

Supplementary Information

Synthesis of 1-Azido-3-heteroaryl Bicyclo[1.1.1]pentanes via Azidoheteroarylation of [1.1.1]Propellane

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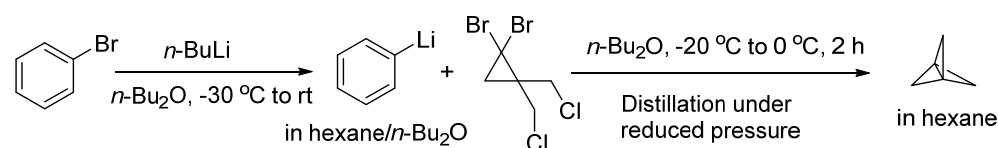
1. General information

Commercially available reagents and solvents were used without any purification. The progress of the reactions was monitored by TLC with silica gel plates, and the visualization was carried out under UV light (254 nm). Melting points were determined using a Büchi B-540 capillary melting point apparatus. NMR spectra were recorded using Varian Mercury Plus 400 MHz or Bruker Avance III 600 MHz spectrometers. Chemical shifts of ^1H NMR were reported relative to the solvent signal (CDCl_3 : $\delta = 7.26$ ppm; $\text{DMSO}-d_6$: $\delta = 2.50$ ppm). Chemical shifts of ^{13}C NMR were reported relative to the solvent signal (CDCl_3 : $\delta = 77.00$ ppm; $\text{DMSO}-d_6$: $\delta = 39.50$ ppm). HRMS spectra were recorded on an electrospray ionization quadrupole time-of-flight (ESI-Q-TOF) mass spectrometer. Column chromatography was performed on silica gel (300-400 mesh).

2. Synthesis of substrates 1

The substrates (**1a-1i**, **1m-1x**),^[1] (**1j-1l**, **1y**, **1z**, **1ab**),^[2] **1aa**,^[3] were prepared following the literature procedure, and the NMR data of all these compounds were compared with the corresponding reported data.

3. Preparation of the solution of [1.1.1]propellane in hexane



a) Preparation of phenyl lithium in hexane/ $n\text{-Bu}_2\text{O}$

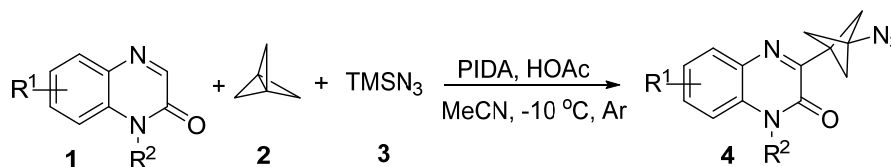
A 100 ml three-neck round bottom flask equipped with a magnetic stirring bar was charged with bromobenzene (100mmol, 1.0 equiv.). After the flask was evacuated and backfilled with argon three times, anhydrous dibutyl ether (20 mL) was added. Then the flask was cooled down to $-30\text{ }^\circ\text{C}$ and $n\text{-BuLi}$ (100 mmol, 1.0 equiv., 2.5 M in hexane) was added dropwise via addition funnel. After the addition

was complete, the mixture was allowed to warm to rt, and stirred at rt for 1 h. The mixture was used in the next step.

b) Preparation of the solution of [1.1.1]propellane in hexane

A solution of the above prepared Phenyl lithium in hexane/*n*-Bu₂O (65 mL) was added dropwise to a suspension of 1,1-dibromo-2,2-bis(chloromethyl)cyclopropane (45.0 mmol) in anhydrous dibutyl ether (20 mL) via addition funnel under argon at -20 °C. After the addition was complete, the mixture was allowed to warm to 0 °C and stirred for 2 h, then the addition funnel was swapped out for a distillation head with attached 100 mL round bottom flask in a -78 °C bath (dry ice/acetone). A vacuum was slowly applied to the system and the distillate collected, while maintaining the reaction/distillation flask below 0 °C. Approximately 35 mL of distillate was collected. The concentration can be checked by NMR by taking a 200 uL aliquot of the stock solution and determining the ratio of [1.1.1]propellane to an added dibromomethane as standard (typically concentrations are 0.5-0.7 M with this protocol).

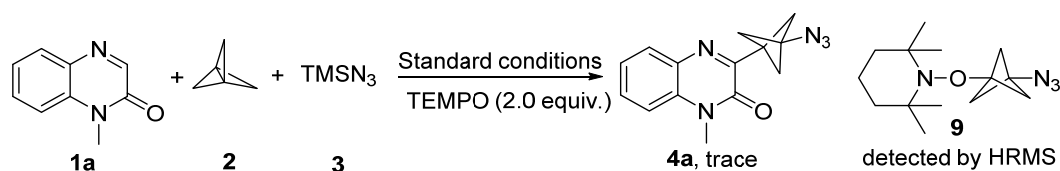
4. General method



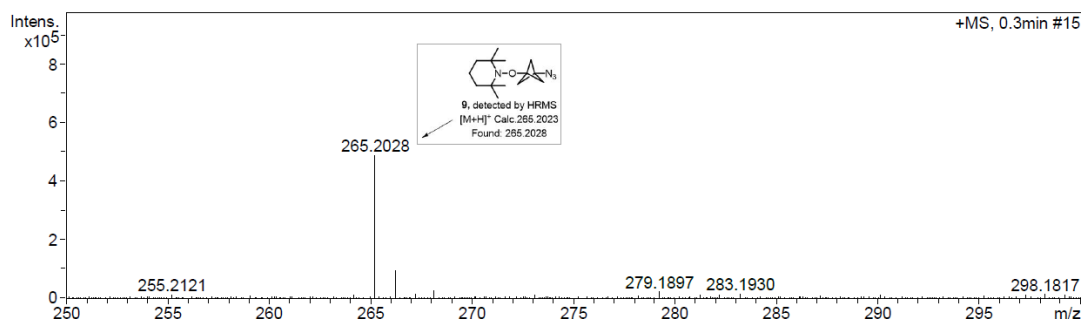
An oven-dried 25 mL Schlenk tube fitted with a magnetic stirring bar was charged with **1** (0.3 mmol, 1.0 equiv.), PIDA (0.9 mmol, 3.0 equiv.), and HOAc (0.6 mmol, 2.0 equiv.) in anhydrous MeCN (1.5 mL) under argon atmosphere. The mixture was cooled down to -10 °C and [1.1.1]propellane **2** (0.45mmol, 1.5 equiv.) was added, then TMSN₃ **3** (0.9 mmol, 3.0 equiv.) was added dropwise under stirring. The reaction mixture was stirred at -10 °C until consumption of starting material (monitored by TLC). After the reaction was complete, it was quenched with saturated NaHCO₃ solution (5 mL) at room temperature, and then extracted with ethyl acetate (10 mL × 3). The organic layers were combined, washed with brine, dried over Na₂SO₄ filtered, and then concentrated in vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate to afford the desired product **4**.

5. Control experiments

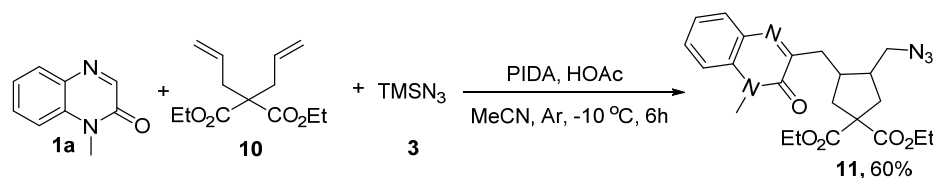
a) Radical inhibiting experiment



An oven-dried 25 mL Schlenk tube was charged with **1a** (0.3 mmol, 1.0 equiv.), PIDA (0.9 mmol, 3.0 equiv.), TEMPO (0.6 mmol, 2.0 equiv.), and HOAc (0.6 mmol, 2.0 equiv.) in anhydrous MeCN (1.5 mL) under argon atmosphere. The mixture was cooled down to -10 °C and [1.1.1]propellane **2** (0.45 mmol, 1.5 equiv.) was added, then TMSN₃ **3** (0.9 mmol, 3.0 equiv.) was added dropwise under stirring. The reaction mixture was stirred at -10 °C under argon atmosphere for 6 h. Only trace amount of product was detected and the corresponding adducts **9** was detected by the HRMS. HRMS (ESI) m/z: calcd for C₁₄H₂₅N₄O [M+H]⁺ 265.2023, found: 265.2028.



b) Radical clock cyclization experiment



An oven-dried 25 mL Schlenk tube was charged with **1a** (0.3 mmol, 1.0 equiv.), PIDA (0.9 mmol, 3.0 equiv.), HOAc (0.6 mmol, 2.0 equiv.) and diethyl 2,2-diallylmalonate **10** (0.6 mmol, 2.0 equiv.) in anhydrous MeCN (1.5 mL) under argon atmosphere. The mixture was cooled down to -10 °C then

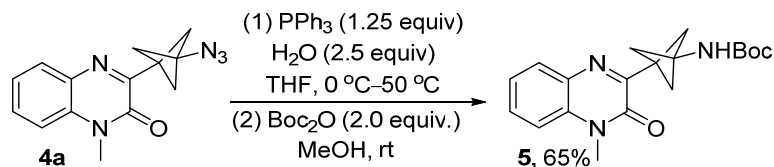
TMSN₃ **3** (0.9 mmol, 3.0 equiv.) was added dropwise under stirring. The reaction mixture was stirred at -10 °C for 6 h. After the reaction was complete, it was quenched with saturated NaHCO₃ solution (5 mL) at room temperature, and then extracted with ethyl acetate (10 mL × 3). The organic layers were combined, washed with brine, dried over Na₂SO₄ filtered, and then concentrated in vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate to afford the desired product **11** as a yellow liquid (79 mg, 60%); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.50(m, 1H), 7.39 – 7.27 (m, 2H), 4.26 – 4.10 (m, 4H), 3.70 (s, 3H), 3.55 – 3.45 (m, 1H), 3.32 – 3.20 (m, 1H), 3.09 – 2.98 (m, 1H), 2.96 – 2.78 (m, 2H), 2.60 – 2.42 (m, 3H), 2.34 – 2.24 (m, 1H), 2.18 – 2.08 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 172.4, 172.4, 159.0, 154.7, 133.0, 132.6, 129.8, 129.8, 123.6, 113.6, 61.6, 61.6, 58.6, 51.7, 40.9, 38.9, 38.3, 37.1, 33.6, 29.1, 14.0. The spectra data matched those previously reported.^[4]

6. Gram-scale synthesis and derivatization of **4a**

a) Gram-scale synthesis of **4a**

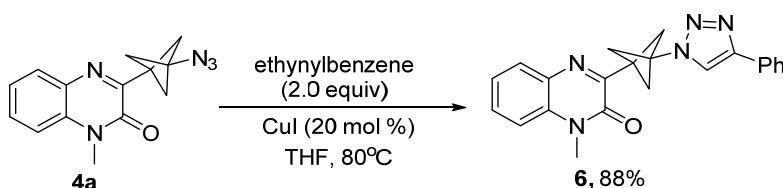
An oven-dried 100 mL two-necked flask equipped with a magnetic stir bar was charged with **1a** (6.0 mmol, 1.0 equiv.), PIDA (18 mmol, 3.0 equiv.), and HOAc (12 mmol, 2.0 equiv.) in anhydrous MeCN (30 mL) under argon atmosphere. The mixture was cooled down to -10 °C and [1.1.1]propellane **2** (9.0 mmol, 1.5 equiv.) was added, then TMSN₃ **3** (18 mmol, 3.0 equiv.) was added dropwise under stirring. The reaction mixture was stirred at -10 °C under argon atmosphere for 6 h. After the reaction was complete, it was quenched with saturated NaHCO₃ solution (15 mL) at room temperature, and then extracted with ethyl acetate (30 mL × 3). The organic layers were combined, washed with brine, dried over Na₂SO₄ filtered, and then concentrated in vacuum. The residue was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate to afford the desired product **4a** as a yellow solid (0.995 g, 62%).

b) Synthesis of tert-butyl(3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl) bicyclo[1.1.1]pentan-1-yl) carbamate **5^[5]**



To a 50 mL Schlenk tube equipped with a stir bar were added **4a** (0.3 mmol, 1.0 equiv.), THF (3 mL) and H₂O (0.75 mmol, 2.5 equiv.). After the tube was evacuated and backfilled with argon three times, a solution of PPh₃ (0.38 mmol, 1.25 equiv.) in THF (1.5 mL) was added dropwise at 0 °C. The mixture was warmed up to 50 °C and stirred for 5 h. The solvent was removed under reduced pressure, then MeOH (3 mL) was added, followed by addition of Boc₂O (0.6 mmol, 2.0 equiv.). The mixture was stirred at rt for 12 h, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v) to give **5** as a yellow liquid (67 mg, 65%); ¹H NMR (600 MHz, Chloroform-*d*) δ 7.84 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.35 – 7.30 (m, 1H), 7.29 – 7.25 (m, 1H), 5.04 (br, 1H), 3.66 (s, 3H), 2.52 (s, 6H), 1.48 (s, 9H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 156.2, 154.6, 133.4, 132.8, 130.1, 130.0, 123.5, 113.5, 54.6, 46.5, 28.6, 28.4. HRMS (ESI) *m/z*: calcd for C₁₉H₂₃N₃NaO₃ [M+Na]⁺ 364.1632, found: 364.1636.

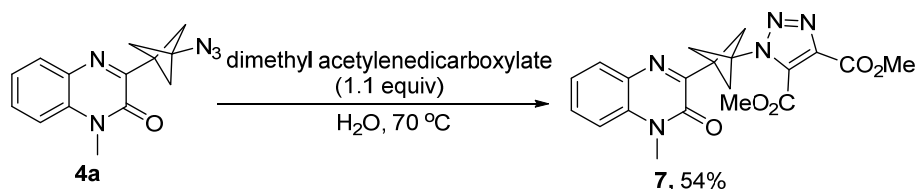
c) Synthesis of 1-methyl-3-(3-(4-phenyl-1H-1,2,3-triazol-1-yl)bicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1H)-one **6^[6]**



A 25 mL seal tube equipped with a magnetic stirring bar was charged with **4a** (0.3 mmol, 1.0 equiv.), ethynylbenzene (0.6 mmol, 2.0 equiv.), CuI (0.06 mmol, 20 mol %) and THF (3 mL). The mixture was stirred at 80 °C for 12 h. Then the mixture was cooled to room temperature, and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel, eluting with petroleum ether/ethyl acetate 2:1 (v/v) to give **6** as a white solid (97 mg, 88%); M.p.: 235–237 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.92 – 7.79 (m, 4H), 7.62 – 7.54 (m, 1H), 7.47 – 7.30 (m, 5H), 3.70 (s, 3H), 2.94 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 154.5, 154.4, 147.6, 133.4, 132.7, 130.5,

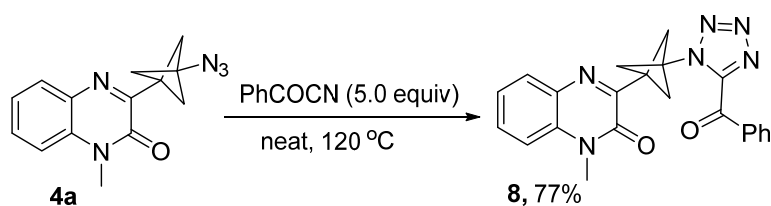
130.4, 130.2, 128.8, 128.1, 125.8, 123.8, 118.3, 113.7, 55.2, 50.4, 38.6, 28.7. HRMS (ESI) m/z : calcd for $C_{22}H_{20}N_5O$ $[M+H]^+$ 370.1662, found: 370.1663.

d) Synthesis of dimethyl-11-(3-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)bicyclo[1.1.1]pentan-1-yl)-1H-1,2,3-triazole-4,5-dicarboxylate **7^[7]**



A 10 mL seal tube was equipped with a magnetic stirring bar was charged with **4a** (0.3 mmol, 1.0 equiv.) and dimethyl acetylenedicarboxylate (0.33 mmol, 1.1 equiv.) in water (2.4 mL) was heated at $70\text{ }^\circ\text{C}$ with constant stirring for 1 h. The resulting mixture was cooled to room temperature and stirred further with ethyl acetate (5 mL). The organic layer was separated, dried over Na_2SO_4 and the resulting mixture was purified by flash chromatography on silica gel, eluting with petroleum ether/ethyl acetate 2:1 (v/v) to give **7** as a white solid (66 mg, 54%); M.p.: $217\text{--}219\text{ }^\circ\text{C}$; 1H NMR (400 MHz, Chloroform- d) δ 7.86 (d, $J = 7.9$ Hz, 1H), 7.62 – 7.54 (m, 1H), 7.41 – 7.29 (m, 2H), 4.04 (s, 3H), 3.96 (s, 3H), 3.69 (s, 3H), 2.95 (s, 6H). ^{13}C NMR (100 MHz, Chloroform- d) δ 160.3, 159.5, 154.4, 153.9, 138.4, 133.4, 132.7, 131.7, 130.6, 130.2, 123.8, 113.7, 55.6, 53.7, 52.6, 51.2, 39.0, 28.7. HRMS (ESI) m/z : calcd for $C_{20}H_{19}N_5NaO_5$ $[M+Na]^+$ 432.1278, found: 432.1297.

e) Synthesis of 3-(3-(5-benzoyl-1H-tetrazol-1-yl)bicyclo[1.1.1]pentan-1-yl)-1-methyl quinoxalin-2(1H)-one **8^[8]**

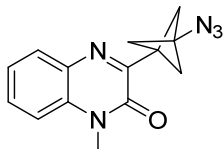


A 10 mL seal tube was equipped with a magnetic stirring bar was charged with **4a** (0.3 mmol, 1.0 equiv.) and benzoyl cyanide (1.5 mmol, 5.0 equiv.). The mixture was stirred at $120\text{ }^\circ\text{C}$ for 36 h. Then the mixture was cooled to room temperature and purified by flash column chromatography on silica gel, eluting with petroleum ether/ethyl acetate 5:1 (v/v) to give **8** as a yellow solid (92 mg, 77%); M.p.: $216\text{--}218\text{ }^\circ\text{C}$; 1H NMR (400 MHz, Chloroform- d) δ 8.30 (d, $J = 7.6$ Hz, 2H), 7.86 (d, $J = 7.6$ Hz, 1H), 7.75 – 7.68 (m, 1H), 7.61 – 7.53 (m, 3H), 7.39 – 7.30 (m, 2H), 3.70 (s, 3H), 3.02 (s, 6H). ^{13}C NMR (100 MHz, Chloroform- d) δ 181.5, 154.4, 154.0, 150.3, 135.2, 134.8, 133.4, 132.7, 130.9, 130.6, 130.2, 128.9, 123.8,

113.7, 55.6, 50.7, 39.4, 28.7. HRMS (ESI) m/z : calcd for $C_{22}H_{19}N_6O_2$ $[M+H]^+$ 399.1564, found: 399.1580.

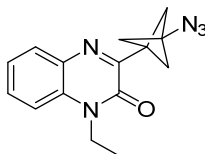
7. Characterization of products

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-methylquinoxalin-2(1H)-one (4a)



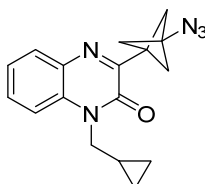
Eluent in chromatography: petroleum ether/ethyl acetate 50:1 to 20:1, **4a** was isolated as a yellow solid (55 mg, 69%); M.p.: 96-98 °C; 1H NMR (400 MHz, Chloroform-*d*) δ 7.84 (dd, J = 8.0, 0.8 Hz, 1H), 7.57 – 7.51 (m, 1H), 7.37 – 7.27 (m, 2H), 3.67 (s, 3H), 2.51 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.0, 154.4, 133.4, 132.7, 130.3, 130.1, 123.7, 113.6, 54.3, 52.0, 37.7, 28.7. HRMS (ESI) m/z : calcd for $C_{14}H_{14}N_5O$ $[M+H]^+$ 268.1193, found: 268.1189.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-ethylquinoxalin-2(1H)-one (4b)



Eluent in chromatography: petroleum ether/ethyl acetate 50:1 to 20:1, **4b** was isolated as a yellow solid (55 mg, 65%); M.p.: 62-64 °C; 1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, J = 8.0 Hz, 1H), 7.58 – 7.51 (m, 1H), 7.38 – 7.29 (m, 2H), 4.29 (q, J = 7.2 Hz, 2H), 2.52 (s, 6H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.1, 153.9, 133.0, 132.3, 130.3, 130.2, 123.5, 113.5, 54.3, 52.0, 37.7, 37.0, 12.4. HRMS (ESI) m/z : calcd for $C_{15}H_{15}N_5NaO$ $[M+Na]^+$ 304.1169, found: 304.1173.

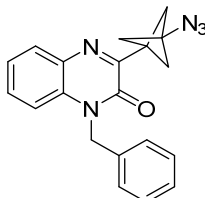
3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-(cyclopropylmethyl)quinoxalin-2(1H)-one (4c)



Eluent in chromatography: petroleum ether/ethyl acetate 100:1 to 50:1, **4c** was isolated as a yellow solid (61 mg, 67%); M.p.: 54-56 °C; 1H NMR (400 MHz, Chloroform-*d*) δ 7.85 (dd, J = 4.0, 0.8 Hz, 1H), 7.57

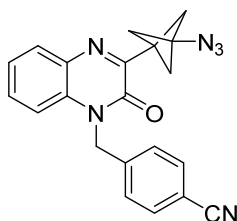
- 7.50 (m, 1H), 7.41 (d, $J = 8.4$ Hz, 1H), 7.36 – 7.30 (m, 1H), 4.15 (d, $J = 7.2$ Hz, 2H), 2.51 (s, 6H), 1.34 – 1.21 (m, 1H), 0.56 – 0.52 (m, 4H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.2, 154.4, 132.9, 132.8, 130.2, 130.1, 123.4, 113.9, 54.3, 52.0, 45.8, 37.7, 9.5, 4.2. HRMS (ESI) m/z : calcd for $\text{C}_{17}\text{H}_{17}\text{N}_5\text{NaO}$ $[\text{M}+\text{Na}]^+$ 330.1325, found: 330.1317.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-benzylquinoxalin-2(1H)-one (4d)



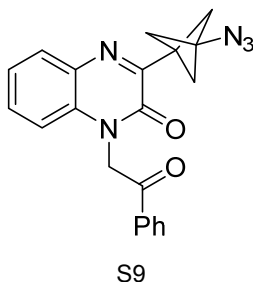
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4d** was isolated as a white solid (67 mg, 65%); M.p.: 85-87 °C; ^1H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, $J = 8.0, 1.4$ Hz, 1H), 7.45 – 7.37 (m, 1H), 7.36 – 7.18 (m, 7H), 5.46 (s, 2H), 2.55 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 155.2, 154.4, 135.0, 132.9, 132.7, 130.3, 130.1, 128.9, 127.7, 126.7, 123.7, 114.4, 54.3, 52.0, 45.5, 37.7. HRMS (ESI) m/z : calcd for $\text{C}_{20}\text{H}_{17}\text{N}_5\text{NaO}$ $[\text{M}+\text{Na}]^+$ 366.1325, found: 366.1337.

4-((3-(3-azidobicyclo[1.1.1]pentan-1-yl)-2-oxoquinoxalin-1(2H)-yl)methyl)benzonitrile (4e)



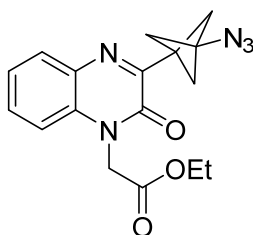
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4e** was isolated as a white solid (60 mg, 55%); M.p.: 163-165 °C; ^1H NMR (600 MHz, Chloroform-*d*) δ 7.88 (d, $J = 8.0$ Hz, 1H), 7.62 (d, $J = 7.8$ Hz, 2H), 7.46 – 7.41 (m, 1H), 7.37 – 7.30 (m, 3H), 7.09 (d, $J = 8.4$ Hz, 1H), 5.50 (s, 2H), 2.54 (s, 6H). ^{13}C NMR (150 MHz, Chloroform-*d*) δ 155.2, 154.3, 140.5, 133.0, 132.8, 132.4, 130.5, 130.5, 127.5, 124.1, 118.3, 113.8, 111.9, 54.4, 52.0, 45.3, 37.7. HRMS (ESI) m/z : calcd for $\text{C}_{21}\text{H}_{16}\text{N}_6\text{NaO}$ $[\text{M}+\text{Na}]^+$ 391.1278, found: 391.1289.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-(2-oxo-2-phenylethyl)quinoxalin-2(1H)-one (4f)



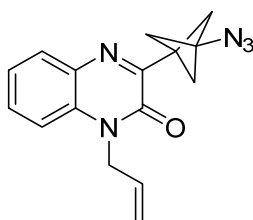
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4f** was isolated as a yellow liquid (38 mg, 35%); ¹H NMR (400 MHz, Chloroform-*d*) δ 8.07 (d, *J* = 7.4 Hz, 2H), 7.88 (dd, *J* = 8.0, 0.8 Hz 1H), 7.72 – 7.65(m, 1H), 7.60 – 7.52 (m, 2H), 7.49 – 7.40 (m, 1H), 7.36 – 7.29 (m, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 5.71 (s, 2H), 2.52 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 190.9, 154.8, 154.1, 134.4, 132.9, 132.8, 130.3, 130.3, 129.1, 128.1, 123.8, 113.5, 54.4, 52.0, 48.0, 37.6, 29.7. HRMS (ESI) *m/z*: calcd for C₂₁H₁₇N₃NaO₂ [M+Na]⁺ 394.1274, found: 394.1277.

ethyl 2-(3-(3-azidobicyclo[1.1.1]pentan-1-yl)-2-oxoquinoxalin-1(2*H*)-yl)acetate (4g)



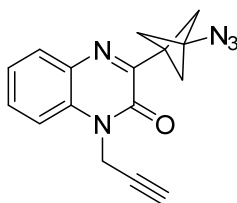
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4g** was isolated as a yellow liquid (63 mg, 62%); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.86 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54 – 7.48 (m, 1H), 7.37 – 7.31 (m, 1H), 7.05 (d, *J* = 8.2 Hz, 1H), 4.99 (s, 2H), 4.25 (q, *J* = 7.2 Hz, 2H), 2.51 (s, 6H), 1.28 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 167.0, 154.9, 153.9, 132.8, 132.5, 130.4, 130.4, 124.0, 113.0, 62.1, 54.3, 52.0, 43.1, 37.6, 14.1. HRMS (ESI) *m/z*: calcd for C₁₇H₁₇N₃NaO₃ [M+Na]⁺ 362.1224, found: 362.1233.

1-allyl-3-(3-azidobicyclo[1.1.1]pentan-1-yl)quinoxalin-2(1*H*)-one (4h)



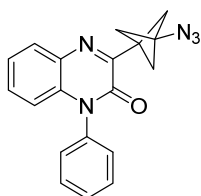
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4h** was isolated as a yellow liquid (53 mg, 60%); ¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 8.0 Hz, 1H), 7.53 – 7.47 (m, 1H), 7.31 (t, *J* = 7.6 Hz, 1H), 7.28 – 7.24 (m, 1H), 5.99 – 5.84 (m, 1H), 5.26 (d, *J* = 8.0 Hz, 1H), 5.15 (d, *J* = 16.0 Hz, 1H), 4.86 (d, *J* = 5.0 Hz, 2H), 2.51 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 155.0, 153.9, 132.8, 132.5, 130.4, 130.2, 130.0, 123.6, 118.1, 114.1, 54.3, 51.9, 44.2, 37.6. HRMS (ESI) *m/z*: calcd for C₁₆H₁₅N₃NaO [M+Na]⁺ 316.1169, found: 316.1183.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-(prop-2-yn-1-yl)quinoxalin-2(1H)-one (4i)



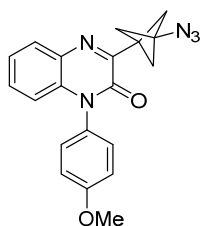
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4i** was isolated as a yellow solid (31 mg, 35%); M.p.: 289-290 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.86 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.54 (m, 1H), 7.45 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.34 (m, 1H), 5.01 (d, *J* = 2.4 Hz, 2H), 2.51 (s, 6H), 2.30 (t, *J* = 2.4 Hz, 1H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 155.0, 153.4, 132.9, 131.9, 130.4, 130.2, 124.0, 114.1, 76.6, 73.3, 54.3, 52.0, 37.7, 31.1. HRMS (ESI) *m/z*: calcd for C₁₆H₁₃N₅NaO [M+Na]⁺ 314.1012, found: 314.1025.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-phenylquinoxalin-2(1H)-one (4j)



Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4j** was isolated as a white solid (68 mg, 69%); M.p.: 108-110 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.93 – 7.85 (m, 1H), 7.66 – 7.52 (m, 3H), 7.38 – 7.27 (m, 4H), 6.72 – 6.64 (m, 1H), 2.53 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 155.8, 154.2, 135.4, 134.1, 132.5, 130.3, 129.9, 129.6, 129.5, 128.1, 123.9, 115.4, 54.4, 52.0, 37.6. HRMS (ESI) *m/z*: calcd for C₁₉H₁₅N₅NaO [M+Na]⁺ 352.1169, found: 352.1180.

