Electronic Supplementary Material (ESI) for ChemComm.


# $Cp^*Co^{III}$-catalyzed formal [4 + 2] cycloaddition of benzamides to afford quinazolinone derivatives

Jingshu Yang, [‡a] Xiao Hu, [‡a] Zijie Liu,[b,c] Xueyuan Li,[a] Yi Dong,*[b,c] and Gang Liu*[a]

[a] School of Pharmaceutical Sciences, Tsinghua University, Haidian District, Beijing 100084,. China. E-mail: gangliu27@tsinghua.edu.cn.

b. State Key Laboratory of Bioactive Substance and Function of Natural Medicines, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050, China. E-mail: dongyi@imm.ac.cn.

c. Beijing Key Laboratory of Active Substances Discovery and Druggability Evaluation, Institute of Materia Medica, Chinese Academy of Medical Sciences and Peking Union Medical College, Beijing 100050, China.

‡ These authors contributed equally.

# *Table of cotent*

# General methods

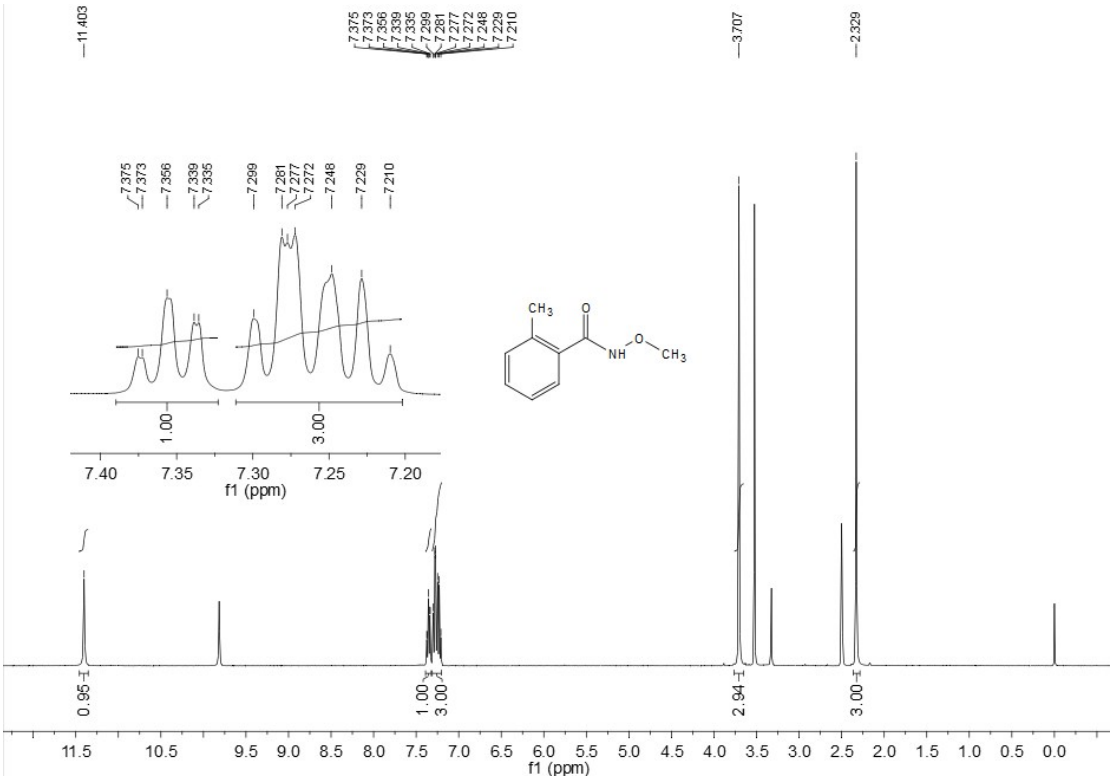
Dried solvent, such as DCM, DCE, MeOH and THF were purchased from domestic corporations and used without purification. [Cp*Co(CO)$I_2$] was purchased from domestic corporation, $AgSbF_6$, $AgNtf_2$, AgOAc， $AgBF_4$ and AgOTf were purchased from Alfa. Analytical thin layer chromatography (TLC) plates, preparative TLC and the silica gel for column chromatography were phased from Qingdao Haiyang Chemical and Special Silica Gel Co, Ltd.

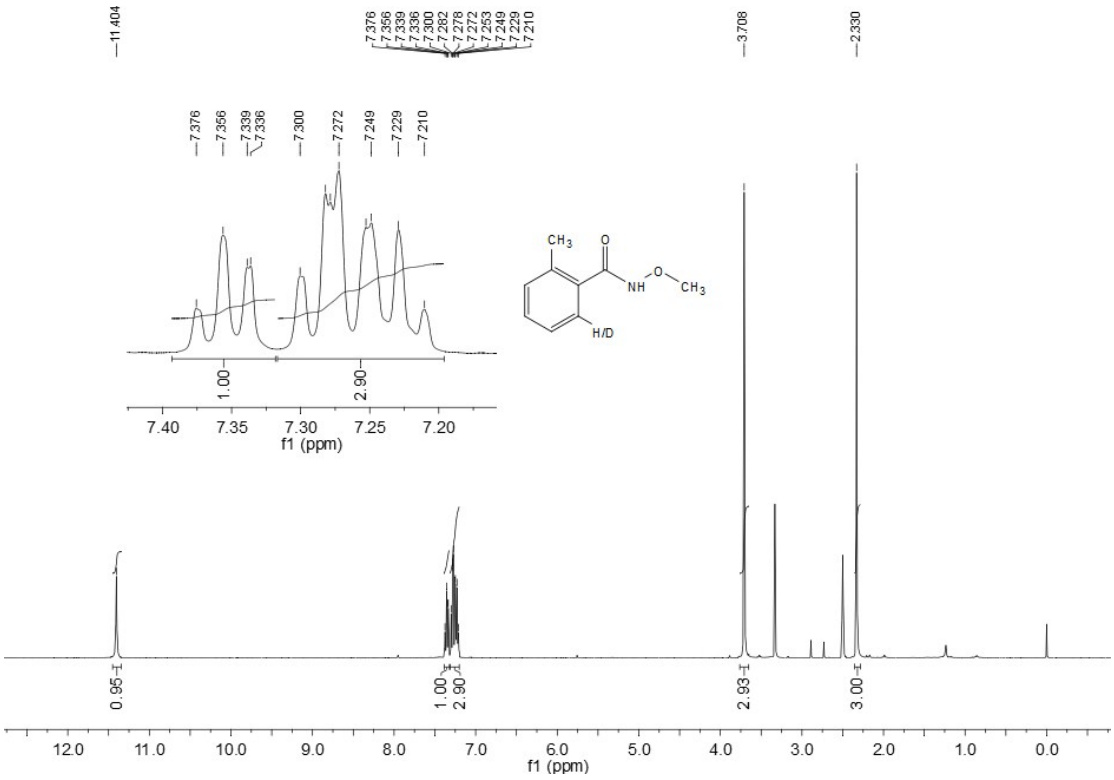
High-resolution LC-MS was carried out by Agilent LC/MSD TOF using a column of Agilent ZORBAX SB-C18 (rapid resolution, 3.5 μm, 2.1 × 30 mm) at a flow of 0.40 mL/min. The solvent was MeOH/water (75:25 (v/v)), containing 5 mmol/L ammonium formate. The ion source is electrospray ionization (ESI).

Proton nuclear magnetic resonance ($^1$H NMR) and carbon nuclear magnetic resonance ($^{13}$C NMR) spectroscopy were performed on Bruker Advance 400M NMR spectrometers or 500M NMR spectrometers. Chemical shifts of $^1$H NMR spectra are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ = 7.260, singlet) and DMSO-*d6* (δ = 2.500, quintet). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); m (multiplets), etc. The number of protons (n) for a given resonance is indicated by nH. Carbon nuclear magnetic resonance spectra ($^{13}$C NMR) are reported as in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ = 77.230, triplet) and DMSO-*d6* (δ = 39.510, septet).

# H/D exchange experiment

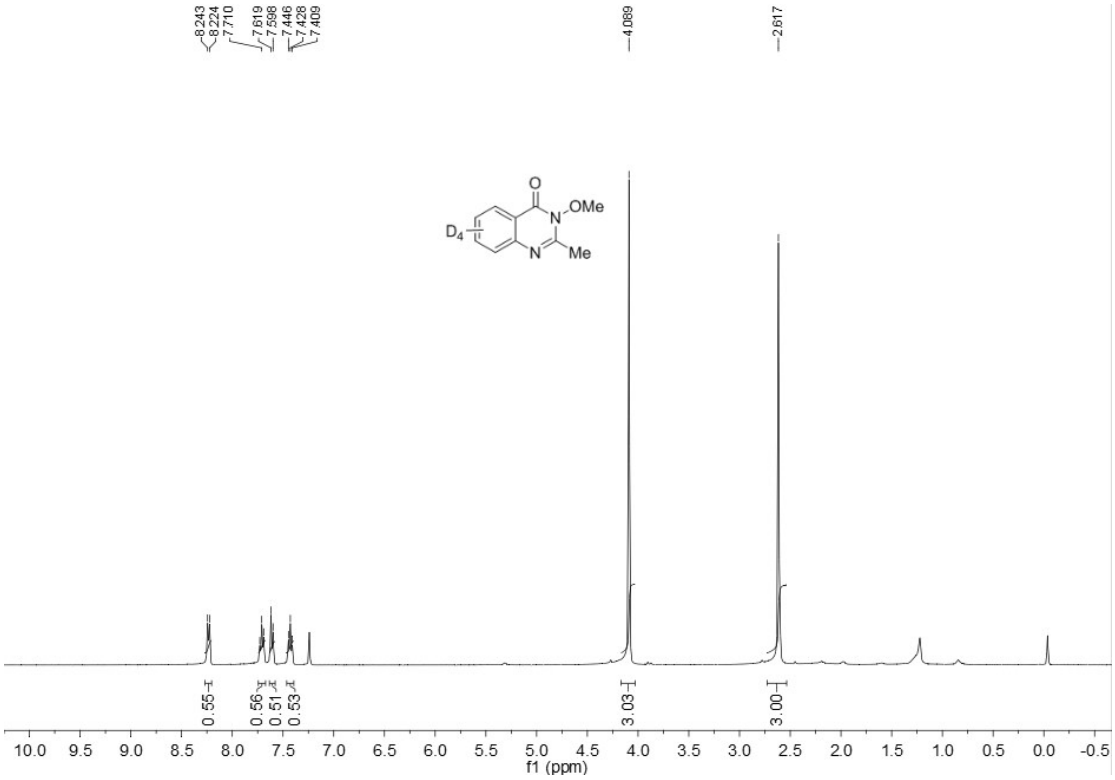
A mixture of [Cp*Co(CO)$I_2$](5.0 mol%), $AgNTf_2$ (10 mol%), $Zn(OAc)_2$ (1 eq) and benzamide **1s** (0.2 mmol) in 2.0 mL DCE and 0.5 mL [D4]-MeOH was heated to 120°C, and stirred overnight. Then the reaction mixture was cooled to room temperature and filtered, the filtrate was concentrated and the residue was purified with flash column chromatography. 10% deuteration on phenyl C−H was detected.




11.404
7.376
7.356
7.339
7.336
7.300
7.282
7.278
7.272
7.253
7.249
7.229
7.210
3.708
2.330
CH3
O
NH
O
CH3
H/D
1.00
2.90
7.40
7.35
7.30
7.25
7.20
f1 (ppm)
0.95
1.00
2.90
2.93
3.00
12.0
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

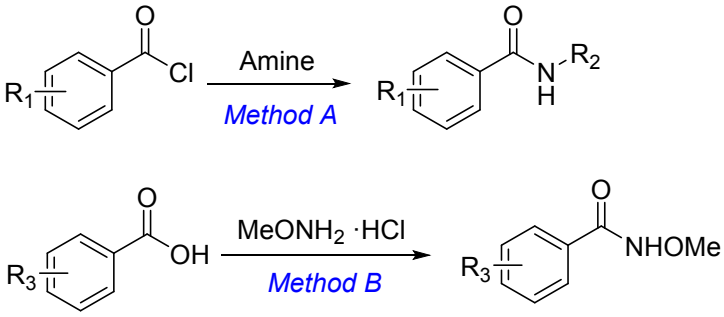
# KIE experiment

The parallel reactions with **1m** and deuterated substract **1m-$d_5$** under the standard conditions were proceeded: A mixture of [Cp*Co(CO)$I_2$](5.0 mol%), $AgNTf_2$ (10 mol%), $Zn(OAc)_2$ (1 eq) and benzamide **1m** or **1m-$d_5$** (0.2 mmol) and 3-methyl-1,4,2-dioxazol-5-one (0.24 mmol) in 2.0 mL DCE was heated to 120°C 1h. Then the two reaction mixtures were combined, cooled to room temperature and filtered, the filtrate was concentrated and the residue was purified with flash column chromatography. KIE value ($k_H/K_D$ = 1.2) was determined by $^1$H NMR analysis.

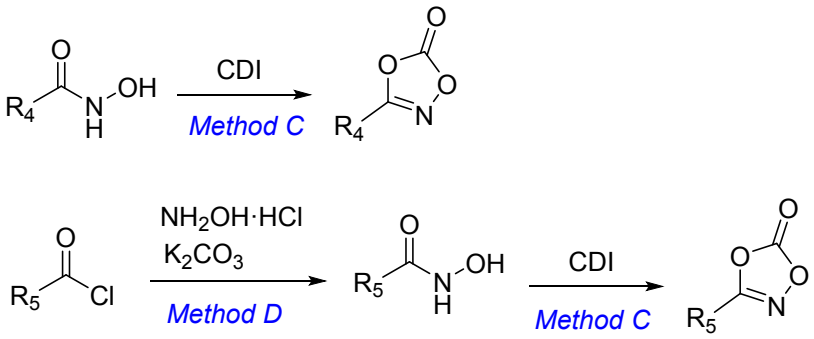


## General procedure for synthesis of amides and dioxazolones:

### *A. General procedure for synthesis of amides*




### *B. General procedure for synthesis of dioxazolones*




***Method A***: Acyl chloride (10 mmol) and trimethylamine (1.67 mL, 12 mmol) were dissolved in 20 mL DCM at 0 °C, then amine (12 mmol) was added. The reaction was allowed to warm to room temperature and stirred overnight. The reaction was quenched by water. DCM was used to extract the product from the aqueous layer. The combined organic layer was washed with water (3×50 mL), dried over $Na_2SO_4$, filtered and concentrated. The crude product was purified by silica gel chromatography.

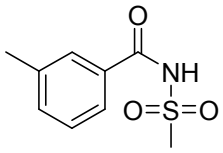
***Method B***: To a suspension of 1,1-Carbonyldiimidazole (2.43 g, 15 mmol) in THF (30 mL) was added carboxylic acid (10 mmol) and hydroxylamine hydrochloride (1.67 g, 20 mmol), and stirred at room temperature overnight. When the starting material was consumed completely, the reaction mixture was filtered and washed with THF. The filtrate was concentrated and purified by silica gel chromatography.

***Method C***[1]: To a solution of hydroxamic acid (10 mmol) in DCM (100 mL) was added 1,1-Carbonyldiimidazole (1.62 g, 10 mmol). The resulting solution was stirred at room temperature and for 0.5h. Then the mixture was quenched with 1 M HCl, extracted with dichloromethane, washed by water and dried over anhydrous $Na_2SO_4$. The solvent was evaporated under the reduced pressure to afford the crude product.

***Method D***: Hydroxylamine hydrochloride (2.48 g, 36 mmol) was added to a biphasic mixture of

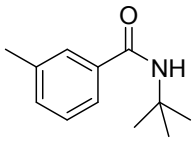
$K_2CO_3$ (8.28 g, 60 mmol) in a 2:1 mixture of EtOAc (120 mL) and $H_2O$ (60 mL). The resulting solution was cooled to 0 °C followed by dropwise addition of acyl chloride (30 mmol) dissolved in a minimum amount of EtOAc. The reaction was allowed to warm to room temperature and stirred for 2 h. EtOAc was used to extract the product from the aqueous layer. The combined organic layer was washed with water (3×50 mL), dried over $Na_2SO_4$, filtered and concentrated to afford the crude product.

**3-methyl-*N*-(methylsulfonyl) benzamide (1ab)**



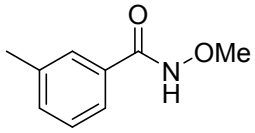
**Method A**. White solid (2.0 g, 94%), $\mathbf{R_f}$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 12.06 (br s, 1H), 7.77 (s, 1H), 7.75 – 7.67 (m, 1H), 7.59 – 7.22 (m, 2H), 3.36 (s, 3H), 2.37 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 166.5, 138.0, 133.8, 131.7, 128.9, 128.5, 125.6, 41.3, 20.8. **MS** (m/z) $[M + H]^+$: 214.25.

## *N*-(*tert*-butyl)-3-methylbenzamide (1ac)



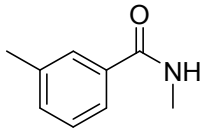
**Method A**. White solid (1.2 g, 63%), $\mathbf{R_f}$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 7.68 (s, 1H), 7.60 (s, 1H), 7.59 – 7.52 (m, 1H), 7.30 (dd, *J* = 8.8, 4.3 Hz, 2H), 2.34 (s, 3H), 1.37 (s, 9H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 166.4, 137.2, 135.9, 131.2, 127.9, 127.8, 124.5, 50.7, 28.6, 20.9. **MS** (m/z) $[M + H]^+$: 192.27.

***N*-methoxy-3-methylbenzamide (1a)**



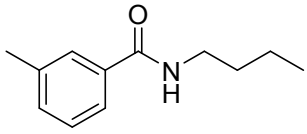
**Method B.** White solid (1.6 g, 97%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.92 (br s, 1H), 7.57 (s, 1H), 7.51 (d, *J* = 6.6 Hz, 1H), 7.38 – 7.28 (m, 2H), 3.89 (s, 3H), 2.39 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.9, 138.8, 133.0, 131.8, 128.7, 127.8, 124.0, 64.7, 21.5. **MS** (m/z) $[M + H]^+$: 166.19.

***N*,3-dimethylbenzamide (1b)**



**Method A**. White solid (1.3 g, 87%), $\mathbf{R_f}$ = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 8.37 (s, 1H), 7.64 (s, 1H), 7.63 – 7.57 (m, 1H), 7.40 – 7.20 (m, 2H), 2.77 (d, *J* = 4.6 Hz, 3H), 2.35 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 166.7, 137.5, 134.5, 131.5, 128.1, 127.6, 124.1, 26.2, 21.0. **MS** (m/z) $[M + H]^+$: 150.19.

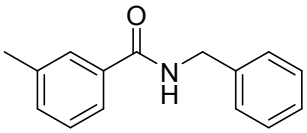
***N*-butyl-3-methylbenzamide (1c)**



**Method B.** Colourless soil (1.8 g, 94%), $\mathbf{R_f}$ = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.58 (s, 1H), 7.52 (dd, *J* = 4.8, 3.6 Hz, 1H), 7.29 (dd, *J* = 4.0, 1.7 Hz, 2H), 6.17 (br s, 1H), 3.44 (dd, *J* = 12.9, 7.1 Hz, 2H), 2.38 (s, 3H), 1.66 – 1.54 (m, 2H), 1.41 (dq, *J* = 14.5, 7.3 Hz, 2H), 0.95 (t, *J* = 7.3 Hz, 3H). **$^{13}$C**

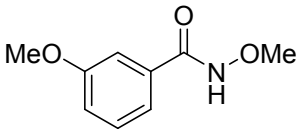
**NMR** (101 MHz, $CDCl_3$) δ 167.9, 138.5, 135.0, 132.1, 128.5, 127.8, 123.9, 39.9, 31.9, 21.5, 20.3, 13.9. **MS** (m/z) $[M + H]^+$: 192.15.

***N*-benzyl-3-methylbenzamide (1d)**



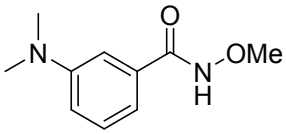
**Method B.** White solid (2.1 g, 93%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.62 (s, 1H), 7.57 (dd, *J* = 6.0, 2.6 Hz, 1H), 7.35 (d, *J* = 4.3 Hz, 4H), 7.33 – 7.27 (m, 3H), 6.53 (br s, 1H), 4.72 – 4.58 (m, 2H), 2.38 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 167.7, 138.6, 138.4, 134.5, 132.4, 128.9, 128.6, 128.0, 127.9, 127.7, 124.0, 44.2, 21.5. **MS** (m/z) $[M + H]^+$: 226.12.

***N*,3-dimethoxybenzamide (1e)**



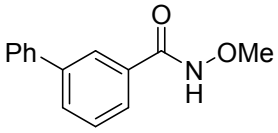
**Method B.** Colourless oil (1.0 g, 55%), $\mathbf{R_f}$ = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.75 (br s, 1H), 7.39 – 7.28 (m, 2H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.06 (dd, *J* = 8.2, 2.4 Hz, 1H), 3.89 (s, 3H), 3.84 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.6, 160.0, 133.3, 129.9, 118.9, 118.6, 112.4, 64.8, 55.6. **MS** (m/z) $[M + H]^+$: 182.19.

**3-(dimethylamino)-*N*-methoxybenzamide (1f)**



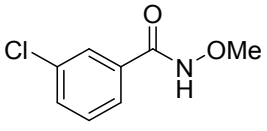
**Method B.** White solid (1.3 g, 67%), $\mathbf{R_f}$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.01 (s, 1H), 7.25 – 7.20 (m, 1H), 7.14 (s, 1H), 6.96 (d, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.2 Hz, 1H), 3.86 (d, *J* = 1.4 Hz, 3H), 2.98 (s, 3H), 2.97 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 167.3, 150.6, 132.8, 129.4, 116.0, 114.4, 111.3, 64.9, 64.7, 40.7. **MS** (m/z) $[M + H]^+$: 195.23.

***N*-methoxy-[1,1'-biphenyl]-3-carboxamide (1g)**



**Method B.** White solid (1.6 g, 70%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.32 (br s, 1H), 7.97 (s, 1H), 7.74 – 7.67 (m, 2H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.51 – 7.39 (m, 3H), 7.38 – 7.33 (m, 1H), 3.87 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.7, 142.0, 140.1, 132.4, 130.8, 129.3, 129.0 , 128.0, 127.3 , 126.0, 125.8, 64.6. **MS** (m/z) $[M + H]^+$: 228.26.

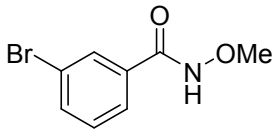
**3-chloro-*N*-methoxybenzamide (1h)**



**Method B.** White solid (1.2 g, 65%), $\mathbf{R_f}$ = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.91 (br s, 1H), 7.73 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.50 (d, *J* = 8.1 Hz, 1H), 7.42 – 7.34 (m, 1H), 3.88 (s, 3H). **$^{13}$C NMR** (101

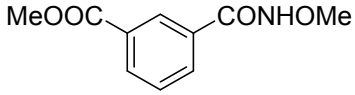
MHz, $CDCl_3$) δ 165.4, 135.1, 133.7, 132.3, 130.2, 127.5, 125.3, 64.8. **MS** (m/z) $[M + H]^+$: 186.01.

**3-bromo-*N*-methoxybenzamide (1i)**



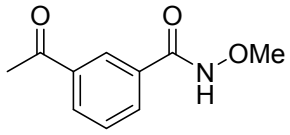
**Method B.** White solid (1.9 g, 83%), $\mathbf{R_f}$ = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.95 (s, 1H), 7.91 (d, *J* = 1.5 Hz, 1H), 7.69 (d, *J* = 7.8 Hz, 1H), 7.60 (dd, *J* = 8.0, 0.7 Hz, 1H), 7.28 – 7.23 (m, 1H), 3.83 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.1, 135.1, 133.7, 130.4, 130.3, 125.8, 122.8, 64.5. **MS** (m/z) $[M + H]^+$: 229.97.

**Methyl 3-(methoxycarbamoyl) benzoate (1j)**



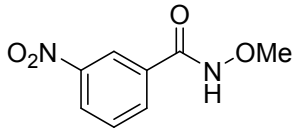
**Method B.** White solid (1.3 g, 62%), $\mathbf{R_f}$ = 0.5 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 11.98 (s, 1H), 8.34 (s, 1H), 8.10 (s, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.74 – 7.41 (m, 1H), 3.98 – 3.84 (m, 3H), 3.73 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 165.7, 163.1, 132.8, 132.1, 131.7, 129.9, 129.2, 127.8, 63.3, 52.4. **MS** (m/z) $[M + H]^+$: 210.11.

**3-acetyl-*N*-methoxybenzamide (1k)**



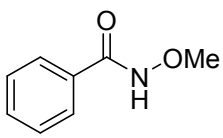
**Method B.** White solid (0.9 g, 47%), $\mathbf{R_f}$= 0.3 (EtOAc/Petroleum ether = 3:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.93 (s, 1H), 8.35 (s, 1H), 8.06 (d, *J* = 7.7 Hz, 1H), 8.02 (d, *J* = 7.7 Hz, 1H), 7.55 – 7.50 (m, 1H), 3.88 (s, 3H), 2.62 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 197.9, 160.4, 137.3, 132.4, 132.1, 131.7, 129.2, 126.8, 64.8, 26.8. **MS** (m/z) [M + H]+: 194.21.

***N*-methoxy-3-nitrobenzamide (1l)**



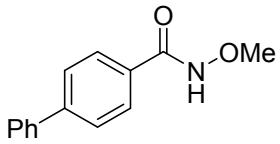
**Method B.** White solid (1.2 g, 61%), $\mathbf{R_f}$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 12.14 (s, 1H), 8.56 (s, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 7.81 – 7.77 (m, 1H), 3.75 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 161.8, 147.8, 133.6, 133.5, 130.4, 126.3, 121.8, 63.5. **MS** (m/z) $[M + H]^+$: 197.05.

***N*-methoxybenzamide (1m)**



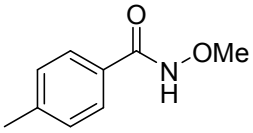
**Method B.** White solid (1.5 g, 99%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 11.72 (br s, 1H), 7.75 (d, *J* = 7.7 Hz, 2H), 7.58 – 7.52 (m, 1H), 7.50 – 7.44 (m, 2H), 3.71 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 164.1, 132.3, 131.6, 128.4, 127.0, 63.2. **MS** (m/z) $[M + H]^+$: 152.17.

***N*-methoxy-[1,1'-biphenyl]-4-carboxamide (1n)**



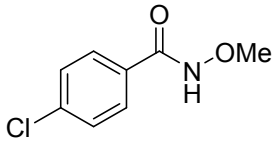
**Method B.** White solid (2.0 g, 88%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 11.81 (s, 1H), 7.85 (d, *J* = 8.1 Hz, 2H), 7.81 – 7.75 (m, 2H), 7.72 (d, *J* = 7.6 Hz, 2H), 7.52 – 7.46 (m, 2H), 7.43 – 7.36 (m, 1H), 3.73 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 163.8, 159.3, 143.1, 139.0, 131.0, 129.0, 128.1, 127.7, 126.9, 126.7, 63.3. **MS** (m/z) $[M + H]^+$: 228.26.

***N*-methoxy-4-methylbenzamide (1o)**



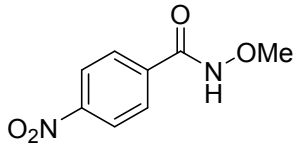
**Method B.** White solid (1.6 g, 97%), $\mathbf{R_f}$ = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.98 (br s, 1H), 7.64 (d, *J* = 7.9 Hz, 2H), 7.20 (d, *J* = 6.2 Hz, 2H), 3.85 (d, *J* = 3.4 Hz, 3H), 2.38 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.7, 142.6, 129.4, 129.1, 127.2, 64.5, 21.6. **MS** (m/z) $[M + H]^+$: 166.21.

**4-chloro-*N*-methoxybenzamide (1p)**



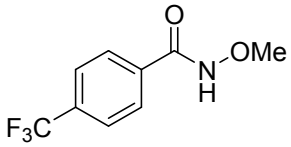
**Method B.** White solid (1.1 g, 59%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.7 (br s, 1H), 7.7 (d, *J* = 8.5 Hz, 2H), 7.4 (d, *J* = 8.5 Hz, 2H), 3.89 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.1, 138.5, 130.0, 129.1, 128.6, 64.6. **MS** (m/z) $[M + H]^+$: 186.22.

***N*-methoxy-4-nitrobenzamide (1q)**



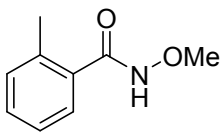
**Method B.** White solid (1.5 g, 77%), $\mathbf{R_f}$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 12.11 (br s, 1H), 8.32 (d, *J* = 8.6 Hz, 2H), 7.98 (d, *J* = 8.6 Hz, 2H), 3.73 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 162.3, 149.3, 138.0, 128.6, 123.7, 63.4. **MS** (m/z) $[M + H]^+$: 197.16.

***N*-methoxy-4-(trifluoromethyl) benzamide (1r)**



**Method B.** White solid (2.0 g, 91%), $\mathbf{R_f}$ = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 11.99 (s, 1H), 7.95 (d, *J* = 8.1 Hz, 2H), 7.84 (d, *J* = 7.9 Hz, 2H), 3.73 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 162.8, 136.1, 131.5 (q, *J* = 32.4 Hz), 128.0, 125.5 (d, *J* = 3.5 Hz), 123.8 (d, *J* = 272.5 Hz), 63.3. **MS** (m/z) $[M + H]^+$: 220.03.

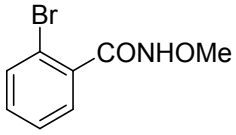
***N*-methoxy-2-methylbenzamide (1s)**



**Method B.** White solid (1.2 g, 73%), $\mathbf{R_f}$ = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.28 (br s, 1H), 7.35 – 7.28 (m, 2H), 7.24 – 7.13 (m,

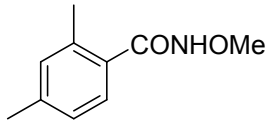
2H), 3.85 (s, 3H), 2.42 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.2, 137.0, 132.7, 131.2, 130.7, 127.2, 125.8, 64.7, 19.6. **MS** (m/z) $[M + H]^+$: 166.19.

**2-bromo-*N*-methoxybenzamide (1t)**



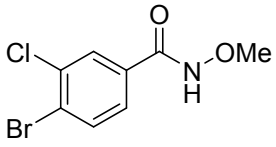

**Method B.** White solid (2.0 g, 88%), $R_f$ = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.67 (br s, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.48 (d, *J* = 7.1 Hz, 1H), 7.35 (dd, *J* = 10.7, 4.1 Hz, 1H), 7.32 – 7.27 (m, 1H), 3.91 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.4, 160.2, 133.5, 132.0, 130.0, 127.7, 120.0, 64.9. **MS** (m/z) $[M + H]^+$: 229.97.

***N*-methoxy-2,4-dimethylbenzamide (1u)**



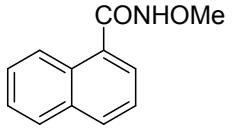

**Method B.** White solid (1.3 g, 73%), $R_f$ = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz) δ 11.38 (s, 1H), 7.22 (dd, *J* = 15.2, 7.3 Hz, 1H), 7.06 (dd, *J* = 22.8, 11.1 Hz, 2H), 3.71 (s, 3H), 2.34 (d, *J* = 10.4 Hz, 2H), 2.30 (d, *J* = 10.0 Hz, 4H). **$^{13}$C NMR** (101 MHz) δ 166.0, 139.5, 135.9, 131.2, 131.1, 127.4, 126.0, 63.2, 20.8, 19.1. **MS** (m/z) $[M + H]^+$: 180.21.

**4-bromo-3-chloro-*N*-methoxybenzamide (1v)**



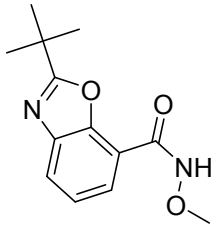

**Method B.** White solid (2.1 g, 80%), $R_f$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.6 (s, 1H), 7.9 (d, *J* = 1.9 Hz, 1H), 7.7 (d, *J* = 8.3 Hz, 1H), 7.5 (dd, *J* = 8.3, 1.9 Hz, 1H), 3.9 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 168.0, 135.3, 134.2, 132.1, 129.1, 126.9, 126.4, 64.5. **MS** (m/z) $[M + H]^+$: 263.93.

***N*-methoxy-1-naphthamide (1w)**




**Method B.** White solid (1.5 g, 75%), $R_f$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 11.73 (s, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.99 (dd, *J* = 8.0, 6.5 Hz, 1H), 7.64 – 7.58 (m, 3H), 7.57 – 7.52 (m, 1H), 3.82 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 165.5, 133.2, 131.5, 130.5, 129.9, 128.4, 127.1, 126.5, 125.8, 125.0(X2), 63.4. **MS** (m/z) $[M + H]^+$: 202.21.

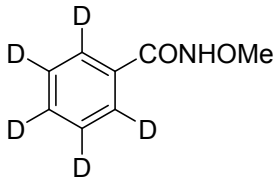
**2-(*tert*-butyl)-*N*-methoxybenzo[*d*]oxazole-7-carboxamide (1x)**




**Method B.** Yellow oil (2.0 g, 81%), $R_f$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (500 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.3 Hz, 1H), 7.85 (d, *J* = 7.5 Hz, 1H), 7.45 – 7.42 (m, 1H), 7.32 (s, 1H), 3.98 (s, 3H), 1.55 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ

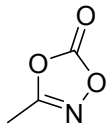
173.3, 162.0, 147.3, 141.5, 126.1, 124.7, 124.0, 114.6, 65.0, 34.4, 28.6. **MS** (m/z) $[M + H]^+$: 249.13 .

***N*-methoxybenzamide-2,3,4,5,6-$d_5$ (1m-$d_5$)**



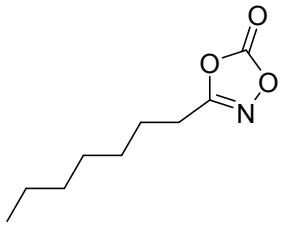

To a suspension of toluene-$d_8$ (0.5g, 5 mmol) in $H_2O$ (20 mL) was added $MgSO_4$ (1.2 g, 10 mmol) and $KMnO_4$ (3.16 g, 20 mmol), and refluxed overnight. When the starting material was consumed completely, the reaction mixture was filtered and washed with EtOAc. The filtrate was concentrated and purified by silica gel chromatography to benzoic acid-$d_5$. The title compound was given from benzoic acid-$d_5$ according to method B. Yellow oil (1.2 g, 77%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ11.74 (s, 1H), 3.71 (s, 3H). **MS** (m/z) $[M + H]^+$: 157.12.

**3-methyl-1,4,2-dioxazol-5-one (2a)**



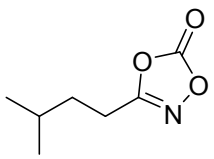
**Method C.** Colourless oil (0.7 g, 69%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 2.35 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 163.9, 154.2, 10.6.

**3-heptyl-1,4,2-dioxazol-5-one (2b)**



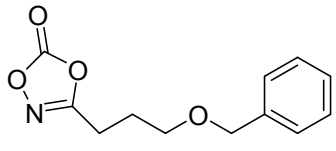
**Method C.** Colourless oil (1.3 g, 70%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 2.62 (t, *J* = 7.5 Hz, 2H), 1.75 – 1.68 (m, 2H), 1.36 – 1.26 (m, 8H), 0.90 – 0.87 (m, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.9, 154.4, 31.6, 28.8, 28.7, 24.9, 24.7, 22.7, 14.2.

