Supporting Information

Photoredox Catalyzed Hydroazolylation of Alkenes *via* Phosphoranyl Radicals

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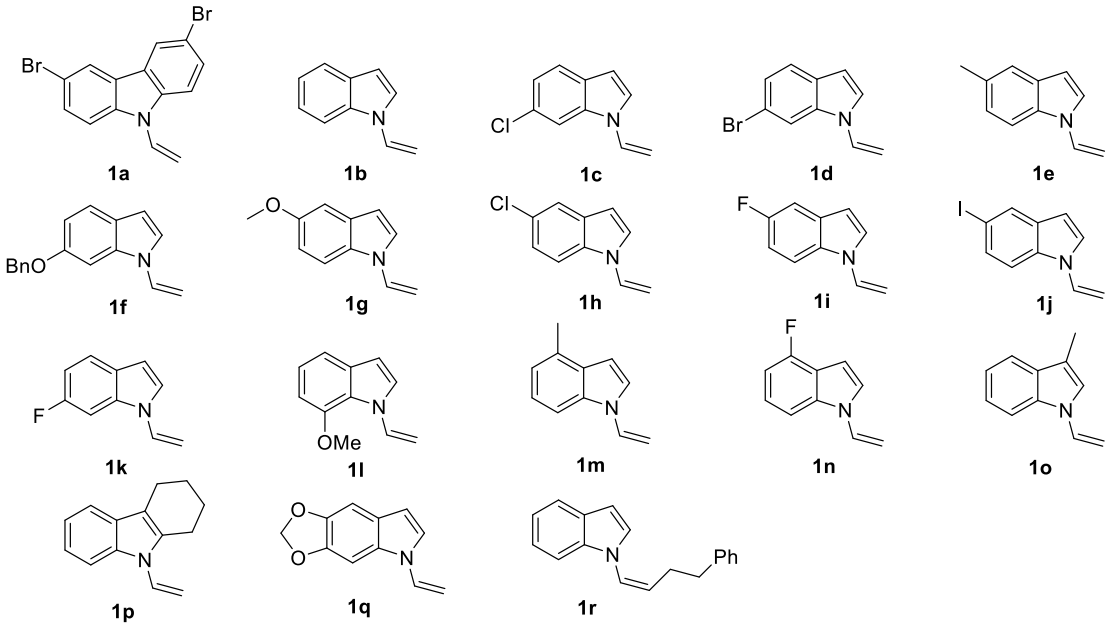
Contents

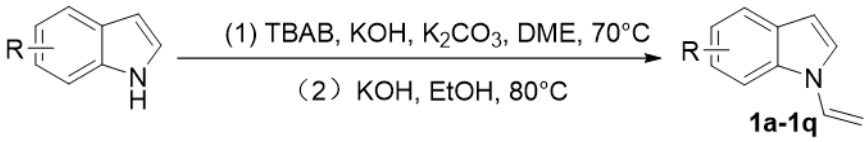
1. General information

All chemicals and reagents were used of commercial grade and were used without further purification. The reactions were monitored by thin-layer chromatography (TLC) using silica gel GF254. Column chromatography was performed with 200–300 mesh silica gel. All yields refer to isolated products after purification. The intermediates and the products synthesized were fully characterized by spectroscopic data. The NMR spectra were recorded on Bruker DRX-400 (^{1}H: 400 MHz, ^{13}C: 101 MHz) using $CDCl_3$ as solvent. The following abbreviation were used to explain the multiplicities: (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, (sept) = septuplet, (dd) = double doublet, (dt) = double triplet, (dq) = double quartet, (ddd) = double-double doublet, (m) = multiplet; Chemical shifts (δ) are expressed in parts per million (ppm) and *J* values are given in hertz (Hz). The melting points were measured by the XT-4A melting point apparatus without correction.

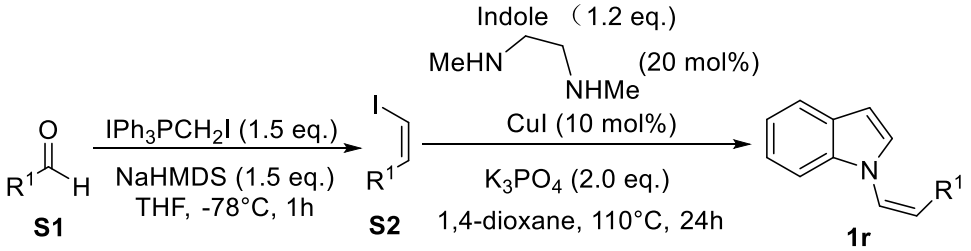
2. Synthesis of substrates **1** and **2** [1]

2.1 Synthesis of *N*-Vinylindole **1**



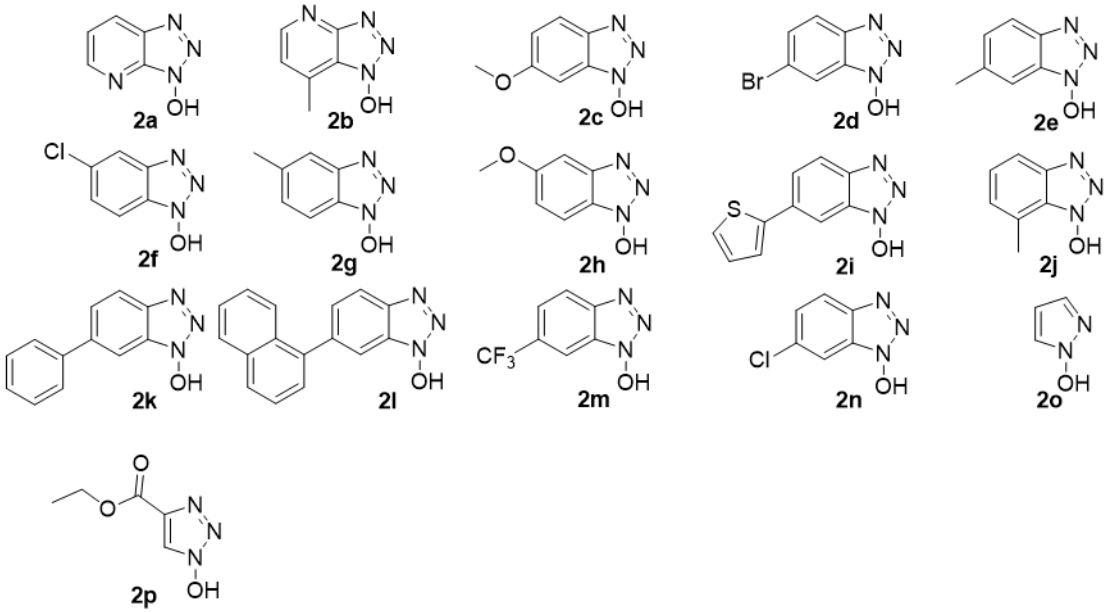


In a round-bottom flask, substrate indole (1.0 equiv.), tetrabutylammonium bromide (TBAB) (0.1 equiv.), KOH (10.0 equiv.), K_2CO_3 (4.0 equiv.) and the solvent DCE (0.27 M) were added. Then, the mixture was stirred at 70℃ for 12 h. After the reaction completion monitored by TLC analysis, the solvent was evaporated under reduced pressure. The mixture of the residue, KOH (4.0 equiv.), and EtOH (0.20 M) were stirred in a preheated oil at 80 ℃ for 3 h. After the reaction completion monitored by TLC analysis, the reaction mixture was filtered and evaporated under vacuum. The residue was purified by a silica-gel column chromatography using petroleum ether/ethyl acetate as an eluent to obtain the product **1a-1q**[1].

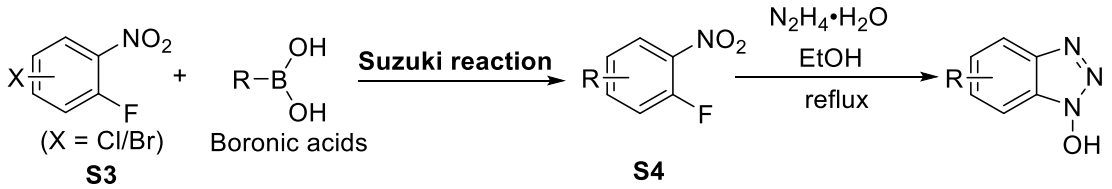


Under nitrogen atmosphere, iodomethyl triphenylphosphonium iodide (10.32 g, 18.50 mmol, 1.5 equiv) was suspended in THF (26.0 mL). At room temperature, sodium bis(trimethylsilyl)amide (2.00 M in THF, 9.2 mL, 18.50 mmol, 1.5 equiv) was added dropwise over 5 min. The reaction was stirred for 30 min then cooled to -78 ℃. A solution of **S1** (12.32 mmol, 1.0 equiv) in THF (26.0 mL) was added dropwise over 15 min. The reaction was then stirred at -78 ℃ for 1 h then quenched with saturated ammonium chloride solution(10.0 mL) then warmed to RT. The crude was diluted with Et_2O (20.0 mL) and saturated salt solution (20.0 mL). The layers were separated, the aqueous layers were extracted with Et_2O (5 × 30.0 mL). The organic layer was washed with sat. $NaHCO_3$(2 × 20.0 mL), then brine (20.0 mL). The organic layers were combined and concentrated under reduced pressure. The compound was purified by column chromatography: SiO_2 using pentane affording **S2.** Then, CuI (10 mol%), **S2**(1.2 equiv.) and K_3PO_4 (2.0 equiv.) were added to pre-dried a flask with a Teflon-lined septum. The flask was then evacuated and backfilled with N_2 (3 cycles). Indole (1.0 equiv.), *N*,*N*-dimethylethane-1,2-diamine (20 mol%), and 1,4-dioxane (0.50 M) were added by syringe at room temperature. The flask was then sealed and the reaction mixture was stirred at 110 ℃ for 24 h. The reaction was cooled to room temperature. Ethyl acetate (10.0 mL) was added and stirred for 10 min. The deposition was separated and washed with ethyl acetate (20.0 mL × 3). The organic phase was combined. The solvent was removed under vacuum. The crude product was purified by colum chromatography on silica gel to give corresponding *N*-alkenyl indolproducts**1r**.

2.2 Synthesis of 1-Hydroxybenzotriazole **2a-2l**



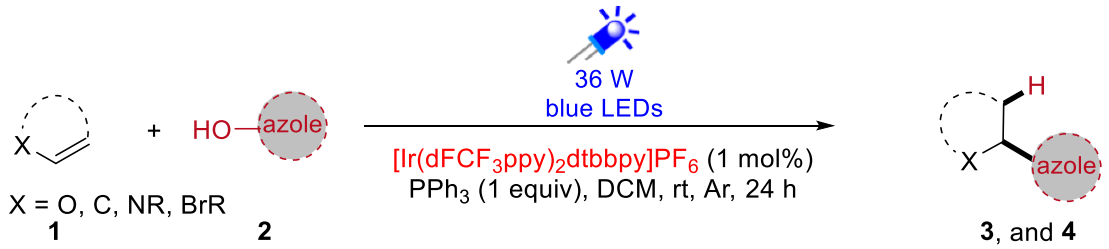
2m-2p were purchased from reagent company.



To a solution of **S3** (3.0 mmol, 1.0 equiv.) and boronic acid (6.0 mmol, 2.0 equiv.) in 1,4-dioxane (5 Vol) was added 2M Na_2CO_3 (9.0 mmol, 3.0 equiv.) and purged with argon for 5 min, Pd $(PPh_3)_4$ (0.3 mmol, 0.1 equiv.) was added and stirred at 100 ℃ in oil bath for 16 h under argon atmosphere. After completion of the reaction, monitored by TLC, the reaction mixture was diluted with water (20 mL) and extracted with EtOAc (3 ×40 mL). The combined organic extracts were washed with water (2 ×10 mL) and brine (2 ×10 mL), dried over anhydrous Na_2SO_4 and filtered. The solvent was removed under vacuum. The crude product was purified by colum chromatography on silica gel to give corresponding products **S4**. Then, **S4** (3 mmol, 1.0 equiv.) and N_2H_4•H_2O (6mmol, 2.0 equiv.) in absolute EtOH (8 mL) were added to 30.0 mL reaction tube. Afterwards, reflux reaction at 80 ℃ for 24 hours . Concentrate the solvent under reduced pressure , dissolve the residue in a 10% Na_2CO_3 aqueous solution (20 mL), extract the solution with Et2O (20mL) to remove any starting material. Acidify with

concentrated HCl to precipitate the product, filter the solution, rinse the precipitate with water, dry the precipitate to obtain 1-hydroxybenzotriazole**2a-2l**.

3. General Procedure for preparing compounds **3a-3zc** and **4a-4p**



Under Ar atmosphere, *N*-vinylcarbazole **1** (0.20mmol, 1.0 equiv), 1-Hydroxybenzotriazole **2** (0.22 mmol, 1.1 equiv), Ph_3P (0.20 mmol, 1.0 equiv), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%, 0.002 mmol) in DCM (2.0 mL, 0.1 M) were added to 10.0 mL reaction tube. The mixture was stirred at 490 nm blue light (LEDs, 36W) and monitored by TLC. After stirring for 24h. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residues were purified by flash column chromatography on silica gel to provide the products **3,** and **4**. The products were further identified by NMR spectroscopy.

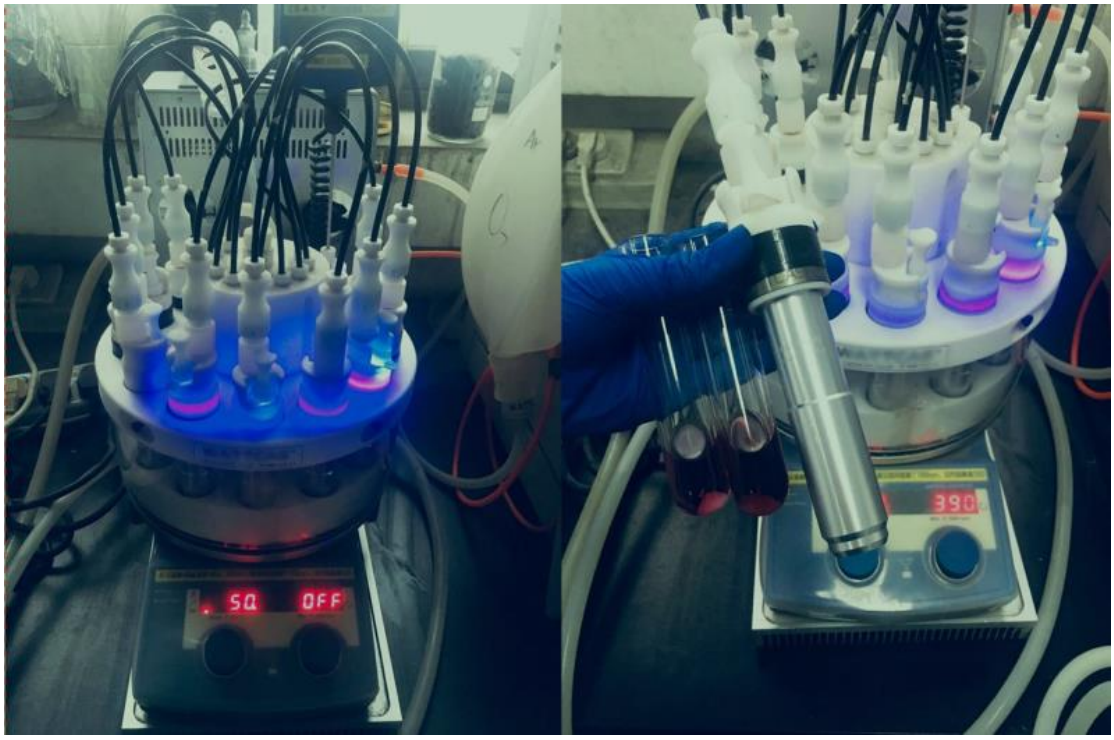


Figure S1. Details for the photochemical reaction setup.

The light Source and the Material of the Irradiation Vessel

Manufacturer: Xi'an WATTECS experimental equipment Co. Ltd

Model: WP-TEC-1020SL

Broadband source: X = 490 nm (light power: 36W).

Material of the irradiation vessel: borosilicate reaction tube (10 ml)

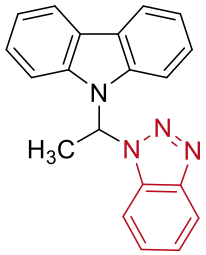
Distance from the light source to the irradiation vessel: 2.0 cm

Not use any filters

4. Spectroscopic Data of **3a-3zc**, **4a-4p**.

4.1 Spectroscopic Data of **(3a)**

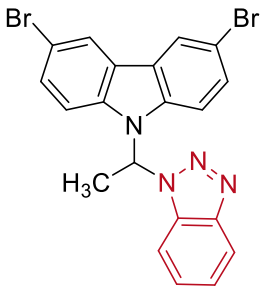
9-(1-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **3a** as white solid (50.0 mg, 80% yield). **MP**: 169.8-171.9 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.99 (d, *J* = 7.8 Hz, 2H), 7.94 (d, *J* = 8.3 Hz, 1H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.34 (t, *J* = 8.4 Hz, 2H), 7.29 (q, *J* = 6.8 Hz, 1H), 7.20–7.12 (m, 3H), 7.05 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 1H), 6.90 (d, *J* = 8.3 Hz, 1H), 2.55 (d, *J* = 6.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 138.6, 132.8, 128.0, 126.5, 124.4, 124.0, 120.8, 120.5, 120.1, 109.8, 109.6, 65.0, 17.9. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{20}H_{16}N_4Na$ $[M+Na]^+$, 335.1267; found, 335.1264. Data consistent with those previously reported[2].

4.2 Spectroscopic Data of **(3b)**

9-(1-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)ethyl)-3,6-dibromo-9*H*-carbazole

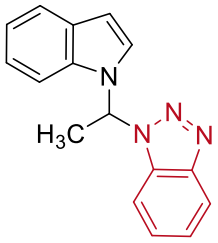


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **3b** as white solid (75.2 mg, 80% yield). **MP**: 232.4-234.3 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.12 (S, 2H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.52 (dd, *J* = 8.8, 2.0 Hz, 2H), 7.40 (d, *J* = 8.8 Hz, 2H), 7.33–7.27 (m, 2H), 7.26–7.19 (m,

1H), 6.91 (d, *J* = 8.2 Hz, 1H), 2.62 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 137.6, 132.6, 130.0, 128.4, 124.8, 124.6, 123.8, 120.5, 113.9, 111.2, 109.3, 65.0, 18.1. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{20}H_{14}Br_2N_4Na$ $[M+Na]^+$, 490.9477; found, 490.9473.

4.3 Spectroscopic Data of **(3c)**

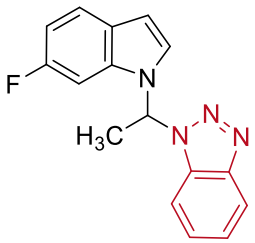
1-(1-(1*H*-Indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3c** as purple solid (38.3 mg, 73% yield). **MP**: 111.8-113.3 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09–8.07 (m, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.55 (d, *J* = 3.4 Hz, 1H), 7.51 (d, *J* = 8.4 Hz, 1H), 7.41 (q, *J* =7.1 Hz, 1H), 7.37–7.32 (m, 2H), 7.27–7.22 (m, 2H), 7.19 (ddd, *J* = 8.0, 7.1, 1.1 Hz, 1H), 6.70 (d, *J* = 3.6 Hz, 1H), 2.49 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 135.7, 131.6, 129.1, 128.0, 124.4, 123.9, 122.9, 121.5, 121.0, 120.3, 109.7, 109.6, 104.2, 65.9, 20.1. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{16}H_{14}N_4Na$ $[M+Na]^+$, 285.1111; found, 285.1109; Data consistent with those previously reported[2].

4.4 Spectroscopic Data of **(3d)**

1-(1-(6-Fluoro-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole

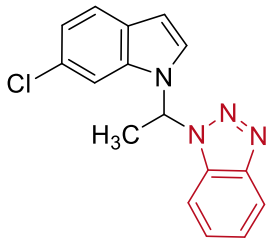


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3d** as purple solid (30.8 mg, 55% yield). **MP**: 158.3-

159.6 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.2 Hz, 1H), 7.50 (dd, *J* = 8.7, 5.4 Hz, 1H), 7.46 (d, *J* = 3.5 Hz, 1H), 7.37–7.29 (m, 2H), 7.25 (q, *J* = 6.8 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 7.13 (dd, *J* = 9.7, 2.3 Hz, 1H), 6.90–6.85 (m, 1H), 6.60 (d, *J* = 2.7 Hz, 1H), 2.44 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.2 (d, $J_{C\text{-}F}$ = 238.3 Hz), 146.6, 135.8 (d, *J* = 11.9 Hz), 131.5 128.1, 125.4, 124.5, 124.3 (d, *J* = 3.8 Hz), 122.3 (d, *J* = 10.0 Hz), 120.4, 109.8, 109.6 (d, *J* = 3.9 Hz), 104.3, 96.4 (d, *J* = 22.8 Hz), 66.0, 20.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -118.65. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{16}H_{13}FN_4Na$ $[M+Na]^+$, 303.1016; found, 303.1014.

4.5 Spectroscopic Data of **(3e)**

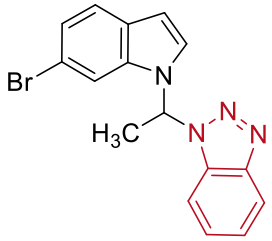
1-(1-(6-Chloro-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3e** as purple oil (40.4 mg, 68% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.3 Hz, 1H), 7.30 (d, *J* = 8.5 Hz, 1H), 7.25 (d, *J* = 3.5 Hz, 2H), 7.17–7.10 (m, 2H), 7.09–7.04 (m, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 6.89 (dd, *J* = 8.4, 1.8 Hz, 1H), 6.40 (d, *J* = 3.4 Hz, 1H), 2.23 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 136.1, 131.6, 129.0, 128.2, 127.6, 124.6, 124.5, 122.4, 121.7, 120.5, 109.7, 109.5, 104.4, 65.8, 20.2. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{16}H_{13}ClN_4Na$ $[M+Na]^+$, 319.0721; found, 319.0713.

4.6 Spectroscopic Data of **(3f)**

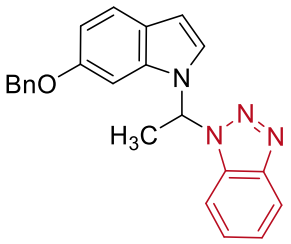
1-(1-(6-Bromo-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3f** as purple oil (47.8 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.3 Hz, 1H), 7.63 (s, 1H), 7.46–7.42 (m, 2H), 7.38–7.30 (m, 2H), 7.26 (d, *J* = 6.8 Hz, 1H), 7.23 (dd, *J* = 8.4, 1.7 Hz, 1H), 7.18 (d, *J* = 7.2 Hz, 1H), 6.59 (d, *J* = 2.7 Hz, 1H), 2.43 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 136.5, 131.6, 128.2, 127.9, 124.6, 124.4, 122.7, 120.5, 116.6, 112.6, 109.5, 104.4, 65.8, 20.3. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{16}H_{13}BrN_4Na$ $[M+Na]^+$, 363.0216; found, 363.0218.

4.7 Spectroscopic Data of **(3g)**

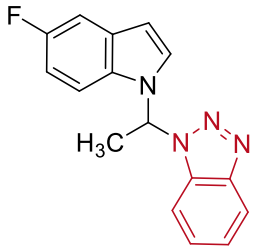
1-(1-(6-(Benzyloxy)-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3g** as yellow solid (55.3 mg, 75% yield). **MP**: 113.2-114.6 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86–7.82 (m, 1H), 7.29–7.24 (m, 3H), 7.21–7.17 (m, 3H), 7.14–7.03 (m, 4H), 6.95–6.92 (m, 1H), 6.78 (s, 1H), 6.67 (dd, *J* = 8.7, 2.2 Hz, 1H), 6.38 (d, *J* = 3.3 Hz, 1H), 4.88–4.81 (m, 2H), 2.21 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.0, 146.6 , 137.2, 136.5 131.5, 128.6, 128.0, 128.0, 127.7, 124.4, 123.3, 122.8, 122.0, 120.3, 111.5, 109.8, 104.1, 94.8, 70.6, 66.1, 20.0. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{23}H_{20}N_4ONa$ $[M+Na]^+$, 391.1529; found, 391.1530.

4.8 Spectroscopic Data of **(3h)**

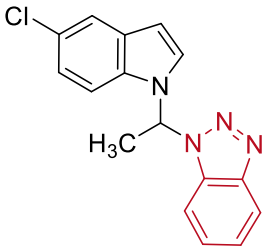
1-(1-(5-Fluoro-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3h** as purple solid (39.2 mg, 70% yield). **MP**: 157.3-158.8 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04–8.01 (m, 1H), 7.54 (d, *J* = 3.4 Hz, 1H), 7.35–7.28 (m, 4H), 7.23 (dd, *J* = 9.3, 2.5 Hz, 1H), 7.16–7.14 (m, 1H), 6.91 (td, *J* = 9.0, 2.5 Hz, 1H), 6.59 (d, *J* = 2.6 Hz, 1H), 2.43 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 158.5 (d $J_{C\text{-}F}$= 234.7 Hz), 146.7, 132.3, 131.5, 129.6 (d, *J* = 10.2 Hz), 128.1, 125.6, 124.5, 120.5, 111.3 (d, *J* = 26.1 Hz), 110.4 (d, *J* =9.5 Hz), 109.6, 106.4 (d, *J* = 23.3 Hz), 104.1 (d, *J* = 4.5 Hz), 66.3, 20.1. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -123.38. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{16}H_{13}FN_4Na$ $[M+Na]^+$, 303.1016; found, 303.1019.

4.9 Spectroscopic Data of **(3i)**

1-(1-(5-Chloro-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole

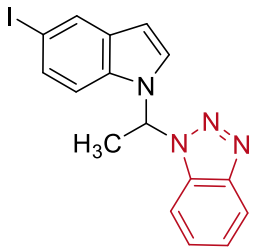


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3i** as yellow solid (38.0 mg, 64% yield). **MP**: 160.3-167.8 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04–8.01 (m, 1H), 7.55 (d, *J* = 2.0 Hz, 1H), 7.51 (d, *J* = 3.4 Hz, 1H), 7.35–7.28 (m, 4H), 7.16–7.10 (m, 2H), 6.57 (d, *J* = 2.6 Hz, 1H), 2.43 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 134.1, 131.5, 130.2, 128.2, 126.7, 125.3, 124.5, 123.2, 120.9, 120.5, 110.7, 109.5, 103.8, 66.1, 20.1.

HRMS (TOF-ESI$^+$): m/z calcd for $C_{16}H_{13}ClN_4Na$ $[M+Na]^+$, 319.0721; found, 319.0715.

4.10 Spectroscopic Data of **(3j)**

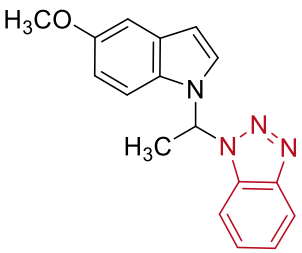
1-(1-(5-Iodo-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3j** as yellow solid (50.5 mg, 65% yield). **MP**: 161.3-162.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.04–8.01 (m, 1H), 7.93 (d, *J* = 1.7 Hz, 1H), 7.45 (d, *J* = 3.5 Hz, 1H), 7.41 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.35–7.27 (m, 3H), 7.20 (d, *J* = 8.7 Hz, 1H), 7.15–7.13 (m, 1H), 6.55 (d, *J* = 2.6 Hz, 1H), 2.44 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 134.8, 131.6, 131.5, 131.2, 130.3, 128.2, 124.8, 124.5, 120.5, 111.6, 109.5, 103.5, 84.6, 66.0, 20.1. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{16}H_{13}$ IN_4Na $[M+Na]^+$, 411.0077; found, 411.0071.

4.11 Spectroscopic Data of **(3k)**

1-(1-(5-Methoxy-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole

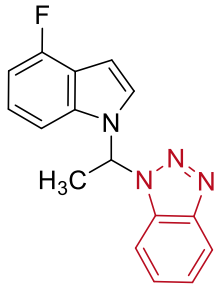


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3k** as yellow solid (42.1 mg, 72% yield). **MP**: 112.4-113.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.96–7.93 (m, 1H), 7.40 (d, *J* = 3.4 Hz, 1H), 7.24–7.19 (m, 4H), 7.09–7.06 (m, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 6.75 (dd, *J* = 9.0, 2.5

Hz, 1H), 6.49 (d, *J* = 2.6 Hz, 1H), 3.73 (s, 3H), 2.35 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 154.9, 146.6, 131.5, 130.9, 129.7, 128.0, 124.5, 124.4, 120.3, 113.0, 110.4, 109.8, 103.8, 103.2, 66.3, 55.9, 20.1. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{17}H_{16}N_4ONa$ $[M+Na]^+$, 315.1216; found, 315.1211.

4.12 Spectroscopic Data of **(3l)**

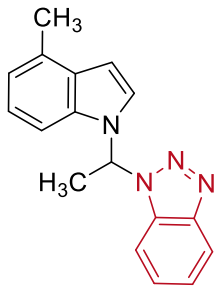
1-(1-(4-Fluoro-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3l** as purple solid (33.6 mg, 60% yield). **MP**: 161.3-162.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05–8.02 (m, 1H), 7.46 (d, *J* = 3.4 Hz, 1H), 7.36–7.29 (m, 3H), 7.22 (d, *J* = 8.3 Hz, 1H,), 7.19–7.16 (m, 1H), 7.10 (td, *J* = 8.1, 5.1 Hz, 1H), 6.79 (dd, *J* = 9.4, 7.9 Hz, 1H), 6.72 (d, *J* = 3.5 Hz, 1H), 2.46 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.5 (d, $J_{C\text{-}F}$ = 246.8 Hz), 146.6, 138.2, 131.5, 128.2, 124.5, 123.9 123.7 (d, *J* = 7.6 Hz), 120.5, 118.2 (d, *J* = 22.7 Hz), 109.5, 106.0, 105.7 (t, *J* = 6.3Hz), 100.3, 66.2, 20.2. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -121.16. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{16}H_{13}FN_4Na$ $[M+Na]^+$, 303.1016; found, 303.1009.

4.13 Spectroscopic Data of **(3m)**

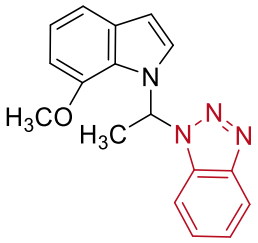
1-(1-(4-Methyl-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3m** as yellow solid (42.6 mg, 77% yield). **MP**: 114.2-115.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07–8.05 (m, 1H), 7.51 (d, *J* = 3.4 Hz, 1H), 7.40–7.30 (m, 4H), 7.25–7.22 (m, 1H), 7.17–7.13 (m, 1H) , 6.97 (d, *J* = 7.2 Hz, 1H), 6.70 (d, *J* = 4.3 Hz, 1H), 2.57 (s, 3H), 2.48 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 135.5, 131.6, 131.0, 128.9, 128.0, 124.4, 123.3, 123.0, 121.1, 120.3, 109.8, 107.1, 102.7, 66.0, 20.2, 18.7. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{17}H_{16}N_4Na$ $[M+Na]^+$, 299.1267; found, 299.1262.

4.14 Spectroscopic Data of **(3n)**

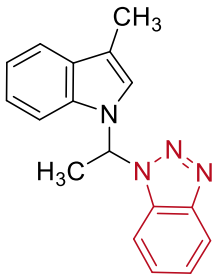
1-(1-(7-Methoxy-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3n** as yellow solid (40.9 mg, 70% yield). **MP**: 114.2-115.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.23 (q, *J* = 6.7 Hz, 1H), 8.03 (d, *J* = 8.1 Hz, 1H), 7.42 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.37–7.29 (m, 3H), 7.21 (d, *J* = 7.0 Hz, 1H), 7.06 (t, *J* = 7.9 Hz, 1H), 6.76 (d, *J* = 7.0 Hz, 1H), 6.52 (d, *J* = 3.4 Hz, 1H), 4.07 (s, 3H), 2.42 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz $CDCl_3$) δ 147.1, 146.1, 132.6, 130.8, 127.8, 125.1, 124.6, 124.3, 121.0, 120.0, 114.4, 109.8, 104.9, 103.8, 65.9, 55.6, 21.9. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{17}H_{16}N_4ONa$ $[M+Na]^+$, 315.1216; found, 315.1213.

4.15 Spectroscopic Data of **(3o)**

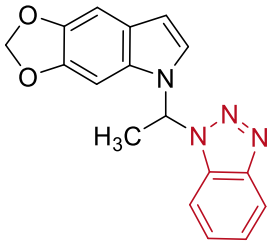
1-(1-(3-Methyl-1*H*-indol-1-yl)ethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3o** as yellow solid (40.9 mg, 74% yield). **MP**: 113.1-114.8 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 7.2 Hz, 1H), 7.54 (d, *J* = 7.7 Hz, 1H), 7.42 (d, *J* = 8.3 Hz, 1H), 7.35–7.27 (m, 3H), 7.25–7.17 (m, 3H), 7.13 (ddd, *J* = 8.0, 7.1, 1.0 Hz, 1H), 2.42 (d, *J* = 6.8 Hz, 3H), 2.33 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 136.1, 131.7, 129.5, 127.9, 124.3, 122.8, 121.2, 120.3, 120.3, 119.6, 113.5, 109.9, 109.4, 65.7, 20.3, 10.0. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{17}H_{16}N_4Na$ $[M+Na]^+$, 299.1267; found, 299.1269.

4.16 Spectroscopic Data of **(3p)**

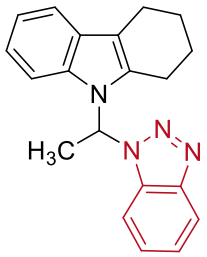
5-(1-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)ethyl)-5*H*-[1,3]dioxolo[4,5-f]indole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3p** as yellow solid (46.6 mg, 76% yield). **MP**: 170.1-171.8 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97–7.93 (m, 1H), 7.30 (d, *J* = 3.4 Hz, 1H), 7.25–7.17 (m, 2H), 7.14 (q, *J* = 6.8 Hz, 1H), 7.07–7.03 (m, 1H), 6.88 (s, 1H), 6.78 (s, 1H), 6.44 (d, *J* = 2.6 Hz, 1H), 5.80 (dd, *J* = 14.2, 1.3 Hz, 2H), 2.32 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 145.6, 143.8, 131.4, 130.9, 128.0, 124.4, 122.9, 122.5, 120.3, 109.8, 104.2, 100.9, 99.8, 91.0, 66.5, 20.0. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{17}H_{14}N_4O_2Na$ $[M+Na]^+$, 329.1009; found, 329.1005.

4.17 Spectroscopic Data of **(3q)**

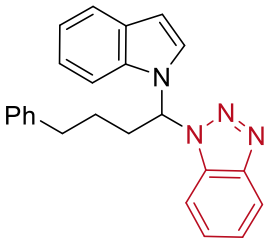
9-(1-(1*H*-Benzo[*d*][1,2,3]triazol-1-yl)ethyl)-2,3,4,9-tetrahydro-1*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3q** as yellow solid (44.3 mg, 70% yield). **MP**: 166.4-167.9 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.28 (dd, *J* = 5.7, 3.4 Hz, 1H), 7.13–7.05 (m, 3H), 6.92–6.87 (m, 2H), 6.84 (q, *J* = 6.8 Hz, 1H), 6.71 (d, *J* = 7.8 Hz, 1H), 2.76–2.69 (m, 1H), 2.55–2.51 (m, 2H), 2.33 (d, *J* = 6.8 Hz, 3H), 2.25–2.18 (m, 1H), 1.81–1.75 (m, 1H), 1.70–1.61 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.6, 135.0, 134.1, 132.8, 128.4, 128.0, 124.4, 121.9, 120.1, 120.0, 118.4, 112.5, 110.0, 109.7, 65.3, 23.4, 23.0, 22.8, 21.1, 19.6. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{20}H_{20}N_4Na$ $[M+Na]^+$, 339.1580; found, 339.1583.

4.18 Spectroscopic Data of **(3r)**

1-(1-(1*H*-Indol-1-yl)-4-phenylbutyl)-1*H*-benzo[*d*][1,2,3]triazole

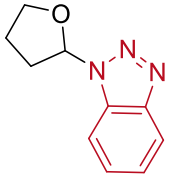


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 10) afforded **3r** as yellow solid (47.6 mg, 65% yield). **MP**: 165.4-166.6 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.97 (d, *J* = 8.1 Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 7.40 (d, *J* = 3.4 Hz, 1H), 7.32–7.12 (m, 7H), 7.10–7.01 (m, 4H), 6.56 (d, *J* = 3.4 Hz, 1H), 2.98–2.80 (m, 2H), 2.67 (t, *J* = 7.4 Hz, 2H), 1.71–1.63 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.4, 141.0, 136.0, 131.9, 128.9, 128.7, 128.5, 128.0, 126.3, 124.4, 124.1, 122.9, 121.5, 120.8, 120.4, 109.6, 109.4, 104.3, 69.1,

35.1, 32.9, 27.2. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{24}H_{22}N_4Na$ $[M+Na]^+$, 389.1737; found, 389.1729.

4.19 Spectroscopic Data of **(3s)**

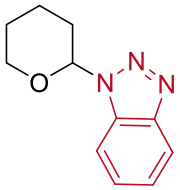
1-(Tetrahydrofuran-2-yl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **3s** as colorless oil (27.6 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.5 Hz, 1H), 7.71 (d, *J* = 8.3 Hz, 1H), 7.52–7.47 (m, 1H), 7.38 (t, *J* = 8.1 Hz, 1H), 6.51 (dd, *J* = 6.8, 2.4 Hz, 1H), 4.13–4.00 (m, 2H), 3.20–3.13 (m, 1H), 2.57–2.47 (m, 1H), 2.45–2.35 (m, 1H), 2.23–2.13 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 133.0, 127.6, 124.3, 120.0, 110.5, 88.0, 69.4, 30.9, 24.5. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{10}H_{11}N_3ONa$ $[M+Na]^+$, 212.0794; found, 212.0791. Data consistent with those previously reported[3].

4.20 Spectroscopic Data of **(3t)**

1-(tetrahydro-2*H*-pyran-2-yl)-1*H*-benzo[*d*][1,2,3]triazole

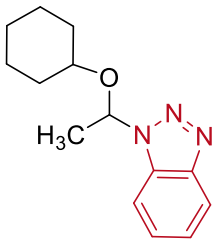


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **3t** as colorless oil (30.5 mg, 75% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.48 (t, *J* = 8.1 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 6.04 (dd, *J* = 8.3, 2.9 Hz, 1H), 3.97–3.91 (m, 1H), 3.81–3.76 (m, 1H), 2.66–2.57 (m, 1H), 2.25–2.16 (m, 2H) 1.89–1.80 (m, 1H), 1.78–1.72 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 132.6, 127.6, 124.3, 120.1, 111.2,

85.8, 67.0, 29.4, 25.1, 21.8. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{11}H_{13}N_3ONa$ $[M+Na]^+$, 226.0951; found, 226.0947. Data consistent with those previously reported[3].

4.21 Spectroscopic Data of **(3u)**

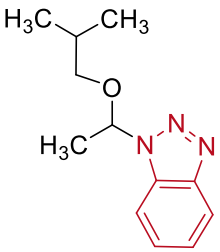
1-(1-(Cyclohexyloxy)ethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **3u** as colorless oil (38.3 mg, 78% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 8.4 Hz, 1H), 7.74 (d, *J* = 8.3 Hz, 1H), 7.49 (t, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.7 Hz, 1H), 6.04 (dd, *J* = 8.3, 2.9 Hz, 1H), 3.24–3.17 (m, 1H), 2.04–2.00 (m, 1H), 1.82 (d, *J* = 6.2 Hz, 3H), 1.76–1.69 (m, 1H), 1.57–1.52(m, 1H), 1.46–1.36 (m,3H), 1.21–1.11 (m, 3H), 1.06–0.96 (m, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.0, 131.3, 127.3, 124.2, 120.1, 111.7, 84.8, 75.9, 32.8, 31.2, 25.5, 24.0, 23.8, 21.9. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{14}H_{19}N_3ONa$ $[M+Na]^+$, 268.1420; found, 268.1415. Data consistent with those previously reported[3].

4.22 Spectroscopic Data of **(3v)**

1-(1-Isobutoxyethyl)-1*H*-benzo[*d*][1,2,3]triazole

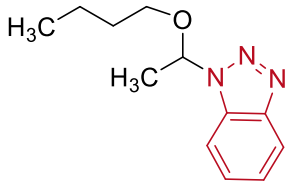


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **3v** as colorless oil (32.9 mg, 70% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 9.6 Hz, 1H), 7.79 (d, *J* = 9.5 Hz, 1H), 7.50–7.46 (m, 1H), 7.41–7.37 (m, 1H), 6.26–6.21 (m, 1H), 3.26 (dd, *J* = 9.1, 7.3 Hz, 1H), 2.93–2.89

(m, 1H), 1.87 (d, *J* = 5.2 Hz, 3H), 1.84–1.75 (m, 1H), 0.83 (d, *J* = 7.7 Hz, 3H), 0.79 (d, *J* = 7.7 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.0, 131.2, 127.5, 124.3, 120.2, 111.4, 87.7, 75.7, 28.3, 21.2, 19.3. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{12}H_{17}N_3ONa$ $[M+Na]^+$, 242.1264; found, 242.1261. Data consistent with those previously reported[3].

4.23 Spectroscopic Data of (**3w**)

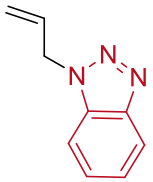
1-(1-Butoxyethyl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **3w** as colorless oil (32.9 mg, 69% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.50–7.46 (m, 1H), 7.41–7.37 (m, 1H), 6.24 (q, *J* = 6.1 Hz, 1H), 3.50–3.44 (m, 1H), 3.19–3.13 (m, 1H), 1.86 (d, *J* = 6.1 Hz, 3H), 1.52–1.45 (m, 2H), 1.34–1.21 (m, 2H), 0.80 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 131.5, 127.8, 124.6, 120.5, 111.7, 87.8, 69.2, 31.7, 21.6, 19.6, 14.1. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{12}H_{17}N_3ONa$ $[M+Na]^+$, 242.1264; found, 242.1259. Data consistent with those previously reported[3].

4.24 Spectroscopic Data of (**3x**)

1-Allyl-1*H*-benzo[*d*][1,2,3]triazole

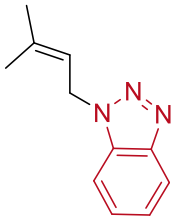


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 30) afforded **3x** as colorless oil (23.9 mg, 75% yield).**^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.5 Hz, 1H), 7.56 (dt, *J* = 8.4, 1.1 Hz, 1H), 7.50 (ddd, *J* = 8.2, 6.8, 0.9 Hz, 1H), 7.37 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 8.15–8.07 (m, 1H) , 5.36–5.34 (m, 1H), 5.32 (t, *J* = 1.1 Hz, 1H), 5.02 (d, *J* = 6.7 Hz, 2H). **^{13}C NMR** (100 MHz,

$CDCl_3$) δ 143.5, 130.2, 128.1, 128.0, 124.7, 123.7, 120.3, 109.0, 81.3. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_9H_9N_3Na$ $[M+Na]^+$, 182.0689; found, 182.0687. Data consistent with those previously reported[4].

