Supporting information for

Bis(2-methoxyethyl)ether promoted intramolecular acceptorless dehydrogenative coupling to construct structurally diverse quinazolinones by molecular oxygen

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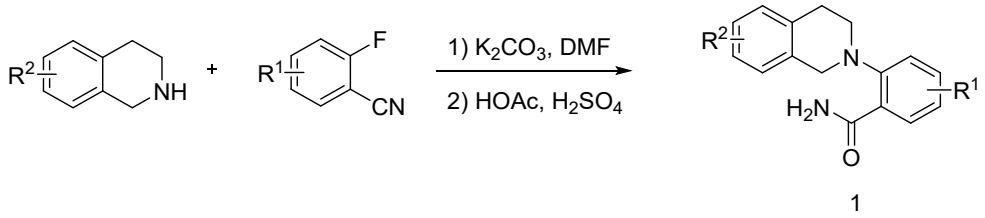
1. General information

Unless otherwise noted, all reagents, catalysts and solvents were purchased from commercial suppliers and used without further purification. Column chromatography was performed with silica gel (200-300 mesh). NMR spectra were recorded on Bruker AVANCE III (400 MHz) spectrometers. $CDCl_3$ or DMSO-*d*6 was the solvent used for the NMR analysis, with tetramethyl silane as an internal standard. Chemical shifts were reported up field to TMS (0.00 ppm) for ^1H NMR and relative to $CDCl_3$ (77.0 ppm) for ^{13}C NMR. HRMS spectra were acquired using a waters G2-XS QTof mass spectrometer.

2. General procedure for synthesis of substrates

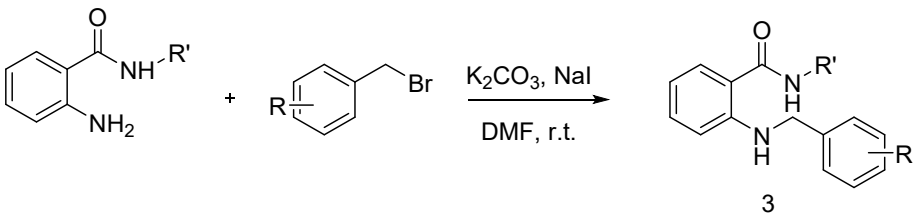
2.1 A typical procedure for the synthesis of 1[1]



1

To a solution of K_2CO_3 (6.6 mmol) in DMF (5 mL), 1,2,3,4-tetrahydroisoquinoline (6.6 mmol) and 2-fluorobenzonitrile (6 mmol) were added. The reaction mixture was stirred at 140 °C for 12 h. The mixture was poured into water (100 mL), and followed by the extraction with ethyl acetate (25 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The residue was added to a mixture of AcOH-H_2SO_4 (3 mL, V/V = 2: 1). The resulting mixture was stirred at 120 °C for 2 h and then slowly poured into ice-cold water (100 mL). The pH of the solution was adjusted to 7 by adding aqueous NaOH solution (1 M). The solution was extracted with ethyl acetate (20 mL × 3). The combined organic layer was dried over anhydrous $MgSO_4$ and concentrated under vacuum. The residue was purified by silica gel flash column chromatography to give compound **1**.

2.2 A typical procedure for the synthesis of 3 [2]



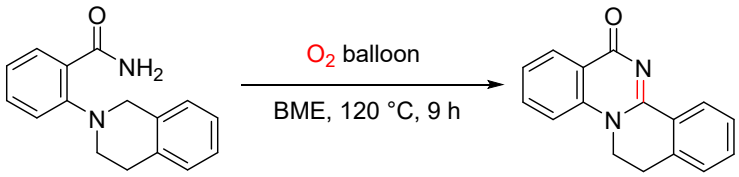
3

A mixture of 2-aminobenzamide (1.5 mmol), K_2CO_3 (1.5 mmol), NaI (1.5 mmol), and benzyl bromide (2.0 mmol) in DMF (10 mL) was stirred at room temperature for 24 hours. The reaction mixture was poured into water and extracted with EtOAc. The organic layer was washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by silica gel flash column chromatography to give compound **3**.

3. General procedure for the synthesis of compound 2 or 4 or 6

The substrate 2-(3,4-dihydroisoquinolin-2(1H)-yl)benzamide **1** or 2-(benzylamino)benzamide **3** (0.5 mmol), or analogue **5**, BME (1 mL) were added to a 10 mL Schlenk tube. The tube was evacuated and filled with oxygen three times. The mixture was stirred at 120 °C for 2 hours under oxygen atmosphere with an O_2 balloon. After cooling, the mixture was subjected to a silica gel column chromatography to isolate product **2** or **4** or **6**.

4. Gram-scale synthesis of compound 2a

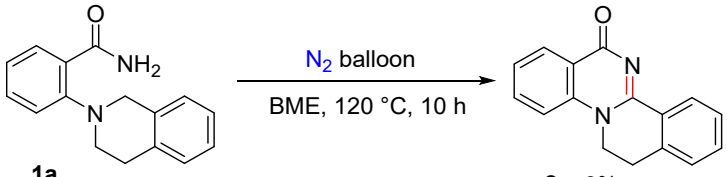


1a
1.26 g, 5 mmol

2a
1.12 g, 90% yield

2-(3,4-Dihydroisoquinolin-2-yl)benzamide (**1a,** 1.26 g, 5 mmol) and BME (10 mL) were added to a 25 mL round-bottom flask. The flask was evacuated and filled with oxygen three times. The mixture was stirred at 120 °C for 9 hours under oxygen atmosphere with an O_2 balloon. After cooling, the mixture was subjected to a silica gel column chromatography to isolate product **2a** (1.12 g, 90% yield).

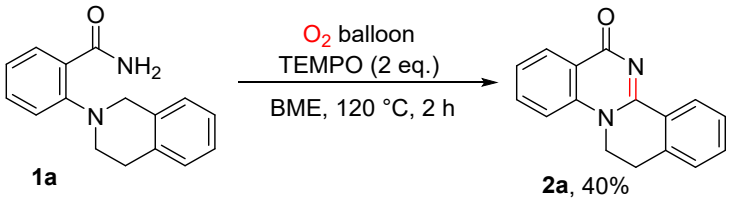
5. Control experiments



1a

2a, 0%

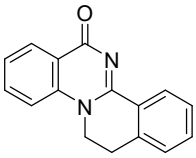
2-(3,4-Dihydroisoquinolin-2(1H)-yl)benzamide **1a** (0.3 mmol) and BME (1 mL) were added to a 10 mL Schlenk tube. The tube was evacuated and filled with nitrogen three times. The mixture was stirred at 120 °C for 10 hours under nitrogen atmosphere with a N_2 balloon. After cooling, the product **2a** was not detected.



2-(3,4-Dihydroisoquinolin-2(1H)-yl)benzamide **1a** (0.3 mmol), BME (1 mL), and 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO, 0.6 mmol) were added to a 10 mL Schlenk tube. The tube was evacuated and filled with oxygen three times. The mixture was stirred at 120 °C for 2 hours under oxygen atmosphere with an O_2 balloon. After cooling, the mixture was subjected to silica gel column chromatography to isolate product **2a** (30 mg, 40%).

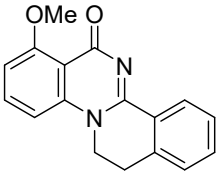
6. Analytical data of the products

12,13-dihydro-6H-isoquinolino[2,1-*a*]quinazolin-6-one (2a) [1]



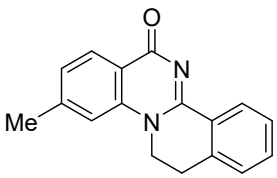
94% yield (117 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.53 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 8.38 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.77-7.70 (m, 1H), 7.57-7.37 (m, 4H), 7.28 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 4.35 (t, J = 6.8 Hz, 2H), 3.25 (t, J = 6.4 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.94, 155.57, 141.20, 136.27, 134.29, 133.22, 130.04, 129.56, 129.31, 128.29, 127.48, 126.33, 120.85, 114.40, 43.77, 27.59.

7-methoxy-12,13-dihydro-6H-isoquinolino[2,1-*a*]quinazolin-6-one (2b)



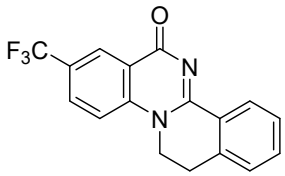
82% yield (114 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.37 (dd, J_1 = 8.0 Hz, J_2 = 1.5 Hz, 1H), 7.51 (t, J = 8.4 Hz, 1H), 7.42-7.36 (m, 1H), 7.28 (t, J = 8.0 Hz, 1H), 7.21 (d, J = 7.2 Hz, 1H), 7.01 (d, J = 8.4 Hz, 1H), 6.80 (d, J = 8.4 Hz, 1H), 4.19 (t, J = 6.8 Hz, 2H), 3.93 (s, 3H), 3.19 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.84, 160.68, 153.60, 143.27, 135.79, 133.91, 132.34, 129.11, 128.94, 127.48, 126.83, 110.34, 107.14, 105.61, 56.40, 43.95, 27.04. **HRMS** (ESI) calcd. for $C_{17}H_{15}N_2O_2$ ($[M+H]^+$): 279.1134, Found: 279.1140.

9-methyl-12,13-dihydro-6H-isoquinolino[2,1-*a*]quinazolin-6-one (2c) [1]



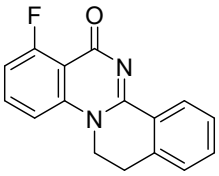
82% yield (108 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.49 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 7.48 (dt, J = 7.6, 1.2 Hz, 1H), 7.38-7.20 (m, 4H), 4.32 (t, J = 6.8 Hz, 2H), 3.25 (t, J = 6.4 Hz, 2H), 2.51 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 169.43, 154.85, 144.82, 140.77, 135.83, 132.60, 129.48, 129.11, 128.58, 127.67, 127.19, 126.99, 118.08, 113.99, 43.19, 27.08, 22.42.

8-(trifluoromethyl)-12,13-dihydro-6H-isoquinolino[2,1-*a*]quinazolin-6-one (2d) [1]



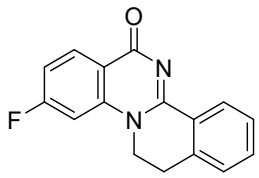
77% yield (122 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.75 (s, 1H), 8.65 (d, J = 7.6 Hz, 1H), 8.00 (d, J = 8.8 Hz, 1H), 7.70 (d, J = 8.8 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 1H), 7.36 (d, J = 7.6 Hz, 1H), 4.43 (t, J = 6.8 Hz, 2H), 3.35 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.34, 155.98, 142.89, 135.82, 133.26, 130.11 (q, J = 3.3 Hz), 129.91, 128.71, 128.05, 127.79, 127.10, 126.90 (q, J = 3.8 Hz), 126.87 (q, J = 270.3 Hz), 120.27, 114.75, 43.70, 27.11.

7-fluoro-12,13-dihydro-6H-isoquinolino[2,1-*a*]quinazolin-6-one (2e)



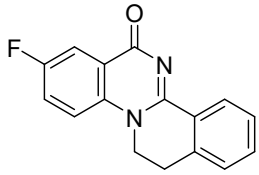
80% yield (107 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.48 (d, J = 8.0 Hz, 1H), 7.70-7.65 (m, 1H), 7.52 (t, J = 7.2 Hz, 1H), 7.39-7.29 (m, 3H), 7.15-7.06 (m, 1H), 4.34 (t, J = 6.8 Hz, 2H), 3.31 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 160.75, 154.73, 142.89, 135.80, 134.12 (d, J =11.0 Hz), 132.88, 129.54, 128.87(d, J =35.9 Hz), 127.8, 126.98, 126.14, 122.46, 112.76 (d, J =21.0 Hz), 109.69, 44.10, 27.07. **HRMS** (ESI) calcd. for $C_{16}H_{12}FN_2O$ ($[M+H]^+$): 267.0934, Found: 267.0938.

9-fluoro-12,13-dihydro-6H-isoquinolino[2,1-*a*]quinazolin-6-one (2f)



79% yield (105 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.27-8.12 (m, 2H), 7.54 (t, J = 7.2 Hz, 1H), 7.46-.40 (m, 2H), 7.34-7.29 (m, 2H), 4.08 (t, J = 6.8 Hz, 2H), 3.21 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 164.36, 164.13, 161.85 (d, J = 246.4 Hz), 147.72 (d, J = 11.7 Hz), 138.21, 132.67, 132.48 (d, J = 3.2 Hz), 129.09, 128.99, 127.46, 127.11, 119.88 (d, J = 2.9 Hz), 117.07 (d, J = 12.0 Hz), 112.84 (d, J = 28.0 Hz), 48.93, 28.42. **HRMS** (ESI) calcd. for $C_{16}H_{12}FN_2O$ ($[M+H]^+$): 267.0934, Found: 267.0940.

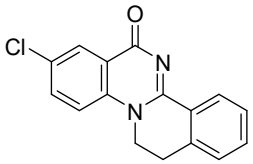
8-fluoro-12,13-dihydro-6H-isoquinolino[2,1-*a*]quinazolin-6-one (2g)



80% yield (107 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.59 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.61-7.43 (m, 4H), 7.33 (d, J = 7.6 Hz, 1H), 4.38 (t, J = 6.8 Hz, 2H), 3.30 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.56, 161.45(d, J = 249.1 Hz), 155.04, 137.27, 135.54, 132.86, 129.76, 128.95, 127.98, 126.95, 122.30 (d, J = 7.0 Hz), 121.83 (d, J = 24.4 Hz), 116.14 (d,

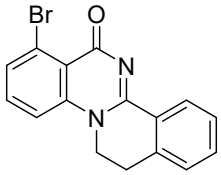
J = 7.7 Hz), 114.19 (d, J = 22.6 Hz), 43.63, 27.12 **HRMS** (ESI) calcd. for $C_{16}H_{12}FN_2O$ ([M+H]$^+$): 267.0934, Found: 267.0940.

8-chloro-12,13-dihydro-6H-isoquinolino[2,1-*a*]quinazolin-6-one (2h) [3]



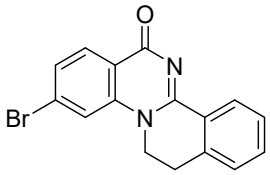
76% yield (107 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.58 (d, J = 8.0 Hz, 1H), 8.42 (d, J = 2.8 Hz, 1H), 7.72 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 1H), 7.62-7.51 (m, 2H), 7.46 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 7.2 Hz, 1H), 4.38 (t, J = 6.8 Hz, 2H), 3.32 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.17, 155.24, 139.27, 135.69, 133.91, 133.83, 132.98, 131.90, 129.81, 128.42, 128.00, 127.03, 121.63, 115.66, 43.56, 27.11.

7-bromo-12,13-dihydro-6H-isoquinolino[2,1-*a*]quinazolin-6-one (2i)



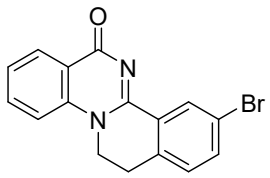
79% yield (129 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.46 (dd, J = 8.0, 1.6 Hz, 1H), 7.73-7.71 (m, 1H), 7.52-7.47 (m, 2H), 7.44 (t, J = 7.6 Hz, 1H), 7.34 (d, J = 7.6, 2H), 4.31 (t, J = 6.8 Hz, 2H), 3.31 (t, J = 6.4 Hz, 2H).**^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.73, 155.47, 141.71, 135.75, 133.05, 130.59, 129.81, 129.24, 128.86, 128.73, 127.98, 127.08, 119.13, 117.17, 43.57, 27.10. **HRMS** (ESI) calcd. for $C_{16}H_{12}BrN_2O$ ([M+H]$^+$): 327.0133, Found: 327.0139.

9-bromo-12,13-dihydro-6H-isoquinolino[2,1-*a*]quinazolin-6-one (2j) [1]



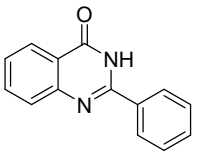
82% yield (134 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.57 (dd, J = 8.0, 1.2 Hz, 1H), 8.29 (d, J = 8.4 Hz, 1H), 7.76 (d, J = 1.6 Hz, 1H), 7.60 (dd, J = 8.4, 1.6 Hz, 1H), 7.56 (dt, J = 7.6, 1.6 Hz, 1H), 7.45 (t, J = 8.0 Hz, 1H), 7.34 (d, J = 7.6 Hz, 1H), 4.34 (t, J = 6.8 Hz, 2H), 3.31 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 168.72, 155.45, 141.69, 135.74, 133.04, 130.58, 129.79, 129.23, 128.84, 128.72, 127.97, 127.06, 119.12, 117.15, 43.56, 27.09.

3-bromo-12,13-dihydro-6H-isoquinolino[2,1-*a*]quinazolin-6-one (**2k**)



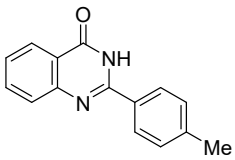
84% yield (137 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.71 (d, J = 2.0 Hz, 1H), 8.39 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.82-7.75 (m, 1H), 7.66-7.45 (m, 3H), 7.20 (d, J = 8.0 Hz, 1H), 4.38 (t, J = 6.8 Hz, 2H), 3.27 (t, J = 6.8 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): 170.02, 154.60, 141.41, 136.46, 135.38, 134.81, 133.05, 131.65, 129.84, 129.50, 127.02, 122.64, 121.28, 114.80, 43.97, 27.54. **HRMS** (ESI) calcd. for $C_{16}H_{12}BrN_2O$ ([M+H]$^+$): 327.0133, Found: 327.0130.

2-phenylquinazolin-4(3H)-one (4a) [4]



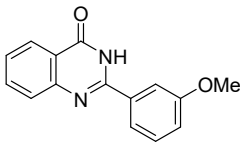
65% yield (72 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.55 (s, 1H), 8.24 – 8.14 (m, 3H), 7.86-7.84 (m, 1H), 7.76 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.63 – 7.50 (m, 4H).**^{13}C NMR** (100 MHz, DMSO-d_6): δ = 162.97, 153.04, 149.45, 135.35, 133.43, 132.14, 129.34, 128.49, 128.23, 127.33, 126.58, 121.69.

2-(p-tolyl)quinazolin-4(3H)-one (4b) [4]



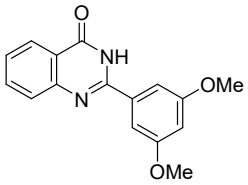
67% yield (79 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.40 (s, 1H), 8.03 (dd, J_1 = 20.4 Hz, J_2 = 7.6 Hz, 3H), 7.78-7.70 (m, 1H), 7.64 (d, J = 8.4 Hz, 1H), 7.47-7.38 (m, 1H), 7.27 (d, J = 8.0 Hz, 2H), 2.30 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 162.11, 152.06, 148.66, 141.31, 134.45, 129.71, 129.05, 127.52, 127.26, 126.27, 125.68, 120.72, 20.85.

2-(3-methoxyphenyl)quinazolin-4(3H)-one (4c) [5]



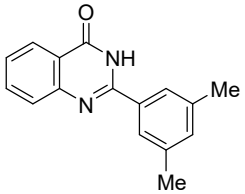
71% yield (90 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.56 (s, 1H), 8.17 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.90-7.71 (m, 4H), 7.59-7.42 (m, 2H), 7.16 (dd, J_1 = 8.0 Hz, J_2= 2.4 Hz, 1H), 3.88 (s, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 163.10, 160.18, 152.89, 135.49, 134.86, 130.61, 128.39, 127.50, 126.71, 121.85, 120.97, 118.46, 113.35, 56.24.