**3-isopentyl-1,4,2-dioxazol-5-one (2c)**



**Method C and D.** Colourless oil (1.3 g, 83%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 2.67 – 2.58 (m, 2H), 1.69 – 1.63 (m, 1H), 1.59 (dt, *J* = 7.3, 2.7 Hz, 2H), 0.94 (d, *J* = 6.3 Hz, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 167.1, 154.4, 33.2, 27.5, 22.9, 22.1.

**3-(3-(benzyloxy)propyl)-1,4,2-dioxazol-5-one (2d)**

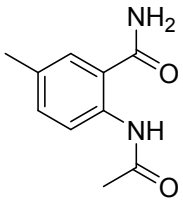


**Method C and D**. Yellow oil (2.0 g, 85%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ7.37 – 7.33 (m, 2H), 7.33 – 7.28 (m, 3H), 4.50 (s, 2H), 3.56 (t, *J* = 5.7 Hz, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.06 – 1.90 (m, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 166.7, 154.3, 138.0, 128.6, 128.0, 127.8, 73.3, 68.1, 24.9, 22.2.

**General procedure for Co(III)-catalyzed C($sp^2$)–H amidation of benzamides to afford quinazolinone derivatives**:

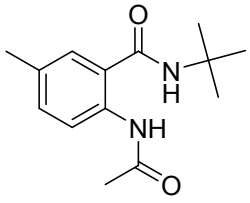
A mixture of [Cp*Co(CO)$I_2$] (5.0 mol%), $AgNTf_2$ (10 mol%), $Zn(OAc)_2$ (1 eq) and benzamide (0.2 mmol), and dioxazolone (0.24 mmol) in 2.0 mL DCE was heated to 120°C, and stirred overnight. Then the reaction mixture was cooled to room temperature and filtered, the filtrate was concentrated and the residue was purified with silica gel to afford quinazolinone derivatives.

**2-acetamido-5-methylbenzamide (3aa')**



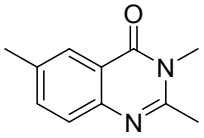
White solid (4.5 mg, 12%), $\mathbf{R_f}$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.50 (br s, 1H), 8.68 (s, 1H), 7.80 (s, 1H), 7.75 (d, *J* = 7.1 Hz, 1H), 7.41 – 7.33 (m, 2H), 2.95 (d, *J* = 4.8 Hz, 3H), 2.42 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 168.5, 155.1, 138.8, 133.9, 132.5, 128.8, 128.5, 125.1, 26.5, 21.5. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{10}H_{13}O_2N_2$, 193.0972, found: 193.0973. **mp** 112−113 °C.

**2-acetamido-*N*-(*tert*-butyl)-5-methylbenzamide (3ca')**



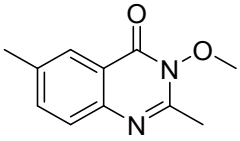
White solid (31 mg, 63%), $\mathbf{R_f}$ = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 10.71 (s, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 7.19 (d, *J* = 8.5 Hz, 1H), 7.14 (s, 1H), 6.14 (s, 1H), 2.29 (s, 3H), 2.14 (s, 3H), 1.46 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 169.0, 168.9, 136.7, 132.6, 132.2, 127.0, 122.2, 121.6, 52.1, 28.8, 25.3, 20.9. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{14}H_{21}O_2N_2$, 249.1603, found: 249.1598. **mp** 148−150 °C.

**2,3,6-trimethylquinazolin-4(3*H*)-one (3da)**



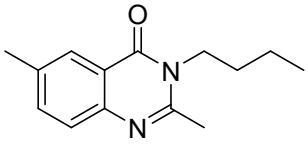
White solid (14 mg, 37%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.54 – 7.42 (m, 2H), 3.60 (s, 3H), 2.59 (s, 3H), 2.45 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.4, 153.7, 145.3, 136.6, 135.8, 126.5, 126.3, 120.0, 31.1, 23.7, 21.4. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{11}H_{13}O_1N_2$, 189.1028, found: 189.1022. **mp** 100−101 °C.

**3-methoxy-2,6-dimethylquinazolin-4(3*H*)-one (3ea)**



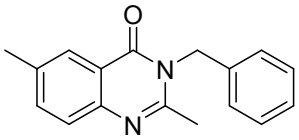
White solid (1.8 g, 88%), $\mathbf{R_f}$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.70 – 7.42 (m, 2H), 4.11 (s, 3H), 2.62 (s, 3H), 2.48 (s, 3H). **$^{13}$C NMR** (100 MHz, $CDCl_3$) δ 158.0, 152.6, 144.6, 136.9, 136.0, 127.0, 126.1, 122.4, 64.2, 21.4, 20.1. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{11}H_{13}N_2O_2$, 205.0972, found: 205.0971. **mp** 126−127°C.

**3-butyl-2,6-dimethylquinazolin-4(3*H*)-one (4)**



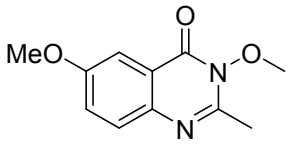
Colourless oil (28 mg, 60%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.02 (s, 1H), 7.61 – 7.40 (m, 2H), 4.28 – 3.88 (m, 2H), 2.64 (s, 3H), 2.46 (s, 3H), 1.70 (ddd, *J* = 12.5, 8.7, 6.6 Hz, 2H), 1.52 – 1.39 (m, 2H), 0.99 (t, *J* = 7.3 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.1, 153.5, 145.1, 136.7, 135.8, 126.3 (X2), 120.3, 44.6, 30.9, 23.1, 21.4, 20.4, 13.9. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{14}H_{19}O_1N_2$, 231.1499, found: 231.1492.

**3-benzyl-2,6-dimethylquinazolin-4(3*H*)-one (5)**



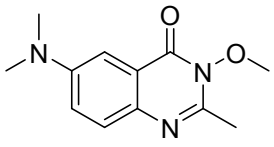
White solid (35 mg, 67%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.10 (s, 1H), 7.61 – 7.52 (m, 2H), 7.35 – 7.25 (m, 3H), 7.22 – 7.17 (m, 2H), 5.40 (s, 2H), 2.54 (s, 3H), 2.49 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.5, 153.9, 145.3, 136.9, 136.1 (X2), 129.1, 127.8, 126.7 (X2), 126.6, 120.2, 47.3, 23.5, 21.4. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{17}H_{17}O_1N_2$, 265.1342 found: 265.1335. **mp** 100−101 °C.

**3,6-dimethoxy-2-methylquinazolin-4(3*H*)-one (6)**



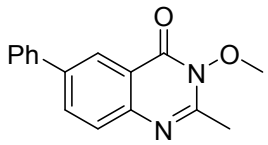
White solid (34 mg, 78%), $\mathbf{R_f}$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 2.7 Hz, 1H), 7.80 (d, *J* = 8.9 Hz, 1H), 7.56 (dd, *J* = 9.0, 2.7 Hz, 1H), 4.35 (s, 3H), 4.15 (s, 3H), 2.85 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 158.2, 157.7, 151.0, 141.1, 128.6, 124.8, 123.4, 106.0, 64.1, 55.9, 19.8. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{11}H_{13}N_2O_3$, 221.0926, found: 221.0921. **mp** 147−149 °C.

**6-(dimethylamino)-3-methoxy-2-methylquinazolin-4(3*H*)-one (7)**



Yellow solid (35 mg, 75%), $\mathbf{R_f}$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 9.0 Hz, 1H), 7.33 (d, *J* = 3.0 Hz, 1H), 7.19 (dd, *J* = 9.0, 3.0 Hz, 1H), 4.09 (s, 3H), 3.04 (s, 6H), 2.58 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 158.1, 149.0, 149.0, 137.6, 127.9, 123.5, 120.5, 105.7, 64.1, 40.7(X2), 19.8. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{12}H_{16}N_3O_2$, 234.1237, found: 234.1235. **mp** 115−116 °C.

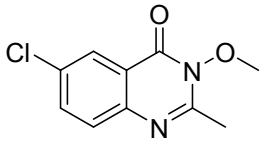
**3-methoxy-2-methyl-6-phenylquinazolin-4(3*H*)-one (8)**



Yellow solid (50 mg, 94%), $\mathbf{R_f}$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.45 (s, 1H), 7.95 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.69 – 7.64 (m, 3H), 7.47 – 7.42 m, 2H), 7.38 – 7.7.34 (m, 1H), 4.11 (s, 3H), 2.63 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.9, 153.3, 145.6, 139.4 (X2), 133.3, 129.1, 128.0, 127.6, 127.2, 124.5,

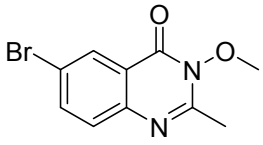
122.9, 64.2, 20.1. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{16}H_{15}N_2O_2$, 267.1128, found: 267.1126. **mp** 129−130 °C.

**6-chloro-3-methoxy-2-methylquinazolin-4(3*H*)-one (9)**



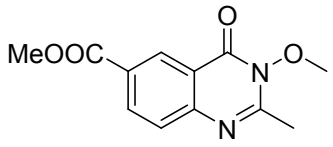
White solid (44 mg, 98%), $\mathbf{R_f}$ = 0.7 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 1.6 Hz, 1H), 7.61 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.53 (d, *J* = 8.7 Hz, 1H), 4.08 (s, 3H), 2.60 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 156.8, 153.8, 145.0, 134.8, 132.4, 128.8, 125.9, 123.7, 64.2, 20.0. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{10}H_{10}ClN_2O_2$, 225.0425, found: 225.0427. **mp** 144−146 °C.

**6-bromo-3-methoxy-2-methylquinazolin-4(3*H*)-one (10)**



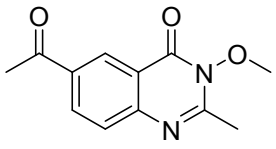
White solid (53 mg, 99%), $\mathbf{R_f}$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.33 (s, 1H), 7.87 – 7.61 (m, 1H), 7.46 (d, *J* = 8.7 Hz, 1H), 4.08 (s, 3H), 2.59 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 156.7, 154.0, 145.3, 137.6, 129.1, 129.0, 124.0, 120.0, 64.3, 20.1. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{10}H_{10}BrN_2O_2$, 268.9920, found: 268.9918. **mp** 148–150 °C.

**Methyl 3-methoxy-2-methyl-4-oxo-3,4-dihydroquinazoline-6-carboxylate (11)**



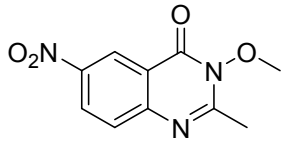
Yellow solid (43 mg, 87%), $\mathbf{R_f}$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.31 (d, *J* = 8.5 Hz, 1H), 7.63 (d, *J* = 8.5 Hz, 1H), 4.11 (s, 3H), 3.94 (s, 3H), 2.64 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.9, 157.4, 155.7, 149.3, 134.8, 129.2, 128.1, 127.4, 122.4, 64.3, 52.5, 20.3. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{12}H_{13}N_2O_4$, 249.0875, found: 249.0870. **mp** 172−174 °C.

**6-acetyl-3-methoxy-2-methylquinazolin-4(3*H*)-one (12)**



Yellow solid (40 mg, 87%), $\mathbf{R_f}$ = 0.5 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.71 (s, 1H), 8.24 (d, *J* = 8.5 Hz, 1H), 7.61 (d, *J* = 8.6 Hz, 1H), 4.10 (s, 3H), 2.64 (s, 3H), 2.62 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 196.5, 157.5, 155.8, 149.5, 134.7, 133.1, 128.1, 127.7, 122.2, 64.3, 26.7, 20.2. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{12}H_{13}N_2O_3$, 233.0921, found: 233.0917. **mp** 150–152 °C.

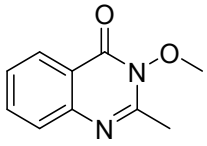
**3-methoxy-2-methyl-6-nitroquinazolin-4(3*H*)-one (13)**



Yellow solid (47 mg, 99%), $\mathbf{R_f}$ = 0.7 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.08 (d, *J* = 2.5 Hz, 1H), 8.48 (dd, *J* = 9.0, 2.6 Hz, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 4.14 (s, 3H), 2.68 (s, 3H). **$^{13}$C NMR** (101 MHz,

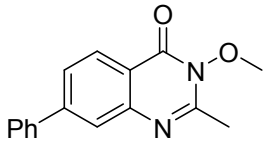
$CDCl_3$) δ 157.2, 156.7, 150.4, 145.4, 128.9, 128.5, 123.4, 122.8, 64.5, 20.4. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{10}H_{10}N_3O_4$, 236.0666, found: 236.0664. **mp** 150–152 °C.

**3-methoxy-2-methylquinazolin-4(3*H*)-one (14)**



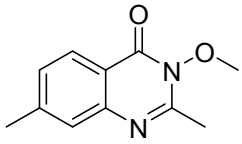
White solid (31 mg, 81%), $\mathbf{R_f}$ = 0.5 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.21 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.72 – 7.66 (m, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.40 (dd, *J* = 11.2, 3.9 Hz, 1H), 4.08 (s, 3H), 2.60 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.8, 153.4, 146.5, 134.4, 127.1, 126.7, 126.5, 122.6, 64.2, 20.1. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{10}H_{11}N_2O_2$, 191.0820, found: 191.0815. **mp** 88–89 °C.

**3-methoxy-2-methyl-7-phenylquinazolin-4(3*H*)-one (15)**



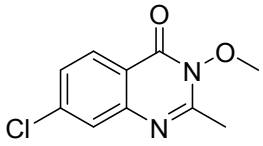
White solid (48 mg, 91%), $\mathbf{R_f}$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 8.3 Hz, 1H), 7.77 (s, 1H), 7.60 (d, *J* = 7.7 Hz, 3H), 7.44 – 7.39 (m, 2H), 7.37 – 7.32 (m, 1H), 4.07 (s, 3H), 2.59 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.5, 153.7, 147.0, 146.7, 139.3, 129.0, 128.4, 127.3, 127.0, 125.4, 124.9, 121.2, 64.1, 20.0. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{16}H_{15}N_2O_2$, 267.1128, found: 267.1125. **mp** 107−108 °C.

**3-methoxy-2,7-dimethylquinazolin-4(3*H*)-one (16)**



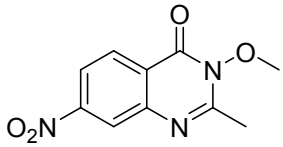
Yellow solid (30 mg, 74%), $\mathbf{R_f}$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.2 Hz, 1H), 7.31 (s, 1H), 7.23 – 7.05 (m, 1H), 4.03 (s, 3H), 2.53 (s, 3H), 2.39 (s, 3H). **$^{13}$C NM**R (101 MHz, $CDCl_3$) δ 157.6, 153.3, 146.4, 145.2, 127.9, 126.7, 126.3, 120.0, 64.0, 21.8, 19.9. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{11}H_{13}O_2N_2$, 205.0972, found: 205.0972. **mp** 132–133 °C.

**7-chloro-3-methoxy-2-methylquinazolin-4(3*H*)-one (17)**



Yellowsolid (38 mg, 85%), $\mathbf{R_f}$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.16 (d, *J* = 8.6 Hz, 1H), 7.61 (d, *J* = 1.8 Hz, 1H), 7.38 (dd, *J* = 8.6, 1.9 Hz, 1H), 4.10 (s, 3H), 2.62 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.3, 154.9, 147.4, 140.7, 128.2, 127.2, 126.8, 121.1, 64.3, 20.1. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{10}H_{10}ClN_2O_2$, 225.0425, found: 225.0428. **mp** 168−170 °C.

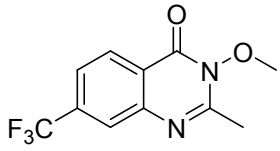
**3-methoxy-2-methyl-7-nitroquinazolin-4(3*H*)-one (18)**



Yellow solid (46 mg, 98%), $\mathbf{R_f}$ = 0.5 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.41 (d, *J* = 2.0 Hz, 1H), 8.38 (d, *J* = 8.8 Hz, 1H),

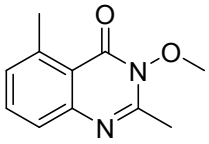
8.17 (dd, *J* = 8.8, 1.7 Hz, 1H), 4.13 (s, 3H), 2.66 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 156.7, 156.1, 151.6, 146.9, 128.6, 126.7, 122.8, 120.2, 64.4, 20.2. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{10}H_{10}N_3O_4$, 236.0666, found: 236.0664. **mp** 172−174 °C.

**3-methoxy-2-methyl-7-(trifluoromethyl) quinazolin-4(3*H*)-one (19)**



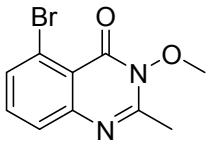
Yellow solid (49 mg, 94%), $R_f$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.37 (d, *J* = 8.4 Hz, 1H), 7.93 (s, 1H), 7.65 (d, *J* = 8.4 Hz, 1H), 4.13 (s, 3H), 2.67 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.1, 155.2, 146.4, 136.2 (q, *J* = 33.0 Hz, -$CF_3$), 128.0, 125.0, 124.8 (q, *J* = 4.0 Hz), 122.6 (q, *J* = 3.4 Hz), 122.1, 64.4, 20.1. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{11}H_{10}F_3N_2O_2$, 259.0696, found: 259.0689. **mp** 102– 103 °C.

**3-methoxy-2,5-dimethylquinazolin-4(3*H*)-one (20)**



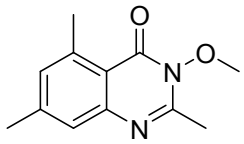
White solid (27 mg, 65%), $R_f$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.52 – 7.7.47 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 1H), 7.12 (d, *J* = 7.3 Hz, 1H), 4.04 (s, 3H), 2.82 (s, 3H), 2.55 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 158.3, 153.0, 147.9, 141.2, 133.4, 129.0, 125.2, 120.9, 63.9, 22.7, 19.9. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{11}H_{13}N_2O_2$, 205.0972, found: 205.0971. **mp** 111−112 °C.

**5-bromo-3-methoxy-2-methylquinazolin-4(3*H*)-one (21)**



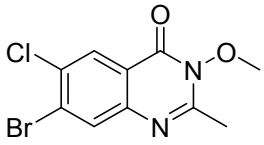
Yellow solid (48 mg, 90%), $R_f$ = 0.4 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.65 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.54 (dd, *J* = 8.2, 1.0 Hz, 1H), 7.49 – 7.42 (m, 1H), 4.08 (s, 3H), 2.58 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.4, 156.1, 154.1, 148.7, 134.1, 133.1, 127.2, 121.2, 64.1, 20.1. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{10}H_{10}BrN_2O_2$, 268.9933, found: 268.9920. **mp** 140−141 °C.

**3-methoxy-2,5,7-trimethylquinazolin-4(3*H*)-one (22)**



White solid (40 mg, 91%), $R_f$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.18 (s, 1H), 6.95 (s, 1H), 4.03 (s, 3H), 2.77 (s, 3H), 2.53 (s, 3H), 2.35 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 158.2, 153.0, 148.0, 144.3, 140.9, 130.5, 125.0, 118.4, 63.9, 22.6, 21.6, 19.9. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{12}H_{15}N_2O_2$, 219.1128, found: 219.1128. **mp** 172−174 °C.

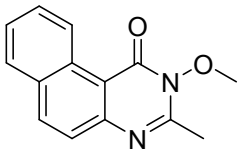
**3-methoxy-2,7-dimethylquinazolin-4(3*H*)-one (23)**



White solid (60 mg, 99%), $R_f$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.30 (s, 1H), 7.96 (d, *J* = 1.5 Hz, 1H), 4.11 (s, 3H), 2.64 (d,

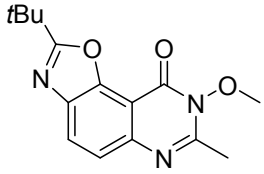
*J* = 0.7 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 156.5, 155.1, 145.4, 133.0, 132.3, 129.6, 127.5, 122.6, 64.4, 20.2. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{10}H_9BrClN_2O_2$, 302.9530, found: 302.9533. **mp** 208−210 °C.

**2-methoxy-3-methylbenzo[*f*]quinazolin-1(2*H*)-one (24)**



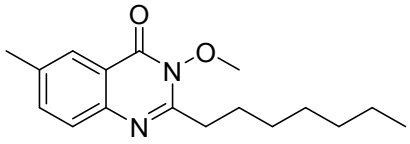
White solid (48 mg, 99%), **$R_f$** = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 9.78 (d, *J* = 8.6 Hz, 1H), 8.03 – 7.93 (m, 1H), 7.79 (d, *J* = 8.0 Hz, 1H), 7.67 (ddd, *J* = 8.5, 7.1, 1.3 Hz, 1H), 7.62 – 7.45 (m, 2H), 4.11 (s, 3H), 2.61 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.9, 153.9, 148.3, 135.6, 131.3, 130.8, 128.7, 128.2, 126.6(X2), 125.6, 115.6, 64.0, 19.9. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{14}H_{13}N_2O_2$, 241.0972, found: 241.0970. **mp** 115−116 °C.

**2-(*tert*-butyl)-8-methoxy-7-methyloxazolo[5,4-*f*] quinazolin-9(8*H*)-one (25)**



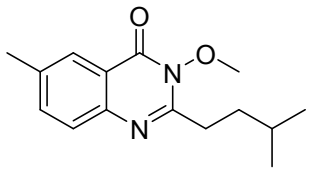
White solid (44 mg, 77%), **$R_f$** = 0.3 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.00 (d, *J* = 8.7 Hz, 1H), 7.57 (d, *J* = 8.7 Hz, 1H), 4.15 (s, 3H), 2.65 (s, 3H), 1.55 (s, 9H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 175.6, 154.8, 152.9, 147.5, 144.6, 139.8, 125.8, 123.6, 109.2, 64.4, 34.6, 28.7, 20.1. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{15}H_{18}N_3O_3$, 288.1352, found: 288.1343. **mp** 128–129 °C.

**2-heptyl-3-methoxy-6-methylquinazolin-4(3*H*)-one (26)**



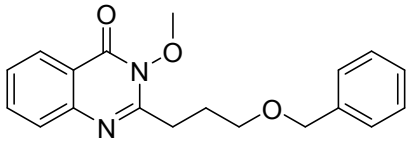
White solid (52 mg, 90%), **$R_f$** = 0.7 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.05 (s, 1H), 7.59 – 7.52 (m, 2H), 4.10 (s, 3H), 2.86 (t, *J* = 7.7 Hz, 2H), 2.47 (s, 3H), 1.89 – 1.77 (m, 2H), 1.49 – 1.40 (m, 2H), 1.39 – 1.26 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.3, 158.1, 155.8, 136.8, 135.9, 127.1, 126.1, 122.3, 64.5, 32.8, 31.8, 29.5, 29.1, 27.0, 22.8, 21.4, 14.2. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{17}H_{25}N_2O_2$, 289.1918, found: 289.1911. **mp** 61–62 °C.

**2-isopentyl-3-methoxy-6-methylquinazolin-4(3*H*)-one (27)**



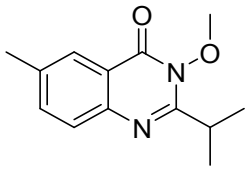
White solid (47 mg, 91%), **$R_f$** = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 0.8 Hz, 1H), 7.52 – 7.42 (m, 2H), 4.05 (s, 3H), 2.79 (dd, *J* = 10.1, 5.6 Hz, 2H), 2.40 (s, 3H), 1.71 – 1.61 (m, 3H), 0.97 – 0.90 (m, 6H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.9, 155.6, 144.4, 136.5, 135.7, 127.0, 125.9, 122.1, 64.2, 35.6, 30.8, 28.0, 22.4, 21.2. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{15}H_{21}N_2O_2$,261.1598, found:261.1597. **mp** 46−47 °C.

**2-(3-(benzyloxy)propyl)-3-methoxyquinazolin-4(3*H*)-one (28)**



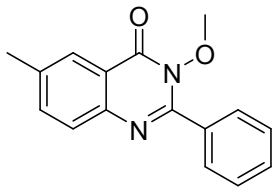
Yellow oil (61 mg, 94%), $\mathbf{R_f}$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.75 – 7.71 (m, 1H), 7.67 – 7.63 (m, 1H), 7.47 – 7.42 (m, 1H), 7.33 – 7.30 (m, 4H), 7.28 (dd, *J* = 6.2, 2.4 Hz, 1H), 4.52 (s, 2H), 4.10 (s, 3H), 3.65 (t, *J* = 6.0 Hz, 2H), 3.04 – 3.00 (m, 2H), 2.22 – 2.17 (m, 2H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ158.1, 155.9, 146.6, 138.5, 134.4, 128.5, 127.7 (X2), 127.4, 126.7, 126.5, 122.6, 73.0, 69.3, 64.4, 29.4, 26.5. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{19}H_{21}N_2O_3$, 325.1547, found: 325.1561.

**2-isopropyl-3-methoxy-6-methylquinazolin-4(3*H*)-one (29)**



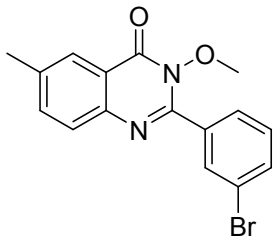
Colourless oil (26 mg, 56%), $\mathbf{R_f}$ = 0.8 (EtOAc/Petroleum ether = 1:1).**$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.04 (s, 1H), 7.58 (d, *J* = 8.3 Hz, 1H), 7.53 (dd, *J* = 8.3, 1.6 Hz, 1H), 4.10 (s, 3H), 3.33 (m, 1H), 2.47 (s, 3H), 1.38 (s, 3H), 1.36 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.5, 158.3, 144.6, 136.6, 135.8, 127.4, 126.0, 122.2, 64.6, 30.4, 21.4, 20.8. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{13}H_{17}N_2O_2$, 233.1285, found: 233.1280.

**3-methoxy-2,6-dimethylquinazolin-4(3*H*)-one (32)**



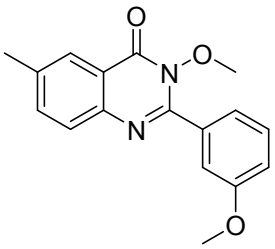
White solid (43 mg, 81%), $\mathbf{R_f}$ = 0.7 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.13 (s, 1H), 7.89 (dd, *J* = 7.9, 1.6 Hz, 2H), 7.69 (d, *J* = 8.3 Hz, 1H), 7.60 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.55 – 7.49 (m, 3H), 3.76 (s, 3H), 2.52 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 158.2, 152.5, 144.7, 137.5, 136.2, 132.2, 130.8, 129.5, 128.5, 127.9, 126.3, 122.5, 64.2, 21.5. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{16}H_{15}N_2O_2$, 267.1128, found: 267.1128. **mp** 111–112 °C.

**2-(3-bromophenyl)-3-methoxy-6-methylquinazolin-4(3*H*)-one (33)**



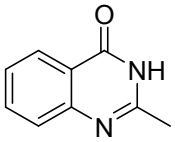
White solid (36 mg, 52%), $\mathbf{R_f}$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.07 – 8.04 (m, 1H), 7.89 – 7.76 (m, 1H), 7.66 (d, *J* = 8.2 Hz, 2H), 7.59 (dd, *J* = 8.4, 1.8 Hz, 1H), 7.40 – 7.34 (m, 1H), 3.78 (s, 3H), 2.51 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 157.9, 150.8, 144.5, 137.9, 136.2, 134.0, 133.9, 132.5, 129.9, 128.2, 128.0, 126.3, 122.5, 122.4, 64.3, 21.5. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{16}H_{14}BrN_2O_2$, 345.0233, found: 345.0228. **mp** 118−119°C.

**3-methoxy-2-(3-methoxyphenyl)-6-methylquinazolin-4(3*H*)-one (34)**



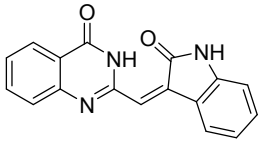
White solid (40 mg, 68%), $\mathbf{R_f}$ = 0.6 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 7.67 (d, *J* = 8.3 Hz, 1H), 7.58 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.46 (d, *J* = 7.7 Hz, 1H), 7.40 (dd, *J* = 9.8, 6.0 Hz, 2H), 7.14 – 6.99 (m, 1H), 3.86 (s, 3H), 3.77 (s, 3H), 2.50 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.4, 158.1, 152.3, 144.6, 137.5, 136.1, 133.4, 129.5, 127.9, 126.2, 122.5, 121.8, 116.9, 114.7, 64.2, 55.6, 21.4. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{17}H_{17}N_2O_3$, 297.1234, found: 297.1229. **mp** 113−114 °C.

**2-methylquinazolin-4(3*H*)-one (35)**



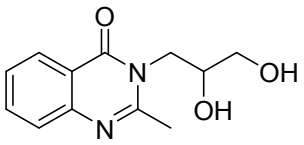
To a suspension of **14** (38 mg, 0.2 mmol) in THF (5 mL) and MeOH (5 mL) was added Pd/C (10%, 320 mg) and stirred at room temperature under a $H_2$ atmosphere. After the starting material was consumed completely, the reaction mixture was filtered and washed with MeOH. The filtrate was concentrated and purified by silica gel chromatography to afford **35** (30 mg, 94%) as white solid. $\mathbf{R_f}$ = 0.3 (EtOAc/Petroleum ether = 3:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 12.18 (br s, 1H), 8.07 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.79 – 7.73 (m, 1H), 7.56 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.1 (m, 1H), 2.34 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 161.7, 154.2, 149.0, 134.2, 126.6, 125.8, 125.6, 120.6, 21.4. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_9H_9N_2O_1$, 161.0713, found: 161.0709. **mp** 198–200 °C.

**(*Z*)-2-((2-oxoindolin-3-ylidene)methyl)quinazolin-4(3*H*)-one (36)**



To a suspension of **35** (160 mg, 1 mmol) in AcOH (5 mL) was added isatin (147 mg, 1 mmol) and stirred at 120°C until the starting material was consumed completely, the reaction mixture was filtered and washed with MeOH to obtain compound **36**[2] as orange solid (260 mg, 90%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 14.40 (br s, 1H), 11.49 (br s, 1H), 8.18 (d, *J* = 7.8 Hz, 1H), 7.95 (d, *J* = 7.5 Hz, 1H), 7.92 – 7.86 (m, 1H), 7.79 (d, *J* = 7.7 Hz, 1H), 7.67 – 7.56 (m, 2H), 7.40 – 7.34 (m, 1H), 7.13 – 7.07 (m, 1H), 6.95 – 6.90 (m, 1H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 168.8, 160.8, 150.4, 148.9, 141.6, 134.7, 134.3, 131.7, 130.0, 128.0 (X2), 126.0, 123.3, 122.6, 122.0, 121.5, 110.6. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{17}H_{12}O_2N_3$, 290.0931, found: 290.0924. **mp** >220 °C.

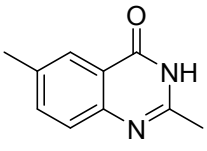
**3-(2,3-dihydroxypropyl)-2-methylquinazolin-4(3*H*)-one (37)**



To a magnetically stirred mixture of **35** (160 mg, 1 mmol) and glycidol (74 mg, 1 mmol) was added $Zn(ClO_4)_2{\cdot}6H_2O$ (7.5 mg, 2 mol%) under

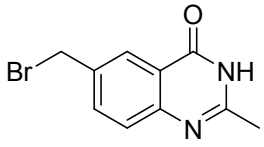
neat condition at room temperature and the stirring was continued for 30 minutes. The crude reaction mixture was purifed by flash column chromatography to obtain **37** [3] as white solid (222 mg, 95%). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 8.09 (dd, *J* = 7.9, 0.9 Hz, 1H), 7.79 – 7.75 (m, 1H), 7.57 (d, *J* = 8.1 Hz, 1H), 7.48 – 7.44 (m, 1H), 5.09 – 5.04 (m, 1H), 4.79 – 4.74 (m, 1H), 4.33 – 4.24 (m, 1H), 3.85 (dd, *J* = 14.8, 5.5 Hz, 2H), 3.44 (d, *J* = 4.3 Hz, 2H), 2.65 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 161.4, 156.2, 147.2, 134.1, 126.4, 126.0, 126.0, 120.1, 68.8, 64.2, 47.7, 23.6. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{12}H_{15}N_2O_3$, 235.1085, found:235.1077. **mp** 142–144 °C.

**2,6-dimethylquinazolin-4(3*H*)-one (39)**



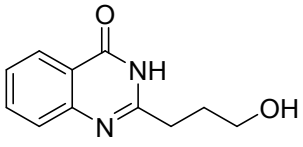
To a suspension of **3ea** (40.8 mg, 0.2 mmol) in THF (5 mL) and MeOH (5 mL) was added Pd/C (10%, 320 mg) and stirred at room temperature under $H_2$ atmosphere overnight. When the starting material was consumed completely, the reaction mixture was filtered and washed with MeOH. The filtrate was concentrated and purified by silica gel chromatography to afford **39** (32 mg, 92%) as white solid. $\mathbf{R_f}$ = 0.3 (EtOAc/Petroleum ether = 3:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 12.09 (s, 1H), 7.86 (s, 1H), 7.58 (dd, *J* = 8.3, 1.8 Hz, 1H), 7.46 (d, *J* = 8.3 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 161.6, 153.3, 146.9, 135.5, 135.3, 126.4, 125.0, 120.4, 21.3, 20.7. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{10}H_{11}N_2O_1$, 175.0871, found: 175.0866. **mp** 205–206 °C.

**6-(bromomethyl)-2-methylquinazolin-4(3*H*)-one (40)**



A mixture of **39** (52.2 mg, 0.3 mmol), *N*-bromosuccinimide (59 mg, 0.33 mmol) and benzoyl peroxide (9 mg, 0.036 mmol) in 20 mL chloroform was stirred at 60°C under infrared heat lamp, and the white precipitate was formed after 2h. The reaction mixture was cooled by ice bath and then filtered. The filter cake was washed with chloroform three times (3 × 15 mL) and dried, compound **40** was obtained as white solid (48 mg, 64%).[4] $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 2:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 12.30 (br s, 1H), 8.15 (d, *J* = 1.8 Hz, 1H), 7.82 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.61 – 7.50 (m, 1H), 4.86 (s, 2H), 2.36 (s, 3H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 161.3, 155.1, 148.3, 135.8, 135.4, 126.8, 126.3, 120.5, 33.8, 21.4. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{10}H_{10}BrN_2O$, 252.9982, found: 252.9971. **mp** >220 °C.

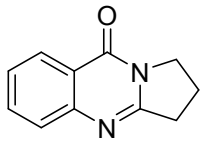
**2-(3-hydroxypropyl)quinazolin-4(3*H*)-one (42)**



To a suspension of **28** (64 mg, 0.2 mmol) in THF (5 mL) and MeOH (5 mL) was added Pd/C (10%, 320 mg) and stirred at room temperature under

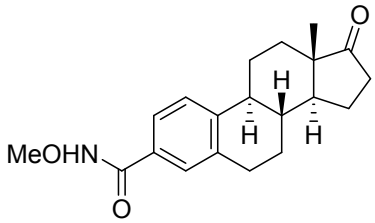
$H_2$ atmosphere overnight. When the starting material was consumed completely, the reaction mixture was filtered and washed with MeOH. The filtrate was concentrated and purified by silica gel chromatography. White solid (37 mg, 91%), $\mathbf{R_f}$ = 0.4 (DCM/MeOH = 25:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 8.07 (dd, *J* = 7.9, 1.1 Hz, 1H), 7.78 – 7.73 (m, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 7.47 – 7.41 (m, 1H), 3.47 (t, *J* = 6.4 Hz, 2H), 2.67 – 2.61 (m, 2H), 1.92 – 1.84 (m, 2H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 161.9, 157.6, 148.9, 134.3, 126.7, 125.9, 125.7, 120.8, 60.1, 31.3, 29.8. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{11}H_{13}N_2O_2$, 205.0972, found: 205.0973.