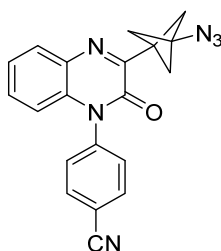
3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-(4-methoxyphenyl)quinoxalin-2(1H)-one (4k)



Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4k** was isolated as a white solid (68 mg, 63%); M.p.: 129-131 °C; ¹H NMR (600 MHz, Chloroform-*d*) δ 7.87 (dd, *J* = 8.0, 1.6 Hz, 1H), 7.36 – 7.29 (m, 2H), 7.21 – 7.17 (m, 2H), 7.13 – 7.09 (m, 2H), 6.73 (dd, *J* = 8.2, 1.2 Hz, 1H), 3.89 (s, 3H), 2.52 (s, 6H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 160.1, 155.8, 154.5, 134.6, 132.6, 129.9, 129.6, 129.2, 127.8, 123.7, 115.5, 115.5, 55.6, 54.4, 52.0, 37.6. HRMS (ESI) *m/z*: calcd for C₂₀H₁₇N₅NaO₂ [M+Na]⁺

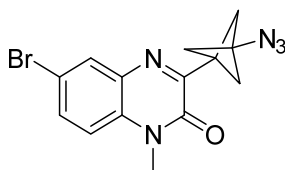
382.1274, found: 382.1286.

4-(3-(3-azidobicyclo[1.1.1]pentan-1-yl)-2-oxoquinoxalin-1(2H)-yl)benzotrile (4l)



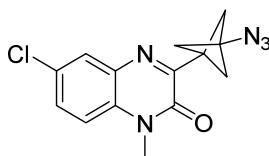
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4l** was isolated as a white solid (65 mg, 61%); M.p.: 161-162 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.97 – 7.88 (m, 3H), 7.47 (d, *J* = 8.4 Hz, 2H), 7.40 – 7.33 (m, 2H), 6.63 – 6.57 (m, 1H), 2.51 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 155.7, 153.6, 139.5, 134.1, 133.2, 132.5, 130.2, 130.1, 129.7, 124.4, 117.6, 114.7, 113.7, 54.4, 52.0, 37.5. HRMS (ESI) *m/z*: calcd for C₂₀H₁₄N₆NO [M+Na]⁺ 377.1121, found: 377.1128.

3-(3-(3-azidobicyclo[1.1.1]pentan-1-yl)-6-bromo-1-methylquinoxalin-2(1H)-one (4m)



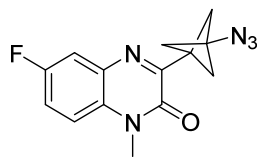
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4m** was isolated as a yellow solid (48 mg, 47%); M.p.: 128-130 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 2.4 Hz, 1H), 7.62 (dd, *J* = 8.8, 2.2 Hz, 1H), 7.16 (d, *J* = 8.8 Hz, 1H), 3.64 (s, 3H), 2.50 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 156.4, 154.0, 133.4, 133.0, 132.4, 132.4, 116.2, 115.0, 54.3, 52.0, 37.7, 28.8. HRMS (ESI) *m/z*: calcd for C₁₄H₁₃BrN₅O [M+H]⁺ 346.0298, found: 346.0311.

3-(3-(3-azidobicyclo[1.1.1]pentan-1-yl)-6-chloro-1-methylquinoxalin-2(1H)-one (4n)



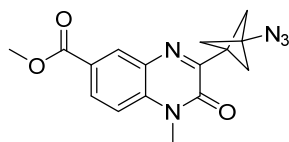
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4n** was isolated as a yellow solid (51 mg, 56%); M.p.: 123-124 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 (d, *J* = 2.4 Hz, 1H), 7.49 (dd, *J* = 8.8, 2.4 Hz, 1H), 7.22 (d, *J* = 8.8 Hz, 1H), 3.65 (s, 3H), 2.50 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 156.4, 154.0, 133.1, 132.0, 130.2, 129.3, 129.0, 114.8, 54.3, 52.0, 37.7, 28.9. HRMS (ESI) *m/z*: calcd for C₁₄H₁₂ClN₅NaO [M+Na]⁺ 324.0623, found: 324.0633.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-6-fluoro-1-methylquinoxalin-2(1H)-one (4o)



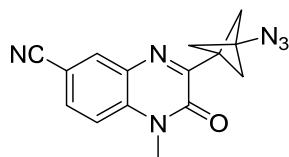
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4o** was isolated as a yellow solid (55 mg, 64%); M.p.: 123-125 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.54 (dd, *J* = 8.6, 2.8 Hz, 1H), 7.33 – 7.22 (m, 2H), 3.66 (s, 3H), 2.50 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 158.7 (d, *J* = 243.9 Hz), 156.6, 154.1, 133.3 (d, *J* = 11.1 Hz), 130.1 (d, *J* = 2.1 Hz), 118.0 (d, *J* = 24.1 Hz), 115.5 (d, *J* = 22.5 Hz), 114.7 (d, *J* = 8.8 Hz), 54.3, 52.0, 37.8, 28.9. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -118.8. HRMS (ESI) *m/z*: calcd for C₁₄H₁₂FN₅NaO [M+Na]⁺ 308.0918, found: 308.0923.

Methyl 3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carboxylate (4p)



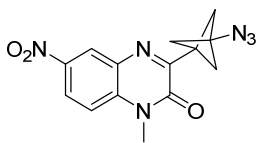
Eluent in chromatography: petroleum ether/ethyl acetate 20:1 to 10:1, **4p** was isolated as a white solid (36 mg, 37%); M.p.: 187-188 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.52 (s, 1H), 8.19 (d, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 1H), 3.95 (s, 3H), 3.69 (s, 3H), 2.51 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 166.0, 156.1, 154.3, 136.6, 132.0, 131.9, 131.0, 125.6, 113.7, 54.3, 52.4, 52.0, 37.7, 28.9. HRMS (ESI) *m/z*: calcd for C₁₆H₁₅N₅NaO₃ [M+Na]⁺ 348.1067, found: 348.1074.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-methyl-2-oxo-1,2-dihydroquinoxaline-6-carbonitrile (4q)



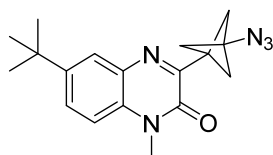
Eluent in chromatography: petroleum ether/ethyl acetate 20:1 to 10:1, **4q** was isolated as a yellow solid (36 mg, 41%); M.p.: 140-141 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.15 (s, 1H), 7.77 (d, *J* = 8.4 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 1H), 3.68 (s, 3H), 2.51 (s, 6H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 157.5, 153.9, 136.6, 134.4, 132.7, 132.3, 117.8, 114.7, 107.2, 54.4, 52.0, 37.7, 29.0. HRMS (ESI) *m/z*: calcd for C₁₅H₁₂N₆NaO [M+Na]⁺ 315.0965, found: 315.0964.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-methyl-6-nitroquinoxalin-2(1H)-one (4r)



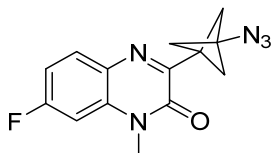
Eluent in chromatography: petroleum ether/ethyl acetate 20:1 to 10:1, **4r** was isolated as a yellow solid (40 mg, 43%); M.p.: 133-134 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.72 (d, *J* = 2.4 Hz, 1H), 8.39 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.40 (d, *J* = 9.0 Hz, 1H), 3.72 (s, 3H), 2.52 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 157.8, 153.9, 143.3, 138.0, 131.8, 125.7, 124.7, 114.2, 54.4, 52.0, 37.7, 29.3. HRMS (ESI) *m/z*: calcd for C₁₄H₁₃N₆O₃ [M+H]⁺ 313.1044, found: 313.1030.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-6-(tert-butyl)-1-methylquinoxalin-2(1H)-one (4s)



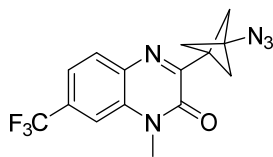
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4s** was isolated as a white solid (73 mg, 75%); M.p.: 123-125 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.84 (s, 1H), 7.60 (d, *J* = 8.3 Hz, 1H), 7.29 – 7.21 (m, 1H), 3.66 (s, 3H), 2.51 (s, 6H), 1.38 (s, 9H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 154.9, 154.5, 147.1, 132.5, 131.0, 128.1, 126.5, 113.2, 54.3, 52.0, 37.8, 34.5, 31.3, 28.6. HRMS (ESI) *m/z*: calcd for C₁₈H₂₁N₅ NaO [M+Na]⁺ 346.1638, found: 346.1650.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-7-fluoro-1-methylquinoxalin-2(1H)-one (4t)



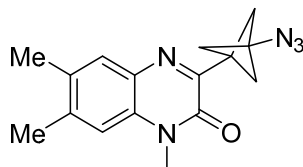
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4t** was isolated as a white solid (51 mg, 60%); M.p.: 119-120 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.81 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.05 (td, *J* = 8.4, 2.6 Hz, 1H), 6.97 (dd, *J* = 10.0, 2.4 Hz, 1H), 3.62 (s, 3H), 2.49 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 163.3 (d, *J* = 251.1 Hz), 154.3, 153.9 (d, *J* = 3.5 Hz), 134.9 (d, *J* = 11.7 Hz), 132.0 (d, *J* = 10.4 Hz), 129.5 (d, *J* = 2.2 Hz), 111.5 (d, *J* = 23.4 Hz), 100.5 (d, *J* = 27.8 Hz), 54.2, 52.0, 37.6, 28.9. ¹⁹F NMR (376 MHz, Chloroform-*d*) δ -106.9. HRMS (ESI) *m/z*: calcd for C₁₄H₁₂FN₅NaO [M+Na]⁺ 308.0918, found: 308.0923.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-methyl-7-(trifluoromethyl)quinoxalin-2(1H)-one (4u)



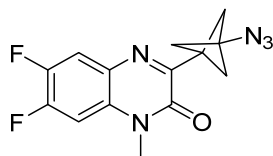
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4u** was isolated as a white solid (72 mg, 72%); M.p.: 106-107 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.95 (d, *J* = 8.4 Hz, 1H), 7.57 (d, *J* = 8.4 Hz, 1H), 7.52 (s, 1H), 3.70 (s, 3H), 2.52 (s, 6H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 157.8, 154.1, 134.4, 133.4, 131.7 (q, *J* = 32.8 Hz), 130.8, 123.6 (q, *J* = 272.8 Hz), 120.2 (q, *J* = 3.6 Hz), 111.0 (q, *J* = 4.1 Hz), 54.4, 52.0, 37.8, 28.9. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -62.4. HRMS (ESI) *m/z*: calcd for C₁₅H₁₃F₃N₅O [M+H]⁺ 336.1067, found: 336.1079.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1,6,7-trimethylquinoxalin-2(1H)-one (4v)



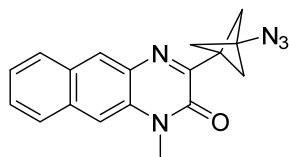
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4v** was isolated as a white solid (62 mg, 70%); M.p.: 137-139 °C; ¹H NMR (600 MHz, Chloroform-*d*) δ 7.60 (s, 1H), 7.05 (s, 1H), 3.64 (s, 3H), 2.49 (s, 6H), 2.41 (s, 3H), 2.33 (s, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 154.6, 153.7, 140.2, 132.6, 131.4, 131.1, 130.1, 114.2, 54.2, 52.0 37.7, 28.6, 20.6, 19.0. HRMS (ESI) *m/z*: calcd for C₁₆H₁₇N₅NaO [M+Na]⁺ 318.1325, found: 318.1328.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-6,7-difluoro-1-methylquinoxalin-2(1H)-one (4w)



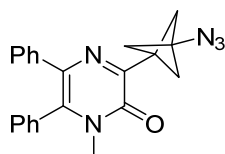
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4w** was isolated as a yellow solid (57 mg, 63%); M.p.: 113-115 °C; ¹H NMR (600 MHz, Chloroform-*d*) δ 7.68 – 7.63 (m, 1H), 7.08 (dd, *J* = 11.2, 7.0 Hz, 1H), 3.62 (s, 3H), 2.49 (s, 6H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 155.7 (d, *J* = 3.6 Hz), 154.0, 151.4 (dd, *J* = 253.8, 14.4 Hz), 146.7 (dd, *J* = 247.4, 13.8 Hz), 130.6 (dd, *J* = 8.8, 1.4 Hz), 129.0 (dd, *J* = 9.2, 3.0 Hz), 117.7 (dd, *J* = 18.1, 2.2 Hz), 102.2 (d, *J* = 23.2 Hz), 54.3, 52.0, 37.7, 29.2. ¹⁹F NMR (565 MHz, Chloroform-*d*) δ -130.3 (d, *J* = 22.4 Hz), -141.9 (d, *J* = 22.4 Hz). HRMS (ESI) *m/z*: calcd for C₁₄H₁₂F₂N₅O [M+H]⁺ 304.1004, found: 304.1003.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-methylbenzo[g]quinoxalin-2(1H)-one (4x)



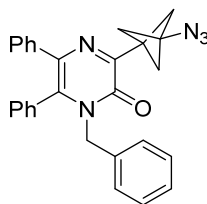
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4x** was isolated as a yellow solid (38 mg, 40%); M.p.: 160-162 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 8.35 (s, 1H), 7.96 (d, *J* = 8.3 Hz, 1H), 7.90 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.54 (m, 2H), 7.52 – 7.45 (m, 1H), 3.72 (s, 3H), 2.55 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 155.7, 154.3, 133.6, 132.0, 131.7, 129.7, 129.3, 128.5, 128.0, 127.1, 125.4, 110.0, 54.5, 52.0, 37.9, 28.6. HRMS (ESI) *m/z*: calcd for C₁₈H₁₅N₅NaO [M+Na]⁺ 340.1169, found: 340.1178.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-methyl-5,6-diphenylpyrazin-2(1H)-one (4y)



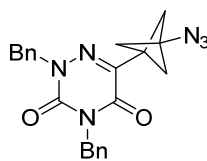
Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4y** was isolated as a yellow solid (65 mg, 60%); M.p.: 147-149 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.35(m, 3H), 7.22 – 7.08 (m, 7H), 3.29 (s, 3H), 2.51 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 155.2, 151.7, 137.7, 137.6, 132.6, 132.4, 129.9, 129.5, 129.2, 129.1, 127.7, 127.0, 54.0, 52.1, 37.3, 33.7. HRMS (ESI) *m/z*: calcd for C₂₂H₁₉N₅NaO [M+Na]⁺ 392.1482, found: 392.1489.

3-(3-azidobicyclo[1.1.1]pentan-1-yl)-1-benzyl-5,6-diphenylpyrazin-2(1H)-one (4z)



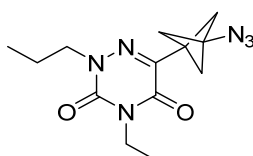
Eluent in chromatography: petroleum ether/ethyl acetate 50:1, **4z** was isolated as a yellow liquid (84 mg, 63%); ¹H NMR (600 MHz, Chloroform-*d*) δ 7.36 – 7.33 (m, 1H), 7.26 – 7.20 (m, 5H), 7.15 – 7.10 (m, 5H), 6.99 (d, *J* = 7.4 Hz, 2H), 6.89 – 6.84 (m, 2H), 5.12 (s, 2H), 2.55 (s, 6H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 154.9, 152.5, 137.6, 137.5, 135.9, 132.8, 131.9, 130.4, 129.4, 129.2, 128.5, 128.4, 127.6, 127.4, 127.0, 126.9, 54.1, 52.1, 48.6, 37.4. HRMS (ESI) *m/z*: calcd for C₂₈H₂₄N₅O [M+H]⁺ 446.1975, found: 446.1972.

6-(3-azidobicyclo[1.1.1]pentan-1-yl)-2,4-dibenzyl-1,2,4-triazine-3,5(2H,4H)-dione (4aa)



Eluent in chromatography: petroleum ether/ethyl acetate 20:1, **4aa** was isolated as a yellow solid (66 mg, 54%); M.p.: 72-74 °C; ¹H NMR (400 MHz, Chloroform-*d*) δ 7.48 (d, *J* = 6.4 Hz, 2H), 7.43 – 7.28 (m, 8H), 5.06 (d, *J* = 14.2 Hz, 4H), 2.35 (s, 6H). ¹³C NMR (100 MHz, Chloroform-*d*) δ 155.2, 148.9, 140.7, 135.4, 135.4, 129.5, 128.8, 128.7, 128.6, 128.3, 128.1, 55.4, 54.0, 52.0, 44.0, 34.5. HRMS (ESI) *m/z*: calcd for C₂₂H₂₀N₆NaO₂ [M+Na]⁺ 423.1540, found: 423.1560.

6-(3-azidobicyclo[1.1.1]pentan-1-yl)-4-ethyl-2-propyl-1,2,4-triazine-3,5(2H,4H)-dione (4ab)

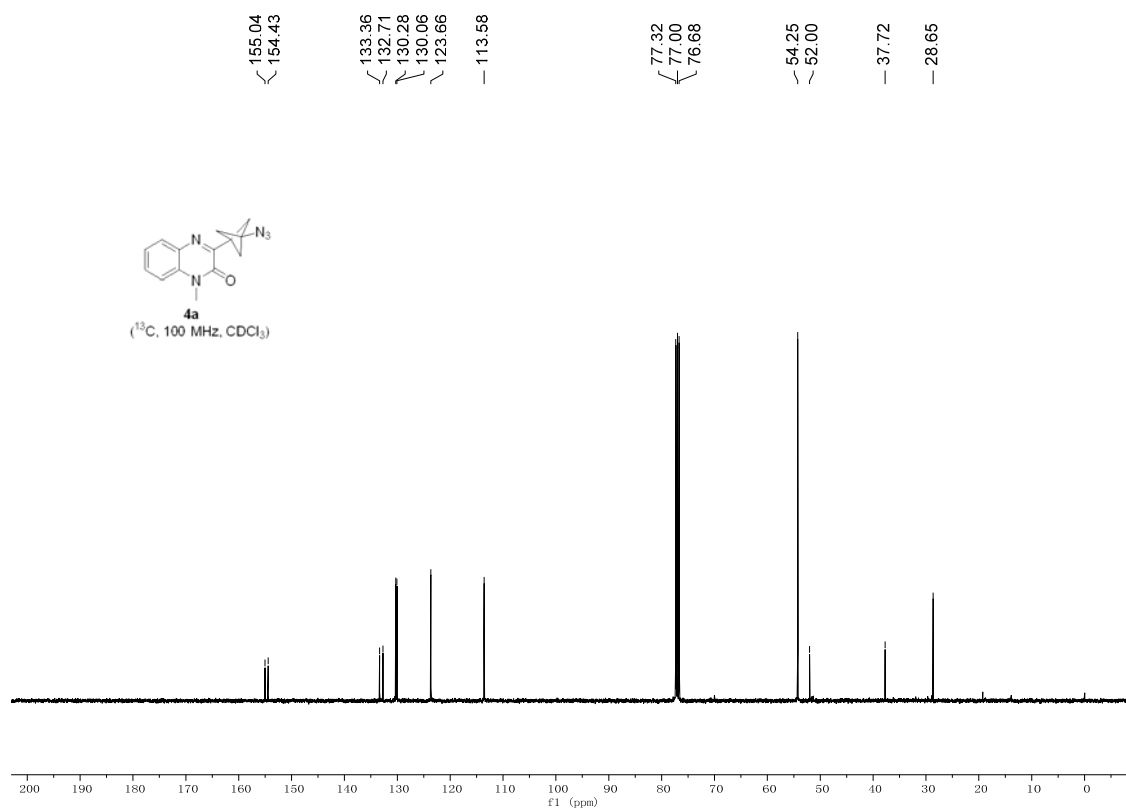
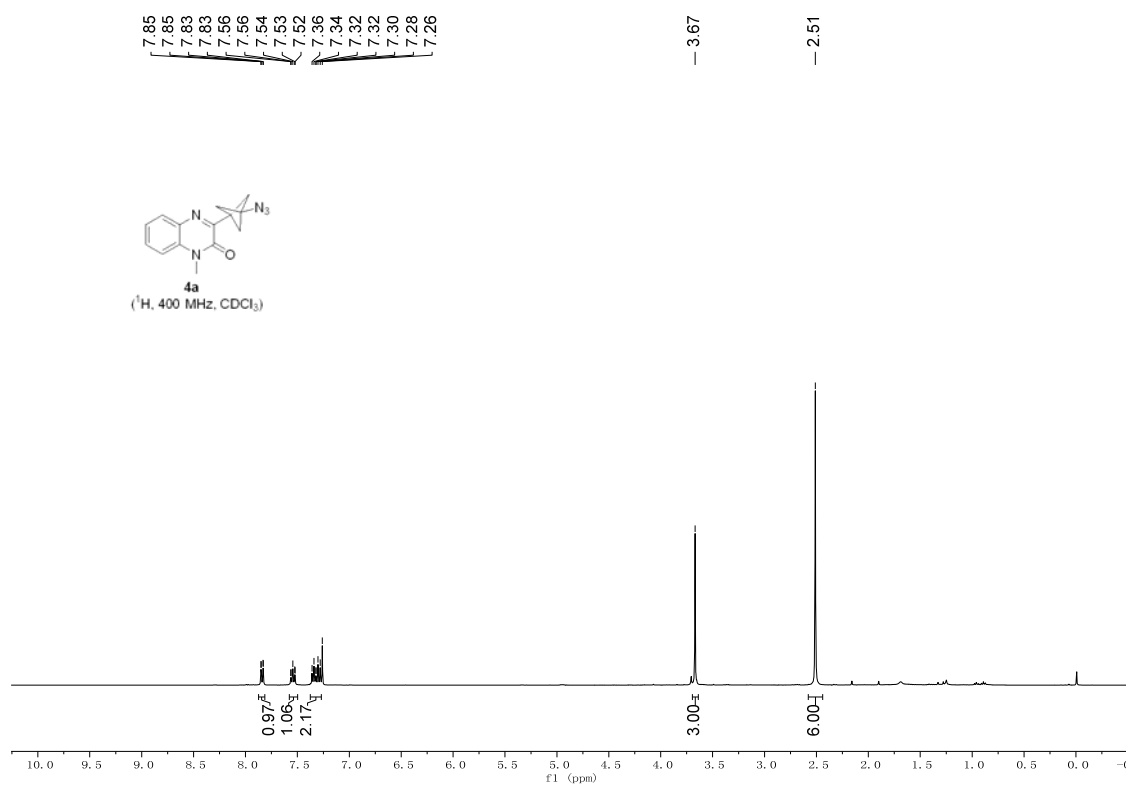


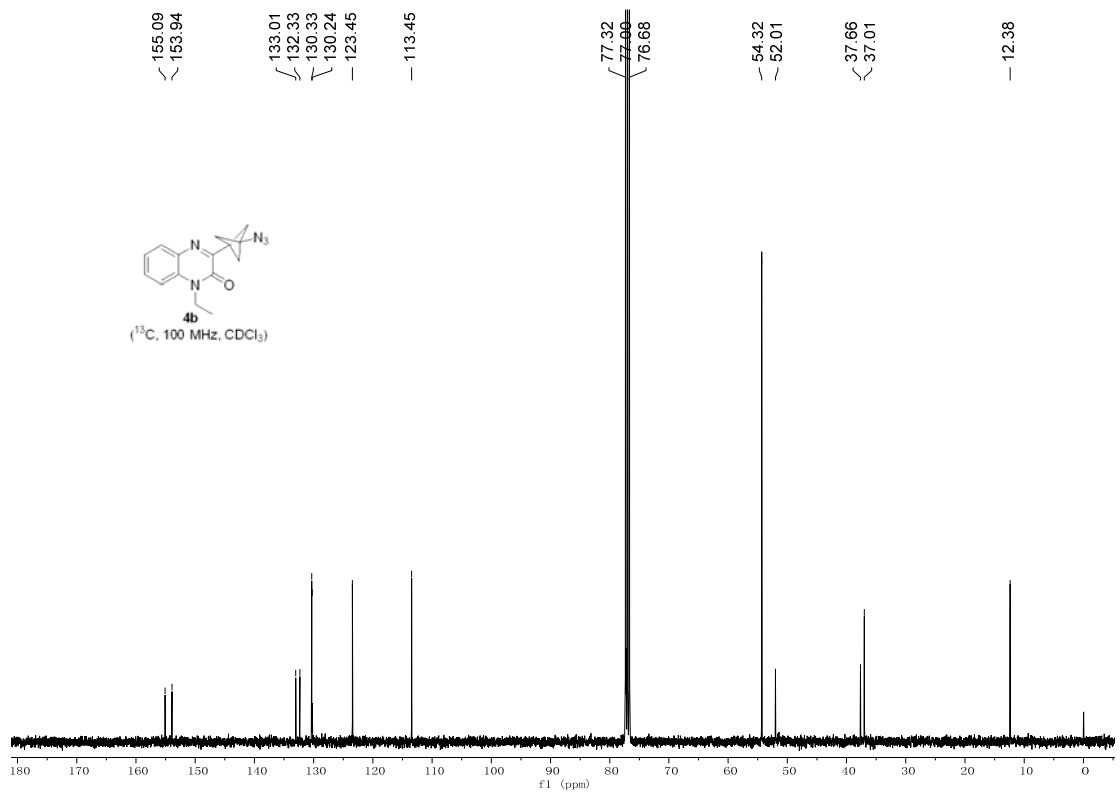
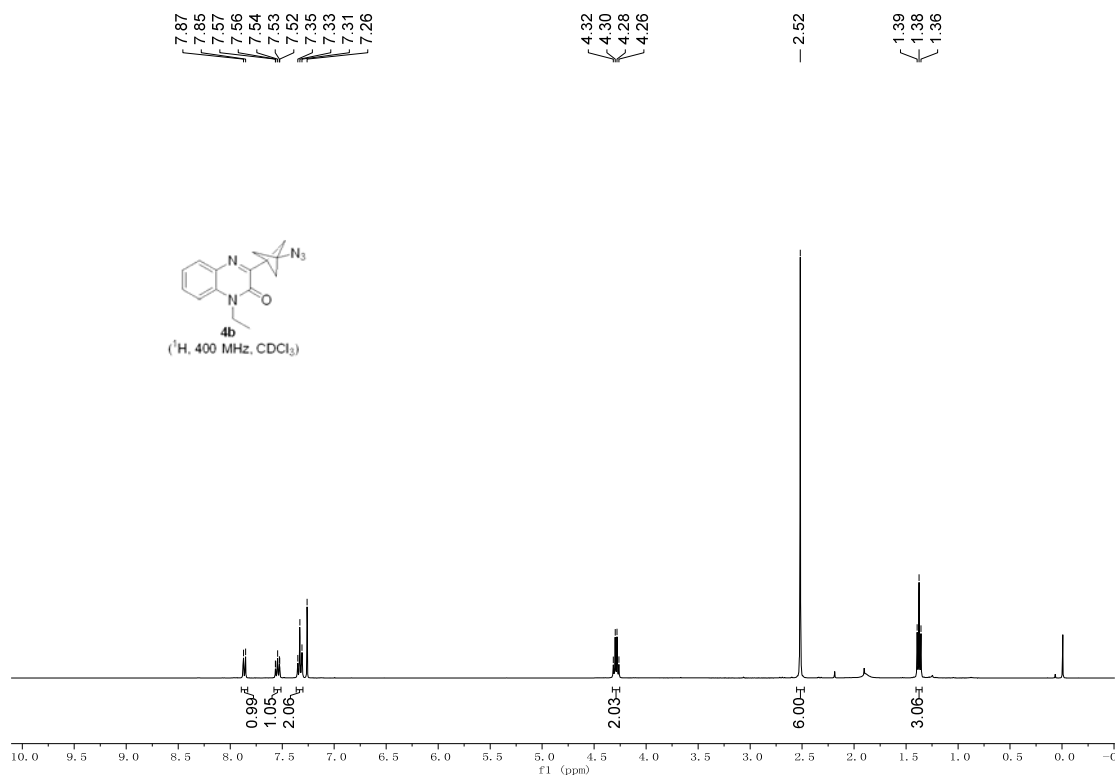
Eluent in chromatography: petroleum ether/ethyl acetate 50:1, **4ab** was isolated as a colorless liquid (39 mg, 45%); ¹H NMR (600 MHz, Chloroform-*d*) δ 3.99 (q, *J* = 7.2 Hz, 2H), 3.86 – 3.82 (m, 2H), 2.34 (s, 6H), 1.67 – 1.63 (m, 2H), 1.31 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.4 Hz, 3H). ¹³C NMR (150 MHz, Chloroform-*d*) δ 155.5, 148.6, 140.2, 54.0, 52.0, 47.0, 42.3, 34.5, 20.6, 13.3, 11.3. HRMS (ESI) *m/z*: calcd for C₁₃H₁₉N₆O₂ [M+H]⁺ 291.1564, found: 291.1565.

