Copper-catalyzed radical reaction of 2-azido-*N*-arylacrylamides with 1-(trifluoromethyl) -1,2-benziodoxole and 1-azidyl-1,2-benziodoxole

Tonghao Yang, Haizhen Zhu and Wei Yu*

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University

Lanzhou, 730000, P. R. China

Email: yuwei@lzu.edu.cn; Fax: +86-931-8912582;

Supplementary Information

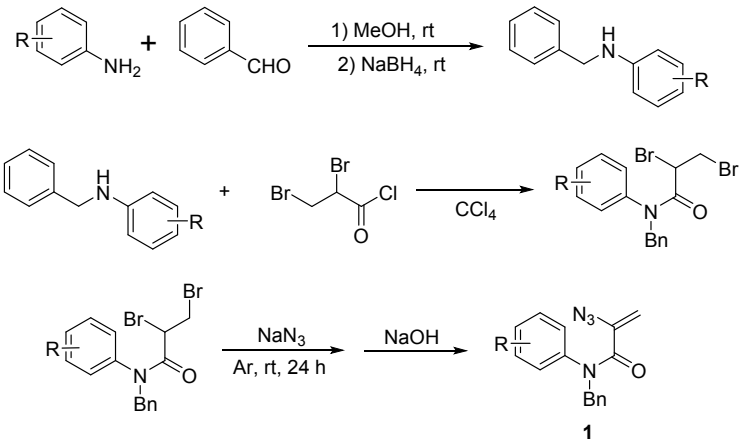
Contents

General methods

The ^{1}H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker AM-400 MHz spectrometer and Bruker AM-300 MHz spectrometer with $CDCl_3$ as the solvent. The chemical shifts in ^{1}H NMR spectra were determined with $Si(CH_3)_4$ as the internal standard (δ = 0.00 ppm). The chemical shifts in ^{13}C NMR spectra were determined based on the chemical shift of $CDCl_3$ (δ = 77.00 ppm). The EI-MS spectra were measured on an HP 5988A spectrometer by direct inlet at 70 eV. The high resolution mass spectra (HRMS) were measured on a Bruker micrOTOF QII by ESI. The Fourier transformation infrared spectra (FT-IR) were measured on a NEXUS 670 spectrometer. Melting points were measured on an XT-4 melting point apparatus and were uncorrected. Flash column chromatography was carried out on silica gel (200-300 mesh). 1-(Trifluoromethyl)-1,2-benziodoxole (Togni's reagent) and 1-azidyl-1,2-benziodoxole (Zhdankin's reagent) were prepared according to the reported methods.[1,2]

General experimental procedures

General procedure for the preparation of 2-azido-*N*-arylacrylamides (compounds 1)



Scheme 1

2-Azido-*N*-arylacrylamides (**1a-1q**) were prepared from arylamines following the procedures given below.

A solution of arylamine (20 mmol) and benzaldehyde (20 mmol, 2 mL) in CH_3OH (250 mL) was stirred at room temperature for 48 h. The reaction flask was then cooled down with an ice-salt bath, and into the flask was added 2.22 g of $NaBH_4$ (60 mmol). The mixture was stirred at temperature for 4 h. After the reaction finished, the reaction mixture was poured into a saturated aqueous $NaHSO_3$ solution (150 mL), and was extracted with ethyl acetate (3× 50 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, and evaporated under reduced pressure on a rotary evaporator. The obtained crude product was purified by column

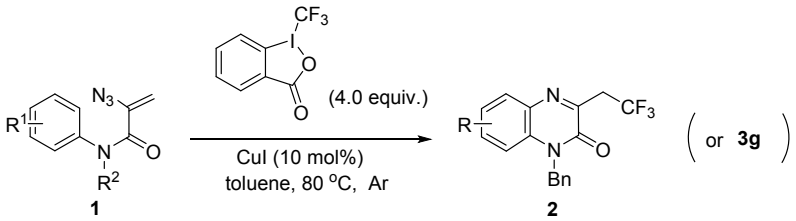
chromatography on silica gel to give the secondary arylamine.[3]

To a stirred solution of secondary arylamine (15 mmol) in 30 mL CCl_4 (held in a 100 mL flask immersed in an ice-salt bath) was added over 30 min a solution of 2,3-dibromopropanoyl chloride (15 mmol, 3.75 g) in 10 mL CCl_4. The mixture was stirred at room temperature for 12 h. After that, the mixture was poured into a saturated aqueous $NaHCO_3$ solution (50 mL), and the aqueous phase was extracted with CH_2Cl_2 (3× 30 mL). The combined organic phases were then washed with brine, dried over Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The thus obtained crude product was purified by column chromatography on silica gel (with petroleum ether and ethyl acetate (15:1) as effluent unless otherwise specified) to give 2,3-dibromo-*N*-aryllpropanamide.[4]

A solution of 2,3-dibromo-*N*-aryllpropanamide (10 mmol) and NaN_3 (12 mmol, 0.78 g) in DMSO (50 mL) was stirred overnight at room temperature under an argon atmosphere. Then to the solution was injected with a syringe an aqueous NaOH solution (1.5 mL of water containing 0.60 g of NaOH (15 mmol)). 24 h later, the mixture was poured into a saturated aqueous $NaHCO_3$ solution (50 mL), and was extracted with ethyl acetate (3× 50 mL). The combined organic phases were washed with brine (6× 100 mL), dried over Na_2SO_4, and concentrated under reduced pressure on a rotary evaporator. The residual was treated with silica gel column chromatography (with petroleum ether and ethyl acetate (15:1) as effluent) to give **1**.[5]

Compounds **1r-1t** were prepared from the corresponding starting materials following the same procedure.

General procedure for the reaction of 1 with Togni's reagent

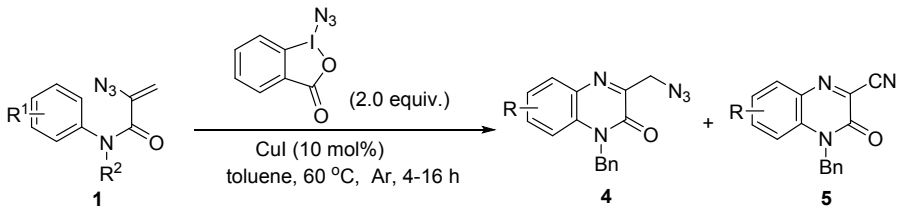


1 2

Scheme 2

A mixture of **1** (0.5 mmol), 1-(trifluoromethyl)-1,2-benziodoxole (2.0 mmol, 632 mg) and CuI (0.05 mmol, 9.5 mg) in 5 mL toluene was stirred at 80 °C under an argon atmosphere for 16 h. The reaction mixture was then cooled to room temperature, and was poured into a saturated K_2CO_3 aqueous solution (10 mL). The aqueous phase was extracted with ethyl acetate (3×10 mL), and the combined organic layers were washed sequentially with saturated K_2CO_3 aqueous solution (10 mL) and brine, and then dried over Na_2SO_4. The solvent was evaporated under reduced pressure on a rotary evaporator, and the residual was purified by column chromatography on silica gel (with petroleum and ether ethyl acetate (10:1) as effluent unless otherwise specified) to give product **2** (or **3g**).

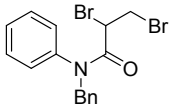
General procedure for the reaction of 1 with Zhdankin's reagent



Scheme 3

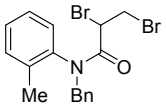
A mixture of **1** (0.5 mmol), 1-azidyl-1,2-benziodoxole (1.0 mmol, 289 mg) and CuI (0.05 mmol, 9.5 mg) in 5 mL toluene was stirred at 60 °C (in an oil bath) under an argon atmosphere until **1** was consumed completely as indicated by TLC (4-16 h). The reaction mixture was then cooled down to room temperature, and was poured into a saturated aqueous K_2CO_3 solution (10 mL). The aqueous phase was extracted with ethyl acetate (3× 10 mL), and the combined organic layers were washed sequentially with saturated aqueous K_2CO_3 solution (10 mL) and brine, and then dried over Na_2SO_4. The solvent was evaporated under reduced pressure on a rotary evaporator, and the residual was purified by silica gel column chromatography (with petroleum ether and ethyl acetate (5:1) as effluent) to give products **4** and **5**.

Characterization data for 2,3-dibromo-*N*-arylpropanamides, and 2-azido-*N*-arylacrylamides



***N*-Benzyl-2,3-dibromo-*N*-phenylpropanamide**

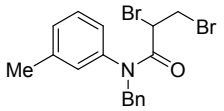
Yellow solid: m.p. = 86–87 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.37–7.35 (m, 3H), 7.29–7.26 (m, 3H), 7.24–7.22 (m, 2H), 7.11 (d, *J* = 4.0 Hz , 2H), 4.99 (d, *J* = 16.4 Hz, 1H), 4.89 (d, *J* = 16.4 Hz, 1H), 4.31 (dd, *J* = 4.0 Hz, *J* = 12.0 Hz, 1H), 4.18 (dd, *J* = 8.0 Hz, *J* = 12.0 Hz, 1H), 3.54 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.7, 140.5, 136.5, 129.8, 128.8, 128.6, 128.5, 127.7, 53.8, 39.4, 30.6; HRMS (ESI): calcd. for $C_{16}H_{15}Br_2NO$+ H = 397.9573, found 397.9577.



***N*-Benzyl-2,3-dibromo-*N*-(*o*-tolyl)propanamide**

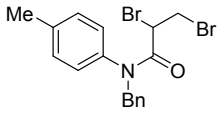
White solid: m.p.= 105–106 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.32–7.20 (m, 7H), 7.13–7.06 (m, 1H), 6.95 (d, *J* = 7.6 Hz, 0.6H), 6.77 (d, *J* = 7.6 Hz , 0.4H), 5.65 (d, *J* = 10.0 Hz, 0.4H), 5.47 (d, *J* = 10.0 Hz, 0.6H), 4.41–4.37 (m, 0.45H), 4.22–4.07 (m, 2H), 4.05–4.01 (m, 0.55H), 3.55–3.51 (m, 1H), 3.33 (s, 1.3H), 3.24 (s, 1.7); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 167.4, 167.0, 155.3, 154.8, 136.8, 136.7, 130.3, 130.2, 128.9, 128.8, 128.2, 128.2, 127.4, 120.5, 112.1, 111.6, 55.4, 55.3, 52.2, 52.2, 40.4, 38.7, 31.1, 30.2; HRMS (ESI): calcd. for $C_{17}H_{17}Br_2NO$+ H = 425.9699, found:

425.9698.



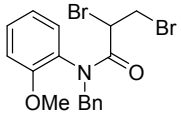
***N*-Benzyl-2,3-dibromo-*N*-(m-tolyl)propanamide**

Brown solid: m.p.= 90–91 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.31–7.24 (m, 6H), 7.16 (d, *J* = 8.4 Hz, 1H), 6.93 (s, 1H), 6.88 (d, *J* = 8.4 Hz, 1H), 4.94–4.86 (m, 2H), 4.34 (dd, *J* = 4.0 Hz, *J* = 12.0 Hz, 1H), 4.17(dd, *J* = 8.0 Hz, *J* = 12.0 Hz, 1H), 3.54 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 2.31 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.3, 140.1, 139.6, 136.3, 129.3, 129.2, 128.8, 128.5, 128.2, 127.3, 125.2, 53.5, 39.3, 30.5, 21.0; HRMS (ESI): calcd. for $C_{17}H_{17}Br_2NO$+ H = 409.9750, found: 409.9749.



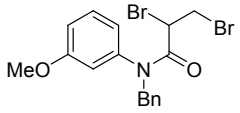
***N*-Benzyl-2,3-dibromo-*N*-(p-tolyl)propanamide**

Yellow solid: m.p. = 64–66 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.30–7.22 (m, 5H), 7.14 (d, *J* = 8.4 Hz, 2H), 6.98–6.96 (m, 2H), 4.96 (d, *J* = 14.0 Hz, 1H), 4.87 (d, *J* = 14.0 Hz, 1H), 4.34 (dd, *J* = 4.0 Hz, *J* = 12.0 Hz, 1H), 4.16 (dd, *J* = 12.0 Hz, *J* = 12.0 Hz, 1H), 3.54 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 2.35 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.4, 138.5, 137.5, 136.3, 130.1, 128.6, 128.2, 128.0, 127.3, 63.5, 39.2, 30.5, 20.7; HRMS (ESI): calcd. for $C_{17}H_{17}Br_2NO$+ H = 409.9750, found: 409.9755.



***N*-Benzyl-2,3-dibromo-*N*-(2-methoxyphenyl)propanamide**

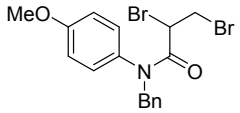
Green solid: m.p. = 115–116 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.36–7.29 (m, 1H), 7.27–7.19 (m, 5H), 6.99–6.93 (m, 1.55H), 6.86–6.80 (m, 1.45H), 5.65 (d, *J* = 10.4 Hz, 0.4H), 5.41 (d, *J* = 10.4 Hz, 0.6H), 4.45(dd, *J* = 4.0 Hz, *J* = 12.0 Hz, 0.4H), 4.29 (d, *J* = 14.4 Hz, 0.6H), 4.19–4.11 (m, 2H), 3.83 (s, 1.3H), 3.76 (s, 1.7H) 3.55–3.51 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 167.4, 167.0, 155.3, 154.8, 136.8, 136.7, 128.9, 128.8, 128.2, 128.2, 127.4, 120.5, 112.1, 111.6, 55.4, 55.3, 52.2, 52.2, 40.4, 38.7, 31.1, 30.2; HRMS (ESI): calcd. for $C_{17}H_{17}Br_2NO_2$+ H = 425.9699, found: 425.9698.



***N*-Benzyl-2,3-dibromo-*N*-(3-methoxyphenyl)propanamide**

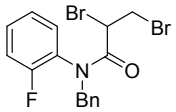
White solid: m.p. = 74–75 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.31–7.23 (m, 6H), 6.90–6.88 (m, 1H), 6.70 (d, *J* = 7.2 Hz, 1H), 6.60 (s, 1H), 4.98 (d, *J* = 14.0 Hz, 1H), 4.88 (d, *J* = 14.0 Hz, 1H), 4.36 (dd, *J* = 4.0 Hz, *J* = 12.0 Hz, 1H), 4.17 (dd, *J* = 9.2 Hz, *J* = 12.0 Hz, 1H), 3.70 (s, 3H), 3.55 (dd, *J* = 3.6 Hz, *J* = 8.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.7, 160.3, 141.4, 136.5, 130.4, 128.8, 128.4,

127.6, 120.5, 114.9, 113.9, 55.3, 53.6, 39.4, 30.6; HRMS (ESI): calcd. for $C_{17}H_{17}Br_2NO_2$+ H = 425.9699, found: 425.9704.



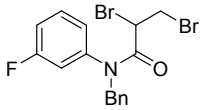
***N*-Benzyl-2,3-dibromo-*N*-(4-methoxyphenyl)propanamide**

Colorless transparent liquid: R_f = 0.47 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.29–7.21 (m, 5H), 6.99 (br, 2H), 6.83 (dd, *J* = 2.0 Hz, *J* = 7.6 Hz, 2H), 4.98 (d, *J* = 14.4 Hz, 1H), 4.87 (d, *J* = 14.4 Hz, 1H), 4.38 (dd, *J* = 4.0 Hz, *J* = 12.0 Hz, 1H), 4.18 (dd, *J* = 9.2 Hz, *J* = 11.6 Hz, 1H), 3.78 (s, 3H), 3.53 (dd, *J* = 4.0 Hz, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.9, 159.4, 136.5, 132.8, 128.7, 128.4, 127.5, 114.7, 55.3, 53.7, 39.3, 30.6; HRMS (ESI): calcd. for $C_{17}H_{17}Br_2NO_2$+ H = 425.9699, found: 425.9704.



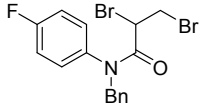
***N*-Benzyl-2,3-dibromo-*N*-(2-fluorophenyl)propanamide**

Colorless oil: R_f = 0.57 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.38–7.33 (m, 1.2H), 7.28–7.27 (m, 1.2H), 7.25–7.15 (m, 4.3H), 7.09–7.03 (m, 1.55H), 6.90 (dt, *J* = 2.0 Hz, *J* = 7.6 Hz, 0.45H), 5.64 (d, *J* = 14.4 Hz, 0.5H), 5.43 (d, *J* = 14.4 Hz, 0.5H), 4.42–4.38 (m, 1H), 4.25–4.14 (m, 2H), 3.57–3.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.9, 166.8, 158.4 (d, *J* = 250 Hz), 157.6 (d, *J* = 250 Hz), 131.9, 130.9, 130.9, 130.8, 128.9, 128.9, 128.8, 128.5, 128.4, 127.7, 127.7, 124.8, 124.7, 124.7, 117.4, 117.2, 117.1, 116.9, 52.8, 52.7, 39.9, 38.2, 30.7, 29.9; HRMS (ESI): calcd. for $C_{16}H_{14}Br_2FNO$+ H, 413.9499, found 413.9505.



***N*-Benzyl-2,3-dibromo-*N*-(3-fluorophenyl)propanamide**

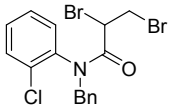
Colorless transparent liquid: R_f = 0.60 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.36–7.29 (m, 4H), 7.26–7.21 (m, 2H), 7.08 (dt, *J* = 2.0 Hz, *J* = 8.4 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 1H), 6.85 (d, *J* = 9.2 Hz, 1H), 4.98 (d, *J* = 14.4 Hz, 1H), 4.87 (d, *J* = 14.4 Hz, 1H), 4.31 (dd, *J* = 4.0 Hz, *J* = 12.0 Hz, 1H), 4.16 (dd, *J* = 8.8 Hz, *J* = 12.0 Hz, 1H), 3.55 (dd, *J* = 4.0 Hz, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.4, 162.7 (d, *J* = 249 Hz), 141.8, 141.7, 136.1, 130.9, 130.9, 128.7, 128.5, 127.8, 124.5, 116.2, 116.1, 116.0, 115.9, 55.6, 39.1, 30.4; HRMS (ESI): calcd. for $C_{16}H_{14}Br_2FNO$+H = 413.9499, found 413.9500.



***N*-Benzyl-2,3-dibromo-*N*-(4-fluorophenyl)propanamide**

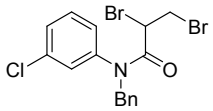
Yellow oil: R_f = 0.56 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.30–7.27 (m, 3.0 H), 7.22–7.20 (m, 2H), 7.05–7.01 (m, 4.0 H), 4.97 (d, *J* = 14.4 Hz, 1H), 4.85 (d, *J* = 14.4 Hz, 1H), 4.28 (dd, *J* = 4.0 Hz, *J* = 12.0 Hz, 1H),

4.16 (dd, *J* = 8.8 Hz, *J* = 12.0 Hz, 1H), 3.55 (dd, *J* = 4.0 Hz, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.7, 162.3 (d, *J* = 249 Hz), 136.2, 136.2, 130.4, 128.8, 128.6, 128.5, 127.8, 127.7, 116.8, 116.6, 53.7, 39.1, 30.5; HRMS (ESI): calcd. for $C_{16}H_{14}Br_2FNO$+ H = 413.9499, found 413.9504.



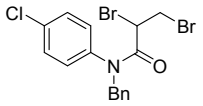
***N*-Benzyl-2,3-dibromo-*N*-(2-chlorophenyl)propanamide**

Brown solid: m.p. = 131–133 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.54–7.51 (m, 1H), 7.35–7.25 (m, 2.40H), 7.24–7.12 (m, 4.60H), 7.02 (dd, *J* = 2.0 Hz, *J* = 7.6 Hz, 0.6H), 6.86 (dd, *J* = 2.0 Hz, *J* = 7.6 Hz, 0.4H), 5.84 (d, *J* = 14.4 Hz, 0.40H), 5.67 (d, *J* = 14.4 Hz, 0.60H), 4.35-4.31 (m, 0.40H), 4.18–3.99 (m, 2.60H), 3.54 (dd, *J* = 4.0 Hz, *J* = 9.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.6, 166.5, 136.9, 136.9, 135.9, 135.8, 133.0, 132.9, 132.4, 131.4, 131.0, 130.6, 130.3, 130.2, 129.0, 129.0, 128.4, 128.3, 127.7, 127.6, 127.5, 127.3, 51.8, 51.8, 40.5, 38.1, 30.9, 29.7; HRMS (ESI): calcd. for $C_{16}H_{14}Br_2ClNO$+ H = 429.9203, found 429.9208.



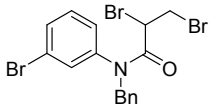
***N*-Benzyl-2,3-dibromo-*N*-(3-chlorophenyl)propanamide**

Yellow solid: m.p. = 67–68 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.37–7.33 (m, 1H), 7.31–7.27 (m, 4H), 7.23–7.21 (m, 1H), 7.14 (s, 1H), 6.98 (d, *J* = 7.2 Hz, 1H), 4.99–4.87 (m, 2H), 4.29 (dd, *J* = 3.6 Hz, *J* = 11.6 Hz, 1H), 4.17 (dd, *J* = 8.8 Hz, *J* = 11.6 Hz, 1H), 3.54 (dd, *J* = 3.6 Hz, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.5, 141.5, 135.9, 135.2, 130.7, 129.3, 128.8, 128.7, 128.6, 127.8, 127.0, 53.7, 39.1, 30.4; HRMS (ESI): calcd. for $C_{16}H_{14}Br_2ClNO$+H = 429.9203, found 429.9209.



***N*-Benzyl-2,3-dibromo-*N*-(4-chlorophenyl)propanamide**

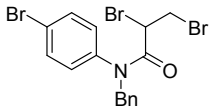
Yellow oil: R_f = 0.53 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.34–7.26 (m, 5H), 7.22-7.20 (m, 2H), 7.03 (d, *J* = 8.0 Hz, 2H), 4.96 (d, *J* = 14.4 Hz, 1H), 4.86 (d, *J* = 14.4 Hz, 1H), 4.28 (dd, *J* = 3.6 Hz, *J* = 11.6 Hz, 1H), 4.16 (dd, *J* = 8.8 Hz, *J* = 11.6 Hz, 1H), 3.55 (dd, *J* = 3.6 Hz, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.5, 138.8, 136.1, 134.9, 130.0, 128.8, 128.6, 127.8, 53.7, 39.1, 30.5; HRMS (ESI): calcd. for $C_{16}H_{14}Br_2ClNO$+ H = 429.9203, found 429.9207.



***N*-Benzyl-2,3-dibromo-*N*-(3-bromophenyl)propanamide**

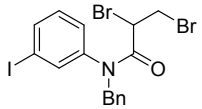
White solid: m.p. =101–103 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.51–7.49 (m, 1H), 7.31–7.26 (m, 4H), 7.24–7.20 (m, 3H), 7.01 (d, *J* = 8.0 Hz, 1H), 4.28 (dd, *J* =

3.6 Hz, *J* = 11.6 Hz, 1H), 4.15 (dd, *J* = 8.8 Hz, *J* = 11.6 Hz, 1H) (m, 1H), 3.54 (dd, *J* = 3.6 Hz, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.3, 141.5, 135.9, 132.0, 131.7, 130.9, 128.7, 128.6, 127.8, 127.4, 122.9, 53.7, 39.1, 30.4; HRMS (ESI): calcd. for $C_{16}H_{14}Br_3NO$+Na = 499.8477, found 499.8490.



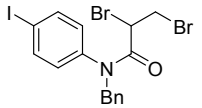
_N_-Benzyl-2,3-dibromo-_N_-(4-bromophenyl)propanamide

Yellow oil: R_f = 0.53 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.49 (d, *J* = 8.8 Hz, 2H), 7.31–7.26 (m, 3H), 7.22–7.20 (m, 2H), 6.97 (d, *J* = 8.0 Hz, 2H), 4.97 (d, *J* = 14.4 Hz, 1H), 4.85 (d, *J* = 14.4 Hz, 1H), 4.27(dd, *J* = 3.6 Hz, *J* = 11.6 Hz, 1H), 4.16(dd, *J* = 8.8 Hz, *J* = 11.6 Hz, 1H), 3.55 (dd, *J* = 3.6 Hz, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.4, 139.3, 136.1, 133.0, 130.3, 128.8, 128.6, 127.8, 123.0, 53.6, 39.1, 30.5; HRMS (ESI): calcd. for $C_{16}H_{14}Br_3NO$+H = 473.8698, found 473.8703.



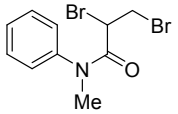
_N_-Benzyl-2,3-dibromo-_N_-(3-iodophenyl)propanamide

White solid: m.p. = 101–103 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.72–7.69 (m, 1H), 7.50 (s, 1H), 7.33–7.29 (m, 3H), 7.26–7.20 (m, 2H), 7.10–7.00 (m, 2H), 4.90 (br, 2H), 4.28(dd, *J* = 3.6 Hz, *J* = 11.6 Hz, 1H), 4.16(dd, *J* = 8.8 Hz, *J* = 11.6 Hz, 1H), 3.56 (dd, *J* = 3.6 Hz, *J* = 8.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.5, 141.5, 138.0, 136.0, 131.0, 128.8, 128.6, 127.8, 94.3, 53.8, 39.2, 30.5; HRMS (ESI): calcd. for $C_{16}H_{14}Br_2INO$+H = 521.8560, found 521.8564.



_N_-Benzyl-2,3-dibromo-_N_-(4-iodophenyl)propanamide

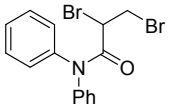
Yellow oil: R_f = 0.53 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.69 (d, *J* = 8.8 Hz, 1.45H), 7.37–7.35 (m, 0.90H), 7.31–7.26 (m, 3.0H), 7.24–7.20 (m, 1.90H), 7.10 (s, 0.45H), 6.83 (d, *J* = 8.0 Hz, 1.30H), 5.01–4.83 (m, 2H), 4.33–4.26 (m, 1H), 4.20–4.13 (m, 1H), 3.57–3.53 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.4, 140.1, 139.1, 136.1, 129.8, 128.8, 128.6, 128.5, 127.8, 127.6, 94.7, 53.8, 53.6, 39.4, 39.2, 30.6, 30.5; HRMS (ESI): calcd. for $C_{16}H_{14}Br_2INO$+H = 521.8560, found 521.8555.



2,3-Dibromo-_N_-methyl-_N_-phenylpropanamide

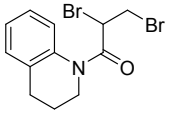
Colorless transparent liquid: R_f = 0.47 (petroleum ether : ethyl acetate = 5:1); effluent for silica gel chromatography: petroleum ether and ethyl acetate (20:1).^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.51–7.41 (m, 3H), 7.35 (d, *J* = 7.6 Hz, 2H), 4.37–4.33 (m, 1H), 4.12–4.07 (m, 1H), 3.52 (dd, *J* = 4.0 Hz, *J* = 8.0 Hz, 1H), 3.35 (s, 3H); ^{13}C

NMR ($CDCl_3$, 100 MHz, δ ppm): 166.4, 142.0, 129.9, 128.6, 127.3, 38.9, 38.0, 30.4; HRMS (ESI): calcd. for $C_{10}H_{11}Br_2NO$+ H = 319.9280, found: 319.9285.



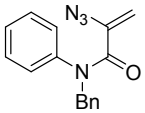
2,3-Dibromo-*N*,*N*-diphenylpropanamide

Yellow oil; R_f = 0.47 (petroleum ether : ethyl acetate = 5:1). Effluent for silica gel chromatography: petroleum ether and ethyl acetate (40:1). ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.49–7.40 (m, 5H), 7.37–7.30 (m, 4H), 7.24–7.20 (m, 1H), 4.54 (dd, *J* = 4.0 Hz, *J* = 11.6 Hz, 1H), 4.43 (dd, *J* = 4.0 Hz, *J* = 11.6 Hz, 0.20H), 4.20 (dd, *J* = 9.2 Hz, *J* = 11.6 Hz, 1H), 3.90 (dd, *J* = 9.2 Hz, *J* = 11.6 Hz, 0.2H), 3.66 (dd, *J* = 4.4 Hz, *J* = 10.0 Hz, 0.2H), 3.59 (dd, *J* = 4.4 Hz, *J* = 10.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 169.8, 166.8, 141.9, 141.2, 130.1, 129.0, 128.7, 126.7, 126.0, 40.8, 40.1, 30.6, 29.5; HRMS (ESI): calcd. for $C_{15}H_{13}Br_2NO$+H = 381.9437, found 381.9452.



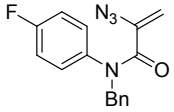
2,3-Dibromo-1-(3,4-dihydroquinolin-1(2*H*)-yl)propan-1-one

Light yellow liquid；R_f = 0.56 (petroleum ether : ethyl acetate= 5:1). Effluent for silica gel chromatography: petroleum ether and ethyl acetate (20:1). ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.36 (d, *J* = 7.2 Hz, 1H), 7.27–7.24 (m, 3H), 5.00 (dd, *J* = 3.6 Hz, *J* = 11.6 Hz, 1H), 4.50–4.48 (m, 0.30H), 4.19–3.91 (m, 2.50H), 3.75–3.67 (m, 1.40H), 3.62–3.59 (m, 0.80H), 2.79–2.69 (m, 2H), 2.09–1.92 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 166.8, 138.1, 135.0, 128.7, 126.8, 126.7, 123.7, 43.5, 40.0, 30.9, 29.8, 26.2, 23.6; HRMS (ESI): calcd. for $C_{12}H_{13}Br_2NO$+H = 345.9437, found 345.9433.



2-Azido-*N*-benzyl-*N*-phenylacrylamide (1a)

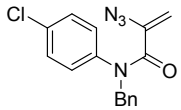
Yellow oil: R_f = 0.45 (petroleum ether : ethyl acetate = 5:1); ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.30–7.20 (m, 8H), 7.01–6.99 (m, 2H), 4.97 (s, 2H), 4.92 (d, *J* = 2.0 Hz, 1H), 4.88 (d, *J* = 2.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm $CDCl_3$): 164.0, 141.9, 140.0, 136.4, 129.1, 128.4, 128.3, 127.5, 127.4, 126.9, 106.4, 53.4; FT-IR (KBr, cm^{-1}): 2107, 1652.5; HRMS (ESI): calcd. for $C_{16}H_{14}N_4O$+H = 279.1248, found 279.1245.



2-Azido-*N*-benzyl-*N*-(4-fluorophenyl)acrylamide (1b)

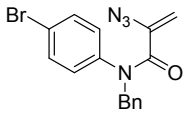
Yellow solid: m.p. = 41–42 °C; ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.27–7.24 (m, 3H) , 7.20–7.18 (m, 2H), 6.96 (d, *J* = 6.4 Hz, 4H), 4.97 (s, 1H), 4.93 (s, 2H), 4.92 (d, *J* = 2.0 Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 164.0, 161.4 (d, *J* = 247 Hz), 139.9, 137.7, 136.1, 128.9, 128.8, 128.6, 128.5, 128.4, 127.7, 116.1, 115.9, 106.4, 53.5; FT-IR (KBr, cm^{-1}): 2108.8, 1642.4; ESI-HRMS: m/z calcd for $C_{16}H_{13}FN_4O$+H

= 297.1152, found 297.1143.



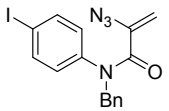
2-Azido-*N*-benzyl-*N*-(4-chlorophenyl)acrylamide (1c)

Colorless oil: R_f = 0.45 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.29–7.24 (m, 5H), 7.20–7.18 (m, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 5.00 (d, *J* = 2.0 Hz, 1H), 4.94 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 164.0, 140.5, 140.0, 136.2, 133.4, 129.4, 128.6, 128.5, 128.4, 127.7, 106.6, 53.5; FT-IR (KBr, cm^{-1}): 2107.8, 1652.4; ESI-HRMS: m/z calcd for $C_{16}H_{13}ClN_4O$+H = 313.0856, found 313.0849.



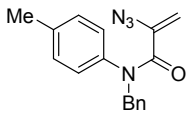
2-Azido-*N*-benzyl-*N*-(4-bromophenyl)acrylamide (1d)

Colorless oil: R_f = 0.53 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.38 (d, *J* = 8.4 Hz, 2H), 7.25–7.18 (m, 3H), 7.18–7.16(m, 2H), 6.87 (d, *J* = 8.8 Hz, 2H), 5.01 (d, *J* = 2.4 Hz, 1H), 4.95 (d, *J* = 2.0 Hz, 1H), 4.94 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 152.7, 137.2, 135.0, 134.0, 133.7, 133.6, 132.5, 129.3, 128.4, 126.9, 117.7, 116.4, 113.6, 46.7; FT-IR (KBr, cm^{-1}): 2109.8, 1646.4; ESI-HRMS: m/z calcd for $C_{16}H_{13}BrN_4O$+H = 357.0351, found 357.0344.



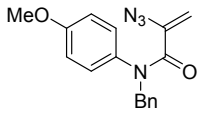
2-Azido-*N*-benzyl-*N*-(4-iodophenyl)acrylamide (1e)

Yelow solid: m.p. = 49–51 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.59 (d, *J* = 8.4 Hz, 2H), 7.25–24 (m, 3H), 7.20–7.18 (m, 2H), 6.75 (d, *J* = 8.8 Hz, 2H), 5.00 (d, *J* = 2.0 Hz, 1H), 5.00–4.93 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 163.8, 141.7, 139.8, 138.3, 136.1, 128.8, 128.5, 128.4, 127.7, 106.8, 92.7, 53.4; FT-IR (KBr, cm^{-1}): 2105.6, 1649.1; ESI-HRMS: m/z calcd for $C_{16}H_{13}IN_4O$+H = 405.0212, found 405.0207.



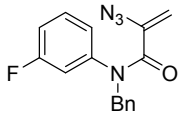
2-Azido-*N*-benzyl-*N*-(p-tolyl)acrylamide (1f)

Yellow solid: m.p. = 36–37 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.27–7.20 (m, 5H), 7.07 (d, *J* = 8.4 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.94 (s, 2H), 4.89–4.88 (m, 2H), 2.31 (s, 3H) ; ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 164.0, 139.9, 139.2, 137.4, 136.5, 129.7, 128.4, 128.3, 126.7, 106.1, 53.4, 20.8; FT-IR (KBr, cm^{-1}): 2107.3, 1651.4; ESI-HRMS: m/z calcd for $C_{17}H_{16}N_4O$+H = 293.1400, found 293.1397.



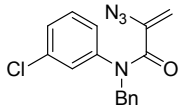
2-Azido-*N*-benzyl-*N*-(4-methoxyphenyl)acrylamide (1g)

Colorless oil: R_f = 0.30 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.28–7.25 (m, 3H), 7.22–7.20 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.78 (d, *J* = 8.8 Hz, 2H), 4.92 (s, 2H), 4.89 (m, 2H), 3.78 (s, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 164.3, 158.8, 140.2, 136.6, 134.6, 128.7, 128.5, 128.4, 127.6, 114.3, 106.0, 55.4, 53.7; FT-IR (KBr, cm^{-1}): 2105.9, 1650.6; ESI-HRMS: m/z calcd for $C_{17}H_{16}N_4O_2$+H = 309.1346, found 309.1351.



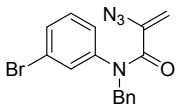
2-Azido-*N*-benzyl-*N*-(3-fluorophenyl)acrylamide (1h)

Colorless oil: R_f = 0.53 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.28–7.25 (m, 4H), 7.22–7.16 (m, 2H), 6.97 (dt, *J* = 9.6 Hz, *J* = 2.4 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 6.76 (dt, *J* = 3.6 Hz, *J* = 8.0 Hz, 1H), 5.00 (d, *J* = 2.4 Hz, 1H), 4.99–4.97 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 164.0, 162.6 (d, *J* = 247 Hz), 143.6, 143.5, 140.5, 136.2, 130.4, 128.6, 128.4, 127.7, 122.9, 122.9, 114.8, 114.6, 114.4, 114.2, 106.7, 53.6; FT-IR (KBr, cm^{-1}): 2111.8, 1657.1; ESI-HRMS: m/z calcd for $C_{16}H_{13}FN_4O$+H = 297.1146, found. 297.1147.



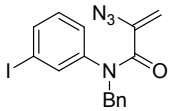
2-Azido-*N*-benzyl-*N*-(3-chlorophenyl)acrylamide (1i)

Yellow solid: m.p. = 46–47 °C; ^{1}H NMR($CDCl_3$, 400 MHz, δ ppm): 7.26–7.22 (m, 5H), 7.19–7.17 (m, 2H), 6.93–6.91 (m, 2H), 4.99 (d, *J* = 2.0 Hz, 1H), 4.93–4.92 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 163.9, 140.5, 140.0, 136.2, 133.4, 129.4, 128.6, 128.5, 128.4, 127.7, 106.6, 53.5; FT-IR (KBr, cm^{-1}): 2108.6, 1655.9; ESI-HRMS: m/z calcd for $C_{16}H_{13}ClN_4O$+H = 313.0856, found 313.0849.



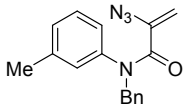
2-Azido-*N*-benzyl-*N*-(3-bromophenyl)acrylamide (1j)

Yellow solid: m.p. = 42–43 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.43–7.41 (m, 1H), 7.33–7.28 (m, 3H), 7.26–7.22 (m, 3H), 7.17 (t, *J* = 8.0 Hz, 1H), 6.95–6.93 (m, 3H), 5.07 (d, *J* = 2.0 Hz, 1H), 4.99 (d, *J* = 2.0 Hz, 1H), 4.97 (s, 2H) ; ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 163.9, 145.4, 140.0, 136.1, 130.7, 130.3, 130.0, 128.6, 128.4, 127.7, 125.9, 122.5, 106.9, 53.2; FT-IR (KBr, cm^{-1}): 2107.8, 1655.2; ESI-HRMS: m/z calcd for $C_{16}H_{13}BrN_4O$+H = 357.0351, found 357.0344.



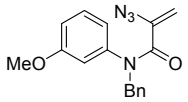
2-Azido-*N*-benzyl-*N*-(3-iodophenyl)acrylamide (1k)

Colorless oil: R_f = 0.50 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.59 (dt, *J* = 7.6 Hz, 1.6 Hz, 1H), 7.41 (t, *J* = 2.0 Hz 1H), 7.29–27 (m, 3H), 7.20–7.18 (m, 2H), 7.01 (t, *J* = 8.0 Hz, 1H), 6.95–6.92 (m, 1H), 5.04 (d, *J* = 2.0 Hz, 1H), 4.97 (d, *J* = 2.0 Hz, 1H), 4.94 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 163.8, 143.2, 139.9, 136.6, 136.1, 135.8, 130.5, 128.5, 128.4, 127.7, 126.5, 106.9, 93.8, 53.6; FT-IR (KBr, cm^{-1}): 2104.9, 1654.5; ESI-HRMS: m/z calcd for $C_{16}H_{13}IN_4O$+H = 405.0212, found 405.0207.



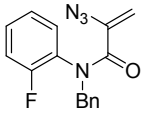
2-Azido-*N*-benzyl-*N*-(m-tolyl)acrylamide (1l)

Yellow solid: m.p. = 36–37 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.27–7.21 (m, 5H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 1H), 6.83 (s, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 4.95 (s, 2H), 4.91 (d, *J* = 1.6 Hz, 1H), 4.89 (d, *J* = 1.6 Hz, 1H), 2.28 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 164.0, 141.9, 139.9, 139.2, 136.5, 128.9, 128.4, 128.3, 127.4, 127.4, 124.0, 106.3, 53.5, 21.1; FT-IR (KBr, cm^{-1}): 2109.5, 1652.6; ESI-HRMS: m/z calcd for $C_{17}H_{16}N_4O$+H = 293.1397, found 293.1402;



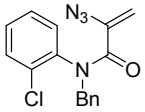
2-Azido-*N*-benzyl-*N*-(3-methoxyphenyl)acrylamide (1m)

Colorless oil: R_f = 0.44 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.21–7.29 (m, 5H), 7.18 (t, *J* = 8.0 Hz, 1H), 6.79 (dd, *J* = 8.4 Hz, 2.4 Hz, 1H), 6.62–6.59 (m, 1H), 6.53 (t, *J* = 2.0 Hz, 1H), 4.95 (s, 3H), 4.90 (d, *J* = 2.0 Hz, 1H), 3.70 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 164.0, 160.0, 143.2, 140.1, 136.6, 129.8, 128.5, 128.4, 127.5, 119.4, 113.0, 112.9, 106.3, 55.3, 53.5; FT-IR (KBr, cm^{-1}): 2109.6, 1653.8; ESI-HRMS: m/z calcd for $C_{17}H_{16}N_4O_2$+H = 309.1346, found 309.1349.



2-Azido-*N*-benzyl-*N*-(2-fluorophenyl)acrylamide (1o)

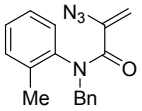
Colorless oil: R_f = 0.53 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.25–7.21 (m, 6.60H), 7.07–7.01 (m, 2.20H), 6.98–6.94 (m, 1.10H), 5.94 (s, 0.10H), 5.61 (s, 0.10H), 5.19 (d, *J* = 1.6 Hz, 1H), 4.88 (s, 2H), 4.68 (d, *J* = 1.6 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 164.5, 157.4 (d, *J* = 248 Hz), 139.6, 136.1, 129.6, 129.6, 129.3, 128.8, 128.5, 124.8, 124.6, 116.7, 116.5, 105.9, 52.7; FT-IR (KBr, cm^{-1}): 2111.6, 1662.2; ESI-HRMS: m/z calcd for $C_{16}H_{13}FN_4O$+H = 297.1152, found 207.1143.



2-Azido-*N*-benzyl-*N*-(2-chlorophenyl)acrylamide (1p)

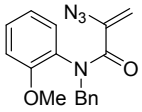
Brown solid:m.p.= 38–39 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.44–7.41 (m,

1.10H), 7.26–7.23 (m, 4.40H), 7.23–7.19 (m, 2.20H), 7.14–7.10 (m, 1.10H), 6.84–6.82 (m, 1.10H), 5.96 (d, *J* = 1.6 Hz, 0.10H), 5.59 (s, 0.10H), 5.56 (d, *J* = 2.0 Hz, 0.20H), 5.48 (d, *J* = 14.4 Hz, 0.85H), 4.82 (s, 2H), 4.36 (d, *J* = 14.4 Hz, 1.0H), 4.23(d, *J* = 14.4 Hz, 0.10H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 165.5, 164.1, 139.3, 138.9, 135.8, 132.4, 131.5, 130.5, 130.4, 130.4, 129.7, 129.4, 129.20, 128.4, 127.7, 127.4, 122.2, 121.5, 105.7, 52.0, 51.7; FT-IR (KBr, cm^{-1}): 2108.7, 1656.3; ESI-HRMS: m/z calcd for $C_{16}H_{13}ClN_4O$+H = 313.0856, found 313.0849.



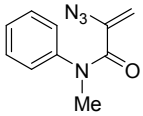
2-Azido-*N*-benzyl-*N*-(o-tolyl)acrylamide (1p)

Colorless oil: R_f = 0.53 (petroleum ether : EtOAc = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.26–7.24 (m , 3H), 7.21–7.19 (m, 4H), 7.10–7.08 (m, 1H), 6.81 (d, *J* = 7.6 Hz, 1H), 5.21 (d, *J* = 14.0 Hz, 1H), 4.83 (d, *J* = 1.6 Hz 2H), 4.50 (d, *J* = 14.0 Hz, 1H), 2.06 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 164.1, 140.3, 140.0, 136.1, 135.5, 131.3, 129.4, 129.0, 128.3, 128.2, 127.7, 126.6, 105.8, 52.9, 17.5; FT-IR (KBr, cm^{-1}): 2107.2, 1648.8; ESI-HRMS: m/z calcd for $C_{17}H_{16}N_4O$+H = 293.1397, found 293.1394.



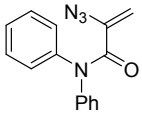
2-Azido-*N*-benzyl-*N*-(2-methoxyphenyl)acrylamide (1q)

Green solid: m.p. = 54–56 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.25–7.19 (m, 6H), 6.92 (dd, *J* = 7.6 Hz, 2.0 Hz, 1H), 6.86–6.82 (m, 2H), 5.10 (d, *J* = 14.4 Hz, 1H), 4.74 (s, 1H), 4.69 (d, *J* = 14.4 Hz, 1H), 4.55 (s, 1H), 3.69 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 165.2, 154.3, 139.3, 136.6, 131.1, 131.9, 128.9, 128.8, 128.1, 128.1, 127.3, 120.7, 111.8, 105.0, 55.3, 52.5; FT-IR (KBr, cm^{-1}): 2108.4, 1653.5; ESI-HRMS: m/z calcd for $C_{17}H_{16}N_4O_2$+H = 309.1346, found 309.1351.



2-Azido-*N*-methyl-*N*-phenylacrylamide (1r)

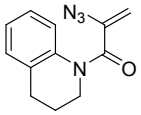
Yellow oil: R_f = 0.53 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.38 (t, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.2 Hz, 1H), 7.17 (d, *J* = 7.6 Hz, 2H), 4.90 (s, 2H), 3.38 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 164.1, 143.6, 139.9, 129.4, 127.4, 126.0, 106.4, 37.8; FT-IR (KBr, cm^{-1}): 2112.9, 1655.1; ESI-HRMS: m/z calcd for $C_{10}H_{10}N_4O$+H = 309.1346, found. 309.1351.



2-Azido-*N*,*N*-diphenylacrylamide (1s)

Yellow oil: R_f = 0.53 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.36–7.34 (m, 4H), 7.28–7.21 (m, 2.50H), 7.21–7.17 (m, 3.50H), 6.13 (d, *J* = 2.4 Hz, 0.10H), 5.79 (d, *J* = 2.0 Hz, 0.10H), 5.15 (d, *J* = 2.0 Hz, 0.90H), 5.03

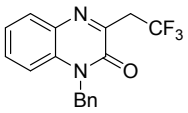
(d, J = 2.0 Hz, 0.90H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 164.2, 142.5, 140.6, 129.2, 129.1, 127.1, 127.0, 126.8, 107.6; FT-IR (KBr, cm^{-1}): 2105.3, 1666.8; ESI-HRMS: m/z calcd for $C_{15}H_{12}N_4O$+H = 265.1084, found 265.1083.



2-Azido-1-(3,4-dihydroquinolin-1(2*H*)-yl)prop-2-en-1-one (1t)

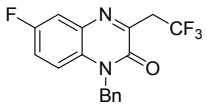
Colorless oil: R_f = 0.45 (petroleum ether : ethyl acetate = 5:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.21 (d, J = 6.8 Hz, 1H), 7.16–7.11 (m, 3H), 5.07 (d, J = 2.4 Hz, 1H), 5.04 (d, J = 2.0 Hz, 1H), 3.83 (t, J = 6.4 Hz, 2H), 2.78 (t, J = 6.4 Hz, 2H), 2.01 (q, J = 6.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 163.7, 140.8, 138.1, 131.6, 128.5, 126.1, 125.5, 123.7, 106.2, 44.3, 26.6, 23.7; FT-IR (KBr, cm^{-1}): 2109.4, 1647.2; ESI-HRMS: m/z calcd for $C_{12}H_{12}N_4O$+H = 229.1084, found 229.1085.

Characterization data for compounds 2, 3g, 4 and 5



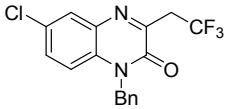
1-Benzyl-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2a)

White solid: m.p. = 109–112 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.90 (dd, J = 8.0 Hz, 1.6 Hz, 1H), 7.47 (dt, J = 1.6 Hz, 8.0 Hz, 1H)，7.33–7.22 (m, 7H), 5.51 (s, 2H), 3.90 (q, J = 10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.6, 150.7, 134.8, 132.7, 132.7, 131.2, 130.7, 129.0, 127.8, 126.8, 125.1, 124.0, 114.5, 46.2, 37.4 (q, J = 30 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, δ ppm): -63.66 (dt, J= 3.0, 12.0 Hz); ESI-HRMS: m/z calcd for $C_{17}H_{13}F_3N_2O$+H = 319.1058, found 319.1051.



1-Benzyl-6-fluoro-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2b)

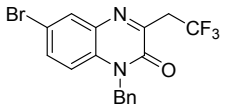
White solid: m.p. = 108–110 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.61–7.59 (m, 1H), 7.34–7.27 (m, 3H), 7.24–7.20 (m, 4H), 5.50 (s, 2H), 3.91 (q, J = 10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 158.7 (d, J = 253 Hz), 154.3, 152.3, 152.2, 134.6, 133.2, 133.1, 129.4, 129.3, 129.1, 128.0, 126.8, 126.7, 126.3, 123.6, 119.0, 118.9, 116.1, 115.9, 115.8, 115.7, 46.4, 37.5 (q, J = 30 Hz); ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -62.81 (t, J = 10.0Hz, 3F), -118.03–-118.08 (m, 1F); ESI-HRMS: m/z calcd for $C_{17}H_{12}F_4N_2O$+H = 337.0964, found 337.0956.



1-Benzyl-6-chloro-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2c)

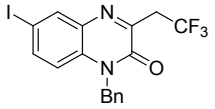
Yellow solid: m.p. = 149–151 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.90 (d, J = 2.0 Hz, 1H), 7.82 (d, J = 2.0 Hz,

0.05H), 7.41 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 1 H), 7.34–7.26 (m, 3H), 7.20–7.19 (m, 3H), 5.47 (s, 2H), 4.67 (s, 0.10H), 3.89 (q, *J* = 10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.2, 152.1, 134.5, 133.1, 131.4, 131.1, 130.0, 129.4, 129.0, 128.0, 126.7, 126.3, 123.6, 115.7, 46.3, 37.6 (q, *J* = 30 Hz); ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -62.81(t, *J* = 12.0Hz); ESI-HRMS: m/z calcd for $C_{17}H_{12}ClF_3N_2O$+H = 353.0669, found 353.0659.



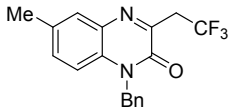
1-Benzyl-6-bromo-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2d)

White solid: m.p. = 118–121 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.06 (d, *J* = 2.0 Hz, 1H), 7.54 (dd, *J* = 2.0 Hz, 9.2 Hz, 1H), 7.30 (m, 3H), 7.20–7.19 (m, 2H), 7.14 (d, *J* = 8.8 Hz, 1H), 5.47 (s, 2H), 3.90 (q, *J* = 10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.2, 152.1, 152.0, 134.4, 134.8, 133.4, 133.0, 131.8, 129.1, 128.6, 128.5, 128.0, 126.7, 126.3, 123.5, 116.6, 116.0, 46.3, 37.4 (q, *J* = 30 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, δ ppm): -63.53 (t, *J* = 12.4 Hz); ESI-HRMS: m/z calcd for $C_{17}H_{12}F_3IN_2O$+H = 445.0025, found 445.0021.



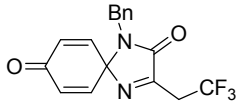
1-Benzyl-6-iodo-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2e)

Brown solid: m.p. = 143–146 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.25 (d, *J* = 1.6 Hz, 0.80H), 8.18 (d, *J* = 1.6 Hz, 0.2H), 7.72–7.66 (m, 1H), 7.33–7.27 (m, 3.0H), 7.21–7.18 (m, 2.0H), 7.02–6.98 (m, 1.20H), 5.46 (s, 2H), 4.67 (s, 0.2H), 3.89 (q, *J* = 10.4 Hz, 1.60H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 157.9, 154.2, 153.2, 151.8, 151.8, 139.5, 139.1, 139.0, 138.7, 134.4, 133.6, 132.5, 129.1, 128.0, 128.0, 126.8, 126.7, 116.3, 116.2, 86.7, 46.2, 46.1, 37.0 (q, *J* = 30 Hz) ; ^{19}F NMR ($CDCl_3$, 282 MHz, δ ppm) -63.54 (t, *J* = 12.0 Hz); ESI-HRMS: m/z calcd for $C_{17}H_{12}F_3IN_2O$+H = 445.0025, found 445.0021.



1-Benzyl-6-methyl-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2f)

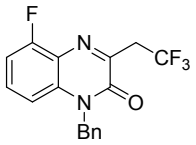
Yellow solid: m.p. = 132–135 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.71 (s, 1H), 7.31–7.27 (m, 4H), 7.22–7.20 (m, 2H), 7.16 (d, *J* = 8.4 Hz, 1H), 5.49 (s, 2H), 3.89 (q, *J* = 10.4 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.5, 150.5, 150.5, 135.0, 133.9, 132.6, 132.3, 130.5, 130.4, 128.9, 127.8, 126.9, 126.5, 114.3, 46.1, 37.5 (q, *J* = 30 Hz), 20.5; ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -62.82 (t, *J* = 12.8 Hz); ESI-HRMS: m/z calcd for $C_{18}H_{15}F_3N_2O$+H = 333.1215, found 337.1207.



1-Benzyl-3-(2,2,2-trifluoroethyl)-1,4-diazaspiro[4.5]deca-3,6,9-triene-2,8-dione

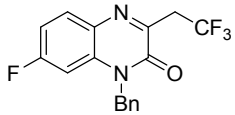
(3g)

White solid: m.p. = 158–160 °C. Effluent for silica gel chromatography: petroleum ether and ethyl acetate (1:1). ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.28–7.26 (m, 3H), 7.18–7.16 (m, 2H), 6.33 (d, *J* = 10.0 Hz, 2H), 5.96 (d, *J* = 10.0 Hz, 2H), 4.53 (s, 2H), 3.60 (q, *J* = 9.6 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 183.6, 165.3, 165.3, 162.6, 141.7, 135.4, 132.3, 128.8, 128.8, 128.4, 125.3, 122.5, 82.2, 45.2, 33.5 (q, *J* = 30 Hz); ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -62.85 (t, *J* = 12.8 Hz); ESI-HRMS: m/z calcd for $C_{17}H_{13}F_3N_2O_2$+H = 335.1007, found 335.1001.



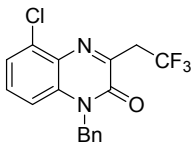
1-Benzyl-5-fluoro-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2h-1)

White solid: m.p. = 136–138 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.45–7.39 (m, 1H), 7.34–7.26 (m, 3H), 7.22–7.20 (m, 2H), 7.08–7.05 (m, 2H), 5.49 (s, 2H), 3.94 (q, *J* = 10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 158.7 (d, *J* = 257 Hz), 154.4, 150.7, 134.5, 134.4, 131.7, 131.6, 129.0, 128.0, 126.8, 126.8, 126.3, 123.5, 122.7, 122.6, 110.4, 110.2, 110.2, 46.6, 37.6 (q, *J* = 30 Hz); ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -62.83 (t, *J* = 12.0Hz, 3F), -102.81–-102.85 (m, 1F); ESI-HRMS: m/z calcd for $C_{17}H_{12}F_4N_2O$+H = 337.0959, found 337.0964.



1-Benzyl-7-fluoro-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2h-2)

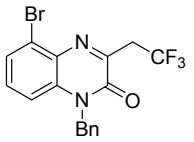
White solid: m.p. = 138–140 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.88 (dd, *J* = 6.0 Hz, *J* = 8.8 Hz, 1H), 7.35–7.26 (m, 3H), 7.24–7.22 (m, 2H), 7.04 (dt, *J* = 2.4 Hz, *J* = 8.4 Hz, 1H), 6.96 (dd, *J* = 2.4 Hz, *J* = 10.0 Hz, 1H), 5.44 (s, 2H), 3.87 (q, *J* = 10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 165.0, 162.5, 154.5, 149.5, 134.4, 134.3, 132.7, 132.6, 129.5, 129.1, 128.6, 128.4, 128.1, 126.8, 126.4, 123.7, 112.2, 111.9, 101.6, 101.4, 46.5, 37.4 (q, *J* = 30 Hz) ; ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -62.96 (t, *J* = 11.6 Hz, 3F), -105.24–-105.30 (m, 1F); ESI-HRMS: m/z calcd for $C_{17}H_{12}F_4N_2O$+H = 305.0896, found 305.0900.



1-Benzyl-5-chloro-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2i-1)

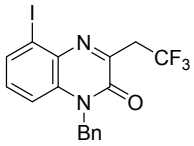
Yellow solid; m.p. = 134–136 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.42–7.35 (m, 2.10H), 7.34–7.27 (m, 3.15H), 7.22–7.17 (m, 3.15H), 5.94 (s, 2.10H), 4.74 (s, 0.10H), 3.94 (q, *J* = 10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.2, 151.0, 151.0, 135.5, 134.5, 134.2, 131.1, 129.4, 129.0, 127.9, 126.7, 126.7, 126.3, 125.0, 124.9, 123.6, 113.5, 113.4, 46.5, 37.6 (q, *J* = 30 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, δ ppm): -63.55 (t, *J* = 12.0 Hz); ESI-

HRMS: m/z calcd for $C_{17}H_{12}ClF_3N_2O$+H = 353.0669, found 353.0659.



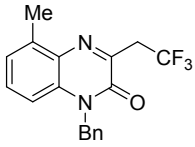
1-Benzyl-5-bromo-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2j-1)

Yellow solid: m.p. = 119–121 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.59 (d, *J* = 7.6 Hz, 1H), 7.34–7.27 (m, 4H), 7.22 (d, 3H), 5.49 (s, 2H), 3.94 (q, *J* = 10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.2, 151.3, 134.5, 134.0, 131.4, 130.3, 129.0, 128.2, 127.9, 126.7, 126.4, 126.3, 123.6, 114.2, 46.5, 37.6 (q, *J* = 30 Hz); ^{19}F NMR ($CDCl_3$, 282 MHz, δ ppm): -63.52(t, *J* = 12.0 Hz); ESI-HRMS: m/z calcd for $C_{17}H_{12}BrF_3N_2O$+H = 397.0163, found 397.0156.



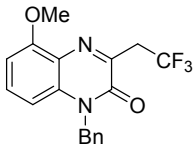
1-benzyl-5-iodo-3-(2,2,2-trifluoroethyl)quinoxalin-2(1H)-one (2k-1)

Light yellow solid: m.p. = 153–156 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.89(d, *J* = 7.2 Hz, 1H), 7.33–7.26 (m, 4H), 7.19–7.17 (m, 2H), 7.11 (t, *J* = 8.0 Hz, 1H), 5.49 (s, 2H), 3.94 (q, *J* = 10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.4, 151.4, 151.3, 134.7, 134.5, 133.0, 132.3, 131.8, 129.1, 128.0, 126.7, 126.3, 115.3, 104.3, 46.4, 37.3 (q, *J* = 30 Hz); ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -62.85 (dt, *J* =4.0Hz, 12.4Hz); ESI-HRMS: m/z calcd for $C_{17}H_{12}F_3IN_2O$+H = 445.0025, found 445.0021.



1-Benzyl-5-methyl-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2l-1)

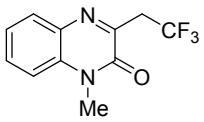
Yellow solid: m.p. = 111–114 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.36–7.25 (m, 4H), 7.23–7.19 (m, 3H), 7.10 (d, *J* = 8.4 Hz, 1H), 5.50 (s, 2H), 4.71 (s, 0.10H), 3.91 (q, *J* = 10.4 Hz, 2H), 2.68 (s, 2.85H), 2.65 (s, 0.15H); ^{13}C NMR($CDCl_3$, 100 MHz, δ ppm): 154.5, 148.6, 148.6, 139.6, 135.1, 132.8, 131.3, 130.8, 128.9, 127.7, 126.8, 126.5, 125.2, 123.9, 112.4, 46.2, 37.3 (q, *J* = 30 Hz), 17.4; ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -63.01 (t, *J* = 11.6 Hz); ESI-HRMS: m/z calcd for $C_{18}H_{15}F_3N_2O$+H = 333.1215, found 333.1207.



1-Benzyl-5-methoxy-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2m-1)

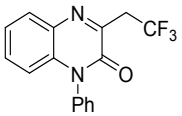
White solid: m.p. = 174–176 °C (recrystallized from petroleum ether and CH_2Cl_2); ^{1}H

NMR ($CDCl_3$, 400 MHz, δ ppm): 7.40 (t, *J* = 8.4 Hz, 1H), 7.33–7.30 (m, 3H), 7.22–7.20 (m, 2H), 6.85 (d, *J* = 8.4 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 1H), 5.49 (s, 2H), 4.02 (s, 3H), 3.96 (q, *J* = 10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 156.7, 154.8, 148.3, 134.9, 134.3, 132.0, 128.9, 127.7, 126.7, 123.5, 106.8, 105.5, 56.5, 46.5, 37.6 (q, *J* = 30 Hz); ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -62.90 (t, *J* = 12.0Hz); ESI-HRMS: m/z calcd for $C_{18}H_{15}F_3N_2O_2$+H = 349.1164, found 349.1156.



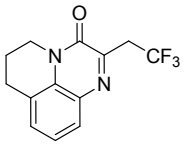
1-Methyl-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2r)

White solid: m.p. = 169–172 °C (recrystallized from petroleum ether and CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.90 (dd, *J* = 1.6 Hz *J* = 8.0 Hz, 1H), 7.62 (dt, *J* = 1.6 Hz, *J* = 8.0 Hz 1H), 7.40 (dt, *J* = 1.6 Hz, *J* = 8.0 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 3.85 (q, *J* = 10.4 Hz, 2H), 3.73 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.5, 150.5, 133.4, 132.4, 131.2, 130.5, 126.5, 124.0, 123.7, 113.7, 37.5 (q, *J* = 30 Hz), 29.4; ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -63.63 (t, *J* = 12.0 Hz); ESI-HRMS: m/z calcd for $C_{11}H_9F_3N_2O$+H = 243.0745, found 243.0737.



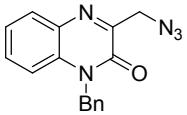
1-Phenyl-3-(2,2,2-trifluoroethyl)quinoxalin-2(1*H*)-one (2s)

Light yellow solid: m.p. = 158–159 °C (recrystallized from petroleum ether and CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.93 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 7.63–7.59 (m, 2H), 7.40–7.32 (m, 3H), 7.30–7.27 (m, 2H), 6.70 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 3.86 (q, *J* = 10.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.1, 151.3, 151.3, 135.4, 134.2, 132.3, 130.7, 130.3, 130.2, 130.0, 129.6, 128.1, 126.5, 126.4, 124.0, 123.7, 115.5, 37.2 (q, *J* = 30 Hz); ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -62.80 (t, *J* = 11.6 Hz); ESI-HRMS: m/z calcd for $C_{16}H_{11}F_3N_2O$+H = 337.0959, found 337.0964.



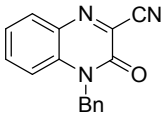
2-(2,2,2-Trifluoroethyl)-6,7-dihydropyrido[1,2,3-de]quinoxalin-3(5*H*)-one (2t)

Light yellow solid: m.p. = 169–172 °C (recrystallized from petroleum ether and CH_2Cl_2); ^1H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.71 (d, *J* = 8.0 Hz, 1H), 7.33 (d, *J* = 6.4 Hz, 1H), 7.25 (t, *J* = 8.0 Hz, 1H), 4.14 (t, *J* = 6.0 Hz, 2H), 3.84 (q, *J* = 10.4 Hz, 2H), 2.98 (t, *J* = 6.0 Hz, 2H), 2.14 (quint, *J* = 6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 153.8, 150.0, 150.0, 132.2, 130.0, 129.7, 128.0, 126.5, 124.7, 123.7, 123.3, 42.0, 37.2 (q, *J* = 30 Hz), 26.3, 20.2; ^{19}F NMR ($CDCl_3$, 377 MHz, δ ppm): -62.93 (t, *J* = 12.0Hz); ESI-HRMS: m/z calcd for $C_{13}H_{11}F_3N_2O$+H = 269.0896, found 269.0894.



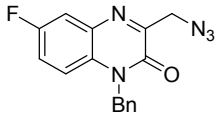
3-(Azidomethyl)-1-benzylquinoxalin-2(1*H*)-one (4a)

White solid:m.p. = 61–63 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.96 (dd, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 7.48 (dt, *J* = 2.0 Hz, *J* = 8.0 Hz, 1H), 7.37–7.27 (m, 5H), 7.25–7.23 (m, 2H), 5.52 (s, 2H), 4.67 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.2, 134.8, 132.7, 130.8, 130.6, 129.0, 127.8, 126.8, 124.0, 114.5, 51.8, 45.9; ESI-HRMS: m/z calcd for $C_{16}H_{13}N_5O$+Na = 314.1012, found: 314.1007.



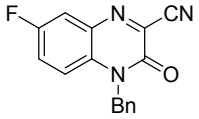
4-Benzyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5a)

Brown solid: m.p. = 175–178 °C; ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.96 (d, *J* = 10.0 Hz, 1H), 7.66 (t, *J* = 10.0 Hz, 1H), 7.45–7.25 (m, 7H), 5.53 (s, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 153.1, 134.6, 133.9, 133.7, 133.4, 133.1, 131.9, 129.1, 128.2, 127.0, 125.0, 115.0, 114.0, 46.5; HRMS (ESI): calcd. for $C_{16}H_{11}N_3O$+Na = 284.0794, found: 284.0798.



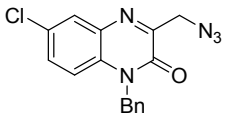
3-(Azidomethyl)-1-benzyl-6-fluoroquinoxalin-2(1*H*)-one (4b)

Yellow oil: R_f = 0.37 (petroleum ether : EtOAc = 3:1); ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.65 (dd, *J* = 2.4 Hz, *J* = 8.4 Hz, 1H), 7.35–7.28 (m , 3H), 7.24–7.21 (m, 4H), 5.50 (s, 2H), 4.66 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 158.7 (d, *J* = 244 Hz), 155.8, 153.8, 134.5, 133.3, 133.1, 129.2, 129.1, 129.0, 128.0, 126.7, 118.8, 116.1, 115.8, 115.8, 115.7, 51.7, 46.1; HRMS (ESI): calcd. for $C_{16}H_{12}FN_5O$+Na = 332.0918, found 332.0923.



4-Benzyl-7-fluoro-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5b)

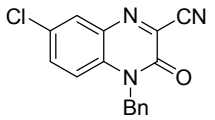
Light yellow solid: m.p. = 205–208 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.65 (dd, *J* = 2.4 Hz, *J* = 8.0 Hz, 1H), 7.42–7.33 (m , 5H), 7.31–7.21 (m, 2H), 5.52 (s, 2H) ; ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 158.9 (d, *J* = 246 Hz), 152.7, 135.3, 133.7, 133.6, 133.5, 130.2, 129.3, 129.1, 128.4, 126.9, 126.8, 122.9, 122.6, 117.0, 116.7, 116.4, 116.4, 113.7, 46.8; HRMS (ESI): calcd. for $C_{16}H_{10}FN_3O$+Na = 302.0700, found 302.0702.



3-(Azidomethyl)-1-benzyl-6-chloroquinoxalin-2(1*H*)-one (4c)

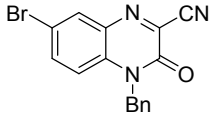
White solid: m.p. = 128–130 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.13 (d, *J* = 1.6 Hz, 1H), 7.41 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 1H), 7.34–7.26 (m , 3H), 7.22–7.20 (m,

3H), 5.48 (s, 2H), 4.64 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 155.7, 153.8, 134.4, 133.1, 131.2, 130.8, 129.8, 129.4, 129.1, 128.0, 126.7, 115.7, 57.6, 46.0; HRMS (ESI): calcd. for $C_{16}H_{12}ClN_5O$+Na = 348.0623, found 348.0626.



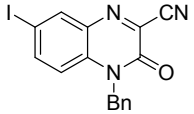
4-Benzyl-7-chloro-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5c)

Yellow solid: m.p. = 195–198 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.95 (d, *J* = 2.4 Hz, 1H), 7.58 (dd, *J* = 2.4 Hz, *J* = 9.2 Hz, 1H), 7.37–7.30 (m, 4H), 7.25–7.23 (m, 2H), 5.50 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 152.7, 135.1, 134.5, 133.6, 133.4, 132.0, 130.9, 130.6, 129.3, 128.4, 126.9, 116.2, 113.7, 46.8; HRMS (ESI): calcd. for $C_{16}H_{10}ClN_3O$+Na = 318.0405, found 318.0413.



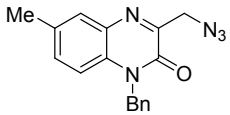
4-Benzyl-7-bromo-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5d)

Yellow solid: m.p. = 197–200 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.10 (d, *J* = 2.4 Hz, 1H), 7.71 (dd, *J* = 2.4 Hz, *J* = 8.8 Hz, 1H), 7.36–7.30 (m, 3H), 7.27–7.23 (m, 3H), 5.50 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 152.7, 137.2, 135.0, 134.0, 133.7, 133.6, 132.5, 129.3, 128.4, 126.9, 117.7, 116.4, 113.6, 46.7; HRMS (ESI): calcd. for $C_{16}H_{10}BrN_3O$+Na = 363.9879, found 363.9882.



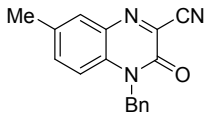
4-Benzyl-7-iodo-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5e)

Yellow solid: m.p. = 202–204 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 8.29 (d, *J* = 1.6 Hz, 1H), 7.86 (dd, *J* = 1.6 Hz, *J* = 9.2 Hz, 1H), 7.34–7.30 (m, 3H), 7.24–7.22 (m, 2H), 7.12 (d, *J* = 8.8 Hz, 1H), 5.48 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 152.7, 142.7, 140.1, 134.7, 133.9, 133.6, 133.1, 129.2, 128.4, 126.9, 116.6, 113.7, 87.7, 46.6; HRMS (ESI): calcd. for $C_{16}H_{10}IN_3O$+ Na = 409.9761, found 409.9767.



3-(Azidomethyl)-1-benzyl-6-methylquinoxalin-2(1*H*)-one (4f)

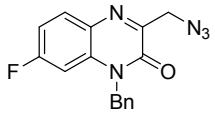
Light yellow solid: m.p. = 122–124 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.75 (s, 1H), 7.33–7.28 (m, 4H), 7.24–7.22 (m, 2H), 7.18 (d, *J* = 8.8 Hz, 1H), 5.49 (s, 2H), 4.65 (s, 2H), 2.42 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.1, 154.1, 134.9, 134.0, 132.6, 132.1, 130.4, 130.4, 129.0, 127.8, 126.8, 114.3, 51.8, 45.8, 20.6; HRMS (ESI): calcd. for $C_{17}H_{15}N_5O$+ Na = 328.1169, found 328.1172.



4-Benzyl-7-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5f)

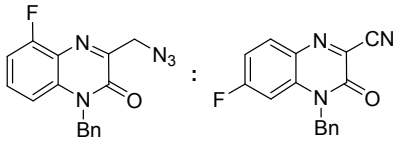
Yellow solid: It is easily oxidized red solid in air. ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm):

7.74 (s, 1H), 7.45 (dd, J = 1.6 Hz, J = 8.8 Hz, 1H), 5.51 (s, 2H), 2.44 (s, 3H); HRMS (ESI): calcd. for $C_{17}H_{13}N_3O$+ Na = 298.0951, found 298.0955.



3-(Azidomethyl)-1-benzyl-7-fluoroquinoxalin-2(1*H*)-one (5h)

White solid: m.p. = 136–138 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.92 (dd, J = 6.0 Hz, J = 8.8 Hz, 1H), 7.35–7.27 (m, 3H), 7.24–7.22 (m, 2H), 7.05 (dt, J = 2.4 Hz, 8.4 Hz, 1H), 6.97 (dd, J = 2.4 Hz, 10.0 Hz, 1H), 5.44 (s, 2H), 4.63 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 163.5 (d, J = 251 Hz), 154.1, 153.1, 153.1, 134.2, 134.1, 132.6, 132.5, 129.4, 129.4, 129.1, 128.1, 126.8, 112.2, 111.9, 101.7, 101.4, 51.6, 46.2; HRMS (ESI): calcd. for $C_{16}H_{12}FN_5O$+Na = 332.0918, found 332.0922.

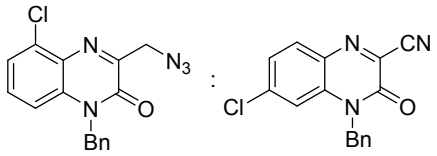


5 : 2

3-(Azidomethyl)-1-benzyl-5-fluoroquinoxalin-2(1*H*)-one (4h-1)

4-Benzyl-6-fluoro-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5h-2)

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.95 (dd, J = 2.4 Hz, J = 8.8 Hz, 0.37H), 7.45–7.39 (m, 1.26 H), 7.38–7.26 (m, 5.52H), 7.25–7.22 (m, 2.70H), 7.14–7.13 (m, 0.37H), 7.09–7.02 (m, 2.70H), 5.50 (s, 2H), 5.45 (s, 0.37H), 4.63 (s, 2H); ^{13}C NMR ($CDCl_3$, 400 MHz, δ ppm): 160.0, 157.4, 154.4, 154.4, 154.1, 134.5, 134.4, 134.4, 133.4, 131.4, 131.3, 129.3, 129.0, 128.5, 128.0, 127.0, 126.8, 122.6, 122.5, 113.7, 113.4, 110.4, 110.2, 110.2, 102.1, 101.9, 51.9, 46.9, 46.3; HRMS (ESI): calcd. for $C_{16}H_{12}FN_5O$+Na = 332.0918, found 332.0923; HRMS (ESI): calcd. for $C_{16}H_{10}FN_3O$+Na = 302.0700, found 302.0704.

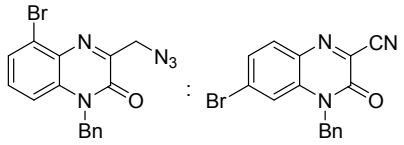


5 : 3

3-(Azidomethyl)-1-benzyl-5-chloroquinoxalin-2(1*H*)-one (4i-1)

4-Benzyl-6-chloro-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5i-2)

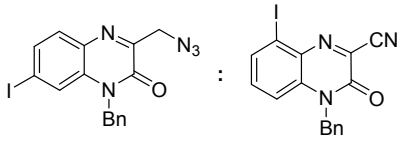
^{1}H NMR (400 MHz, $CDCl_3$): 7.87 (d, J = 9.2 Hz, 0.60H), 7.43–7.27 (m, 8.0H), 7.25 (s, 1H), 7.22– 7.20 (m, 3.20H), 5.50 (s, 2H), 5.46 (s, 1.20H), 4.65 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): 154.7, 153.9, 152.8, 141.1, 134.5, 132.9, 130.8, 129.3, 129.0, 128.5, 127.9, 127.0, 126.7, 125.6, 124.9, 114.9, 113.8, 113.4, 51.5, 46.7, 46.2; HRMS (ESI): calcd. for $C_{16}H_{12}ClN_5O$+Na = 348.0623, found 348.0628. HRMS (ESI): calcd. for $C_{16}H_{10}ClN_3O$+Na = 318.0405, found 318.0410.



3 : 1

3-(Azidomethyl)-1-benzyl-5-bromoquinoxalin-2(1*H*)-one (4j-1) and
4-Benzyl-8-bromo-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5j-2)

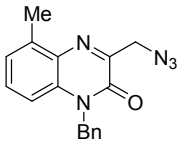
^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.77 (d, *J* = 8.4 Hz, 0.33H), 7.61 (dd, *J* = 1.2Hz, *J* = 7.6 Hz, 1.00H), 7.54–7.49 (m, 0.66H), 7.34–7.27 (m, 5.33H), 7.25–7.23 (m, 1.33H), 7.20–7.18 (m , 2H), 5.49 (s, 2H), 5.44 (s, 0.66H), 4.63 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9, 153.8, 152.7, 134.4, 134.2, 133.9, 134.4, 134.2, 133.9, 133.4, 132.8, 131.8, 131.1, 130.3, 129.6, 129.2, 129.0, 128.5, 128.4, 128.2, 127.9, 127.0, 126.7, 126.2, 118.0, 114.2, 113.8, 51.2, 46.6, 46.2; HRMS (ESI): calcd. for $C_{16}H_{10}BrN_3O$+Na=363.9879, found 363.9882. calcd.for $C_{16}H_{12}BrN_5O$+Na=394.0097, found 394.0101.