2-(3,5-dimethoxyphenyl)quinazolin-4(3H)-one (4d) [6]



67% yield (95 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.54 (s, 1H), 8.16 (dd, J_1 = 8.0 Hz, J_2 =1.2 Hz, 1H), 7.88-7.80 (m, 1H), 7.76 (dd, J_1 = 8.4 Hz, J_2= 1.2 Hz, 1H), 7.57-7.50 (m, 1H), 7.39 (d, J = 2.4 Hz, 2H), 6.70 (t, J = 2.0 Hz, 1H), 3.85 (s, 6H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 162.88, 161.13, 161.13, 152.47, 135.25, 135.17, 128.21, 127.31, 126.50, 121.69, 106.11, 104.40, 56.17.

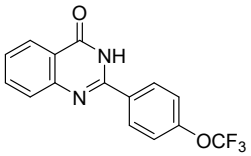
2-(3,5-dimethylphenyl)quinazolin-4(3H)-one (4e) [7]



65% yield (81 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.46 (s, 1H), 8.19 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 7.90-7.82 (m, 3H), 7.78 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 7.58-7.52 (m, 1H), 7.26 (s, 1H), 2.40 (s, 6H);

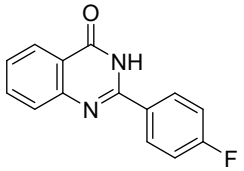
^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.64, 152.92, 149.25, 138.23, 135.06, 133.21, 133.02, 127.92, 126.96, 126.31, 125.95, 121.43, 21.36.

2-(4-(trifluoromethoxy)phenyl)quinazolin-4(3H)-one (4f) [7]



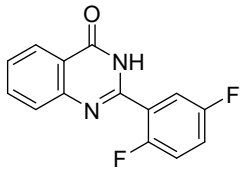
78% yield (119 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.66 (s, 1H), 8.31 (d, J = 8.8 Hz, 2H), 8.17 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 7.90-7.84 (m, 1H), 7.76 (dd, J_1 = 8.4 Hz, J_2 =1.2 Hz, 1H), 7.61-7.52 (m, 3H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 172.97, 151.68, 138.60, 135.12, 130.54, 130.07, 127.91, 127.26, 126.31, 121.42, 121.32, 113.20, 92.53.

2-(4-fluorophenyl)quinazolin-4(3H)-one (4g) [4]



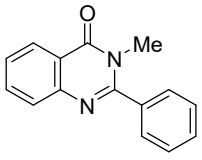
65% yield (78 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.59 (s, 1H), 8.31-8.22 (m, 2H), 8.16 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.89-7.81 (m, 1H), 7.74 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.56-7.49 (m, 1H), 7.40 (t, J = 8.8 Hz, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 165.75 (d, J = 247.8 Hz), 162.67, 151.83, 149.12, 135.12, 130.89 (d, J =9.0 Hz), 129.71, 127.94, 127.09, 126.32, 121.36, 116.11 (d, J = 21.90 Hz).

2-(2,5-difluorophenyl)quinazolin-4(3H)-one (4h) [8]



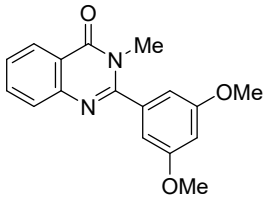
74% yield (96 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.67 (s, 1H), 8.19 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 7.92-7.83 (m, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.69-7.55 (m, 2H), 7.52-7.44 (m, 2H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 161.73, 159.25 (d, J = 241.8 Hz), 157.32 (d, J = 247.5 Hz), 149.09, 148.77, 135.00, 127.88, 127.60, 126.19, 123.81 (dd, J_1 = 15.8 Hz, J_2 = 8.5 Hz), 121.52, 119.64 (dd, J_1 = 23.7 Hz, J_2 = 8.8 Hz), 118.33 (dd, J_1 = 24.4 Hz, J_2 = 8.9 Hz), 117.67 (dd, J_1 = 25.8 Hz, J_2 = 2.8 Hz).

3-methyl-2-phenylquinazolin-4(3H)-one (4i) [4]



66% yield (78 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.39 (d, J = 8.0 Hz, 1H), 7.80 (s, 2H), 7.67-7.54 (m, 6H), 3.56 (s, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 162.66, 156.08, 147.27, 135.35, 134.26, 130.03, 128.84, 127.96, 127.44, 126.95, 126.63, 120.48, 34.23.

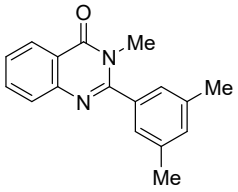
2-(3,5-dimethoxyphenyl)-3-methylquinazolin-4(3H)-one (4j) [9]



72% yield (107 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 8.21 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 7.90-7.83 (m, 1H), 7.70 (dt, J_1 = 8.4 Hz, J_2 = 0.8 Hz, 1H), 7.62-7.56 (m, 1H), 6.84 (d, J = 2.4 Hz, 2H), 6.70 (t, J = 2.4 Hz, 1H), 3.83 (s, 6H), 3.39 (s, 3H). **^{13}C NMR** (100 MHz, DMSO-

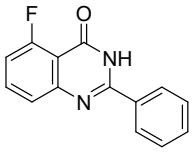
d_6): δ = 162.06, 160.92, 156.36, 147.49, 137.66, 134.87, 127.70, 127.44, 126.59, 120.76, 106.70, 102.03, 56.03, 34.19.

2-(3,5-dimethylphenyl)-3-methylquinazolin-4(3H)-one (4k) [9]



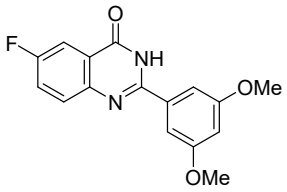
77% yield (102 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 8.18 (dd, J_1 = 8.0 Hz, J_2 =1.2 Hz, 1H), 7.85-7.81 (m, 1H), 7.66 (dd, J_1 = 8.4 Hz, J_2 =1.2 Hz, 1H), 7.56-7.50 (m, 1H), 7.26 (s, 2H), 7.18 (s, 1H), 3.37 (s, 5H), 2.39-2.35 (m, 6H); **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 162.00, 156.65, 147.44, 138.02, 135.63, 134.66, 131.43, 127.48, 127.13, 126.43, 126.15, 120.44, 34.26, 21.20.

5-fluoro-2-phenylquinazolin-4(3H)-one (4l) [10]



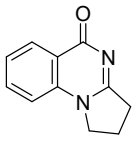
75% yield (90 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 12.57 (s, 1H), 8.17–8.15 (m, 2H), 7.81-7.76 (m, 1H), 7.59 – 7.52 (m, 4H), 7.27-7.21 (m, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 162.35 (d, J = 261.0 Hz), 160.12, 153.79, 151.39, 135.61 (d, J = 10.7 Hz), 132.73, 132.19, 129.14, 128.38, 124.08, 113.30 (d, J = 20.2 Hz), 110.96 (d, J = 6.1 Hz).

2-(3,5-dimethoxyphenyl)-6-fluoroquinazolin-4(3H)-one (4m) [4]



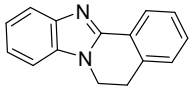
70% yield (105 mg). **^{1}H NMR** (400 MHz, DMSO-d_6):12.62 (s, 1H), 7.85–7.81 (m, 2H), 7.75-7.70 (m, 1H), 7.37 (d, J = 2.4 Hz, 2H), 6.70 (t, J = 2.0 Hz, 1H), 3.84 (s, 6H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 161.75 (d, J = 243.9 Hz), 161.01, 151.92, 145.92, 134.88, 132.19 (d, J = 17.5 Hz), 129.15, 123.69 (d, J = 24.1 Hz), 122.8 (d, J = 8.0 Hz), 111.13 (d, J = 23.2 Hz), 105.99, 104.27, 56.29.

2,3-dihydropyrrolo[1,2-*a*]quinazolin-5(1H)-one (6a) [1]



74% yield (69 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.30 (dt, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.75-7.66 (m, 1H), 7.48-7.40 (m, 1H), 7.22 (d, J = 8.0 Hz, 1H), 4.27 (t, J = 7.6 Hz, 2H), 3.20 (t, J = 8.4Hz, 2H), 2.44 (q, J = 8.0 Hz, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 170.17, 166.46, 138.66, 133.67, 128.83, 125.88, 118.77, 114.51, 48.75, 32.83, 18.70.

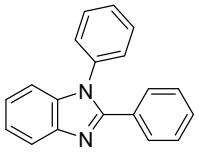
5,6-dihydrobenzo[4,5]imidazo[2,1-*a*]isoquinoline (6b) [4]



79% yield (87 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.35-8.34 (m, 1H), 7.93-7.80 (m, 1H), 7.47-7.26 (m, 6H), 4.34 (t, J = 8.0 Hz, 2H), 3.35-3.23 (m, 2H).

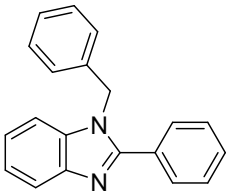
^{13}C NMR (100 MHz, $CDCl_3$): δ = 149.13, 143.91, 134.67, 134.31, 130.19, 128.12, 127.77, 126.66, 125.67, 122.71, 122.50, 119.76, 109.09, 40.42, 28.26.

1,2-diphenyl-1H-benzo[*d*]imidazole (6c) [4]



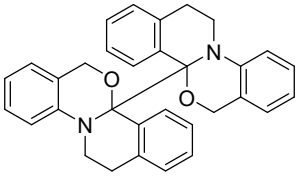
66% yield (89 mg). **^{1}H NMR** (400 MHz, DMSO-d_6): δ = 7.81-7.79 (m, 1H), 7.58–7.52 (m, 5H), 7.44-7.26 (m, 7H), 7.20–7.18 (m, 1H). **^{13}C NMR** (100 MHz, DMSO-d_6): δ = 152.50, 143.22, 137.75, 137.13, 130.70, 130.50, 130.19, 129.79, 129.51, 129.02, 128.19, 124.01, 123.40, 120.06, 111.13.

1-benzyl-2-phenyl-1H-benzo[d]imidazole (6d) [11]



28% yield (39.8 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.90 (d, J = 8.0 Hz, 1H), 7.73-7.71 (m, 2H), 7.51-7.46 (m, 3H), 7.38-7.22 (m, 6H), 7.15-7.12 (m, 2H), 5.48 (s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): 154.19, 143.16, 136.40, 136.06, 130.05, 129.96, 129.28, 129.09, 128.79, 127.80, 125.98, 123.08, 122.72, 120.00, 110.57, 48.40.

12,12',13,13'-tetrahydro-6H,6'H-4b,4'b-bibenzo[4,5][1,3]oxazino[2,3-*a*]isoquinoline (6e) [4]



65% yield (154 mg). **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 8.16 (dd, J_1 = 7.6 Hz, J_2=1.6 Hz, 2H), 7.61 (dd, J_1 = 7.2 Hz, J_2= 2.4 Hz, 2H), 7.56-7.51 (m, 2H), 7.44-7.39 (m, 6H), 7.33-7.20 (m, 4H), 4.66 (d, J = 11.6 Hz, 2H), 4.52-4.43 (m, 2H), 4.12-4.01 (m, 2H), 3.91-3.63 (m, 2H), 3.31-3.21 (m, 2H), 3.16-3.05 (m, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 165.74, 141.31, 138.50, 137.76, 132.51, 130.79, 129.41, 129.07, 128.84, 128.34, 127.35, 127.15, 125.97, 61.96, 50.19, 28.59.

Reference:

[1]. Sun, Y. Hu, S. Z. Nie, Y. Y. Yan, X. J. Zhang, M. Yan, *Adv. Synth. Catal.,* 2013, **355**, 2179–2184.

[2]. Hikawa, Y. Ino, H. Suzuki, Y. Yokoyama, *J. Org. Chem.* 2012, **77**, 7046–7051.

[3]. Q. Y. Li, S. Y. Cheng, H. T. Tang, Y. M. Pan, *Green Chem.*, 2019, **21**, 5517–5520.

[4]. S. M. Patel, H. Chada, S. Biswal, S. Sharma, D. S. Sharada, *Synthesis* 2019, **51**, 3160–3170.

[5]. J. K. Laha, K. S. S. Tummalapalli, A. Nair, N. Patel, *J. Org. Chem.* 2015, **80**, 11351–11359.

[6]. R. Sharma, R. A. Vishwakarma, S. B. Bharate, *Adv. Synth. Catal*. 2016, **358**, 3027–3033.

[7]. K. Upadhyaya, R. K. Thakur, S. K. Shukla, R. P. Tripathi, J. *Org. Chem.* 2016, **81**, 5046–5055.

[8]. S. Hao, J. Yang, P. Liu, J. Xu, C. Yang, F. Li, *Org. Lett.* 2021, **23**, 2553–2558.

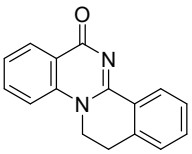
[9]. Y. Jang, S. B. Lee, J. Hong, S. Chun, J. Lee, S. Hong, *Org. Biomol. Chem*. 2020, **18**, 5435–5441.

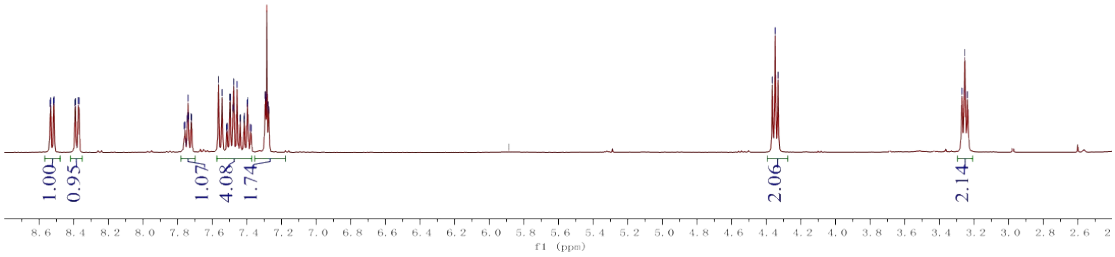
[10]. H. Hikawa, Y. Ino, H. Suzuki, Y. Yokoyama, *J. Org. Chem.* 2012, **77**, 7046–7051.

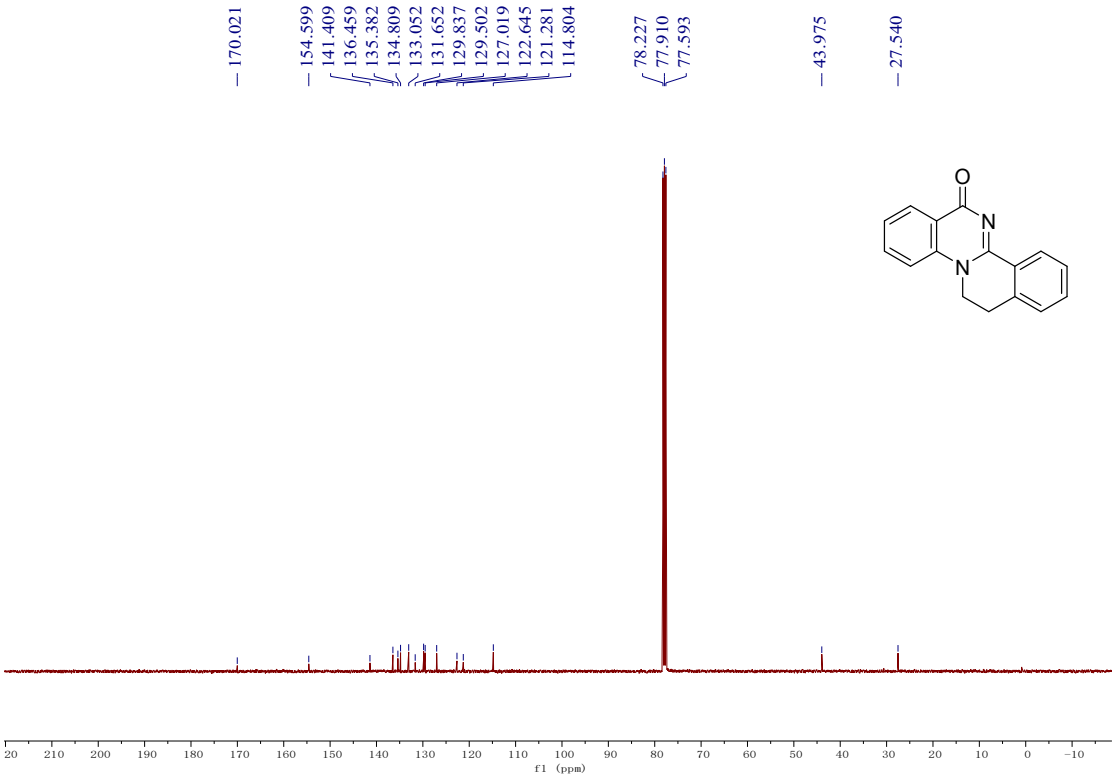
[11]. P. H. Wang, J. Y. Wang, C. T. Au, R.H. Qiu, X. H. Xu, S. F. Yin, *Adv. Synth. Catal.* 2016, **358**, 1302–1308

