Electronic Supplementary Material (ESI) for Green Chemistry.


# *Supporting information*

## Metal-Free Visible-Light-Initiated Direct C3 Alkylation of Quinoxalin-2(1*H*)-ones and Coumarins with Unactivated Alkyl Iodides

Jun Sun, Hua Yang,* and Bo Zhang*

*State Key Laboratory of Natural Medicines, China Pharmaceutical University, Nanjing 210009, China*

*E-mail: zb3981444@cpu.edu.cn; yanghuacpu@126.com*

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## *General*

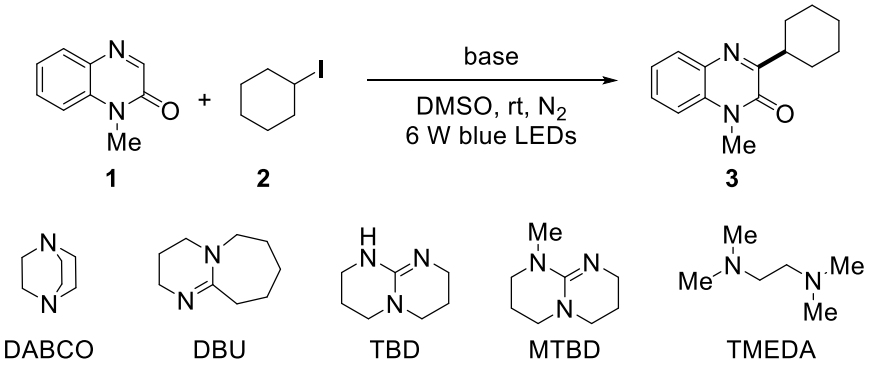
All manipulations were conducted with a standard *Schlenk* tube under a nitrogen atmosphere. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Anhydrous cyclohexane, dimethyl sulfoxide and $CH_2Cl_2$ were purchased from J&K Chemical or Energy Chemical and used as received. These solvents were dried and degassed by commercial suppliers. Alkyl halides were purchased from commercial sources or prepared according to the reported method.[1] Quinoxalinone substrates were prepared according to the reported method.[2] Coumarin substrates were prepared according to the reported method.[3]

Flash column chromatography was carried out on silica gel (200-300 mesh). Thin layer chromatography (TLC) was performed using silica gel 60 $F_{254}$ plates.

$^1$H NMR spectra were recorded on a *Bruker AV-300, AV-400 or AV-500* spectrometer at room temperature. Chemical shifts (in ppm) were referenced to tetramethylsilane (δ = 0 ppm) in $CDCl_3$ as an internal standard. $^{13}$C NMR spectra were obtained by the same NMR spectrometer and were calibrated with $CDCl_3$ (δ = 77.00 ppm). $^{19}$F NMR spectra were obtained by the same NMR spectrometer and using $CFCl_3$ as external standard. Data for $^1$H NMR are reported as follows: chemical shifts (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet or unresolved, br s = broad singlet), coupling constant (Hz) and integration. Data for $^{13}$C NMR are reported in terms of chemical shift and multiplicity where appropriate. High-Resolution Mass Spectrometry (HRMS) were performed on an *Aglient 6545 Q-TOF* for HRMS. The yields were determined on a *METTLER TOLEDO ME 104* balance (accuracy: 0.1 mg). Melting points (Mp) were determined on an RY-1G and are uncorrected.

## *Optimization of reaction conditions*

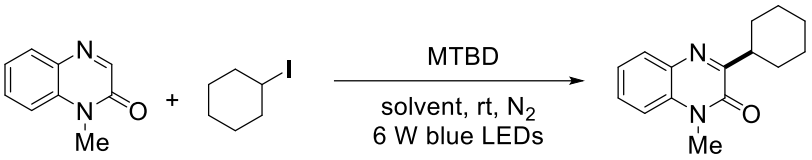
## *Table S1. Alkylation of 1: evaluation of bases*[a]




| entry | base | yield[b] (%) |
|---|---|---|
| 1 | DABCO | 0 |
| 2 | DBU | 22 |
| 3 | TBD | 25 |
| 4 | MTBD | 55 |
| 5 | $Et_3N$ | 0 |
| 6 | TMEDA | trace |
| 7 | $K_2CO_3$ | 0 |
| 8 | $Na_2CO_3$ | 0 |

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), and base (0.4 mmol) in DMSO (2.0 mL) were irradiated with 6 W blue LEDs at room temperature under $N_2$. [b]Isolated yields.

## *Table S2. Alkylation of 1: evaluation of solvents*[a]




**1** **2** **3**

| entry | solvent | yield[b] (%) |
|---|---|---|
| 1 | $CH_3CN$ | 14 |
| 2 | EtOAc | 13 |
| 3 | DMF | 15 |
| 4 | $CH_2Cl_2$ | 22 |
| 5 | THF | 11 |
| 6 | MeOH | 0 |

[a]Reaction conditions: **1** (0.2 mmol), **2** (0.6 mmol), and MTBD (0.4 mmol) in solvent (2.0 mL) were irradiated with 6 W blue LEDs at room temperature under $N_2$. [b]Isolated yields.

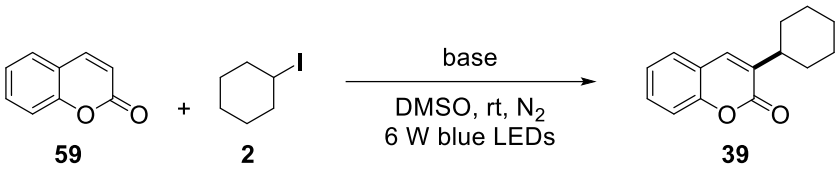
## *Table S3. Alkylation of 1: evaluation of other reaction parameters* [a]


**1** **2** **3**

| entry | MTBD (equiv) | **2** (equiv) | irradiation time (h) | yield[b] (%) |
|---|---|---|---|---|
| 1 | 3.0 | 3.0 | 12 | 56 |
| 2 | 5.0 | 3.0 | 12 | 58 |
| 3 | 3.0 | 4.0 | 12 | 74 |
| 4 | 4.0 | 4.0 | 12 | 75 |
| 5 | 5.0 | 4.0 | 12 | 78 |
| 6 | 2.0 | 5.0 | 12 | 57 |
| 7 | 3.0 | 5.0 | 12 | 68 |
| 8 | 4.0 | 5.0 | 12 | 71 |
| 9 | 5.0 | 5.0 | 12 | 88 |
| 10 | 5.0 | 5.0 | 3 | 62 |
| 11 | 5.0 | 5.0 | 6 | 82 |
| 12 | none | 5.0 | 12 | 0 |
| 13[c] | 5.0 | 5.0 | 12 | 0 |
| 14[d] | 5.0 | 5.0 | 12 | 0 |

[a]Reaction conditions: **1** (0.2 mmol), **2**, and MTBD in solvent (2.0 mL) were irradiated with 6 W blue LEDs at room temperature under $N_2$. [b]Isolated yields. [c]The reaction was conducted in the dark. [d]The reaction was conducted under air.

## *Table S4. Alkylation of 58: evaluation of bases*[a]




| entry | base | yield[b] (%) |
|---|---|---|
| 1 | DABCO | 0 |
| 2 | DBU | trace |
| 3 | TBD | 45 |
| 4 | MTBD | 80 |

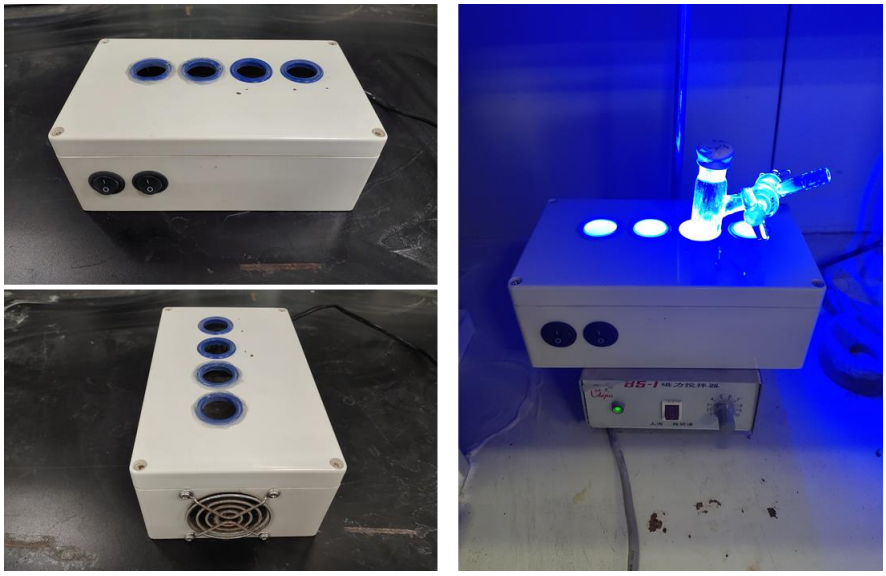
[a]Reaction conditions: **59** (0.2 mmol), **2** (0.6 mmol), and base (0.4 mmol) in DMSO (2.0 mL) were irradiated with 6 W blue LEDs at room temperature under $N_2$. [b]Isolated yields.

## *General procedure for direct C3 alkylation of quinoxalin-2(1H)-ones with alkyl iodides (GP1):*

Quinoxalin-2(1*H*)-one (0.2 mmol, 1.0 equiv), alkyl iodide (1.0 mmol, 5.0 equiv), and MTBD (1.0 mmol, 5.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous DMSO (2.0 mL) was added with a syringe, and the reaction mixture was irradiated with 6 W blue LEDs at room temperature under $N_2$ for 12 h. After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the product.

## *General procedure for direct C3 alkylation of coumarins with alkyl iodides (GP2):*

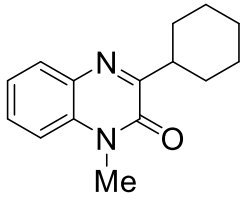
Coumarin (0.2 mmol, 1.0 equiv), alkyl halide (0.6 mmol, 3.0 equiv), and MTBD (0.4 mmol, 2.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous DMSO (2.0 mL) was added with a syringe, and the reaction mixture was irradiated with 6 W blue LEDs at room temperature under $N_2$ for 12 h. After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel to afford the product.



Reaction setup (4x6 W blue LEDs)

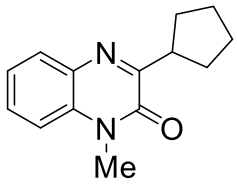
## *Physical data of the compounds*

**3-Cyclohexyl-1-methylquinoxalin-2(1*H*)-one (3)[4]**



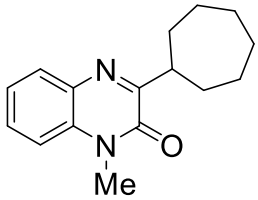

According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.0 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **3** as white solid (42.4 mg, 88%). Mp: 98-100 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 7.9 Hz, 1H), 7.51 (t, *J* = 7.7 Hz, 1H), 7.36-7.26 (m, 2H), 3.70 (s, 3H), 3.38-3.31 (m, 1H), 1.95 (d, *J* = 12.0 Hz, 2H), 1.87 (d, *J* = 12.6 Hz, 2H) , 1.77 (d, *J* = 12.6 Hz, 1H), 1.63-1.42 (m, 4H), 1.37-1.23 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.2, 154.5, 132.9, 132.8, 129.7, 129.3, 123.4, 113.4, 40.7, 30.5, 29.0, 26.3, 26.1; **HRMS** (ESI) calculated for $C_{15}H_{18}N_2O$ $[M+Na]^+$ m/z 265.1311, found 265.1314.

**3-Cyclopentyl-1-methylquinoxalin-2(1*H*)-one (4)[5]**



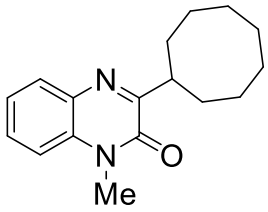

According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.4 mg, 0.2 mmol, 1.0 equiv), iodocyclopentane (196.0 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **4** as white solid (35.8 mg, 79%). Mp: 89-91 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.54-7.46 (m, 1H), 7.36-7.27 (m, 2H), 3.77-3.63 (m, 4H), 2.13-2.00 (m, 2H), 1.98-1.87 (m, 2H), 1.86-1.77 (m, 2H), 1.75-1.65 (m, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 163.7, 155.0, 132.9, 132.7, 129.7, 129.3, 123.3, 113.4, 42.7, 30.8, 29.0, 25.9; **HRMS** (ESI) calculated for $C_{14}H_{16}N_2O$ $[M+H]^+$ m/z 229.1335, found 229.1340.

**3-Cycloheptyl-1-methylquinoxalin-2(1*H*)-one (5)**



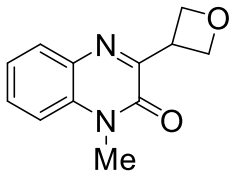

According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.1 mg, 0.2 mmol, 1.0 equiv), iodocycloheptane (224.1 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **5** as white solid (48.2 mg, 94%). Mp: 81-83 °C; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54-7.46 (m, 1H), 7.35-7.27 (m, 2H), 3.70 (s, 3H), 3.53-3.43 (m, 1H), 2.02-1.92 (m, 2H), 1.89-1.76 (m, 4H), 1.75-1.67 (m, 2H) 1.66-1.55 (m, 4H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 165.3, 154.4, 132.8, 132.7, 129.7, 129.3, 123.4, 113.4, 42.4, 32.2, 29.0, 28.1, 27.1; **HRMS** (ESI) calculated for $C_{16}H_{20}N_2O$ $[M+H]^+$ m/z 257.1648, found 257.1644.

**3-Cyclooctyl-1-methylquinoxalin-2(1*H*)-one (6)**



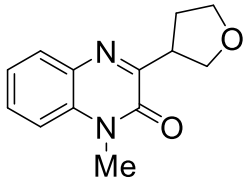

According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.2 mg, 0.2 mmol, 1.0 equiv), iodocyclooctane (238.1 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **6** as white solid (49.2 mg, 91%). Mp: 56-58 °C; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54-7.46 (m, 1H), 7.35-7.27 (m, 2H), 3.70 (s, 3H), 3.50-3.51 (m, 1H),1.91-1.84 (m, 4H), 1.83-1.76 (m, 2H), 1.74-1.57 (m, 8H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.7, 154.4, 132.8, 132.7, 129.7, 129.2, 123.4, 113.4, 40.4, 30.5, 29.0, 26.6, 26.5, 25.9; **HRMS** (ESI) calculated for $C_{17}H_{22}N_2O$ $[M+H]^+$ m/z 271.1805, found 271.1803.

**1-Methyl-3-(oxetan-3-yl)quinoxalin-2(1*H*)-one (7)**



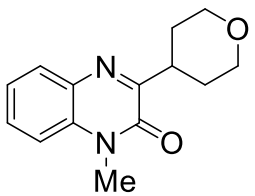
According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.1 mg, 0.2 mmol, 1.0 equiv), 3-iodooxetane (184.0 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3:1) to afford the desired product **7** as yellow solid (31.1 mg, 72%). Mp: 105-107 °C; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.92-7.86 (m, 1H), 7.60-7.53 (m, 1H), 7.41-7.30 (m, 2H), 5.11-5.00 (m, 4H), 4.72-4.61 (m, 1H), 3.68 (s, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 158.0, 154.1, 132.8, 132.4, 130.1, 129.9, 123.7, 113.5, 74.3, 38.1, 28.8; **HRMS** (ESI) calculated for $C_{12}H_{12}N_2O_2$ $[M+Na]^+$ m/z 239.0791, found 239.0788.

**1-Methyl-3-(tetrahydrofuran-3-yl)quinoxalin-2(1*H*)-one (8)**



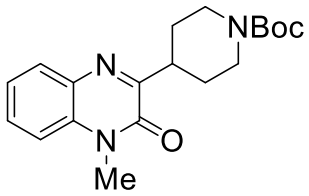
According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.3 mg, 0.2 mmol, 1.0 equiv), 3-iodotetrahydrofuran (198.0 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3:1) to afford the desired product **8** as white solid (39.0 mg, 85%). Mp: 110-112 °C; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.58-7.50 (m, 1H), 7.38-7.28 (m, 2H), 4.29-4.18 (m, 1H), 4.10-3.89 (m, 4H), 3.71 (s, 3H), 2.52-2.25 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.0, 154.9, 133.0, 132.5, 130.0, 129.9, 123.6, 113.5, 71.3, 68.6, 42.3, 30.0, 29.1; **HRMS** (ESI) calculated for $C_{13}H_{14}N_2O_2$ $[M+H]^+$ m/z 231.1128, found 231.1124.

**1-Methyl-3-(tetrahydro-2*H*-pyran-4-yl)quinoxalin-2(1*H*)-one (9)[6]**



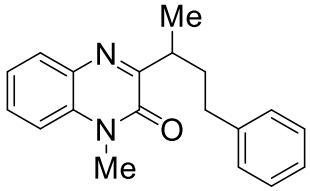
According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.2 mg, 0.2 mmol, 1.0 equiv), 4-iodotetrahydro-2*H*-pyran (212.0 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 2:1) to afford the desired product **9** as white solid (47.6 mg, 98%). Mp: 174-176 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.7 Hz, 1H), 7.52 (t, *J* = 7.4 Hz, 1H), 7.39-7.28 (m, 2H), 4.09 (d, *J* = 10.9 Hz, 2H), 3.70 (s, 3H), 3.66-3.53 (m, 3H), 1.93 (dt, *J* = 24.2, 7.8 Hz, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.8, 154.2, 132.7, 132.6, 129.8, 129.6, 123.4, 113.4, 67.7, 38.0, 29.9, 28.9; **HRMS** (ESI) calculated for $C_{14}H_{16}N_2O_2$ $[M+H]^+$ m/z 245.1285, found 245.1280.

***tert*-Butyl 4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)piperidine-1-carboxylate (10)[7]**




According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.4 mg, 0.2 mmol, 1.0 equiv), *tert*-butyl 4-iodopiperidine-1-carboxylate (311.1 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 2:1) to afford the desired product **10** as white solid (65.7 mg, 96%). Mp: 180-182 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.58-7.49 (m, 1H), 7.37-7.29 (m, 2H), 4.43-4.09 (m, 2H), 3.71 (s, 3H), 3.52-3.42 (m, 1H), 2.92 (t, *J* = 11.2 Hz, 2H), 1.94 (d, *J* = 12.0 Hz, 2H), 1.83-1.70 (m, 2H), 1.48 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 162.1, 154.7, 154.3, 132.8, 132.6, 129.8, 129.7, 123.5, 113.5, 79.2, 43.7, 38.8, 29.3, 29.0, 28.4; **HRMS** (ESI) calculated for $C_{19}H_{25}N_3O_3$ $[M+Na]^+$ m/z 366.1788, found 366.1782.

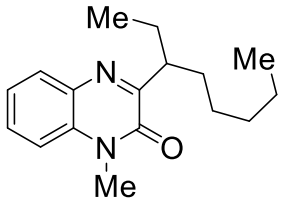
**1-Methyl-3-(4-phenylbutan-2-yl)quinoxalin-2(1*H*)-one (11)**




According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.2 mg, 0.2 mmol, 1.0

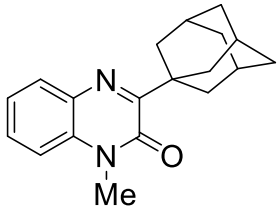
equiv), (3-iodobutyl)benzene (260.1 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **11** as pale yellow oil (30.9 mg, 53%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.87-7.81 (m, 1H), 7.55-7.48 (m, 1H), 7.33 (t, *J* = 7.6 Hz, 1H), 7.28 (d, *J* = 8.3 Hz, 1H), 7.25-7.16 (m, 4H), 7.15-7.09 (m, 1H), 3.69 (s, 3H), 3.64-3.54 (m, 1H), 2.75-2.58 (m, 2H), 2.35-2.23 (m, 1H), 1.95-1.85 (m, 1H), 1.34 (d, *J* = 6.9 Hz, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 164.1, 154.6, 142.5, 132.9, 132.7, 129.8, 129.5, 128.4, 128.1, 125.5, 123.4, 113.4, 36.2, 36.1, 33.9, 29.0, 18.5; **HRMS** (ESI) calculated for $C_{19}H_{20}N_2O$ $[M+H]^+$ m/z 293.1648, found 293.1643.

**1-Methyl-3-(octan-3-yl)quinoxalin-2(1*H*)-one (12)**




According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.0 mg, 0.2 mmol, 1.0 equiv), 3-iodooctane (480.1 mg, 2.0 mmol, 10.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **12** as colorless oil (29.0 mg, 53%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.55-7.48 (m, 1H), 7.36-7.27 (m, 2H), 3.71 (s, 3H), 3.45-3.37 (m, 1H), 1.93-1.80 (m, 2H), 1.74-1.58 (m, 2H), 1.35-1.19 (m, 6H), 0.91-0.79 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.0, 155.0, 132.8, 132.7, 129.7, 129.3, 123.3, 113.4, 43.1, 32.9, 32.0, 29.1, 27.2, 26.1, 22.5, 14.0, 12.0; **HRMS** (ESI) calculated for $C_{17}H_{24}N_2O$ $[M+H]^+$ m/z 273.1961, found 273.1957.

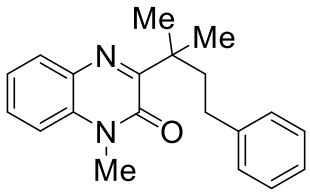
**3-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-1-methylquinoxalin-2(1*H*)-one (13)[5]**




According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.2 mg, 0.2 mmol, 1.0 equiv), (3*s*,5*s*,7*s*)-1-iodoadamantane (262.1 mg, 1.0 mmol, 5.0 equiv), and MTBD

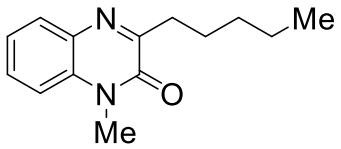
(144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 20:1) to afford the desired product **13** as white solid (38.6 mg, 66%). Mp: 186-188 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.52-7.46 (m, 1H), 7.33-7.23 (m, 2H), 3.65 (s, 3H), 2.27-2.20 (m, 6H), 2.14-2.07 (m, 3H), 1.86-1.76 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.7, 153.5, 132.9, 132.3, 130.0, 129.4, 123.1, 113.2, 41.9, 38.7, 37.0, 28.6, 28.5; **HRMS** (ESI) calculated for $C_{19}H_{22}N_2O$ $[M+H]^+$ m/z 295.1805, found 295.1800.

**1-Methyl-3-(2-methyl-4-phenylbutan-2-yl)quinoxalin-2(1*H*)-one (14)**




According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.0 mg, 0.2 mmol, 1.0 equiv), (3-iodo-3-methylbutyl)benzene (548.1 mg, 2.0 mmol, 10.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 8:1) to afford the desired product **14** as yellow oil (18.2 mg, 30%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.54-7.48 (m, 1H), 7.35-7.30 (m, 1H), 7.23 (dd, *J* = 8.4, 0.9 Hz, 1H), 7.16-7.02 (m, 5H), 3.60 (s, 3H), 2.53-2.46 (m, 2H), 2.39-2.32 (m, 2H), 1.53 (s, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.2, 153.6, 142.8, 133.3, 132.2, 130.1, 129.5, 128.5, 127.9, 125.3, 123.1, 113.2, 42.8, 41.7, 31.7, 28.7, 26.4; $C_{20}H_{22}N2O$ $[M+H]^+$ m/z 307.1805, found 307.1802.

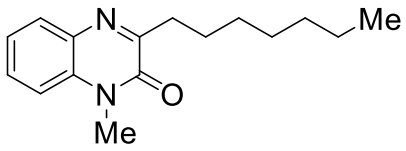
**1-Methyl-3-pentylquinoxalin-2(1*H*)-one (15)[8]**




According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.4 mg, 0.2 mmol, 1.0 equiv), 1-iodopentane (198.0 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **15** as yellow solid (39.9 mg, 87%). Mp: 75-77 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.55-7.48 (m, 1H), 7.37-7.27 (m, 2H), 3.70 (s, 3H), 2.94 (t, *J* = 7.6 Hz, 2H), 1.79 (p, *J* = 7.6 Hz, 2H), 1.48-1.35 (m, 4H), 0.92 (t, *J* = 7.0 Hz, 3H); **$^{13}$C**

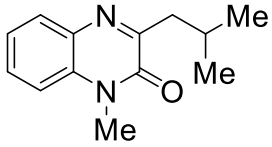
**NMR** (101 MHz, $CDCl_3$) δ 161.3, 154.8, 133.0, 132.7, 129.5, 129.4, 123.4, 113.5, 34.3, 31.7, 28.9, 26.5, 22.5, 14.0; **HRMS** (ESI) calculated for $C_{14}H_{18}N_2O$ $[M+H]^+$ m/z 231.1492, found 231.1486.

**3-Heptyl-1-methylquinoxalin-2(1*H*)-one (16)[6]**



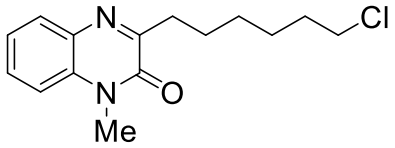

According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.3 mg, 0.2 mmol, 1.0 equiv), 1-iodoheptane (226.1 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **16** as pale yellow solid (44.9 mg, 87%). Mp: 73-75 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.54-7.48 (m, 1H), 7.37-7.25 (m, 2H), 3.69 (s, 3H), 2.93 (t, *J* = 7.6 Hz, 2H), 1.78 (p, *J* = 7.6 Hz, 2H), 1.49-1.26 (m, 8H), 0.88 (t, *J* = 6.8 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.3, 154.8, 133.0, 132.6, 129.5, 129.4, 123.4, 113.4, 34.3, 31.7, 29.5, 29.1, 28.9, 26.8, 22.6, 14.0; **HRMS** (ESI) calculated for $C_{16}H_{22}N_2O$ $[M+H]^+$ m/z 259.1805, found 259.1799.

**3-Isobutyl-1-methylquinoxalin-2(1*H*)-one (17)[9]**



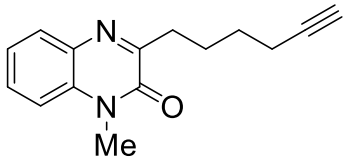

According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.1 mg, 0.2 mmol, 1.0 equiv), 1-iodo-2-methylpropane (184.0 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **17** as yellow oil (27.3 mg, 63%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.55-7.49 (m, 1H), 7.37-7.28 (m, 2H), 3.70 (s, 3H), 2.83 (d, *J* = 7.1 Hz, 2H), 2.40-2.27 (m, 1H), 1.01 (d, *J* = 6.7 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.7, 155.0, 133.0, 132.6, 129.6, 129.5, 123.5, 113.5, 42.9, 29.0, 26.8, 22.7; **HRMS** (ESI) calculated for $C_{13}H_{16}N_2O$ $[M+H]^+$ m/z 217.1335, found 217.1331.

**3-(6-Chlorohexyl)-1-methylquinoxalin-2(1*H*)-one (18)**



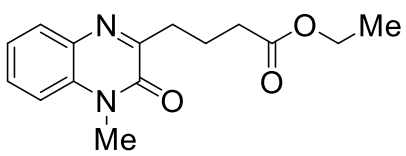

According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.3 mg, 0.2 mmol, 1.0 equiv), 1-chloro-6-iodohexane (246.5 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **18** as pale yellow oil (45.1 mg, 81%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.54-7.48 (m, 1H), 7.37-7.26 (m, 2H), 3.69 (s, 3H), 3.54 (t, *J* = 6.8 Hz, 2H), 2.94 (t, *J* = 7.6 Hz, 2H), 1.86-1.75 (m, 4H), 1.55-1.44 (m, 4H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 160.9, 154.8, 133.0, 132.6, 129.5, 129.5, 123.5, 113.5, 45.1, 34.1, 32.4, 29.0, 28.7, 26.6, 26.5; **HRMS** (ESI) calculated for $C_{15}H_{19}ClN_2O$ $[M+H]^+$ m/z 279.1259, found 279.1256.

**3-(Hex-5-yn-1-yl)-1-methylquinoxalin-2(1*H*)-one (19)[10]**



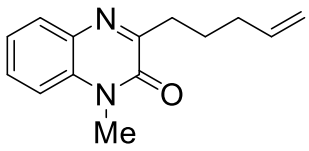

According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.1 mg, 0.2 mmol, 1.0 equiv), 6-iodohex-1-yne (208.0 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **19** as white solid (38.8 mg, 81%). Mp: 82-84 °C; **$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.56-7.48 (m, 1H), 7.38-7.27 (m, 2H), 3.70 (s, 3H), 2.96 (t, *J* = 7.8 Hz, 2H), 2.27 (td, *J* = 7.1, 2.6 Hz, 2H), 1.99-1.86 (m, 3H), 1.69 (p, *J* = 7.2 Hz, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 160.6, 154.8, 133.0, 132.6, 129.6, 129.5, 123.5, 113.5, 84.3, 68.3, 33.6, 29.0, 28.3, 25.7, 18.3; **HRMS** (ESI) calculated for $C_{15}H_{16}N_2O$ $[M+H]^+$ m/z 241.1335, found 241.1330.

**Ethyl 4-(4-methyl-3-oxo-3,4-dihydroquinoxalin-2-yl)butanoate (20)[11]**



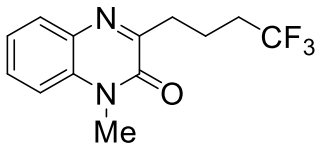
According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.0 mg, 0.2 mmol, 1.0 equiv), ethyl 4-iodobutanoate (242.0 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **20** as yellow solid (30.2 mg, 55%). Mp: 101-103 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 8.0, 1.1 Hz, 1H), 7.56-7.49 (m, 1H), 7.37-7.28 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.70 (s, 3H), 2.99 (t, *J* = 7.4 Hz, 2H), 2.47 (t, *J* = 7.6 Hz, 2H), 2.17 (p, *J* = 7.5 Hz, 2H), 1.25 (t, *J* = 7.1 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 173.4, 160.0, 154.8, 133.0, 132.6, 129.7, 129.7, 123.5, 113.5, 60.3, 33.8, 33.2, 29.0, 21.6, 14.2; **HRMS** (ESI) calculated for $C_{15}H_{18}N_2O_3$ $[M+H]^+$ m/z 275.1390, found 275.1393.

**1-Methyl-3-(pent-4-en-1-yl)quinoxalin-2(1*H*)-one (21)**




According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.2 mg, 0.2 mmol, 1.0 equiv), 5-iodopent-1-ene (196.0 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **21** as white solid (31.5 mg, 69%). Mp: 57-59 °C; **$^1$H NMR** (500 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.9, 1.0 Hz, 1H), 7.53-7.47 (m, 1H), 7.34-7.25 (m, 2H), 5.92-5.82 (m, 1H), 5.10-5.02 (m, 1H), 5.00-4.95 (m, 1H), 3.68 (s, 3H), 2.95 (t, *J* = 7.5 Hz, 2H), 2.21 (q, *J* = 7.2 Hz, 2H), 1.91 (p, *J* = 7.6 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.8, 154.7, 138.2, 132.9, 132.6, 129.5, 129.4, 123.4, 114.8, 113.4, 33.6, 33.5, 28.9, 25.8; **HRMS** (ESI) calculated for $C_{14}H_{16}N_2O$ $[M+H]^+$ m/z 229.1335, found 229.1334.

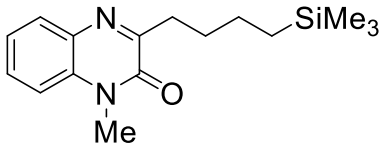
**1-Methyl-3-(4,4,4-trifluorobutyl)quinoxalin-2(1*H*)-one (22)**




According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.0 mg, 0.2 mmol, 1.0 equiv), 1,1,1-trifluoro-4-iodobutane (238.0 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **22** as white solid (42.6 mg, 79%). Mp: 79-81 °C; **$^1$H NMR** (400 MHz, $CDCl_3$)

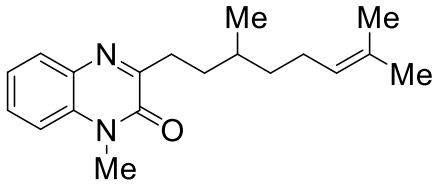
δ 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.57-7.50 (m, 1H), 7.38-7.28 (m, 2H), 3.69 (s, 3H), 3.01 (t, *J* = 7.4 Hz, 2H), 2.33-2.20 (m, 2H), 2.15-2.05 (m, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 159.1, 154.7, 133.0, 132.6, 129.8, 129.7, 127.1 (q, *J* = 275.0 Hz), 123.6, 113.6, 33.3 (q, *J* = 28.4 Hz), 32.5, 29.0, 18.6 (q, *J* = 3.1 Hz); **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ -66.31; **HRMS** (ESI) calculated for $C_{13}H_{13}F_3N_2O$ $[M+H]^+$ m/z 271.1053, found 271.1048.

**1-Methyl-3-(4-(trimethylsilyl)butyl)quinoxalin-2(1*H*)-one (23)**




According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.1 mg, 0.2 mmol, 1.0 equiv), (4-iodobutyl)trimethylsilane (256.2 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **23** as white solid (54.6 mg, 95%). Mp: 102-104 °C; **$^{1}$H NMR** (300 MHz, $CDCl_3$) δ 7.85 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.57-7.50 (m, 1H), 7.39-7.28 (m, 2H), 3.72 (s, 3H), 2.97 (t, *J* = 7.8 Hz, 2H), 1.83 (p, *J* = 7.5 Hz, 2H), 1.56-1.44 (m, 2H), 0.65-0.57 (m, 2H), 0.01 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.4, 154.9, 133.1, 132.7, 129.6, 129.4, 123.5, 113.5, 34.2, 30.7, 29.0, 24.0, 16.5, -1.7; **HRMS** (ESI) calculated for $C_{16}H_{24}N_2OSi$ $[M+H]^+$ m/z 289.1731, found 289.1725.

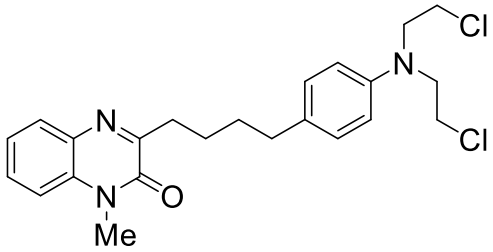
**3-(3,7-Dimethyloct-6-en-1-yl)-1-methylquinoxalin-2(1*H*)-one (24)**




According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.1 mg, 0.2 mmol, 1.0 equiv), 8-iodo-2,6-dimethyloct-2-ene (266.2 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **24** as pale yellow oil (37.0 mg, 62%). **$^{1}$H NMR** (300 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.54-7.46 (m, 1H), 7.36-7.24 (m, 2H), 5.16-5.06 (m, 1H), 3.69 (s, 3H), 3.04-2.85 (m, 2H), 2.10-1.92 (m, 2H), 1.87-1.76 (m, 1H), 1.67 (s, 3H), 1.63-1.54 (m, 5H), 1.49-1.38 (m, 1H), 1.28-1.21 (m, 1H), 0.99 (d, *J* = 6.2 Hz, 3H); **$^{13}$C NMR**

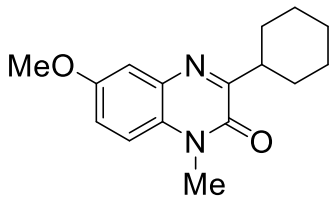
(101 MHz, $CDCl_3$) δ 161.6, 154.8, 133.0, 132.7, 131.0, 129.5, 129.4, 124.9, 123.5, 113.5, 36.9, 33.7, 32.5, 32.0, 29.0, 25.7, 25.5, 19.4, 17.6; **HRMS** (ESI) calculated for $C_{19}H_{26}N_2O$ $[M+H]^+$ m/z 299.2118, found 299.2112.

**3-(4-(4-(Bis(2-chloroethyl)amino)phenyl)butyl)-1-methylquinoxalin-2(1*H*)-one (25)**




According to **GP1** with 1-methylquinoxalin-2(1*H*)-one (32.2 mg, 0.2 mmol, 1.0 equiv), *N*,*N*-bis(2-chloroethyl)-4-(4-iodobutyl)aniline (400.1 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **25** as white solid (34.5 mg, 40%). Mp: 142-144 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.55-7.48 (m, 1H), 7.36-7.27 (m, 2H), 7.09 (d, *J* = 8.6 Hz, 2H), 6.61 (d, *J* = 8.6 Hz, 2H), 3.74-3.65 (m, 7H), 3.64-3.56 (m, 4H), 2.98 (t, *J* = 8.0 Hz, 2H), 2.60 (t, *J* = 8.0 Hz, 2H), 1.89-1.79 (m, 2H), 1.78-1.68 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.0, 154.8, 144.0, 133.0, 132.7, 131.8, 129.6, 129.5, 123.5, 113.5, 112.0, 53.6, 40.5, 34.6, 34.1, 31.6, 29.0, 26.5; **HRMS** (ESI) calculated for $C_{23}H_{27}Cl_2N_3O$ $[M+H]^+$ m/z 432.1604, found 432.1595.

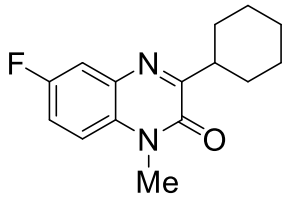
**3-Cyclohexyl-6-methoxy-1-methylquinoxalin-2(1*H*)-one (26)[8]**




According to **GP1** with 6-methoxy-1-methylquinoxalin-2(1*H*)-one (38.2 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (129.3 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **26** as white solid (39.1 mg, 72%). Mp: 104-106 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.30 (d, *J* = 2.7 Hz, 1H), 7.19 (d, *J* = 9.1 Hz, 1H), 7.11(dd, *J* =9.1, 2.7 Hz, 1H), 3.88

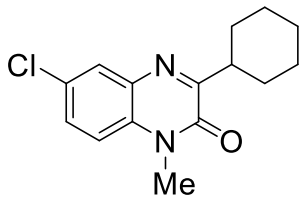
(s, 3H), 3.67 (s, 3H), 3.38-3.31 (m, 1H), 1.96 (d, *J* = 12.0 Hz, 2H), 1.87 (d, *J* = 12.6 Hz, 2H) , 1.77 (d, *J* = 12.6 Hz, 1H), 1.62-1.41 (m, 4H), 1.37-1.23 (m, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 164.8, 155.7, 154.1, 133.5, 127.0, 118.4, 114.3, 111.1, 55.7, 40.7, 30.5, 29.1, 26.2, 26.1; **HRMS** (ESI) calculated for $C_{16}H_{20}N_2O_2$ $[M+H]^+$ m/z 273.1598, found 273.1597.

**3-Cyclohexyl-6-fluoro-1-methylquinoxalin-2(1*H*)-one (27)[8]**




According to **GP1** with 6-fluoro-1-methylquinoxalin-2(1*H*)-one (35.6 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **27** as pale yellow solid (37.0 mg, 71%). Mp: 110-112 °C; **$^{1}$H NMR** (300 MHz, $CDCl_3$) δ 7.56-7.49 (m, 1H), 7.28-7.22 (m, 2H), 3.69 (s, 3H), 3.38-3.32 (m, 1H), 1.94 (d, *J* = 11.4 Hz, 2H), 1.86 (d, *J* = 12.3 Hz, 2H) , 1.77 (d, *J* = 12.3 Hz, 1H), 1.63-1.41 (m, 4H), 1.37-1.23 (m, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 165.8, 160.2, 156.9, 154.1, 133.5 (d, *J* = 11.3Hz), 129.5 (d, *J* = 2.2Hz), 117.0 (d, *J* = 24.0Hz), 115.2 (d, *J* = 21.7Hz), 114.5 (d, *J* = 8.2Hz), 40.8, 30.4, 29.2, 26.2, 26.1; **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ -119.51; **HRMS** (ESI) calculated for $C_{15}H_{17}FN_2O$ $[M+H]^+$ m/z 261.1398, found 261.1407.

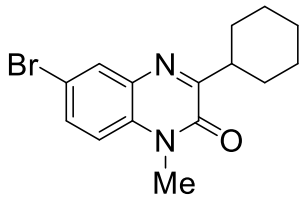
**6-Chloro-3-cyclohexyl-1-methylquinoxalin-2(1*H*)-one (28)[8]**




According to **GP1** with 6-chloro-1-methylquinoxalin-2(1*H*)-one (38.9 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **28** as white solid (35.4 mg, 64%). Mp: 124-126 °C; **$^{1}$H NMR** (300 MHz, $CDCl_3$) δ 7.83 (d, *J* = 2.4 Hz, 1H), 7.45 (dd, *J* = 8.9, 2.4 Hz, 1H), 7.20 (d, *J* = 8.9 Hz, 1H), 3.68 (s, 3H), 3.37-3.28 (m, 1H), 1.94 (d, *J* = 10.7 Hz, 2H), 1.86 (d, *J* = 12.1 Hz, 2H) , 1.77 (d, *J* =

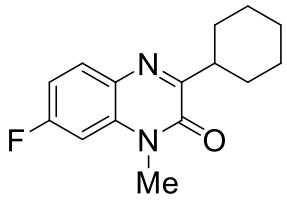
12.1 Hz, 1H), 1.62-1.41 (m, 4H), 1.37-1.23 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.7, 154.1, 133.4, 131.5, 129.3, 129.1, 128.6, 114.5, 40.8, 30.4, 29.2, 26.2, 26.1; **HRMS** (ESI) calculated for $C_{15}H_{17}ClN_2O$ $[M+H]^+$ m/z 277.1102, found 277.1099.

**6-Bromo-3-cyclohexyl-1-methylquinoxalin-2(1*H*)-one (29)[5]**




According to **GP1** with 6-bromo-1-methylquinoxalin-2(1*H*)-one (47.8 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **29** as white solid (30.1 mg, 47%). Mp: 118-120 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.73-7.65 (m, 1H), 7.49-7.38 (m, 2H), 3.65 (s, 3H), 3.34-3.27 (m, 1H), 1.94 (d, *J* = 12.3 Hz, 2H), 1.86 (d, *J* = 12.6 Hz, 2H) , 1.76 (d, *J* = 12.6 Hz, 1H), 1.60-1.42 (m, 4H), 1.35-1.23 (m, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 164.6, 154.1, 133.9, 131.7, 131.0, 126.6, 123.2, 116.5, 40.8, 30.4, 29.2, 26.2, 26.1; **HRMS** (ESI) calculated for $C_{15}H_{17}BrN_2O$ $[M+H]^+$ m/z 321.0597, found 321.0599.

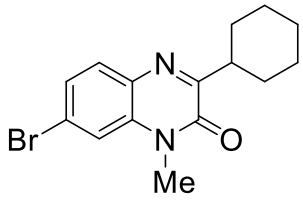
**3-Cyclohexyl-7-fluoro-1-methylquinoxalin-2(1*H*)-one (30)[5]**




According to **GP1** with 7-fluoro-1-methylquinoxalin-2(1*H*)-one (35.6 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **30** as white solid (26.5 mg, 51%). Mp: 113-115 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.79 (dd, *J* = 8.8, 6.0 Hz, 1H), 7.02 (td, *J* = 8.8, 2.6 Hz, 1H), 6.96 (dd, *J* = 10.1, 2.6 Hz, 1H), 3.65 (s, 3H), 3.33-3.26 (m, 1H), 1.94 (d, *J* = 12.5 Hz, 2H), 1.86 (d, *J* = 12.6 Hz, 2H) , 1.76 (d, *J* = 12.6 Hz, 1H), 1.61-1.41 (m, 4H), 1.37-1.23 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.0, 163.1 (d, *J* = 4.0 Hz), 161.5, 154.3, 134.2 (d, *J* = 12.1 Hz), 131.5 (d, *J* = 2.2 Hz), 129.6 (d, *J* = 2.0 Hz), 111.1 (d, *J* = 23.2 Hz), 100.4 (d, *J* = 27.2 Hz), 40.6,

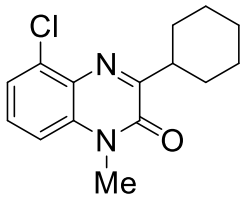
30.4, 29.2, 26.2, 26.1; **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -108.73; **HRMS** (ESI) calculated for $C_{15}H_{17}FN_2O$ $[M+H]^+$ m/z 261.1398, found 261.1399.

**7-Bromo-3-cyclohexyl-1-methylquinoxalin-2(1*H*)-one (31)[5]**



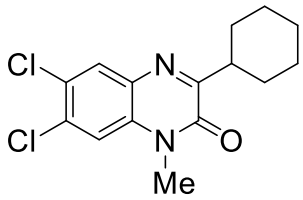

According to **GP1** with 7-bromo-1-methylquinoxalin-2(1*H*)-one (47.8 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **31** as white solid (57.7 mg, 90%). Mp: 120-122 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 2.0 Hz, 1H), 7.57 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 3.66 (s, 3H), 3.35-3.29 (m, 1H), 1.93 (d, *J* = 11.5 Hz, 2H), 1.85 (d, *J* = 12.6 Hz, 2H) , 1.76 (d, *J* = 12.6 Hz, 1H), 1.61-1.41 (m, 4H), 1.37-1.23 (m, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 165.6, 154.1, 133.6, 132.1, 132.0, 131.9, 115.9, 114.8, 40.7, 30.4, 29.1, 26.2, 26.0; **HRMS** (ESI) calculated for $C_{15}H_{17}BrN_2O$ $[M+H]^+$ m/z 321.0597, found 321.0589.

**5-Chloro-3-cyclohexyl-1-methylquinoxalin-2(1*H*)-one (32)**



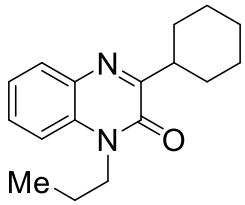

According to **GP1** with 5-chloro-1-methylquinoxalin-2(1*H*)-one (38.9 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **32** as white solid (45.9 mg, 83%). Mp: 126-128 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.35 (m, 2H), 7.21-7.15 (m, 1H), 3.69 (s, 3H), 3.36-3.30 (m, 1H), 1.98 (d, *J* = 12.9 Hz, 2H), 1.88 (d, *J* = 12.9 Hz, 2H) , 1.76 (d, *J* = 12.5 Hz, 1H), 1.67-1.58 (m, 2H), 1.54-1.42 (m, 2H) 1.38-1.23 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.6, 154.1, 134.7, 134.3, 129.4, 129.2, 124.3, 112.3, 41.2, 30.4, 29.4, 26.2, 26.1; **HRMS** (ESI) calculated for $C_{15}H_{17}ClN_2O$ $[M+H]^+$ m/z 277.1102, found 277.1093.

**6,7-Dichloro-3-cyclohexyl-1-methylquinoxalin-2(1*H*)-one (33)[8]**



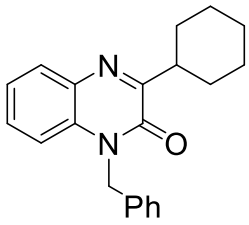

According to **GP1** with 6,7-dichloro-1-methylquinoxalin-2(1*H*)-one (45.8 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **33** as white solid (31.7 mg, 51%). Mp: 127-129 °C; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.92 (s, 1H), 7.36 (s, 1H), 3.65 (s, 3H), 3.34-3.27 (m, 1H), 1.93 (d, *J* = 11.1 Hz, 2H), 1.86 (d, *J* = 12.6 Hz, 2H) , 1.77 (d, *J* = 12.6 Hz, 1H), 1.57-1.40 (m, 4H), 1.35-1.23 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 165.8, 153.9, 133.3, 132.3, 131.9, 130.6, 127.1, 114.9, 40.8, 30.4, 29.3, 26.2, 26.1; **HRMS** (ESI) calculated for $C_{15}H_{16}Cl_2N_2O$ $[M+H]^+$ m/z 311.0712, found 311.0718.

**3-Cyclohexyl-1-propylquinoxalin-2(1*H*)-one (34)[5]**



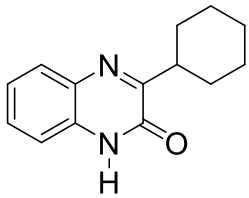

According to **GP1** with 1-propylquinoxalin-2(1*H*)-one (37.8 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **34** as pale yellow oil (41.1 mg, 76%). **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.9 Hz, 1H), 7.49 (t, *J* = 7.9 Hz, 1H), 7.35-7.27 (m, 2H), 4.25-4.17 (m, 2H), 3.37-3.30 (m, 1H), 1.96 (d, *J* = 11.7 Hz, 2H), 1.87 (d, *J* = 12.6 Hz, 2H) , 1.83-1.73 (m, 3H), 1.62-1.43 (m, 4H), 1.35-1.25 (m, 1H), 1.05 (t, *J* = 7.4 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.2, 154.2, 133.1, 132.0, 129.9, 129.2, 123.1, 113.4, 43.7, 40.7, 30.5, 26.3, 26.1, 20.6, 11.4; **HRMS** (ESI) calculated for $C_{17}H_{22}N_2O$ $[M+Na]^+$ m/z 271.1805, found 271.1802.

**1-Benzyl-3-cyclohexylquinoxalin-2(1*H*)-one (35)[12]**



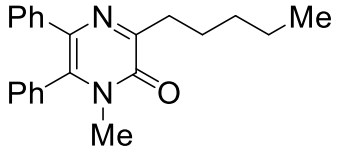

According to **GP1** with 1-benzylquinoxalin-2(1*H*)-one (47.5 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **35** as whitw solid (61.1 mg, 96%). Mp: 134-136 °C; **$^{1}$H NMR** (300 MHz, $CDCl_3$) δ 7.84 (dd, *J* = 7.9, 1.5 Hz, 1H), 7.41-7.20 (m, 8H), 5.48 (s, 2H), 3.46-3.34 (m, 1H), 2.01 (d, *J* = 12.0 Hz, 2H), 1.88 (d, *J* = 12.4 Hz, 2H) , 1.82-1.73 (m, 1H), 1.68-1.43 (m, 4H), 1.40-1.28 (m, 1H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 164.3, 154.5, 135.4, 133.1, 132.1, 129.8, 129.3, 128.8, 127.6, 126.9, 123.4, 114.2, 45.9, 40.8, 30.5, 26.3, 26.1; **HRMS** (ESI) calculated for $C_{21}H_{22}N_2O$ $[M+H]^+$ m/z 319.1805, found 319.1803.

**3-Cyclohexylquinoxalin-2(1*H*)-one (36)[12]**



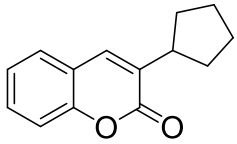

According to **GP1** with quinoxalin-2(1*H*)-one (29.2 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 3:1) to afford the desired product **36** as white solid (21.1 mg, 46%). Mp: 175-177 °C; **$^{1}$H NMR** (400 MHz, $d_6$-DMSO) δ 12.32 (s, 1H), 7.70 (d, *J* = 9.3 Hz, 1H), 7.46 (t, *J* = 8.2 Hz, 1H), 7.30-7.22 (m, 2H), 3.21-3.11 (m, 1H), 1.91-1.75 (m, 4H), 1.71 (d, *J* = 12.5 Hz, 1H) , 1.50-1.29 (m, 4H), 1.29-1.20 (m, 1H); **$^{13}$C NMR** (75 MHz, $d_6$-DMSO) δ 165.3, 154.6, 132.1, 132.0, 129.8, 128.6, 123.5, 115.6, 39.9, 30.5, 26.3, 26.2; **HRMS** (ESI) calculated for $C_{14}H_{16}N_2O$ $[M+H]^+$ m/z 229.1335, found 229.1334.

**1-Methyl-3-pentyl-5,6-diphenylpyrazin-2(1*H*)-one (37)**



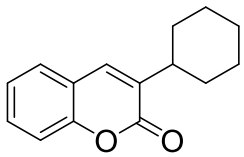

According to **GP1** with 1-methyl-5,6-diphenylpyrazin-2(1*H*)-one (52.4 mg, 0.2 mmol, 1.0 equiv), 1-iodopentane (132 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **37** as white solid (13.9 mg, 21%). Mp: 55-57 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.43-7.33 (m, 3H), 7.23-7.17 (m, 2H), 7.17-7.03 (m, 5H), 3.31 (s, 3H), 2.94 (t, *J* = 8 Hz, 2H), 1.88-1.76 (m, 2H), 1.50-1.36 (m, 4H), 0.93 (t, *J* = 6.9 Hz, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 158.1, 155.6, 137.9, 136.1, 132.6, 132.1, 130.0, 129.2, 128.9, 127.6, 126.7, 33.8, 33.7, 31.7, 26.4, 22.5, 14.0; **HRMS** (ESI) calculated for $C_{22}H_{24}N_2O$ $[M+H]^+$ m/z 333.1961, found 333.1960.

**3-Cyclopentyl-2*H*-chromen-2-one (38)[13]**




According to **GP2** with 2*H*-chromen-2-one (29.1 mg, 0.2 mmol, 1.0 equiv), iodocyclopentane (117.7 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **38** as white solid (29.8 mg, 70%). Mp: 68-70 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.40 (m, 3H), 7.30 (d, *J* = 8.1 Hz, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 3.20-3.09 (m, 1H), 2.15-2.03 (m, 2H), 1.85-1.68 (m, 4H), 1.64-1.52 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.7, 152.8, 136.0, 133.4, 130.4, 127.2, 124.1, 119.5, 116.3, 40.7, 31.7, 25.0; **HRMS** (ESI) calculated for $C_{14}H_{14}O_2$ $[M+H]^+$ m/z 215.1067, found 215.1065.

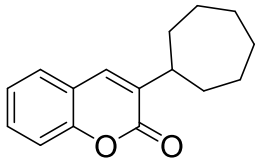
**3-Cyclohexyl-2*H*-chromen-2-one (39)[5]**




According to **GP2** with 2*H*-chromen-2-one (29.2 mg, 0.2 mmol, 1.0 equiv),

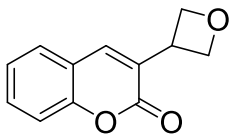
iodocyclohexane (78 μL, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **39** as white solid (36.5 mg, 80%). Mp: 93-95 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.48-7.40 (m, 3H), 7.29 (d, *J* = 9.6 Hz, 1H), 7.27-7.20 (m, 1H), 2.82-2.70 (m, 1H), 1.98 (d, *J* = 11.5Hz, 2H), 1.90-1.81 (m, 2H), 1.81-1.72 (m, 1H), 1.51-1.37 (m, 2H), 1.36-1.18 (m, 3H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 161.5, 152.6, 136.3, 134.7, 130.3, 127.2, 124.1, 119.6, 116.2, 38.1, 32.0, 26.4, 26.1; **HRMS** (ESI) calculated for $C_{15}H_{16}O_2$ $[M+H]^+$ m/z 229.1223, found 229.1217.

**3-Cycloheptyl-2*H*-chromen-2-one (40)[13]**



According to **GP2** with 2*H*-chromen-2-one (29.4 mg, 0.2 mmol, 1.0 equiv), iodocycloheptane (134.5 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **40** as white solid (25.7 mg, 53%). Mp: 82-84 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.49-7.39 (m, 3H), 7.28 (d, *J* = 8.7 Hz, 1H), 7.26-7.20 (m, 1H), 2.99-2.87 (m, 1H), 2.00-1.89 (m, 2H), 1.85-1.75 (m, 2H), 1.74-1.65 (m, 2H), 1.64-1.51 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.3, 152.5, 136.2, 136.1, 130.2, 127.1, 124.0, 119.5, 116.1, 40.0, 34.1, 27.6, 26.8; **HRMS** (ESI) calculated for $C_{16}H_{18}O_2$ $[M+H]^+$ m/z 243.1380, found 243.1373.

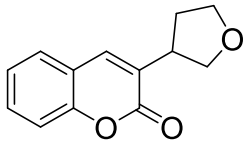
**3-(Oxetan-3-yl)-2*H*-chromen-2-one (41)**



According to **GP2** with 2*H*-chromen-2-one (29.6 mg, 0.2 mmol, 1.0 equiv), 3-iodooxetane (110.4 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 8:1) to afford the desired product **41** as white solid (22.1 mg, 55%). Mp: 98-100 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.69 (s, 1H), 7.52 (t, *J* = 7.0 Hz, 2H), 7.32 (dd, *J* = 13.9, 7.6 Hz, 2H), 5.12-5.01 (m, 2H), 4.79

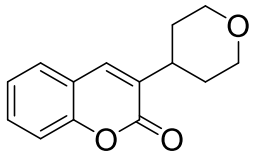
(t, *J* = 6.5 Hz, 2H), 4.37 (p, *J* = 7.5 Hz, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.7, 152.9, 137.4, 131.1, 128.5, 127.5, 124.5, 118.8, 116.4, 75.6, 35.3; **HRMS** (ESI) calculated for $C_{12}H_{10}O_3$ $[M+H]^+$ m/z 203.0703, found 203.0697.

**3-(Tetrahydrofuran-3-yl)-2*H*-chromen-2-one (42)[13]**



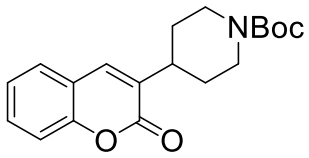
According to **GP2** with 2*H*-chromen-2-one (29.3 mg, 0.2 mmol, 1.0 equiv), 3-iodotetrahydrofuran (118.8 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 8:1) to afford the desired product **42** as white solid (25.8 mg, 60%). Mp: 106-108 °C; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.52-7.45 (m, 2H), 7.34-7.30 (m, 1H), 7.29-7.25 (m, 1H), 4.14-4.07 (m, 1H), 4.06-3.99 (m, 1H), 3.97-3.90 (m, 1H), 3.88-3.82 (m, 1H), 3.64-3.56 (m, 1H), 2.42-2.31 (m, 1H), 2.09-1.99 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.3, 152.8, 137.2, 130.9, 130.2, 127.4, 124.3, 119.1, 116.2, 72.0, 67.6, 39.3, 31.4; **HRMS** (ESI) calculated for $C_{13}H_{12}O_3$ $[M+Na]^+$ m/z 239.0679, found 239.0674.

**3-(Tetrahydro-2*H*-pyran-4-yl)-2*H*-chromen-2-one (43)[13]**



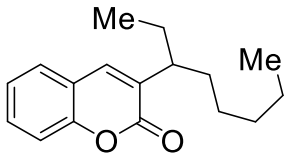
According to **GP2** with 2*H*-chromen-2-one (29.3 mg, 0.2 mmol, 1.0 equiv), 4-iodotetrahydro-2*H*-pyran (127.2 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 8:1) to afford the desired product **43** as white solid (27.5 mg, 60%). Mp: 114-116 °C; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.45 (m, 3H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.30-7.26 (m, 1H), 4.09 (dd, *J* = 11.4, 4.2 Hz, 2H), 3.58 (td, *J* = 11.9, 1.7 Hz, 2H), 3.04 (tt, *J* = 12.0, 3.2 Hz, 1H), 1.94-1.87 (m, 2H), 1.74-1.66 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.3, 152.8, 136.8, 132.8, 130.8, 127.5, 124.3, 119.4, 116.4, 68.0, 35.5, 31.6; **HRMS** (ESI) calculated for $C_{14}H_{14}O_3$ $[M+Na]^+$ m/z 253.0835, found 253.0826.

***tert*-Butyl 4-(2-oxo-2*H*-chromen-3-yl)piperidine-1-carboxylate (44)[13]**



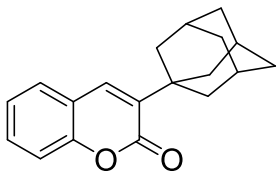

According to **GP2** with 2*H*-chromen-2-one (29.6 mg, 0.2 mmol, 1.0 equiv), *tert*-butyl 4-iodopiperidine-1-carboxylate (186.7 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 8:1) to afford the desired product **44** as white solid (30.3 mg, 46%). Mp: 142-144 °C; **$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.53-7.43 (m, 3H), 7.35-7.30 (m, 1H), 7.28-7.23 (m, 1H), 4.27 (s, 2H), 3.01-2.75 (m, 3H), 2.00-1.91 (m, 2H), 1.61-1.51 (m, 2H), 1.48 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.3, 154.7, 152.7, 136.9, 132.8, 130.8, 127.4, 124.3, 119.3, 116.3, 79.5, 44.2, 36.5, 30.7, 28.4; **HRMS** (ESI) calculated for $C_{19}H_{23}NO_4$ $[M+Na]^+$ m/z 352.1519, found 352.1520.

**3-(Octan-3-yl)-2*H*-chromen-2-one (45)**



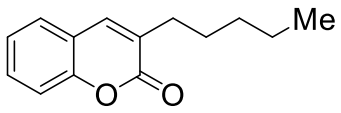

According to **GP2** with 2*H*-chromen-2-one (29.5 mg, 0.2 mmol, 1.0 equiv), 3-iodooctane (115.9 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **45** as colorless oil (32.6 mg, 63%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.41 (m, 3H), 7.31 (d, *J* = 8.9 Hz, 1H), 7.28-7.23 (m, 1H), 2.81 (p, *J* = 7.0 Hz, 1H), 1.74-1.59 (m, 4H), 1.33-1.19 (m, 6H), 0.91-0.82 (m, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.6, 152.8, 137.9, 132.9, 130.4, 127.2, 124.1, 119.5, 116.3, 41.6, 33.4, 31.9, 26.9, 26.6, 22.5, 14.0, 11.6; **HRMS** (ESI) calculated for $C_{17}H_{22}O_2$ $[M+H]^+$ m/z 259.1693, found 259.1686.

**3-((3*r*,5*r*,7*r*)-Adamantan-1-yl)-2*H*-chromen-2-one (46)**



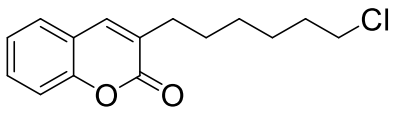
According to **GP2** with 2*H*-chromen-2-one (29.3 mg, 0.2 mmol, 1.0 equiv), (3*s*,5*s*,7*s*)-1-iodoadamantane (157.3 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **46** as white solid (26.1 mg, 47%). Mp: 184-186 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.41 (m, 3H), 7.30-7.20 (m, 2H), 2.17-2.04 (m, 9H), 1.82-1.76 (m, 5H), 1.70-1.59 (m, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 159.5, 152.9, 137.1, 136.9, 130.4, 127.6, 123.9, 119.5, 115.9, 39.8, 37.1, 36.7, 28.5; **HRMS** (ESI) calculated for $C_{19}H_{20}O_2$ $[M+Na]^+$ m/z 303.1356, found 303.1339.

**3-Pentyl-2*H*-chromen-2-one (47)[14]**




According to **GP2** with 2*H*-chromen-2-one (29.3 mg, 0.2 mmol, 1.0 equiv), 1-iodopentane (118.8 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **47** as colorless oil (25.8 mg, 60%). **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.42 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.27-7.22 (m, 1H), 2.56 (t, *J* = 7.6 Hz, 2H), 1.65 (p, *J* = 7.4 Hz, 2H), 1.41-1.32 (m, 4H), 0.96-0.88 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.8, 153.0, 138.3, 130.4, 130.0, 127.0, 124.2, 119.5, 116.3, 31.4, 30.8, 27.6, 22.4, 14.0; **HRMS** (ESI) calculated for $C_{14}H_{16}O_2$ $[M+Na]^+$ m/z 239.1043, found 239.1038.

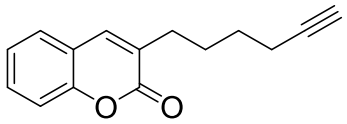
**3-(6-Chlorohexyl)-2*H*-chromen-2-one (48)**




According to **GP2** with 2*H*-chromen-2-one (29.2 mg, 0.2 mmol, 1.0 equiv), 1-chloro-6-iodohexane (147.9 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **48** as pale yellow solid (27.6 mg, 52%). Mp: 49-51 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51-7.42 (m, 3H), 7.31 (d, *J* = 8.1 Hz, 1H), 7.29-7.23 (m, 1H), 3.54 (t, *J* = 6.7 Hz, 2H), 2.58 (t, *J* = 7.6 Hz, 2H), 1.79 (p, *J* = 6.7 Hz, 2H), 1.67 (p, *J* = 7.6 Hz, 2H), 1.55-1.38 (m, 4H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.7, 153.0, 138.5, 130.5, 129.7,

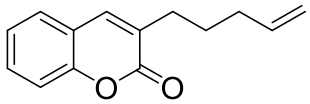
127.1, 124.2, 119.5, 116.3, 45.0, 32.4, 30.7, 28.4, 27.8, 26.5; **HRMS** (ESI) calculated for $C_{15}H_{17}ClO_2$ $[M+H]^+$ m/z 265.0990, found 265.0990.

**3-(Hex-5-yn-1-yl)-2*H*-chromen-2-one (49)**



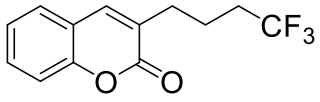
According to **GP2** with 2*H*-chromen-2-one (29.6 mg, 0.2 mmol, 1.0 equiv), 6-iodohex-1-yne (124.8 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **49** as white solid (20.4 mg, 45%). Mp: 70-72 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.51 (s, 1H), 7.49-7.42 (m, 2H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 1H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.26 (td, *J* = 6.9, 2.5 Hz, 2H), 1.97 (t, *J* = 2.4 Hz, 1H), 1.79 (p, *J* = 7.5 Hz, 2H), 1.64 (q, *J* = 7.2 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.7, 153.1, 138.5, 130.5, 129.4, 127.1, 124.2, 119.4, 116.4, 84.1, 68.5, 30.3, 27.9, 27.0, 18.2; **HRMS** (ESI) calculated for $C_{15}H_{14}O_2$ $[M+Na]^+$ m/z 249.0886, found 249.0870.

**3-(Pent-4-en-1-yl)-2*H*-chromen-2-one (50)[15]**



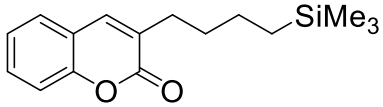
According to **GP2** with 2*H*-chromen-2-one (29.1 mg, 0.2 mmol, 1.0 equiv), 5-iodopent-1-ene (117.6 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **50** as white solid (17.1 mg, 40%). Mp: 46-48 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.50-7.41 (m, 3H), 7.31 (d, *J* = 8.3 Hz, 1H), 7.28-7.22 (m, 1H), 5.90-5.78 (m, 1H), 5.09-5.03 (m, 1H), 5.02-4.98 (m, 1H), 2.62-2.55 (m, 2H), 2.16 (q, *J* = 7.3 Hz, 2H), 1.76 (p, *J* = 7.5 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.7, 153.1, 138.6, 138.0, 130.5, 129.6, 127.1, 124.2, 119.5, 116.4, 115.1, 33.2, 30.3, 27.1; **HRMS** (ESI) calculated for $C_{14}H_{14}O_2$ $[M+H]^+$ m/z 215.1067, found 215.1066.

**3-(4,4,4-Trifluorobutyl)-2*H*-chromen-2-one (51)**



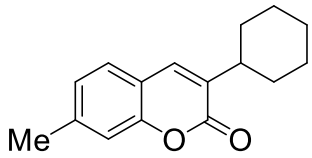
According to **GP2** with 2*H*-chromen-2-one (29.4 mg, 0.2 mmol, 1.0 equiv), 1,1,1-trifluoro-4-iodobutane (142.8 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **51** as white solid (27.2 mg, 53%). Mp: 64-66 °C; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.52-7.43 (m, 2H), 7.32 (d, *J* = 8.3 Hz, 1H), 7.27 (t, *J* = 7.5 Hz, 1H), 2.65 (t, *J* = 7.6 Hz, 2H), 2.19 (dt, *J* = 16.3, 9.0 Hz, 2H), 1.95 (p, *J* = 7.8 Hz, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.5, 153.2, 139.3, 130.9, 128.1, 127.3, 127.0 (q, *J* = 275.0 Hz), 124.4, 119.2, 116.4, 33.2 (q, *J* = 28.6 Hz), 29.8, 20.5 (q, *J* = 2.9 Hz); **$^{19}$F NMR** (376 MHz, $CDCl_3$) δ -66.07; **HRMS** (ESI) calculated for $C_{13}H_{11}F_3O_2$ $[M+Na]^+$ m/z 279.0603, found 279.0612.

**3-(4-(Trimethylsilyl)butyl)-2*H*-chromen-2-one (52)**



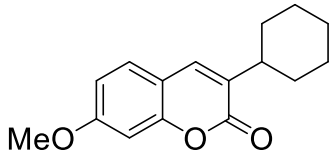
According to **GP2** with 2*H*-chromen-2-one (29.4 mg, 0.2 mmol, 1.0 equiv), (4-iodobutyl)trimethylsilane (153.7 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **52** as white solid (36.8 mg, 67%). Mp: 88-90 °C; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.40 (m, 3H), 7.30 (d, *J* = 8.3 Hz, 1H), 7.25 (t, *J* = 7.4 Hz, 1H), 2.62-2.52 (m, 2H), 1.67 (p, *J* = 7.5 Hz, 2H), 1.41 (dt, *J* = 15.7, 7.6 Hz, 2H), 0.60-0.51 (m, 2H), -0.01 (s, 9H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.8, 153.0, 138.2, 130.3, 130.0, 127.0, 124.1, 119.5, 116.3, 31.8, 30.5, 23.6, 16.4, -1.7; **HRMS** (ESI) calculated for $C_{16}H_{22}O_2Si$ $[M+Na]^+$ m/z 297.1281, found 229.1265.

**3-Cyclohexyl-7-methyl-2*H*-chromen-2-one (53)[16]**



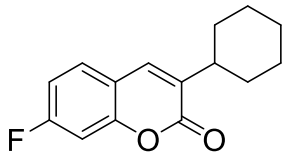
According to **GP2** with 7-methyl-2*H*-chromen-2-one (32.0 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (78 μL, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **53** as pale yellow solid (21.3 mg, 44%). Mp: 78-80 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.41 (s, 1H), 7.32 (d, *J* = 7.8 Hz, 1H), 7.13-7.01 (m, 2H), 2.80-2.70 (m, 1H), 2.43 (s, 3H), 1.97 (d, *J* = 11.8 Hz, 2H), 1.89-1.73 (m, 3H), 1.51-1.38 (m, 2H), 1.36-1.18 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.8, 152.8, 141.4, 136.3, 133.6, 126.9, 125.3, 117.2, 116.4, 38.1, 32.1, 26.5, 26.2, 21.6; **HRMS** (ESI) calculated for $C_{16}H_{18}O_2$ $[M+H]^+$ m/z 243.1380, found 243.1379.

**3-Cyclohexyl-7-methoxy-2*H*-chromen-2-one (54)[13]**




According to **GP2** with 7-methoxy-2*H*-chromen-2-one (35.2 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (78 μL, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **54** as white solid (33.5 mg, 65%). Mp: 103-105 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.39 (s, 1H), 7.33 (d, *J* = 8.5 Hz, 1H), 6.84-6.77 (m, 2H), 3.85 (s, 3H), 2.78-2.68 (m, 1H), 1.96 (d, *J* = 11.5 Hz, 2H), 1.88-1.72 (m, 3H), 1.50-1.37 (m, 2H), 1.34-1.20 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.8, 161.7, 154.3, 136.4, 131.3, 128.1, 113.3, 112.2, 100.3, 55.6, 38.0, 32.1, 26.5, 26.1; **HRMS** (ESI) calculated for $C_{16}H_{18}O_3$ $[M+H]^+$ m/z 259.1329, found 259.1321.

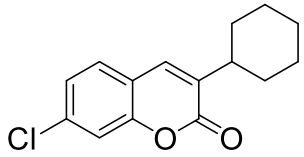
**3-Cyclohexyl-7-fluoro-2*H*-chromen-2-one (55)**




According to **GP2** with 7-fluoro-2*H*-chromen-2-one (32.9 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (78 μL, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **55** as white solid (36.8 mg, 75%). Mp: 132-134 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ

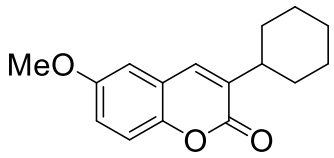
7.46-7.38 (m, 2H), 7.05-6.95 (m, 2H), 2.80-2.70 (m, 1H), 1.97 (d, *J* = 12.8 Hz, 2H), 1.90-1.73 (m, 3H), 1.51-1.38 (m, 2H), 1.36-1.18 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 164.8, 162.3, 161.1, 153.7 (d, *J* = 12.9 Hz), 135.79 (d, *J* = 1.1 Hz), 133.6 (d, *J* = 3.1 Hz), 128.7 (d, *J* = 10.2 Hz), 116.3 (d, *J* = 2.8 Hz), 112.2 (d, *J* = 22.9 Hz), 103.9 (d, *J* = 25.6 Hz), 38.1, 32.0, 26.5, 26.1; **$^{19}$F NMR** (282 MHz, $CDCl_3$) δ -107.34; **HRMS** (ESI) calculated for $C_{15}H_{15}FO_2$ $[M+H]^+$ m/z 247.1129, found 247.1128.

**7-Chloro-3-cyclohexyl-2*H*-chromen-2-one (56)[13]**




According to **GP2** with 7-chloro-2*H*-chromen-2-one (36.3 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (78 μL, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **56** as white solid (28.8 mg, 55%). Mp: 142-144 °C; **$^{1}$H NMR** (400 MHz, $CDCl_3$) δ 7.45-7.35 (m, 2H), 7.29 (d, *J* = 2 Hz, 1H), 7.22 (dd, *J* = 8.3, 2.0 Hz, 1H), 2.80-2.69 (m, 1H), 1.97 (d, *J* = 11.8 Hz, 2H), 1.90-1.73 (m, 3H), 1.51-1.38 (m, 2H), 1.36-1.18 (m, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.8, 152.9, 136.1, 135.5, 134.9, 128.1, 124.7, 118.2, 116.5, 38.2, 32.0, 26.4, 26.0; **HRMS** (ESI) calculated for $C_{15}H_{15}ClO_2$ $[M+H]^+$ m/z 263.0833, found 263.0826.