**2,3-dihydropyrrolo[2,1-*b*]quinazolin-9(1*H*)-one (43)**



To a solution of **42** (204 mg, 1.0 mmol) and triphenylphosphine (340 mg, 1.3 mmol) in THF (3 mL), a solution of DEAD (190 mg, 1.1 mmol) in THF (2 mL) was added in a dropwise fashion, and the reaction mixture was stirred for 3h. The reaction mixture was concentrated, and the residue was purified by silica gel. White solid (167 mg, 90%), $\mathbf{R_f}$ = 0.2 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, DMSO-*d6*) δ 8.11 (d, *J* = 7.9 Hz, 1H), 7.80-7.74 (m, 1H), 7.60 (d, *J* = 8.1 Hz, 1H), 7.50 – 7.44 (m, 1H), 4.06 (t, *J* = 7.2 Hz, 2H), 3.08 (t, *J* = 7.9 Hz, 2H), 2.16 (dd, *J* = 14.9, 7.6 Hz, 2H). **$^{13}$C NMR** (101 MHz, DMSO-*d6*) δ 160.4, 160.0, 149.0, 134.1, 126.6, 125.9, 125.7, 120.1, 46.3, 31.8, 18.9. **HRMS** (ESI): m/z (M + $H^+$) calcd for $C_{11}H_{11}N_2O$, 187.0866, found: 187.0867. **mp** 106–107 °C.

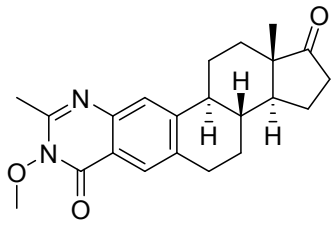
**(8*R*,9*S*,13*S*,14*S*)-*N*-methoxy-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[a]phenanthrene-3-carboxamide (46)**



Ethyl (8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthrene-3-carboxylate (326 mg, 1 mmol)[5] was added to a biphasic mixture of LiOH (72 mg, 3 mmol) in a 2:1 mixture of THF (9 mL) and $H_2O$ (4.5 mL). The resulting solution was stirred at room temperature overnight. The solvent was evaporated under the reduced pressure and EtOAc was used to extract the product from the aqueous layer. The combined organic layer was washed with water (3×50 mL), dried over $Na_2SO_4$, filtered and concentrated to afford the corresponding carboxylic acid (200 mg, 67%), which was used to produce the title compound according to method B as white solid (203 mg, 62%), $\mathbf{R_f}$ = 0.5 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.67 (br s, 1H), 7.55 – 7.45 (m, 2H), 7.35 – 7.33 (m, 1H), 3.89 (s, 3H), 2.99 – 2.89 (m, 2H), 2.52 (dd, *J* = 18.7, 8.5 Hz, 1H), 2.44 (dd, *J* = 9.9, 2.3 Hz,

1H), 2.36 – 2.30 (m, 1H), 2.17 (dd, *J* = 18.5, 9.3 Hz, 1H), 2.09 – 2.02 (m, 2H), 1.98 (dd, *J* = 9.6, 1.9 Hz, 1H), 1.60 – 1.46 (m, 6H), 0.92 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 220.7, 144.4, 137.4, 131.1, 128.0, 125.9, 125.4, 124.2, 64.8, 50.6, 48.0, 44.7, 38.0, 36.0, 31.7, 29.4, 26.4, 25.7, 21.7, 14.0. **MS** (m/z) $[M + H]^+$: 328.19.

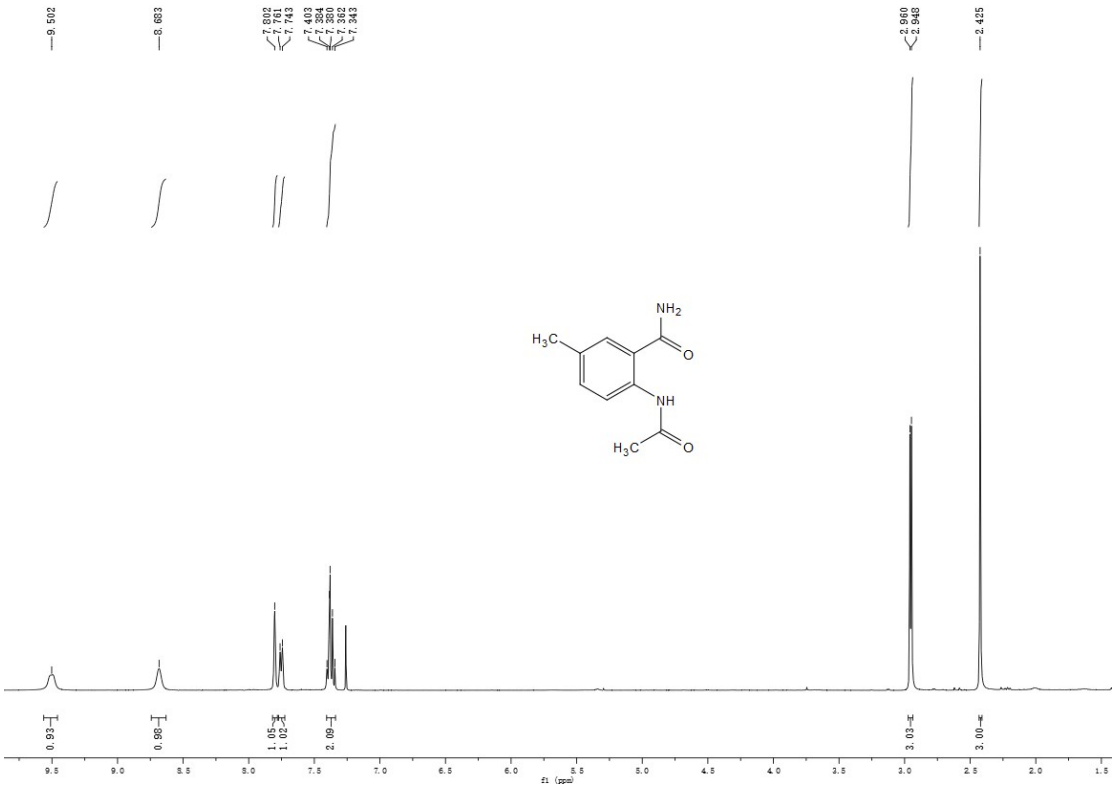
**(3a*S*,3b*R*,11b*S*,13a*S*)-8-methoxy-9,13a-dimethyl-3,3a,3b,4,5,8,11b,12,13,13a-decahydro-1*H*-cyclopenta[5,6]naphtho[2,1-*g*]quinazoline-1,7(2*H*)-dione (47)**



White solid (67 mg, 92%), **$R_f$** = 0.5 (EtOAc/Petroleum ether = 1:1). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.97 (s, 1H), 7.57 (s, 1H), 4.10 (s, 3H), 3.11 – 2.97 (m, 2H), 2.63 (s, 3H), 2.56 – 2.49 (m, 1H), 2.43 – 2.36 (m, 1H), 2.17 (d, *J* = 10.1 Hz, 1H), 2.10 – 1.96 (m, 4H), 1.64 – 1.50 (m, 6H), 0.91 (s, 3H). **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 220.4, 157.4, 153.6, 148.5, 143.3, 136.8, 126.2, 122.6, 119.9, 64.5, 50.8, 48.0, 44.9, 37.6, 35.9, 31.6, 29.1, 26.3, 25.6, 21.8, 19.5, 13.9. **HRMS** (ESI): m/z ($M + H^+$) calcd for $C_{22}H_{27}N_2O_3$, 367.2027, found: 367.2016. **mp** 168–170 °C.

**Reference:**


1. Y. Park, K. T. Park, J. G. Kim, S. Chang, *J. Am. Chem. Soc.*, 2015, **137**, 4534
2. Uehata K, Kimura N, Hasegawa K, et al. *J. Nat. Prod.,* 2013, **76**, 2034.
3. Kumar D, Jadhavar P S, Nautiyal M, et al. *RSC Adv*., 2015, **5**, 30819
4. Zhan X, Xu Y, Qi Q, et al. *Chem. Biodivers.*, 2018, **15**, e1700513.
5. Liang A, Han S, Wang L, et al. *Adv. Synth. Catal*., 2015, **357**, 3104.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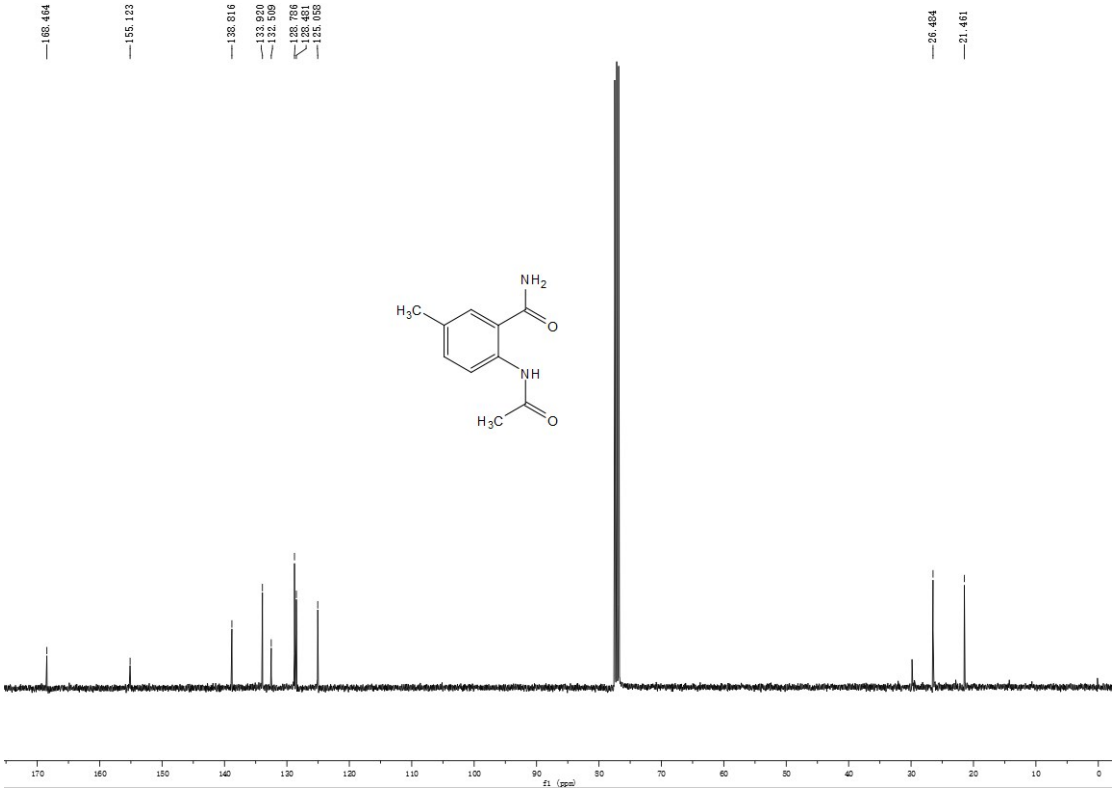
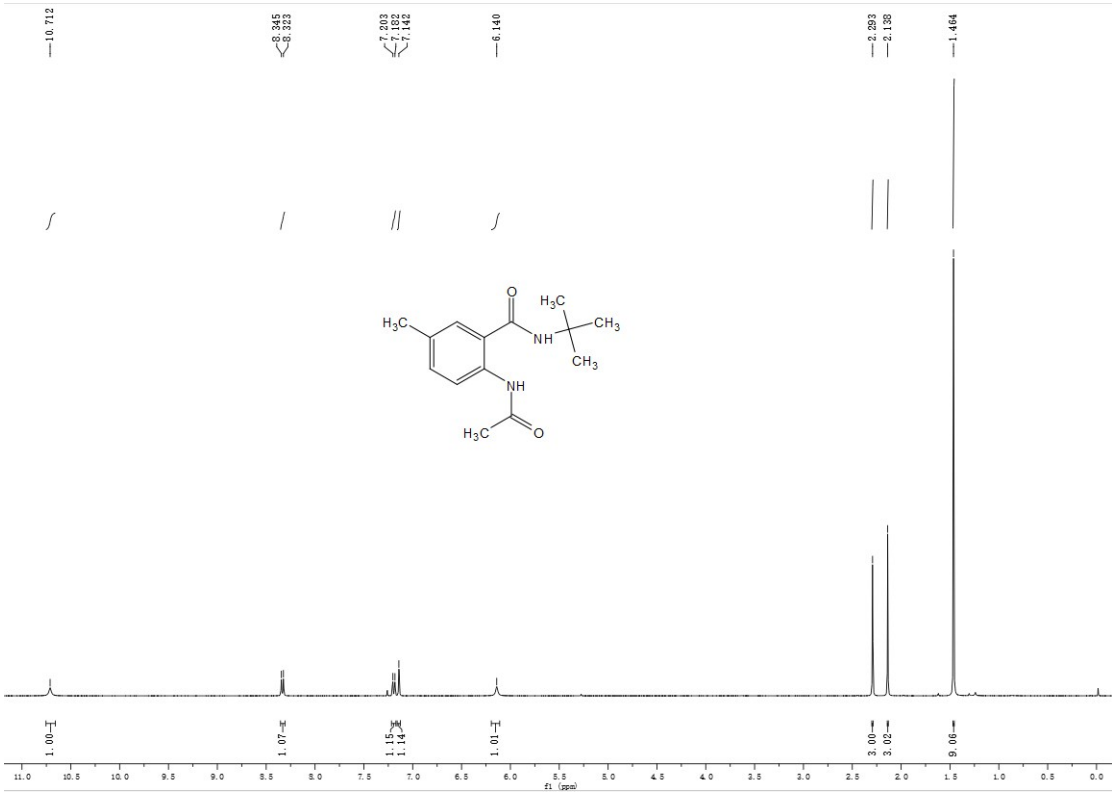
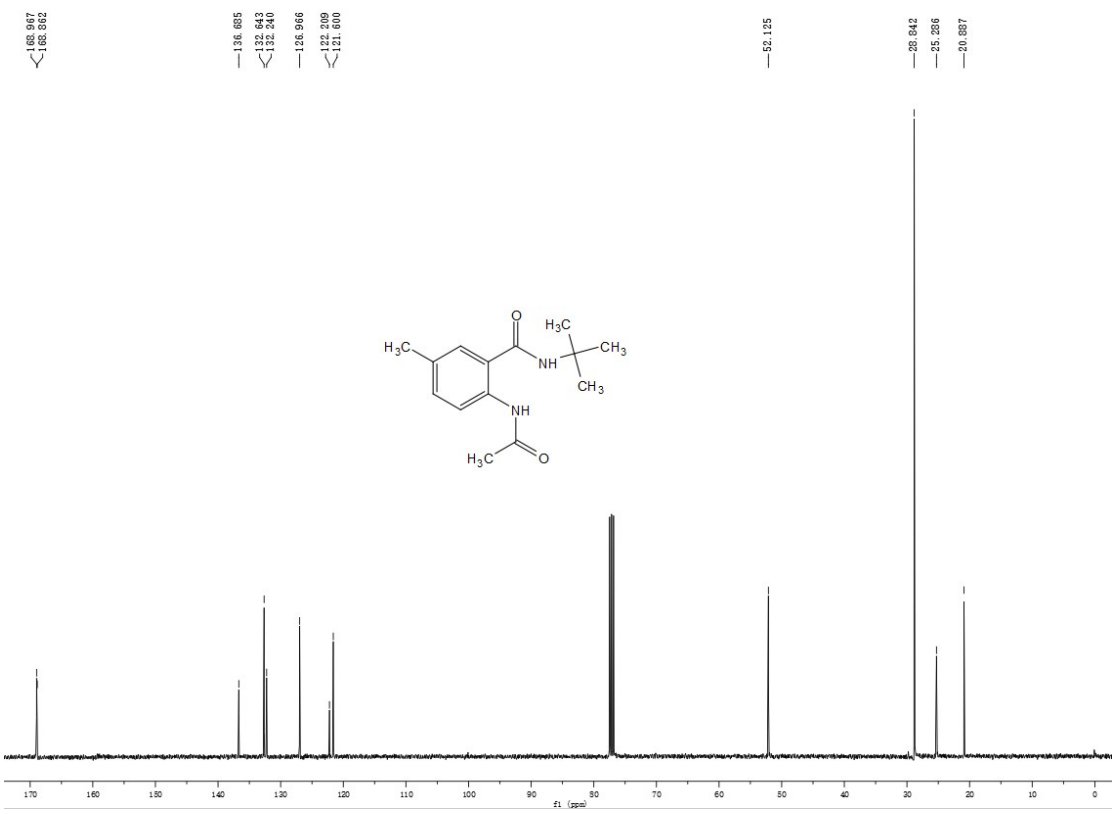
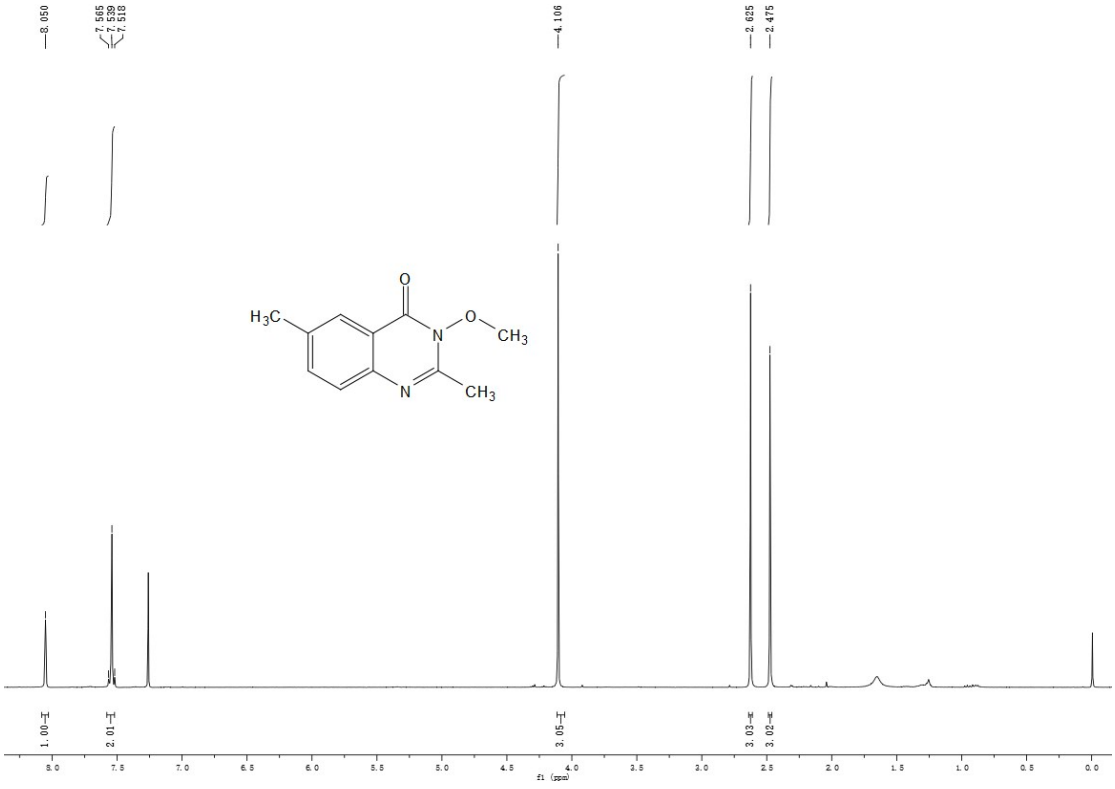
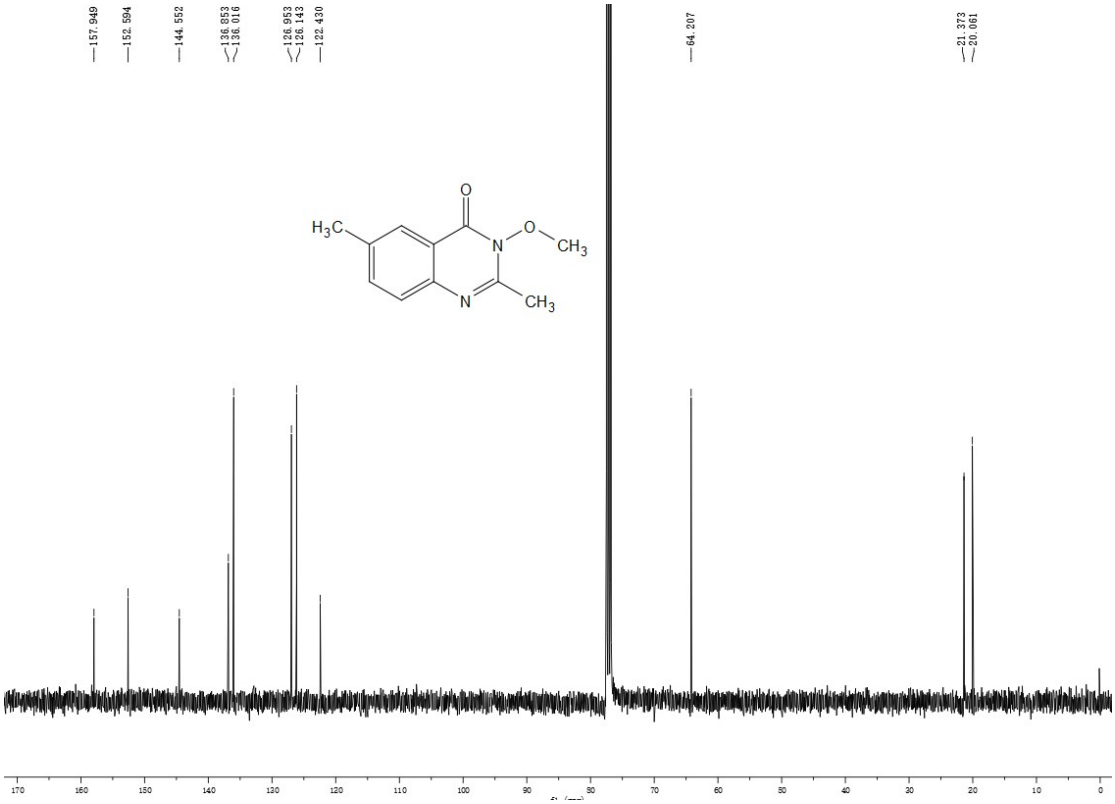
8.683
7.802
7.761
7.743
7.403
7.384
7.380
7.362
7.343
2.960
2.948
2.425
NH2
H3C
O
NH
H3C
O
0.93
0.98
1.05
1.02
2.09
3.03
3.00
f1 (ppm)

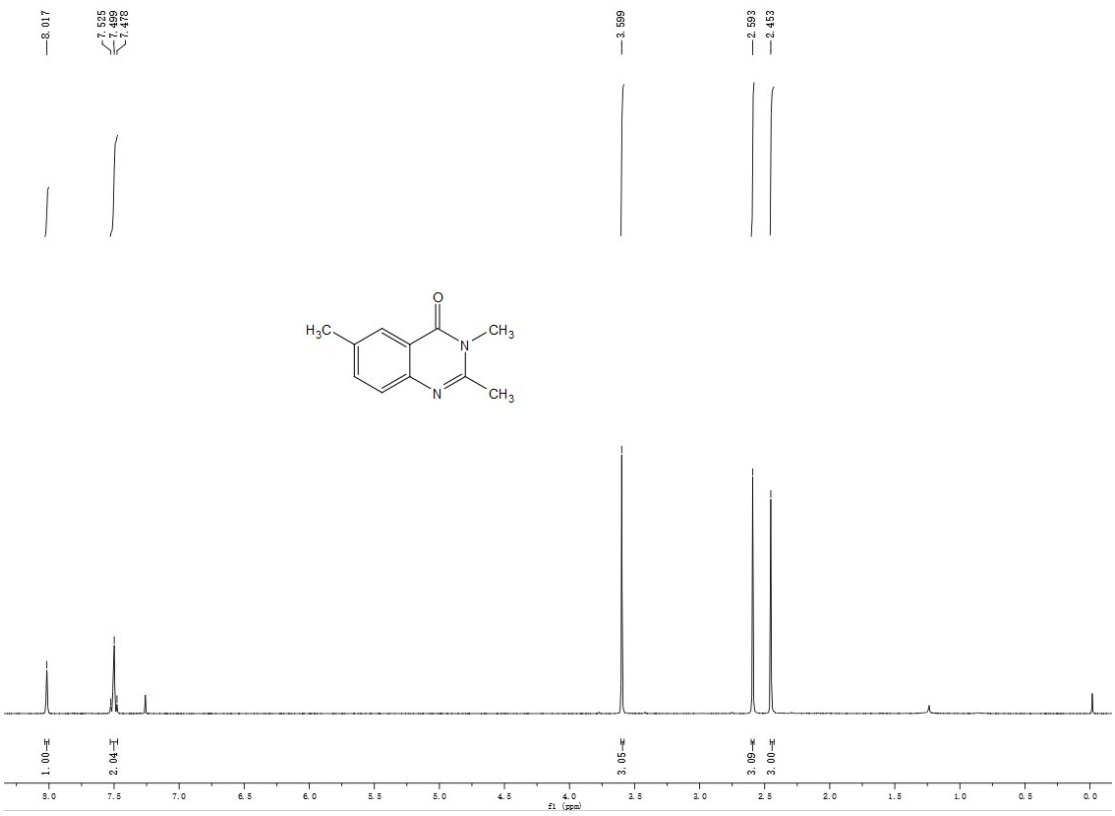

168.464
155.123
138.816
133.920
132.509
128.786
128.481
125.058
26.494
21.461
NH2
H3C
O
NH
H3C
O
f1 (ppm)

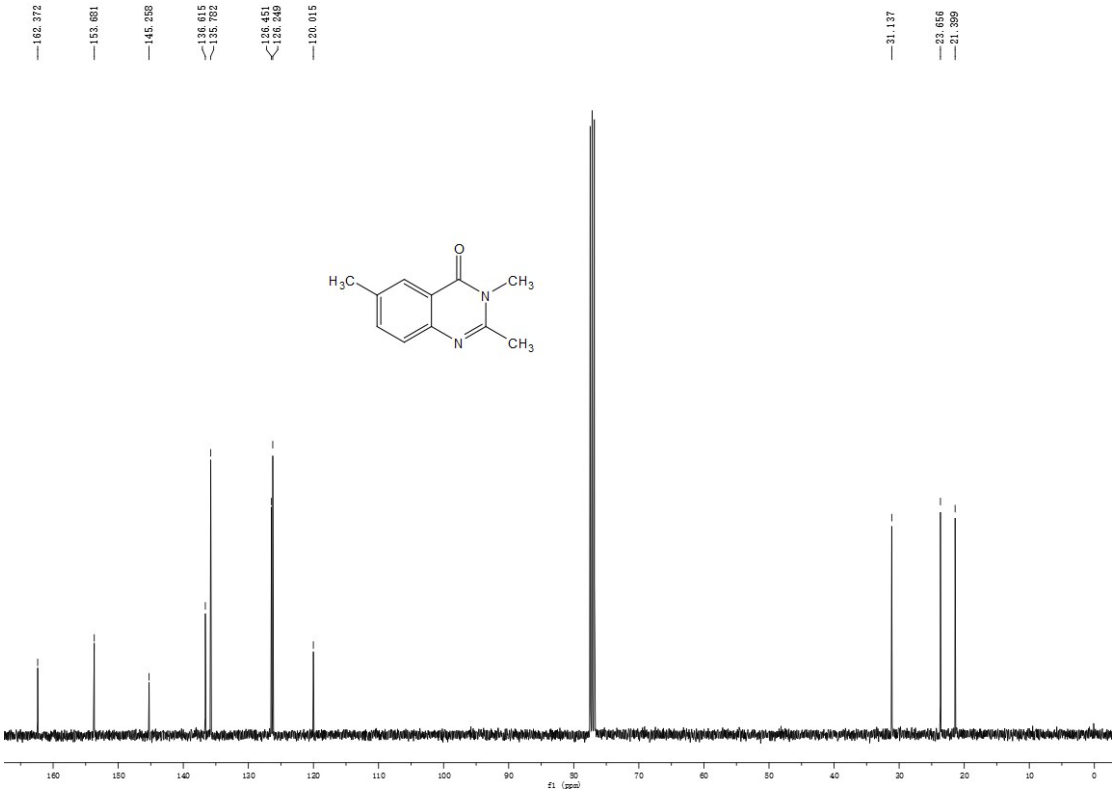

10.712
8.345
8.323
7.203
7.192
7.142
6.140
2.293
2.138
1.464
1.00
1.07
1.15
1.14
1.01
3.00
3.02
9.06
f1 (ppm)


168.967
168.862
136.685
132.643
132.240
126.966
122.209
121.600
52.125
28.842
25.286
20.887
f1 (ppm)


8.050
7.565
7.539
7.518
4.106
2.625
2.475
O
H3C
N
O
CH3
N
CH3
1.00
2.01
3.05
3.03
3.02
f1 (ppm)


157.949
152.594
144.552
136.853
136.016
126.953
126.143
122.430
64.207
21.373
20.061
O
H3C
N
O
CH3
N
CH3


8.017
7.595
7.490
7.478
3.599
2.593
2.453
O
H3C
N
CH3
CH3
1.00
2.04
3.05
3.09
3.00
f1 (ppm)


162.372
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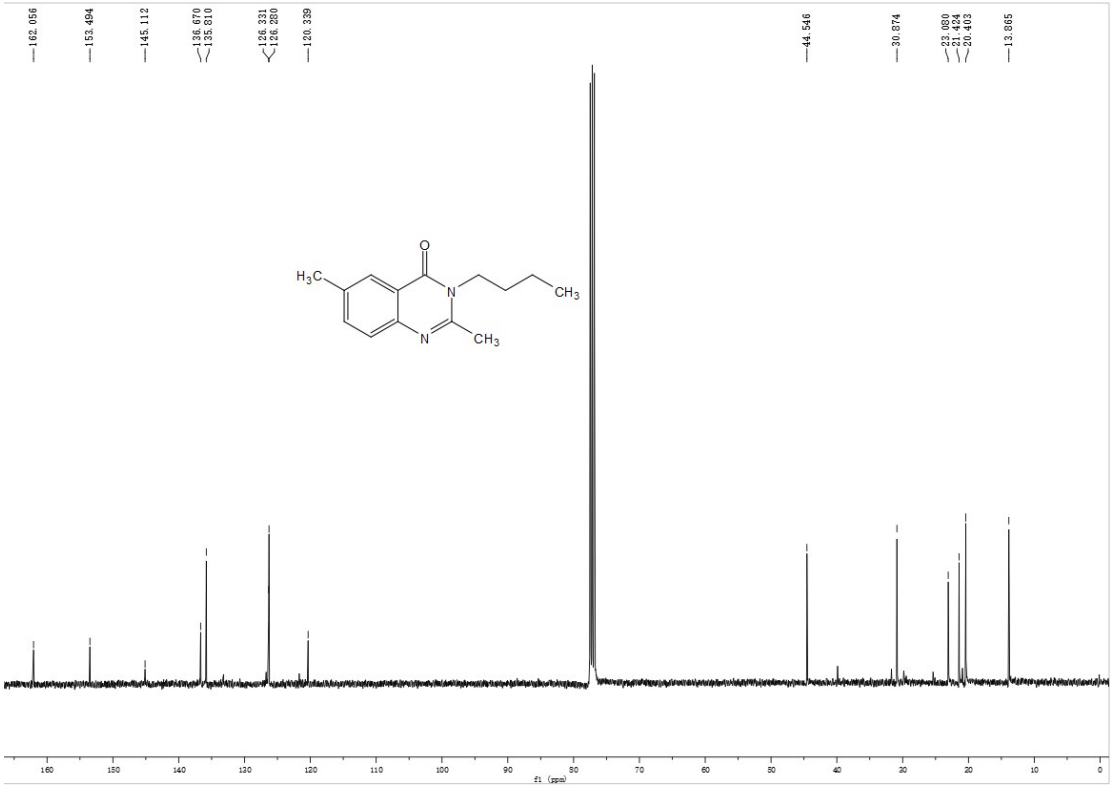
145.258
136.615
135.782
126.451
126.249
120.015
31.137
23.656
21.399
O
H3C
N
CH3
CH3
f1 (ppm)


