Supporting Information

CF_3SO_3H-Enabled Cascade Ring-Opening/Dearomatization of Indole Derivatives to Polycyclic Heterocycles

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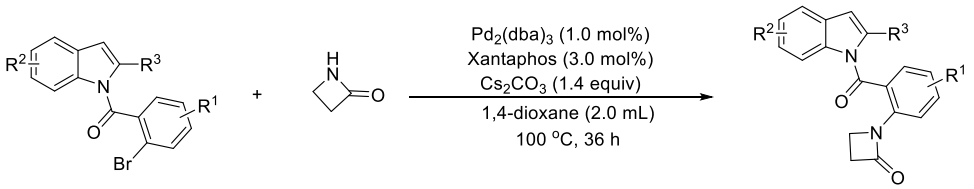
1. General Information

All commercially available reagents were used without purification unless otherwise noted. The starting materials A were synthesized according to the previous literature.[1,2] The information of some commercially available reagents is as follows: $Pd_2(dba)_3$ (98%, LOT: BD21135), Azetidin-2-one (97%, LOT: BD71042), Xantaphos (98%, LOT: BD18689), CuI (99.68%, LOT: BD122226) and *Trans-N1,N2*-Dimethylcyclohexane-1,2-diamine (96%, LOT: BD10761) were purchased from Shanghai Bepharm Science&Technology Co.,Ltd. Cs_2CO_3 (98%, LOT: P1628564) was purchased from Damas-beta. Column chromatography was performed using silica gel (200 - 300 mesh). Visualization of the compounds was accomplished with UV light (254 nm) or iodine. ^1H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ operating at 400 MHz and 100 MHz, respectively. Proton chemical shifts are reported relative to the residual proton signals of the deuterated solvent $CDCl_3$ (7.26 ppm) or TMS. Carbon chemical shifts were internally referenced to the deuterated solvent signals in $CDCl_3$ (77.10 ppm). Chemical shifts are reported in δ (parts per million) values. Coupling constants *J* are reported in Hz. Proton coupling patterns were described as singlet (s), doublet (d), triplet (t), quartet (q), and multiple (m). High - resolution mass spectra were recorded on a Liquid Chromatograph Mass Spectrometer (LCMS - IT - TOF).

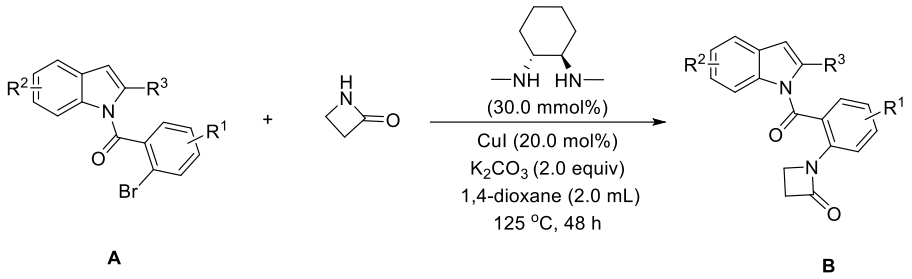
2. General Procedure for Preparation of Substrate and Characterization Data

General Procedure A



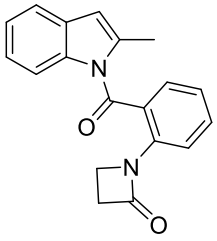
In a golvebox, charge a 10 mL oven dried sealed tube with $Pd_2(dba)_3$ (9.2 mg, 1.0 mol%), Xantphos (17.4 mg, 3.0 mol %), **A** (1.0 mmol), 2-azetidinone (144 mg, 2.0 mmol) and Cs_2CO_3 (460 mg, 1.4 equiv) in anhydrous 1,4-dioxane (2.0 mL). Then reaction tube was taken out and stirred at 100 ^oC for 36 h. The solvent was removed under *vacuum*. Purified by Silica gel column chromatography eluting with ethyl acetate/petroleum ether.

General Procedure B



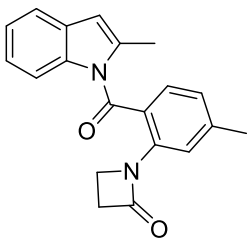
A (1.0 mmol), CuI (38.1 mg, 0.2 mmol), K_2CO_3 (276.4 mg, 2.0 mmol), *N*, *N* '-dimethylcyclohexane-1,2-diamine (47.4 μL, 0.3 mmol), 2-azetidinone (144 mg, 2.0 mmol) and 1,4-dioxane (2.0 mL) were charged to an oven dried 25 mL sealed tube under argon atmosphere. After being heated at 125 °C for 2 days, the solvent was removed under *vacuum*. The residue was purified through silica gel column chromatography eluting with ethyl acetate/petroleum ether to furnish **B**.

1-(2-(2-Methyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S1)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S1** (231 mg, 76%) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.55 (ddd, *J* = 8.4, 7.4, 1.6 Hz, 1H), 7.44 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.40 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.24 – 7.13 (m, 3H), 7.05 (ddd, *J* = 7.7, 7.2, 1.3 Hz, 1H), 6.40 (s, 1H), 3.52 (dd, *J* = 5.7, 3.3 Hz, 1H), 3.28 (dd, *J* = 5.9, 3.2 Hz, 1H), 3.02 – 2.84 (m, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.7, 165.3, 138.2, 136.9, 135.8, 132.2, 129.8, 129.5, 126.4, 124.7, 123.4, 123.1, 120.6, 119.8, 114.8, 109.7, 40.6, 36.7, 16.5. HRMS m/z (ESI$^+$): Calculated for $C_{19}H_{16}N_2O_2$ ([M+H]$^+$): 305.1285, found 305.1287.

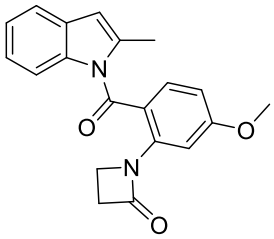
1-(5-Methyl-2-(2-methyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S2)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S2** (232 mg, 73%) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (s, 1H), 7.47 (d, *J* = 7.6 Hz, 1H), 7.31 (d, *J* = 7.9 Hz, 1H), 7.24 – 7.14 (m, 2H), 7.12 – 7.00 (m, 2H), 6.42 (s, 1H), 3.55 – 3.51 (m, 1H), 3.36 – 3.22 (m, 1H), 2.93 (dd, *J* = 12.9, 4.6 Hz, 2H), 2.46 (s, 3H), 2.41 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 165.3, 143.1, 138.2, 136.9, 135.9,

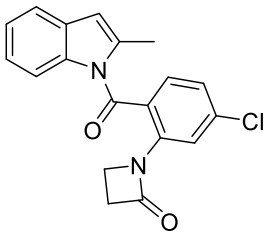
129.8, 129.7, 125.6, 123.9, 123.2 (X 2), 121.1, 119.8, 114.7, 109.4, 40.6, 36.6, 21.7, 16.4. HRMS m/z (ESI^+): Calculated for $C_{20}H_{18}N_2O_2$ ($[M+H]^+$): 319.1441, found 319.1442.

1-(5-Methoxy-2-(2-methyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S3)



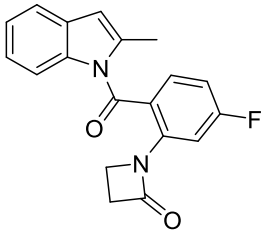
The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S3** (114 mg, 34%) as orange solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 7.6 Hz, 1H), 7.39 (d, J = 2.4 Hz, 1H), 7.35 (d, J = 8.7 Hz, 1H), 7.24 – 7.13 (m, 2H), 7.07 (ddd, J = 8.4, 6.9, 1.3 Hz, 1H), 6.75 (dd, J = 8.7, 2.5 Hz, 1H), 6.42 (s, 1H), 3.91 (s, 3H), 3.52 (td, J = 5.9, 3.4 Hz, 1H), 3.30 (td, J = 6.0, 3.3 Hz, 1H), 2.95 (dddd, J = 13.3, 9.5, 5.8, 3.2 Hz, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 165.5, 162.8, 138.3, 137.9, 136.9, 131.8, 129.7, 123.04, 123.01, 119.8, 118.8, 114.5, 110.7, 109.1, 105.6, 55.7, 40.9, 36.7, 16.2. HRMS m/z (ESI^+): Calculated for $C_{20}H_{18}N_2O_3$ ($[M+H]^+$): 335.1390, found 335.1395.

1-(5-Chloro-2-(2-methyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S4)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S4** (122 mg, 36%) as yellow oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 2.0 Hz, 1H), 7.53 – 7.44 (m, 1H), 7.34 (d, J = 8.3 Hz, 1H), 7.30 – 7.21 (m, 2H), 7.19 (d, J = 1.7 Hz, 1H), 7.11 (ddd, J = 8.5, 7.2, 1.3 Hz, 1H), 6.44 (s, 1H), 3.54 (td, J = 5.8, 3.6 Hz, 1H), 3.35 (td, J = 5.9, 3.4 Hz, 1H), 3.11 – 2.86 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 165.3, 138.1, 137.9, 136.9, 136.8, 130.7, 129.9, 124.6, 124.4, 123.54, 123.49, 120.4, 120.0, 114.7, 110.0, 40.8, 36.9, 16.6. HRMS m/z (ESI^+): Calculated for $C_{19}H_{15}ClN_2O_2$ ($[M+H]^+$): 339.0895, found 339.0898.

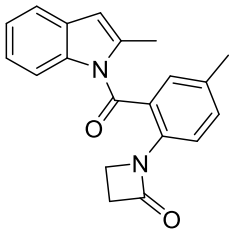
1-(5-Fluoro-2-(2-methyl-1*H*-indene-1-carbonyl)phenyl)azetidin-2-one (S5)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S5** (242 mg, 75%) as white solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J =

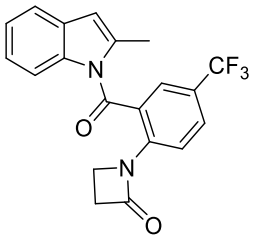
10.2, 2.5 Hz, 1H), 7.53 – 7.45 (m, 1H), 7.39 (dd, *J* = 8.7, 6.0 Hz, 1H), 7.25 – 7.16 (m, 2H), 7.16 – 7.04 (m, 1H), 6.98 – 6.85 (m, 1H), 6.44 (s, 1H), 3.53 (td, *J* = 5.9, 3.7 Hz, 1H), 3.37 (td, *J* = 5.9, 3.7 Hz, 1H), 3.00 (dd, *J* = 5.9, 5.9 Hz, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.8, 165.4, 164.6 (d, *J* = 251.5 Hz), 138.0, 137.9 (d, *J* = 11.5 Hz), 136.8, 131.7 (d, *J* = 10.0 Hz), 129.8, 123.48, 123.45, 122.0 (d, *J* = 3.2 Hz), 114.7, 111.7 (d, *J* = 22.2 Hz), 109.9, 107.8 (d, *J* = 26.1 Hz), 41.0, 37.0, 16.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -(99.59–112.14) (m). HRMS m/z (ESI^+): Calculated for $C_{19}H_{15}FN_2O_2$ ($[M+H]^+$): 323.1190, found 323.1193.

1-(4-Methyl-2-(2-methyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S6)



The compound was synthesized according to the procedure **B**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S6** (172 mg, 54%) as Plum solid. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.65 (d, *J* = 8.3 Hz, 1H), 7.52 – 7.43 (m, 1H), 7.38 (dd, *J* = 8.5, 2.1 Hz, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 7.23 – 7.13 (m, 2H), 7.08 (ddd, *J* = 8.2, 7.2, 1.3 Hz, 1H), 6.40 (s, 1H), 3.50 (td, *J* = 5.8, 3.3 Hz, 1H), 3.22 (dt, *J* = 6.1, 3.1 Hz, 1H), 2.90 (ddd, *J* = 16.1, 5.6, 3.6 Hz, 2H), 2.40 (s, 3H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 167.9, 165.1, 138.3, 136.9, 134.8, 133.4, 132.8, 129.8, 129.7, 126.7, 123.29, 123.25, 120.8, 119.8, 114.7, 109.6, 40.6, 36.6, 20.8, 16.4. HRMS m/z (ESI^+): Calculated for $C_{20}H_{18}N_2O_2$ ($[M+H]^+$): 319.1441, found 319.1441.

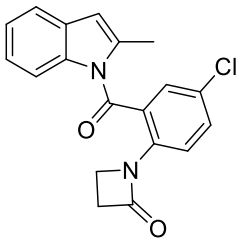
1-(2-(2-Methyl-1*H*-indole-1-carbonyl)-4-(trifluoromethyl)phenyl)azetidin-2-one (S7)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S7** (78 mg, 21%) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.06 (d, *J* = 8.5 Hz, 1H), 7.77 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.63 (d, *J* = 2.1 Hz, 1H), 7.46 (d, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.21 (ddd, *J* = 8.4, 7.4, 1.4 Hz, 1H), 7.16 – 7.07 (m, 1H), 6.44 (s, 1H), 3.56 (td, *J* = 5.5 Hz, 3.3 Hz 1H), 3.39 (td, *J* = 5.3, 3.1 Hz, 1H), 3.07 – 2.96 (m, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 166.3, 165.5, 138.50, 138.49 137.5, 136.8, 129.9, 128.7 (q, *J* = 3.6 Hz), 127.0 (q, *J* = 3.1 Hz) 126.6 (q, *J* = 4.0 Hz), 126.2 (q, *J* = 33.9 Hz), 123.9 (q, J = 2.9 Hz), 123.4

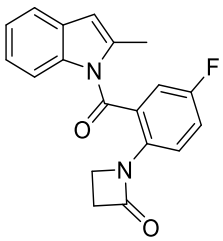
(q, *J* = 272.4 Hz) 120.5, 120.1, 114.9, 110.8, 40.9, 37.2, 16.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.27. HRMS m/z (ESI^+): Calculated for $C_{20}H_{15}F_3N_2O_2$ ($[M+H]^+$): 373.1158, found 373.1160.

1-(4-Chloro-2-(2-methyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S8)



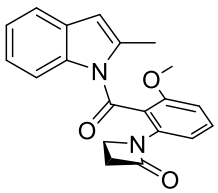
The compound was synthesized according to the procedure **B**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S8** (91 mg, 27%) as yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.8 Hz, 1H), 7.50 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.48 – 7.43 (m, 1H), 7.37 (d, *J* = 2.4 Hz, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 7.20 (ddd, *J* = 8.3, 7.5, 1.1 Hz, 1H), 7.10 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 1H), 6.45 (s, 1H), 3.50 (td, *J* = 5.9, 3.6 Hz, 1H), 3.29 (td, *J* = 5.9, 3.4 Hz, 1H), 2.95 (ddd, *J* = 9.3, 5.5, 3.7 Hz, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.2, 137.8, 136.7, 134.3, 132.0, 129.9, 129.8 129.0, 127.4, 123.72, 123.67, 122.0, 120.0, 114.8, 110.3, 40.8, 36.9, 16.6. HRMS m/z (ESI^+): Calculated for $C_{19}H_{15}ClN_2O_2$ ($[M+H]^+$): 339.0895, found 339.0894.

1-(4-Fluoro-2-(2-methyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S9)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S9** (196 mg, 61%) as yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 9.0, 4.7 Hz, 1H), 7.45 (d, *J* = 7.5 Hz, 1H), 7.32 – 7.23 (m, 1H), 7.23 – 7.12 (m, 2H), 7.14 (dd, *J* = 8.1 Hz, 2.9 Hz, 1H), 7.10 – 7.05 (m, 1H), 6.42 (s, 1H), 3.49 (td, *J* = 5.7, 3.1 Hz, 1H), 3.20 (td, *J* = 5.7, 3.1 Hz, 1H), 3.01 – 2.80 (m, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.2, 165.1, 159.0 (d, *J* = 247.7 Hz), 137.9, 136.7, 132.1 (d, *J* = 3.2 Hz), 129.9, 128.1 (d, *J* = 6.5 Hz), 123.6, 123.5, 122.9 (d, *J* = 7.9 Hz), 120.0, 119.2 (d, *J* = 22.5 Hz), 116.1 (d, *J* = 24.2 Hz), 114.7, 110.2, 40.9, 36.8, 16.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.60 (dd, *J* = 7.9, 4.6 Hz). HRMS m/z (ESI^+): Calculated for $C_{19}H_{15}FN_2O_2$ ($[M+H]^+$): 323.1190, found 323.1191.

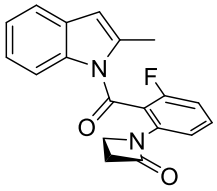
1-(3-Methoxy-2-(2-methyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S10)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S10** (267 mg,

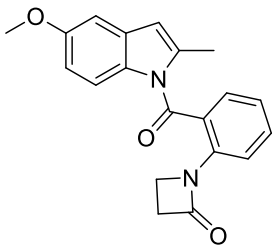
80%) white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.9 Hz, 1H), 7.45 (ddd, J = 8.4, 7.6, 1.0 Hz, 1H), 7.21 – 7.02 (m, 4 H), 6.97 (d, J = 2.9 Hz, 1H), 6.40 (s, 1H), 3.80 (s, 3H), 3.43 (td, J = 5.2, 3.1 Hz 1H), 3.03 (td, J = 5.2, 3.1 Hz, 1H), 2.94 – 2.71 (m, 2H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 165.1, 156.9, 138.3, 136.8, 129.8, 128.9, 128.5, 123.4, 123.3, 123.0, 119.8, 118.4, 114.6, 113.7, 109.6, 55.8, 40.8, 36.6, 16.3. HRMS m/z (ESI^+): Calculated for $C_{20}H_{18}N_2O_3$ ($[M+H]^+$): 335.1390, found 335.1389.

1-(3-Fluoro-2-(2-methyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S11)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S11** (219 mg, 68%) as pink solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J = 1.6 Hz, 1H), 7.50 – 7.33 (m, 3H), 7.20 (d, J = 8.4 Hz, 1H), 7.12 (ddd, J = 8.3, 7.4, 1.0 Hz, 1H), 7.02 (ddd, J = 8.4, 7.2, 1.3 Hz, 1H), 6.46 (s, 1H), 3.50 (td, J = 5.8, 3.7 Hz, 1H), 3.32 (td, J = 5.8, 3.6 Hz, 1H), 3.10 – 2.99 (m, 2H), 2.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.4, 165.3, 137.7, 136.8, 136.1, 133.9 (d, J = 33.2 Hz), 129.9 (d, J = 21.7 Hz), 128.7, 123.8 (d, J = 5.8 Hz), 123.2 (d, J = 273.5 Hz), 121.0, 120.8 (d, J = 7.7 Hz), 120.1, 117.3 (d, J = 4.0 Hz), 114.9, 110.5, 40.8, 37.1, 16.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.07. HRMS m/z (ESI^+): Calculated for $C_{19}H_{15}FN_2O_2$ ($[M+H]^+$): 323.1190, found 323.1193.

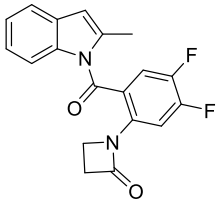
1-(2-(5-Methoxy-2-methyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S12)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S12** (254 mg, 76%) as goldenrod solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.3 Hz, 1H), 7.56 (ddd, J = 8.5, 7.6, 1.0 Hz, 1H), 7.41 (dd, J = 7.7, 1.6 Hz, 1H), 7.24 (ddd, J = 8.4 7.6, 1.1 Hz, 1H), 7.17 (d, J = 9.1 Hz, 1H), 6.95 (d, J = 2.6 Hz, 1H), 6.70 (dd, J = 9.0, 2.6 Hz, 1H), 6.36 (s, 1H), 3.84 (s, 3H), 3.55 (td, J = 5.8, 3.5 Hz, 1H), 3.33 (td, J = 5.8, 3.3 Hz, 1H), 3.05 – 2.87 (ddd, J = 9.7, 5.6, 3.6 Hz, 2H), 2.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.4, 165.3, 156.3, 138.8, 135.7, 132.0, 131.5, 130.9, 129.4, 126.3, 124.6,

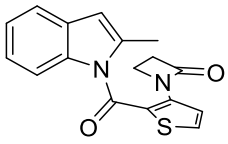
120.6, 115.7, 111.4, 109.9, 102.9, 55.6, 40.6, 36.7, 16.6. HRMS m/z (ESI$^+$): Calculated for $C_{20}H_{18}N_2O_3$ ([M+H]$^+$): 335.1390, found 335.1393.

1-(4,5-Difluoro-2-(2-methyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S13)



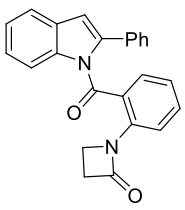
The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S13** (207 mg, 61%) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 (dd, J = 11.4, 7.0 Hz, 1H), 7.47 (d, J = 7.7 Hz, 1H), 7.25 – 7.14 (m, 3H), 7.10 (ddd, J = 8.3, 7.1, 1.3 Hz, 1H), 6.44 (s, 1H), 3.47 (td, J = 5.9, 3.5 Hz, 1H), 3.28 (td, J = 5.9, 3.3 Hz, 1H), 2.96 (ddd, J = 10.5, 5.5, 3.6 Hz, 2H), 2.39 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 165.3, 152.1 (dd, J = 255.2, 13.3 Hz), 146.7 (dd, J = 250.0, 13.1 Hz), 137.8, 136.6, 133.0 (dd, J = 8.2, 4.1 Hz), 129.9, 123.8, 123.7, 122.2 (dd, J = 8.8, 3.6 Hz), 120.1, 118.3 (dd, J = 19.3, 2.1 Hz), 114.5, 110.3 (dd, J = 19.6 2.5 Hz), 110.1, 41.2, 37.1, 16.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -129.19 (ddd, J = 22.2, 11.4, 8.1 Hz), -139.92 (ddd, J = 22.2, 9.7, 6.9 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{19}H_{14}F_2N_2O_2$ ([M+H]$^+$): 341.1096, found 341.1099.

1-(2-(2-Methyl-1*H*-indole-1-carbonyl)thiophen-3-yl)azetidin-2-one (S14)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S14** (96 mg, 31%) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.73 (d, J = 5.3 Hz, 1H), 7.56 (d, J = 5.4 Hz, 1H), 7.46 (d, J = 7.7 Hz, 1H), 7.21 – 7.03 (m, 3H), 6.42 (s, 1H), 3.44 – 3.35 (m, 2H), 3.01 – 2.95 (m, 2H), 2.48 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 161.4, 139.7, 137.8, 136.7, 131.7, 129.4, 123.0, 122.9, 122.4, 120.0, 118.3, 113.6, 108.7, 41.7, 37.6, 15.1. HRMS m/z (ESI$^+$): Calculated for $C_{17}H_{14}N_2O_2S$ ([M+H]$^+$): 311.0849, found 311.0850.

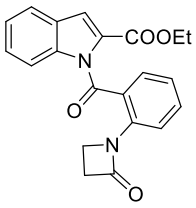
1-(2-(2-Phenyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S15)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S15** (274 mg, 75%) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (dd, J = 7.3, 3.7 Hz, 1H),

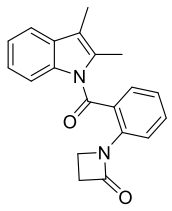
7.63 (dd, *J* = 5.9, 3.1 Hz, 1H), 7.58 (dd, *J* = 8.3, 1.1 Hz, 1H), 7.42 – 7.29 (m, 4H), 7.27 (d, *J* = 2.1 Hz, 2H), 7.22 – 7.13 (m, 3H), 6.99 (dd, *J* = 7.6, 1.1 Hz, 1H), 6.72 (s, 1H), 3.50 (s, 2H), 2.98 (t, *J* = 4.7 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.8, 165.3, 141.2, 138.0, 136.4, 132.9, 132.2, 130.5, 129.5, 128.8, 127.9, 127.7, 125.7, 124.9, 123.9, 123.8, 120.7, 120.7, 115.4, 111.5, 41.3, 36.7. HRMS m/z (ESI^+): Calculated for $C_{24}H_{18}N_2O_2$ ($[M+H]^+$): 367.1441, Found 367.1444.

Ethyl 1-(2-(2-oxoazetidin-1-yl)benzoyl)-1*H*-indole-2-carboxylate (S16)



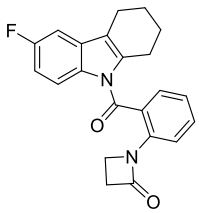
The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S16** (236 mg, 65%) as White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, *J* = 8.3 Hz, 1H), 8.11 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.8 Hz, 1H), 7.46 (ddd, *J* = 7.7, 5.2, 2.9 Hz, 2H), 7.34 (dd, *J* = 7.5, 2.0 Hz, 1H), 7.28 (s, 1H), 7.07 – 6.99 (m, 2H), 3.98 (q, *J* = 7.1 Hz, 2H), 3.87 (t, *J* = 4.9 Hz, 2H), 3.08 (t, *J* = 4.7 Hz, 2H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 166.5, 161.0, 139.1, 137.7, 132.5, 131.2, 128.7, 127.8, 127.4, 124.8, 124.3, 123.1, 122.5, 121.2, 116.6, 115.2, 61.5, 41.7, 37.0, 14.0. HRMS m/z (ESI^+): Calculated for $C_{21}H_{18}N_2O_4$ ($[M+H]^+$): 363.1339, Found 363.1343.

1-(2-(2,3-Dimethyl-1*H*-indole-1-carbonyl)phenyl)azetidin-2-one (S17)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S17** (255 mg, 85%) as Light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.53 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.46 – 7.40 (m, 1H), 7.36 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.20 (dd, *J* = 7.2, 5.0 Hz, 3H), 7.12 – 7.04 (m, 1H), 3.51 (td, *J* = 5.8, 3.4 Hz, 1H), 3.35 (td, *J* = 5.8, 3.2 Hz, 1H), 3.03 – 2.83 (m, 2H), 2.29 (s, 3H), 2.20 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.5, 165.3, 136.1, 135.8, 133.1, 131.9, 131.3, 129.5, 126.7, 124.5, 123.6, 123.2, 120.6, 118.1, 116.0, 114.7, 40.7, 36.7, 13.6, 8.8. HRMS m/z (ESI^+): Calculated for $C_{20}H_{18}N_2O_2$ ($[M+H]^+$): 319.1441, Found 319.1443.

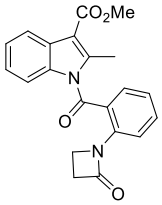
1-(2-(6-Fluoro-2,3,4,9-tetrahydro-1*H*-carbazole-9-carbonyl)phenyl)azetidin-2-one (S18)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S18** (189 mg, 52%) as White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.3 Hz, 1H), 7.52

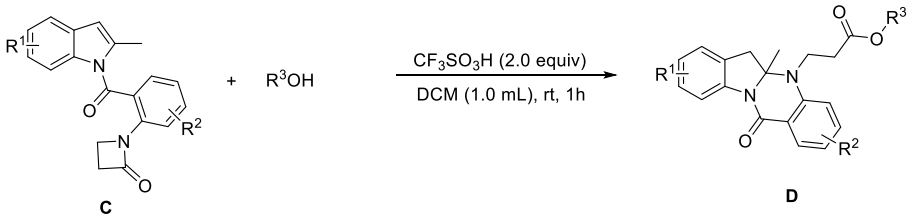
(dd, *J* = 8.1, 1.9 Hz, 2H), 7.34 (d, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 8.6 Hz, 1H), 6.85 (dd, *J* = 9.2, 2.3 Hz, 1H), 3.70 – 3.50 (m, 1H), 3.38 (q, *J* = 4.9 Hz, 1H), 3.11 – 2.87 (m, 2H), 2.58 (d, *J* = 23.8 Hz, 3H), 2.35 (d, *J* = 17.9 Hz, 1H), 1.95 – 1.68 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.0, 165.3, 159.7 (d, *J* = 239.9 Hz), 137.5 (d, *J* = 1.9 Hz), 135.6, 132.6, 131.8, 131.7 (d, *J* = 10.1 Hz), 129.2, 126.2, 124.4, 120.5, 118.6, 116.3 (d, *J* = 9.1 Hz), 111.1 (d, *J* = 24.3 Hz), 103.7 (d, *J* = 23.7 Hz), 40.7, 36.8, 25.7, 23.5, 21.9, 21.1. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -119.57. HRMS m/z (ESI^+): Calculated for $C_{22}H_{19}FN_2O_2$ ($[M+H]^+$): 363.1503, Found 363.1495.

Methyl 2-methyl-1-(2-(2-oxoazetidin-1-yl)benzoyl)-1*H*-indole-3-carboxylate (S19)



The compound was synthesized according to the procedure **A**. Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **S19** (174 mg, 48%) as White solid.^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.0 Hz, 1H), 7.65 – 7.59 (m, 1H), 7.51 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.39 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.28 – 7.21 (m, 2H), 7.16 – 7.09 (m, 2H), 3.98 (s, 3H), 3.65 (s, 1H), 3.33 (s, 1H), 2.97 (d, *J* = 22.4 Hz, 2H), 2.81 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 165.8, 165.1, 146.3, 135.9, 135.9, 133.2, 130.2, 127.3, 126.6, 125.0, 123.9, 123.9, 121.5, 120.2, 114.0, 110.9, 51.4, 40.2, 36.5, 15.0. HRMS m/z (ESI^+): Calculated for $C_{21}H_{18}N_2O_4$ ($[M+H]^+$): 363.1339, Found 363.1321.

3. Ring-Opening/Hydroamination of Indole Derivatives and Characterization Data

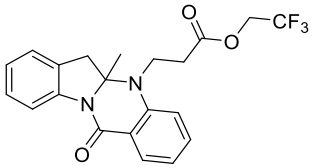


Under argon, charge a 10 mL flame-dried resealable Schlenk tube with compound **C** (0.2 mmol) and R^3OH (3.0 equiv) in anhydrous DCM (1.0 mL). The reaction mixture was cooled to 0 ^oC and stirred for 5 min. Then CF_3SO_3H (2.0 equiv) was added dropwise to the above mixture at 0 ^oC and stirred for further 5 min. Afterwards, the reaction was warmed to room temperature and stirred for 1 h. The

reaction was quenched carefully with saturated solution of Na_2CO_3, diluted with water. The aqueous was extracted with DCM (3 times), the combined organic layers were washed with brine, dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by silica column chromatography eluting with the ethyl acetate/petroleum ether.

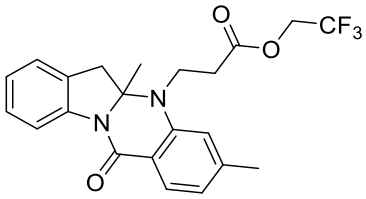
2,2,2-Trifluoroethyl

3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3aa)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3aa** (75 mg, 93%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, J = 7.9 Hz, 1H), 8.13 (dd, J = 7.7, 1.7 Hz, 1H), 7.47 (ddd, J = 8.6, 7.3, 1.7 Hz, 1H), 7.35 – 7.26 (m, 2H), 7.10 (ddd, J = 8.4, 7.5, 1.1 Hz, 1H), 7.00 (dd, J = 7.5, 0.9 Hz, 1H), 6.72 (d, J = 8.0 Hz, 1H), 4.64 – 4.38 (m, 2H), 3.75 – 3.59 (m, 3H), 3.23 (d, J = 14.6 Hz, 1H), 2.98 – 2.75 (m, 2H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 160.0, 145.2, 141.0, 134.0, 129.4, 128.3, 127.2, 124.7, 124.1, 122.8 (q, J = 277.7 Hz), 119.5, 118.7, 116.8, 112.3, 82.6, 60.6 (q, J = 36.8 Hz), 43.3, 41.4, 33.2, 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.70 (t, J = 8.3 Hz). HRMS m/z (ESI+): Calculated for $C_{21}H_{19}F_3N_2O_3$ ($[M+H]^+$): 405.1420, found 405.1419.

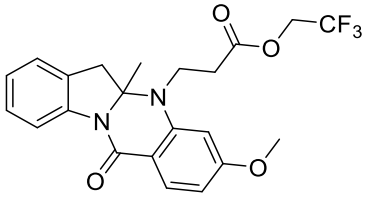
2,2,2-Trifluoroethyl-3-(3,5*a*-dimethyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ba)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ba** (67 mg, 80%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.21 (d, J = 8.0 Hz, 1H), 7.93 (d, J = 7.8 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.00 (ddd, J = 8.5, 7.5, 1.1 Hz, 1H), 6.73 (dd, J = 8.0, 1.4 Hz, 1H), 6.43 (s, 1H), 4.62 – 4.28 (m, 2H), 3.70 – 3.49 (m, 3H), 3.12 (d, J = 14.6 Hz, 1H), 2.88 – 2.71 (m, 2H), 2.32 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 160.1, 145.2, 144.8, 141.1, 129.3, 128.2, 127.2, 124.7, 123.9, 122.8 (q, J = 277.6 Hz), 120.6, 116.7, 116.2, 112.8, 82.6, 60.6 (q, J = 36.7 Hz), 43.3, 41.3, 33.3, 22.3, 20.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.68 (t, J = 8.4 Hz). HRMS m/z (ESI^+): Calculated for $C_{22}H_{21}F_3N_2O_3$ ($[M+H]^+$): 419.1577, found 419.1579.

2,2,2-Trifluoroethyl

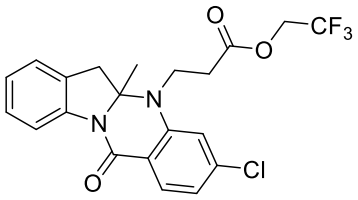
3-(3-methoxy-5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ca)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ca** (75 mg, 86%) as light yellow oil. ^{1}H NMR (400 MHz,$CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.6 Hz, 1H), 7.22 – 7.17 (m, 2H), 6.99 (ddd, J = 8.4, 7.5, 1.1 Hz, 1H), 6.46 (dd, J = 8.7, 2.2 Hz, 1H), 6.14 (d, J = 2.2 Hz, 1H), 4.60 – 4.24 (m, 2H), 3.79 (s, 3H), 3.62 – 3.51 (m, 3H), 3.12 (d, J = 14.6 Hz, 1H), 2.93 – 2.70 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 164.5, 160.0, 146.8, 141.2, 131.3, 128.2, 127.0, 124.6, 123.8, 122.8 (q, J = 278.4 Hz), 116.6, 112.1, 104.3, 98.7, 82.7, 60.6 (q, J = 36.7 Hz), 55.4, 43.3, 41.5, 33.2, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.69 (t, J = 8.3 Hz). HRMS m/z (ESI^+): Calculated for $C_{22}H_{21}F_3N_2O_4$ ($[M+H]^+$): 435.1526, found 435.1530.

2,2,2-Trifluoroethyl

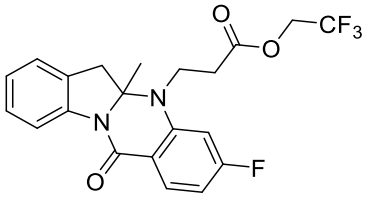
3-(3-chloro-5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3da)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3da** (72 mg, 82%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 7.9 Hz, 1H), 7.97 (d, J = 8.3 Hz, 1H), 7.33 – 7.19 (m, 2H), 7.03 (ddd, J = 8.7, 7.4, 1.1 Hz, 1H), 6.89 (dd, J = 8.3, 1.8 Hz, 1H), 6.62 (d, J = 1.8 Hz, 1H), 4.59 – 4.30 (m, 2H), 3.75 – 3.46 (m, 3H), 3.15 (d, J = 14.7 Hz, 1H), 2.99 – 2.65 (m, 2H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 159.2, 146.1, 140.8, 140.2, 130.7, 128.3, 127.0, 124.7, 124.3, 122.7 (q, J = 277.9 Hz), 119.8, 117.1, 116.8, 112.4, 82.9, 60.7 (q, J = 36.9 Hz), 43.2, 41.4, 33.0, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.68 (t, J = 8.3 Hz). HRMS m/z (ESI^+): Calculated for $C_{21}H_{18}ClF_3N_2O_3$ ($[M+H]^+$): 439.1030, found 439.1033.

2,2,2-Trifluoroethyl

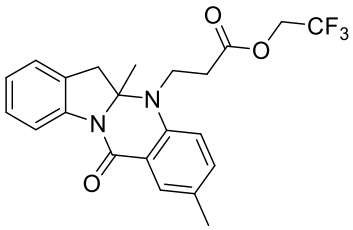
3-(3-fluoro-5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ea)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ea** (78 mg, 93%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.19 (d, J = 8.0 Hz, 1H), 8.04 (dd, J = 8.6, 6.6 Hz, 1H), 7.26 – 7.18 (m, 2H), 7.01 (ddd, J = 8.4, 7.5, 1.1 Hz, 1H), 6.59 (ddd, J = 8.4, 7.3, 2.3 Hz, 1H), 6.33 (dd, J = 11.2, 2.3 Hz, 1H), 4.62 – 4.14 (m, 2H), 3.78 – 3.35 (m, 3H), 3.14 (d, J = 14.6 Hz, 1H), 2.96 – 2.56 (m, 2H), 1.28 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 166.8 (d, J = 251.6 Hz), 159.2, 147.2 (d, J = 11.0 Hz), 140.9, 131.9 (d, J = 11.2 Hz), 128.3, 126.9, 124.7, 124.2, 122.7 (q, J = 277.1 Hz), 116.8, 114.9 (d, J = 2.2 Hz), 106.7 (d, J = 22.4 Hz), 99.6 (d, J = 27.0 Hz), 82.9, 60.7 (q, J = 36.8 Hz), 43.2, 41.6, 32.9, 21.2. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.68 (t, J = 8.6 Hz), -103.78 (dt, J = 11.6, 7.6 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{21}H_{18}F_4N_2O_3$ ([M+H]$^+$): 423.1326, found 423.1331.

2,2,2-Trifluoroethyl

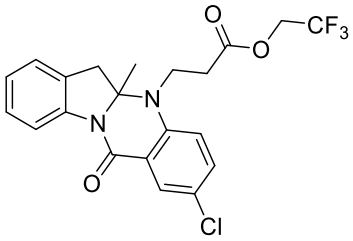
3-(2,5*a*-dimethyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3fa)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3fa** (70 mg, 84%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 2.2 Hz, 1H), 7.30 – 7.18 (m, 3H), 7.01 (ddd, J = 8.3, 7.5, 1.1 Hz, 1H), 6.55 (d, J = 8.3 Hz, 1H), 4.57 – 4.30 (m, 2H), 3.60 (d, J = 14.6 Hz, 1H), 3.55 (td, J = 6.9, 2.3 Hz, 2H), 3.12 (d, J = 14.6 Hz, 1H), 2.89 – 2.70 (m, 2H), 2.26 (s, 3H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.1, 160.2, 143.1, 141.1, 134.7, 129.5, 129.0, 128.2, 127.4, 124.7, 124.0, 122.8 (q, J = 277.8 Hz), 118.6, 116.8, 112.4, 82.6, 60.6 (q, J = 36.7 Hz), 43.3, 41.5, 33.2, 20.6, 20.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.68 (d, J = 8.3 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{22}H_{21}F_3N_2O_3$ ([M+H]$^+$): 419.1577, found 419.1582.

2,2,2-Trifluoroethyl

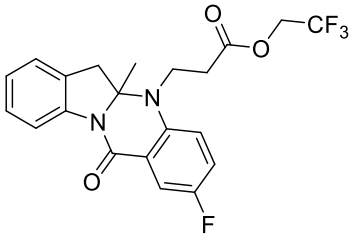
3-(2-chloro-5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ga)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ga** (59 mg, 67%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 1H), 8.01 (d, J = 2.6 Hz, 1H), 7.32 (dd, J = 8.8, 2.6 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.03 (ddd, J = 8.4, 7.5, 1.0 Hz, 1H), 6.59 (d, J = 8.8 Hz, 1H), 4.68 – 4.32 (m, 2H), 3.78 – 3.48 (m, 3H), 3.15 (d, J = 14.6 Hz, 1H), 2.92 – 2.64 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 158.8, 143.7, 140.7, 133.7, 128.9, 128.3, 127.2, 125.0, 124.7, 124.4, 122.7 (q, J = 278.1 Hz), 119.9, 116.9, 113.8, 82.8, 60.7 (q, J = 36.8 Hz), 43.2, 41.5, 33.0, 21.0. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.70 (t, J = 8.4 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{21}H_{18}ClF_3N_2O_3$ ([M+H]$^+$): 439.1030, found 439.1032.

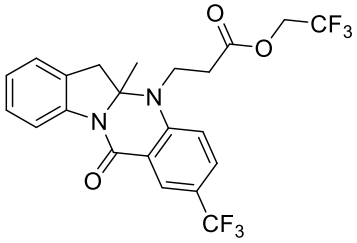
2,2,2-Trifluoroethyl

3-(2-fluoro-5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ha)



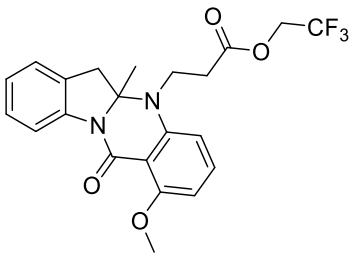
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ha** (81 mg, 96%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 1H), 7.74 (dd, J = 8.6, 3.1 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.11 (ddd, J = 8.9, 7.8, 3.1 Hz, 1H), 7.03 (ddd, J = 8.3, 7.5, 1.1 Hz, 1H), 6.60 (dd, J = 9.0, 4.0 Hz, 1H), 4.52 – 4.33 (m, 2H), 3.66 – 3.48 (m, 3H), 3.14 (d, J = 14.7 Hz, 1H), 2.87 – 2.69 (m, 2H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.9, 158.9 (d, J = 2.4 Hz), 156.7 (d, J = 239.4 Hz), 141.6 (d, J = 1.8 Hz), 140.7, 128.2, 127.3, 124.8, 124.4, 122.8 (q, J = 277.4 Hz), 120.8 (d, J = 23.2 Hz), 120.0 (d, J = 6.9 Hz), 116.8, 115.4 (d, J = 24.0 Hz), 113.7 (d, J = 7.0 Hz), 82.8, 60.6 (q, J = 36.8 Hz), 43.2, 41.7, 33.1, 20.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.69 (t, J = 8.3 Hz), -(117.29 – 128.64) (m). HRMS m/z (ESI$^+$): Calculated for $C_{21}H_{18}F_4N_2O_3$ ([M+H]$^+$): 423.1326, found 423.1328.

2,2,2-Trifluoroethyl 3-(5*a*-methyl-12-oxo-2-(trifluoromethyl)-5*a*,6-dihydroindolo[2,1-*b*] quinazolin-5(12*H*)-yl)propanoate (3ia)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ia** (87 mg, 92%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 2.3 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.60 (dd, J = 8.6, 2.3 Hz, 1H), 7.30 – 7.19 (m, 2H), 7.04 (ddd, J = 8.4, 7.5, 1.1 Hz, 1H), 6.72 (d, J = 8.6 Hz, 1H), 4.55 – 4.35 (m, 2H), 3.73 – 3.57 (m, 3H), 3.18 (d, J = 14.6 Hz, 1H), 2.93 – 2.72 (m, 2H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 158.7, 147.4, 140.6, 130.7 (q, J = 3.6 Hz), 128.4, 126.9, 126.8 (q, J = 4.8 Hz), 124.8, 124.6, 124.2 (q, J = 271.1Hz), 122.7 (q, J = 277.4 Hz), 121.4 (q, J = 33.6 Hz), 118.2, 116.9, 112.4, 82.8, 60.7 (q, J = 36.8 Hz), 43.1, 41.5, 32.9, 21.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -61.82, -73.70 (t, J = 8.4 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{22}H_{18}F_6N_2O_3$ ([M+H]$^+$): 473.1294, found 473.1296.

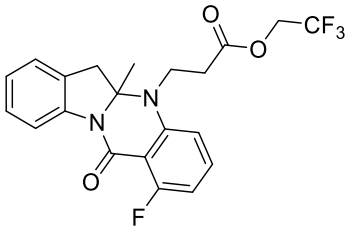
2,2,2-Trifluoroethyl 3-(1-methoxy-5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*] quin-azolin-5(12*H*)-yl)propanoate (3ja)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ja** (66 mg, 76%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 7.34 1H), 7.30 (dd, J = 8.4, 3.1 Hz, 1H), 7.22 – 7.17 (m, 2H), 6.99 (ddd, J = 8.5, 7.4, 1.1 Hz, 1H), 6.50 (d, J = 8.4 Hz, 1H), 6.27 (d, J = 8.3 Hz, 1H), 4.54 – 4.33 (m, 2H), 3.91 (s, 3H), 3.70 – 3.43 (m, 3H), 3.11 (d, J = 14.7 Hz, 1H), 3.00 – 2.63 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 162.0, 158.6, 147.6, 141.3, 134.1, 128.2, 127.1, 124.3, 123.7, 122.8 (q, J = 278.2 Hz), 117.2, 107.7, 105.2, 103.6, 82.0, 60.6 (q, J = 36.8 Hz), 56.2, 43.7, 41.8, 33.4, 20.6. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.68 (t, J = 8.3 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{22}H_{21}F_3N_2O_4$ ([M+H]$^+$): 435.1526, found 435.1557.

2,2,2-Trifluoroethyl

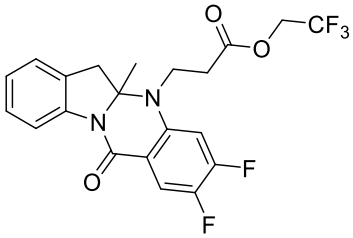
3-(1-fluoro-5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ka)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ka** (78 mg, 93%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, J = 8.0 Hz, 1H), 8.15 (d, J = 8.0 Hz, 1H), 7.25 – 7.21 (m, 2H), 7.15 (dd, J = 8.0, 1.5 Hz, 1H), 7.04 (ddd, J = 8.4, 7.5, 1.1 Hz, 1H), 6.85 (s, 1H), 4.58 – 4.25 (m, 2H), 3.81 – 3.54 (m, 3H), 3.17 (d, J = 14.6 Hz, 1H), 2.93 – 2.67 (m, 2H), 1.29 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 158.7, 145.3, 140.6, 135.4 (d, J = 32.1 Hz), 130.1, 128.4, 127.1, 124.7 (d, J = 14.5 Hz), 123.7 (q, J = 274.6 Hz), 122.7 (d, J = 280.3 Hz), 121.3 (d, J = 1.1 Hz), 116.9, 116.0 (d, J = 3.8 Hz), 109.0 (d, J = 4.1 Hz), 82.9, 60.7 (q, J = 36.8 Hz), 43.2, 41.4, 32.9, 21.3. ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.22, -73.73 (t, J = 8.3 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{21}H_{18}F_4N_2O_3$ ([M+H]$^+$):423.1326, found 423.1323.

2,2,2-Trifluoroethyl

3-(2,3-difluoro-5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3la)

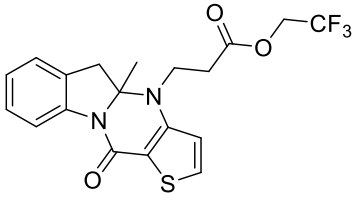


Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3la** (77 mg, 88%) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 8.0 Hz, 1H), 7.85 (dd, J = 10.3, 8.9 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.03 (ddd, J = 8.3, 7.5, 1.1 Hz, 1H), 6.45 (dd, J = 12.2, 6.1 Hz, 1H), 4.58 – 4.19 (m, 2H), 3.72 – 3.44 (m, 3H), 3.14 (d, J = 14.7 Hz, 1H), 2.93 – 2.64 (m, 2H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.7, 158.2 (d, J = 2.0 Hz), 154.1 (dd, J = 253.8, 14.0 Hz), 144.3 (dd, J = 242.1, 13.2 Hz), 142.6 (dd, J = 8.9, 1.6 Hz), 140.6, 128.4, 126.9, 124.8, 124.5, 122.7 (q, J = 277.5 Hz), 118.0 (dd, J = 19.3, 2.8 Hz), 116.8, 114.8 (dd, J = 4.9, 2.8 Hz), 101.7 (d, J = 22.5 Hz), 83.0, 60.7 (q, J = 36.9 Hz), 43.2, 41.8, 32.9, 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.69 (t, J = 8.3 Hz), -127.92 (ddd, J = 21.6, 12.0, 8.8 Hz), -148.69 (ddd, J = 22.2, 10.4, 6.2 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{21}H_{17}F_5N_2O_3$ ([M+H]$^+$): 441.1232, found 441.1235.

2,2,2-Trifluoroethyl

3-(4*a*-methyl-11-oxo-4*a*,5-dihydrothieno[3',2':4,5]pyrimido[1,2-*a*]indol-4(11*H*)-yl)propanoate

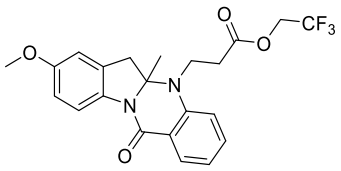
(3ma)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ma** (66 mg, 81%) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 1H), 7.44 (d, J = 5.3 Hz, 1H), 7.20 – 7.15 (m, 2H), 6.96 (ddd, J = 8.6, 7.5, 1.1 Hz, 1H), 6.57 (d, J = 5.2 Hz, 1H), 4.63 – 4.13 (m, 2H), 3.68 – 3.40 (m, 3H), 3.10 (d, J = 14.7 Hz, 1H), 2.80 – 2.77 (m, 2H), 1.30 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.8, 157.3, 150.8, 141.0, 133.4, 128.2, 126.9, 124.8, 123.4, 122.8 (q, J = 277.4 Hz), 116.1, 115.6, 111.2, 84.9, 60.6 (q, J = 36.8 Hz), 43.0, 42.3, 34.2, 19.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.67 (t, J = 8.5 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{19}H_{17}F_3N_2O_3S$ ([M+H]$^+$): 411.0985, found 411.0993.

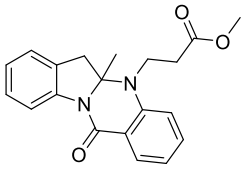
2,2,2-Trifluoroethyl

3-(8-methoxy-5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3na)



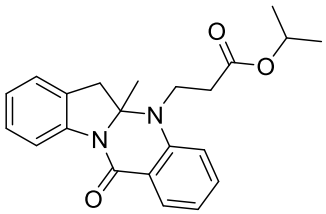
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3na** (66 mg, 76%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J = 8.6 Hz, 1H), 8.04 (dd, J = 7.7, 1.7 Hz, 1H), 7.38 (ddd, J = 8.7, 7.3, 1.7 Hz, 1H), 6.91 (ddd, J = 8.3, 7.7, 1.2 Hz, 1H), 6.80 – 6.72 (m, 2H), 6.63 (d, J = 8.3 Hz, 1H), 4.53 – 4.33 (m, 2H), 3.73 (s, 3H), 3.64 – 3.54 (m, 3H), 3.10 (d, J = 14.7 Hz, 1H), 2.93 – 2.70 (m, 2H), 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 159.3, 156.7, 145.0, 134.7, 133.7, 129.2, 128.8, 122.8 (q, J = 278.0 Hz),119.5, 118.8, 117.5, 112.6, 112.2, 111.1, 82.7, 60.6 (q, J = 36.8 Hz), 55.7, 43.5, 41.3, 33.2, 20.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.68 (t, J = 8.4 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{22}H_{21}F_3N_2O_4$ ([M+H]$^+$): 435.1526, found 435.1537.

Methyl 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ab)



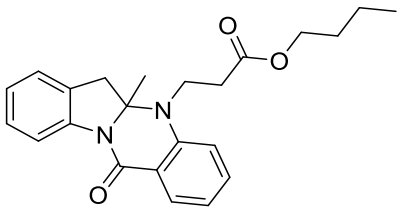
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ab** (52 mg, 77%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.0 Hz, 1H), 8.14 (dd, J = 7.7, 1.7 Hz, 1H), 7.48 (ddd, J = 8.6, 7.3, 1.8 Hz, 1H), 7.32 – 7.29 (m, 2H), 7.11 (ddd, J = 8.4, 7.5, 1.1 Hz, 1H), 7.06 – 6.95 (ddd, J = 8.5, 7.4 1.2 Hz, 1H), 6.76 (d, J = 8.2 Hz, 1H), 3.73 (s, 3H), 3.72 – 3.58 (m, 3H), 3.24 (d, J = 14.6 Hz, 1H), 2.83 (dt, J = 16.5, 7.6 Hz, 1H), 2.74 (dt, J = 16.4, 7.9 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 160.1, 145.4, 141.1, 133.9, 129.2, 128.2, 127.4, 124.7, 124.0, 119.2, 118.4, 116.8, 112.4, 82.6, 52.0, 43.4, 41.8, 33.5, 20.9. HRMS m/z (ESI$^+$): Calculated for $C_{20}H_{20}N_2O_3$ ([M+H]$^+$): 337.1547, found 337.1547.

Isopropyl 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ac)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ac** (61 mg, 84%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 7.9 Hz, 1H), 8.12 (dd, J = 7.7, 1.7 Hz, 1H), 7.46 (ddd, J = 8.6, 7.3, 1.8 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.09 (ddd, J = 8.3, 7.5, 1.1 Hz, 1H), 6.97 (ddd, J = 8.5, 7.5, 1.1 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 5.07 – 5.01 (m, 1H), 3.72 (d, J = 14.8 Hz, 1H), 3.67 – 3.58 (m, 2H), 3.22 (d, J = 14.7 Hz, 1H), 2.88 – 2.53 (m, 2H), 1.34 (s, 3H), 1.23 (dd, J = 10.1, 6.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 160.2, 145.5, 141.1, 133.9, 129.2, 128.2, 127.4, 124.7, 124.0, 119.1, 118.4, 116.8, 112.4, 82.5, 68.6, 43.4, 41.8, 34.1, 21.9, 21.8, 20.9. HRMS m/z (ESI$^+$): Calculated for $C_{22}H_{24}N_2O_3$ ([M+H]$^+$): 365.1860, found 365.1864.

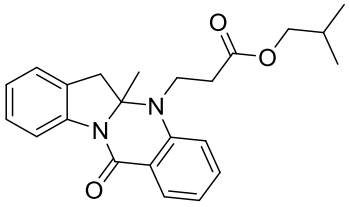
Butyl 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ad)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ad** (42 mg, 56%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.9 Hz, 1H), 8.04 (dd, J = 7.8, 1.7 Hz, 1H), 7.38 (ddd, J = 8.7, 7.3, 1.7 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.01 (ddd, J = 8.6, 7.5, 1.1 Hz, 1H), 6.89 (ddd, J = 8.4 7.5, 0.9 Hz, 1H), 6.67 (d, J = 8.4 Hz, 1H), 4.05 – 4.02 (m, 2H), 3.63 (d, J = 14.7 Hz, 1H), 3.59 – 3.49 (m, 2H), 3.14

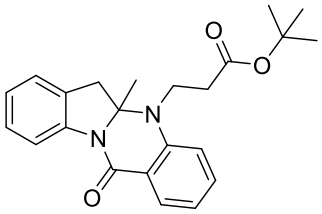
(d, *J* = 14.7 Hz, 1H), 2.83 – 2.46 (m, 2H), 1.60 – 1.45 (m, 2H), 1.33 – 1.26 (m, 2H), 1.26 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 160.1, 145.5, 141.1, 133.9, 129.2, 128.2, 127.4, 124.7, 124.0, 119.1, 118.4, 116.8, 112.4, 82.5, 64.9, 43.4, 41.8, 33.8, 30.6, 20.9, 19.1, 13.7. HRMS m/z (ESI^+): Calculated for $C_{23}H_{26}N_2O_3$ ($[M+H]^+$): 379.2016, found 379.2028.

Isobutyl 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ae)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ae** (41 mg, 54%) as red brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, *J* = 7.9 Hz, 1H), 8.05 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.39 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.04 (ddd, *J* = 8.7, 7.6, 1.1 Hz, 1H), 6.90 (ddd, *J* = 8.6, 7.5, 1.3 Hz, 1H), 6.68 (d, *J* = 8.3 Hz, 1H), 3.82 (dd, *J* = 6.7, 1.7 Hz, 2H), 3.72 – 3.48 (m, 3H), 3.14 (d, *J* = 14.7 Hz, 1H), 2.82 – 2.56 (m, 2H), 1.84 (m, 1H), 1.26 (s, 3H), 0.83 (dd, *J* = 6.7, 1.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 160.1, 145.5, 141.1, 133.9, 129.2, 128.2, 127.4, 124.7, 124.0, 119.1, 118.4, 116.8, 112.4, 82.5, 71.1, 43.4, 41.8, 33.8, 27.7, 20.9, 19.1. HRMS m/z (ESI^+): Calculated for $C_{23}H_{26}N_2O_3$ ($[M+H]^+$): 379.2016, found 379.2025.

