Supporting Information

Chemo- and regioselective defluorinative annulation of (trifluoromethyl)alkenes with pyrazolones: synthesis and insecticidal activity of 6-fluoro-1,4-dihydropyrano[2,3-*c*]pyrazoles

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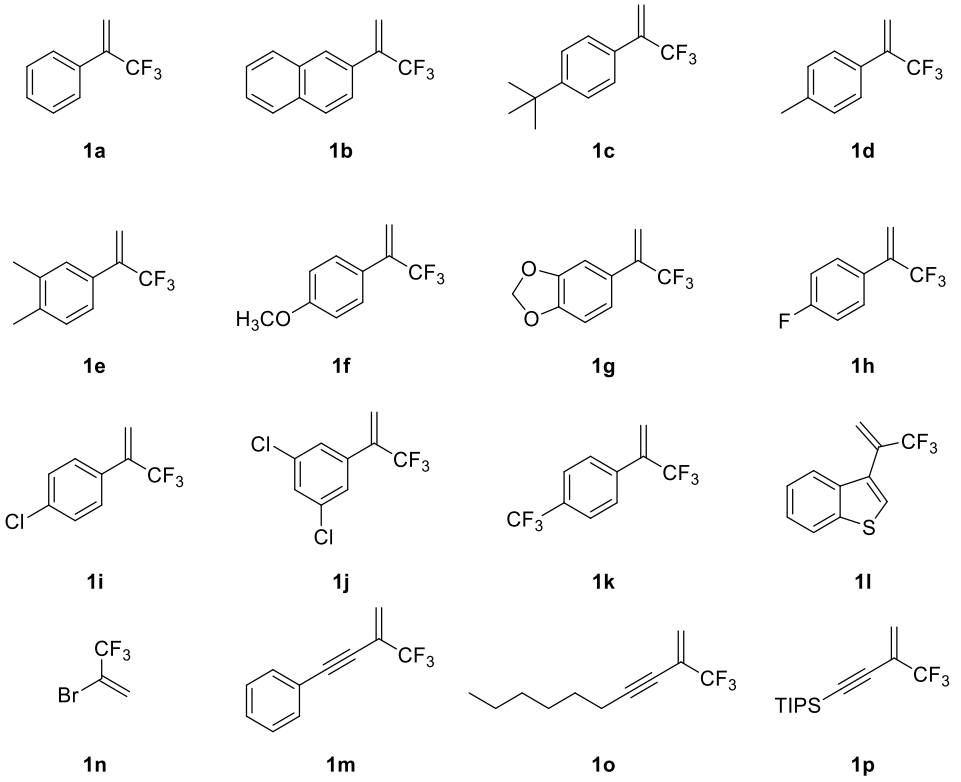
A. General Information

Melting points were measured using a melting point instrument and are uncorrected. Chemical shifts were reported in ppm from the solvent resonance as the internal standard ($CDCl_3$ δ_H = 7.26 ppm, δ_C = 77.16 ppm). Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quint)quintet), m (multiplet). Coupling constants were reported in Hertz (Hz). IR spectra were obtained with an infrared spectrometer on either potassium bromide pellets or liquid films between two potassium bromide pellets. HRMS was carried out on a high-resolution mass spectrometer (Agilent 6210 ESI/TOF MS or Thermo Q Exactive Plus). TLC was performed using commercially available 100−400 mesh silica gel plates (GF_{254}). X-ray structural analyses were conducted on Bruker APEX-II CCD Diffractometer.

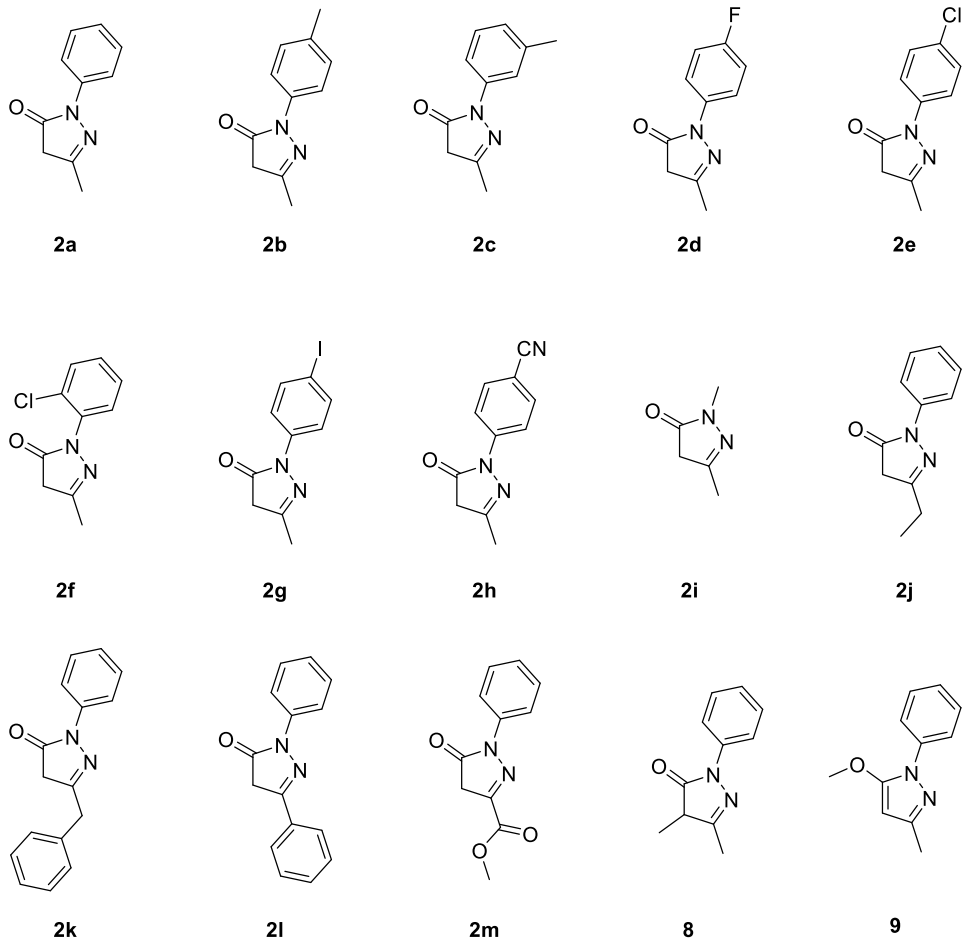
Materials. Tetrahydrofuran (THF) and toluene were distilled from sodium/benzophenone; 1,2-dichloroethane (DCE) was distilled from calcium hydride; acetonitrile (CH_3CN) was distilled from phosphorus pentoxide. Other commercially available reagents were purchased and used without further purification. Analytical thin-layer chromatography was performed on 0.20 mm silica gel plates (GF_{254}) using UV light as a visualizing agent. Flash column chromatography was carried out using silica gel (200–300 mesh) with the indicated solvent system. All reactions were conducted in oven-dried Schlenk tubes. All the reaction temperatures reported are oil bath temperatures. For the biological activity assays, the *Plutella xylostella* (diamondback moth) has been in continuous colony at the glasshouse and raised with artificial feed for three generations.

B. Synthesis of (Trifluoromethyl)alkenes and Pyrazolone

(Trifluoromethyl)alkene **1n** was purchased directly, and (trifluoromethyl)alkenes **1a**[1], **1b**[1], **1c**[2], **1d**[2], **1e**[2], **1f**[3], **1g**[1], **1h**[1], **1i**[1], **1j**[2], **1k**[4], **1l**[5], **1m**[6], **1o**[7], **1p**[8] were synthesized according to the reported literatures.

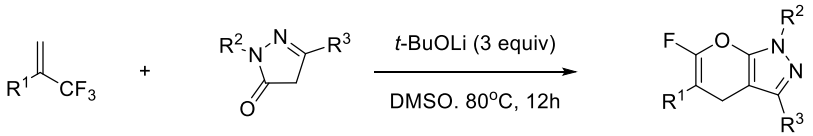


In the scope of substrates, substituted pyrazolones **2c**[9], **2d**[9], **2g**[9], **2h**[10], **2j**[10], **2k**[9], **2l**[10], **2m**[11] ,**8**[12] , **9**[13] were synthesized according to the reported literatures. **2a, 2b, 2e, 2f, 2i** were bought and used directly.



C. General Procedures

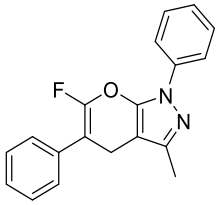
Defluorinative cyclization of (trifluoromethyl)alkenes with pyrazolones



A 25 mL oven-dried graduated tube equipped with a magnetic stirring bar, pyrazolones **1** (0.4mmol), (trifluoromethyl)alkenes **2** (0.6 mmol), *t*-BuOLi (1.2 mmol), and DMSO (4 mL) was vigorously stirred at 80 ℃ for 12 h. Then the mixture was stopped stirring, quenched with H_2O (15 mL) and extracted with EtOAc (15 mL×3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated in vacuo. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided the product **3**.

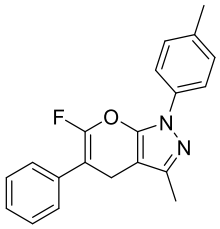
D. Analysis Data of Products

6-Fluoro-3-methyl-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3a)



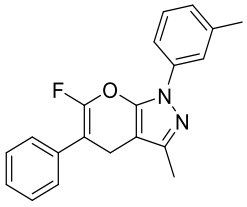
41.3 mg, 67% yield; yellow solid, mp: 89-90 °C; eluting with petroleum ether/ethyl acetate = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.63-7.64 (m, 2H), 7.30-7.38 (m, 6H), 7.17-7.23 (m, 2H), 3.55 (d, *J* = 5.5 Hz, 2H), 2.20 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3 (d, $^{1}J_{F\text{-}C}$ = 259.6 Hz), 146.1, 144.8 (d, $^{3}J_{F\text{-}C}$ = 7.6 Hz), 137.8, 134.4 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 129.2, 128.5, 127.4, 127.3, 126.3, 120.5, 95.6, 87.5 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 22.8 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 12.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.1 (s, 1F); IR (KBr): 3052, 2921, 1694, 1600, 1513, 1226, 1132, 1066 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{15}FN_2O$+H, 307.1241; found, 307.1236.

6-Fluoro-3-methyl-5-phenyl-1-(p-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3b)



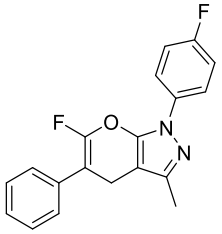
52.3 mg, 82% yield; yellow solid, mp: 124-125 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.5 Hz, 2H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.29 (t, *J* = 7.0 Hz, 1H), 7.23 (d, *J* = 8.0 Hz, 2H), 3.59 (d, *J* = 3.5 Hz, 2H), 2.37 (s, 3H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3 (d, $^{1}J_{F\text{-}C}$ = 260.8 Hz), 145.7, 144.6 (d, $^{3}J_{F\text{-}C}$ = 7.6 Hz), 136.16, 135.43, 134.5 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 129.8, 128.5, 127.4 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 127.3, 120.6, 95.3, 87.5 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 22.9 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 21.0, 12.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.2 (s, 1F); IR (KBr): 3053, 2924, 1694, 1519, 1227, 1112 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{17}FN_2O$+H, 321.1398; found, 321.1393.

6-Fluoro-3-methyl-5-phenyl-1-(*o*-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3c)



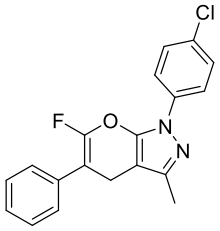
101.7 mg, 79% yield; yellow solid, mp: 102-103 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.49 (d, *J* = 10.0 Hz, 1H), 7.44 (d, *J* = 10.0 Hz, 2H), 7.39 (t, *J* = 5.0 Hz, 2H), 7.27-7.33 (m, 2H), 7.08 (d, *J* = 7.5 Hz, 1H), 3.58 (d, *J* = 4.0 Hz, 2H), 2.41 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3 (d, $^{1}J_{F\text{-}C}$ = 260.8 Hz), 145.9, 144.7 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 139.3, 137.8, 134.5 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 129.0, 128.5, 127.4 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 127.3, 127.1, 121.2, 117.6, 95.5, 87.5 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 22.8 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 21.5, 12.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.1 (s, 1F); IR (KBr): 2920, 1693, 1609, 1511, 1391, 1224, 1123 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{17}FN_2O$+H, 321.1398; found, 321.1393.

6-Fluoro-1-(4-fluorophenyl)-3-methyl-5-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3d)



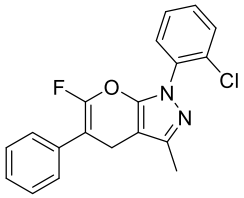
88.6 mg, 68% yield; yellow solid, mp: 118-119 °C; eluting with petroleum ether/ethyl acetate = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66-7.67 (m, 2H), 7.37-7.44 (m, 4H), 7.29 (t, *J* = 6.5 Hz, 1H), 7.12 (t, *J* = 8.5 Hz, 2H), 3.57 (s, 2H), 2.25 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 160.9 (d, $^{1}J_{F\text{-}C}$ = 245.7 Hz), 152.2 (d, $^{1}J_{F\text{-}C}$ = 259.6 Hz), 146.1, 144.6 (d, $^{3}J_{F\text{-}C}$ = 7.6 Hz), 134.3 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 134.0 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 128.5, 127.4 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 127.3, 122.2, 116.0 (d, $^{2}J_{F\text{-}C}$ = 22.7 Hz), 95.5, 87.6 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 22.8, 12.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.2 (s, 1F), -115.8 (s, 1F); IR (KBr): 2923, 1692, 1629, 1519, 1394, 1224, 1122 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{14}F_2N_2O$+H, 325.1147; found, 325.1143.

1-(4-Chlorophenyl)-6-fluoro-3-methyl-5-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3e)



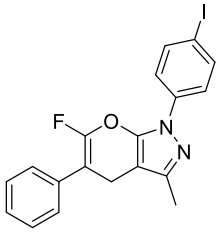
42.0 mg, 59% yield; yellow solid, mp: 124-125 °C; eluting with petroleum ether/ethyl acetate = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58-7.61 (m, 2H), 7.30-7.37 (m, 6H), 7.21-7.24 (m, 1H), 3.50 (d, *J* = 5.0 Hz, 2H), 2.81 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ152.1 (d, $^{1}J_{F\text{-}C}$ = 260.8 Hz), 146.4, 144.7 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 136.5, 134.3 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 131.6, 129.3, 128.5, 127.4, 127.3 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 121.3, 95.9, 87.6 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 22.8 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 12.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.2 (s, 1F); IR (KBr): 2925, 1694, 1611, 1509, 1406, 1226, 1094 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{14}ClFN_2O$+H, 341.0852; found, 341.0851.

1-(2-Chlorophenyl)-6-fluoro-3-methyl-5-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3f)



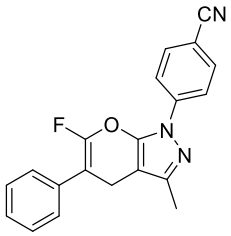
57.8 mg, 85% yield; yellow oil; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.44 (m, 1H), 7.34-7.38 (m, 3H), 7.27-7.31 (m, 4H), 7.18-7.21 (m, 1H), 3.53 (d, *J* = 5.0 Hz, 2H), 2.19 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3 (d, $^{1}J_{F\text{-}C}$ = 260.8 Hz), 146.8, 146.0 (d, $^{3}J_{F\text{-}C}$ = 7.6 Hz), 134.6, 134.5 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 131.6, 130.4, 130.3, 129.3, 128.5, 127.6, 127.4 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 127.3, 94.4, 87.5 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 23.1 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.5 (s, 1F); IR (KBr): 3057, 2923, 1699, 1532, 1227, 1116 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{14}ClFN_2O$+H, 341.0852; found, 341.0849.

6-Fluoro-1-(4-iodophenyl)-3-methyl-5-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3g)



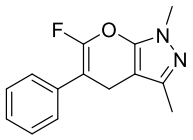
54.3 mg, 64% yield; yellow solid, mp: 133-134 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.5 Hz, 2H), 7.22–7.42 (m, 6H), 7.21-7.23 (m, 1H), 3.49 (d, *J* = 5.0 Hz, 2H), 2.17 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1 (d, $^{1}J_{F\text{-}C}$ = 260.8 Hz), 146.5, 144.7 (d, $^{3}J_{F\text{-}C}$ = 7.6 Hz), 138.2, 137.6, 134.2 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 128.6, 127.5, 127.3 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 121.8, 96.0, 90.4, 87.6 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 27.7 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.2(s, 1F); IR (KBr): 2918, 1689, 1506, 1396, 1222, 1064 cm^{-1}; HRMS (ESI, m/z): $[M+H]^+$ Calcd. for $C_{19}H_{14}FIN_2O$+H, 433.0208; found, 433.0201.

4-(6-Fluoro-3-methyl-5-phenylpyrano[2,3-*c*]pyrazol-1(4*H*)-yl)benzonitrile (3h)



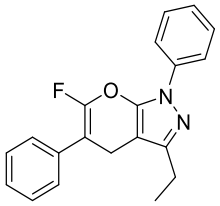
54.8 mg, 40% yield; white solid, mp: 188-189 °C; eluting with petroleum ether/ethyl acetate = 10:1 ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.89 (d, *J* = 8.5, 2H), 7.69 (d, *J* = 8.5 Hz, 2H), 7.38–7.44 (m, 4H), 7.31 (t, *J* = 7.0 Hz, 1H), 3.56 (d, *J* = 5.5 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 151.9 (d, $^{1}J_{F\text{-}C}$ = 262.1 Hz), 147.8, 145.3 (d, $^{3}J_{F\text{-}C}$ = 7.6 Hz), 141.2, 133.9 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 133.4, 128.6, 127.6, 127.3 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 119.5 118.5, 109.0, 96.9, 87.8 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 22.7 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.2 (s, 1F); IR (KBr): 2921, 2219, 1695, 1601, 1513, 1410, 1220 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{14}FN_3O$+H, 332.1194; found, 332.1190.

6-Fluoro-1,3-dimethyl-5-phenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3i)



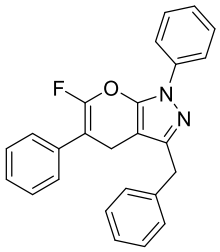
39.7 mg, 81% yield; yellow solid, mp: 79-80 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29-7.36 (m, 4H), 7.18-7.22 (m, 1H), 3.60 (s, 3H), 3.45 (d, *J* = 5.0 Hz, 2H), 2.11 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3 (d, $^{1}J_{F\text{-}C}$ = 259.6 Hz), 145.5 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 144.1, 134.7 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 128.5, 127.4 (d, $^{3}J_{F\text{-}C}$ = 5.0 Hz), 127.2, 93.3, 87.5 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 33.6, 23.0 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 12.7; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.8 (s, 1F); IR (KBr): 2928, 1691, 1557, 1488, 1226 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{14}H_{13}FN_2O$+H, 245.1084; found, 245.1081.

3-Ethyl-6-fluoro-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3j)



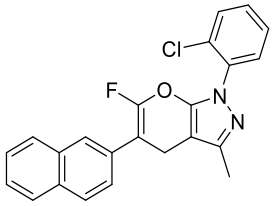
71.1 mg, 55% yield; yellow solid, mp: 89-90 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 8.0 Hz, 2H), 7.37-7.45 (m, 6H), 7.24-7.30 (m, 2H), 3.63 (d, *J* = 5.5 Hz, 2H), 2.66 (q, *J* = 7.5 Hz, 2H), 1.29 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.3 (d, $^{1}J_{F\text{-}C}$ = 259.6 Hz), 151.3, 144.8 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 137.9, 134.5 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 129.2, 128.5, 127.4 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 127.3, 126.2, 120.6, 94.8, 87.5 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 23.1 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 21.4, 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.1 (s, 1F); IR (KBr): 2924, 1697, 1600, 1517, 1450, 1404, 1345, 1227, 1132 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{17}FN_2O$+H, 321.1398; found, 321.1394.

3-Benzyl-6-fluoro-1,5-diphenyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3k)



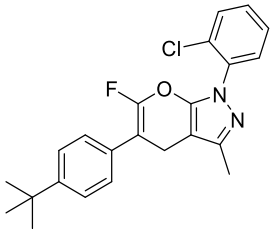
62.0 mg, 40% yield; yellow solid, mp: 107-108 °C; eluting with petroleum ether/ethyl acetate = 10:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.0 Hz, 2H), 7.51 (t, *J* = 7.2 Hz, 2H), 7.28-7.41 (m, 11H), 4.06 (s, 2H), 3.36 (d, *J* = 5.2 Hz, 2H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1 (d, $^{1}J_{F\text{-}C}$ = 260.8 Hz), 148.7, 145.0 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 138.3, 137.9, 134.4 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 129.3, 128.8, 128.6, 128.5, 127.4, 127.3, 126.5, 126.4, 120.7, 95.5, 87.6 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 34.7, 22.9 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.4 (s, 1F); IR (KBr): 3049, 2922, 1696, 1599, 1512, 1403, 1225, 1128, 1068 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{25}H_{19}FN_2O$+H, 383.1554; found, 383.1548.

1-(2-Chlorophenyl)-6-fluoro-3-methyl-5-(naphthalen-2-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3n)



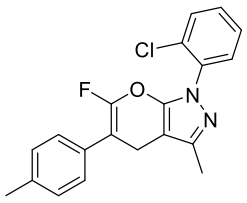
142.2 mg, 91% yield; yellow solid, mp: 107-108 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80–7.83 (m, 4H), 7.57 (d, *J* = 9.0 Hz, 1H), 7.44–7.51 (m, 4H), 7.33–7.35 (m, 2H), 3.68 (d, *J* = 4.5 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.6 (d, $^{1}J_{F\text{-}C}$ = 260.8 Hz), 146.8, 146.0 (d, $^{1}J_{F\text{-}C}$ = 6.3 Hz), 134.6, 133.3, 132.5, 132.0 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 131.6, 130.5, 130.3, 129.3, 128.0, 128.0, 127.6, 126.4, 126.2, 126.2, 125.5 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 94.4, 87.6 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 23.1 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -98.8 (s, 1F); IR (KBr): 2922, 1690, 1529, 1386, 1236, 1117 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{23}H_{16}ClFN_2O$+H, 391.1008; found, 391.1004.

5-(4-(*tert*-Butyl)phenyl)-1-(2-chlorophenyl)-6-fluoro-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3o)



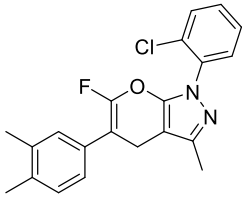
126.4 mg, 80% yield; yellow oil; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.53 (m, 1H), 7.45–7.47 (m, 1H), 7.36–7.42 (m, 6H), 3.61 (d, *J* = 5.0 Hz, 2H), 2.28 (s, 3H), 1.33 (s, 9H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2 (d, $^{1}J_{F-C}$ = 260.8 Hz), 150.3, 146.8, 146.1 (d, $^{3}J_{F-C}$ = 7.6 Hz), 134.6, 131.6, 131.4 (d, $^{4}J_{F-C}$ = 3.8 Hz), 130.4, 130.3, 129.3, 127.5 127.0 (d, $^{4}J_{F-C}$ = 3.8 Hz), 125.4, 94.4, 87.3 (d, $^{2}J_{F-C}$ = 13.9 Hz), 34.6, 31.3, 22.9 (d, $^{4}J_{F-C}$ = 2.5 Hz), 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.7 (s, 1F); IR (KBr): 3055, 2960, 1696, 1575, 1528, 1395, 1229, 1104, 1044 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{23}H_{22}ClFN_2O$+H, 397.1478; found, 397.1473.

1-(2-Chlorophenyl)-6-fluoro-3-methyl-5-(*p*-tolyl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3p)



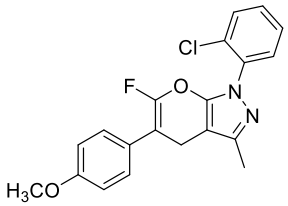
89.9 mg, 63% yield; yellow solid, mp: 110-111ºC; eluting with petroleum ether/ethyl acetate = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49-7.51 (m, 1H), 7.44-7.46 (m, 1H), 7.34-7.36 (m, 2H), 7.31-7.33 (m, 2H), 7.18 (d, *J* = 8.0 Hz, 2H), 3.59 (d, *J* = 1.3 Hz, 2H), 2.34 (s, 3H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1 (d, $^{1}J_{F-C}$ = 260.8 Hz), 146.7, 146.1 (d, $^{1}J_{F-C}$ = 6.3 Hz), 137.1, 134.7, 131.6, 131.5 (d, $^{3}J_{F-C}$ = 2.5 Hz), 130.4, 130.2, 129.3, 129.2, 127.5, 127.2 (d, $^{4}J_{F-C}$ = 5.0 Hz), 94.4, 87.4 (d, $^{3}J_{F-C}$ = 13.9 Hz), 23.1 (d, $^{3}J_{F-C}$ = 3.8 Hz), 21.2, 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.8 (s, 1F); IR (KBr): 3052, 2921, 1694, 1600, 1513, 1226, 1132, 1066 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{16}ClFN_2O$+H, 355.1008; found, 355.1004.

1-(2-Chlorophenyl)-5-(3,4-dimethylphenyl)-6-fluoro-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3q)



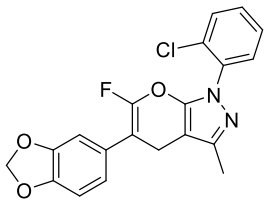
95.2 mg, 65% yield; yellow solid, mp: 114-115 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.53 (m, 1H), 7.45–7.47 (m, 1H), 7.36–7.38 (m, 2H), 7.20 (m, 3H), 3.59 (d, *J* = 5.5 Hz, 2H), 2.28 (s, 6H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1 (d, $^{1}J_{F\text{-}C}$ = 259.6 Hz), 146.7, 146.1 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 136.7, 135.8, 134.7, 131.9 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 131.6, 130.4, 130.2, 129.8, 129.3, 128.5 (d, $^{2}J_{F\text{-}C}$ = 3.8 Hz), 127.5, 124.8 (d, $^{2}J_{F\text{-}C}$ = 3.8 Hz), 94.4, 87.4 (d, $^{2}J_{F\text{-}C}$ = 15.1 Hz), 23.2 (d, $^{2}J_{F\text{-}C}$ = 3.8 Hz), 19.9, 19.5, 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.9 (s, 1F); IR (KBr): 2924, 1693, 1626, 1528, 1446, 1391, 1230, 1118, 1032 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{21}H_{18}ClFN_2O$+H, 369.1165; found, 369.1162.

1-(2-Chlorophenyl)-6-fluoro-5-(4-methoxyphenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3r).



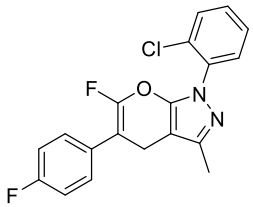
95.8 mg, 65% yield; yellow solid, mp: 87-88 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.53 (m, 1H), 7.45–7.47 (m, 1H), 7.36 (d, *J* = 7.5 Hz, 4H), 6.92 (d, *J* = 8.5 Hz, 2H), 3.81 (s, 3H), 3.58 (d, *J* = 5.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 152.0 (d, $^{1}J_{F\text{-}C}$ = 259.6 Hz), 146.72, 146.1 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 134.7, 131.6, 130.4, 130.2, 129.3, 128.5 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 127.5, 126.7 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 113.9, 94.3, 87.0 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 55.3, 23.2 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -100.5 (s, 1F); IR (KBr): 2840, 1693, 1605, 1516, 1228, 1181, 1097, 1034 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{16}ClFN_2O_2$+H, 371.0957; found, 371.0954.

5-(Benzo[*d*][1,3]dioxol-5-yl)-1-(2-chlorophenyl)-6-fluoro-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3s)



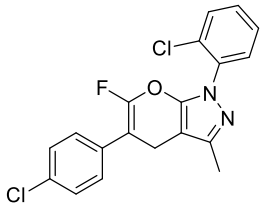
117.0 mg, 76% yield; yellow solid, mp: 118-119 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51–7.52 (m, 1H), 7.45–7.46 (m, 1H), 7.36–7.38 (m, 2H), 6.81–6.94 (m, 3H), 5.96 (s, 2H), 3.55 (d, *J* = 4.5 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.1 (d, $^{1}J_{F\text{-}C}$ = 259.6 Hz), 147.8, 146.7, 146.0 (d, $^{3}J_{F\text{-}C}$ = 7.6 Hz), 134.6, 131.6, 130.4, 130.3, 129.3, 128.2 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 127.5, 120.9 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 108.3, 108.1 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 101.2, 94.3, 87.3 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 23.4 (d, $^{3}J_{F\text{-}C}$ = 3.8 Hz), 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.8(s, 1F); IR (KBr): 2900, 1694, 1623, 1493, 1442, 1391, 1337, 1238, 1100, 1039 cm^{-1}; HRMS (APCI, m/z): $[M]^+$ Calcd. for $C_{20}H_{14}ClFN_2O_3$+H, 385.0750; found, 385.0745.

1-(2-Chlorophenyl)-6-fluoro-5-(4-fluorophenyl)-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3t)



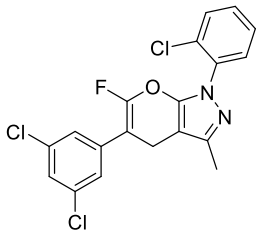
112.2 mg, 77% yield; yellow oil; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50-7.52 (m, 1H), 7.44-7.46 (m, 1H), 7.35–7.40 (m, 4H), 7.05 (t, *J* = 8.5 Hz, 2H), 3.57 (d, *J* = 5.0 Hz, 2H), 2.27 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, $^{1}J_{F\text{-}C}$ = 247.0 Hz), 152.3 (d, $^{1}J_{F\text{-}C}$ = 259.6 Hz), 146.7, 145.9 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 134.6, 131.6, 130.4, 130.3, 129.3, 129.1 (d, $^{3}J_{F\text{-}C}$ = 7.6 Hz), 129.1 (d, $^{3}J_{F\text{-}C}$ = 5.0 Hz), 127.6, 115.4 (d, $^{2}J_{F\text{-}C}$ = 20.2 Hz), 94.2 (d, $^{4}J_{F\text{-}C}$ = 1.3 Hz), 86.8 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 23.2 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 12.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -99.7 (s,1F), -114.4 (s, 1F); IR (KBr): 3065,2925, 1702, 1584, 1511, 1232, 1126 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{19}H_{13}ClF_2N_2O$+H, 359.0757; found, 359.0753.

1-(2-Chlorophenyl)-5-(4-chlorophenyl)-6-fluoro-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3u)



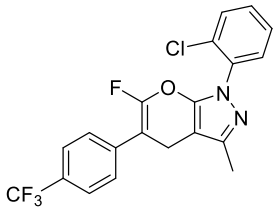
128.7 mg, 86% yield, yellow solid, mp: 101-102 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.52 (m, 1H), 7.44–7.46 (m, 1H), 7.34–7.37 (m, 6H), 3.58 (d, *J* = 5.0 Hz, 2H), 2.28 (s, 1H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.4 (d, $^{1}J_{F\text{-}C}$ = 260.8 Hz), 146.7, 145.8 (d, $^{1}J_{F\text{-}C}$ = 7.6 Hz), 134.6, 133.0, 132.9 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 131.6, 130.4, 130.3, 129.3, 128.7, 128.6, 127.6, 94.1, 86.7 (d, $^{2}J_{F\text{-}C}$ = 13.9 Hz), 22.9 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -98.4 (s, 1F); IR (KBr): 2924, 1692, 1517, 1232, 1097 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{19}H_{13}Cl_2FN_2O$+H, 375.0462; found, 375.0459.

1-(2-Chlorophenyl)-5-(3,5-dichlorophenyl)-6-fluoro-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3v)



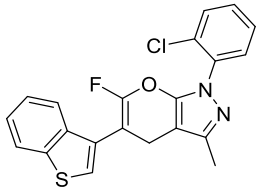
126.9 mg, 77% yield, yellow solid, mp: 134-135 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.53 (m, 1H), 7.44–7.46 (m, 1H), 7.36–7.38 (m, 2H), 7.32 (s, 2H), 7.26 (t, *J* = 2.0 Hz, 1H), 3.57 (d, *J* = 5.0 Hz, 2H), 2.28 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.1 (d, $^{1}J_{F\text{-}C}$ = 263.3 Hz), 146.7, 145.5 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 137.5 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 135.1, 134.5, 131.5, 130.4, 130.4, 129.2, 127.6, 127.2, 125.8 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 93.9, 86.0 (d, $^{2}J_{F\text{-}C}$ = 12.6 Hz), 22.8 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -95.8 (s, 1F); IR (KBr): 2921, 1689, 1558, 1433, 1233, 1126 cm^{-1}; HRMS (APCI, m/z): $[M+H]^-$ Calcd. for $C_{19}H_{12}Cl_3FN_2O+H^-$, 409.0072; found, 409.0070.

1-(2-Chlorophenyl)-6-fluoro-3-methyl-5-(4-(trifluoromethyl)phenyl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3w)



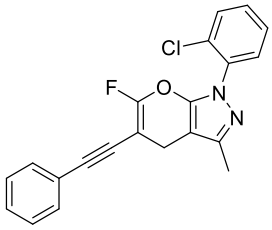
150.8 mg, 92% yield; yellow oil; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (dd, *J* = 4.0, 5.0 Hz, 4H), 7.52–7.54 (m, 1H), 7.46–7.48 (m, 1H), 7.38–7.40 (m, 2H), 3.64 (d, *J* = 5.0 Hz, 2H), 2.29 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.0 (d, $^{1}J_{F\text{-}C}$ = 263.3 Hz), 146.7, 145.7 (d, $^{3}J_{F\text{-}C}$ = 7.6 Hz), 138.3, 134.5, 131.6, 130.4, 130.4, 129.3, 127.6, 127.6 (d, $^{4}J_{F\text{-}C}$ = 1.3 Hz), 125.4 (q, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 124.1 (d, $^{1}J_{F\text{-}C}$ = 273.4 Hz), 94.1, 86.8 (d, $^{2}J_{F\text{-}C}$ = 12.6 Hz), 22.8 (d, $^{4}J_{F\text{-}C}$ = 3.8 Hz), 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -62.6 (s, 3F), -97.3 (s, 1F); IR (KBr): 2923, 1688, 1572, 1391, 1324, 1267, 1119 cm^{-1}; HRMS (ESI, m/z): $[M+Na]^+$ Calcd. for $C_{20}H_{13}ClF_4N_2O$+H, 409.0725; found, 409.0722.

5-(Benzo[*b*]thiophen-3-yl)-1-(2-chlorophenyl)-6-fluoro-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3x)



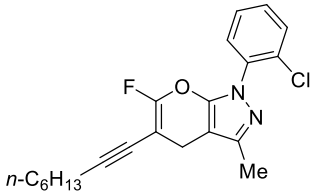
58.6 mg, 37% yield; yellow solid, mp: 141-142 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 1H), 7.53–7.55 (m, 1H), 7.48–7.50 (m, 1H), 7.38–7.40 (m, 5H), 3.63 (d, *J* = 5.0 Hz, 2H), 2.26 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 152.2 (d, $^{1}J_{F\text{-}C}$ = 259.6 Hz), 146.7, 146.3 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 140.0, 137.5, 134.6, 131.7, 130.5, 130.4, 130.0, 129.3, 127.6, 124.9, 124.6, 124.3, 122.9, 122.8 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 94.4, 82.6 (d, $^{2}J_{F\text{-}C}$ = 18.9 Hz), 24.4 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -95.6 (s, 1F); IR (KBr): 3069, 2924, 1705, 1529, 1246, 1102, 1039 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{14}ClFN_2OS$+H, 397.0572; found, 397.0569.