7. NMR spectra

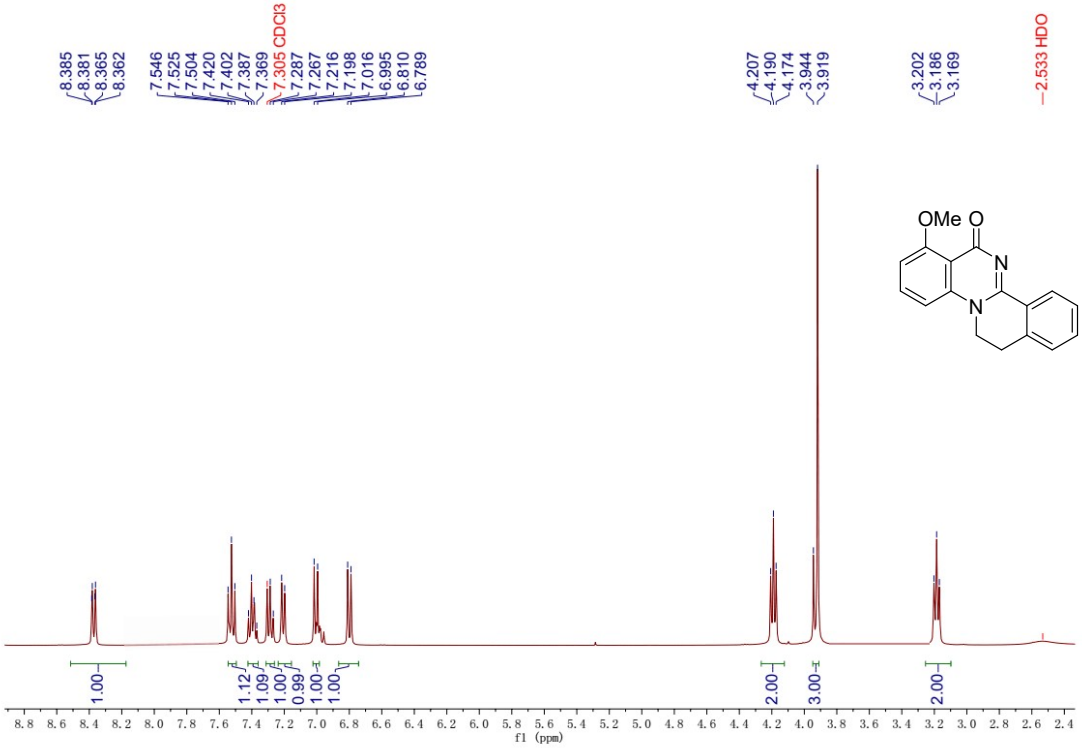
2a







2b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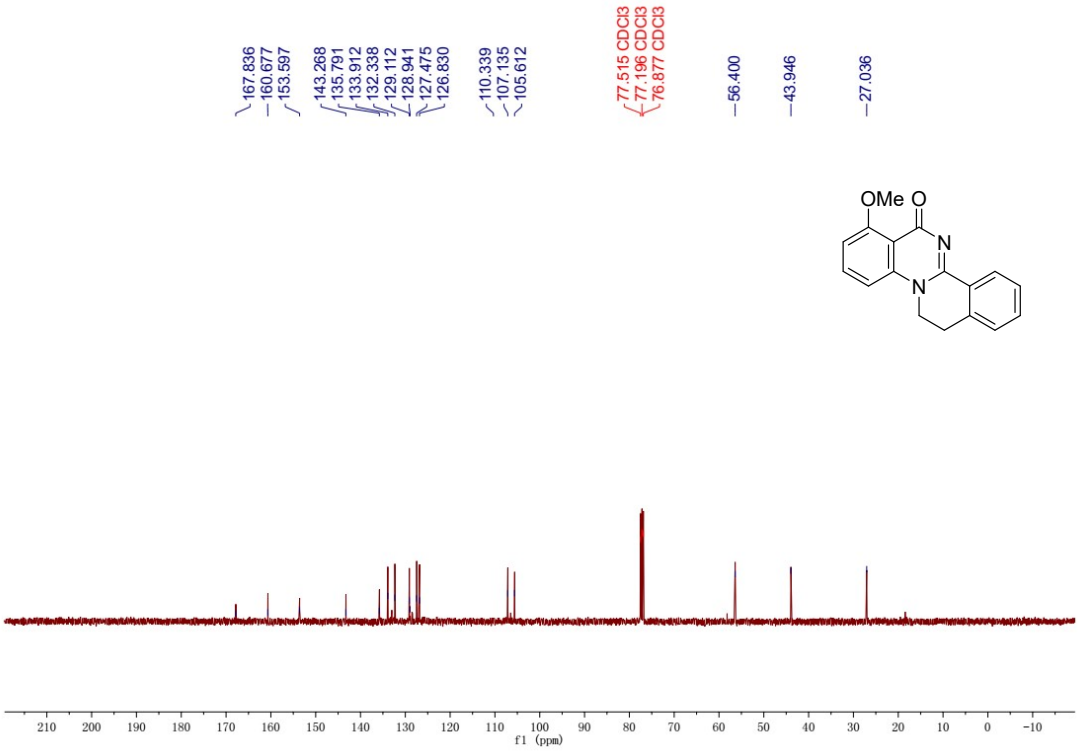
7.287
7.267
7.216
7.198
7.016
6.995
6.810
6.789
4.207
4.190
4.174
3.944
3.919
3.202
3.186
3.169
2.533 HDO
OMe O
N
N
1.00
1.12
1.09
1.00
0.99
1.00
1.00
2.00
3.00
2.00
f1 (ppm)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105.612
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76.877 CDCl3
56.400
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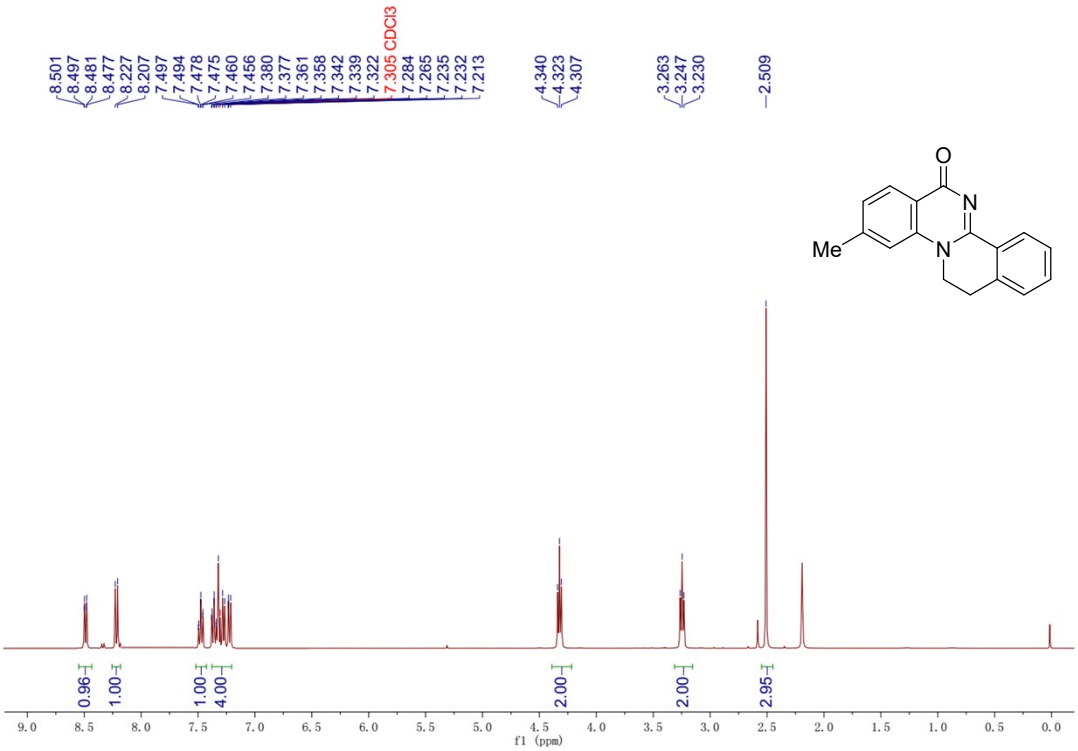
27.036
OMe O
N
N
f1 (ppm)

2c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1.00
4.00
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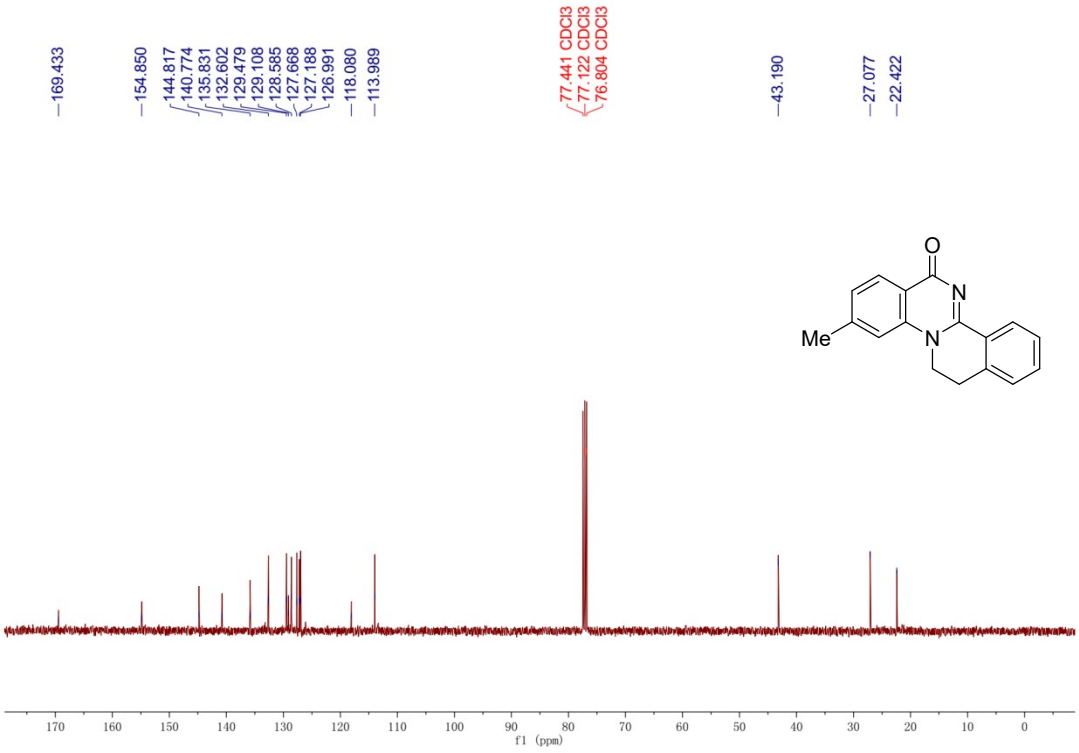
2.95
f1 (ppm)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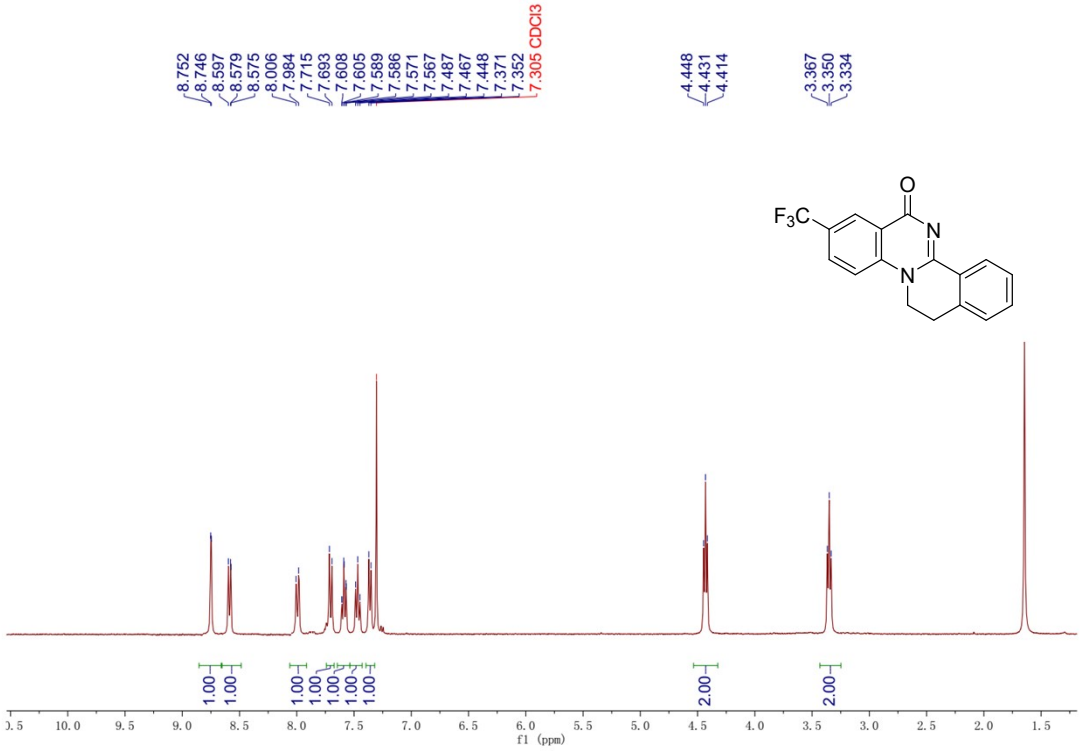
O
N
N
Me
f1 (ppm)

2d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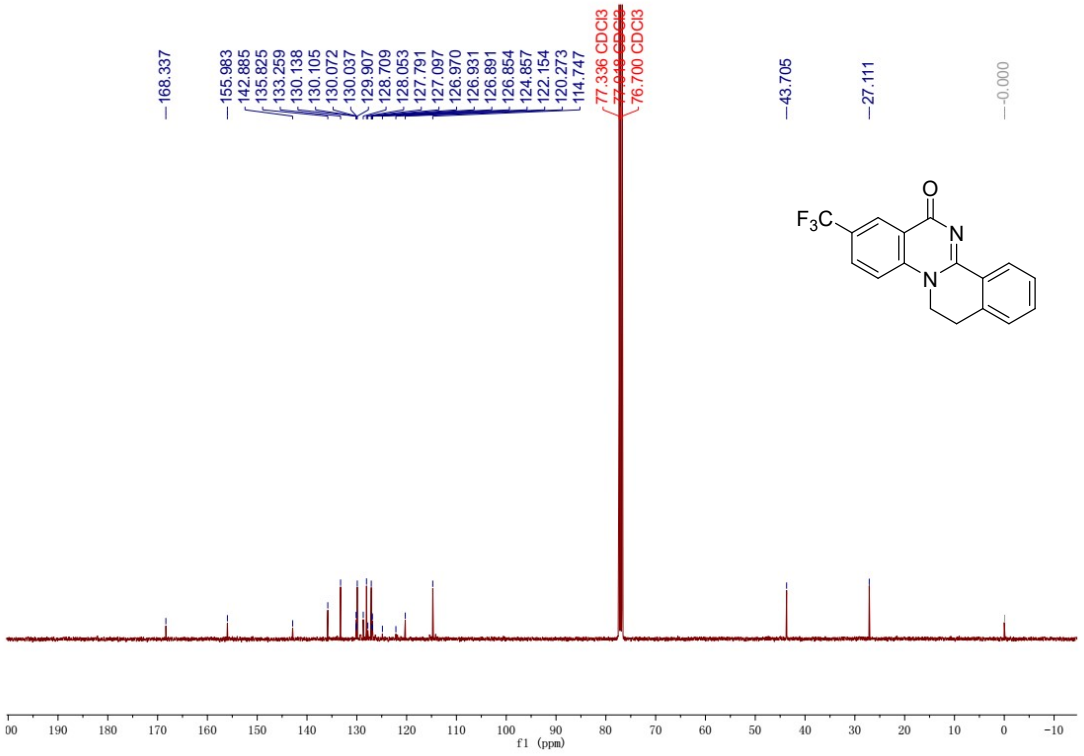
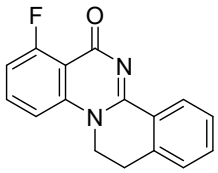
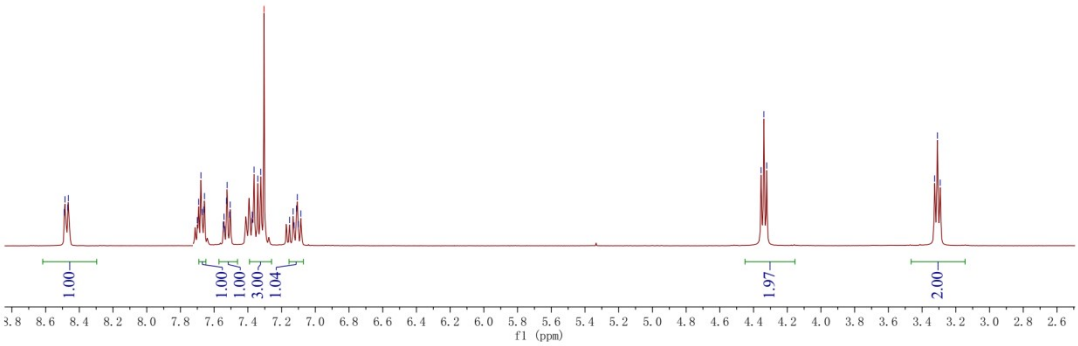
1.00
2.00
2.00
f1 (ppm)


168.337
155.983
142.885
135.825
133.259
130.138
130.105
130.072
130.037
129.907
128.709
128.053
127.791
127.097
126.970
126.931
126.891
126.854
124.857
122.154
120.273
114.747
77.336 CDCl3
76.700 CDCl3
43.705
27.111
0.000
F3C
O
N
N
f1 (ppm)

2e


8.4692
8.4655
8.4590
8.4554
7.7697
7.7622
7.7605
7.7608
7.7616
7.7577
7.7457
7.7420
7.7376
7.7269
7.7232
7.7094
7.7047
7.7771
7.7740
7.3632
7.3414
7.3235
7.3044 CDCl3
7.1527
7.1317
7.1259
7.1115
7.1065
7.1005
7.0980
4.3554
4.3387
4.3220
3.3525
3.3359
3.3294

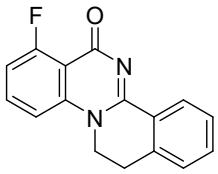

F
O
N
N

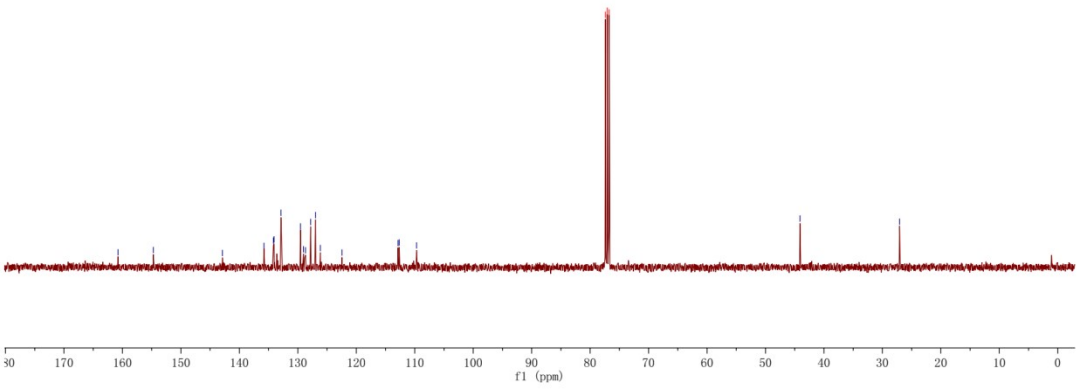

1.00
1.00
1.00
3.00
1.04
1.97
2.00
f1 (ppm)


160.746
154.726
142.894
135.800
134.173
134.063
132.883
129.539
129.045
128.691
127.801
126.981
126.144
122.457
112.860
112.645
109.691