6 : 1

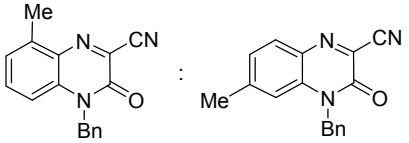
3-(Azidomethyl)-1-benzyl-7-iodoquinoxalin-2(1*H*)-one (4k-2)
4-Benzyl-8-iodo-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5k-1)

^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.90 (d, *J* = 6.4 Hz , 1.00H), 7.76–7.70 (m, 0.33 H), 7.60 (d, *J* = 8.4 Hz, 0.17H), 7.38–7.27 (m, 4.83H), 7.20–7.18 (m, 2.0H), 7.13 (t, *J* = 8.4 Hz, 1.0H), 5.49 (s, 2H), 5.45 (s, 0.33H), 4.64 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.9, 154.0, 134.8, 134.5, 134.3, 132.9, 132.6, 132.4, 131.5, 129.3, 129.0, 128.5, 127.9, 127.1, 126.7, 124.2, 115.3, 104.0, 51.1, 46.6, 46.2; HRMS (ESI): calcd. for $C_{16}H_{12}IN_5O$+Na = 439.9979, found 439.9984, calcd. for $C_{16}H_{10}IN_3O$+Na = 409.9761, found 409.9767.



3-(Azidomethyl)-1-benzyl-5-methylquinoxalin-2(1*H*)-one (4l)

White solid: m.p. = 69–72 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.35–7.29 (m, 3 H), 7.25–7.17 (m, 4H), 7.11 (d, *J* = 8.4 Hz, 1H), 5.48 (s, 2H), 4.59 (s, 2H), 2.72 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 154.0, 152.2, 139.3, 135.0, 132.7, 131.2, 130.5, 128.8, 127.6, 126.7, 125.2, 112.4, 51.1, 45.9, 17.6; HRMS (ESI): calcd. for $C_{17}H_{15}N_5O$+Na = 328.1169, found 328.1173.

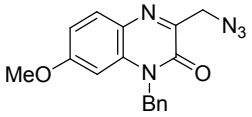


10 : 9

4-Benzyl-8-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5l-1)
4-Benzyl-6-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5l-2)

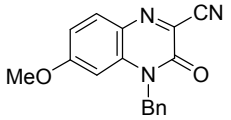
^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.82 (d, *J* = 8.4 Hz, 1H), 7.51 (t, *J* = 8.0 Hz, 1H), 5.52 (s, 2H), 5.50 (s, 1.80H), 2.69 (s, 3H), 2.47 (s, 2.70H); HRMS (ESI): calcd. for $C_{17}H_{13}N_3O$+ Na = 298.0951, found: 298.0955, 298.0950. These compounds are

unstable. There were isolated as yellow solid, but then quickly became red.



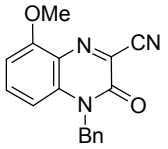
3-(azidomethyl)-1-benzyl-7-methoxyquinoxalin-2(1*H*)-one (4m)

R_f = 0.44 (petroleum ether : ethyl acetate = 3:1); ^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.84 (d, *J* = 12.0 Hz, 1H), 6.91 (dd, *J* = 6.4 Hz, *J* = 12.0 Hz, 1H), 6.71 (d, *J* = 6.4 Hz, 1H), 5.48 (s, 2H), 4.63 (s, 2H), 3.79 (s, 3H); HRMS (ESI): calcd. for $C_{17}H_{15}N_5O_2$+ Na = 344.1118, found: 344.1122. **4m** was isolated as white oil, but quickly became yellow.



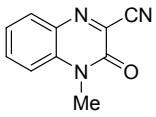
4-Benzyl-6-methoxy-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5m-2)

^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 7.83 (d, *J* = 12.0 Hz, 1H), 7.35–7.28 (m, 5H), 6.87 (dd, *J* = 3.2 Hz, *J* = 12.0 Hz, 1H), 6.71 (d, *J* = 3.2 Hz, 1H), 5.48 (s, 2H), 3.83 (s, 3H); HRMS (ESI): calcd. for $C_{17}H_{13}N_3O_2$+ Na = 314.0900, found: 314.0910. **5m-2** was isolated as light yellow solid, but quickly became yellow oil.



4-Benzyl-8-methoxy-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5m-1)

Yellow solid: m.p. = 189–192 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.58 (t, *J* = 8.4 Hz, 1H), 7.33–7.30 (m, 3H), 7.25–7.23 (m, 2H), 6.92 (d, *J* = 8.4 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 5.50 (s, 2H), 4.05 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, δ ppm): 157.5, 153.3, 136.0, 135.0, 134.1, 130.8, 129.1, 128.1, 126.9, 124.5, 106.8, 105.9, 56.7, 46.8; HRMS (ESI): calcd. for $C_{17}H_{13}N_3O_2$+Na = 314.0900, found 314.0905.



4-methyl-3-oxo-3,4-dihydroquinoxaline-2-carbonitrile (5r)

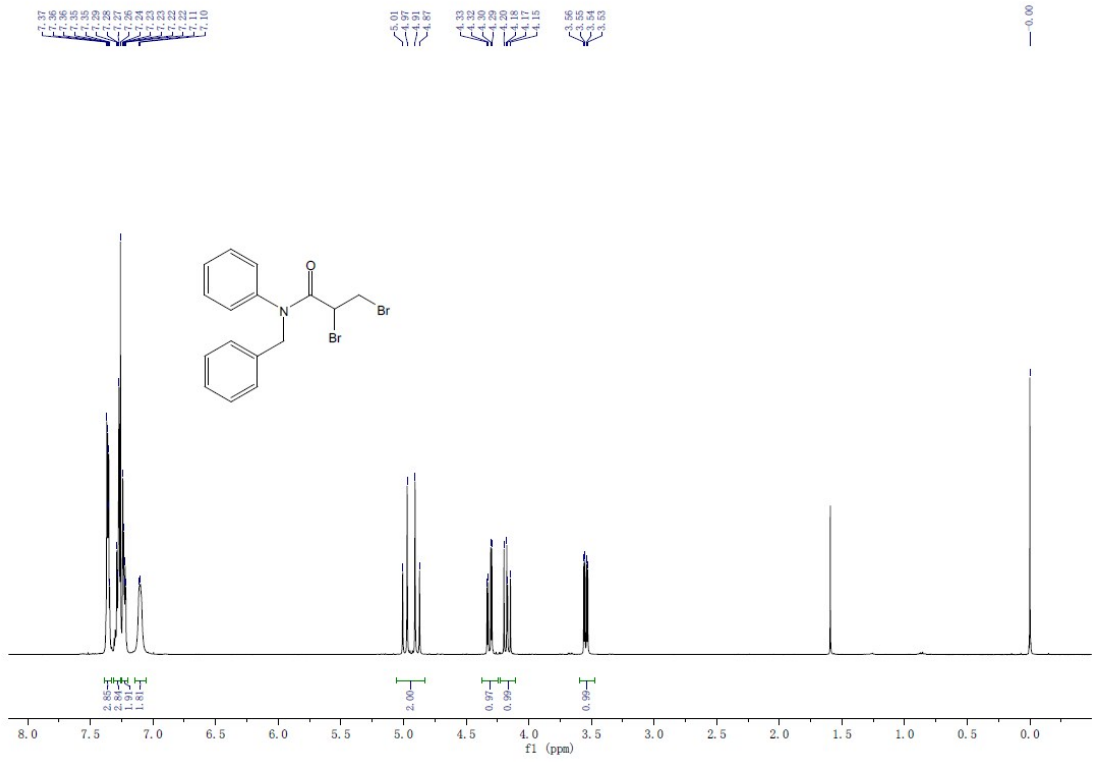
Yellow solid. It is easily oxidized red solid in air . ^{1}H NMR ($CDCl_3$, 400 MHz, δ ppm): 7.96 (dd, *J* = 1.6 Hz, *J* = 8.4 Hz, 1H), 7.78 (dt, *J* = 1.6 Hz, *J* = 8.4 Hz, 1H), 7.48 (dt, *J* = 1.6 Hz, 8.4 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 1H), 3.77 (s, 3H); HRMS (ESI): calcd. for $C_{10}H_7N_3O$+ Na = 208.0481, found: 208.0483.

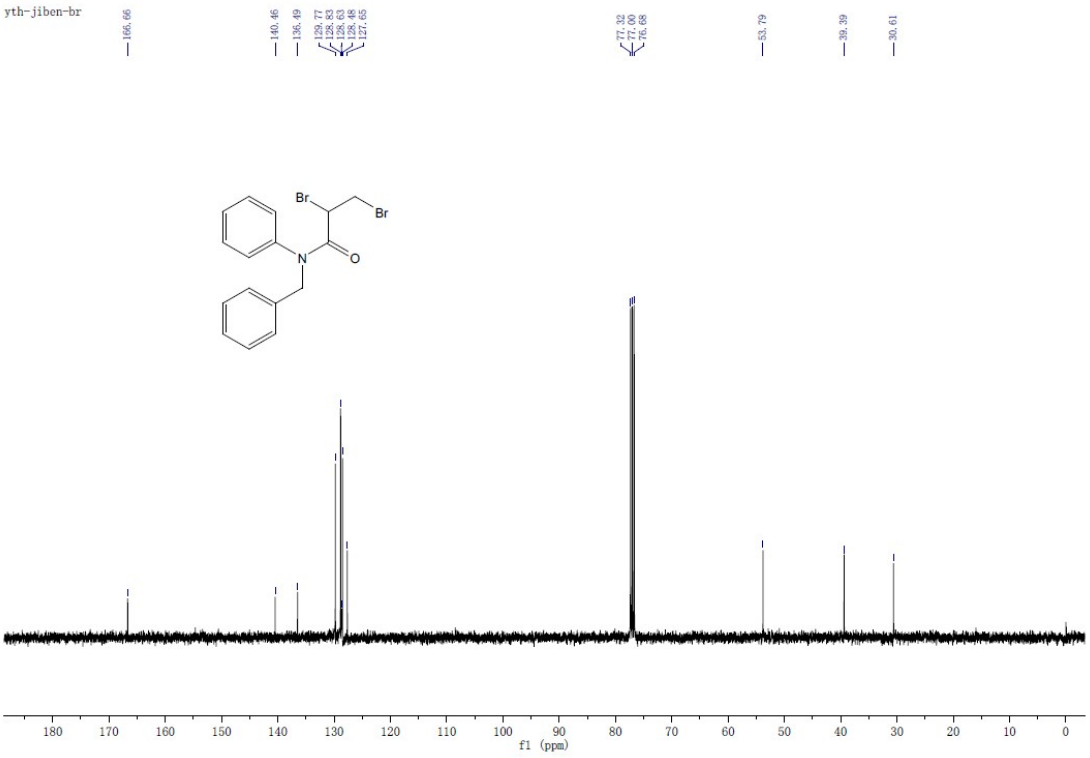
Reference

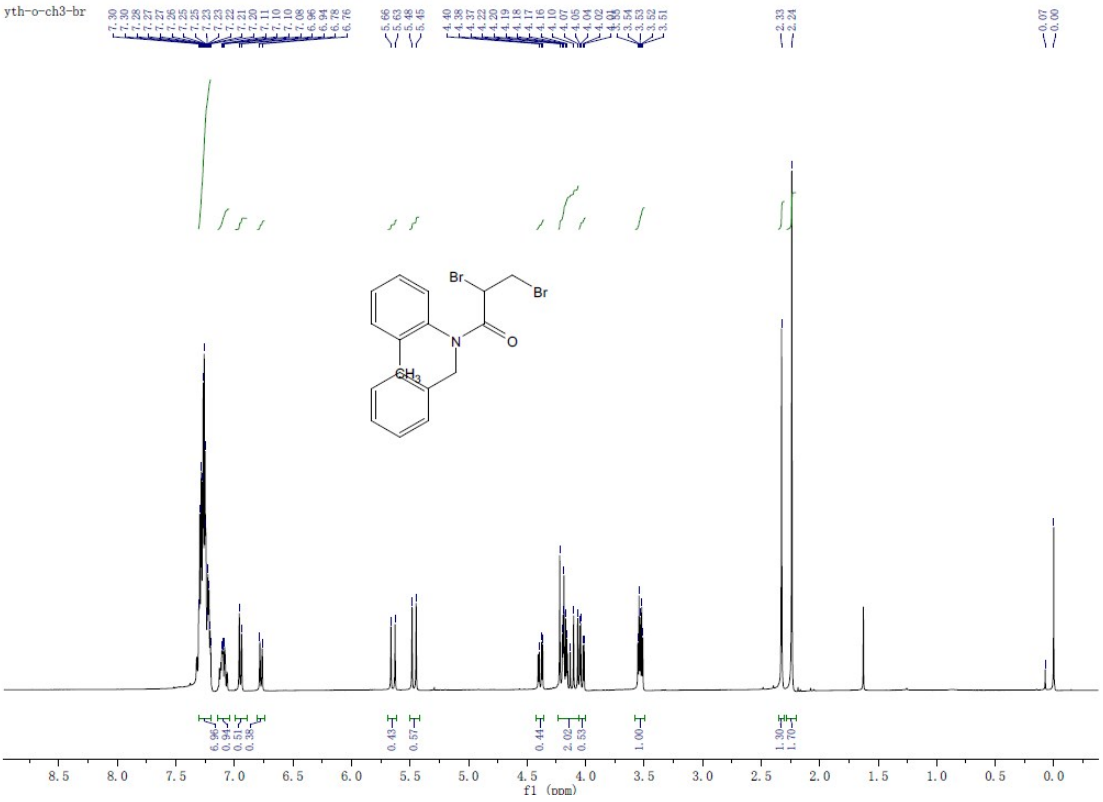
1. A. T. Parsons, T. D. Senecal, and S. L. Buchwald, *Angew. Chem. Int. Ed,* 2012, **51**, 2947–2950.
2. M. Victoria Vita and J. Waser, *Org. Lett*, 2013, **15**, 3246–3249.
3. D. Li, T. Yang, H. Su, W. Yu, *Adv. Synth. Catal.* 2015**, 357**, 2529–2539.
4. P. Truitt, E. E. Richardson, L. M. Long, W. J. Middleton, *J. Am. Chem. Soc.*, 1949**, 71**, 3479–3480.

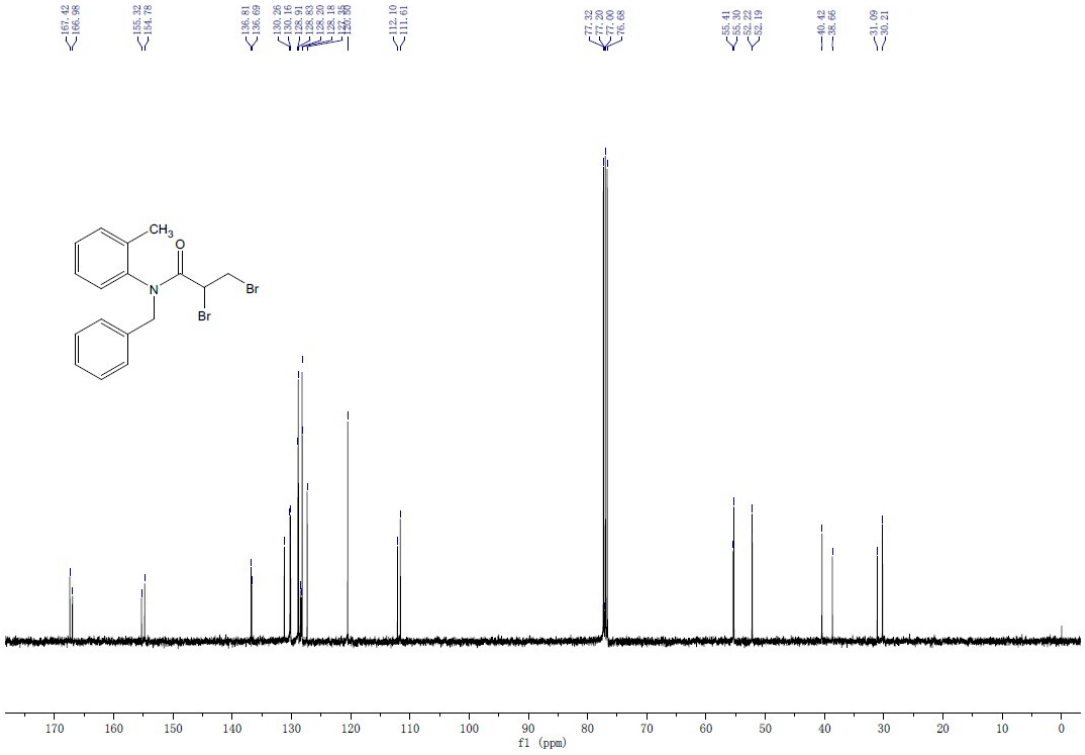
5. N. Jiang, J. Fan, T. Liu, J. Cao, B. Qiao, J. Wang, P. Gao and X. Peng, *Chem. Commun.*, 2013, **49**, 10620–10622.

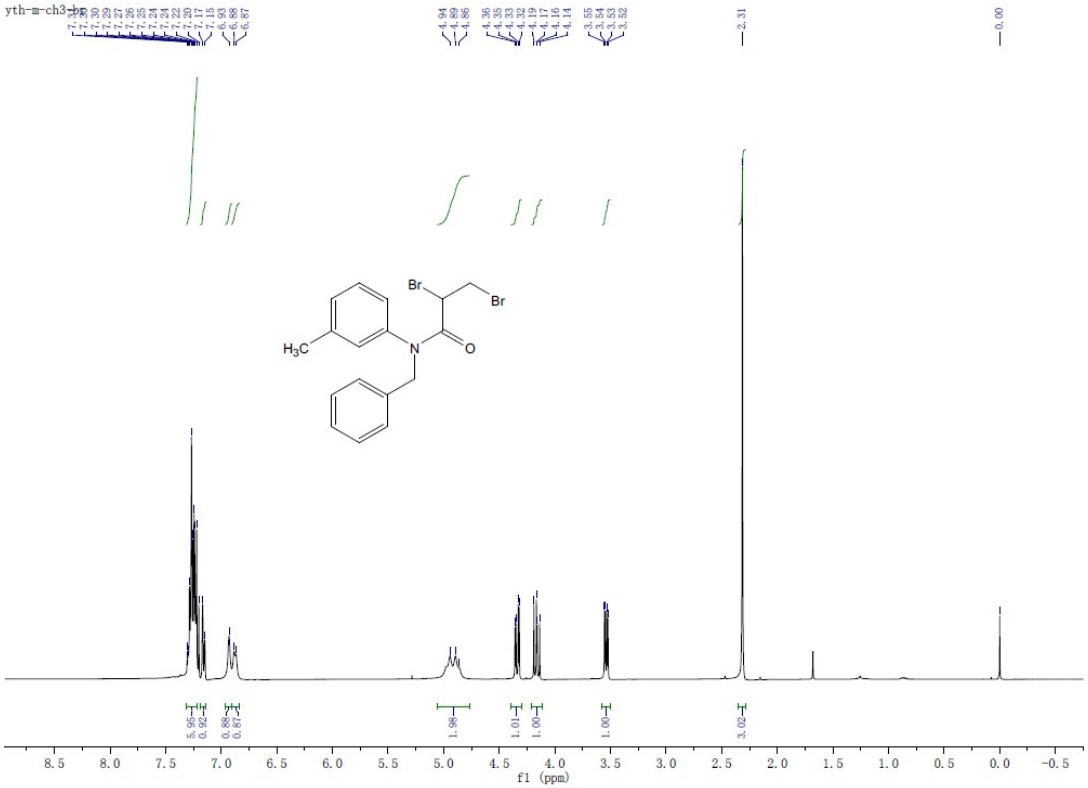
Copies of ^{1}H NMR and ^{13}C NMR spectra

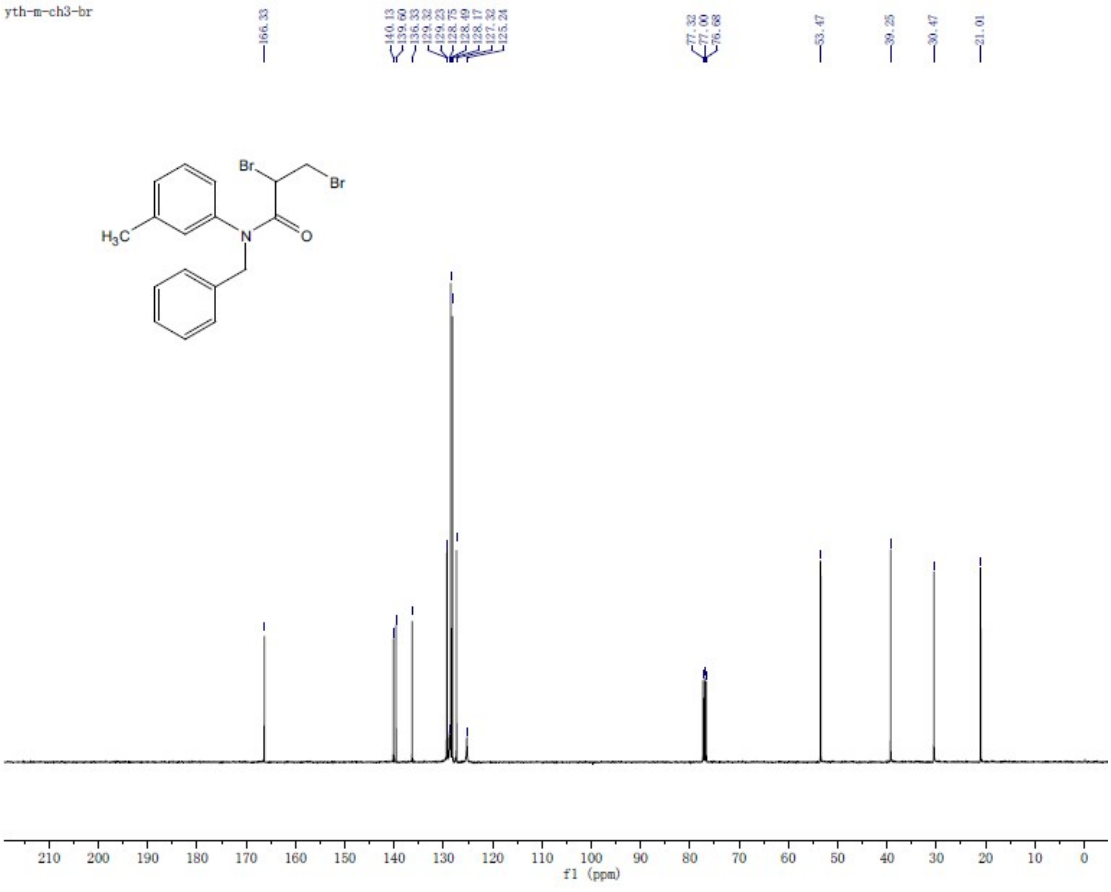


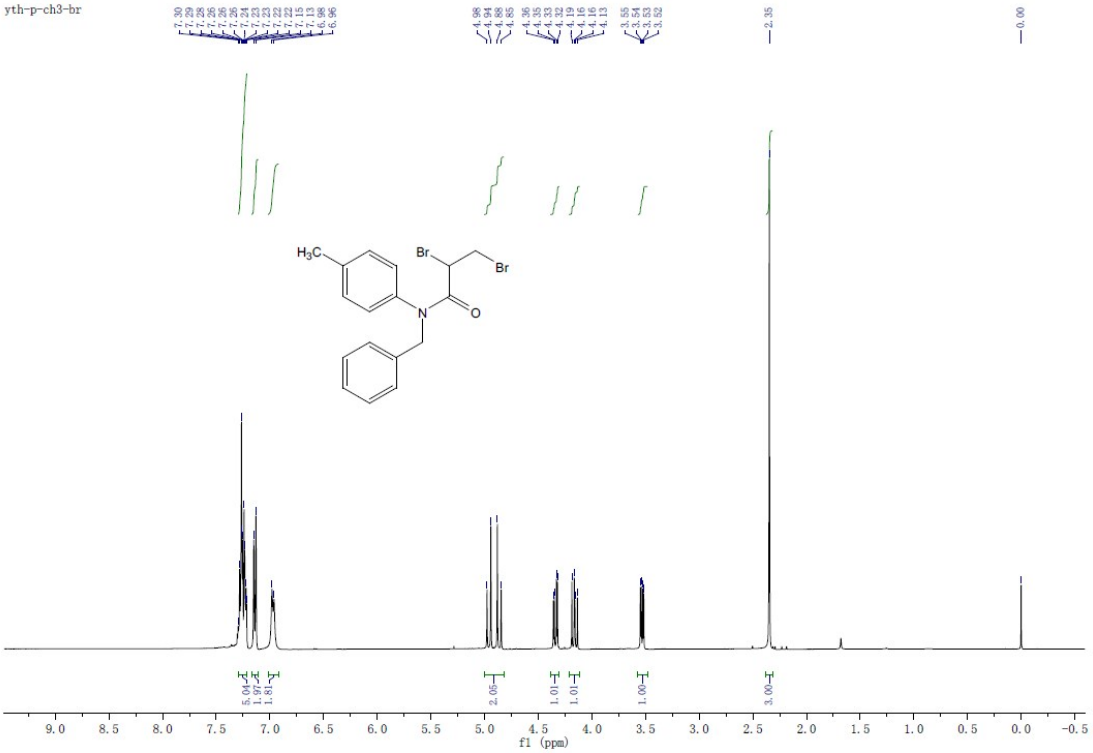


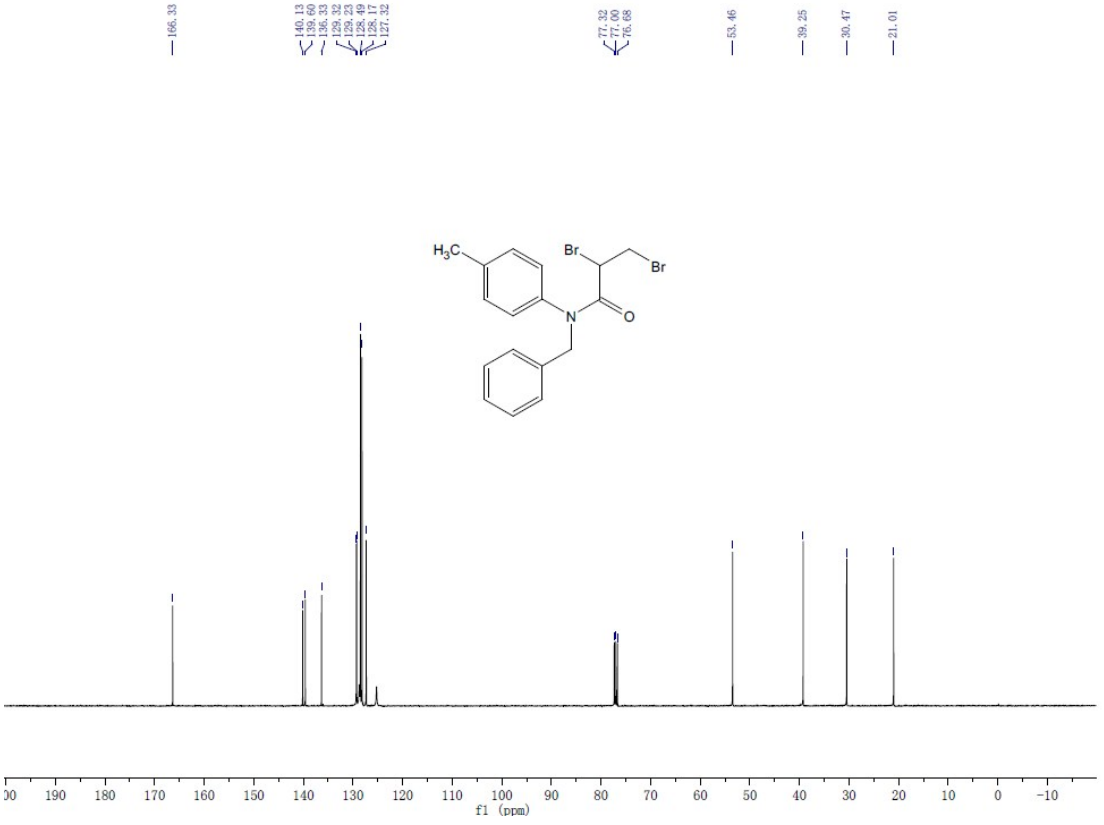

yth-o-ch3-br
Br
Br
N
O
CH3
f1 (ppm)

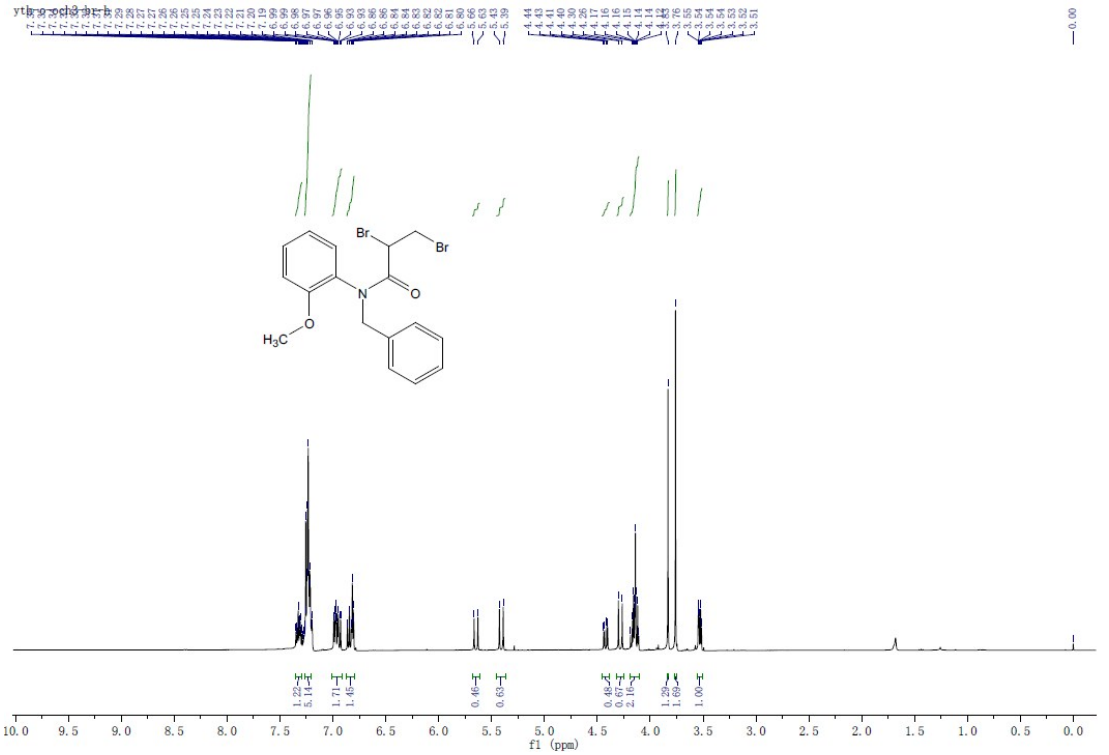

CH3
O
N
Br
Br
f1 (ppm)

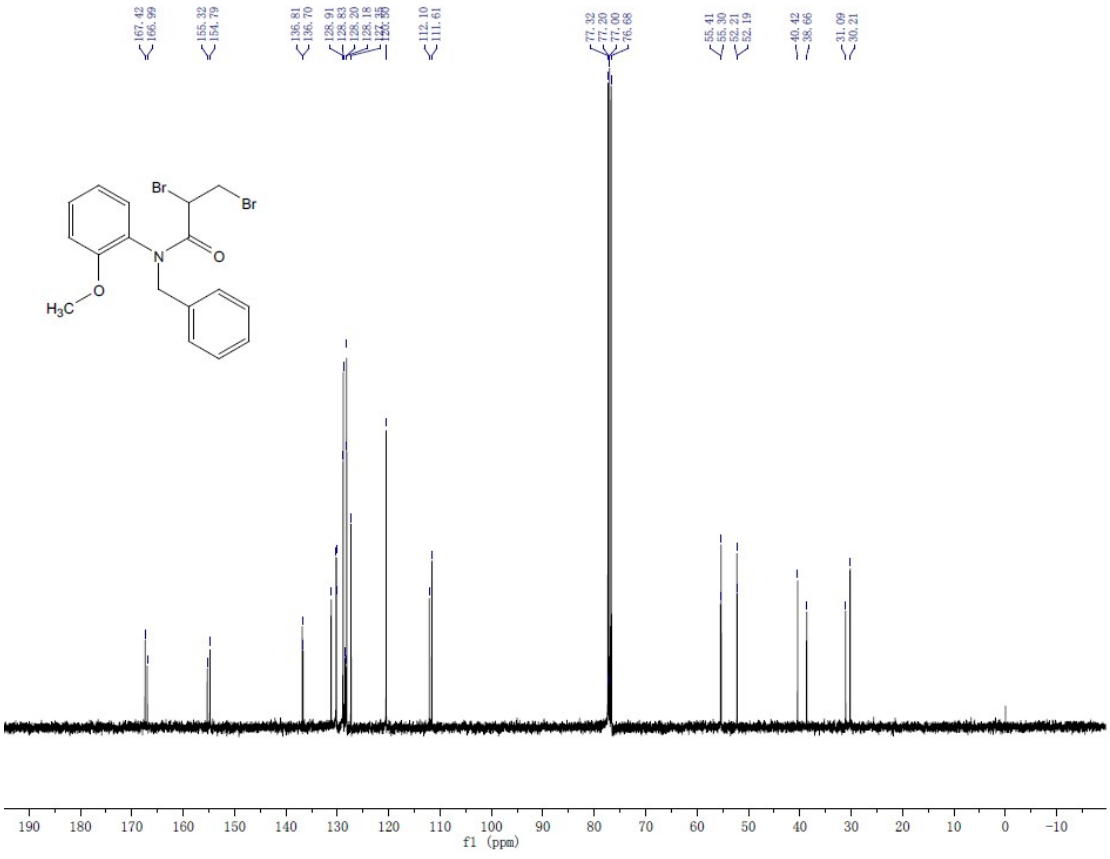

yth-m-ch3-br
Br
Br
H3C
N
O
f1 (ppm)

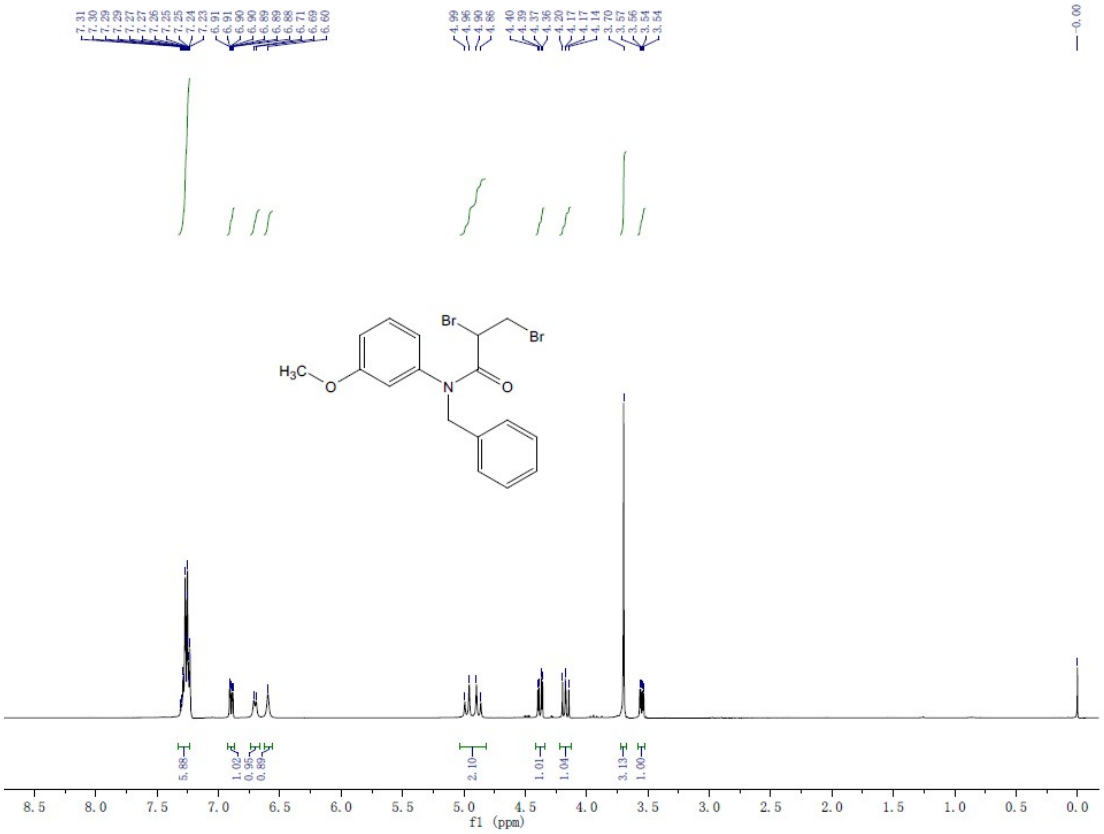

yth-m-ch3-br
Br
Br
H3C
N
O
f1 (ppm)

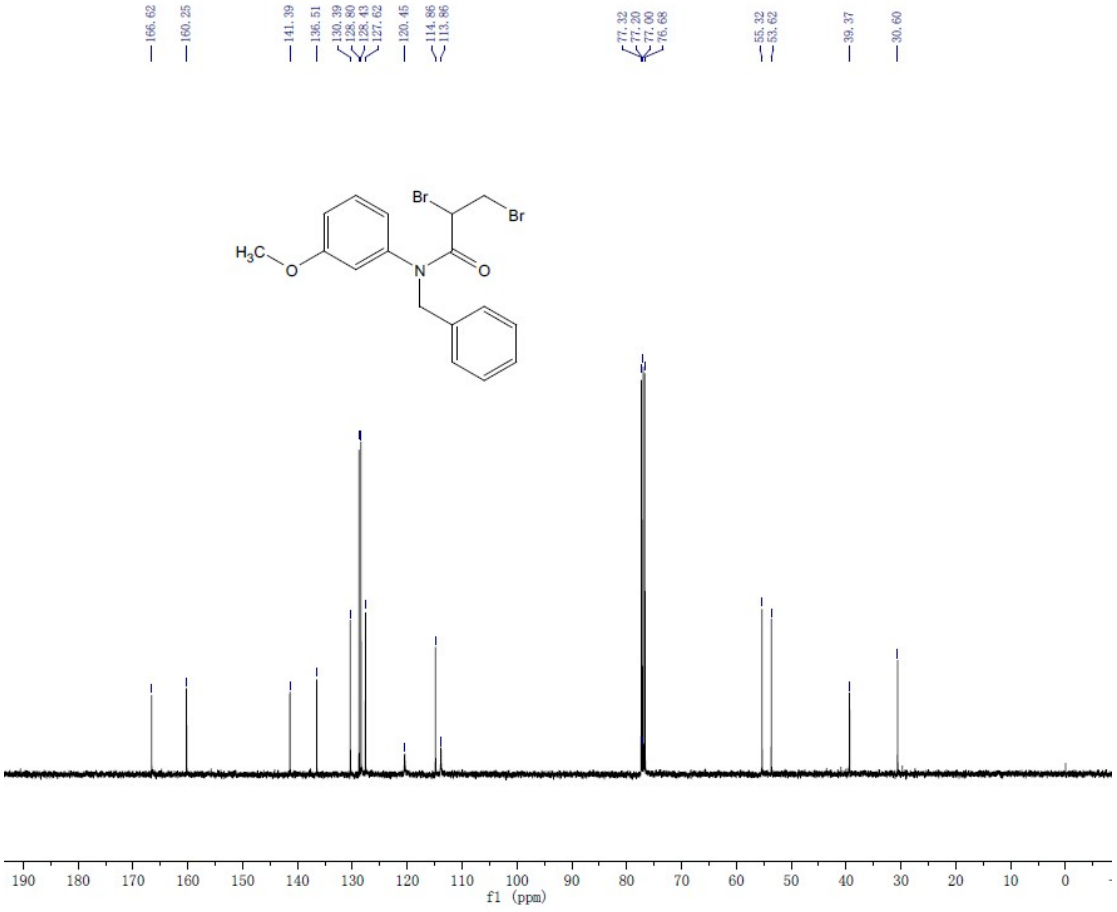

yth-p-ch3-br
H3C
Br
Br
N
O
f1 (ppm)

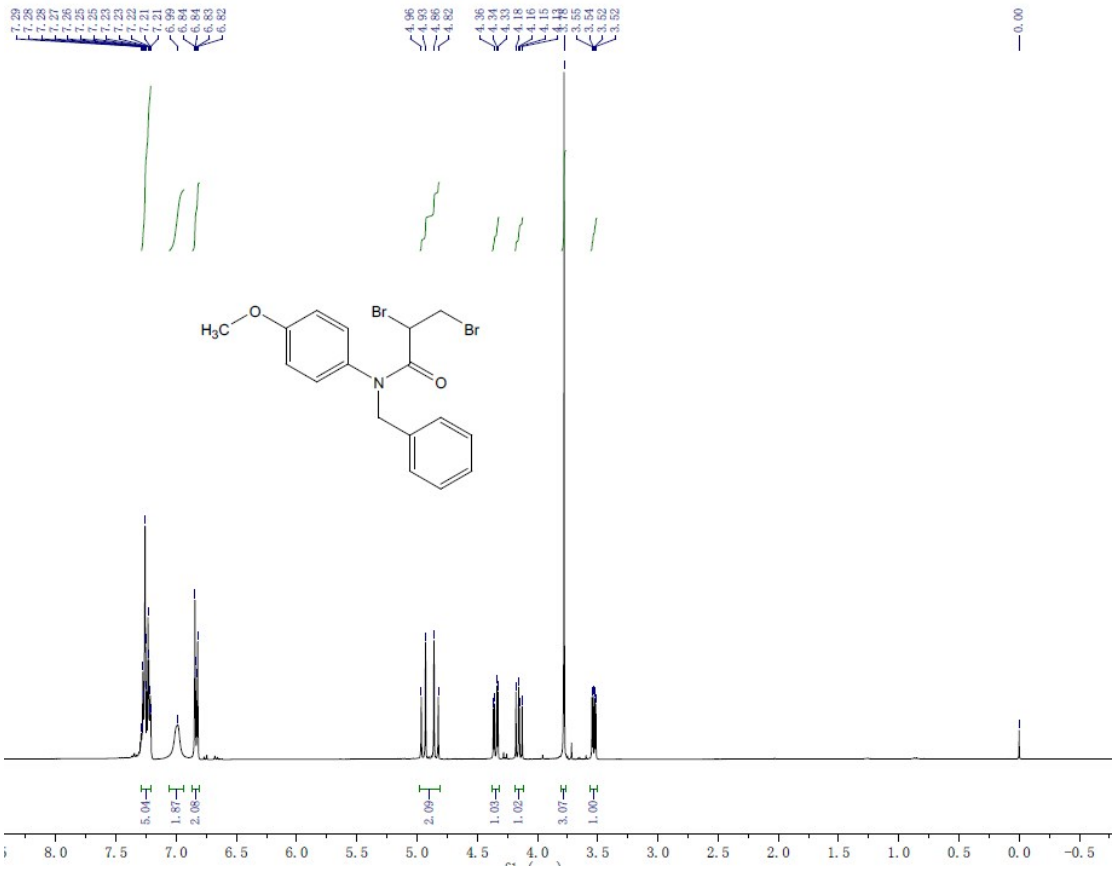

H3C
Br
Br
N
O
f1 (ppm)

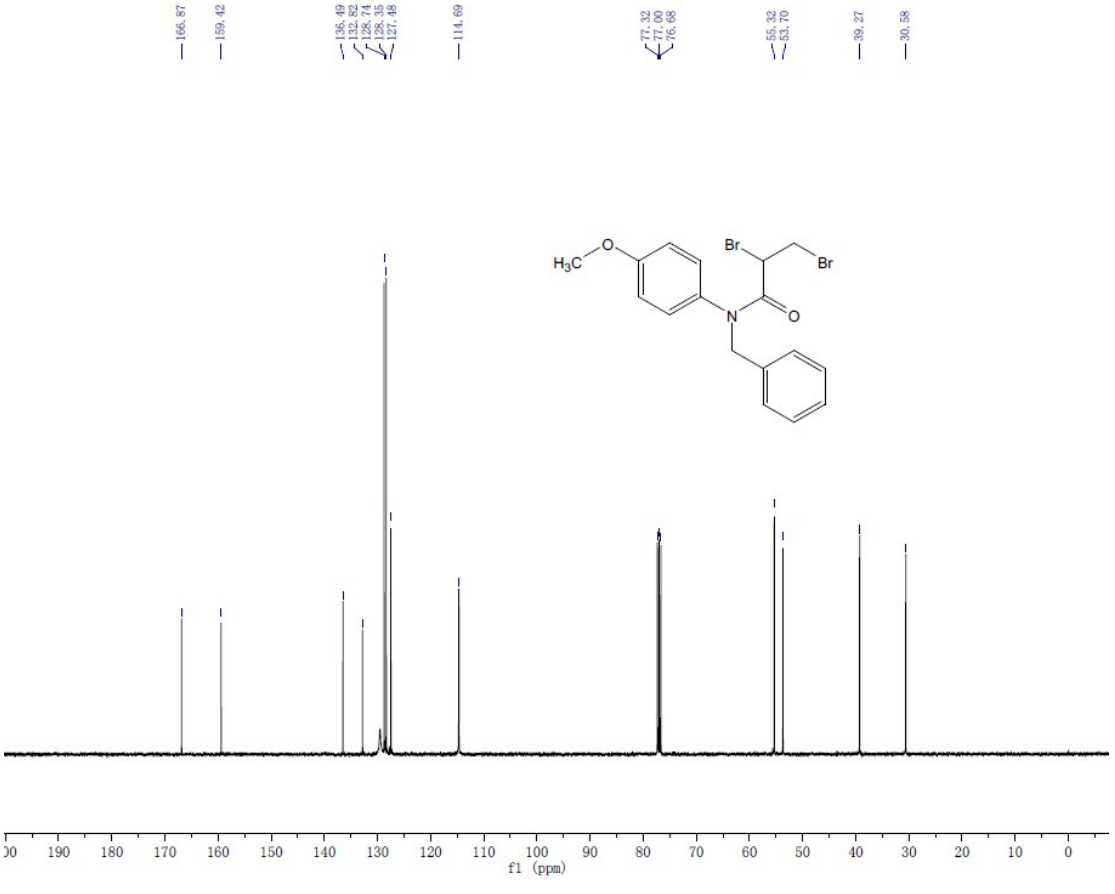

Br
Br
O
N
O
H3C
f1 (ppm)

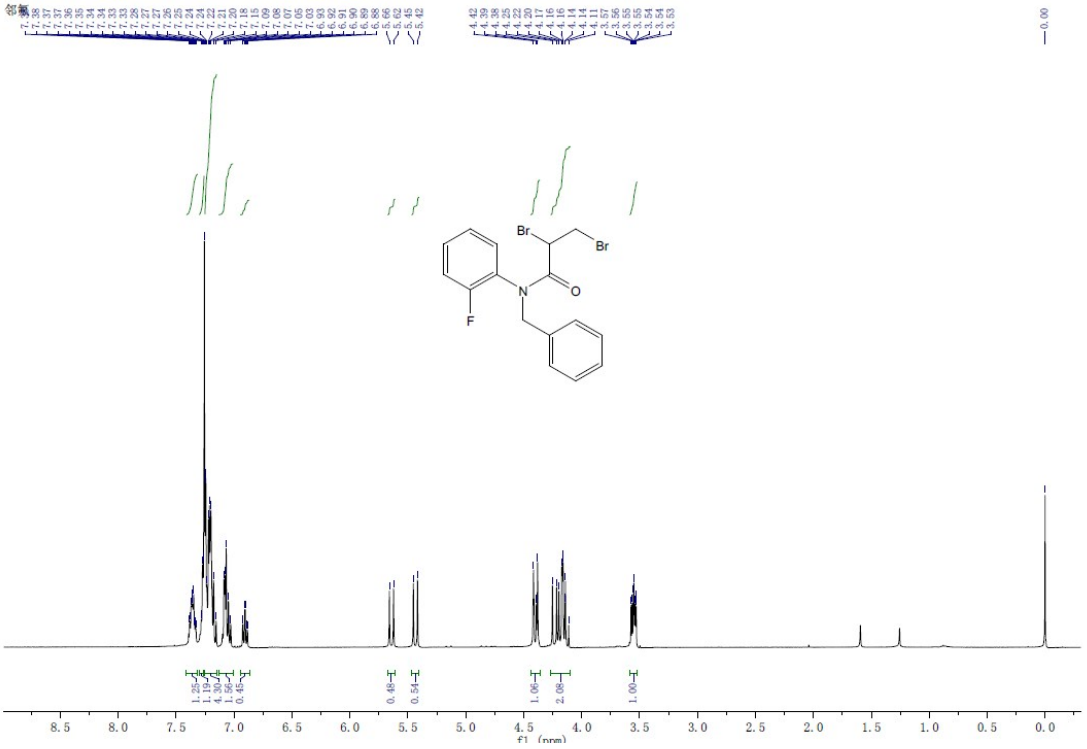

Br
Br
O
N
O
H3C
f1 (ppm)

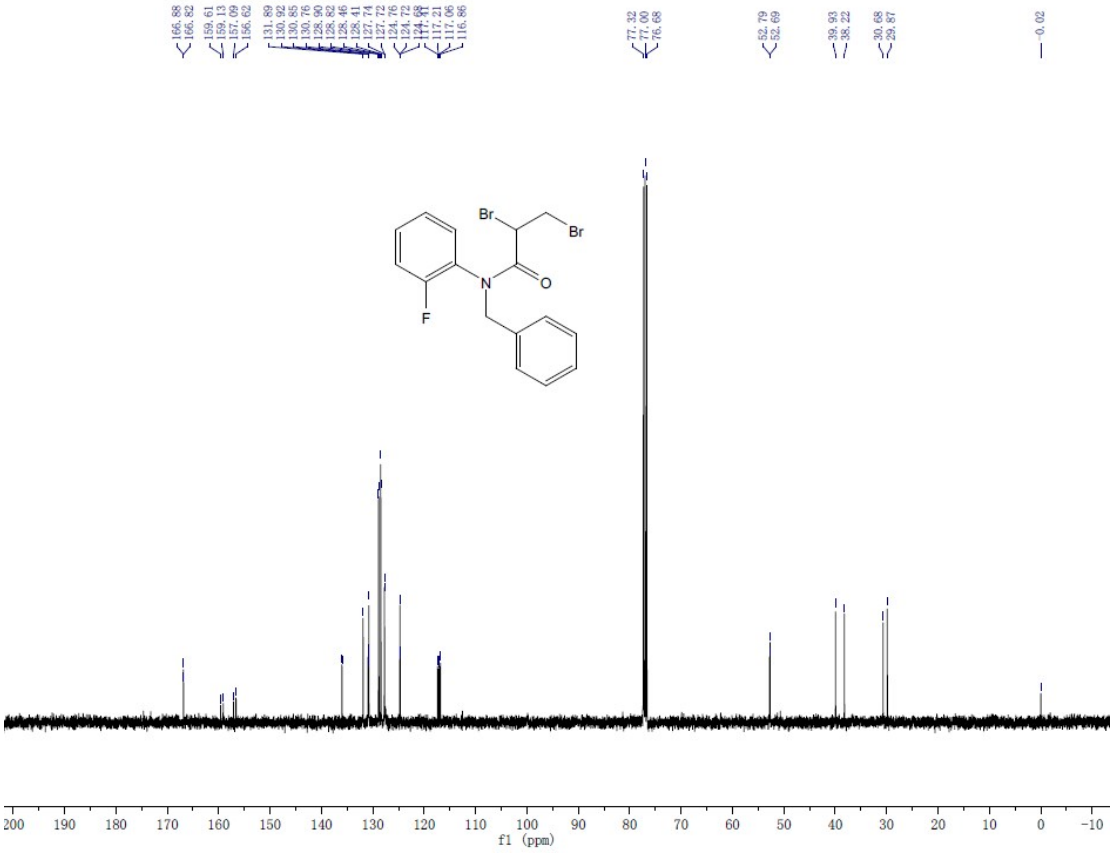

7.31
7.30
7.29
7.29
7.27
7.27
7.26
7.25
7.25
7.24
7.23
6.91
6.90
6.90
6.89
6.89
6.88
6.71
6.69
6.60
4.99
4.96
4.90
4.86
4.40
4.39
4.37
4.36
4.20
4.17
4.17
4.14
3.70
3.57
3.56
3.54
3.54
0.00
Br
Br
H3C
O
N
O
5.88
1.02
0.95
0.89
2.10
1.01
1.04
3.13
1.00
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

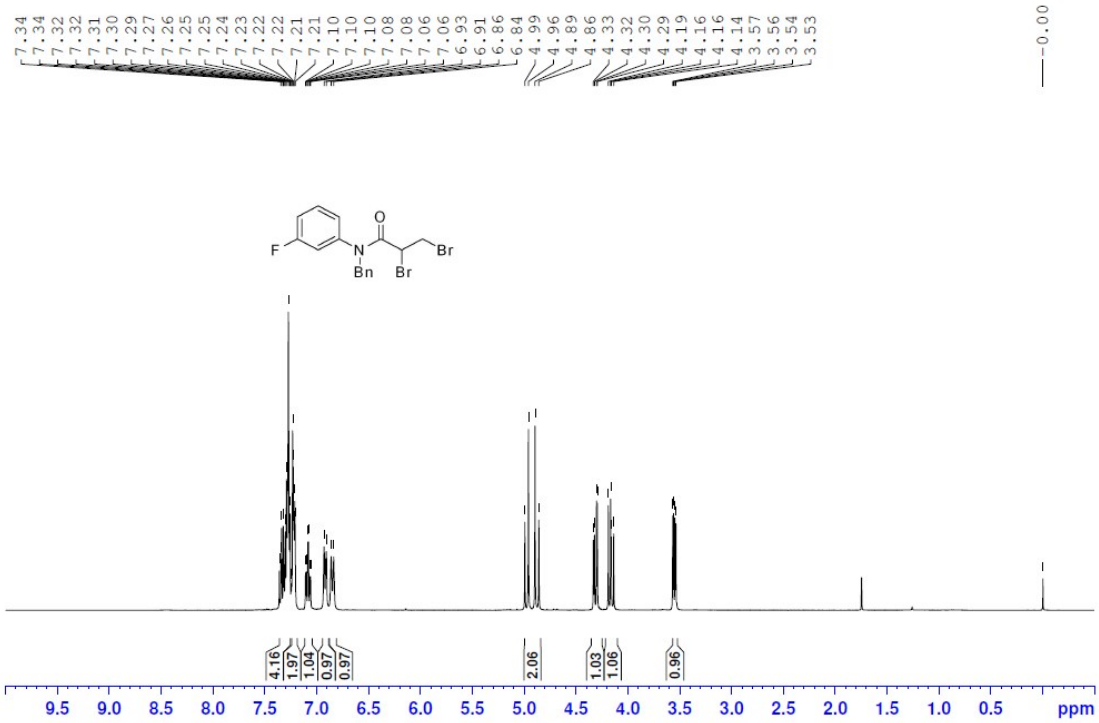

166.62
160.25
141.39
136.51
130.39
128.80
128.43
127.62
120.45
114.86
113.86
77.32
77.20
77.00
76.68
55.32
53.62
39.37
30.60
Br
Br
H3C
O
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

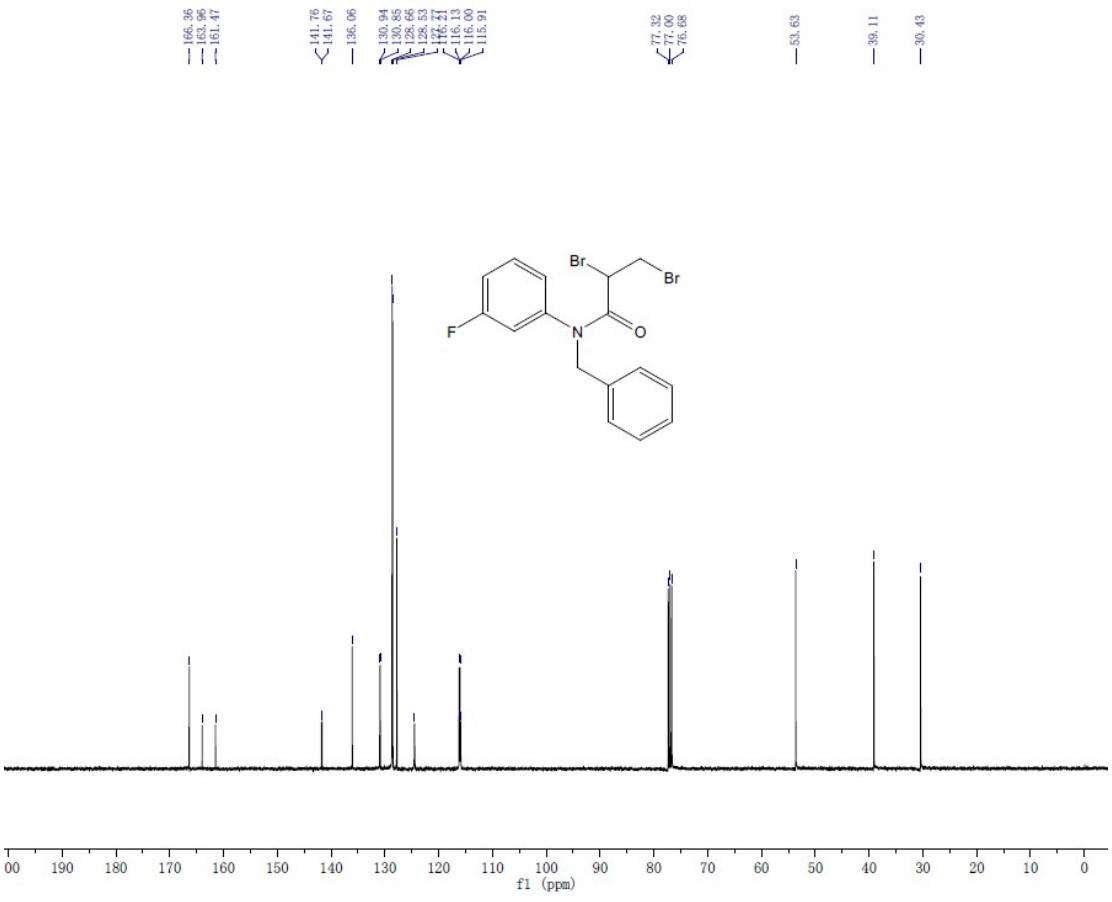

7.29
7.28
7.28
7.27
7.26
7.25
7.25
7.23
7.22
7.21
7.21
6.85
6.84
6.83
6.82
4.96
4.93
4.86
4.82
4.36
4.34
4.33
4.18
4.16
4.15
3.78
3.55
3.54
3.52
3.52
0.00
Br
Br
O
H3C
N
O
5.04
1.87
2.08
2.09
1.03
1.02
3.07
1.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5

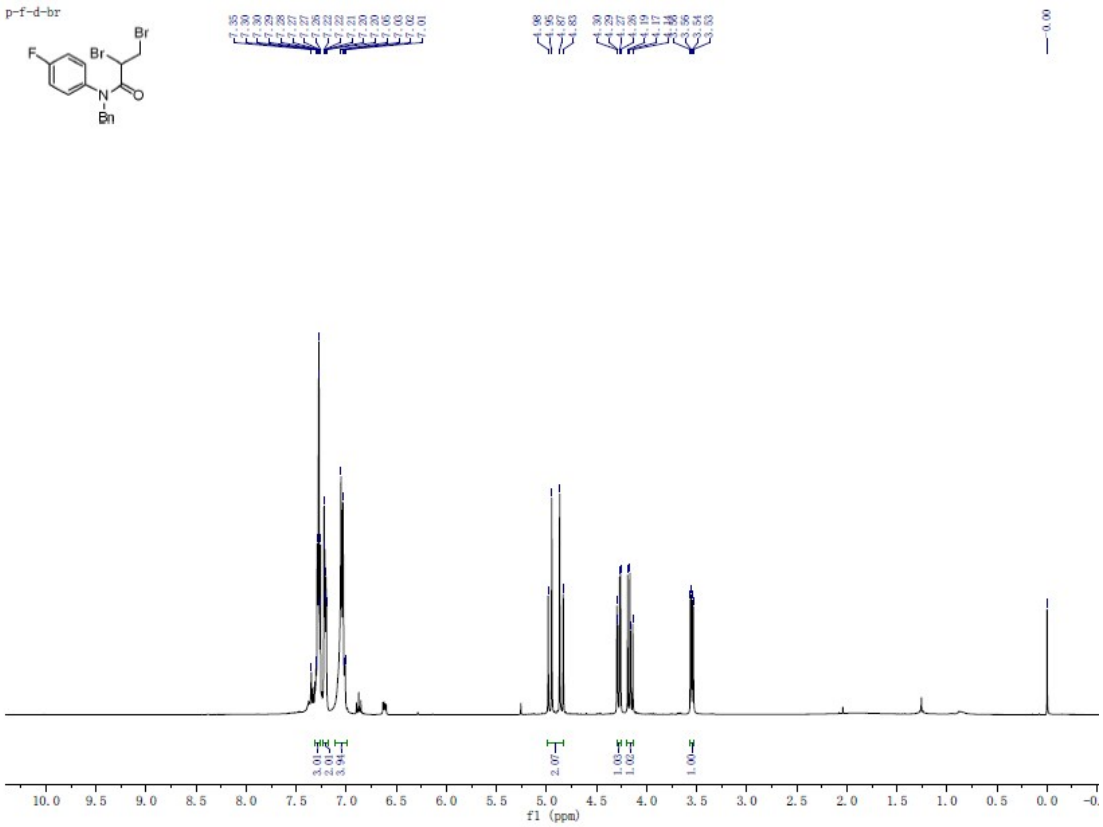

166.87
159.42
136.49
132.82
128.74
128.15
127.48
114.69
77.32
77.00
76.68
55.32
53.70
39.27
30.58
Br
Br
O
H3C
N
O
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

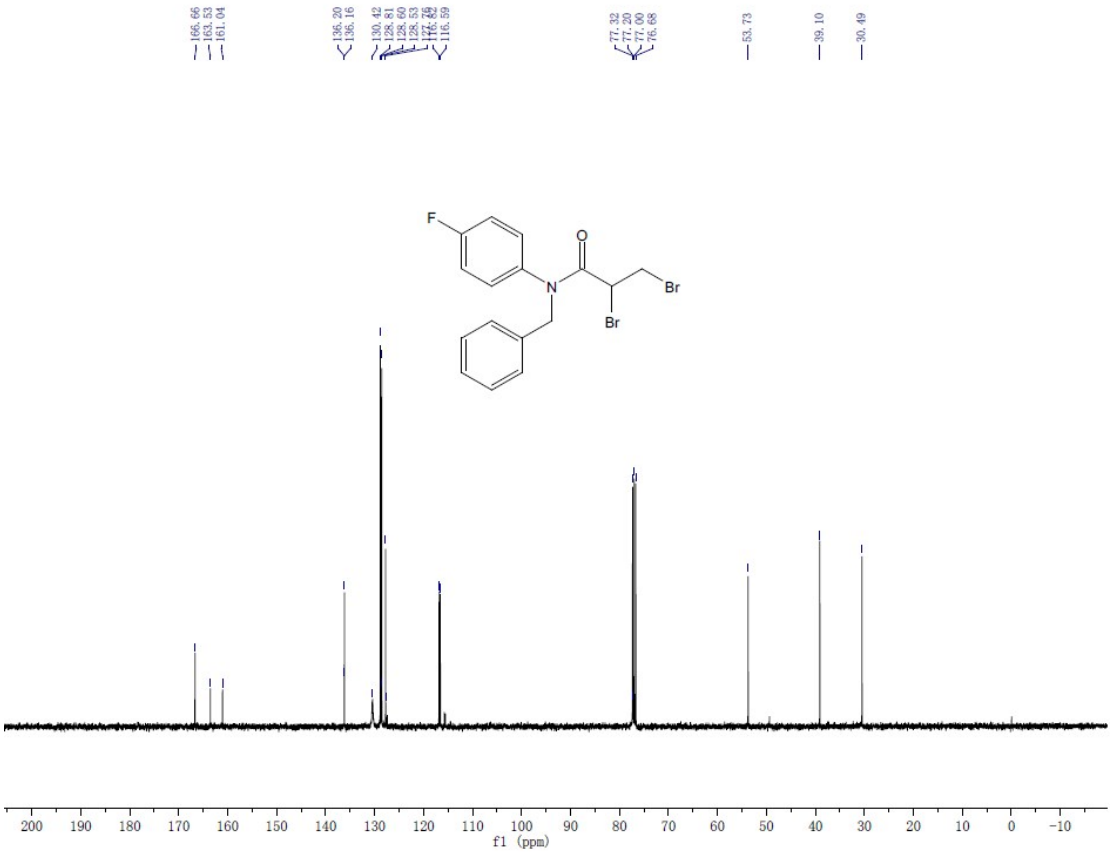

Br
Br
N
O
F
f1 (ppm)

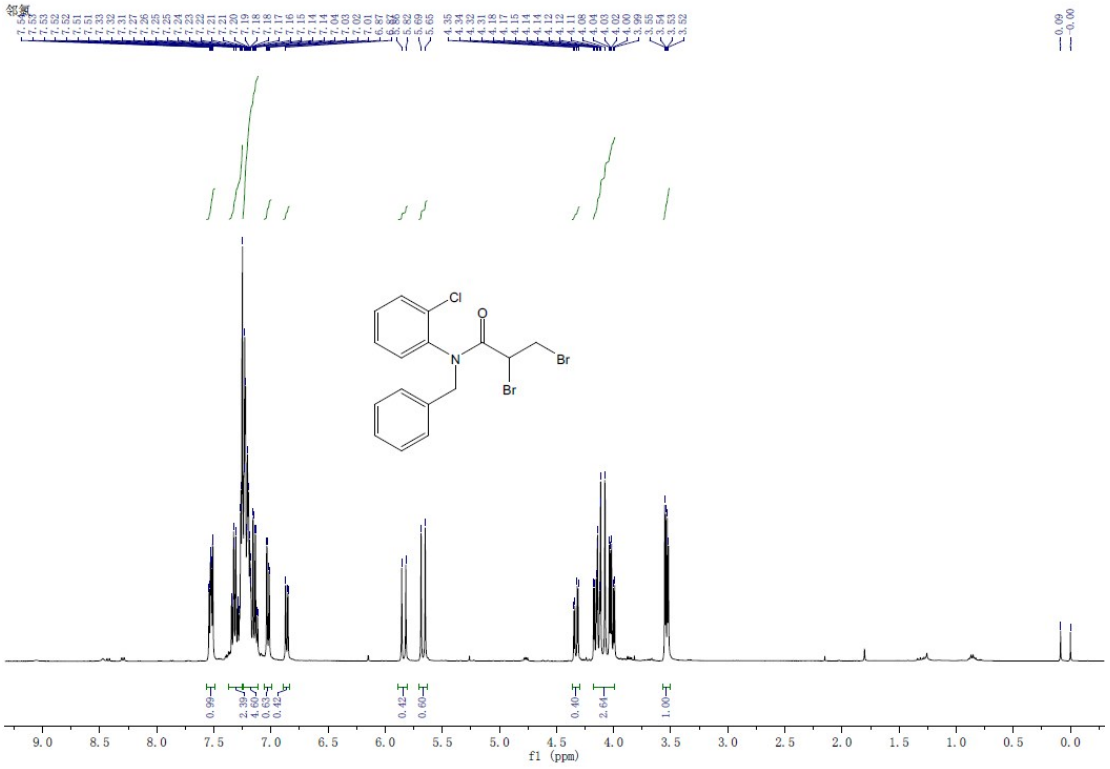

Br
Br
N
O
F
f1 (ppm)

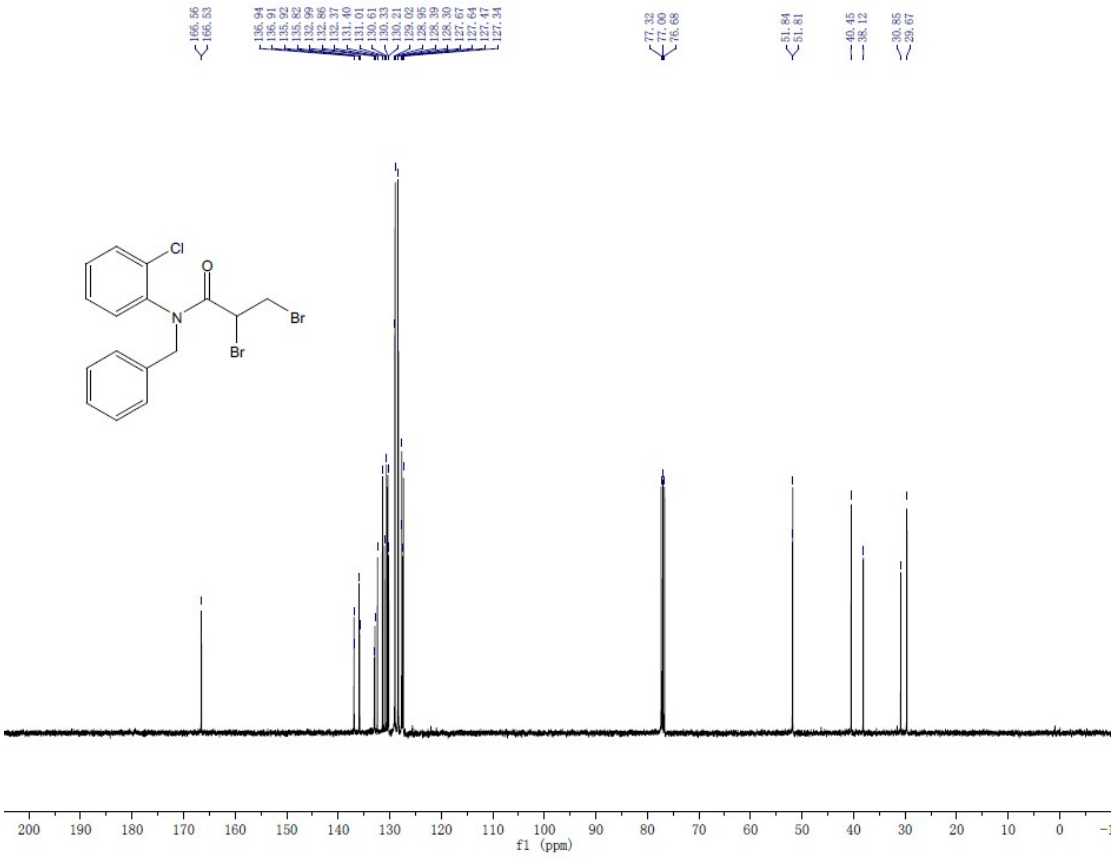

7.34
7.34
7.32
7.32
7.31
7.30
7.29
7.27
7.26
7.25
7.25
7.24
7.23
7.22
7.22
7.21
7.21
7.10
7.10
7.10
7.08
7.08
7.06
7.06
6.93
6.91
6.86
6.84
4.99
4.96
4.89
4.86
4.33
4.32
4.30
4.29
4.19
4.16
4.16
4.14
3.57
3.56
3.54
3.53
0.00
F
N
Bn
O
Br
Br
4.16
1.97
1.04
0.97
0.97
2.06
1.03
1.06
0.96
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm

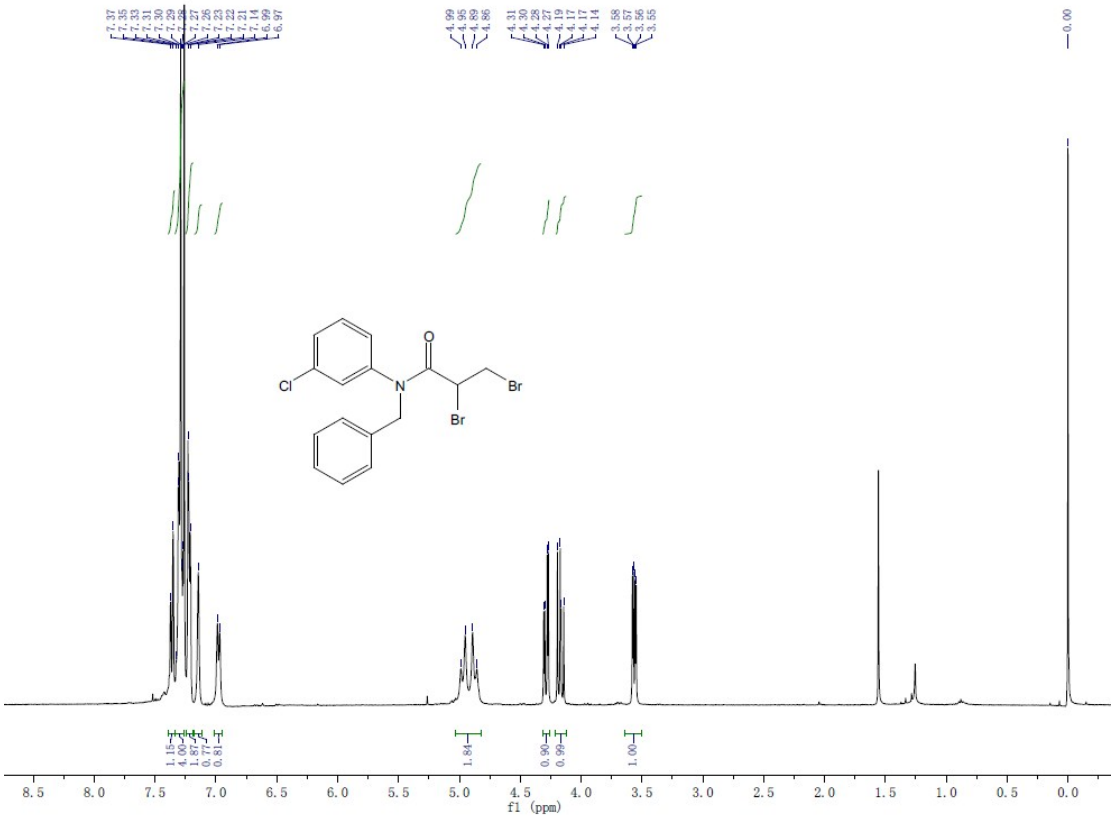

166.36
163.96
161.47
141.76
141.67
136.06
130.94
130.85
128.66
128.53
127.77
116.21
116.13
116.00
115.91
77.32
77.00
76.68
53.63
39.11
30.43
Br
Br
F
N
O
00
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