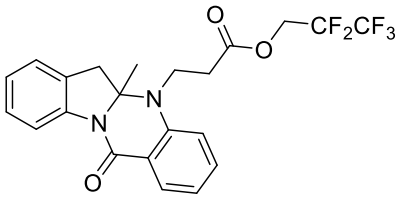
***tert*-Butyl 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3af)**



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3af** (15 mg, 20%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31 (d, *J* = 7.9 Hz, 1H), 8.12 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.46 (ddd, *J* = 8.6, 7.2, 1.7 Hz, 1H), 7.31 – 7.26 (m, 2H), 7.12 (ddd, *J* = 8.7 7.6, 1.1 Hz, 1H), 6.97 (ddd, *J* = 8.4, 7.5 Hz, 1.2 1H), 6.75 (d, *J* = 8.3 Hz, 1H), 3.70 (d, *J* = 14.7 Hz, 1H), 3.62 – 3.58 (m, 2H), 3.23 (d, *J* = 14.7 Hz, 1H), 2.73 (dt, *J* = 16.4, 6.8 Hz, 1H), 2.61 (dt, *J* = 16.1, 7.8 Hz, 1H), 1.45 (s, 9H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 160.2, 145.6, 141.1, 133.9, 129.2, 128.2, 127.4, 124.7, 124.0, 119.0, 118.3, 116.8, 112.4, 82.5, 81.4, 43.4, 41.9, 34.9, 28.1, 20.9. HRMS m/z (ESI^+): Calculated for $C_{23}H_{26}N_2O_3$ ($[M+H]^+$): 379.2016, found 379.2025.

2,2,3,3,3-Pentafluoropropyl

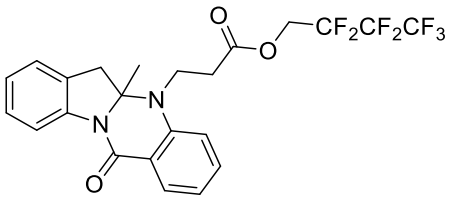
3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ag)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ag** (84 mg, 92%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.0 Hz, 1H), 8.05 (dd, J = 7.7, 1.7 Hz, 1H), 7.39 (ddd, J = 8.6, 7.5, 1.7 Hz, 1H), 7.24 - 7.19 (m, 2H), 7.02 (ddd, J = 8.4, 7.4, 1.4 Hz, 1H), 6.91 (ddd, J = 8.6, 7.5, 1.3 Hz, 1H), 6.64 (d, J = 8.3 Hz, 1H), 4.61 – 4.40 (m, 2H), 3.84 – 3.49 (m, 3H), 3.14 (d, J = 14.6 Hz, 1H), 3.01 – 2.62 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 160.0, 145.2, 141.0, 134.0, 129.4, 128.3, 127.2, 124.7, 124.1, 119.8, 119.5, 118.6, 116.8, 112.2, 111.7, 82.6, 59.4 (t, J = 27.7 Hz), 43.3, 41.4, 33.2, 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -83.79, -123.40 (t, J = 12.9 Hz). HRMS m/z (ESI^+): Calculated for $C_{22}H_{19}F_5N_2O_3$ ($[M+H]^+$): 455.1389, found 455.1419.

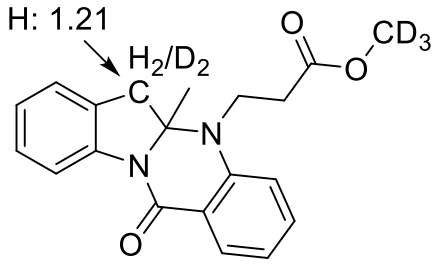
2,2,3,3,4,4,4-Heptafluorobutyl

3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ah)



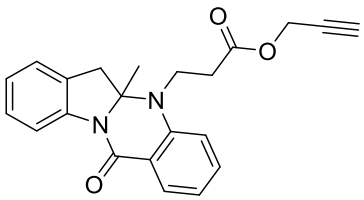
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ah** (84 mg, 83%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 7.9 Hz, 1H), 8.04 (dd, J = 7.7, 1.7 Hz, 1H), 7.37 (ddd, J = 8.7, 7.4, 1.7 Hz, 1H), 7.22 – 7.17 (m, 2H), 7.00 (ddd, J = 8.6, 7.4, 1.1 1H), 6.90 (ddd, J = 8.4, 7.5, 1.2 Hz, 1H), 6.63 (d, J = 8.3 Hz, 1H), 4.64 – 4.43 (m, 2H), 3.66 – 3.52 (m, 3H), 3.12 (d, J = 14.6 Hz, 1H), 2.88 – 2.63 (m, 2H), 1.24 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 160.0, 145.2, 141.0, 134.0, 129.3, 128.2, 127.2, 124.7, 124.1, 119.5, 118.6, 116.8, 116.6 – 115.4 (m), 113.8 (t, J = 31.1 Hz), 112.2, 111.4 (t, J = 31.1 Hz), 82.6, 59.5 (t, J = 26.9 Hz), 43.3, 41.4, 33.2, 20.9. ^{19}F NMR (376 MHz, $CDCl_3$) δ -80.82 (t, J = 9.2 Hz), -120.43 (td, J = 9.3, 4.6 Hz), -127.60 (d, J = 3.8 Hz). HRMS m/z (ESI^+): Calculated for $C_{23}H_{19}F_7N_2O_3$ ($[M+H]^+$): 505.1357, found 505.1382.

Methyl-d3 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate(3ai)



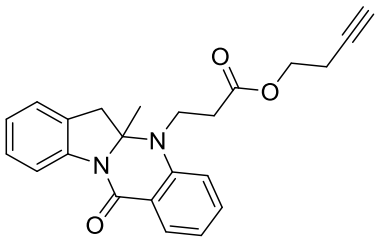
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ai** (56 mg, 82%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, J = 7.9 Hz, 1H), 8.14 (dd, J = 7.7, 1.7 Hz, 1H), 7.49 (ddd, J = 8.6, 7.2, 1.7 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.12 (ddd, J = 8.6, 7.4, 1.1 Hz, 1H), 7.00 (ddd, J = 8.7, 7.5, 0.9 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 3.77 – 3.70 (m, 0.56H), 3.69 – 3.59 (m, 2H), 3.30 – 3.18 (m, 0.65H), 2.84 (dt, J = 16.6, 7.6, Hz, 1H), 2.74 (dt, J = 16.4, 7.9 Hz, 1H), 1.36 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.0, 160.1, 145.4, 141.1, 133.9, 129.2, 128.2, 127.3, 124.7, 124.0, 119.2, 118.5, 116.8, 112.4, 82.5, 43.4, 41.8, 33.5, 20.9, 20.8. HRMS m/z (ESI^+): Calculated for: **D3**: $C_{20}H_{18}D_3N_2O_3$ ($[M+H]^+$): 340.1735, found 340.1730, **D4**: $C_{20}H_{17}D_4N_2O_3$ ($[M+H]^+$): 341.1798, found 341.1795, **D5**: $C_{20}H_{16}D_5N_2O_3$ ($[M+H]^+$): 342.1861, found 342.1837.

Prop-2-yn-1-yl 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3aj)



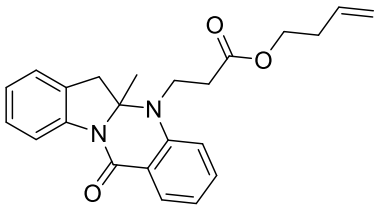
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3aj** (62 mg, 86%) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, J = 8.2 Hz, 1H), 8.04 (dd, J = 7.7, 1.7 Hz, 1H), 7.38 (ddd, J = 8.3, 7.3, 1.7 Hz, 1H), 7.23 – 7.19 (m, 2H), 7.01 (ddd, J = 8.6, 7.5, 1.1 Hz, 1H), 6.90 (ddd, J = 8.5, 7.5, 0.9 Hz, 1H), 6.65 (d, J = 8.4, 1H), 4.67 – 4.58 (m, 2H), 3.63 (d, J = 14.7 Hz, 1H), 3.60 – 3.54 (m, 2H), 3.14 (d, J = 14.7 Hz, 1H), 2.85 – 2.62 (m, 2H), 2.34 (t, J = 2.5 Hz, 1H). 1.25 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.8, 160.1, 145.3, 141.0, 133.9, 129.3, 128.2, 127.4, 124.7, 124.1, 119.3, 118.6, 116.8, 112.4, 82.6, 77.2, 75.3, 52.4, 43.4, 41.7, 33.5, 20.9. HRMS m/z (ESI^+): Calculated for $C_{22}H_{20}N_2O_3$ ($[M+H]^+$): 361.1547, found 361.1567.

But-3-yn-1-yl 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3ak)



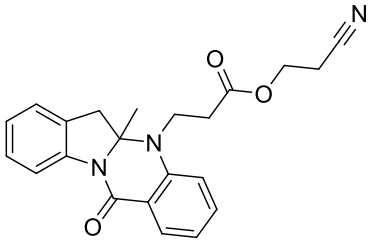
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ak** (70 mg, 93%) as light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 8.0 Hz, 1H), 8.05 (dd, J = 7.7, 1.7 Hz, 1H), 7.39 (ddd, J = 8.8, 7.3, 1.7 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.02 (ddd, J = 8.6, 7.5, 1.1 Hz, 1H), 6.90 (ddd, J = 8.7, 7.5 1.1 Hz, 1H), 6.67 (d, J = 8.3 Hz, 1H), 4.15 (t, J = 6.7 Hz, 2H), 3.63 (d, J = 14.7 Hz, 1H), 3.60 – 3.54 (m, 2H), 3.15 (d, J = 14.7 Hz, 1H), 2.83 – 2.62 (m, 2H), 2.46 (td, J = 6.7, 2.6 Hz, 2H), 1.91 (t, J = 2.7 Hz, 1H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.3, 160.1, 145.4, 141.1, 133.9, 129.3, 128.2, 127.3, 124.7, 124.1, 119.2, 118.5, 116.8, 112.4, 82.6, 79.8, 70.1, 62.6, 43.4, 41.7, 33.7, 20.9, 19.0. HRMS m/z (ESI$^+$): Calculated for $C_{23}H_{22}N_2O_3$ ([M+H]$^+$): 375.1703, found 375.1712.

But-3-en-1-yl 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3al)



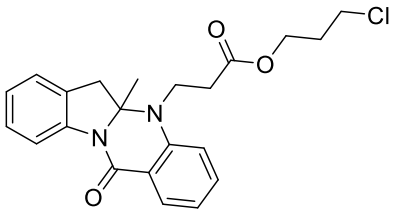
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3al** (48 mg, 63%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.9, 1H), 8.05 (dd, J = 7.7, 1.7 Hz, 1H), 7.38 (ddd, J = 8.5, 7.3, 1.7 Hz, 1H), 7.24 – 7.19 (m, 2H), 7.01 (ddd, J = 8.7, 7.5, 1.1 Hz, 1H), 6.90 (ddd, J = 8.6, 7.5, 0.9 Hz, 1H), 6.67 (d, J = 8.3 Hz, 1H), 5.73 – 5.63(m, 1H), 5.10 – 4.96 (m, 2H), 4.10 (t, J = 6.7 Hz, 2H), 3.62 (d, J = 14.7 Hz, 1H), 3.60 – 3.53 (m, 2H), 3.14 (d, J = 14.7 Hz, 1H), 2.80 – 2.58 (m, 2H), 2.34 – 2.28 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.6, 160.1, 145.4, 141.1, 133.9, 133.7, 129.2, 128.2, 127.3, 124.7, 124.0, 119.2, 118.4, 117.5, 116.8, 112.4, 82.5, 64.0, 43.4, 41.8, 33.8, 33.0, 20.9. HRMS m/z (ESI$^+$): Calculated for $C_{23}H_{24}N_2O_3$ ([M+H]$^+$): 377.1860, found 377.1869.

2-Cyanoethyl 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3am)



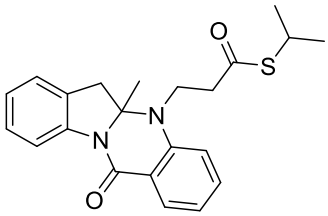
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3am** (62 mg, 83%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 8.5, 1.1 Hz, 1H), 8.05 (dd, J = 7.7, 1.7 Hz, 1H), 7.40 (ddd, J = 8.6, 7.3, 1.7 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.02 (ddd, J = 8.6, 7.4, 1.1 Hz, 1H), 6.91 (ddd, J = 8.7, 7.5, 0.9 Hz, 1H), 6.66 (d, J = 8.1 Hz, 1H), 4.31 – 4.17 (m, 2H), 3.63 (d, J = 14.7 Hz, 1H), 3.60 – 3.55 (m, 2H), 3.15 (d, J = 14.7 Hz, 1H), 2.84 – 2.66 (m, 2H), 2.63 (t, J = 6.3 Hz, 2H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.0, 160.1, 145.3, 141.0, 134.0, 129.3, 128.2, 127.3, 124.7, 124.1, 119.4, 118.6, 116.7, 116.6, 112.4, 82.6, 59.1, 43.3, 41.5, 33.4, 20.9, 18.0. HRMS m/z (ESI$^+$): Calculated for $C_{22}H_{21}N_3O_3$ ([M+H]$^+$): 376.1656, found 376.1660.

3-Chloropropyl 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoate (3an)



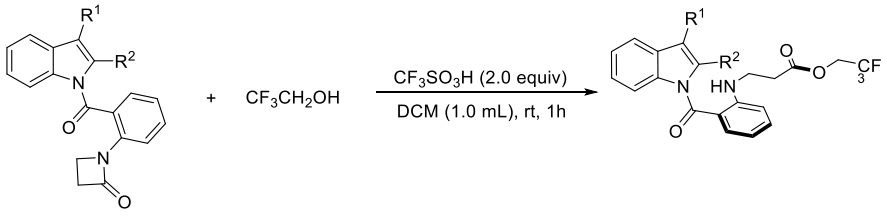
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3an** (45 mg, 56%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.23 (d, J = 7.8 Hz, 1H), 8.05 (dd, J = 7.7, 1.7 Hz, 1H), 7.39 (ddd, J = 8.6, 7.3, 1.7 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.02 (ddd, J = 8.6, 7.5, 1.1 Hz, 1H), 6.90 (ddd, J = 8.4, 7.6, 0.9 Hz, 1H), 6.66 (d, J = 8.2 Hz, 1H), 4.21 -4.18 (m, 2H), 3.65 – 3.55 (m, 3H), 3.49 (t, J = 6.3 Hz, 2H), 3.15 (d, J = 14.7 Hz, 1H), 2.88 – 2.44 (m, 2H), 2.00 – 1.97 (m, 2H), 1.26 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.5, 160.1, 145.4, 141.0, 133.9, 129.3, 128.2, 127.3, 124.7, 124.1, 119.3, 118.5, 116.8, 112.4, 82.6, 61.7, 43.4, 41.7, 41.1, 33.6, 31.4, 20.9. HRMS m/z (ESI$^+$): Calculated for $C_{22}H_{23}ClN_2O_3$ ([M+H]$^+$): 399.1470, found 399.1666.

S-isopropyl 3-(5*a*-methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanethioate (3ao)

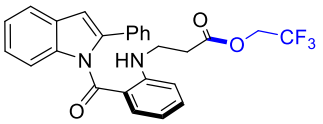


Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **3ao** (59 mg, 78%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, J = 7.8, 1.3 Hz, 1H), 8.04 (dd, J = 7.7, 1.7 Hz, 1H), 7.39 (ddd, J = 8.6, 7.3, 1.7 Hz, 1H), 7.22 – 7.18 (m, 2H), 7.00 (ddd, J = 8.6, 7.5, 1.1 Hz, 1H), 6.89 (ddd, J = 8.5, 7.5, 0.9 Hz, 1H), 6.67 (d, J = 8.3 Hz, 1H), 3.64 – 3.59 (m, 1H) 3.58 – 3.48 (m, 3H), 3.13 (d, J = 14.7 Hz, 1H), 2.93 – 2.76 (m, 2H), 1.25 (s, 3H), 1.21 (dd, J = 12.6, 6.9 Hz, 6H) . ^{13}C NMR (100 MHz, $CDCl_3$) δ 197.6, 160.1, 145.3, 141.1, 134.0, 129.2, 128.2, 127.3, 124.7, 124.0, 119.2, 118.3, 116.8, 112.3, 82.5, 43.3, 43.0, 42.0, 35.1, 22.9, 22.8, 21.0. HRMS m/z (ESI$^+$): Calculated for $C_{22}H_{24}N_2O_2S$ ([M+H]$^+$): 381.1631, found 381.1639.

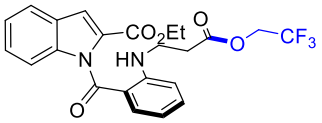
4 Ring-Opening of Indole Derivatives and Characterization Data



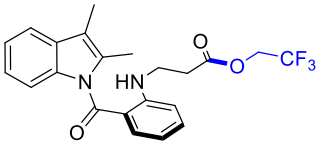
Under argon, charge a 10 mL flame-dried resealable Schlenk tube with **1** (0.2 mmol) and R^3OH (3.0 equiv) in anhydrous DCM (1.0 mL). The reaction mixture was cooled to 0 ^{o}C and stirred for 5 min. Then CF_3SO_3H (2.0 equiv) was added dropwise to the above mixture at 0 ^{o}C and stirred for further 5 min. Afterwards, the reaction was warmed to room temperature and stirred for 1 h. The reaction was quenched carefully with saturated solution of Na_2CO_3, diluted with water. The aqueous was extracted with DCM (3 times), the combined organic layers were washed with brine, dried over sodium sulfate, filtered and concentrated under reduced pressure. The crude product was purified by silica column chromatography eluting with the ethyl acetate/petroleum ether.



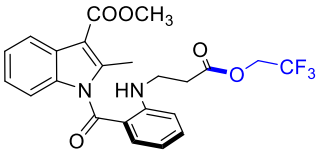
S-4oa: 74%



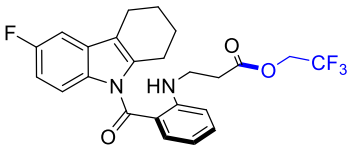
S-4pa: 75%



S-4qa: 88%

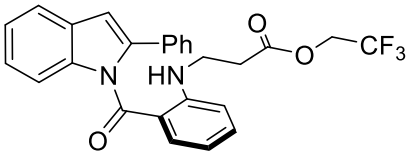


S-4ra: 94.2%



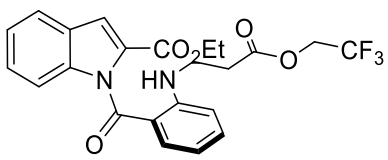
S-4sa: 89%

2,2,2-Trifluoroethyl 3-((2-(2-phenyl-1*H*-indole-1-carbonyl)phenyl)amino)propanoate (S-4oa)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **4oa** (69 mg, 74%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (dd, J = 5.9, 2.1 Hz, 1H), 7.54 (dd, J = 7.4, 1.5 Hz, 1H), 7.37 – 7.20 (m, 5H), 7.19 – 7.03 (m, 5H), 6.71 (s, 1H), 6.64 (d, J = 8.5 Hz, 1H), 6.40 (dd, J = 7.5, 2.3 Hz, 1H), 4.39 (q, J = 8.4 Hz, 2H), 3.53 (q, J = 6.5 Hz, 2H), 2.69 (t, J = 6.8 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.7, 170.0, 150.8, 141.6, 138.3, 135.7, 134.1, 133.0, 129.3, 128.4, 127.8, 127.6, 123.6, 122.9 (q, J = 277.1 Hz), 122.5, 120.8, 115.6, 115.4, 113.3, 111.2, 108.3, 60.5 (q, J = 36.7 Hz), 38.2, 33.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ -73.68 (t, J = 8.1 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{26}H_{21}F_3N_2O_3$ ([M+H]$^+$): 467.1577, Found 467.1600.

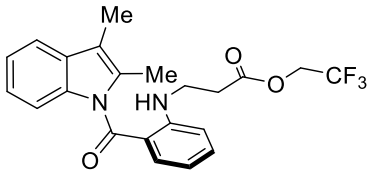
Ethyl 1-(2-((3-oxo-3-(2,2,2-trifluoroethoxy)propyl)amino)benzoyl)-1*H*-indole-2-carboxylate (S-4pa)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **4pa** (69.5 mg, 75%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (dd, J = 5.8, 2.1 Hz, 1H), 7.75 – 7.56 (m, 1H), 7.40 – 7.28 (m, 3H), 7.28 – 7.20 (m, 1H), 7.16 (t, J = 7.1 Hz, 1H), 7.04 (dd, J = 8.0, 1.6

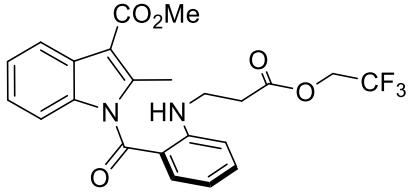
Hz, 1H), 6.74 (d, *J* = 8.6 Hz, 1H), 6.58 – 6.36 (m, 1H), 4.45 (q, J = 8.4 Hz, 2H), 4.08 (q, *J* = 7.1 Hz, 2H), 3.62 (q, *J* = 6.6 Hz, 2H), 2.79 (t, *J* = 6.8 Hz, 2H), 1.12 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 171.2, 170.1, 161.0, 151.1, 138.8, 136.0, 133.0, 130.8, 127.0, 126.5, 122.9 (q, *J* = 277.7 Hz), 122.6, 120.1, 115.6, 115.3, 114.0, 113.1, 111.3, 61.2, 60.5 (q, *J* = 36.7 Hz), 38.2, 33.5, 14.0. ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -73.70 (d, *J* = 8.3 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{23}H_{21}F_3N_2O_5$ ([M+H]$^+$): 463.1475, Found 463.1463.

2,2,2-Trifluoroethyl 3-((2-(2,3-dimethyl-1*H*-indole-1-carbonyl)phenyl)amino)propanoate (S-4qa)



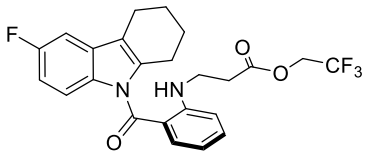
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **4qa** (74 mg, 88%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 (dd, *J* = 15.0, 7.5 Hz, 3H), 7.21 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.07 (ddd, *J* = 7.7, 6.0, 1.6 Hz, 1H), 7.02 – 6.90 (m, 2H), 6.76 (d, *J* = 8.5 Hz, 1H), 6.51 (t, *J* = 7.5 Hz, 1H), 4.42 (q, *J* = 8.4 Hz, 2H), 3.57 (d, *J* = 7.3 Hz, 2H), 2.74 (td, *J* = 6.8, 1.5 Hz, 2H), 2.25 (s, 3H), 2.16 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) *δ* 171.1, 170.2, 150.1, 136.5, 135.1, 134.0, 133.1, 130.5, 122.9 (q, *J* = 278.5 Hz), 122.6, 121.8, 118.0, 116.1, 115.6, 114.1, 113.5, 111.4, 60.5 (q, *J* = 36.8 Hz), 38.3, 33.5, 12.5, 8.7. ^{19}F NMR (376 MHz, $CDCl_3$) *δ* -73.68 (d, *J* = 8.4 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{22}H_{21}F_3N_2O_3$ ([M+H]$^+$): 419.1577, Found 419.1602.

Methyl 2-methyl-1-(2-((3-oxo-3-(2,2,2-trifluoroethoxy)propyl)amino)benzoyl)-1*H*-indole-3-carbo xylate (S-4ra)



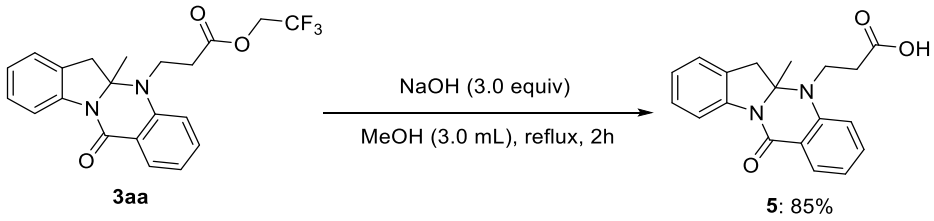
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **4ra** (87 mg, 94%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.25 (dd, *J* = 5.9, 1.8 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.50 (ddd, *J* = 8.6, 7.0, 1.6 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.18 – 7.10 (m, 2H), 7.08 (d, *J* = 8.3 Hz, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.56 (t, *J* = 7.6 Hz, 1H), 4.56 (q, *J* = 8.4 Hz, 2H), 4.00 (s, 3H), 3.75 (q, *J* = 6.5 Hz, 2H), 2.90 (t, *J* = 6.8 Hz, 2H), 2.73 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 171.2, 170.0, 166.1, 151.8, 145.1, 137.0, 136.2, 134.3, 126.6, 123.3, 122.9, 122.9 (q, *J* = 273.2 Hz) 121.5, 115.8, 113.6, 112.3, 111.7, 108.1, 60.6 (q, *J* = 36.7 Hz), 51.1, 38.2, 33.4, 13.8. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.70 (t, *J* = 8.5 Hz). HRMS m/z (ESI$^+$): Calculated for $C_{23}H_{21}F_3N_2O_5$ ([M+H]$^+$): 463.1475, Found 463.1463.

2,2,2-Trifluoroethyl 3-((2-(6-fluoro-2,3,4,9-tetrahydro-1*H*-carbazole-9-carbonyl)phenyl)amino)propanoate (S-4sa)



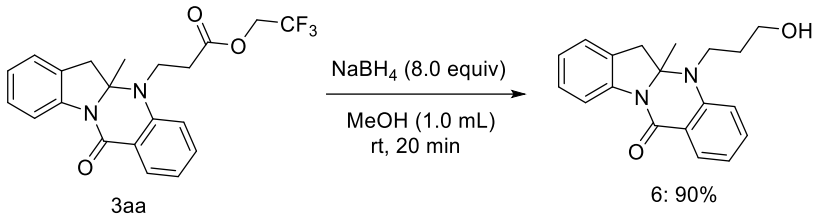
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **4sa** (82 mg, 89%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (ddd, *J* = 8.7, 7.1, 1.6 Hz, 1H), 7.33 – 7.28 (m, 1H), 7.18 (dd, *J* = 9.0, 4.4 Hz, 1H), 7.08 (td, *J* = 8.3, 3.9 Hz, 2H), 6.87 – 6.79 (m, 2H), 6.67 – 6.62 (m, 1H), 4.52 (qd, *J* = 8.4, 1.6 Hz, 2H), 3.64 (q, *J* = 6.4 Hz, 2H), 2.83 (t, *J* = 6.7 Hz, 2H), 2.73 (s, 1H), 2.67 (dq, *J* = 6.4, 3.2, 2.3 Hz, 2H), 2.52 (s, 1H), 1.93 – 1.86 (m, 2H), 1.82 (ddp, *J* = 9.1, 5.9, 3.1, 2.5 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.2, 169.1, 158.1 (d, *J* = 238.6 Hz), 148.6, 136.9, 133.8, 132.3, 131.9, 129.7 (d, *J* = 9.6 Hz), 121.8 (q, *J* = 277.3 Hz), 115.7 (d, *J* = 3.9 Hz), 115.2, 114.6, 113.9 (d, *J* = 9.1 Hz), 110.4, 109.3 (d, *J* = 25.1 Hz), 102.4 (d, *J* = 23.5 Hz), 59.4 (q, *J* = 36.8 Hz), 37.3, 32.4, 24.2, 22.3, 21.3, 20.0. ^{19}F NMR (376 MHz, Chloroform-*d*) δ -73.73, -121.39 (dt, *J* = 9.0, 4.5 Hz). HRMS m/z (ESI^+): Calculated for $C_{24}H_{22}F_4N_2O_3$ ($[M+H]^+$): 463.1639, Found 463.1631.

5 Derivatization experiments and Characterization Data

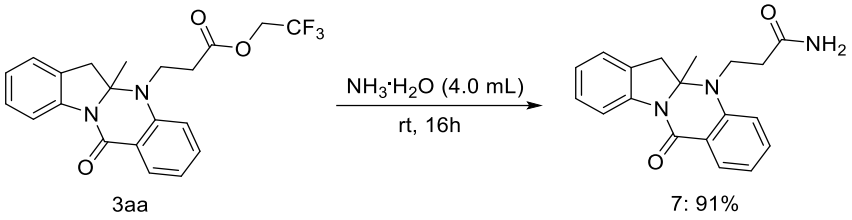


3aa **5**: 85%

To a solution of **3aa** (80.9 mg, 0.2 mmol) in MeOH (3.0 mL) was added NaOH (3.0 equiv, 0.6 mmol, 24 mg), then heated to reflux for 2 h. The reaction was cooled to room temperature. The residue was added water, then the water layer was adjust to pH = 3-4 with 1M HCl and extracted with EtOAc (3 times). The combined EtOAc layer was washed with brine, dried with Na_2SO_4 and concentrated. Purified by column chromatography (PE/EA = 2:1) to afford desired acid 5 (55 mg, 85% yield).

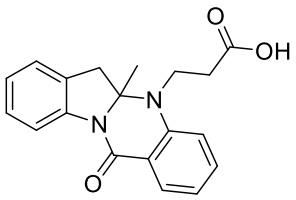


To a solution of **3aa** (80.9 mg, 0.2 mmol) in MeOH (1.0 mL) was added $NaBH_4$ (8.0 equiv, 1.6 mmol, 60.5 mg) at room temperature and reacted at room temperature for 20 min. the reaction reached completion according to the TLC analysis. The residue was added water and extracted with EtOAc (3 times). The combined EtOAc layer was washed with brine, dried with Na_2SO_4 and concentrated. Purified by silica gel column chromatography (PE/EA = 5:1) to afford **6** (55 mg, 90% yield).



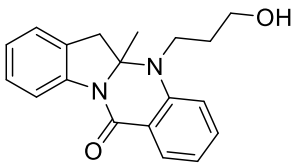
The **3aa** (80.9 mg, 0.2 mmol) was added to $NH_3.H_2O$ (4.0 mL) and stir for 16 hours at room temperature. After the reaction reached completion according to the TLC analysis. The residue was extracted with EtOAc (3 times). The combine EtOAc layer was washed with brine, dried with Na_2SO_4 and concentrated. Purified by silica gel column chromatography (PE/EA = 2:1) to afford **7** (58 mg, 91% yield).

3-(5*a*-Methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propanoic acid (5)



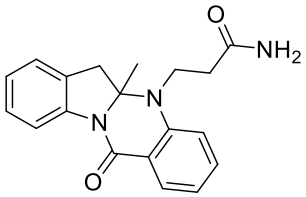
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **5** (55 mg, 85%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.96 (s, 1H), 8.30 (d, J = 8.0 Hz, 1H), 8.12 (dd, J = 7.8, 1.6 Hz, 1H), 7.45 (ddd, J = 8.9, 7.8, 1.7 Hz, 1H), 7.34 – 7.26 (m, 2H), 7.09 (ddd, J = 8.6, 7.4, 1.3 Hz, 1H), 6.97 (ddd, J = 8.5, 7.5, 1.3 Hz, 1H), 6.74 (d, J = 8.3 Hz, 1H), 3.73 – 3.58 (m, 3H), 3.21 (d, J = 14.6 Hz, 1H), 2.86 (dt, J = 16.8, 6.8 Hz, 1H), 2.75 (dt, J = 16.4, 7.8 Hz, 1H), 1.33 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 176.1, 160.4, 145.4, 140.9, 134.2, 129.3, 128.3, 127.4, 124.7, 124.3, 119.3, 118.3, 117.0, 112.4, 82.6, 43.3, 41.6, 33.5, 20.8. HRMS m/z (ESI$^+$): Calculated for $C_{19}H_{18}N_2O_3$ ([M+H]$^+$): 323.1391, found 323.1394.

5-(3-Hydroxypropyl)-5*a*-methyl-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-12(5*H*)-one (6)



Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **6** (55 mg, 90%) as light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, J = 8.0 Hz, 1H), 8.04 (dd, J = 7.7, 1.7 Hz, 1H), 7.37 (ddd, J = 8.7, 7.3, 1.7 Hz, 1H), 7.27 – 7.19 (m, 2H), 7.02 (ddd, J = 8.6, 7.5, 1.1 Hz, 1H), 6.87 (ddd, J = 8.7, 7.5, 1.1 Hz, 1H), 6.75 (d, J = 8.3 Hz, 1H), 3.76 – 3.70 (m, 2H), 3.62 (d, J = 14.7 Hz, 1H), 3.48 – 3.27 (m, 2H), 3.13 (d, J = 14.8 Hz, 1H), 1.99 – 1.81 (m, 2H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.6, 146.2, 141.0, 134.0, 128.9, 128.1, 127.6, 124.8, 124.1, 118.6, 117.9, 116.7, 112.9, 82.6, 59.7, 43.4, 43.0, 31.3, 20.7. HRMS m/z (ESI$^+$): Calculated for $C_{19}H_{20}N_2O_2$ ([M+H]$^+$): 309.1598, found 309.1606.

3-(5*a*-Methyl-12-oxo-5*a*,6-dihydroindolo[2,1-*b*]quinazolin-5(12*H*)-yl)propenamide (7)



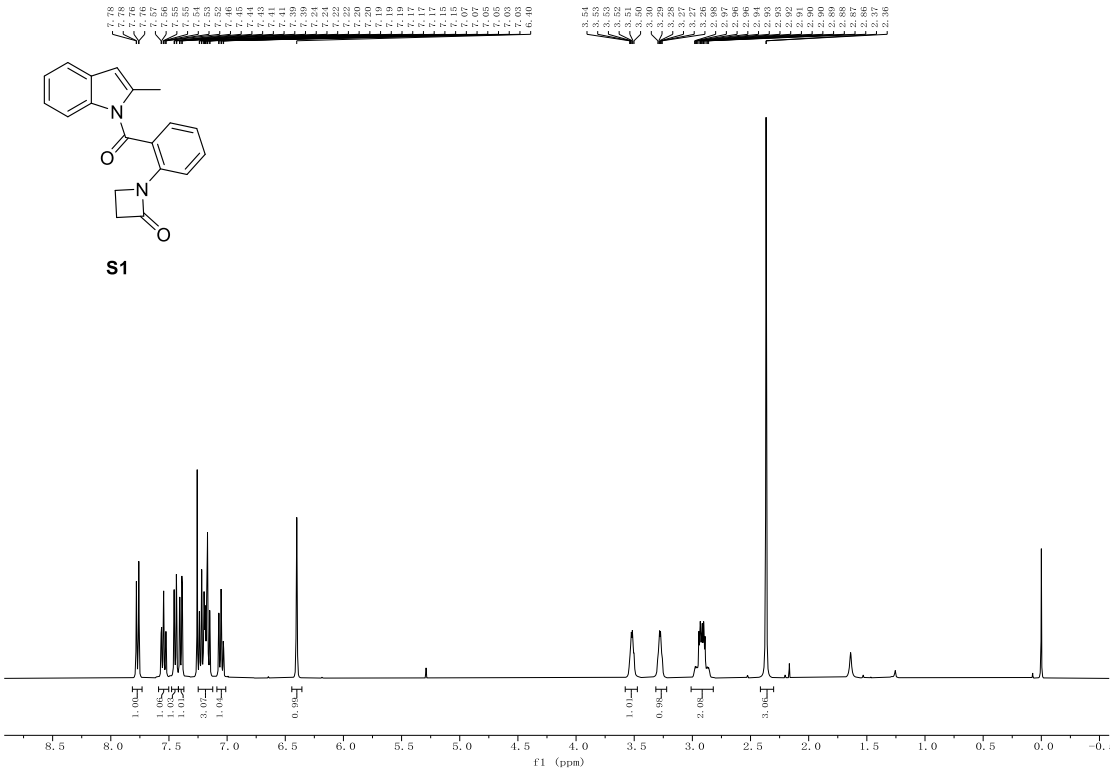
Purified by silica gel column chromatography (EtOAc/petroleum ether: 1:5) afforded **7** (58 mg, 91%) as white solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.0 Hz, 1H), 8.10 (dd, J = 7.7, 1.7 Hz, 1H), 7.42 (ddd, J = 8.8, 7.4, 1.7 Hz, 1H), 7.33 – 7.25 (m, 2H), 7.09 (ddd, J = 8.7, 7.5, 1.1 Hz, 1H), 6.96 (ddd, J = 8.6, 7.5, 0.9 Hz, 1H), 6.73 (d, J = 8.2 Hz, 1H), 5.75 (s, 1H), 5.47 (s, 1H), 3.87 – 3.46 (m, 3H), 3.19 (d, J = 14.8 Hz, 1H), 2.77 – 2.42 (m, 2H), 1.31 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.8, 160.2, 145.5, 140.9, 134.0, 129.2, 128.1, 127.6, 124.8, 124.1, 119.2, 118.5, 116.7, 112.4, 82.6, 43.4, 42.0, 34.7, 20.8. HRMS m/z (ESI$^+$): Calculated for $C_{19}H_{19}N_3O_2$ ([M+H]$^+$): 322.1550, found 322.1551.

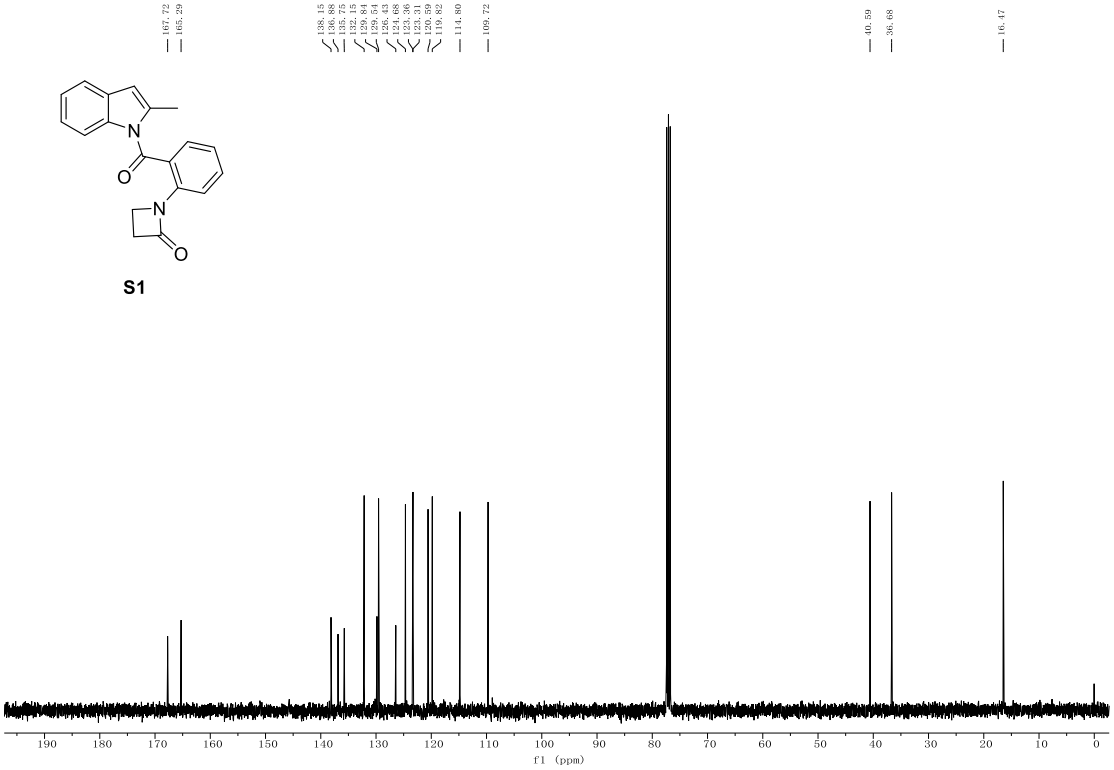
Reference:

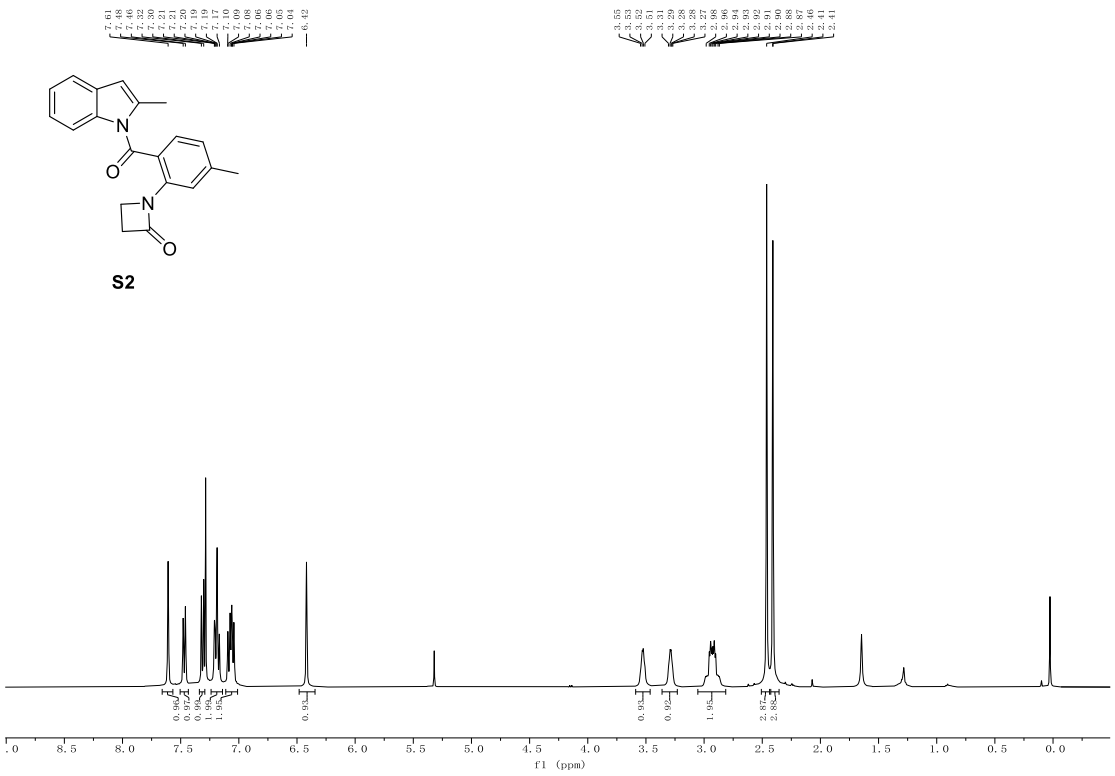
1. Shen, C.; Liu, R. R.; Fan, R. J.; Li, Y. L.; Xu, T. F.; Gao, J. R.; Jia, Y. X., Enantioselective Arylative Dearomatization of Indoles via Pd-Catalyzed Intramolecular Reductive Heck Reactions. *J. Am. Chem. Soc.* **2015,** *137*, 4936-4939.

2. Wang, J.; Liu, Y.; Xiong, Z.; Zhong, L.; Ding, S.; Li, L.; Zhao, H.; Chen, C.; Shang, Y., Palladium-catalysed dearomative aryl/cycloimidoylation of indoles. *Chem. Commun*. **2020,** *56*, 3249-3252.

6 ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra



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7.20
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7.17
7.10
7.09
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7.06
7.05
7.05
7.04
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3.55
3.53
3.52
3.51
3.31
3.29
3.28
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3.27
2.98
2.96
2.94
2.93
2.92
2.91
2.90
2.88
2.87
2.46
2.41
2.41
0.96
0.97
0.96
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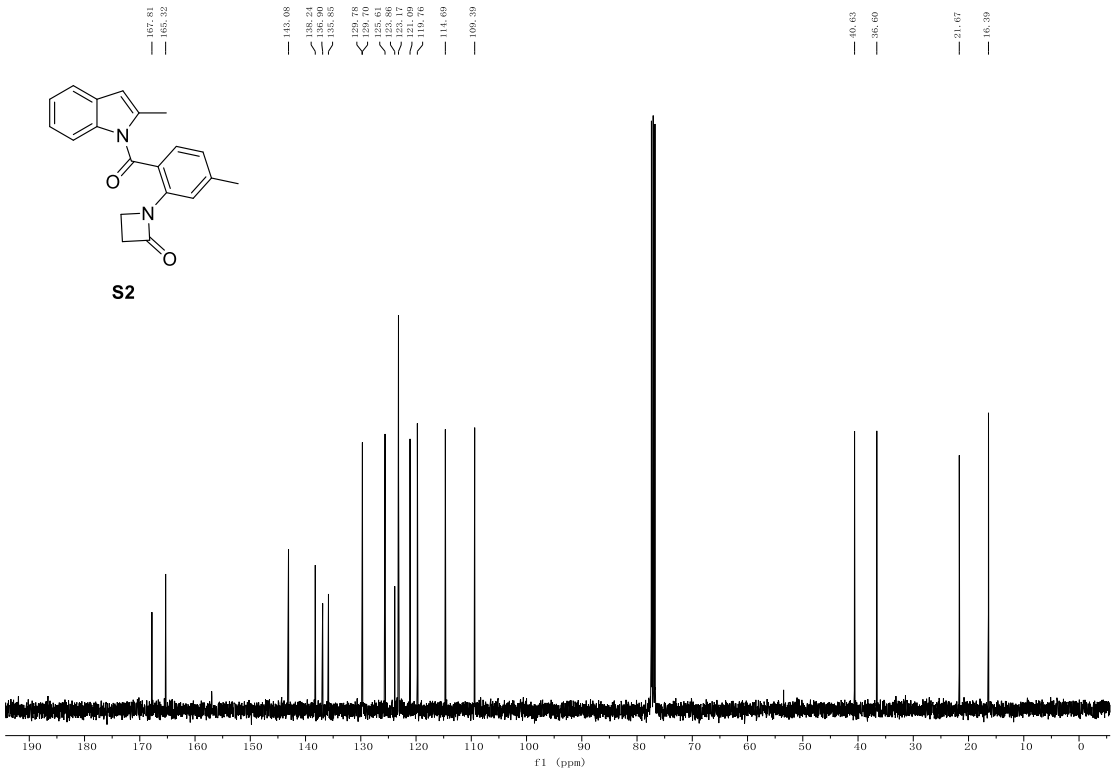
1.95
0.94
0.94
0.92
1.95
2.87
2.88
f1 (ppm)

S2


167.81
165.32
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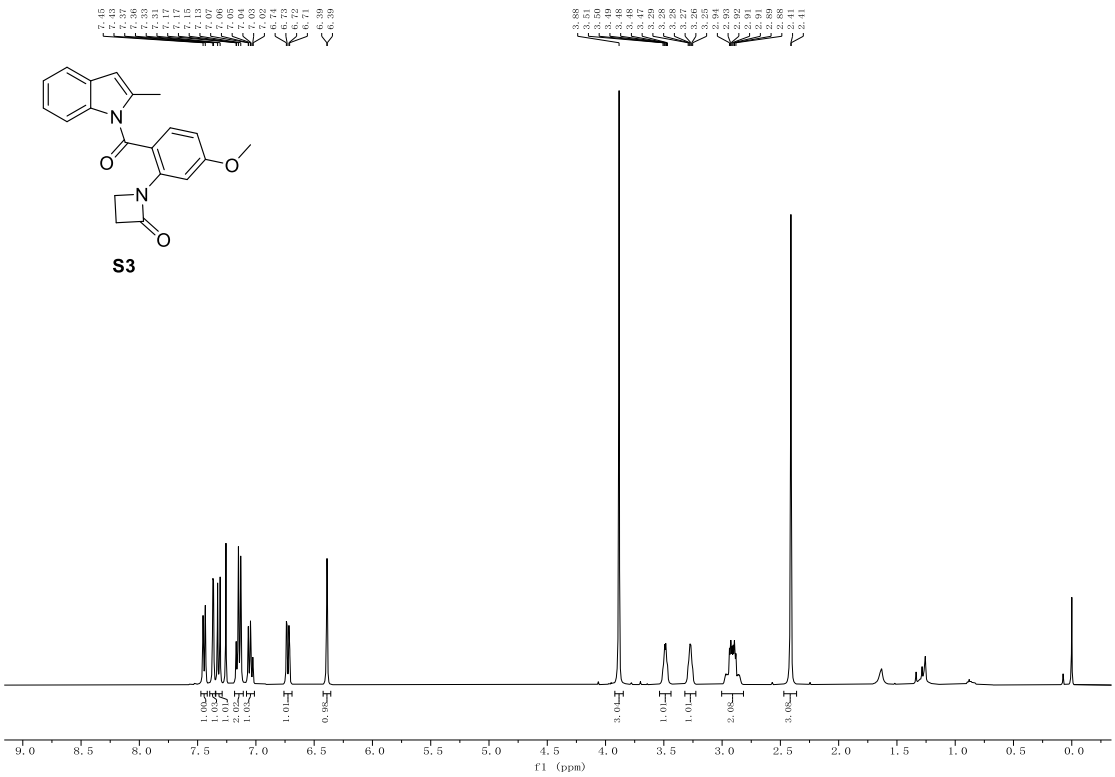
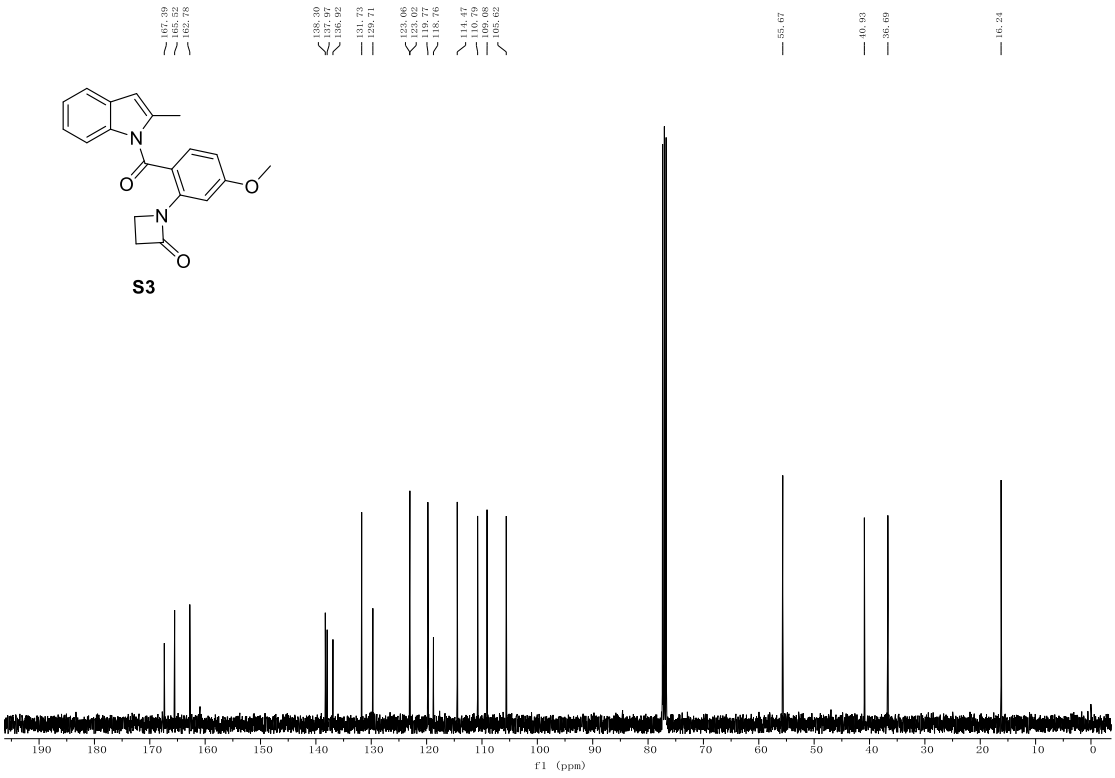
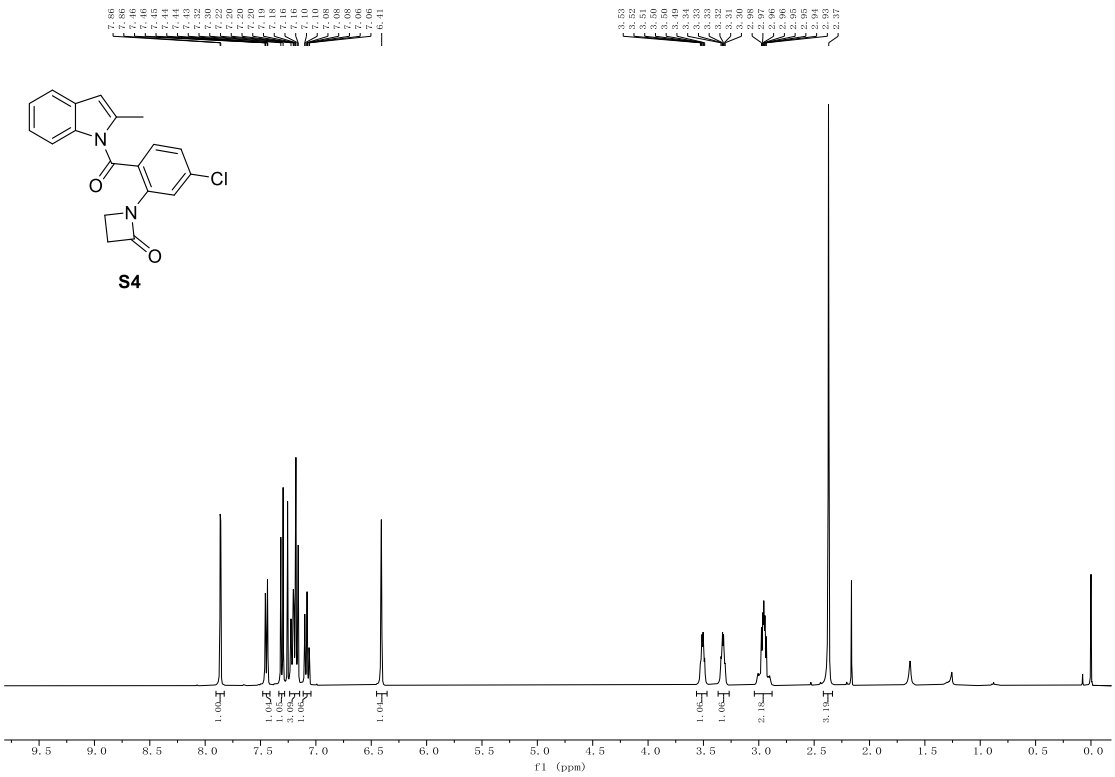
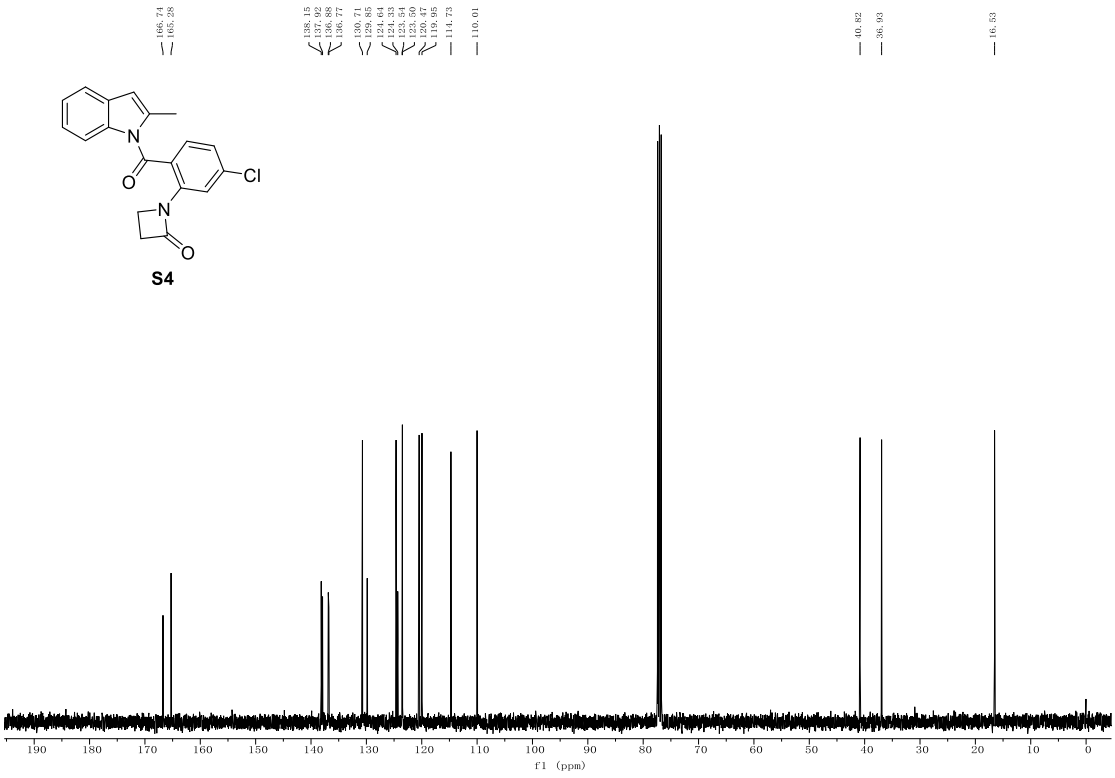
138.24
136.90
135.85
129.78
129.70
125.61
123.86
123.17
121.09
110.76
114.69
109.39
40.63
36.60
21.67
16.39
f1 (ppm)

