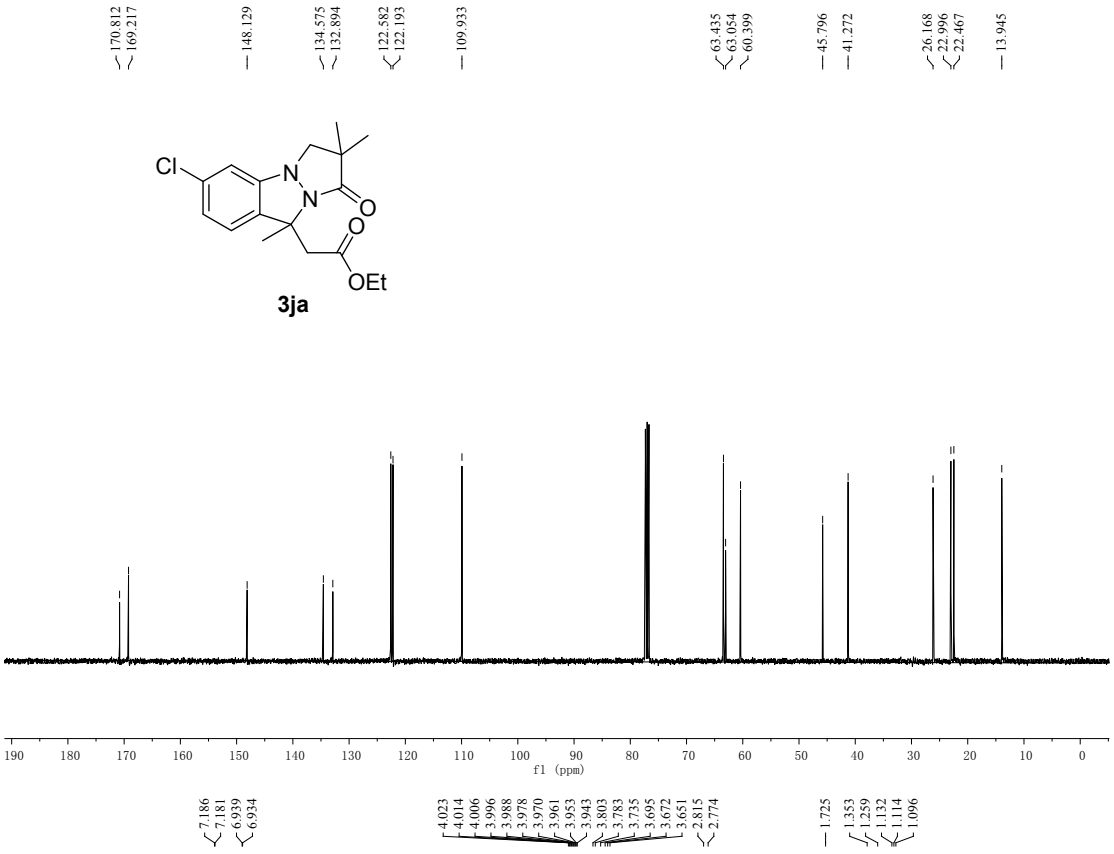
1.283
1.092
1.074
1.056
N
N
O
O
OEt
3ia
1.15
1.02
1.00
1.95
0.90
1.13
1.02
1.05
3.09
3.03
3.08
3.14
3.05
f1 (ppm)


170.639
169.407
147.127
138.936
131.584
123.081
121.356
110.192
63.794
60.267
45.780
41.697
25.990
22.854
22.524
21.473
13.914
N
N
O
O
OEt
3ia
f1 (ppm)
6.988
6.968
6.919
6.915
6.899
6.894
6.667
6.663
3.996
3.987
3.976
3.969
3.958
3.952
3.940
3.934
3.923
3.913
3.898
3.581
3.542
3.465
3.425
2.858
2.789
1.760
1.314
1.273
1.103
1.085
1.067
Cl
N
N
O
O
OEt
3ja
1.08
1.05
1.00
2.35
1.13
1.15
1.14
1.13
3.33
3.33
3.44
3.38
f1 (ppm)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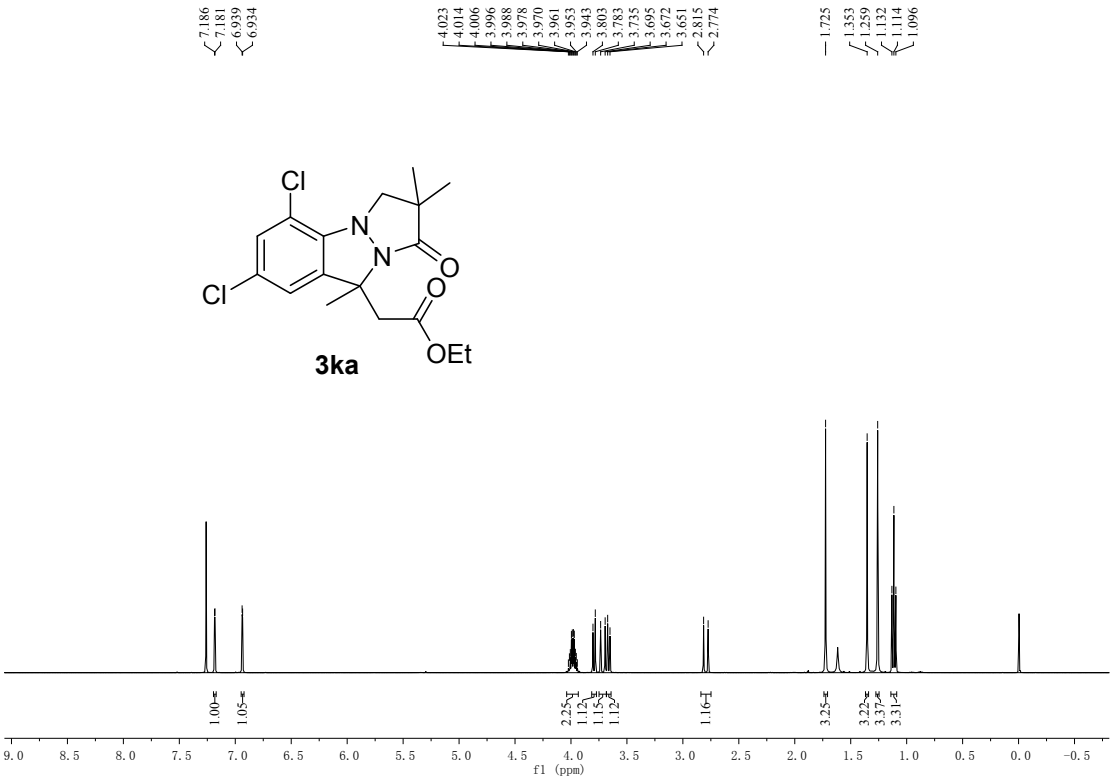
169.217
148.129
134.575
132.894
122.582
122.193
109.933
63.435
63.054
60.399
45.796
41.272
26.168
22.996
22.467
13.945
Cl
N
N
O
O
OEt
3ja
f1 (ppm)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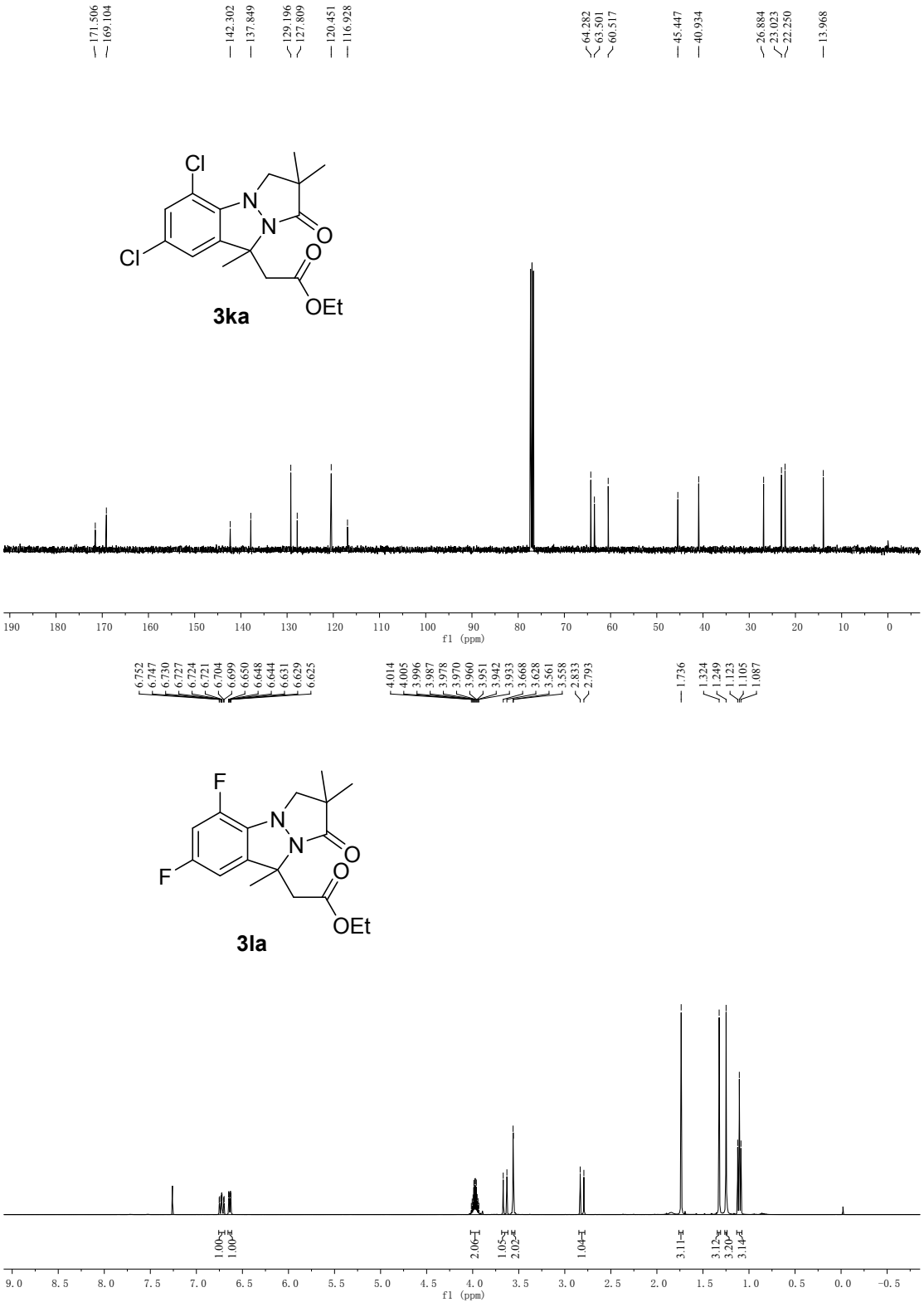
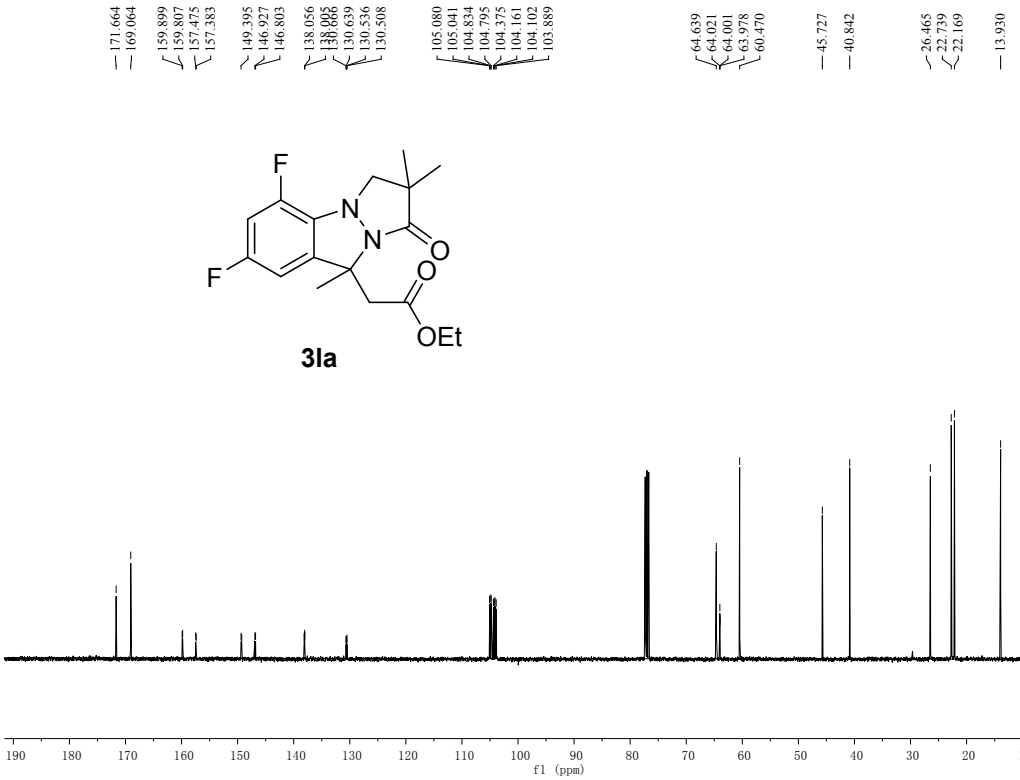
7.181
6.939
6.934
4.023
4.014
4.006
3.996
3.988
3.978
3.970
3.961
3.953
3.943
3.803
3.783
3.735
3.695
3.672
3.651
2.815
2.774
1.725
1.353
1.259
1.132
1.114
1.096
Cl
Cl
N
N
O
O
OEt
3ka
1.00
1.05
2.25
1.12
1.15
1.12
1.16
3.25
3.22
3.37
3.31
f1 (ppm)