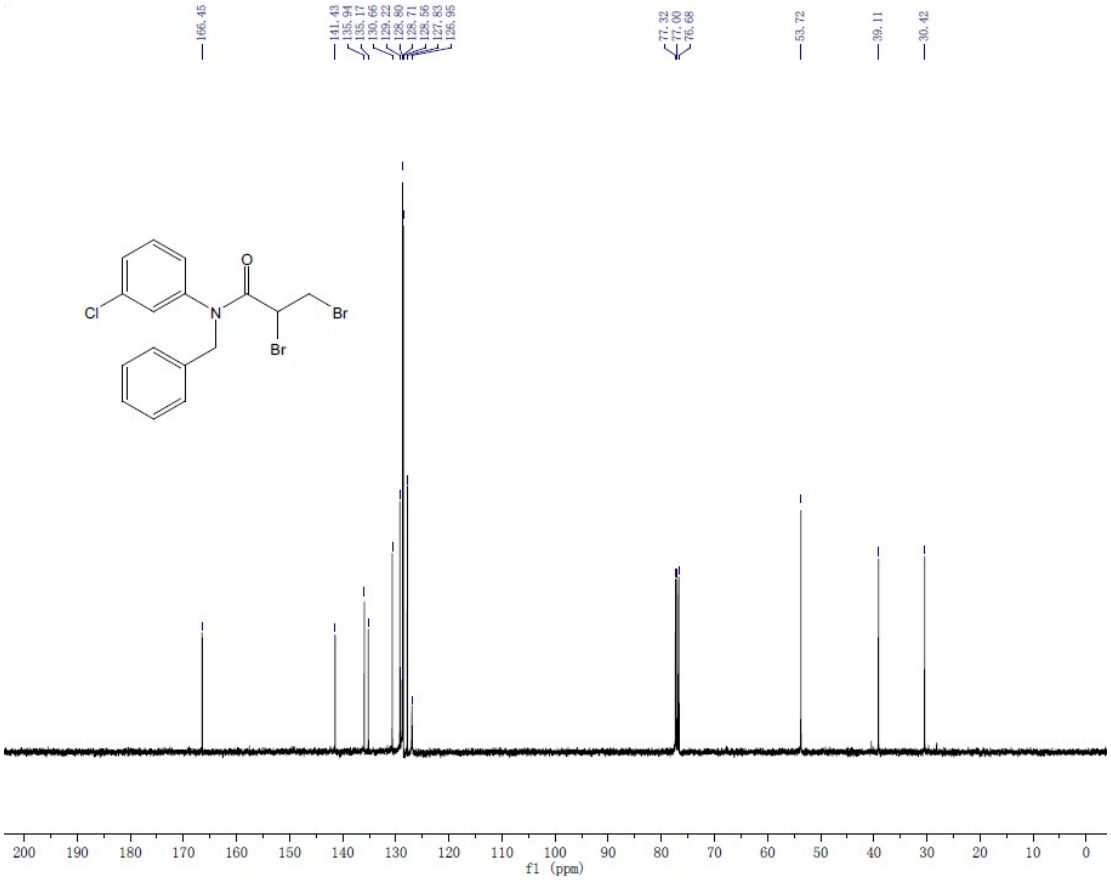

p-f-d-br
F
Br
Br
N
O
Bn
f1 (ppm)

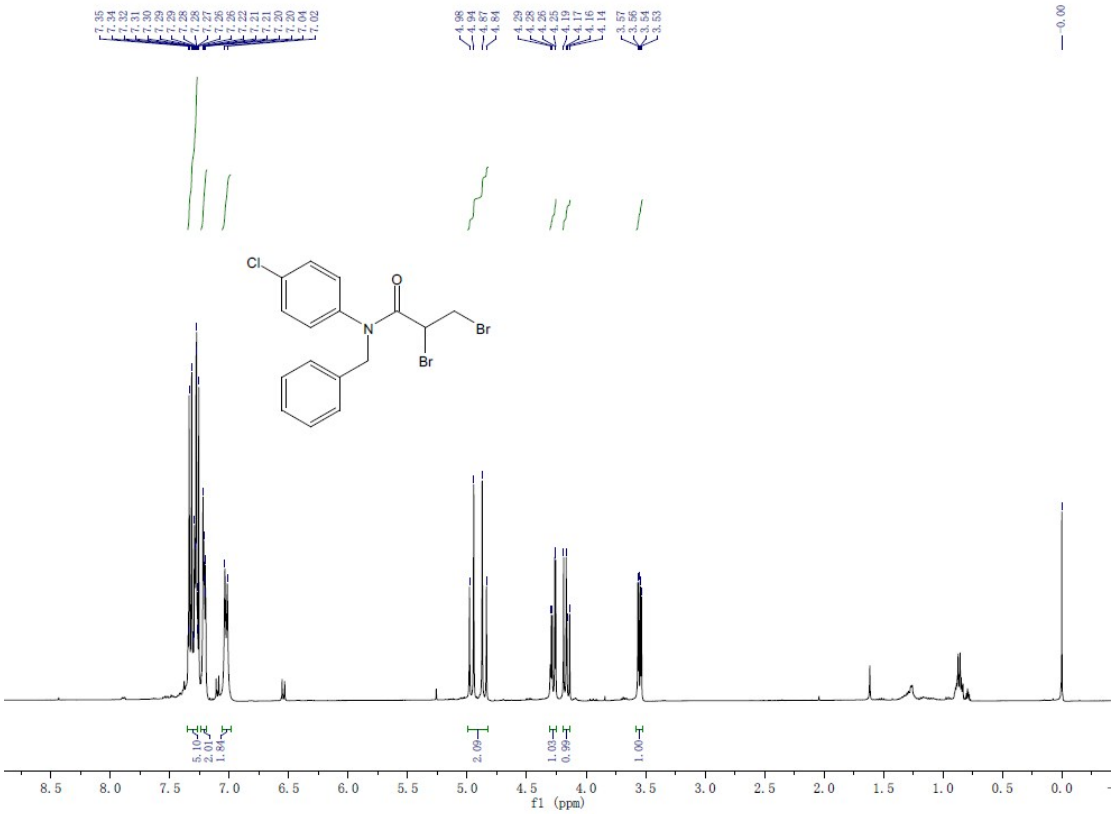

F
O
N
Br
Br
f1 (ppm)

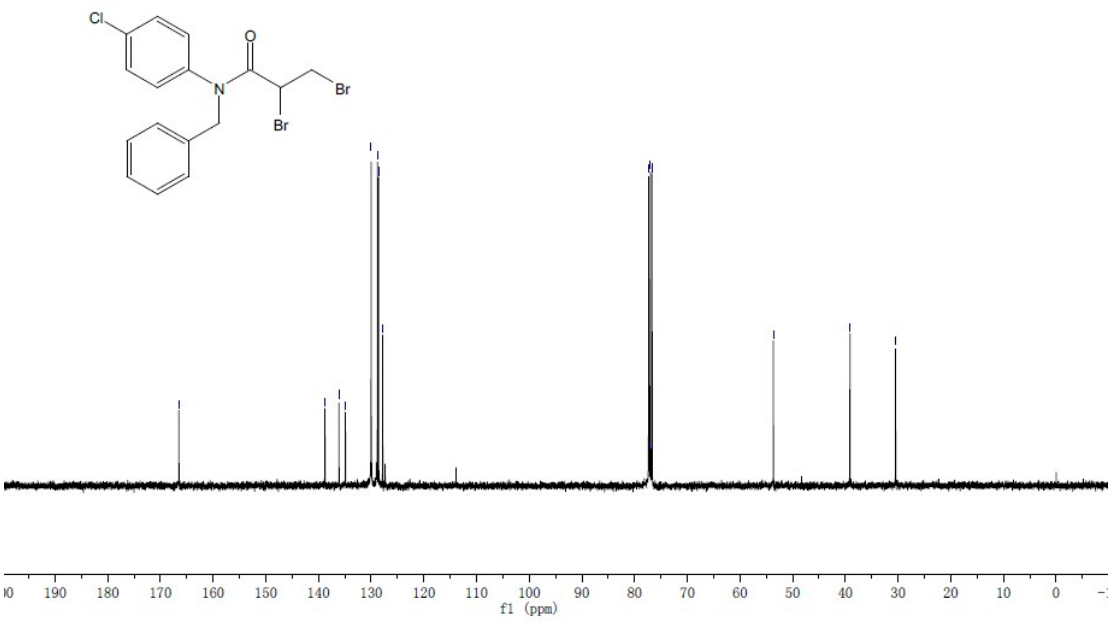

Cl
O
N
Br
Br
f1 (ppm)

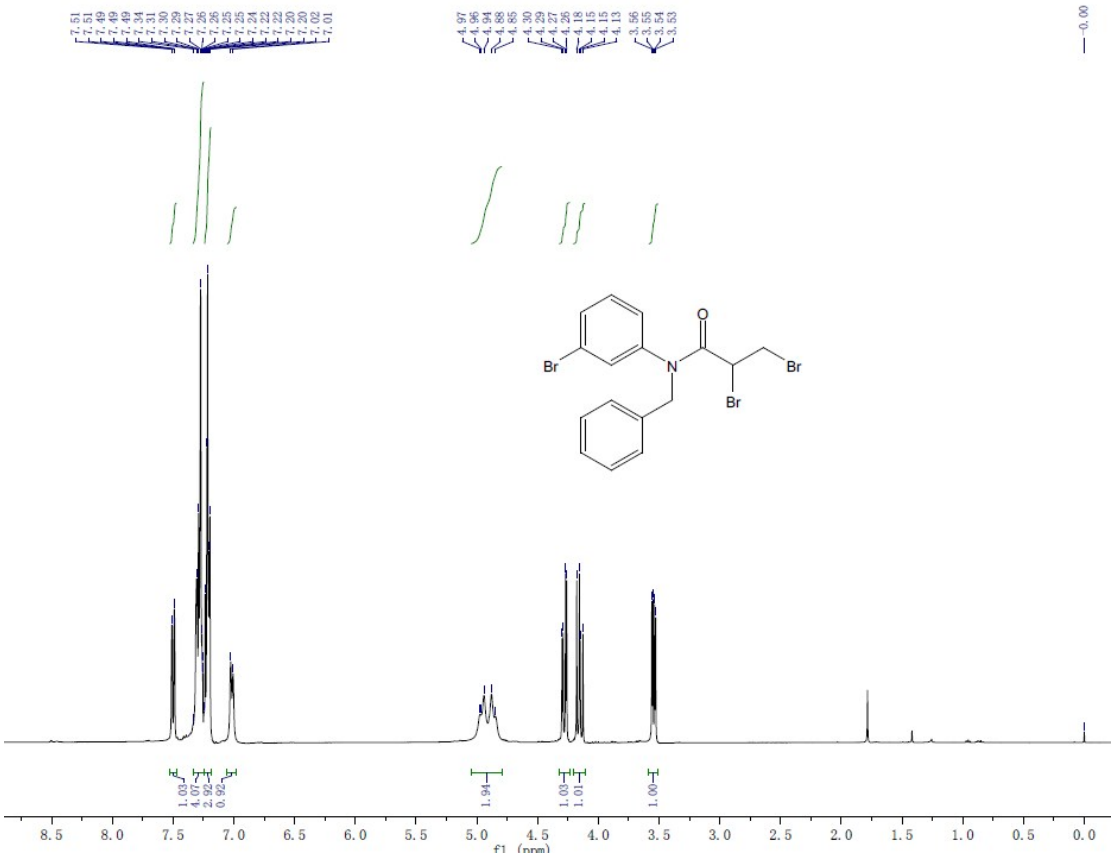

Cl
O
N
Br
Br
f1 (ppm)

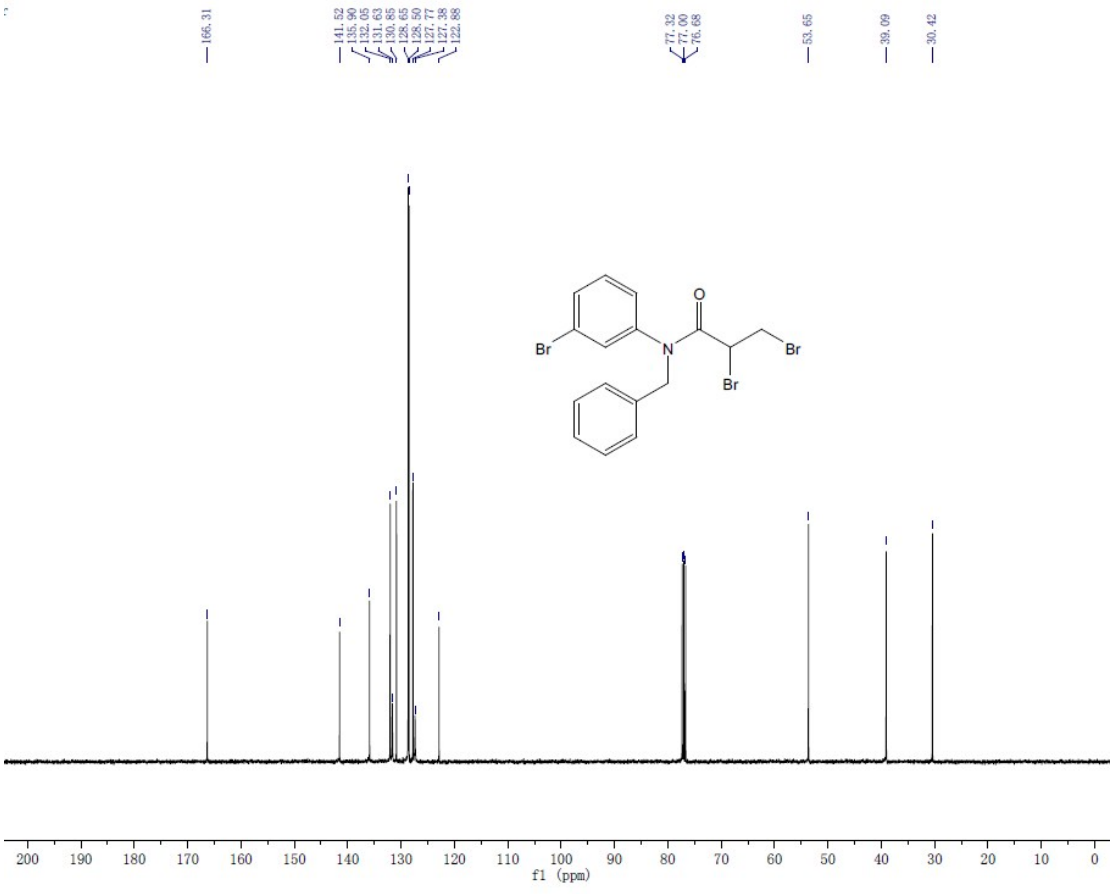

7.37
7.35
7.33
7.31
7.30
7.29
7.27
7.26
7.23
7.22
7.21
7.14
6.99
6.97
4.99
4.96
4.89
4.86
4.31
4.30
4.28
4.27
4.19
4.17
4.17
4.14
3.58
3.57
3.56
3.55
0.00
Cl
N
O
Br
Br
1.15
4.00
1.87
0.77
0.81
1.84
0.90
0.99
1.00
f1 (ppm)

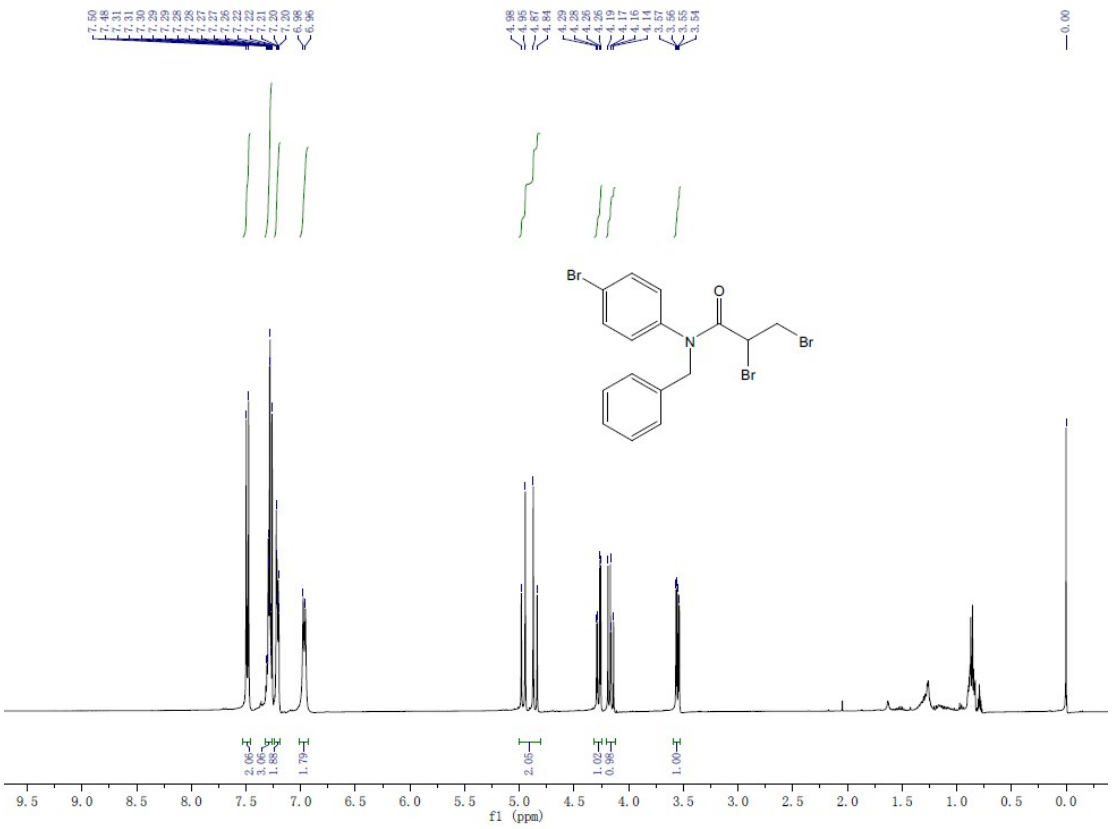

166.45
141.43
135.94
135.17
130.66
129.22
128.80
128.71
128.56
127.83
126.95
77.32
77.00
76.68
53.72
39.11
30.42
Cl
N
O
Br
Br
f1 (ppm)

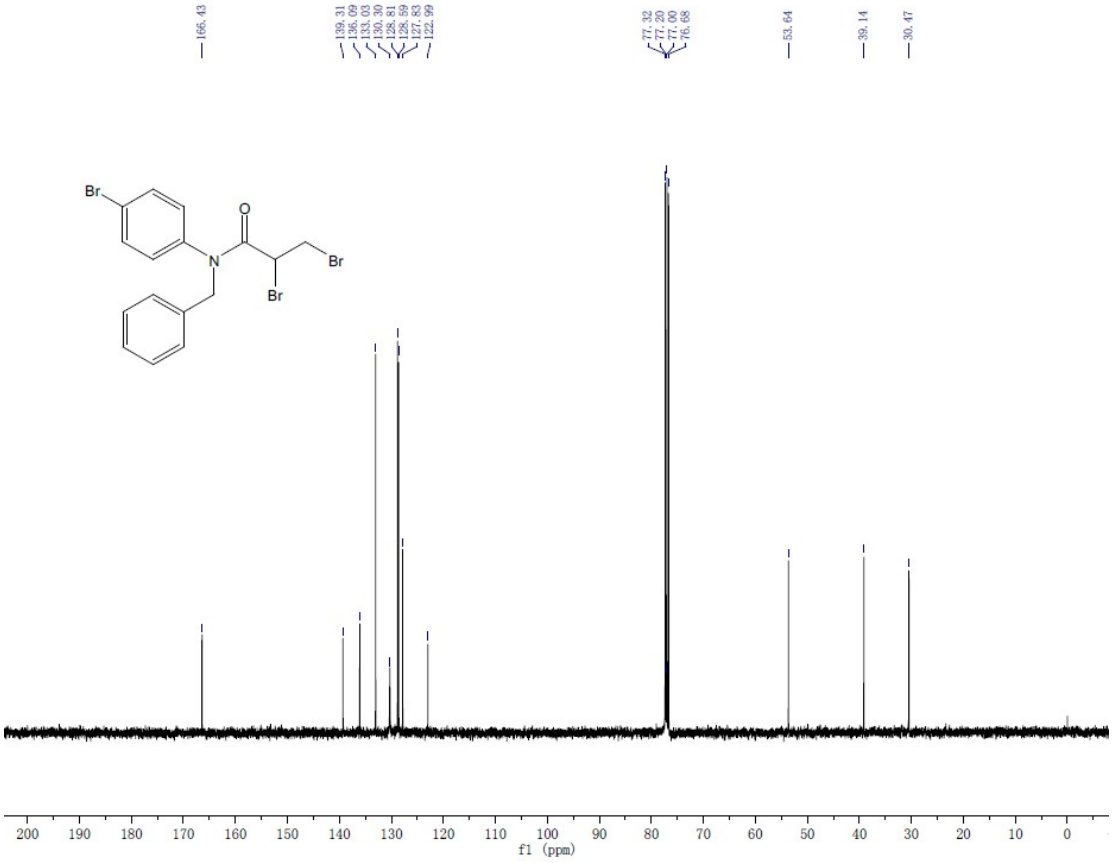

Cl
O
N
Br
Br
f1 (ppm)

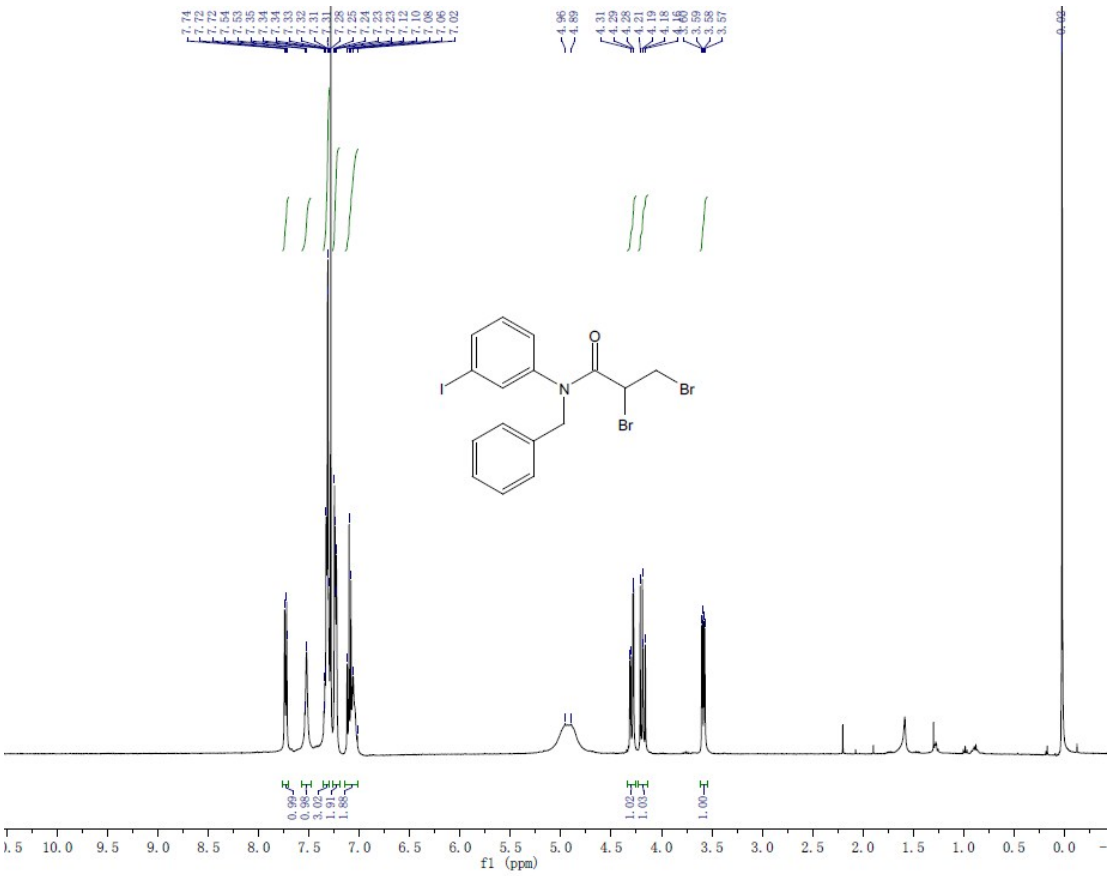

Cl
O
N
Br
Br
f1 (ppm)

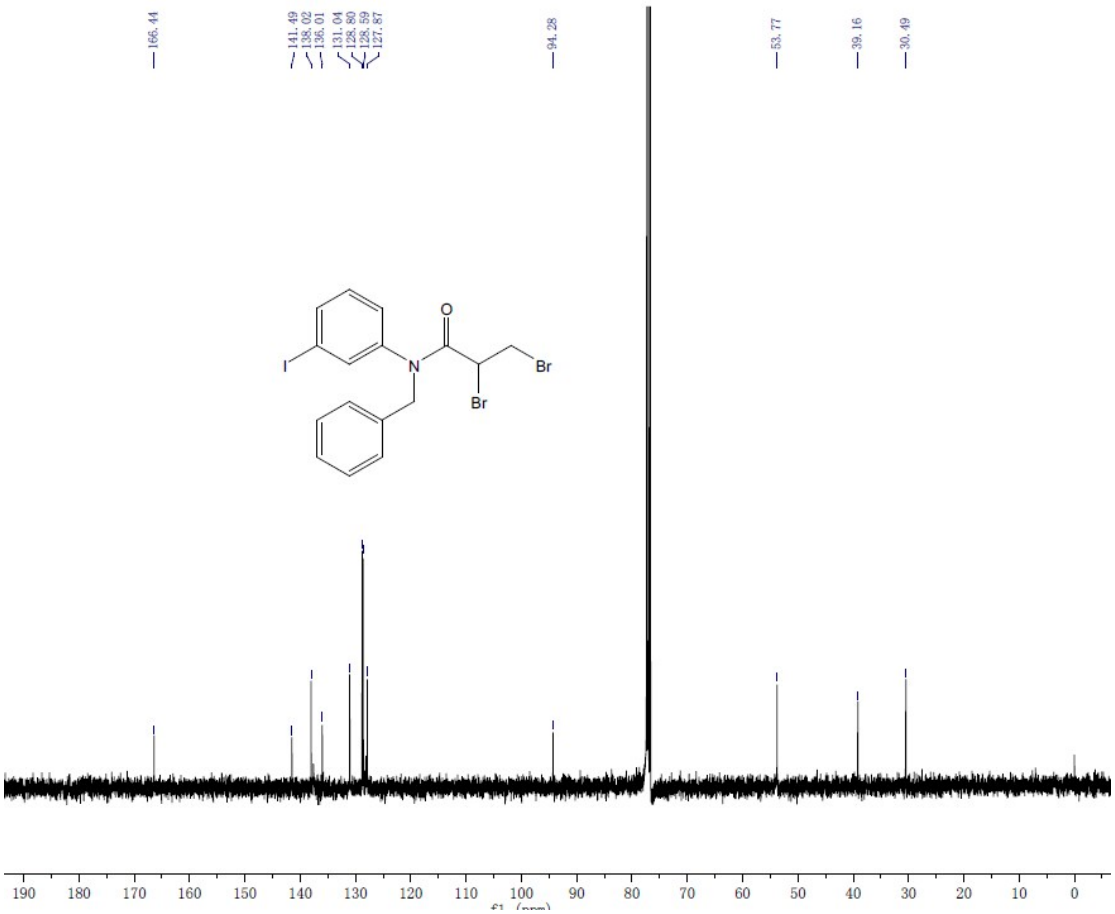

7.51
7.51
7.49
7.49
7.49
7.49
7.34
7.31
7.30
7.29
7.27
7.26
7.26
7.25
7.25
7.24
7.22
7.22
7.20
7.20
7.02
7.01
4.97
4.96
4.94
4.88
4.85
4.30
4.29
4.27
4.26
4.18
4.15
4.15
4.13
3.56
3.55
3.54
3.53
0.00
Br
N
O
Br
Br
1.03
4.07
2.92
0.92
1.94
1.03
1.01
1.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

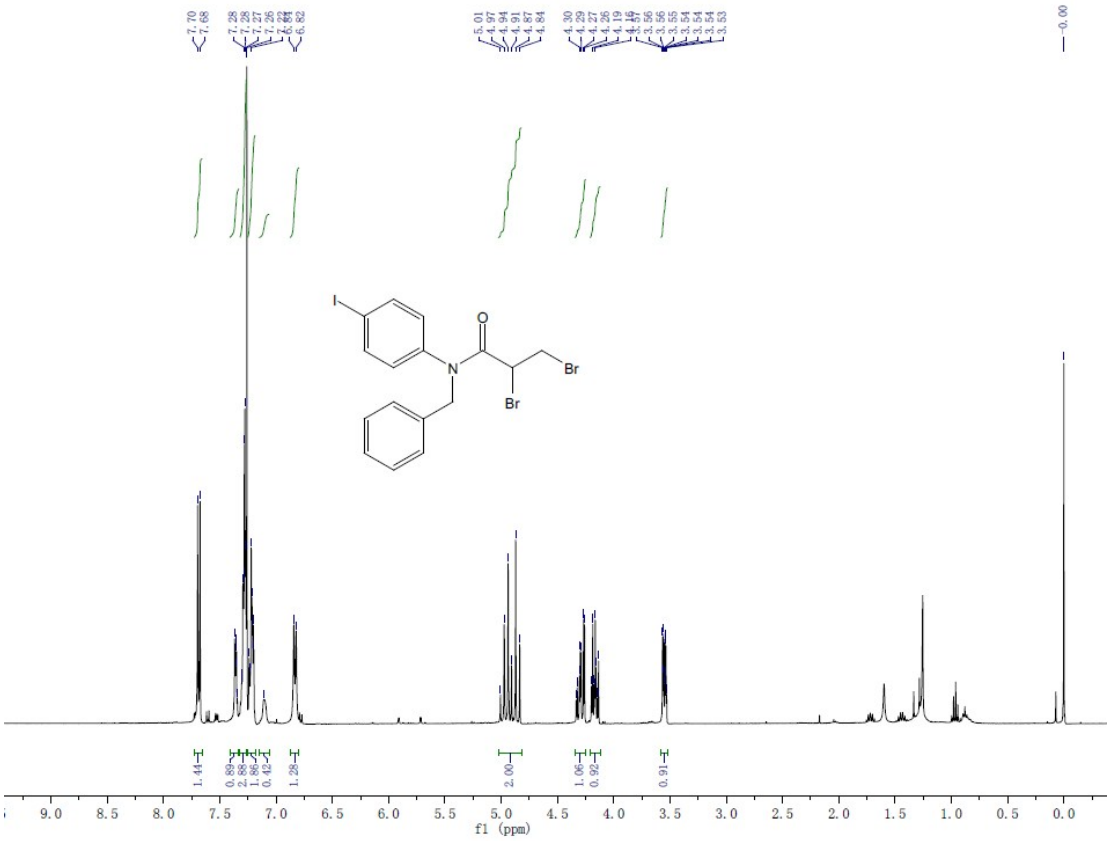

166.31
141.52
135.99
132.65
131.63
130.85
128.65
128.50
127.77
127.38
122.88
77.32
77.00
76.68
53.65
39.09
30.42
Br
N
O
Br
Br
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

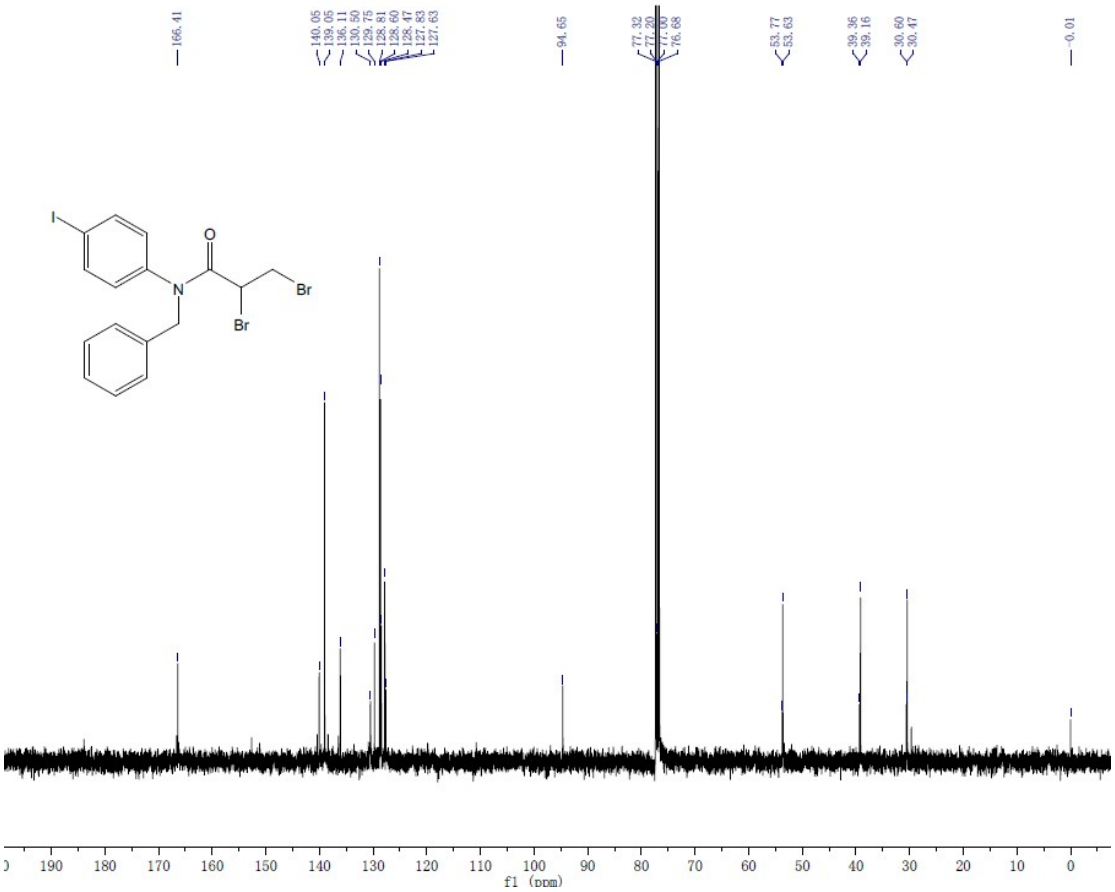

Br
O
N
Br
Br
f1 (ppm)

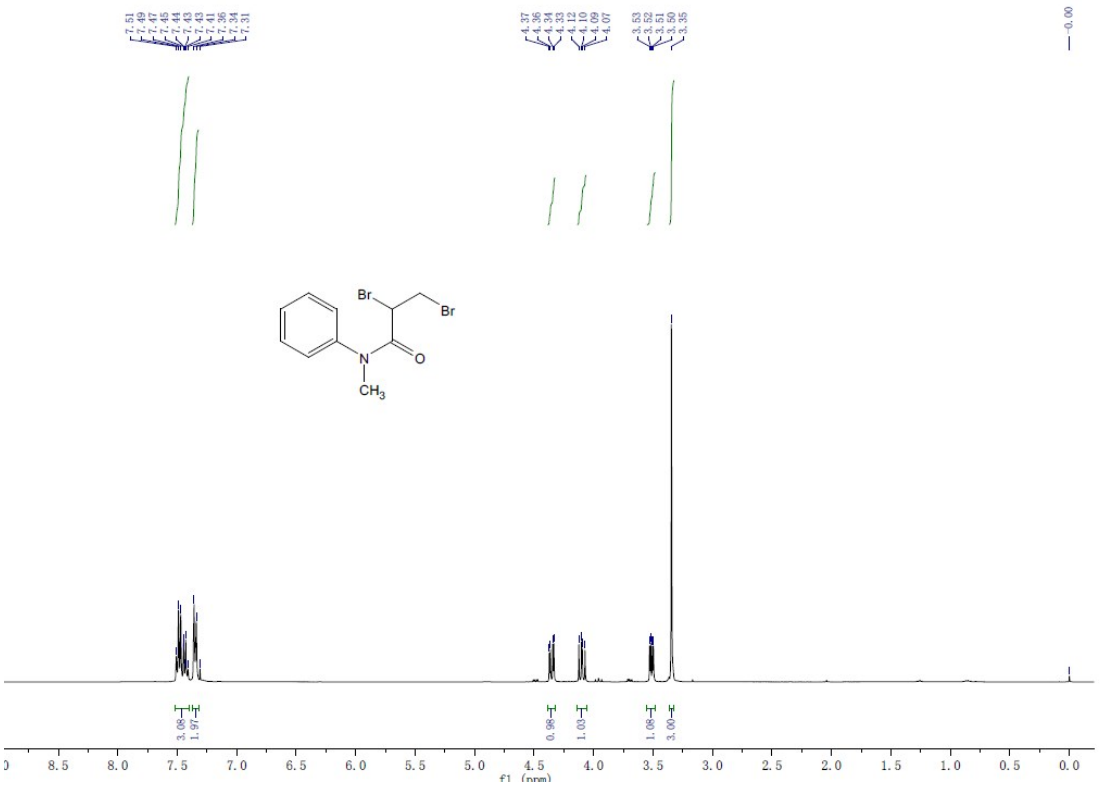

Br
O
N
Br
Br
f1 (ppm)

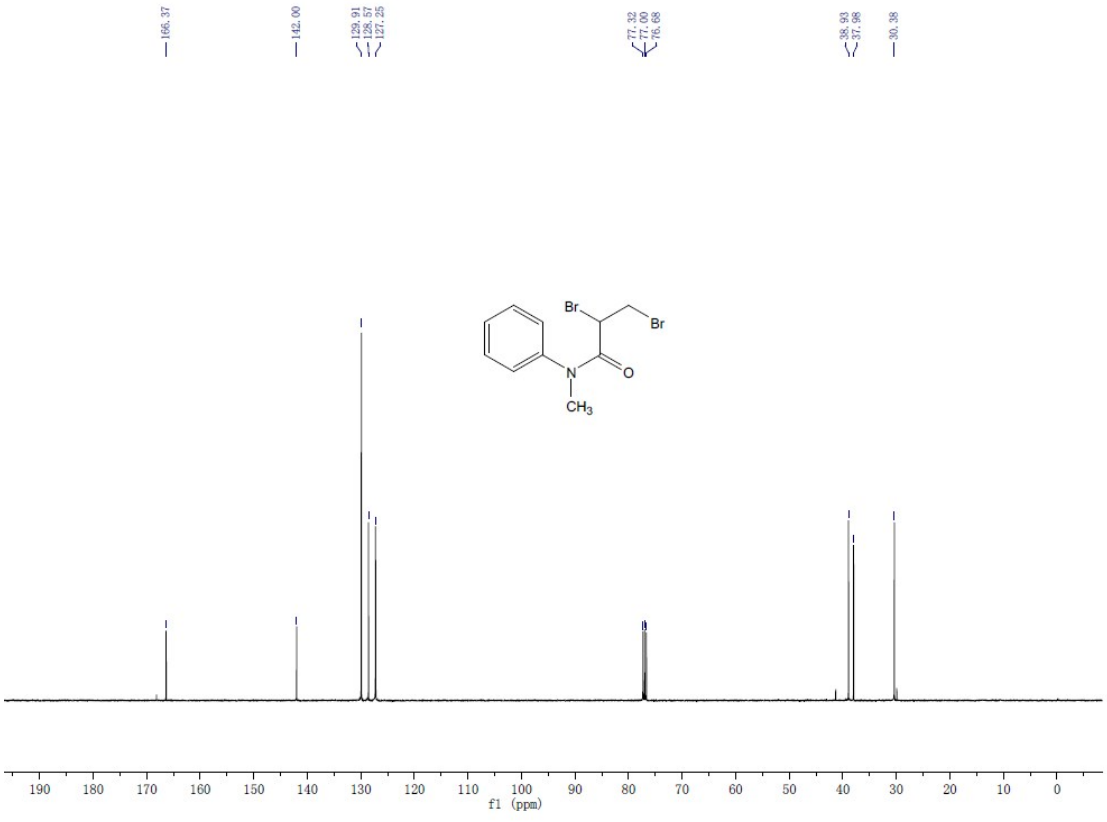

7.74
7.72
7.72
7.54
7.53
7.35
7.34
7.34
7.33
7.32
7.31
7.31
7.28
7.25
7.24
7.23
7.23
7.12
7.10
7.08
7.06
7.02
4.96
4.89
4.31
4.29
4.28
4.21
4.19
4.18
3.59
3.58
3.57
0.00
I
N
O
Br
Br
0.99
0.98
3.02
1.91
1.88
1.02
1.03
1.00
f1 (ppm)

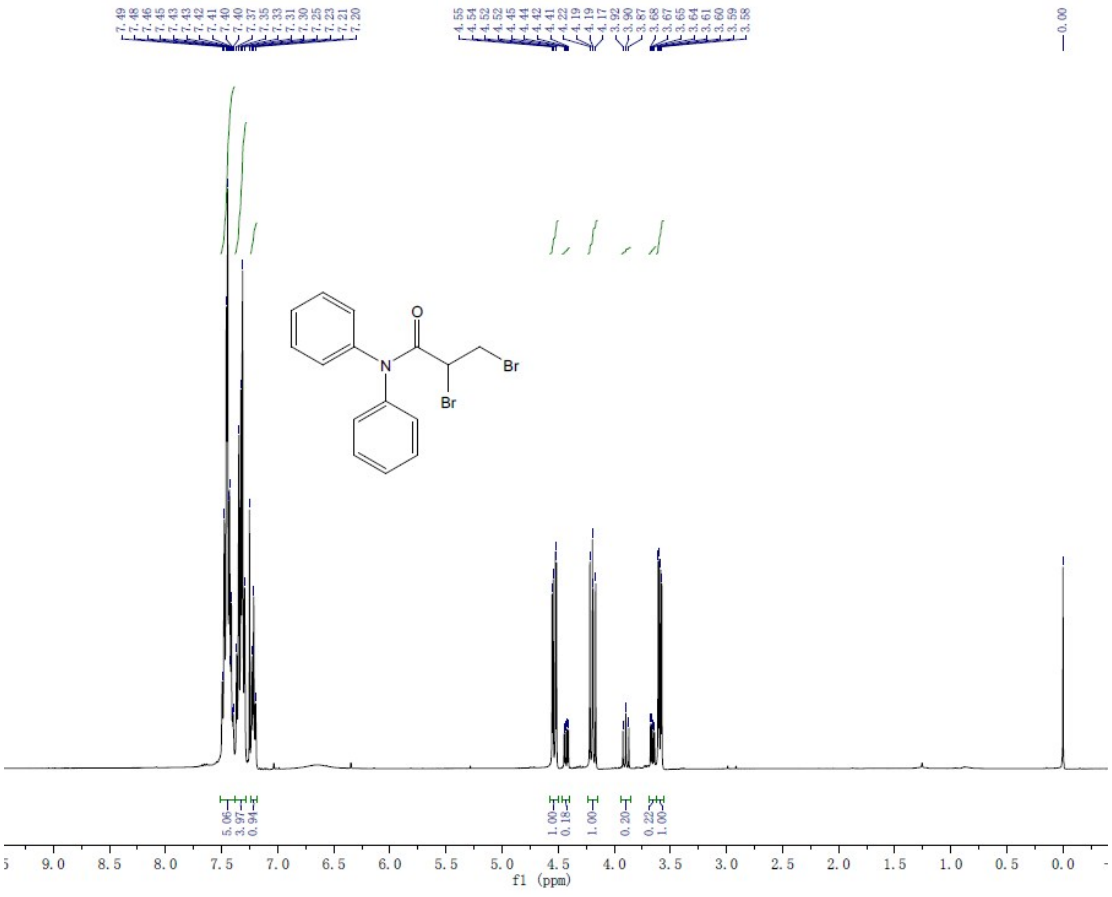

166.44
141.49
138.02
136.01
131.04
128.80
128.59
127.87
94.28
53.77
39.16
30.49
I
N
O
Br
Br
f1 (ppm)

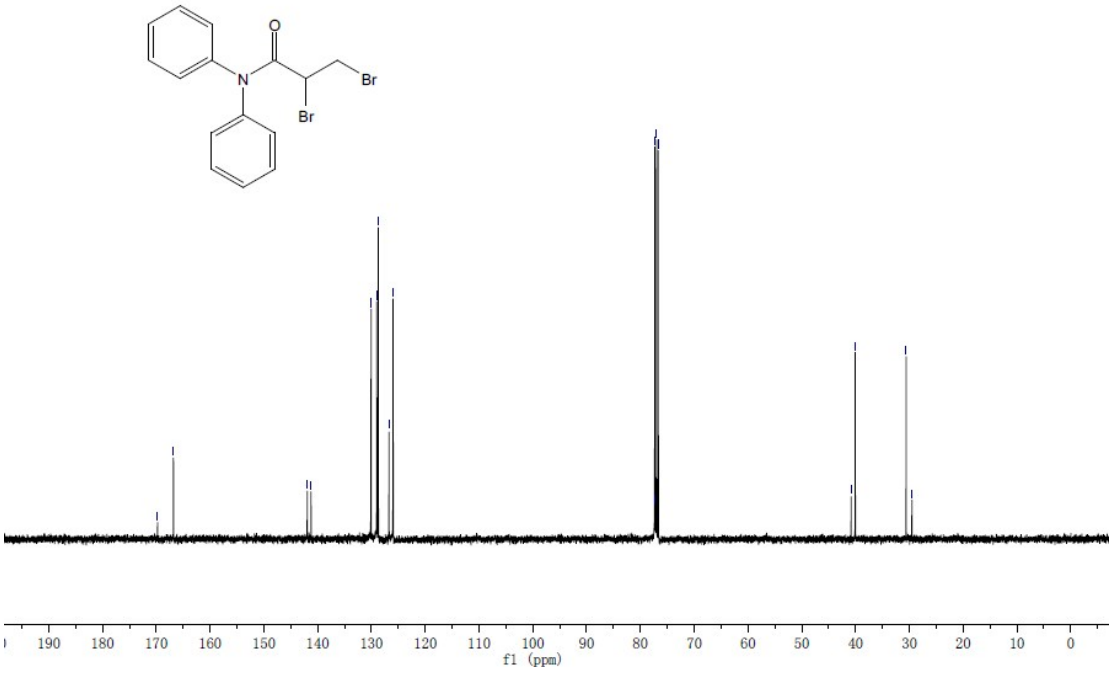

7.70
7.68
7.28
7.28
7.27
7.26
6.84
6.82
5.01
4.97
4.94
4.91
4.87
4.84
4.30
4.29
4.27
4.26
4.19
4.18
3.56
3.55
3.54
3.54
3.53
-0.00
I
O
N
Br
Br
1.44
0.89
2.88
1.85
0.42
1.28
2.00
1.06
0.92
0.91
f1 (ppm)

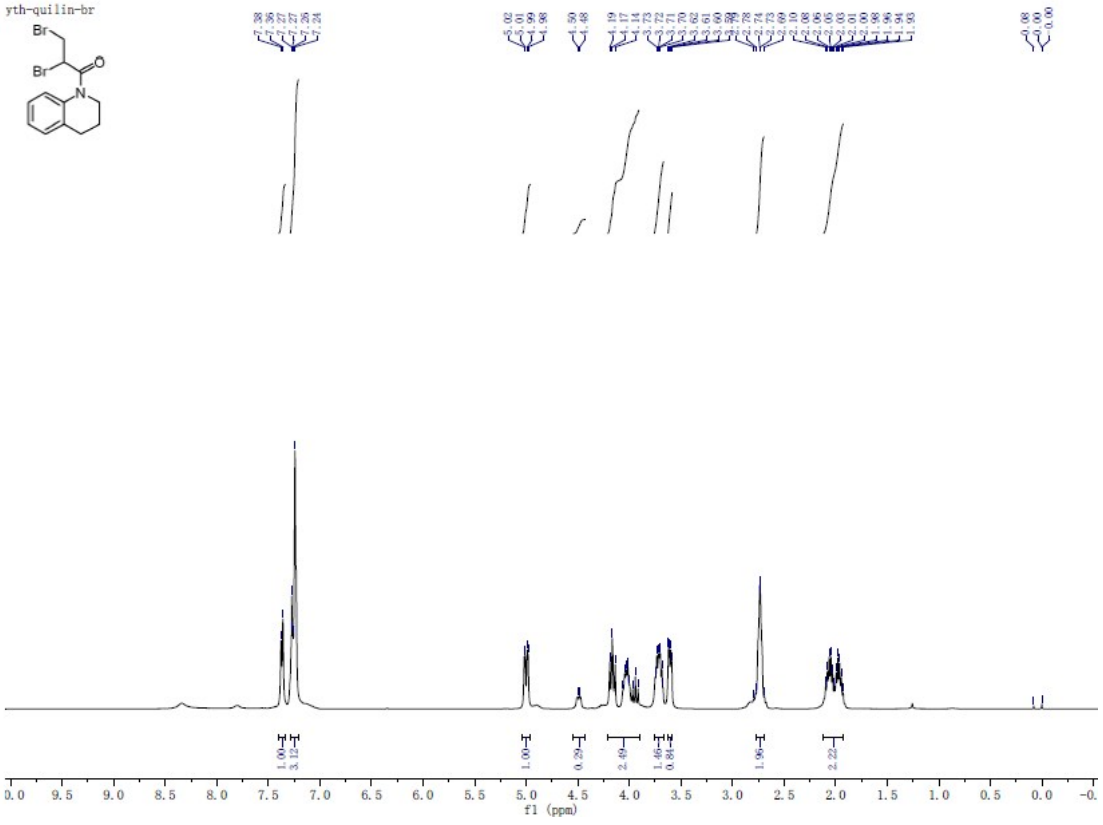

166.41
140.05
139.05
136.11
130.50
129.75
128.81
128.60
128.47
127.83
127.63
94.65
77.32
77.20
77.00
76.68
53.77
53.63
39.36
39.16
30.60
30.47
-0.01
I
O
N
Br
Br
f1 (ppm)

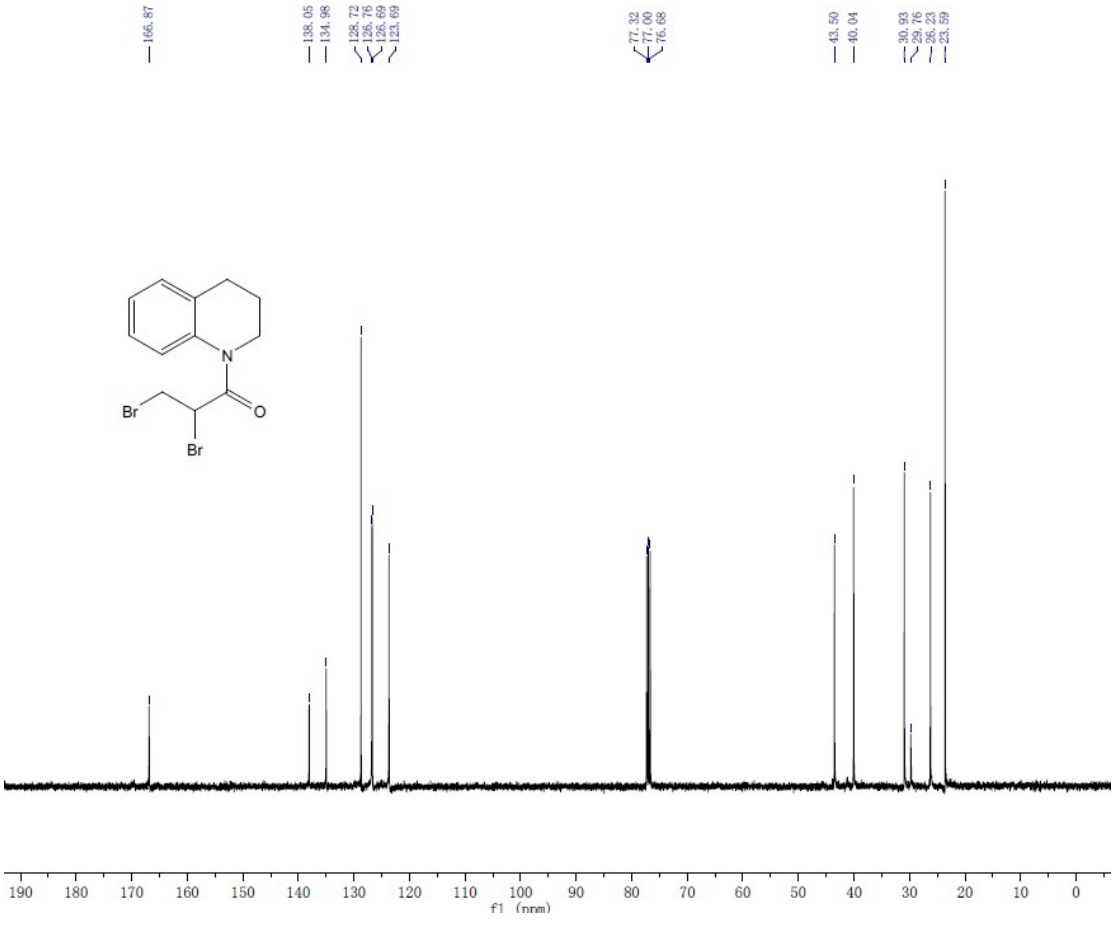

7.51
7.49
7.47
7.45
7.44
7.43
7.43
7.41
7.36
7.34
7.31
4.37
4.36
4.34
4.33
4.12
4.10
4.09
4.07
3.53
3.52
3.51
3.50
3.35
0.00
Br
Br
N
O
CH3
3.08
1.97
0.98
1.03
1.08
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


166.37
142.00
129.91
128.57
127.25
77.32
77.00
76.68
38.93
37.98
30.38
Br
Br
N
O
CH3
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

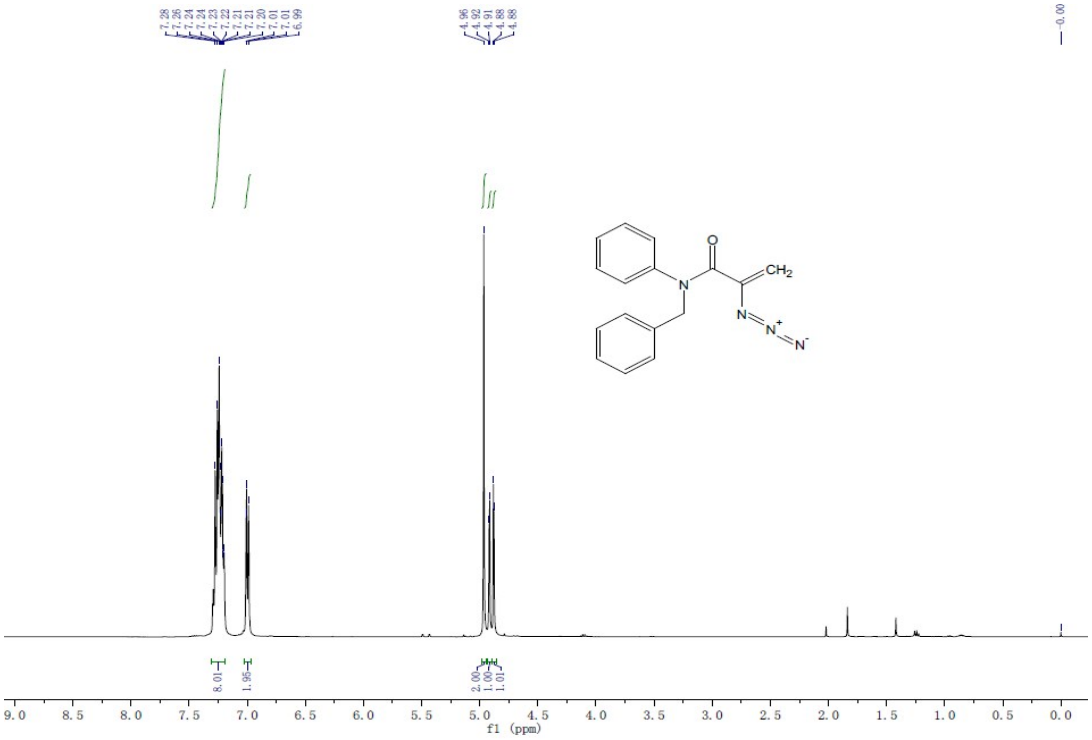

O
N
Br
Br
f1 (ppm)

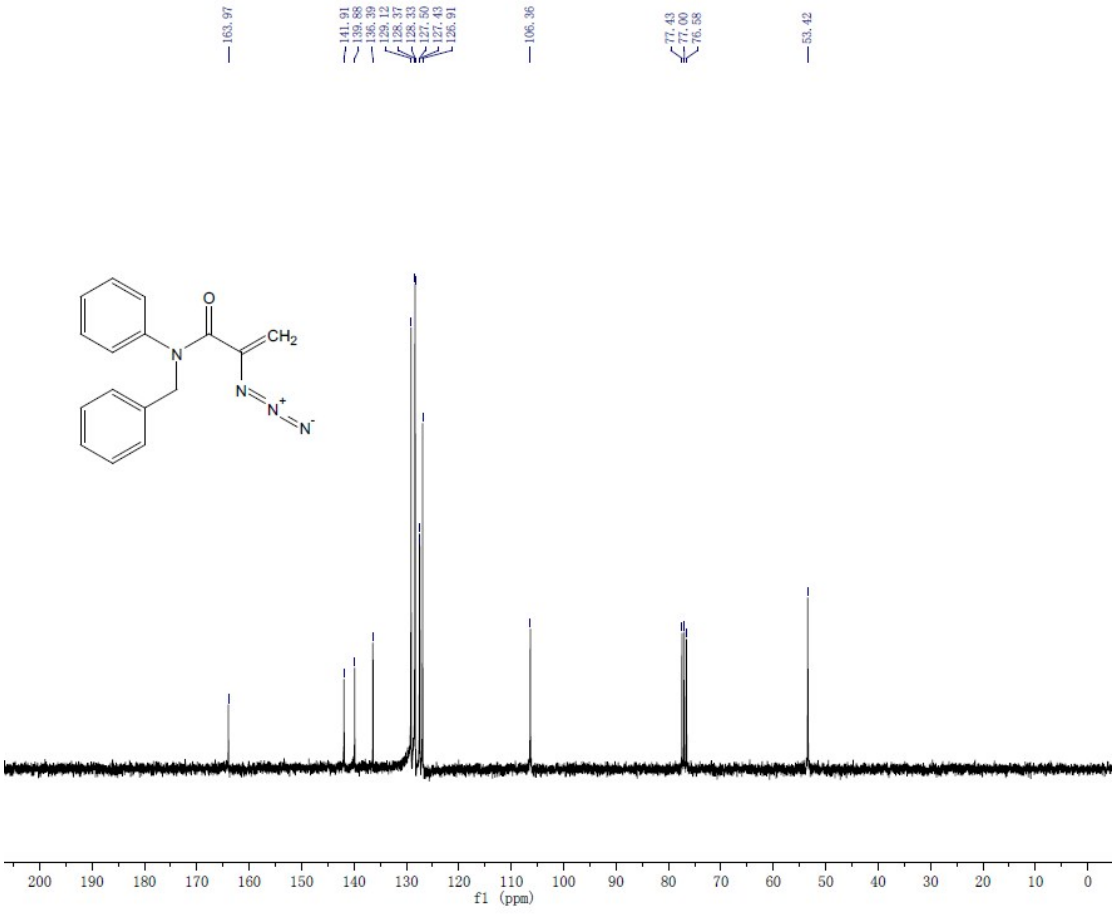

O
N
Br
Br
f1 (ppm)

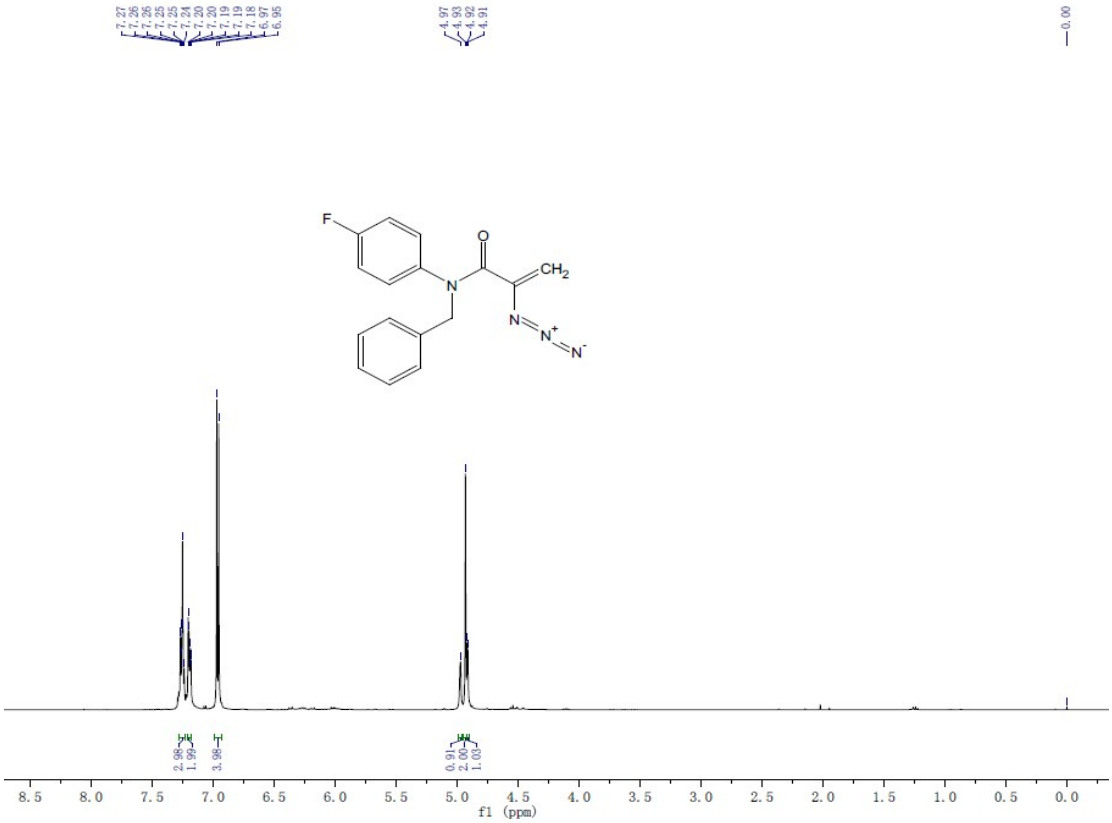

yth-quilin-br
Br
Br
O
N
f1 (ppm)

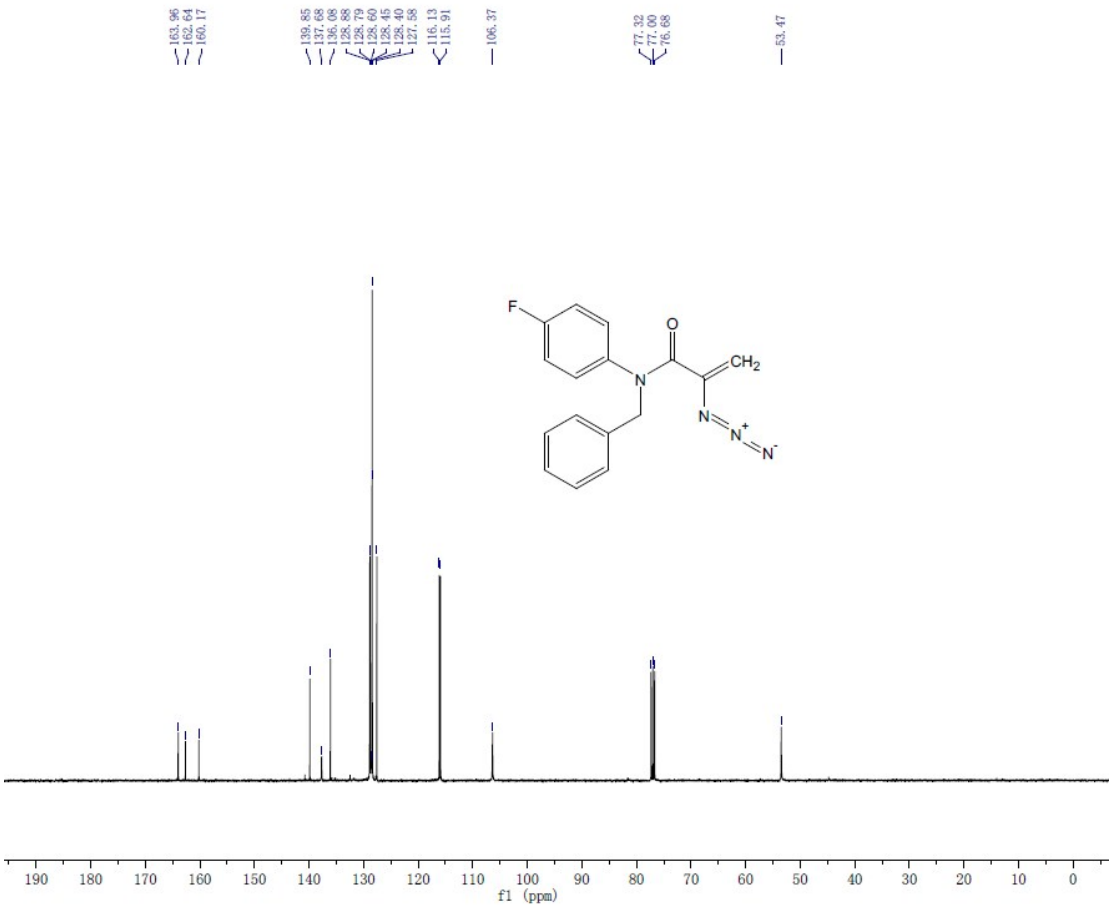

166.87
138.05
134.98
128.72
126.76
125.69
123.69
77.32
77.00
76.68
43.50
40.04
30.93
29.76
26.23
23.59
Br
Br
O
N
f1 (ppm)

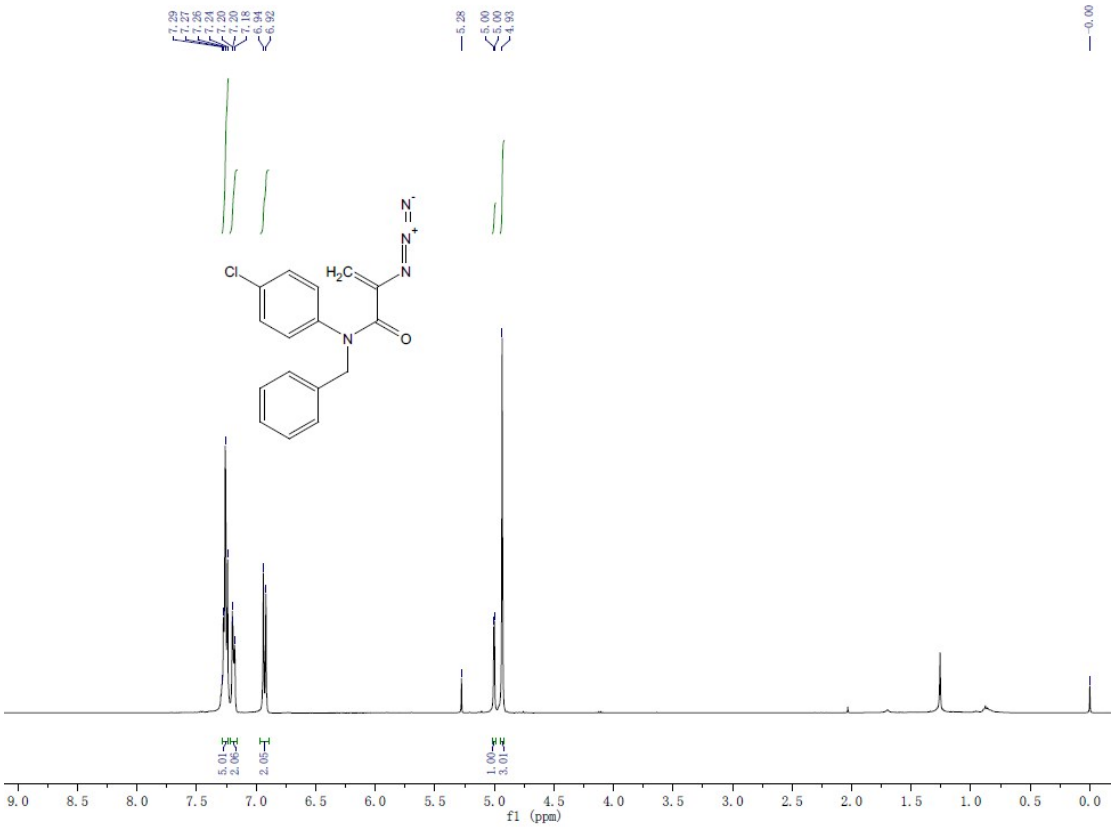
Copies of ^{1}H NMR and ^{13}C NMR spectra of substrates 1

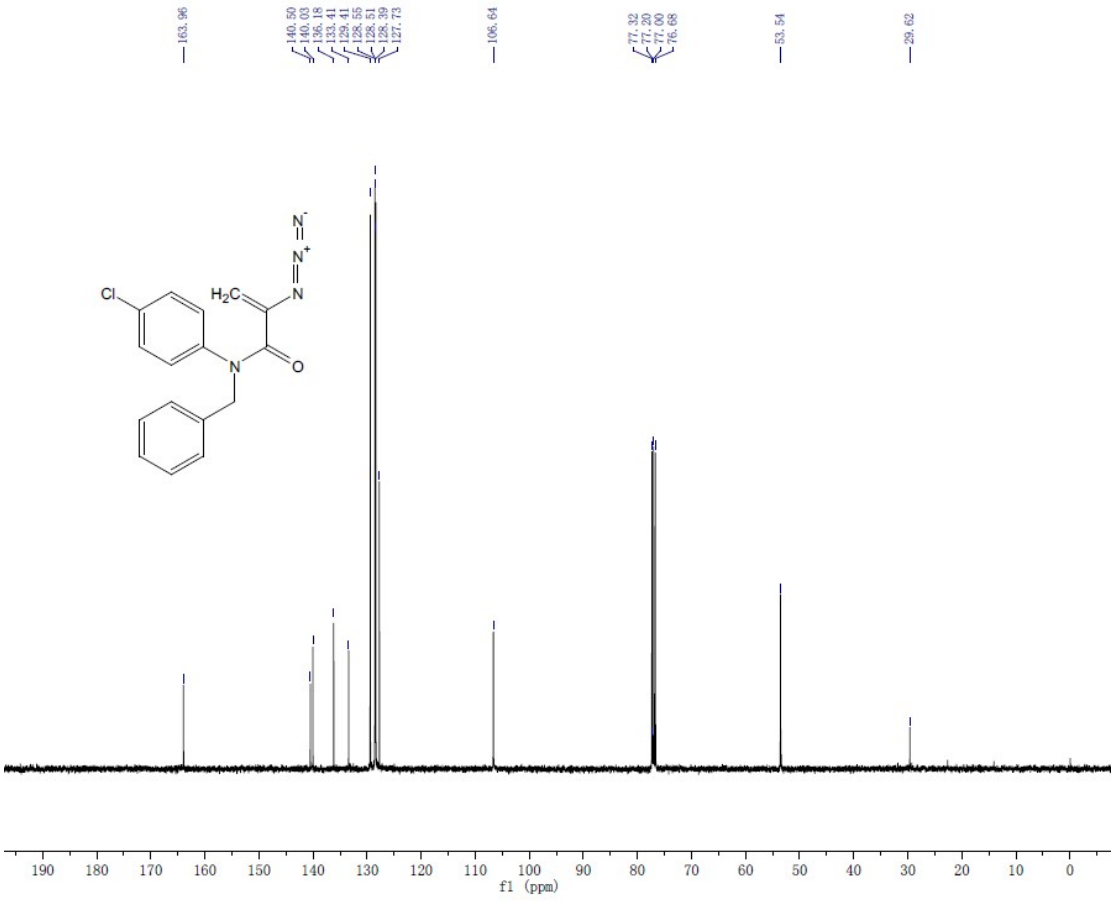




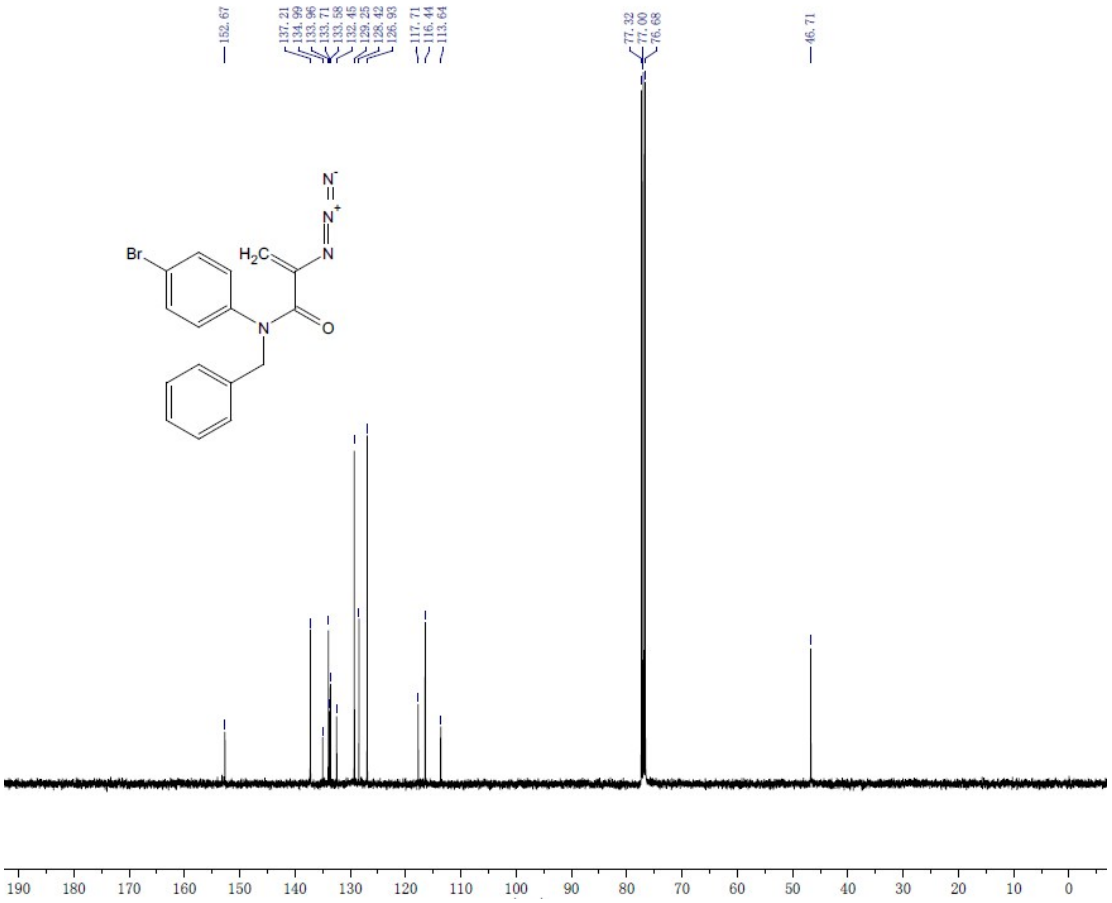

7.27
7.26
7.26
7.25
7.25
7.24
7.20
7.20
7.19
7.19
7.18
6.97
6.95
4.97
4.93
4.92
4.91
0.00
F
O
N
CH2
N
N+
N-
2.98
1.99
3.98
0.91
2.00
1.03
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