1-(2-Chlorophenyl)-6-fluoro-3-methyl-5-(phenylethynyl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3z)



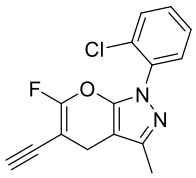
114.5 mg, 79% yield; yellow solid, mp: 80-81 °C; eluting with petroleum ether/ethyl acetate = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.52 (m, 1H), 7.43–7.46 (m, 3H), 7.36–7.38 (m, 2H), 7.30–7.32 (m, 3H), 3.48 (d, *J* = 5.0 Hz, 2H), 2.25 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.8 (d, $^{1}J_{F\text{-}C}$ = 264.6 Hz), 146.6, 145.4 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 134.4, 131.6, 131.4, 130.4, 130.4, 129.2, 128.3, 127.6, 123.0, 93.9, 93.7 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 81.8 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 73.1 (d, $^{2}J_{F\text{-}C}$ = 16.4 Hz), 22.9, 12.9; ^{19}F NMR (471 MHz, $CDCl_3$) δ -89.3 (s, 1F); IR (KBr): 2924, 1686, 1620, 1527, 1389, 1261, 1121 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{14}ClFN_2O$+H, 365.0852; found, 365.0850.

1-(2-Chlorophenyl)-6-fluoro-3-methyl-5-(oct-1-yn-1-yl)-1,4-dihydropyrano[2,3-*c*]pyrazole (3aa)



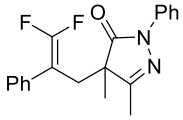
97.1 mg, 65% yield; yellow oil; eluting with petroleum ether/ethyl acetate = 10:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48–7.50 (m, 1H), 7.40–7.42 (m, 1H), 7.34–7.36 (m, 2H), 3.35 (d, *J* = 5.0 Hz, 2H), 2.34 (t, *J* = 8.0 Hz, 2H), 2.23 (s, 3H), 1.52–1.58 (m, 2H), 1.38–1.44 (m, 2H), 1.28–1.34 (m, 4H), 0.90 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 157.6 (d, $^{1}J_{F\text{-}C}$ = 262.1 Hz), 146.5, 145.5 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 134.5, 131.6, 130.4, 130.3, 129.2, 127.5, 94.9 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 94.0, 73.7 (d, $^{2}J_{F\text{-}C}$ = 16.4 Hz), 72.7 (d, $^{4}J_{F\text{-}C}$ = 1.3 Hz), 31.3, 28.7, 28.5, 23.2 (d, $^{4}J_{F\text{-}C}$ = 1.3 Hz), 22.5, 19.5, 14.0, 12.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -92.3 (s, 1F); IR (KBr): 2927, 2858, 1691, 1530, 1257, 1111 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{21}H_{22}ClFN_2O$+H, 373.1478; found, 373.1474.

1-(2-Chlorophenyl)-5-ethynyl-6-fluoro-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazole (3ab')



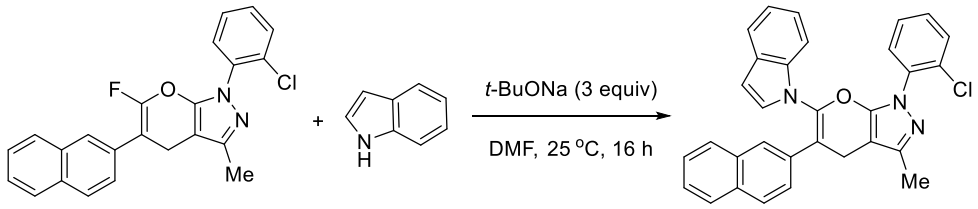
64.5 mg, 56% yield; yellow solid, mp: 107-108 ºC; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50–7.52 (m, 1H), 7.36–7.43 (m, 3H), 3.41 (d, *J* = 5.0 Hz, 2H), 3.11 (s, 1H), 2.24 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 159.0 (d, $^{1}J_{F\text{-}C}$ = 265.9 Hz), 146.5, 145.2 (d, $^{3}J_{F\text{-}C}$ = 6.3 Hz), 134.3, 131.6, 130.4, 130.4, 129.2, 127.6, 93.8, 81.8 (d, $^{4}J_{F\text{-}C}$ = 5.0 Hz), 76.3 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 72.6 (d, $^{2}J_{F\text{-}C}$ = 16.4 Hz), 22.6 (d, $^{4}J_{F\text{-}C}$ = 1.3 Hz), 12.8; ^{19}F NMR (471 MHz, $CDCl_3$) δ -89.0 (s, 1F); IR (KBr): 2921, 2855, 1688, 1623, 1528, 1390, 1340, 1264 1088, 1038 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{15}H_{10}ClFN_2O$+H, 289.0539; found, 289.0534.

4-(3,3-Difluoro-2-phenylallyl)-4,5-dimethyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (10)



100.5 mg, 74% yield; yellow oil; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.44 (m, 2H), 7.19–7.22 (m, 2H), 7.00–7.07 (m, 6H), 2.94 (dt, *J* = 3.0, 3.0 Hz, 1H), 2.69 (dd, *J* = 2.0, 2.0 Hz, 1H), 1.86 (s, 3H), 1.22 (s, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.6, 162.8, 154.1 (t, $^{1}J_{F\text{-}C}$ = 291.1 Hz), 137.7, 131.1 (dd, $^{4}J_{F\text{-}C}$ = 3.8, 2.5 Hz), 128.9 (t, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 128.5, 128.2, 128.0, 124.8, 118.7, 89.1 (dd, $^{2}J_{F\text{-}C}$ = 20.2, 17.6 Hz), 54.1 (t, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 33.9 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz), 21.0, 13.5 (d, $^{4}J_{F\text{-}C}$ = 2.5 Hz); ^{19}F NMR (471 MHz, $CDCl_3$) δ -88.7 (d, $^{3}J_{F\text{-}H}$ = 37.7 Hz, 1F), -89.8 (d, $^{3}J_{F\text{-}H}$ = 37.7 Hz, 1F); IR (KBr): 2968, 1712, 1595, 1497, 1450, 1399, 1365, 1296, 1240, 1140 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. for $C_{20}H_{18}F_2N_2O$+H, 341.1460; found, 341.1457.

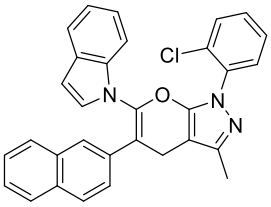
E. Further Derivations



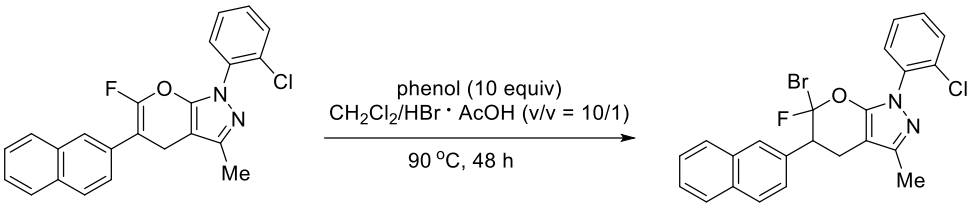
3n **4**: 87%

A 25 mL oven-dried tube equipped with a magnetic stirring bar, **3n** (77.7 mg, 0.2 mmol), indole (46.9 mg, 0.4 mmol), *t*-BuONa (57.7 mg, 0.6 mmol), and DMF (2 mL) was vigorously stirred at room temperature for 16 h. Then the mixture was stopped stirring, added water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 5:1) provided product **4** in 87% isolated yield.

1-(2-Chlorophenyl)-6-(1*H*-indol-1-yl)-3-methyl-5-(naphthalen-2-yl)-1,4-dihydropyrano[2,3-*c*] pyrazole (4)



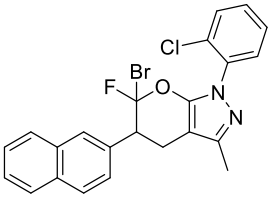
84.9 mg, 87% yield; yellow solid, mp: 96-98 °C; eluting with petroleum ether/ethyl acetate = 5:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.72 (m, 3H), 7.43–7.56 (m, 7H), 7.32–7.36 (m, 2H), 7.13–7.19 (m, 2H), 6.90–6.93 (m, 2H), 6.42 (d, *J* = 3.6 Hz, 1H), 4.00 (s, 2H), 2.41 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 146.8, 140.3, 136.0, 135.0, 134.9, 133.2, 132.5, 131.7, 130.4, 130.2, 129.4, 128.6, 128.1, 128.0, 127.9, 127.6, 127.6, 126.2, 126.1, 125.9, 125.0, 122.8, 121.0, 120.9, 111.5, 108.6, 104.8, 93.9, 25.9, 13.0; IR (KBr): 3055, 2924, 1669, 1521, 1453, 1389, 1303, 1223, 1119 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. For $C_{31}H_{22}ClN_3O$+H, 488.1524; found, 488.1520.



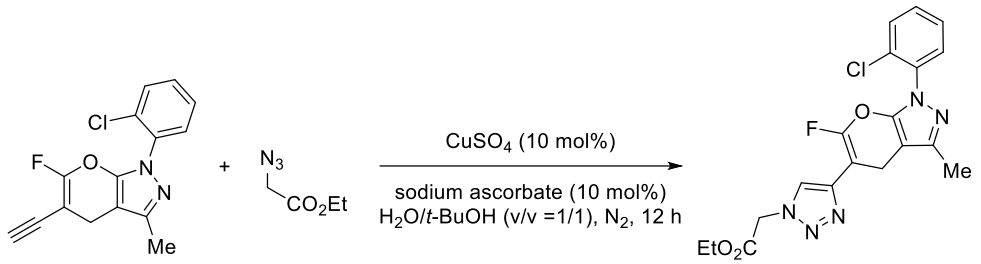
3n **5**: 73%

A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, **3n** (77.7 mg, 0.2 mmol) and phenol (188.2 mg, 2.0 mmol) were dissolved in 4 mL of dichloromethane, and the HBr (0.4 mL, 33 wt.% in AcOH) was added dropwise. The resulting mixture was vigorously stirred at 90 ℃ for 48 h. Then the mixture was stopped stirring, added water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 10:1) provided product **5** in 73% isolated yield.

6-Bromo-1-(2-chlorophenyl)-6-fluoro-3-methyl-5-(naphthalen-2-yl)-1,4,5,6-tetrahydropyrano[2,3-*c*]pyrazole (5)



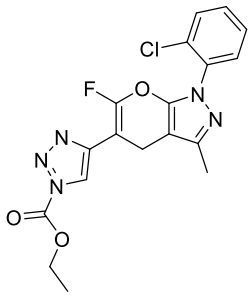
69.0 mg, 73% yield; colorless oil; eluting with petroleum ether/ethyl acetate = 10:1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (s, 1H), 7.88–7.98 (m, 3H), 7.50–7.62 (m, 5H), 7.40–7.42 (m, 2H), 3.65–3.70 (m, 1H), 3.38–3.45 (m, 1H), 2.97 (dt, J = 13.6, 5.6 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.9, 145.9 (d, $^3J_{F\text{-}C}$ = 6.1 Hz), 134.6, 133.3, 133.1, 132.1, 131.7, 130.4, 130.3, 129.5, 129.2, 128.2, 128.0, 127.7, 127.6, 127.4, 126.6, 126.4, 122.2 (d, $^1J_{F\text{-}C}$ = 284.8 Hz), 96.1, 51.8 (d, $^2J_{F\text{-}C}$ = 17.2 Hz), 23.3 (d, $^3J_{F\text{-}C}$ = 5.1 Hz), 12.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.9 (s, 1F); IR (KBr): 2923, 1617, 1523, 1489, 1441, 1390, 1304, 1262, 1212, 1164, 1105 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. For $C_{23}H_{17}BrClFN_2O$+H, 471.0270; found, 471.0264.



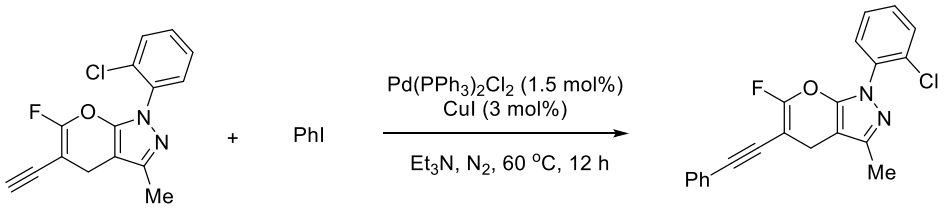
3ab' **6** **7**: 69%

A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, **3ab'** (86.6 mg, 0.3 mmol) and azidoacetic acid ethyl ester **6** (77.5 mg, 0.6 mmol) were dissolved in 2 mL of a 1:1 water/*tert*-butanol mixture. Sodium ascorbate (5.9 mg, 0.03 mmol, 300μL of freshly prepared 0.1 M solution in water) and copper(II) sulfate pentahydrate (7.5 mg, 0.03 mmol, 300μL of freshly prepared 0.1 M solution in water) were added. The mixture was vigorously stirred at 60 °C for 12 h. Then the mixture was stopped stirring, added water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate = 1:1) provided product **7** in 69% isolated yield.

Ethyl-2-(4-(1-(2-chlorophenyl)-6-fluoro-3-methyl-1,4-dihydropyrano[2,3-*c*]pyrazol-5-yl)-1*H*-1,2,3-triazol-1-yl)acetate (7)



111.4 mg, 69% yield; white solid, eluting with petroleum ether/ethyl acetate = 1:1; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 3.5 Hz, 1H), 7.43–7.45 (m, 1H), 7.37–7.39 (m, 1H), 7.29–7.32 (m, 2H), 5.11 (s, 2H), 4.17–4.20 (m, 2H), 3.79 (s, 2H), 2.23 (s, 3H), 1.21–1.23 (m, 3H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 166.2, 152.8 (d, $^1J_{F\text{-}C}$ = 260.8 Hz), 147.1, 145.5 (d, $^3J_{F\text{-}C}$ = 7.6 Hz), 141.5, 134.5, 131.5, 130.4, 130.3, 129.3, 127.6, 122.3 (d, $^2J_{F\text{-}C}$ = 11.3 Hz), 94.6, 90.0 (d, $^2J_{F\text{-}C}$ = 13.9 Hz), 62.5, 51.0, 29.7, 20.0 (d, $^4J_{F\text{-}C}$ = 2.5 Hz), 14.06, 12.91; ^{19}F NMR (471 MHz, $CDCl_3$) δ -92.7 (s, 1F); IR (KBr): 2986, 2920, 2852, 1751, 1709, 1529, 1489, 1464, 1391, 1253, 1206, 1121 cm^{-1}; HRMS (APCI, m/z): $[M+H]^+$ Calcd. For $C_{18}H_{15}ClFN_5O_3$+H, 404.0920; found, 404.0915.



3ab' **3z**: 83% yield

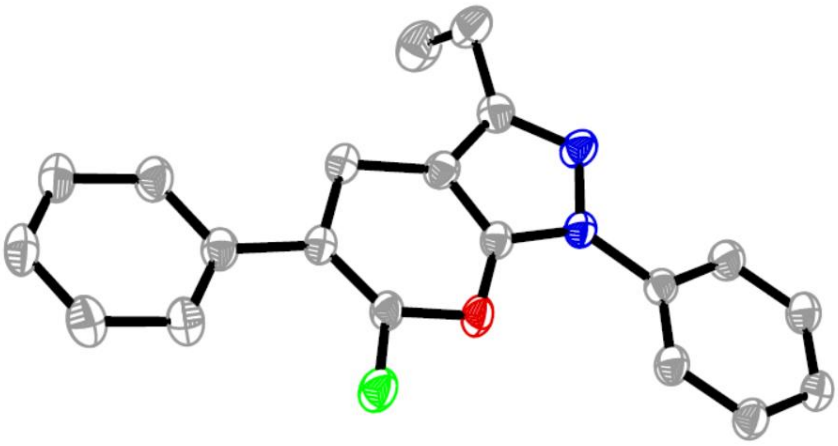
A 25 mL oven-dried Schlenk tube equipped with a magnetic stirring bar, **3ab'** (115.4 mg, 0.4 mmol), $Pd(PPh_3)_2Cl_2$ (4.9 mg, 1.5 mol%), CuI (2.3 mg, 0.012 mmol) were added. The tube was evacuated and filled with N_2, then THF (2 mL) and Et_3N (1 mmol, 138 μL) was added. The mixture was sealed and vigorously stirred at 60 °C for 12 h. Then the mixture was stopped stirring, added water (15 mL), extracted with EtOAc (15 mL × 3). The combined organic phases were dried over anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. Further purification by flash column chromatography on silica gel (eluting with petroleum ether/ethyl acetate) provided defluorination product **3z** in 83% isolated yield.

F. X-ray Crystallographic Data

The preparation of crystal of **3j**

The obtained compound **3j** (71.1 mg, 55% yield) was dissolved in the appropriate amount of CH_2Cl_2 to form a saturated solution in a test tube at room temperature. Then petroleum ether (15 mL) was added to the solution slowly along the tube wall, resulting in a two-phase mixture. Finally, sealed the test tube with a rubber plug. Then the colorless crystal of **3j** was formed after the two-phase mixture has diffused.

The X-ray crystallographic structures for **3j**. ORTEP representation with 50% probability thermal ellipsoids. Solvent and hydrogen are omitted for clarity. Crystal data have been deposited to CCDC, number 2171272.



Empirical formula	$C_{20}H_{17}FN_2O$
Formula weight	320.35
Temperature	170 K
Crystal system, Space group	Triclinic, P-1
Unit cell dimensions	a = 5.0036(15) Å alpha = 86.545(10) deg. b = 14.799(4) Å beta = 86.339(9) deg. c = 21.367(7) Å gamma = 83.061(11) deg.
Volume	1565.2(8) $Å^3$
Z	4
ρ_{calc}g/cm3	1.359
μ	0.093 mm^{-1}
F(000)	672.0
Crystal size	0.11 × 0.05 × 0.02 mm^3
Radiation	MoK\a (λ = 0.71073)
Theta range for data collection	1.913 to 25.026 deg.
Index ranges	$-5 \le h \le 5$, $-17 \le k \le 16$, $-25 \le l \le 25$
Reflections collected	15038
Independent reflections	5420 [R_{int} = 0.0746, R_{sigma} = 0.0930]
Data/restraints/parameters	5420/0/435
Goodness-of-fit on F^2	1.117
Final R indexes [I>=2σ (I)]	R_1 = 0.1143, wR_2 = 0.2975
Final R indexes [all data]	R_1 = 0.1835, wR_2 = 0.3519

G. Biological activity assays against *Plutella xylostella*

All of the tested compounds were dissolved in DMSO, and diluted with distilled water containing 0.1% Tween-80 to a solution at a concentration of 0.1 mg/mL. The leaf disks (at a diameter of 1.8 cm) were excised from cabbages, dipped in the test solution for 30 s, and allowed to dry naturally. For blank control experiments, leaf disks were dipped in the solution of distilled water containing 0.1% Tween-80 and 0.01% DMSO for 30 s, and allowed to dry naturally. The treated leaf disks were placed in petri dishes lined with filter paper. 30 second-instar larvae of *Plutella xylostella* raised in our laboratory were transferred to each petri dish. Petri dishes were kept in an incubator at 26 ℃ and 85 % relative humidity under a photoperiod of 16:8 h (light/dark). Mortalities were determined 48 h later after the treatment of the leaf disks. Three independent biological replicates were carried out for each experiment.

The corrected mortality (%) was obtained as follows:

$$\text{mortality} = \frac{\text{mortality in treatment} - \text{mortality in blank control}}{1 - \text{mortality in blank control}} \times 100\%$$

H. References

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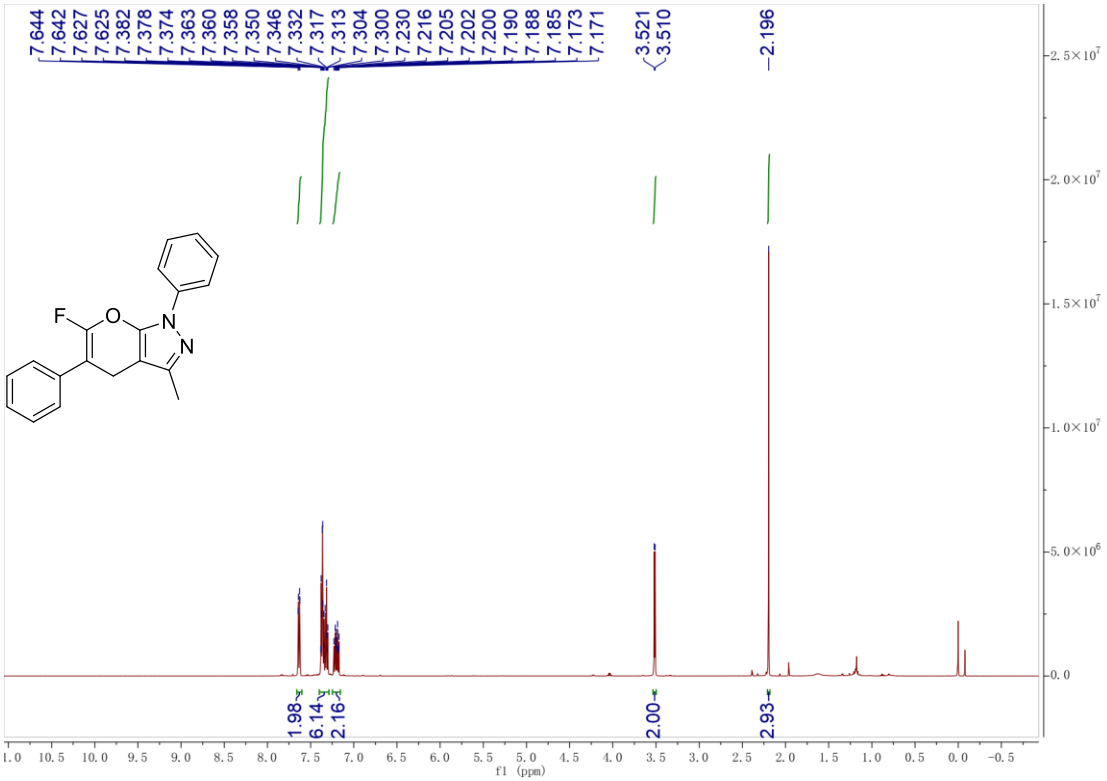
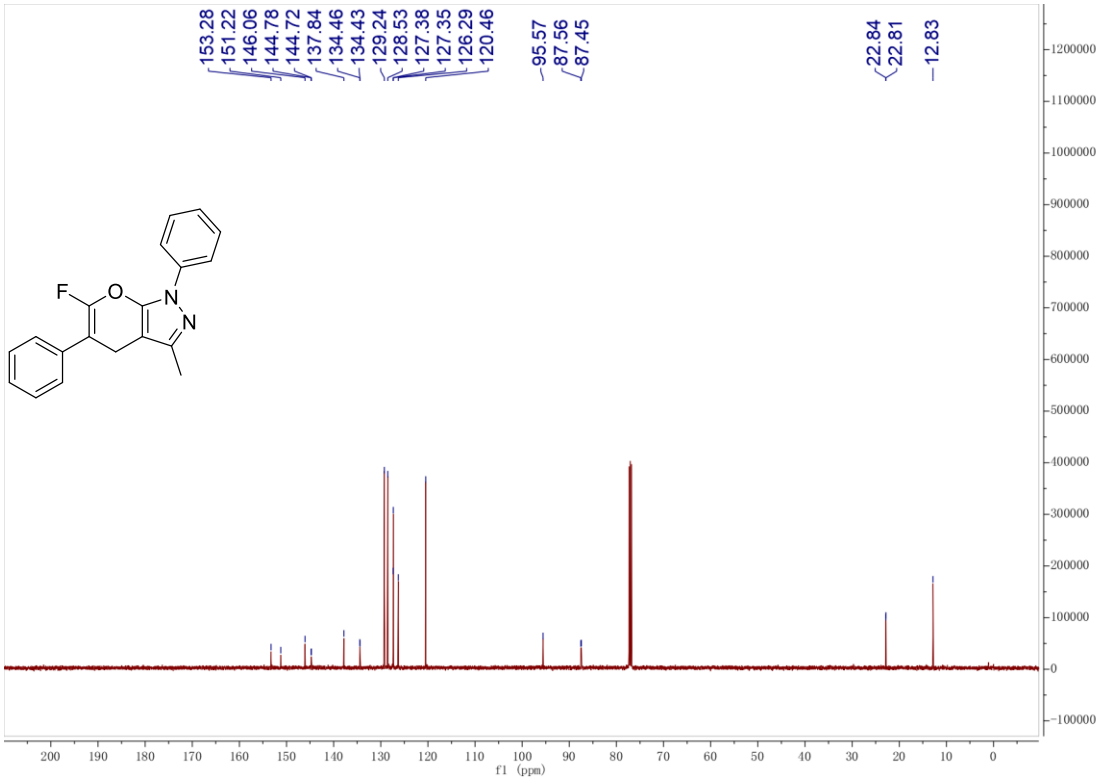
H. NMR Spectrum of New Compounds

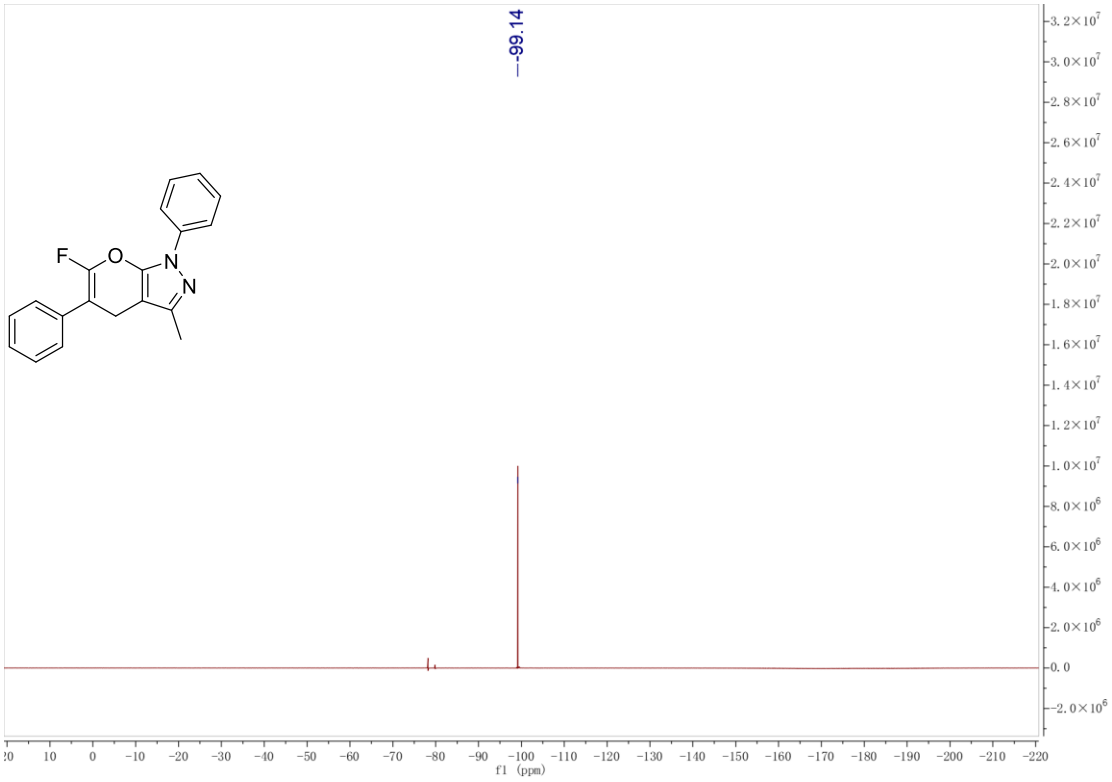
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3a



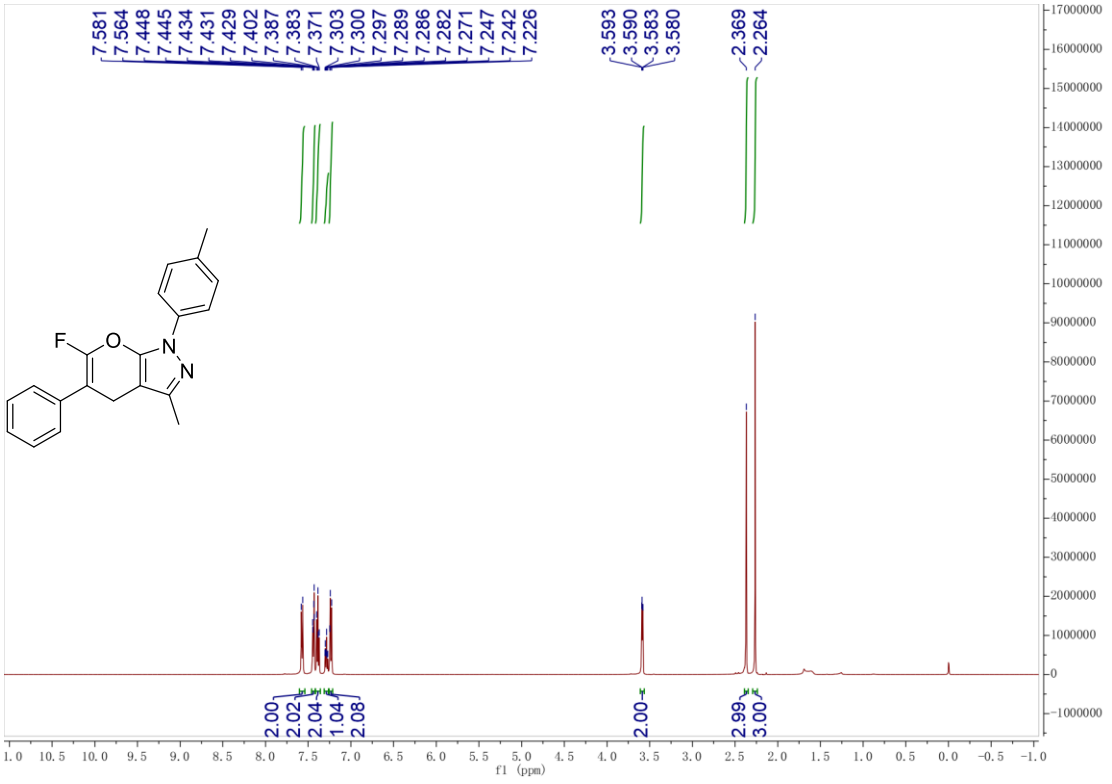
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3a



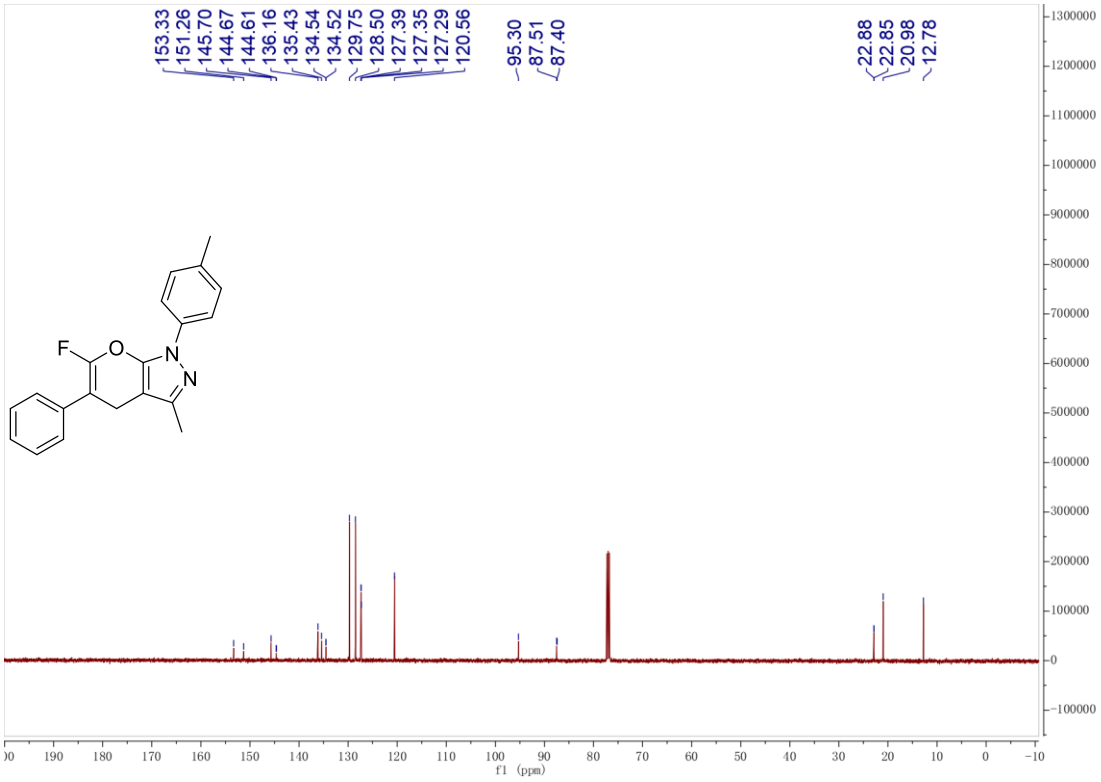
^{19}F NMR Spectrum (471 MHz, $CDCl_3$) for 3a



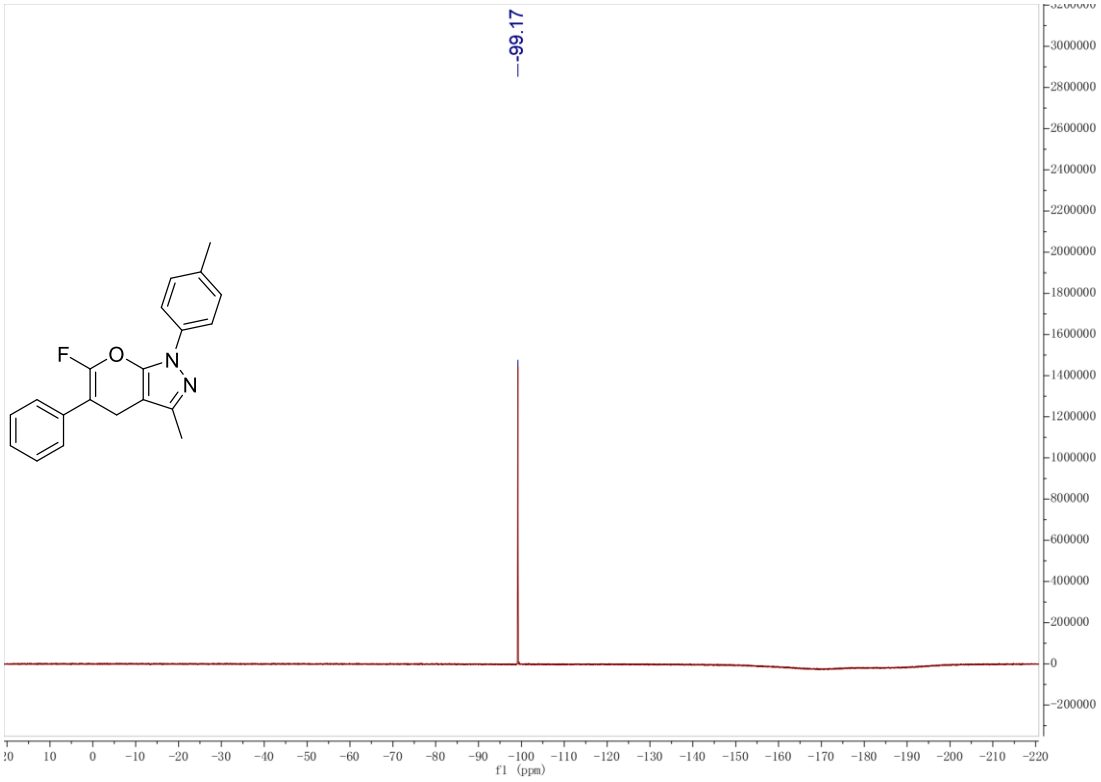
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3b