171.506
169.104
142.302
137.849
129.196
127.809
120.451
116.928
64.282
63.501
60.517
45.447
40.934
26.884
23.023
22.250
13.968
Cl
Cl
N
N
O
O
OEt
3ka
f1 (ppm)
6.752
6.747
6.730
6.727
6.724
6.721
6.704
6.699
6.650
6.648
6.644
6.631
6.629
6.625
4.014
4.005
3.996
3.987
3.978
3.970
3.960
3.951
3.942
3.933
3.668
3.628
3.561
3.558
2.833
2.793
1.736
1.324
1.249
1.123
1.105
1.087
F
F
N
N
O
O
OEt
3la
1.00
1.00
2.06
1.05
2.02
1.04
3.11
3.12
3.20
3.14
f1 (ppm)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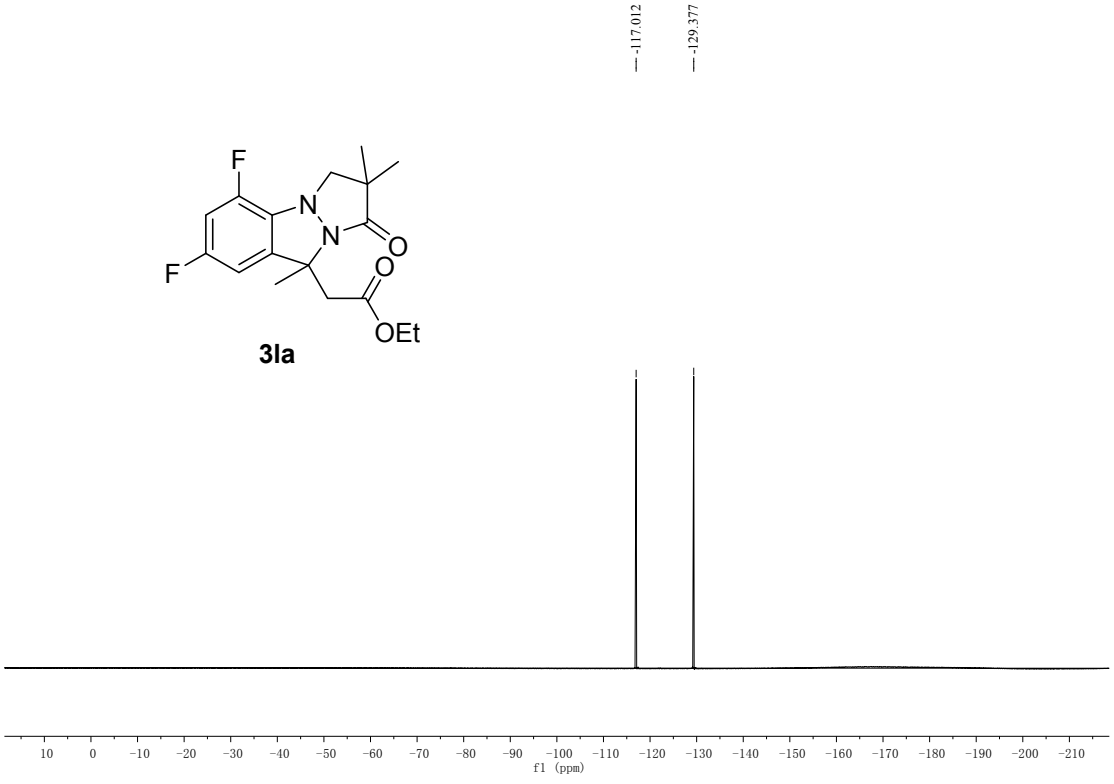
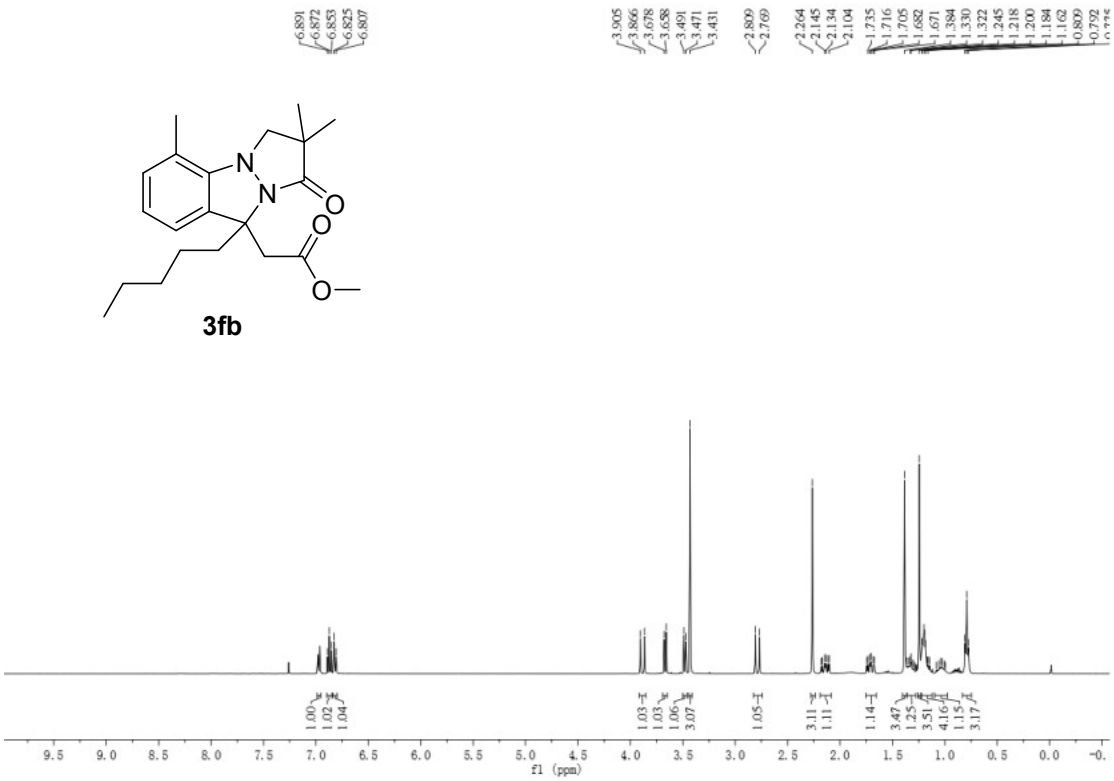
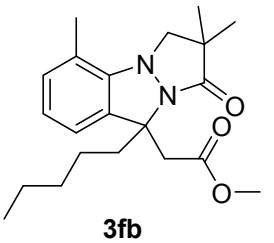
159.899
159.807
157.475
157.383
149.395
146.927
146.803
138.056
130.639
130.536
130.508
105.080
105.041
104.834
104.795
104.375
104.161
104.102
103.889
64.639
64.021
64.001
63.978
60.470
45.727
40.842
26.465
22.739
22.169
13.930
F
F
N
N
O
O
OEt
3la
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

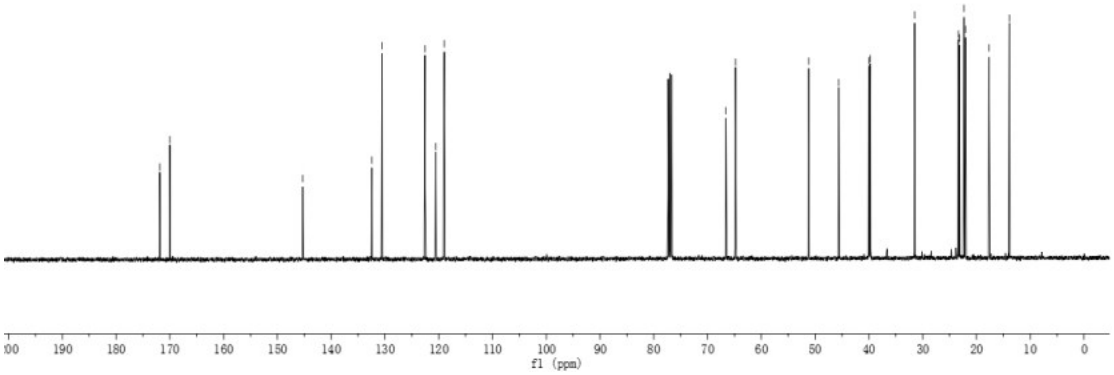

-117.012
-129.377
F
F
N
N
O
O
OEt
3la
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