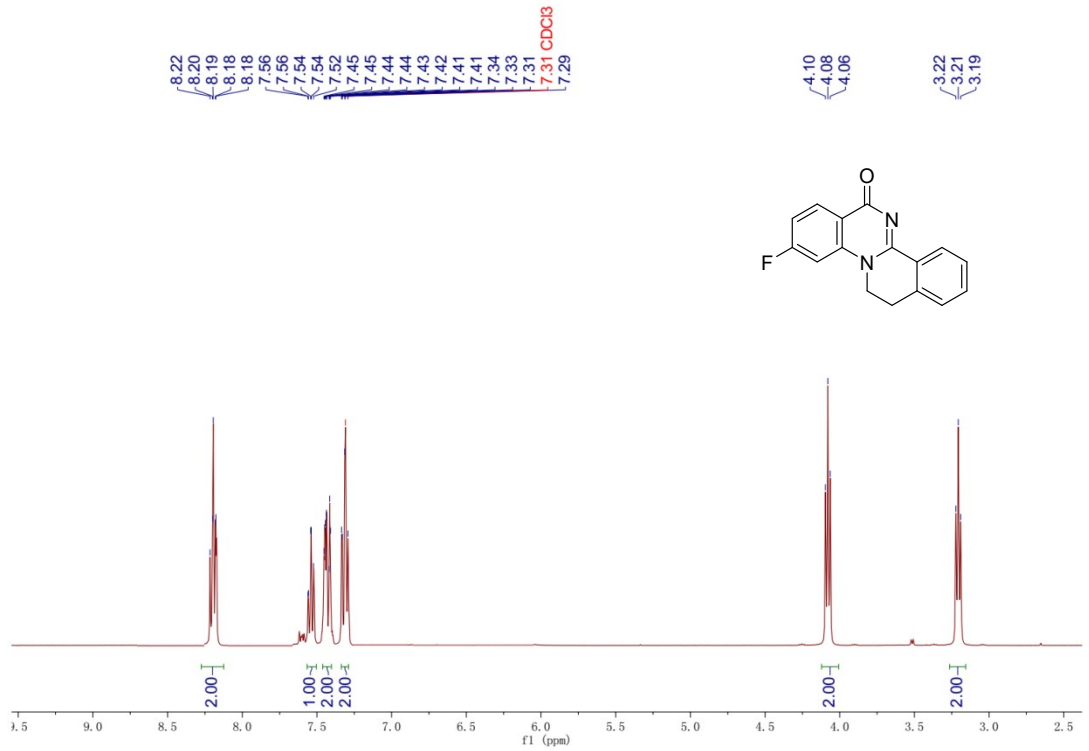

77.379 CDCl3
77.060 CDCl3
76.743 CDCl3

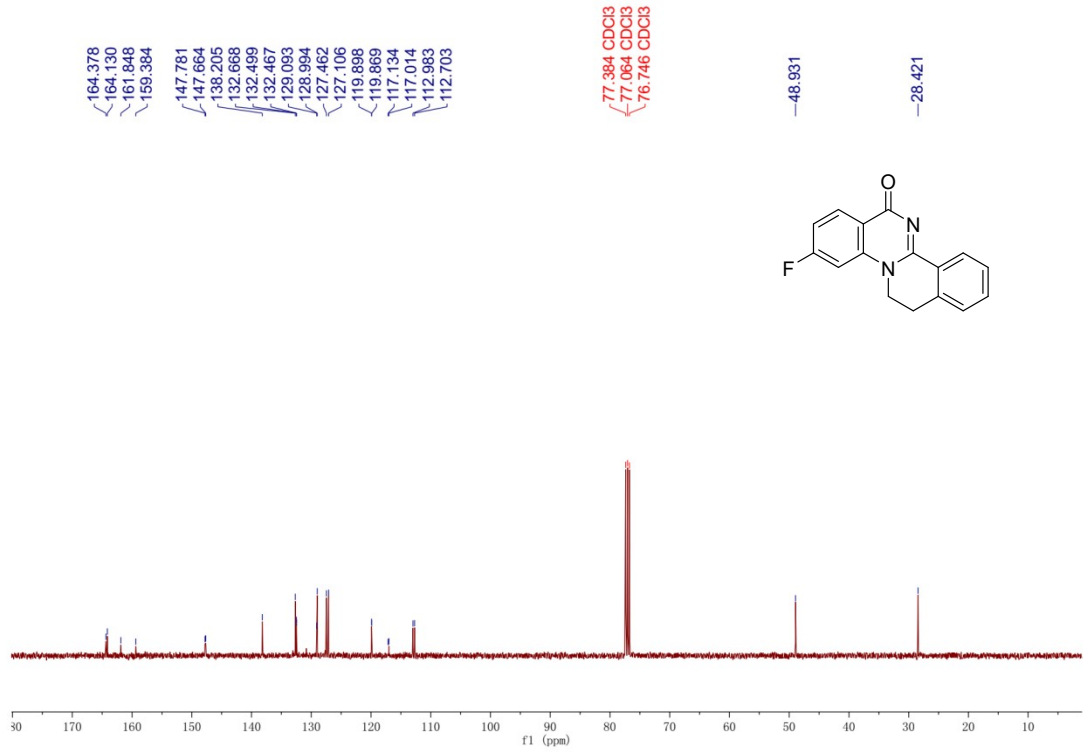

44.102
27.075


F
O
N
N

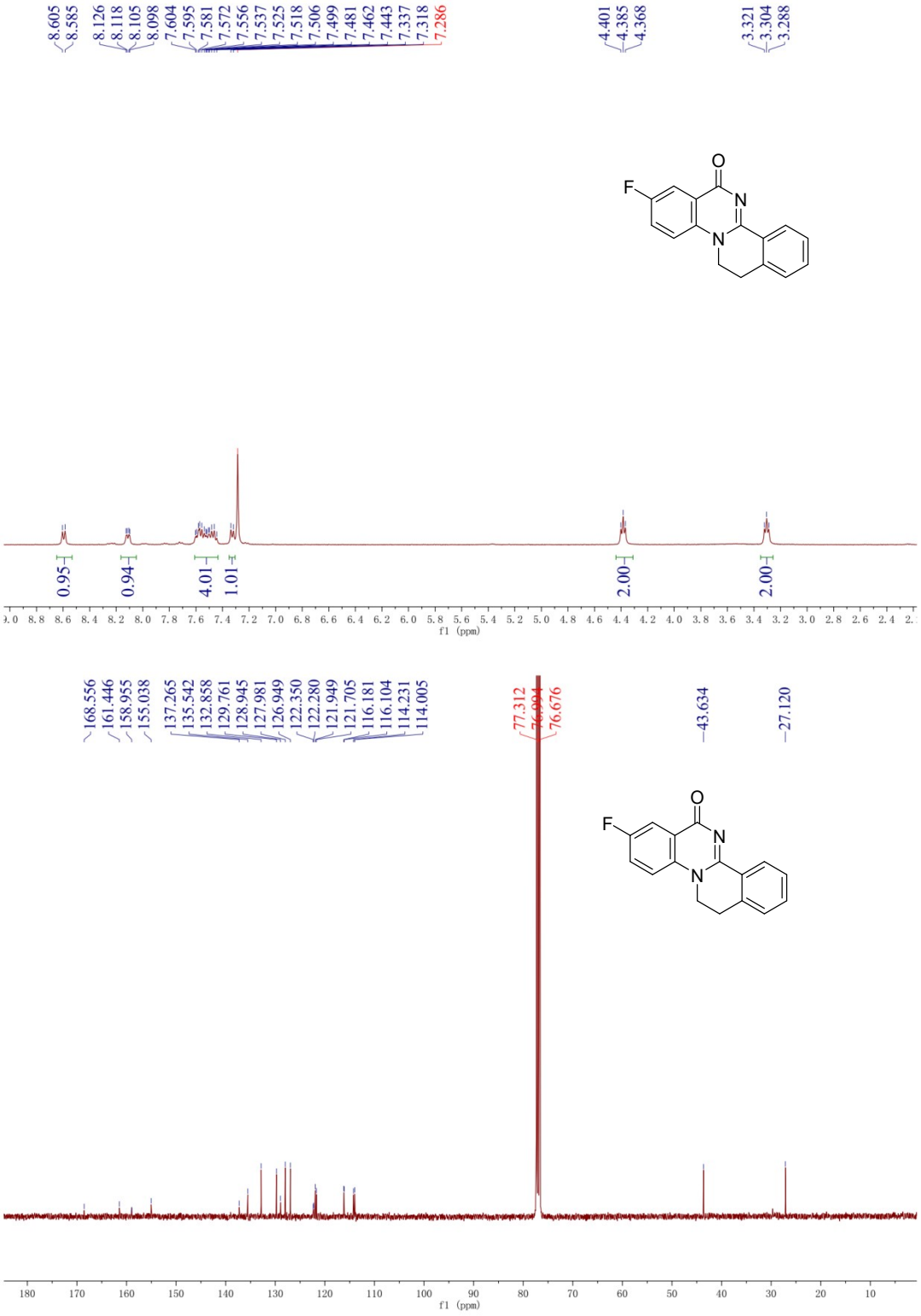

f1 (ppm)

2f

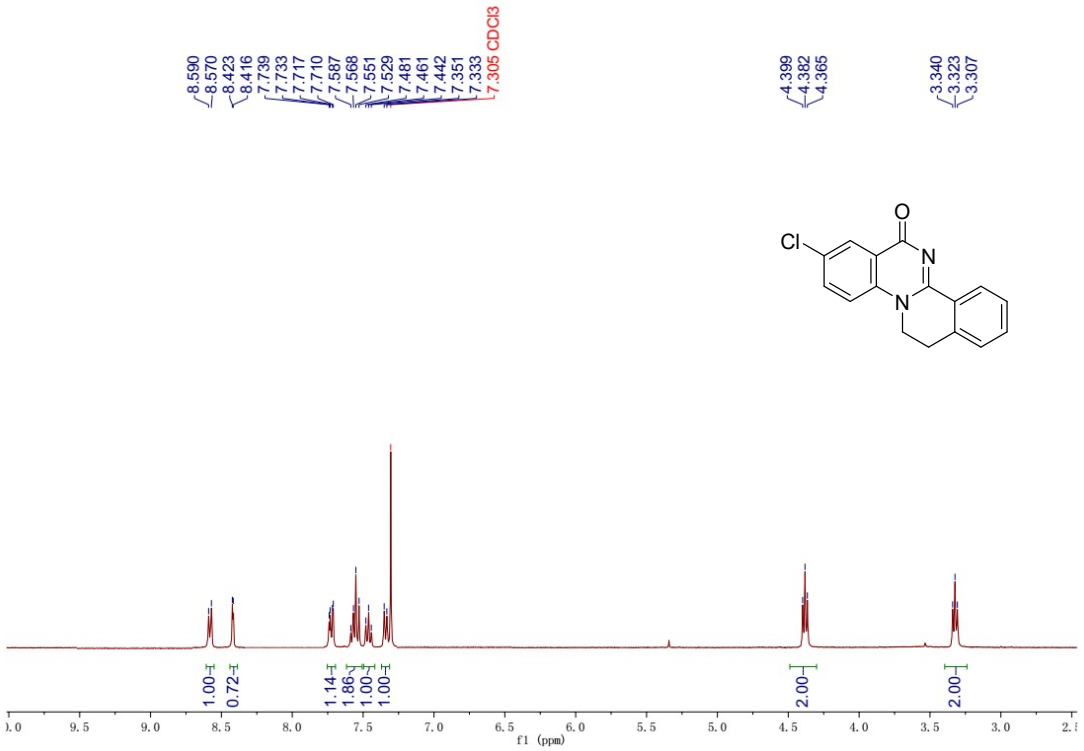

8.22
8.20
8.19
8.18
8.18
7.56
7.56
7.54
7.54
7.52
7.45
7.44
7.44
7.43
7.42
7.41
7.41
7.34
7.33
7.31
7.31 CDCl3
7.29
4.10
4.08
4.06
3.22
3.21
3.19
O
N
F
N
2.00
1.00
2.00
2.00
2.00
2.00
f1 (ppm)

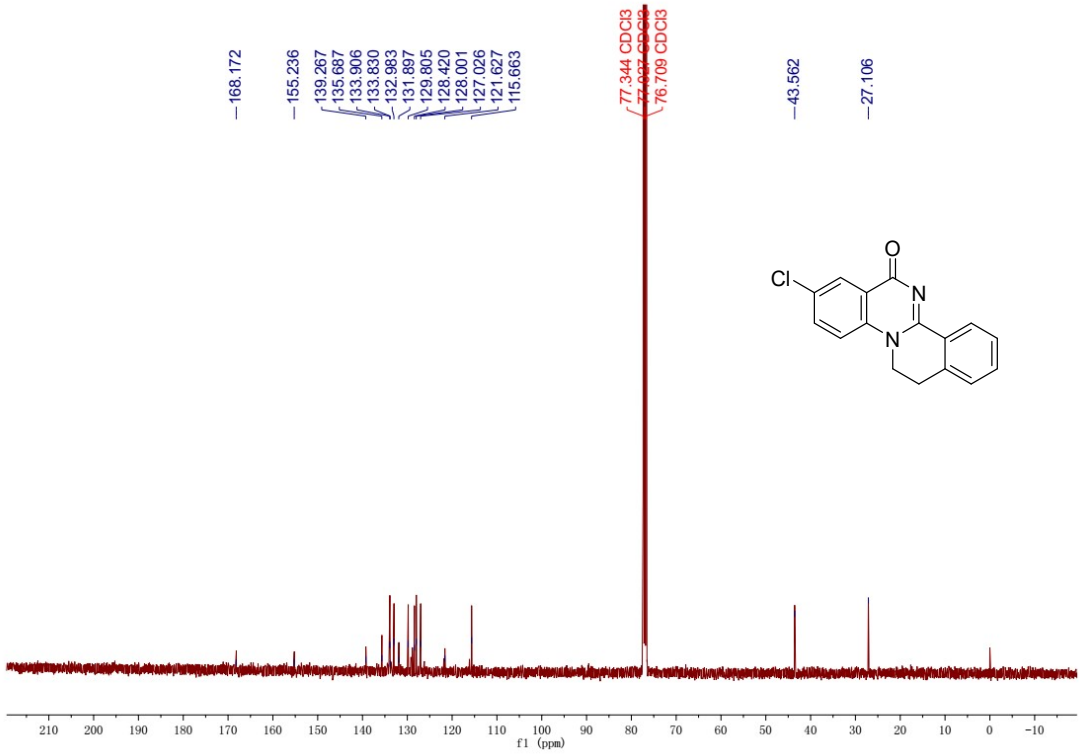

164.378
164.130
161.848
159.384
147.781
147.664
138.205
132.668
132.499
132.467
129.093
128.994
127.462
127.106
119.898
119.869
117.134
117.014
112.983
112.703
77.384 CDCl3
77.064 CDCl3
76.746 CDCl3
48.931
28.421
O
N
F
N
f1 (ppm)

2g

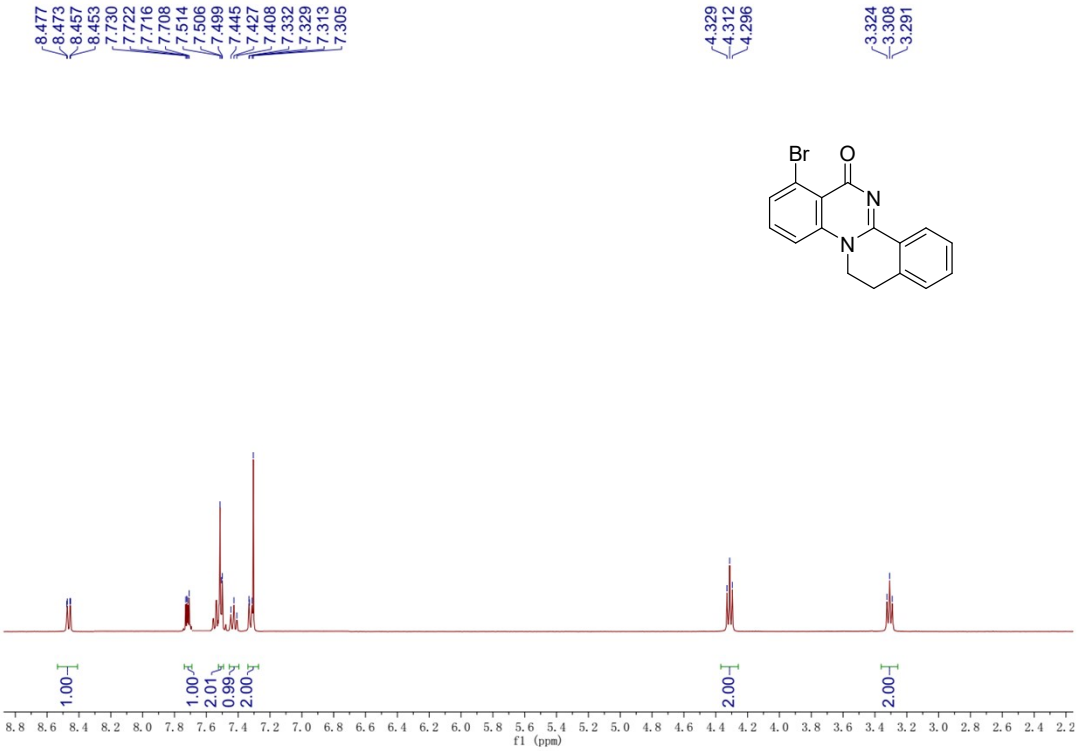

8.605
8.585
8.126
8.118
8.105
8.098
7.604
7.595
7.581
7.572
7.556
7.537
7.525
7.518
7.506
7.499
7.481
7.462
7.443
7.337
7.318
7.286
4.401
4.385
4.368
3.321
3.304
3.288
F
O
N
N
0.95
0.94
4.01
1.01
2.00
2.00
f1 (ppm)
168.556
161.446
158.955
155.038
137.265
135.542
132.858
129.761
128.945
127.981
126.949
122.350
122.280
121.949
121.705
116.181
116.104
114.231
114.005
77.312
76.994
76.676
43.634
27.120
F
O
N
N
f1 (ppm)

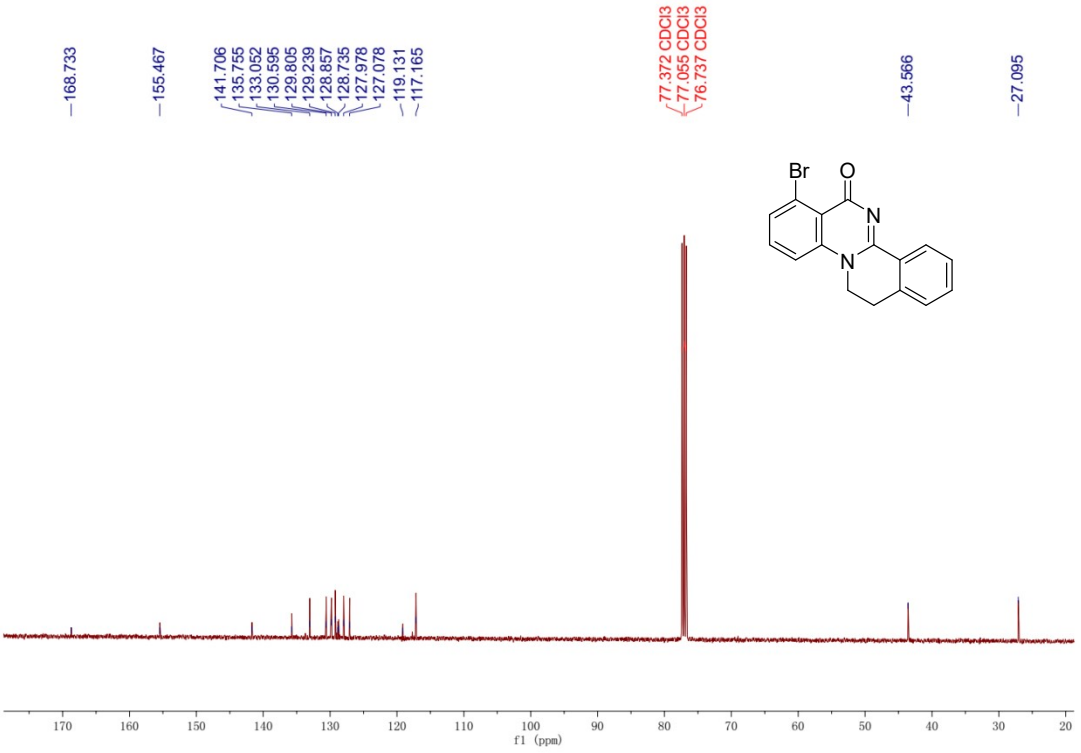
2h


8.590
8.570
8.423
8.416
7.739
7.733
7.717
7.710
7.587
7.568
7.551
7.529
7.481
7.461
7.442
7.351
7.333
7.305 CDCl3
4.399
4.382
4.365
3.340
3.323
3.307
Cl
O
N
N
1.00
0.72
1.14
1.86
1.00
1.00
2.00
2.00
f1 (ppm)