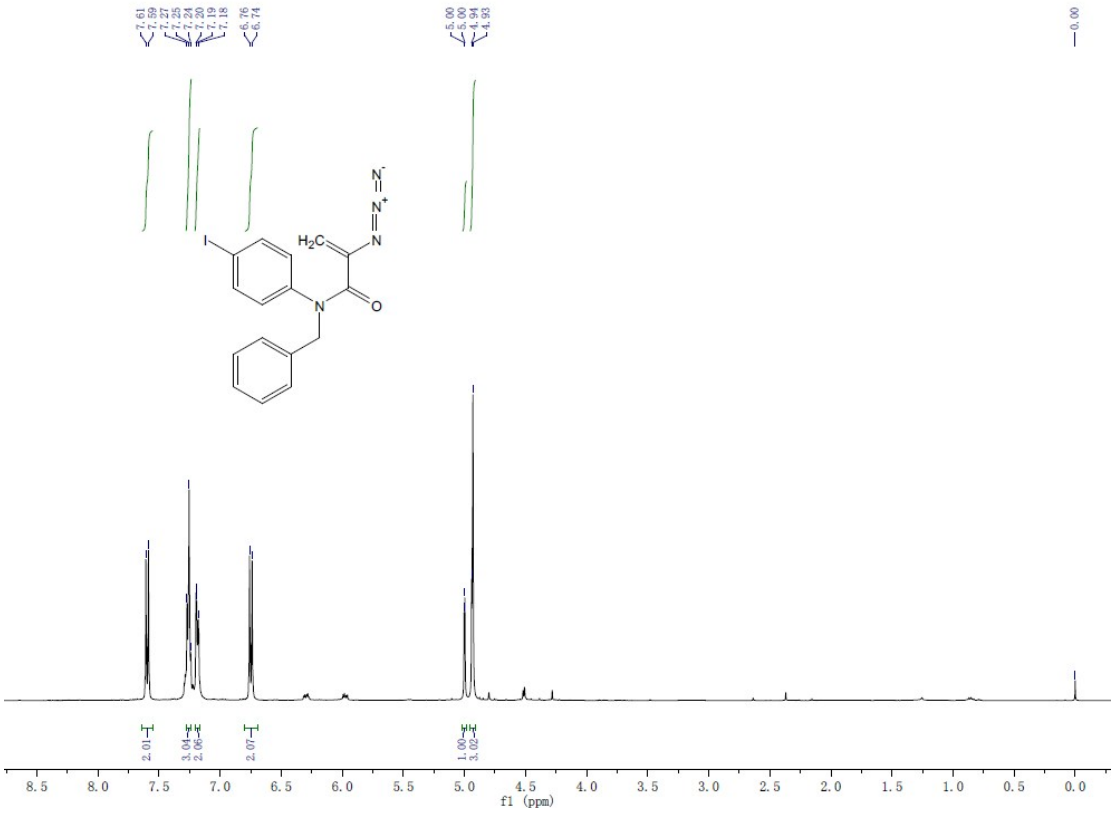

163.96
162.64
160.17
139.85
137.68
136.08
128.88
128.79
128.60
128.45
128.40
127.58
116.13
115.91
106.37
77.32
77.00
76.68
53.47
F
O
N
CH2
N
N+
N-
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

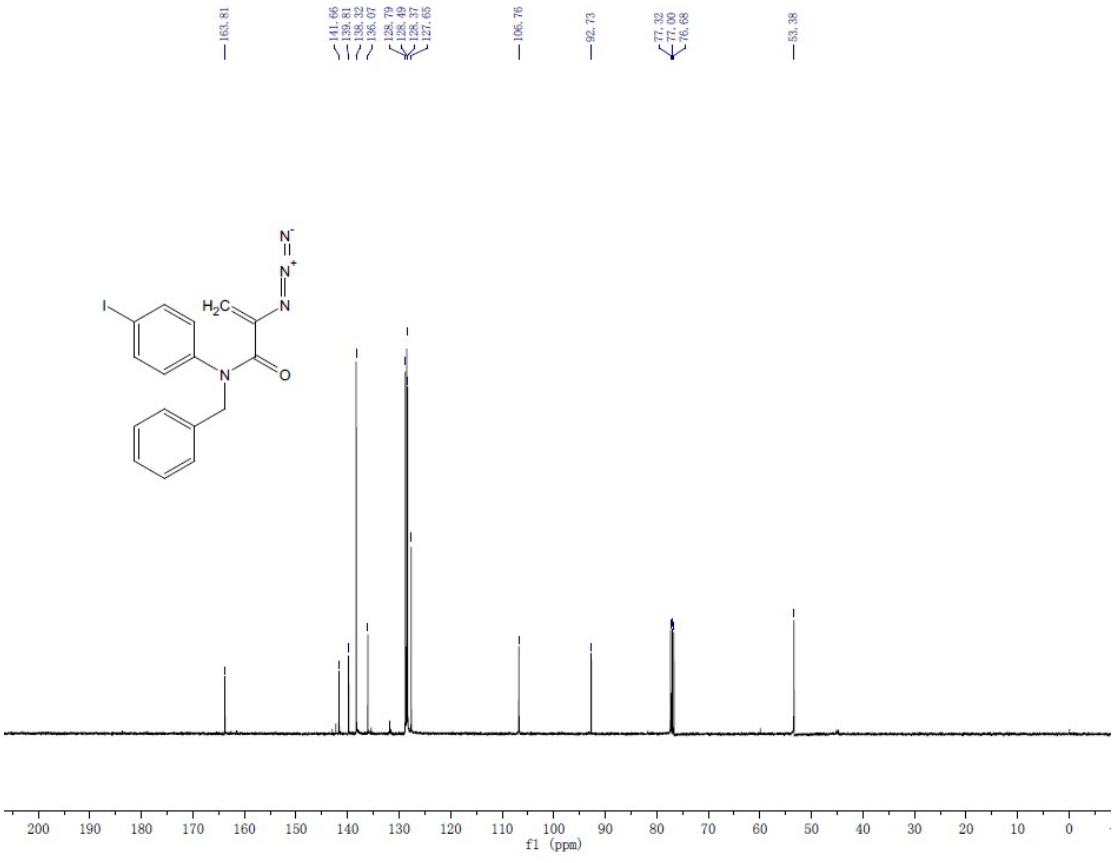

7.29
7.27
7.25
7.24
7.20
7.20
7.18
6.94
6.92
5.28
5.00
5.00
4.93
-0.00
Cl
H2C
N
N
N
O
5.01
2.06
2.08
1.00
3.01
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

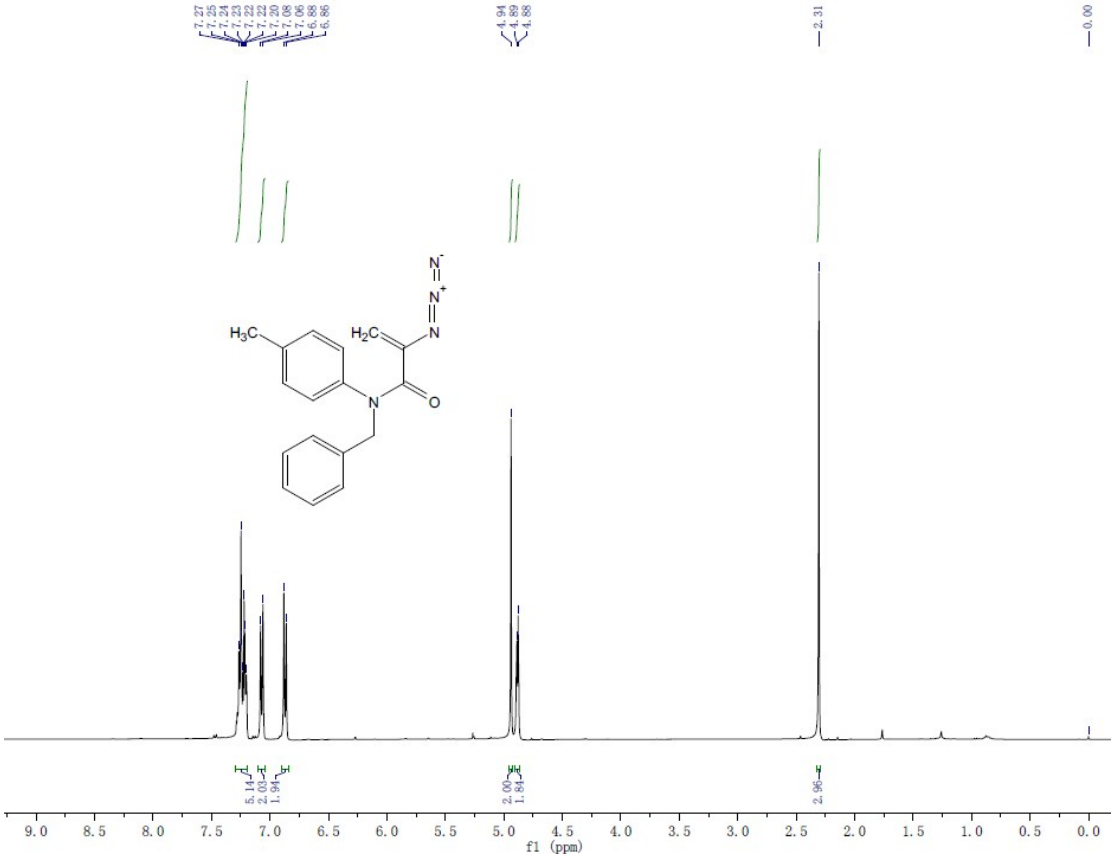

163.96
140.50
140.03
136.18
133.41
129.41
128.55
128.51
128.39
127.73
106.64
77.32
77.20
77.00
76.68
53.54
29.62
Cl
H2C
N
N
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

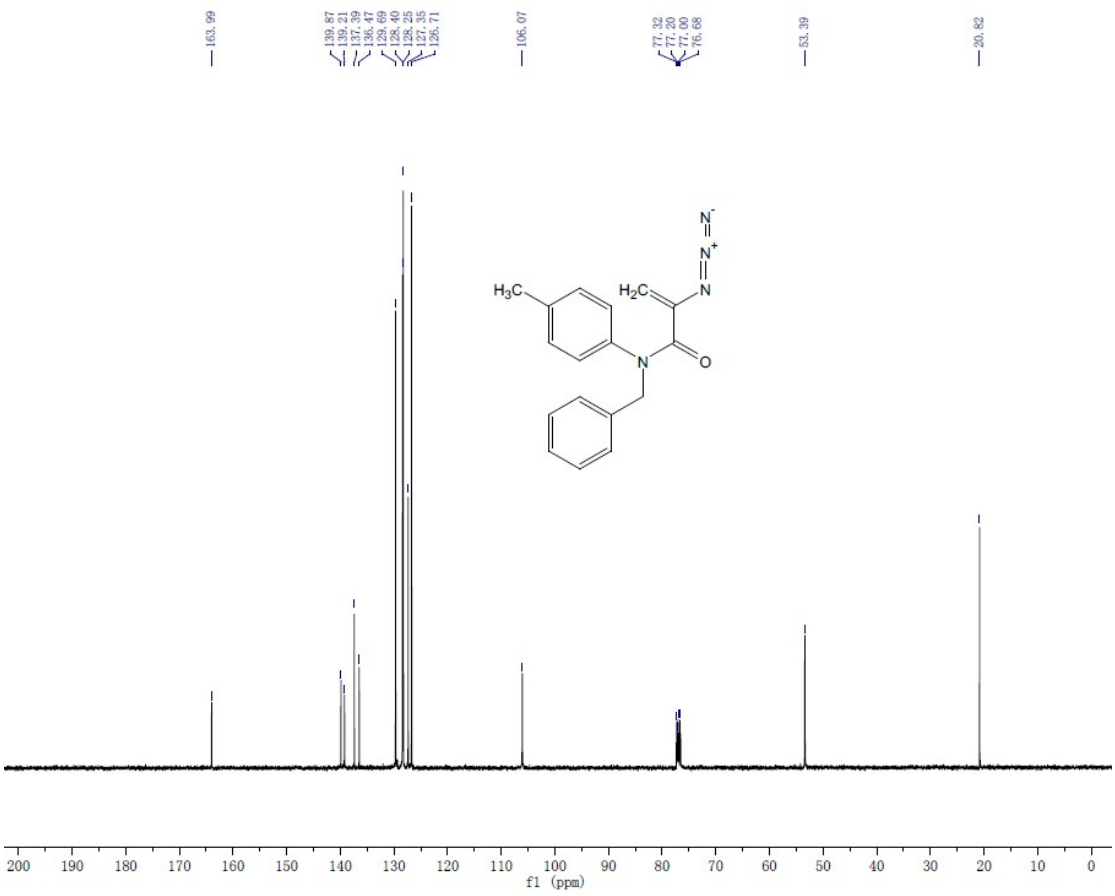

7.39
7.37
7.25
7.23
7.22
7.18
7.18
7.16
7.16
6.67
6.65
6.65
4.98
4.98
4.92
-0.01
Br
O
CH2
N
N+
N-
2.00
3.05
2.01
2.02
0.94
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

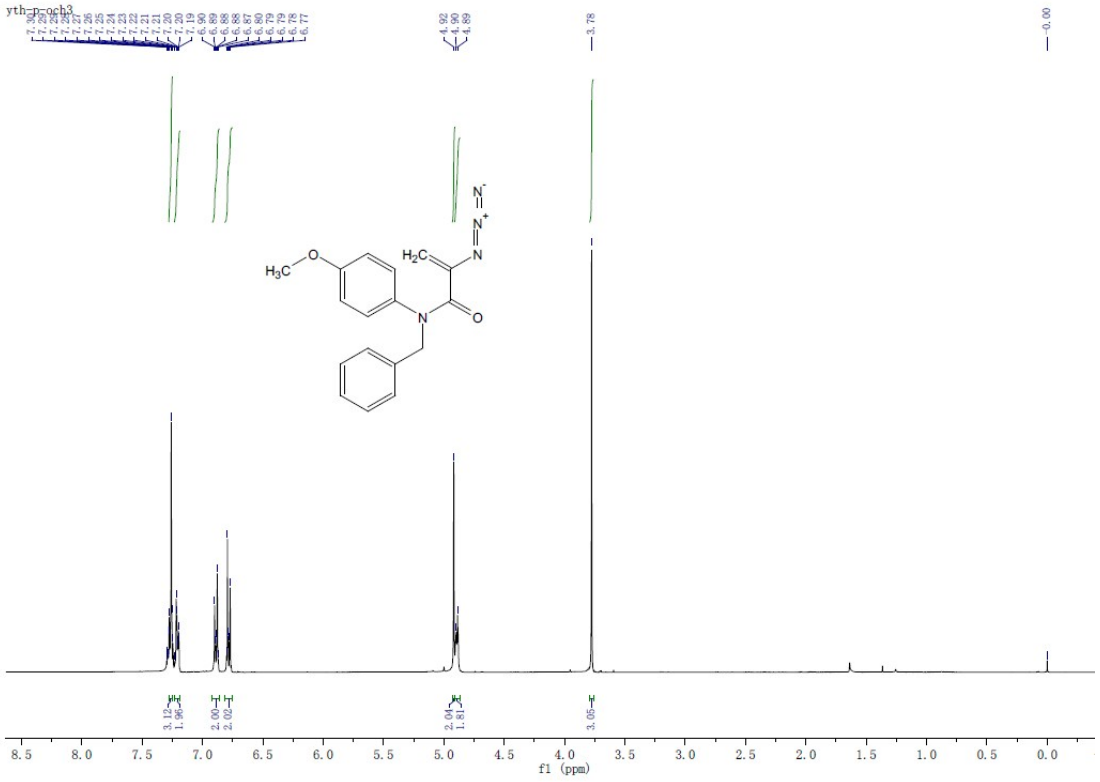

152.67
137.21
134.99
133.96
133.71
133.58
133.45
129.25
128.42
126.93
117.71
116.44
113.64
77.32
77.00
76.68
46.71
N-
N+
Br
H2C
N
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0

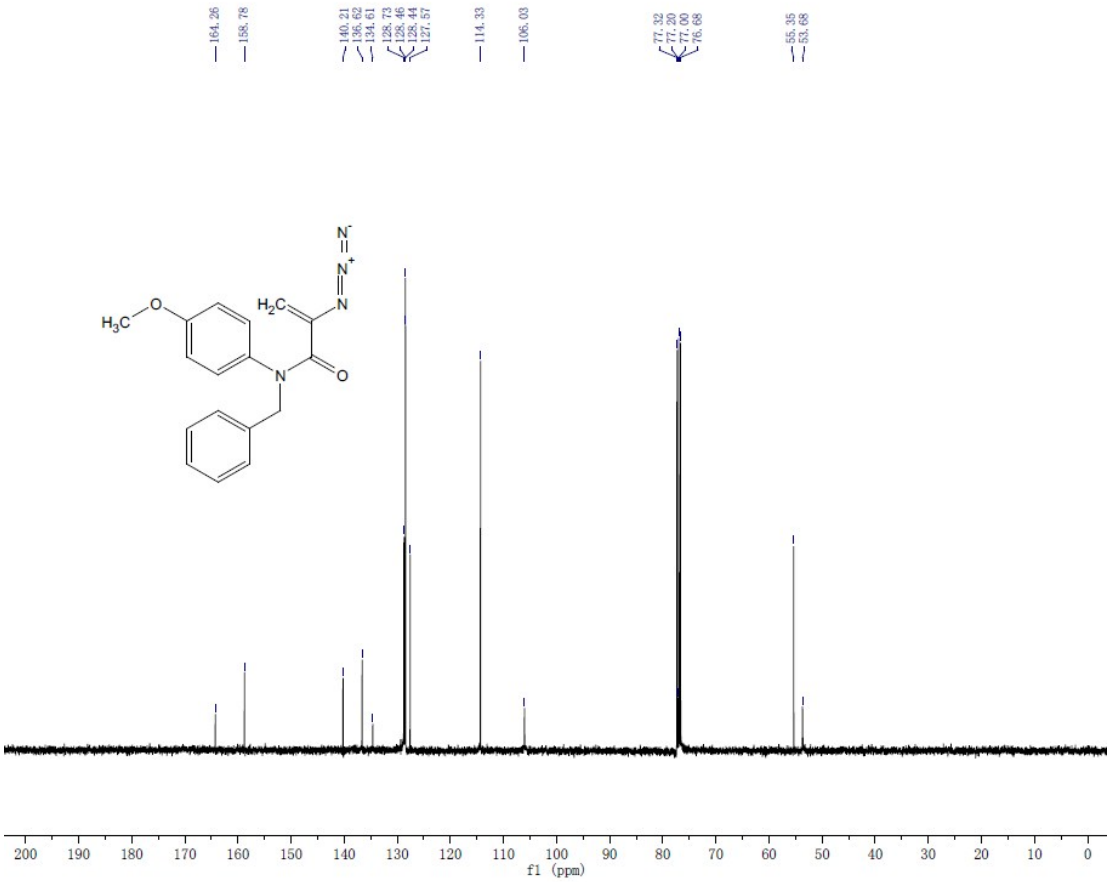

7.61
7.59
7.27
7.25
7.24
7.20
7.19
7.18
6.76
6.74
5.00
5.00
4.94
4.93
0.00
I
H2C
N
N
O
2.01
3.04
2.06
2.07
1.00
3.02
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

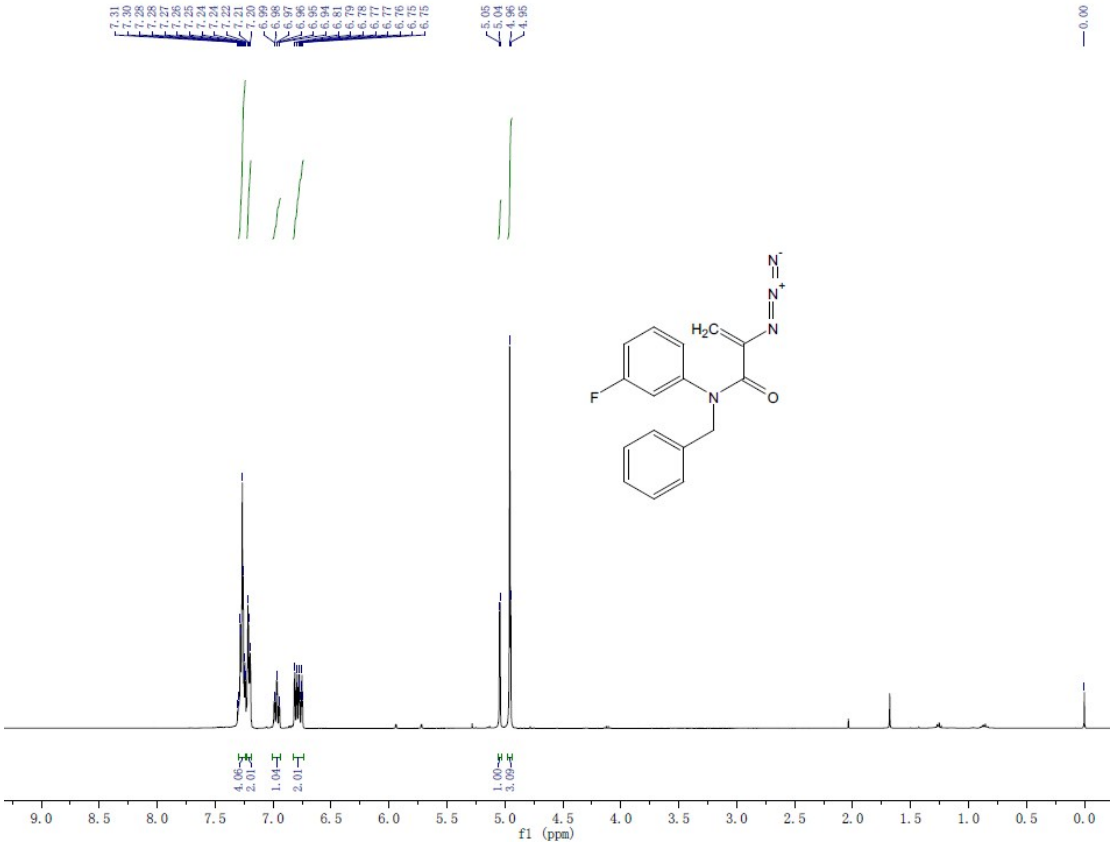

163.81
141.66
139.81
138.32
136.07
128.79
128.49
128.37
127.65
106.76
92.73
77.32
77.00
76.68
53.38
I
H2C
N
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

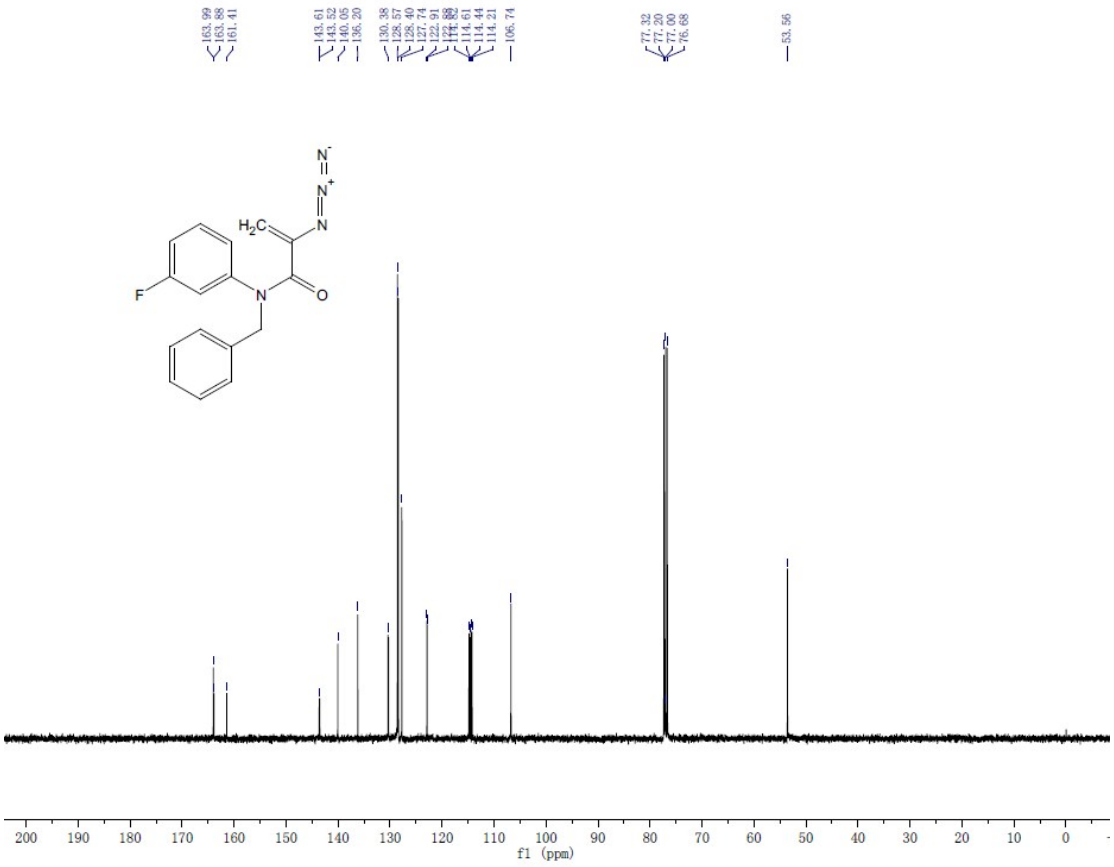

7.27
7.25
7.24
7.23
7.22
7.22
7.20
7.08
7.06
6.88
6.86
4.94
4.89
4.88
2.31
0.00
5.14
2.03
1.94
2.00
1.84
2.96
f1 (ppm)

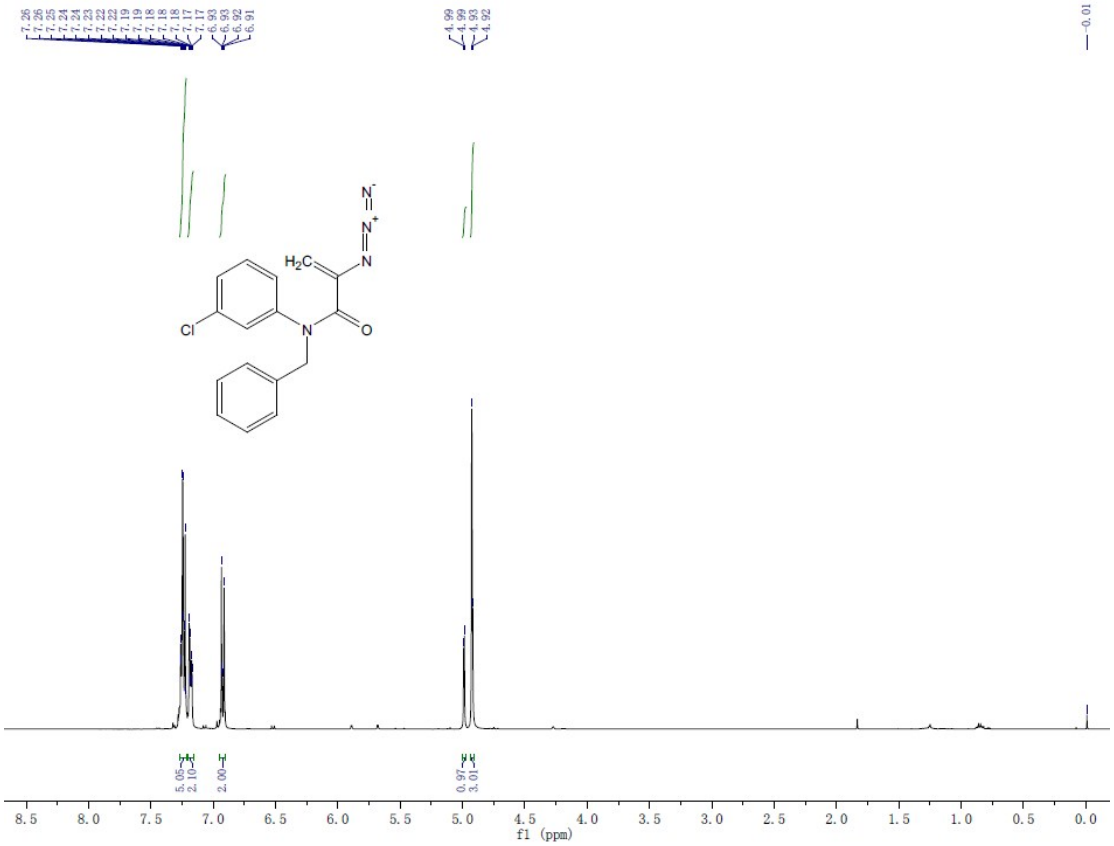

163.99
139.87
139.21
137.39
136.47
129.69
128.40
128.25
127.35
126.71
106.07
77.32
77.20
77.00
76.68
53.39
20.82
f1 (ppm)

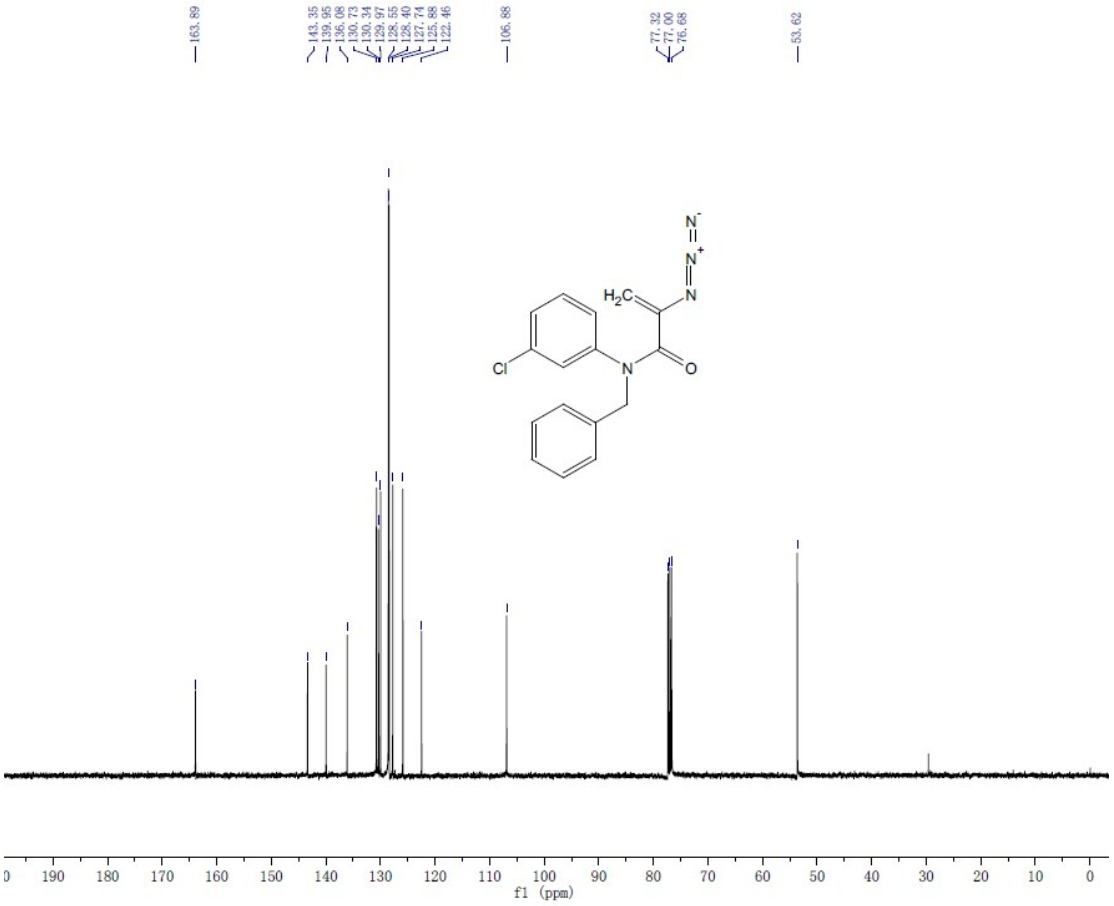

yth-p-och3
7.30
7.28
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
6.90
6.89
6.88
6.87
6.80
6.79
6.78
6.77
4.92
4.90
4.89
3.78
-0.00
3.12
1.96
2.00
2.02
2.04
1.81
3.05
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
H3C
O
H2C
N
N
O

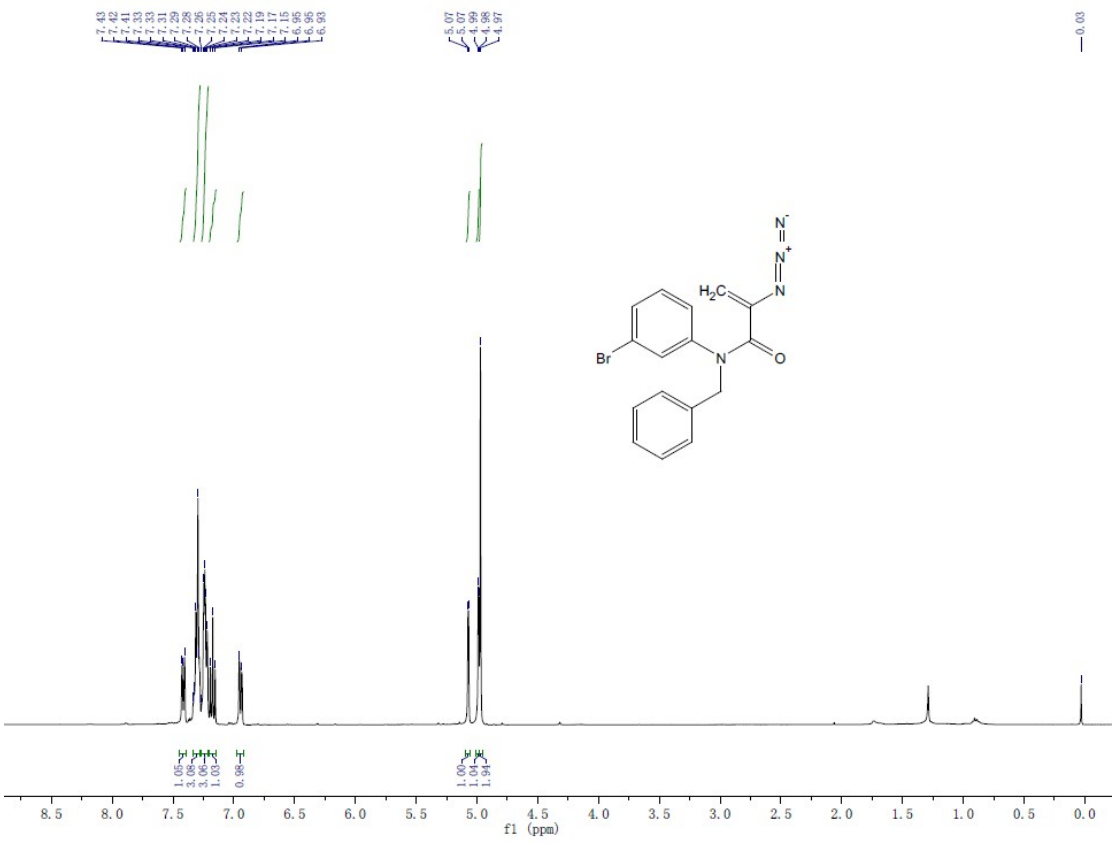

164.26
158.78
140.21
136.62
134.61
128.73
128.46
128.44
127.57
114.33
106.03
77.32
77.20
77.00
76.68
55.35
53.68
H3C
O
H2C
N
N
O
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

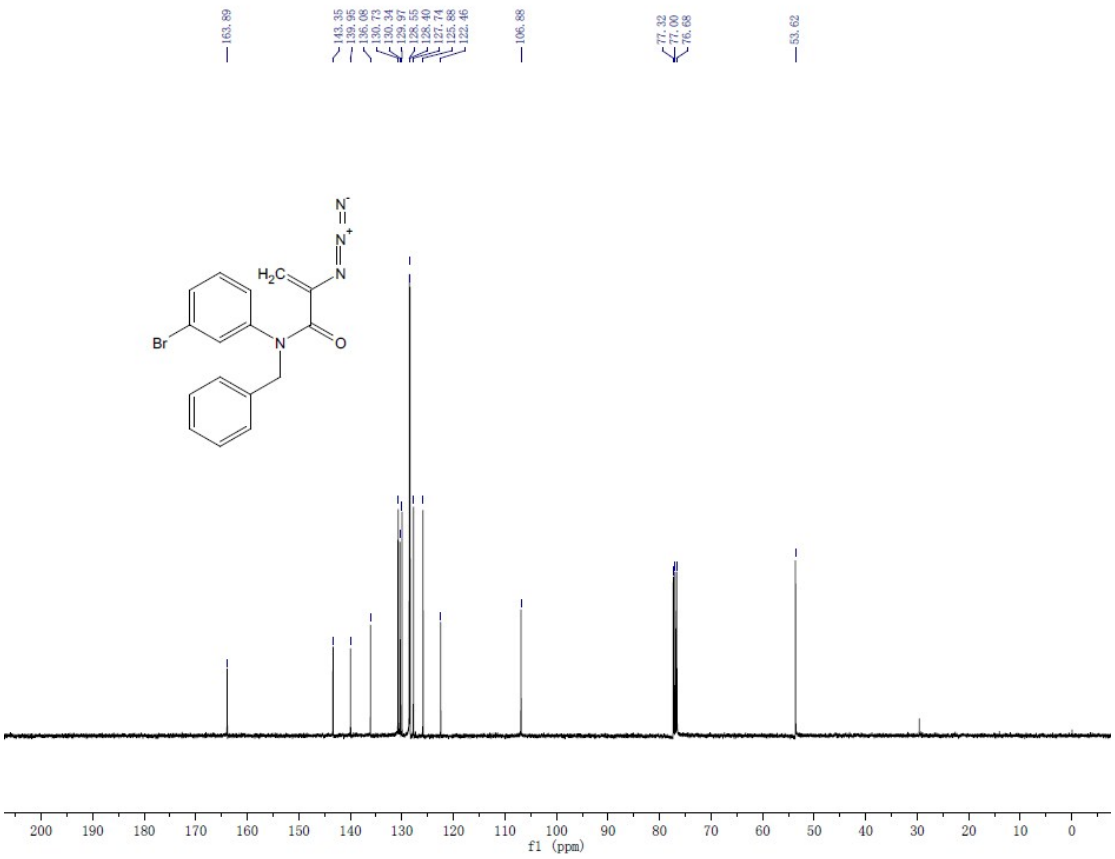

7.31
7.30
7.29
7.28
7.27
7.26
7.25
7.24
7.23
7.22
7.21
7.20
6.99
6.98
6.97
6.96
6.95
6.94
6.81
6.79
6.78
6.77
6.77
6.76
6.75
6.75
5.05
5.04
4.96
4.95
0.00
4.06
2.01
1.04
2.01
1.00
3.09
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
F
N
O
H2C
N
N+
N-

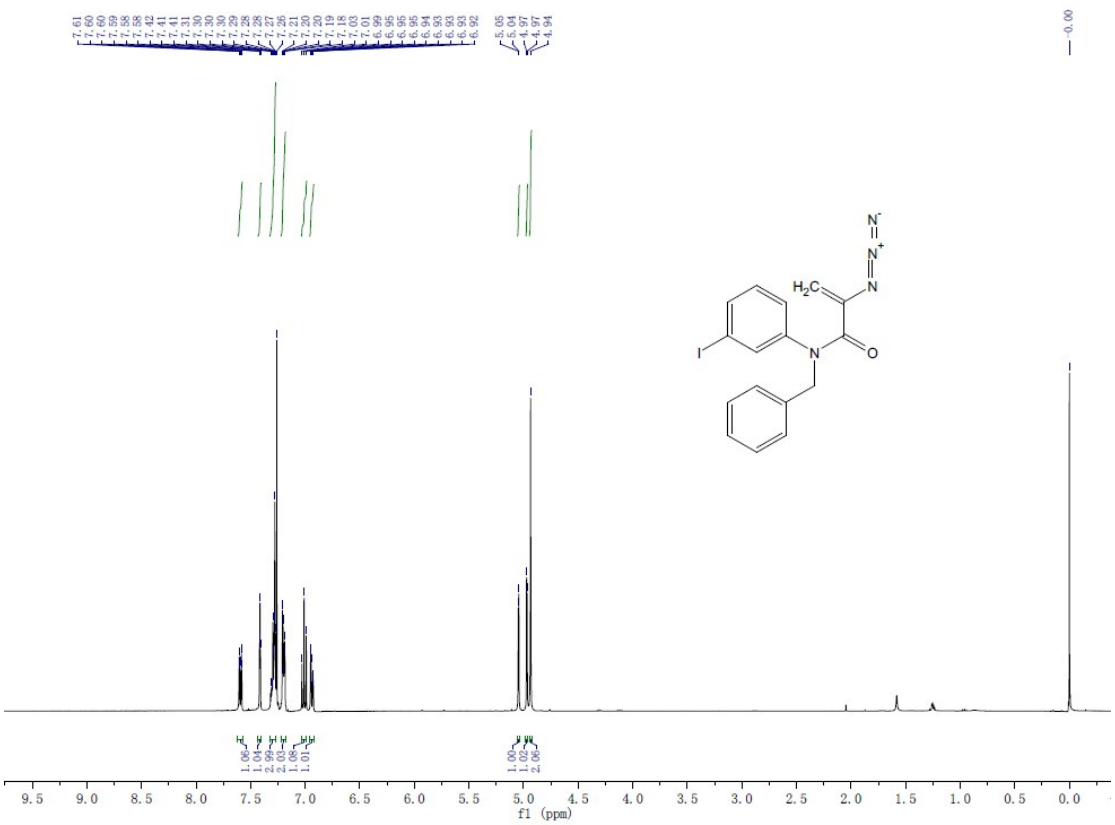

163.99
163.88
161.41
143.61
143.52
140.05
136.20
130.38
128.57
128.40
127.74
127.71
122.91
114.61
114.44
114.21
106.74
77.32
77.20
77.00
76.68
53.56
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)
F
N
O
H2C
N
N+
N-

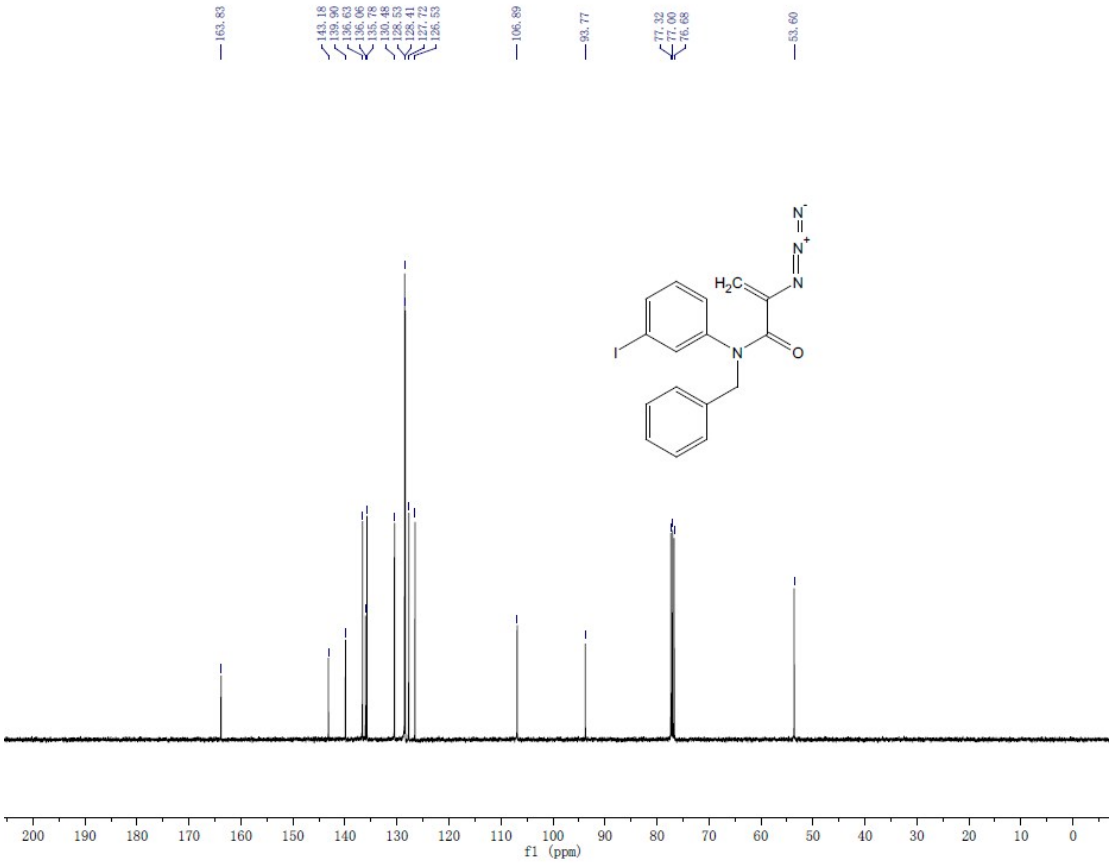

7.26
7.25
7.24
7.23
7.22
7.19
7.18
7.17
6.93
6.92
6.91
4.99
4.93
4.92
-0.01
5.05
2.10
2.00
0.97
3.01
f1 (ppm)

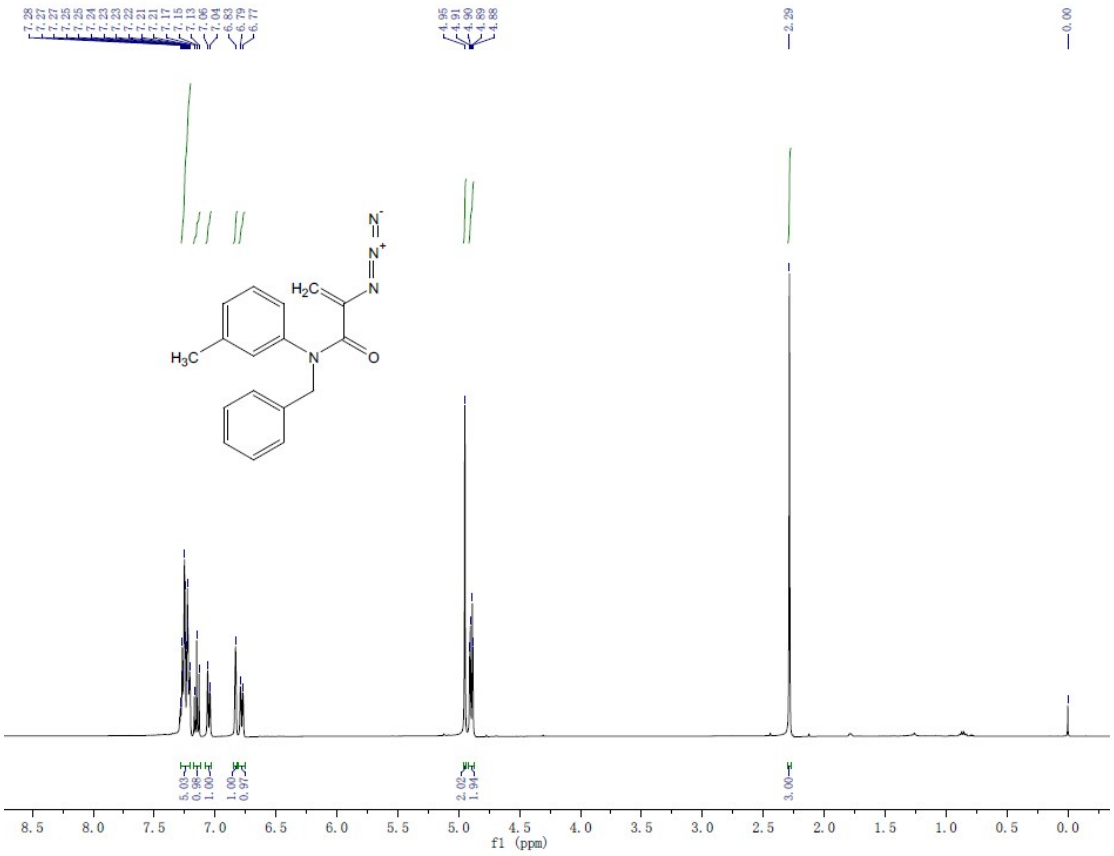

163.89
143.35
139.95
136.08
130.73
130.34
129.67
128.55
128.40
127.74
125.88
122.46
106.88
77.32
77.00
76.68
53.62
f1 (ppm)

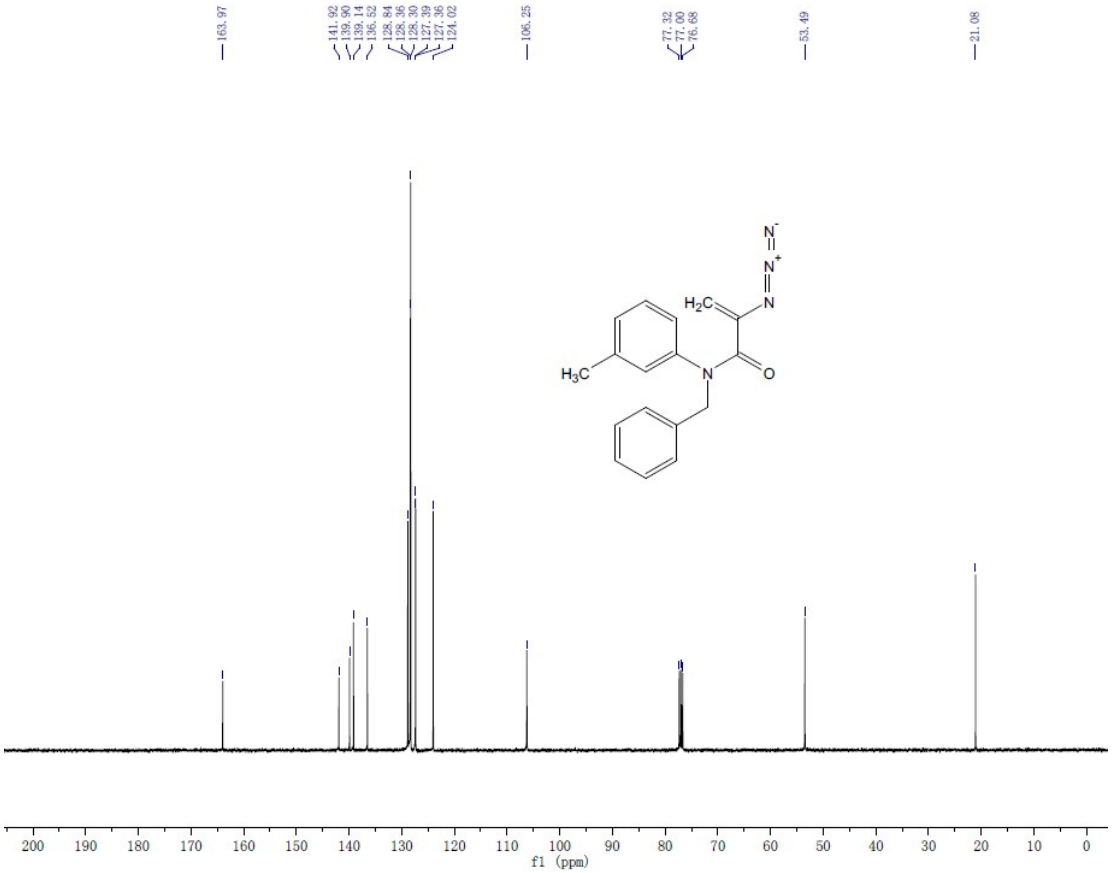

7.43
7.42
7.41
7.33
7.33
7.31
7.29
7.28
7.25
7.25
7.24
7.23
7.22
7.19
7.17
7.15
6.95
6.95
6.93
5.07
5.07
4.99
4.98
4.97
0.03
1.05
3.08
3.06
1.03
0.98
1.00
1.04
1.94
Br
N
O
H2C
N
N+
N-
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

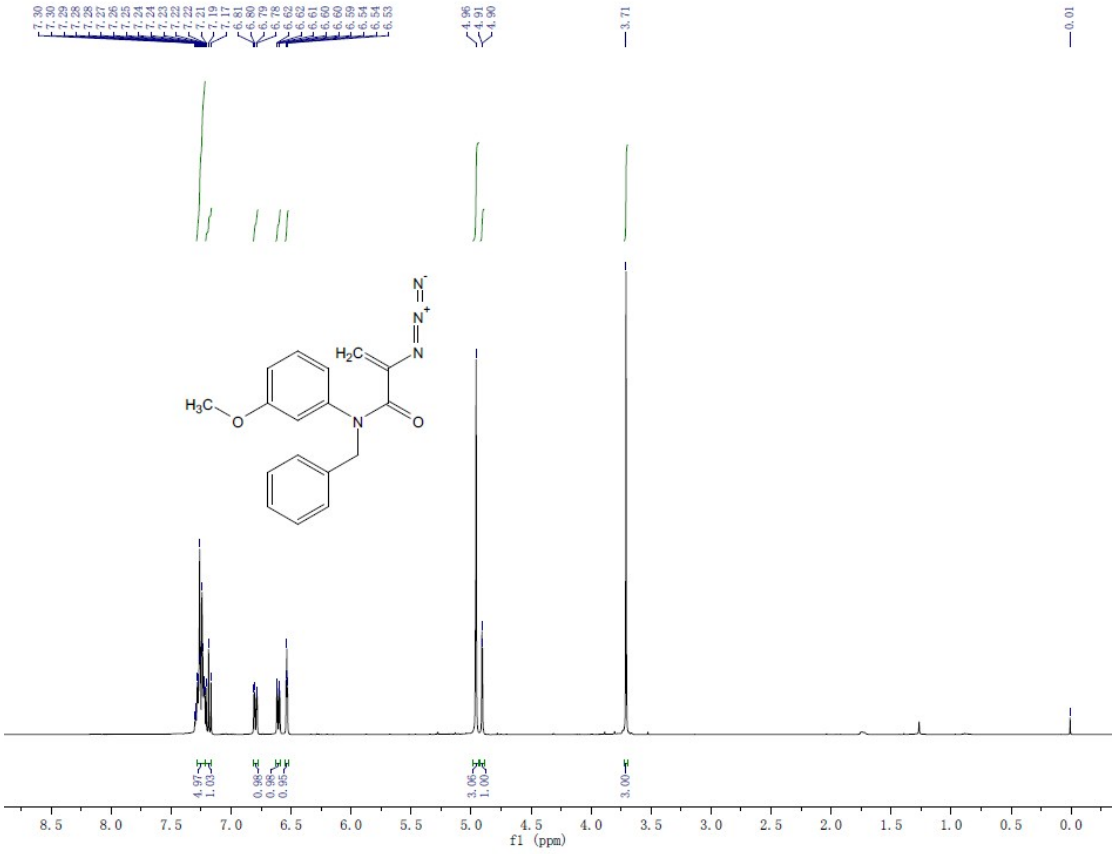

163.89
143.35
139.95
136.09
130.73
130.34
129.97
128.55
128.40
127.74
125.88
122.46
106.88
77.32
77.00
76.68
53.62
Br
N
O
H2C
N
N+
N-
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

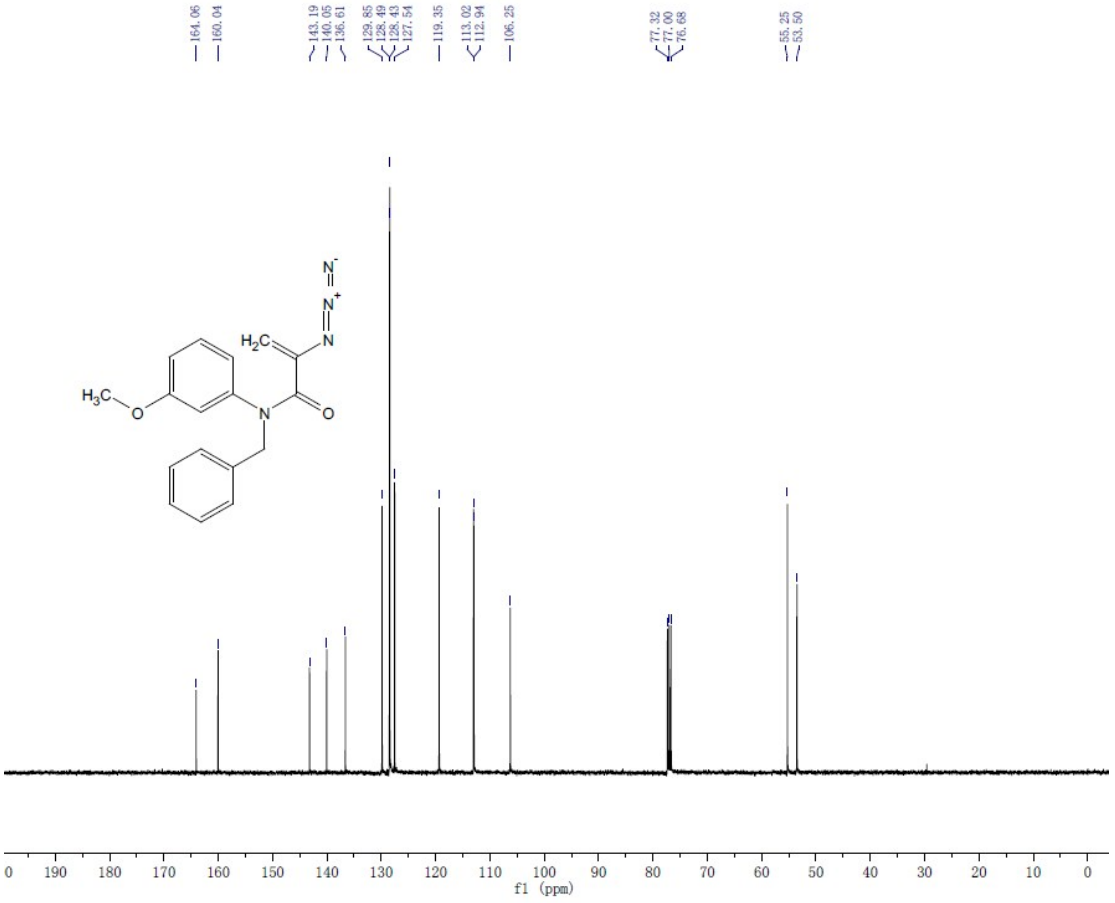

7.61
7.60
7.59
7.59
7.58
7.58
7.42
7.41
7.41
7.31
7.30
7.30
7.29
7.28
7.28
7.27
7.25
7.21
7.20
7.20
7.19
7.18
7.03
7.01
6.99
6.95
6.95
6.94
6.93
6.93
6.93
6.92
5.05
5.04
4.97
4.97
4.94
-0.00
1.06
1.04
2.99
2.03
1.06
1.01
1.00
1.02
2.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)
N
N
N
H2C
I
N
O

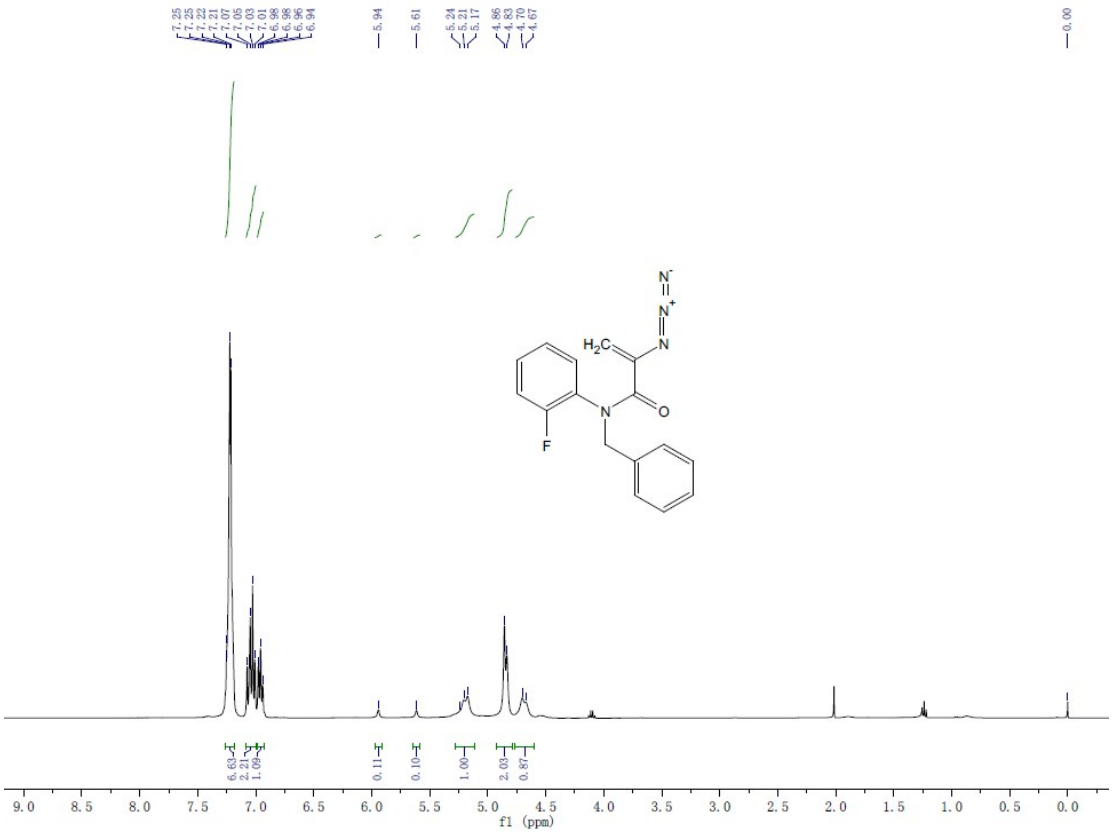

163.83
143.18
139.90
136.63
136.06
135.78
130.48
128.53
128.41
127.72
126.53
106.89
93.77
77.32
77.00
76.68
53.60
N
N
N
H2C
I
N
O
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

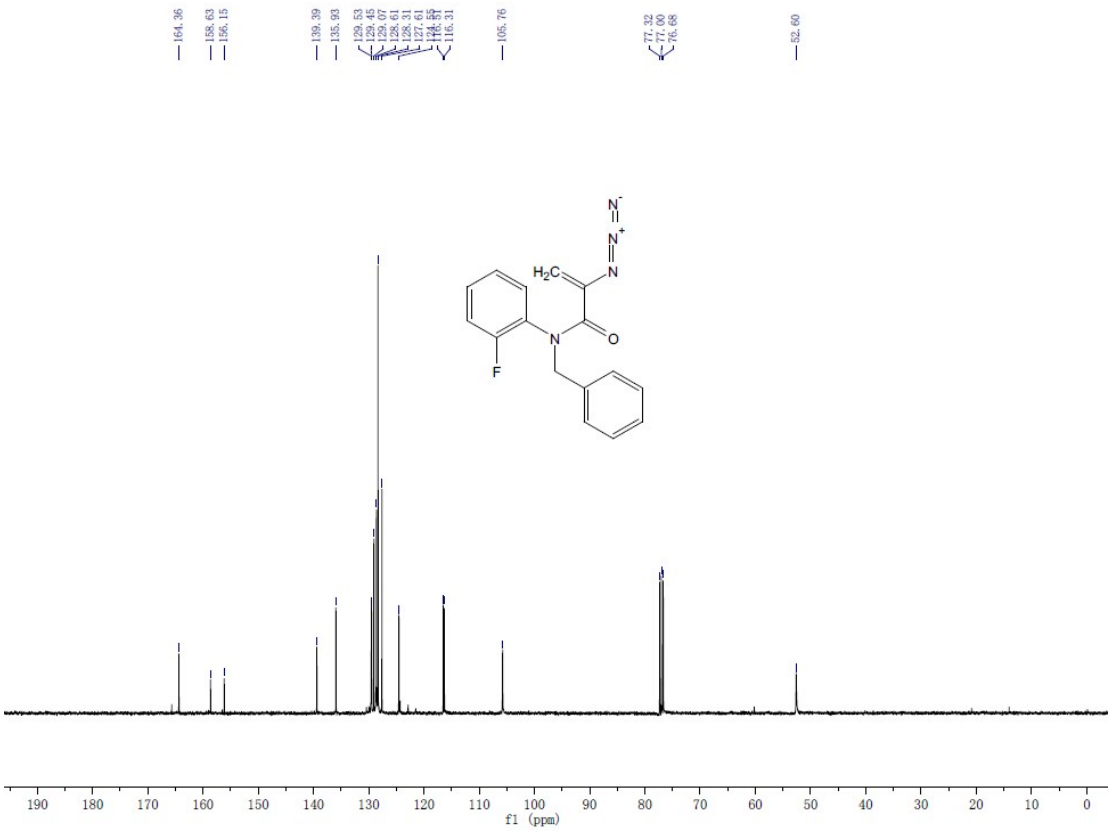

7.28
7.27
7.27
7.25
7.25
7.24
7.23
7.23
7.22
7.21
7.21
7.17
7.15
7.13
7.06
7.04
6.83
6.79
6.77
4.95
4.91
4.90
4.89
4.88
2.29
0.00
5.03
0.98
1.00
1.00
0.97
2.02
1.94
3.00
f1 (ppm)

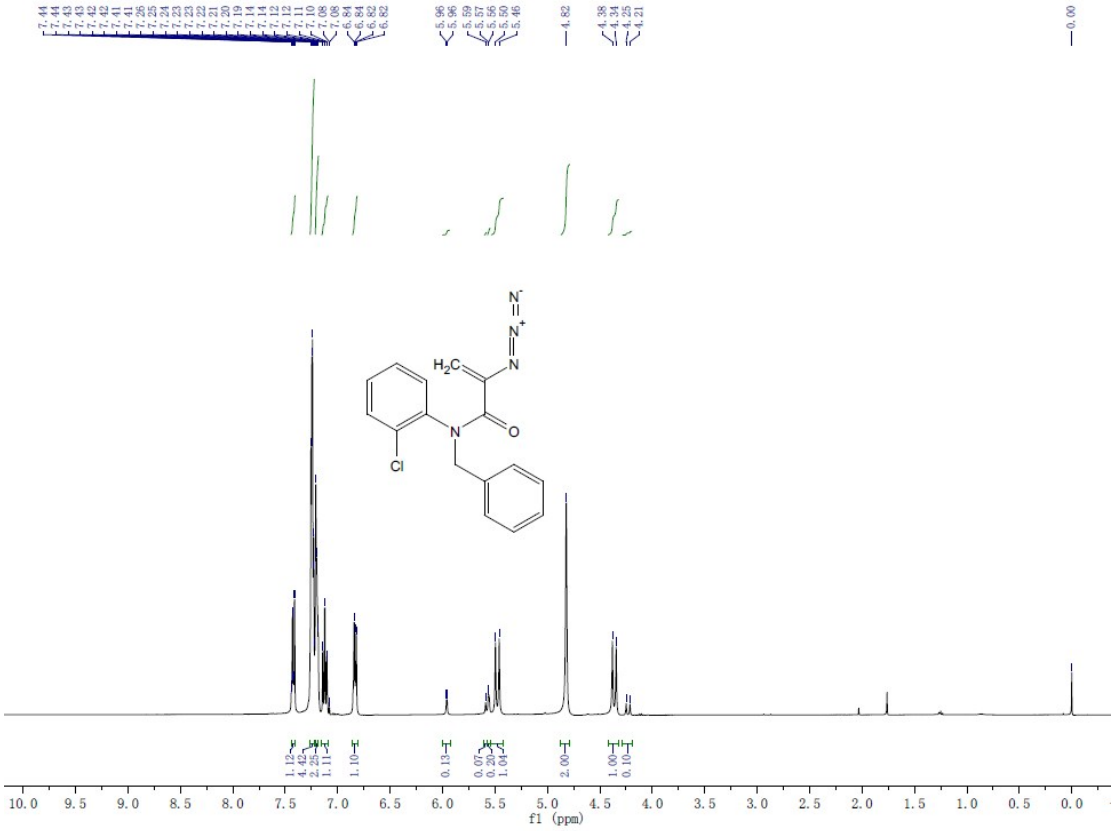

163.97
141.92
139.90
139.14
136.52
128.84
128.36
128.30
127.39
127.36
124.02
106.25
77.32
77.00
76.68
53.49
21.08
f1 (ppm)

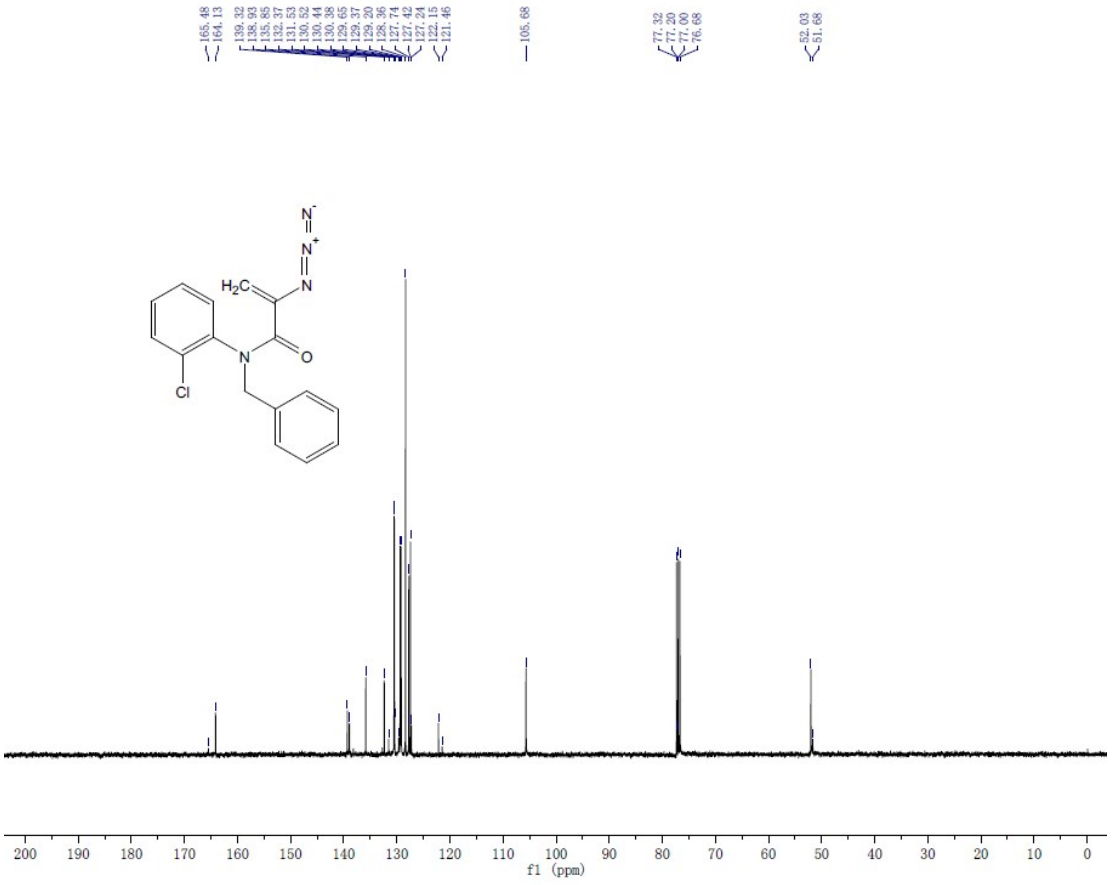

7.30
7.30
7.29
7.28
7.28
7.27
7.26
7.25
7.24
7.24
7.23
7.22
7.22
7.21
7.19
7.17
6.81
6.80
6.79
6.78
6.62
6.62
6.61
6.60
6.60
6.59
6.54
6.54
6.53
4.96
4.91
4.90
3.71
0.01
4.97
1.03
0.98
0.98
0.95
3.06
1.00
3.00
f1 (ppm)

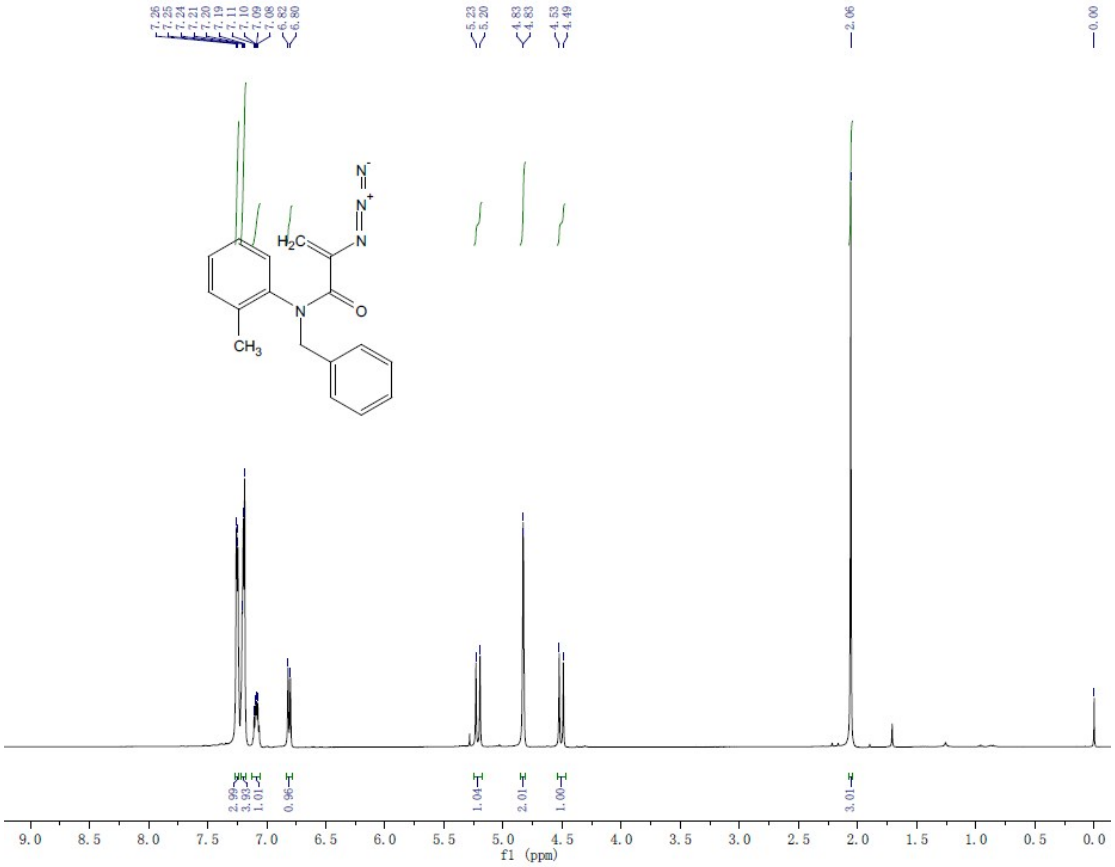

164.06
160.04
143.19
140.05
136.61
129.85
128.49
128.43
127.54
119.35
113.02
112.94
106.25
77.32
77.00
76.68
55.25
53.50
f1 (ppm)