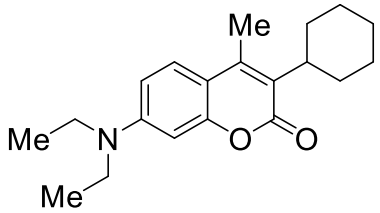
**3-Cyclohexyl-6-methoxy-2*H*-chromen-2-one (57)**




According to **GP2** with 6-methoxy-2*H*-chromen-2-one (35.2 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (78 μL, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **57** as white solid (22.5 mg, 44%). Mp: 87-89 °C; **$^{1}$H NMR** (300 MHz, $CDCl_3$) δ 7.40 (s, 1H), 7.23 (d, *J* = 9.0 Hz, 1H), 7.03 (dd, *J* = 9.0, 2.9 Hz, 1H), 6.89 (d, *J* = 2.9 Hz, 1H), 3.84 (s, 3H), 2.80-2.69 (m, 1H), 2.04-1.92 (m, 2H), 1.90-1.73 (m, 3H), 1.54-1.21 (m, 5H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.7, 155.9, 147.1, 136.1, 135.2, 120.0, 118.0, 117.3, 109.6, 55.8, 38.2, 32.1, 26.5, 26.2; **HRMS** (ESI) calculated for $C_{16}H_{18}O_3$

$[M+H]^+$ m/z 259.1329, found 259.1323.

**3-Cyclohexyl-7-(diethylamino)-4-methyl-2*H*-chromen-2-one (58)[13]**




According to **GP2** with 7-(diethylamino)-4-methyl-2*H*-chromen-2-one (46.3 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (78 μL, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv). The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **58** as yellow solid (23.2 mg, 37%). Mp: 95-97 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.40 (d, *J* = 9.0 Hz, 1H), 6.57 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.47 (d, *J* = 2.6 Hz, 1H), 3.39 (q, *J* = 7.1 Hz, 4H), 2.82 (s, 1H), 2.36 (s, 3H), 2.17 (q, *J* = 11.4, 10.6 Hz, 2H), 1.82 (d, *J* = 9.2 Hz, 2H), 1.77-1.61 (m, 2H), 1.54 (d, *J* = 12.5 Hz, 2H), 1.34 (d, *J* = 7.2 Hz, 2H), 1.19 (t, *J* = 7.1 Hz, 6H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.3, 154.5, 149.3, 146.1, 125.6, 124.1, 109.8, 108.2, 97.3, 44.6, 39.4, 29.4, 27.1, 25.8, 14.6, 12.4; **HRMS** (ESI) calculated for $C_{20}H_{27}NO_2$ $[M+Na]^+$ m/z 336.1934, found 336.1950.

## *Evaluation of other substrates:*


1-Methylquinoxalin-2(1*H*)-one (32.5 mg, 0.2 mmol, 1.0 equiv), iodobenzene (112 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous DMSO (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated with 6 W blue LEDs at room temperature for 12 h. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **67** (11.0 mg, 23%).

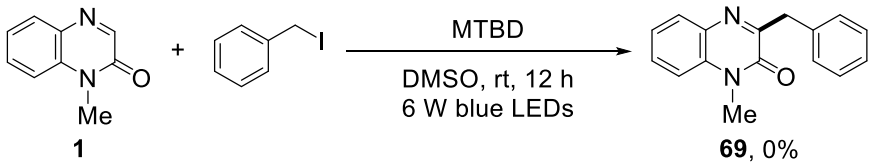
**1-Methyl-3-phenylquinoxalin-2(1*H*)-one** (**67**) **[17]**: white solid; Mp: 90-92 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 8.31 (s, 2H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.55 (t, *J* = 7.6 Hz,

1H), 7.48 (s, 3H), 7.40-7.29 (m, 2H), 3.76 (s, 3H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 154.7, 154.1, 136.0, 133.3, 133.0, 130.4, 130.3, 129.5, 128.0, 123.7, 113.5, 29.3; **HRMS** (ESI) calculated for $C_{15}H_{12}N_2O$ $[M+H]^+$ m/z 237.1022, found 237.1032.


**59** **68**, 10%

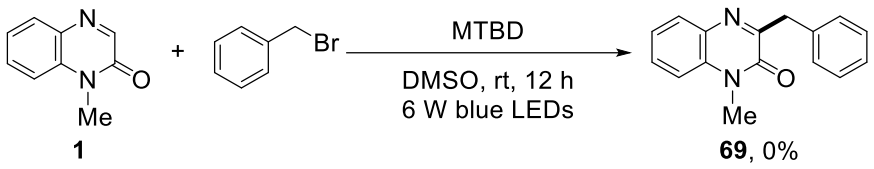
2*H*-Chromen-2-one (29.4 mg, 0.2 mmol, 1.0 equiv), iodobenzene (68 μL, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous DMSO (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated with 6 W blue LEDs at room temperature for 12 h. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **68** (4.5 mg, 10%).

**3-Phenyl-2*H*-chromen-2-one** (**68**) [18]: white solid; Mp: 134-136 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.82 (s, 1H), 7.71 (d, *J* = 6.9 Hz, 2H), 7.53 (t, *J* = 8.1 Hz, 2H), 7.49-7.40 (m, 3H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.30 (t, *J* = 7.5 Hz, 1H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 160.6, 153.5, 139.8, 134.7, 131.4, 128.8, 128.5, 128.5, 128.4, 127.9, 124.5, 119.7, 116.4; **HRMS** (ESI) calculated for $C_{15}H_{10}O_2$ $[M+H]^+$ m/z 223.0754, found 223.0759.

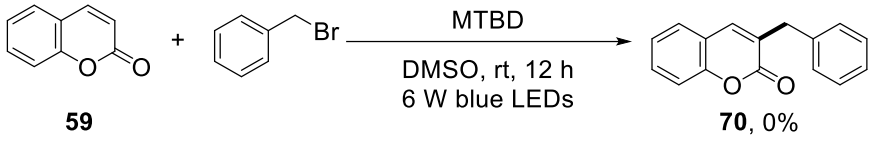



**1** **69**, 0%

1-Methylquinoxalin-2(1*H*)-one (32.3 mg, 0.2 mmol, 1.0 equiv), (iodomethyl)benzene (124 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous DMSO (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated with 6 W blue LEDs at room temperature for 12 h. This reaction did not afford any targeted product, and the starting heterocycles were completely recovered.




1-Methylquinoxalin-2(1*H*)-one (32.5 mg, 0.2 mmol, 1.0 equiv), (bromomethyl)benzene (118 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous DMSO (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated with 6 W blue LEDs at room temperature for 12 h. This reaction did not afford any targeted product, and the starting heterocycles were completely recovered.




2*H*-Chromen-2-one (29.5 mg, 0.2 mmol, 1.0 equiv), (bromomethyl)benzene (72 μL, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous DMSO (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated with 6 W blue LEDs at room temperature for 12 h. This reaction did not afford any targeted product, and the starting heterocycles were completely recovered.

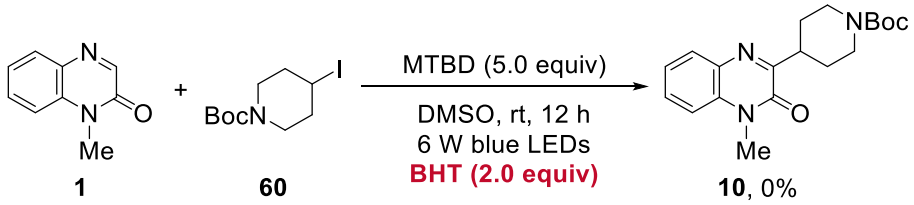
## *Lager scale experiments:*


1-Methylquinoxalin-2(1*H*)-one (480.5 mg, 3.0 mmol, 1.0 equiv), iodocyclohexane (1940 μL, 15.0 mmol, 5.0 equiv), and MTBD (2154 μL, 15.0 mmol, 5.0 equiv) were placed in a dry 25 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous DMSO (5.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated with 6 W blue LEDs at room temperature for 12 h. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10:1) to afford the desired product **3** (0.58 g, 80%).

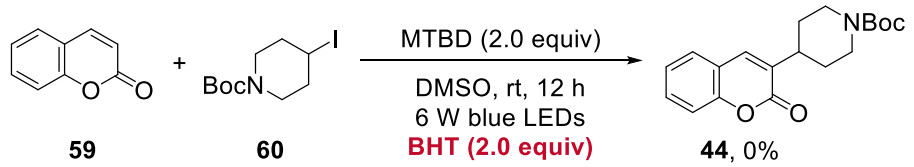

2*H*-Chromen-2-one (438.4 mg, 3.0 mmol, 1.0 equiv), iodocyclohexane (1164 μL, 9.0 mmol, 3.0 equiv), and MTBD (862 μL, 6.0 mmol, 2.0 equiv) were placed in a dry 25 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous DMSO (5.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated with 6 W blue LEDs at room temperature for 12 h. The crude reaction mixture was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30:1) to afford the desired product **39** (0.52 g, 75%).

## *Mechanistic studies*

### *1) Radical inhibition and trapping experiments:*

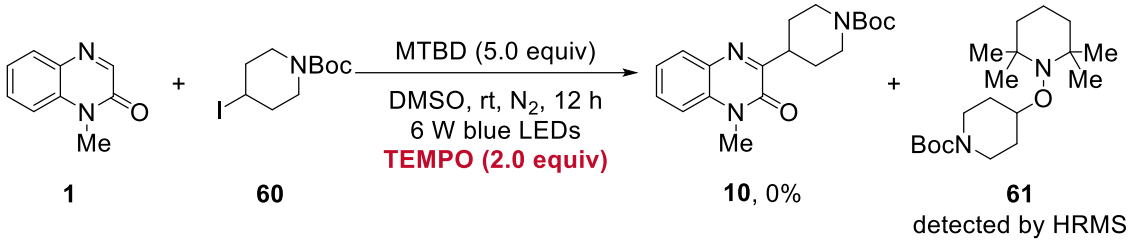



1-Methylquinoxalin-2(1*H*)-one (32.5 mg, 0.2 mmol, 1.0 equiv), *tert*-butyl 4-iodopiperidine-1-carboxylate (311.1 mg, 1.0 mmol, 5.0 equiv), MTBD (144 μL, 1.0 mmol, 5.0 equiv), and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (88.1 mg, 0.4 mmol, 2.0 equiv) were placed in a 10 mL Schlenk tube under $N_2$. Then DMSO (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. In this reaction, the formation of **10** was completely suppressed.

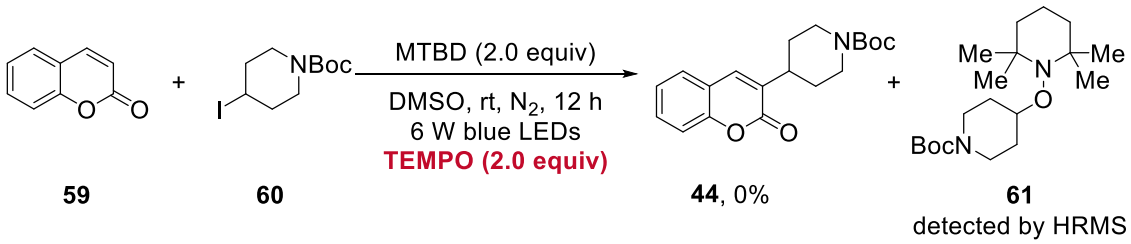



2*H*-Chromen-2-one (29.4 mg, 0.2 mmol, 1.0 equiv), *tert*-butyl 4-iodopiperidine-1-carboxylate (186.7 mg, 0.6 mmol, 3.0 equiv), MTBD (58 μL, 0.4 mmol, 2.0 equiv), and 2,6-di-*tert*-butyl-4-methylphenol (BHT) (88.4 mg, 0.4 mmol,

2.0 equiv) were placed in a 10 mL Schlenk tube under $N_2$. Then DMSO (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. In this reaction, the formation of **44** was completely suppressed.

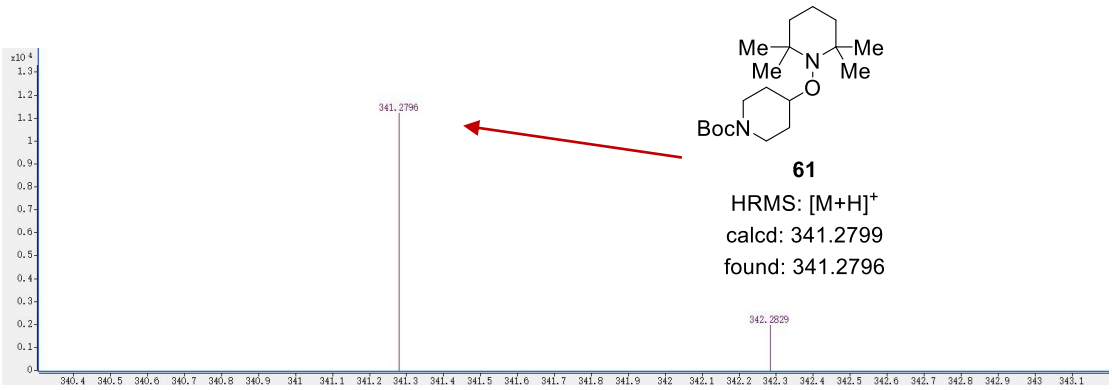



1-Methylquinoxalin-2(1*H*)-one (32.2 mg, 0.2 mmol, 1.0 equiv), *tert*-butyl 4-iodopiperidine-1-carboxylate (311.1 mg, 1.0 mmol, 5.0 equiv), MTBD (144 μL, 1.0 mmol, 5.0 equiv), and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (62.5 mg, 0.4 mmol, 2.0 equiv) were placed in a 10 mL Schlenk tube under $N_2$. Then DMSO (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. In this reaction, the formation of **10** was completely suppressed.

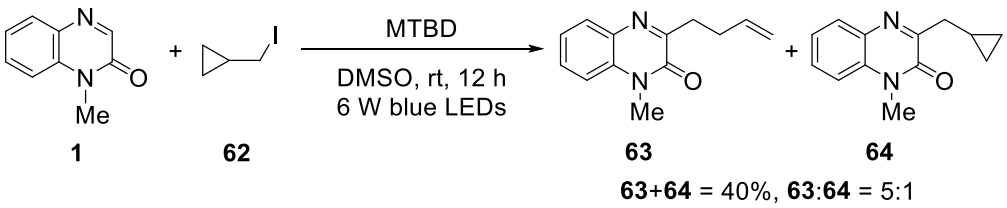



2*H*-Chromen-2-one (29.5 mg, 0.2 mmol, 1.0 equiv), *tert*-butyl 4-iodopiperidine-1-carboxylate (186.7 mg, 0.6 mmol, 3.0 equiv), MTBD (58 μL, 0.4 mmol, 2.0 equiv), and 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (62.5 mg, 0.4 mmol, 2.0 equiv) were placed in a 10 mL Schlenk tube under $N_2$. Then DMSO (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. In this reaction, the formation of **44** was completely suppressed.

Moreover, high-resolution mass spectra analysis of these two reaction mixtures showed that the TEMPO-trapped product **61** was formed. This result indicated that C-radicals are generated in the current reaction conditions.

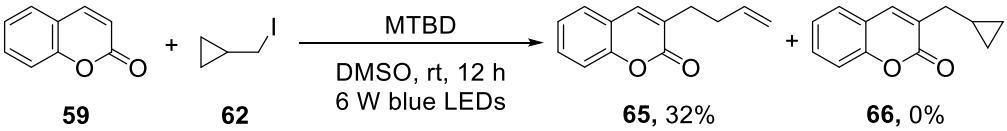



## *2) Radical clock experiments:*




1-Methylquinoxalin-2(1*H*)-one (32.5 mg, 0.2 mmol, 1.0 equiv), (iodomethyl)cyclopropane (182.0 mg, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv) were placed in a 10 mL Schlenk tube under $N_2$. Then DMSO (2.0 mL) was added with a syringe. The reaction mixture was irradiated with 6 W blue LEDs at room temperature under $N_2$ for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford a mixture of **63** and **64** (17.0 mg, 40%, **63**:**64** = 5:1).

**3-(But-3-en-1-yl)-1-methylquinoxalin-2(1*H*)-one** (**63**): **$^1$H NMR** (300 MHz, $CDCl_3$) δ 7.83 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.57-7.47 (m, 1H), 7.38-7.26 (m, 2H), 6.04-5.88 (m, 1H), 5.11 (dd, *J* = 17.1, 1.6 Hz, 1H), 5.00 (d, *J* = 10.2 Hz, 1H), 3.69 (s, 3H), 3.05 (dd, *J* = 8.7, 6.7 Hz, 2H), 2.64-2.52 (m, 2H); **$^{13}$C NMR** (75 MHz, $CDCl_3$) δ 160.2, 154.7, 137.6, 133.1, 132.7, 129.6, 129.6, 123.4, 115.1, 113.5, 33.4, 30.5, 28.9; **HRMS** (ESI) calculated for $C_{13}H_{14}N_2O$ $[M+H]^+$ m/z 215.1179, found 215.1180.



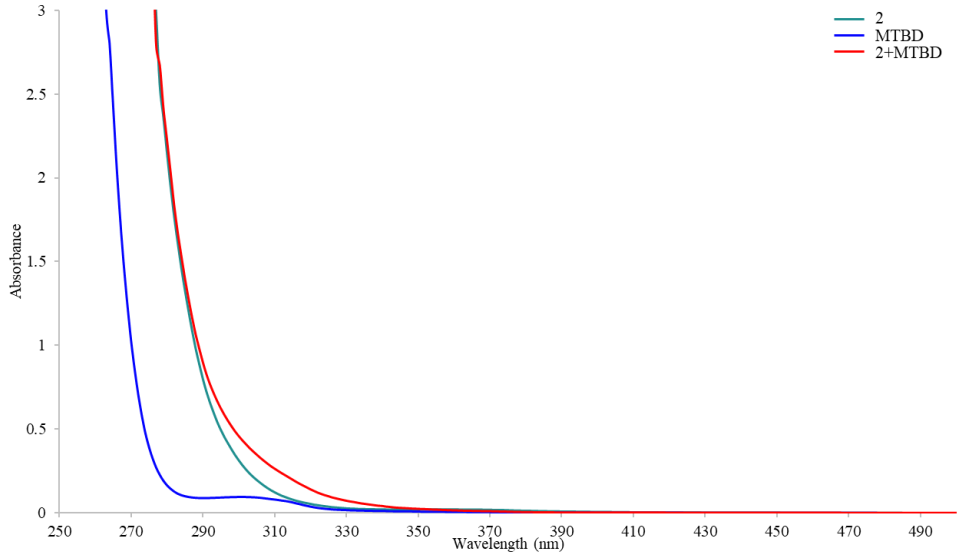

2*H*-Chromen-2-one (29.5 mg, 0.2 mmol, 1.0 equiv), (iodomethyl)cyclopropane (109.3 mg, 0.6 mmol, 3.0 equiv), and MTBD (58 μL, 0.4 mmol, 2.0 equiv) were placed in a

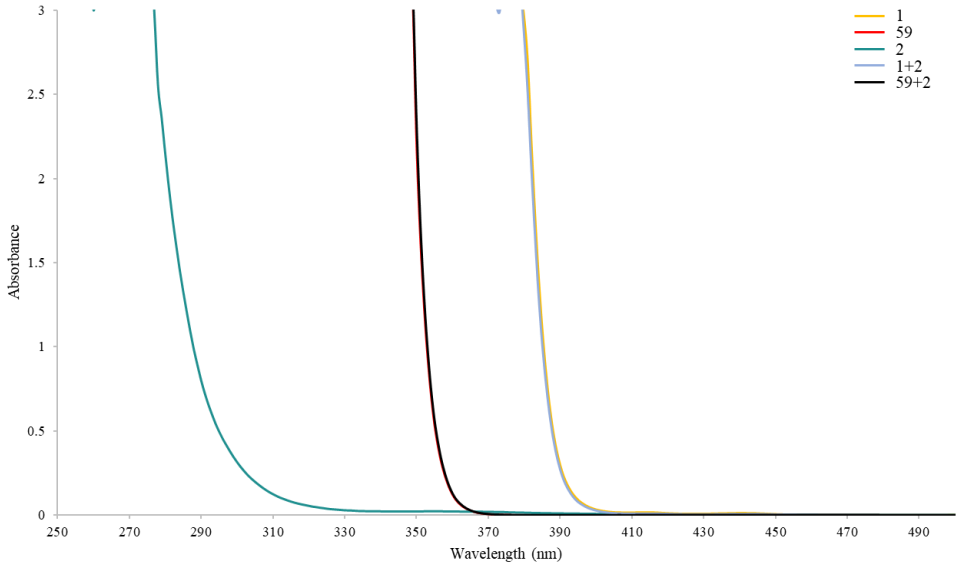
10 mL Schlenk tube under $N_2$. Then DMSO (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30/1) to afford the ring-opening product **65** as white solid (12.8 mg, 32%).

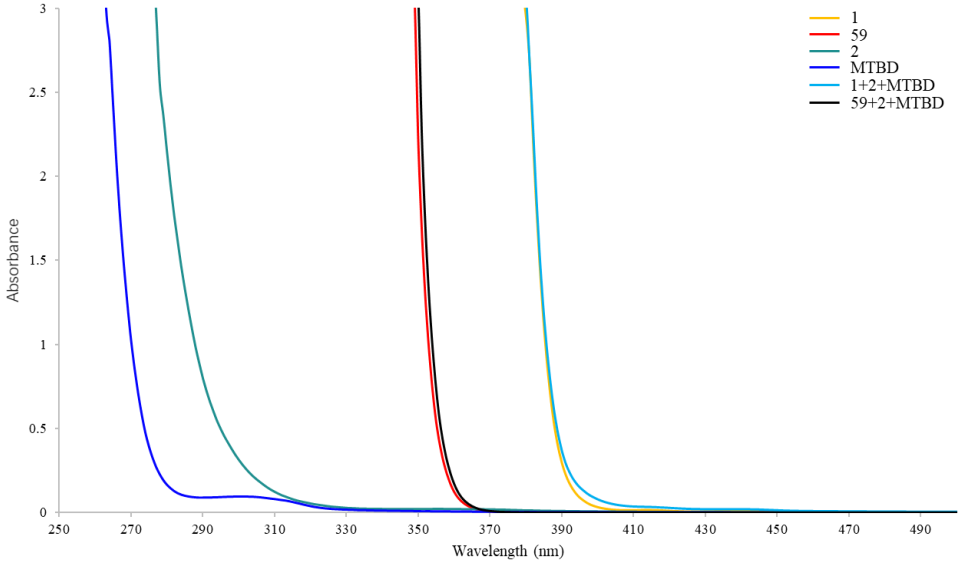
**3-(But-3-en-1-yl)-2*H*-chromen-2-one (65)**: white solid; Mp: 52-54 °C; **$^1$H NMR** (400 MHz, $CDCl_3$) δ 7.52-7.42 (m, 3H), 7.31 (d, *J* = 8.2 Hz, 1H), 7.27-7.22 (m, 1H), 5.92-5.77 (m, 1H), 5.12-4.99 (m, 2H), 2.68 (t, *J* = 7.4 Hz, 2H), 2.47-2.39 (m, 2H); **$^{13}$C NMR** (101 MHz, $CDCl_3$) δ 161.7, 153.1, 138.9, 137.1, 130.6, 129.0, 127.2, 124.2, 119.4, 116.4, 115.8, 31.9, 30.2; **HRMS** (ESI) calculated for $C_{13}H_{12}O_2$ $[M+H]^+$ m/z 201.0910, found 201.0901.

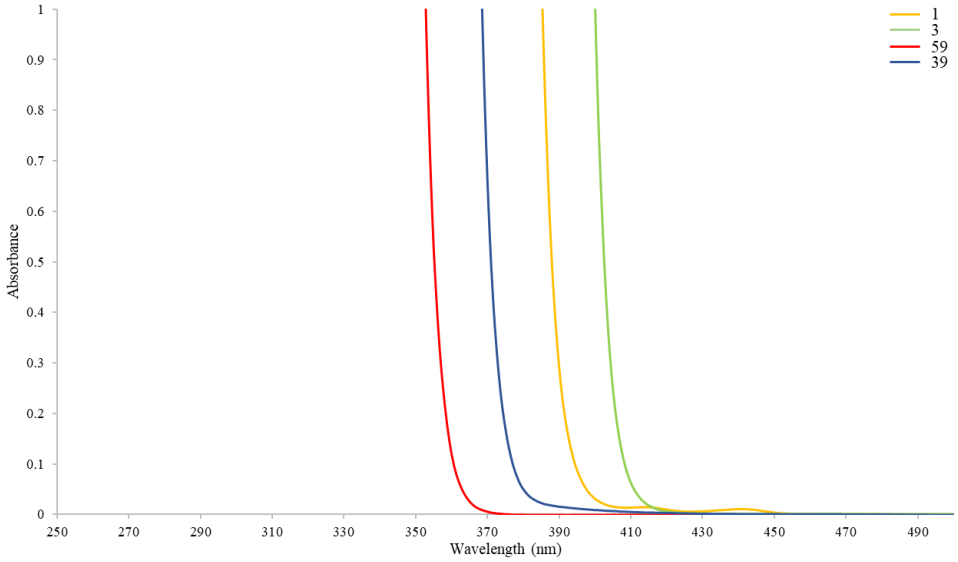
## *3) UV-vis spectroscopic measurements:*

We investigated whether the EDA complexes could be formed in the current reaction. The UV-vis experiments were performed on Agilent Cary 100 UV-visible spectrophotometer with a quartz cuvette (10 mm path length). We observed that after mixing of 1-methylquinoxalin-2(1*H*)-one **1**, 2*H*-chromen-2-one **59**, iodocyclohexane **2**, and MTBD in DMSO, the optical absorption spectrum did not show a red-shift. On the basis of these observations, we supposed that EDA complex was unlikely responsible for generating radical intermediates in the current reaction system.



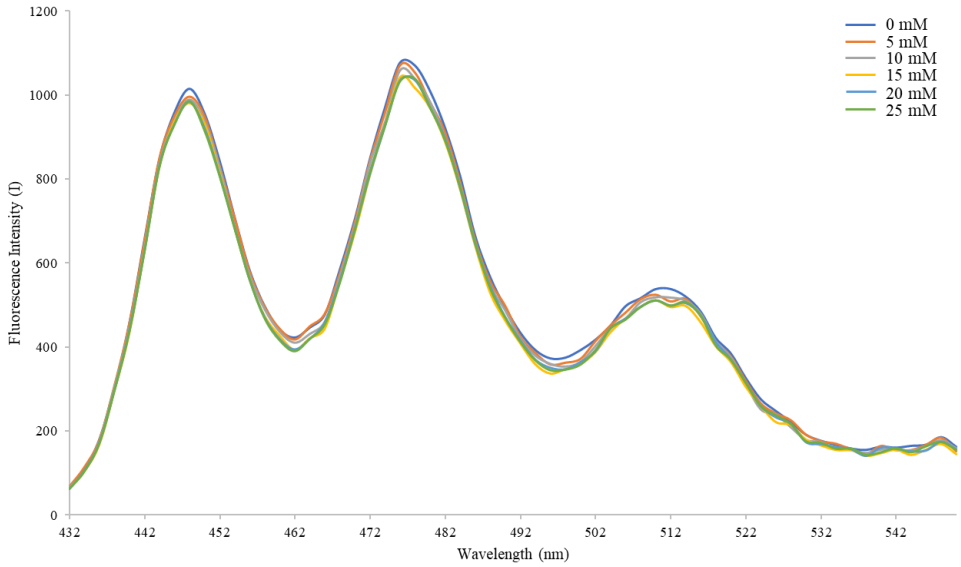

Absorbance
Wavelength (nm)
1
59
2
1+2
59+2


Absorbance
Wavelength (nm)
1
59
2
MTBD
1+2+MTBD
59+2+MTBD

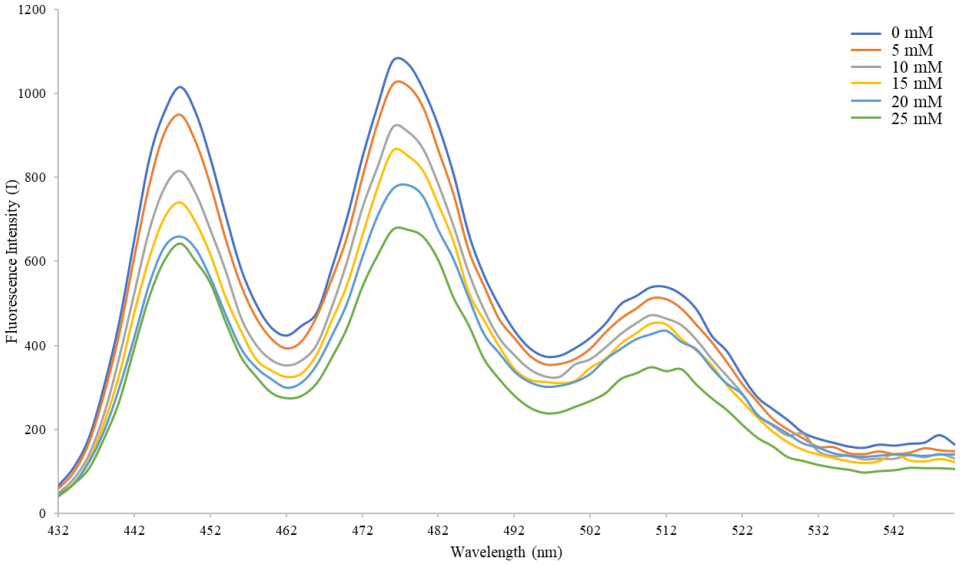



## *4) Stern-Volmer fluorescence quenching experiments*

Emission intensities were recorded using a spectrofluorimeter. All solutions were excited at 414 nm and the emission intensity at 478 nm was observed. DMSO was degassed with a stream of argon for 15 min. In a typical experiment, 2.0 mL of solution of **1** (1.0 mM) in DMSO was added to the appropriate amount of iodocyclohexane and MTBD respectively in a screw-top 1.0 cm quartz cuvette and the emission spectra of the sample was collected.

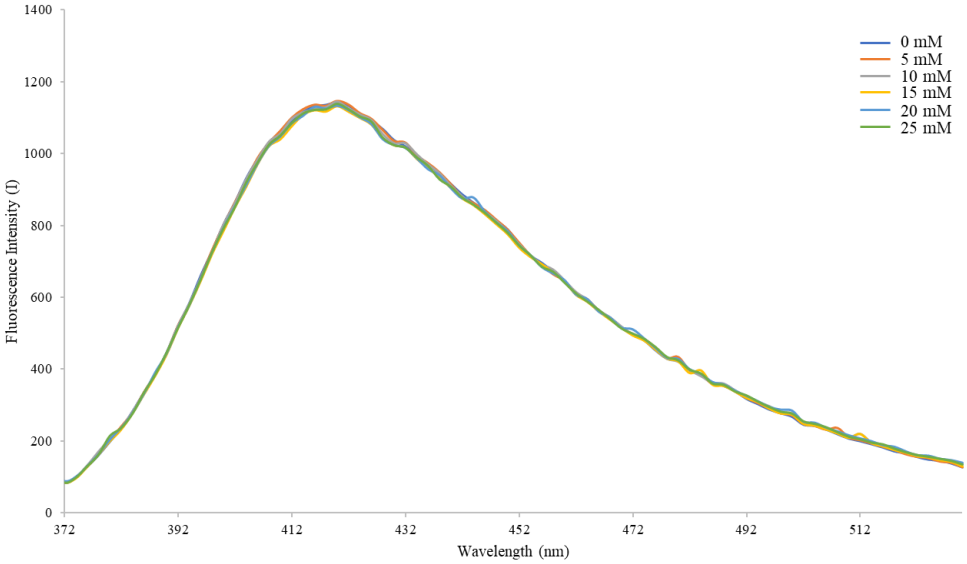



The fluorescence emission spectra of **1** with different concentration of iodocyclohexane **2** excited at 414 nm

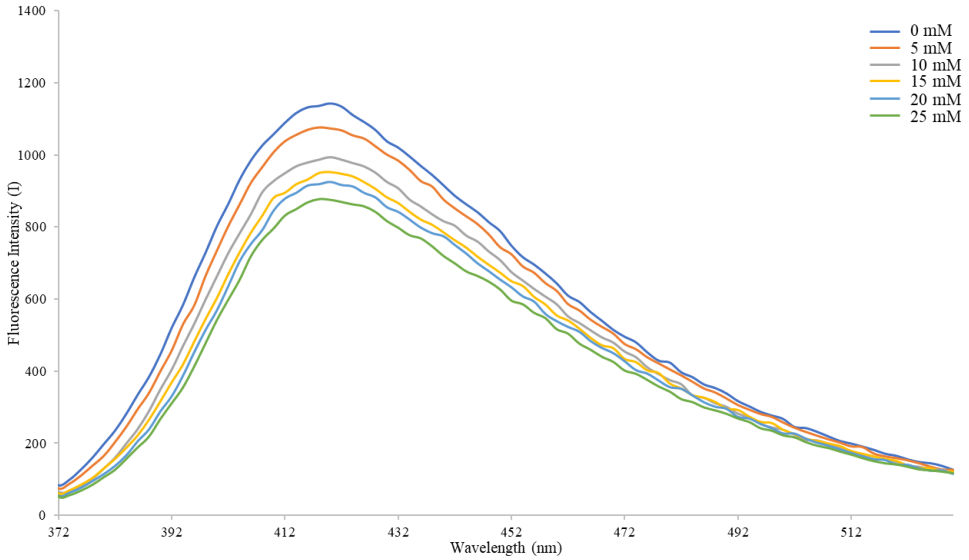



The fluorescence emission spectra of **1** with different concentration of MTBD excited at 414 nm

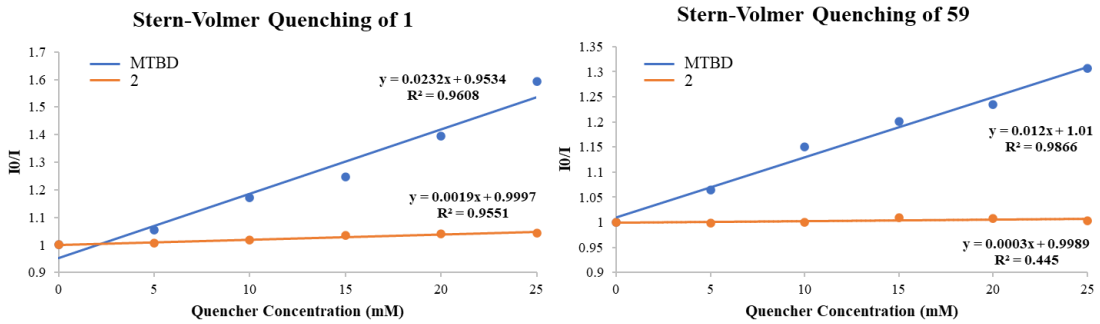
All solutions were excited at 360 nm and the emission intensity at 420 nm was observed. DMSO was degassed with a stream of argon for 15 min. In a typical experiment, 2.0 mL of solution of **59** (1.0 mM) in DMSO was added to the appropriate amount of iodocyclohexane and MTBD respectively in a screw-top 1.0 cm quartz cuvette and the emission spectra of the sample was collected.




The fluorescence emission spectra of **59** with different concentration of iodocyclohexane **2** excited at 360 nm

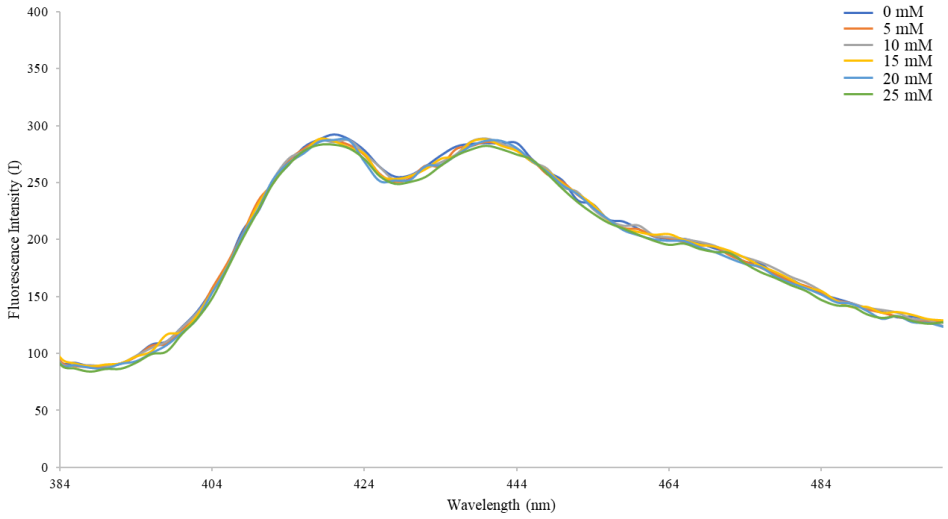



The fluorescence emission spectra of **59** with different concentration of MTBD excited at 360 nm



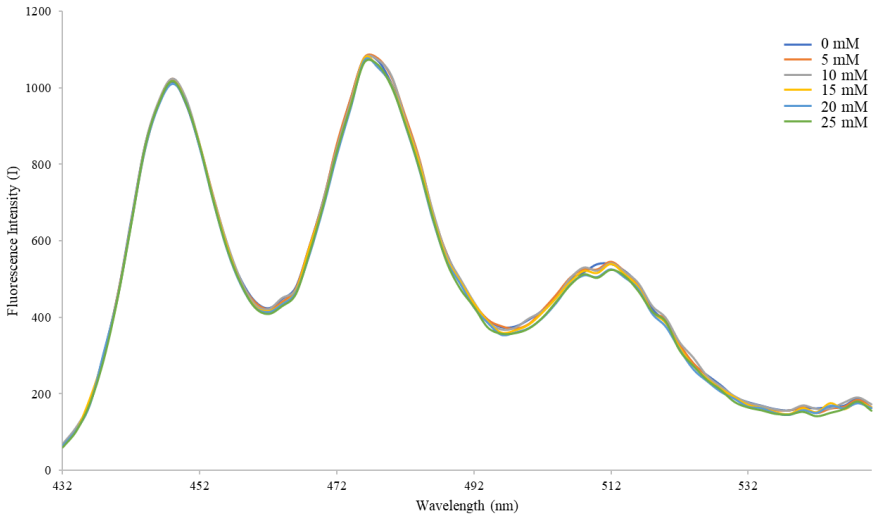

Stern-Volmer fluorescence quenching plot

All solutions were excited at 375 nm and the emission intensity at 418 nm was observed. DMSO was degassed with a stream of argon for 15 min. In a typical experiment, 2.0 mL of solution of lepidine (1.0 mM) in DMSO was added to the appropriate amount of MTBD in a screw-top 1.0 cm quartz cuvette and the emission spectra of the sample was collected. These results show that the fluorescence of lepidine could not be gradually quenched with the increase of the concentration of MTBD, which are consistent with our experimental observations that lepidine did not participate in the current alkylation reaction.



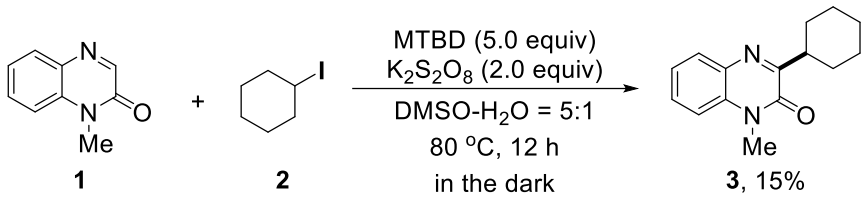

The fluorescence emission spectra of lepidine with different concentration of MTBD excited at 375 nm

All solutions were excited at 414 nm and the emission intensity at 478 nm was observed. DMSO was degassed with a stream of argon for 15 min. In a typical experiment, 2.0 mL of solution of **1** (1.0 mM) in DMSO was added to the appropriate amount of $Et_3N$ in a screw-top 1.0 cm quartz cuvette and the emission spectra of the sample was collected. These results show that the fluorescence of **1** could not be gradually quenched with the increase of the concentration of $Et_3N$, which are consistent with our experimental observations that the alkylation reaction did not work in the presence of $Et_3N$.

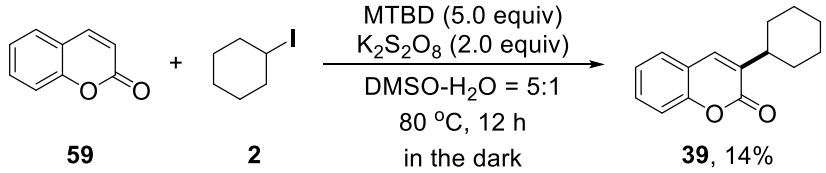



The fluorescence emission spectra of **1** with different concentration of $Et_3N$ excited at 414 nm

## *5) Conducting the reaction in the presence of $K_2S_2O_8$ in the dark:*




1-Methylquinoxalin-2(1*H*)-one (32.3 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), MTBD (144 μL, 1.0 mmol, 5.0 equiv), and $K_2S_2O_8$ (108.2 mg, 0.4 mmol, 2.0 equiv) were placed in a 10 mL Schlenk tube under $N_2$. Then DMSO (2.0 mL) and $H_2O$ (0.4 mL) were added with a syringe. The reaction mixture was stirred in the dark at 80°C under $N_2$ for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 10/1) to afford the desired product **3** (7.3 mg, 15%).

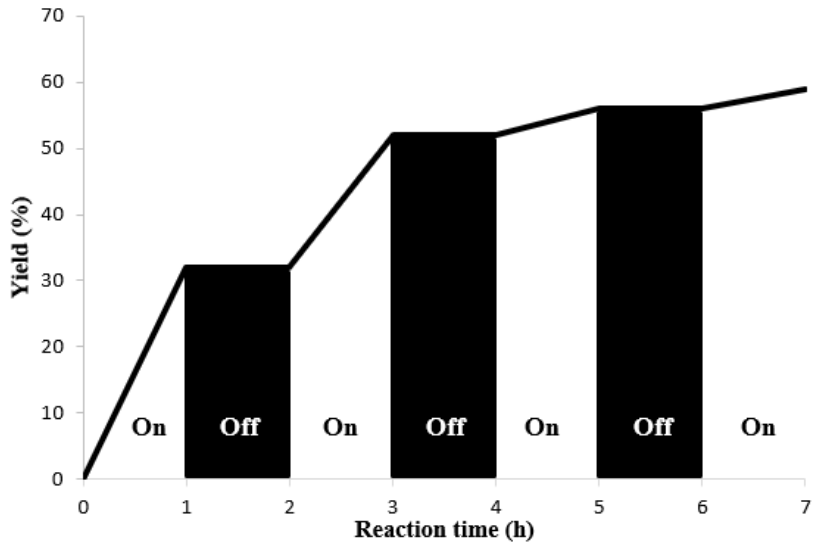



2*H*-Chromen-2-one (29.6 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (78 μL, 0.6 mmol, 3.0 equiv), MTBD (58 μL, 0.4 mmol, 2.0 equiv), and $K_2S_2O_8$ (108.3 mg, 0.4 mmol, 2.0 equiv) were placed in a 10 mL Schlenk tube under $N_2$. Then DMSO (2.0 mL) and $H_2O$ (0.4 mL) were added with a syringe. The reaction mixture was stirred in the dark at 80°C under $N_2$ for 12 h. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was purified by flash silica gel column chromatography (petroleum ether/EtOAc = 30/1) to afford the desired product **39** (6.4 mg, 14%).

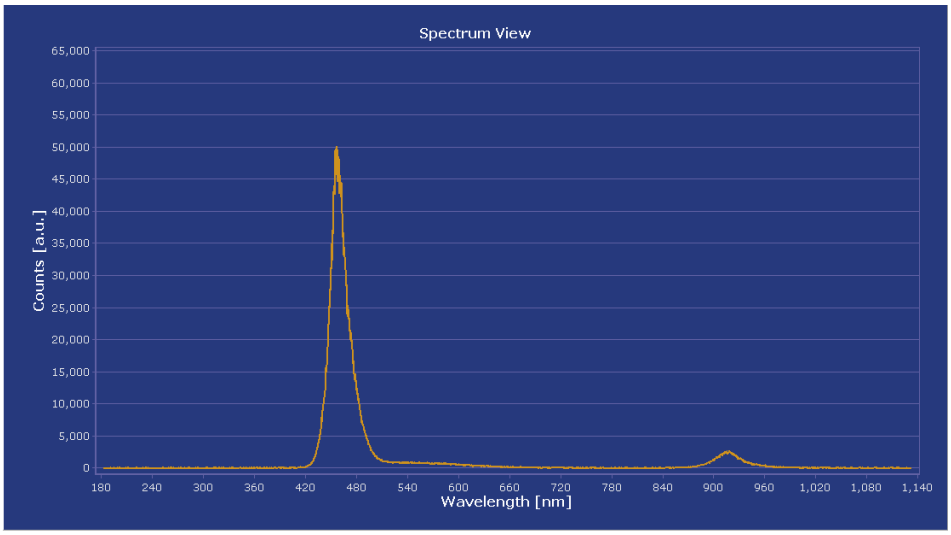
## *6) Visible light on/off experiments:*

1-Methylquinoxalin-2(1*H*)-one (32.3 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv) were placed in a dry 10 mL Schlenk tube under a nitrogen atmosphere. Then anhydrous DMSO (2.0 mL) was added with a syringe. The reaction mixture was stirred and irradiated by using 6 W blue LEDs at room temperature. The process of photocatalytic reaction with and without light was monitored by $^1$H NMR using dibromomethane as internal

standard. The results suggest that the formation of **3** requires continuous visible light irradiation.




## *7) The emission spectra for the light source:*




The emission spectra for 6 W blue LEDs

## *8) Determination of quantum yield:*

1-Methylquinoxalin-2(1*H*)-one (32.6 mg, 0.2 mmol, 1.0 equiv), iodocyclohexane (130 μL, 1.0 mmol, 5.0 equiv), and MTBD (144 μL, 1.0 mmol, 5.0 equiv) were placed in a quartz cuvette (10 mm path length). Anhydrous DMSO (2.0 mL) was added with a syringe. Then the solution was degassed with a stream of nitrogen for 10 min. The reaction mixture was stirred and irradiated by using a 30 W blue LED (λ = 420 nm, PLS-LED100B) at room temperature for 600 s. After completion of the reaction, the solution was measured the unit area photon flux (photosynthetic active radiation meter, Apogee MQ-200). The yield of product **3** formed was determined by $^{1}$H NMR spectroscopic analysis using dibromomethane as an internal standard. The quantum yield is calculated using the following equation:

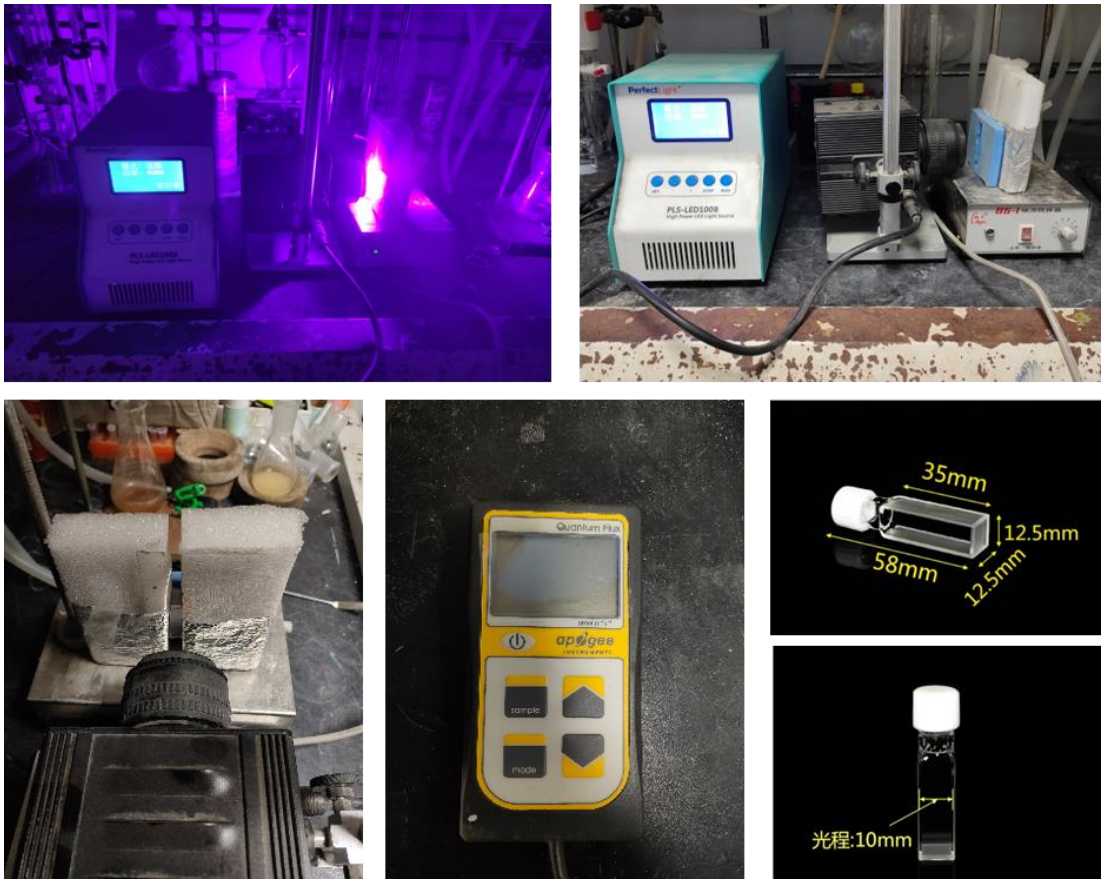
$$\Phi = \frac{\text{mol of product formed}}{\text{flux} \bullet S \bullet t}$$

Where Φ is quantum yield, S ($m^2$) is the irradiation area and t (s) is the reaction time.

Experiment: 1-methylquinoxalin-2(1*H*)-one **1** (32.6 mg), iodocyclohexane (130 μL), and MTBD (144 μL) after 600s, the unite area photon flux was 604 $\mu mol \cdot s^{-1} \cdot m^{-2}$ (average of three experiments), the irradiation area was $3.0 \times 10^{-4} m^2$, and the yield of product **3** was 78%.

Sample quantum yield calculation:

$$\Phi = \frac{0.156 \times 10^{3}}{604 \times 3.0 \times 10^{-4} \times 600} = 1.43$$




Experimental setup for determining quantum yield

## *References:*


[1] a) C. W. Cheung, F. E. Zhurkin, X. Hu, *J. Am. Chem. Soc.* **2015**, *137*, 4932; b) M. Murai, C. Mizuta, R. Taniguchi, K. Takai, *Org. Lett.* **2017**, *19*, 6104.

[2] J. Wang, B. Sun, L. Zhang, T. Xu, Y. Xie, C. Jin, *Asian Journal of Organic Chemistry* **2019**, *8*, 1942.

[3] C. Jin, Z. Yan, B. Sun, J. Yang, *Org. Lett.* **2019**, *21*, 2064.

[4] C. Huang, J. Li, C. Li, *Nat. Commun.* **2021**, *12*, 4010.

[5] M. Tian, Y. Wang, X. Bu, Y. Wang, X. Yang, *Catal. Sci. Technol.* **2021**, *11*, 4272.

[6] K. Niu, L. Song, Y. Hao, Y. Liu, Q. Wang, *Chem. Commun.* **2020**, *56*, 11673.

[7] Z. Yan, B. Sun, X. Zhang, X. Zhuang, J. Yang, W. Su, C. Jin, *Chem. Asian J.* **2019**, *14*, 3344.

[8] K. Niu, Y. Hao, L. Song, Y. Liu, Q. Wang, *Green Chem.* **2021**, *23*, 302.

[9] B. Wang, H. Yao, X. Zhong, Z. Yan, S. Lin, *Tetrahedron Lett.* **2021**, *64*, 152720.

[10] L. Xie, L. Jiang, J. Tan, Y. Wang, X. Xu, B. Zhang, Z. Cao, W. He. *ACS Sustainable Chem. Eng.* **2019**, *7*, 14153.

[11] W. Zhang, Y. Pan, C. Yang, L. Chen, X. Li, J. Cheng, *J. Org. Chem.* **2019**, *84*, 7786.

[12] S. Singh, N. Dagar, S. R. Roy, *Org. Biomol. Chem.* **2021**, *19*, 5383.

[13] L. Liu, N. Pang, W. Sheng, L. Su, L. Liu, J. Dong, Y. Zhou, S. Yin, *Adv. Synth. Catal.* **2019**, *361*, 4126.

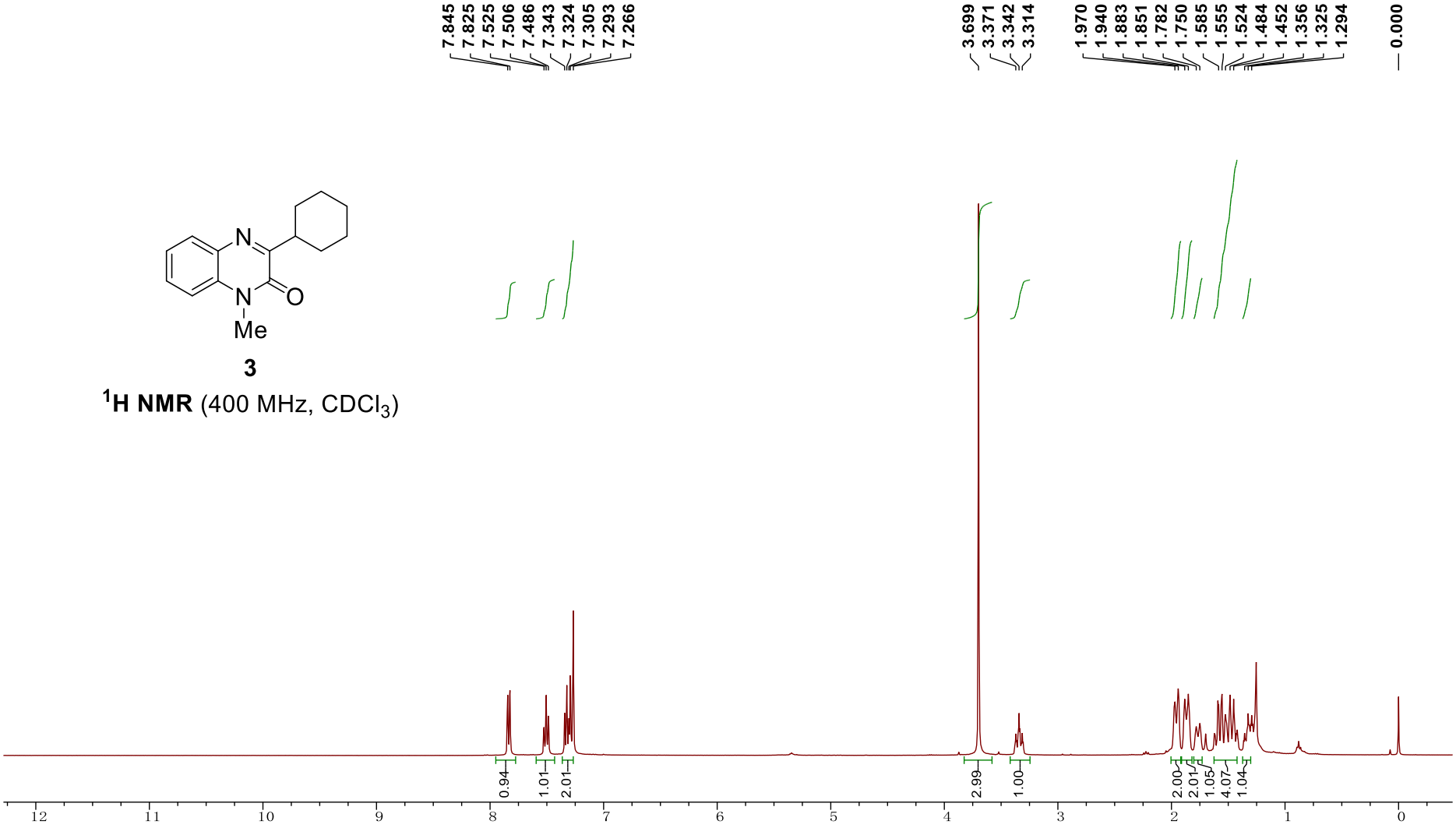
[14] D. Villemin, D. Goussu, *Heterocycles* **1989**, *29*, 1255.

[15] D. D. P. Kranz, A. G. Griesbeck, R. Alle, R. Perez-Ruiz, J. M. Neudörfl, K. Meerholz, H. Schmalz, *Angew. Chem. Int. Ed.* **2012**, *51*, 6000.

[16] A. Ling, L. Zhang, R. X. Tan, Z. Liu, *J. Org. Chem.* **2018**, *83*, 14489.

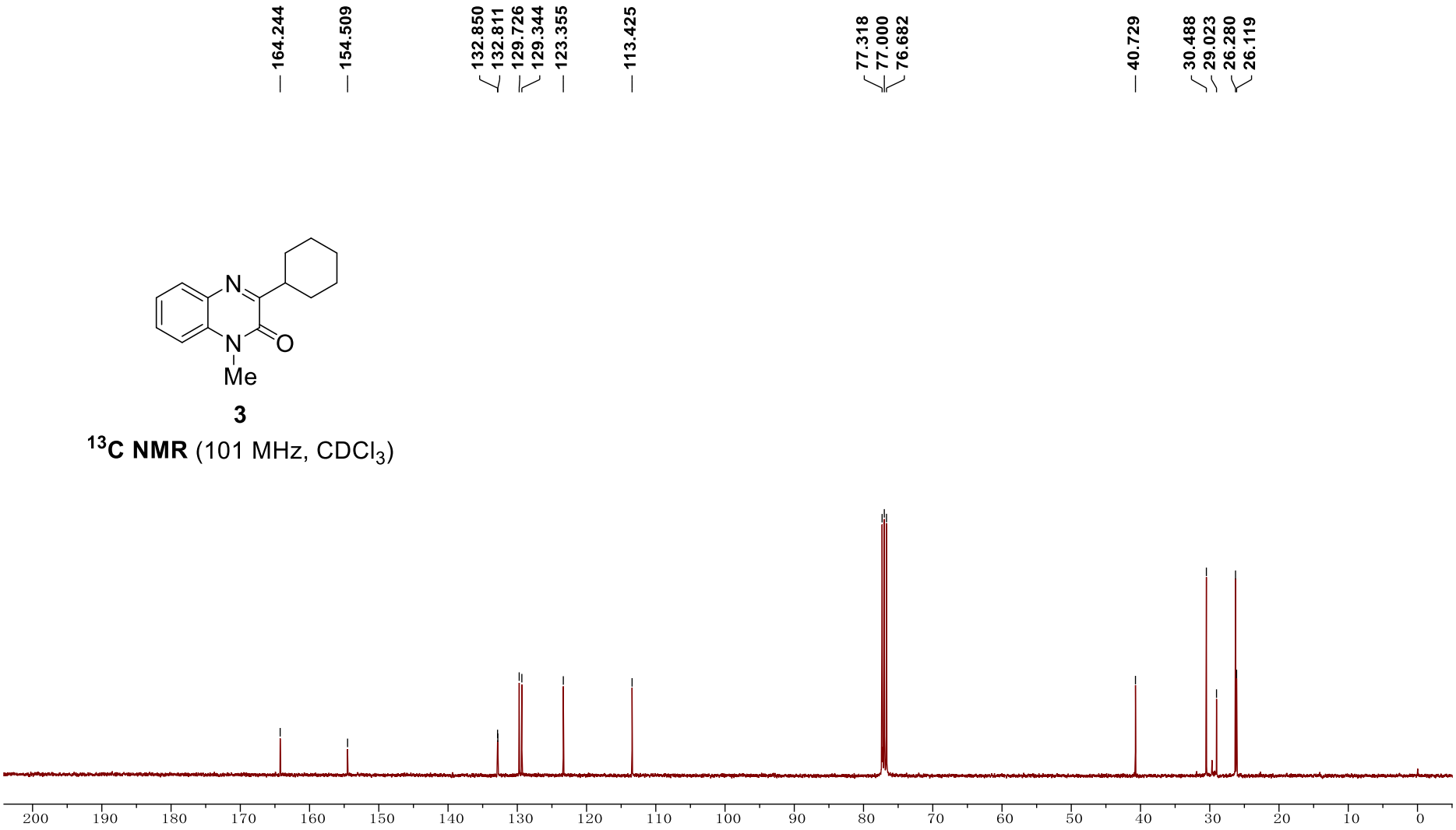
[17] Y. Wu, X. Chu, D. Yang, C. Ma, *SynOpen* **2021**, *5*, 114.

[18] V. N. Shinde, K. Rangan, D. Kumar, A. Kumar, *J. Org. Chem.* **2021**, *86*, 9755.



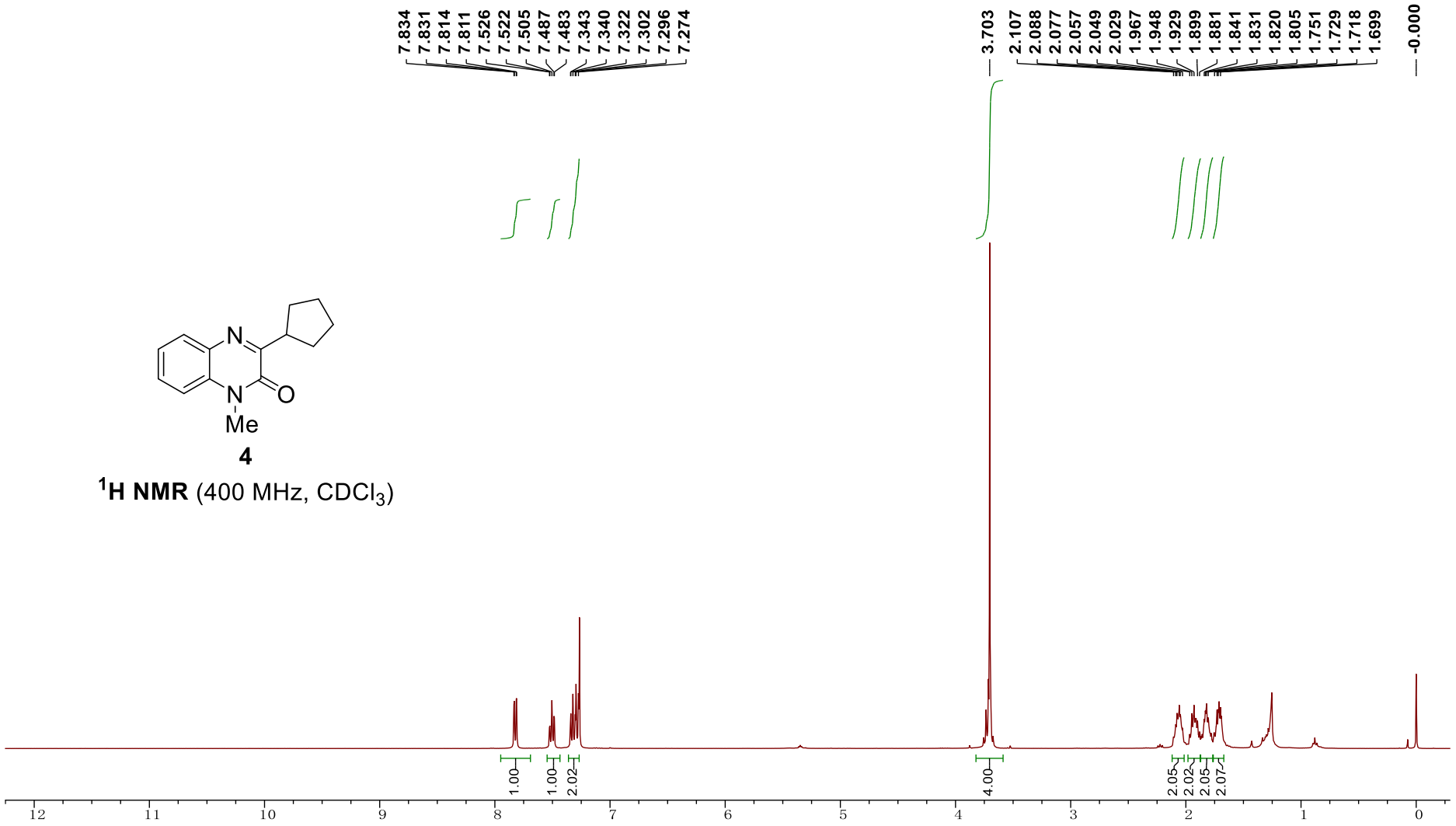

**3**

**$^1$H NMR** (400 MHz, $CDCl_3$)



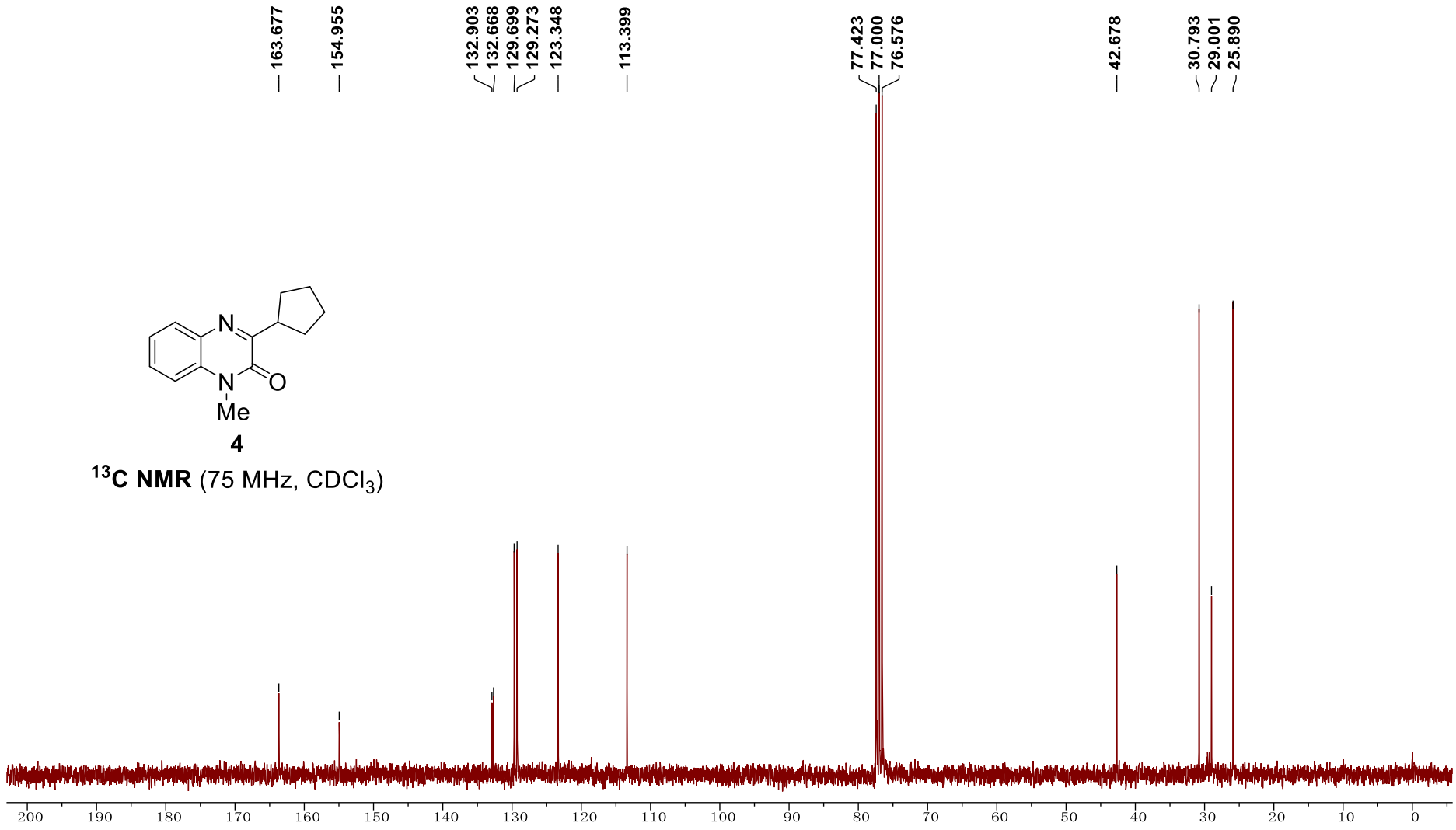

**3**

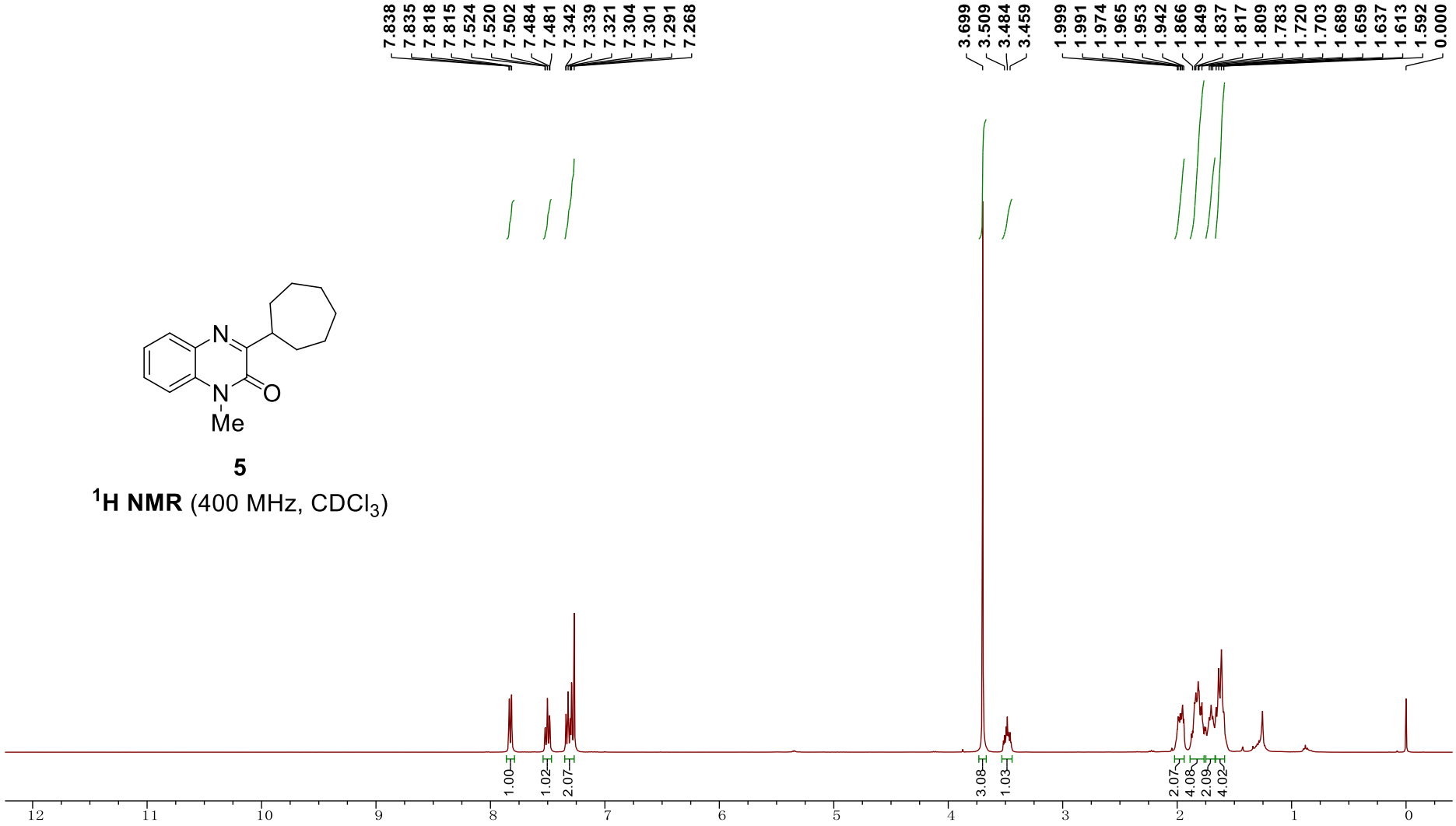
**$^{13}$C NMR** (101 MHz, $CDCl_3$)