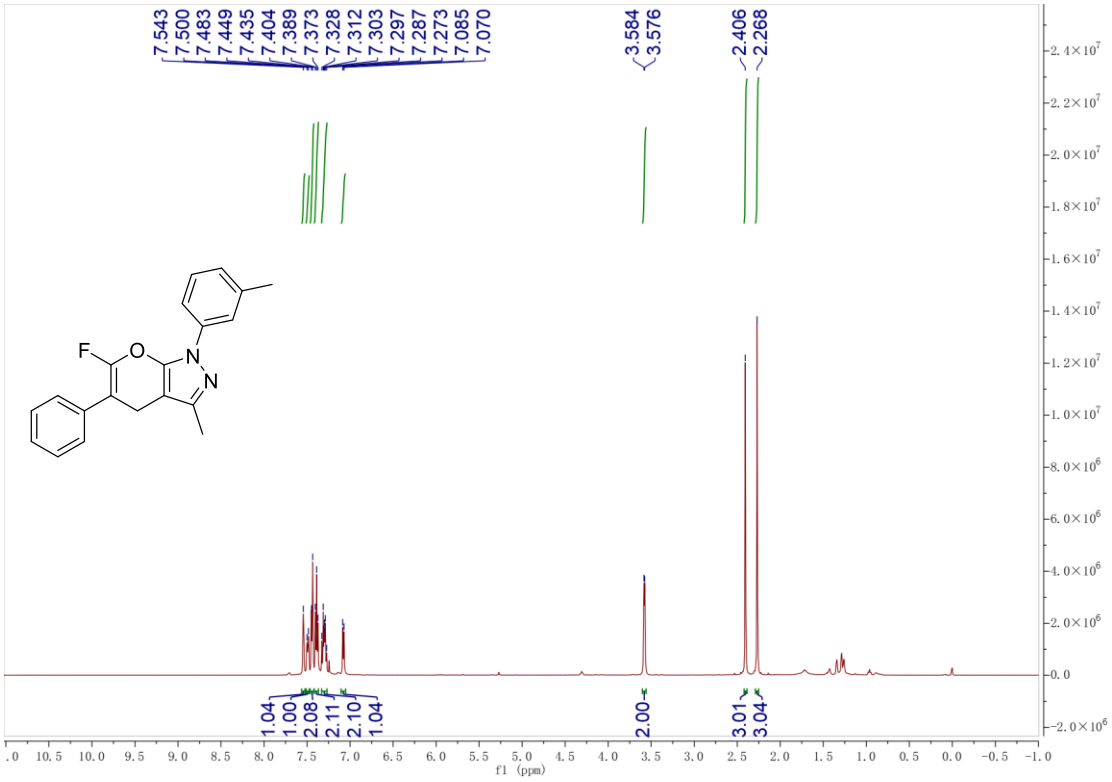
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3b



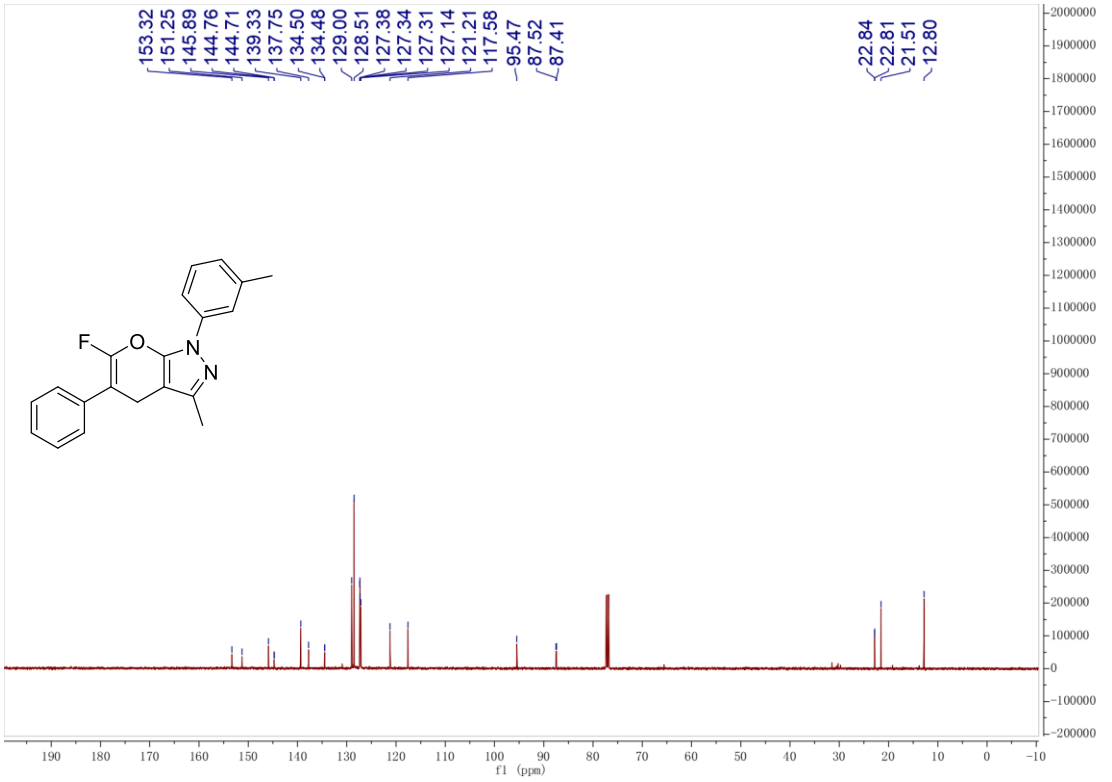
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3b



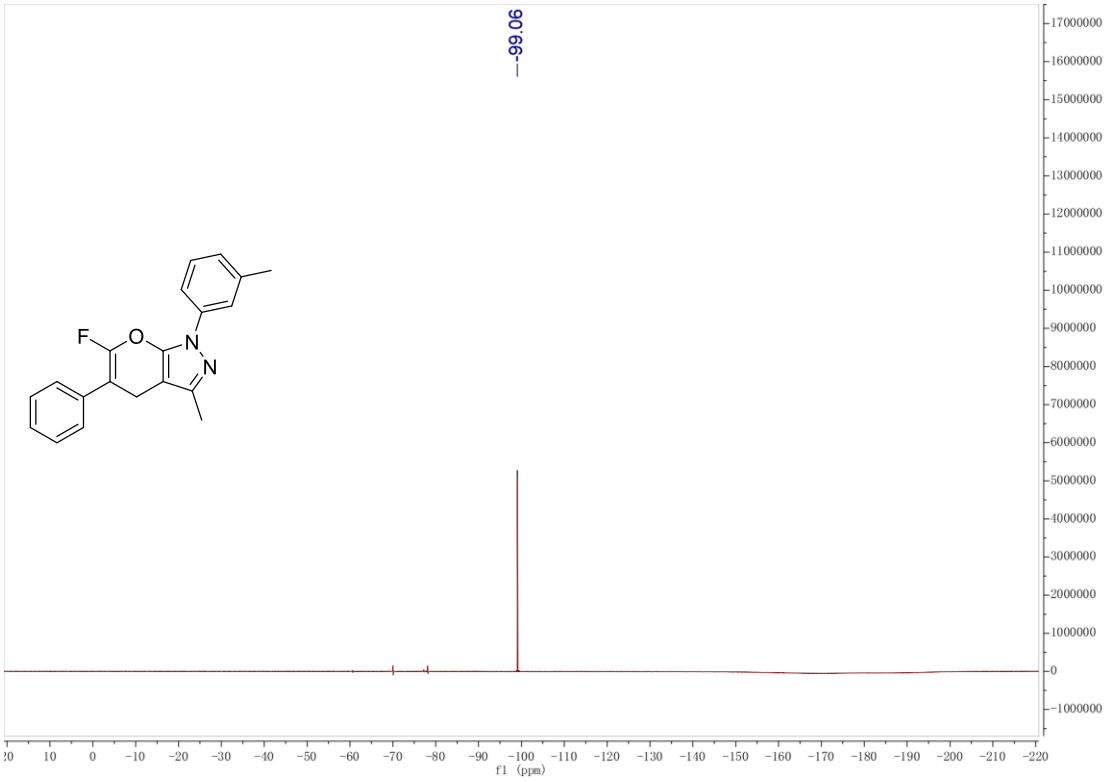
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3c



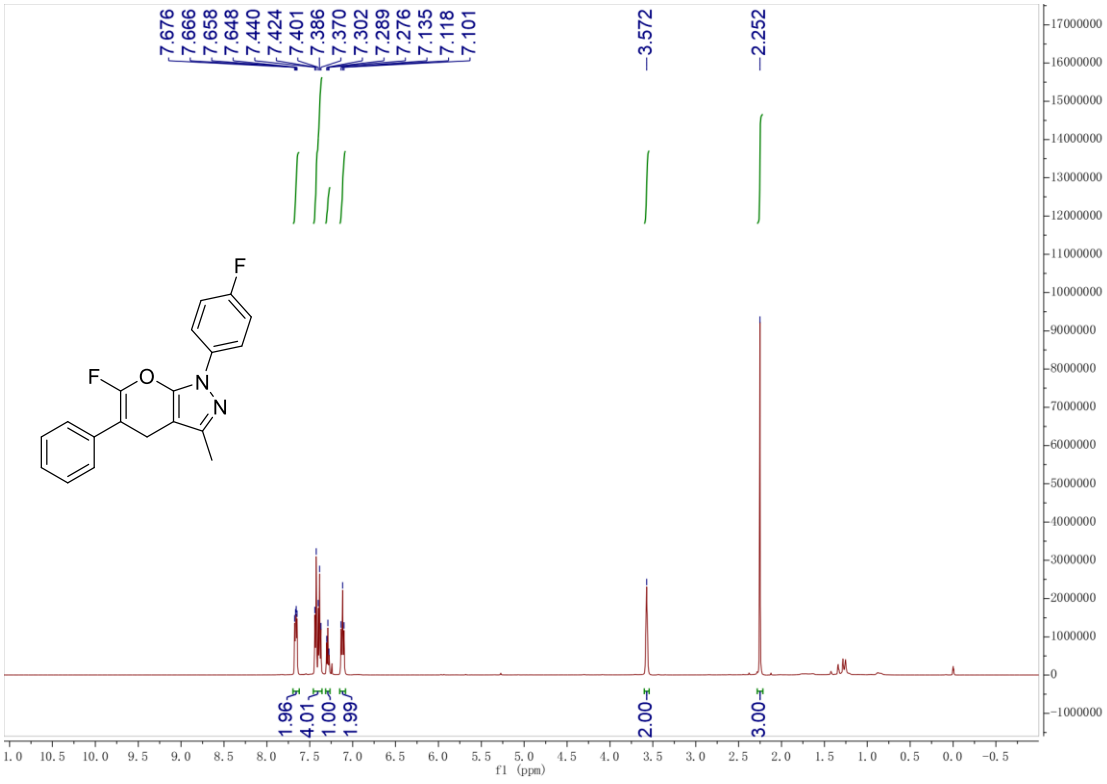
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3c



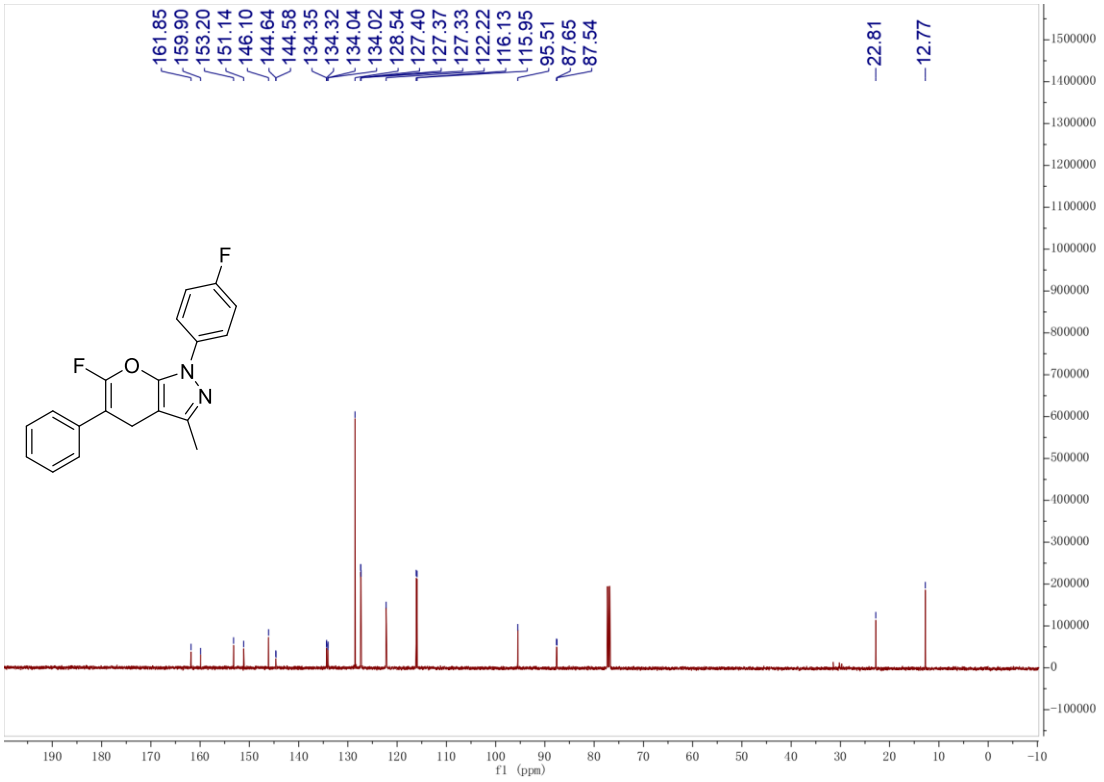
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3c



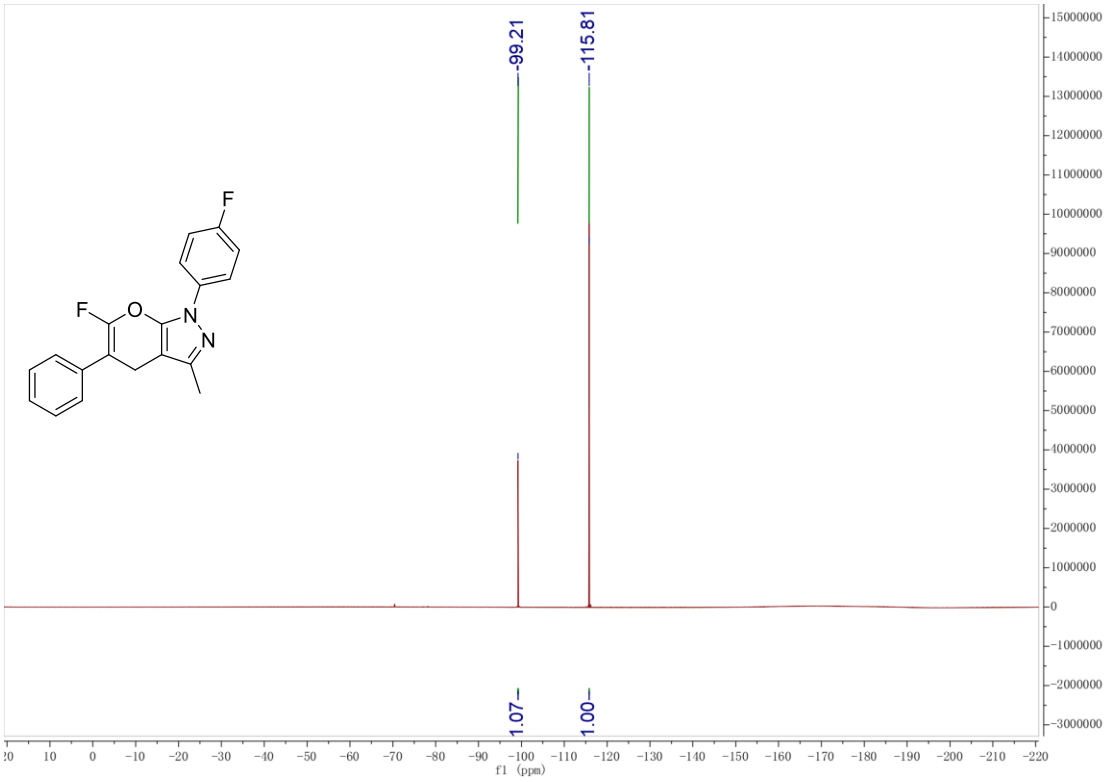
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3d



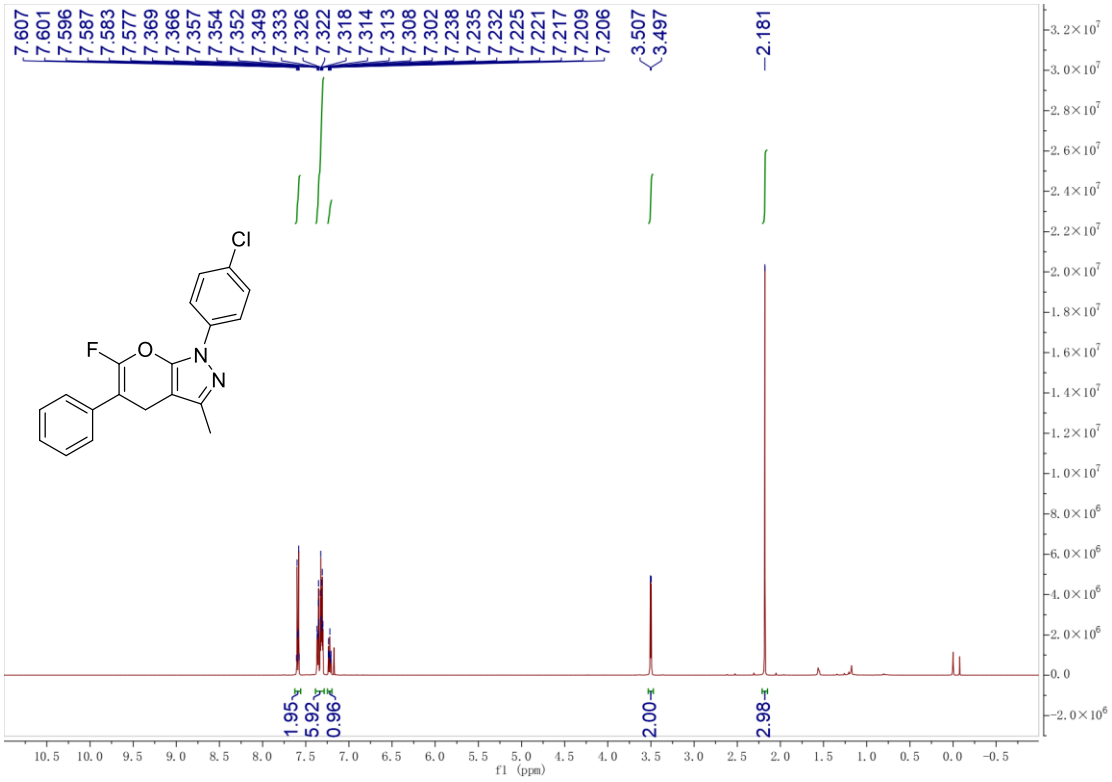
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3d



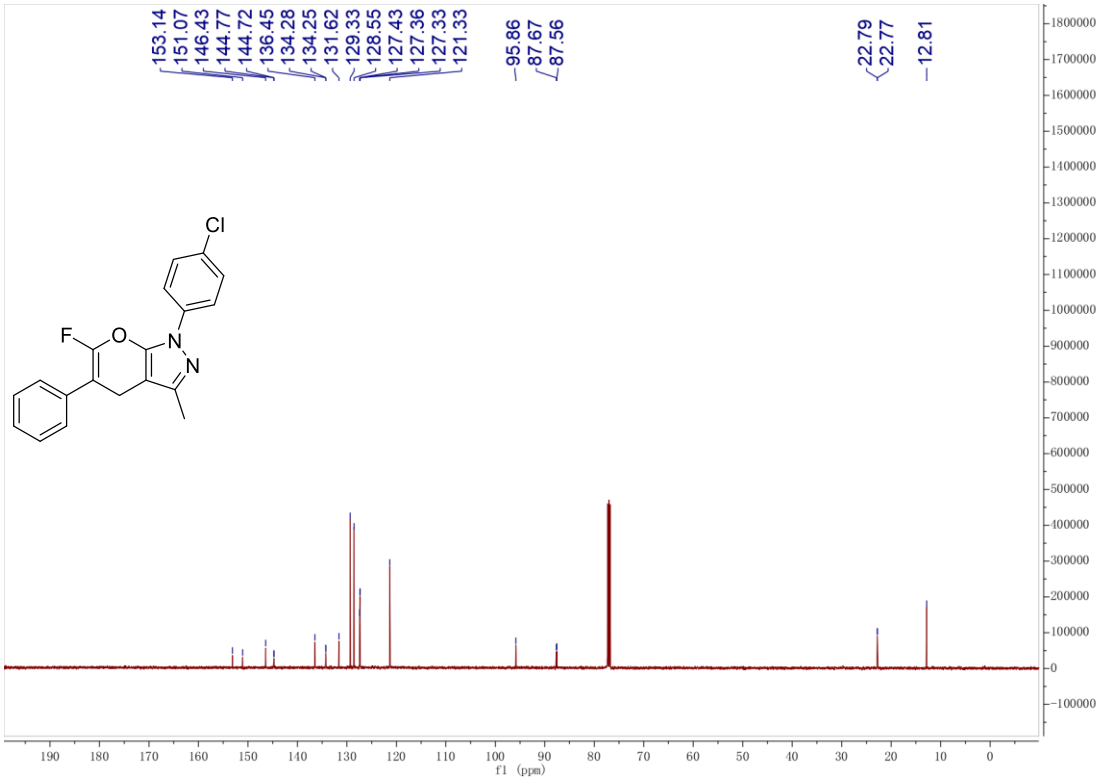
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3d



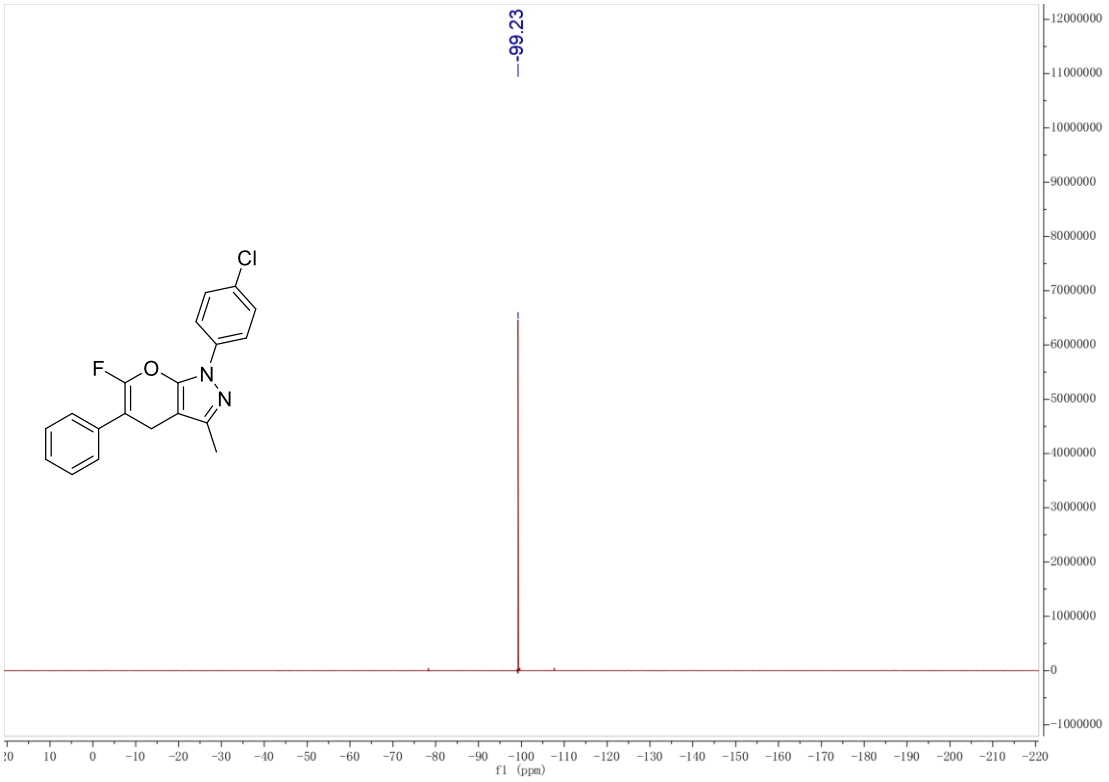
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3e



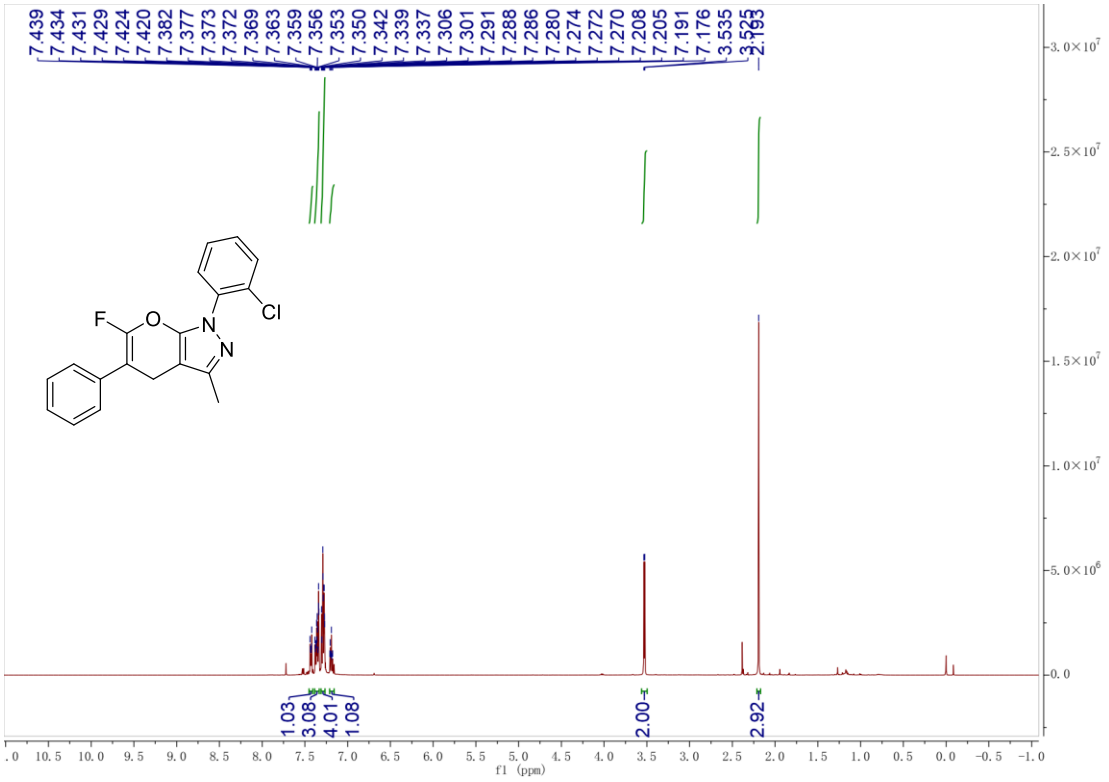
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3e



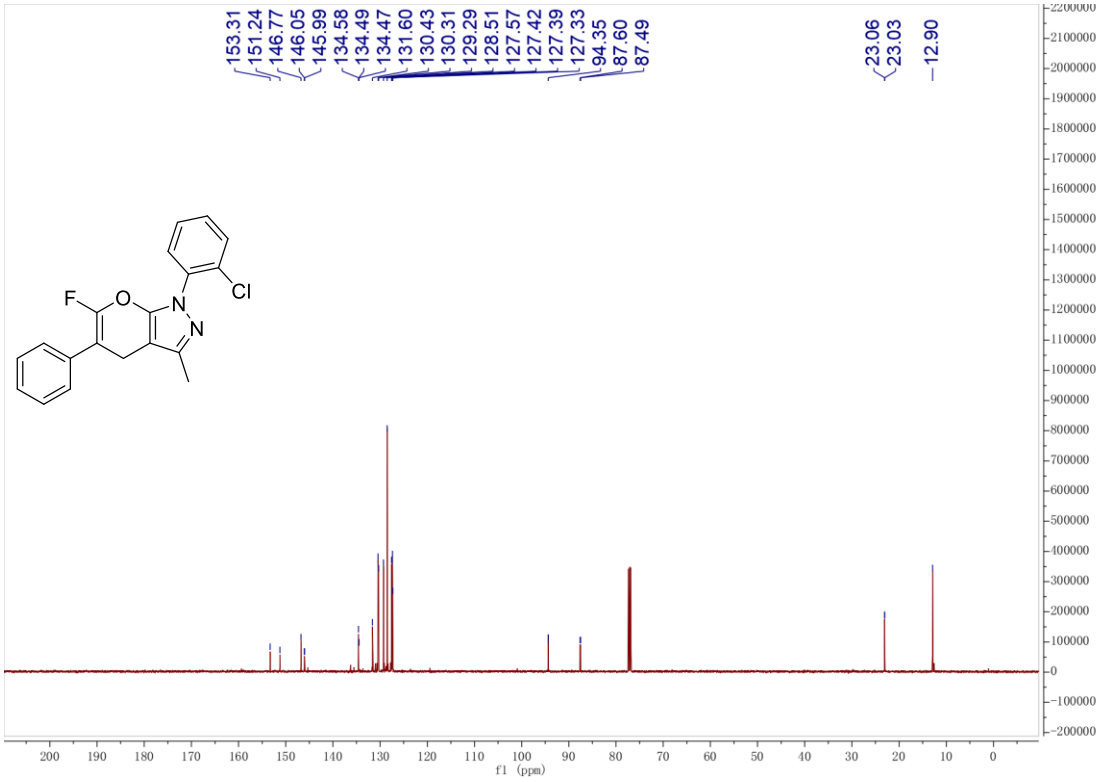
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3e



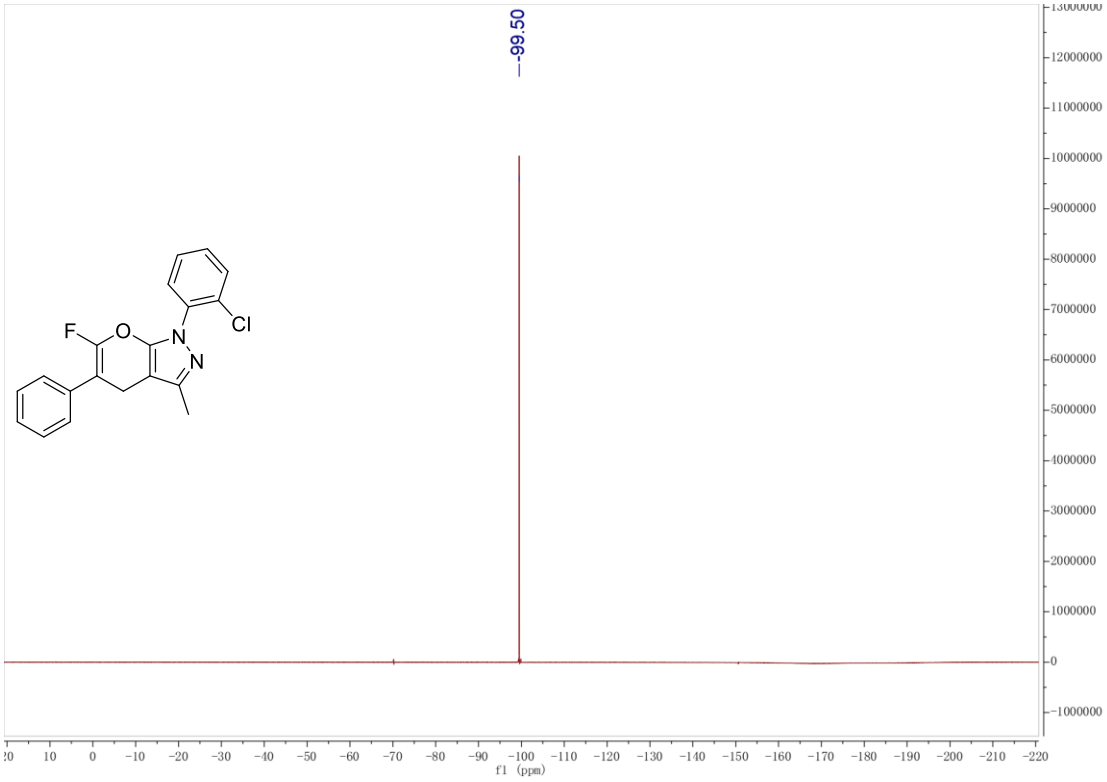
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3f



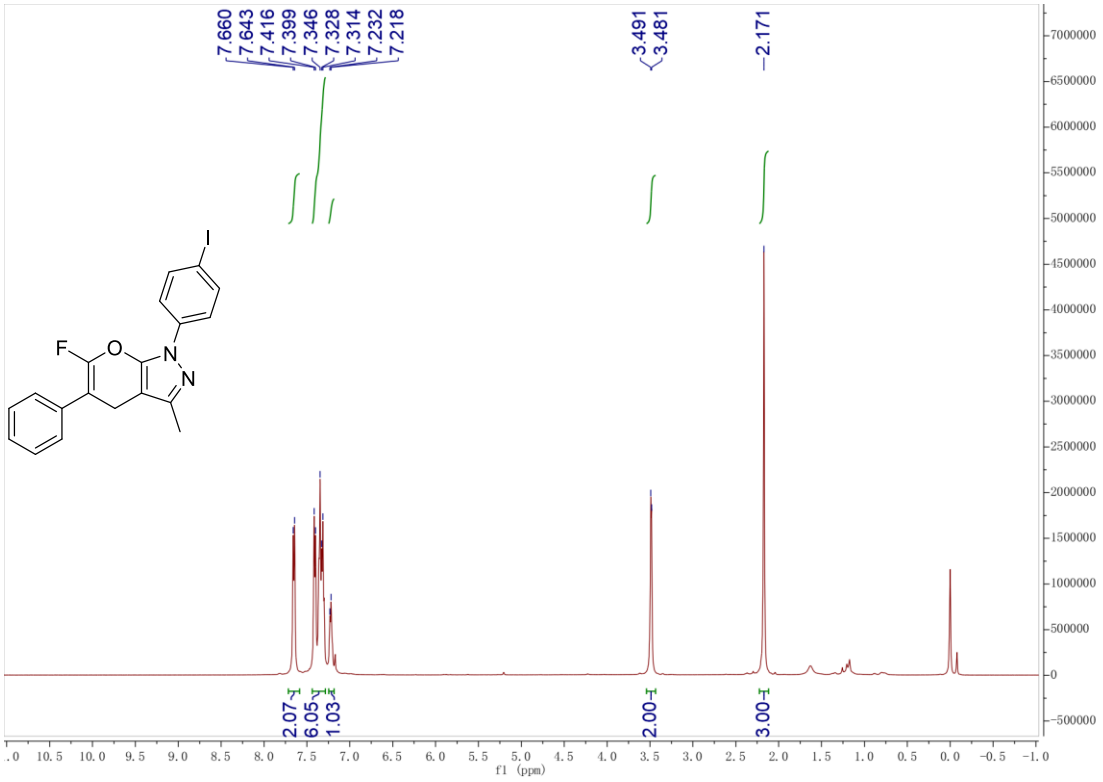
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3f