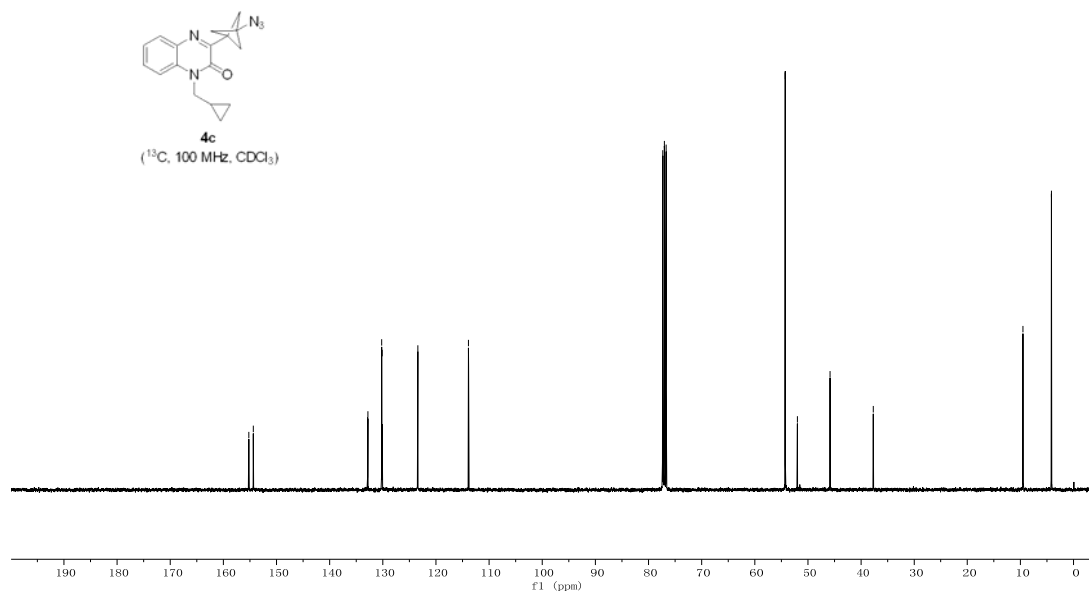
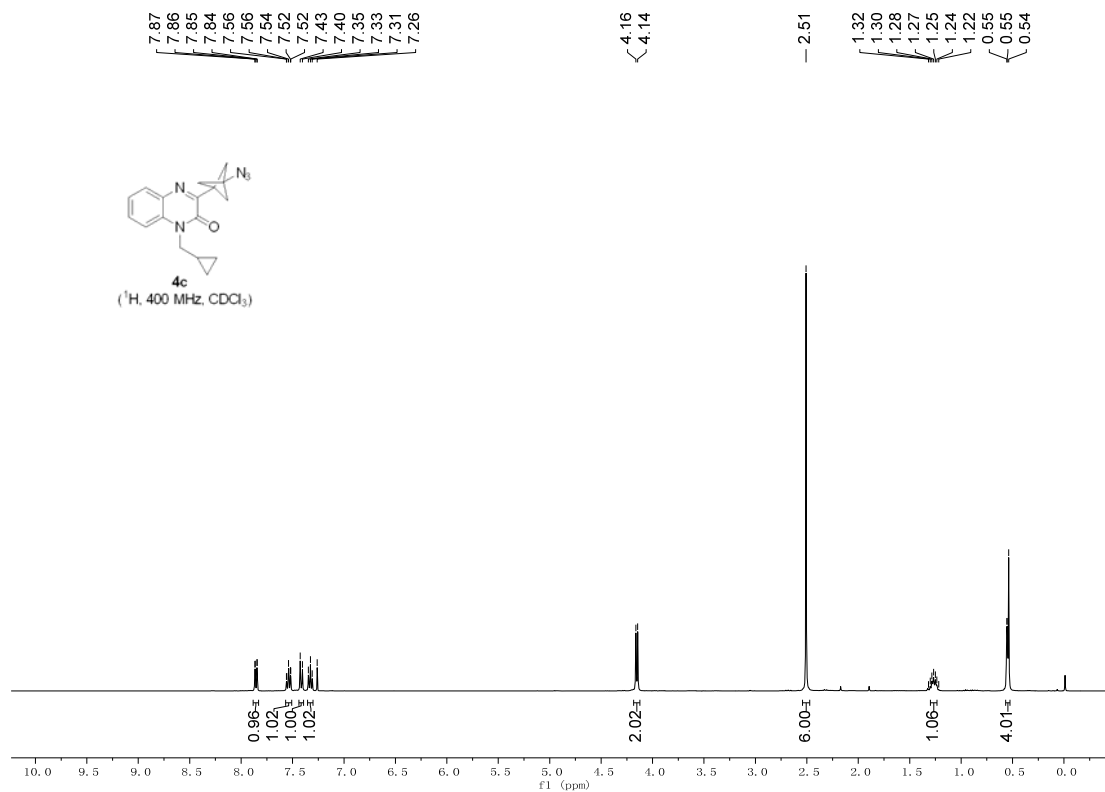
8. References

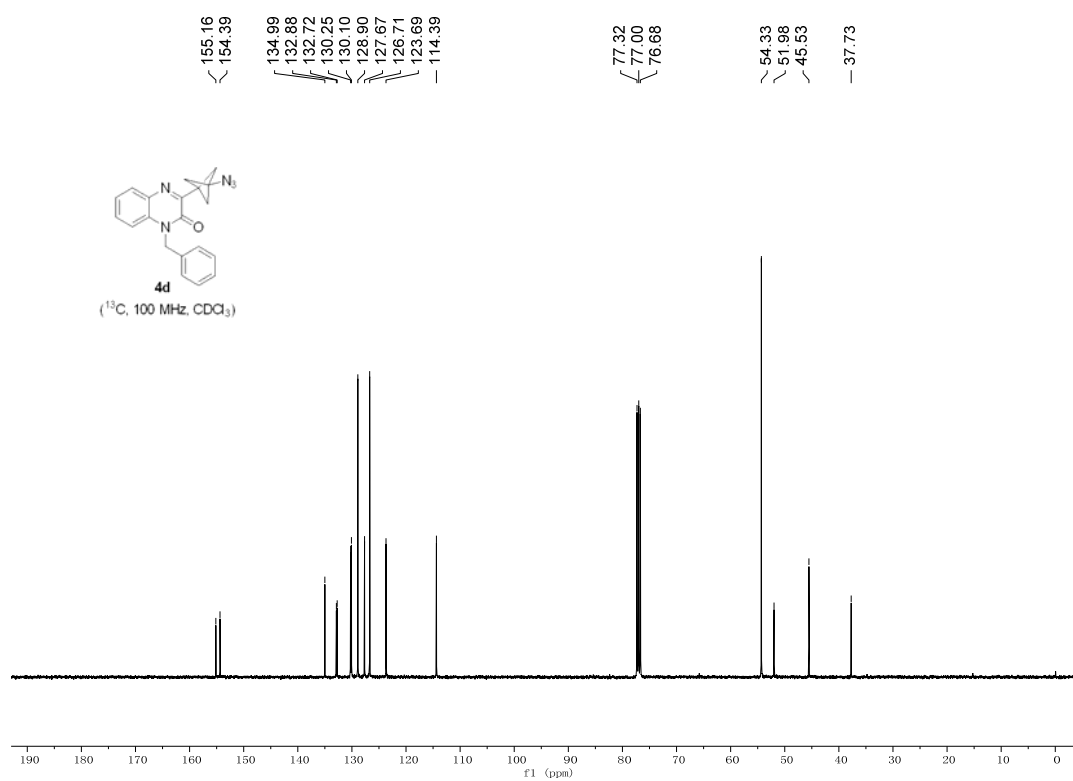
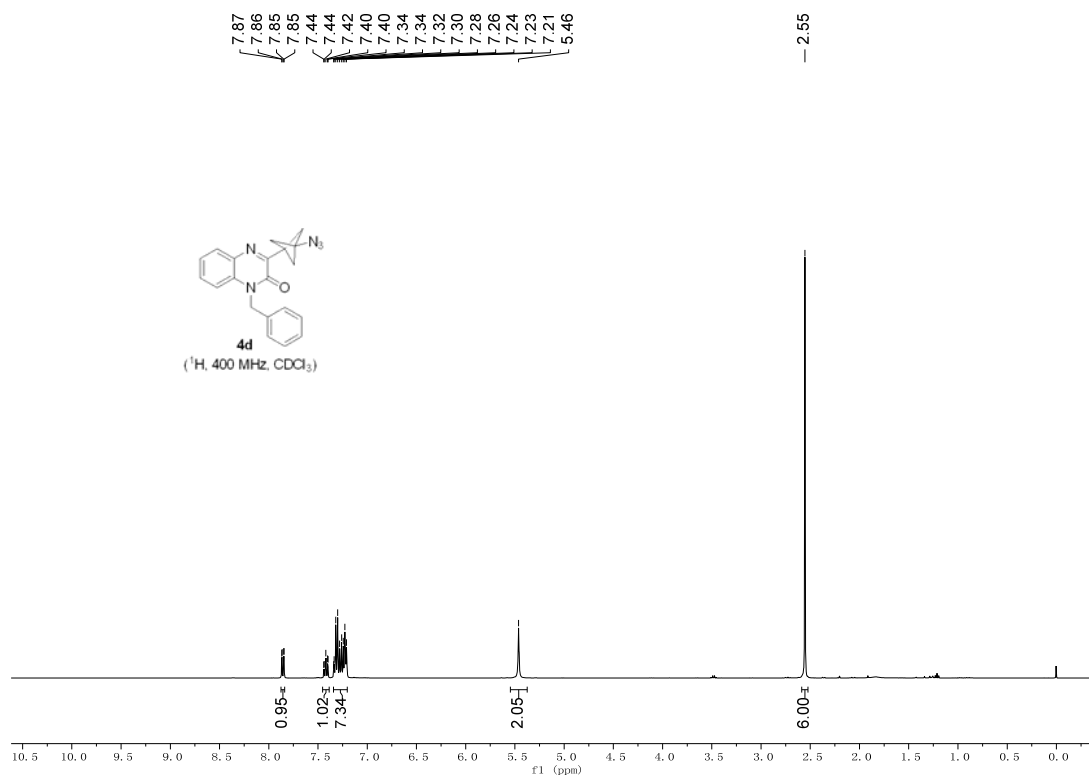
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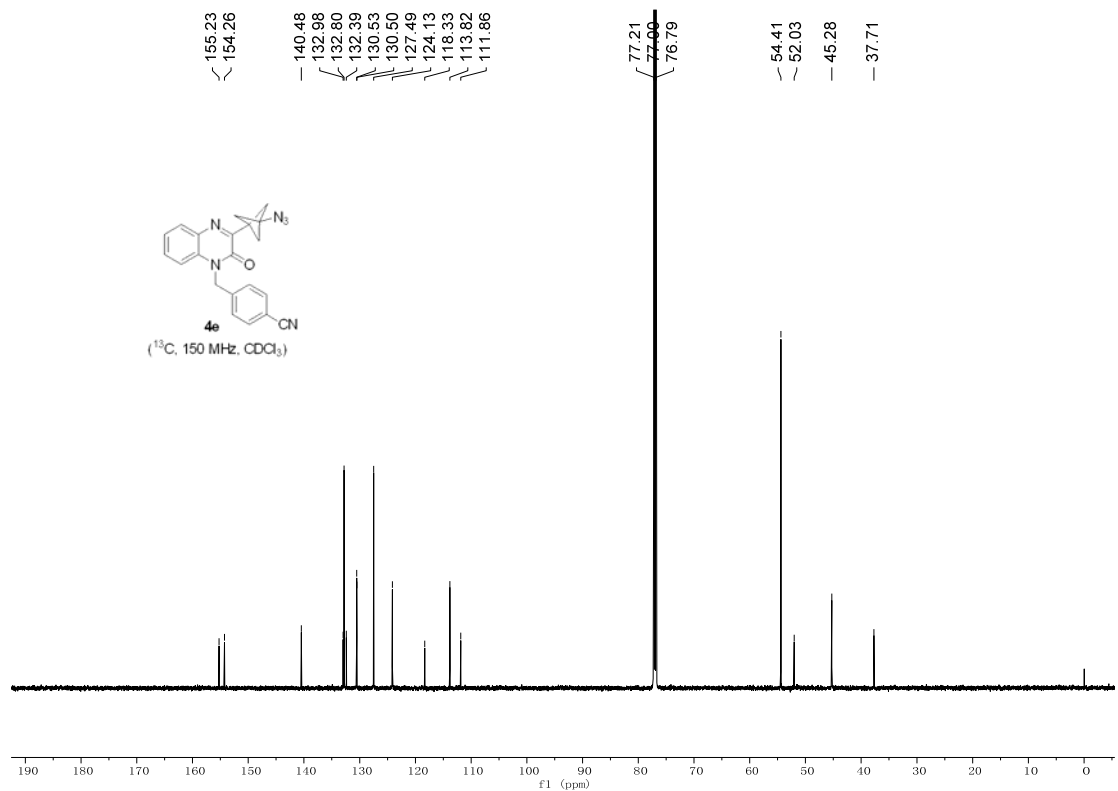
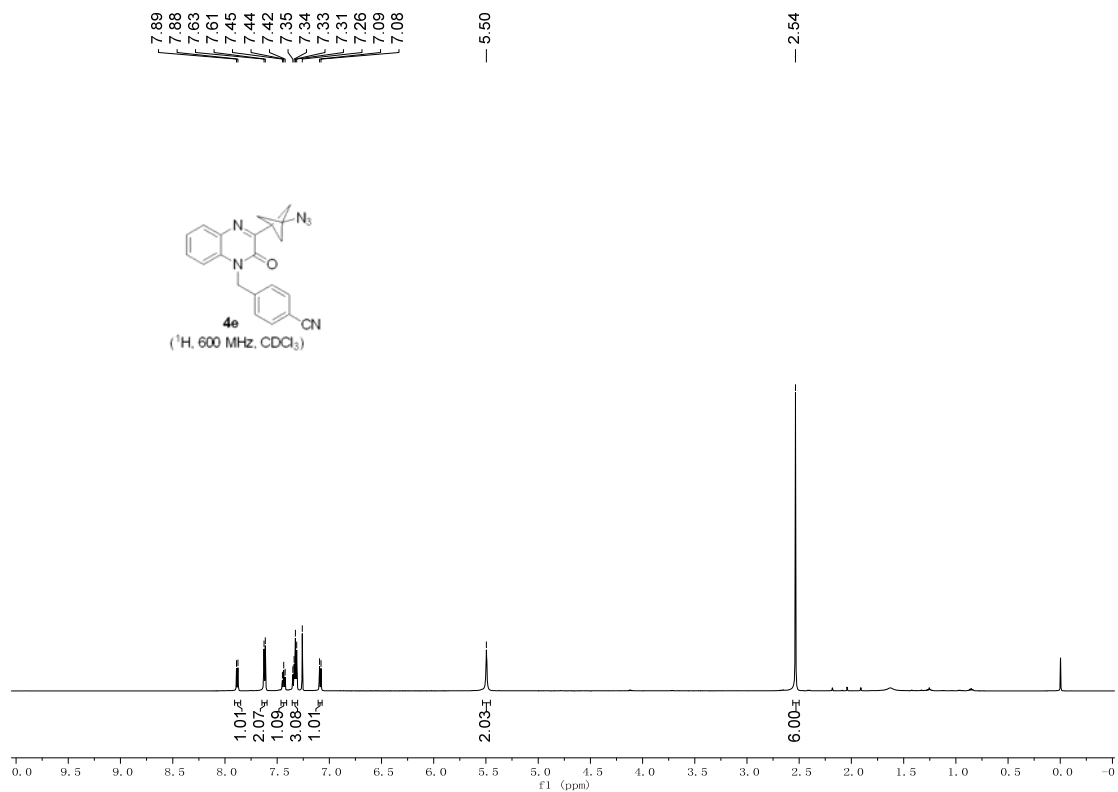
9. Copies of ^1H , ^{13}C NMR, and ^{19}F NMR spectra of products

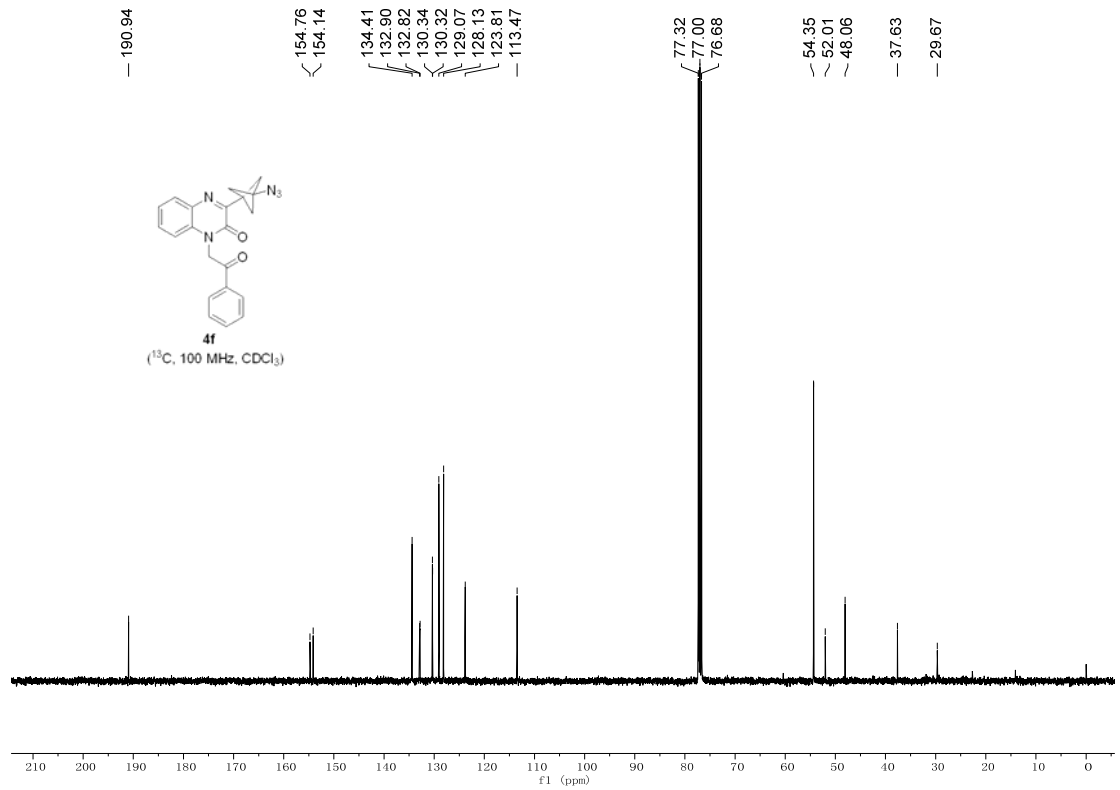
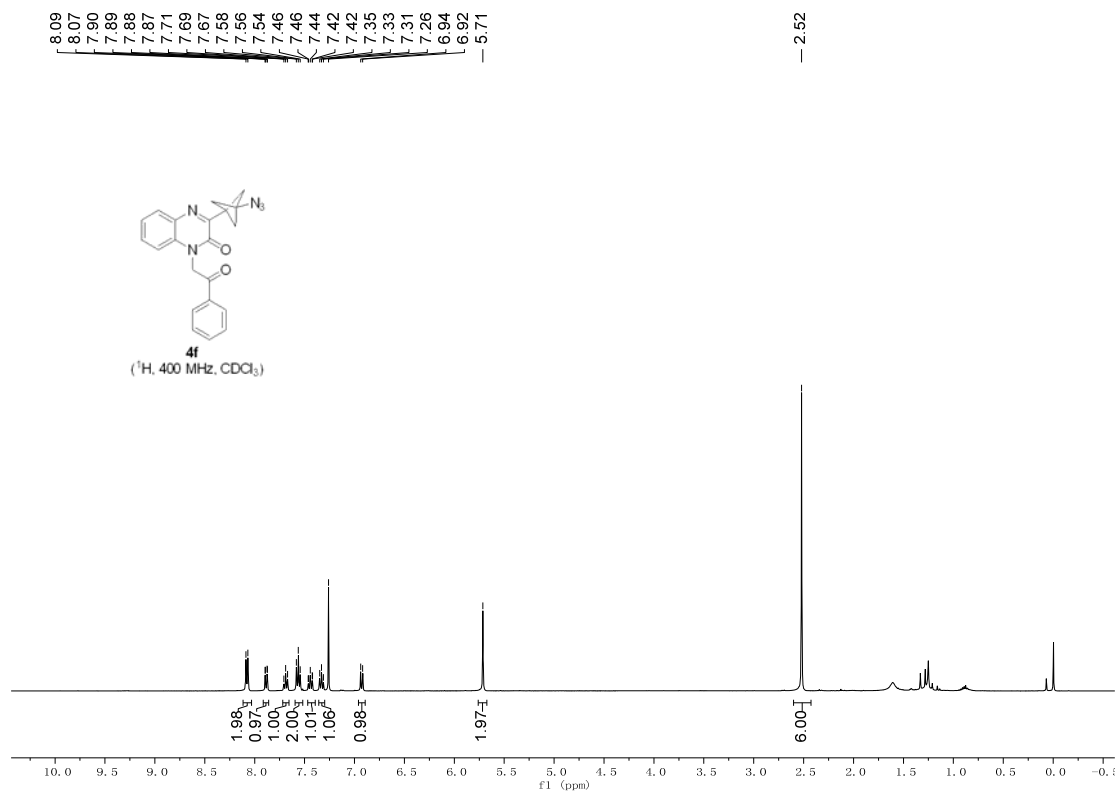


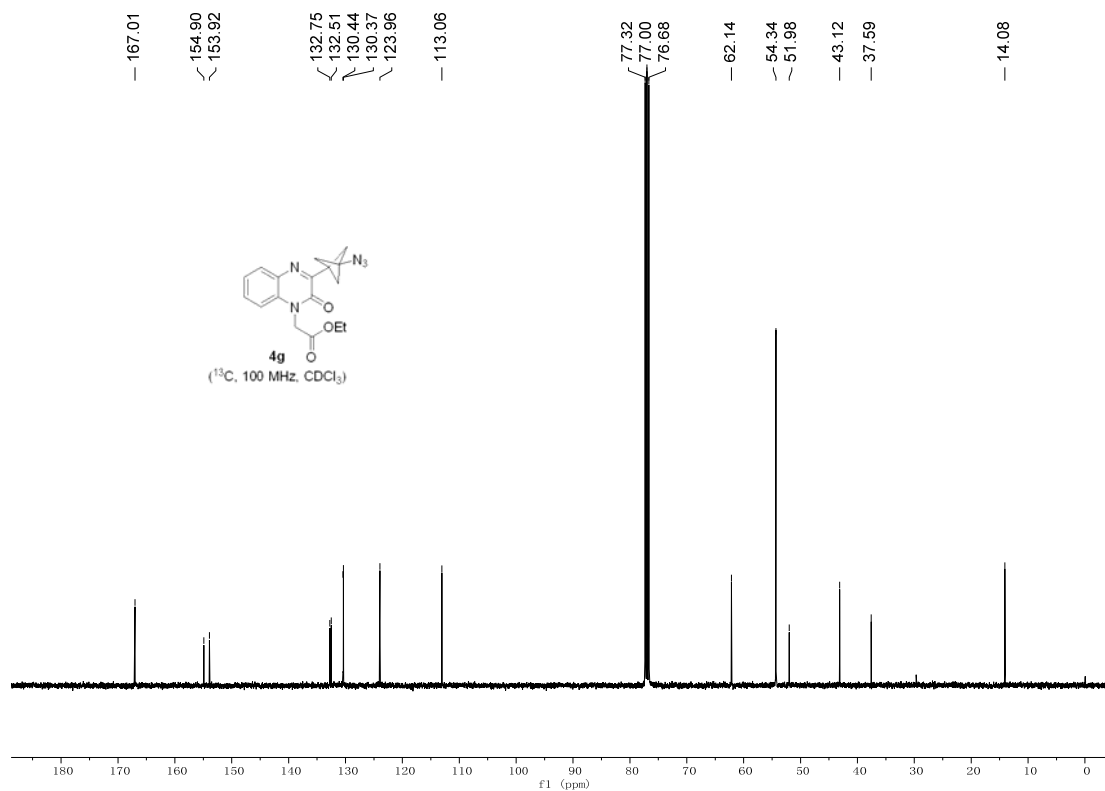
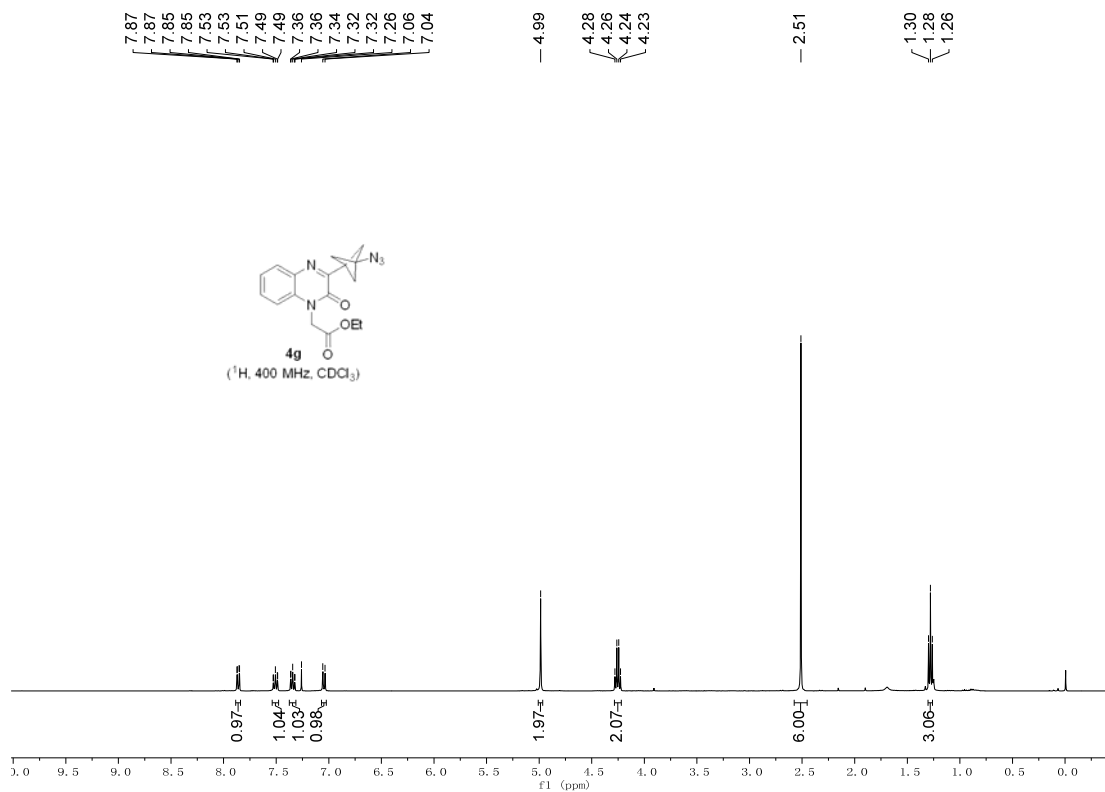