**4**

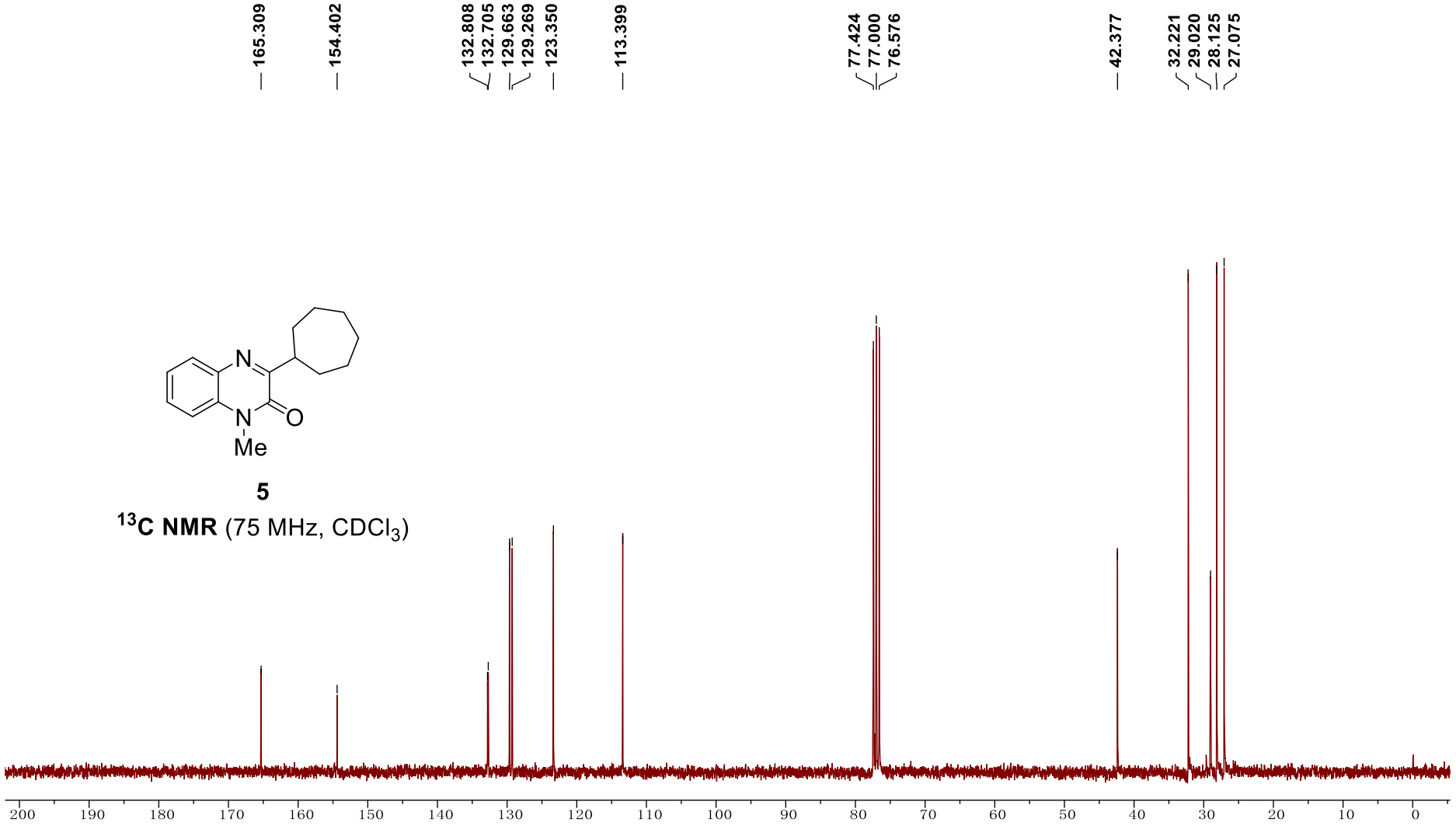
**$^1$H NMR** (400 MHz, $CDCl_3$)

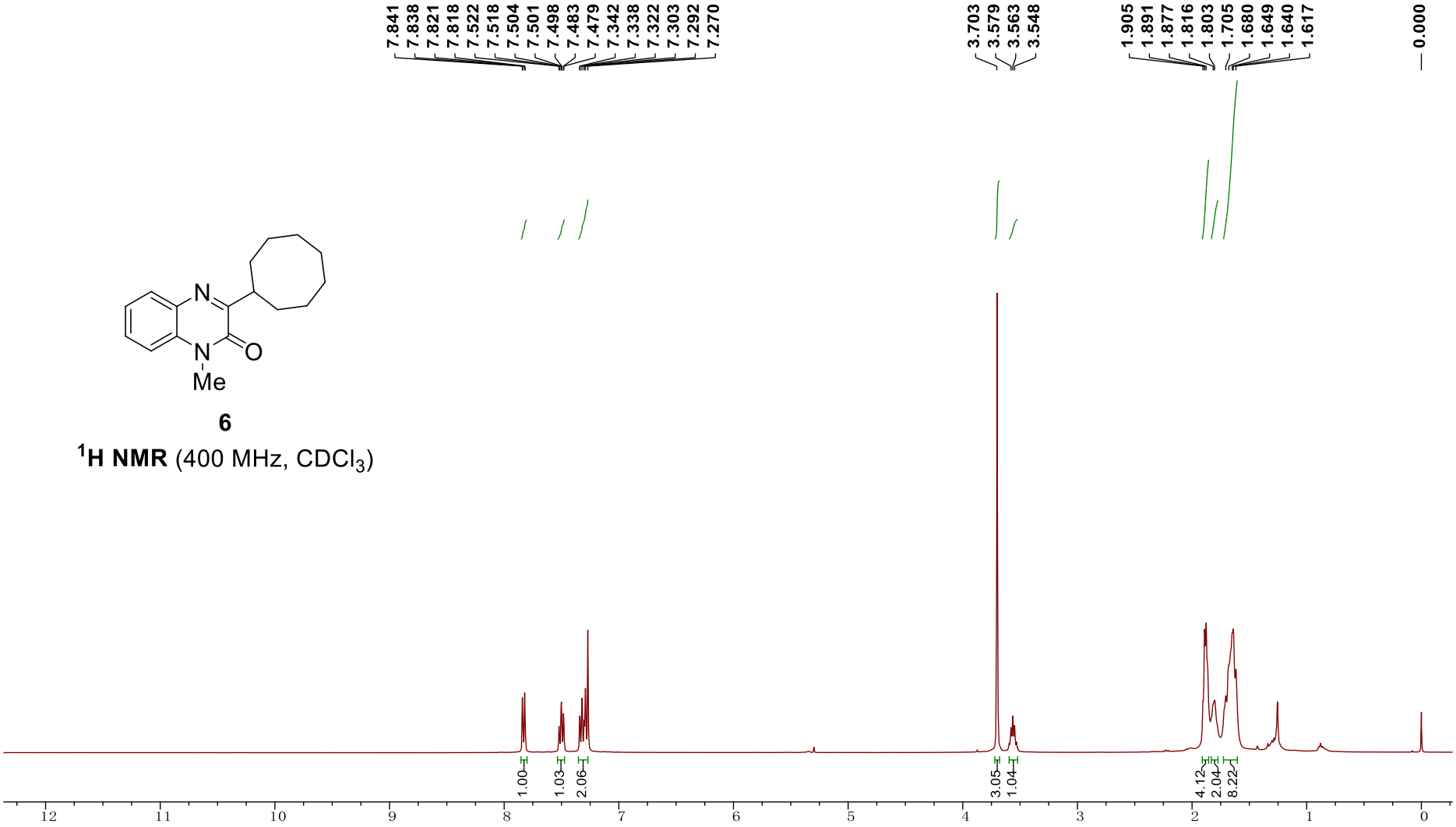

163.677
154.955
132.903
132.668
129.699
129.273
123.348
113.399
77.423
77.000
76.576
42.678
30.793
29.001
25.890
N
N
O
Me
4
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0




**5**

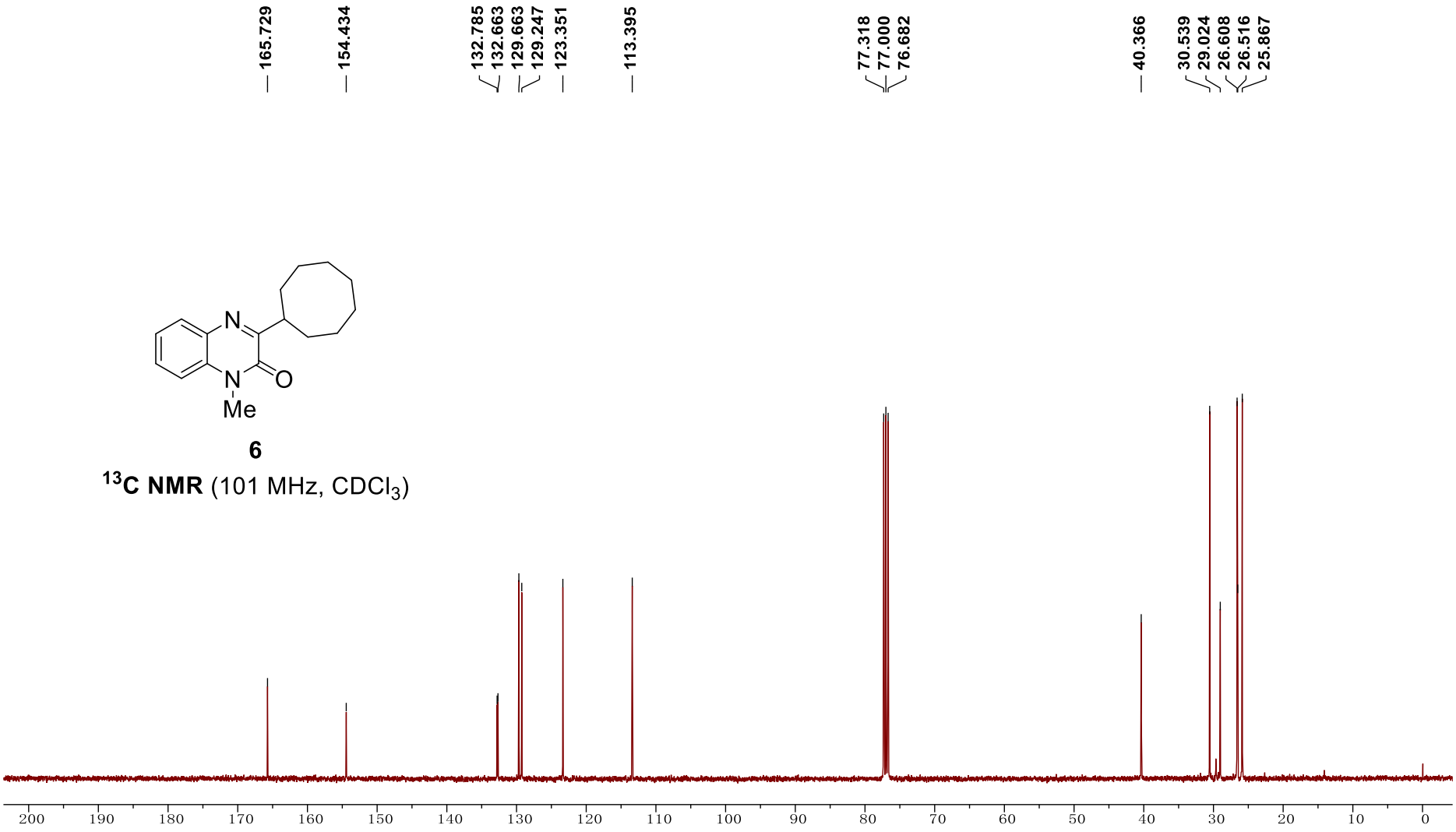
**$^1$H NMR** (400 MHz, $CDCl_3$)


165.309
154.402
132.808
132.705
129.663
129.269
123.350
113.399
77.424
77.000
76.576
42.377
32.221
29.020
28.125
27.075
N
N
O
Me
5
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



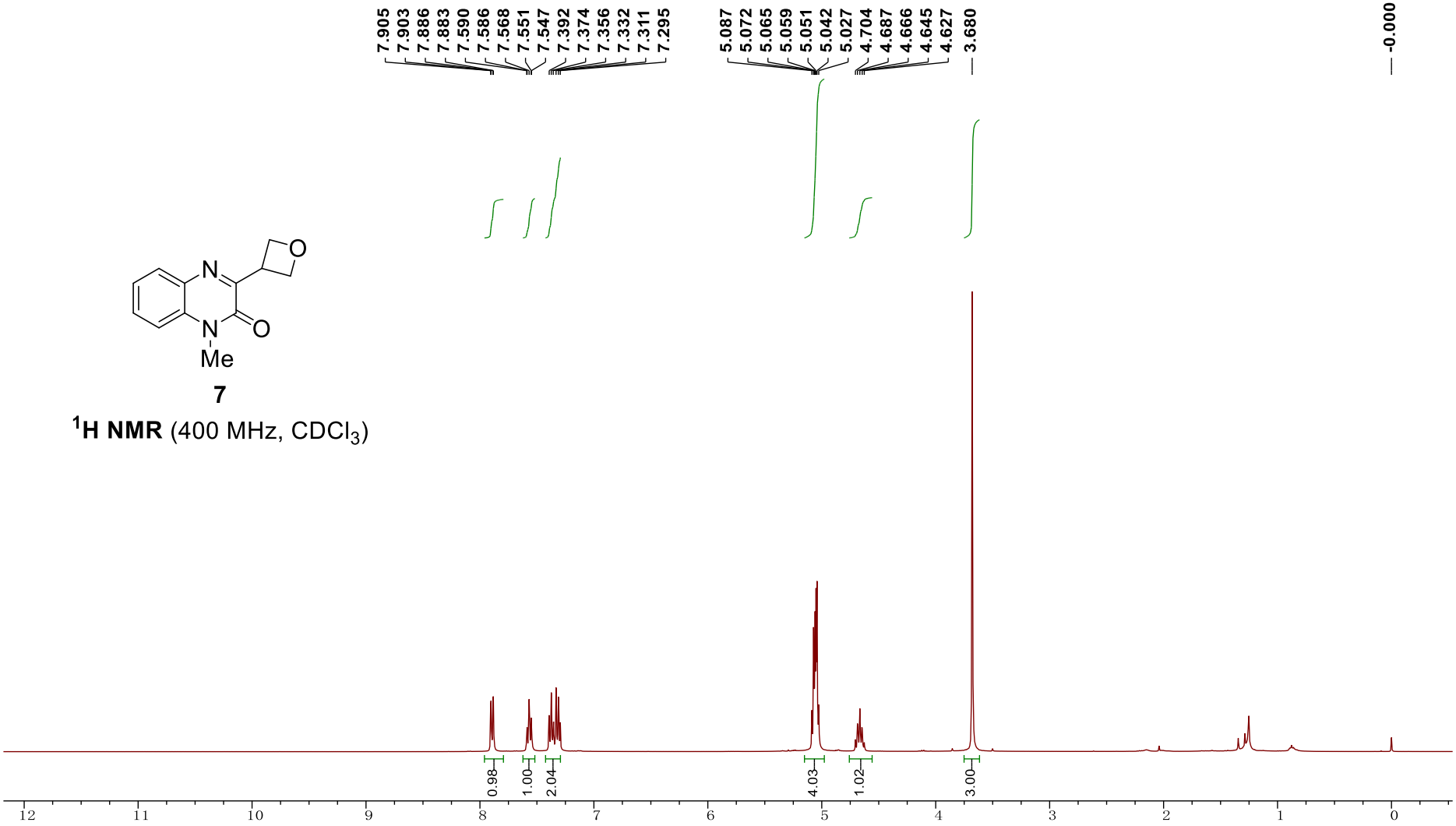

**6**

**$^1$H NMR** (400 MHz, $CDCl_3$)



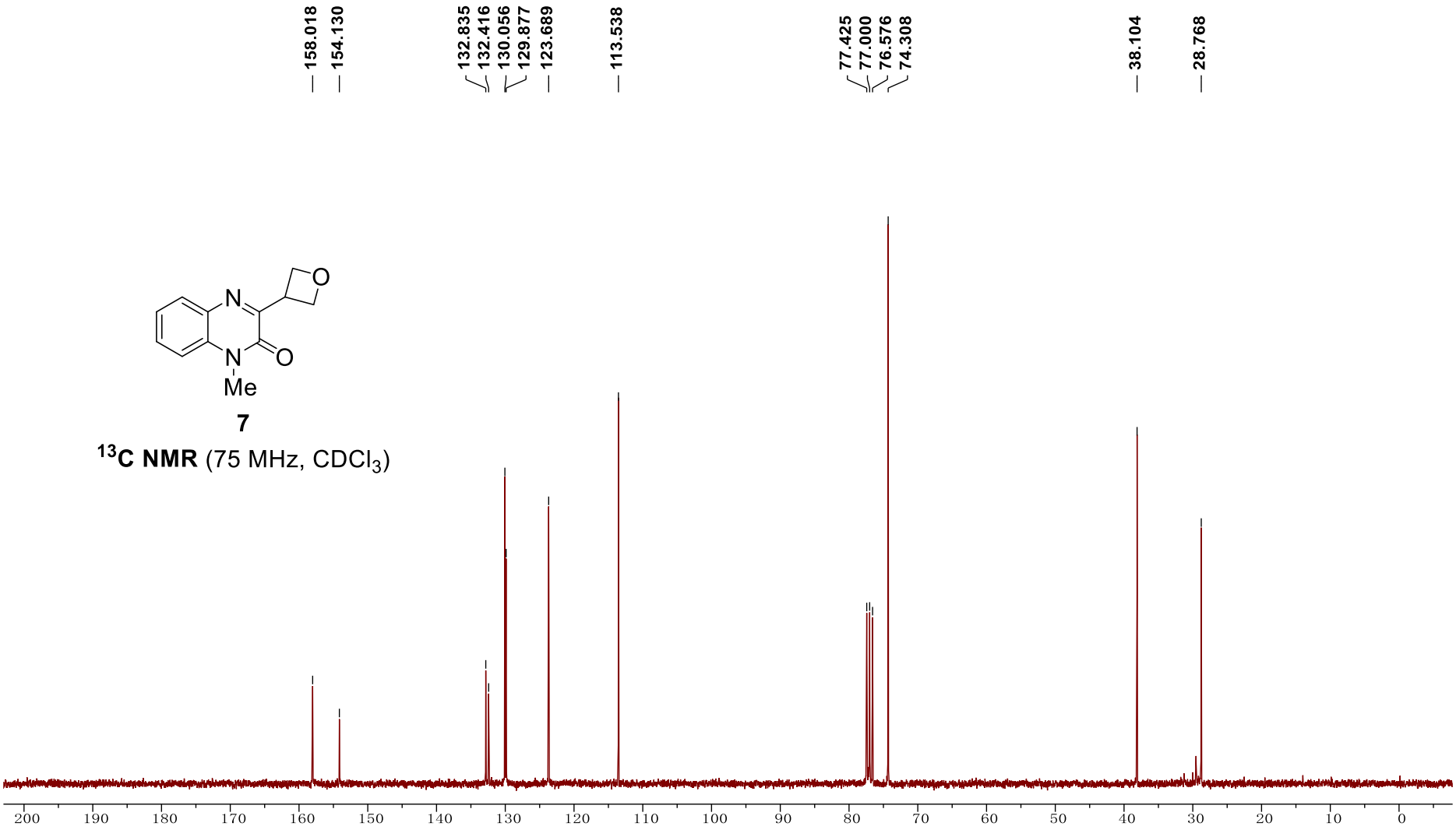

**6**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



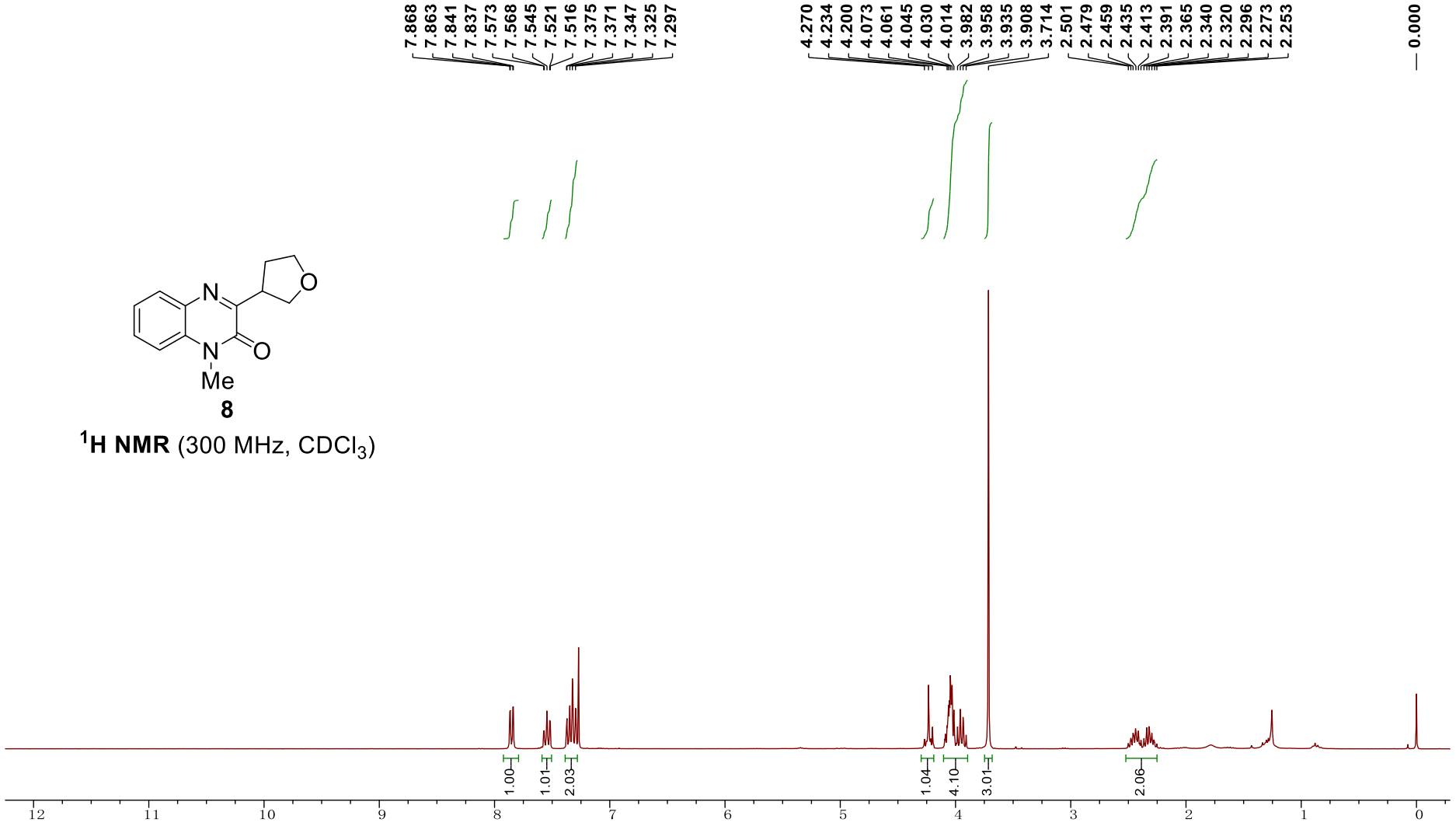

**7**

**$^1$H NMR** (400 MHz, $CDCl_3$)



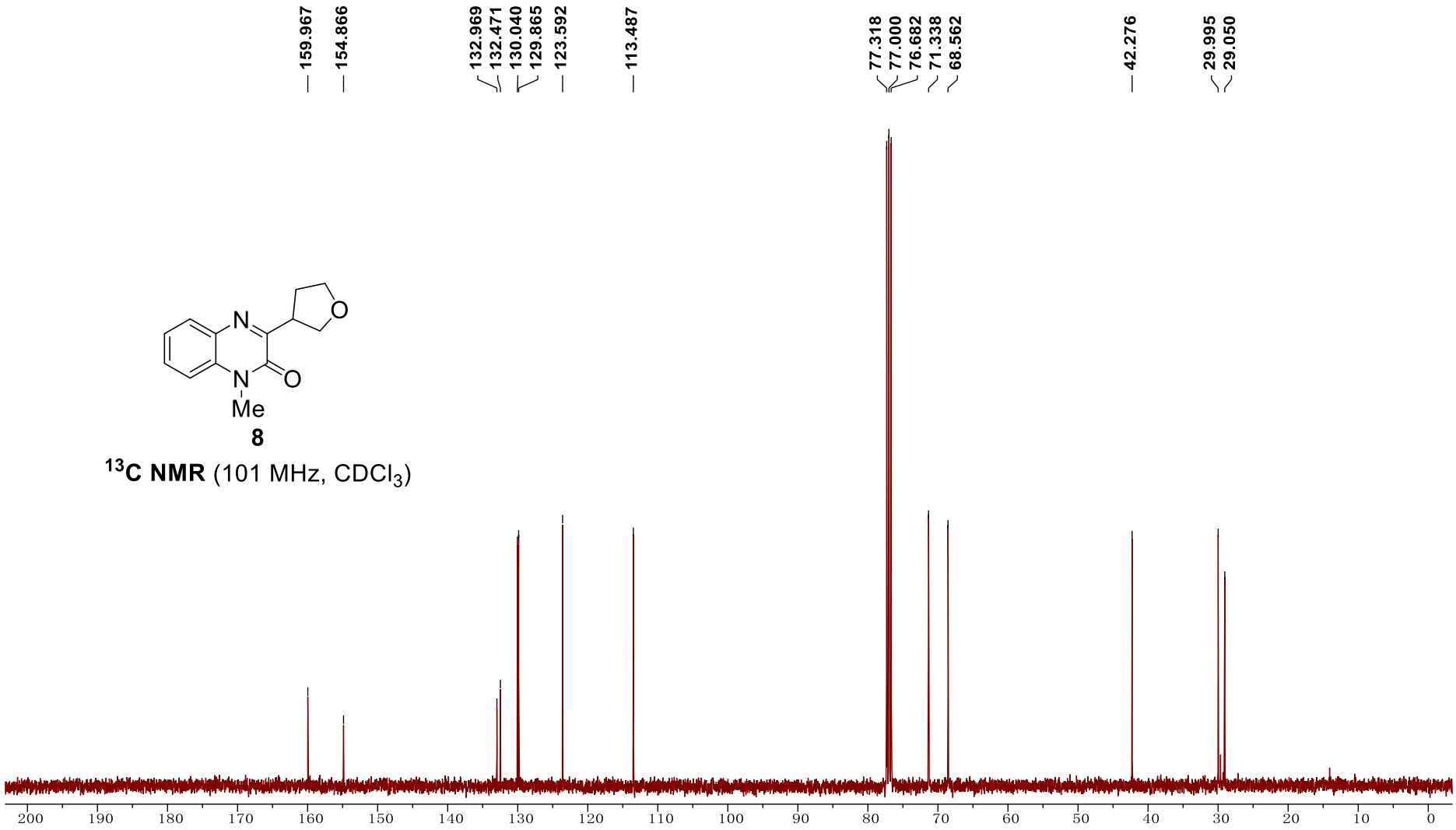

**7**

**$^{13}$C NMR** (75 MHz, $CDCl_3$)



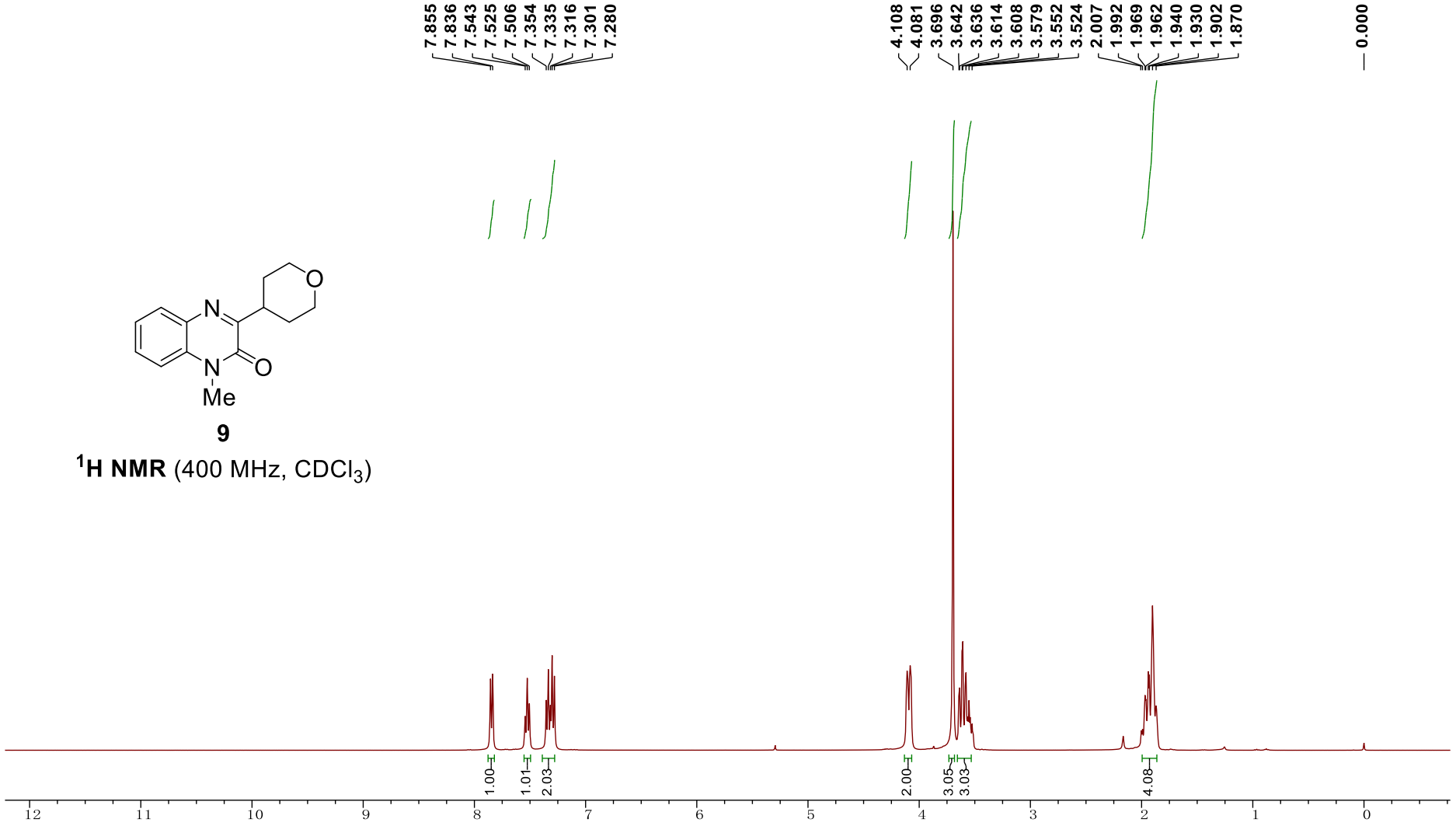

**8**

**$^1$H NMR** (300 MHz, $CDCl_3$)



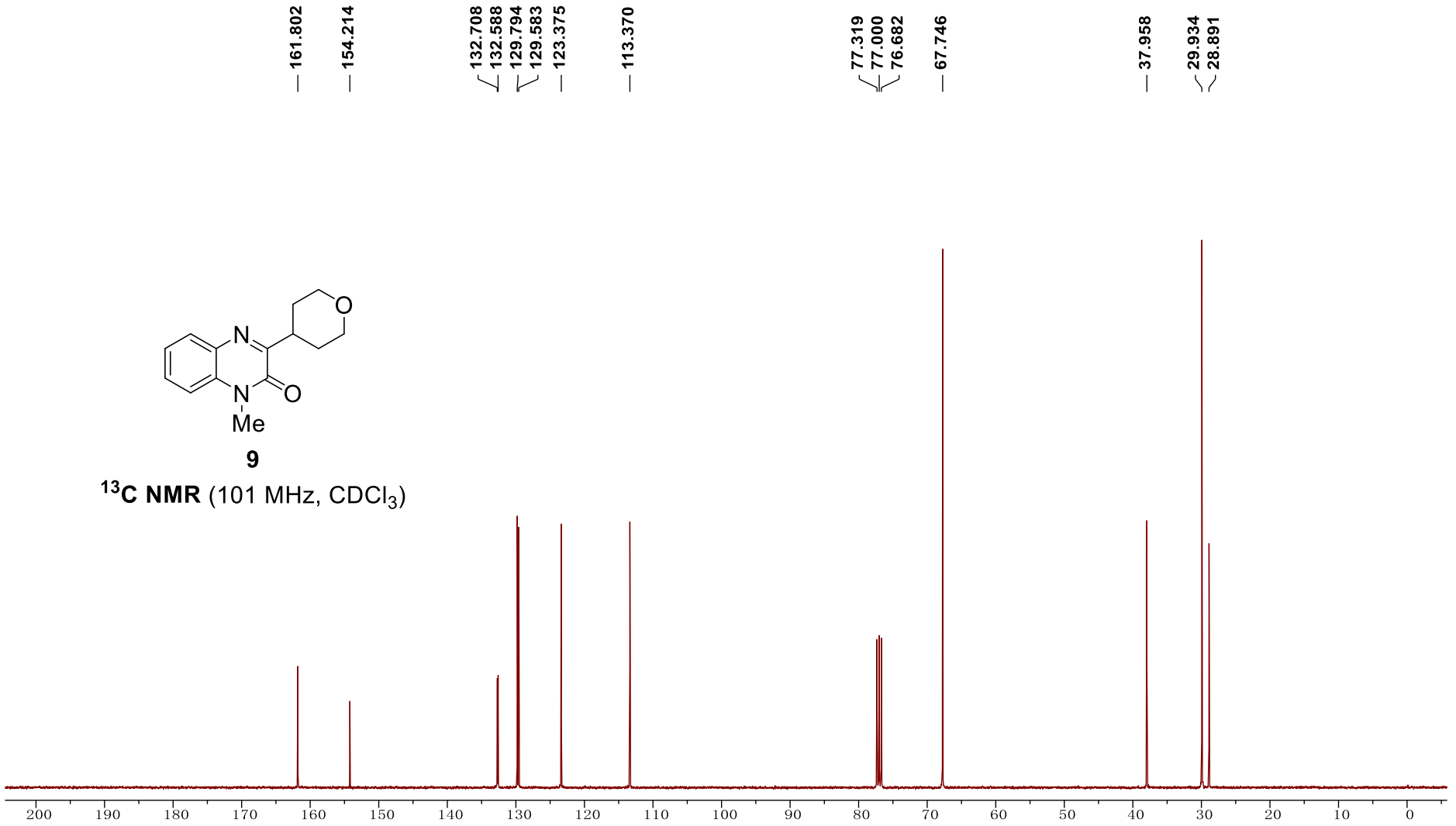

**8**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)




**9**

**$^1$H NMR** (400 MHz, $CDCl_3$)




**9**

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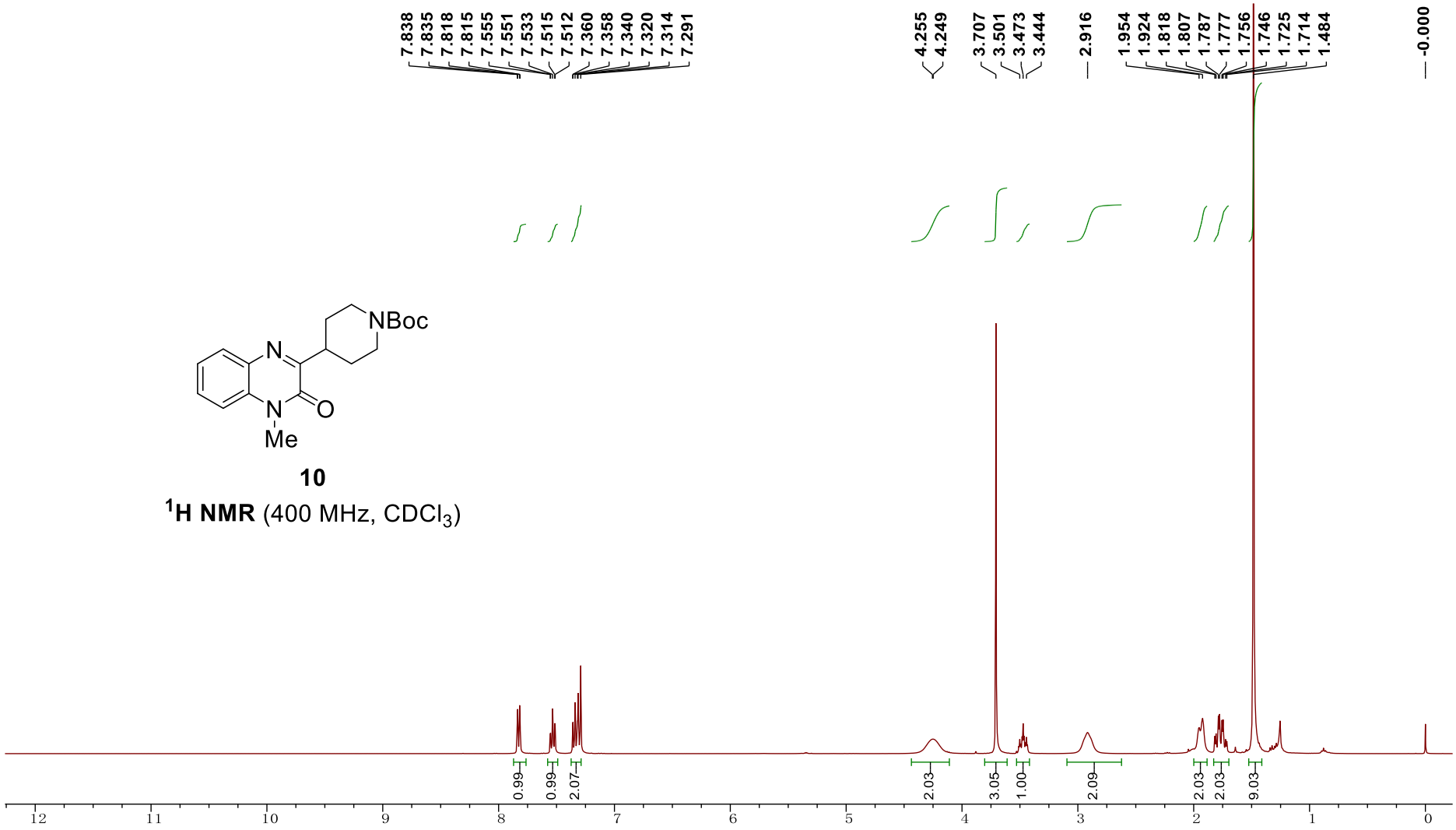
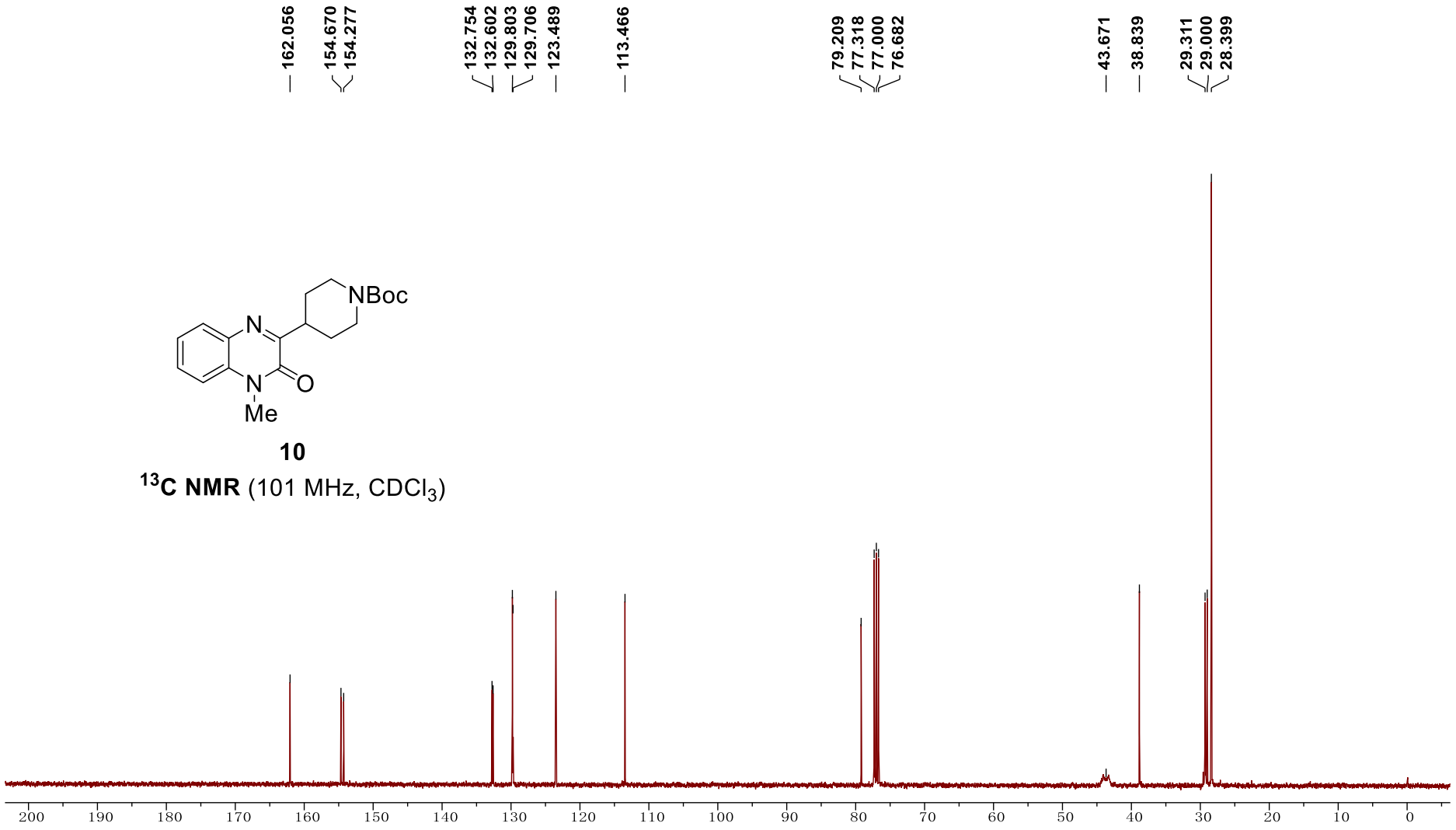


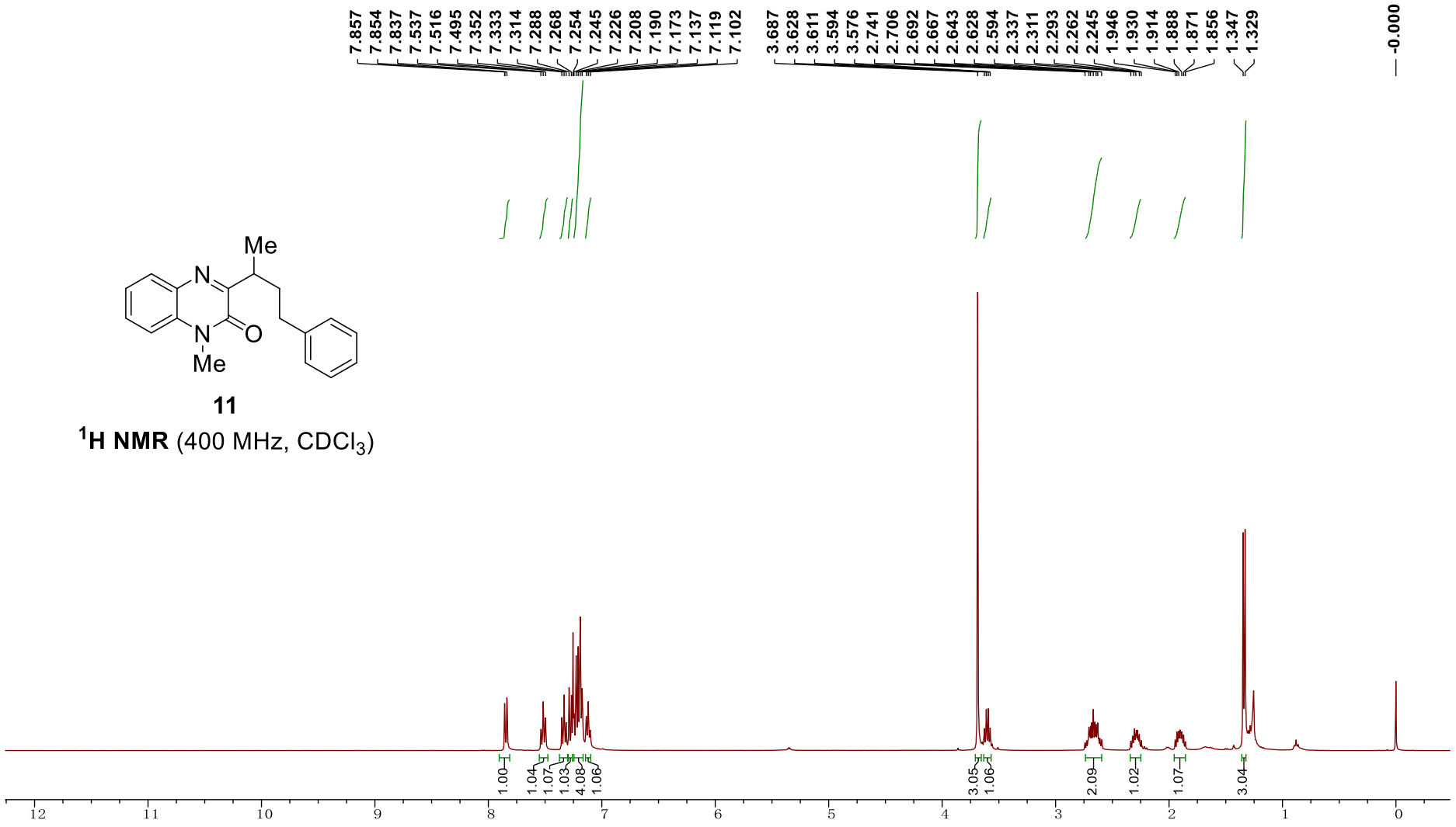

**10**

**$^1$H NMR** (400 MHz, $CDCl_3$)



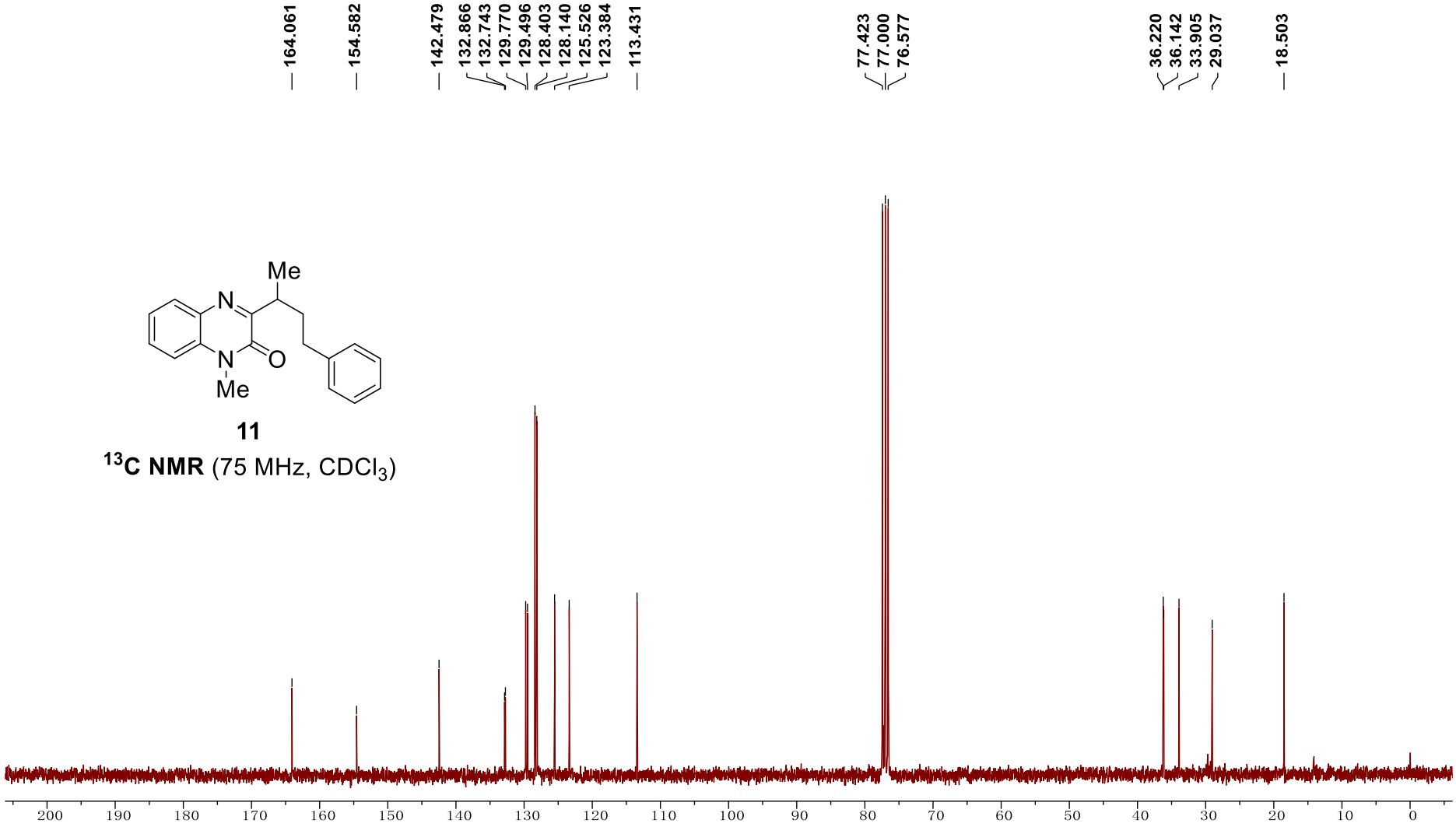

**10**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



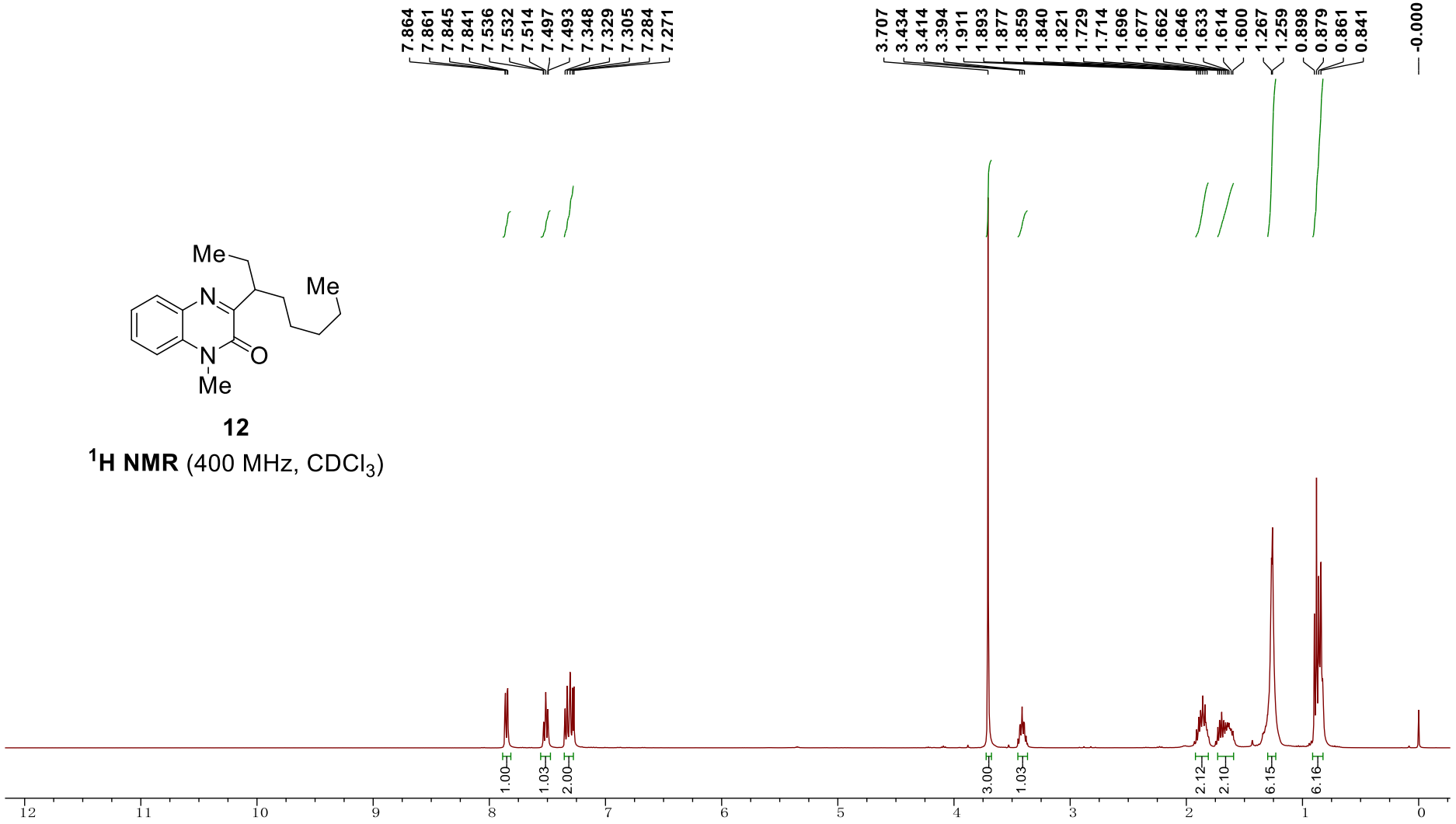

**11**

**$^1$H NMR** (400 MHz, $CDCl_3$)



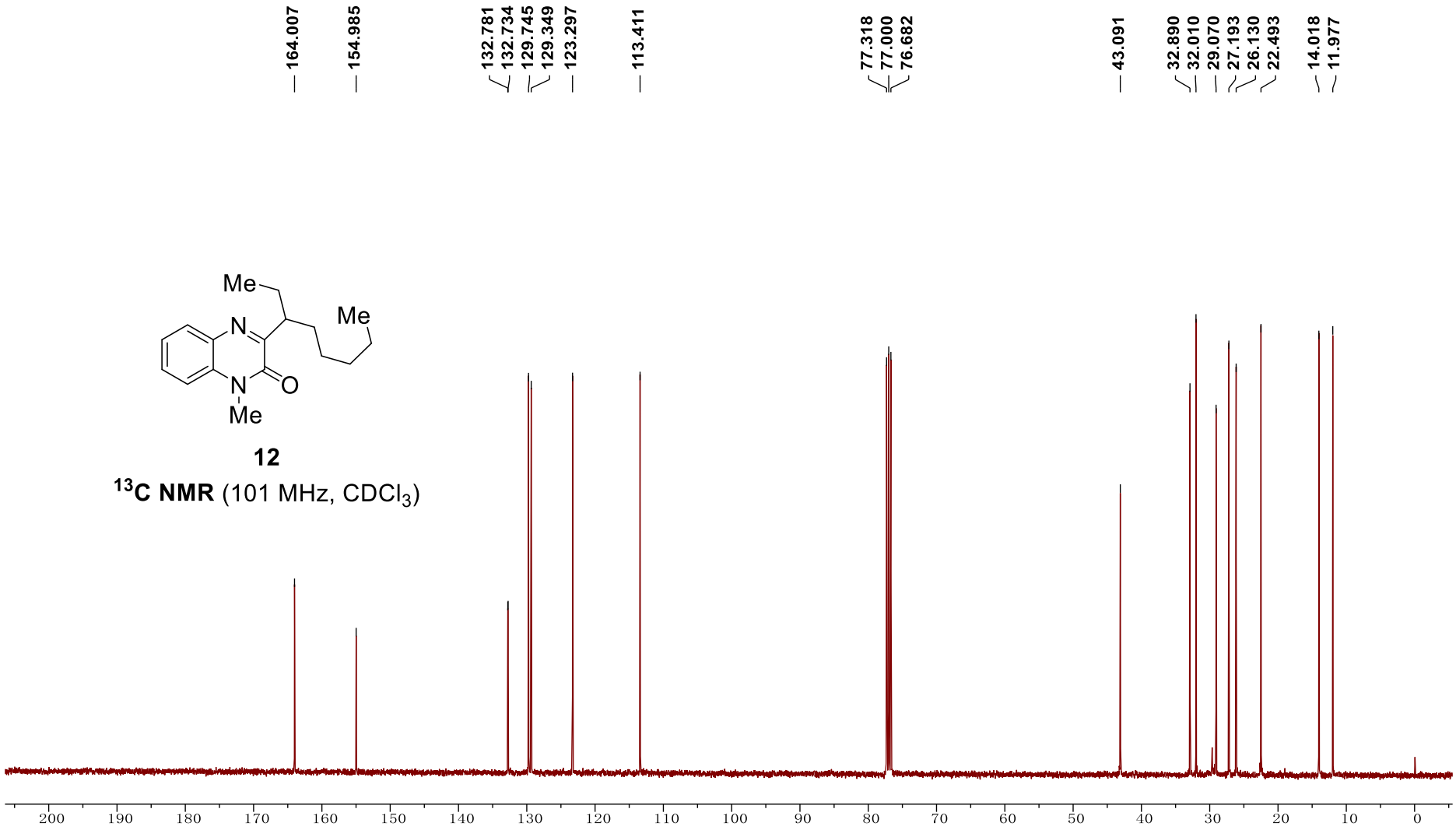

**11**

**$^{13}$C NMR** (75 MHz, $CDCl_3$)




**12**

**$^1$H NMR** (400 MHz, $CDCl_3$)




**12**

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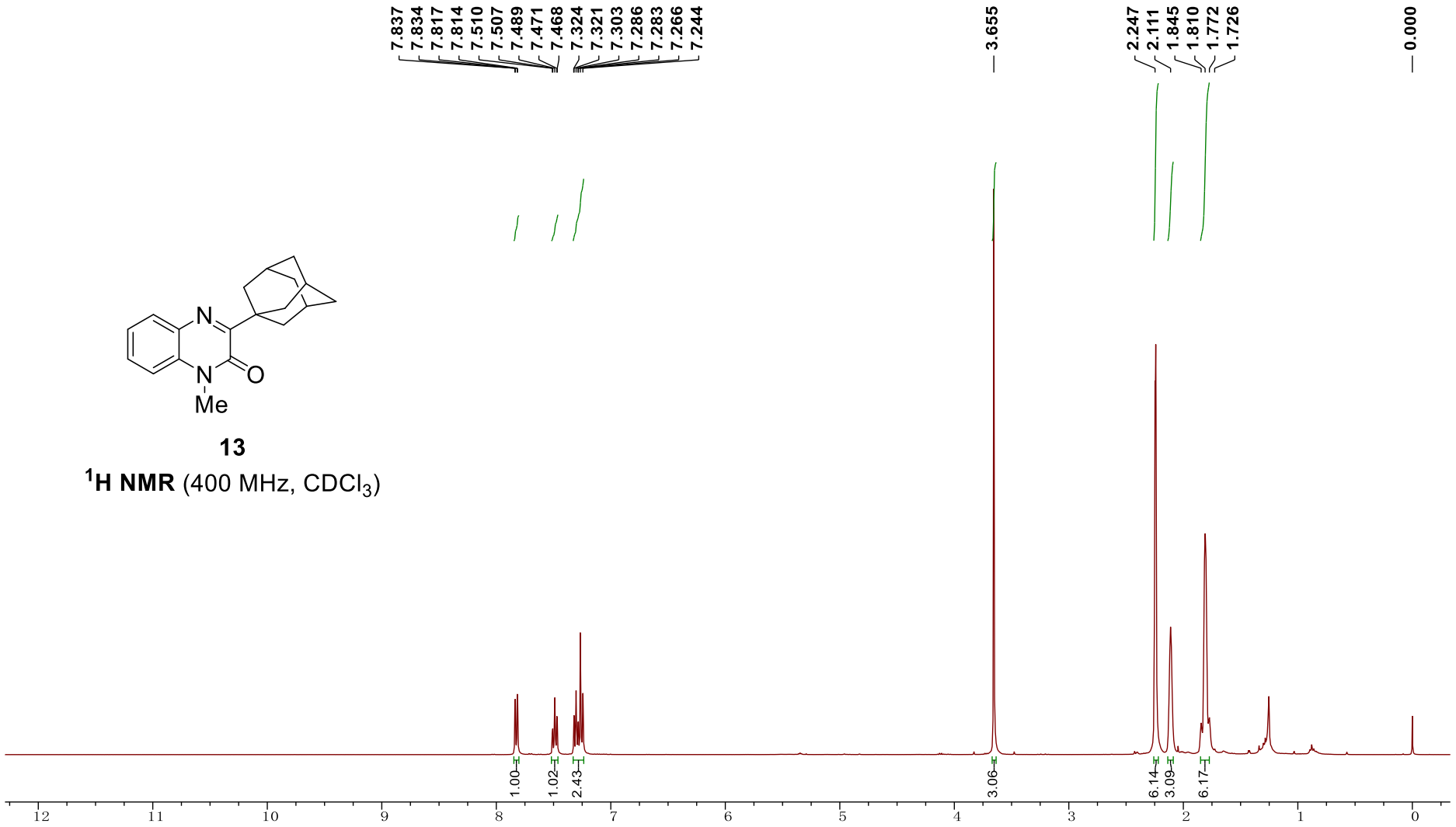
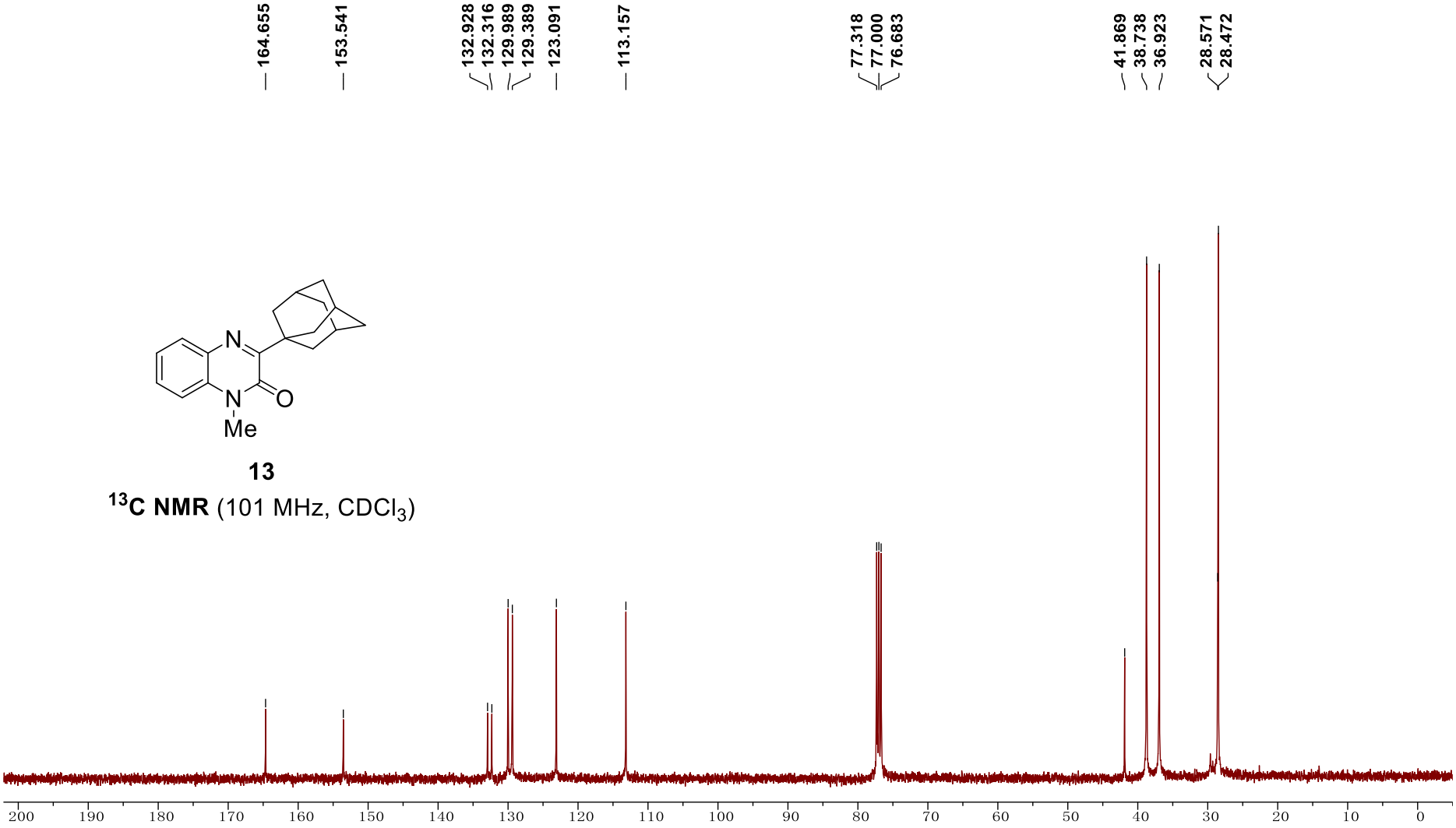


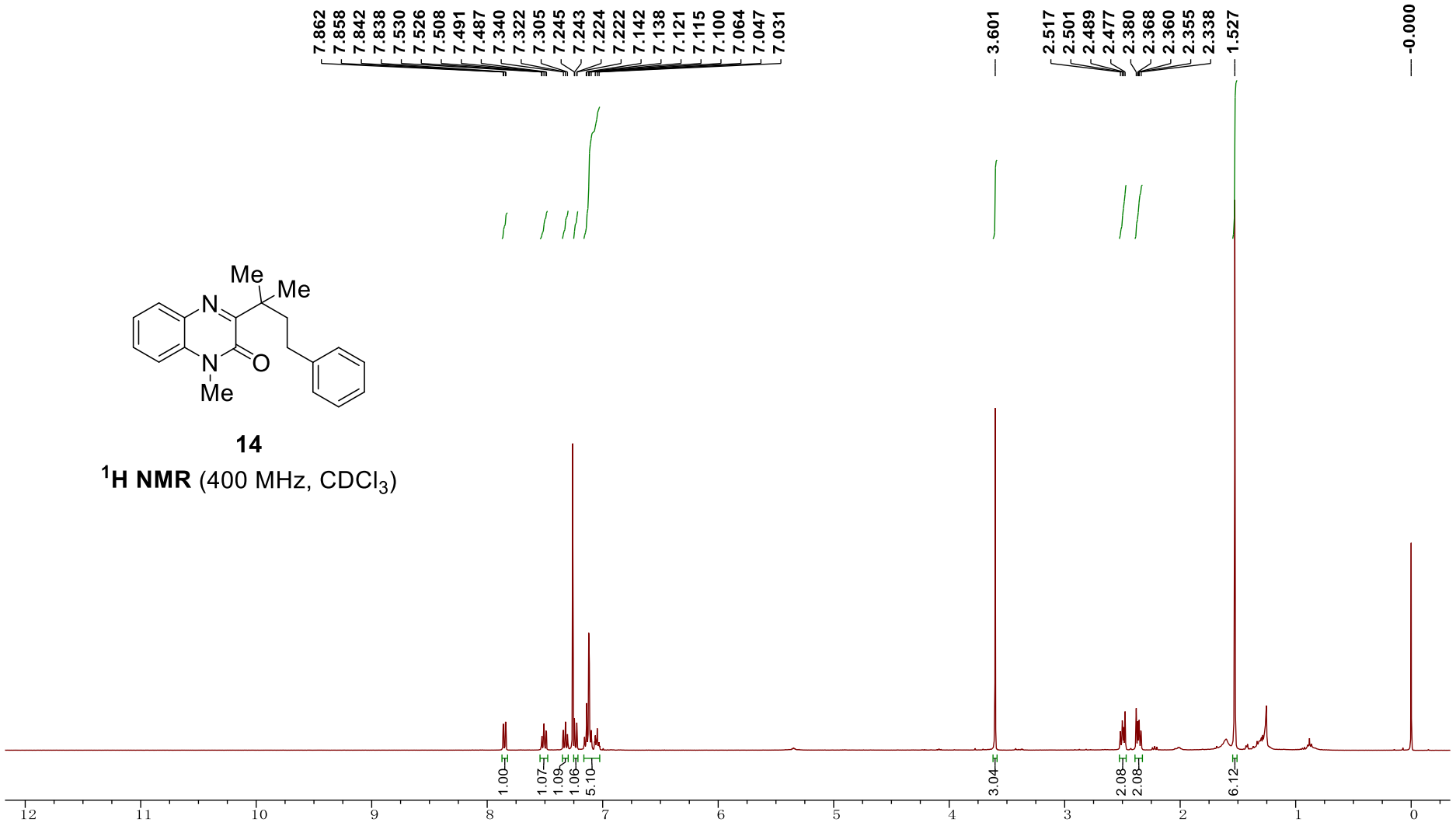

**13**

**$^1$H NMR** (400 MHz, $CDCl_3$)



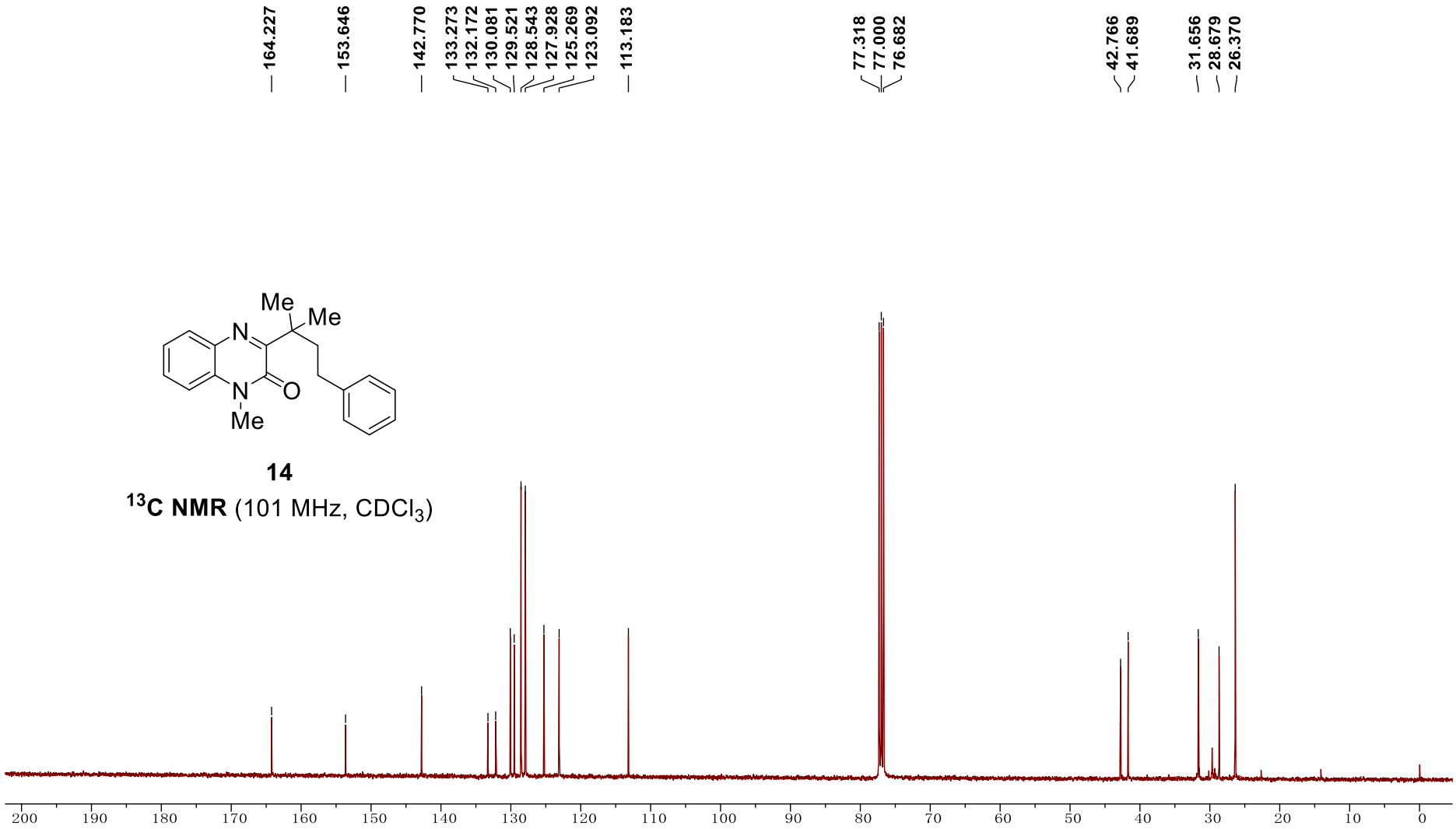

**13**

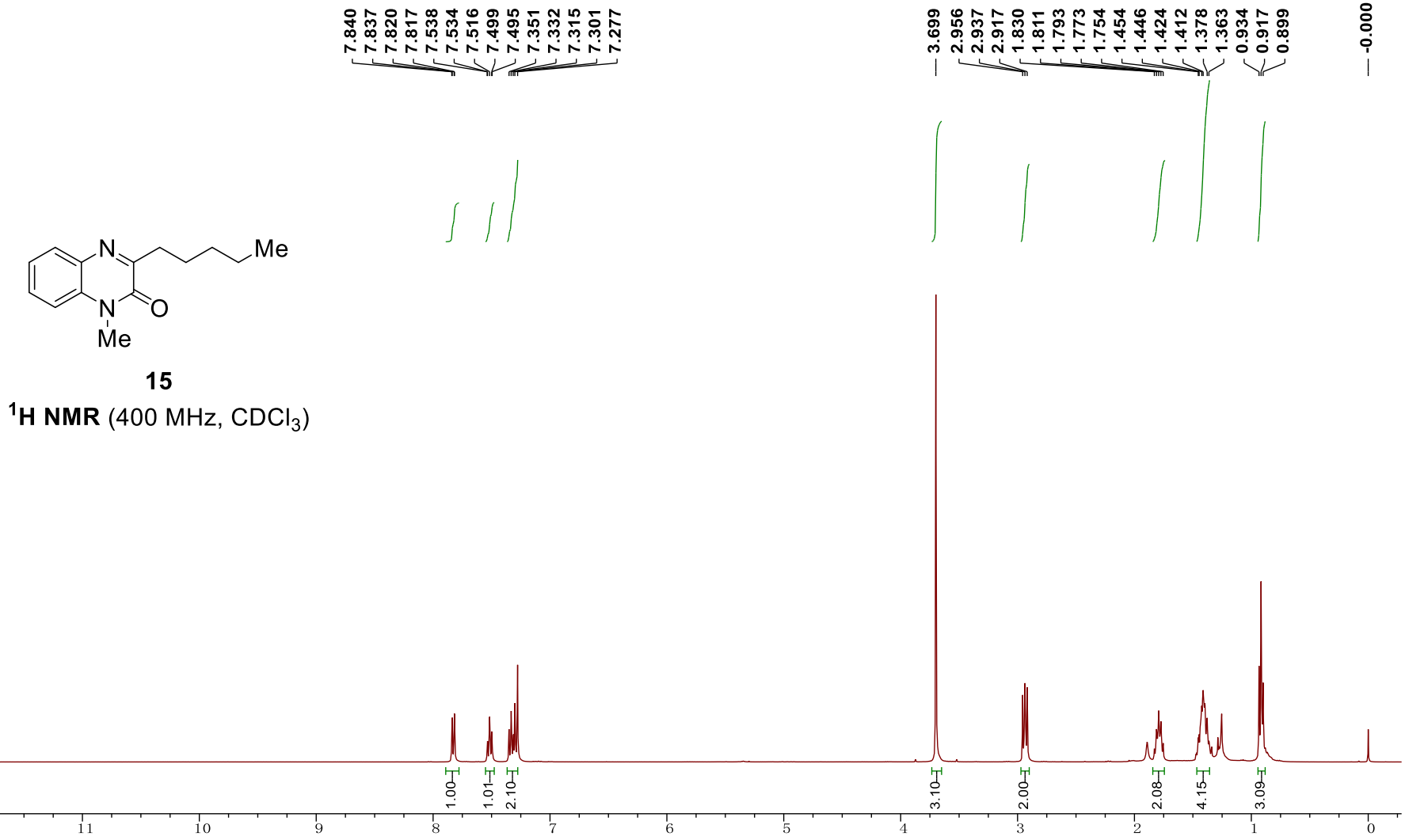
**$^{13}$C NMR** (101 MHz, $CDCl_3$)