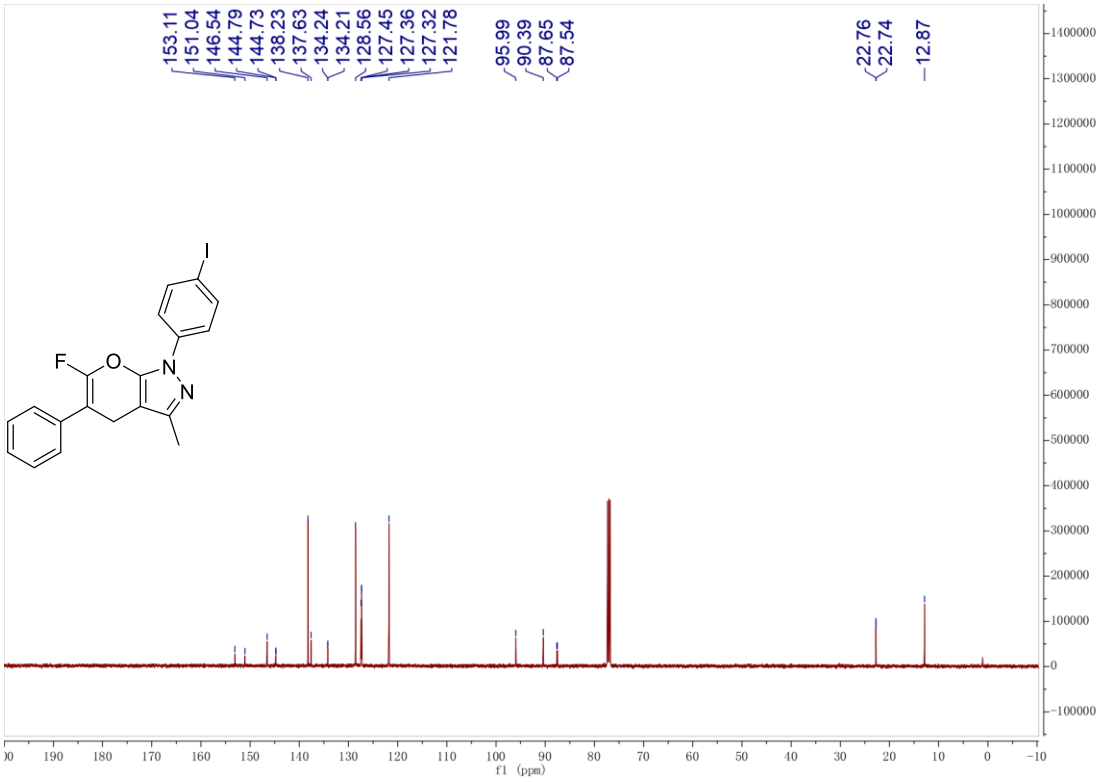
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3f



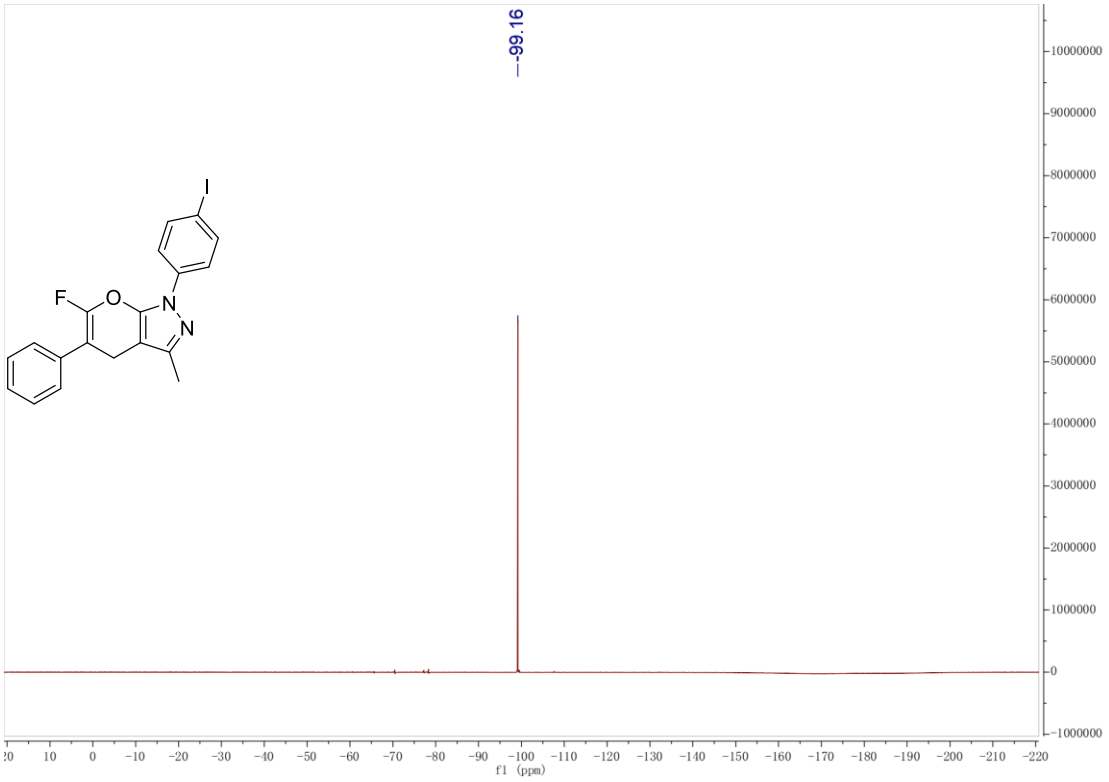
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3g



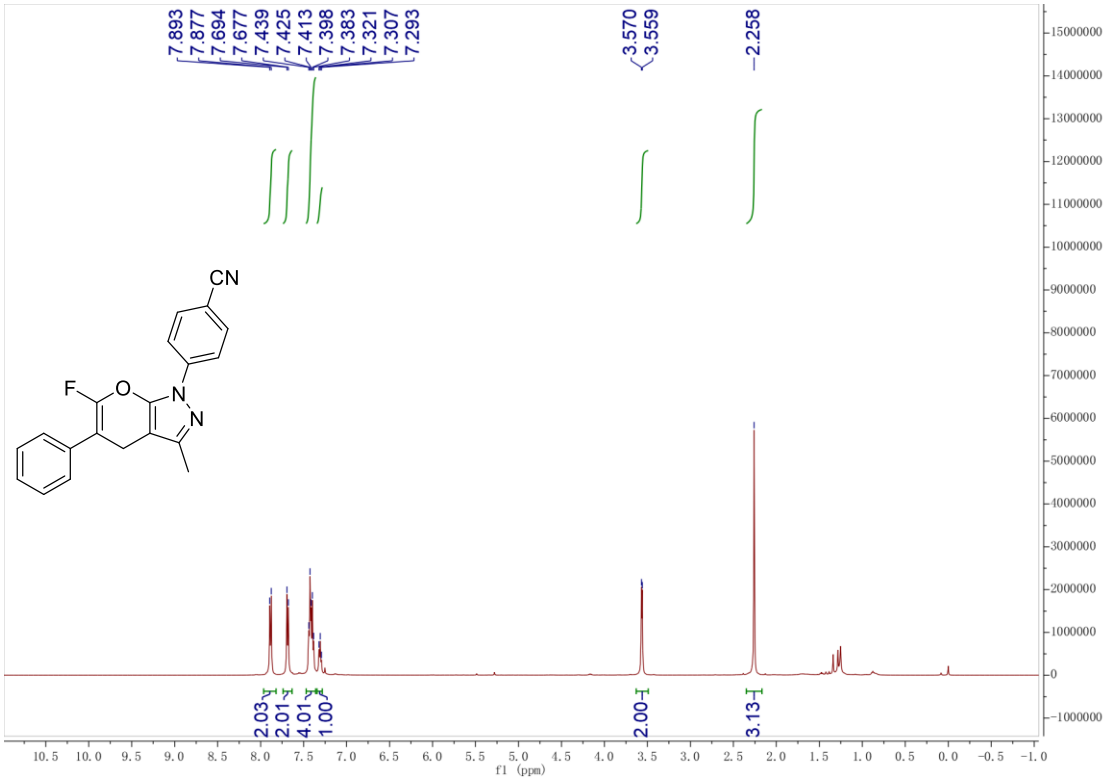
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3g



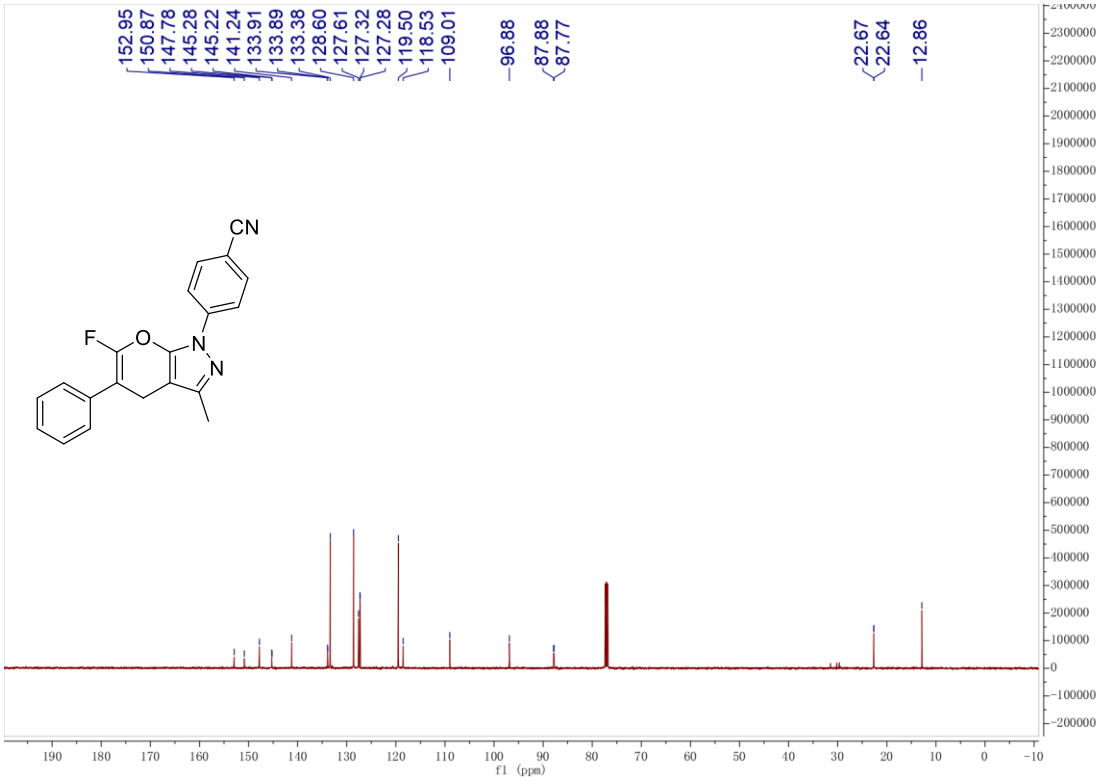
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3g



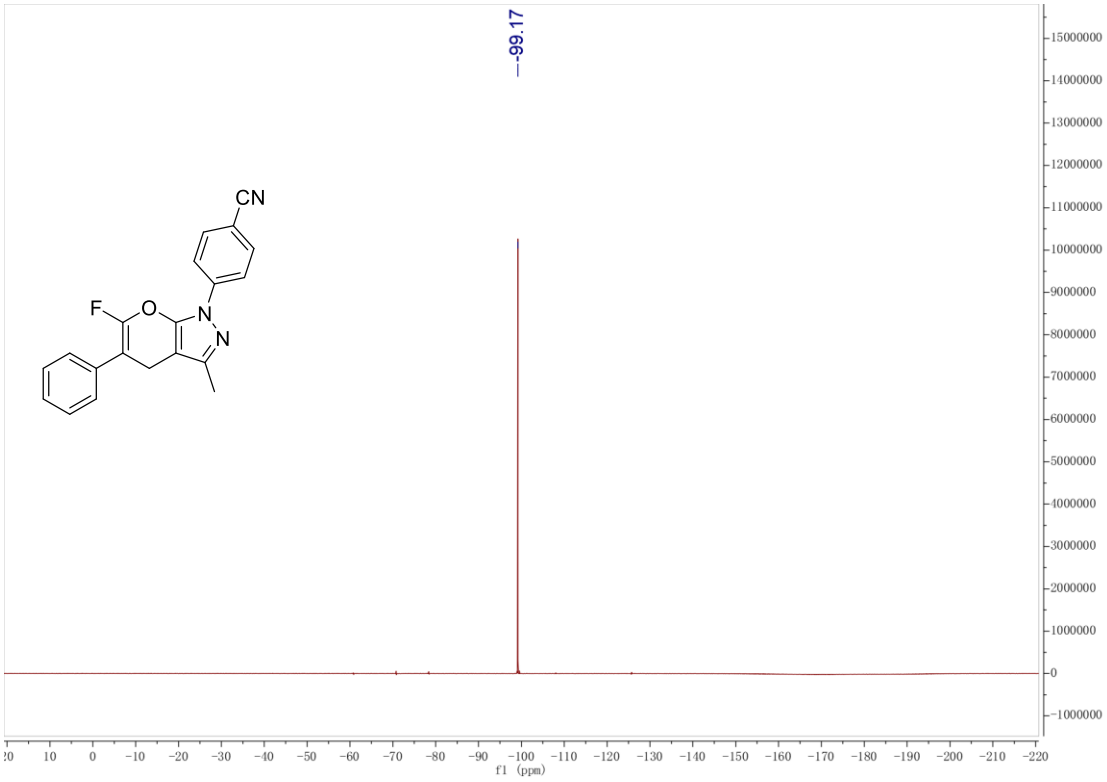
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3h



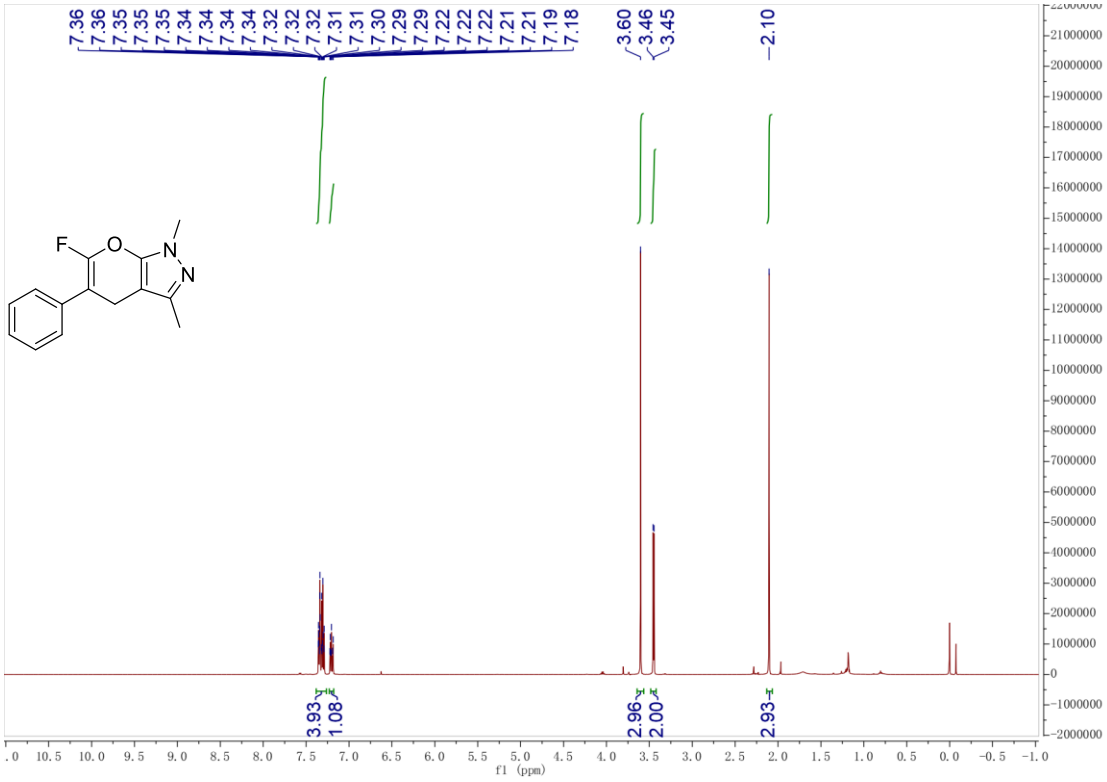
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3h



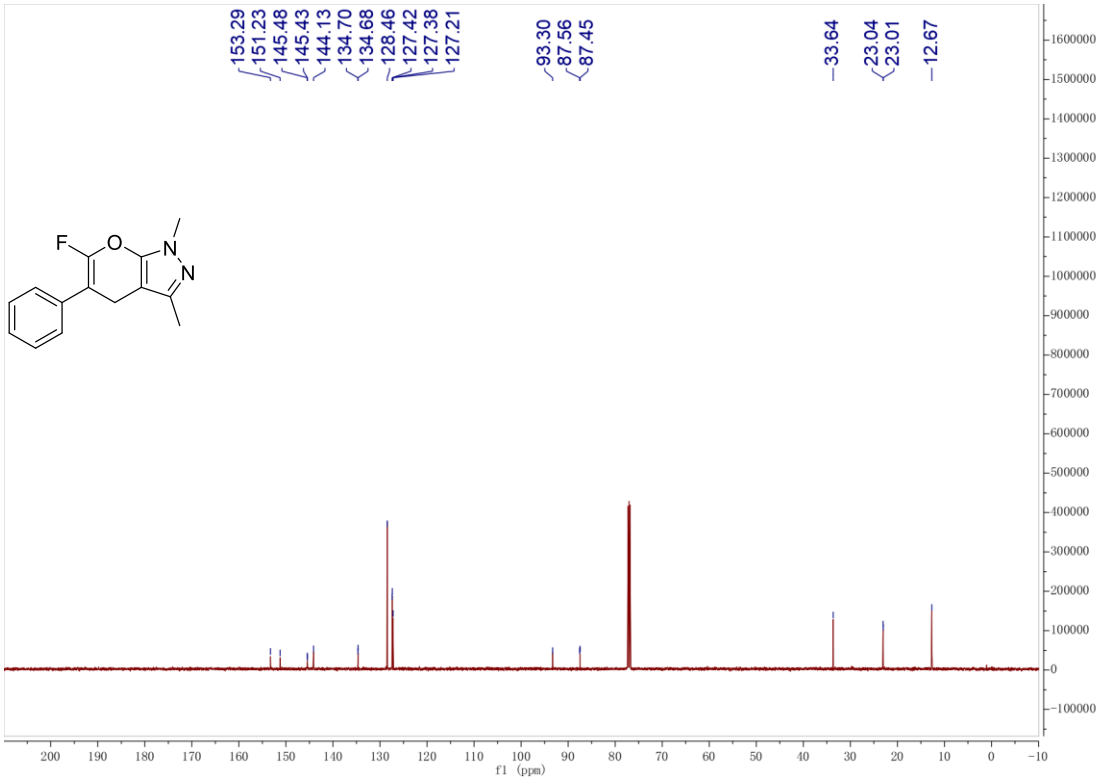
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3h



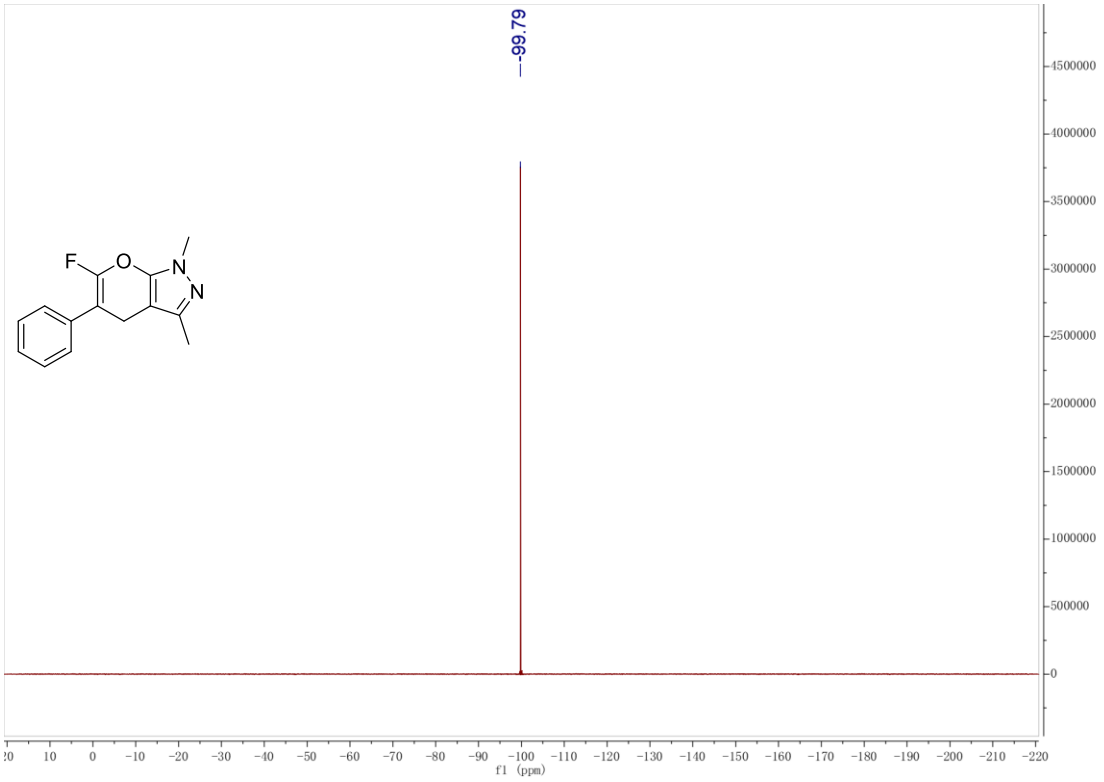
^{1}H NMR Spectrum (500 MHz, $CDCl_3$) for 3i



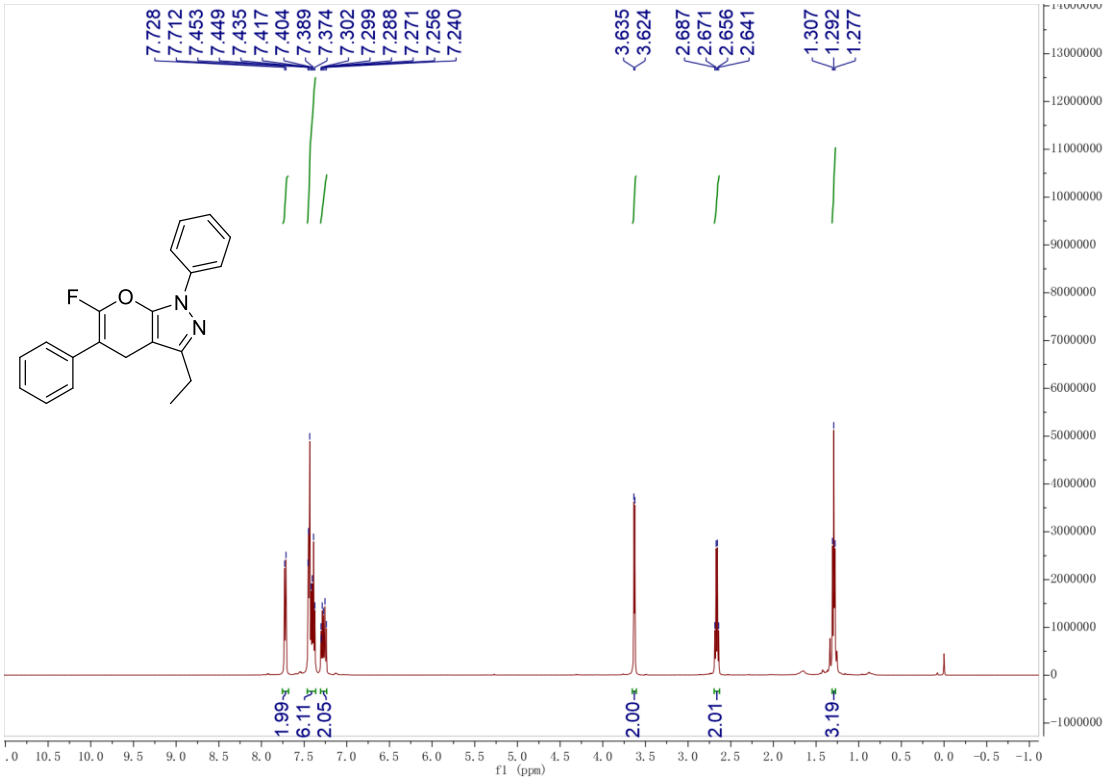
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3i



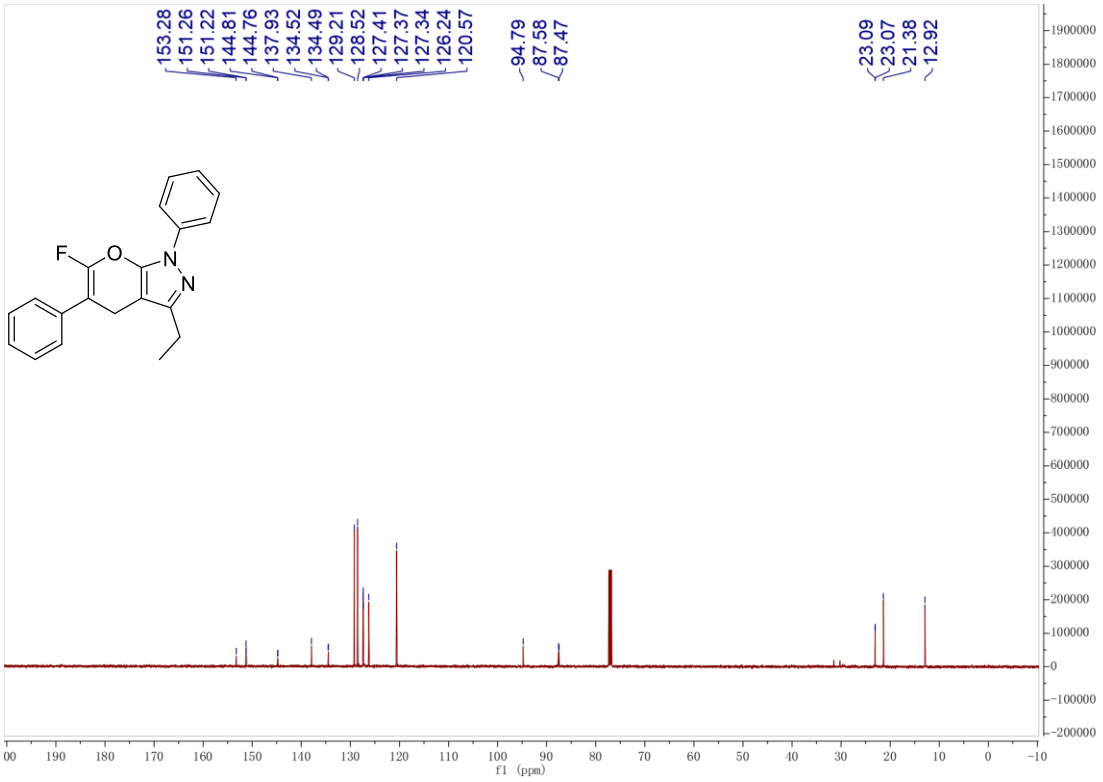
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3i



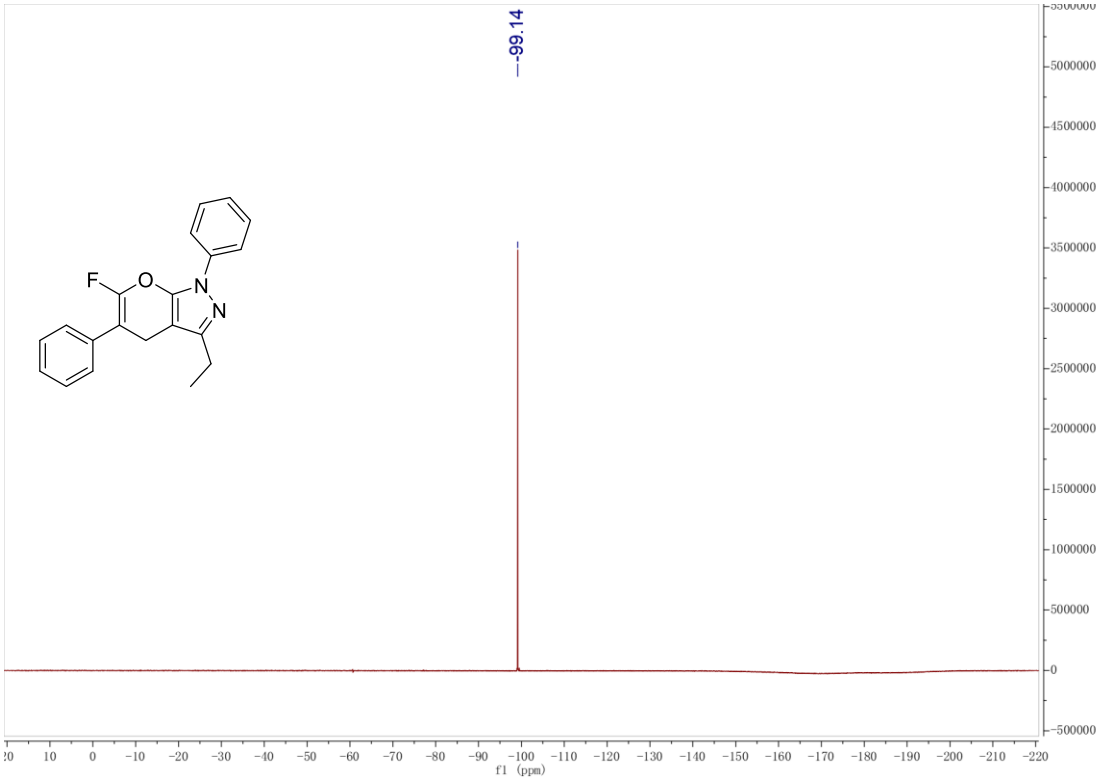
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3j



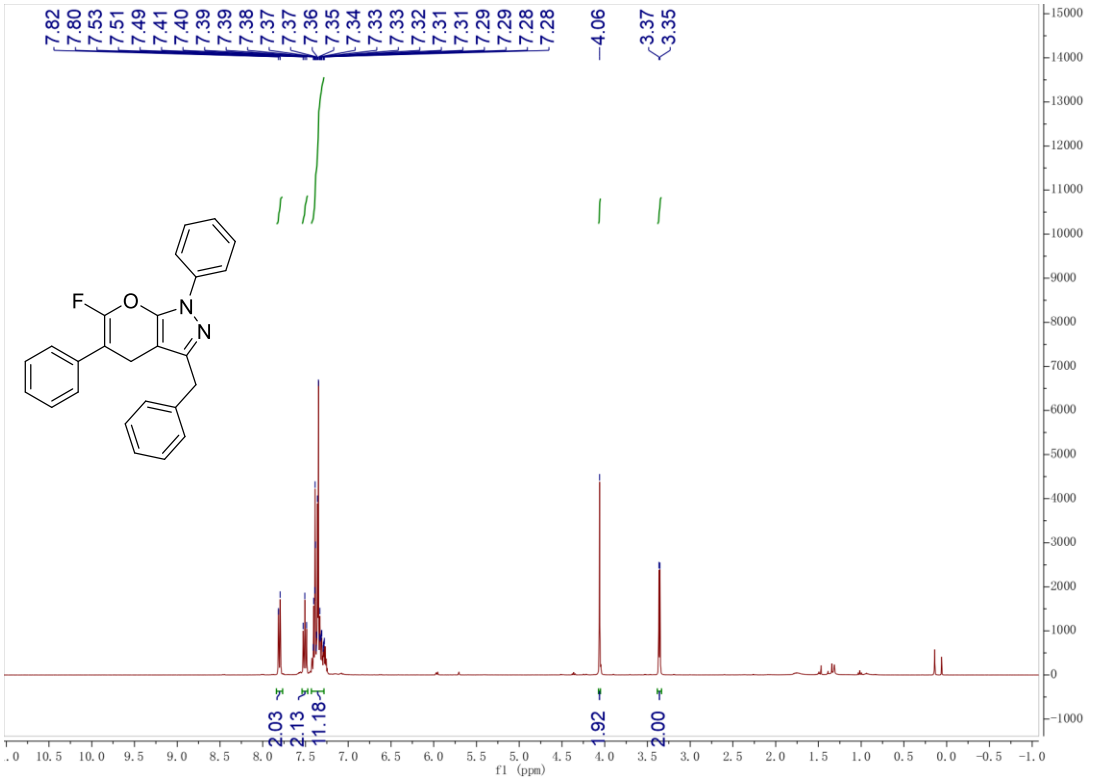
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3j



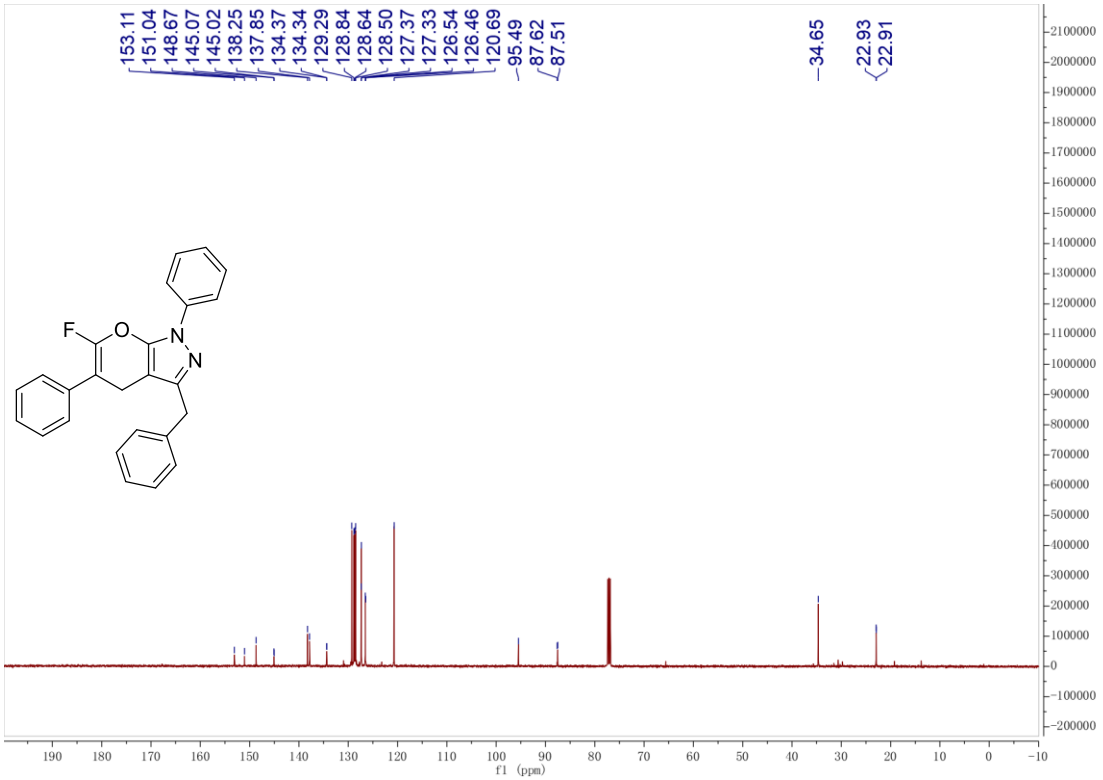
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3j