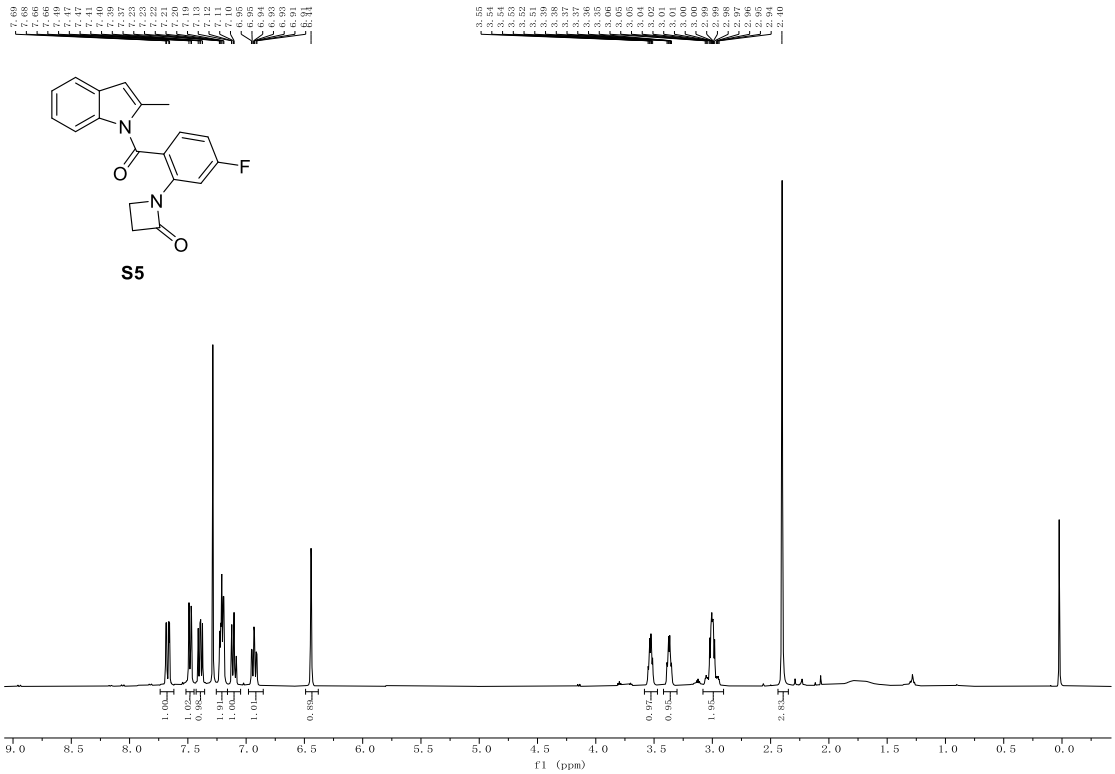
S2

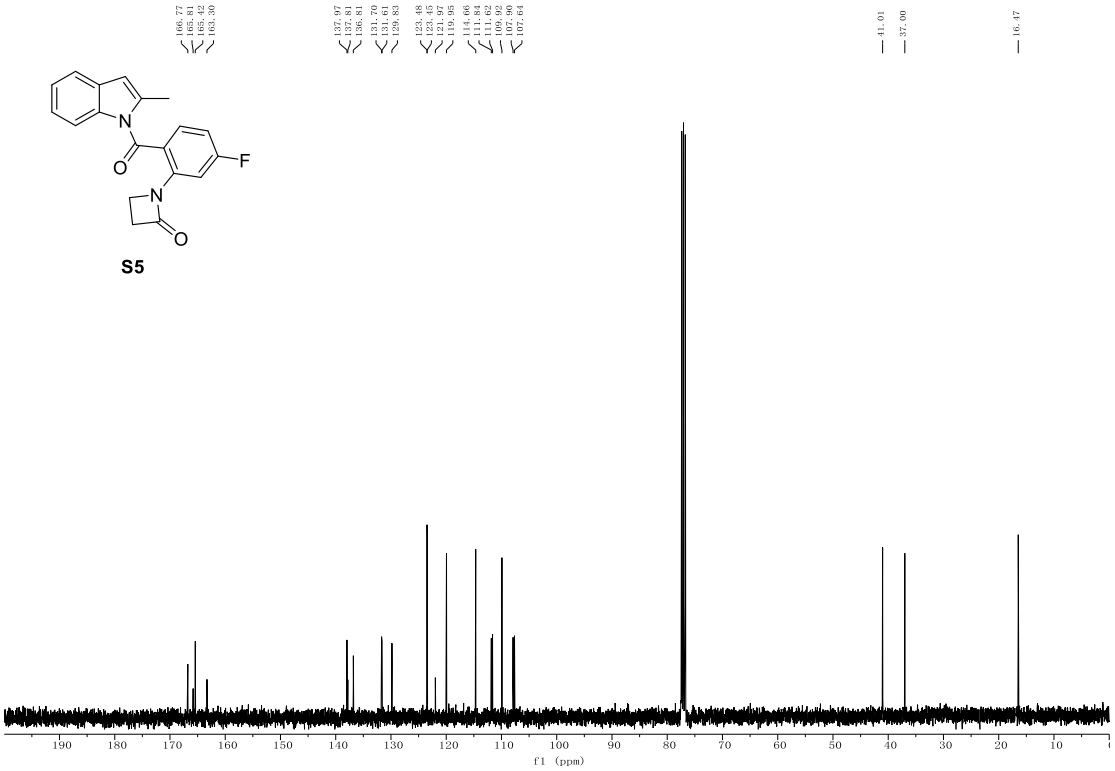

S3
f1 (ppm)

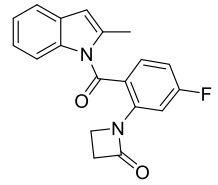

S3
f1 (ppm)


Cl
S4
f1 (ppm)

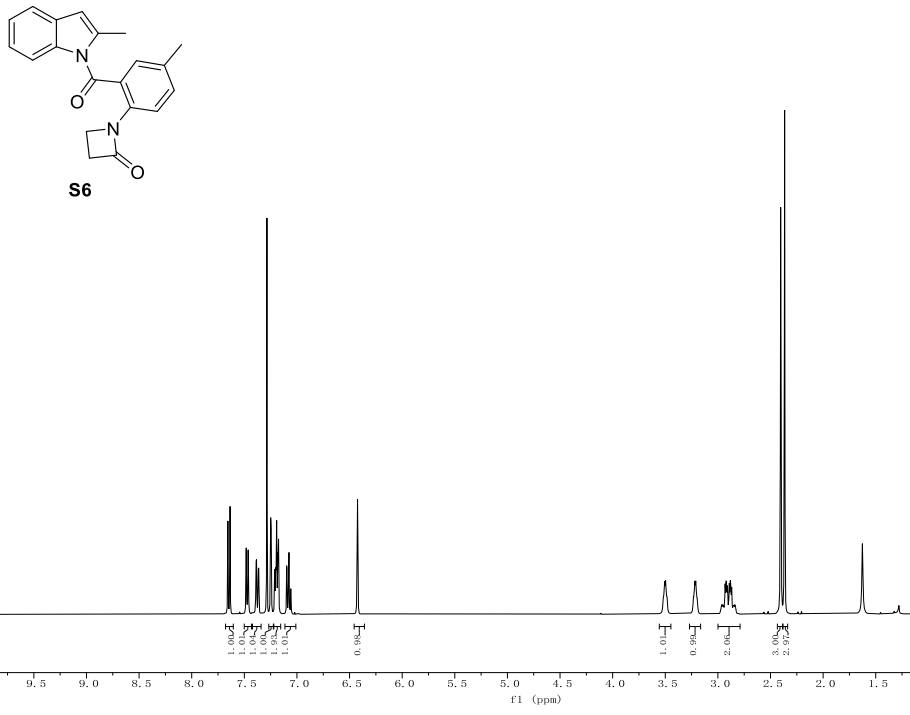

Cl
S4
f1 (ppm)


F
O
N
O
S5
f1 (ppm)

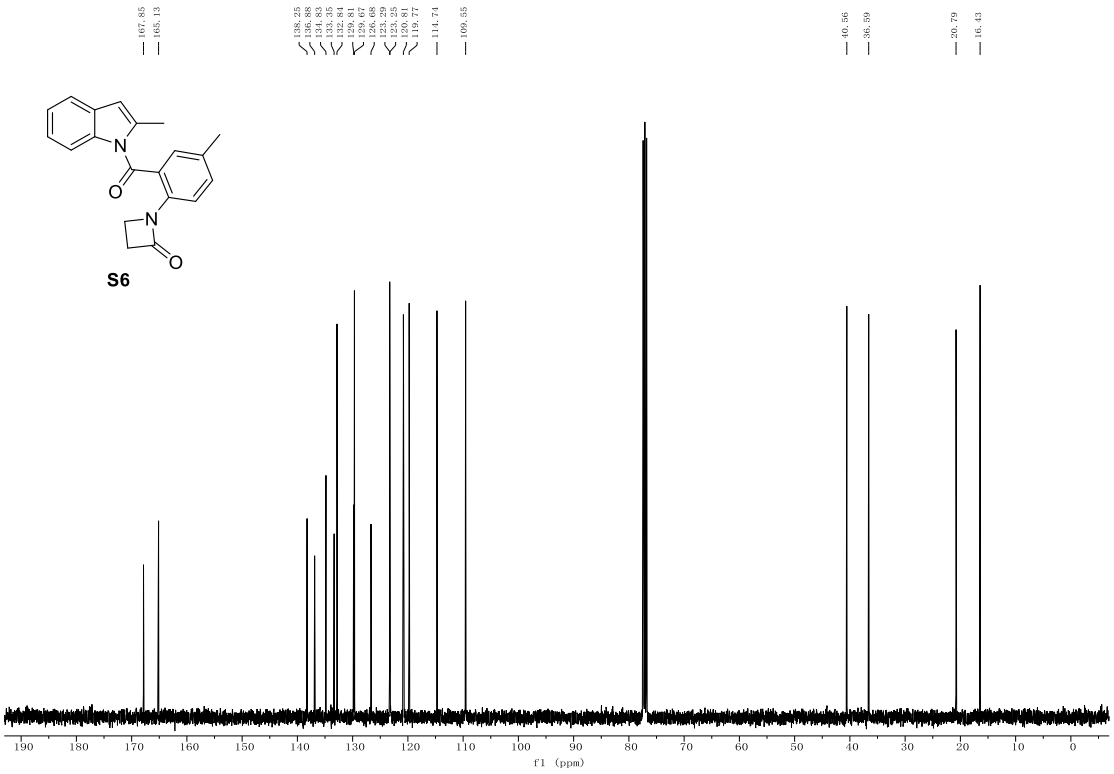

F
O
N
O
S5
f1 (ppm)



S5



S6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165.13
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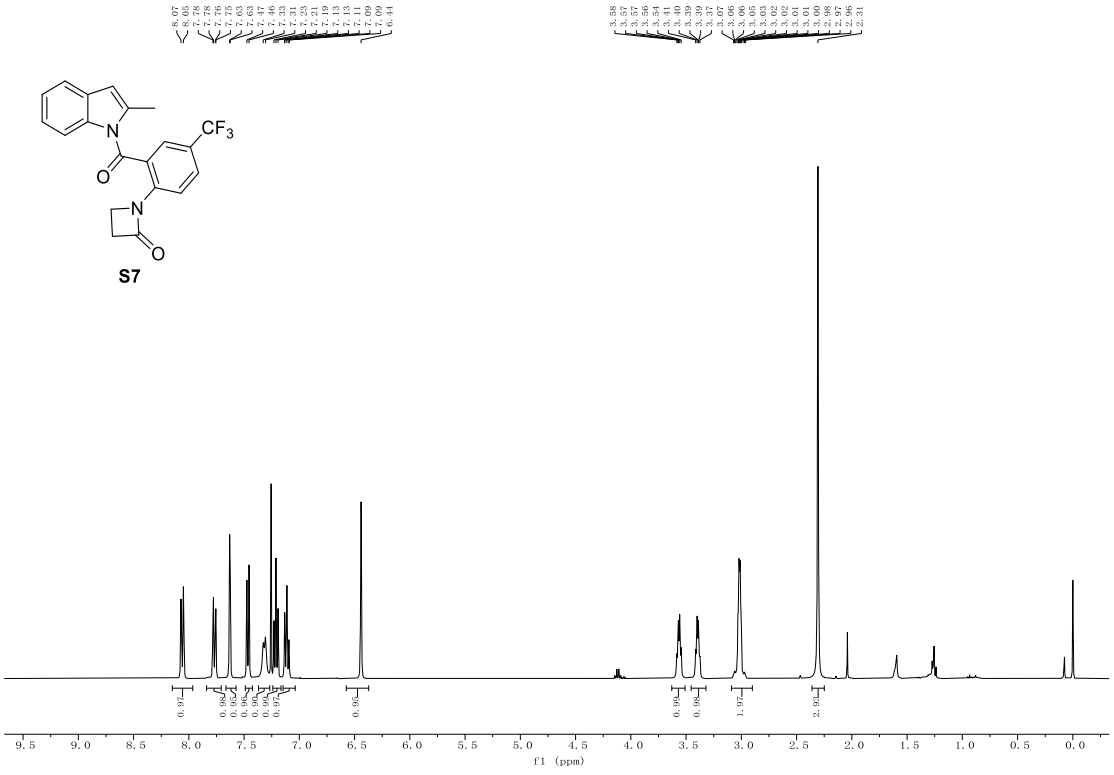
132.84
130.81
129.67
126.68
123.29
122.25
120.81
119.77
114.74
109.55
40.56
36.59
20.79
16.43
S6
f1 (ppm)


8.07
8.05
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7.76
7.75
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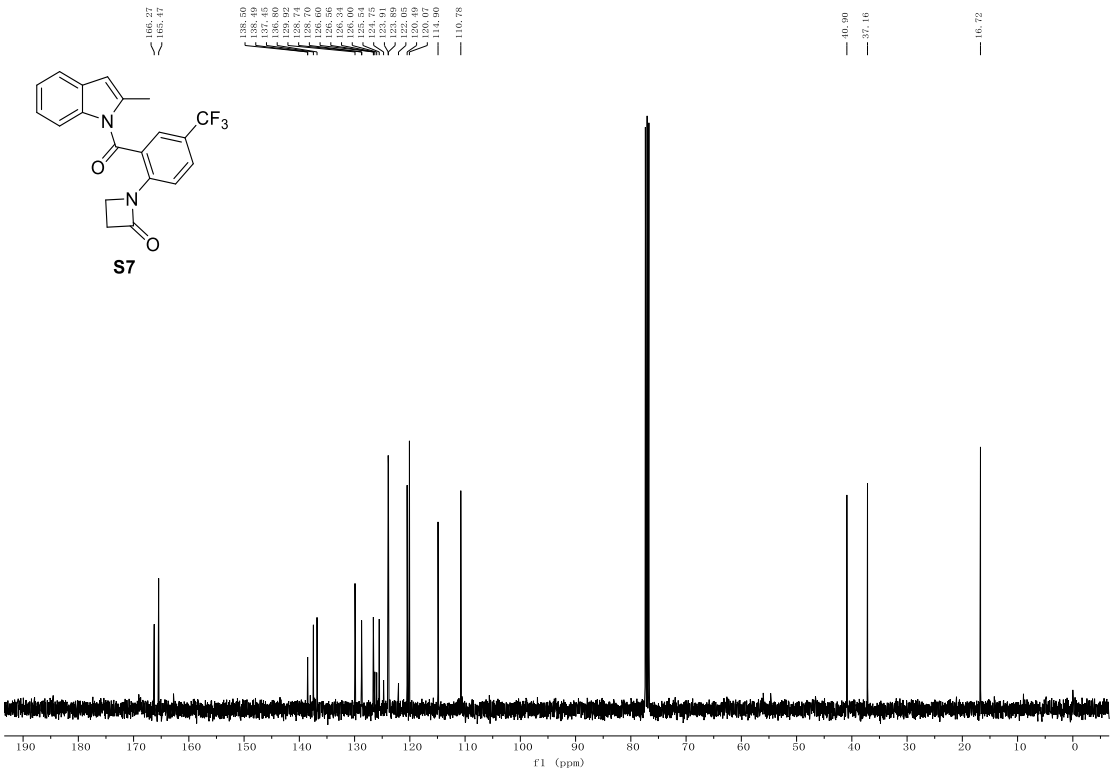
7.63
7.47
7.46
7.33
7.31
7.23
7.21
7.19
7.15
7.13
7.11
7.09
7.09
6.44
3.58
3.57
3.57
3.56
3.54
3.41
3.40
3.39
3.39
3.37
3.07
3.06
3.06
3.05
3.03
3.02
3.00
3.01
3.01
3.00
2.98
2.97
2.96
2.31
CF3
S7
0.97
0.98
0.95
0.96
0.96
0.97
0.97
0.96
0.98
1.97
2.93
f1 (ppm)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165.47
138.50
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136.80
129.92
128.74
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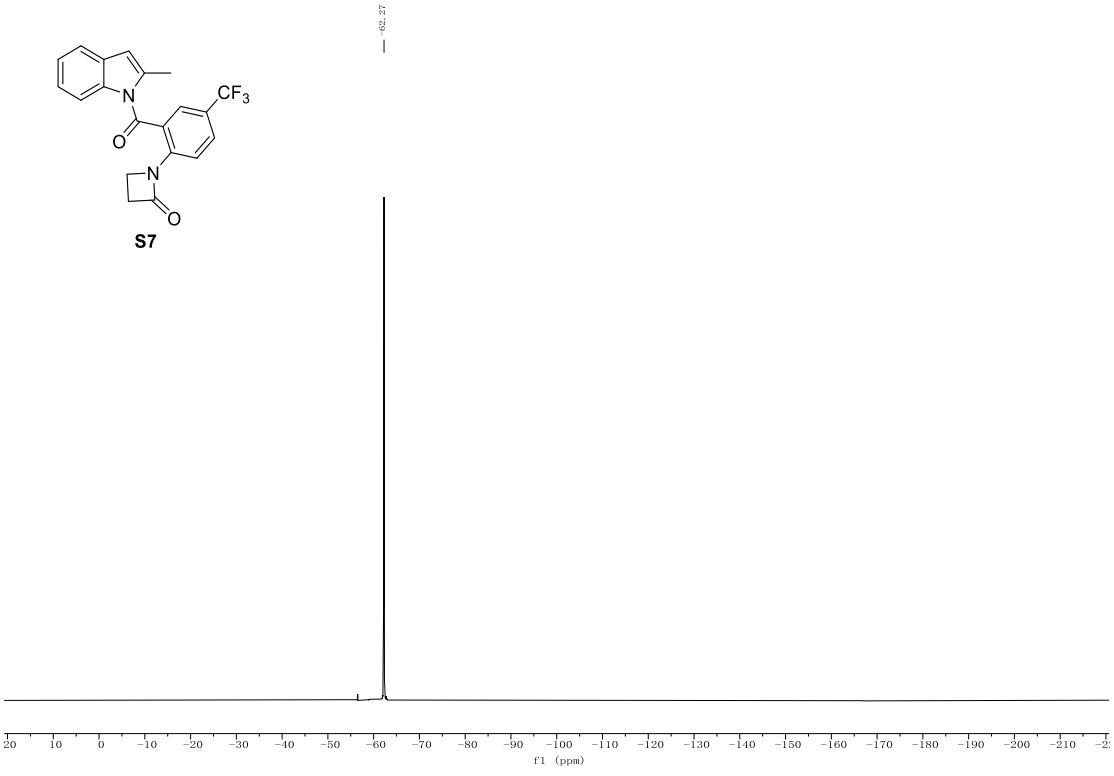
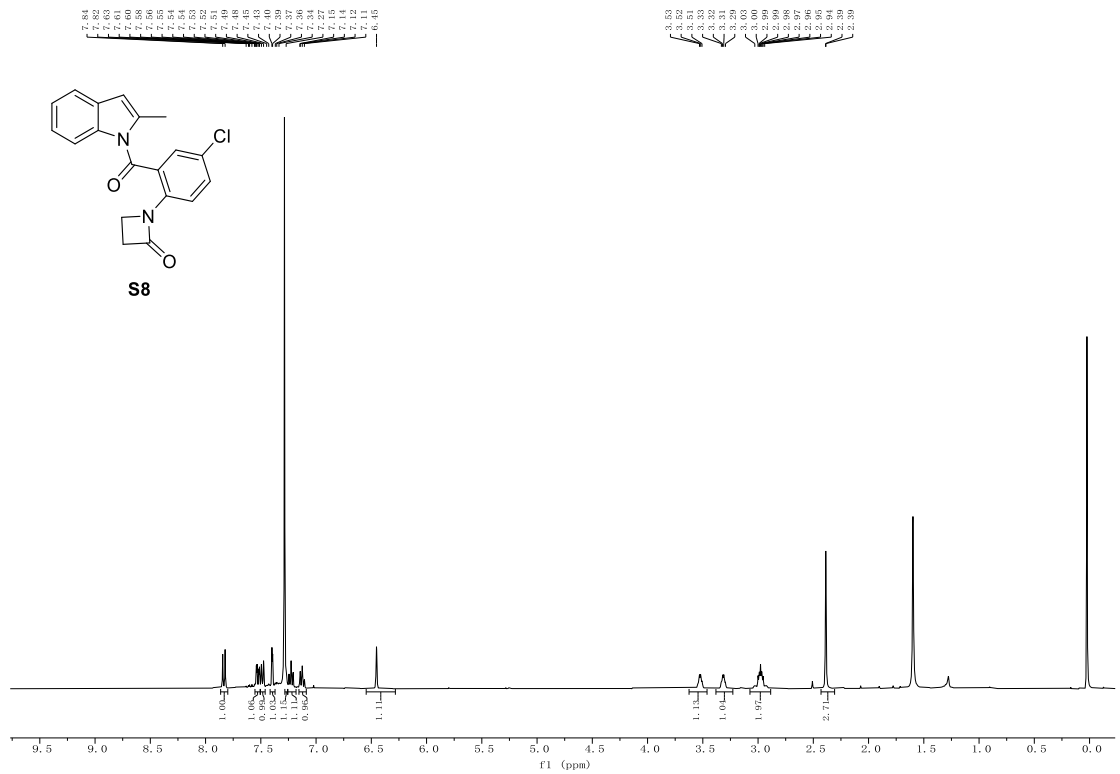
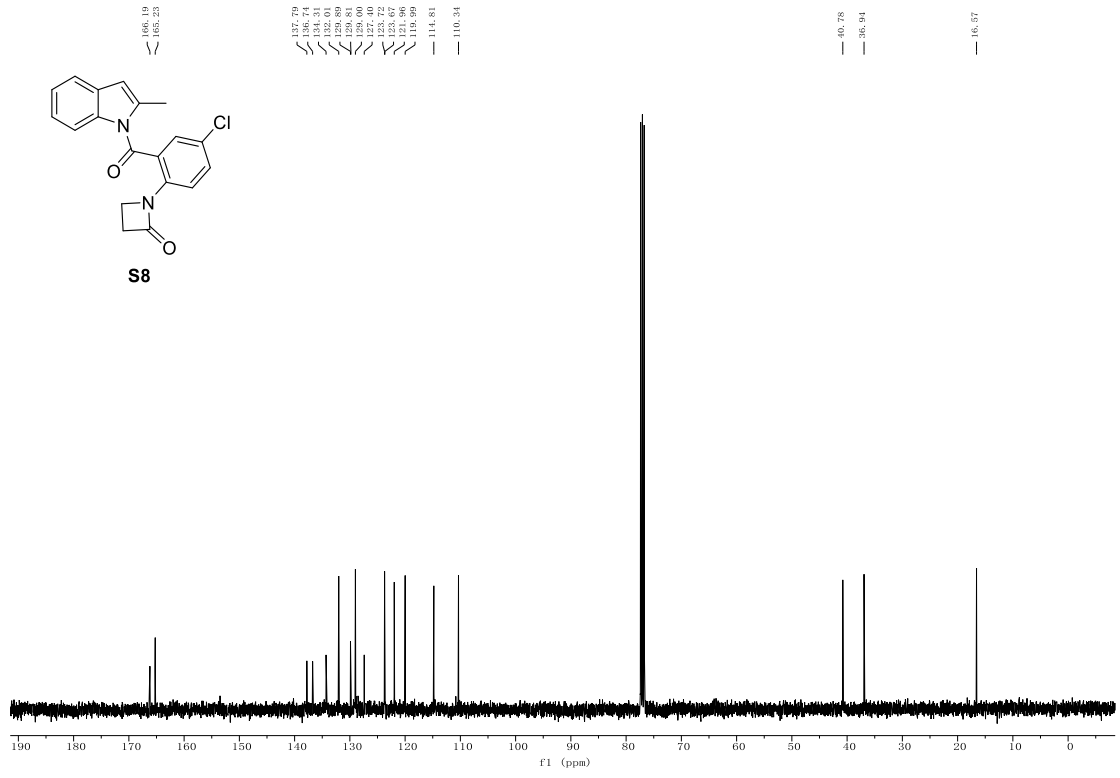
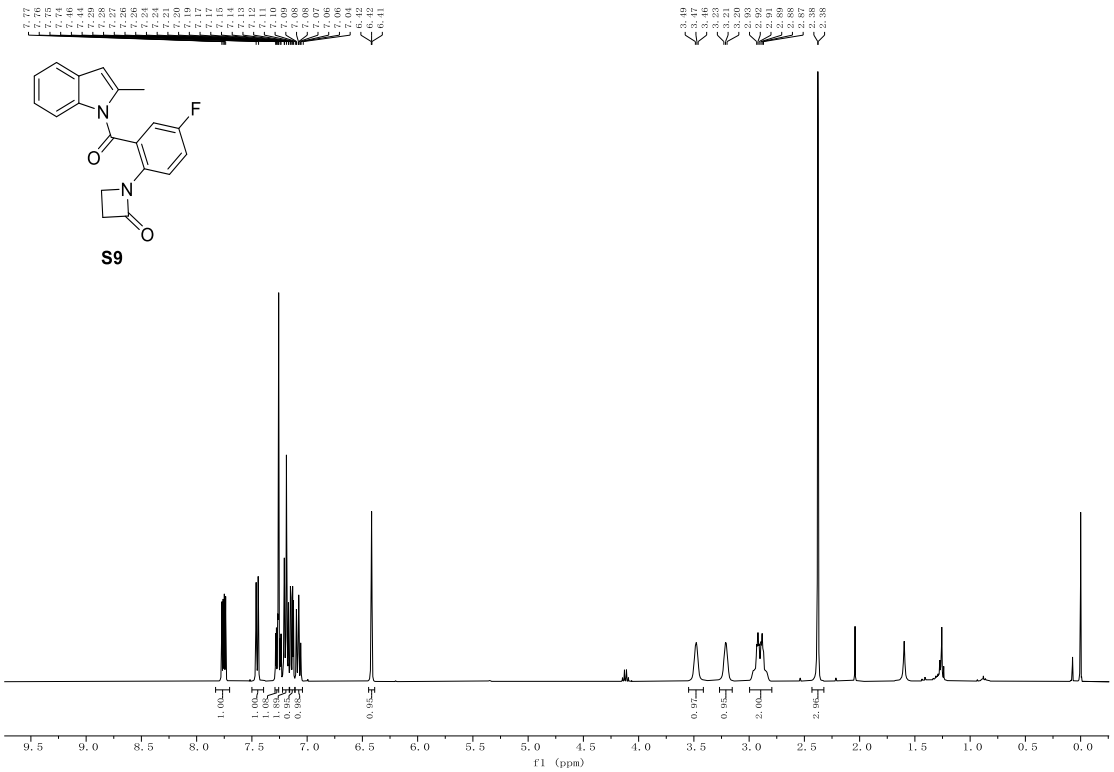
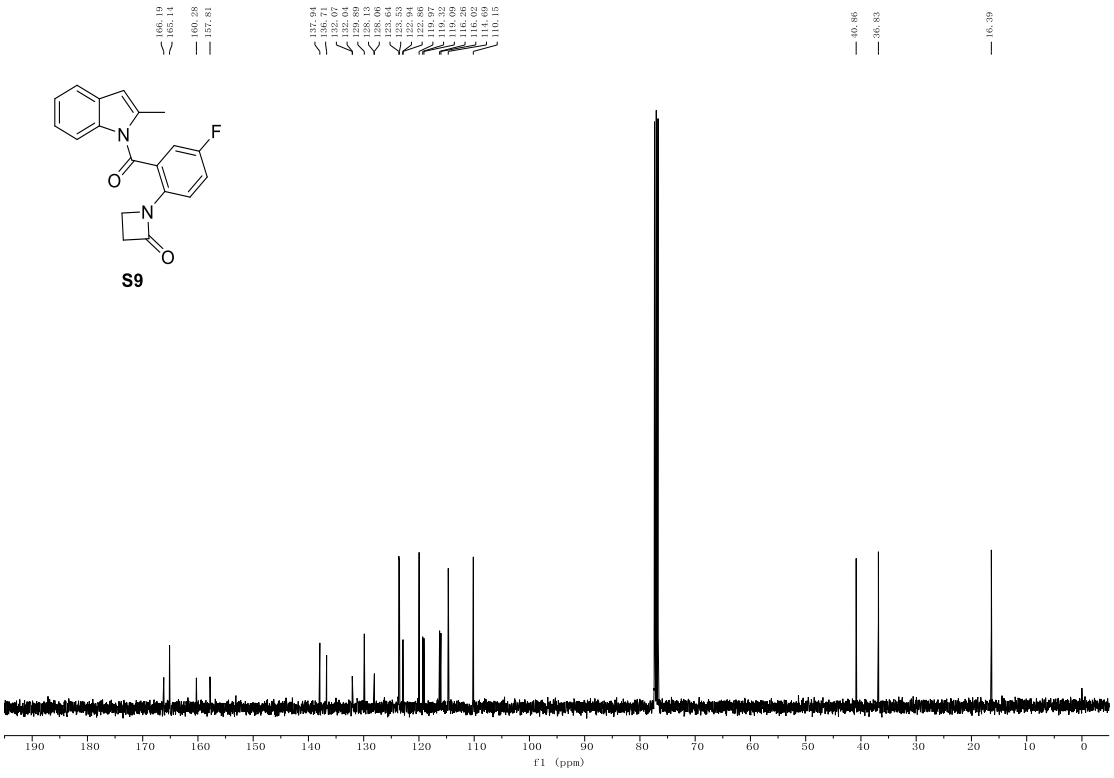
126.60
126.56
126.34
126.00
125.54
124.75
123.91
122.98
122.05
120.49
120.07
114.90
110.78
40.90
37.16
16.72
CF3
O
N
O
N
O
S7
f1 (ppm)

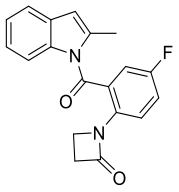

62.27
CF3
O
N
O
N
O
S7
f1 (ppm)


Cl
N
O
N
O
S8
f1 (ppm)


Cl
N
O
N
O
S8
f1 (ppm)

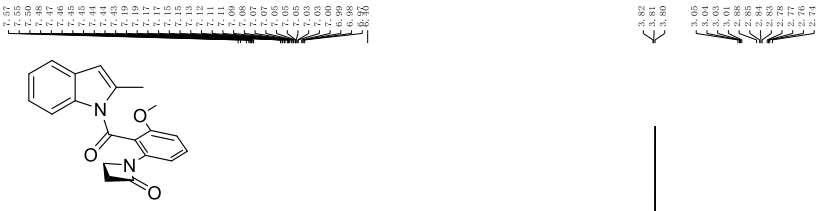

S9
f1 (ppm)


S9
f1 (ppm)



S9

115.58
115.60
115.60
115.62
f1 (ppm)


7.57
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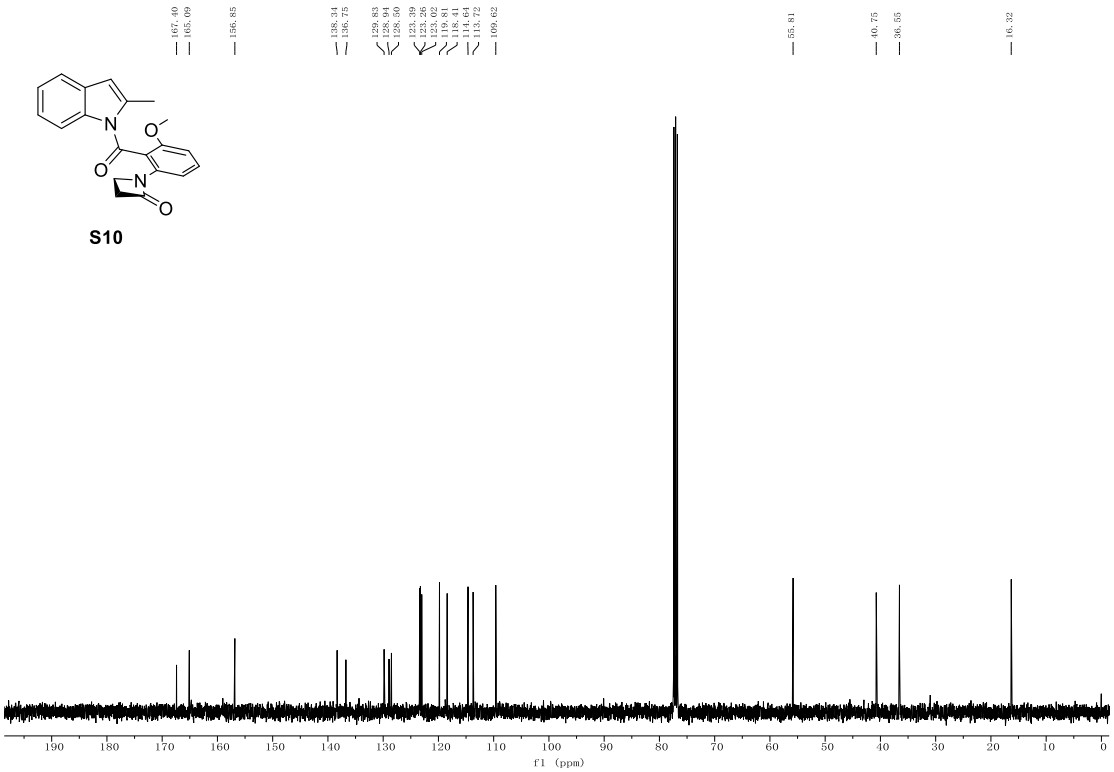
7.46
7.45
7.45
7.44
7.44
7.43
7.19
7.17
7.17
7.15
7.15
7.13
7.12
7.11
7.09
7.08
7.07
7.07
7.05
7.05
7.03
7.03
7.00
6.99
6.98
6.97
6.96
3.82
3.81
3.80
3.05
3.04
3.03
3.01
2.88
2.85
2.84
2.83
2.78
2.77
2.76
2.74

S10

0.98
0.97
4.11
1.02
0.96
3.16
1.00
0.98
2.02
2.90
f1 (ppm)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165.09
156.85
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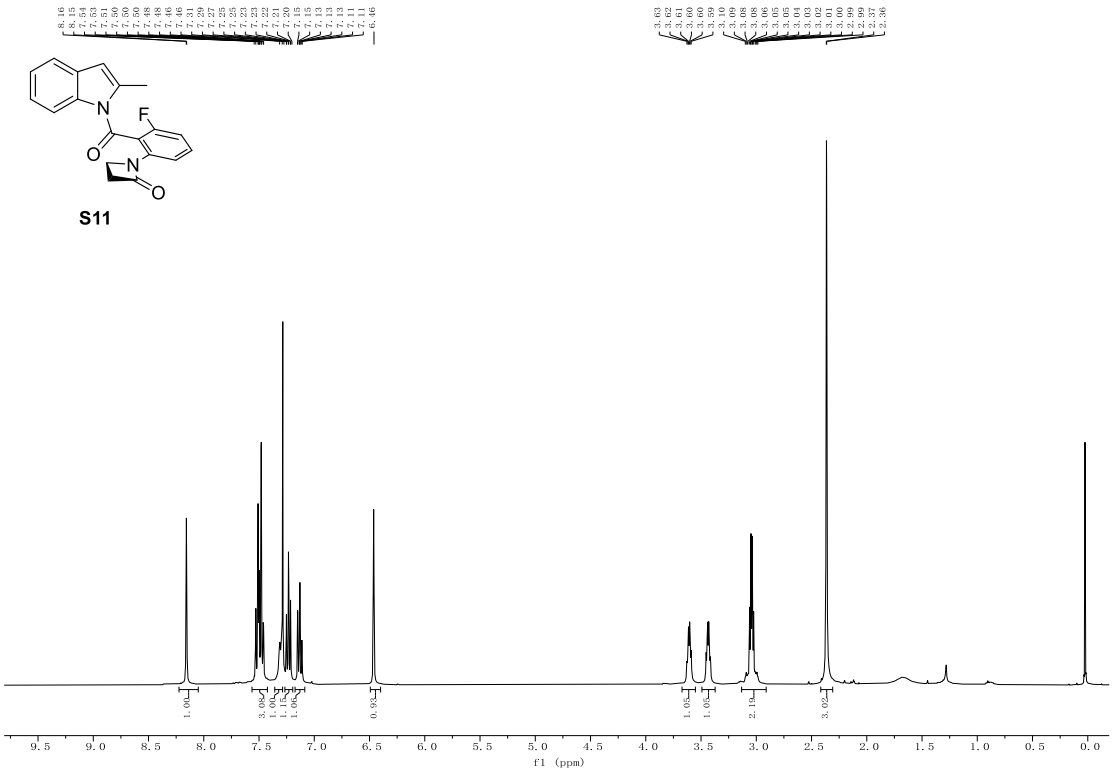
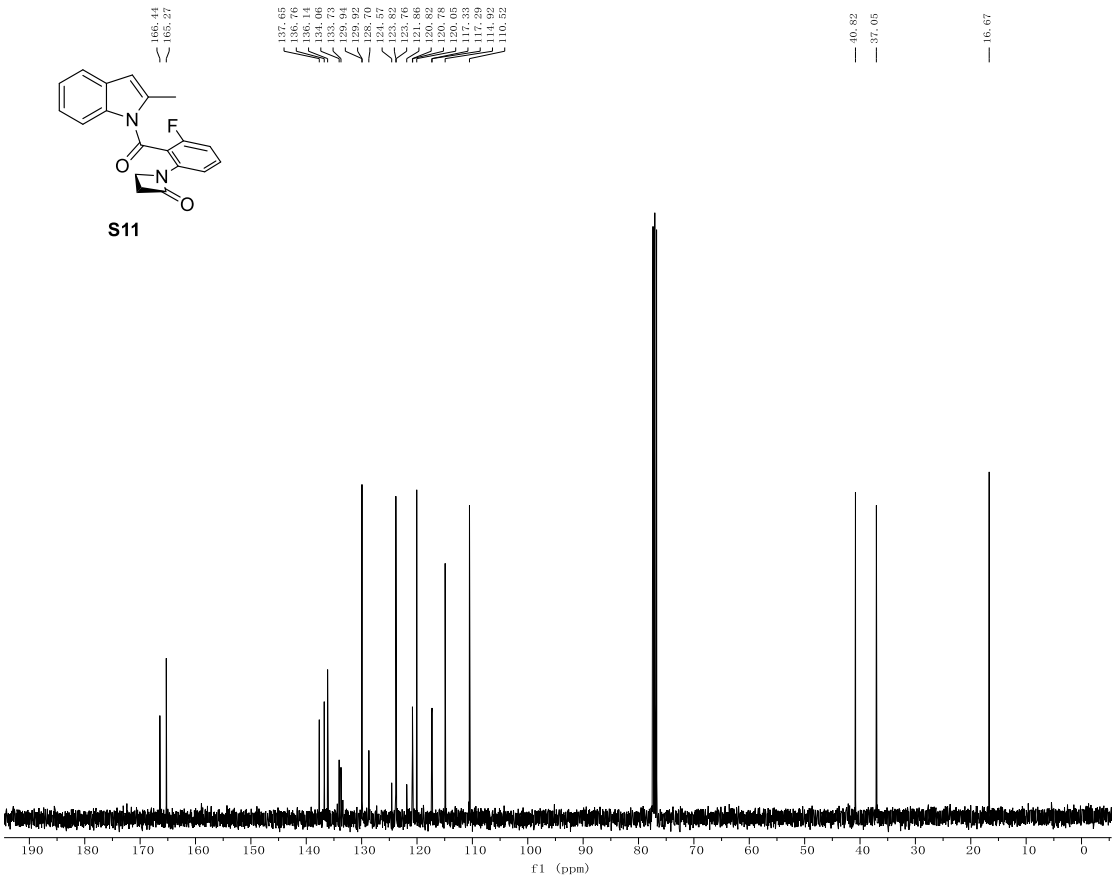
136.75
129.83
128.94
128.50
123.39
123.25
122.02
119.81
118.41
114.64
113.72
109.62
55.81
40.75
36.55
16.32
f1 (ppm)

S10


f1 (ppm)

S11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165.27
137.65
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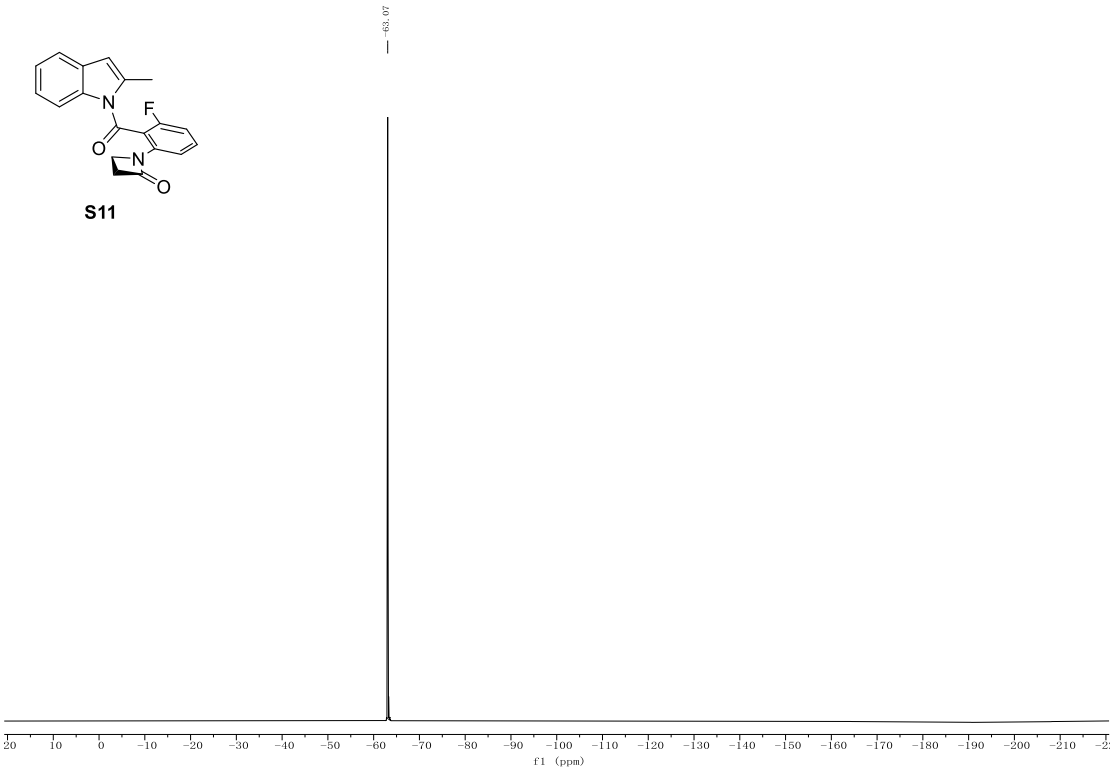
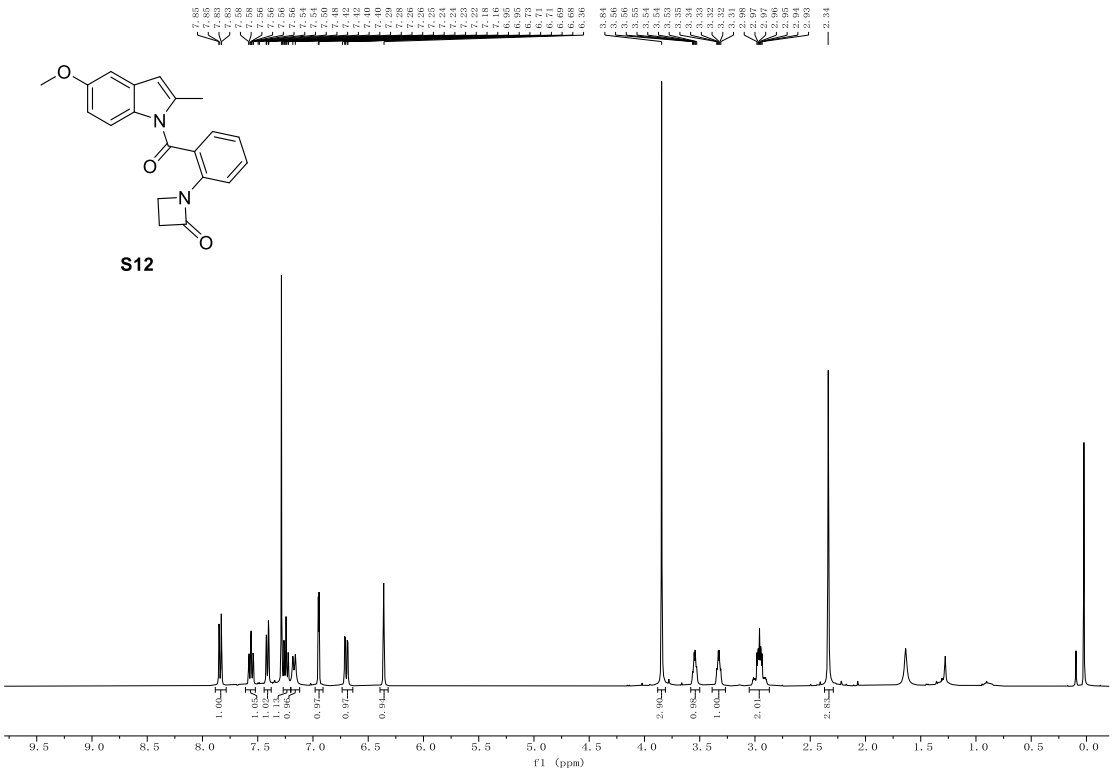
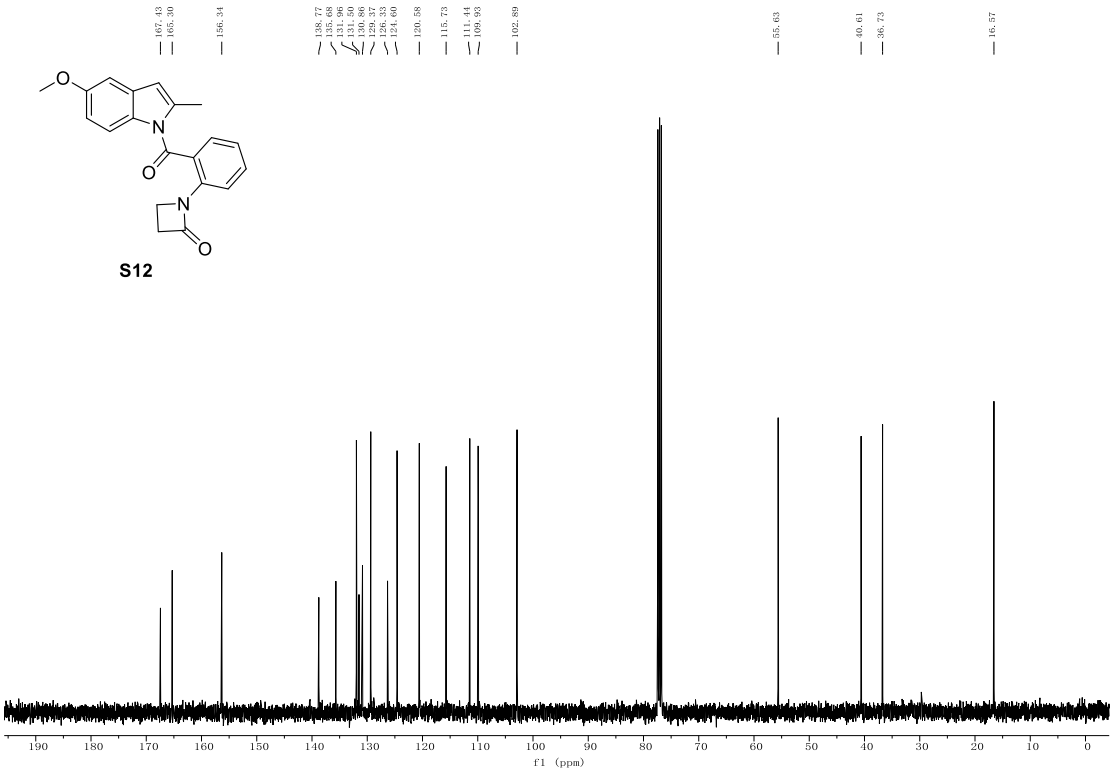
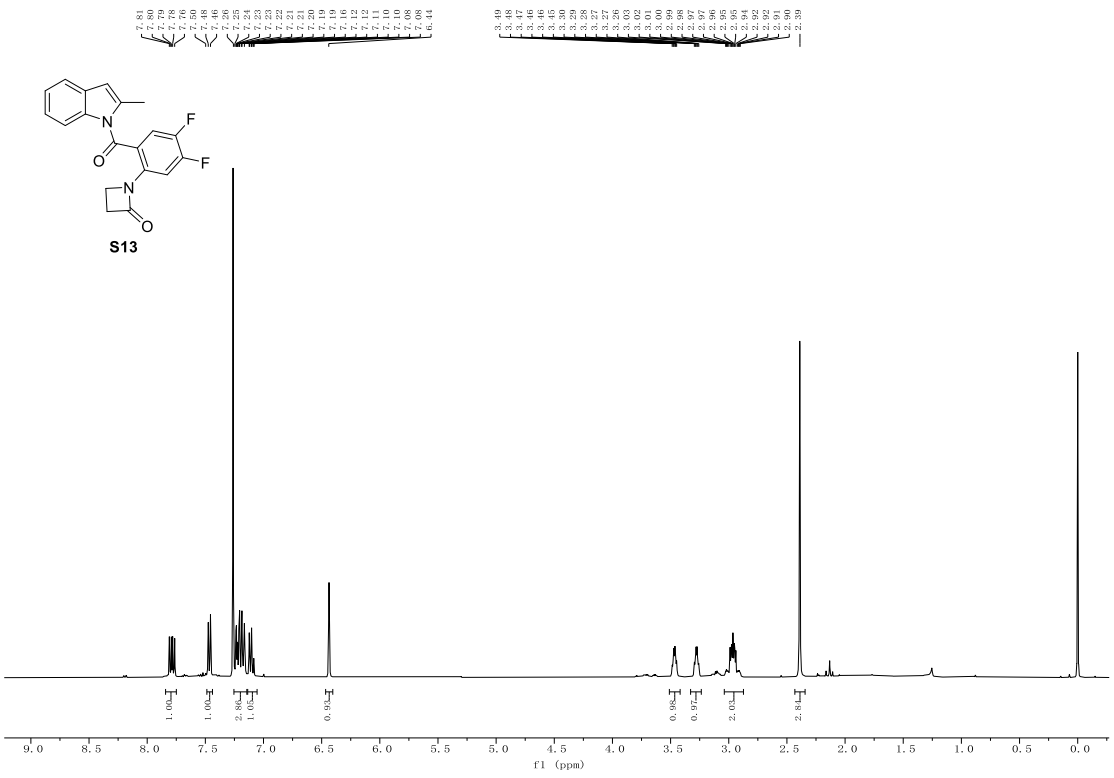
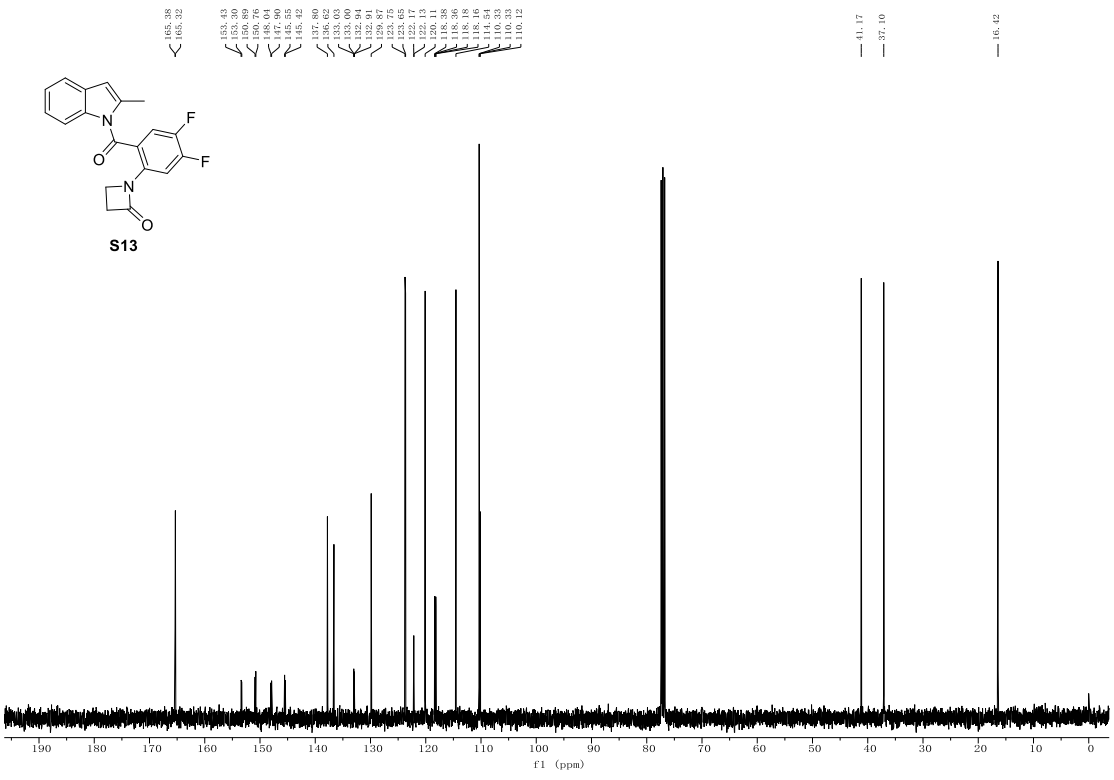
136.14
134.06
133.73
129.94
129.92
128.70
124.57
123.82
123.76
121.86
120.82
120.78
120.05
117.33
117.29
114.32
110.52
40.82
37.05
16.67
F
O
N
O
S11
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

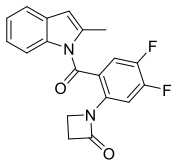

-63.07
F
O
N
O
S11
20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


S12
f1 (ppm)

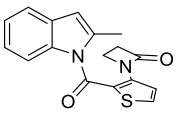

S12
f1 (ppm)


S13
f1 (ppm)

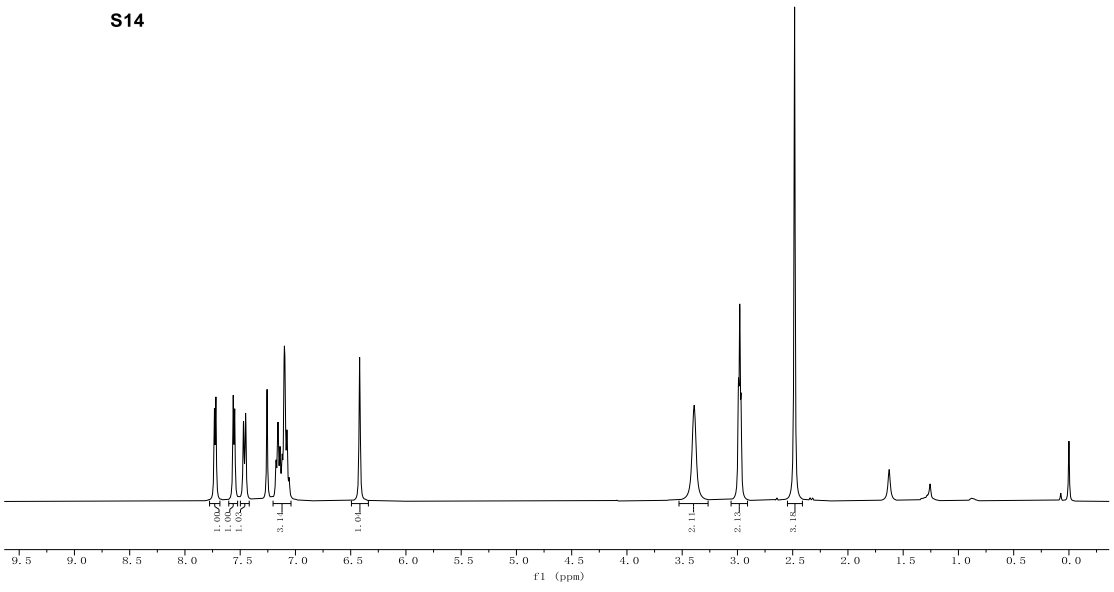

S13
f1 (ppm)