4.25 Spectroscopic Data of (**3y**)

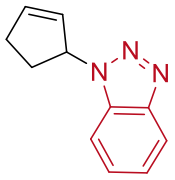
1-(3-Methylbut-2-en-1-yl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 30) afforded **3y** as colorless oil (27.3 mg, 73% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.3 Hz, 1H), 7.50–7.43 (m, 2H), 7.35 (ddd, *J* = 8.1, 6.4, 1.5 Hz, 1H), 5.46 (ddt, *J* = 8.4, 6.8, 1.5 Hz, 1H), 5.26 (d, *J* = 7.1 Hz, 2H), 1.90 (s, 3H), 1.78 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.3, 138.6, 127.2, 123.9, 120.1, 117.8, 109.8, 46.7, 25.8, 18.3. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{11}H_{13}N_3Na$ $[M+Na]^+$, 210.1002; found, 210.1005. Data consistent with those previously reported[5].

4.26 Spectroscopic Data of (**3za**)

1-(Cyclopent-2-en-1-yl)-1*H*-benzo[*d*][1,2,3]triazole

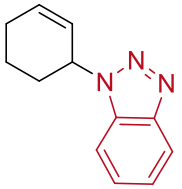


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 40) afforded **3za** as colorless oil (15.9 mg, 43% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.00 (dd, *J* = 8.4, 1.0 Hz, 1H), 7.55 (dt, *J* = 8.3, 1.1 Hz, 1H), 7.51–7.47 (m, 1H), 7.37 (ddd, *J* = 8.2, 6.8, 1.2 Hz, 1H), 6.32–6.29 (m, 1H), 5.91–5.88 (m, 1H), 5.75–5.72 (m, 1H), 2.67–2.58 (m, 1H), 2.46–2.35 (m, 2H), 2.31–2.22 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 142.0, 128.5, 127.9, 127.7, 124.6, 120.3, 109.3, 96.8,

31.5, 29.0. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{11}H_{11}N_3Na$ $[M+Na]^+$, 208.0845; found, 208.0844. Data consistent with those previously reported[6].

4.27 Spectroscopic Data of (**3zb**)

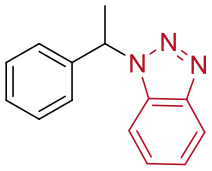
1-(Cyclohex-2-en-1-yl)-1*H*-benzo[*d*][1,2,3]triazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 40) afforded **3zb** as colorless oil (19.9 mg, 50% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.52–7.48 (m, 1H), 7.38 (ddd, *J* = 8.1, 6.8, 1.2 Hz, 1H), 6.17 (dt, *J* = 10.1, 3.7 Hz, 1H), 5.89 (ddd, *J* = 10.1, 4.2, 2.2 Hz, 1H), 5.14 (q, *J* = 4.5 Hz, 1H), 3.49 (d, *J* = 5.4 Hz, 2H), 2.26–2.19 (m, 1H), 2.14–1.93 (m, 2H), 1.87–1.79 (m, 1H), 1.75–1.66 (m, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 143.5, 136.3, 128.7, 128.0, 124.6, 123.3, 120.3, 109.2, 83.8, 27.2, 25.3, 18.1. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{12}H_{13}N_3Na$ $[M+Na]^+$, 222.1002; found, 222.1005. Data consistent with those previously reported[7].

4.28 Spectroscopic Data of (**3zc**)

1-(1-Phenylethyl)-1*H*-benzo[*d*][1,2,3]triazole

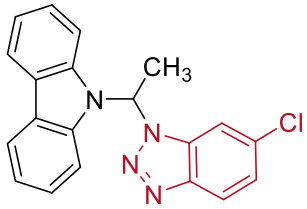


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 50) afforded **3zc** as colorless oil (5.8 mg, 13% yield). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.98–7.95 (m, 1H), 7.28–7.16(m, 8H), 5.96 (q, *J* = 7.1 Hz, 1H), 2.09 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 146.5, 140.2, 132.5, 129.0, 128.3, 127.1, 126.3, 123.9, 120.0, 110.2, 59.1, 21.2. **HRMS** (TOF-ESI$^+$): m/z calcd for

C14H13N3Na [M+Na]+, 246.1002; found, 246.1000. Data consistent with those previously reported[8].

4.29 Spectroscopic Data of (**4a**)

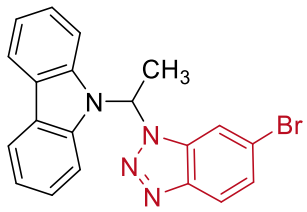
9-(1-(6-chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4a** as yellow solid (52.0 mg, 75% yield). **MP**: 193.1-194.3 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 7.3 Hz, 2H), 7.81 (s, 1H), 7.29–7.22 (m, 4H), 7.17 (q, *J* = 6.8 Hz, 1H), 7.12–7.08 (m, 2H), 6.91 (dd, *J* = 8.7, 1.6 Hz, 1H), 6.65 (d, *J* = 8.8 Hz, 1H), 2.46 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 138.5, 131.5, 130.4, 129.0, 126.6, 123.9, 120.9, 120.7, 119.5, 110.8, 109.4, 65.4, 17.9. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{20}H_{15}ClN_4Na$ $[M+Na]^+$, 369.0877; found, 369.0876.

4.30 Spectroscopic Data of (**4b**)

9-(1-(6-Bromo-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole

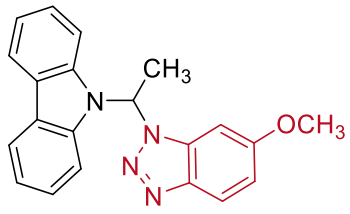


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4b** as yellow solid (53.2 mg, 68% yield). **MP**: 197.3-198.6 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.08 (d, *J* = 7.8 Hz, 2H), 7.46–7.40 (m, 4H), 7.36 (q, *J* = 6.8 Hz, 1H), 7.30–7.27 (m, 2H), 7.23 (dd, *J* = 8.8, 1.7 Hz, 1H), 6.78 (d, *J* = 8.8 Hz, 1H), 2.65 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ

147.8, 138.5, 131.8, 131.5, 126.6, 124.0, 122.8, 121.0, 120.7, 117.9, 111.1, 109.4, 65.4, 18.0. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{20}H_{15}BrN_4Na$ $[M+Na]^+$, 413.0372; found, 413.0375.

4.31 Spectroscopic Data of (**4c**)

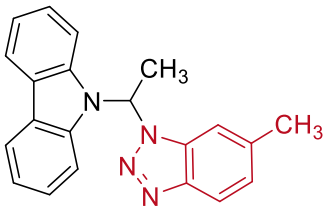
9-(1-(6-Methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4c** as yellow solid (52.0 mg, 76% yield). **MP**: 155.4-156.5 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 2H), 7.82 (d, *J* = 9.1 Hz, 1H), 7.55 (d, *J* = 8.2 Hz, 2H), 7.44–7.40 (m, 2H), 7.33–7.24 (m, 3H), 6.82 (dd, *J* = 9.1, 2.2 Hz, 1H), 6.14 (s, 1H), 3.30 (s, 3H), 2.68 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1, 141.9, 138.8, 134.0, 126.5, 123.9, 120.8, 120.8, 120.5, 116.7, 109.6, 90.2, 64.9, 55.2, 18.0. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{21}H_{18}N_4ONa$ $[M+Na]^+$, 365.1373; found, 365.1370.

4.32 Spectroscopic Data of (**4d**)

9-(1-(6-Methyl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole

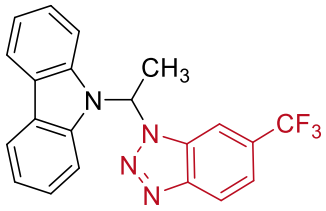


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4d** as white solid (49.0 mg, 75% yield). **MP**: 152.7-153.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.77 (s, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.41 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 2H), 7.34 (q, *J* = 6.8 Hz, 1H), 7.26 (dd,

J = 14.9, 1.0 Hz, 2H), 6.97 (dd, *J* = 8.5, 1.5 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 2.62 (d, *J* = 6.8 Hz, 3H), 2.37 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 138.7, 134.5, 131.4, 130.2, 126.5, 123.9, 120.8, 120.4, 119.1, 109.6, 109.3, 65.0, 21.5, 17.9. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{21}H_{18}N_4Na$ $[M+Na]^+$, 349.1424; found, 349.1418.

4.33 Spectroscopic Data of (**4e**)

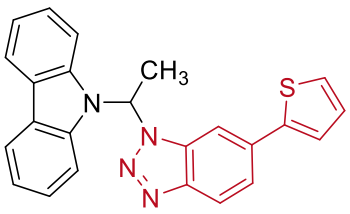
9-(1-(6-(Trifluoromethyl)-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4e** as yellow solid (51.0 mg, 67% yield). **MP**: 190.3-191.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.14 (d, *J* = 8.7 Hz, 1H), 8.09 (d, *J* = 7.8 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 7.50–7.41(m, 4H), 7.34–7.27 (m, 3H), 2.69 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.8, 138.6 132.1, 126.7, 124.1, 121.4(d, *J* = 3.0 Hz), 121.3, 121.0, 120.9, 109.5, 108.1 (d, *J* = 4.8 Hz), 65.5, 18.0. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.14. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{21}H_{15}F_3N_4Na$ $[M+Na]^+$, 403.1141; found, 403.1146.

4.34 Spectroscopic Data of (**4f**)

9-(1-(6-(Thiophen-2-yl)-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole

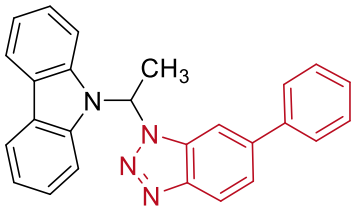


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4f** as white solid (47.3 mg, 60% yield). **MP**: 208.9-210.0 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.21 (s, 1H), 8.09 (d, *J* = 7.8 Hz, 2H), 7.50 (d,

J = 8.3 Hz, 2H), 7.45–7.36 (m, 4H), 7.30–7.28 (m, 2H), 7.25–7.23 (m, 2H), 7.04 (dd, *J* = 5.1, 3.7 Hz, 1H), 6.92 (d, *J* = 8.7 Hz, 1H), 2.66 (d, *J* = 6.8 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.3, 143.4, 138.6, 132.3, 131.4, 128.3, 127.2, 126.6, 125.4, 123.9, 123.8, 120.9, 120.6, 116.4, 110.2, 109.6, 65.2, 18.0. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{24}H_{18}N_4SNa$ $[M+Na]^+$, 417.1144; found, 417.1136.

4.35 Spectroscopic Data of (**4g**)

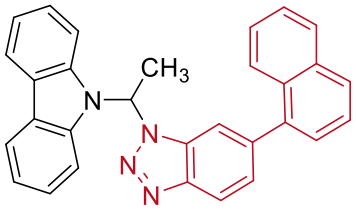
9-(1-(6-Phenyl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4g** as white solid (48.2 mg, 62% yield). **MP**: 205.2-206.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.19 (s, 1H), 8.10 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.52–7.48 (m, 2H), 7.47–7.38 (m, 6H), 7.34 (d, *J* = 7.3 Hz, 1H), 7.29 (d, *J* = 6.9 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 1H), 2.67 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.5, 140.4, 138.7, 138.3, 132.3, 129.0, 128.3, 127.7, 127.5, 126.6, 124.0, 120.9, 120.6, 118.0, 110.0, 109.6, 65.2, 18.0, 1.2. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{26}H_{20}N_4Na$ $[M+Na]^+$, 411.1580; found, 411.1547.

4.36 Spectroscopic Data of (**4h**)

9-(1-(6-(Naphthalen-1-yl)-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole

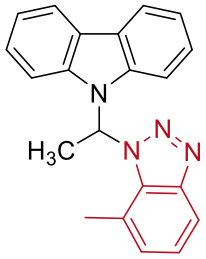


Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4h** as white solid (67.5 mg, 77% yield). **MP**: 203.4-

204.7 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.13 (d, *J* = 4.5 Hz, 2H), 8.11 (s, 1H), 7.87 (dd, *J* = 11.9, 7.5 Hz, 2H), 7.69 (d, *J* = 8.5 Hz, 1H), 7.62 (d, *J* = 8.3 Hz, 2H), 7.50–7.43 (m, 5H), 7.37–7.28 (m, 5H), 7.12 (d, *J* = 8.5 Hz, 1H), 2.71 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 147.1, 139.1, 138.8, 137.5, 133.9, 132.3, 131.7, 130.9, 128.5, 128.2, 127.5, 126.6, 126.4, 126.0, 125.8, 125.5, 124.0, 121.0, 120.9, 120.6, 109.8, 109.4, 65.1, 18.0. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{30}H_{22}N_4Na$ $[M+Na]^+$, 461.1737; found, 461.1730.

4.37 Spectroscopic Data of (**4i**)

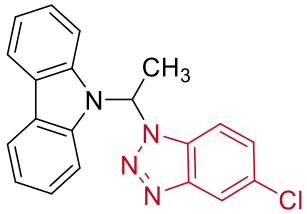
9-(1-(7-Methyl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4i** as white solid (47.0 mg, 72% yield). **MP**: 154.3-155.8 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.7 Hz, 2H), 7.54 (d, *J* = 8.3 Hz, 2H), 7.42 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 2H), 7.36 (q, *J* = 6.8 Hz, 1H), 7.28–7.24 (m, 2H), 7.08–6.99 (m, 2H), 6.82 (d, *J* = 8.2 Hz, 1H), 2.77 (s, 3H), 2.64 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 138.7, 133.0, 128.0, 126.5, 124.4, 123.9, 120.8, 120.4, 109.7, 107.0, 65.0, 18.0, 16.8. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{21}H_{18}N_4Na$ $[M+Na]^+$, 349.1424; found, 349.1417.

4.38 Spectroscopic Data of (**4j**)

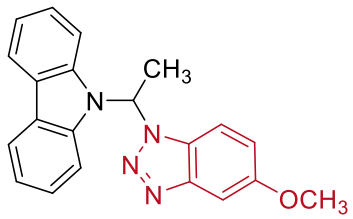
9-(1-(6-Chloro-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4j** as white solid (49.9 mg, 72% yield). **MP**: 198.4-199.8 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.9 Hz, 2H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.41 (d, *J* = 8.2 Hz, 2H), 7.35 (ddd, *J* = 8.2, 7.0, 1.2 Hz, 2H), 7.24–7.18 (m, 3H), 7.13 (dd, *J* = 8.9, 1.8 Hz, 1H), 6.91 (s, 1H), 2.54 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.2, 138.6, 134.5, 133.4, 126.6, 125.8, 124.1, 121.1, 120.9, 120.7, 109.7, 109.5, 65.2, 17.9. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{20}H_{15}ClN_4Na$ $[M+Na]^+$, 369.0877; found, 369.0875.

4.39 Spectroscopic Data of (**4k**)

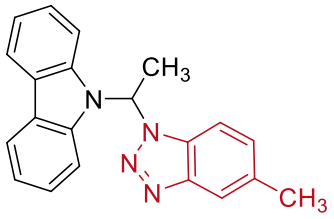
9-(1-(5-Methoxy-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4k** as white solid (50.0 mg, 73% yield). **MP**: 156.3-157.7 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.8 Hz, 2H), 7.76 (d, *J* = 9.1 Hz, 1H), 7.48 (d, *J* = 8.3 Hz, 2H), 7.35 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 2H), 7.24–7.17(m, 3H), 6.75 (dd, *J* = 9.1, 2.2 Hz, 1H), 6.07 (d, *J* = 2.2 Hz, 1H), 3.23 (s, 3H), 2.61 (d, *J* = 6.8 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.1, 141.9, 138.8, 134.0, 126.5, 123.9, 120.8, 120.8, 120.5, 116.7, 109.6, 90.2, 64.9, 55.2, 18.1. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{21}H_{18}N_4ONa$ $[M+Na]^+$, 365.1373; found, 365.1370.

4.40 Spectroscopic Data of (**4l**)

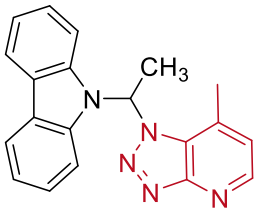
9-(1-(5-Methyl-1*H*-benzo[*d*][1,2,3]triazol-1-yl)ethyl)-9*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4l** as white solid (49.0 mg, 75% yield). **MP**: 196.5-197.9 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.05 (d, *J* = 7.8 Hz, 2H), 7.87 (d, *J* = 8.6 Hz, 1H), 7.51 (d, *J* = 8.3 Hz, 2H), 7.43–7.38 (m, 2H), 7.30 (q, *J* = 6.9 Hz, 1H), 7.24–7.22 (m, 2H), 7.04 (dd, *J* = 8.5, 1.4 Hz, 1H), 6.77 (s, 1H), 2.58 (d, *J* = 6.8 Hz, 3H), 2.19 (s, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 145.3, 138.8, 138.7, 133.4, 126.8, 126.5, 124.0, 120.8, 120.4, 119.6, 109.7, 109.0, 64.8, 22.1, 17.9. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{21}H_{18}N_4Na$ $[M+Na]^+$, 349.1424; found, 349.1420.

4.41 Spectroscopic Data of (**4m**)

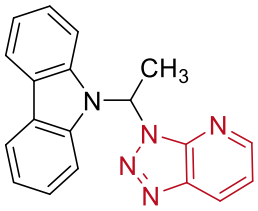
9-(1-(7-Methyl-1*H*-[1,2,3]triazolo[4,5-*b*]pyridin-1-yl)ethyl)-9*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **4m** as yellow solid (53.4 mg, 82% yield). **MP**: 190.0-191.2 °C; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.47 (d, *J* = 4.7 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 2H), 8.03 (d, *J* = 7.7 Hz, 2H), 7.82 (q, *J* = 7.2 Hz, 1H), 7.50 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 2H), 7.28–7.24 (m, 2H), 7.07 (dd, *J* = 4.7, 1.0 Hz, 1H), 2.78 (s, 3H), 2.64 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.5, 145.5, 141.4, 139.3, 137.8, 126.2, 123.9, 120.8, 120.3, 111.3, 62.6, 18.3, 16.6. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{20}H_{18}N_5Na$ $[M+Na]^+$, 350.1376; found, 350.1372.

4.42 Spectroscopic Data of (**4n**)

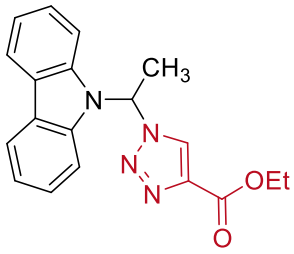
9-(1-(3*H*-[1,2,3]Triazolo[4,5-*b*]pyridin-3-yl)ethyl)-9*H*-carbazole



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 20) afforded **5a** as yellow solid (48.9 mg, 78% yield). **MP**: 192.2-193.6 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.64 (dd, *J* = 4.5, 1.5 Hz, 1H), 8.34 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.16 (d, *J* = 8.4 Hz, 2H), 8.04 (d, *J* = 7.7 Hz, 2H), 7.86 (q, *J* = 7.2 Hz, 1H), 7.51 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 2H), 7.31 (dd, *J* = 8.3, 4.5 Hz, 1H), 7.28–7.25 (m, 2H), 2.66 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 150.7, 145.7, 139.2, 137.1, 128.7, 126.2, 123.9, 120.3, 120.3, 120.3, 111.3, 62.6, 18.3. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{19}H_{15}N_5Na$ $[M+Na]^+$, 336.1220; found, 336.1213.

4.43 Spectroscopic Data of (**4o**)

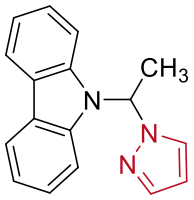
ethyl 1-(1-(9*H*-Carbazol-9-yl)ethyl)-1*H*-1,2,3-triazole-4-carboxylate



Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 30) afforded **4o** as white solid (53.5 mg, 80% yield). **MP**: 152.1-153.3 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.07 (d, *J* = 6.9 Hz, 3H), 7.76 (d, *J* = 8.3 Hz, 2H), 7.48 (ddd, *J* = 8.4, 7.2, 1.3 Hz, 2H), 7.35 (q, *J* = 7.0 Hz, 1H), 7.31–7.27 (m, 2H), 4.41 (q, *J* = 7.1 Hz, 2H), 2.49 (d, *J* = 7.0 Hz, 3H), 1.39 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 160.6, 140.3, 139.1, 137.4, 126.3, 124.0, 120.5, 110.5, 70.1, 61.6, 18.2, 14.3. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{19}H_{18}N_4O_2Na$ $[M+Na]^+$, 357.1322; found, 357.1318.

4.44 Spectroscopic Data of (**4p**)

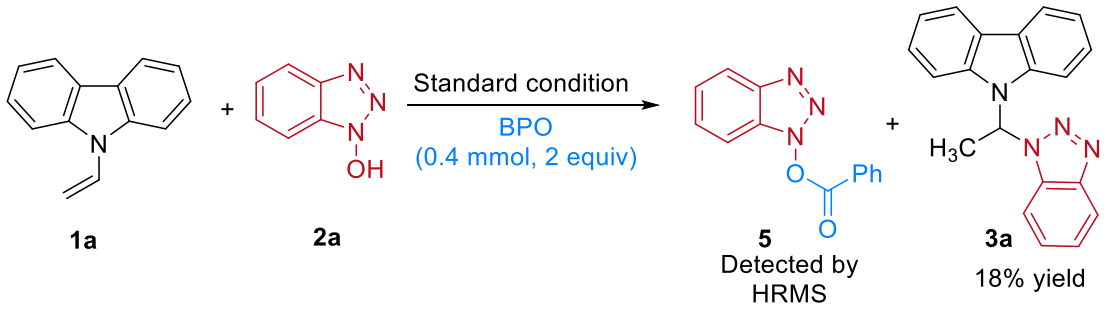
9-(1-(1*H*-Pyrazol-1-yl)ethyl)-9*H*-carbazole



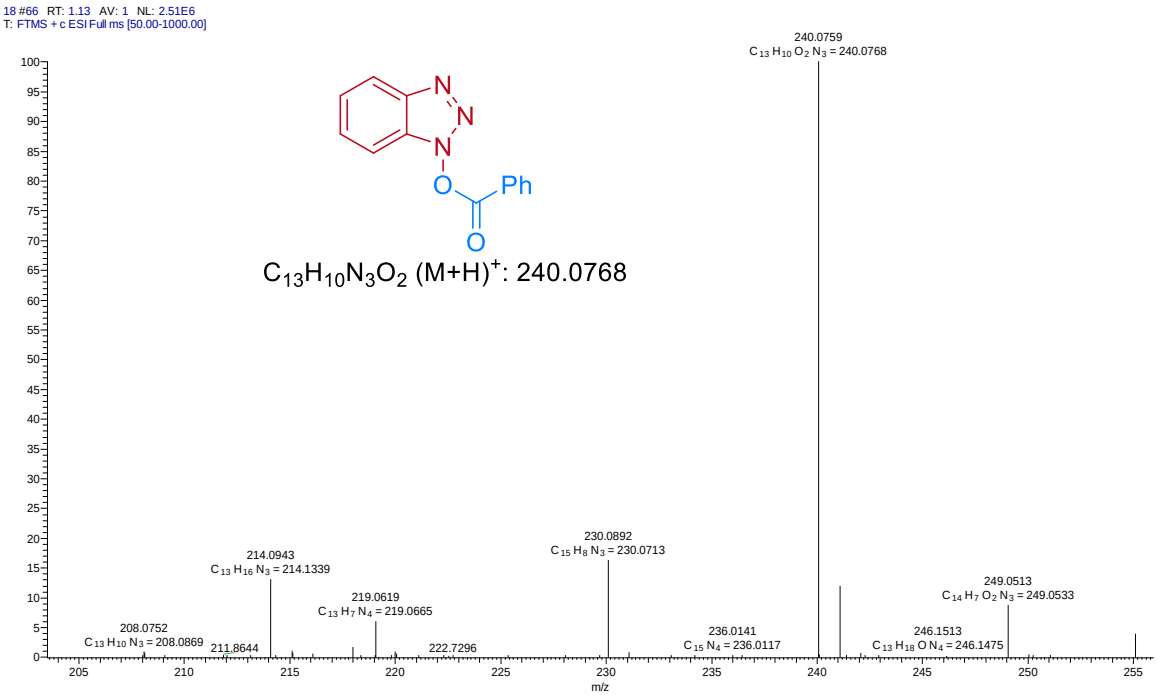
Following the general procedure, purification by flash chromatography on silica gel (eluent: EA: PE = 1: 30) afforded **4p** as white solid (37.1 mg, 71% yield). **MP**: 156.2-157.7 ℃; **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.8 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.43 – 7.41 (m, 2H), 7.27 – 7.24 (m, 3H), 7.16 (s, 1H), 6.87 (q, *J* = 6.4 Hz, 1H), 6.44 (s, 1H), 5.68 (t, *J* = 2.4 Hz, 1H), 2.13 (d, *J* = 6.4 Hz, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 139.6, 134.1, 126.2, 126.0, 123.5, 123.1, 120.5, 119.6, 110.7, 103.5, 88.3, 17.5. **HRMS** (TOF-ESI$^+$): m/z calcd for $C_{19}H_{15}N_3Na$ $[M+Na]^+$, 284.1158; found, 284.1153.

5. Mechanistic studies

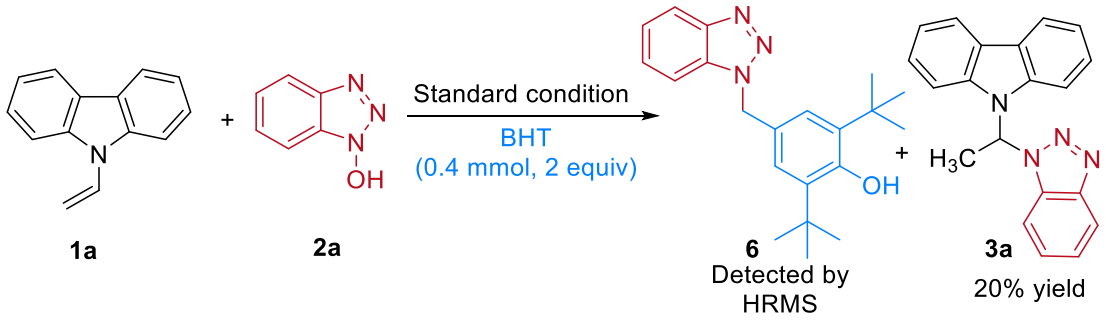
1)



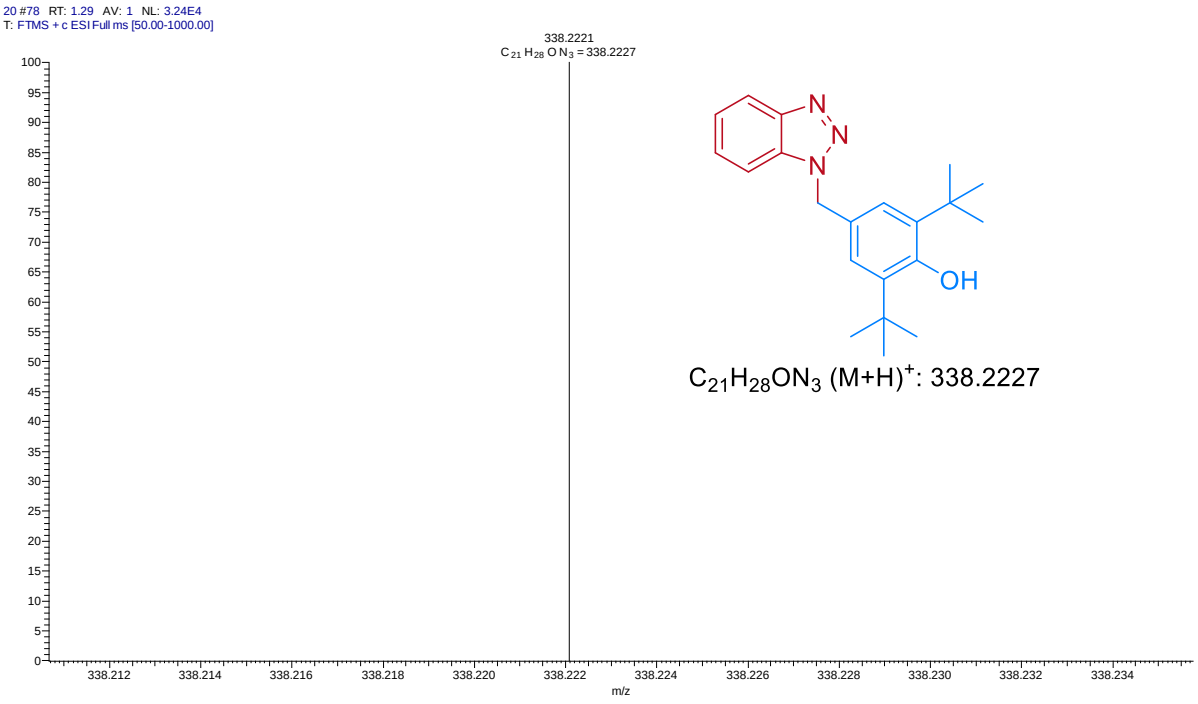
Under Ar atmosphere, *N*-vinylcarbazole **1** (0.2 mmol, 1.0 equiv), 1-Hydroxybenzotriazole **2** (0.22 mmol, 1.1 equiv), Ph_3P (0.2 mmol, 1.0 equiv), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%, 0.001mmol), and BPO (0.4 mmol, 2 equiv) in DCM (0.2mL, 0.1 M) were added to 10.0 mL reaction tube. The mixture was stirred at 490 nm blue light (LEDs, 36W) and monitored by TLC. After stirring for 24h and directly detected by HRMS.



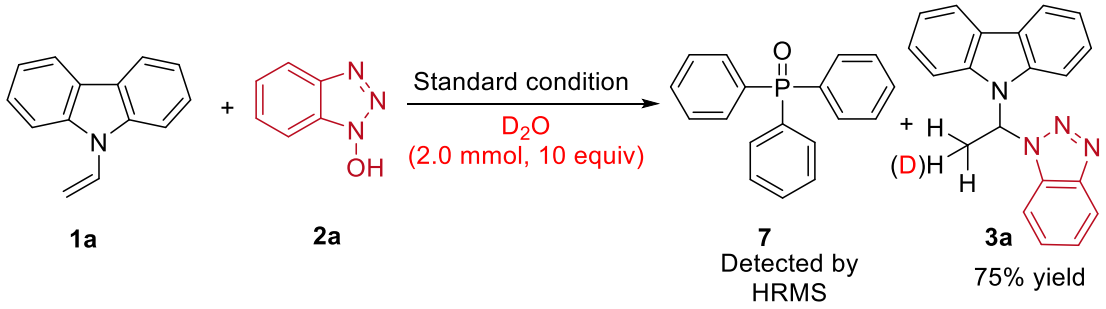
2)



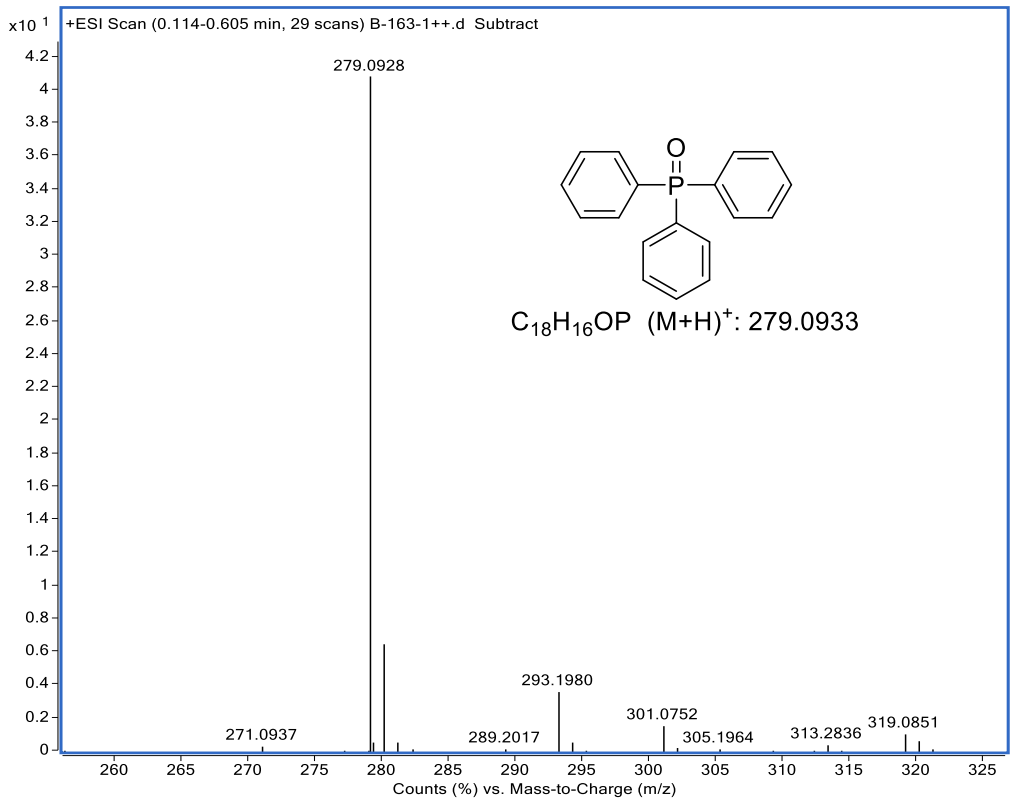
Under Ar atmosphere, N-vinylcarbazole **1** (0.2 mmol, 1.0 equiv), 1-Hydroxybenzotriazole **2** (0.22 mmol, 1.1 equiv), Ph_3P (0.2 mmol, 1.0 equiv), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%, 0.001mmol), and BHT (0.4 mmol, 2 equiv) in DCM (0.2mL, 0.1 M) were added to 10.0 mL reaction tube. The mixture was stirred at 490 nm blue light (LEDs, 36W) and monitored by TLC. After stirring for 24h and directly detected by HRMS.



3)



Under Ar atmosphere, *N*-vinylcarbazole **1** (0.2 mmol, 1.0 equiv), 1-Hydroxybenzotriazole **2** (0.22 mmol, 1.1 equiv), Ph_3P (0.2 mmol, 1.0 equiv), $[Ir(dFCF_3ppy)_2dtbbpy]PF_6$ (1 mol%, 0.001mmol), and D_2O (1.0 mmol, 10 equiv) in DCM (0.2mL, 0.1 M) were added to 10.0 mL reaction tube. The mixture was stirred at 490 nm blue light (LEDs, 36W) and monitored by TLC. After stirring for 24h and found Ph_3PO by HRMS. Then, the reaction was quenched with saturated NaCl solution and extracted with 20.0 mL EtOAc for three times. The organic layers were combined, dried over Na_2SO_4, filtered and evaporated under reduced pressure. The crude product was purified by flash column chromatography (1/20, ethyl acetate/petroleum ether) to afford compound **3a**.



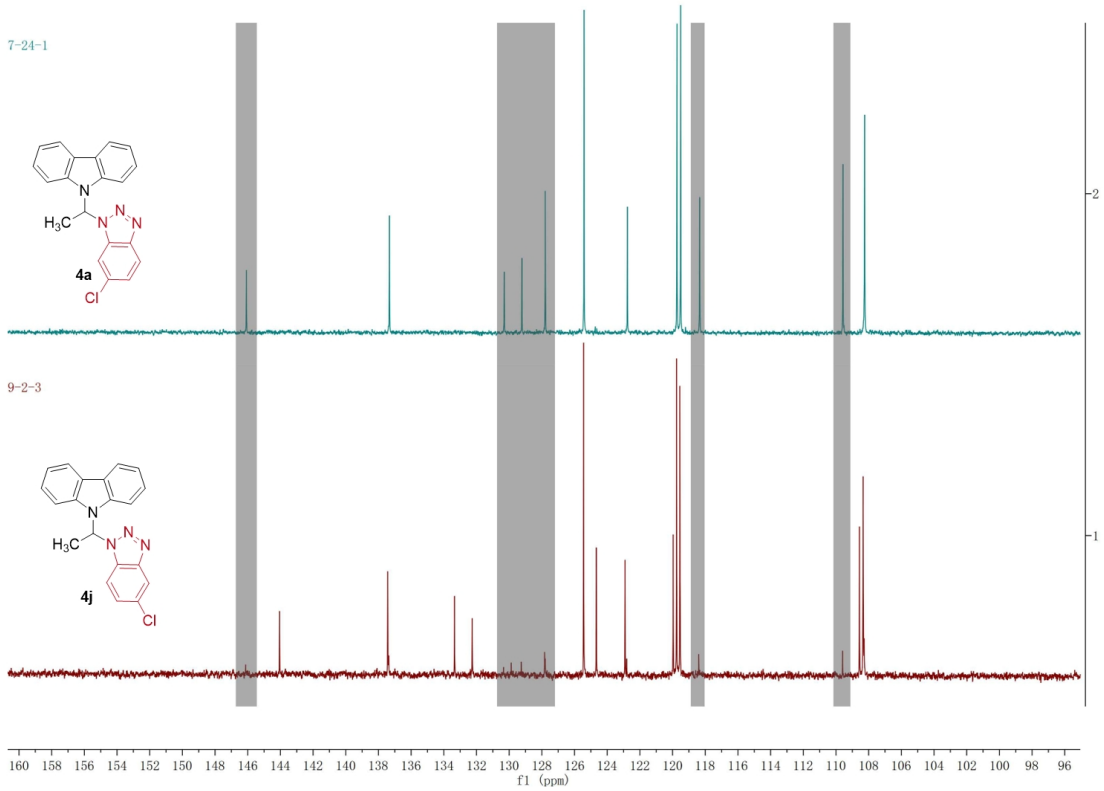


Figure S2. Comparison chart of the CNMR spectrum of compounds **4a** and **4j**. In the spectrum of **4a**, the presence of **4j** was not observed, while in the spectrum of **4j**, a small amount of the **4a** isomer was present.

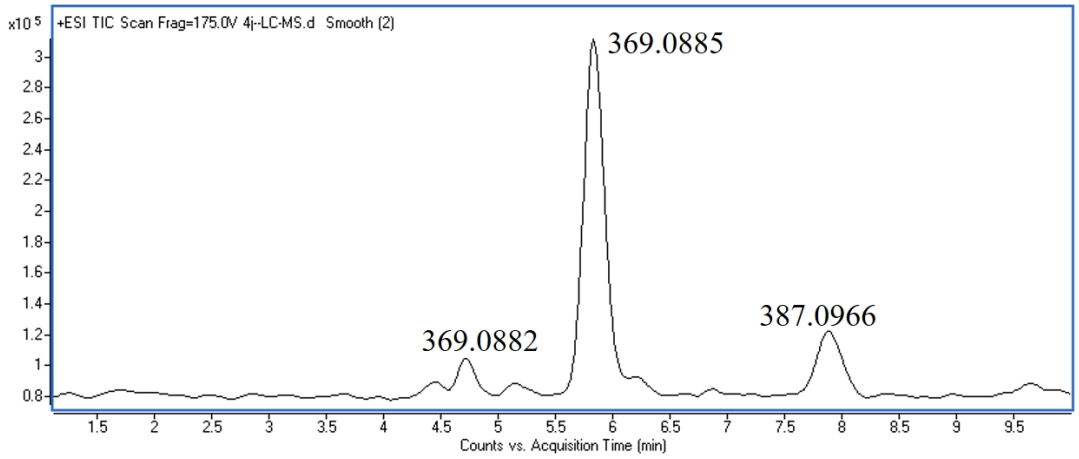
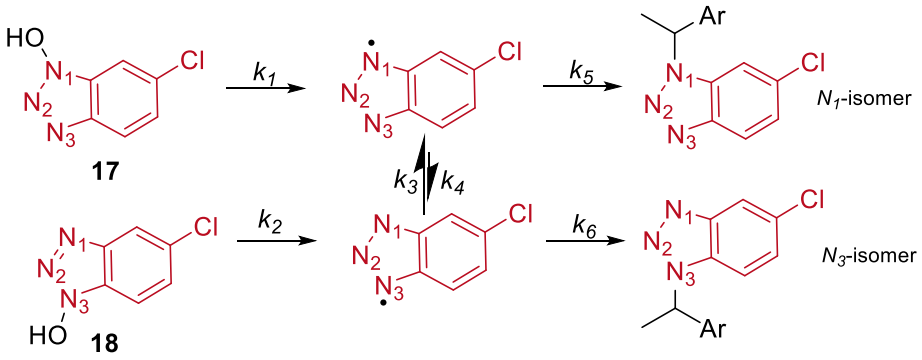
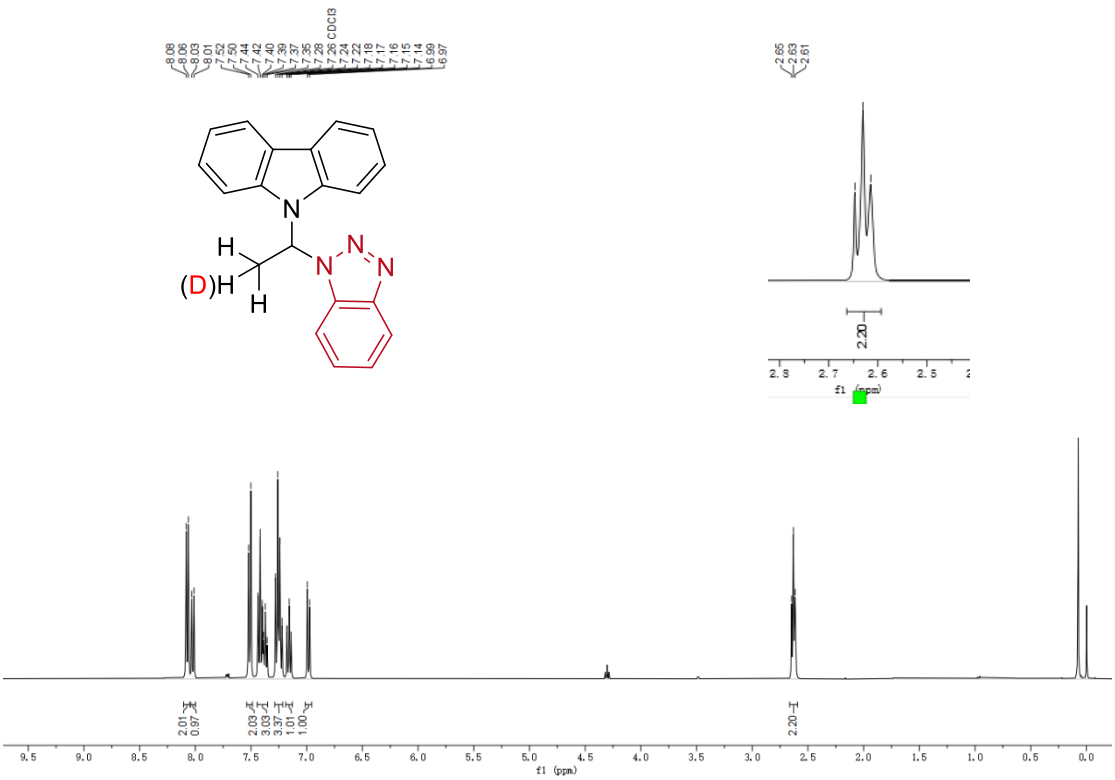


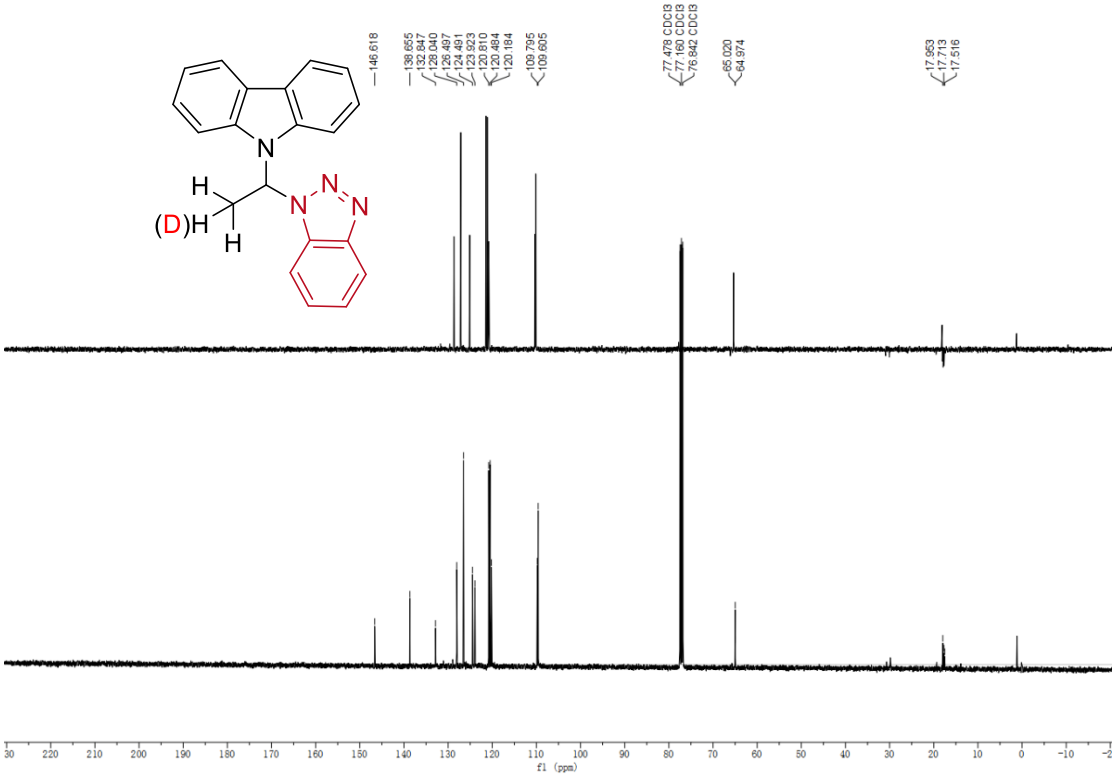
Figure S3. LCMS spectrum of d **4j**. Dissolve a small amount of sample in MeOH to a concentration of 0.1mg/ml, and separate **4j** under the conditions of MeOH: H_2O (80:20) in the mobile phase with a flow rate of 0.8ml/min. HRMS (TOF-ESI$^+$): m/z calcd for **4j** $[M+Na]^+$, 369.0877. The presence of isomeric peaks in the product **4j** was confirmed.