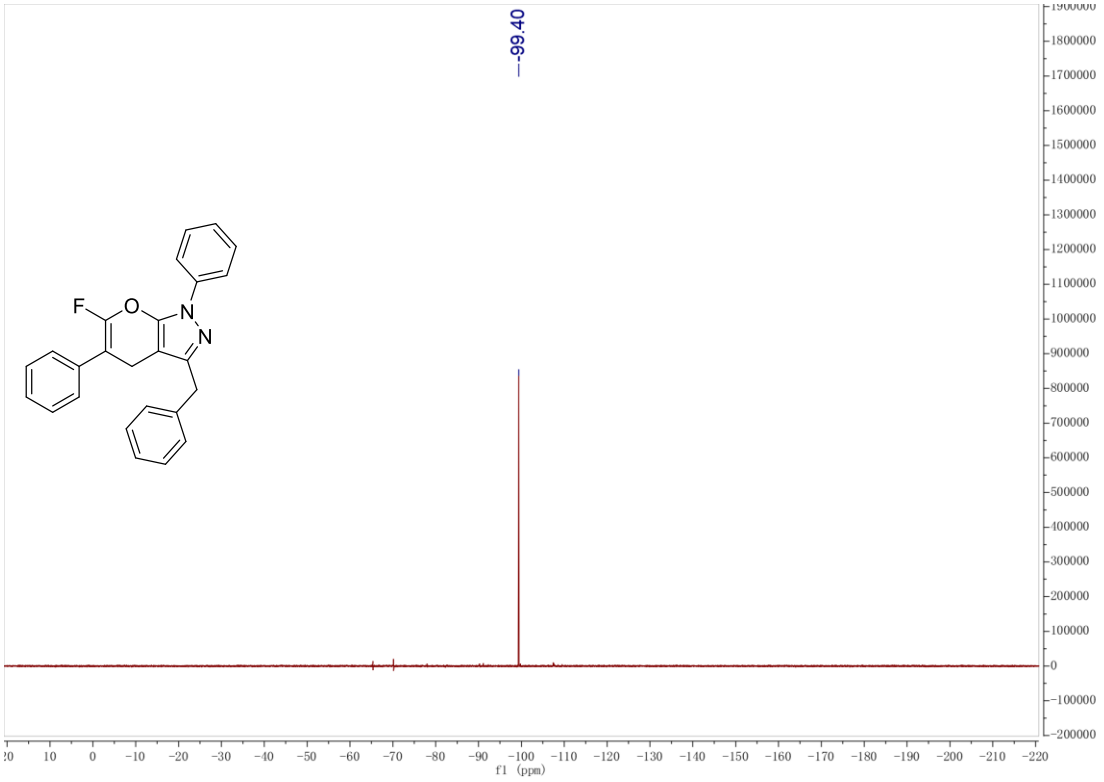
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum for 3k



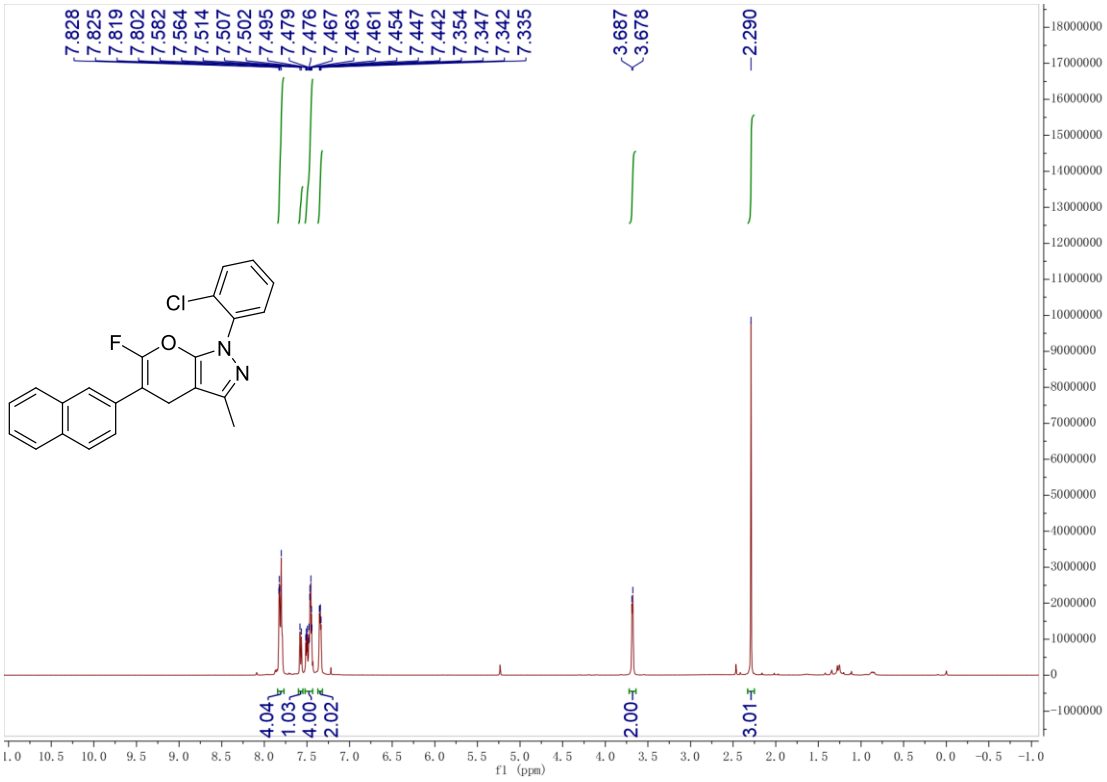
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3k



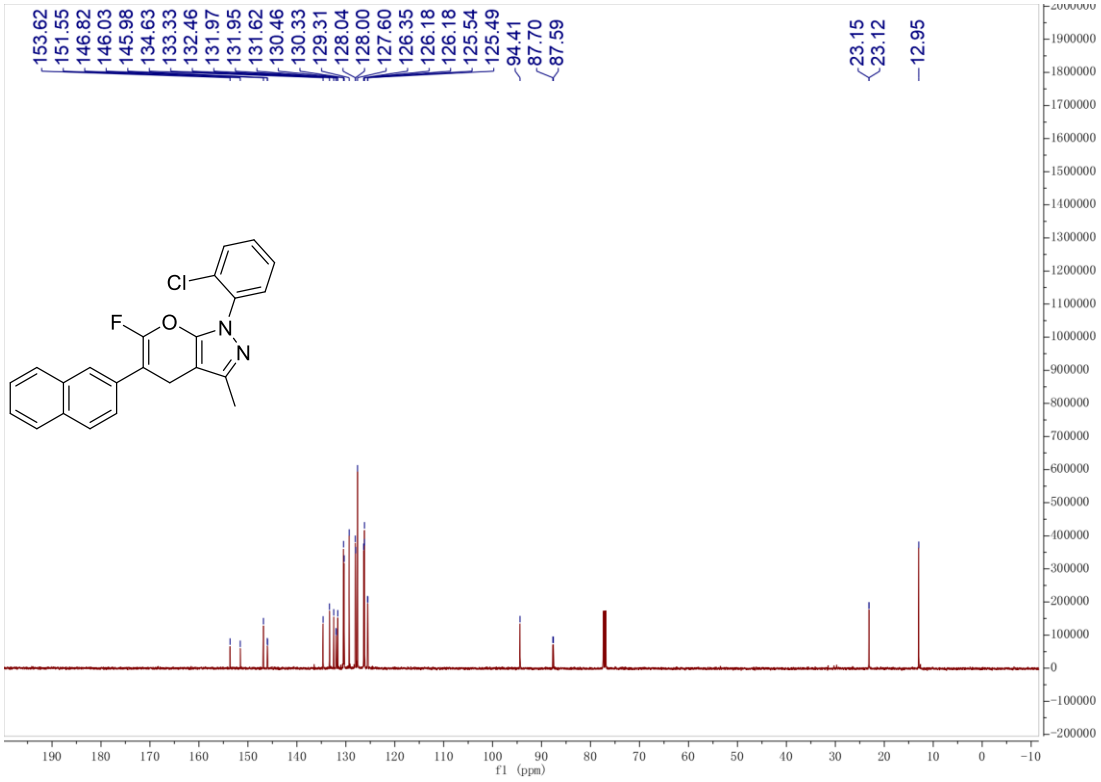
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3k



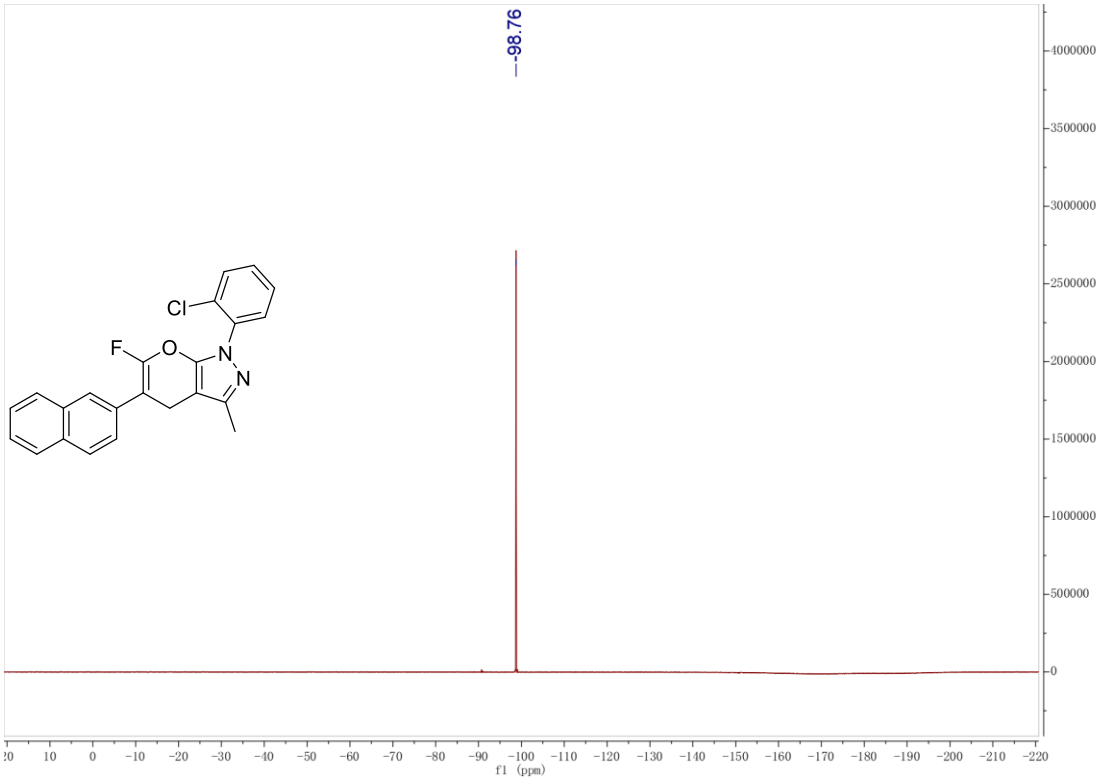
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3n



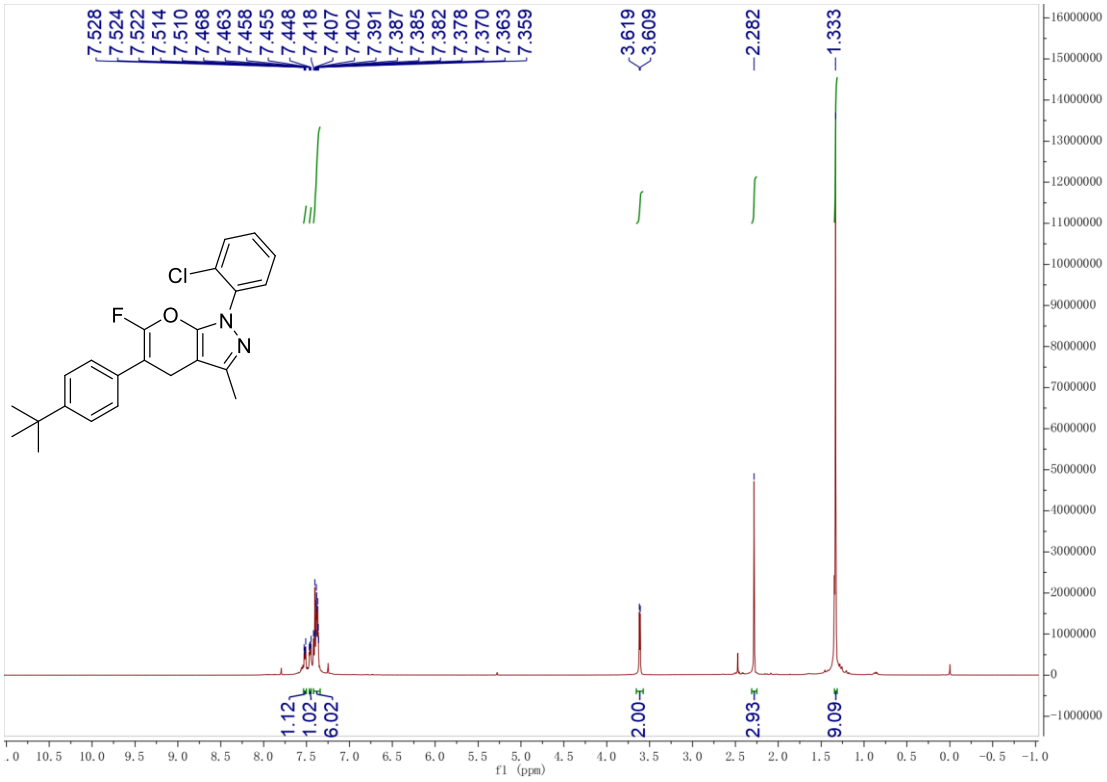
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3n



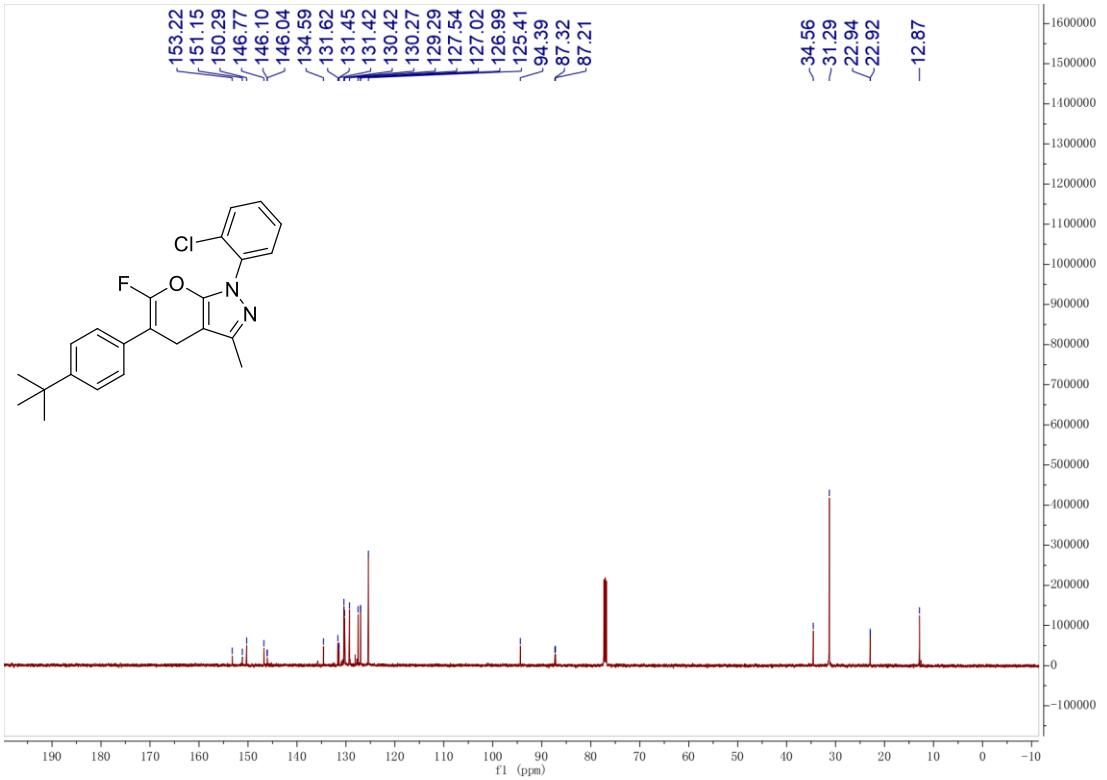
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3n



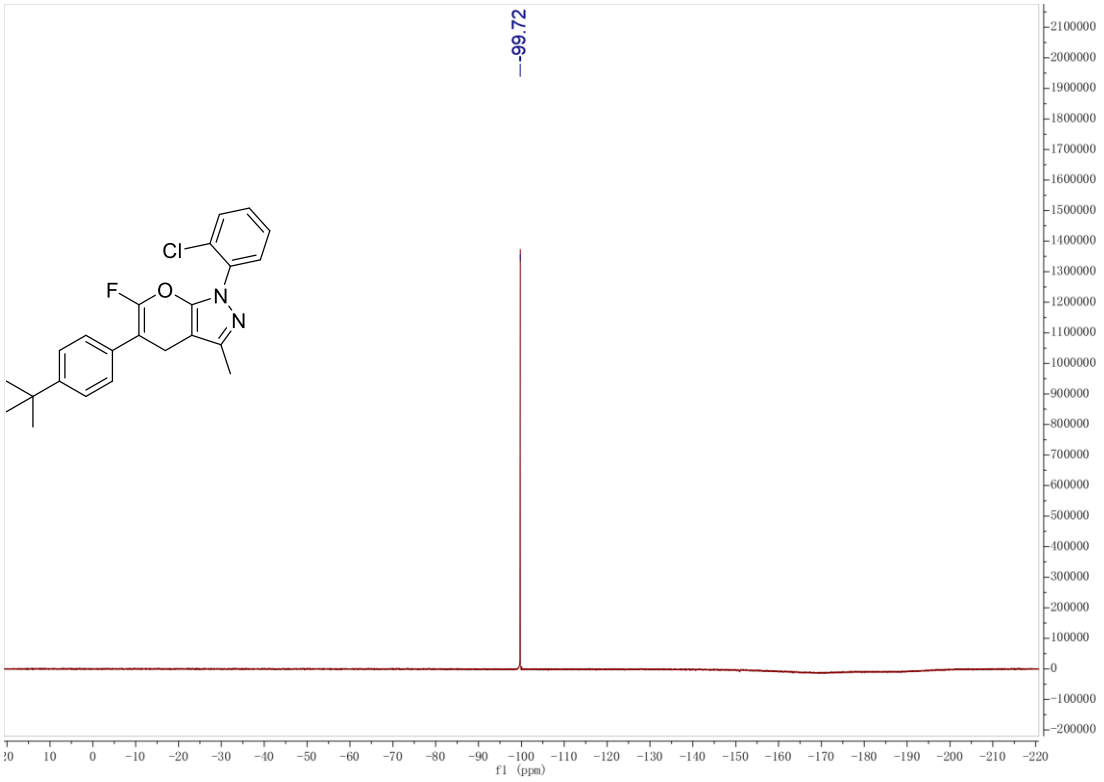
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3o



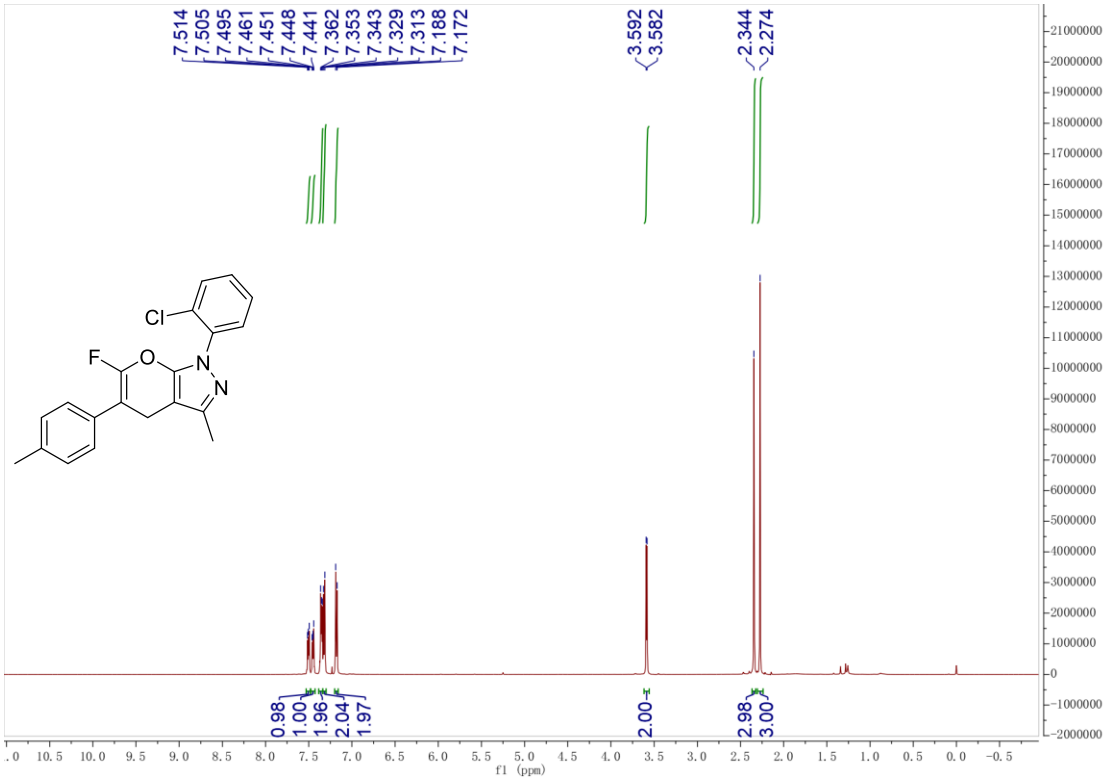
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3o



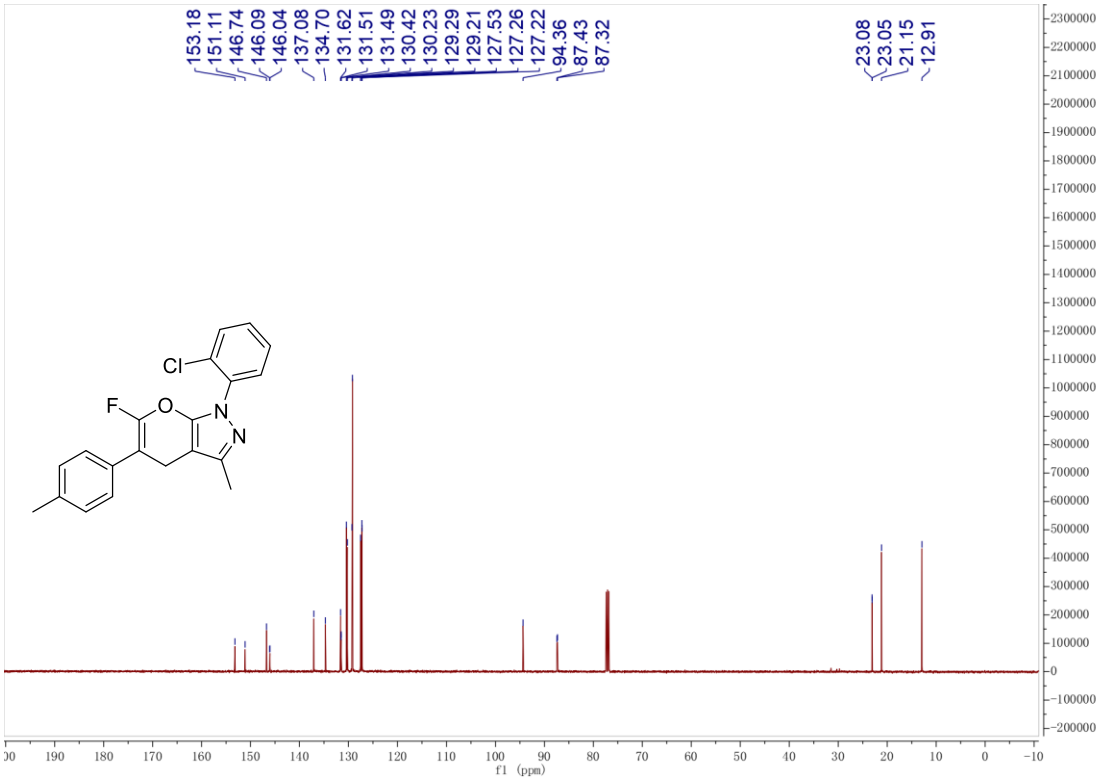
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3o



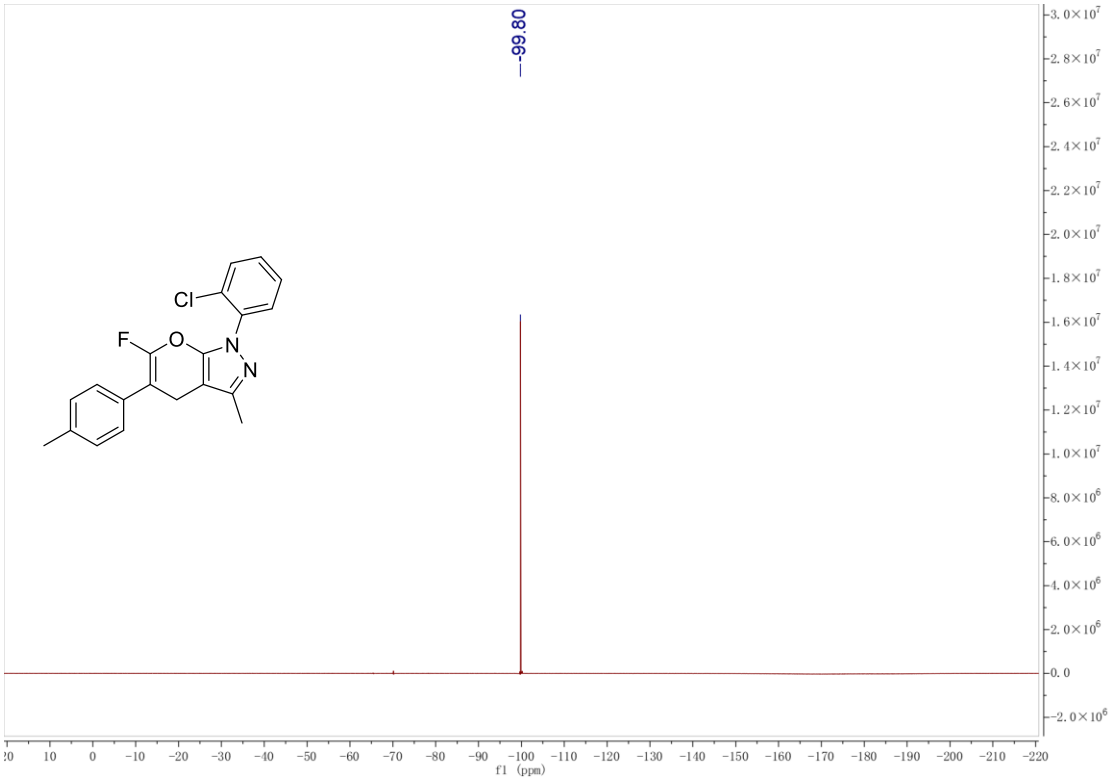
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3p



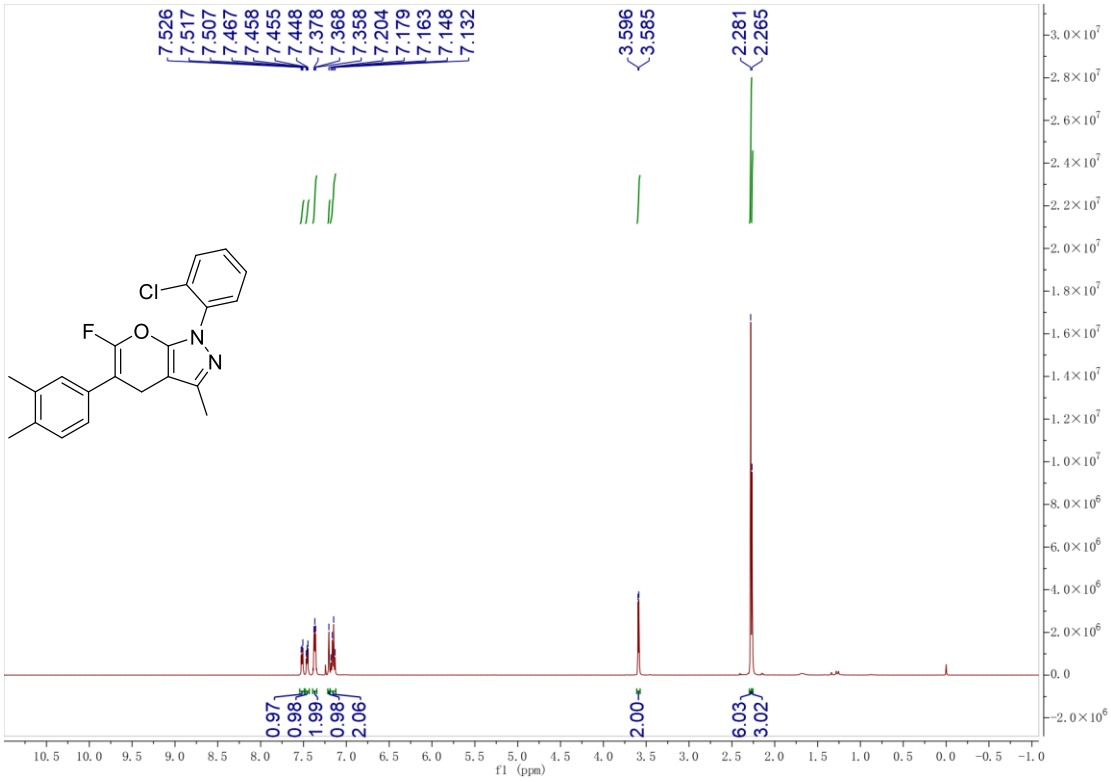
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3p



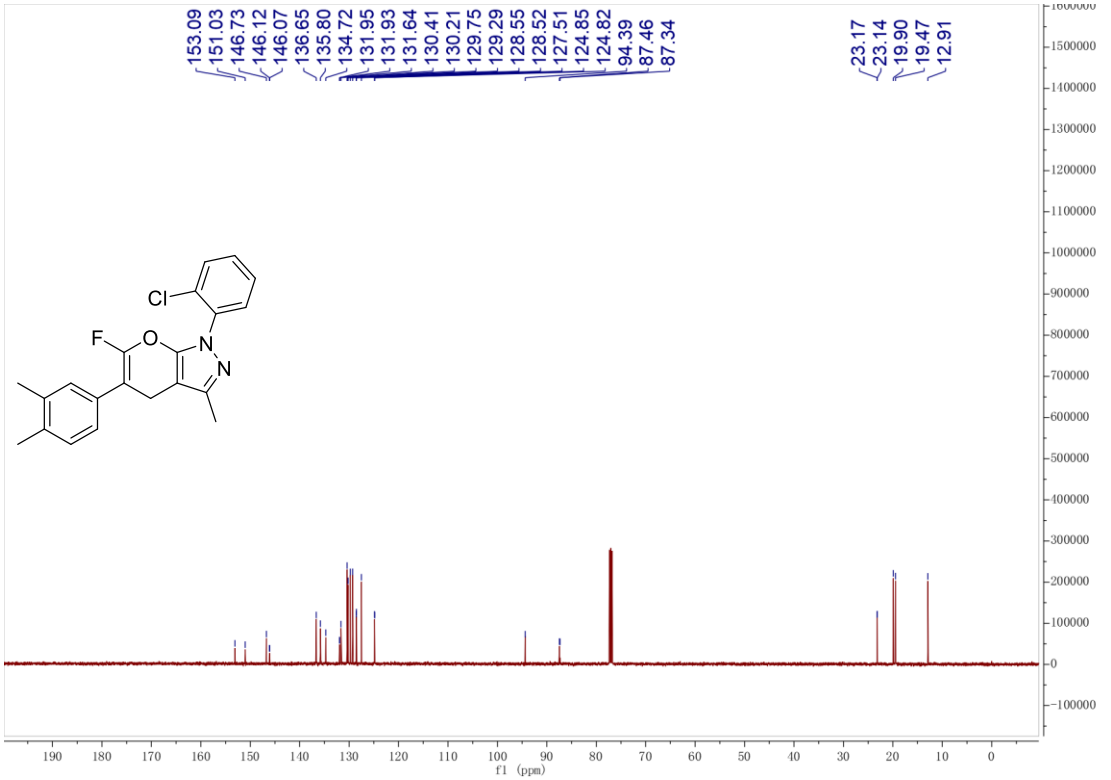
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3p



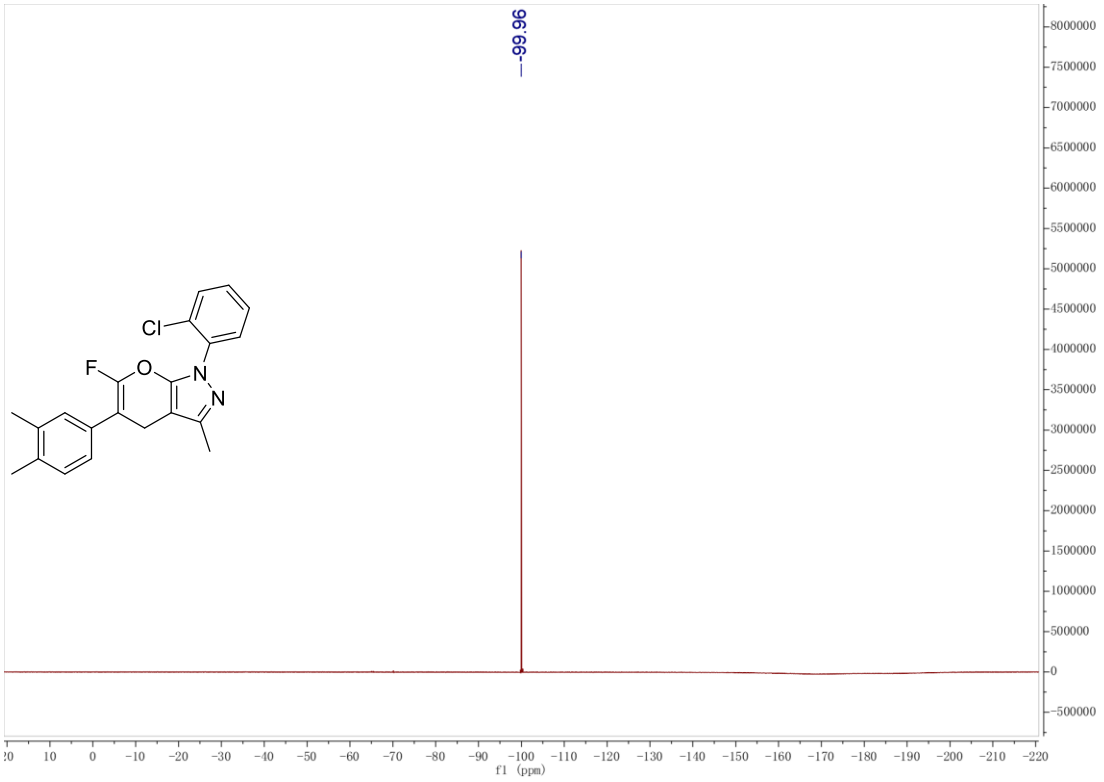
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3q



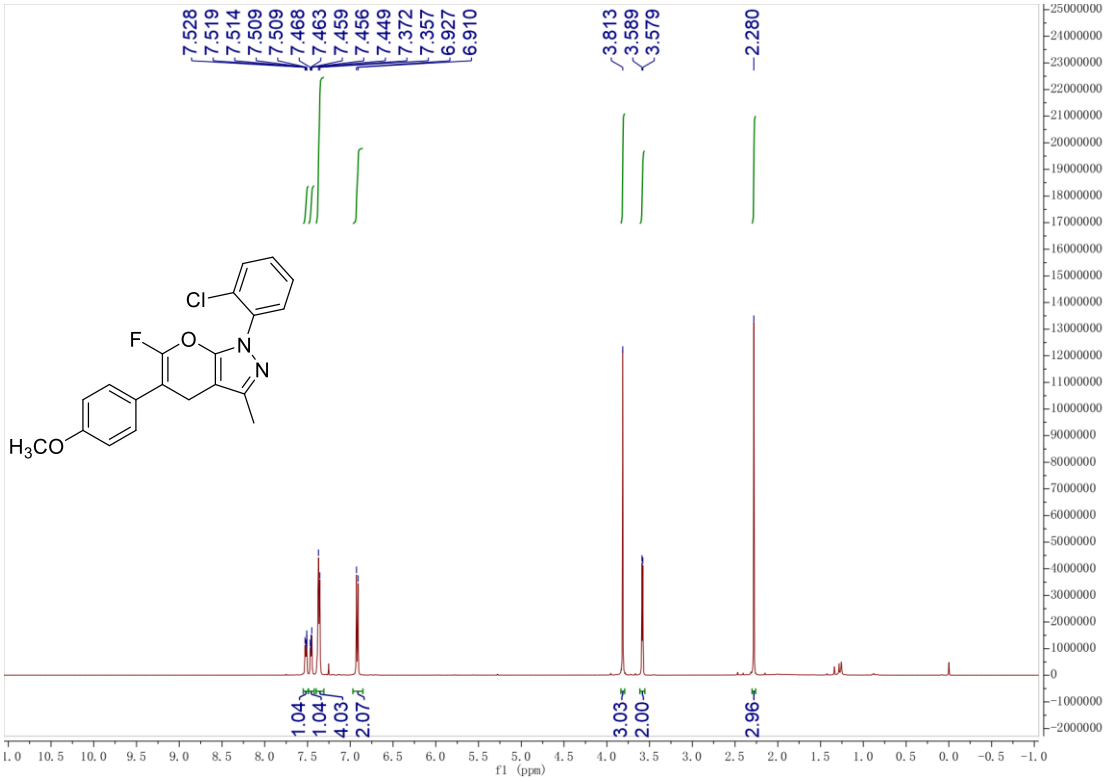
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3q



