# Supporting Information

# Construction of 2-Alkynyl Aza-spiro[4,5]indole Scaffolds via Sequential C–H Activations for Modular Click Chemistry Libraries

Jun Zhang,[a] Mengmeng Wang,[c] Huiying Wang,[c] Hui Xu,[b] Junjie Chen,[b] Ziqiong Guo,[b] Biao Ma,*[,b] Shu-Rong Ban,*[,a] Hui-Xiong Dai*[,b,c,d]

[a] School of Pharmaceutical Science, Shanxi Medical University, 56 Xinjian South Road, Taiyuan 030001, China.

[b] Chinese Academy of Sciences Key Laboratory of Receptor Research, Shanghai Institute of Materia Medica, Shanghai 201203, China.

[c] School of Chinese Materia Medica, Nanjing University of Chinese Medicine, Nanjing, Jiangsu 210023, China

[d] University of Chinese Academy of Sciences, Beijing 100049, China.

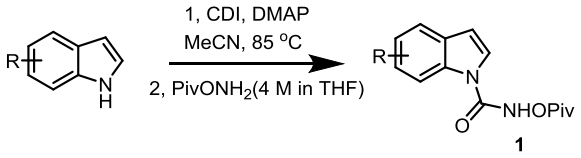
## Contents

# 1. General Information

All reagents were purchased from commercial suppliers with the highest purity grade, and used directly without further purification. $^{1}H$ and $^{13}C$ NMR spectra were Record on Bruker AVANCE III 400, Bruker AVANCE III 500 and Bruker AVANCE III 600 instruments. $^{19}F$ NMR spectra were recorded on Bruker AVANCE III 500 and BRUKER AVANCE NEO 500 instrument and are reported relative to the $CFCl_3$ as the external standard. The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublets, td = triple doublet, dt = double triplet, and br = broad. EI-double focus magnetic-sector high resolution MS (EI-DFS-HRMS) were recorded on a DFS-Thermofischer instrument at the Center for Mass Spectrometry, Shanghai Institute of Material Medica. ESI with TOF analyzer was carried out at the Center for Mass Spectrometry, Shanghai Institute of Organic Chemistry. Solvents were purified prior to use according to conventional procedures. Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Column chromatography was performed on silica gel (200–300 mesh) using a mixture of petroleum ether-ethyl acetate or dichloromethane-methanol as the eluent.

# 2. General Procedure for the Preparation of Substrates

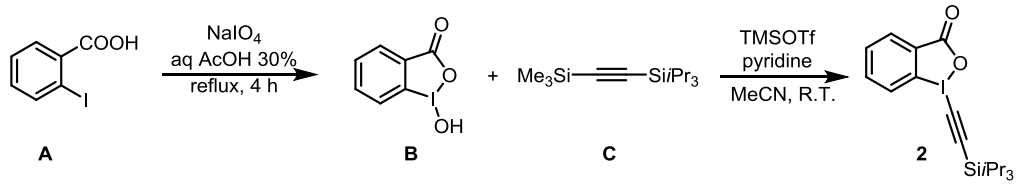
## Preparation of substrates 1[1]




**Preparation of $PivONH_2$ solution**: To a 100 mL round bottle charged with a stirring bar was added $PivONH_2$·TfOH (20.0 mmol) and 5 mL THF. To the system was then added sodium hydroxide (powder, 1.0 equiv). The system was then stirred at room temperature for about 3 h until the system became clear.

**The synthesis of *O*-pivaloyl 1-indolehydroxamic acid:** To a 100 mL round bottle charged with stirring bar, was added indole (5.0 mmol, 1.0 equiv), 1, 1'-carbonyldiimidazole (CDI, 7.5 mmol, 1.5 equiv) and 4-dimethylaminepyridine (DMAP, 20.0 mol%). Then 20 mL anhydrous MeCN was added to the bottle under the protection of nitrogen. The system was refluxed at 85 °C for 10 h. After cooled to room temperature, $PivONH_2$ solution (4 M in THF, 2 equiv) was added and then stirred at 60 °C for another 6 h (when most of indole was consumed as detected by TLC). After reaction, the reaction mixture was extracted with EtOAc. The combined organic layers were dried over $MgSO_4$. The solvent was removed in vacuo and **1a** was obtained by silica gel column chromatography (PE/EtOAc) in 58% yield.

## Preparation of substrates 2[2]

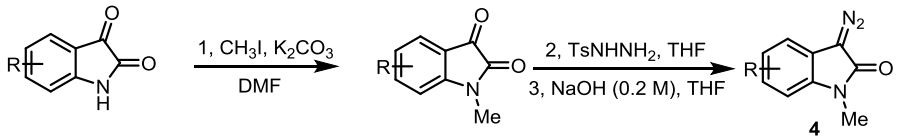


**Step 1:** 2-iodobenzoic acid (**A**) (7.4 g, 30 mmol, 1.0 equiv) and $NaIO_4$ (6.7 g, 31 mmol, 1.0 equiv) were suspended in 30% (v:v) aq. AcOH (45 mL). The mixture was vigorously stirred and refluxed for 4 h. The reaction mixture was then diluted with cold water (120 mL) and allowed to cool to room temperature, protecting it from light. After 1 h, the crude product was collected by filtration, washed on the filter with ice water (3 x 30 mL) and acetone (3 x 30 mL), and air-dried in the dark to give the pure product **B** (7.3 g, 19 mmol, 92%) as a colorless solid.

**Step 2:** Trimethylsilyltriflate (3.6 mL, 20 mmol, 1.1 equiv, freshly distilled) was added dropwise to a stirred solution of 2-iodosylbenzoic acid (**B**) (4.7 g, 18 mmol, 1.0 equiv) in MeCN (140 mL). (Trimethylsilyl)(tri*iso*-propylsilyl)acetylene (**C**) (5.0 g, 20 mmol, 1.1 equiv) was then added dropwise, followed, after 15 min, by the addition of pyridine (1.5 mL, 20 mmol, 1.1 equiv). The mixture was stirred 10 min. The solvent was then removed under reduced pressure and the yellow crude oil was dissolved in dichloromethane (50 mL). The organic layer was washed with 1 M HCl (50 mL) and the aqueous layer was extracted with DCM (50 mL). The organic layers were combined, washed with a saturated solution of $NaHCO_3$ (50 mL), dried over $MgSO_4$, filtered and the solvent was evaporated under reduced pressure. Recrystallization from MeCN afforded **2** (6.3 g, 15 mmol, 83%) as a colorless solid.

## Preparation of substrates 4[3,4,5]

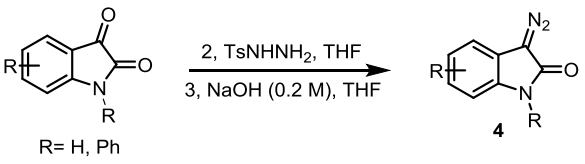
***Method A**:*




**Step 1:** To a stirred solution of isatin (8 mmol) and $K_2CO_3$ (2 eq) in DMF (10 mL) was added $CH_3I$ (2 eq) dropwise at room temperature. Then the mixture was stirred at 40 ℃ for 2-12 h. After completion of the reaction, the mixture was diluted with DCM (50 mL), and cold water (50 mL) was added. The organic layer was separated, washed with brine (50 ml x 2), dried over anhydrous $Na_2SO_4$, and concentrated under reduced pressure to give crude product without further purification.

**Step 2:** A mixture of N-substituted isatin (5 mmol) and $TsNHNH_2$ (1.1 eq) in THF (25 mL) was stirred at 60 ℃ for 2 h, then cooled at room temperature. The mixture solvent was concentrated under reduced pressure, and the pure tosylhydrazone was precipitated from MeOH (15 mL) solution. Then tosylhydrazone was dissolved in THF (25 mL), aq. NaOH (0.2 N) solution was added, and the mixture was stirred at room temperature for 2 h. Water (15 mL) and EtOAc (15 mL) were added and the organic layer was separated. The collected organic layers were washed with brine (10 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure to give the crude products, which was purified by column chromatography eluting with PE/EtOAc (10:1).

***Method B**:*

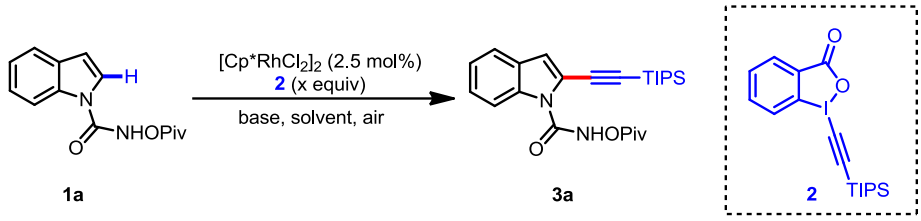



A mixture of isatin derivatives (5 mmol) and $TsNHNH_2$ (1.1 eq) in THF (25 mL) was stirred at

60 ℃ for 2 h, then cooled at room temperature. The mixture solvent was concentrated under reduced pressure, and the pure tosylhydrazone was precipitated from MeOH (15 mL) solution. Then tosylhydrazone was dissolved in THF (25 mL), aq. NaOH (0.2 N) solution was added, and the mixture was stirred at room temperature for 2 h. Water (15 mL) and EtOAc (15 mL) were added and the organic layer was separated. The collected organic layers were washed with brine (10 mL), dried over $Na_2SO_4$, and concentrated under reduced pressure to give the crude products, which was purified by column chromatography eluting with PE/EtOAc (10:1).

# 3. Optimization of Reaction Conditions

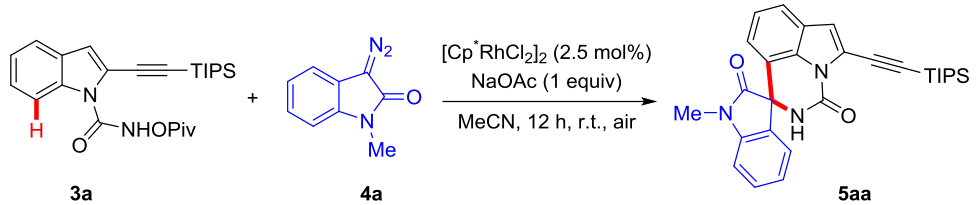
## Table S1. Screening of C2-alkynylation reaction conditions[a,b]




| Entry | Solvent | Temp (°C) | t (h) | Yield (%) of **3a** |
|---|---|---|---|---|
| 1 | DCE | r.t. | 12 | 52 |
| 2 | DCM | r.t. | 12 | 50 |
| 3 | MeCN | r.t. | 12 | 52 |
| 4 | MeOH | r.t. | 12 | 44 |
| 5 | THF | r.t. | 12 | 18 |
| 6 | Toluene | r.t. | 12 | 51 |
| 7[c] | DCE | r.t. | 12 | 66 |
| 8[c] | DCE | 0 | 12 | 80 |
| 9[c] | DCE | 0 | 4 | 79 |
| 10[c,d] | DCE | 0 | 4 | 86 |

[a] Conditions: **1a** (0.10 mmol), **2** (0.10 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), NaOAc (100 mol%), solvent (1.0 mL), r.t., air, 12 h. [b] $^1H$ NMR yields were determined by using $CH_2Br_2$ as internal standard. [c] 1.5 equiv of **2**. [d] 20 mol% NaOAc.

## Table S2. Screening of C7-annulation reaction conditions[a,b]



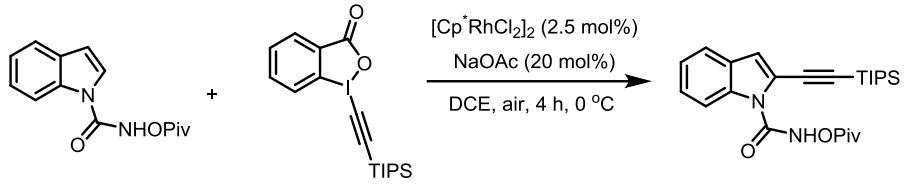

**3a** **4a** **5aa**

| Entry | Variations from the standard conditions | Yield (%) of **5aa** |
|---|---|---|
| 1 | none | 92 |
| 2 | No Rh(III) | 0 |
| 3 | MeOH instead of MeCN | 65 |
| 4 | DCE instead of MeCN | 71 |
| 5 | THF instead of MeCN | 69 |
| 6 | CsOAc (1.0 equiv) | 89 |
| 7 | KOAc (1.0 equiv) | 91 |
| 8 | $AgSbF_6$ (20 mol%) | 0 |
| 9 | MeCN (2 mL) | 92 |
| 10 | MeCN (0.5 mL) | 68 |
| 11 | 60 °C | 77 |
| 12 | **4a** (1.0 equiv) | 73 |

a) Conditions: **3a** (0.10 mmol), **4a** (0.15 mmol), $[Cp^*RhCl_2]_2$ (2.5 mol%), NaOAc (1.0 equiv), MeCN (1.0 mL), r.t., air, 12 h. b) $^1H$ NMR yields were determined by using $CH_2Br_2$ as internal standard.

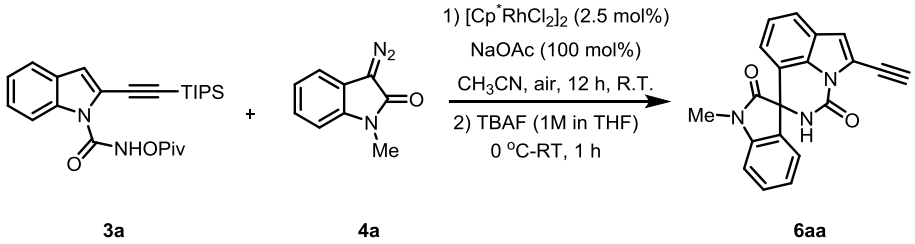
# 4. Experimental Procedures

## General procedure for Rh-catalyzed indole C2-alkynylation (*Step 1*)



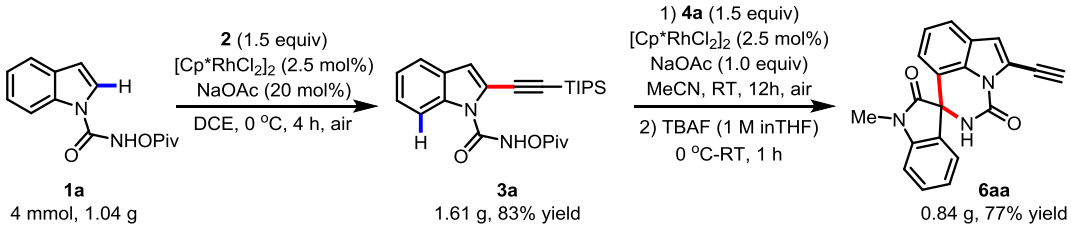

To a solution of **1a** (26.0 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (1.6 mg, 2.5 mol%), NaOAc (1.6 mg, 20 mol%) in DCE (1 mL) was added **2** (64.2 mg , 0.15 mmol). The reaction mixture was stirred at 0 °C for 4 h. After completion of the reaction, the resulting mixture was diluted with 25 mL of EtOAc, and filtered through a celite pad. Evaporation of the solvent followed by purification on silica gel (gradient eluent: PE/EtOAc = 20/1), provided product **3a**.

## General procedure for Rh-catalyzed indole C7-annulation (*Step 2*)




To a solution of **3a** (44.0 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (1.6 mg, 2.5 mol%), NaOAc (8.2 mg, 100 mol%), in MeCN (1 mL) was added **4a** (26.0 mg , 0.15 mmol). The reaction mixture was stirred at room temperature for 12 h. Then, the reaction flask was cooled to 0 °C and TBAF solution (0.12 mL, 1 M solution in THF) was added via a syringe. The reaction mixture was warmed up to ambient temperature and stirred for additional 1 h. After completion of the reaction, the reaction mixture was quenched with $H_2O$ (1.5 mL), and compound was extracted with EtOAc (5 mL × 3). The combined organic extract was dried over $Na_2SO_4$ and the volatiles were evaporated in vacuo. The remaining residue was purified by column chromatography (PE/EtOAc: 1/1) to yield **6aa**.

## Gram-scale Synthesis

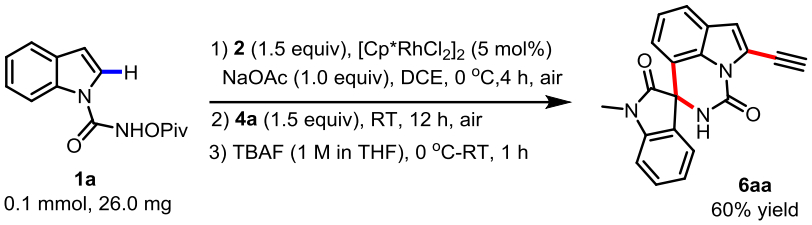



***Step 1:*** Under air atmosphere, to a solution of **1a** (1.04 g, 4.0 mmol), $[Cp^*RhCl_2]_2$ (64.0 mg, 2.5 mol%), NaOAc (65.6 mg, 20 mol%) in DCE (40 mL) was added **2** (2.57 g, 6.0 mmol). The reaction mixture was stirred at 0 °C for 4 h. After completion of the reaction, the resulting mixture was diluted with EtOAc, and filtered through a celite pad. The solvent was removed under

reduced pressure. The residue was purified by column chromatography on silica gel (gradient eluent: PE/EtOAc = 20/1) to give product **3a** in 83% yield.

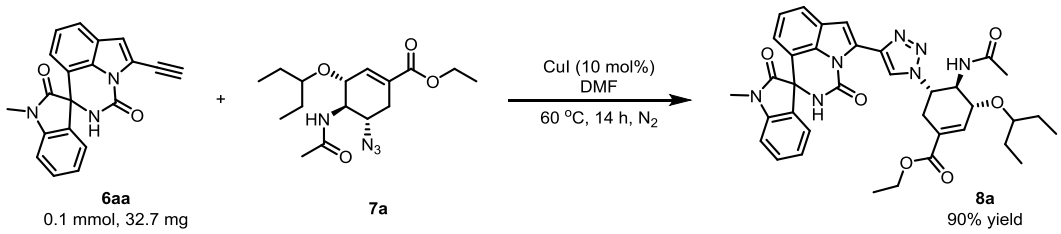
***Step 2:*** Under air atmosphere, to a solution of **3a** (1.61 g, 3.3 mmol), $[Cp^*RhCl_2]_2$ (52.8 mg, 2.5 mol%), NaOAc (270.6 mg, 1 equiv) in MeCN (33 mL) was added **4a** (855.0 mg, 5.0 mmol). The reaction mixture was stirred at room temperature for 12 h. Then, the reaction flask was cooled to 0 °C and TBAF solution (3.96 mL, 1 M solution in THF) was added via a syringe. The reaction mixture was warmed up to ambient temperature and stirred for additional 1 h. After completion of the reaction, the reaction mixture was quenched with $H_2O$ (50 mL), and compound was extracted with EtOAc (100 mL × 3). The combined organic extract was dried over $Na_2SO_4$ and the volatiles were evaporated in vacuo. The remaining residue was purified by column chromatography (PE/EtOAc: 1/1) to yield **6aa**.

## One-pot Synthesis



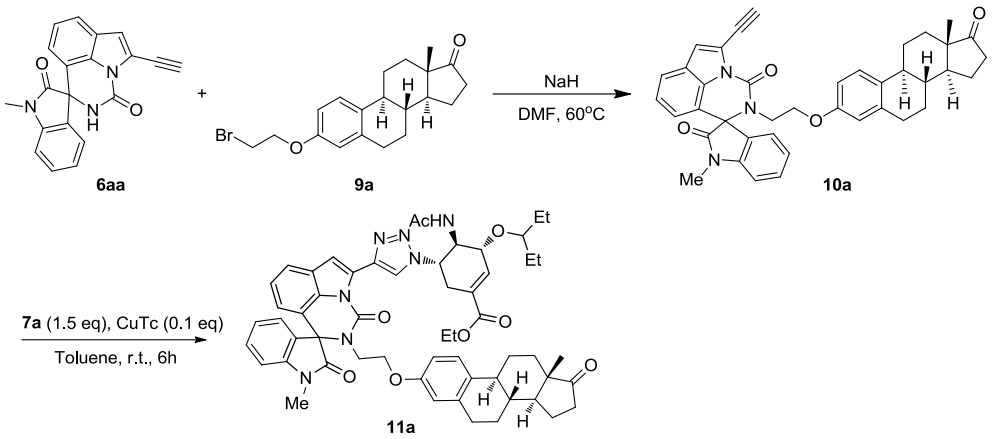

To a solution of **1a** (26.0 mg, 0.1 mmol), $[Cp^*RhCl_2]_2$ (3.2 mg, 5 mol%), NaOAc (8.2 mg, 1 equiv) in DCE (1 mL) was added **2** (64.2 mg , 0.15 mmol). The reaction mixture was stirred at 0 °C for 4 h. Then, **4a** (26.0 mg, 0.15 mmol) was added. The reaction mixture was stirred at room temperature for 12 h. Then, the reaction flask was cooled to 0 °C and TBAF solution (0.12 mL, 1 M solution in THF) was added via a syringe. The reaction mixture was warmed up to ambient temperature and stirred for additional 1 h. After completion of the reaction, the reaction mixture was quenched with $H_2O$ (1.5 mL), and compound was extracted with EtOAc (5 mL × 3). The combined organic extract was dried over $Na_2SO_4$ and the volatiles were evaporated in vacuo. The remaining residue was purified by column chromatography (PE/EtOAc: 1/1) to yield **6aa**.

## The preparation of 8a[6]




Compound **6aa** (32.7 mg, 0.1 mmol), **7a** (33.8 mg, 0.1 mmol, the preparation according to previous reports[7, 8]) and CuI (1.9 mg, 10 mol%) were charged into a Schlenk tube, and DMF (2 mL) was added under argon. The reaction mixture was stirred at 60 °C for 14 h. At ambient temperature, $H_2O$ (5 mL) was added and the compound was extracted with EtOAc (30 mL × 3). The combined organic extract was washed with water (10 mL × 3) and dried over $Na_2SO_4$, and the volatiles were evaporated in vacuo. The remaining residue was purified by column chromatography (PE/EtOAc: 1/5) to yield **8** (60.0 mg, 90%) as a white solid.

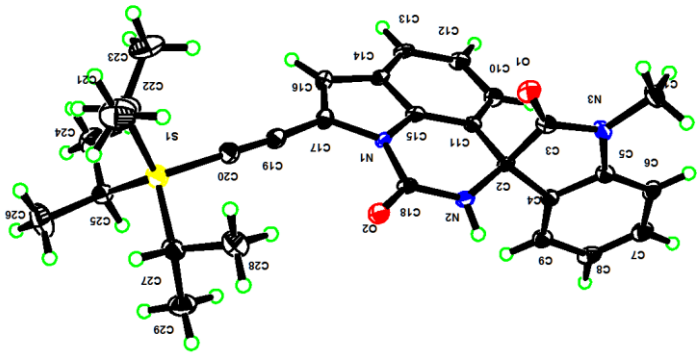
## The preparation of 11a




0°C, NaH (6.0 mg, 1.5 eq) was added into a solution of Compound **6aa** (32.7 mg, 0.1 mmol) in DMF (2 mL) under argon. After 1h, compound **9a** (45.1 mg, 1.2 eq) was added, and the reaction mixture was stirred at 80 °C for 14 h. At ambient temperature, $H_2O$ (5 mL) was added and the reaction was extracted with EtOAc (30 mL × 3). The combined organic extract was washed with water (10 mL × 3) and dried over $Na_2SO_4$, and the volatiles were evaporated in vacuo. The remaining residue was purified by column chromatography (PE/EtOAc: 1/1) to yield **10a** (51.0 mg, 81%) as a pink solid.

Compound **10a** (21 mg, 0.03 mmol), 7**a** (11 mg, 0.03 mmol) and CuTc (1 mg, 10 mol%) were charged into a Schlenk tube, and Toluene (1 mL) was added under argon. The reaction mixture was stirred at r.t. for 6 h. At ambient temperature, $H_2O$ (5 mL) was added and the compound was extracted with EtOAc (30 mL × 3). The combined organic extract was washed with water (10 mL × 3) and dried over $Na_2SO_4$, and the volatiles were evaporated in vacuo. The remaining residue was purified by column chromatography (PE/acetone: 2/1) to yield **11a** (25 mg, 78%) as a white solid.

## 5. X-ray Crystallographic Date of compound 5aa



**Crystal Data** for $C_{29}H_{33}N_3O_2S$ (*M* =487.64 g/mol): monoclinic, space group $P2_1/c$ (no. 14), *a* = 7.7589(12) Å, *b* = 9.054(2) Å, *c* = 37.137(7) Å, *β* = 94.835(6)°, *V* = 2599.6(9) Å$^3$, *Z* = 4, *T* = 140.0 K, μ(MoKα) = 0.155 mm$^{-1}$, *Dcalc* = 1.246 g/cm$^3$, 20910 reflections measured (4.402° ≤ 2Θ ≤ 50.048°), 4610 unique ($R_{int}$ = 0.1032, $R_{sigma}$ = 0.0864) which were used in all calculations. The final $R_1$ was 0.0950 (I > 2σ(I)) and $wR_2$ was 0.2882 (all data).

**Table 1 Crystal data and structure refinement for 22020487TIPS1_0m.**

| | |
|---|---|
| Identification code | 22020487TIPS1_0m |
| Empirical formula | $C_{29}H_{33}N_3O_2S$ |
| Formula weight | 487.64 |
| Temperature/K | 140.0 |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ |
| a/Å | 7.7589(12) |
| b/Å | 9.054(2) |
| c/Å | 37.137(7) |
| α/° | 90 |
| β/° | 94.835(6) |
| γ/° | 90 |
| Volume/Å$^3$ | 2599.6(9) |
| Z | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.246 |
| μ/mm$^{-1}$ | 0.155 |
| F(000) | 1040.0 |
| Crystal size/mm$^3$ | 0.15 × 0.08 × 0.05 |
| Radiation | MoKα (λ = 0.71073) |

| | |
|---|---|
| 2Θ range for data collection/° | 4.402 to 50.048 |
| Index ranges | $-9 \le h \le 9$, $-10 \le k \le 10$, $-44 \le l \le 44$ |
| Reflections collected | 20910 |
| Independent reflections | 4610 [$R_{int}$ = 0.1032, $R_{sigma}$ = 0.0864] |
| Data/restraints/parameters | 4610/0/324 |
| Goodness-of-fit on $F^2$ | 1.039 |
| Final R indexes [I>=2σ (I)] | $R_1$ = 0.0950, $wR_2$ = 0.2583 |
| Final R indexes [all data] | $R_1$ = 0.1223, $wR_2$ = 0.2882 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.57/-0.80 |

**Table 2 Fractional Atomic Coordinates (×10$^4$) and Equivalent Isotropic Displacement Parameters (Å$^2$×10$^3$) for 22020487TIPS1_0m. $U_{eq}$ is defined as 1/3 of of the trace of the orthogonalised $U_{IJ}$ tensor.**

| Atom | *x* | *y* | *z* | U(eq) |
|---|---|---|---|---|
| S1 | 2112(2) | 2374(2) | 4458.0(5) | 28.6(5) |
| O2 | 805(5) | 6039(5) | 3497.5(12) | 23.0(10) |
| O1 | 3261(6) | 6942(5) | 2537.6(12) | 25.0(11) |
| N1 | 3656(6) | 6772(6) | 3535.8(13) | 14.0(10) |
| N2 | 1581(6) | 8037(6) | 3172.6(13) | 18.5(11) |
| N3 | 2887(7) | 9375(6) | 2358.7(13) | 19.2(12) |
| C18 | 1915(7) | 6869(7) | 3406.1(15) | 16.6(13) |
| C11 | 4551(7) | 8897(7) | 3184.9(15) | 14.8(12) |
| C13 | 7801(7) | 8518(7) | 3589.6(17) | 18.4(13) |
| C20 | 3025(9) | 3804(8) | 4183.4(18) | 25.2(15) |
| C15 | 4859(8) | 7791(7) | 3440.3(16) | 15.4(12) |
| C8 | 1558(8) | 13030(8) | 2949.5(18) | 24.8(14) |
| C14 | 6446(8) | 7558(7) | 3644.6(15) | 17.5(13) |
| C2 | 2781(7) | 8908(7) | 2979.6(16) | 15.8(13) |
| C5 | 2419(8) | 10698(7) | 2517.9(16) | 17.7(13) |
| C16 | 6155(8) | 6328(7) | 3875.5(16) | 20.2(14) |
| C3 | 3002(8) | 8245(7) | 2598.8(16) | 18.9(13) |
| C19 | 3616(8) | 4762(8) | 4000.6(18) | 23.8(14) |
| C17 | 4484(8) | 5892(7) | 3819.4(16) | 20.2(14) |
| C10 | 5898(8) | 9844(7) | 3136.9(16) | 20.3(13) |
| C9 | 1795(8) | 11615(7) | 3103.8(17) | 21.6(14) |
| C25 | 2734(9) | 2820(8) | 4950.7(18) | 28.4(16) |
| C4 | 2222(8) | 10466(7) | 2887.3(16) | 17.3(13) |
| C6 | 2229(8) | 12095(7) | 2365.6(18) | 21.7(14) |
| C12 | 7523(8) | 9649(7) | 3336.5(17) | 21.7(14) |
| C27 | -276(9) | 2505(8) | 4367.8(17) | 26.4(15) |
| C1 | 3169(10) | 9228(8) | 1975.9(16) | 27.8(16) |

| | | | | |
|---|---|---|---|---|
| C7 | 1785(8) | 13252(8) | 2585.0(18) | 25.1(14) |
| C29 | -1062(10) | 3834(10) | 4553(2) | 36.9(19) |
| C28 | -839(10) | 2618(9) | 3954.3(18) | 34.4(17) |
| C21 | 1948(12) | -586(11) | 4171(3) | 52(2) |
| C24 | 4696(10) | 2848(10) | 5043(2) | 39.9(19) |
| C22 | 3094(11) | 535(9) | 4351(3) | 45(2) |
| C23 | 4811(11) | 639(11) | 4201(3) | 49(2) |
| C26 | 1853(11) | 1743(11) | 5196.4(19) | 46(2) |

**Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 22020487TIPS1_0m. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.**

| Atom | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{23}$ | $U_{13}$ | $U_{12}$ |
|---|---|---|---|---|---|---|
| S1 | 34.6(9) | 20.0(10) | 32.6(9) | 3.3(7) | 10.5(7) | 1.7(7) |
| O2 | 20(2) | 17(2) | 32(2) | 6(2) | 5.2(18) | -0.8(19) |
| O1 | 35(3) | 11(3) | 29(2) | -3.3(19) | 4(2) | 5(2) |
| N1 | 11(2) | 13(3) | 18(2) | 3(2) | -0.7(19) | 3(2) |
| N2 | 14(2) | 14(3) | 28(3) | 6(2) | 6(2) | 2(2) |
| N3 | 30(3) | 12(3) | 17(2) | 0(2) | 8(2) | 1(2) |
| C18 | 16(3) | 11(3) | 23(3) | -2(2) | 4(2) | 2(3) |
| C11 | 18(3) | 8(3) | 19(3) | -2(2) | 6(2) | 1(2) |
| C13 | 11(3) | 18(4) | 26(3) | -4(3) | 1(2) | 2(2) |
| C20 | 30(3) | 21(4) | 26(3) | 3(3) | 7(3) | 4(3) |
| C15 | 19(3) | 5(3) | 24(3) | -3(2) | 6(2) | 0(2) |
| C8 | 23(3) | 12(3) | 39(4) | -4(3) | 3(3) | 3(3) |
| C14 | 18(3) | 13(3) | 21(3) | -2(3) | 2(2) | 5(2) |
| C2 | 16(3) | 9(3) | 23(3) | 3(2) | 5(2) | 4(2) |
| C5 | 20(3) | 12(3) | 21(3) | -1(2) | 4(2) | -1(2) |
| C16 | 22(3) | 19(4) | 19(3) | 2(3) | -1(2) | 1(3) |
| C3 | 17(3) | 18(4) | 22(3) | -3(3) | 3(2) | -2(3) |
| C19 | 28(3) | 15(4) | 29(3) | 2(3) | 6(3) | 5(3) |
| C17 | 24(3) | 13(3) | 23(3) | 4(3) | 2(3) | 1(3) |
| C10 | 21(3) | 16(3) | 24(3) | 1(3) | 4(3) | -2(3) |
| C9 | 25(3) | 14(3) | 27(3) | 0(3) | 5(3) | 3(3) |
| C25 | 27(3) | 25(4) | 34(3) | 6(3) | 10(3) | 8(3) |
| C4 | 20(3) | 12(3) | 20(3) | 0(2) | 5(2) | 3(2) |
| C6 | 23(3) | 15(4) | 27(3) | 6(3) | 2(2) | 3(3) |
| C12 | 23(3) | 14(4) | 29(3) | -4(3) | 6(3) | -1(3) |
| C27 | 33(4) | 17(4) | 31(3) | 0(3) | 15(3) | 3(3) |
| C1 | 40(4) | 27(4) | 17(3) | 0(3) | 8(3) | 3(3) |
| C7 | 26(3) | 15(4) | 35(3) | 2(3) | 4(3) | 5(3) |

| | | | | | | |
|---|---|---|---|---|---|---|
| C29 | 33(4) | 46(5) | 33(4) | -7(4) | 5(3) | 13(4) |
| C28 | 36(4) | 39(5) | 29(3) | -2(3) | 6(3) | -4(4) |
| C21 | 55(5) | 41(6) | 61(5) | -15(4) | 8(5) | 1(4) |
| C24 | 35(4) | 46(5) | 38(4) | 4(4) | -4(3) | 8(4) |
| C22 | 44(5) | 15(4) | 78(6) | -5(4) | 23(4) | -1(3) |
| C23 | 43(5) | 40(6) | 64(6) | -9(4) | 6(4) | 20(4) |
| C26 | 55(5) | 59(6) | 24(4) | 8(4) | 4(3) | -16(5) |

**Table 4 Bond Lengths for 22020487TIPS1_0m.**

| Atom | Atom | Length/Å | Atom | Atom | Length/Å |
|---|---|---|---|---|---|
| S1 | C20 | 1.827(7) | C15 | C14 | 1.407(8) |
| S1 | C25 | 1.896(7) | C8 | C9 | 1.409(9) |
| S1 | C27 | 1.859(7) | C8 | C7 | 1.394(9) |
| S1 | C22 | 1.887(8) | C14 | C16 | 1.435(9) |
| O2 | C18 | 1.212(8) | C2 | C3 | 1.559(8) |
| O1 | C3 | 1.221(8) | C2 | C4 | 1.507(9) |
| N1 | C18 | 1.398(7) | C5 | C4 | 1.409(8) |
| N1 | C15 | 1.380(8) | C5 | C6 | 1.388(9) |
| N1 | C17 | 1.429(8) | C16 | C17 | 1.354(9) |
| N2 | C18 | 1.378(8) | C19 | C17 | 1.425(9) |
| N2 | C2 | 1.454(8) | C10 | C12 | 1.419(9) |
| N3 | C5 | 1.397(8) | C9 | C4 | 1.372(9) |
| N3 | C3 | 1.355(8) | C25 | C24 | 1.532(11) |
| N3 | C1 | 1.462(8) | C25 | C26 | 1.535(10) |
| C11 | C15 | 1.386(9) | C6 | C7 | 1.388(10) |
| C11 | C2 | 1.513(8) | C27 | C29 | 1.537(10) |
| C11 | C10 | 1.375(9) | C27 | C28 | 1.564(9) |
| C13 | C14 | 1.393(9) | C21 | C22 | 1.473(12) |
| C13 | C12 | 1.394(9) | C22 | C23 | 1.492(11) |
| C20 | C19 | 1.215(10) | | | |

**Table 5 Bond Angles for 22020487TIPS1_0m.**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C20 | S1 | C25 | 108.0(3) | C11 | C2 | C3 | 106.9(5) |
| C20 | S1 | C27 | 106.4(3) | C4 | C2 | C11 | 110.6(5) |
| C20 | S1 | C22 | 109.0(3) | C4 | C2 | C3 | 101.9(5) |
| C27 | S1 | C25 | 109.2(3) | N3 | C5 | C4 | 109.7(5) |
| C27 | S1 | C22 | 115.6(4) | C6 | C5 | N3 | 129.1(5) |
| C22 | S1 | C25 | 108.4(4) | C6 | C5 | C4 | 121.1(6) |
| C18 | N1 | C17 | 130.6(5) | C17 | C16 | C14 | 109.3(5) |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C15 | N1 | C18 | 121.6(5) | O1 | C3 | N3 | 127.6(6) |
| C15 | N1 | C17 | 106.8(5) | O1 | C3 | C2 | 125.0(6) |
| C18 | N2 | C2 | 129.2(5) | N3 | C3 | C2 | 107.4(5) |
| C5 | N3 | C1 | 123.7(5) | C20 | C19 | C17 | 172.9(7) |
| C3 | N3 | C5 | 112.0(5) | C16 | C17 | N1 | 108.5(5) |
| C3 | N3 | C1 | 124.3(5) | C16 | C17 | C19 | 128.4(6) |
| O2 | C18 | N1 | 123.6(6) | C19 | C17 | N1 | 123.2(6) |
| O2 | C18 | N2 | 123.4(5) | C11 | C10 | C12 | 120.5(6) |
| N2 | C18 | N1 | 113.0(5) | C4 | C9 | C8 | 118.7(6) |
| C15 | C11 | C2 | 116.5(5) | C24 | C25 | S1 | 112.7(5) |
| C10 | C11 | C15 | 116.7(6) | C24 | C25 | C26 | 111.2(6) |
| C10 | C11 | C2 | 126.7(6) | C26 | C25 | S1 | 110.4(5) |
| C14 | C13 | C12 | 118.8(6) | C5 | C4 | C2 | 108.0(5) |
| C19 | C20 | S1 | 179.4(6) | C9 | C4 | C2 | 131.0(6) |
| N1 | C15 | C11 | 125.3(5) | C9 | C4 | C5 | 120.6(6) |
| N1 | C15 | C14 | 110.0(5) | C5 | C6 | C7 | 118.1(6) |
| C11 | C15 | C14 | 124.8(6) | C13 | C12 | C10 | 121.5(6) |
| C7 | C8 | C9 | 120.2(6) | C29 | C27 | S1 | 113.3(5) |
| C13 | C14 | C15 | 117.7(6) | C29 | C27 | C28 | 107.4(6) |
| C13 | C14 | C16 | 137.0(6) | C28 | C27 | S1 | 111.9(4) |
| C15 | C14 | C16 | 105.3(5) | C6 | C7 | C8 | 121.3(6) |
| N2 | C2 | C11 | 109.8(5) | C21 | C22 | S1 | 117.7(6) |
| N2 | C2 | C3 | 111.2(5) | C21 | C22 | C23 | 113.3(8) |
| N2 | C2 | C4 | 115.9(5) | C23 | C22 | S1 | 114.3(6) |

**Table 6 Hydrogen Atom Coordinates (Å×10$^4$) and Isotropic Displacement Parameters (Å$^2$× 10$^3$) for 22020487TIPS1_0m.**

| **Atom** | ***x*** | ***y*** | ***z*** | **U(eq)** |
|---|---|---|---|---|
| H2 | 486.18 | 8291.85 | 3135.03 | 22 |
| H13 | 8894.48 | 8404.69 | 3722.09 | 22 |
| H8 | 1243.66 | 13835.59 | 3094.34 | 30 |
| H16 | 7001.39 | 5887.75 | 4041.66 | 24 |
| H10 | 5738.91 | 10634.1 | 2969.07 | 24 |
| H9 | 1661.24 | 11459.56 | 3352.88 | 26 |
| H25 | 2286.77 | 3831.92 | 4997.71 | 34 |
| H6 | 2398.39 | 12254.8 | 2118.2 | 26 |
| H12 | 8444.18 | 10305 | 3296.77 | 26 |
| H27 | -795.7 | 1585.81 | 4461.57 | 32 |
| H1A | 2131.26 | 9553.44 | 1828.4 | 42 |
| H1B | 3407.94 | 8192.79 | 1921.68 | 42 |

| | | | | |
|---|---|---|---|---|
| H1C | 4155.22 | 9840.16 | 1921.24 | 42 |
| H7 | 1631.86 | 14213.25 | 2484.87 | 30 |
| H29A | -817.96 | 3750.27 | 4815.37 | 55 |
| H29B | -2316.11 | 3850.88 | 4492.64 | 55 |
| H29C | -552.92 | 4749.03 | 4468.81 | 55 |
| H28A | -318.64 | 3498.97 | 3854.92 | 52 |
| H28B | -2102.12 | 2689.49 | 3917.82 | 52 |
| H28C | -449.38 | 1737.18 | 3831.14 | 52 |
| H21A | 948.18 | -744.15 | 4310.65 | 78 |
| H21B | 2583.47 | -1515.32 | 4153.84 | 78 |
| H21C | 1550.43 | -243.86 | 3927.43 | 78 |
| H24A | 5175.43 | 1867.36 | 5000.92 | 60 |
| H24B | 4948.92 | 3121.44 | 5296.92 | 60 |
| H24C | 5218.67 | 3572.8 | 4888.83 | 60 |
| H22 | 3387.37 | 97.85 | 4596.22 | 54 |
| H23A | 4742.85 | 1347.27 | 4000.36 | 73 |
| H23B | 5138.23 | -333.19 | 4112.53 | 73 |
| H23C | 5681.33 | 971.6 | 4389.91 | 73 |
| H26A | 595.81 | 1796.48 | 5142.66 | 69 |
| H26B | 2150.31 | 2009.96 | 5449.79 | 69 |
| H26C | 2249.18 | 735.63 | 5153.62 | 69 |

## 6. References

[1] Zhang, L.-B.; Zhu, M.-H.; Ni, S.-F.; Wen, L.-R.; Li, M. *ACS Catal.* **2019**, *9*, 1680.

[2] Brand, J.; Charpentier, J.; Waser, J. *Angew. Chem. Int. Ed.* **2009**, *48*, 9346.

[3] Ma, B.; Wu, P.; Wang, X.; Wang, Z.-Y.; Lin, H.-X.; Dai, H.-X. *Angew. Chem. Int. Ed.* **2019**, *58*, 13335.

[4] Dhara, K.; Mandal, T.; Das, J.; Dash, J. *Angew. Chem. Int. Ed.* **2015**, *54*, 15831.

[5] Oseka, M.; Kimm, M.; Kaabel, S.; Jarving, I.; Rissanen, K.; Kanger, T. *Org. Lett.* **2016**, *18*, 1358.

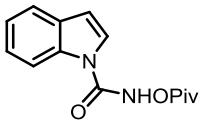
[6] Khake, S. M.; Soni, V.; Gonnade, R. G.; Punji, B. *Chem. Eur. J.* **2017**, *23*, 2907.

[7] Reader, P. W.; Pfukwa, R.; Jokonya, S.; Arnott, G. E.; Klumperman, B. *Polym. Chem.* **2016**, *7*, 6450.

[8] Favalli, N.; Bassi, G.; Zanetti, T.; Scheuermann, J.; Neri, D. *Helv. Chim. Acta* **2019**, *102*, e1900033.

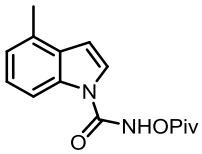
# 7. Analytical Data

## Characterization of Substrates



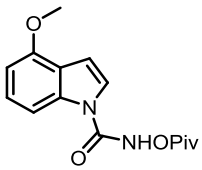

***N*-(pivaloyloxy)-1*H*-indole-1-carboxamide**

**1a**: Pale yellow solid (58% yield, eluent = PE/EtOAc (10/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.85 (s, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.56 (d, *J* = 7.7 Hz, 1H), 7.47 (d, *J* = 3.7 Hz, 1H), 7.36 – 7.30 (m, 1H), 7.29 – 7.23 (m, 1H), 6.61 (d, *J* = 3.7 Hz, 1H), 1.37 (s, 9H).



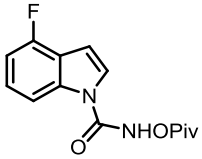

**4-methyl-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide**

**1b**: Yellow solid (54% yield, eluent = PE/EtOAc (10/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.96 (d, *J* = 8.0 Hz, 1H), 7.48 (d, *J* = 3.8 Hz, 1H), 7.29 – 7.20 (m, 1H), 7.07 (d, *J* = 7.3, 1H), 6.69 (d, *J* = 3.7, 1H), 2.52 (s, 3H), 1.38 (s, 9H).



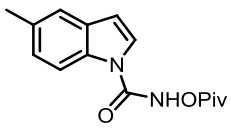

**4-methoxy-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide**

**1c**: White solid (56% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 8.90 (s, 1H), 7.73 (d, *J* = 8.4, 1H), 7.39 (d, *J* = 3.8 Hz, 1H), 7.29 – 7.25 (m, 1H), 6.80 (d, *J* = 3.7 Hz, 1H), 6.70 (d, *J* = 8.0 Hz, 1H), 3.95 (s, 3H), 1.38 (s, 9H).



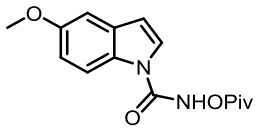

**4-fluoro-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide**

**1d**: Yellow oil (55% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 8.99 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 1H), 7.44 (d, *J* = 3.7 Hz, 1H), 7.33 – 7.18 (m, 1H), 6.94 (t, *J* = 10.0 Hz, 1H), 6.76 – 6.73 (m, 1H), 1.38 (s, 9H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 177.7, 155.9 (d, *J* = 248.4 Hz), 152.2, 137.2 (d, *J* = 9.5 Hz), 125.7 (d, *J* = 7.4 Hz), 123.4, 119.0 (d, *J* = 22.6 Hz), 110.9 (d, *J* = 3.8 Hz), 108.6 (d, *J* = 18.7 Hz), 104.7, 38.5, 27.0. $^{19}$F NMR (470 MHz, Chloroform-*d*) δ -121.3. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{14}FN_2O_3$ 277.0994; Found 277.0989.



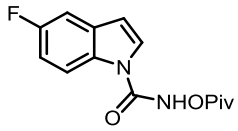

**5-methyl-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide**

**1e**: White solid (58% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.01 (d, *J* = 8.5 Hz, 1H), 7.44 (d, *J* = 3.7 Hz, 1H), 7.36 (s, 1H), 7.15 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.57 (d, *J* = 3.7, 1H), 2.44 (s, 3H), 1.38 (s, 9H).



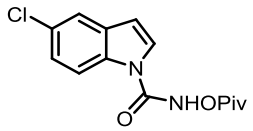

**5-methoxy-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide**

**1f**: White solid (56% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.03 (d, *J* = 9.0 Hz, 1H), 7.44 (d, *J* = 3.7 Hz, 1H), 7.03 (d, *J* = 2.5 Hz, 1H), 6.94 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.57 (d, *J* = 3.6 Hz, 1H), 3.85 (s, 3H), 1.37 (s, 9H).



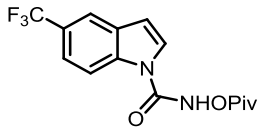

**5-fluoro-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide**

**1g**: White solid (55% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.90 (s, 1H), 8.12 (dd, *J* = 9.0, 4.5 Hz, 1H), 7.49 (d, *J* = 3.8 Hz, 1H), 7.23 (dd, *J* = 8.7, 2.6 Hz, 1H), 7.07 (td, *J* = 9.1, 2.6 Hz, 1H), 6.62 (d, *J* = 3.7, 1H), 1.38 (s, 9H).



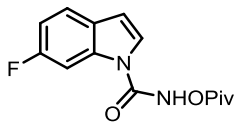

**5-chloro-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide**

**1h**: White solid (57% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.92 (s, 1H), 8.08 (d, *J* = 8.0 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 7.47 (d, *J* = 3.8 Hz, 1H), 7.29 (dd, *J* = 8.8, 2.1 Hz, 1H), 6.59 (d, *J* = 3.8, 1H), 1.38 (s, 9H).




***N*-(pivaloyloxy)-5-(trifluoromethyl)-1*H*-indole-1-carboxamide**

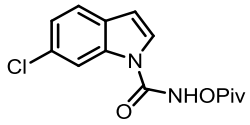
**1i**: White solid (52% yield, eluent = PE/ EtOAc (10/1), mp: 78-80 °C); $^1$H NMR (400 MHz, Chloroform-*d*) δ 9.02 (s, 1H), 8.26 (d, *J* = 8.0, 1H), 7.84 (s, 1H), 7.57 (dd, *J* = 8.8, 1.8 Hz, 1H), 7.54 (d, *J* = 3.7 Hz, 1H), 6.70 (d, *J* = 3.8, 1H), 1.38 (s, 9H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 177.8, 152.0, 136.8, 129.6, 125.7 (q, *J* = 32.5 Hz) 124.9, 124.5 (q, *J* = 270.0 Hz), 121.7 (q, *J* = 3.7 Hz), 118.7 (q, *J* = 4.1 Hz), 115.3, 109.1, 38.5, 27.0. $^{19}$F NMR (375 MHz, Chloroform-*d*) δ -61.07. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{14}F_3N_2O_3$ 327.0962; Found 327.0955.




**6-fluoro-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide**

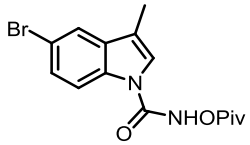
**1j**: White solid (55% yield, eluent = PE/ EtOAc (10/1), mp: 66-68 °C); $^1$H NMR (500 MHz, Chloroform-*d*) δ 8.88 (s, 1H), 7.93 (dd, *J* = 10.0, 2.4 Hz, 1H), 7.50 (dd, *J* = 8.5, 5.3 Hz, 1H), 7.42

(d, *J* = 3.7 Hz, 1H), 7.02 (td, *J* = 8.9, 2.4 Hz, 1H), 6.64 (d, *J* = 3.8, 1H), 1.38 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 177.8, 161.1 (d, *J* = 241.2 Hz), 152.1, 135.5 (d, *J* = 12.6 Hz), 126.1, 123.4 (d, *J* = 4.1 Hz), 121.7 (d, *J* = 10.0 Hz), 111.6 (d, *J* = 24.5 Hz), 108.8, 102.5 (d, *J* = 28.8 Hz), 38.4, 26.9. $^{19}$F NMR (470 MHz, Chloroform-*d*) δ -116.5. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{14}H_{14}FN_2O_3$ 277.0994; Found 277.0988.



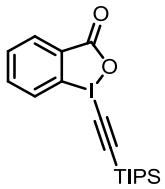

**6-chloro-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide**

**1k**: White solid (56% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.21 (d, *J* = 1.9 Hz, 1H), 7.47 (d, *J* = 8.4 Hz, 1H), 7.42 (d, *J* = 3.7 Hz, 1H), 7.23 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.62 (dd, *J* = 3.7, 0.8 Hz, 1H), 1.38 (s, 9H).



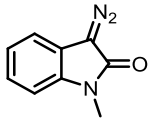

**5-bromo-3-methyl-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide**

**1l**: White solid (55% yield, eluent = PE/ EtOAc (10/1), mp: 93-95 °C); $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.90 (s, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 1.9 Hz, 1H), 7.40 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.18 (d, *J* = 1.5 Hz, 1H), 2.21 (s, 3H), 1.37 (s, 9H). $^{13}$C NMR (100 MHz, Chloroform-d) δ 177.9, 152.0, 134.2, 132.6, 127.7, 122.0, 121.1, 117.8, 116.5, 116.4, 38.4, 27.0, 9.5. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{15}H_{16}BrN_2O_3$ 351.0350; Found 351.0343.



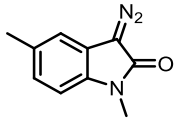

**1-((triisopropylsilyl)ethynyl)-1λ$^3$-benzo[*d*][1,2]iodaoxol-3(1*H*)-one**

**2**: White solid (90% yield); $^1$H NMR (400 MHz, Chloroform-*d*) δ 8.43 – 8.37 (m, 1H), 8.32 – 8.24 (m, 1H), 7.80 – 7.69 (m, 2H), 1.19 – 1.10 (m, 21H).



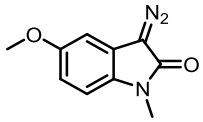

**3-diazo-1-methylindolin-2-one**

**4a**: Red solid (85% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.22 – 7.16 (m, 2H), 7.11 – 7.04 (m, 1H), 6.94 – 6.87 (m, 1H), 3.31 (s, 3H).



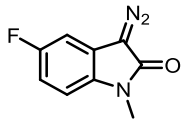

**3-diazo-1,5-dimethylindolin-2-one**

**4b**: Light red solid (87% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.01 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 1H), 6.91 (dd, *J* = 7.6, 1.6, 1H), 3.59 (s, 3H), 2.59 (s, 3H).



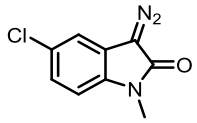
**3-diazo-5-methoxy-1-methylindolin-2-one**

**4c**: Red solid (84% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 6.94 – 6.59 (m, 3H), 3.80 (s, 3H), 3.28 (s, 3H).



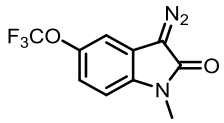
**3-diazo-5-fluoro-1-methylindolin-2-one**

**4d**: Orange solid (88% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 6.97 – 6.87 (m, 2H), 6.82 (dd, *J* = 8.5, 4.2 Hz, 1H), 3.32 (s, 3H).



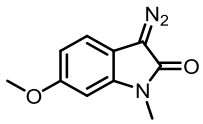
**5-chloro-3-diazo-1-methylindolin-2-one**

**4e**: Red solid (86% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.20 – 7.14 (m, 2H), 6.82 (d, *J* = 8.2, 1H), 3.31 (s, 3H).



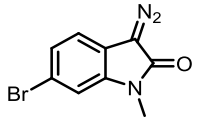
**3-diazo-1-methyl-5-(trifluoromethoxy)indolin-2-one**

**4f**: Orange solid (84% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.12 – 7.00 (m, 2H), 6.88 (d, *J* = 8.4, 1H), 3.32 (s, 3H).



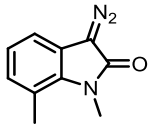
**3-diazo-6-methoxy-1-methylindolin-2-one**

**4g**: Red solid (86% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.06 (d, *J* = 8.3 Hz, 1H), 6.63 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.51 (d, *J* = 2.2 Hz, 1H), 3.83 (s, 3H), 3.29 (s, 3H).



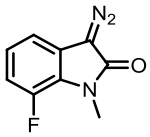
**6-bromo-3-diazo-1-methylindolin-2-one**

**4h**: Orange solid (86% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.21 (dd, *J* = 8.1, 1.7 Hz, 1H), 7.07 – 7.02 (m, 2H), 3.30 (s, 3H).



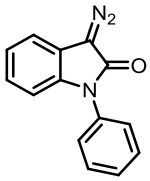
**3-diazo-1,7-dimethylindolin-2-one**

**4i**: Dark yellow solid (87% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.04 – 6.97 (m, 2H), 6.80 (d, *J* = 7.9 Hz, 1H), 3.30 (s, 3H), 2.36 (s, 3H).



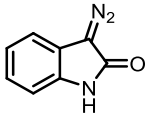
**3-diazo-7-fluoro-1-methylindolin-2-one**

**4j**: Dark yellow solid (88% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.09 – 6.74 (m, 3H), 3.53 (d, *J* = 2.5 Hz, 3H).



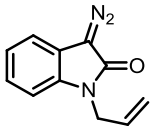
**3-diazo-1-phenylindolin-2-one**

**4k**: Red solid (89% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 7.60 – 7.50 (m, 2H), 7.48 – 7.39 (m, 3H), 7.30 – 7.23 (m, 1H), 7.17 – 7.10 (m, 2H), 6.98 – 6.87 (m, 1H).



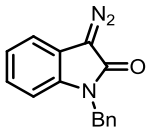
**3-diazoindolin-2-one**

**4l**: Pale red solid (82% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 10.68 (s, 1H), 7.40 (d, *J* = 7.6, 1H), 7.09 (td, *J* = 7.7, 1.3 Hz, 1H), 6.99 (td, *J* = 7.6, 1.1 Hz, 1H), 6.91 (d, *J* = 7.7 Hz, 1H).



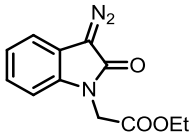
**1-allyl-3-diazoindolin-2-one**

**4m**: Pale red solid (81% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (400 MHz, $CDCl_3$) δ 7.22 (t, *J* = 5.7 Hz, 1H), 7.18 (d, *J* = 7.7 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.88 (ddd, *J* = 22.1, 10.5, 5.3 Hz, 1H), 5.23 (dd, *J* = 13.6, 6.1 Hz, 2H), 4.47 (d, *J* = 5.2 Hz, 2H).



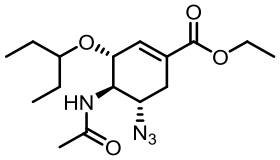
**1-benzyl-3-diazoindolin-2-one**

**4n**: Pale red solid (79% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.36 – 7.32 (m, 4H), 7.31 – 7.27 (m, 1H), 7.25 – 7.22 (m, 1H), 7.13 (td, *J* = 7.6, 1.6 Hz, 1H), 7.09 (td, *J* = 7.5, 1.4 Hz, 1H), 6.93 – 6.70 (m, 1H), 5.06 (s, 2H).



**methyl 2-(3-diazo-2-oxoindolin-1-yl)acetate**

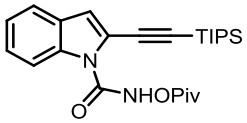
**4o**: Pale red solid (80% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.25 (d, *J* = 7.6 Hz, 1H), 7.21 (dd, *J* = 7.7, 6.9 Hz, 1H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 4.60 (s, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).