Scheme S1. A schematic diagram of the possible N_1/N_3 selectivity. We speculate that the observed N_1/N_3 selectivity may be attributed to two factors: Firstly, from a thermodynamic perspective, the *N* radicals intermediates generated by 6-chloro-1H-benzo[d][1,2,3]triazol-1-ol (**17**) or 5-chloro-1H-benzo[d][1,2,3]triazol-1-ol (**18**) may form a pair of N_1/N_3 equilibrium isomers. However, the N_1 radical intermediate may be relatively more stable compared to the N_3 radical. Secondly, from a kinetic perspective, the rate of the radical addition reaction between the *N* radical of the triazole and the olefin may be faster than the equilibrium transition rate between N_1 and N_3 (k_5, $k_6 > k_3$, k_4). Based on these two assumptions, the rate-determining step of this reaction is the formation of *N* radicals, which quickly completes the subsequent reactions, thus obtaining good *N* reaction selectivity. So, for example, the **4a** product may hardly have the **4j** isomer, while the **4j** product may contain a small amount of the **4a** isomer.



^{1}H-NMR (100 MHz, $CDCl_3$) **spectrum of 3aa**



^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3aa**

6. X-ray Structure and Data of **3a**、**4a**、**4j**

6.1 X-ray Structure and Data of **3a**

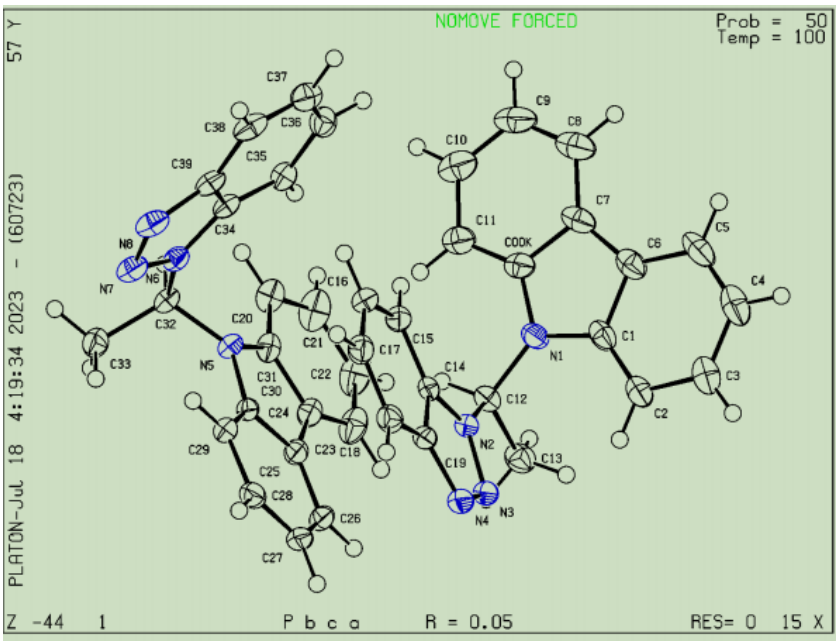


Figure S4. X-Ray crystal structure of **3a**, thermal ellipsoids shown at 50% probability

Datablock: 1

Bond precision: C-C = 0.0023 A Wavelength=0.71073

Cell: a=8.6995(4) b=18.4071(7) c=39.8272(14)
alpha=90 beta=90 gamma=90
Temperature: 100 K

	Calculated	Reported
Volume	6377.6(4)	6377.6(4)
Space group	P b c a	P b c a
Hall group	-P 2ac 2ab	-P 2ac 2ab
Moiety formula	C20 H16 N4	C20 H16 N4
Sum formula	C20 H16 N4	C20 H16 N4
Mr	312.37	312.37
Dx,g cm-3	1.301	1.301
Z	16	16
Mu (mm-1)	0.080	0.080
F000	2624.0	2624.0
F000'	2624.83	
h,k,lmax	11,24,53	11,24,53
Nref	7944	7935
Tmin,Tmax	0.982,0.986	0.700,0.746
Tmin'	0.982	

Correction method= # Reported T Limits: Tmin=0.700 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.999 Theta(max)= 28.323

R(reflections)= 0.0499(5104) wR2(reflections)= 0.1198(7935)

S = 1.028 Npar= 436

Figure S5. Crystal data and structure refinement for **3a**

6.2 X-ray Structure and Data of **4a**

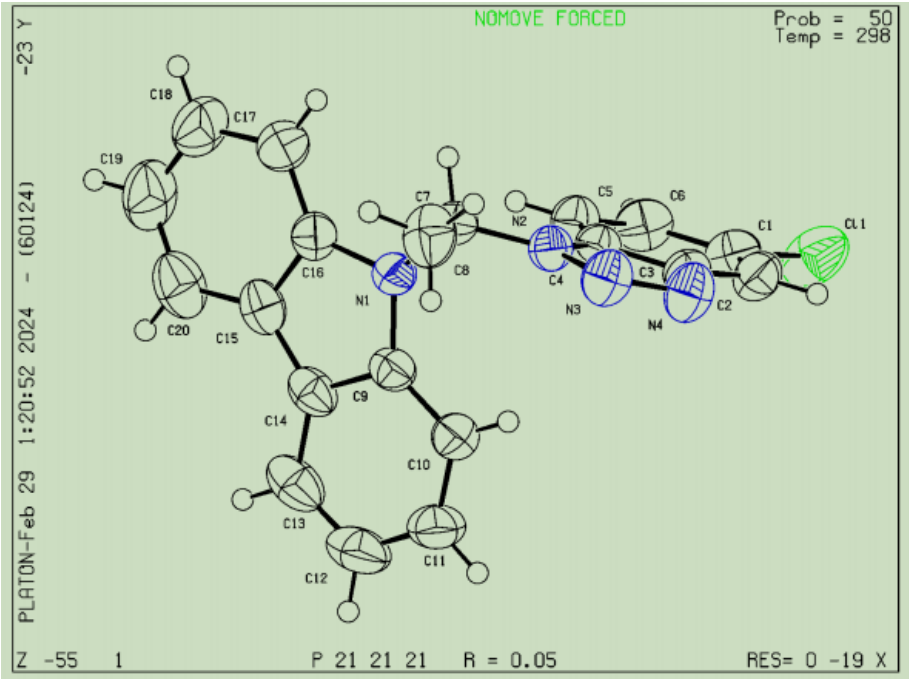


Figure S6. X-Ray crystal structure of **4a**, thermal ellipsoids shown at 50% probability

Datablock: 1

Bond precision: C-C = 0.0049 A Wavelength=0.71073

Cell: a=9.9868(4) b=12.6657(5) c=13.3981(6)
alpha=90 beta=90 gamma=90
Temperature: 298 K

	Calculated	Reported
Volume	1694.72(12)	1694.72(12)
Space group	P 21 21 21	P 21 21 21
Hall group	P 2ac 2ab	P 2ac 2ab
Moiety formula	C20 H15 Cl N4	C20 H15 Cl N4
Sum formula	C20 H15 Cl N4	C20 H15 Cl N4
Mr	346.81	346.81
Dx,g cm-3	1.359	1.359
Z	4	4
Mu (mm-1)	0.235	0.235
F000	720.0	720.0
F000'	720.80	
h,k,lmax	13,16,17	13,16,17
Nref	4223[2400]	4189
Tmin,Tmax	0.940,0.954	0.703,0.746
Tmin'	0.939	

Correction method= # Reported T Limits: Tmin=0.703 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 1.75/0.99 Theta(max)= 28.295

R(reflections)= 0.0510(2857) wR2(reflections)= 0.1071(4189)
S = 1.088 Npar= 227

Figure S7. Crystal data and structure refinement for **4a**

6.3 X-ray Structure and Data of **4j**

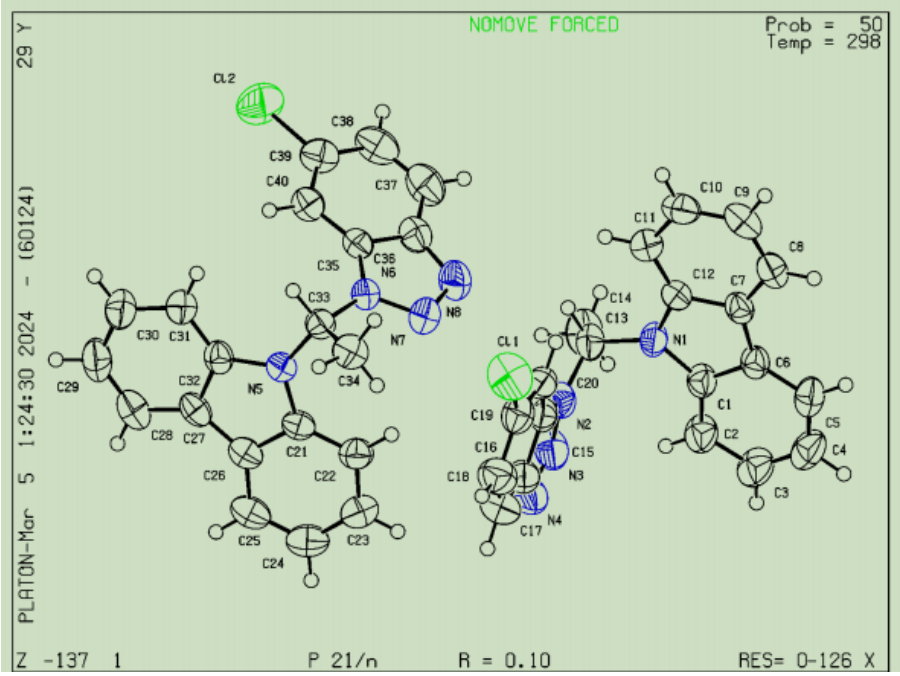


Figure S8. X-Ray crystal structure of **4j**, thermal ellipsoids shown at 50% probability

Datablock: 1

Bond precision: C-C = 0.0056 A Wavelength=0.71073

Cell: a=9.4084(4) b=21.4394(9) c=16.9249(8)
alpha=90 beta=96.024(1) gamma=90
Temperature: 298 K

	Calculated	Reported
Volume	3395.1(3)	3395.1(3)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Moiety formula	C20 H15 Cl N4	C20 H15 Cl N4
Sum formula	C20 H15 Cl N4	C20 H15 Cl N4
Mr	346.81	346.81
Dx,g cm-3	1.357	1.357
Z	8	8
Mu (mm-1)	0.235	0.235
F000	1440.0	1440.0
F000'	1441.61	
h,k,lmax	12,28,22	12,28,22
Nref	8506	8475
Tmin,Tmax	0.952,0.963	0.680,0.746
Tmin'	0.952	

Correction method= # Reported T Limits: Tmin=0.680 Tmax=0.746
AbsCorr = MULTI-SCAN

Data completeness= 0.996 Theta(max)= 28.370

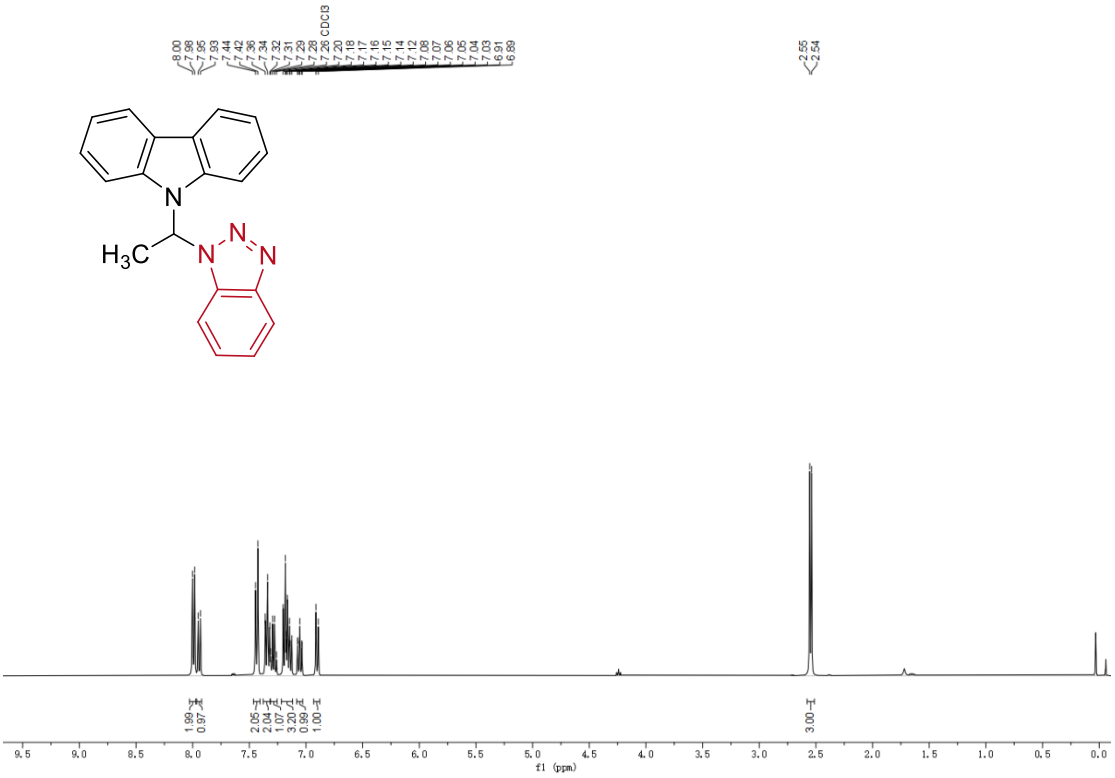
R(reflections)= 0.0981(4232) wR2(reflections)= 0.1840(8475)

S = 1.115 Npar= 453

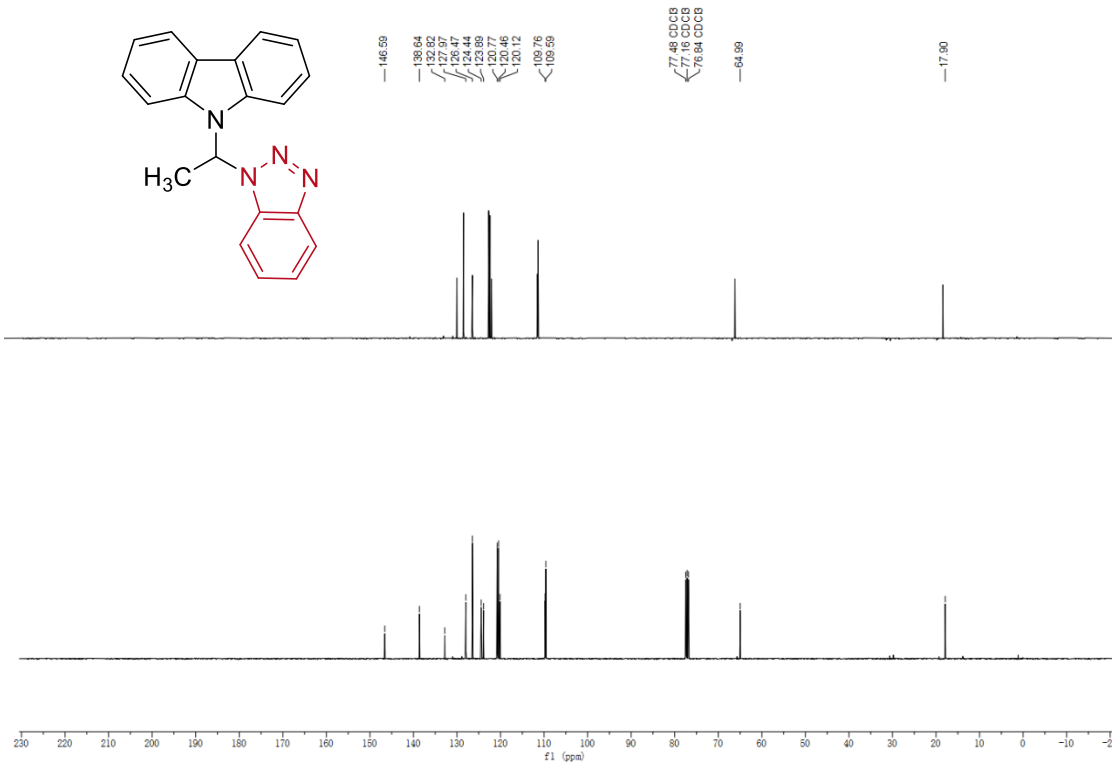
Figure S9. Crystal data and structure refinement for **4j**

Compound **3a**、**4d**、**4j**(50mg) was added to a 10mL sample bottle, following to add DCM (2mL), n-hexane (2.5mL) and toluene (0.1mL), then seal the bottle with a parafilm, and poke 15 small holes on the parafilm, place the sample bottle in a safe place to allow it to volatilize and separate out the single crystal. Take out the single crystal and send it for single crystal diffraction test to obtain relevant data. Instrument model: Intensity data for single crystals of each complex were collected on a BRUKER SMART APEX II CCD detector with graphite-monochromatized Mo Kα radiation (k = 0.071073 nm). The structures were solved by direct method using the program SHELXS-97 and subsequent Fourier difference techniques, and refined anisotropically by full matrix least-squares on F2 using SHELXL-97.

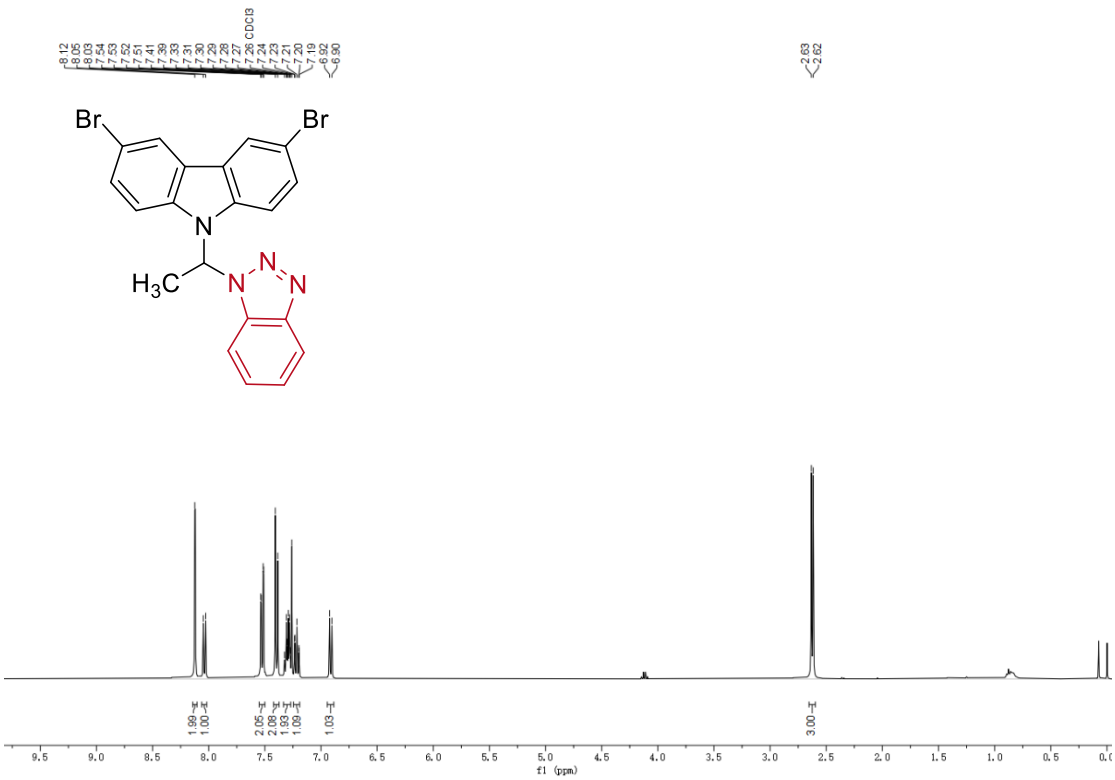
7. ^{1}H NMR and ^{13}C NMR spectra of **3a-3zc** and **4a-4p**



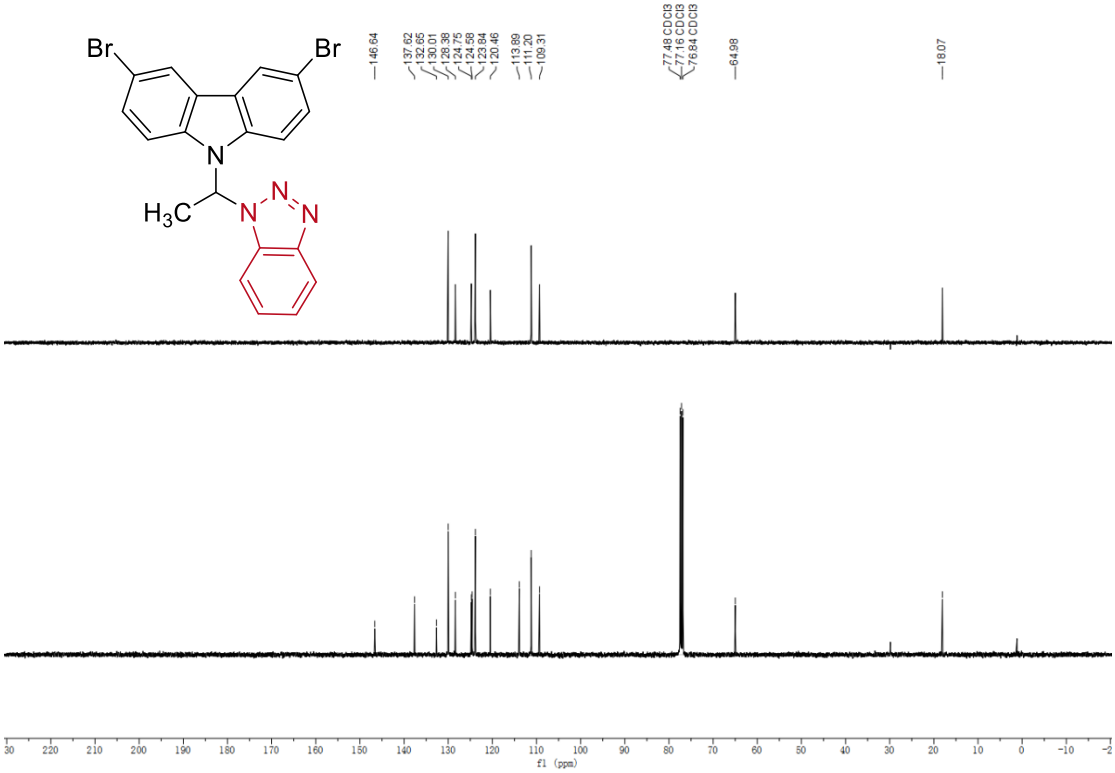
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3a**



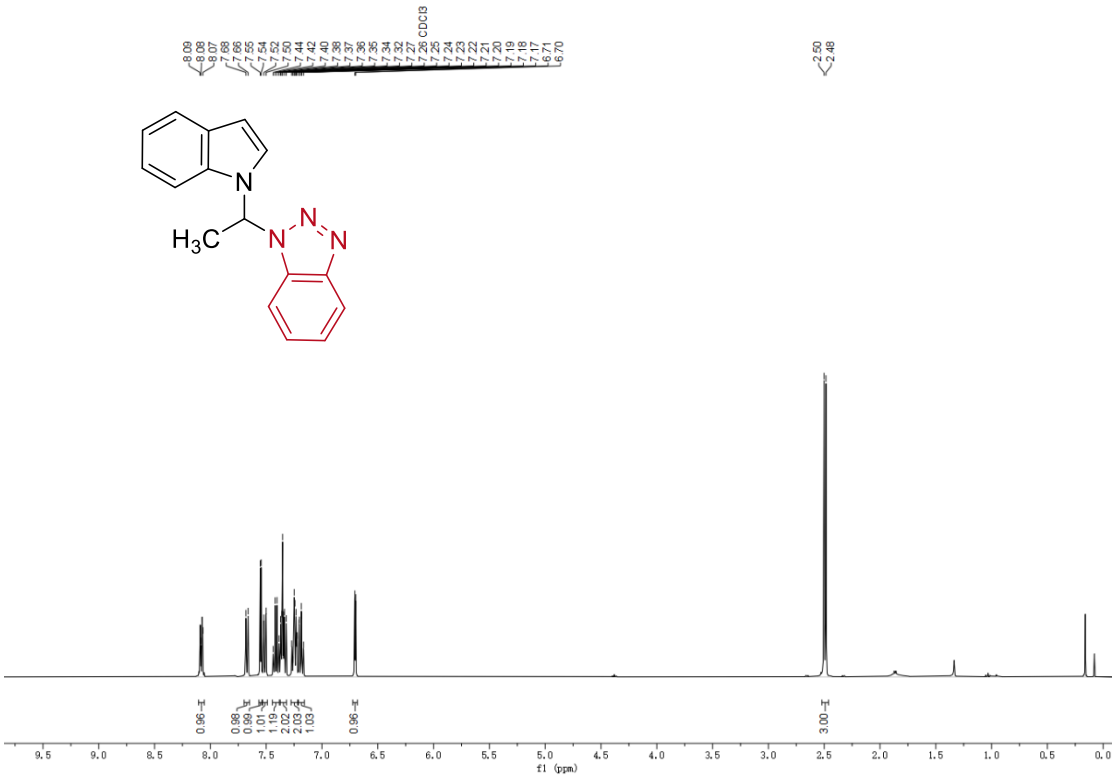
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3a**



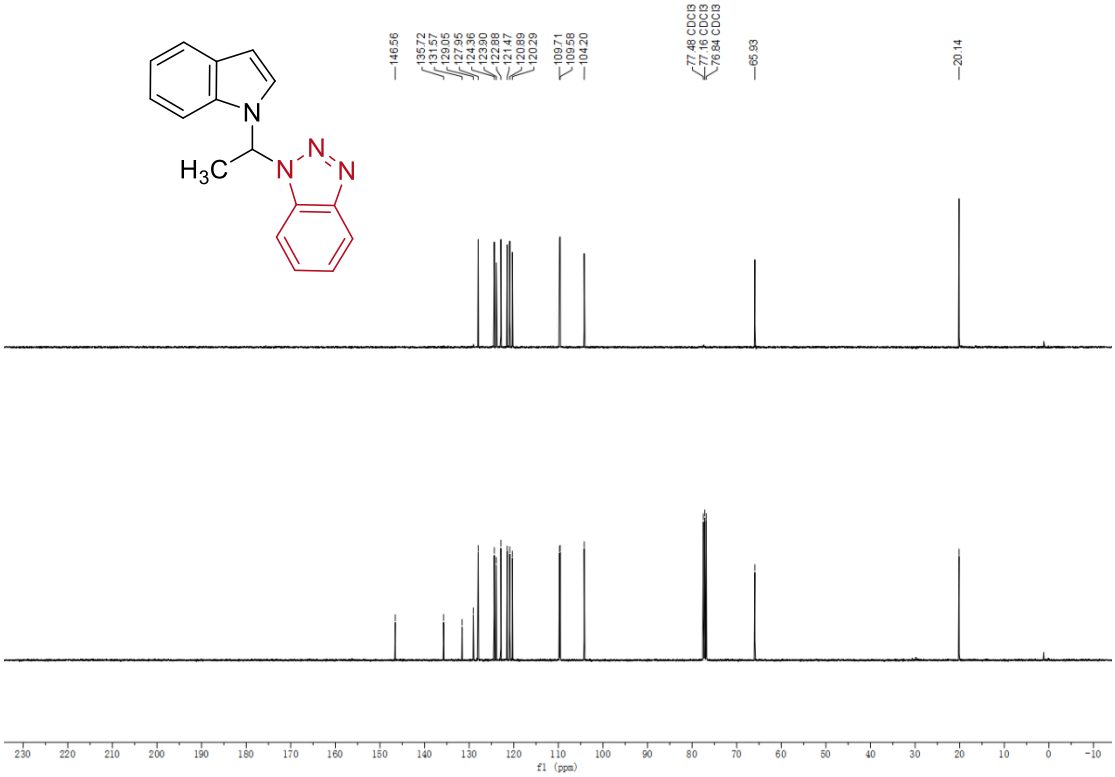
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3b**



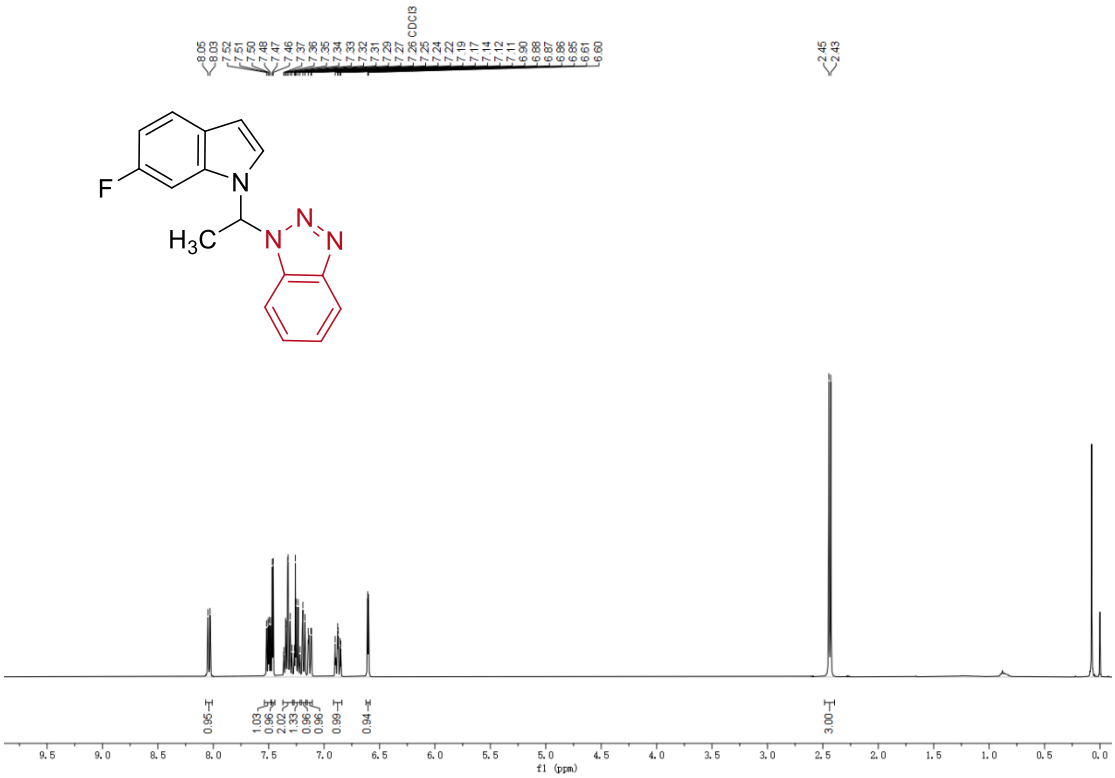
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3b**



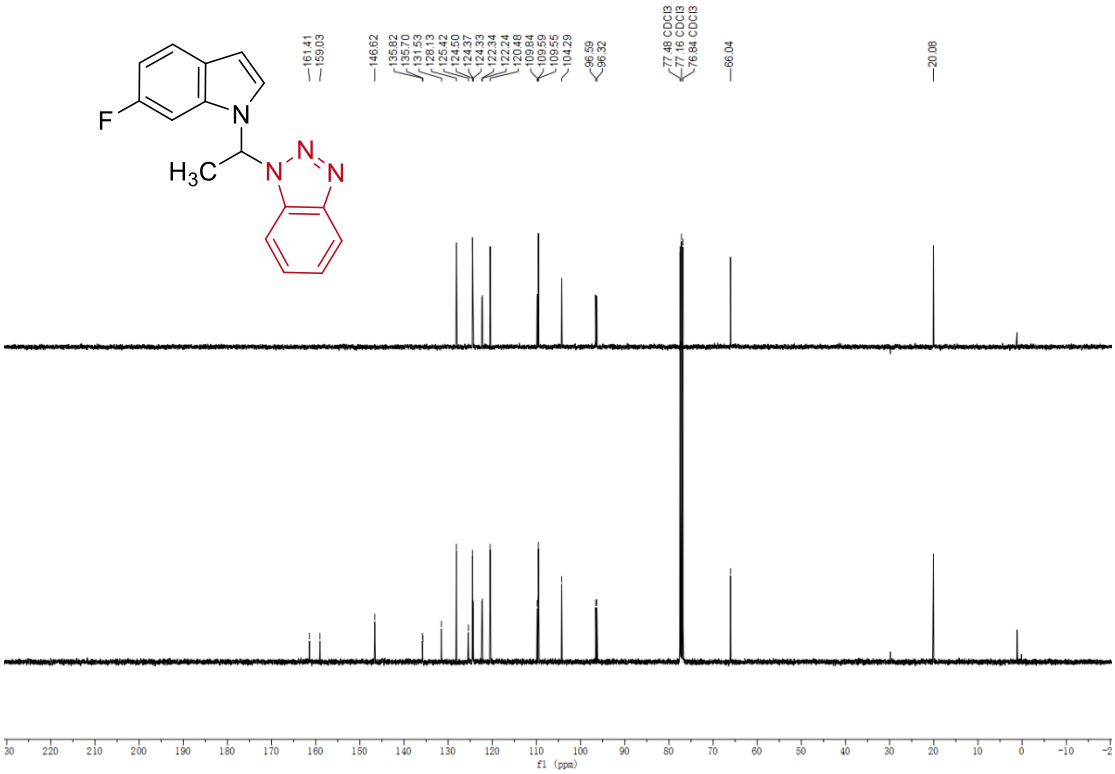
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3c**



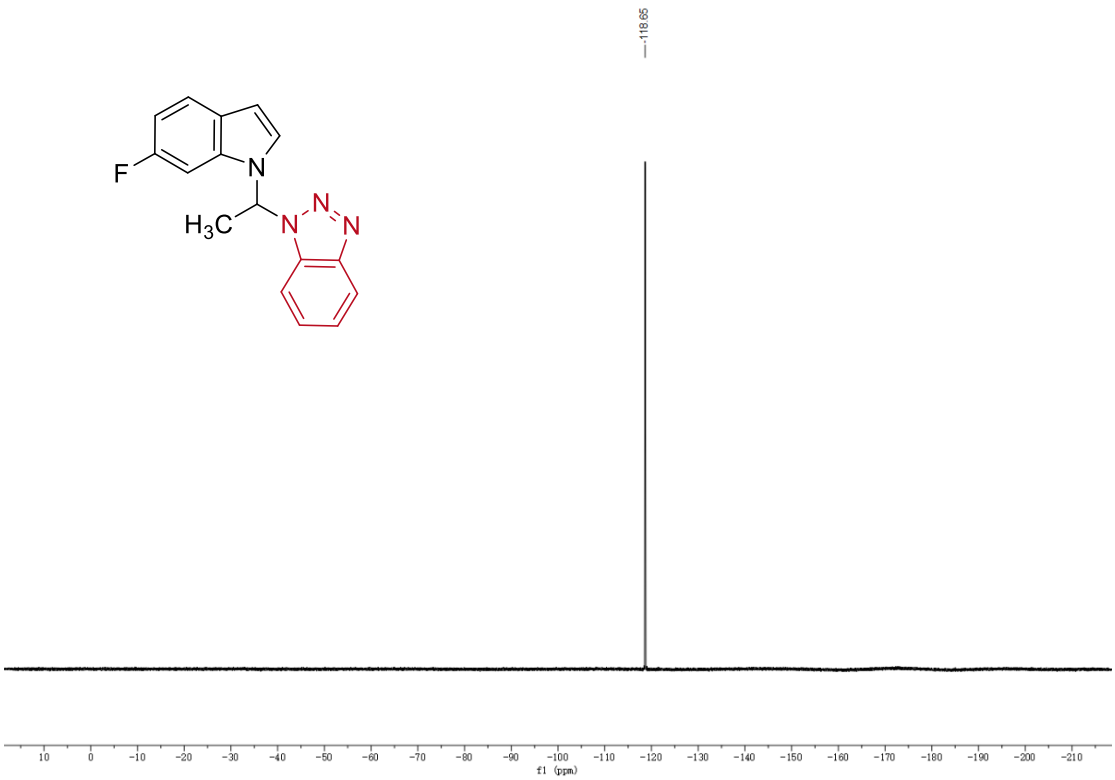
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3c**



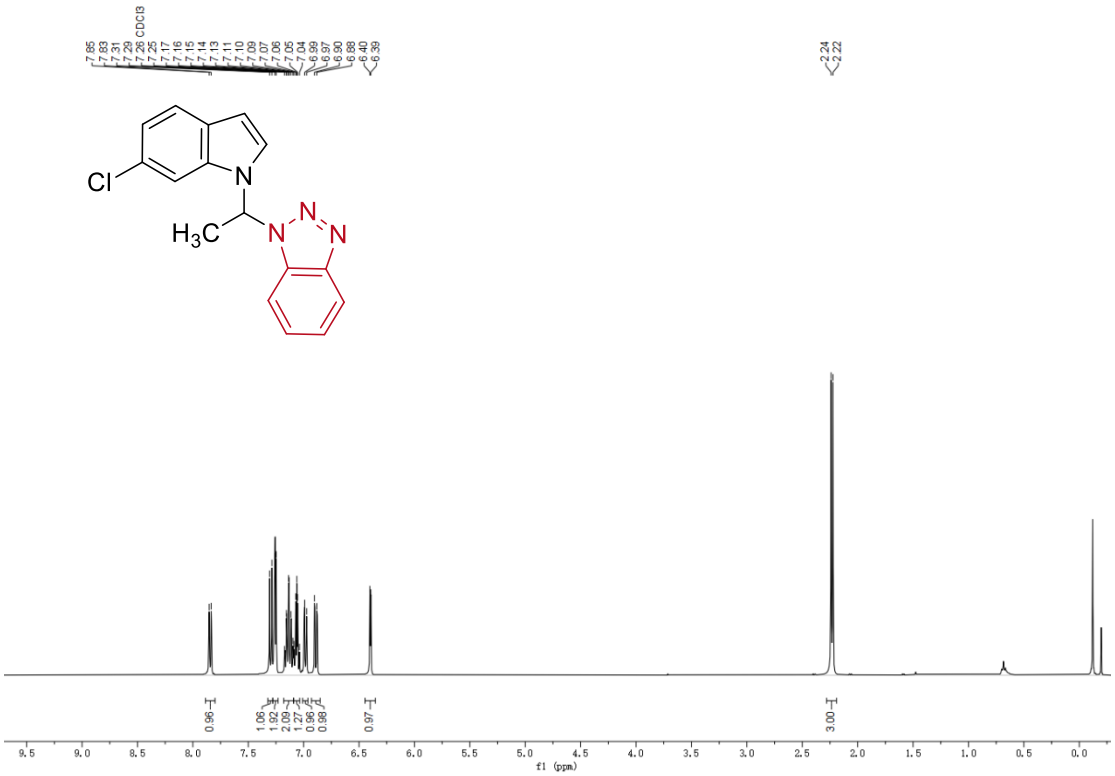
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3d**



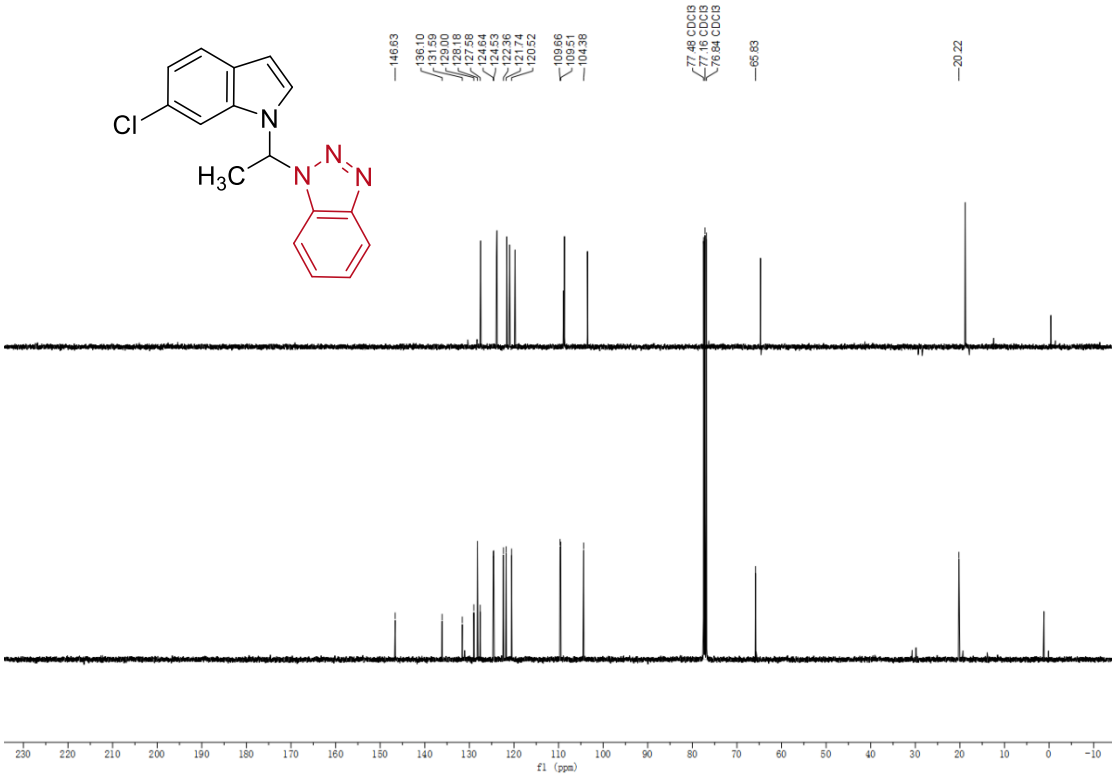
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3d**