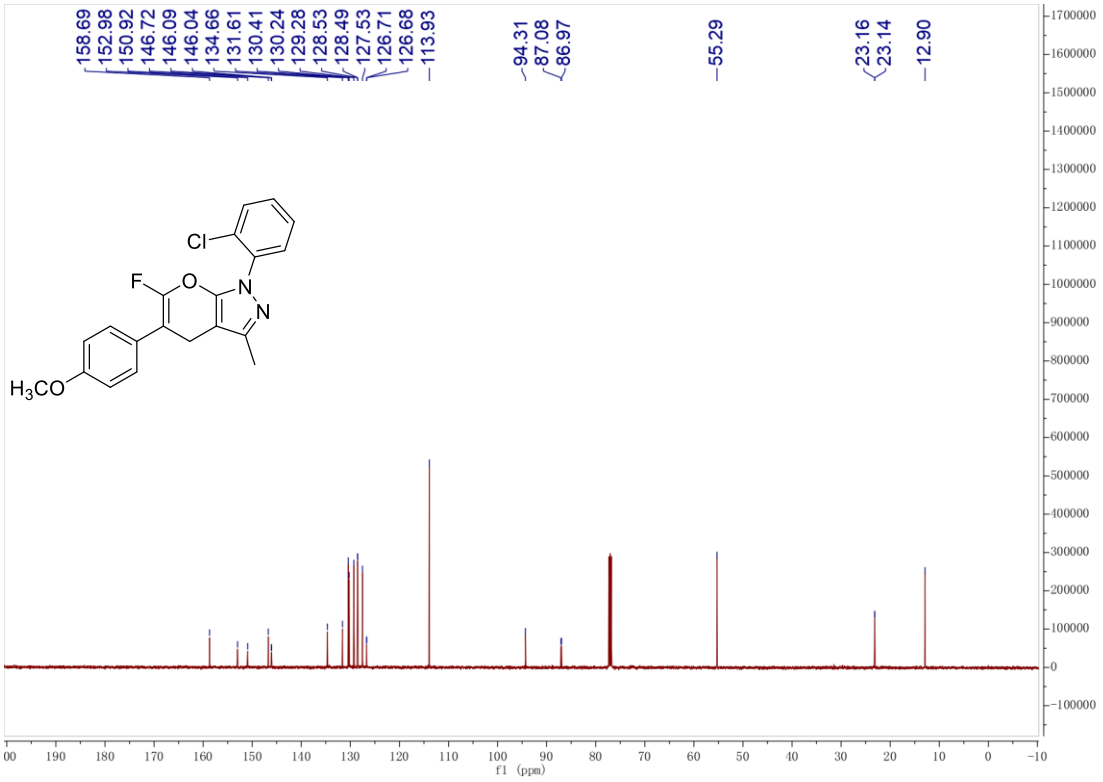
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3q



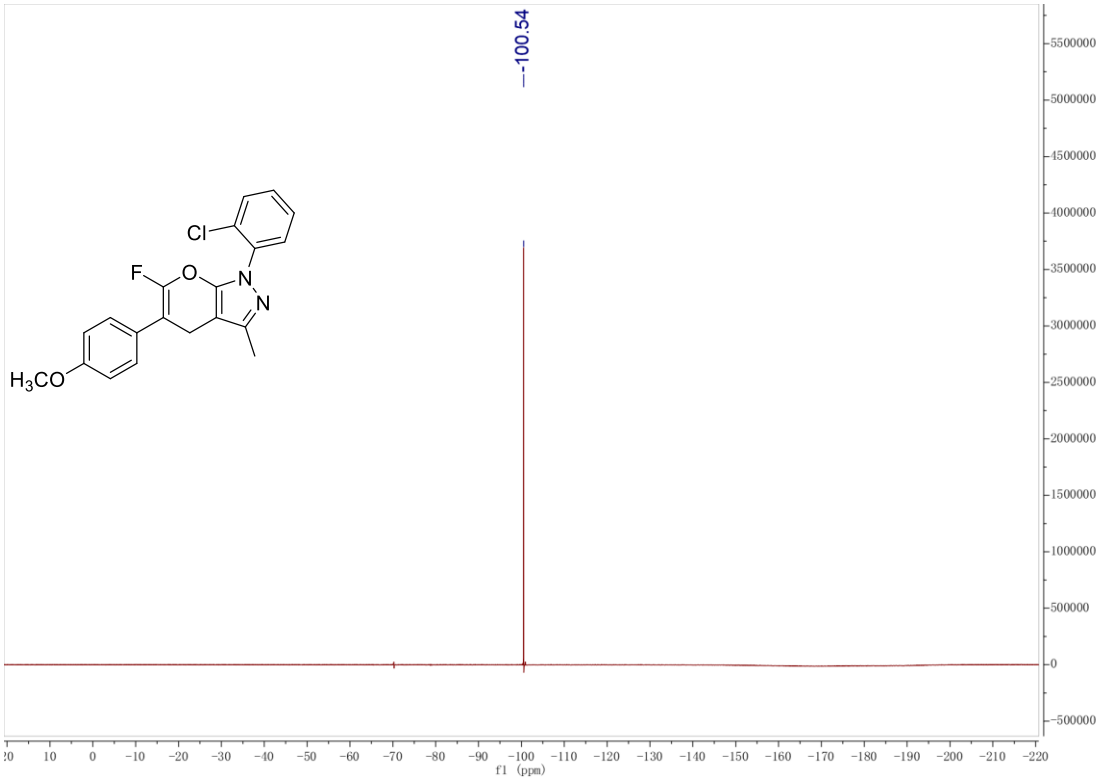
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3r



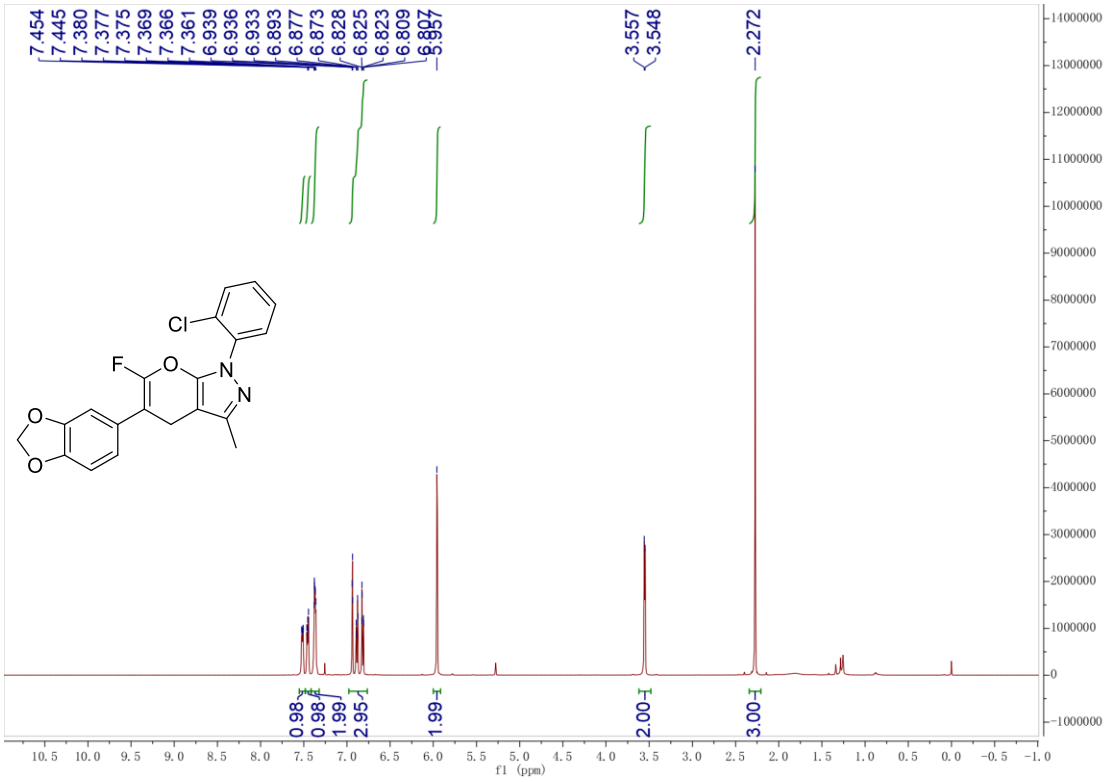
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3r



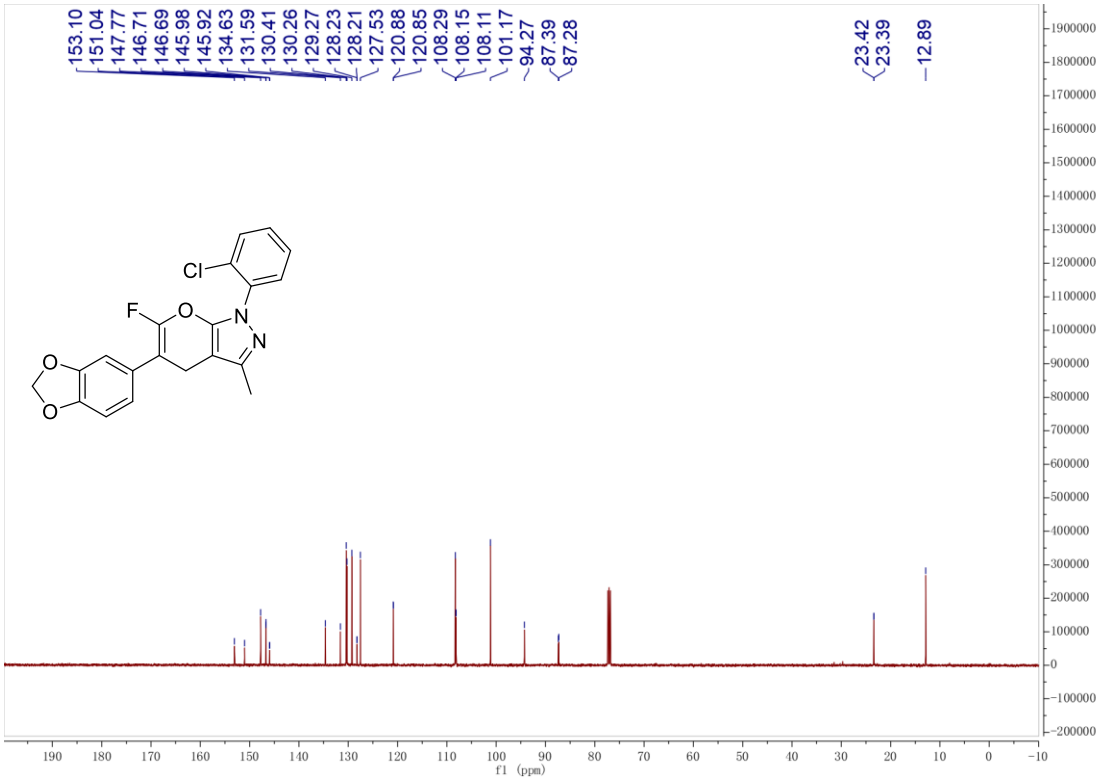
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3r



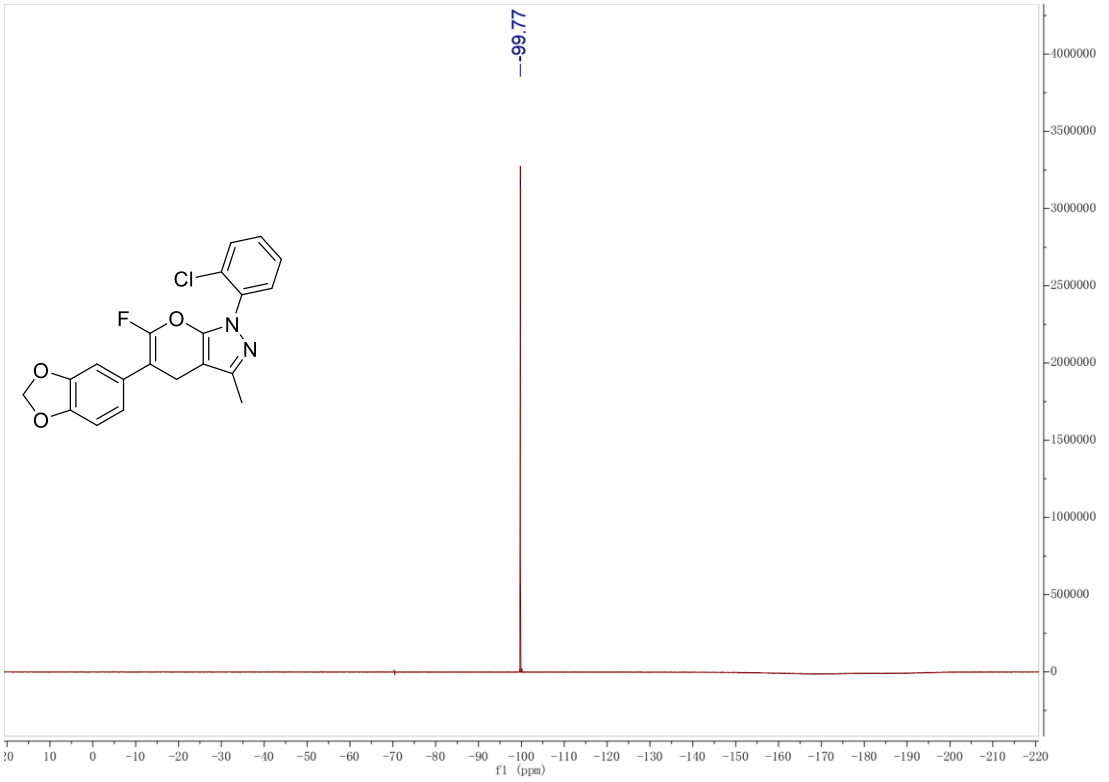
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3s



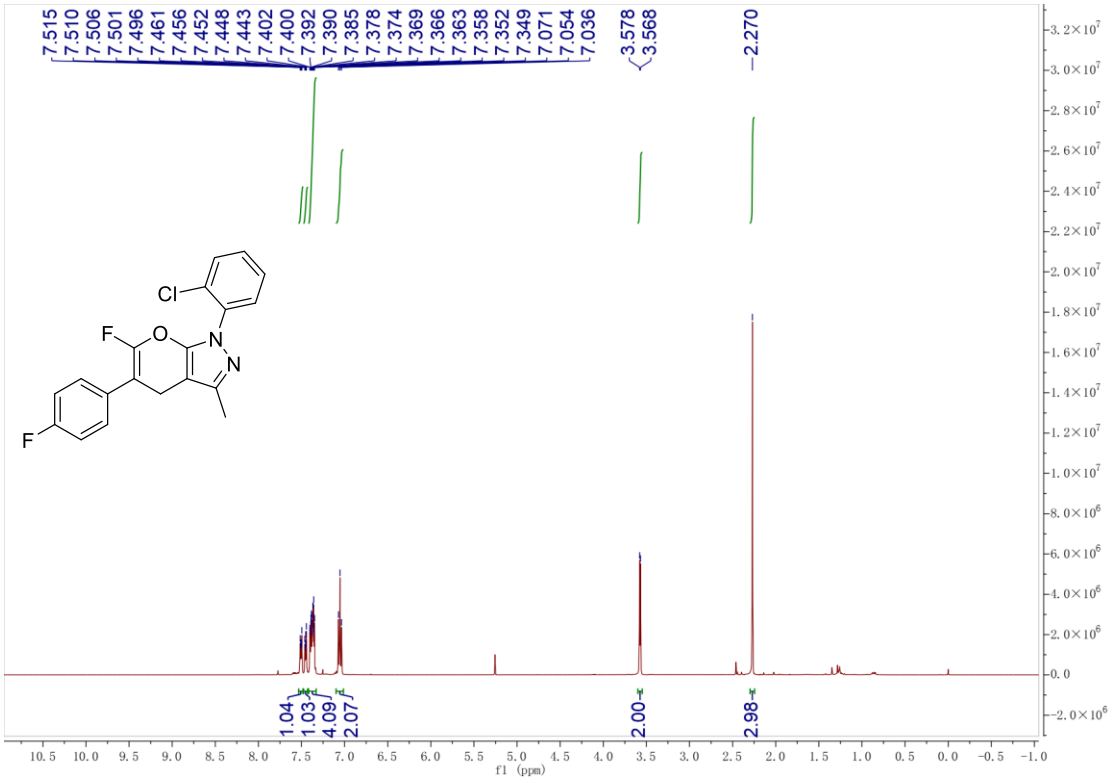
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3s



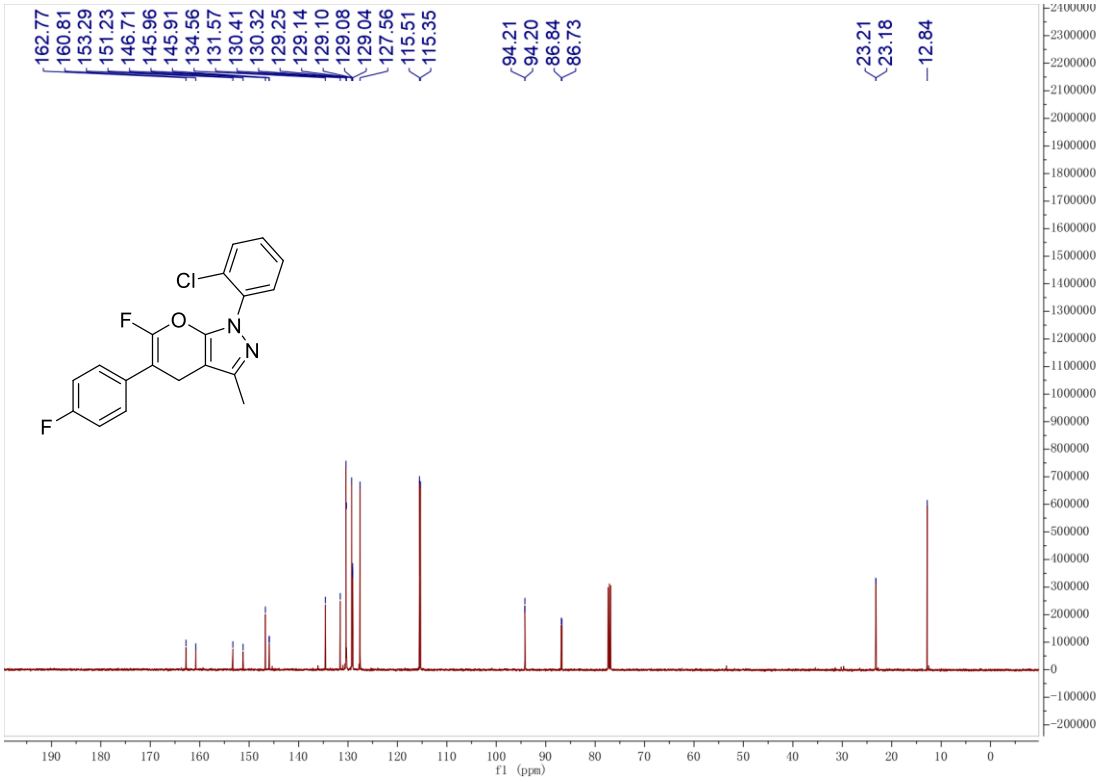
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3s



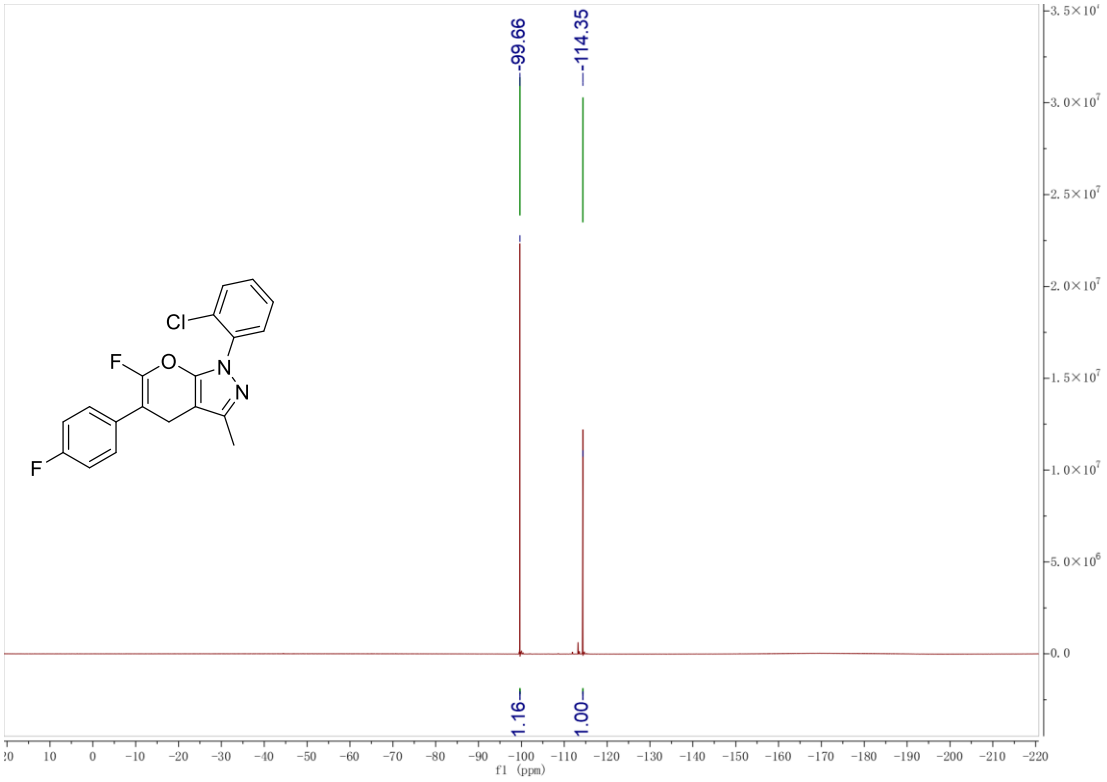
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3t



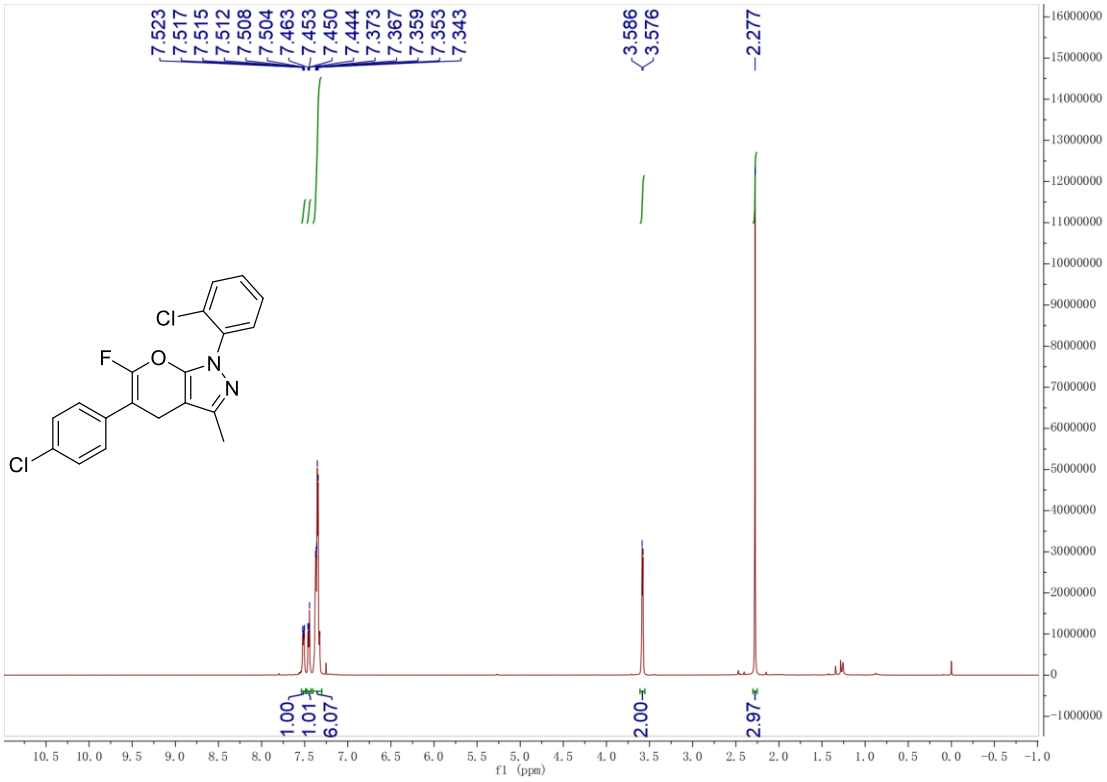
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3t



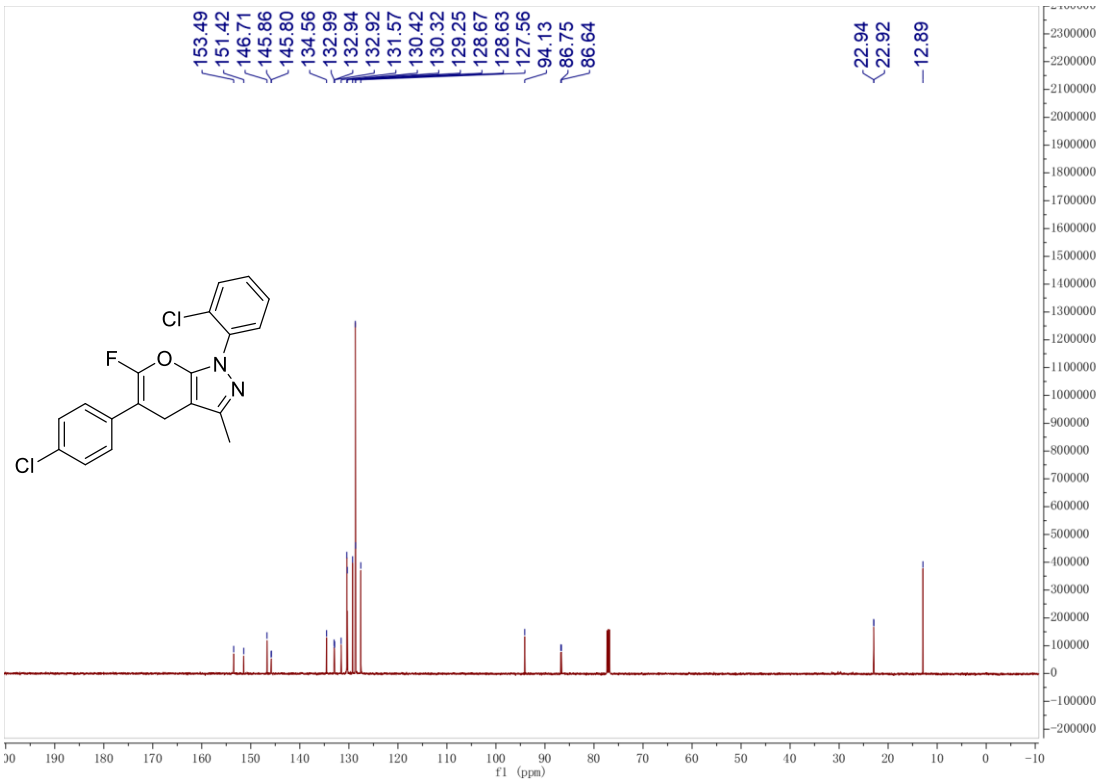
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3t



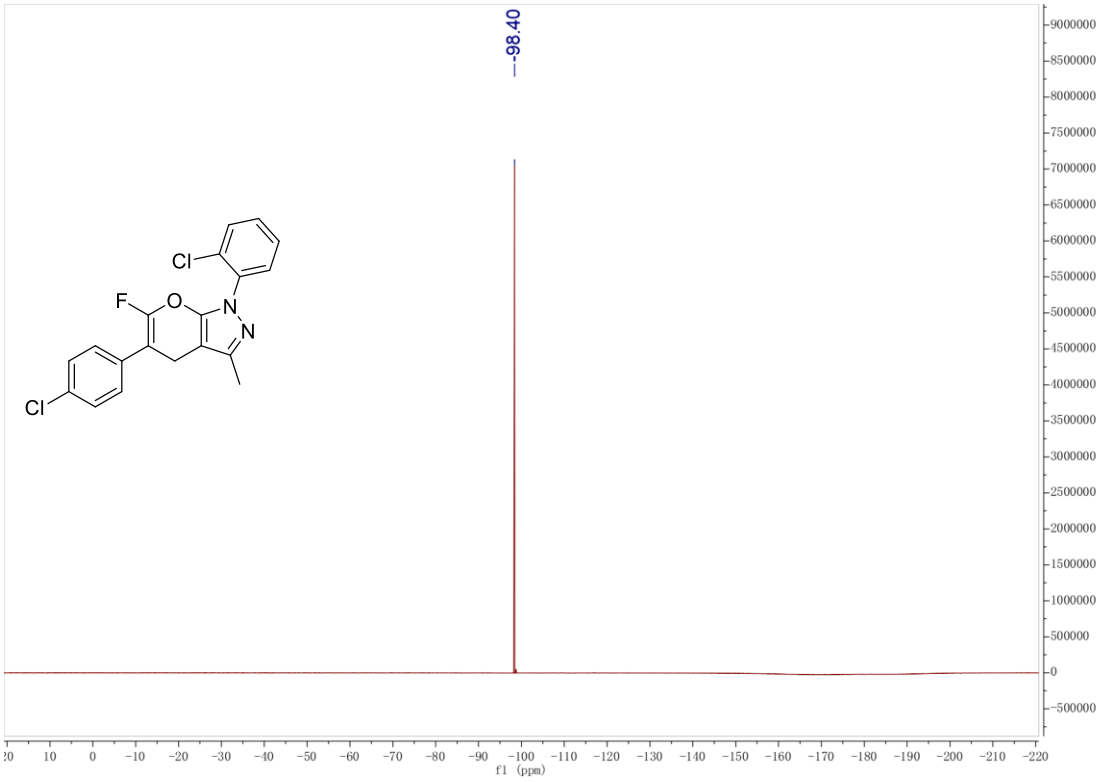
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3u



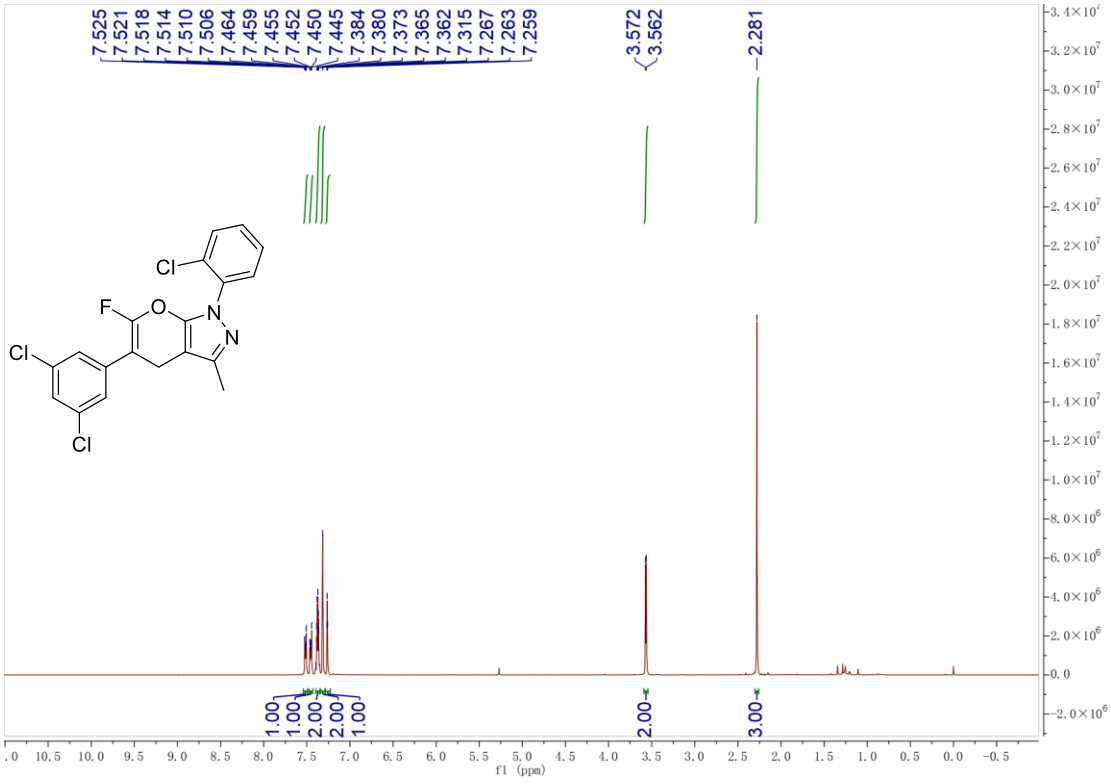
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3u



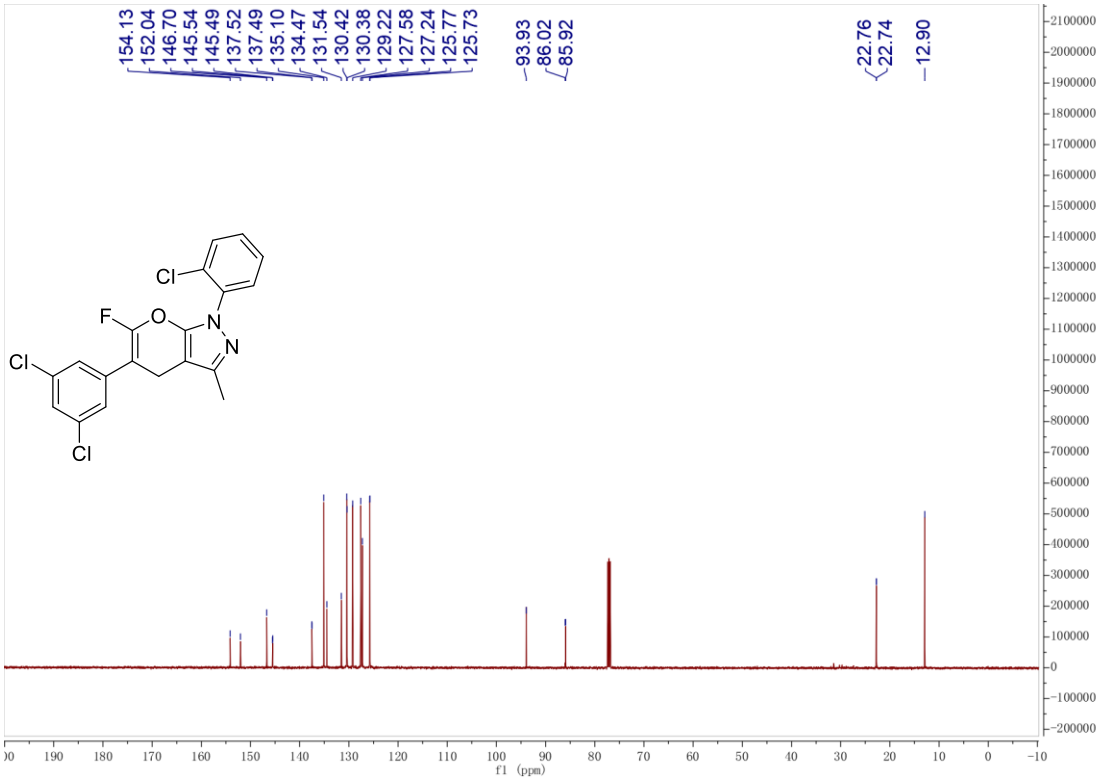
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3u