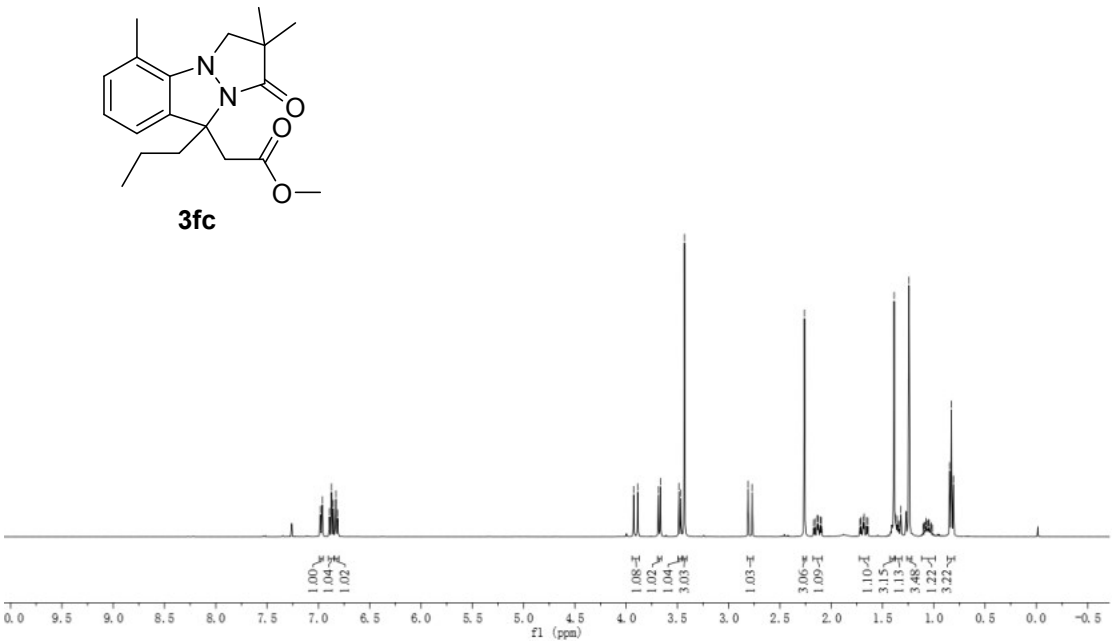
3fb



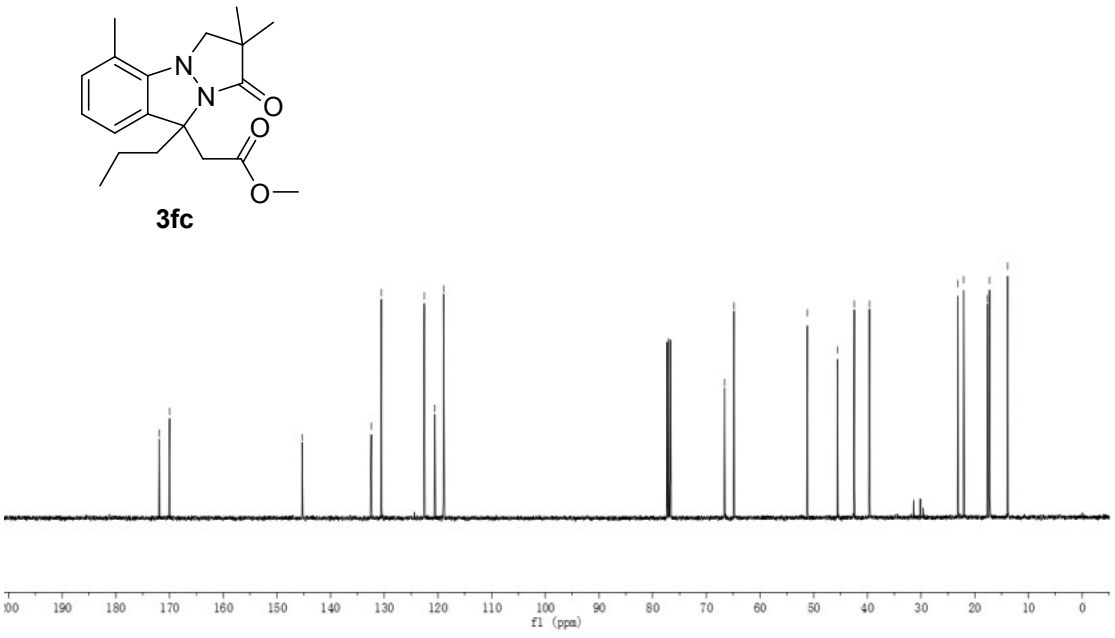


3fb



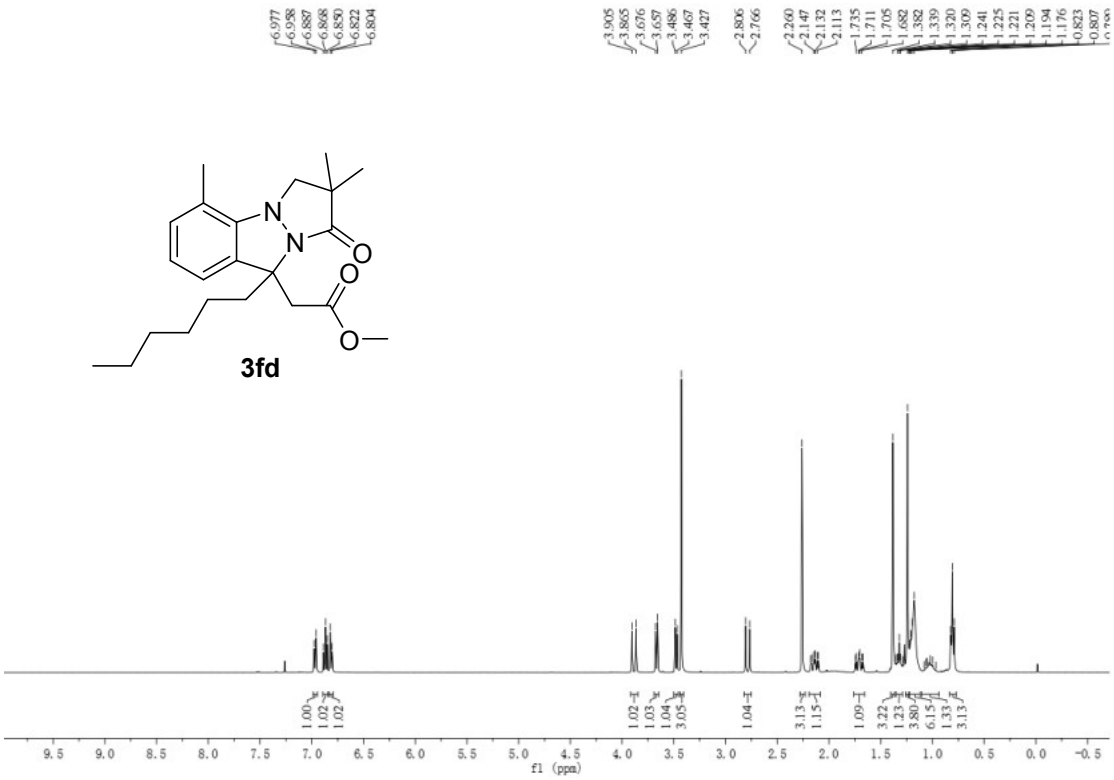


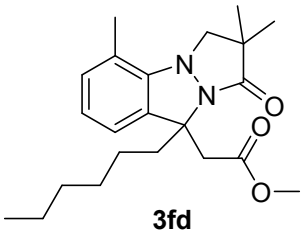
3fc



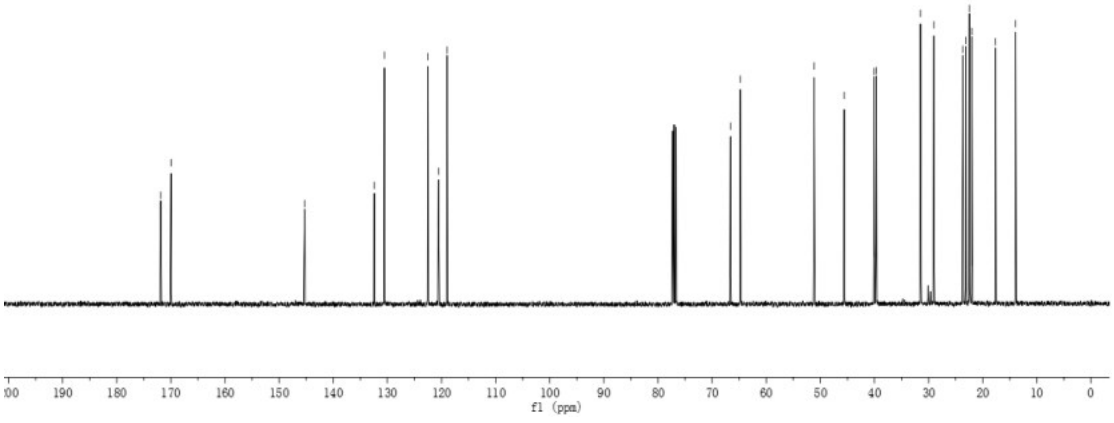
3fc

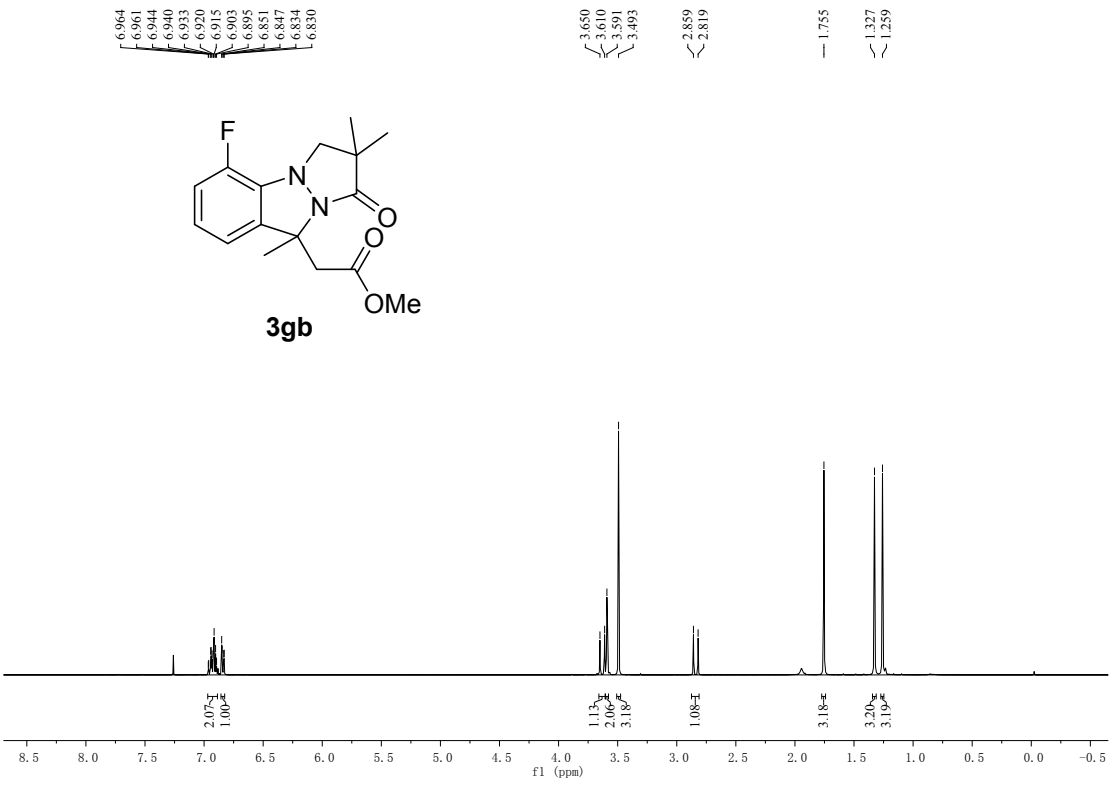
3fd



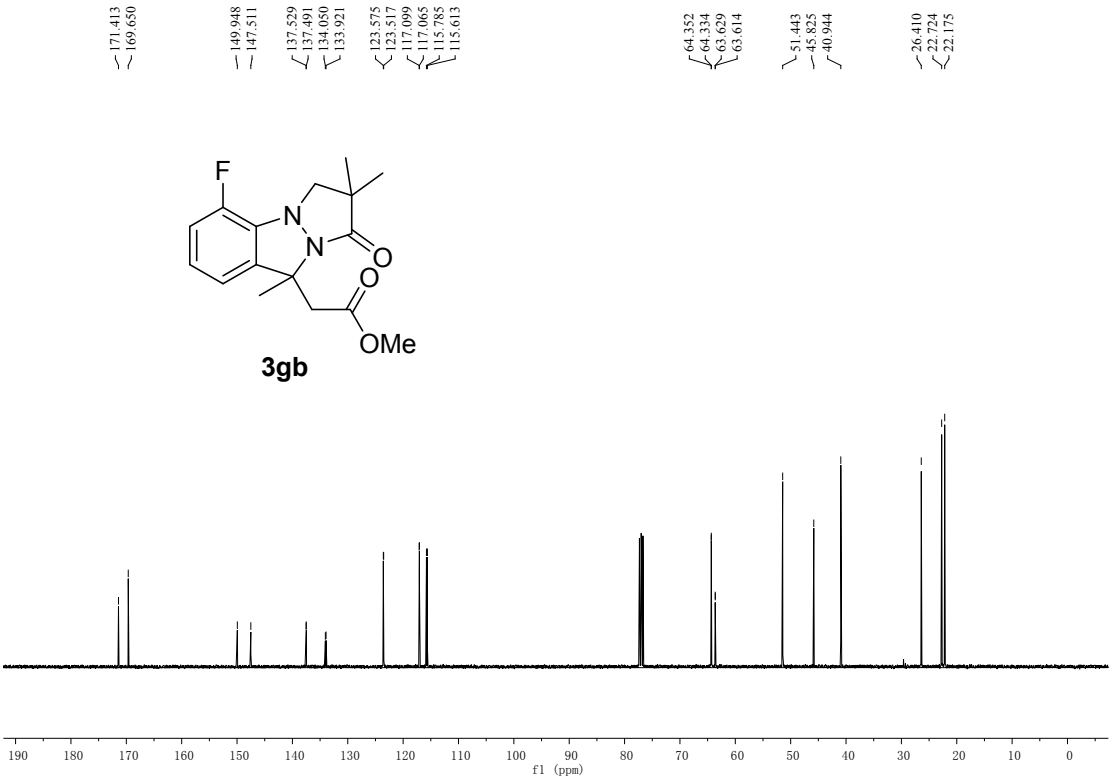


3fd




6.964
6.961
6.944
6.940
6.933
6.920
6.915
6.903
6.895
6.851
6.847
6.834
6.830
3.650
3.610
3.591
3.493
2.859
2.819
1.755
1.327
1.259
F
N
N
O
O
OMe
2.07
1.00
1.13
2.06
3.18
1.08
3.18
3.20
3.19
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

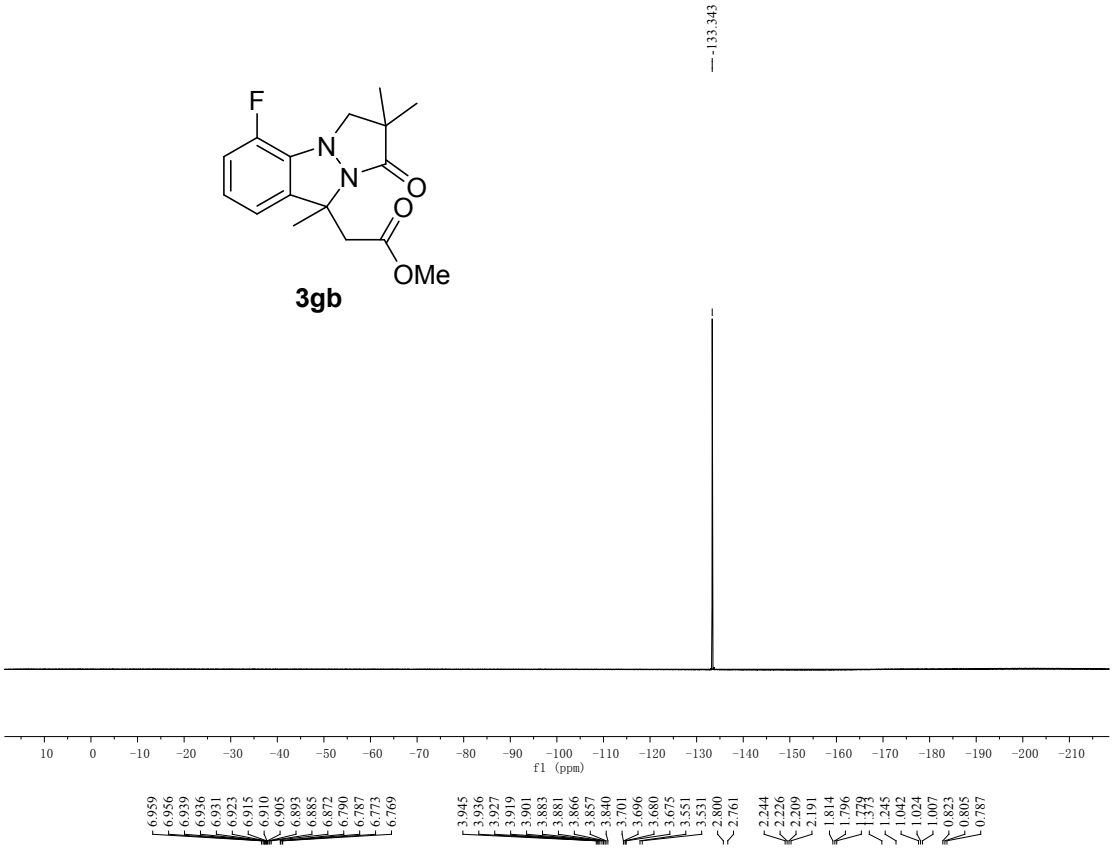
3gb

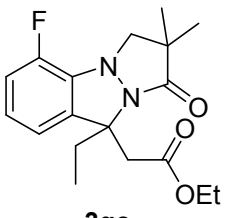

171.413
169.650
149.948
147.511
137.529
137.491
134.050
133.921
123.575
123.517
117.099
117.065
115.785
115.613
64.352
64.334
63.629
63.614
51.443
45.825
40.944
26.410
22.724
22.175
F
N
N
O
O
OMe
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