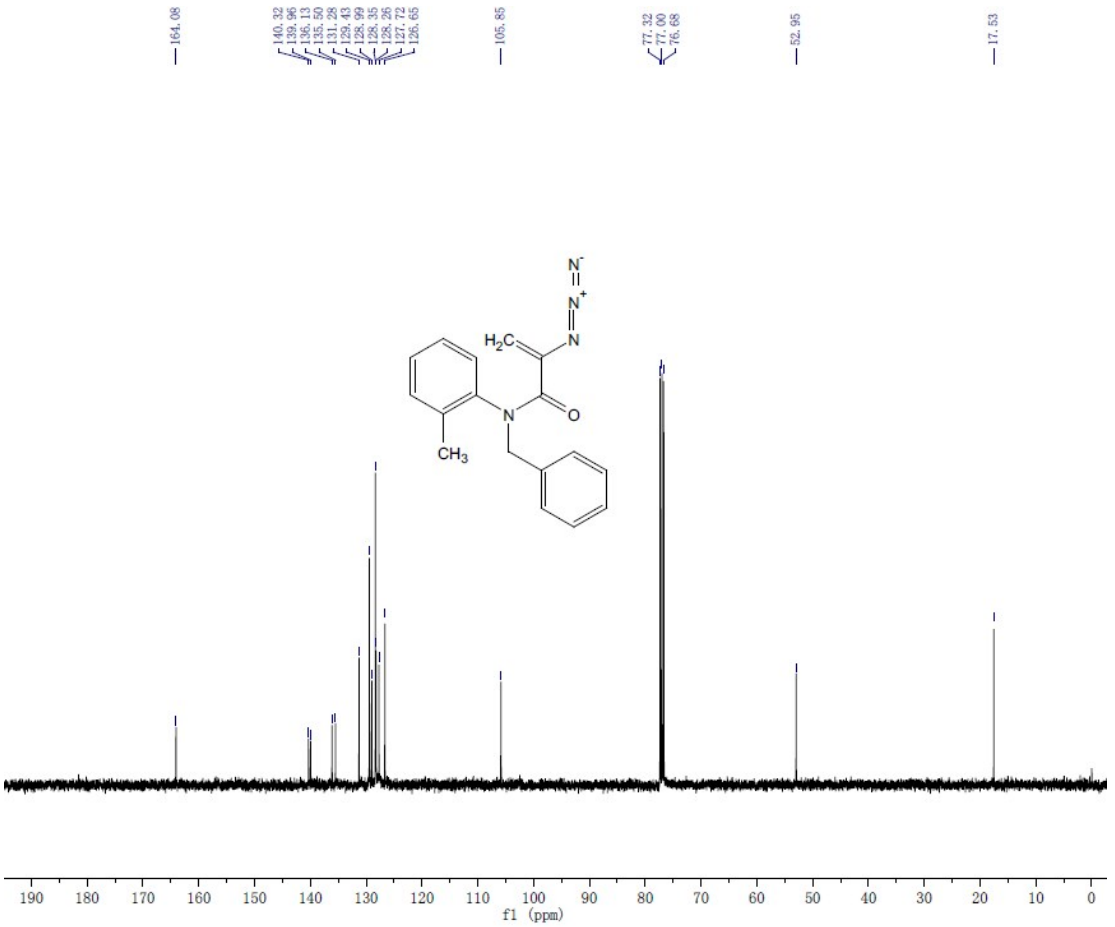

7.25
7.25
7.22
7.21
7.07
7.05
7.03
7.01
6.98
6.98
6.96
6.94
5.94
5.61
5.24
5.21
5.17
4.86
4.83
4.70
4.67
0.00
6.63
2.21
1.09
0.11
0.10
1.00
2.03
0.87
f1 (ppm)

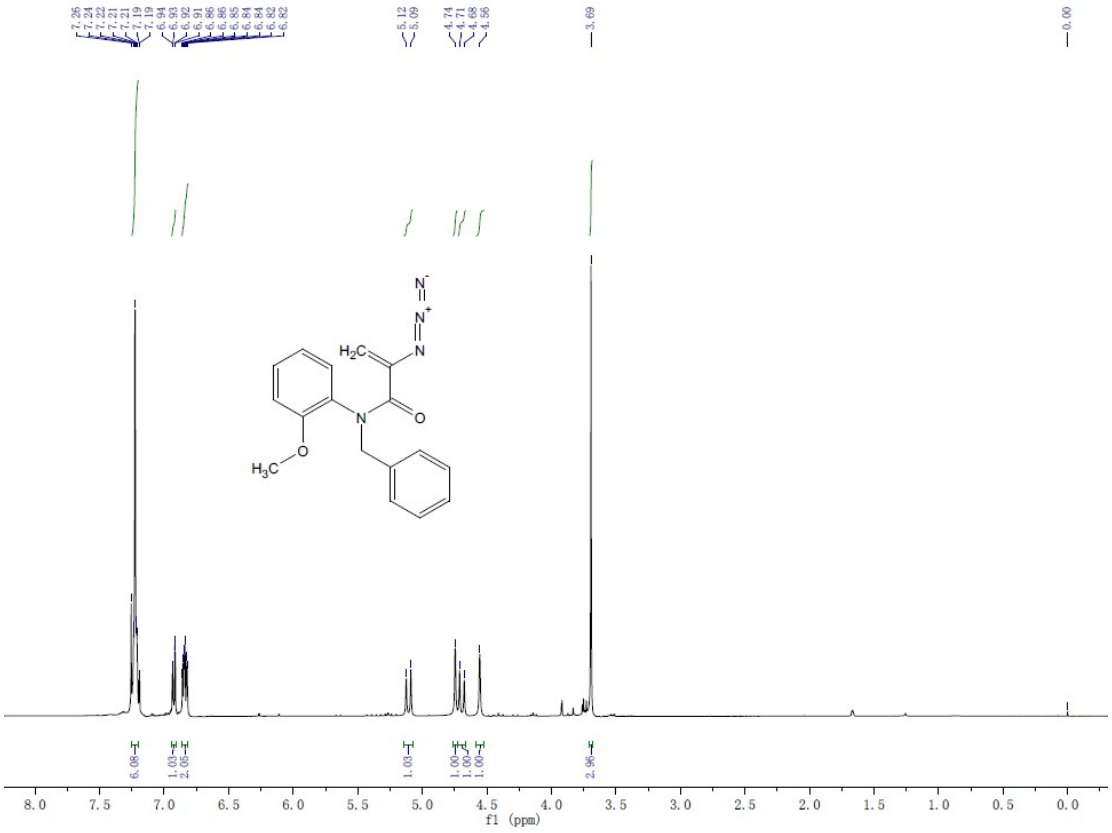

164.36
158.63
156.15
139.39
135.93
129.53
129.45
129.07
128.61
128.31
127.61
116.55
116.31
105.76
77.32
77.00
76.68
52.60
f1 (ppm)

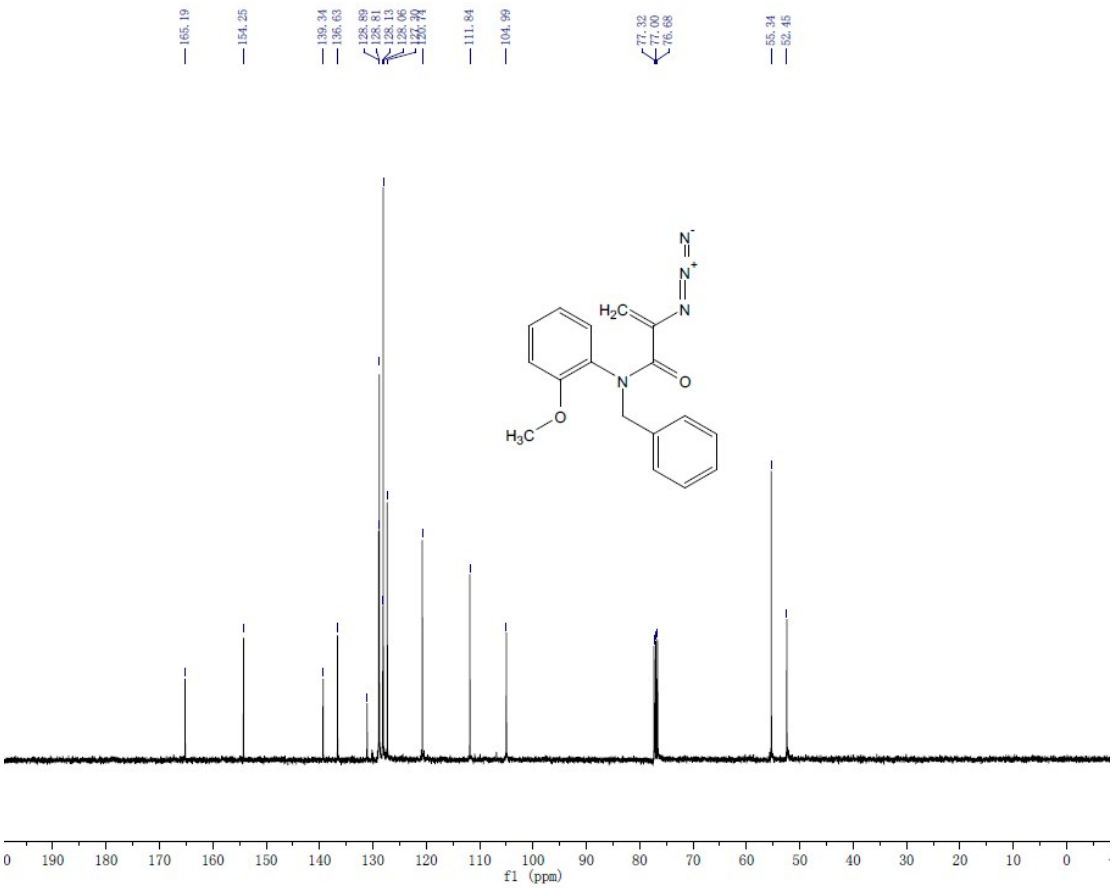

7.44
7.44
7.43
7.43
7.42
7.42
7.41
7.41
7.26
7.25
7.24
7.23
7.22
7.21
7.20
7.19
7.14
7.14
7.12
7.12
7.11
7.10
7.08
6.84
6.84
6.82
6.82
5.96
5.96
5.59
5.57
5.55
5.50
5.46
4.82
4.38
4.34
4.25
4.21
0.00
N
N
N
H2C
O
N
Cl
1.12
4.42
2.25
1.11
1.10
0.13
0.07
0.20
1.04
2.00
1.00
0.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

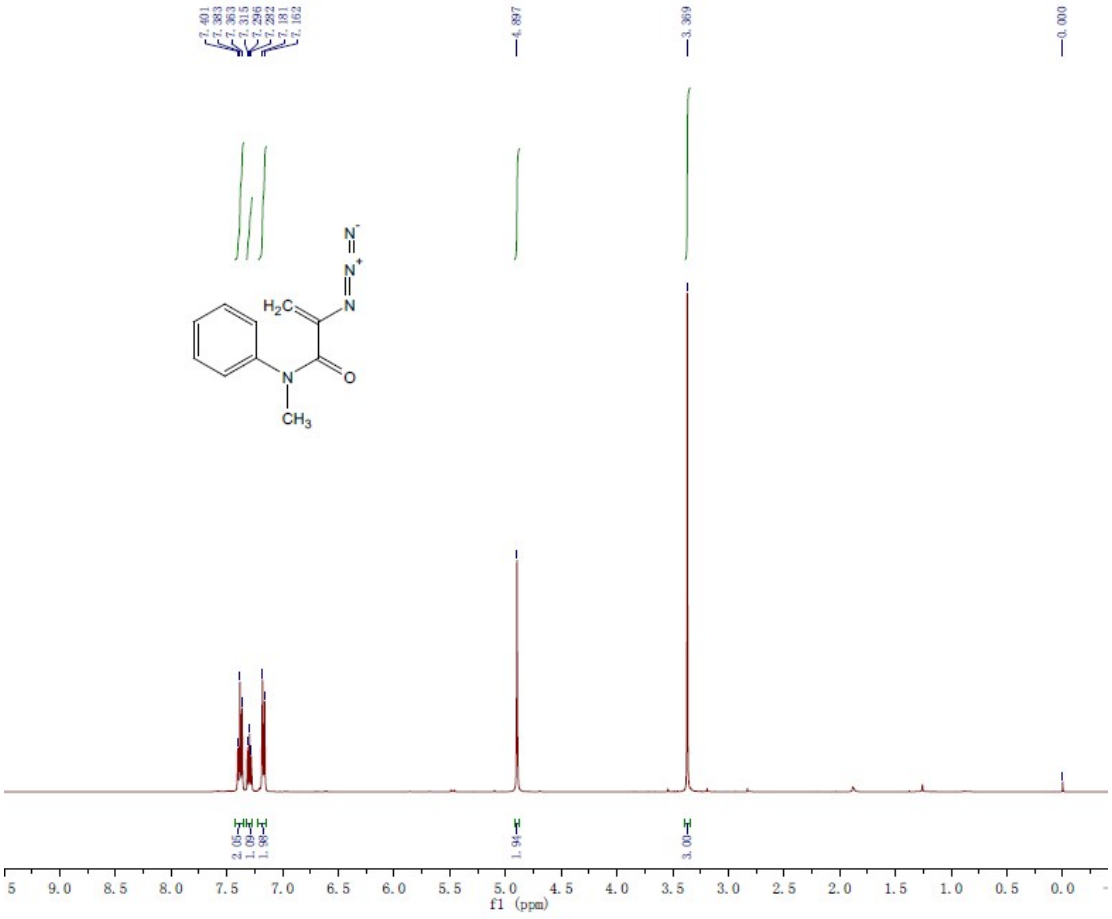

165.48
164.13
139.32
138.93
135.85
132.37
131.53
130.52
130.44
130.38
129.65
129.37
129.20
128.36
127.74
127.43
127.32
127.24
122.15
121.46
105.68
77.32
77.20
77.00
76.68
52.03
51.68
N
N
N
H2C
O
N
Cl
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

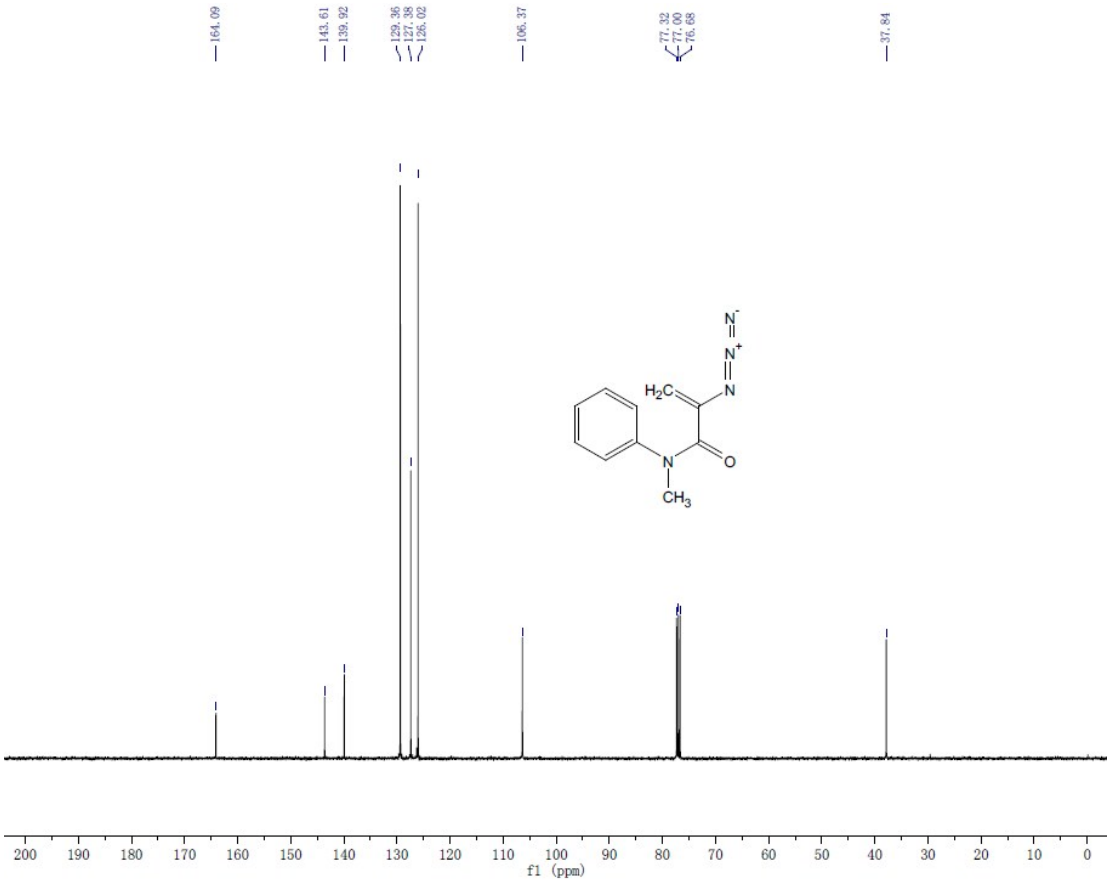

7.26
7.25
7.24
7.21
7.20
7.19
7.11
7.10
7.09
7.08
6.82
6.80
5.23
5.20
4.83
4.83
4.53
4.49
2.06
0.00
2.99
3.93
1.01
0.96
1.04
2.01
1.00
3.01
f1 (ppm)

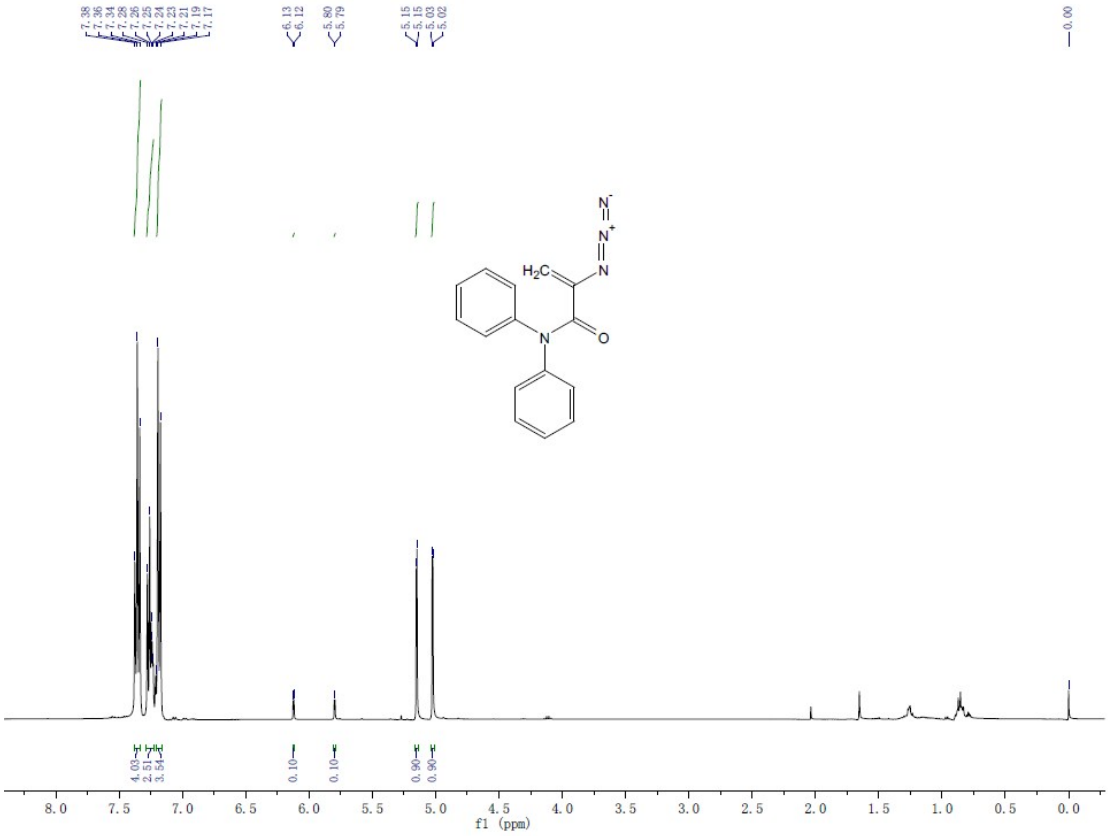

164.08
140.32
139.96
136.13
135.50
131.28
129.43
128.99
128.35
128.26
127.72
126.65
105.85
77.32
77.00
76.68
52.95
17.53
f1 (ppm)

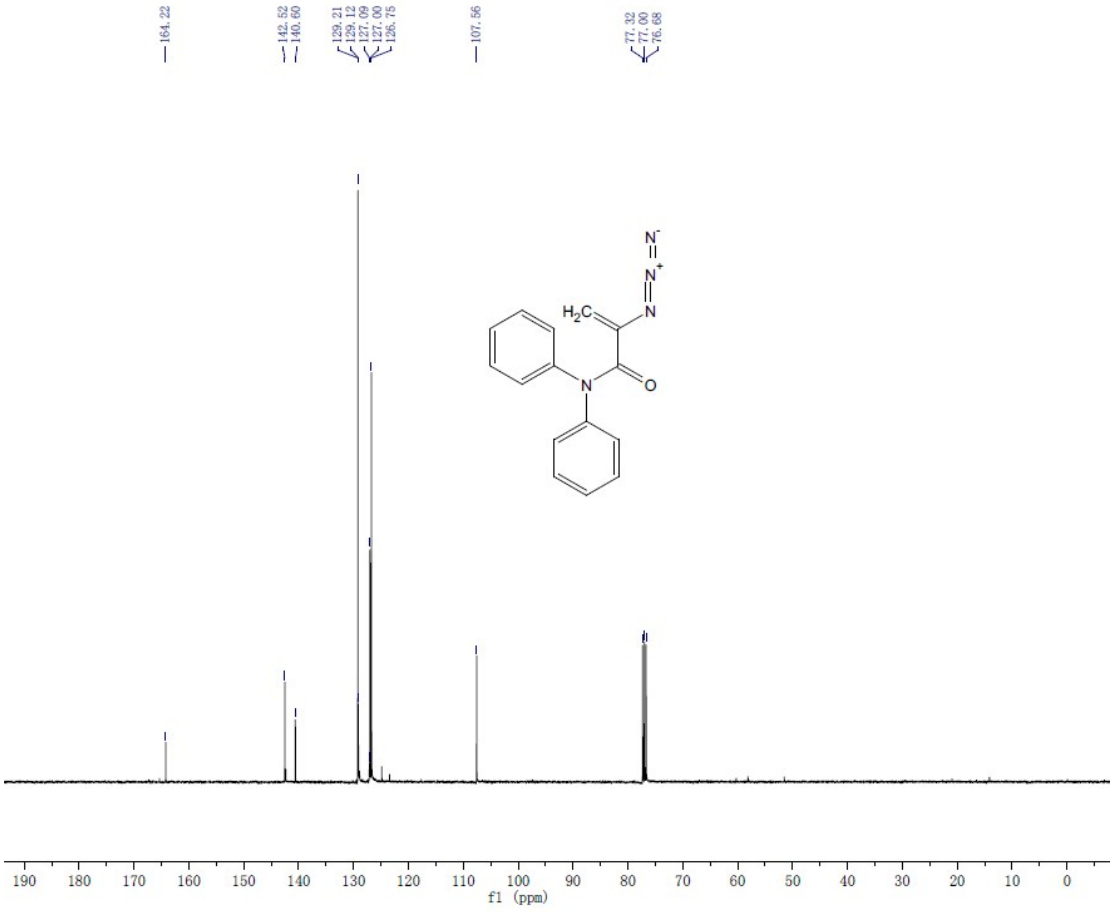

7.26
7.24
7.22
7.21
7.21
7.19
7.19
6.94
6.93
6.92
6.91
6.86
6.85
6.84
6.84
6.82
6.82
5.12
5.09
4.74
4.71
4.68
4.56
3.69
0.00
6.08
1.03
2.05
1.03
1.00
1.00
1.00
2.96
f1 (ppm)

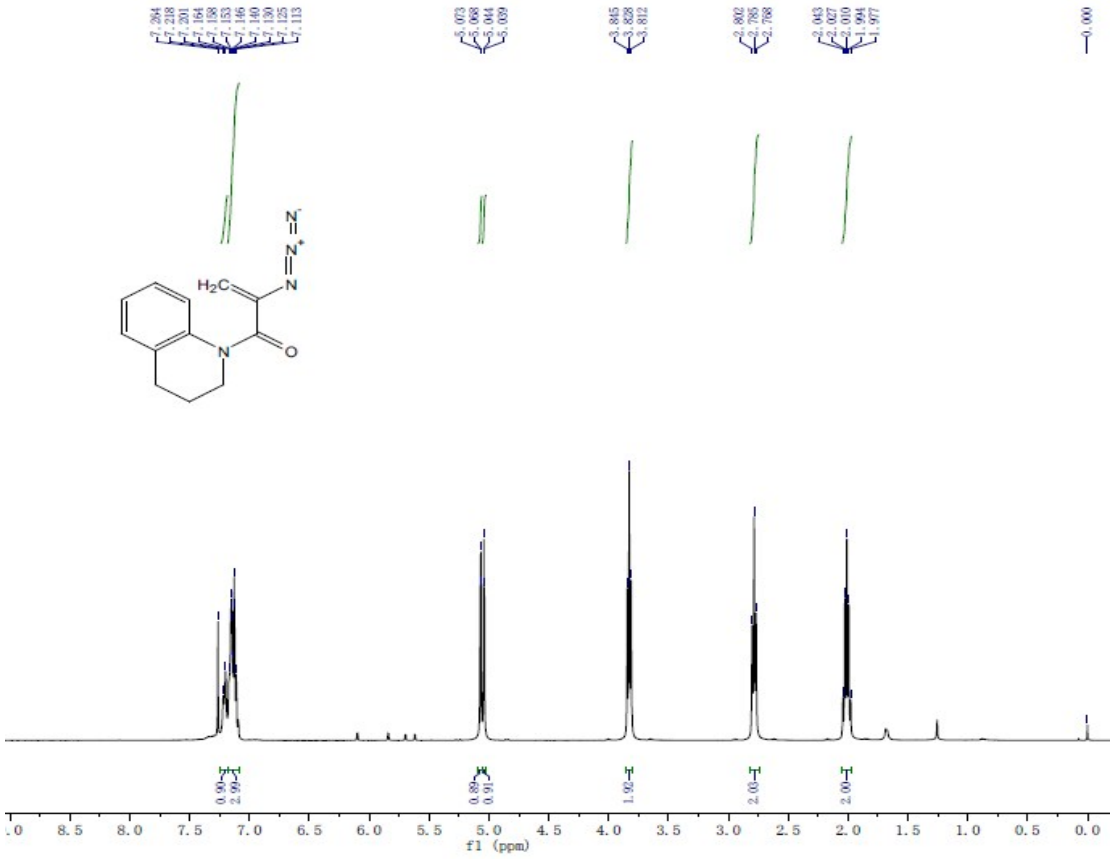

165.19
154.25
139.34
136.63
128.89
128.81
128.13
128.06
127.30
120.74
111.84
104.99
77.32
77.00
76.68
55.34
52.45
f1 (ppm)

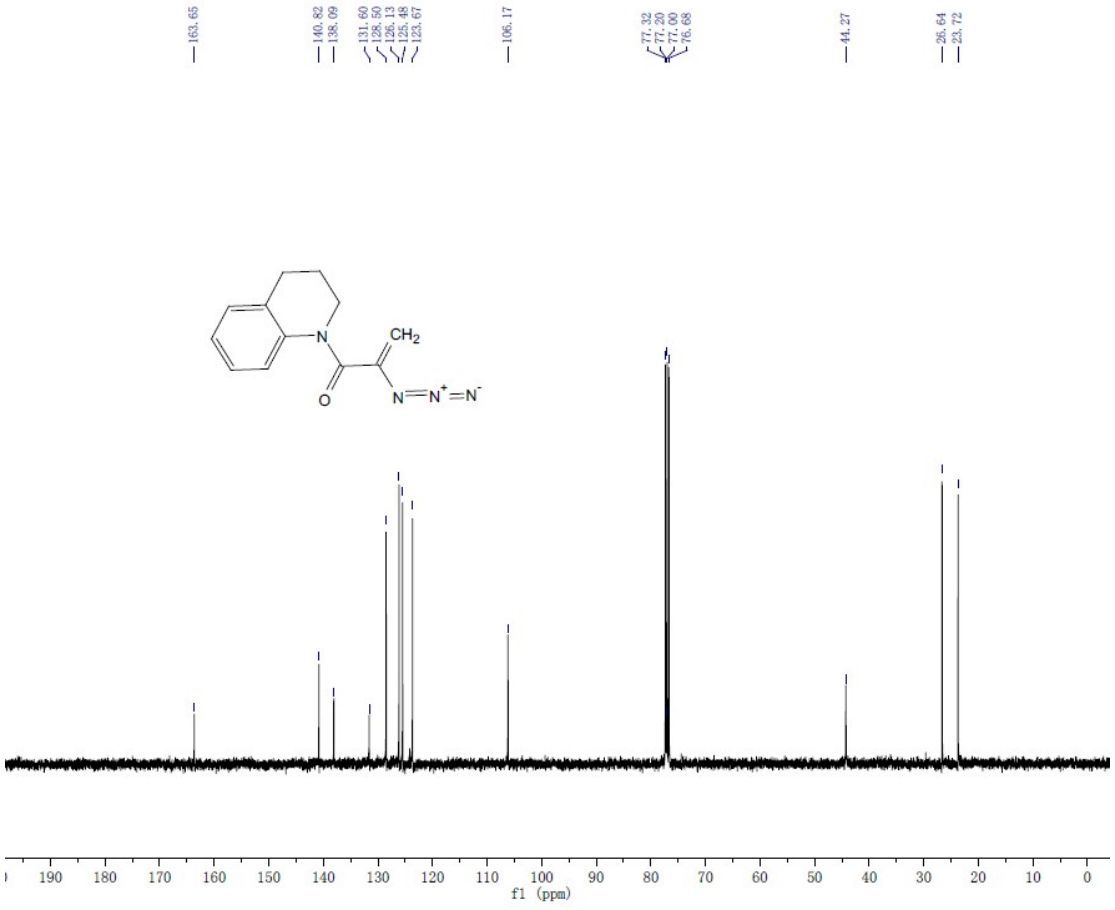

7.401
7.383
7.363
7.315
7.296
7.292
7.181
7.162
6.897
3.369
0.000
2.05
1.09
1.98
1.94
3.00
f1 (ppm)


164.09
143.61
139.92
129.36
127.38
126.02
106.37
77.32
77.00
76.68
37.84
f1 (ppm)


7.38
7.36
7.34
7.28
7.26
7.25
7.24
7.23
7.21
7.19
7.17
6.13
6.12
5.80
5.79
5.15
5.15
5.03
5.02
0.00
4.03
2.51
3.54
0.10
0.10
0.90
0.90
f1 (ppm)

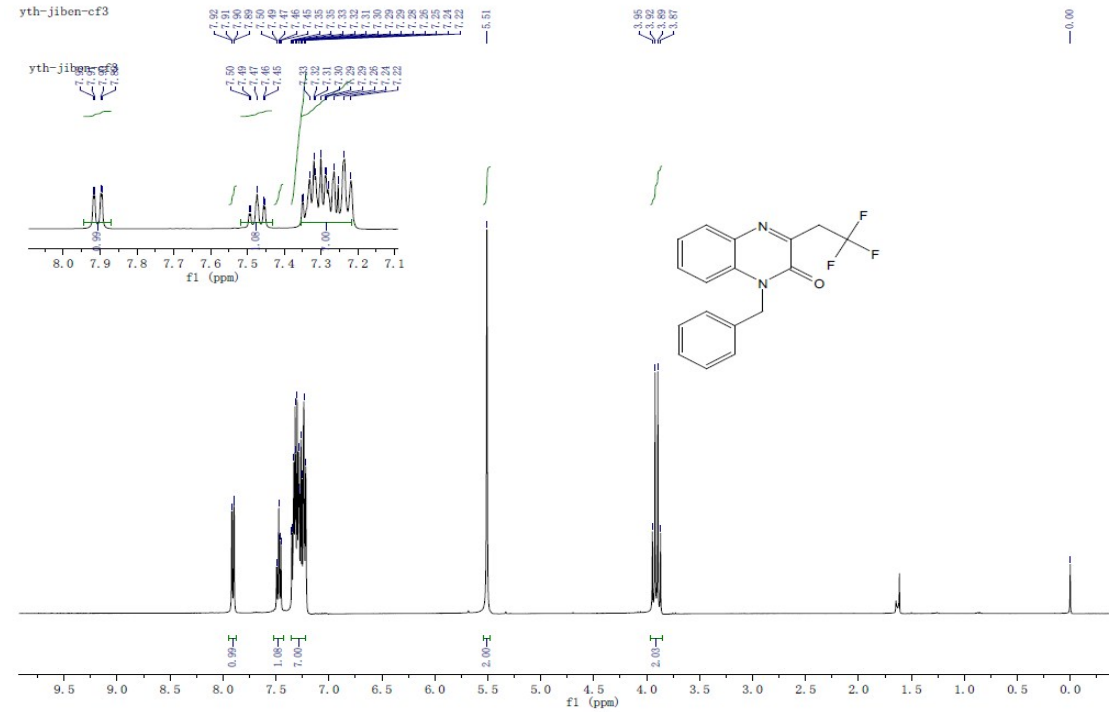

164.22
142.52
140.60
129.21
129.12
127.09
127.00
126.75
107.56
77.32
77.00
76.68
f1 (ppm)

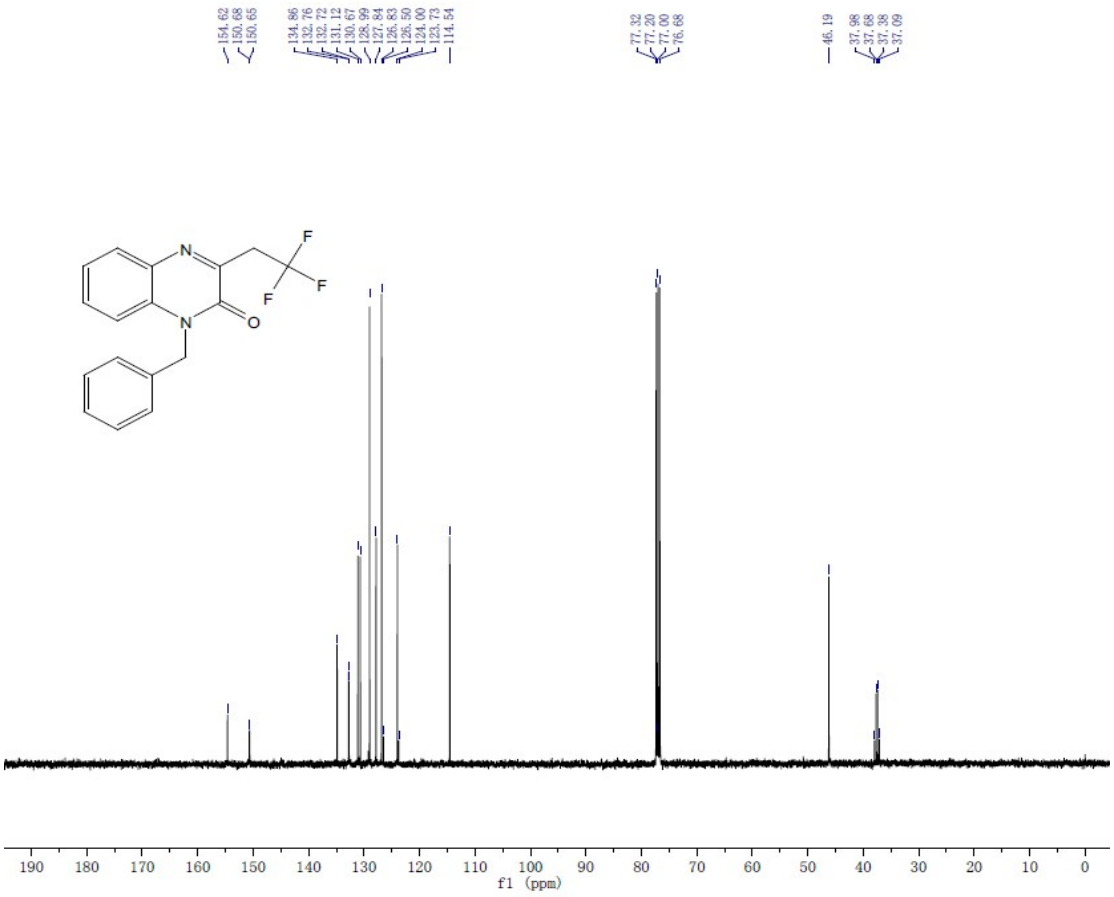

7.264
7.238
7.201
7.164
7.158
7.153
7.146
7.140
7.130
7.125
7.113
5.073
5.068
5.044
5.039
3.845
3.828
3.812
2.802
2.785
2.768
2.043
2.027
2.010
1.994
1.977
0.000
N
N
N
H2C
N
O
0.90
2.99
0.89
0.91
1.92
2.00
2.00
f1 (ppm)

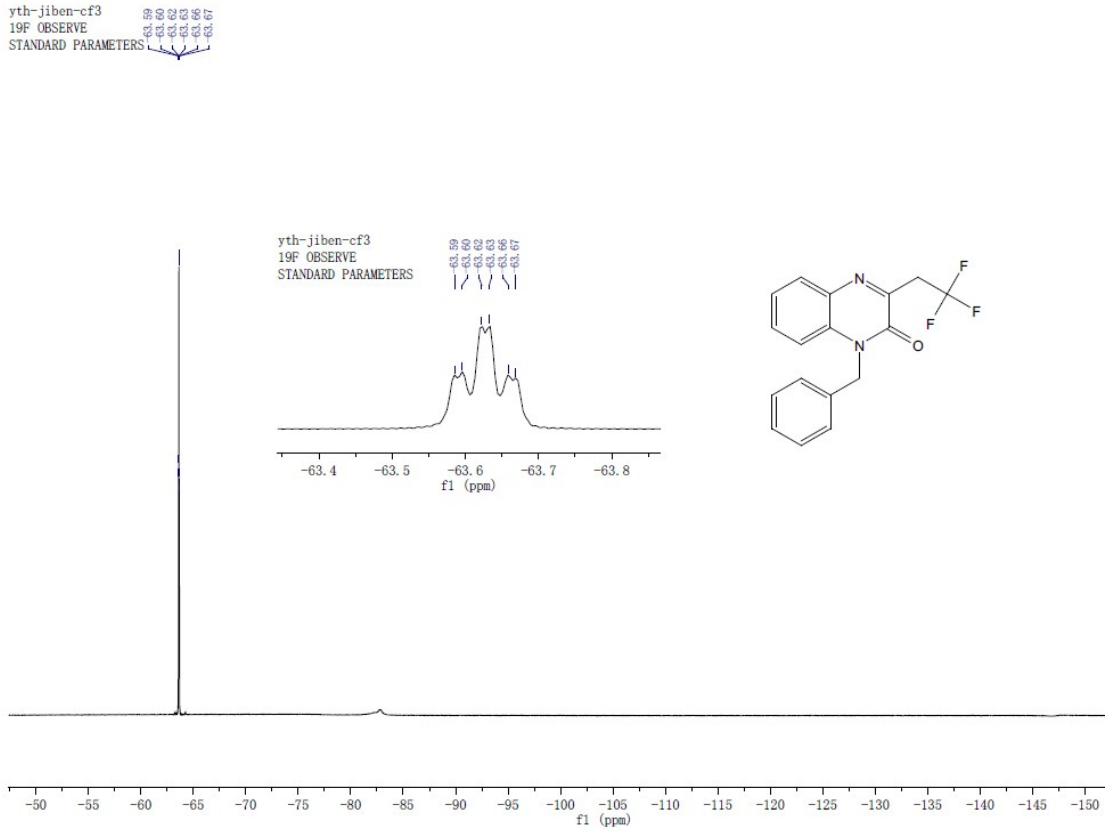

163.65
140.82
138.09
131.60
128.50
126.13
125.48
123.67
106.17
77.32
77.20
77.00
76.68
44.27
26.64
23.72
CH2
N
O
N=N+=N-
f1 (ppm)

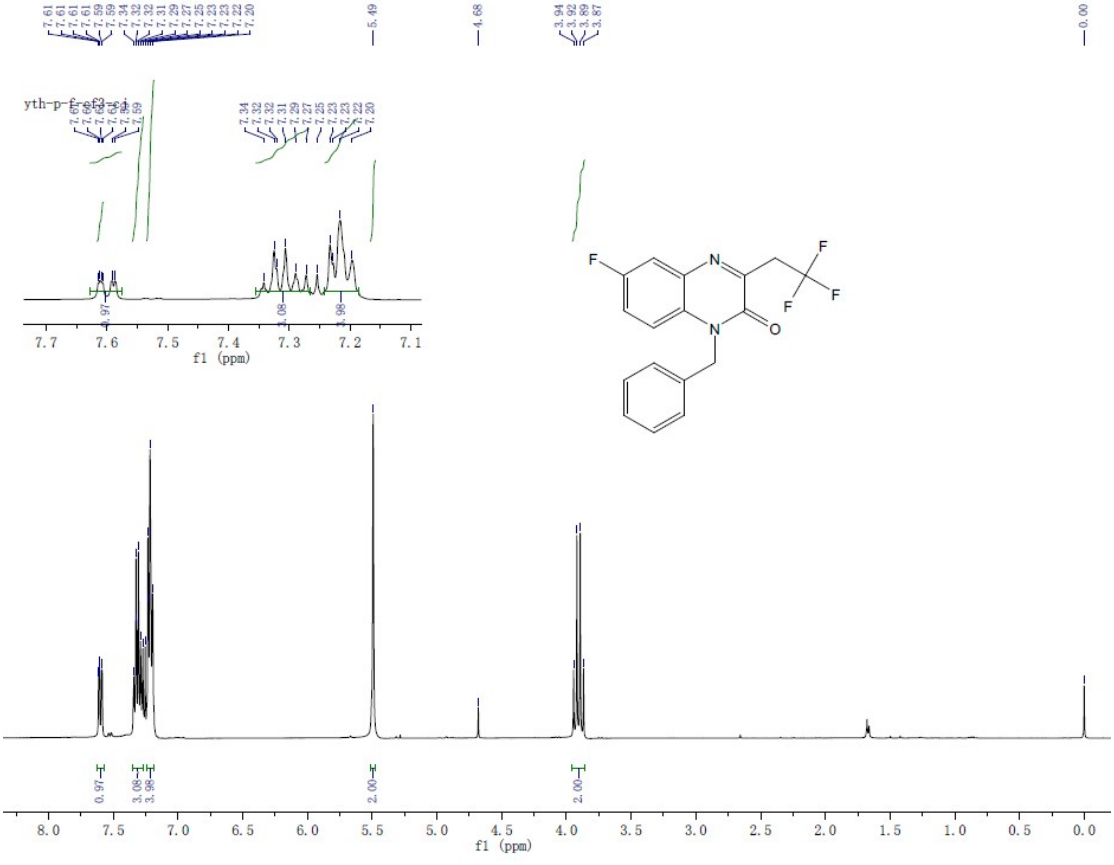
Copies of ^{1}H NMR , ^{13}C NMR and ^{19}F NMR spectra of the products

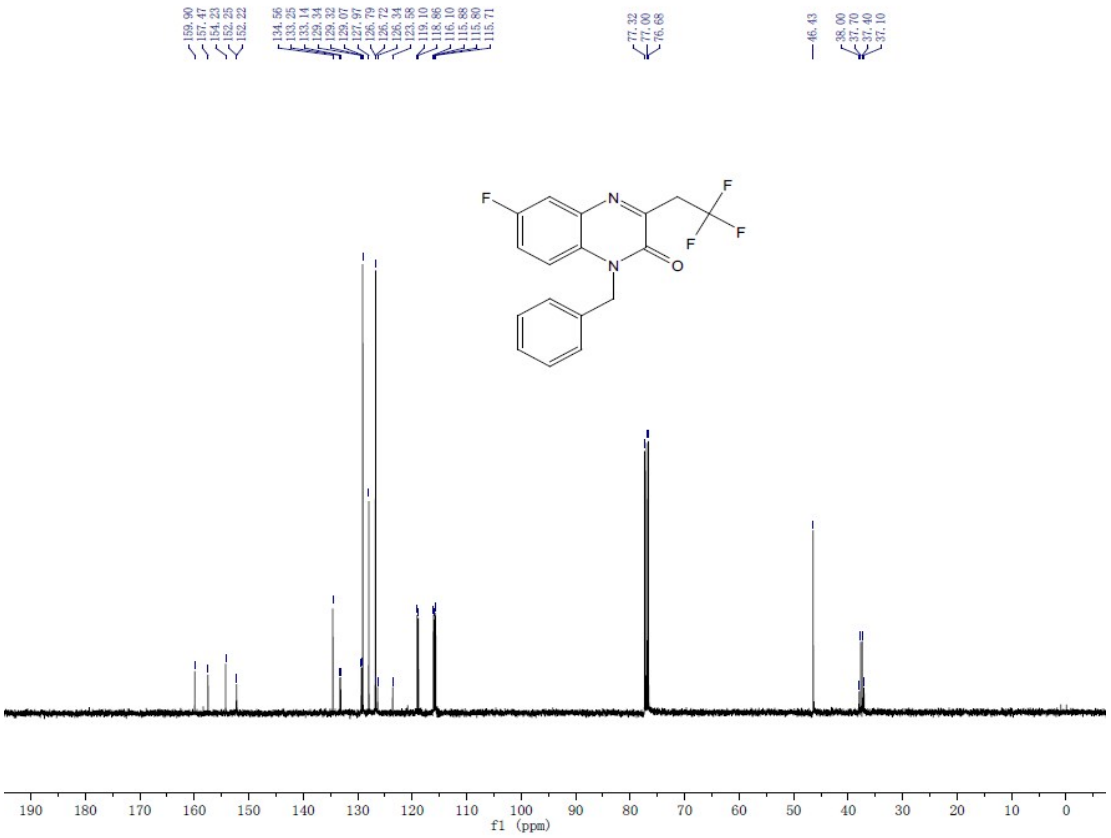
2a

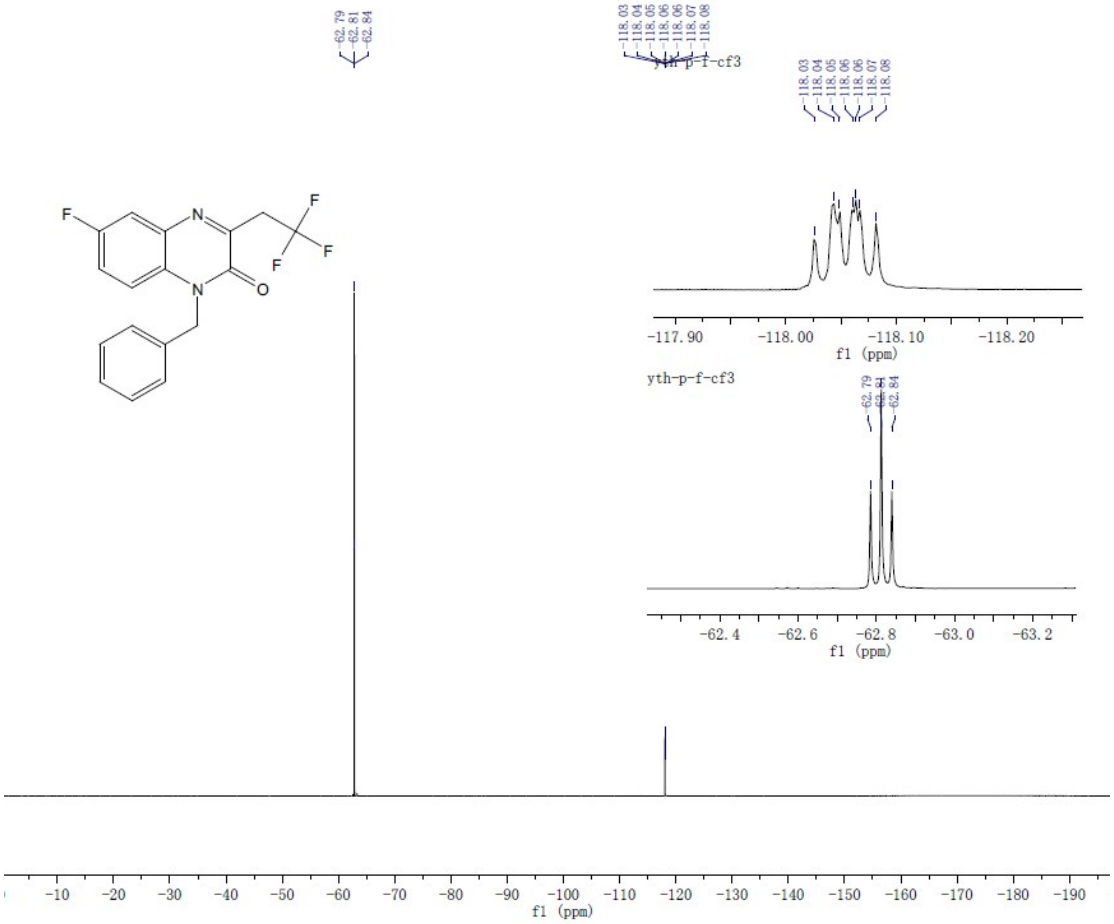


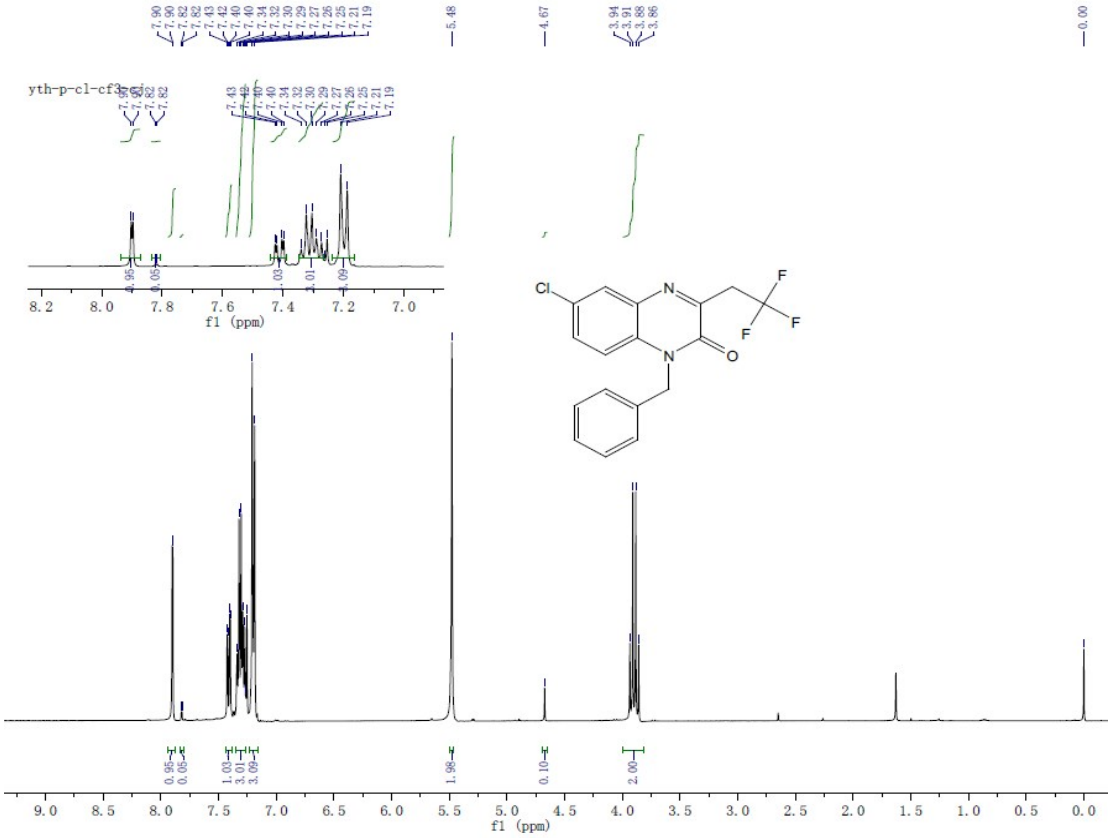


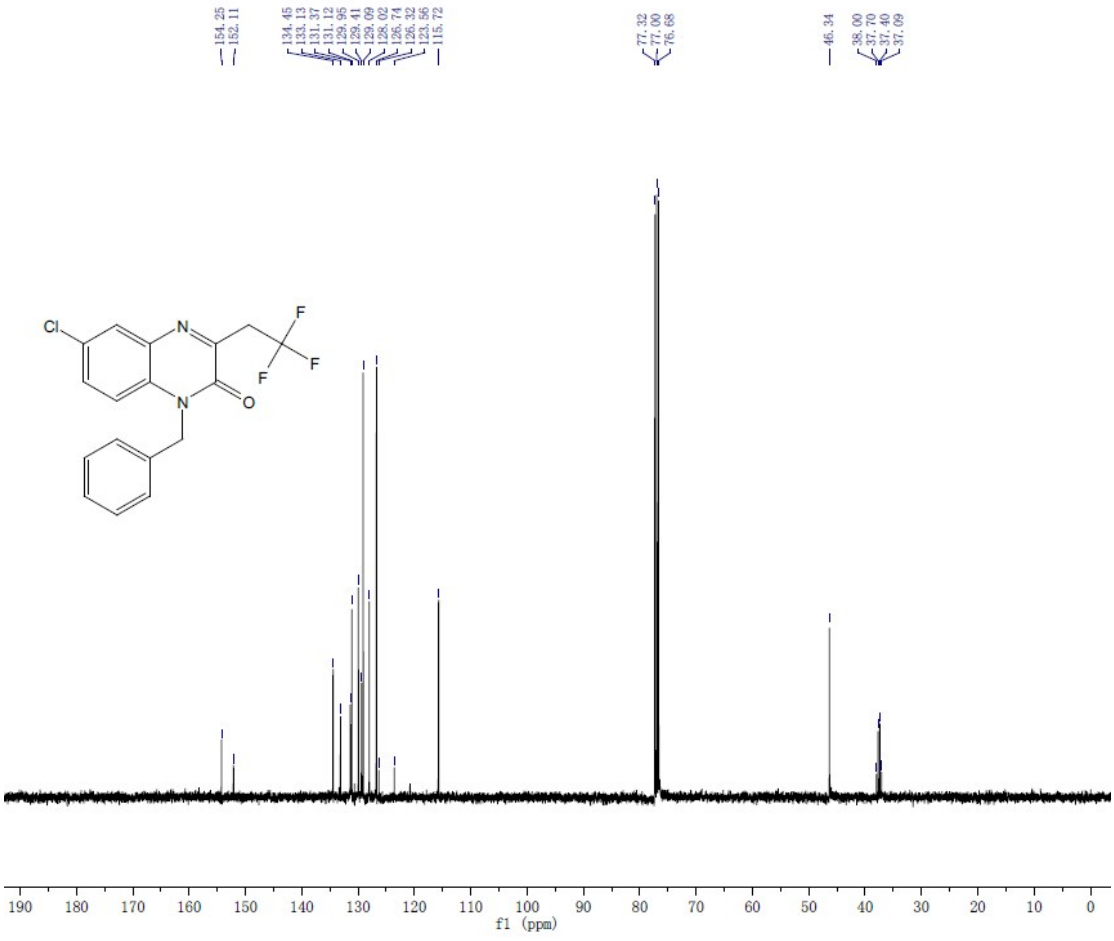

yth-jiben-cf3
19F OBSERVE
STANDARD PARAMETERS
f1 (ppm)


f1 (ppm)

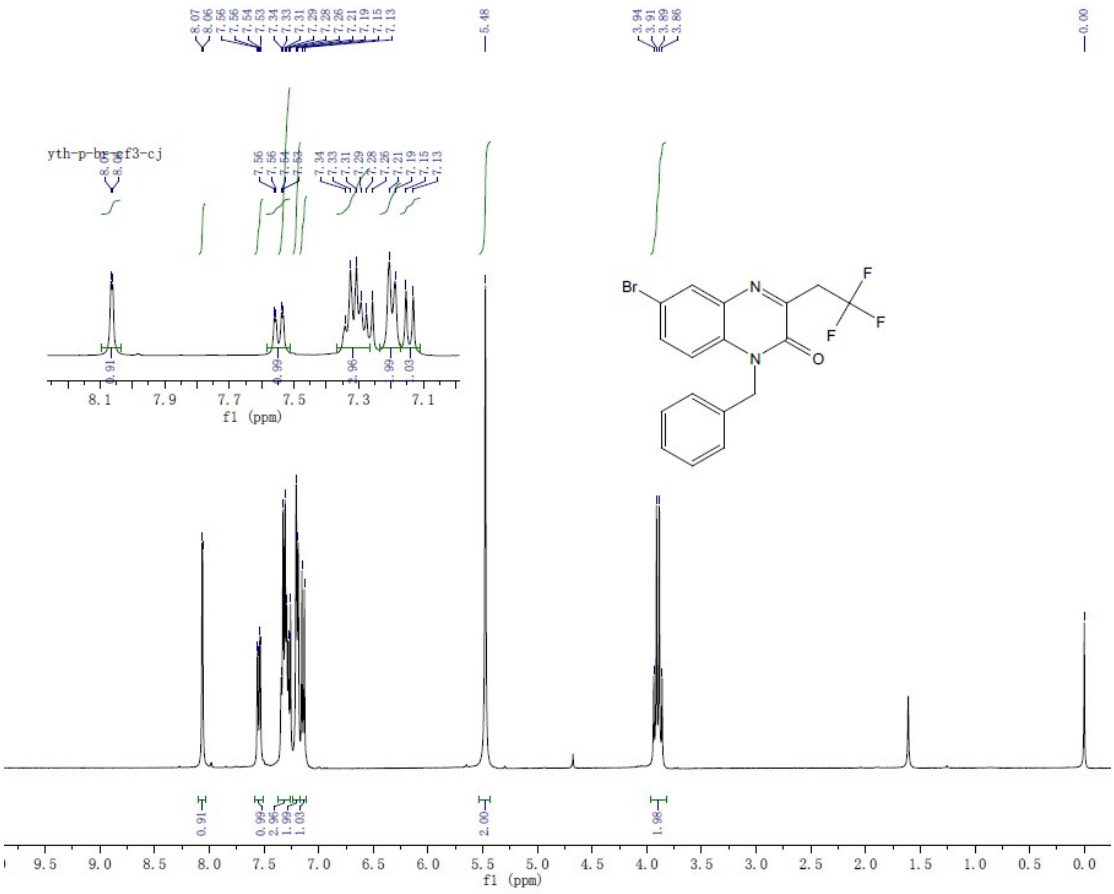

159.90
157.47
154.23
152.25
152.22
134.56
133.25
133.14
129.34
129.32
129.07
127.97
126.79
126.72
126.34
123.58
119.10
118.86
116.10
115.88
115.80
115.71
77.32
77.00
76.68
46.43
38.00
37.70
37.40
37.10
F
N
F
F
F
O
N
f1 (ppm)

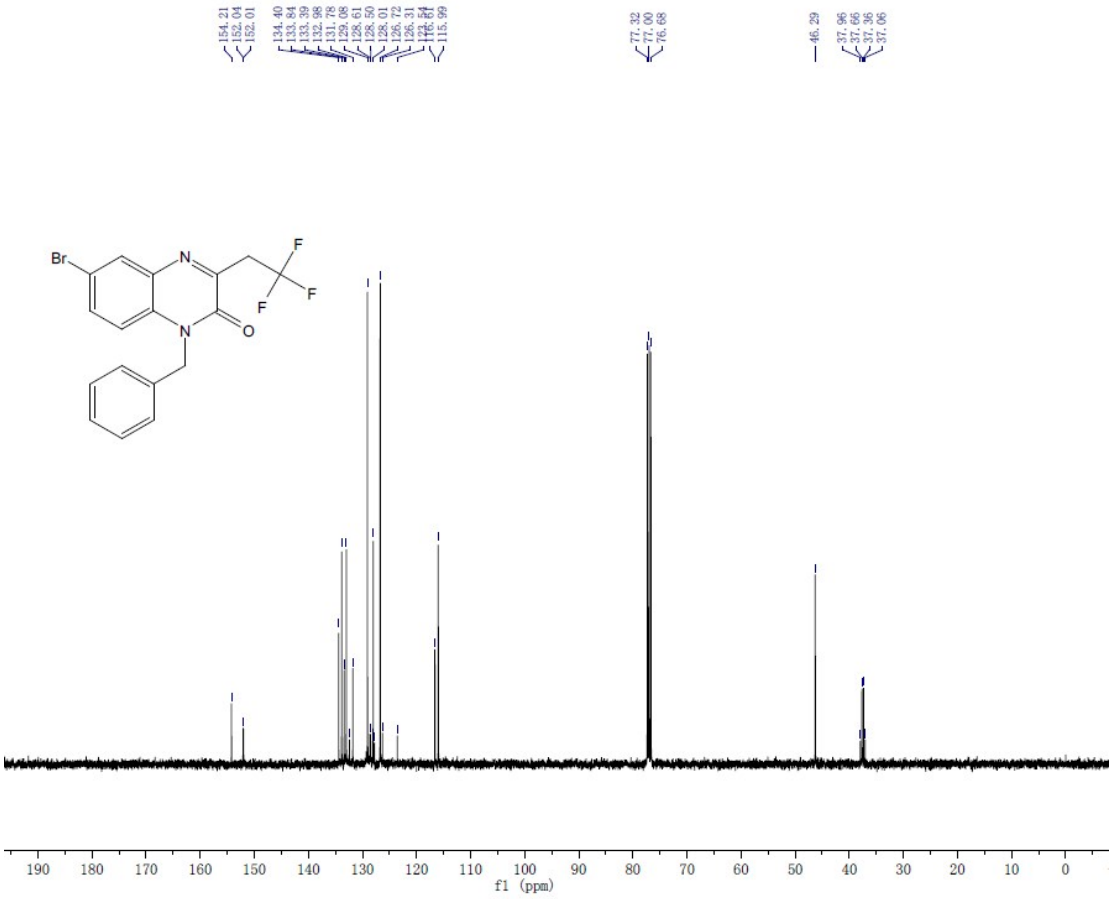

-62.79
-62.81
-62.84
-118.03
-118.04
-118.05
-118.06
-118.06
-118.07
-118.08
yth-p-f-cf3
F
N
F
F
F
O
N
-117.90
-118.00
-118.10
-118.20
f1 (ppm)
yth-p-f-cf3
-62.4
-62.6
-62.8
-63.0
-63.2
f1 (ppm)
f1 (ppm)

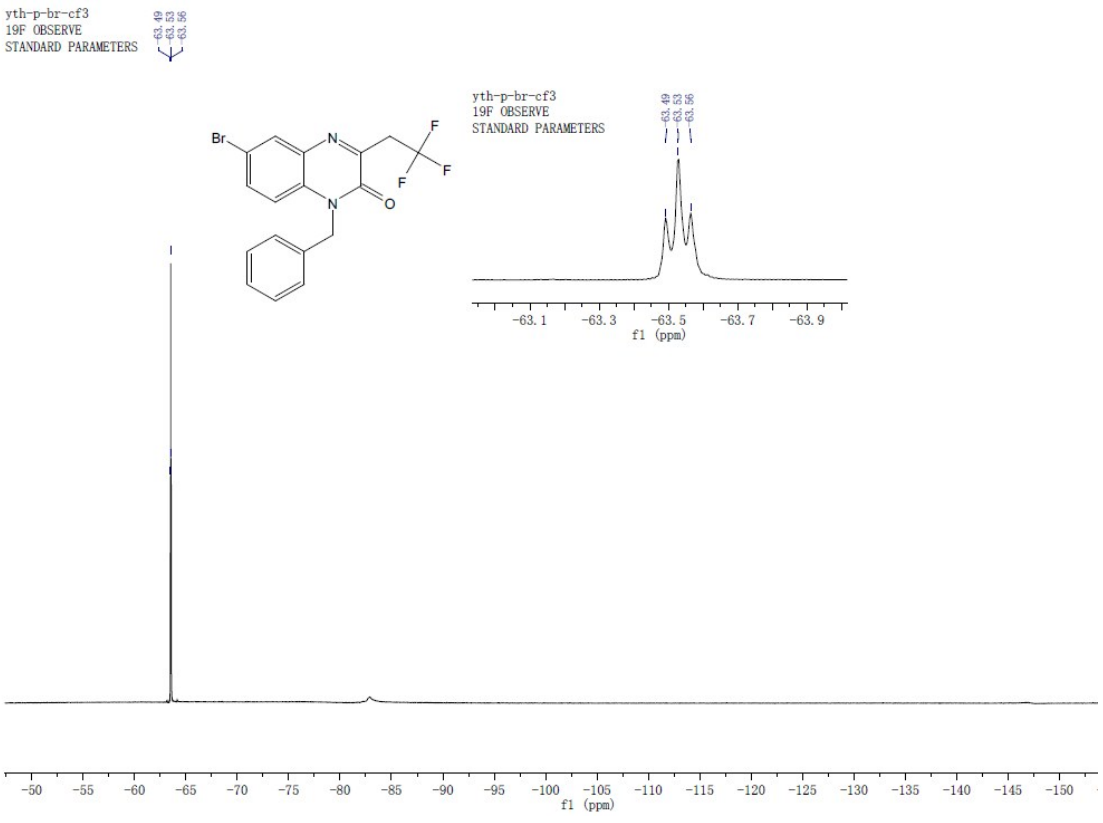

yth-p-cl-cf3-1h
f1 (ppm)

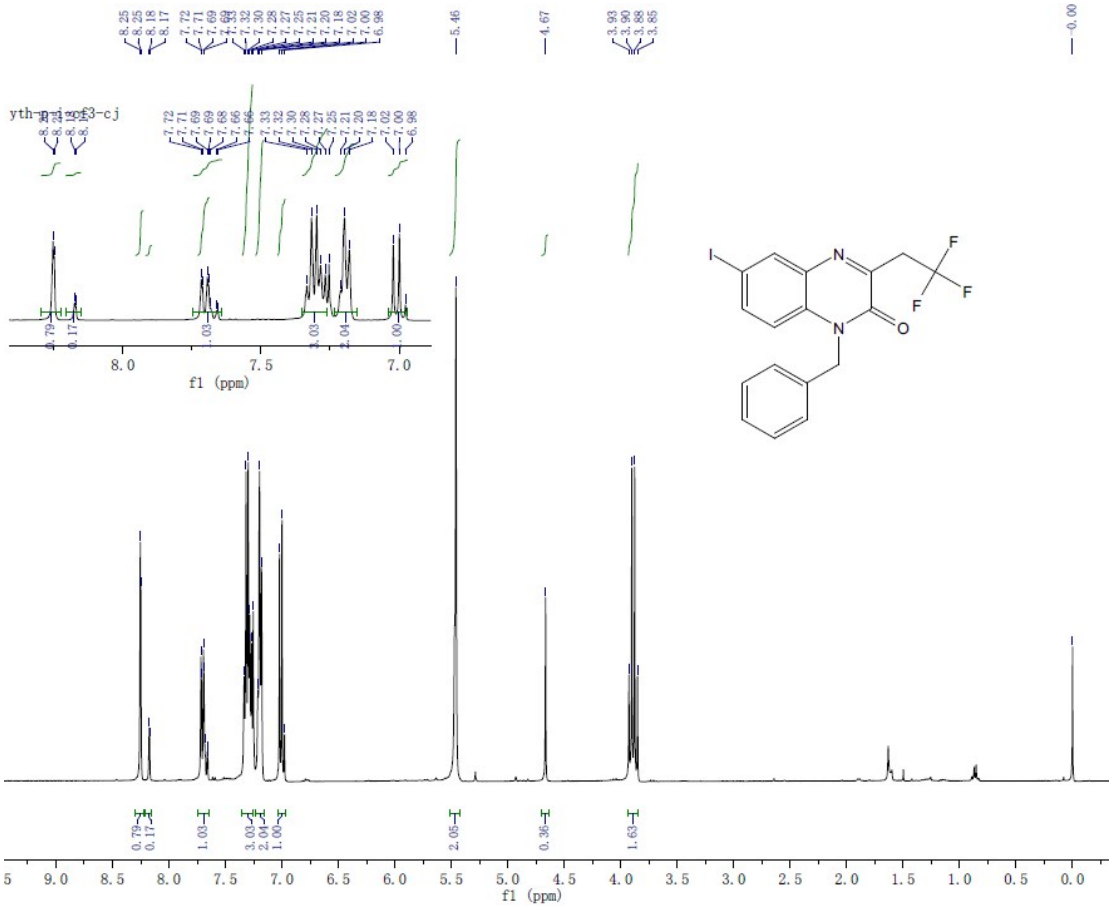

f1 (ppm)

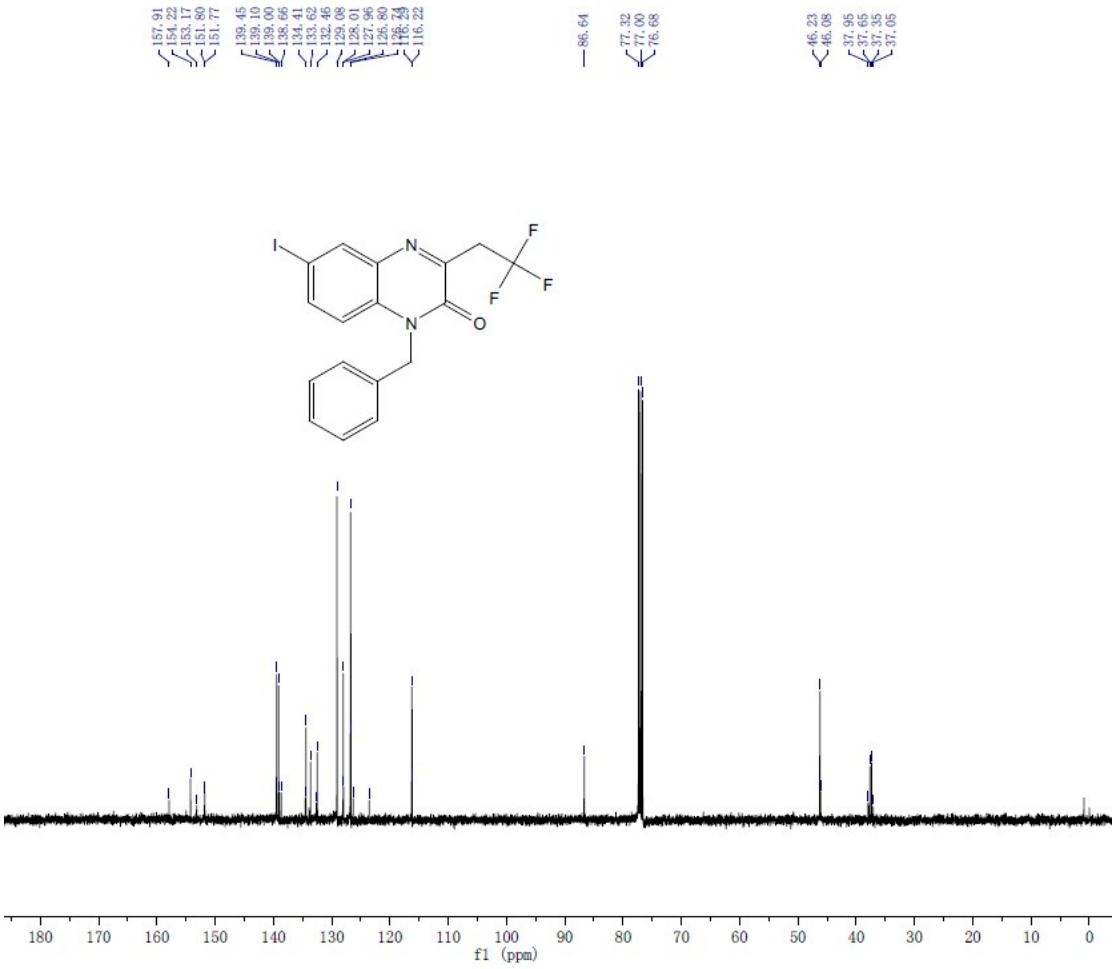

-62.78
-62.81
-62.83
Cl
N
F
F
F
N
O
yth-p-cl-cf3
-62.78
-62.81
-62.83
-62.70
-62.80
-62.90
-63.00
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

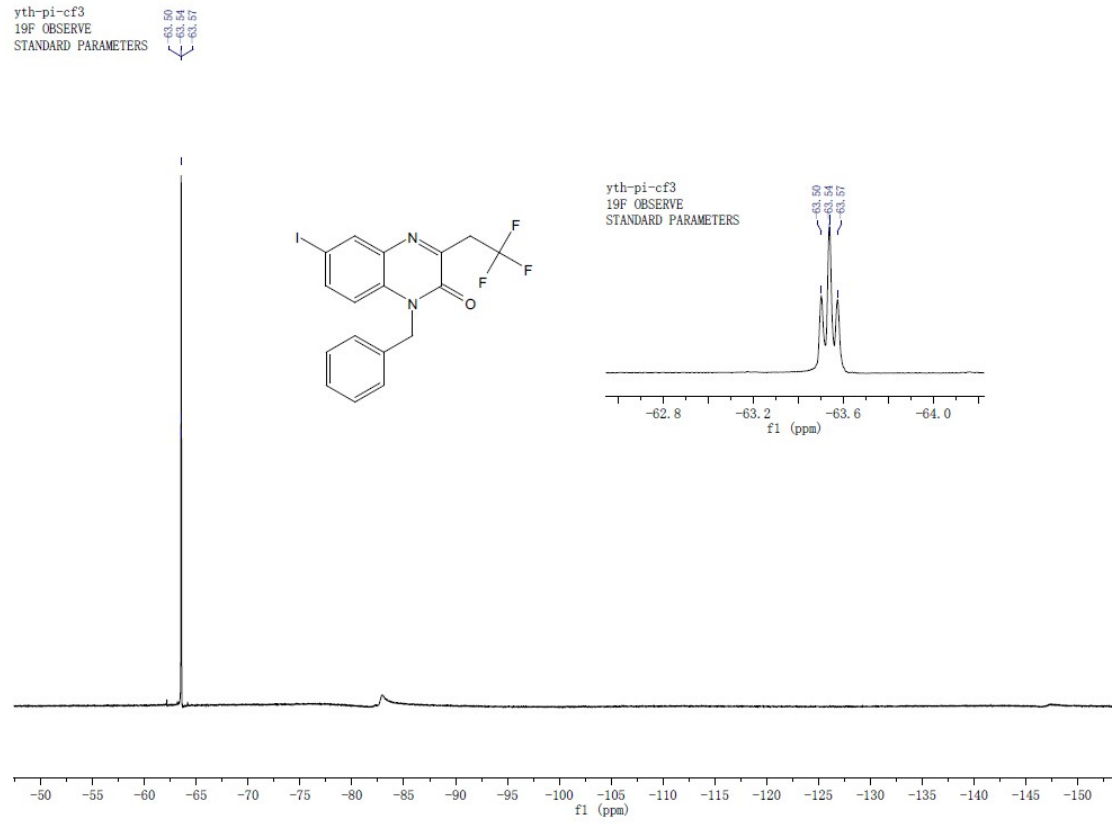

8.07
8.06
7.56
7.56
7.56
7.54
7.53
7.34
7.33
7.31
7.29
7.28
7.26
7.21
7.19
7.15
7.13
5.48
3.94
3.91
3.89
3.86
0.00
yth-p-br-cf3-cj
8.07
8.06
7.56
7.56
7.54
7.53
7.34
7.33
7.31
7.29
7.28
7.26
7.21
7.19
7.15
7.13
0.91
0.99
0.96
0.99
1.03
8.1
7.9
7.7
7.5
7.3
7.1
f1 (ppm)
Br
N
F
F
F
N
O
0.91
0.99
2.96
1.99
1.03
2.00
1.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