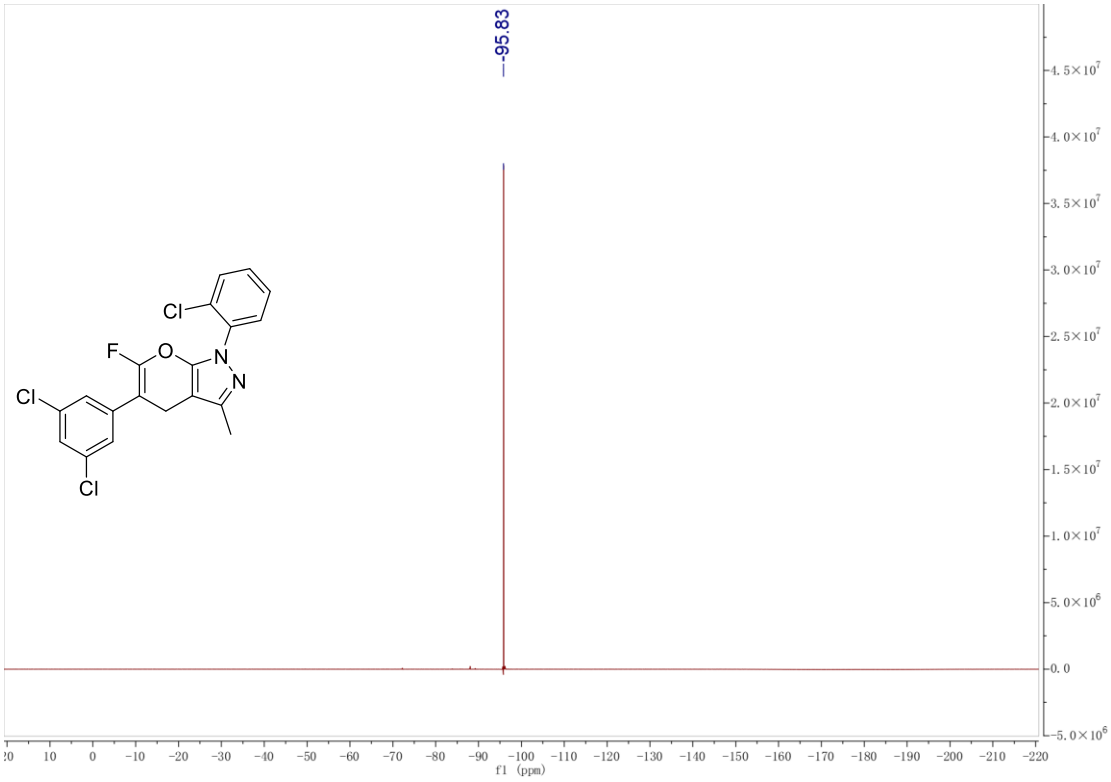
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3v



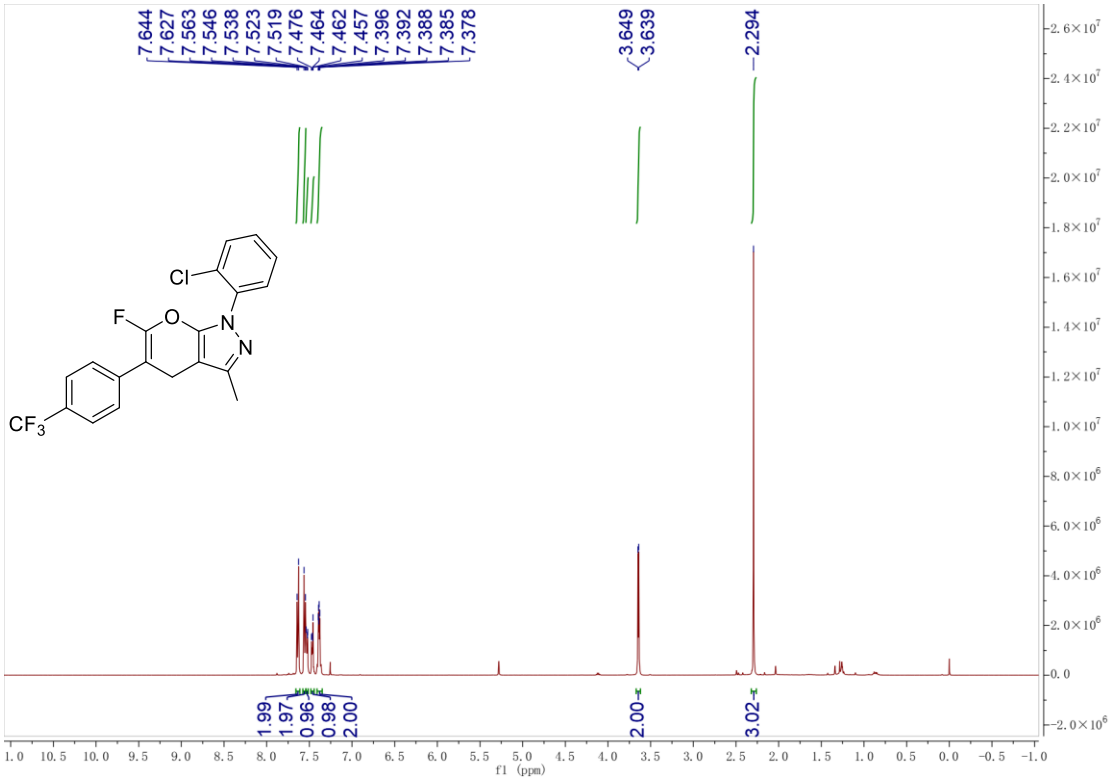
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3v



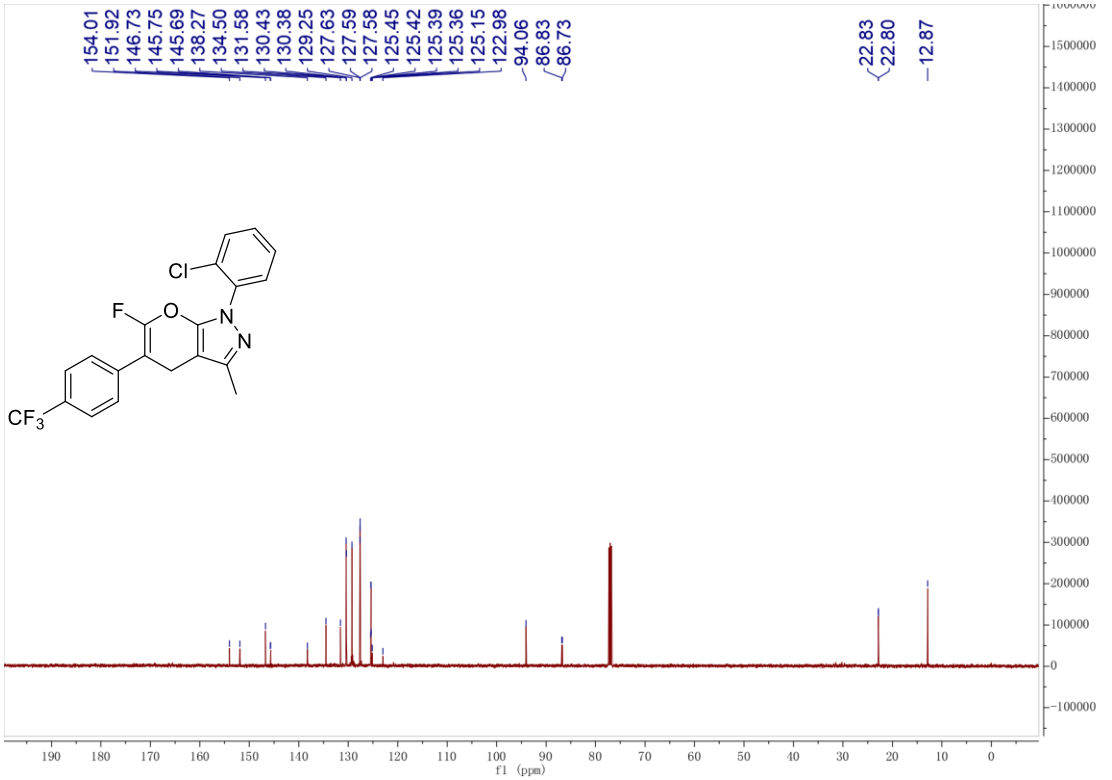
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3v



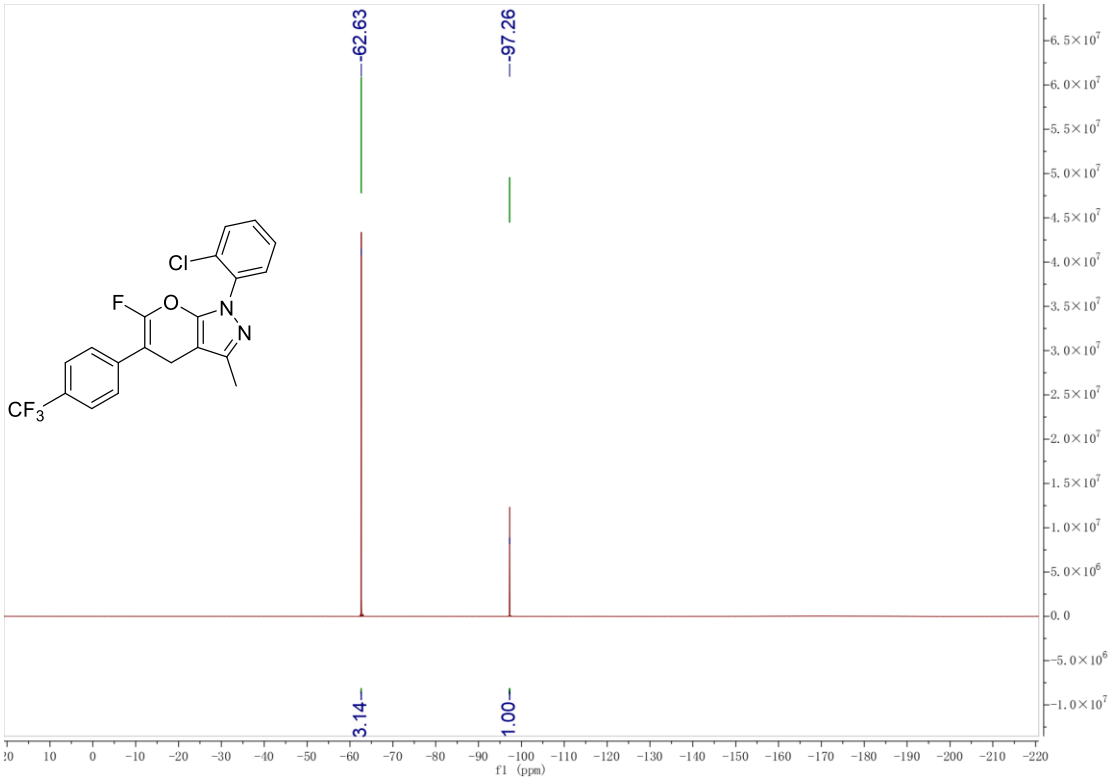
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3w



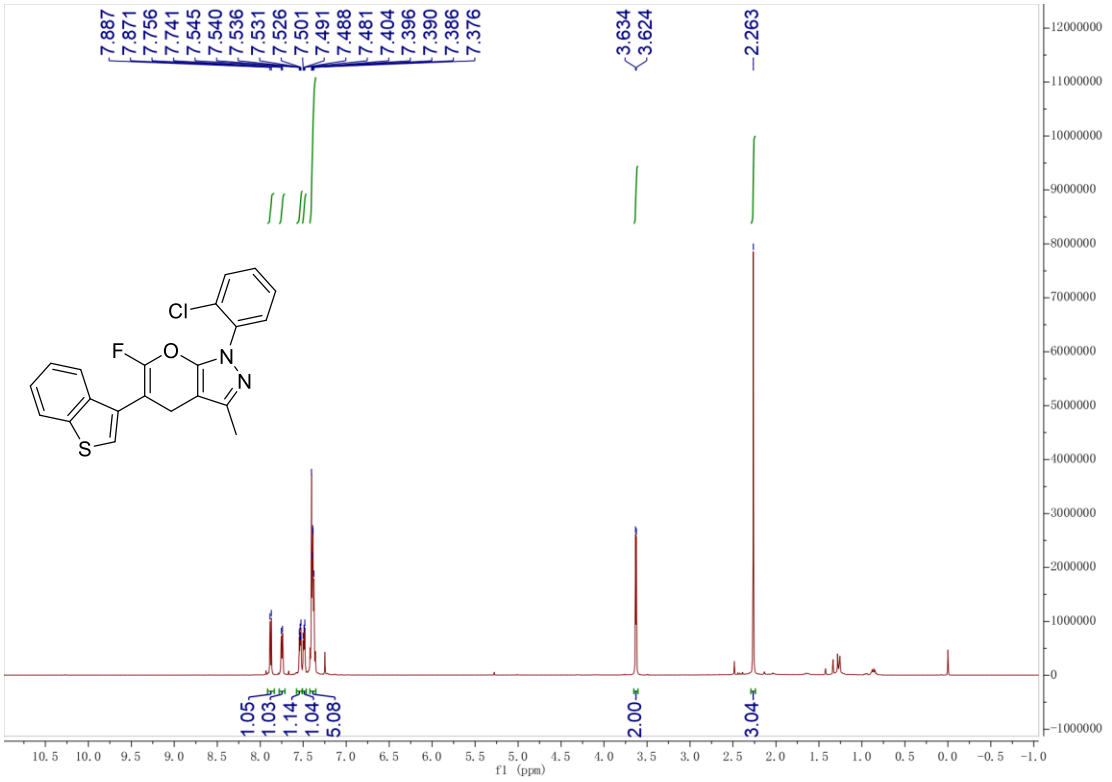
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3w



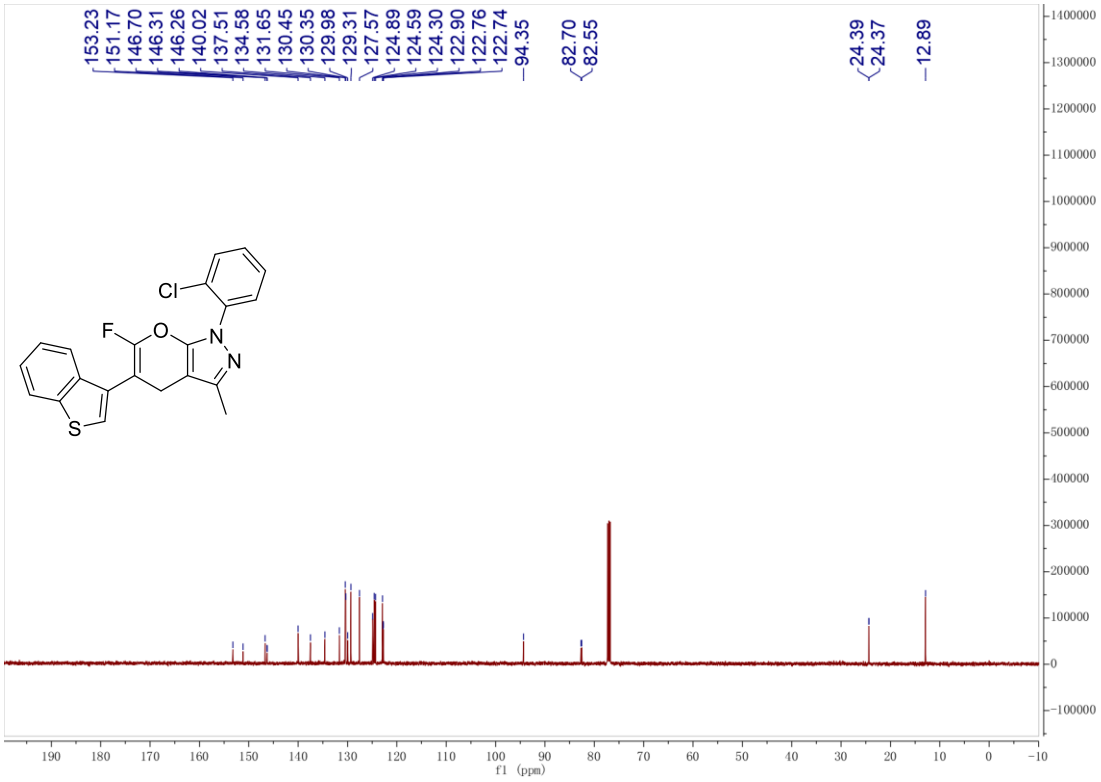
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3w



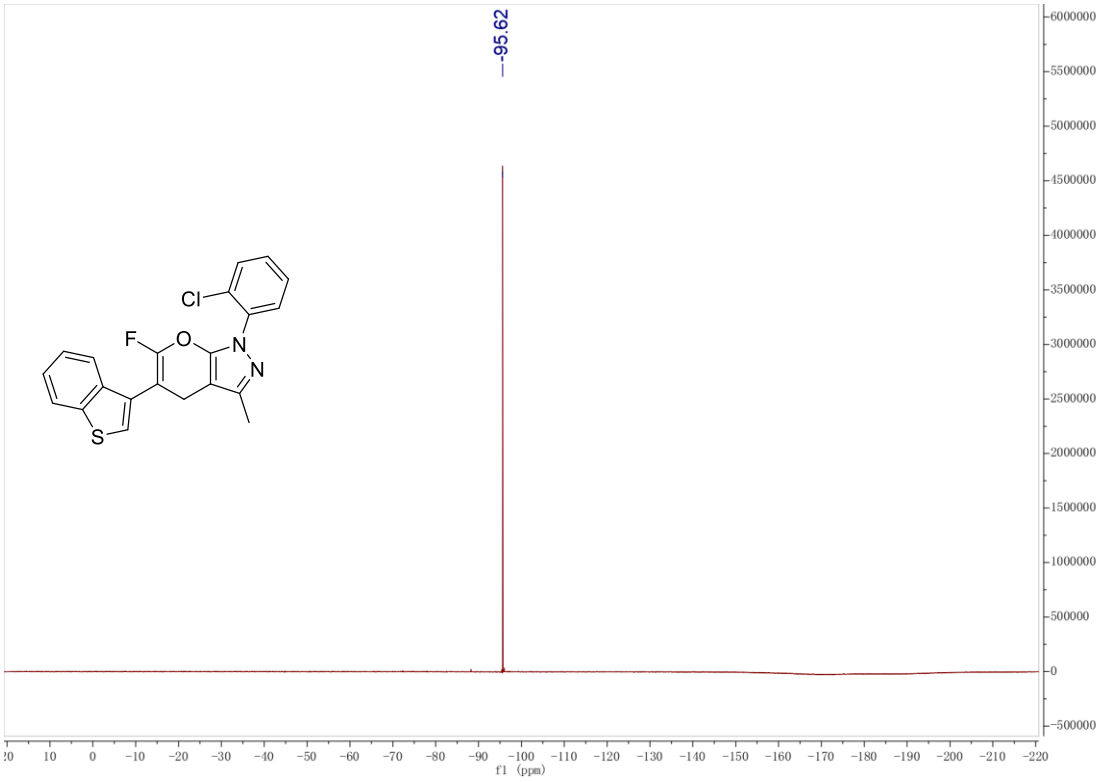
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3x



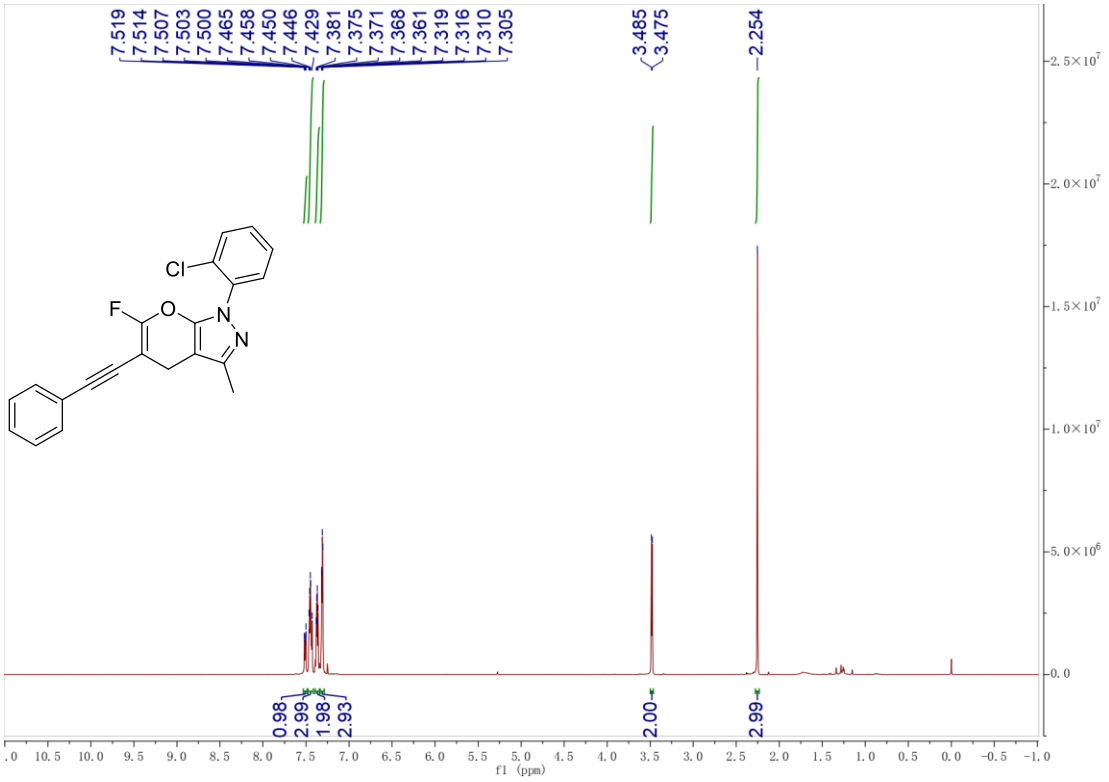
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3x



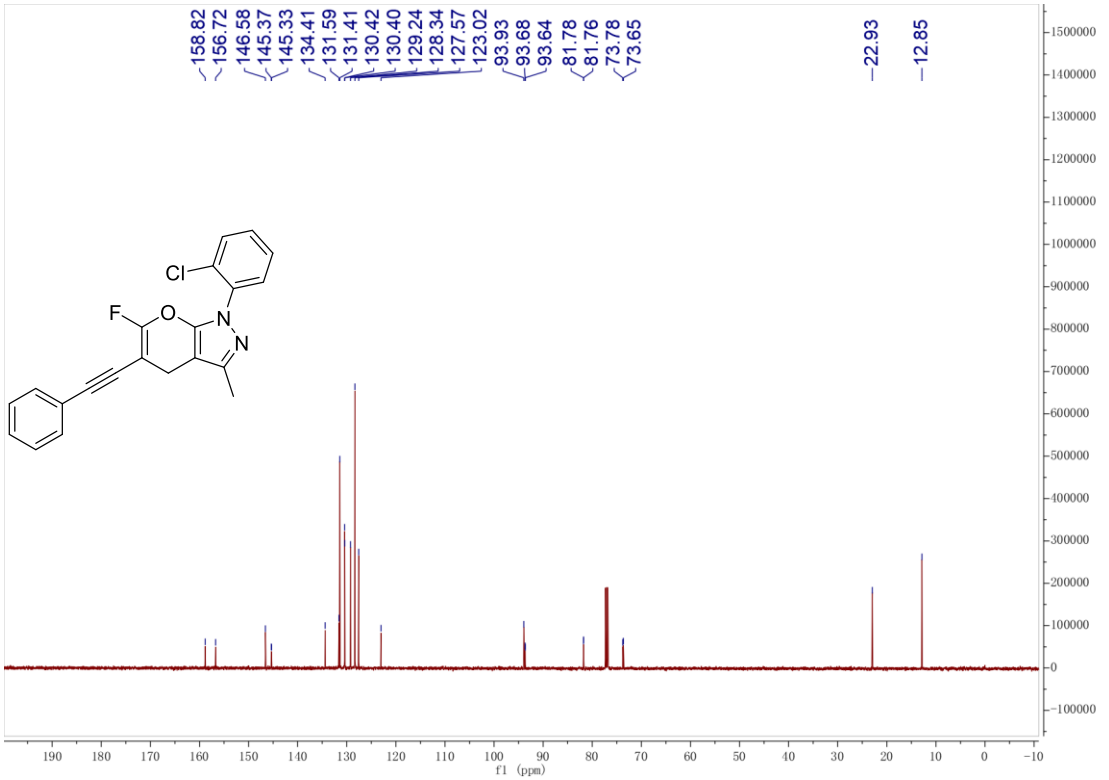
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3x



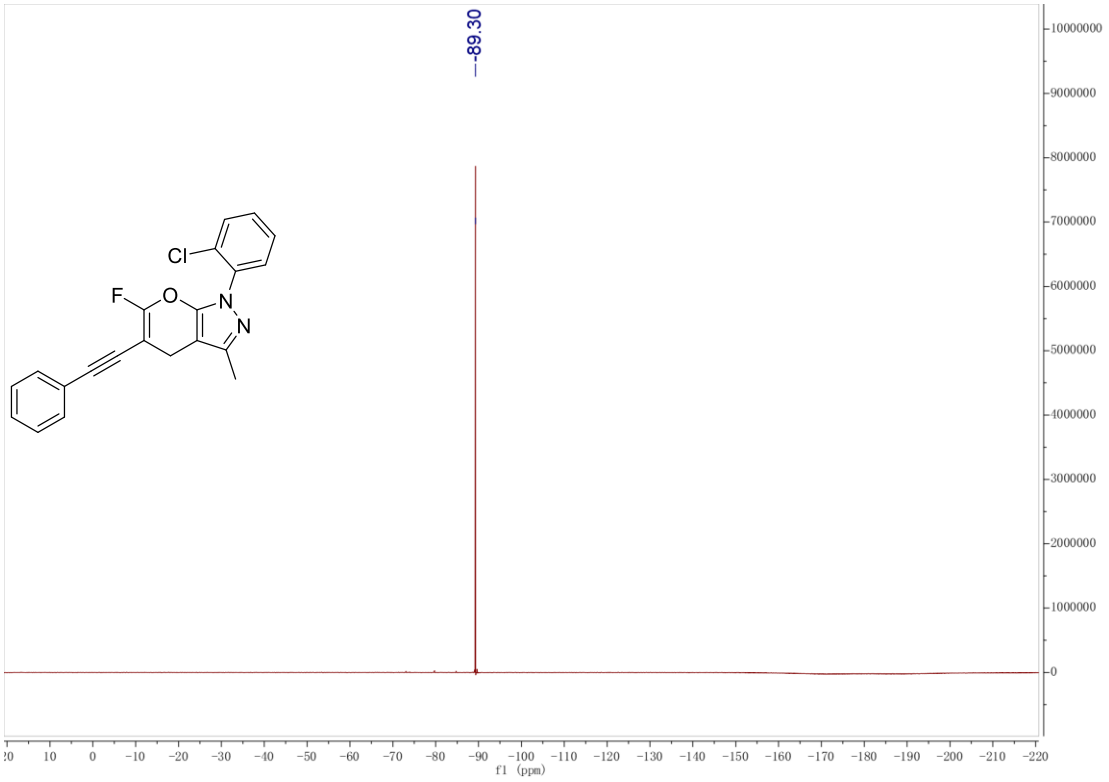
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum for 3z



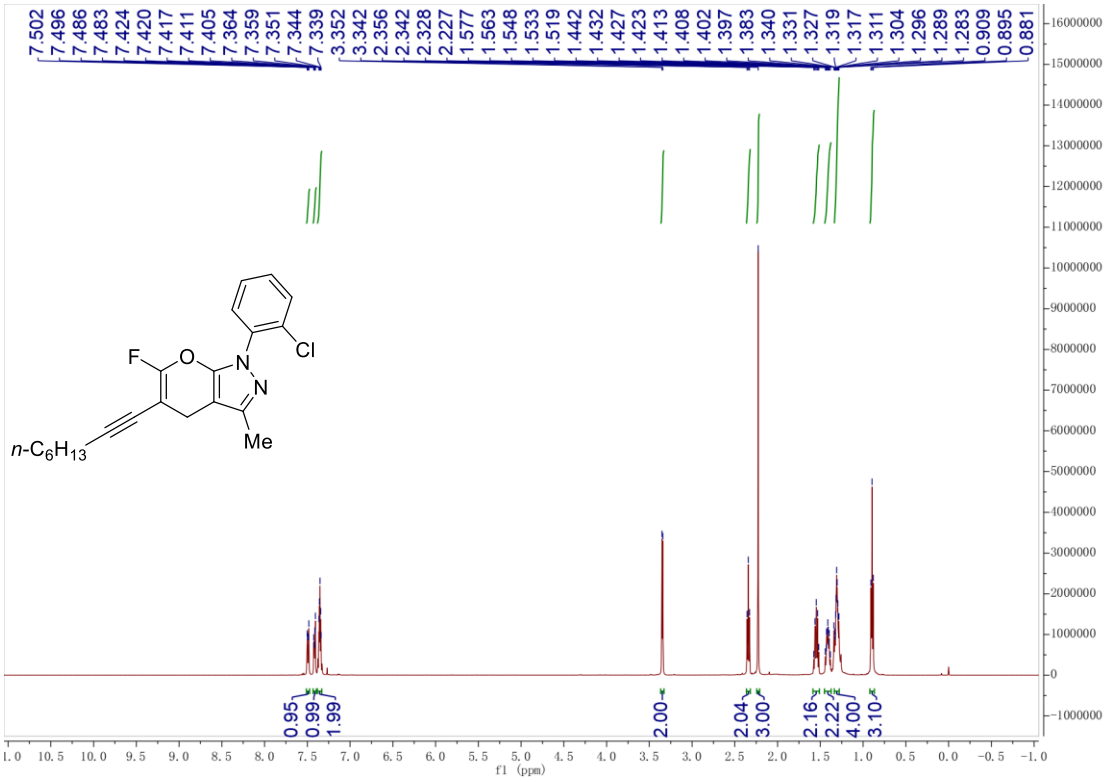
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum for 3z



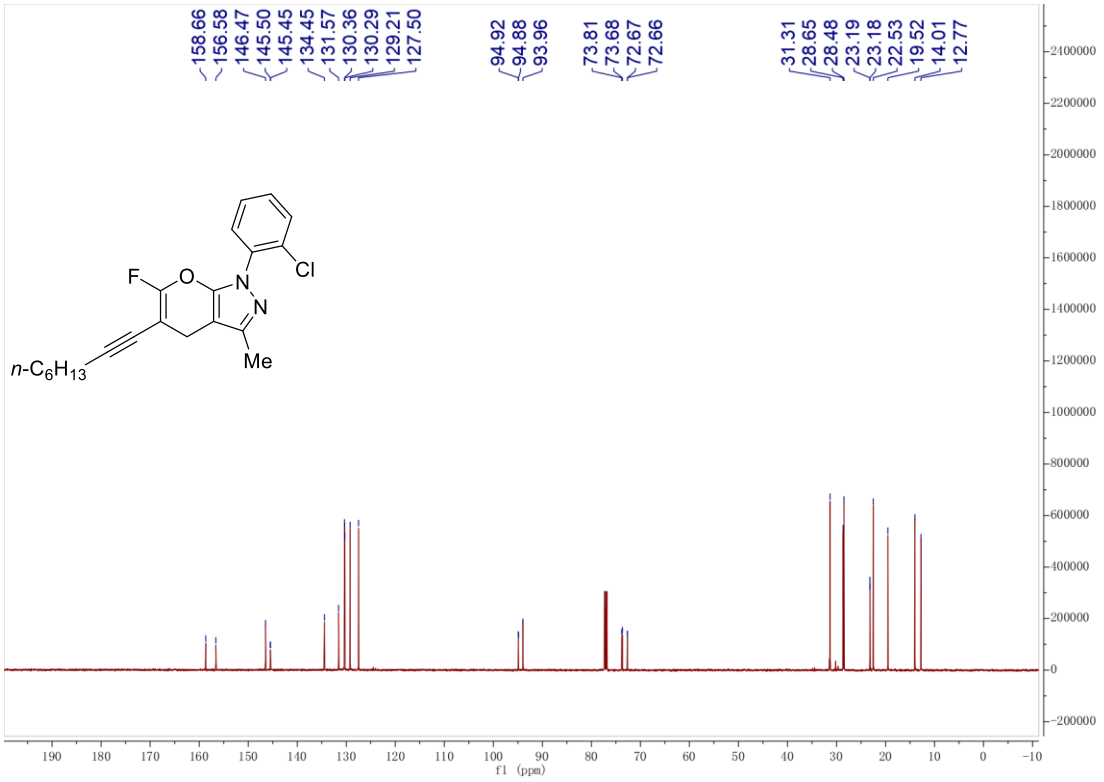
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3z



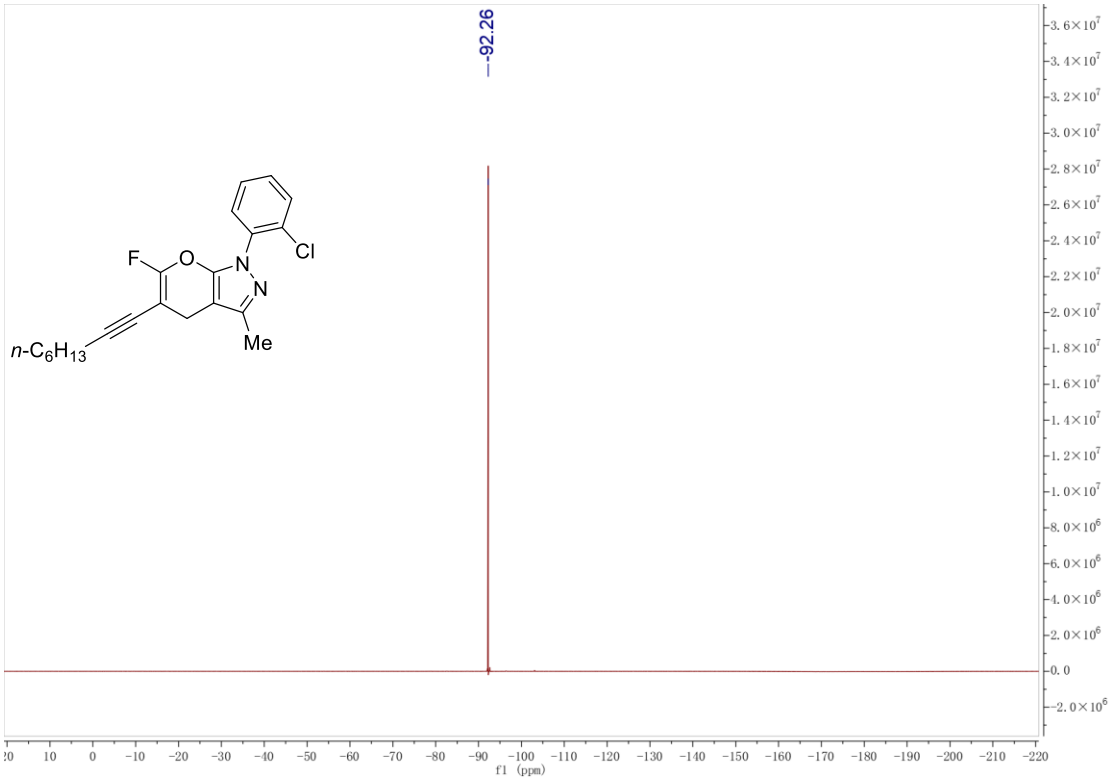
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3aa