8.025
7.543
7.519
7.499
4.096
4.077
4.057
2.642
2.463
1.745
1.727
1.722
1.707
1.699
1.688
1.682
1.668
1.499
1.480
1.461
1.442
1.424
1.405
1.004
0.986
0.968
O
H3C
N
CH3
N
CH3
1.00
2.05
2.03
3.03
3.04
2.04
2.08
3.01
f1 (ppm)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153.494
145.112
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126.280
120.339
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23.080
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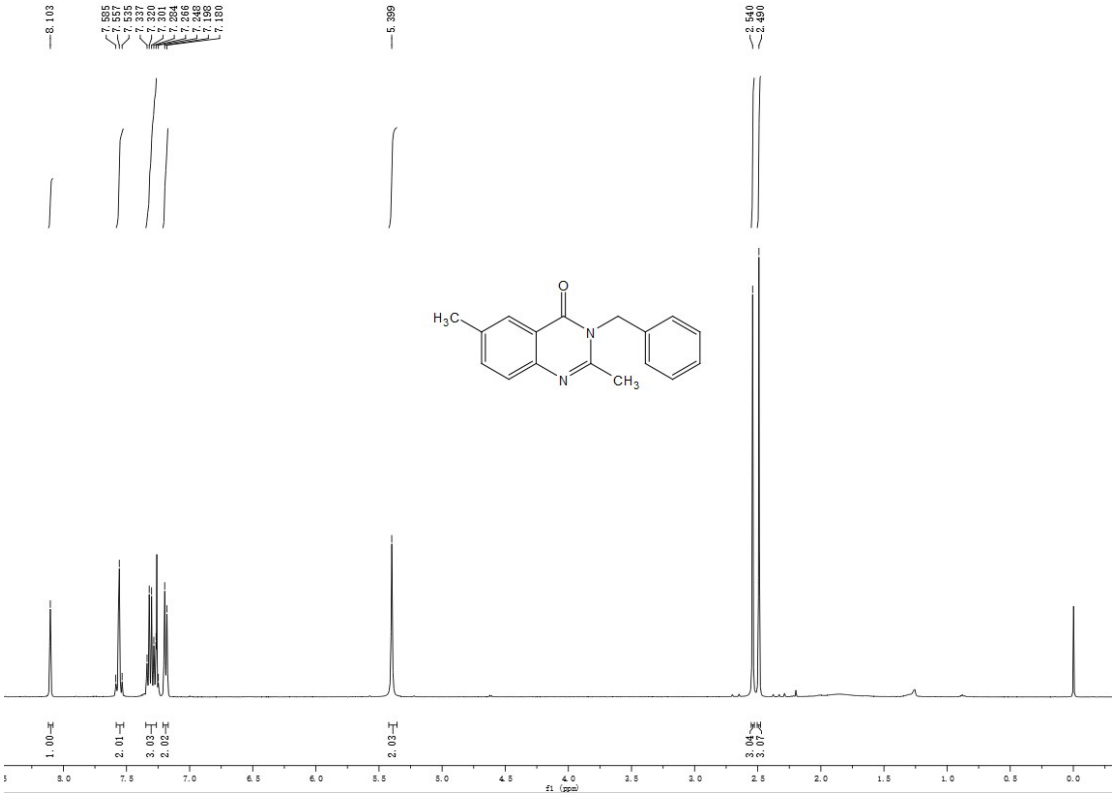
20.403
13.865
O
H3C
N
CH3
N
CH3
f1 (ppm)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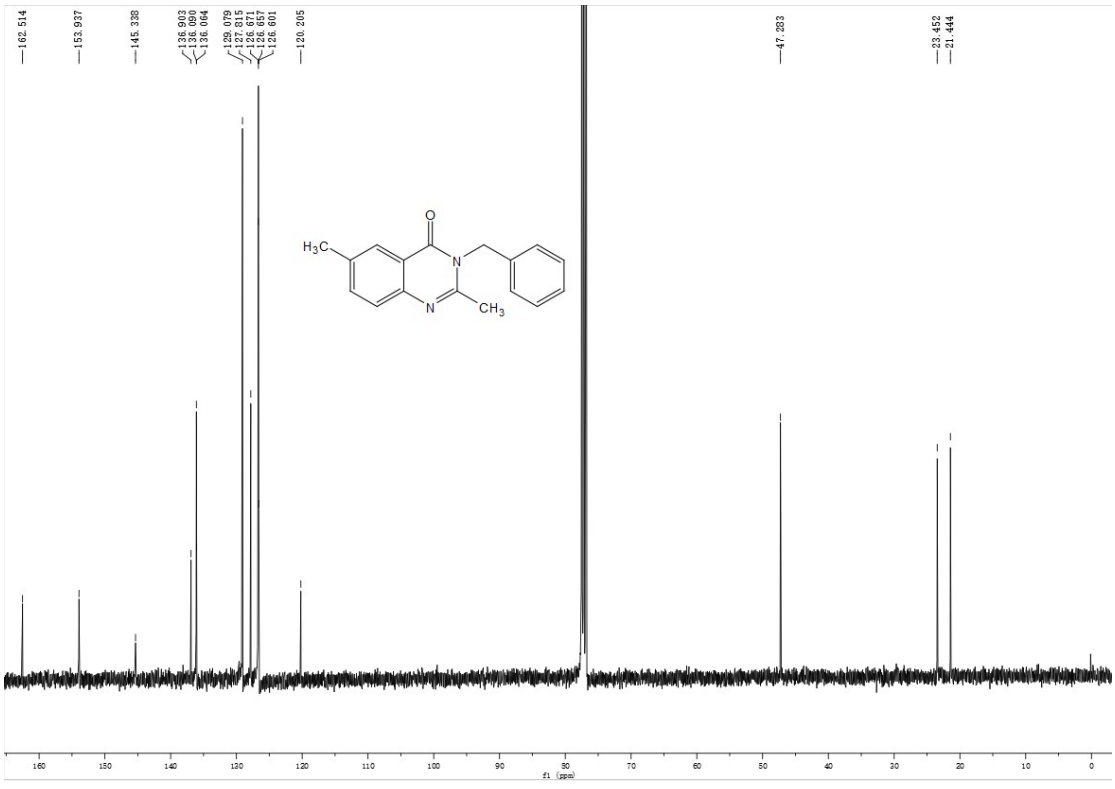
7.557
7.555
7.337
7.320
7.301
7.284
7.196
7.180
5.399
2.540
2.490
O
N
N
H3C
CH3
1.00
2.01
3.03
2.02
2.03
3.04
3.07
f1 (ppm)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153.937
145.338
136.903
136.090
136.064
129.079
127.815
126.671
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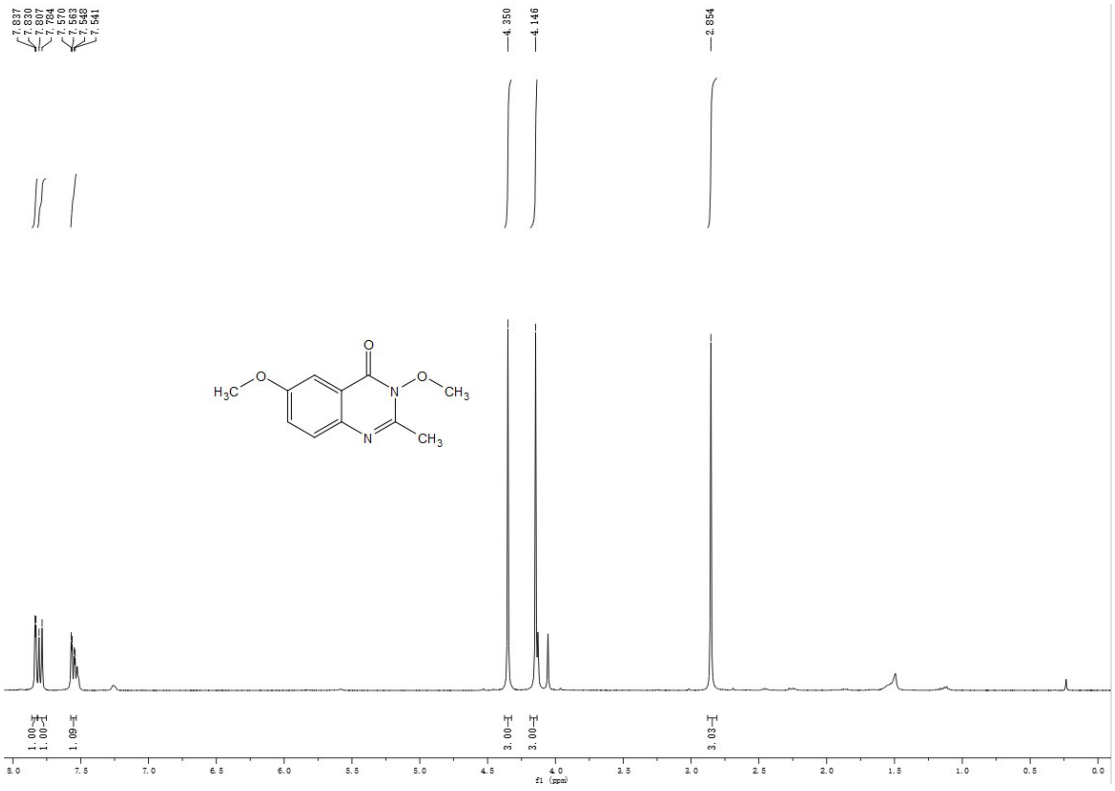
126.601
120.205
47.283
23.452
21.444
O
N
N
H3C
CH3
f1 (ppm)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7.830
7.807
7.784
7.570
7.548
7.543
7.541
4.350
4.146
2.854
O
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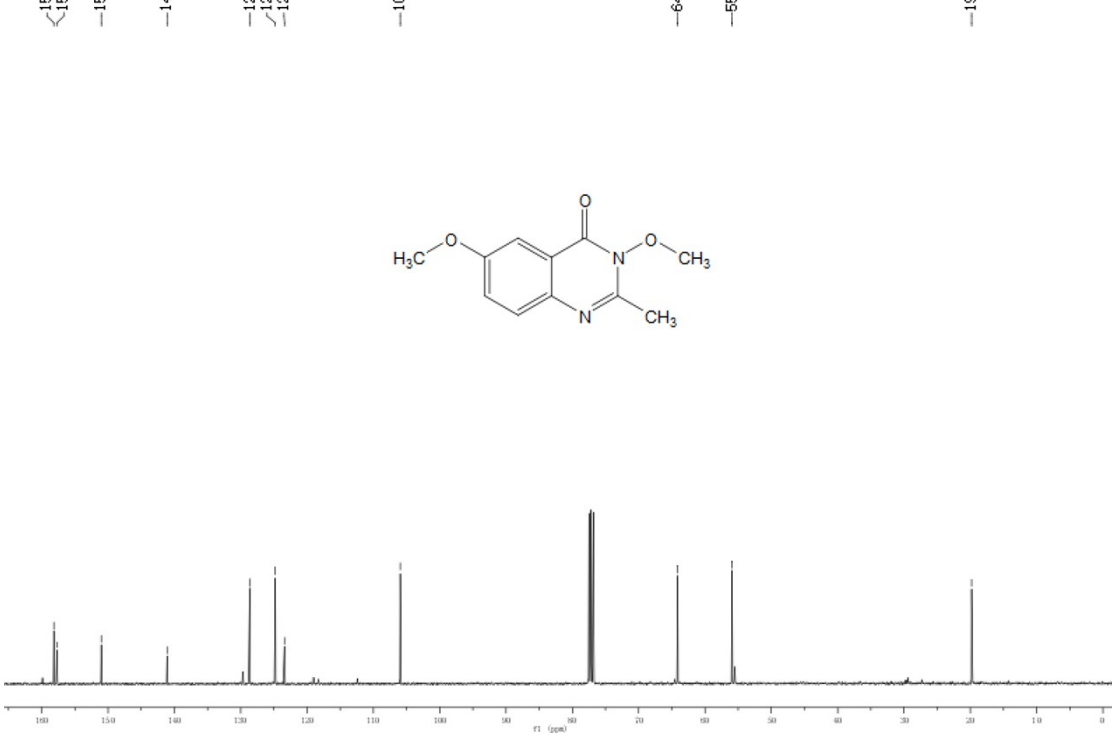
O
N
O
CH3
N
CH3
1.00
1.00
1.09
3.00
3.00
3.03
f1 (ppm)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128.639
124.791
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55.919
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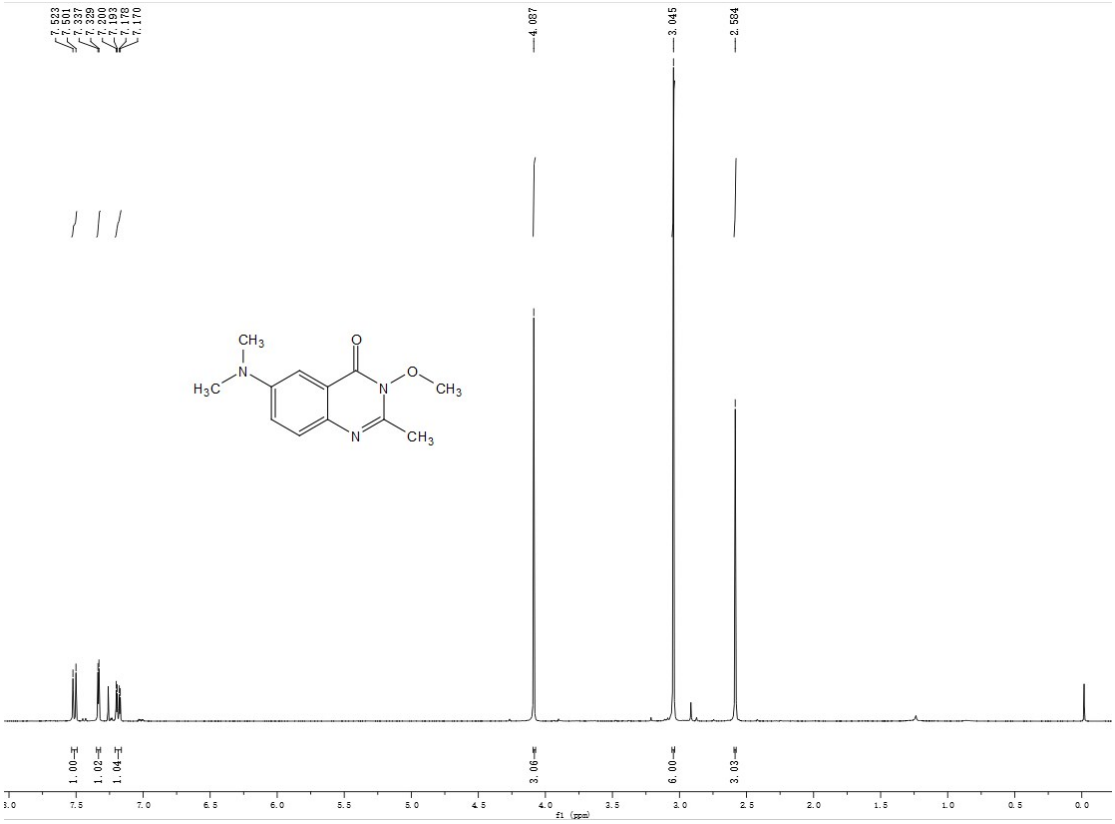
O
H3C
O
N
O
CH3
N
CH3
f1 (ppm)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7.337
7.329
7.200
7.193
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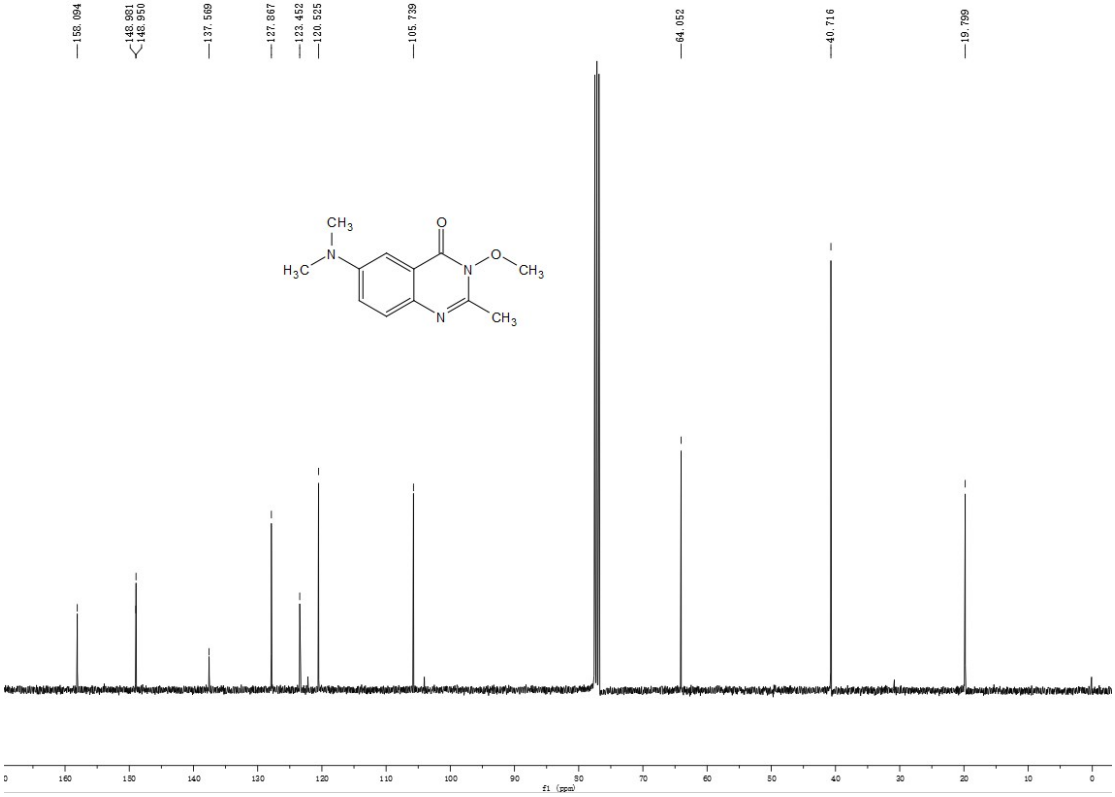
1.04
3.06
6.00
3.03
f1 (ppm)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120.525
105.739
64.052
40.716
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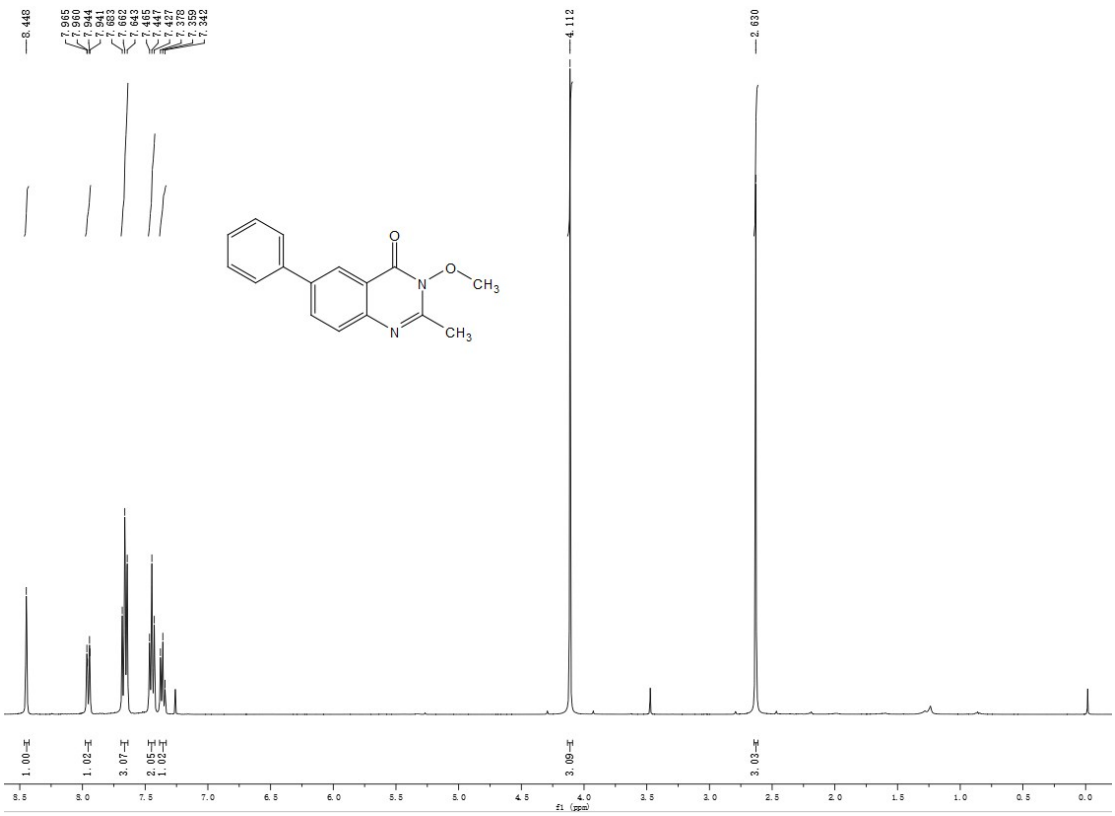
f1 (ppm)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7.960
7.944
7.941
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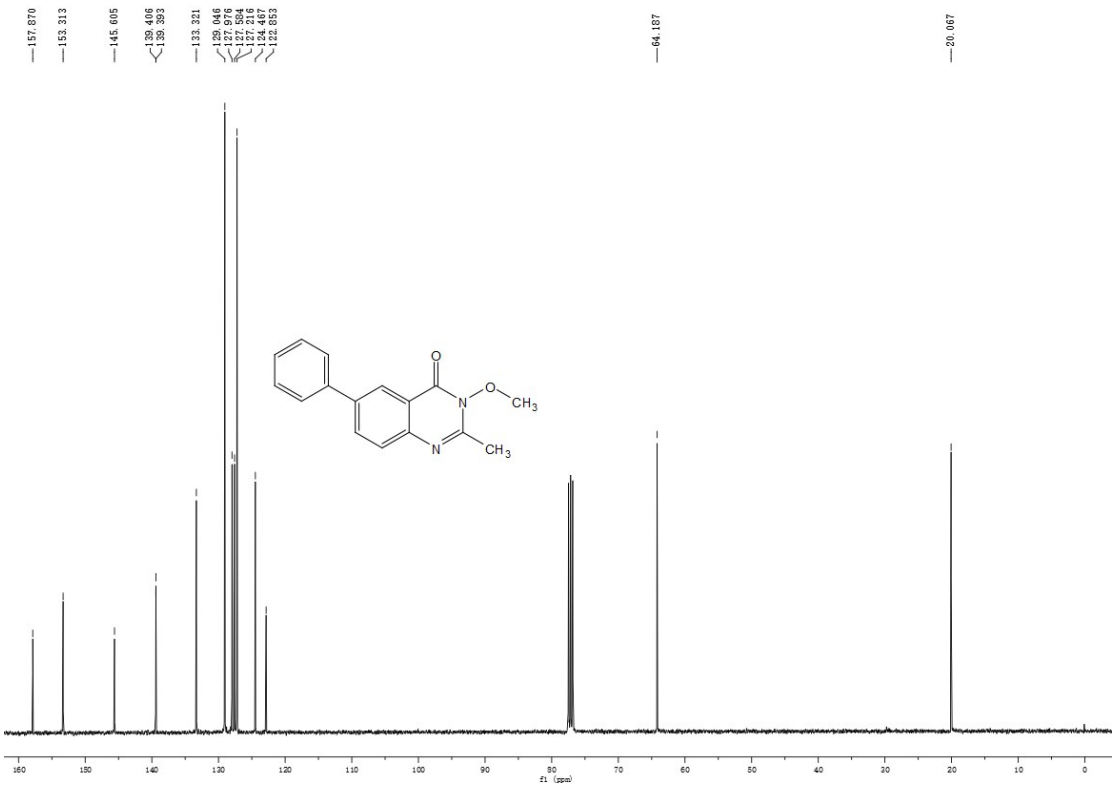
7.662
7.643
7.485
7.447
7.427
7.378
7.359
7.342
4.112
2.630
1.00
1.02
3.07
2.05
1.02
3.09
3.03
f1 (ppm)
O
N
O
CH3
N
CH3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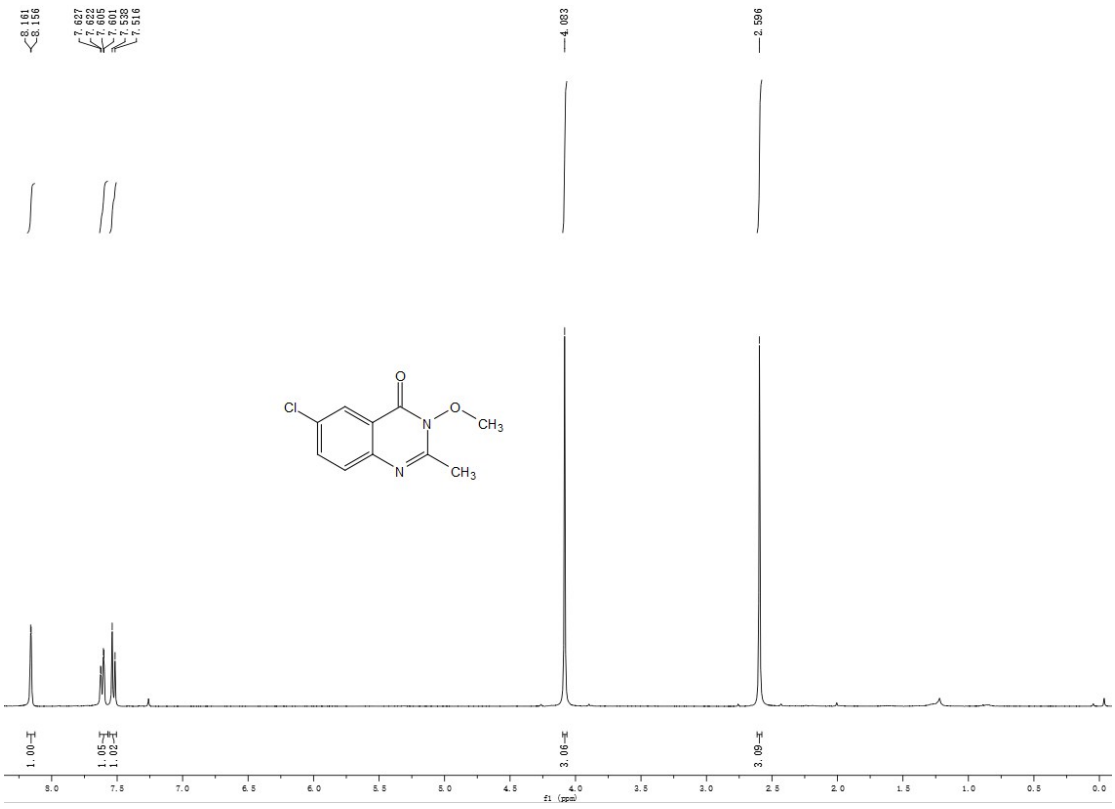
N
O
CH3
N
CH3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CH3
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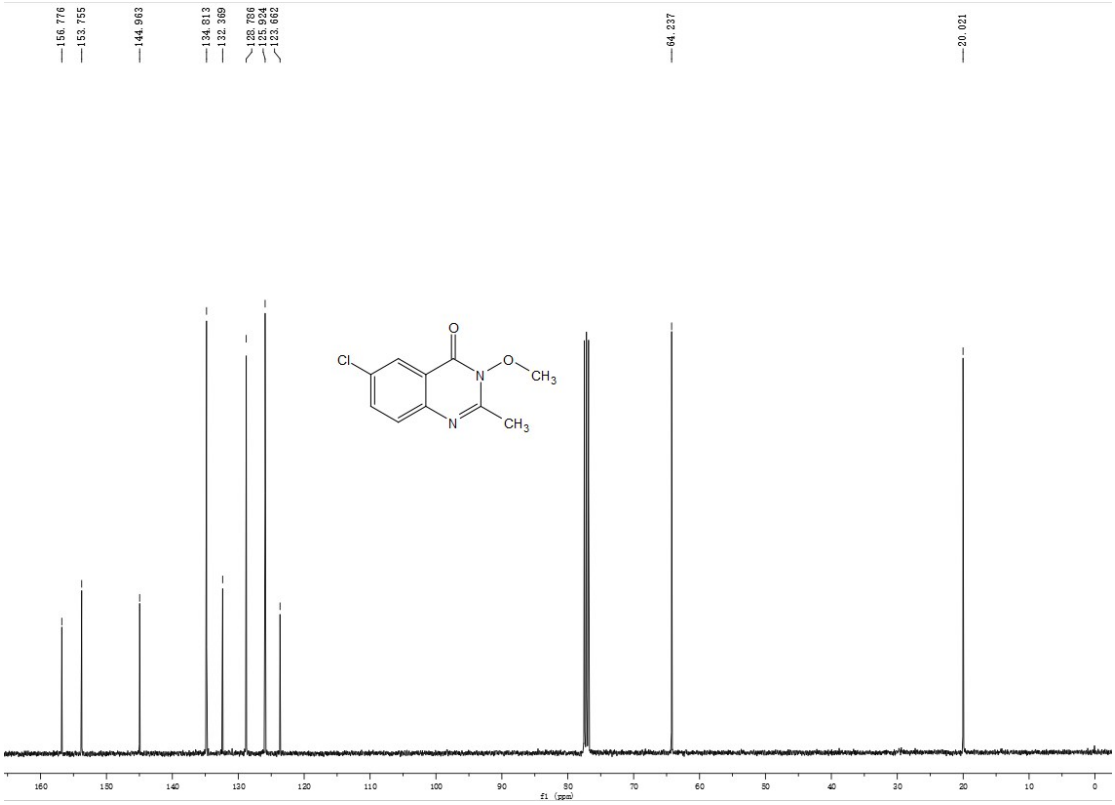
1.02
3.06
3.09
f1 (ppm)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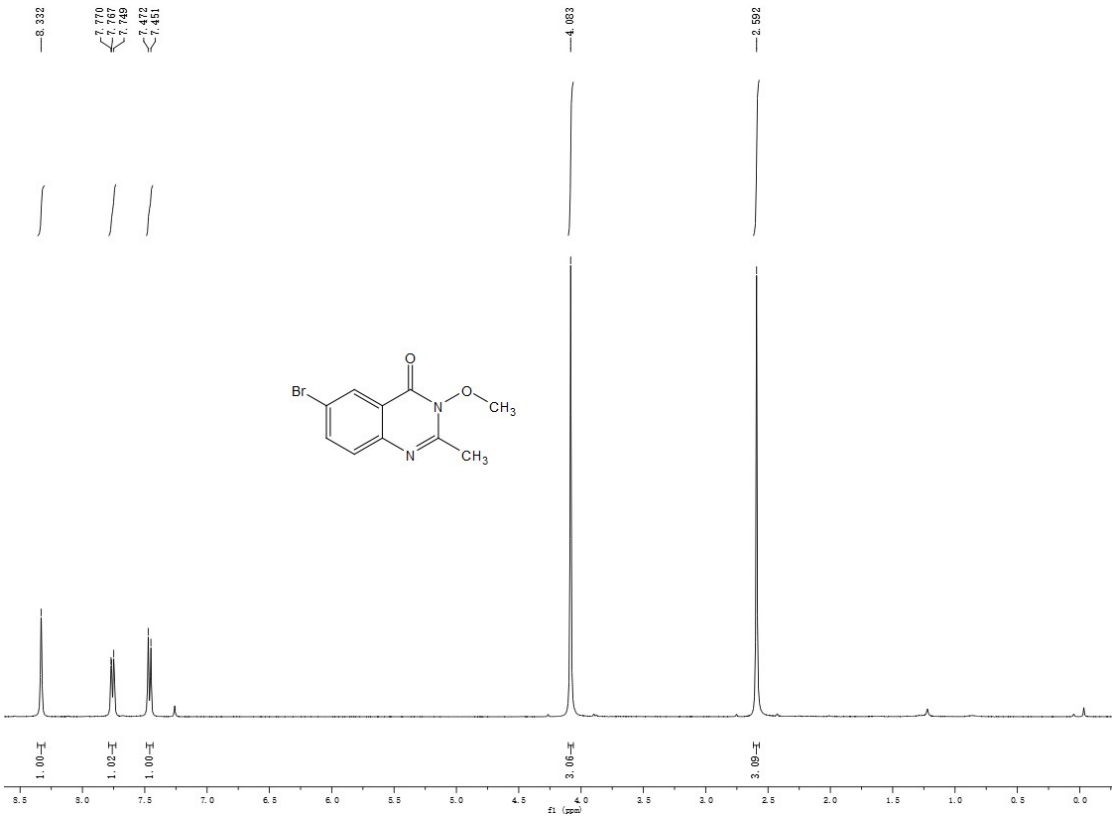
f1 (ppm)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N
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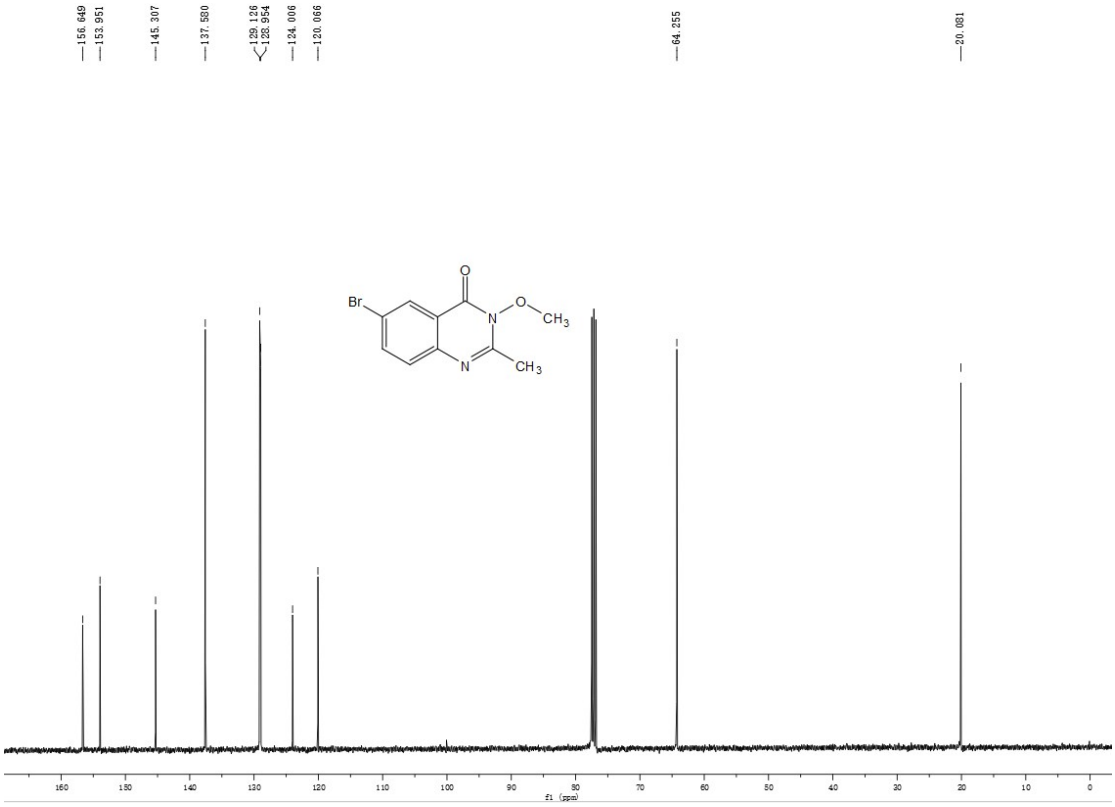
CH3
N
CH3
f1 (ppm)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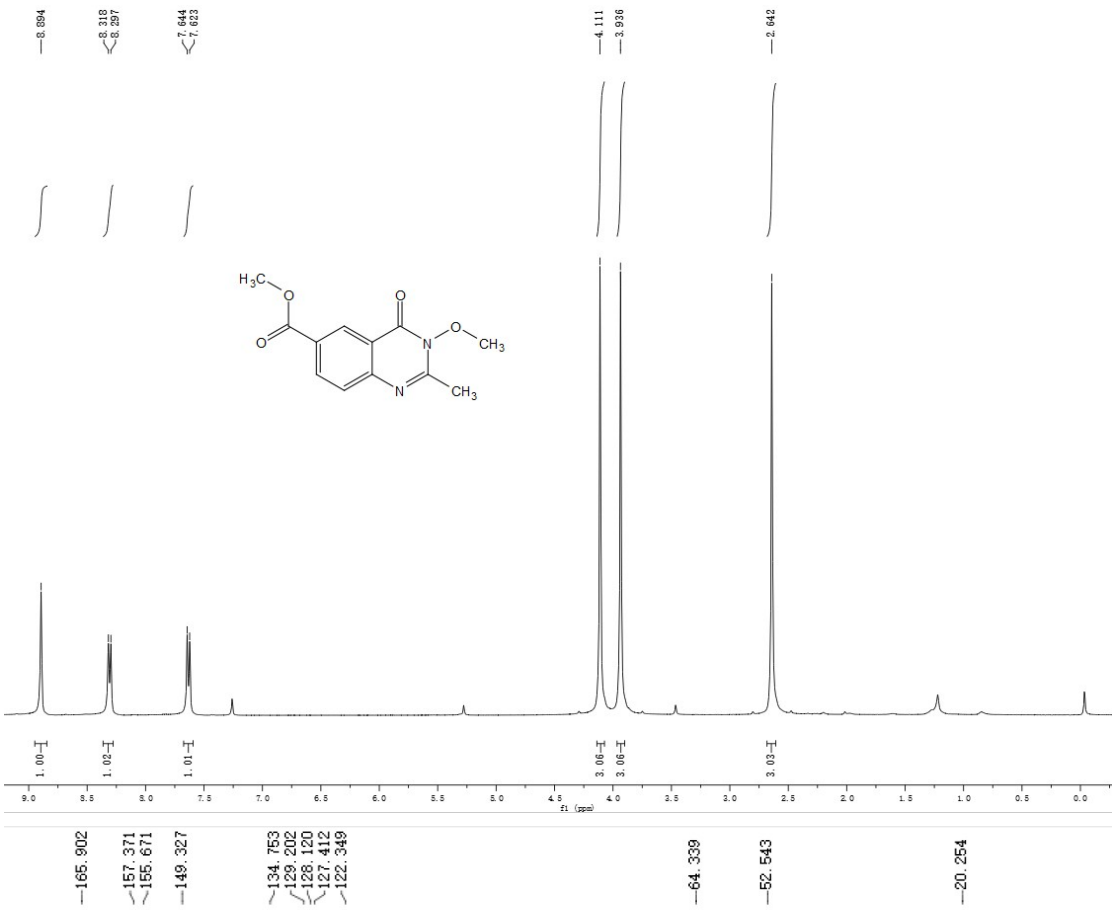
CH3
f1 (ppm)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2.642
1.00
1.02
1.01
3.06
3.06
3.03
f1 (ppm)