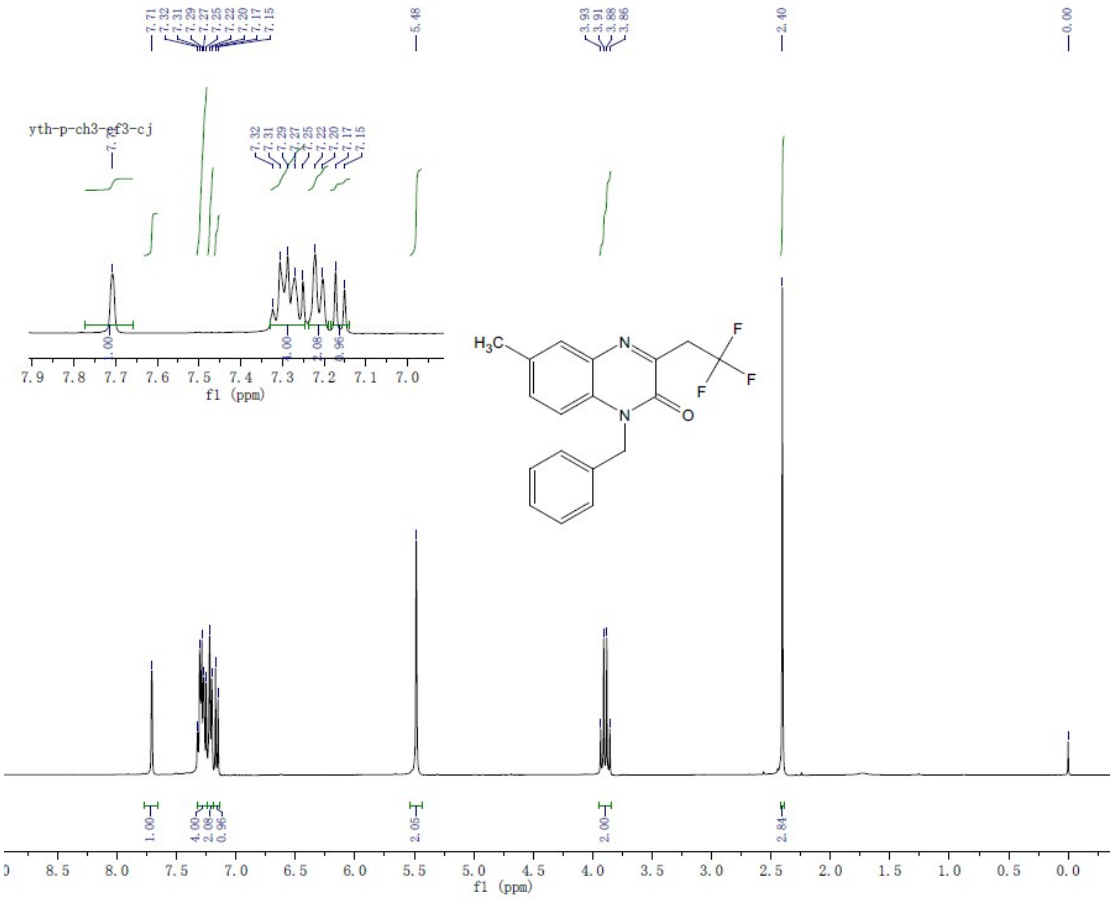

154.21
152.04
152.01
134.40
133.84
133.39
132.98
131.78
129.08
128.61
128.50
128.01
126.72
126.31
115.99
77.32
77.00
76.68
46.29
37.96
37.66
37.35
37.06
Br
N
F
F
F
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

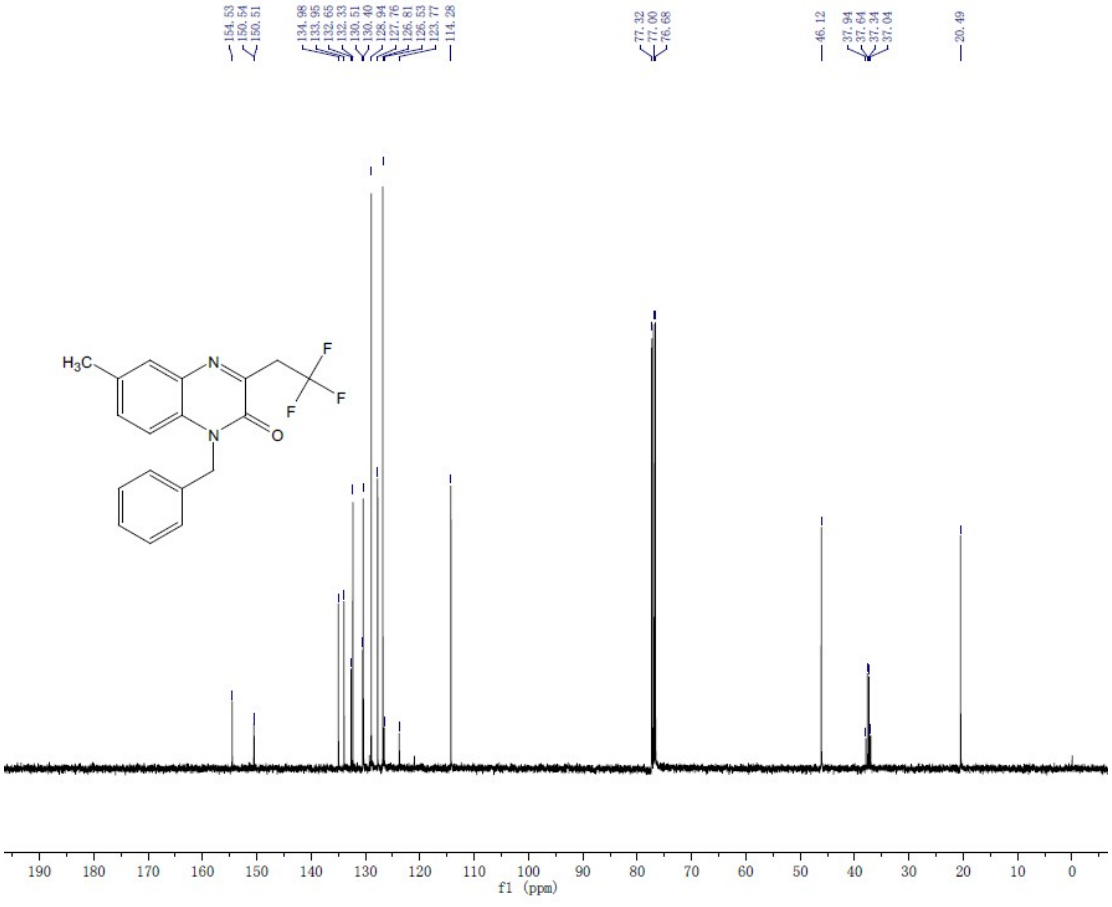

yth-p-br-cf3
19F OBSERVE
STANDARD PARAMETERS
-63.49
-63.53
-63.56
Br
N
F
F
F
N
O
yth-p-br-cf3
19F OBSERVE
STANDARD PARAMETERS
-63.49
-63.53
-63.56
-63.1 -63.3 -63.5 -63.7 -63.9
f1 (ppm)
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)

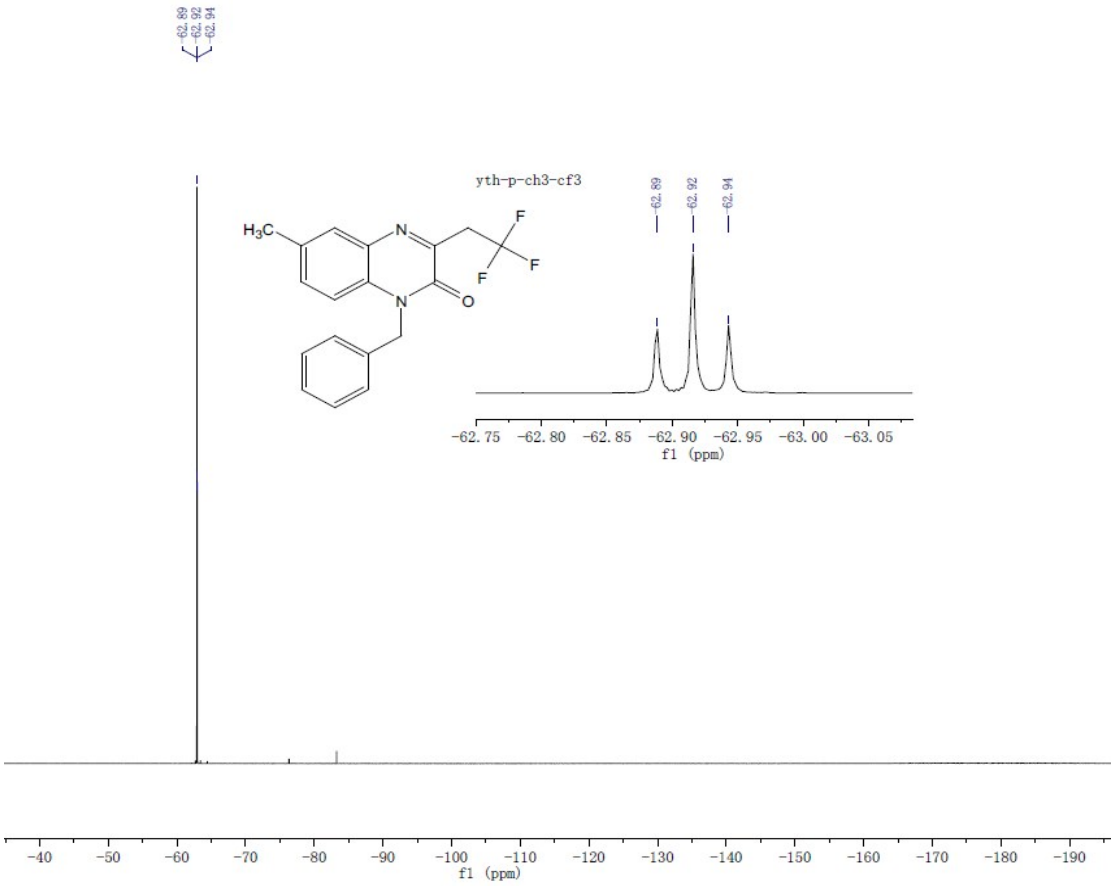

f1 (ppm)
I
N
F
F
F
N
O

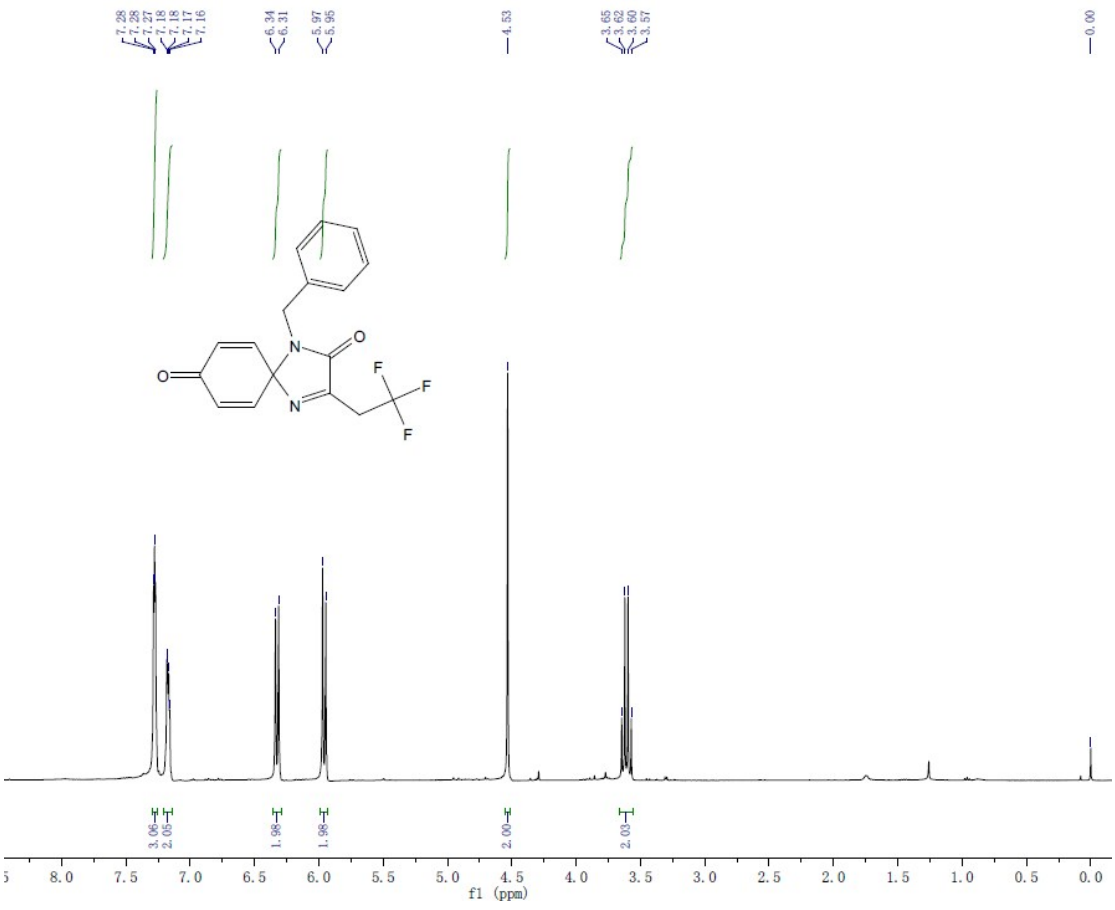

157.91
154.22
153.17
151.80
151.77
139.45
139.10
139.00
136.66
134.41
133.62
132.46
129.08
128.01
127.96
126.80
116.22
86.64
77.32
77.00
76.68
46.23
46.08
37.95
37.65
37.35
37.05
I
N
F
F
F
N
O
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

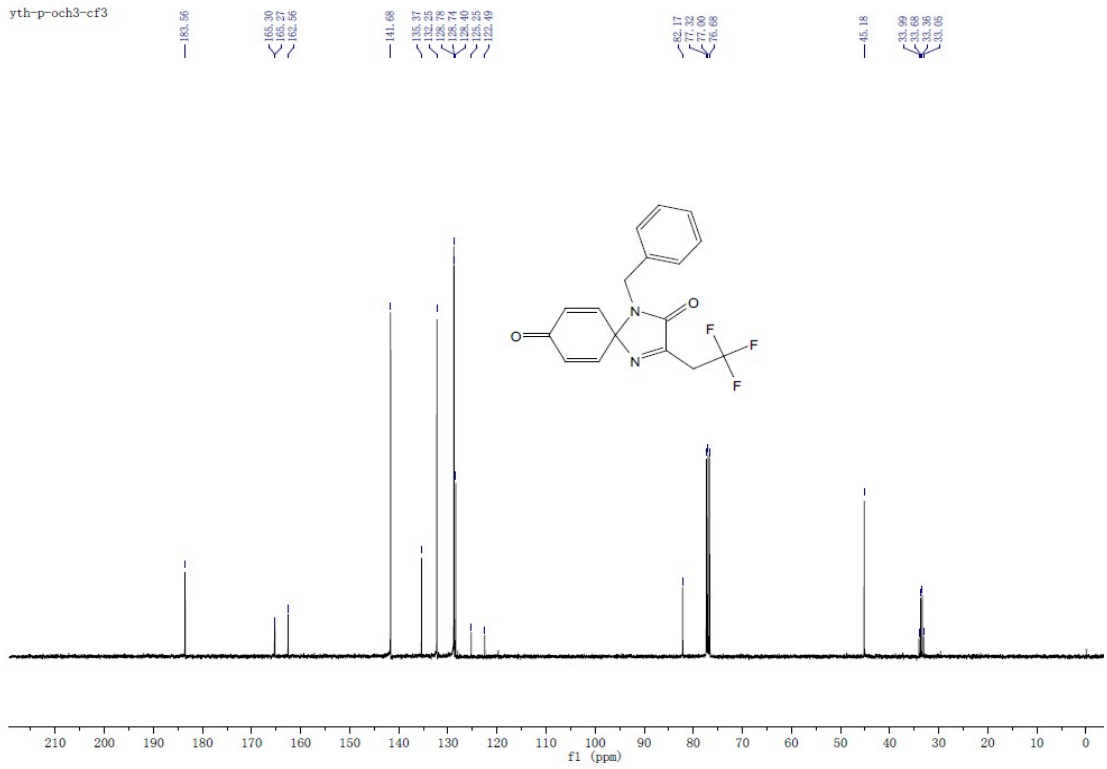

yth-pi-cf3
19F OBSERVE
STANDARD PARAMETERS
-63.50
-63.54
-63.57
I
N
F
F
F
N
O
yth-pi-cf3
19F OBSERVE
STANDARD PARAMETERS
-63.50
-63.54
-63.57
-62.8 -63.2 -63.6 -64.0
f1 (ppm)
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)

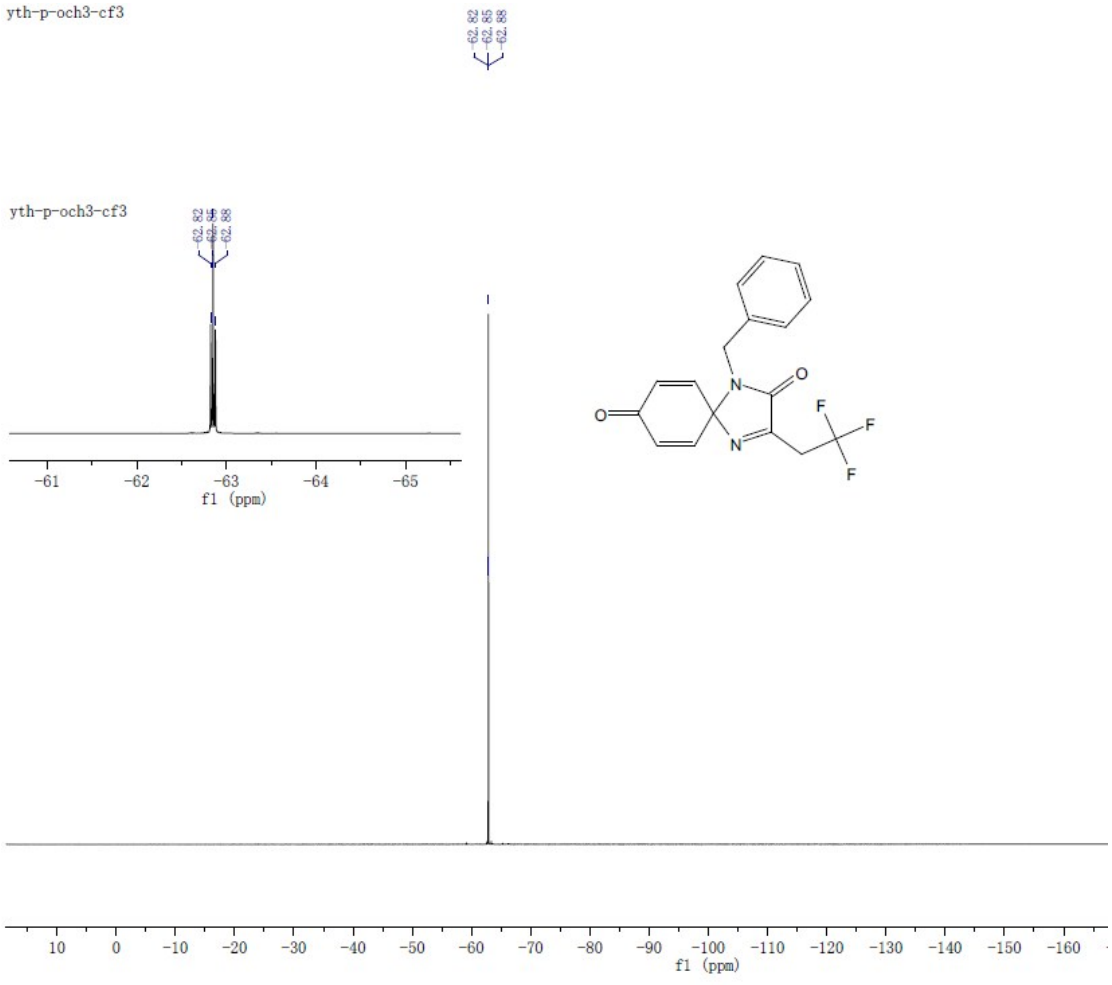

yth-p-ch3-gf3-cj
f1 (ppm)

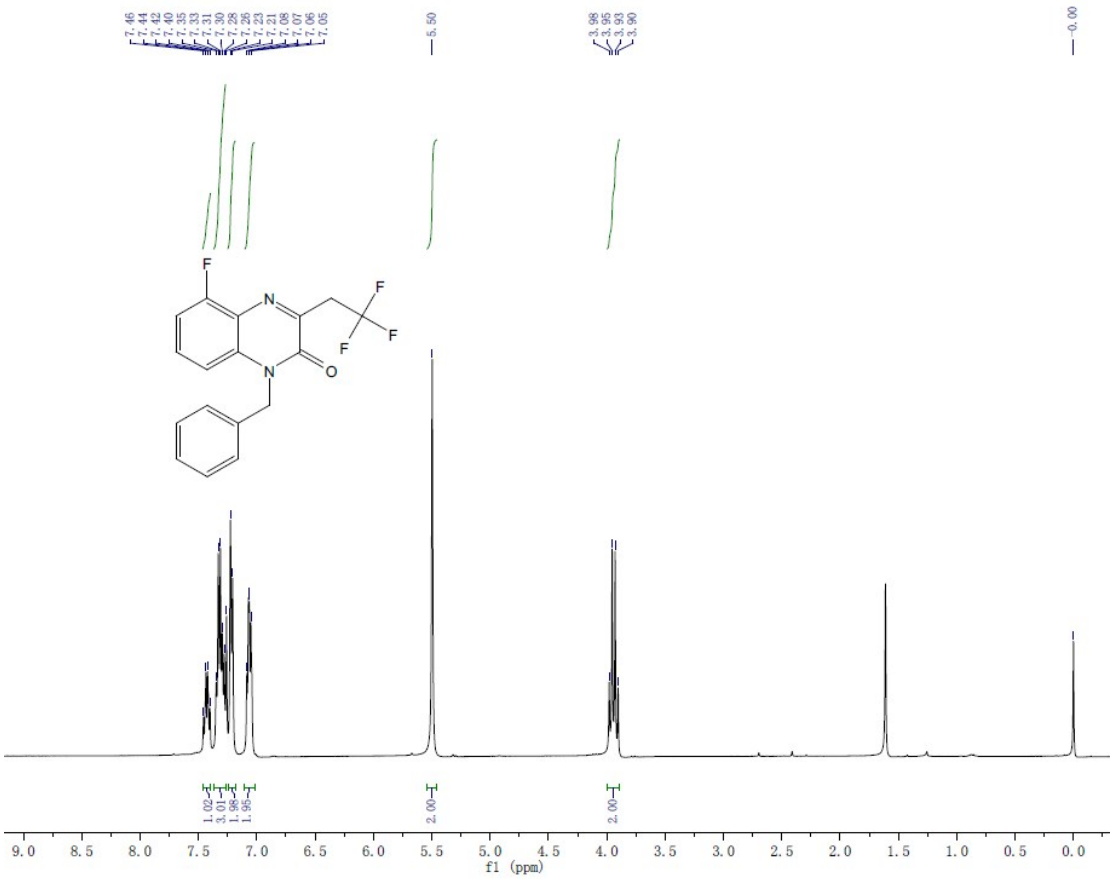

f1 (ppm)

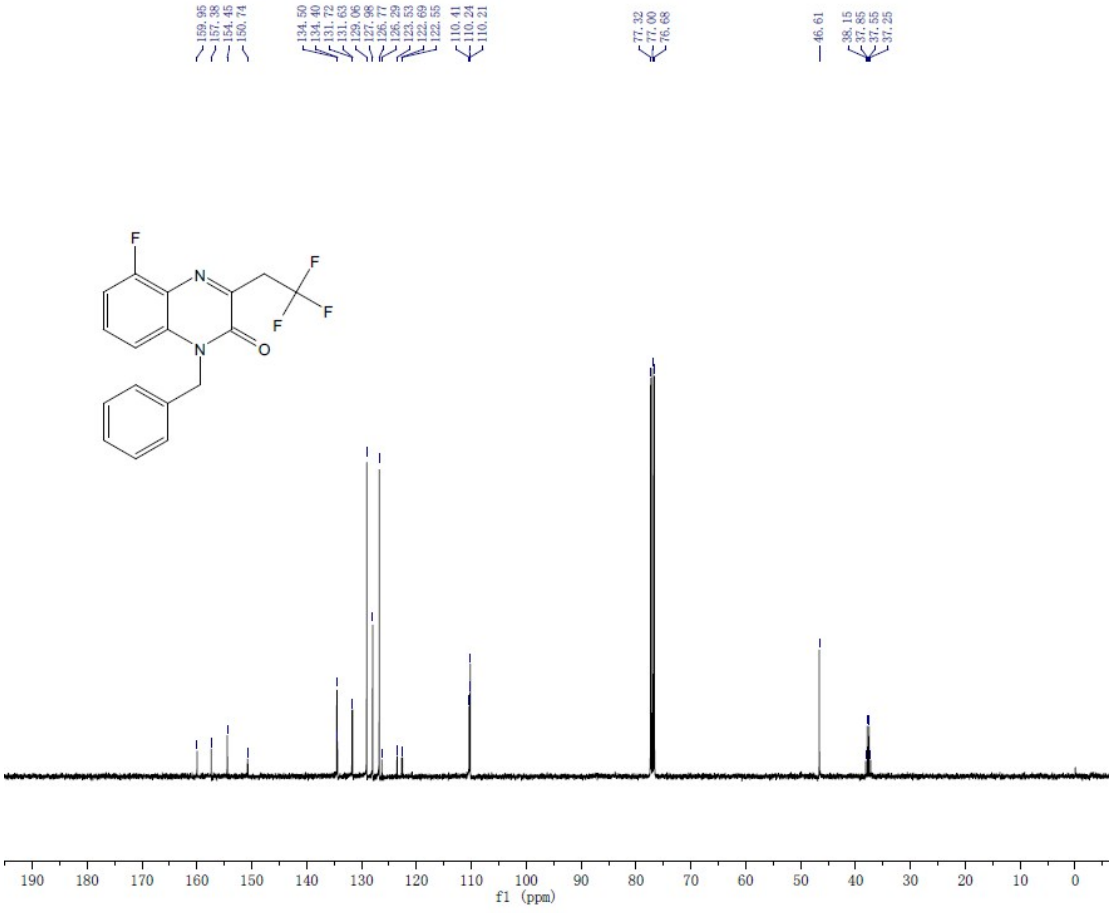

-62.89
-62.92
-62.94
yth-p-ch3-cf3
H3C
N
F
F
F
N
O
-62.89
-62.92
-62.94
-62.75 -62.80 -62.85 -62.90 -62.95 -63.00 -63.05
f1 (ppm)
-40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

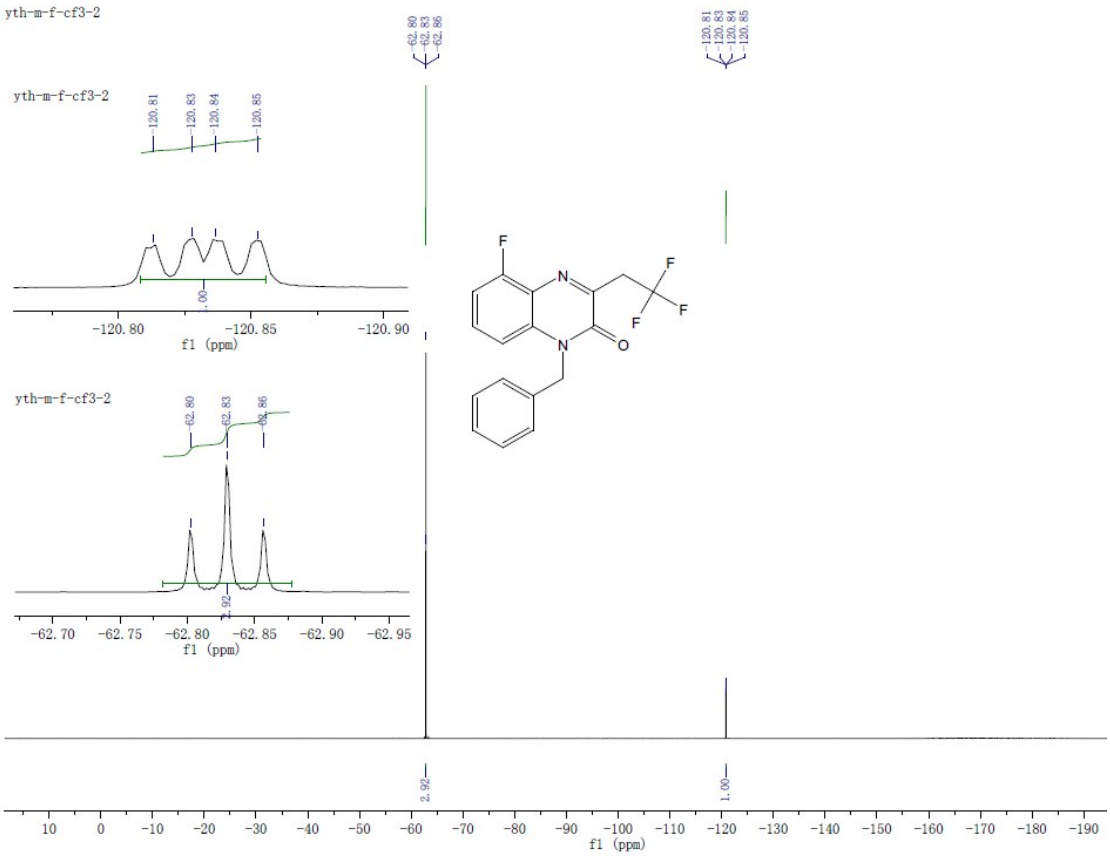

7.28
7.28
7.27
7.18
7.18
7.17
7.16
6.34
6.31
5.97
5.95
4.53
3.65
3.62
3.60
3.57
0.00
O
N
O
F
F
F
N
3.06
2.05
1.98
1.98
2.00
2.03
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

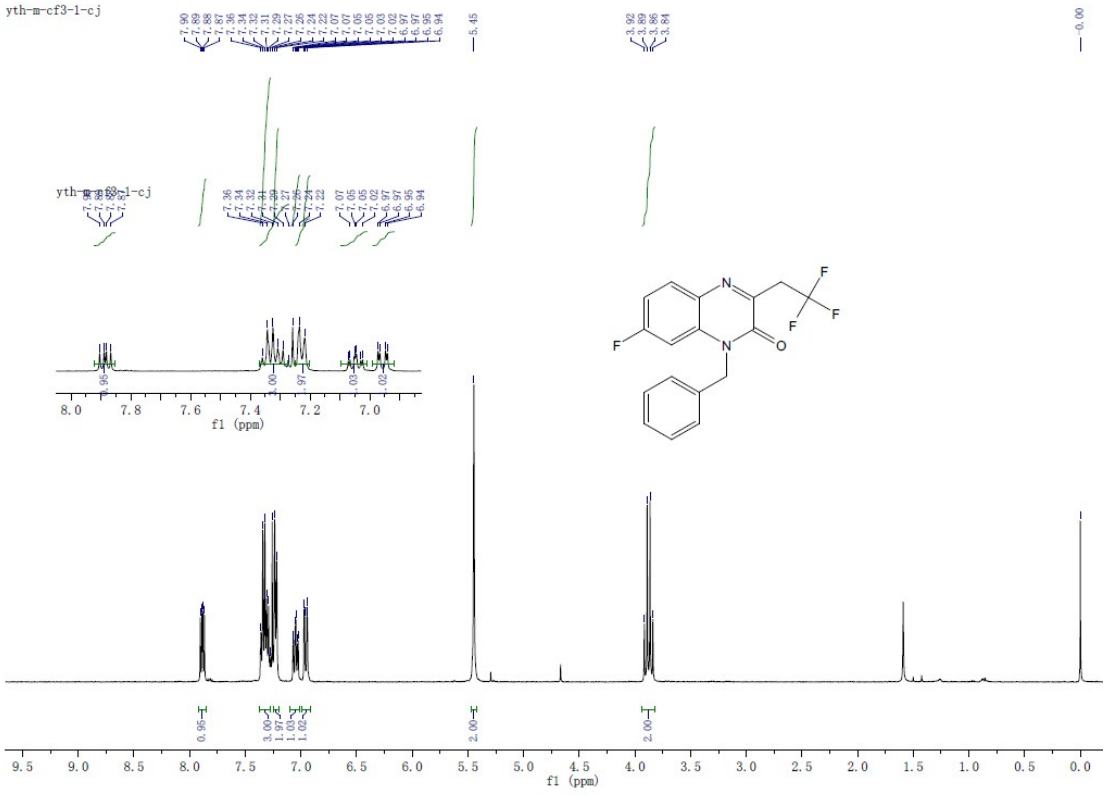

yth-p-och3-cf3
183.56
165.30
165.27
162.56
141.68
135.37
132.25
129.76
128.74
128.40
125.25
122.49
82.17
77.32
77.00
76.68
45.18
33.99
33.68
33.36
33.05
O
N
O
F
F
F
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

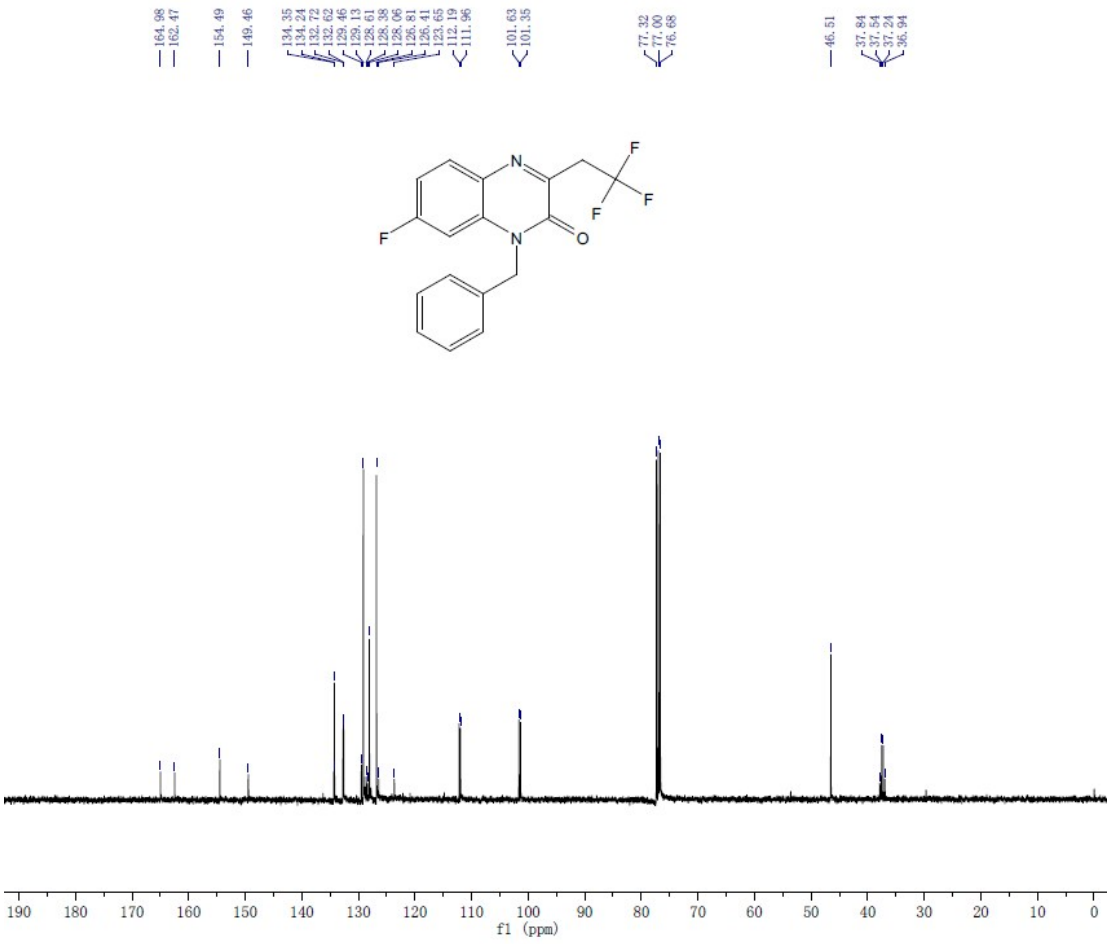

yth-p-och3-cf3
62.82
62.85
62.88
yth-p-och3-cf3
62.82
62.85
62.88
-61 -62 -63 -64 -65
f1 (ppm)
O
N
O
F
F
F
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160
f1 (ppm)

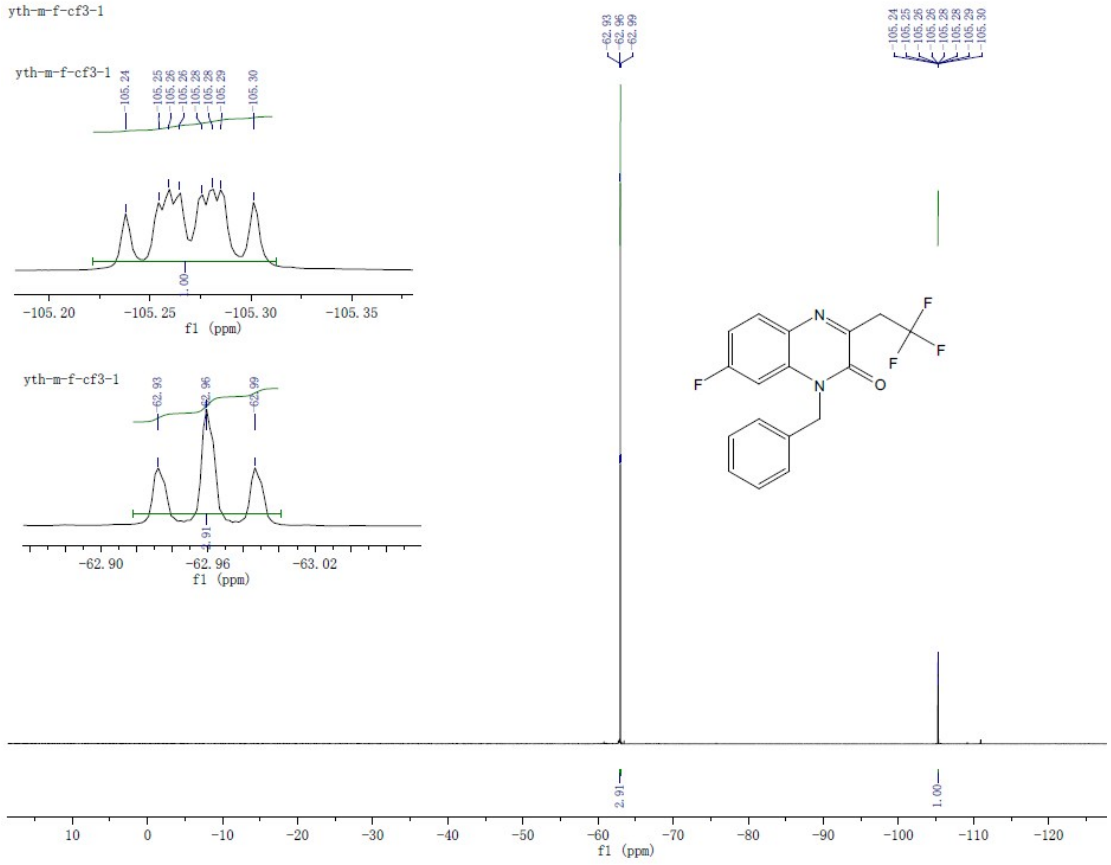

7.46
7.44
7.42
7.40
7.35
7.33
7.31
7.30
7.28
7.26
7.23
7.21
7.08
7.07
7.06
7.05
5.50
3.98
3.95
3.93
3.90
0.00
F
N
F
F
F
N
O
1.02
3.01
1.98
1.96
2.00
2.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

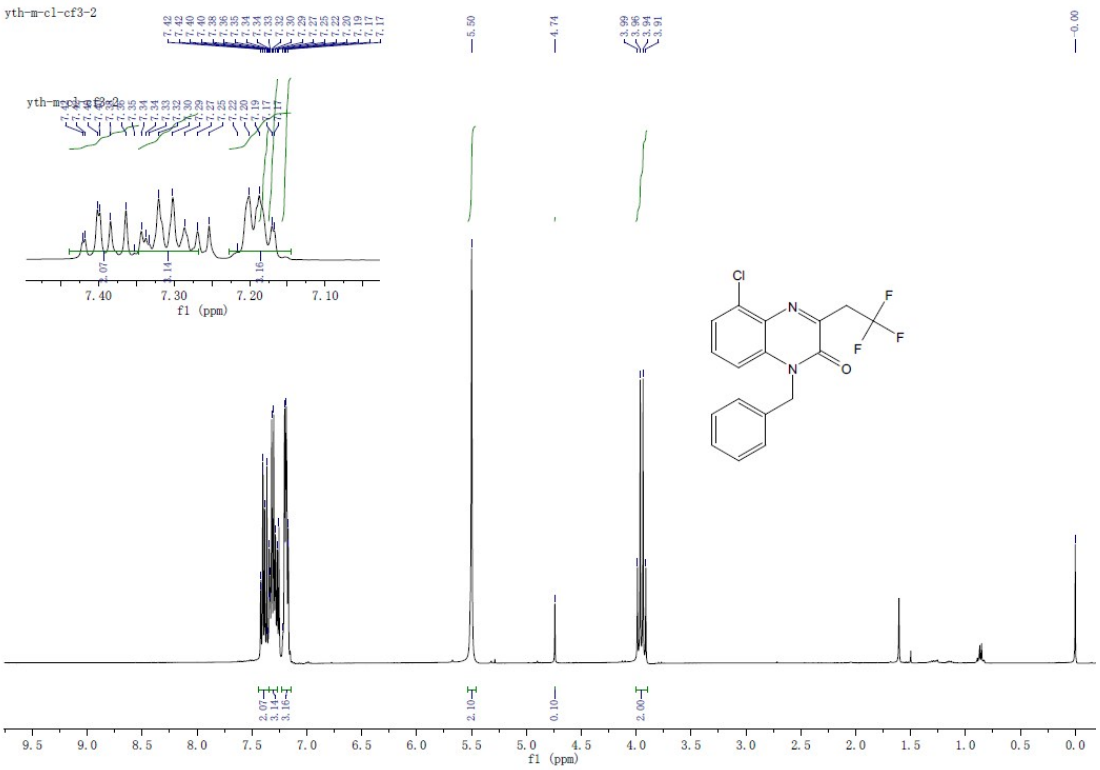

159.95
157.38
154.45
150.74
134.50
134.40
131.72
131.63
129.06
127.98
126.77
126.29
123.53
122.69
122.55
110.41
110.24
110.21
77.32
77.00
76.68
46.61
38.15
37.85
37.55
37.25
F
N
F
F
F
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

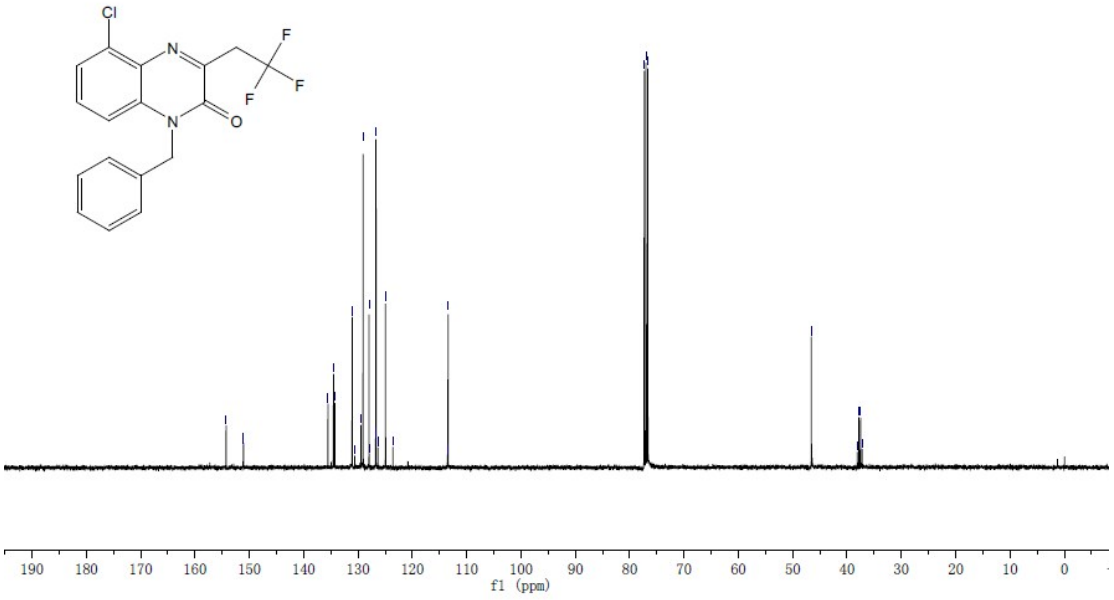

yth-m-f-cf3-2
yth-m-f-cf3-2
yth-m-f-cf3-2
f1 (ppm)
f1 (ppm)

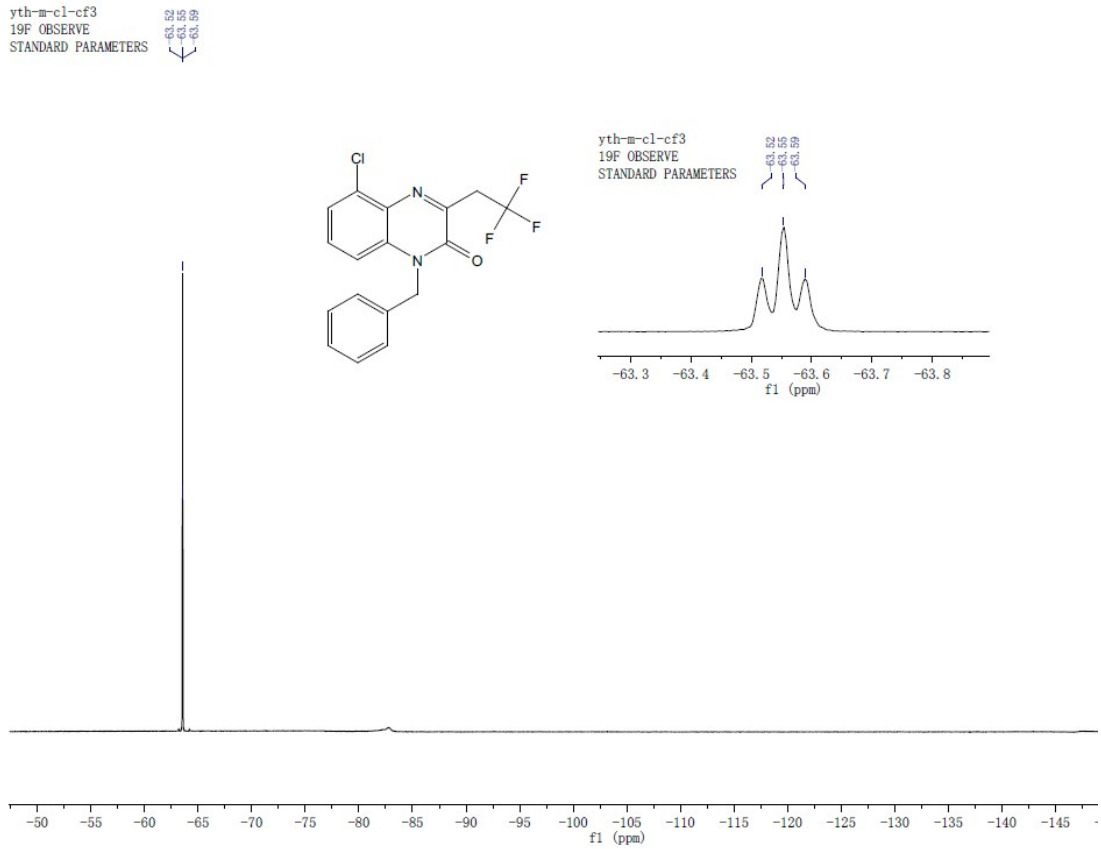

yth-m-cf3-1-cj
f1 (ppm)
f1 (ppm)

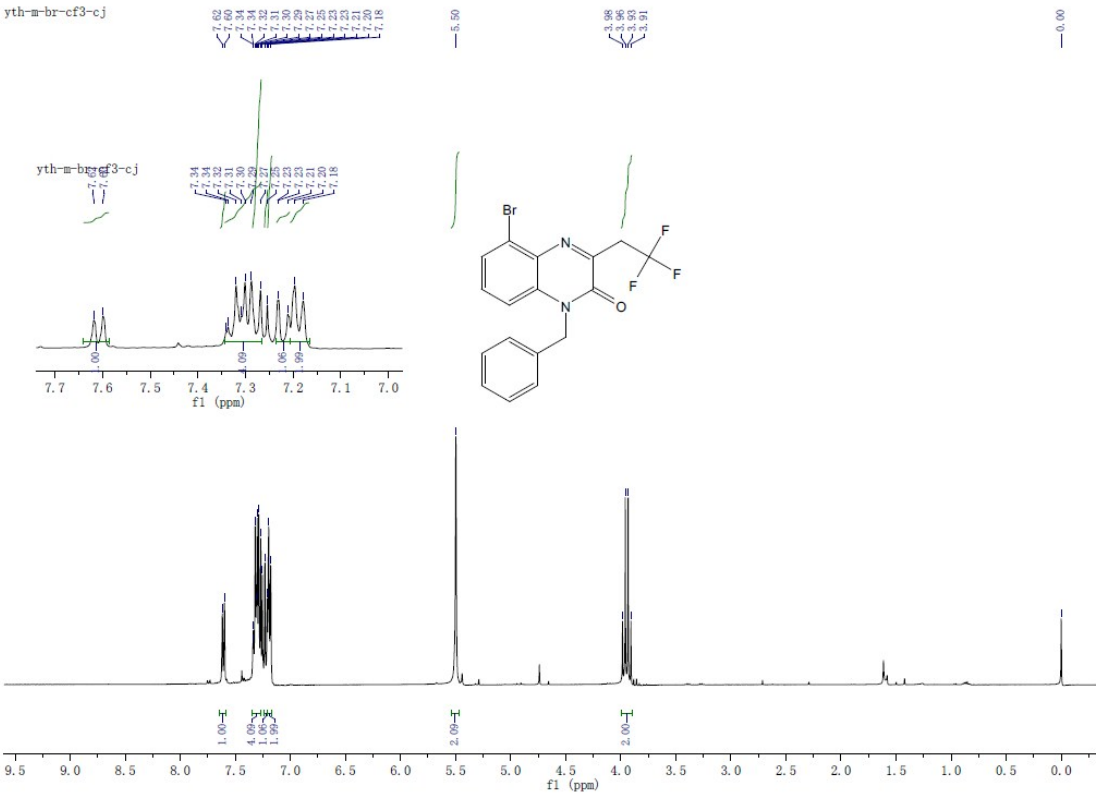

164.98
162.47
154.49
149.46
134.35
134.24
132.72
132.62
129.46
129.13
128.61
128.38
128.06
126.81
126.41
123.65
112.19
111.96
101.63
101.35
77.32
77.00
76.68
46.51
37.84
37.54
37.24
36.94
F
F
F
N
N
O
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


yth-m-f-cf3-1
yth-m-f-cf3-1
105.24
105.25
105.26
105.26
105.28
105.28
105.29
105.30
1.00
-105.20
-105.25
-105.30
-105.35
f1 (ppm)
yth-m-f-cf3-1
62.93
62.96
62.99
2.91
-62.90
-62.96
-63.02
f1 (ppm)
62.93
62.96
62.99
105.24
105.25
105.26
105.26
105.28
105.28
105.29
105.30
F
F
F
N
N
O
F
2.91
1.00
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120
f1 (ppm)

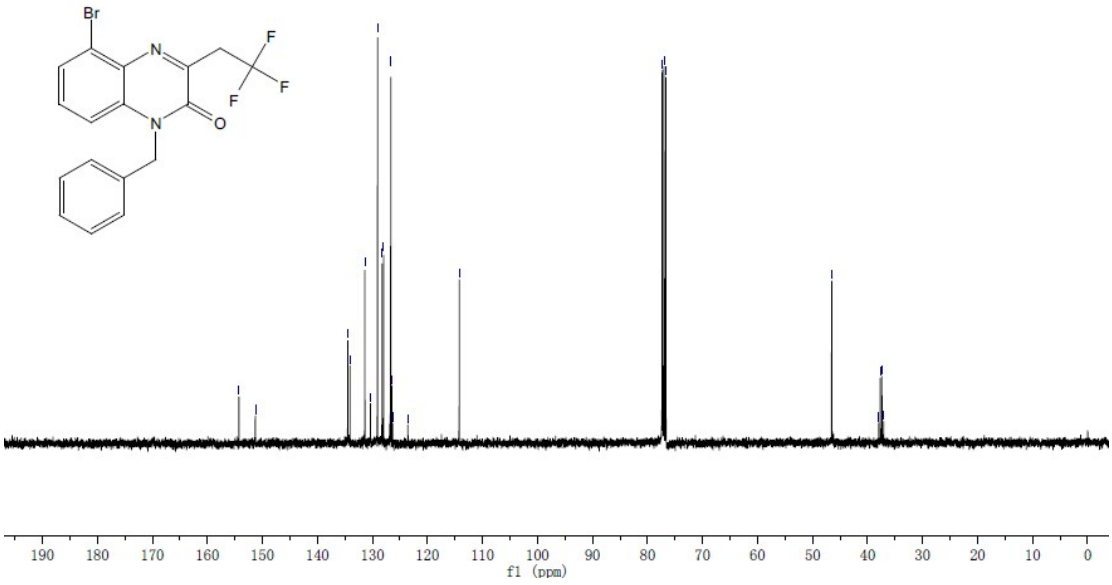

yth-m-cl-cf3-2
f1 (ppm)

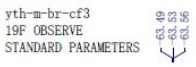

f1 (ppm)

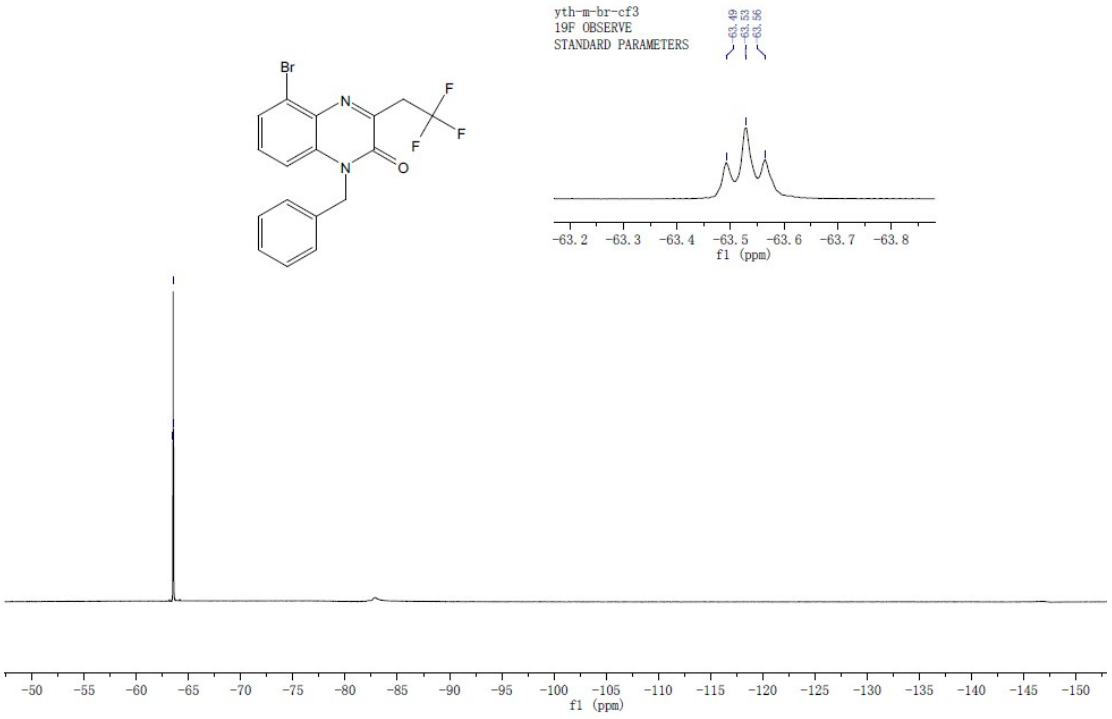

yth-m-cl-cf3
19F OBSERVE
STANDARD PARAMETERS
63.52
63.55
63.59
Cl
N
F
F
F
N
O
yth-m-cl-cf3
19F OBSERVE
STANDARD PARAMETERS
63.52
63.55
63.59
-63.3 -63.4 -63.5 -63.6 -63.7 -63.8
f1 (ppm)
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
f1 (ppm)

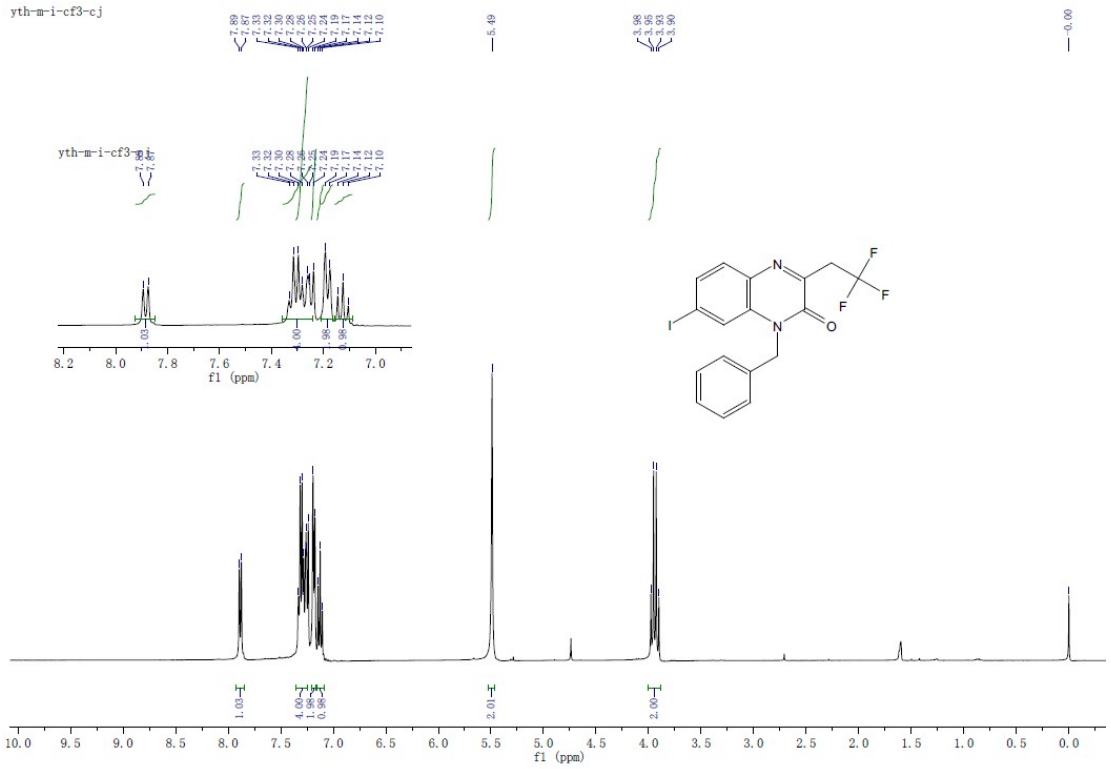

yth-m-br-cf3-cj
7.62
7.60
7.34
7.34
7.32
7.31
7.30
7.29
7.27
7.25
7.23
7.23
7.21
7.20
7.18
5.50
3.98
3.96
3.93
3.91
0.00
yth-m-br-cf3-cj
Br
N
F
F
F
N
O
7.7 7.6 7.5 7.4 7.3 7.2 7.1 7.0
f1 (ppm)
1.00
4.09
1.06
1.99
2.09
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

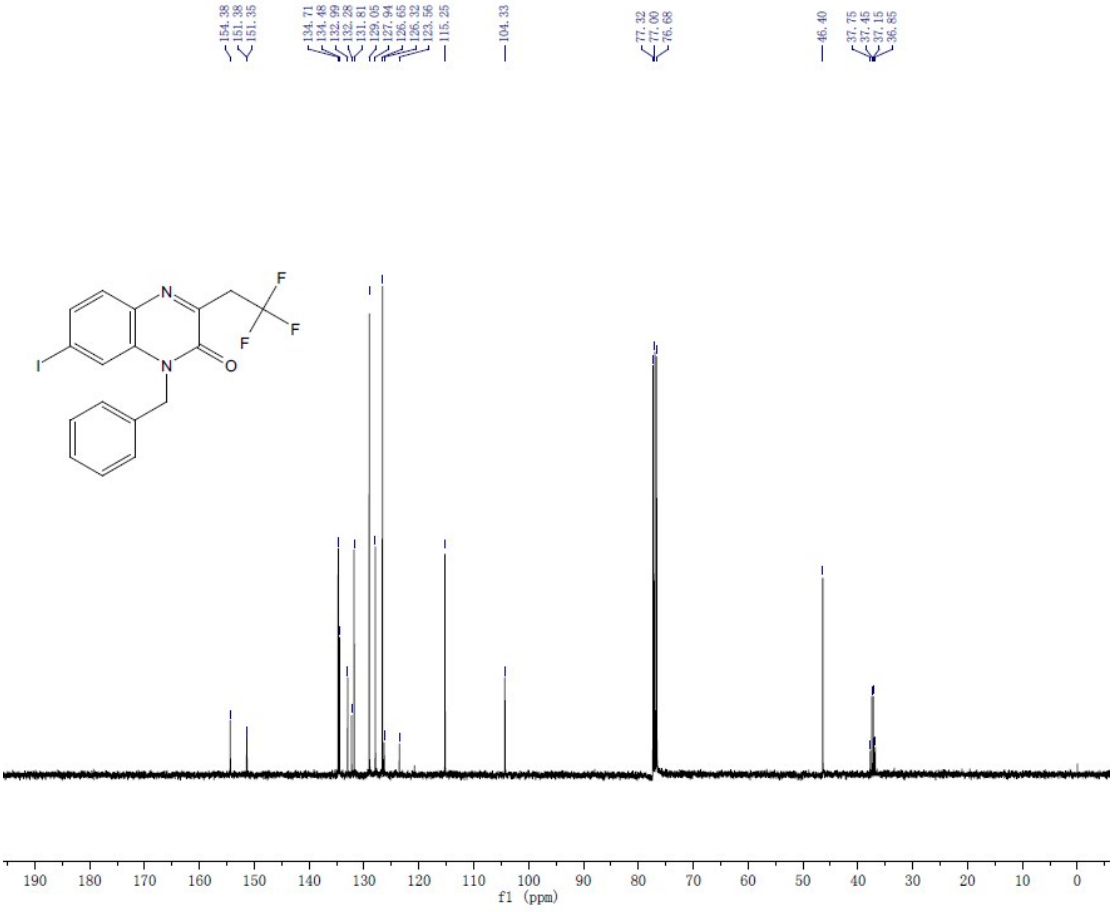

154.27
151.26
134.48
134.06
131.37
130.36
129.07
128.24
127.97
125.67
125.46
126.31
123.55
114.20
77.32
77.00
76.68
46.52
37.99
37.69
37.39
37.09

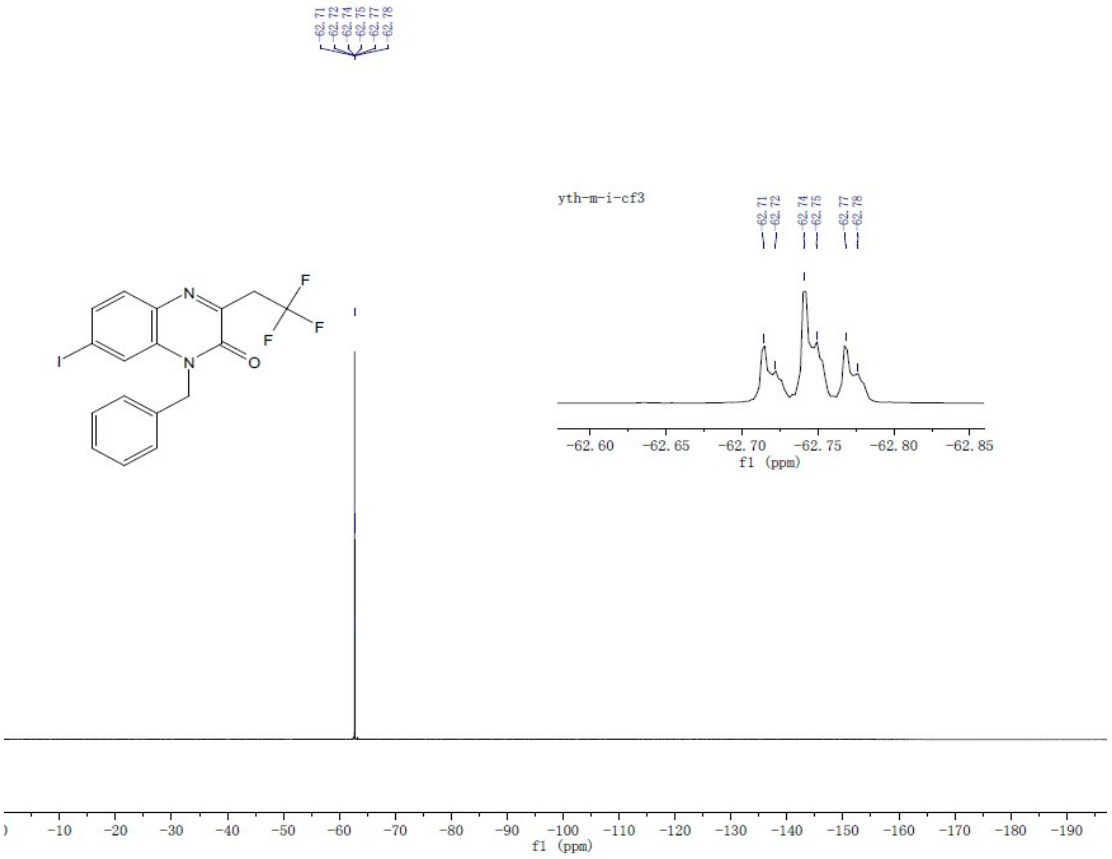

Br
N
F
F
F
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

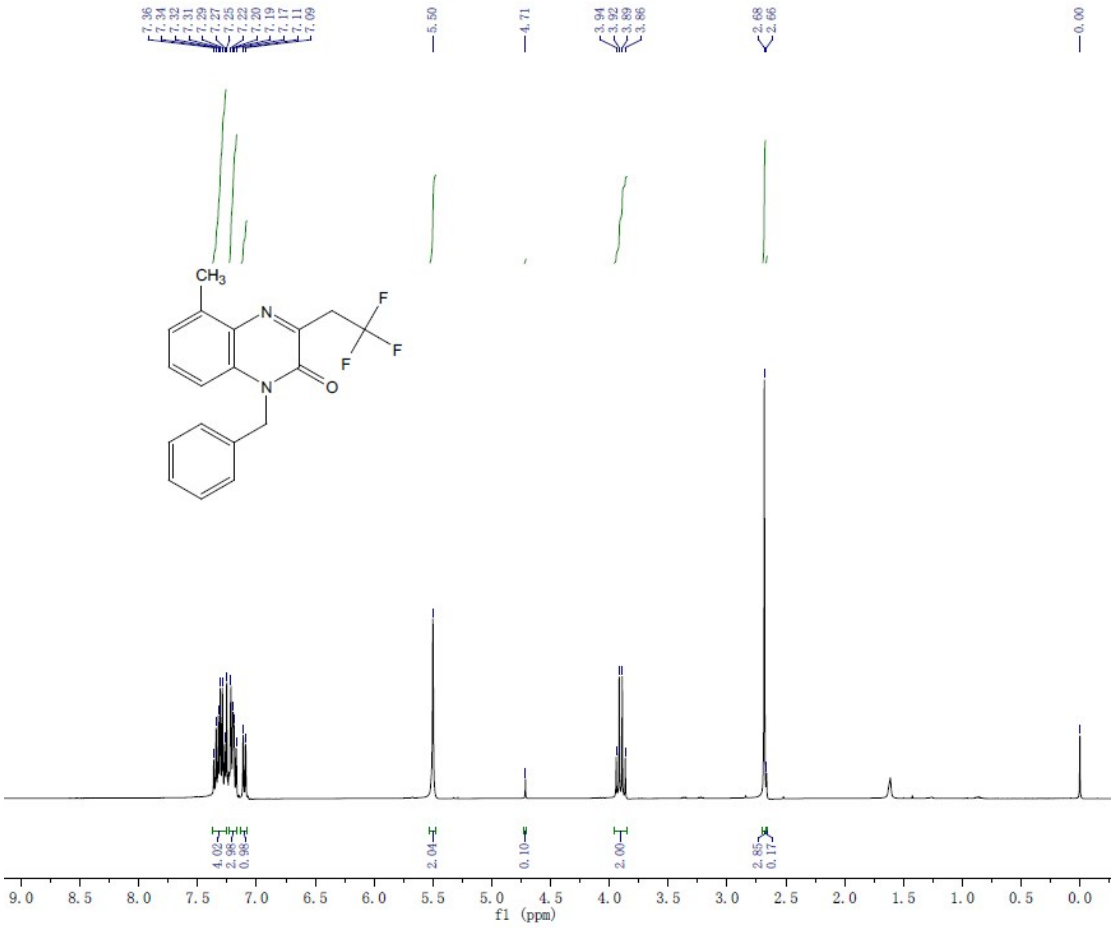

yth-m-br-cf3
19F OBSERVE
STANDARD PARAMETERS
63.49
63.53
63.56

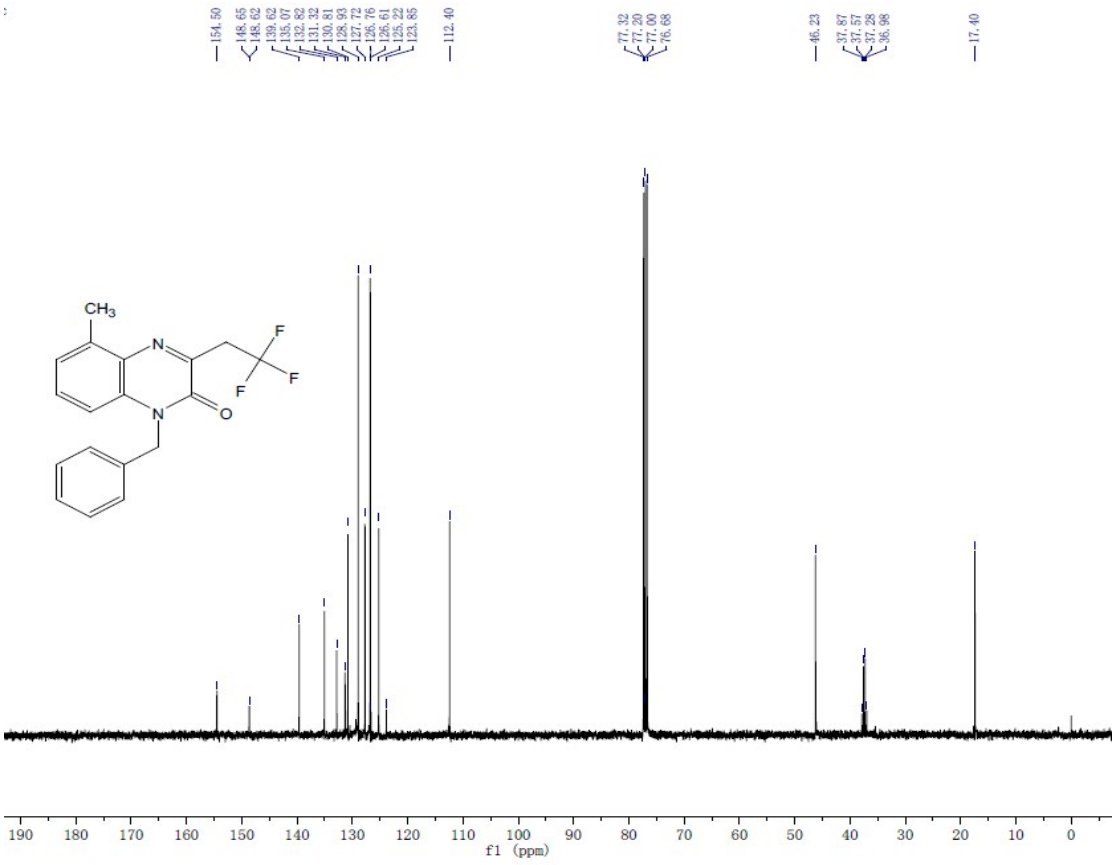

Br
N
F
F
F
N
O
yth-m-br-cf3
19F OBSERVE
STANDARD PARAMETERS
63.49
63.53
63.56
-63.2 -63.3 -63.4 -63.5 -63.6 -63.7 -63.8
f1 (ppm)
-50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -150
f1 (ppm)


yth-m-i-cf3-cj
f1 (ppm)

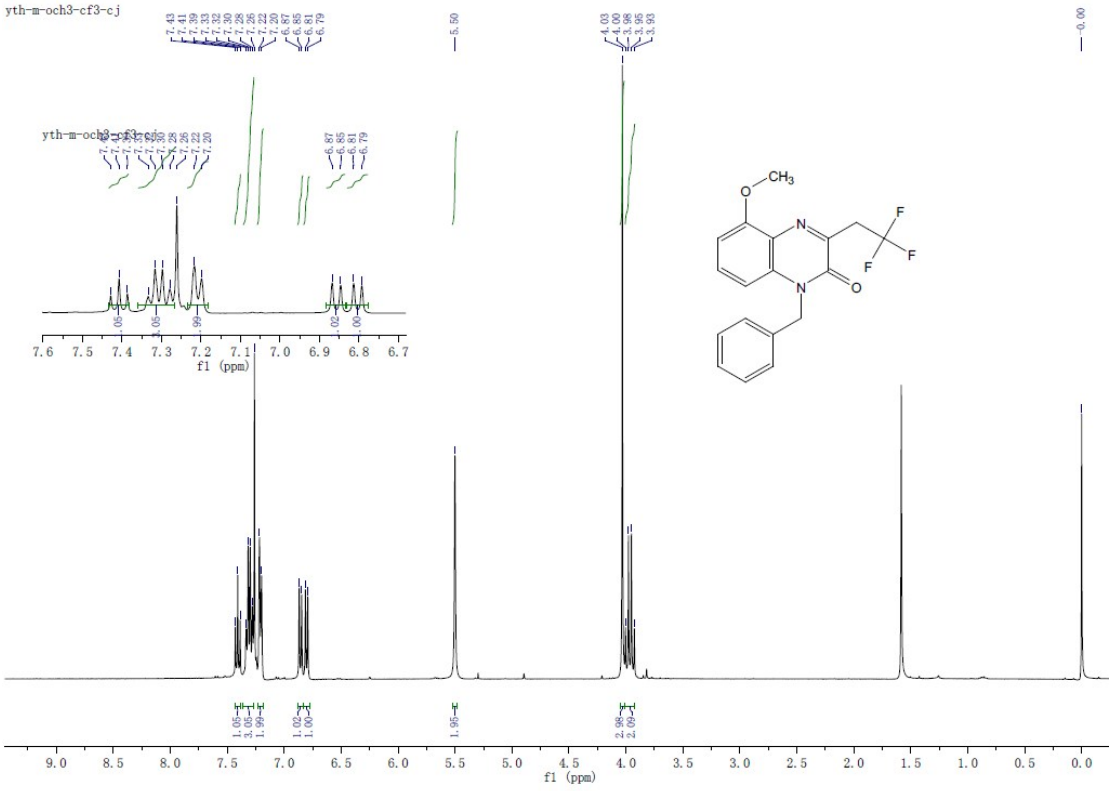

f1 (ppm)