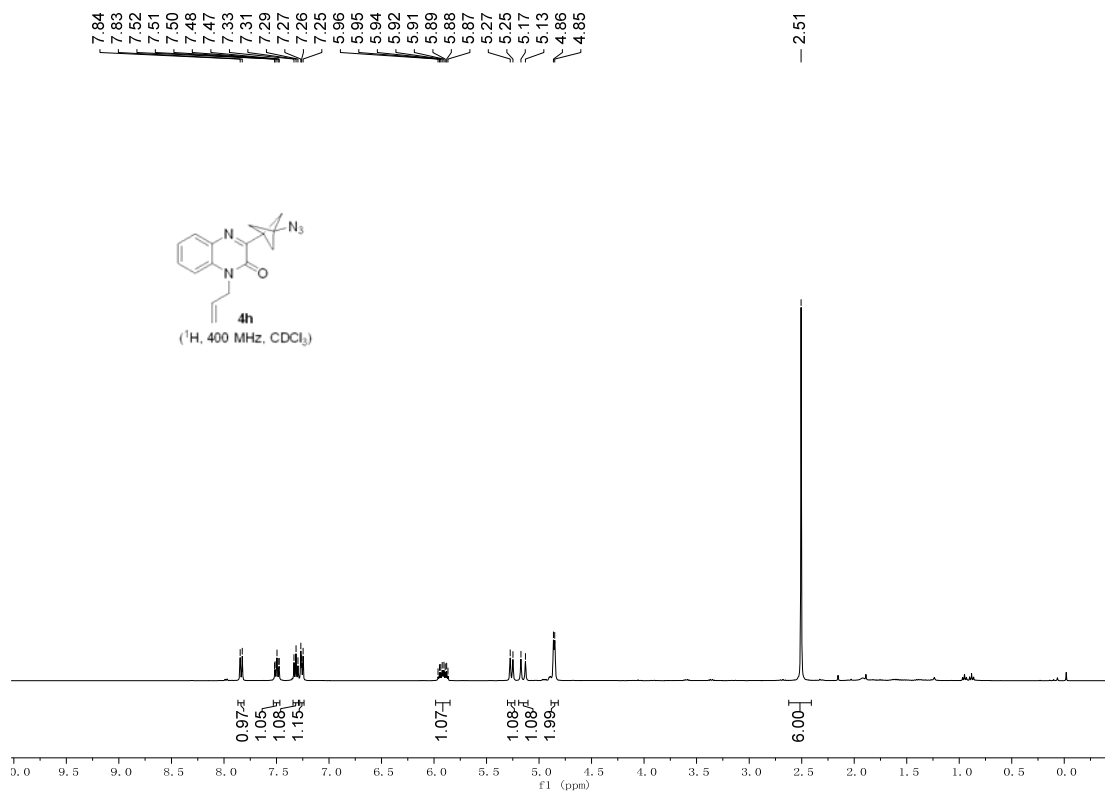


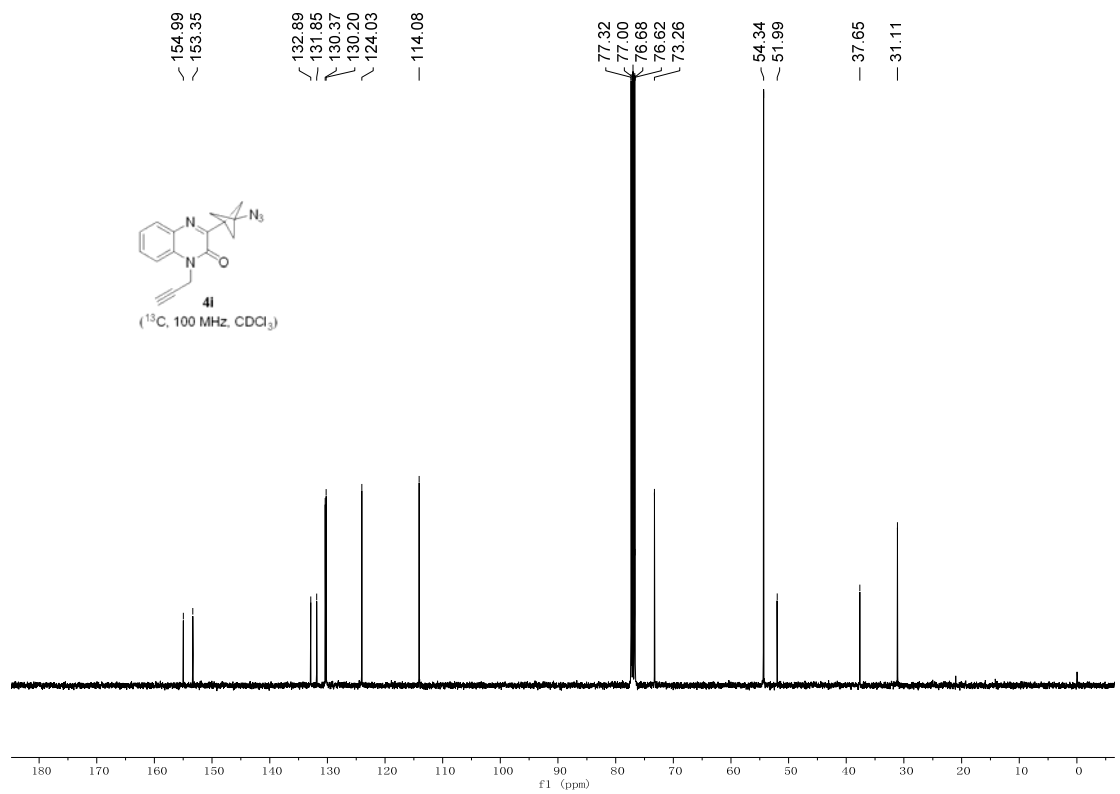
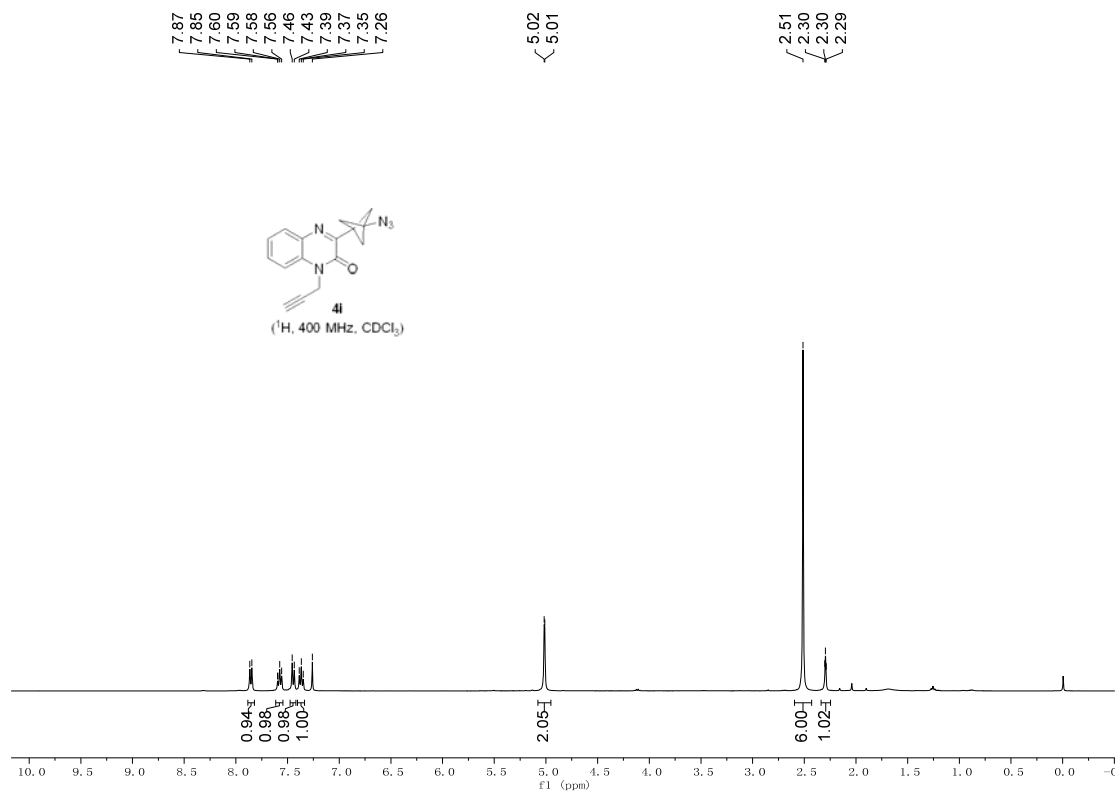


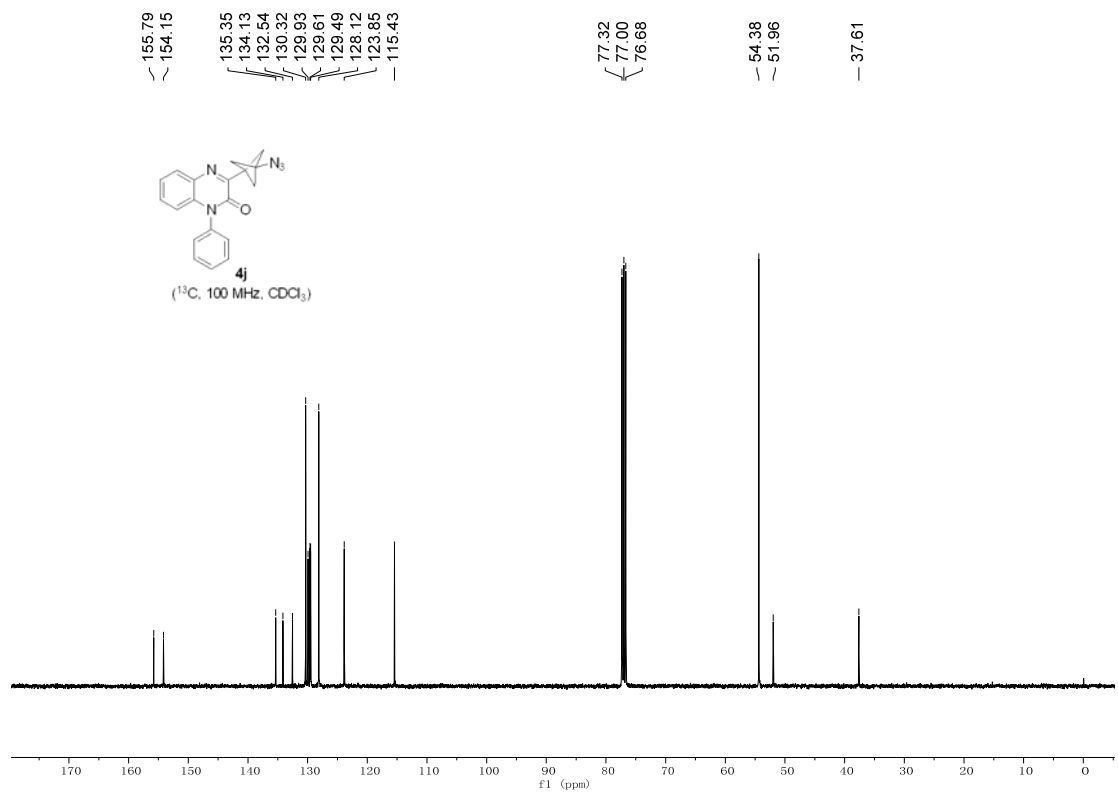
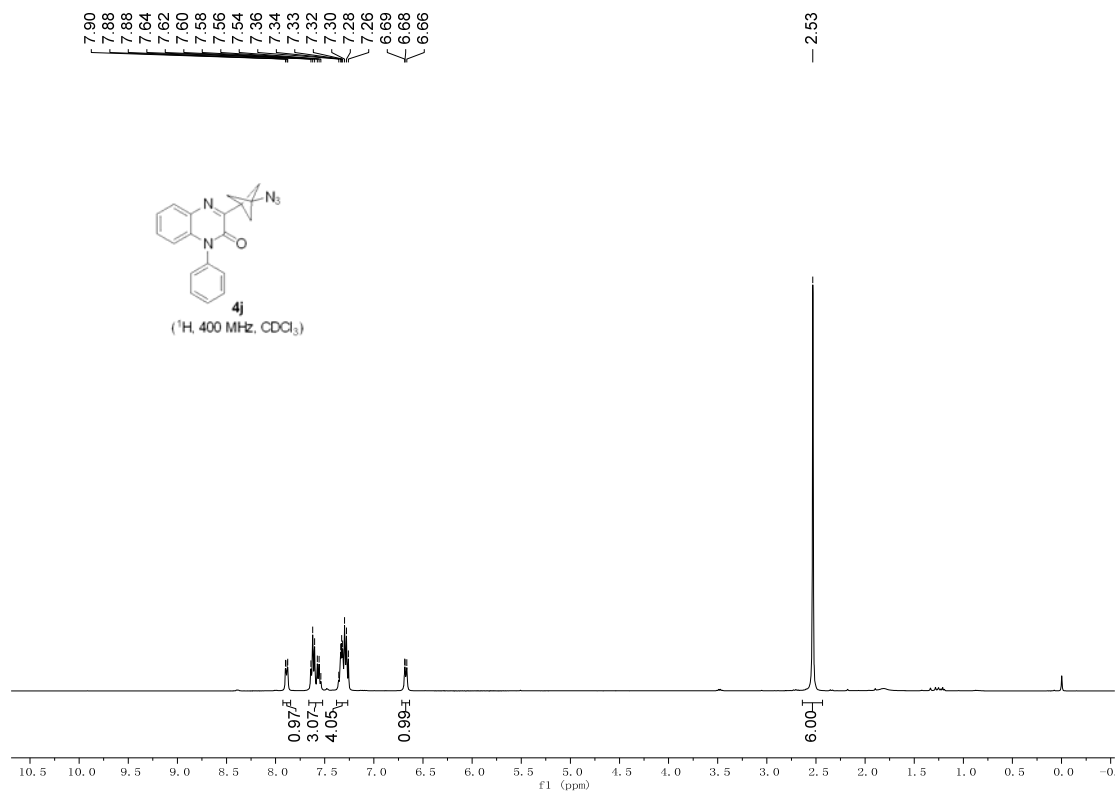


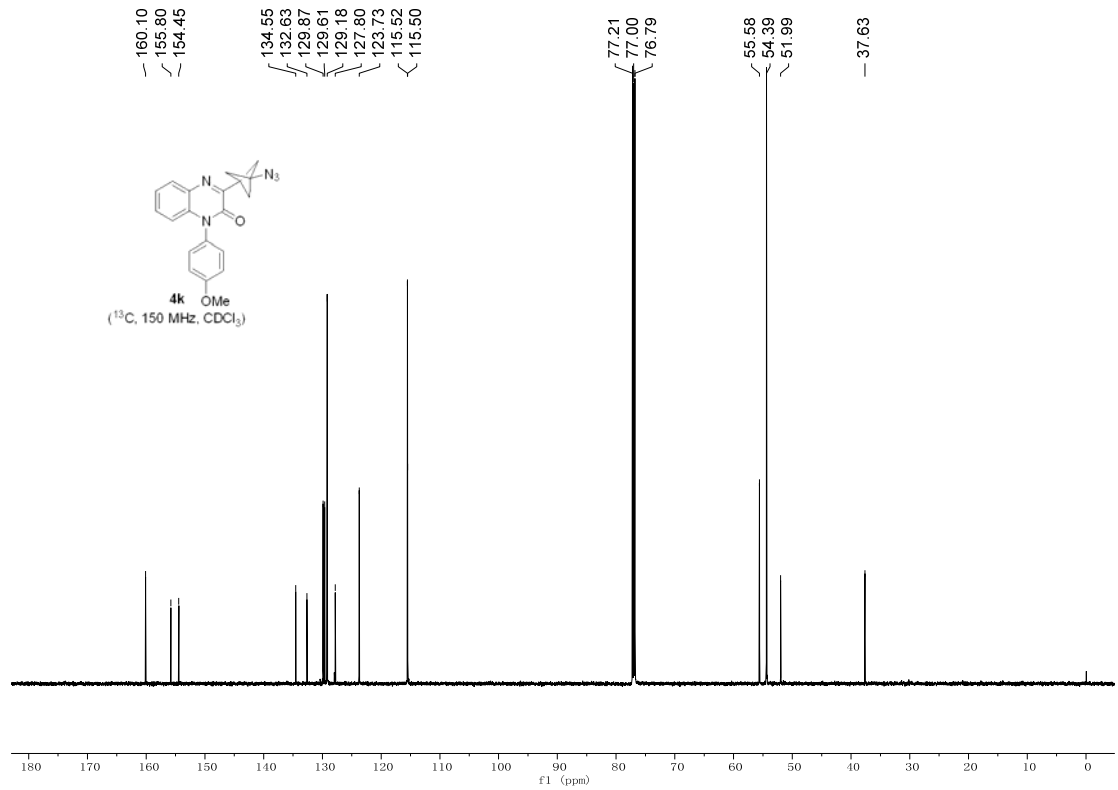
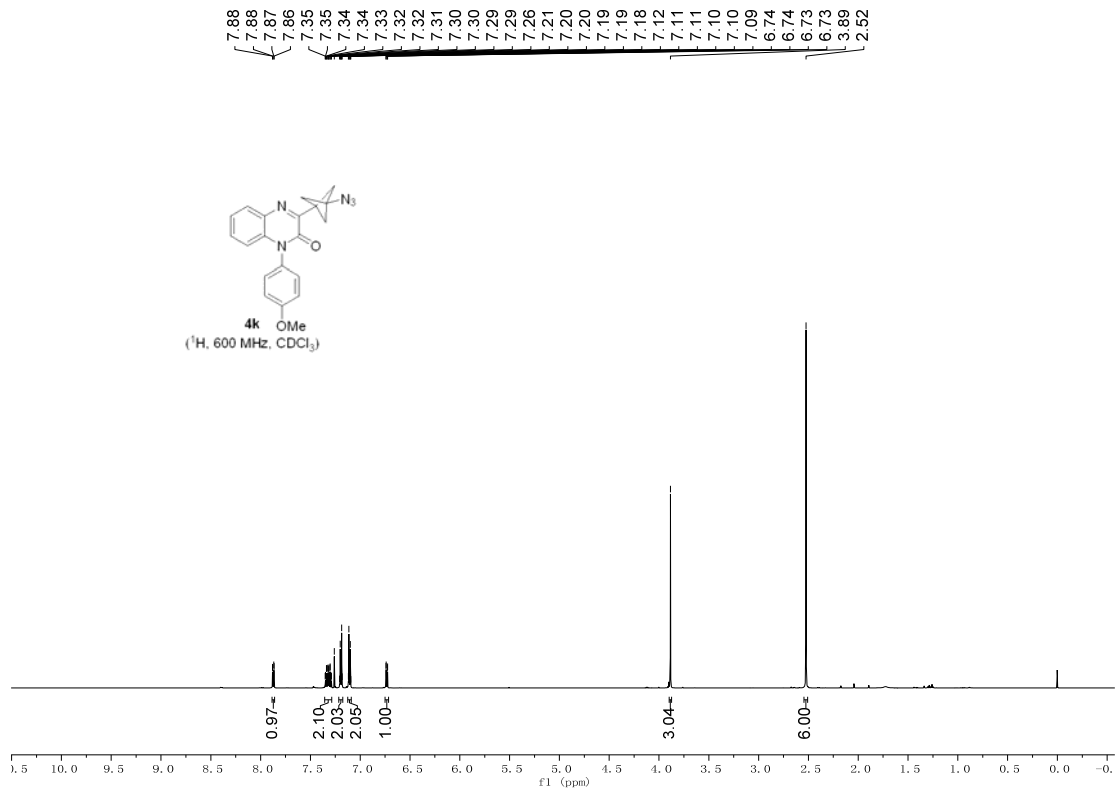


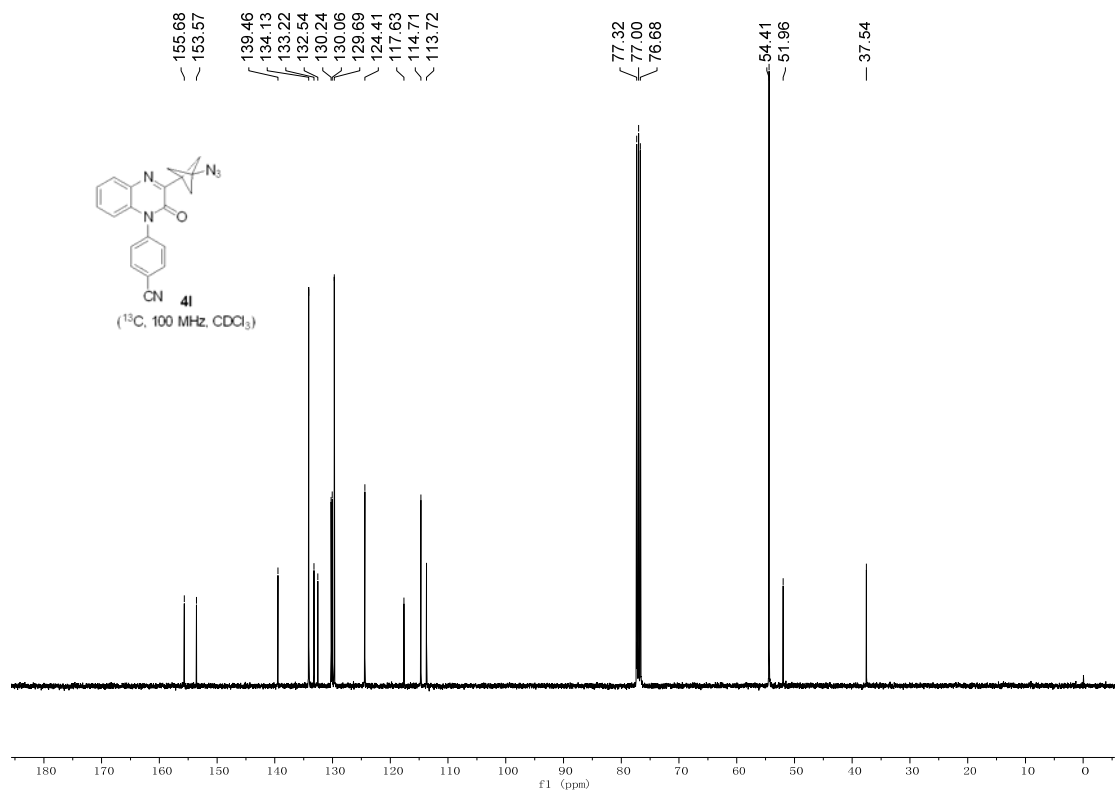
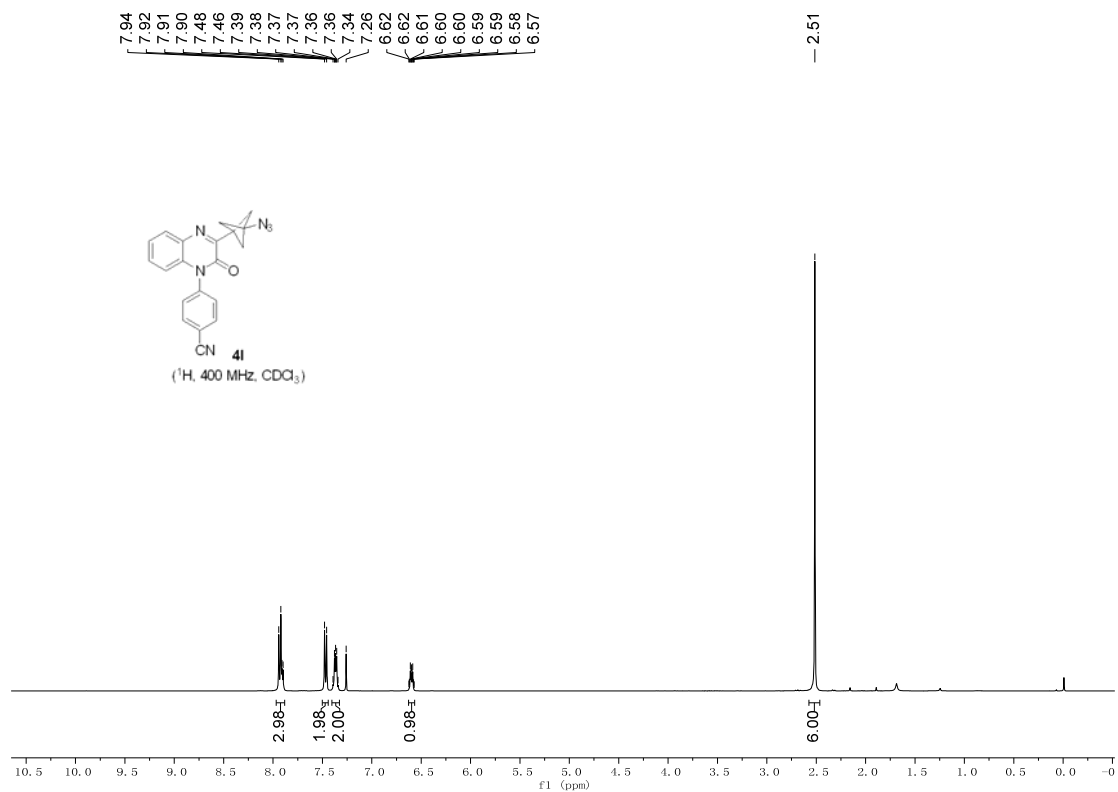


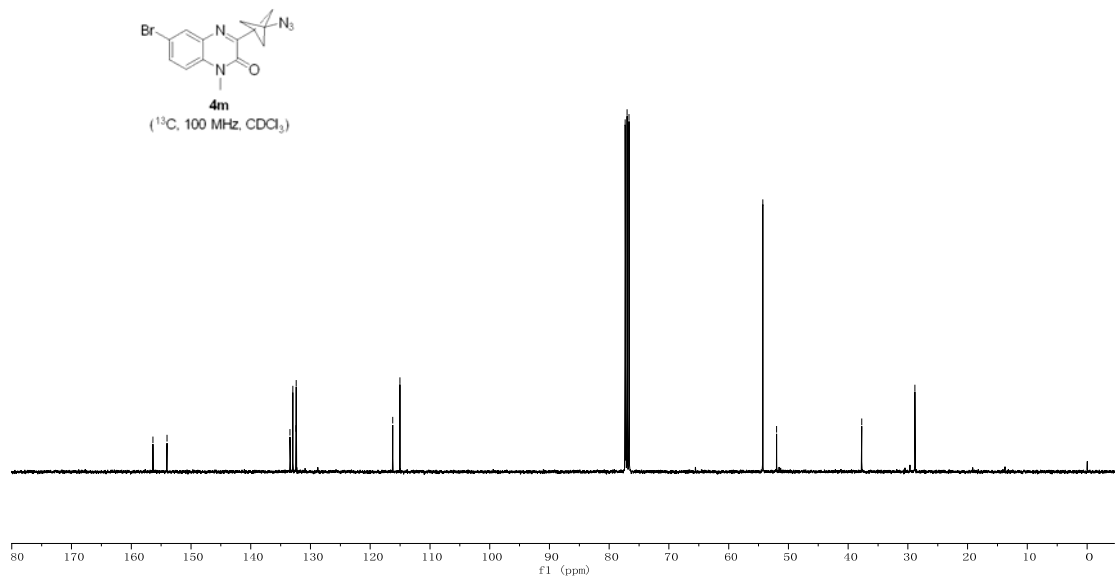
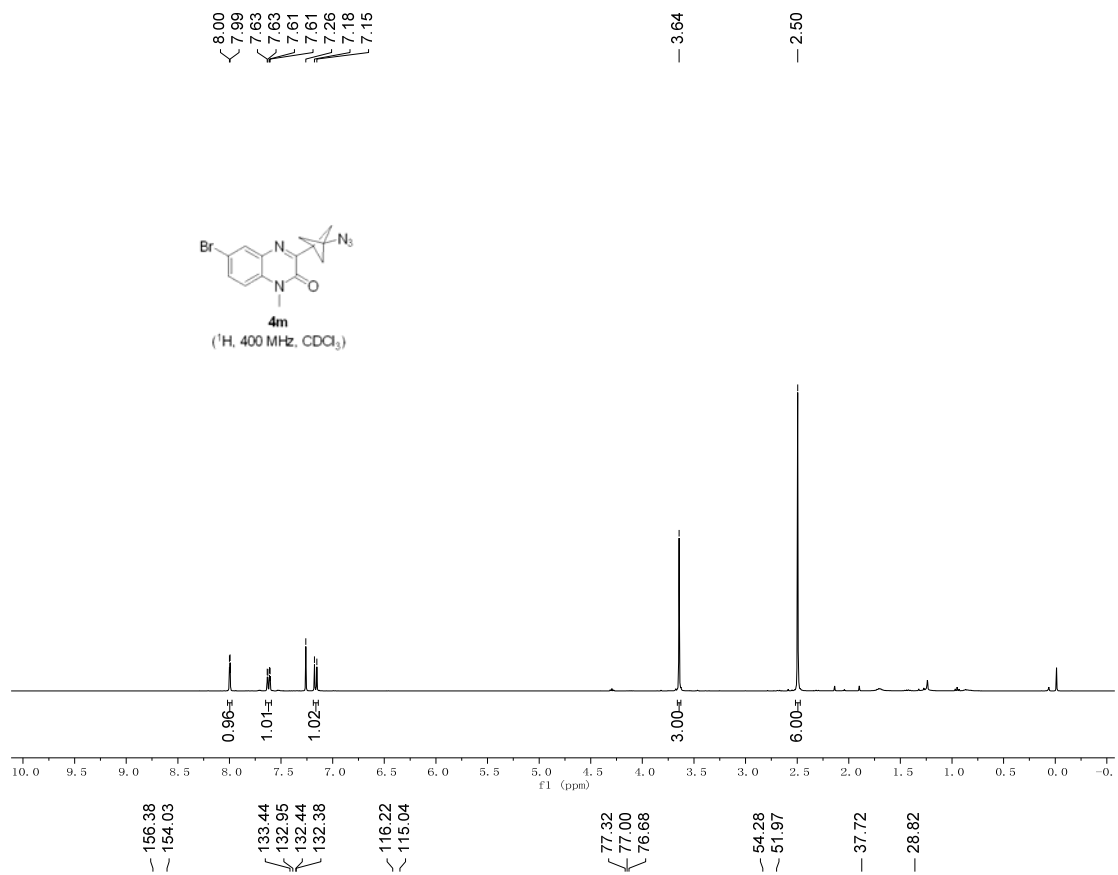