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155.671
149.327
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127.412
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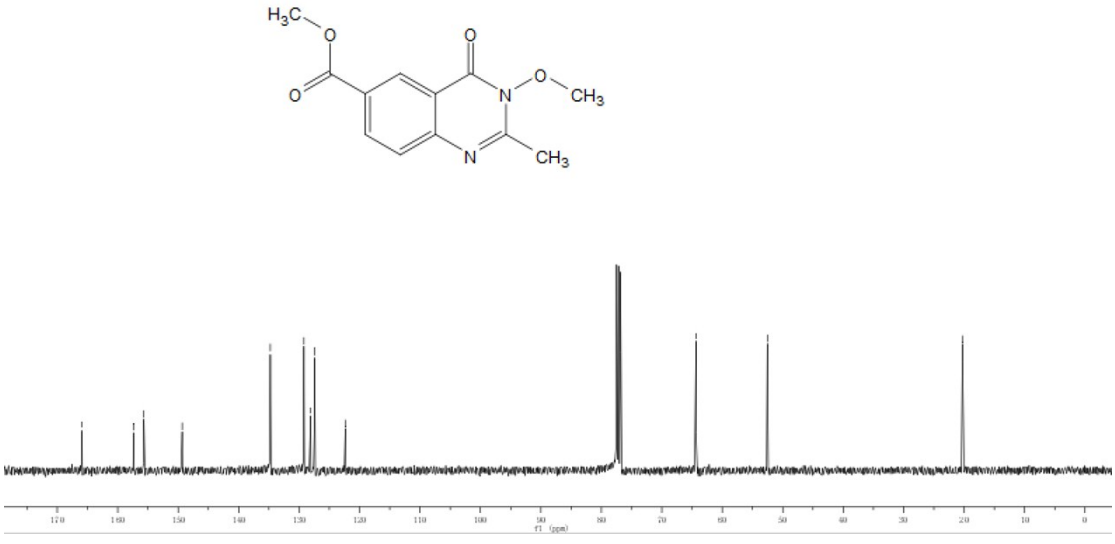
20.254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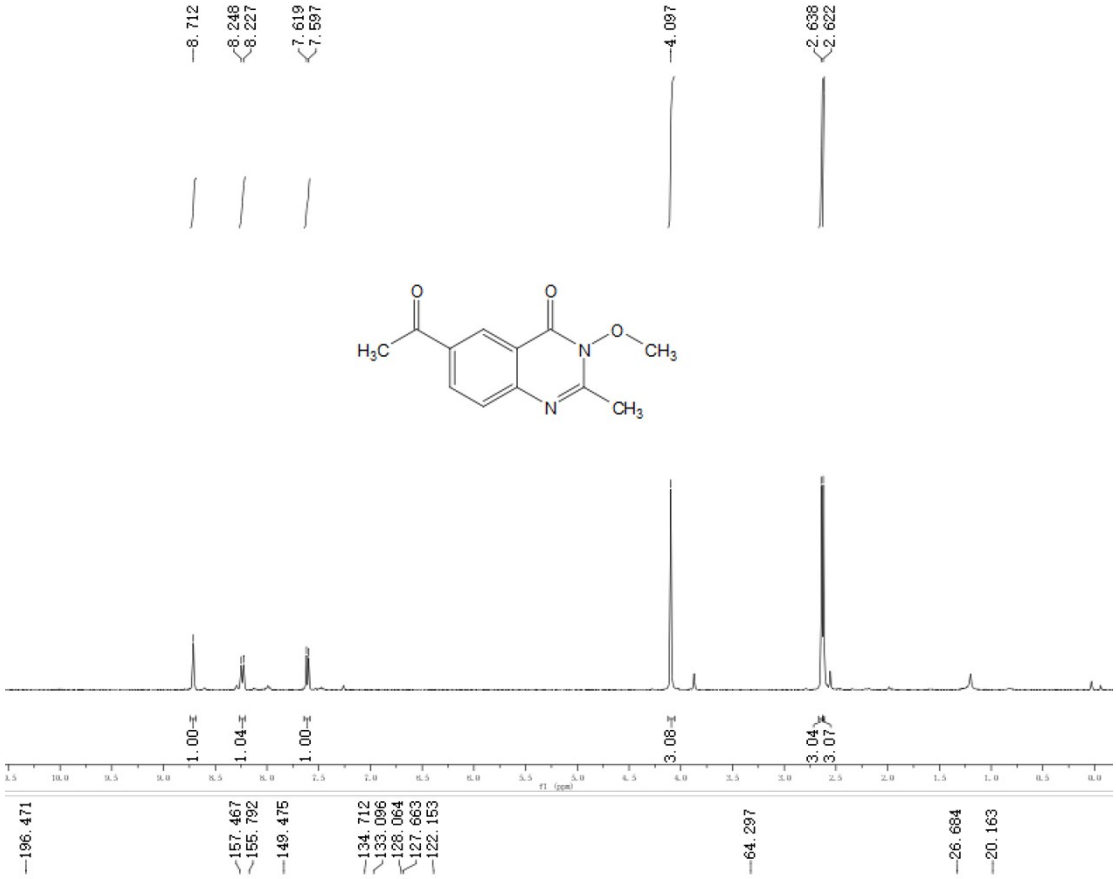
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4.097
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2.622
O
O
H3C
N
O
CH3
N
CH3
1.00
1.04
1.00
3.08
3.04
3.07
f1 (ppm)
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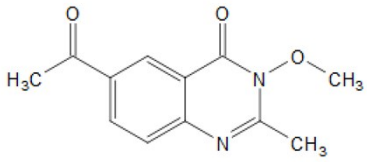
26.684
20.163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O
H3C
N
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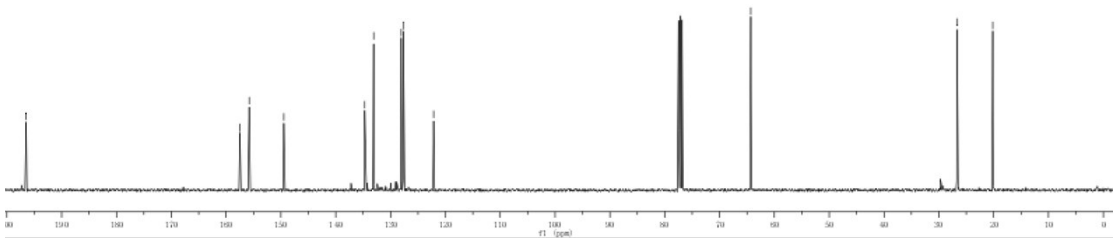
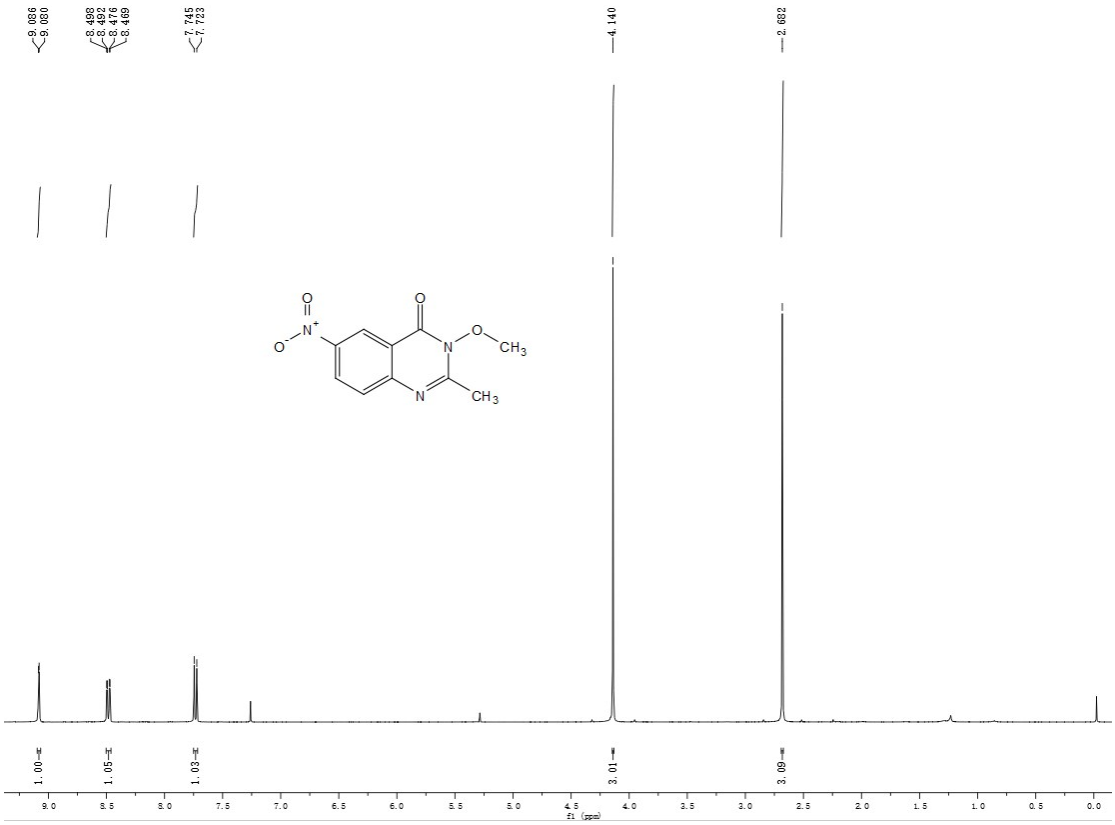
CH3
N
CH3


f1 (ppm)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7.723
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1.00
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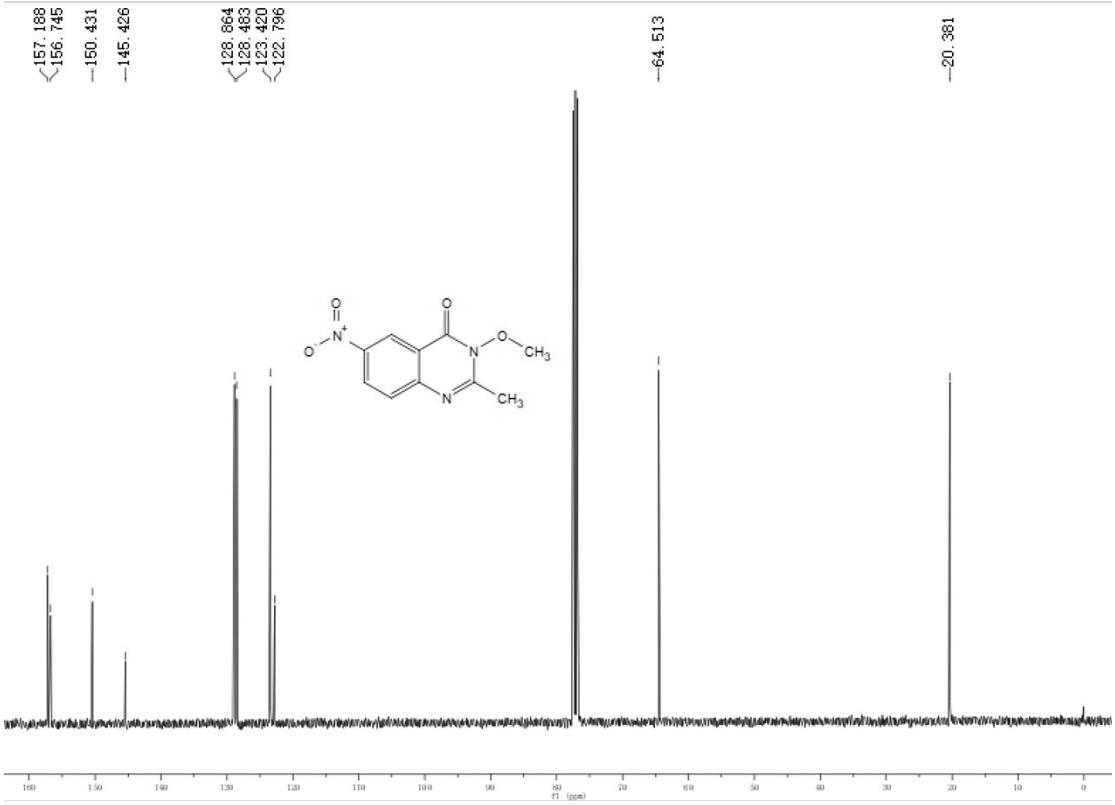
1.03
3.01
3.09
f1 (ppm)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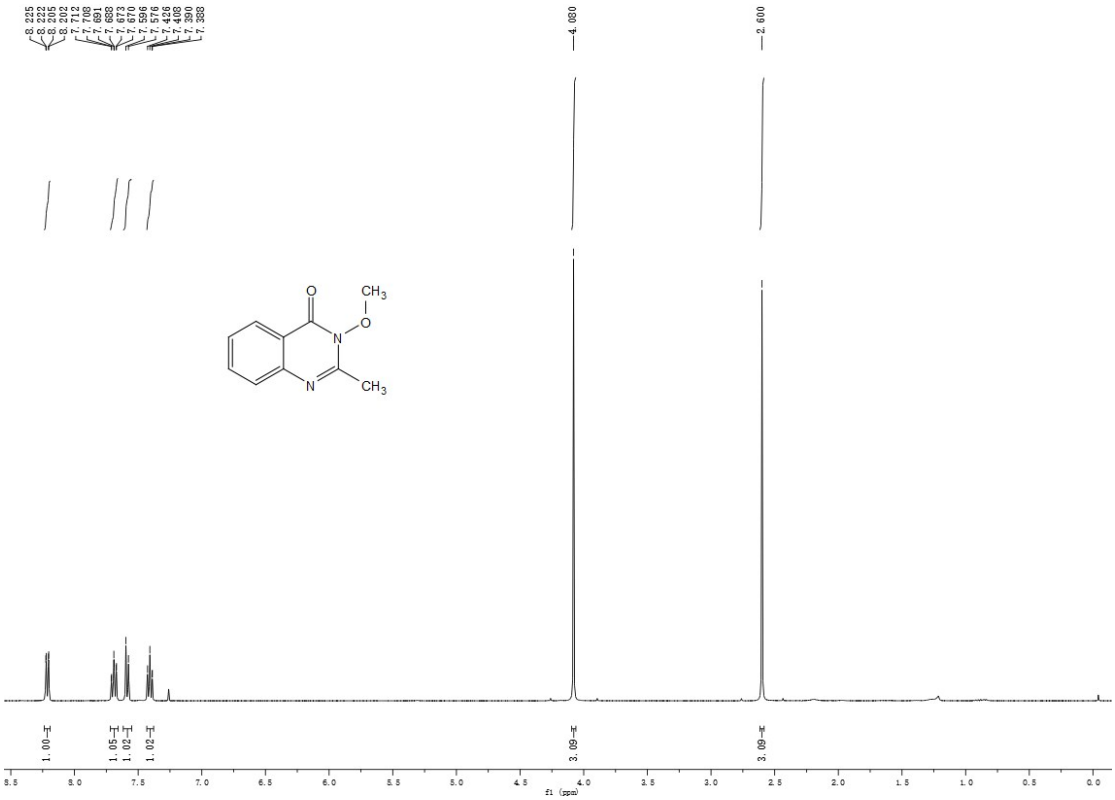
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7.670
7.596
7.576
7.426
7.408
7.390
7.388
4.080
2.600
O
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N
O
N
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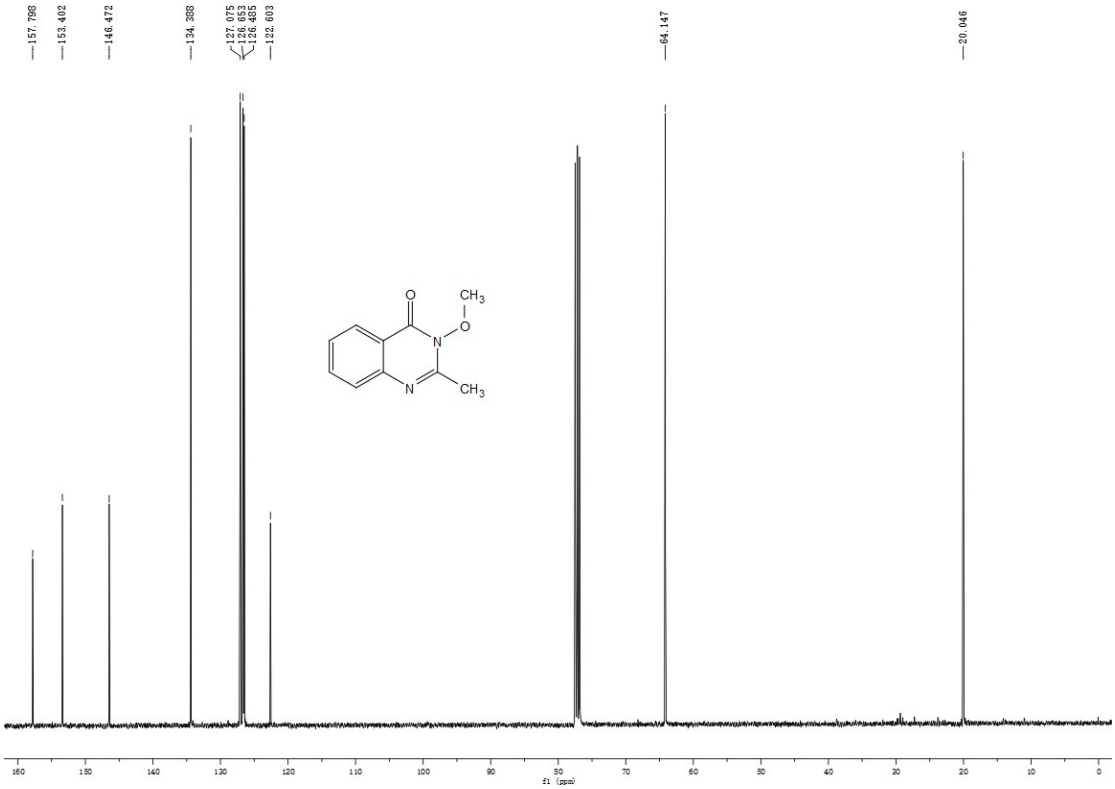
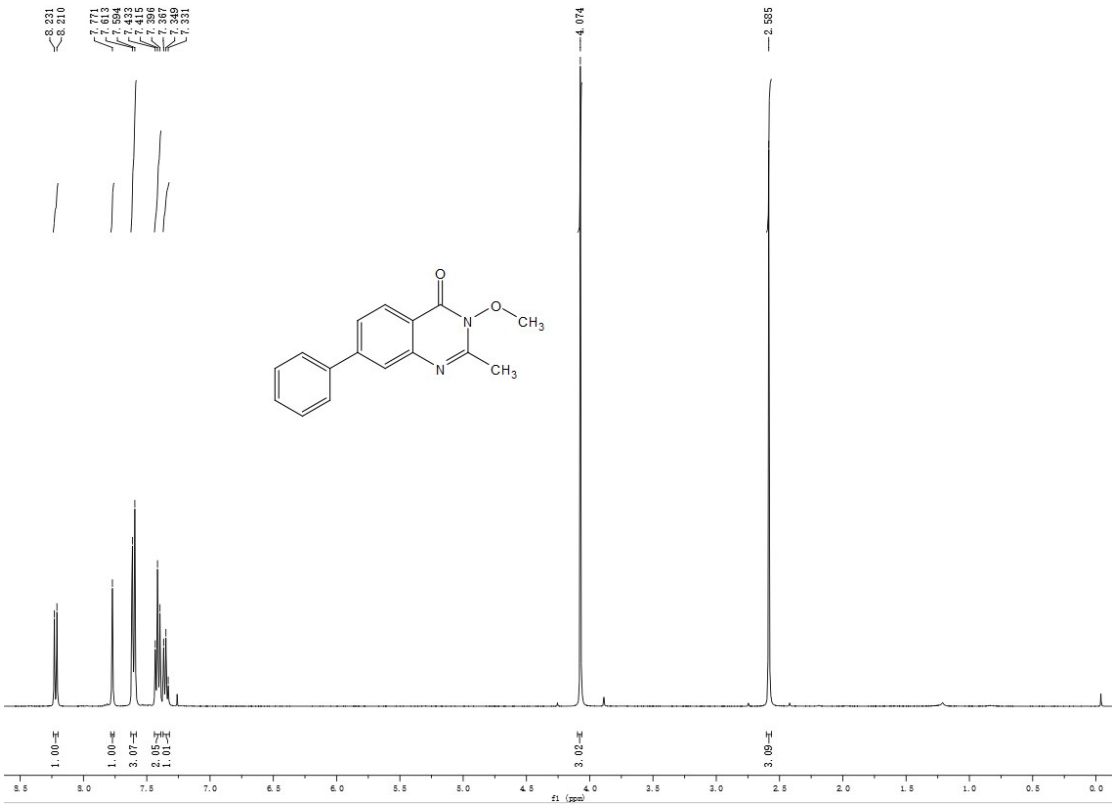
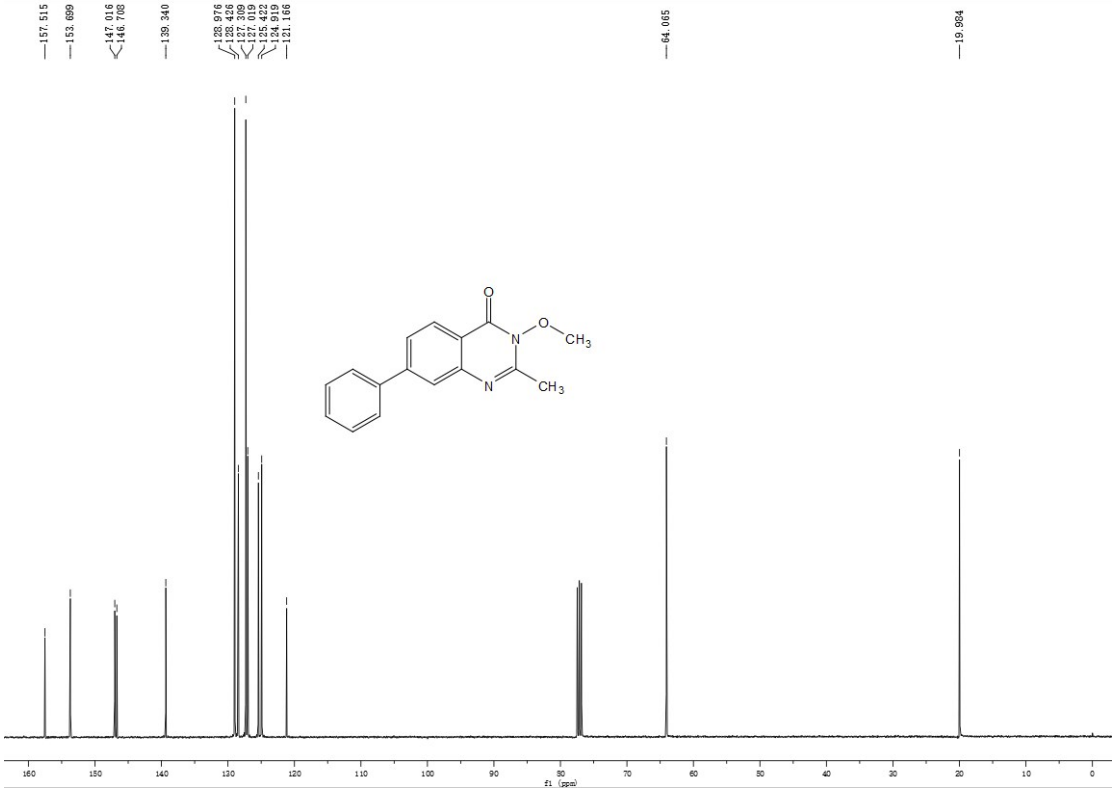
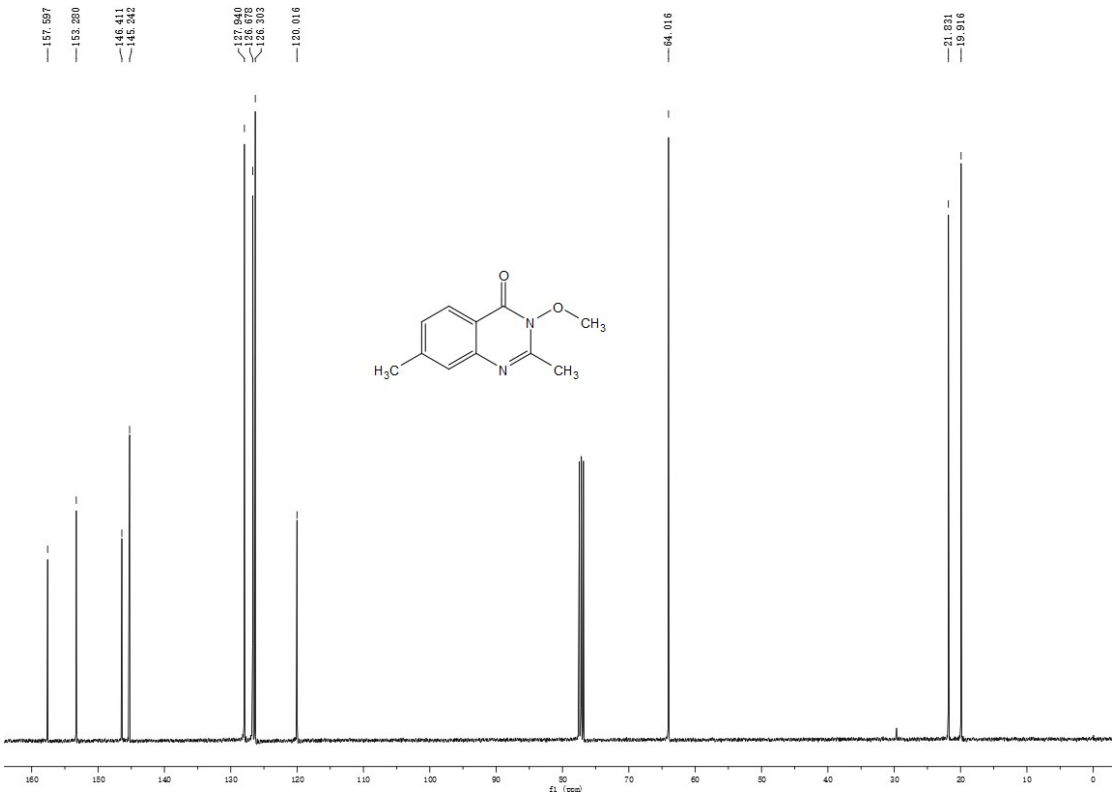
1.00
1.05
1.02
1.02
3.09
3.09
f1 (ppm)


157.798
153.402
146.472
134.388
127.075
126.653
126.485
122.603
64.147
20.046
O
CH3
N
O
N
CH3
f1 (ppm)

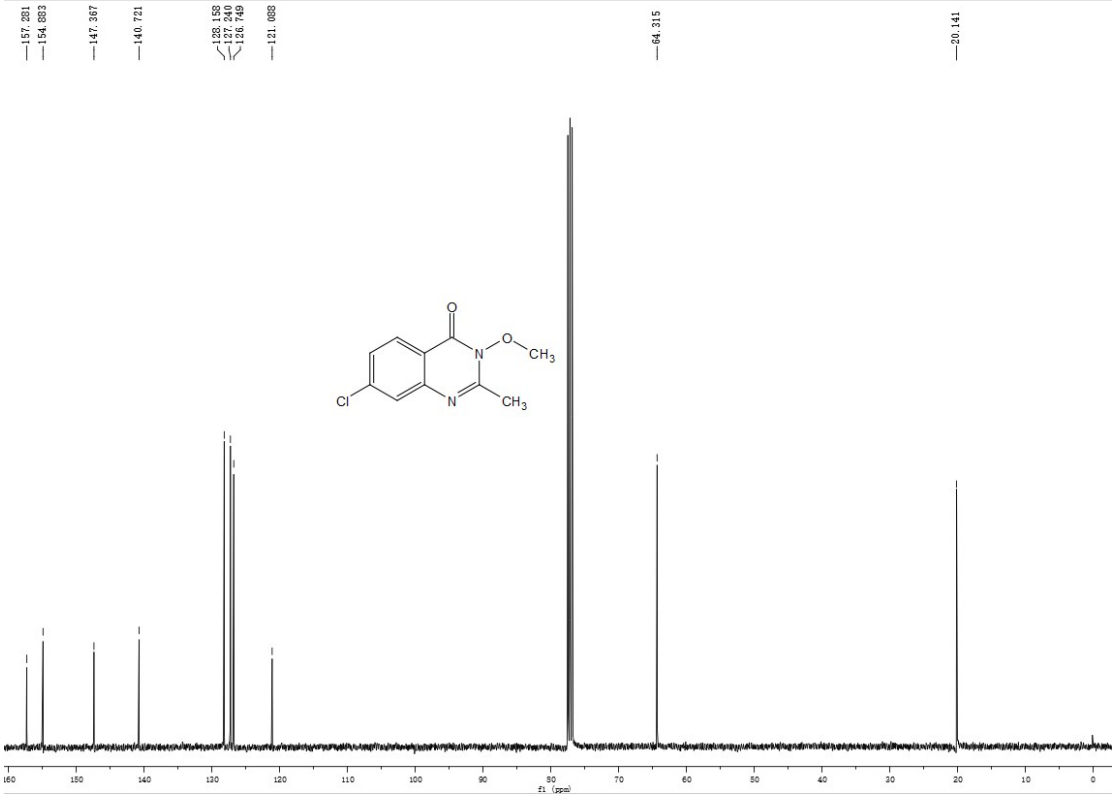

8.231
8.210
7.771
7.613
7.594
7.433
7.415
7.396
7.367
7.349
7.331
4.074
2.585
O
N
O
CH3
N
CH3
1.00
1.00
3.07
2.05
1.01
3.02
3.09
f1 (ppm)

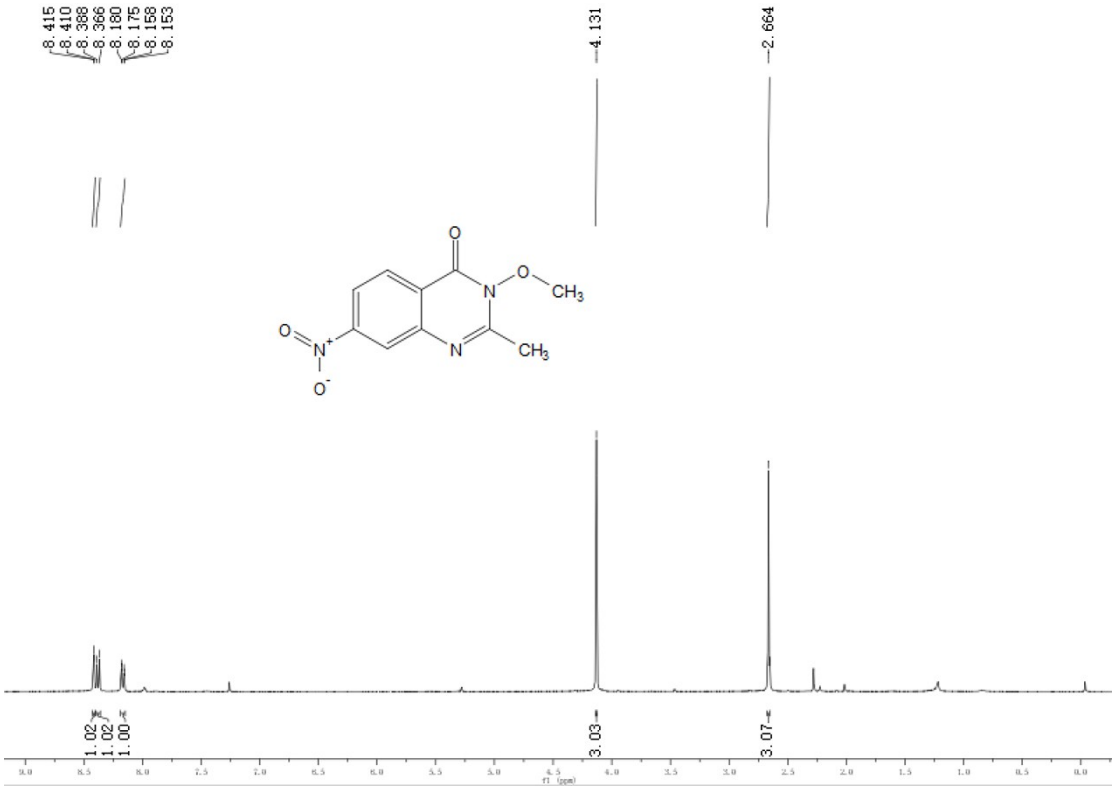

157.515
153.699
147.016
146.708
139.340
128.976
128.426
128.309
127.105
125.422
124.919
121.166
64.065
19.984
O
N
O
CH3
N
CH3
f1 (ppm)

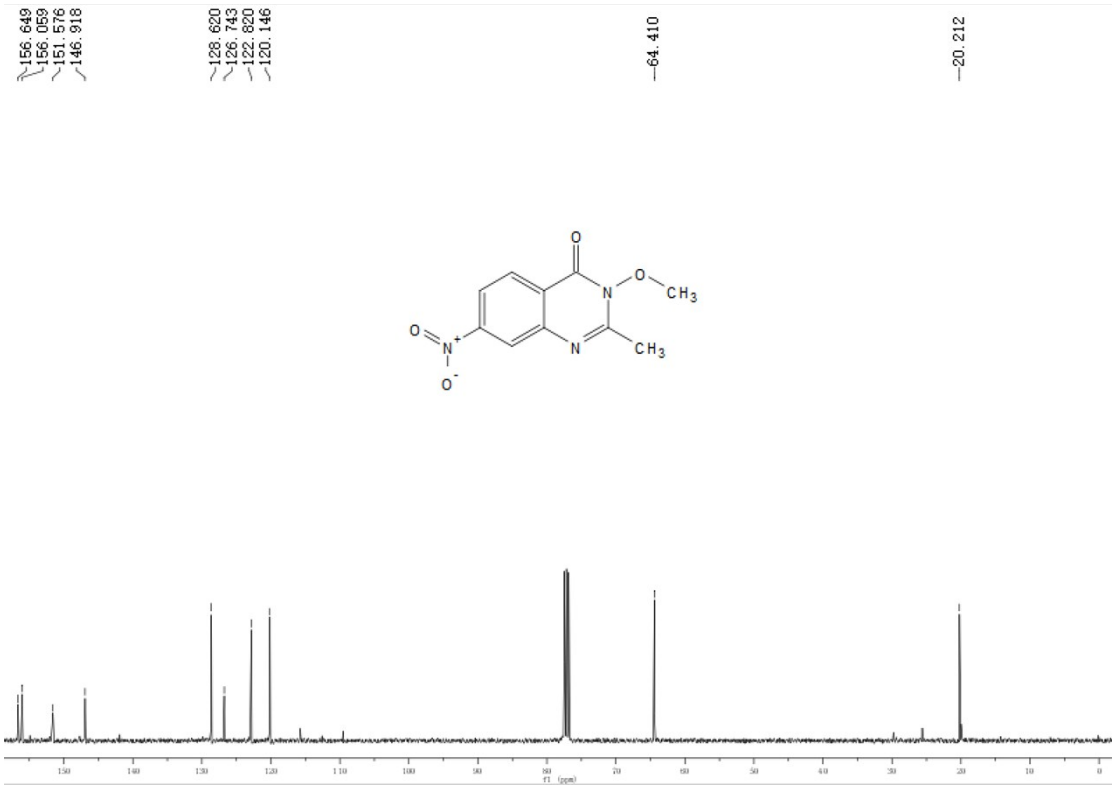

8.035
8.015
7.309
7.176
7.174
7.155
4.026
2.533
2.392
O
N
O
CH3
H3C
N
CH3
1.00
1.00
1.02
3.09
3.03
3.04
f1 (ppm)