**Ethyl (3*R*,4*R*,5*S*)-4-acetamido-5-azido-3-(pentan-3-yloxy)cyclohex-1-ene-1-carboxylate**

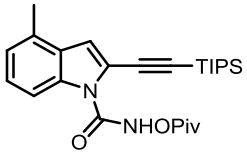
**7a**: White solid (72% yield, eluent = DCM/ MeOH (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 6.82 (t, *J* = 2.5 Hz, 1H), 5.80 (d, *J* = 7.4 Hz, 1H), 4.65 – 4.60 (m, 1H), 4.36 (td, *J* = 10.8, 5.8 Hz, 1H), 4.29 – 4.19 (m, 2H), 3.39 – 3.33 (m, 1H), 3.33 – 3.27 (m, 1H), 2.89 (dd, *J* = 17.7, 5.8, 1H), 2.30 – 2.21 (m, 1H), 2.07 (s, 3H), 1.61 – 1.46 (m, 4H), 1.32 (t, *J* = 7.1 Hz, 3H), 0.96 – 0.90(m, 6H).

## Characterization of products



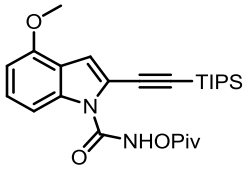

**N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

**3a**: Yellow oil (82% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 10.55 (s, 1H), 8.36 (dd, *J* = 8.5, 1.0 Hz, 1H), 7.52 (dt, *J* = 7.7, 1.0 Hz, 1H), 7.38 (ddd, *J* = 8.5, 7.2, 1.3 Hz, 1H), 7.26 (td, *J* = 7.4, 1.0 Hz, 1H), 7.03 (s, 1H), 1.38 (s, 9H), 1.21 – 1.09 (m, 21H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 176.5, 151.9, 136.8, 128.0, 126.5, 123.7, 120.7, 118.2, 116.9, 116.3, 102.8, 98.2, 38.2, 26.9, 18.5, 11.1. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{25}H_{35}N_2O_3Si$ 439.2422; Found 439.2416.




**4-methyl-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

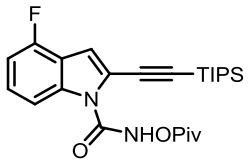
**3b**: Yellow oil (74% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 10.55 (s, 1H), 8.18 (d, *J* = 8.9 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.08 – 7.04 (m, 2H), 2.50 (s, 3H), 1.38 (s, 9H), 1.23 – 1.09 (m, 21H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 176.5, 151.9, 136.7, 130.2, 127.7, 126.6, 124.0, 116.8, 116.3, 113.8, 102.5, 98.4, 38.2, 26.9, 18.5, 18.3, 11.1. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{26}H_{37}N_2O_3Si$ 453.2579; Found 453.2575.




**4-methoxy-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

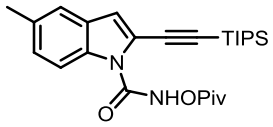
**3c**: Yellow oil (81% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 10.56 (s, 1H), 7.93 (d, *J* = 8.5 Hz, 1H), 7.29 (t, *J* = 8.2 Hz, 1H), 7.16 (d, *J* = 0.7 Hz, 1H), 6.65 (d, *J*

= 8.0 Hz, 1H), 3.91 (s, 3H), 1.37 (s, 9H), 1.21 – 1.08 (m, 21H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 176.4, 152.5, 151.9, 137.9, 127.6, 118.7, 115.6, 115.5, 109.2, 103.5, 102.2, 98.4, 55.3, 38.2, 26.9, 18.5, 11.1. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{26}H_{37}N_2O_4Si$ 469.2528; Found 469.2524.



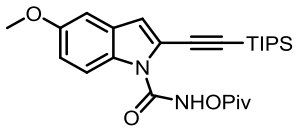

**4-fluoro-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

**3d**: Yellow oil (72% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 10.54 (s, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.30 (td, *J* = 8.3, 5.5 Hz, 1H), 7.11 (d, *J* = 0.8 Hz, 1H), 6.93 (dd, *J* = 9.4, 8.0 Hz, 1H), 1.37 (s, 9H), 1.21 – 1.11 (m, 21H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 176.4, 155.1 (d, *J* = 249.8 Hz), 151.6, 138.4 (d, *J* = 8.7 Hz), 127.2 (d, *J* = 7.2 Hz), 117.4 (d, *J* = 22.2 Hz), 117.1, 113.4, 112.4 (d, *J* = 3.9 Hz), 108.7 (d, *J* = 18.0 Hz), 103.3, 97.6, 38.2, 26.9, 18.5, 11.1. $^{19}$F NMR (470 MHz, Chloroform-*d*) δ -121.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{36}FN_2O_3Si$ 459.2474; Found 459.2485.



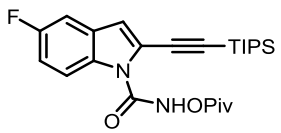

**5-methyl-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

**3e**: Yellow oil (72% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 10.50 (s, 1H), 8.22 (d, *J* = 8.6 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.19 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.95 (d, *J* = 0.8 Hz, 1H), 2.42 (s, 3H), 1.37 (s, 9H), 1.25 – 1.09 (m, 21H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 176.5, 151.9, 135.1, 133.3, 128.2, 128.0, 120.4, 118.0, 116.9, 116.0, 102.6, 98.4, 38.2, 27.0, 21.2, 18.5, 11.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{39}N_2O_3Si$ 455.2724; Found 455.2732.




**5-methoxy-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

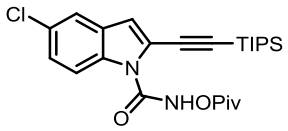
**3f**: Yellow oil (77% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (400 MHz, Chloroform-*d*) δ 10.52 (s, 1H), 8.25 (d, *J* = 9.1 Hz, 1H), 6.99 (dd, *J* = 9.2, 2.6 Hz, 1H), 6.95 (s, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 3.83 (s, 3H), 1.37 (s, 9H), 1.23 – 0.96 (m, 21H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 176.5, 156.4, 151.9, 131.5, 128.8, 117.9, 117.3, 117.2, 115.7, 102.8, 102.4, 98.3, 55.5, 38.2, 26.9, 18.5, 11.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{39}N_2O_4Si$ 471.2674; Found 471.2667.




**5-fluoro-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

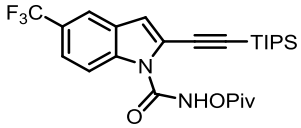
**3g**: Yellow oil (70% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 10.52 (s, 1H), 8.32 (dd, *J* = 9.2, 4.6 Hz, 1H), 7.16 (dd, *J* = 8.4, 2.6 Hz, 1H), 7.09 (td, *J* = 9.1, 2.6 Hz, 1H), 6.98 (s, 1H), 1.37 (s, 9H), 1.21 – 1.09 (m, 21H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ

176.5, 159.6 (d, *J* = 240.6 Hz), 151.6, 133.1, 128.8 (d, *J* = 10.4 Hz), 118.4, 117.5, 117.5 (d, *J* = 14.1 Hz), 114.4 (d, *J* = 25.3 Hz), 105.8 (d, *J* = 23.8 Hz), 103.6, 97.7, 38.2, 26.9, 18.5, 11.1. $^{19}$F NMR (470 MHz, Chloroform-*d*) δ -121.2. HRMS (ESI) m/z: $[M-H]^-$ Calcd for $C_{25}H_{34}FN_2O_3Si$ 457.2328; Found 457.2329.



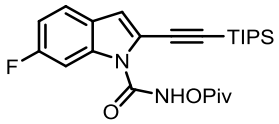

**5-chloro-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

**3h**: Yellow oil (74% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 10.52 (s, 1H), 8.28 (d, *J* = 9.0 Hz, 1H), 7.47 (d, *J* = 2.2 Hz, 1H), 7.31 (dd, *J* = 9.0, 2.1 Hz, 1H), 6.95 (d, *J* = 0.7 Hz, 1H), 1.37 (s, 9H), 1.19 – 1.10 (m, 21H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 176.4, 151.5, 135.0, 129.3, 129.1, 126.6, 120.0, 118.2, 117.4, 117.0, 103.7, 97.6, 38.2, 26.9, 18.5, 11.1. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{35}ClN_2NaO_3Si$ 497.1998; Found 497.1990.



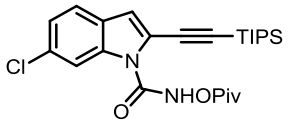

**N-(pivaloyloxy)-5-(trifluoromethyl)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

**3i**: Yellow oil (70% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 10.55 (s, 1H), 8.46 (d, *J* = 8.9 Hz, 1H), 7.81 (s, 1H), 7.60 (dd, *J* = 8.9, 1.8 Hz, 1H), 7.07 (s, 1H), 1.38 (s, 9H), 1.25 – 1.07 (m, 21H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 176.4, 151.3, 138.2, 127.6, 126.1 (q, *J* = 32.5 Hz), 124.4 (q, *J* = 271.9 Hz), 122.9 (q, *J* = 3.7 Hz), 118.8, 118.1 (q, *J* = 4.1 Hz), 117.7, 116.7, 104.2, 97.3, 38.3, 26.9, 18.5, 11.1. $^{19}$F NMR (470 MHz, Chloroform-*d*) δ -61.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{36}F_3N_2O_3Si$ 509.2442; Found 509.2456.




**6-fluoro-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

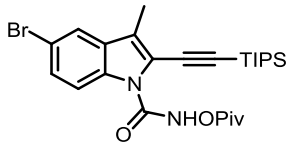
**3j**: Yellow oil (60% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 10.54 (s, 1H), 8.11 (dd, *J* = 10.6, 2.4 Hz, 1H), 7.44 (dd, *J* = 8.7, 5.5 Hz, 1H), 7.02 (td, *J* = 8.9, 2.4 Hz, 1H), 6.99 (d, *J* = 0.8 Hz, 1H), 1.37 (s, 9H), 1.22 – 1.08 (m, 21H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 176.5, 162.2 (d, *J* = 243.3 Hz), 151.7, 137.0 (d, *J* = 13.3 Hz), 124.3, 121.4 (d, *J* = 9.8 Hz), 117.8, 117.4 (d, *J* = 4.5 Hz), 112.4 (d, *J* = 24.8 Hz), 103.7 (d, *J* = 29.4 Hz), 103.0, 97.9, 38.3, 26.9, 18.5, 11.1. $^{19}$F NMR (470 MHz, Chloroform-*d*) δ -113.7. HRMS (ESI) m/z: $[M+Na]^+$ Calcd for $C_{25}H_{35}FN_2NaO_3Si$ 481.2293; Found 481.2304.




**6-chloro-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

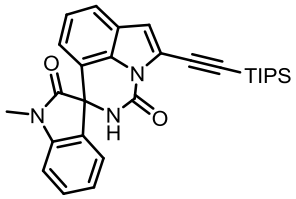
**3k**: Yellow oil (84% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 10.52 (s, 1H), 8.42 (d, *J* = 1.8 Hz, 1H), 7.41 (d, *J* = 8.4 Hz, 1H), 7.23 (dd, *J* = 8.4, 1.9 Hz, 1H), 6.98 (d, *J* = 0.8 Hz, 1H), 1.37 (s, 9H), 1.20 – 1.10 (m, 21H). $^{13}$C NMR (125 MHz, Chloroform-*d*)

δ 176.4, 151.5, 137.0, 132.6, 126.4, 124.5, 121.3, 117.7, 117.6, 116.5, 103.5, 97.7, 38.2, 26.9, 18.5, 11.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{25}H_{36}ClN_2O_3Si$ 475.2178; Found 475.2175.



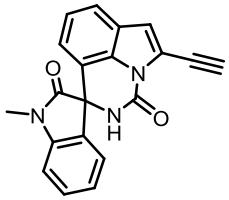

**5-bromo-3-methyl-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide**

**3l**: Yellow oil (84% yield, eluent = PE/ EtOAc (10/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 10.54 (s, 1H), 8.23 (d, *J* = 8.9 Hz, 1H), 7.61 (d, *J* = 2.0 Hz, 1H), 7.45 (dd, *J* = 9.0, 2.0 Hz, 1H), 2.35 (s, 3H), 1.36 (s, 9H), 1.24 – 1.09 (m, 21H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 176.5, 151.7, 135.0, 130.6, 129.4, 126.6, 121.7, 117.8, 116.7, 115.8, 106.5, 97.2, 38.2, 26.9, 18.5, 11.1, 9.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{38}BrN_2O_3Si$ 533.1830; Found 533.1841.



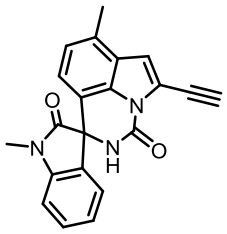

**1-methyl-5'-((triisopropylsilyl)ethynyl)spiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**5aa**: White solid (91% yield, eluent = PE/ EtOAc (2/1), mp: >200 °C); $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.40 (m, 2H), 7.29 – 7.25 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 7.05 (t, *J* = 7.7 Hz, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.45 (d, *J* = 7.4 Hz, 1H), 5.34 (s, 1H), 3.23 (s, 3H), 1.19 – 1.16 (m, 21H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 174.9, 147.7, 143.5, 133.1, 130.8, 130.3, 126.8, 125.3, 124.0, 124.0, 120.6, 120.2, 118.9, 117.2, 115.3, 108.7, 99.8, 96.7, 66.0, 26.7, 18.6, 11.3. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{29}H_{33}O_2N_3Si$ 483.1398; Found 483.1411.



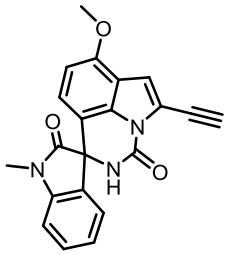

**5'-ethynyl-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6aa**: White solid (81% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.49 – 7.40 (m, 2H), 7.30 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.16 – 7.05 (m, 2H), 6.98 (s, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.50 (d, *J* = 9.0 Hz, 1H), 5.61 (s, 1H), 3.58 (s, 1H), 3.23 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 174.8, 148.0, 143.6, 133.3, 130.9, 129.9, 126.5, 125.4, 124.2, 124.0, 120.9, 119.4, 118.8, 117.3, 116.1, 108.7, 84.5, 74.6, 65.9, 26.7. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{13}O_2N_3$ 327.1002; Found 327.1010.



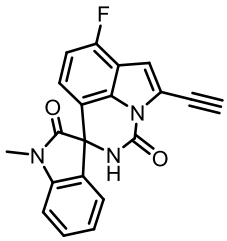
**5'-ethynyl-1,7'-dimethylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6ba**: White solid (86% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.42 (td, *J* = 7.8, 1.3 Hz, 1H), 7.29 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.12 (td, *J* = 7.6, 1.0 Hz, 1H), 7.00 (s, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 6.87 (dd, *J* = 7.5, 1.0 Hz, 1H), 6.40 (d, *J* = 7.6 Hz, 1H), 5.51 (s, 1H), 3.58 (s, 1H), 3.23 (s, 3H), 2.46 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 174.9, 148.2, 143.6, 133.1, 131.2, 130.8, 130.0, 126.3, 125.3, 124.4, 123.9, 119.5, 118.2, 115.0, 114.7, 108.7, 84.3, 74.7, 65.8, 26.7, 18.2. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{15}O_2N_3$ 341.1159; Found 341.1155.



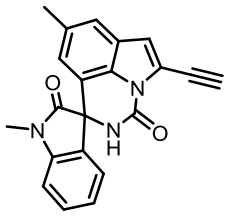
**5'-ethynyl-7'-methoxy-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6ca**: White solid (88% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.43 (td, *J* = 7.8, 1.4 Hz, 1H), 7.30 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.13 (td, *J* = 7.6, 0.9 Hz, 1H), 7.05 (s, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.51 – 6.37 (m, 2H), 5.44 (s, 1H), 3.88 (s, 3H), 3.55 (s, 1H), 3.22 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 175.0, 153.2, 148.2, 143.6, 134.7, 130.8, 130.0, 125.4, 123.9, 120.8, 117.3, 116.7, 113.9, 110.0, 108.7, 104.4, 83.9, 74.7, 65.6, 55.7, 26.7. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{15}O_3N_3$ 357.1108; Found 357.1106.



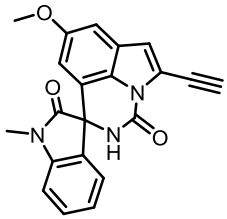
**5'-ethynyl-7'-fluoro-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6da**: White solid (98% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 8.60 (s, 1H), 7.46 (td, *J* = 7.8, 1.3 Hz, 1H), 7.33 (d, *J* = 5.0 Hz, 1H), 7.23 (s, 1H), 7.20 (d, *J* = 7.8 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.94 (dd, *J* = 10.3, 8.1 Hz, 1H), 6.46 (dd, *J* = 8.2, 4.1 Hz, 1H), 4.79 (s, 1H), 3.18 (s, 3H). $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 174.7, 154.0 (d, *J* = 249.8 Hz), 147.2, 143.4, 134.9 (d, *J* = 11.5 Hz), 130.7, 130.4, 124.8, 123.5, 120.6 (d, *J* = 7.6 Hz), 118.5, 114.5 (d, *J* = 4.0 Hz), 114.2 (d, *J* = 23.4 Hz), 110.7, 109.5 (d, *J* = 20.0 Hz), 109.4, 88.2, 74.4, 64.9, 26.5. $^{19}$F NMR (470 MHz, DMSO-$d_6$) δ -120.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{12}O_2N_3F$ 345.0908; Found 345.0908.



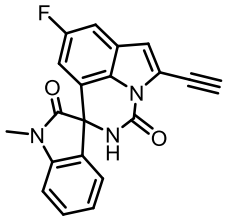
**5'-ethynyl-1,8'-dimethylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6ea**: White solid (86% yield, eluent = PE/ EtOAc (2/1) mp: >200 ºC); $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 8.41 (s, 1H), 7.45 (td, *J* = 7.7, 1.3 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.19 (d, *J* = 7.9 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.06 (s, 1H), 6.28 (d, *J* = 1.3 Hz, 1H), 4.71 (s, 1H), 3.18 (s, 3H), 2.23 (s, 3H). $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 174.8, 147.4, 143.5, 133.5, 131.3, 131.0, 130.2, 125.9, 124.7, 123.4, 120.2, 120.1, 118.0, 117.6, 114.9, 109.3, 87.6, 75.0, 65.2, 26.5, 21.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{15}O_2N_3$ 341.1159; Found 341.1159.



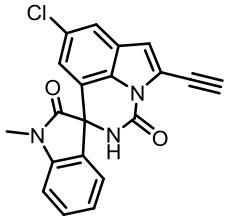
**5'-ethynyl-8'-methoxy-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6fa**: White solid (87% yield, eluent = PE/ EtOAc (2/1) mp: >200 ºC); $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 8.42 (s, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.30 (d, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 7.06 (s, 2H), 6.00 (d, *J* = 2.1 Hz, 1H), 4.72 (s, 1H), 3.67 (s, 3H), 3.18 (s, 3H). $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 174.6, 156.9, 147.4, 143.4, 130.7, 130.3, 127.7, 126.2, 124.6, 123.4, 118.8, 118.2, 115.1, 109.3, 108.9, 102.3, 87.8, 75.0, 65.2, 55.6, 26.5. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{15}O_3N_3$ 357.1108; Found 357.1109.



**5'-ethynyl-8'-fluoro-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

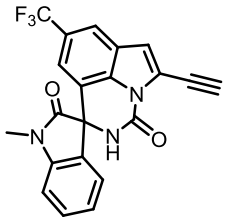
**6ga**: White solid (96% yield, eluent = PE/ EtOAc (2/1) mp: >200 ºC); $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.44 (td, *J* = 7.8, 1.2 Hz, 1H), 7.30 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.17 – 7.07 (m, 2H), 6.96 (d, *J* = 7.9 Hz, 1H), 6.93 (s, 1H), 6.25 (dd, *J* = 9.1, 2.1 Hz, 1H), 5.91 (s, 1H), 3.61 (s, 1H), 3.24 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 174.4, 160.3 (d, *J* = 240.7 Hz), 147.9, 143.5, 131.1, 129.8, 129.3 (d, *J* = 3.8 Hz), 127.1(d, *J* = 10.0 Hz), 125.3, 124.1, 120.2, 118.3(d, *J* = 10.0 Hz), 115.7 (d, *J* = 4.4 Hz), 108.9, 107.9 (d, *J* = 28.5 Hz), 106.6 (d, *J* = 25.2 Hz), 85.2, 74.2, 49.9, 26.8. $^{19}$F NMR (470 MHz, Chloroform-*d*) δ -117.7. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{12}O_2N_3F$ 345.0908; Found 345.0908.



**8'-chloro-5'-ethynyl-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

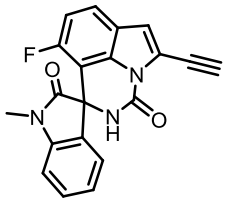
**6ha**: White solid (96% yield, eluent = PE/ EtOAc (2/1) mp: >200 ºC); $^{1}$H NMR (500 MHz,

DMSO-$d_6$) δ 8.60 (s, 1H), 7.62 (d, *J* = 1.7 Hz, 1H), 7.48 (td, *J* = 7.8, 1.2 Hz, 1H), 7.35 (d, *J* = 8.2 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.16 – 7.10 (m, 2H), 6.47 (d, *J* = 1.8 Hz, 1H), 4.81 (s, 1H), 3.19 (s, 3H). $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 204.3, 177.0, 173.5, 161.5, 160.5, 160.4, 158.4, 156.9, 154.8, 153.6, 150.1, 149.6, 149.4, 148.9, 144.5, 139.6, 118.7, 104.5, 95.0, 56.6. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{12}O_2N_3Cl$ 361.0613; Found 361.0613.



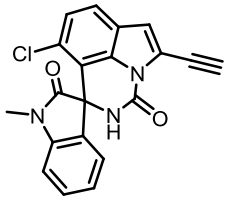
**5'-ethynyl-1-methyl-8'-(trifluoromethyl)spiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6ia**: White solid (94% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.78 (s, 1H), 7.47 (td, *J* = 7.8, 1.3 Hz, 1H), 7.31 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.16 (td, *J* = 7.5, 0.9 Hz, 1H), 7.04 (s, 1H), 7.00 (d, *J* = 7.8 Hz, 1H), 6.69 (s, 1H), 5.81 (s, 1H), 3.61 (s, 1H), 3.25 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 174.3, 147.6, 143.7, 135.0, 131.4, 128.8, 127.0 (q, *J* = 32.4 Hz), 126.2, 125.5, 124.3, 124.1 (q, *J* = 272.1 Hz), 120.7, 118.7 (q, *J* = 4.4 Hz), 118.2, 116.2 (q, *J* = 3.5 Hz), 115.9, 109.1, 85.7, 73.9, 65.7, 26.9. $^{19}$F NMR (470 MHz, Chloroform-*d*) δ -60.8. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{12}O_2N_3F_3$ 395.0876; Found 395.0881.



**5'-ethynyl-9'-fluoro-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

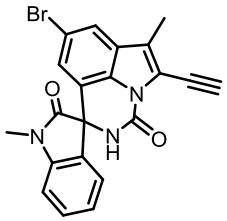
**6ja**: White solid (70% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.44 – 7.38 (m, 2H), 7.27 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.09 (td, *J* = 7.6, 1.0 Hz, 1H), 6.96 (s, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.85 (dd, *J* = 10.8, 8.6 Hz, 1H), 5.47 (s, 1H), 3.59 (s, 1H), 3.30 (s, 3H). $^{13}$C NMR (100 MHz, Chloroform-*d*) δ 173.2, 155.9 (d, *J* = 248.1 Hz), 147.1, 143.0, 134.0 (d, *J* = 8.4 Hz), 130.9, 129.5, 124.8, 123.9, 122.7, 122.2 (d, *J* = 9.3 Hz), 119.3 (d, *J* = 4.5 Hz), 115.8, 112.9 (d, *J* = 23.1 Hz), 108.9, 104.4 (d, *J* = 18.4 Hz), 84.7, 74.3, 63.7, 26.9. $^{19}$F NMR (470 MHz, Chloroform-*d*) δ -122.1. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{12}O_2N_3F$ 345.0908; Found 345.0910.



**9'-chloro-5'-ethynyl-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'H)-dione**

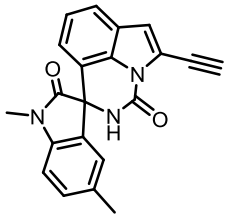
**6ka**: White solid (59% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.46 – 7.37 (m, 2H), 7.18 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 1H), 7.08 (td, *J* = 7.5, 0.9 Hz, 1H), 6.97 (s, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 5.41 (s, 1H), 3.61 (s, 1H), 3.31 (s,

3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 172.6, 146.6, 143.7, 134.5, 130.9, 129.2, 126.8, 126.2, 125.2, 125.0, 123.9, 121.9, 119.1, 115.7, 114.7, 108.8, 85.1, 74.1, 65.7, 26.8. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{12}O_2N_3Cl$ 361.0613; Found 361.0613.



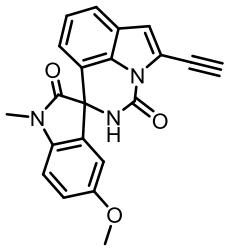

**8'-bromo-5'-ethynyl-1,6'-dimethylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6la**: White solid (82% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^1$H NMR (500 MHz, DMSO-$d_6$) δ 8.48 (s, 1H), 7.80 (s, 1H), 7.47 (t, *J* = 7.7 Hz, 1H), 7.32 (d, *J* = 7.4 Hz, 1H), 7.20 (d, *J* = 7.9 Hz, 1H), 7.12 (t, *J* = 7.5 Hz, 1H), 6.57 (s, 1H), 4.93 (s, 1H), 3.19 (s, 3H), 2.33 (s, 3H). $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 174.3, 146.9, 143.5, 131.3, 130.5, 128.2, 124.8, 124.1, 123.5, 121.9, 121.4, 119.9, 116.6, 115.9, 109.5, 91.1, 73.8, 64.7, 26.6, 9.3. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{14}O_2N_3Br$ 419.0264; Found 419.0263.




**5'-ethynyl-1,5-dimethylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

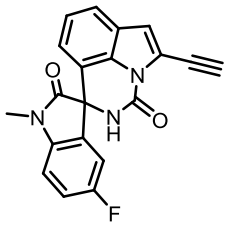
**6ab**: White solid (96% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.9 Hz, 1H), 7.14 (t, *J* = 8.2 Hz, 2H), 7.09 (t, *J* = 7.7 Hz, 1H), 7.02 – 6.95 (m, 2H), 6.52 (d, *J* = 7.5 Hz, 1H), 5.49 (s, 1H), 3.58 (s, 1H), 3.50 (s, 3H), 2.64 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 175.5, 148.0, 141.2, 134.5, 133.3, 130.7, 126.5, 124.2, 123.9, 123.4, 120.8, 120.4, 119.4, 118.8, 117.7, 116.1, 84.5, 74.6, 65.5, 30.1, 19.0. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{15}O_2N_3$ 341.1159; Found 341.1161.




**5'-ethynyl-5-methoxy-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

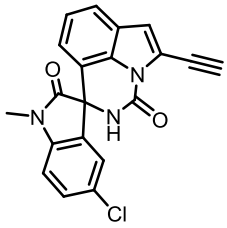
**6ac**: White solid (87% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.98 (s, 1H), 6.94 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.90 (d, *J* = 2.5 Hz, 1H), 6.86 (d, *J* = 8.5 Hz, 1H), 6.52 (dd, *J* = 7.5, 0.8 Hz, 1H), 5.69 (s, 1H), 3.70 (s, 3H), 3.57 (s, 1H), 3.20 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 174.6, 156.9, 148.0, 136.7, 133.3, 131.1, 126.5, 124.3, 120.8, 119.4, 118.8, 117.4, 116.1, 116.0, 111.6,

109.4, 84.5, 74.6, 66.3, 55.7, 26.8. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{15}O_3N_3$ 357.1108; Found 357.1105.



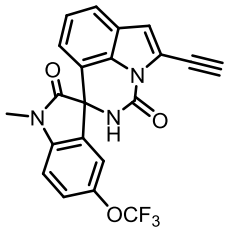
**5'-ethynyl-5-fluoro-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6ad**: White solid (96% yield, eluent = PE/ EtOAc (2/1) mp: >200 ºC); $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.47 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.18 – 7.04 (m, 3H), 6.98 (s, 1H), 6.89 (dd, *J* = 8.5, 4.0 Hz, 1H), 6.50 (dd, *J* = 7.5, 0.8 Hz, 1H), 5.83 (s, 1H), 3.57 (s, 1H), 3.22 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 174.6, 159.7 (d, *J* = 244.1 Hz), 148.0, 139.5, 133.2, 131.4 (d, *J* = 7.6 Hz), 126.6, 124.3, 121.1, 119.2, 118.9, 117.3 (d, *J* = 23.8 Hz), 116.8, 116.2, 113.5 (d, *J* = 25.5 Hz), 109.5 (d, *J* = 8.1 Hz), 84.6, 74.5, 66.0, 26.9. $^{19}$F NMR (470 MHz, Chloroform-*d*) δ -117.8. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{12}O_2N_3F$ 345.0908; Found 345.0909.



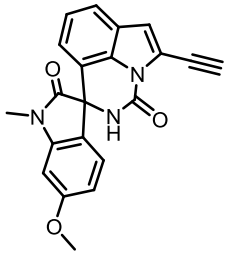
**5-chloro-5'-ethynyl-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6ae**: White solid (96% yield, eluent = PE/ EtOAc (2/1) mp: >200 ºC); $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 7.8 Hz, 1H), 7.39 (dd, *J* = 8.4, 2.1 Hz, 1H), 7.31 (d, *J* = 2.1 Hz, 1H), 7.11 (t, *J* = 7.7 Hz, 1H), 6.98 (s, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.51 (d, *J* = 7.4 Hz, 1H), 5.81 (s, 1H), 3.57 (s, 1H), 3.22 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 174.4, 147.9, 142.0, 133.2, 131.5, 130.8, 129.4, 126.6, 125.9, 124.3, 121.1, 119.3, 118.9, 116.6, 116.2, 109.8, 84.7, 74.5, 65.8, 26.9. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{12}O_2N_3Cl$ 361.0613; Found 361.0617.



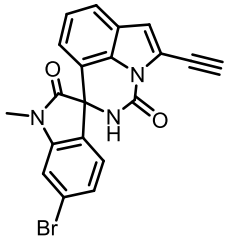
**5'-ethynyl-1-methyl-5-(trifluoromethoxy)spiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6af**: Amorphous (77% yield, eluent = PE/ EtOAc (2/1)); $^1$H NMR (500 MHz, Chloroform-*d*) δ 7.46 (d, *J* = 7.8 Hz, 1H), 7.27 (d, *J* = 6.6 Hz, 1H), 7.20 (d, *J* = 2.3 Hz, 1H), 7.10 (t, *J* = 7.7 Hz, 1H), 6.97 (s, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.48 (d, *J* = 7.4 Hz, 1H), 6.18 (s, 1H), 3.55 (s, 1H), 3.21 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 174.7, 148.0, 145.4, 142.2, 133.1, 131.4, 126.6, 124.4, 123.8, 121.3 (q, *J* = 256.2 Hz), 121.1, 119.2, 118.8, 116.5, 116.2, 109.4, 84.6, 74.4, 65.8, 26.9. $^{19}$F NMR (470 MHz, Chloroform-*d*) δ -58.3. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{14}O_3N_3F_3$ 401.0982; Found 401.0982.



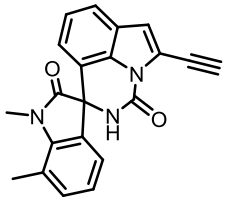
**5'-ethynyl-6-methoxy-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6ag**: White solid (85% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.44 (d, *J* = 7.8 Hz, 1H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.97 (s, 1H), 6.59 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.54 – 6.47 (m, 2H), 5.57 (s, 1H), 3.86 (s, 3H), 3.58 (s, 1H), 3.20 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 175.2, 162.1, 148.1, 145.1, 133.4, 126.5, 126.4, 124.2, 121.6, 120.8, 119.4, 118.8, 117.8, 116.1, 107.5, 96.7, 84.5, 74.6, 65.6, 55.6, 26.7. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{15}O_3N_3$ 357.1108; Found 357.1110.



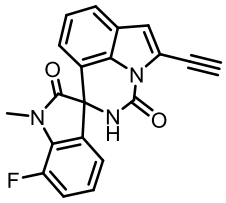
**6-bromo-5'-ethynyl-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6ah**: White solid (75% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 8.45 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.49 (s, 1H), 7.28 (s, 2H), 7.16 – 7.07 (m, 2H), 6.53 (d, *J* = 7.4 Hz, 1H), 4.73 (s, 1H), 3.18 (s, 3H). $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 174.8, 147.3, 145.1, 132.8, 130.3, 126.5, 126.0, 125.8, 124.2, 123.1, 120.6, 119.2, 118.0, 117.3, 115.3, 112.6, 87.8, 74.9, 64.9, 26.7. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{12}O_2N_3Br$ 405.0107; Found 405.0088.



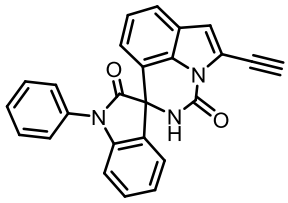
**5'-ethynyl-1,7-dimethylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6ai**: White solid (95% yield, eluent = PE/ EtOAc (2/1) mp: 178-180 °C); $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.45 (dd, *J* = 8.0, 0.8 Hz, 1H), 7.21 (ddd, *J* = 8.1, 1.8, 0.9 Hz, 1H), 7.12 – 7.11 (m, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.98 (s, 1H), 6.84 (d, *J* = 7.9 Hz, 1H), 6.52 (dd, *J* = 7.5, 0.8 Hz, 1H), 5.60 (s, 1H), 3.57 (s, 1H), 3.21 (s, 3H), 2.28 (s, 3H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 174.7, 148.0, 141.1, 133.8, 133.3, 131.1, 130.1, 126.5, 126.0, 124.2, 120.8, 119.4, 118.8, 117.5, 116.1, 108.5, 84.5, 74.6, 66.1, 26.7, 20.9. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{21}H_{15}O_2N_3$ 341.1159; Found 341.1160.



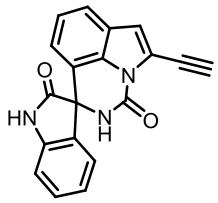
**5'-ethynyl-7-fluoro-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6aj**: White solid (87% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 8.48 (s, 1H), 7.54 (dd, *J* = 7.9, 0.8 Hz, 1H), 7.34 (ddd, *J* = 11.9, 8.4, 1.1 Hz, 1H), 7.23 – 7.02 (m, 4H), 6.61 (dd, *J* = 7.5, 0.8 Hz, 1H), 4.74 (s, 1H), 3.35 (d, *J* = 2.8 Hz, 3H). $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 174.6, 147.5 (d, *J* = 241.2 Hz), 147.2, 134.0, 132.7, 129.9 (d, *J* = 8.4 Hz), 125.8, 124.4 (d, *J* = 6.1 Hz), 124.2, 121.1, 120.7, 119.3, 118.1 (d, *J* = 18.8 Hz), 118.0, 117.4, 115.3, 87.9, 74.9, 65.2, 28.9 (d, *J* = 5.4 Hz). $^{19}$F NMR (470 MHz, DMSO-$d_6$) δ -136.0. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{20}H_{12}O_2N_3F$ 345.0908; Found 345.0909.



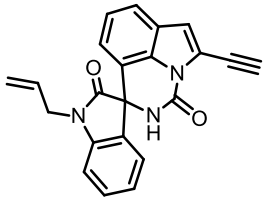
**5'-ethynyl-1-phenylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6ak**: White solid (86% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.54 – 7.49 (m, 2H), 7.48 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.39 – 7.30 (m, 2H), 7.17 – 7.12 (m, 2H), 6.98 (s, 1H), 6.94 (d, *J* = 7.9 Hz, 1H), 6.66 (d, *J* = 7.4 Hz, 1H), 5.95 (s, 1H), 3.56 (s, 1H). $^{13}$C NMR (125 MHz, Chloroform-*d*) δ 174.0, 148.2, 143.5, 133.7, 133.3, 130.7, 129.7, 128.5, 126.7, 126.4, 125.7, 124.5, 124.4, 121.0, 119.3, 118.9, 117.6, 116.2, 110.1, 84.6, 74.6, 66.2. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{25}H_{15}O_2N_3$ 389.1159; Found 389.1160.



**5'-ethynylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

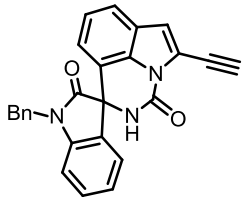
**6al**: White solid (47% yield, eluent = PE/ EtOAc (2/1) mp: >200 °C); $^{1}$H NMR (500 MHz, DMSO-$d_6$) δ 10.64 (s, 1H), 8.53 (s, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.35 (td, *J* = 7.7, 1.3 Hz, 1H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.16 – 7.10 (m, 2H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.47 (d, *J* = 7.4 Hz, 1H), 4.72 (s, 1H). $^{13}$C NMR (125 MHz, DMSO-$d_6$) δ 176.5, 147.5, 142.0, 132.8, 131.6, 130.1, 125.7, 125.1, 124.2, 122.8, 120.3, 118.8, 118.3, 118.0, 115.2, 110.2, 87.7, 75.0, 65.6. HRMS (EI) m/z: $[M]^+$ Calcd for $C_{19}H_{11}O_2N_3$ 313.0846; Found 313.0848.



**1-allyl-5'-ethynylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

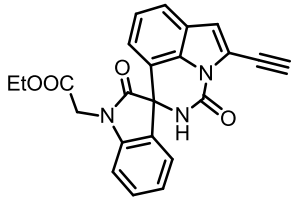
**6am**: White solid (35% yield, eluent = PE/ EtOAc (1/1) mp: >200 °C); $^{1}$H NMR (500 MHz,

$CDCl_3$) δ 7.50 (d, *J* = 7.9 Hz, 1H), 7.43 (t, *J* = 7.8 Hz, 1H), 7.35 (d, *J* = 7.4 Hz, 1H), 7.16 (t, *J* = 5.8 Hz, 1H), 7.13 (t, *J* = 6.0 Hz, 1H), 7.02 (s, 1H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.55 (d, *J* = 7.5 Hz, 1H), 5.89 (ddd, *J* = 22.4, 10.5, 5.4 Hz, 1H), 5.52 (s, 1H), 5.37 – 5.30 (m, 2H), 4.45 (dd, *J* = 16.2, 5.3 Hz, 1H), 4.28 (dd, *J* = 16.2, 5.5 Hz, 1H), 3.63 (s, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 174.5, 148.1, 142.9, 133.5, 130.9, 130.8, 129.9, 126.7, 125.6, 124.4, 124.1, 121.0, 119.3, 119.0, 118.5, 117.5, 116.3, 109.8, 84.7, 74.7, 66.0, 42.8. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{16}N_3O_2$ 354.1237; Found 354.1241.



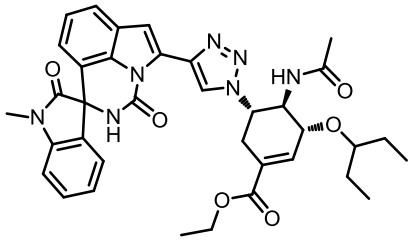

**1-benzyl-5'-ethynylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**

**6an**: yellow oil (69% yield, eluent = PE/ EtOAc (1/1)); $^1$H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.9 Hz, 1H), 7.41 – 7.31 (m, 7H), 7.13 (q, *J* = 7.9 Hz, 2H), 7.03 (s, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.53 (d, *J* = 7.5 Hz, 1H), 5.55 (s, 1H), 5.05 (d, *J* = 15.5 Hz, 1H), 4.79 (d, *J* = 15.5 Hz, 1H), 3.63 (s, 1H). $^{13}$C NMR (126 MHz, $CDCl_3$) δ 174.9, 148.1, 142.8, 135.2, 133.5, 130.9, 129.9, 129.0, 128.1, 127.5, 126.7, 125.6, 124.4, 124.1, 121.1, 119.4, 119.0, 117.5, 116.3, 109.9, 84.7, 74.6, 66.1, 44.3. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{26}H_{18}N_3O_2$ 404.1394; Found 404.1392.



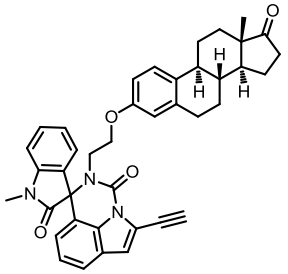

**methyl**
**2-(5'-ethynyl-2,3'-dioxo-2',3'-dihydrospiro[indoline-3,1'-pyrrolo[3,2,1-ij]quinazolin]-1-yl)acetate**

**6ao**: Pink solid (78% yield, eluent = PE/ EtOAc (1/1) mp: >185-188 °C); $^1$H NMR (400 MHz, DMSO-$d_6$) δ 8.62 (s, 1H), 7.53 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.05 (m, 4H), 6.59 (d, *J* = 7.5 Hz, 1H), 4.72 (s, 1H), 4.62 (s, 2H), 4.17 (q, *J* = 7.1 Hz, 2H), 1.20 (t, *J* = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, DMSO-$d_6$) δ 174.8, 167.6, 147.4, 142.2, 132.8, 131.0, 130.3, 125.8, 124.9, 124.2, 123.8, 120.6, 119.4, 118.1, 118.1, 115.4, 109.5, 87.9, 75.0, 65.2, 61.4, 41.3, 14.1. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{23}H_{18}N_3O_4$ 400.1292; Found 400.1297.



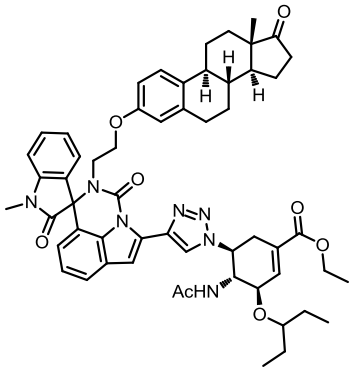

**ethyl(3*R*,4*R*,5*S*)-4-acetamido-5-(4-(1-methyl-2,3'-dioxo-2',3'-dihydrospiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazolin]-5'-yl)-1*H*-1,2,3-triazol-1-yl)-3-(pentan-3-yloxy)cyclohex-1-ene-1-carboxylate**

**8a**: White solid (1: 1 ratio, 90% yield, eluent = DCM/ MeOH (20/1), mp: 165-167 °C); $^{1}$H NMR (400 MHz, Chloroform-*d*) δ 8.39 (s, 1H), 8.30 (s, 1H), 7.50 – 7.28 (m, 6H), 7.24 (s, 2H), 7.11 – 7.02 (m, 4H), 6.98 – 6.90 (m, 2H), 6.87 (s, 1H), 6.83 (s, 1H), 6.54 – 6.37 (m, 4H), 6.32 (s, 1H), 6.14 (s, 1H), 5.64 – 5.54 (m, 1H), 5.45 – 5.35 (m, 1H), 4.89 (d, *J* = 8.8 Hz, 1H), 4.78 (d, *J* = 8.8 Hz, 1H), 4.26 – 4.17 (m, 4H), 3.97 – 3.83 (m, 1H), 3.82 – 3.69 (m, 1H), 3.36 – 3.28 (m, 2H), 3.21 (s, 3H), 3.15 (s, 3H), 3.09 – 3.02 (m, 4H), 1.84 (s, 3H), 1.71 (s, 3H), 1.54 – 1.37 (m, 8H), 1.32 – 1.27 (m, 6H), 0.94 – 0.78 (m, 12H). $^{13}$C NMR (150 MHz, Chloroform-*d*) δ 174.8, 174.7, 171.4, 171.1, 165.3, 165.3, 148.9, 148.7, 143.5, 143.1, 138.3, 138.2, 138.2, 137.9, 134.0, 133.8, 130.5, 130.3, 130.2, 129.5, 129.3, 127.8, 127.6, 127.0, 127.0, 125.1, 125.0, 124.8, 124.8, 123.7, 123.6, 123.5, 123.4, 120.2, 120.1, 117.7, 117.2, 117.0, 108.5, 108.3, 108.0, 82.1, 81.9, 73.0, 72.8, 65.5, 65.3, 60.6, 57.4, 57.0, 56.3, 55.9, 31.2, 31.1, 26.4, 26.2, 25.8, 25.6, 25.1, 24.9, 23.0, 22.7, 22.2, 13.8, 9.1, 9.1, 8.8, 8.7. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{40}N_7O_6$ 666.3035; Found 666.3036.




**5'-ethynyl-1-methyl-2'-(2-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)ethyl)spiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'H)-dione**

(**10a**) Pink solid (51 mg, 1: 1 ratio, 81% yield, eluent = PE/ EA (1/1), mp: 131-133 °C); $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 7.48 (t, *J* = 7.8 Hz, 1H), 7.43 (d, *J* = 7.9 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.9 Hz, 1H), 7.11 (d, *J* = 8.5 Hz, 1H), 7.05 (t, *J* = 7.8 Hz, 1H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.98 (s, 1H), 6.56 – 6.49 (m, 2H), 6.38 (d, *J* = 7.5 Hz, 1H), 4.25 – 4.16 (m, 1H), 4.15 – 4.09 (m, 1H), 3.65 (s, 1H), 3.63 – 3.55 (m, 1H), 3.46 – 3.36 (m, 1H), 3.26 (s, 3H), 2.91 – 2.75 (m, 2H), 2.49 (dd, *J* = 19.1, 8.7 Hz, 1H), 2.39 – 2.31 (m, 1H), 2.25 – 2.09 (m, 1H), 2.13 (dt, *J* = 18.7, 8.9 Hz, 1H), 2.07 – 2.01 (m, 1H), 2.00 – 1.90 (m, 2H), 1.62 – 1.53 (m, 2H), 1.53 – 1.44 (m, 3H), 1.43 – 1.35 (m, 1H), 0.89 (s, 3H). $^{13}$C NMR (101 MHz, Chloroform-*d*) δ 221.0, 174.2, 156.3, 149.1, 143.6, 137.6, 132.6, 132.1, 130.9, 129.5, 126.2, 126.1, 125.7, 124.2, 124.1, 120.8, 119.6, 119.0, 117.5, 116.1, 114.4 , 114.4, 112.2, 112.1, 109.0, 84.5, 74.9, 71.5, 65.0, 50.4, 48.0, 45.5, 43.9, 38.3, 35.8, 31.5, 29.7, 29.6, 26.9, 26.5, 25.9, 21.5, 13.8. HRMS (ESI) m/z: [M+H]+ Calcd for $C_{40}H_{38}N_3O_4$ 624.2857; Found 624.2869.

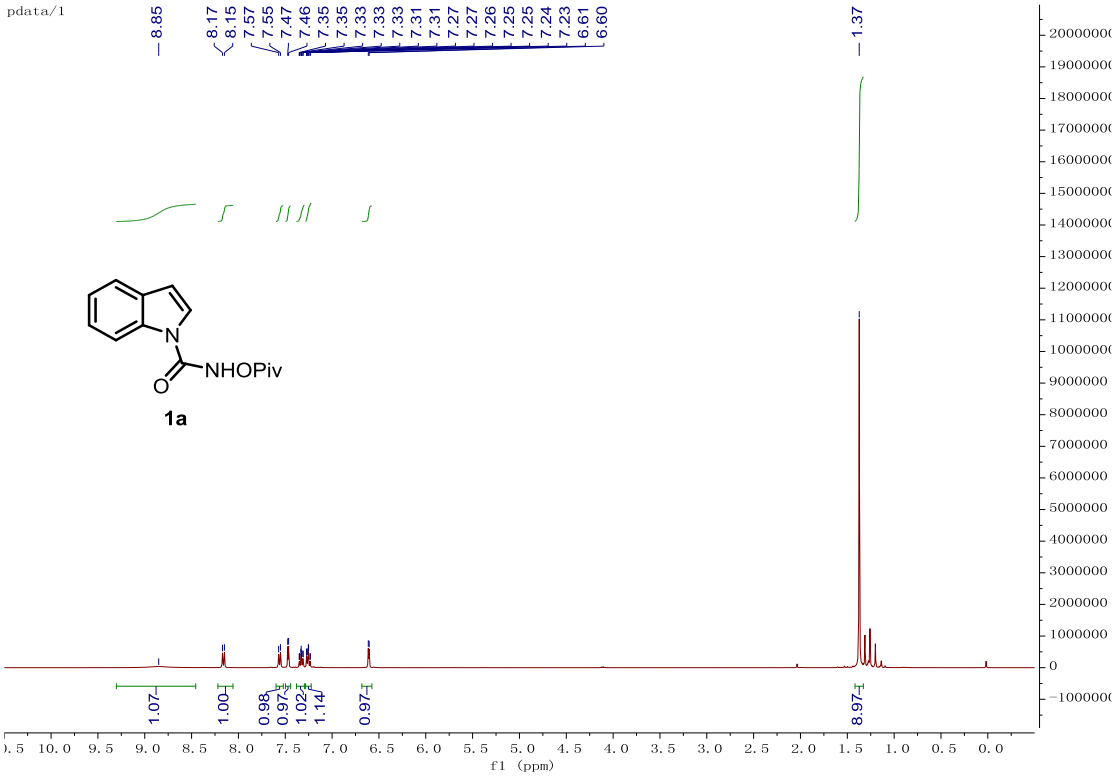


**(3*R*,4*R*,5*S*)-ethyl 4-acetamido-5-(4-(1-methyl-2'-(2-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthren-3-yl)oxy)ethyl)-2,3'-dioxo-2',3'-dihydrospiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazolin]-5'-yl)-1*H*-1,2,3-triazol-1-yl)-3-(pentan-3-yloxy)cyclohex-1-enecarboxylate**

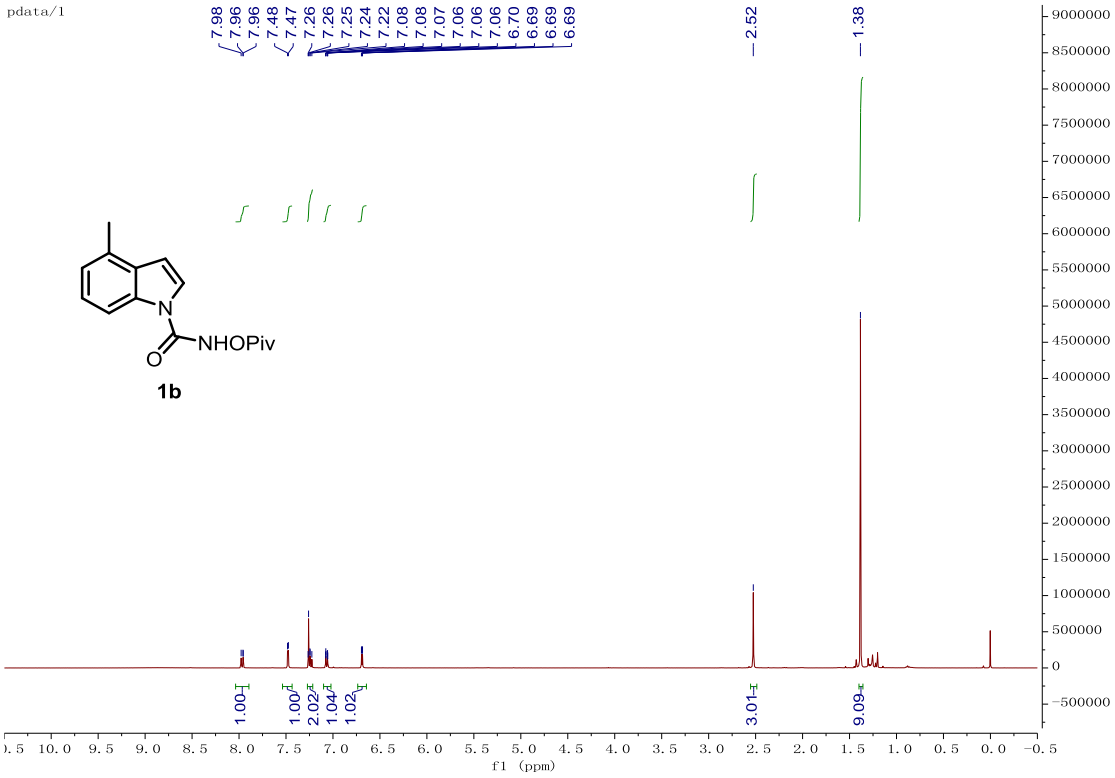
(**11a**) White solid (25 mg, 1: 1 ratio, 78% yield, eluent = PE/ Acetone (2/1), mp: 160-162 °C); $^{1}$H NMR (500 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 8.47 (s, 1H), 7.51 – 7.44 (m, 4H), 7.36 (s, 1H), 7.34 – 7.29 (m, 3H), 7.17 (td, *J* = 7.6, 3.1 Hz, 2H), 7.13 – 7.09 (m, 2H), 7.07 – 7.01 (m, 4H), 6.92 (s, 2H), 6.54 – 6.49 (m, 4H), 6.31 (dd, *J* = 7.5, 3.8 Hz, 2H), 6.03 (dd, *J* = 10.5, 7.2 Hz, 2H), 5.59 – 5.50 (m, 2H), 4.90 (ddd, *J* = 18.1, 9.1, 2.5 Hz, 2H), 4.23 (q, *J* = 7.1 Hz, 4H), 4.20 – 4.08 (m, 2H), 4.06 – 4.00 (m, 2H), 3.94 – 3.89 (m, 1H), 3.88 – 3.82 (m, 1H), 3.69 – 3.57 (m, 2H), 3.41 – 3.35 (m, 4H), 3.27 (s, 3H), 3.26 (s, 3H), 3.15 – 3.12 (m, 4H), 2.84 – 2.81 (m, 4H), 2.49 (dd, *J* = 19.1, 8.7 Hz, 2H), 2.36 – 2.33 (m, 2H), 2.24 – 2.17 (m, 2H), 2.14 (t, *J* = 8.8 Hz, 1H), 2.10 (t, *J* = 8.8 Hz, 1H), 1.98 – 1.91 (m, 4H), 1.84 (s, 3H), 1.83 (s, 3H), 1.64 – 1.59 (m, 2H), 1.56 – 1.44 (m, 16H), 1.42 – 1.35 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 8H), 0.93 (t, *J* = 7.4 Hz, 6H), 0.90 – 0.86 (m, 12H). $^{13}$C NMR (126 MHz, Chloroform-*d*) δ 220.9, 220.9, 174.5, 171.4, 171.3, 165.6, 165.6, 156.2, 149.8, 143.7, 143.6, 138.9, 138.8, 138.5, 138.4, 137.6, 133.6, 133.6, 132.1, 132.1, 131.3, 131.2, 130.8, 129.7, 129.6, 128.1, 128.1, 127.0, 126.2, 125.8, 125.5, 125.5, 124.1, 124.1, 123.9, 120.5, 120.5, 118.4, 117.5, 117.5, 114.4, 114.3, 112.1, 112.0, 109.0, 109.0, 108.8, 82.1, 82.1, 73.3, 73.1, 71.4, 71.3, 65.0, 61.0, 58.1, 57.8, 56.8, 56.6, 50.3, 47.9, 45.5, 43.9, 38.3, 35.8, 31.5, 29.6, 29.6, 26.9, 26.4, 26.3, 25.8, 25.5, 23.3, 23.3, 21.5, 14.2, 13.8, 9.6, 9.2. HRMS (ESI) m/z: [M+H]+ Calcd for $C_{56}H_{64}N_7O_8$ 962.4811; Found 962.4827.