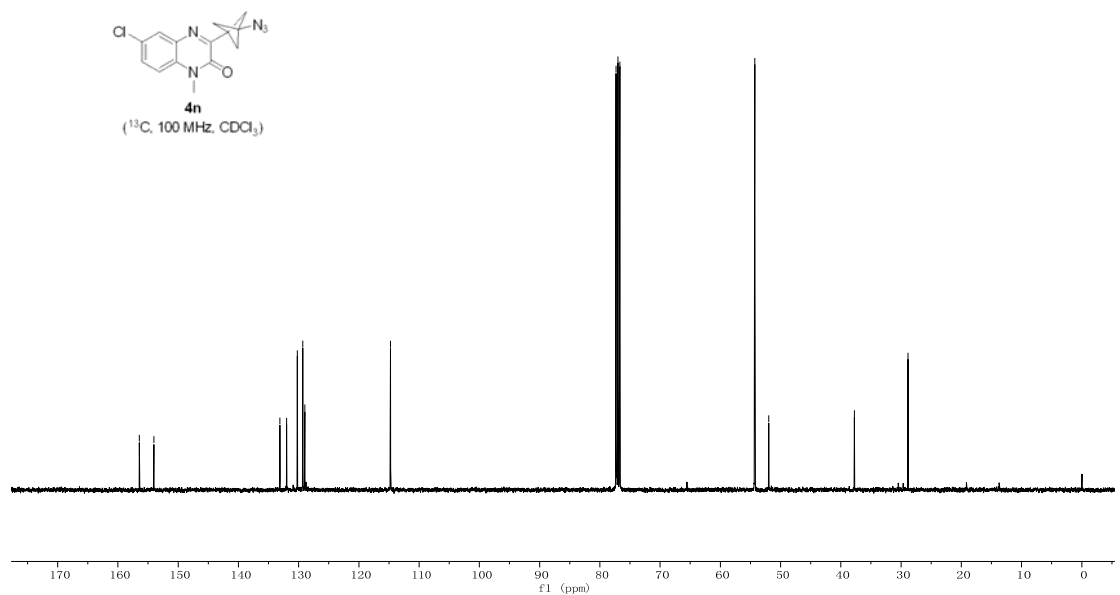
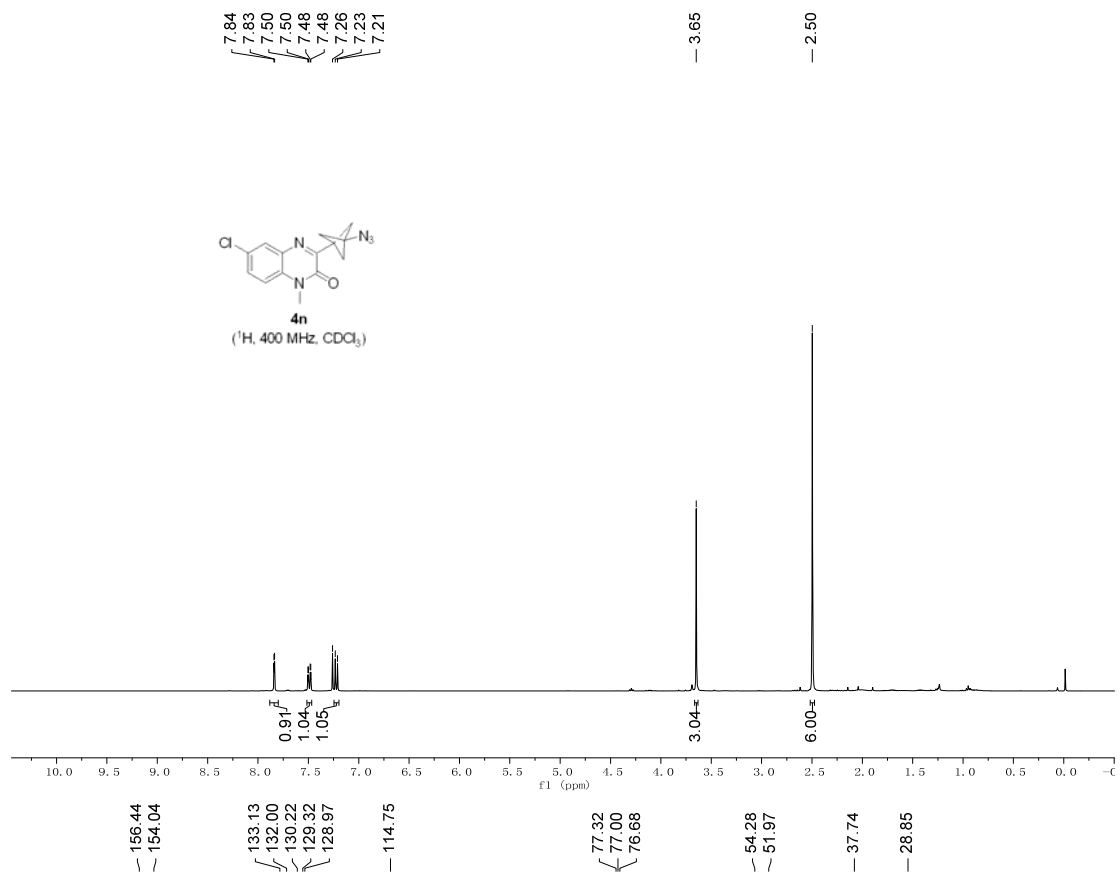


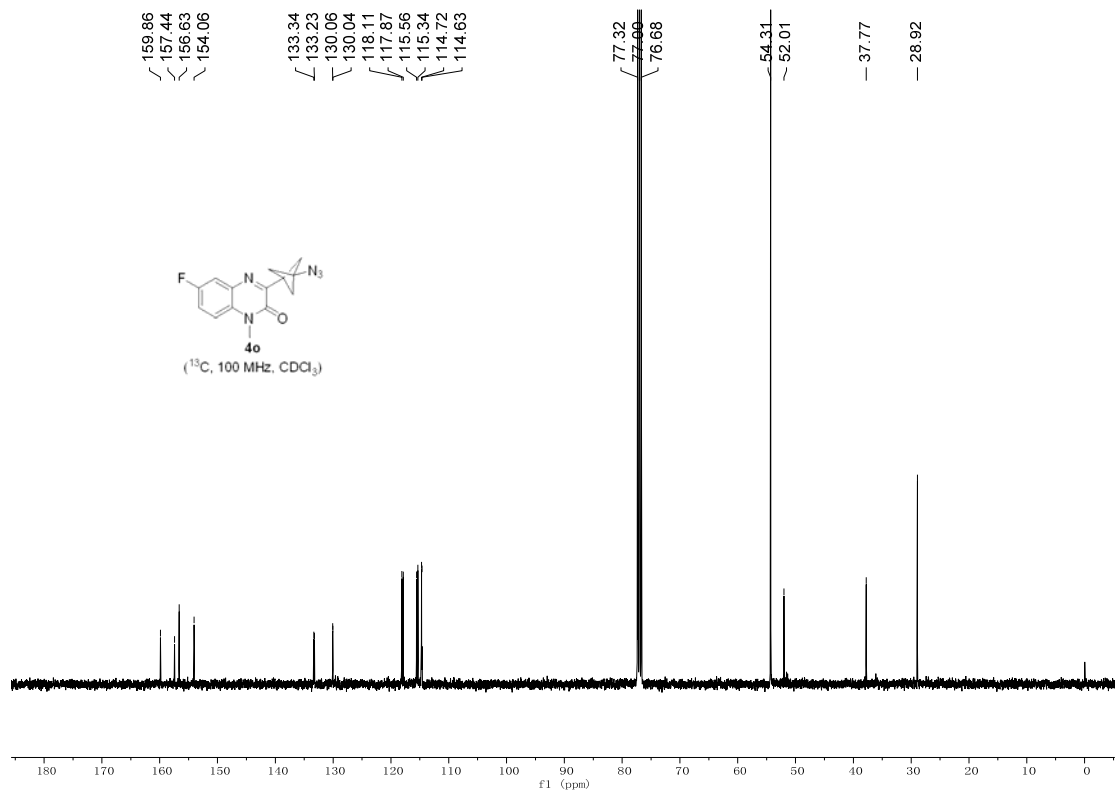
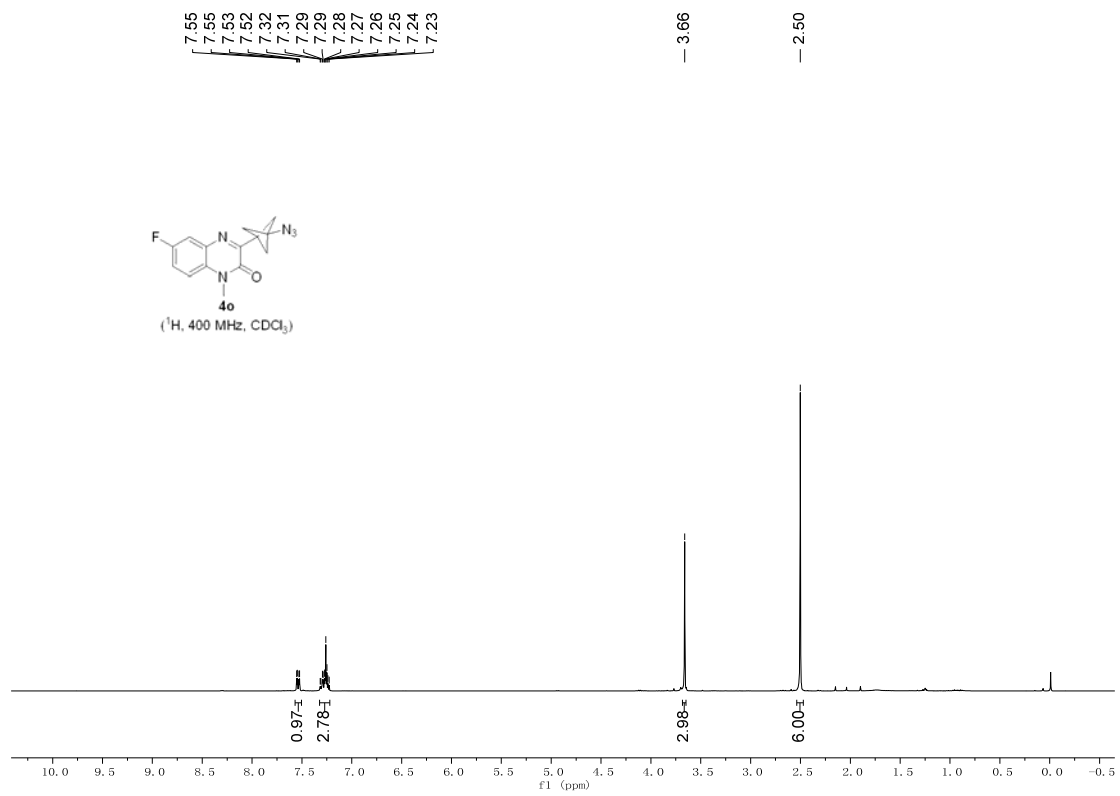


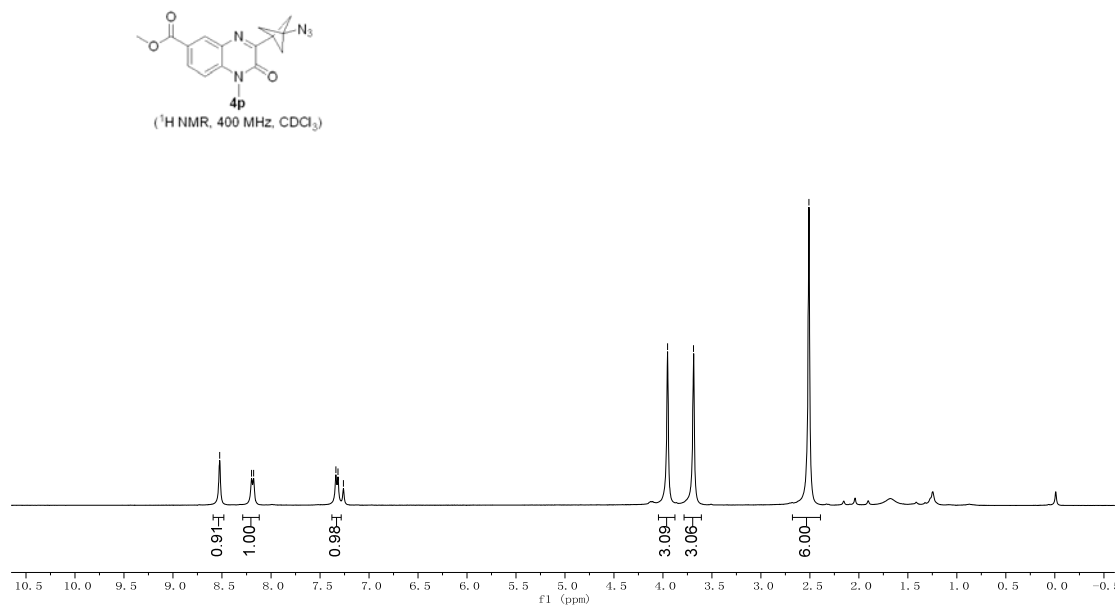
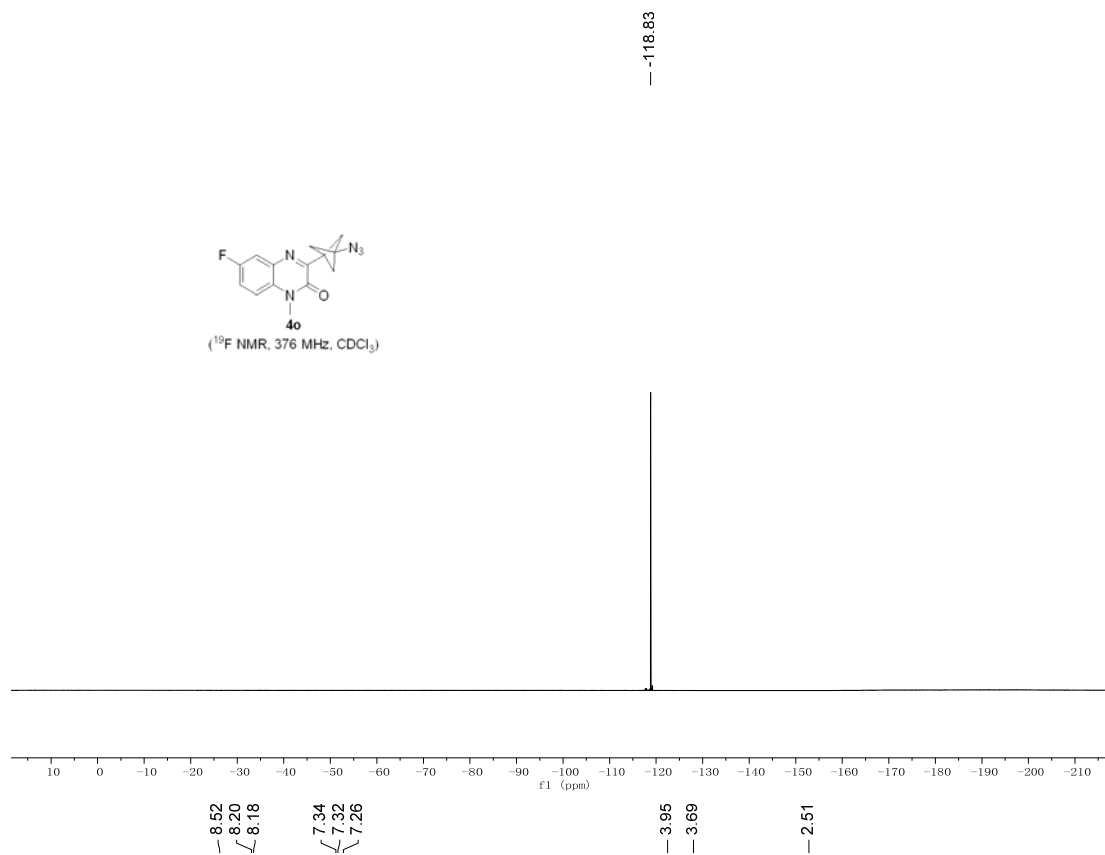


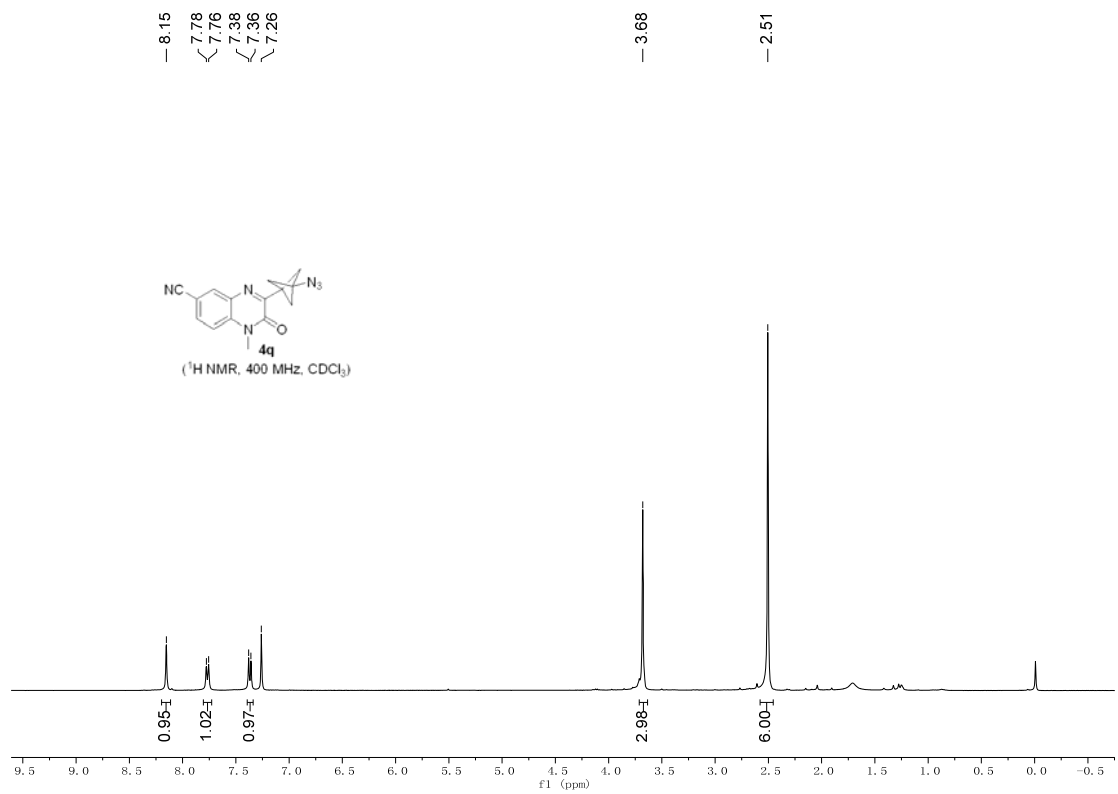
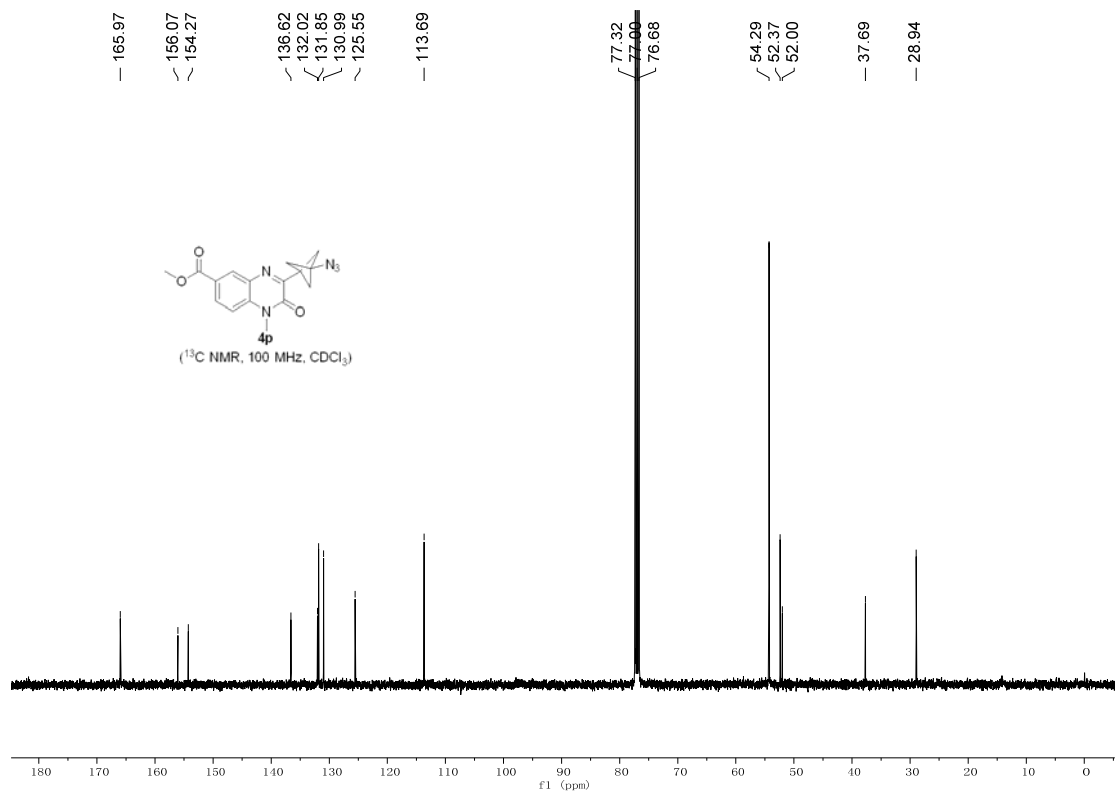


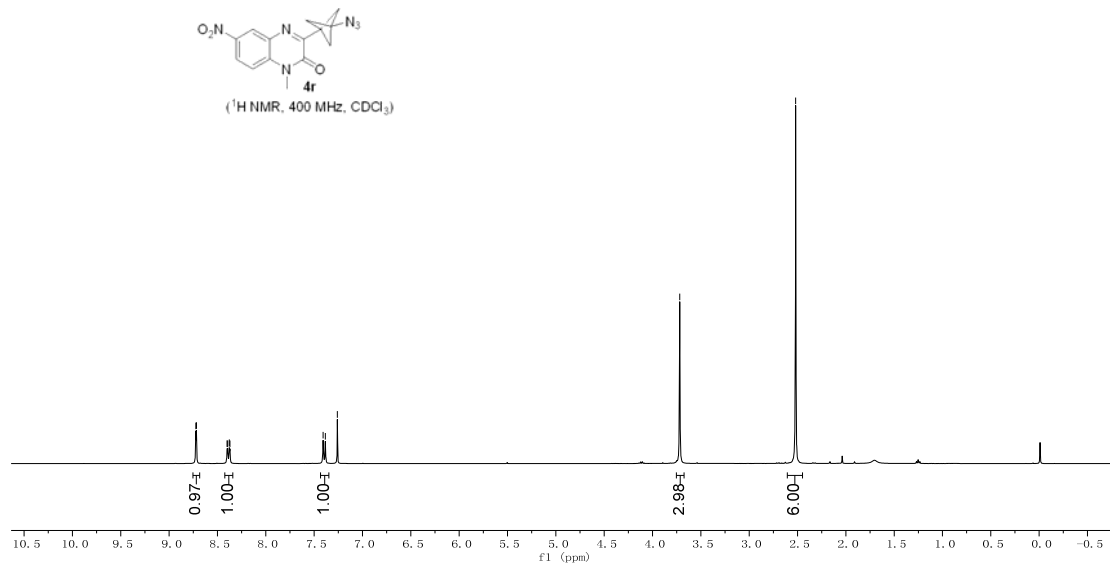
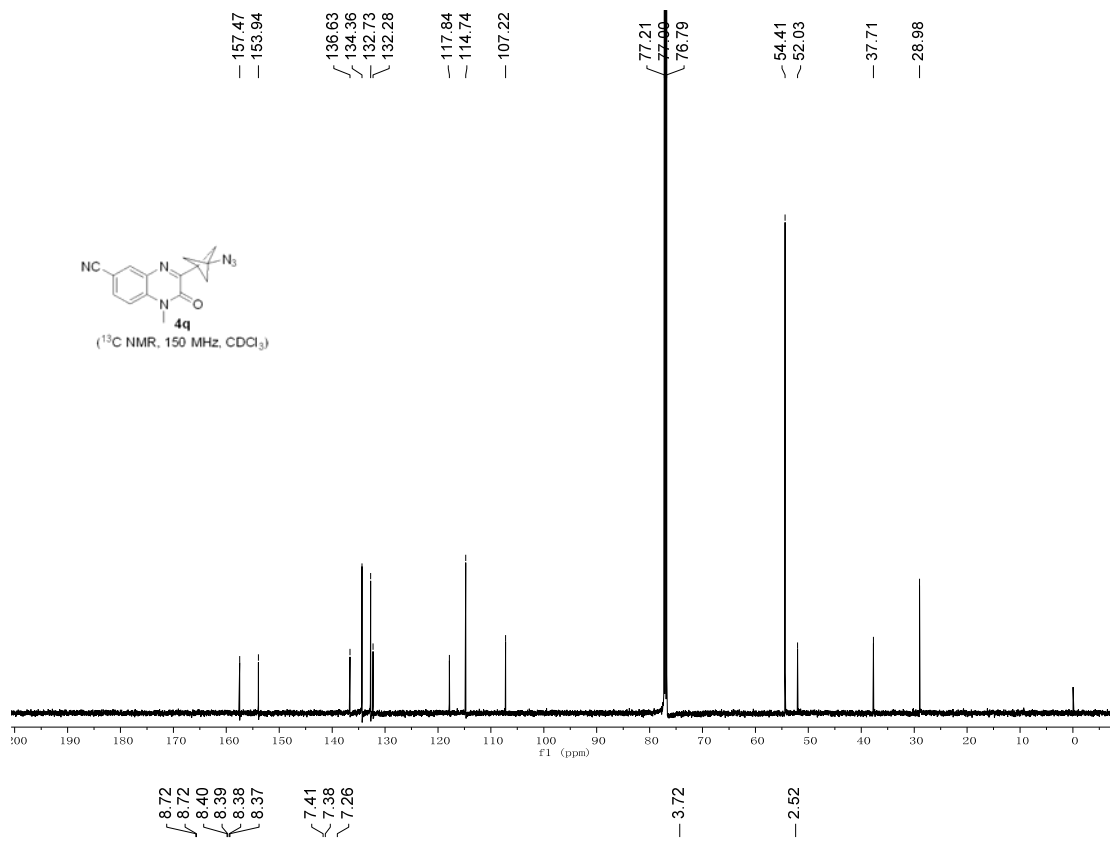