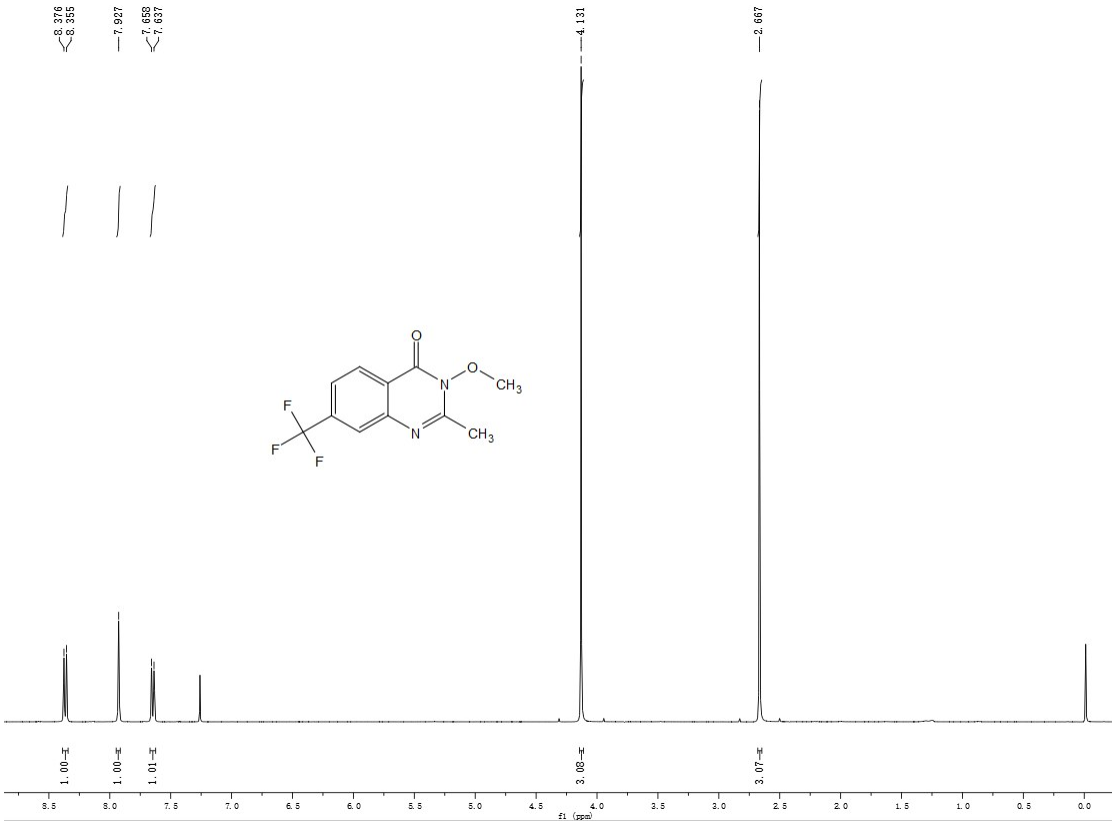

157.597
153.280
146.411
145.242
127.940
126.678
126.303
120.016
64.016
21.831
19.916
O
N
O
CH3
H3C
N
CH3
f1 (ppm)

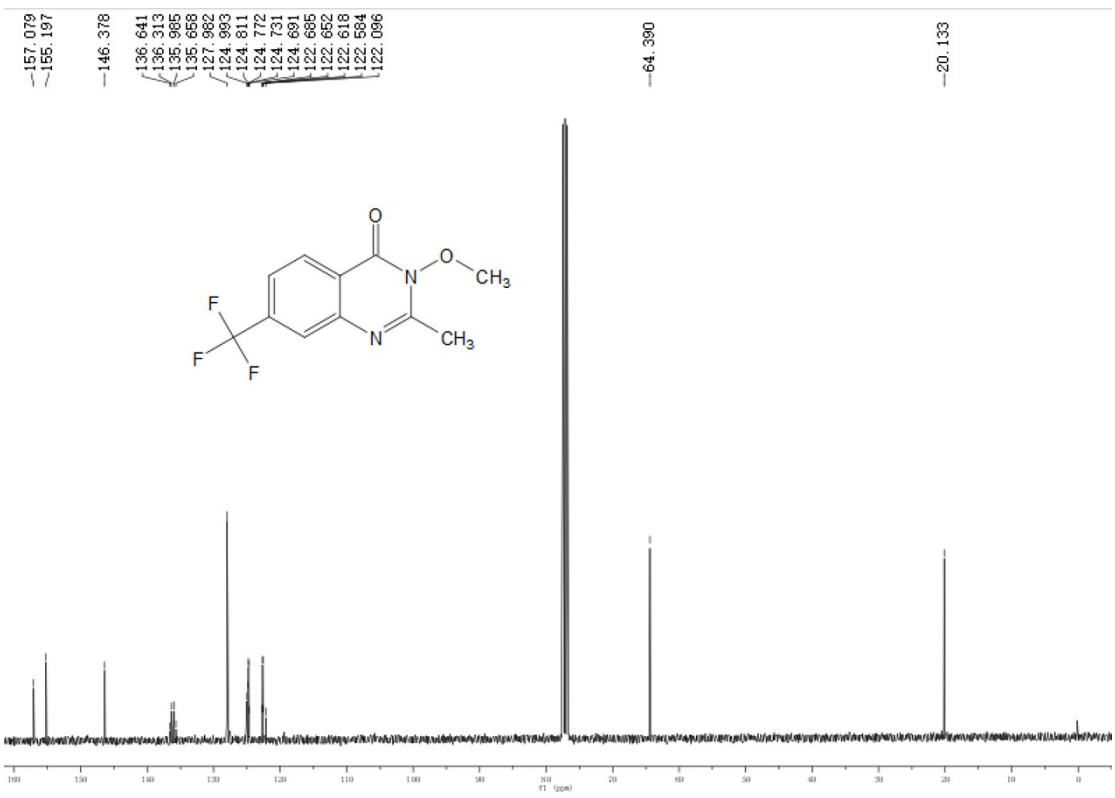

8.169
8.148
7.611
7.607
7.396
7.391
7.374
7.370
4.099
2.619
O
N
O
CH3
Cl
N
CH3
1.00
1.00
1.02
3.08
3.01
f1 (ppm)

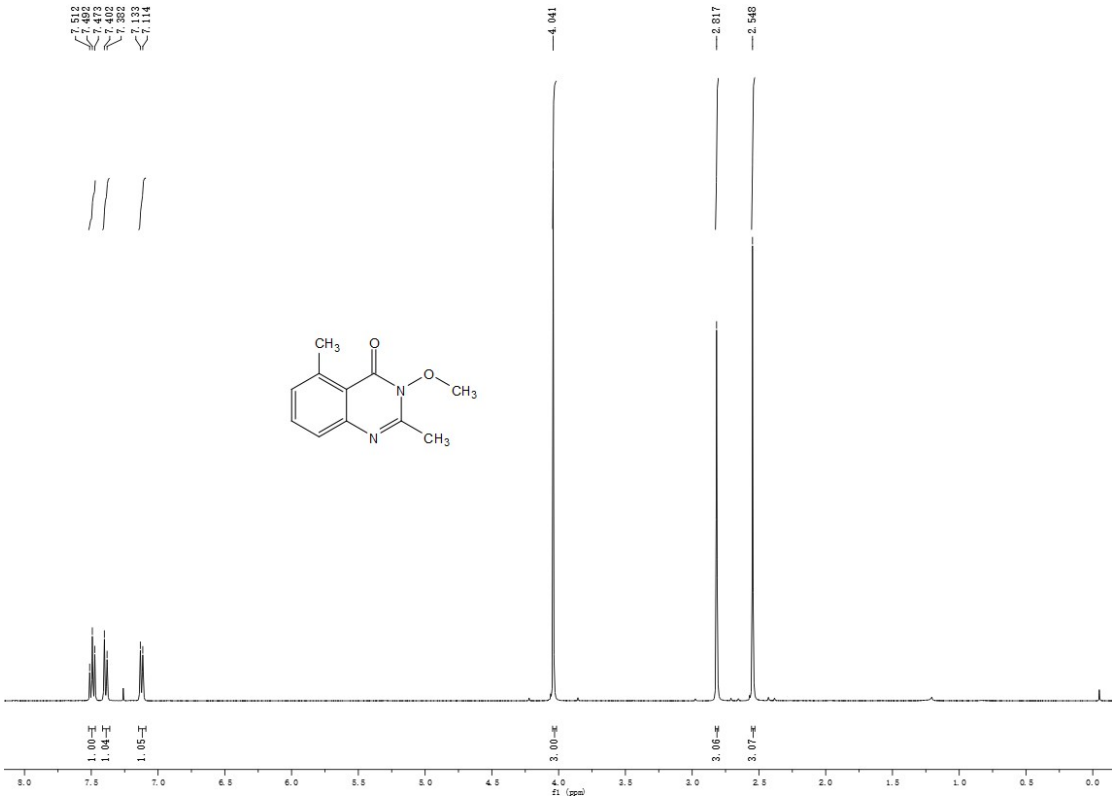

157.281
154.883
147.367
140.721
128.158
127.340
126.749
121.088
64.315
20.141
O
N
O
CH3
Cl
N
CH3
f1 (ppm)

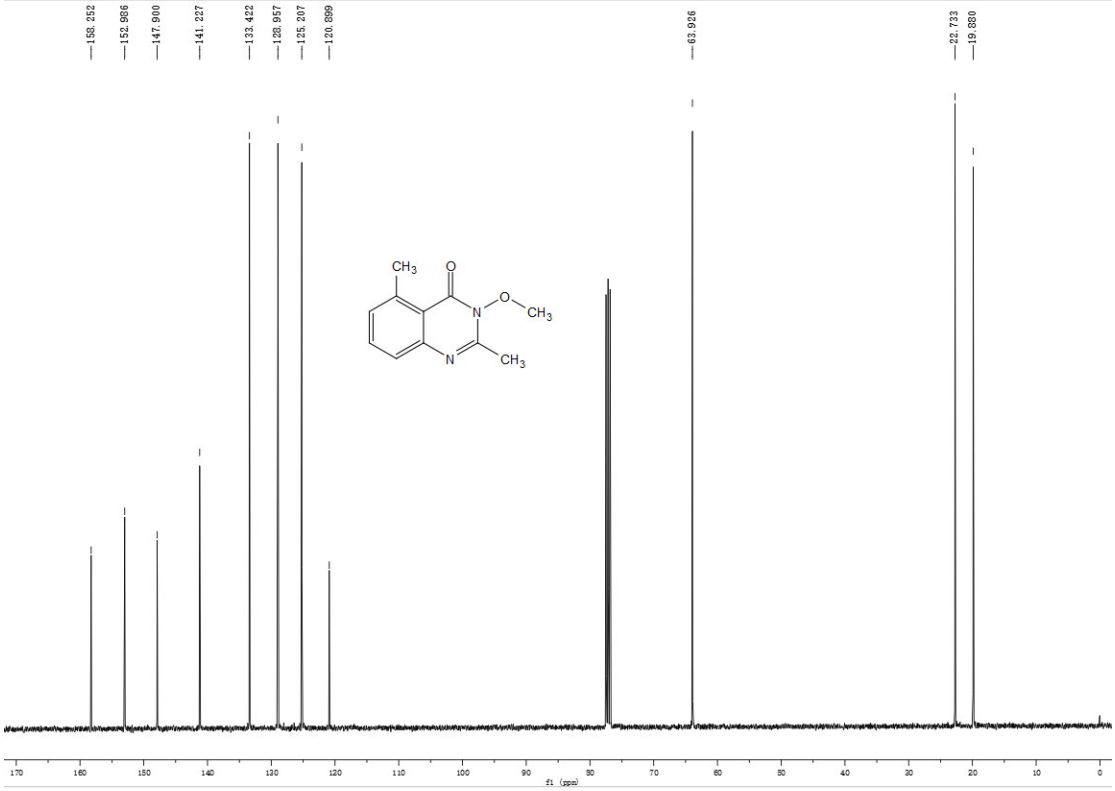

8.415
8.410
8.388
8.366
8.180
8.175
8.158
8.153
4.131
2.664
O
N
O
CH3
O
N+
O-
N
CH3
1.02
1.02
1.00
3.03
3.07

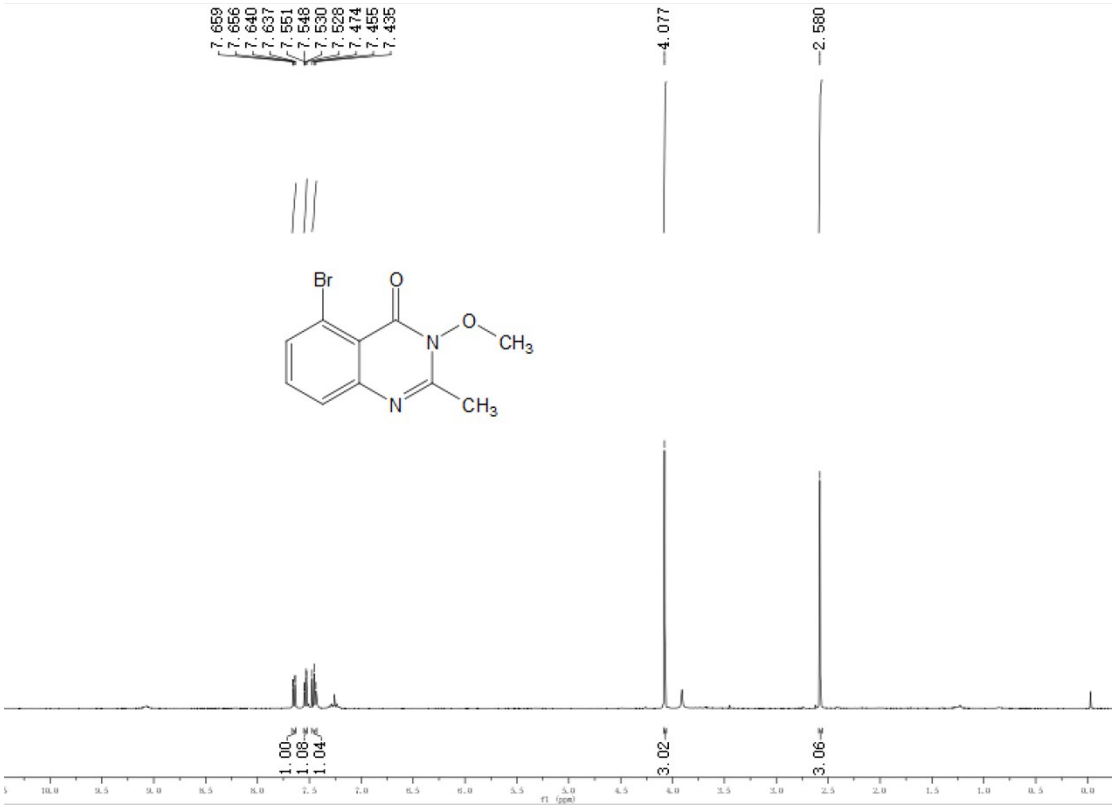

156.649
156.059
151.576
146.918
128.620
126.743
122.820
120.146
64.410
20.212
O
N
O
CH3
O
N+
O-
N
CH3


8.376
8.355
7.927
7.658
7.637
4.131
2.667
O
N
O
CH3
F
F
F
N
CH3
1.00
1.00
1.01
3.08
3.07
f1 (ppm)

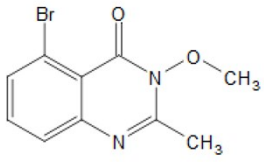

157.079
155.197
146.378
136.641
136.313
135.985
135.658
127.982
124.993
124.811
124.772
124.731
124.691
122.685
122.652
122.618
122.584
122.096
64.390
20.133
O
N
O
CH3
F
F
F
N
CH3
f1 (ppm)

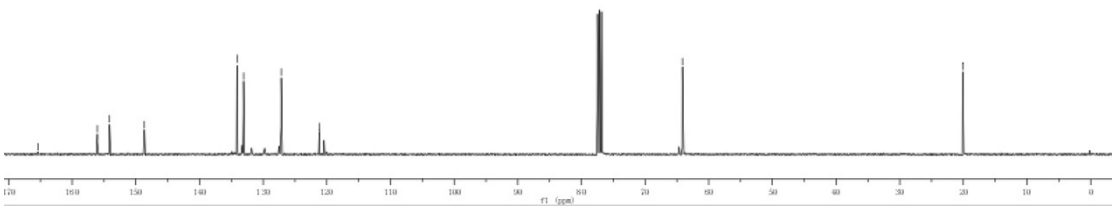

7.512
7.493
7.473
7.402
7.382
7.133
7.114
4.041
2.817
2.548
1.00
1.04
1.05
3.00
3.06
3.07
f1 (ppm)

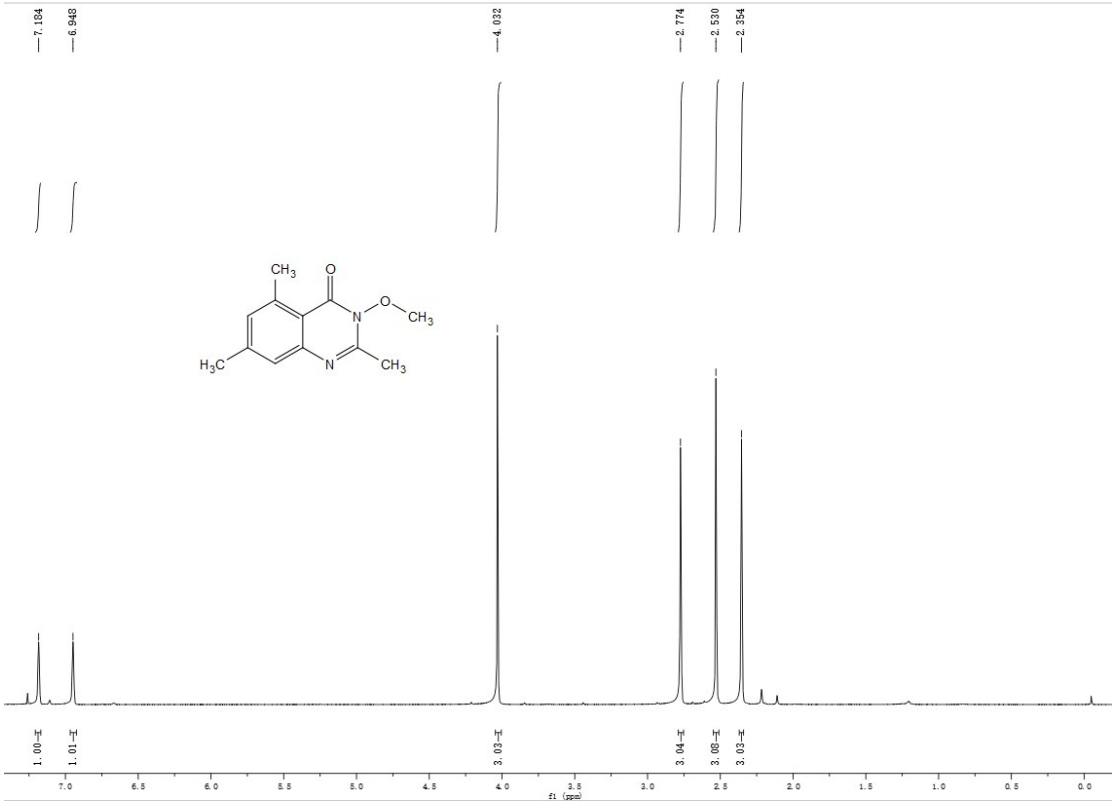

158.252
152.986
147.900
141.227
133.422
128.957
125.207
120.899
63.926
22.733
19.880
f1 (ppm)

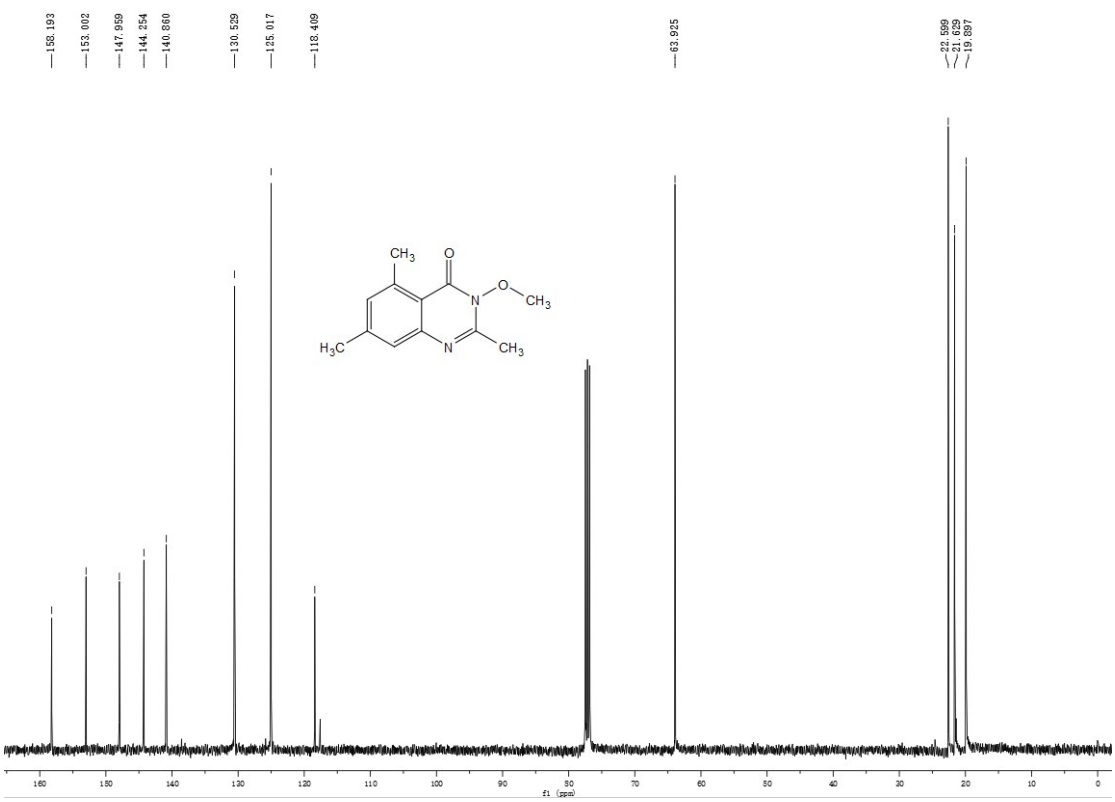

7.659
7.656
7.640
7.637
7.551
7.548
7.530
7.528
7.474
7.455
7.435
4.077
2.580
Br
O
N
O
CH3
N
CH3
1.00
1.08
1.04
3.02
3.06
f1 (ppm)

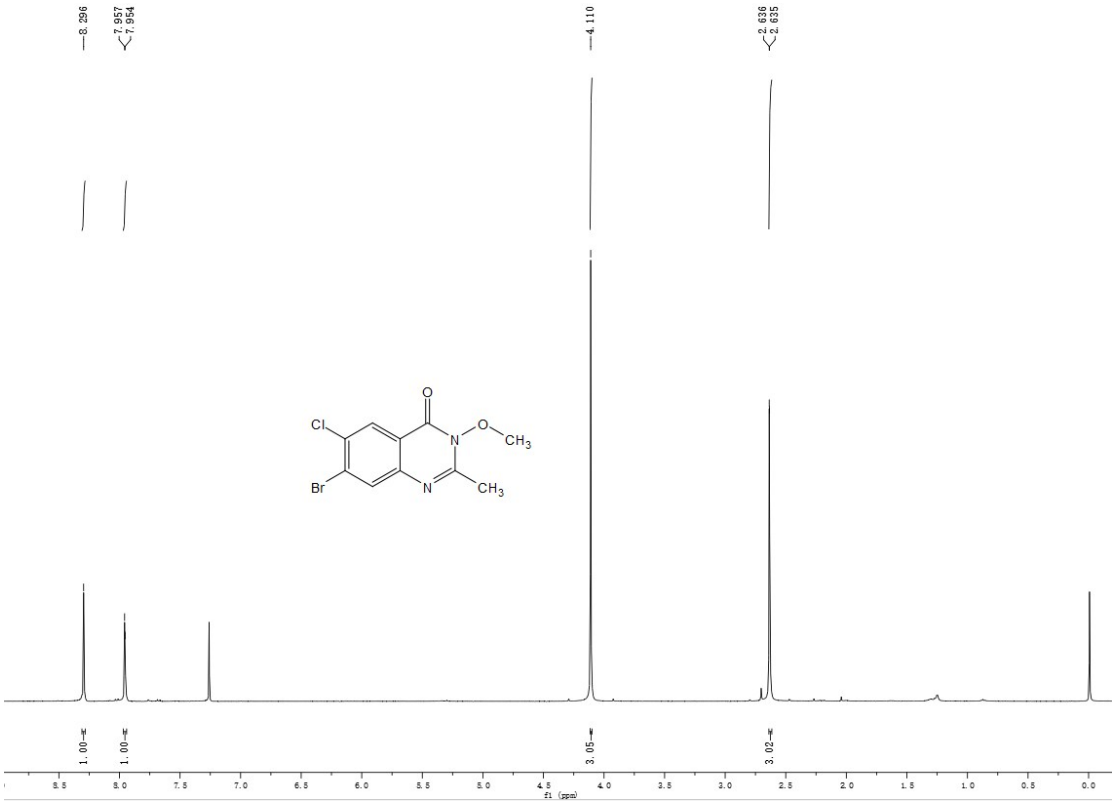

165.408
156.057
154.135
148.662
134.108
133.068
127.156
121.181
64.128
20.104

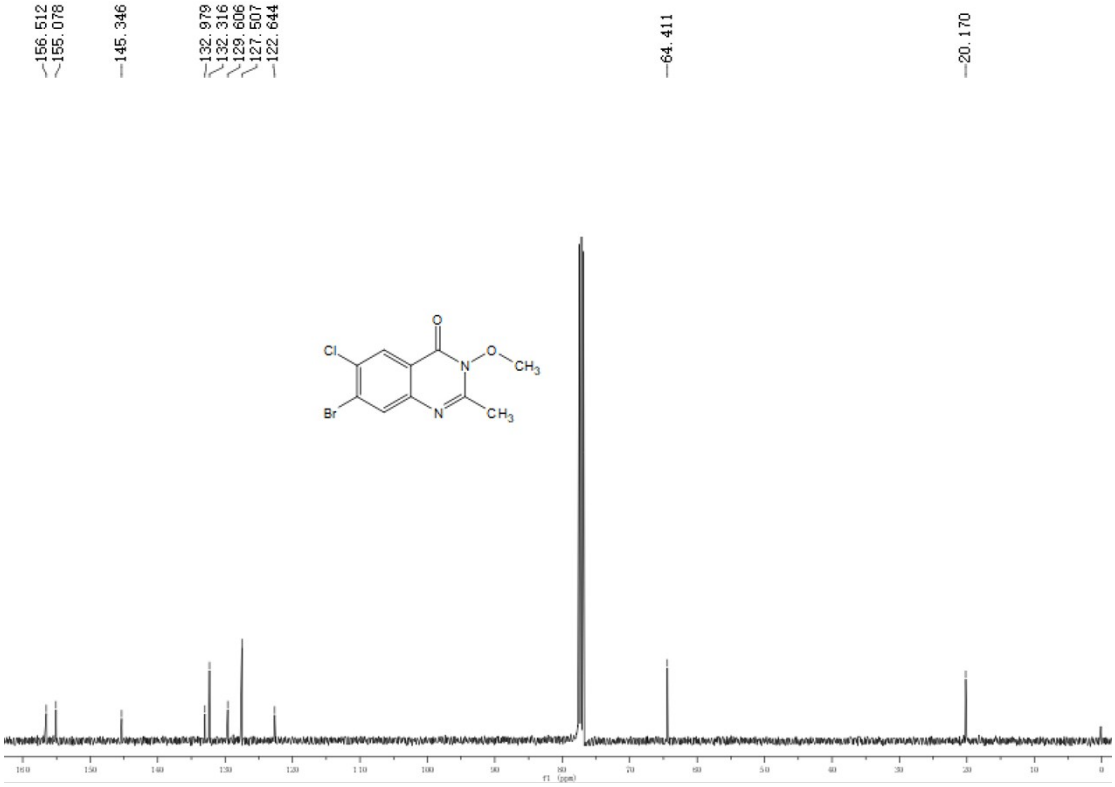

Br
O
N
O
CH3
N
CH3

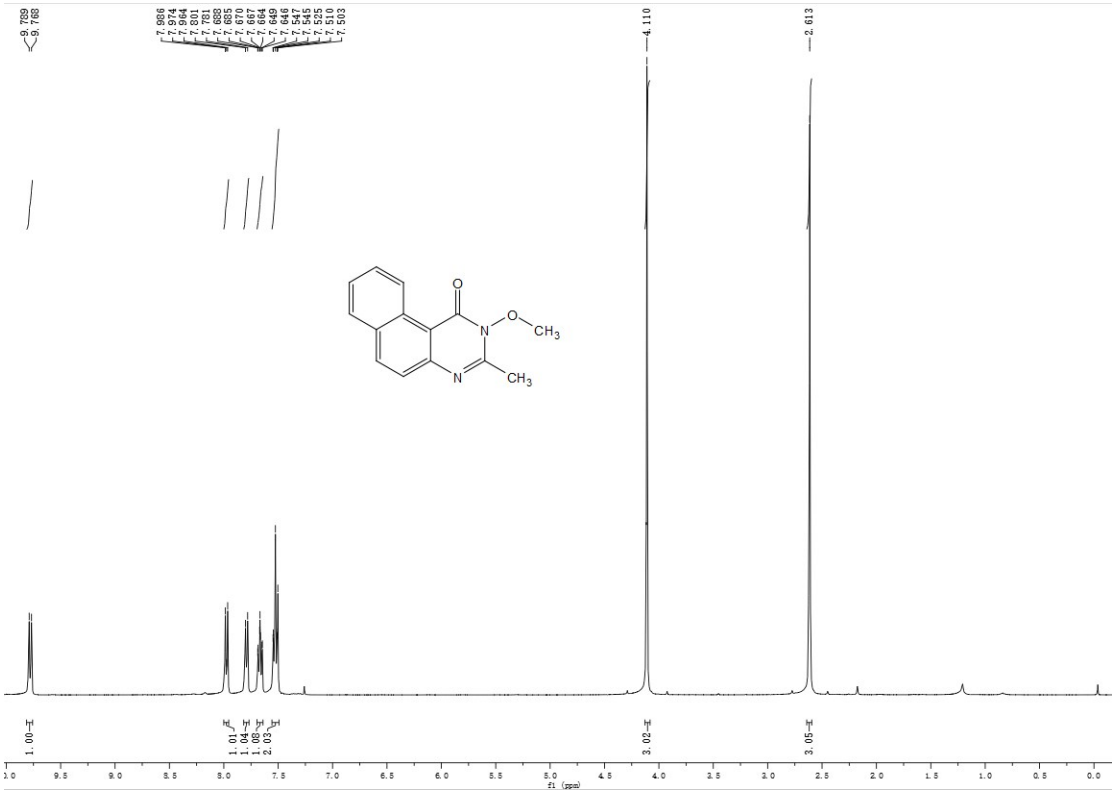

f1 (ppm)

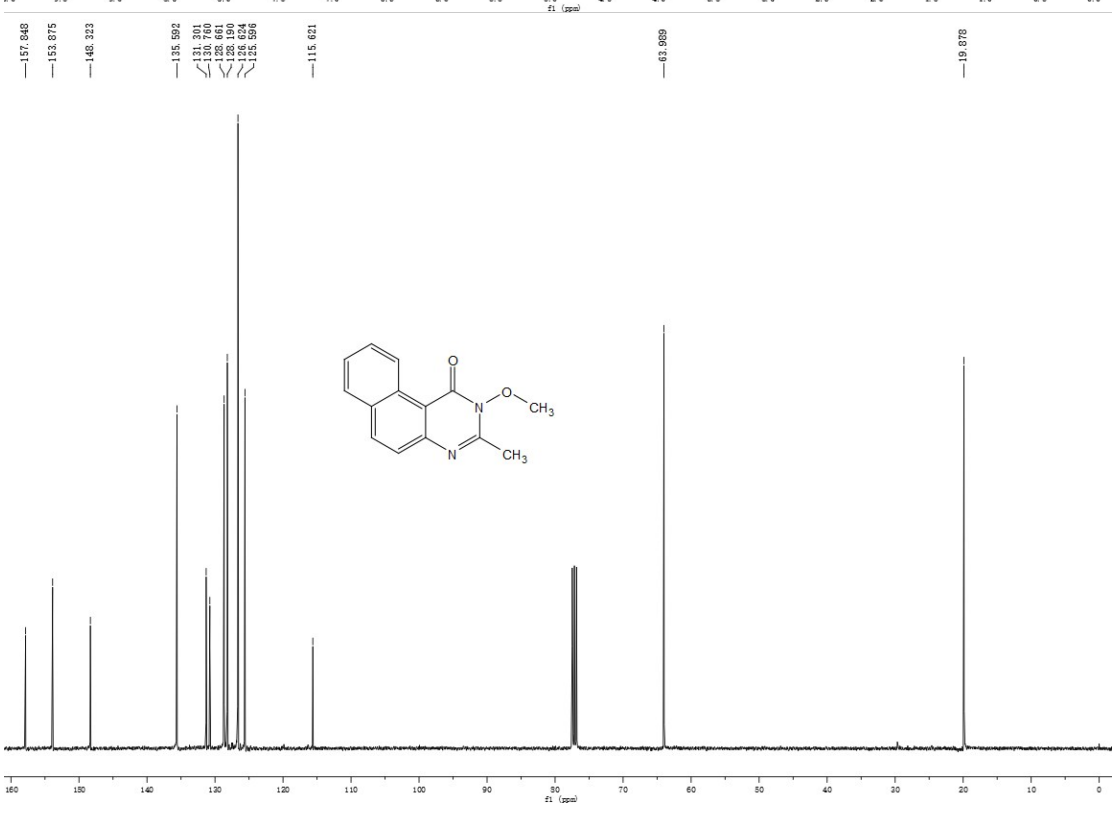

7.184
6.948
4.032
2.774
2.530
2.354
1.00
1.01
3.03
3.04
3.08
3.03
f1 (ppm)


158.193
153.002
147.959
144.254
140.860
130.529
125.017
118.409
63.925
22.599
21.829
19.697
f1 (ppm)


8.296
7.957
7.954
4.110
2.638
2.635
Cl
Br
O
N
O
CH3
N
CH3
1.00
1.00
3.05
3.02
f1 (ppm)


156.512
155.078
145.346
132.979
132.316
129.606
127.507
122.644
64.411
20.170
Cl
Br
O
N
O
CH3
N
CH3
f1 (ppm)


9.789
9.768
7.986
7.974
7.964
7.944
7.801
7.781
7.688
7.685
7.670
7.667
7.664
7.649
7.646
7.547
7.545
7.525
7.510
7.503
4.110
2.613
1.00
1.01
1.04
1.08
2.03
3.02
3.05
f1 (ppm)