# 8. NMR Spectra

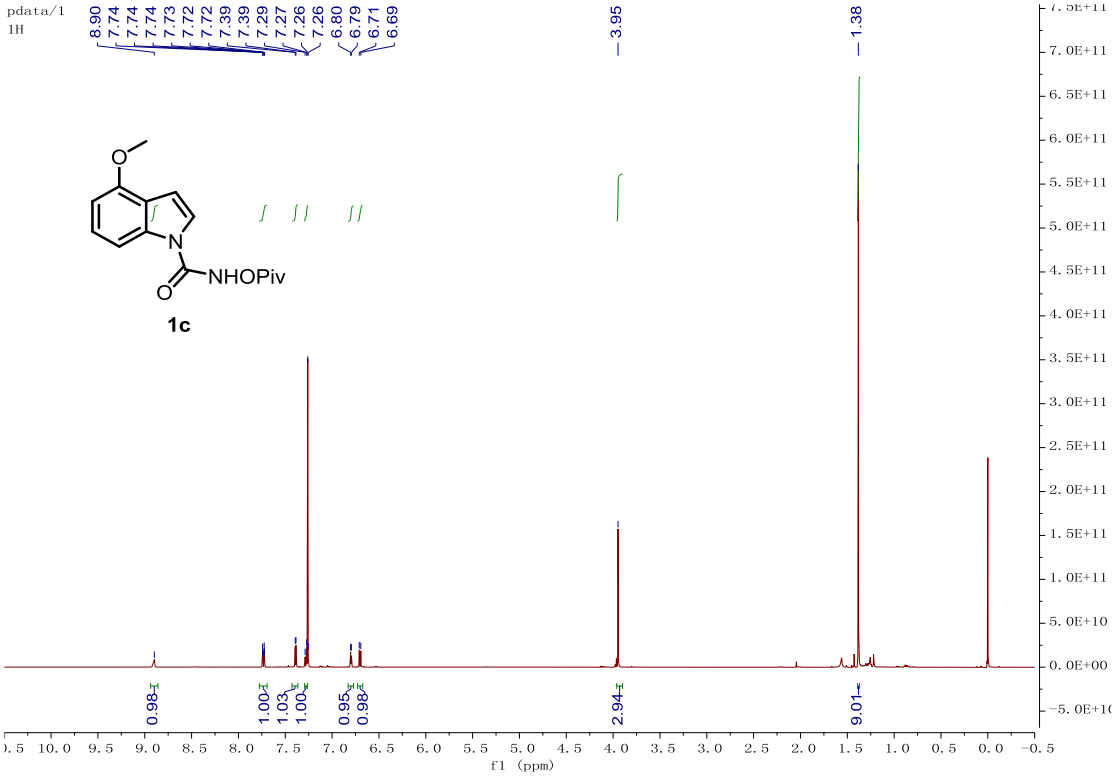
## *N*-(pivaloyloxy)-1*H*-indole-1-carboxamide (1a)



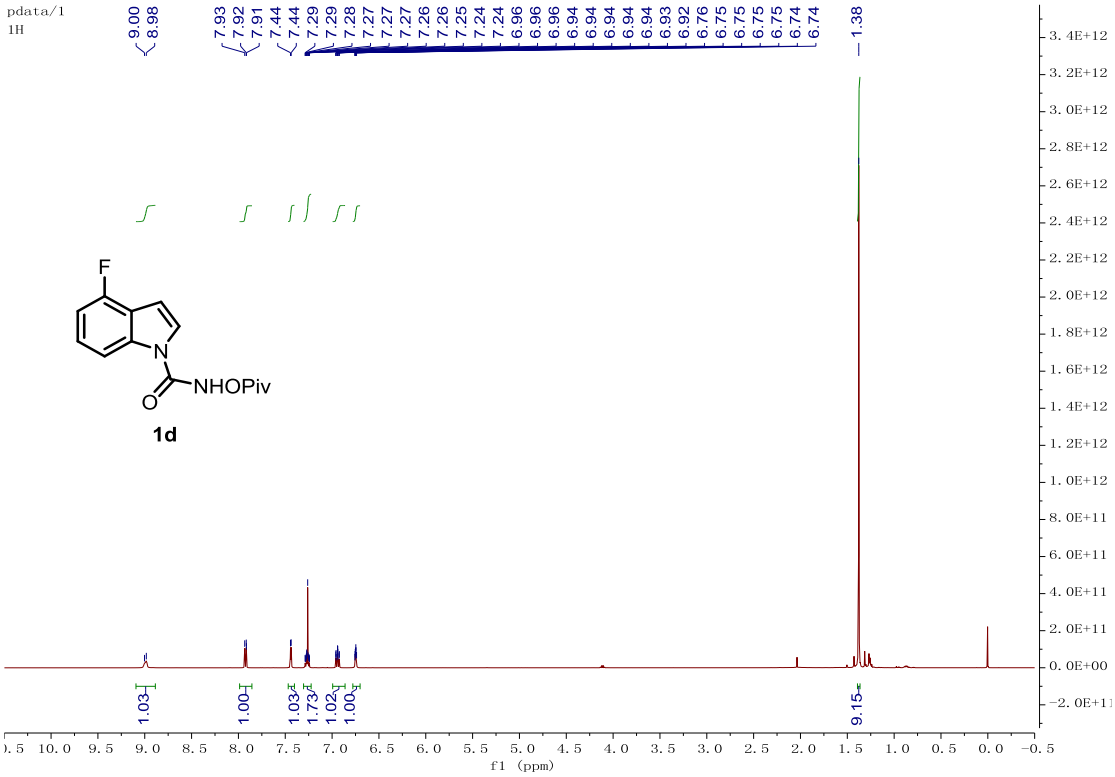

## 4-methyl-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide (1b)

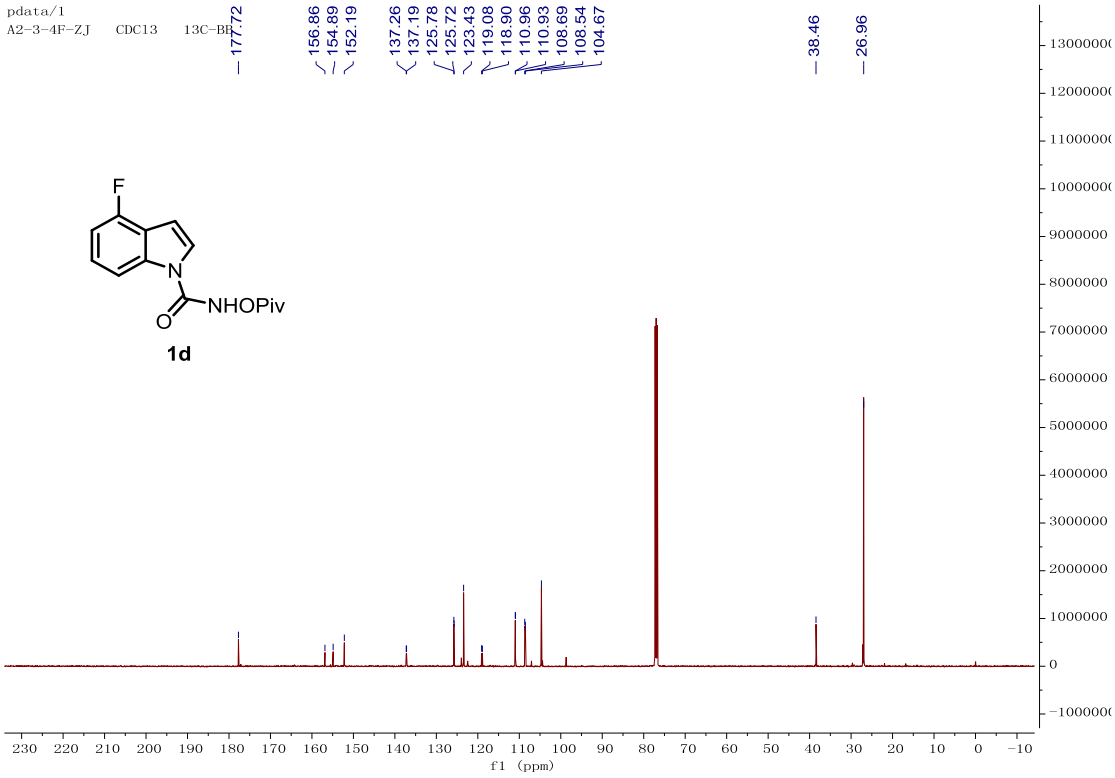


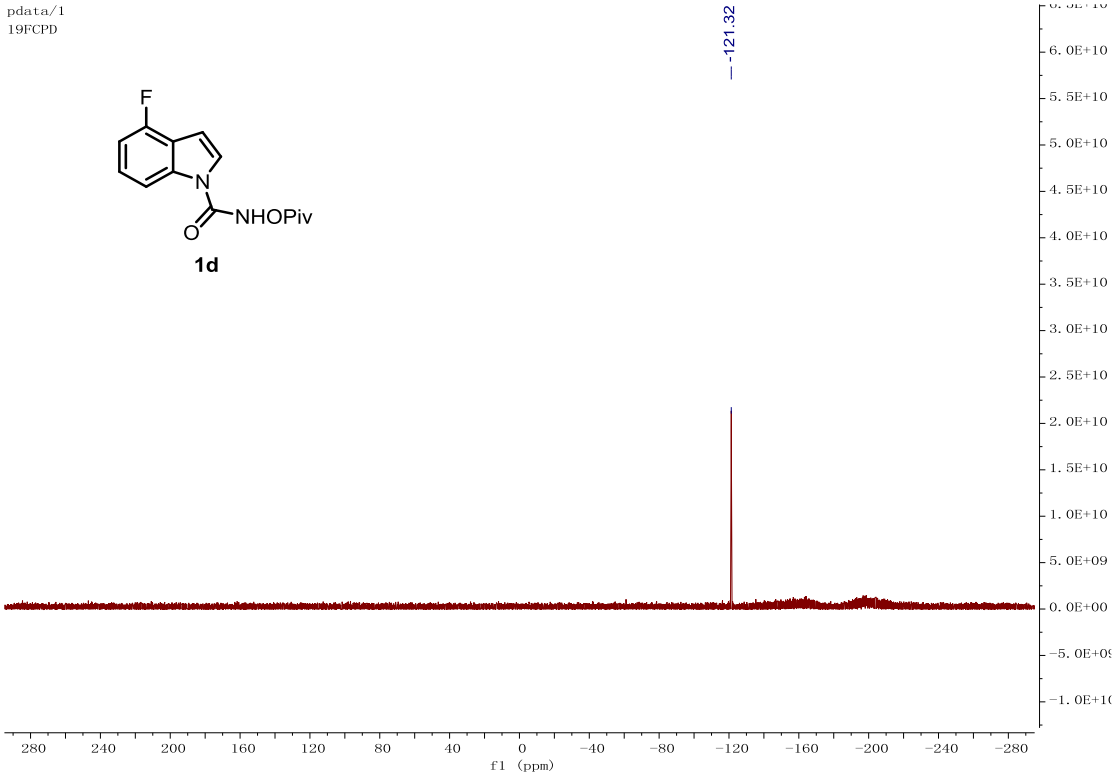
**4-methoxy-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide (1c)**



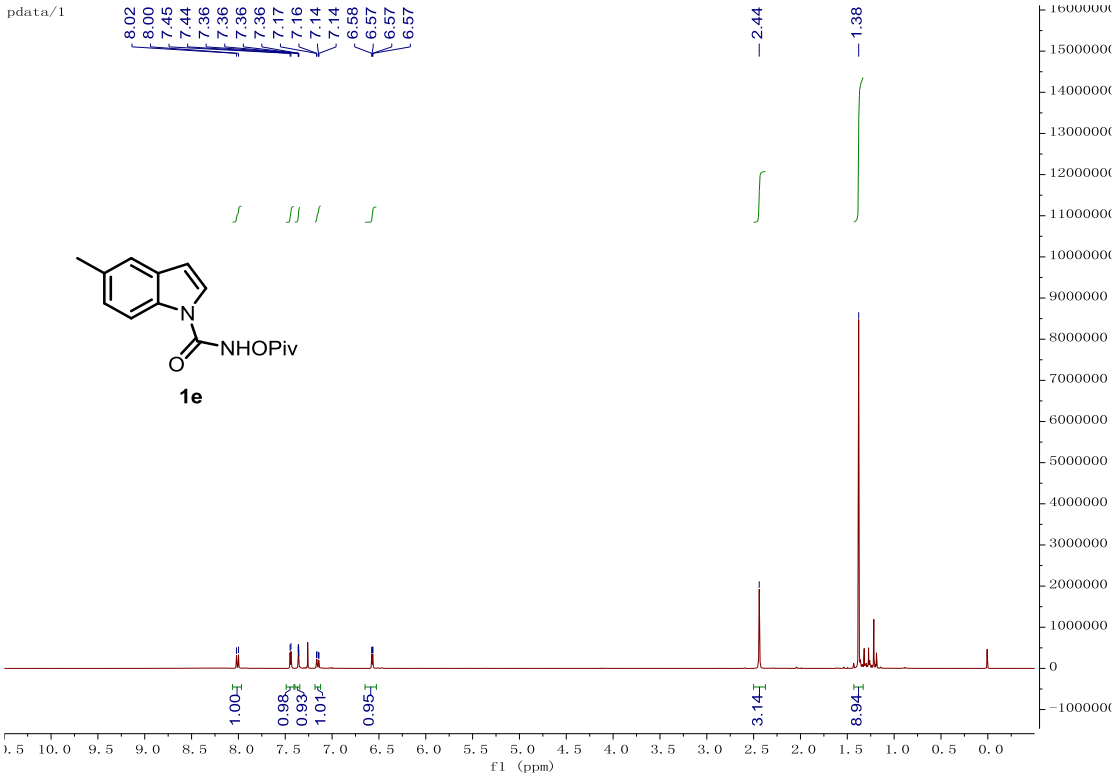

**4-fluoro-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide (1d)**



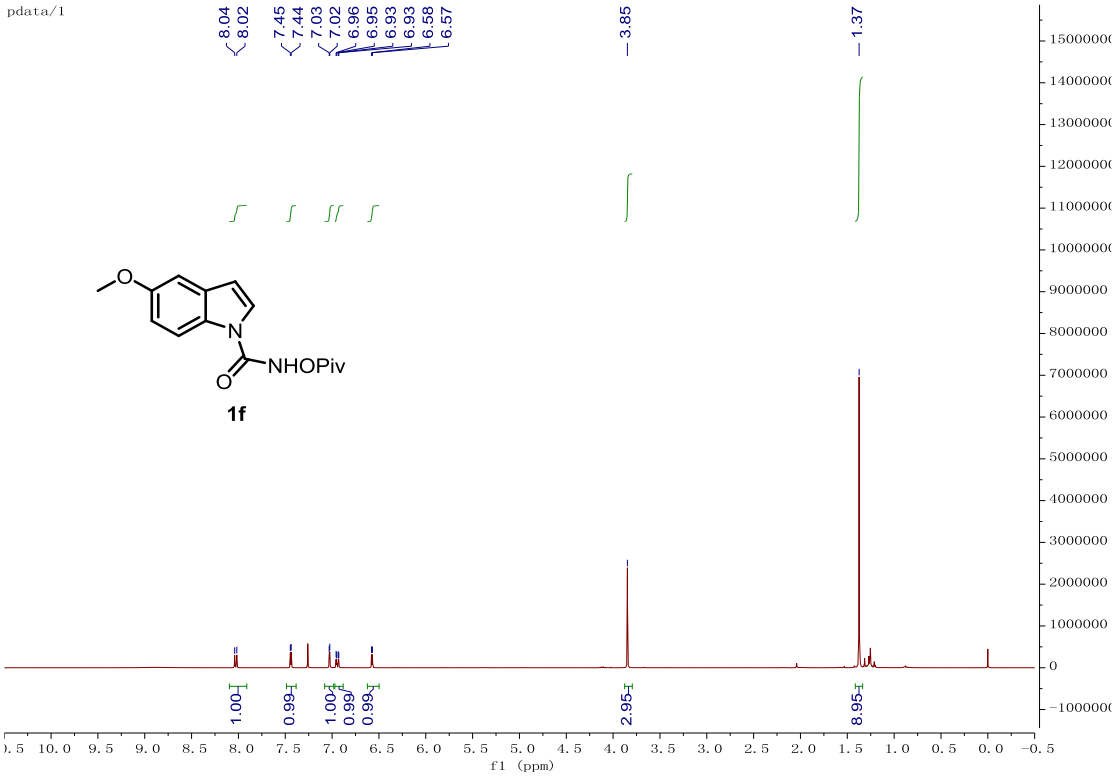

pdata/1
A2-3-4F-ZJ CDC13 13C-BF
177.72
156.86
154.89
152.19
137.26
137.19
125.78
125.72
123.43
119.08
118.90
110.96
110.93
108.69
108.54
104.67
38.46
26.96
F
N
O
NHOPiv
1d
f1 (ppm)


pdata/1
19FCPD
-121.32
F
N
O
NHOPiv
1d
f1 (ppm)

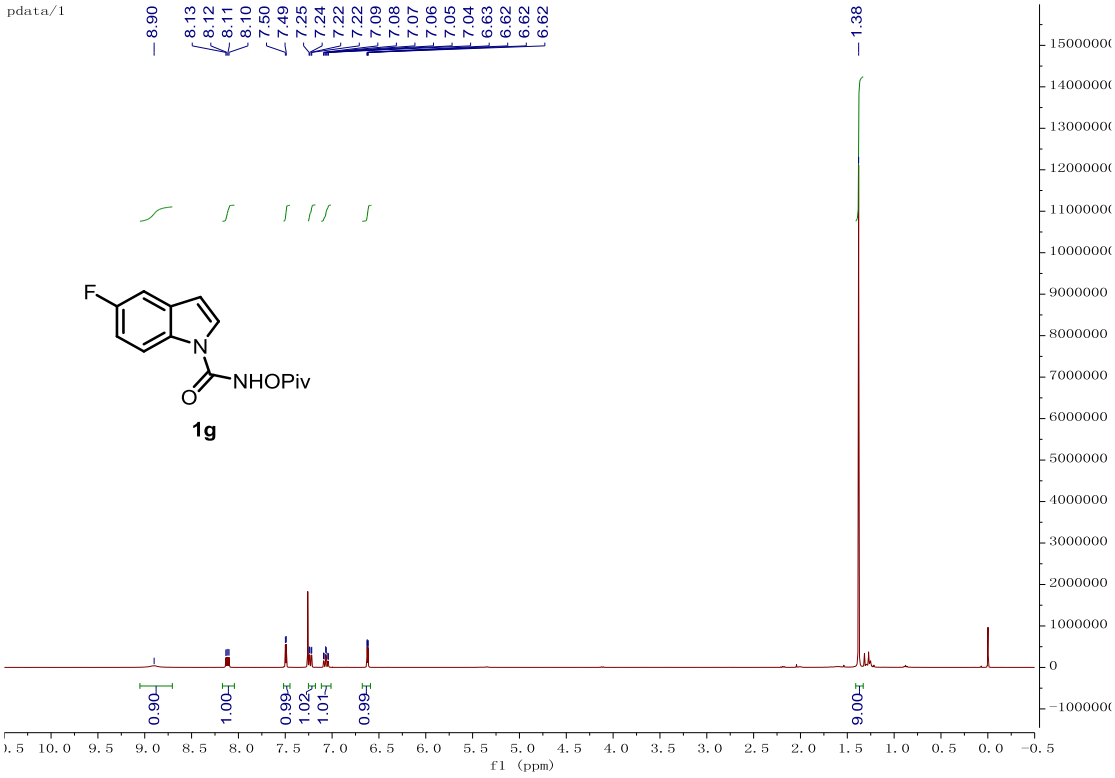
## 5-methyl-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide (1e)



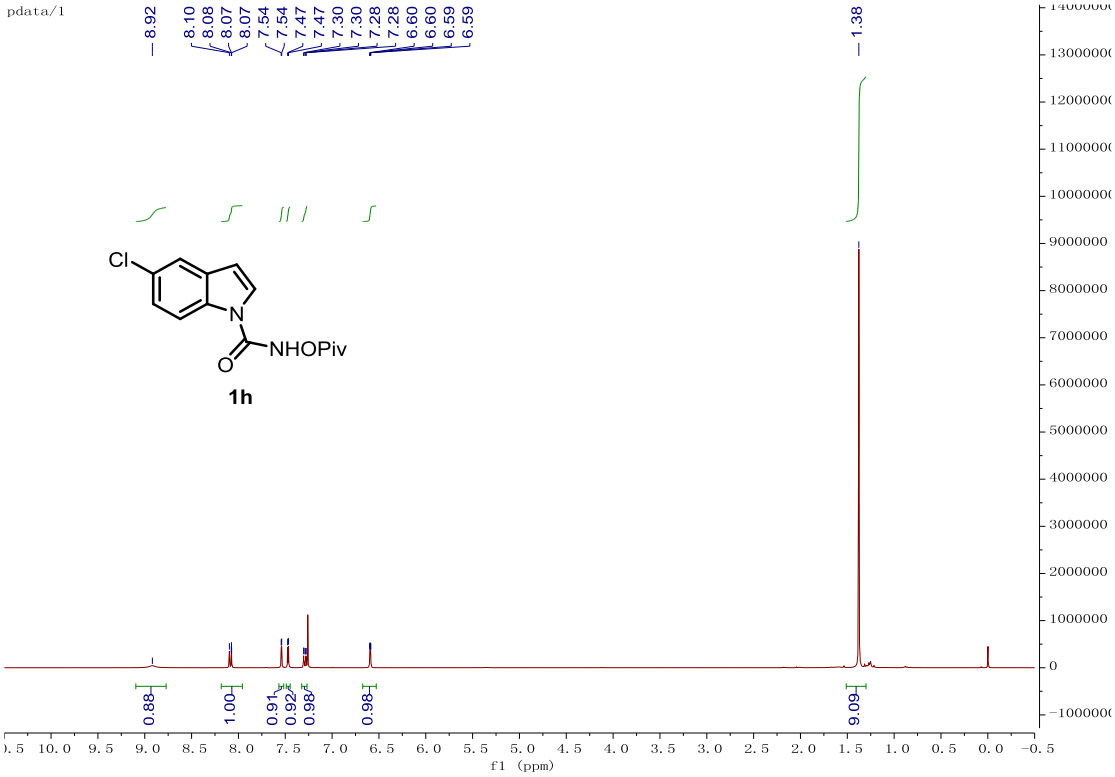

## 5-methoxy-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide (1f)



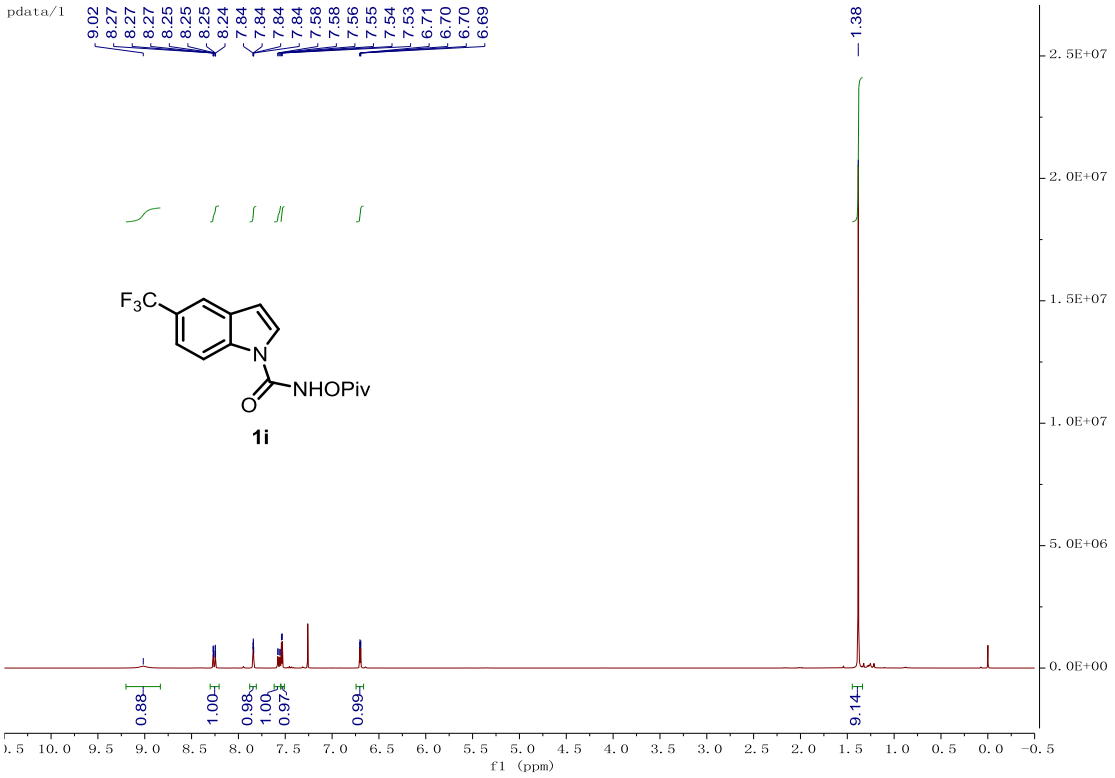
## 5-fluoro-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide (1g)

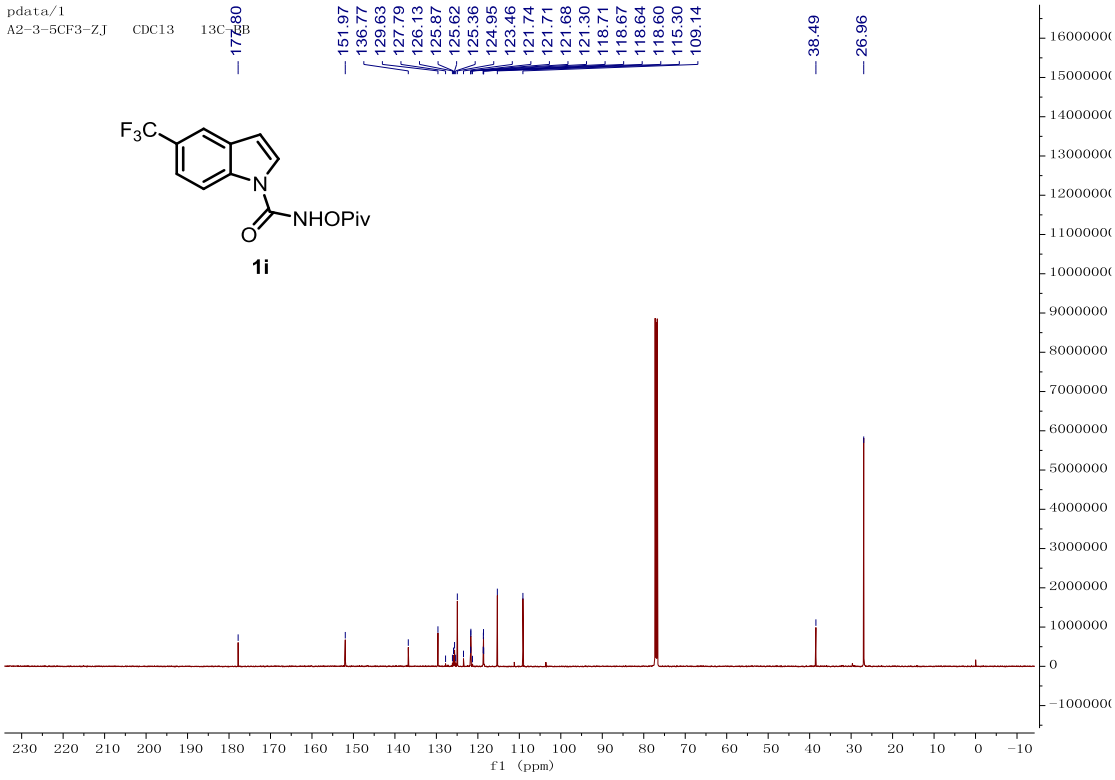


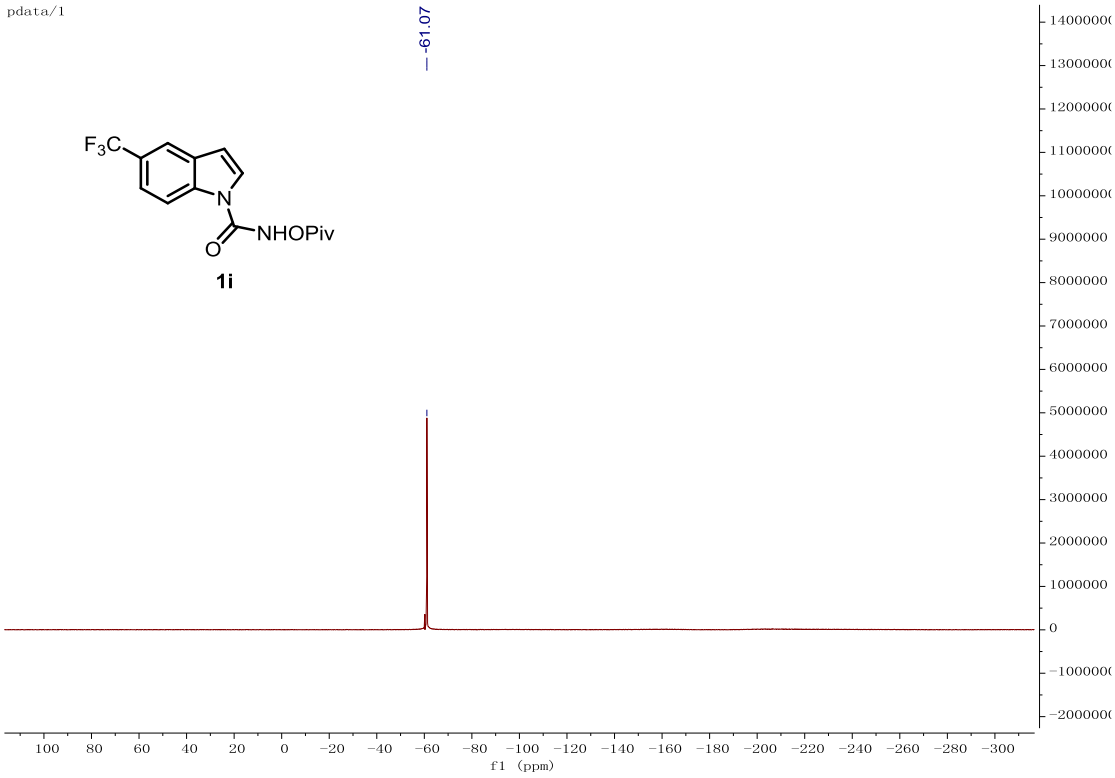

## 5-chloro-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide (1h)



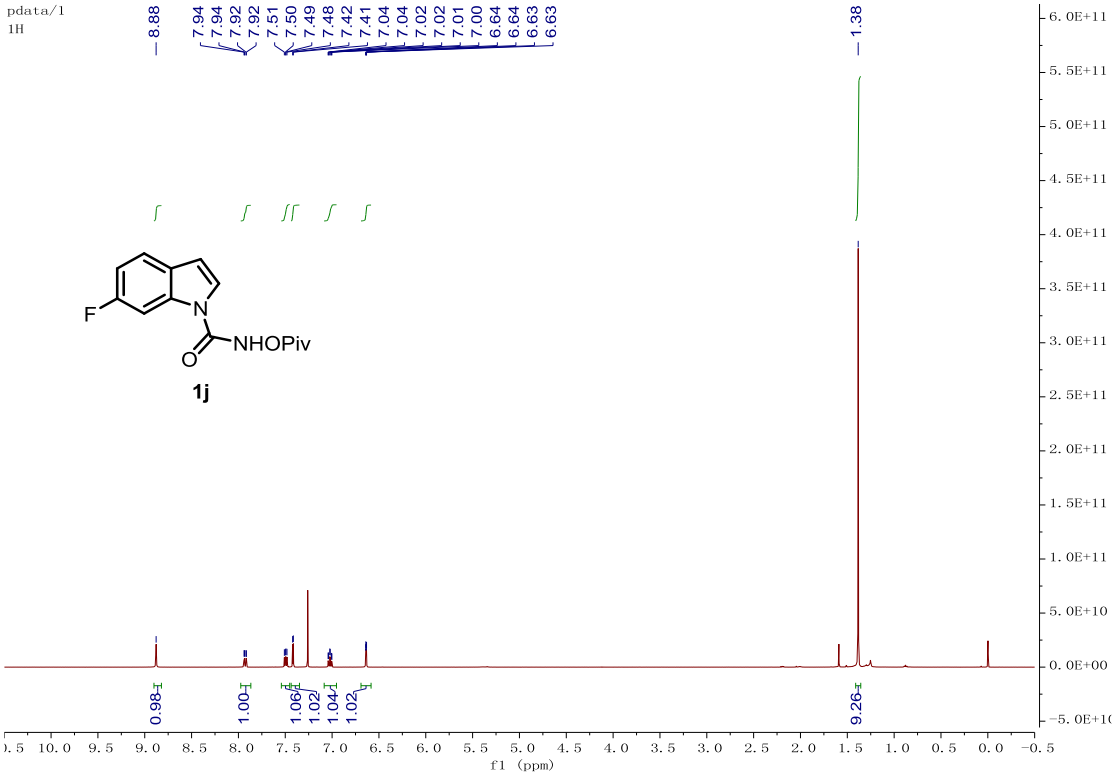
## *N*-(pivaloyloxy)-5-(trifluoromethyl)-1*H*-indole-1-carboxamide (1i)

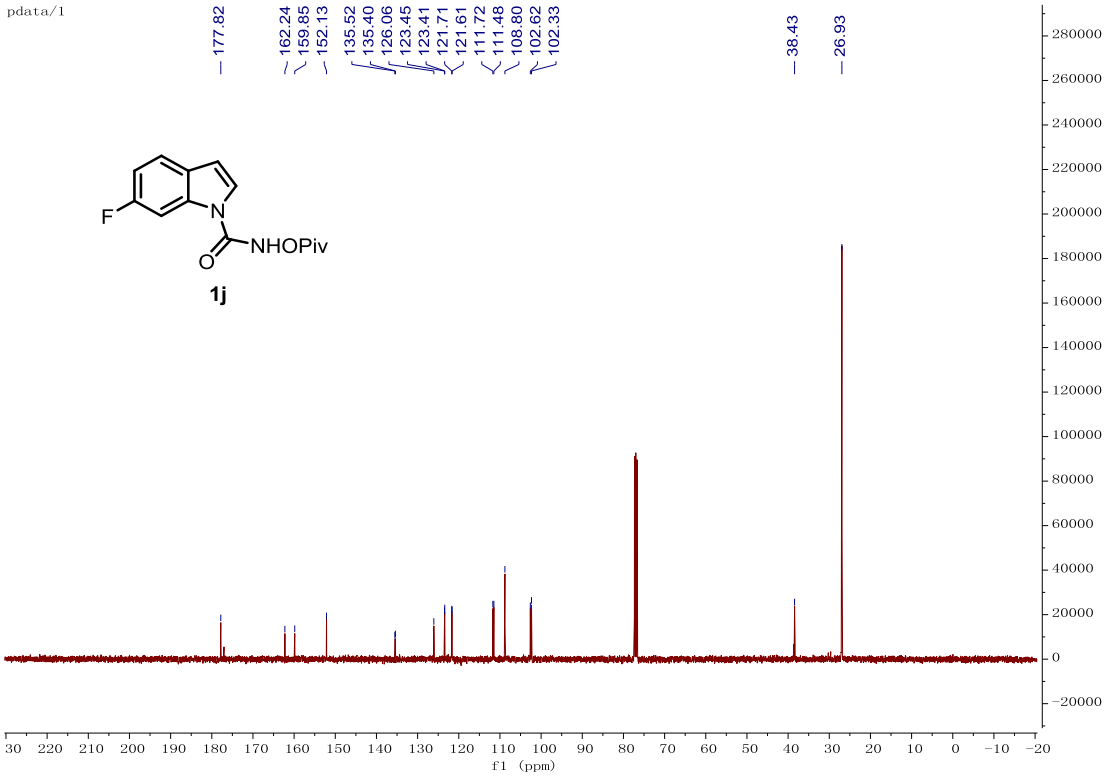


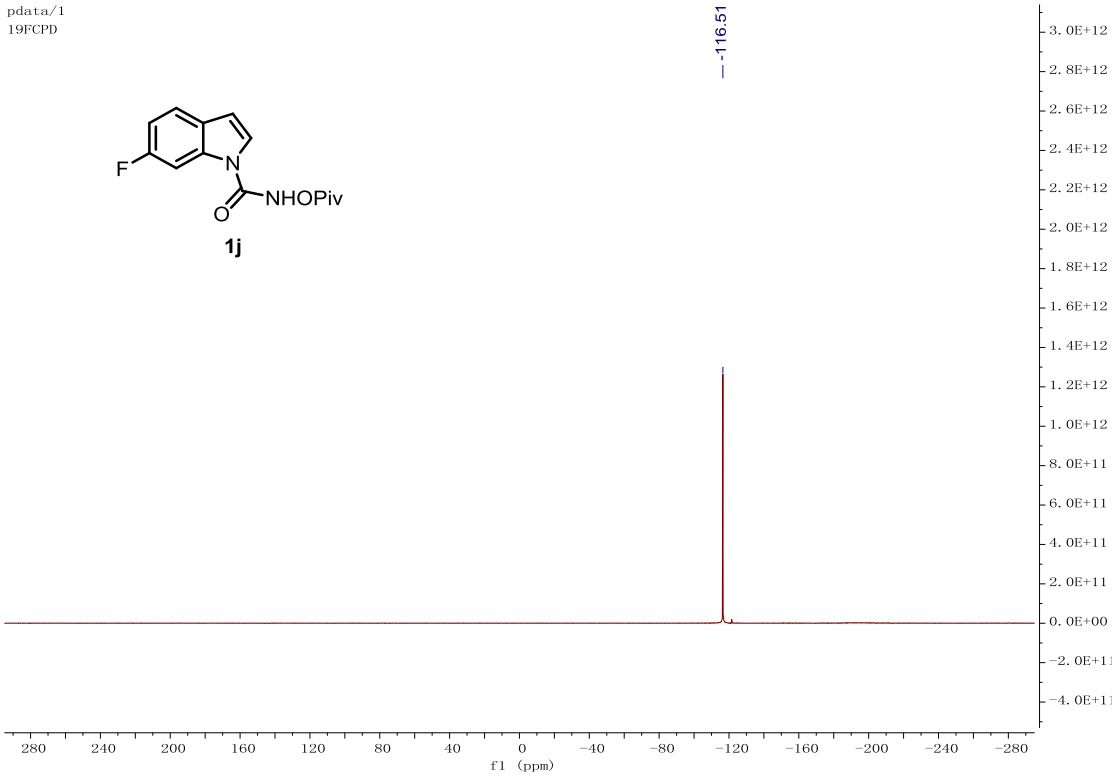





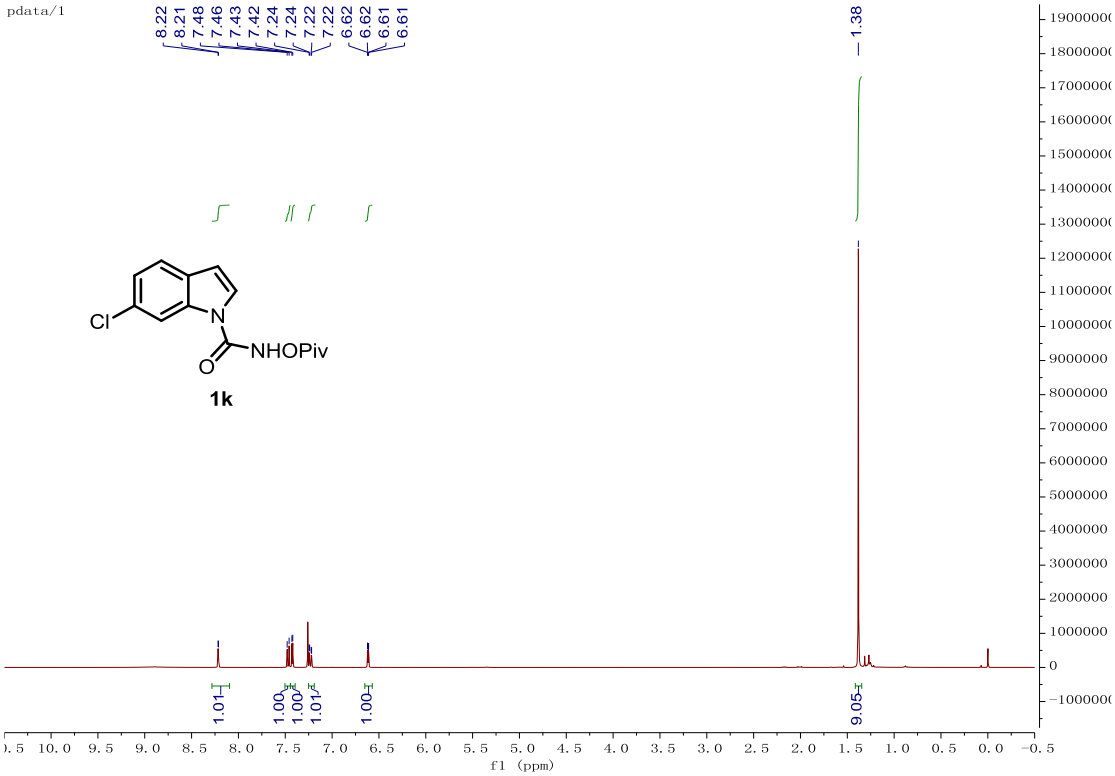

**6-fluoro-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide (1j)**



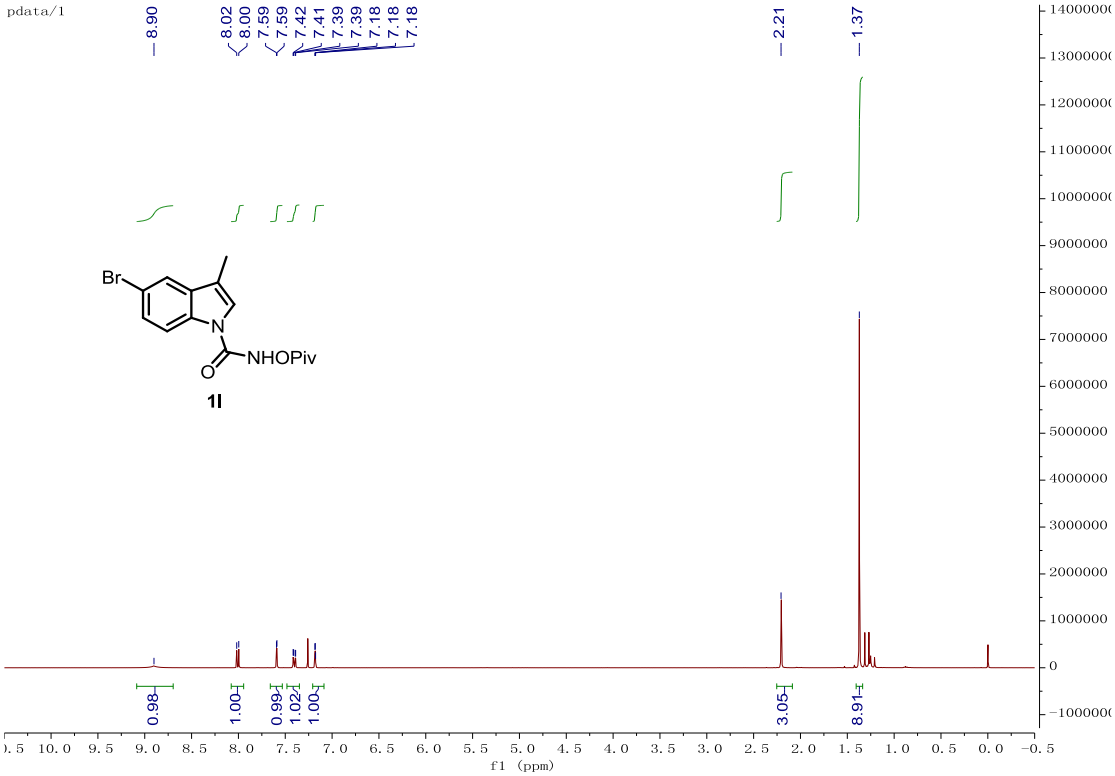

pdata/1
177.82
162.24
159.85
152.13
135.52
135.40
126.06
123.45
123.41
121.71
121.61
111.72
111.48
108.80
102.62
102.33
38.43
26.93
F
N
O
NHOPiv
1j
f1 (ppm)

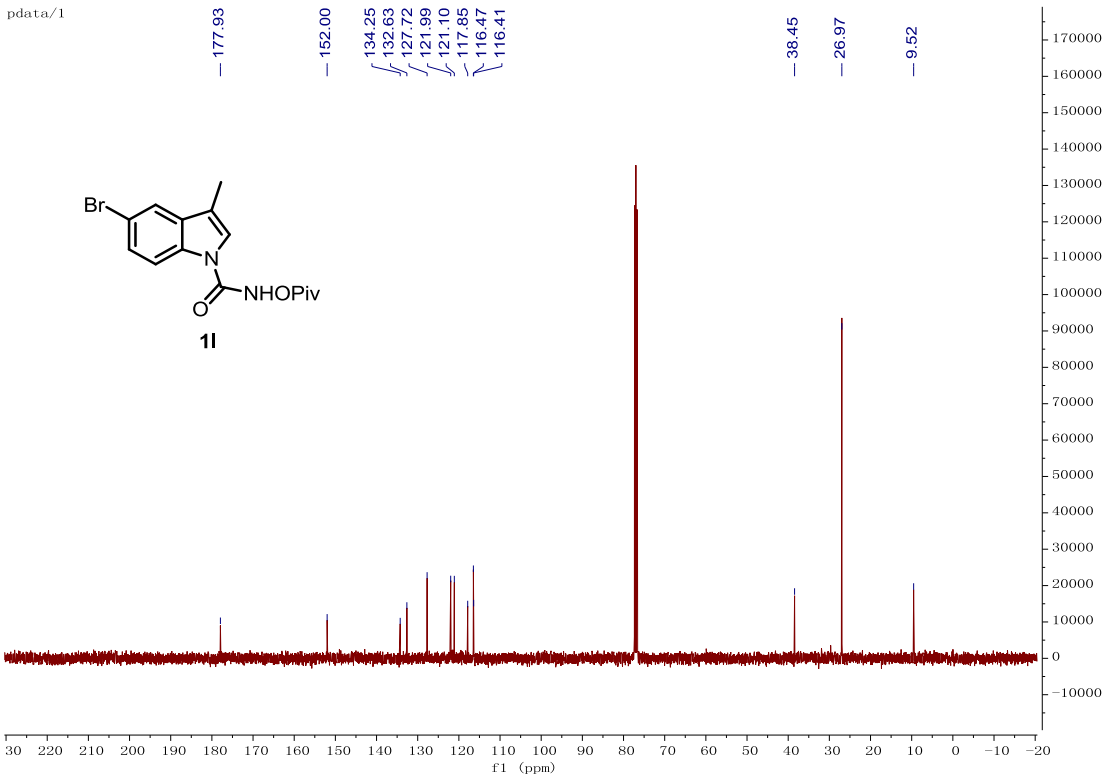

pdata/1
19FCPD
-116.51
F
N
O
NHOPiv
1j
f1 (ppm)

## 6-chloro-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide (1k)

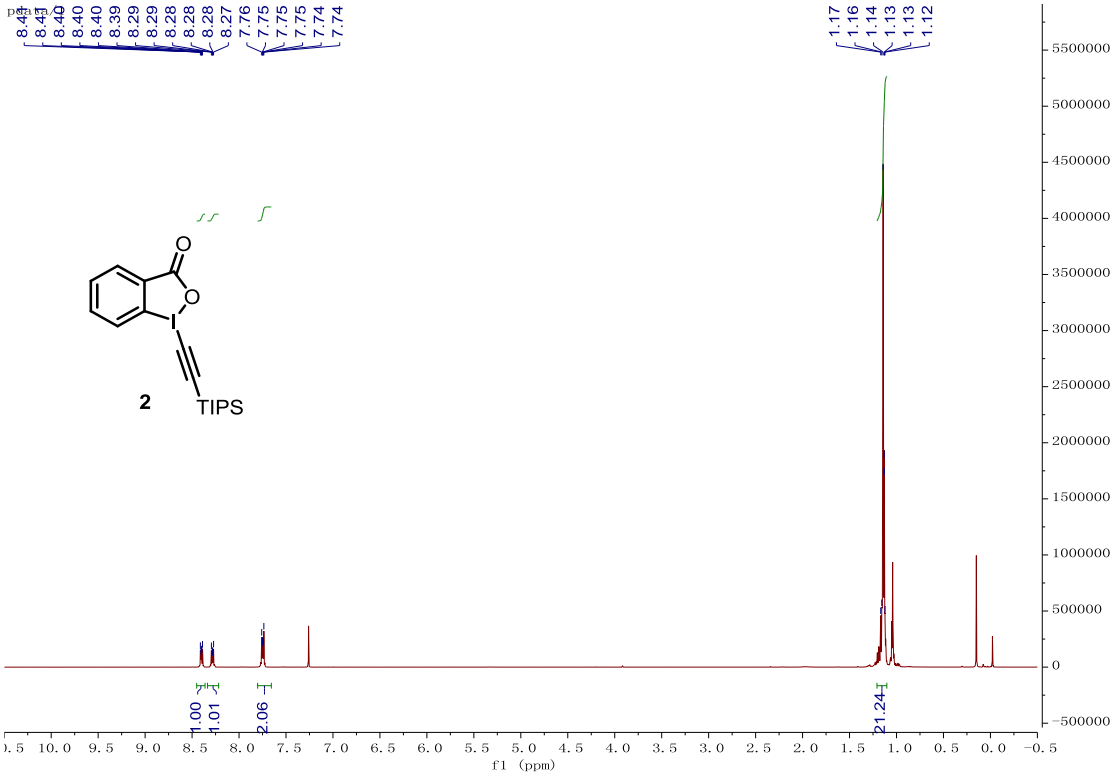



## 5-bromo-3-methyl-*N*-(pivaloyloxy)-1*H*-indole-1-carboxamide (1l)

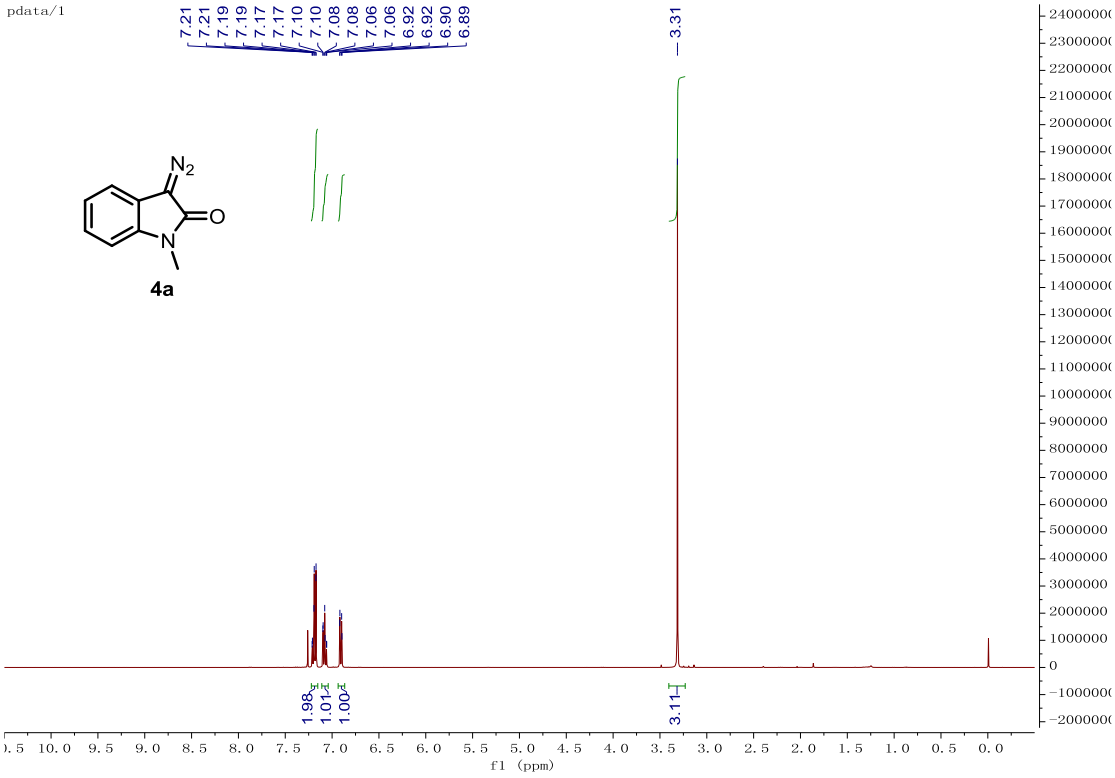




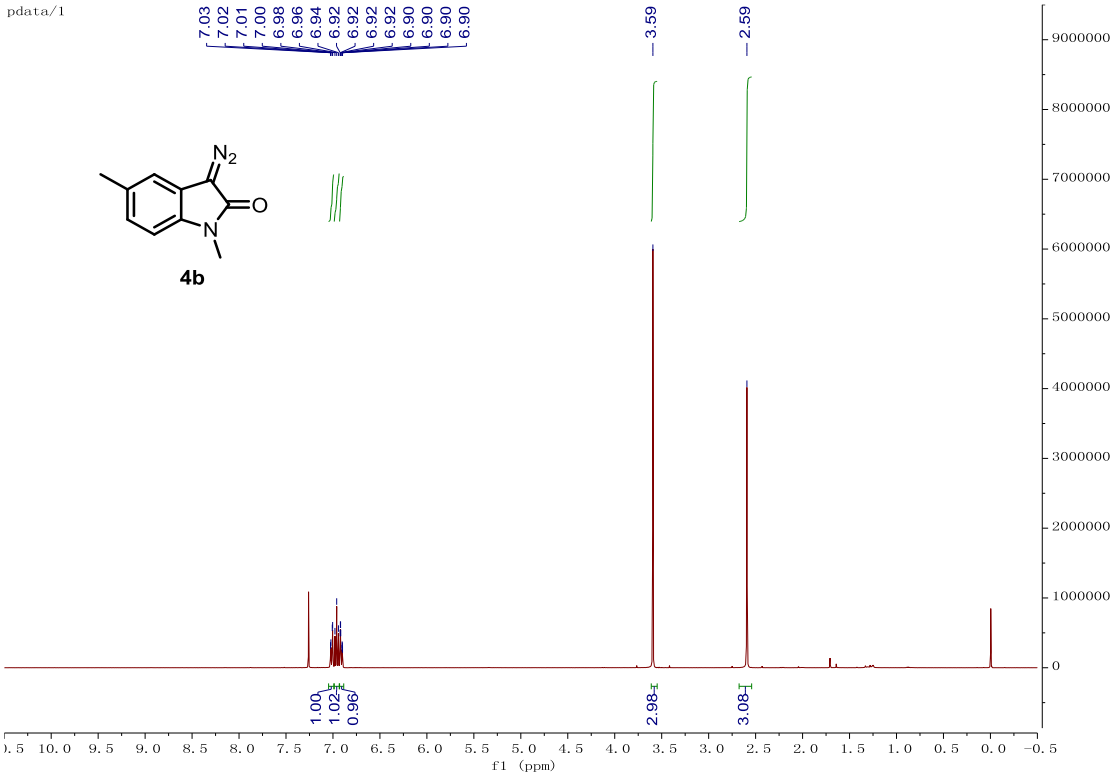

**1-((triisopropylsilyl)ethynyl)-1λ$^3$-benzo[*d*][1,2]iodaoxol-3(1*H*)-one (2)**



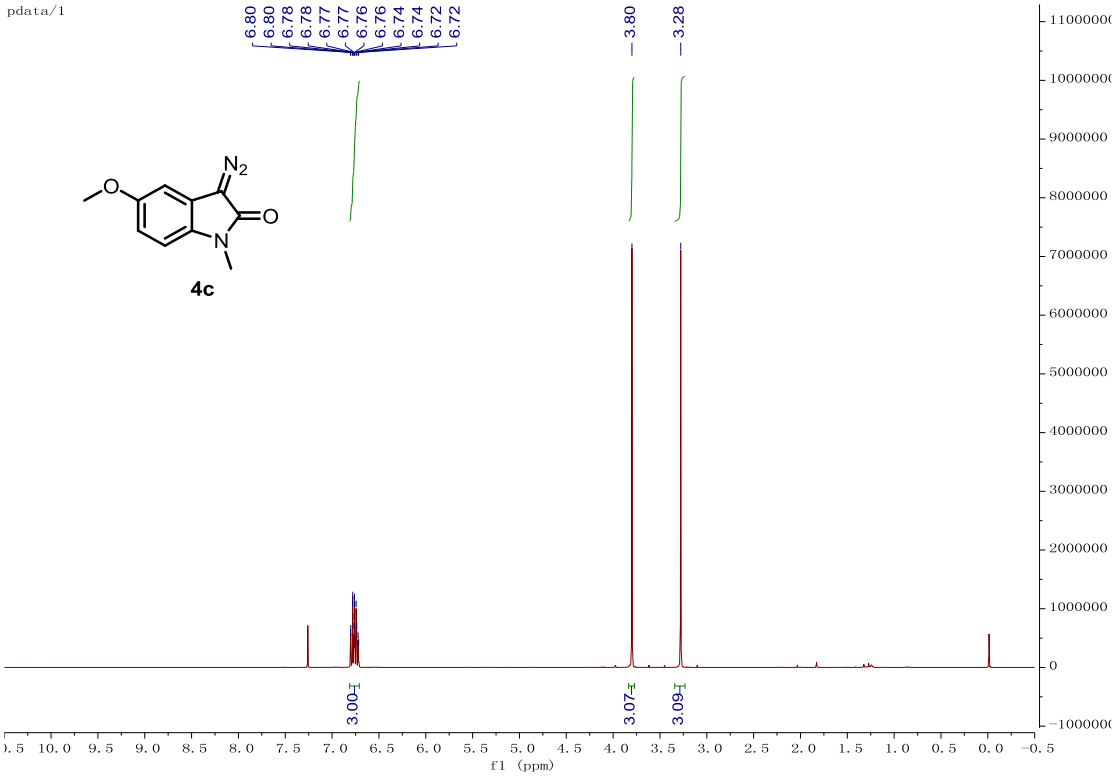
## 3-diazo-1-methylindolin-2-one (4a)