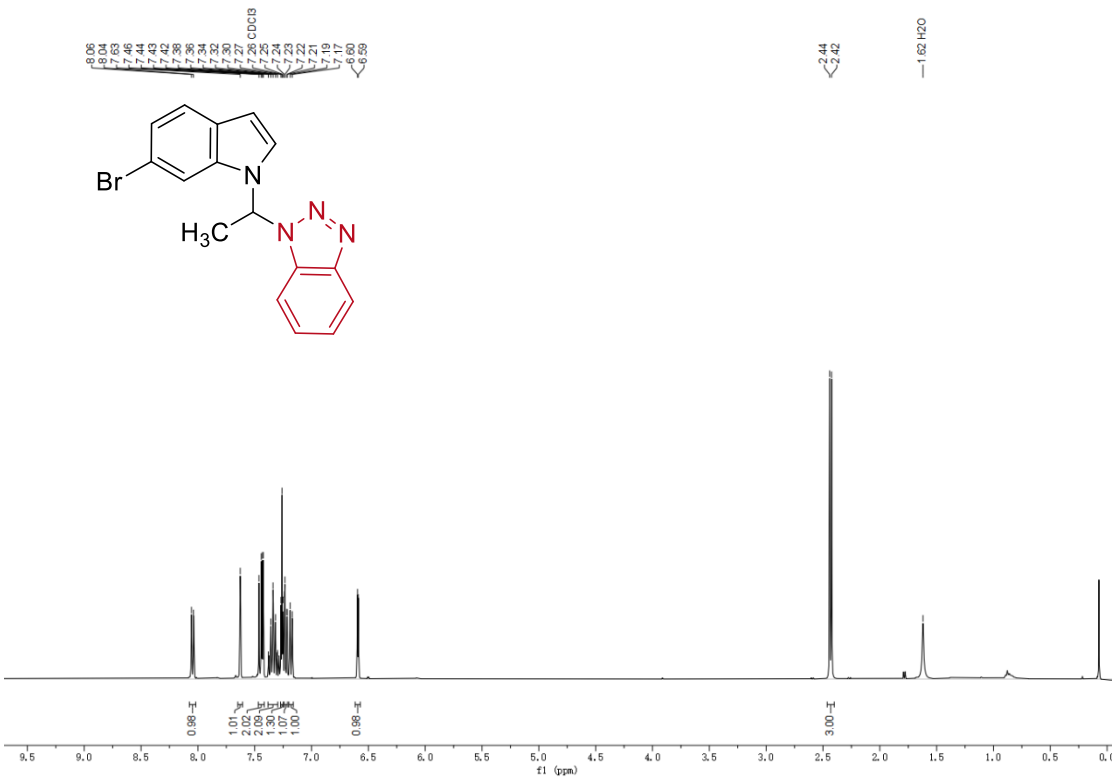
^{19}F-NMR (376 MHz, $CDCl_3$) **spectrum of 3d**



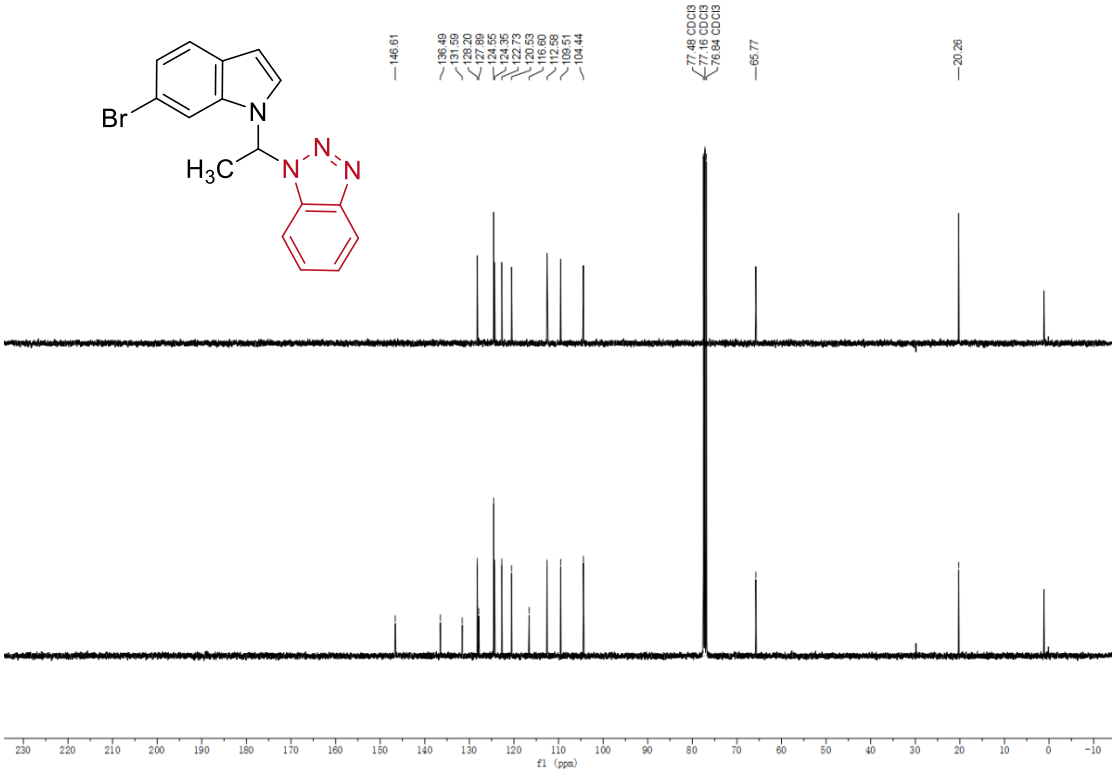
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3e**



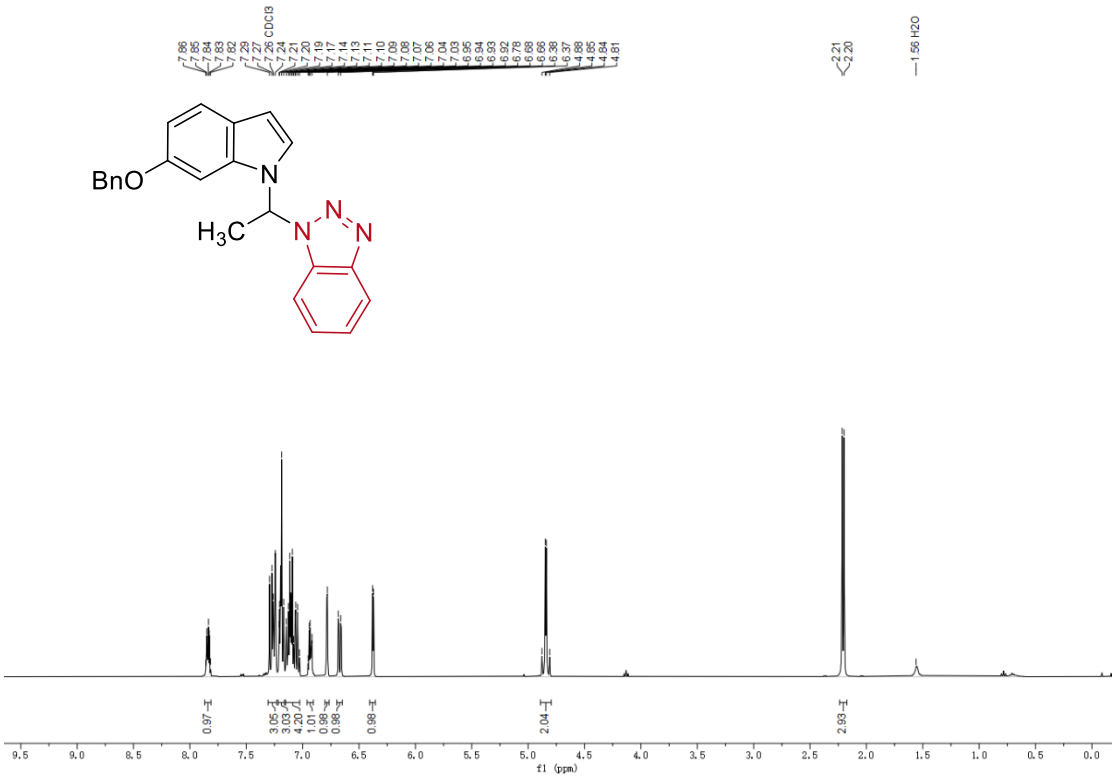
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3e**



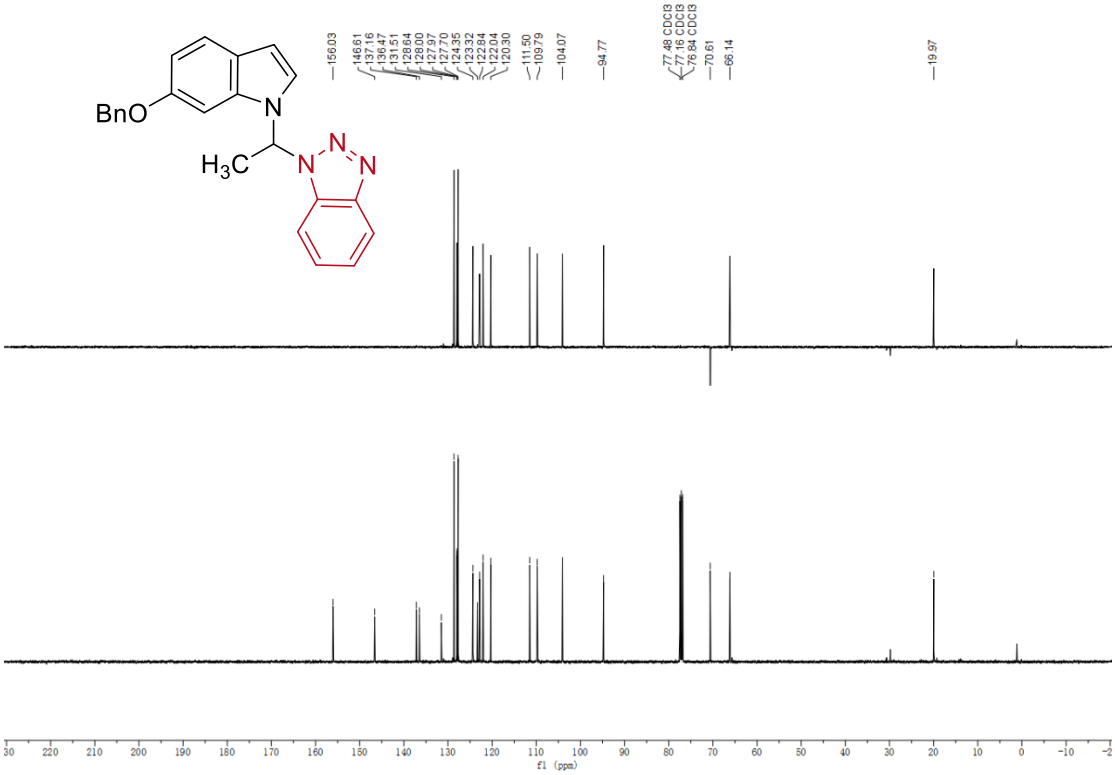
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3f**



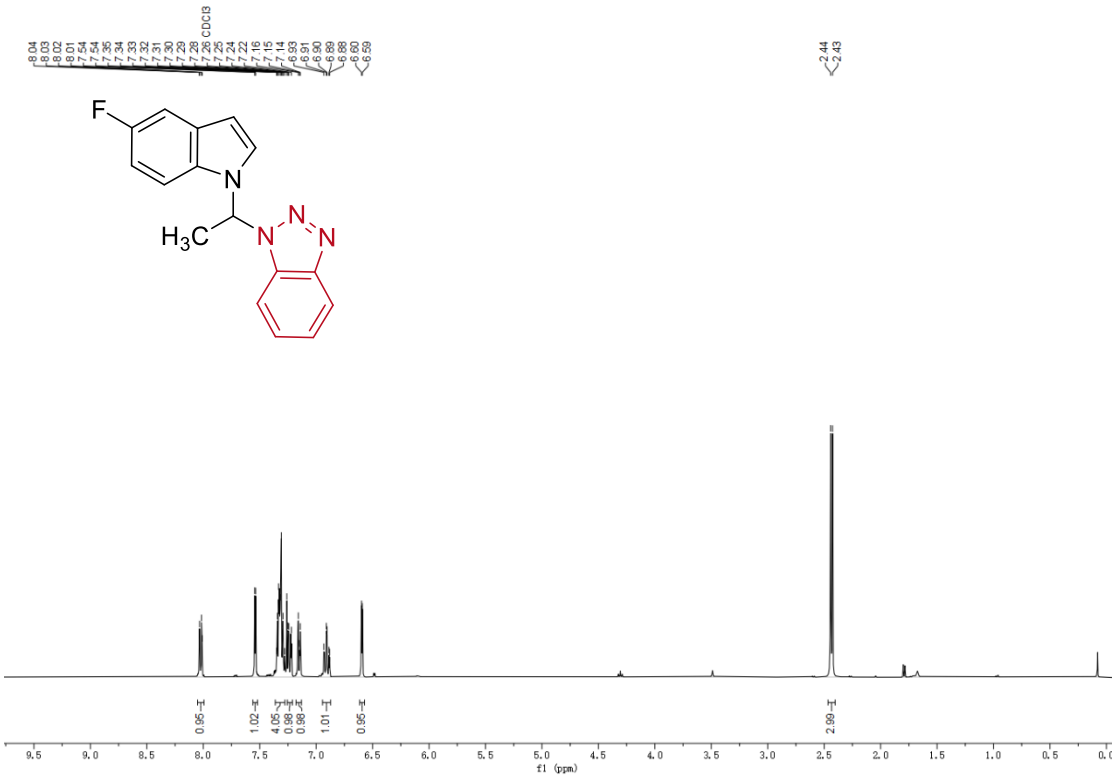
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3f**



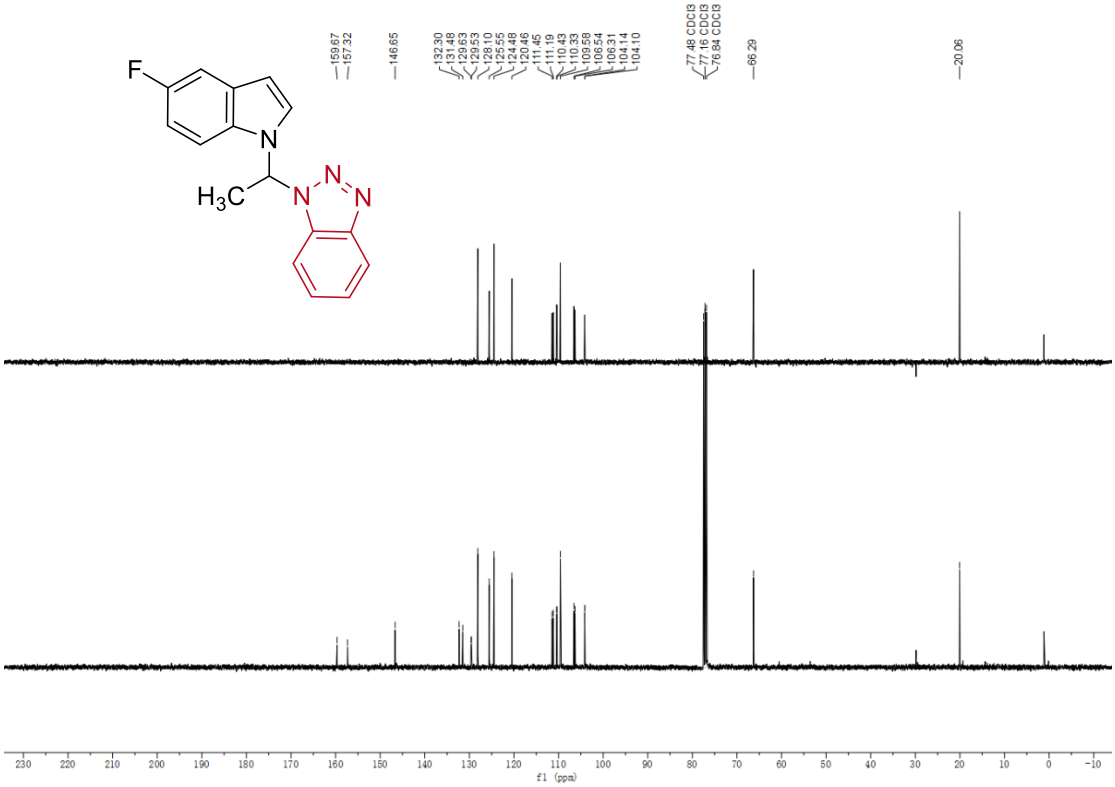
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3g**



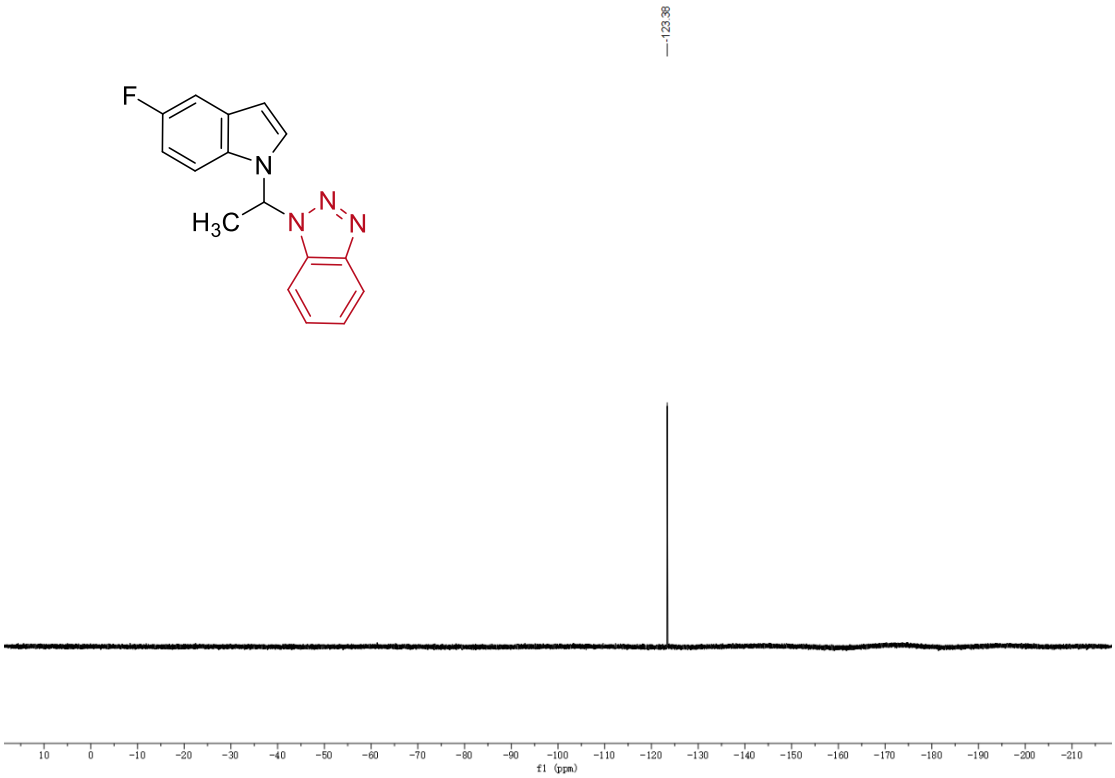
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3g**



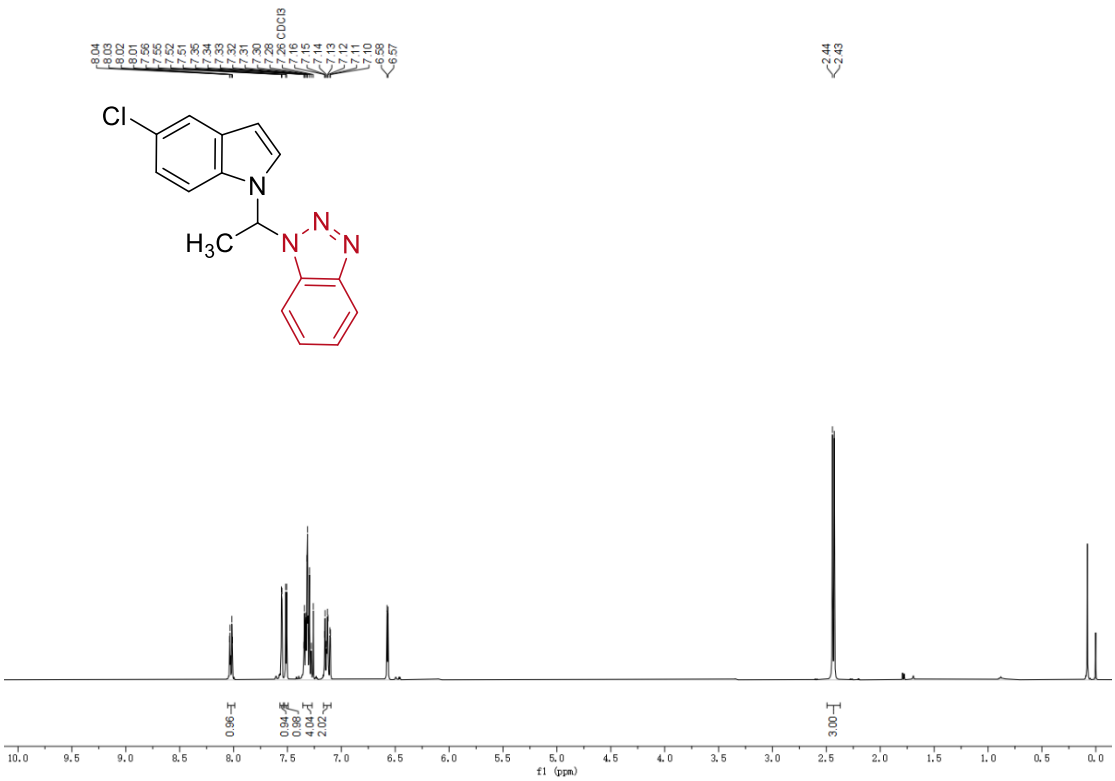
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3h**



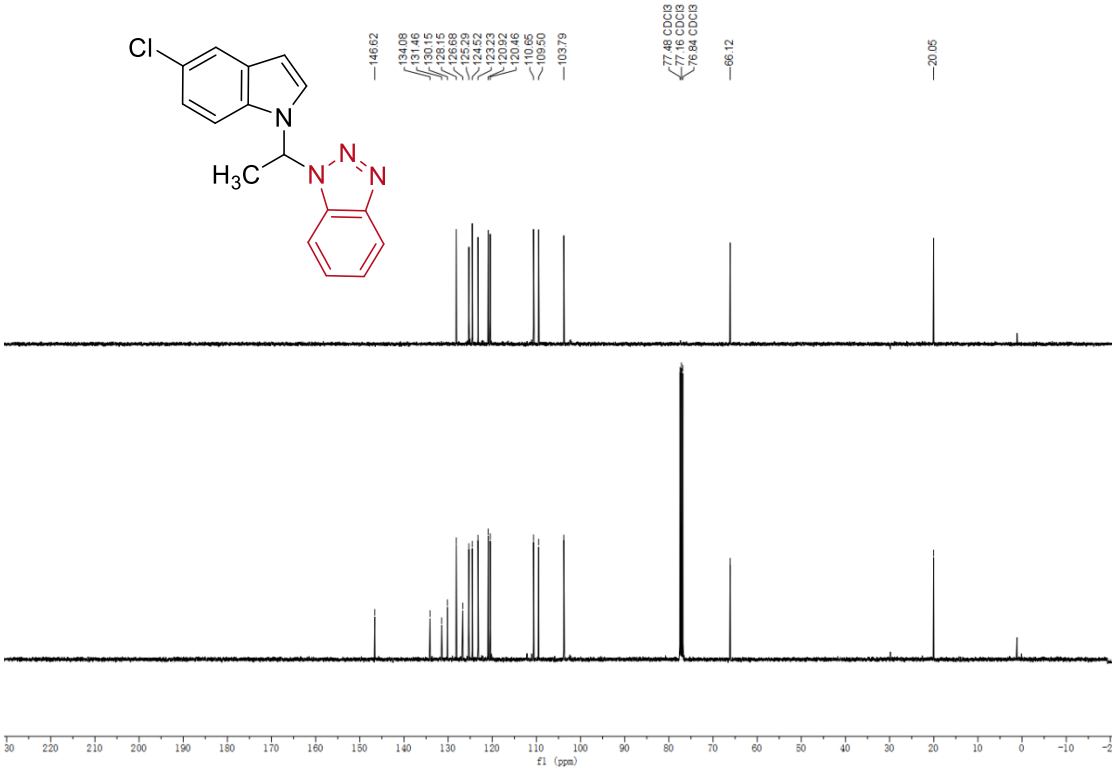
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3h**



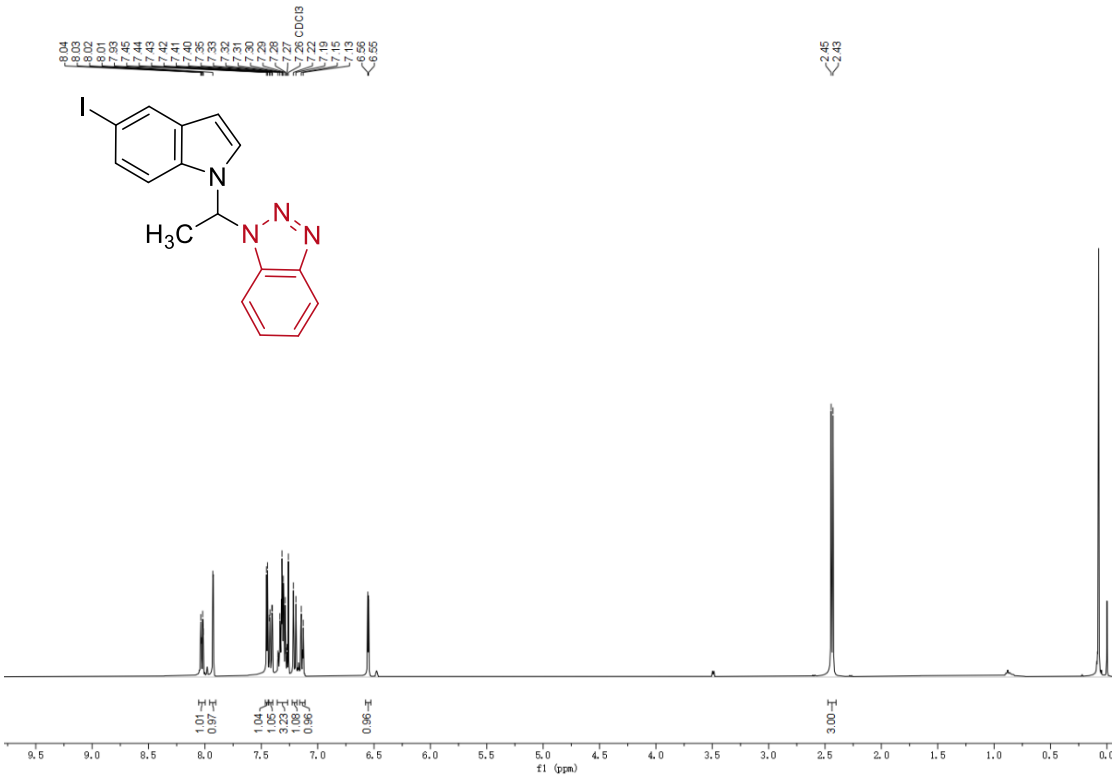
^{19}F-NMR (376 MHz, $CDCl_3$) **spectrum of 3h**



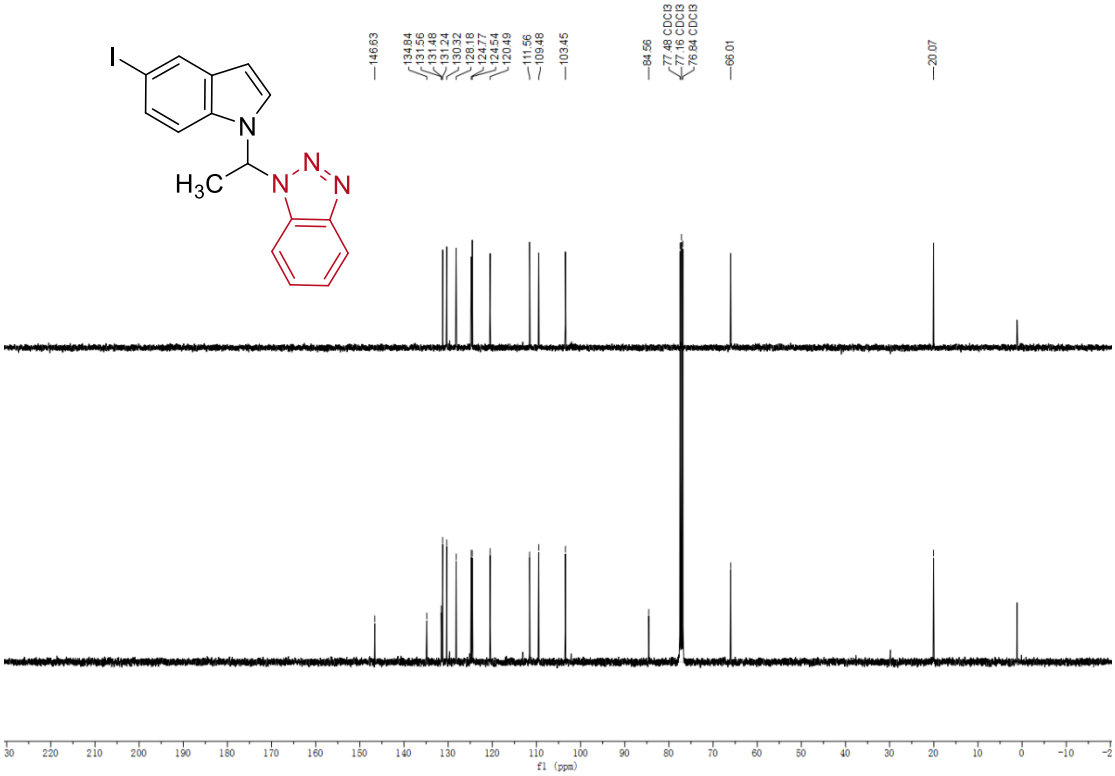
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3i**



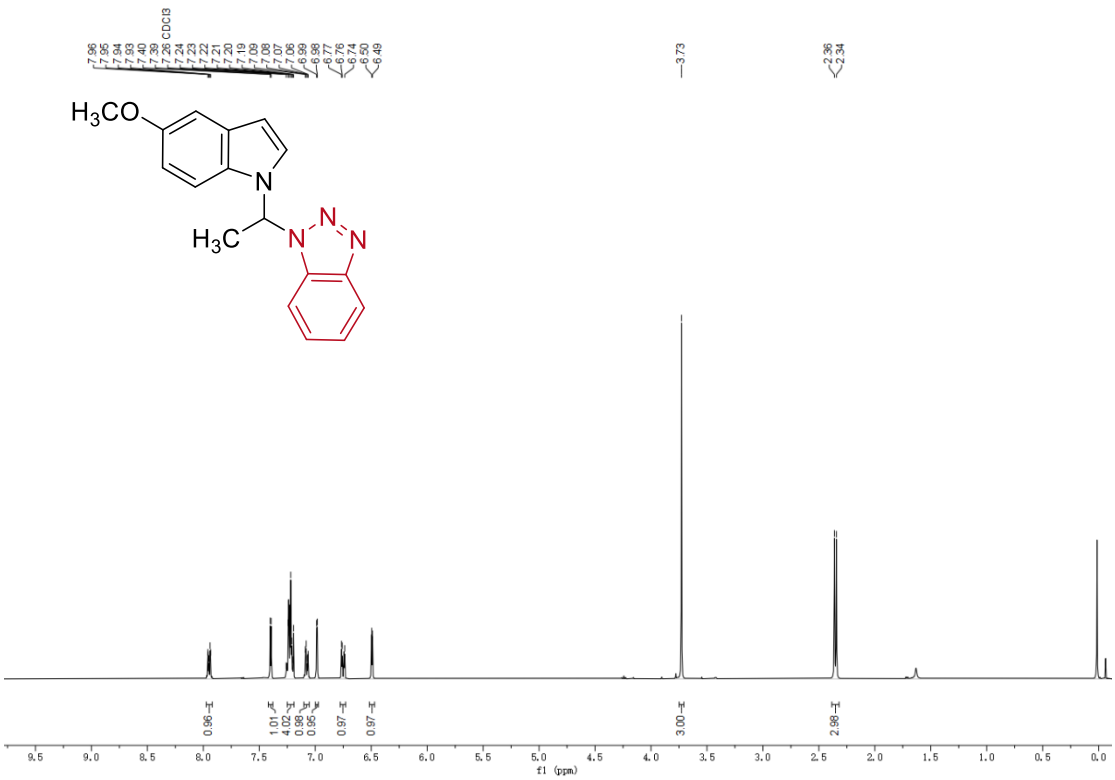
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3i**



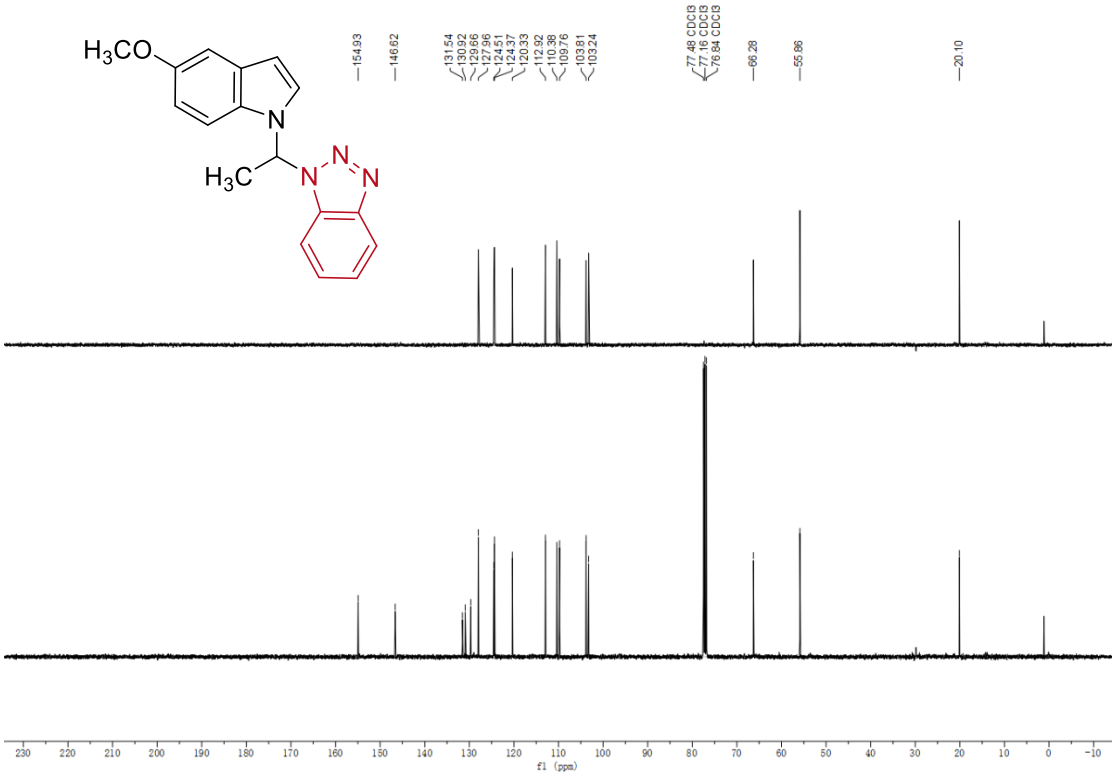
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3j**



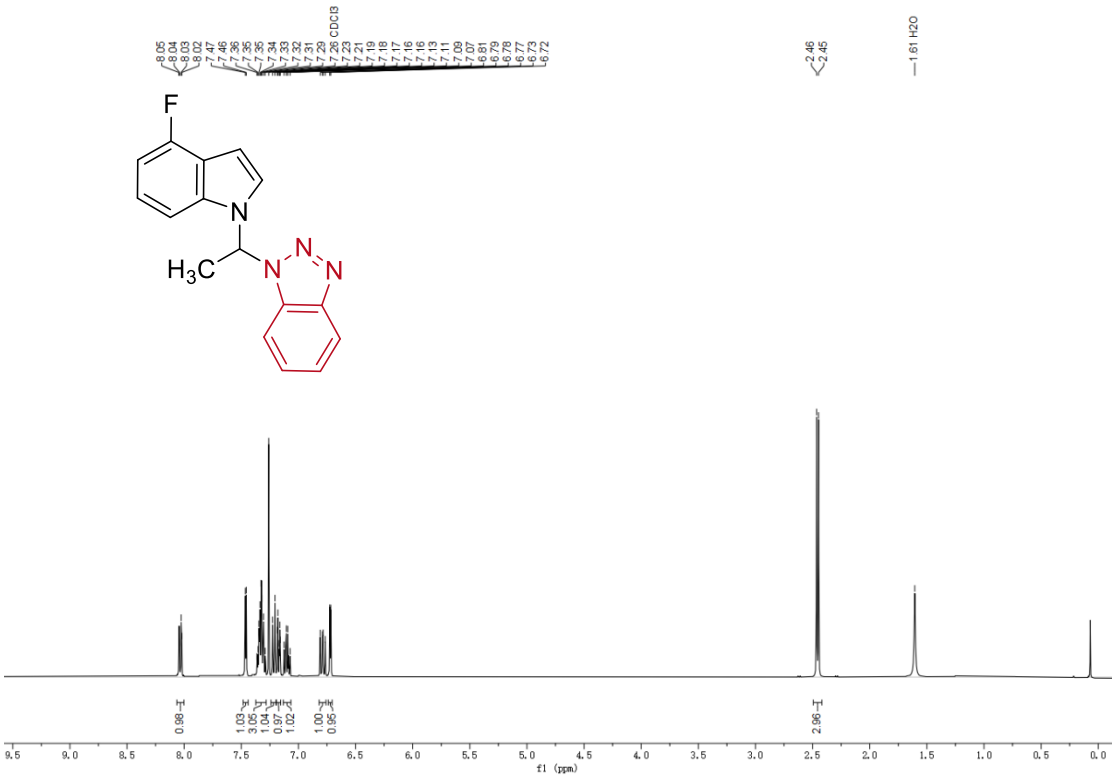
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3j**



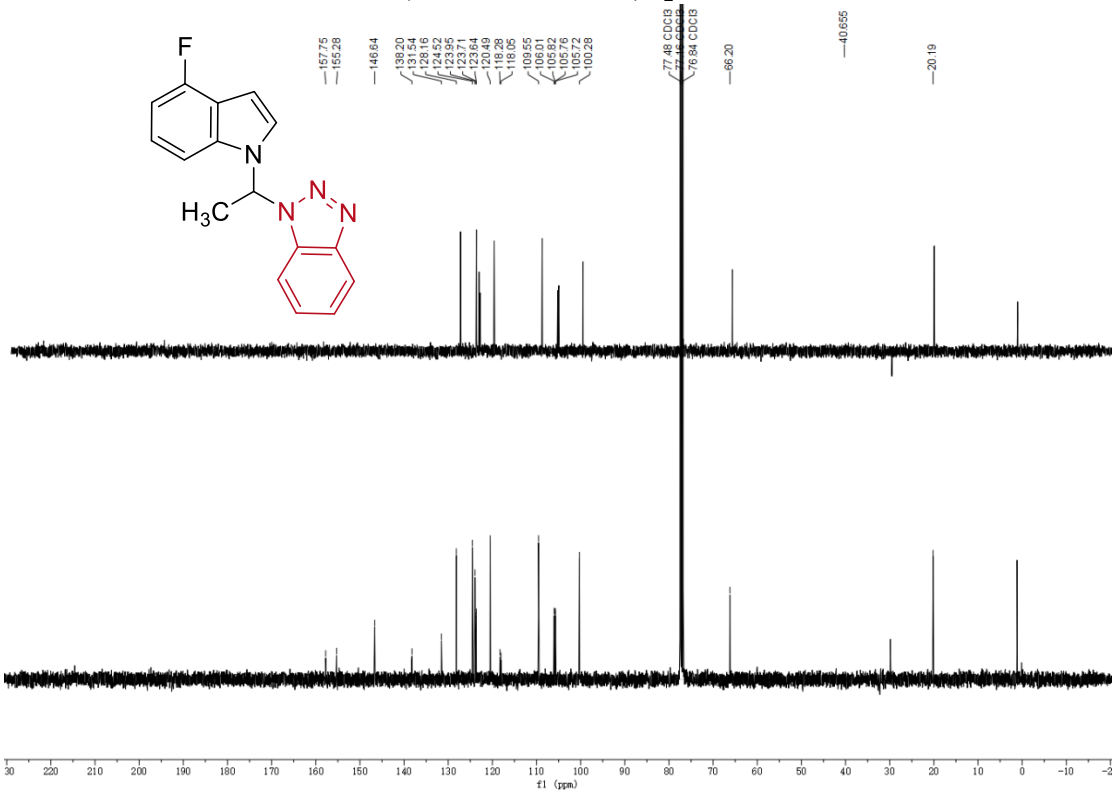
[1]H-NMR (400 MHz, $CDCl_3$) **spectrum of 3k**



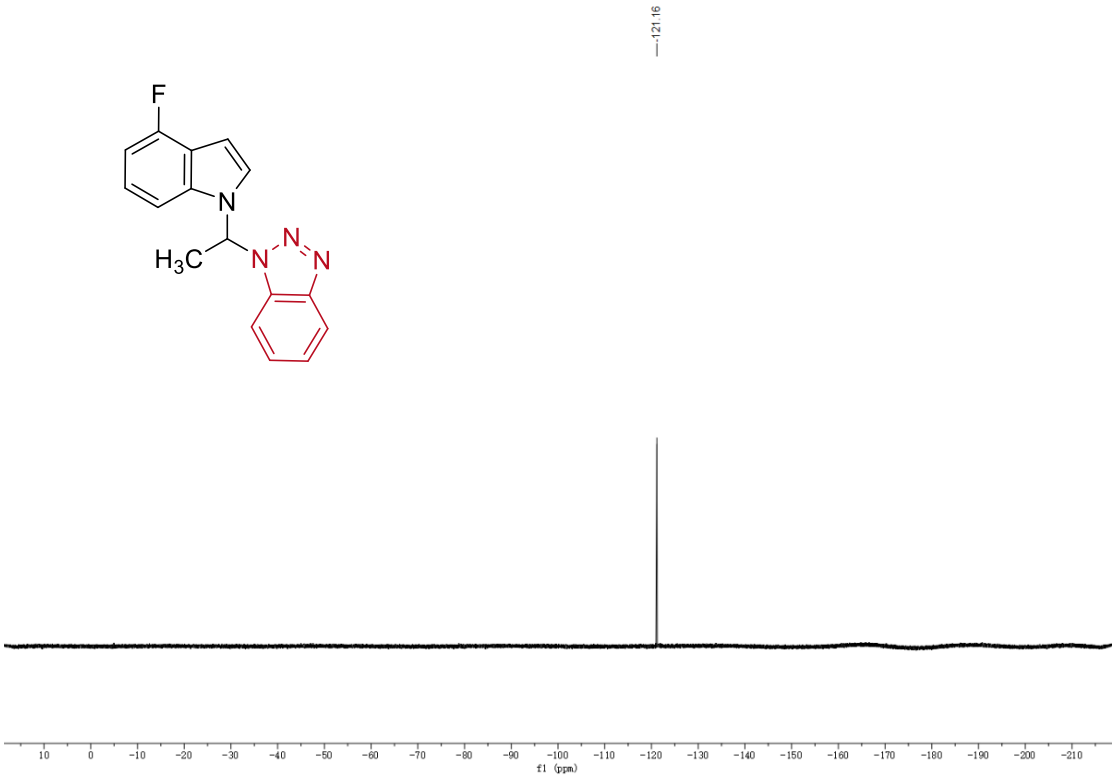
[13]C-NMR (100 MHz, $CDCl_3$) **spectrum of 3k**