3gb

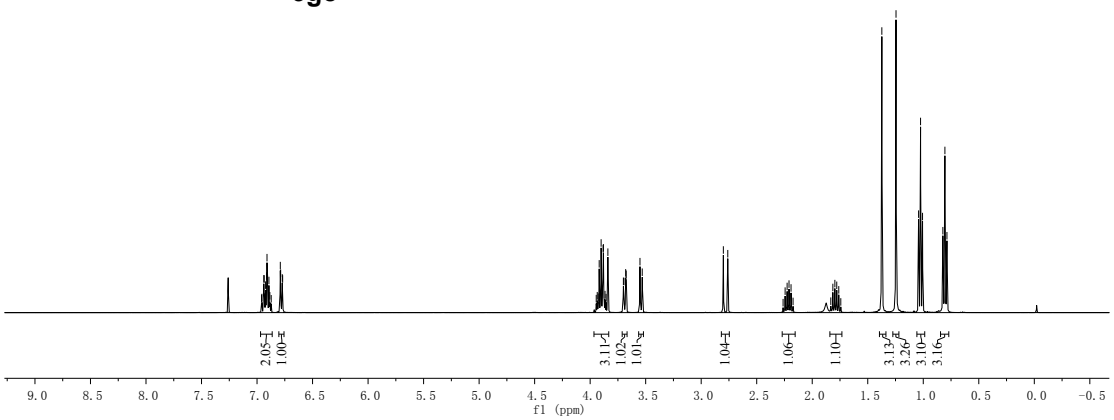
F
N
N
O
O
OMe

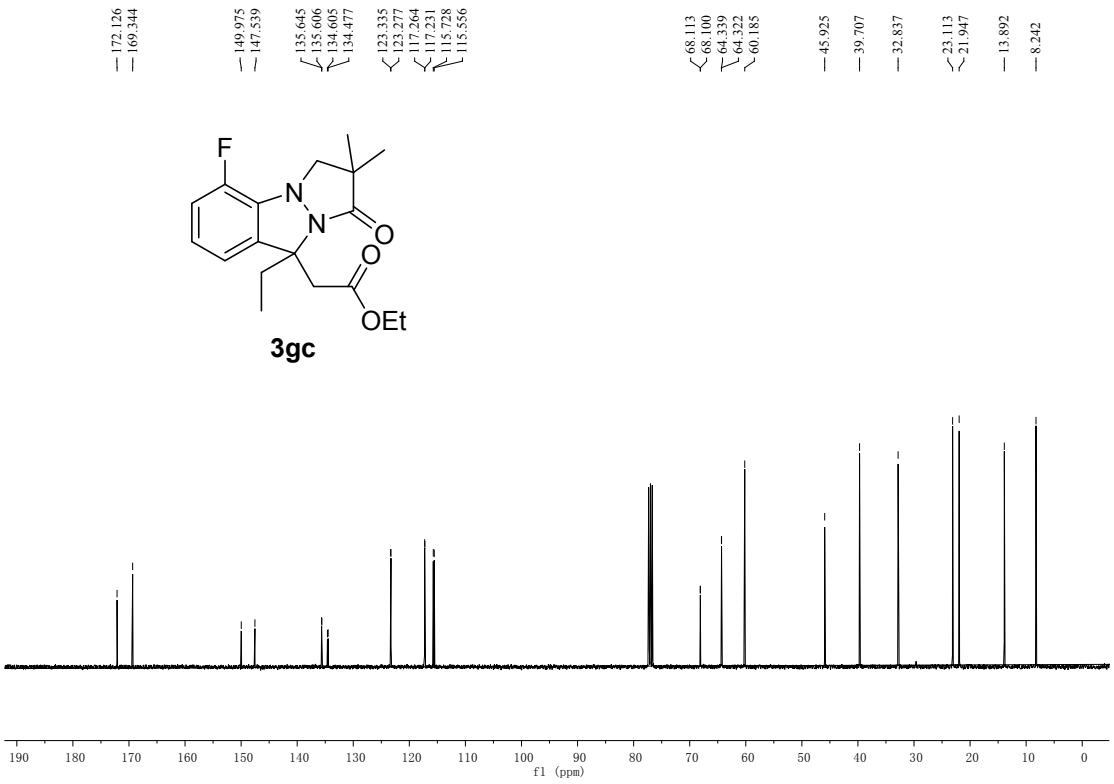
3gb

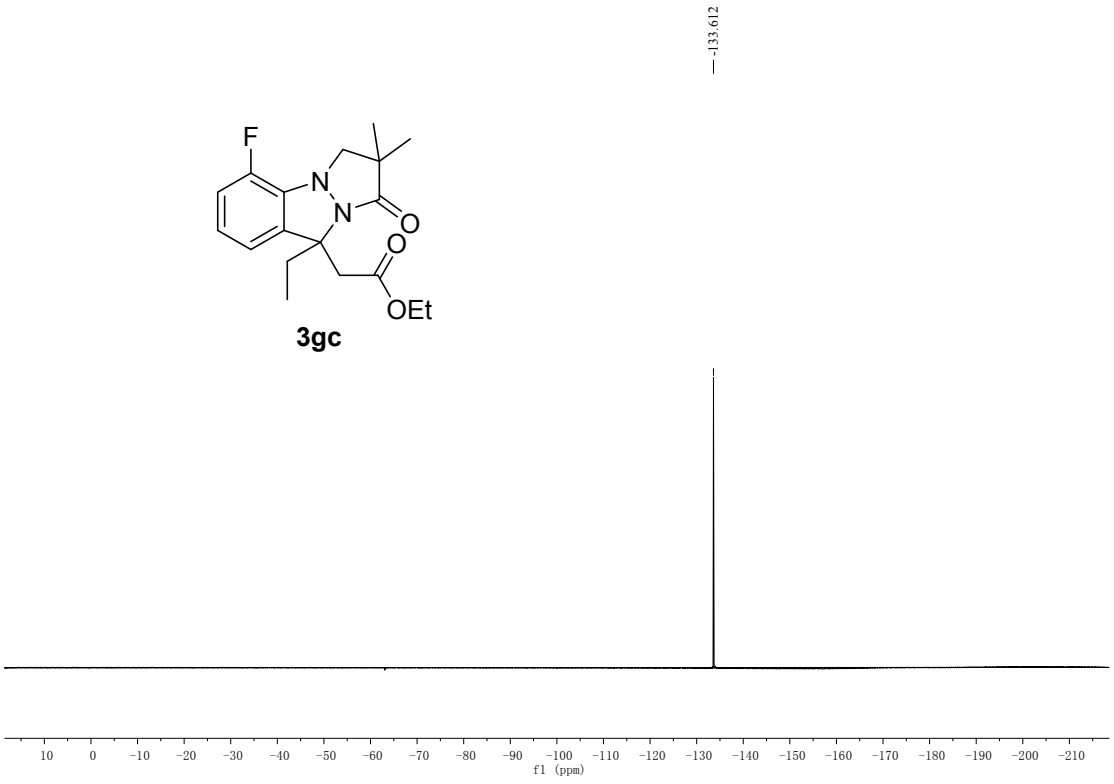

-133.343
f1 (ppm)
6.959
6.956
6.939
6.936
6.931
6.923
6.915
6.910
6.905
6.893
6.885
6.872
6.790
6.787
6.773
6.769
3.945
3.936
3.927
3.919
3.901
3.883
3.881
3.866
3.857
3.840
3.701
3.696
3.680
3.675
3.551
3.531
2.800
2.761
2.244
2.226
2.209
2.191
1.814
1.796
1.245
1.042
1.024
1.007
0.823
0.805
0.787


F
N
N
O
O
OEt

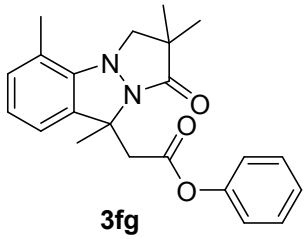
3gc


2.05
1.00
3.11
1.02
1.01
1.04
1.06
1.10
3.13
3.26
3.10
3.16
f1 (ppm)

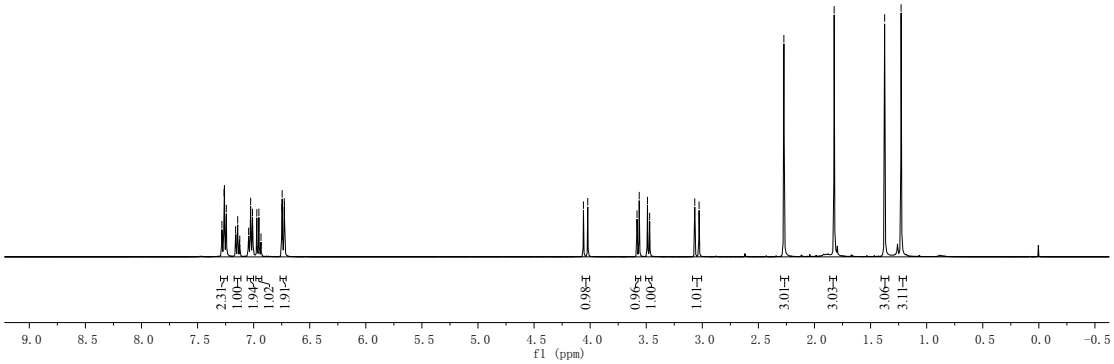

172.126
169.344
149.975
147.539
135.645
135.606
134.605
134.477
123.335
123.277
117.264
117.231
115.728
115.556
68.113
68.100
64.339
64.322
60.185
45.925
39.707
32.837
23.113
21.947
13.892
8.242
F
N
N
O
O
OEt
3gc
f1 (ppm)

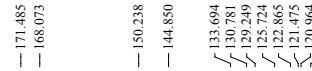

-133.612
F
N
N
O
O
OEt
3gc
f1 (ppm)

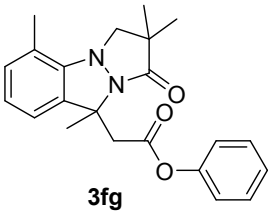

7.283
7.278
7.264
7.244
7.161
7.158
7.142
7.126
7.124
7.045
7.027
7.010
6.972
6.953
6.935
6.749
6.746
6.727
6.725
4.060
4.021
3.582
3.563
3.489
3.469
3.067
3.029
2.273
1.825
1.375
1.228


N
N
O
O
O

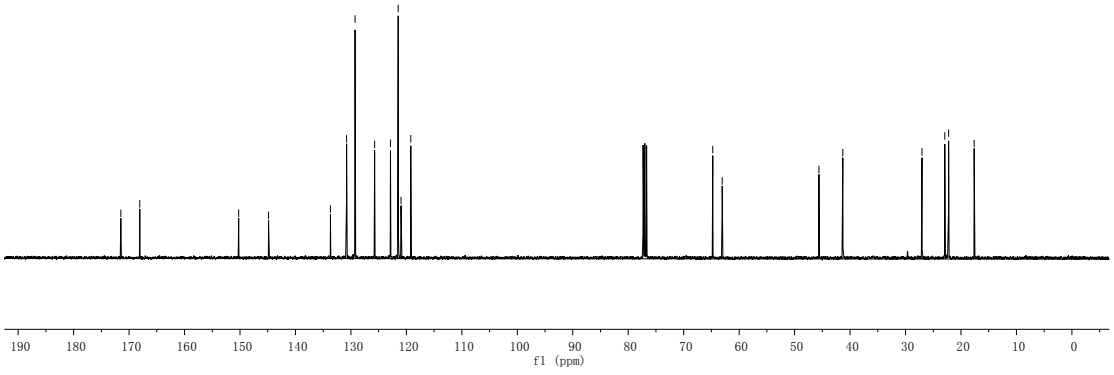
3fg

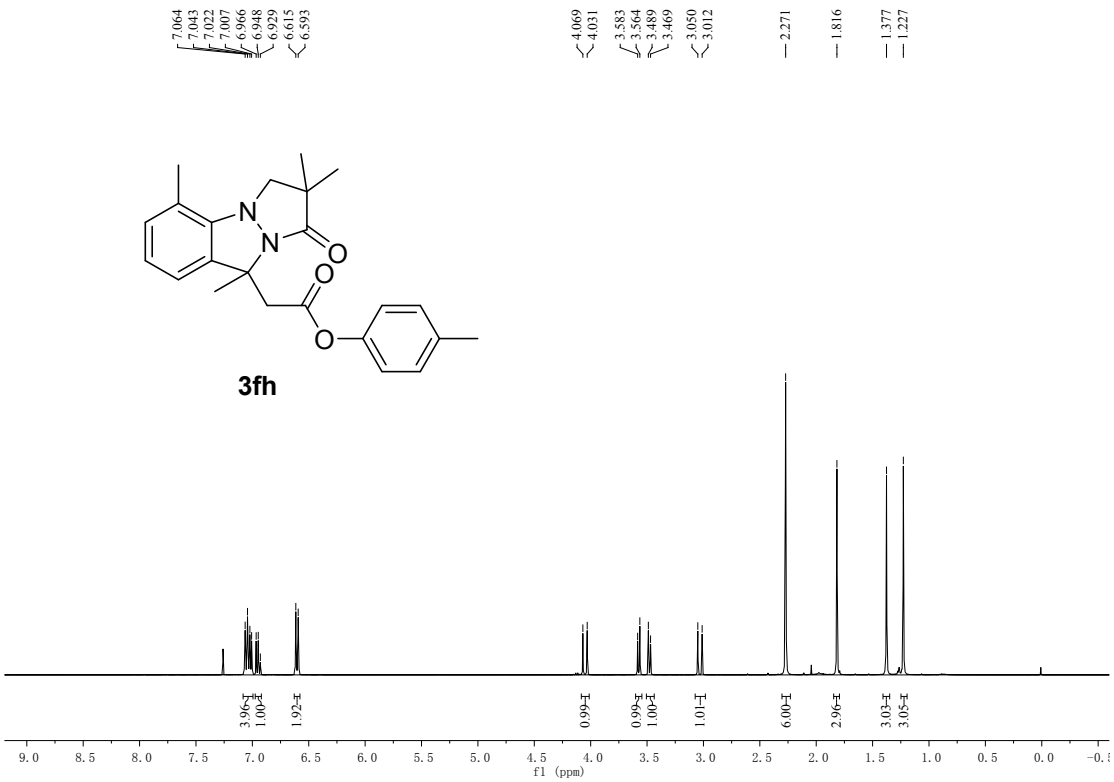

2.31
1.00
1.94
1.02
1.91
0.98
0.96
1.00
1.01
3.01
3.03
3.06
3.11
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)


171.485
168.073
150.238
144.850
133.694
130.781
129.249
125.724
122.865
121.475
120.964
119.205
64.756
63.056
45.616
41.306
27.033
22.916
22.230
17.624