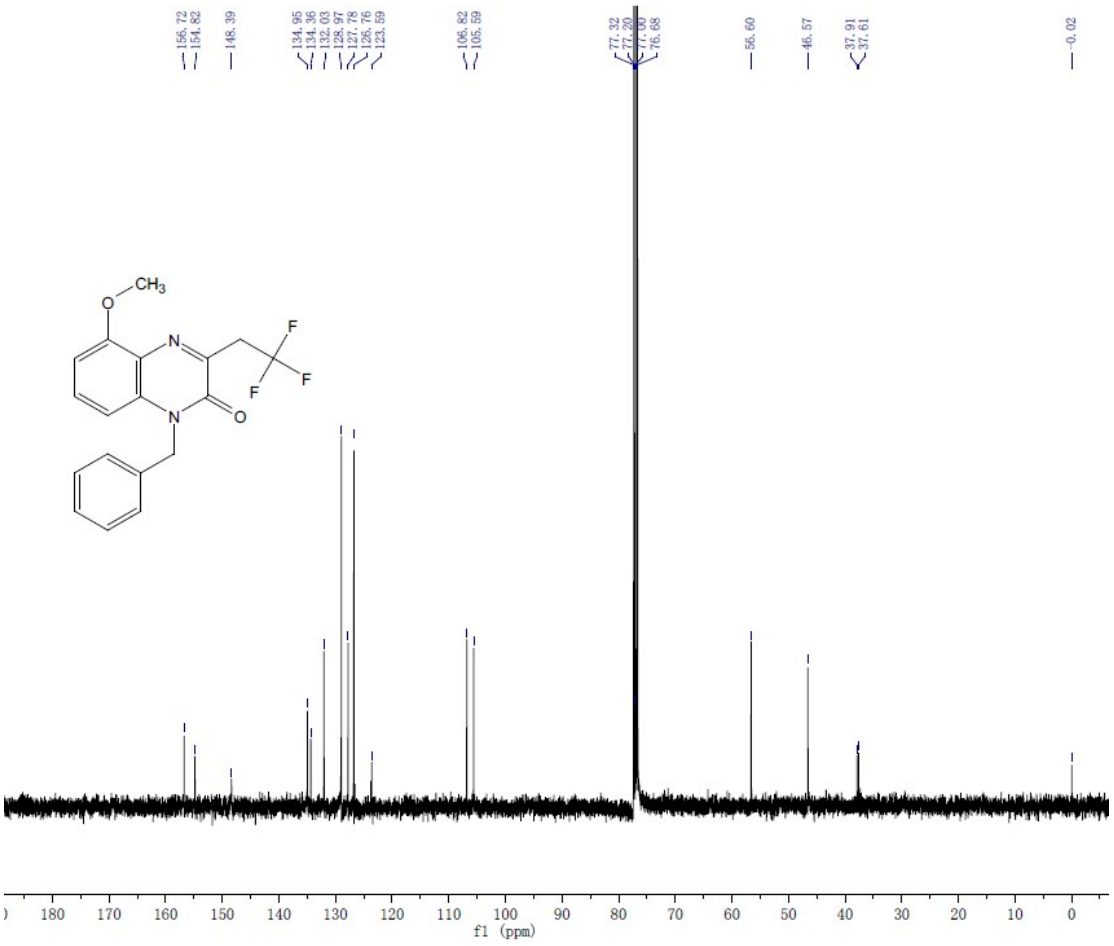

yth-m-i-cf3
f1 (ppm)

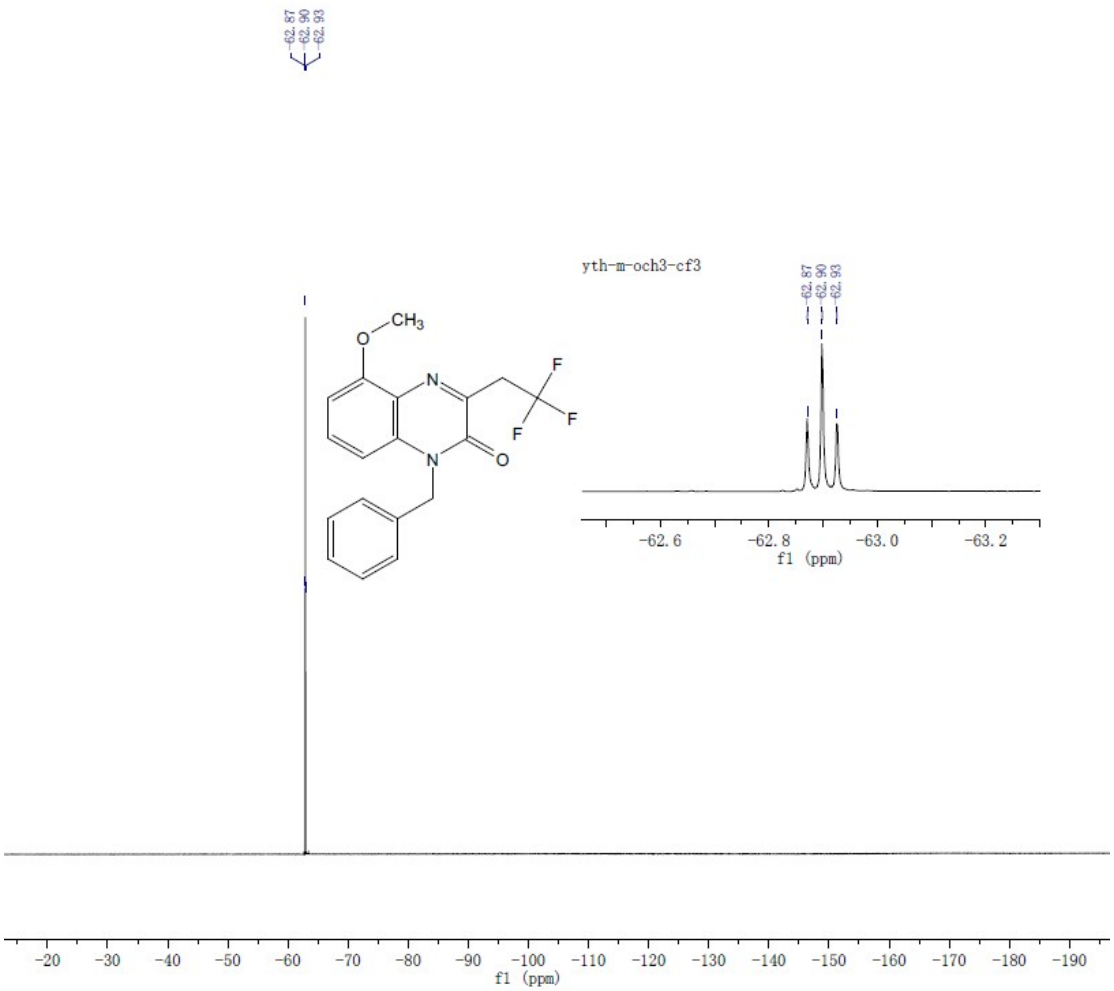

f1 (ppm)

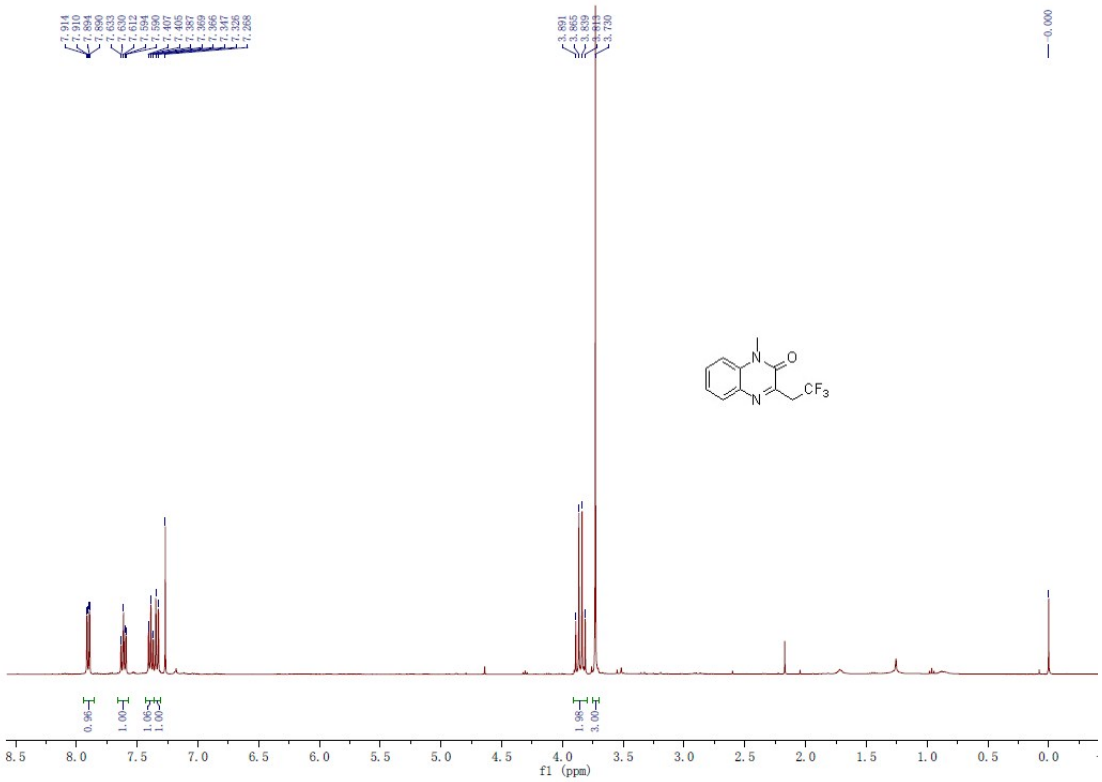

154.80
148.65
148.62
139.62
135.07
132.82
131.32
130.81
128.93
127.72
126.76
126.61
125.22
123.85
112.40
77.32
77.20
77.00
76.68
46.23
37.87
37.57
37.28
36.98
17.40
CH3
N
F
F
F
N
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

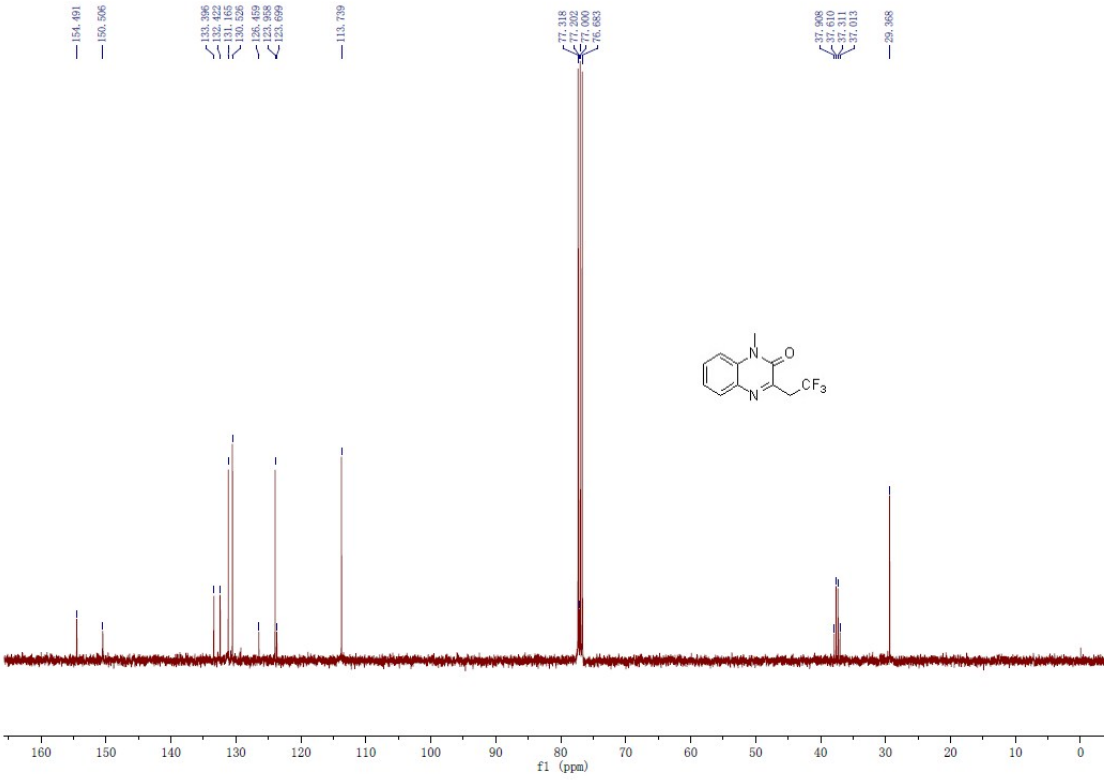

-62.98
-63.01
-63.04
CH3
N
F
F
F
N
O
yth-m-ch3-cf3
-62.98
-63.01
-63.04
-62.90 -62.95 -63.00 -63.05 -63.10 -63.15
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

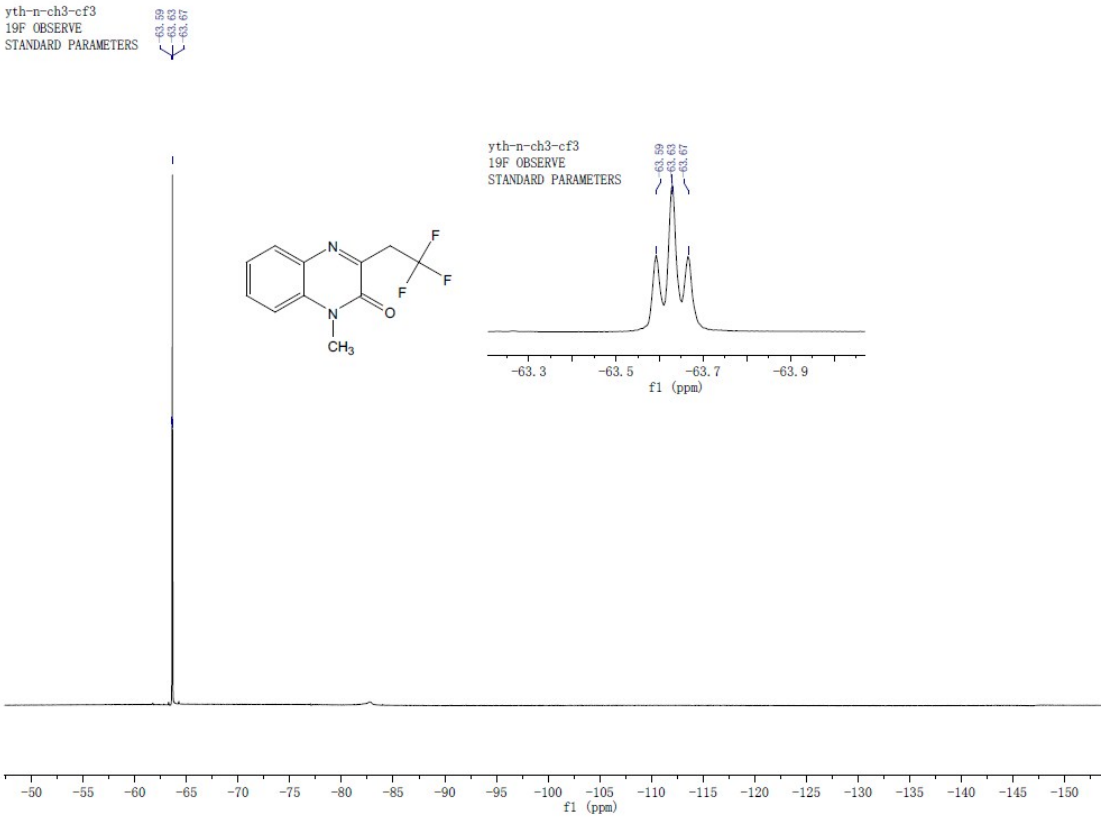

yth-m-och3-cf3-cj
f1 (ppm)

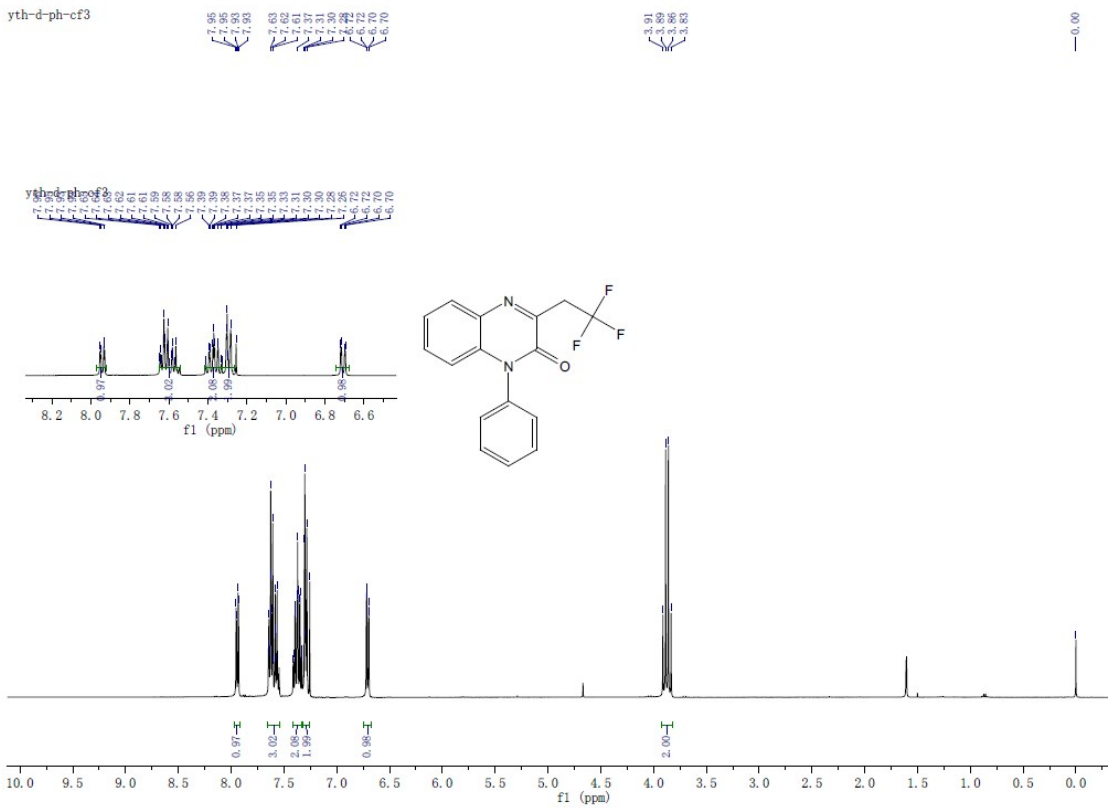

f1 (ppm)

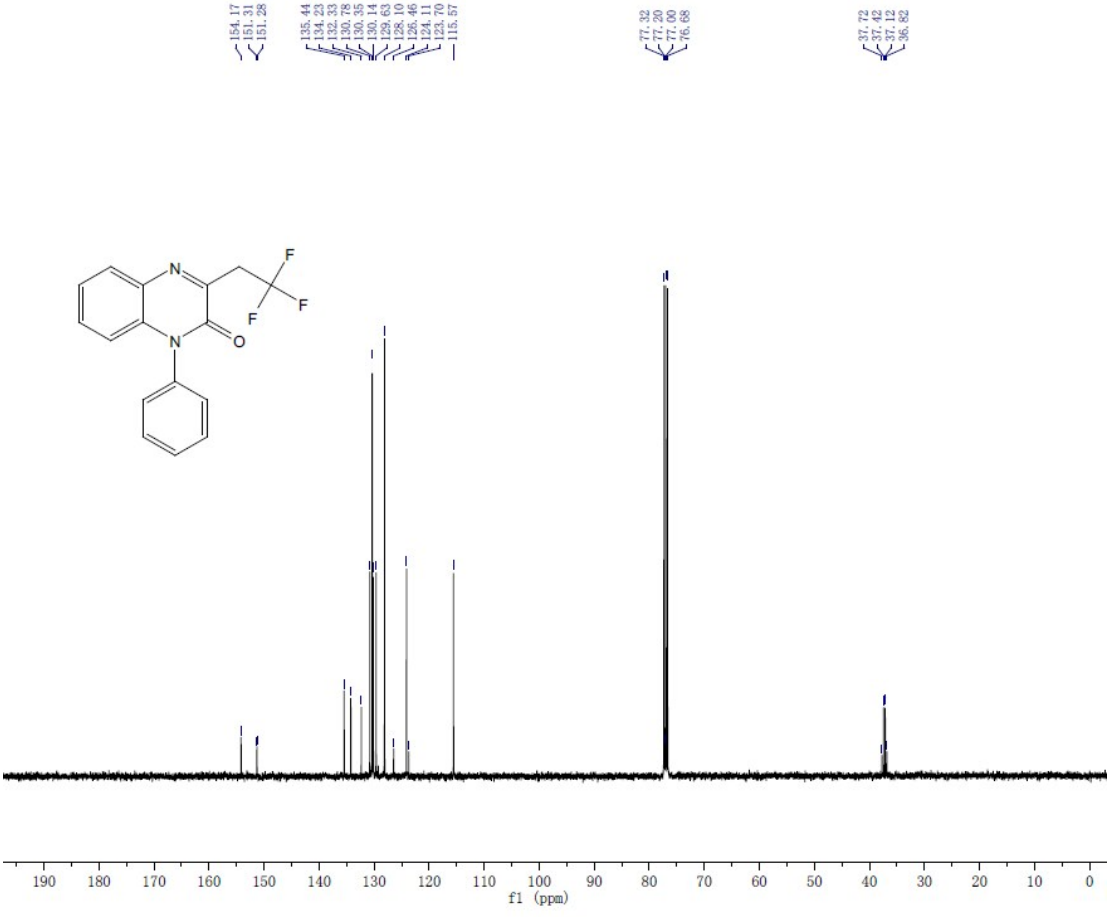

-62.87
-62.90
-62.93
yth-m-och3-cf3
-62.87
-62.90
-62.93
-62.6
-62.8
-63.0
-63.2
f1 (ppm)
O
CH3
N
F
F
F
N
O
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
f1 (ppm)

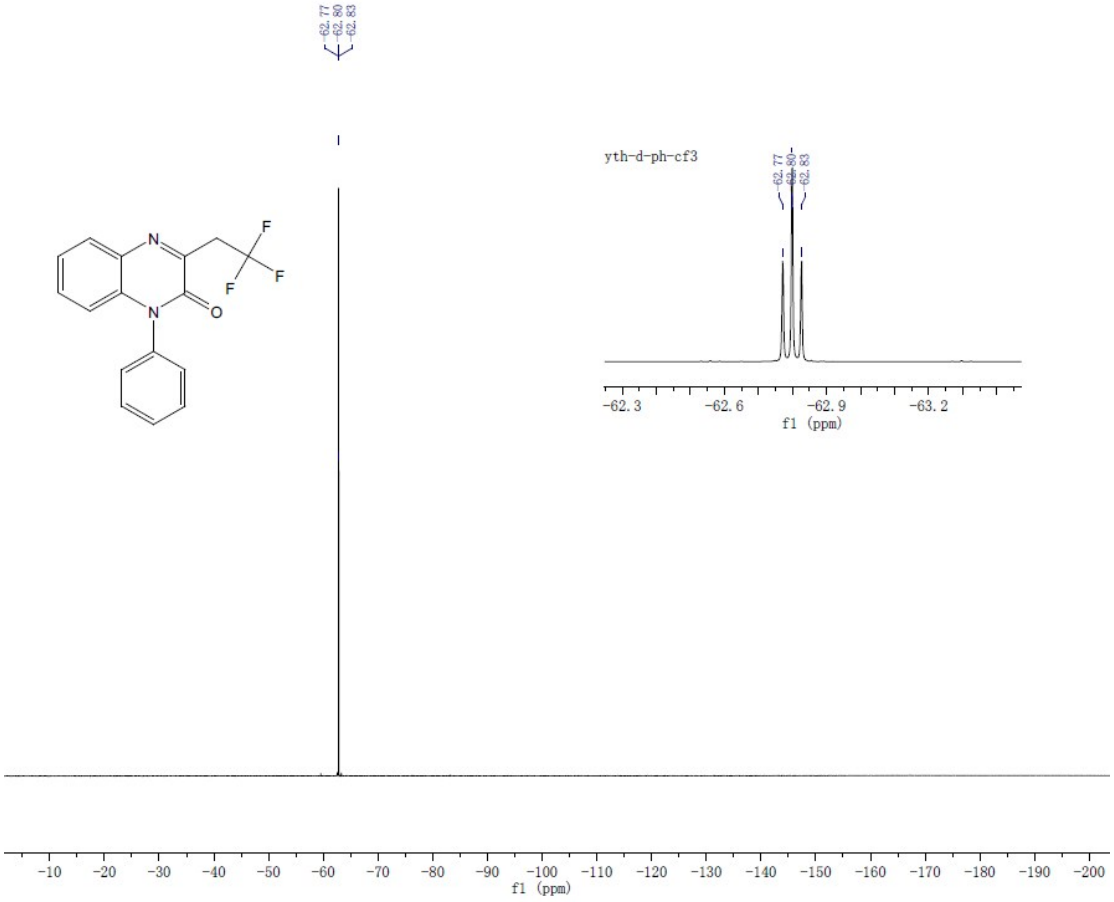

7.914
7.910
7.894
7.890
7.633
7.630
7.612
7.594
7.589
7.407
7.405
7.387
7.369
7.365
7.347
7.326
7.268
3.891
3.885
3.839
3.813
3.730
0.000
N
O
N
CF3
0.96
1.00
1.06
1.00
1.98
3.00
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

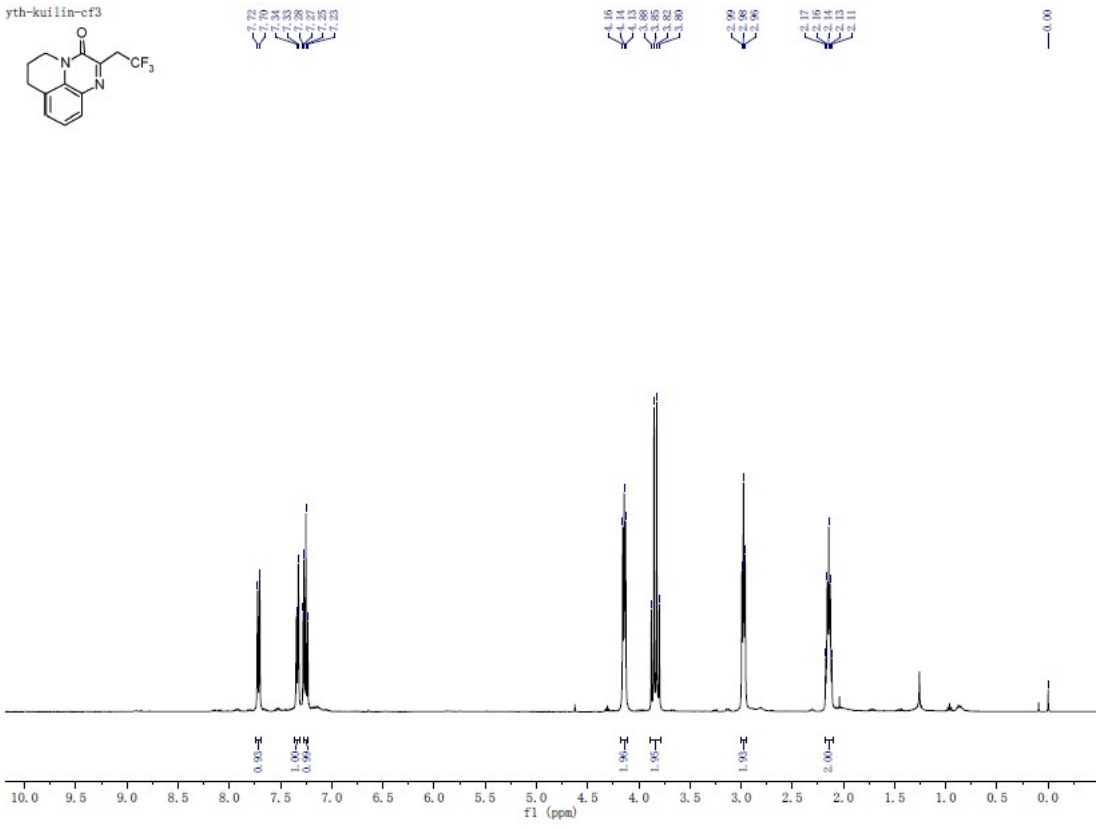

154.491
150.506
133.306
132.422
131.165
130.526
126.459
123.958
123.699
113.739
77.318
77.202
77.000
76.683
37.908
37.610
37.311
37.013
29.368
f1 (ppm)

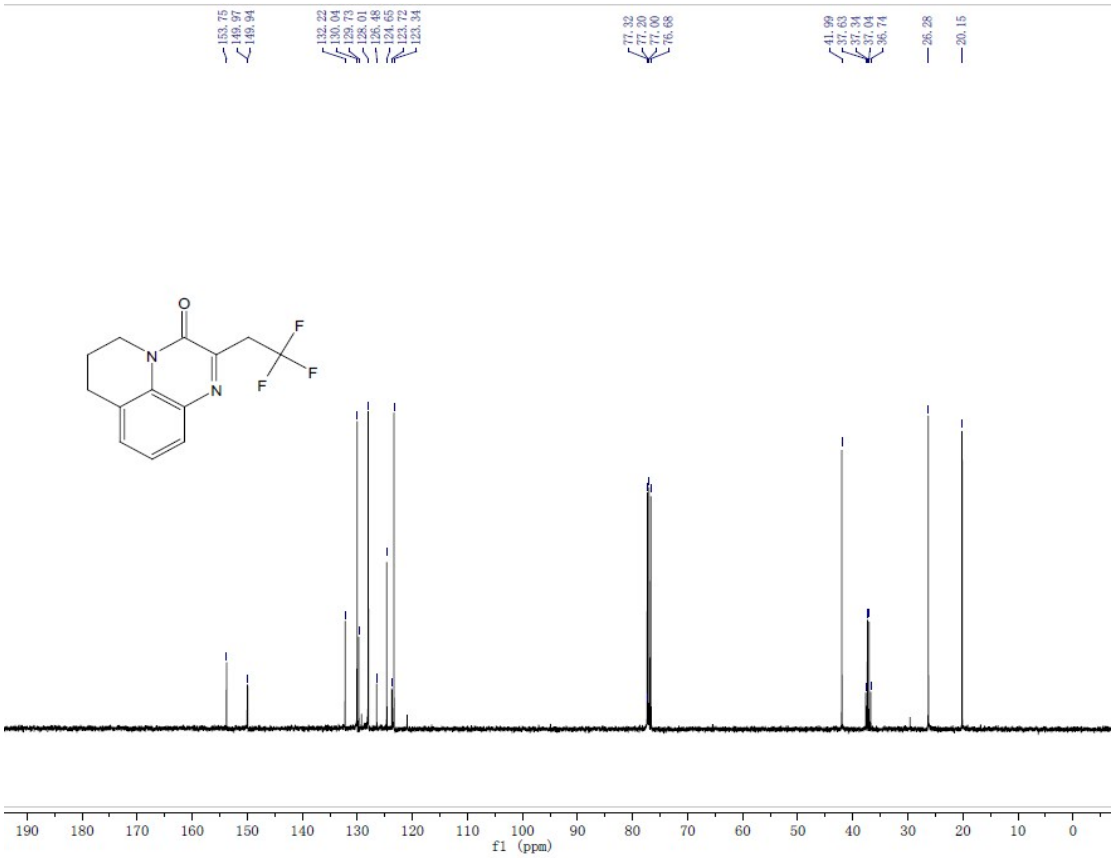

yth-n-ch3-cf3
19F OBSERVE
STANDARD PARAMETERS
63.59
63.63
63.67
f1 (ppm)

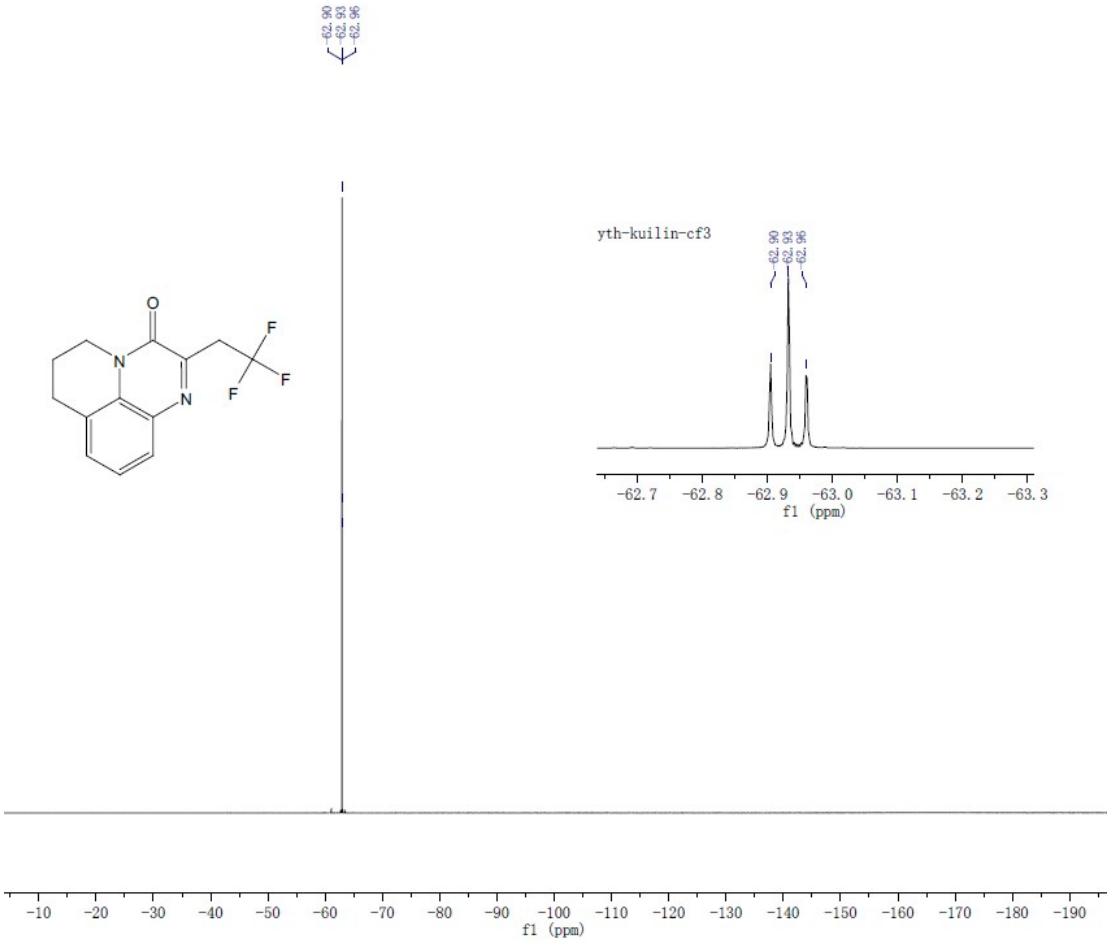

yth-d-ph-cf3
f1 (ppm)

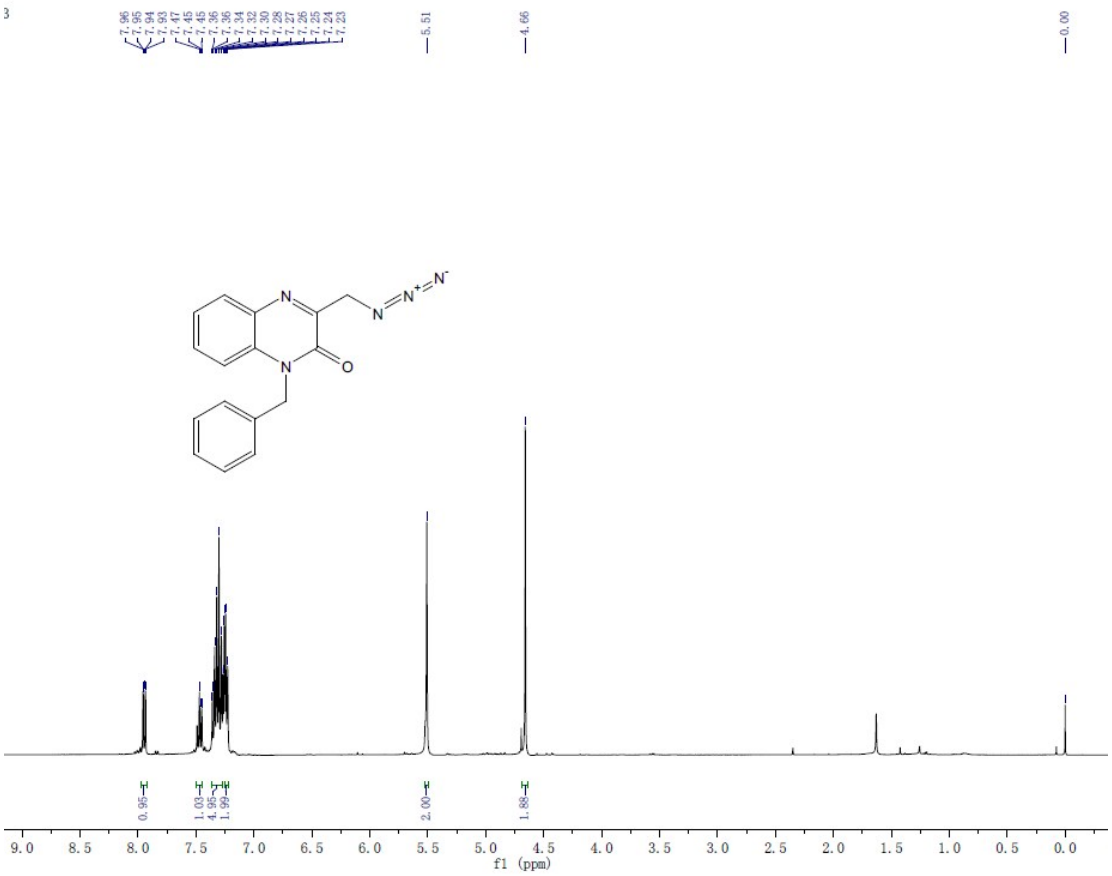

f1 (ppm)

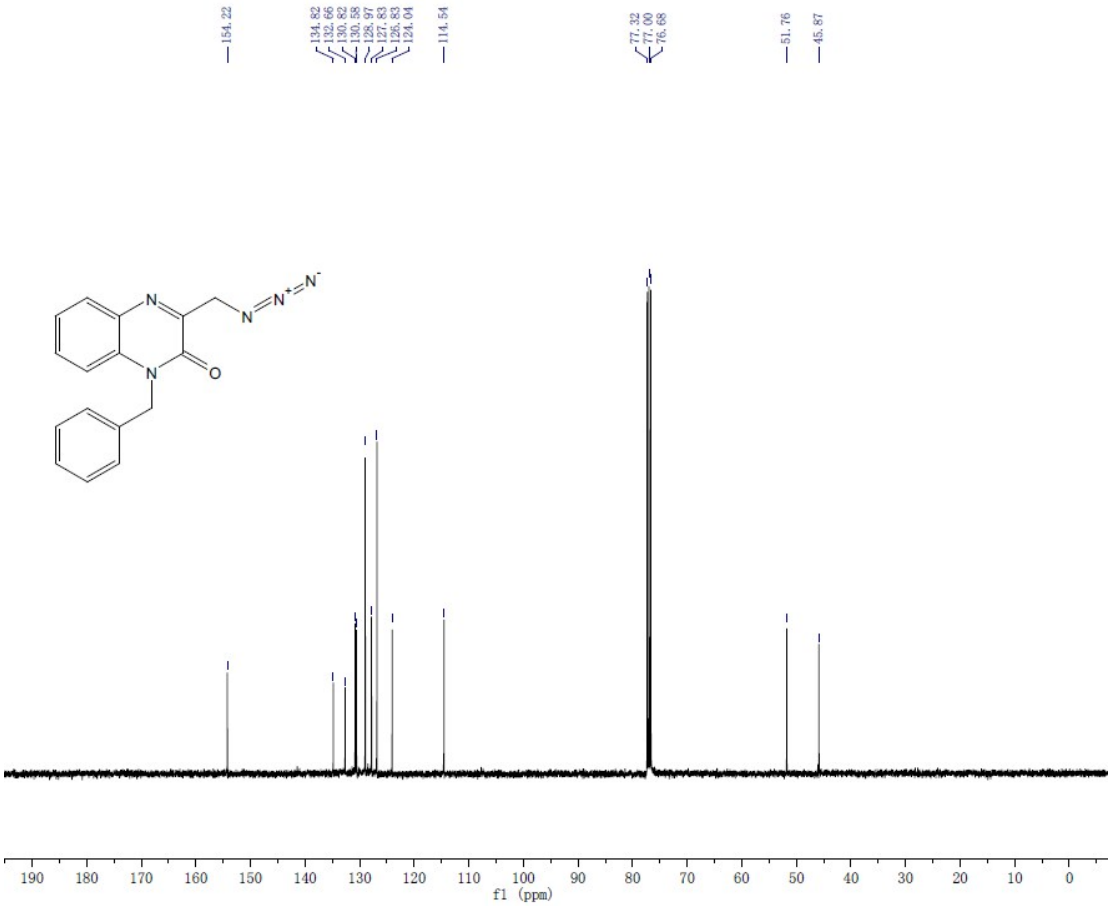

-62.77
-62.80
-62.83
yth-d-ph-cf3
F
F
F
N
N
O
-62.3
-62.6
-62.9
-63.2
f1 (ppm)
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

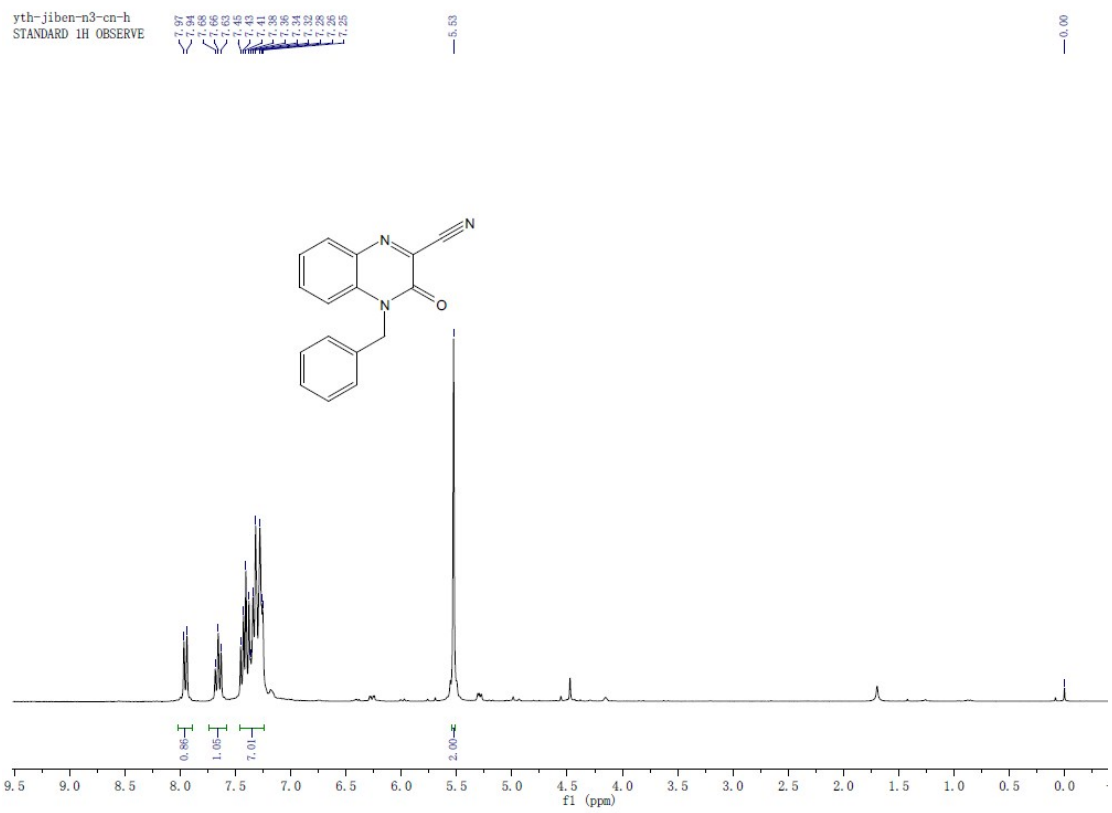

yth-kuilin-cf3
O
N
N
CF3
7.72
7.70
7.34
7.33
7.28
7.27
7.25
7.23
4.16
4.14
4.13
3.88
3.85
3.82
3.80
2.99
2.98
2.96
2.17
2.15
2.14
2.13
2.11
0.00
0.93
1.00
0.99
1.96
1.95
1.93
2.00
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

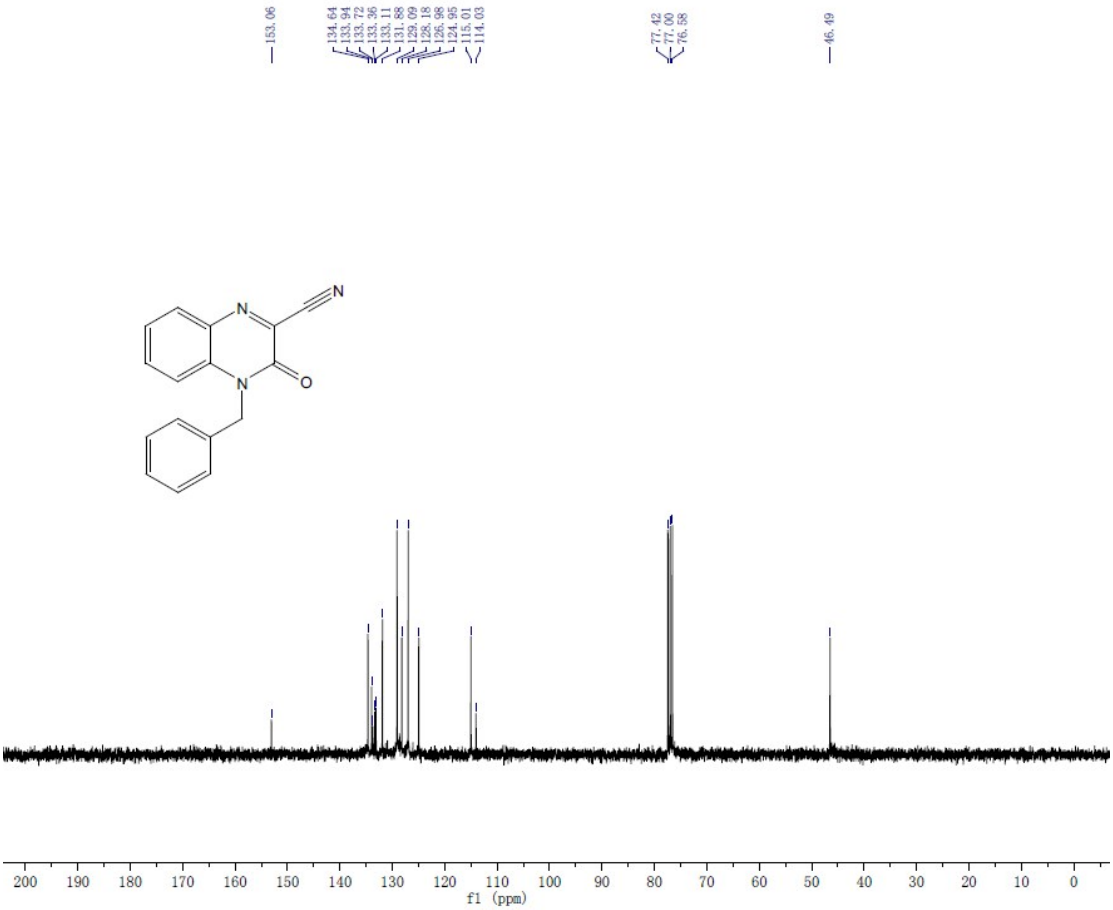

153.75
149.97
149.94
132.22
130.04
129.73
128.01
126.48
124.65
123.72
123.34
77.32
77.20
77.00
76.68
41.99
37.63
37.34
37.04
36.74
26.28
20.15
O
N
N
F
F
F
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

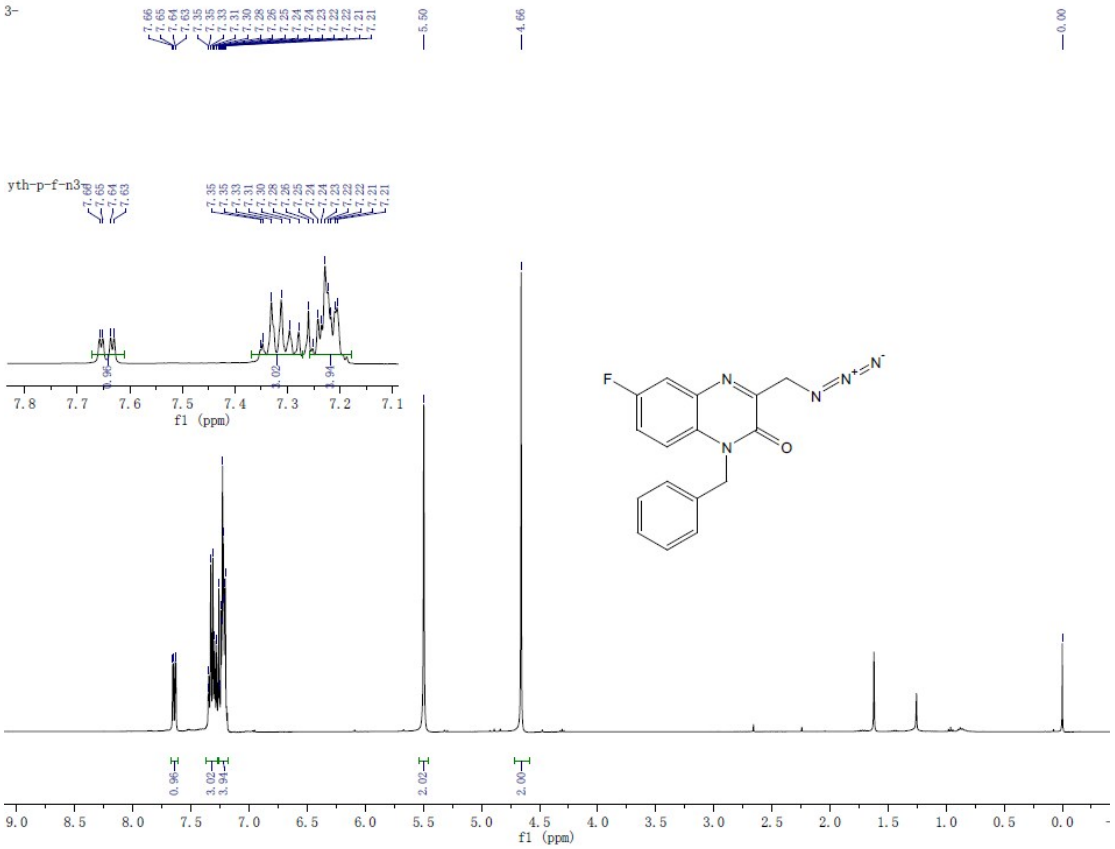

62.90
62.93
62.96
O
N
N
F
F
F
yth-kuilin-cf3
62.90
62.93
62.96
-62.7 -62.8 -62.9 -63.0 -63.1 -63.2 -63.3
f1 (ppm)
-10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190
f1 (ppm)

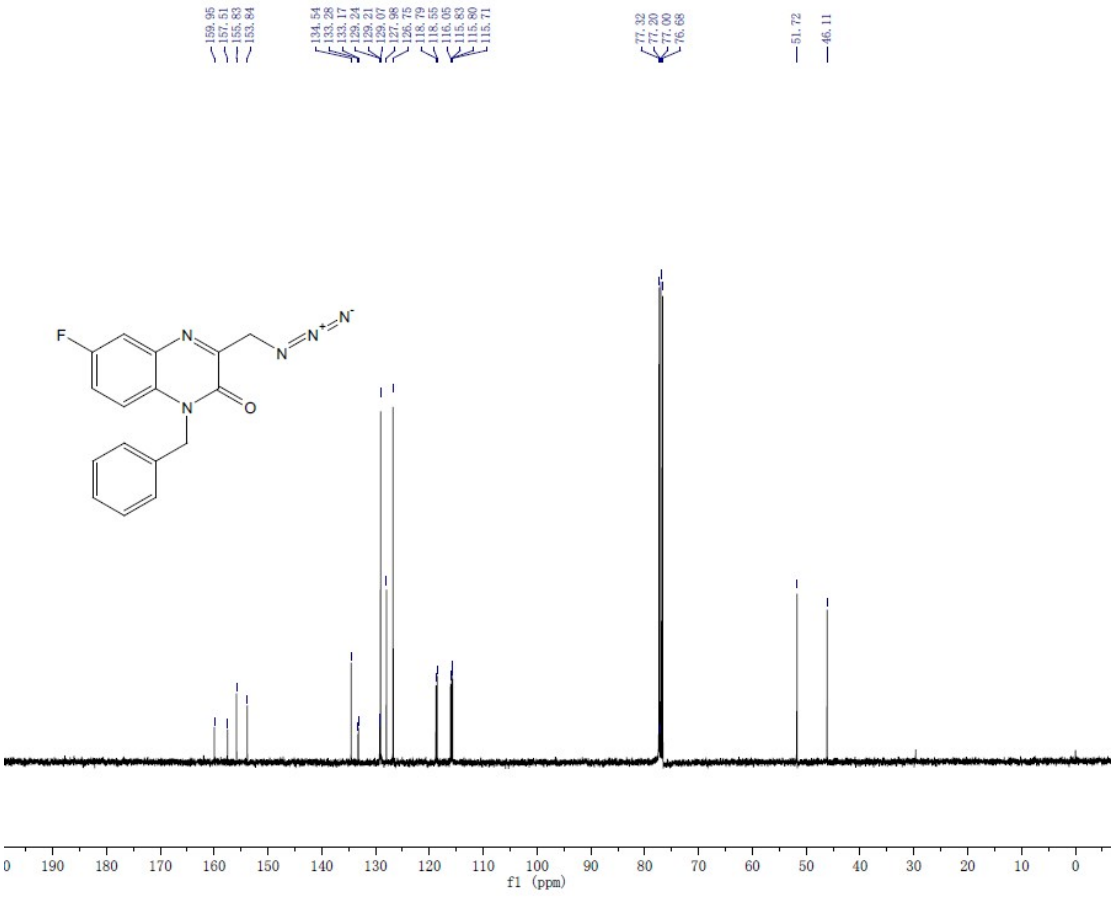

7.96
7.95
7.94
7.93
7.47
7.45
7.45
7.36
7.36
7.34
7.32
7.30
7.28
7.27
7.26
7.25
7.24
7.23
5.51
4.66
0.00
0.95
1.03
4.95
1.99
2.00
1.88
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

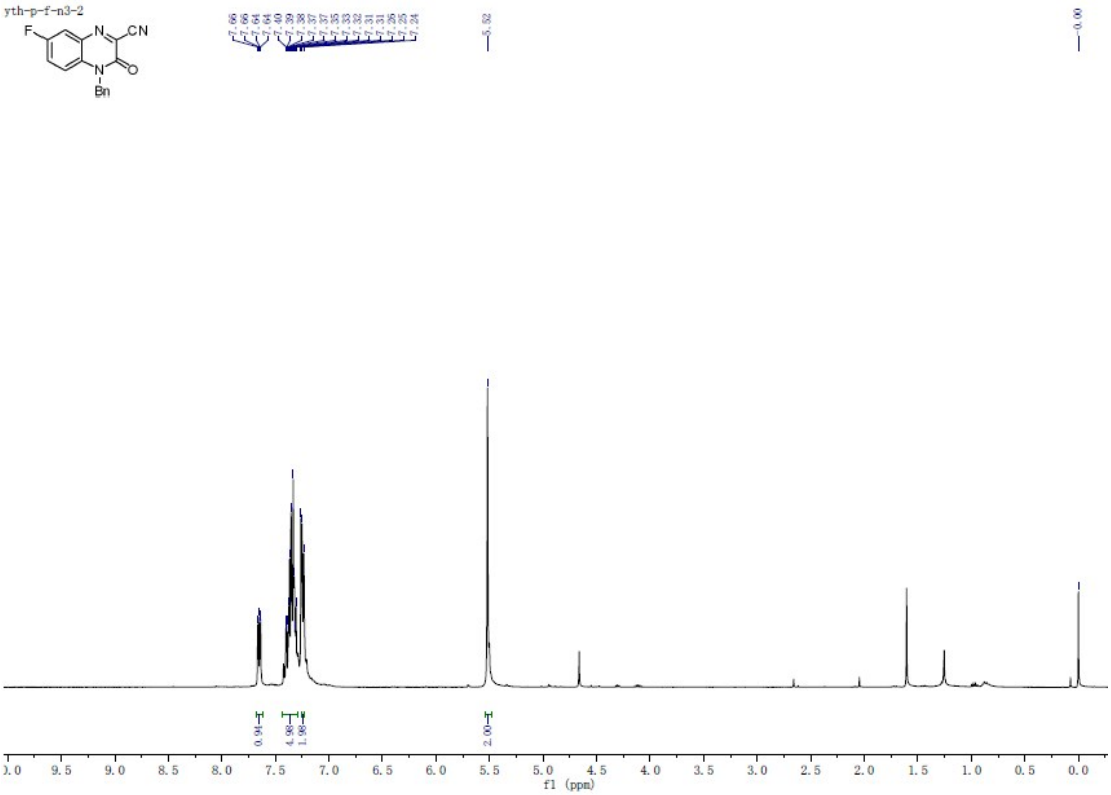

154.22
134.82
132.66
130.82
130.58
128.97
127.83
126.83
124.04
114.54
77.32
77.00
76.68
51.76
45.87
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

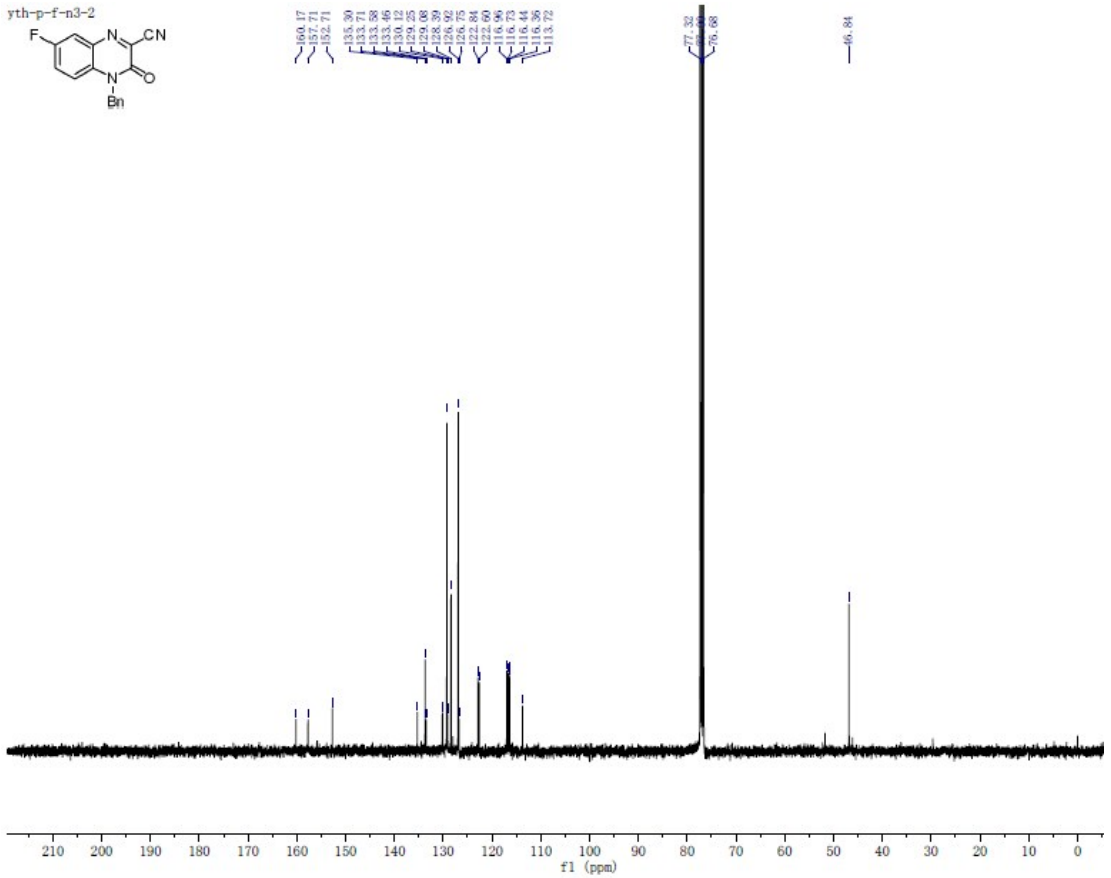

yth-jiben-n3-cn-h
STANDARD 1H OBSERVE
7.97
7.94
7.68
7.66
7.63
7.45
7.43
7.41
7.38
7.36
7.34
7.32
7.28
7.26
7.25
5.53
0.00
N
N
O
N
0.86
1.05
7.01
2.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

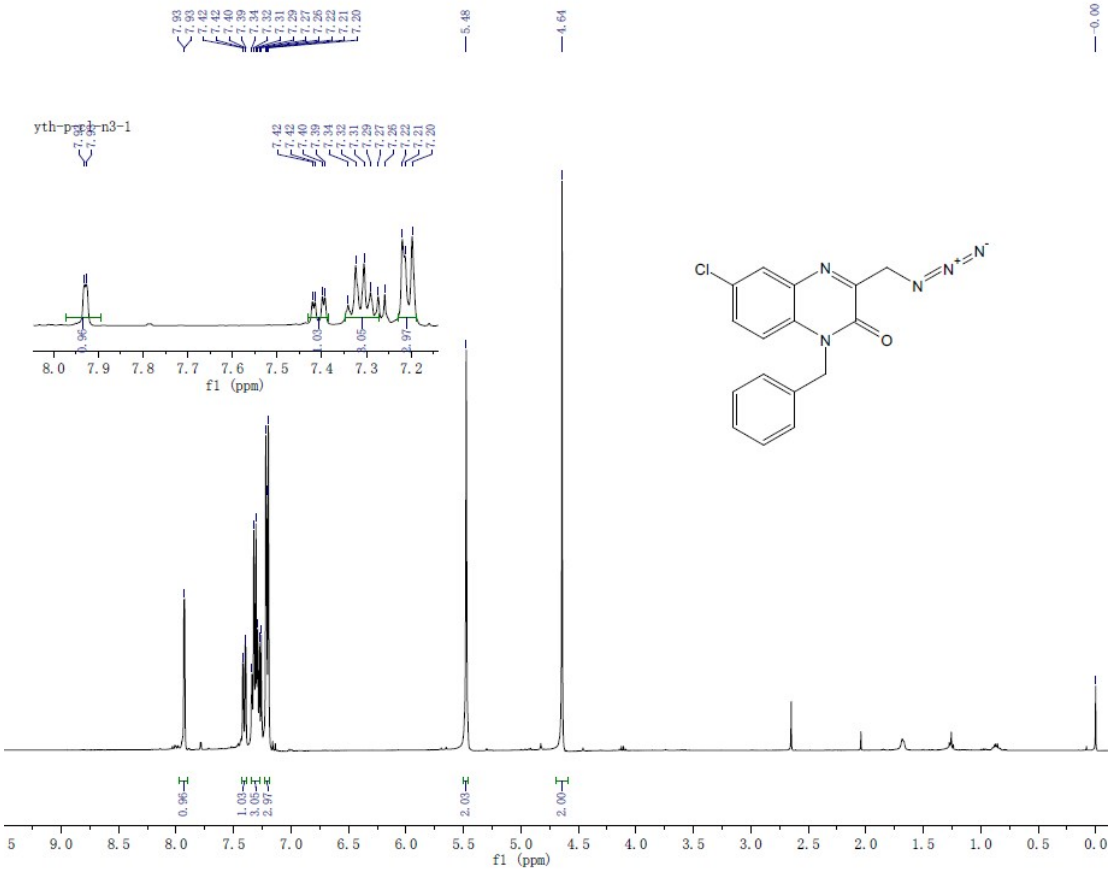

153.06
134.64
133.94
133.72
133.36
133.11
131.88
129.09
128.18
126.98
124.95
115.01
114.03
77.42
77.00
76.58
46.49
N
N
O
N
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

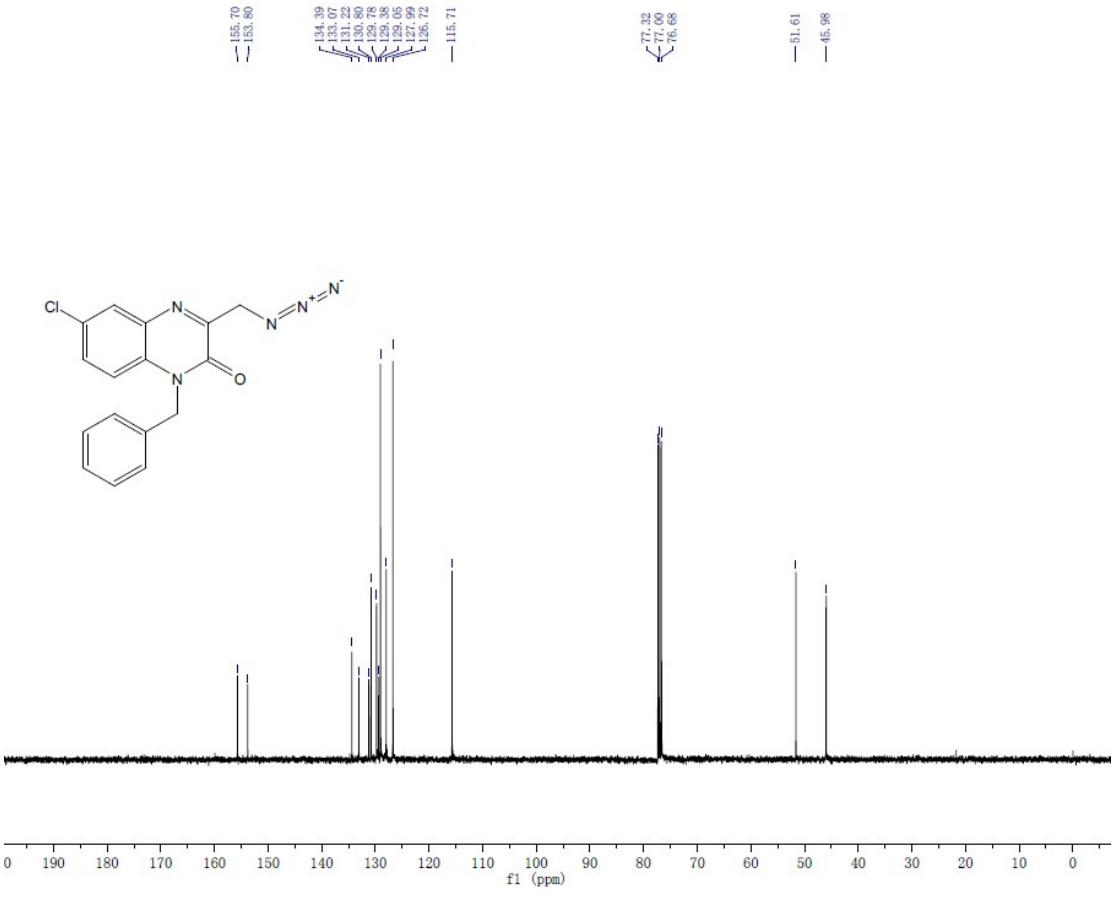

3-
yth-p-f-n3
f1 (ppm)

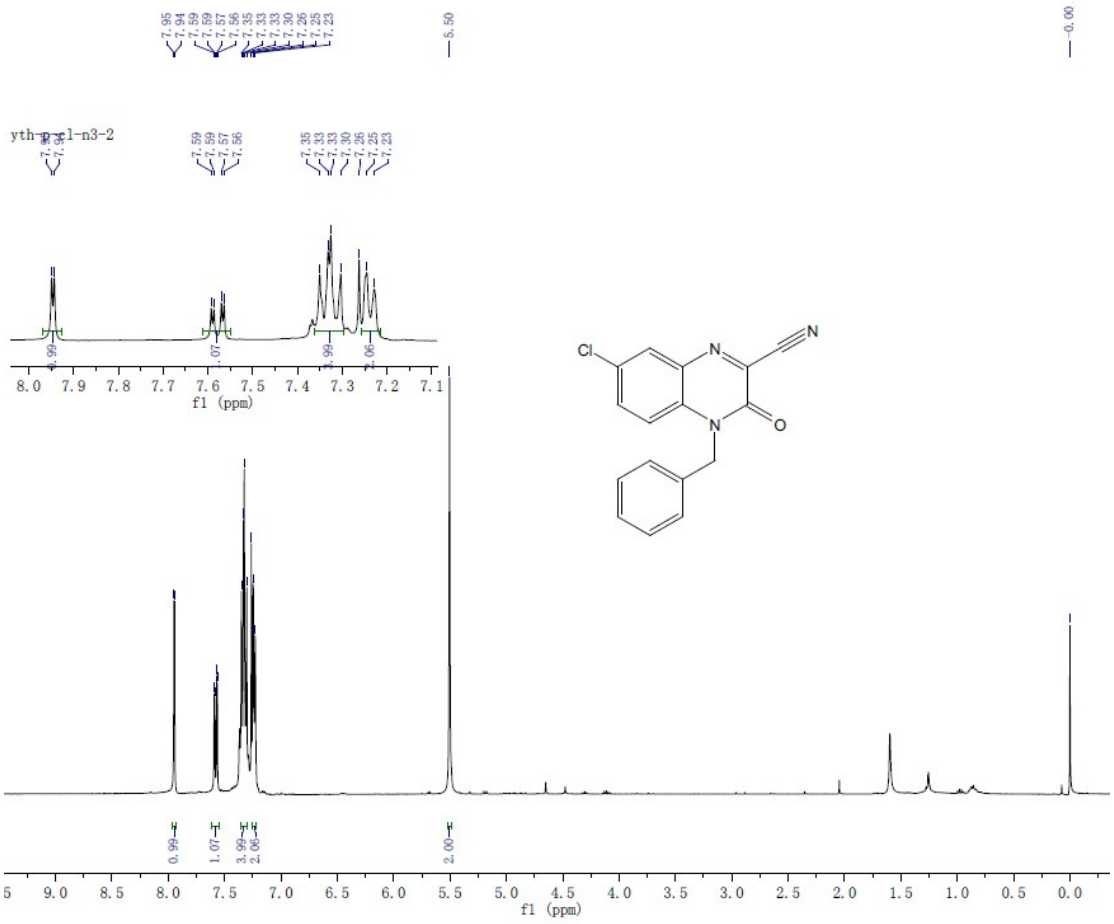

f1 (ppm)

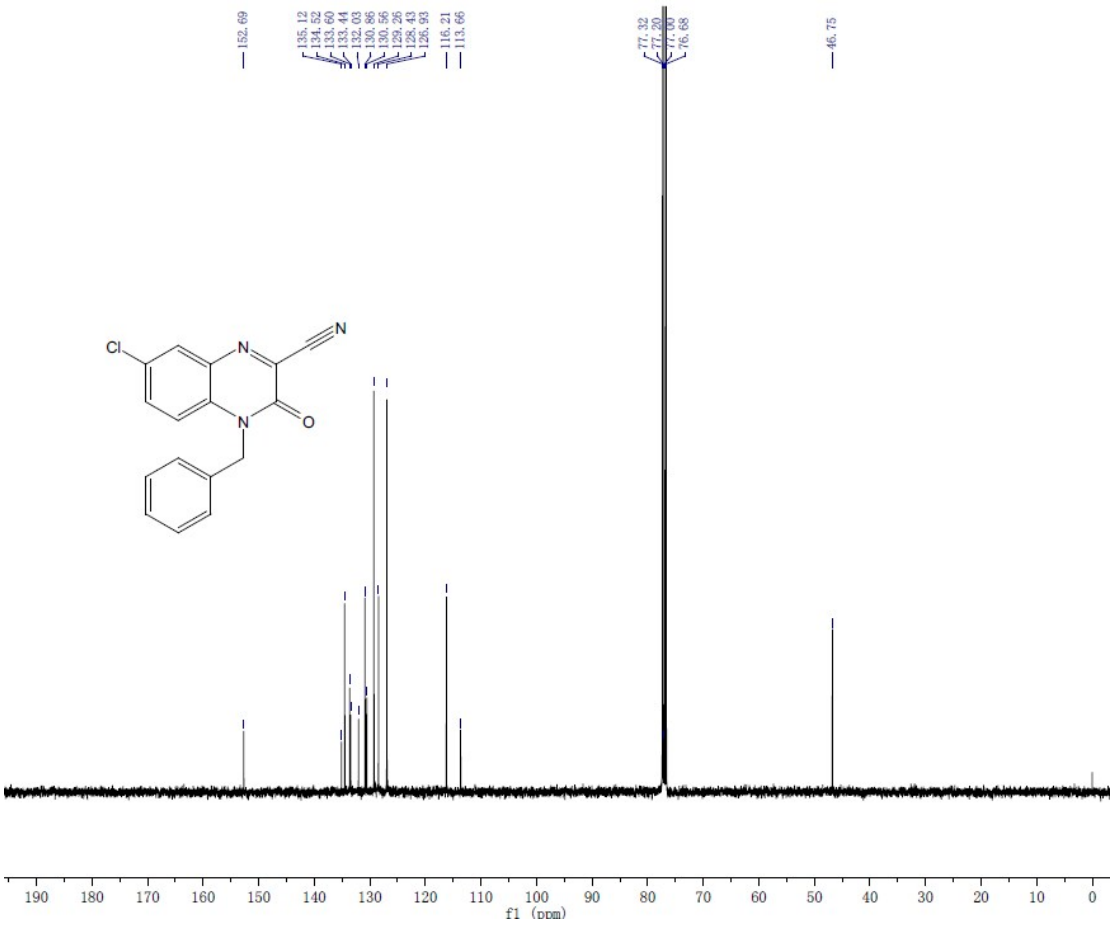

yth-p-f-n3-2
F
CN
O
Bn
7.66
7.64
7.64
7.39
7.38
7.37
7.35
7.33
7.32
7.31
7.25
7.24
5.52
0.00
0.94
4.98
1.98
2.00
f1 (ppm)

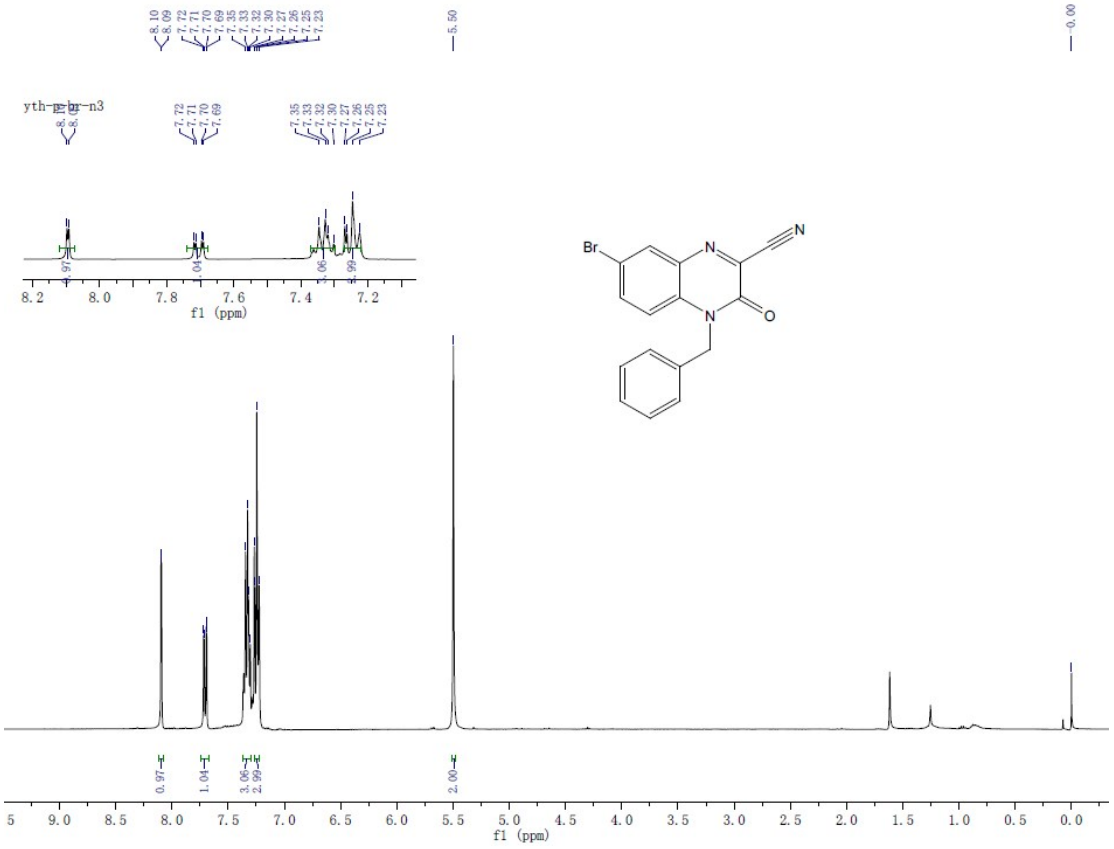

yth-p-f-n3-2
F
CN
O
Bn
160.17
157.71
152.71
135.30
133.71
133.58
133.46
130.12
129.25
129.08
128.99
126.92
126.75
126.84
122.69
116.96
116.73
116.44
116.36
113.72
77.32
77.00
76.68
46.84
f1 (ppm)