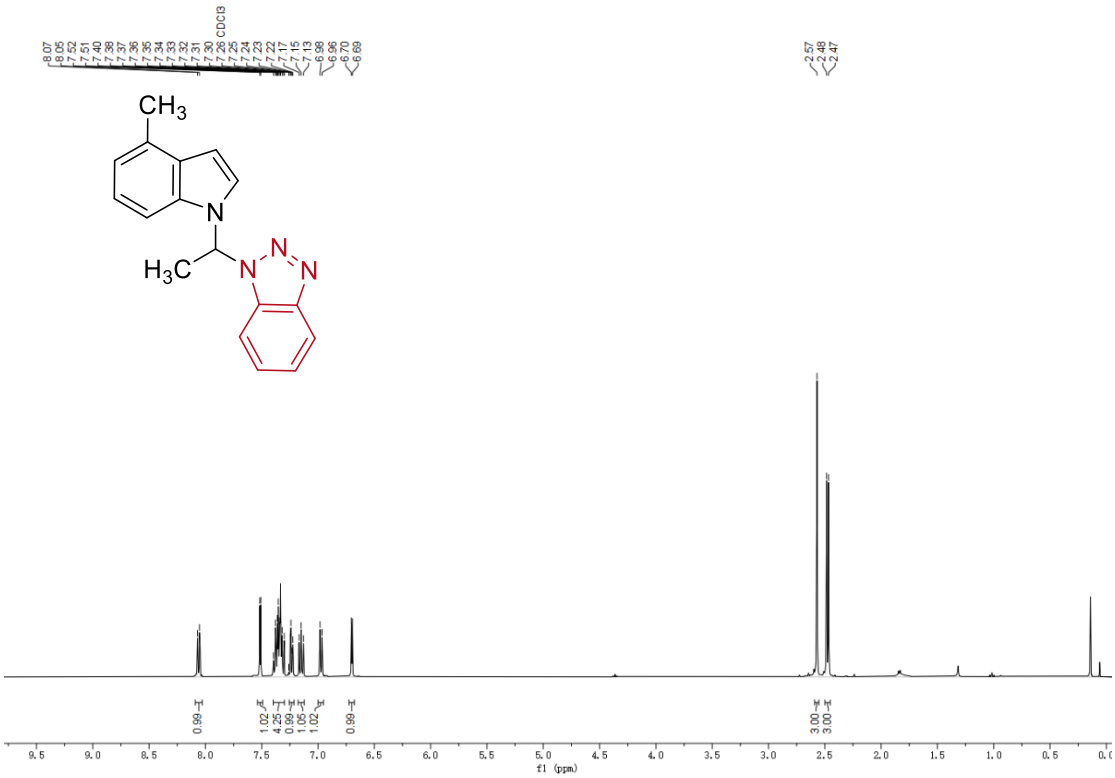
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3l**



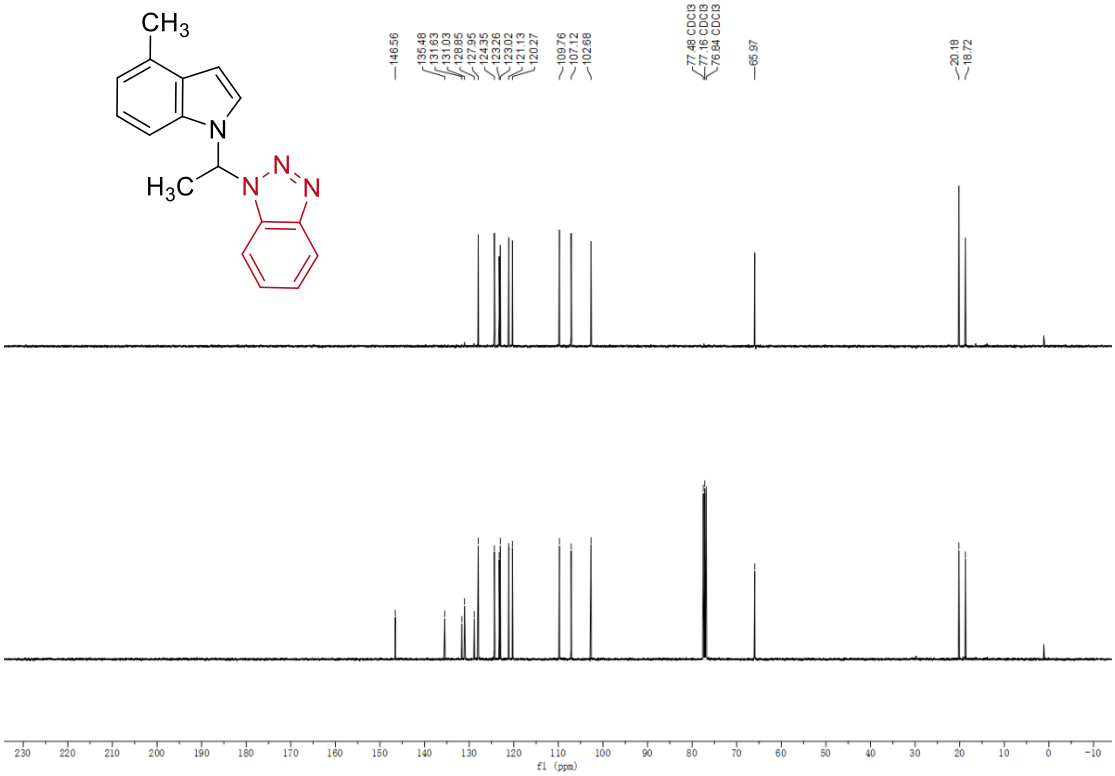
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3l**



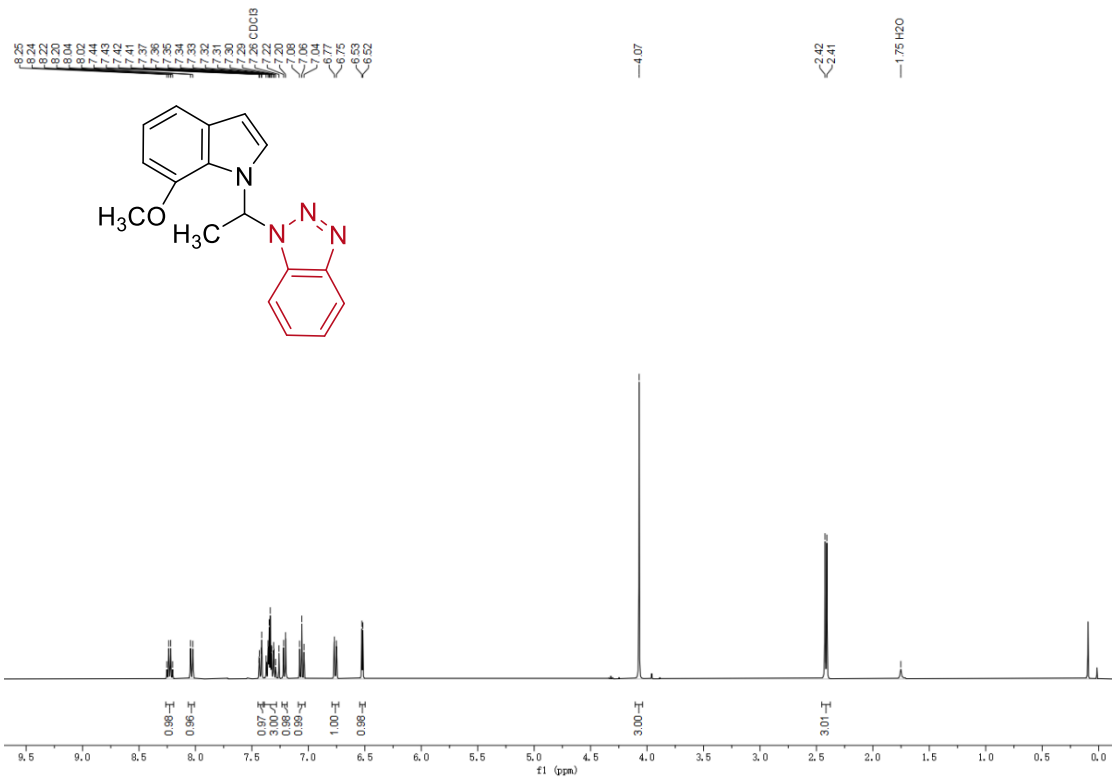
^{19}F-NMR (376 MHz, $CDCl_3$) **spectrum of 3l**



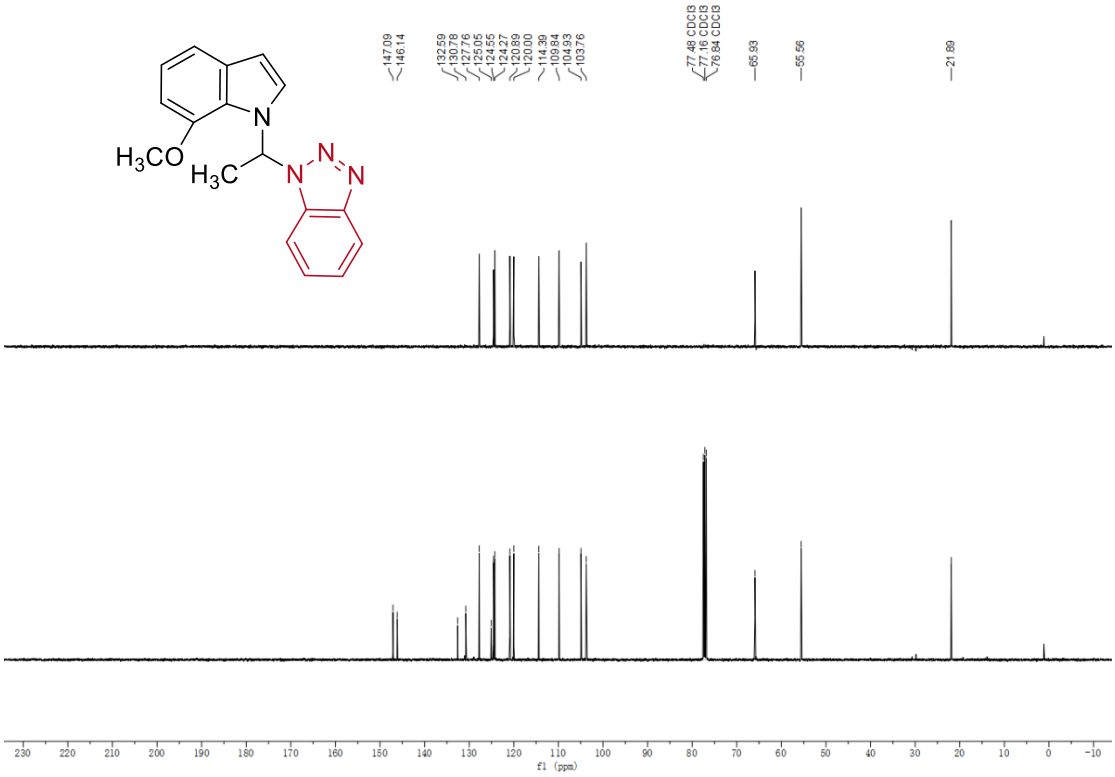
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3m**



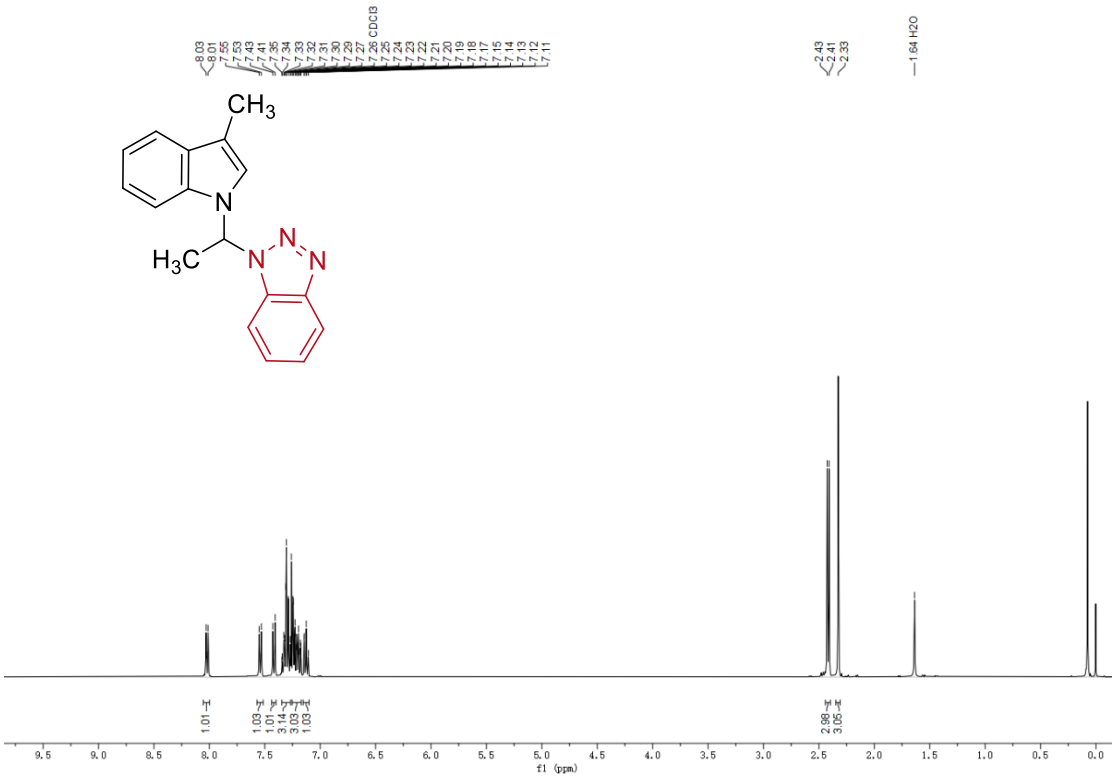
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3m**



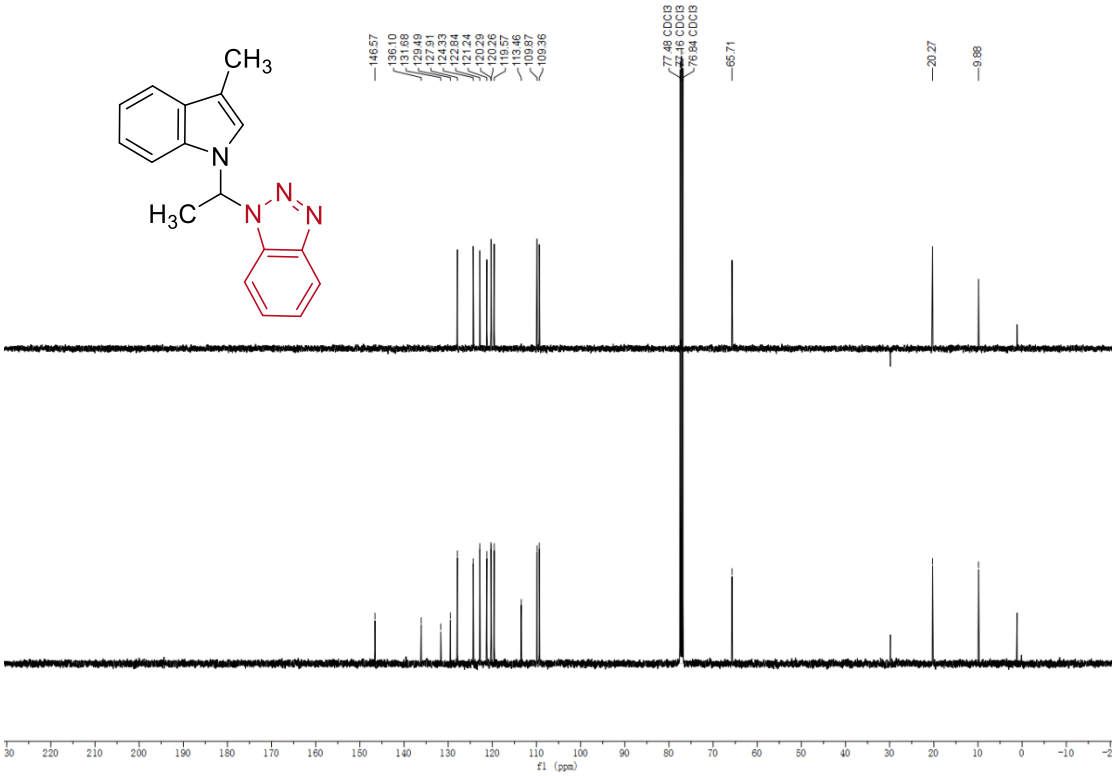
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3n**



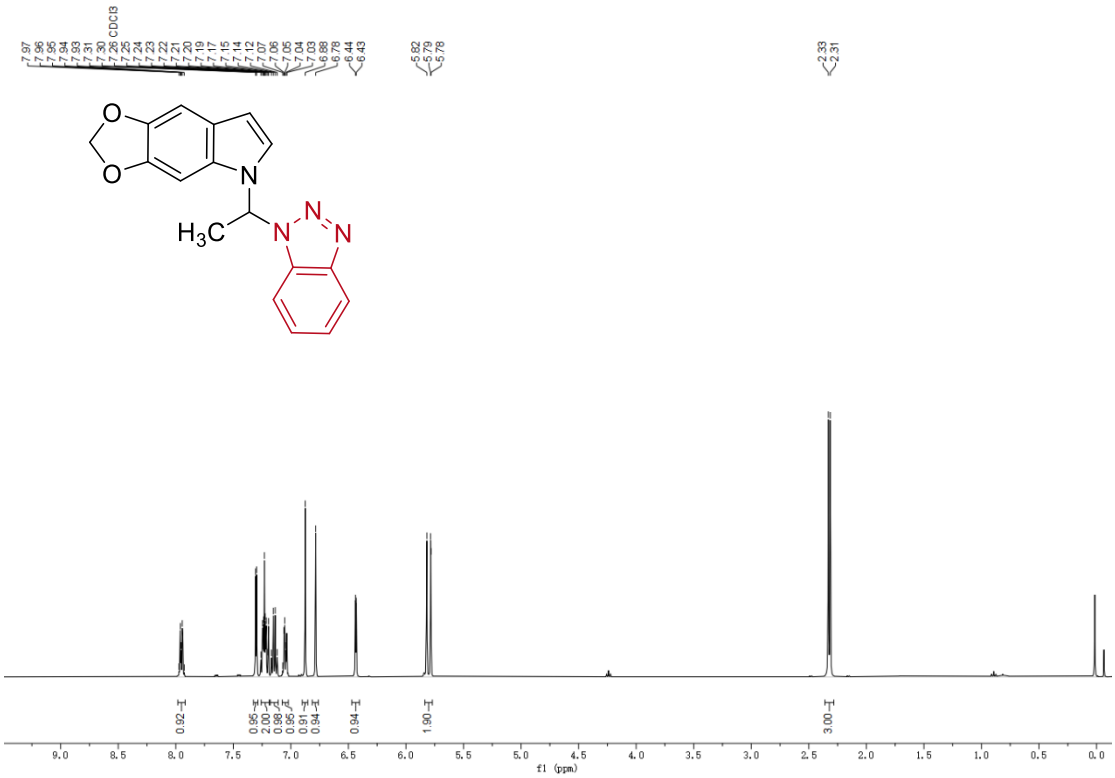
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3n**



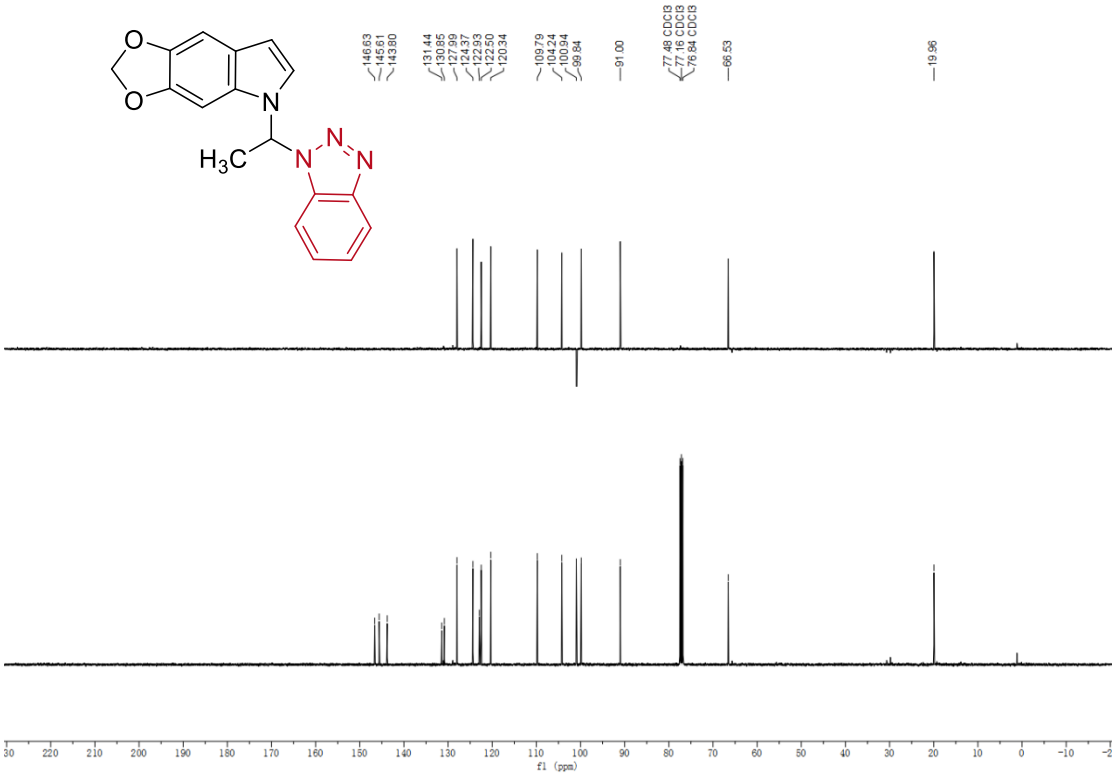
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3o**



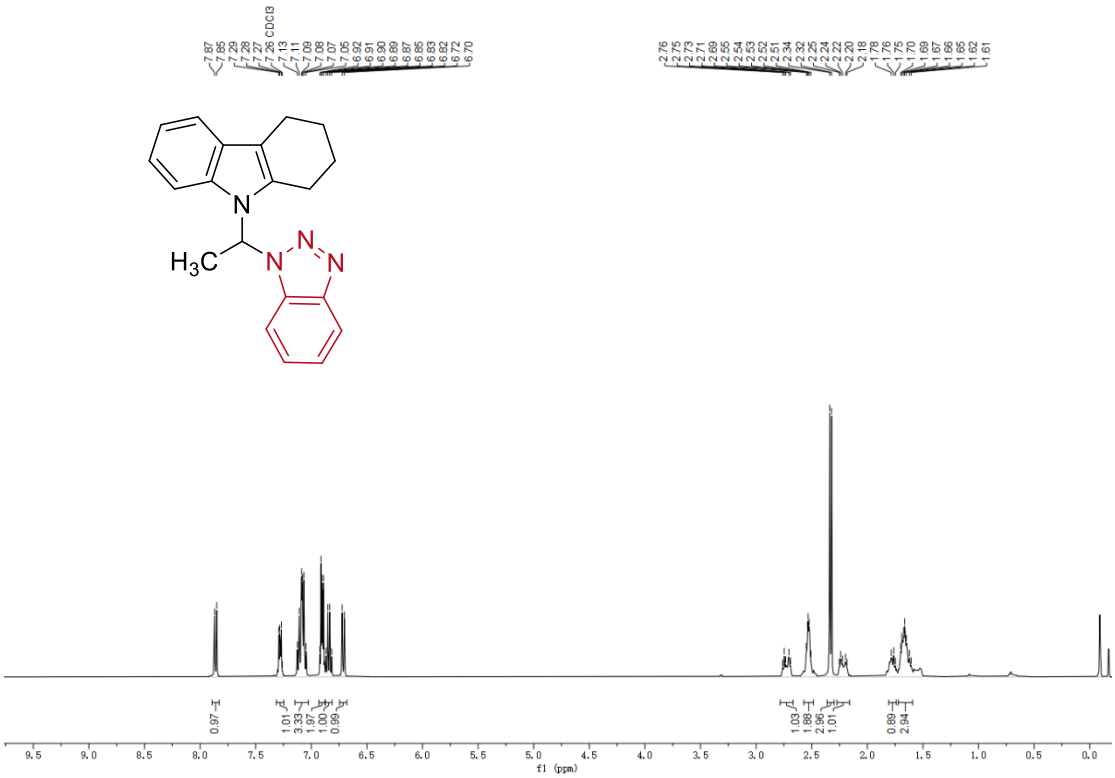
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3o**



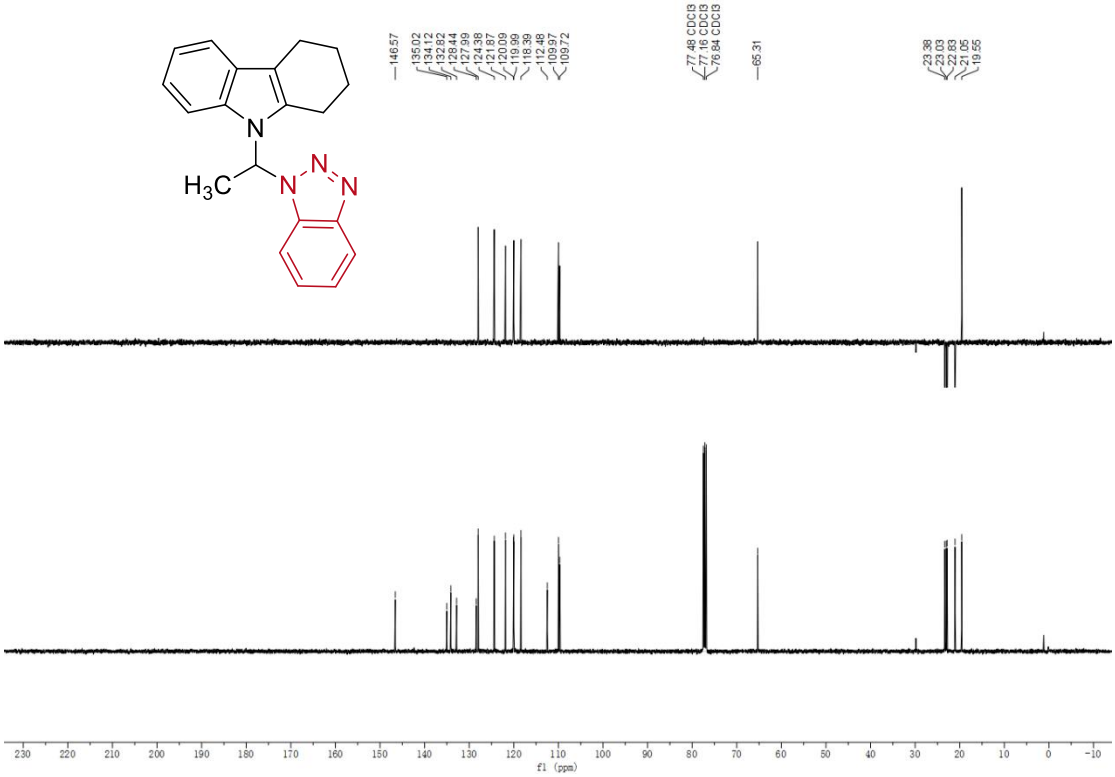
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3p**



^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3p**

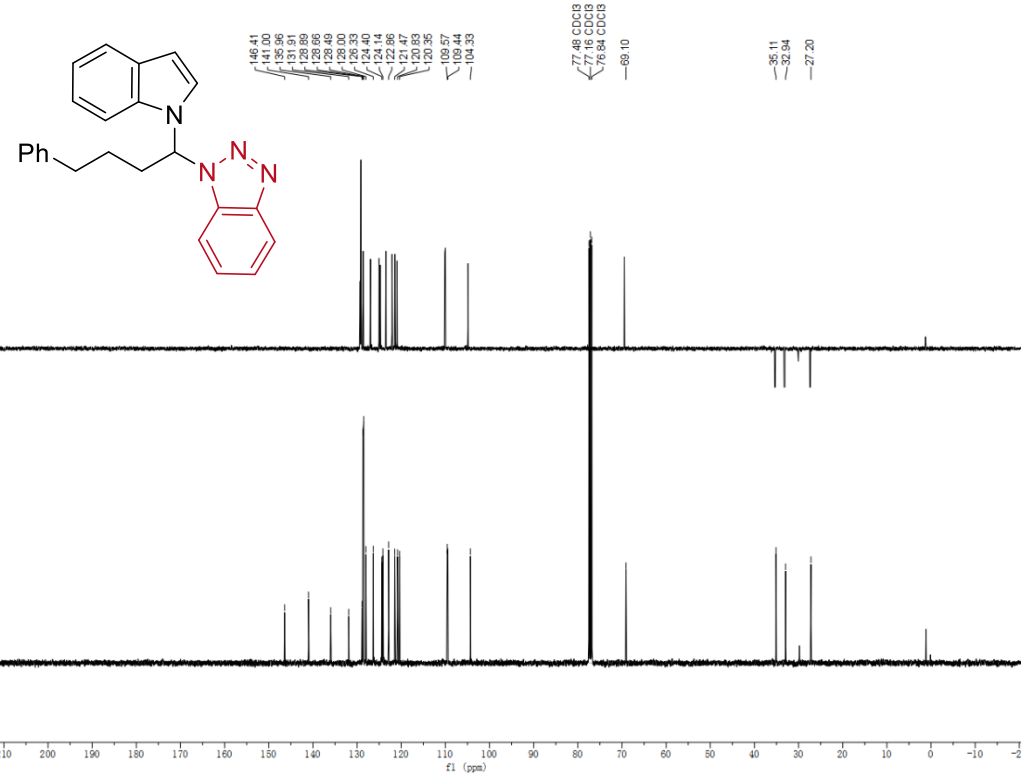


^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3q**

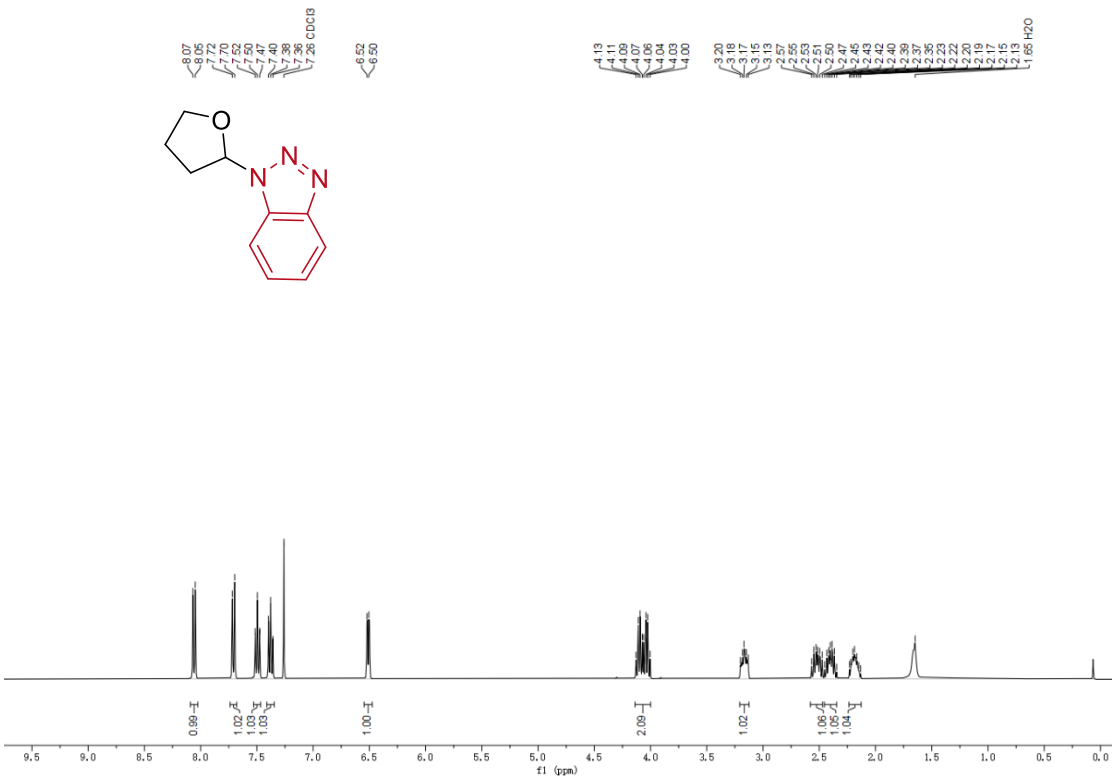


^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3q**

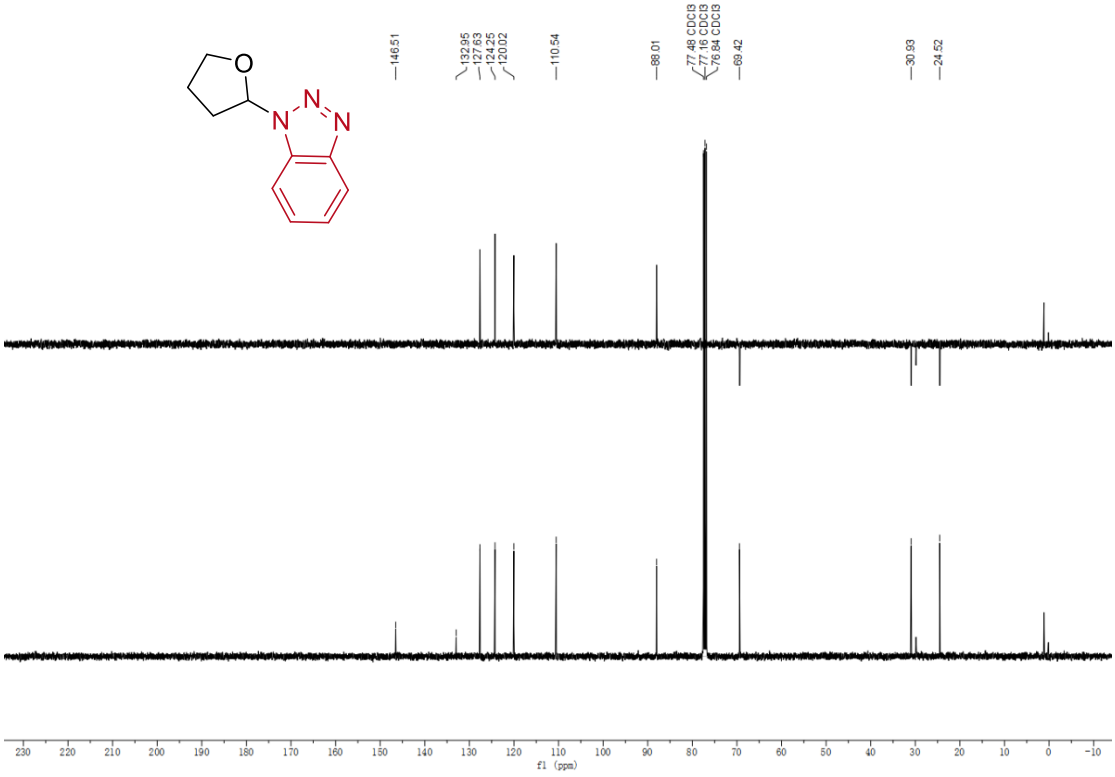
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3r`**



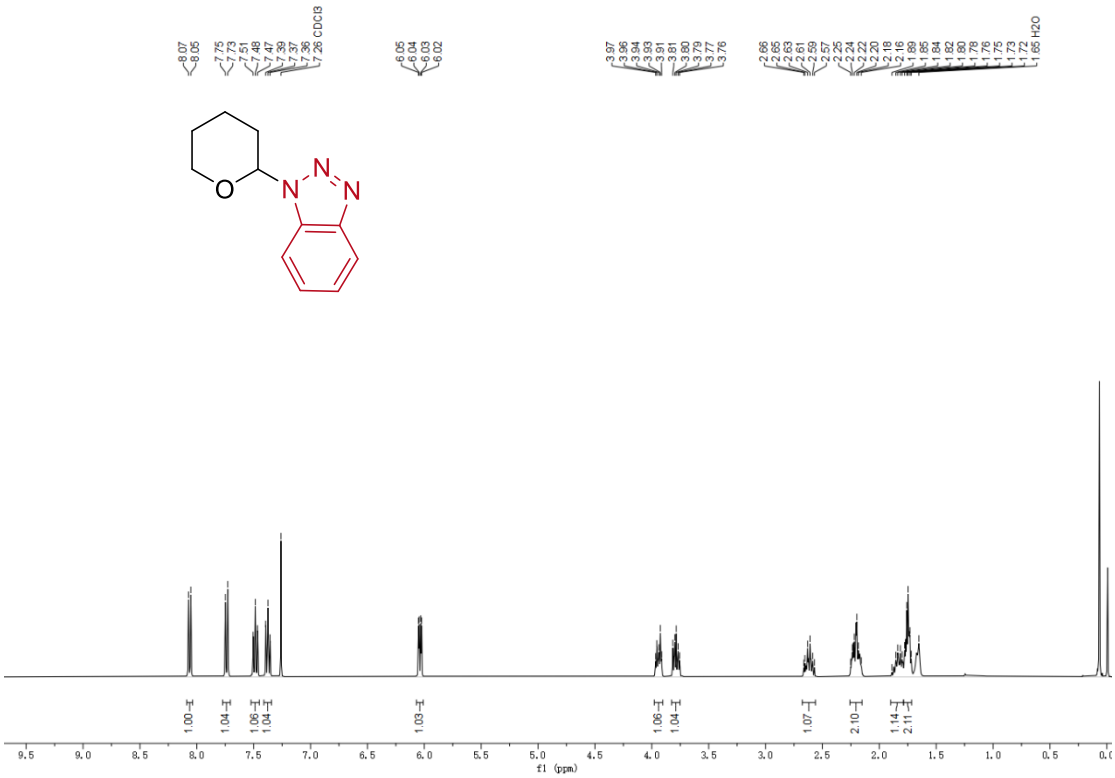
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3r**



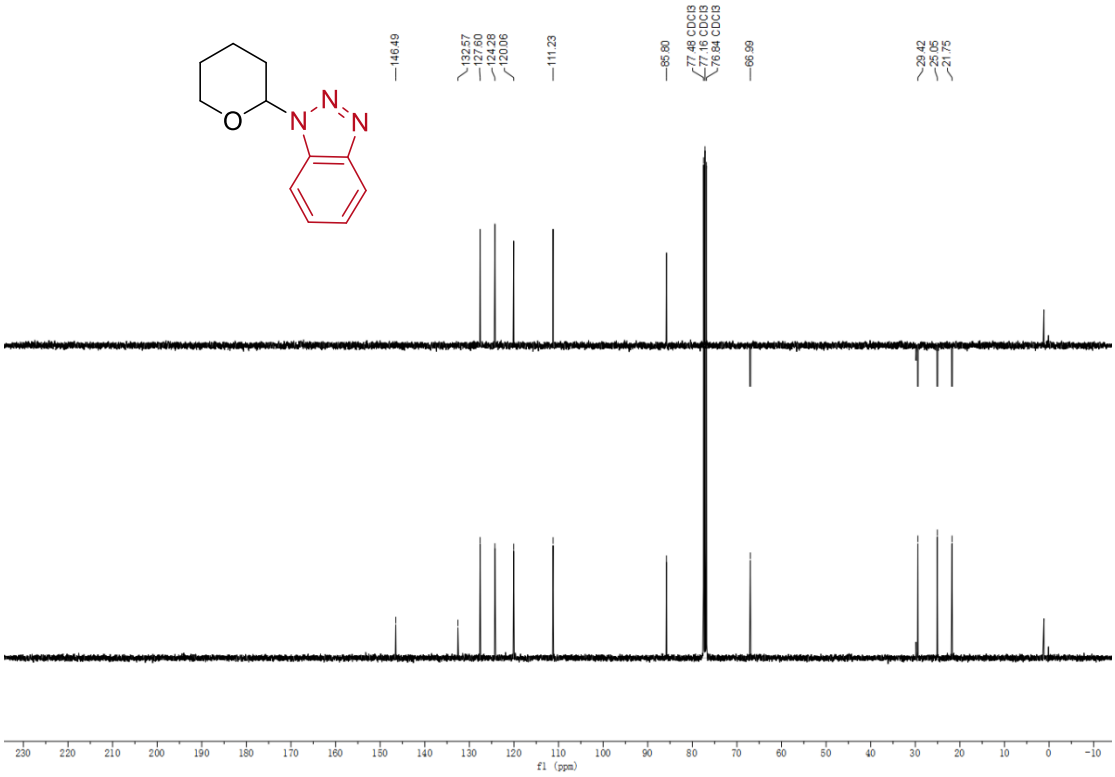
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3s**



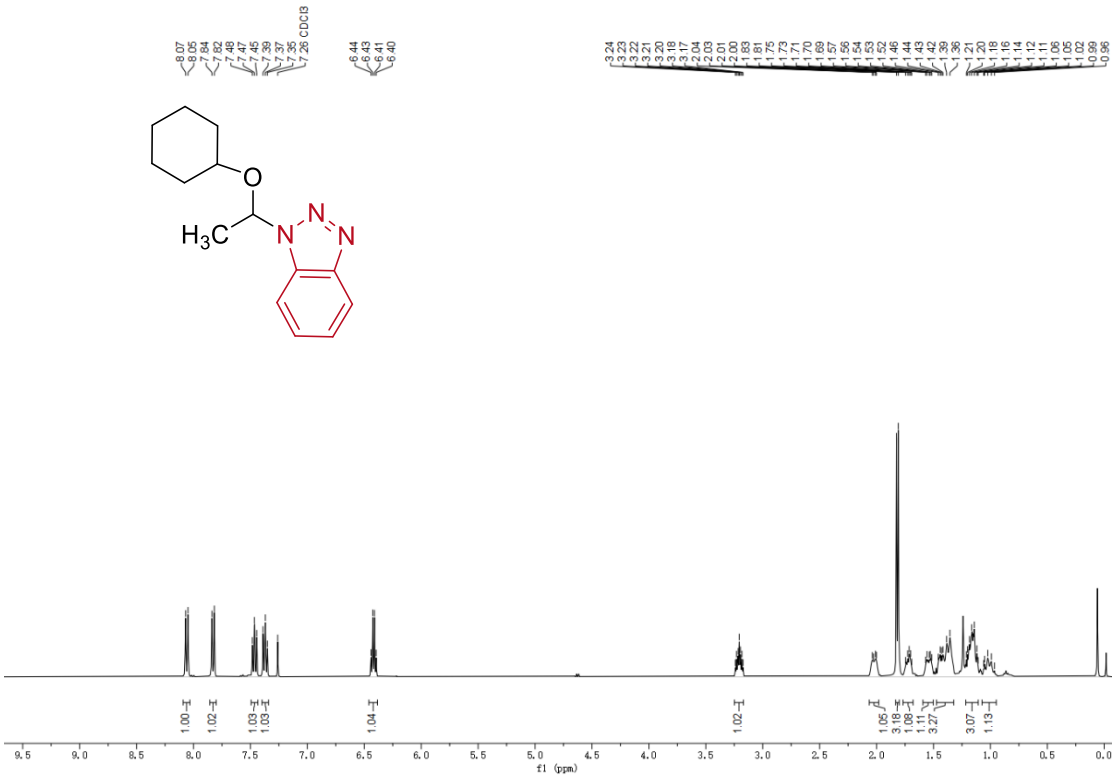
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3s**