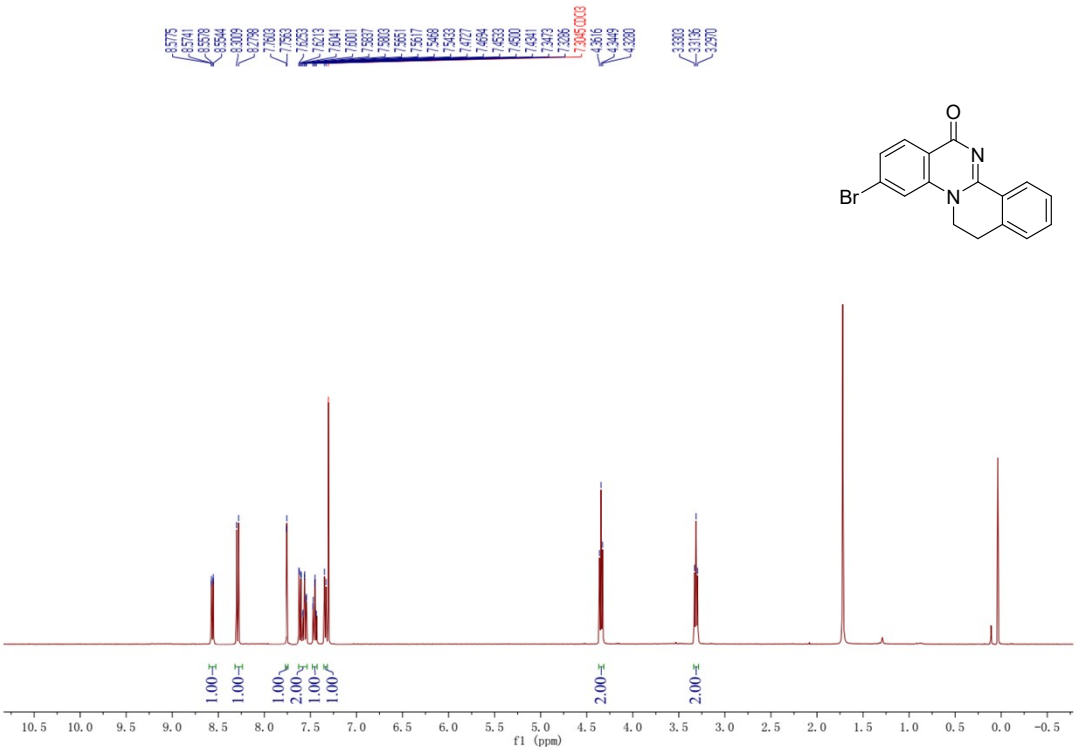

168.172
155.236
139.267
135.687
133.906
133.830
132.983
131.897
129.805
128.420
128.001
127.026
121.627
115.663
77.344 CDCl3
76.709 CDCl3
43.562
27.106
Cl
O
N
N
f1 (ppm)

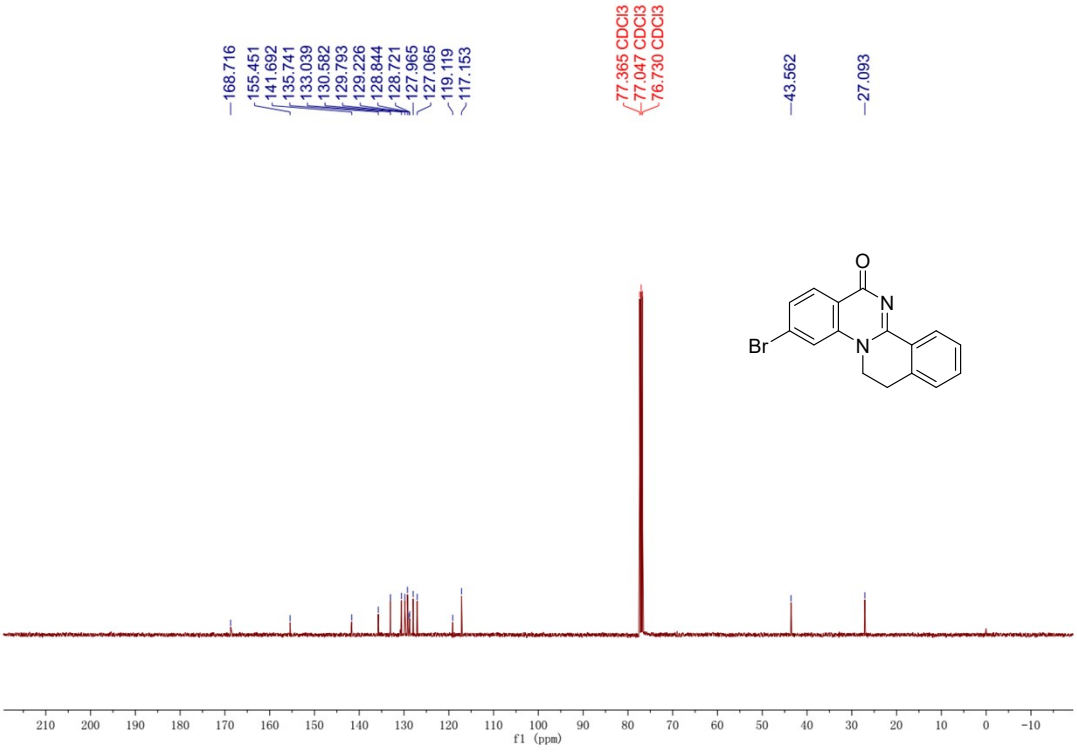
2i


8.477
8.473
8.457
8.453
7.730
7.722
7.716
7.708
7.514
7.506
7.499
7.445
7.427
7.408
7.332
7.329
7.313
7.305
4.329
4.312
4.296
3.324
3.308
3.291
Br
O
N
N
1.00
1.00
2.01
0.99
2.00
2.00
2.00
f1 (ppm)


168.733
155.467
141.706
135.755
133.052
130.595
129.805
129.239
128.857
128.735
127.978
127.078
119.131
117.165
77.372 CDCl3
77.055 CDCl3
76.737 CDCl3
43.566
27.095
Br
O
N
N
f1 (ppm)

2j


8.5775
8.5741
8.5578
8.5544
8.3039
8.2798
7.7603
7.7563
7.6253
7.6213
7.6041
7.6001
7.5837
7.5803
7.5651
7.5617
7.5468
7.5433
7.4727
7.4694
7.4538
7.4500
7.4341
7.3473
7.3206
7.3045 CDCl3
4.3616
4.3449
4.3280
3.3303
3.3136
3.2970
O
N
Br
N
1.00
1.00
1.00
2.00
1.00
1.00
2.00
2.00
f1 (ppm)


168.716
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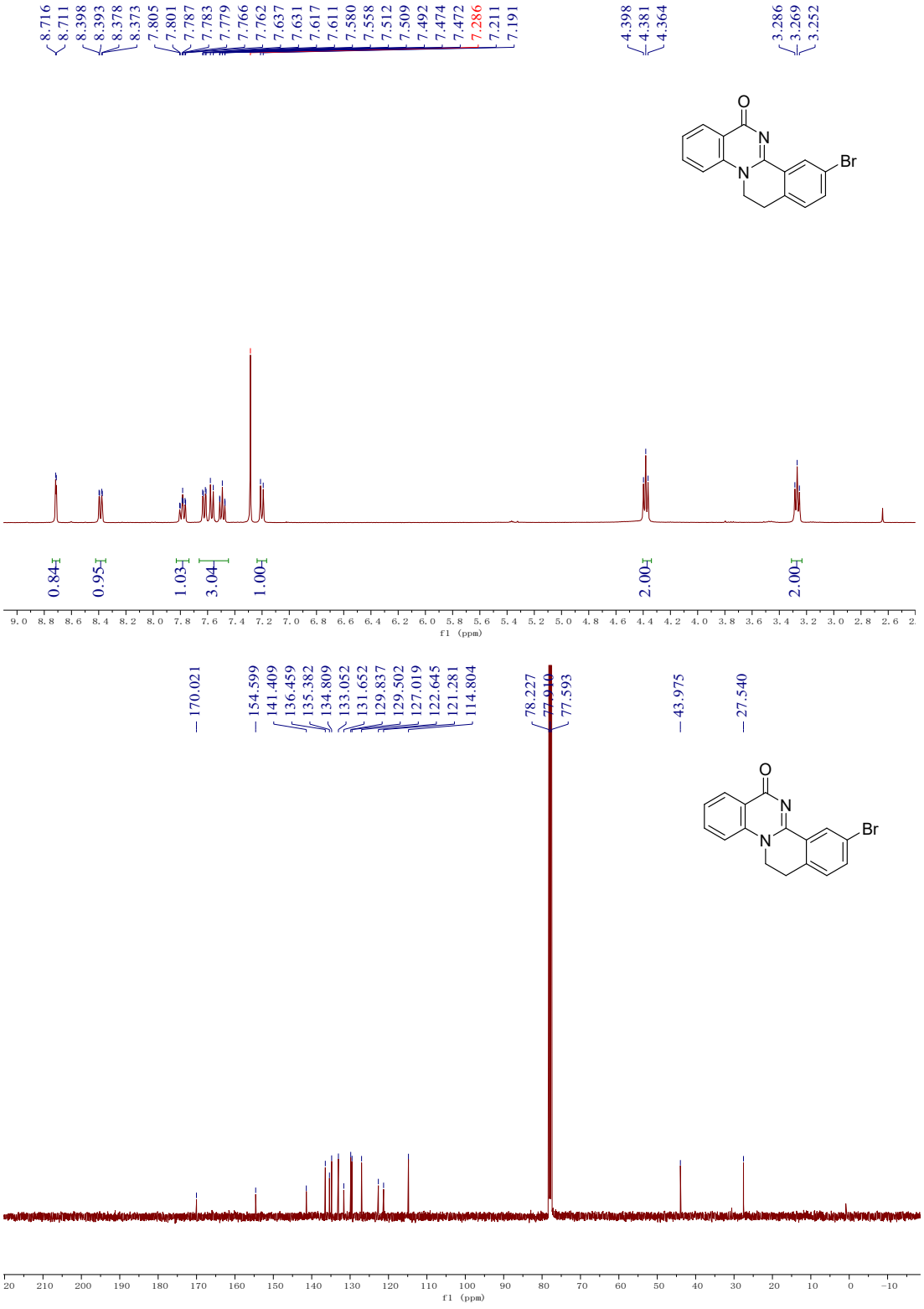
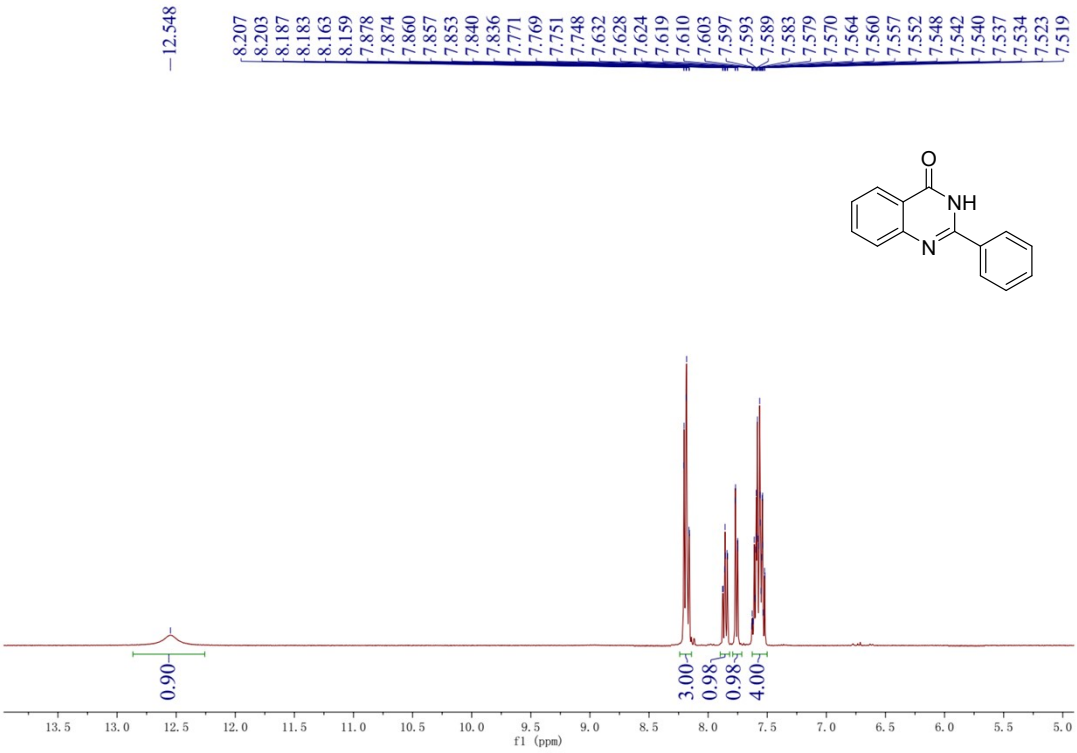
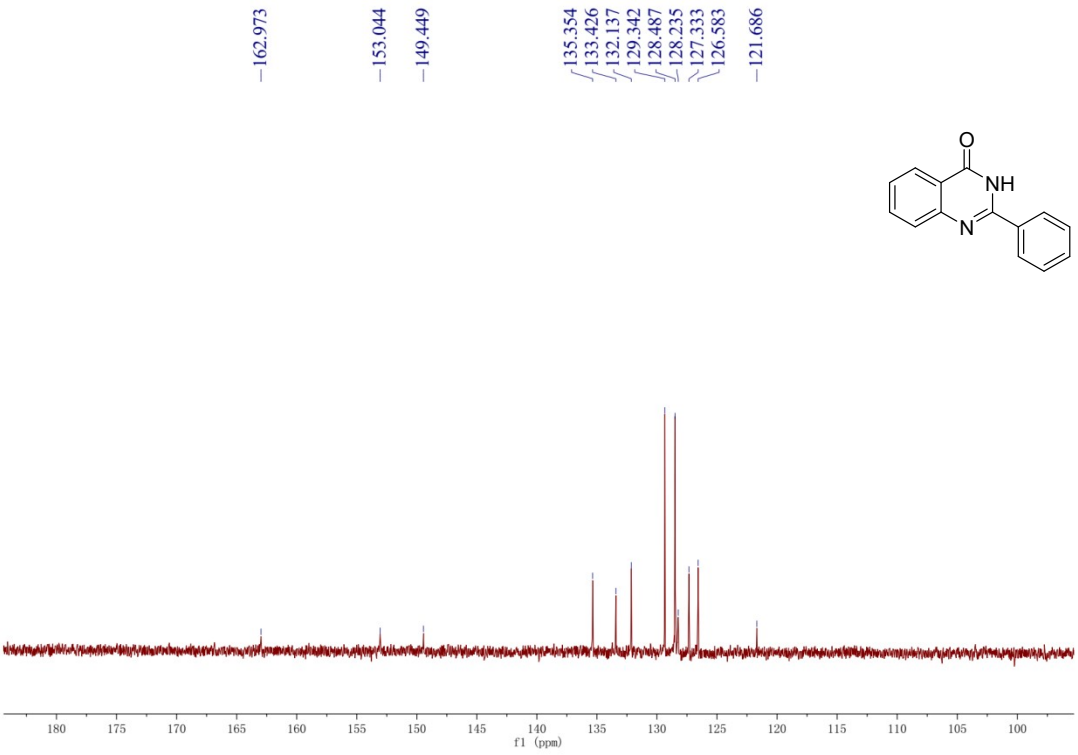
141.692
135.741
133.039
130.582
129.793
129.226
128.844
128.721
127.965
127.065
119.119
117.153
77.365 CDCl3
77.047 CDCl3
76.730 CDCl3
43.562
27.093
O
N
Br
N
f1 (ppm)

2k

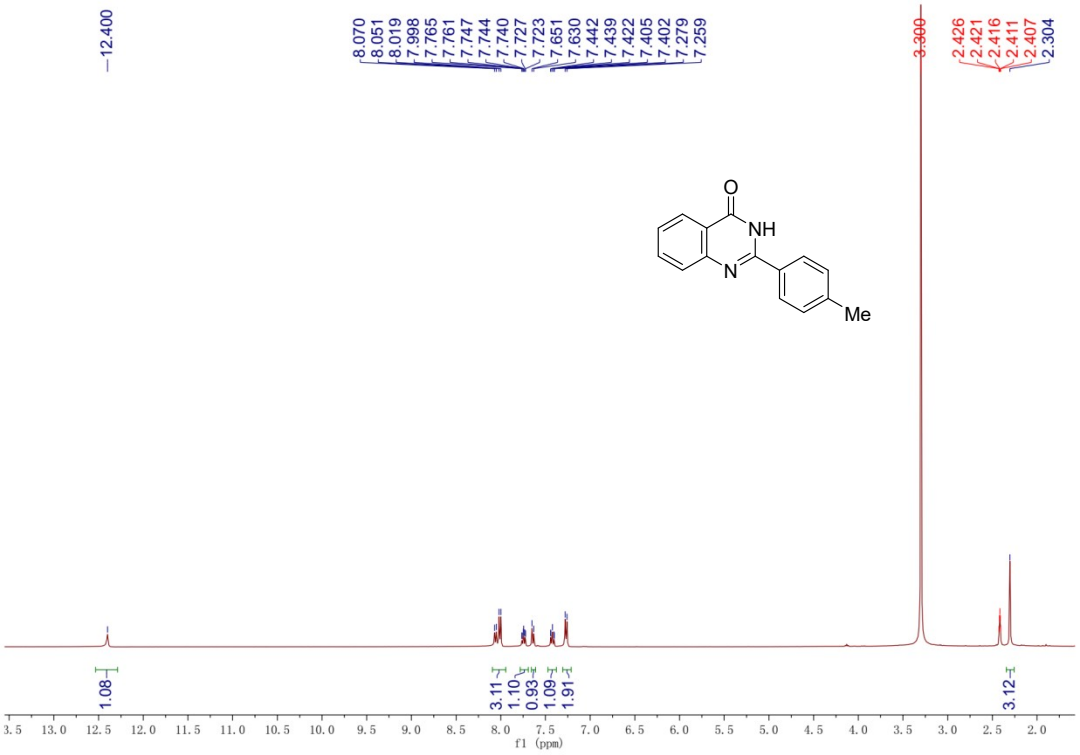

8.716
8.711
8.398
8.393
8.378
8.373
7.805
7.801
7.787
7.783
7.779
7.766
7.762
7.637
7.631
7.617
7.611
7.580
7.558
7.512
7.509
7.492
7.474
7.472
7.286
7.211
7.191
4.398
4.381
4.364
3.286
3.269
3.252
O
N
N
Br
0.84
0.95
1.03
3.04
1.00
2.00
2.00
f1 (ppm)
170.021
154.599
141.409
136.459
135.382
134.809
133.052
131.652
129.837
129.502
127.019
122.645
121.281
114.804
78.227
77.910
77.593
43.975
27.540
O
N
N
Br
f1 (ppm)

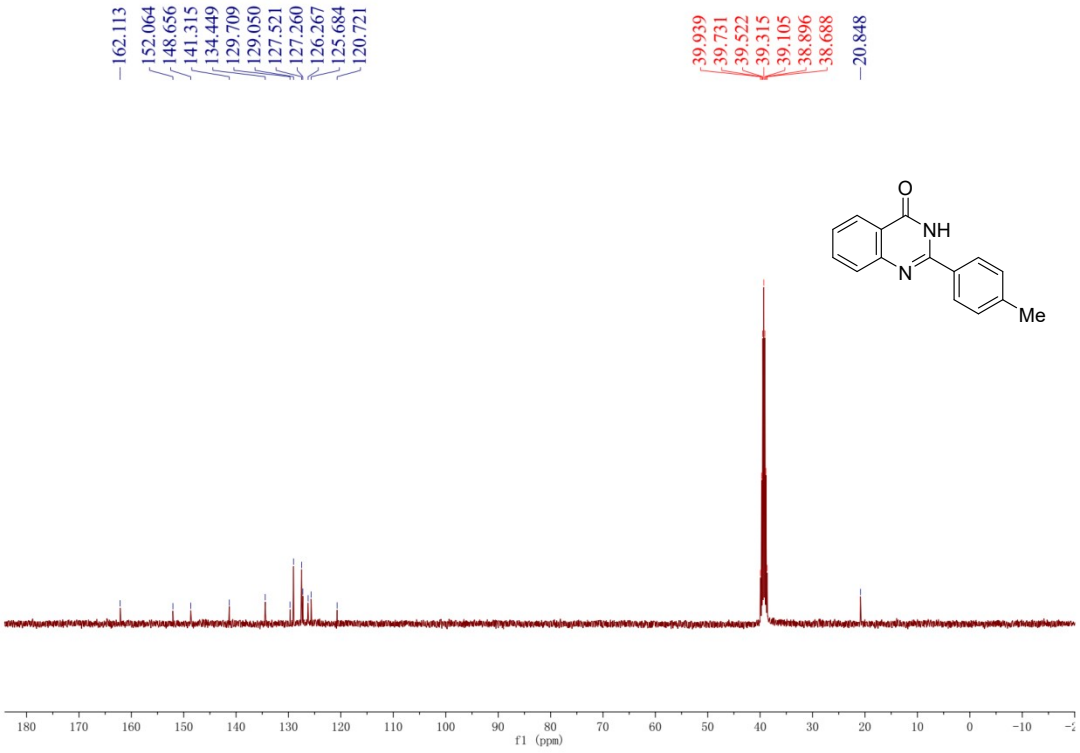
4a


12.548
8.207
8.203
8.187
8.183
8.163
8.159
7.878
7.874
7.860
7.857
7.853
7.840
7.836
7.771
7.769
7.751
7.748
7.632
7.628
7.624
7.619
7.610
7.603
7.597
7.593
7.589
7.583
7.579
7.570
7.564
7.560
7.557
7.552
7.548
7.542
7.540
7.537
7.534
7.523
7.519
O
NH
N
0.90
3.00
0.98
0.98
4.00
13.5 13.0 12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0
f1 (ppm)