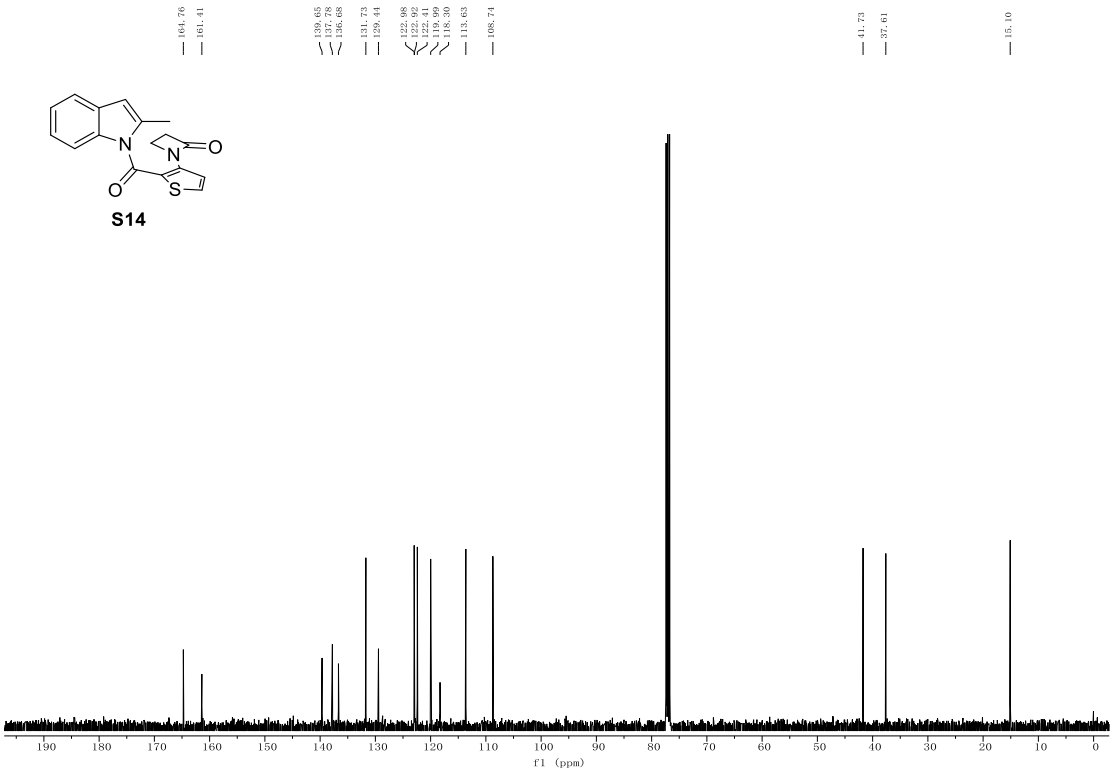


S13



S14

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129.44
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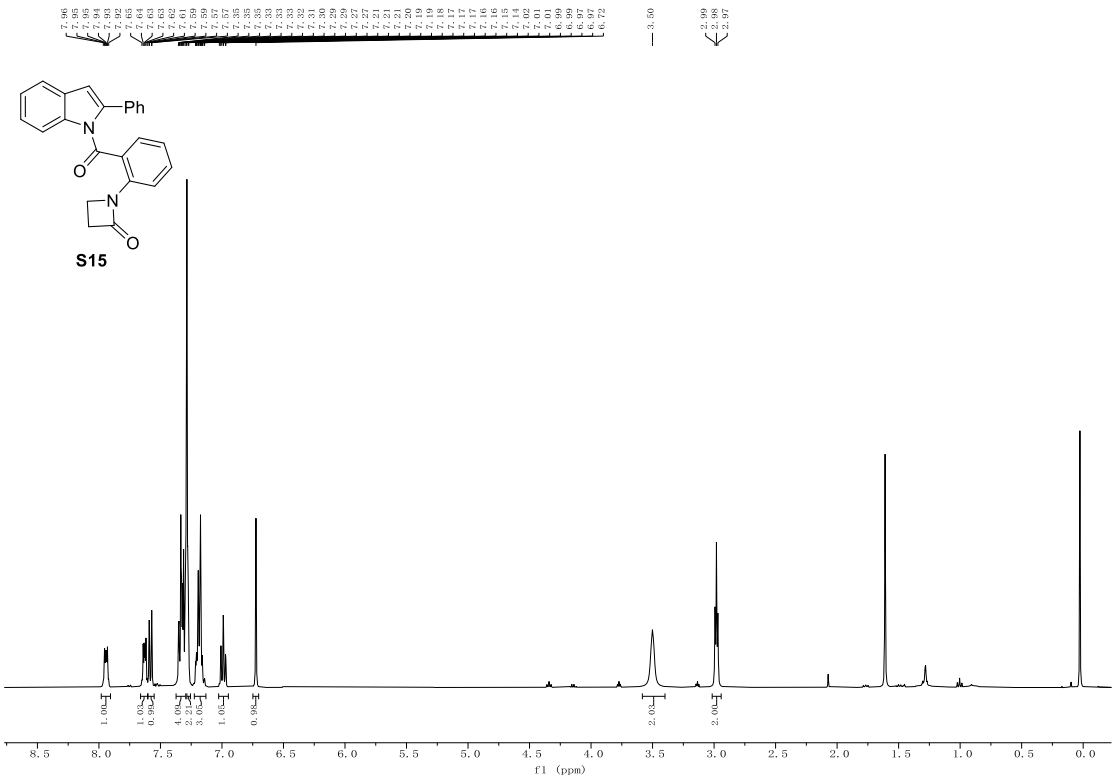
122.41
119.99
118.39
113.63
108.74
41.73
37.61
15.10
S14
f1 (ppm)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7.62
7.61
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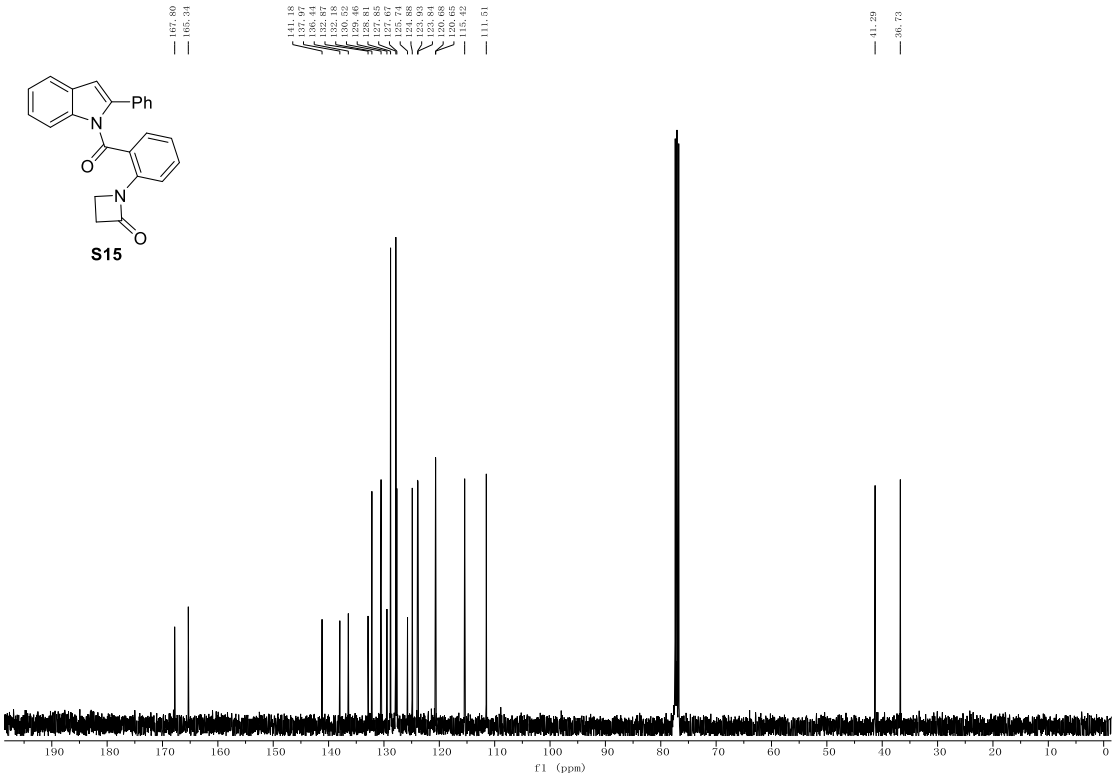
7.35
7.33
7.33
7.32
7.31
7.30
7.29
7.29
7.27
7.27
7.21
7.21
7.20
7.19
7.18
7.17
7.17
7.16
7.16
7.15
7.14
7.02
7.01
7.01
6.99
6.97
6.97
6.72
3.50
2.99
2.98
2.97
Ph
S15
1.00
1.03
0.99
4.00
2.21
3.05
1.04
0.98
2.03
2.00
f1 (ppm)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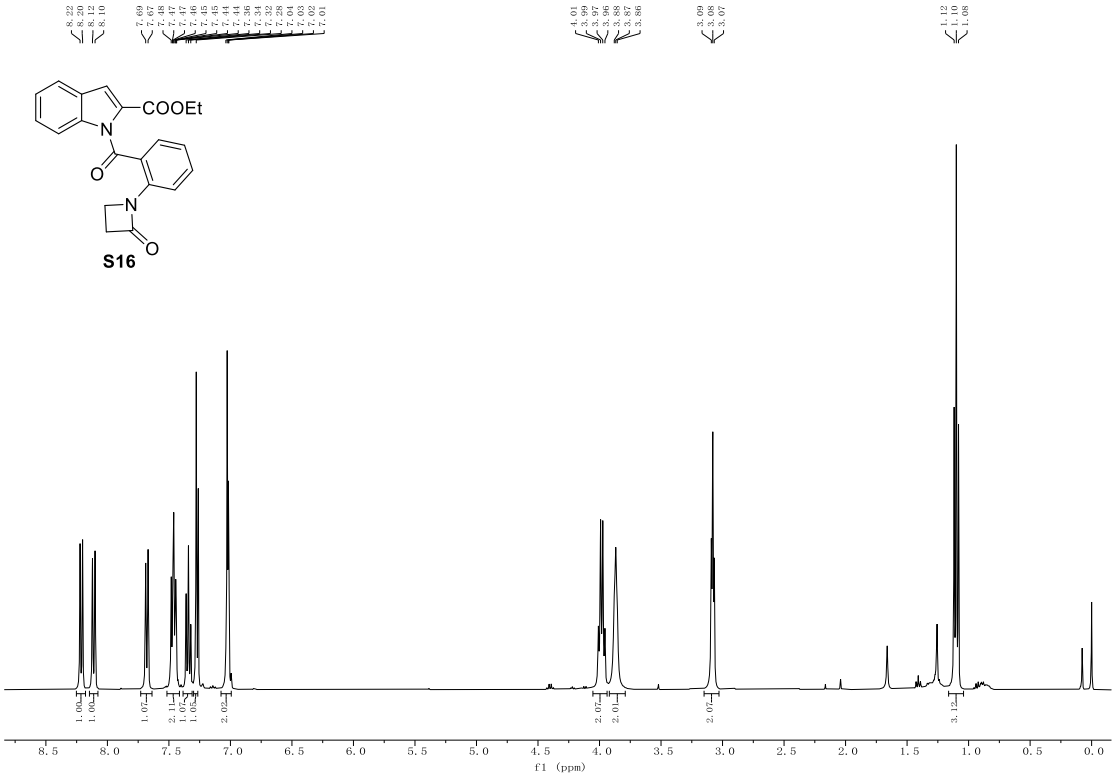
132.87
132.18
130.52
129.46
128.81
127.85
127.67
125.74
124.88
124.55
123.84
120.68
120.63
115.42
111.51
41.29
36.73
Ph
N
O
N
O
S15
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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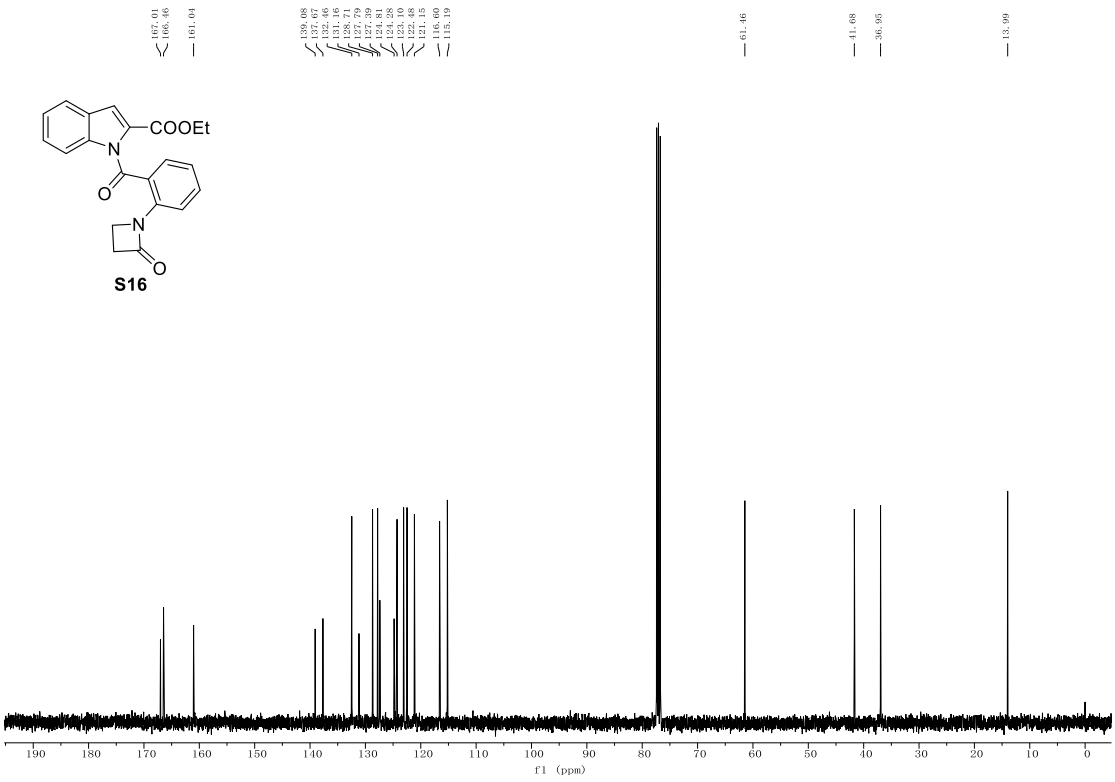
7.45
7.45
7.44
7.44
7.36
7.34
7.32
7.32
7.05
7.04
7.03
7.02
7.01
4.01
3.99
3.97
3.96
3.88
3.87
3.86
3.09
3.08
3.07
1.12
1.10
1.08
COOEt
N
O
N
O
S16
1.00
1.00
1.07
2.11
1.05
1.05
2.02
2.07
2.01
2.07
3.12
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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132.46
131.15
128.71
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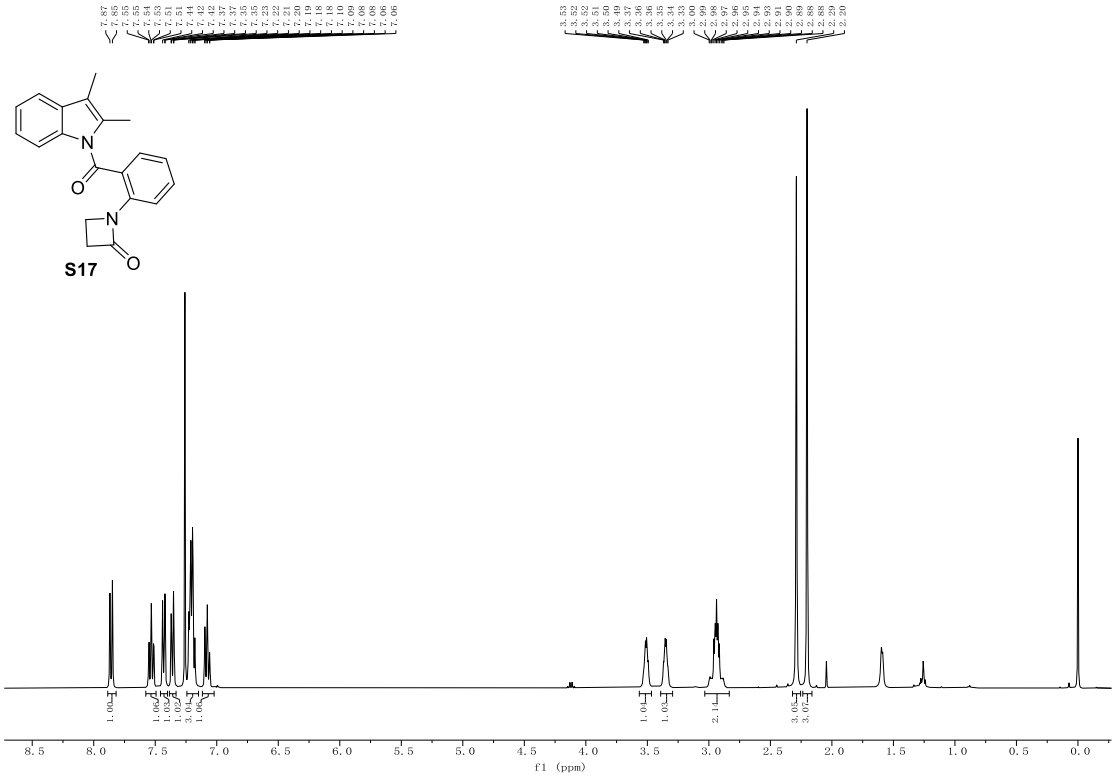
127.39
124.81
124.28
123.10
122.48
121.15
116.09
115.19
61.46
41.68
36.95
13.99
COOEt
N
O
N
O
S16
f1 (ppm)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7.35
7.35
7.23
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7.20
7.19
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7.08
7.08
7.06
7.06
3.53
3.52
3.52
3.51
3.50
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2.88
2.29
2.20
N
O
N
O
S17
1.00
1.08
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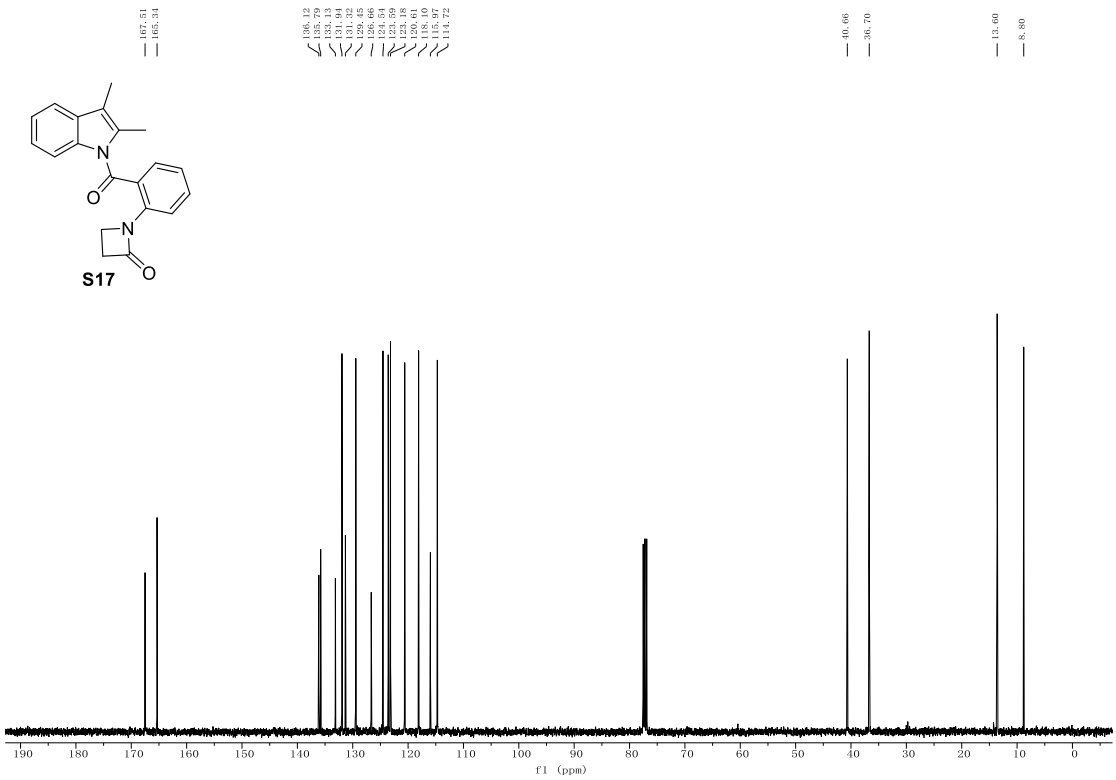
1.02
3.04
1.00
1.04
1.03
2.14
3.05
3.07
f1 (ppm)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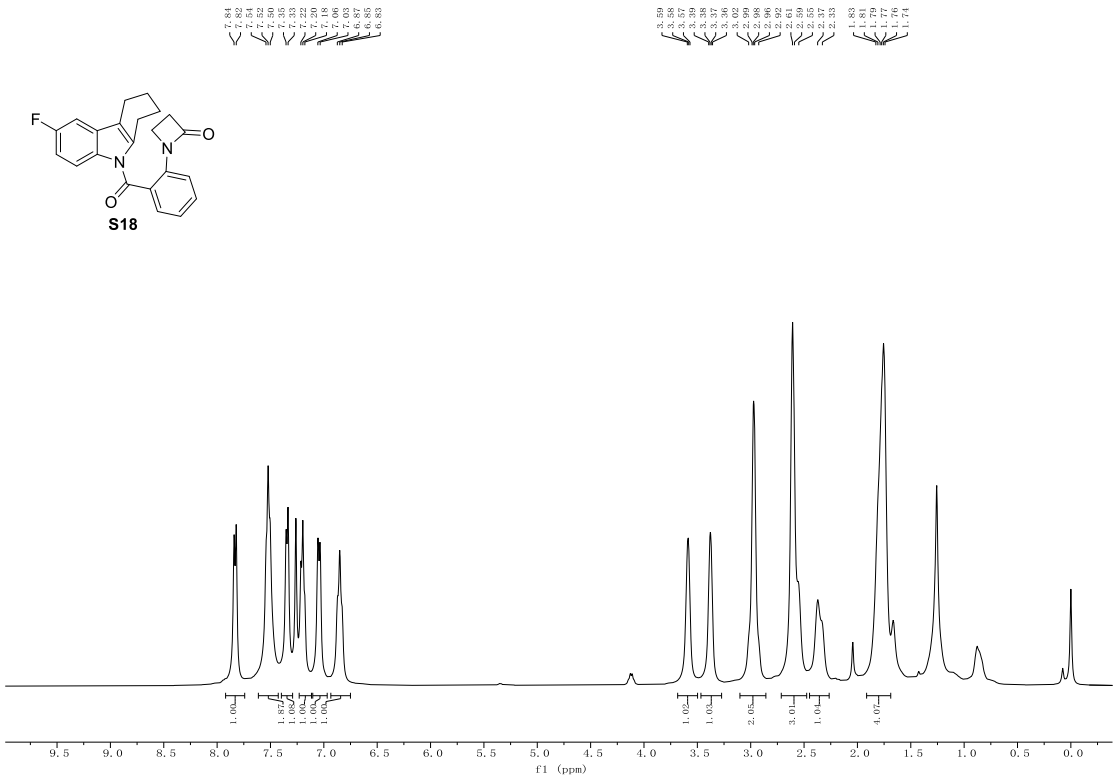
136.12
135.79
133.13
131.84
131.32
129.45
126.66
125.54
123.59
123.18
120.61
118.10
115.57
114.72
40.66
36.70
13.60
8.80
S17
f1 (ppm)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7.82
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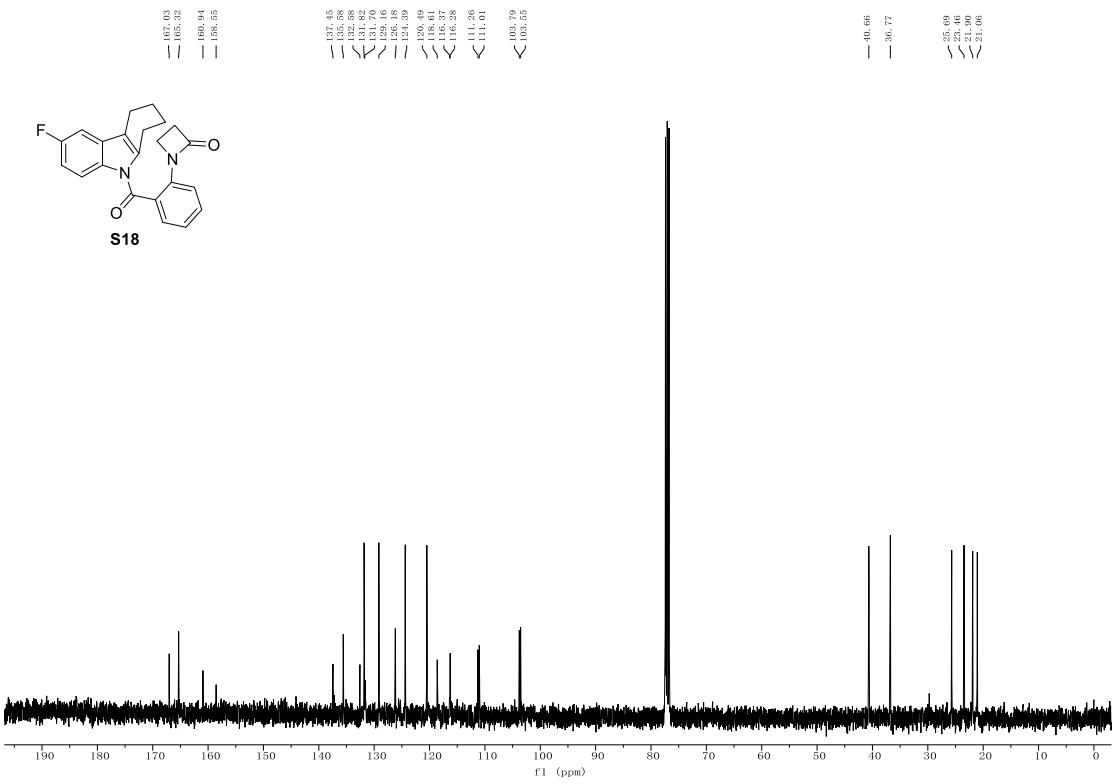
7.52
7.50
7.35
7.33
7.22
7.20
7.18
7.06
7.03
6.87
6.85
6.83
3.59
3.58
3.57
3.39
3.38
3.37
3.36
3.02
2.99
2.98
2.96
2.92
2.61
2.59
2.55
2.37
2.33
1.83
1.81
1.79
1.77
1.76
1.74
F
S18
1.00
1.87
1.04
1.00
1.00
1.02
1.03
2.05
3.01
1.04
4.07
f1 (ppm)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165.32
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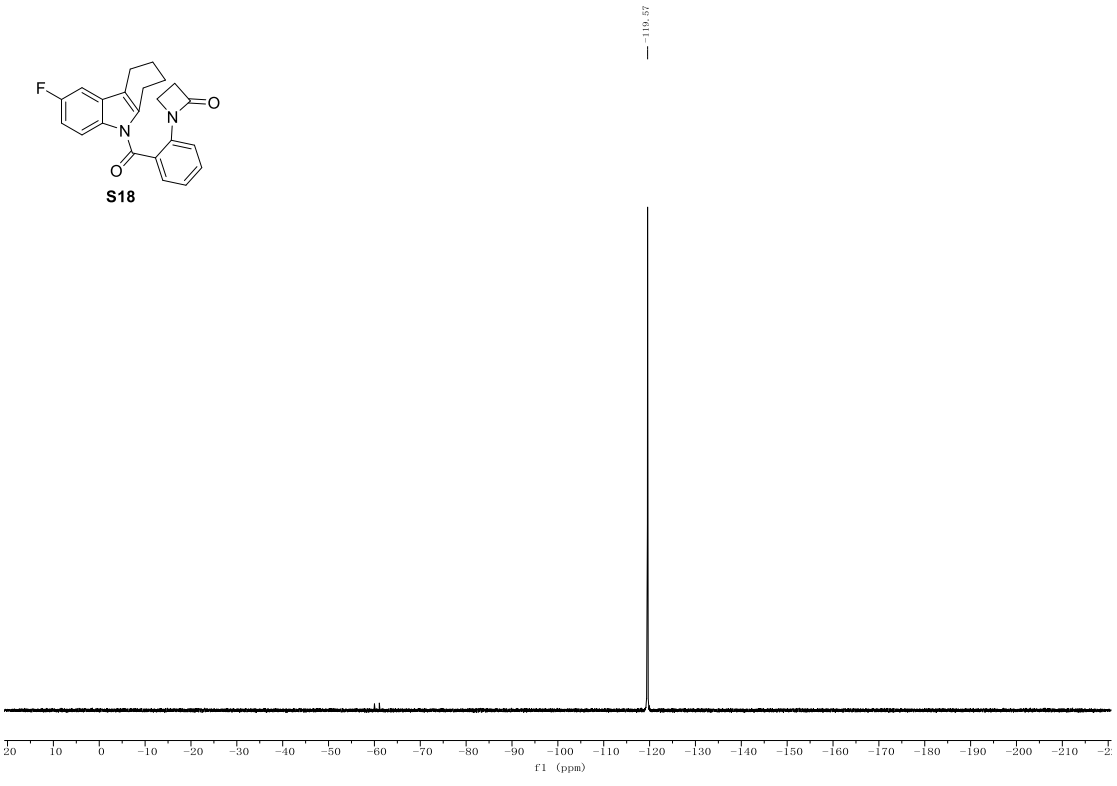
137.45
135.68
132.58
131.82
131.70
129.16
128.18
124.39
120.49
118.61
116.37
116.28
111.26
111.01
103.79
103.55
40.66
36.77
25.69
23.46
21.60
21.06
F
N
O
N
O
S18
f1 (ppm)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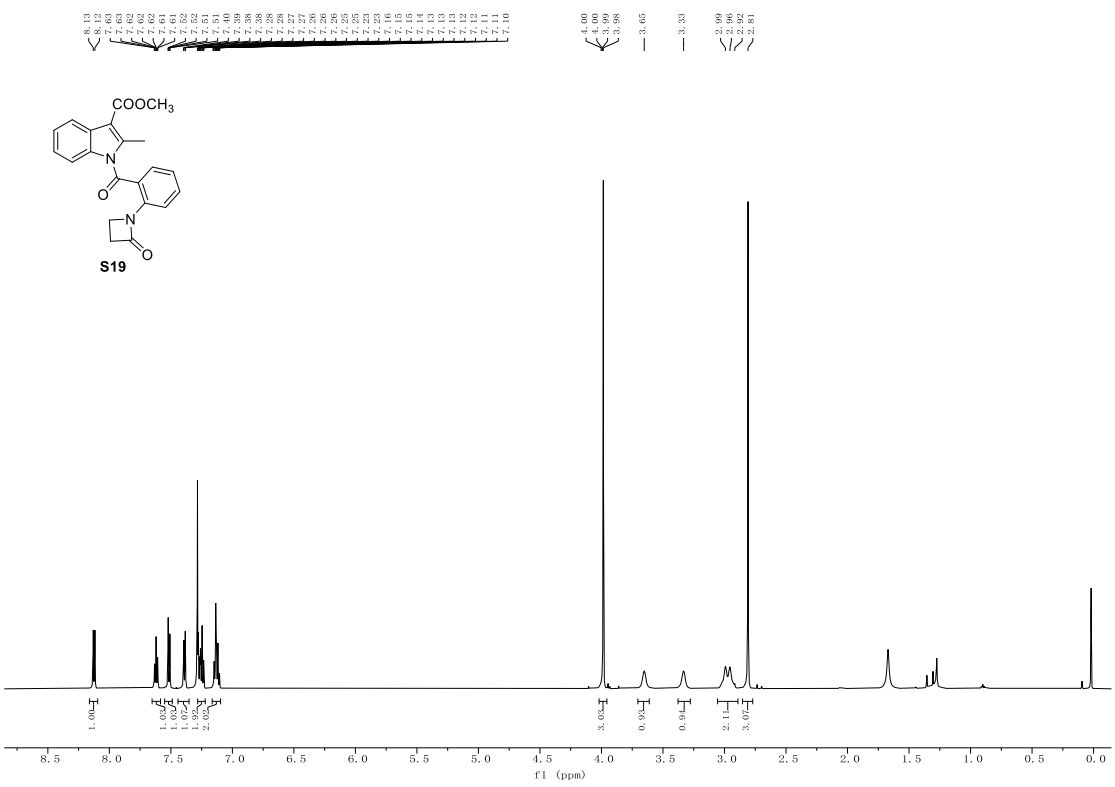
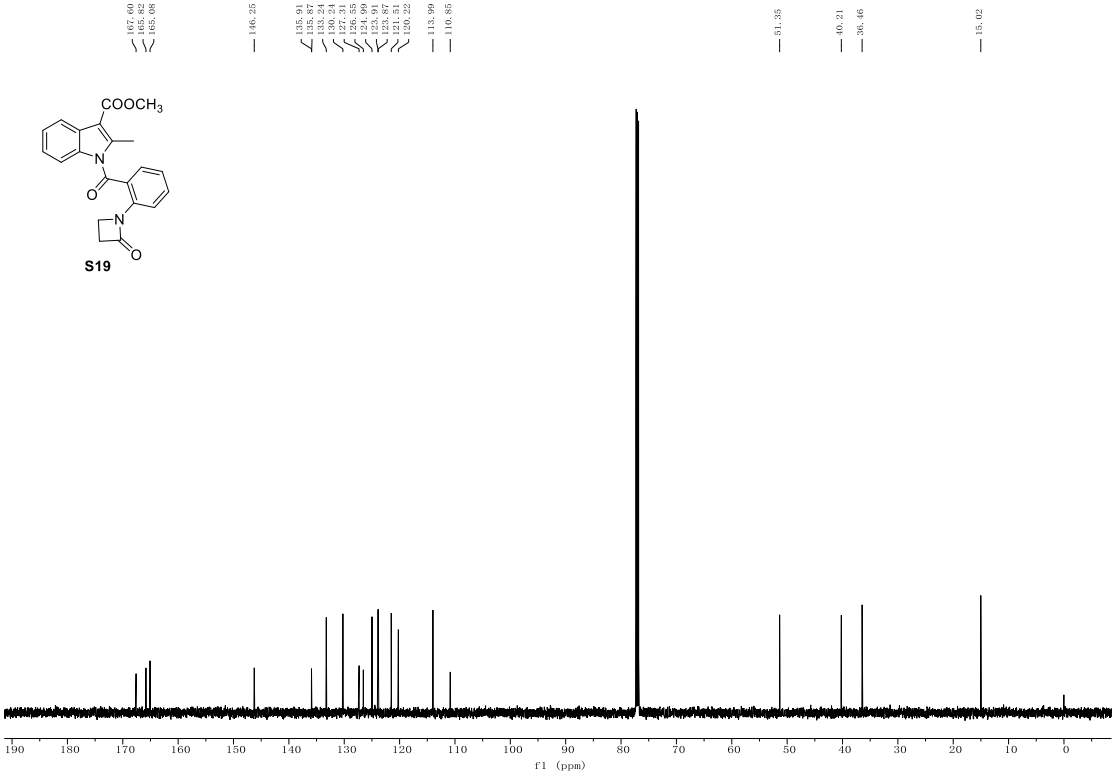
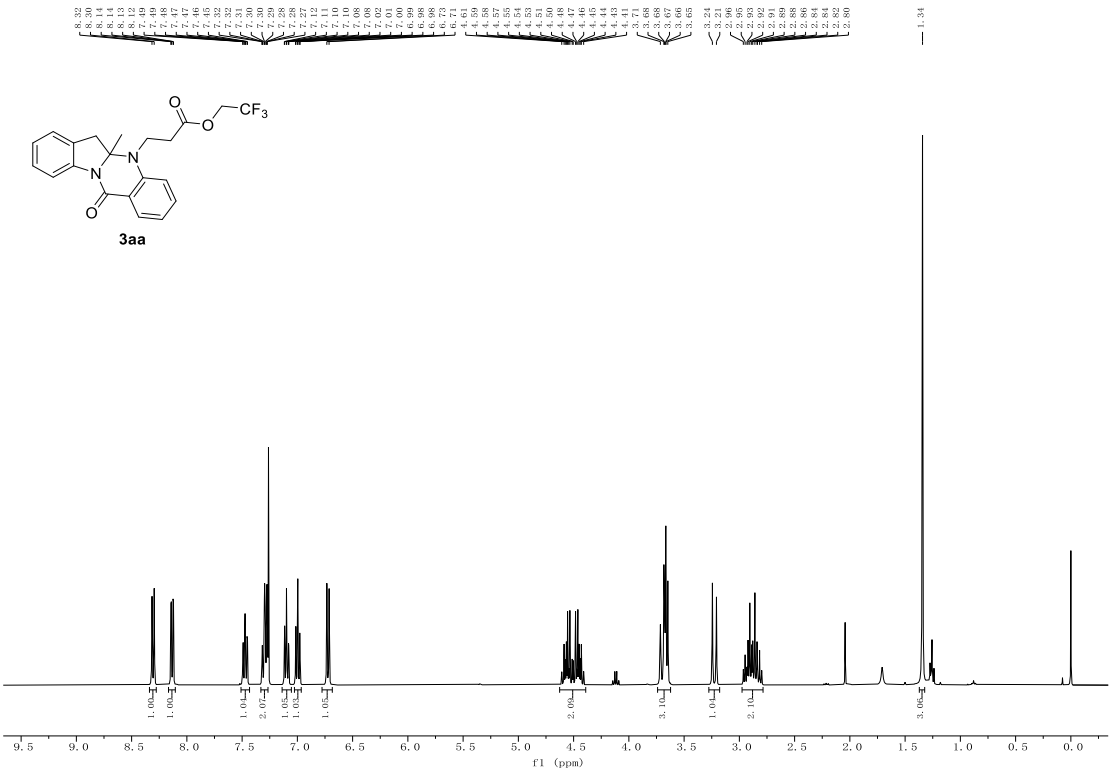
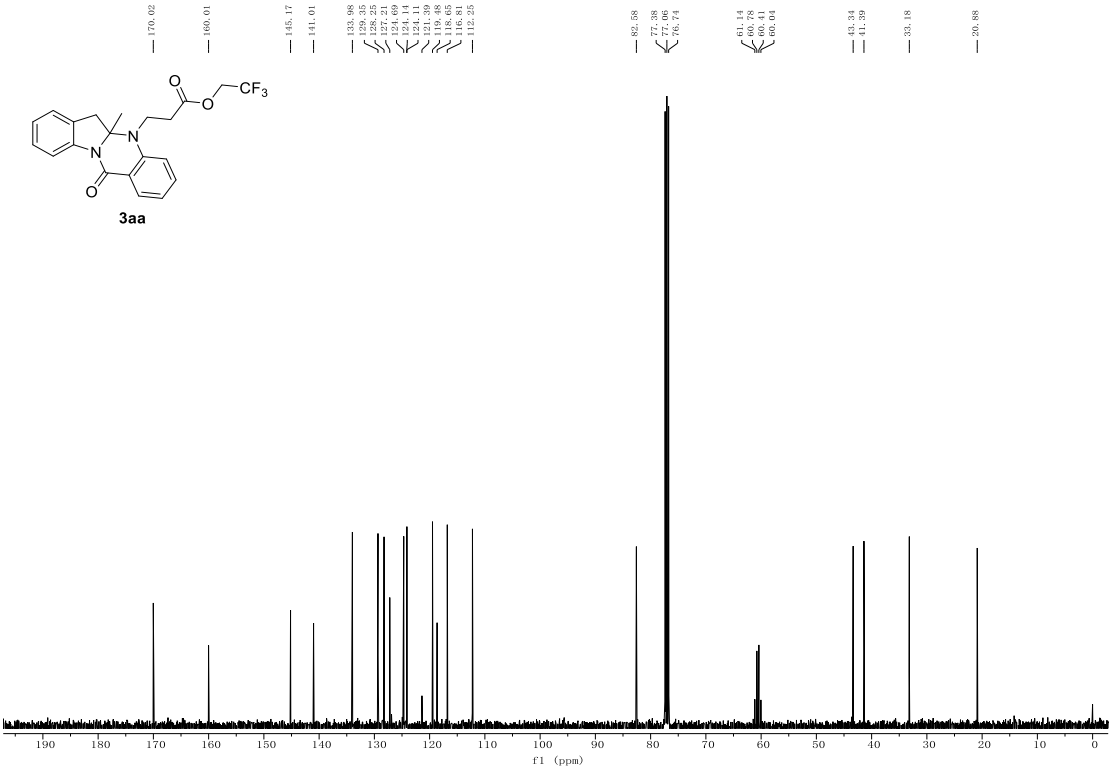
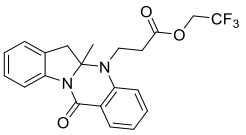
F
N
O
N
O
S18
f1 (ppm)


COOCH3
S19
f1 (ppm)

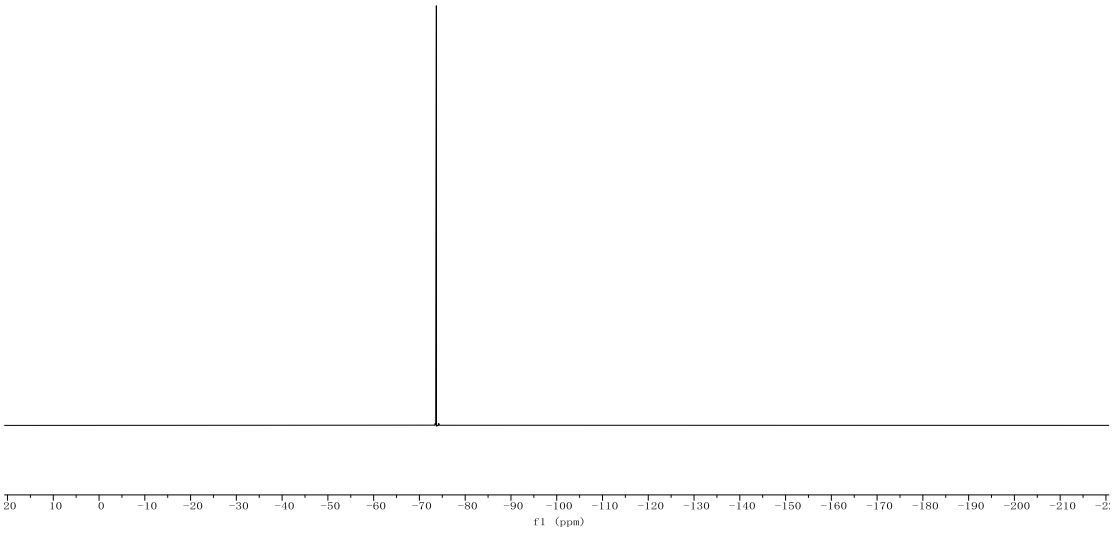

COOCH3
S19
f1 (ppm)

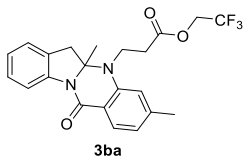

8.32 8.30 8.14 8.14 8.13 8.12 7.49 7.49 7.48 7.47 7.47 7.46 7.45 7.32 7.31 7.30 7.29 7.28 7.28 7.27 7.12 7.11 7.10 7.08 7.08 7.02 7.01 7.00 6.99 6.98 6.73 6.71 4.64 4.59 4.58 4.57 4.55 4.54 4.53 4.51 4.50 4.48 4.47 4.46 4.45 4.44 4.43 4.41 3.71 3.68 3.68 3.67 3.66 3.65 3.24 3.21 2.96 2.95 2.93 2.92 2.91 2.89 2.88 2.86 2.84 2.84 2.84 2.82 2.80 1.34
O
O
CF3
N
N
O
3aa
1.00 1.00 1.04 2.07 1.05 1.03 1.05 2.09 3.10 1.04 2.10 3.06
f1 (ppm)


170.02 160.01 145.17 141.01 133.98 129.35 128.25 127.21 124.69 124.14 124.11 121.39 119.48 118.65 116.81 112.25 82.58 77.38 77.06 76.74 61.14 60.78 60.41 60.04 43.34 41.39 33.18 20.88
O
O
CF3
N
N
O
3aa
f1 (ppm)

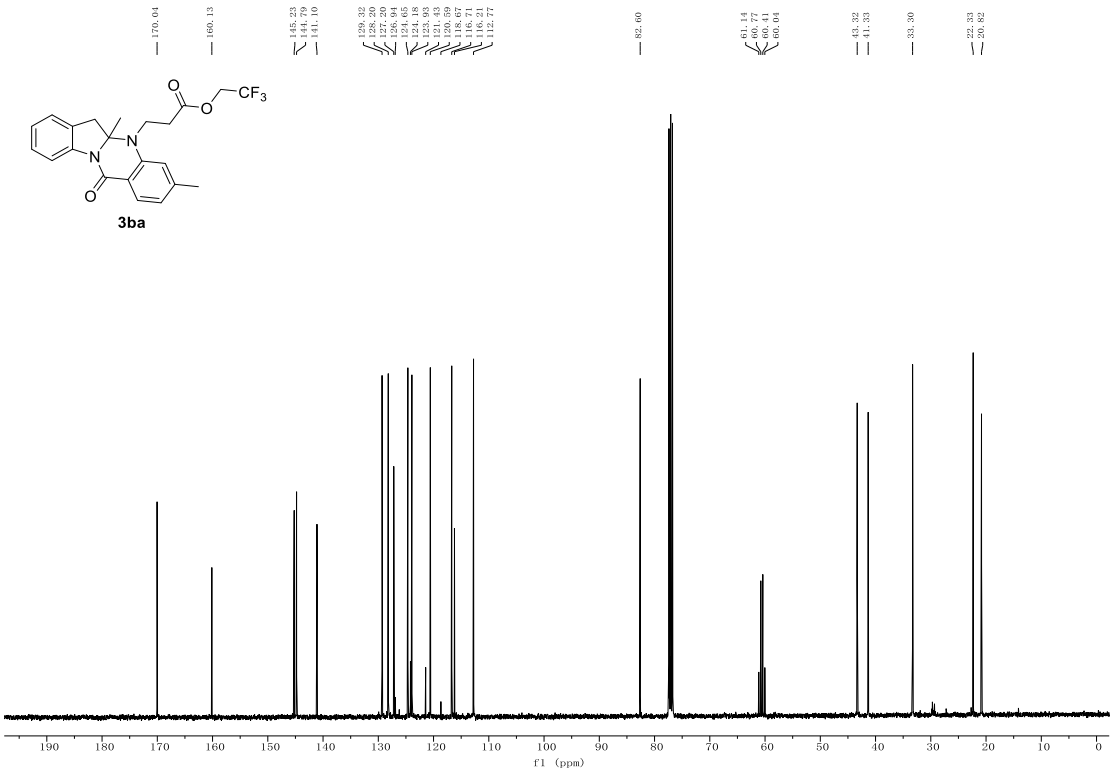


3aa





3ba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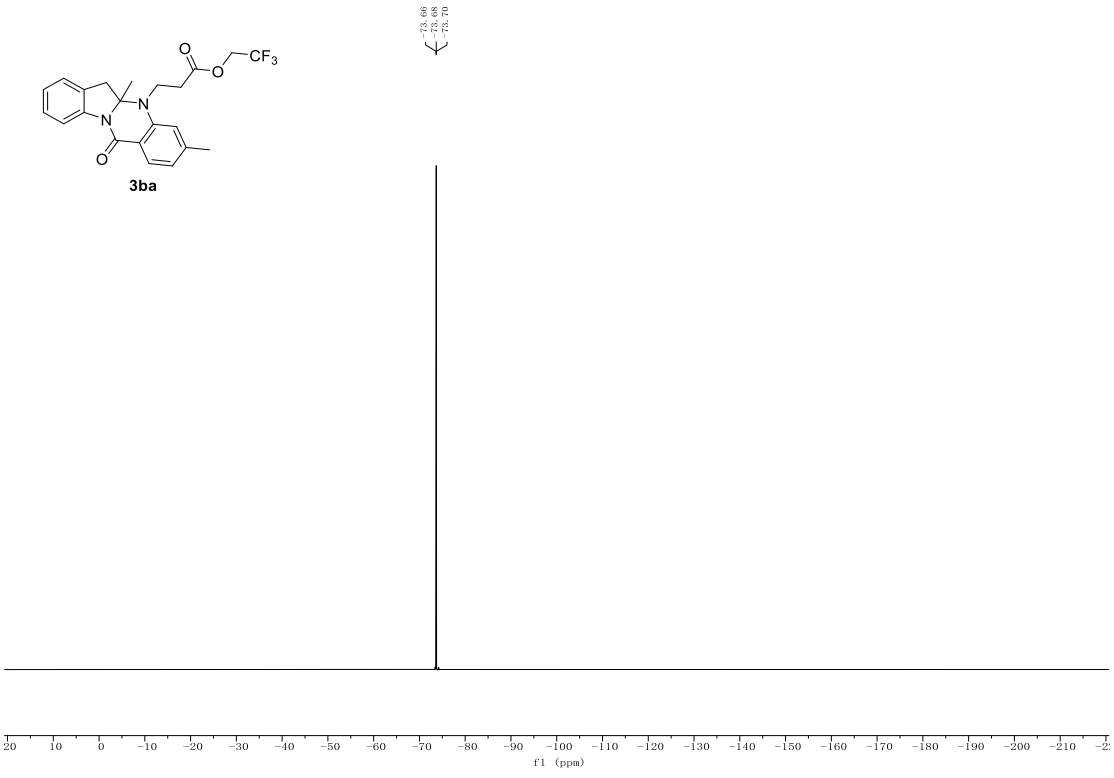
145.23
144.79
141.10
129.32
128.20
127.20
126.94
124.65
124.18
123.93
121.43
120.59
118.67
116.71
116.21
112.77
82.60
61.14
60.77
60.41
60.04
43.32
41.33
33.30
22.33
20.82
O
O
CF3
N
N
O
3ba
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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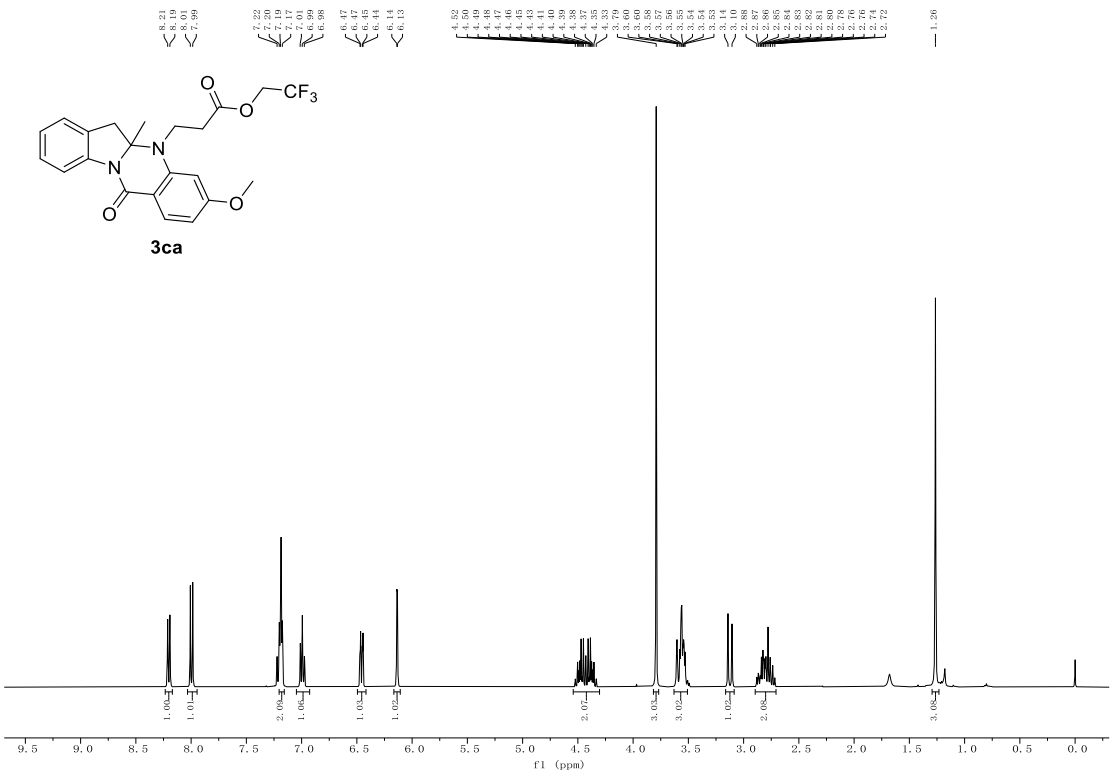
-73.68
-73.70
O
O
CF3
N
N
O
3ba
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
−90
−100
−110
−120
−130
−140
−150
−160
−170
−180
−190
−200
−210
f1 (ppm)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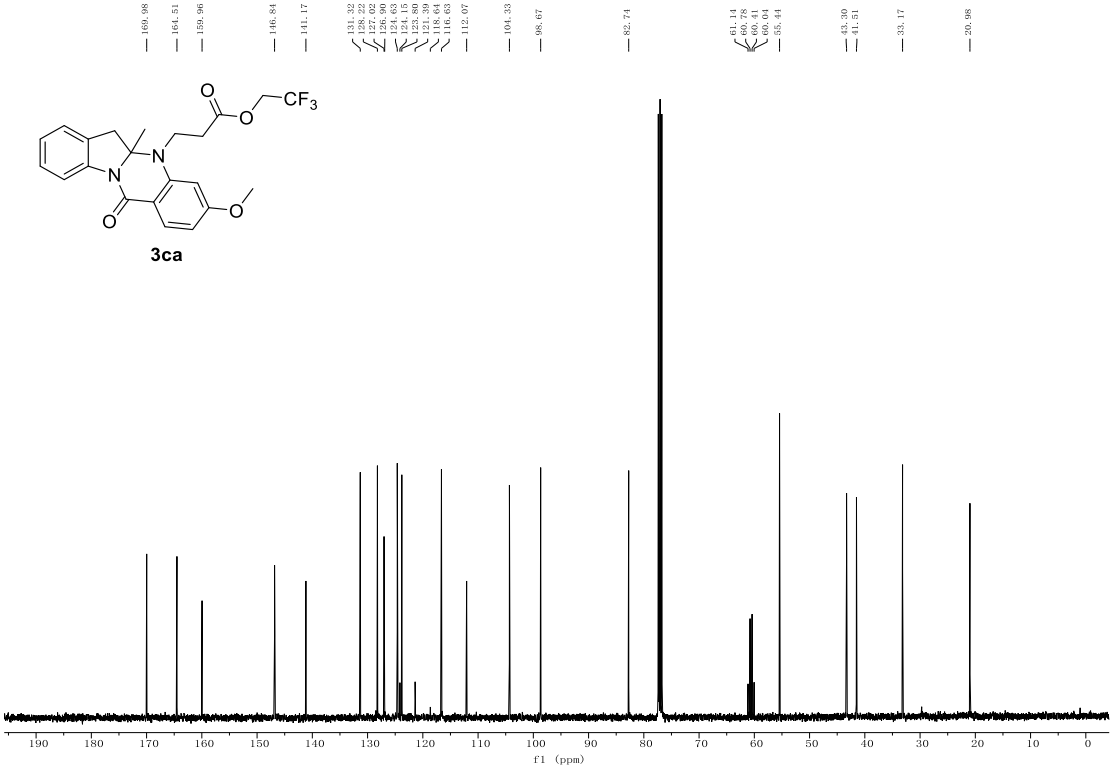
8.19
8.01
7.99
7.22
7.20
7.19
7.17
7.01
6.99
6.98
6.47
6.45
6.44
6.14
6.13
4.52
4.50
4.49
4.48
4.47
4.46
4.45
4.43
4.41
4.40
4.39
4.38
4.37
4.35
4.33
3.79
3.60
3.58
3.57
3.56
3.55
3.54
3.53
3.14
3.10
2.87
2.86
2.85
2.84
2.83
2.82
2.81
2.80
2.78
2.76
2.74
2.72
1.26
O
O
CF3
N
N
O
O
3ca
1.00
1.01
2.09
1.06
1.03
1.02
2.07
3.03
3.02
1.02
2.08
3.08
9.5
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
f1 (ppm)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164.51
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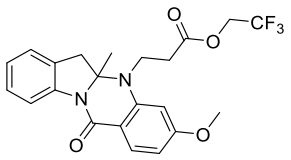
146.84
141.17
131.32
128.22
127.02
126.90
124.65
124.15
123.80
121.39
118.44
116.63
112.07
104.33
98.67
82.74
61.14
60.78
60.41
60.04
55.44
43.30
41.51
33.17
20.98
O
O
CF3
N
N
O
O
3ca
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)