157.648
153.875
148.323
135.592
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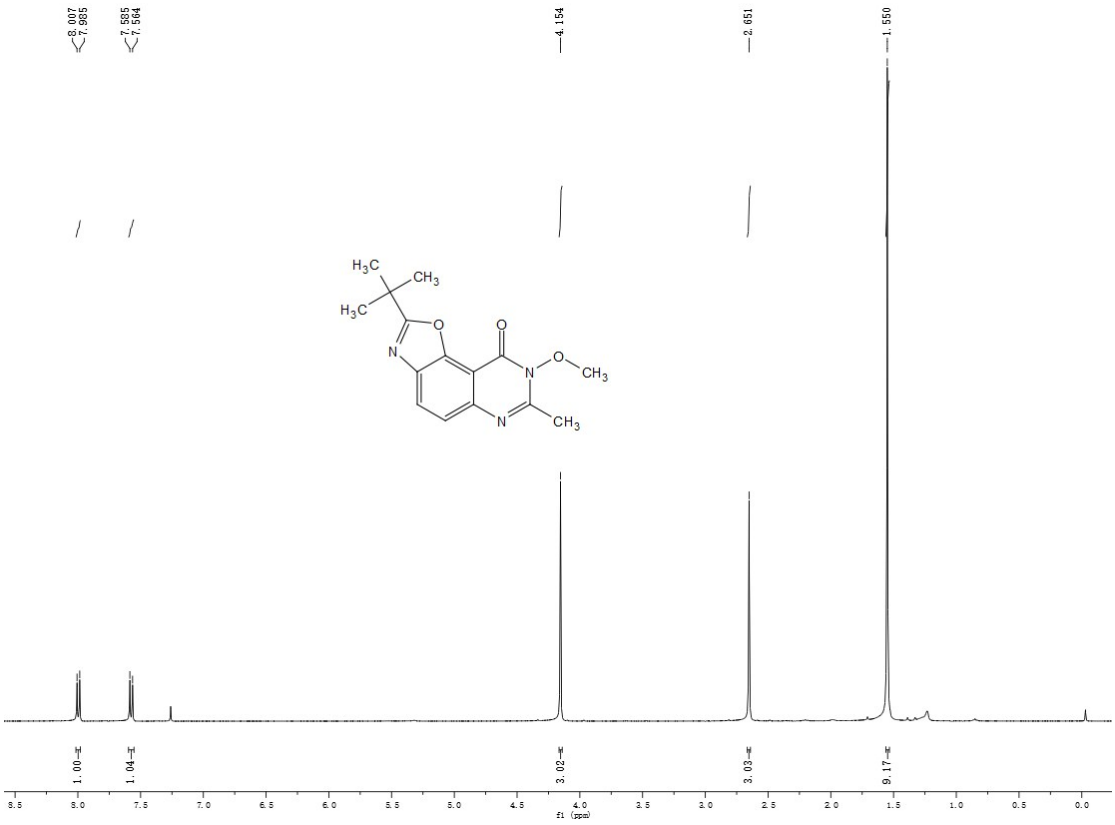
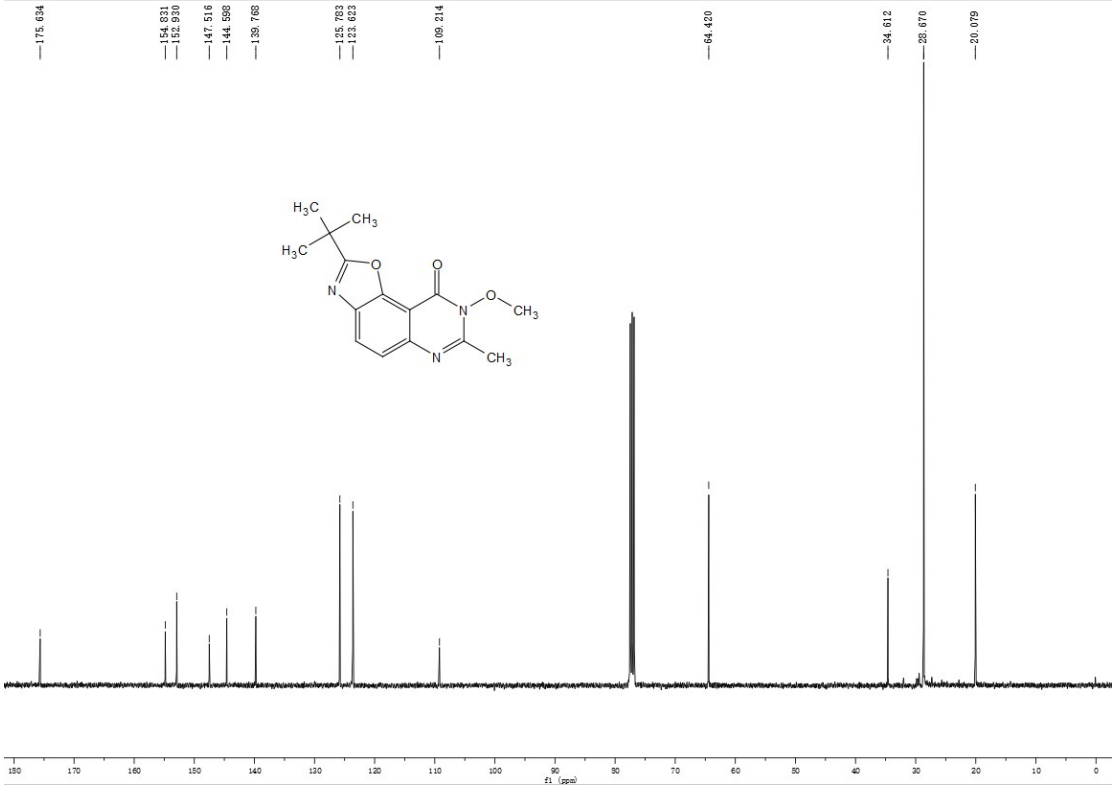
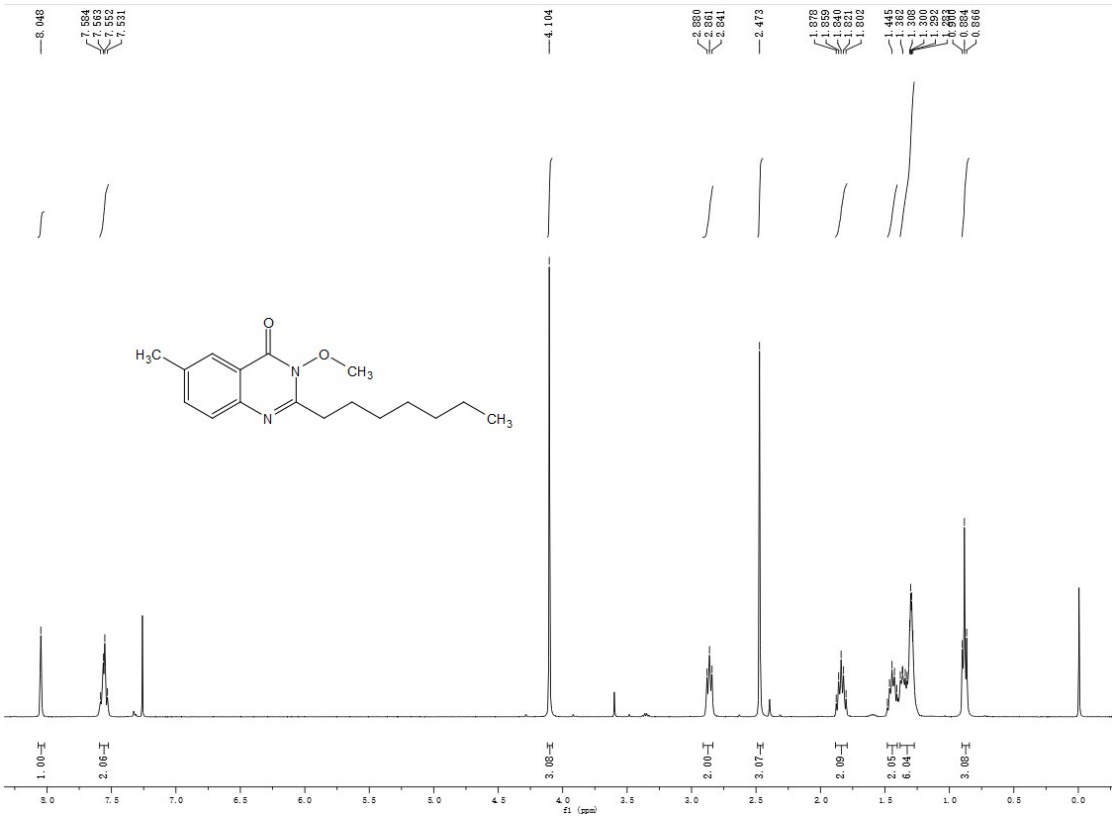
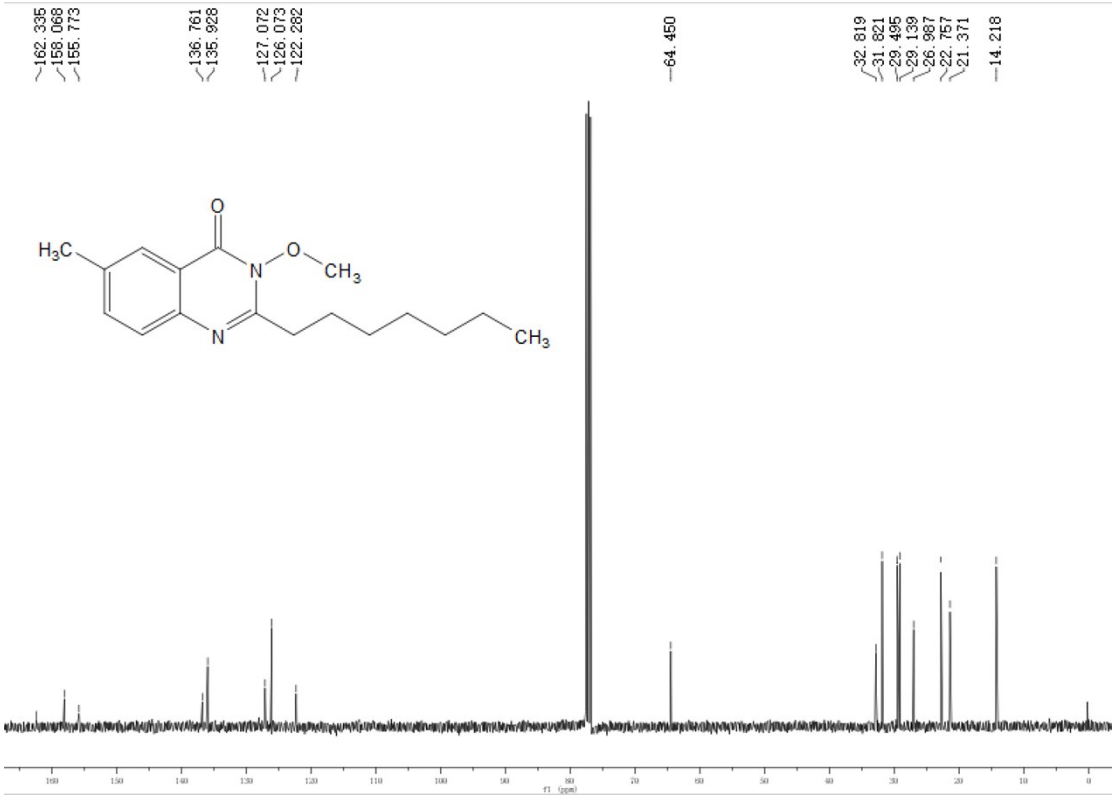
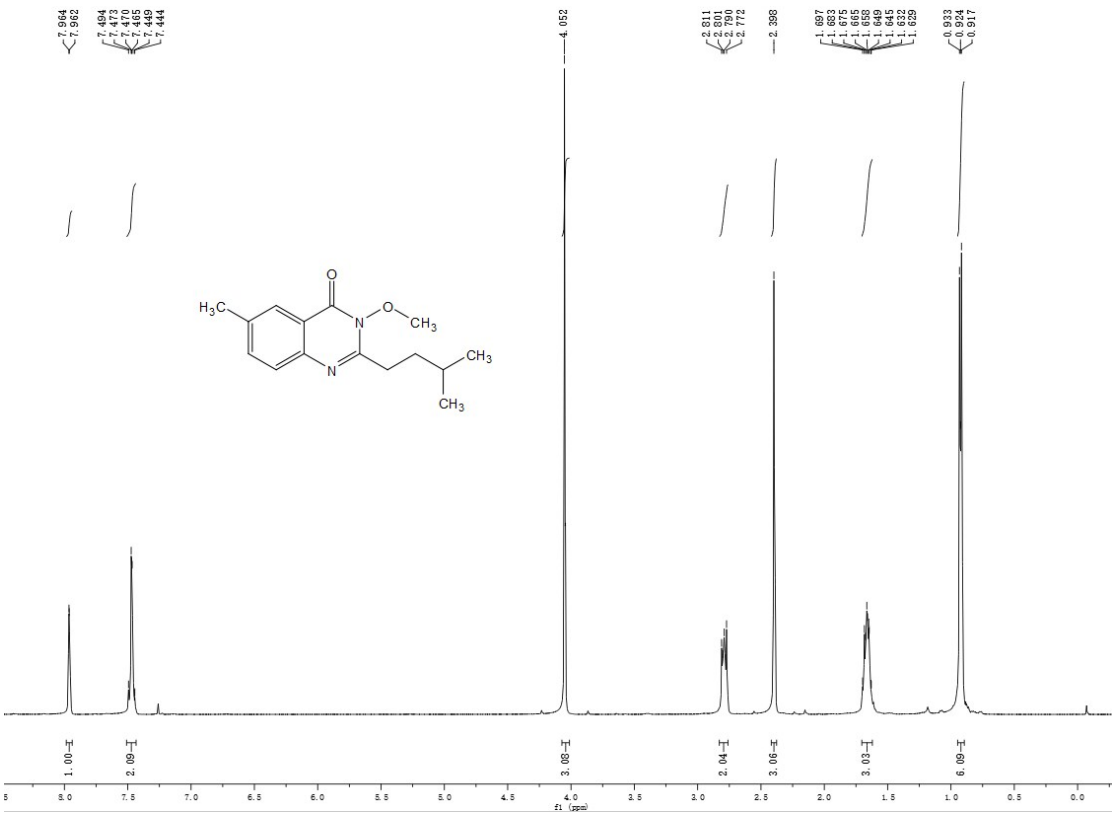
130.760
128.661
128.190
126.624
126.396
115.621
63.989
19.878
f1 (ppm)

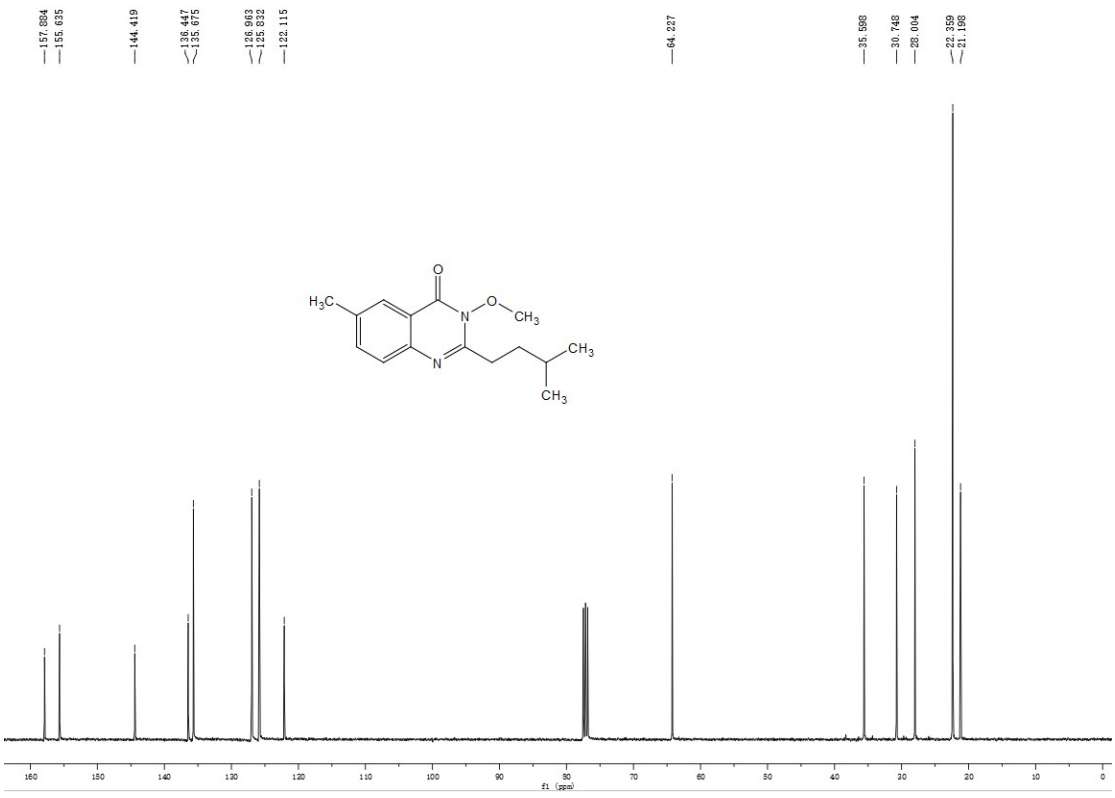

8.007
7.985
7.585
7.564
4.154
2.651
1.550
1.00
1.04
3.02
3.03
9.17
f1 (ppm)


175.634
154.831
152.930
147.516
144.598
139.768
125.783
123.623
109.214
64.420
34.612
29.670
20.079
f1 (ppm)


8.048
7.584
7.563
7.552
7.531
4.104
2.880
2.861
2.841
2.473
1.878
1.859
1.840
1.821
1.802
1.445
1.362
1.300
1.293
0.884
0.866
1.00
2.06
3.08
2.00
3.07
2.09
2.05
6.04
3.08
f1 (ppm)


162.335
158.068
155.773
136.761
135.928
127.072
126.073
122.282
64.450
32.819
31.821
29.495
29.139
26.987
22.757
21.371
14.218
f1 (ppm)


7.964
7.962
7.494
7.473
7.470
7.465
7.449
7.444
4.052
2.811
2.801
2.790
2.772
2.398
1.697
1.683
1.675
1.665
1.655
1.649
1.645
1.632
1.629
0.933
0.924
0.917
1.00
2.09
3.08
2.04
3.06
3.03
6.09
f1 (ppm)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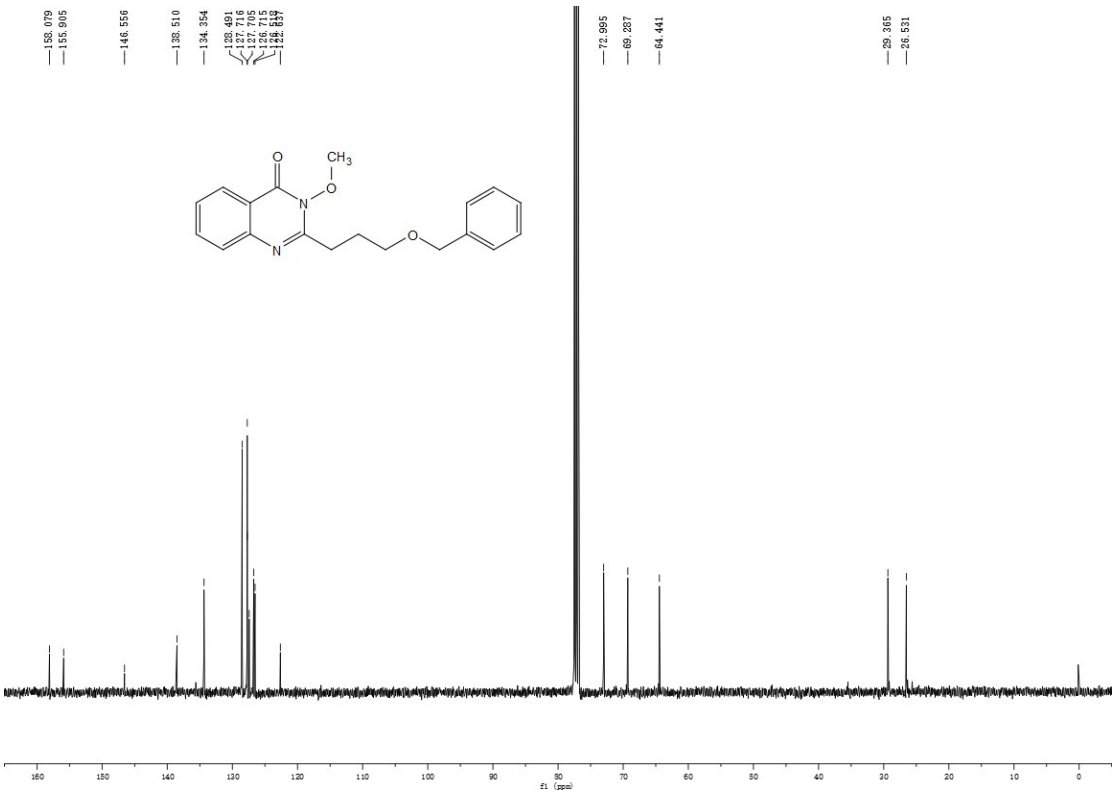
144.419
136.447
135.675
126.963
125.832
122.115
64.227
35.598
30.748
28.004
22.359
21.198
f1 (ppm)


8.269
8.266
8.249
8.246
7.750
7.746
7.729
7.725
7.711
7.708
7.669
7.666
7.649
7.640
7.467
7.464
7.447
7.429
7.427
7.319
7.308
7.293
7.273
7.269
7.266
4.522
4.099
3.665
3.650
3.635
3.038
3.020
3.001
2.234
2.219
2.200
2.182
2.167
O
CH3
N
O
N
O
1.00
1.04
1.09
1.08
4.01
1.05
2.00
3.06
2.09
2.02
2.06
f1 (ppm)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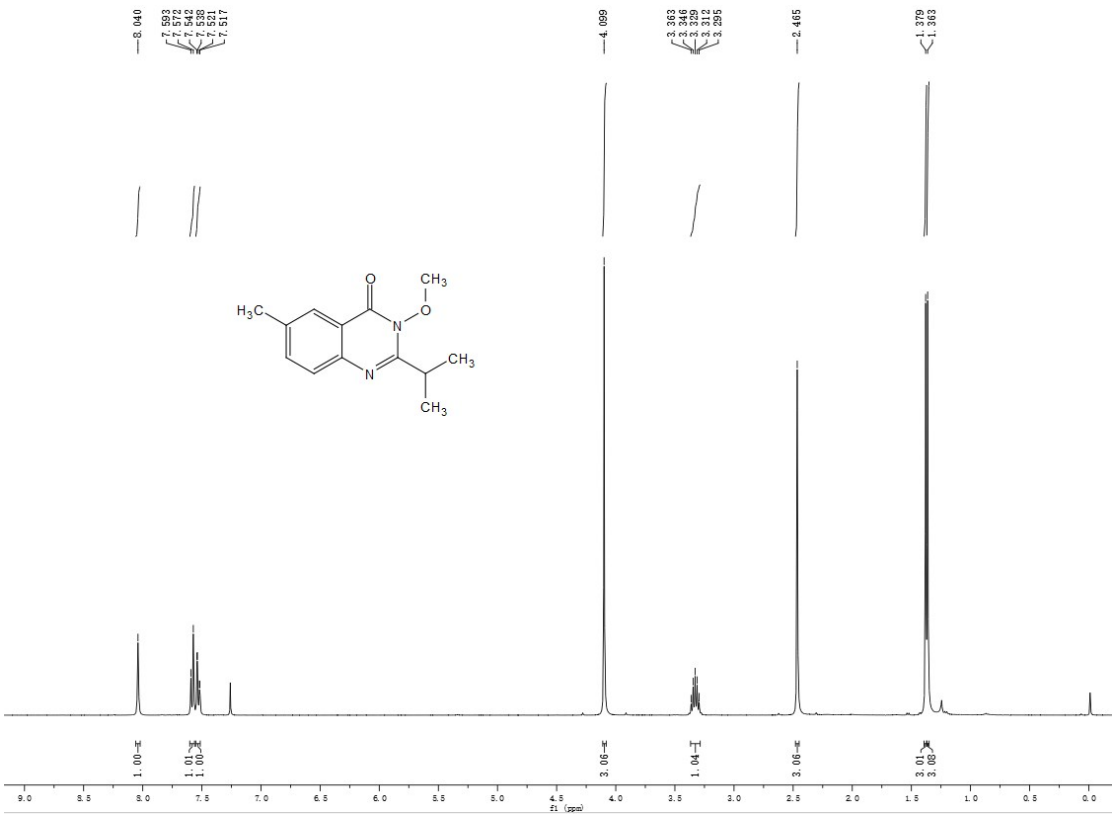
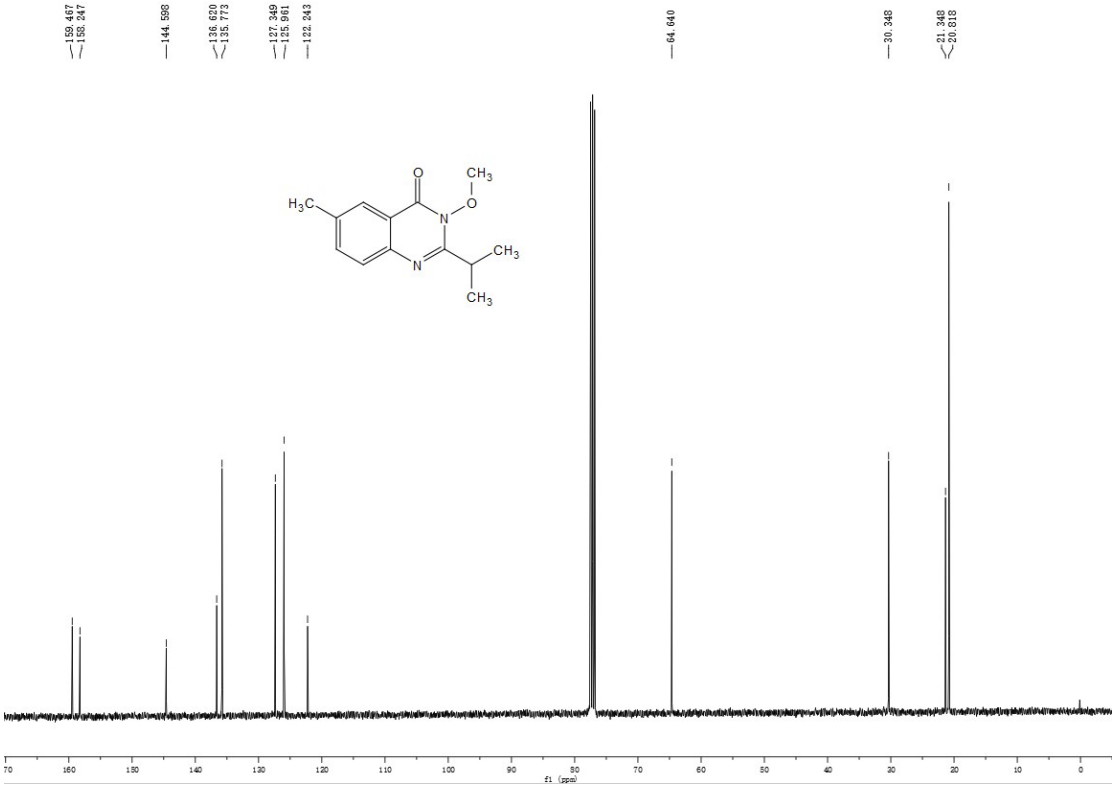
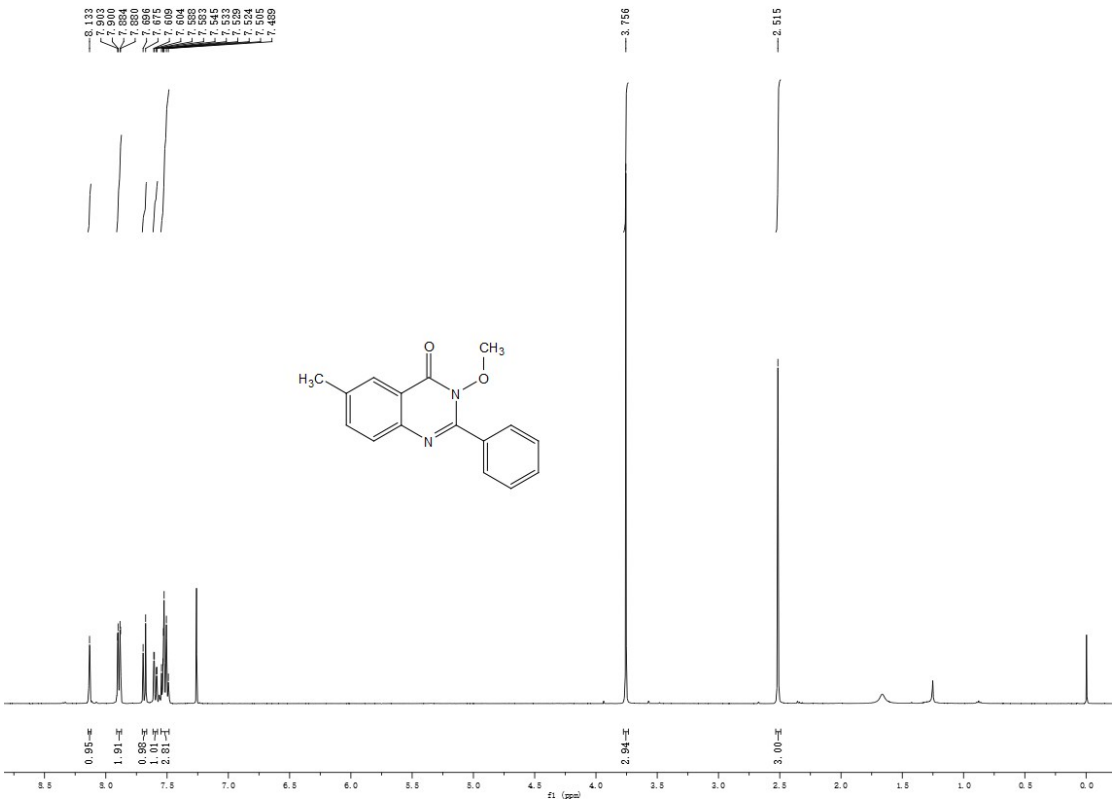
155.905
146.556
138.510
134.354
128.491
127.716
127.705
126.715
72.995
69.287
64.441
29.365
26.531
O
CH3
N
O
N
O
f1 (ppm)


8.040
7.593
7.572
7.542
7.538
7.531
7.517
4.099
3.363
3.346
3.329
3.312
3.295
2.465
1.379
1.363
O
CH3
H3C
O
N
CH3
N
CH3
1.00
1.01
1.00
3.06
1.04
3.06
3.01
3.08
f1 (ppm)


159.467
158.247
144.598
136.620
135.773
127.349
125.961
122.243
64.640
30.348
21.348
20.838
O
CH3
H3C
O
N
CH3
N
CH3
f1 (ppm)


8.133
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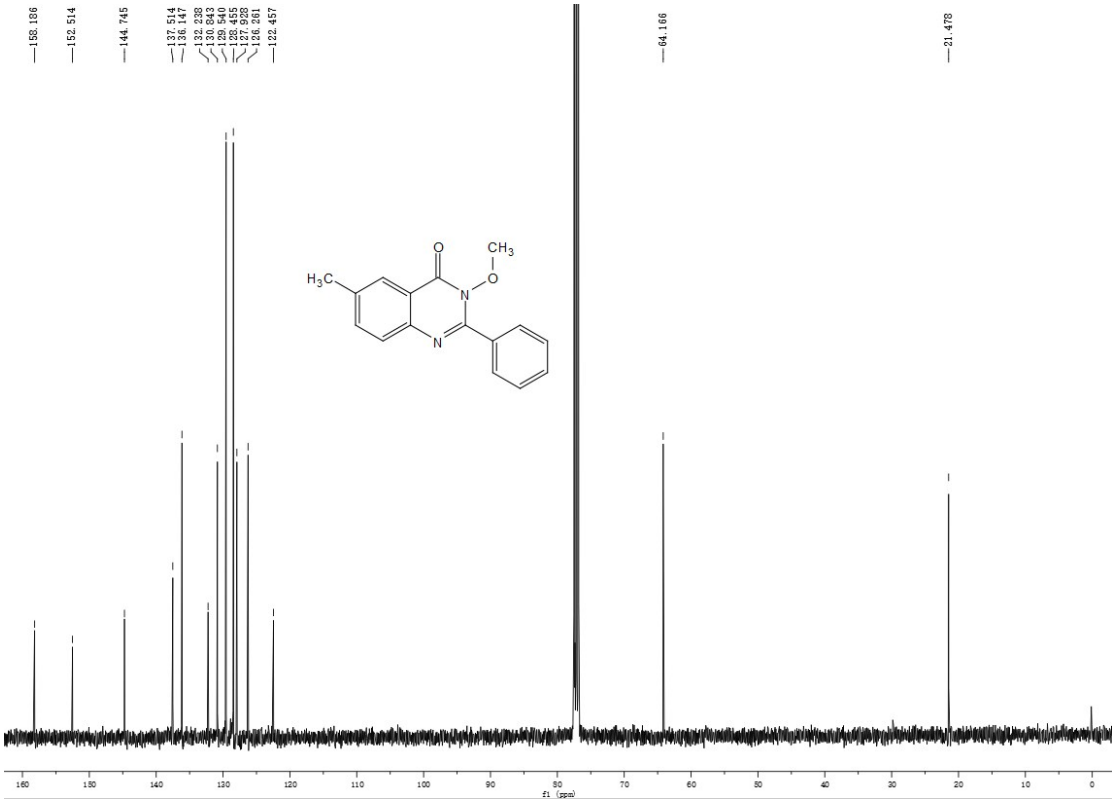
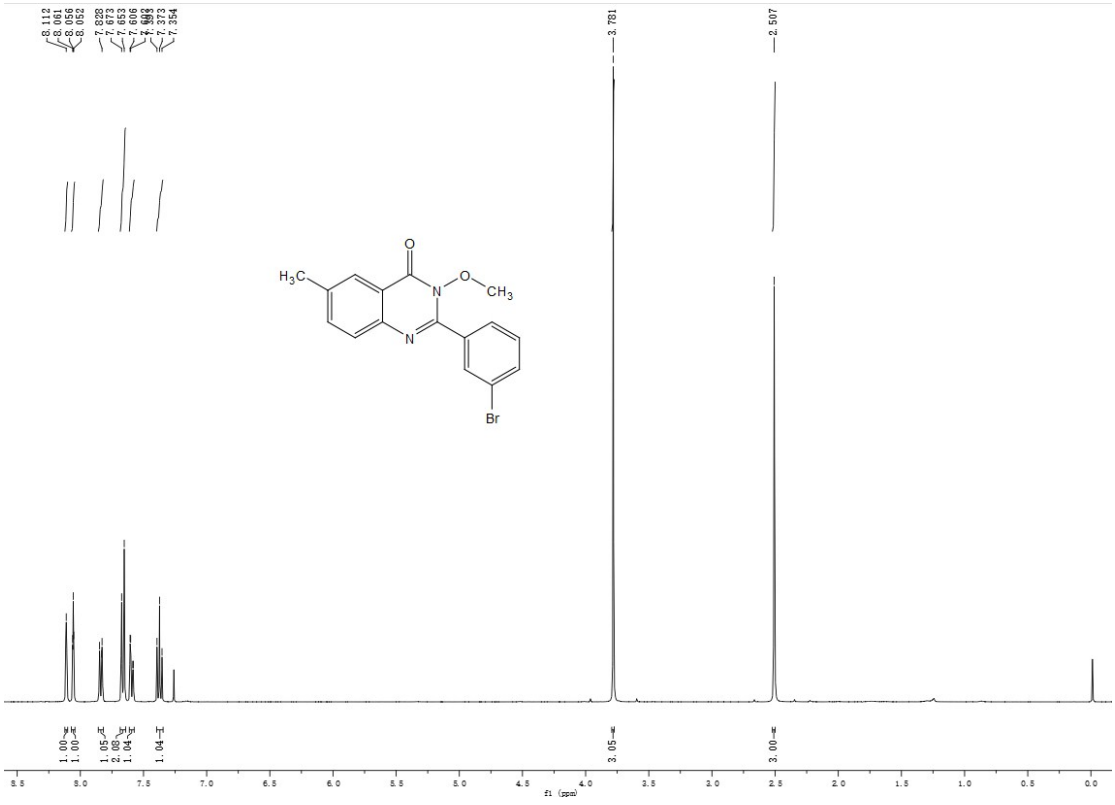
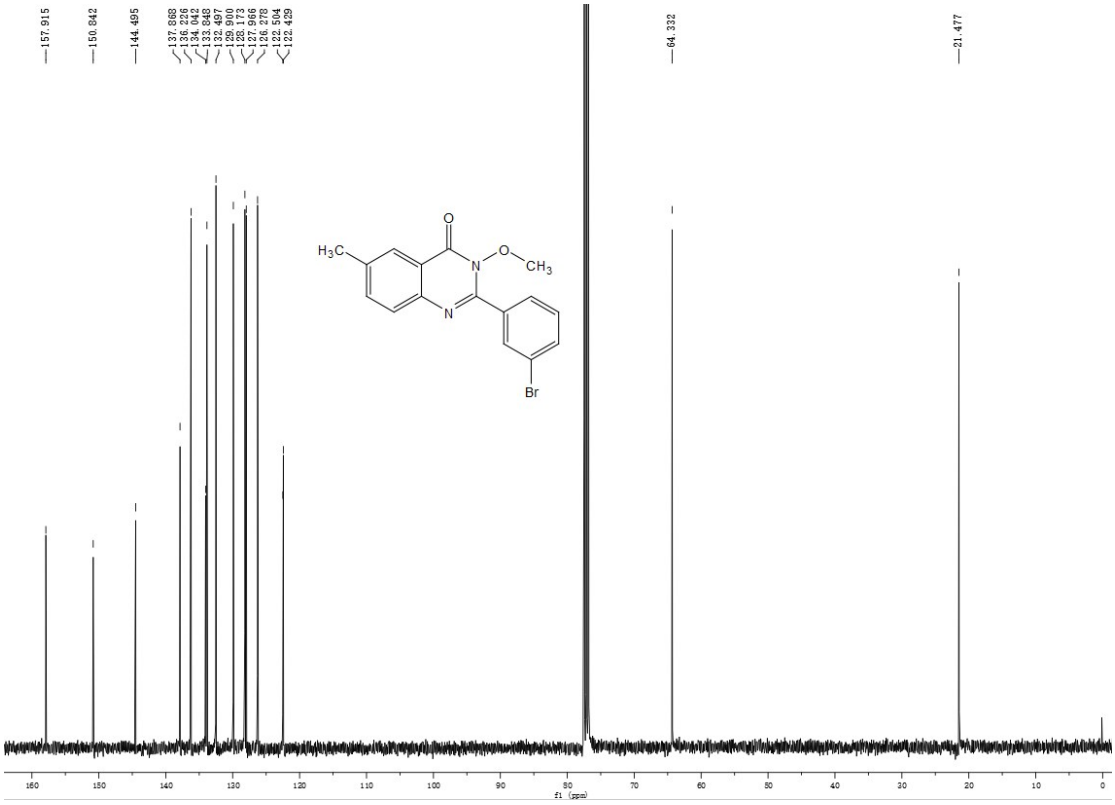
7.900
7.884
7.880
7.696
7.615
7.609
7.604
7.588
7.583
7.545
7.533
7.529
7.524
7.505
7.489
3.756
2.515
O
CH3
H3C
N
O
N
0.95
1.91
0.98
1.01
2.81
2.94
3.00
f1 (ppm)