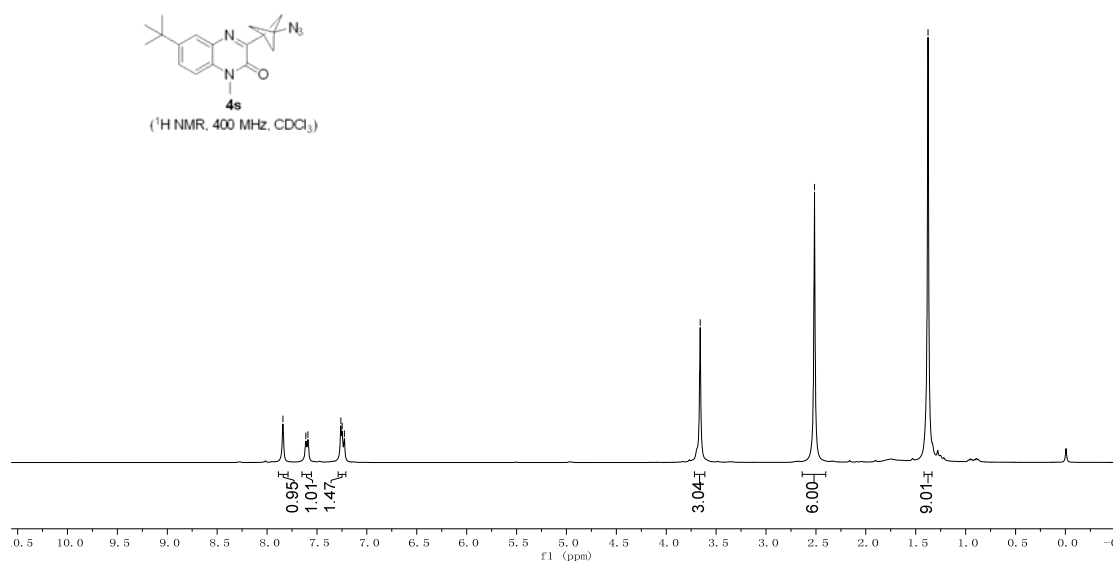
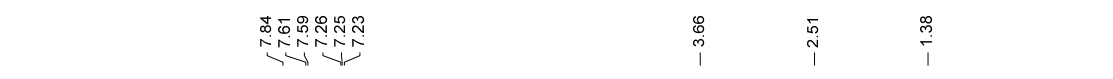
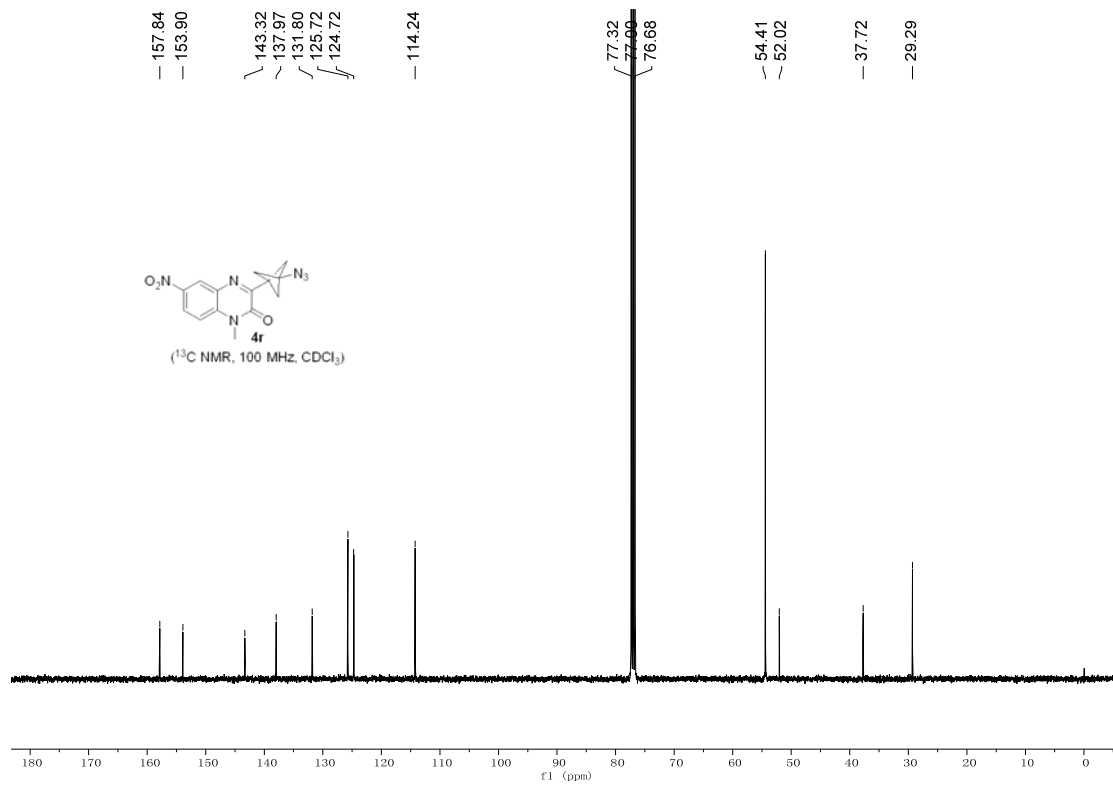


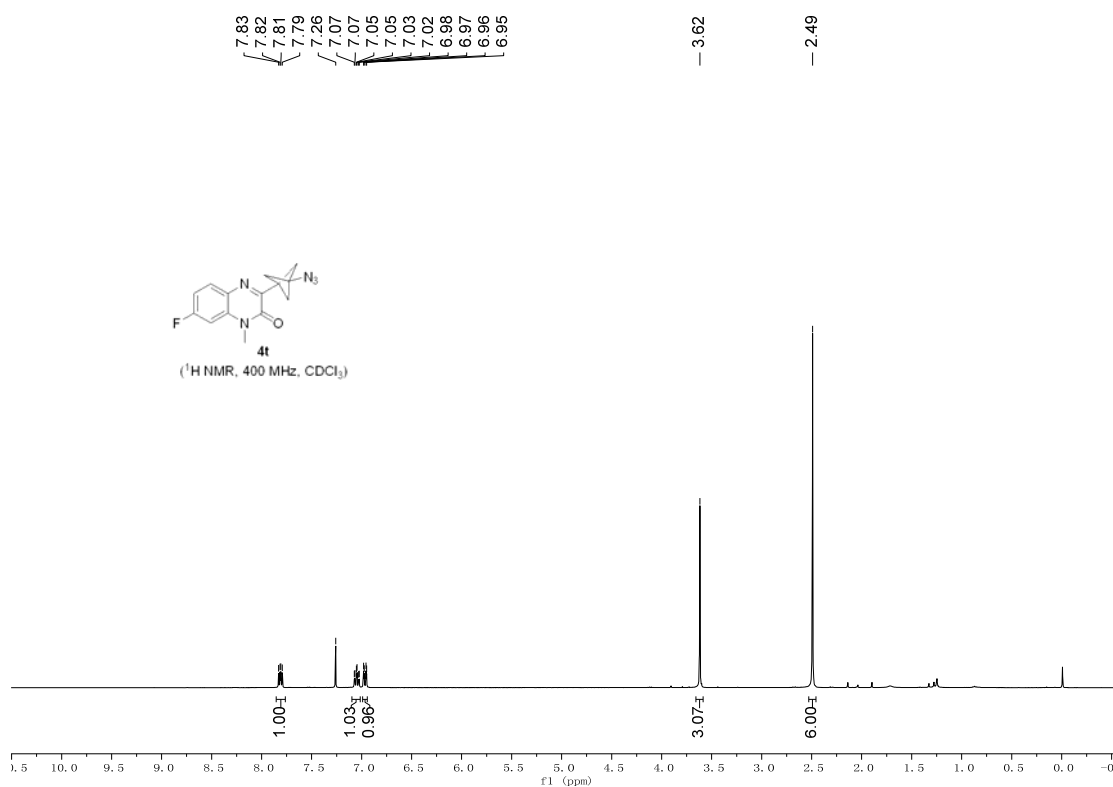
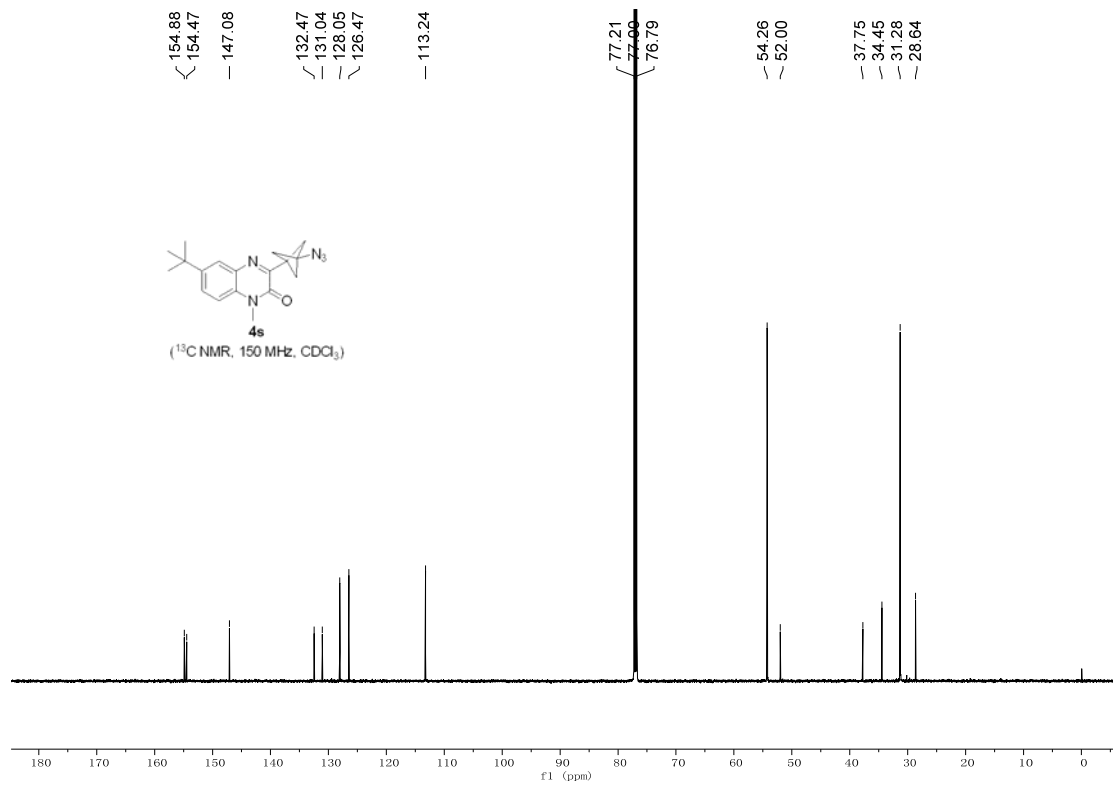


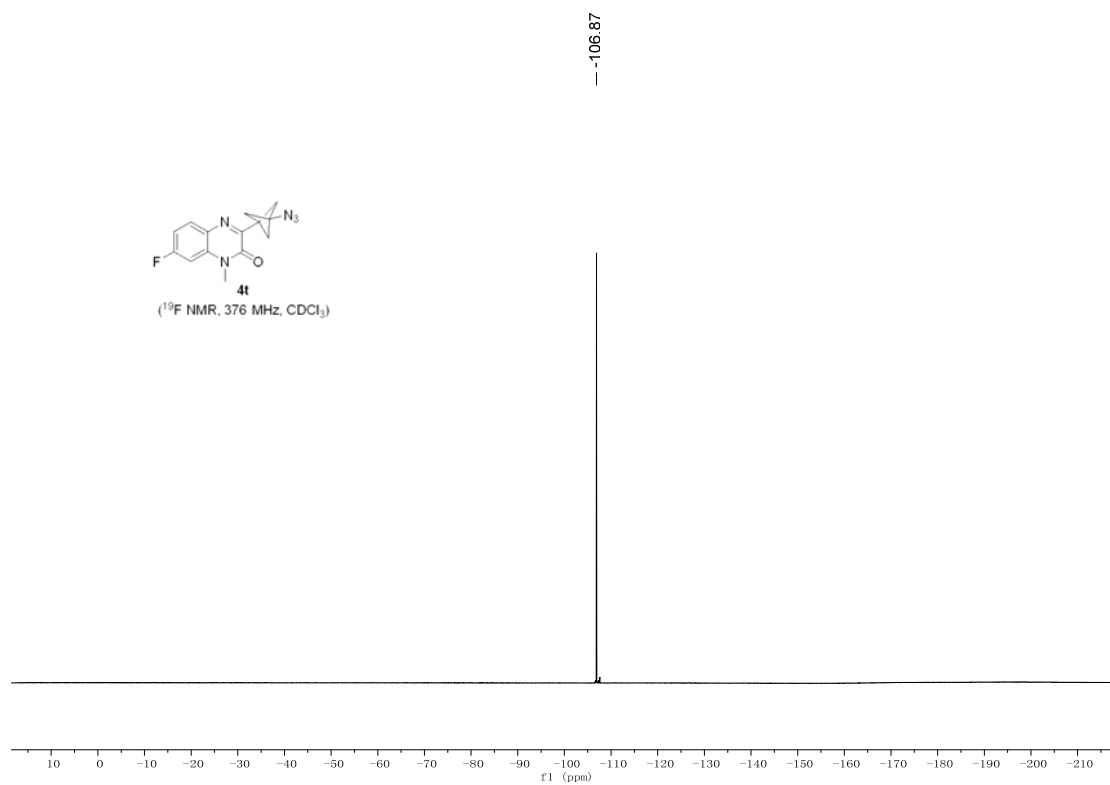
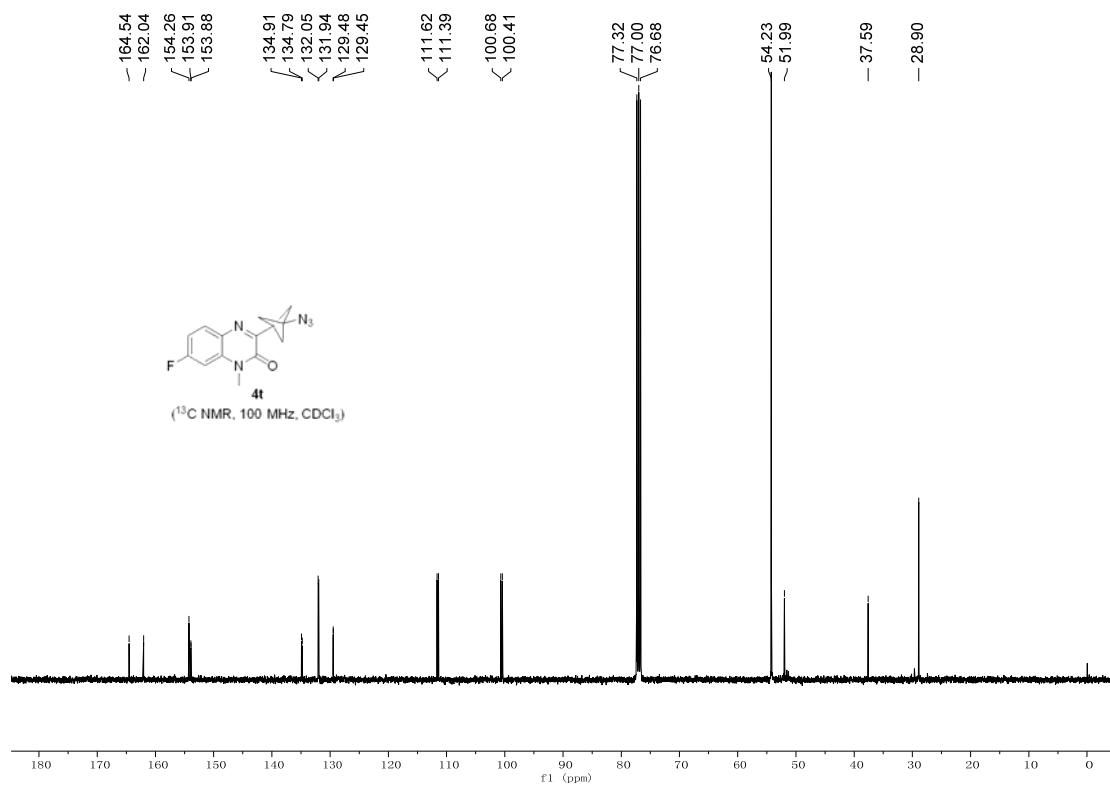


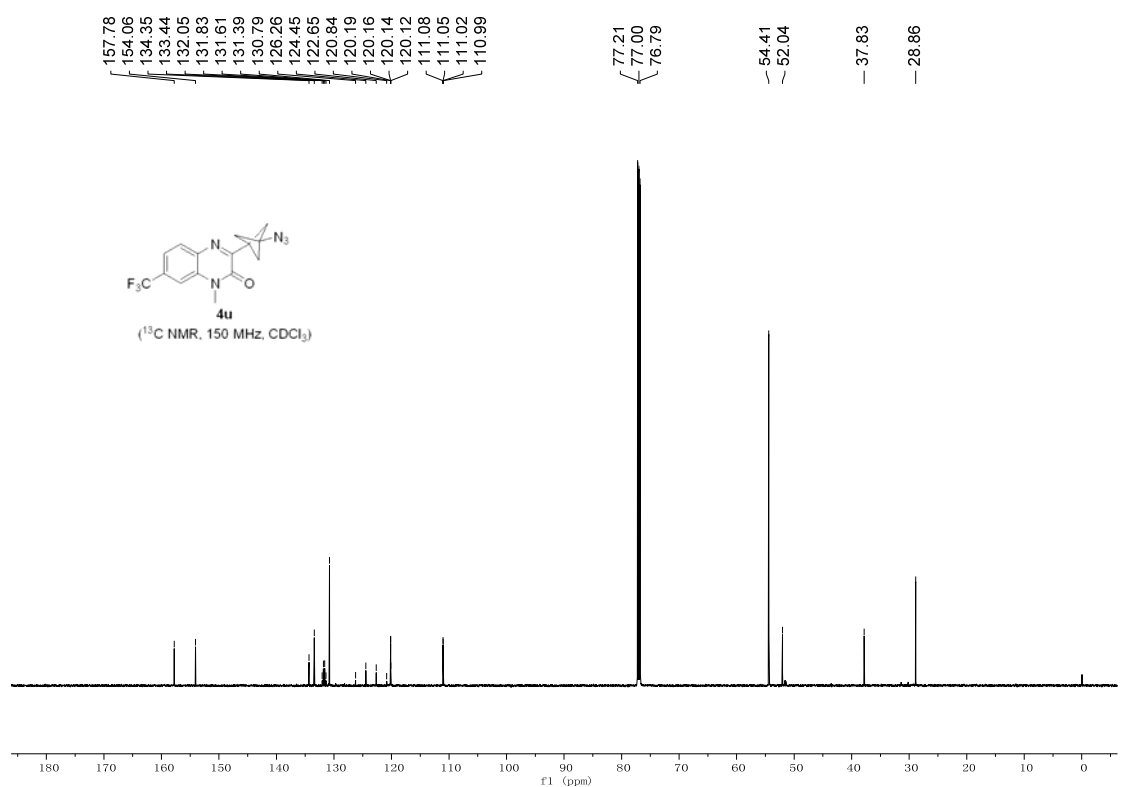
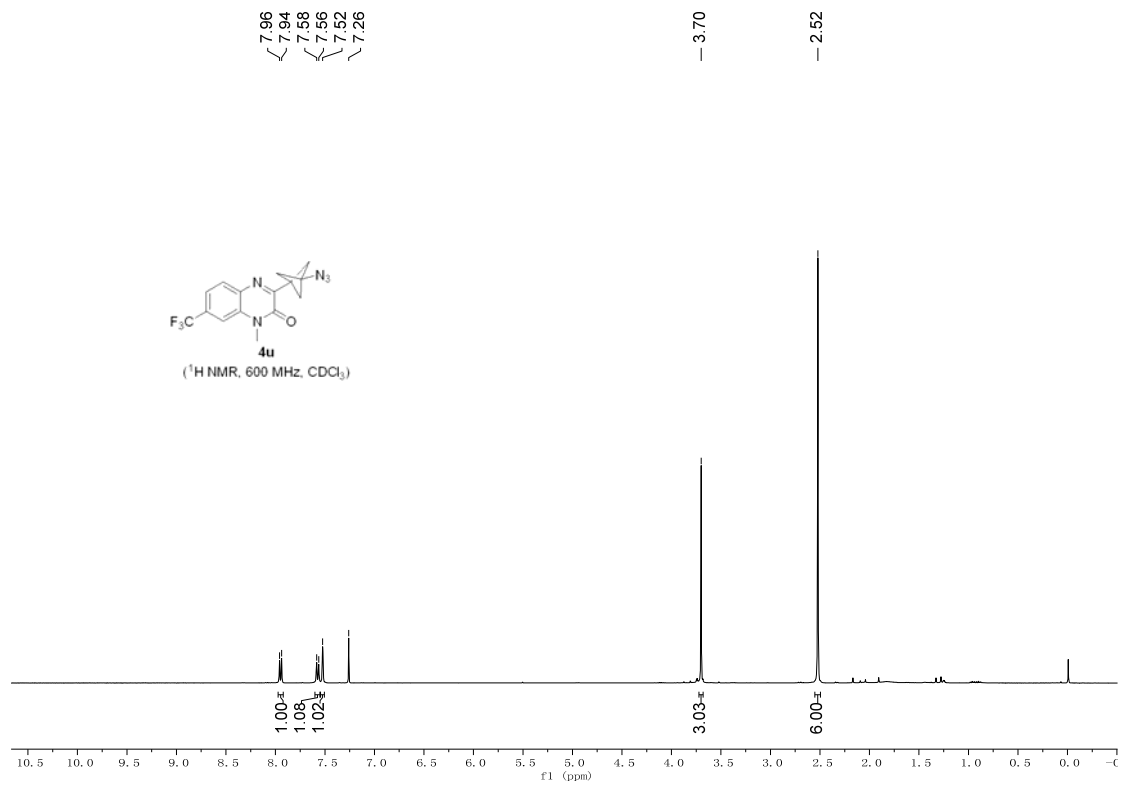


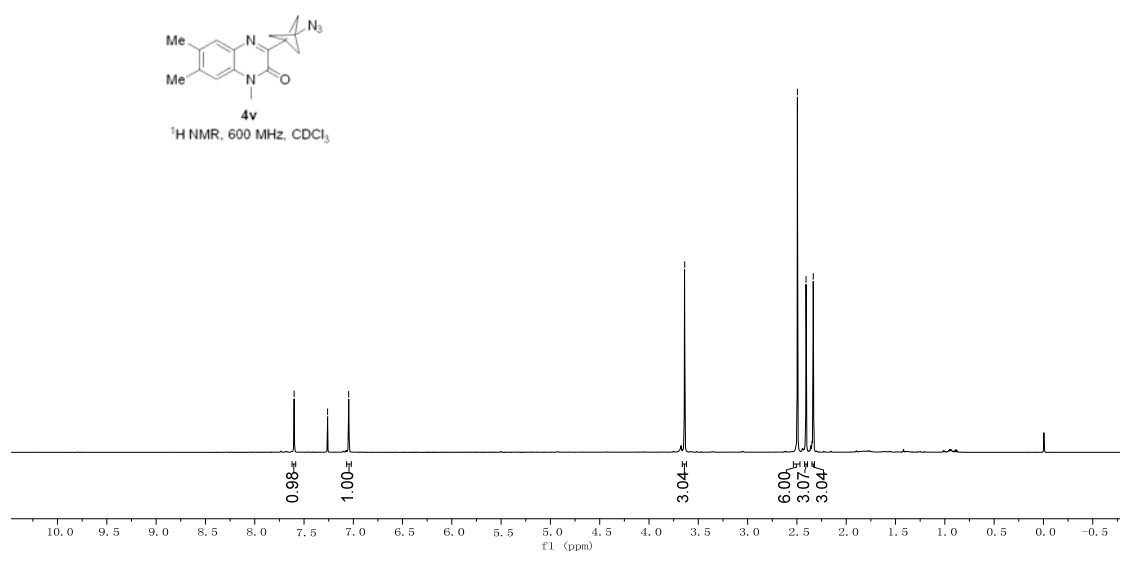
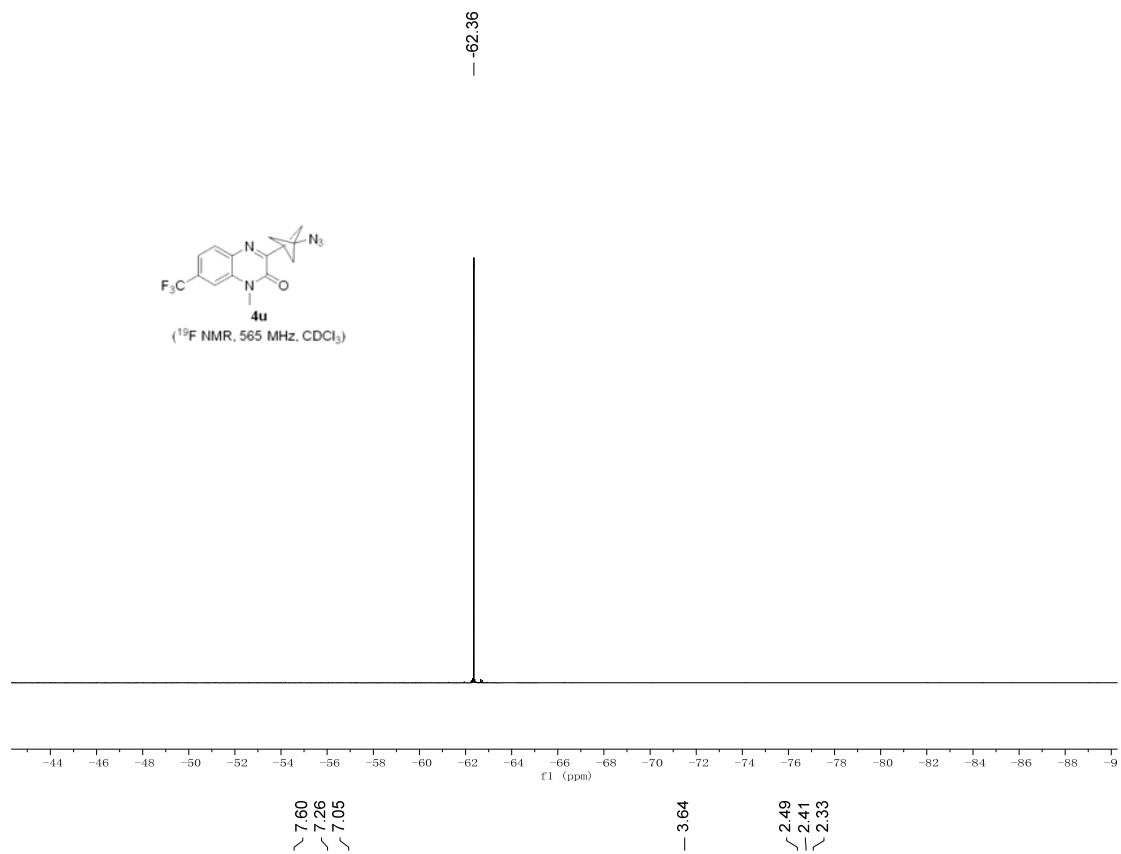