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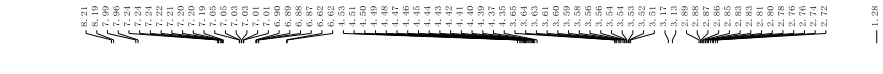
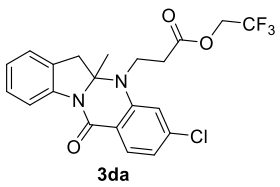
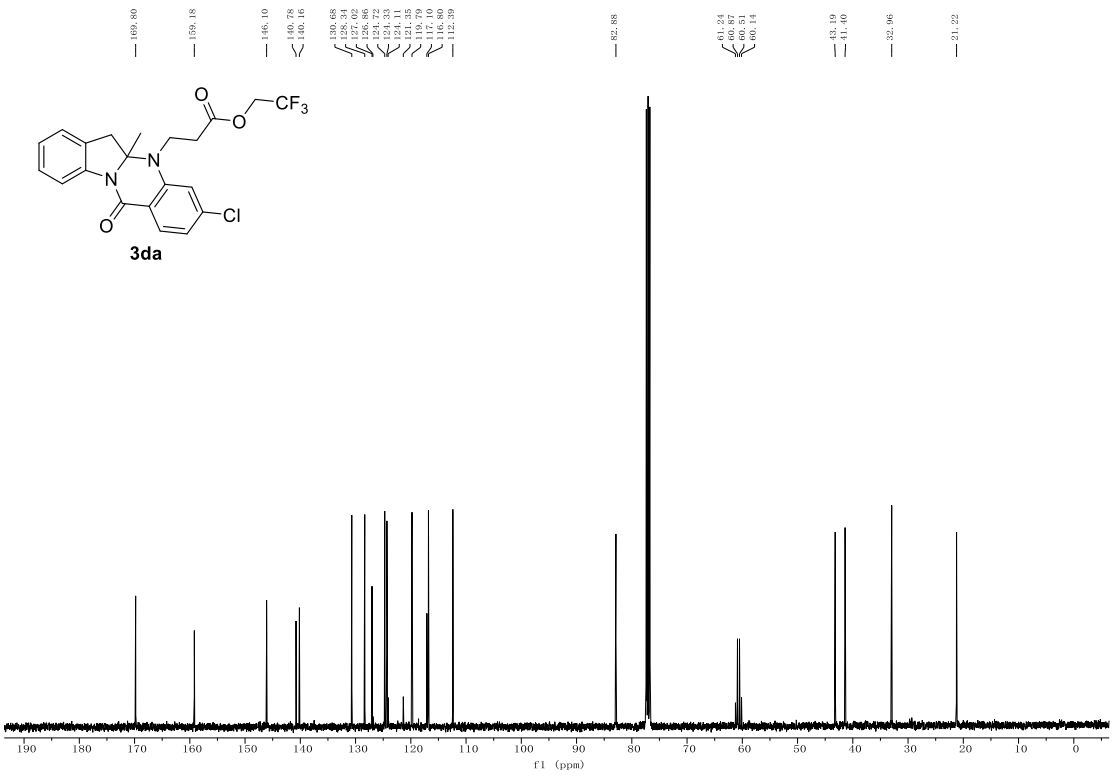




3da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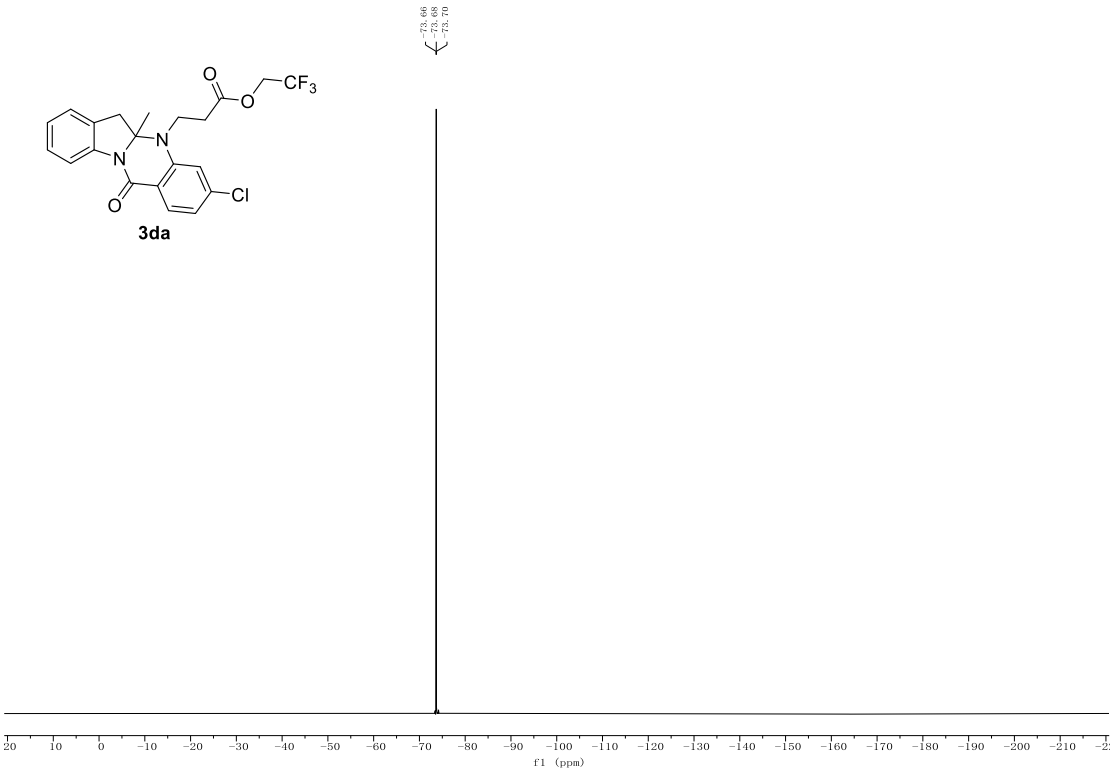
130.68
128.34
127.02
126.86
124.72
124.33
124.11
121.35
119.79
117.10
116.80
112.39
82.88
61.24
60.87
60.51
60.14
43.19
41.40
32.96
21.22
O
O
CF3
N
N
O
Cl
3da
f1 (ppm)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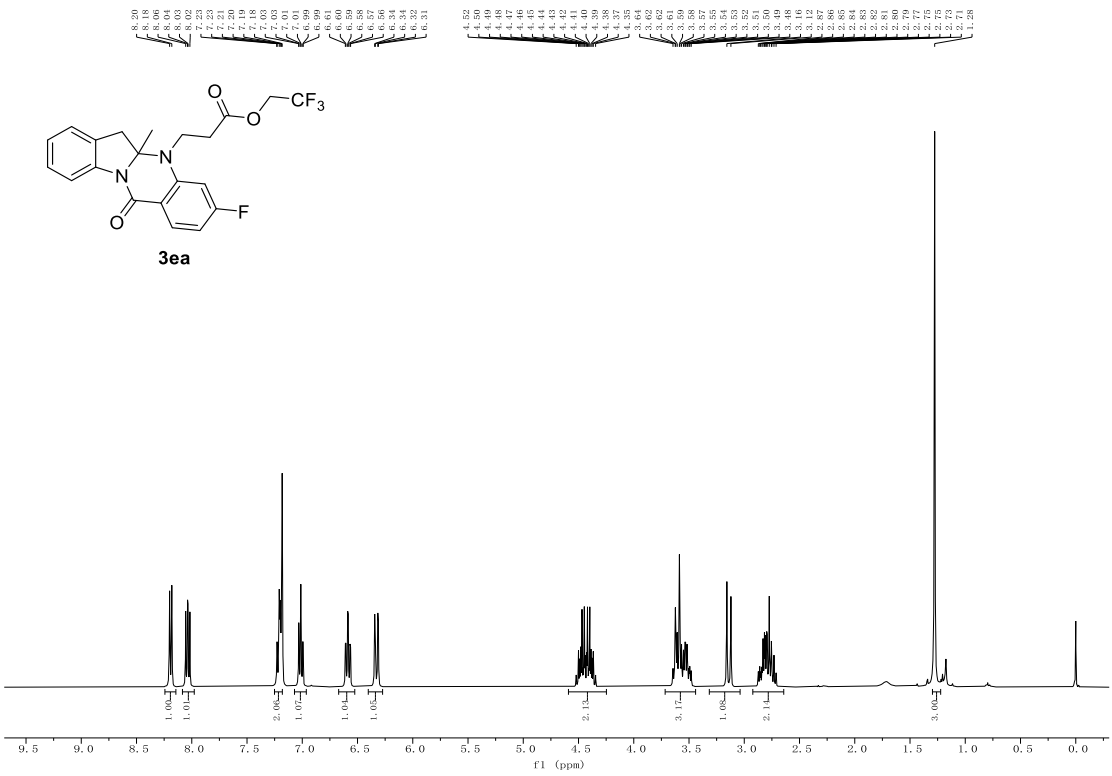
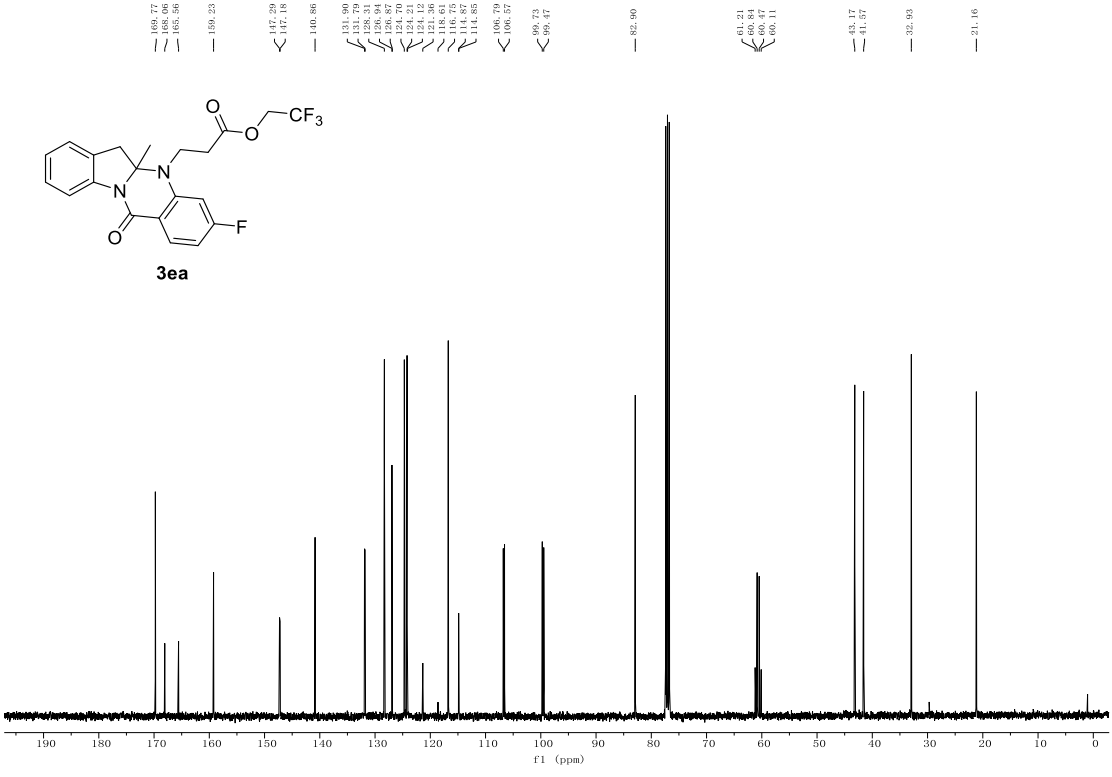
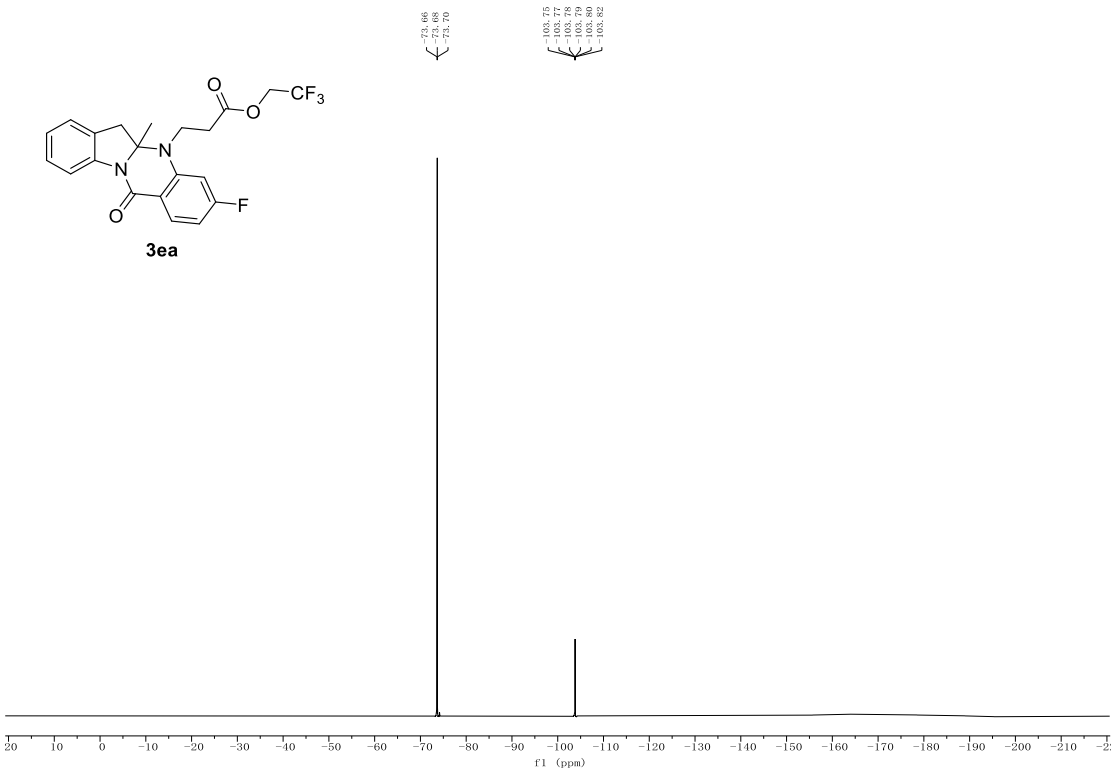
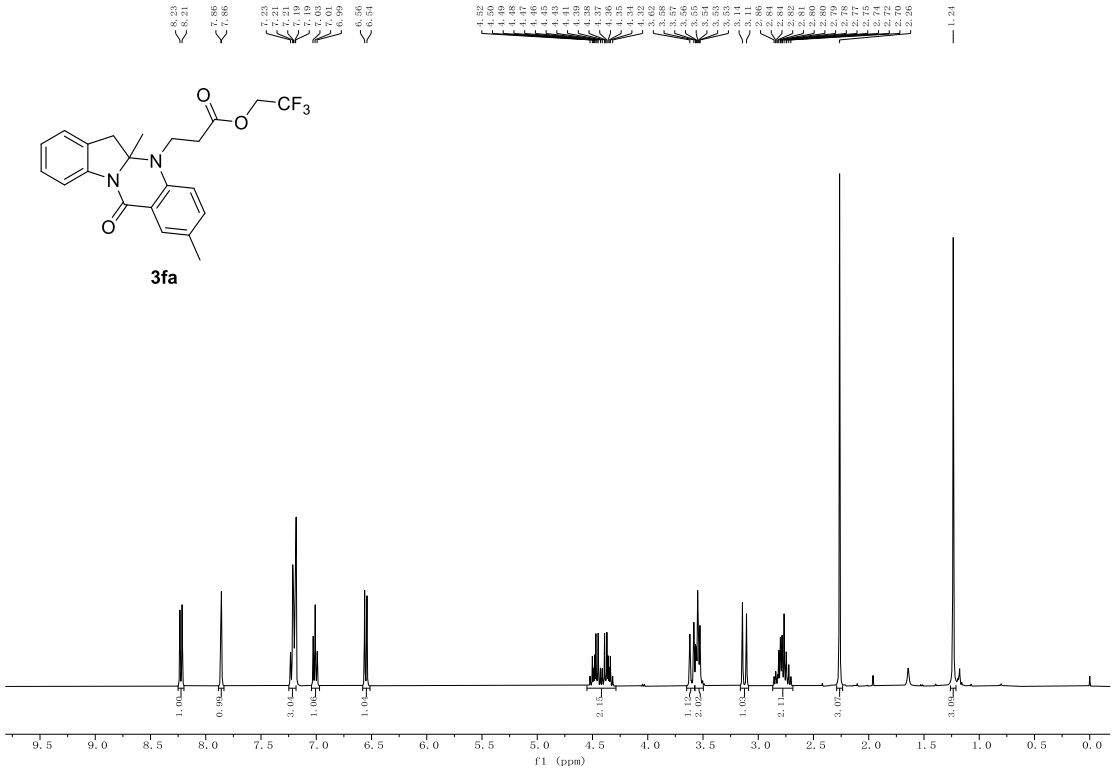
-73.68
-73.70
O
O
CF3
N
N
O
Cl
3da
f1 (ppm)


3ea
f1 (ppm)


3ea
f1 (ppm)


-73.68
-73.68
-73.70
-103.75
-103.77
-103.78
-103.79
-103.80
-103.82
O
O
CF3
N
N
O
F
3ea
f1 (ppm)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7.86
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7.21
7.19
7.19
7.03
7.01
6.99
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6.54
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4.50
4.49
4.48
4.47
4.46
4.45
4.43
4.41
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2.78
2.77
2.75
2.74
2.72
2.70
2.26
1.24
O
O
CF3
N
N
O
3fa
1.00
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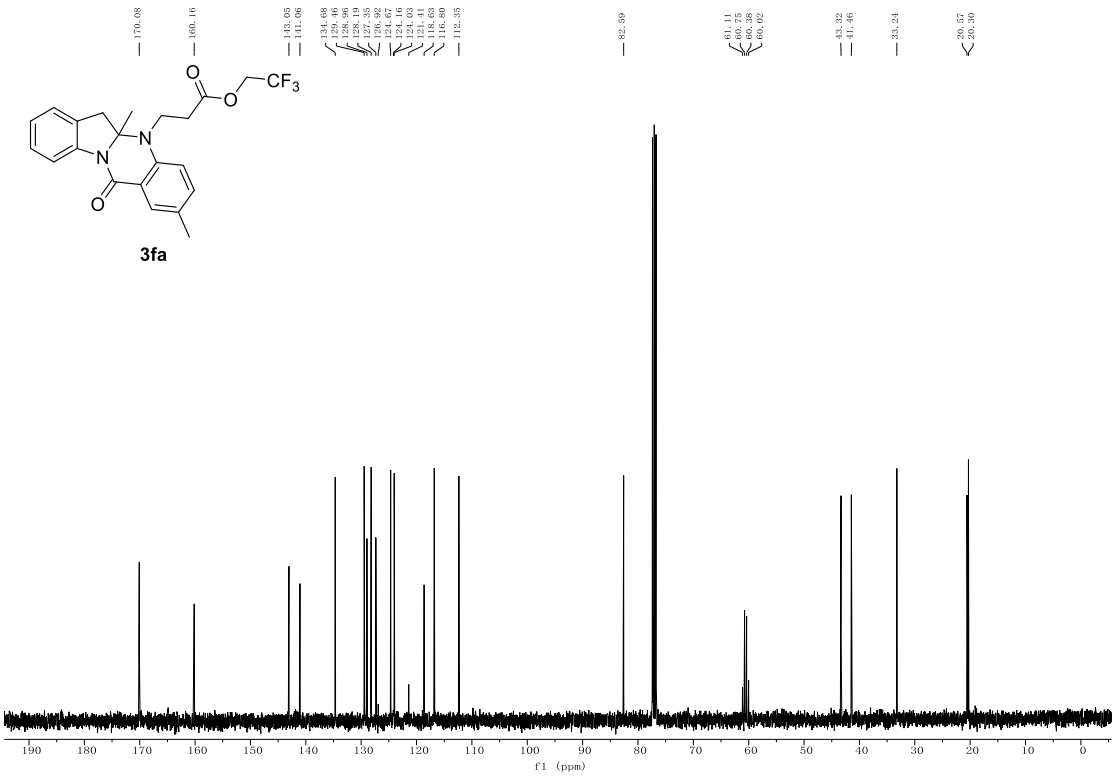
1.04
2.16
1.12
2.05
1.03
2.11
3.07
3.00
f1 (ppm)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128.19
127.35
126.94
124.67
124.16
124.03
123.41
118.63
116.80
112.35
82.59
61.11
60.75
60.38
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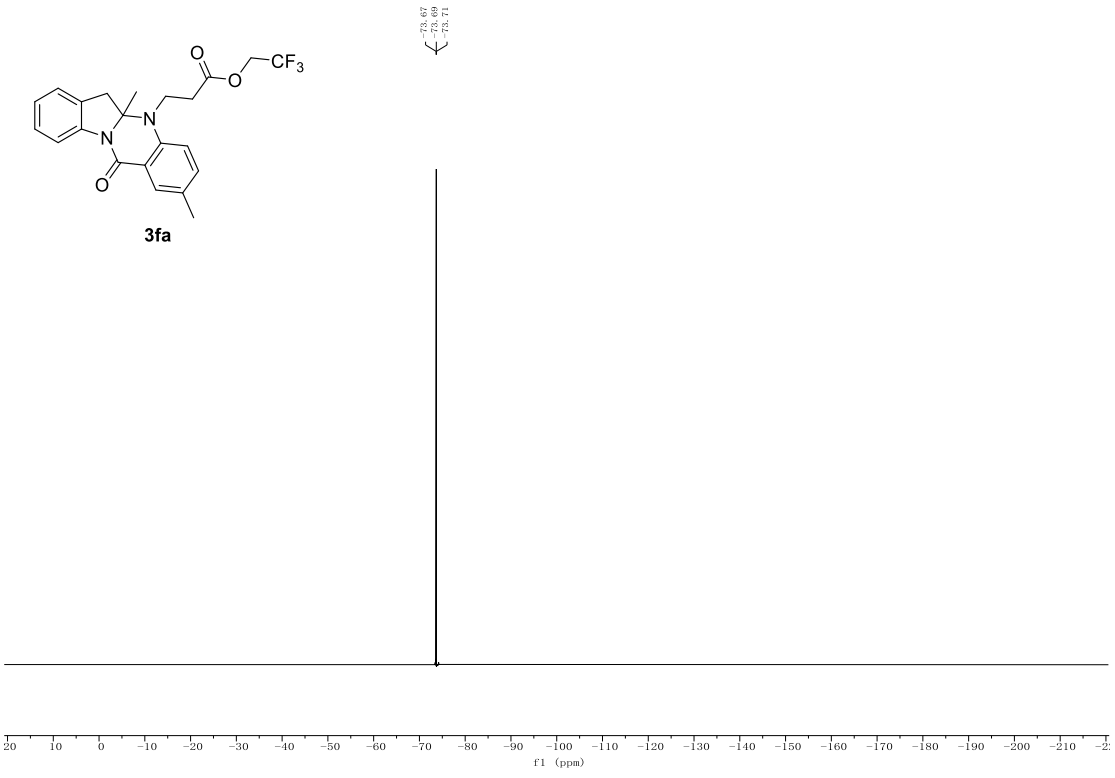
43.32
41.46
33.24
20.57
20.30
O
O
CF3
N
N
O
3fa
f1 (ppm)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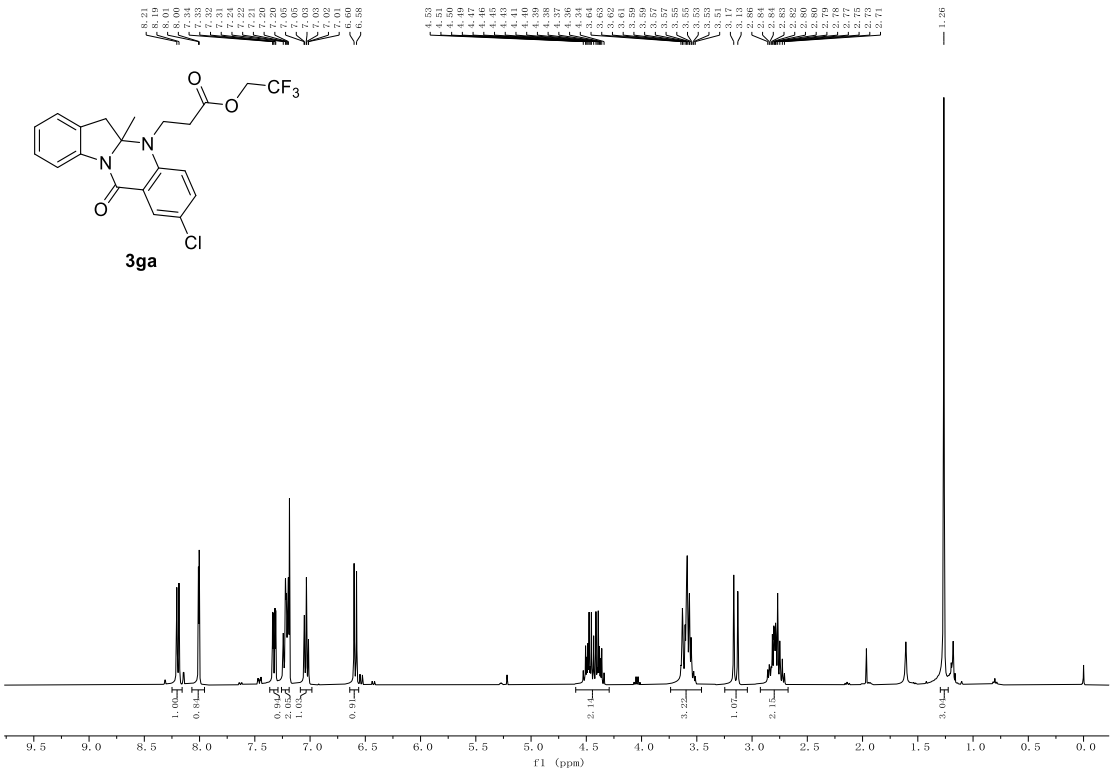
-73.71
O
O
CF3
N
N
O
3fa
f1 (ppm)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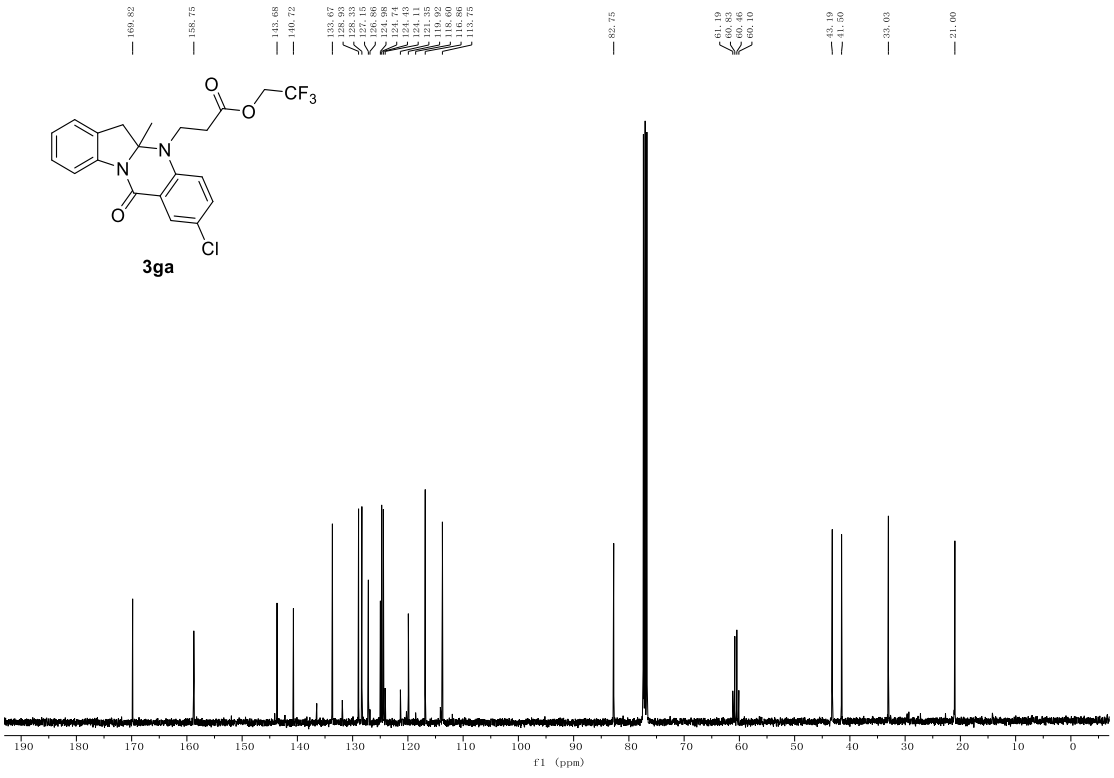
f1 (ppm)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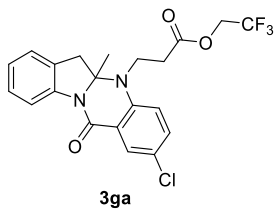
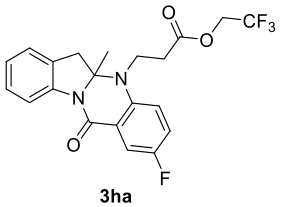
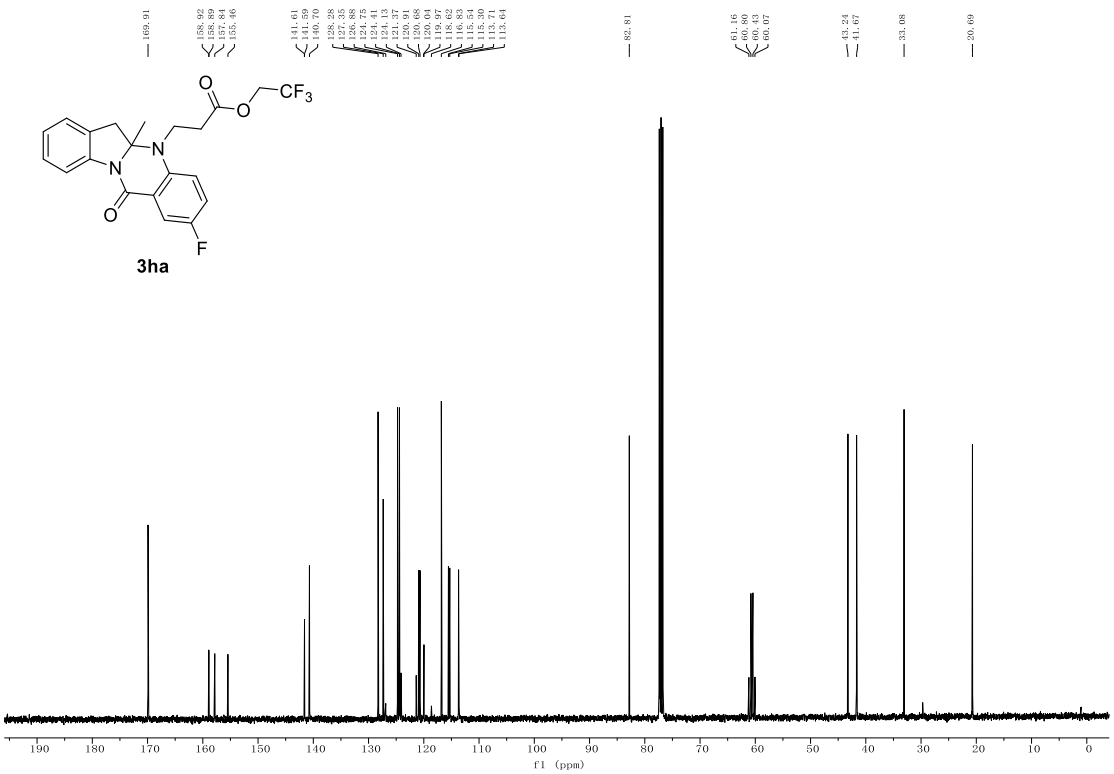


3ga



3ha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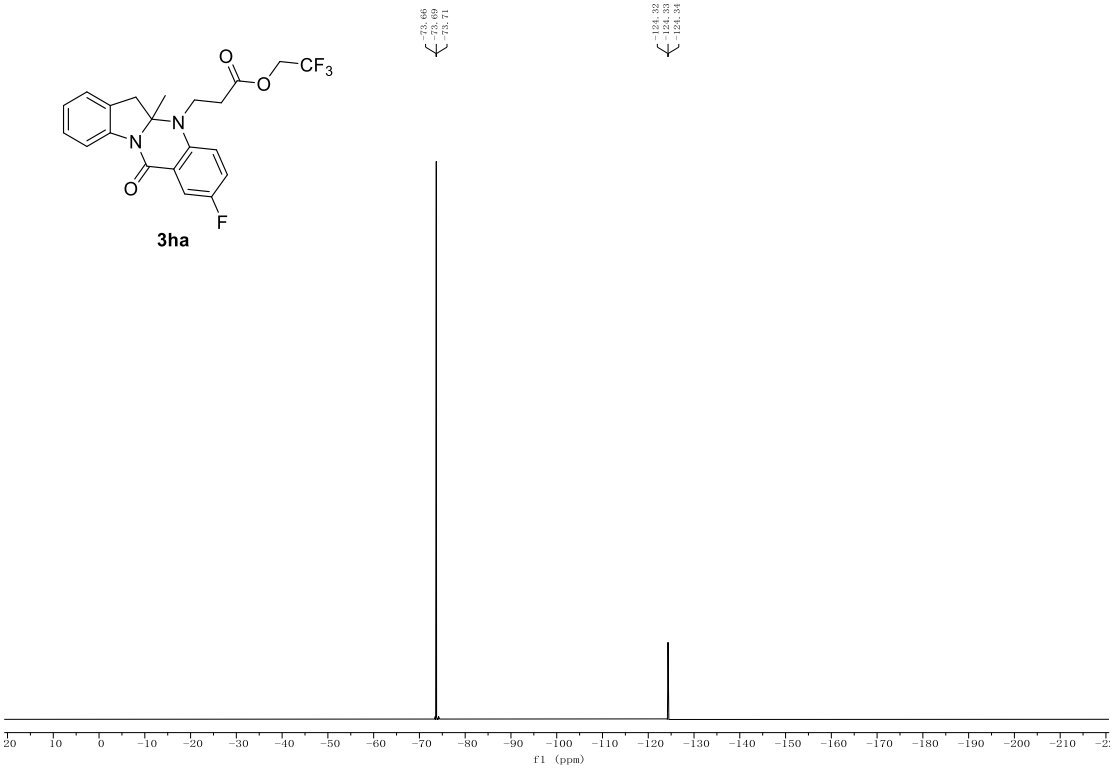
124.75
124.41
124.13
121.37
120.84
120.68
120.04
118.97
118.62
116.83
115.54
115.30
113.77
113.64
82.81
61.16
60.90
60.43
60.07
43.24
41.67
33.08
20.69
O
O
CF3
N
N
O
F
3ha
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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-73.71
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-124.33
-124.34
O
O
CF3
N
N
O
F
3ha
20
10
0
-10
-20
-30
-40
-50
-60
-70
-80
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-100
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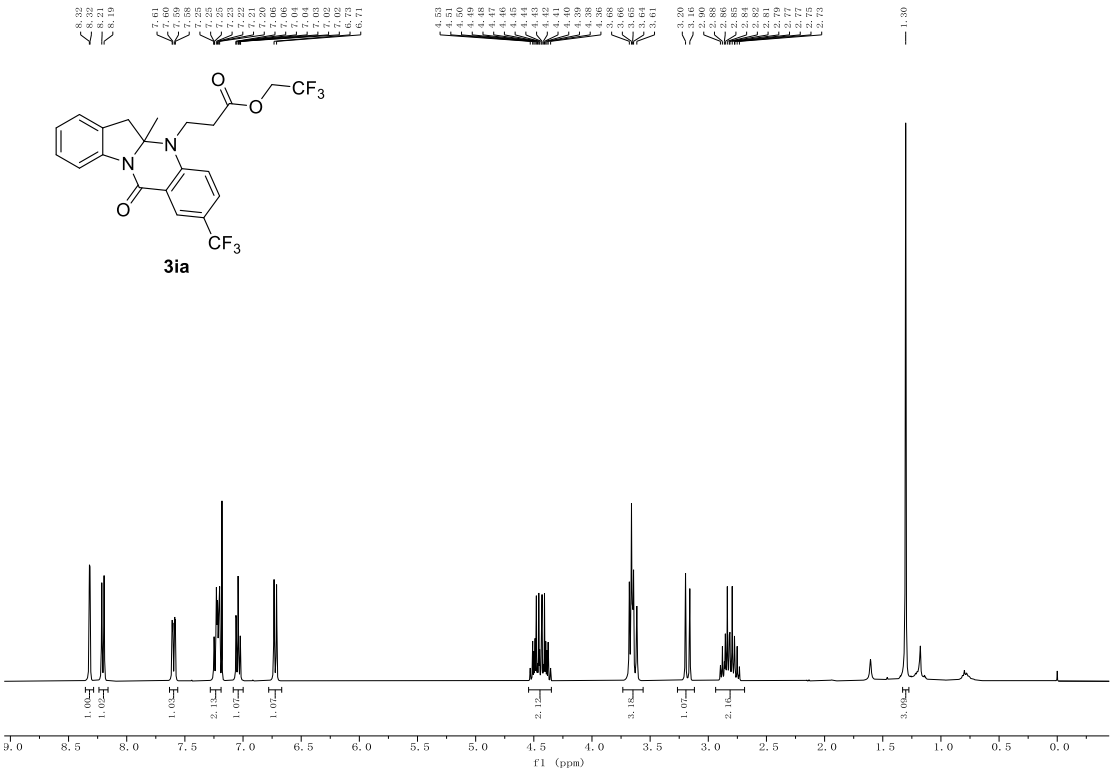
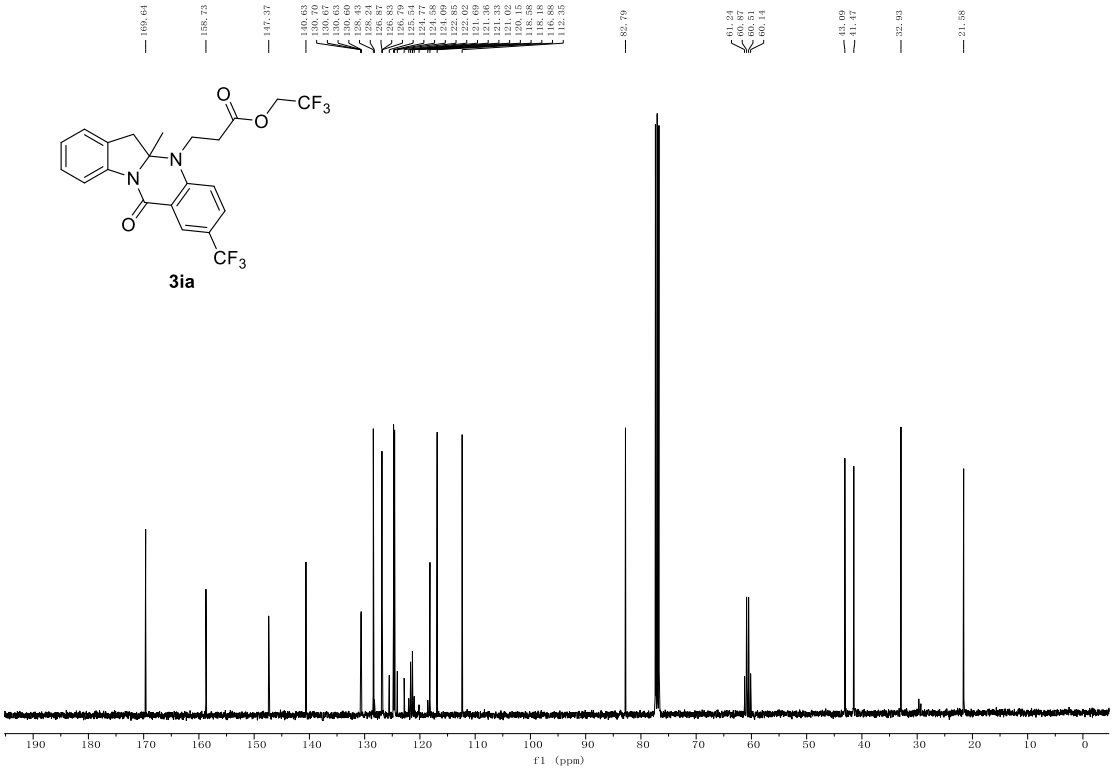
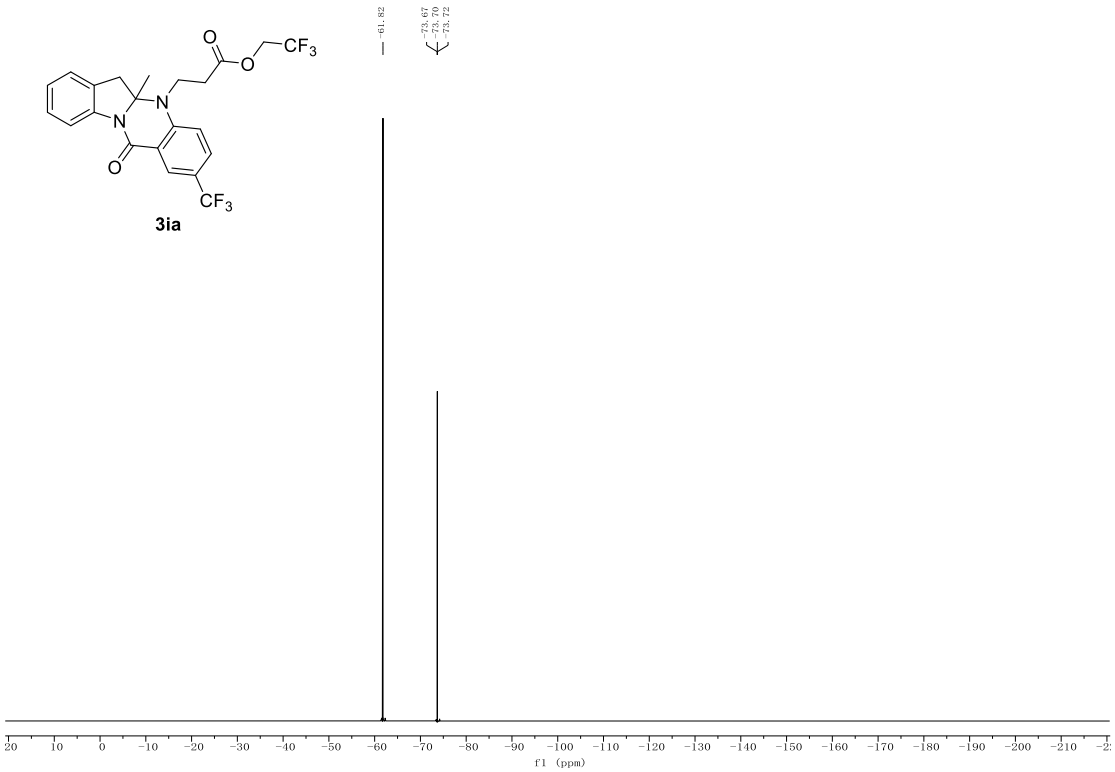
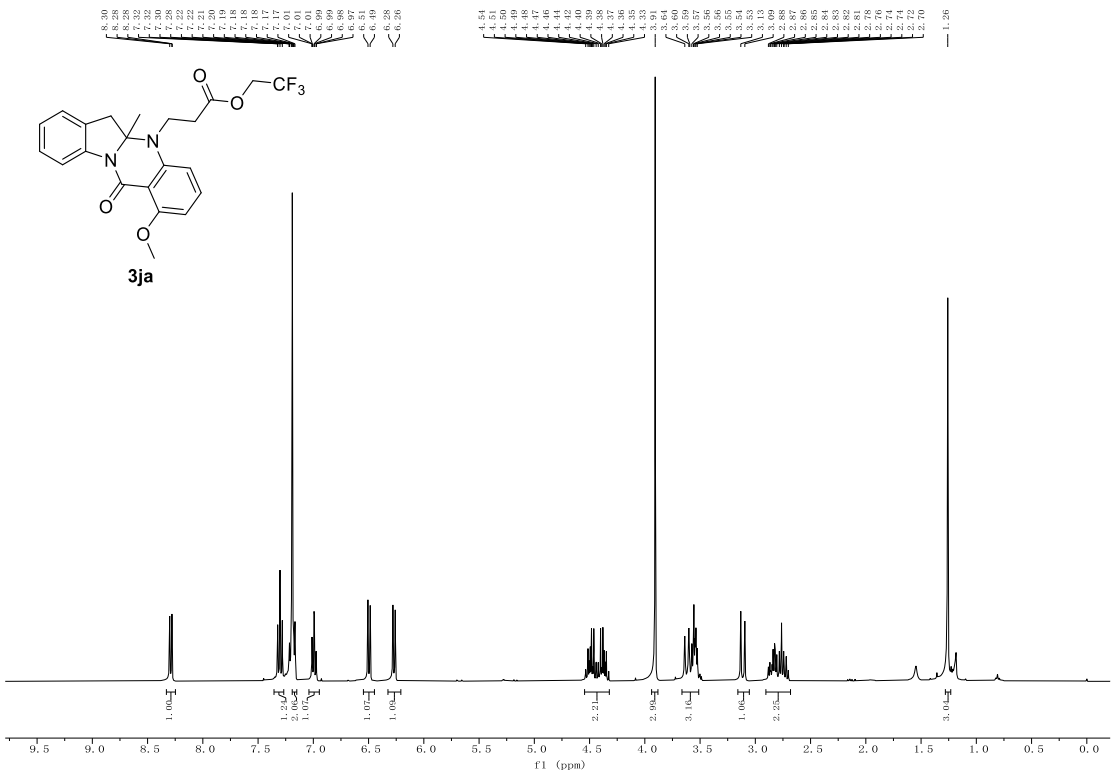
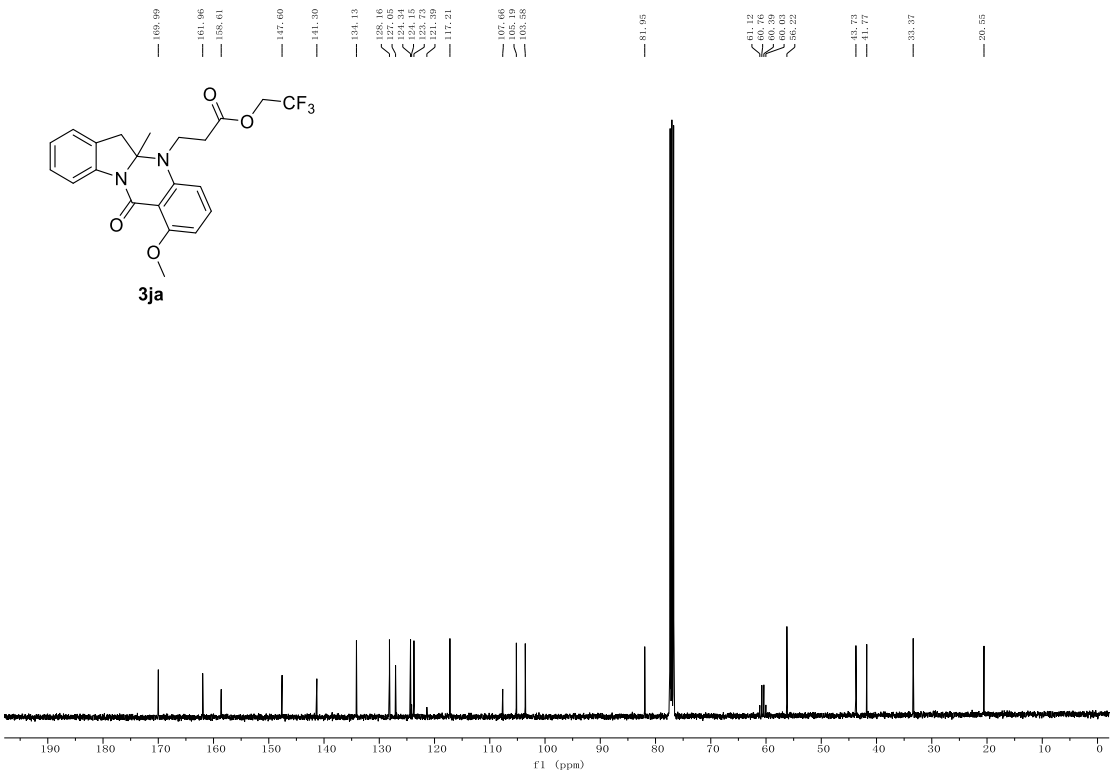
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)


3ia
f1 (ppm)


3ia
f1 (ppm)


O
O
CF3
N
N
O
CF3
3ia
-61.82
-73.67
-73.70
-73.72
f1 (ppm)