N
N
O
O
O

3fg


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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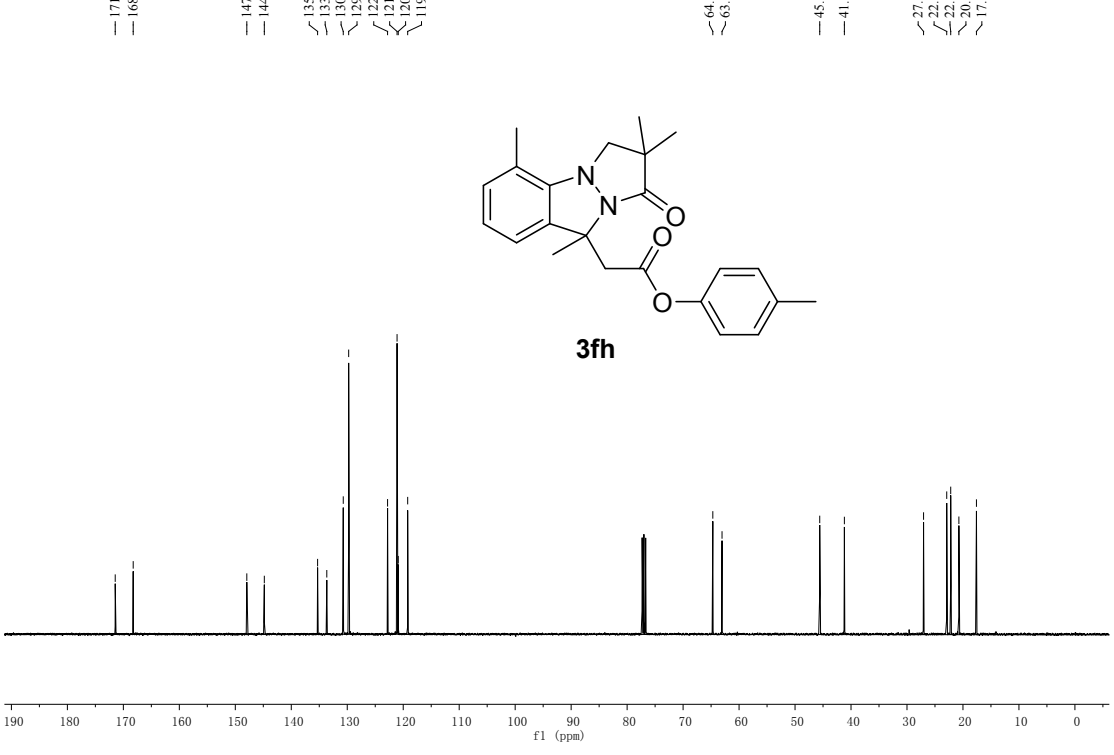
7.043
7.022
7.007
6.966
6.948
6.929
6.615
6.593
4.069
4.031
3.583
3.564
3.489
3.469
3.050
3.012
2.271
1.816
1.377
1.227
3fh
3.96
1.00
1.92
0.99
0.99
1.00
1.01
6.00
2.96
3.03
3.05
f1 (ppm)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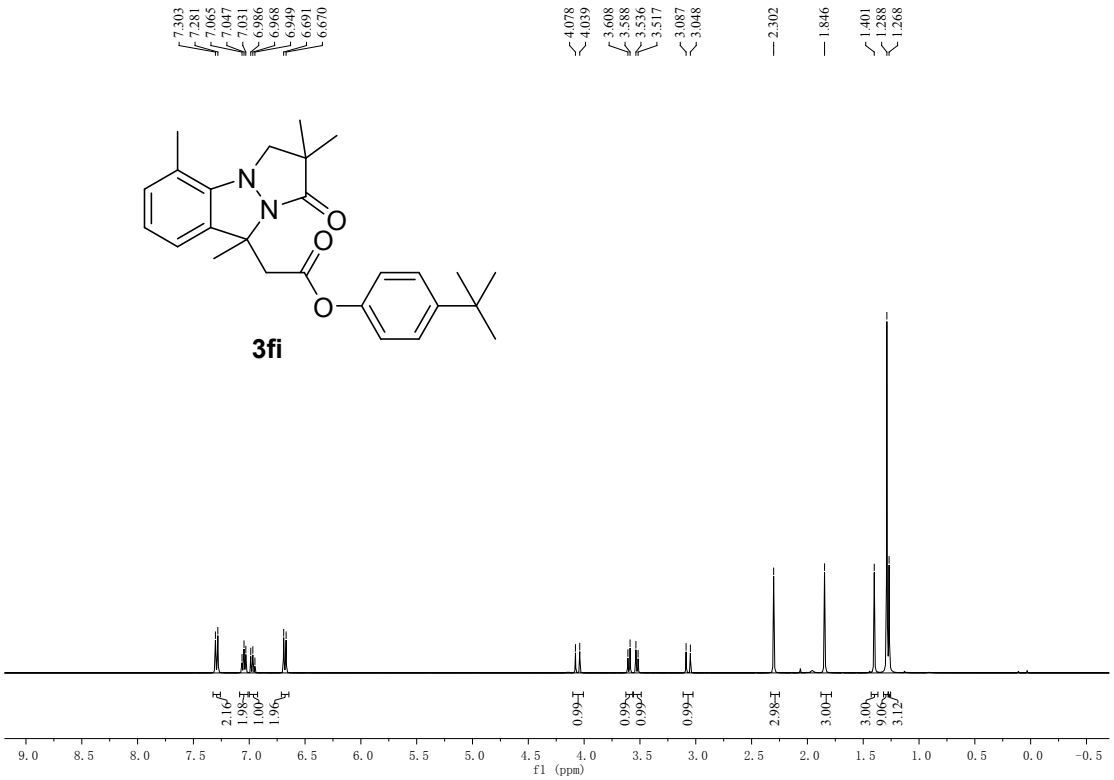
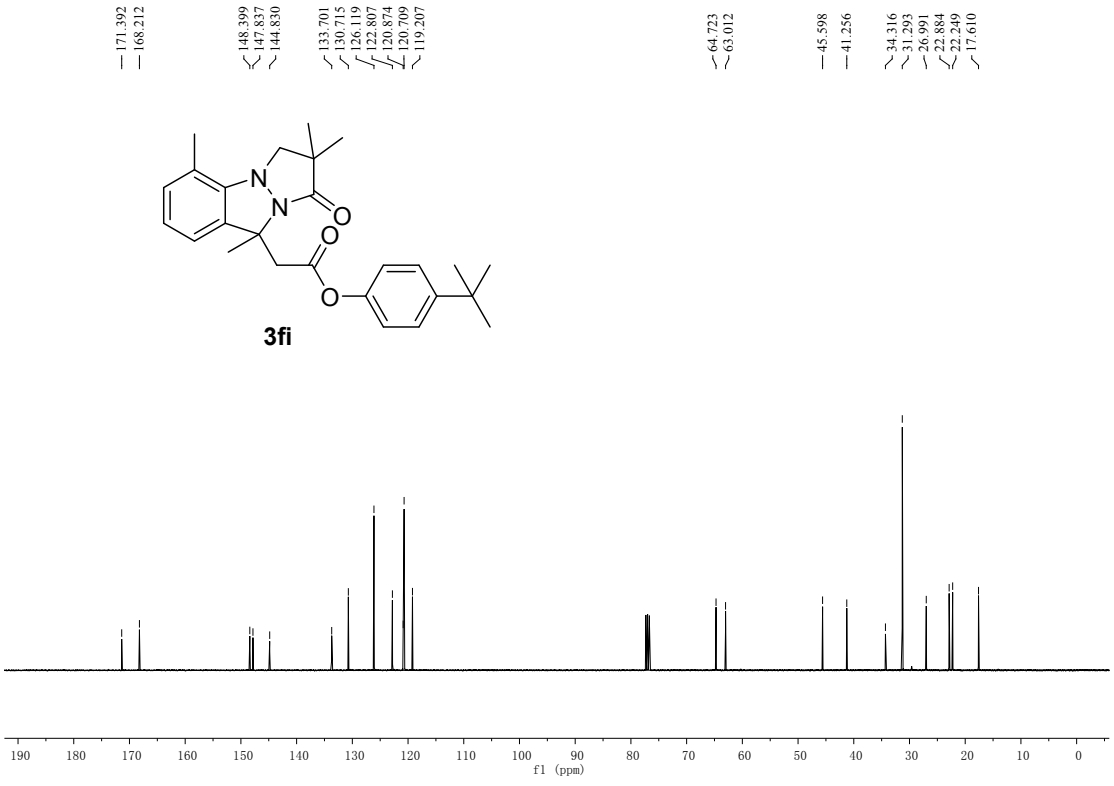
135.297
133.654
130.713
129.746
122.797
121.101
120.889
119.203
64.689
63.043
45.588
41.186
27.039
22.900
22.188
20.730
17.592
3fh
f1 (ppm)


7.303
7.281
7.065
7.047
7.031
6.986
6.968
6.949
6.691
6.670
4.078
4.039
3.608
3.588
3.536
3.517
3.087
3.048
2.302
1.846
1.401
1.288
1.268
2.16
1.98
1.00
1.96
0.99
0.99
0.99
0.99
2.98
3.00
3.00
9.06
3.12
f1 (ppm)

3fi


171.392
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147.837
144.830
133.701
130.715
126.119
122.807
120.874
120.709
119.207
64.723
63.012
45.598
41.256
34.316
31.293
26.991
22.884
22.249
17.610
f1 (ppm)

3fi


7.043
7.024
7.010
6.994
6.966
6.961
6.947
6.939
6.929
6.924
6.918
6.724
6.713
6.707
6.702
6.690
4.001
3.963
3.574
3.555
3.483
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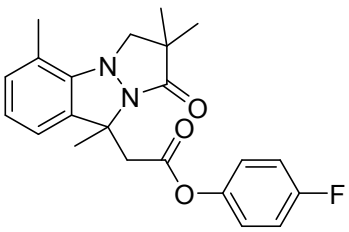
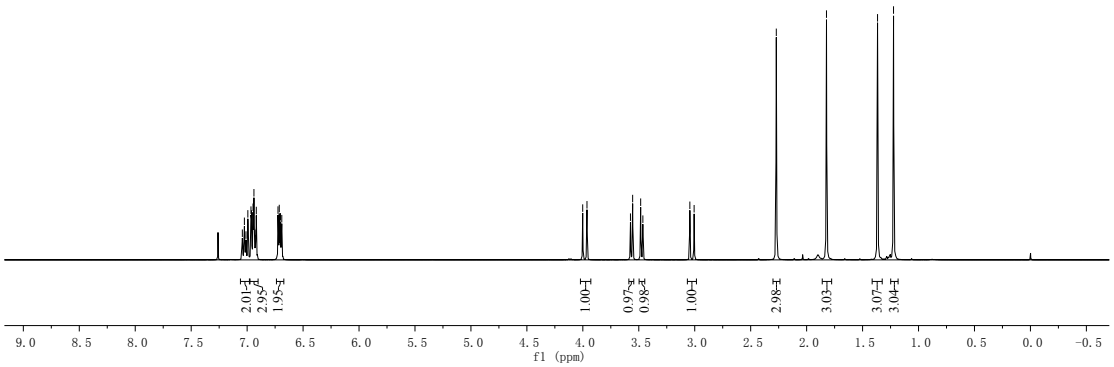
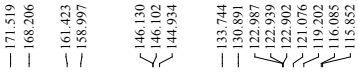
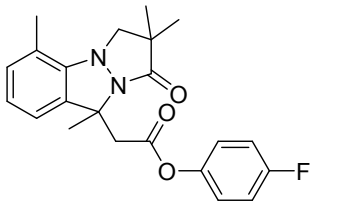
1.823
1.366
1.223


N
N
O
O
O
F

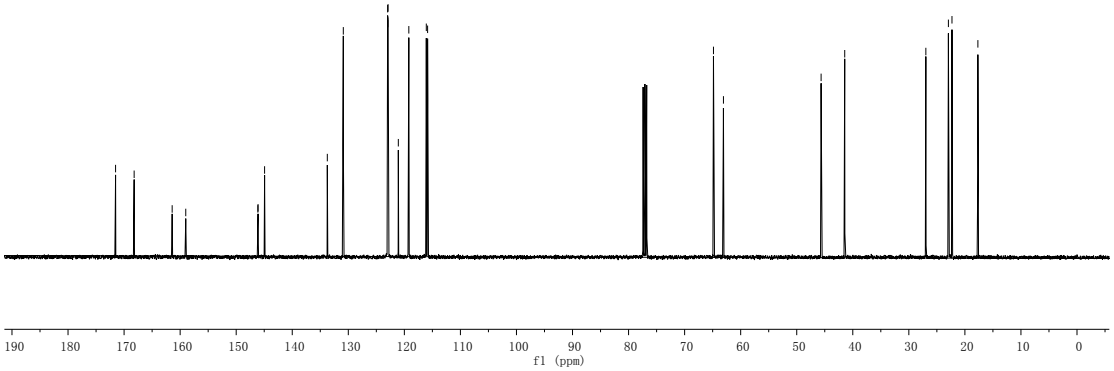
3fj


2.01
2.95
1.95
1.00
0.97
0.98
1.00
2.98
3.03
3.07
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


171.519
168.206
161.423
158.997
146.130
146.102
144.934
133.744
130.891
122.987
122.939
122.902
121.076
119.202
116.085
115.852
64.853
63.074
45.652
41.438
26.965
22.942
22.303
17.682