**14**

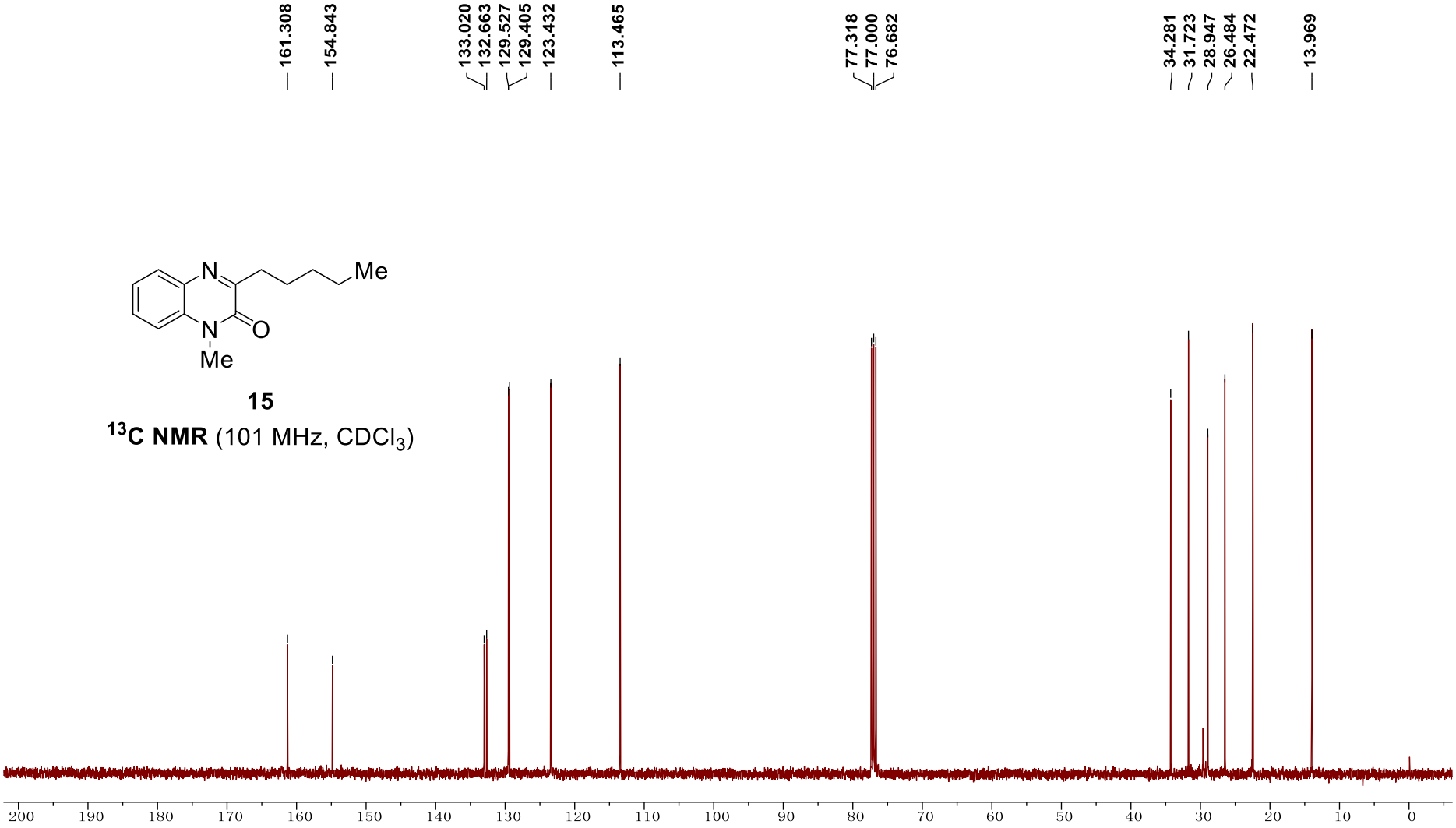
**$^1$H NMR** (400 MHz, $CDCl_3$)

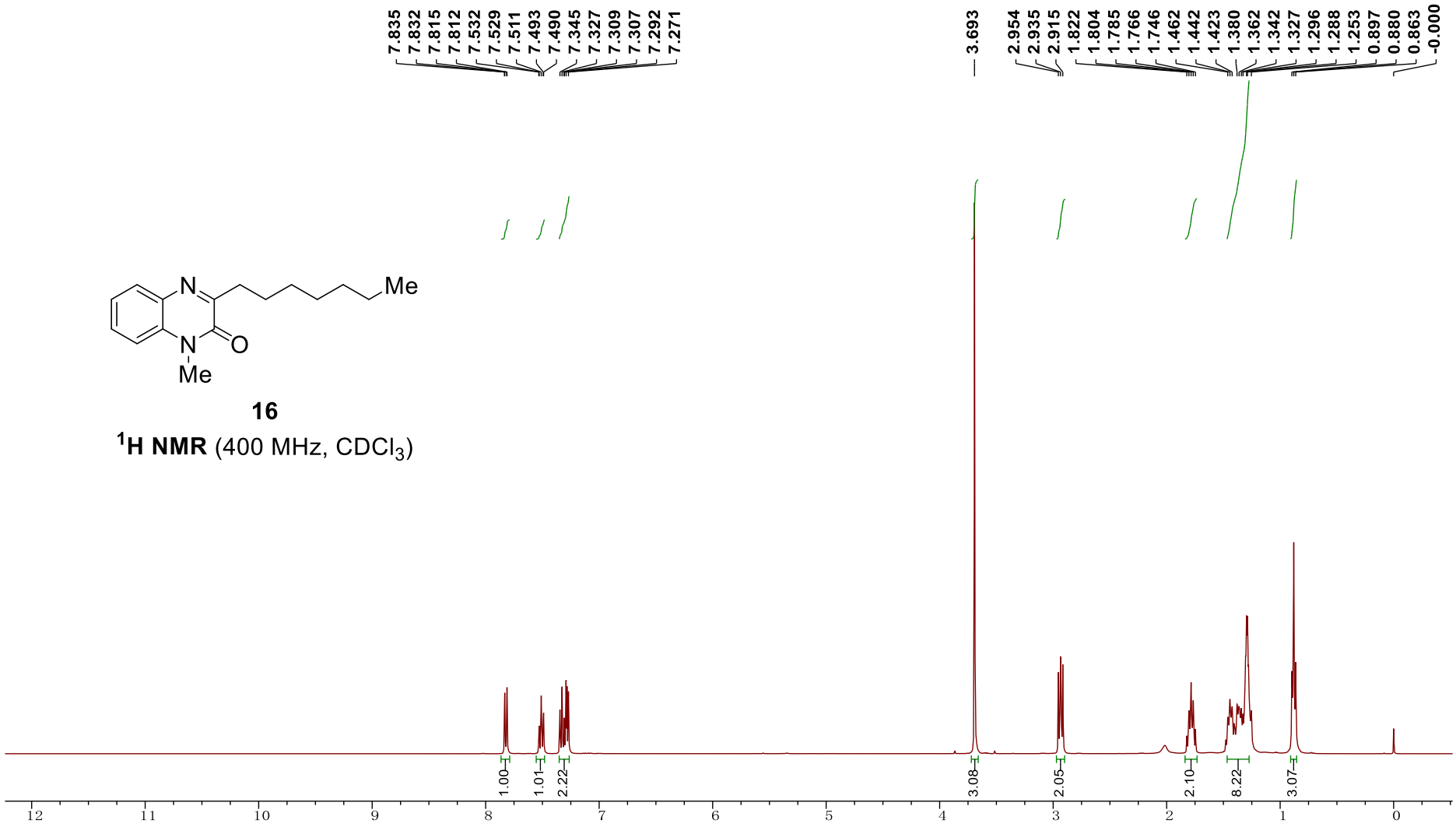

164.227
153.646
142.770
133.273
132.172
130.081
129.521
128.543
127.928
125.269
123.092
113.183
77.318
77.000
76.682
42.766
41.689
31.656
28.679
26.370
Me
Me
N
N
O
Me
14
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0




**15**

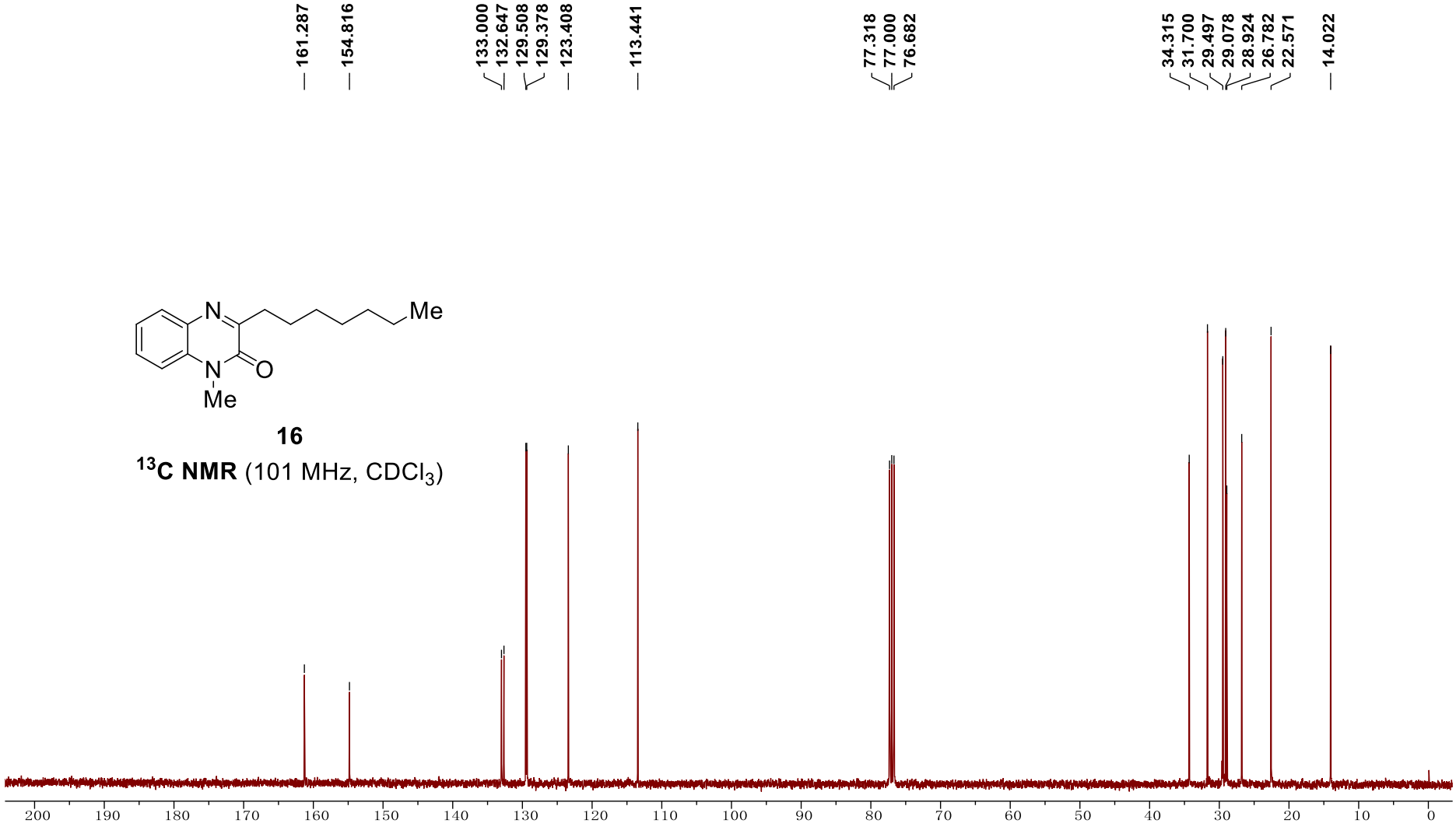
**$^1$H NMR** (400 MHz, $CDCl_3$)

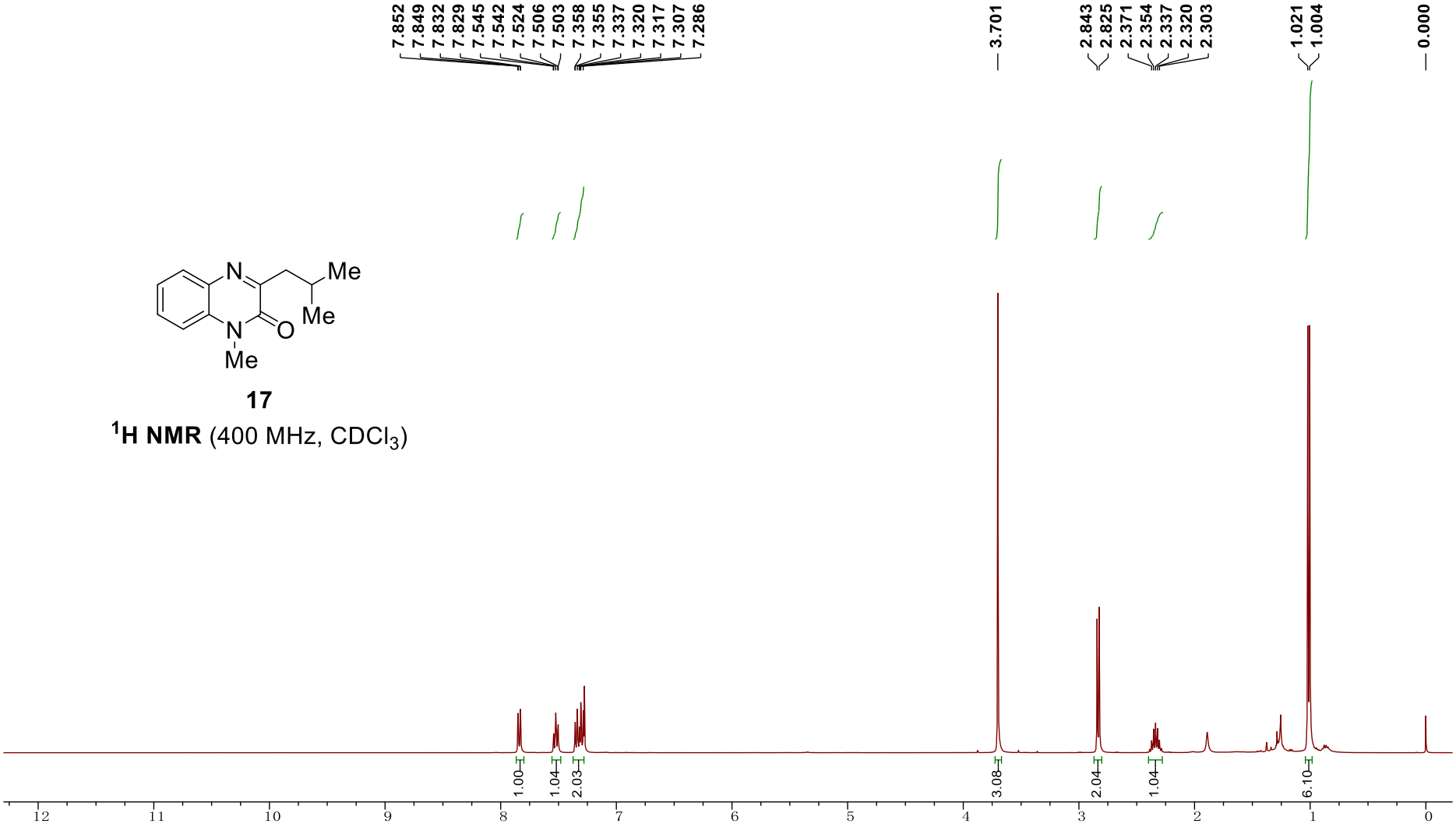

161.308
154.843
133.020
132.663
129.527
129.405
123.432
113.465
77.318
77.000
76.682
34.281
31.723
28.947
26.484
22.472
13.969
N
Me
N
O
Me
15
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0




**16**

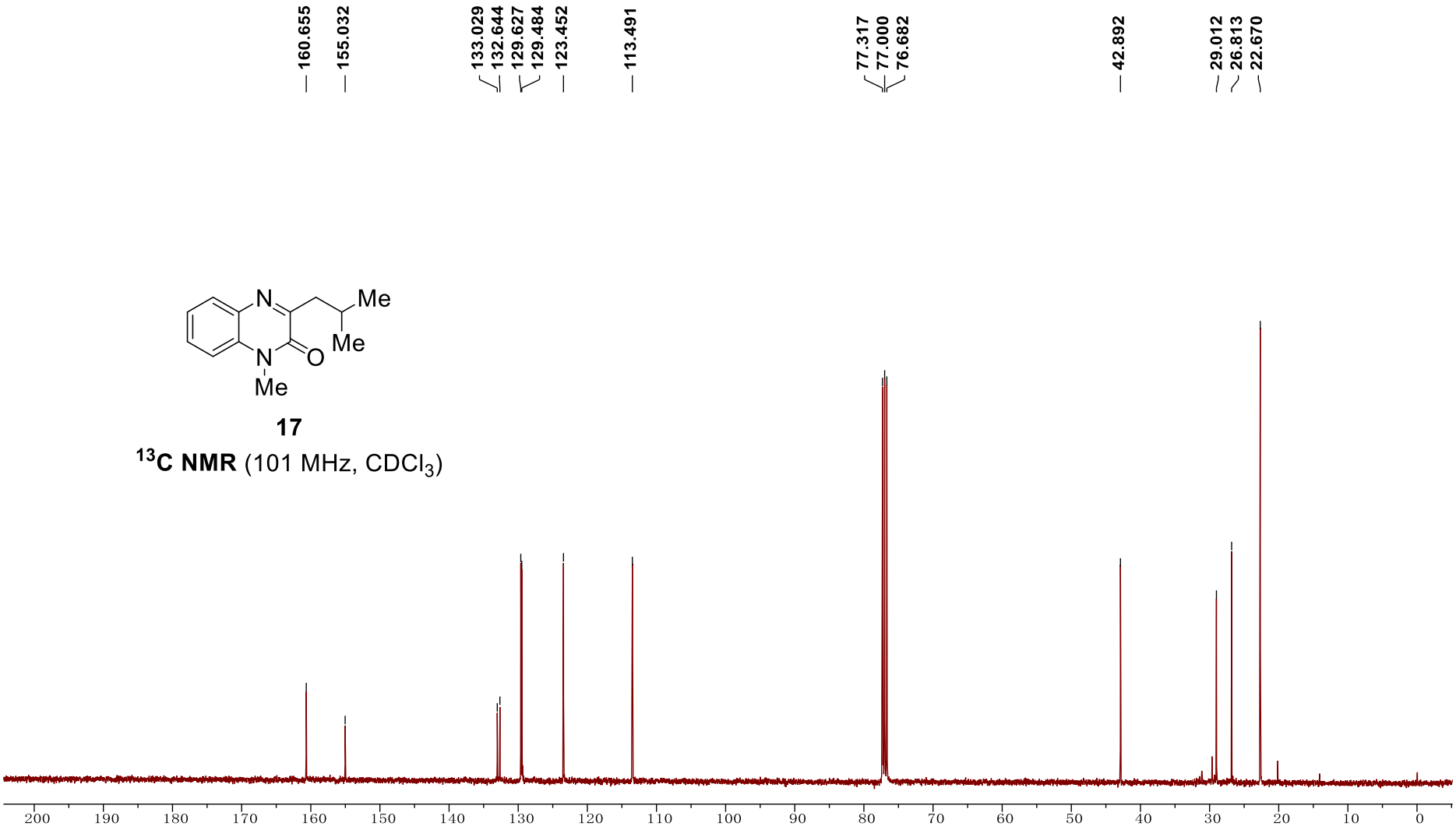
**$^1$H NMR** (400 MHz, $CDCl_3$)

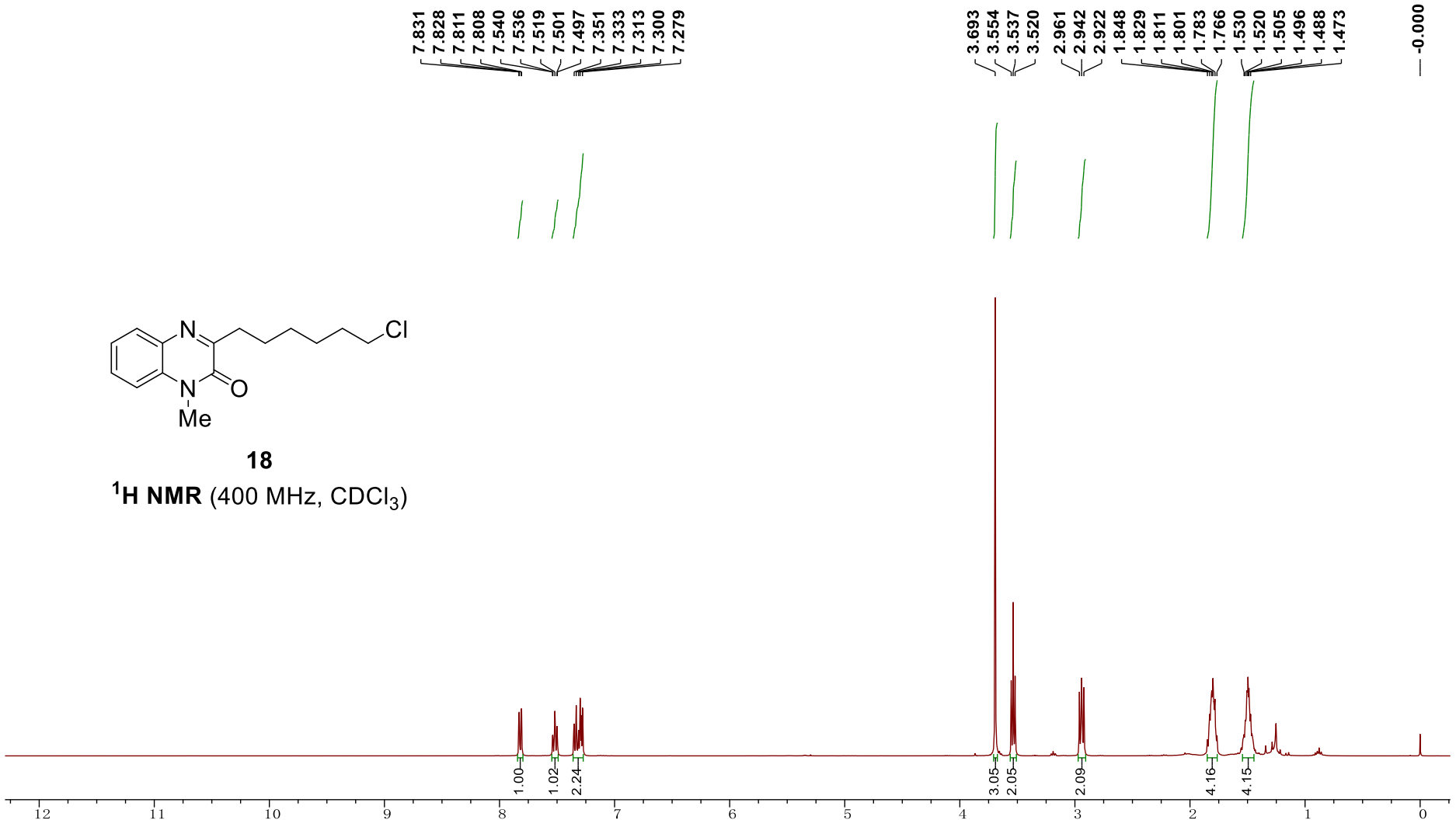

161.287
154.816
133.000
132.647
129.508
129.378
123.408
113.441
77.318
77.000
76.682
34.315
31.700
29.497
29.078
28.924
26.782
22.571
14.022
N
N
O
Me
Me
16
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0




**17**

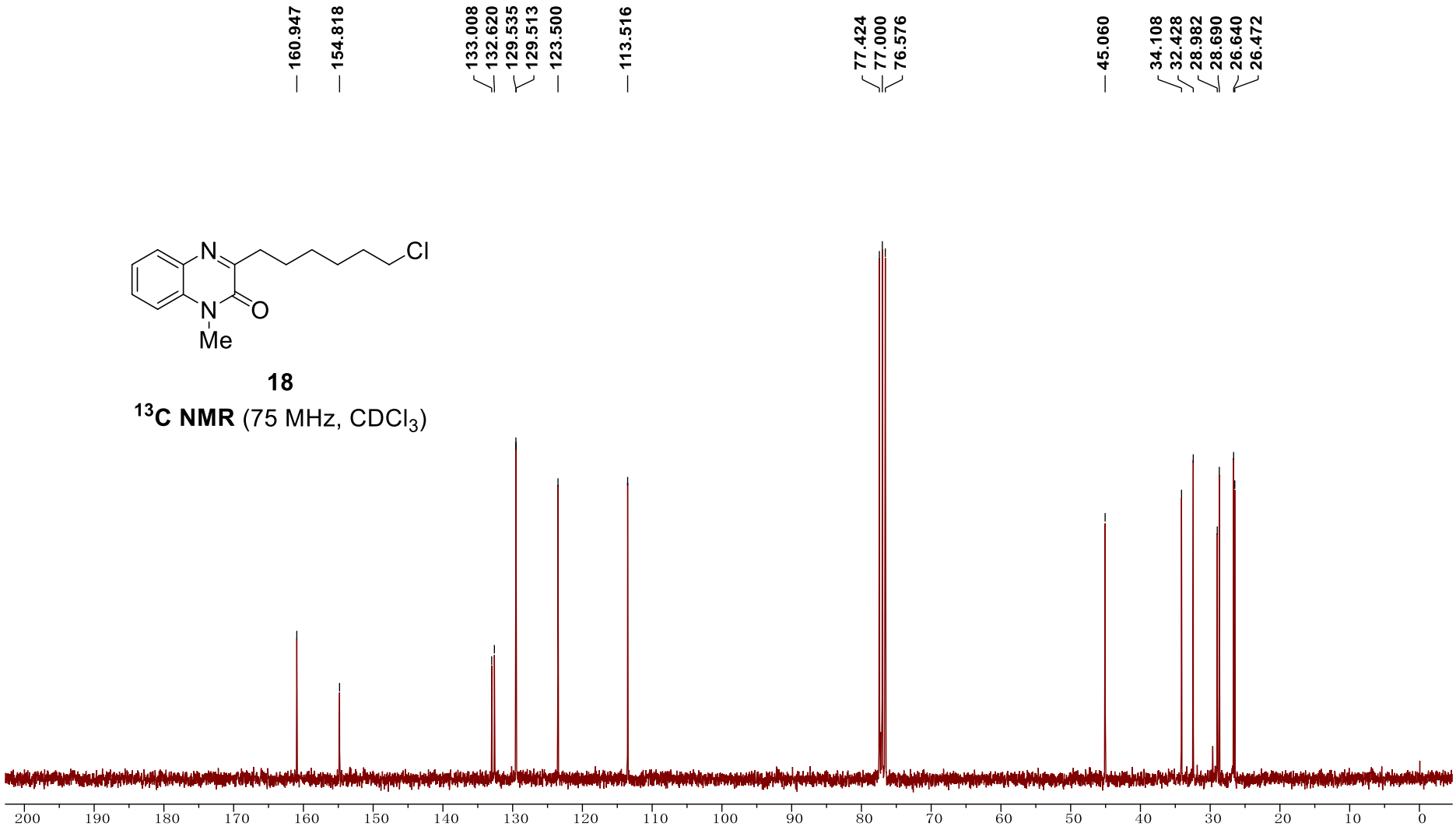
**$^1$H NMR** (400 MHz, $CDCl_3$)

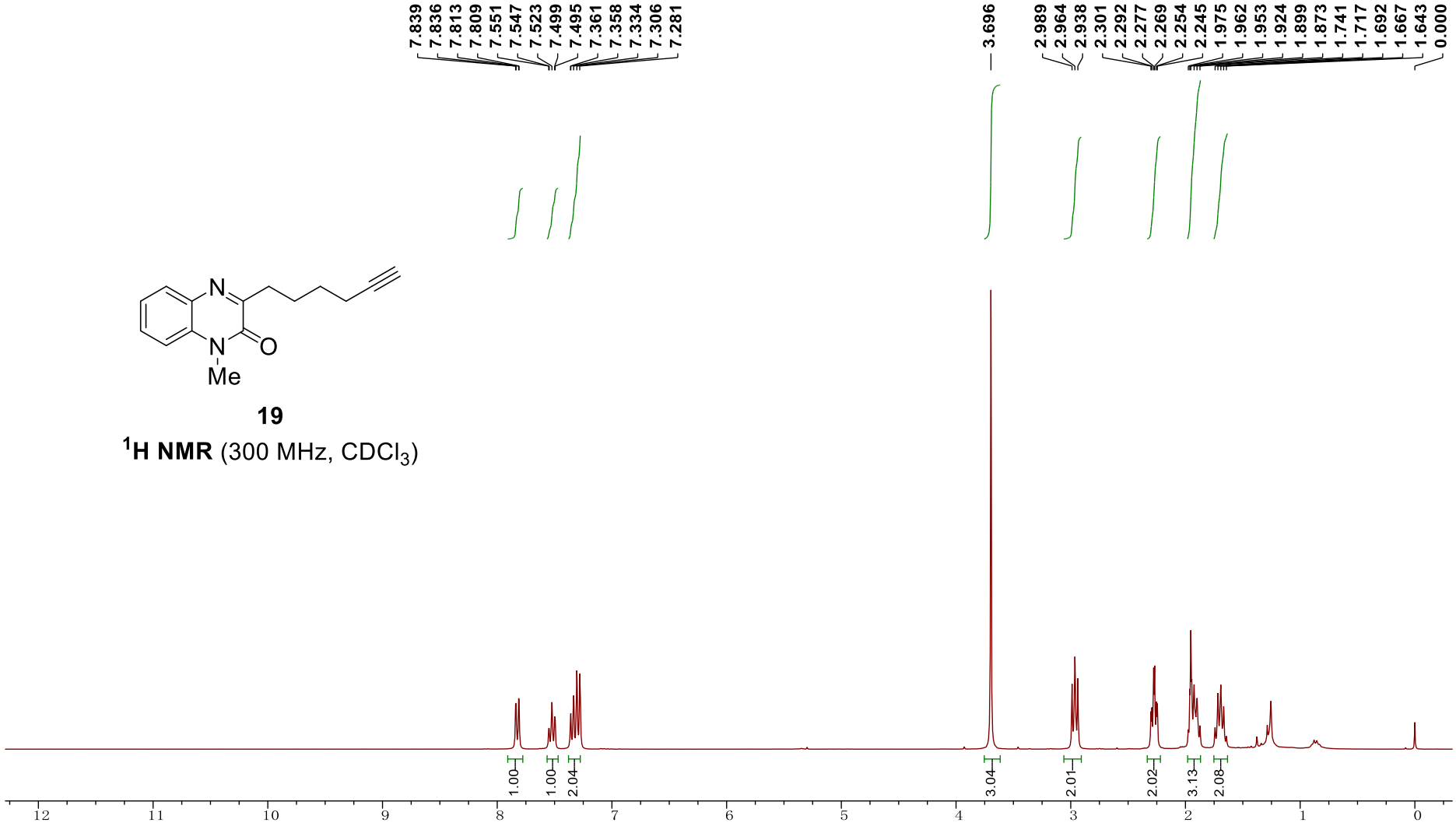

160.655
155.032
133.029
132.644
129.627
129.484
123.452
113.491
77.317
77.000
76.682
42.892
29.012
26.813
22.670
N
Me
Me
N
O
Me
17
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0




**18**

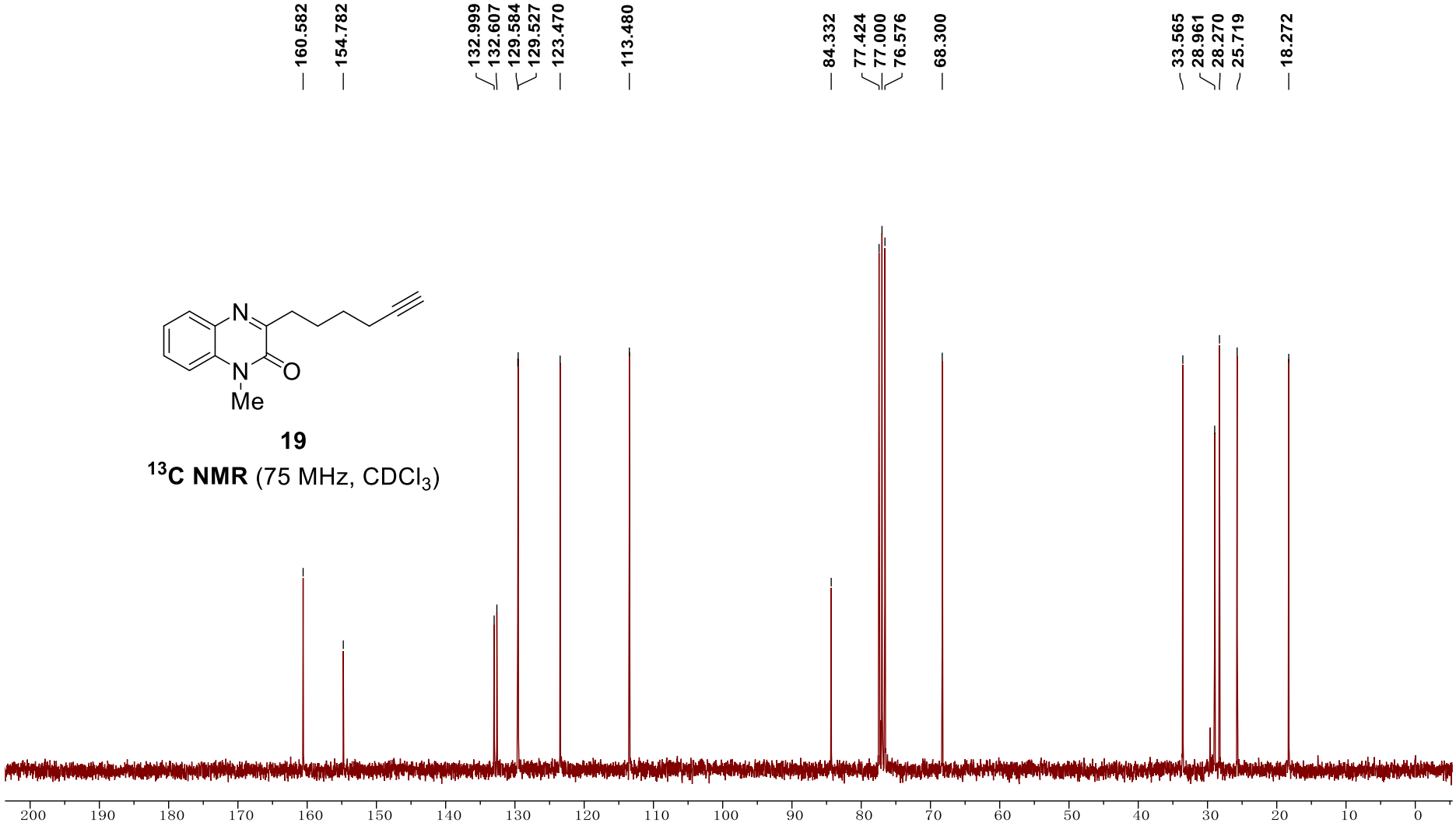
**$^1$H NMR** (400 MHz, $CDCl_3$)

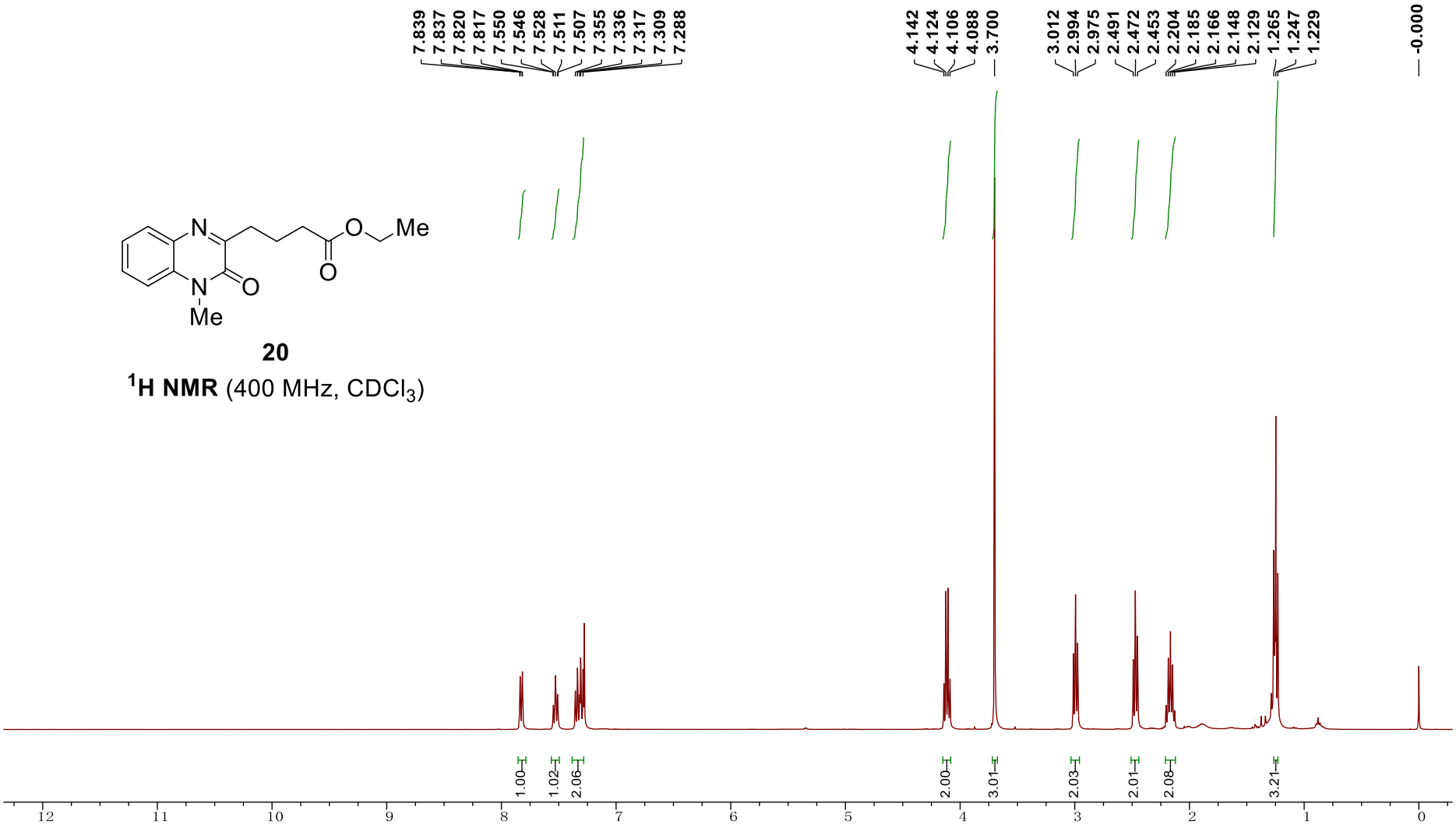

160.947
154.818
133.008
132.620
129.535
129.513
123.500
113.516
77.424
77.000
76.576
45.060
34.108
32.428
28.982
28.690
26.640
26.472
N
Cl
N
O
Me
18
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0




**19**

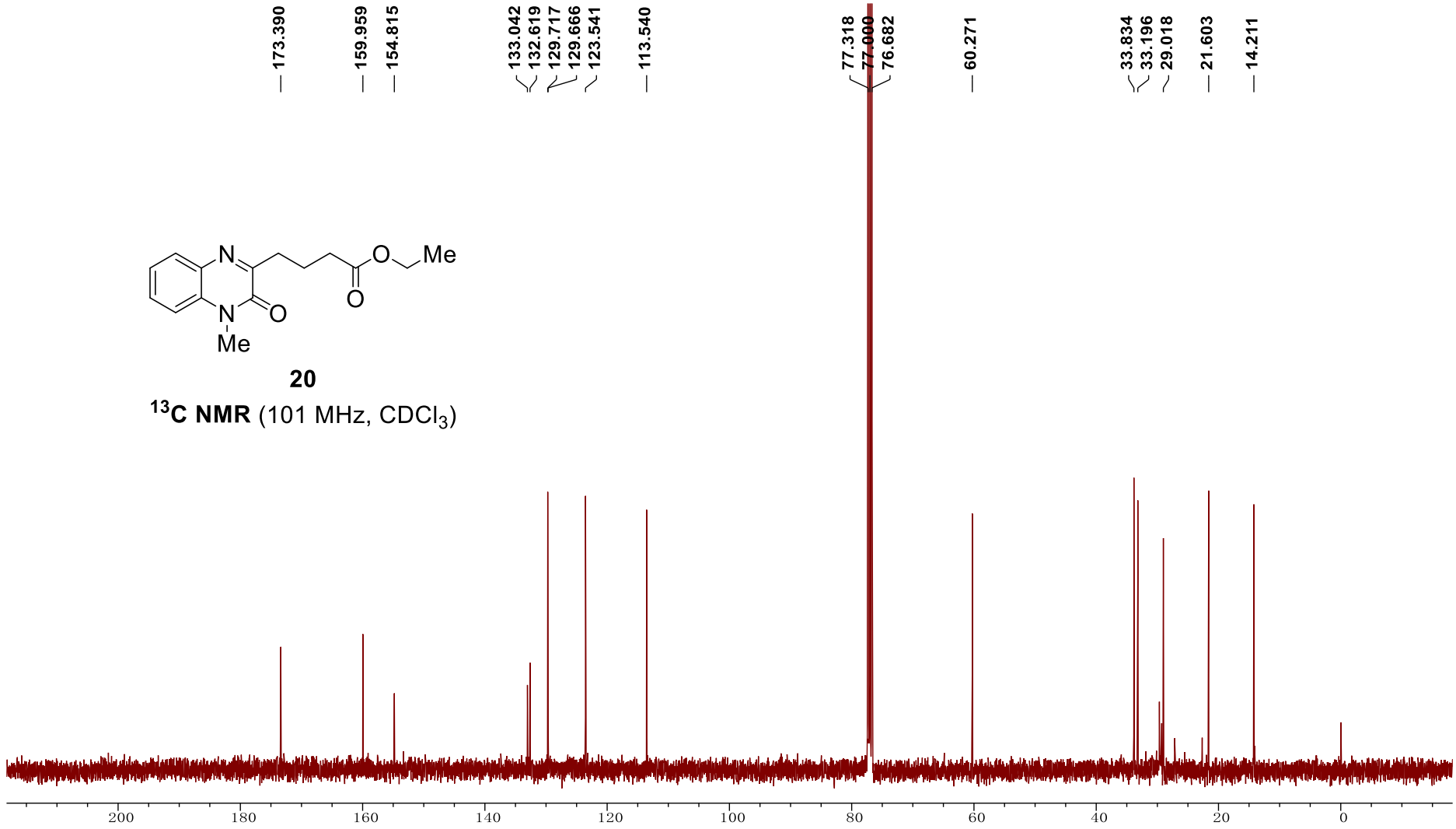
**$^1$H NMR** (300 MHz, $CDCl_3$)


160.582
154.782
132.999
132.607
129.584
129.527
123.470
113.480
84.332
77.424
77.000
76.576
68.300
33.565
28.961
28.270
25.719
18.272
N
N
O
Me
19
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



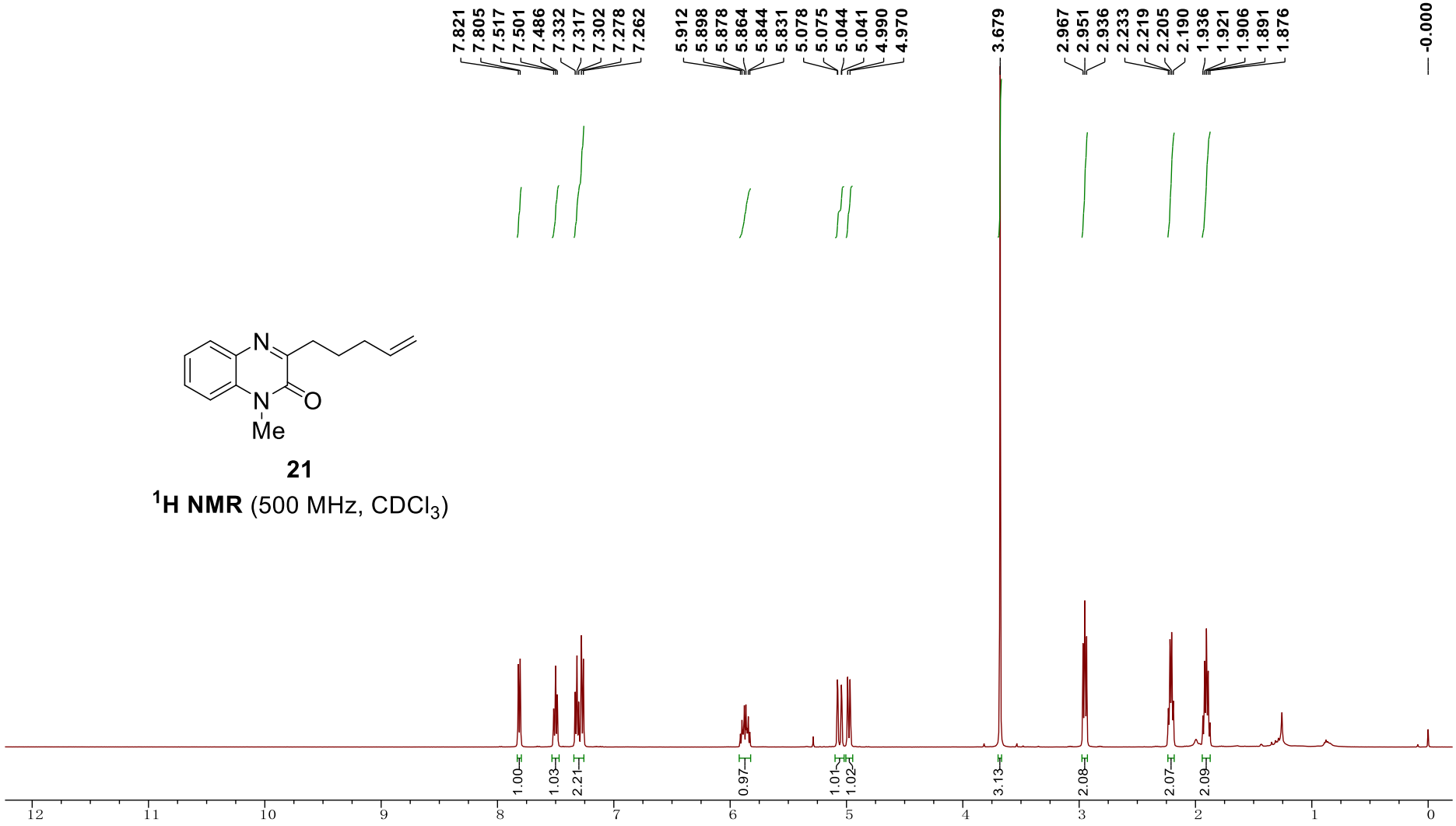

**20**

**$^1$H NMR** (400 MHz, $CDCl_3$)



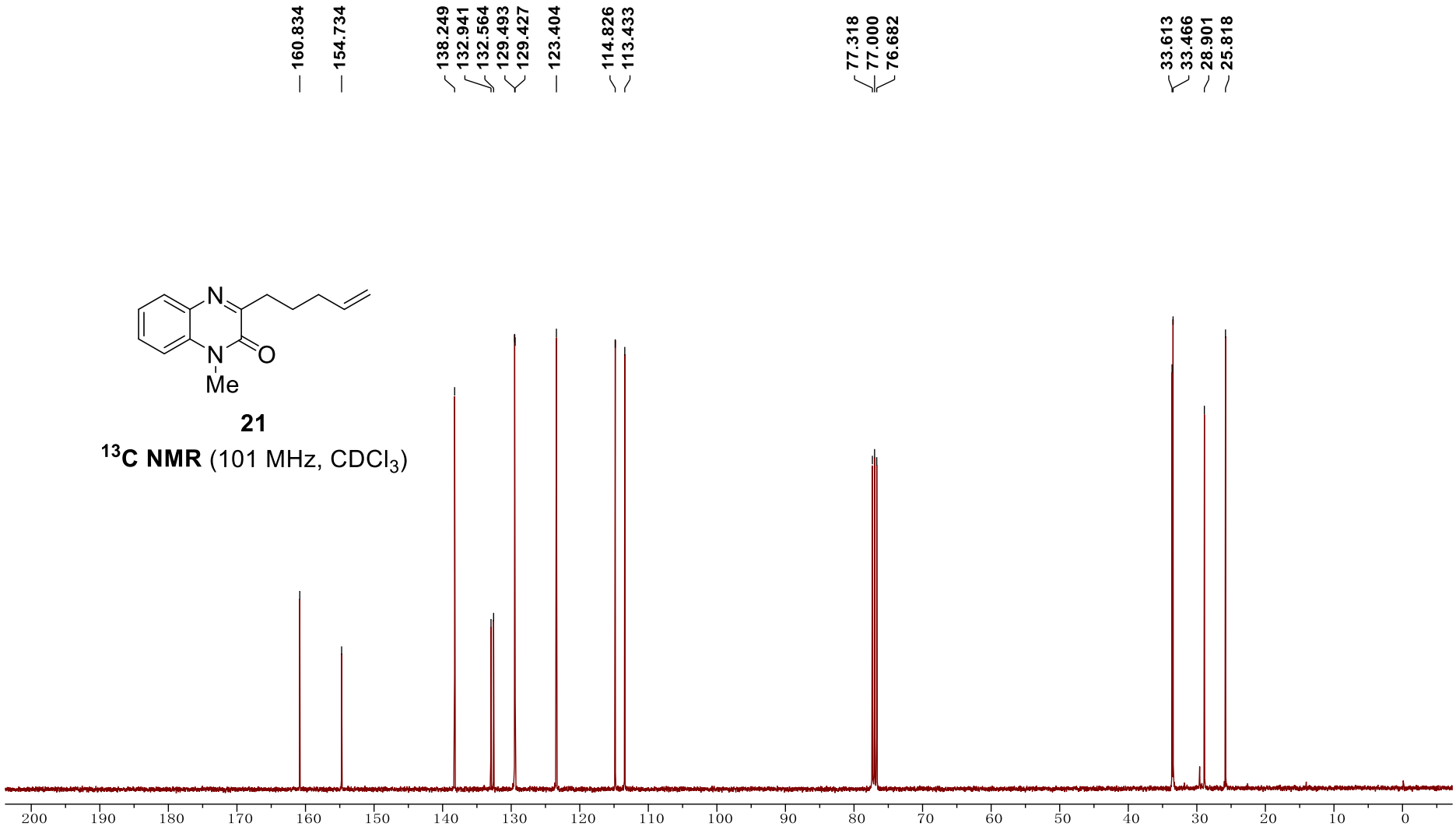

**20**

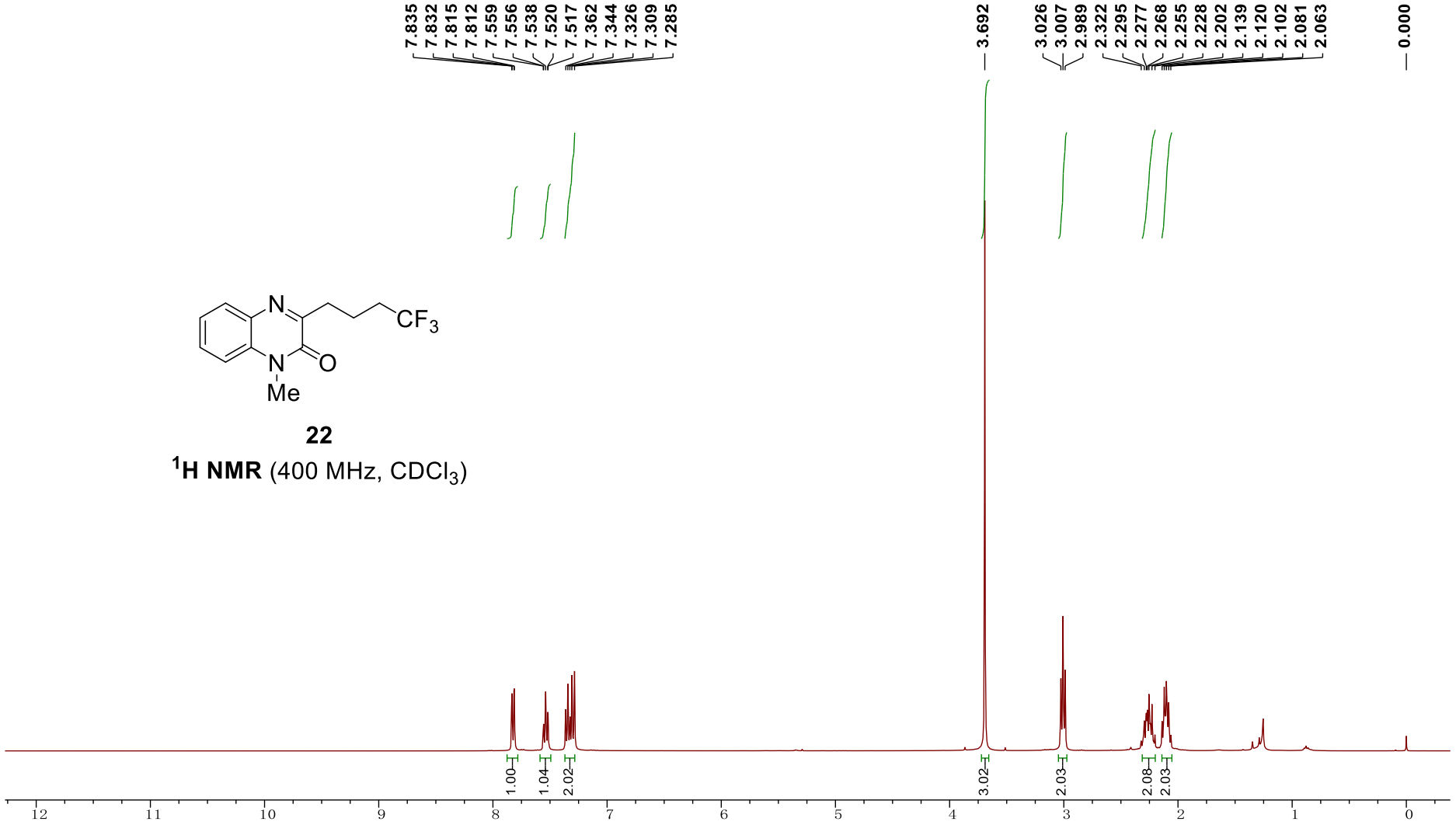
**$^{13}$C NMR** (101 MHz, $CDCl_3$)




**21**

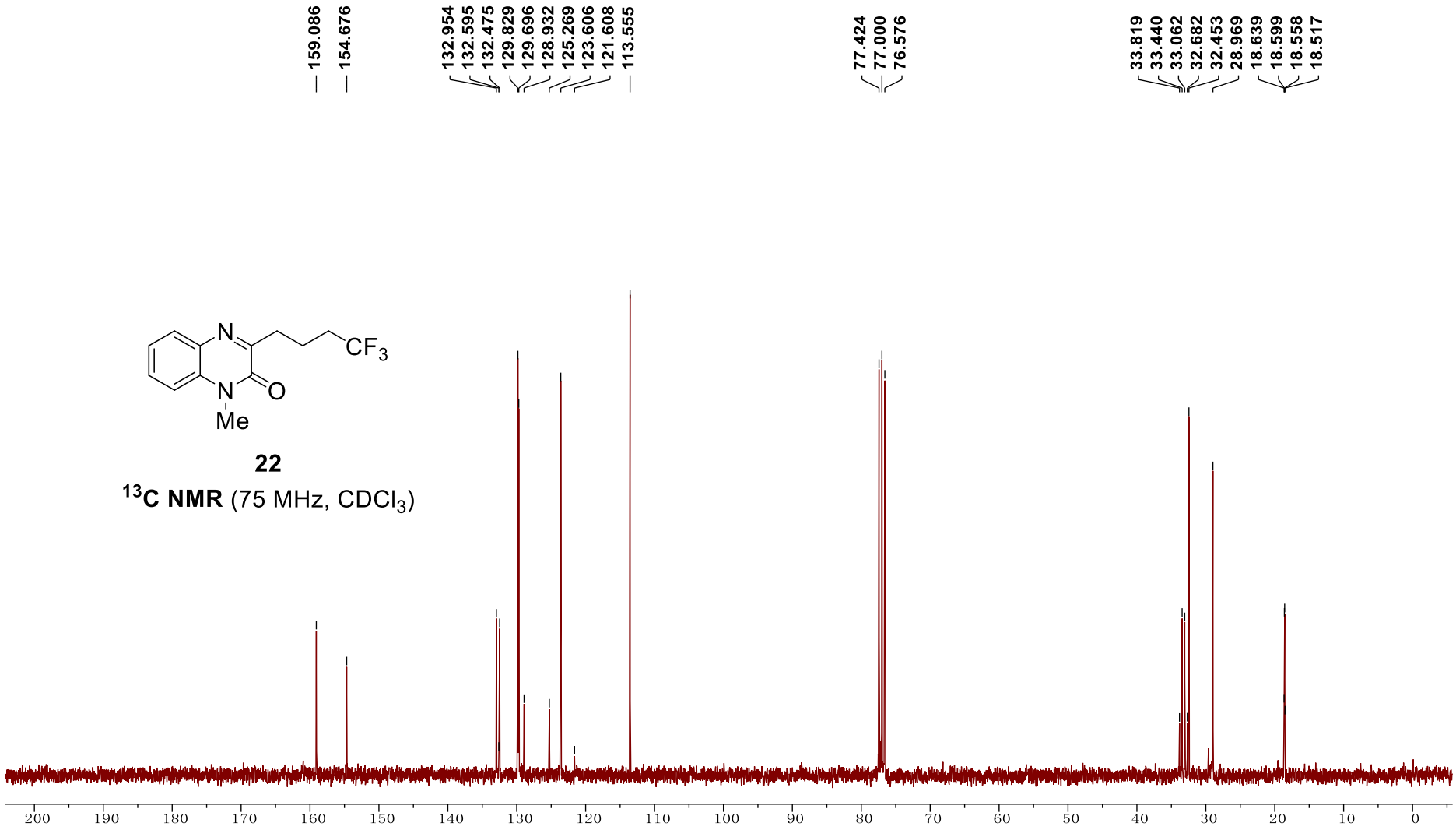
**$^1$H NMR** (500 MHz, $CDCl_3$)


160.834
154.734
138.249
132.941
132.564
129.493
129.427
123.404
114.826
113.433
77.318
77.000
76.682
33.613
33.466
28.901
25.818
N
N
O
Me
21
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



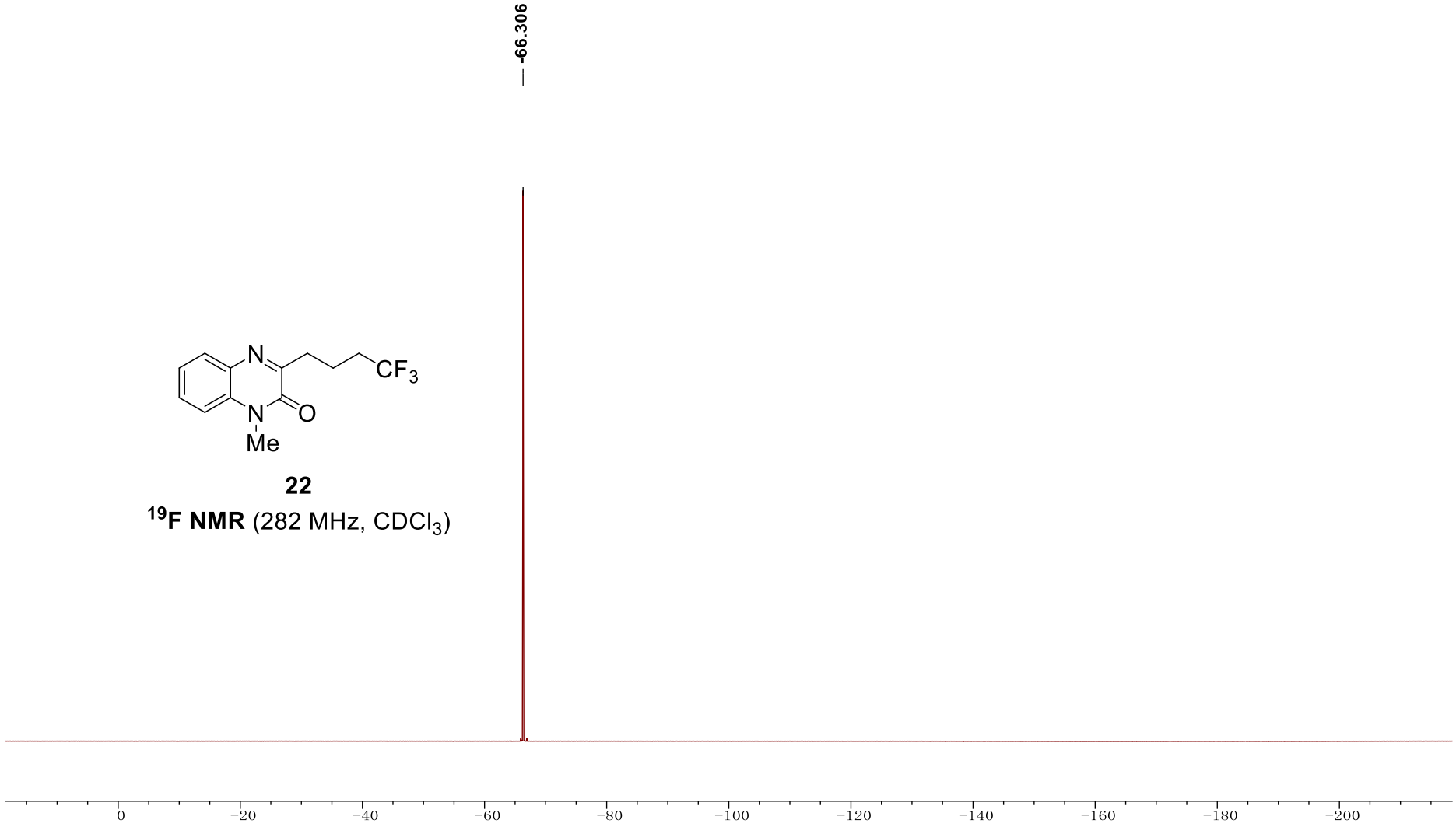

**22**

**$^1$H NMR** (400 MHz, $CDCl_3$)



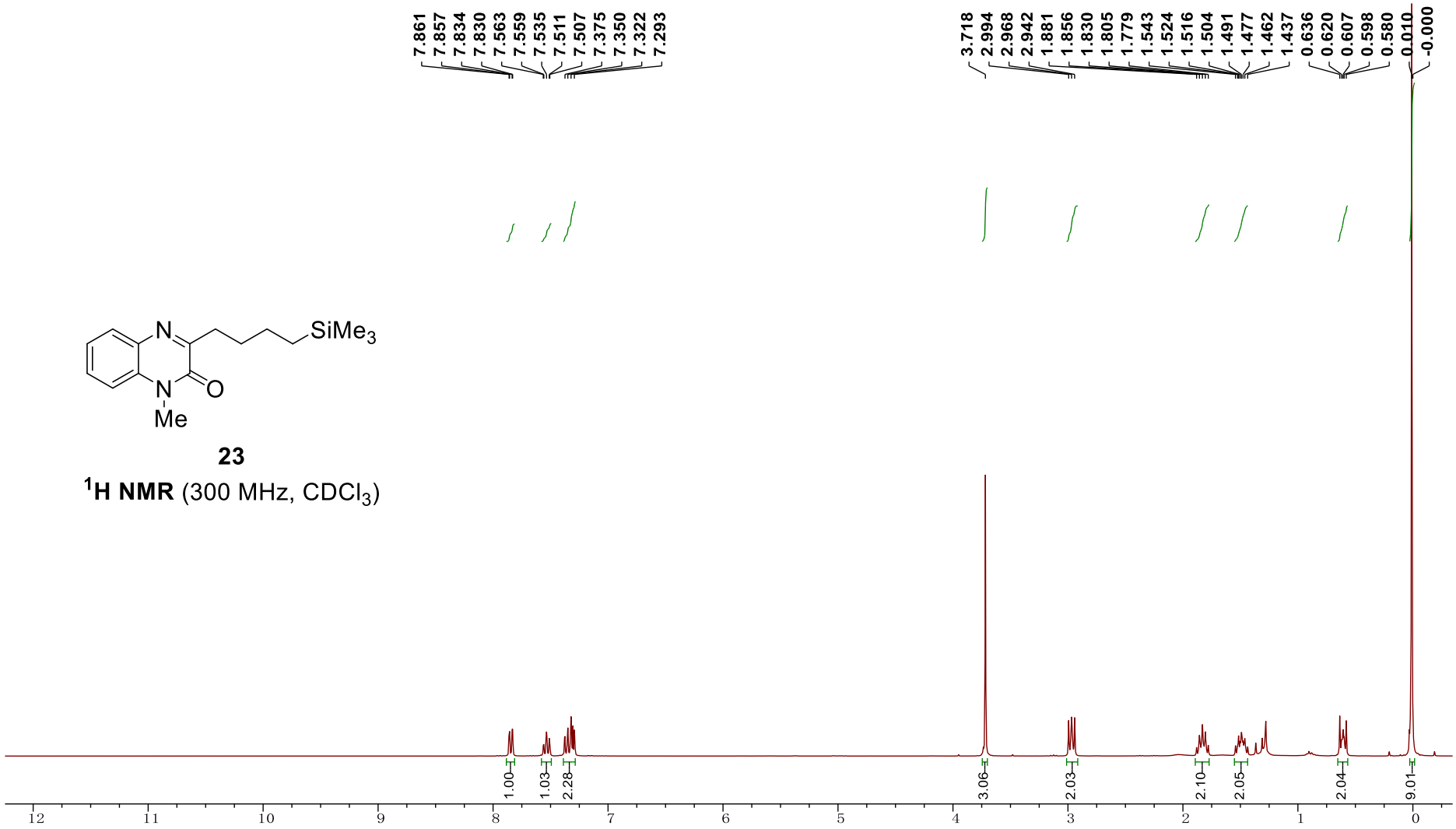

**22**

**$^{13}$C NMR** (75 MHz, $CDCl_3$)



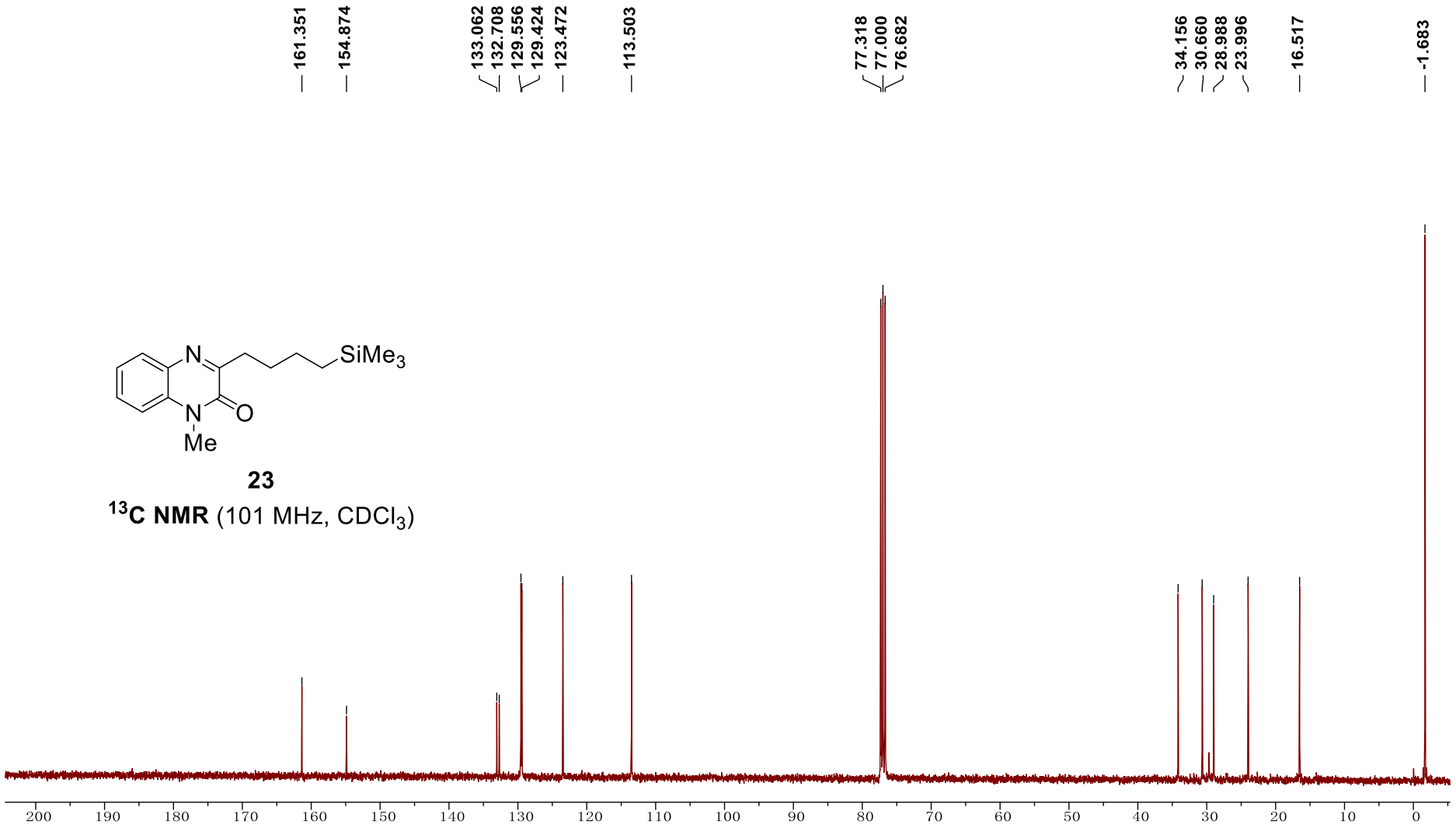

**22**

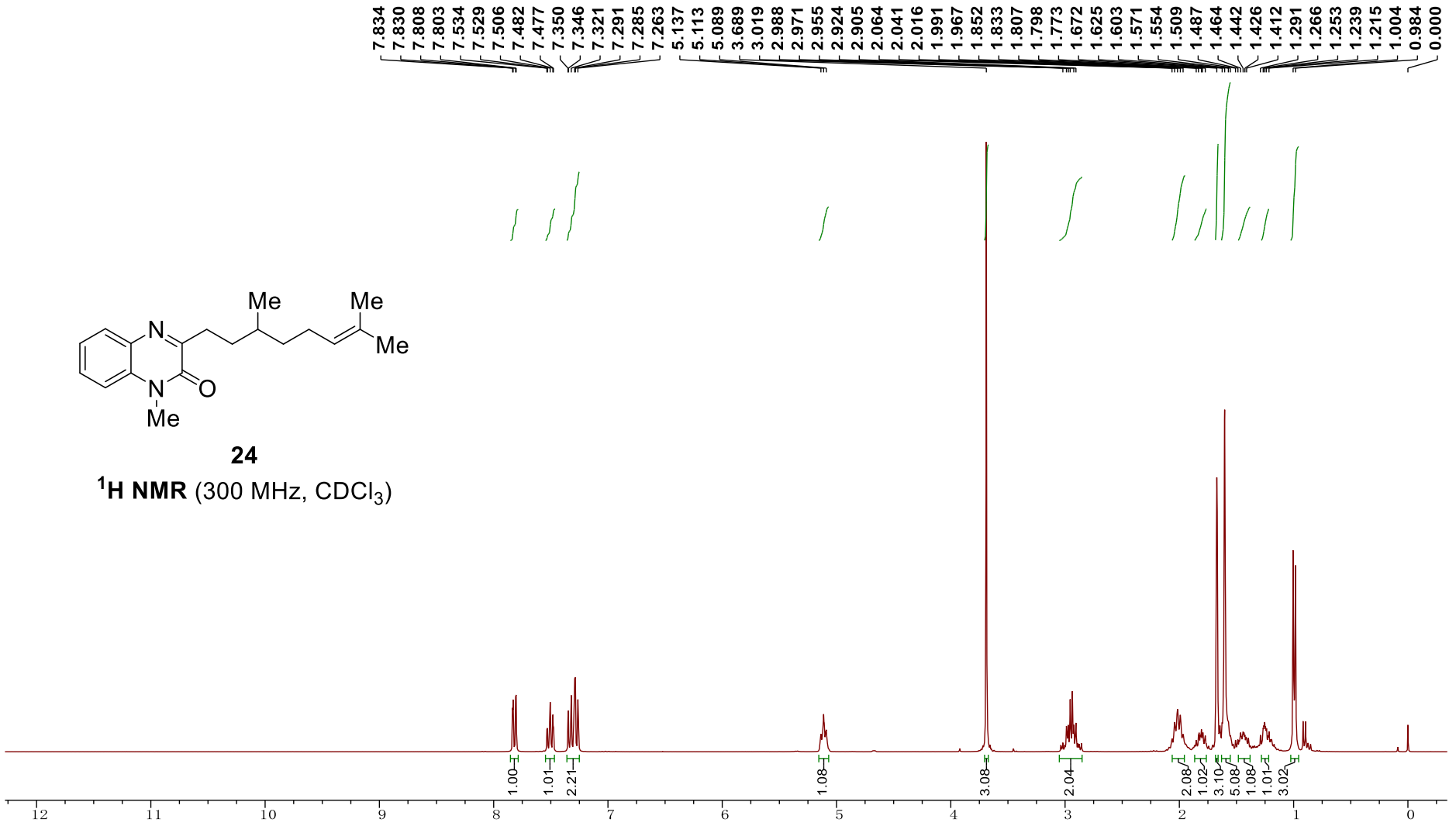
**$^{19}$F NMR** (282 MHz, $CDCl_3$)