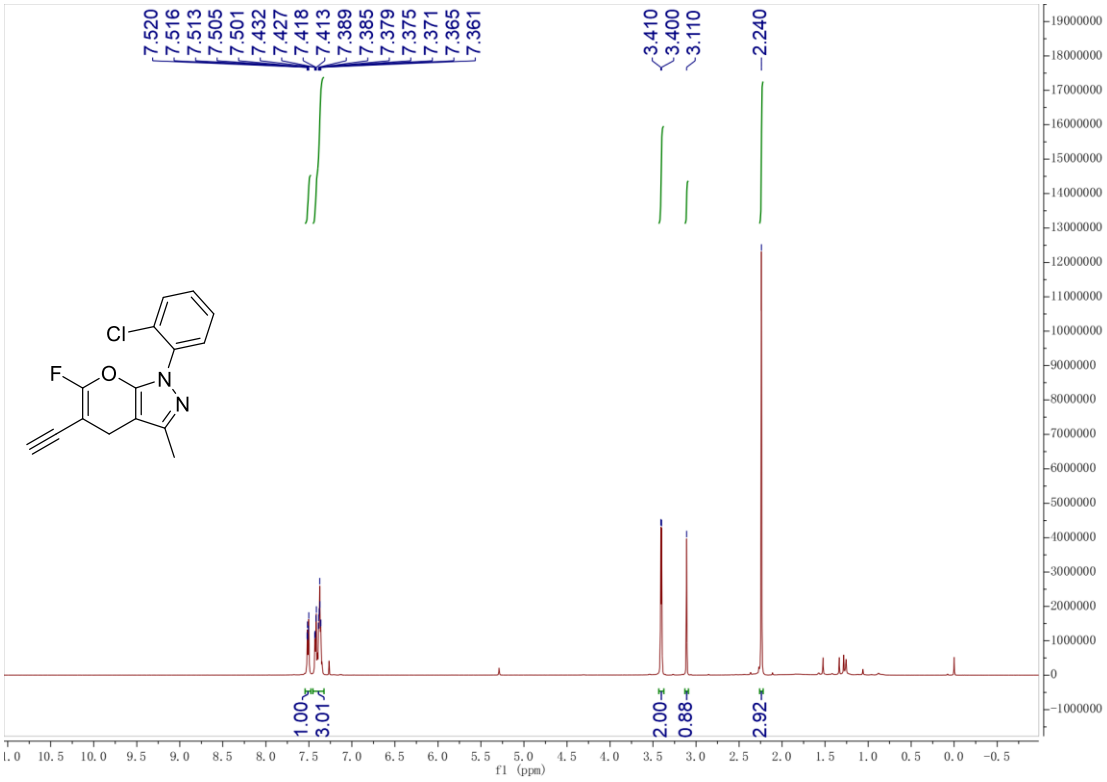
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 3aa



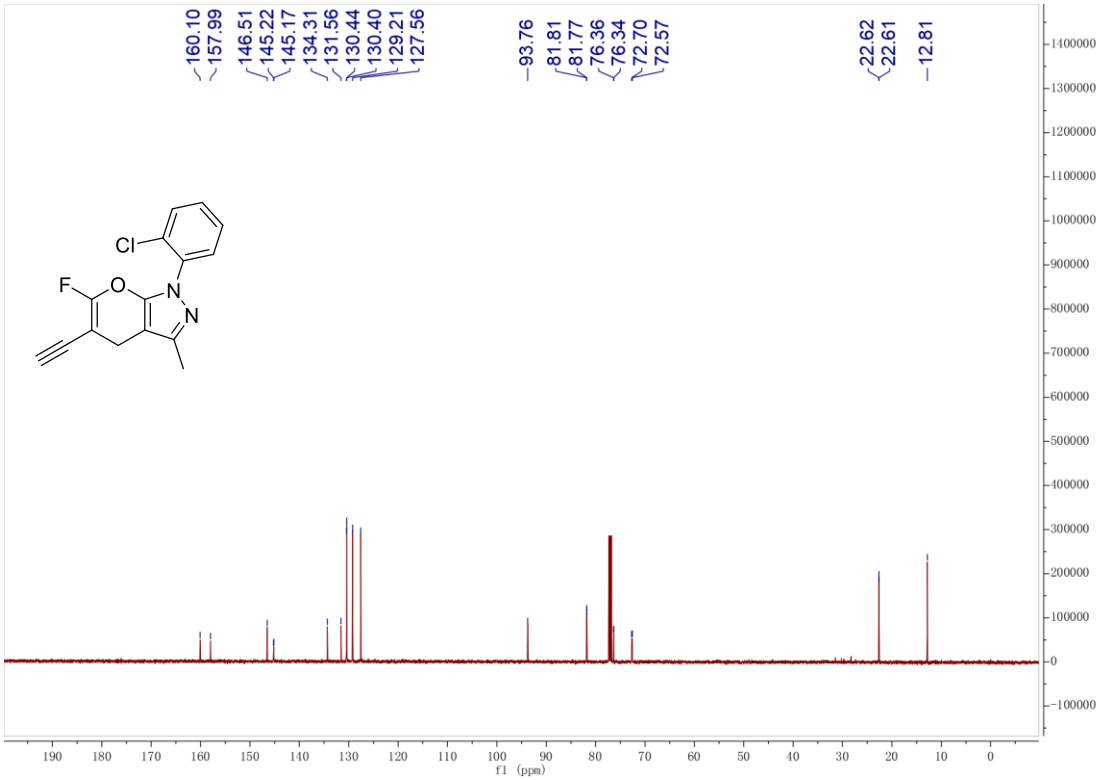
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3aa



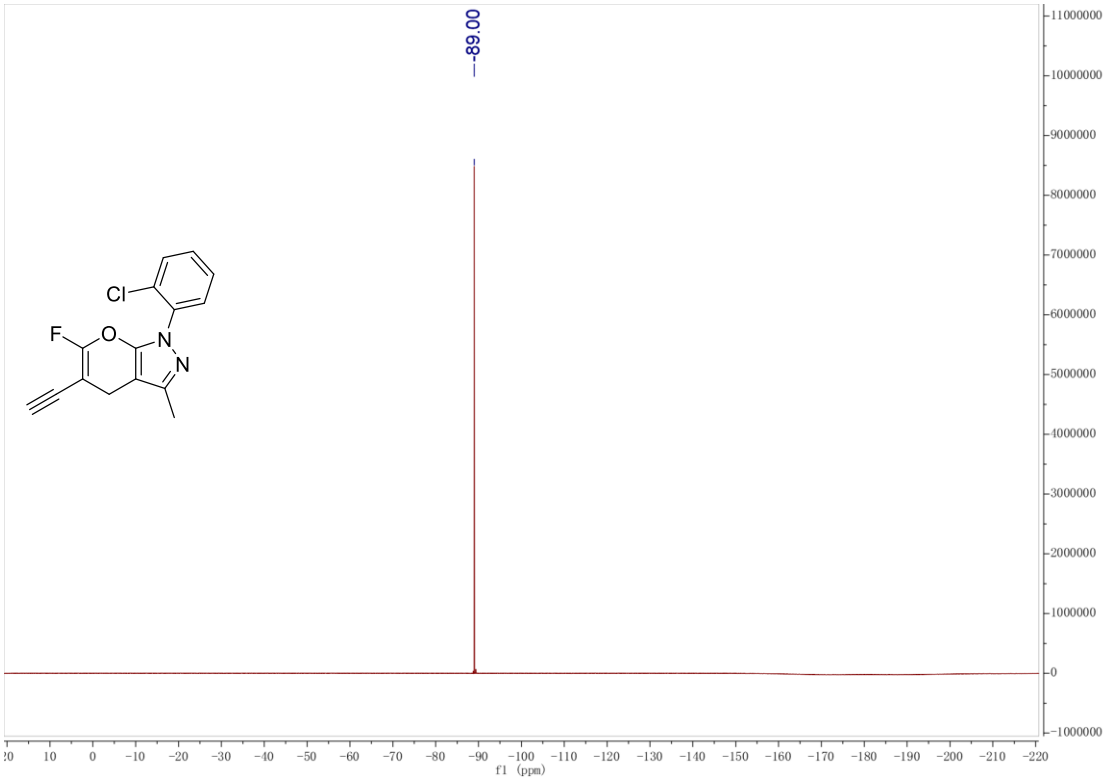
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 3ab'



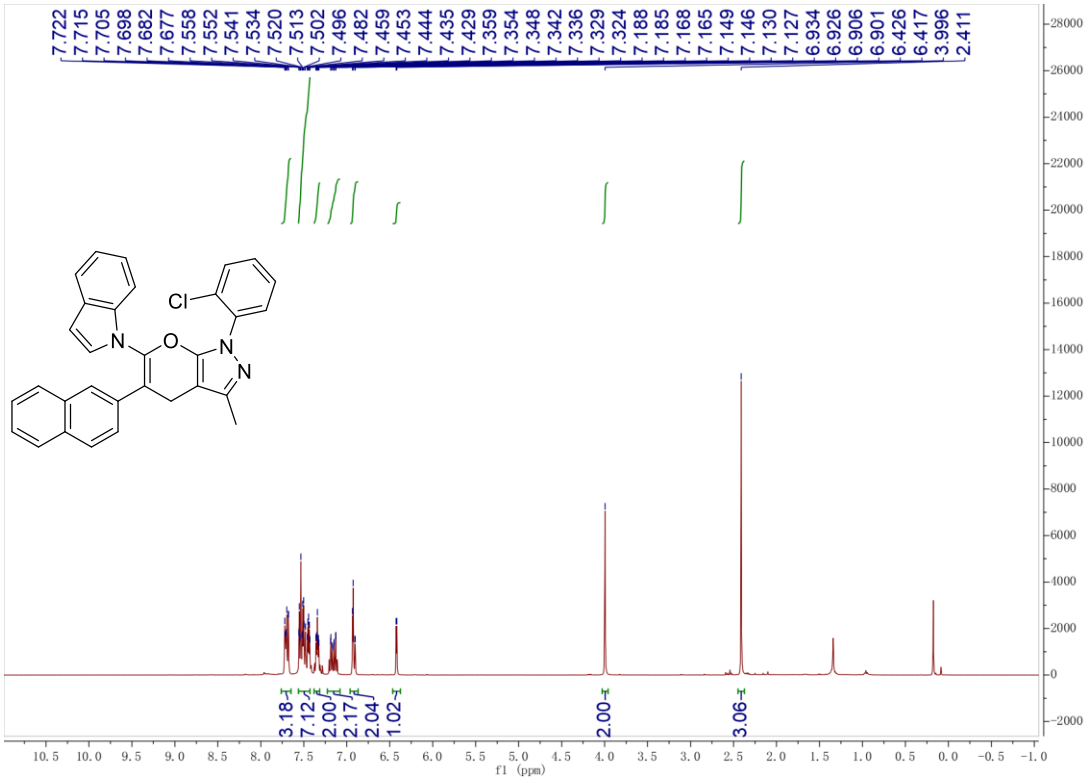
^{13}C NMR (126 MHz, $CDCl_3$) pectrum for 3ab'



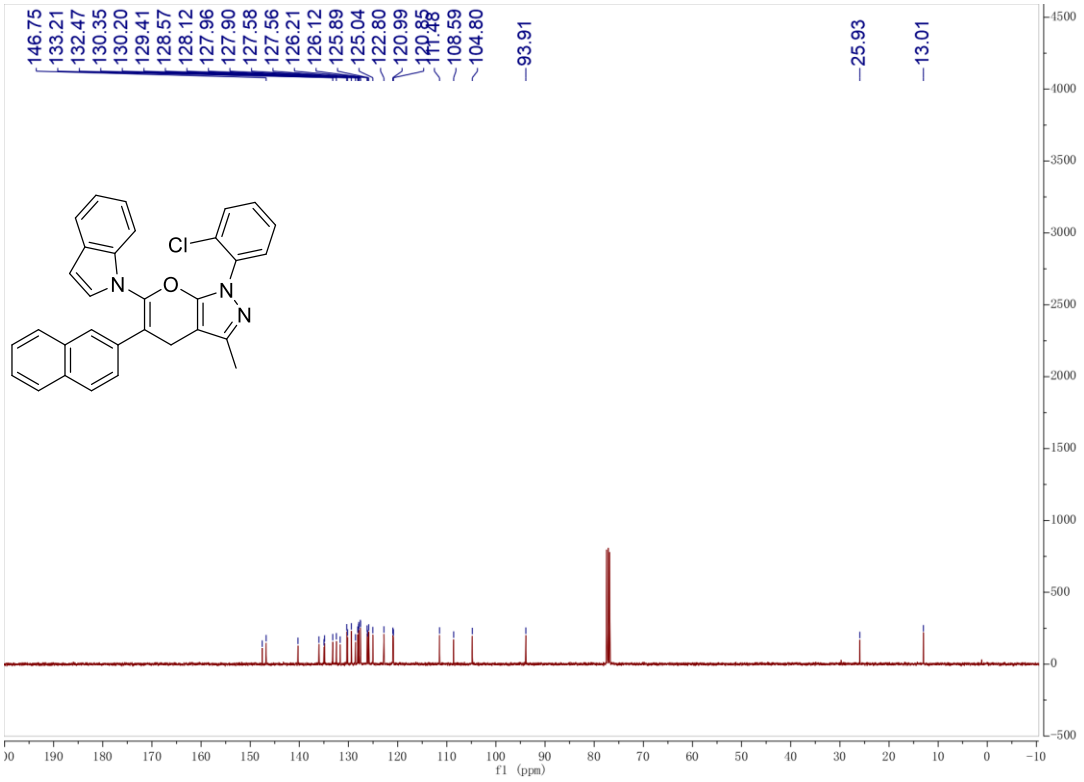
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 3ab'



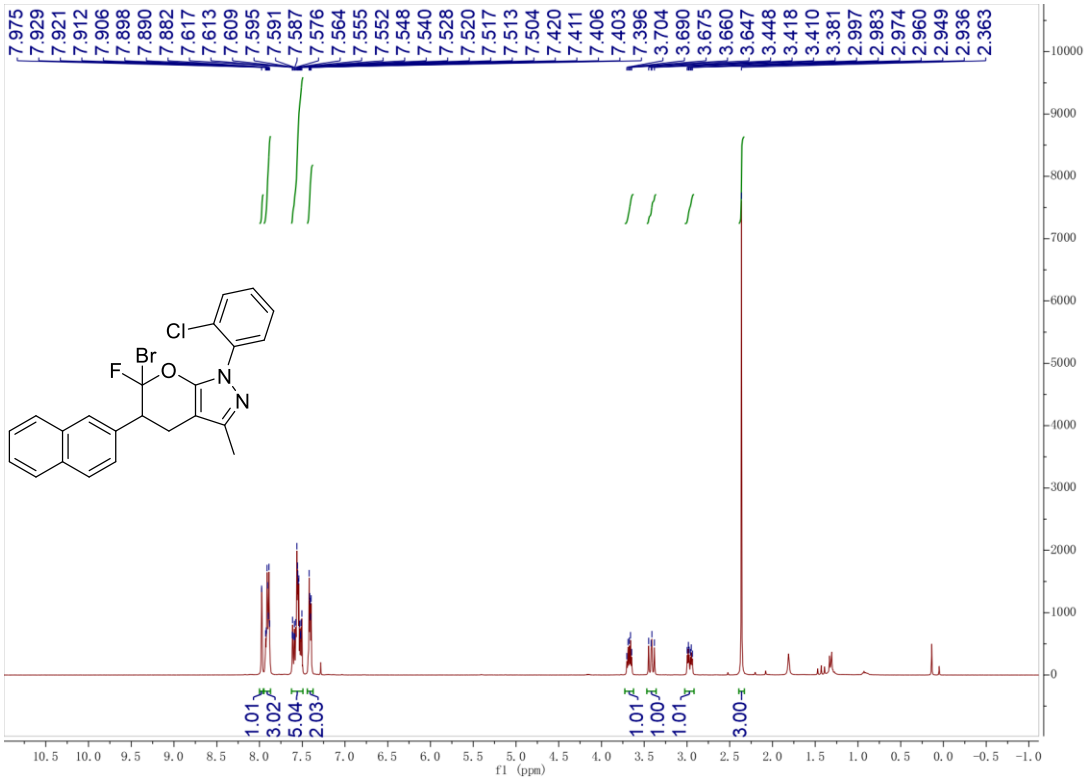
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum for 4



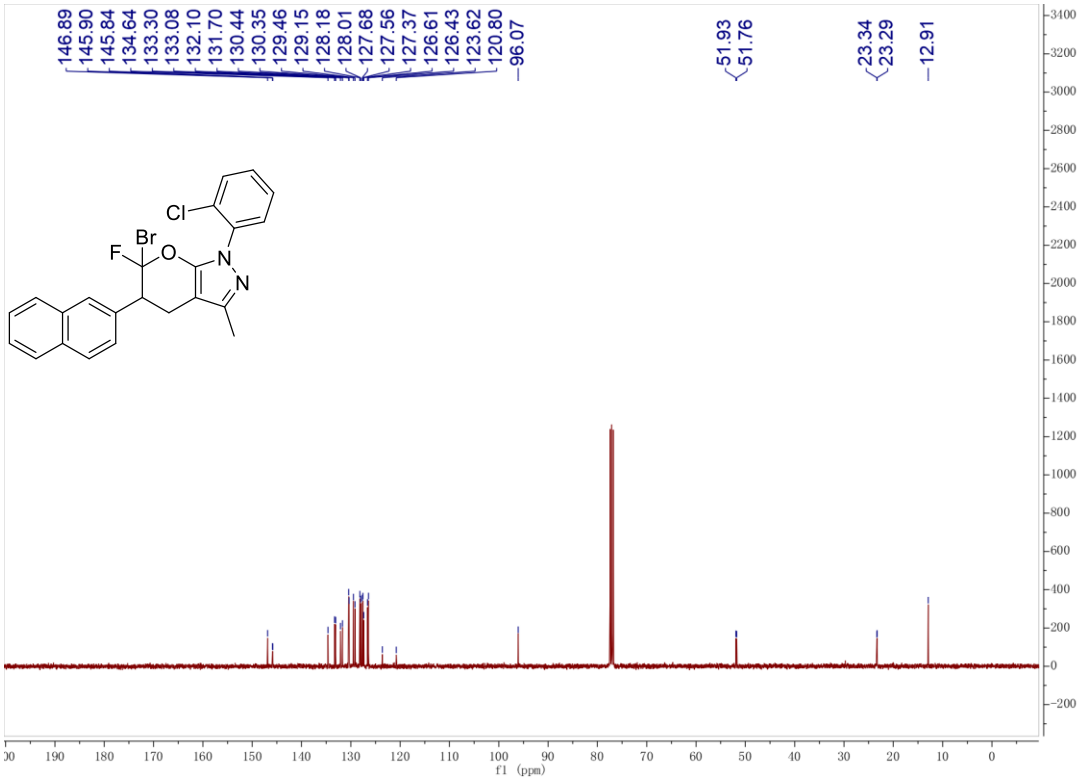
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum for 4



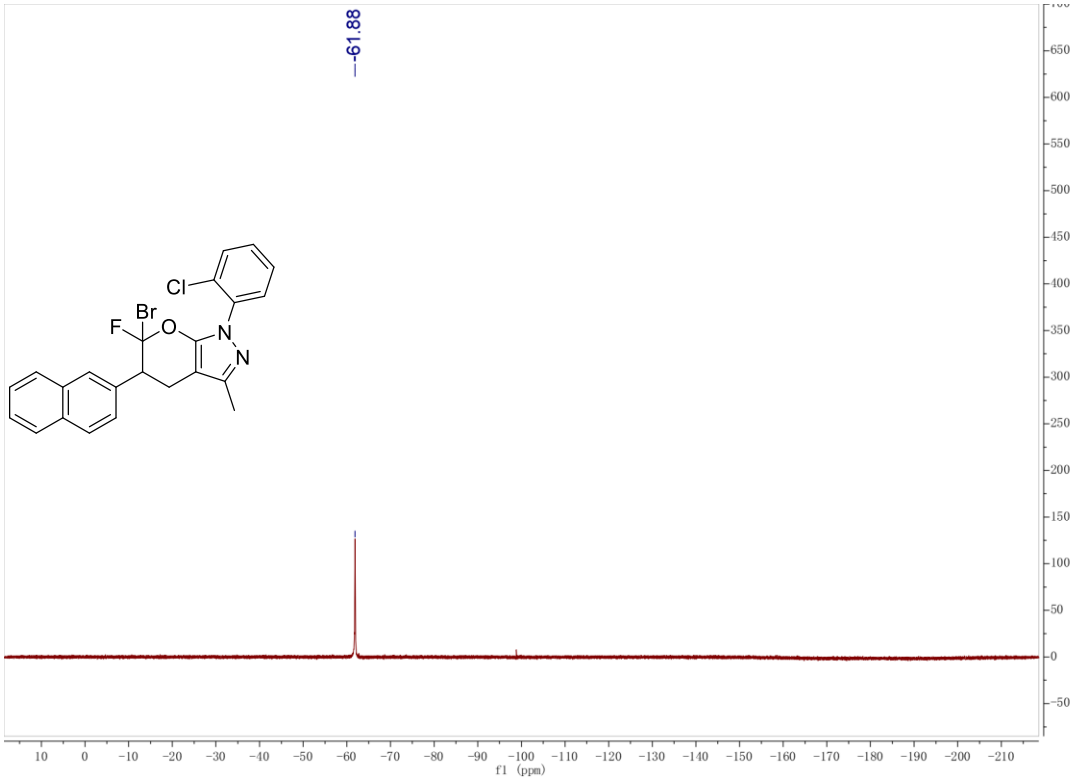
^{1}H NMR (400 MHz, $CDCl_3$) Spectrum for 5



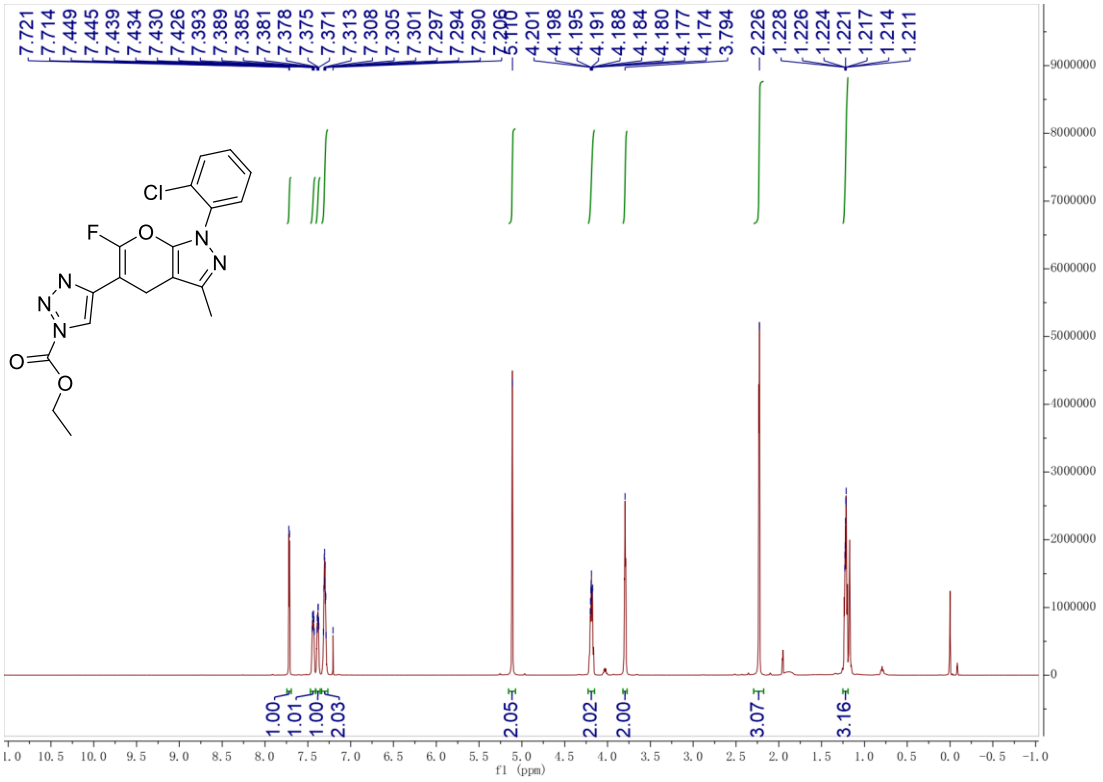
^{13}C NMR (101 MHz, $CDCl_3$) Spectrum for 5



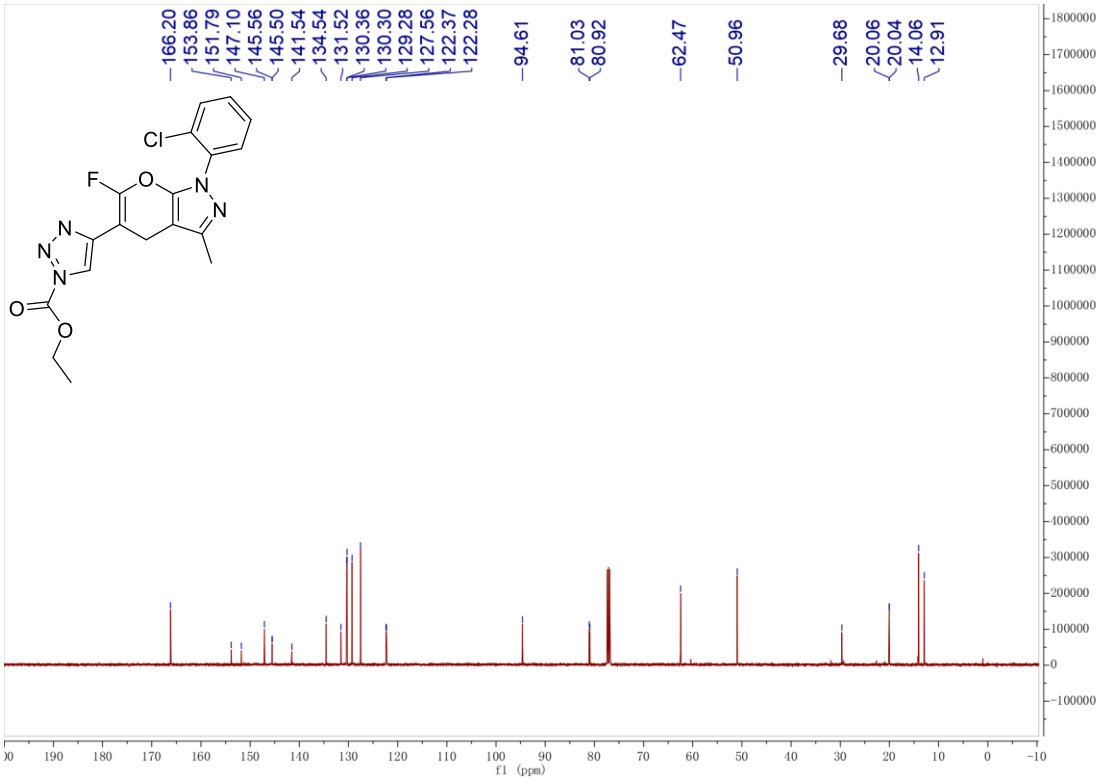
^{19}F NMR (376 MHz, $CDCl_3$) Spectrum for 5



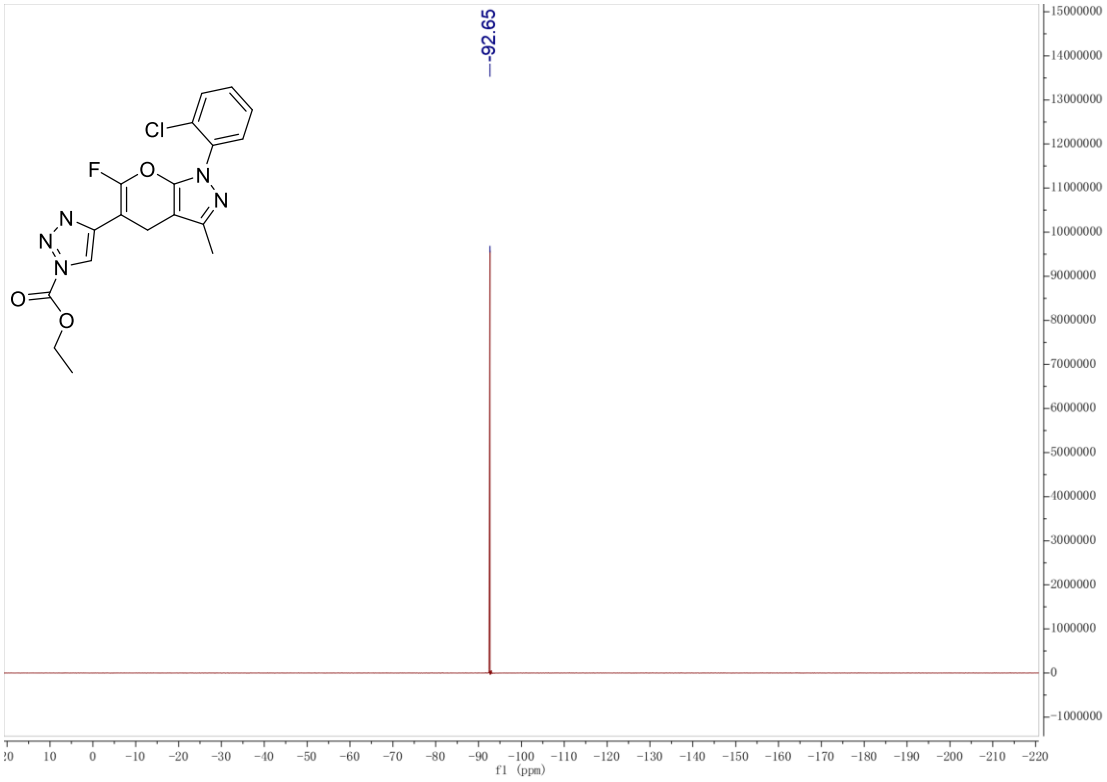
^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 7



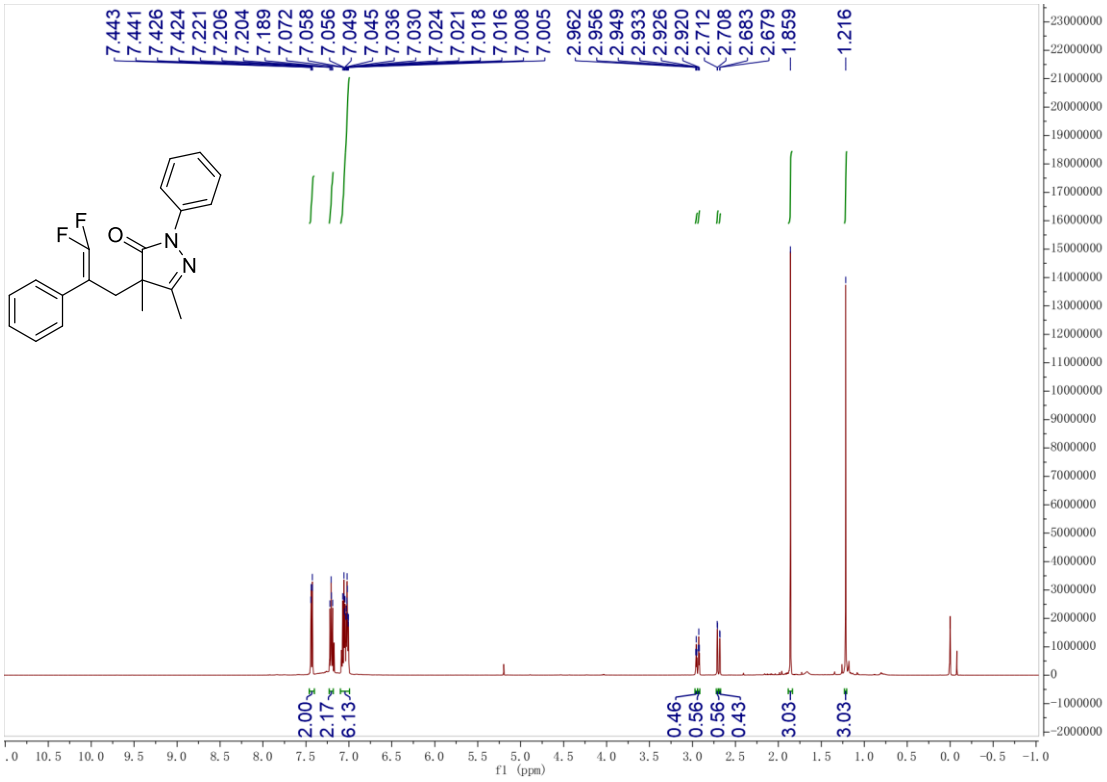
^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 7



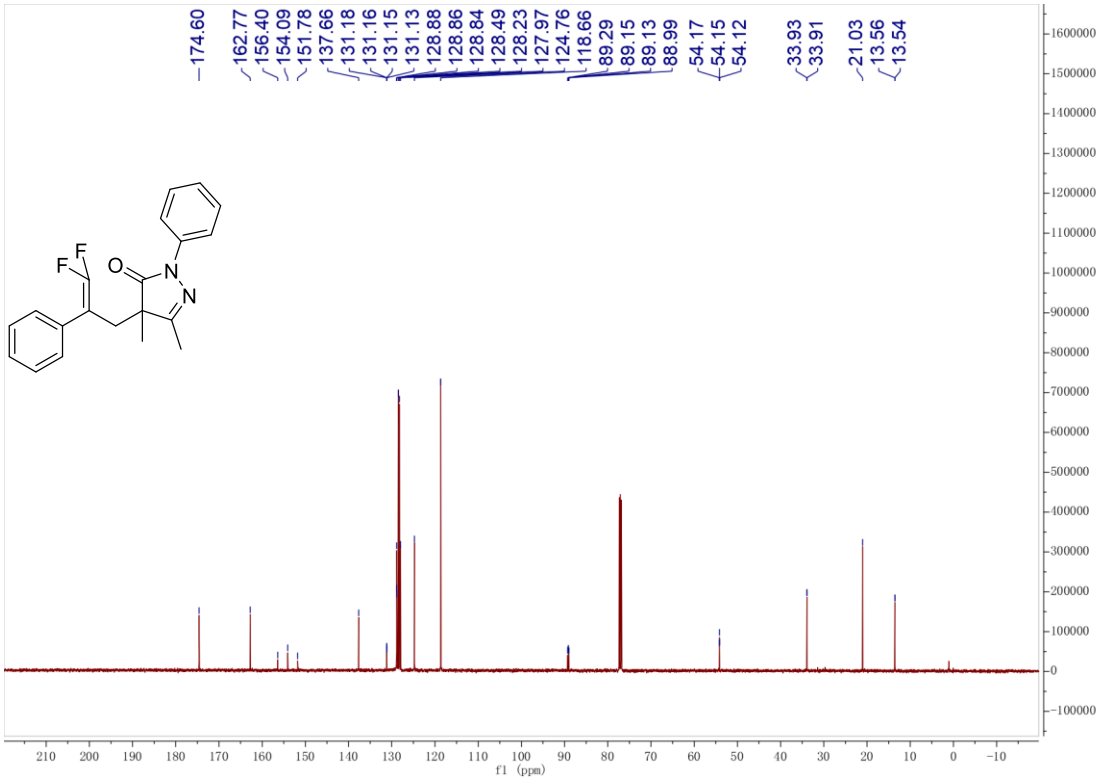
^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 7



^{1}H NMR (500 MHz, $CDCl_3$) Spectrum for 10



^{13}C NMR (126 MHz, $CDCl_3$) Spectrum for 10



^{19}F NMR (471 MHz, $CDCl_3$) Spectrum for 10