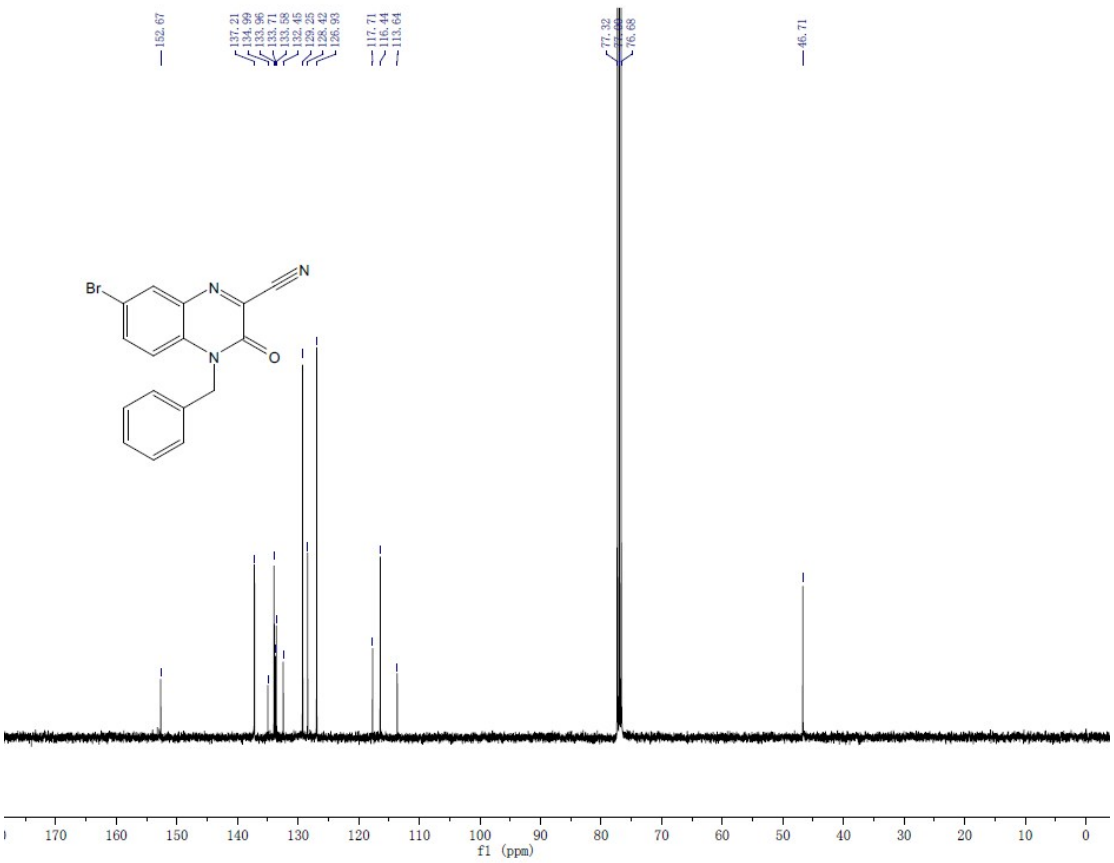

7.93
7.93
7.42
7.42
7.40
7.40
7.39
7.34
7.32
7.31
7.29
7.27
7.26
7.22
7.21
7.20
5.48
4.64
0.00
yth-pyrd-n3-1
f1 (ppm)
Cl
N
O
0.96
1.03
3.05
2.97
2.03
2.00


155.70
153.80
134.39
133.07
131.22
130.80
129.78
129.38
129.05
127.99
126.72
115.71
77.32
77.00
76.68
51.61
45.98
Cl
N
O
f1 (ppm)

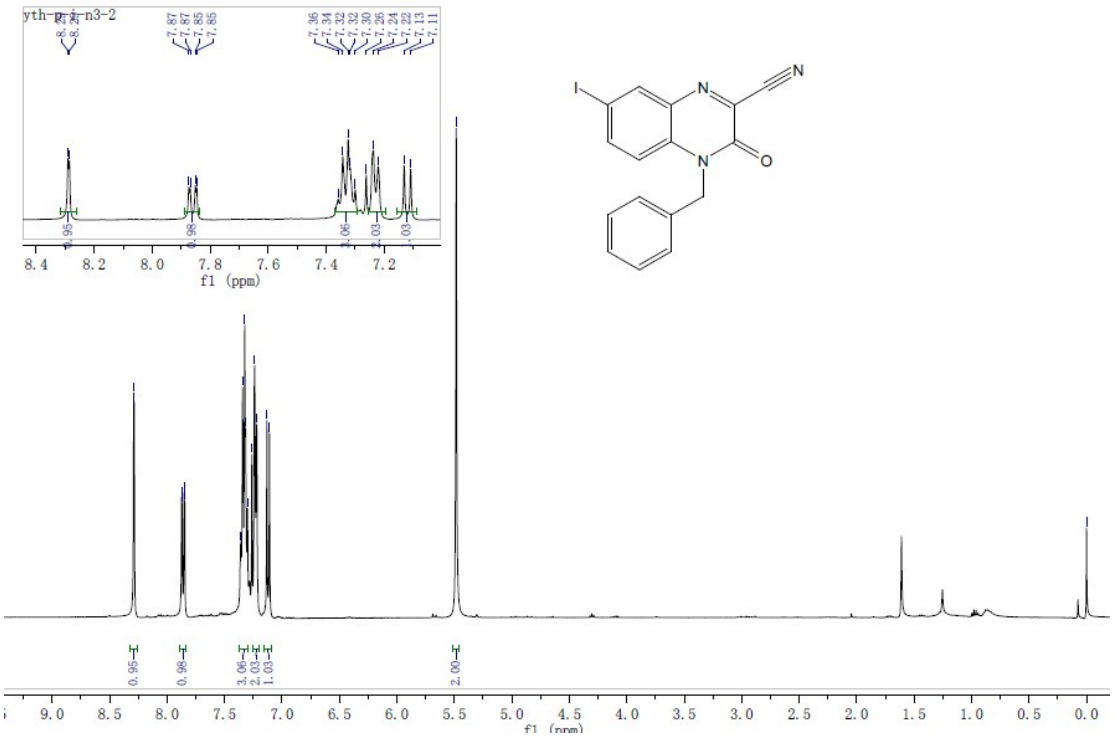

yth-pxl-n3-2
Cl
N
O
f1 (ppm)

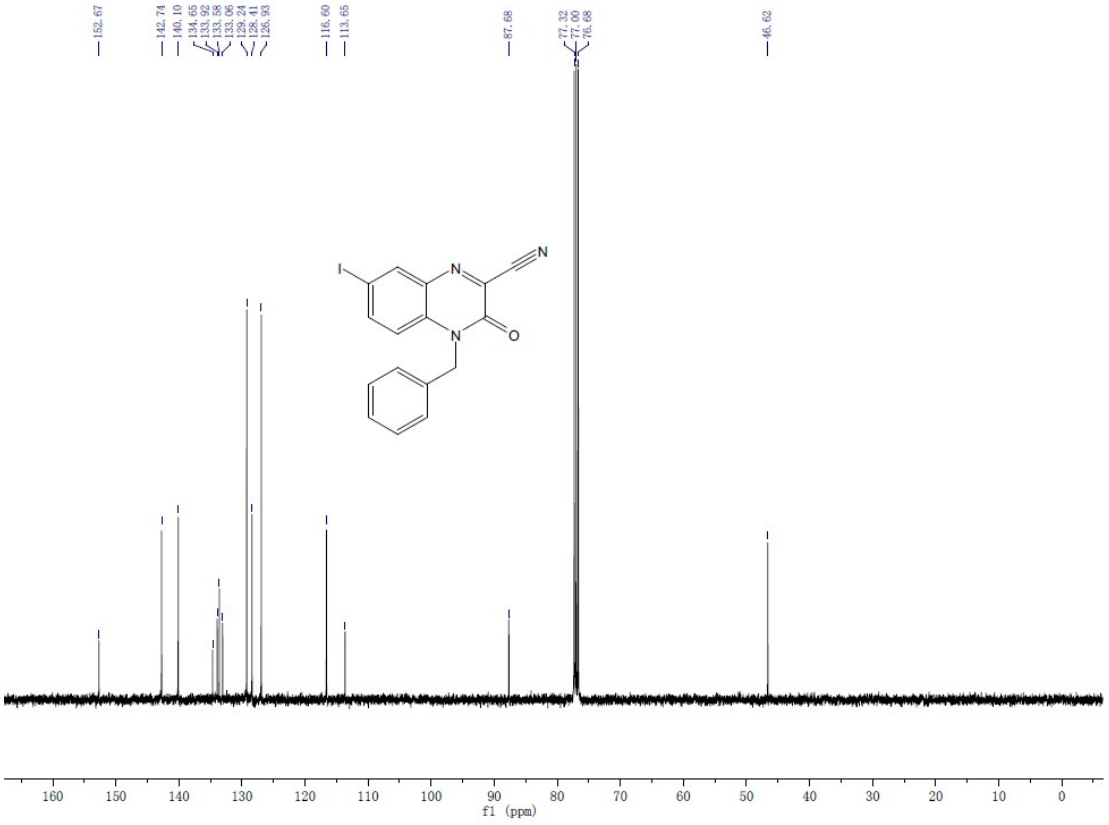

152.69
135.12
134.52
133.60
133.44
132.03
130.86
130.56
129.26
128.43
126.93
116.21
113.66
77.32
77.20
77.00
76.68
46.75
Cl
N
N
O
N
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

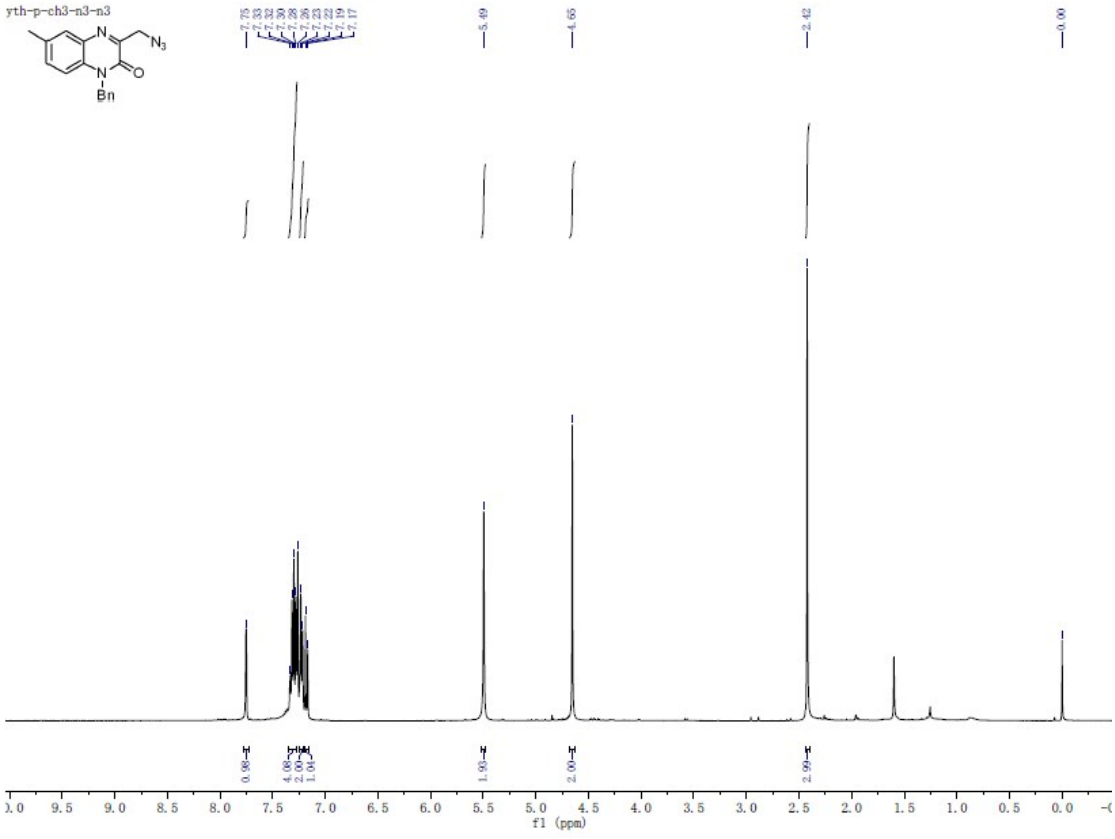

8.10
8.09
7.72
7.71
7.70
7.69
7.35
7.33
7.32
7.30
7.27
7.26
7.25
7.23
5.50
0.00
yth-pr-br-n3
8.2 8.0 7.8 7.6 7.4 7.2
f1 (ppm)
Br
N
N
O
0.97
1.04
3.06
2.99
2.00
5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

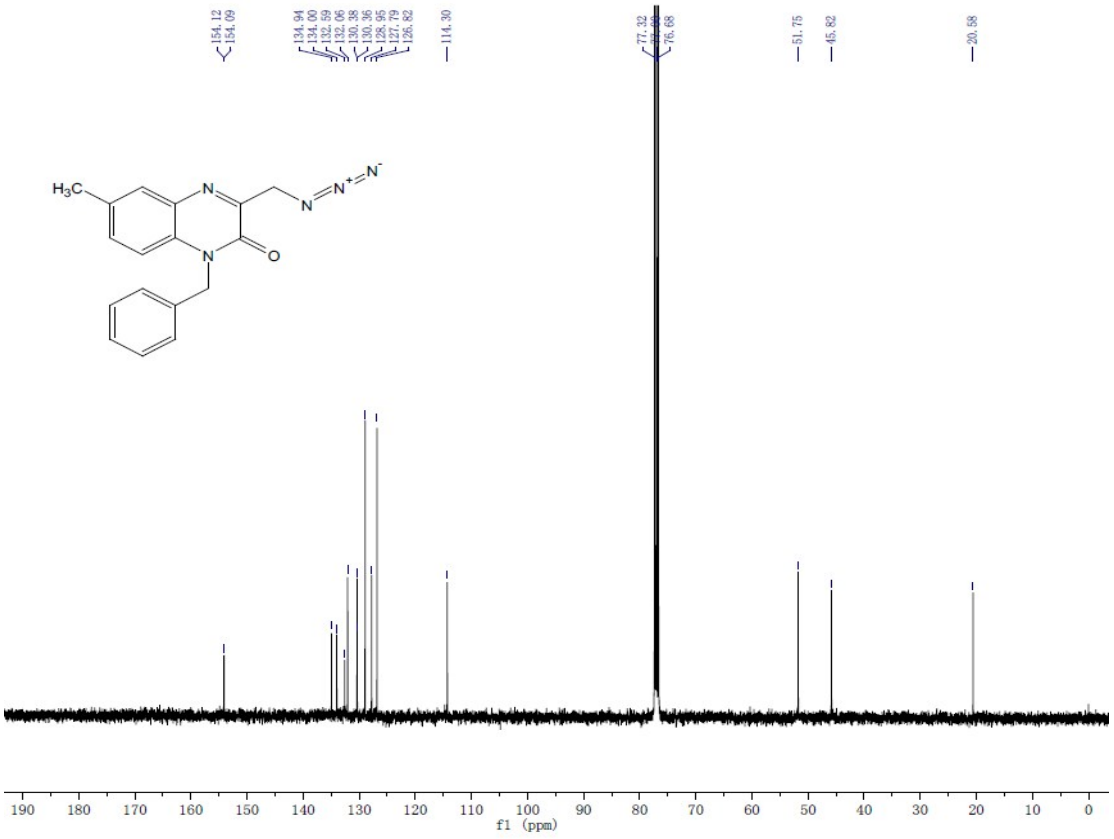

152.67
137.21
134.99
133.96
133.71
133.58
132.45
129.25
128.42
126.93
117.71
116.44
113.64
77.32
76.68
46.71
Br
N
O
N
f1 (ppm)

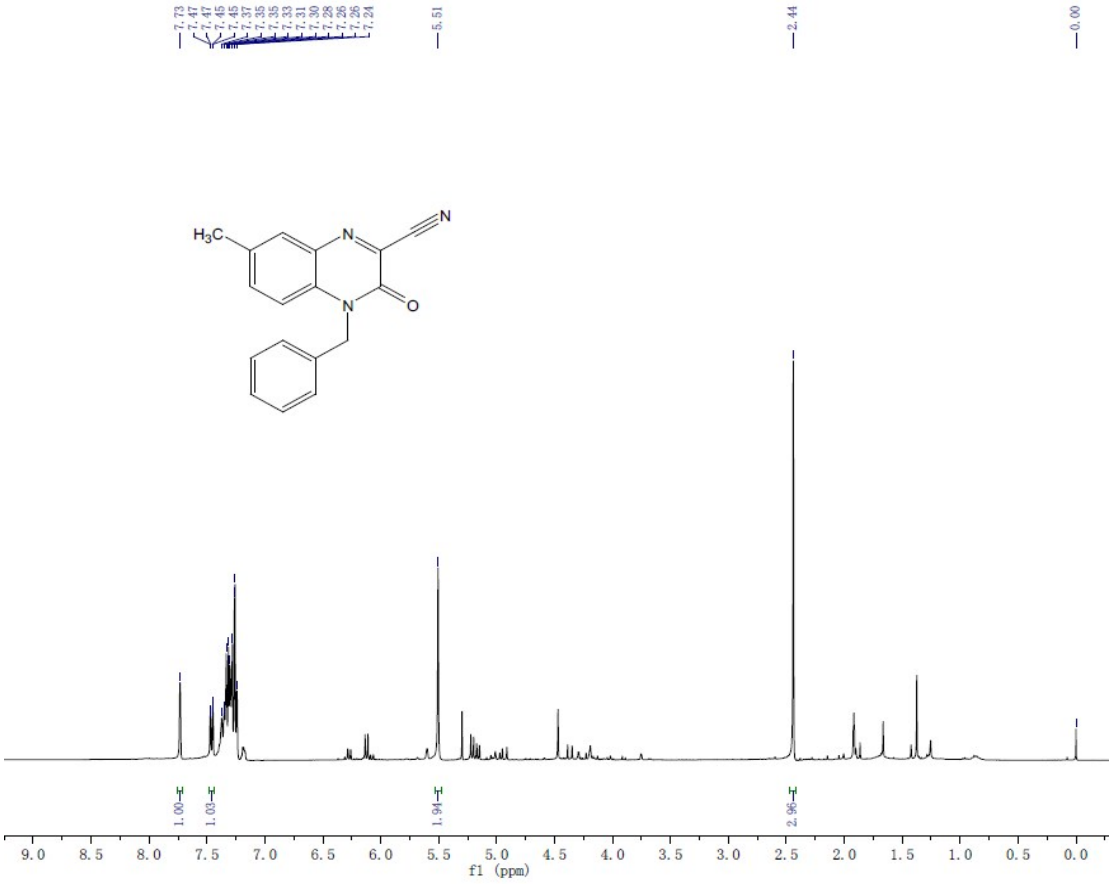

8.29
8.29
7.87
7.87
7.85
7.85
7.36
7.34
7.32
7.32
7.30
7.26
7.24
7.22
7.13
7.11
5.48
0.00

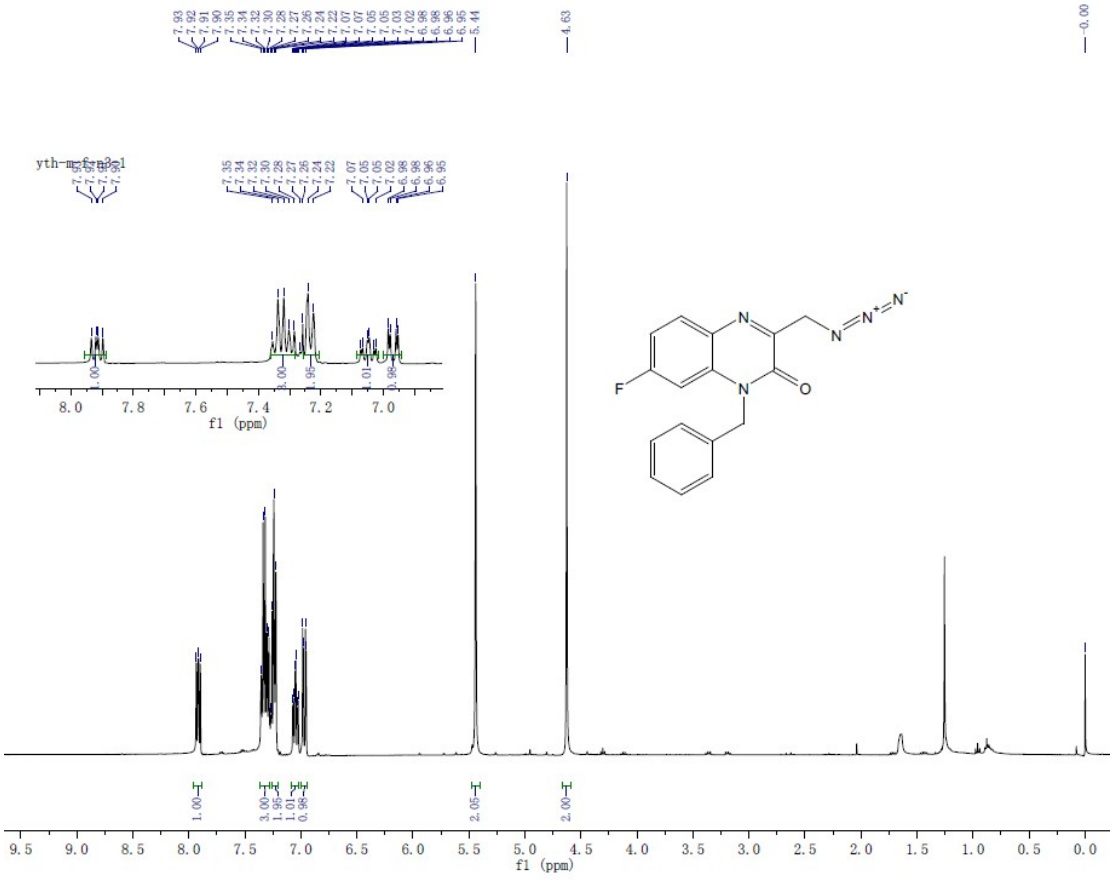

yth-pra-n3-2
8.29
8.29
7.87
7.87
7.85
7.85
7.36
7.34
7.32
7.32
7.30
7.26
7.24
7.22
7.13
7.11
0.95
0.98
3.06
2.03
1.03
2.00
I
N
O
N
f1 (ppm)

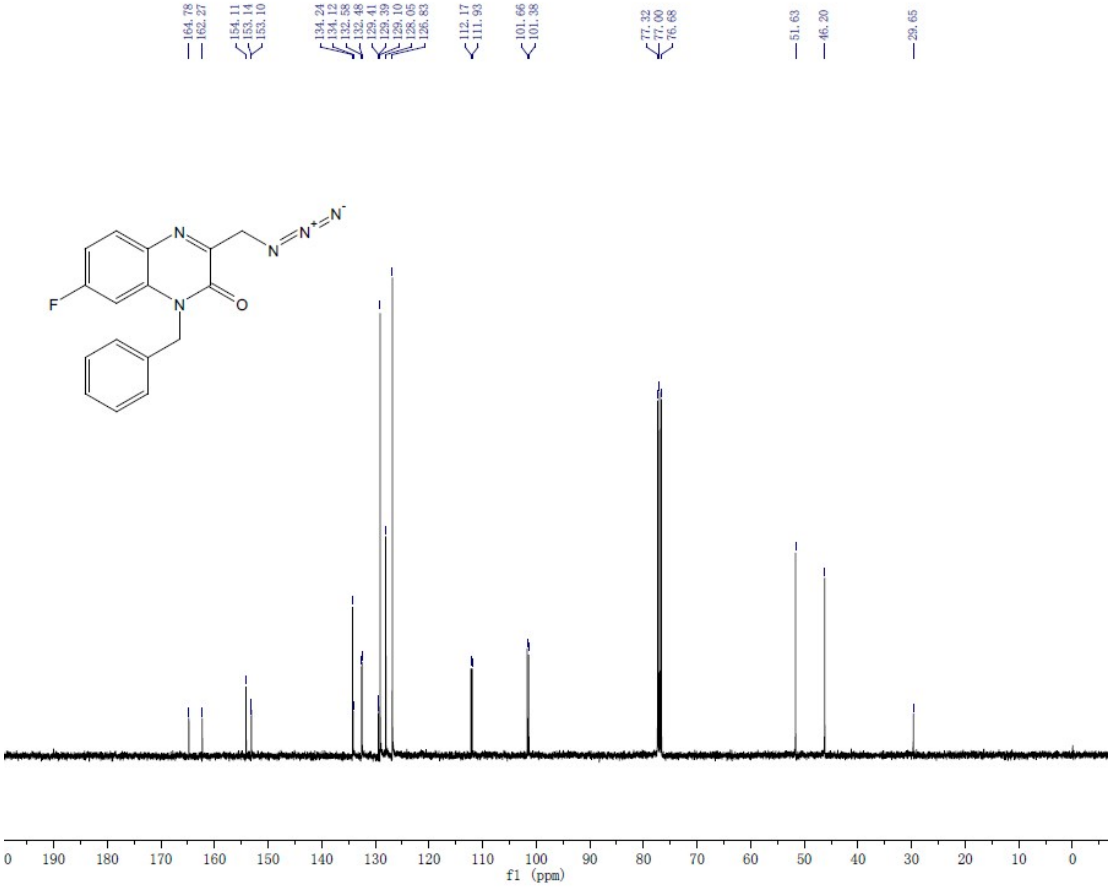

152.67
142.74
140.10
134.65
133.92
133.58
133.06
129.24
128.41
126.93
116.69
113.65
87.68
77.32
77.00
76.68
46.62
I
N
CN
N
O
f1 (ppm)

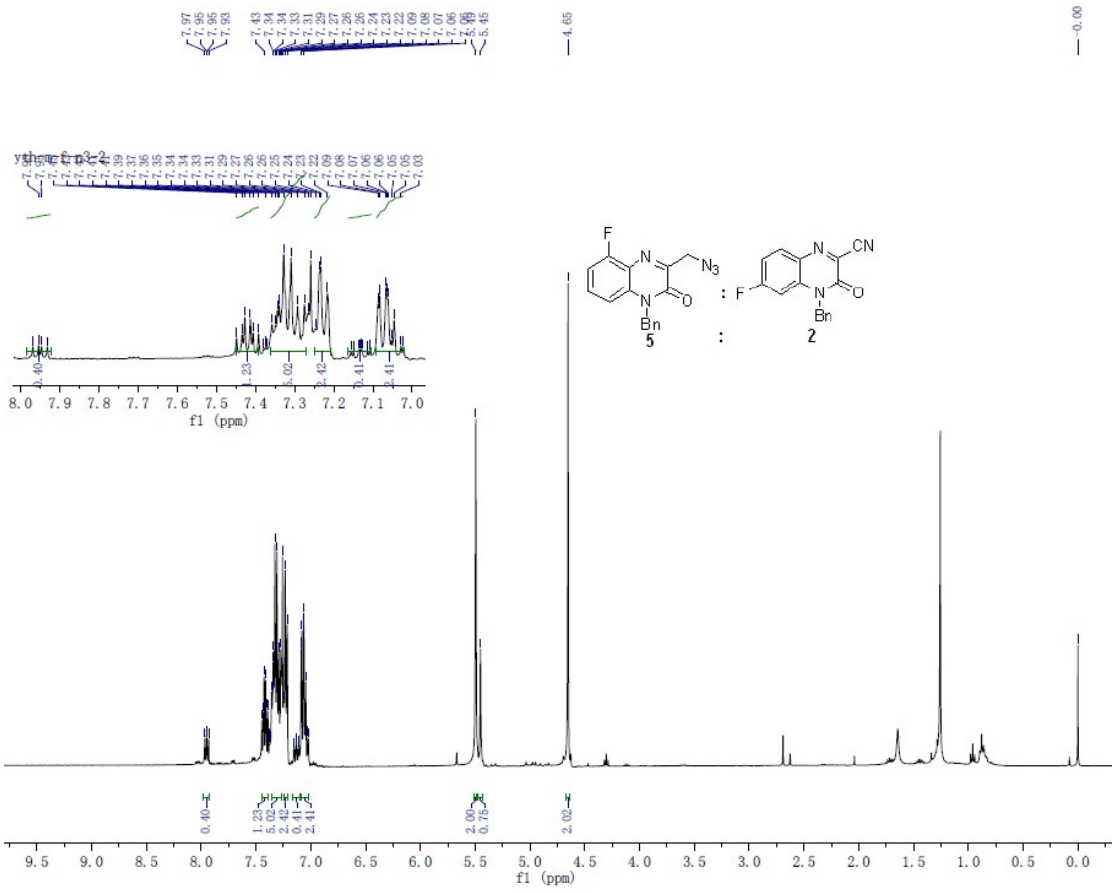

yth-p-ch3-n3-n3
N
N3
N
O
Bn
7.75
7.33
7.32
7.30
7.28
7.26
7.23
7.22
7.19
7.17
5.49
4.65
2.42
0.00
0.98
4.08
2.00
1.04
1.93
2.00
2.99
f1 (ppm)

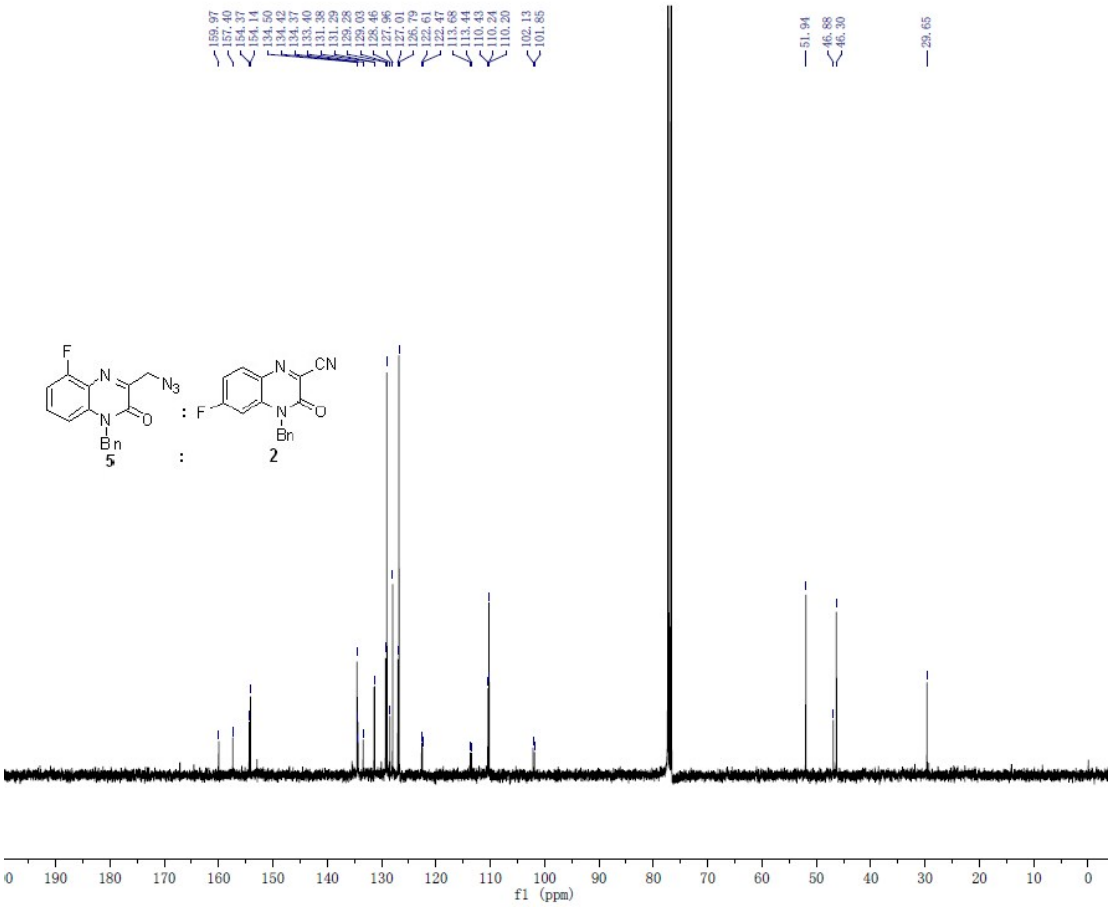

154.12
154.09
134.94
134.00
132.59
132.06
130.38
130.36
126.95
127.79
126.82
114.30
77.32
77.00
76.68
51.75
45.82
20.58
H3C
N
N
N+
N-
O
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

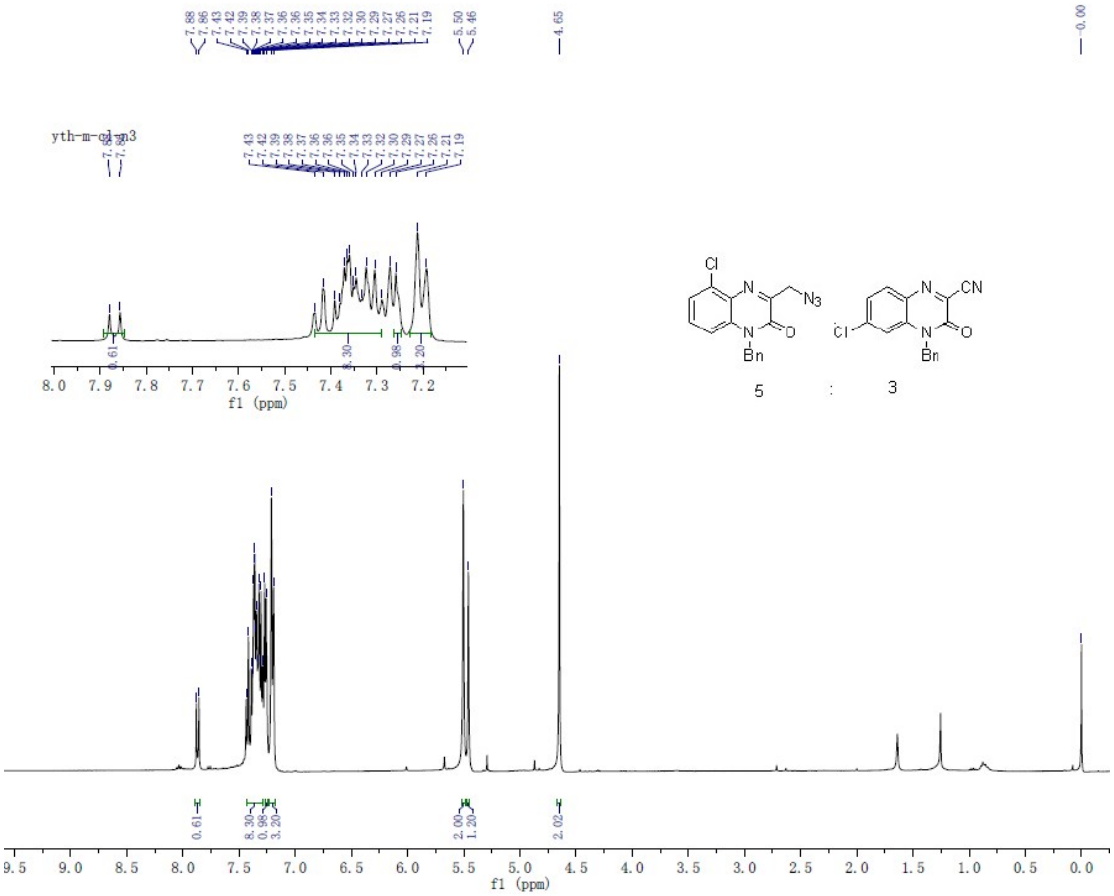

7.73
7.47
7.47
7.45
7.45
7.37
7.35
7.35
7.33
7.31
7.30
7.28
7.26
7.26
7.24
5.51
2.44
0.00
H3C
N
N
O
1.00
1.03
1.94
2.96
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

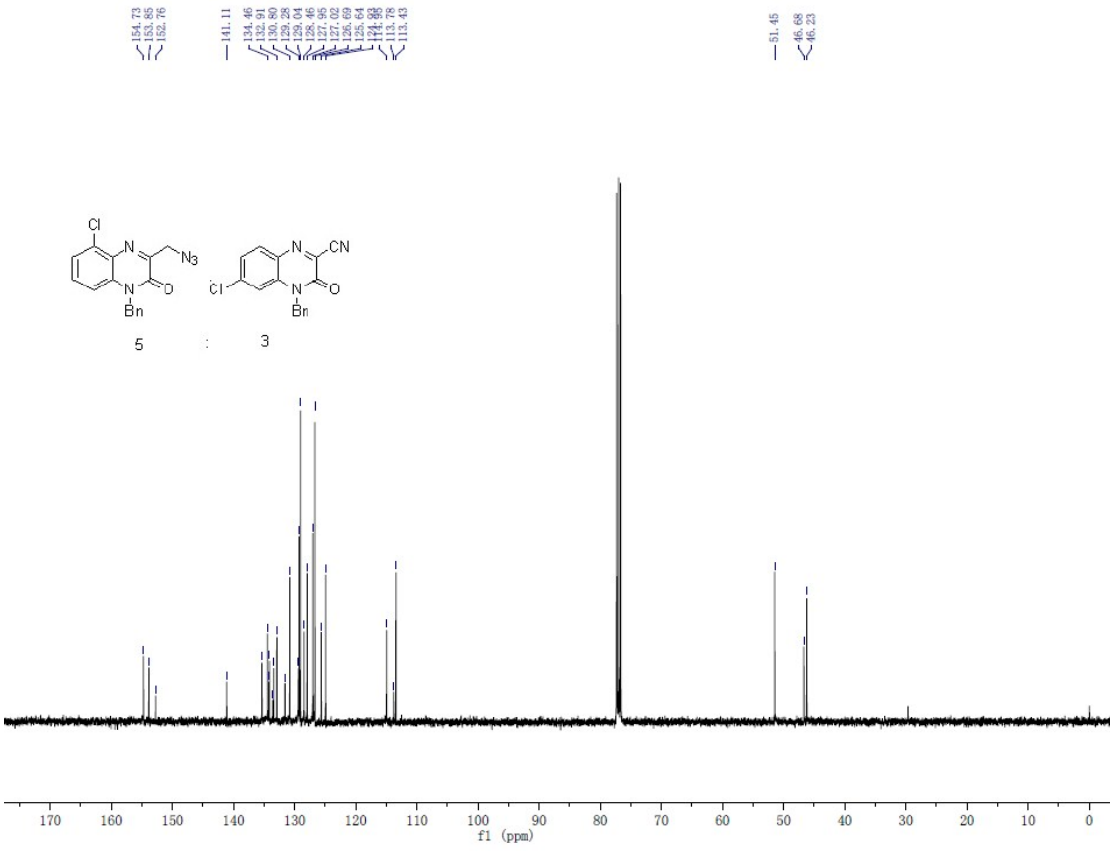

f1 (ppm)

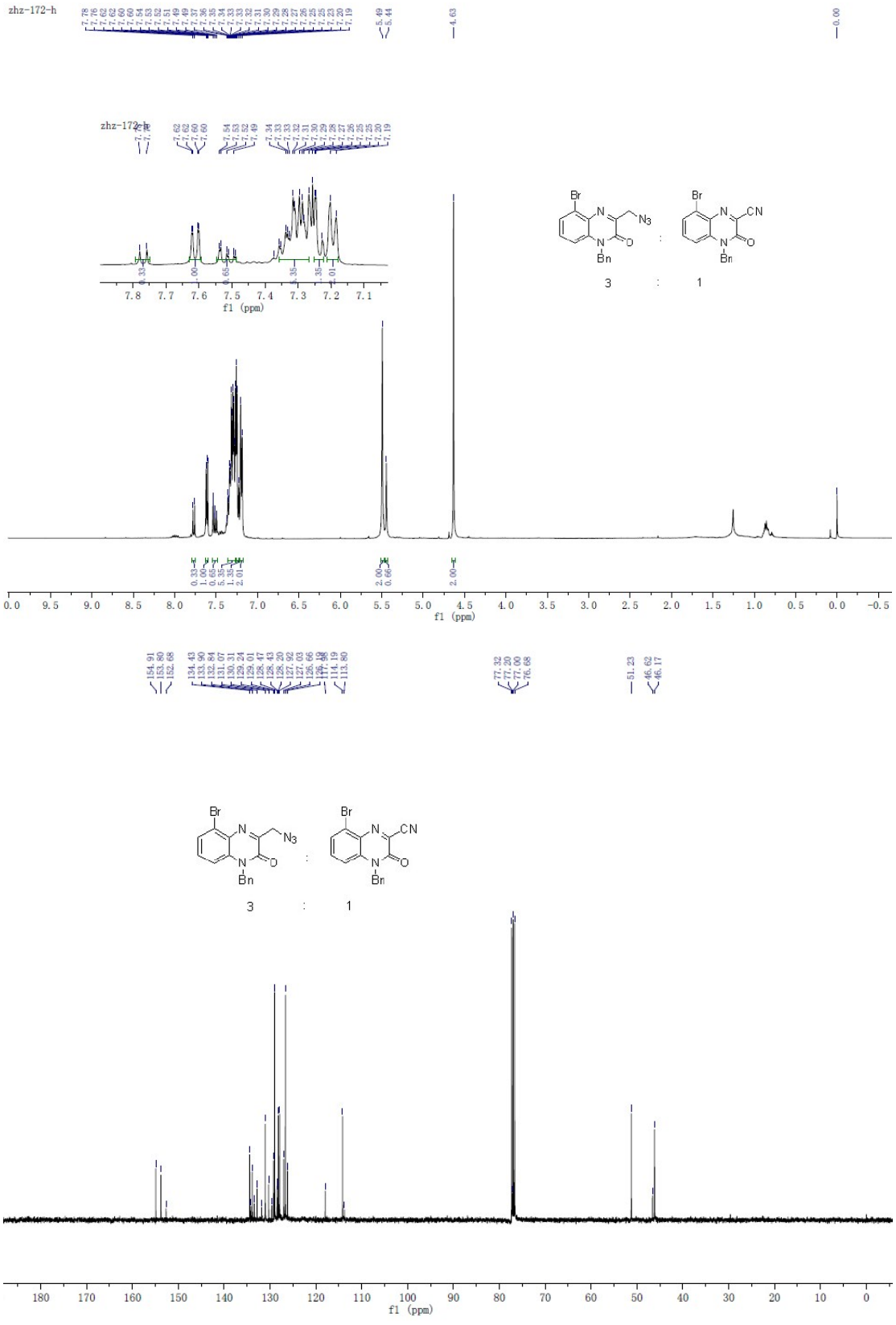

f1 (ppm)


f1 (ppm)

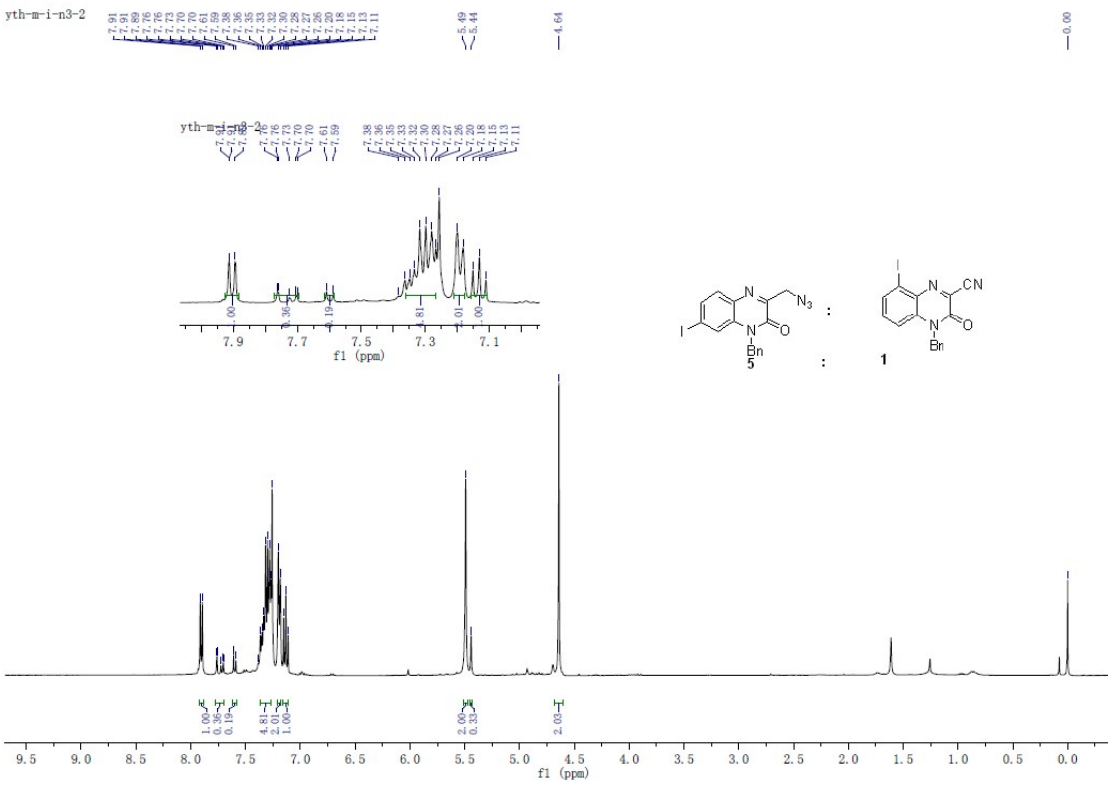

f1 (ppm)

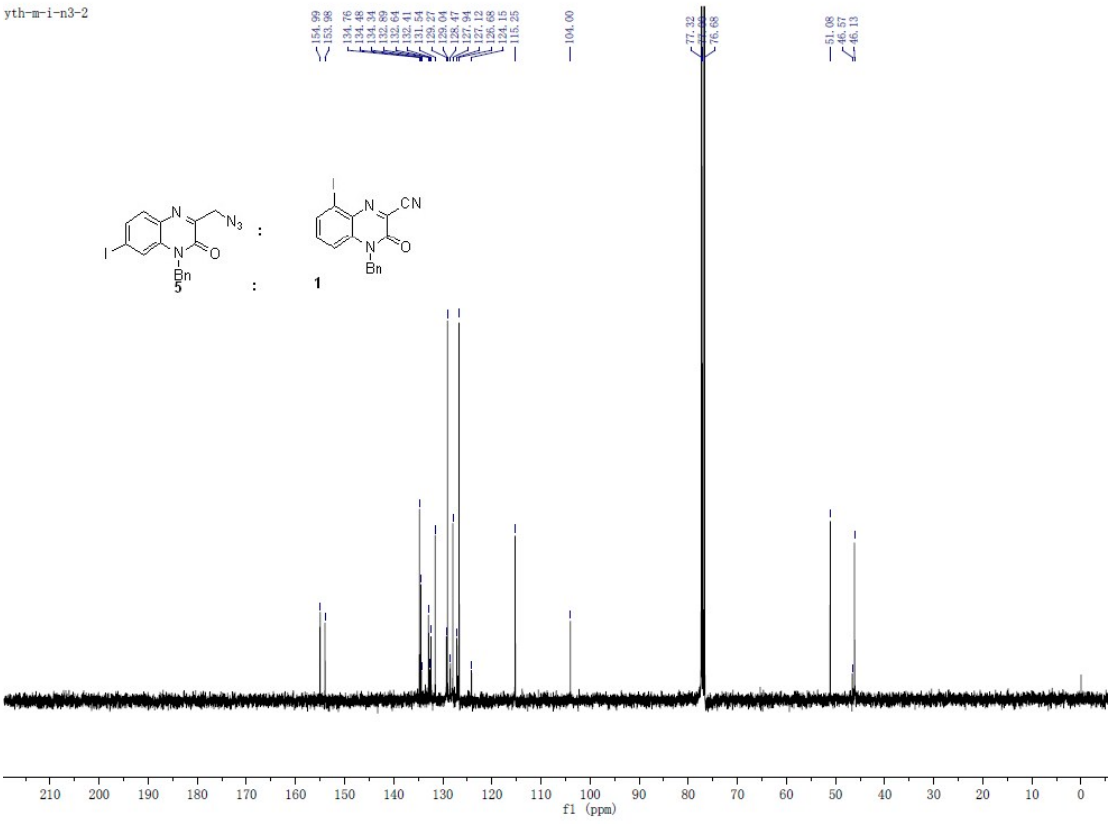

f1 (ppm)
5 : 3

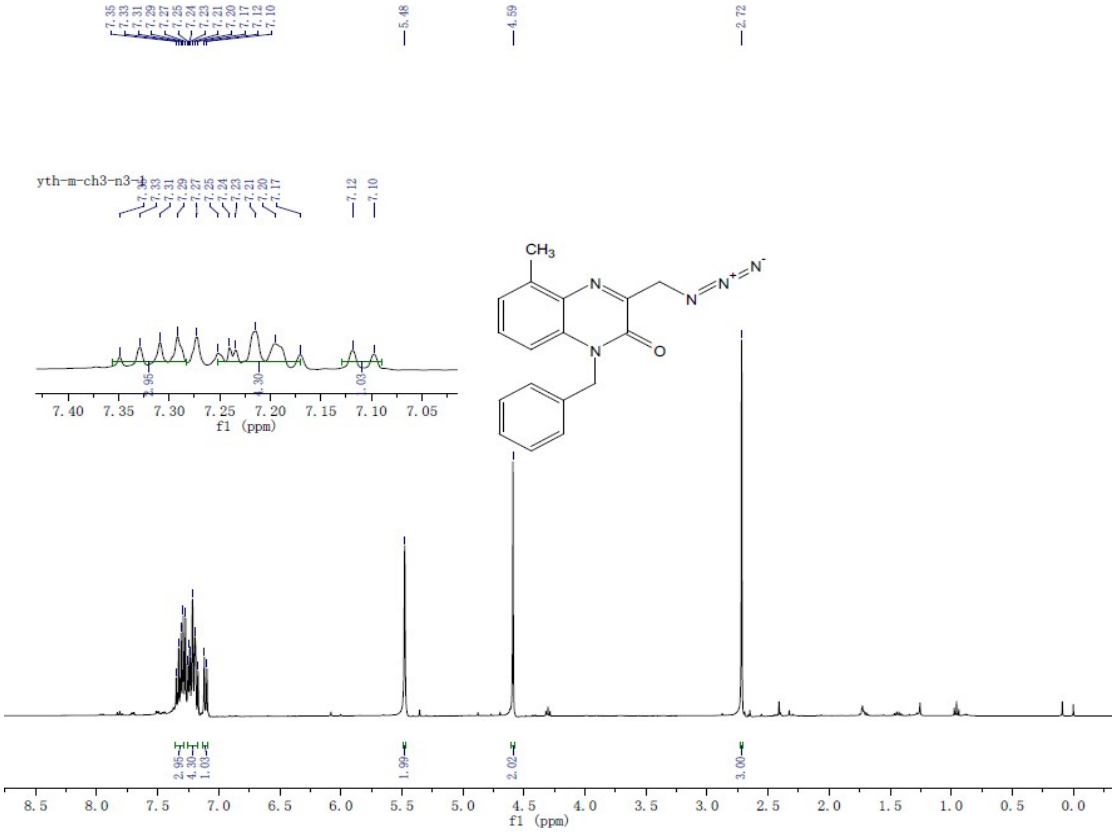

f1 (ppm)
5 : 3

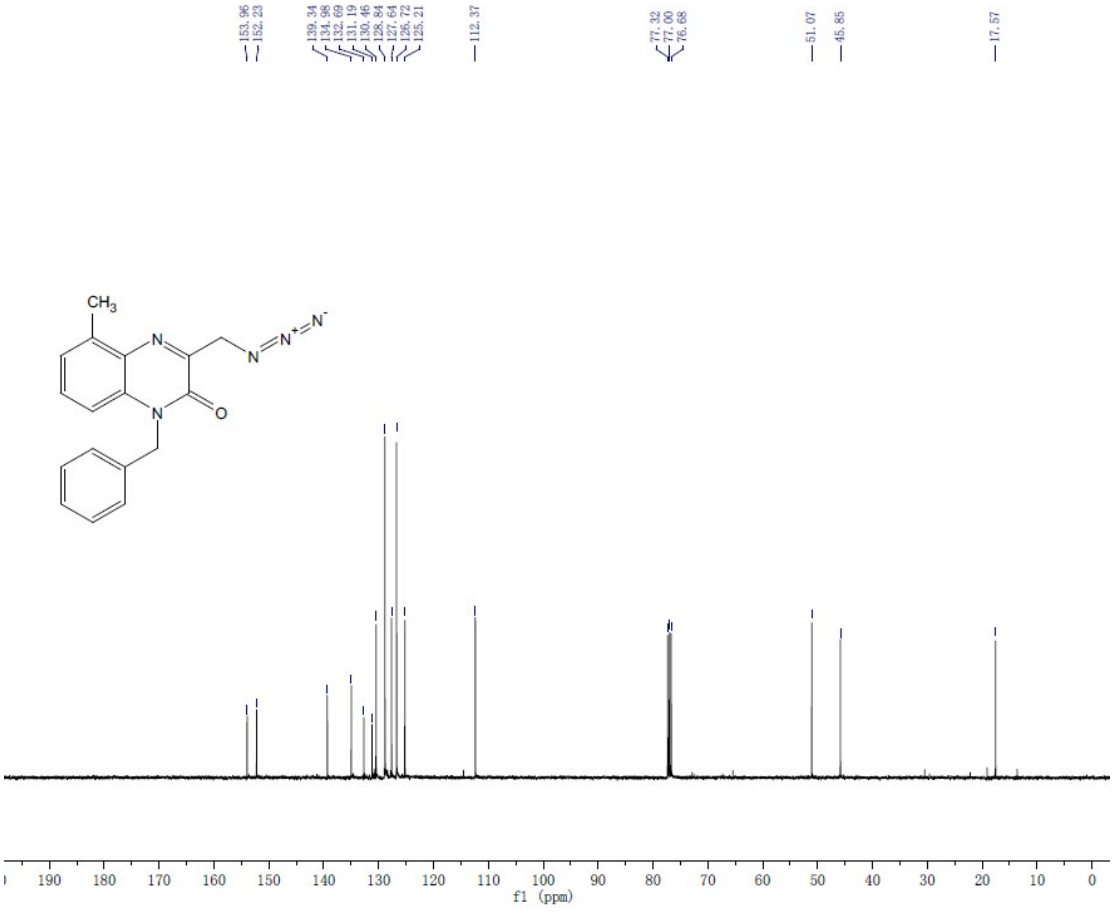

zhz-172-h
f1 (ppm)
3 : 1

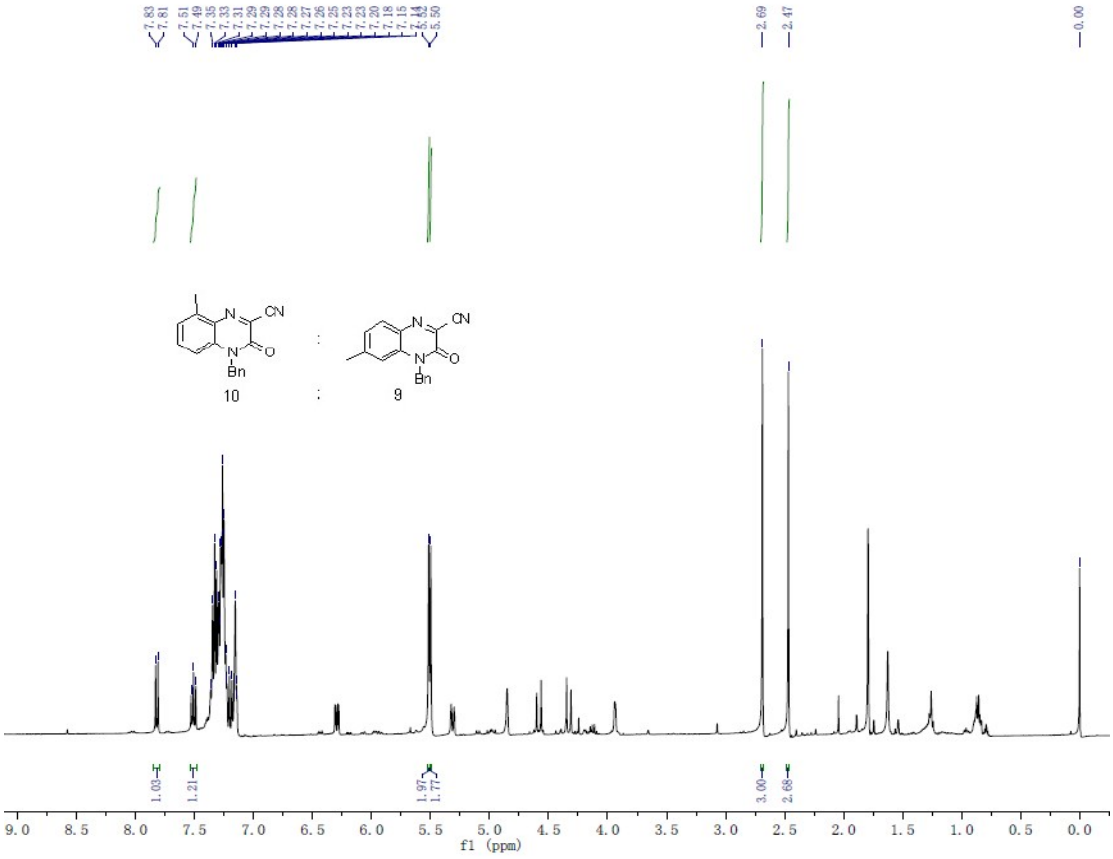
f1 (ppm)
3 : 1

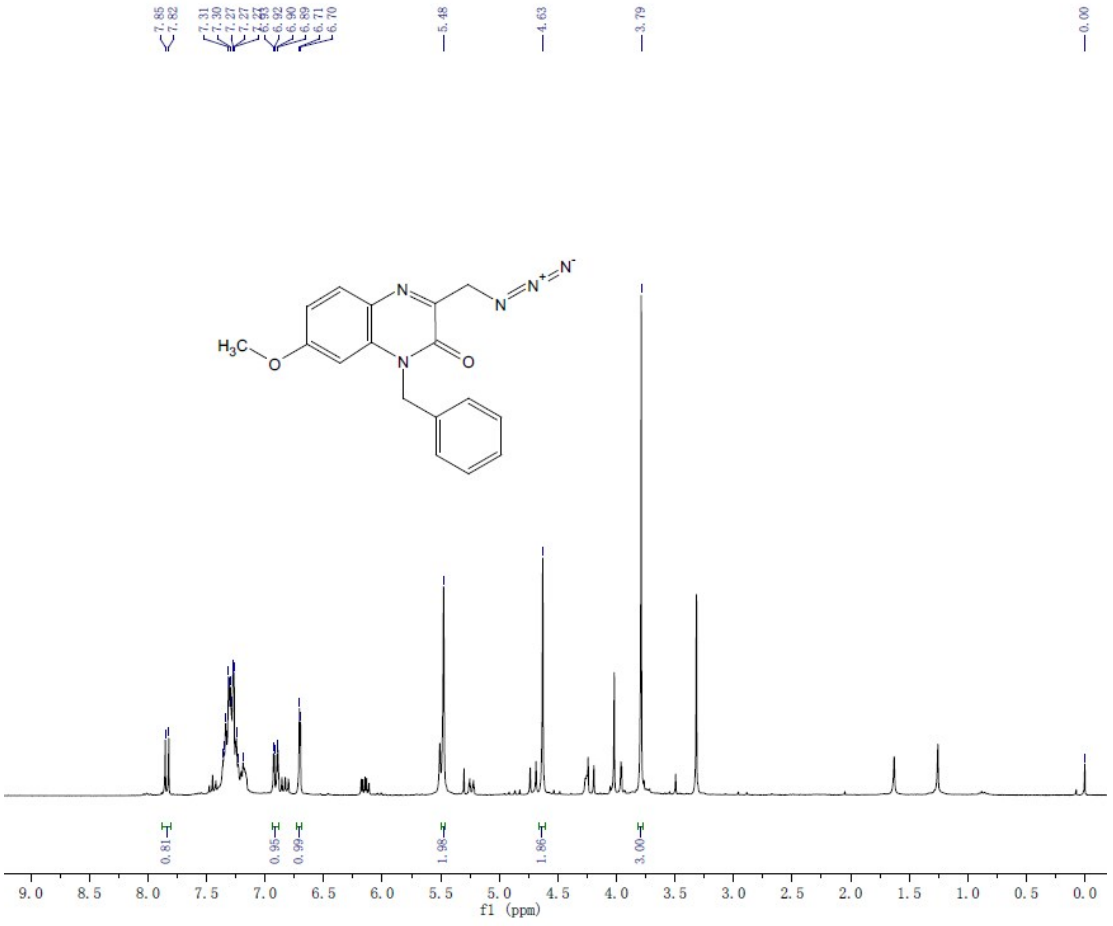

yth-m-i-n3-2
f1 (ppm)
5
1

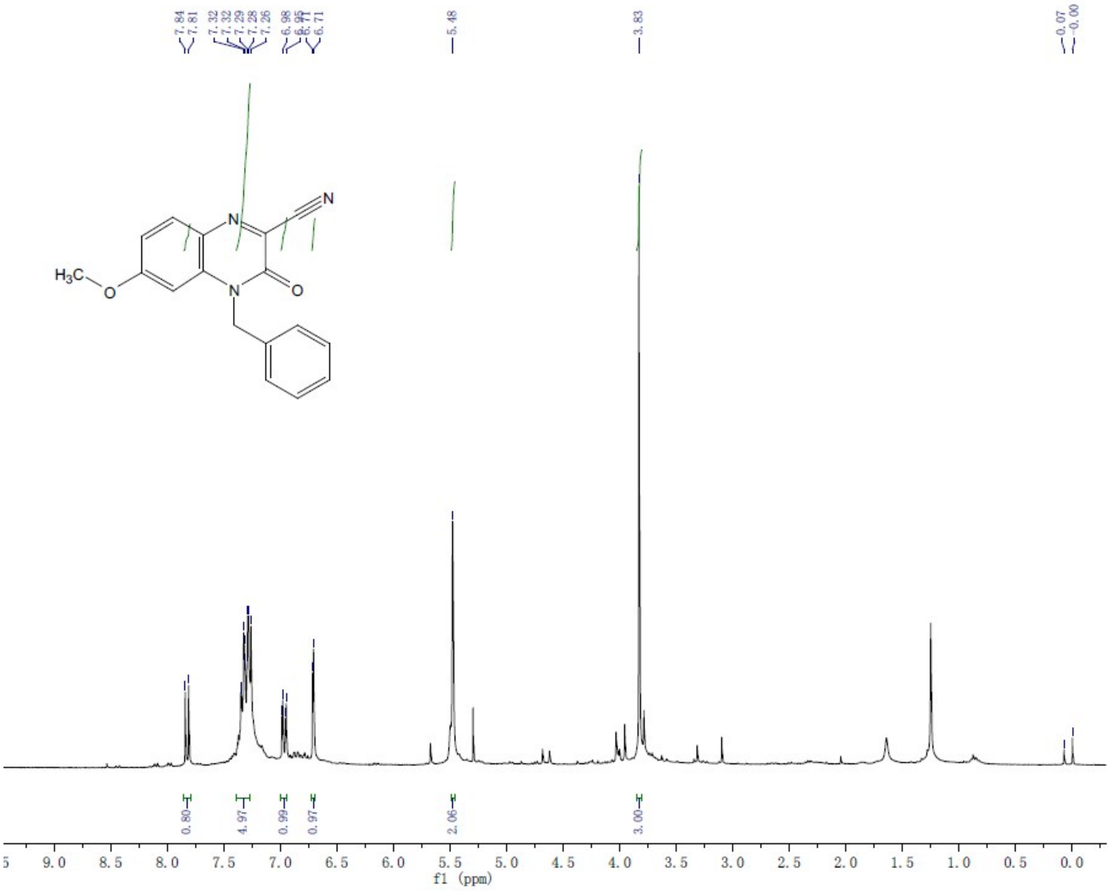

yth-m-i-n3-2
f1 (ppm)
5
1

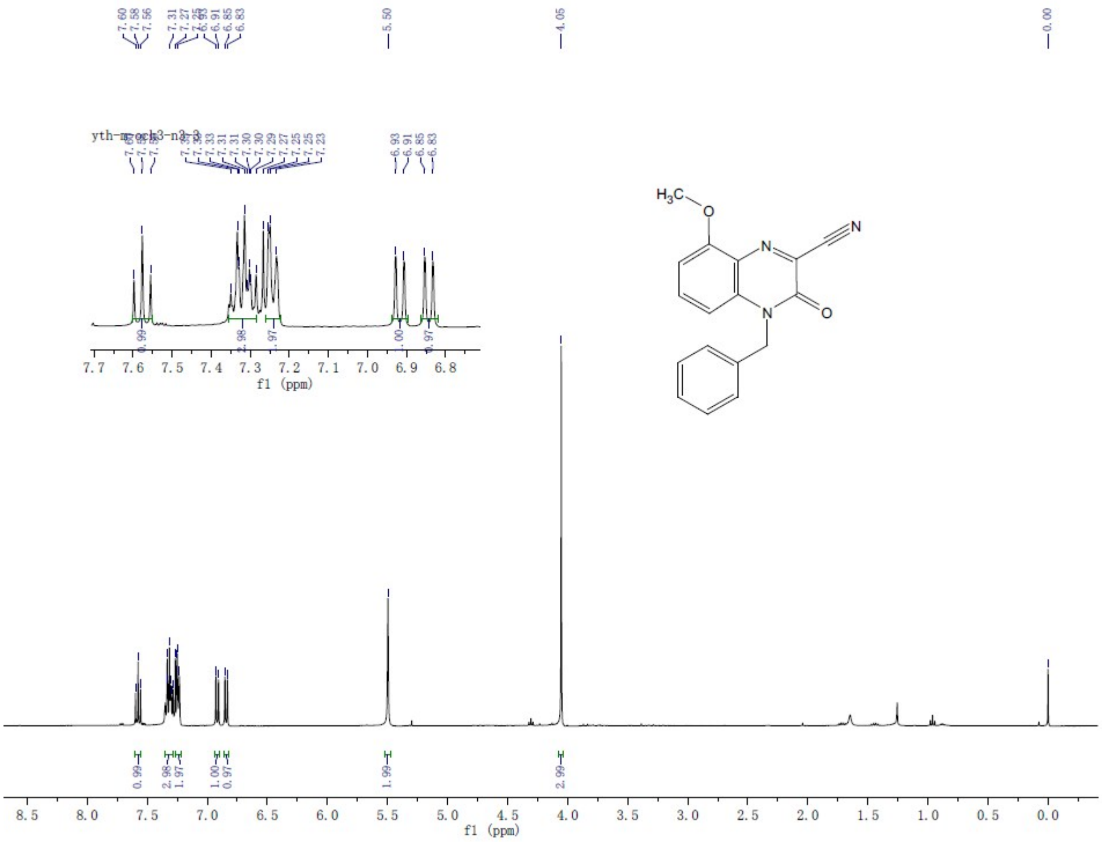

yth-m-ch3-n3-1h
f1 (ppm)

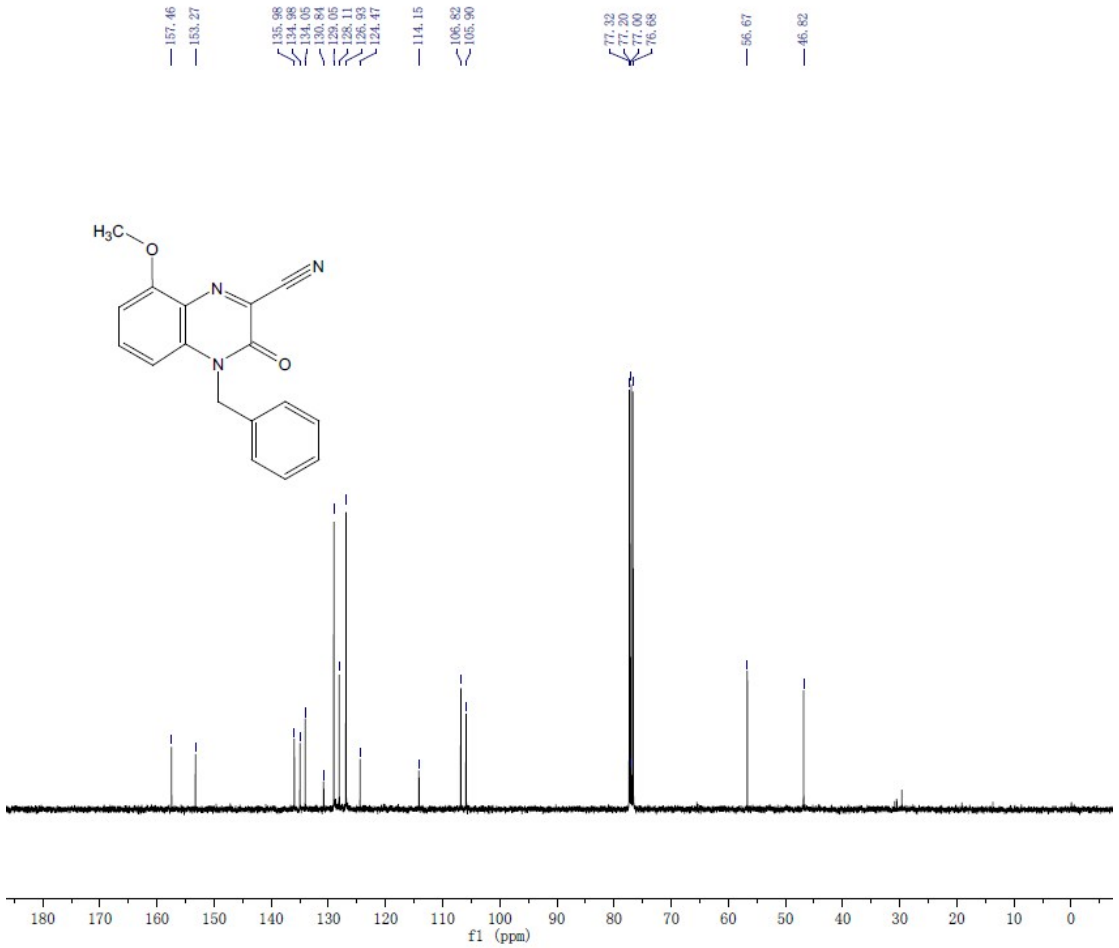

f1 (ppm)

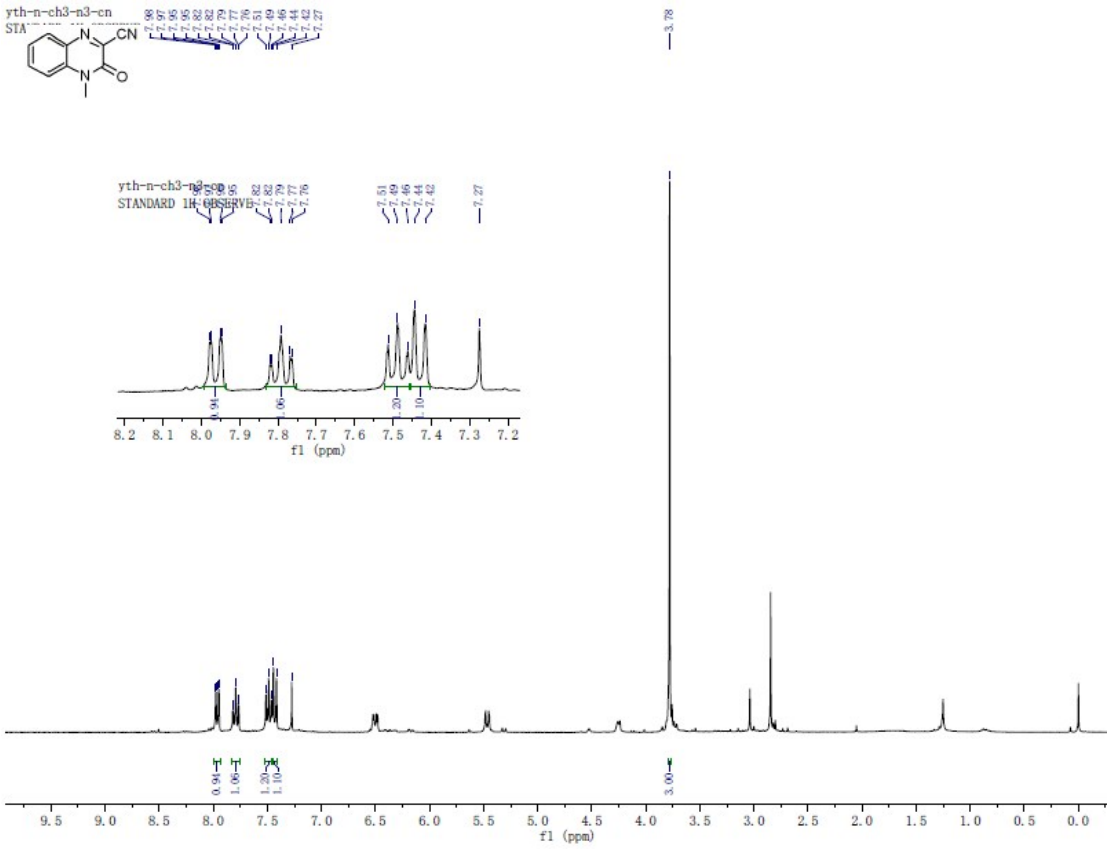

7.83
7.81
7.51
7.49
7.35
7.33
7.31
7.29
7.29
7.28
7.28
7.27
7.26
7.25
7.23
7.23
7.20
7.18
7.15
6.50
2.69
2.47
0.00
CN
N
O
Bn
10
:
9
1.03
1.21
1.97
1.77
3.00
2.68
f1 (ppm)


7.86
7.82
7.31
7.30
7.27
7.27
6.92
6.90
6.89
6.71
6.70
5.48
4.63
3.79
0.00
H3C
O
N
O
N+
N-
0.81
0.95
0.99
1.98
1.86
3.00
f1 (ppm)


f1 (ppm)


yth-m-och3-n2-3
f1 (ppm)
f1 (ppm)


157.46
153.27
135.98
134.98
134.05
130.84
129.05
128.11
126.93
124.47
114.15
106.82
105.90
77.32
77.20
77.00
76.68
56.67
46.82
H3C
O
N
CN
O
N
f1 (ppm)


yth-n-ch3-n3-cn
CN
O
3.78
STANDARD 1H OBSERVE
7.51
7.49
7.46
7.44
7.43
7.27
0.94
1.06
1.20
1.10
3.00
f1 (ppm)