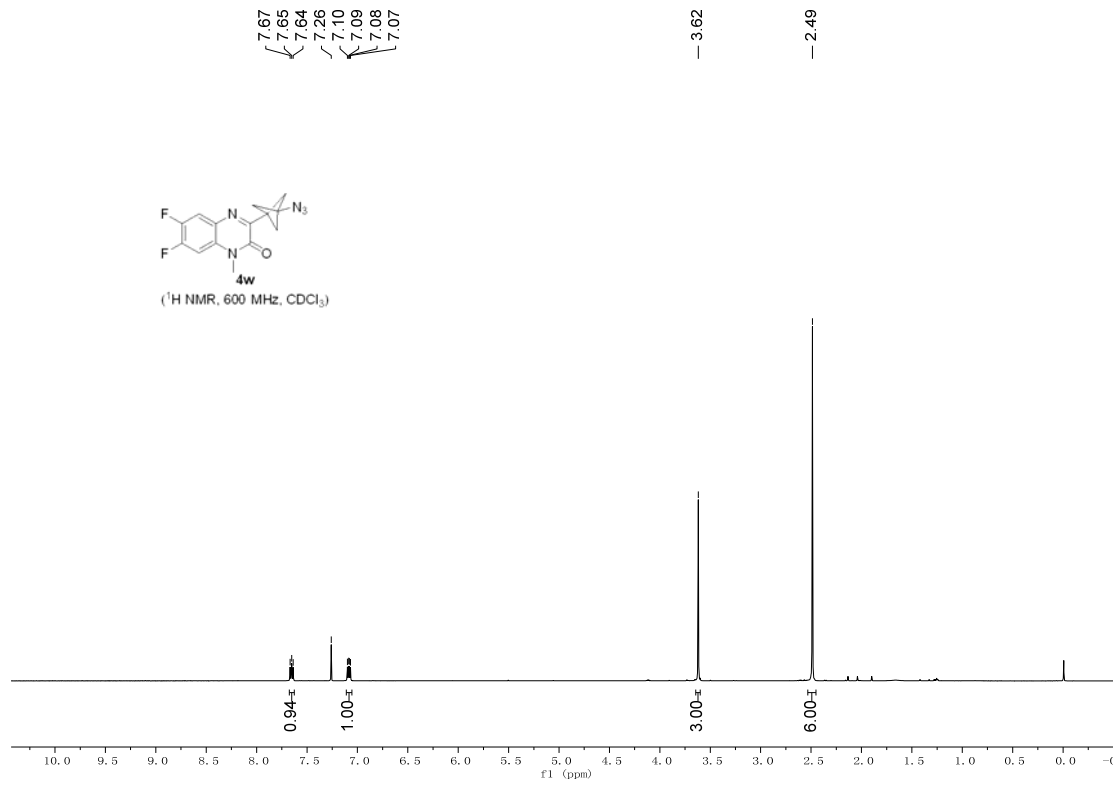
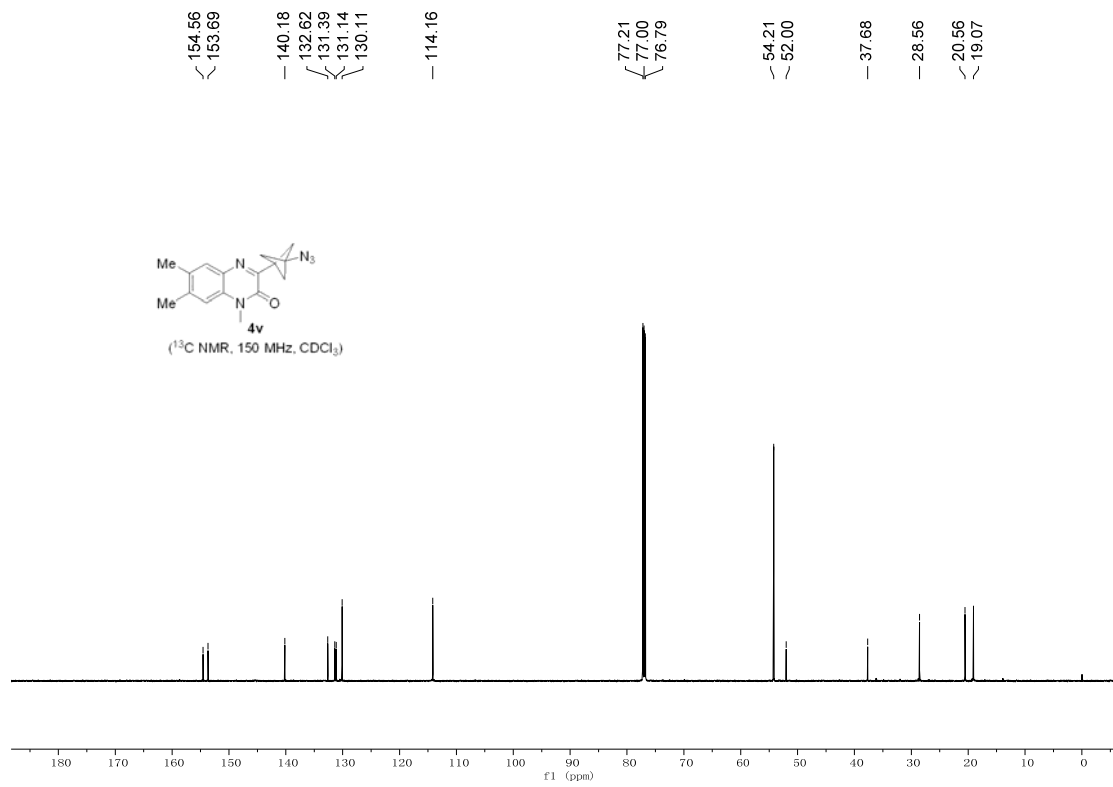


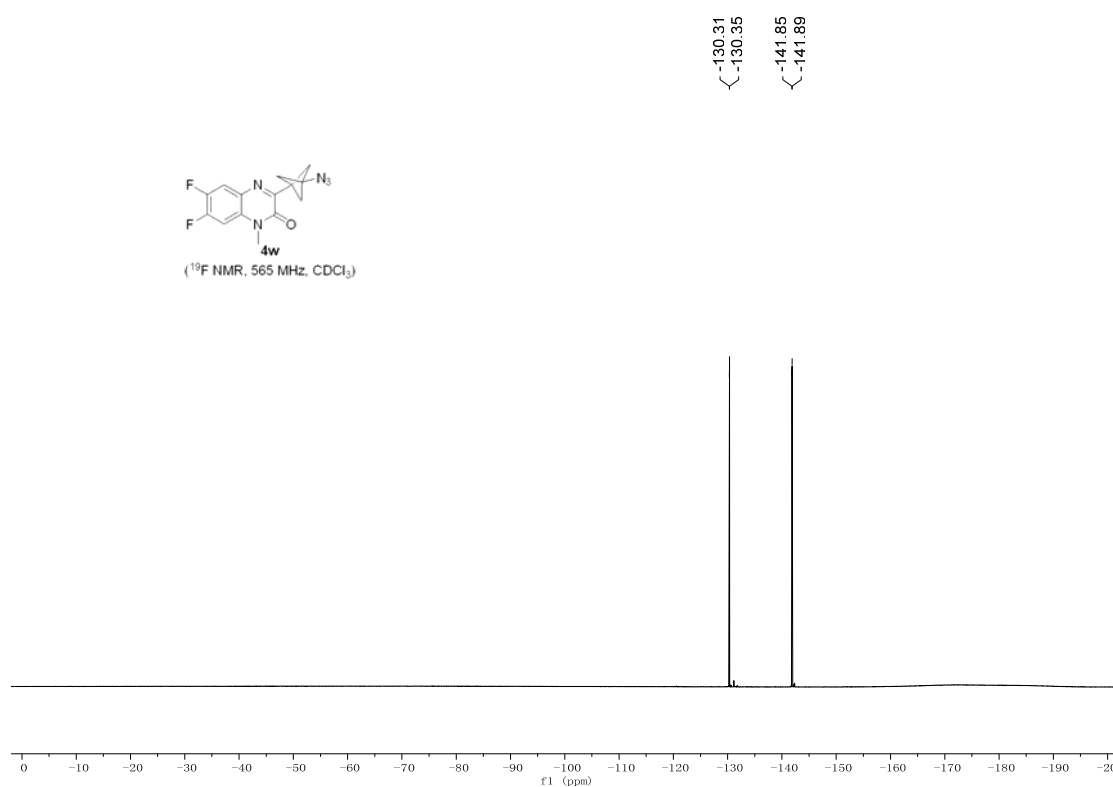
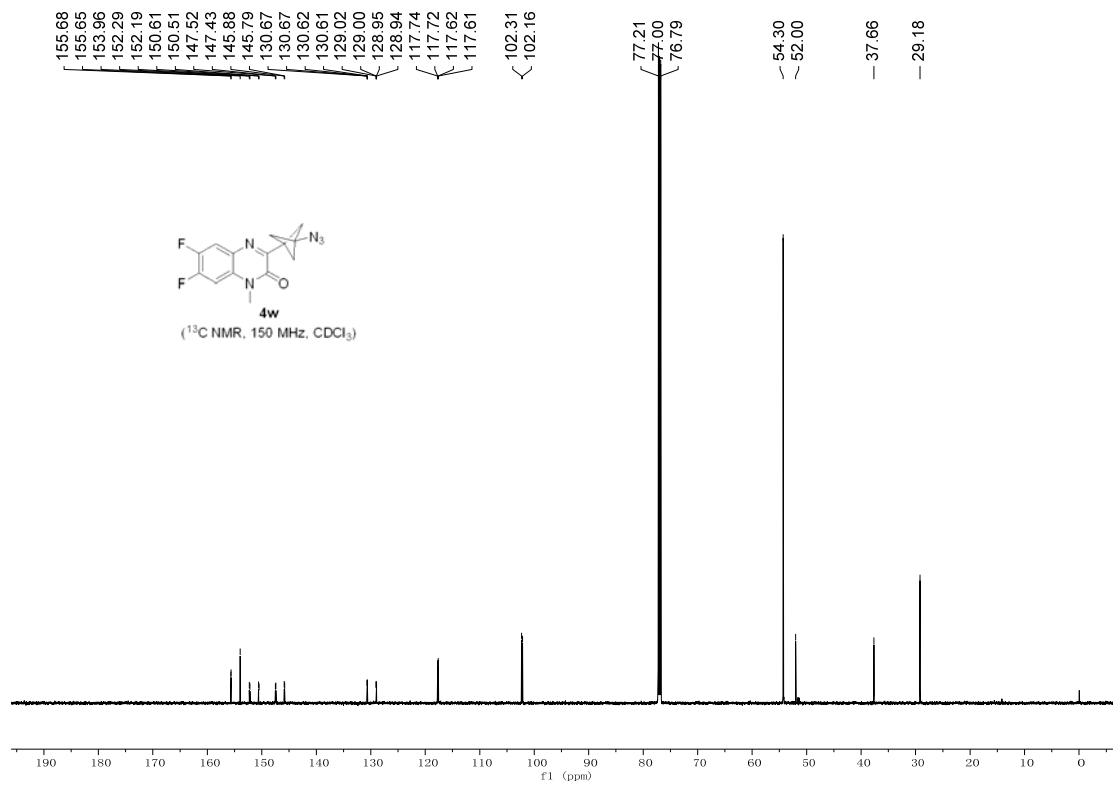


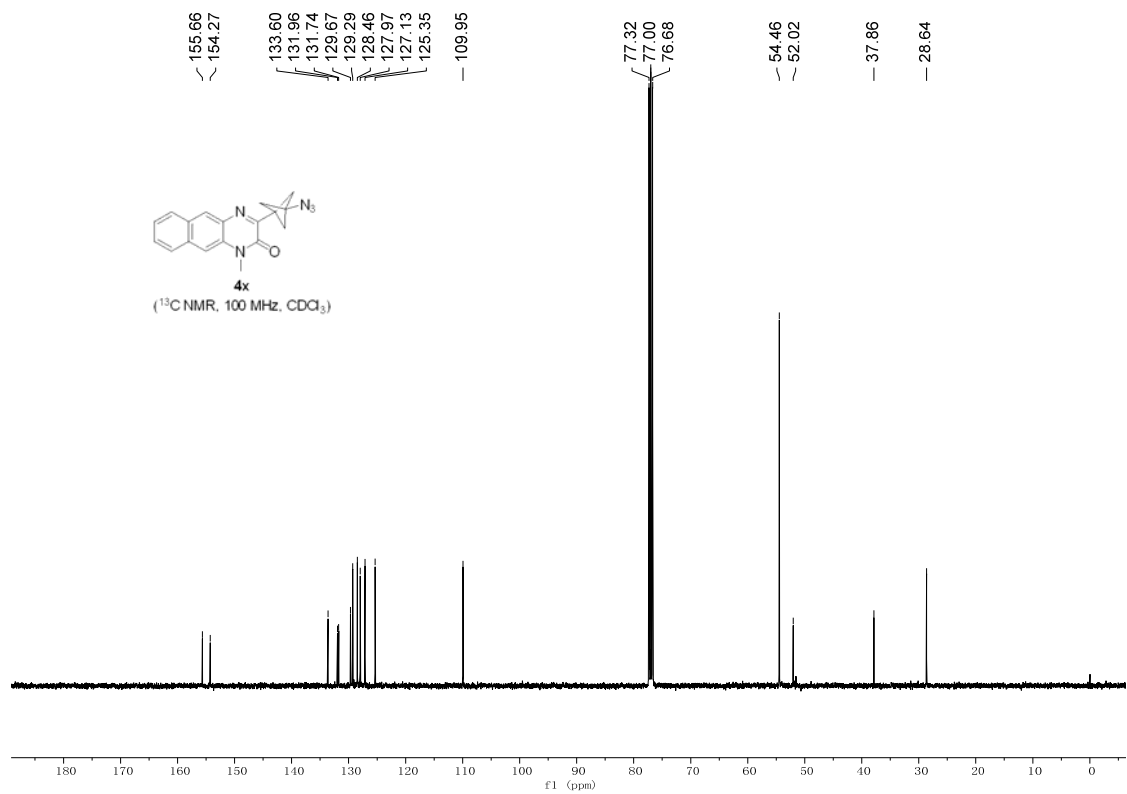
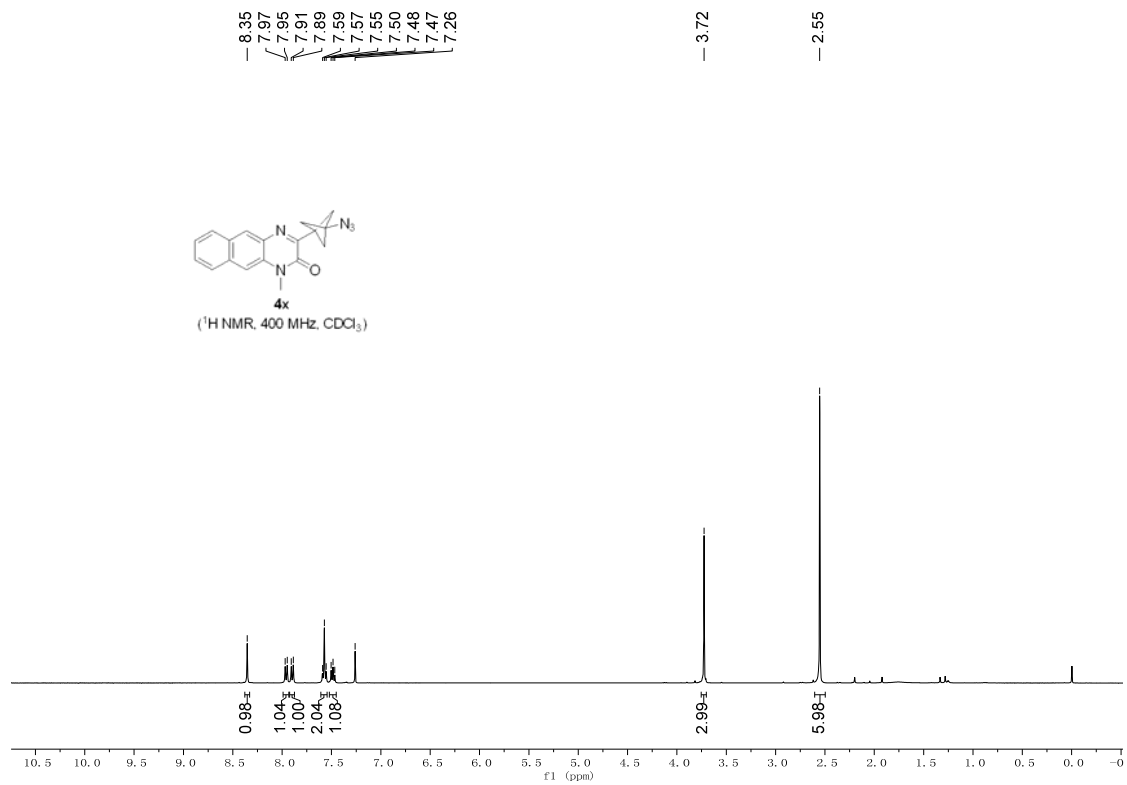


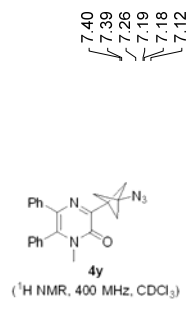




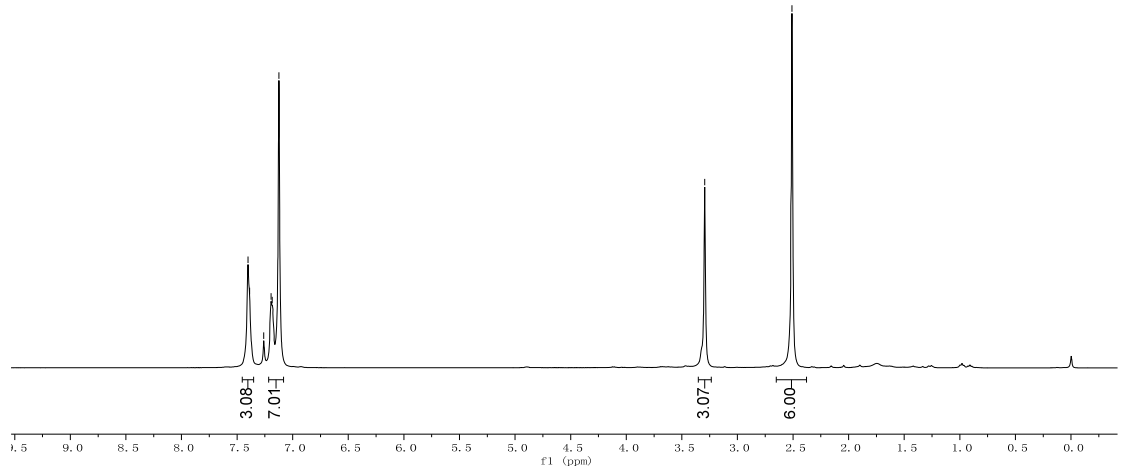








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 — 2.51 —

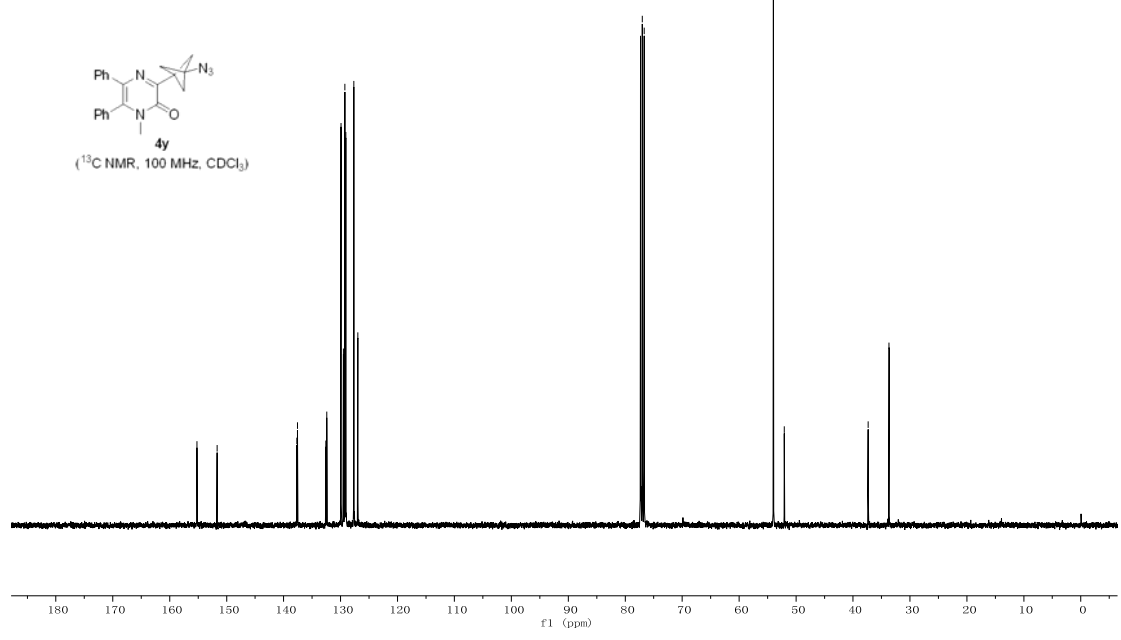
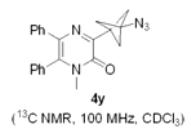