**23**

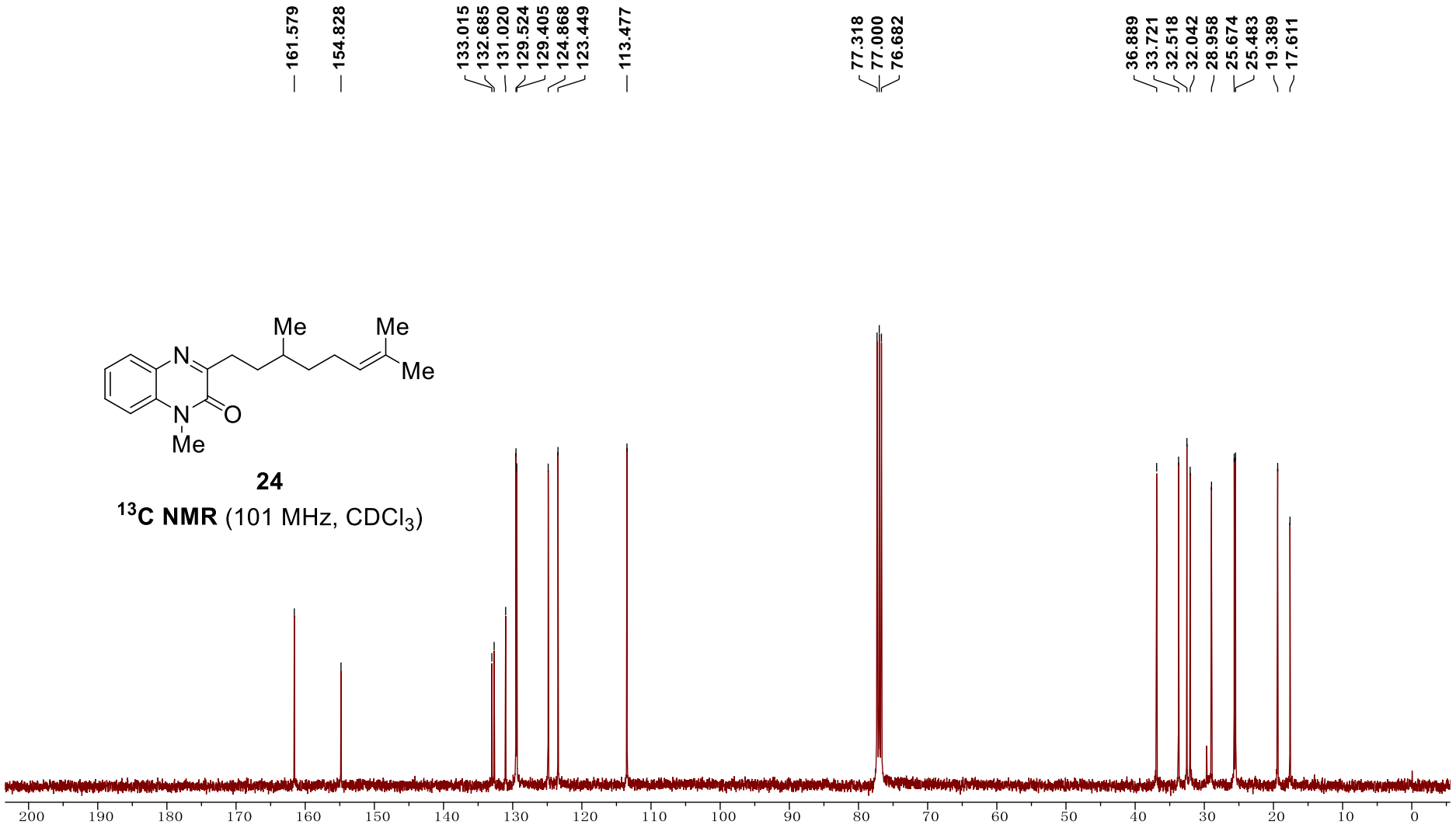
**$^1$H NMR** (300 MHz, $CDCl_3$)

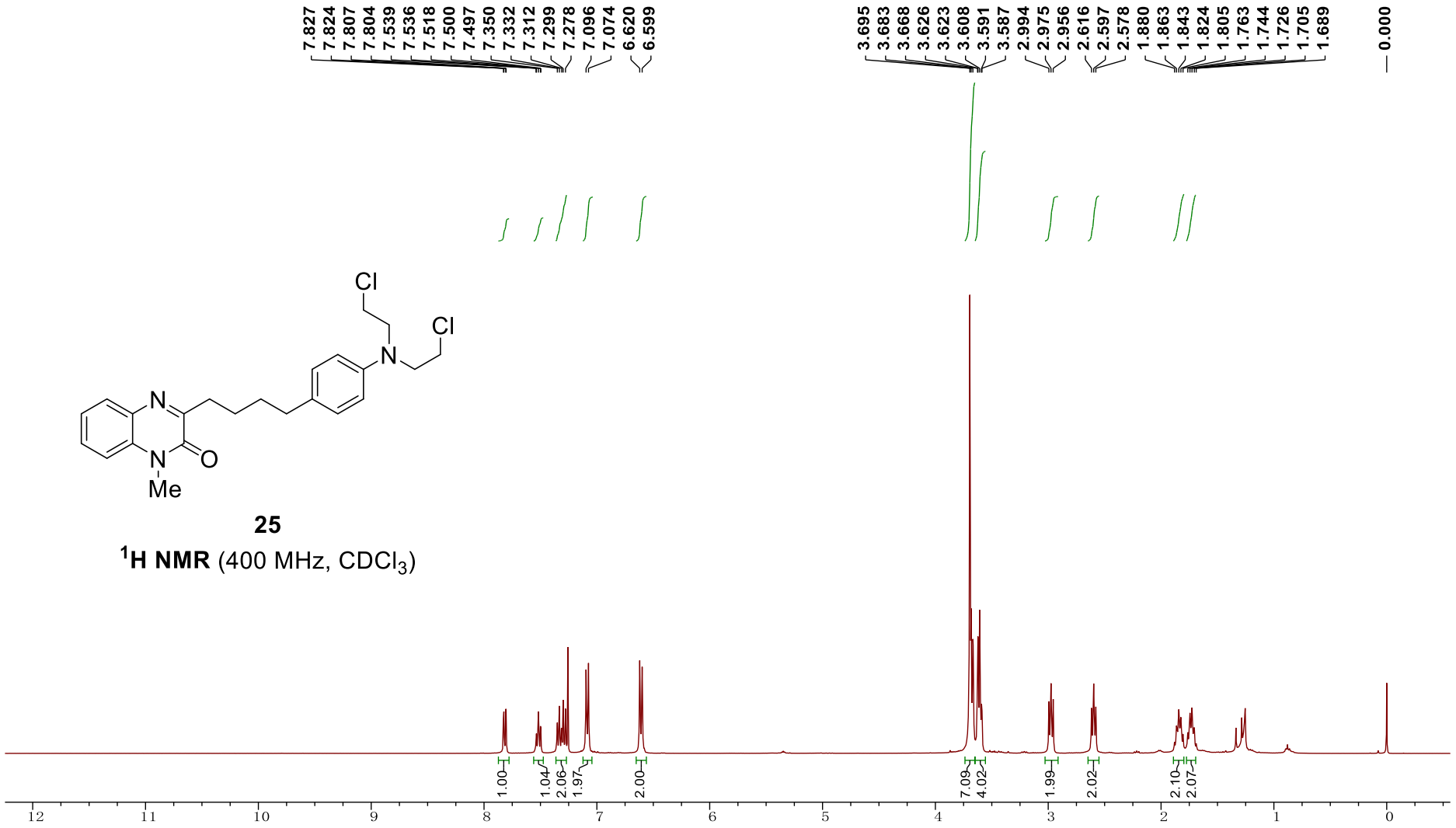

161.351
154.874
133.062
132.708
129.556
129.424
123.472
113.503
77.318
77.000
76.682
34.156
30.660
28.988
23.996
16.517
-1.683
N
SiMe3
N
O
Me
23
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0




**24**

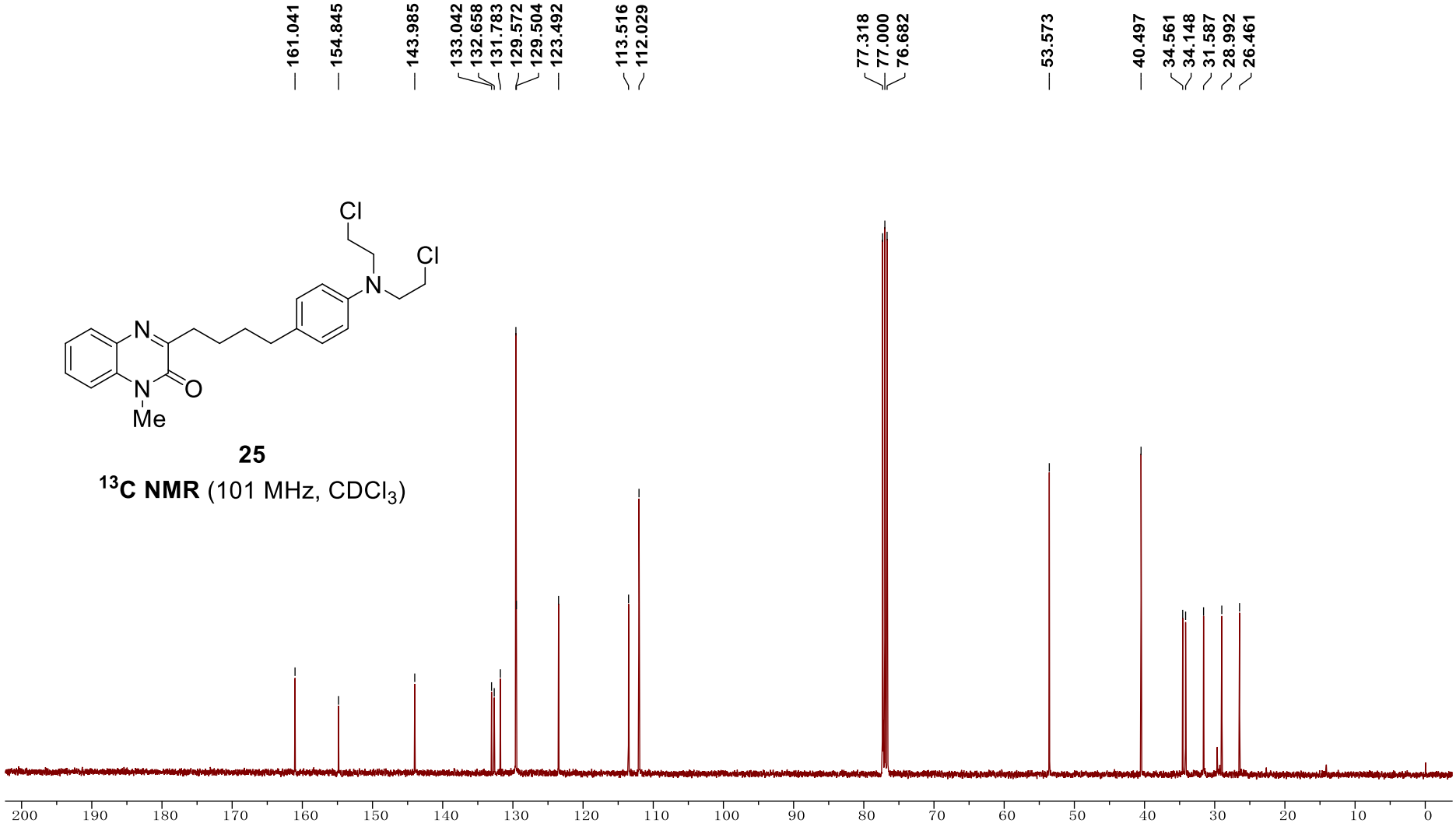
**$^1$H NMR** (300 MHz, $CDCl_3$)


161.579
154.828
133.015
132.685
131.020
129.524
129.405
124.868
123.449
113.477
77.318
77.000
76.682
36.889
33.721
32.518
32.042
28.958
25.674
25.483
19.389
17.611
Me
Me
Me
N
N
O
Me
24
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



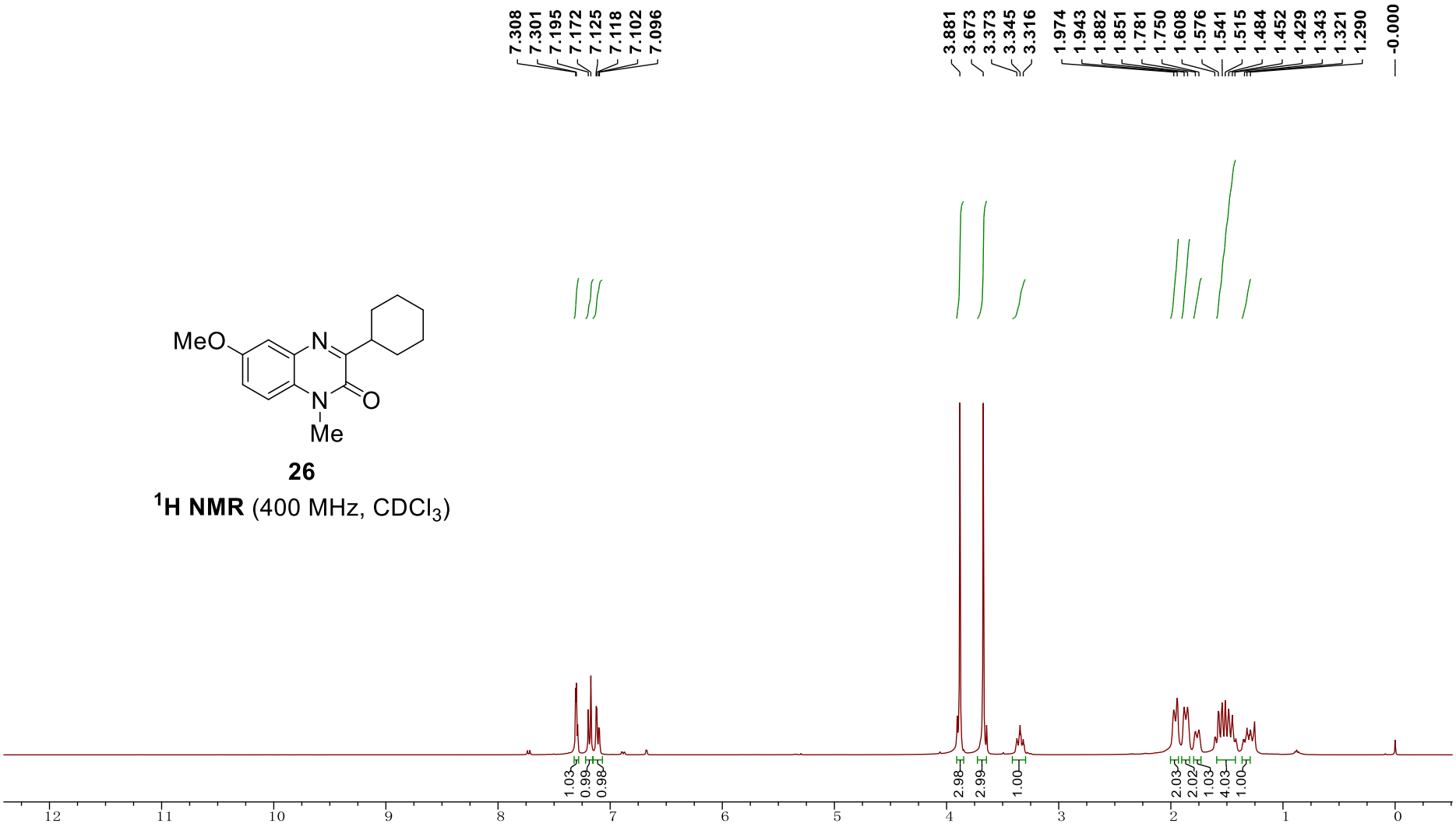

**25**

**$^1$H NMR** (400 MHz, $CDCl_3$)



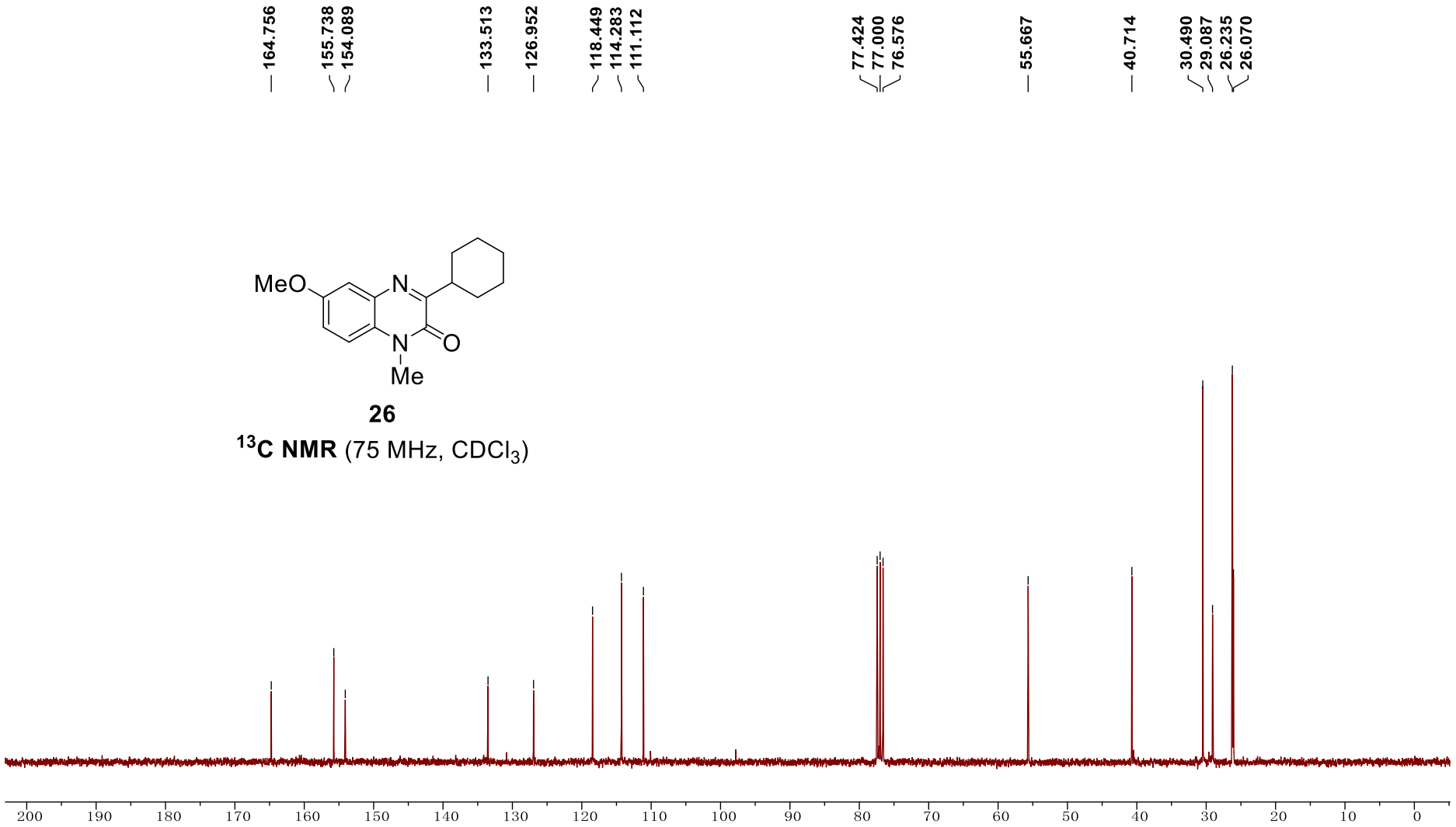

**25**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



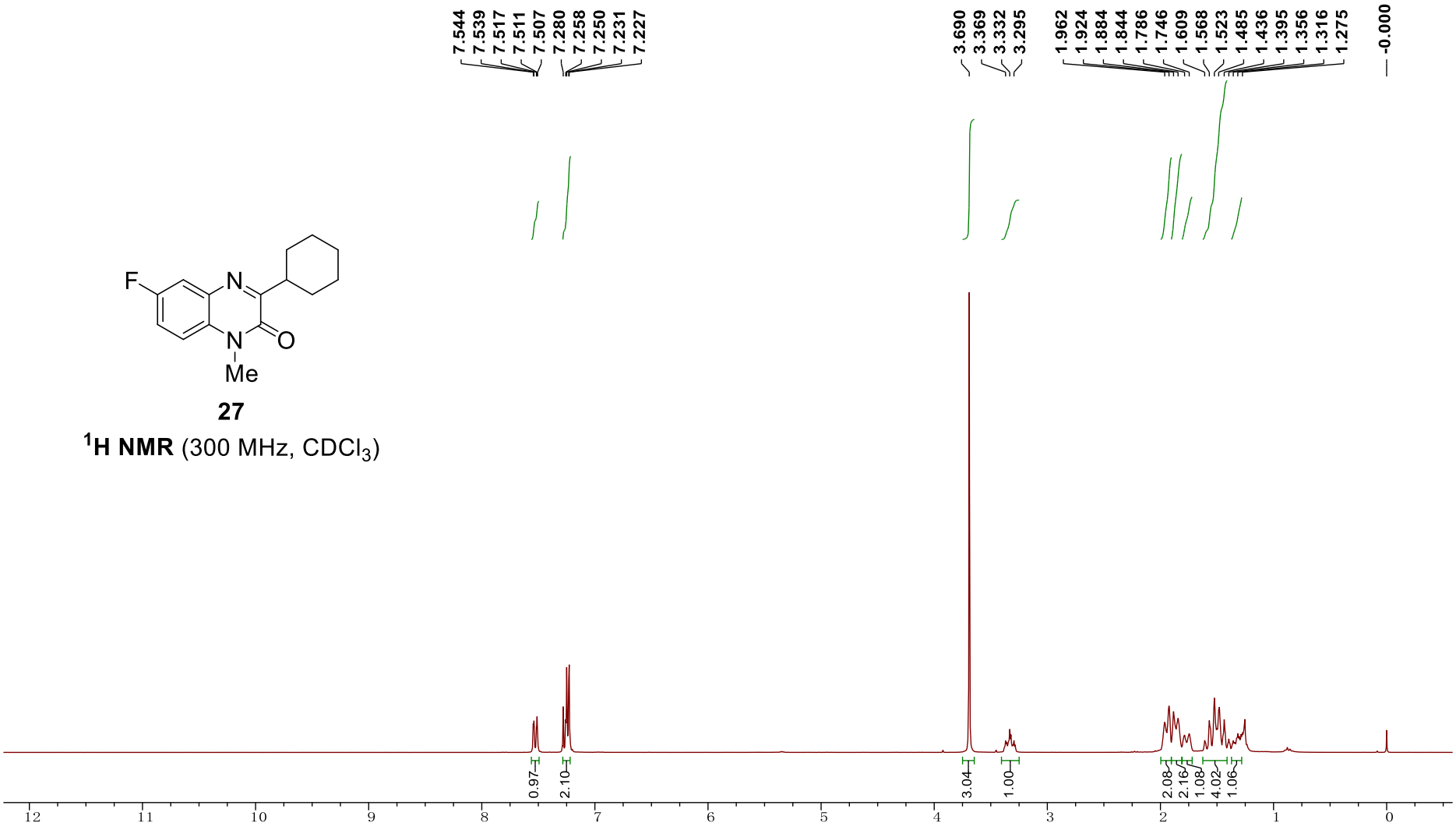

**26**

**$^1$H NMR** (400 MHz, $CDCl_3$)



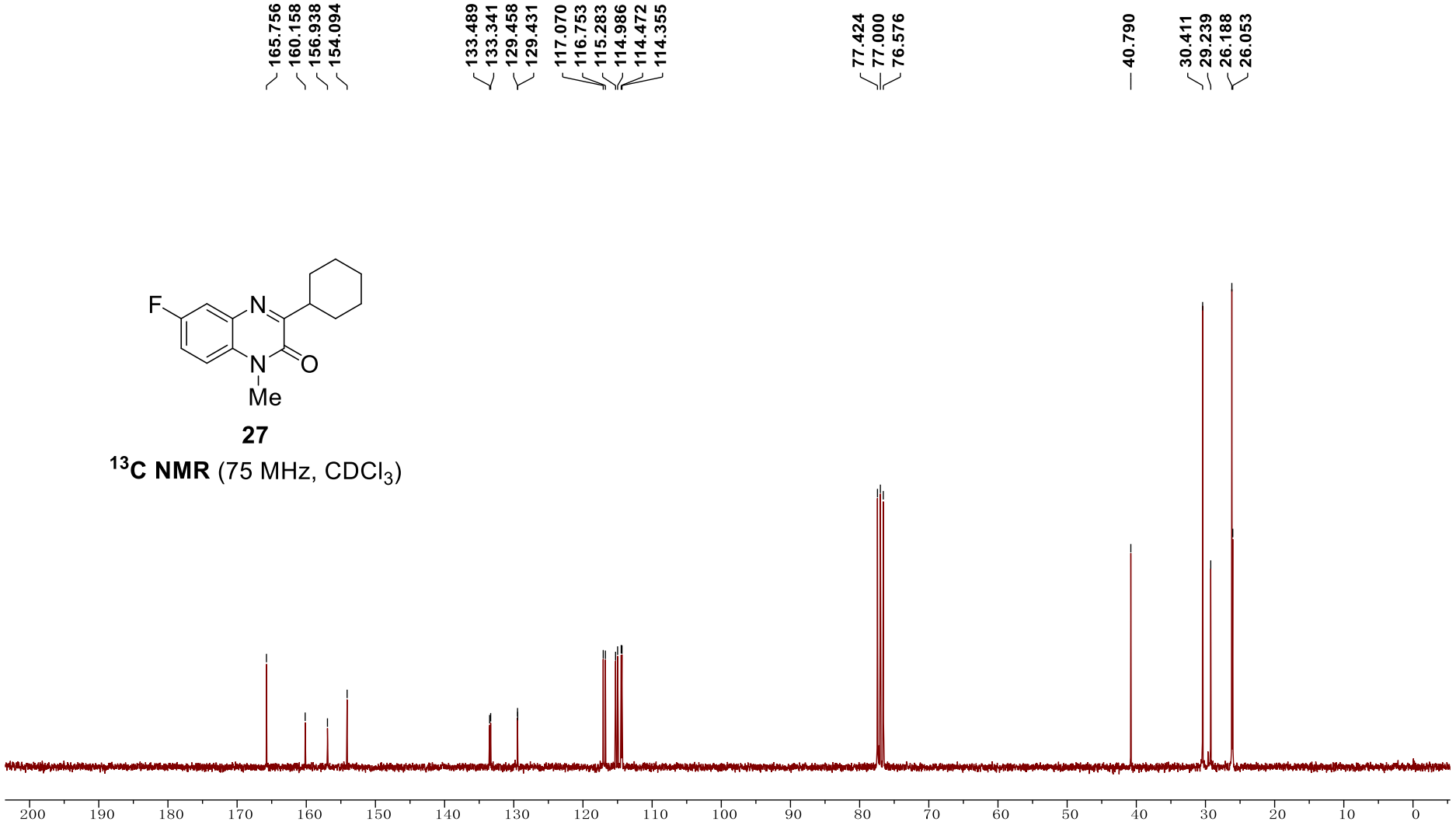

**26**

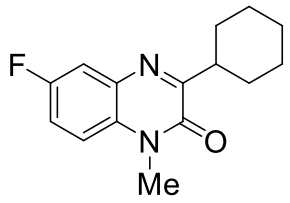
**$^{13}$C NMR** (75 MHz, $CDCl_3$)




**27**

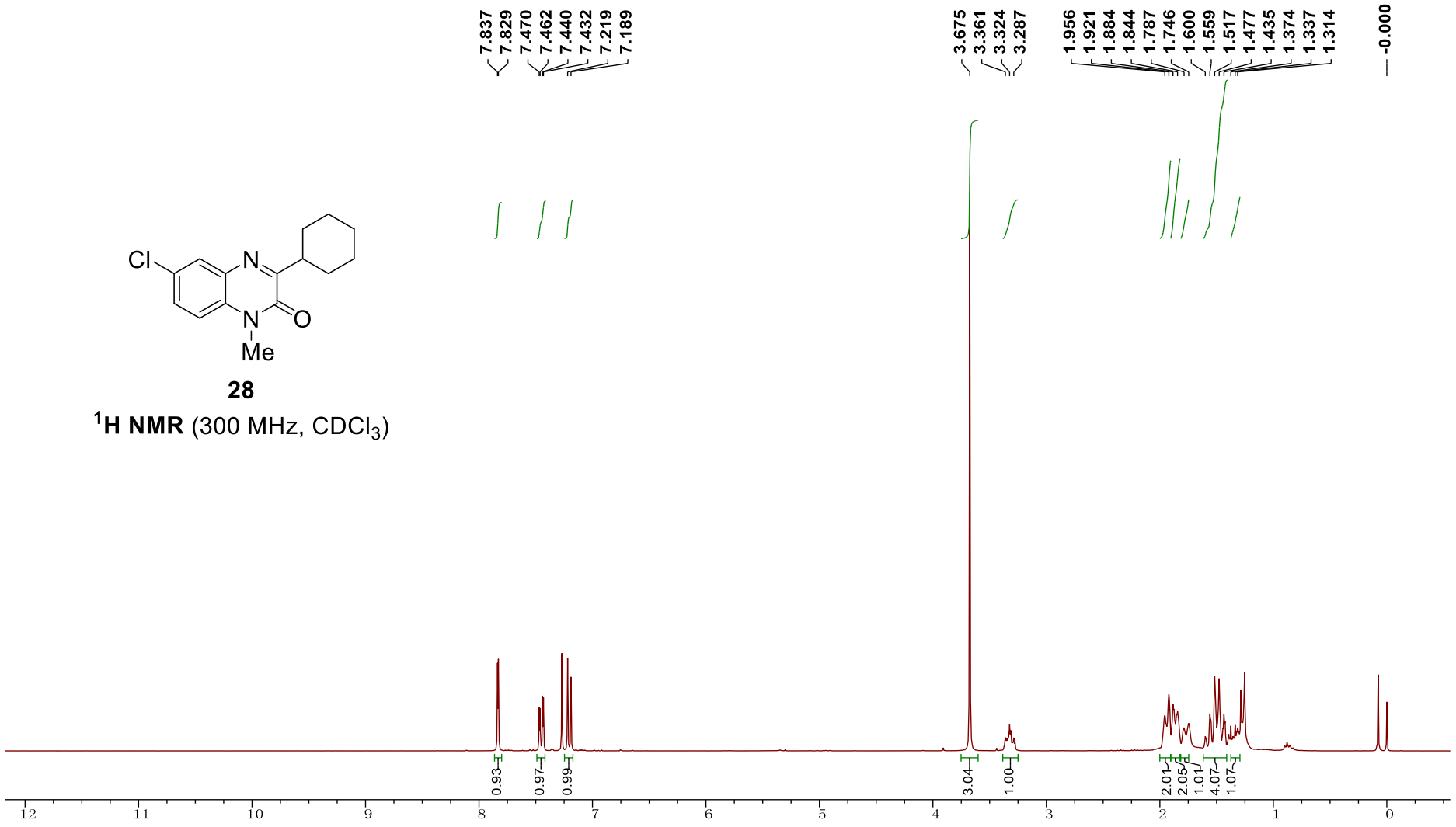
**$^1$H NMR** (300 MHz, $CDCl_3$)


165.756
160.158
156.938
154.094
133.489
133.341
129.458
129.431
117.070
116.753
115.283
114.986
114.472
114.355
77.424
77.000
76.576
40.790
30.411
29.239
26.188
26.053
F
N
N
O
Me
27
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



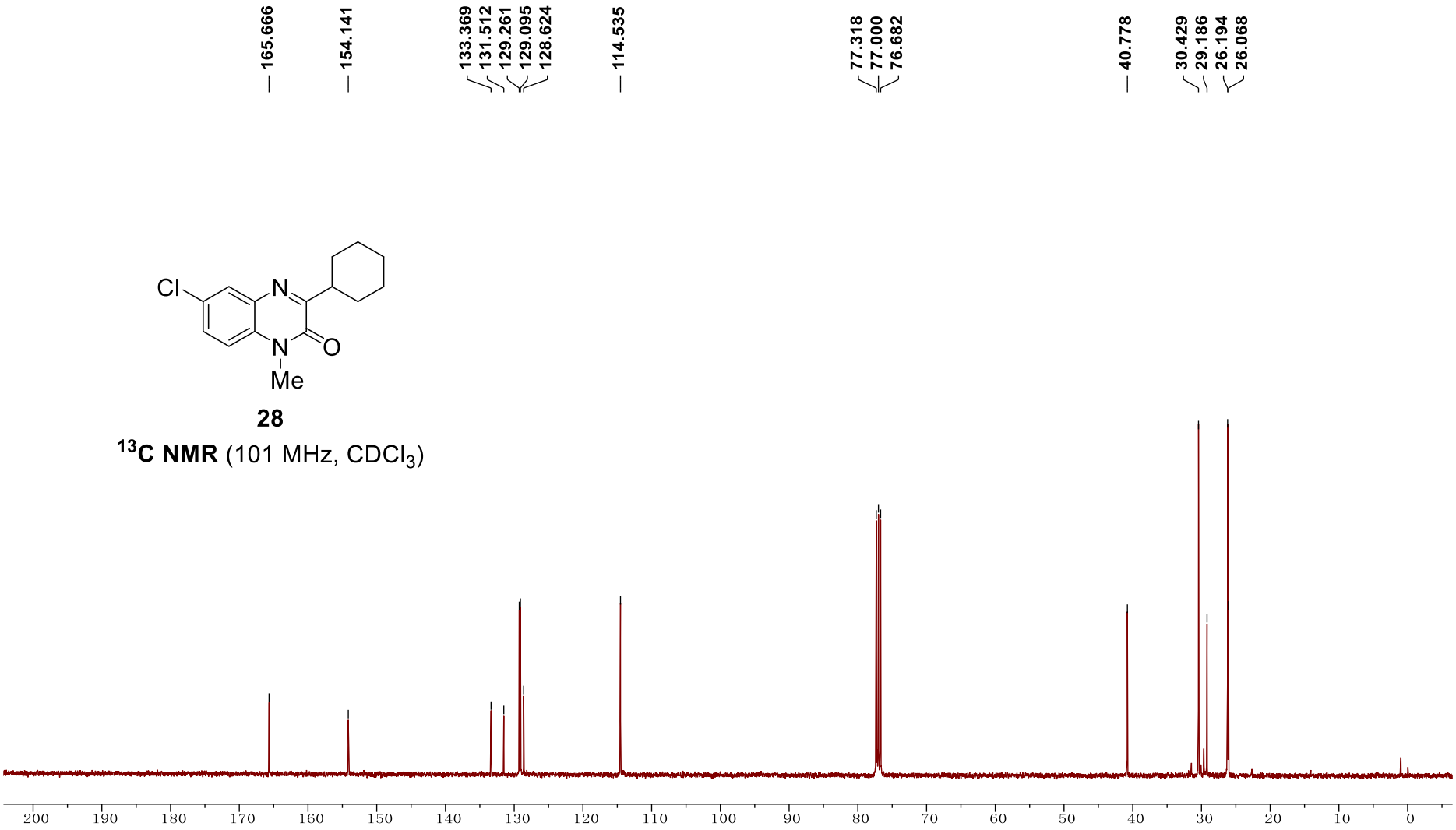

**27**

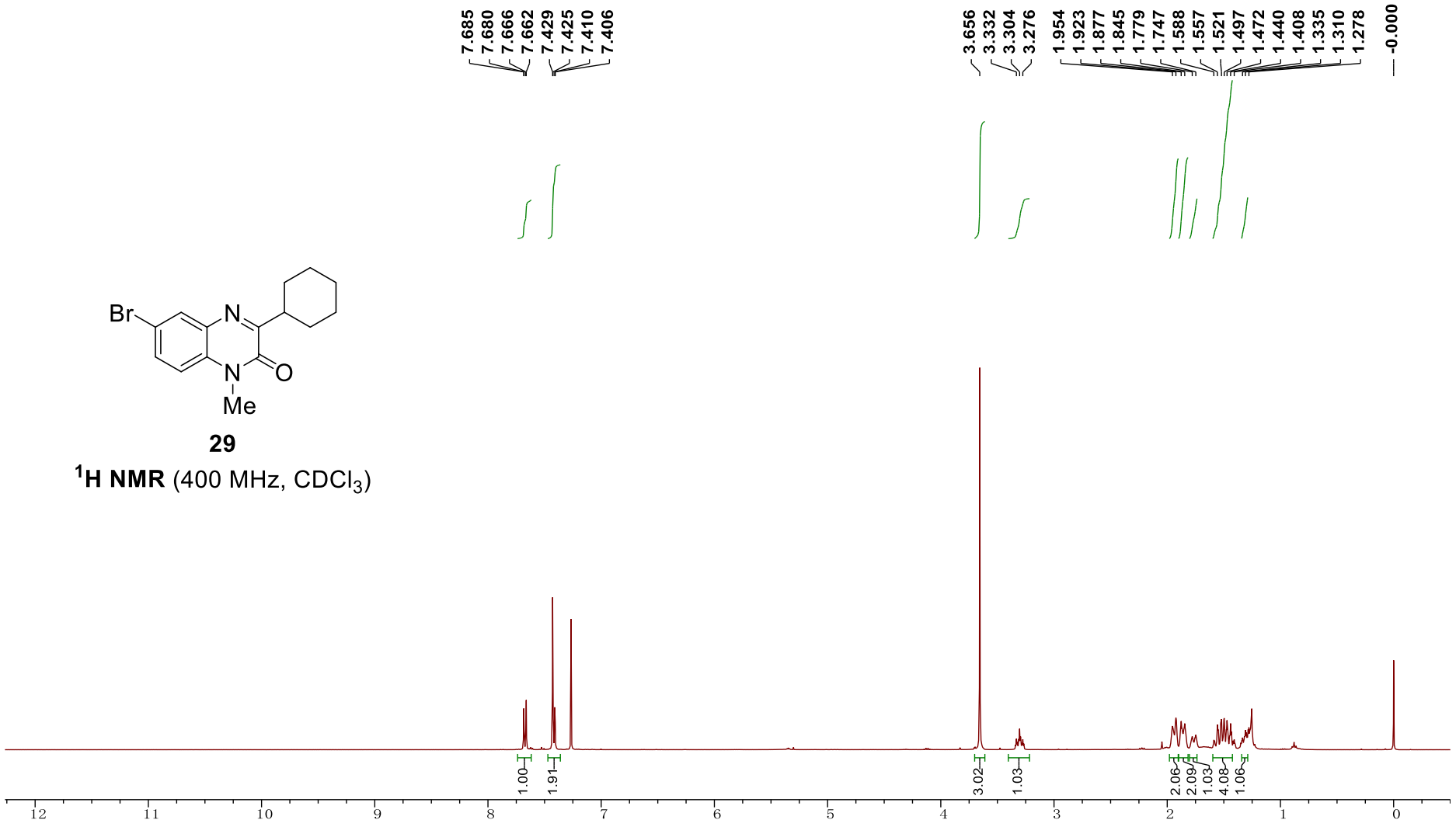
**$^{19}$F NMR** (282 MHz, $CDCl_3$)




**28**

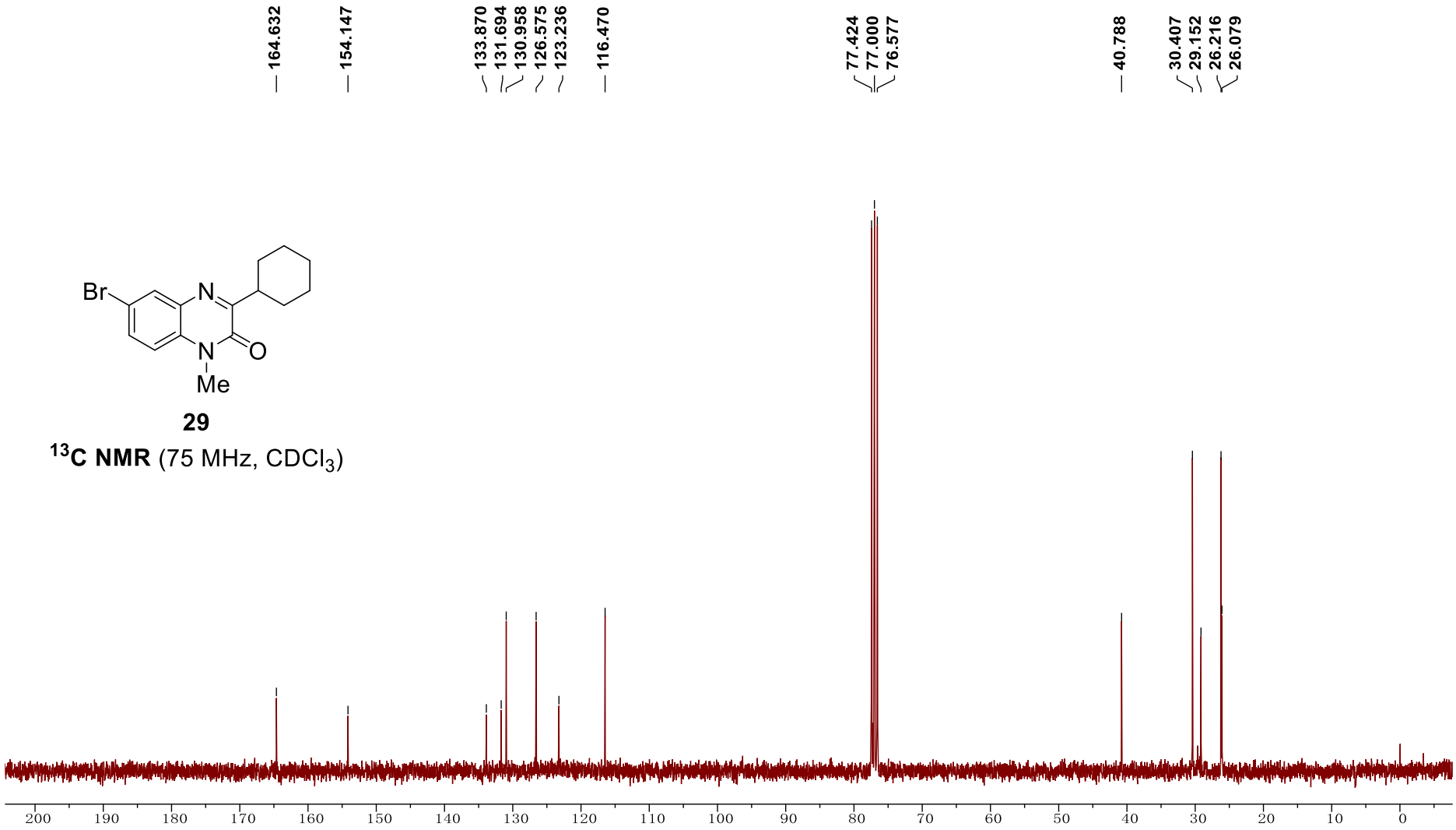
**$^1$H NMR** (300 MHz, $CDCl_3$)


165.666
154.141
133.369
131.512
129.261
129.095
128.624
114.535
77.318
77.000
76.682
40.778
30.429
29.186
26.194
26.068
Cl
N
N
O
Me
28
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



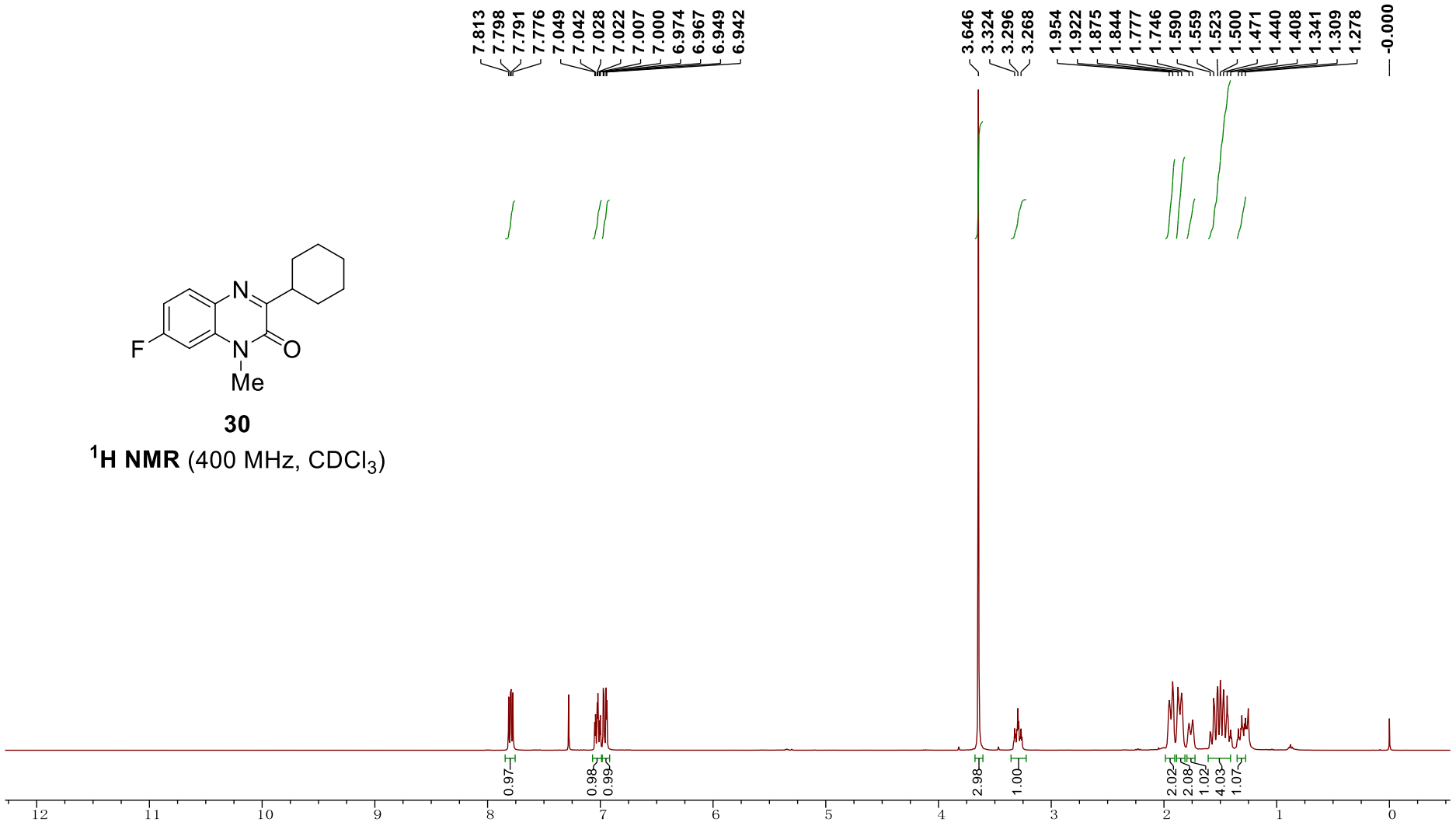

**29**

**$^1$H NMR** (400 MHz, $CDCl_3$)



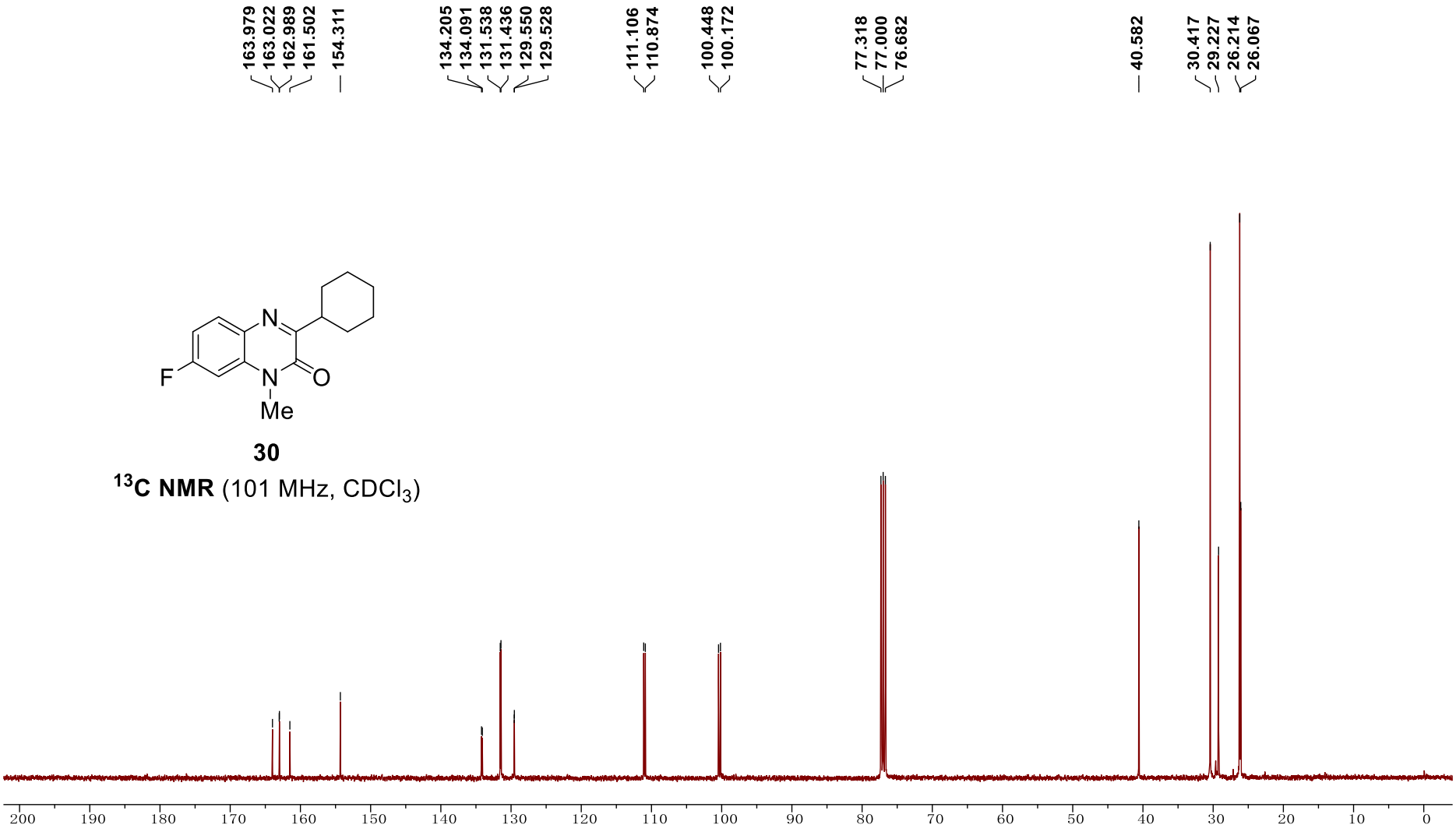

**29**

**$^{13}$C NMR** (75 MHz, $CDCl_3$)



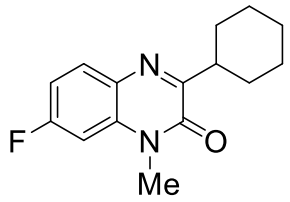

**30**

**$^1$H NMR** (400 MHz, $CDCl_3$)



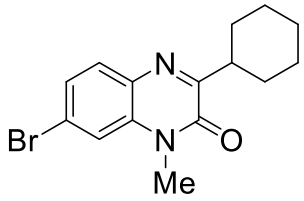

**30**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



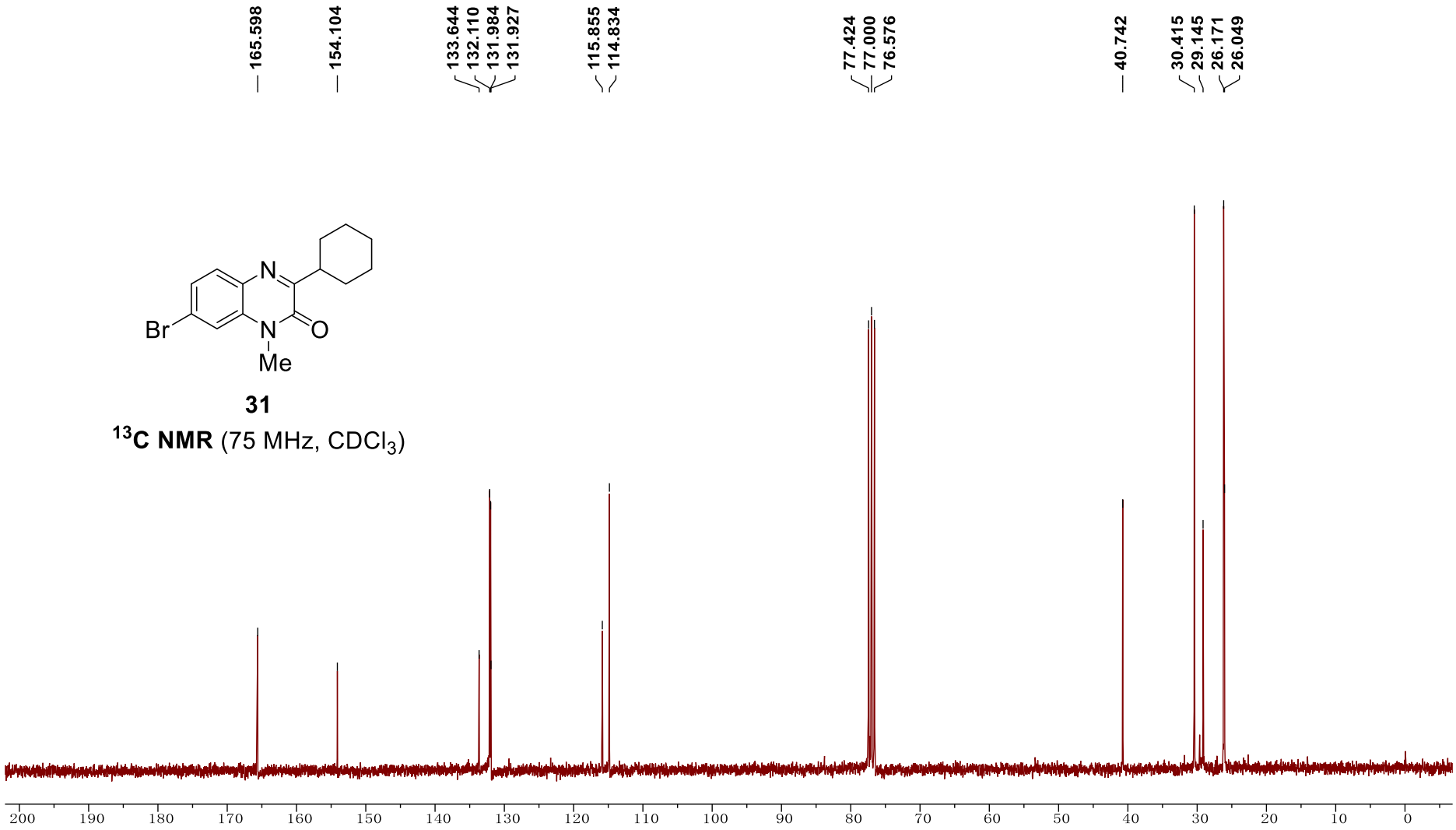

**30**

**$^{19}$F NMR** (376 MHz, $CDCl_3$)



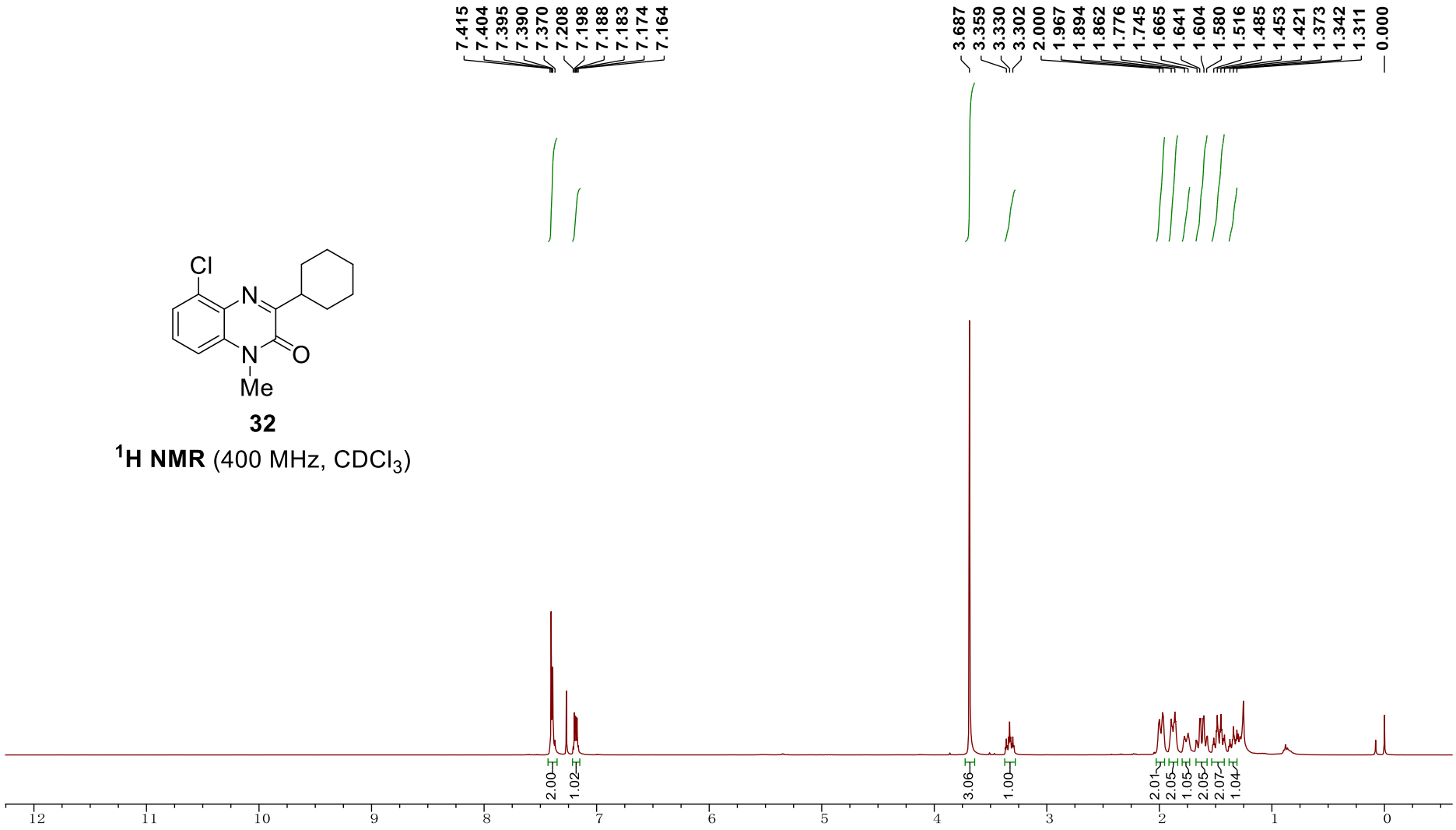

**31**

**$^1$H NMR** (400 MHz, $CDCl_3$)



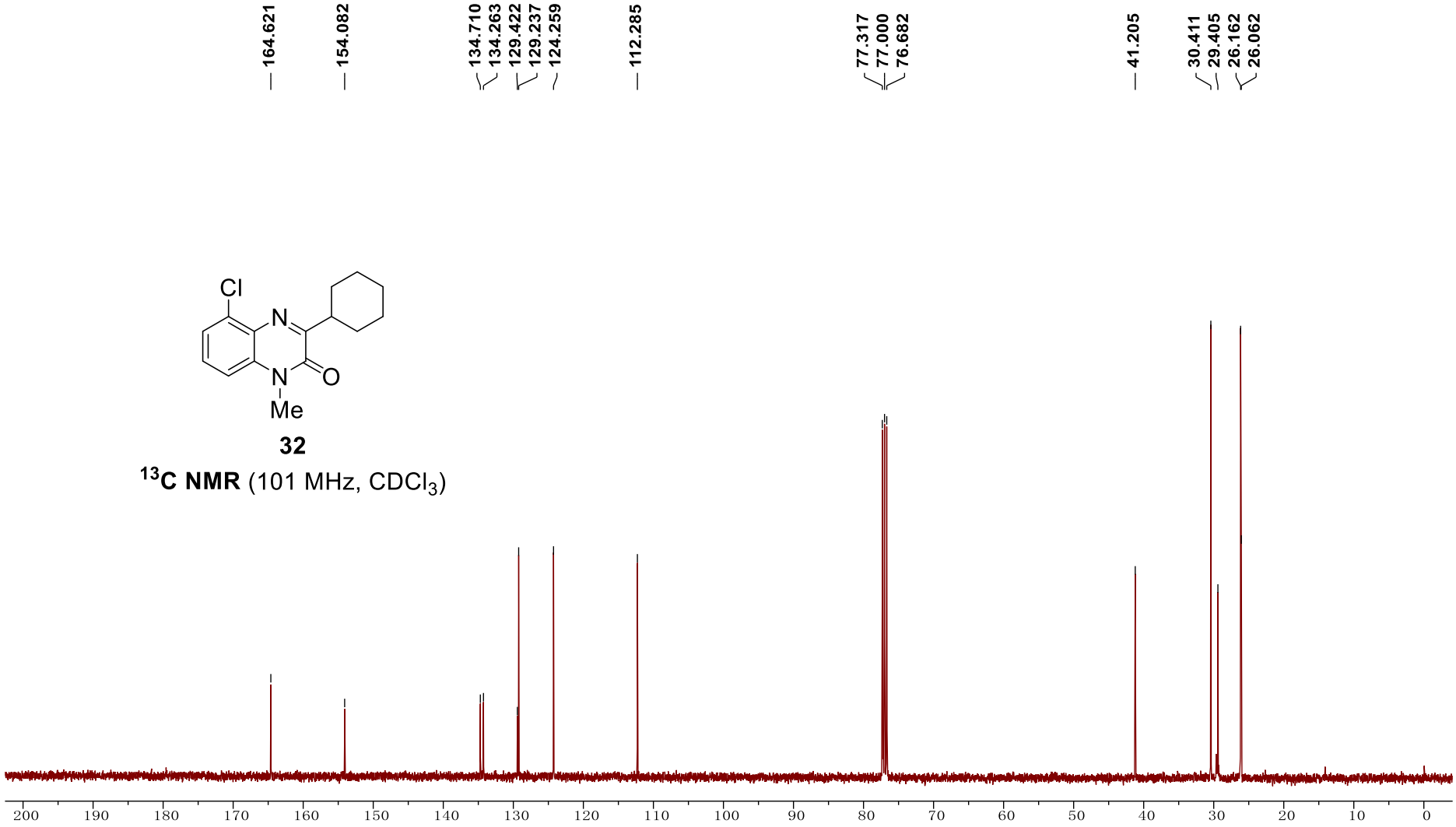

**31**

**$^{13}$C NMR** (75 MHz, $CDCl_3$)



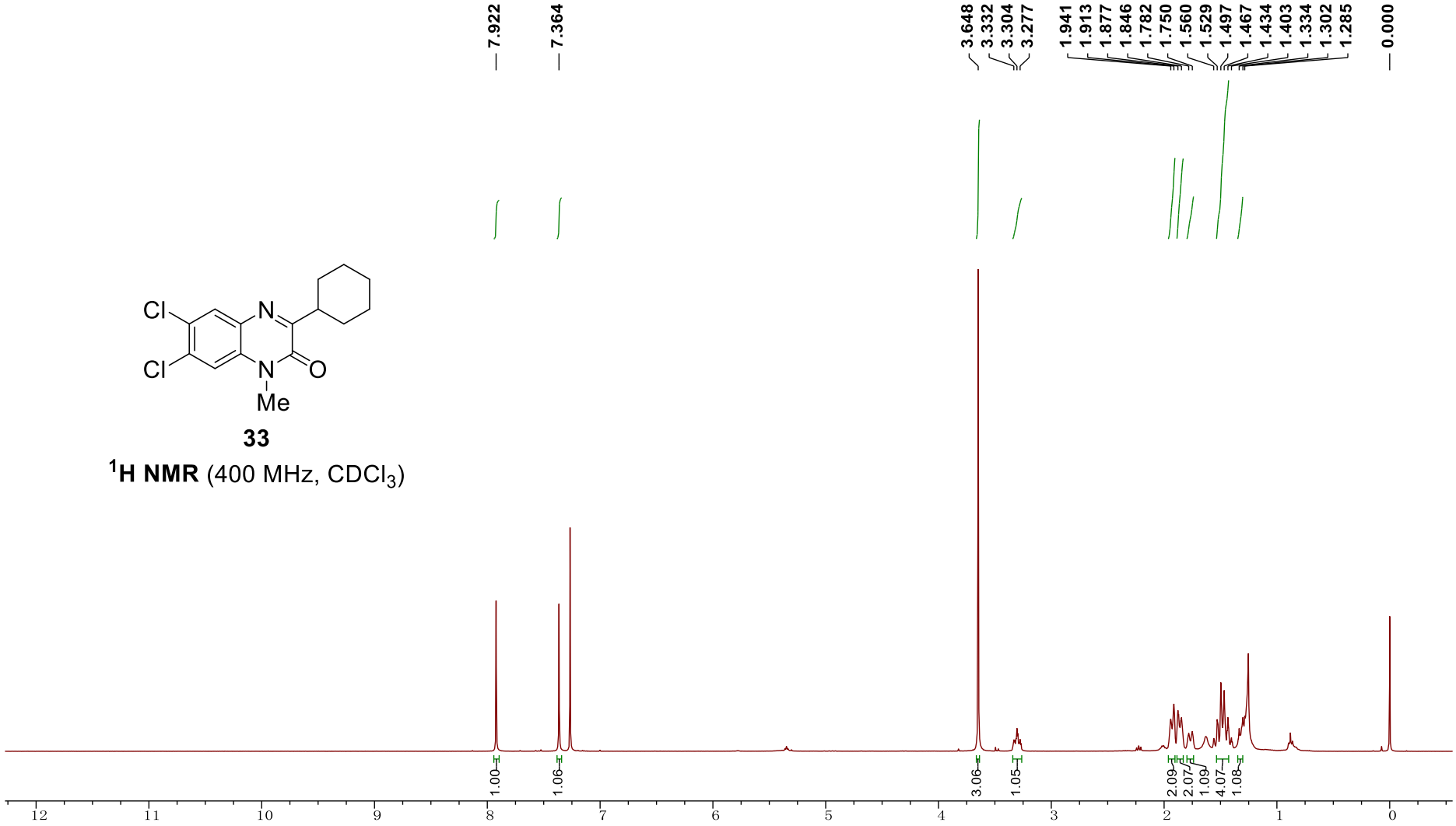

**32**

**$^1$H NMR** (400 MHz, $CDCl_3$)



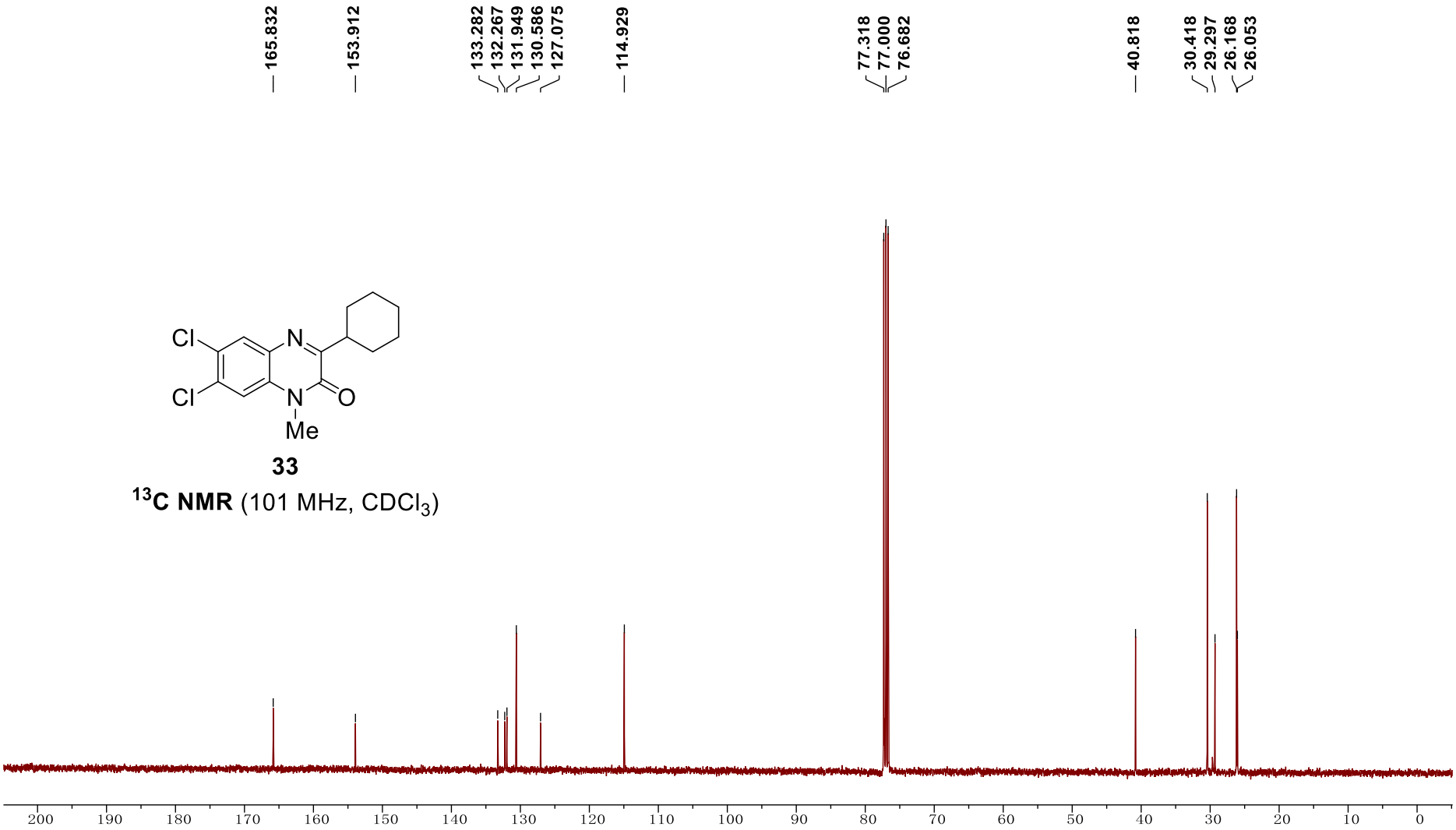

**32**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



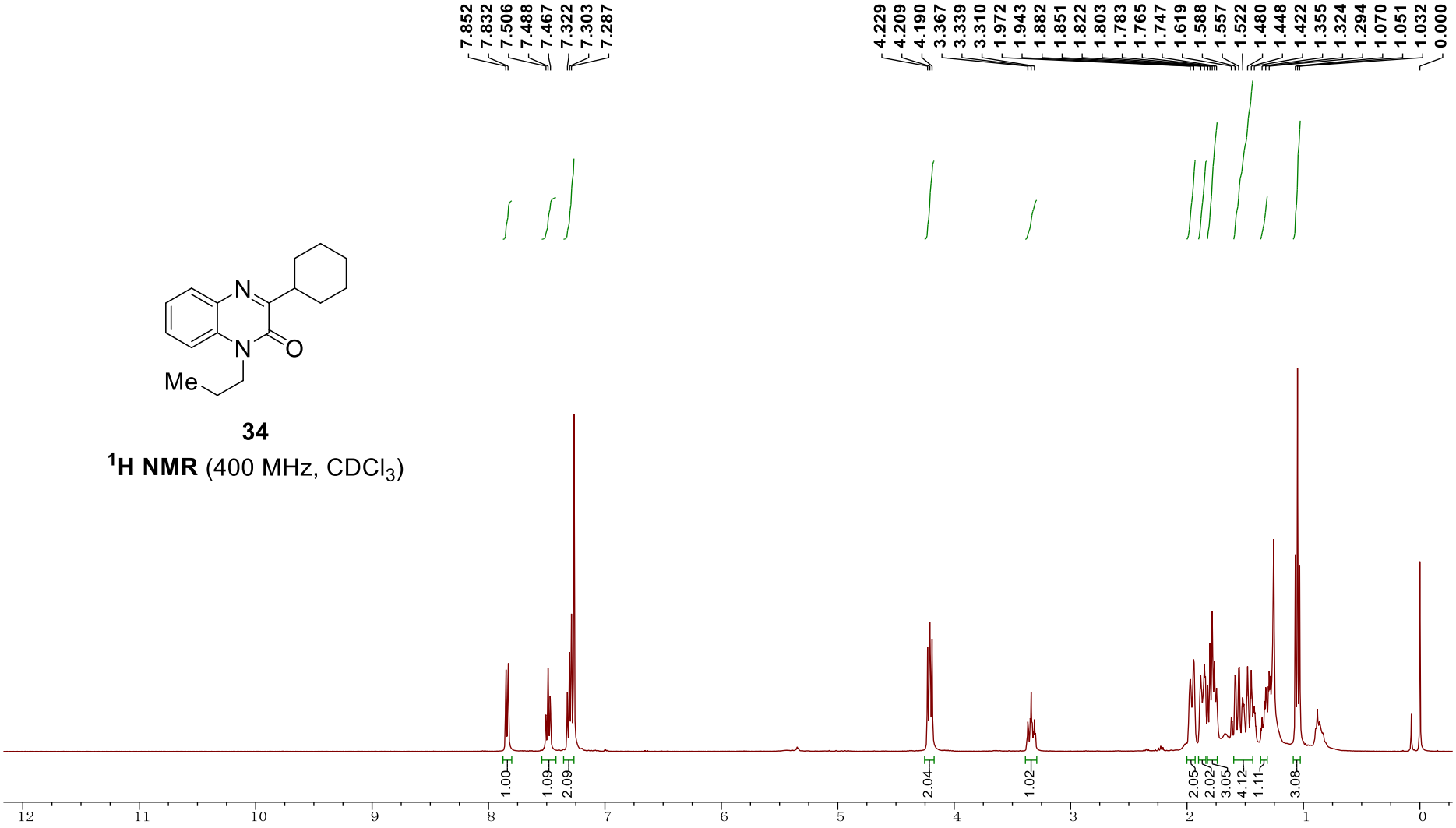

**33**

**$^1$H NMR** (400 MHz, $CDCl_3$)



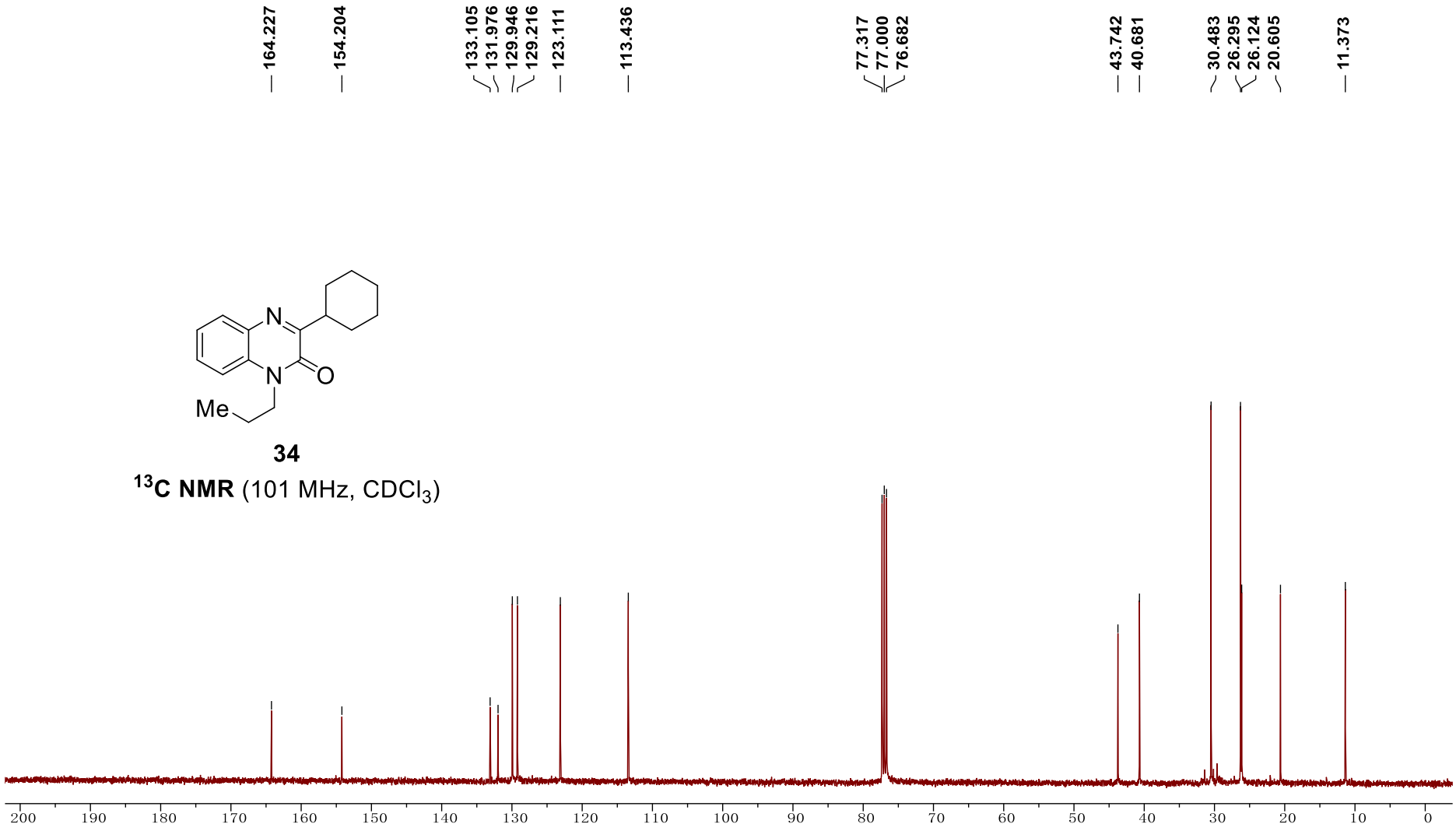

**33**

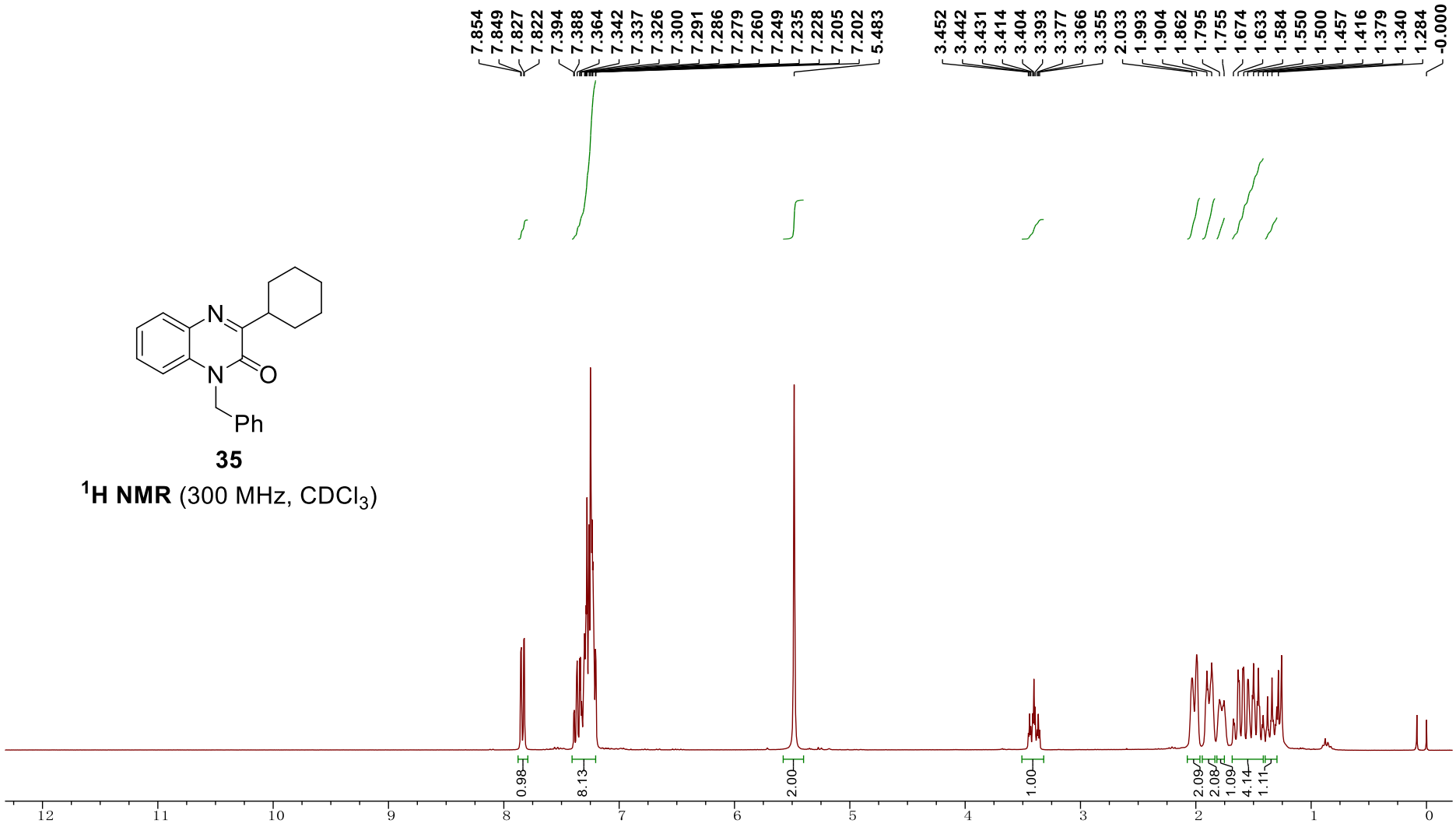
**$^{13}$C NMR** (101 MHz, $CDCl_3$)