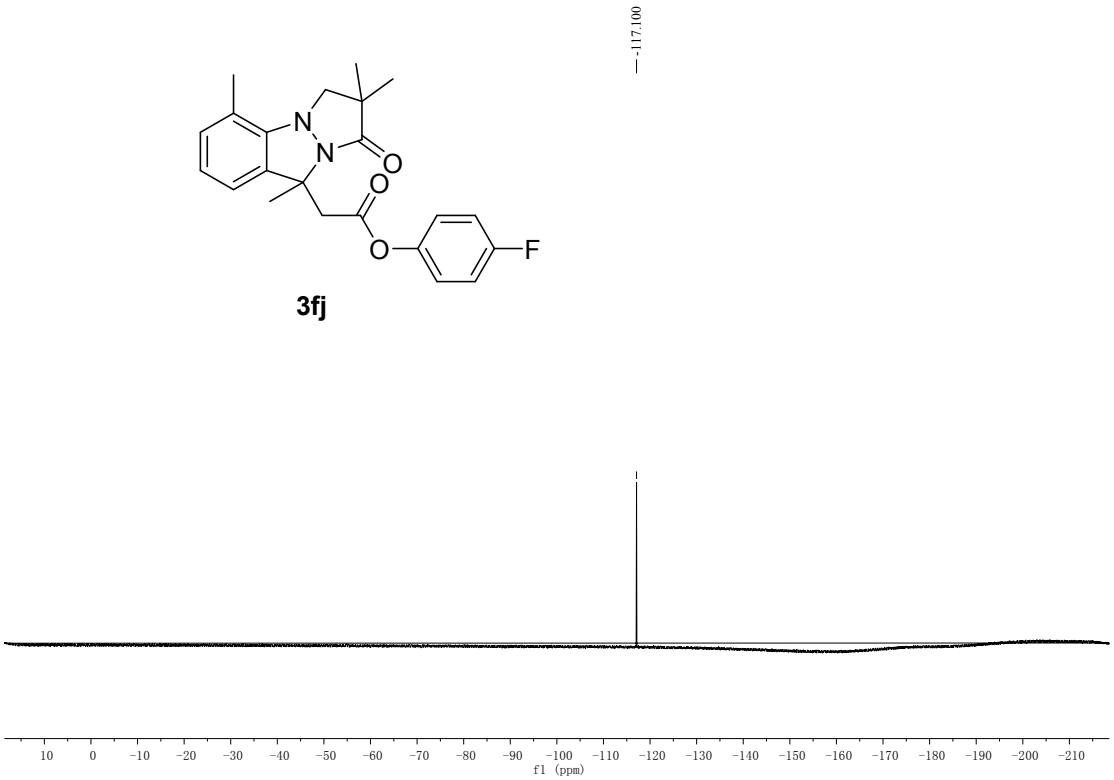

N
N
O
O
O
F

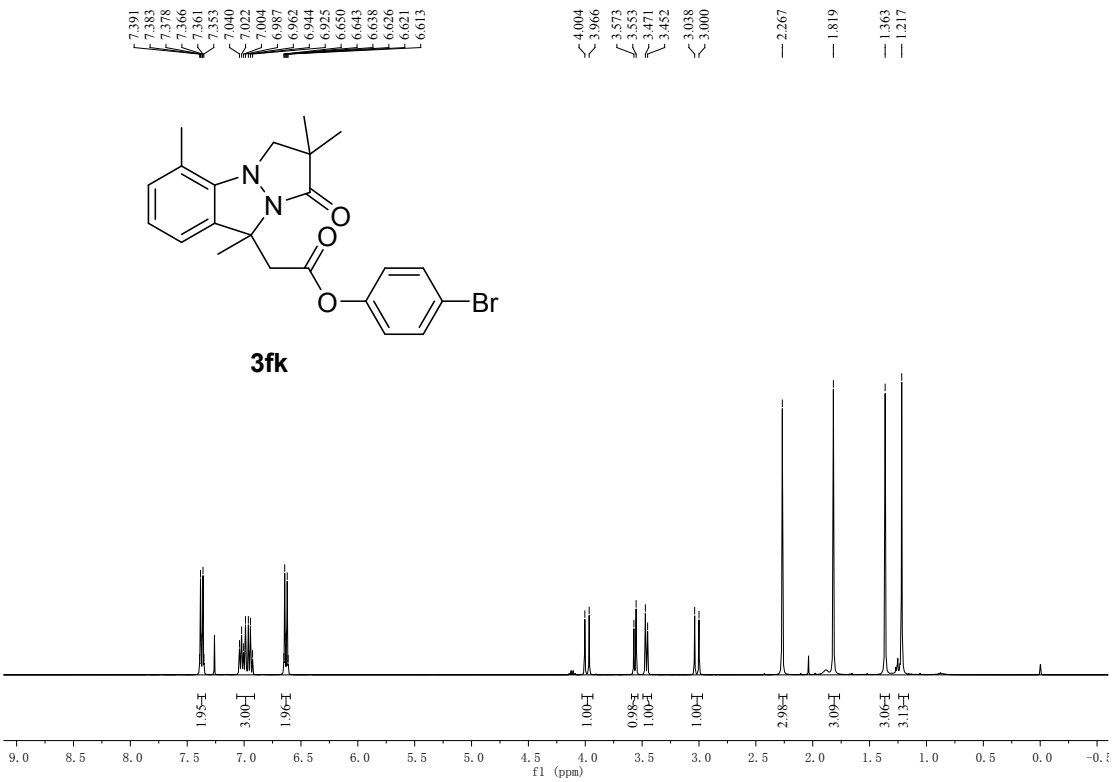
3fj


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

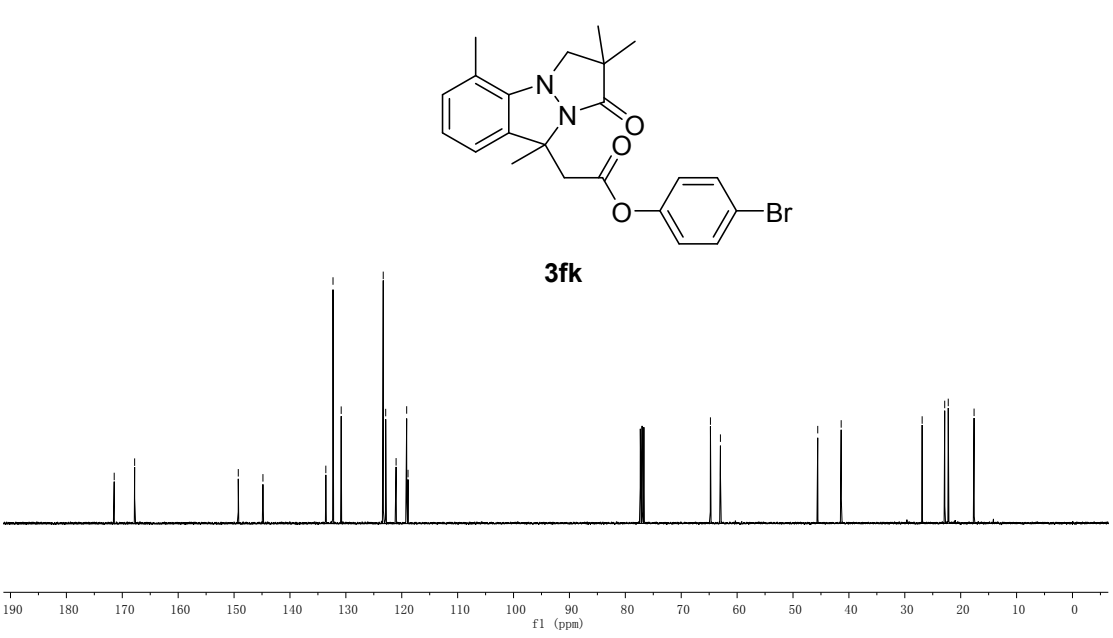
N
N
O
O
O
F

3fj

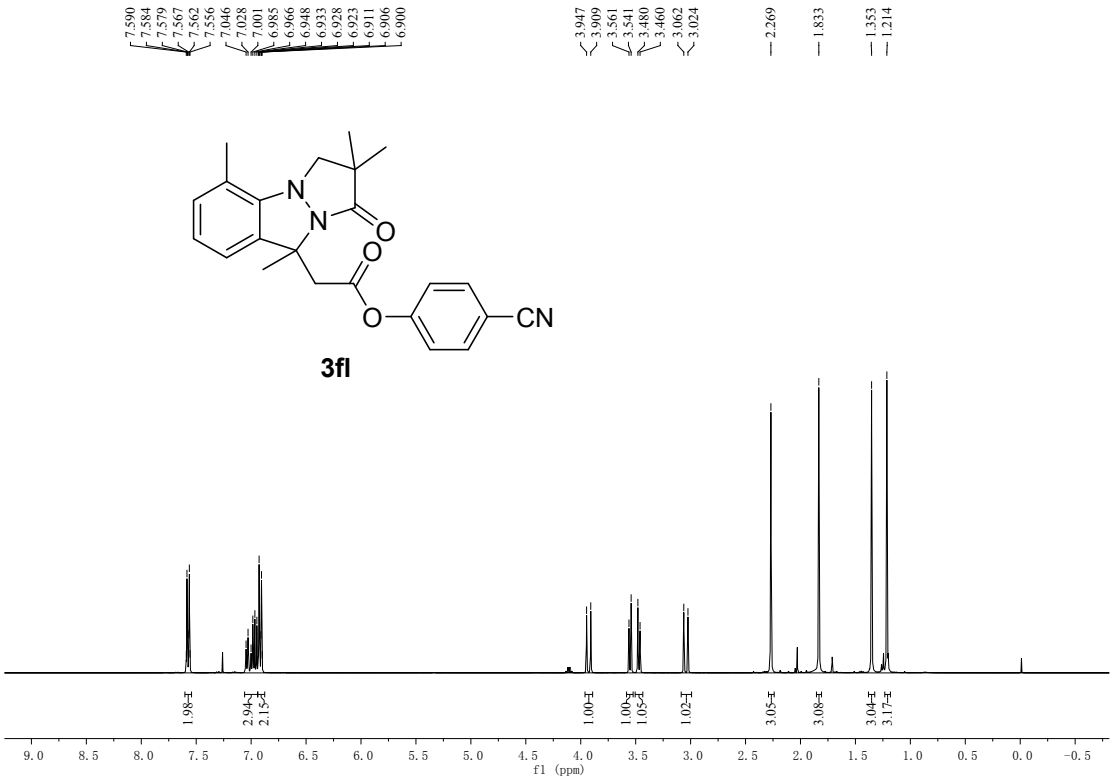

-117.100
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


7.391
7.383
7.378
7.366
7.361
7.353
7.040
7.022
7.004
6.987
6.962
6.944
6.925
6.650
6.643
6.638
6.626
6.621
6.613
4.004
3.966
3.573
3.553
3.471
3.452
3.038
3.000
2.267
1.819
1.363
1.217
N
N
O
O
O
Br
1.95
3.00
1.96
1.00
0.98
1.00
1.00
2.98
3.09
3.06
3.13
f1 (ppm)

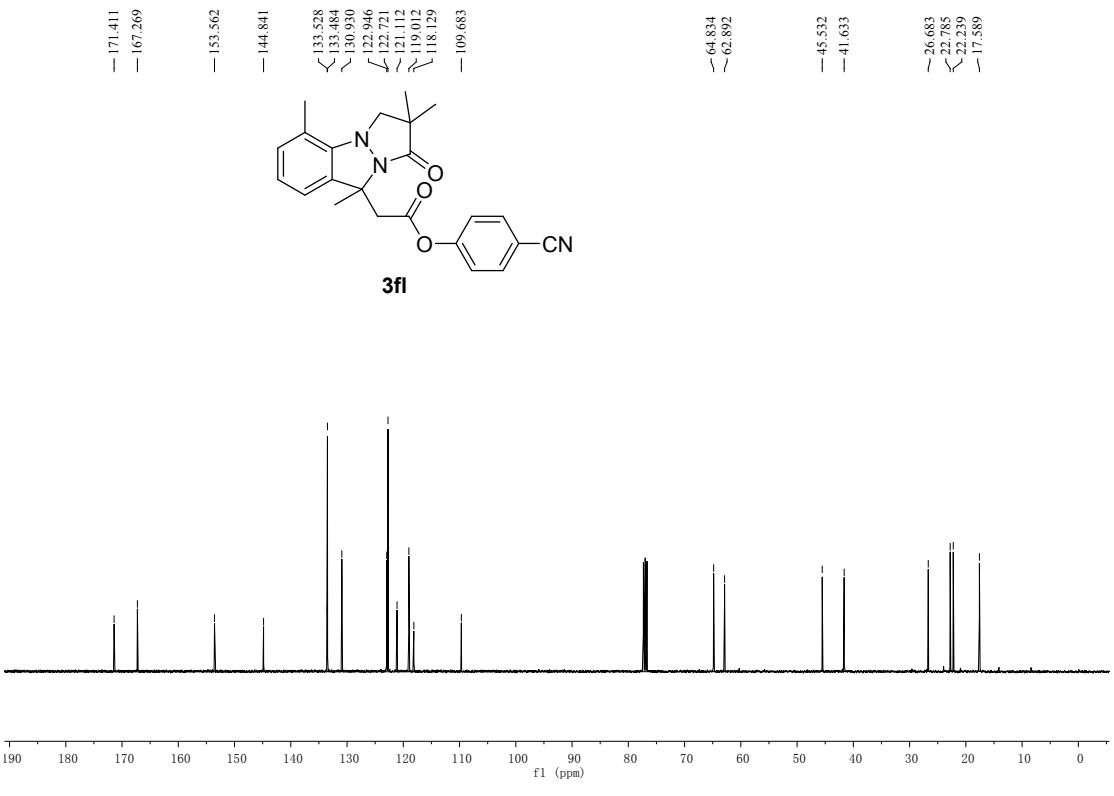
3fk


171.445
167.790
149.246
144.835
133.583
132.298
130.834
123.313
122.873
121.013
119.118
118.881
64.774
62.986
45.575
41.383
26.896
22.860
22.227
17.607
N
N
O
O
O
Br
f1 (ppm)

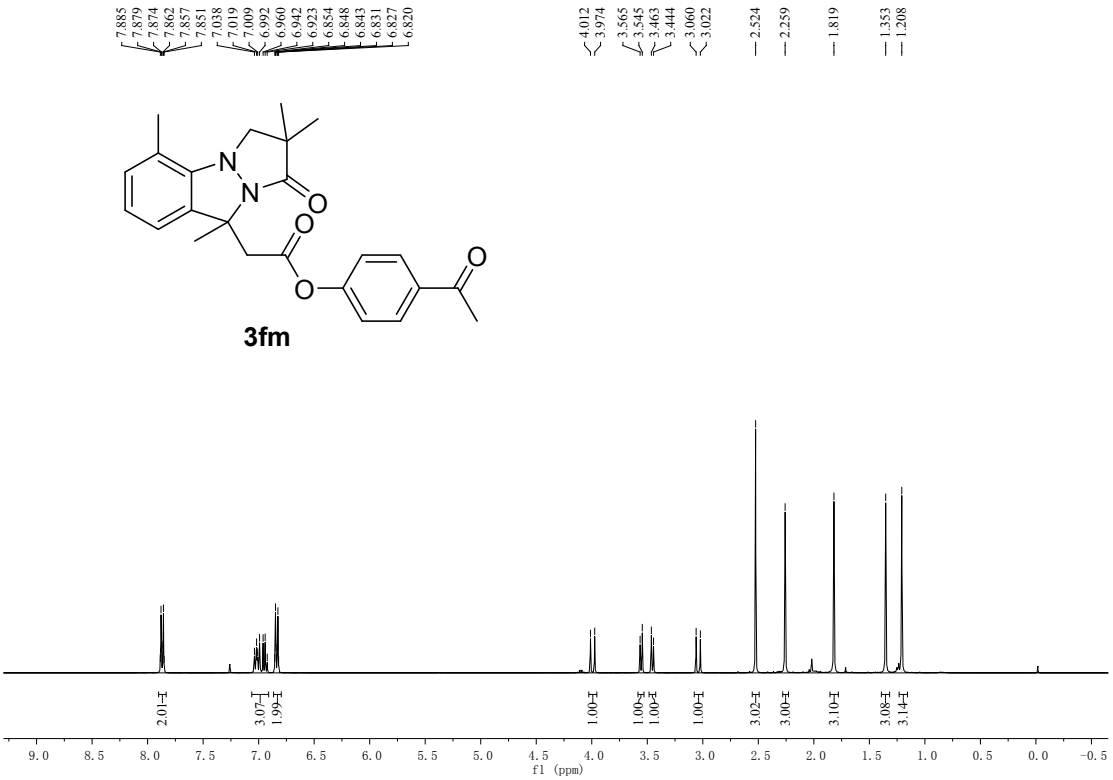
3fk

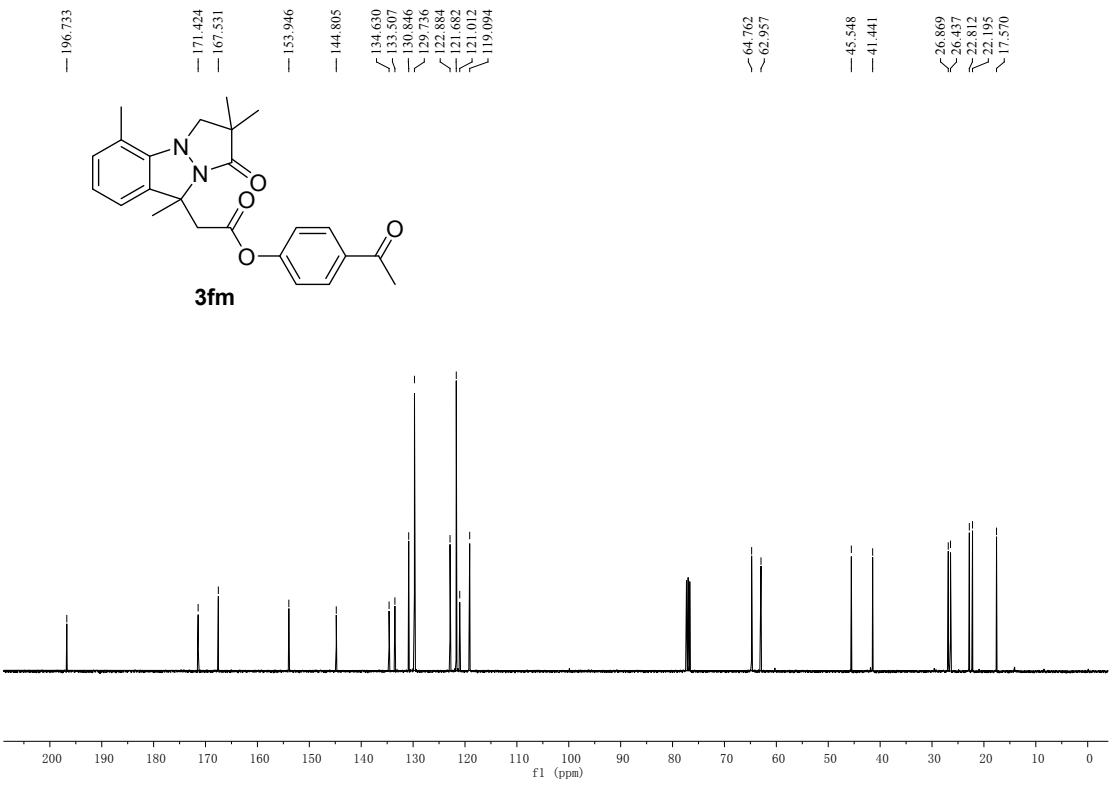

7.590
7.584
7.579
7.567
7.562
7.556
7.046
7.028
7.001
6.985
6.966
6.948
6.933
6.928
6.923
6.911
6.906
6.900
3.947
3.909
3.561
3.541
3.480
3.460
3.062
3.024
2.269
1.833
1.353
1.214
N
N
O
O
O
O
CN
1.98
2.94
2.15
1.00
1.00
1.05
1.02
3.05
3.08
3.04
3.17
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 −0.5
f1 (ppm)