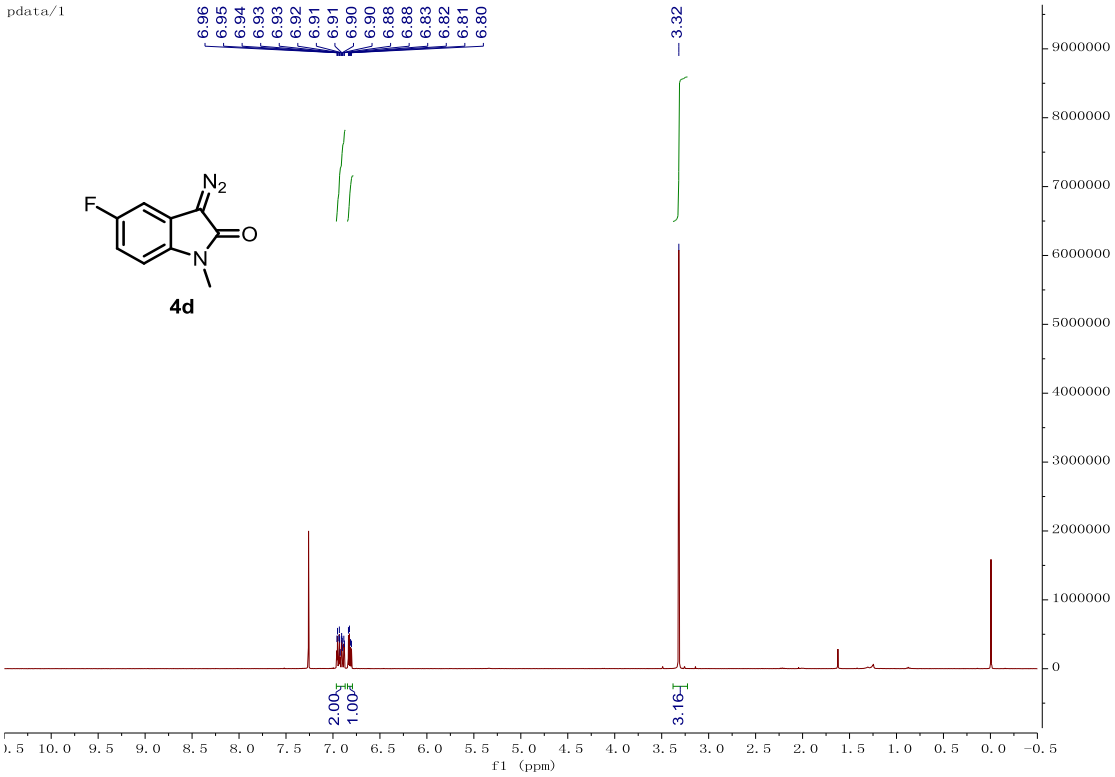

## 3-diazo-1,5-dimethylindolin-2-one (4b)



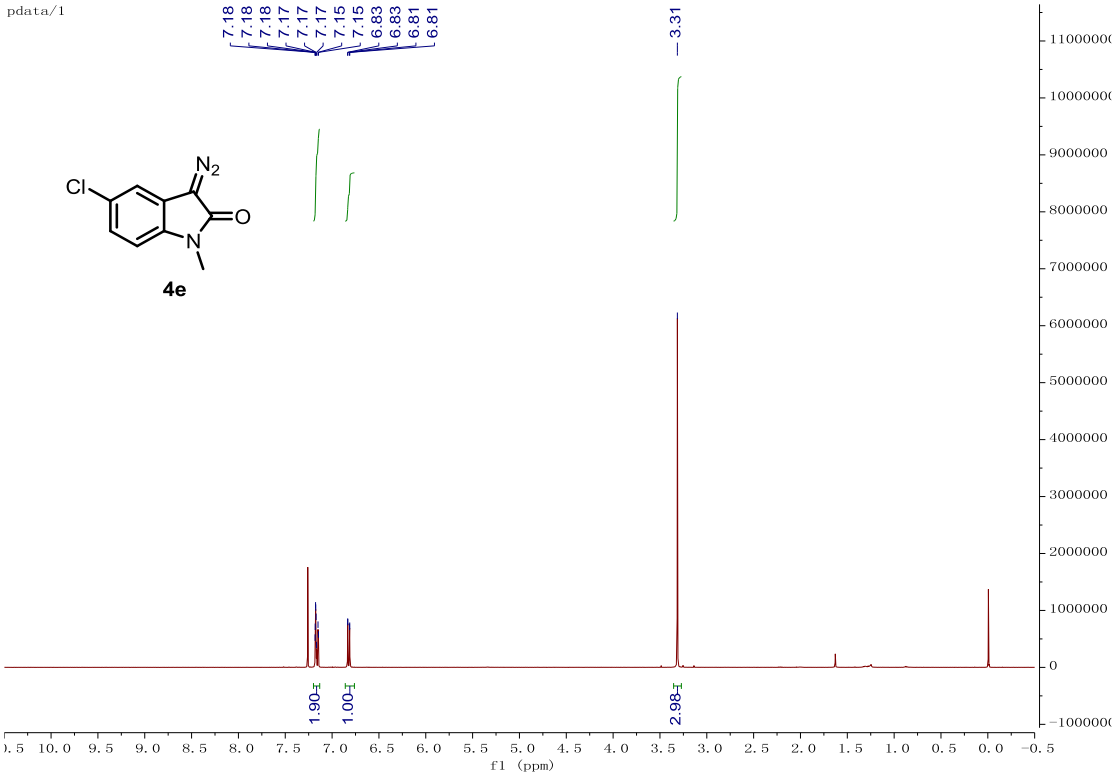
## 3-diazo-5-methoxy-1-methylindolin-2-one (4c)



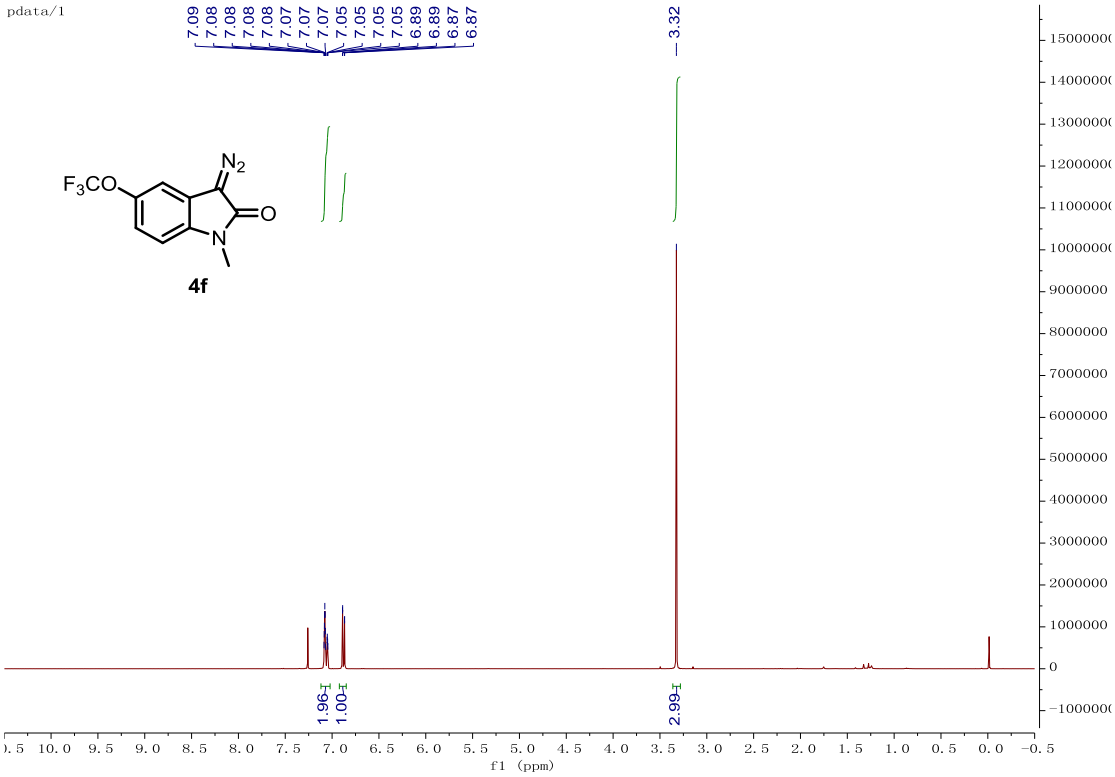

## 3-diazo-5-fluoro-1-methylindolin-2-one (4d)



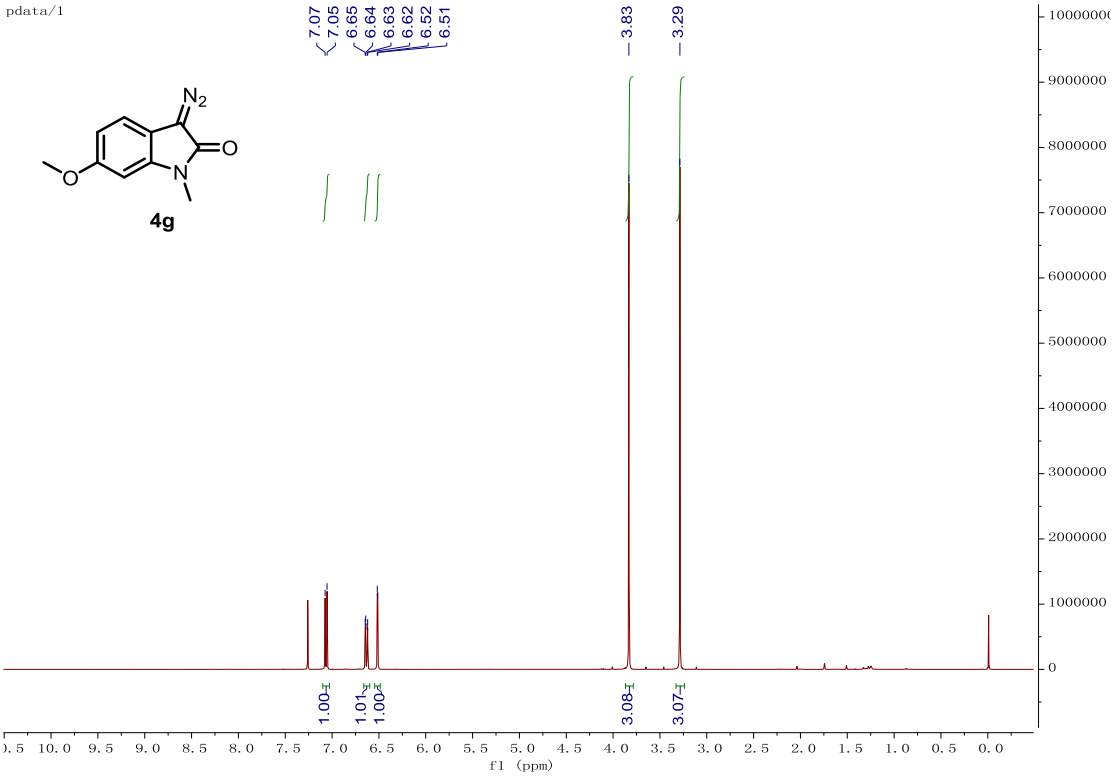
## 5-chloro-3-diazo-1-methylindolin-2-one (4e)



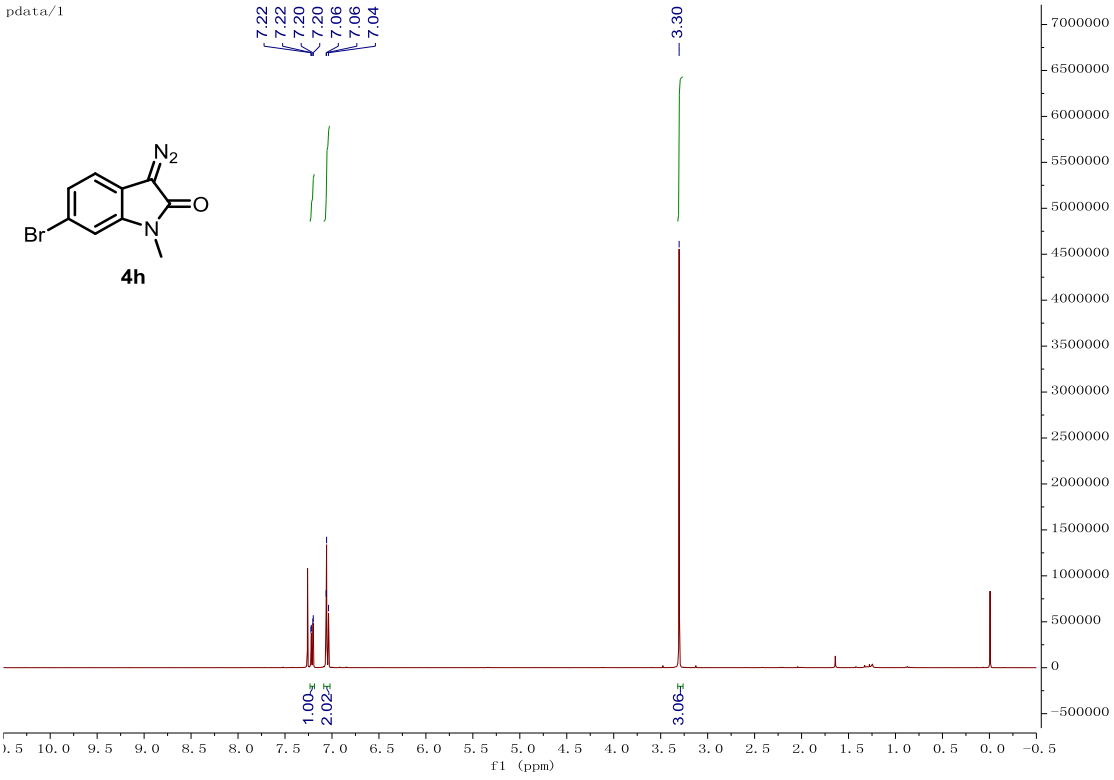

## 3-diazo-1-methyl-5-(trifluoromethoxy)indolin-2-one (4f)



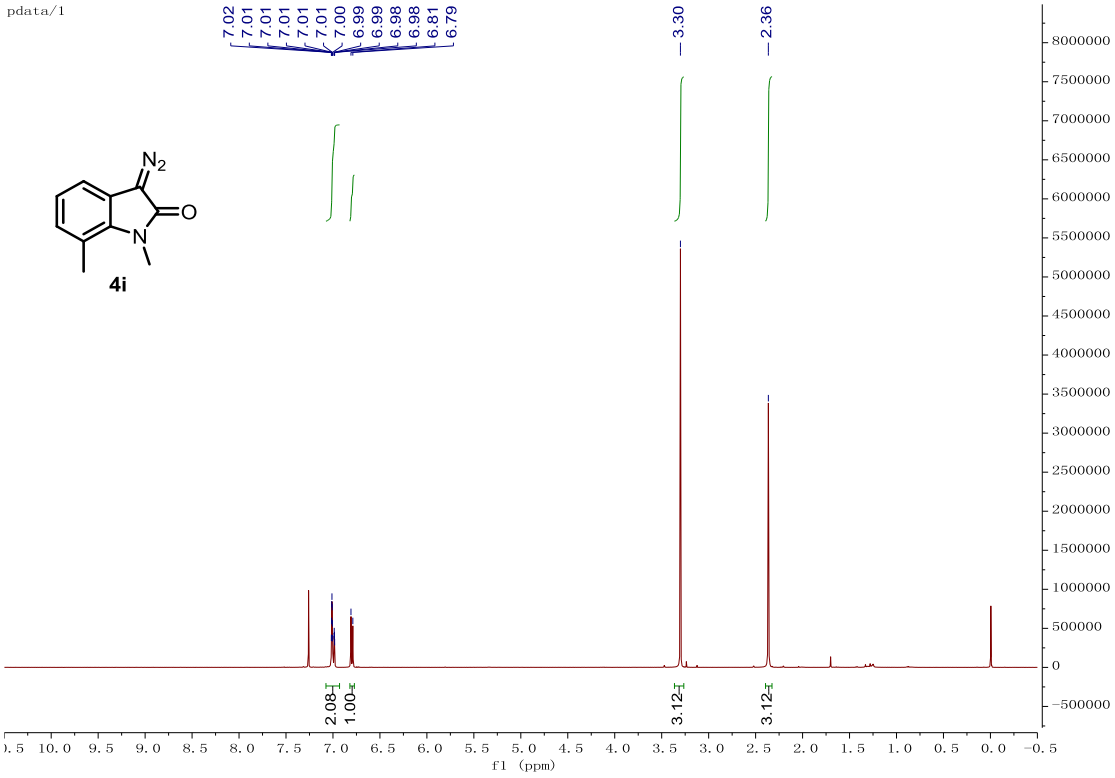
## 3-diazo-6-methoxy-1-methylindolin-2-one (4g)



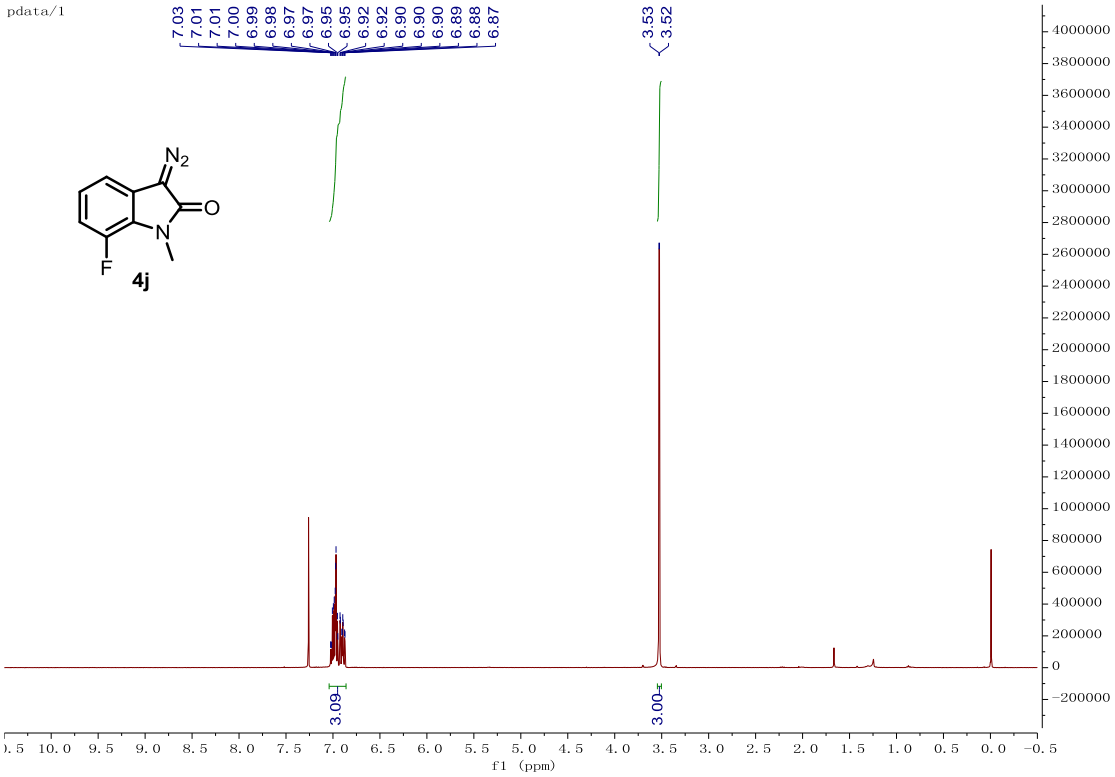

## 6-bromo-3-diazo-1-methylindolin-2-one (4h)



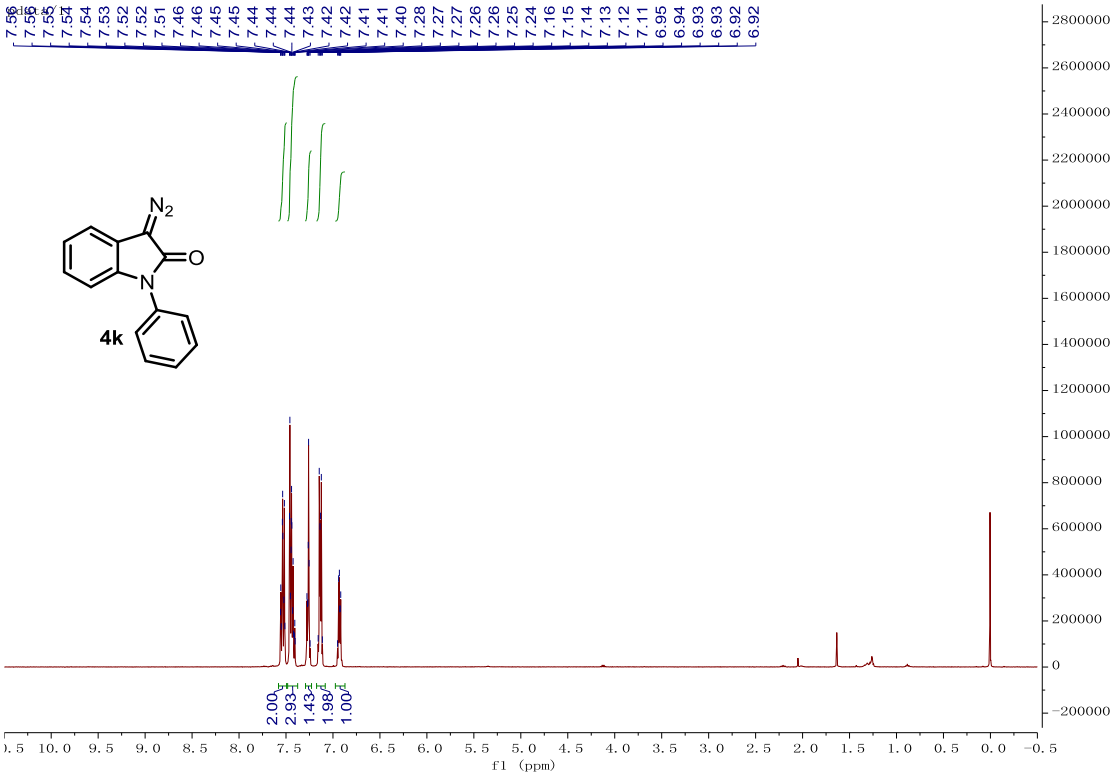
## 3-diazo-1,7-dimethylindolin-2-one (4i)



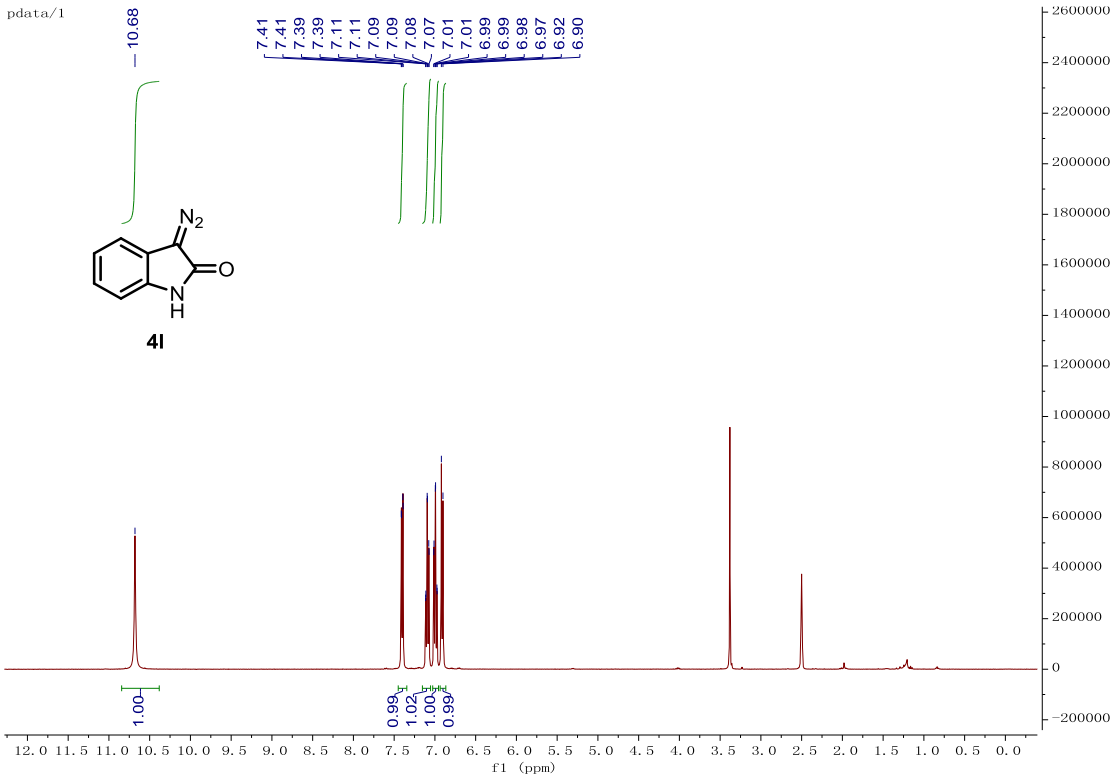

## 3-diazo-7-fluoro-1-methylindolin-2-one (4j)



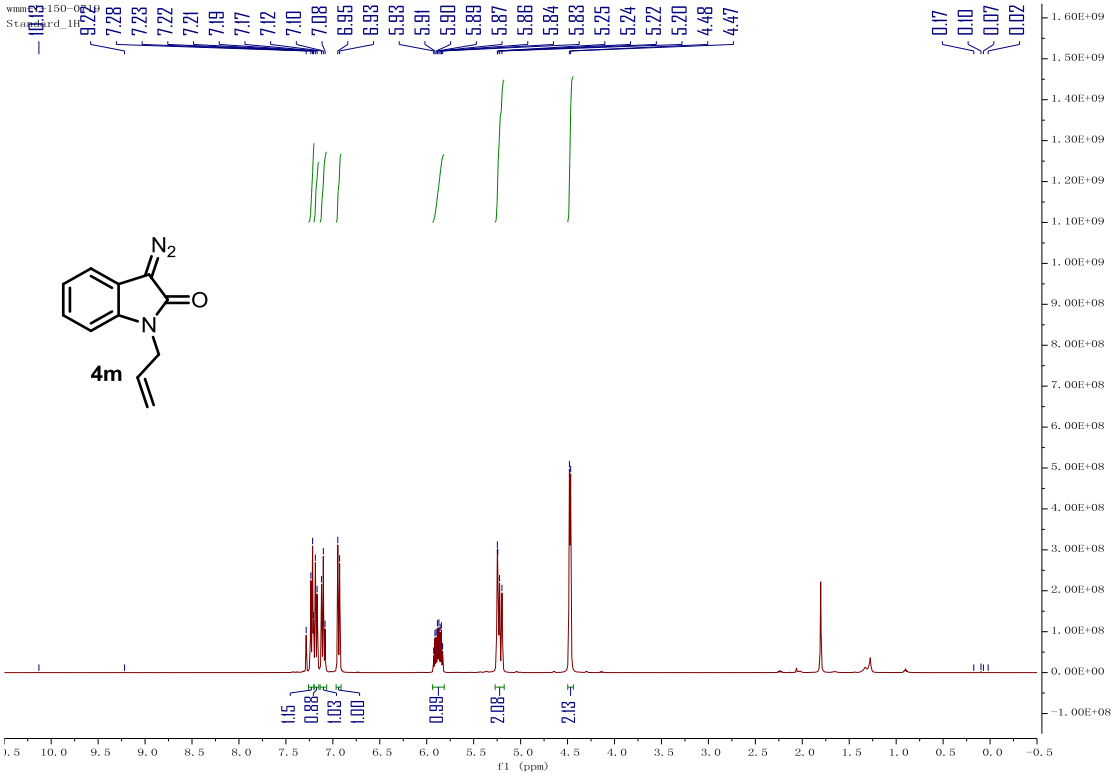
## 3-diazo-1-phenylindolin-2-one (4k)



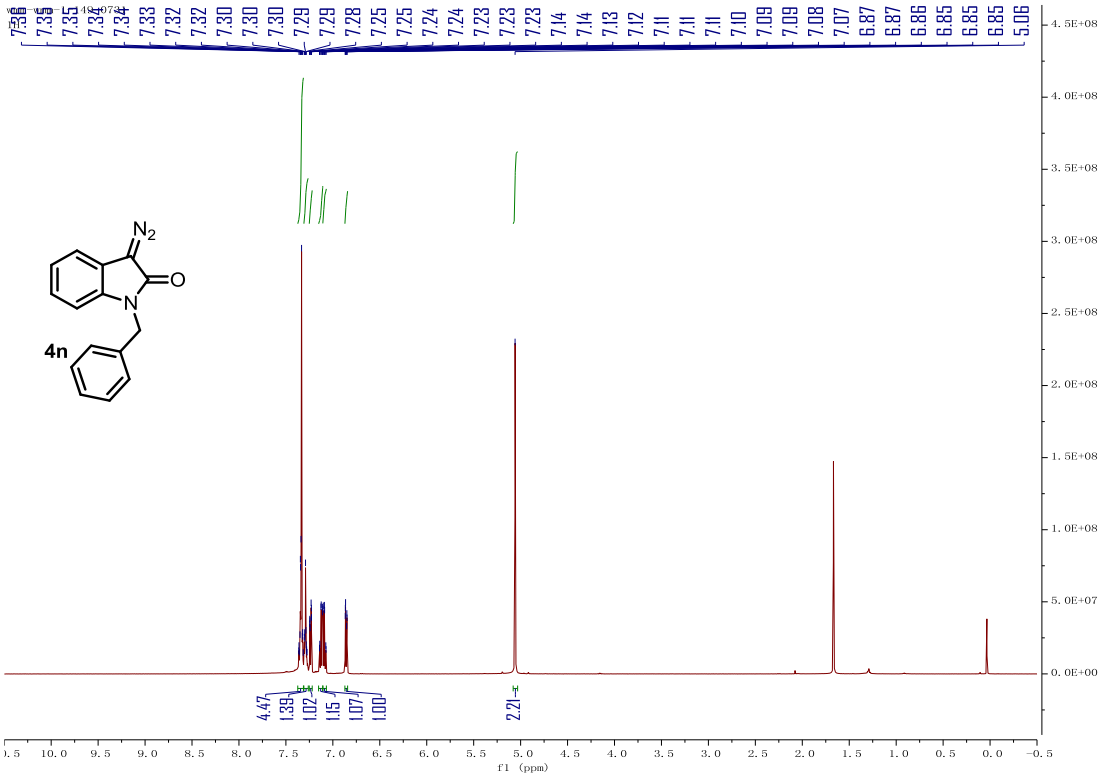

## 3-diazoindolin-2-one (4l)



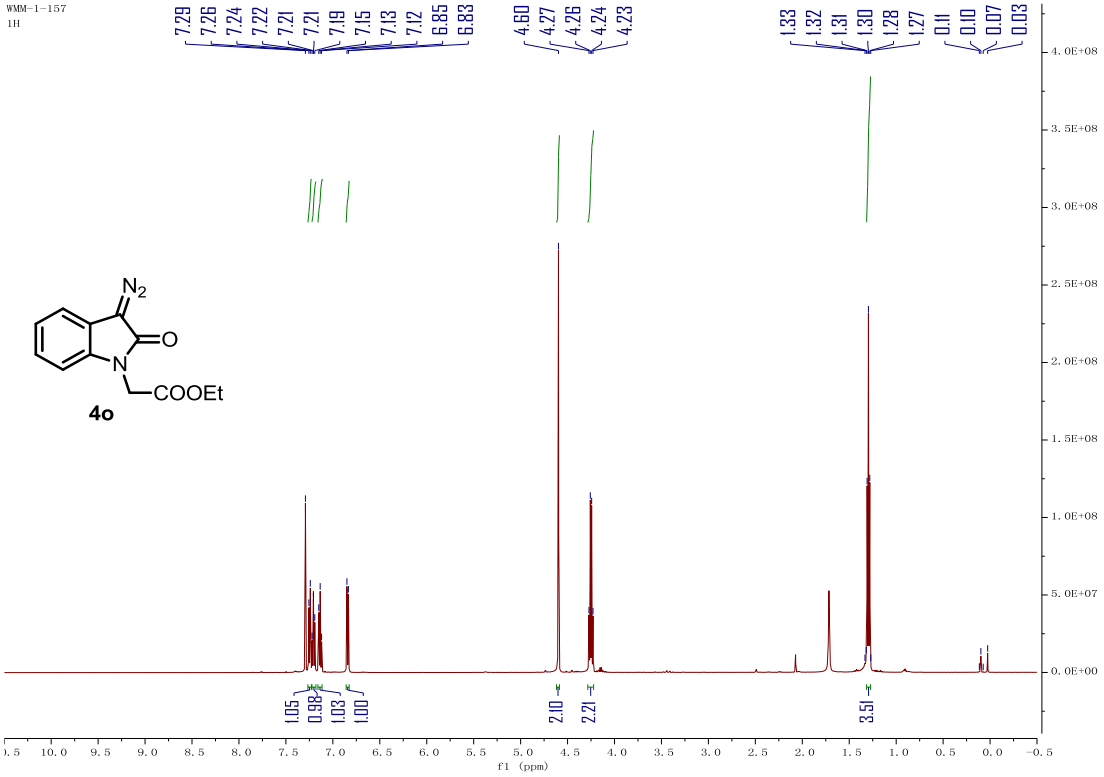
## 1-allyl-3-diazoindolin-2-one (4m)



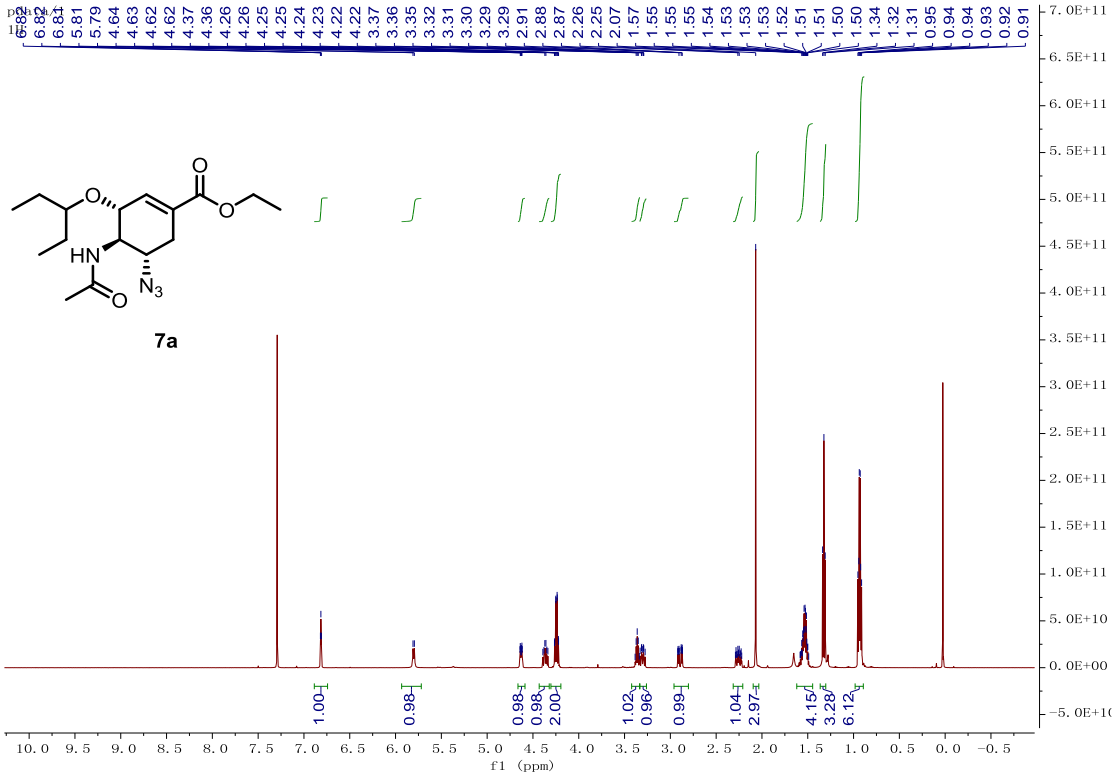

## 1-benzyl-3-diazoindolin-2-one (4n)



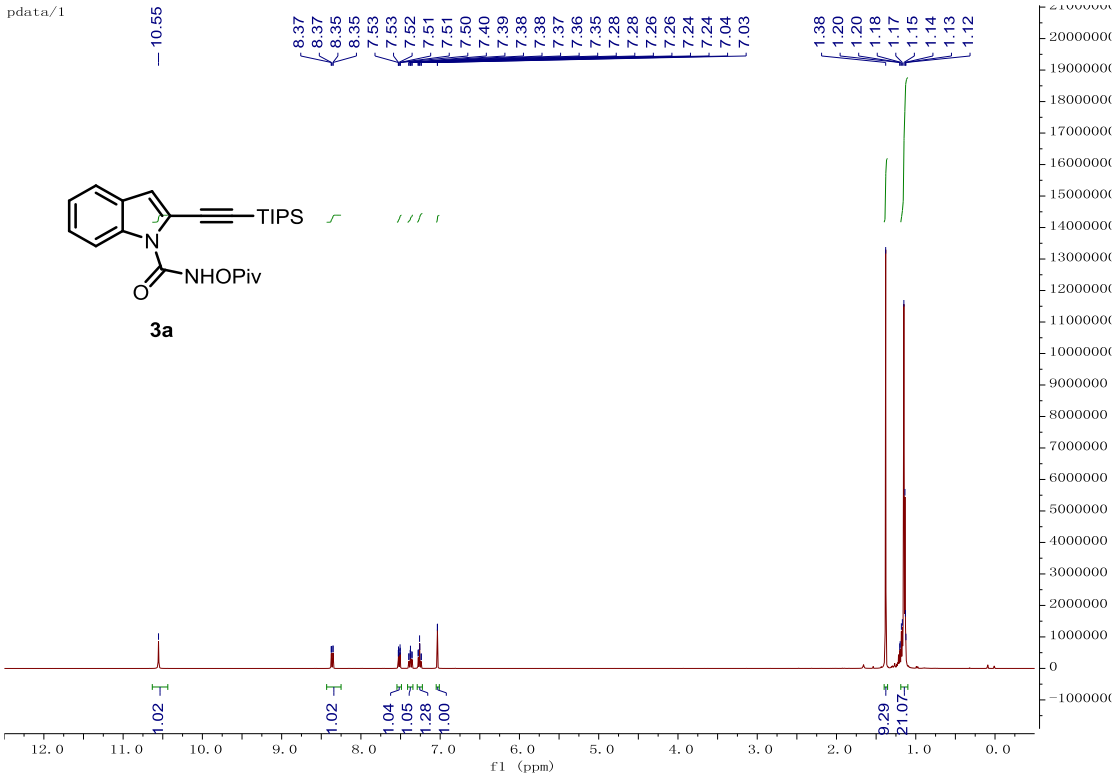
**ethyl 2-(3-diazo-2-oxoindolin-1-yl)acetate (4o)**

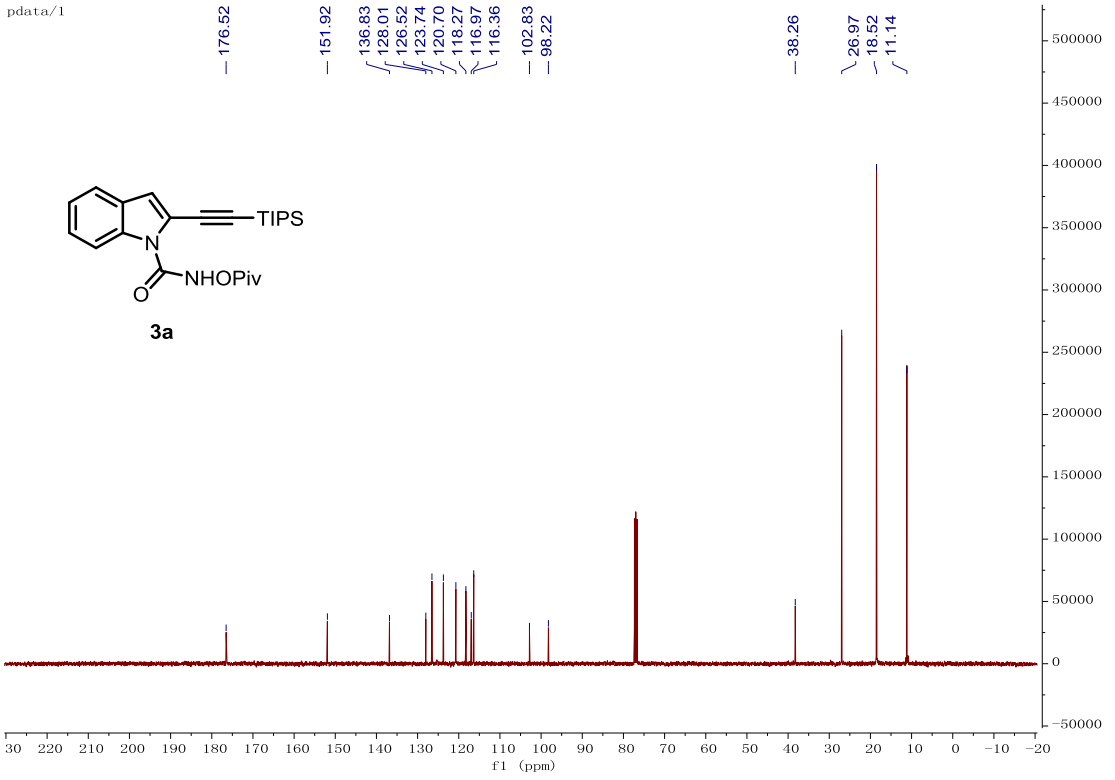



**ethyl (3*R*,4*R*,5*S*)-4-acetamido-5-azido-3-(pentan-3-yloxy)cyclohex-1-ene-1-carboxylate (7a)**

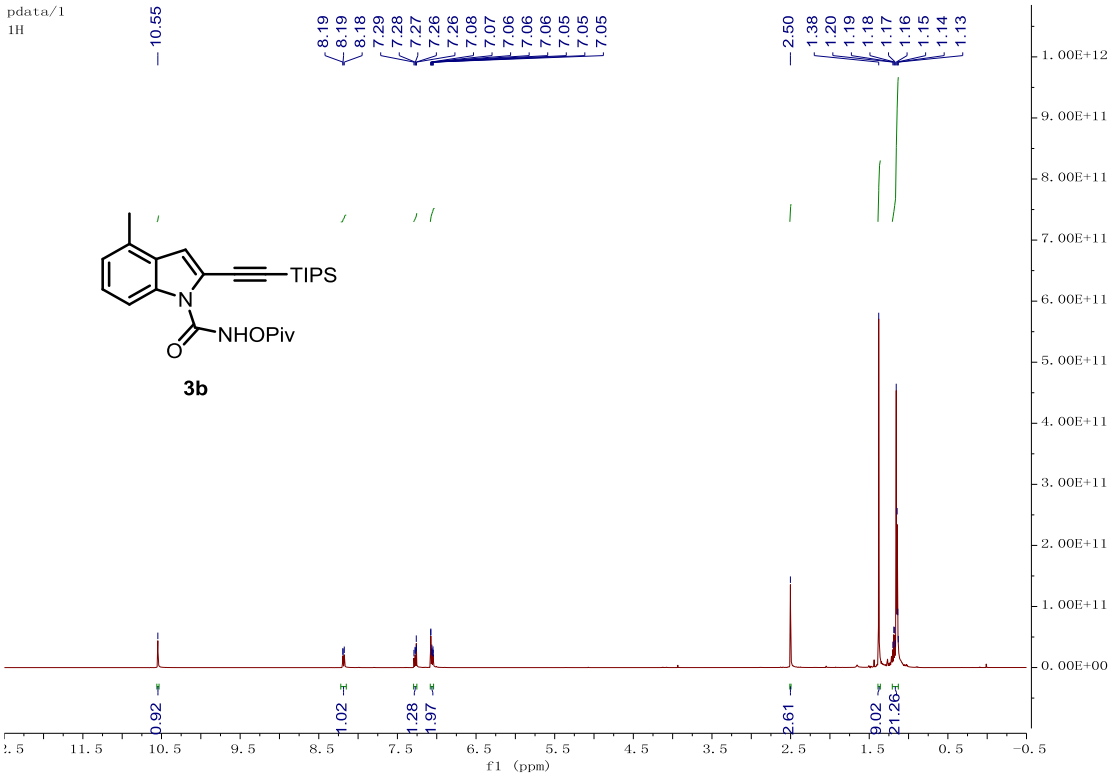


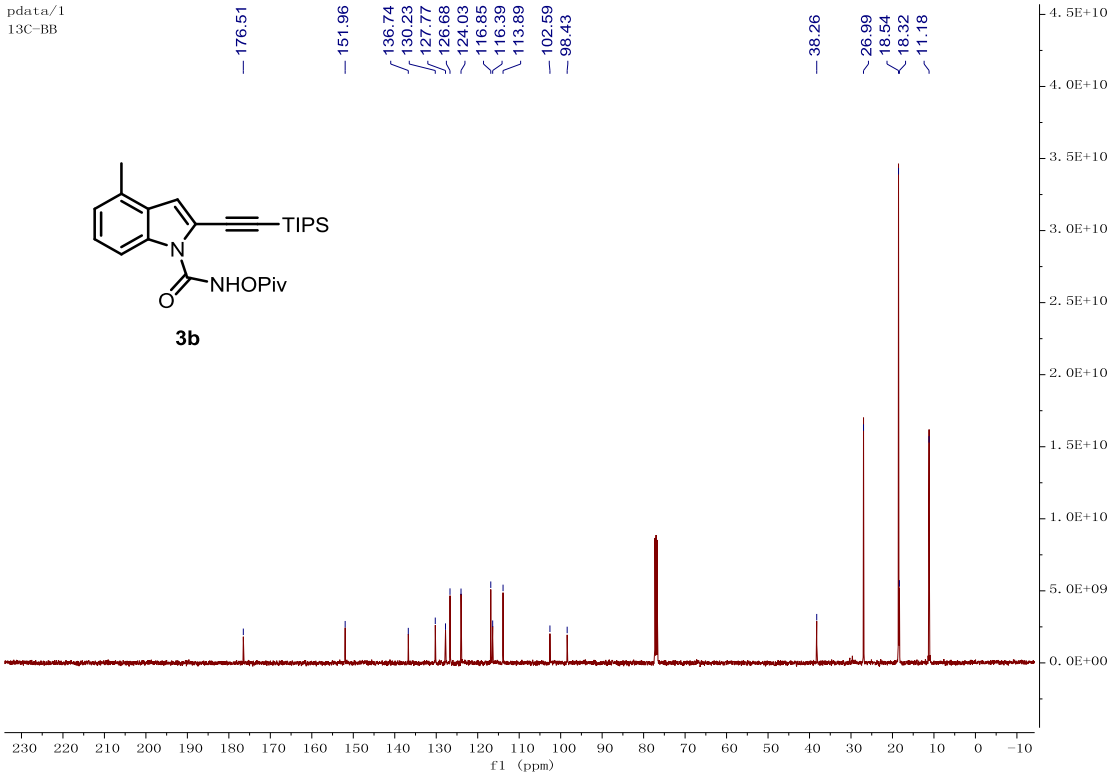
**N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3a)**



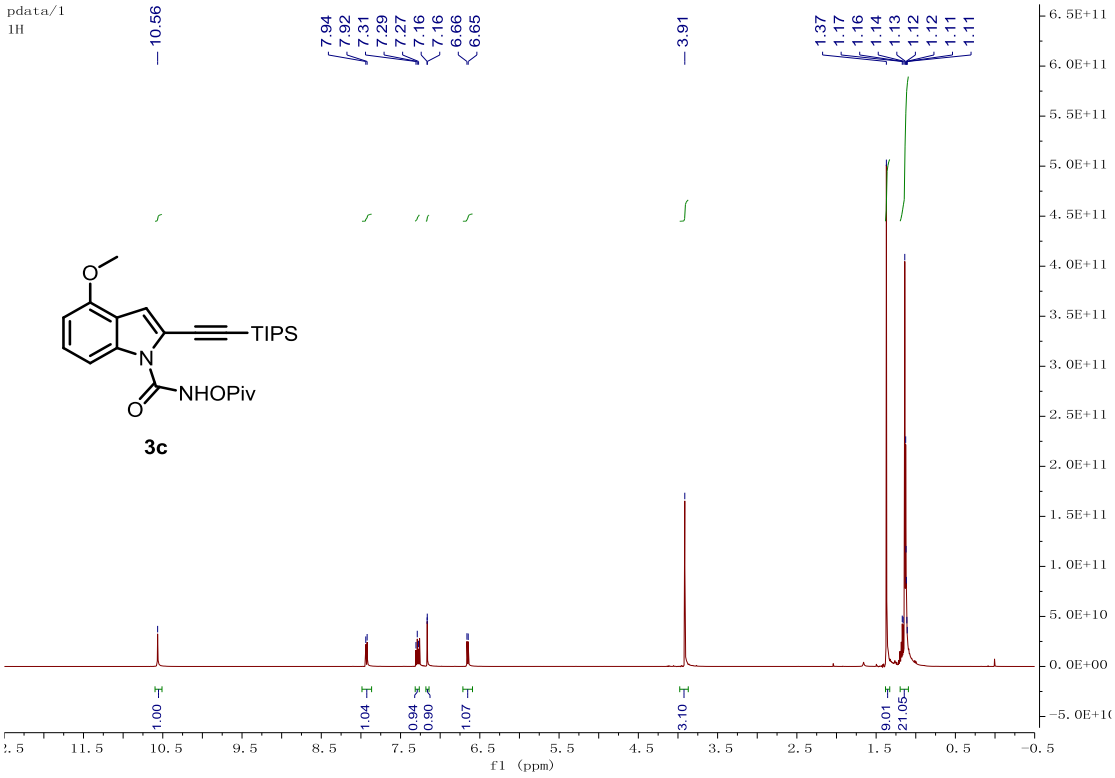



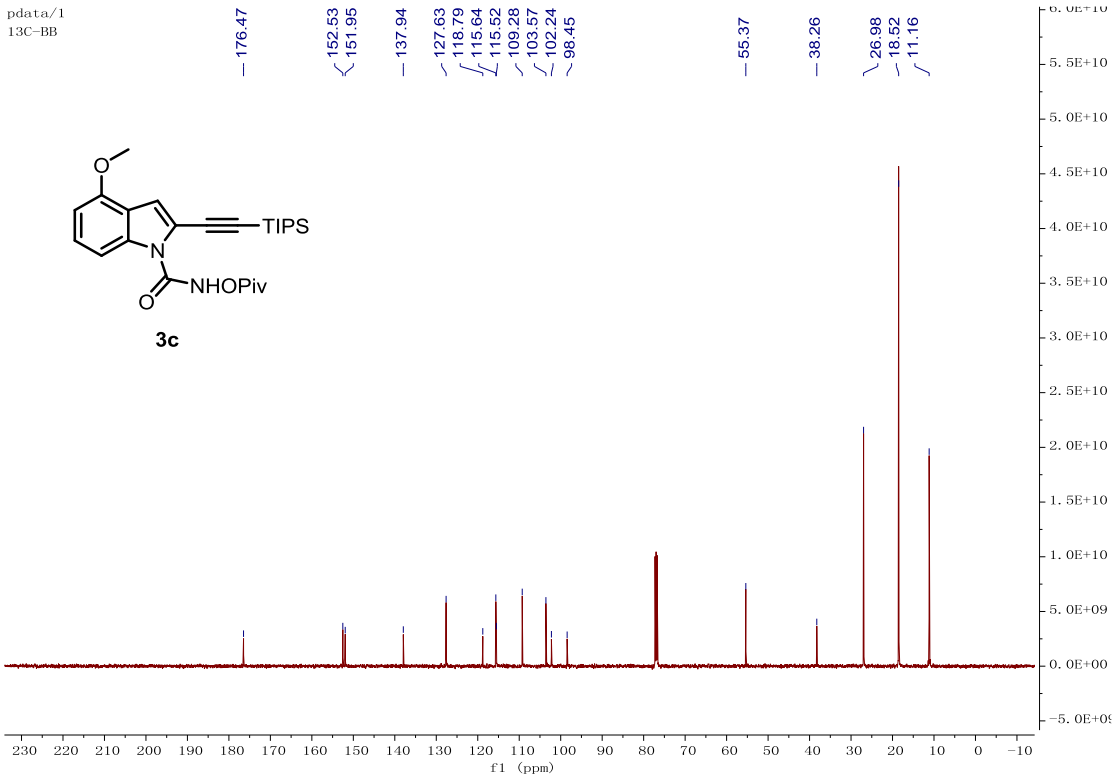
**4-methyl-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3b)**



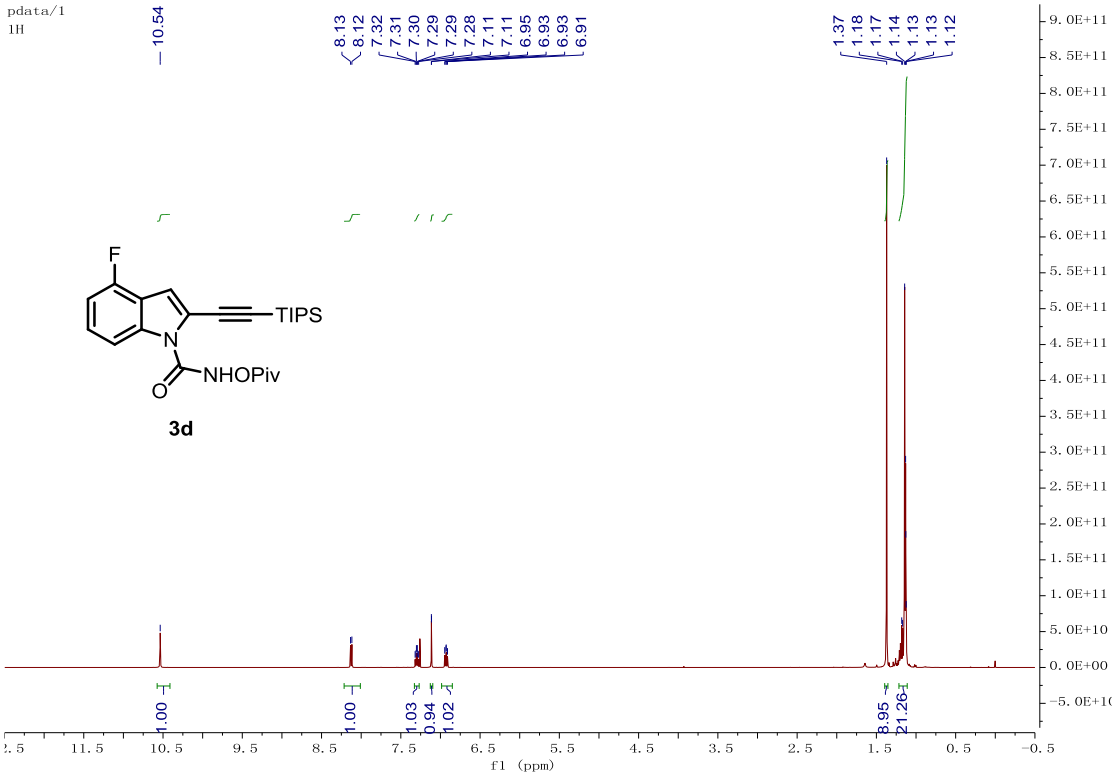



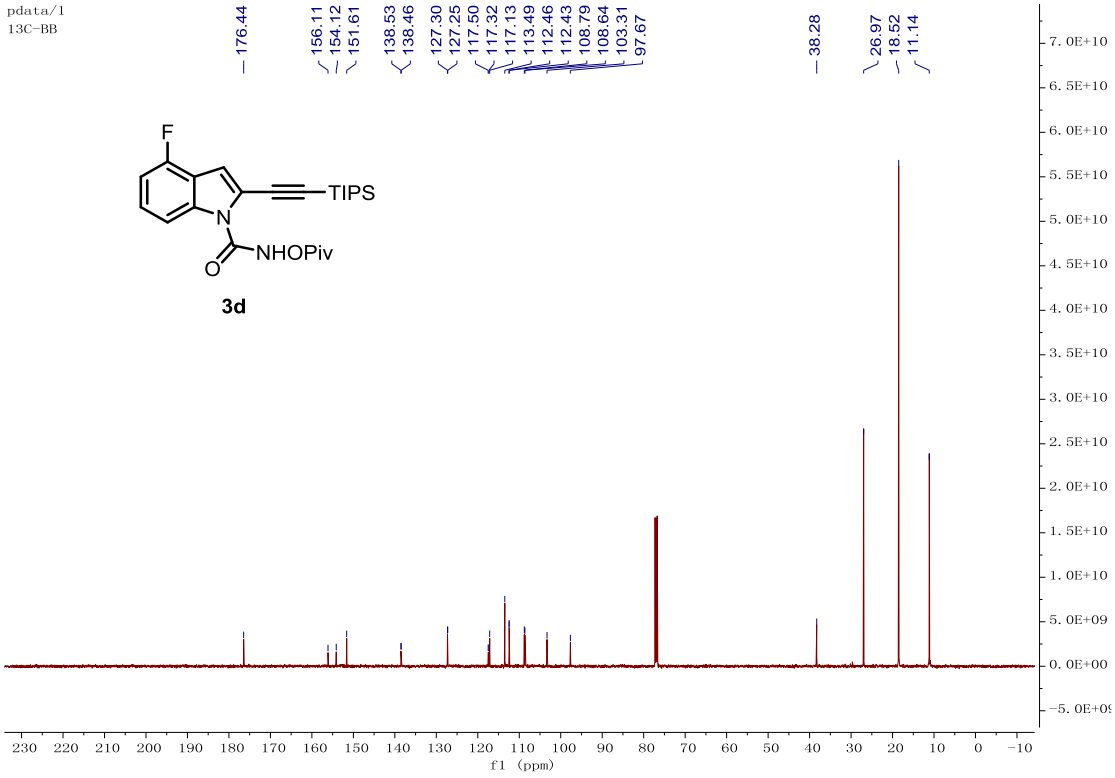
**4-methoxy-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3c)**