**34**

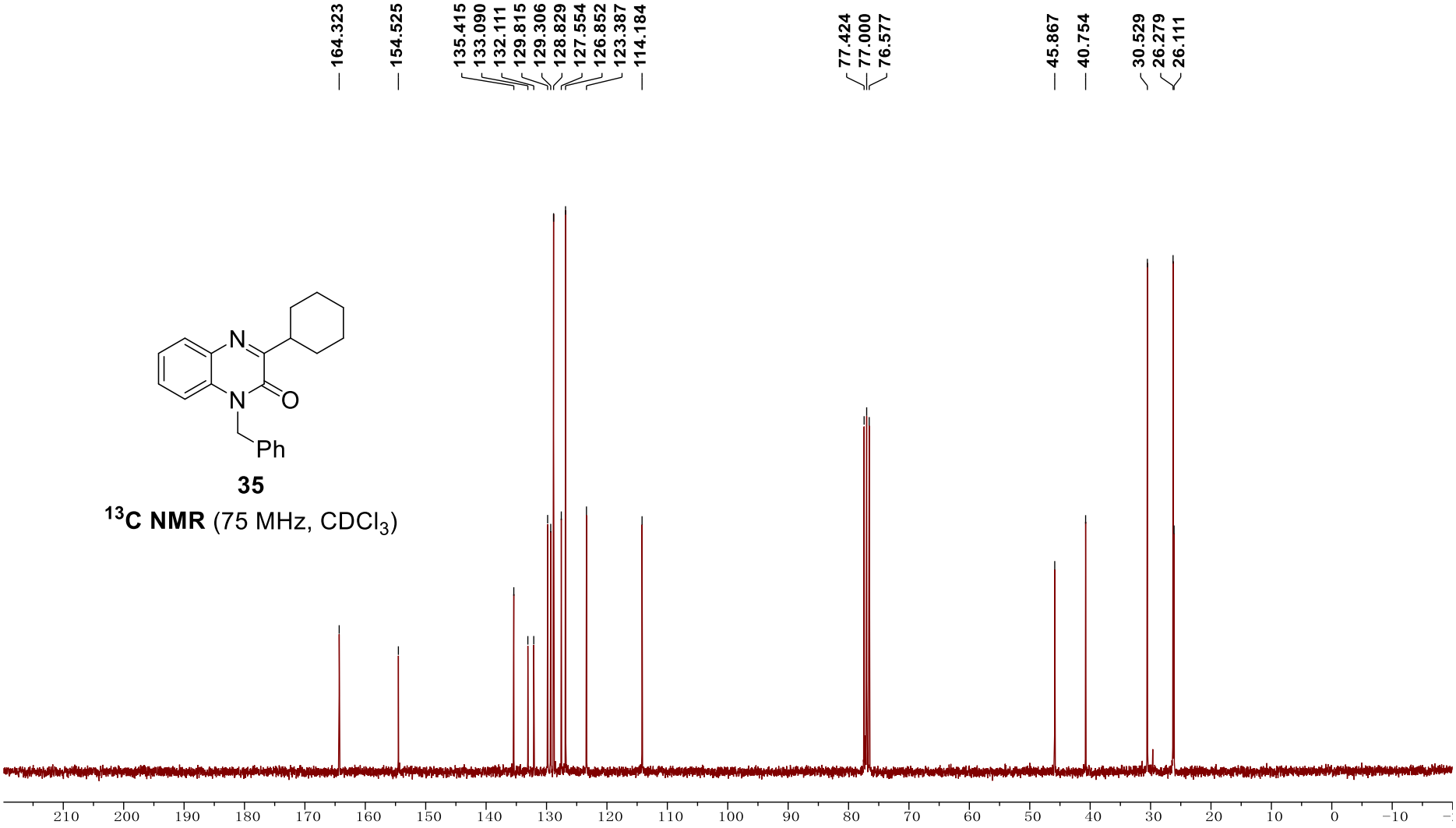
**$^1$H NMR** (400 MHz, $CDCl_3$)

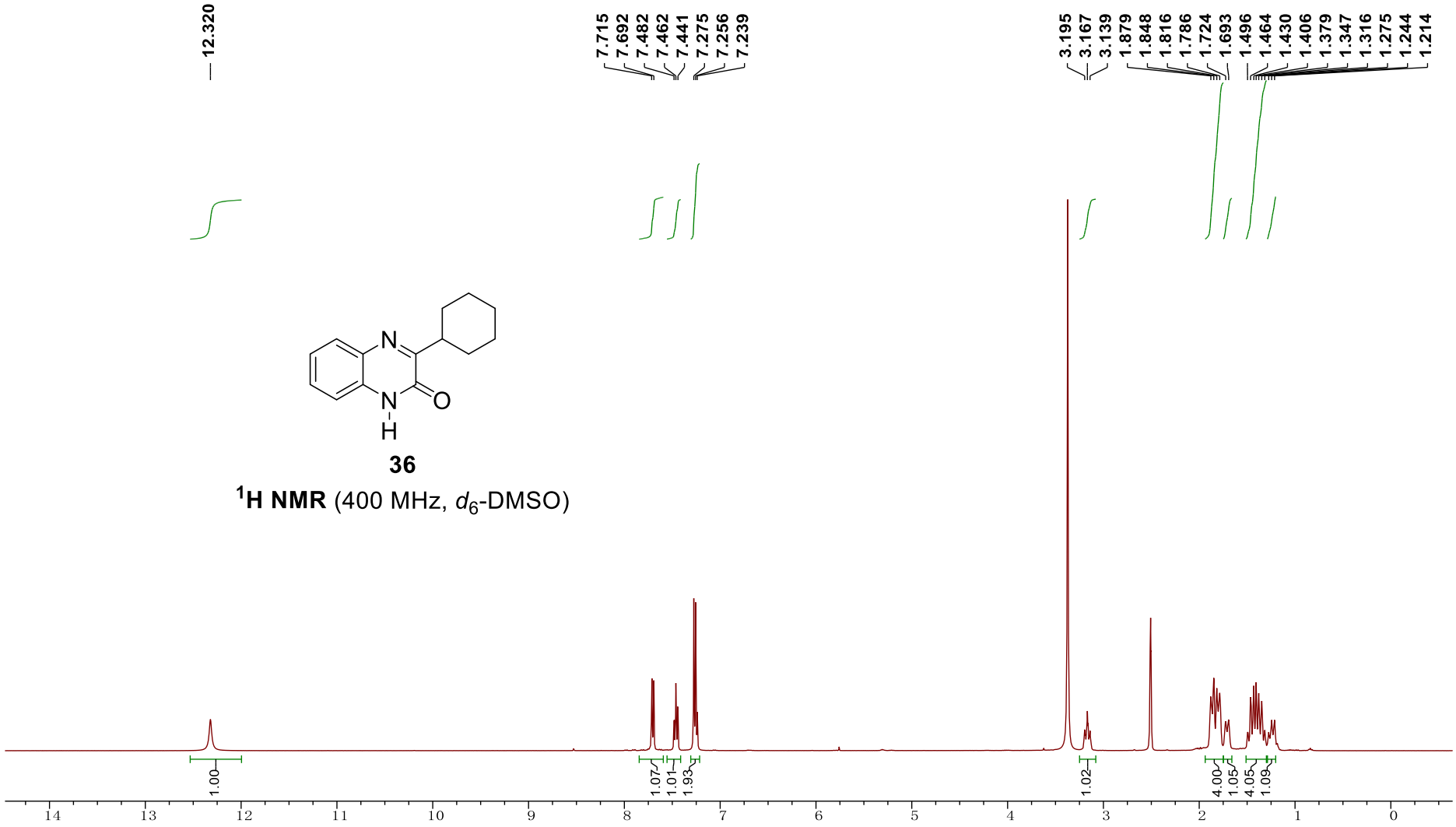

164.227
154.204
133.105
131.976
129.946
129.216
123.111
113.436
77.317
77.000
76.682
43.742
40.681
30.483
26.295
26.124
20.605
11.373
N
N
O
Me
34
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0




**35**

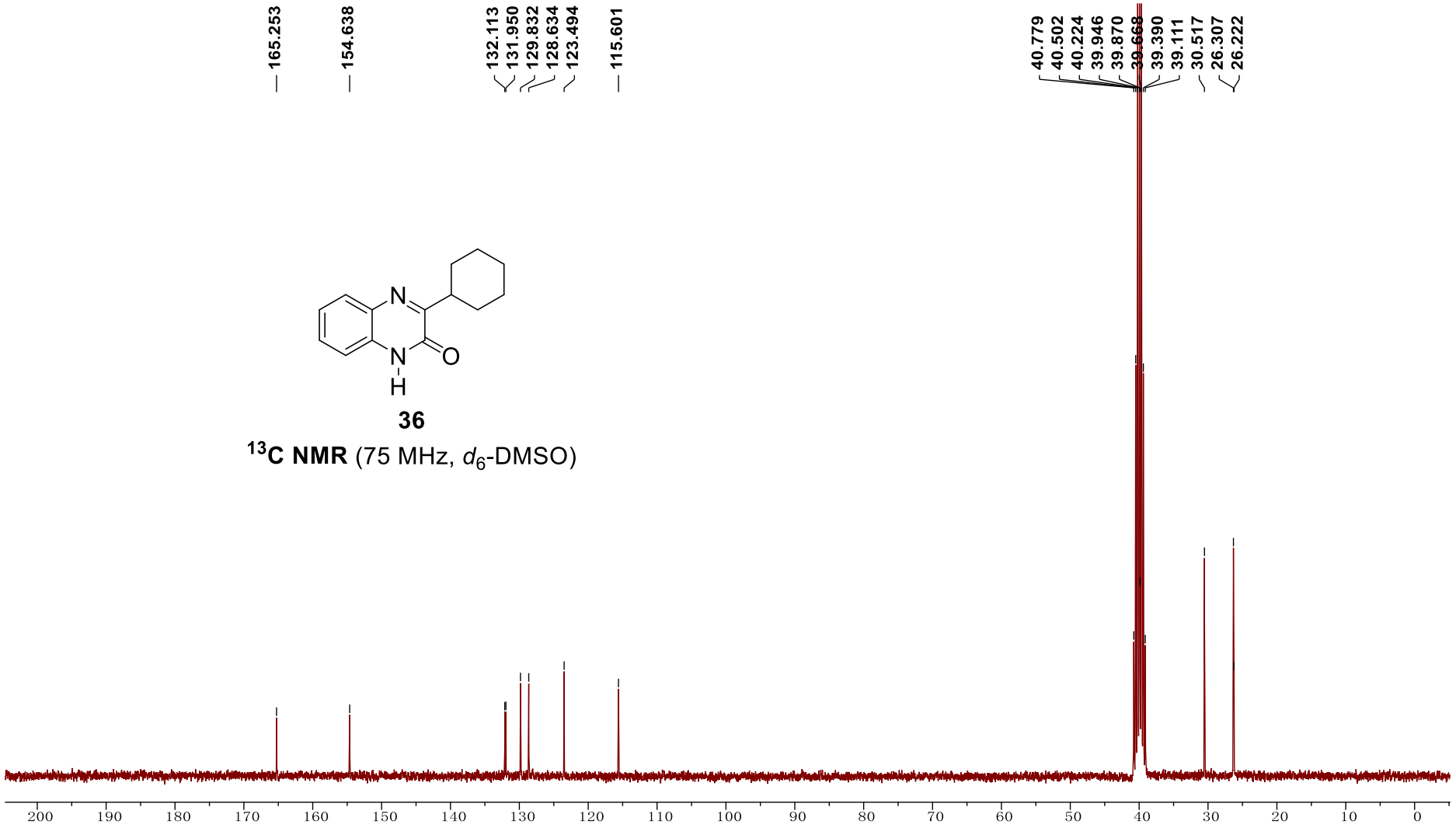
**$^1$H NMR** (300 MHz, $CDCl_3$)


164.323
154.525
135.415
133.090
132.111
129.815
129.306
128.829
127.554
126.852
123.387
114.184
77.424
77.000
76.577
45.867
40.754
30.529
26.279
26.111
N
N
O
Ph
35
13C NMR (75 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



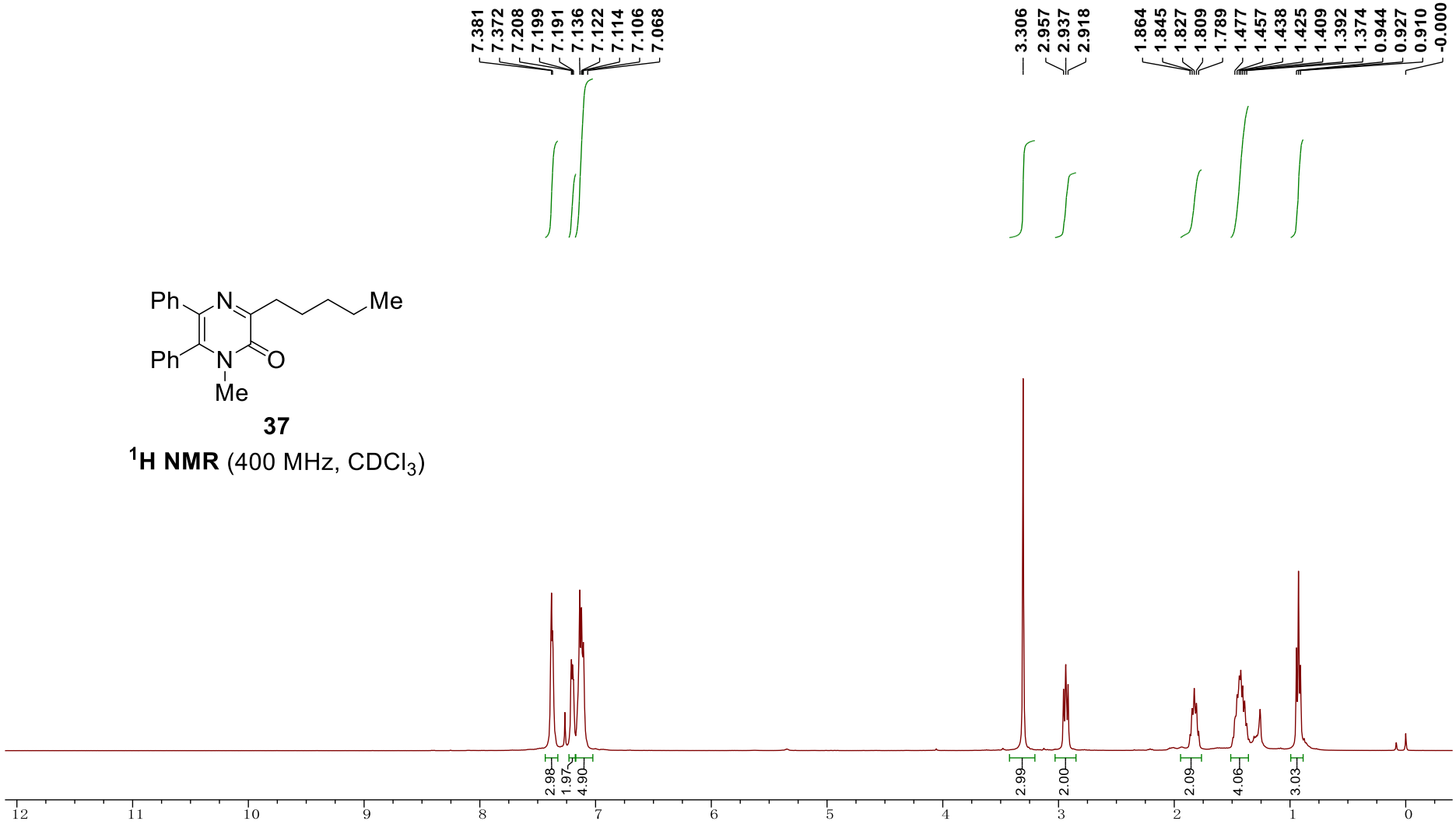

**36**

**$^1$H NMR** (400 MHz, $d_6$-DMSO)



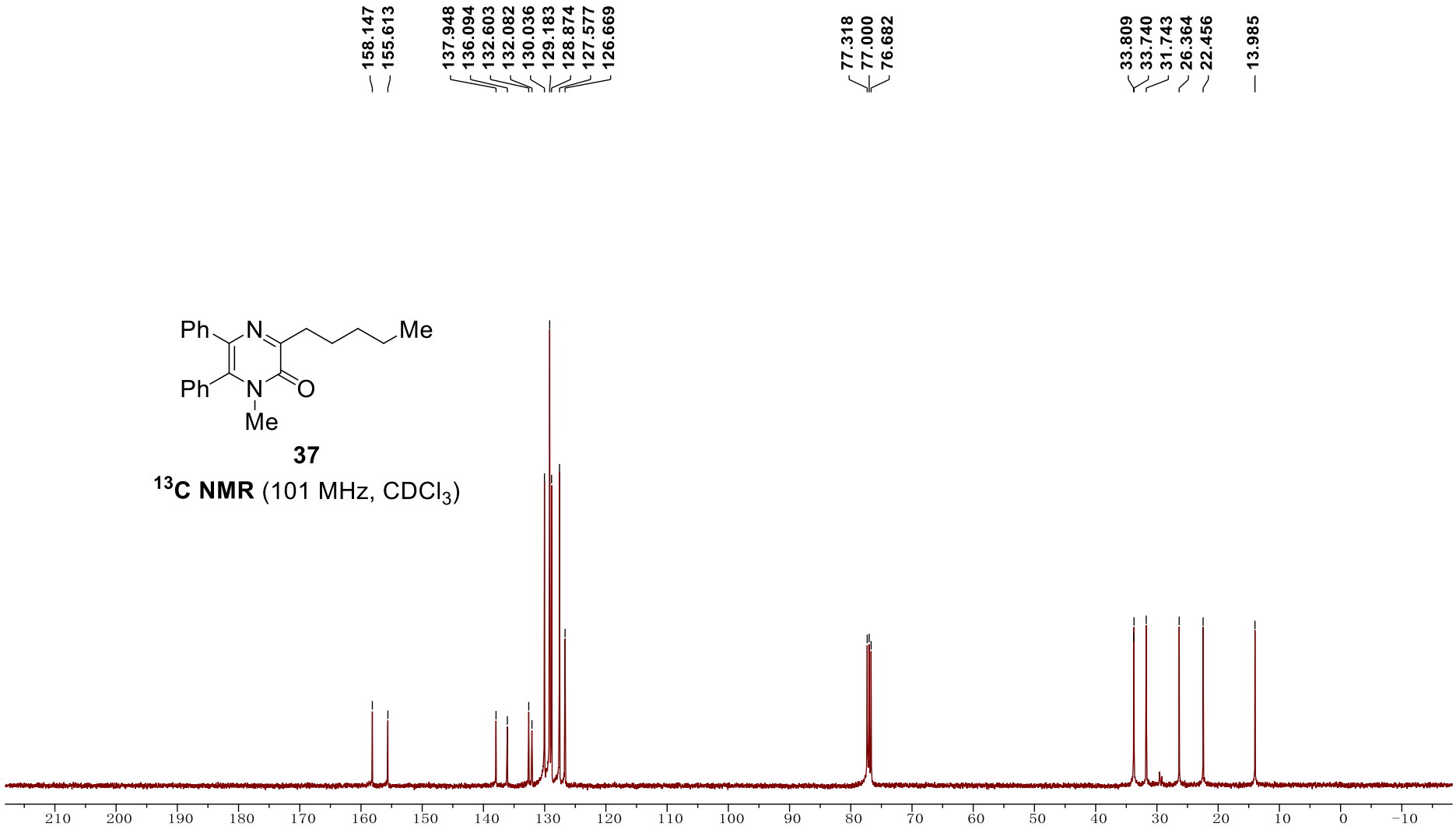

**36**

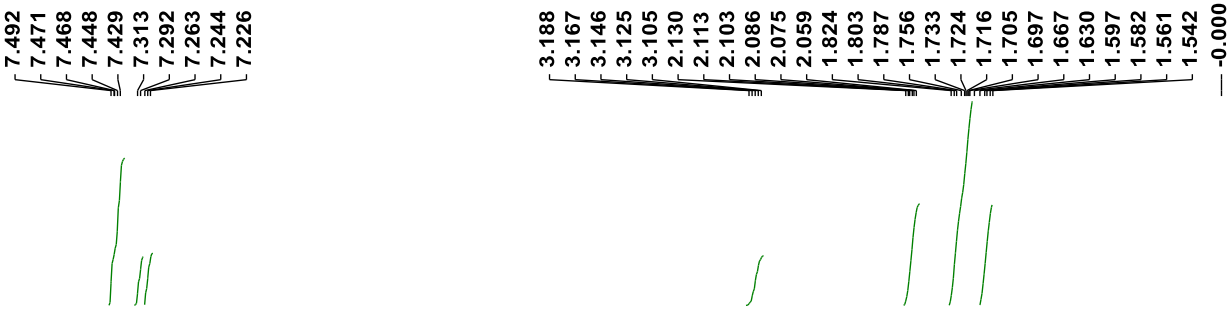
**$^{13}$C NMR** (75 MHz, $d_6$-DMSO)

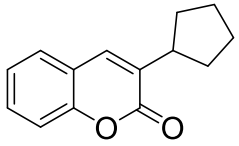



**37**

**$^1$H NMR** (400 MHz, $CDCl_3$)

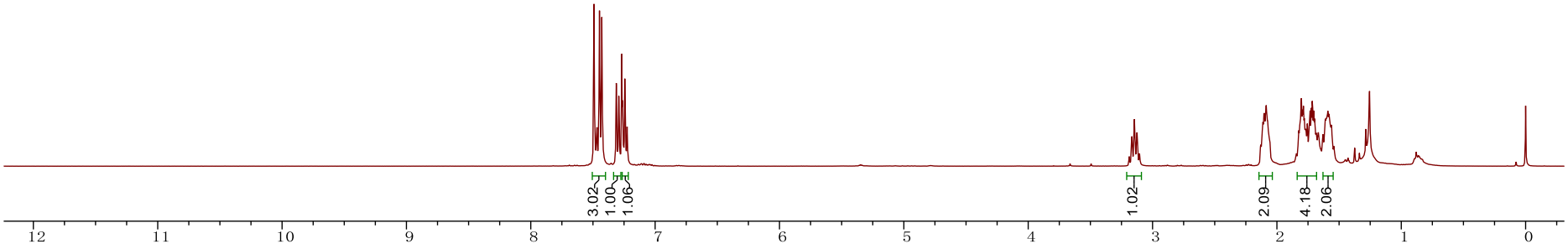

158.147
155.613
137.948
136.094
132.603
132.082
130.036
129.183
128.874
127.577
126.669
77.318
77.000
76.682
33.809
33.740
31.743
26.364
22.456
13.985
Ph
N
Me
Ph
N
O
Me
37
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

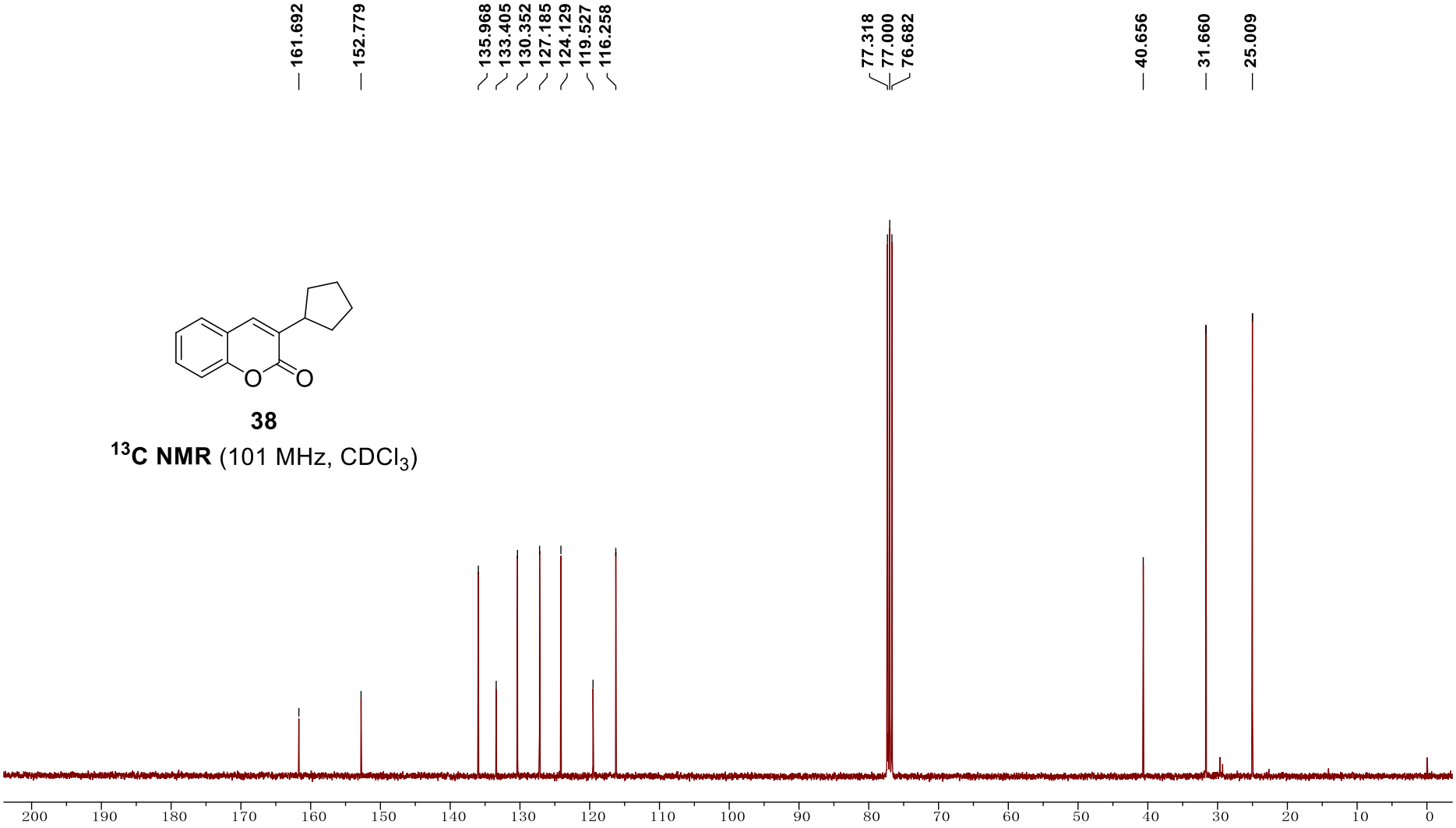


**38**

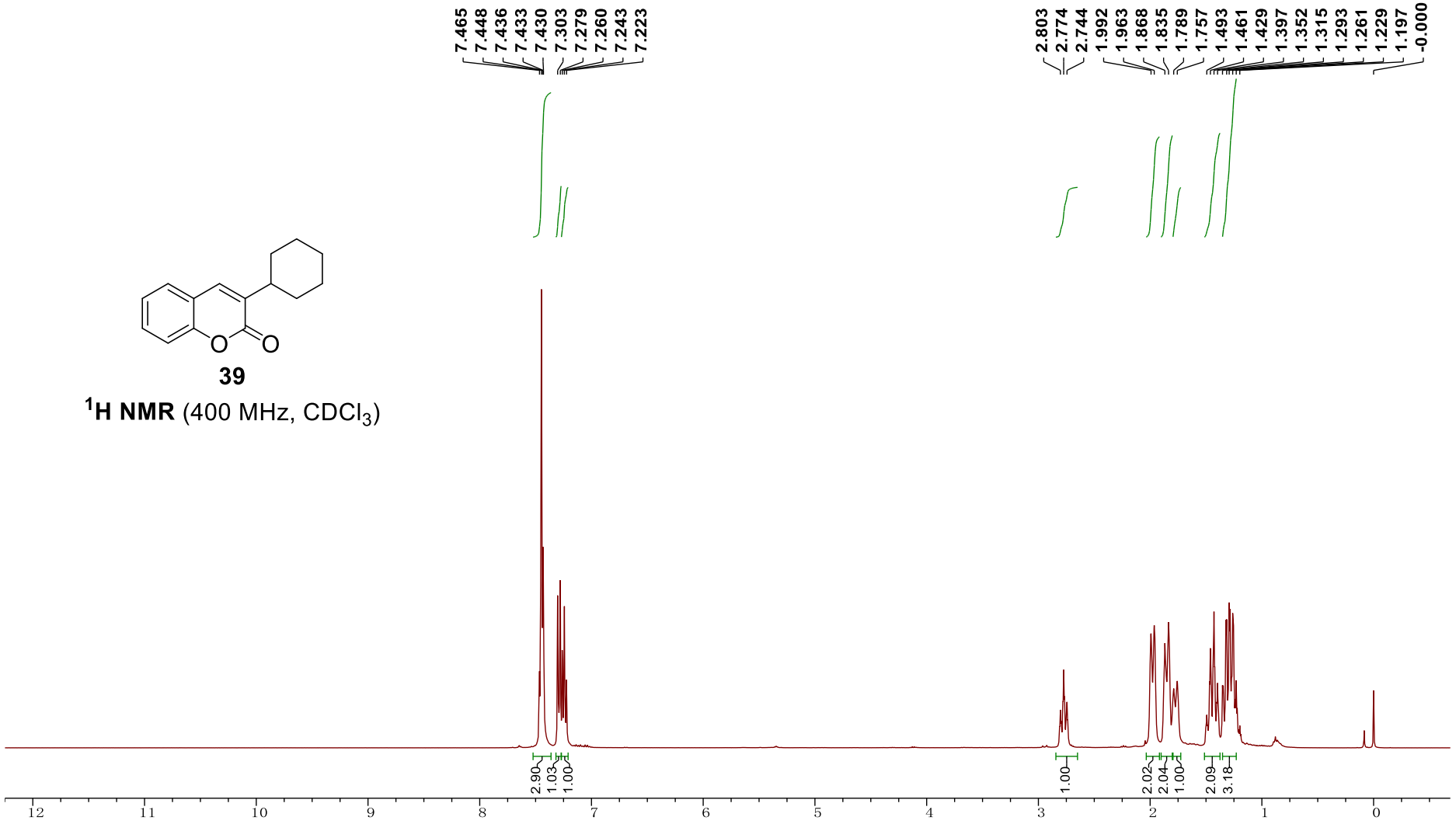
**$^1$H NMR** (400 MHz, $CDCl_3$)





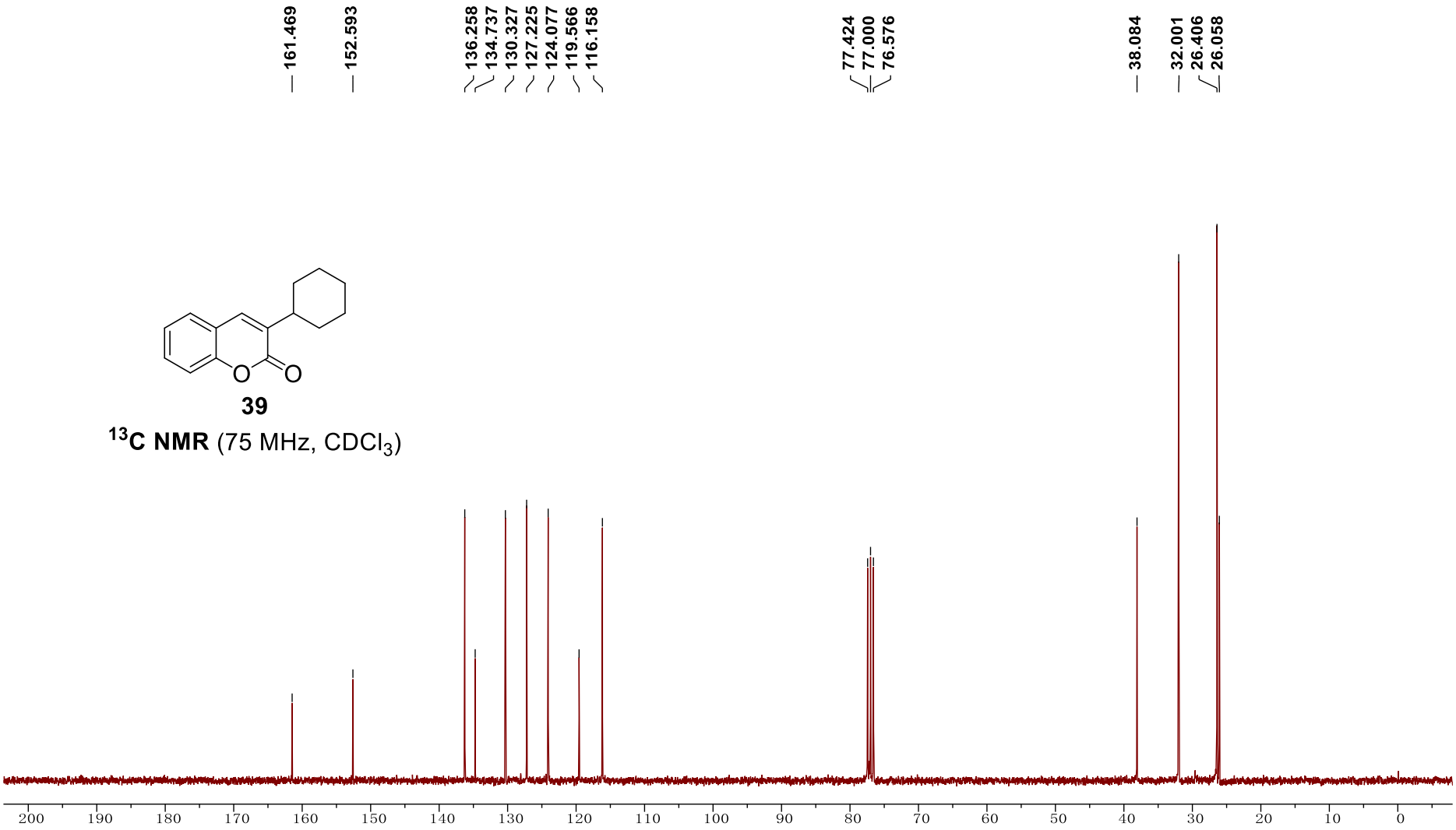

**38**

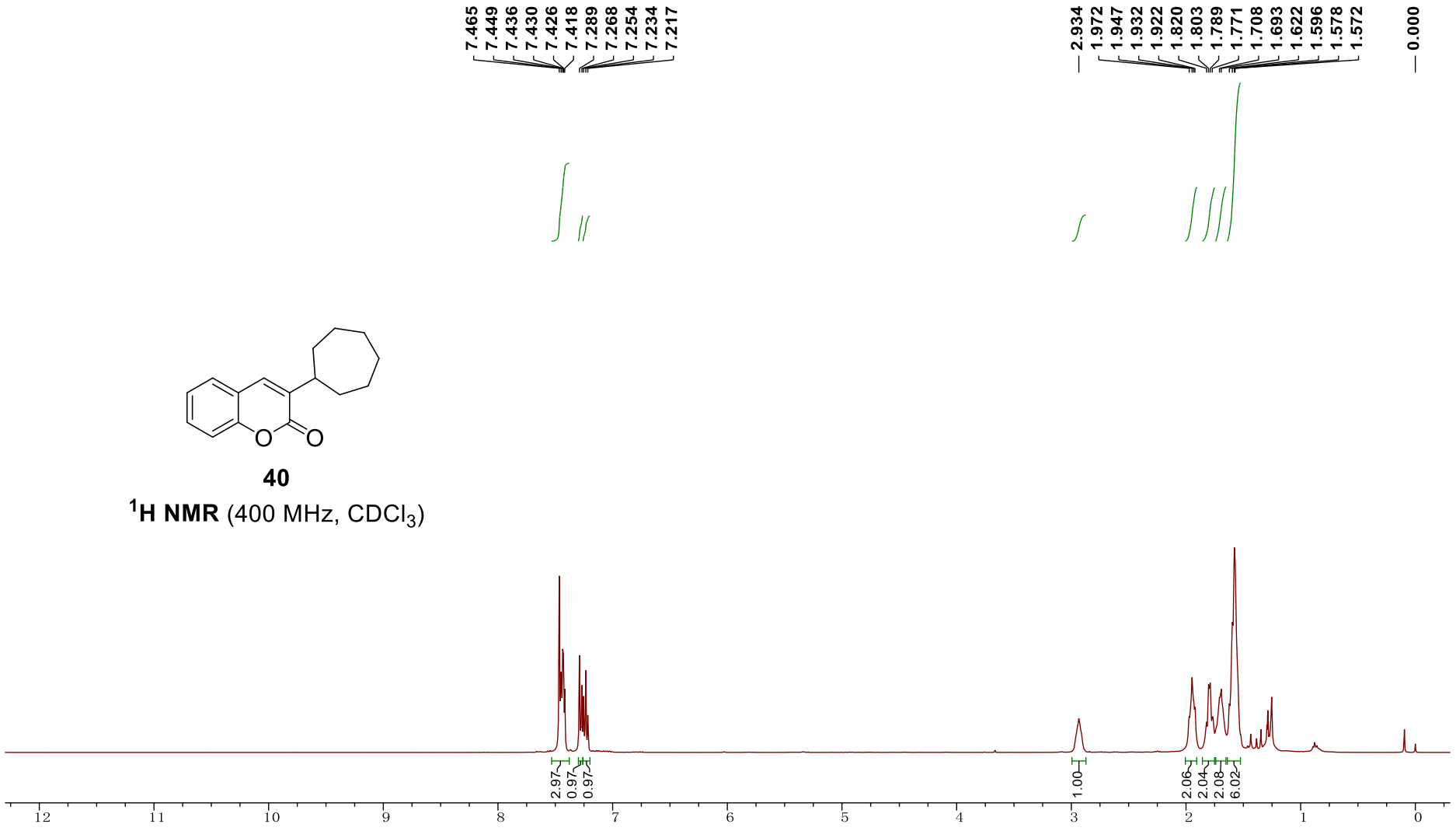
**$^{13}$C NMR** (101 MHz, $CDCl_3$)




**39**

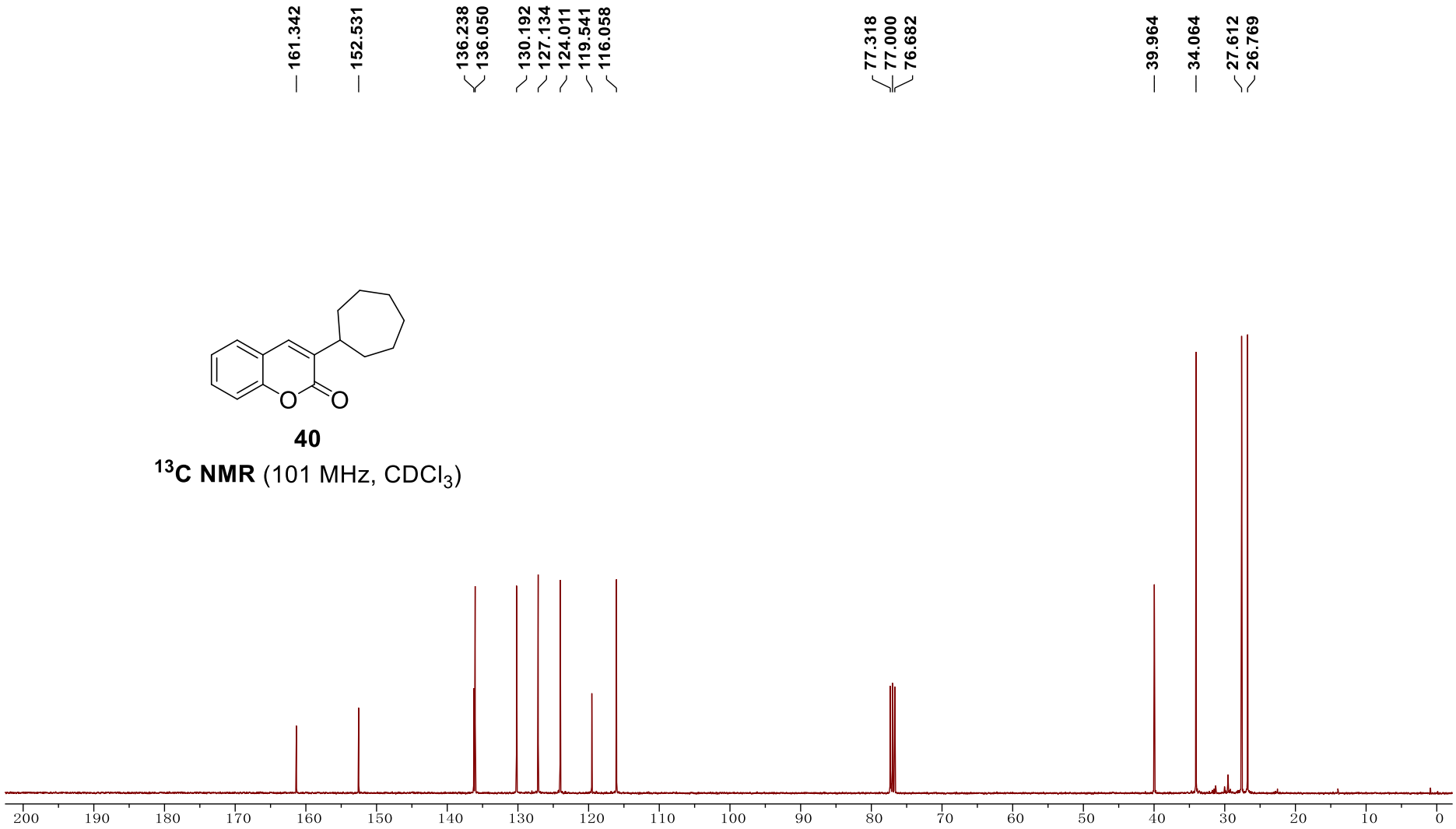
**$^1$H NMR** (400 MHz, $CDCl_3$)


161.469
152.593
136.258
134.737
130.327
127.225
124.077
119.566
116.158
77.424
77.000
76.576
38.084
32.001
26.406
26.058
O
O
39
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



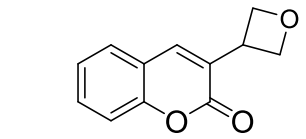

**40**

**$^1$H NMR** (400 MHz, $CDCl_3$)



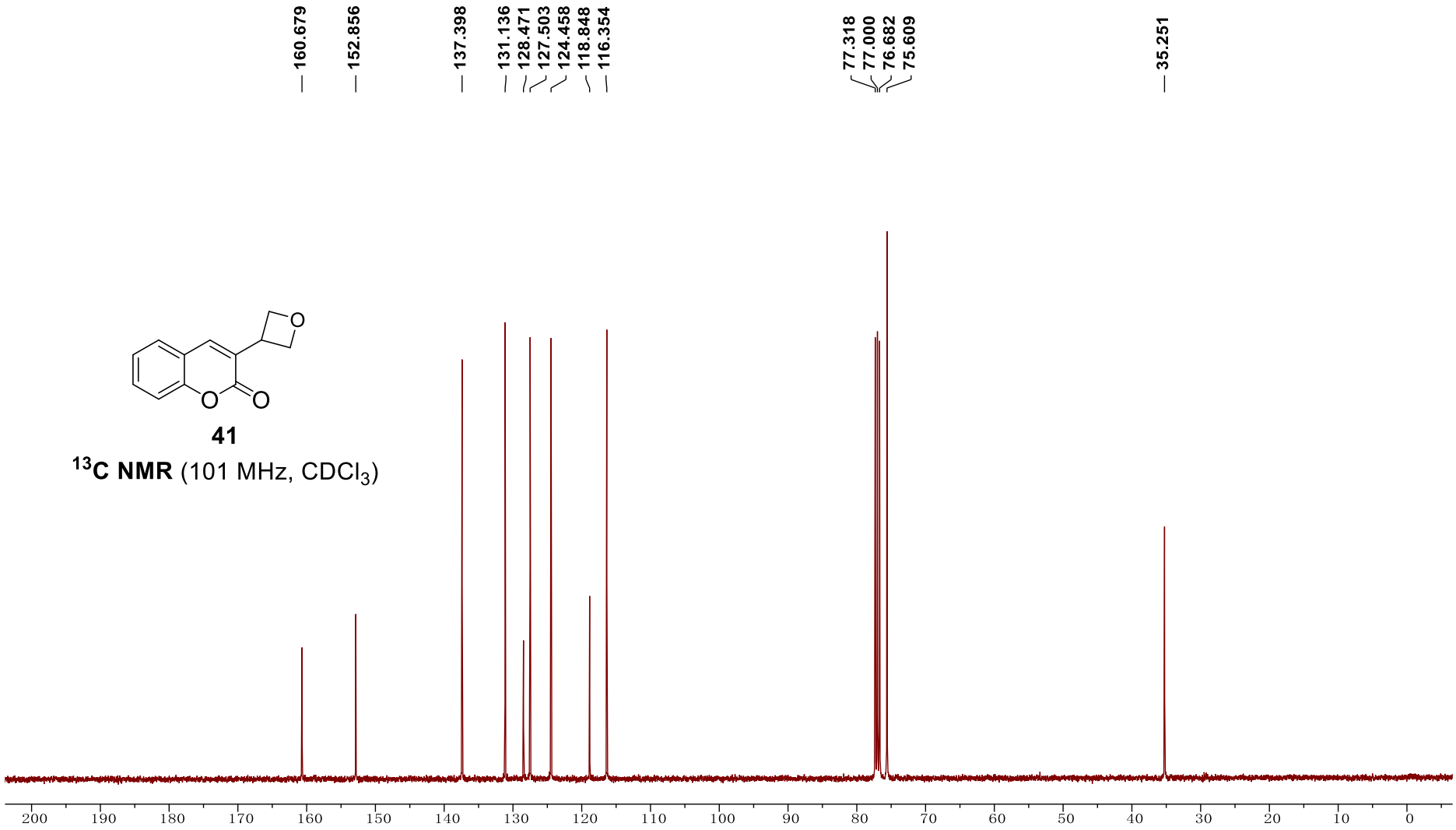

**40**

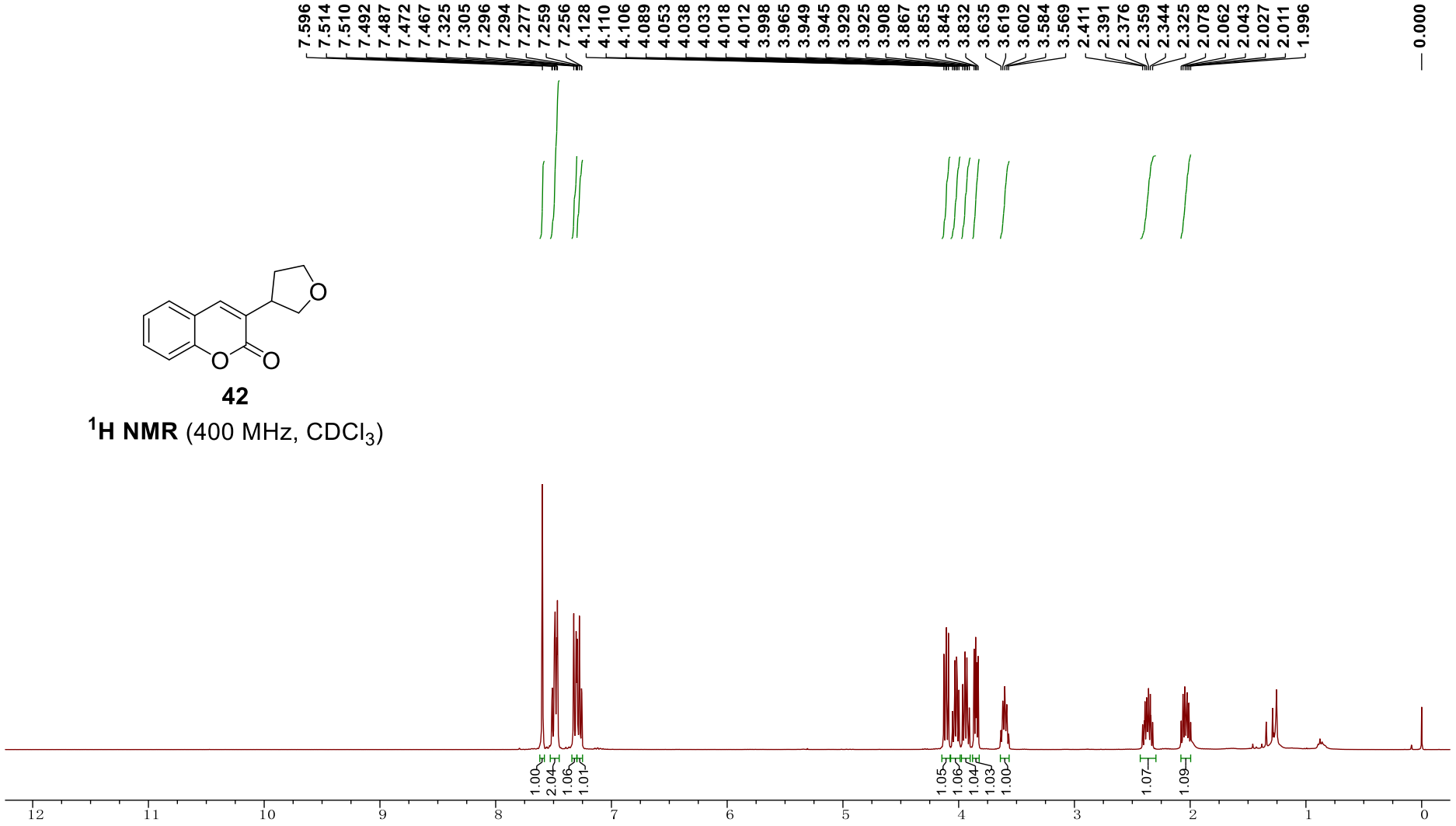
**$^{13}$C NMR** (101 MHz, $CDCl_3$)



**41**

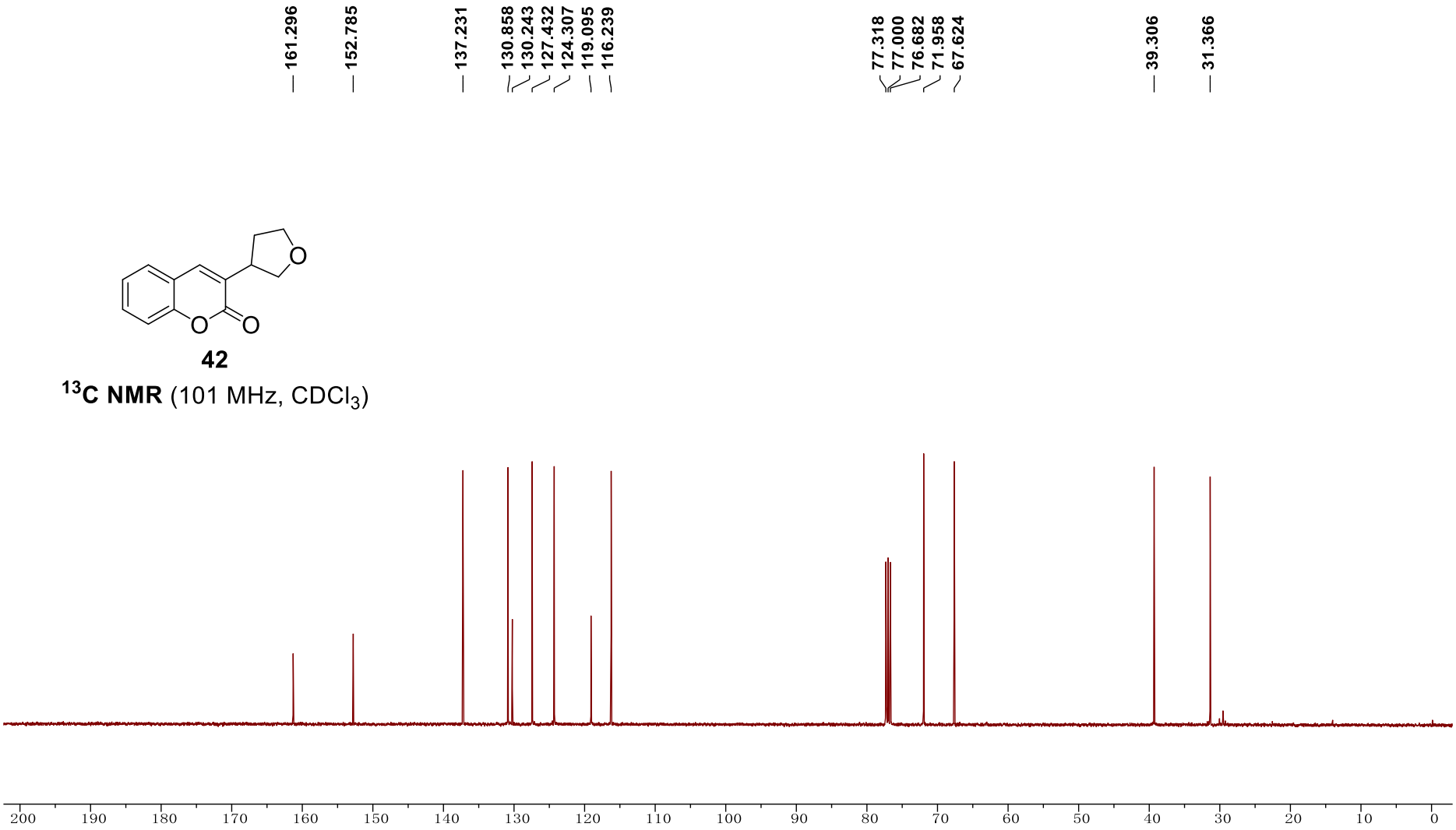
**$^1$H NMR** (400 MHz, $CDCl_3$)


160.679
152.856
137.398
131.136
128.471
127.503
124.458
118.848
116.354
77.318
77.000
76.682
75.609
35.251
O
O
O
41
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0



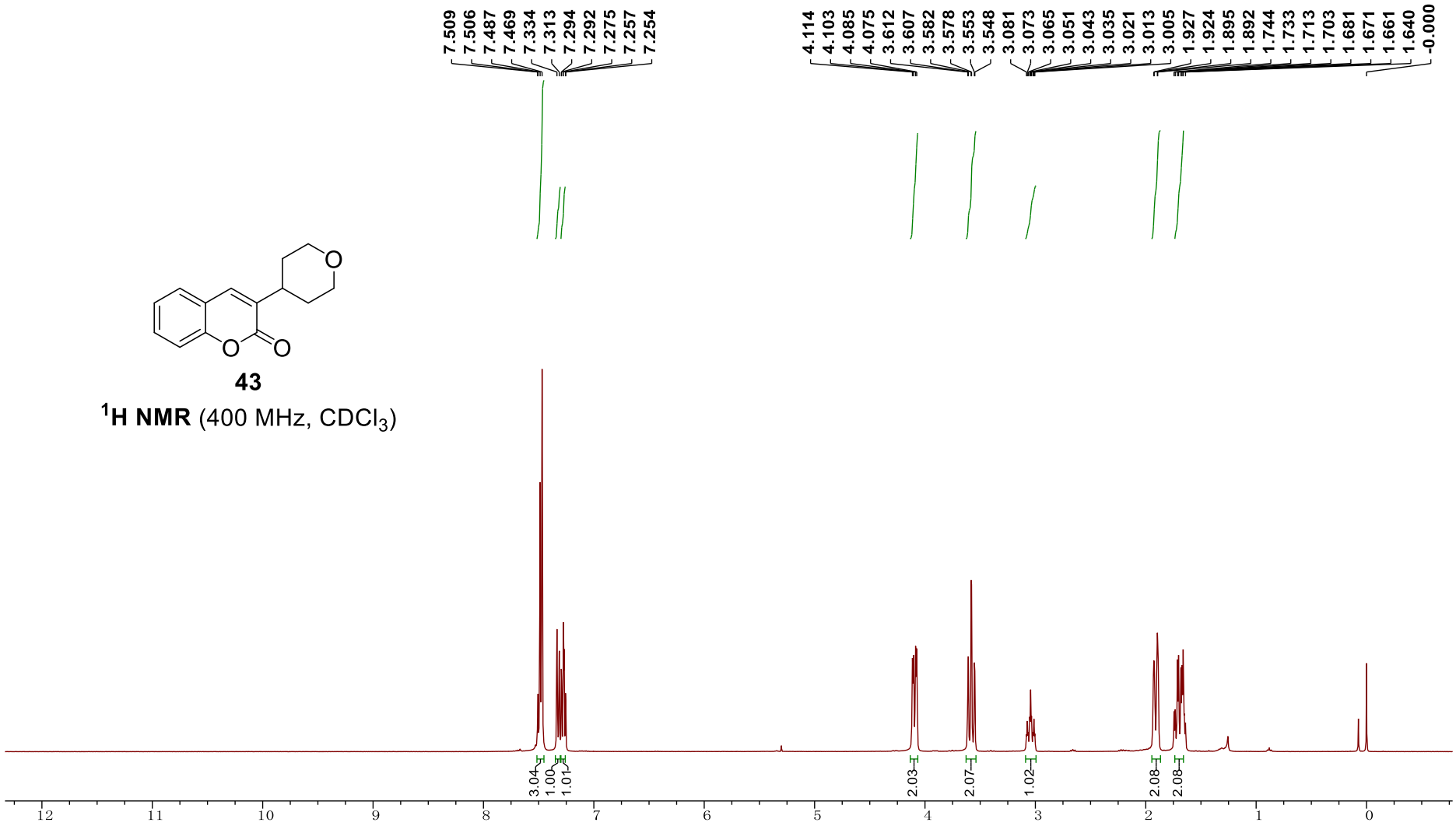

**42**

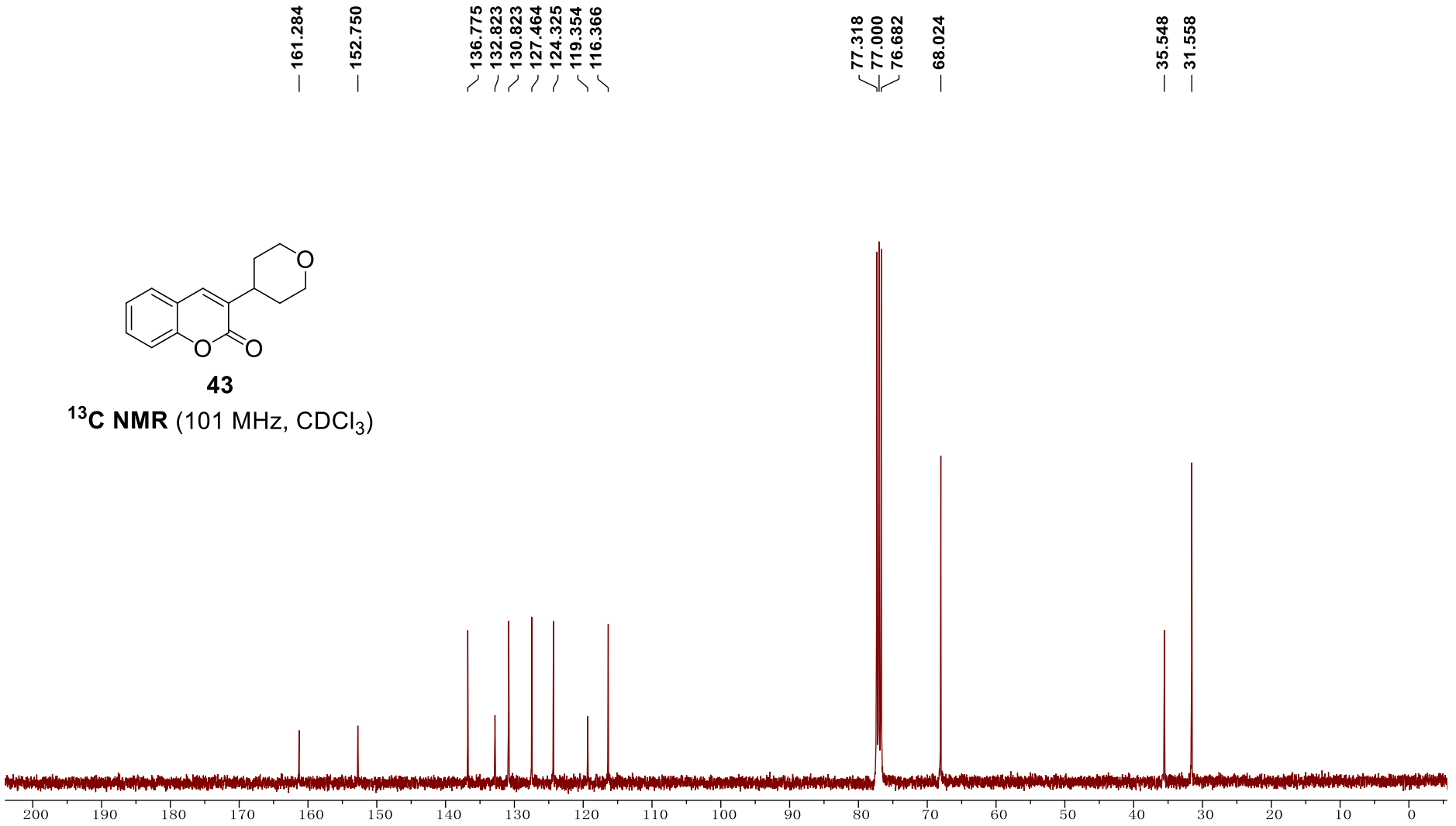
**$^1$H NMR** (400 MHz, $CDCl_3$)




**42**

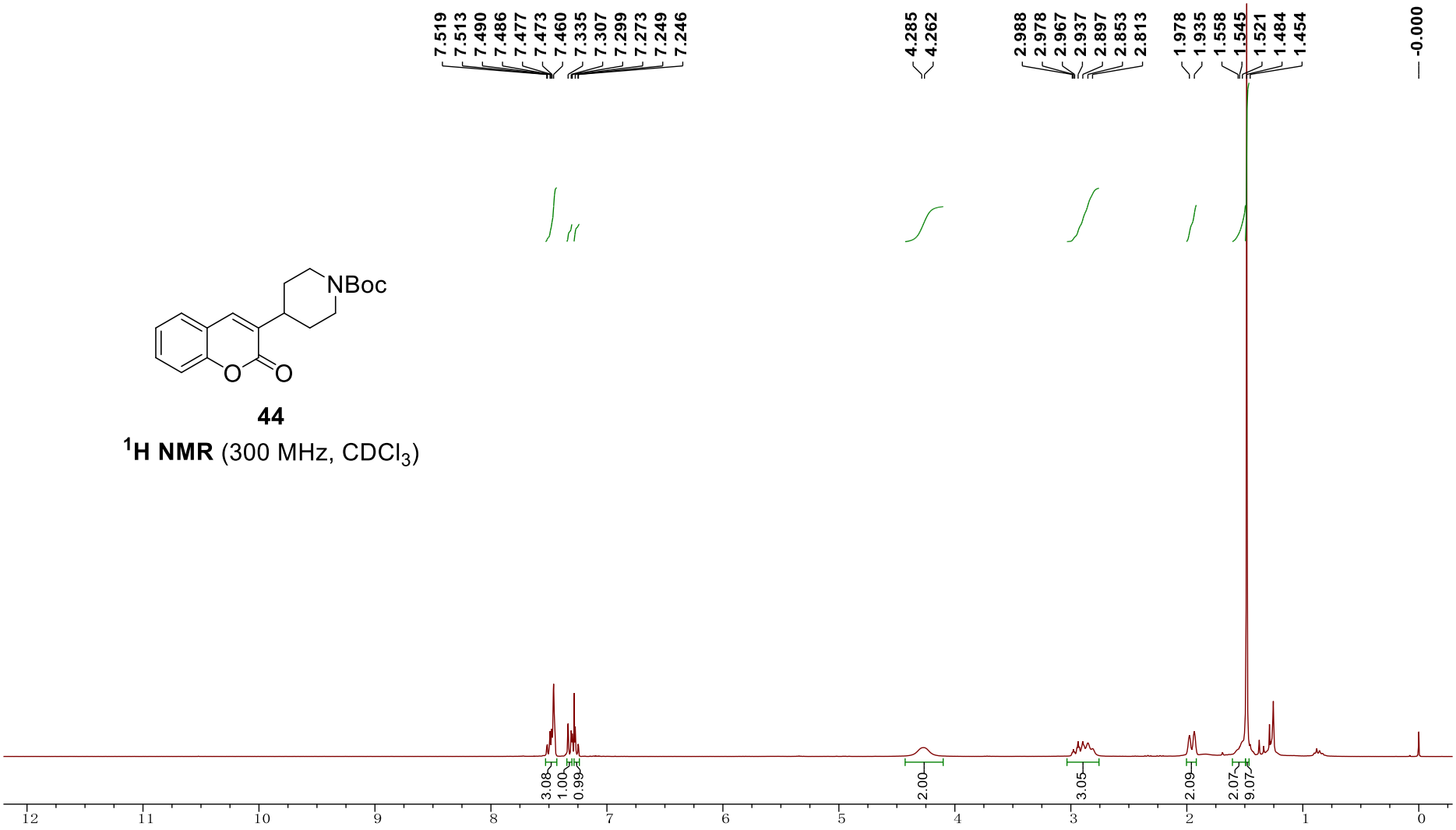
**$^{13}$C NMR** (101 MHz, $CDCl_3$)