O
O
CF3
N
N
O
O
3ja
f1 (ppm)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147.60
141.30
134.13
128.16
127.05
124.34
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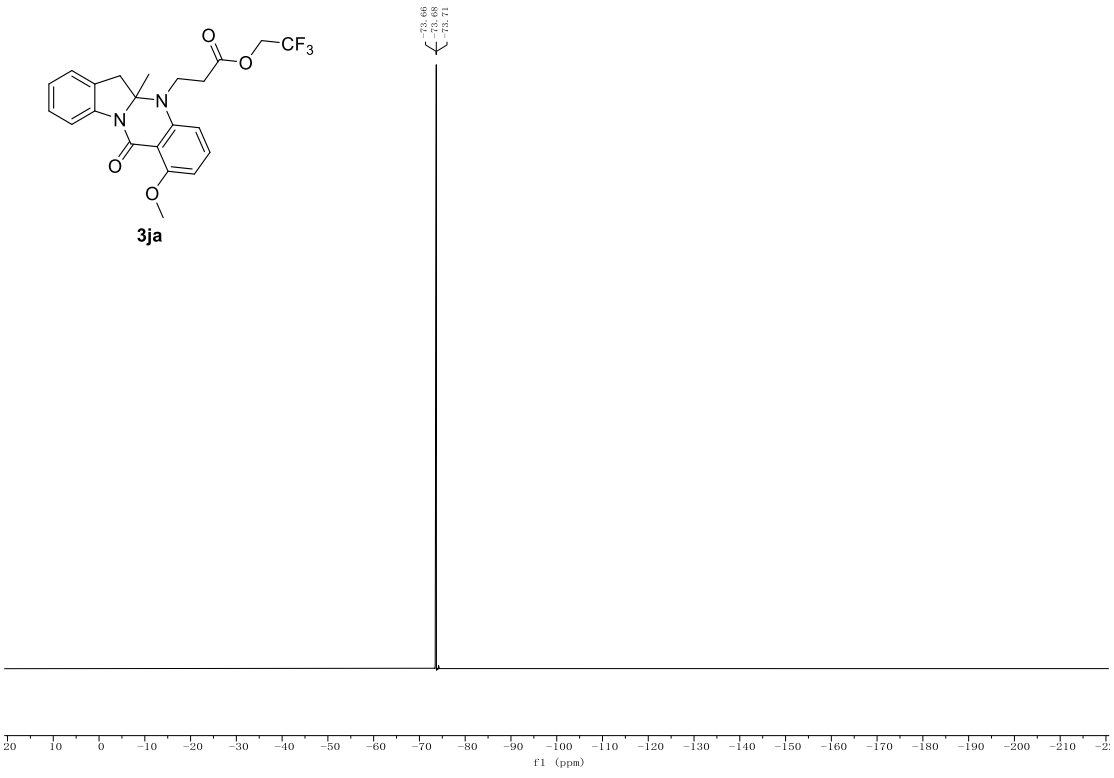
122.73
121.39
117.21
107.66
105.19
103.58
81.95
61.12
60.76
60.39
60.03
56.22
43.73
41.77
33.37
20.55
O
O
CF3
N
N
O
O
3ja
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-73.68
-73.68
-73.71
O
O
CF3
N
N
O
O
3ja
20
10
0
−10
−20
−30
−40
−50
−60
−70
−80
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−140
−150
−160
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−180
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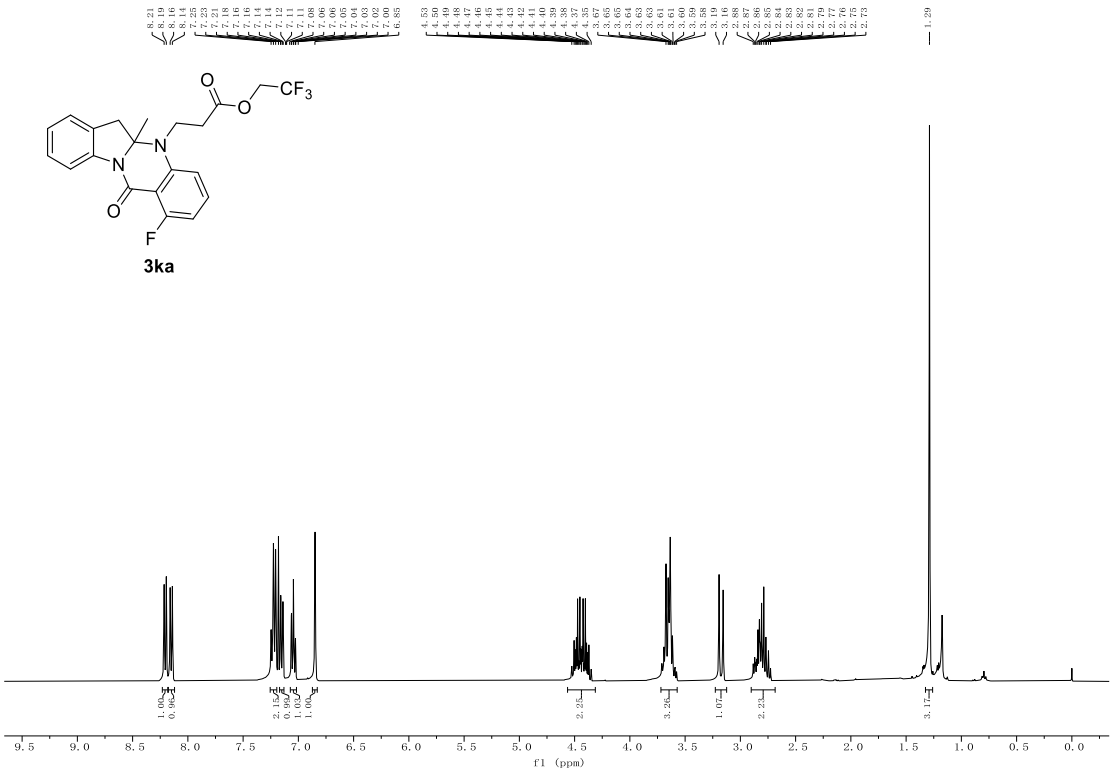
−210
f1 (ppm)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7.08
7.06
7.05
7.04
7.03
7.02
7.00
6.85
4.53
4.50
4.49
4.48
4.47
4.46
4.45
4.44
4.43
4.42
4.41
4.40
4.39
4.38
4.37
4.35
3.67
3.65
3.64
3.63
3.63
3.61
3.61
3.60
3.59
3.58
3.19
3.16
2.88
2.87
2.86
2.85
2.84
2.83
2.82
2.81
2.79
2.77
2.76
2.75
2.73
1.29
O
O
CF3
N
N
O
F
3ka
1.00
0.96
2.15
0.99
1.03
1.00
2.25
3.26
1.07
2.23
3.17
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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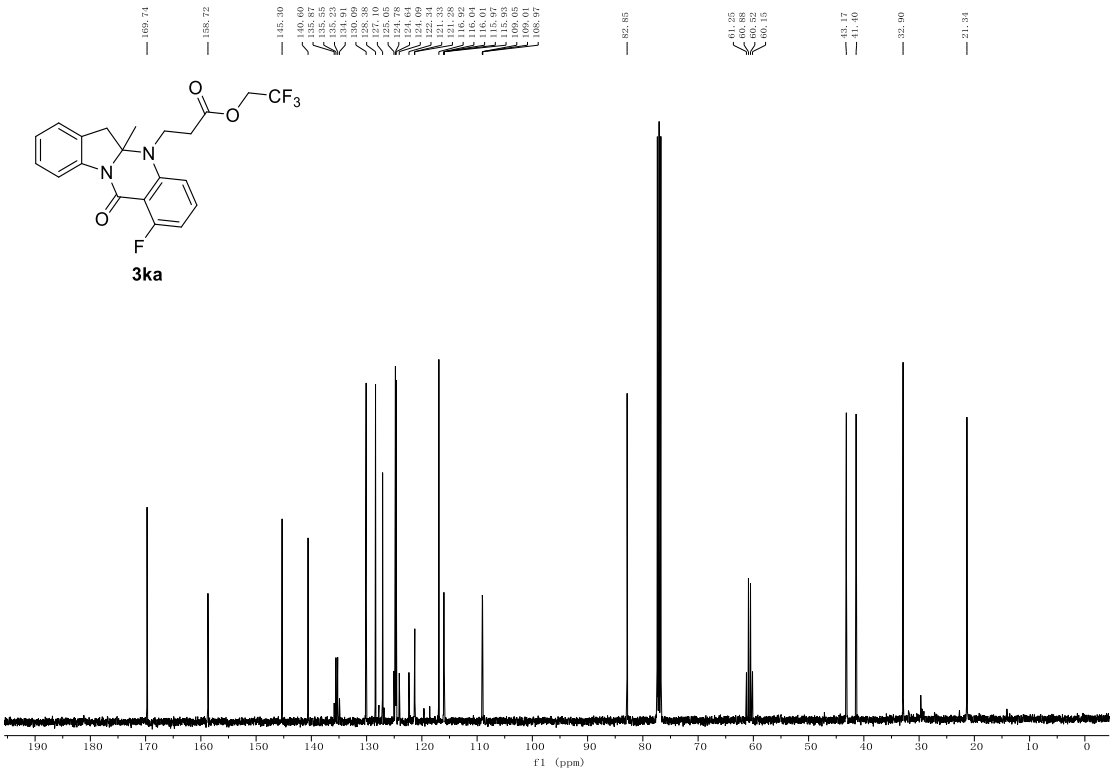
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.91
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127.10
125.05
124.78
124.64
124.09
122.34
121.33
121.08
116.97
116.04
116.01
115.97
115.93
109.05
109.01
108.97
82.85
61.25
60.88
60.52
60.15
43.17
41.40
32.90
21.34
O
O
CF3
N
N
O
F
3ka
190
180
170
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130
120
110
100
90
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70
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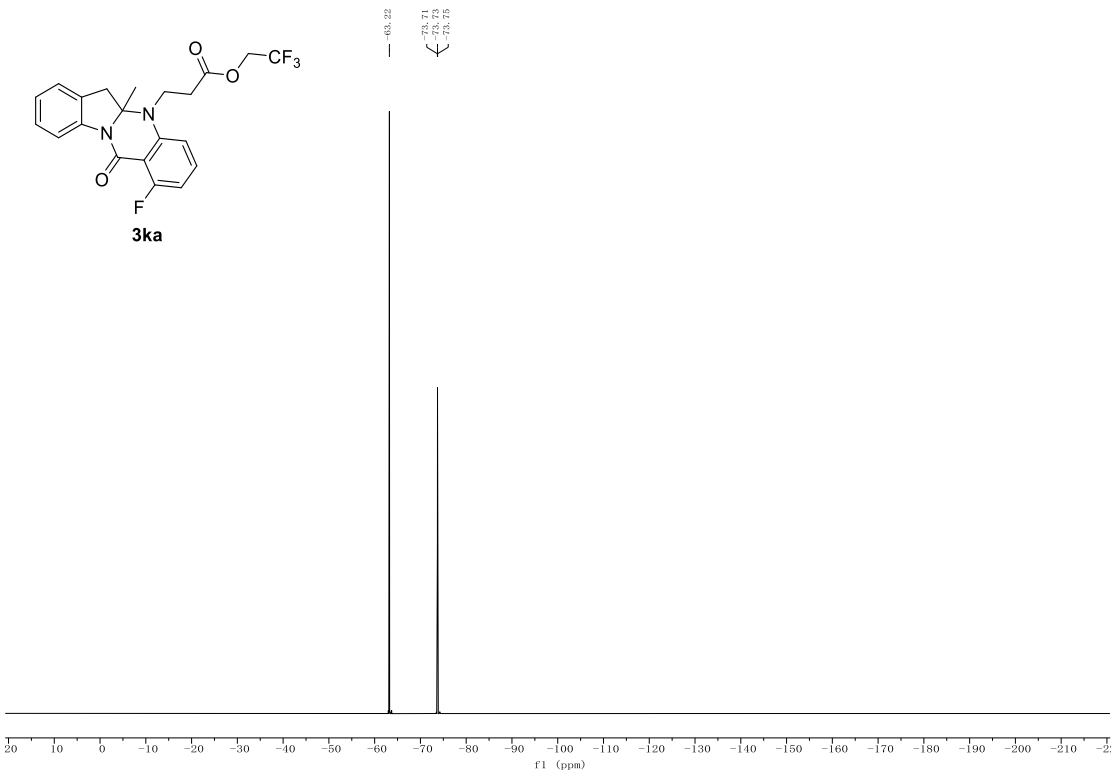
50
40
30
20
10
0
f1 (ppm)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-73.73
-73.75
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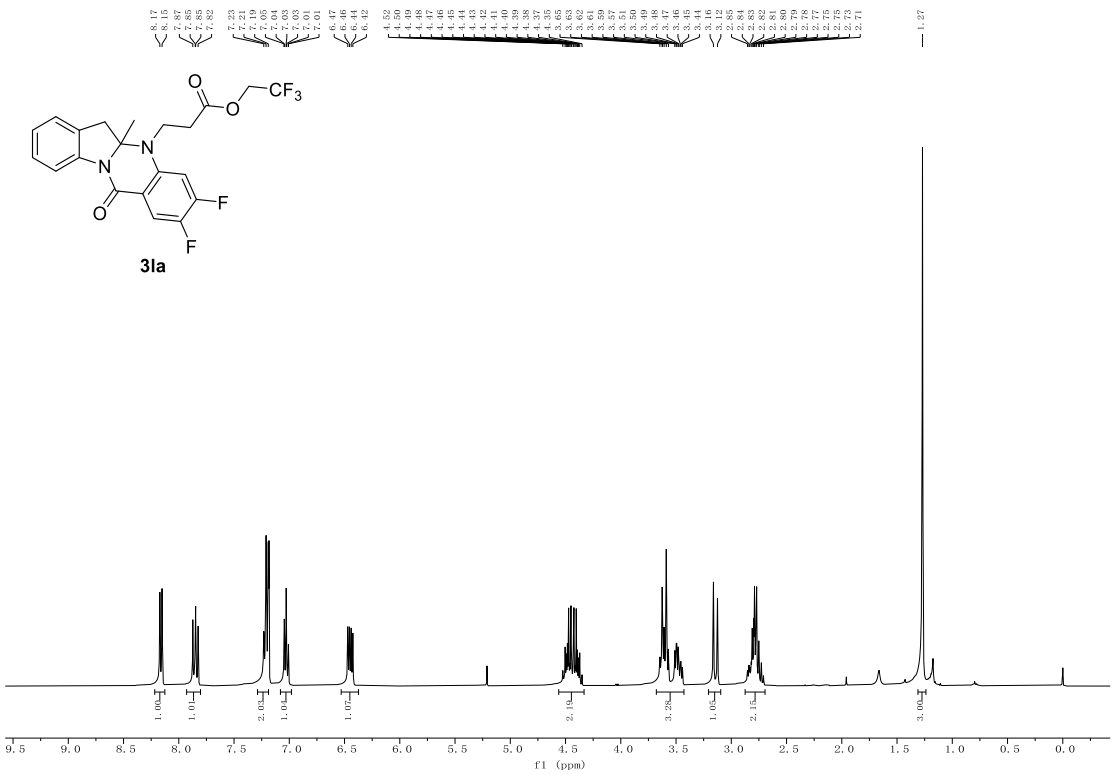
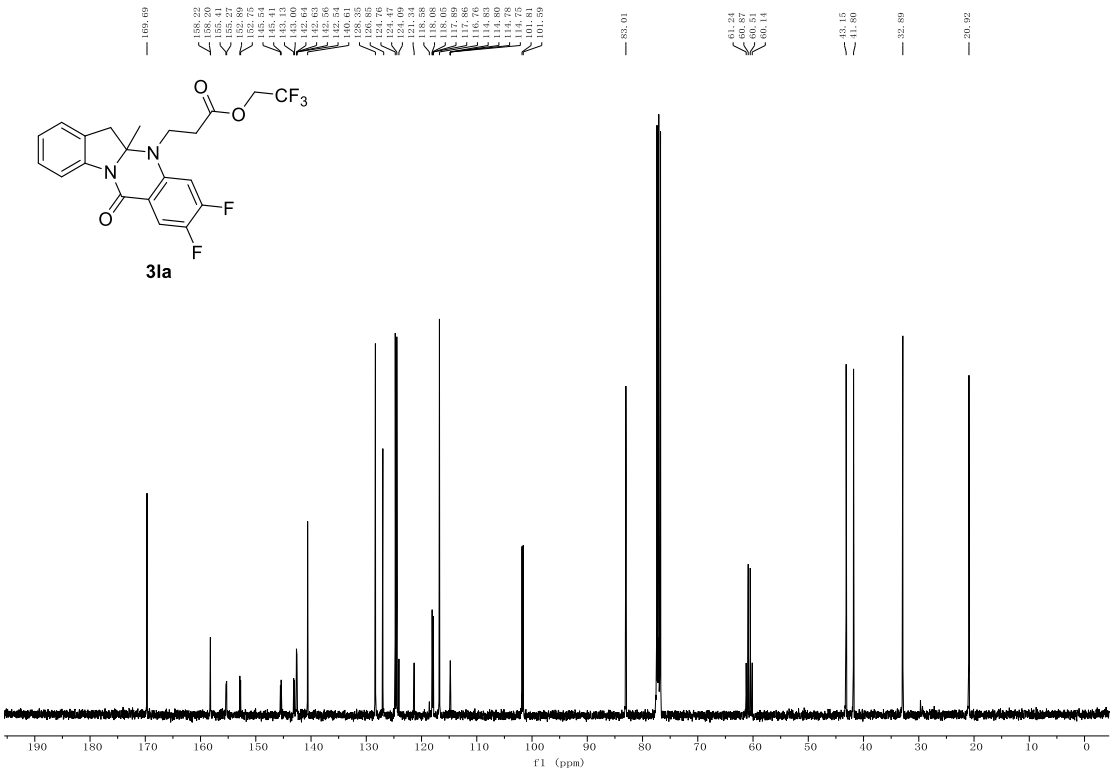
f1 (ppm)


3la
f1 (ppm)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145.54
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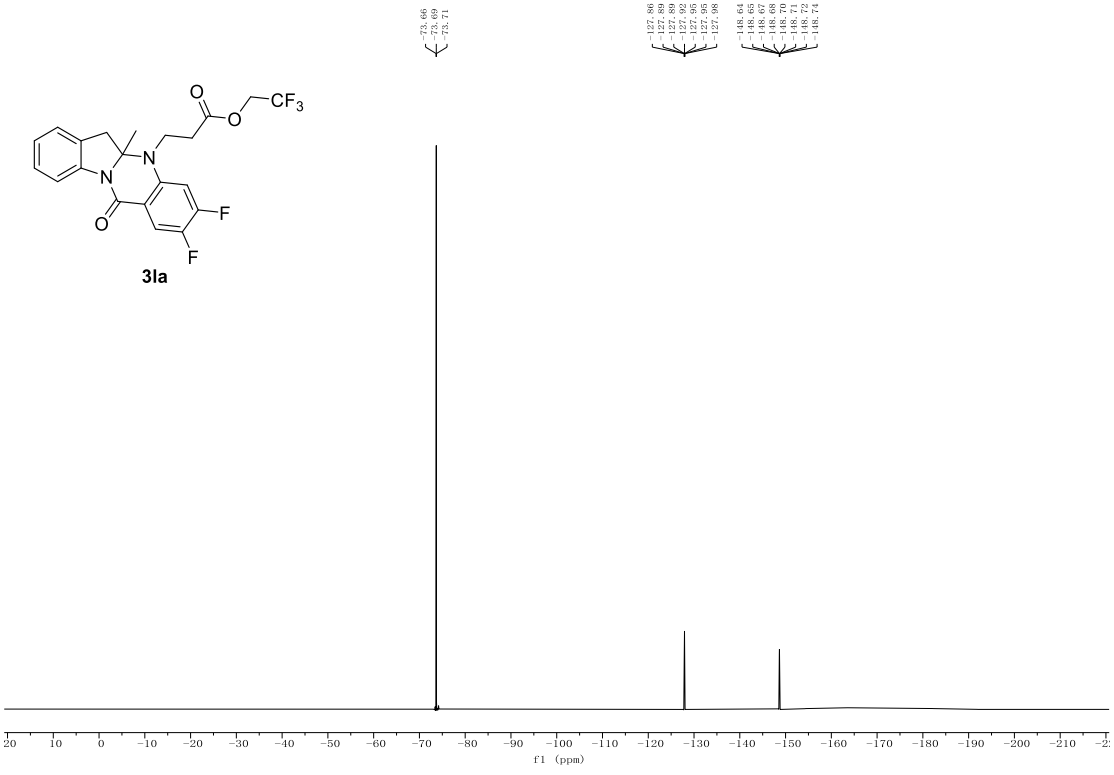
143.13
143.09
142.64
142.63
142.56
142.54
140.61
128.35
126.85
124.75
124.47
124.09
121.34
118.58
118.08
118.05
117.89
117.66
116.76
114.83
114.80
114.78
114.75
101.81
101.59
83.01
61.24
60.87
60.51
60.14
43.15
41.80
32.89
20.92
O
O
CF3
N
N
O
F
F
3la
f1 (ppm)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-73.71
-127.86
-127.89
-127.89
-127.92
-127.95
-127.95
-127.98
-148.64
-148.65
-148.67
-148.68
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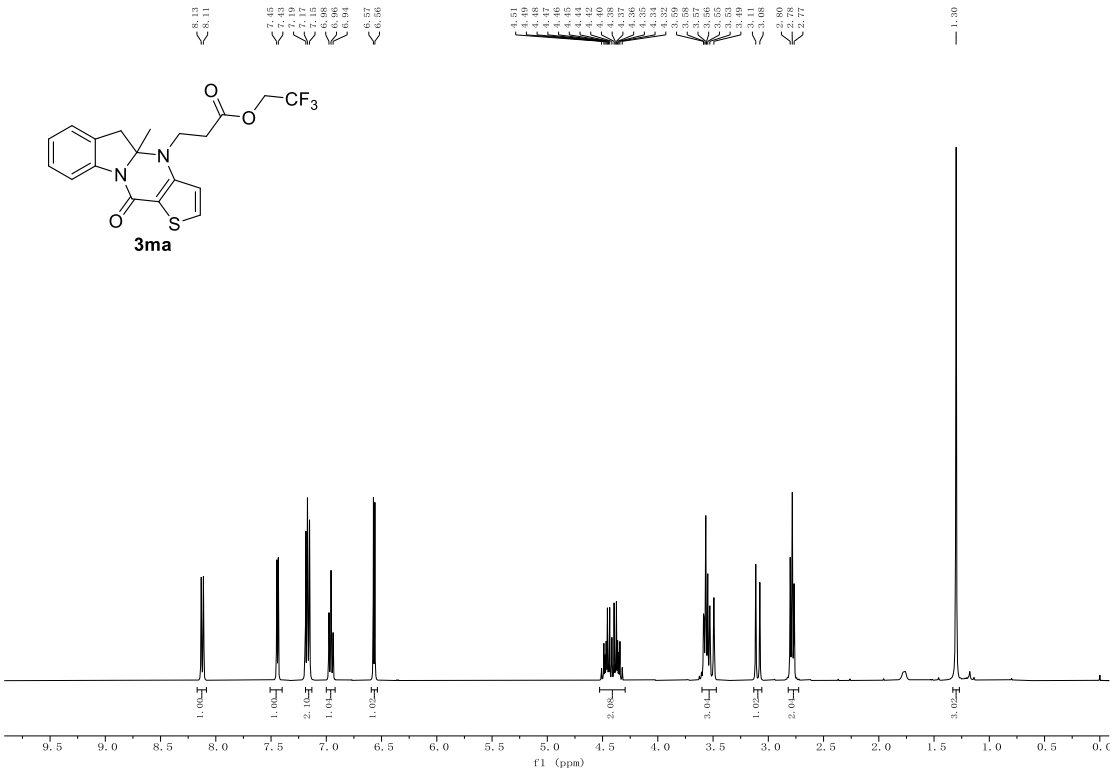
-148.72
-148.74
O
O
CF3
N
N
O
F
F
3la
f1 (ppm)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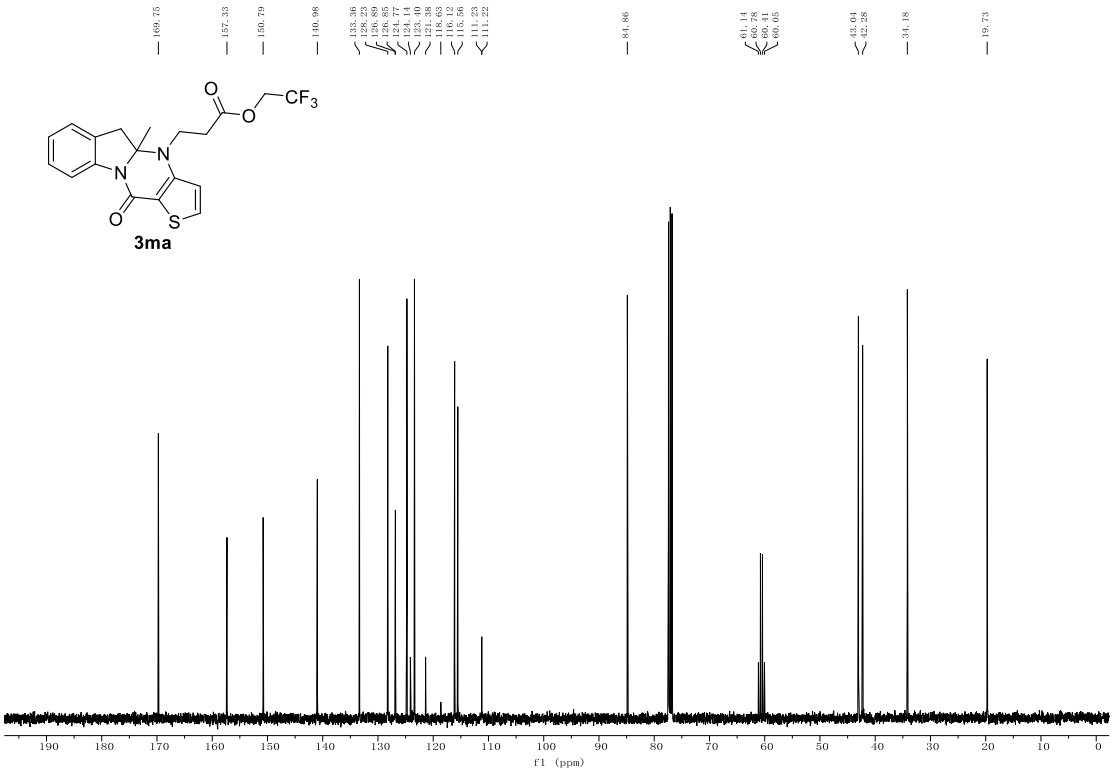
7.43
7.19
7.17
7.15
6.98
6.96
6.94
6.57
6.56
4.51
4.49
4.48
4.47
4.46
4.45
4.44
4.42
4.40
4.38
4.37
4.36
4.35
4.34
4.32
3.59
3.58
3.57
3.56
3.55
3.53
3.49
3.11
3.08
2.80
2.78
2.77
1.30
O
O
CF3
N
N
O
S
3ma
1.00
1.00
2.10
1.04
1.02
2.08
3.04
1.02
2.04
3.02
f1 (ppm)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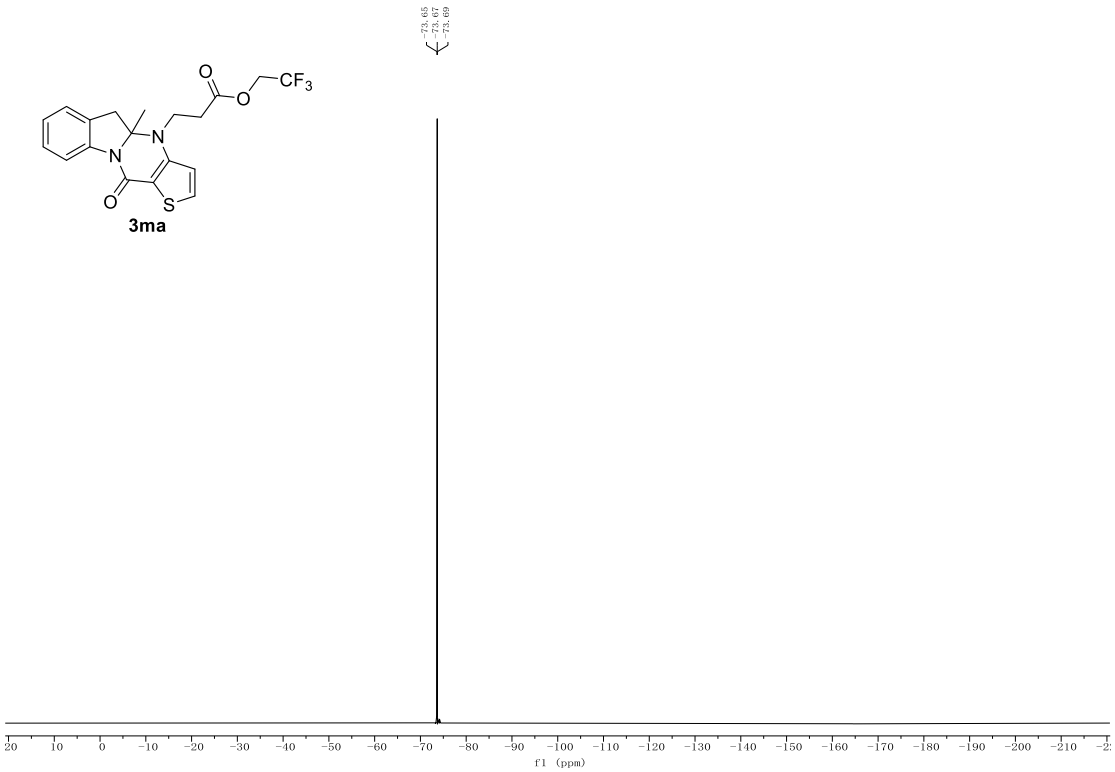
126.85
124.77
124.14
123.40
121.38
118.63
116.12
115.56
111.23
111.22
84.86
61.14
60.78
60.41
60.05
43.04
42.28
34.18
19.73
O
O
CF3
N
N
O
S
3ma
f1 (ppm)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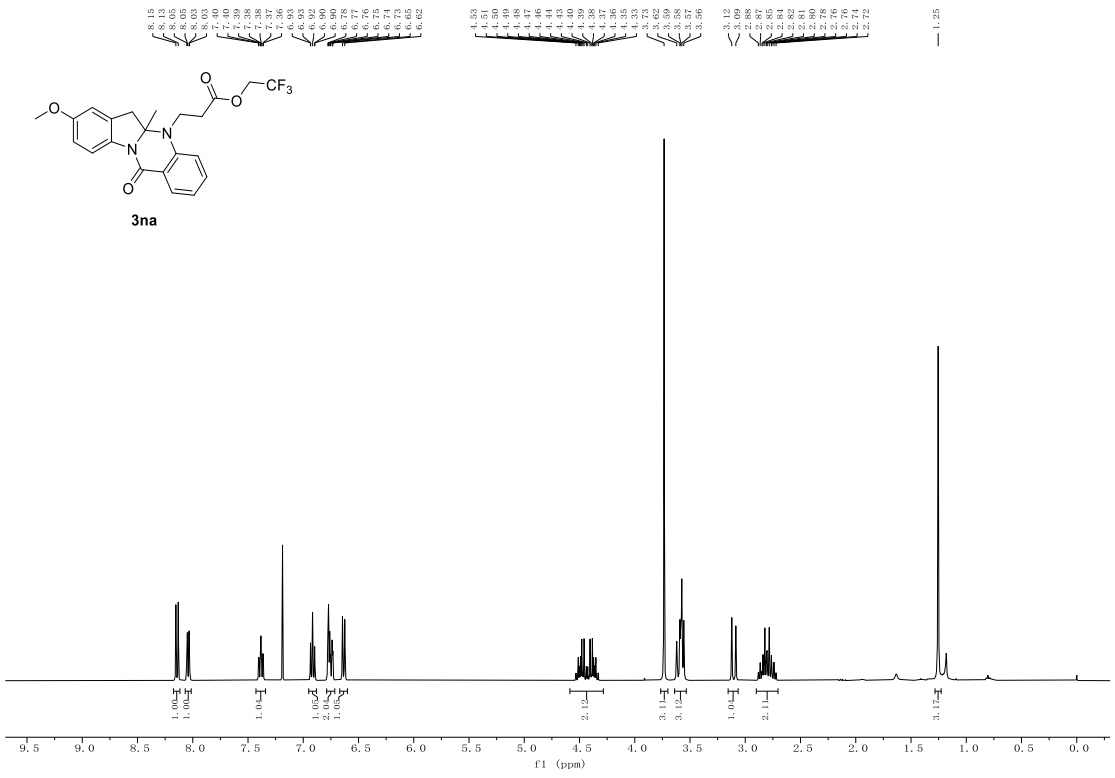
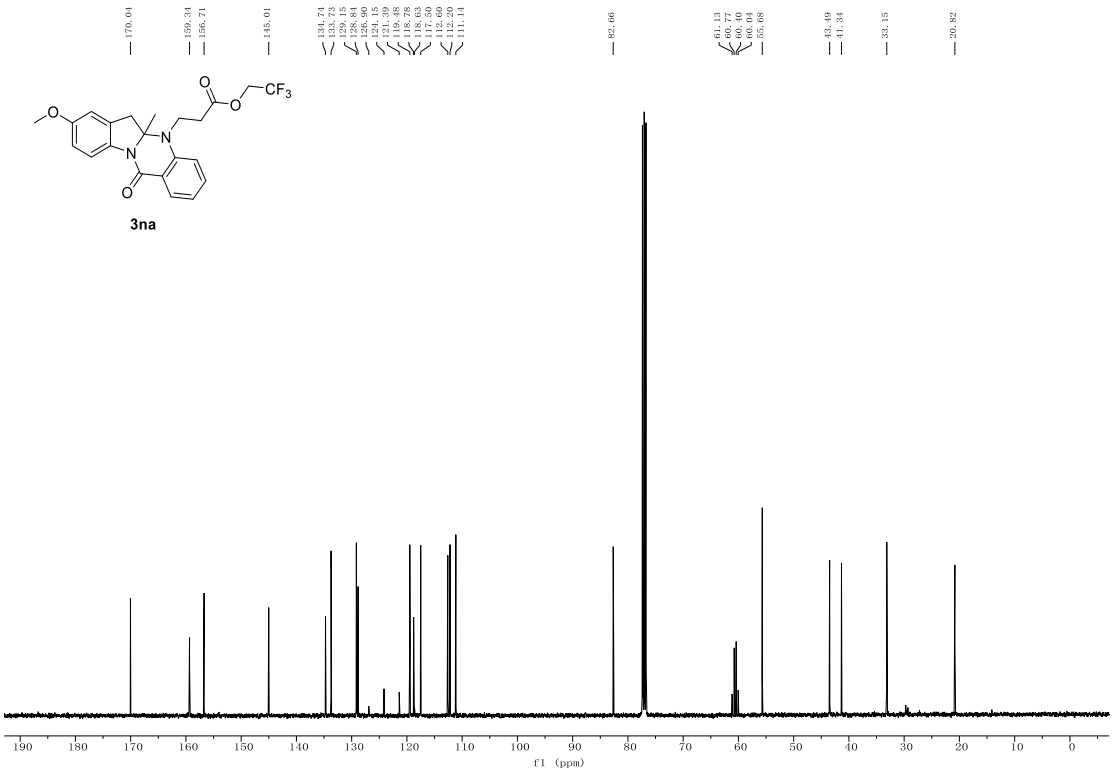
-73.69
3ma
f1 (ppm)


3na
f1 (ppm)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156.71
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134.74
133.73
129.15
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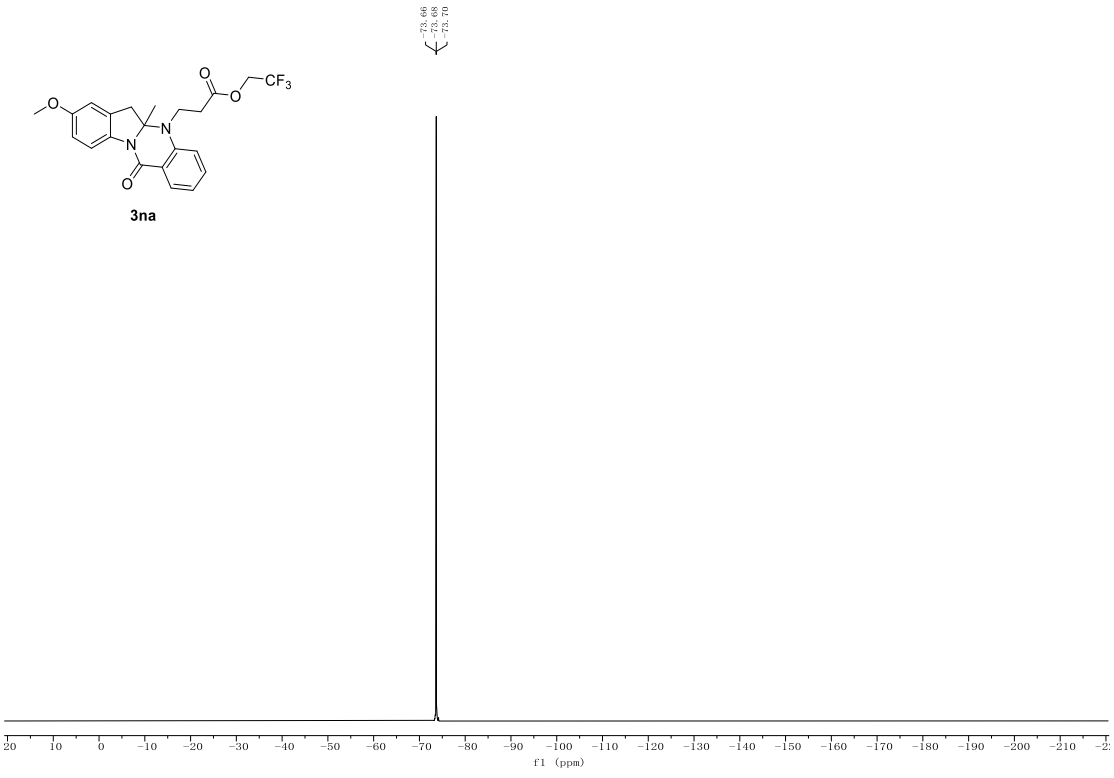
124.15
121.39
119.48
118.75
118.63
117.56
112.60
111.20
111.14
82.66
61.13
60.77
60.40
60.04
55.68
43.49
41.34
33.15
20.82
O
O
CF3
O
N
N
O
3na
f1 (ppm)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73.68
73.70
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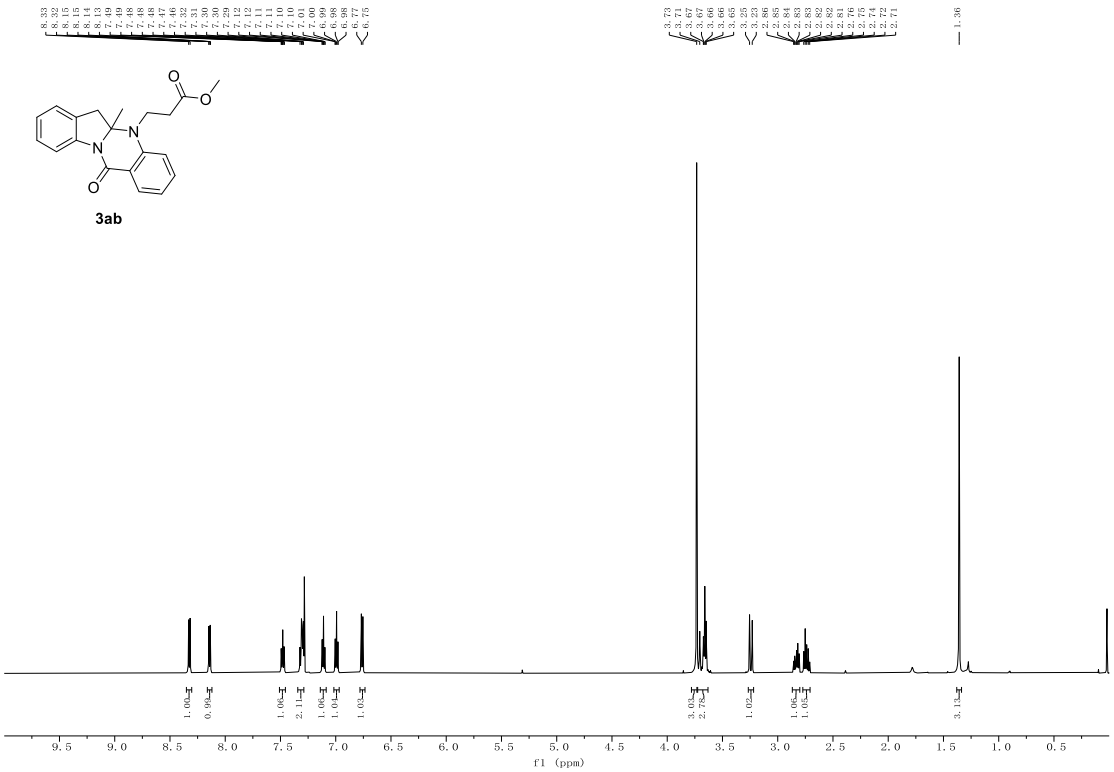
O
CF3
O
N
N
O
3na
f1 (ppm)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8.14
8.13
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7.48
7.48
7.47
7.46
7.32
7.31
7.30
7.29
7.12
7.11
7.11
7.10
7.01
7.00
6.99
6.98
6.77
6.75
3.73
3.71
3.67
3.67
3.66
3.66
3.65
3.25
3.23
2.86
2.85
2.84
2.83
2.82
2.82
2.81
2.76
2.75
2.74
2.72
2.71
1.36
O
O
N
N
O
3ab
1.00
0.99
1.06
2.11
1.06
1.04
1.03
3.03
2.78
1.02
1.06
1.03
3.13
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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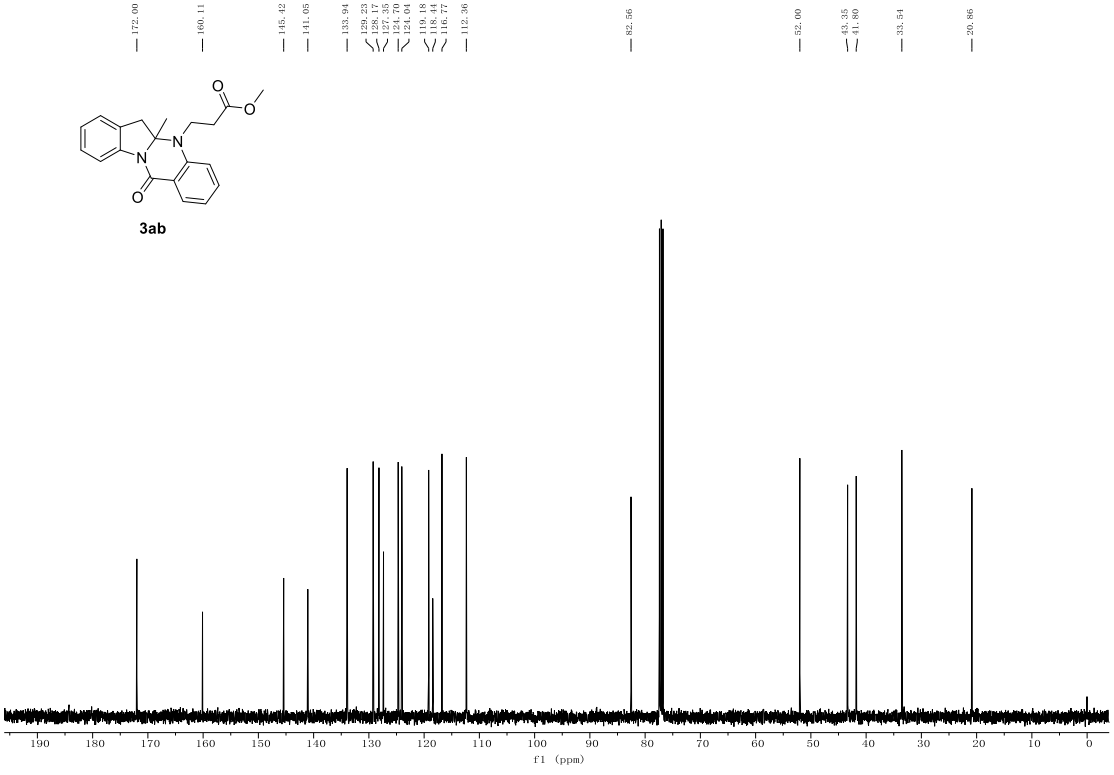
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)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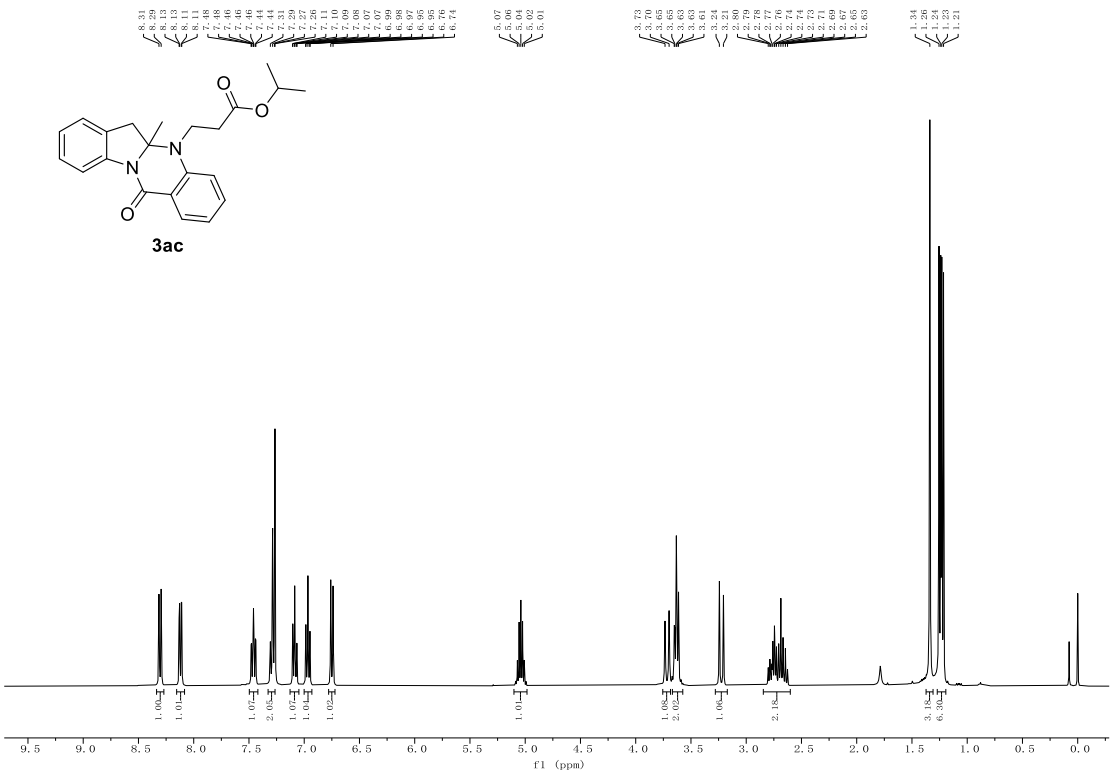
128.17
127.35
124.70
124.64
119.18
118.14
116.77
112.36
82.56
52.00
43.35
41.80
33.54
20.86
O
O
N
N
O
3ab
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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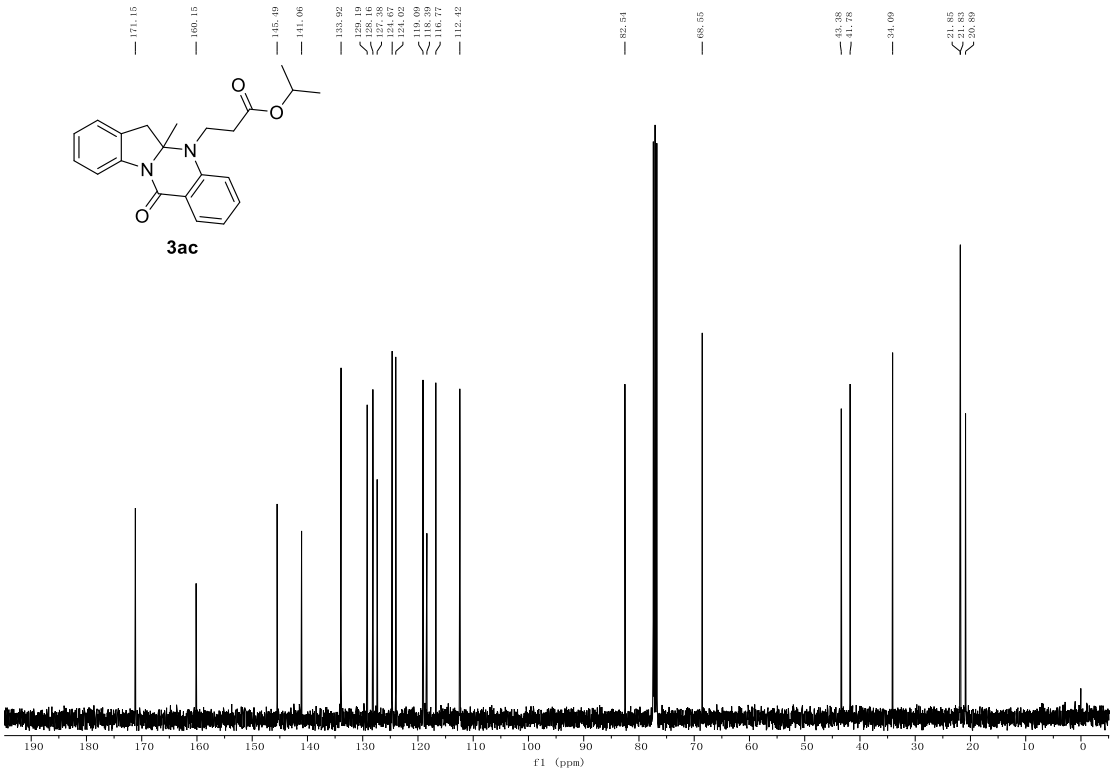
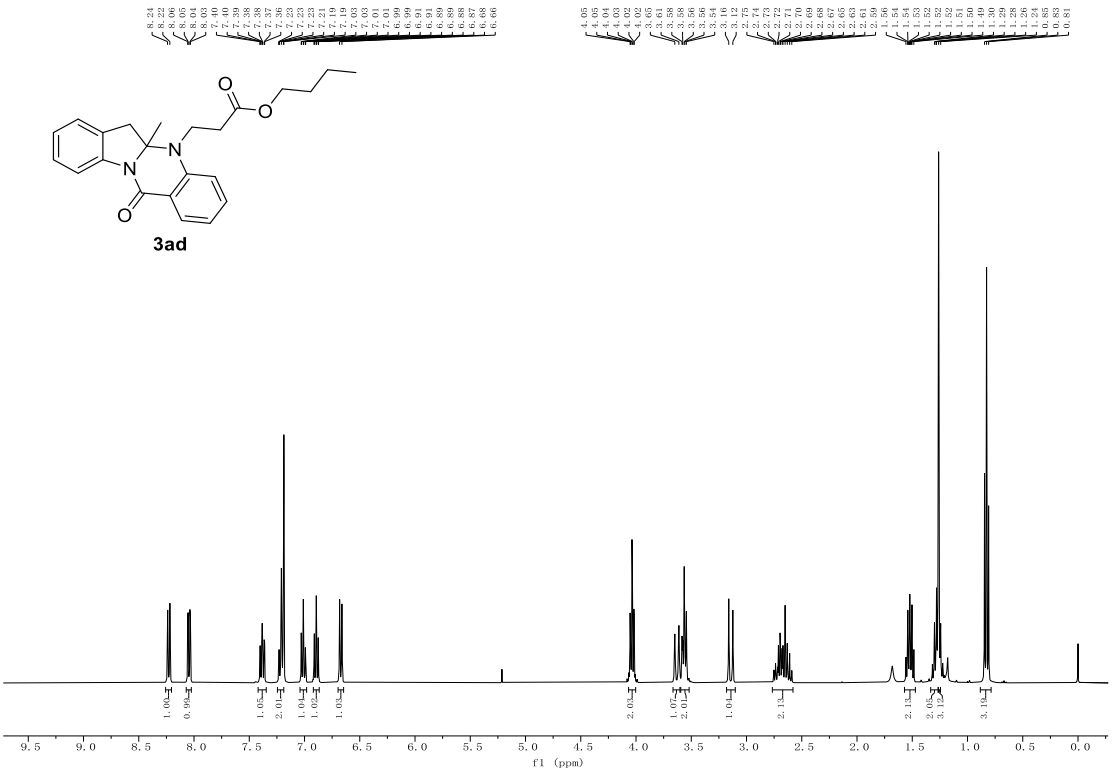
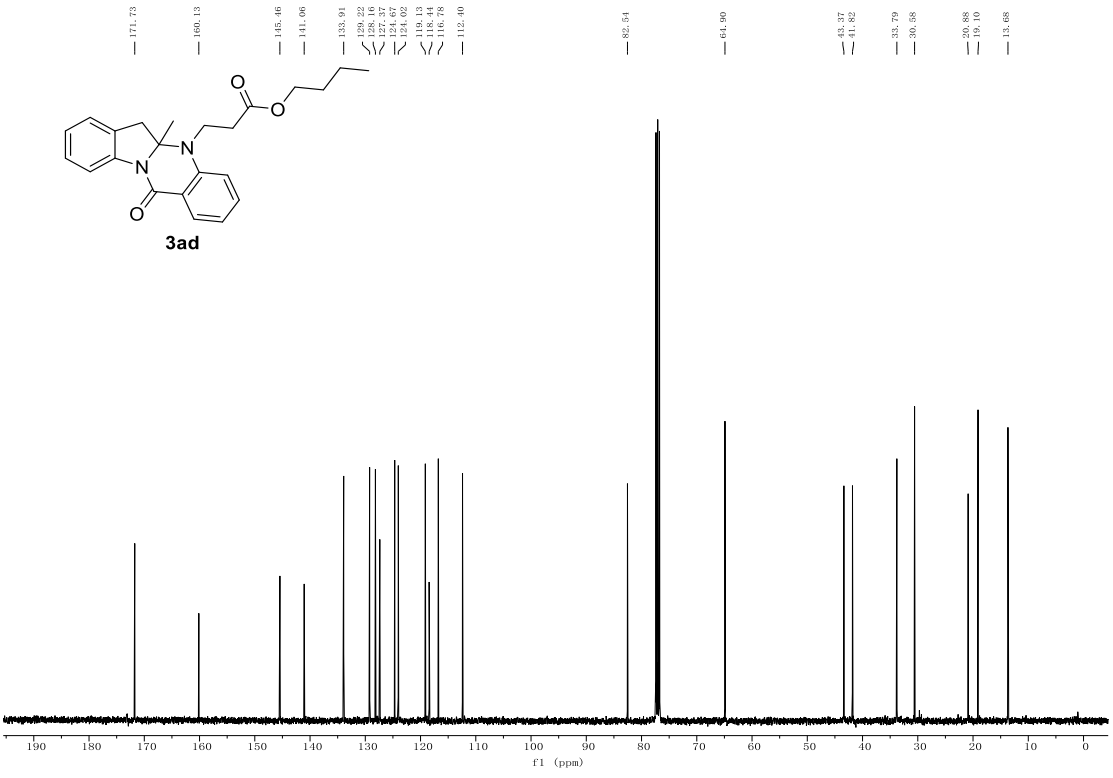
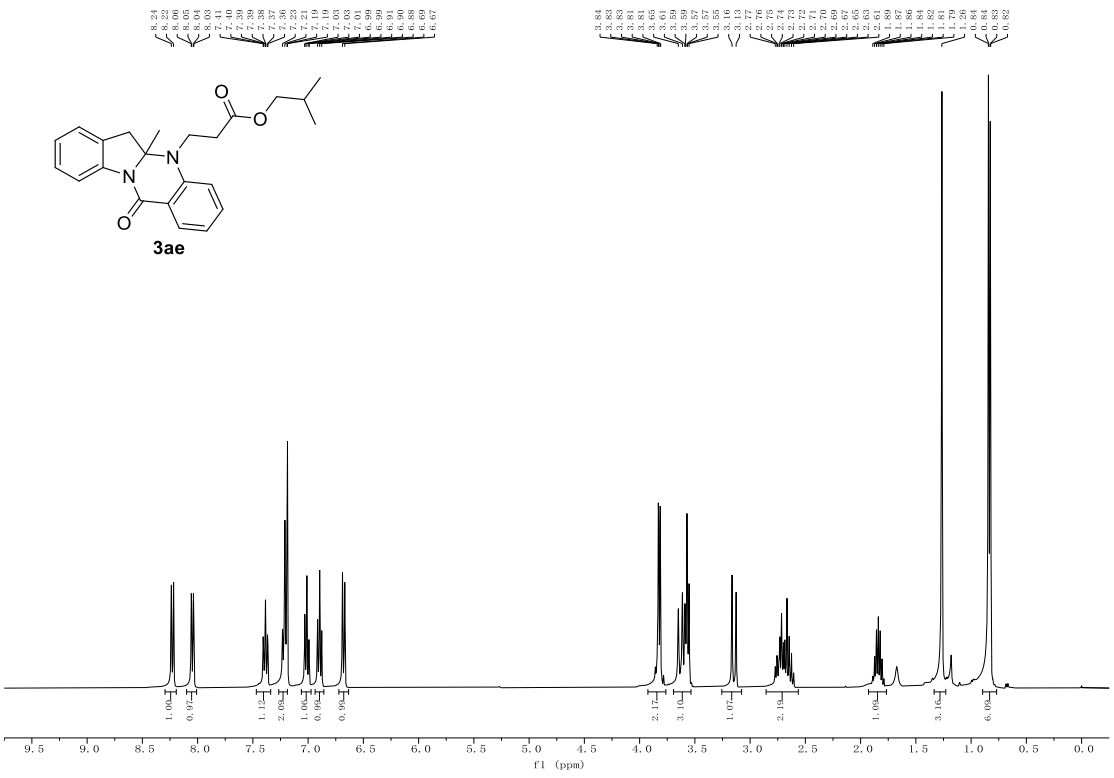
f1 (ppm)


3ac
f1 (ppm)


3ad
f1 (ppm)