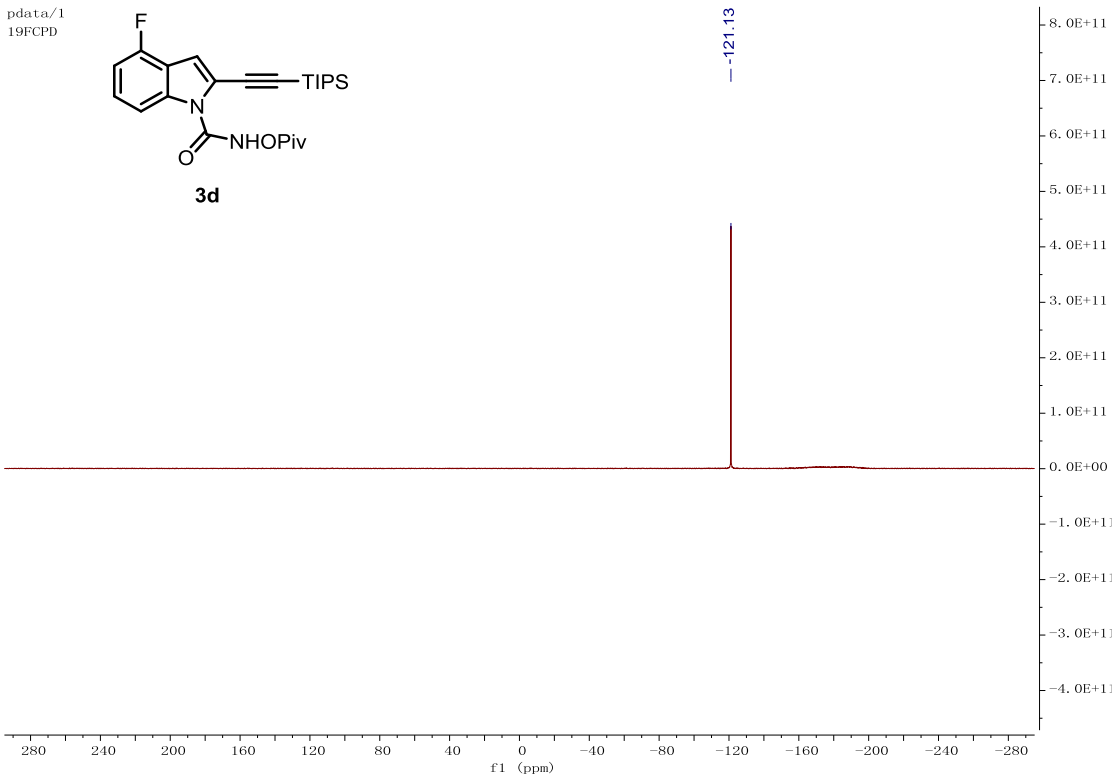


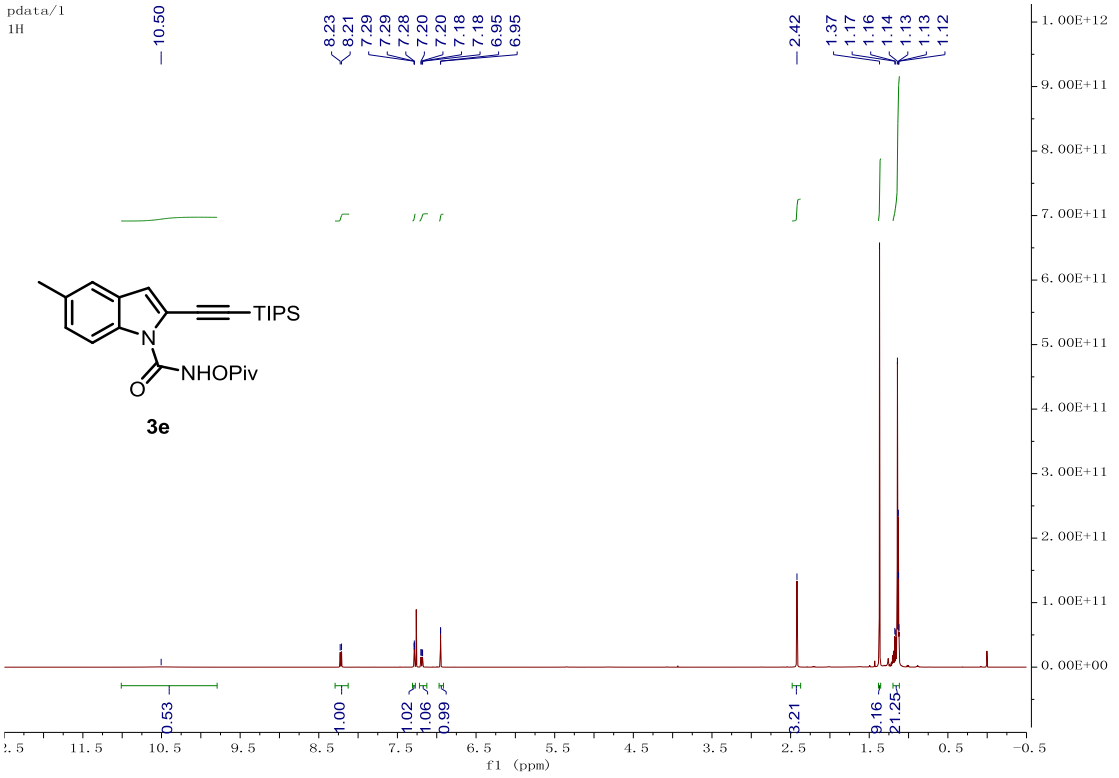
**4-fluoro-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3d)**

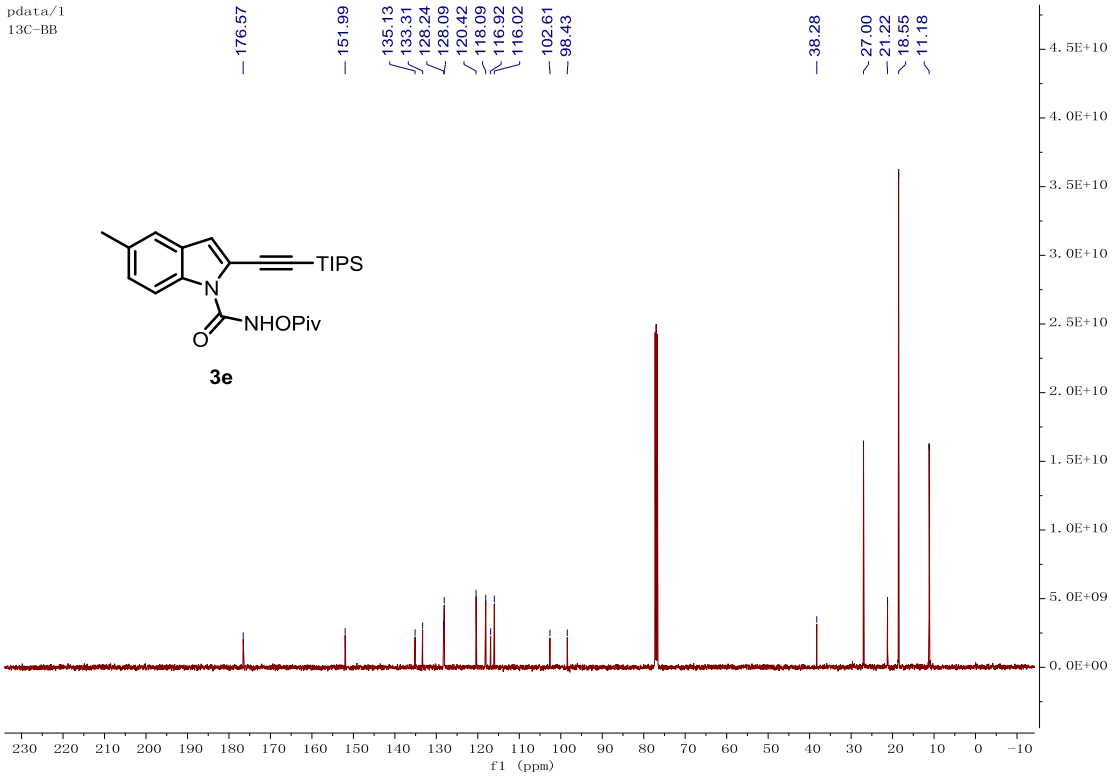


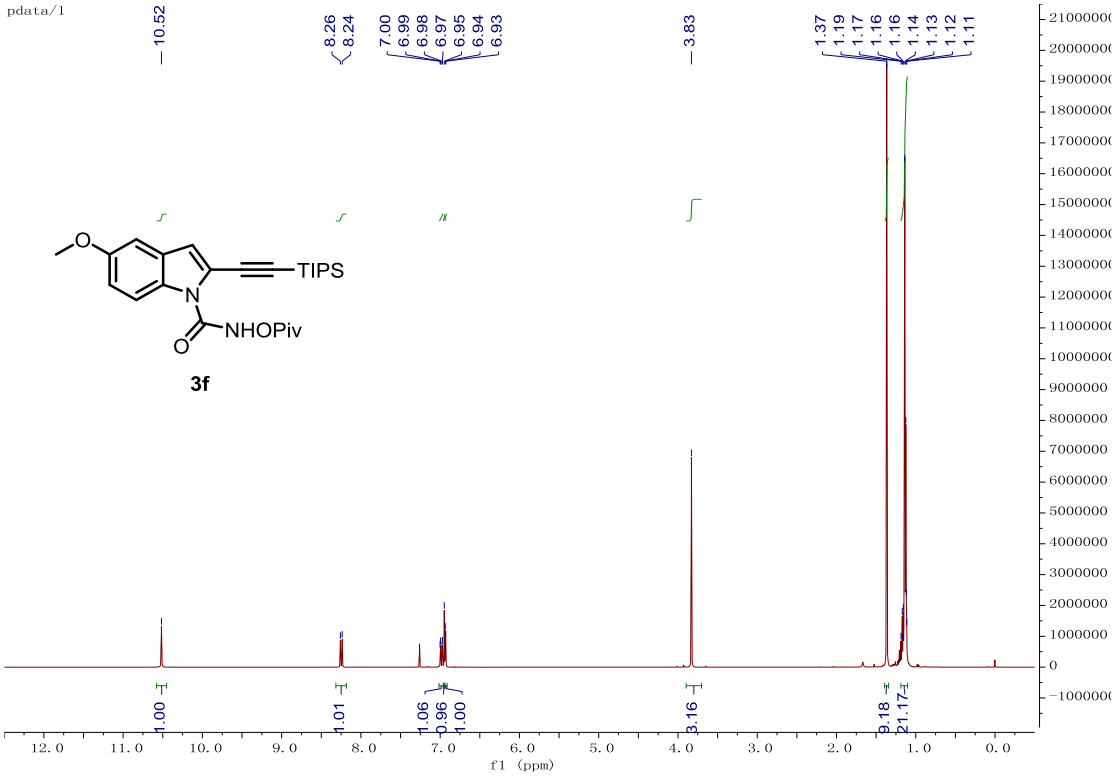


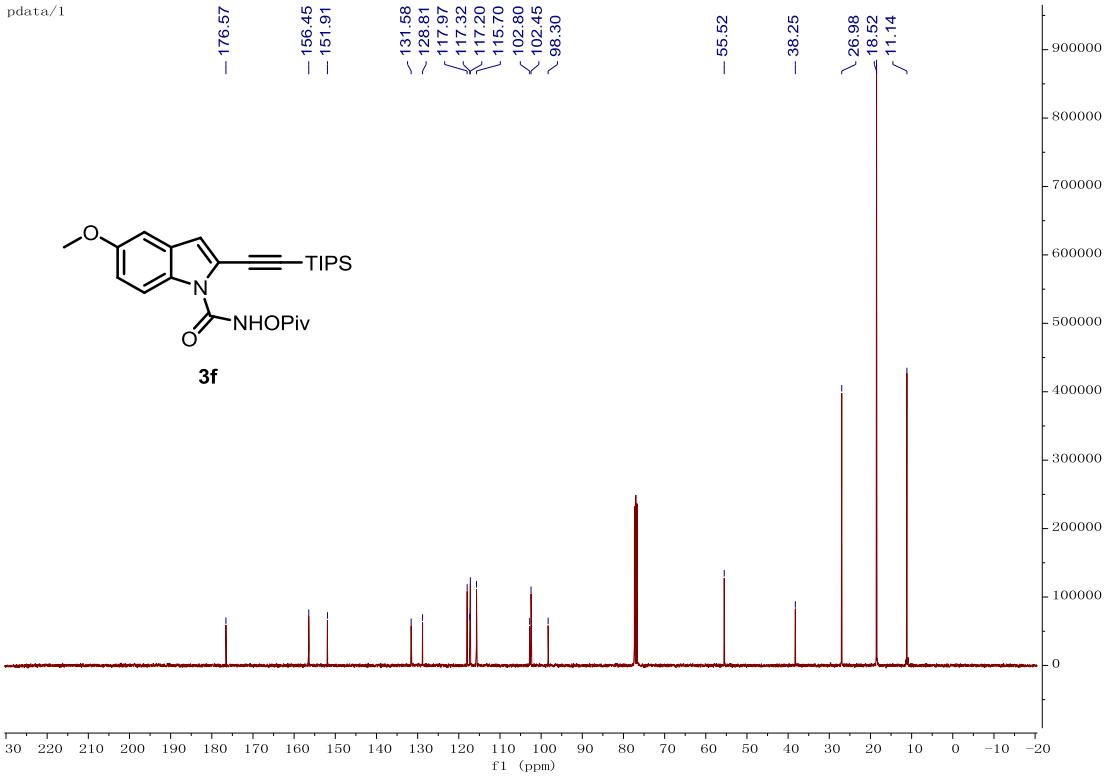

**5-methyl-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3e)**



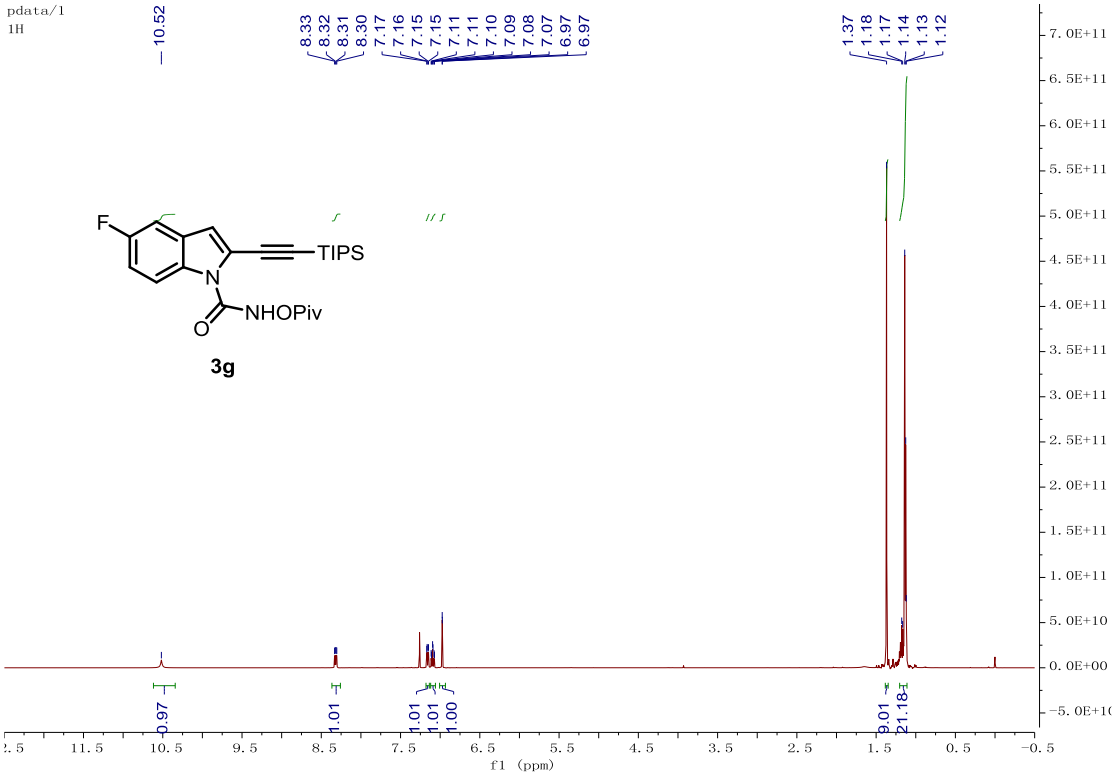


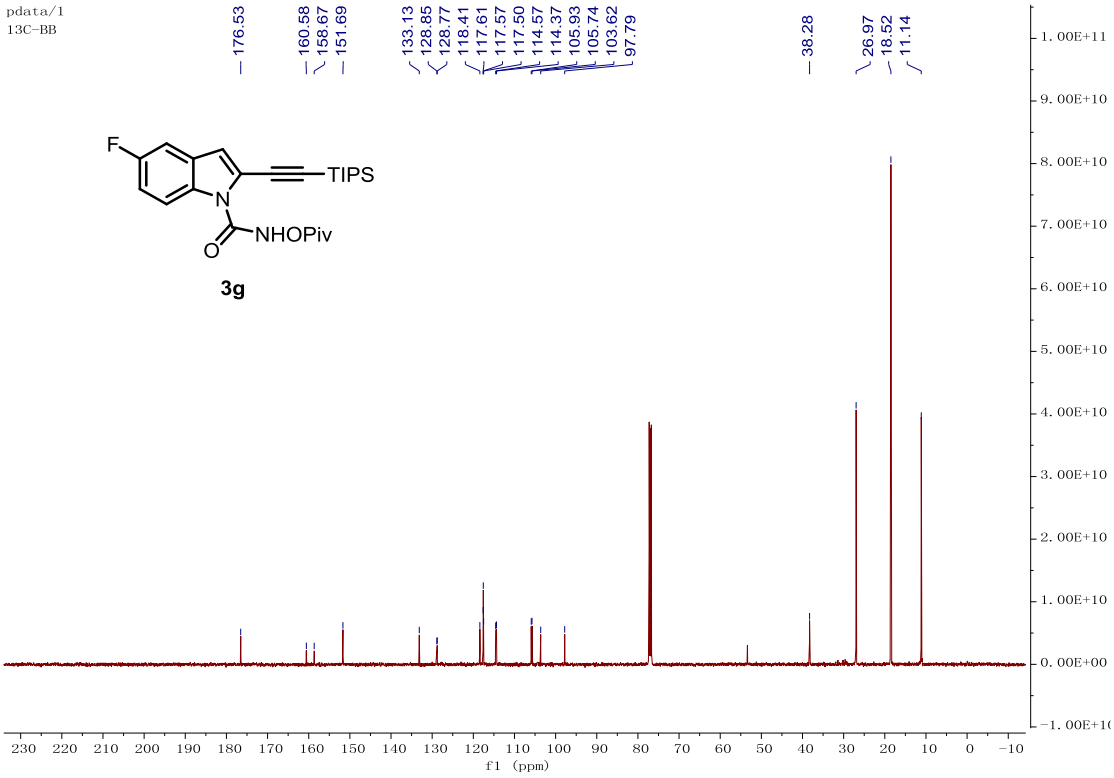

**5-methoxy-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3f)**

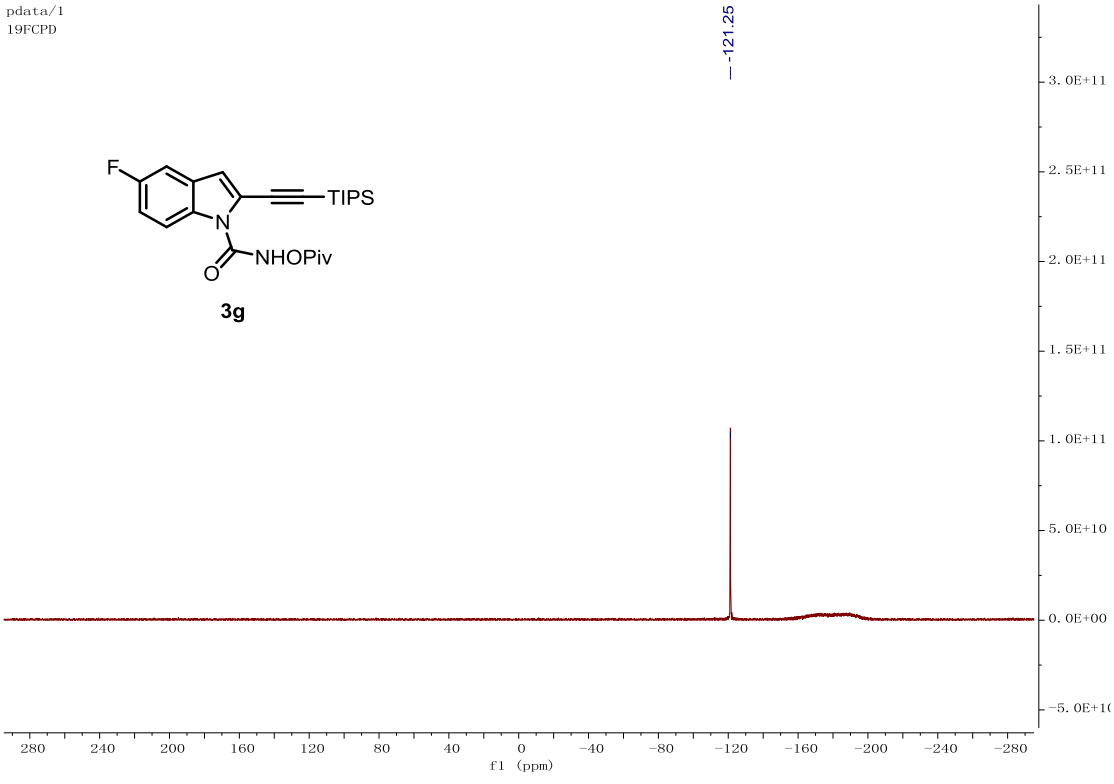




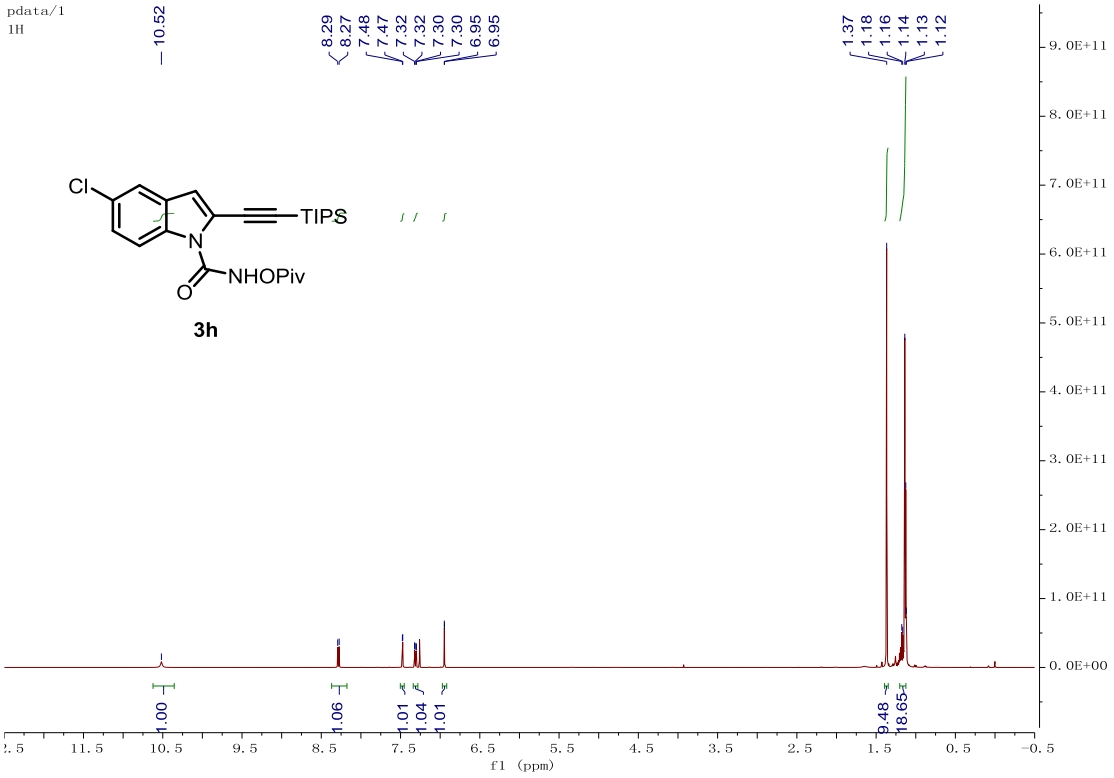

**5-fluoro-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3g)**

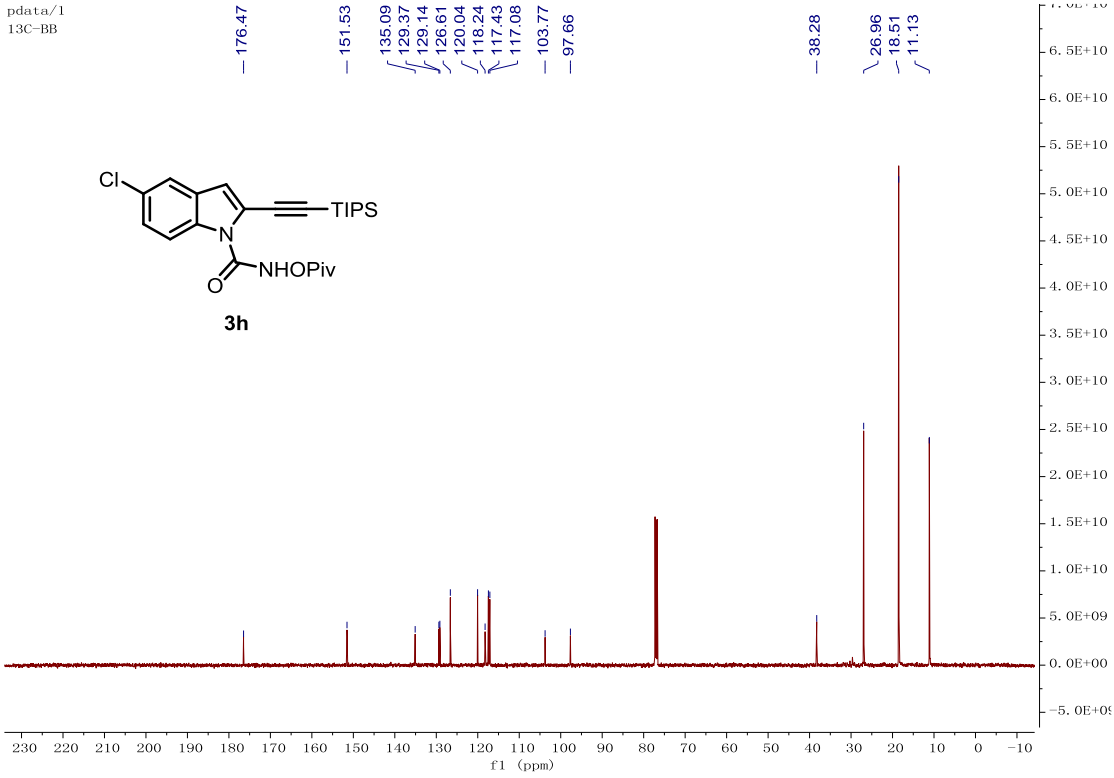



pdata/1
13C-BB
176.53
160.58
158.67
151.69
133.13
128.85
128.77
118.41
117.61
117.57
117.50
114.57
114.37
105.93
105.74
103.62
97.79
38.28
26.97
18.52
11.14
F
TIPS
N
O
NHOPiv
3g
f1 (ppm)

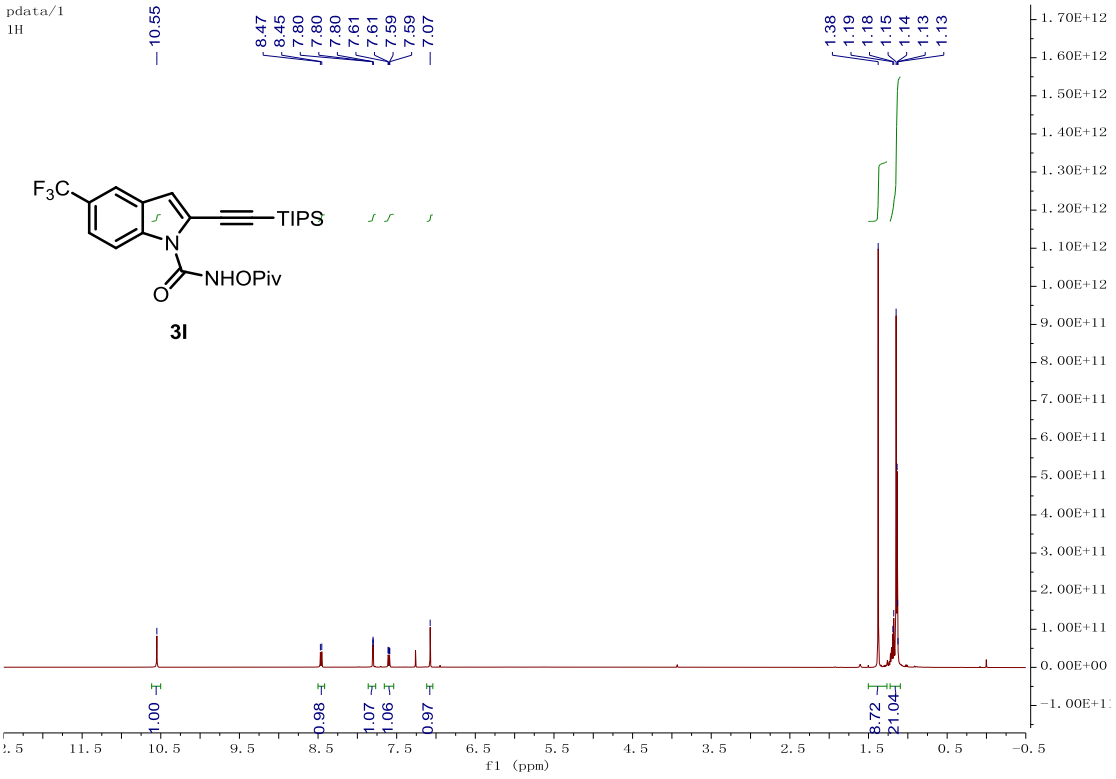

pdata/1
19FCPD
-121.25
F
TIPS
N
O
NHOPiv
3g
f1 (ppm)

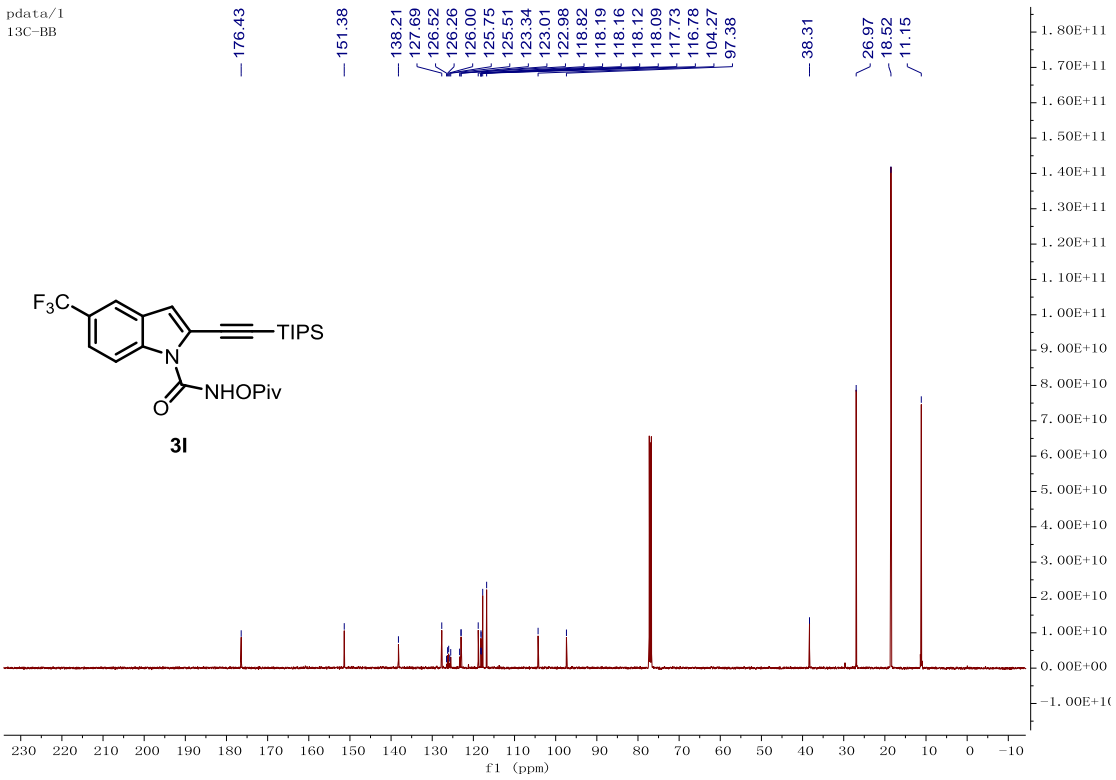
**5-chloro-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3h)**

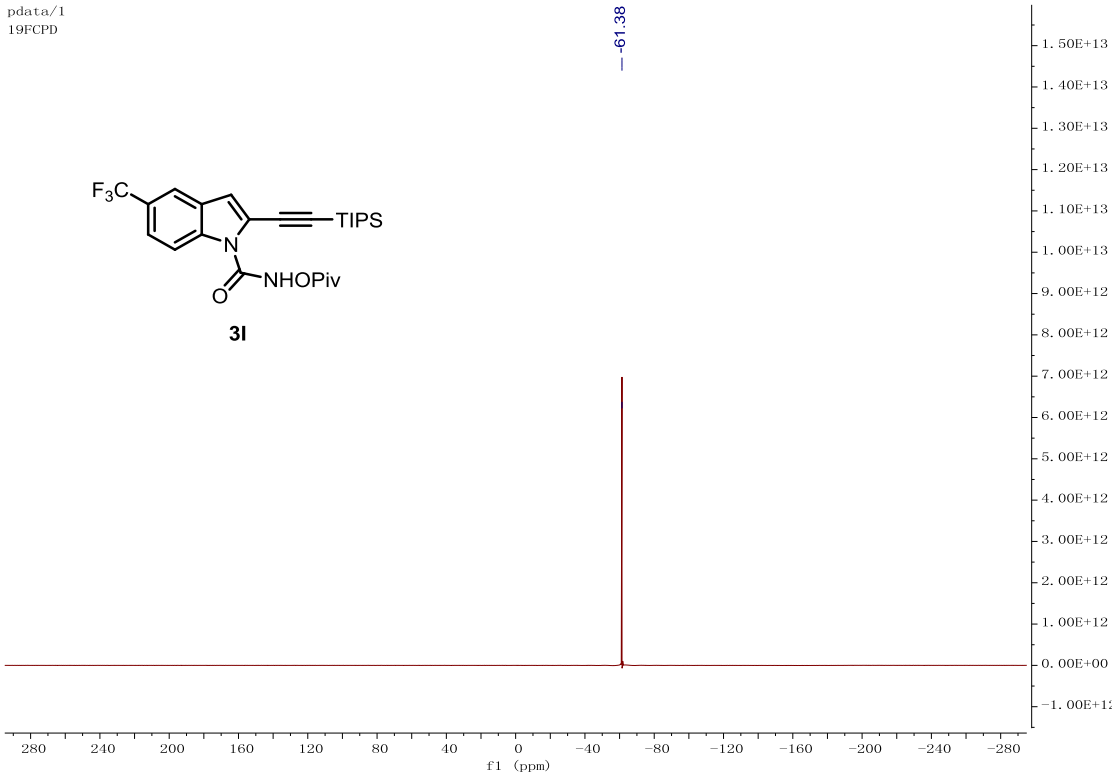


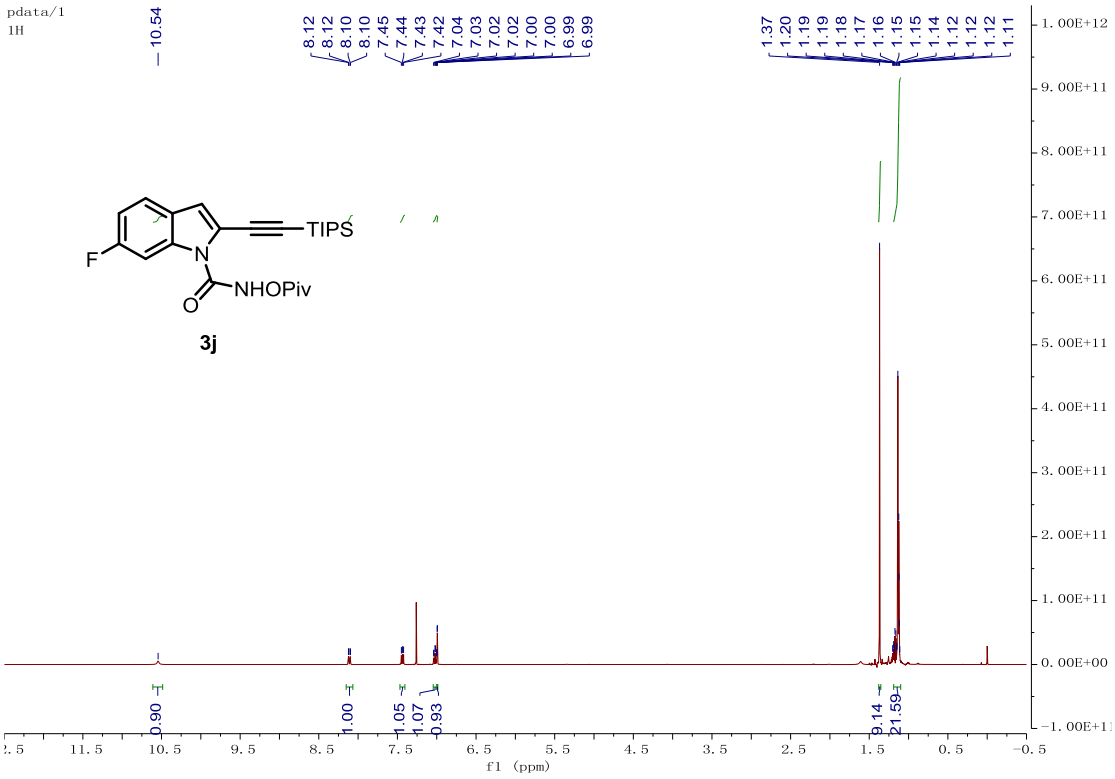
**N-(pivaloyloxy)-5-(trifluoromethyl)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3i)**

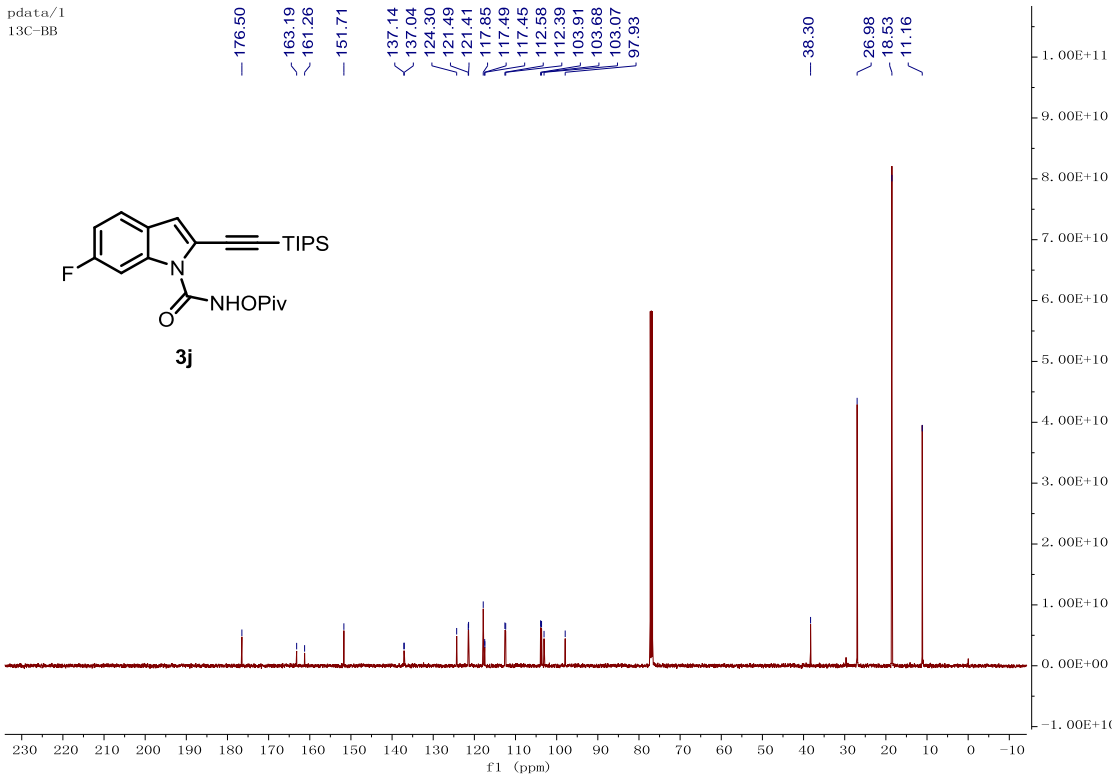


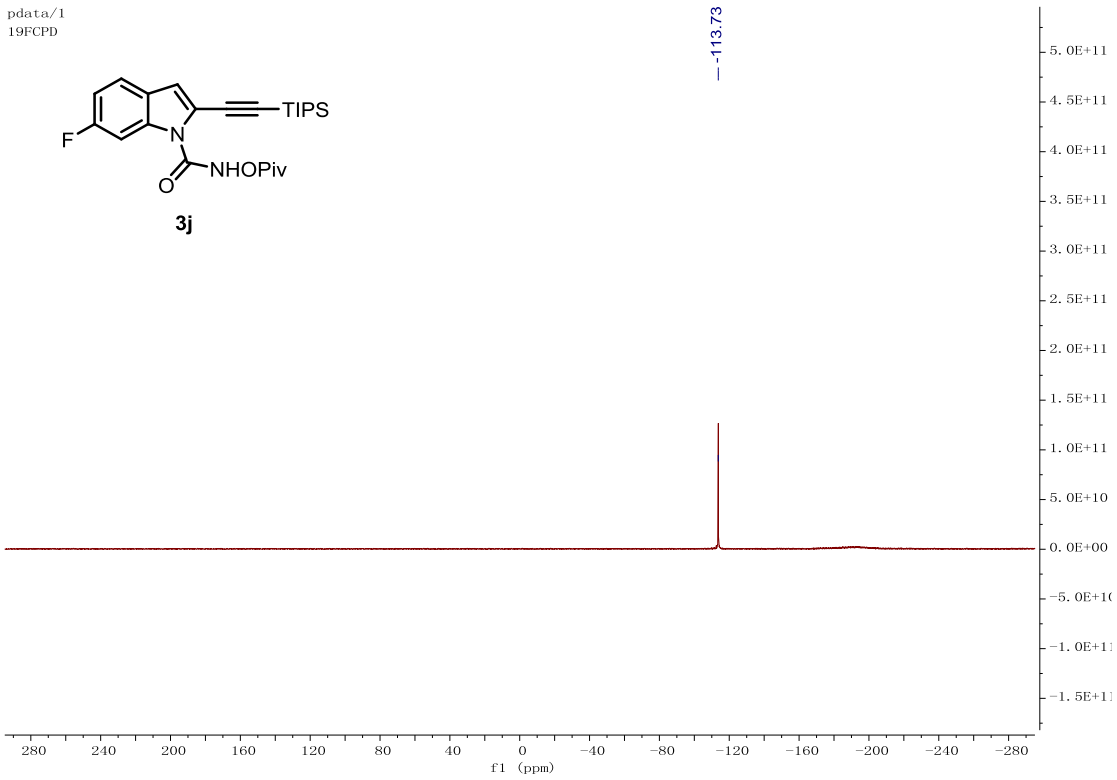




pdata/1
19FCPD
-61.38
F3C
TIPS
N
O
NHOPiv
3l
1.50E+13
1.40E+13
1.30E+13
1.20E+13
1.10E+13
1.00E+13
9.00E+12
8.00E+12
7.00E+12
6.00E+12
5.00E+12
4.00E+12
3.00E+12
2.00E+12
1.00E+12
0.00E+00
280
240
200
160
120
80
40
0
-40
-80
-120
-160
-200
-240
-280
f1 (ppm)

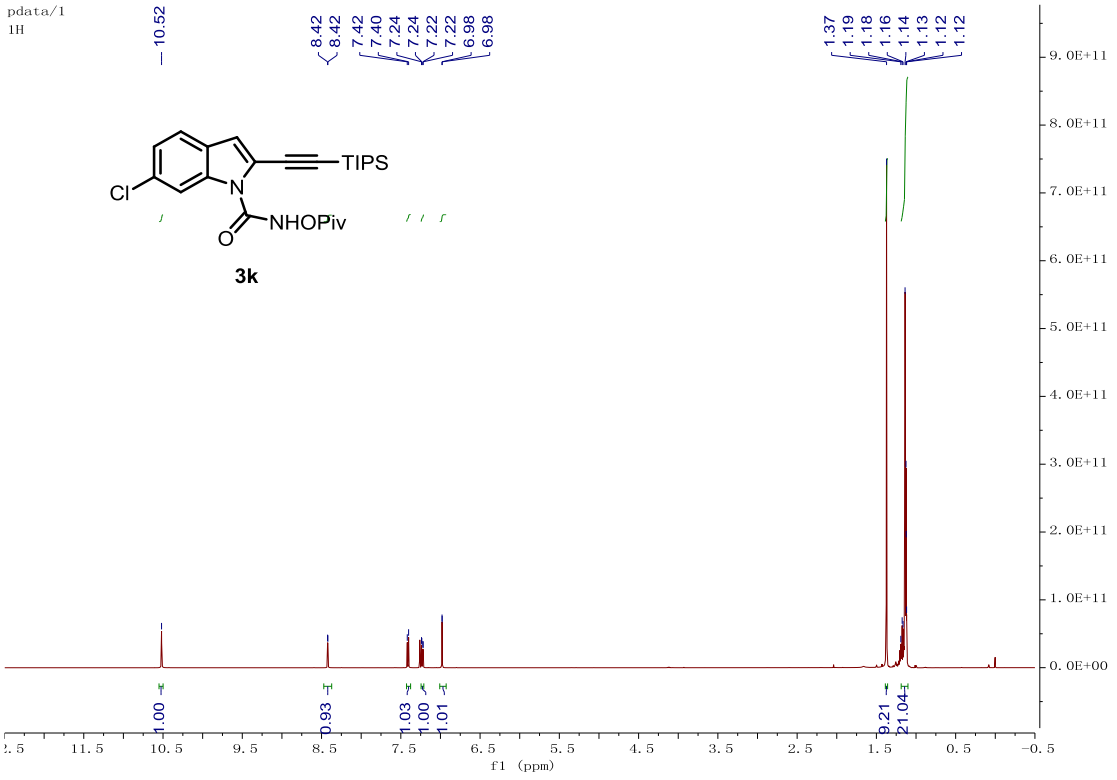
**6-fluoro-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3j)**