7.509
7.506
7.487
7.469
7.334
7.313
7.294
7.292
7.275
7.257
7.254
4.114
4.103
4.085
4.075
3.612
3.607
3.582
3.578
3.553
3.548
3.081
3.073
3.065
3.051
3.043
3.035
3.021
3.013
3.005
1.927
1.924
1.895
1.892
1.744
1.733
1.713
1.703
1.681
1.671
1.661
1.640
-0.000
O
O
O
43
1H NMR (400 MHz, CDCl3)
3.04
1.00
1.01
2.03
2.07
1.02
2.08
2.08
12
11
10
9
8
7
6
5
4
3
2
1
0



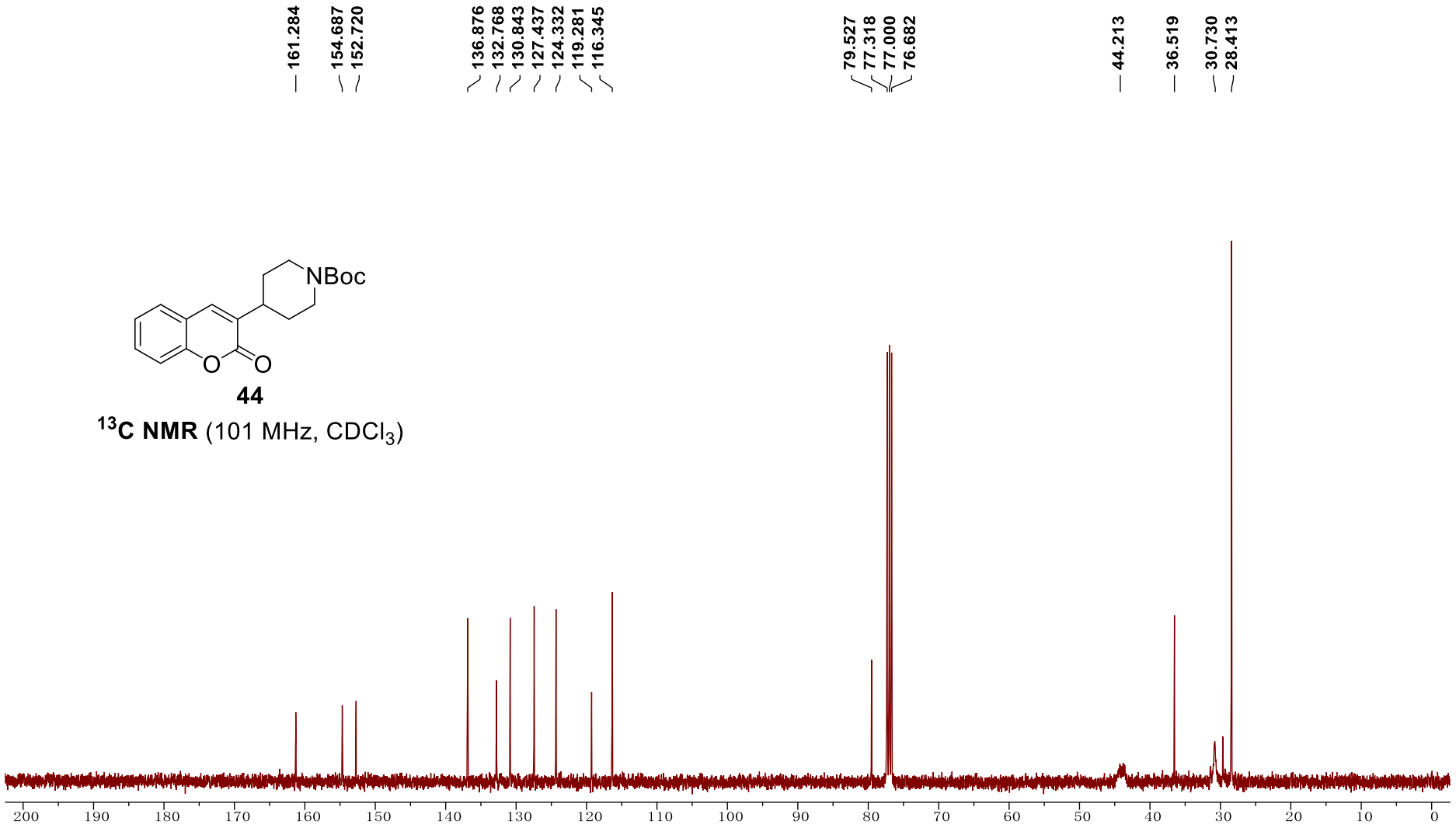

**43**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



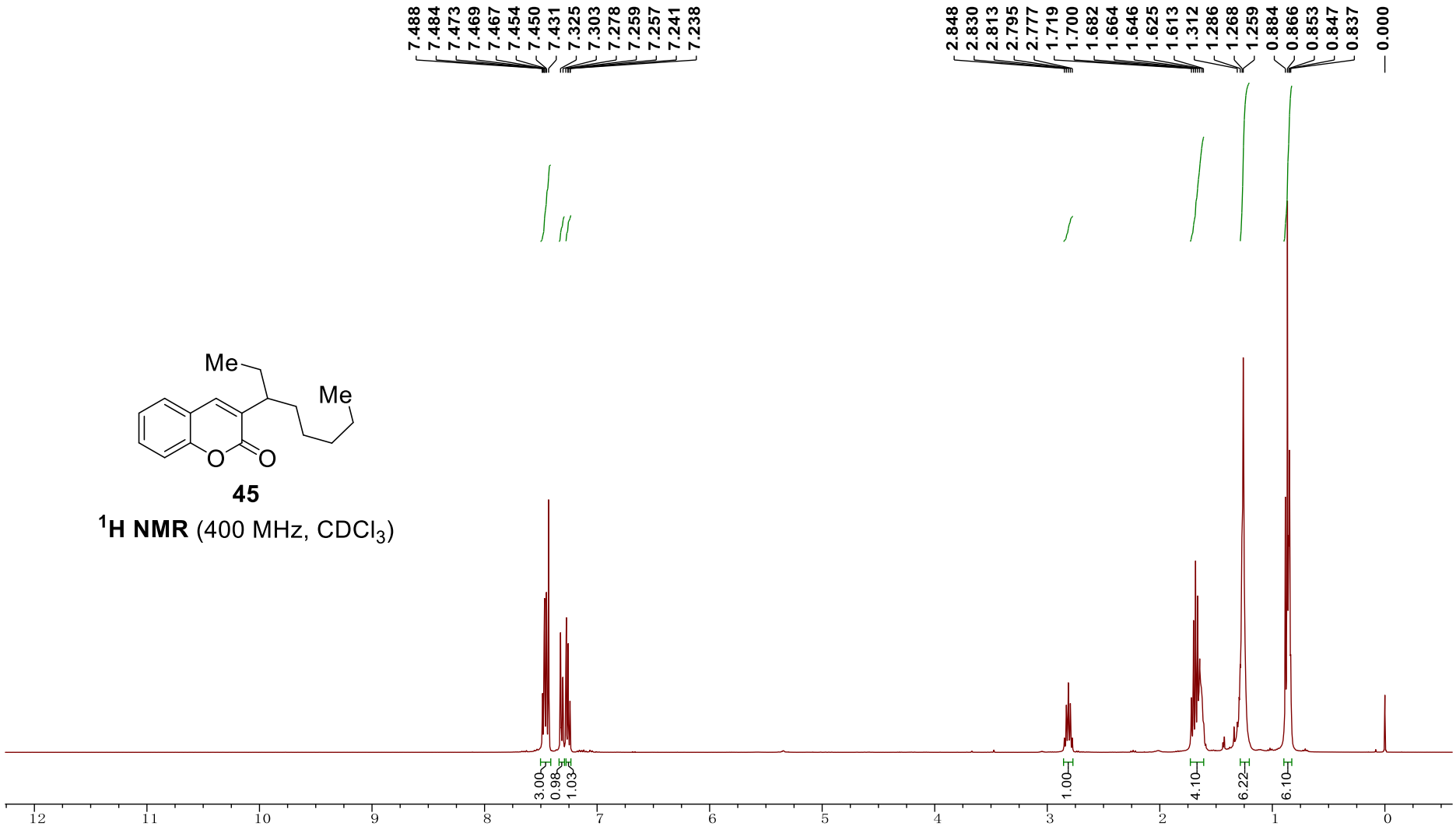

**44**

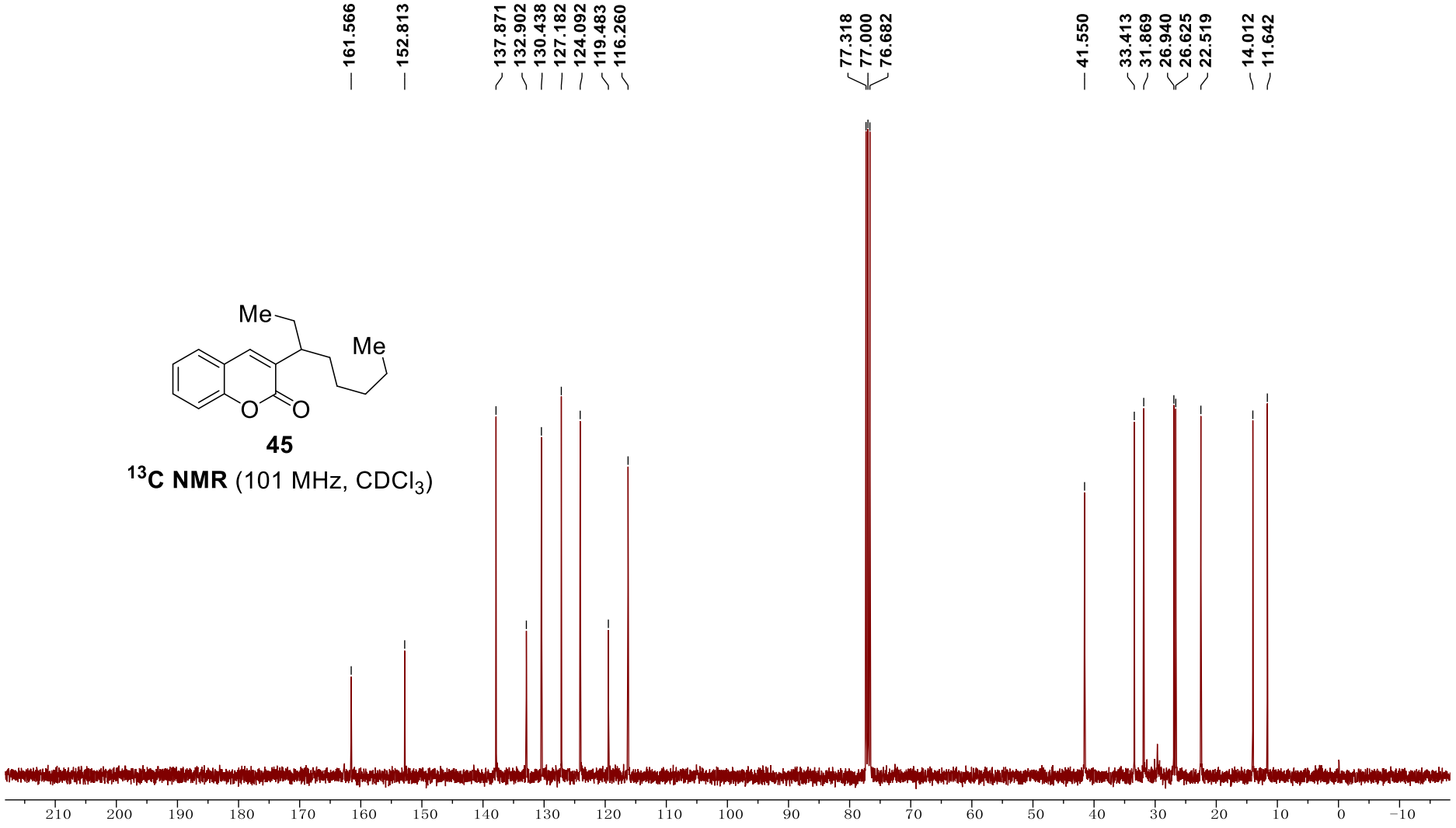
**$^1$H NMR** (300 MHz, $CDCl_3$)

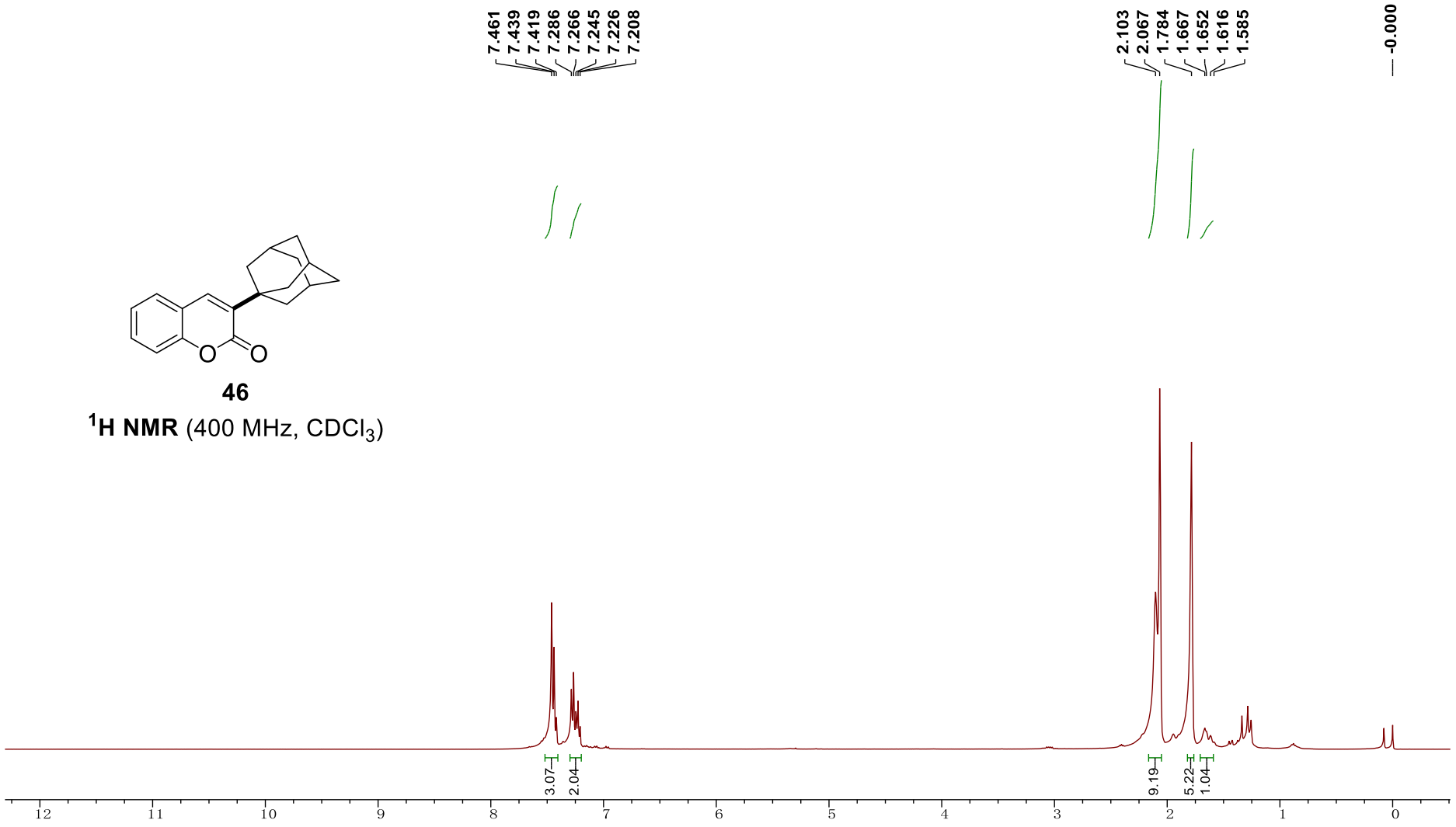



**44**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)

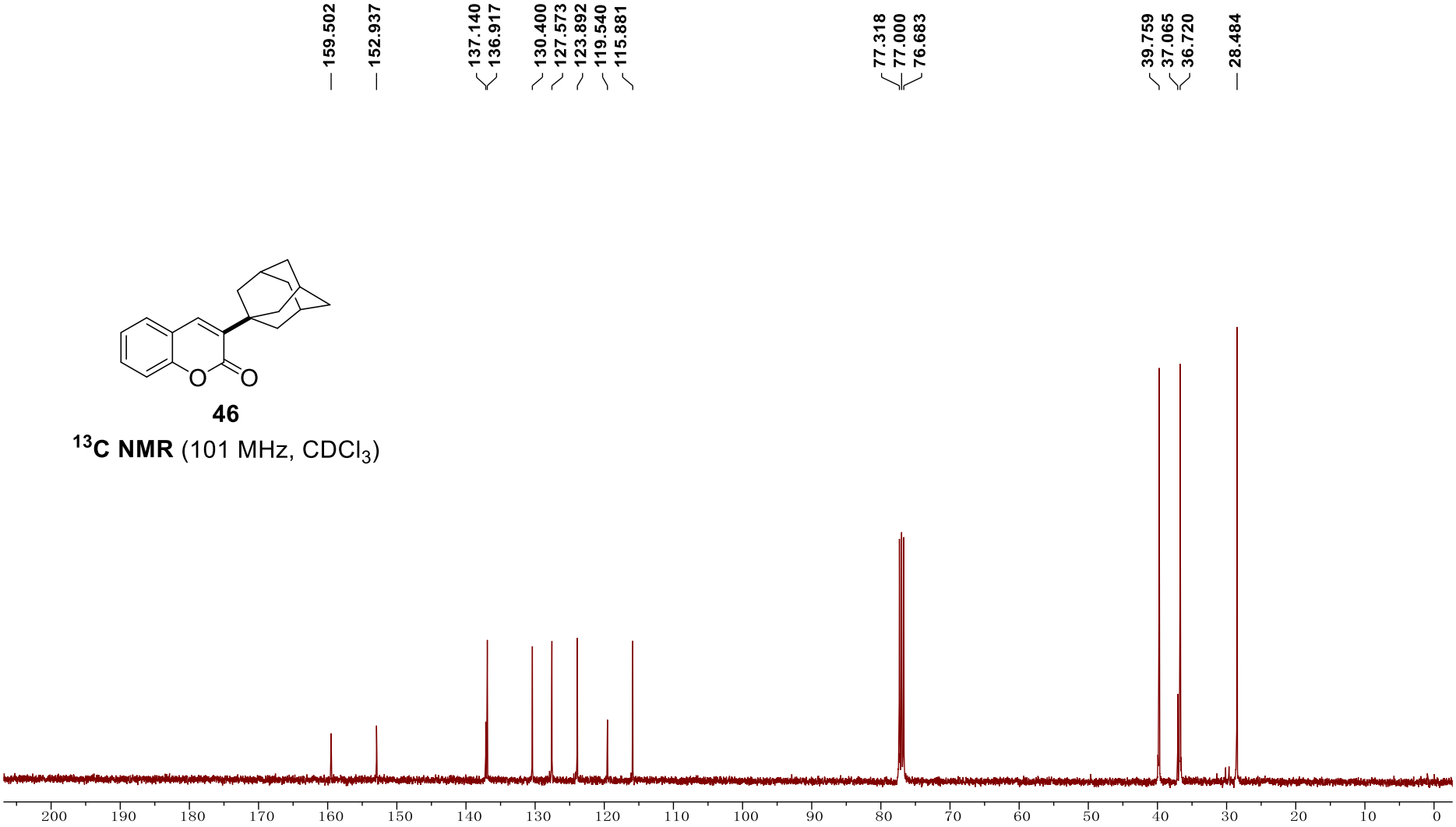

7.488
7.484
7.473
7.469
7.467
7.454
7.450
7.431
7.325
7.303
7.278
7.259
7.257
7.241
7.238
2.848
2.830
2.813
2.795
2.777
1.719
1.700
1.682
1.664
1.646
1.625
1.613
1.312
1.286
1.268
1.259
0.884
0.866
0.853
0.847
0.837
0.000
Me
Me
O
O
45
1H NMR (400 MHz, CDCl3)
3.00
0.98
1.03
1.00
4.10
6.22
6.10
12
11
10
9
8
7
6
5
4
3
2
1
0


161.566
152.813
137.871
132.902
130.438
127.182
124.092
119.483
116.260
77.318
77.000
76.682
41.550
33.413
31.869
26.940
26.625
22.519
14.012
11.642
Me
Me
O
O
45
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



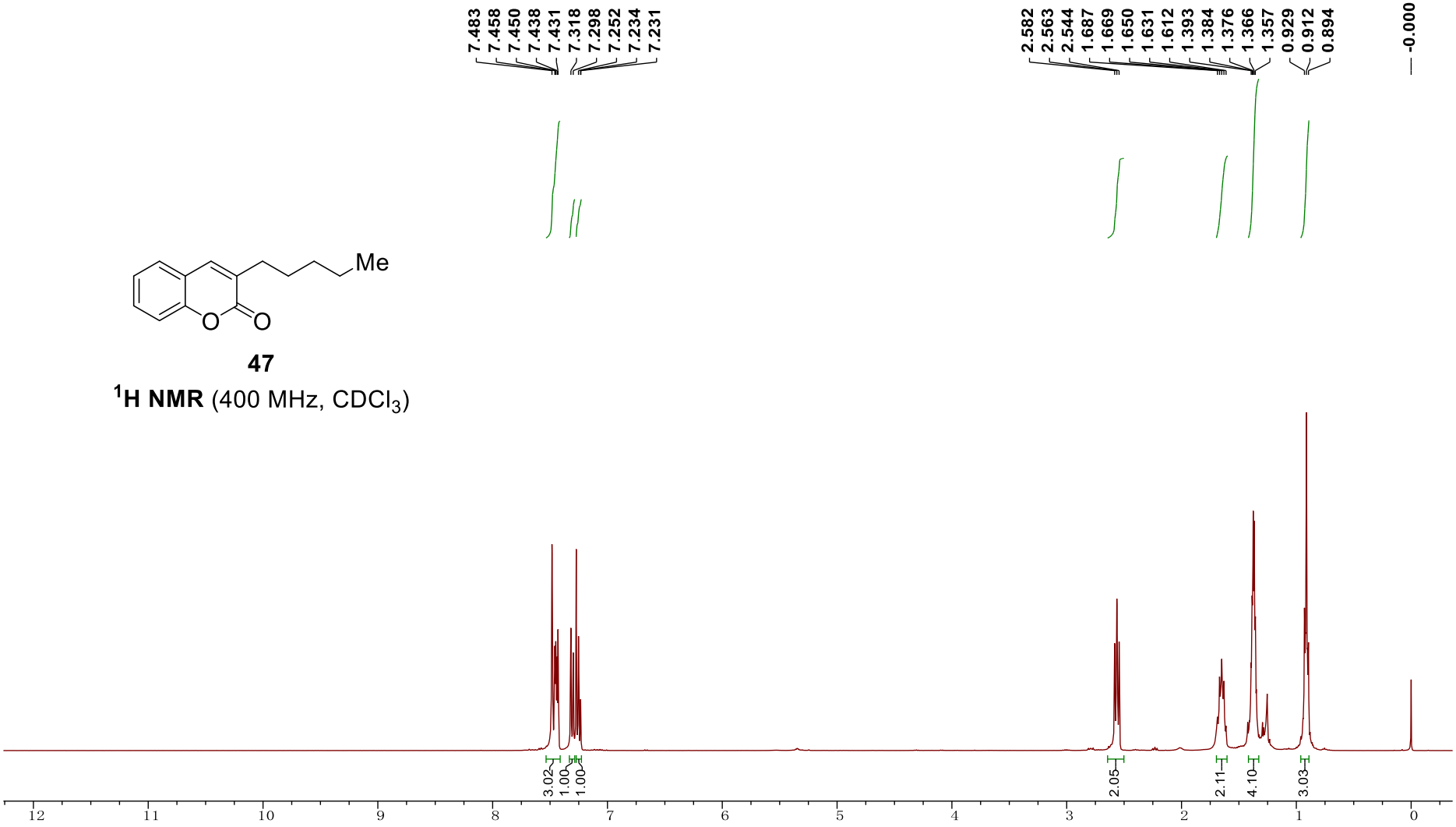

**46**

**$^1$H NMR** (400 MHz, $CDCl_3$)



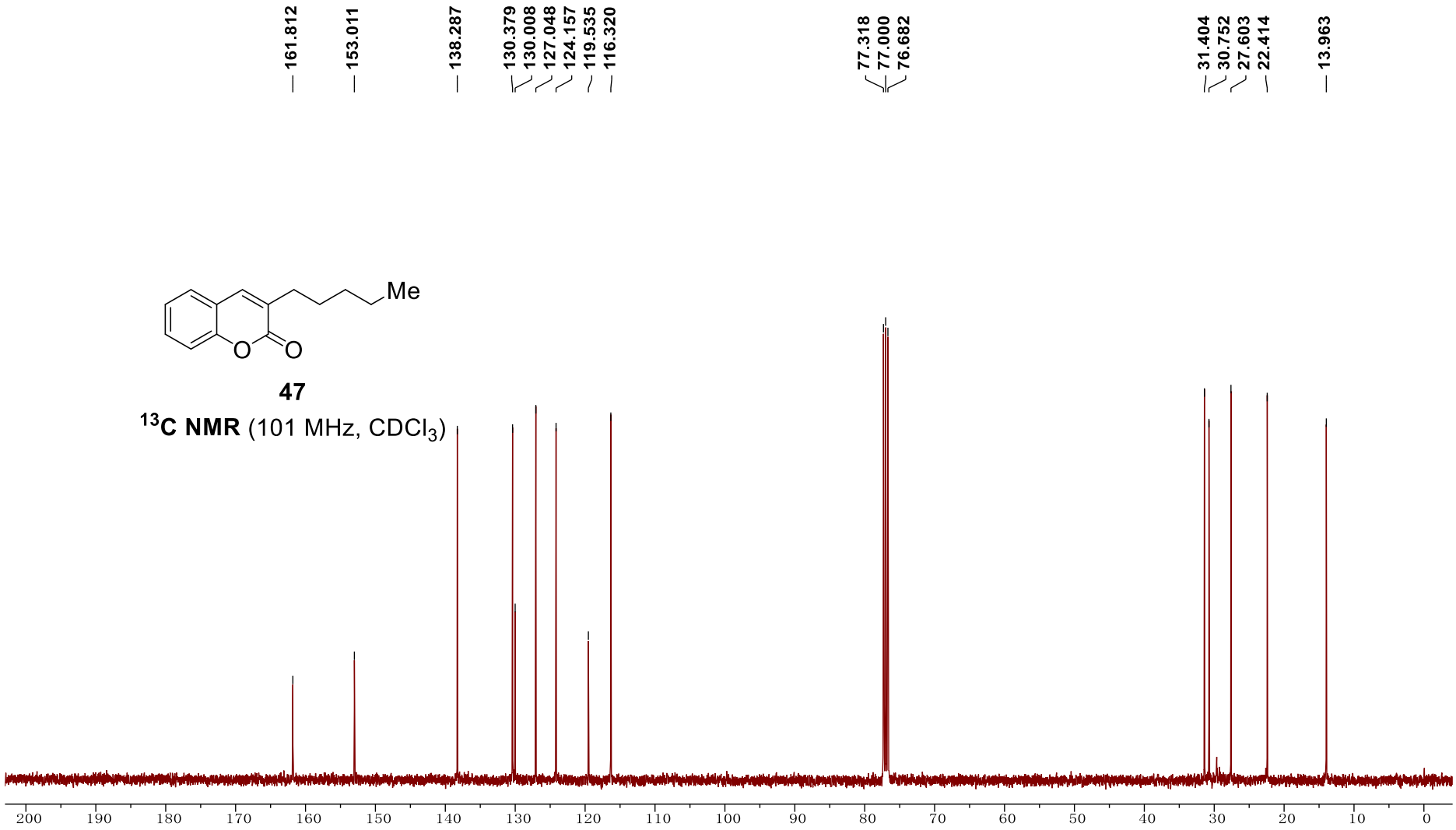

**46**

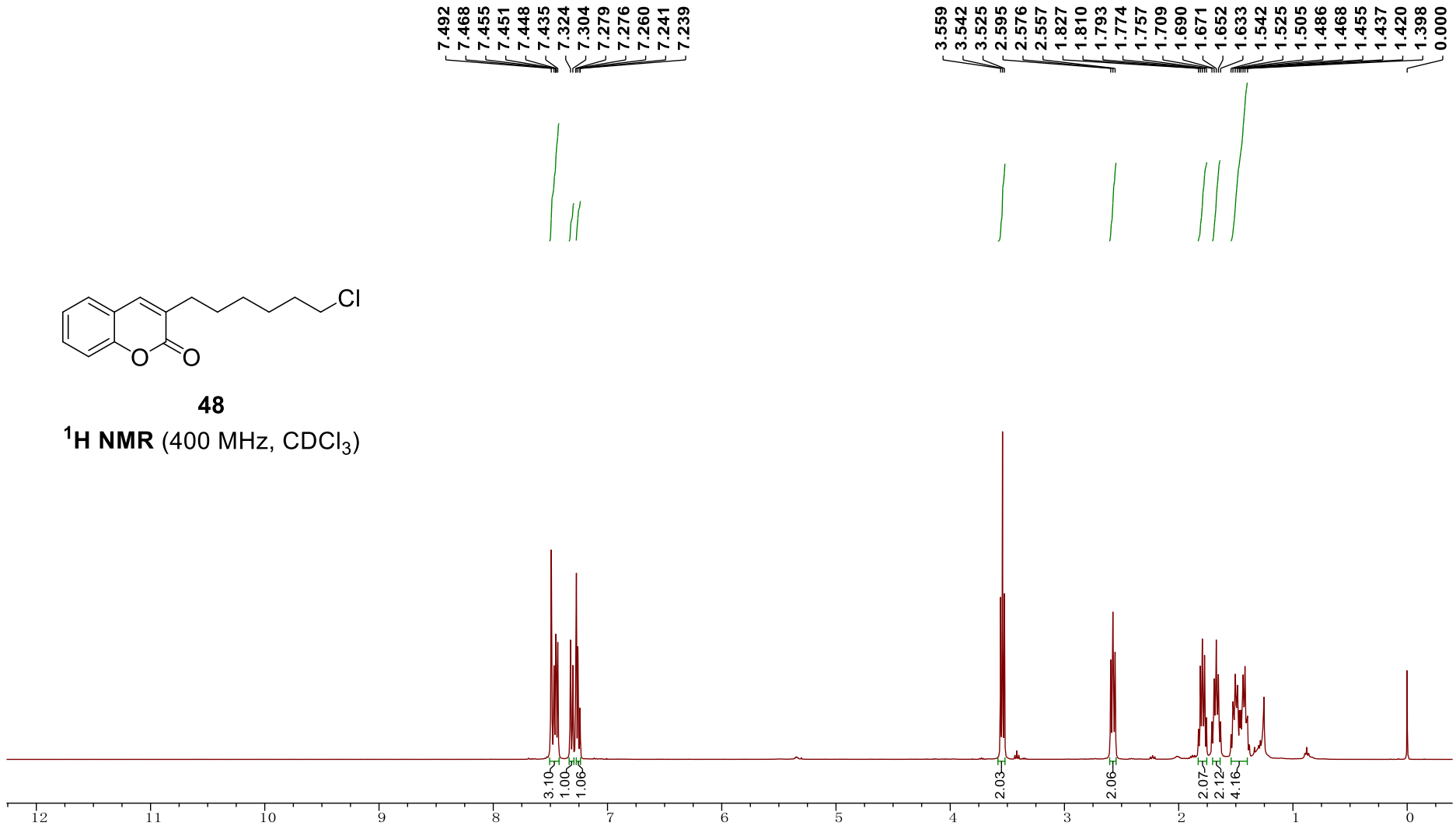
**$^{13}$C NMR** (101 MHz, $CDCl_3$)




**47**

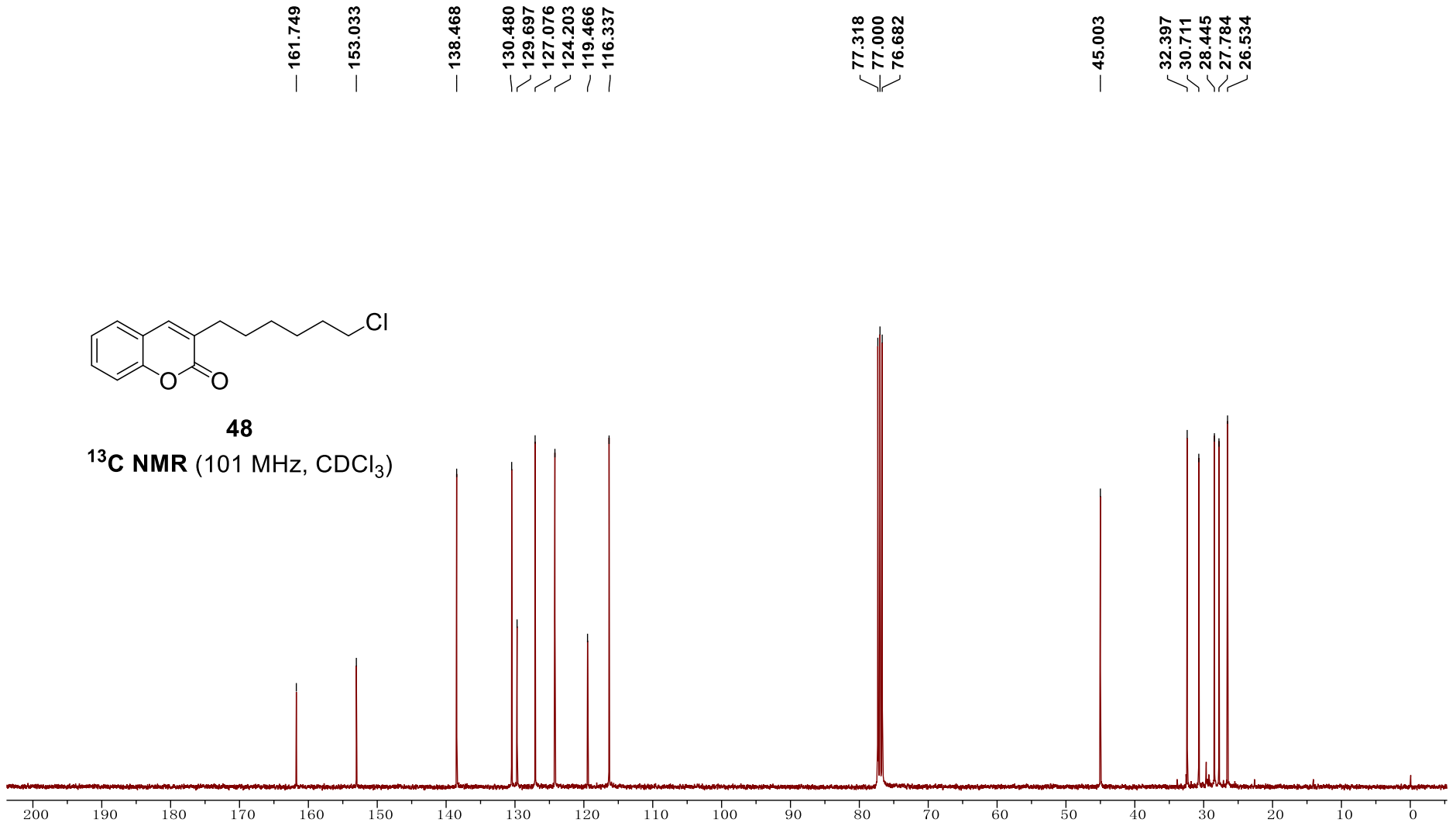
**$^1$H NMR** (400 MHz, $CDCl_3$)

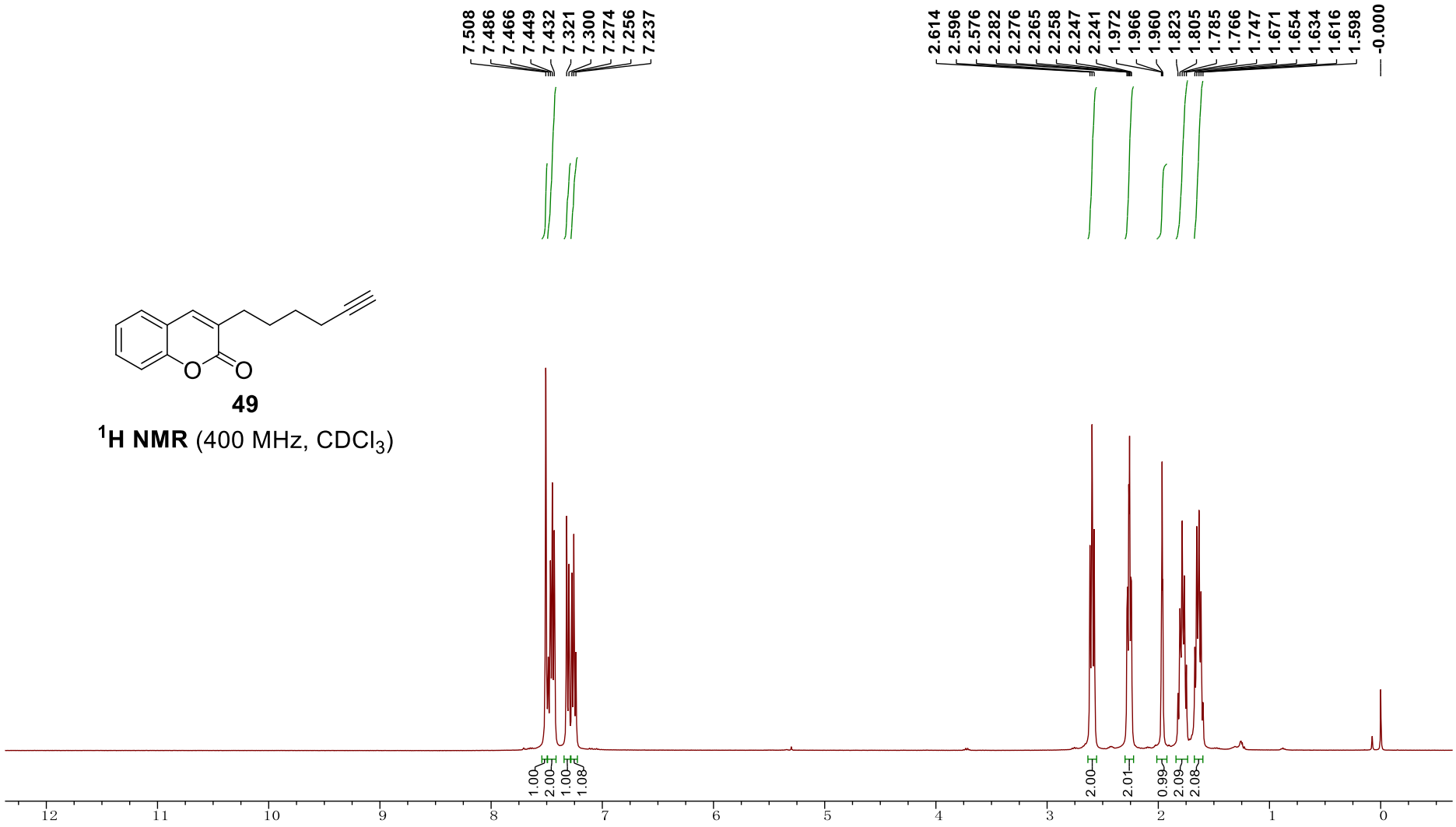

161.812
153.011
138.287
130.379
130.008
127.048
124.157
119.535
116.320
77.318
77.000
76.682
31.404
30.752
27.603
22.414
13.963
Me
O
O
47
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

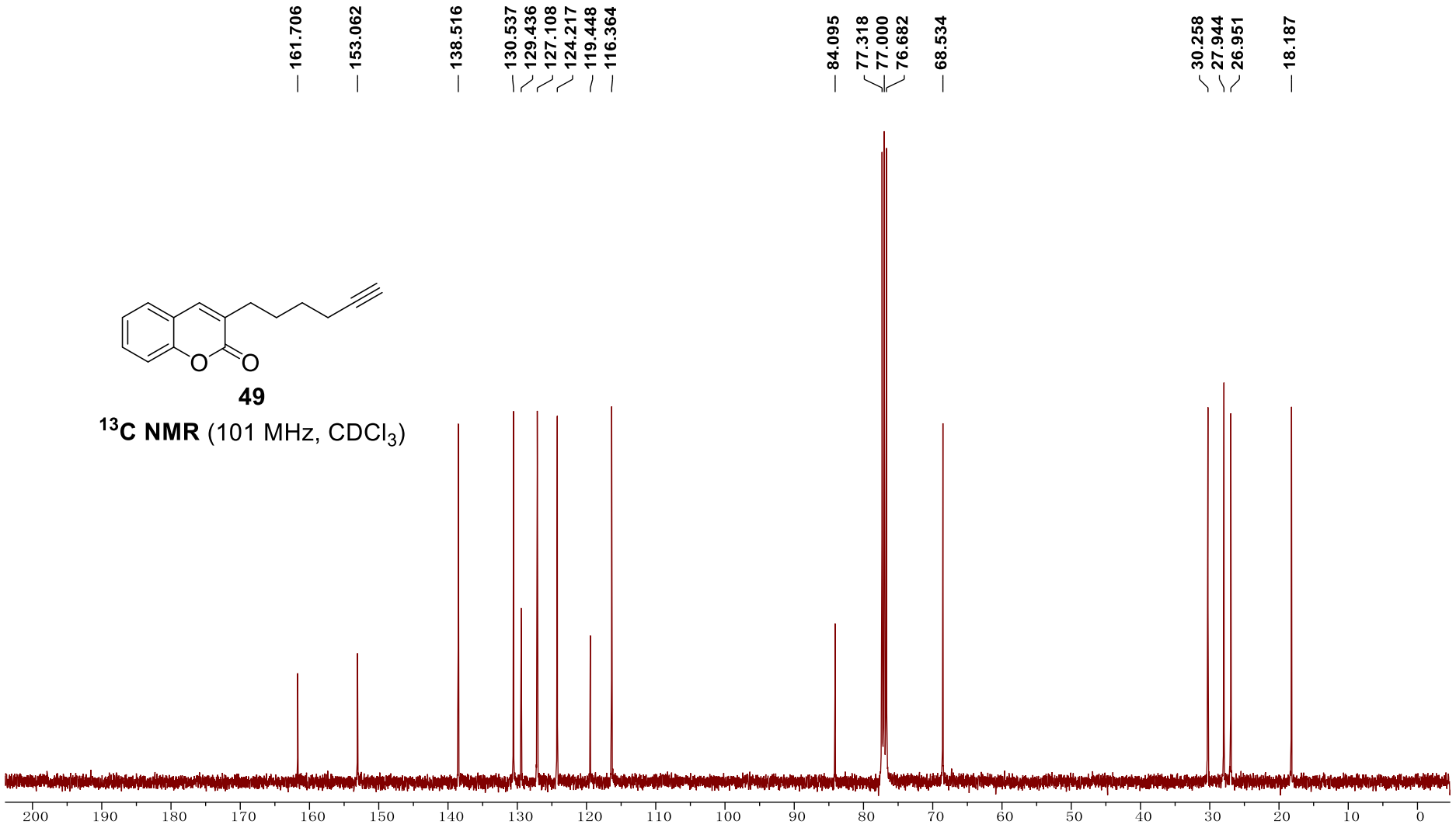


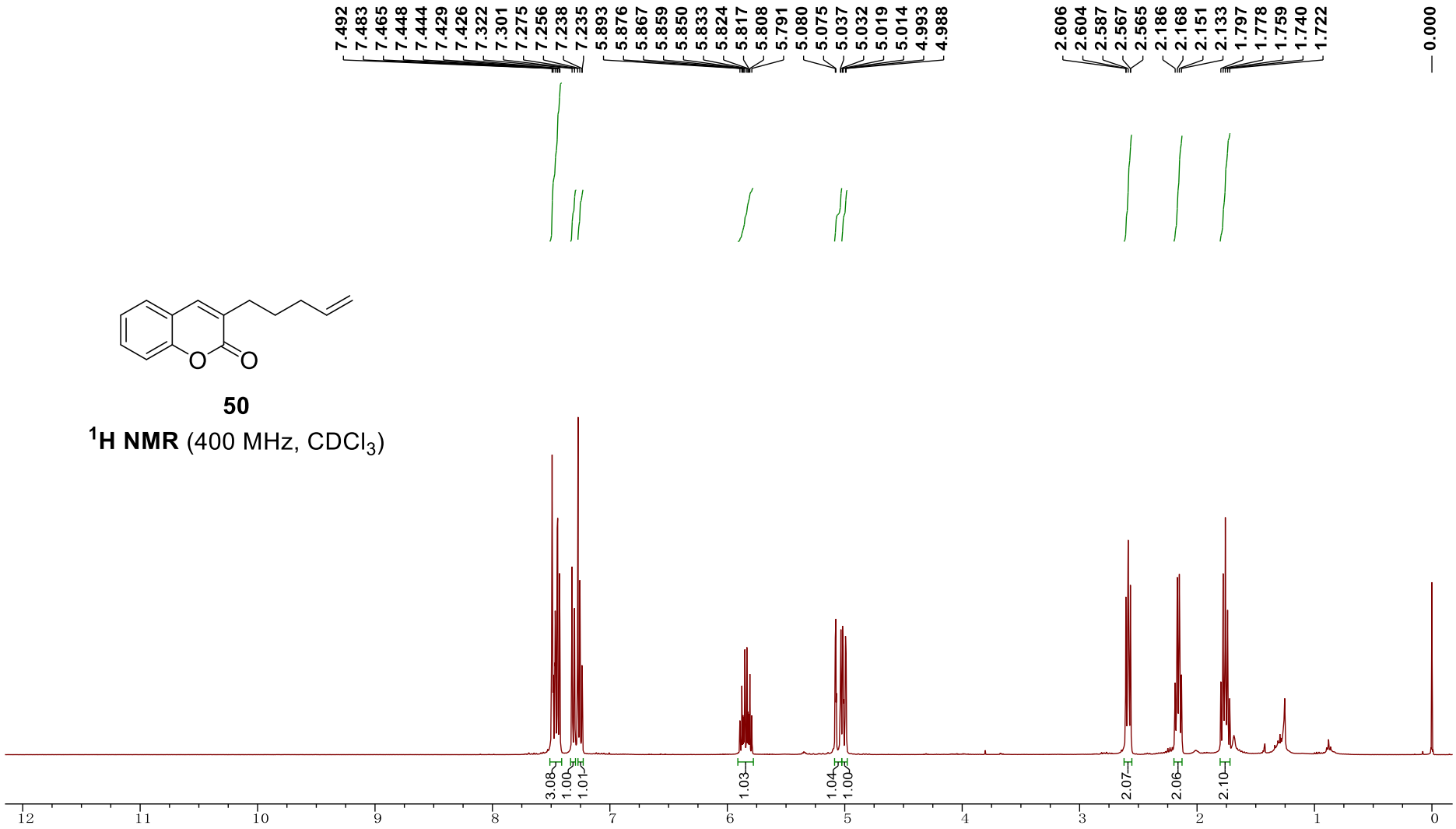

**48**

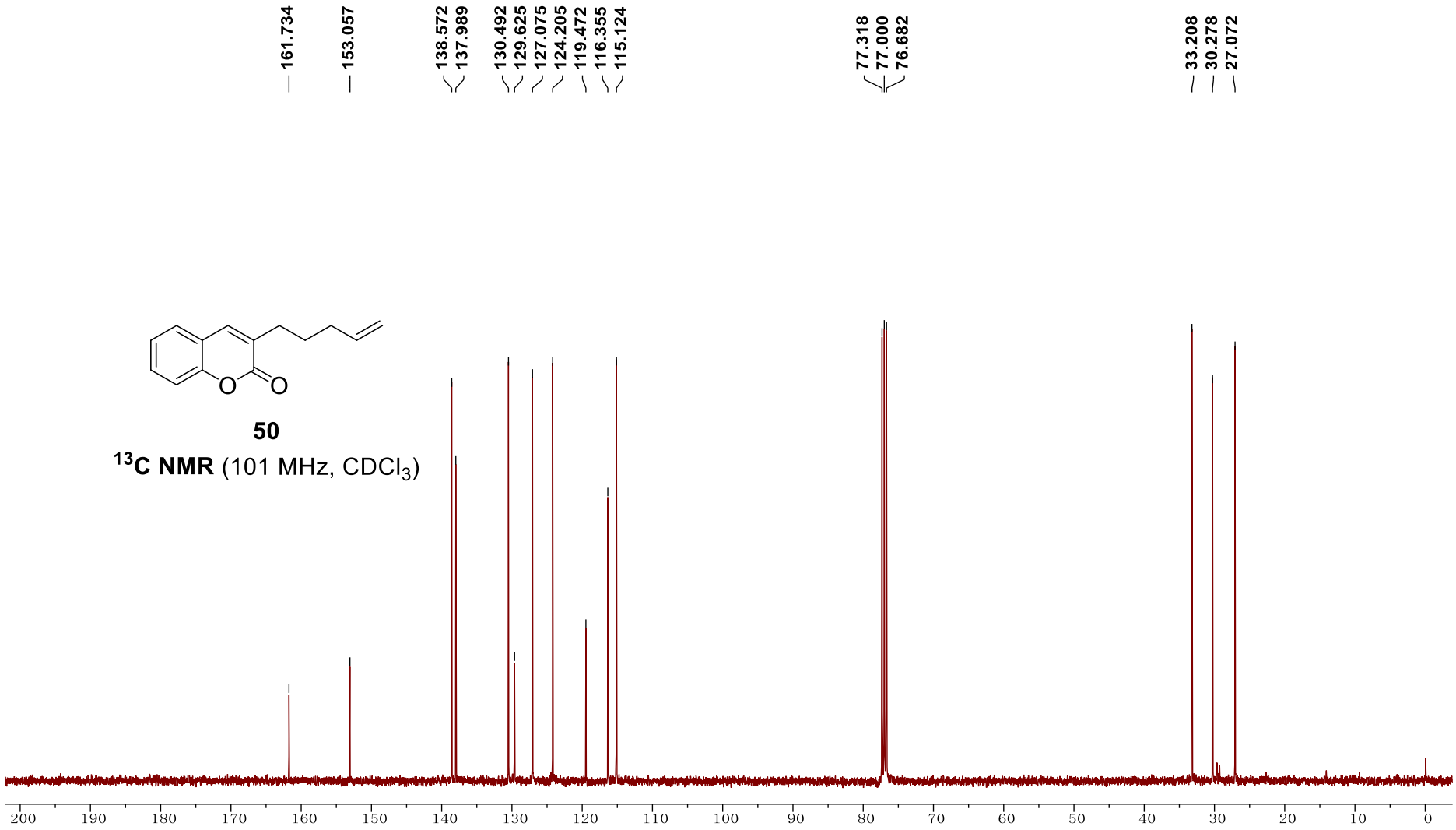
**$^1$H NMR** (400 MHz, $CDCl_3$)

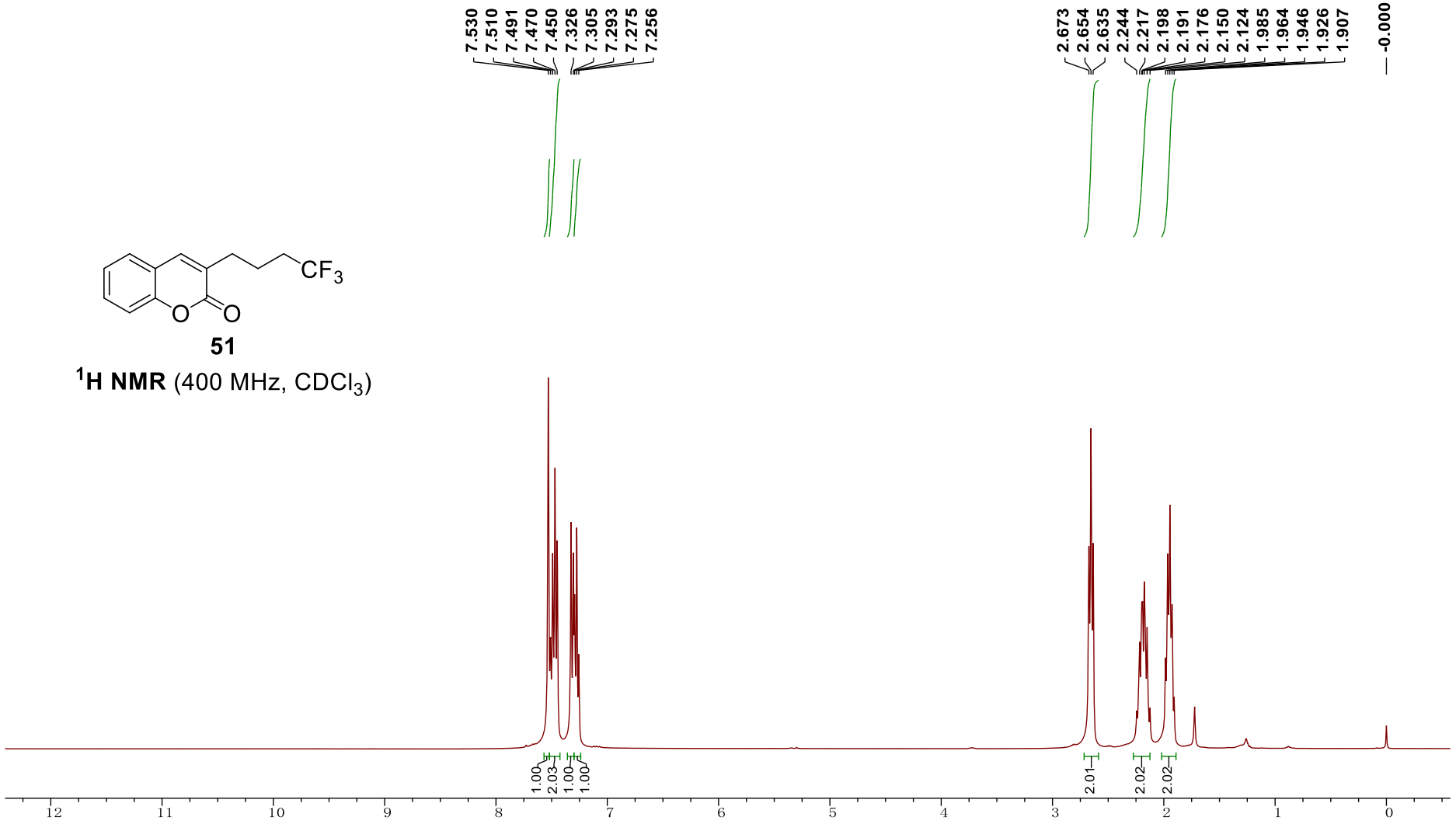

161.749
153.033
138.468
130.480
129.697
127.076
124.203
119.466
116.337
77.318
77.000
76.682
45.003
32.397
30.711
28.445
27.784
26.534
Cl
O
O
48
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.508
7.486
7.466
7.449
7.432
7.321
7.300
7.274
7.256
7.237
2.614
2.596
2.576
2.282
2.276
2.265
2.258
2.247
2.241
1.972
1.966
1.960
1.823
1.805
1.785
1.766
1.747
1.671
1.654
1.634
1.616
1.598
-0.000
O
O
49
1H NMR (400 MHz, CDCl3)
1.00
2.00
1.00
1.08
2.00
2.01
0.99
2.09
2.08
12
11
10
9
8
7
6
5
4
3
2
1
0


161.706
153.062
138.516
130.537
129.436
127.108
124.217
119.448
116.364
84.095
77.318
77.000
76.682
68.534
30.258
27.944
26.951
18.187
O
O
49
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

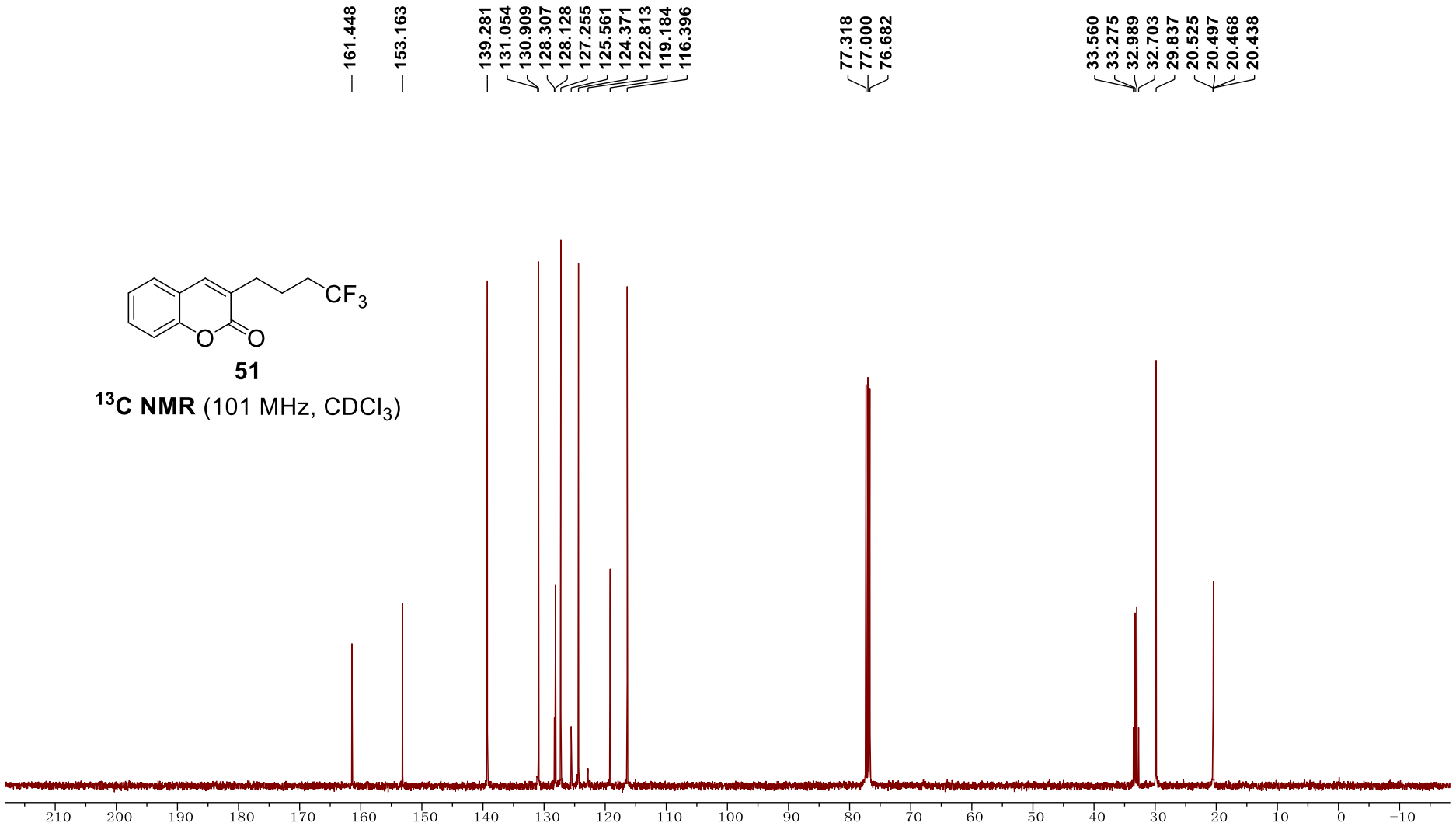

7.492
7.483
7.465
7.448
7.444
7.429
7.426
7.322
7.301
7.275
7.256
7.238
7.235
5.893
5.876
5.867
5.859
5.850
5.833
5.824
5.817
5.808
5.791
5.080
5.075
5.037
5.032
5.019
5.014
4.993
4.988
2.606
2.604
2.587
2.567
2.565
2.186
2.168
2.151
2.133
1.797
1.778
1.759
1.740
1.722
0.000
O
O
50
1H NMR (400 MHz, CDCl3)
3.08
1.00
1.01
1.03
1.04
1.00
2.07
2.06
2.10
12
11
10
9
8
7
6
5
4
3
2
1
0

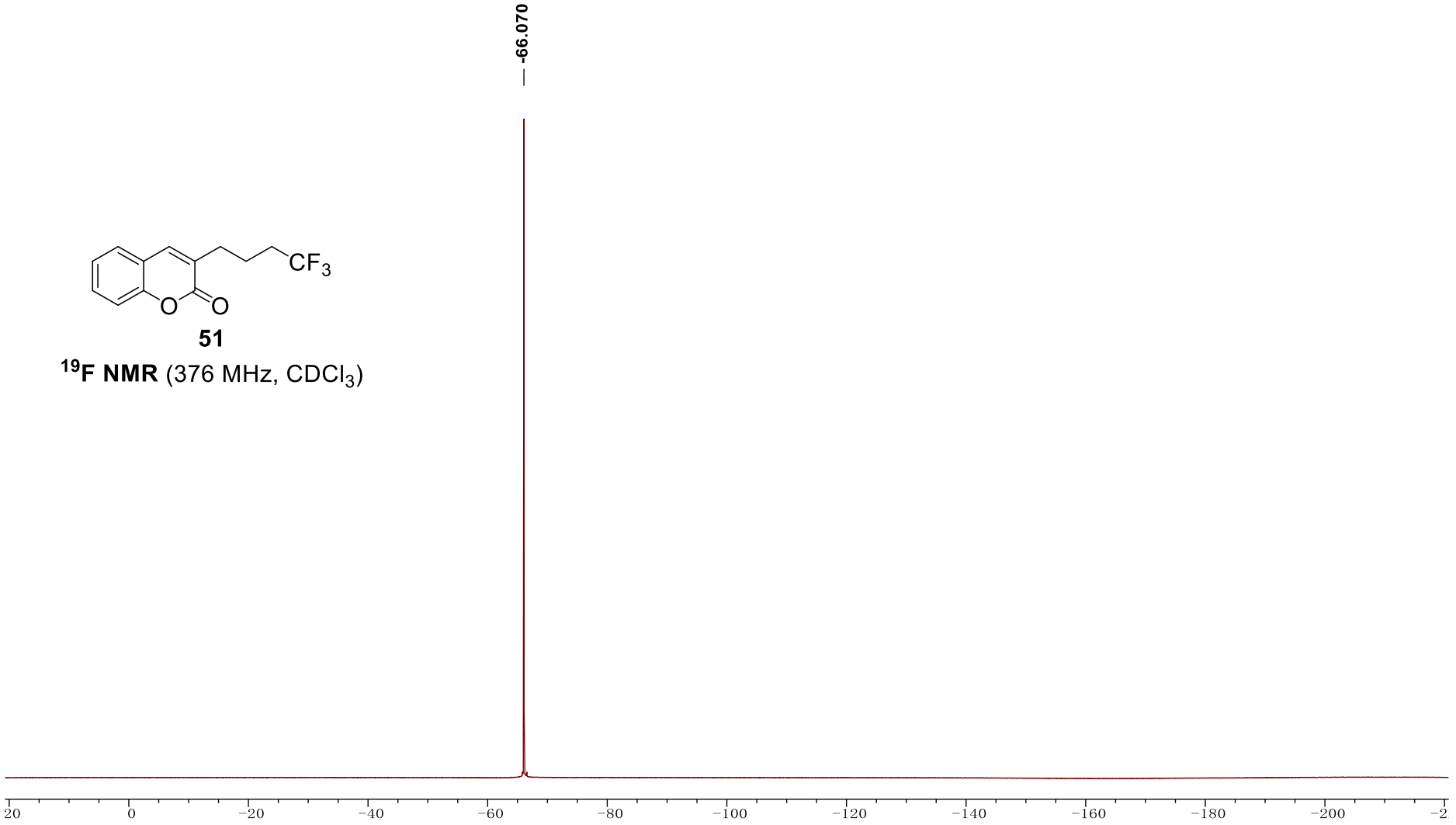

161.734
153.057
138.572
137.989
130.492
129.625
127.075
124.205
119.472
116.355
115.124
77.318
77.000
76.682
33.208
30.278
27.072
O
O
50
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0




**51**

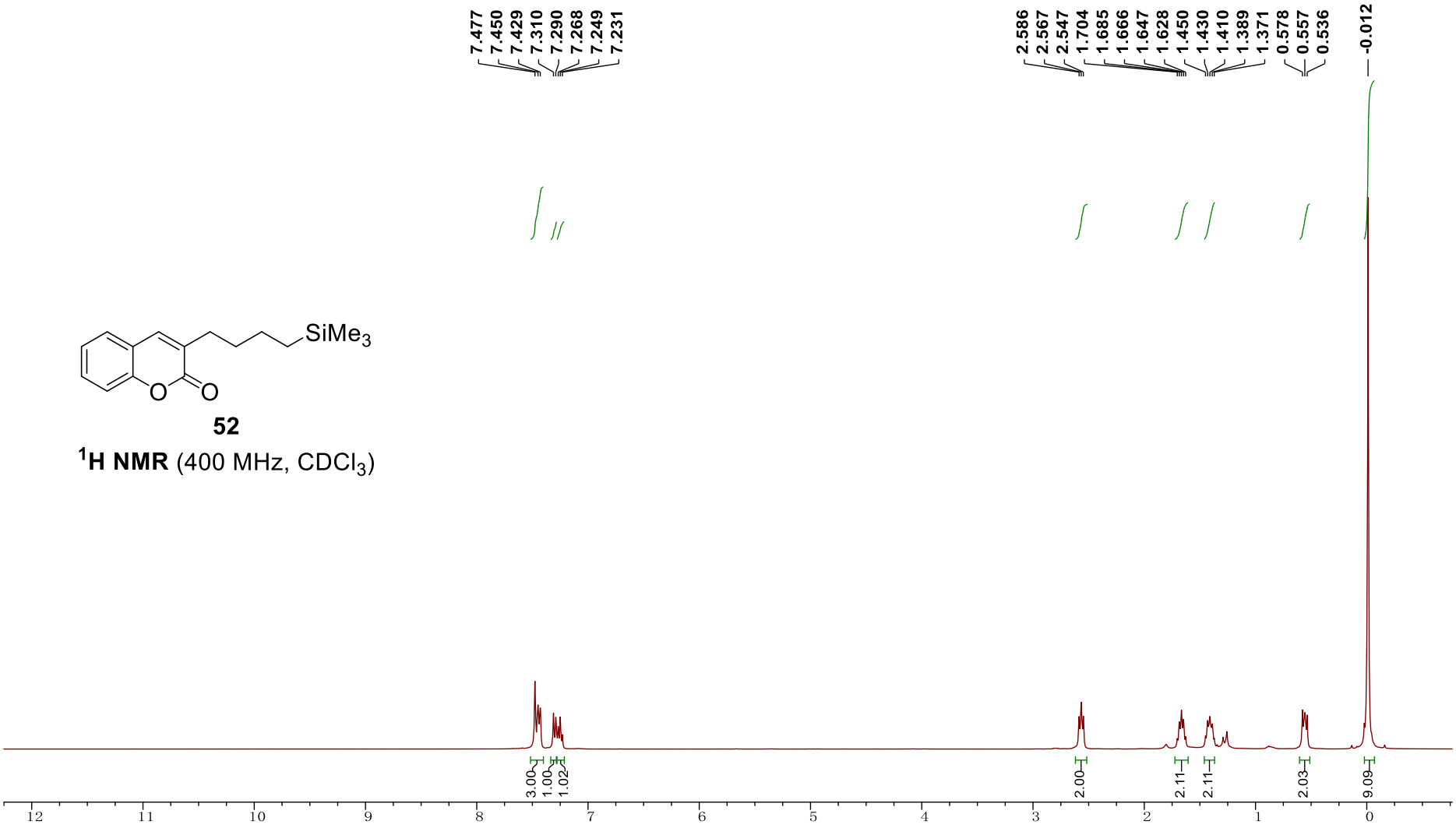
**$^1$H NMR** (400 MHz, $CDCl_3$)


161.448
153.163
139.281
131.054
130.909
128.307
128.128
127.255
125.561
124.371
122.813
119.184
116.396
77.318
77.000
76.682
33.560
33.275
32.989
32.703
29.837
20.525
20.497
20.468
20.438
CF3
O
O
51
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