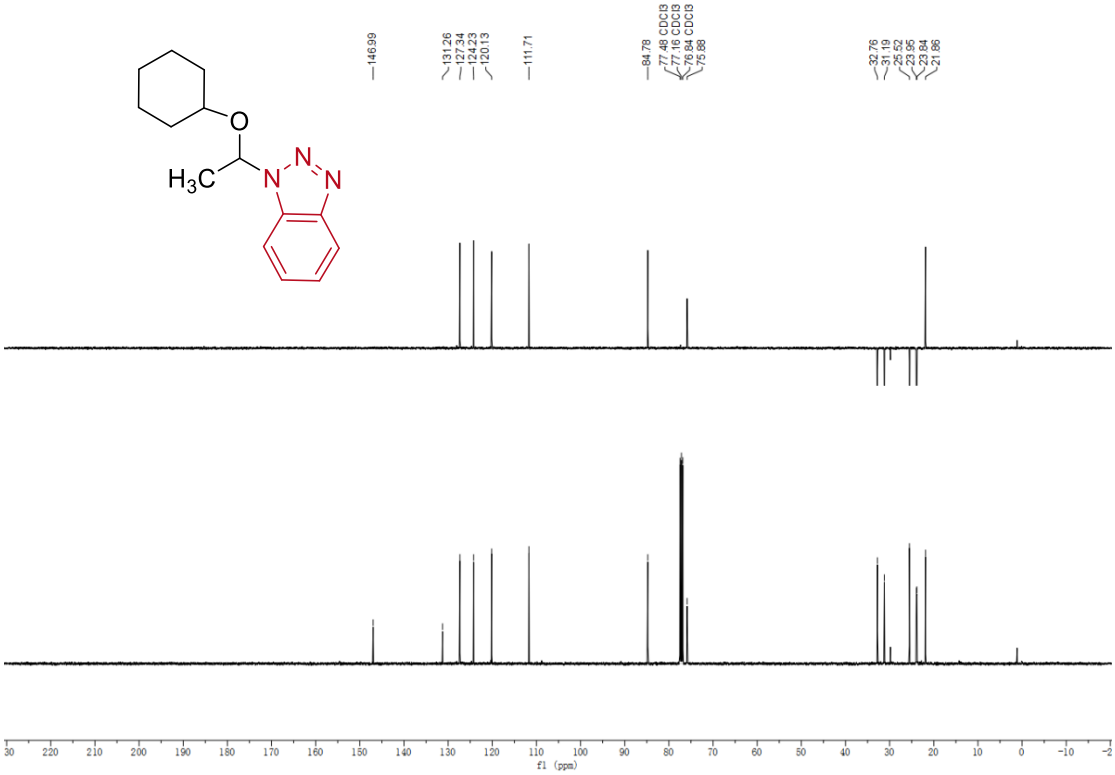
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3t**



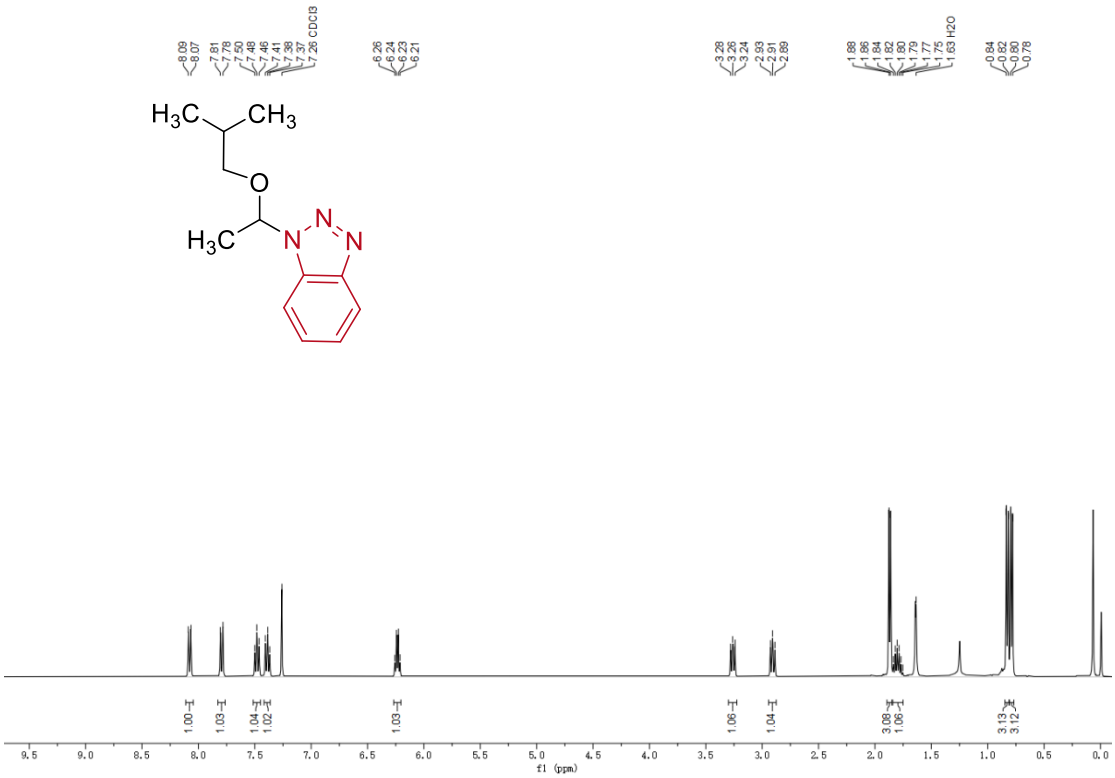
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3t**



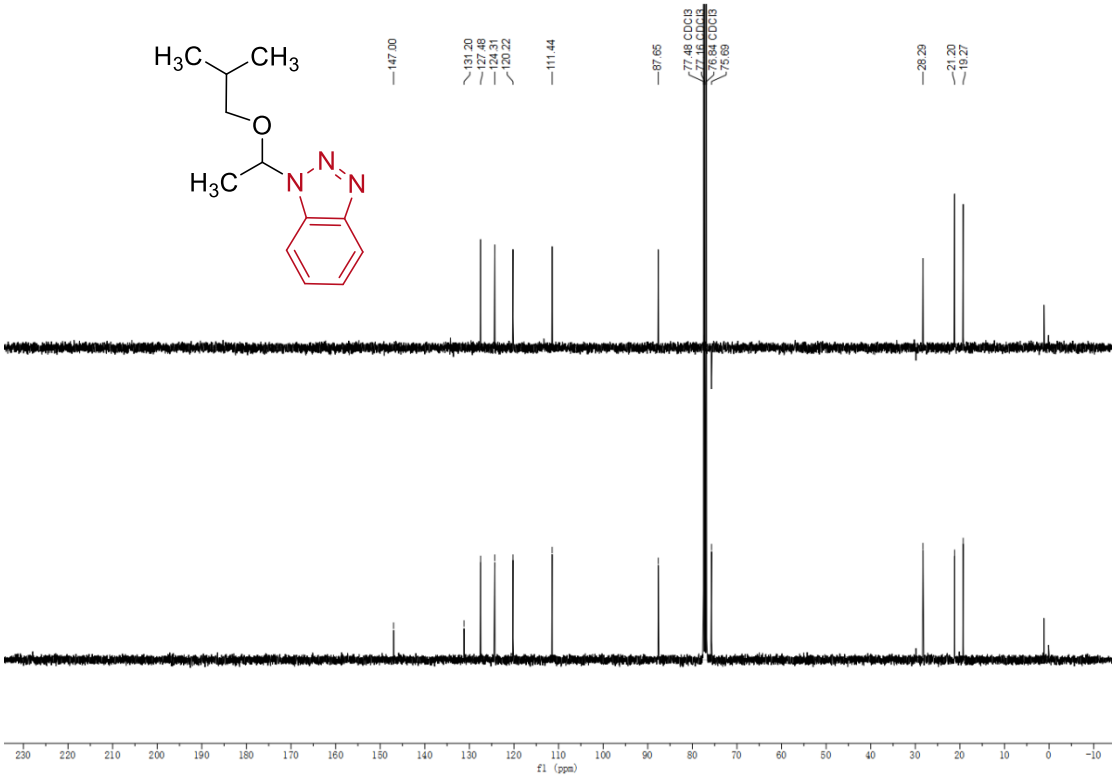
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3u**



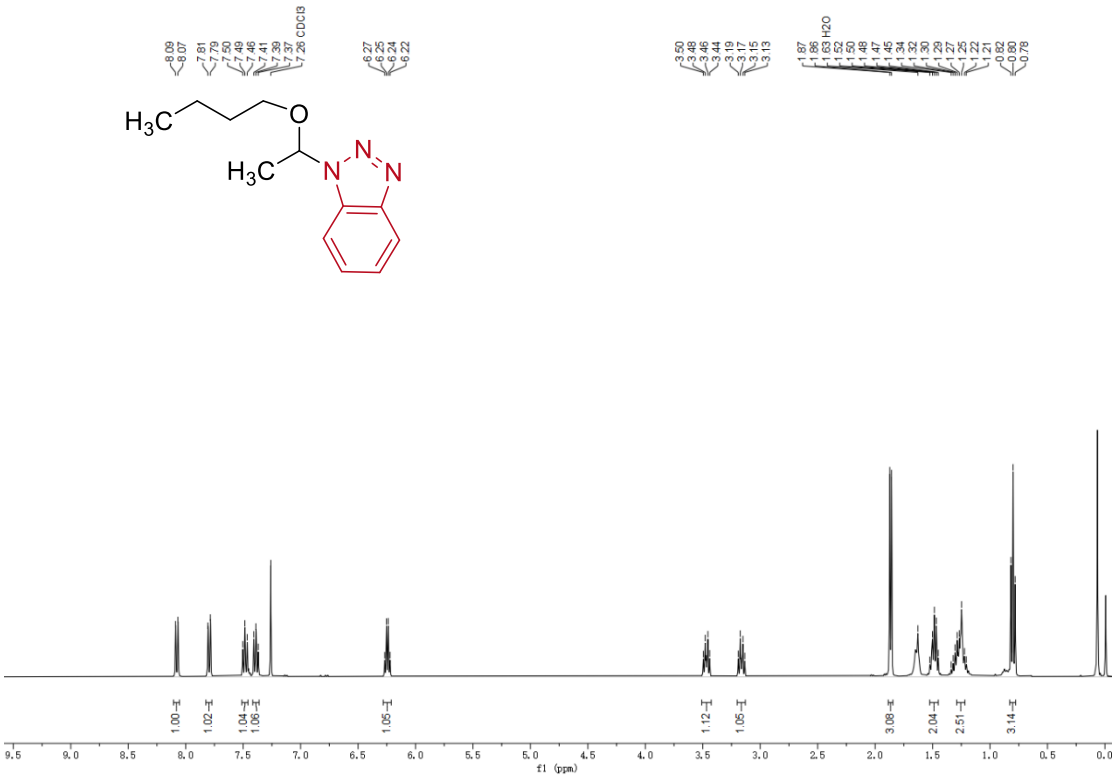
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3u**



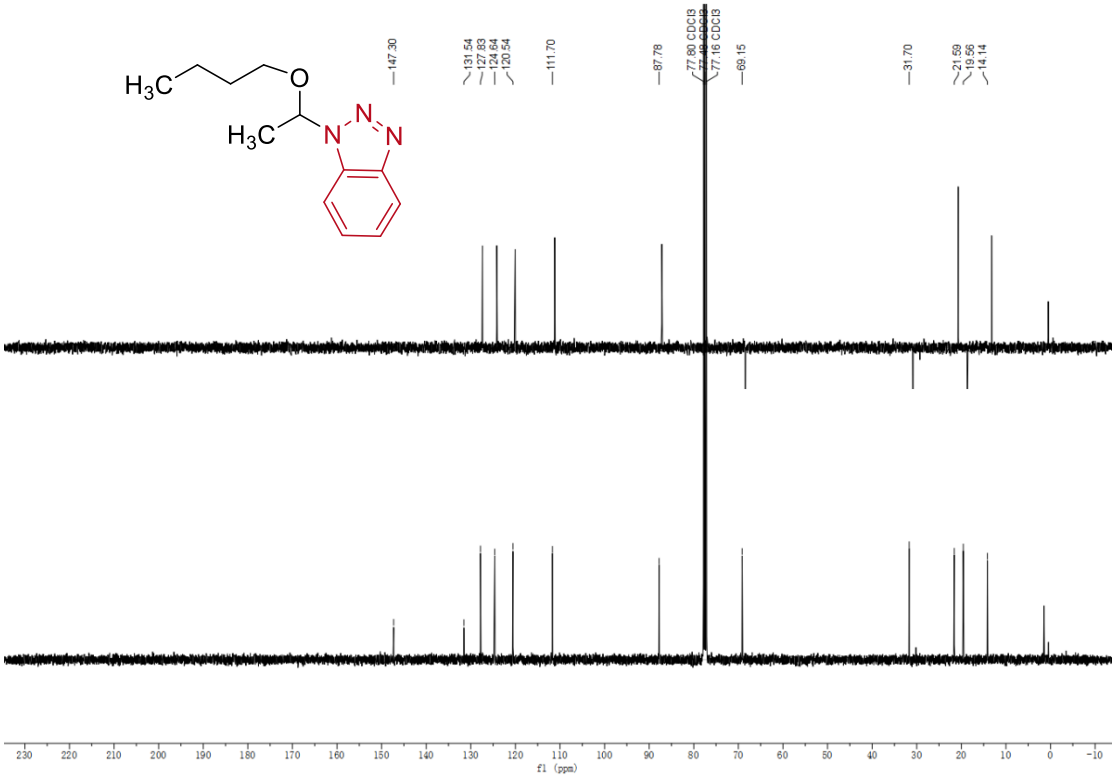
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3v**



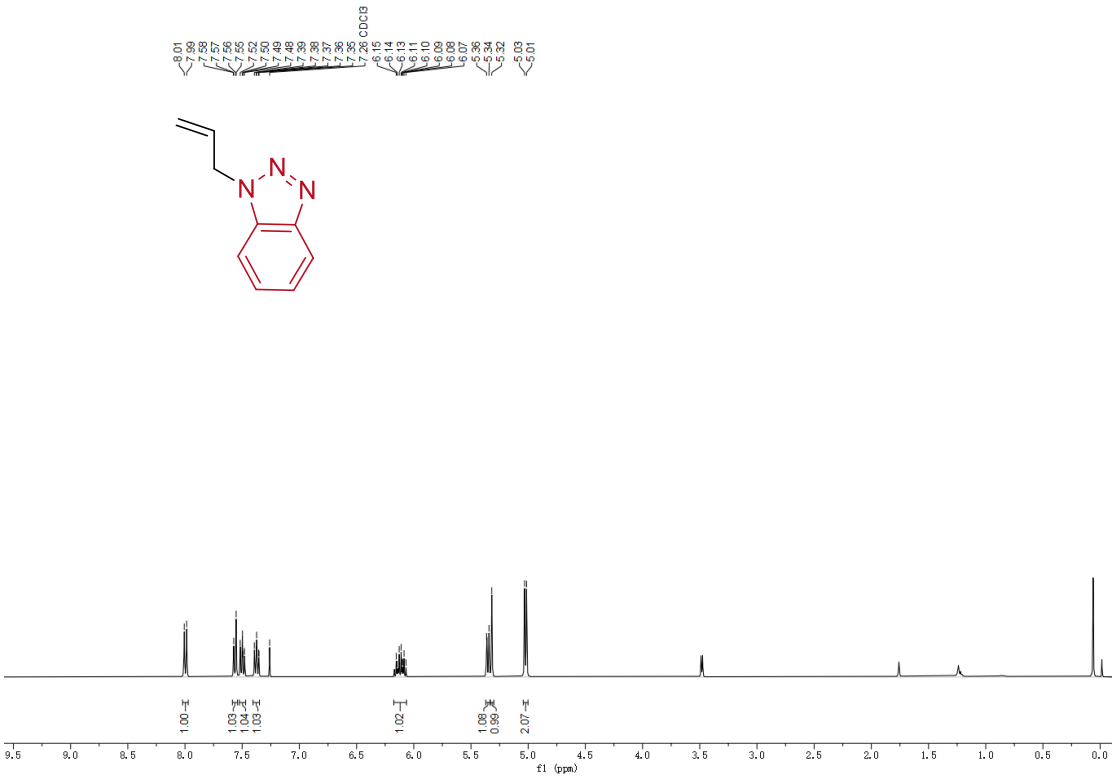
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3v**



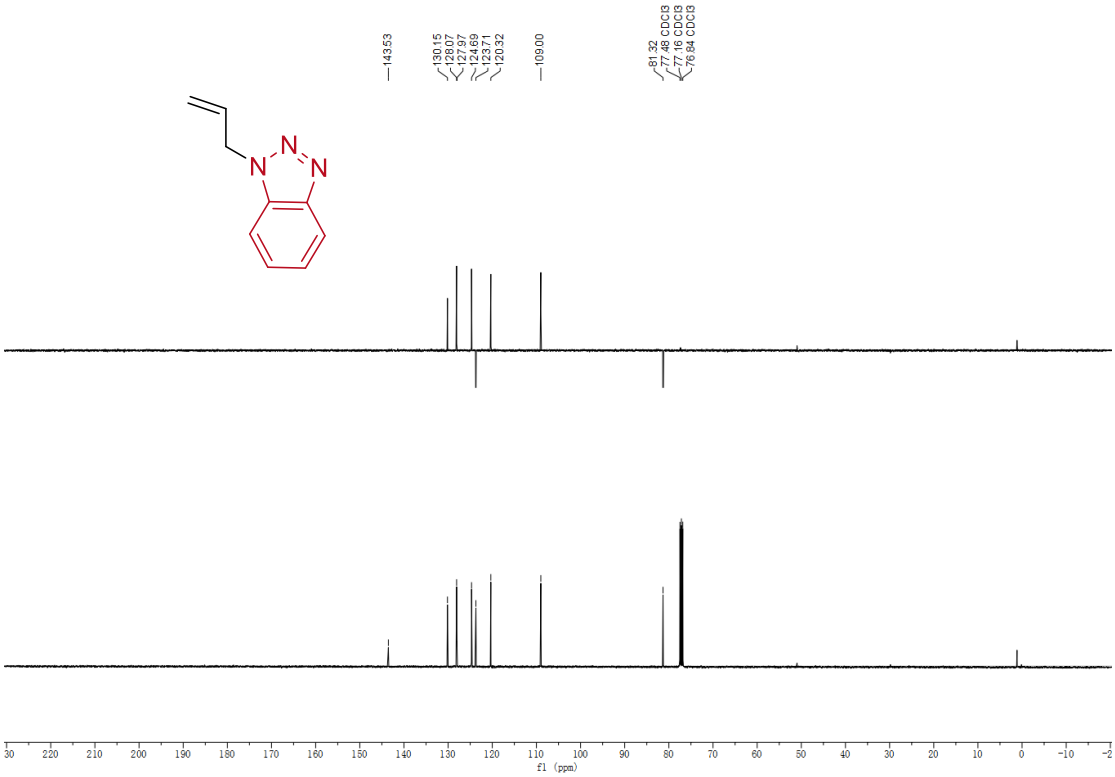
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3w**



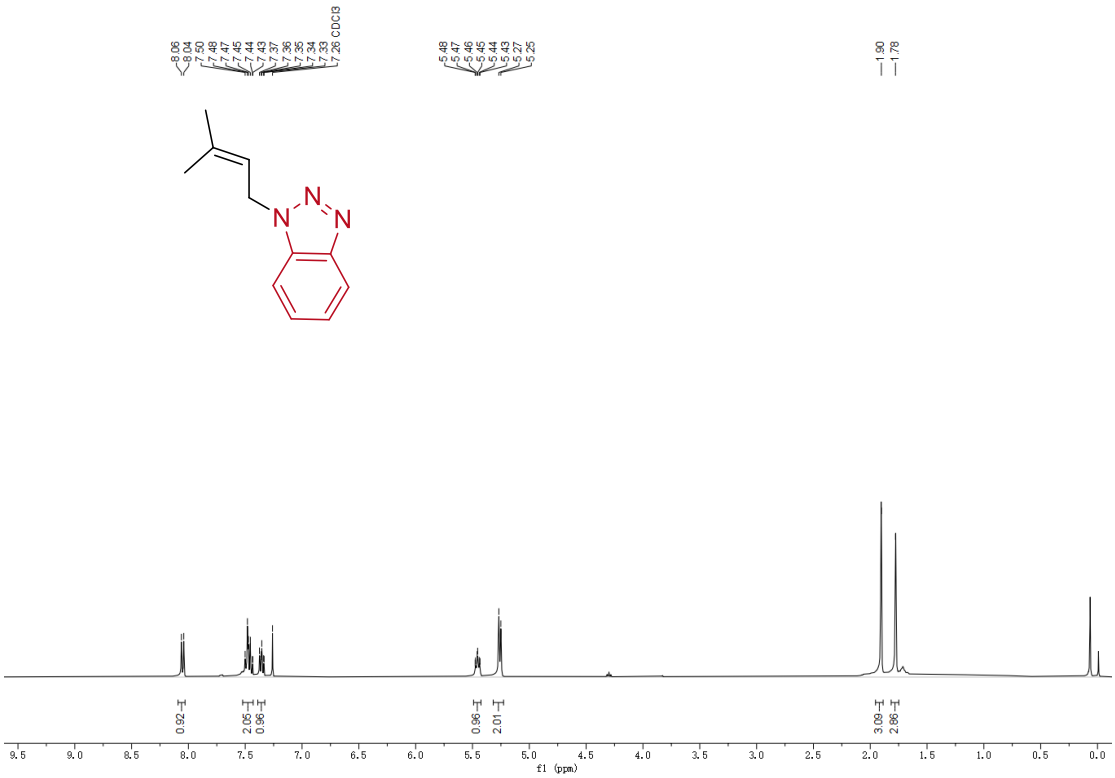
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3w**



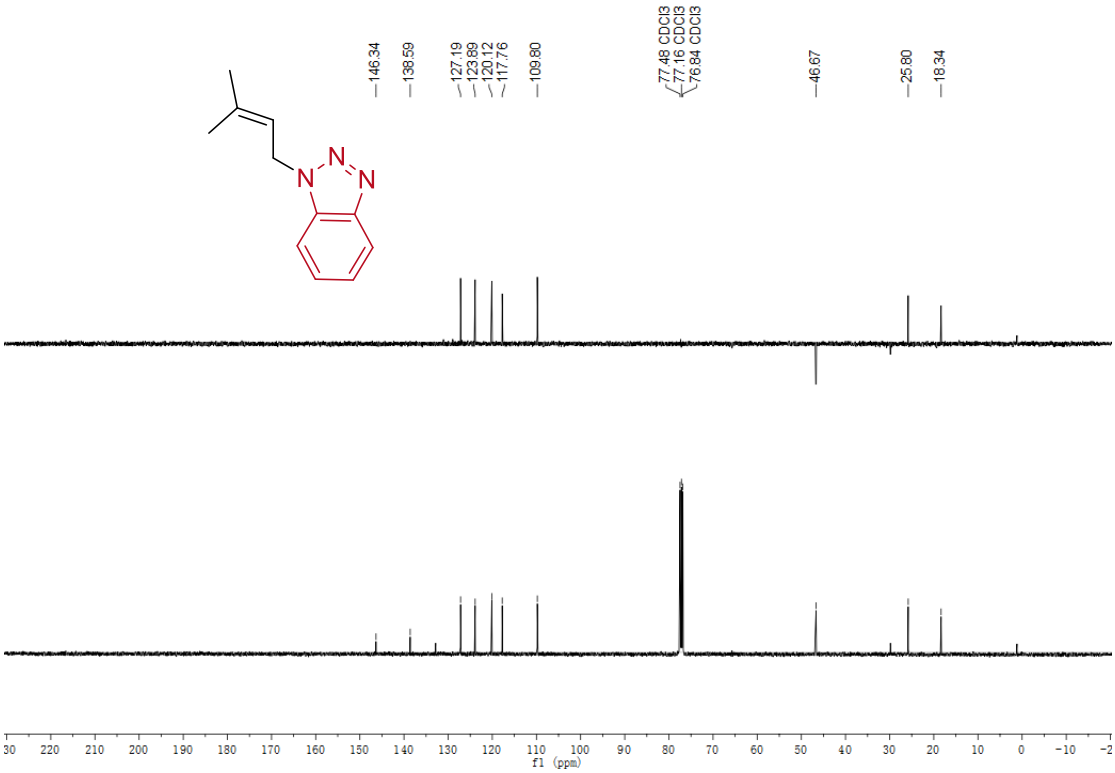
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3x**



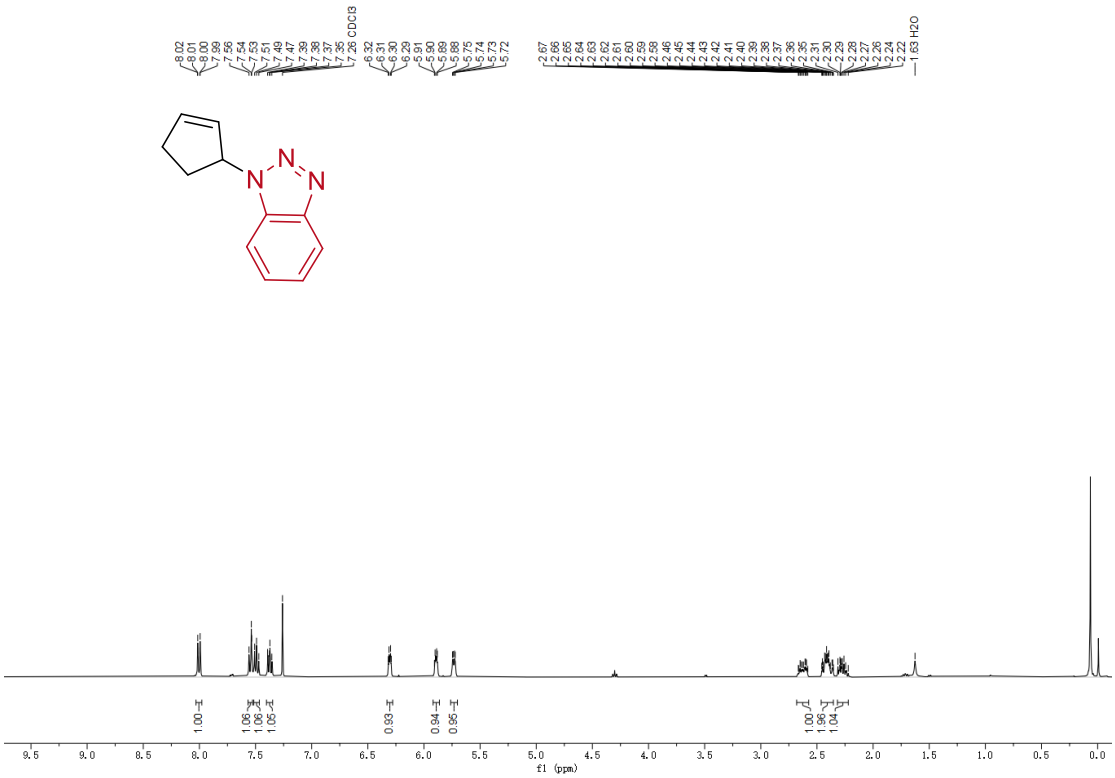
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3x**



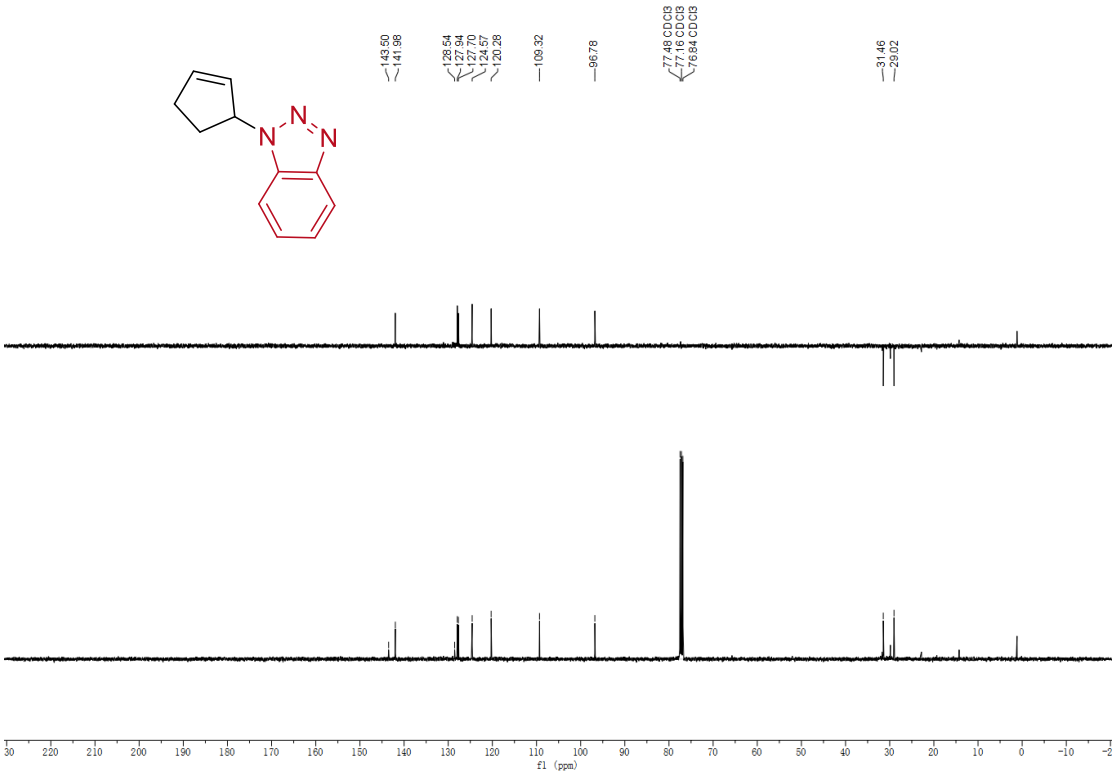
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3y**



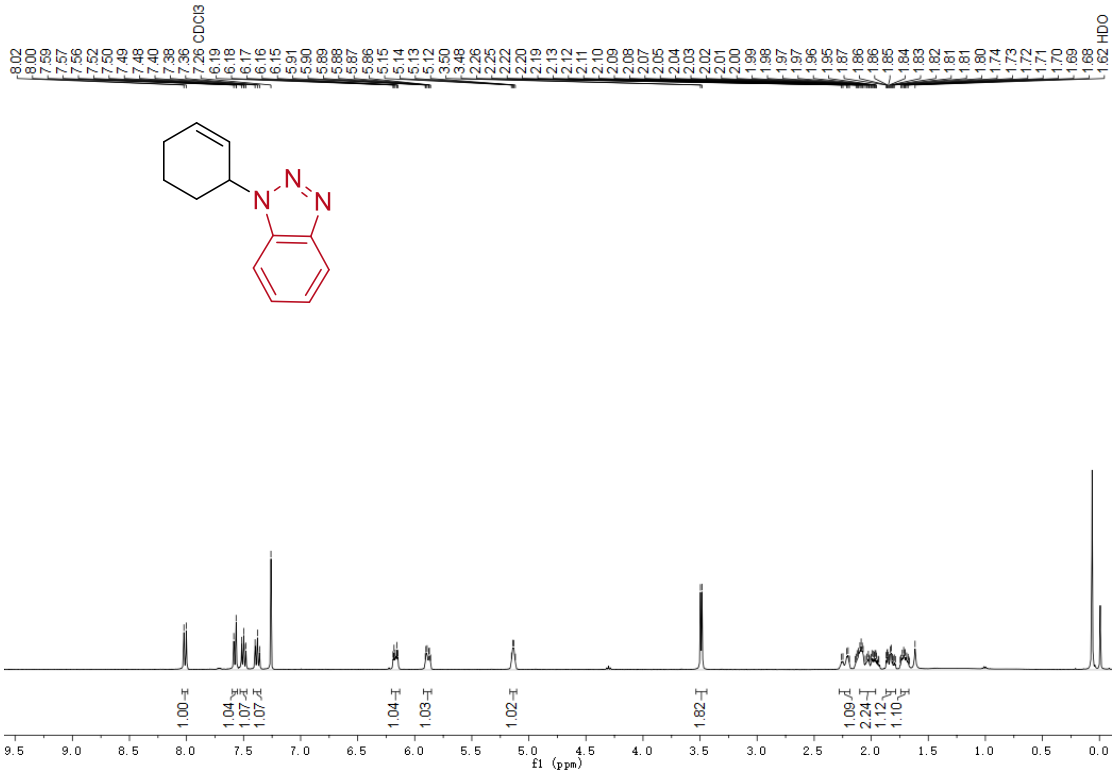
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3y**



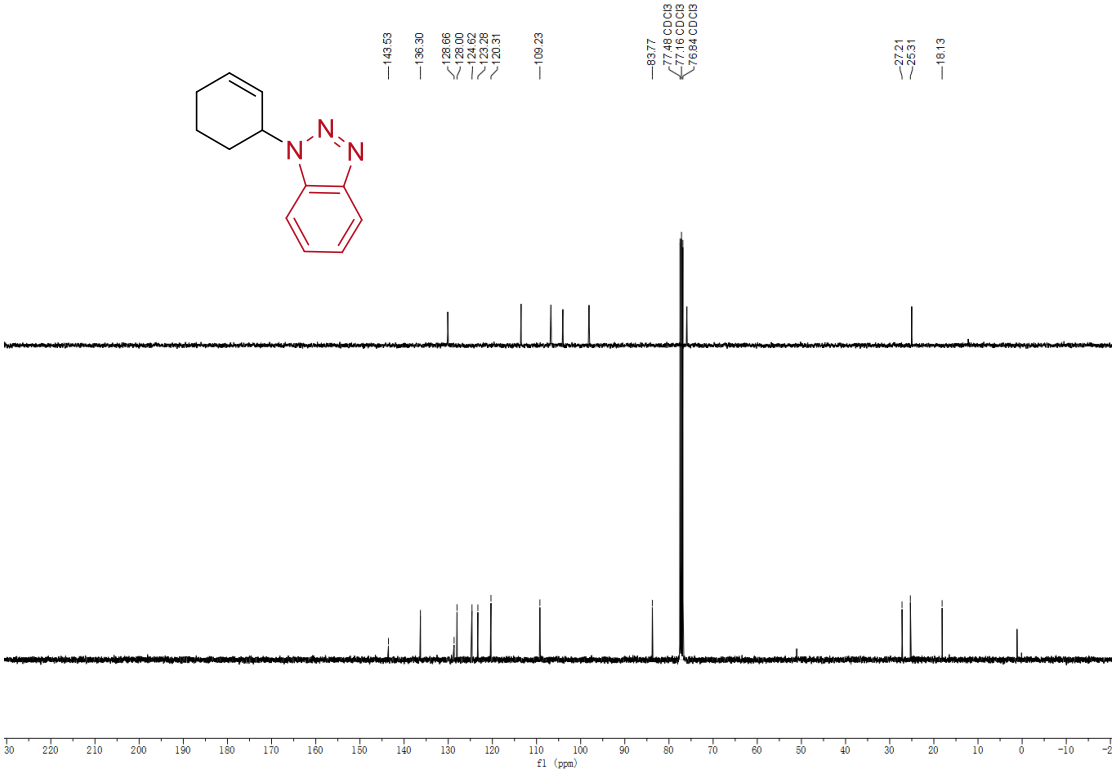
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3za**



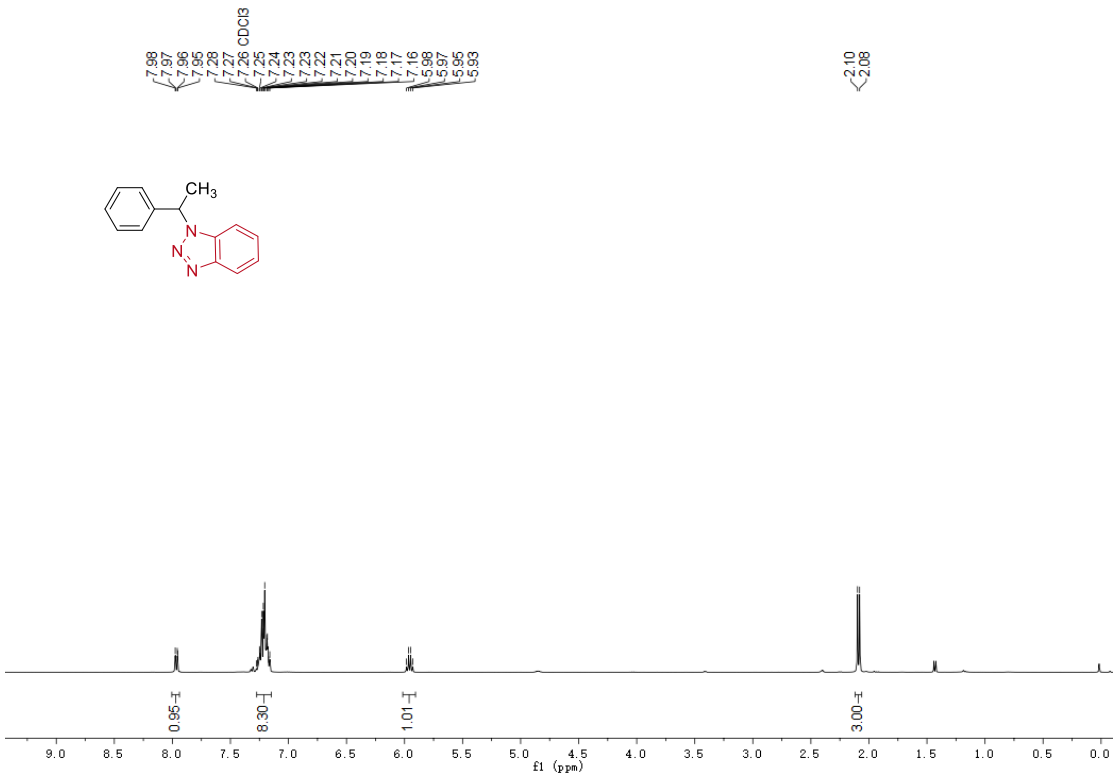
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3za**



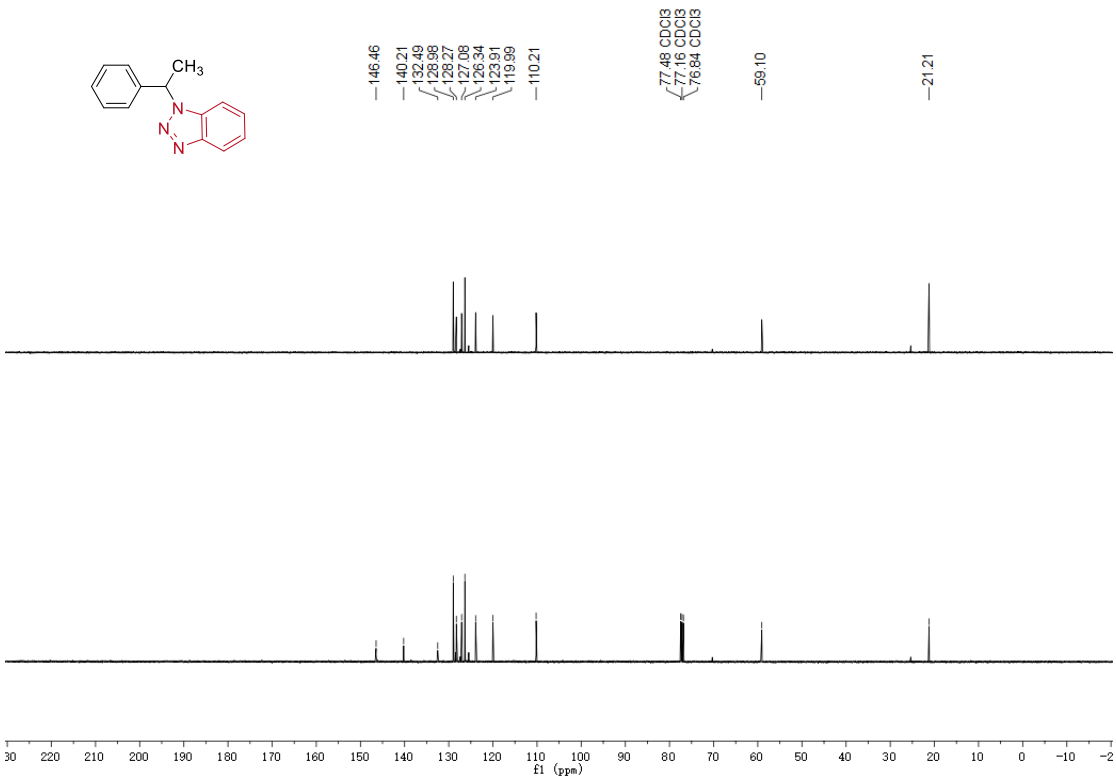
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3zb**



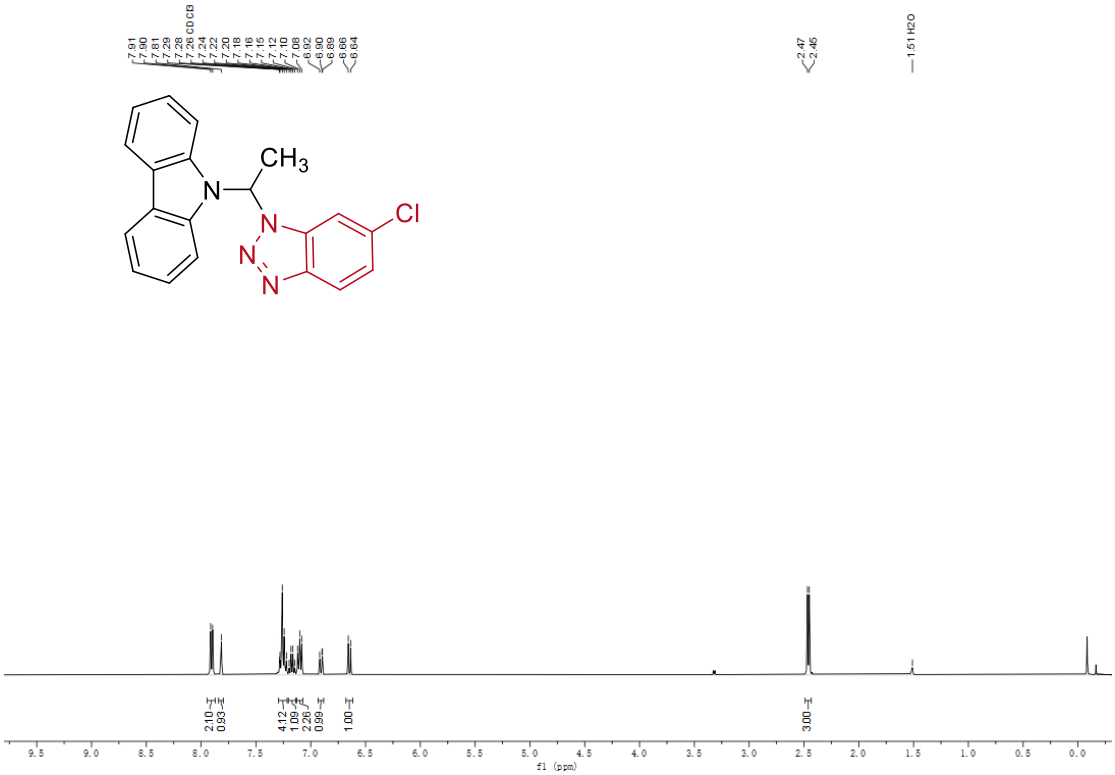
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 3zb**