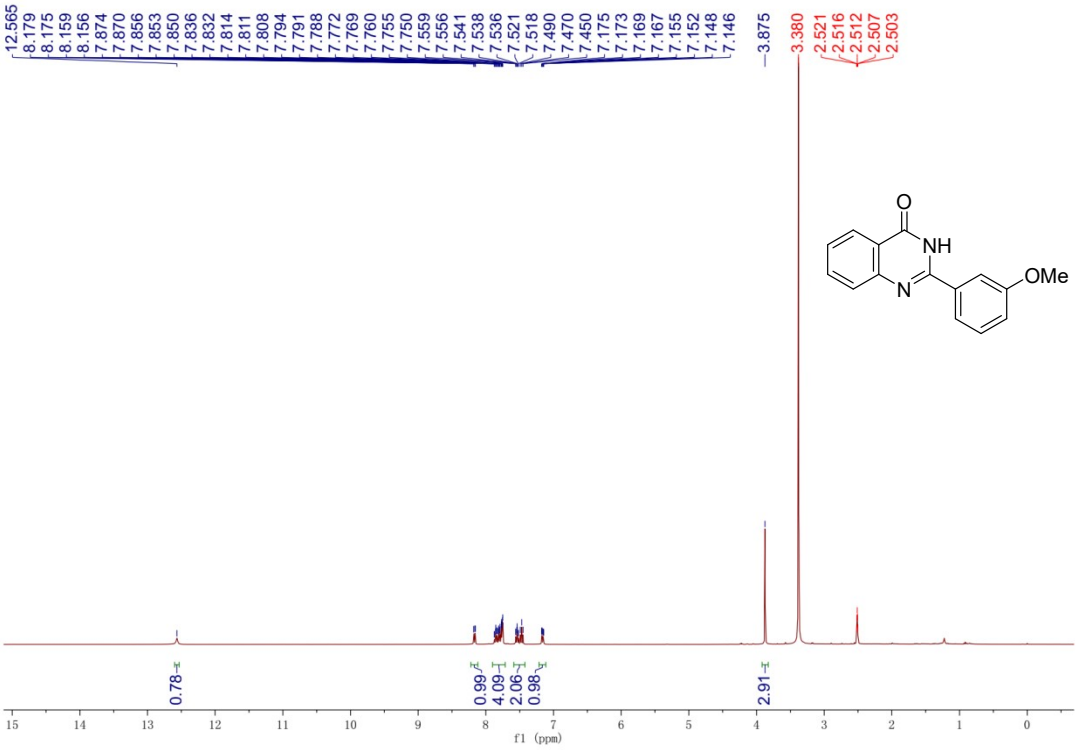

162.973
153.044
149.449
135.354
133.426
132.137
129.342
128.487
128.235
127.333
126.583
121.686
O
NH
N
180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100
f1 (ppm)

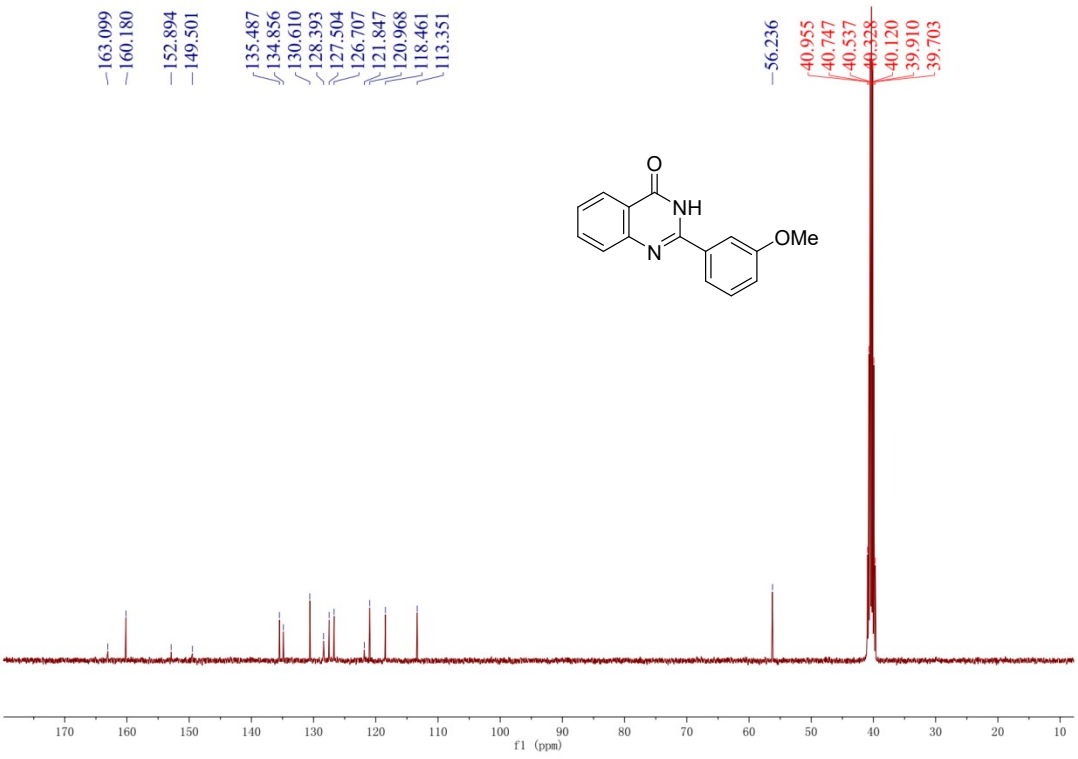
4b


12.400
8.070
8.051
8.019
7.998
7.765
7.761
7.747
7.744
7.740
7.727
7.723
7.651
7.630
7.442
7.439
7.422
7.405
7.402
7.279
7.259
3.300
2.426
2.421
2.416
2.411
2.407
2.304
O
NH
N
Me
1.08
3.11
1.10
0.93
1.09
1.91
3.12
f1 (ppm)


162.113
152.064
148.656
141.315
134.449
129.709
129.050
127.521
127.260
126.267
125.684
120.721
39.939
39.731
39.522
39.315
39.105
38.896
38.688
20.848
O
NH
N
Me
f1 (ppm)

4c


12.565
8.179
8.175
8.159
8.156
7.874
7.870
7.856
7.853
7.850
7.836
7.832
7.814
7.811
7.808
7.794
7.791
7.788
7.772
7.769
7.760
7.755
7.750
7.559
7.556
7.541
7.538
7.536
7.521
7.518
7.490
7.470
7.450
7.175
7.173
7.169
7.167
7.155
7.152
7.148
7.146
3.875
3.380
2.521
2.516
2.512
2.507
2.503
O
NH
N
OMe
0.78
0.99
4.09
2.06
0.98
2.91
f1 (ppm)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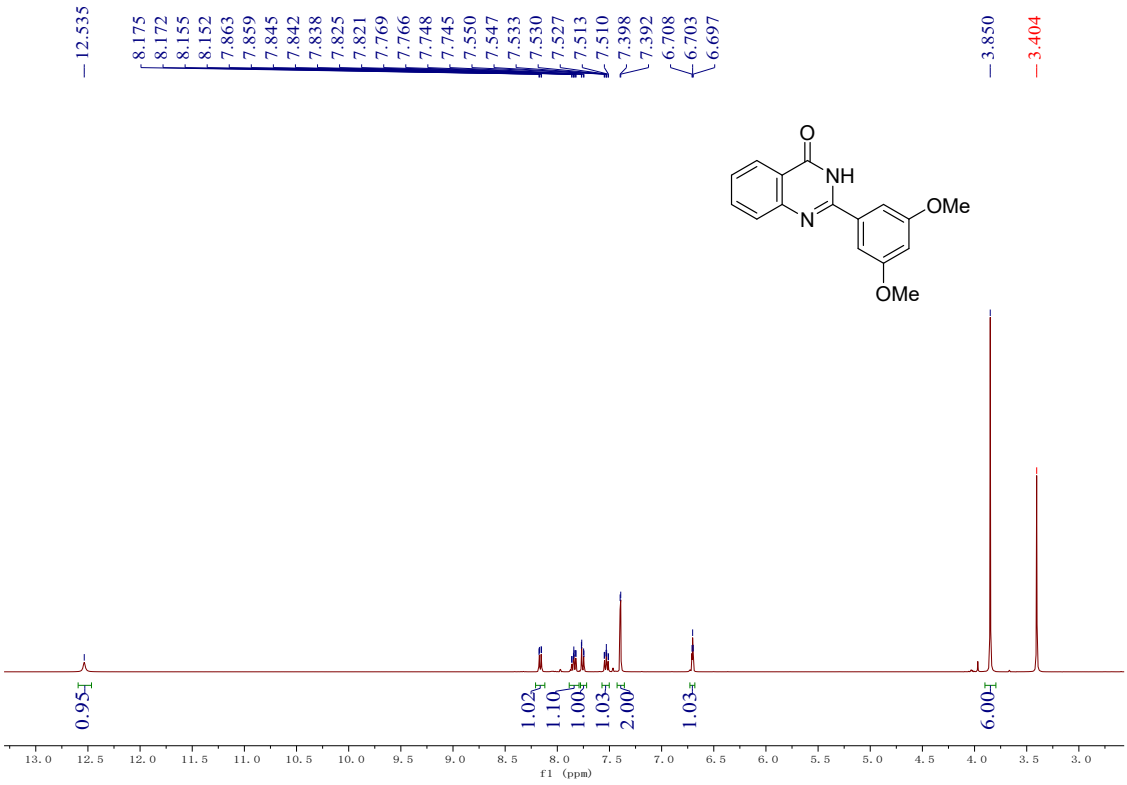
160.180
152.894
149.501
135.487
134.856
130.610
128.393
127.504
126.707
121.847
120.968
118.461
113.351
56.236
40.955
40.747
40.537
40.328
40.120
39.910
39.703
O
NH
N
OMe
f1 (ppm)

4d


12.535
8.175
8.172
8.155
8.152
7.863
7.859
7.845
7.842
7.838
7.825
7.821
7.769
7.766
7.748
7.745
7.550
7.547
7.533
7.530
7.527
7.513
7.510
7.398
7.392
6.708
6.703
6.697
3.850
3.404
O
NH
N
OMe
OMe
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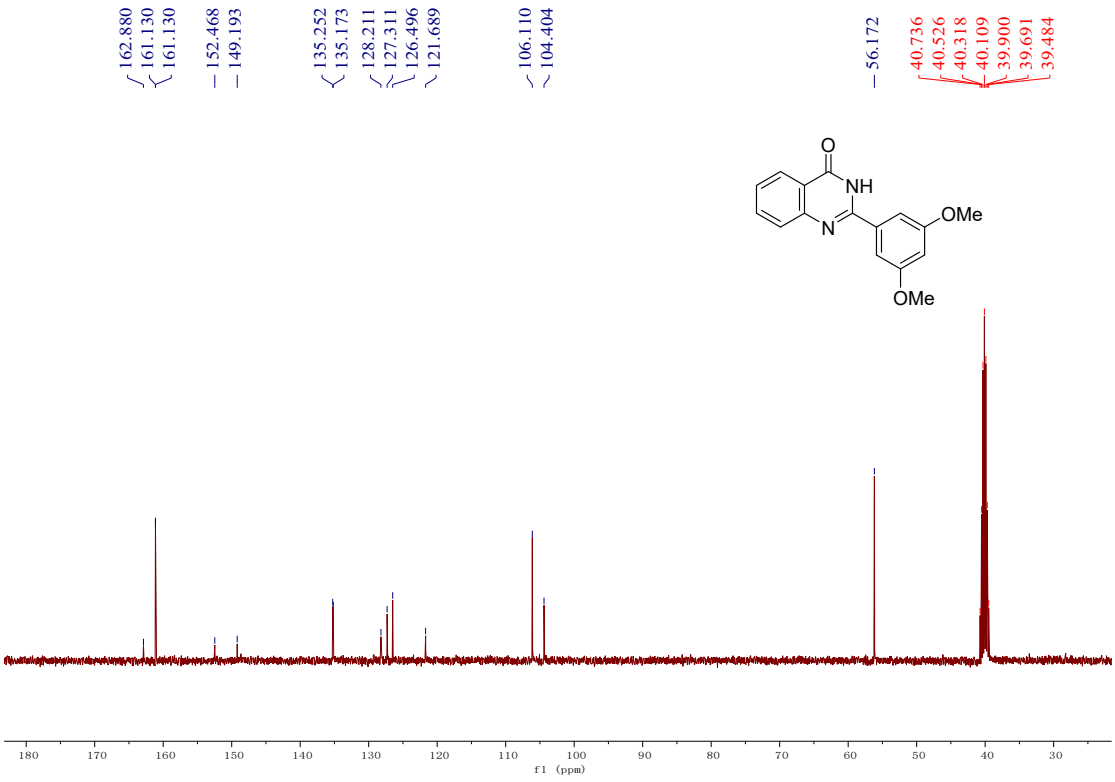
1.02
1.10
1.00
1.03
2.00
1.03
6.00
f1 (ppm)


162.880
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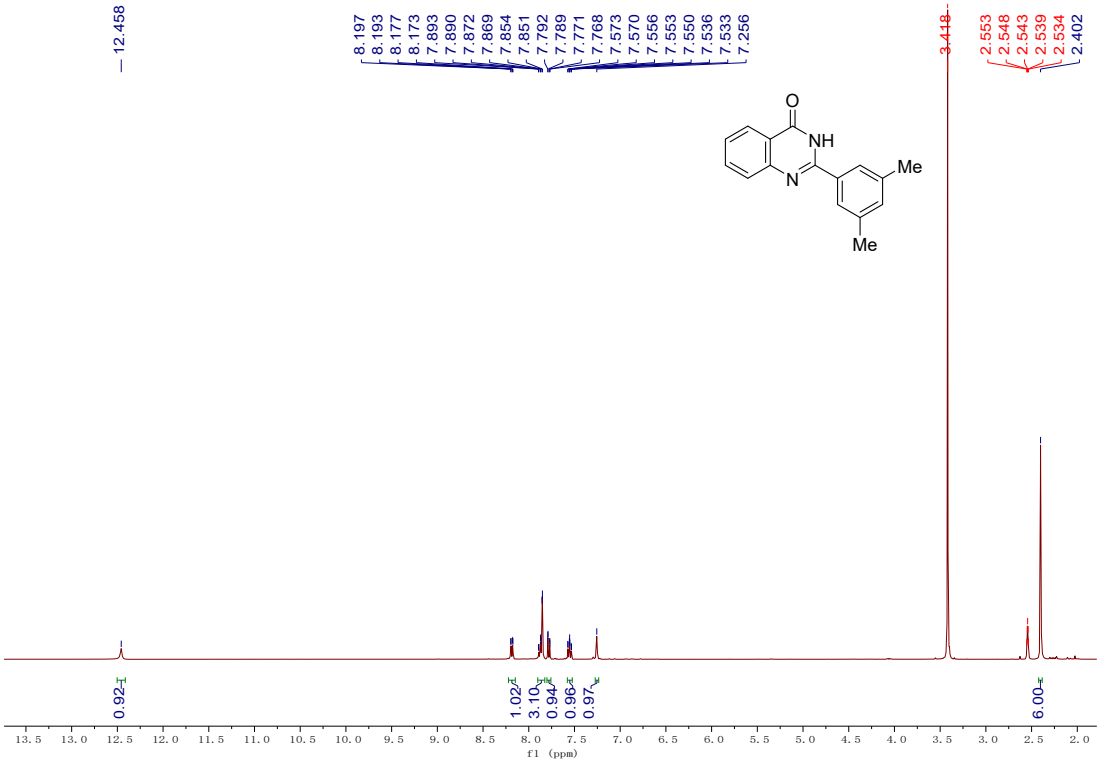
161.130
152.468
149.193
135.252
135.173
128.211
127.311
126.496
121.689
106.110
104.404
56.172
40.736
40.526
40.318
40.109
39.900
39.691
39.484
O
NH
N
OMe
OMe
f1 (ppm)