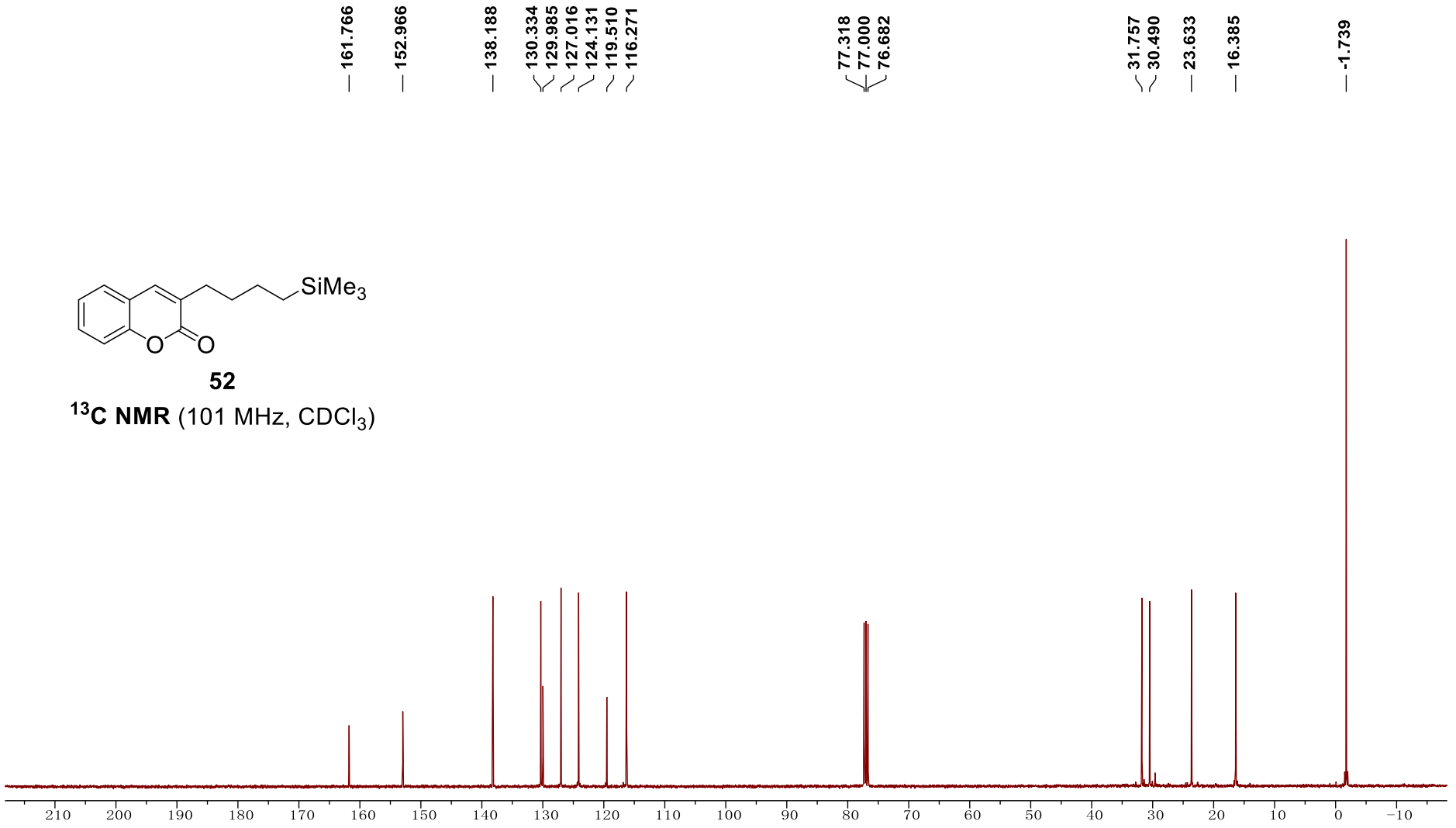

**51**

**$^{19}$F NMR** (376 MHz, $CDCl_3$)



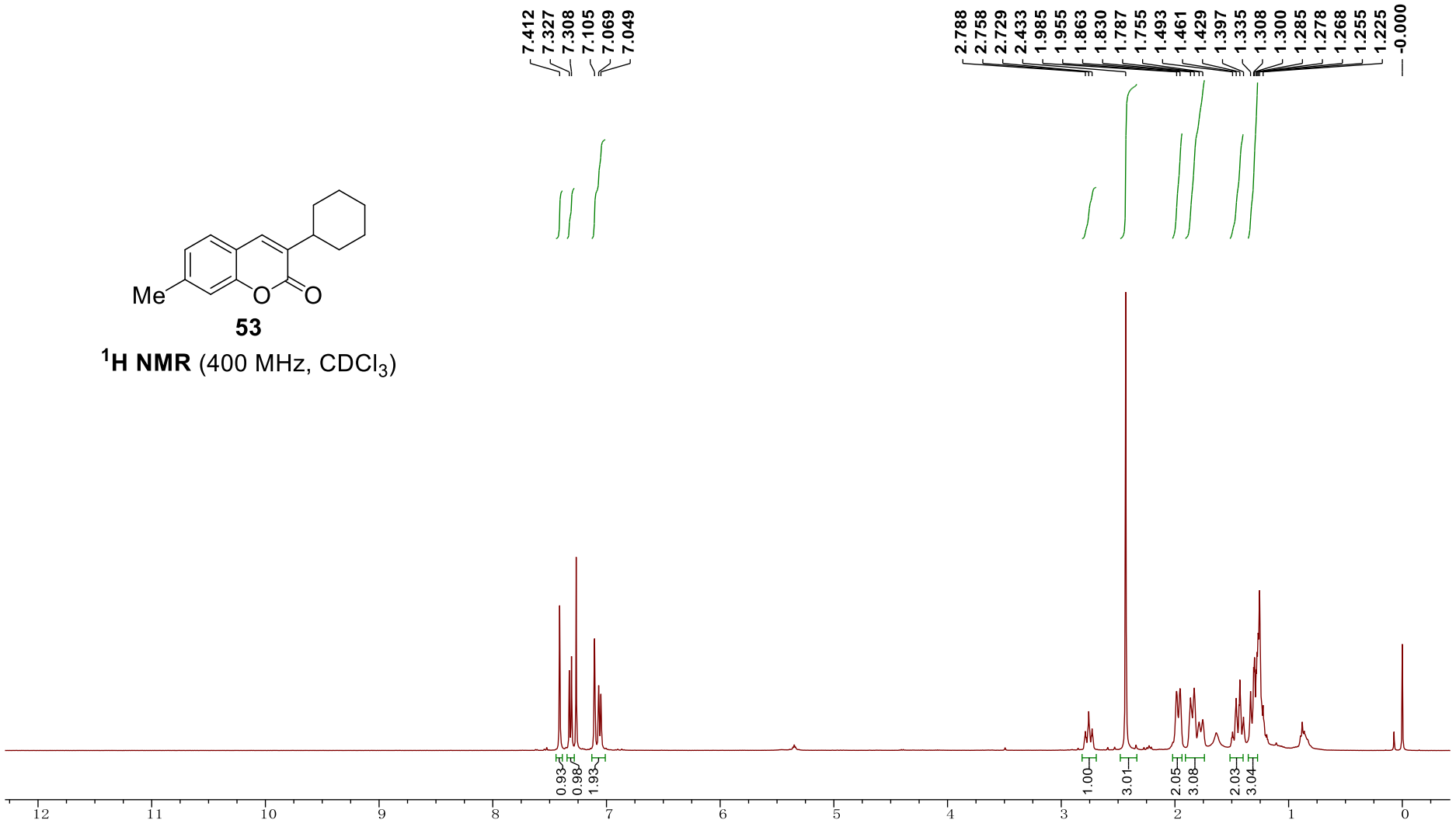

**52**

**$^1$H NMR** (400 MHz, $CDCl_3$)



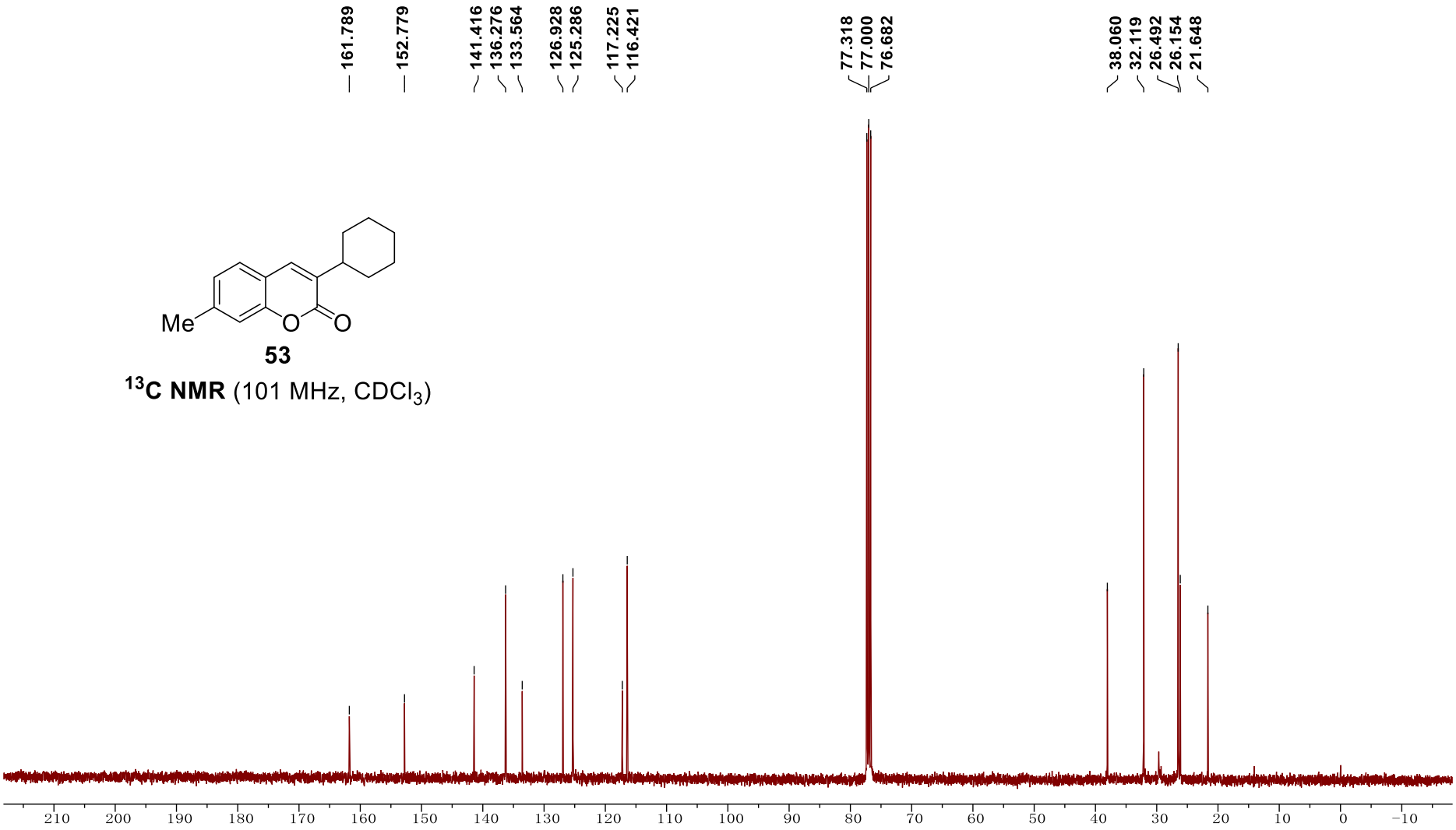

**52**

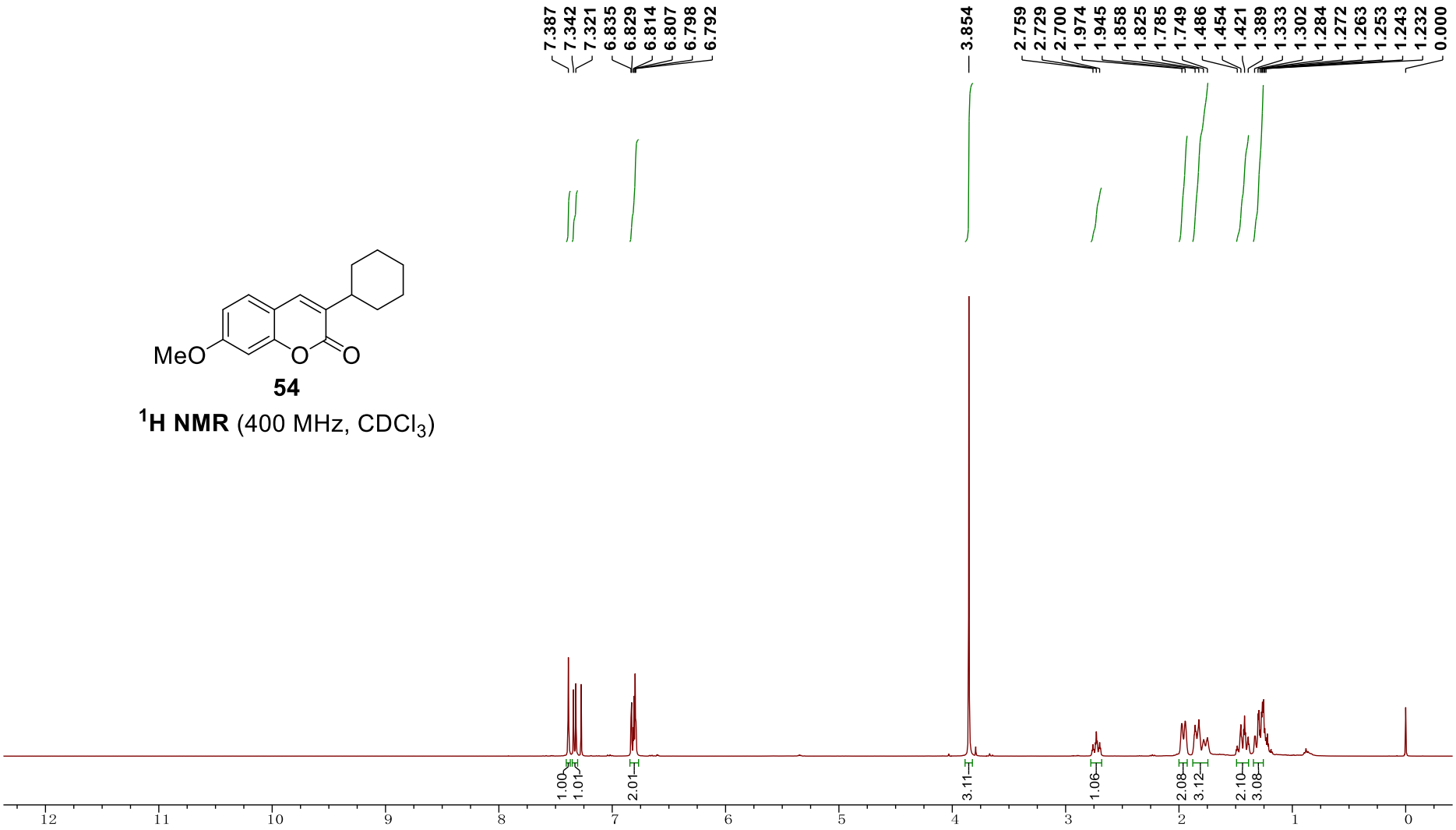
**$^{13}$C NMR** (101 MHz, $CDCl_3$)




**53**

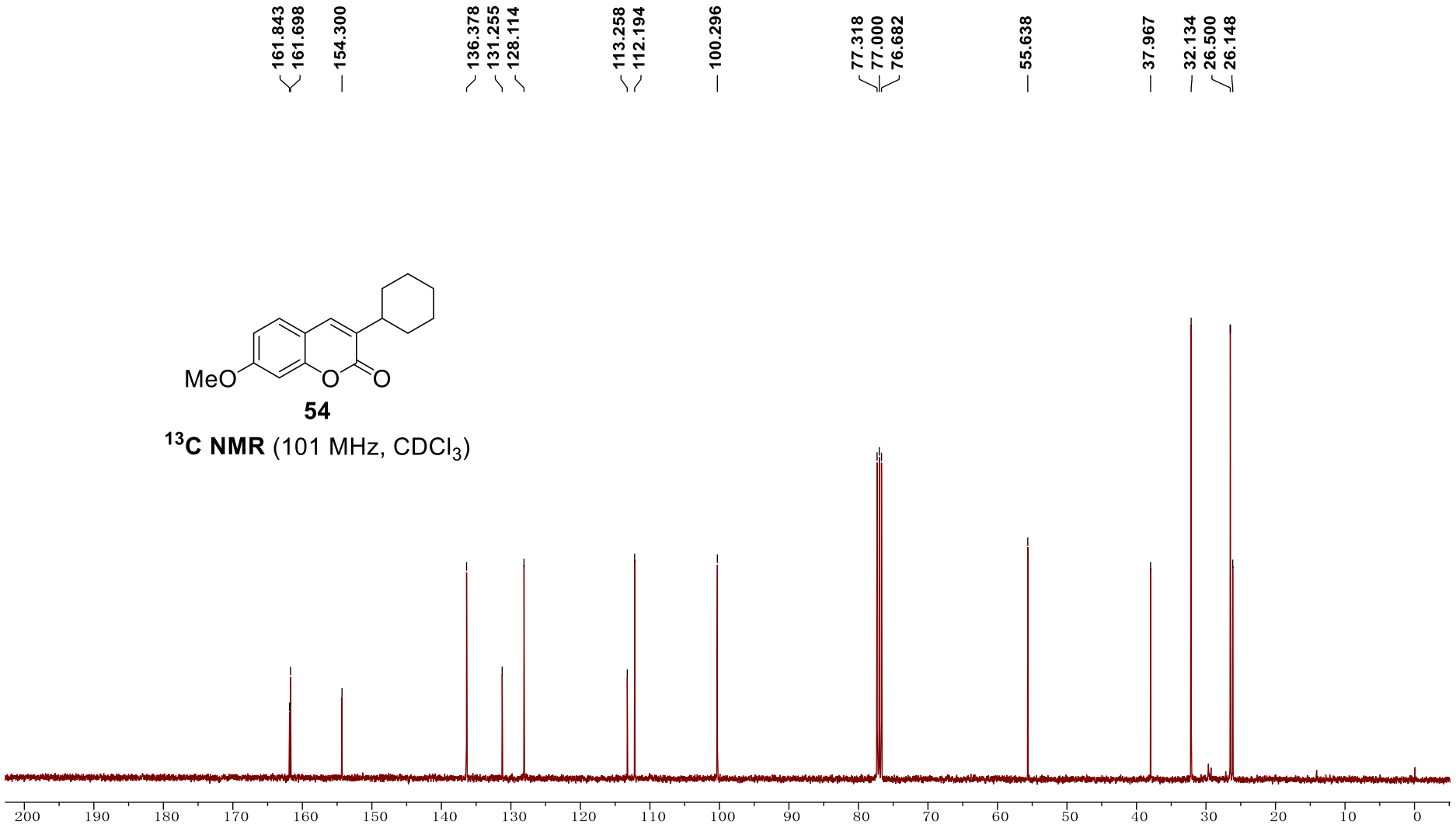
**$^1$H NMR** (400 MHz, $CDCl_3$)

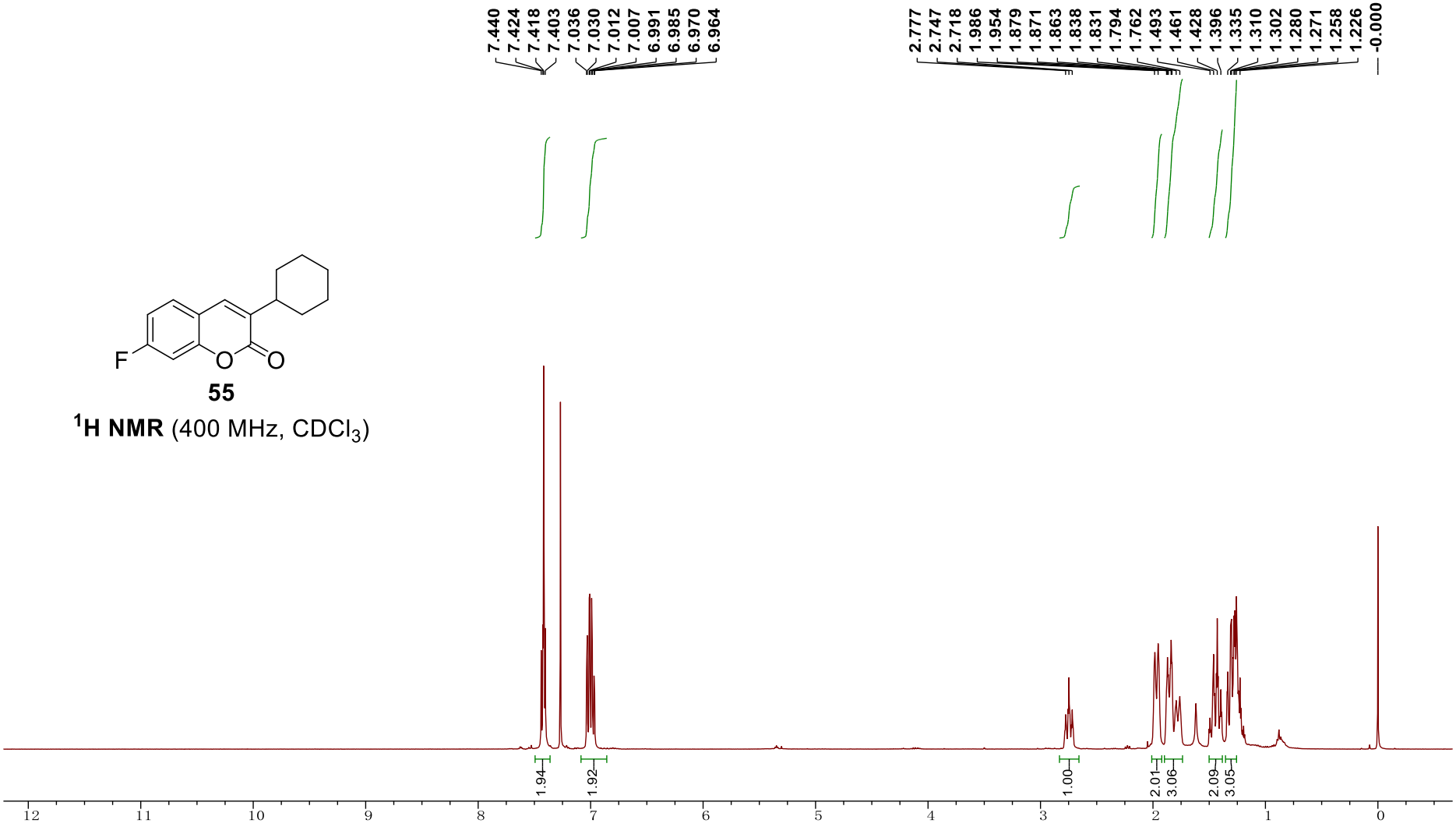

161.789
152.779
141.416
136.276
133.564
126.928
125.286
117.225
116.421
77.318
77.000
76.682
38.060
32.119
26.492
26.154
21.648
Me
O
O
53
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10

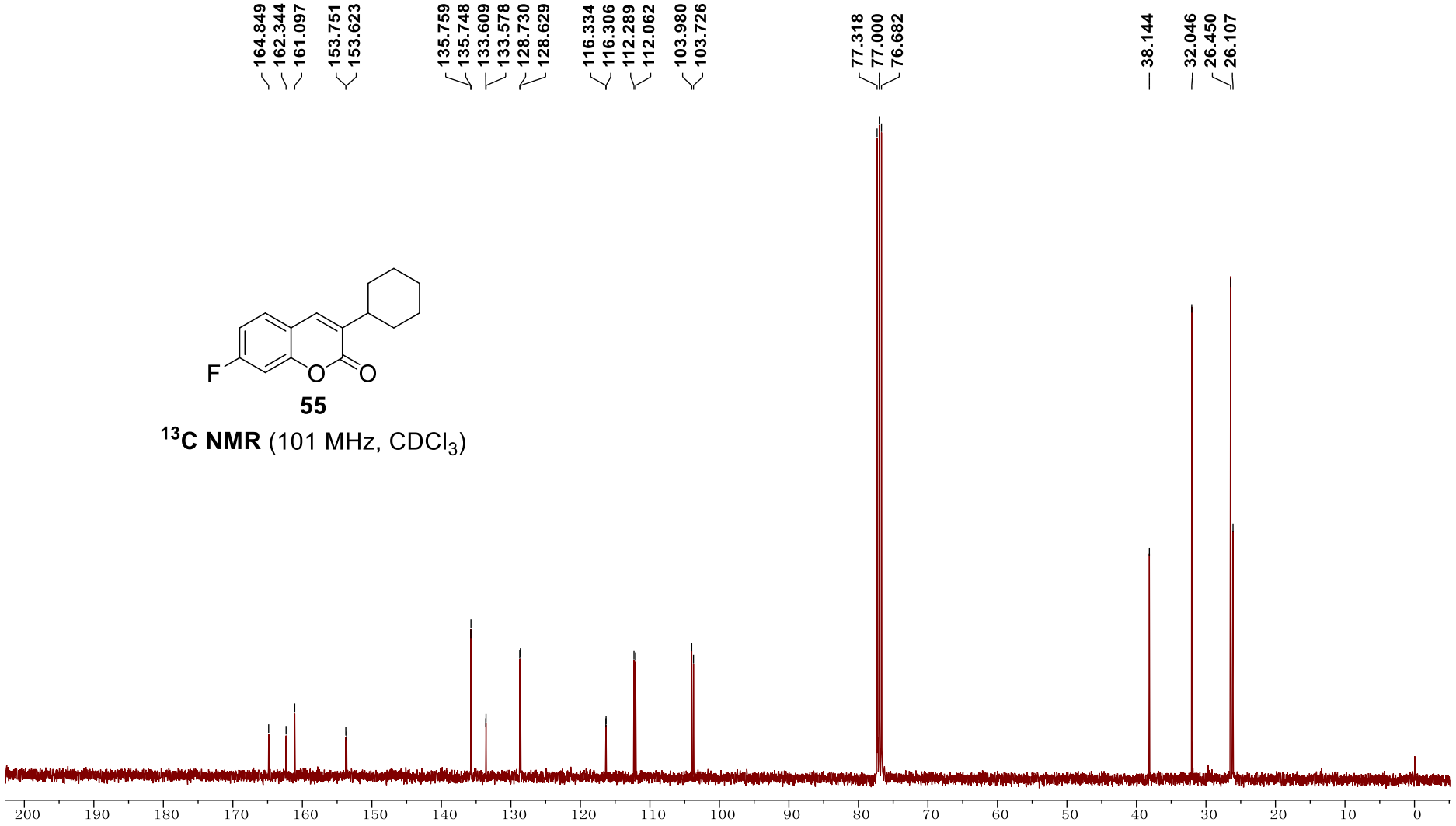



**54**

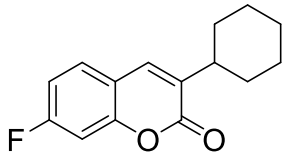
**$^1$H NMR** (400 MHz, $CDCl_3$)


161.843
161.698
154.300
136.378
131.255
128.114
113.258
112.194
100.296
77.318
77.000
76.682
55.638
37.967
32.134
26.500
26.148
MeO
O
O
54
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0


7.440
7.424
7.418
7.403
7.036
7.030
7.012
7.007
6.991
6.985
6.970
6.964
2.777
2.747
2.718
1.986
1.954
1.879
1.871
1.863
1.838
1.831
1.794
1.762
1.493
1.461
1.428
1.396
1.335
1.310
1.302
1.280
1.271
1.258
1.226
-0.000
F
O
O
55
1H NMR (400 MHz, CDCl3)
1.94
1.92
1.00
2.01
3.06
2.09
3.05
12
11
10
9
8
7
6
5
4
3
2
1
0

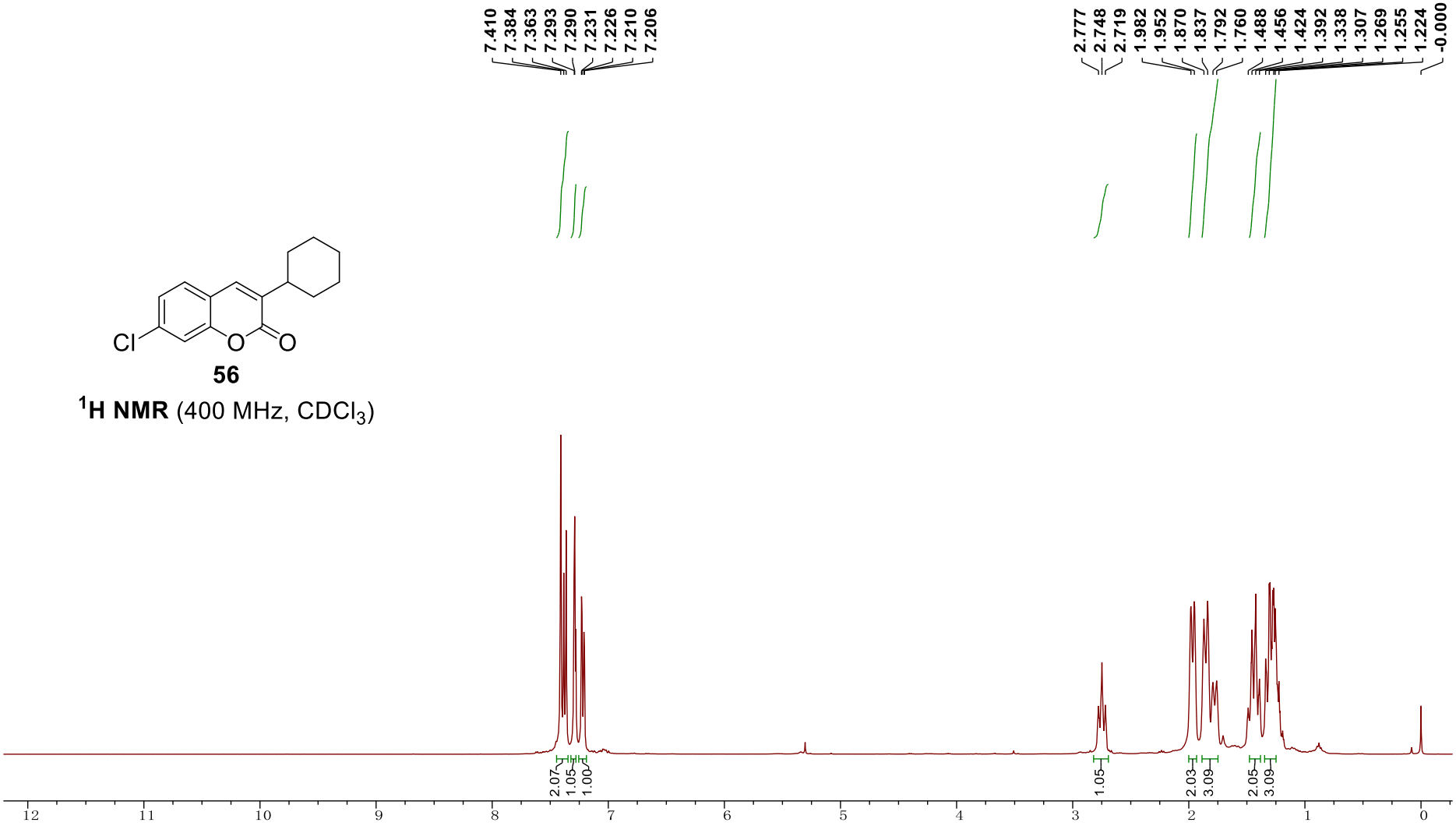


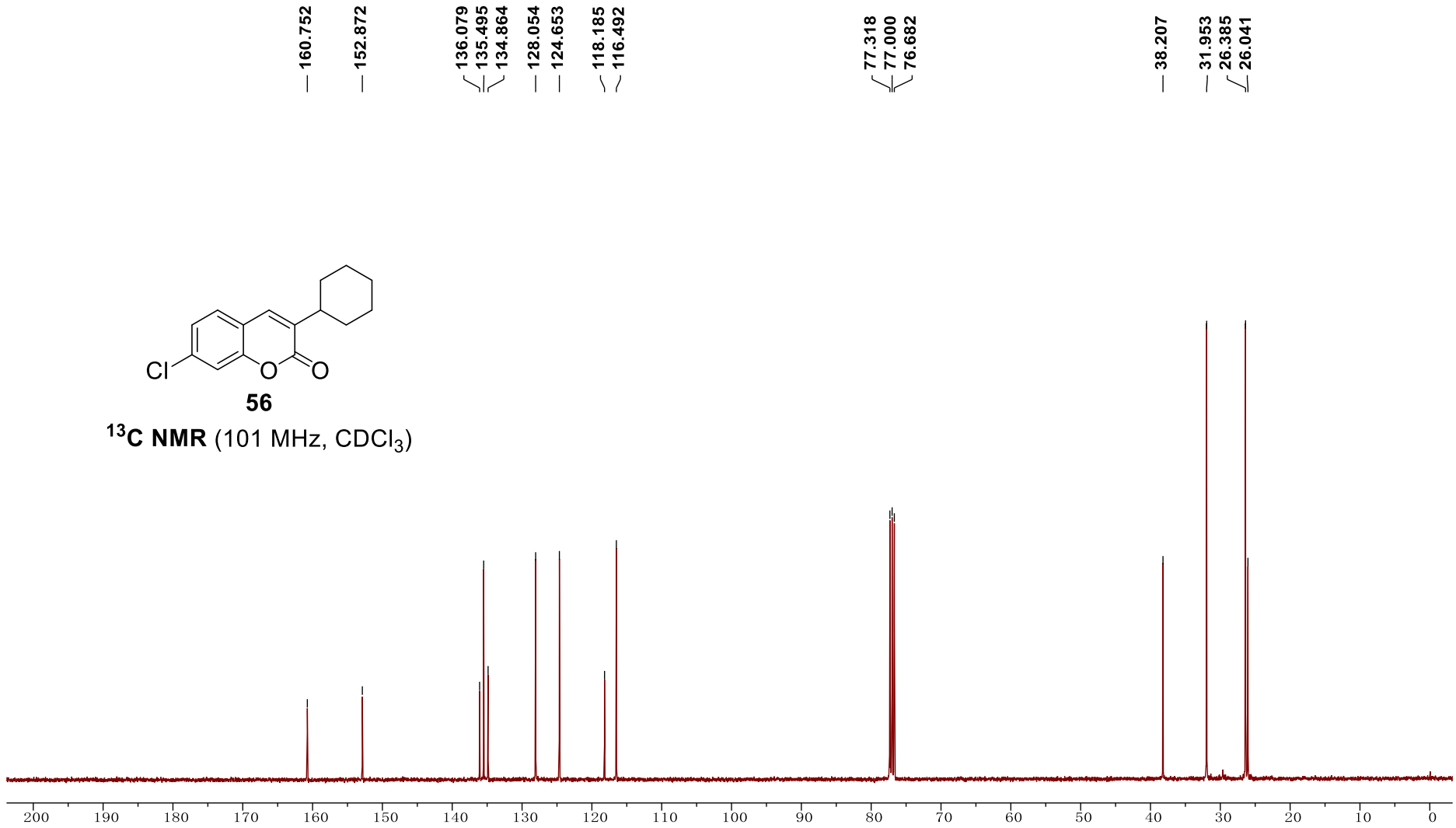

**$^{13}$C NMR** (101 MHz, $CDCl_3$)




**55**

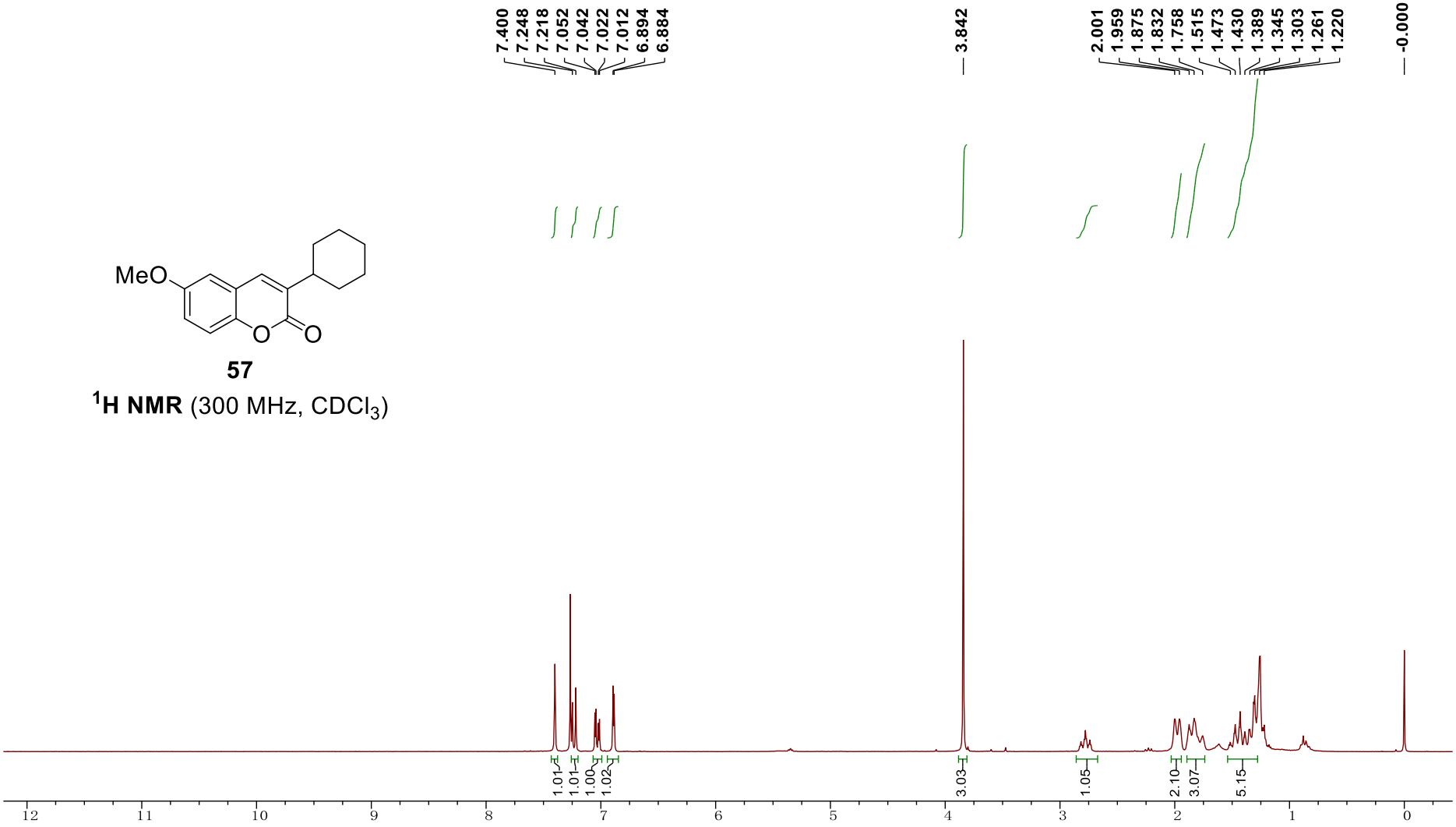
**$^{19}$F NMR** (282 MHz, $CDCl_3$)


7.410
7.384
7.363
7.293
7.290
7.231
7.226
7.210
7.206
2.777
2.748
2.719
1.982
1.952
1.870
1.837
1.792
1.760
1.488
1.456
1.424
1.392
1.338
1.307
1.269
1.255
1.224
-0.000
Cl
O
O
56
1H NMR (400 MHz, CDCl3)
2.07
1.05
1.00
1.05
2.03
3.09
2.05
3.09
12
11
10
9
8
7
6
5
4
3
2
1
0



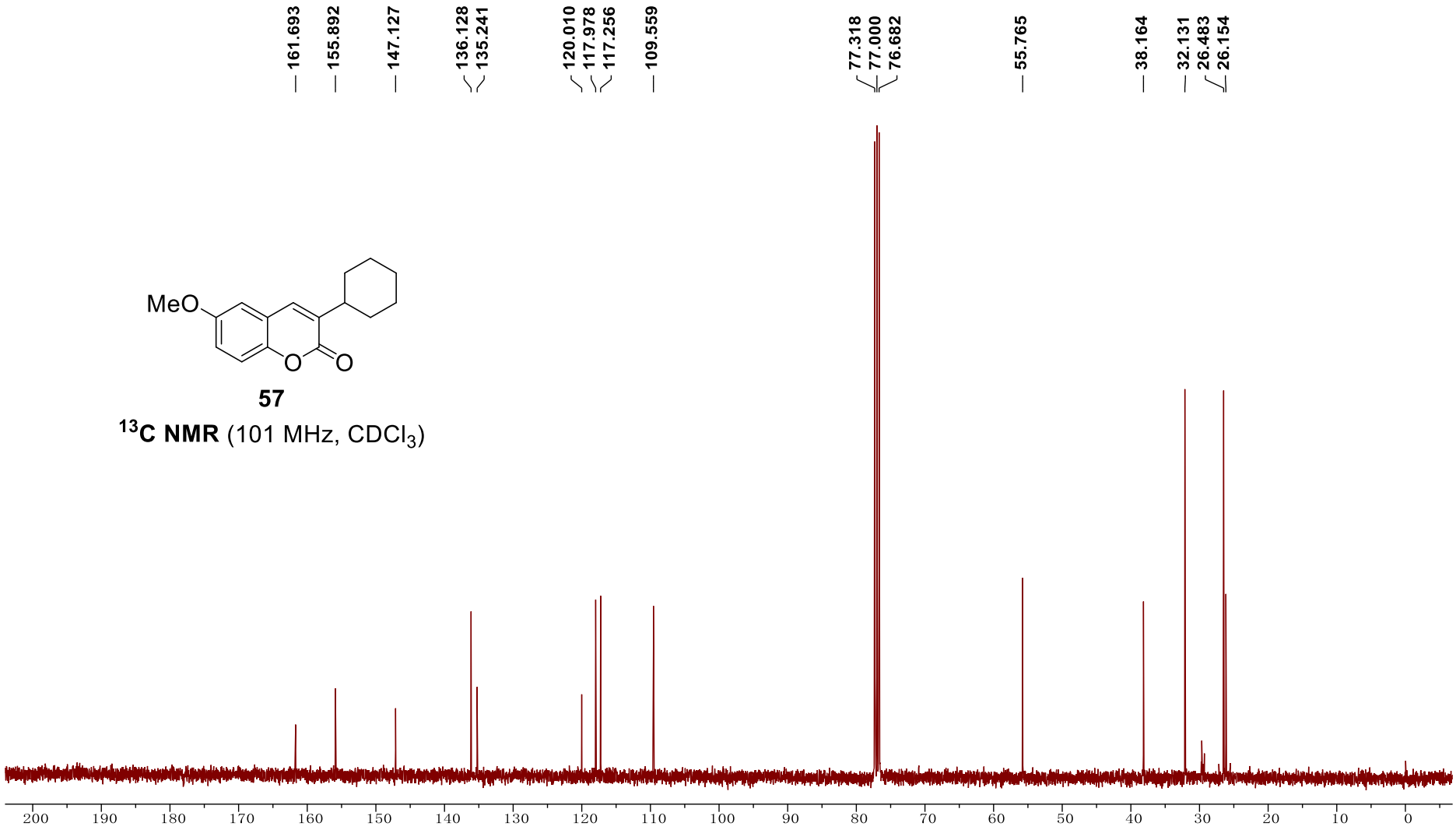

**56**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



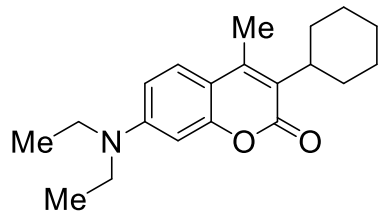

**57**

**$^1$H NMR** (300 MHz, $CDCl_3$)



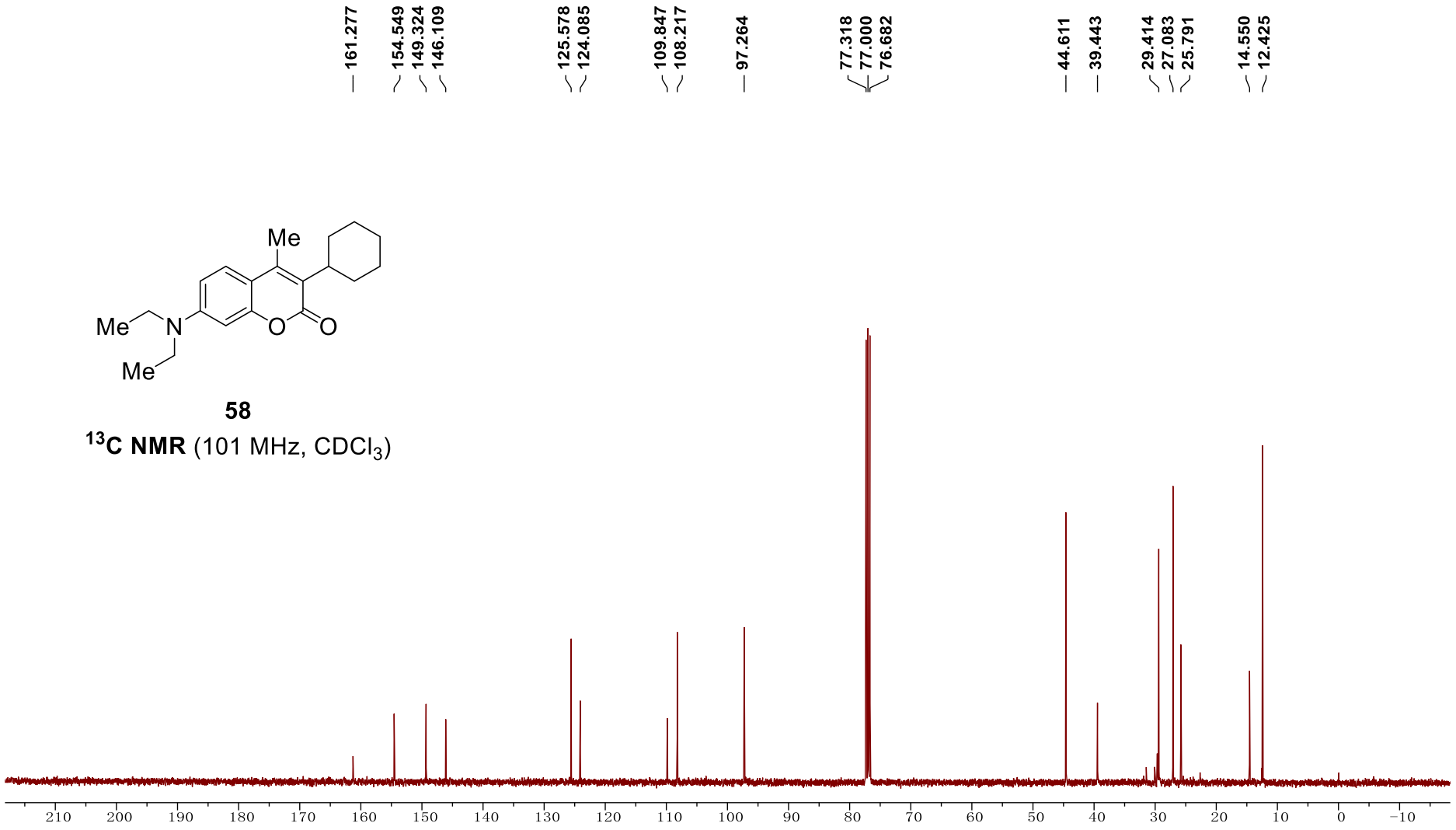

**57**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)



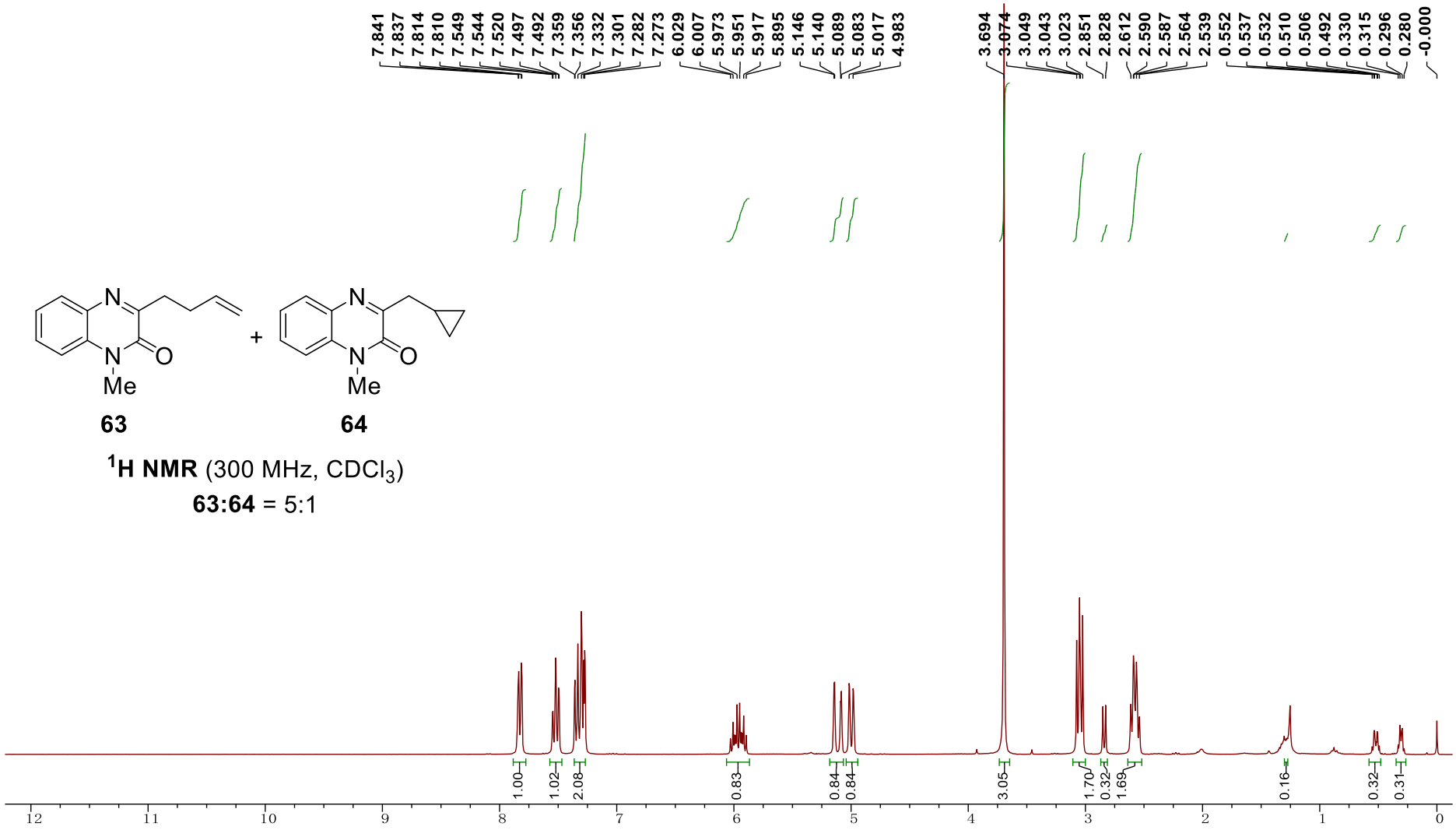

**58**

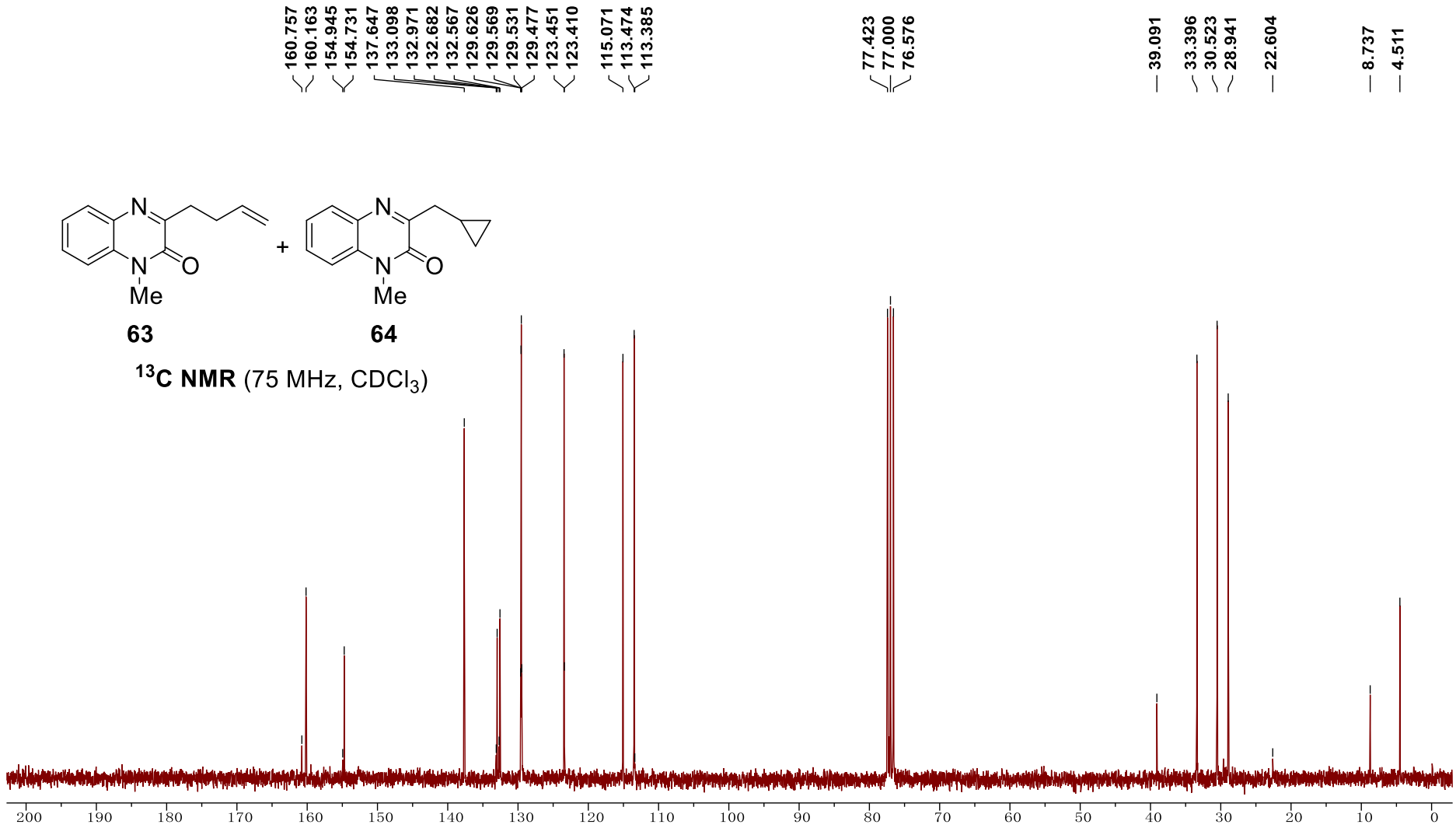
**$^1$H NMR** (400 MHz, $CDCl_3$)

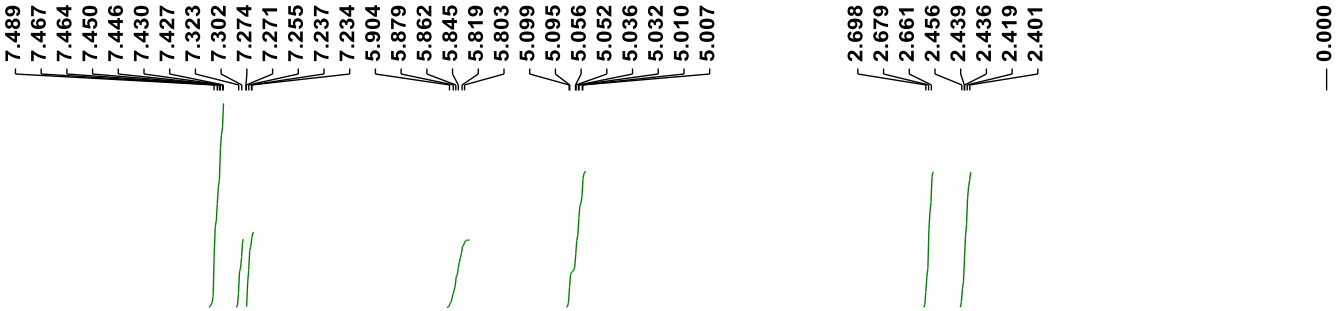


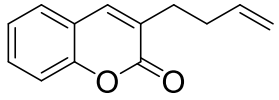

**58**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)


7.841
7.837
7.814
7.810
7.549
7.544
7.520
7.497
7.492
7.359
7.356
7.332
7.301
7.282
7.273
6.029
6.007
5.973
5.951
5.917
5.895
5.146
5.140
5.089
5.083
5.017
4.983
3.694
3.074
3.049
3.043
3.023
2.851
2.828
2.612
2.590
2.587
2.564
2.539
0.552
0.537
0.532
0.510
0.506
0.492
0.330
0.315
0.296
0.280
-0.000
N
O
N
Me
+
N
O
N
Me
63
64
1H NMR (300 MHz, CDCl3)
63:64 = 5:1
1.00
1.02
2.08
0.83
0.84
0.84
3.05
1.70
0.32
1.69
0.16
0.32
0.31
12
11
10
9
8
7
6
5
4
3
2
1
0

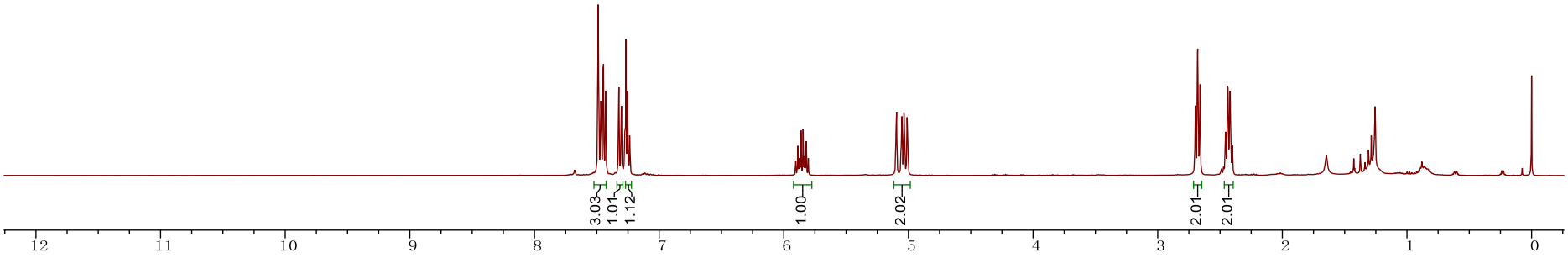

160.757
160.163
154.945
154.731
137.647
133.098
132.971
132.682
132.567
129.626
129.569
129.531
129.477
123.451
123.410
115.071
113.474
113.385
77.423
77.000
76.576
39.091
33.396
30.523
28.941
22.604
8.737
4.511
N
N
O
Me
+
N
N
O
Me
63
64
13C NMR (75 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

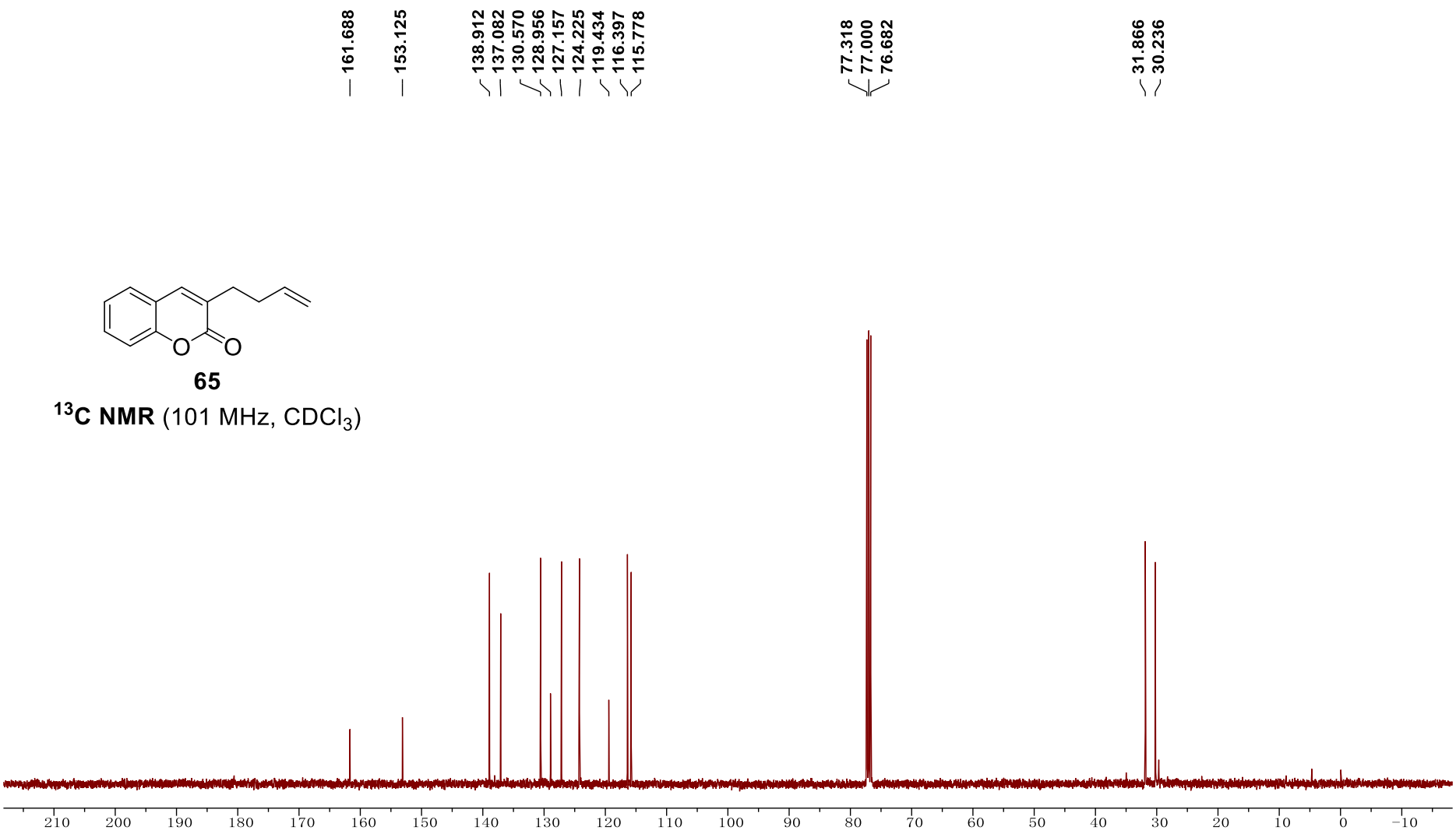


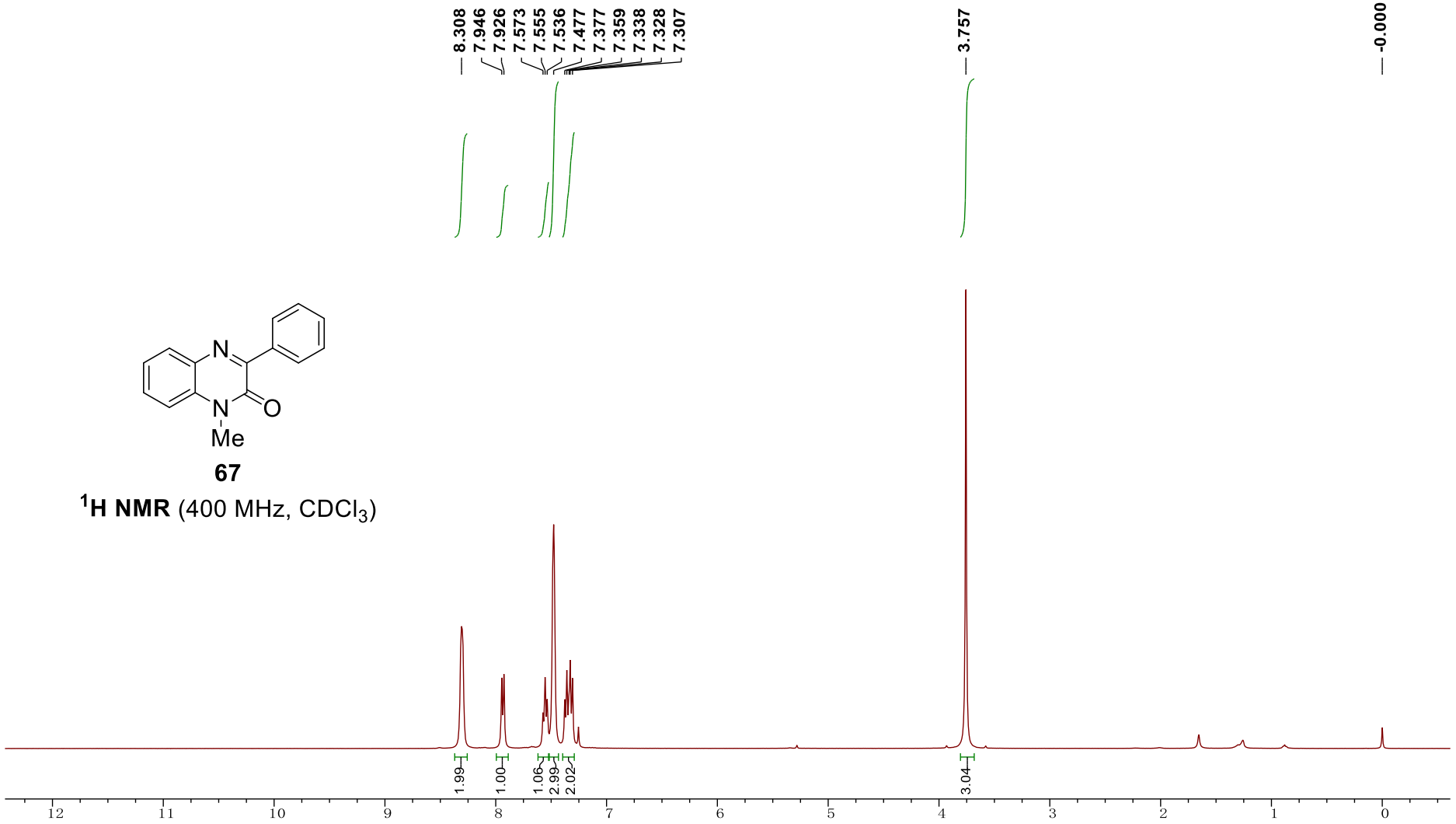



**65**

**$^1$H NMR** (400 MHz, $CDCl_3$)

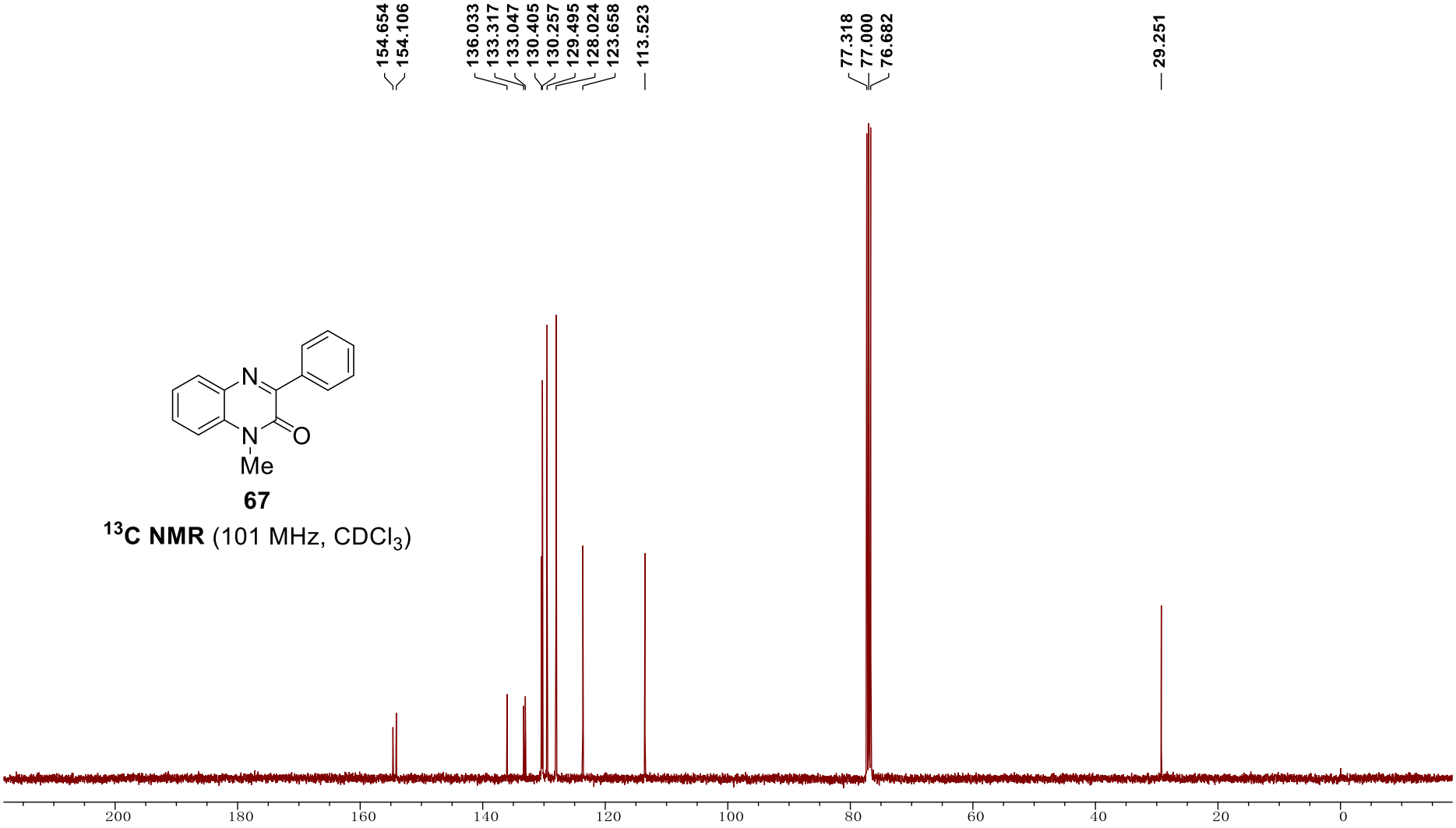



161.688
153.125
138.912
137.082
130.570
128.956
127.157
124.225
119.434
116.397
115.778
77.318
77.000
76.682
31.866
30.236
O
O
65
13C NMR (101 MHz, CDCl3)
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
−10



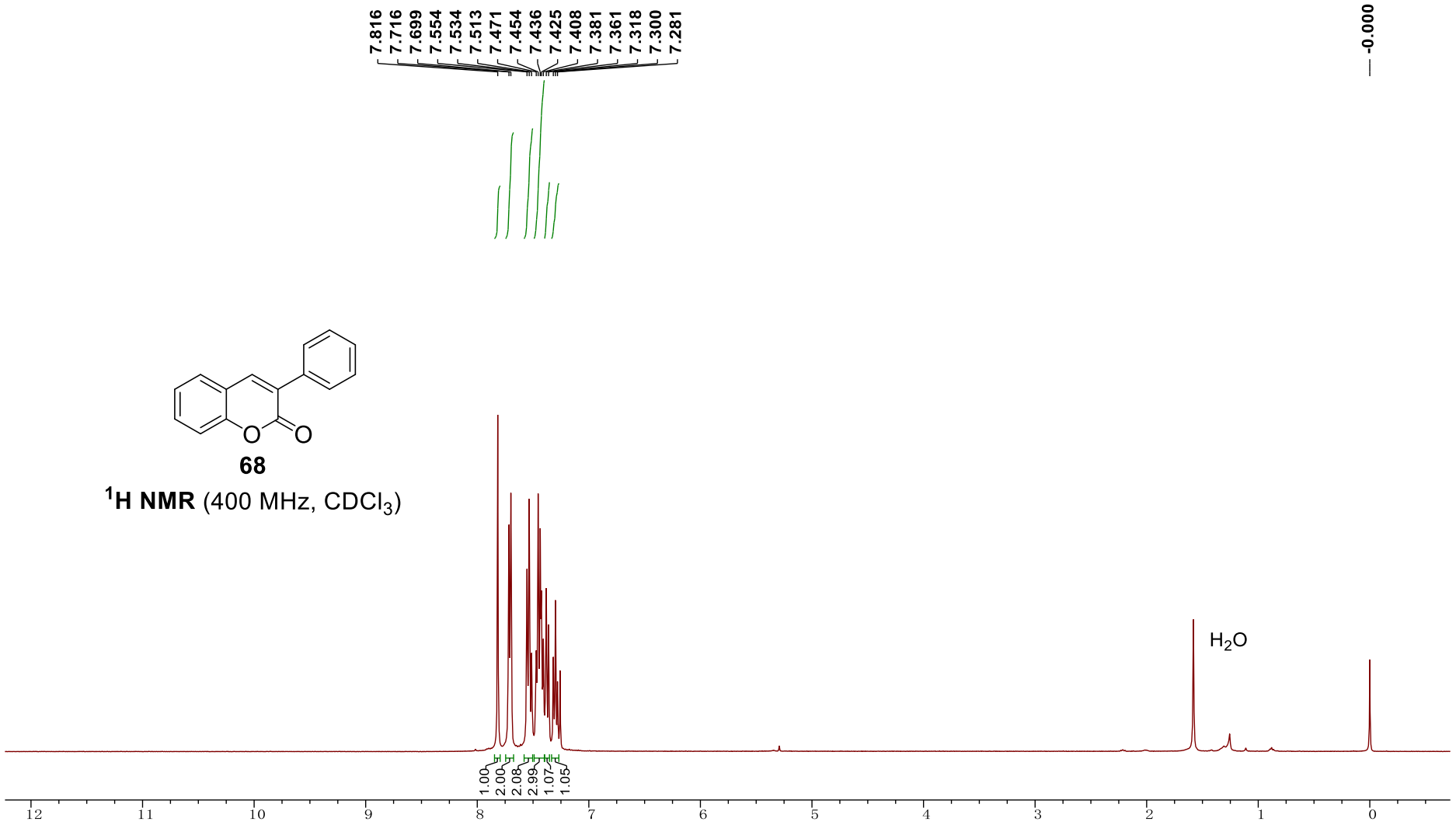

**67**

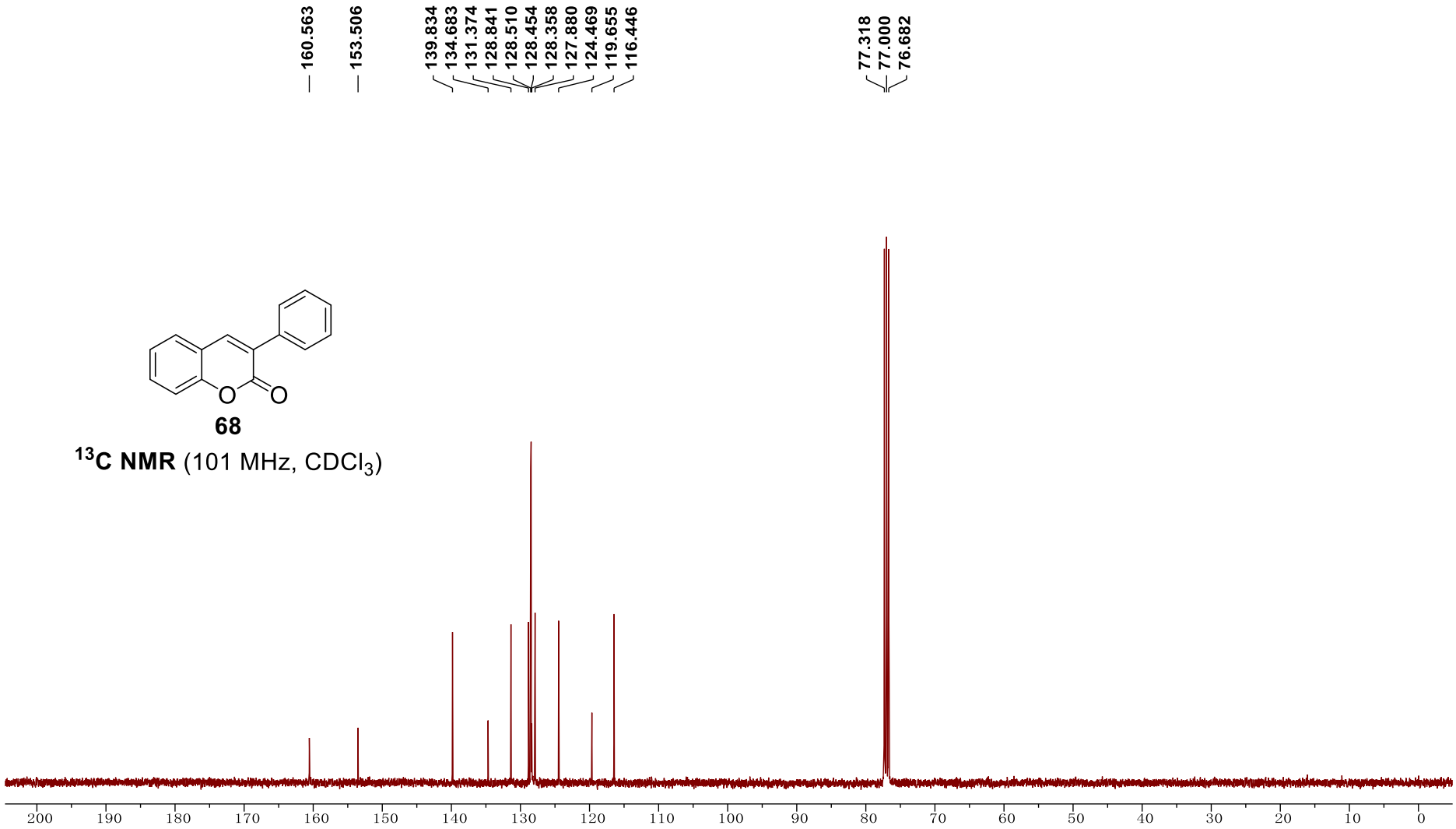
**$^1$H NMR** (400 MHz, $CDCl_3$)




**67**

**$^{13}$C NMR** (101 MHz, $CDCl_3$)


7.816
7.716
7.699
7.554
7.534
7.513
7.471
7.454
7.436
7.425
7.408
7.381
7.361
7.318
7.300
7.281
-0.000
O
O
68
1H NMR (400 MHz, CDCl3)
H2O
1.00
2.00
2.08
2.99
1.07
1.05
12
11
10
9
8
7
6
5
4
3
2
1
0


160.563
153.506
139.834
134.683
131.374
128.841
128.510
128.454
128.358
127.880
124.469
119.655
116.446
77.318
77.000
76.682
O
O
68
13C NMR (101 MHz, CDCl3)
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0