3ad
f1 (ppm)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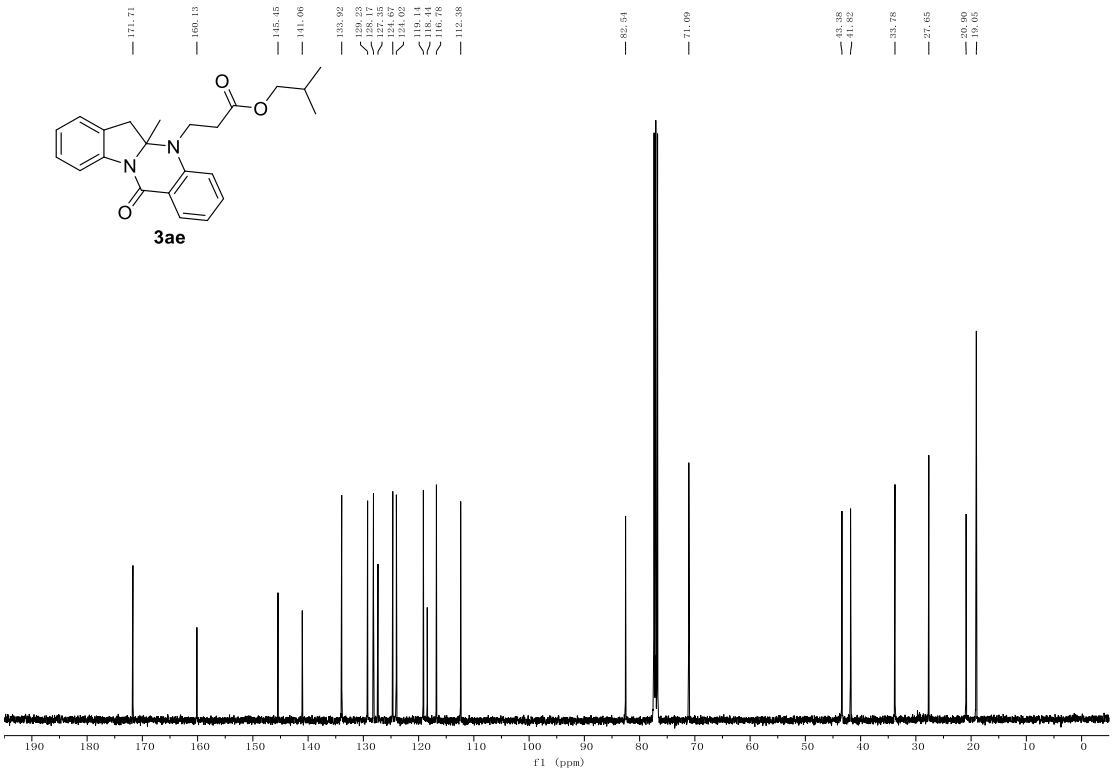
f1 (ppm)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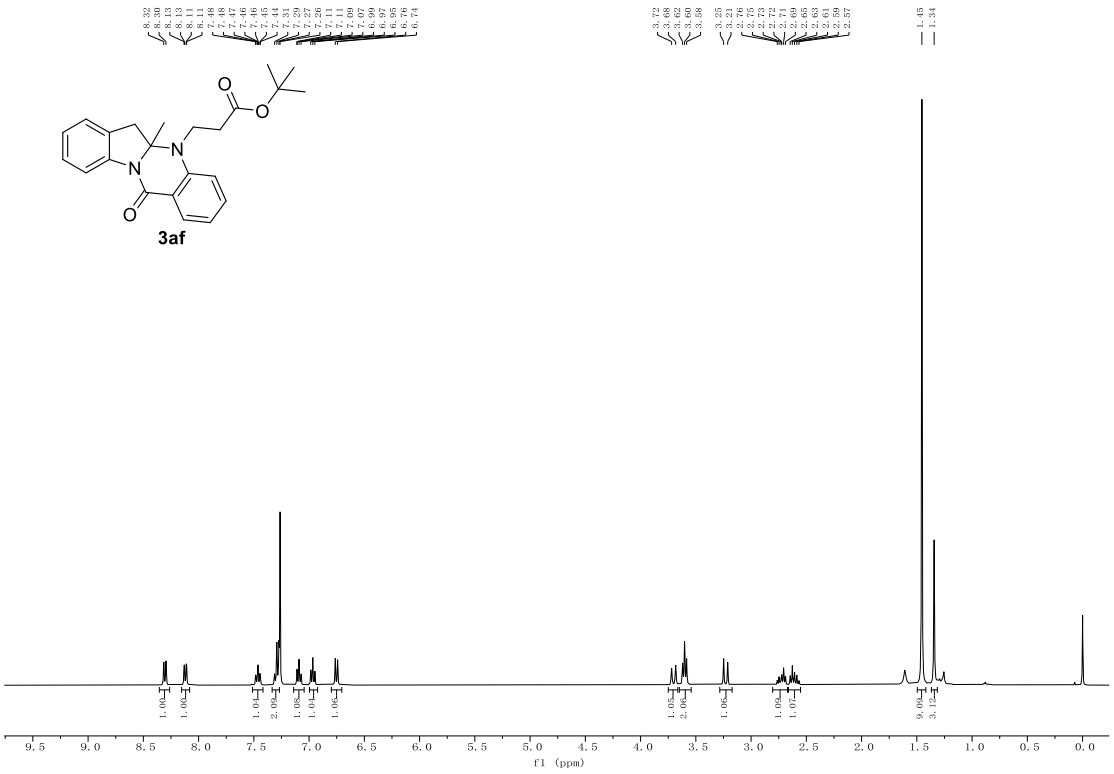
f1 (ppm)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8.13
8.13
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8.11
7.48
7.47
7.46
7.46
7.45
7.44
7.31
7.29
7.27
7.26
7.11
7.11
7.09
7.07
6.99
6.97
6.95
6.76
6.74
3.72
3.68
3.62
3.60
3.58
3.25
3.21
2.76
2.75
2.73
2.72
2.71
2.69
2.65
2.63
2.61
2.59
2.57
1.45
1.34
O
O
N
N
O
3af
1.04
1.00
1.04
2.09
1.08
1.04
1.06
1.05
2.06
1.06
1.09
1.07
9.09
3.12
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
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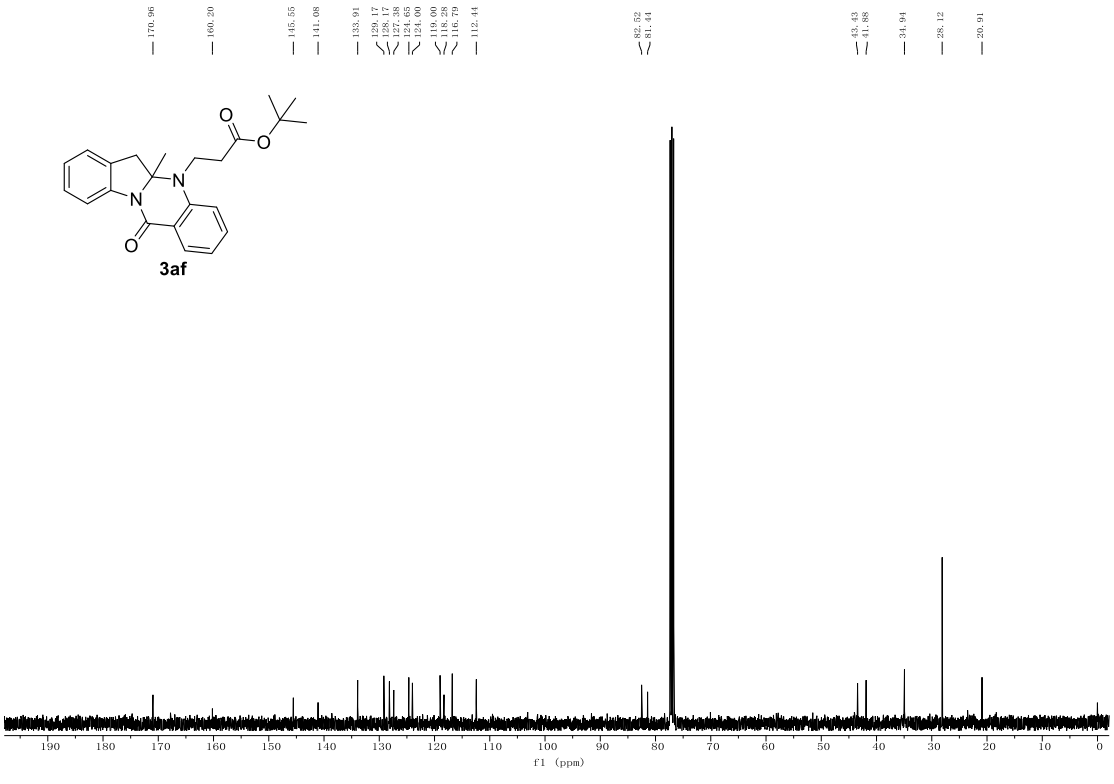
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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128.17
127.38
124.65
124.00
119.00
118.28
116.79
112.44
82.52
81.44
43.43
41.88
34.94
28.12
20.91
O
O
N
N
O
3af
190
180
170
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150
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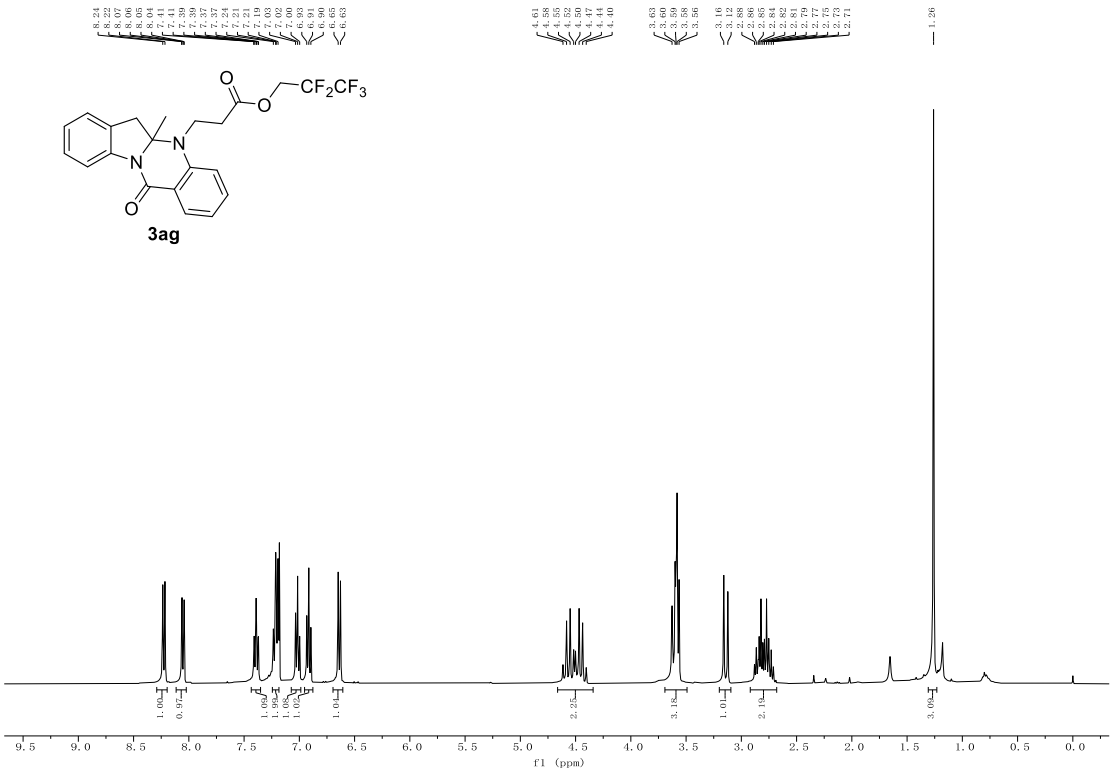
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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7.37
7.37
7.24
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7.21
7.19
7.03
7.02
7.00
6.93
6.91
6.90
6.65
6.63
4.61
4.58
4.55
4.52
4.50
4.47
4.44
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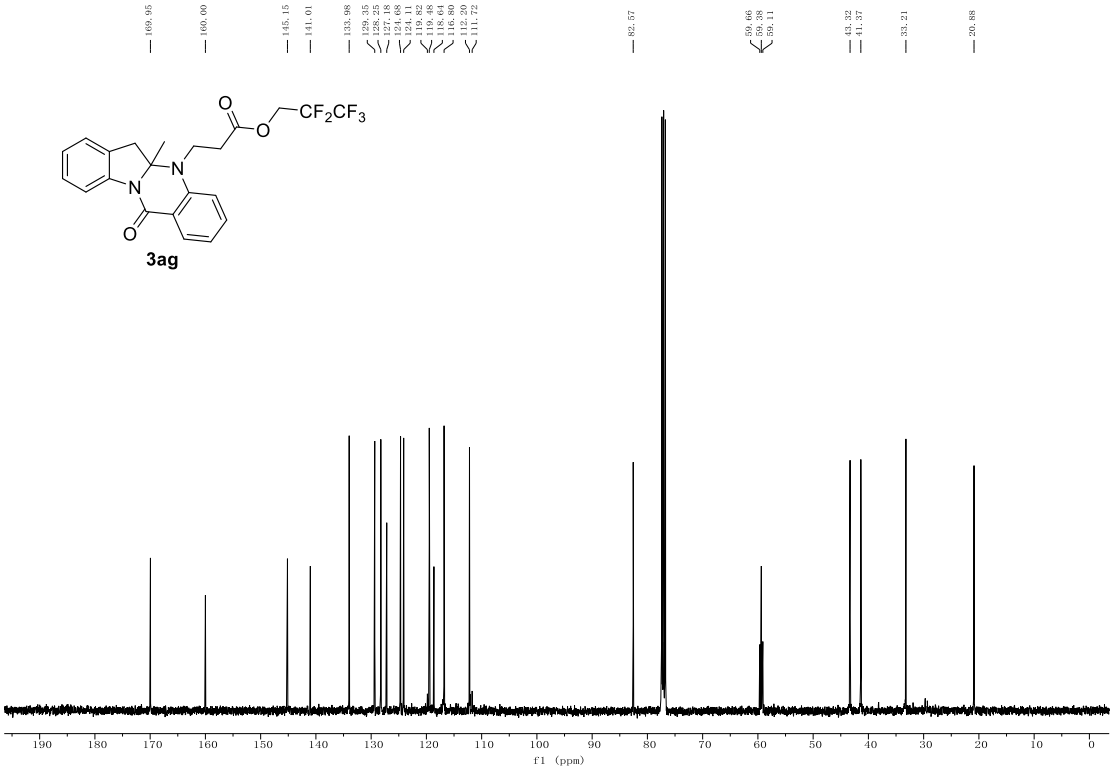
3.63
3.60
3.58
3.58
3.56
3.16
3.12
2.88
2.86
2.85
2.84
2.82
2.81
2.79
2.77
2.75
2.73
2.71
1.26
O
O
CF2CF3
N
N
O
3ag
1.00
0.97
1.09
1.99
1.08
1.02
1.04
2.25
3.18
1.01
2.19
3.09
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.35
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127.18
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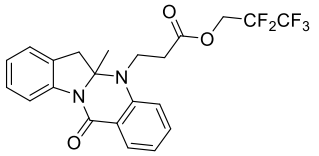
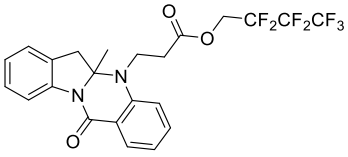
124.11
119.82
119.48
118.64
116.80
112.00
111.72
82.57
59.66
59.38
52.11
43.32
41.37
33.21
20.88
O
O
CF2CF3
N
N
O
3ag
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


O
O
CF2CF3
N
N
O

3ag

-83.79
-123.36
-123.39
-126.43
f1 (ppm)


O
O
CF2CF2CF3
N
N
O

3ah

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8.21
8.05
8.05
8.03
7.39
7.38
7.37
7.36
7.35
7.22
7.20
7.19
7.17
7.02
7.00
6.98
6.91
6.90
6.88
6.64
6.62
4.64
4.61
4.58
4.54
4.53
4.52
4.50
4.46
4.43
3.62
3.59
3.58
3.57
3.55
3.14
3.11
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2.83
2.82
2.81
2.79
2.78
2.75
2.74
2.73
2.72
2.70
1.24
1.00
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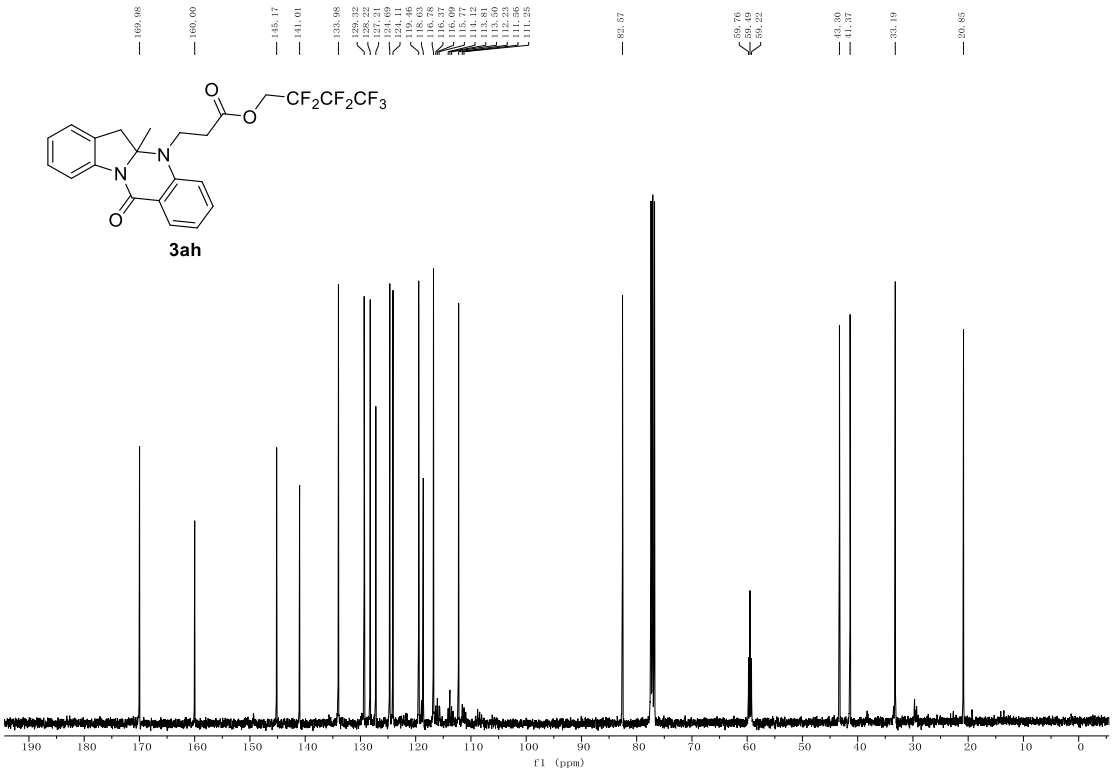
1.08
1.03
1.05
2.32
3.02
1.02
2.38
3.00
f1 (ppm)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127.21
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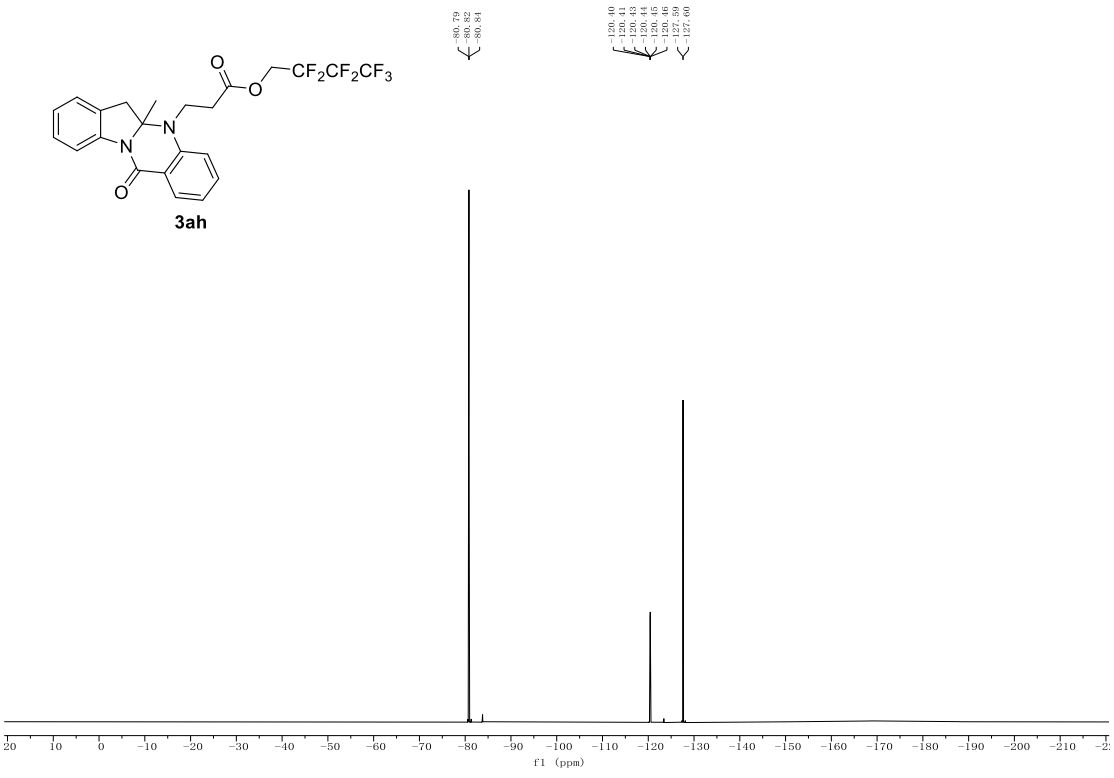
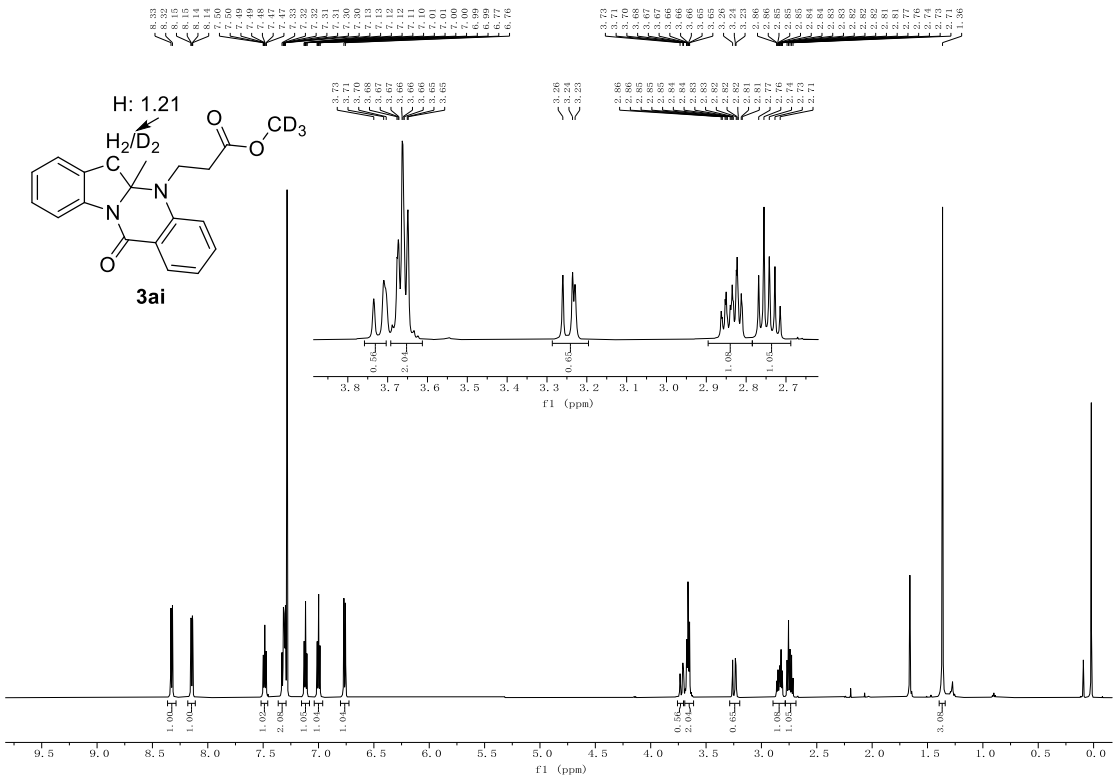
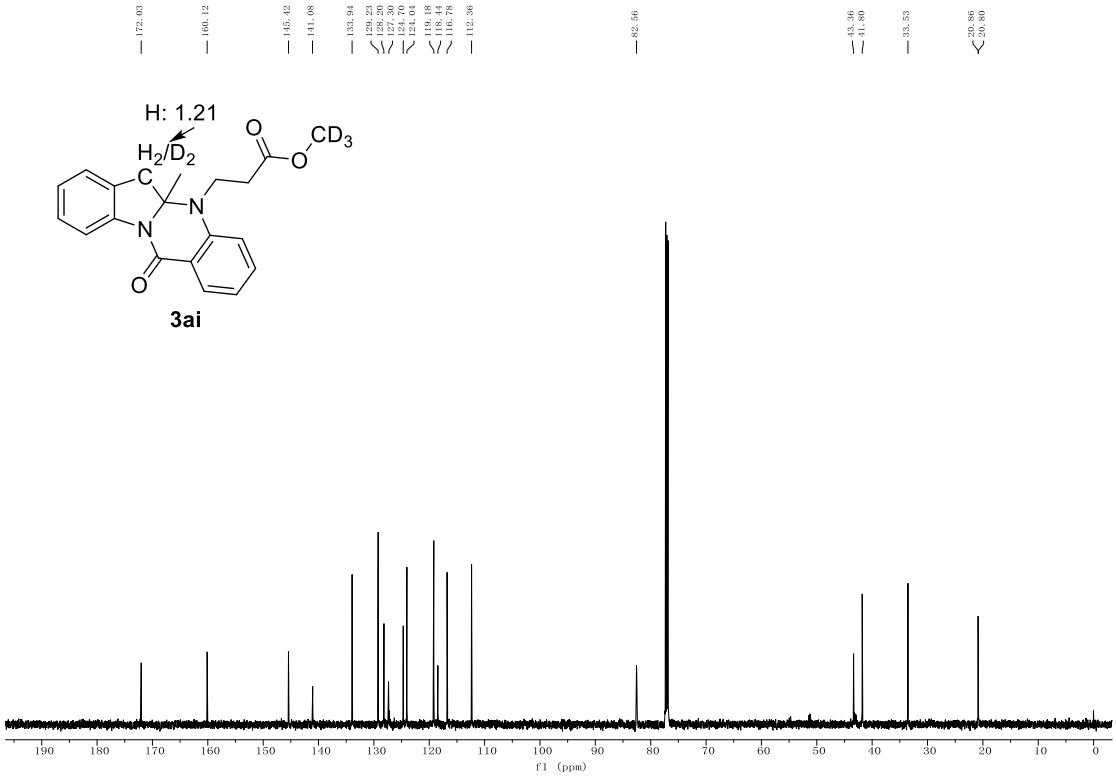
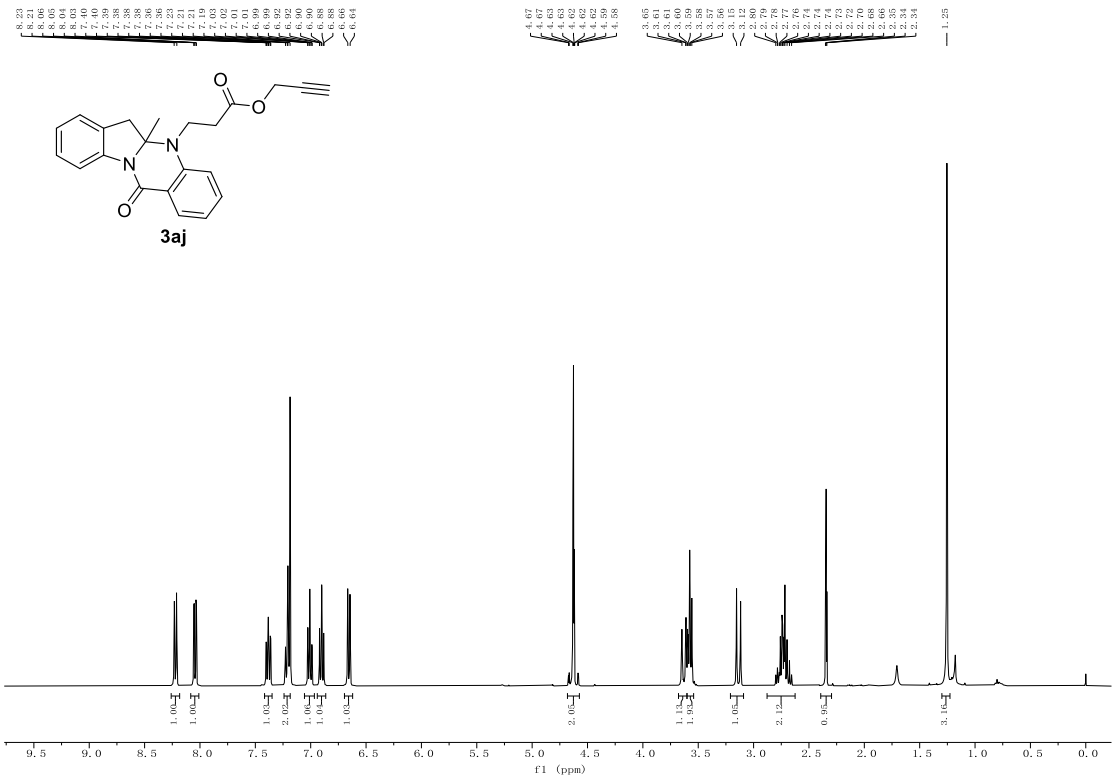
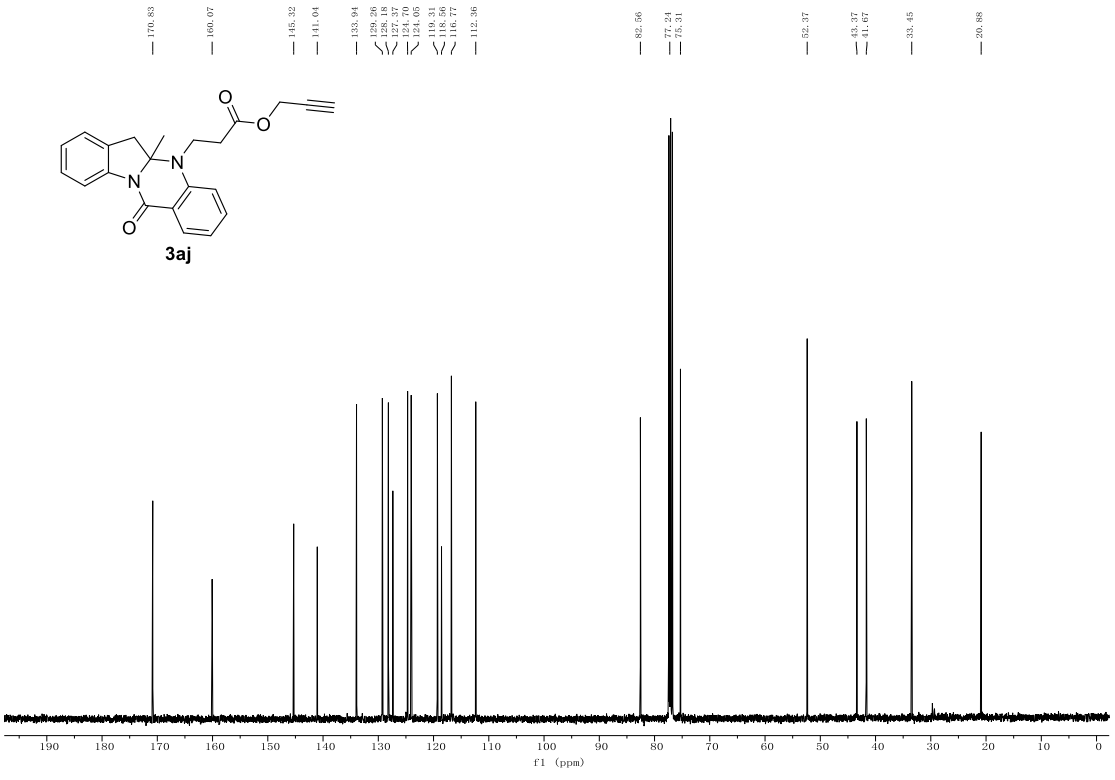
118.05
116.78
116.37
116.09
115.77
114.12
113.81
113.50
112.23
111.56
111.25
82.57
59.76
59.49
59.22
43.30
41.37
33.19
20.85
O
O
CF2CF2CF3
N
N
O
3ah
f1 (ppm)

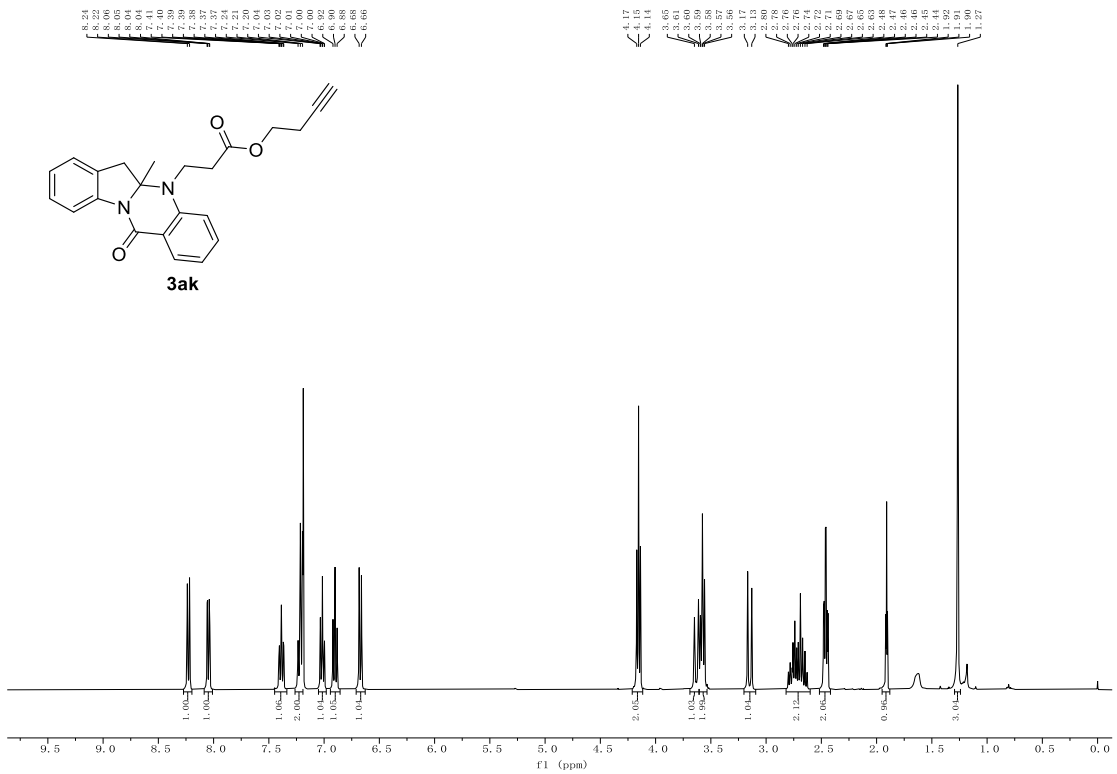

80.79
80.82
80.84
120.40
120.41
120.43
120.44
120.45
120.46
127.39
127.60
O
O
CF2CF2CF3
N
N
O
3ah
f1 (ppm)

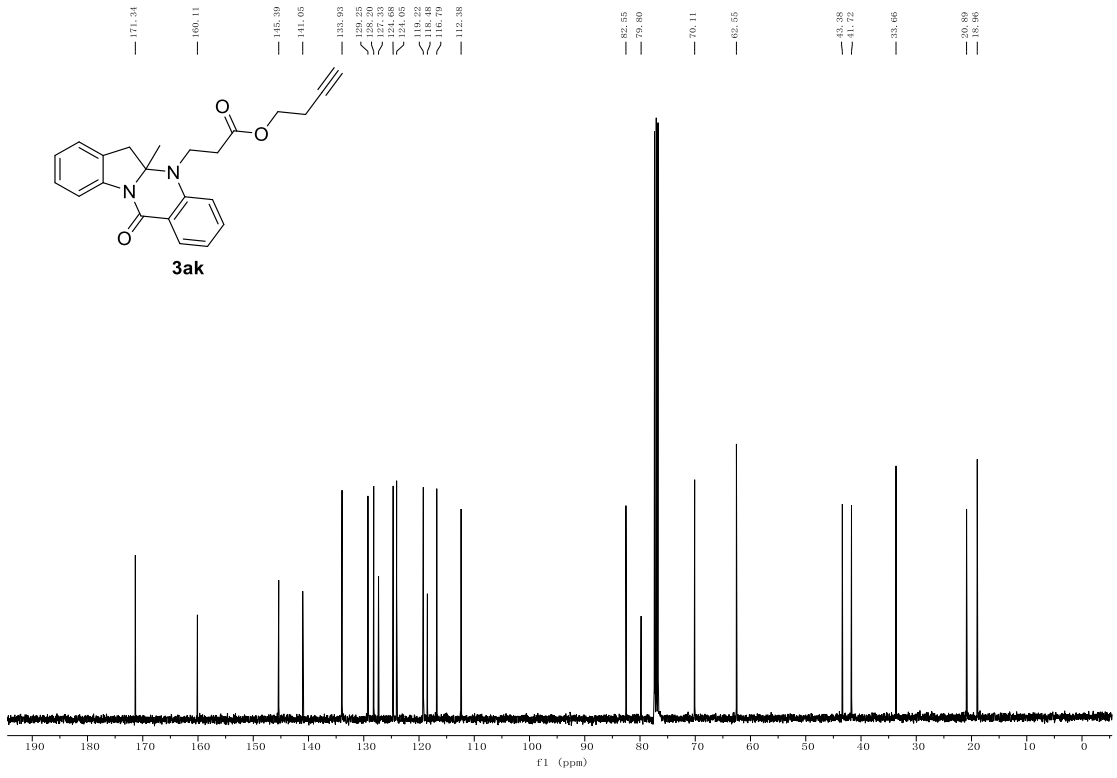

H: 1.21
H2/D2
CD3
3ai
f1 (ppm)

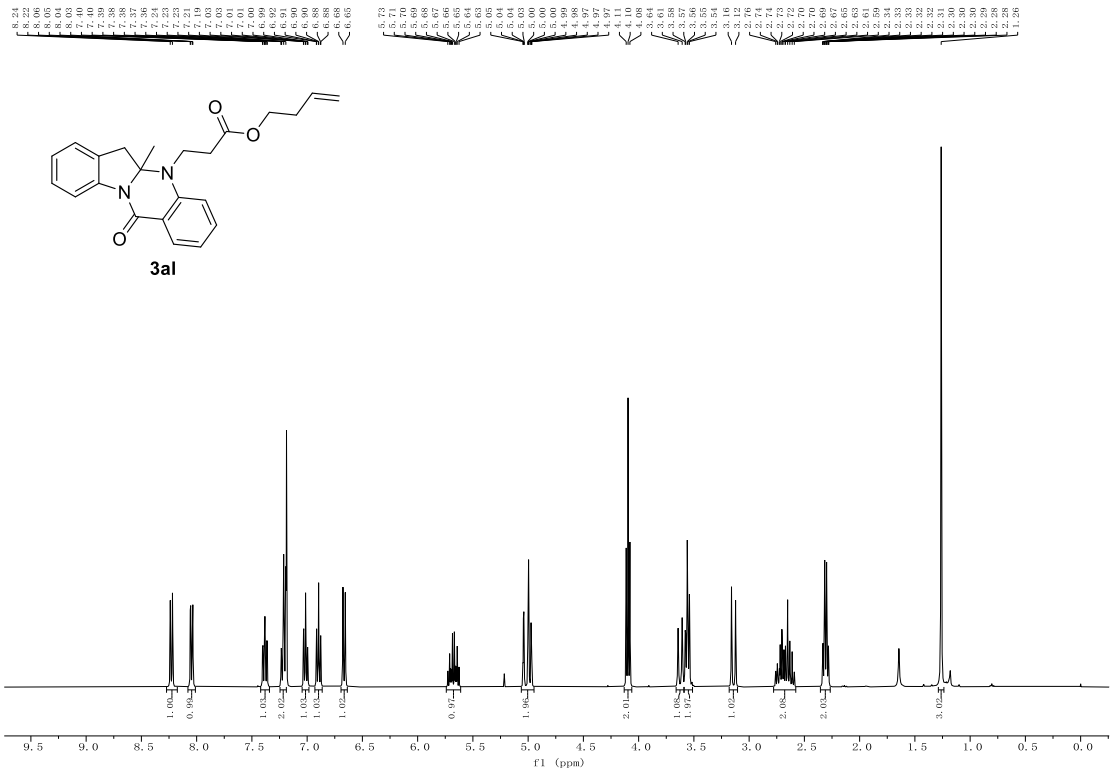

H: 1.21
H2/D2
CD3
3ai
f1 (ppm)

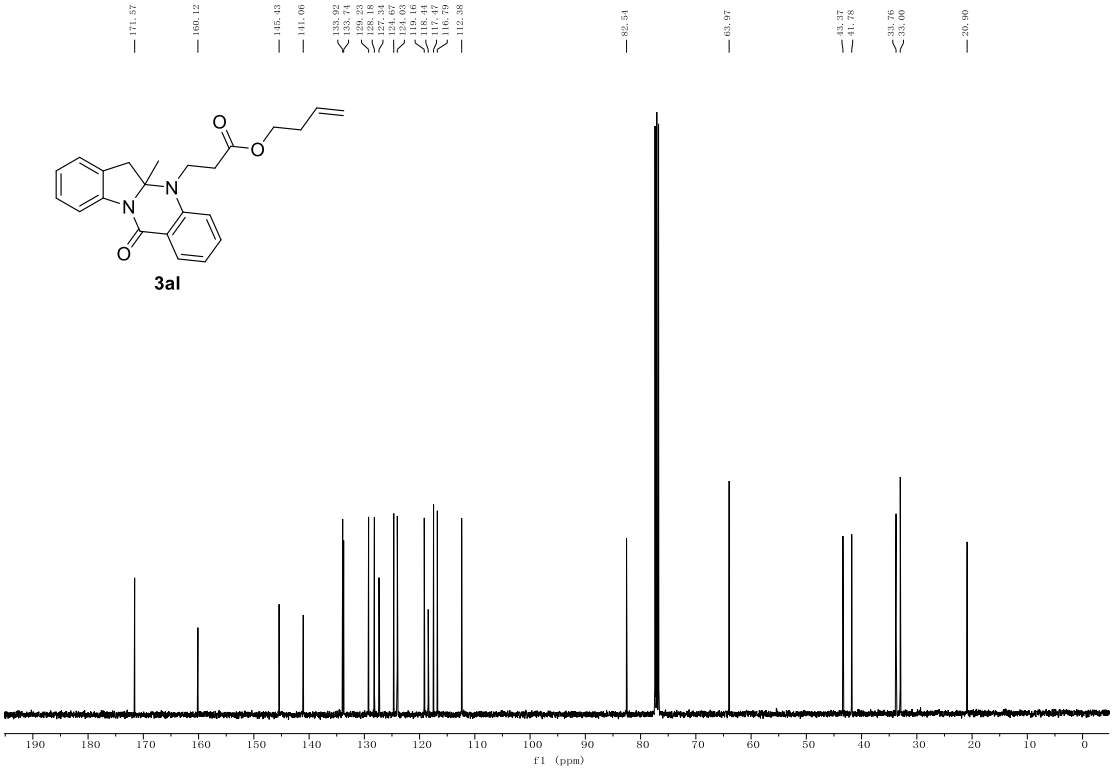

3aj
f1 (ppm)

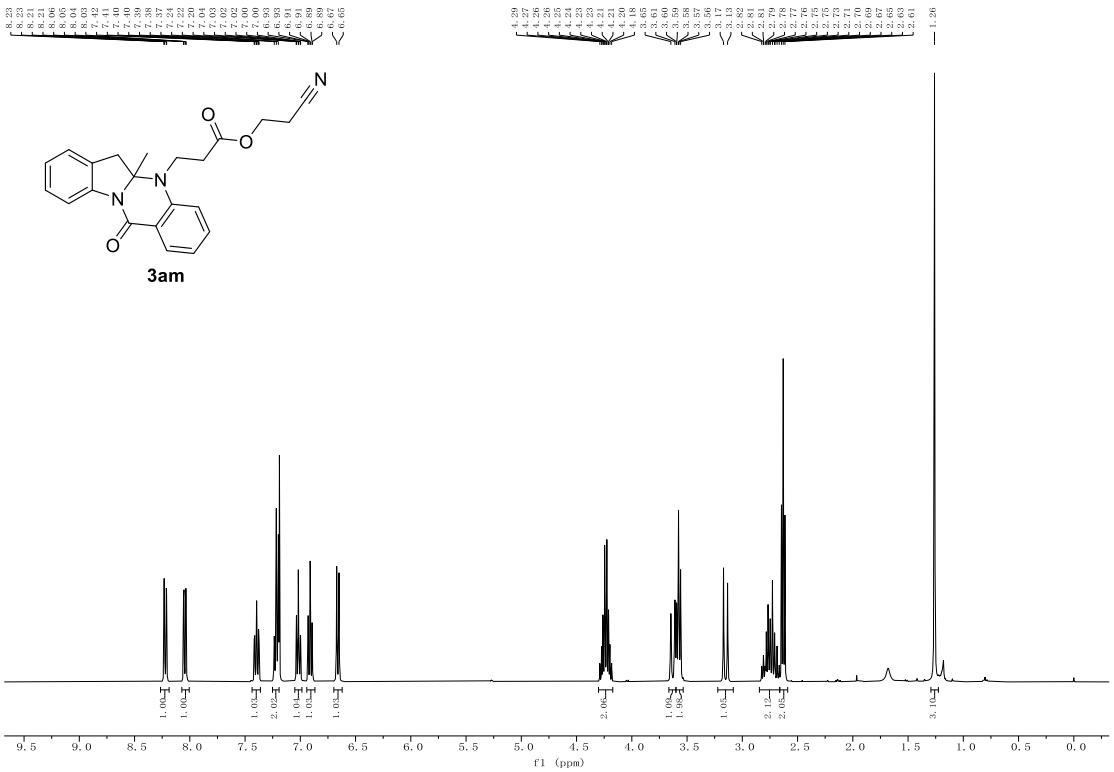

3aj
f1 (ppm)

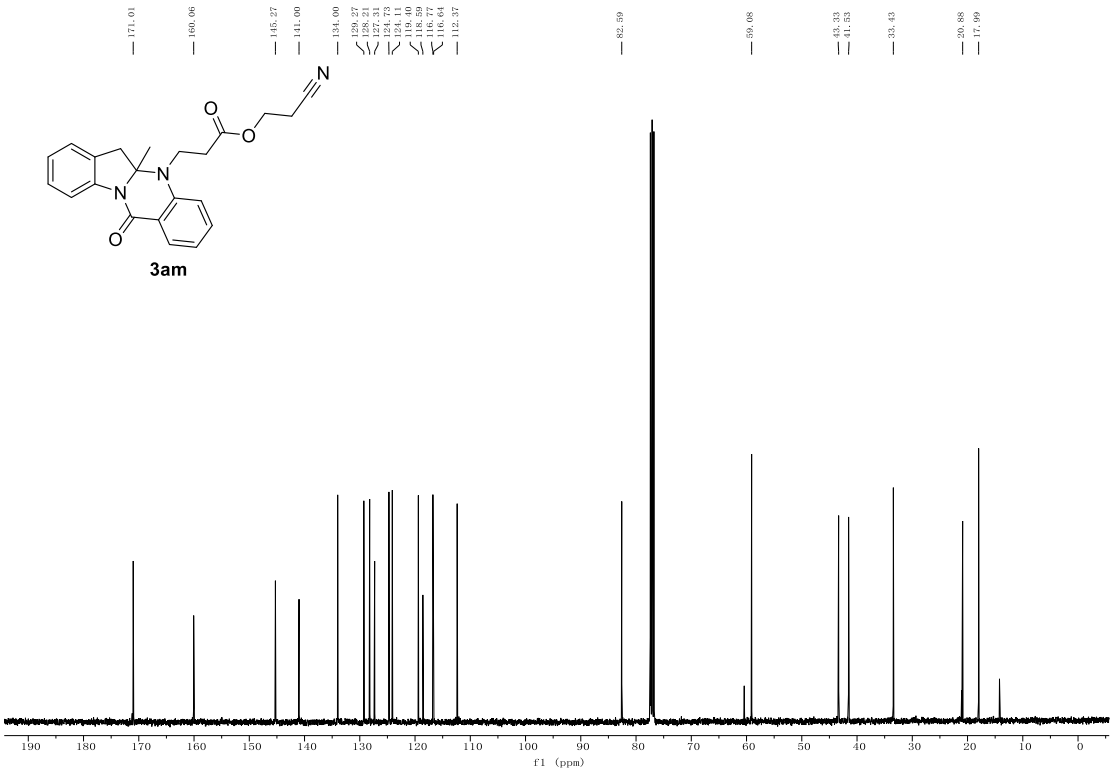

3ak
f1 (ppm)

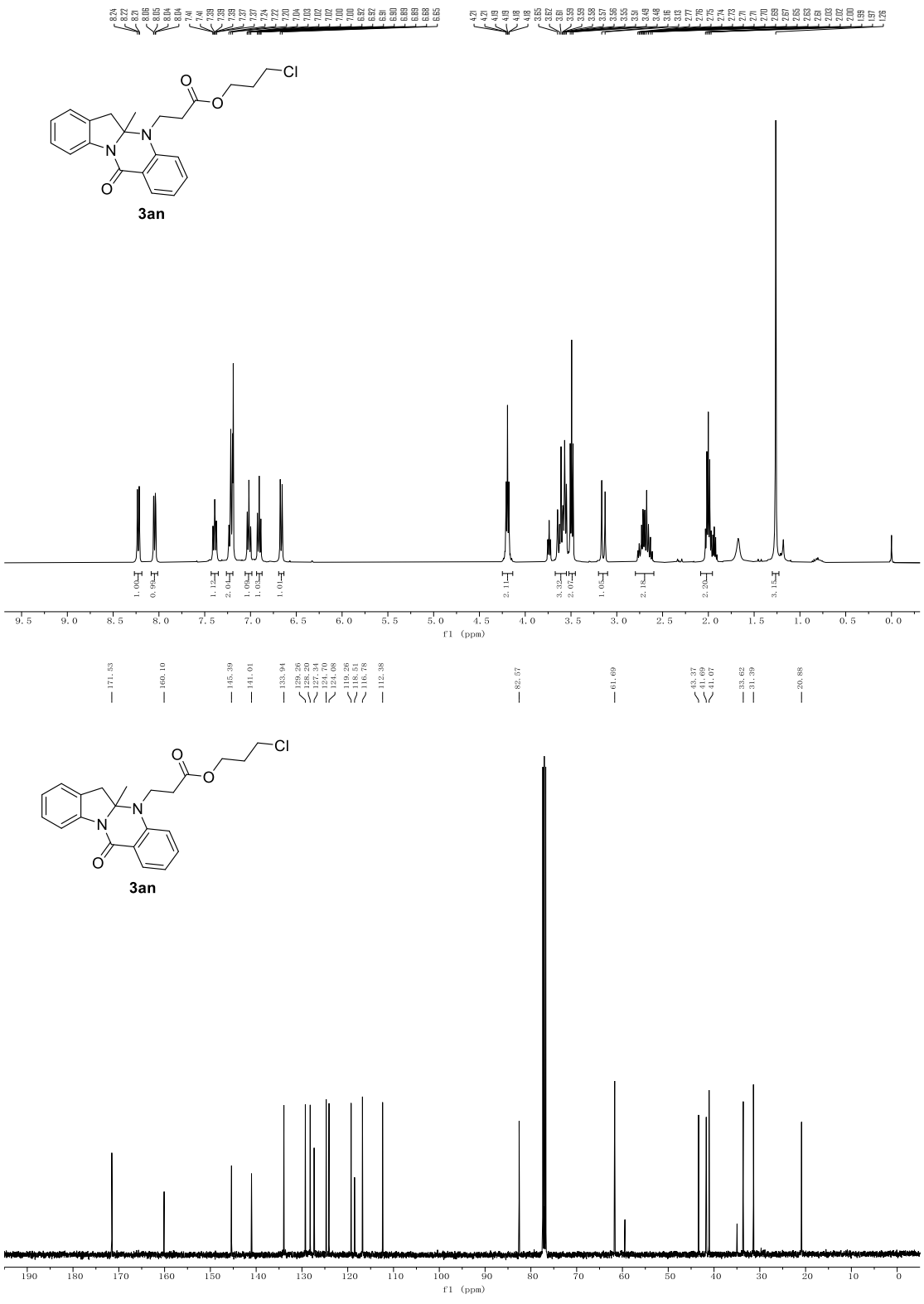

3ak
f1 (ppm)

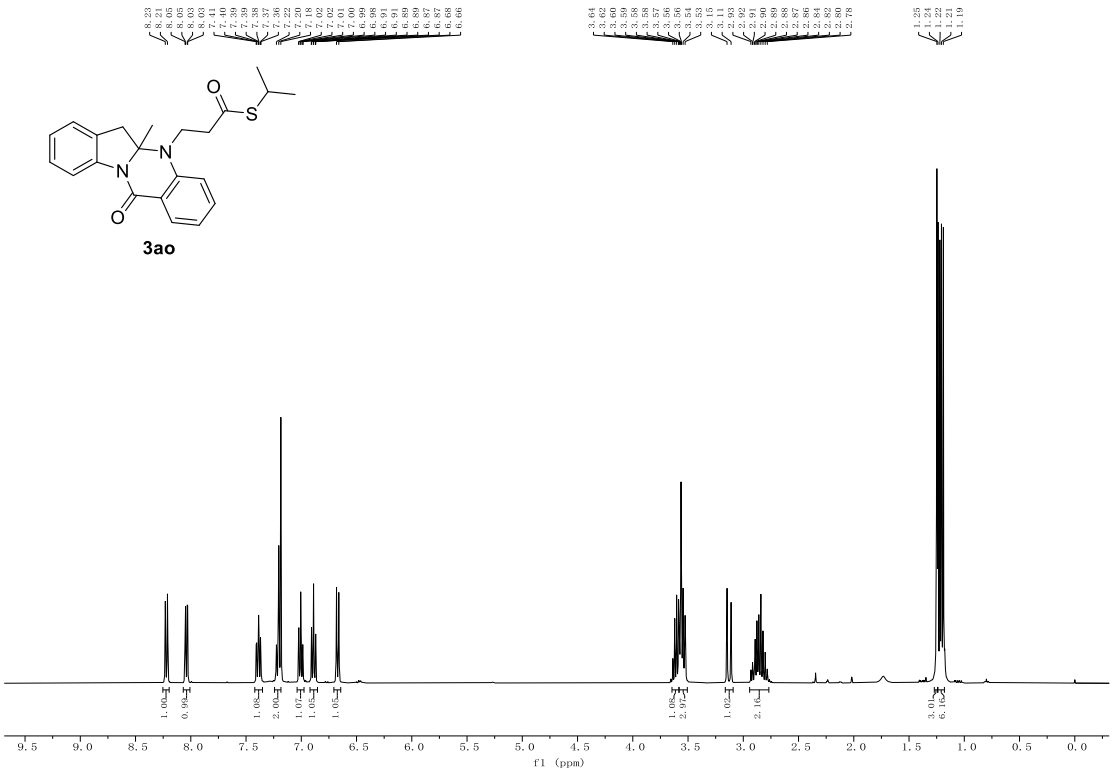

3al
f1 (ppm)

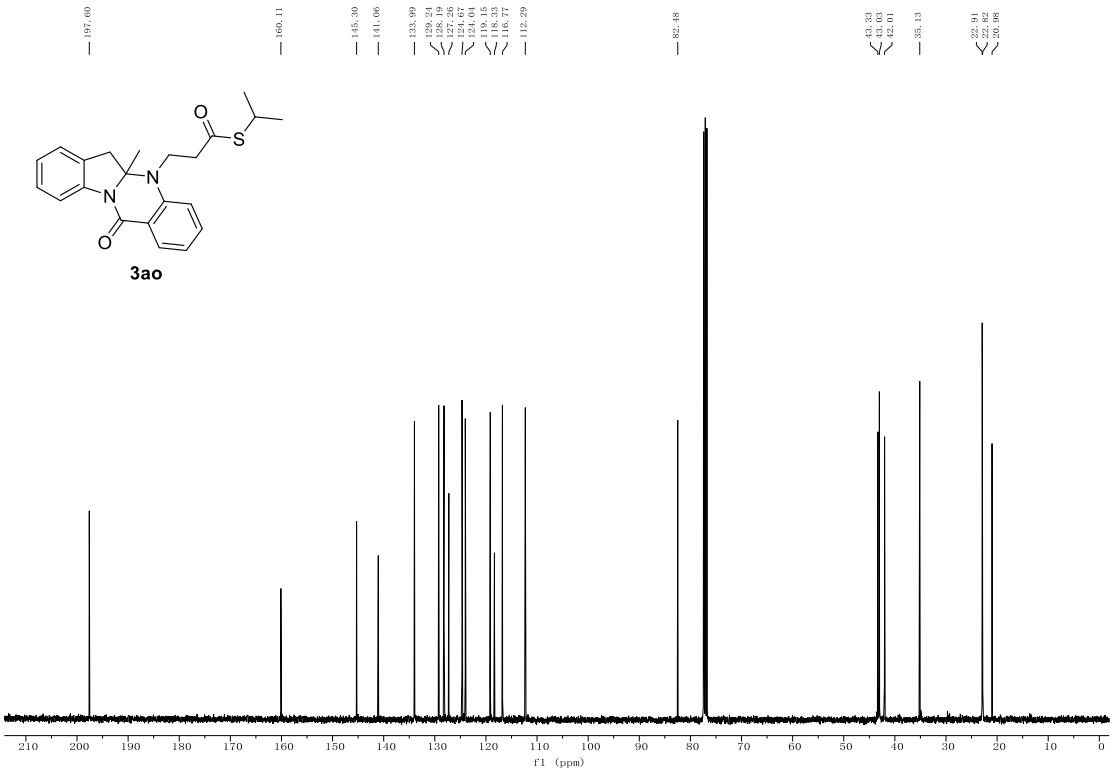

3al
f1 (ppm)

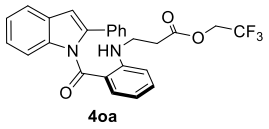

3am
f1 (ppm)


3am
f1 (ppm)

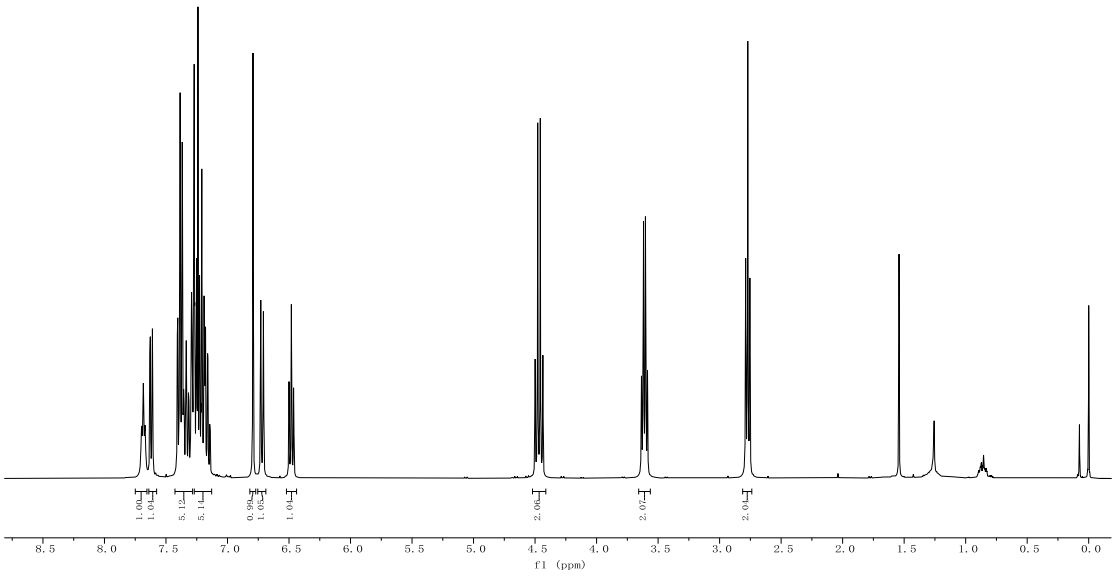

Cl
O
O
N
N
O
3an
1.04
0.99
1.12
2.04
1.09
1.03
1.01
2.11
3.22
2.07
1.05
2.18
2.20
3.15
f1 (ppm)
171.53
160.10
145.39
141.01
133.94
129.26
128.20
127.84
124.70
124.08
119.26
118.51
116.78
112.38
82.57
61.69
43.37
41.69
41.07
33.62
31.39
20.88
f1 (ppm)

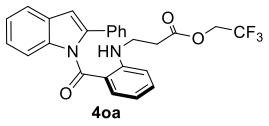

8.23
8.21
8.05
8.05
8.03
8.03
7.41
7.40
7.39
7.39
7.38
7.37
7.36
7.22
7.20
7.18
7.02
7.02
7.01
7.00
6.99
6.98
6.91
6.91
6.89
6.89
6.87
6.87
6.68
6.66
3.64
3.62
3.60
3.59
3.58
3.58
3.57
3.56
3.56
3.54
3.53
3.15
3.11
2.93
2.92
2.91
2.90
2.89
2.89
2.88
2.87
2.86
2.84
2.82
2.80
2.78
1.25
1.24
1.22
1.21
1.19
O
S
N
N
O
3ao
1.00
0.99
1.08
2.04
1.07
1.03
1.05
1.08
2.97
1.02
2.16
3.01
6.16
9.5 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
f1 (ppm)