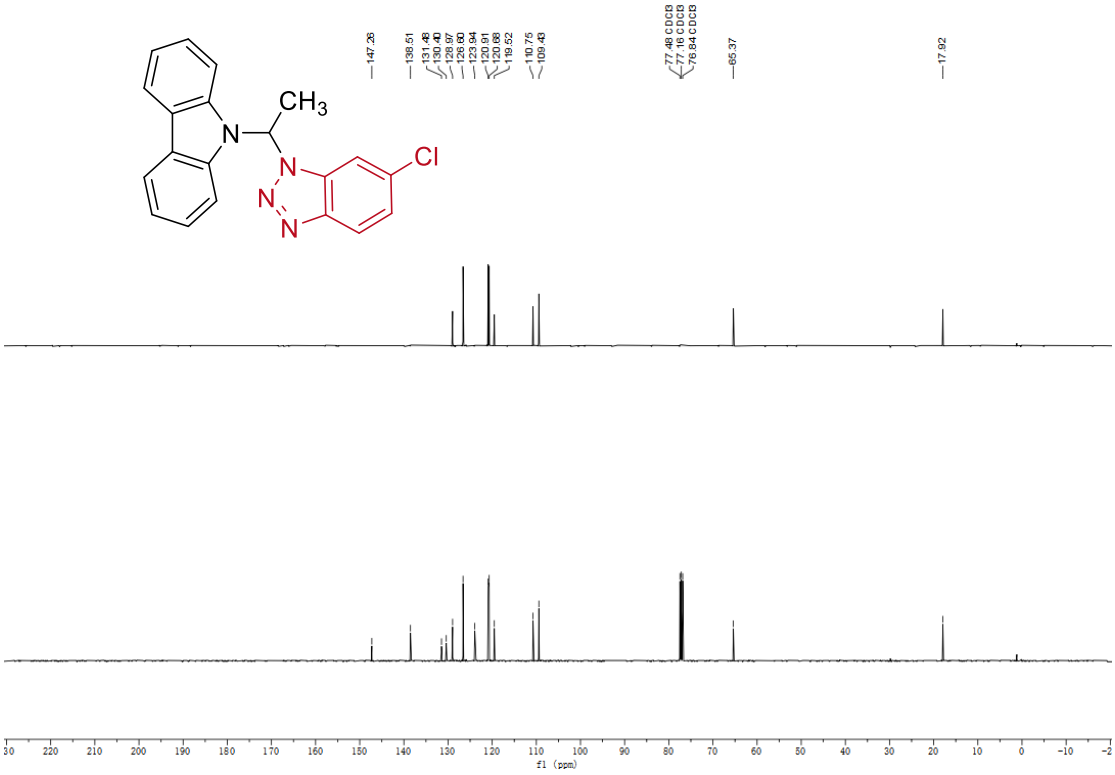
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3zc**



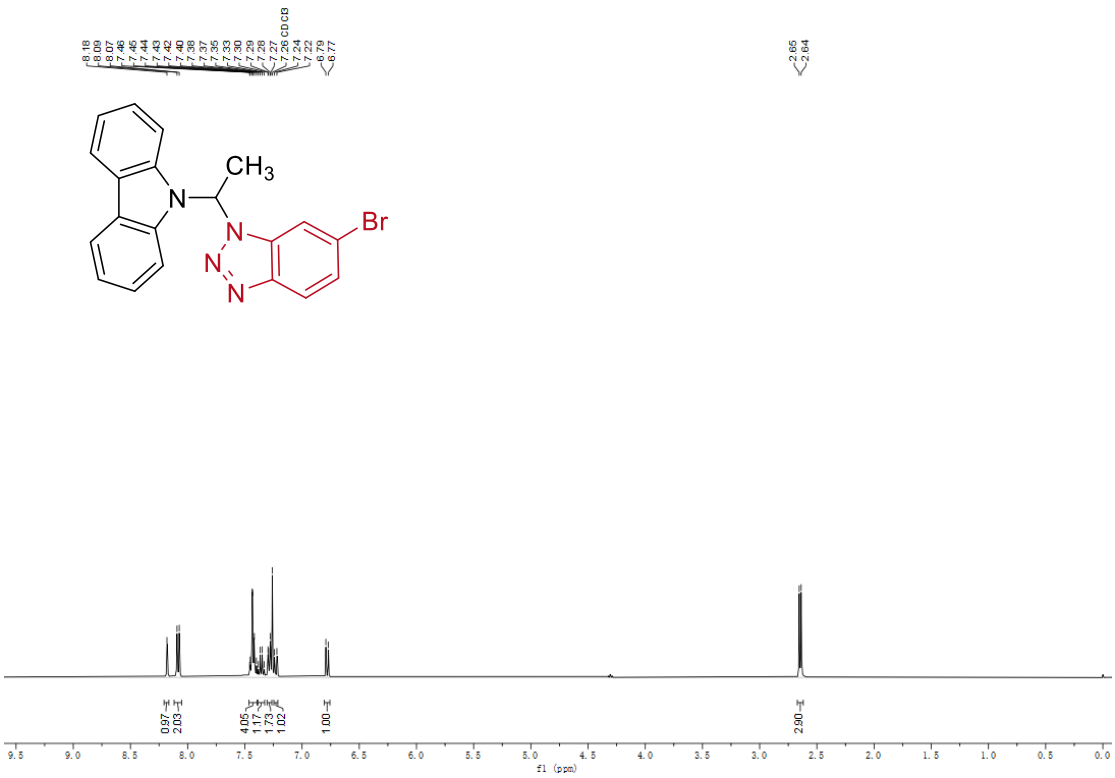
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 3zc**



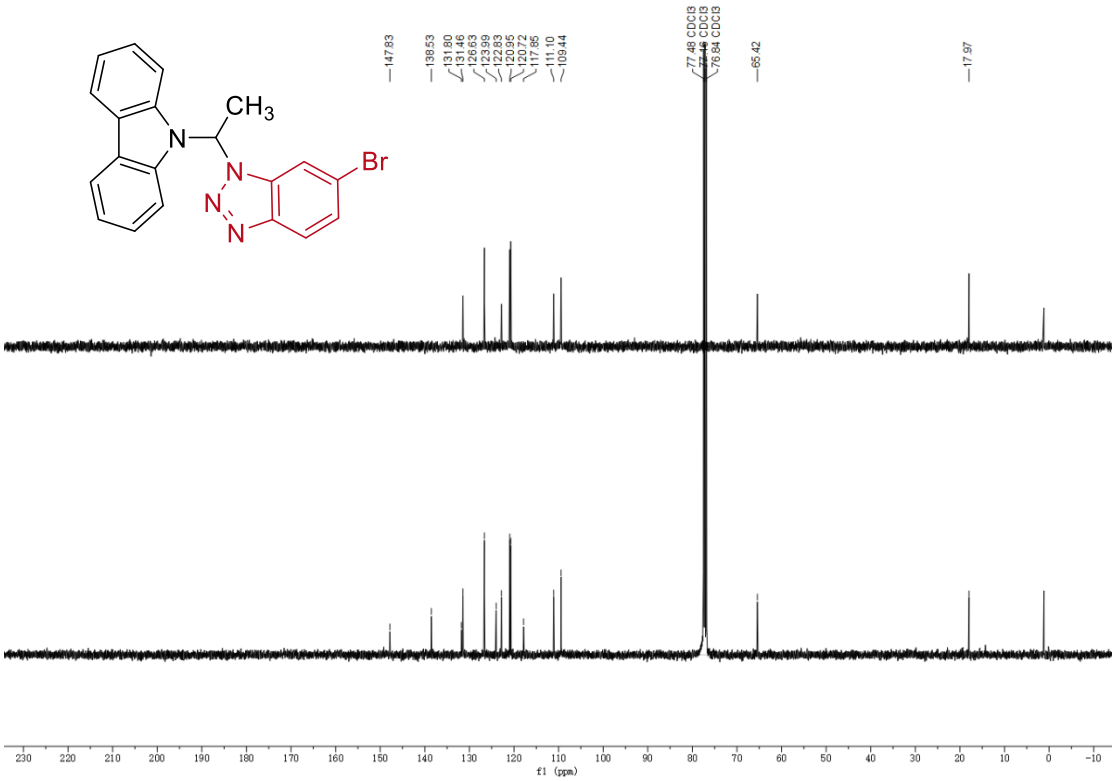
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4a**



^{13}C-NMR (100MHz, $CDCl_3$) **spectrum of 4a**



^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4b**



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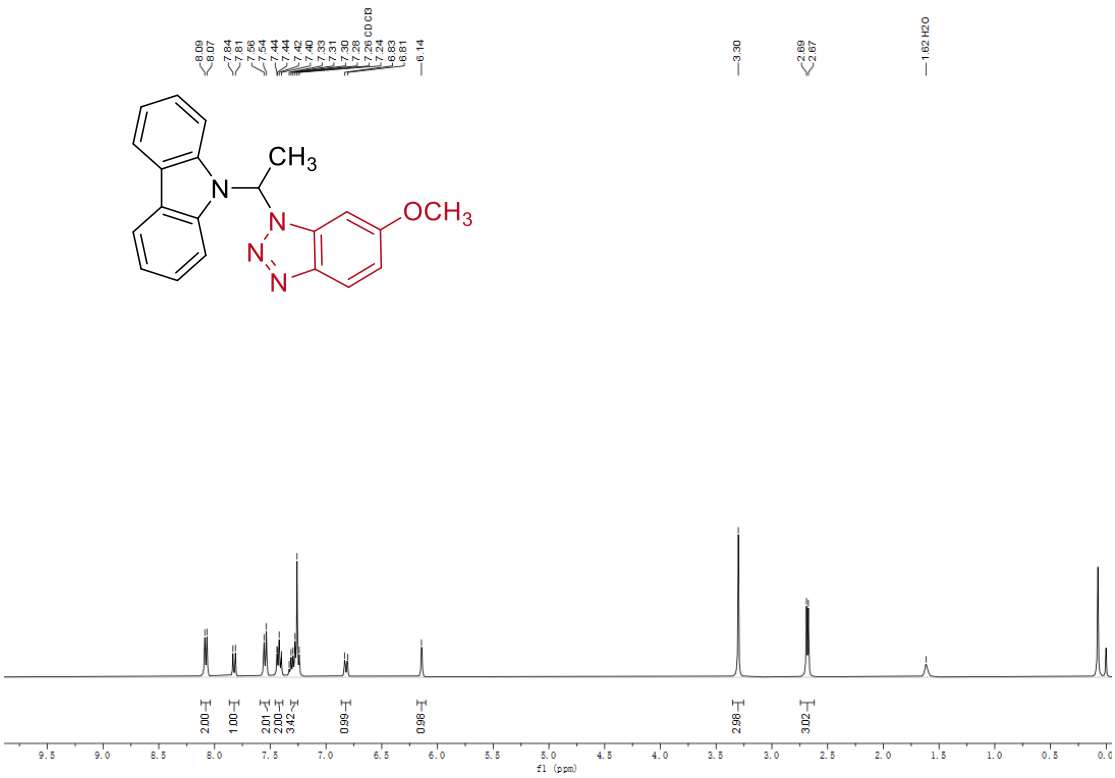
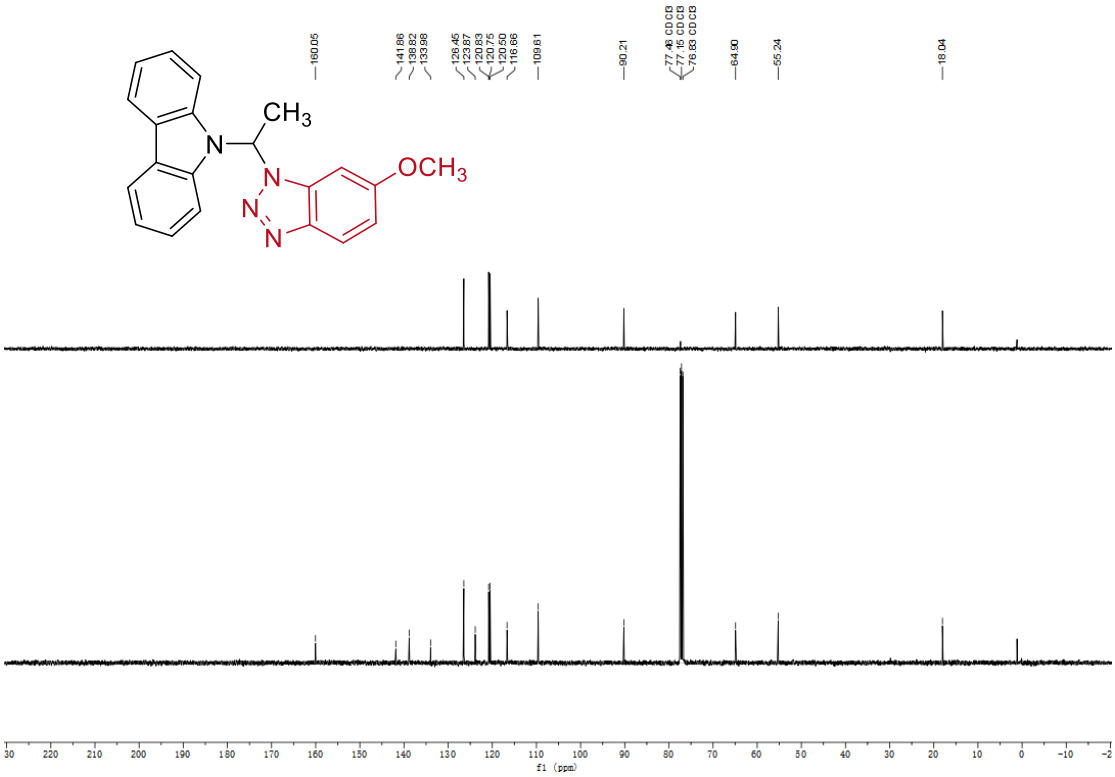
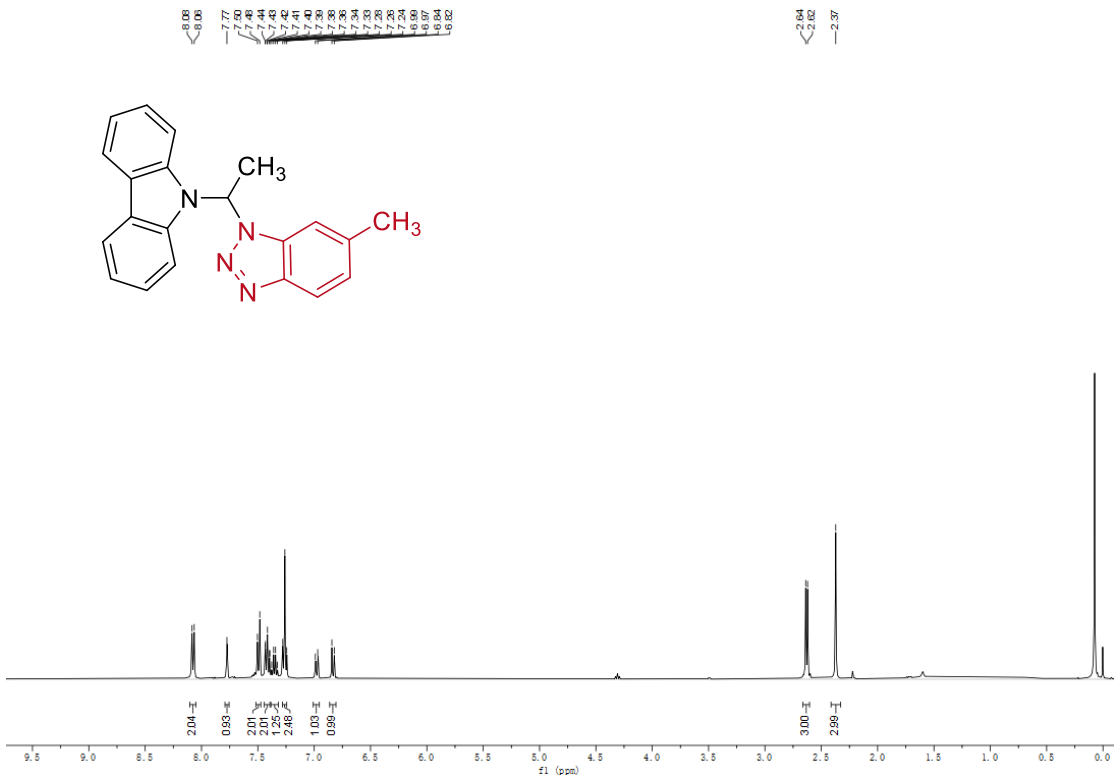


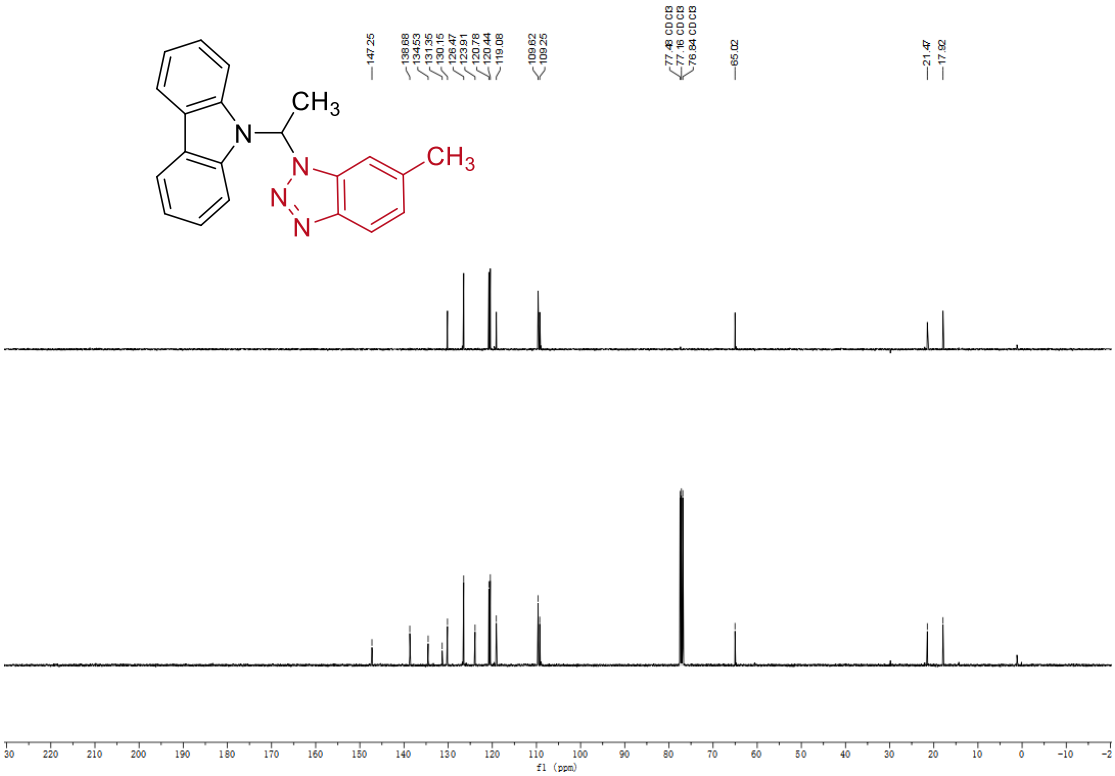
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4c**



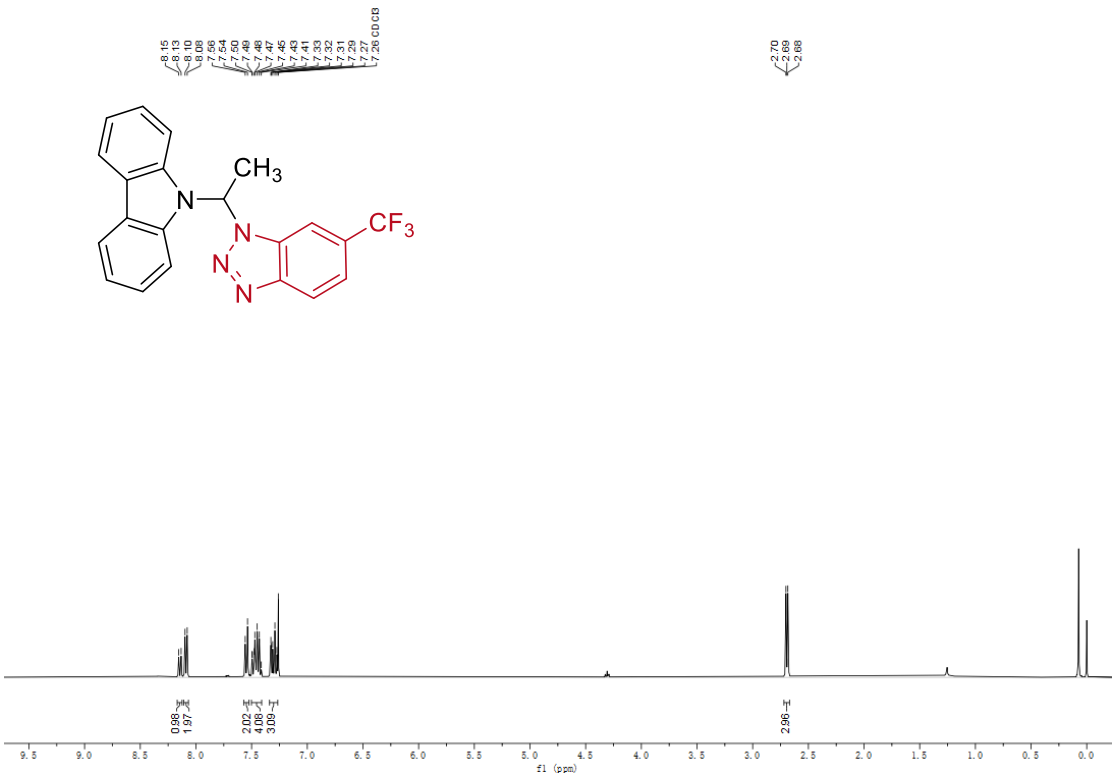
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 4c**



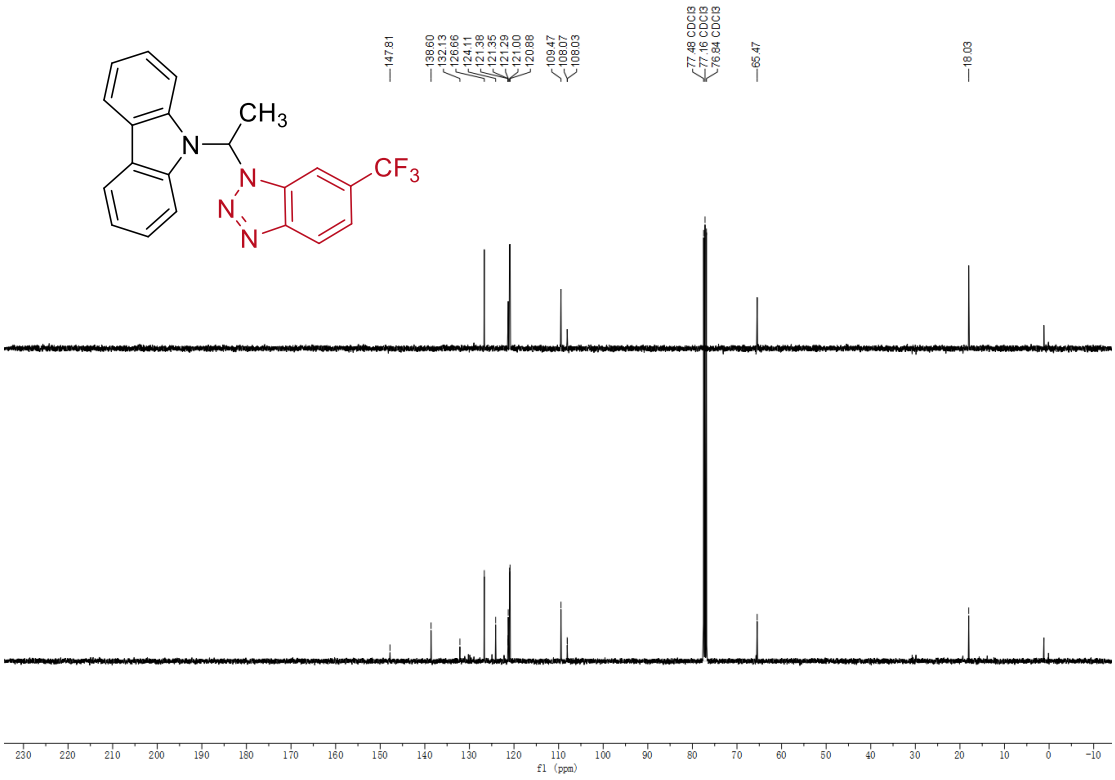
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4d**



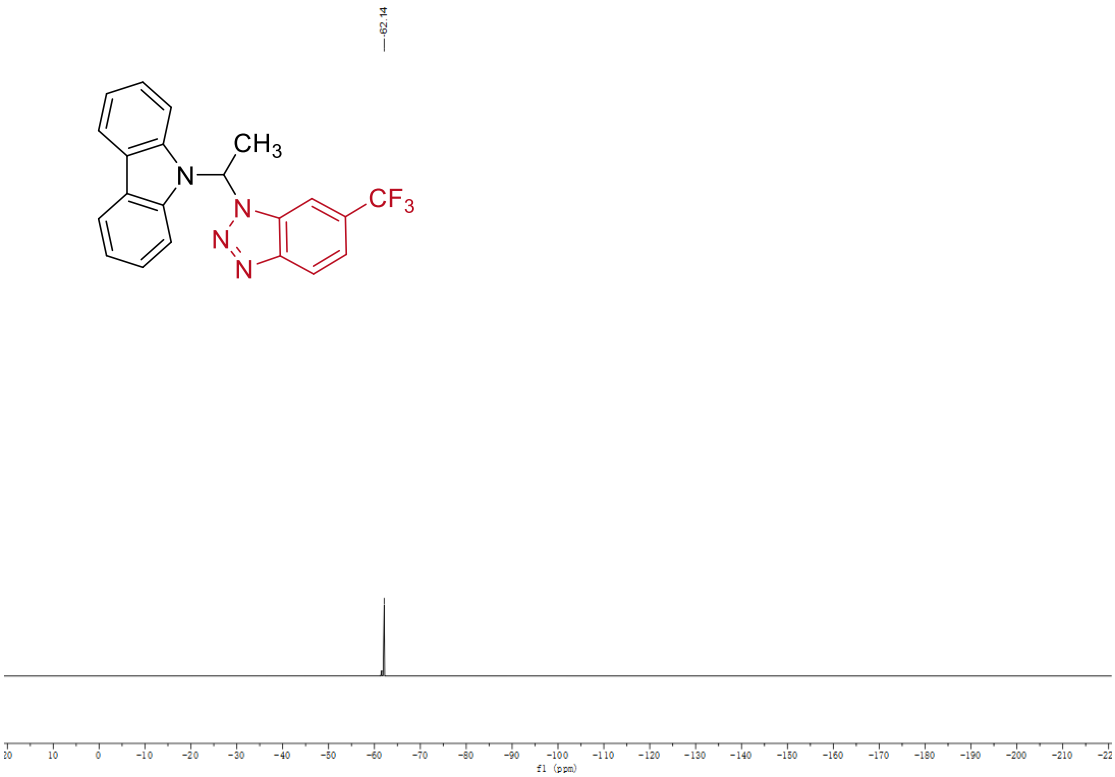
^{13}C-NMR (100MHz, $CDCl_3$) **spectrum of 4d**



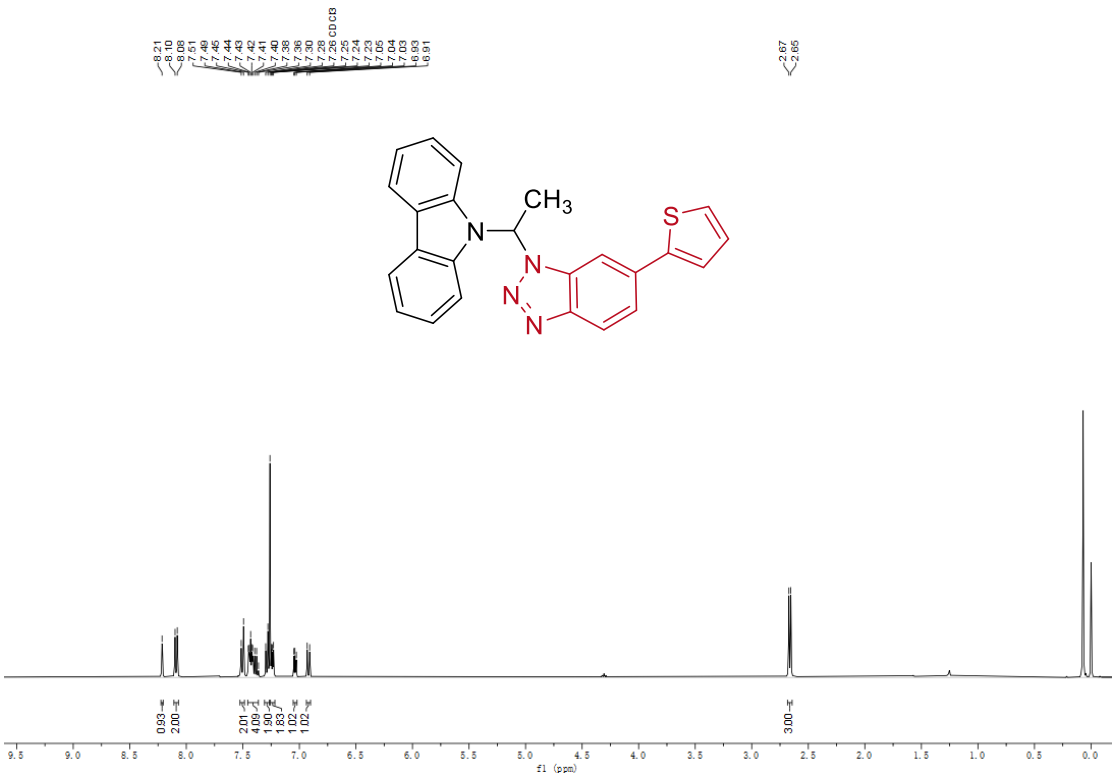
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4e**



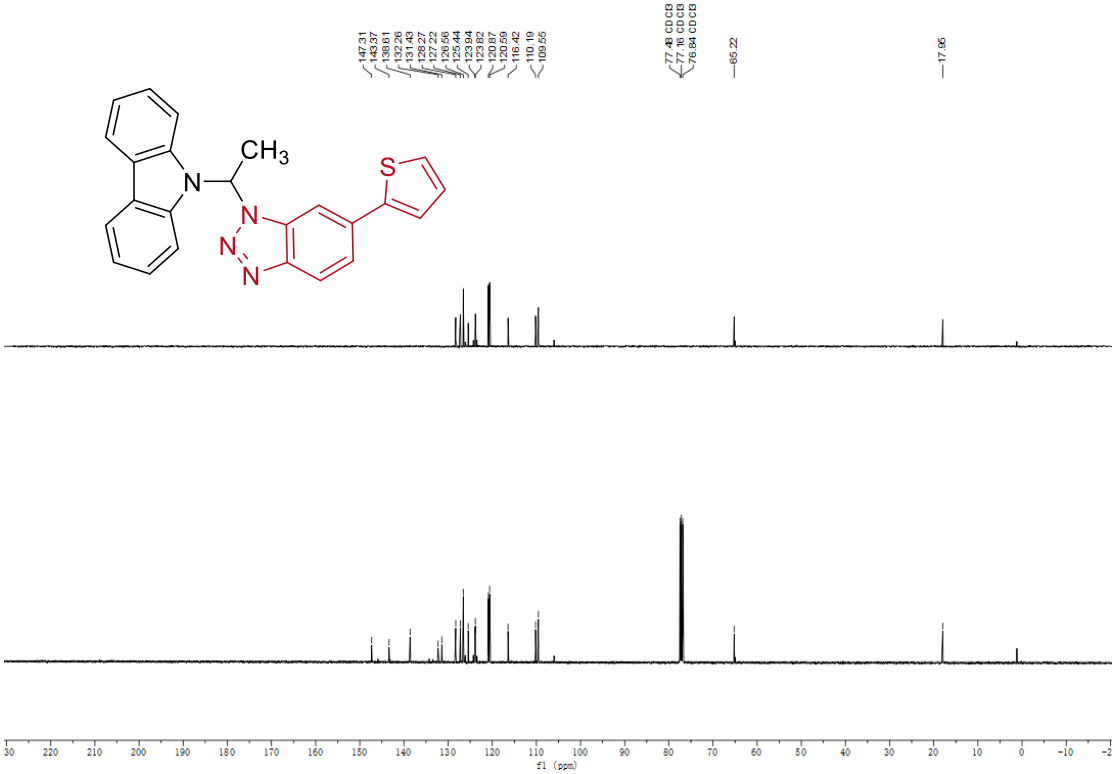
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 4e**



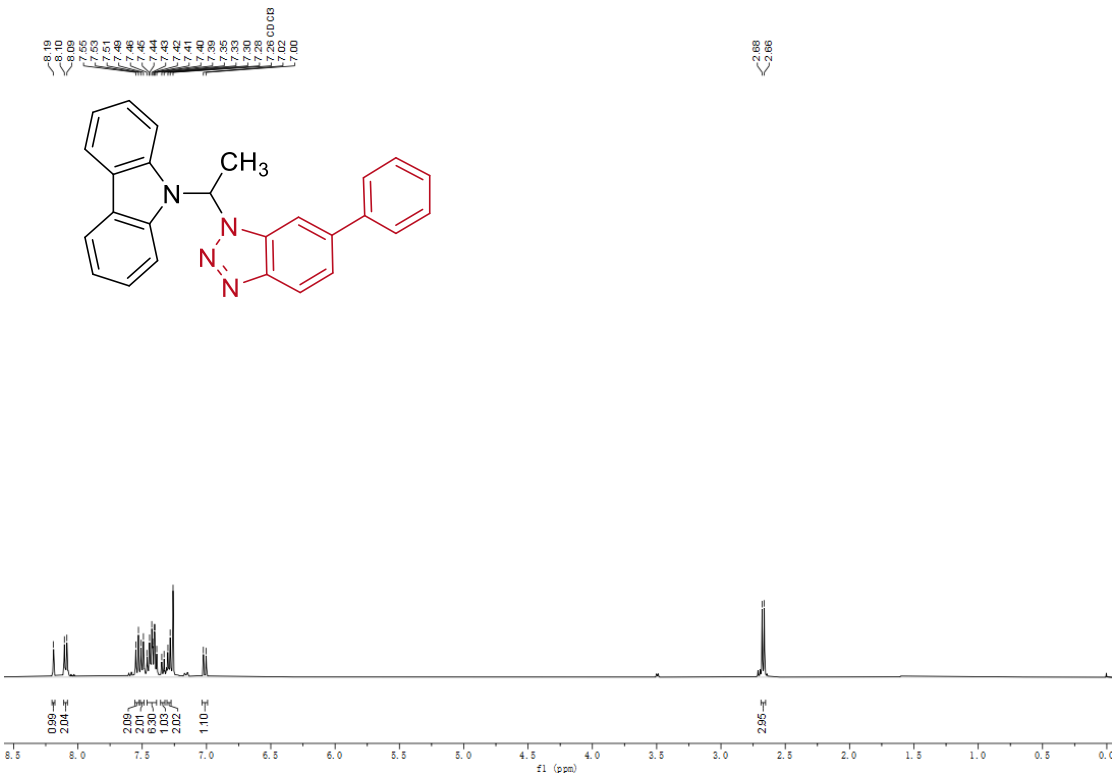
^{19}F-NMR (376.5 MHz, $CDCl_3$) **spectrum of 4e**



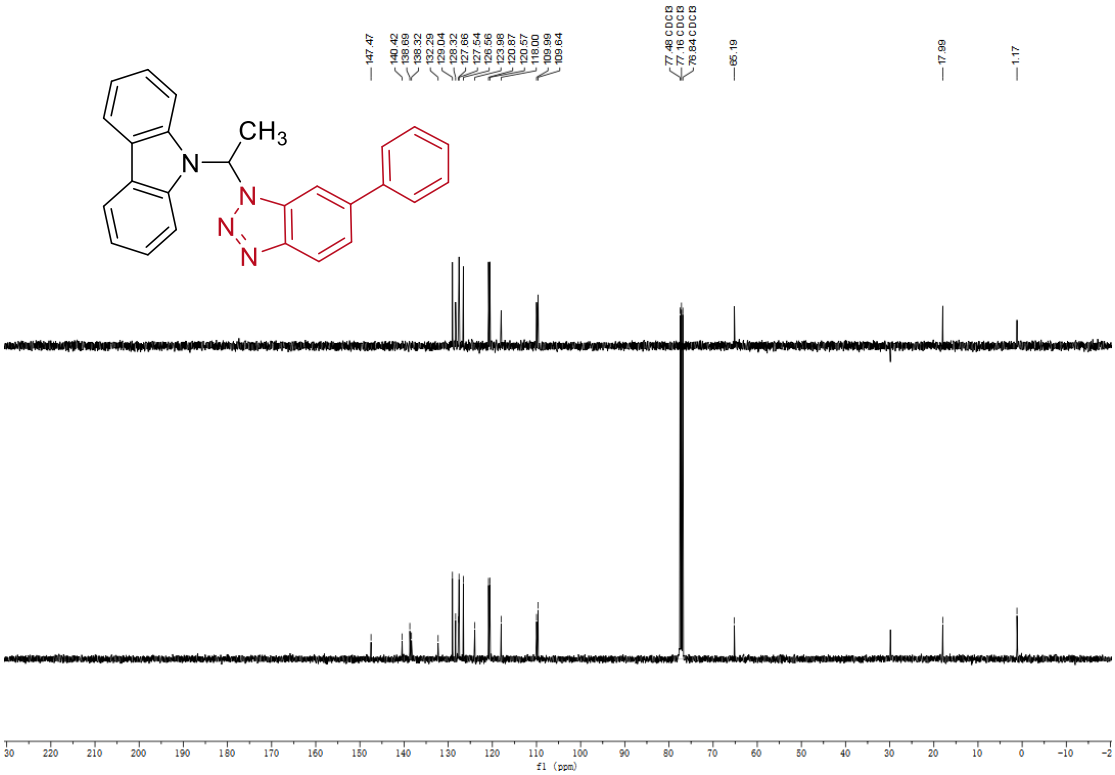
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4f**



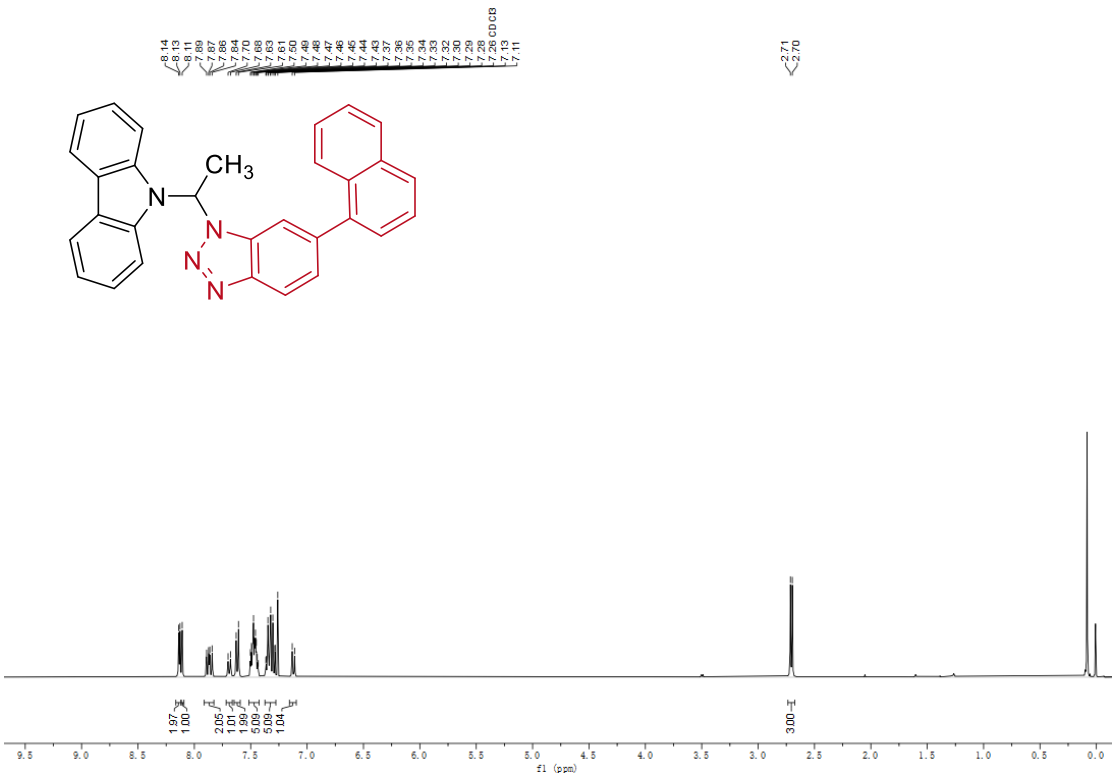
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 4f**



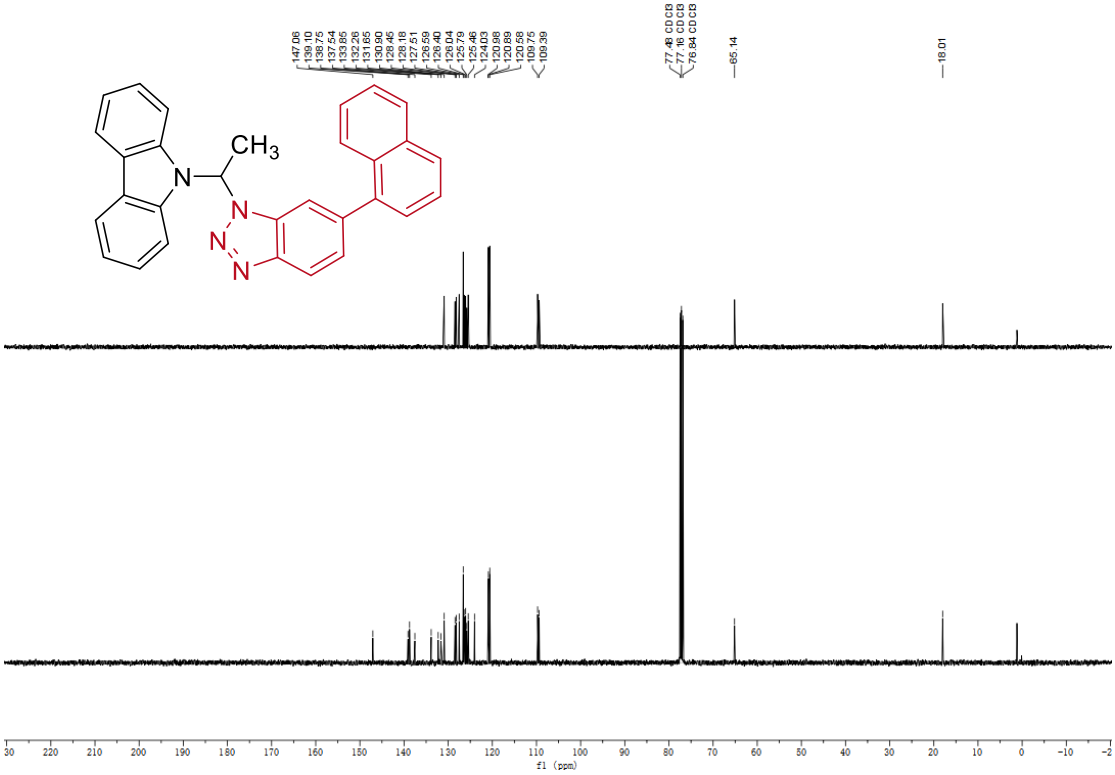
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4g**