4e


12.458
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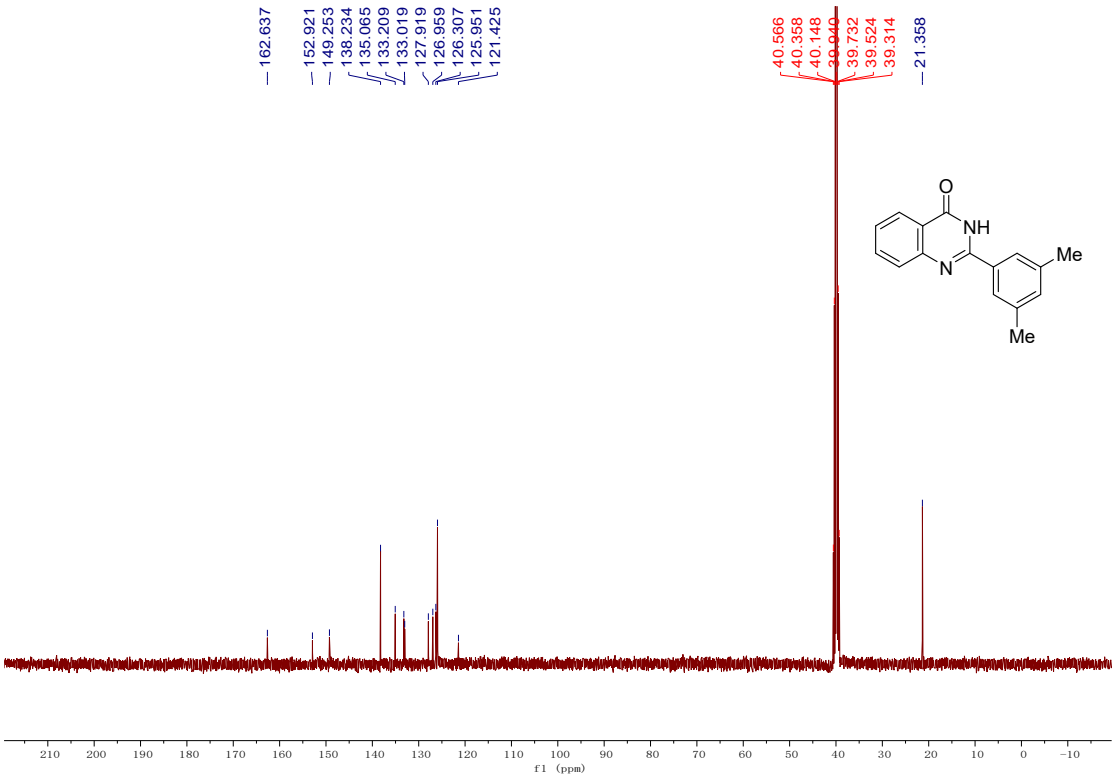
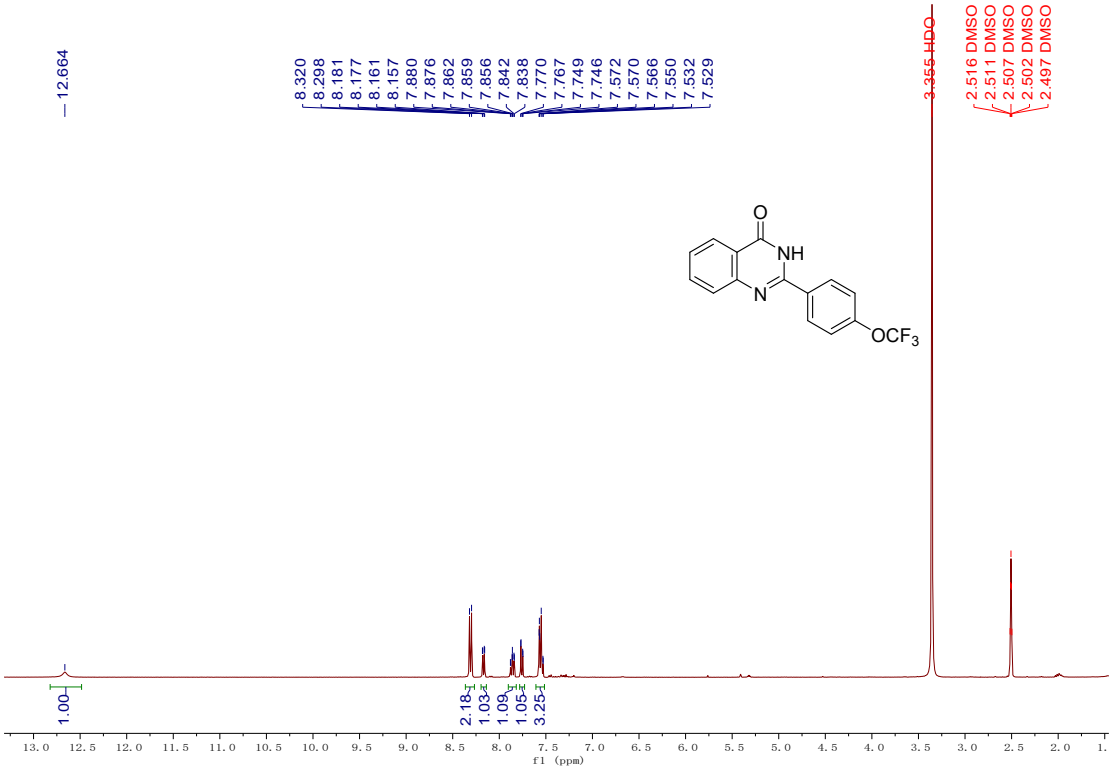
8.177
8.173
7.893
7.890
7.872
7.869
7.854
7.851
7.792
7.789
7.771
7.768
7.573
7.570
7.556
7.553
7.550
7.536
7.533
7.256
3.418
2.553
2.548
2.543
2.539
2.534
2.402
O
NH
N
Me
Me
0.92
1.02
3.10
0.94
0.96
0.97
6.00
f1 (ppm)


162.637
152.921
149.253
138.234
135.065
133.209
133.019
127.919
126.959
126.307
125.951
121.425
40.566
40.358
40.148
39.940
39.732
39.524
39.314
21.358
O
NH
N
Me
Me
f1 (ppm)

4f


12.664
8.320
8.298
8.181
8.177
8.161
8.157
7.880
7.876
7.862
7.859
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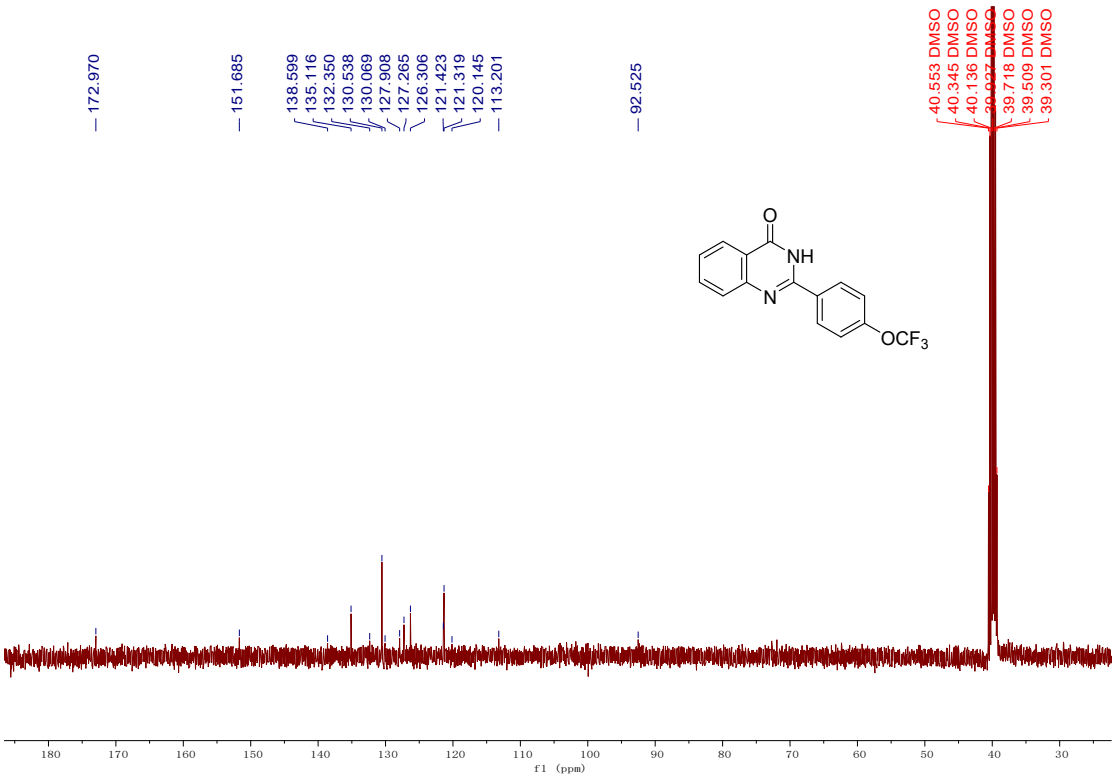
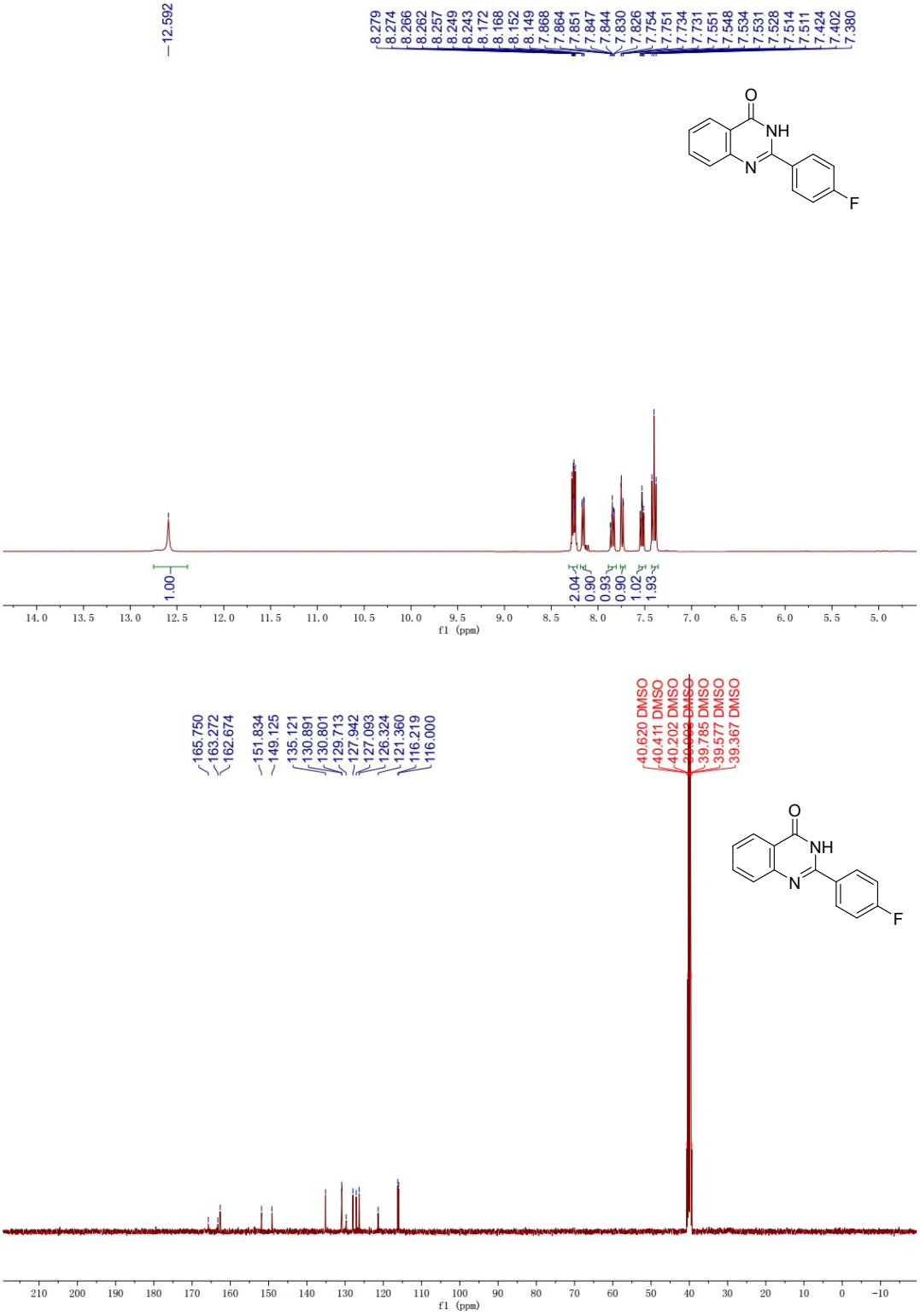
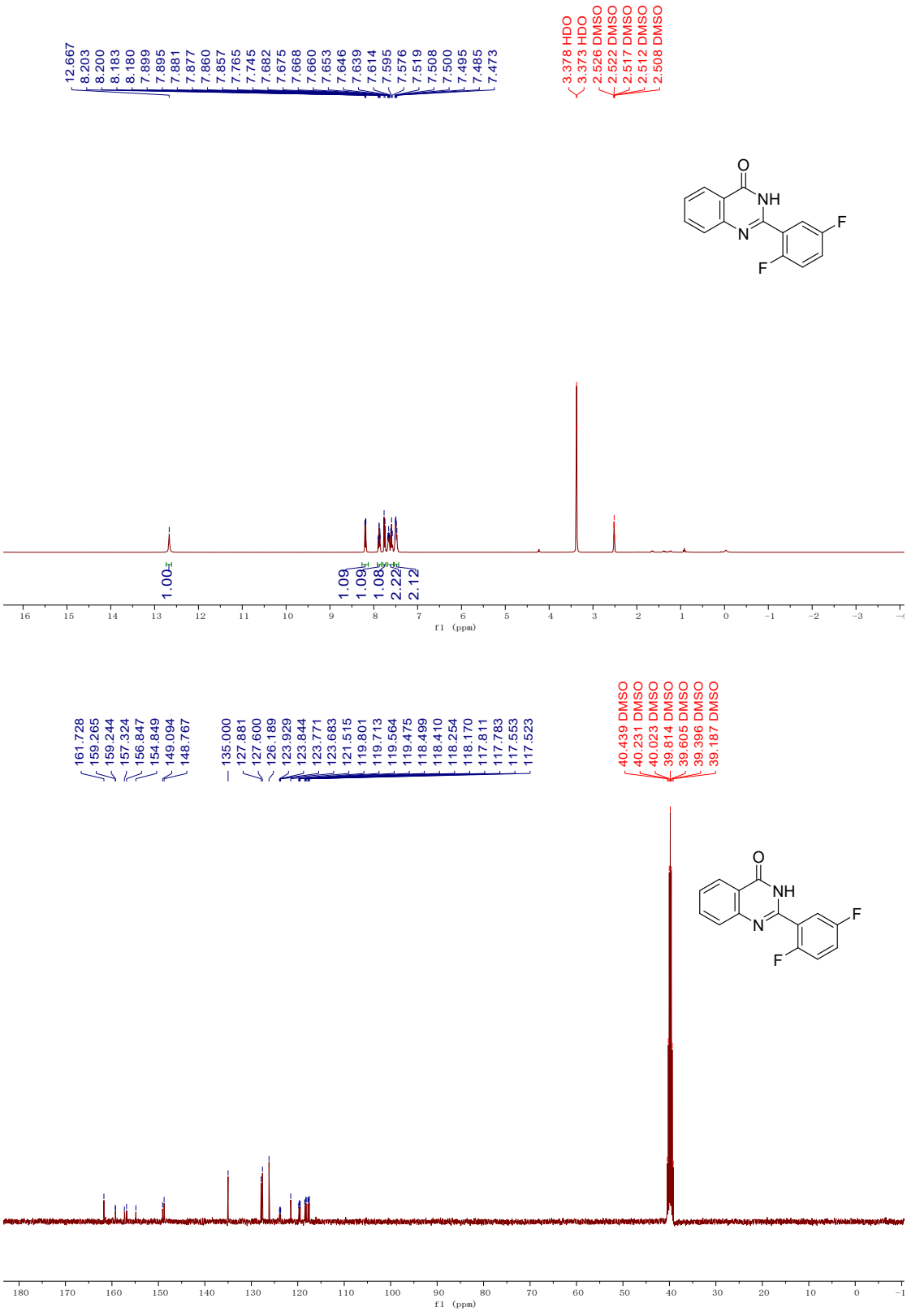
7.842
7.838
7.770
7.767
7.749
7.746
7.572
7.570
7.566
7.550
7.532
7.529
3.355 HDO
2.516 DMSO
2.511 DMSO
2.507 DMSO
2.502 DMSO
2.497 DMSO
O
NH
N
OCF3
1.00
2.18
1.03
1.09
1.05
3.25
f1 (ppm)


172.970
151.685
138.599
135.116
132.350
130.538
130.069
127.908
127.265
126.306
121.423
121.319
120.145
113.201
92.525
40.553 DMSO
40.345 DMSO
40.136 DMSO
39.718 DMSO
39.509 DMSO
39.301 DMSO
O
NH
N
OCF3
f1 (ppm)

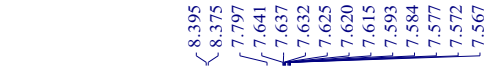
4g

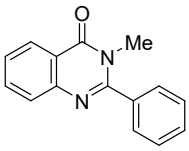

12.592
8.279
8.274
8.266
8.262
8.257
8.249
8.243
8.172
8.168
8.152
8.149
7.868
7.864
7.851
7.847
7.844
7.830
7.826
7.754
7.751
7.734
7.731
7.551
7.548
7.534
7.531
7.528
7.514
7.511
7.424
7.402
7.380
O
NH
N
F
1.00
2.04
0.90
0.93
0.90
1.02
1.93
f1 (ppm)
165.750
163.272
162.674
151.834
149.125
135.121
130.891
130.801
129.713
127.942
127.093
126.324
121.360
116.219
116.000
40.620 DMSO
40.411 DMSO
40.202 DMSO
39.785 DMSO
39.577 DMSO
39.367 DMSO
f1 (ppm)

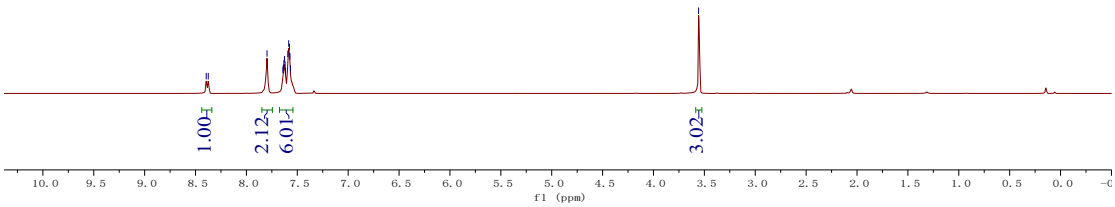
4h


12.667
8.203
8.200
8.183
8.180
7.899
7.895
7.881
7.877
7.860
7.857
7.765
7.745
7.682
7.675
7.668
7.660
7.653
7.646
7.639
7.614
7.595
7.576
7.519
7.508
7.500
7.495
7.485
7.473
3.378 HDO
3.373 HDO
2.526 DMSO
2.522 DMSO
2.517 DMSO
2.512 DMSO
2.508 DMSO
O
NH
N
F
F
1.00
1.09
1.09
1.08
2.22
2.12
f1 (ppm)
161.728
159.265
159.244
157.324
156.847
154.849
149.094
148.767
135.000
127.881
127.600
126.189
123.929
123.844
123.771
123.683
121.515
119.801
119.713
119.564
119.475
118.499
118.410
118.254
118.170
117.811
117.783
117.553
117.523
40.439 DMSO
40.231 DMSO
40.023 DMSO
39.814 DMSO
39.605 DMSO
39.396 DMSO
39.187 DMSO
O
NH
N
F
F
f1 (ppm)

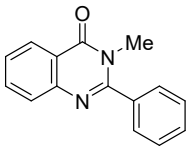
4i

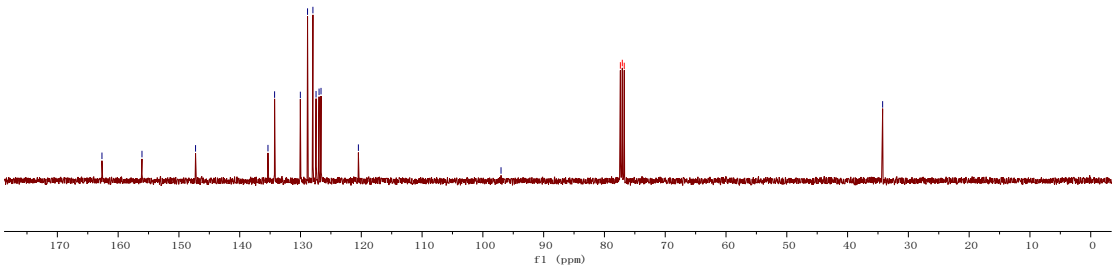

8.395
8.375
7.797
7.641
7.637
7.632
7.625
7.620
7.615
7.593
7.584
7.577
7.572
7.567
3.557