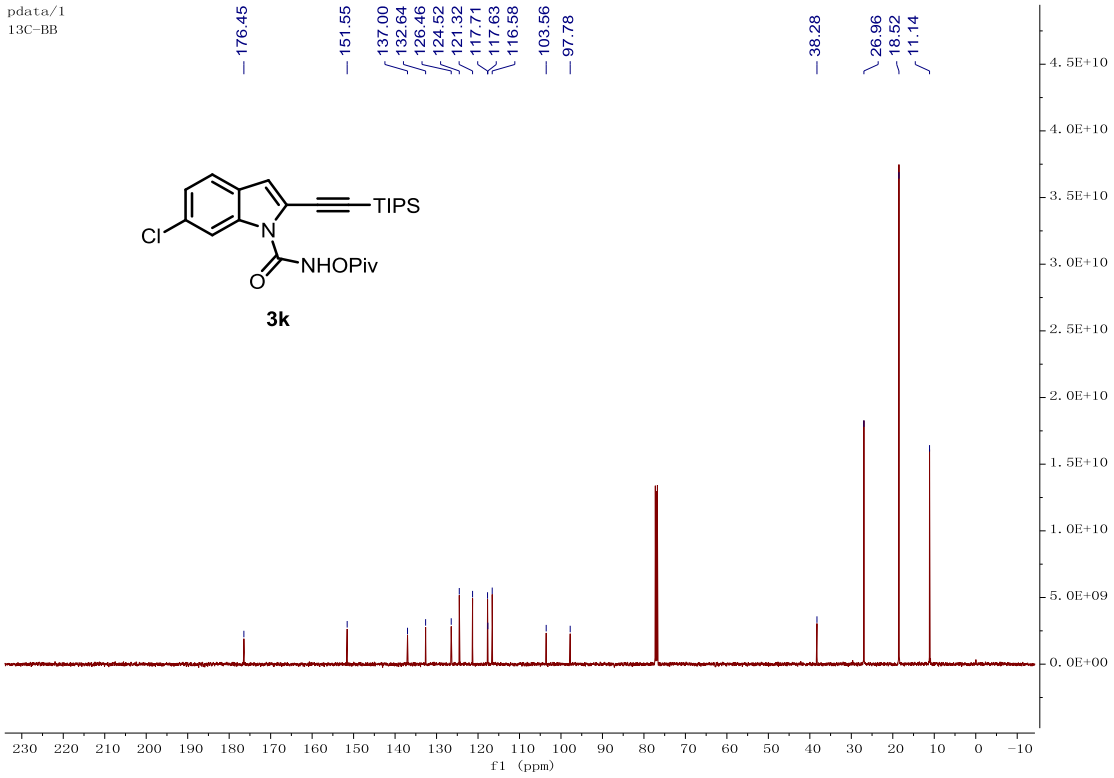


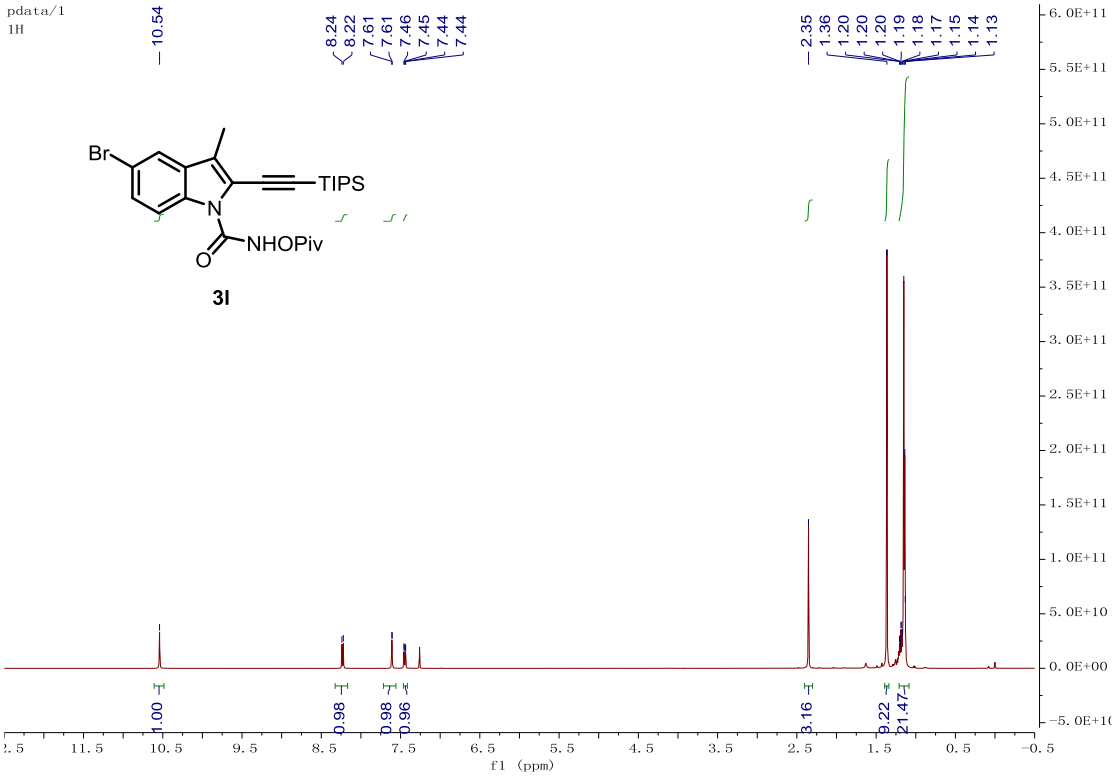


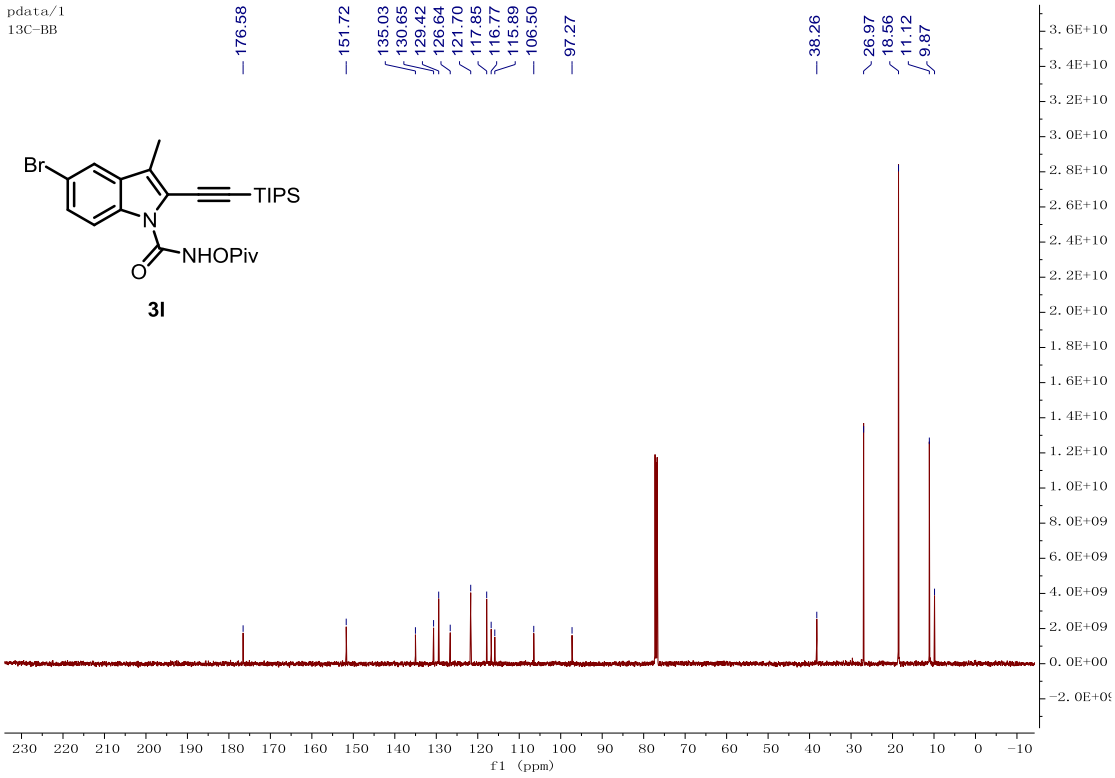

**6-chloro-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3k)**



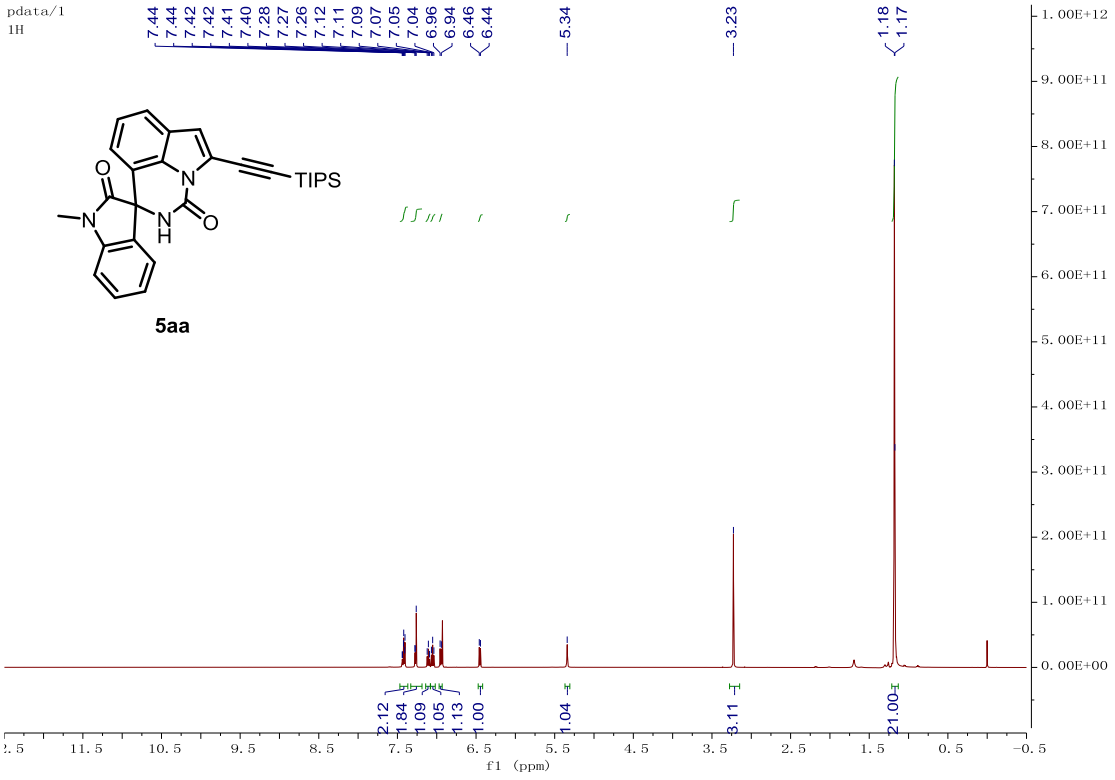


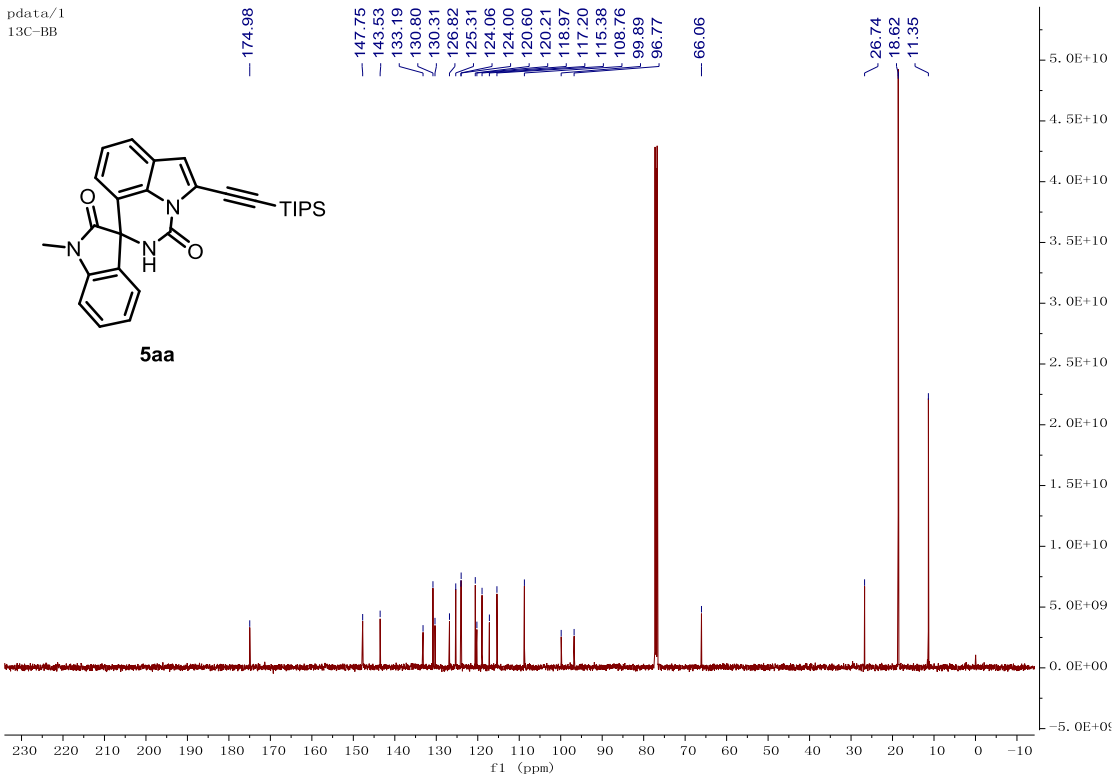

**5-bromo-3-methyl-N-(pivaloyloxy)-2-((triisopropylsilyl)ethynyl)-1*H*-indole-1-carboxamide (3l)**



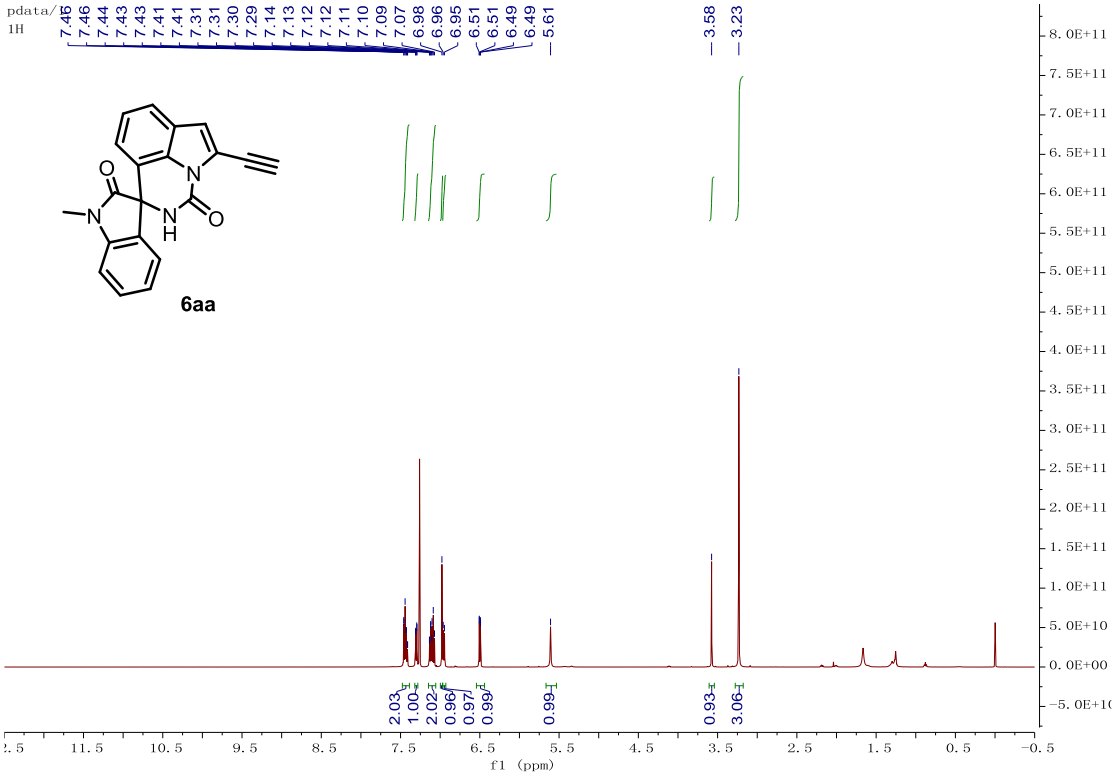


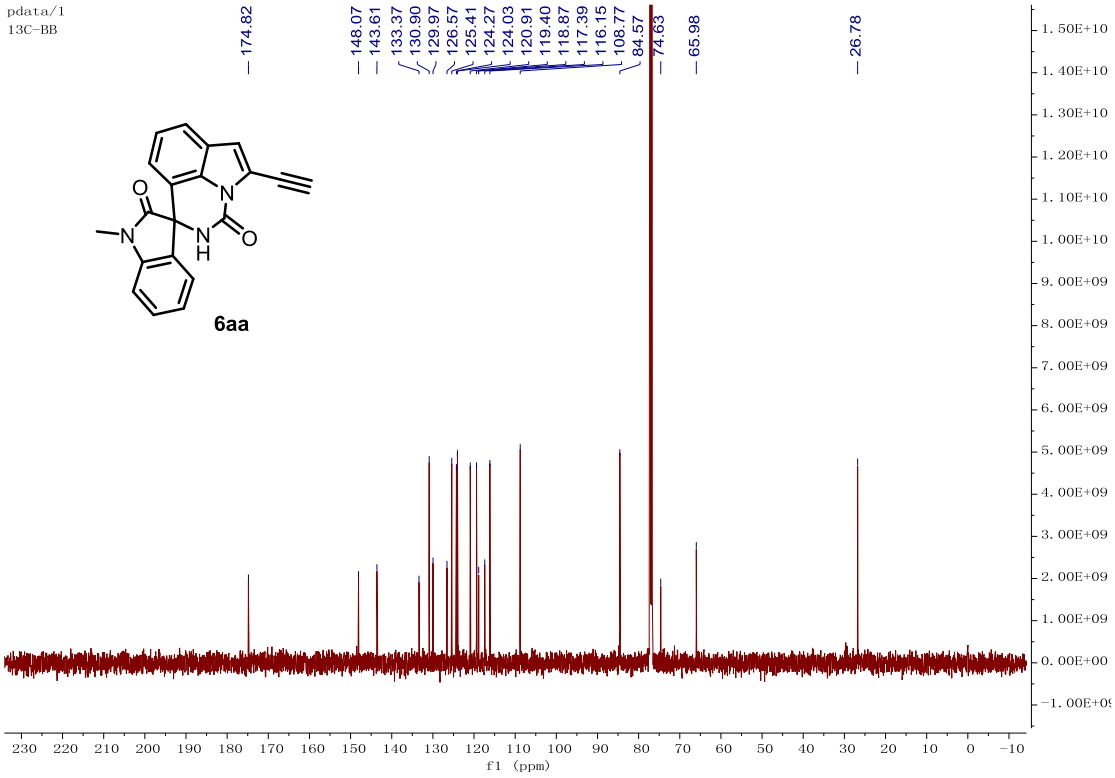

**1-methyl-5'-((triisopropylsilyl)ethynyl)spiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (5aa)**



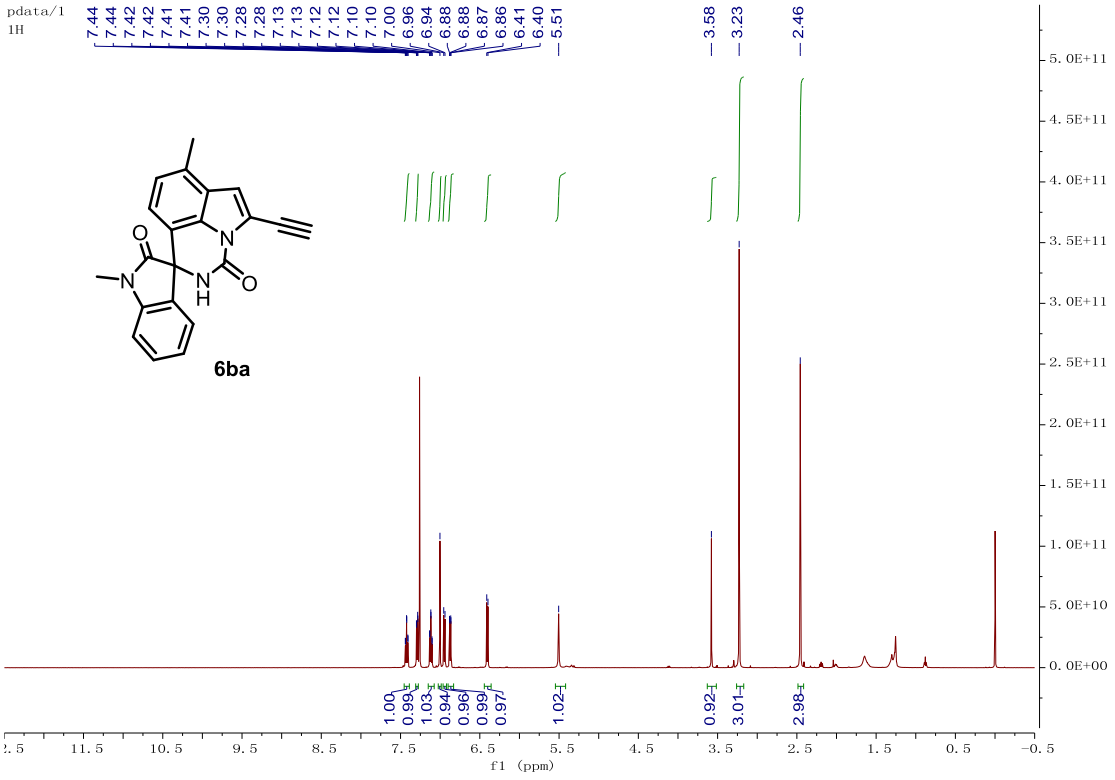


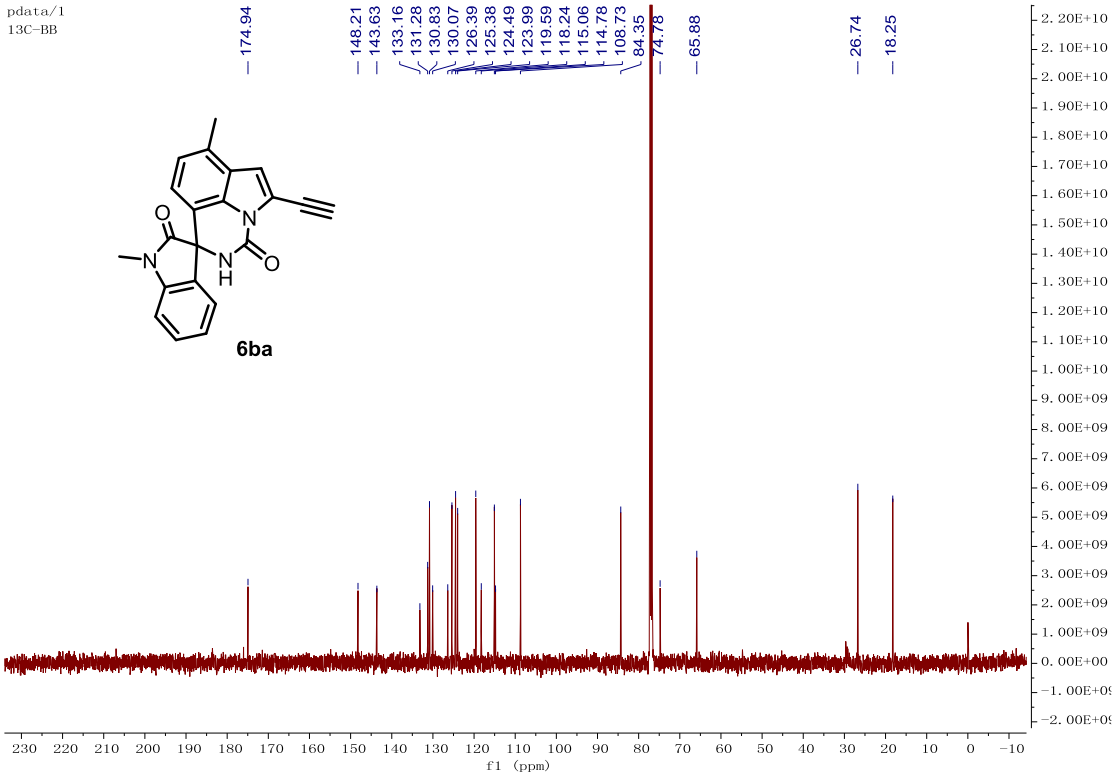

**5'-ethynyl-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6aa)**



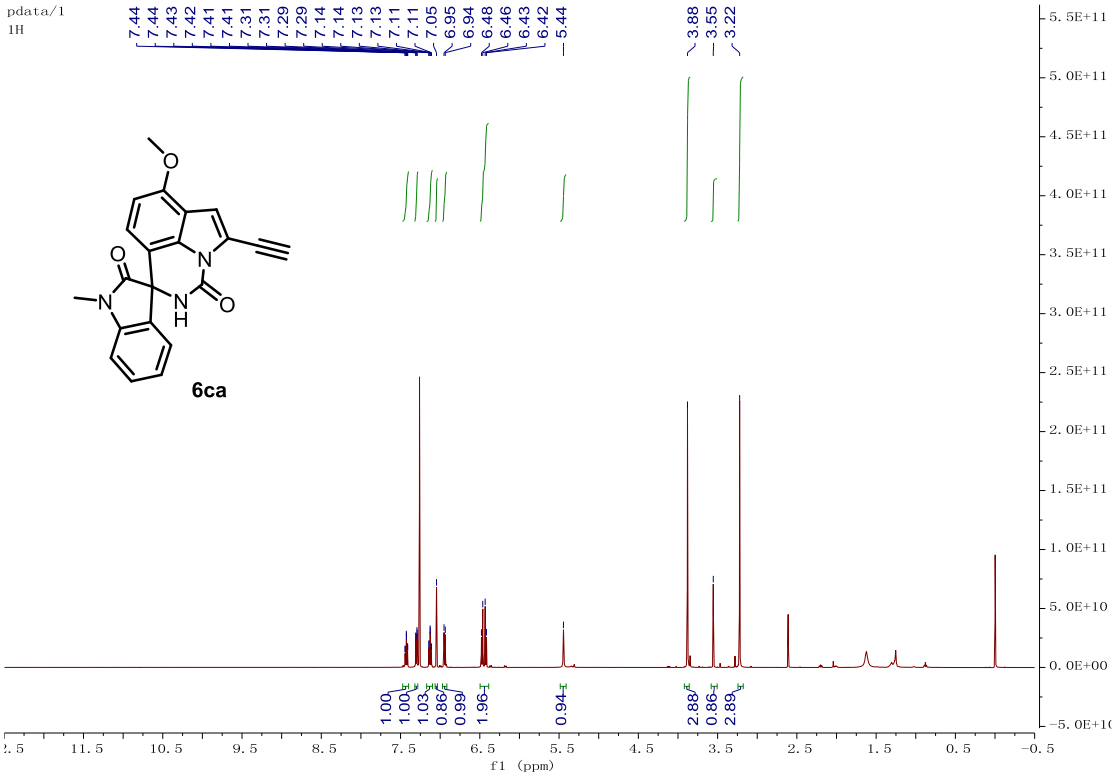


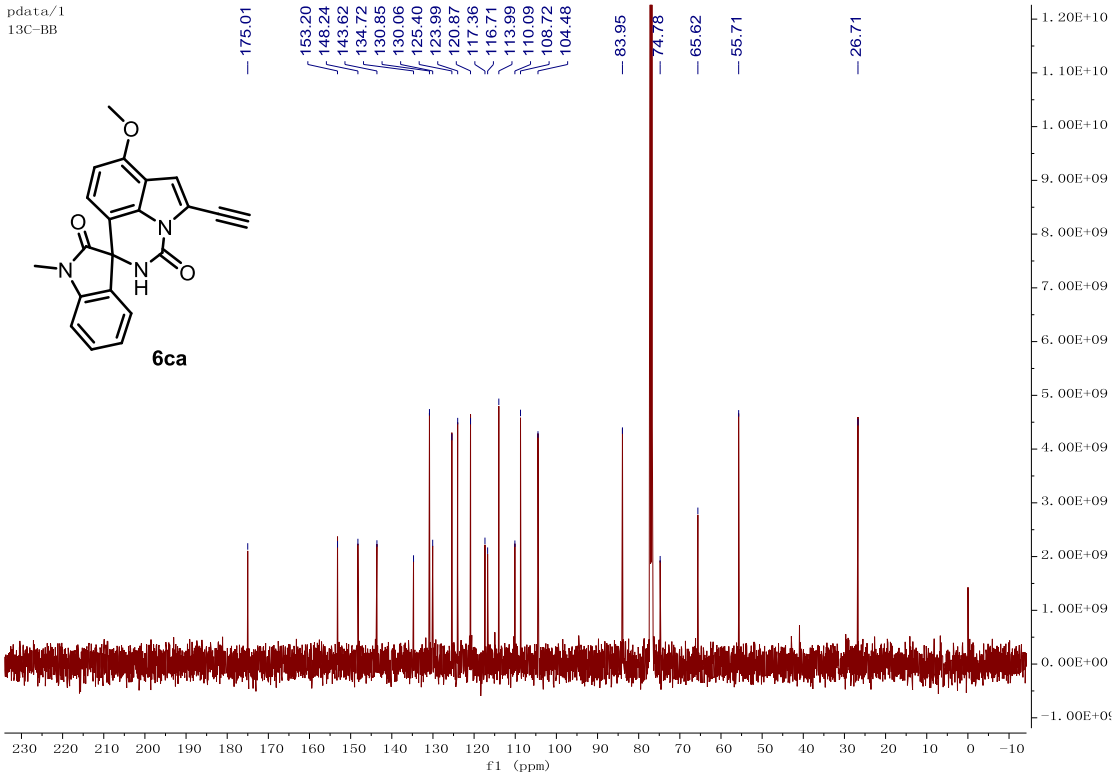

**5'-ethynyl-1,7'-dimethylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ba)**



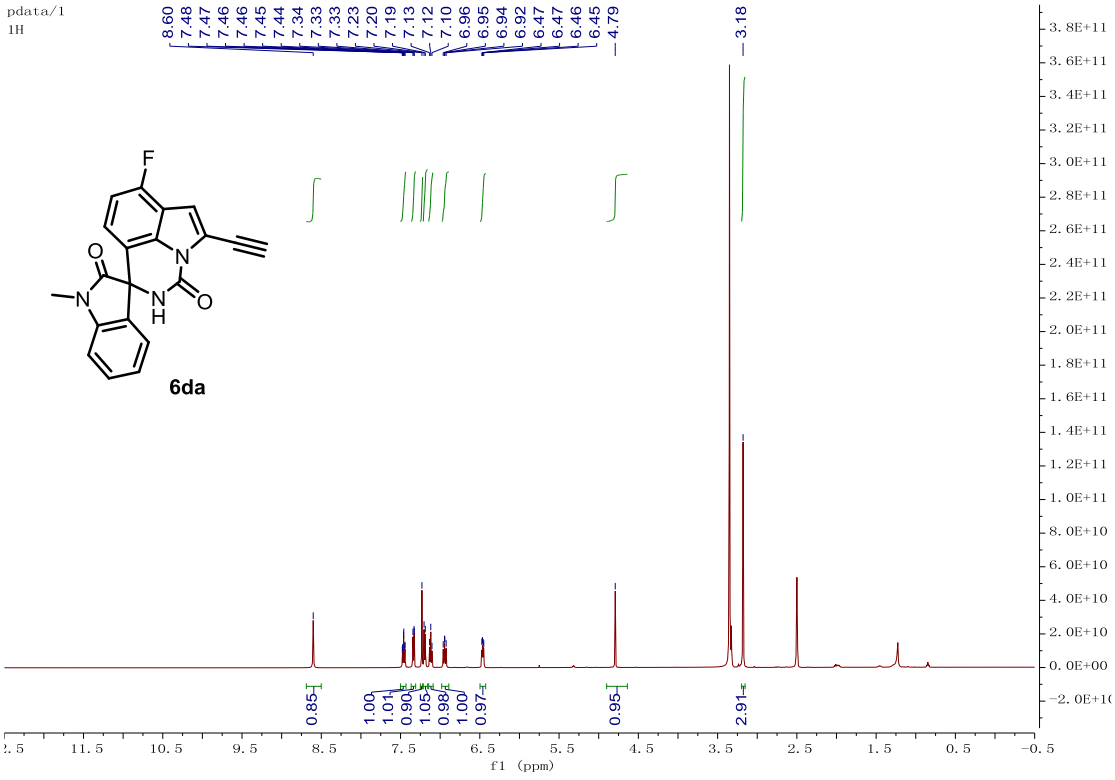


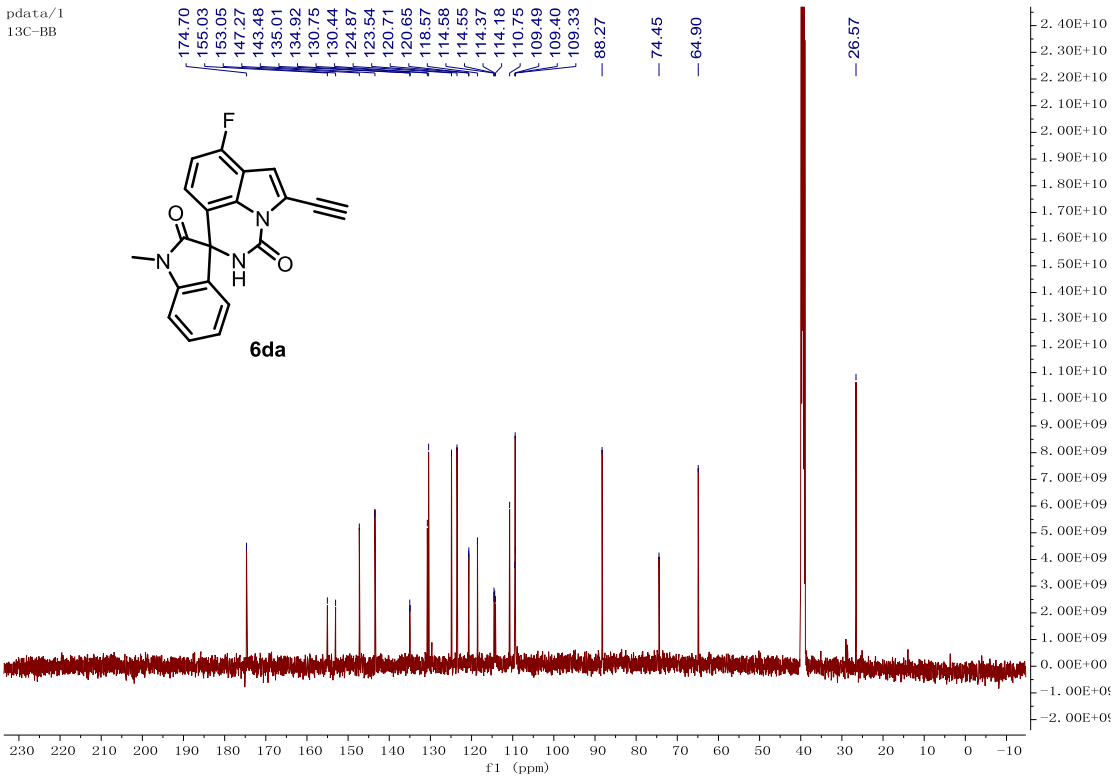

**5'-ethynyl-7'-methoxy-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ca)**

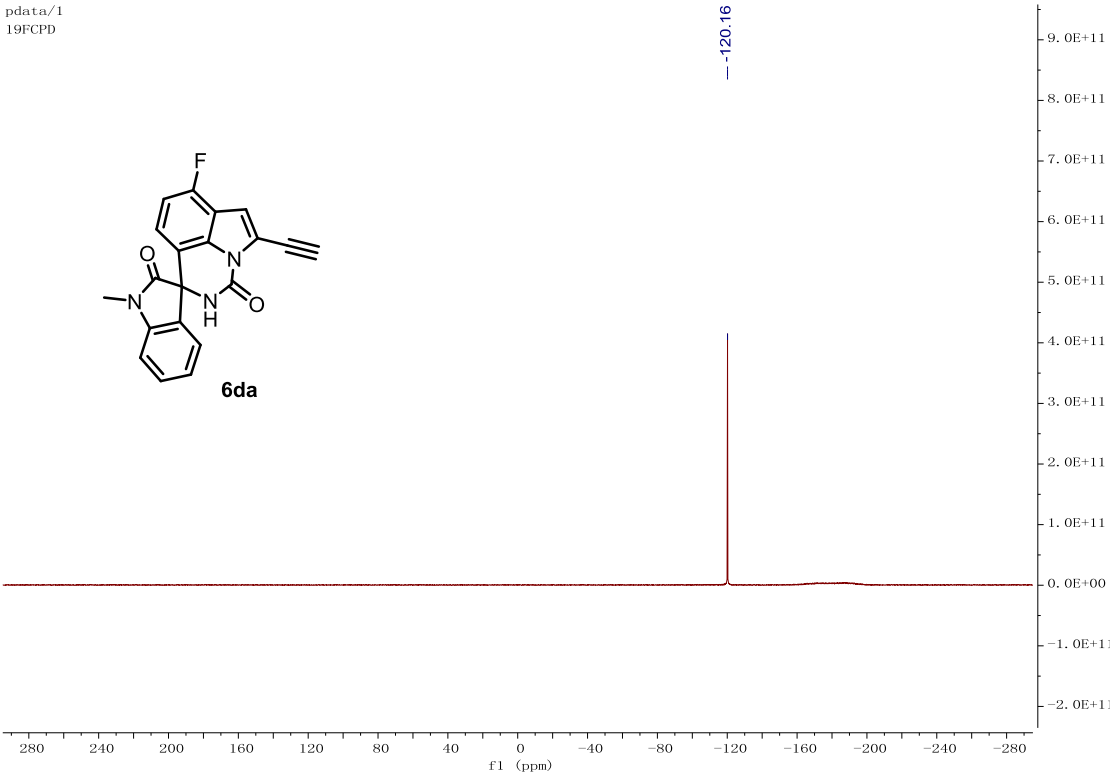




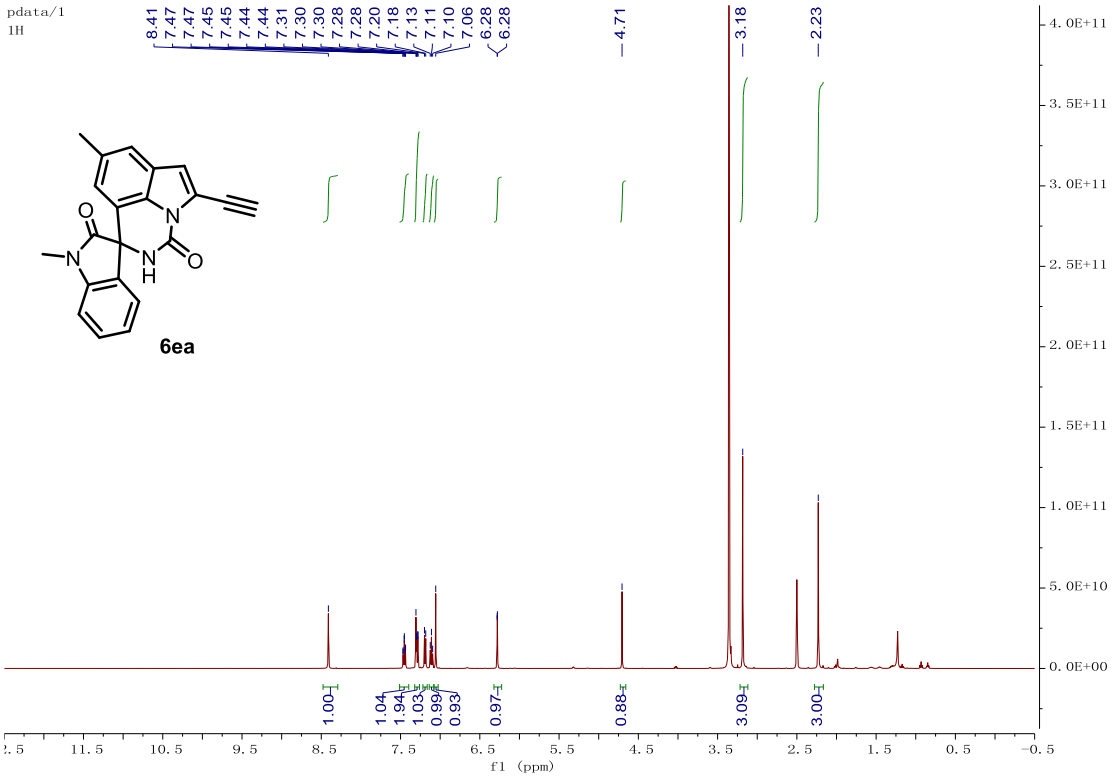

**5'-ethynyl-7'-fluoro-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6da)**

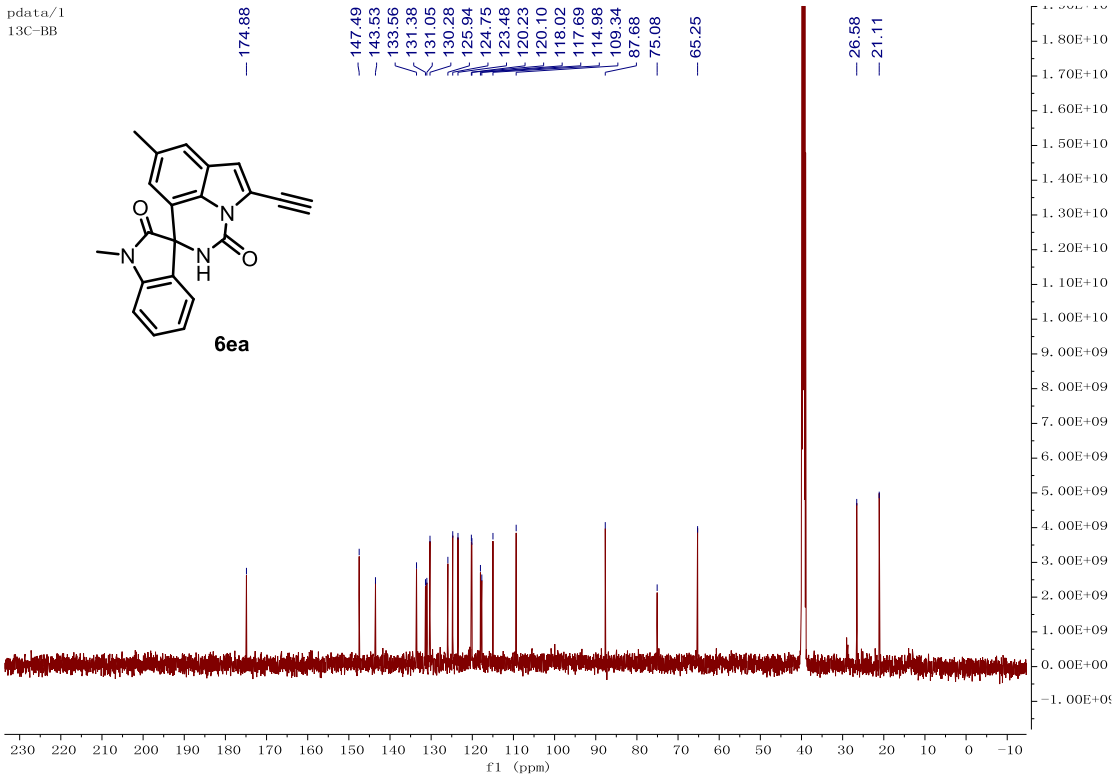



pdata/1
13C-BB
174.70
155.03
153.05
147.27
143.48
135.01
134.92
130.75
130.44
124.87
123.54
120.71
120.65
118.57
114.58
114.55
114.37
114.18
110.75
109.49
109.40
109.33
88.27
74.45
64.90
26.57
F
O
N
N
H
O
N
6da
f1 (ppm)

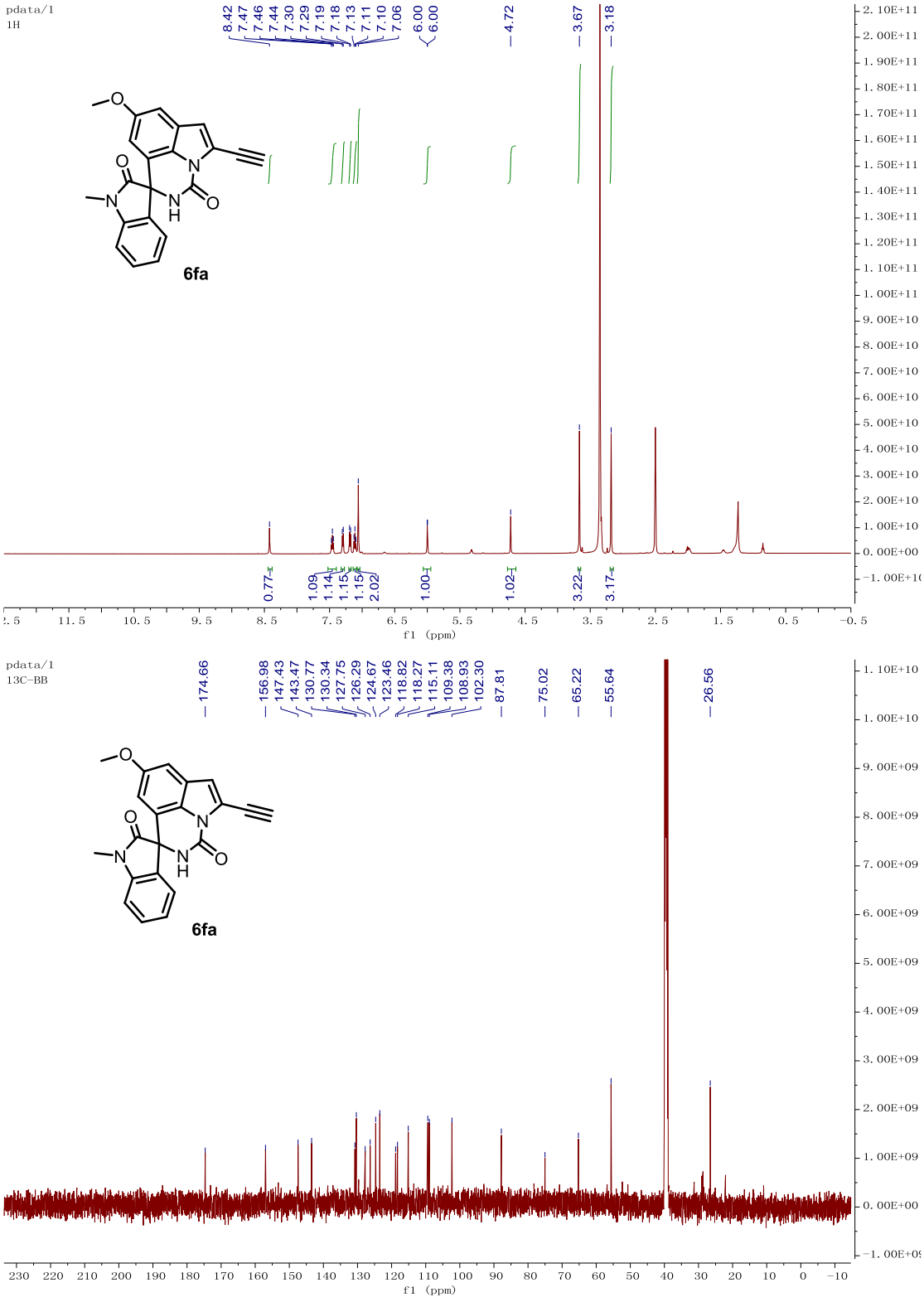

pdata/1
19FCPD
-120.16
F
O
N
N
H
O
N
6da
f1 (ppm)

**5'-ethynyl-1,8'-dimethylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ea)**

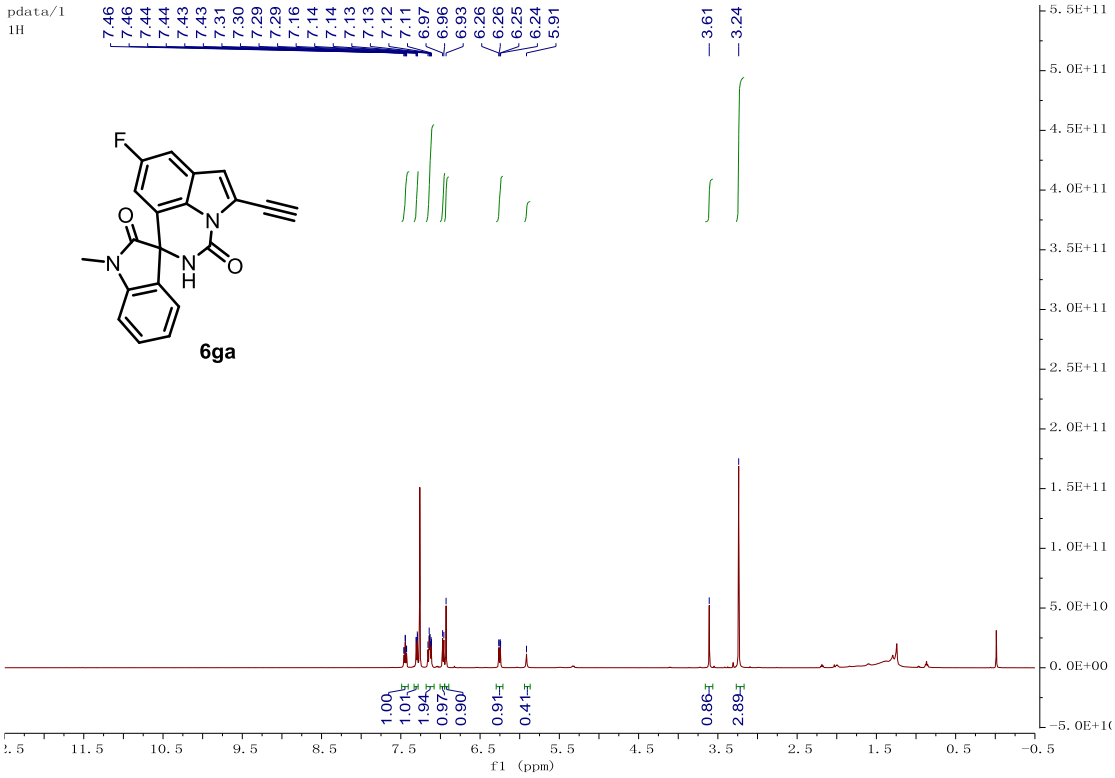


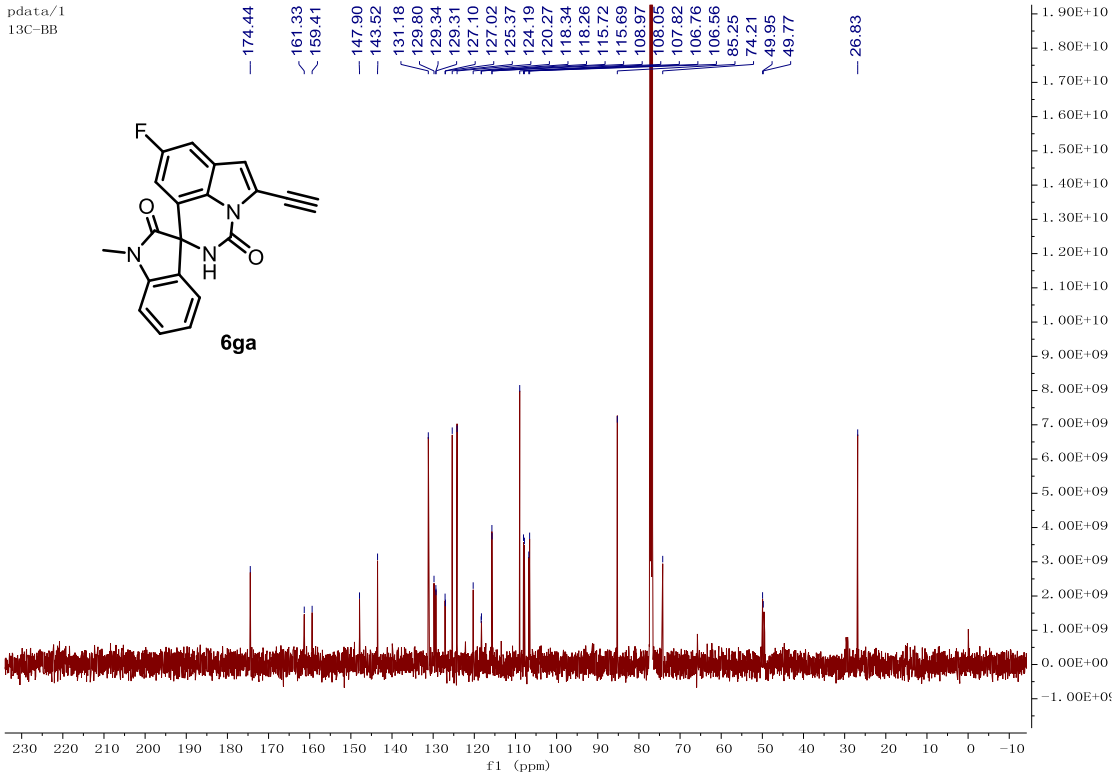



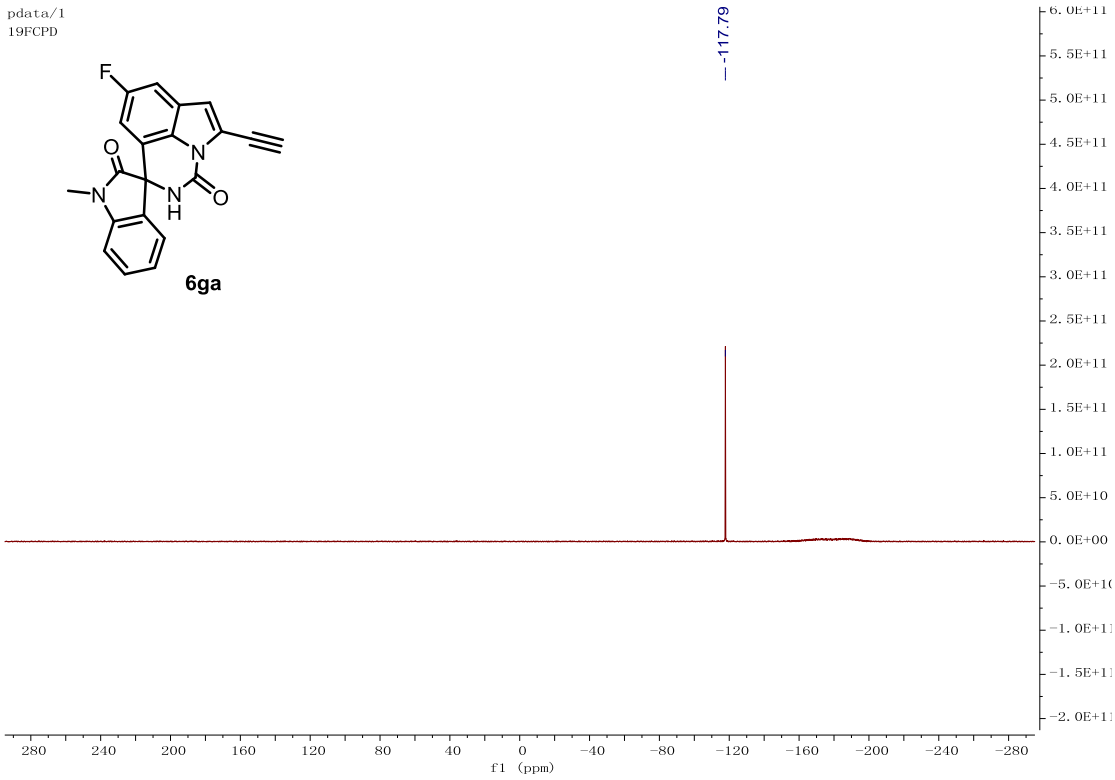
**5'-ethynyl-8'-methoxy-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6fa)**



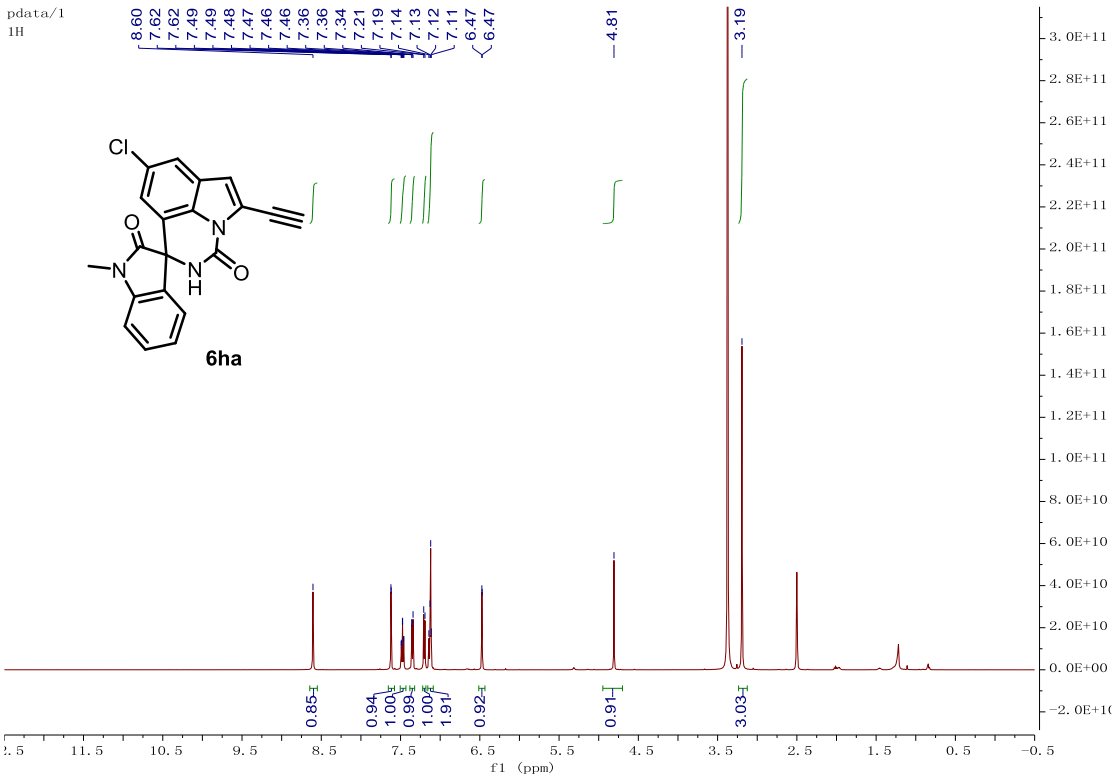
**5'-ethynyl-8'-fluoro-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ga)**

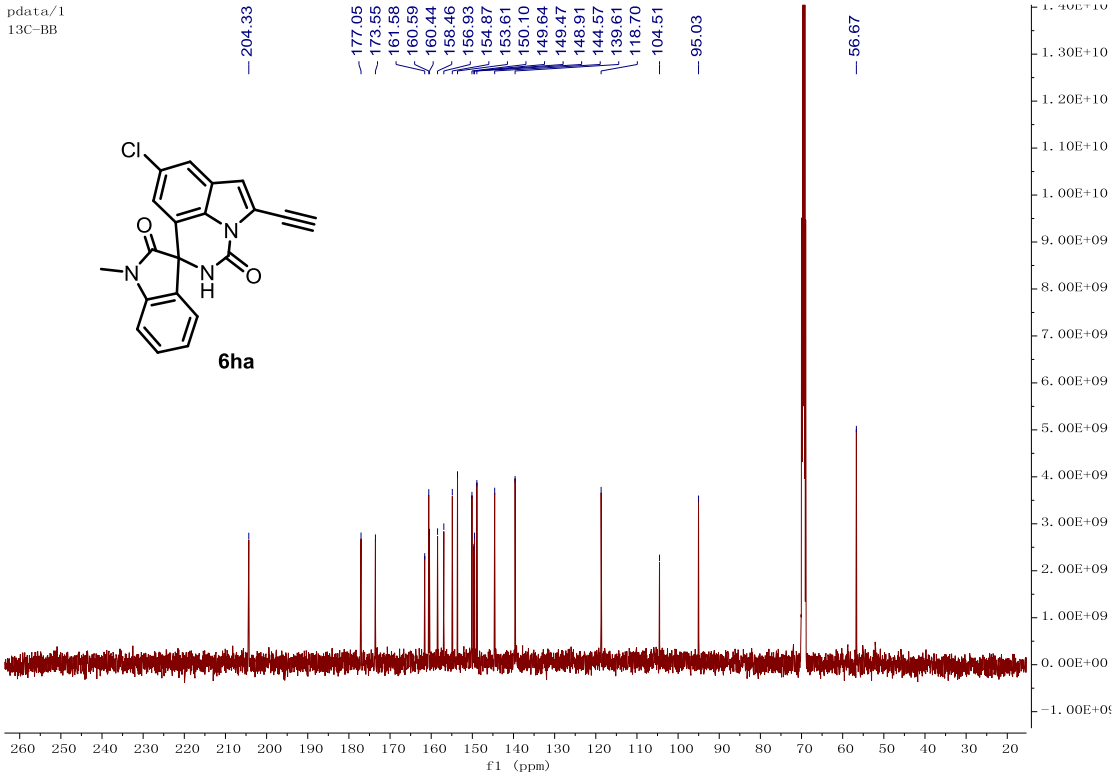


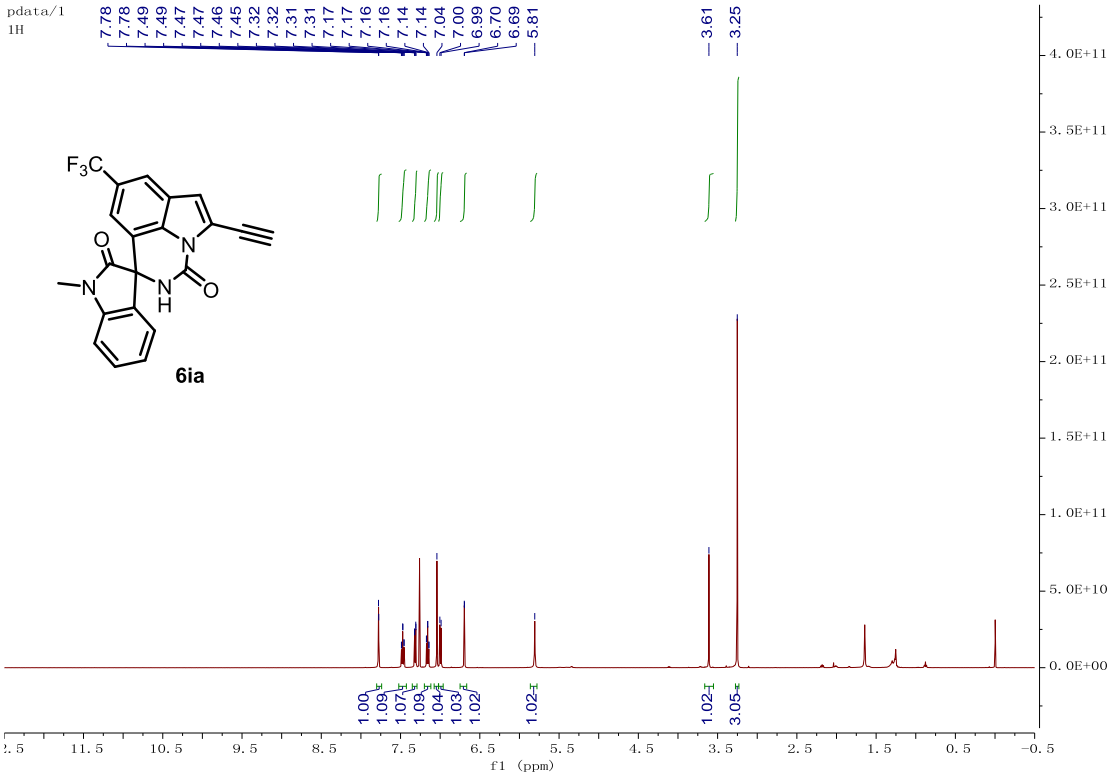


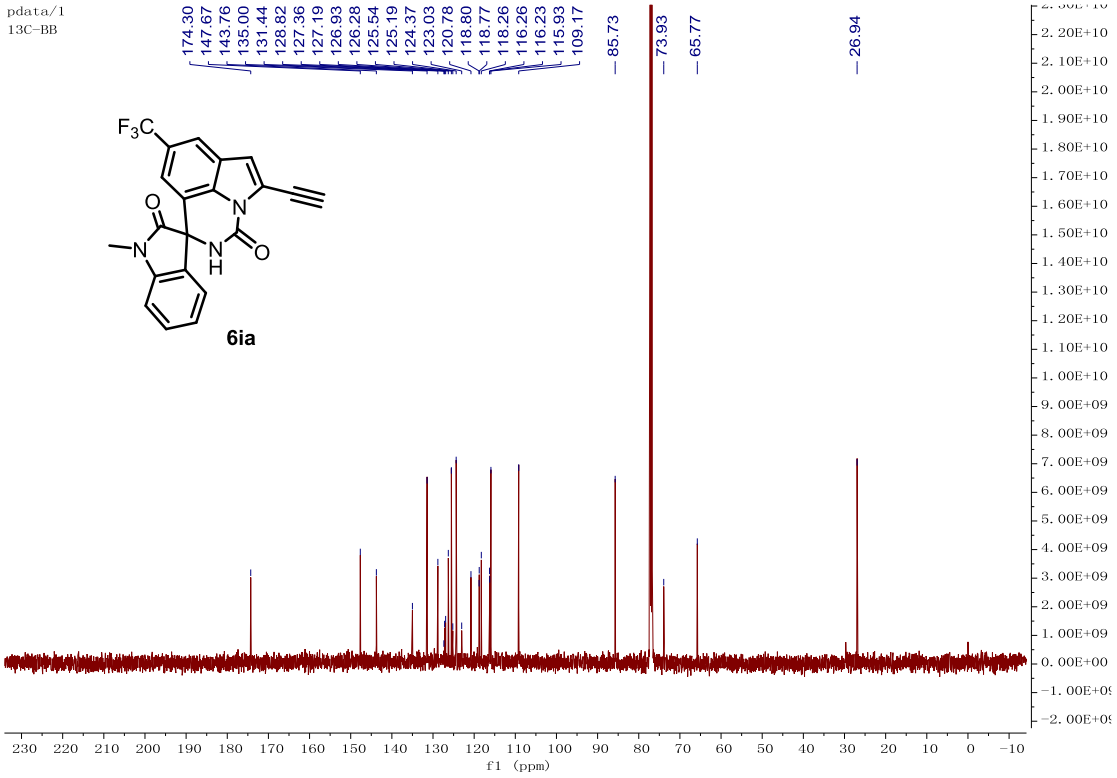

**8'-chloro-5'-ethynyl-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ha)**

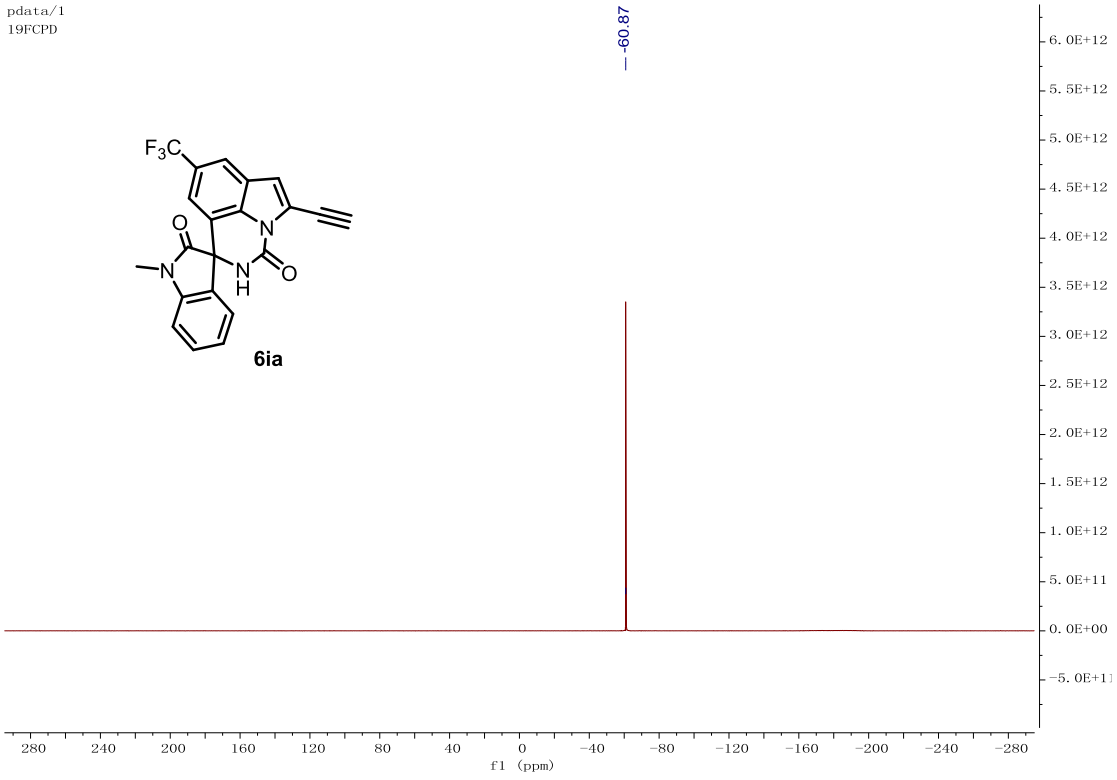




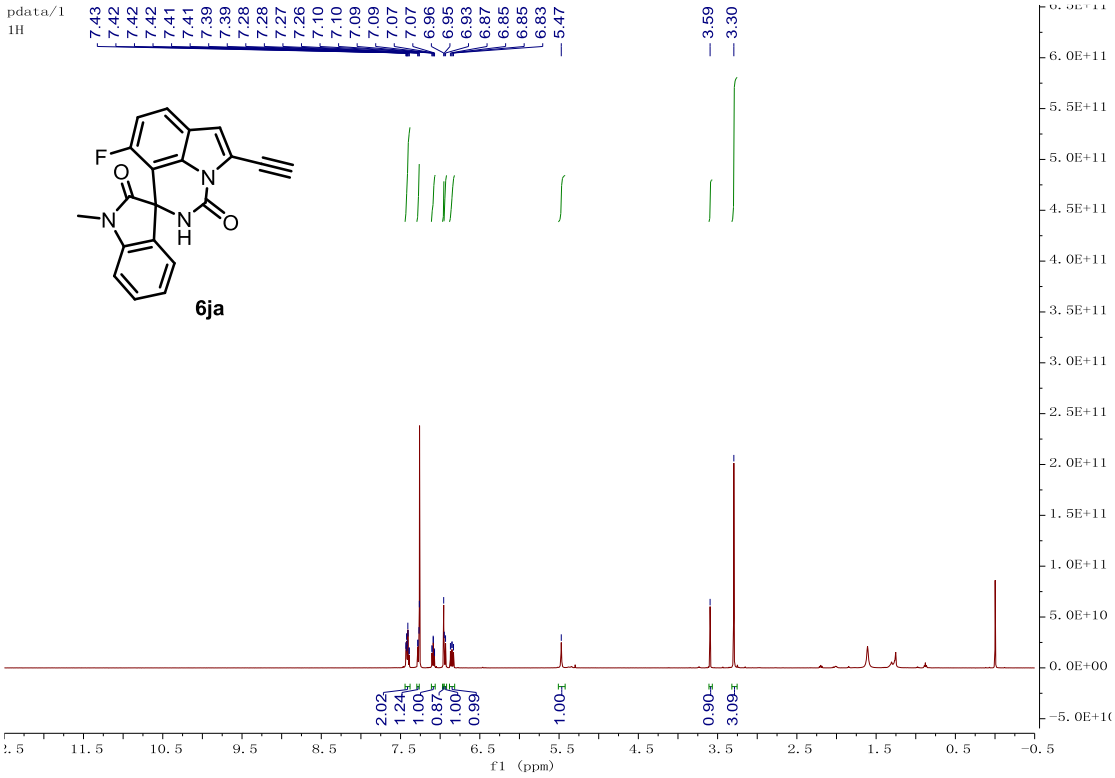

**5'-ethynyl-1-methyl-8'-(trifluoromethyl)spiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ia)**

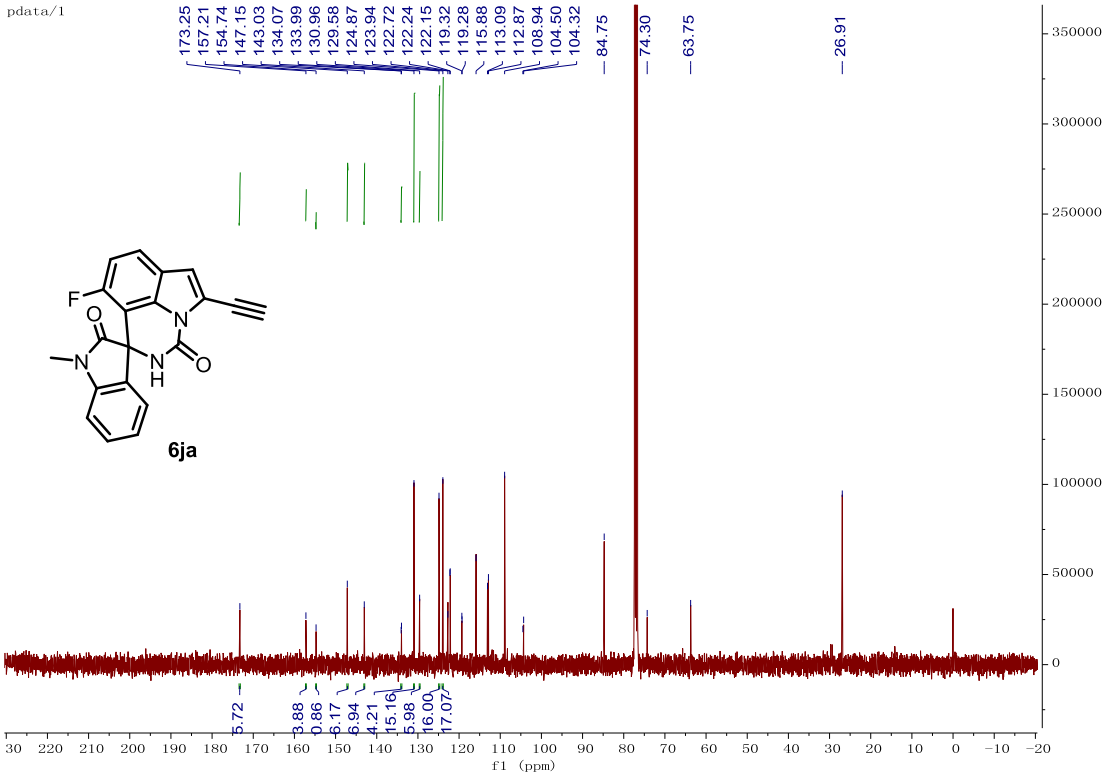


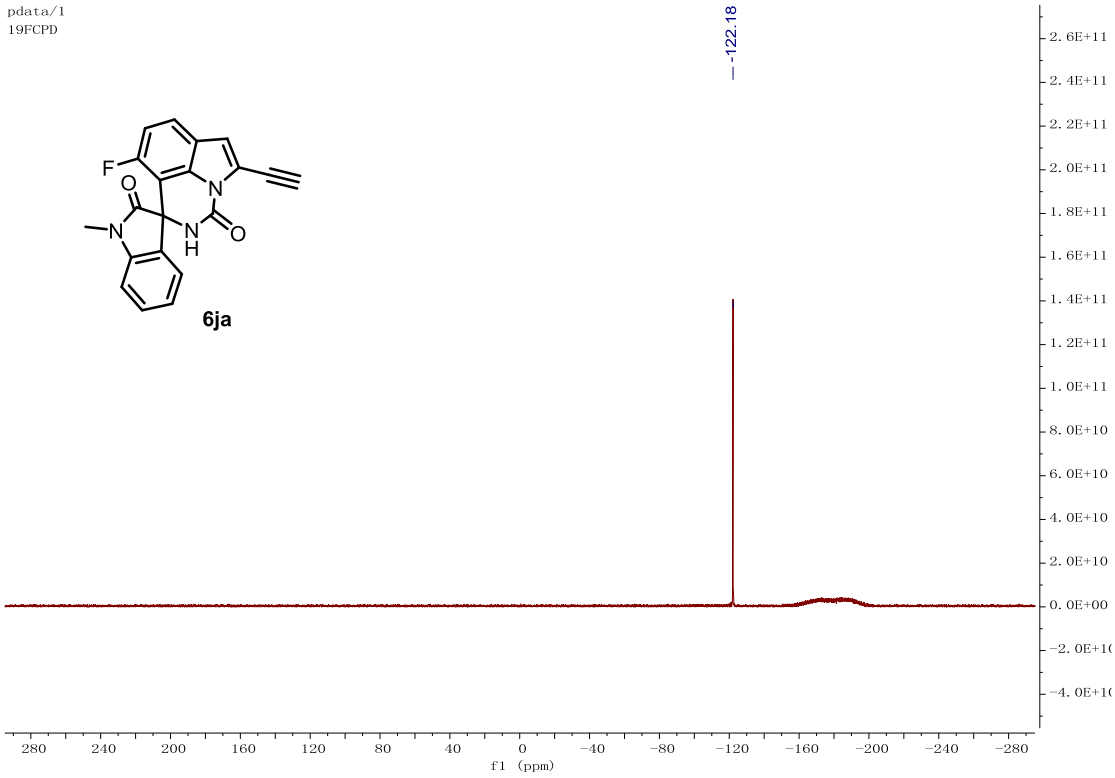

pdata/1
13C-BB
174.30
147.67
143.76
135.00
131.44
128.82
127.36
127.19
126.93
126.28
125.54
125.19
124.37
123.03
120.78
118.80
118.77
118.26
116.23
115.93
109.17
85.73
73.93
65.77
26.94
F3C
O
N
N
H
O
6ia
f1 (ppm)


pdata/1
19FCPD
-60.87
F3C
O
N
N
H
O
6ia
f1 (ppm)