158.186
152.514
144.745
137.514
136.147
132.238
130.843
129.540
128.455
127.928
126.261
122.457
64.166
21.478
O
CH3
H3C
N
O
N
f1 (ppm)


8.112
8.081
8.056
8.052
7.828
7.673
7.653
7.606
7.373
7.354
3.781
2.507
O
H3C
N
O
CH3
N
Br
1.00
1.00
1.05
2.05
1.04
1.04
3.05
3.00
f1 (ppm)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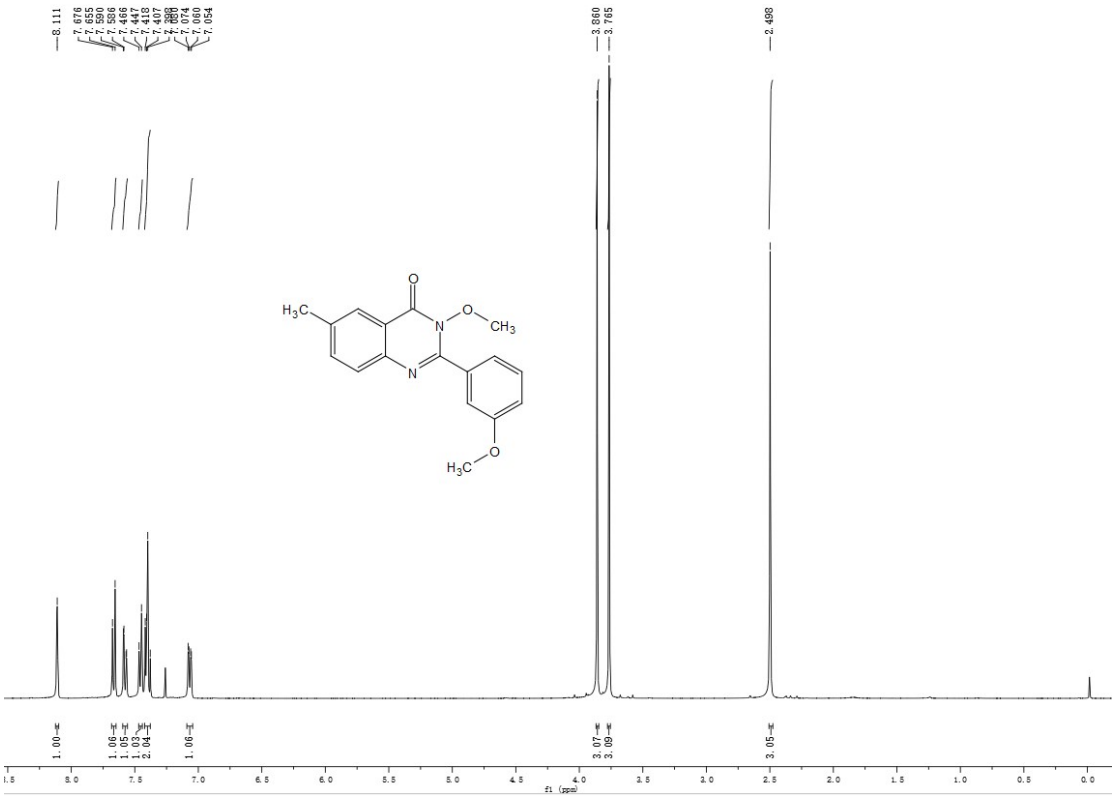
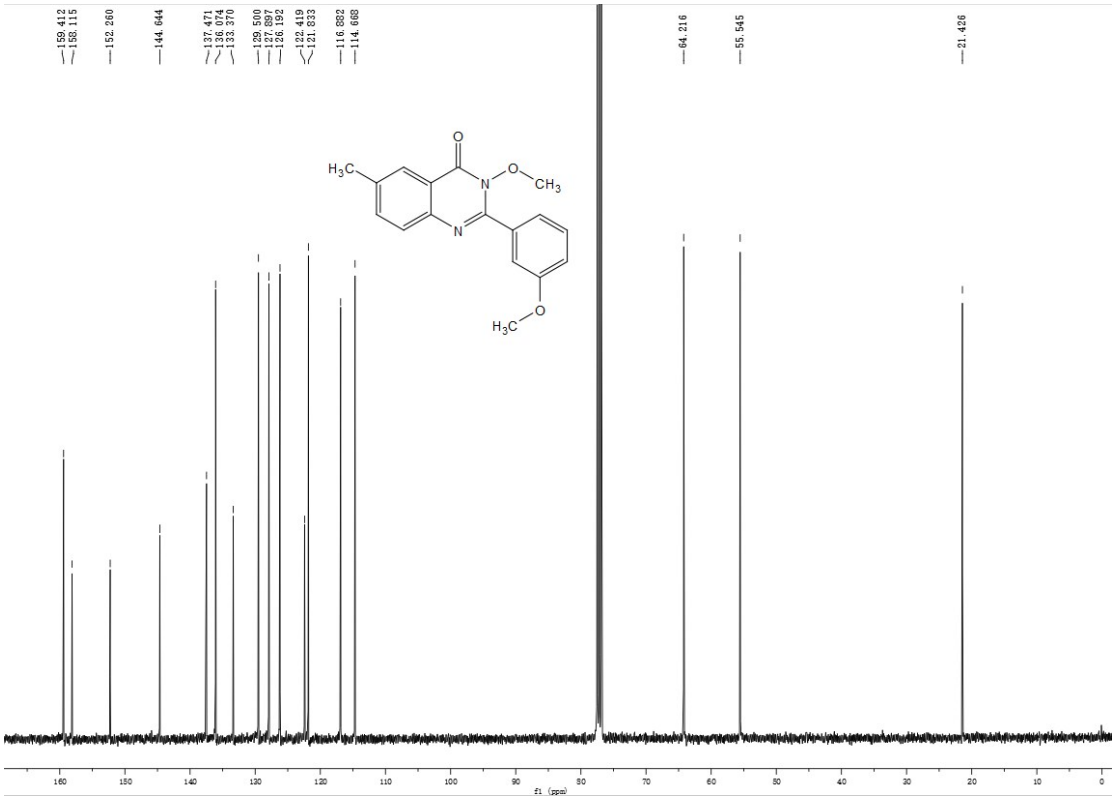
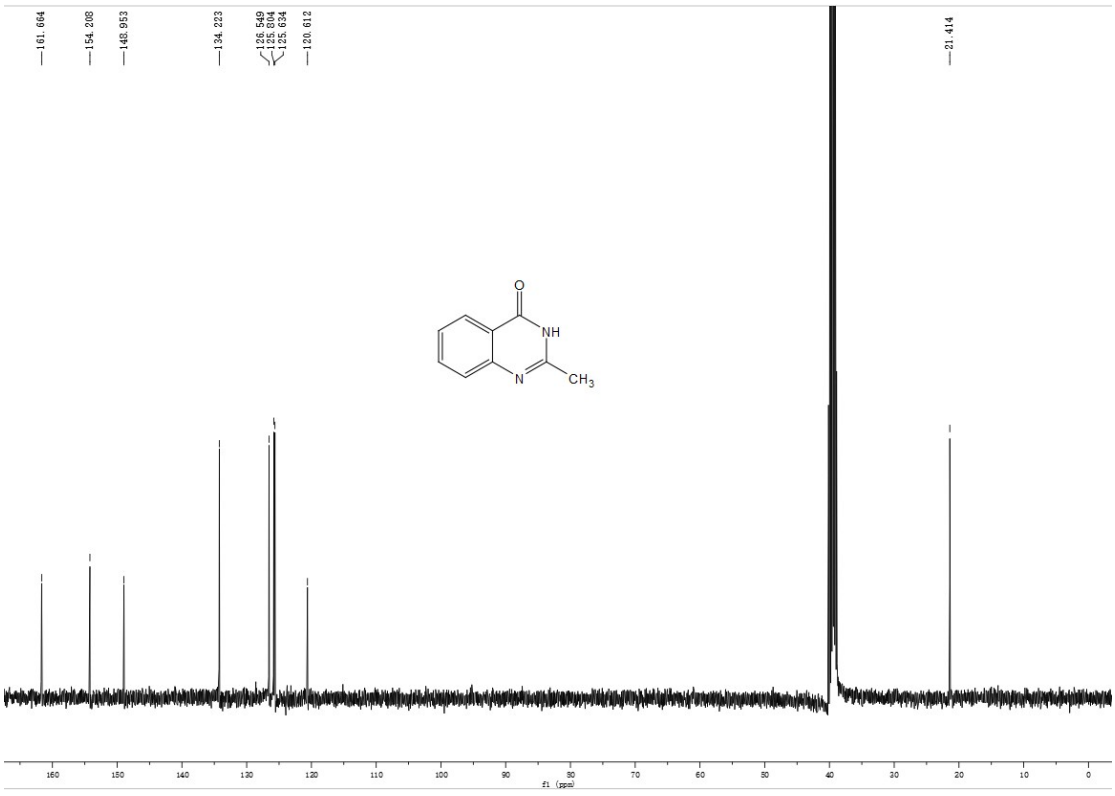
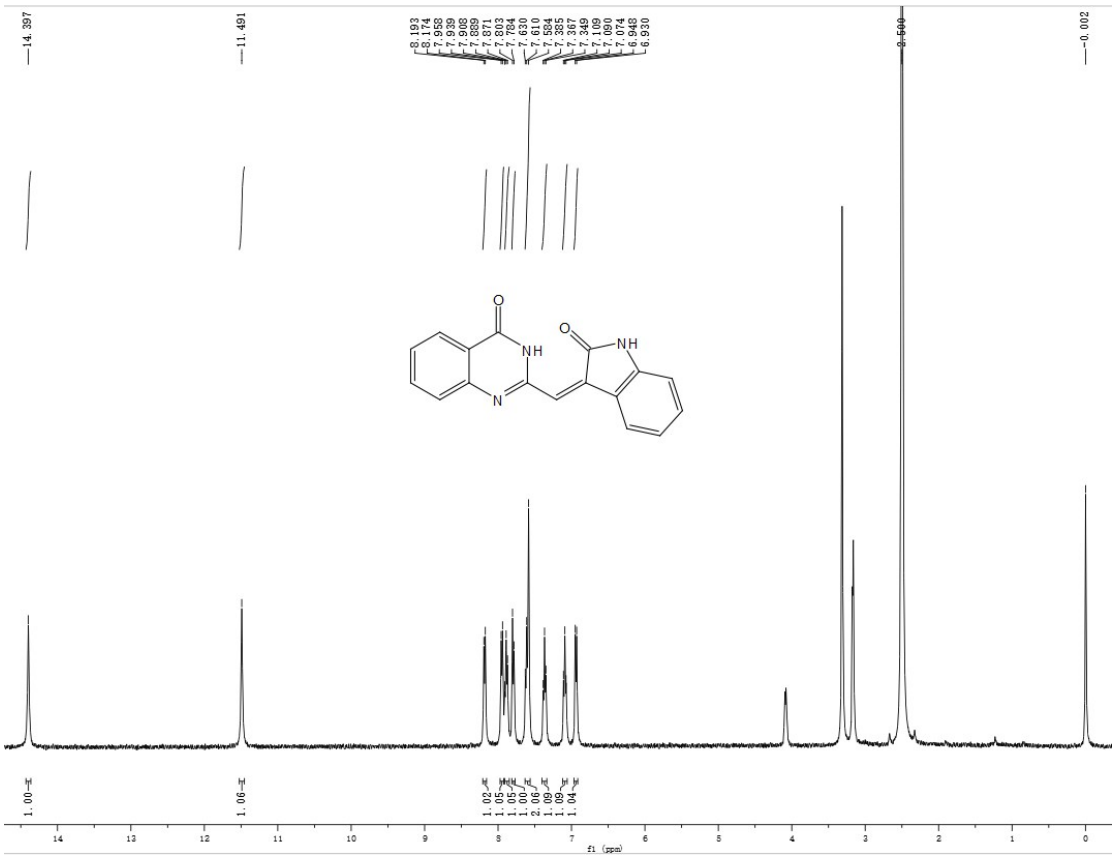
144.495
137.868
135.226
134.042
133.848
132.497
129.900
129.173
127.566
126.278
122.504
122.429
64.332
21.477
O
H3C
N
O
CH3
N
Br
f1 (ppm)

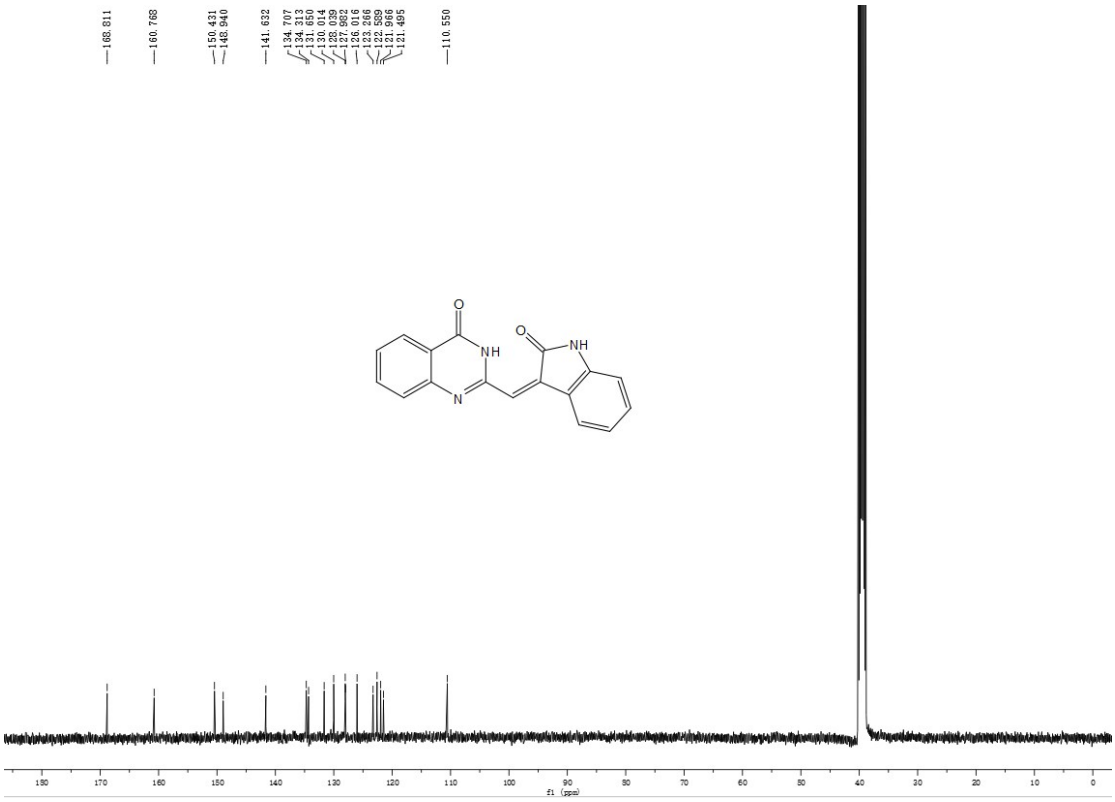

8.111
7.676
7.655
7.590
7.586
7.466
7.447
7.418
7.407
7.074
7.070
7.054
3.860
3.765
2.498
1.00
1.06
1.05
1.03
2.04
1.06
3.07
3.09
3.05
f1 (ppm)

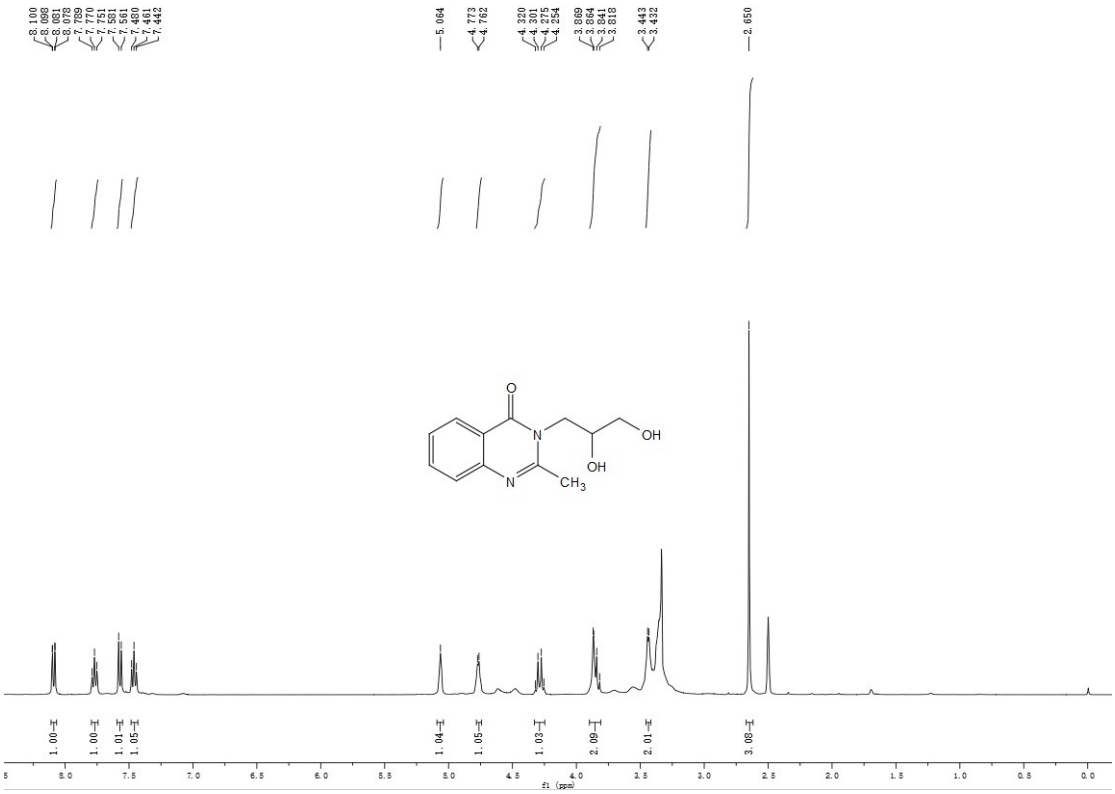

159.412
158.115
152.260
144.644
137.471
136.074
133.370
129.500
127.897
126.192
122.419
121.833
116.882
114.668
64.216
55.545
21.426
f1 (ppm)

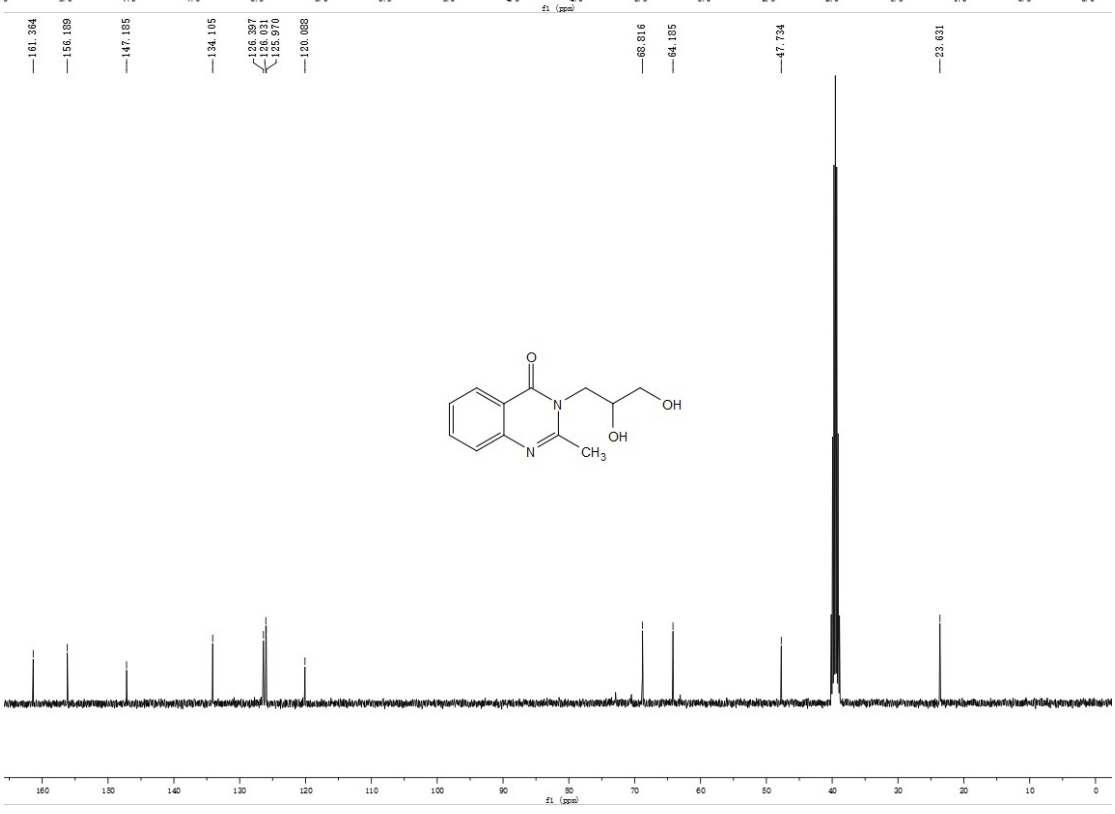

12.179
8.078
8.075
8.058
8.055
7.779
7.775
7.758
7.754
7.740
7.737
7.572
7.552
7.460
7.441
7.423
2.343
O
NH
N
CH3
0.91
1.00
1.03
0.98
1.00
3.12
f1 (ppm)


161.664
154.208
148.953
134.223
126.549
125.804
125.634
120.612
21.414
O
NH
N
CH3
f1 (ppm)

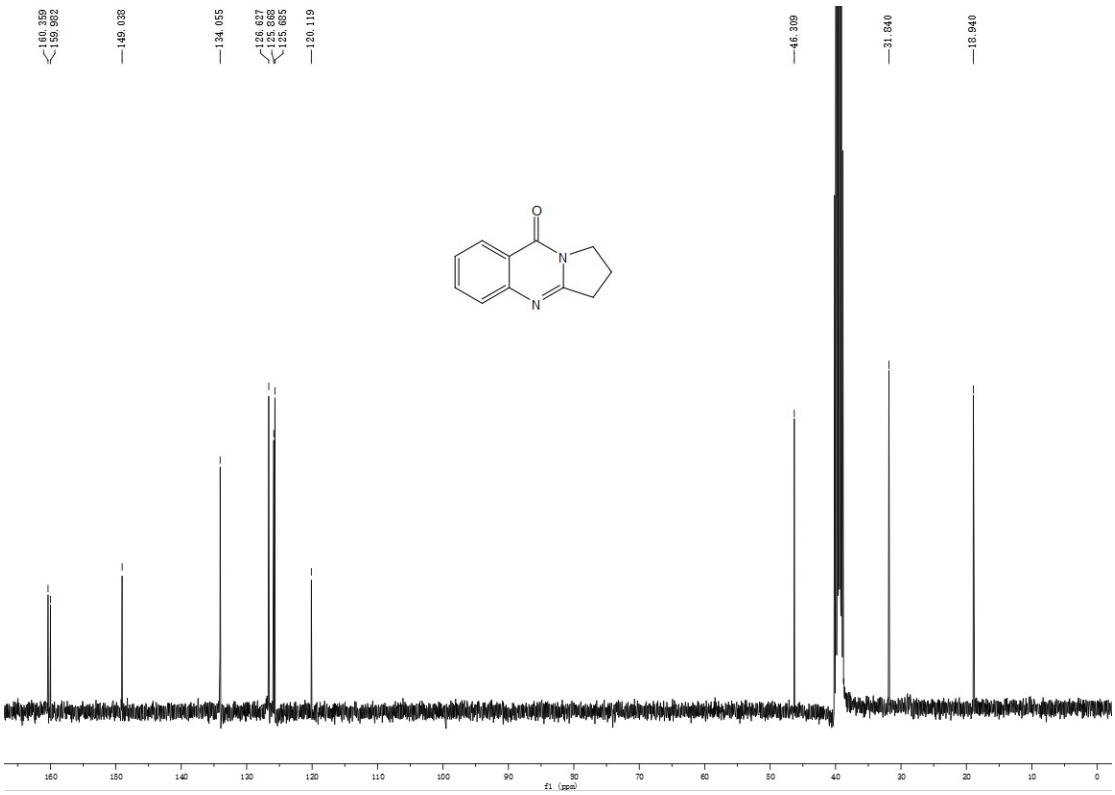

14.397
11.491
8.193
8.174
7.958
7.939
7.908
7.889
7.871
7.803
7.784
7.630
7.610
7.594
7.385
7.367
7.349
7.109
7.090
7.074
6.948
6.930
8.640
0.002
O
NH
O
NH
N
1.00
1.06
1.02
1.05
1.05
1.00
2.00
1.09
1.04
f1 (ppm)

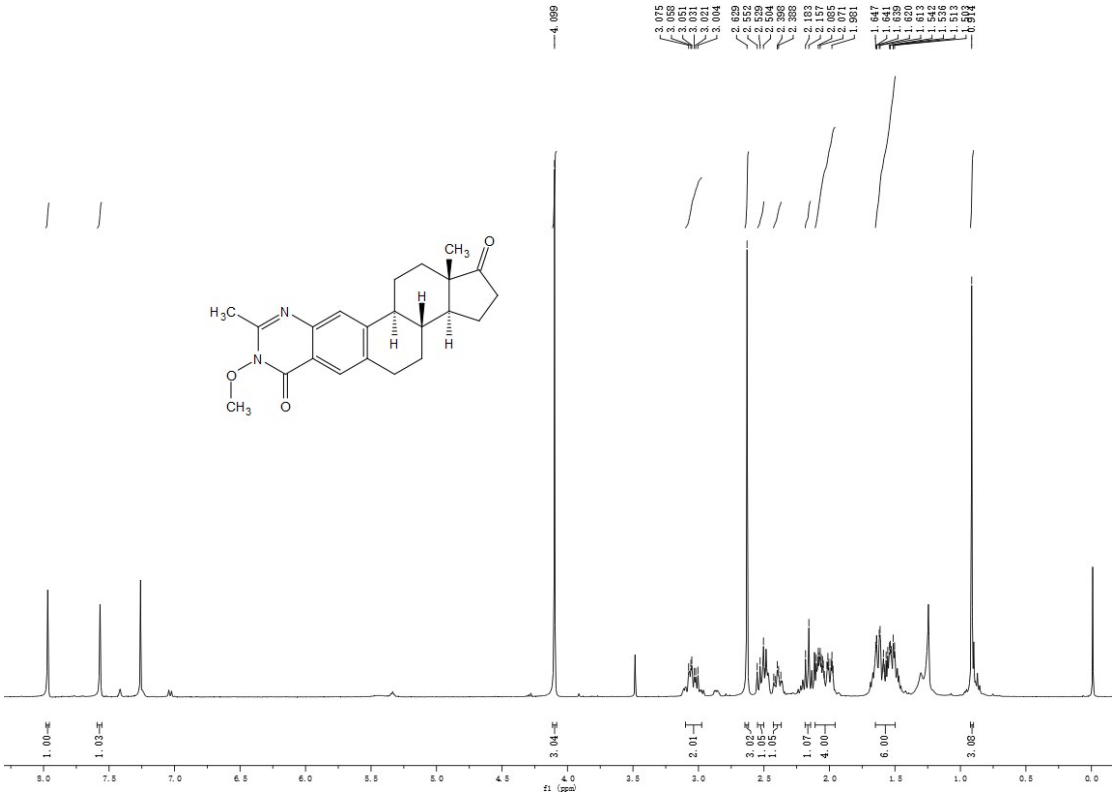

168.811
160.768
150.431
148.940
141.632
134.707
134.313
131.650
130.014
128.039
127.982
126.016
123.266
122.288
121.966
121.495
110.550
O
NH
O
NH
N
f1 (ppm)

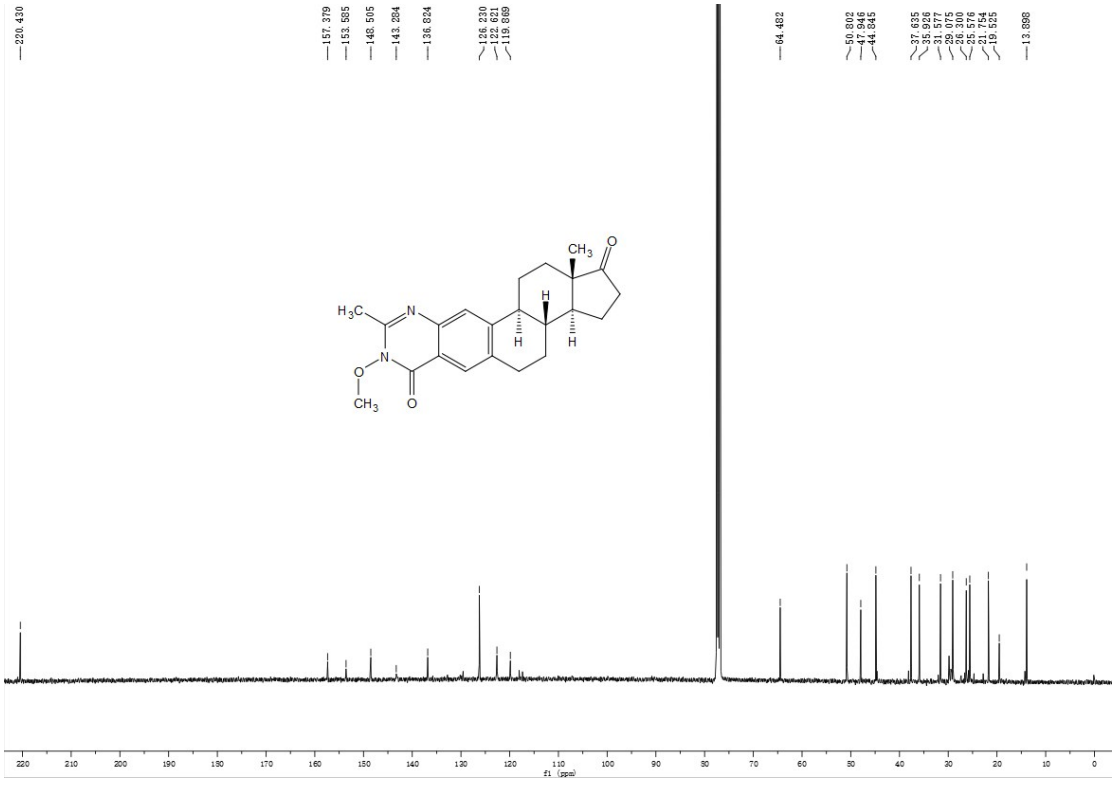

8.100
8.098
8.081
8.078
7.789
7.770
7.751
7.561
7.561
7.480
7.461
7.442
5.064
4.773
4.762
4.320
4.301
4.275
4.254
3.869
3.864
3.841
3.818
3.443
3.432
2.650
O
N
OH
OH
N
CH3
1.00
1.00
1.01
1.05
1.04
1.05
1.03
2.09
2.01
3.08
f1 (ppm)


161.364
156.189
147.185
134.105
126.397
126.031
125.970
120.088
68.816
64.185
47.734
23.631
O
N
OH
OH
N
CH3
f1 (ppm)


8.119
8.099
7.794
7.776
7.756
7.610
7.590
7.486
7.467
7.448
4.075
4.057
4.039
3.099
3.079
3.059
2.206
2.186
2.168
2.149
2.130
O
N
N
1.00
1.06
1.03
1.05
2.09
2.06
2.02
f1 (ppm)


160.359
159.982
149.038
134.055
126.627
125.668
125.685
120.119
46.309
31.840
18.940
O
N
N
f1 (ppm)


4.099
3.075
3.058
3.051
3.031
3.021
3.004
2.629
2.552
2.539
2.524
2.394
2.388
2.183
2.157
2.085
2.077
1.981
1.647
1.641
1.630
1.620
1.613
1.542
1.538
1.533
1.514
0.914
CH3
O
H3C
N
H
H
H
N
O
CH3
O
1.00
1.03
3.04
2.01
3.02
1.05
1.05
1.07
4.00
6.00
3.08
f1 (ppm)


220.430
157.379
153.555
148.505
143.284
136.824
126.230
122.821
119.089
64.482
50.802
47.946
44.845
37.635
35.976
33.577
29.075
26.300
25.576
21.754
19.525
13.898
CH3
O
H3C
N
H
H
H
N
O
CH3
O
f1 (ppm)