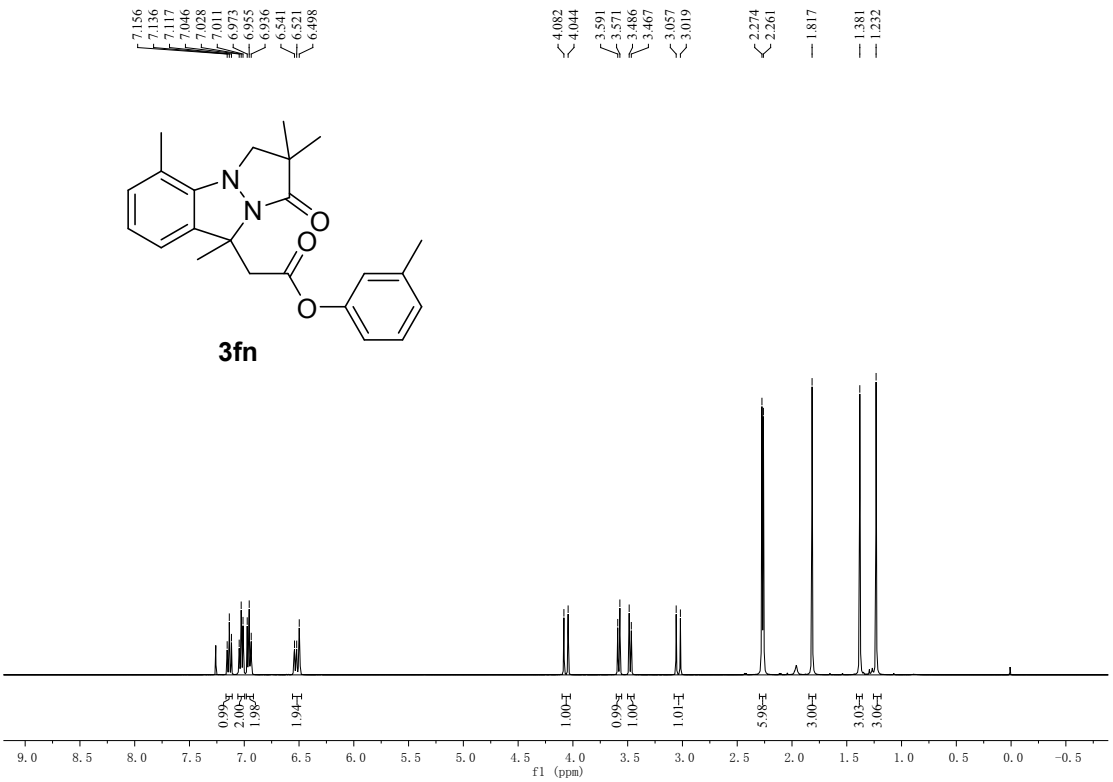
3fl


171.411
167.269
153.562
144.841
133.528
133.484
130.930
122.946
122.721
121.112
119.012
118.129
109.683
64.834
62.892
45.532
41.633
26.683
22.785
22.239
17.589
N
N
O
O
O
O
CN
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

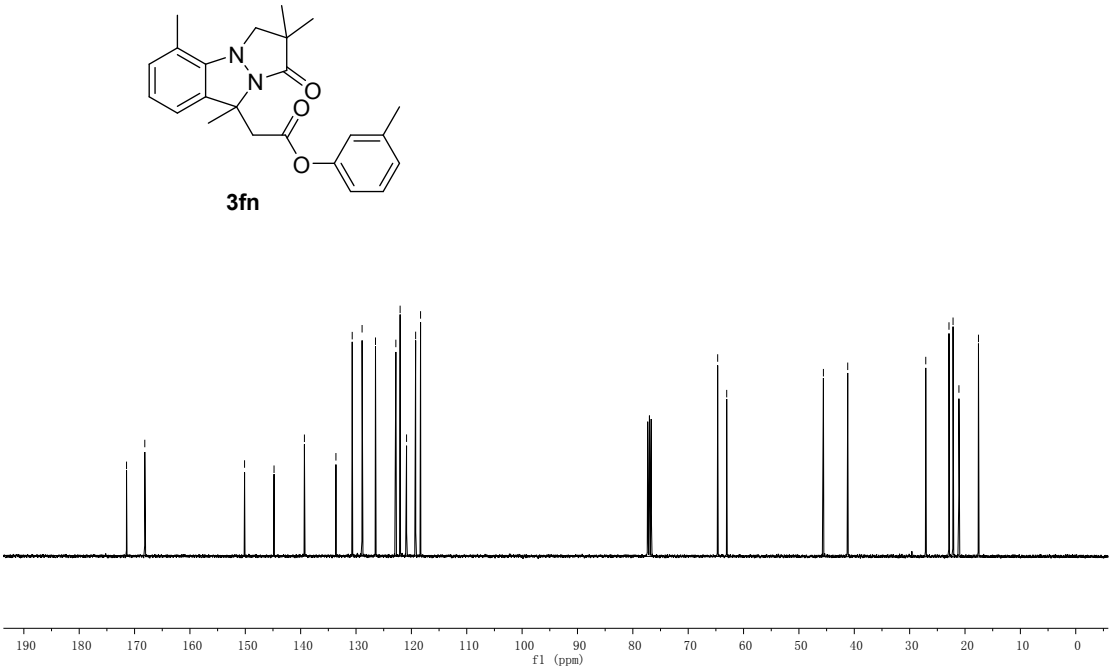
3fl


7.885
7.879
7.874
7.862
7.857
7.851
7.038
7.019
7.009
6.992
6.960
6.942
6.923
6.854
6.848
6.843
6.831
6.827
6.820
4.012
3.974
3.565
3.545
3.463
3.444
3.060
3.022
2.524
2.259
1.819
1.353
1.208
3fm
2.01
3.07
1.99
1.00
1.00
1.00
1.00
3.02
3.00
3.10
3.08
3.14
f1 (ppm)


196.733
171.424
167.531
153.946
144.805
134.630
133.507
130.846
129.736
122.884
121.682
121.012
119.094
64.762
62.957
45.548
41.441
26.869
26.437
22.812
22.195
17.570
3fm
f1 (ppm)

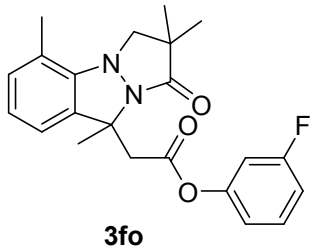

7.156
7.136
7.117
7.046
7.028
7.011
6.973
6.955
6.936
6.541
6.521
6.498
4.082
4.044
3.591
3.571
3.486
3.467
3.057
3.019
2.274
2.261
1.817
1.381
1.232
0.99
2.00
1.98
1.94
1.00
0.99
1.00
1.01
5.98
3.00
3.03
3.06
f1 (ppm)

3fn

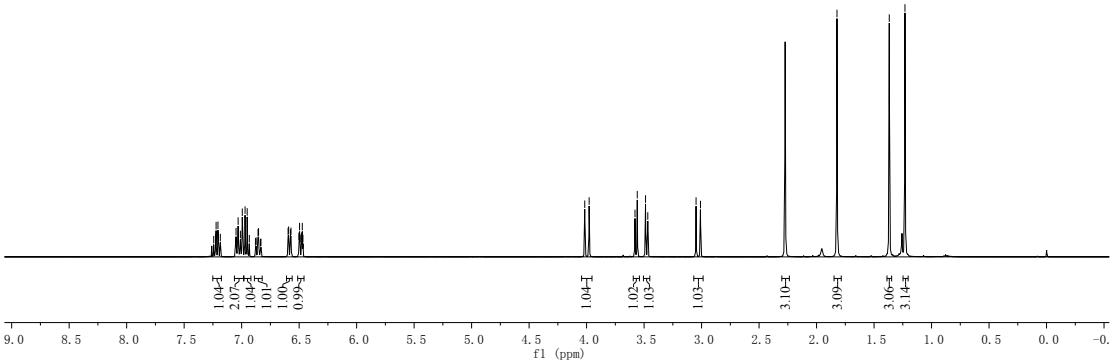

171.451
168.154
150.133
144.809
139.321
133.629
130.689
128.904
126.482
122.805
122.035
120.873
119.231
118.342
64.676
63.045
45.578
41.186
27.090
22.896
22.162
21.100
17.568
f1 (ppm)

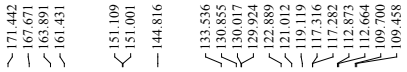
3fn

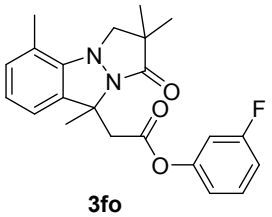

7.243
7.227
7.222
7.206
7.202
7.185
7.049
7.031
7.011
6.994
6.970
6.952
6.933
6.880
6.874
6.857
6.853
6.836
6.832
6.596
6.591
6.576
6.571
6.502
6.496
6.491
6.478
6.473
6.467
4.016
3.978
3.579
3.559
3.487
3.468
3.048
3.010
1.822
1.368
1.231


N
N
O
O
O
F

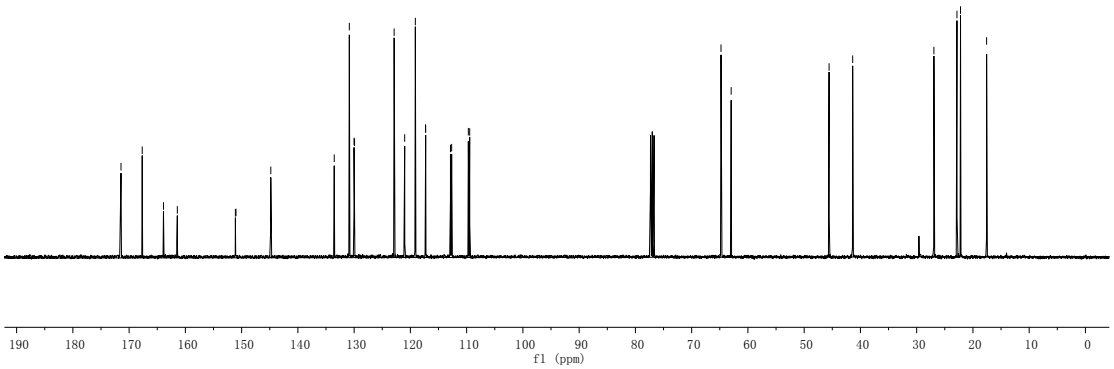
3fo


1.04
2.07
1.04
1.01
1.00
0.99
1.04
1.02
1.03
1.03
3.10
3.09
3.06
3.14
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.
f1 (ppm)


171.442
167.671
163.891
161.431
151.109
151.001
144.816
133.536
130.855
130.017
129.924
122.889
121.012
119.119
117.316
117.282
112.873
112.664
109.700
109.458
64.782
62.978
45.572
41.377
26.936
22.841
22.207
17.568