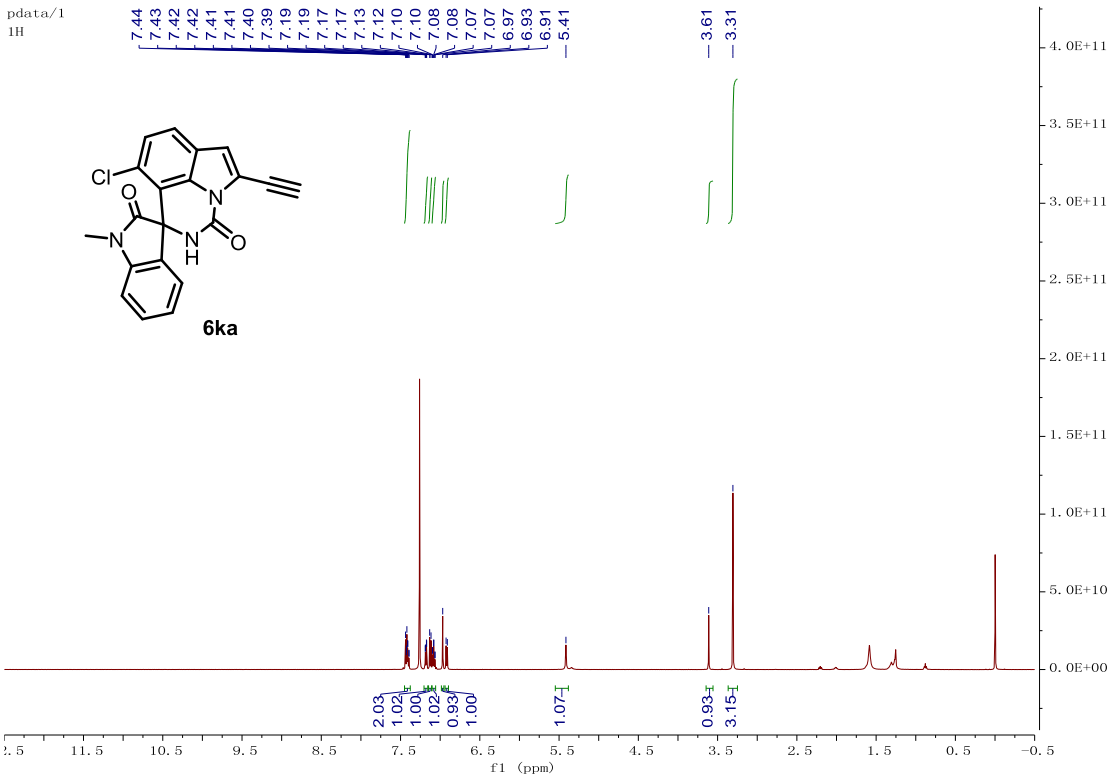
**5'-ethynyl-9'-fluoro-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ja)**

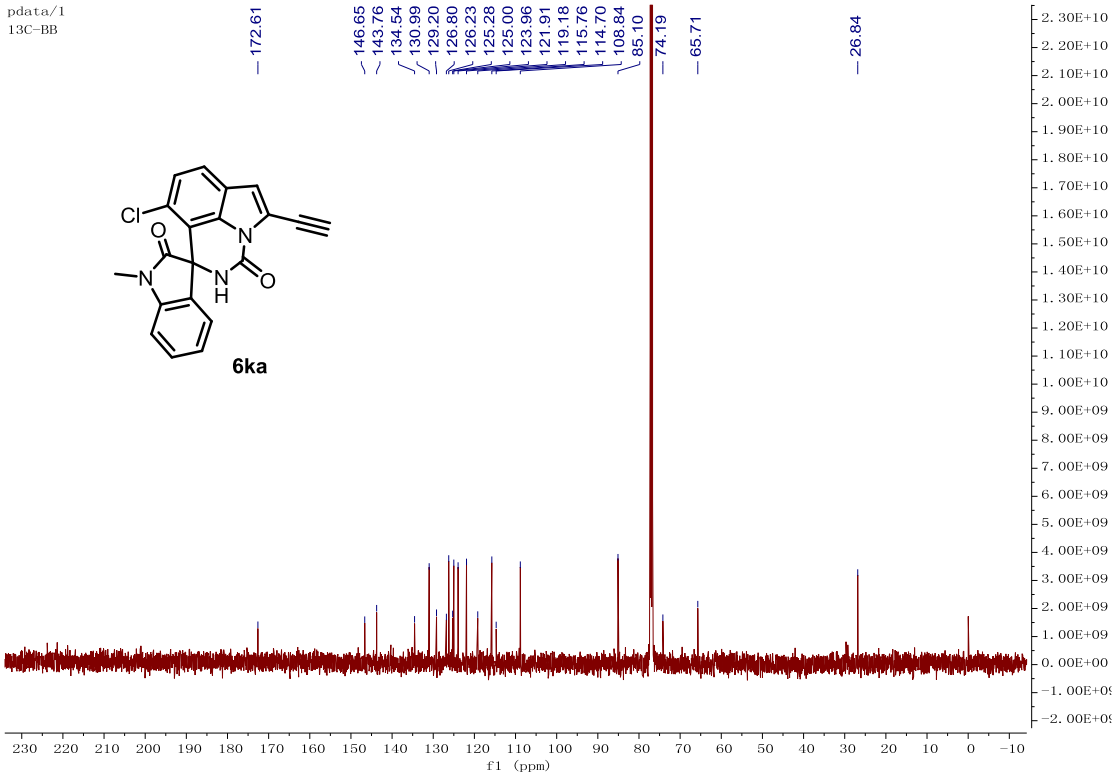


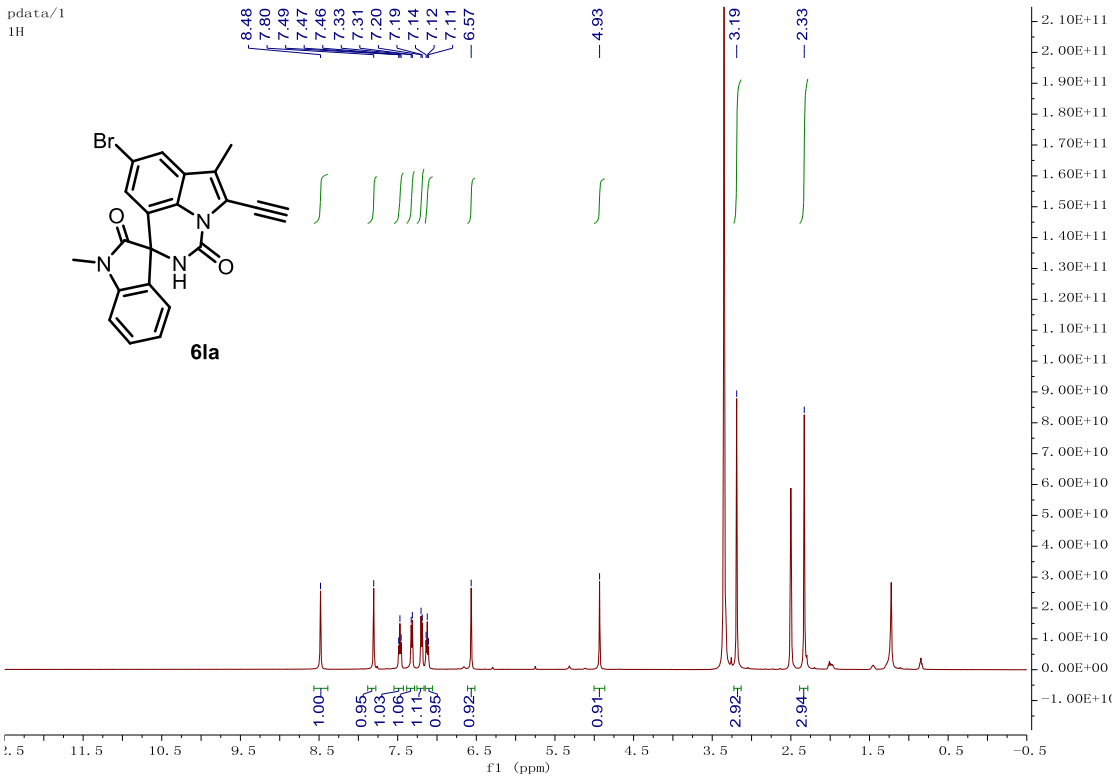


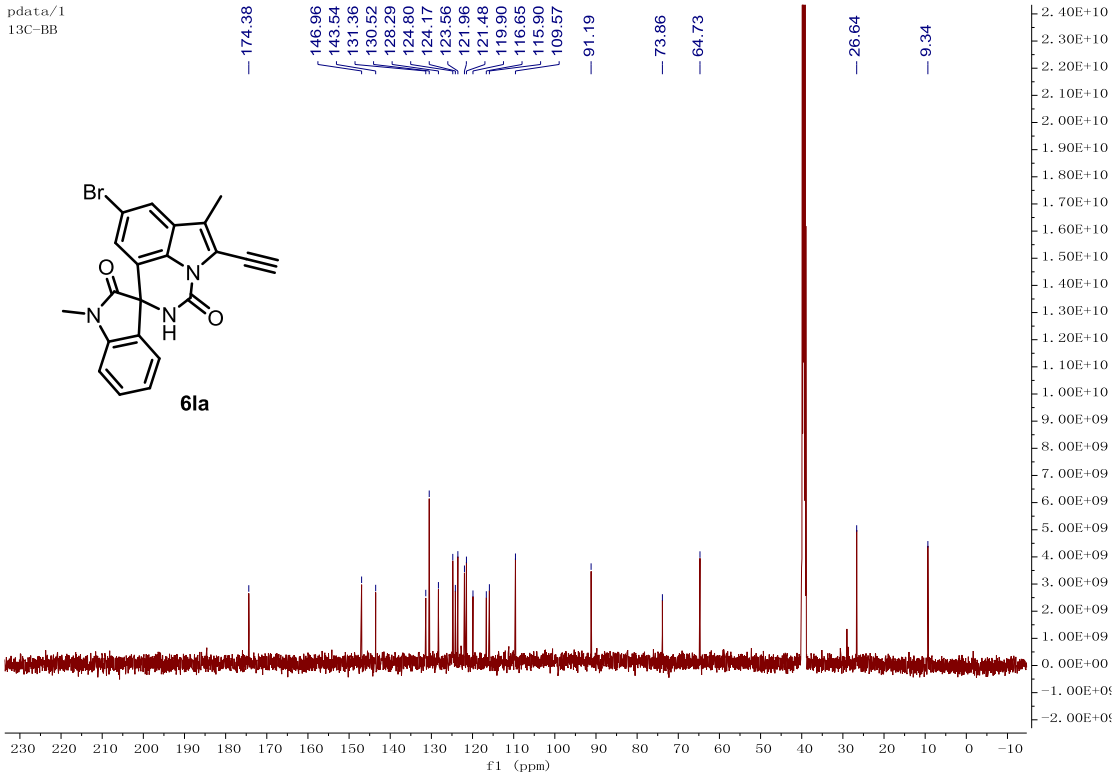

**9'-chloro-5'-ethynyl-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'H)-dion (6ka)**



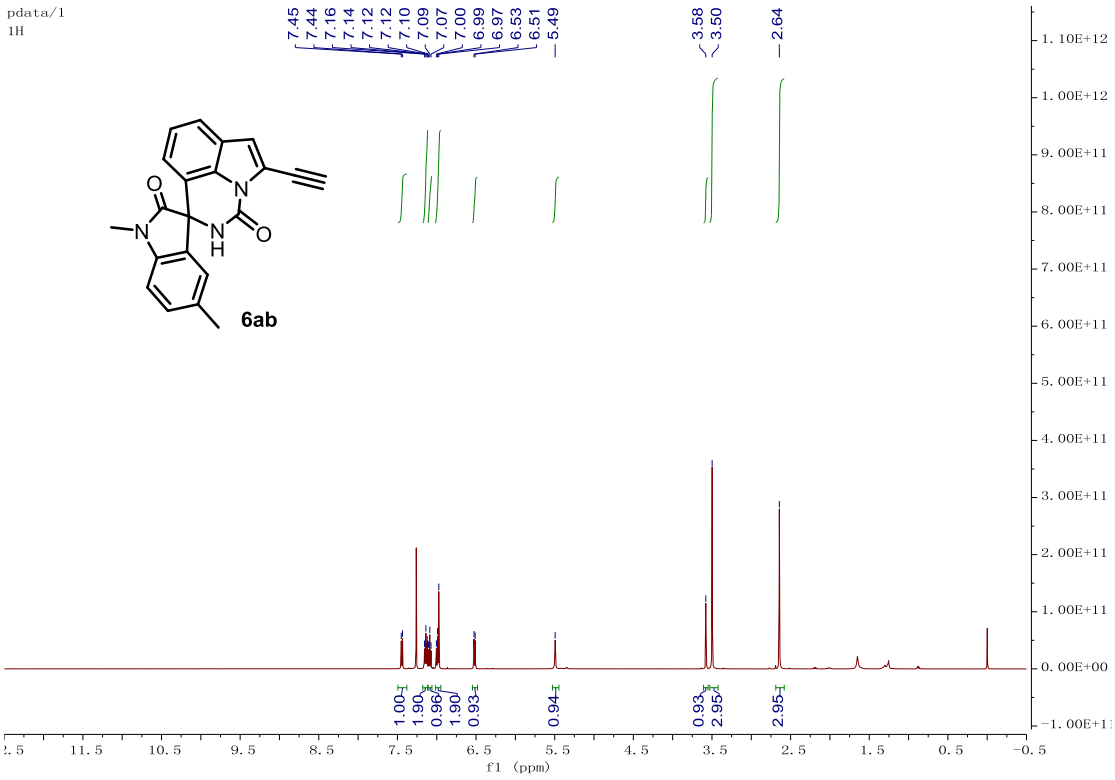


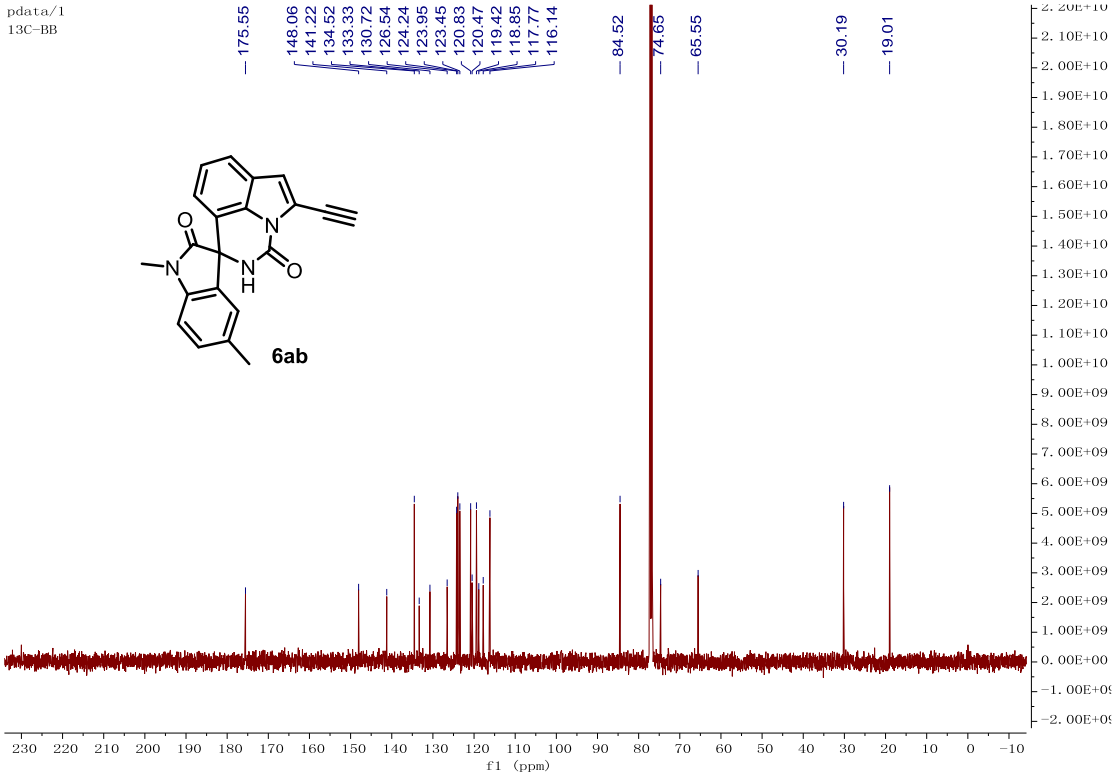

**8'-bromo-5'-ethynyl-1,6'-dimethylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6la)**



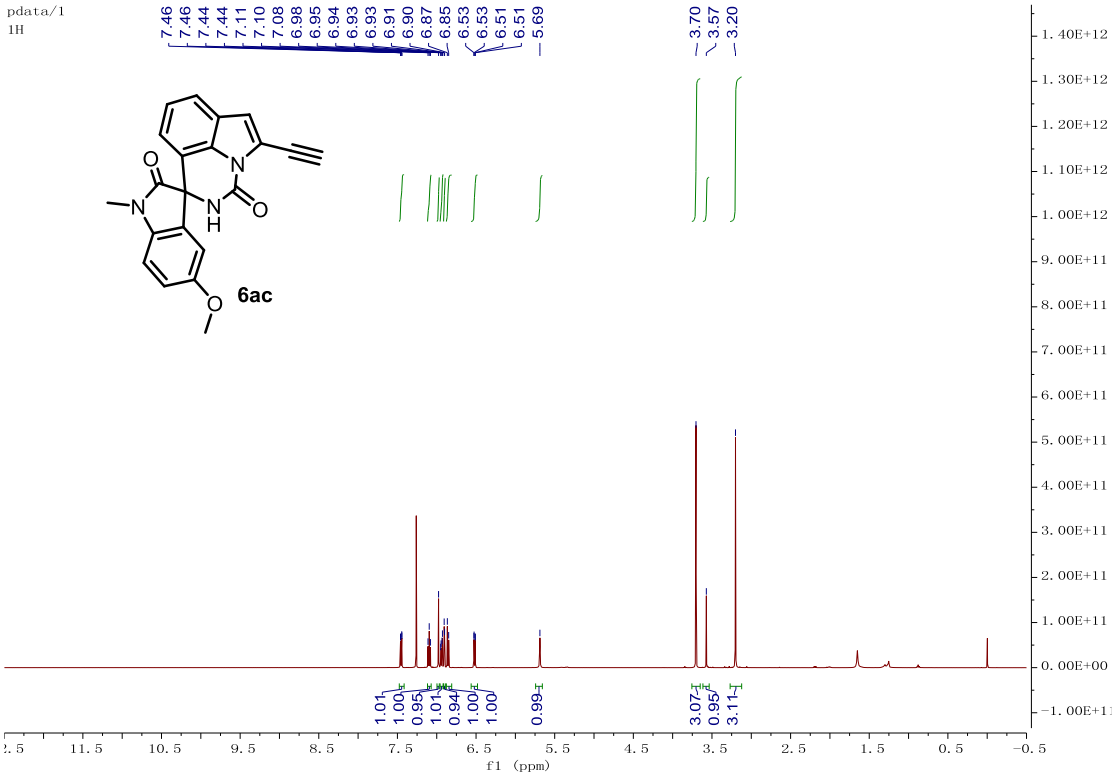


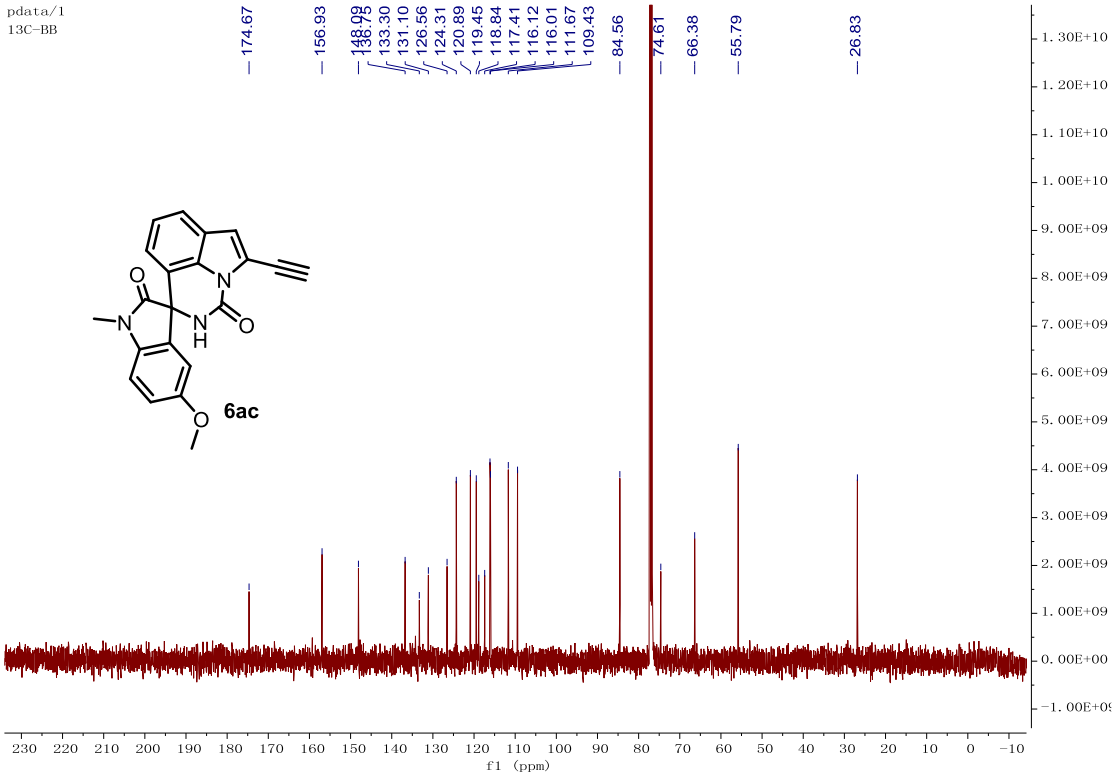

**5'-ethynyl-1,5-dimethylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ab)**



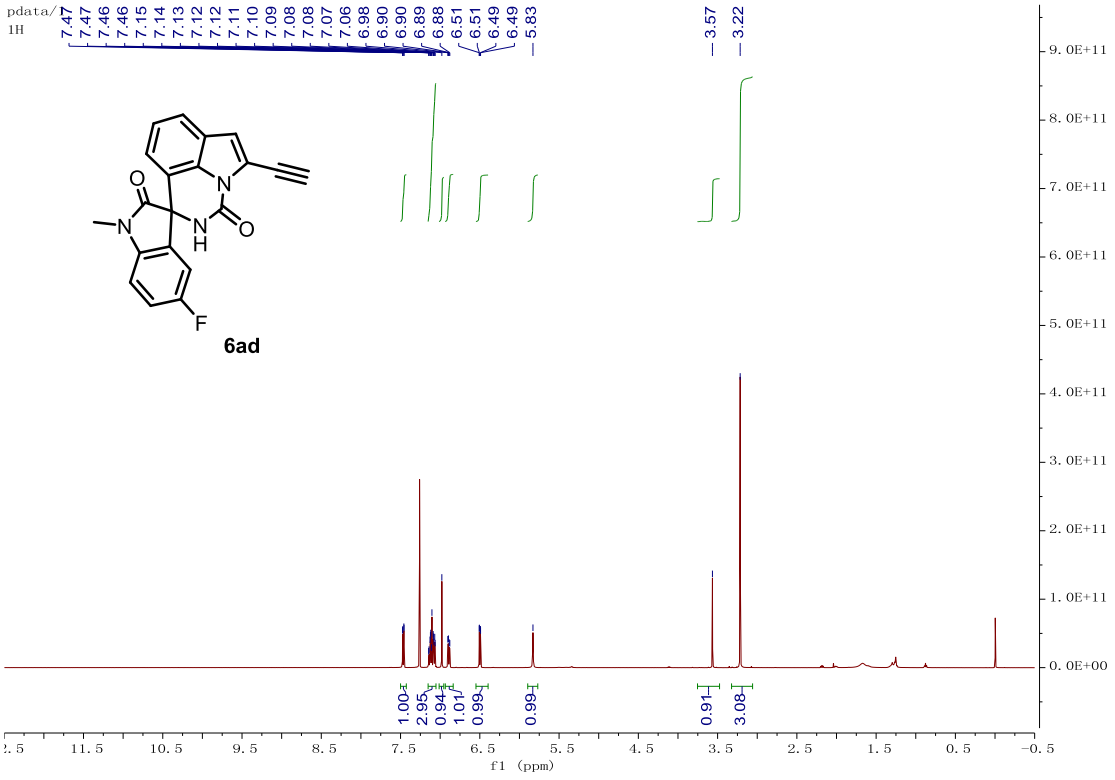


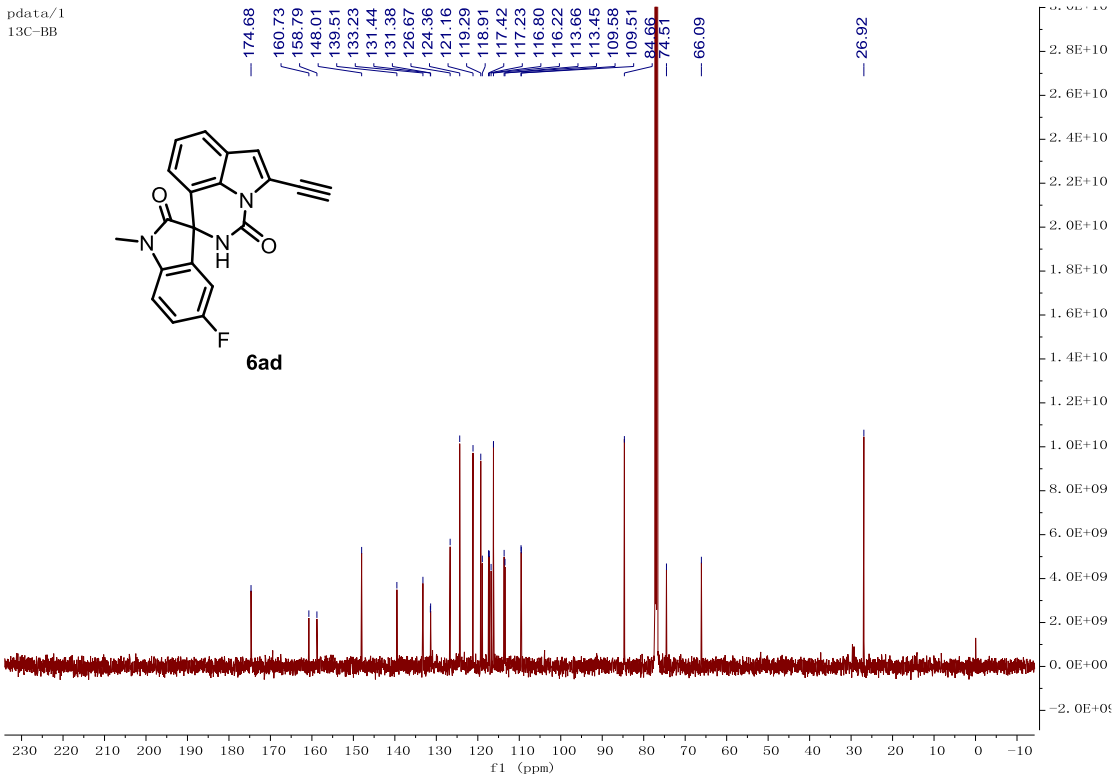

**5'-ethynyl-5-methoxy-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ac)**

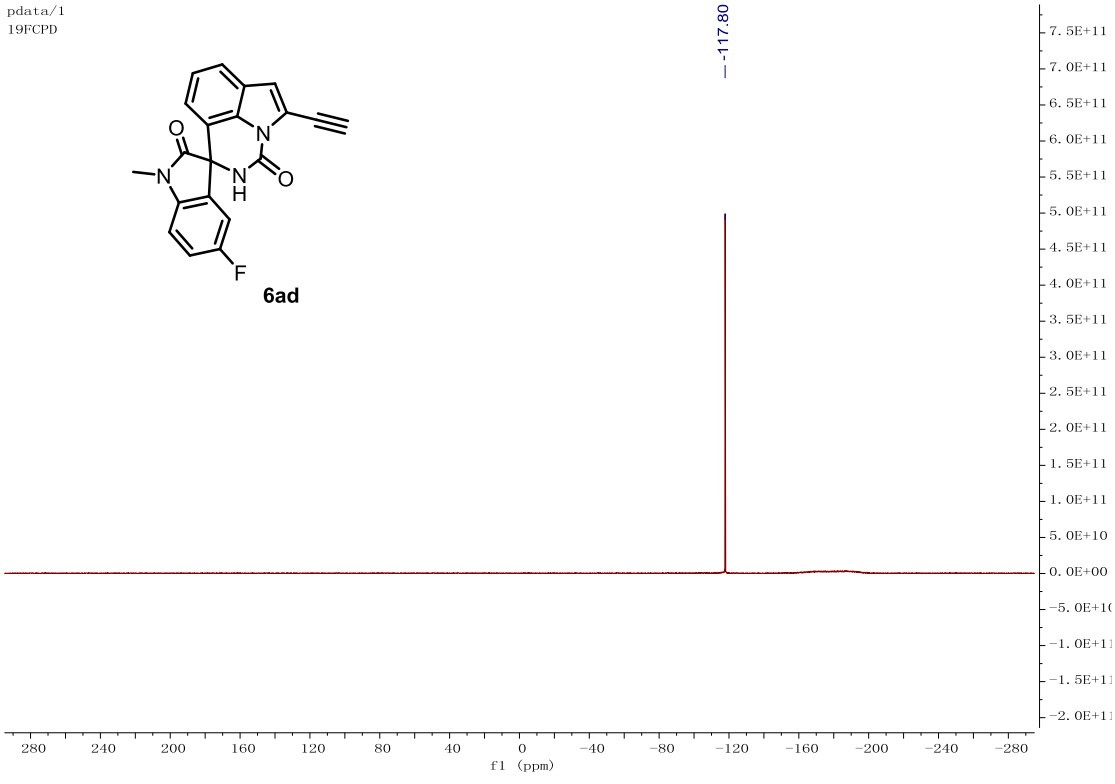




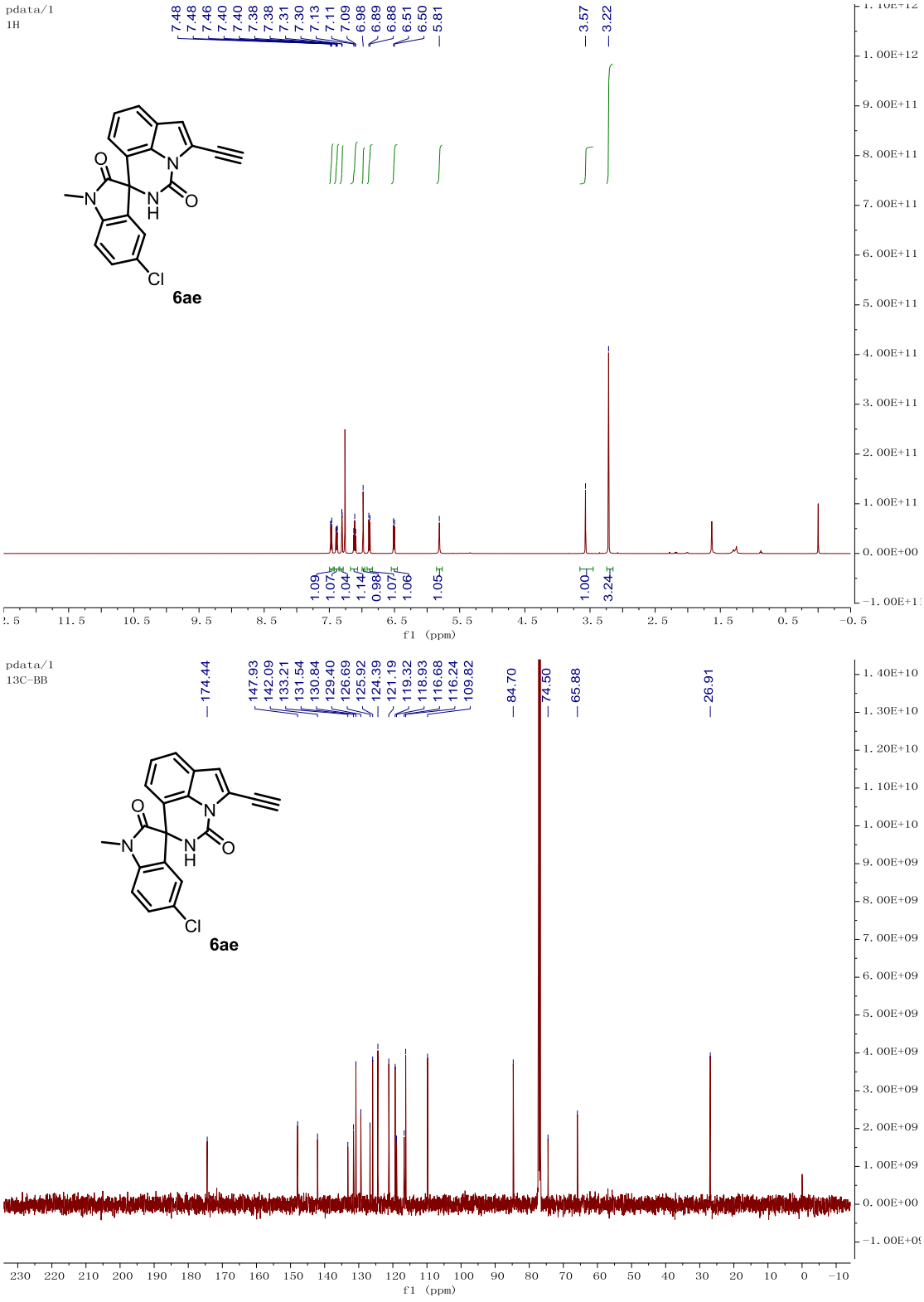

**5'-ethynyl-5-fluoro-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ad)**



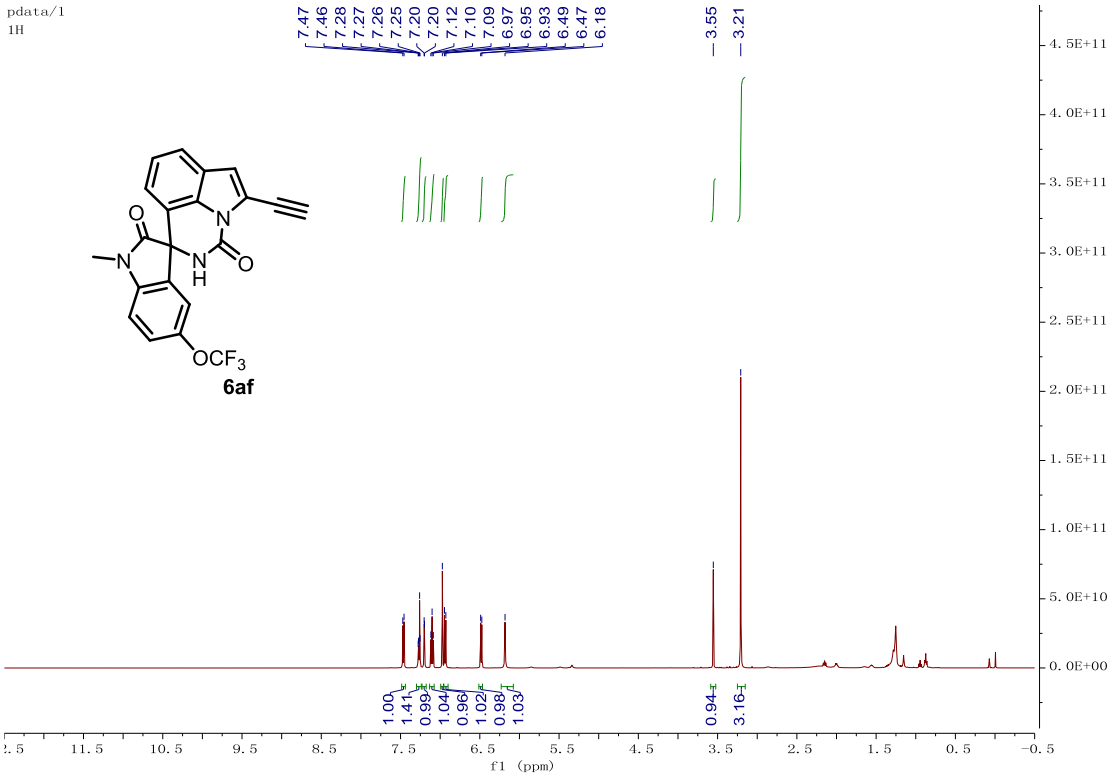

pdata/1
13C-BB
174.68
160.73
158.79
148.01
139.51
133.23
131.44
131.38
126.67
124.36
121.16
119.29
118.91
117.42
117.23
116.80
116.22
113.66
113.45
109.58
109.51
84.66
74.51
66.09
26.92
6ad
f1 (ppm)

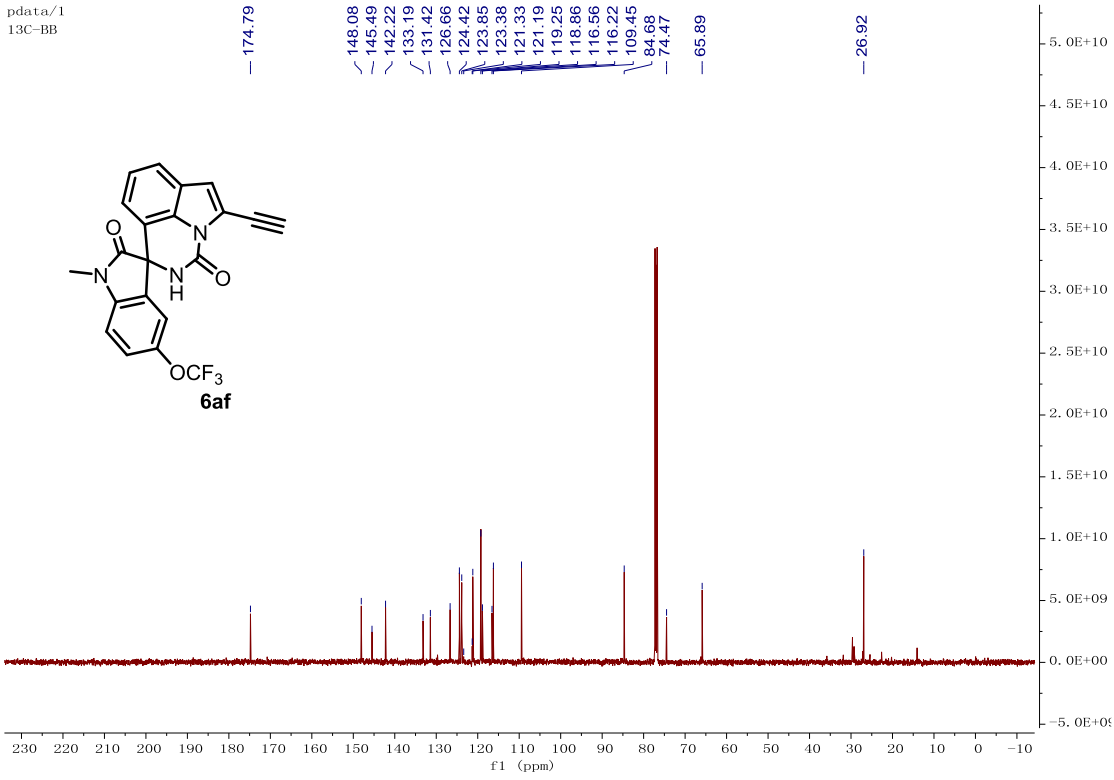

pdata/1
19FCPD
-117.80
6ad
f1 (ppm)

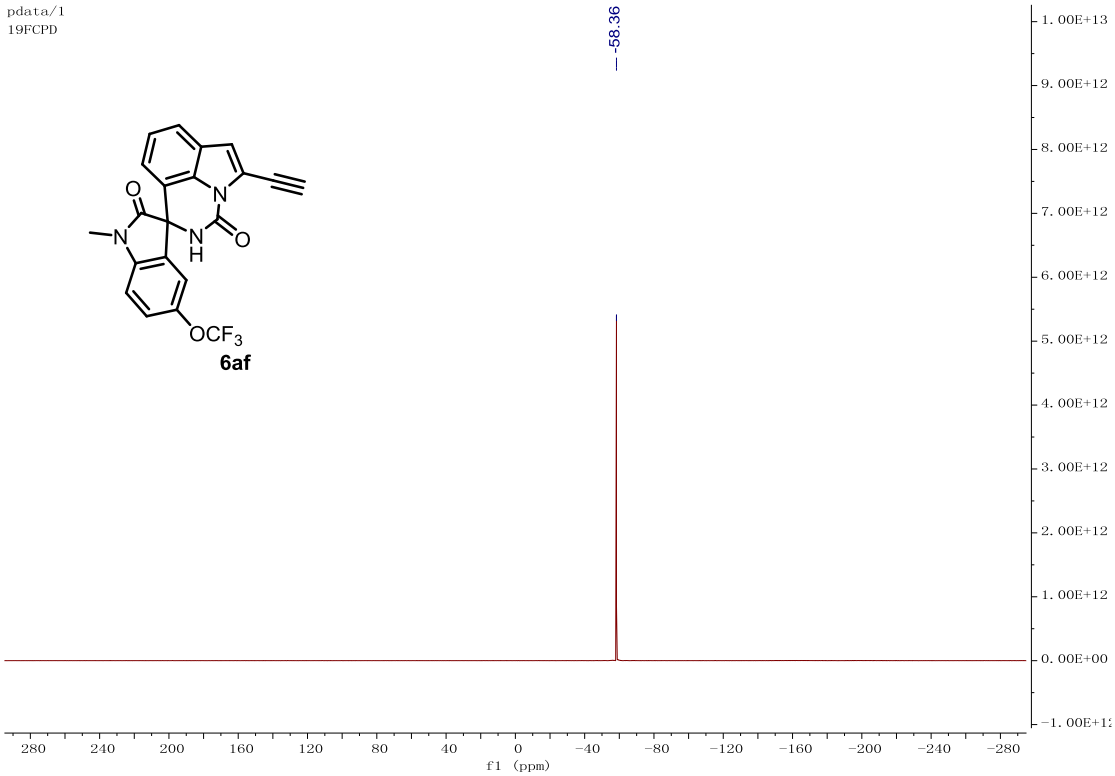
**5-chloro-5'-ethynyl-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-ij]quinazoline]-2,3'(2'H)-dione (6ae)**



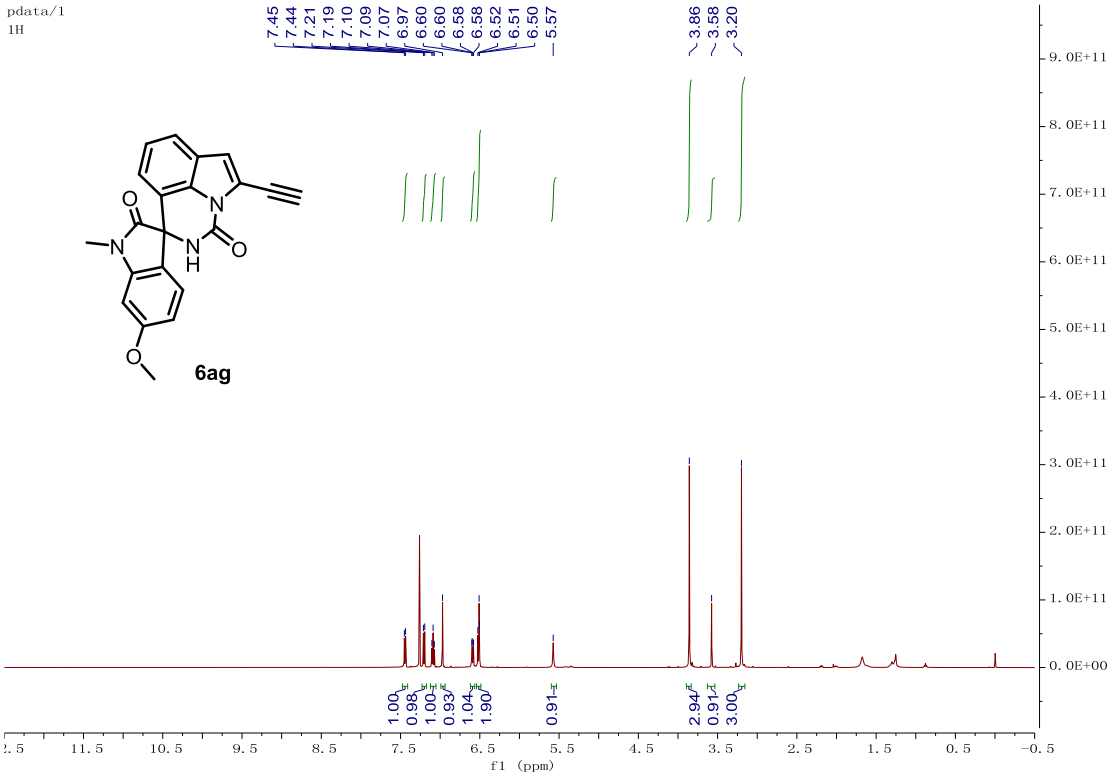
**5'-ethynyl-1-methyl-5-(trifluoromethoxy)spiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6af)**