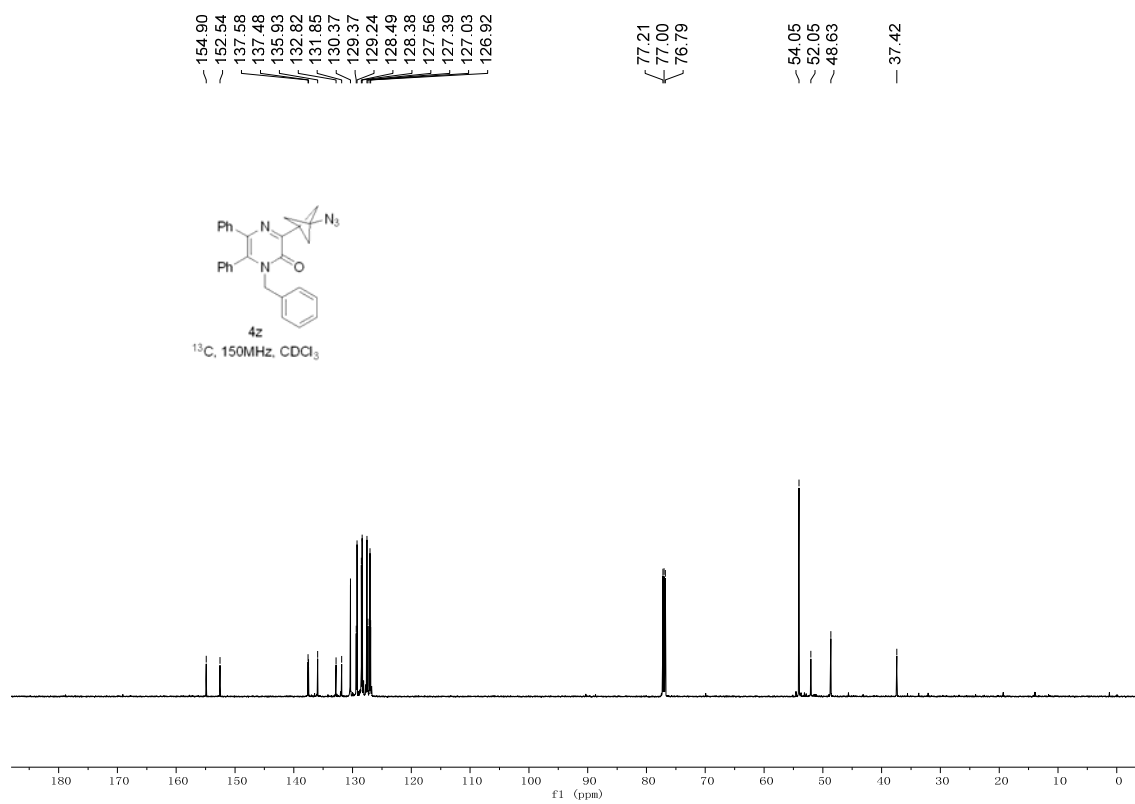
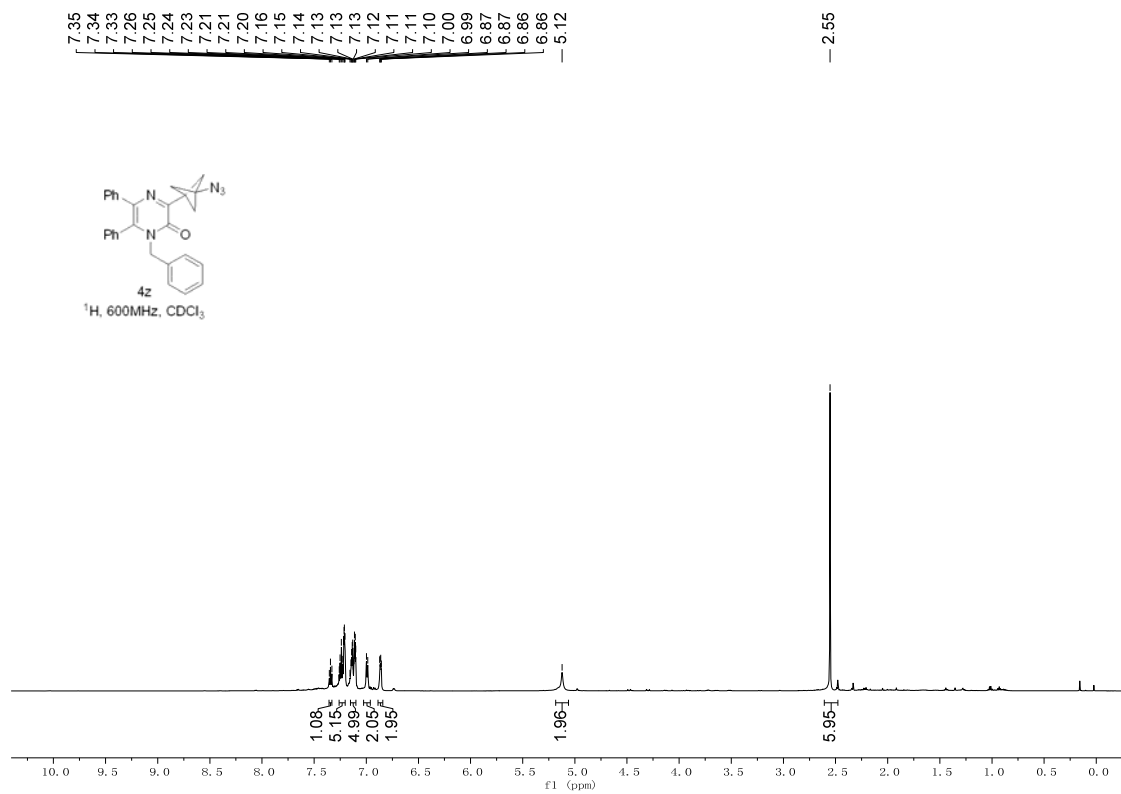
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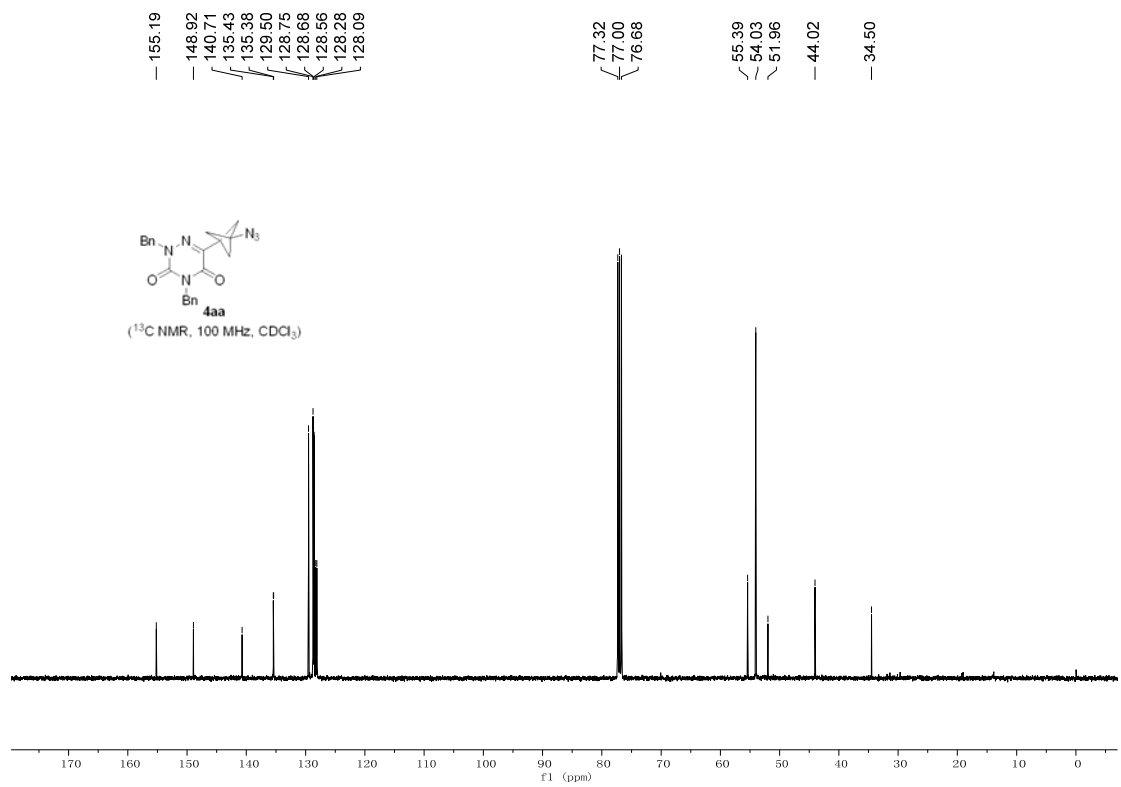
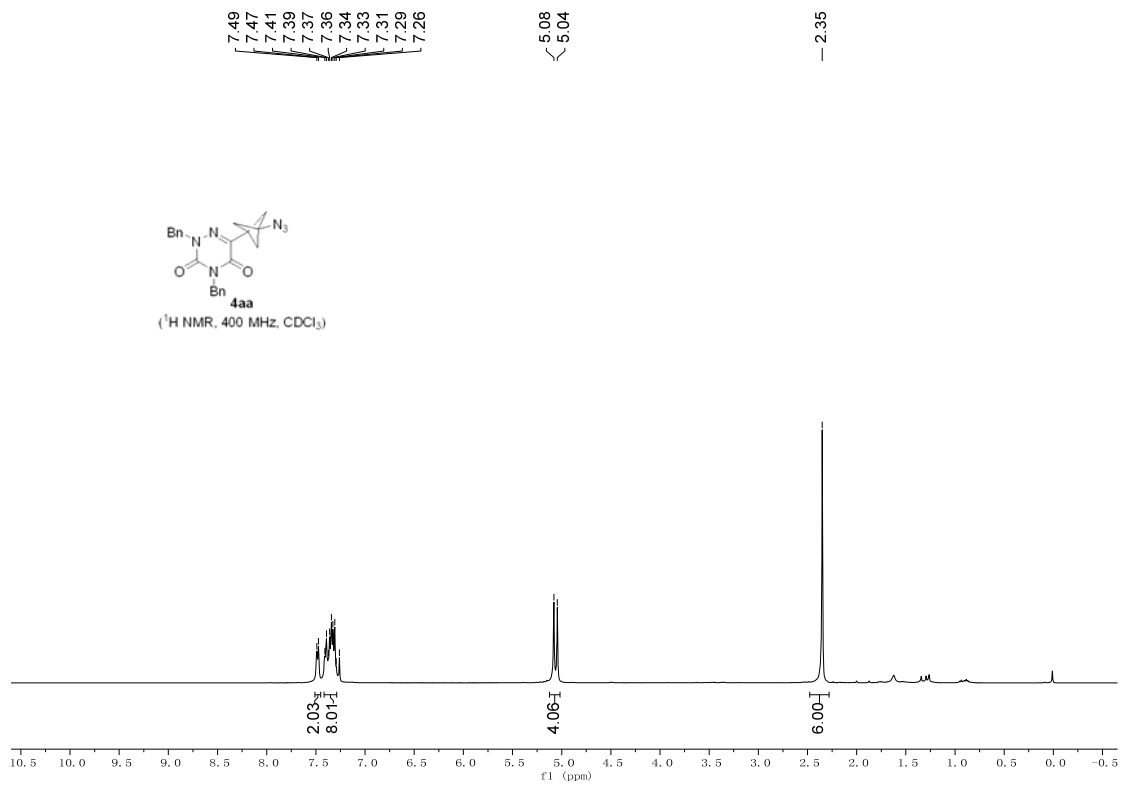
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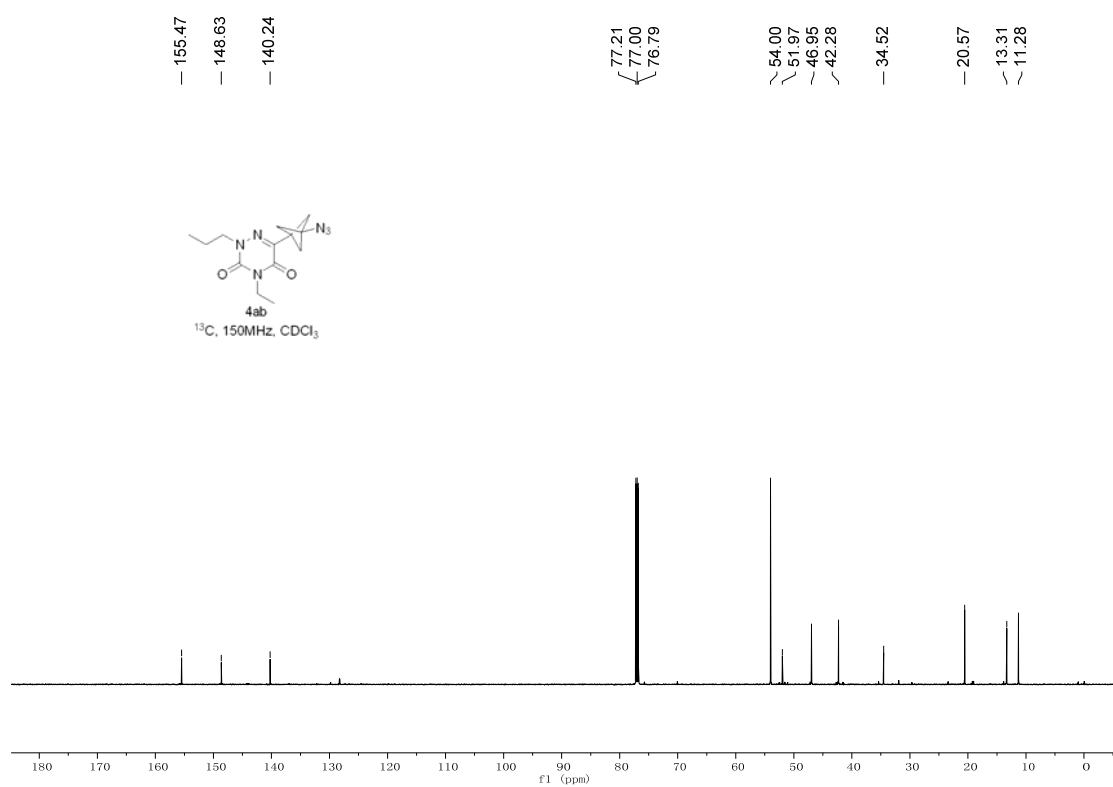
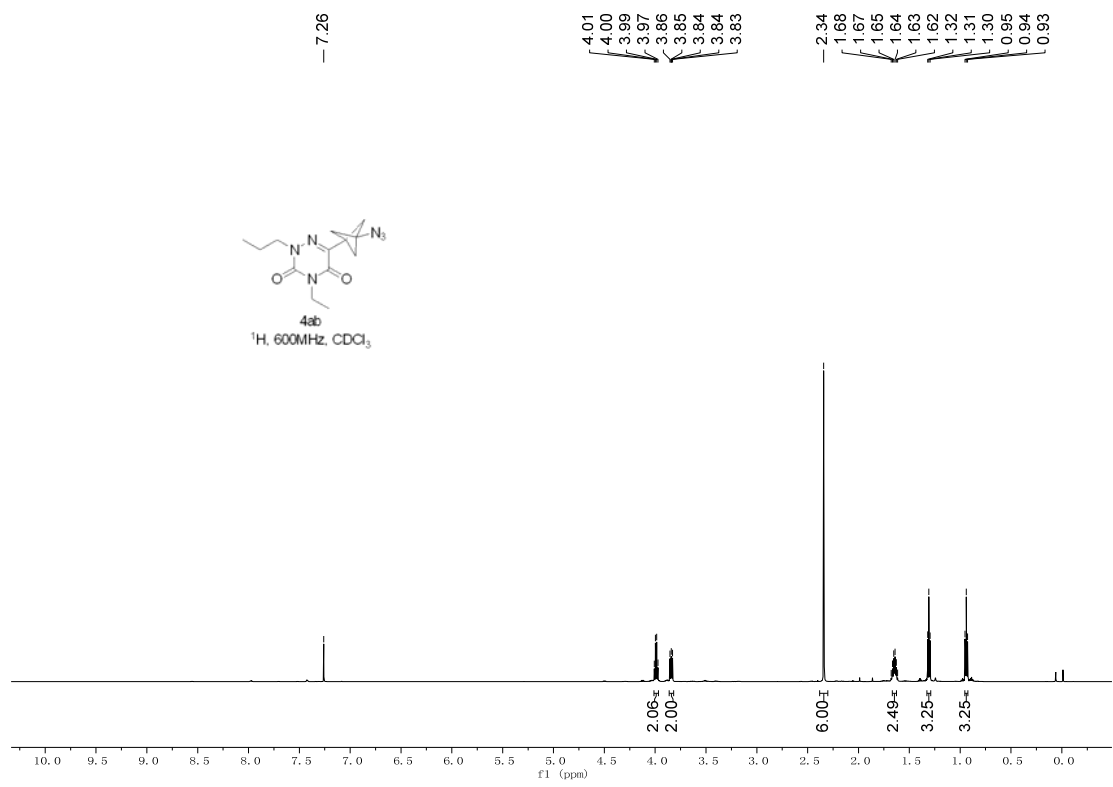
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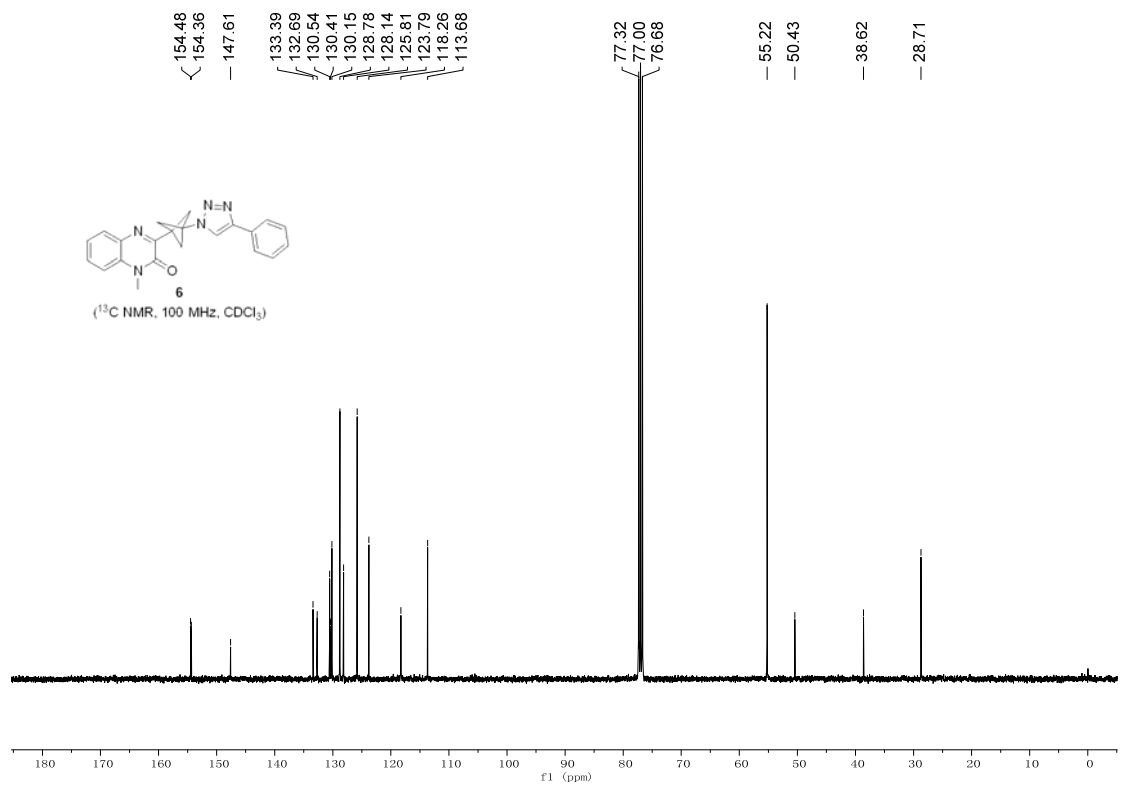
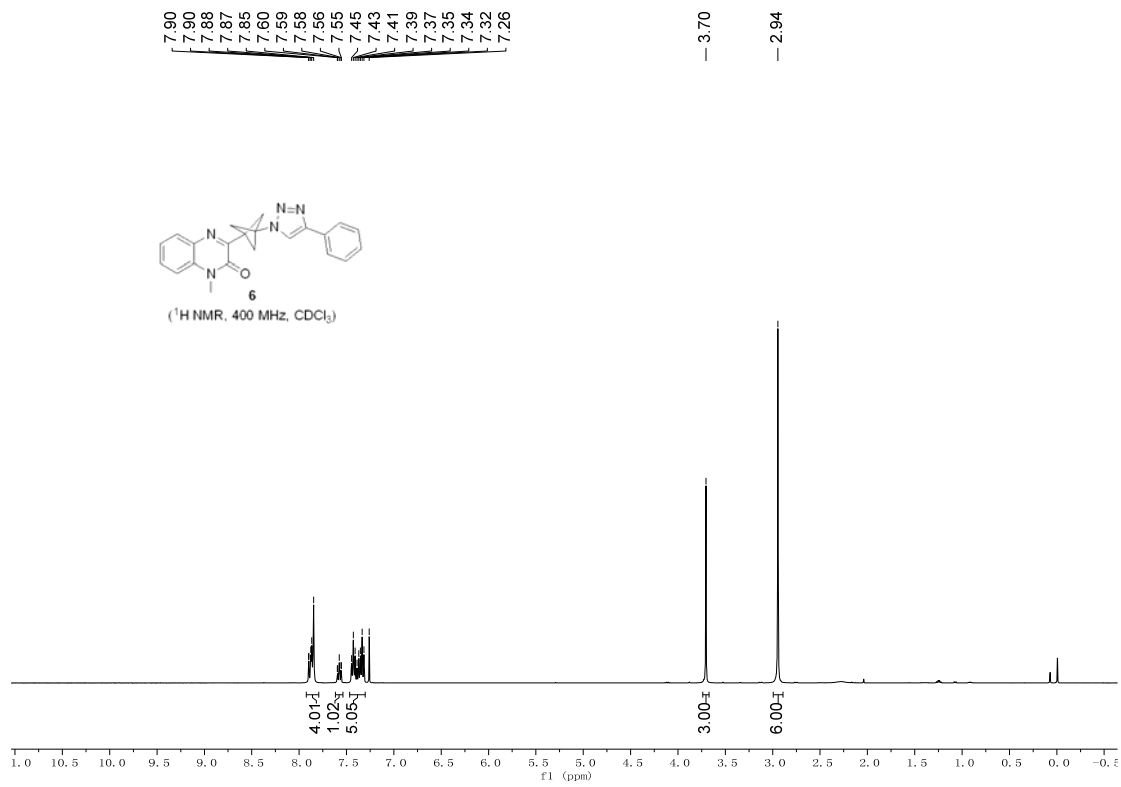
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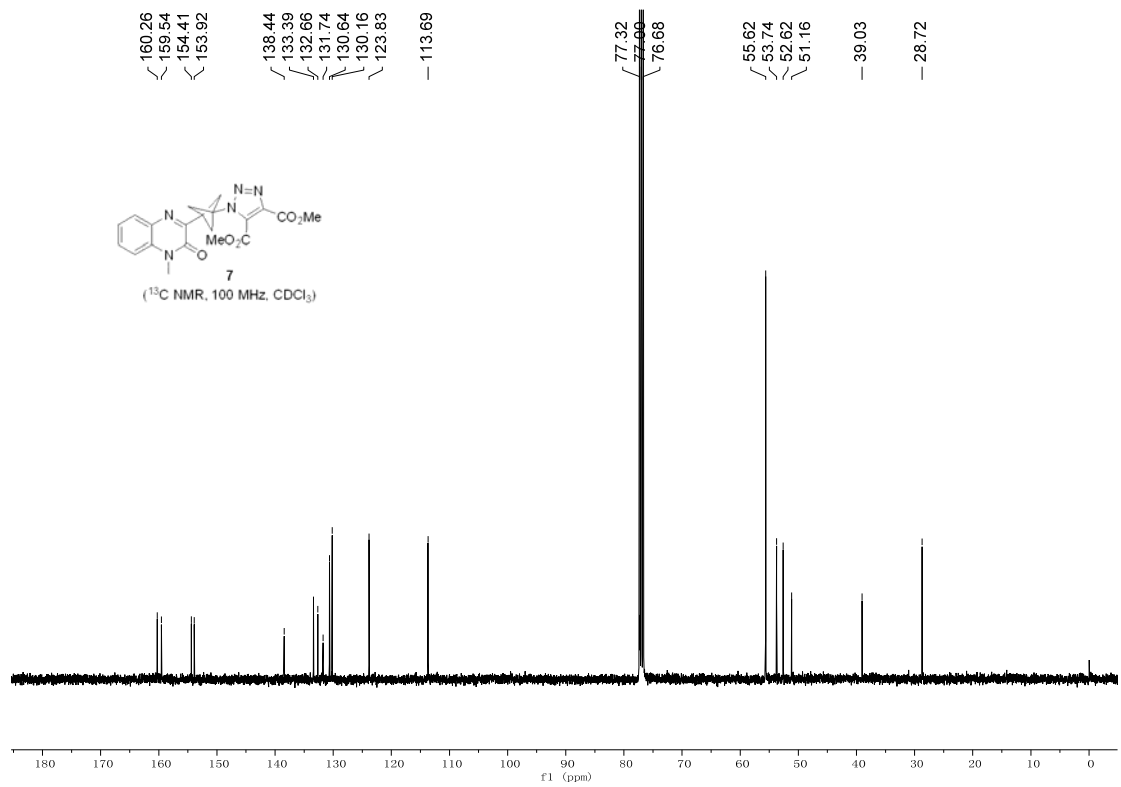
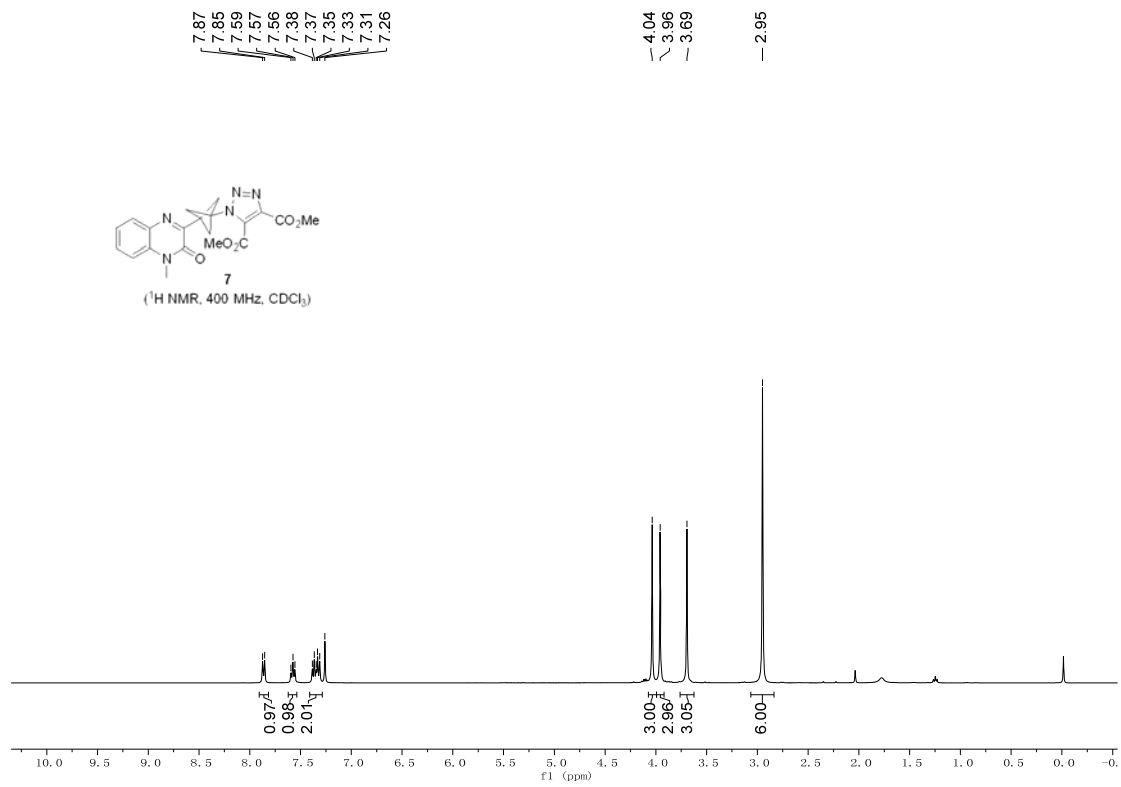


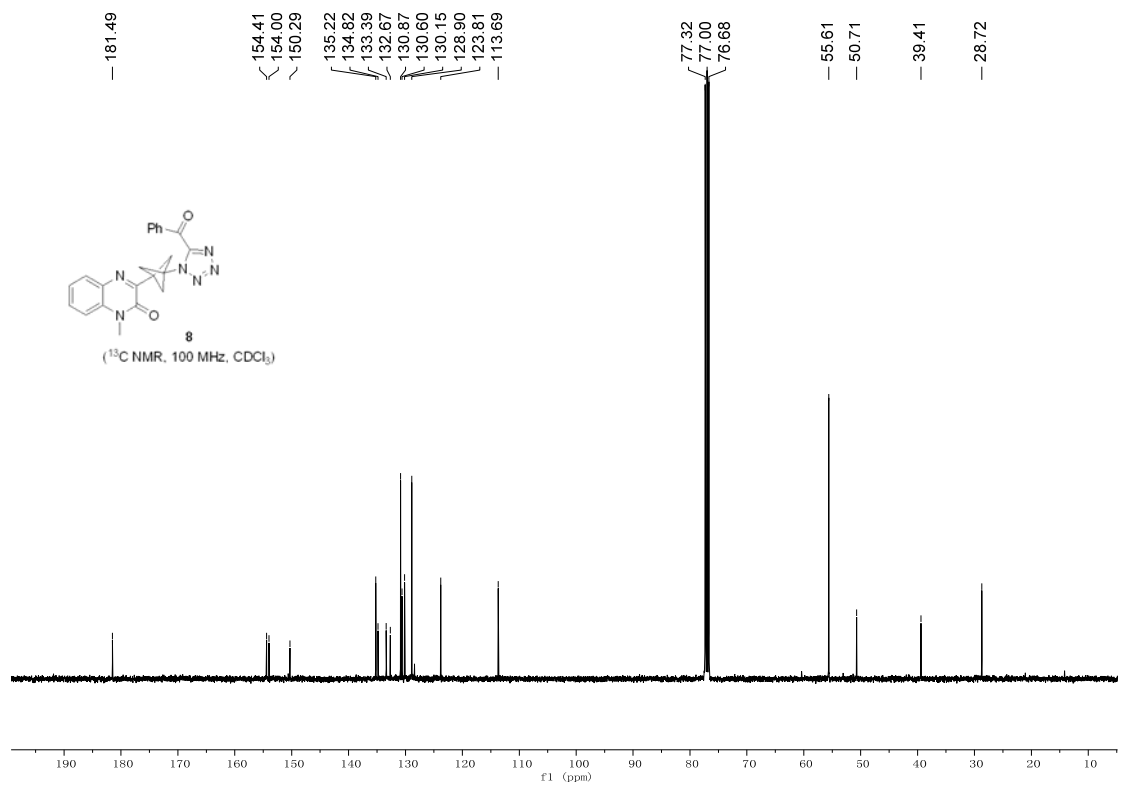
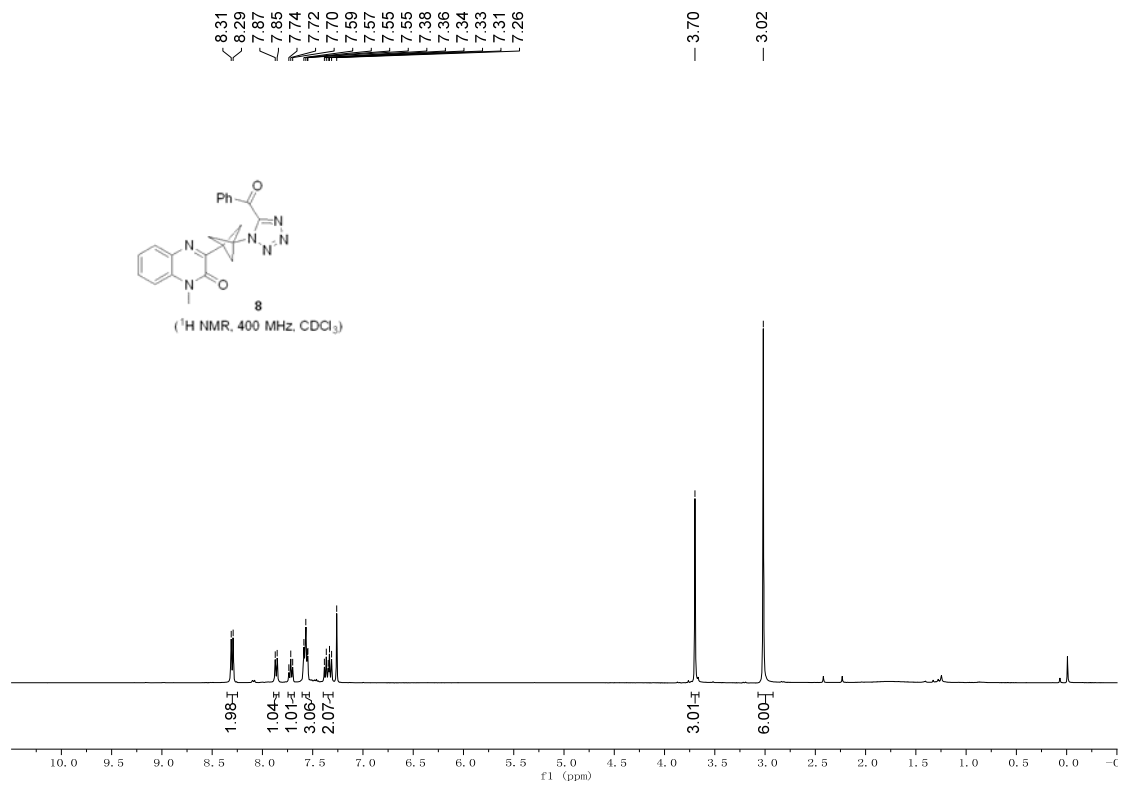




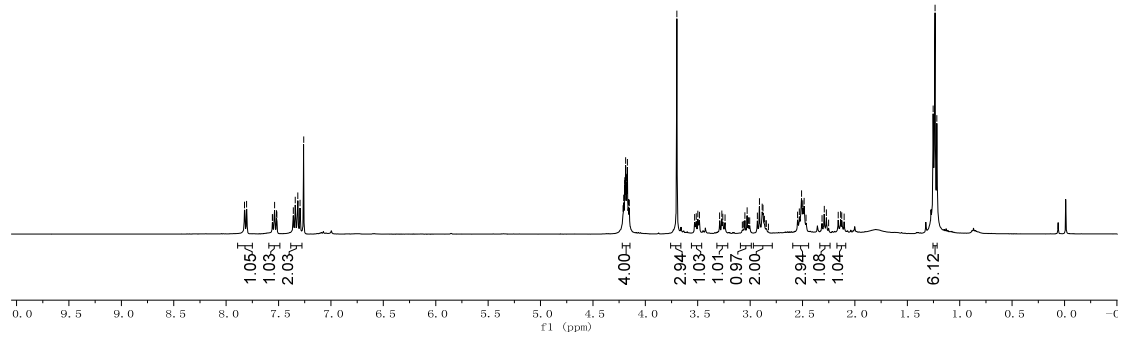
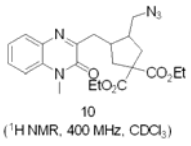








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