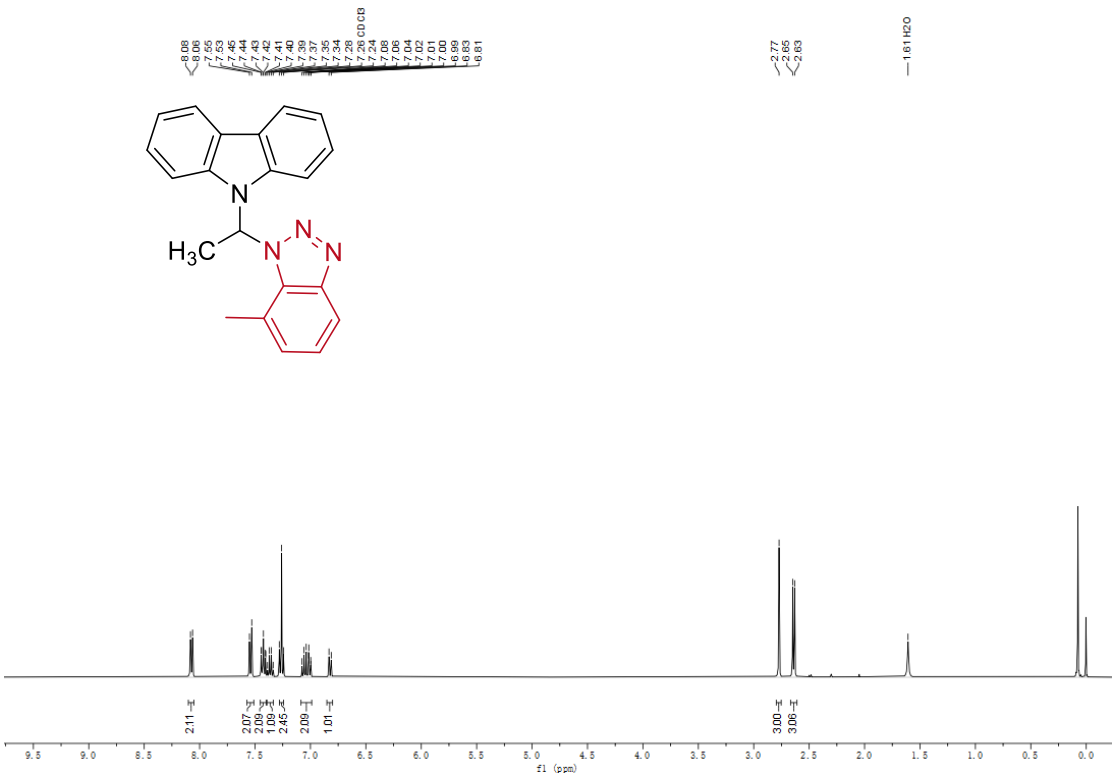
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 4g**



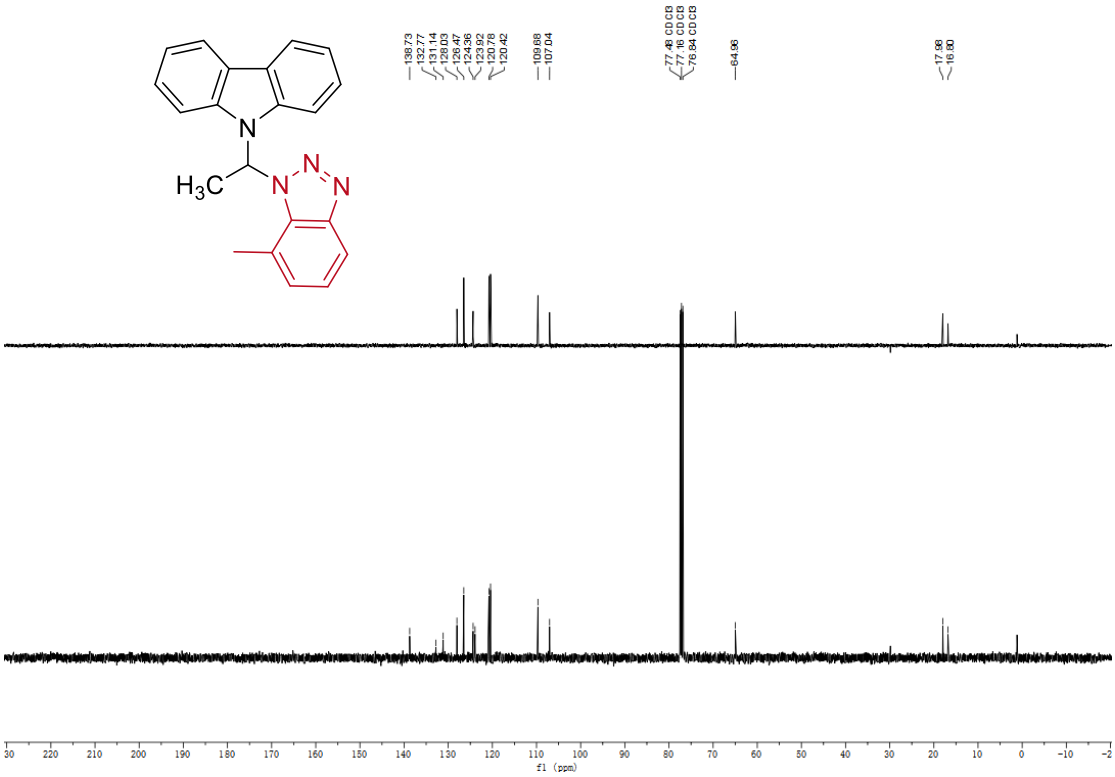
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4h**



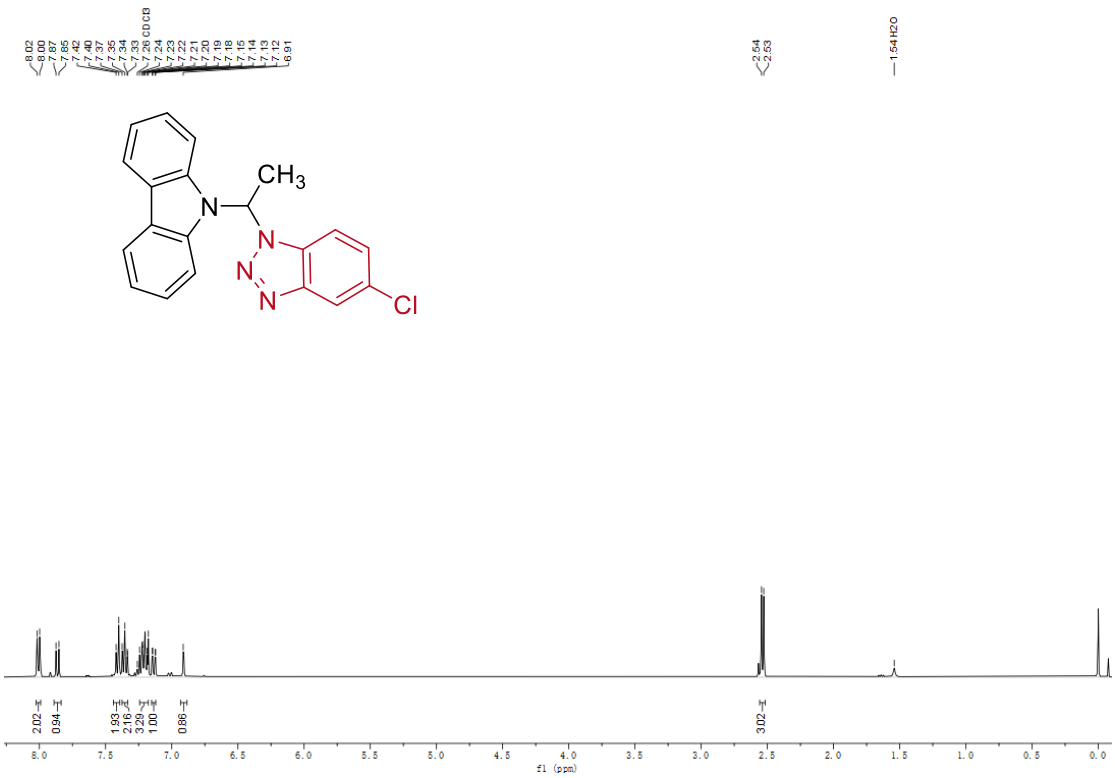
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 4h**



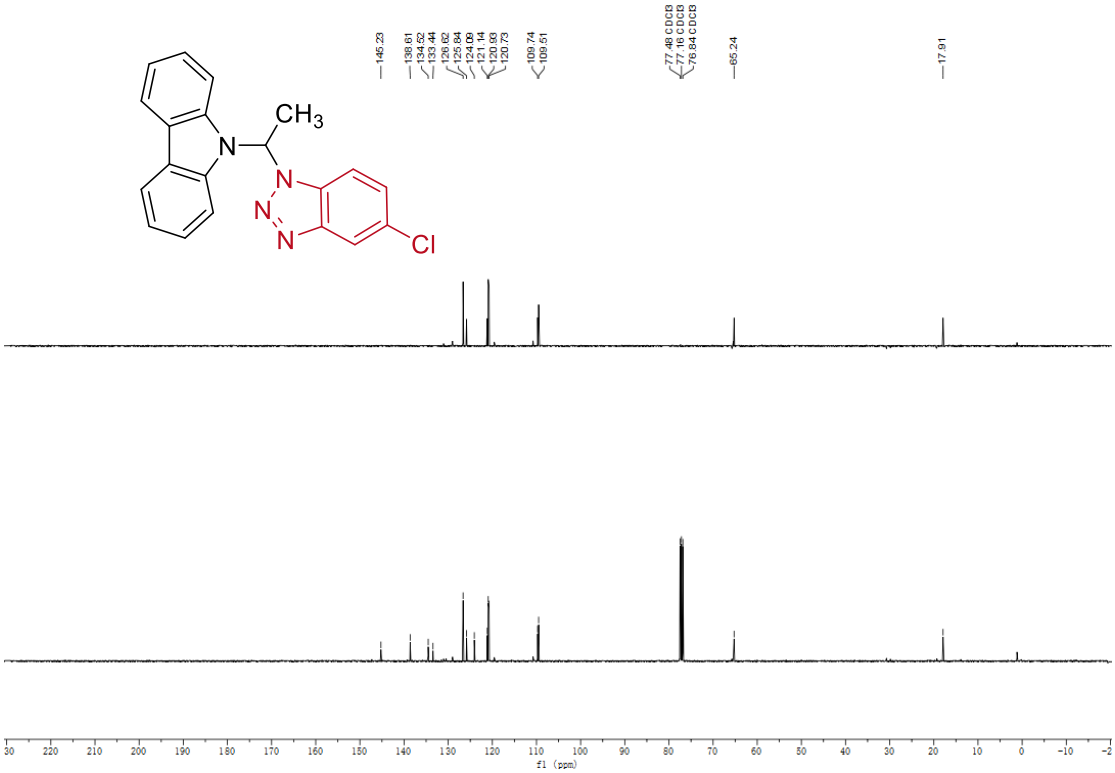
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4i**



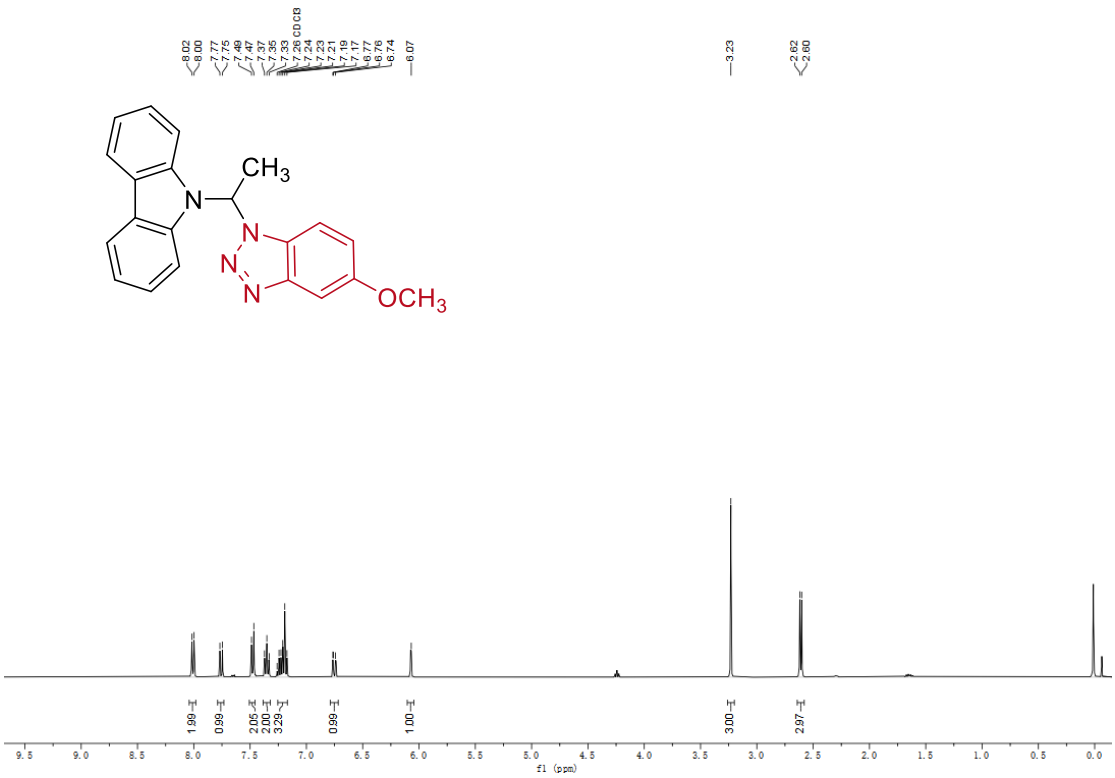
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 4i**



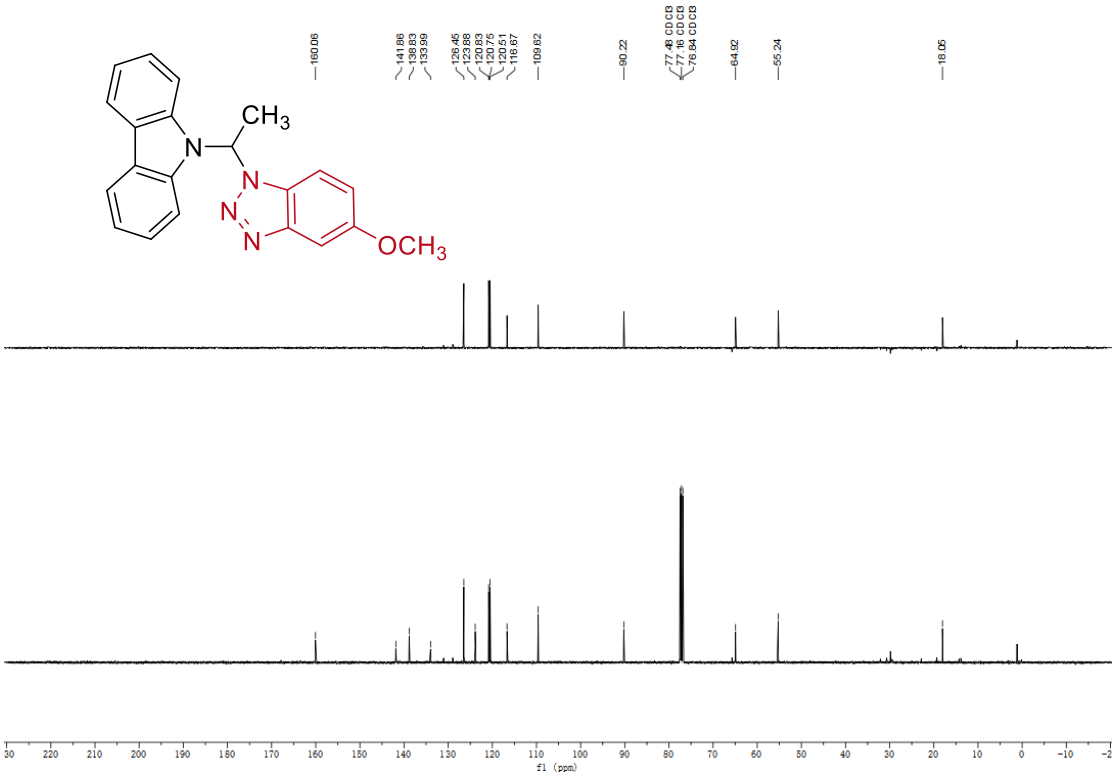
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4j**



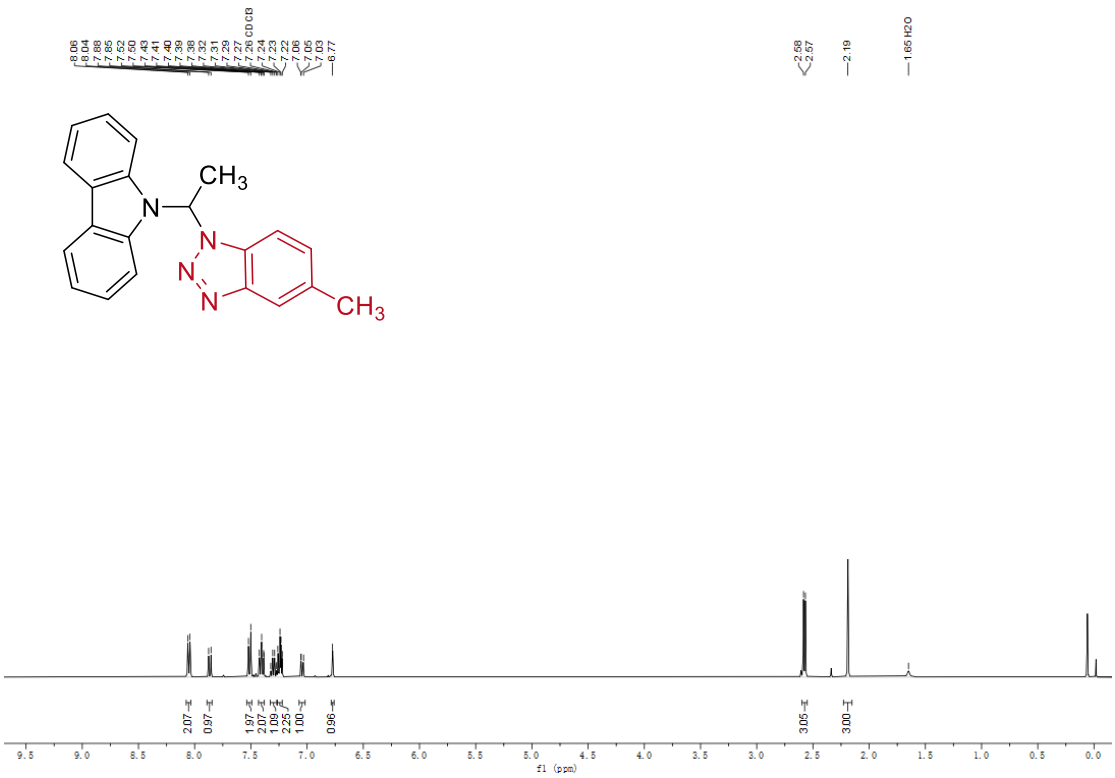
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 4j**



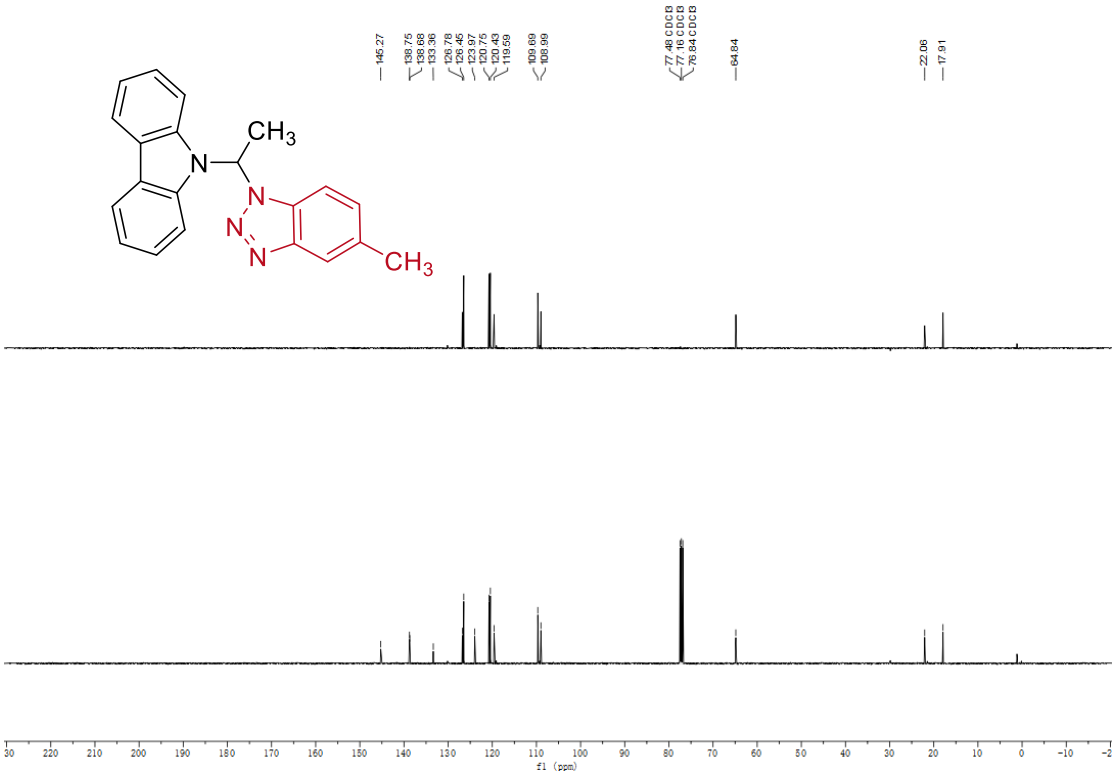
[1]H-NMR (400 MHz, $CDCl_3$) **spectrum of 4k**



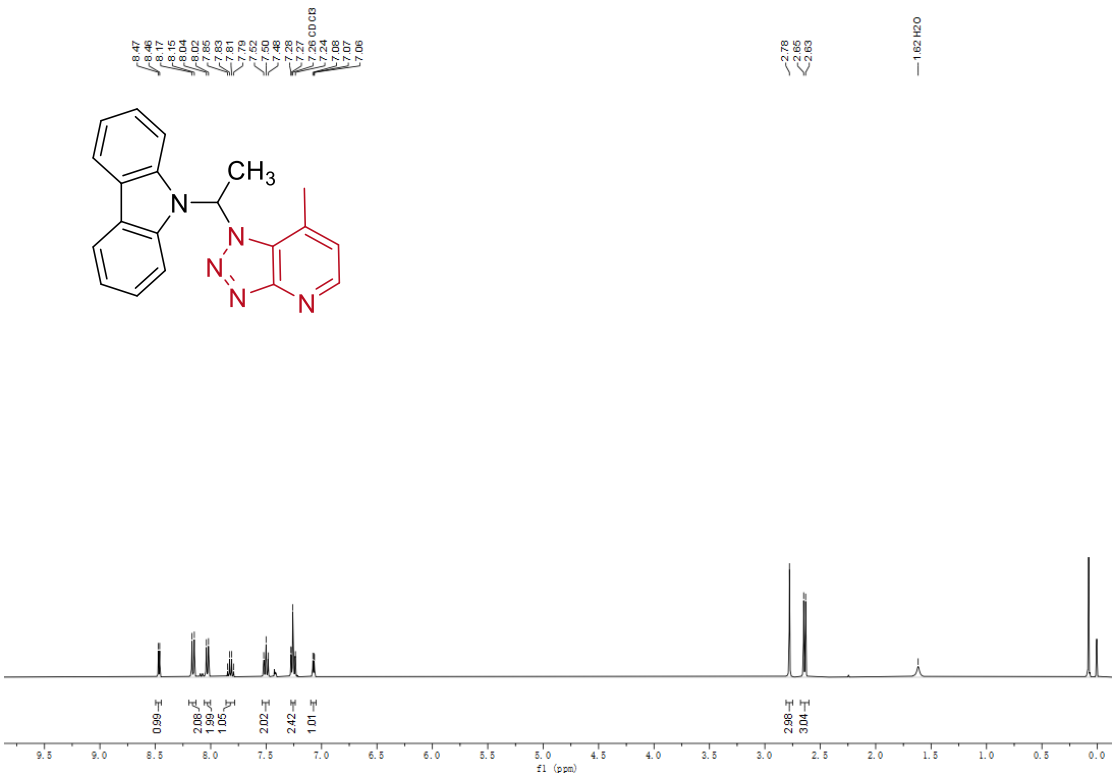
[13]C-NMR (100 MHz, $CDCl_3$) **spectrum of 4k**



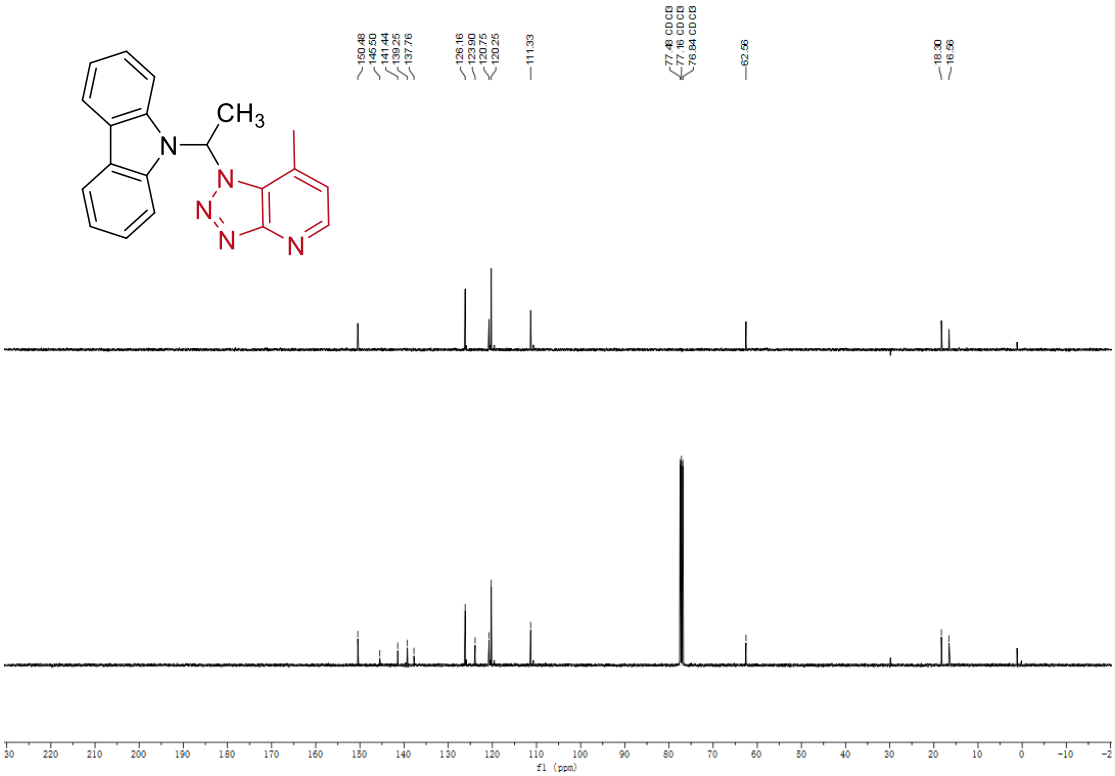
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4l**



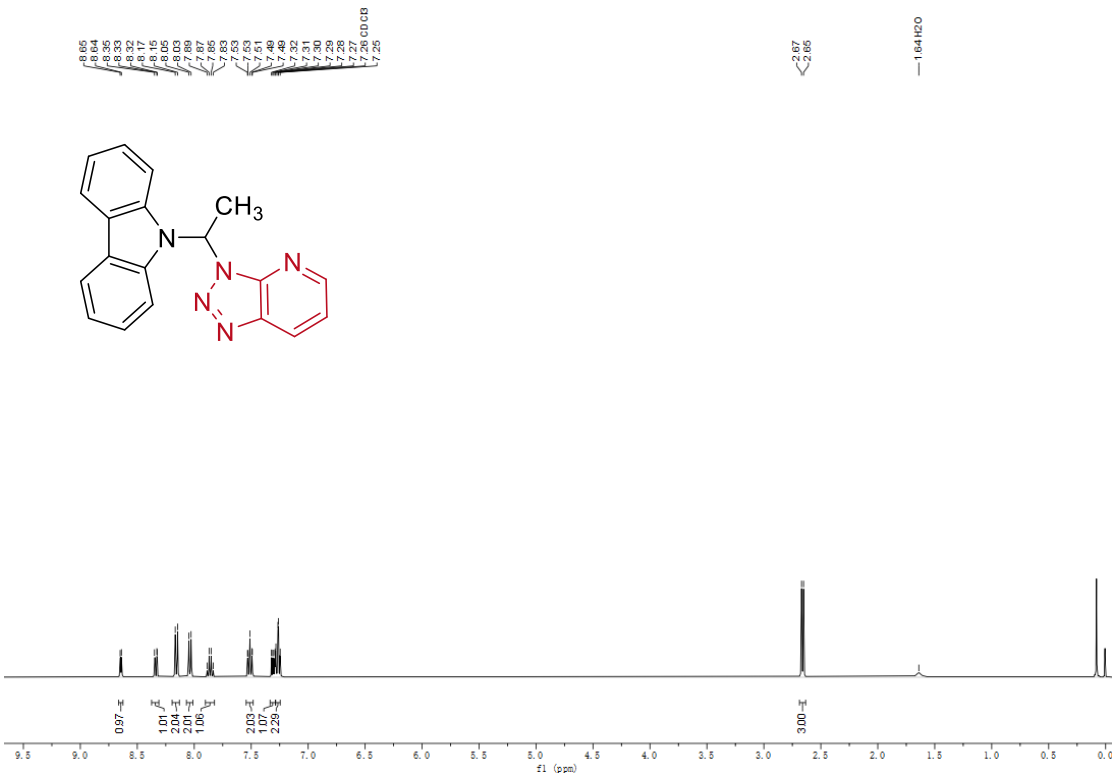
^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 4l**



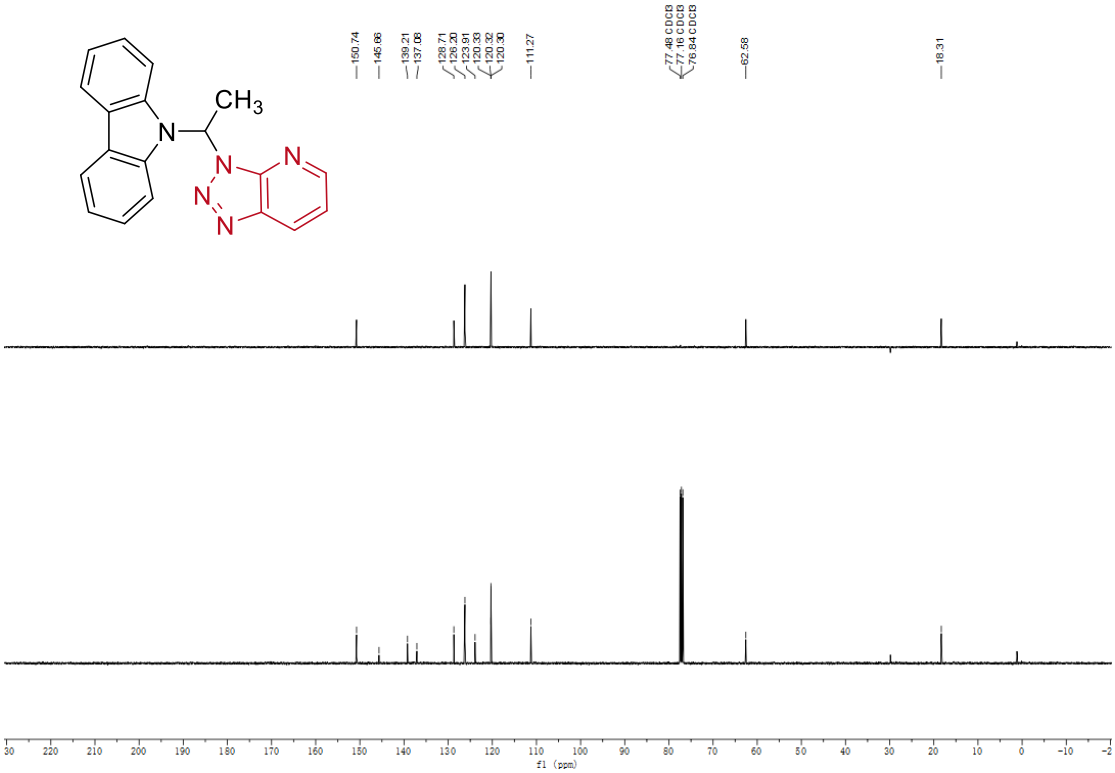
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4m**



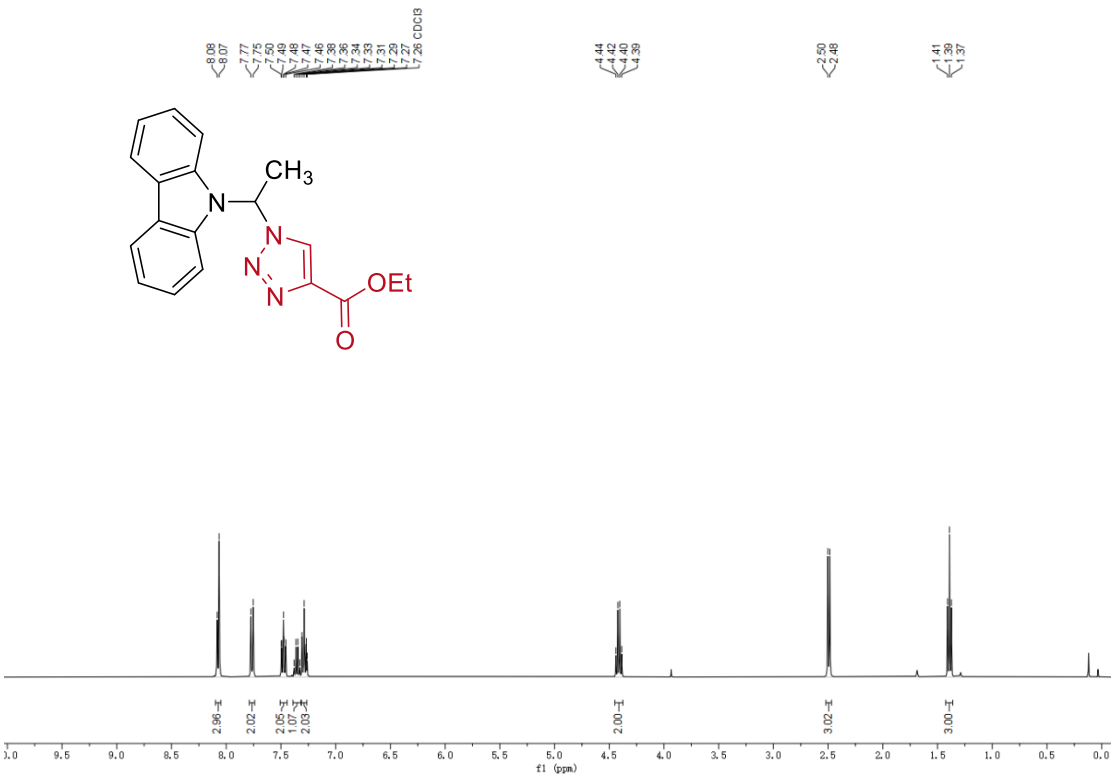
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4m**



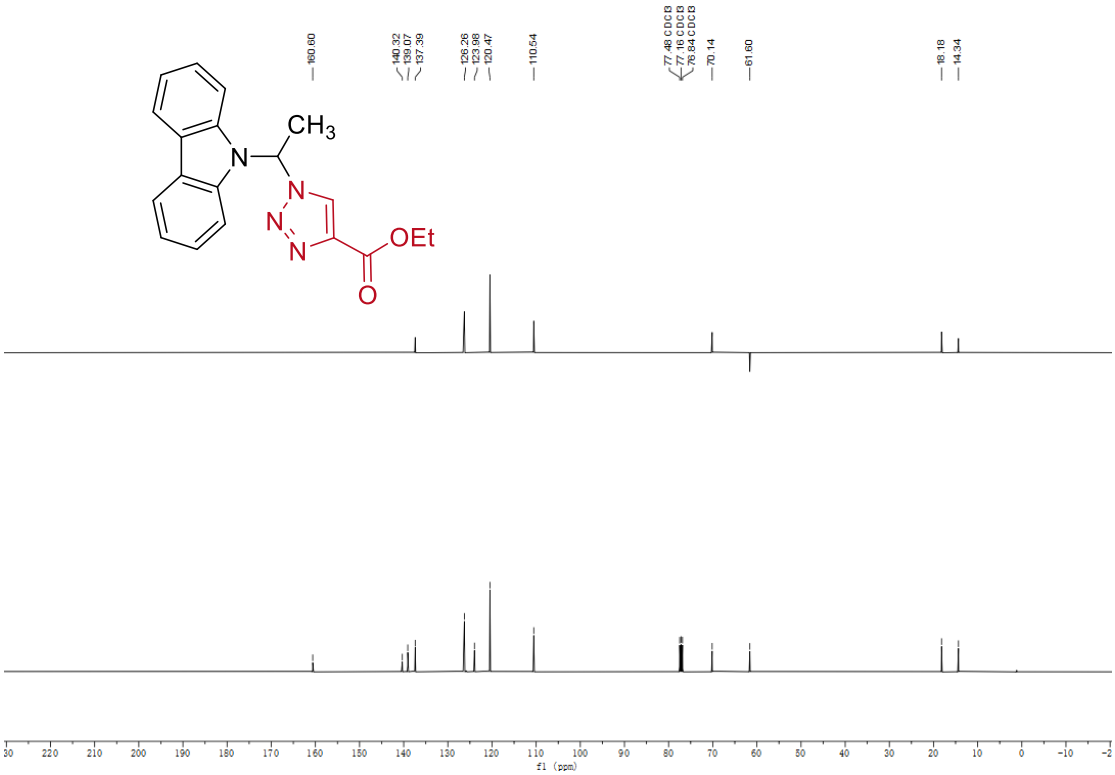
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4n**



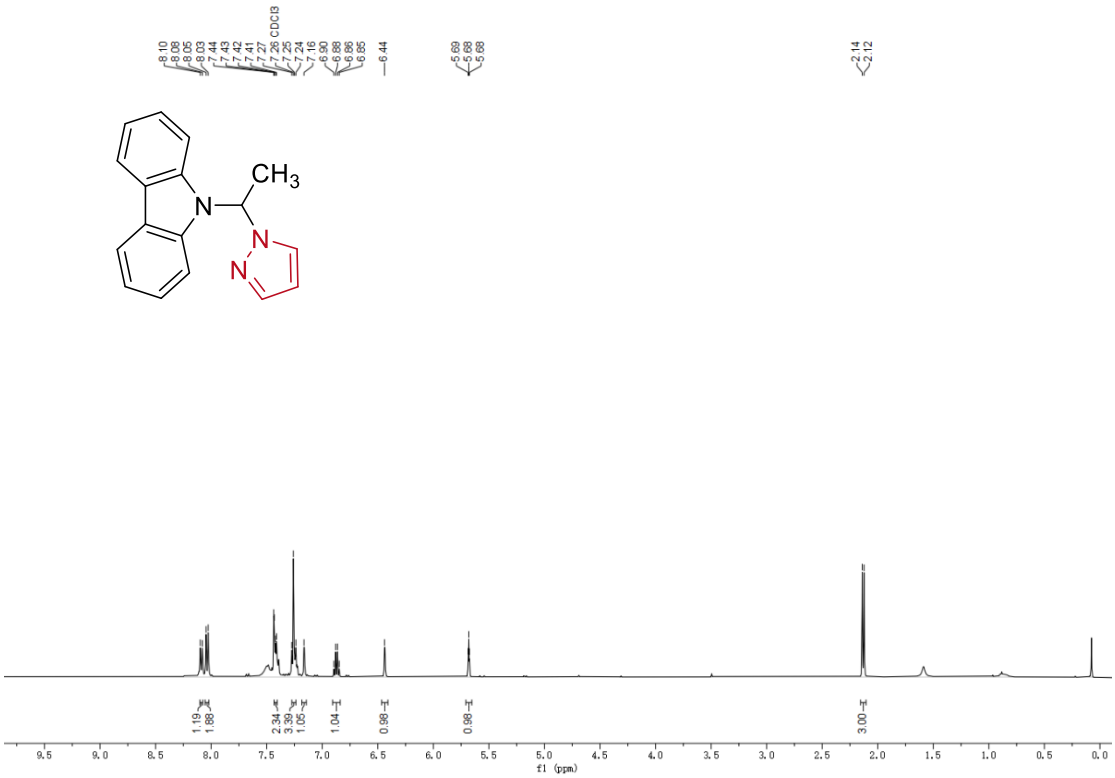
^{13}C-NMR (100MHz, $CDCl_3$) **spectrum of 4n**



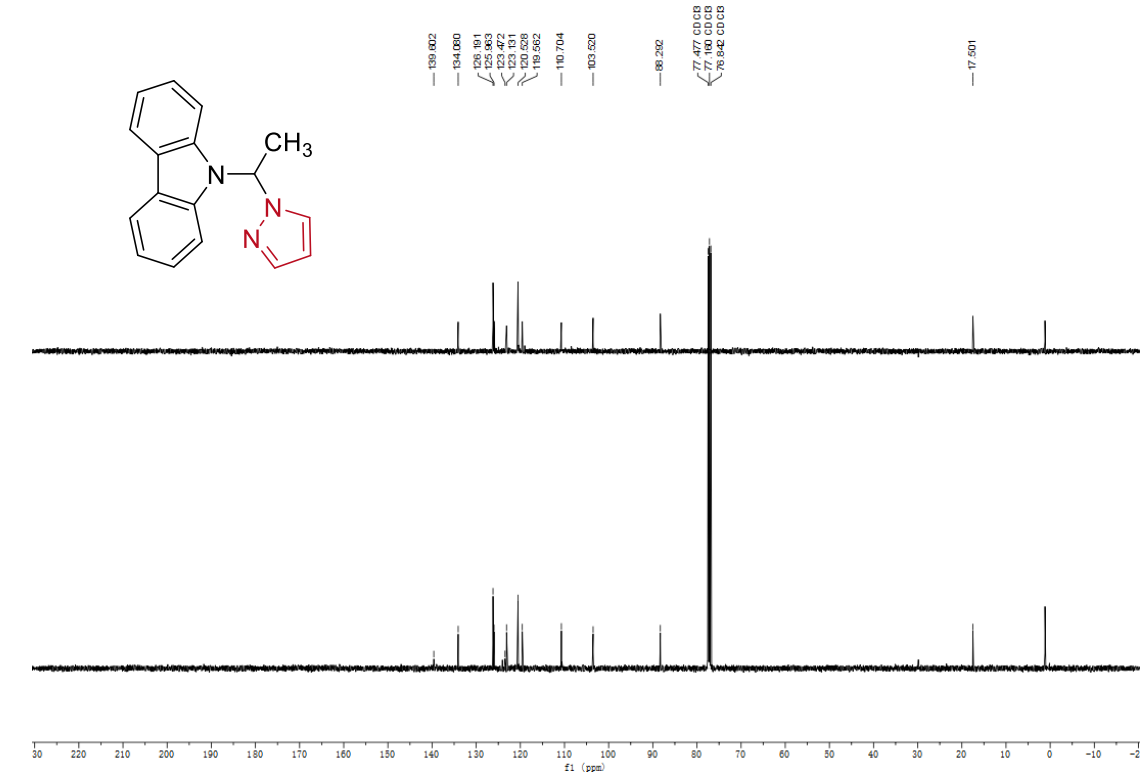
^{1}H-NMR (400 MHz, $CDCl_3$) **spectrum of 4o**



^{13}C-NMR (100 MHz, $CDCl_3$) **spectrum of 4o**



[1]H-NMR (400 MHz, $CDCl_3$) **spectrum of 4p**



[13]C-NMR (100 MHz, $CDCl_3$) **spectrum of 4p**

9. References

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