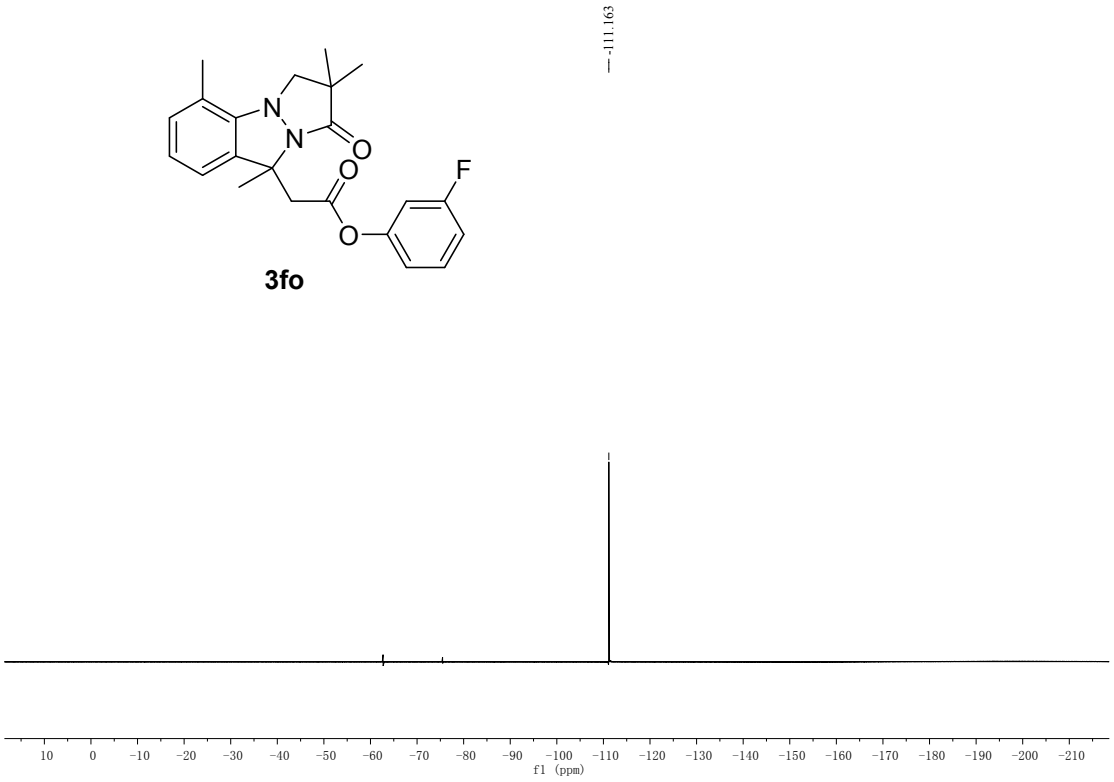

N
N
O
O
O
F

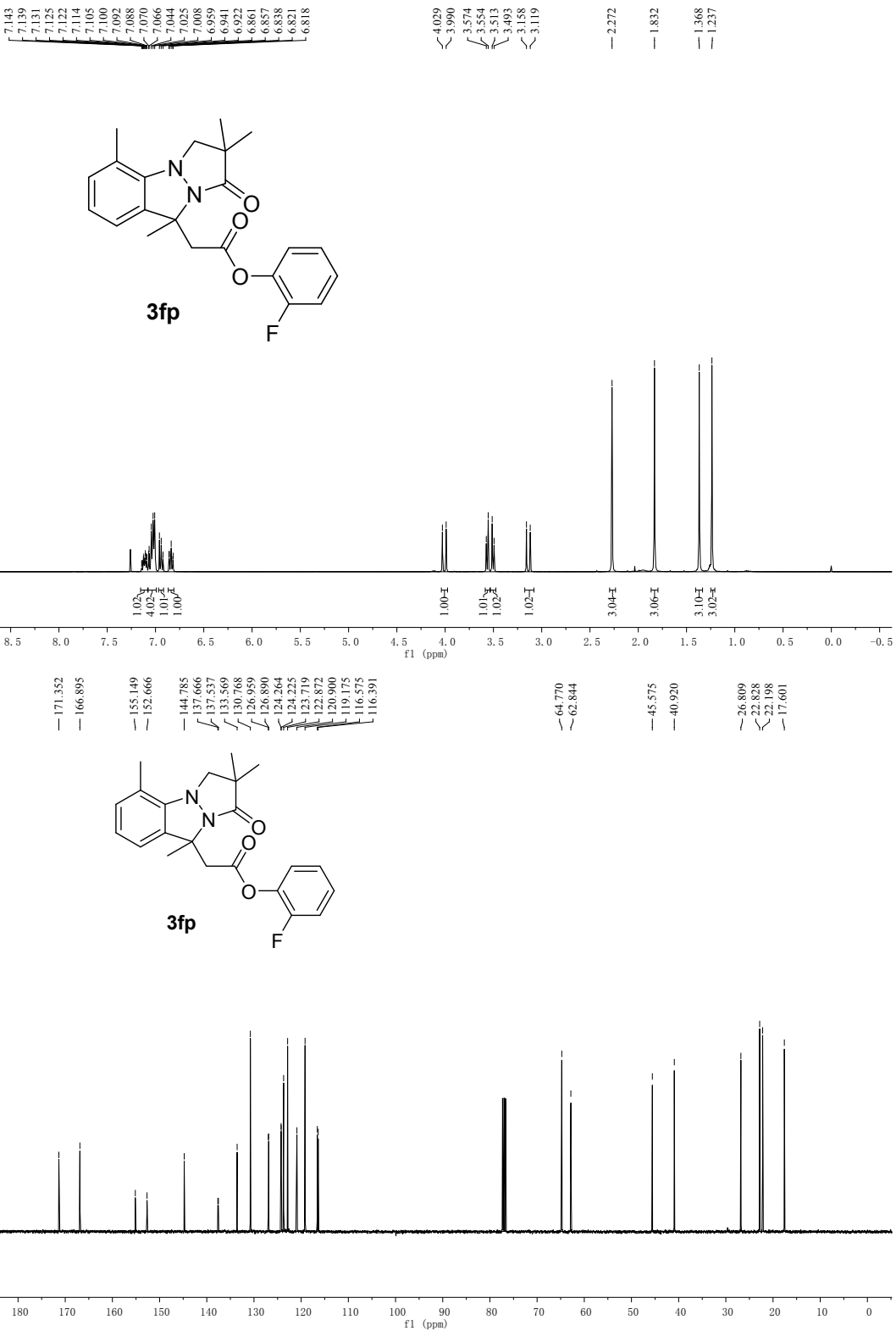
3fo


190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

N
N
O
O
O
F

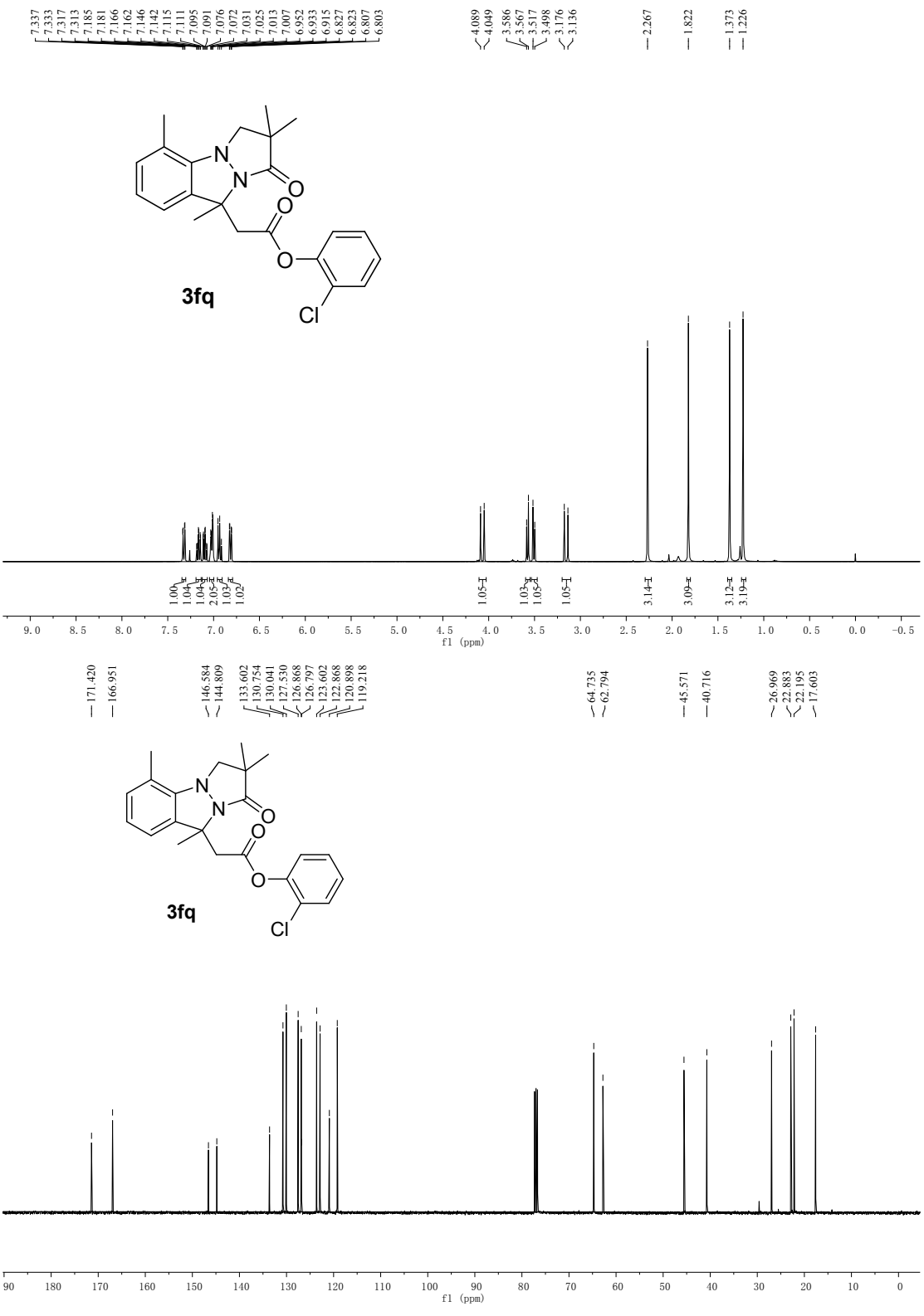
3fo

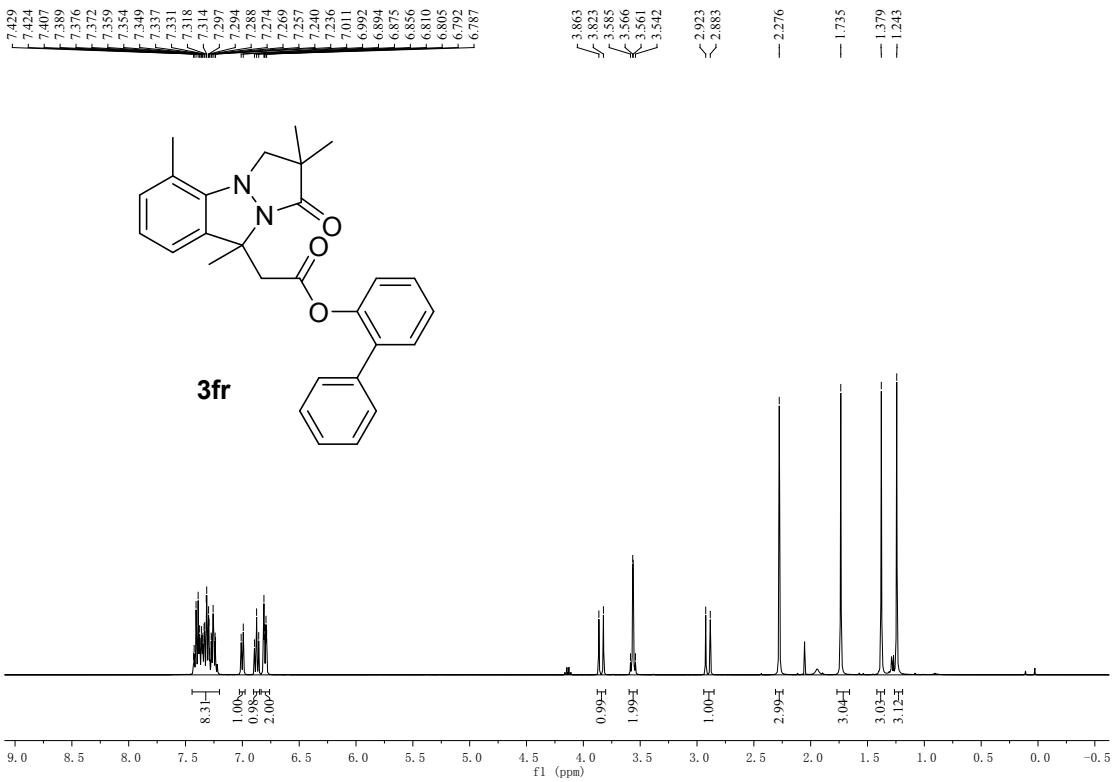

-111.163
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.143
7.139
7.131
7.125
7.122
7.114
7.105
7.100
7.092
7.088
7.070
7.066
7.044
7.025
7.008
6.959
6.941
6.922
6.861
6.857
6.838
6.821
6.818
4.029
3.990
3.574
3.554
3.513
3.493
3.158
3.119
2.272
1.832
1.368
1.237
3fp
1.02
4.02
1.01
1.00
1.00
1.01
1.02
1.02
3.04
3.06
3.10
3.02
f1 (ppm)
171.352
166.895
155.149
152.666
144.785
137.666
137.537
133.569
130.768
126.959
126.890
124.264
124.225
123.719
122.872
120.900
119.175
116.575
116.391
64.770
62.844
45.575
40.920
26.809
22.828
22.198
17.601
3fp
f1 (ppm)


-128.302
N
N
O
O
O
F
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)

3fp


7.337
7.333
7.317
7.313
7.185
7.181
7.166
7.162
7.146
7.142
7.115
7.111
7.095
7.091
7.076
7.072
7.031
7.025
7.013
7.007
6.952
6.933
6.915
6.827
6.823
6.807
6.803
4.089
4.049
3.586
3.567
3.517
3.498
3.176
3.136
2.267
1.822
1.373
1.226
3fq
1.00
1.04
1.04
2.05
1.03
1.02
1.05
1.03
1.05
1.05
3.14
3.09
3.12
3.19
f1 (ppm)
171.420
166.951
146.584
144.809
133.602
130.754
130.041
127.530
126.868
126.797
123.602
122.868
120.898
119.218
64.735
62.794
45.571
40.716
26.969
22.883
22.195
17.603
3fq
f1 (ppm)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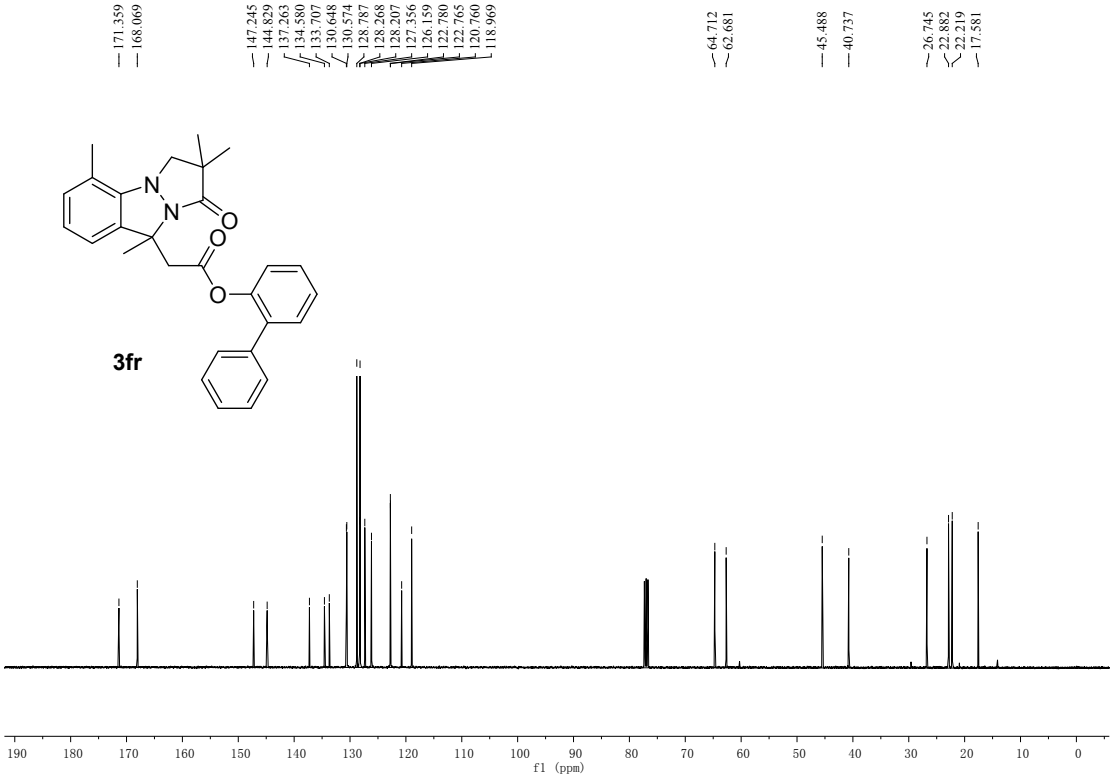
7.376
7.372
7.359
7.354
7.349
7.337
7.331
7.318
7.314
7.297
7.294
7.288
7.274
7.269
7.257
7.240
7.236
7.011
6.992
6.894
6.875
6.856
6.810
6.805
6.792
6.787
3.863
3.823
3.585
3.566
3.561
3.542
2.923
2.883
2.276
1.735
1.379
1.243
3fr
8.31
1.00
0.98
2.00
0.99
1.99
1.00
2.99
3.04
3.03
3.12
f1 (ppm)


171.359
168.069
147.245
144.829
137.263
134.580
133.707
130.648
130.574
128.787
128.268
128.207
127.356
126.159
122.780
122.765
120.760
118.969
64.712
62.681
45.488
40.737
26.745
22.882
22.219
17.581
3fr
f1 (ppm)