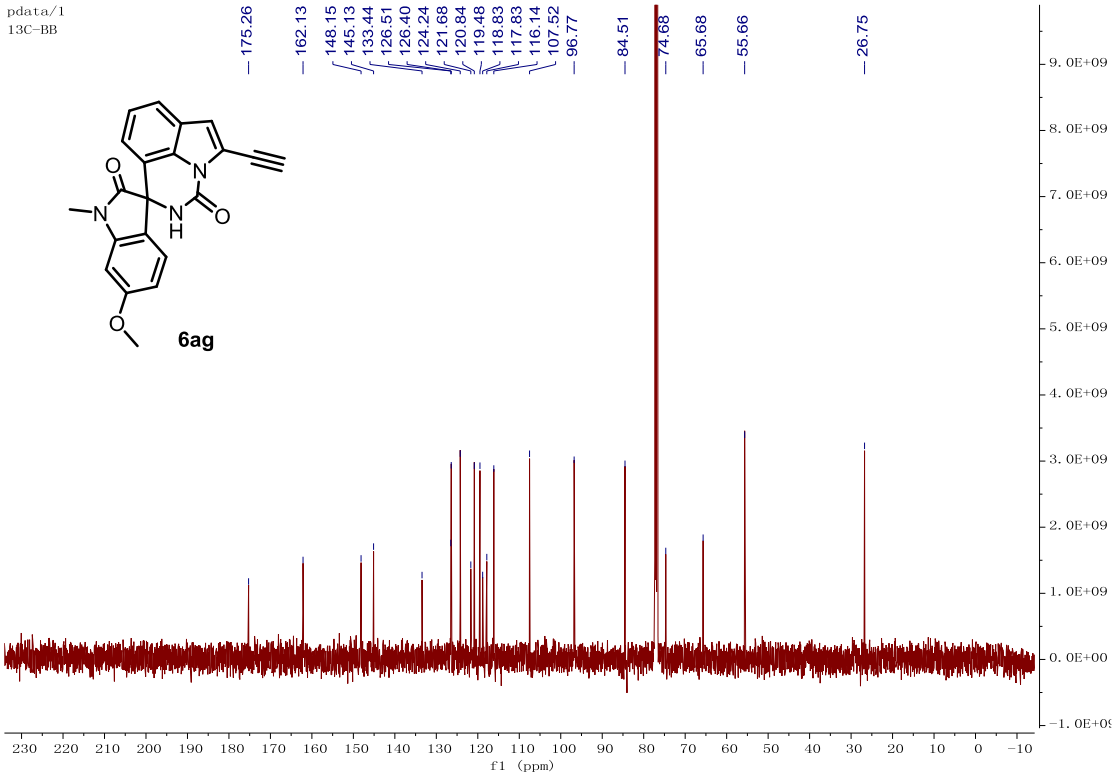


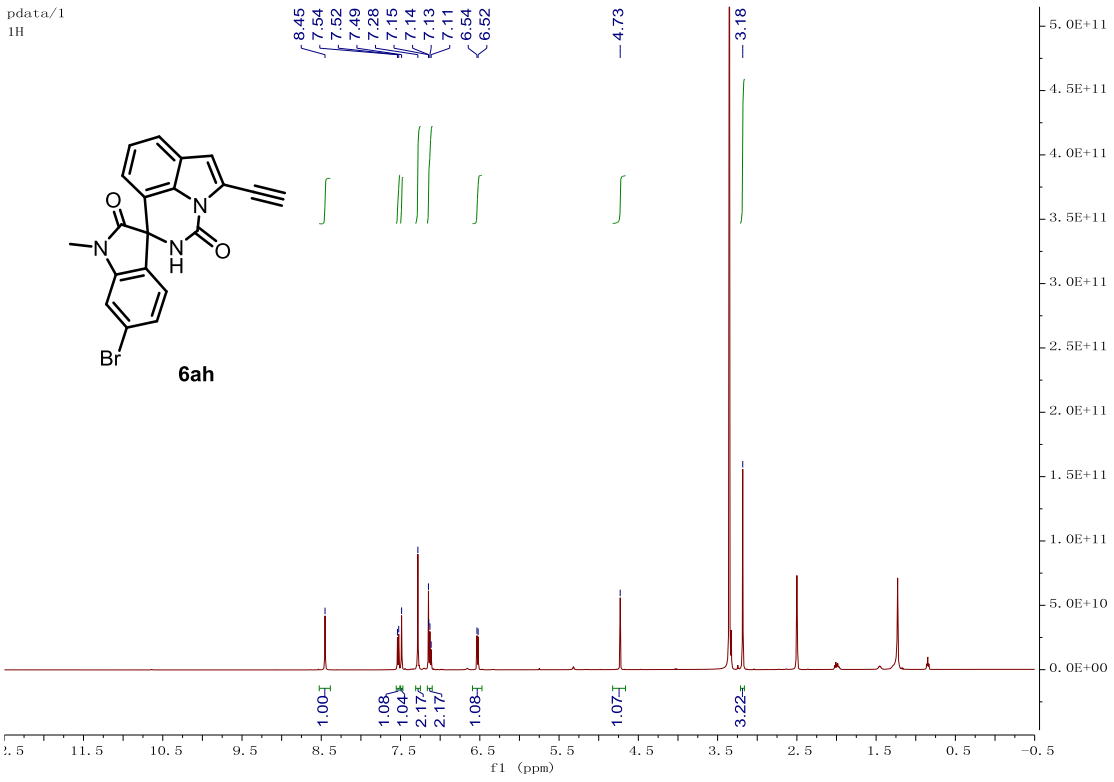


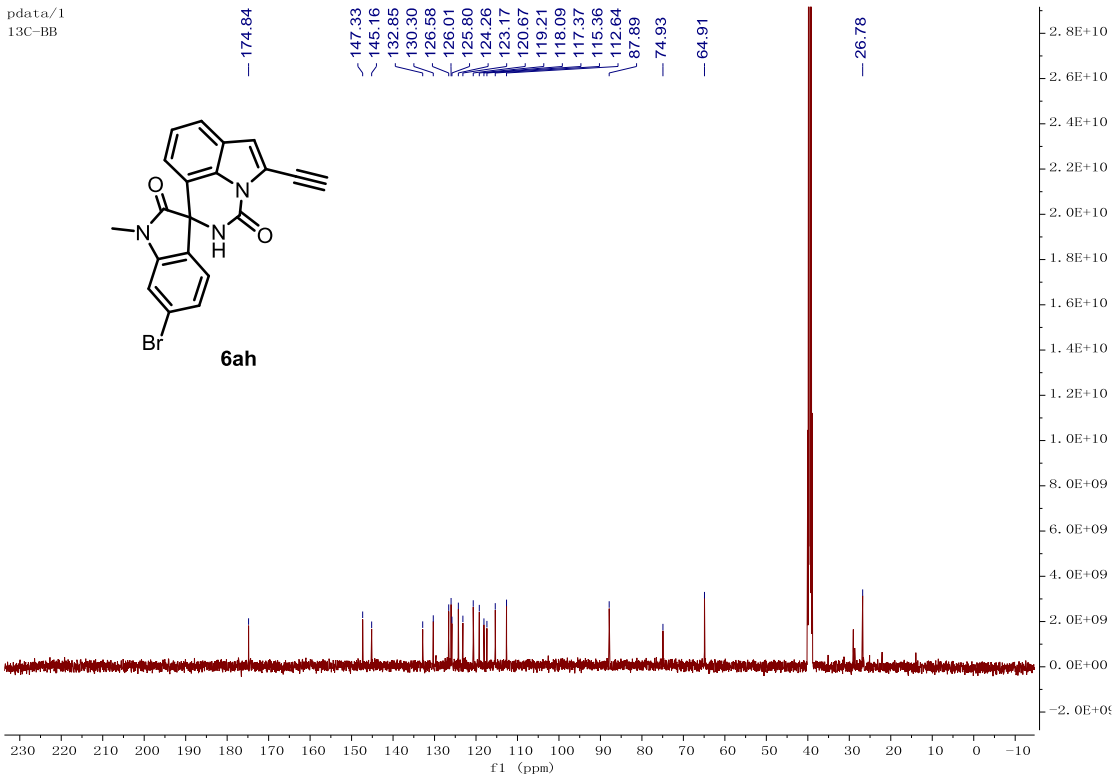

**5'-ethynyl-6-methoxy-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ag)**



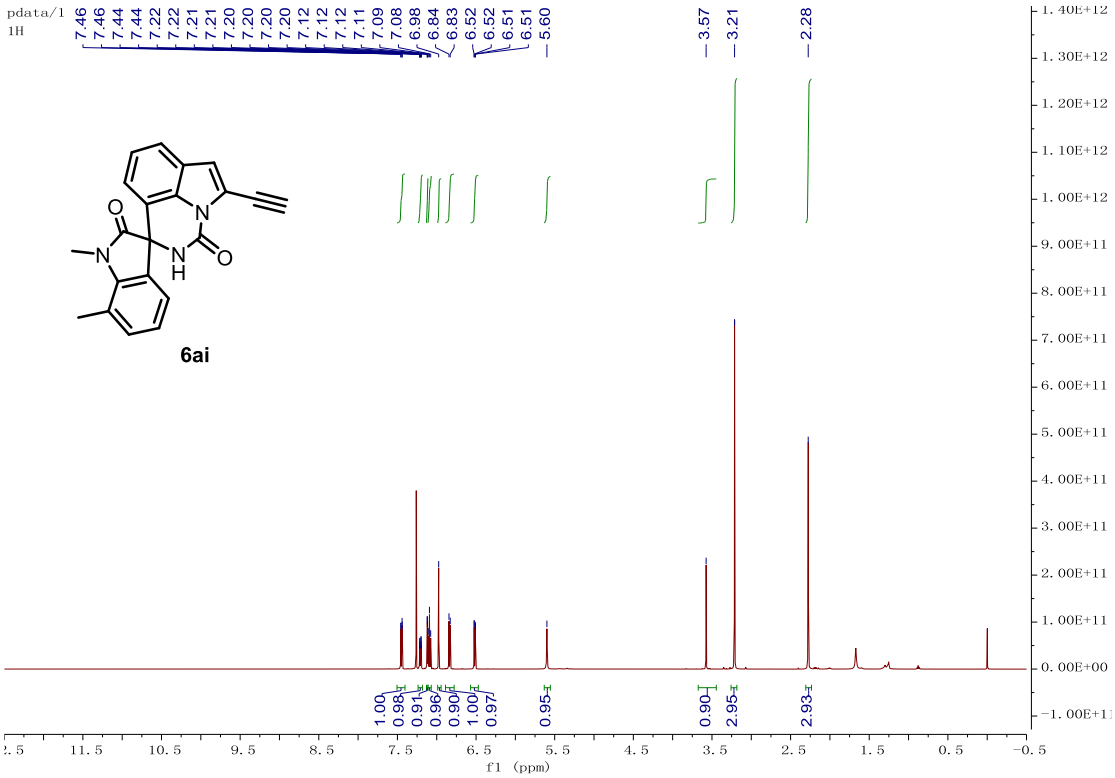


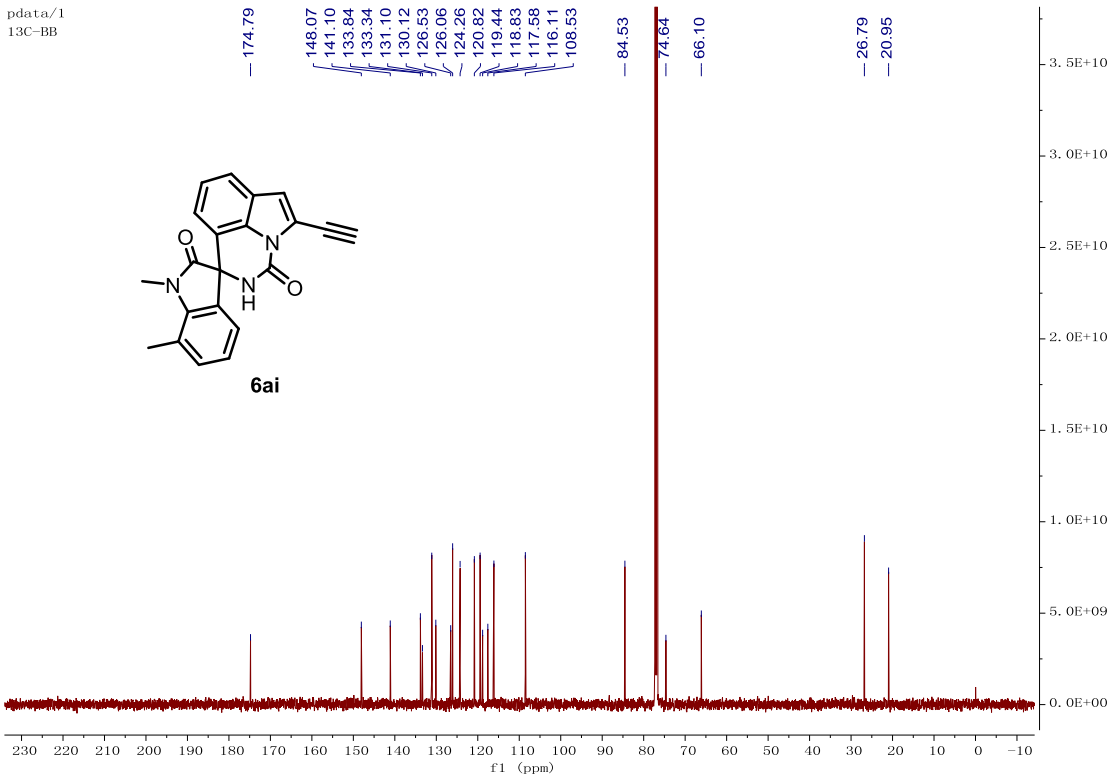

**6-bromo-5'-ethynyl-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ah)**



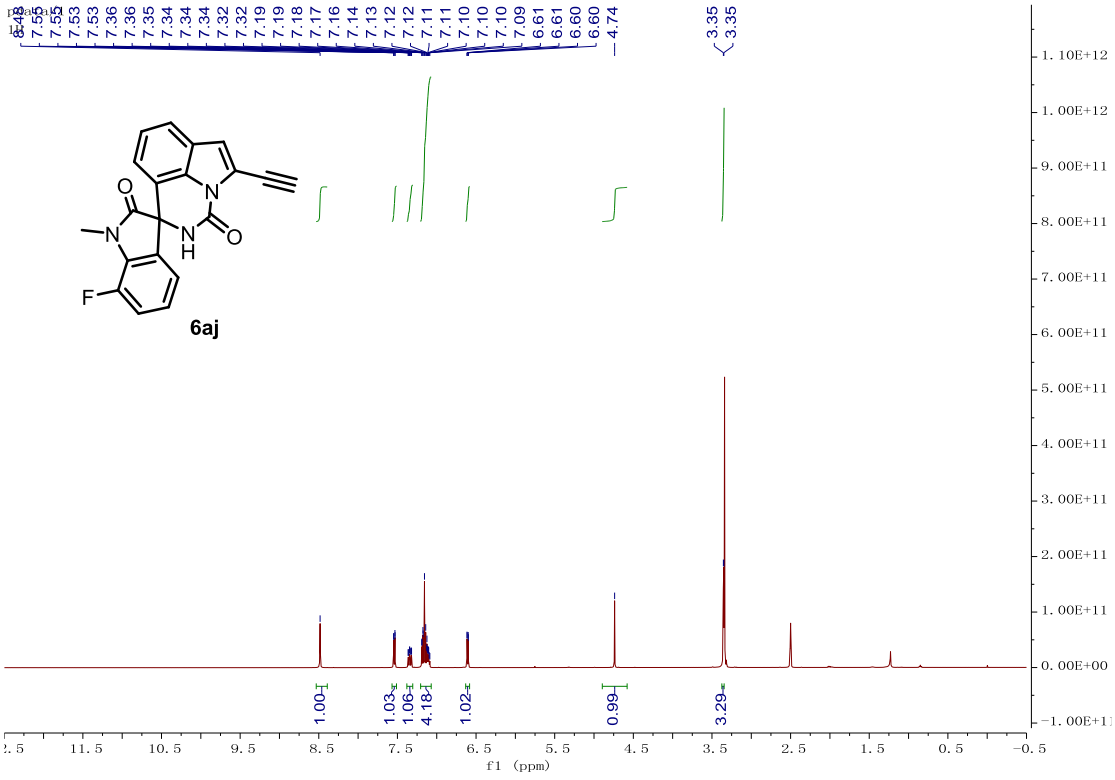


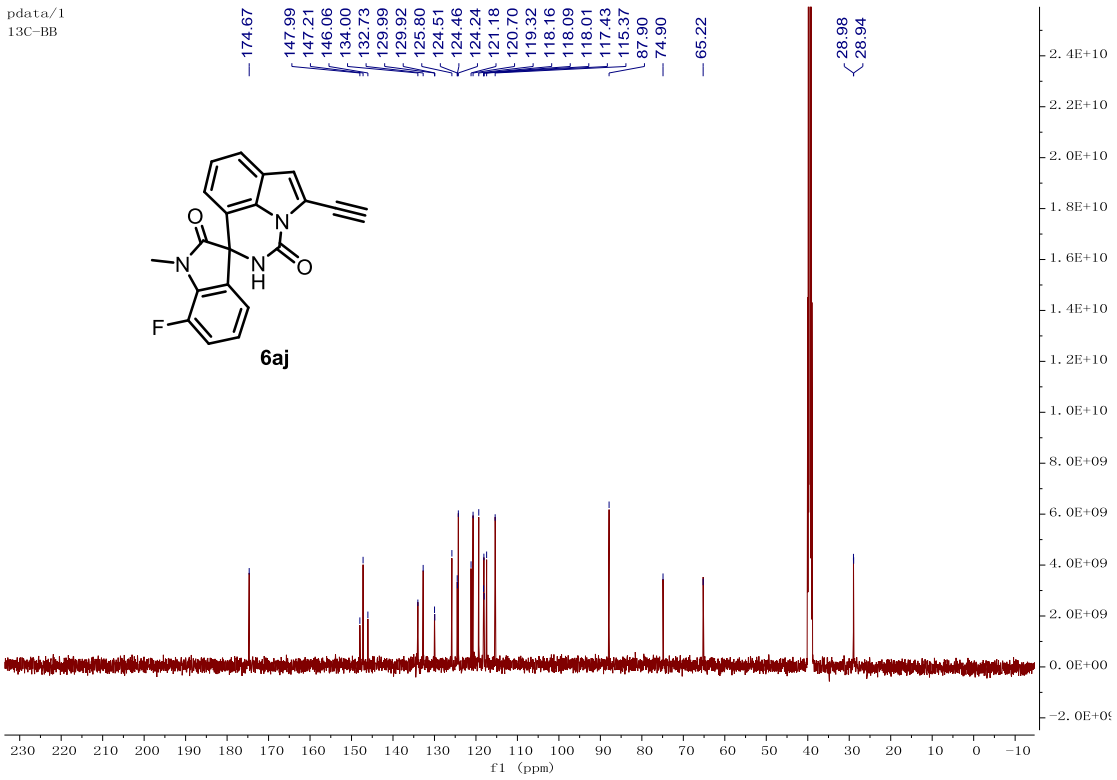

**5'-ethynyl-1,7-dimethylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ai)**

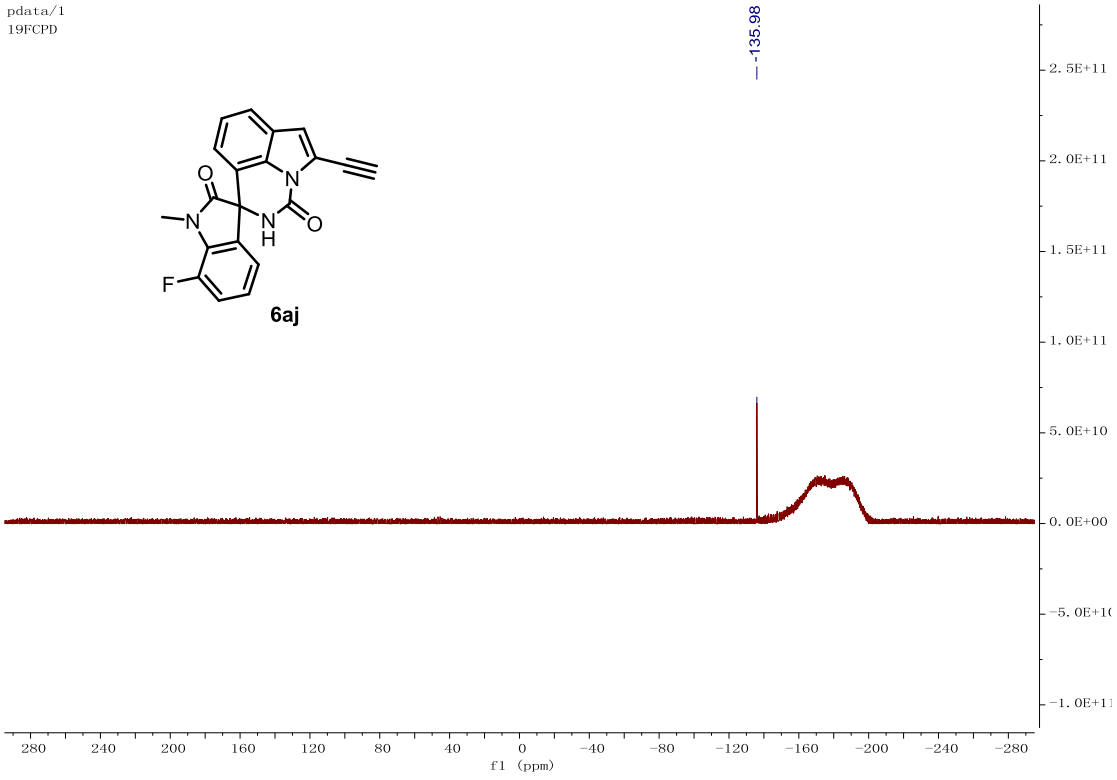




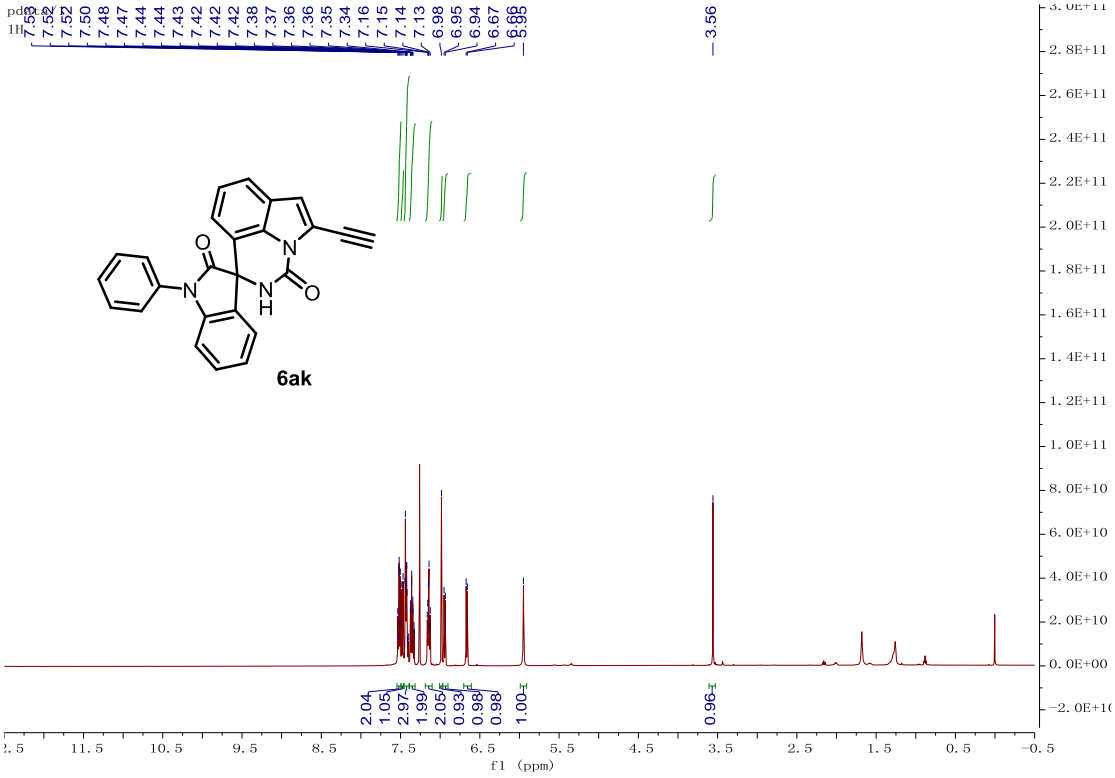

**5'-ethynyl-7-fluoro-1-methylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6aj)**

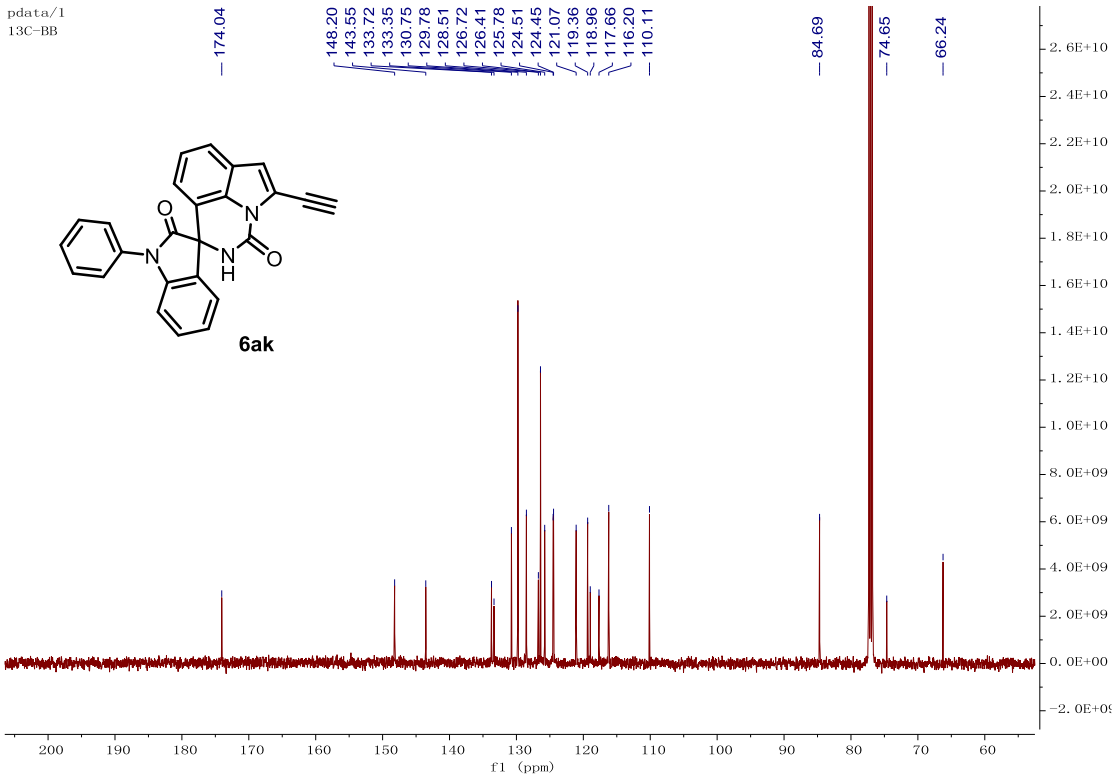



pdata/1
13C-BB
174.67
147.99
147.21
146.06
134.00
132.73
129.99
129.92
125.80
124.51
124.46
124.24
121.18
120.70
119.32
118.16
118.09
118.01
117.43
115.37
87.90
74.90
65.22
28.98
28.94
6aj
f1 (ppm)

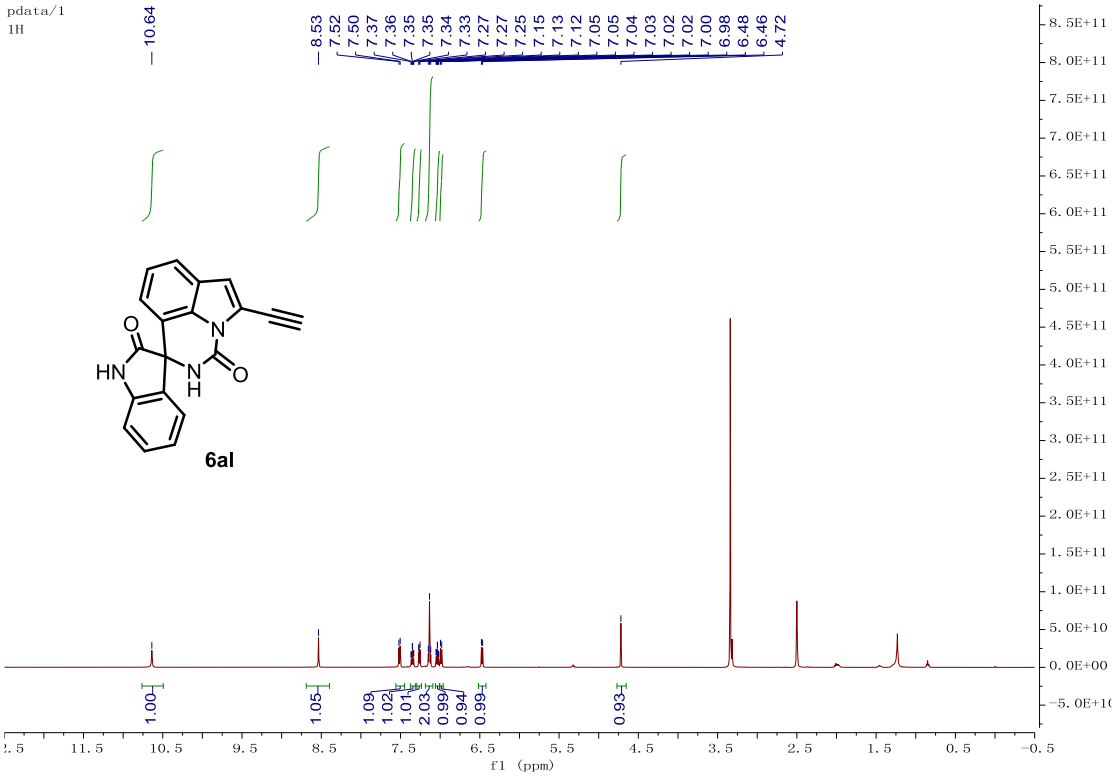

pdata/1
19FCPD
-135.98
6aj
f1 (ppm)

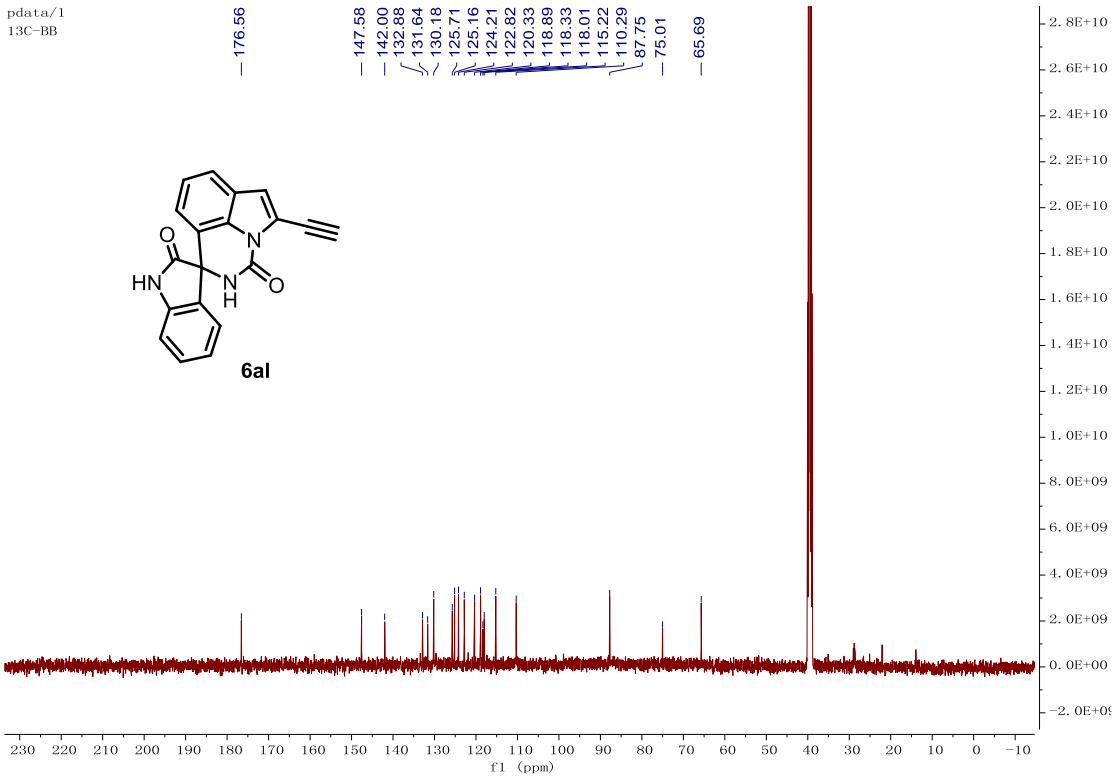
**5'-ethynyl-1-phenylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6ak)**



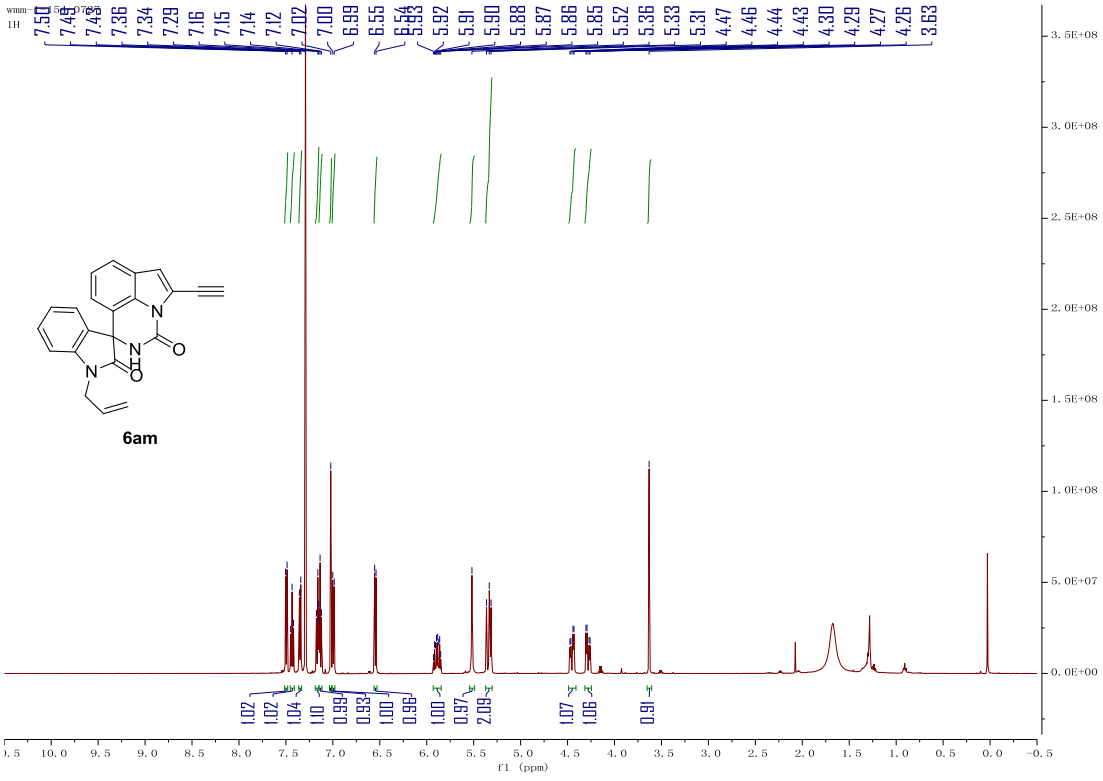



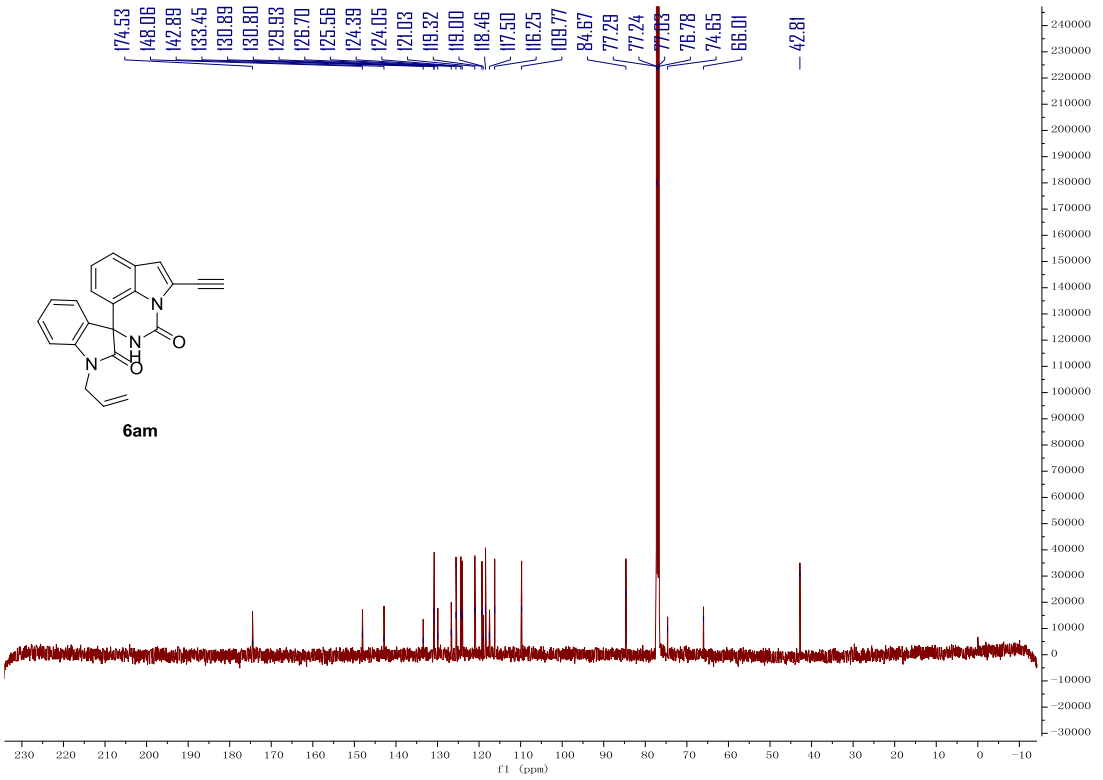
**5'-ethynylspiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione (6al)**



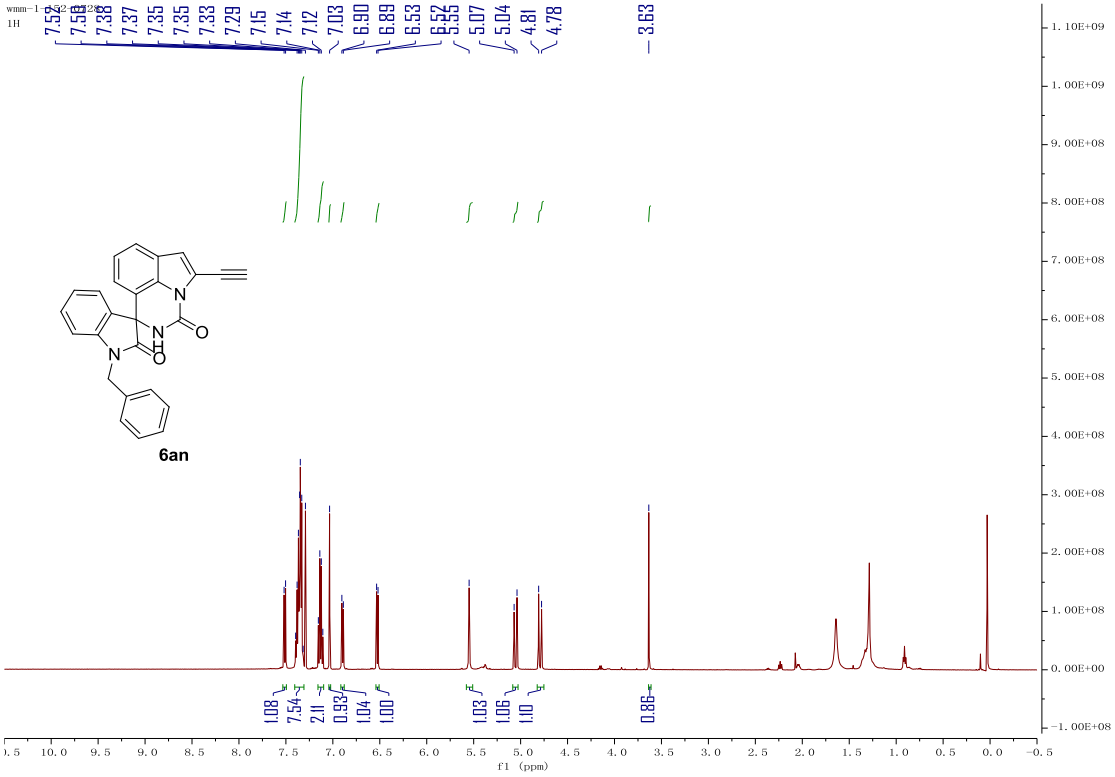



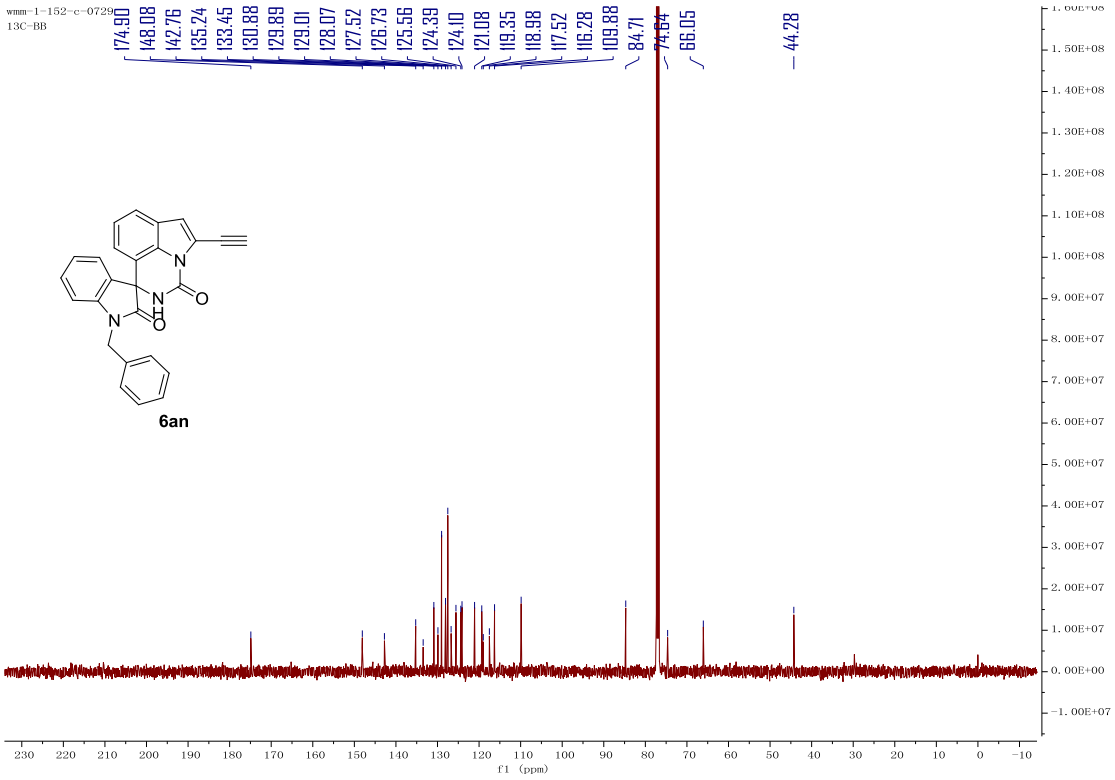
**allyl-5'-ethynylspiro[indoline-3,1'-pyrrolo[3,2,1-ij]quinazoline]-2,3'(2'H)-dione (6am)**



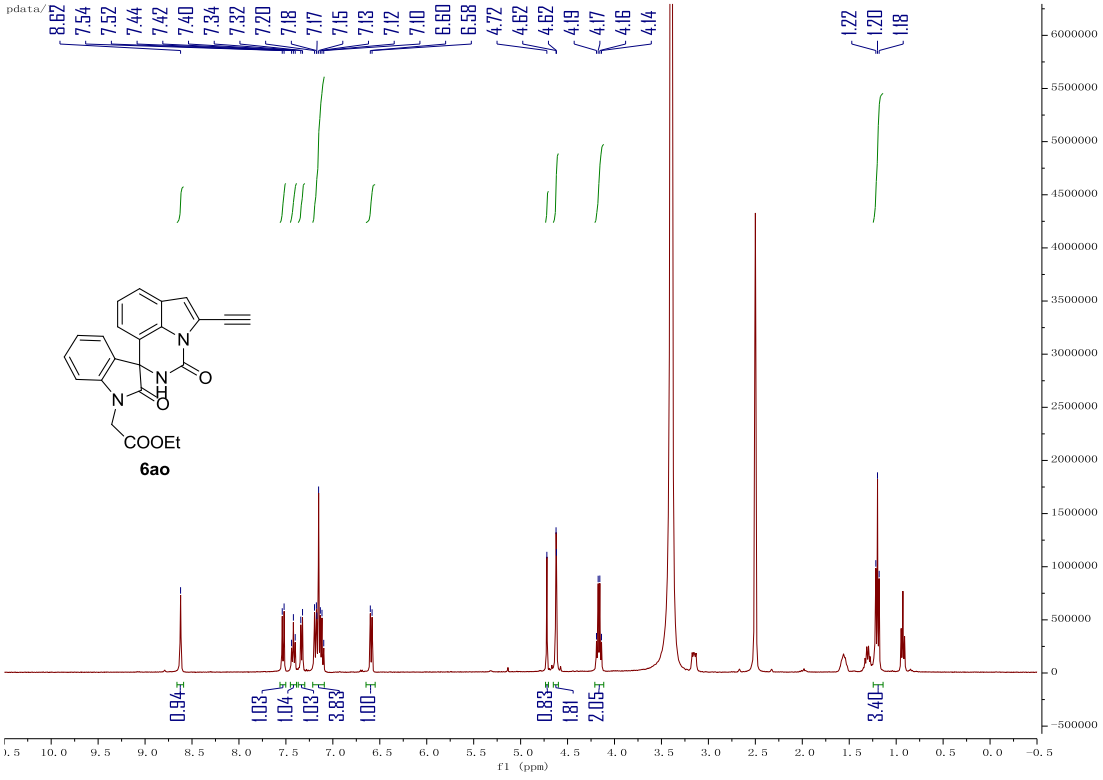



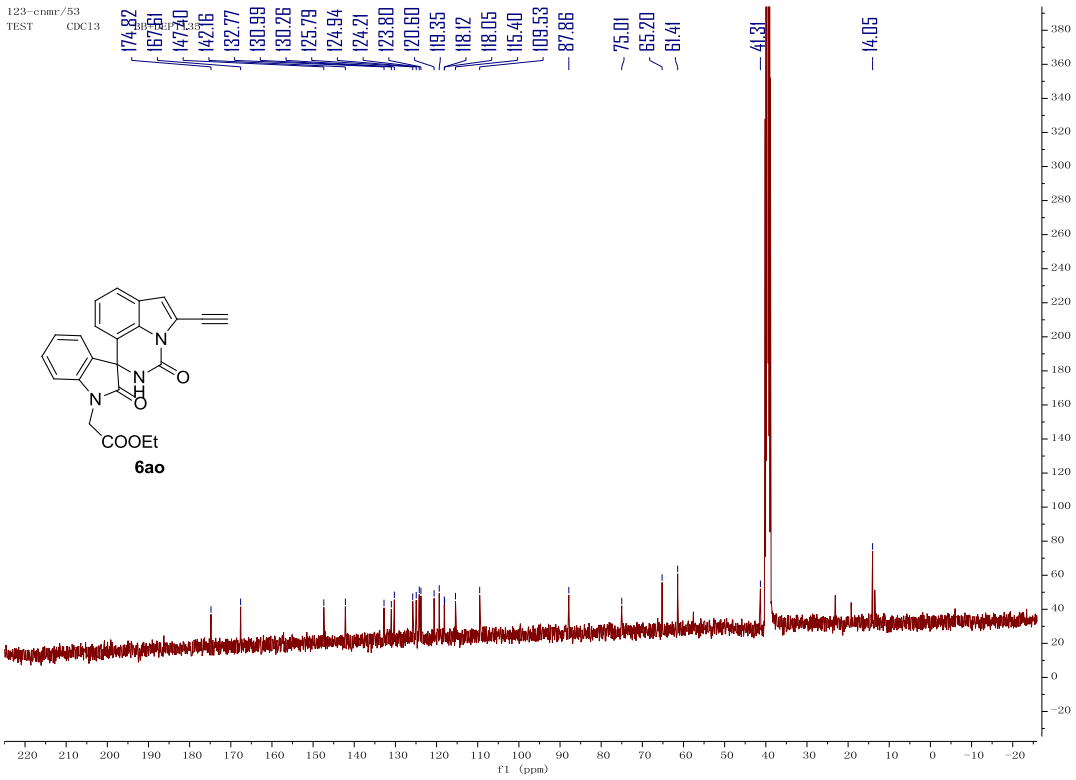
**1-benzyl-5'-ethynylspiro[indoline-3,1'-pyrrolo[3,2,1-ij]quinazoline]-2,3'(2'H)-dione (6an)**



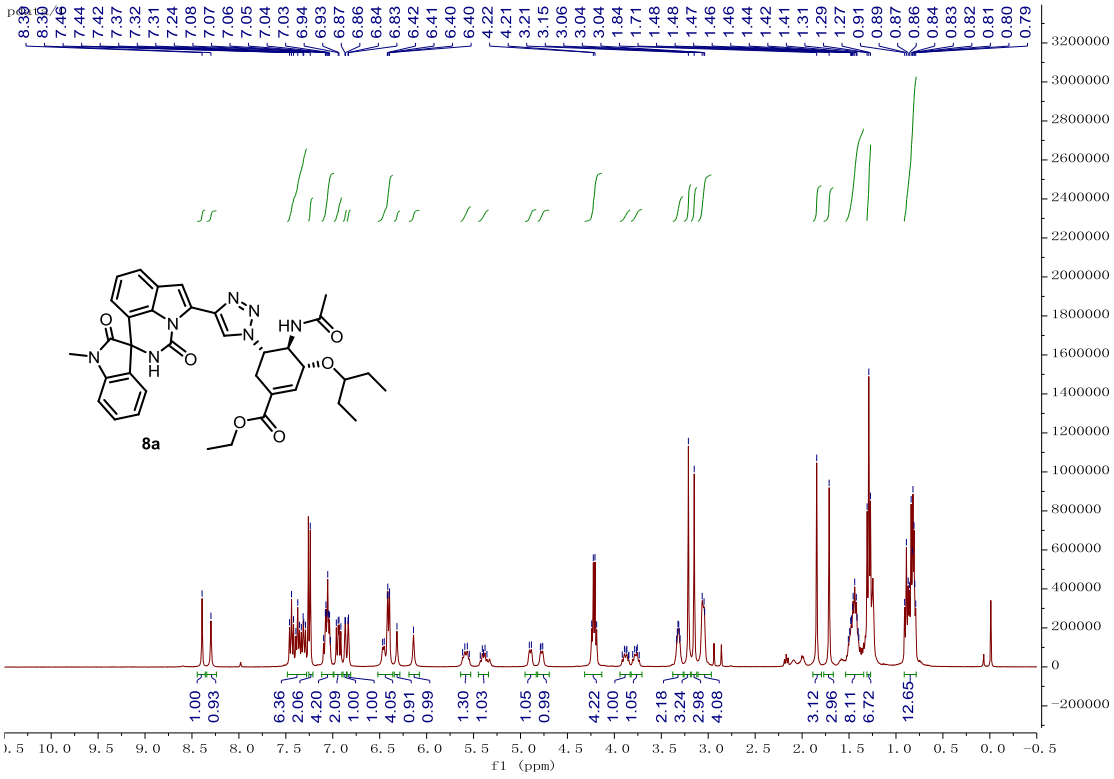



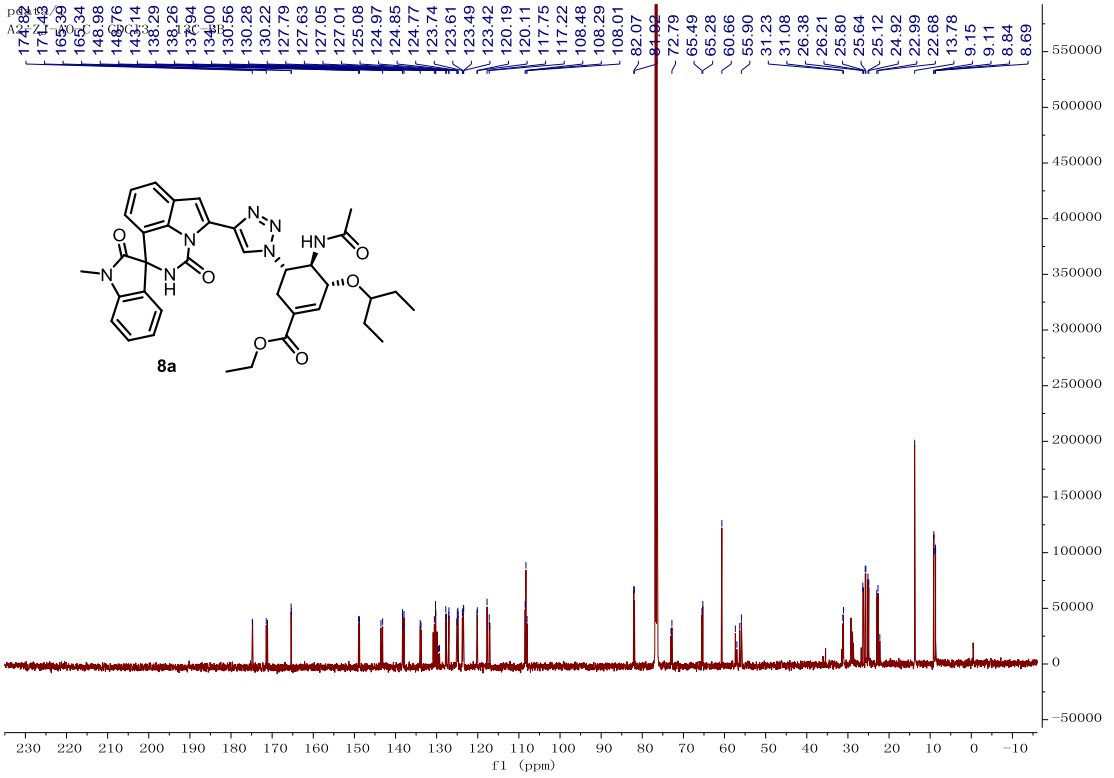
**ethyl 2-(5'-ethynyl-2,3'-dioxo-2',3'-dihydrospiro[indoline-3,1'-pyrrolo[3,2,1-ij]quinazolin]-1-yl)acetate (6ao)**



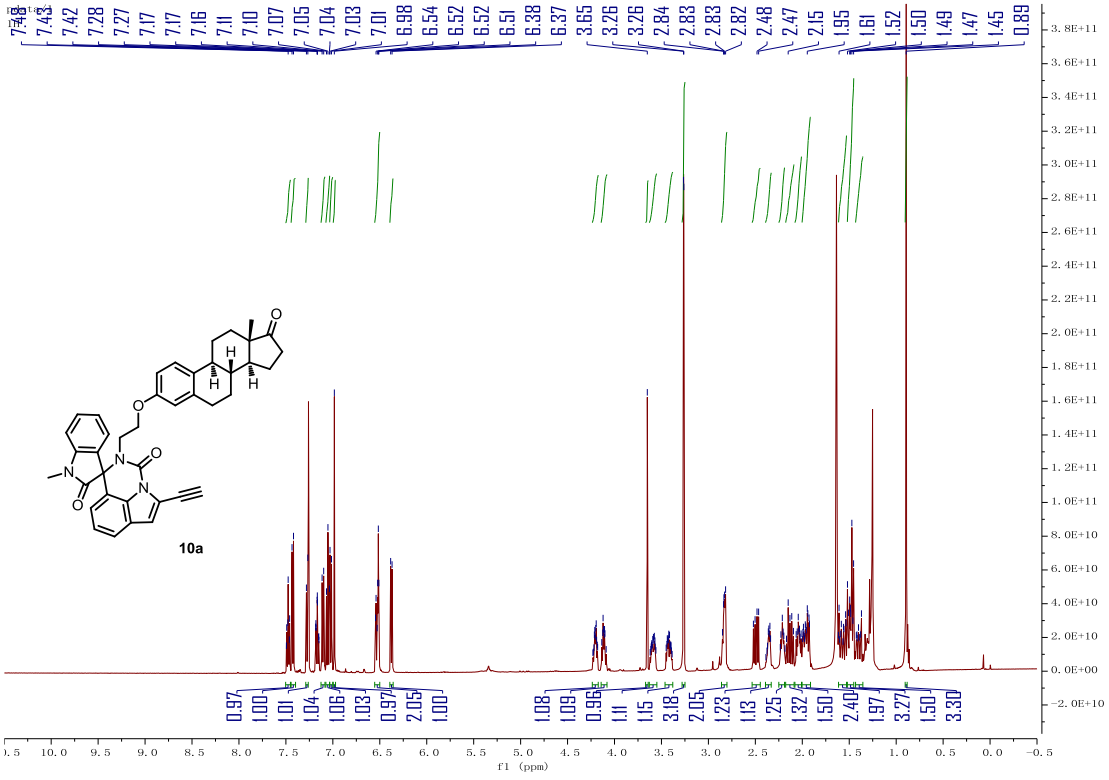



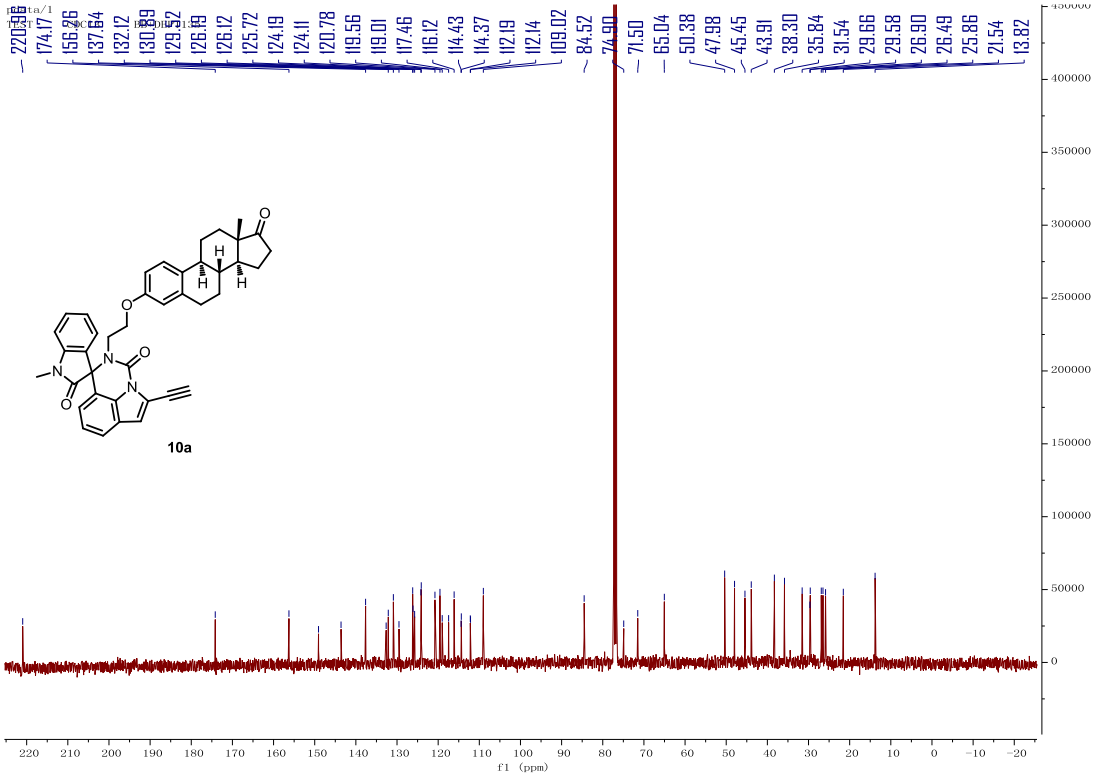
**Ethyl(3*R*,4*R*,5*S*)-4-acetamido-5-(4-(1-methyl-2,3'-dioxo-2',3'-dihydrospiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazolin]-5'-yl)-1*H*-1,2,3-triazol-1-yl)-3-(pentan-3-yloxy)cyclohex-1-ene-1-carboxylate (8a)**



**5'-Ethynyl-1-methyl-2'-(2-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)ethyl)spiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazoline]-2,3'(2'*H*)-dione**



**(3R,4R,5S)-Ethyl 4-acetamido-5-(4-(1-methyl-2'-(2-(((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-3-yl)oxy)ethyl)-2,3'-dioxo-2',3'-dihydrospiro[indoline-3,1'-pyrrolo[3,2,1-*ij*]quinazolin]-5'-yl)-1*H*-1,2,3-triazol-1-yl)-3-(pentan-3-yloxy)cyclohex-1-enecarboxylate**