197.60
160.11
145.30
141.06
133.99
129.24
128.19
127.96
124.67
124.04
119.15
118.33
116.77
112.29
82.48
43.33
43.03
42.01
35.13
22.91
22.82
20.98
O
S
N
N
O
3ao
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

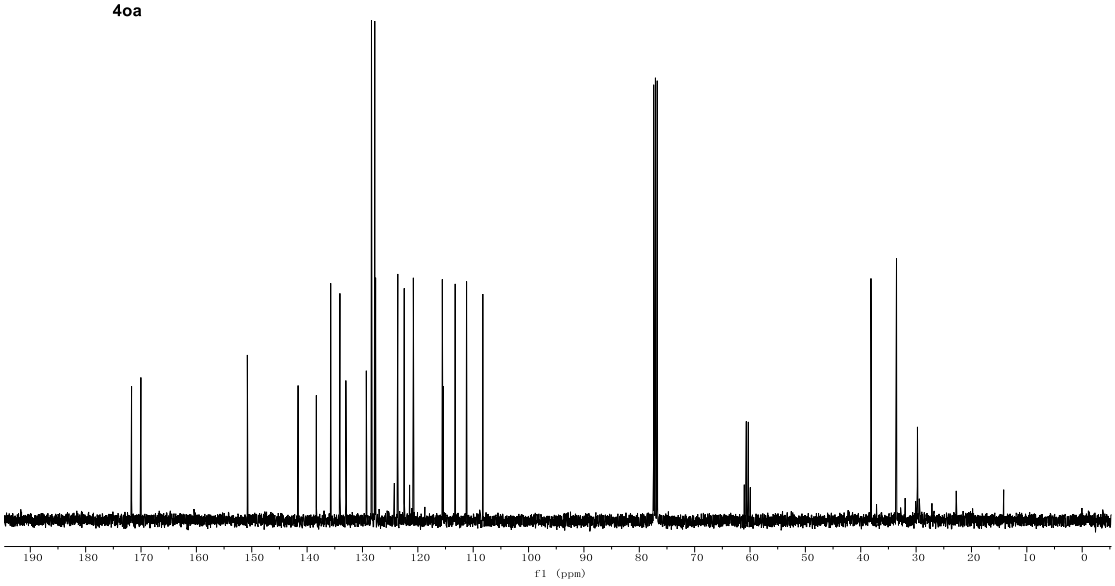


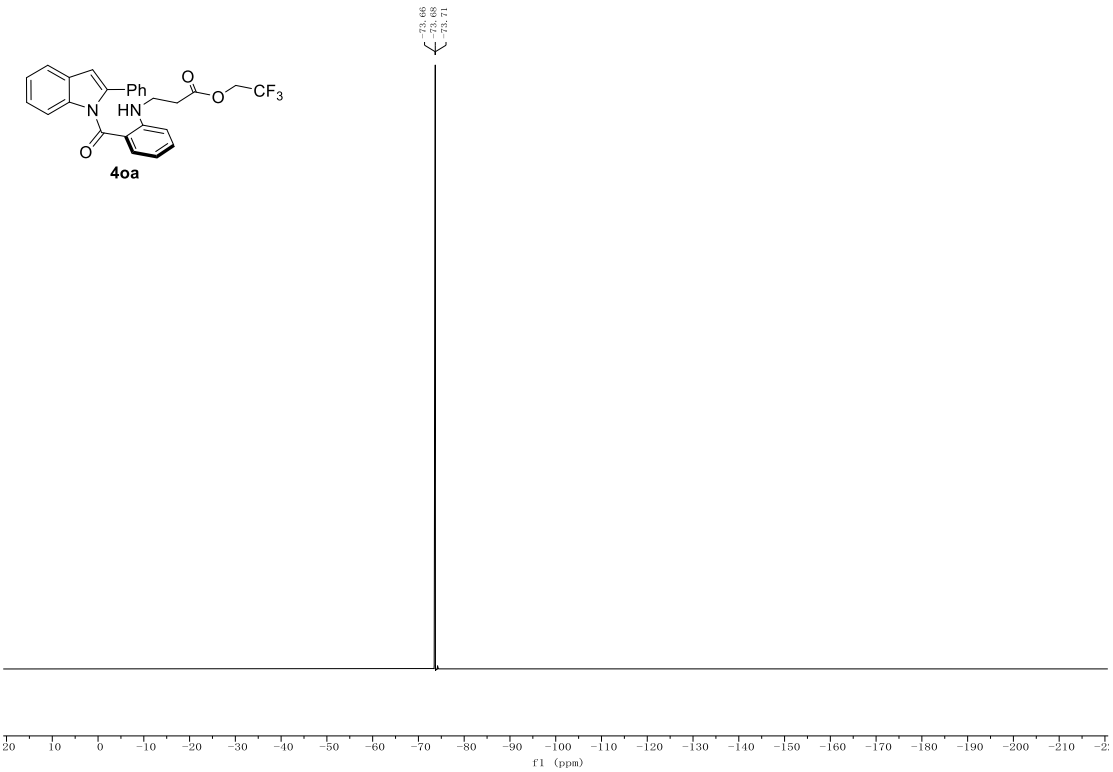
4oa

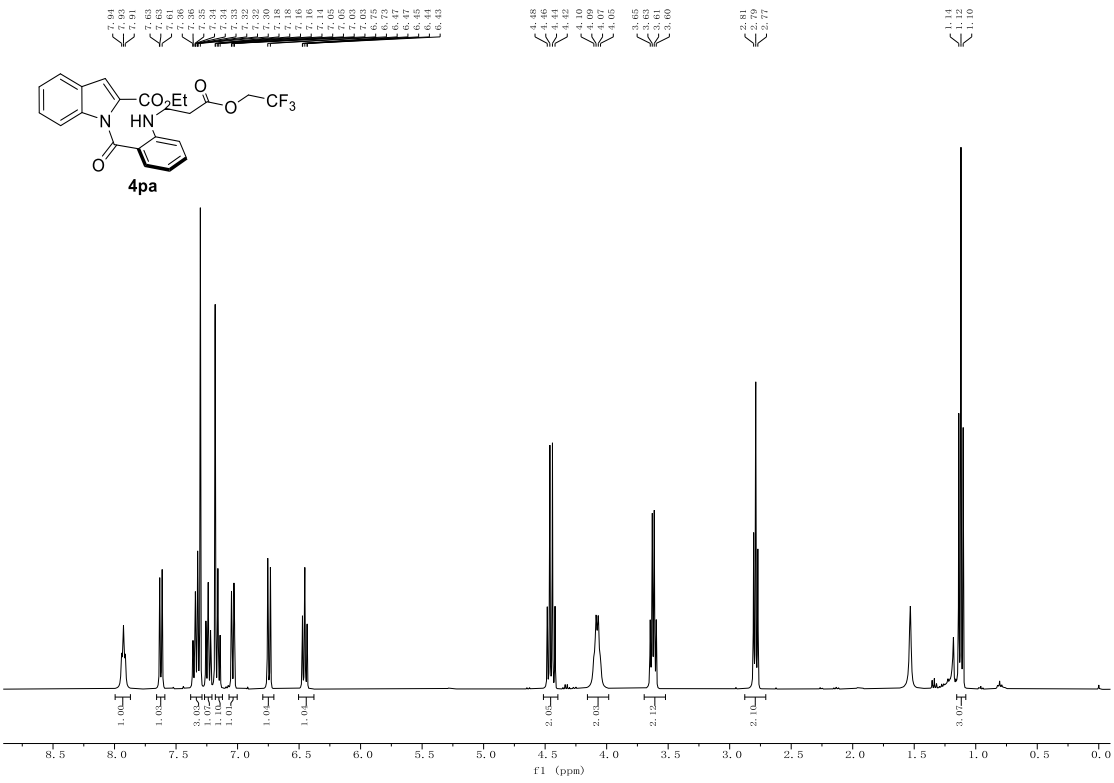


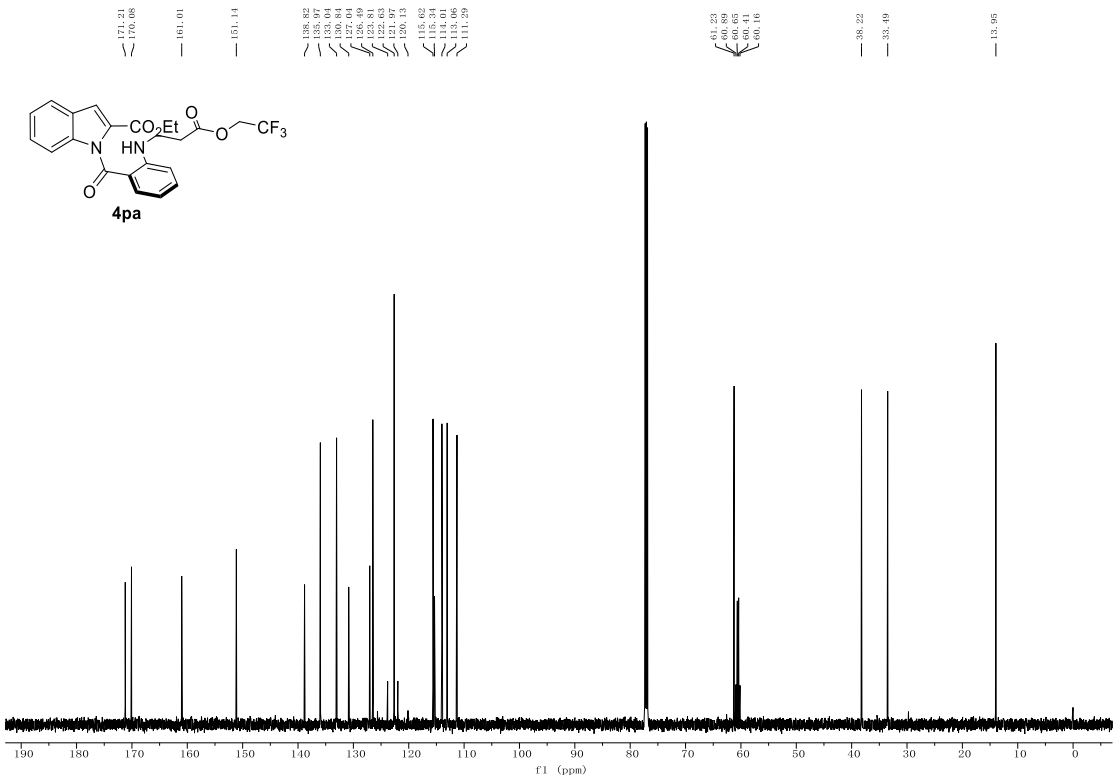


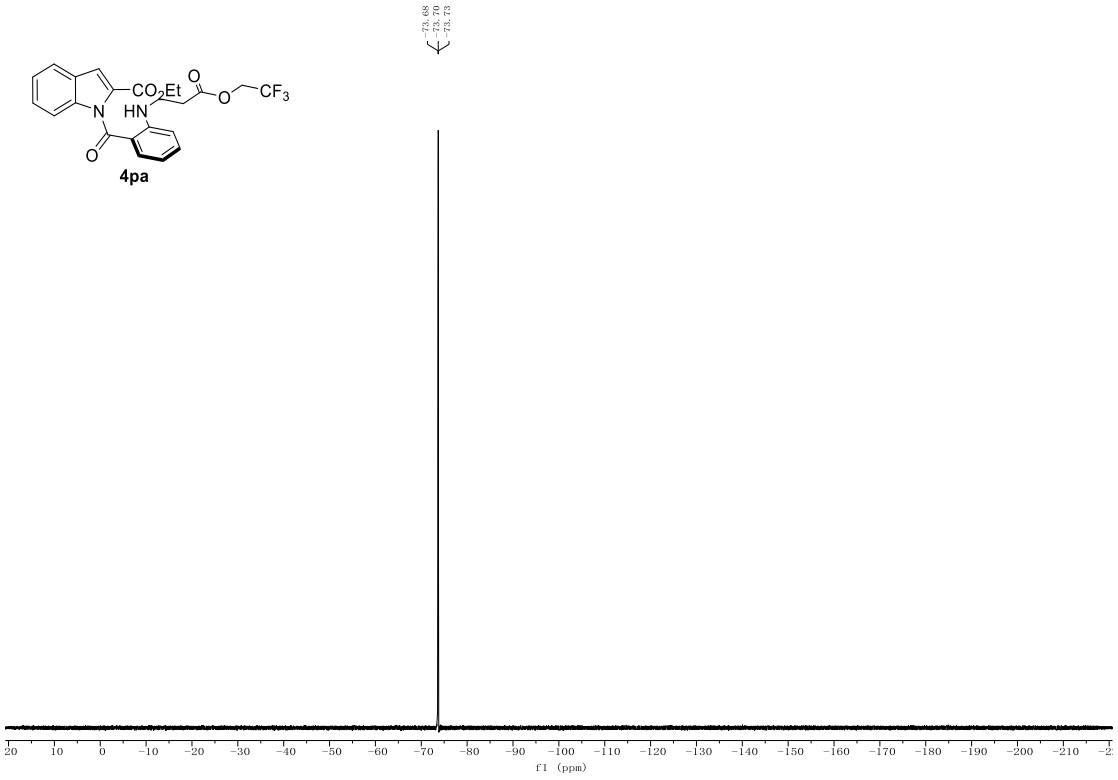
4oa

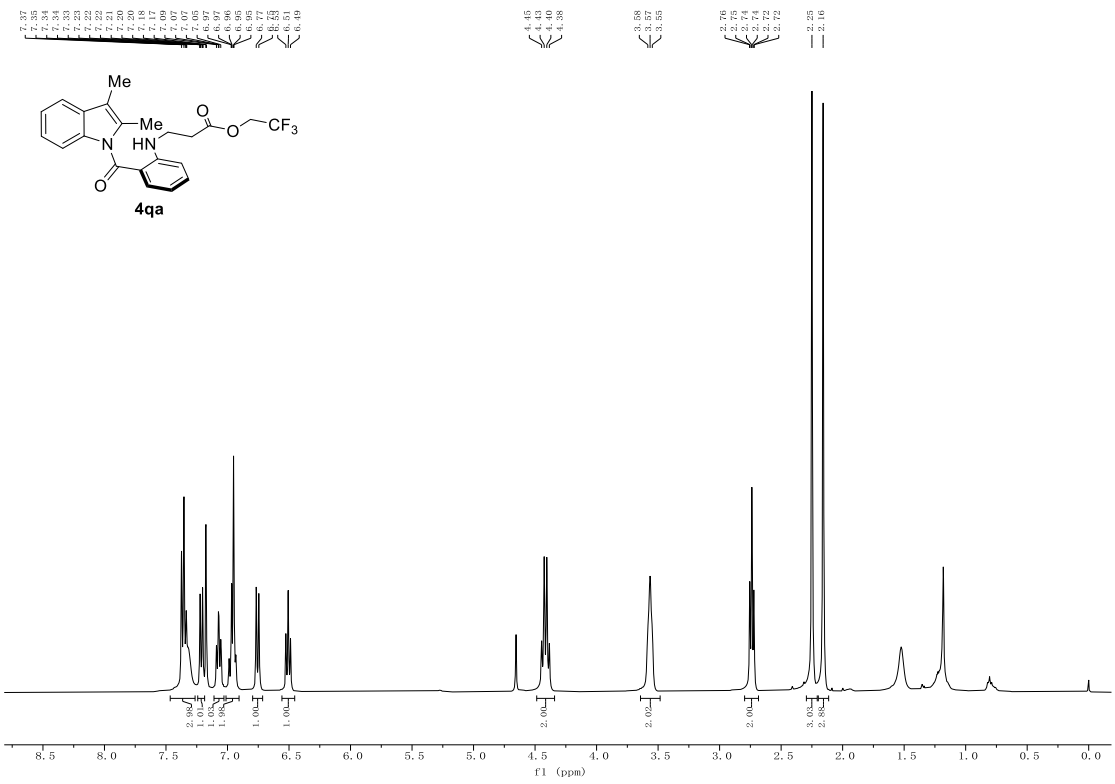


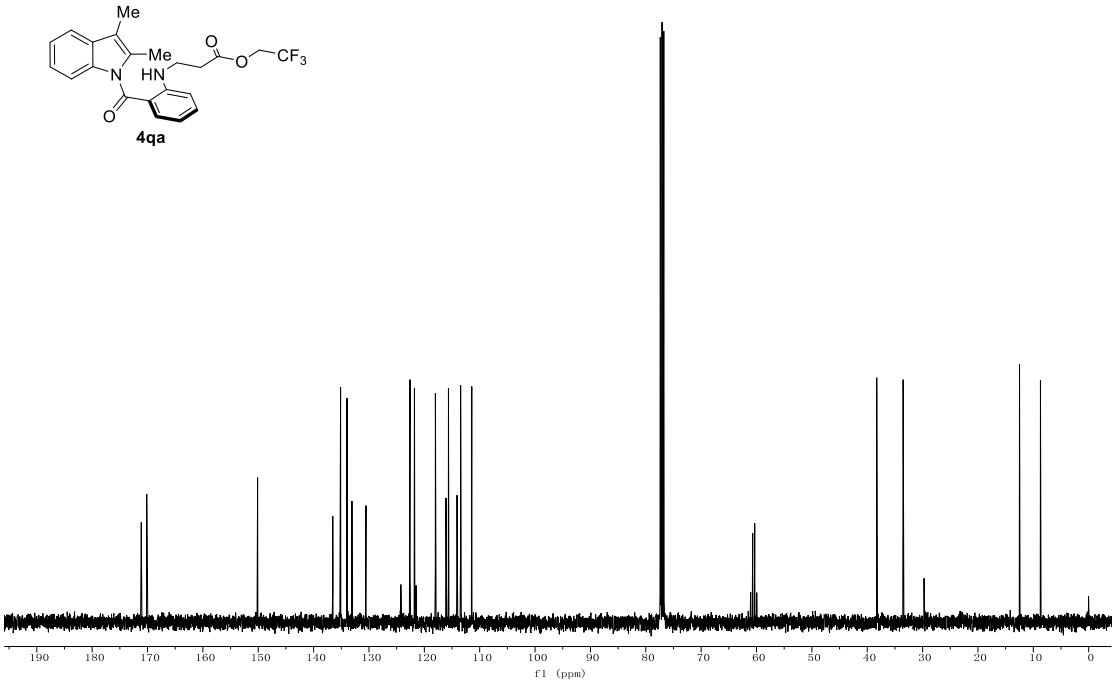

Ph
HN
O
O
CF3
O
4oa
-73.66
-73.68
-73.71
f1 (ppm)

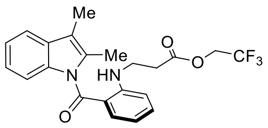

CO2Et
HN
O
O
CF3
O
4pa
f1 (ppm)


171.21
170.08
161.01
151.14
138.82
135.97
133.04
130.84
127.04
126.49
123.81
122.63
121.97
120.13
115.62
115.34
114.01
113.06
111.29
61.23
60.89
60.65
60.41
60.16
38.22
33.49
13.95
CO2Et
O
O
CF3
N
HN
O
4pa
f1 (ppm)

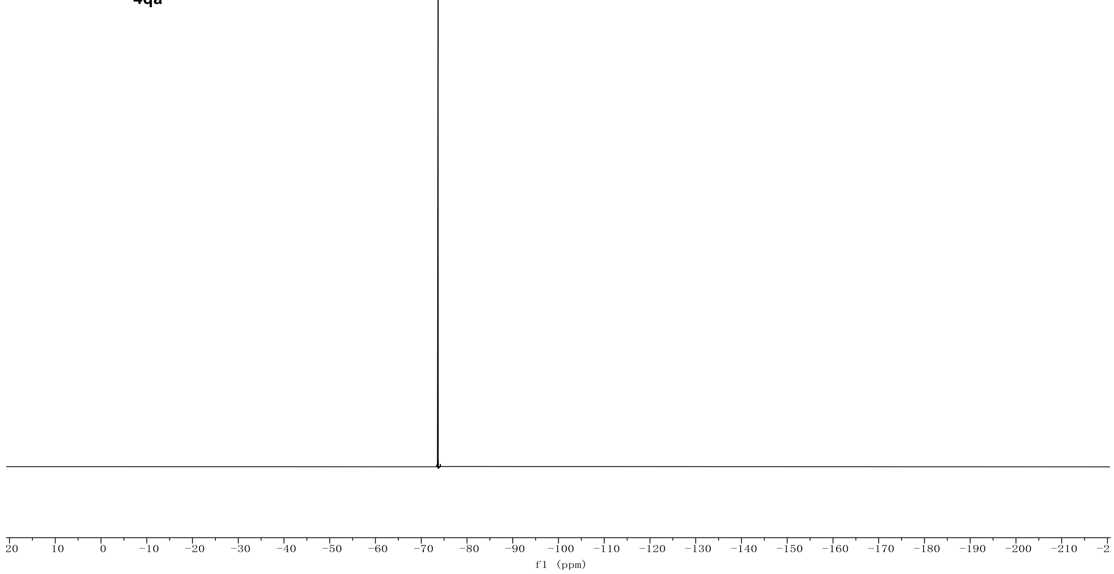

-73.68
-73.70
-73.73
CO2Et
O
O
CF3
N
HN
O
4pa
f1 (ppm)

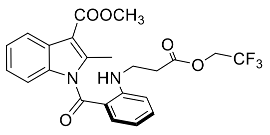

Me
Me
HN
N
O
O
O
CF3
4qa
f1 (ppm)


Me
Me
HN
N
O
O
O
CF3
4qa
f1 (ppm)

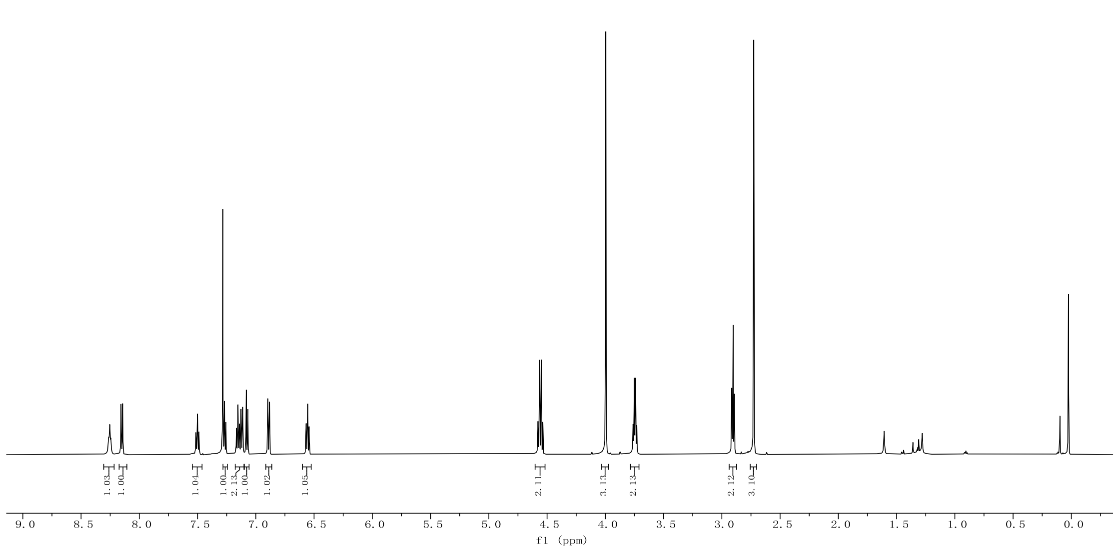

Me
Me
HN
N
O
O
O
CF3

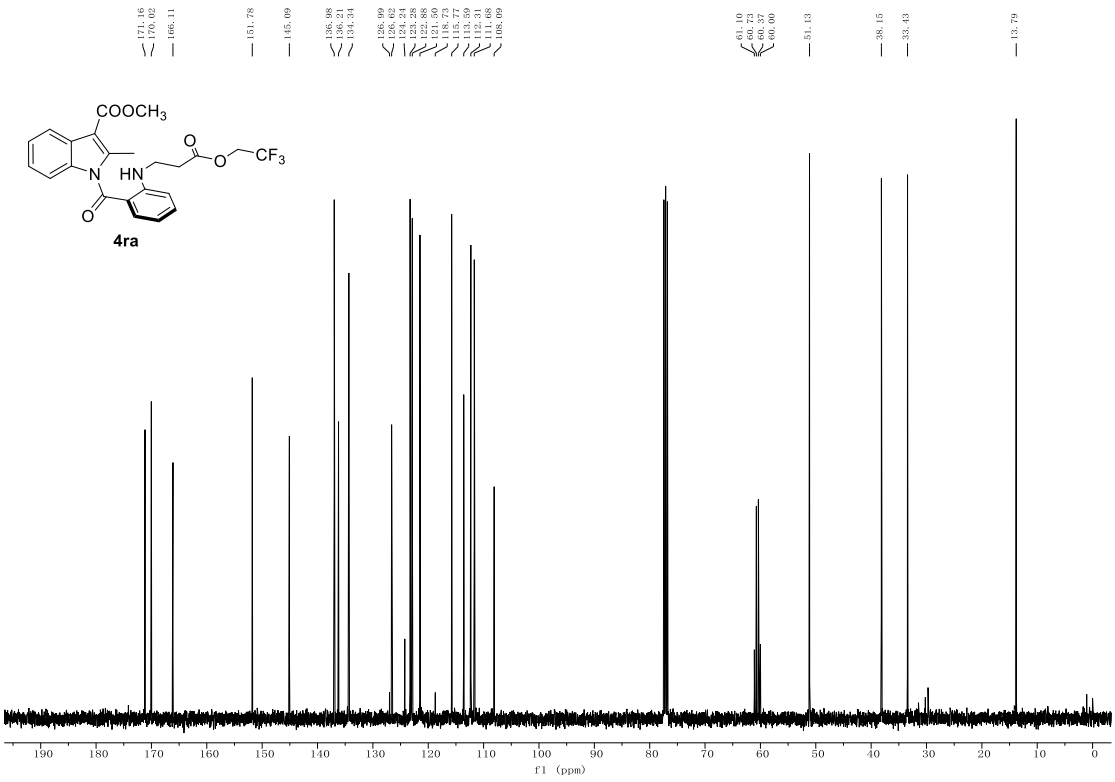
4qa

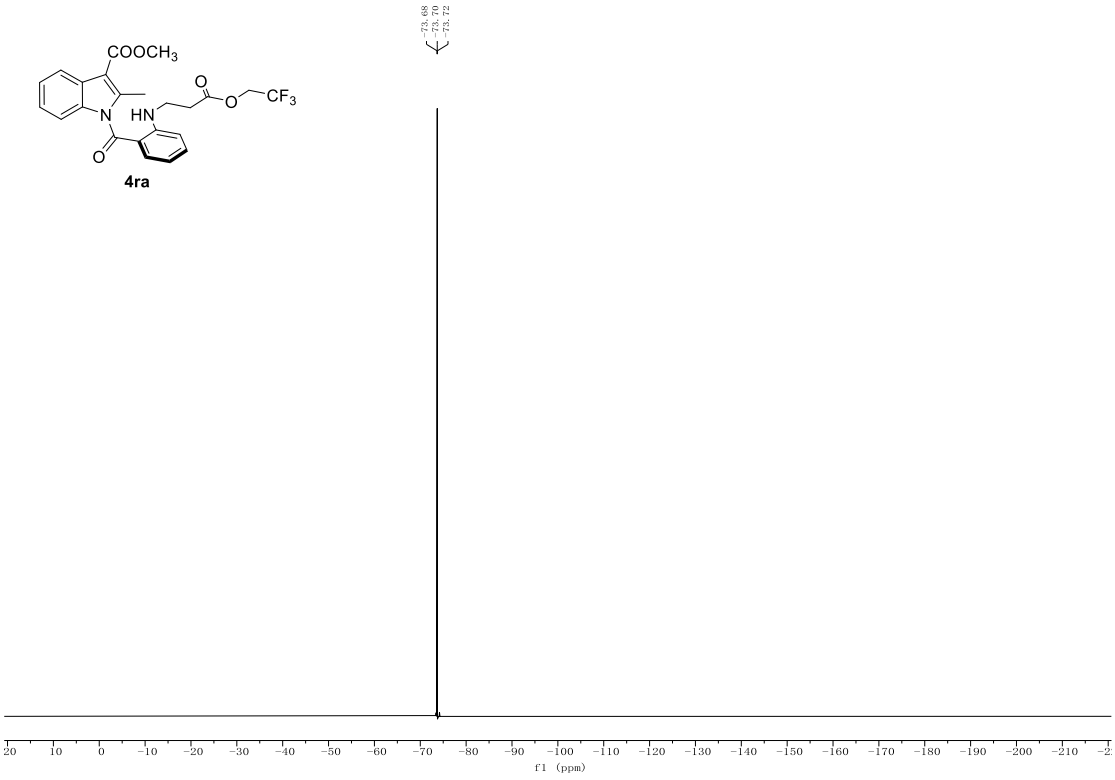

-73.67
-73.69
-73.71
f1 (ppm)

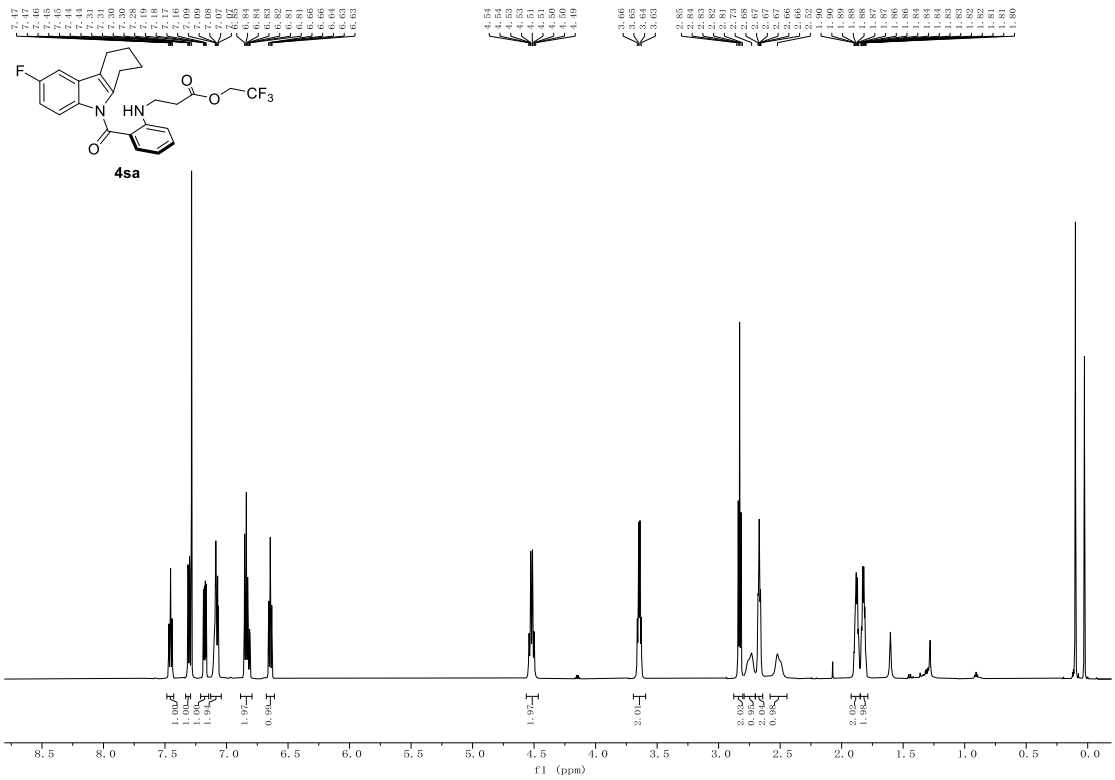

COOCH3
HN
N
O
O
O
CF3

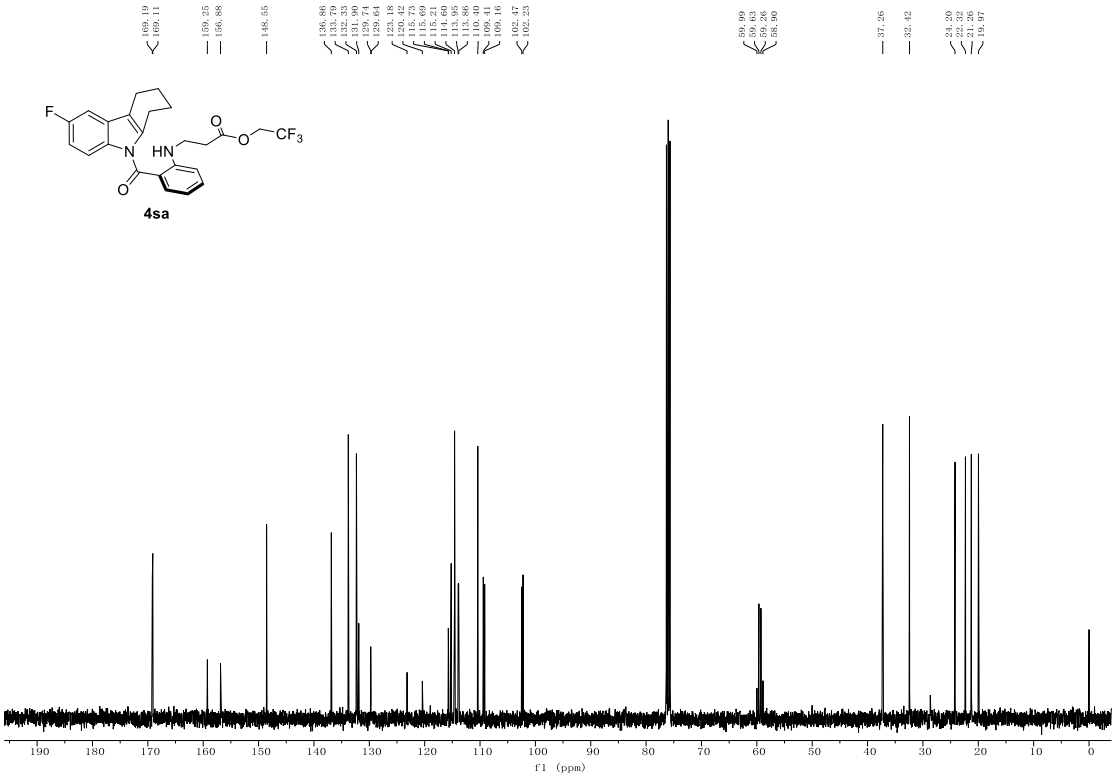
4ra

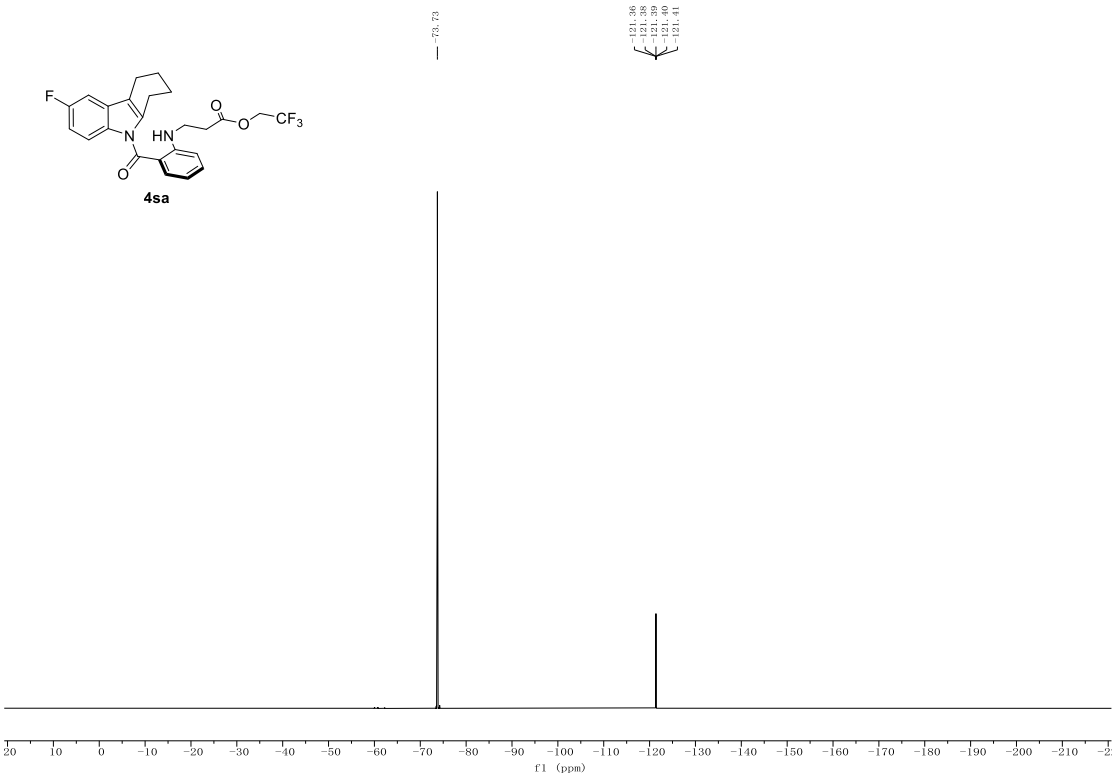

8.26
8.25
8.24
8.16
8.14
7.52
7.51
7.50
7.50
7.49
7.49
7.28
7.27
7.26
7.26
7.24
7.17
7.16
7.15
7.15
7.15
7.14
7.14
7.13
7.12
7.11
7.11
7.08
7.07
6.90
6.88
6.57
6.56
6.54
4.58
4.56
4.55
4.54
4.01
4.00
3.76
3.75
3.74
3.73
2.91
2.90
2.89
2.73
2.71
f1 (ppm)

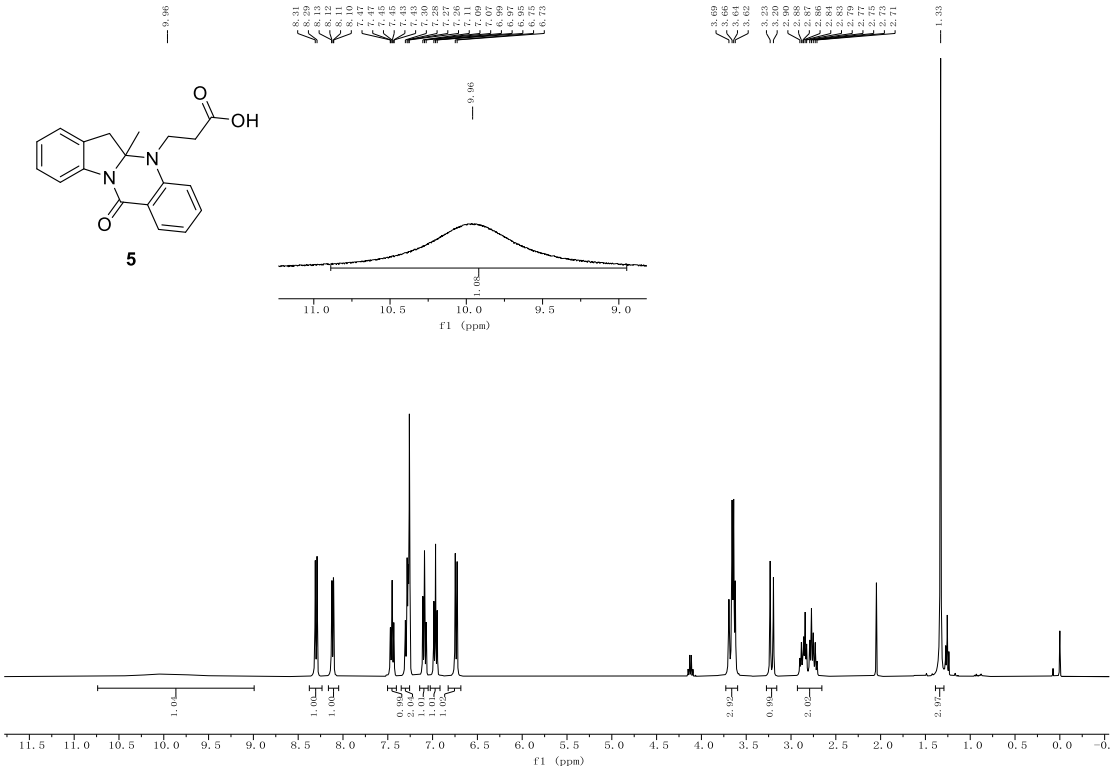

171.16
170.02
166.11
151.78
145.09
136.98
136.21
134.54
126.99
126.62
124.24
123.28
122.88
121.66
118.73
115.77
113.59
111.31
111.68
108.09
61.10
60.73
60.37
60.00
51.13
38.15
33.43
13.79
COOCH3
O
O
CF3
HN
N
O
4ra
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-73.68
-73.70
-73.72
COOCH3
O
O
CF3
HN
N
O
4ra
20
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)


F
N
HN
O
O
O
CF3
4sa
f1 (ppm)


F
N
HN
O
O
O
CF3
4sa
f1 (ppm)


F
HN
O
O
CF3
N
O
4sa
-73.73
121.36
121.38
121.39
121.40
121.41
f1 (ppm)


OH
O
N
N
O
5
9.96
8.31
8.29
8.13
8.12
8.11
8.10
7.47
7.45
7.45
7.43
7.30
7.28
7.26
7.11
7.09
7.07
6.99
6.97
6.95
6.75
6.73
3.69
3.66
3.64
3.62
3.23
3.20
2.90
2.88
2.87
2.86
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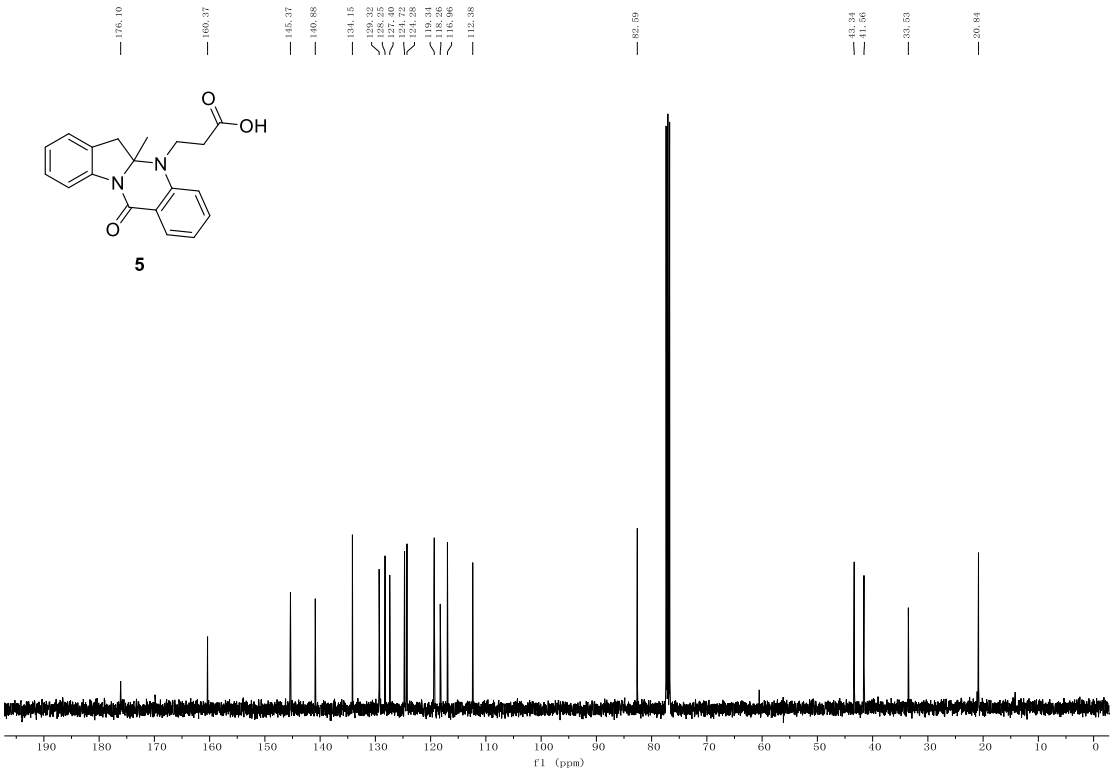
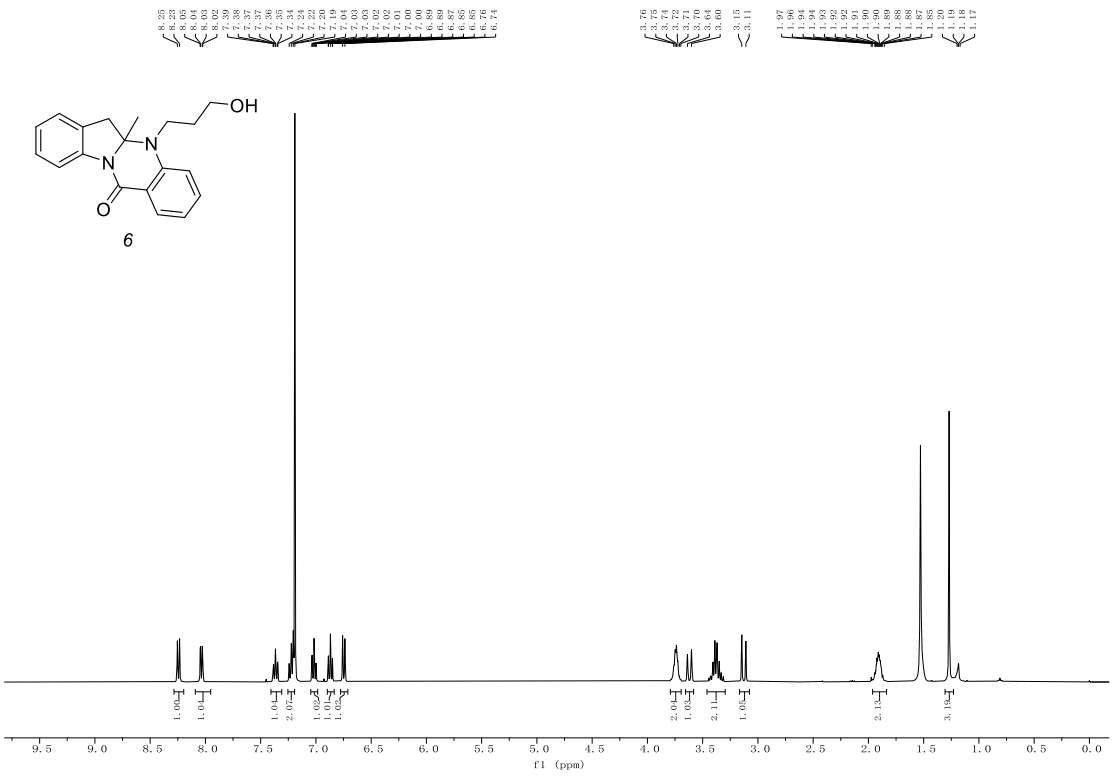
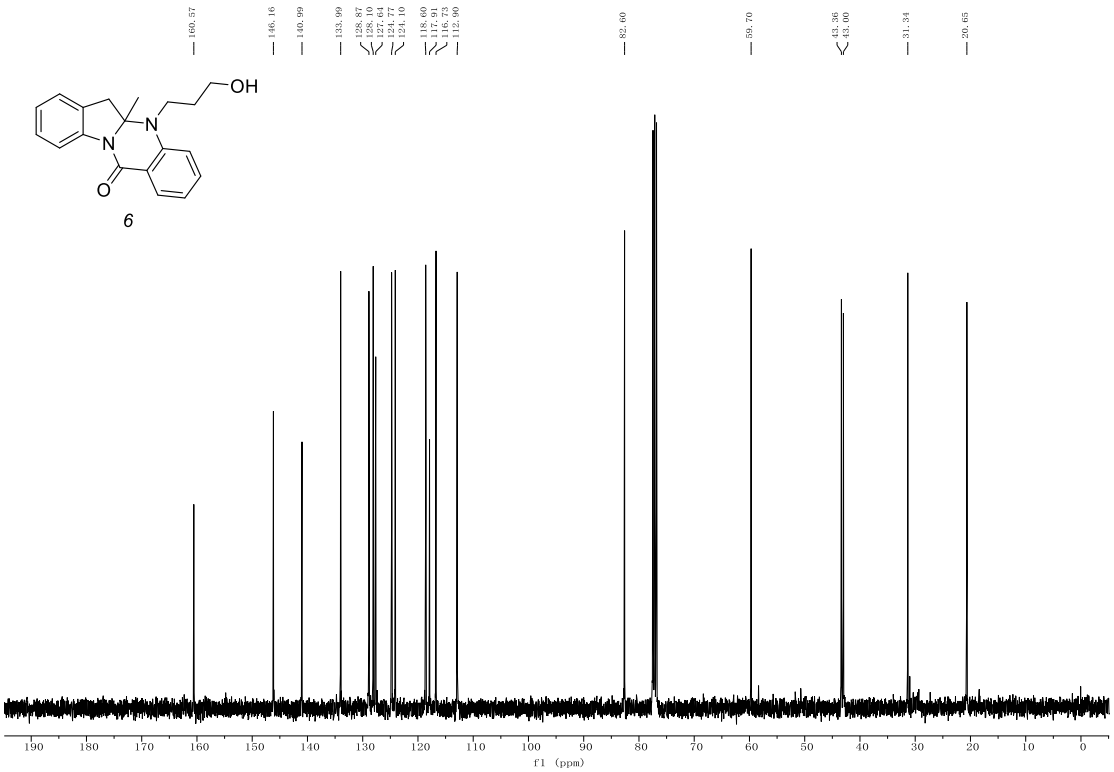
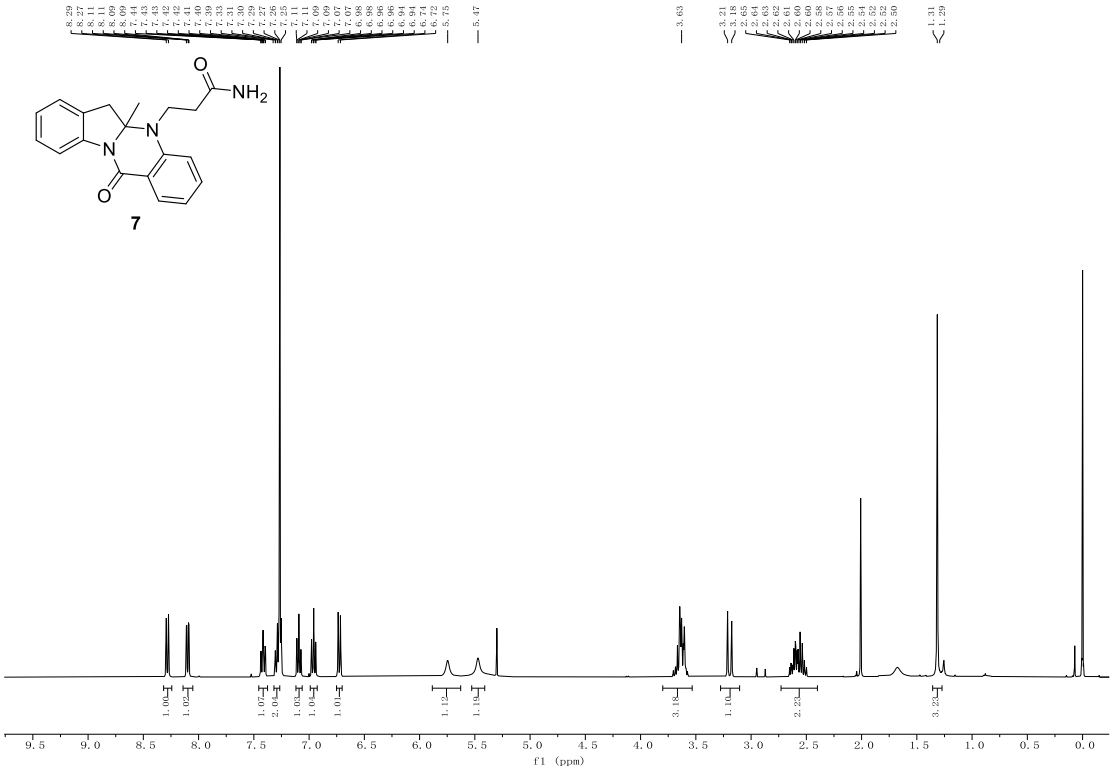
2.83
2.79
2.77
2.75
2.73
2.71
1.33
1.08
f1 (ppm)


176.10
160.37
145.37
140.88
134.15
129.32
128.35
127.49
124.72
124.28
119.34
118.25
116.96
112.38
82.59
43.34
41.56
33.53
20.84
O
OH
N
N
O
5
f1 (ppm)


OH
N
N
O
6
f1 (ppm)


160.57
146.16
140.99
133.99
128.87
128.10
127.64
124.77
124.10
118.60
117.91
116.73
112.90
82.60
59.70
43.36
43.06
31.34
20.65
OH
N
N
O
6
f1 (ppm)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8.27
8.11
8.10
8.09
7.44
7.43
7.43
7.42
7.41
7.40
7.39
7.33
7.31
7.30
7.29
7.27
7.26
7.25
7.11
7.09
7.09
7.07
7.07
6.98
6.98
6.96
6.96
6.94
6.94
6.74
6.72
5.75
5.47
3.63
3.21
3.18
2.65
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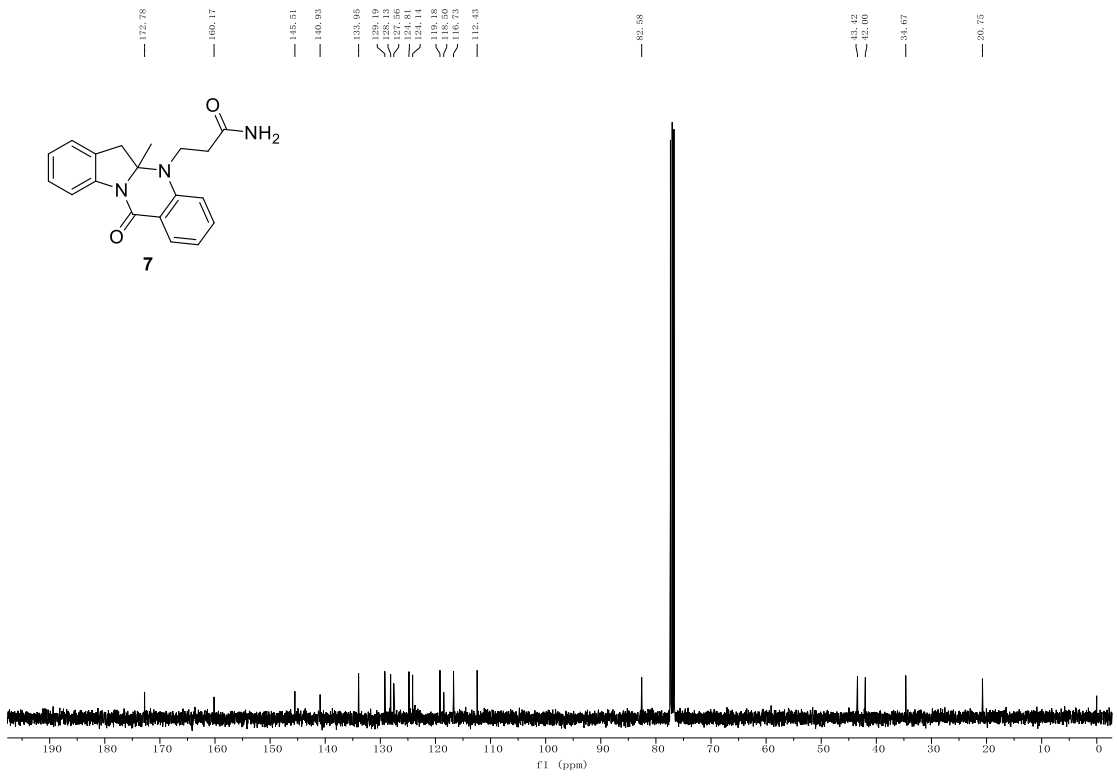
2.63
2.62
2.61
2.60
2.60
2.58
2.57
2.56
2.55
2.54
2.52
2.52
2.50
1.31
1.29
O
NH2
N
N
O
7
1.00
1.02
1.07
2.04
1.02
1.04
1.01
1.12
1.14
3.18
1.10
2.23
3.25
f1 (ppm)


172.78
160.17
145.51
140.93
133.95
129.19
128.13
127.65
124.81
124.14
119.18
118.50
116.73
112.43
82.58
43.42
42.00
34.67
20.75
O
NH2
N
N
O
7
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)