O
N
Me
N

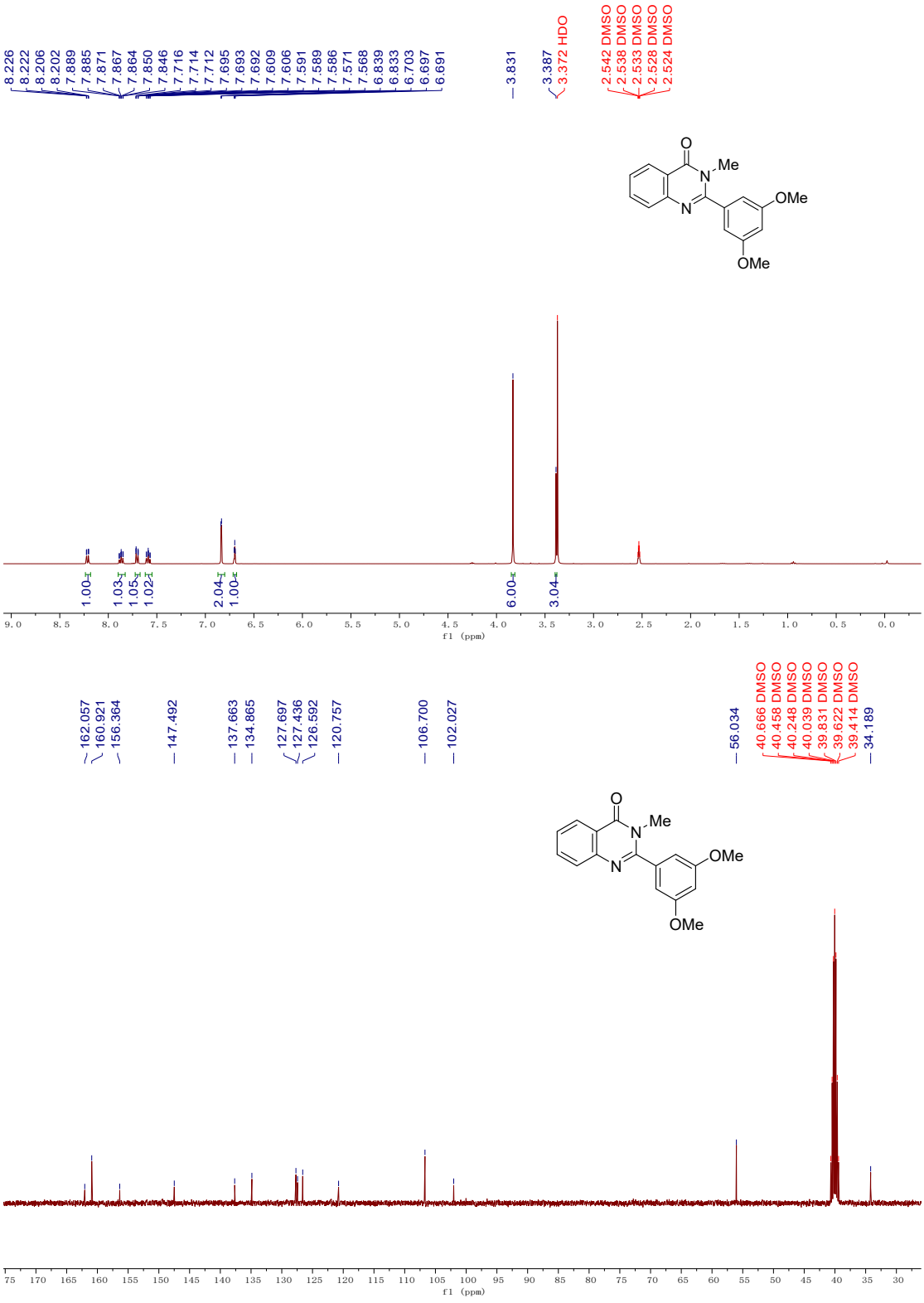

1.00
2.12
6.01
3.02
f1 (ppm)


162.664
156.080
147.266
135.353
134.264
130.027
128.844
127.959
127.444
126.947
126.627
120.477
97.013
77.379
77.062
76.742
34.234

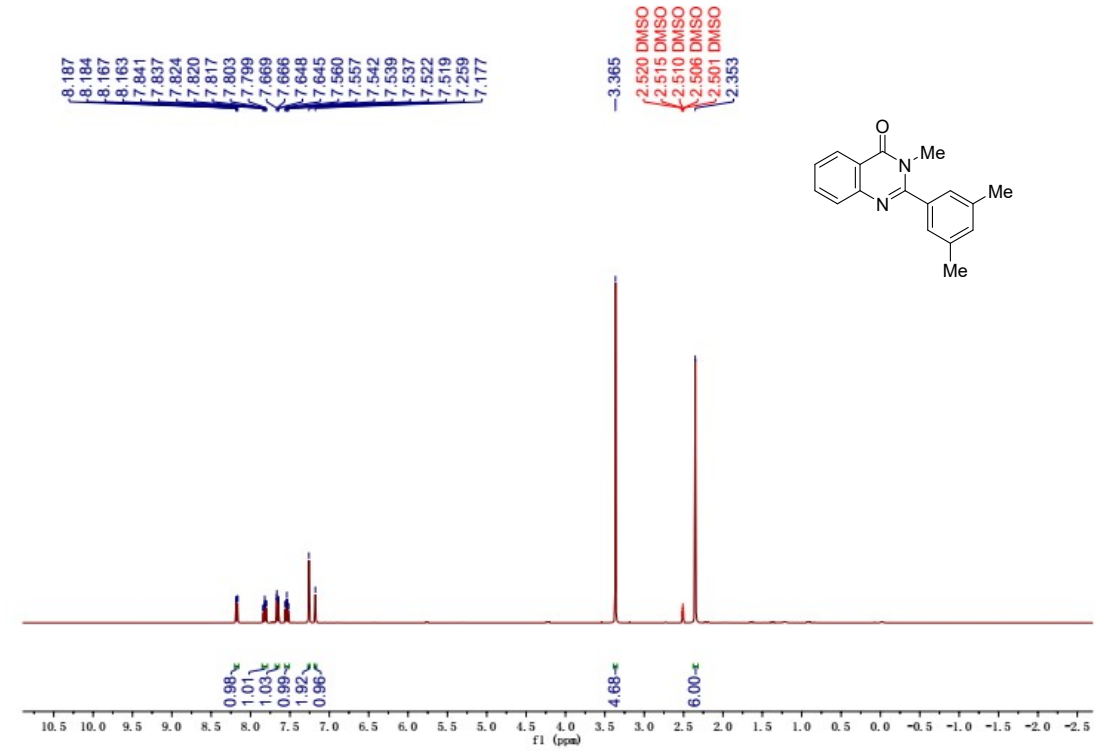

O
N
Me
N

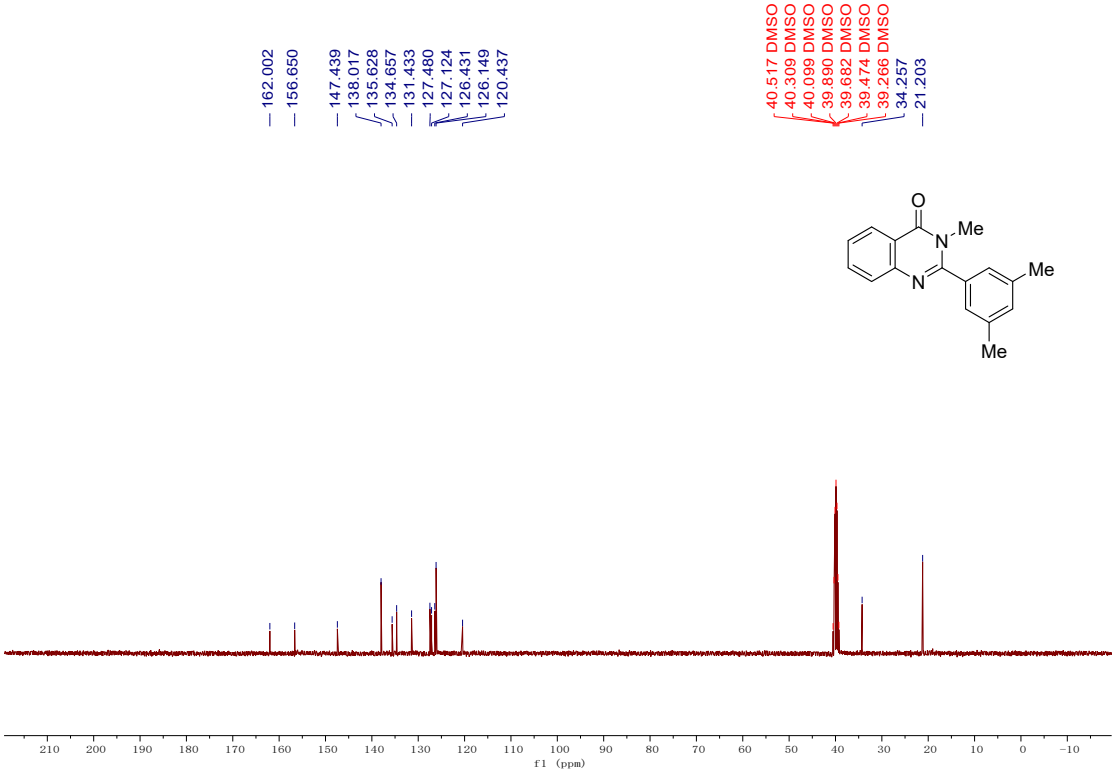

f1 (ppm)

4j

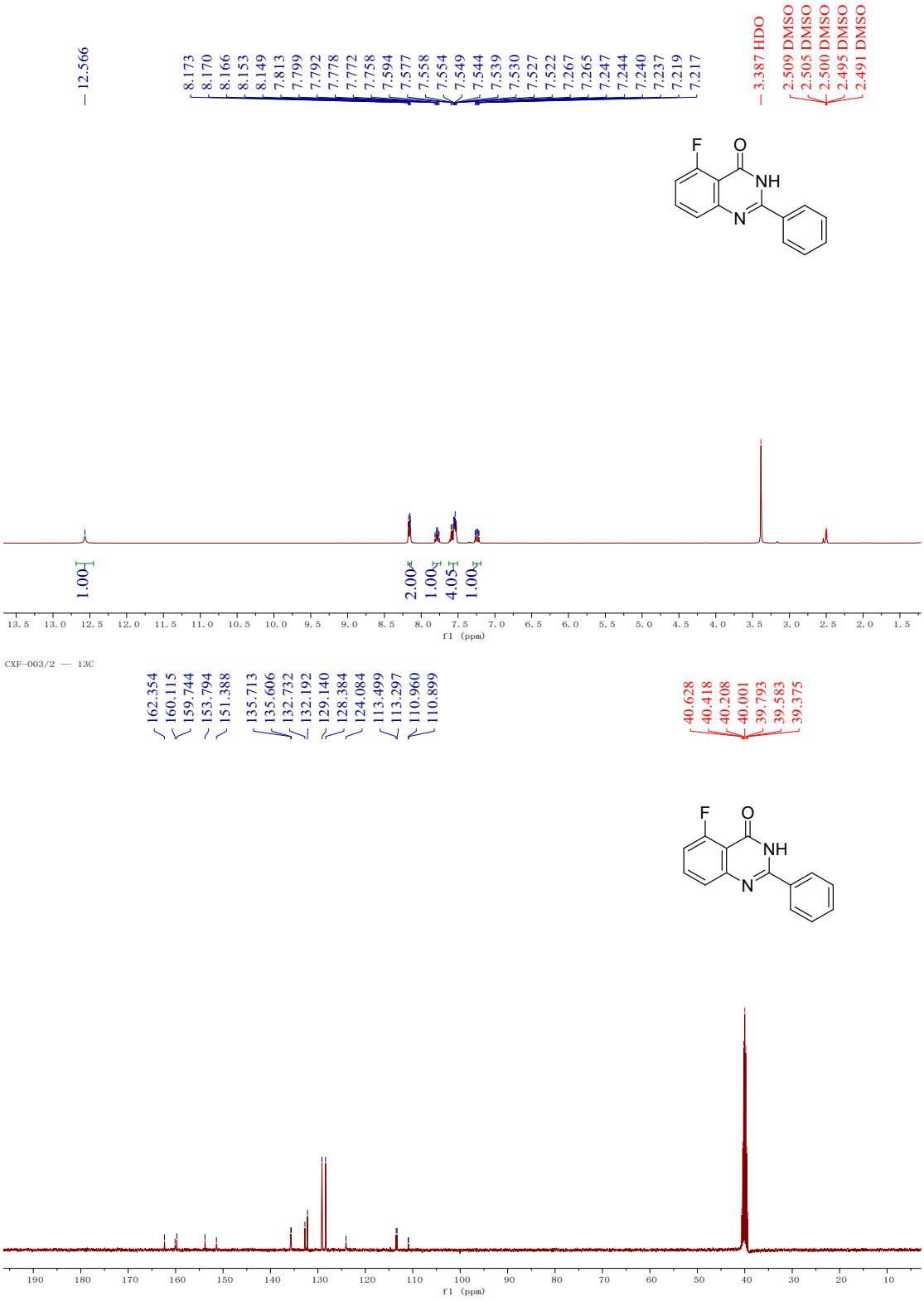

8.226
8.222
8.206
8.202
7.889
7.885
7.871
7.867
7.864
7.850
7.846
7.716
7.714
7.712
7.695
7.693
7.692
7.609
7.606
7.591
7.589
7.586
7.571
7.568
6.839
6.833
6.703
6.697
6.691
3.831
3.387
3.372 HDO
2.542 DMSO
2.538 DMSO
2.533 DMSO
2.528 DMSO
2.524 DMSO
O
N
Me
N
OMe
OMe
1.00
1.03
1.05
1.02
2.04
1.00
6.00
3.04
f1 (ppm)
162.057
160.921
156.364
147.492
137.663
134.865
127.697
127.436
126.592
120.757
106.700
102.027
56.034
40.666 DMSO
40.458 DMSO
40.248 DMSO
40.039 DMSO
39.831 DMSO
39.622 DMSO
39.414 DMSO
34.189
O
N
Me
N
OMe
OMe
f1 (ppm)

4k

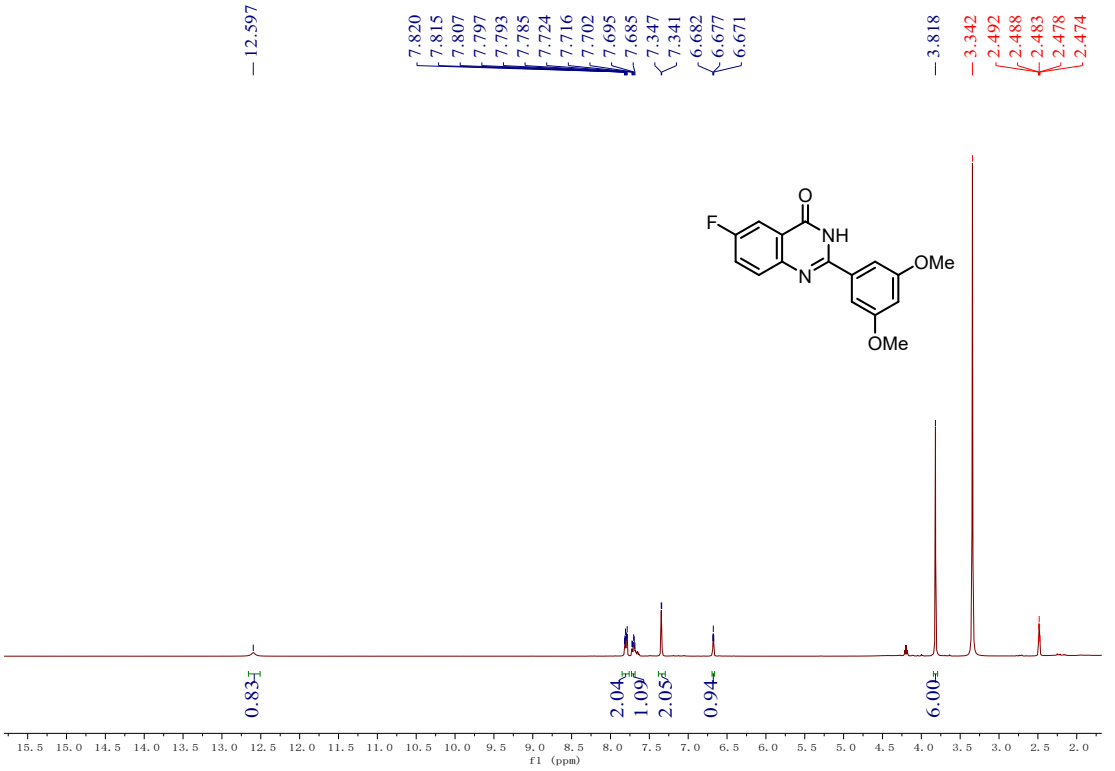

8.187
8.184
8.167
8.163
7.841
7.837
7.824
7.820
7.817
7.803
7.799
7.669
7.666
7.648
7.645
7.560
7.557
7.542
7.539
7.537
7.522
7.519
7.259
7.177
3.365
2.520 DMSO
2.515 DMSO
2.510 DMSO
2.506 DMSO
2.501 DMSO
2.353
O
N
Me
N
Me
Me
0.98
1.01
1.03
0.99
1.92
0.96
4.68
6.00
f1 (ppm)

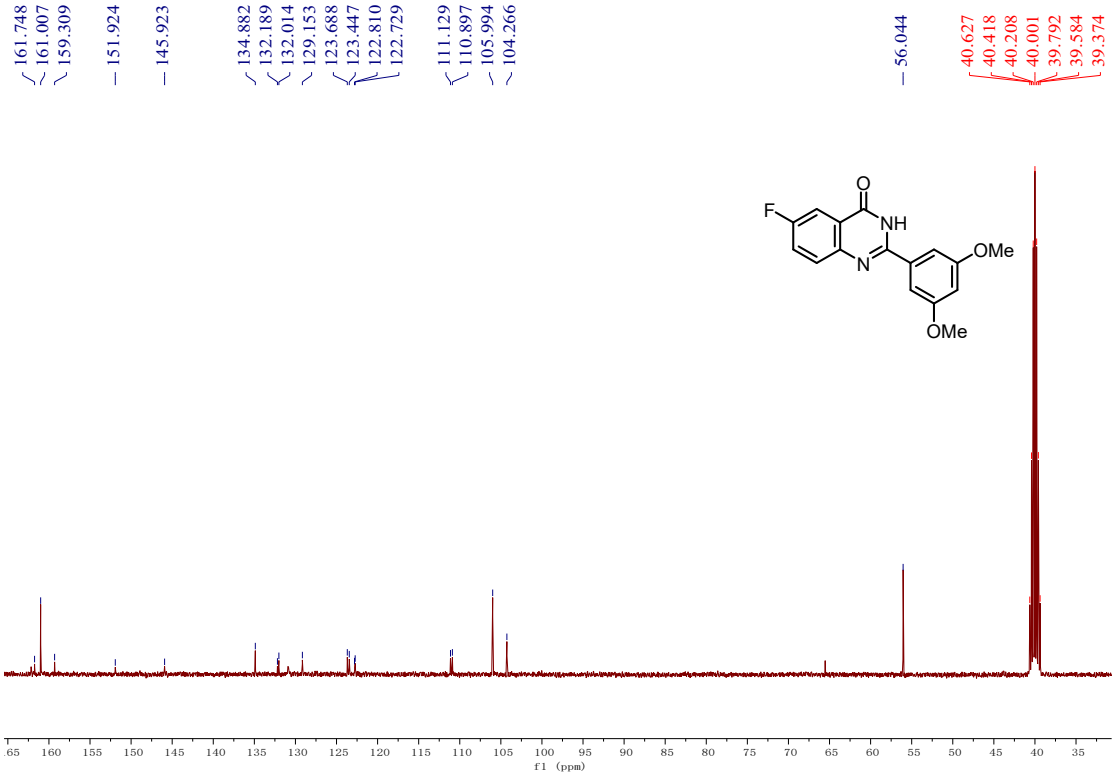

162.002
156.650
147.439
138.017
135.628
134.657
131.433
127.480
127.124
126.431
126.149
120.437
40.517 DMSO
40.309 DMSO
40.099 DMSO
39.890 DMSO
39.682 DMSO
39.474 DMSO
39.266 DMSO
34.257
21.203
O
N
Me
N
Me
Me
f1 (ppm)

4l

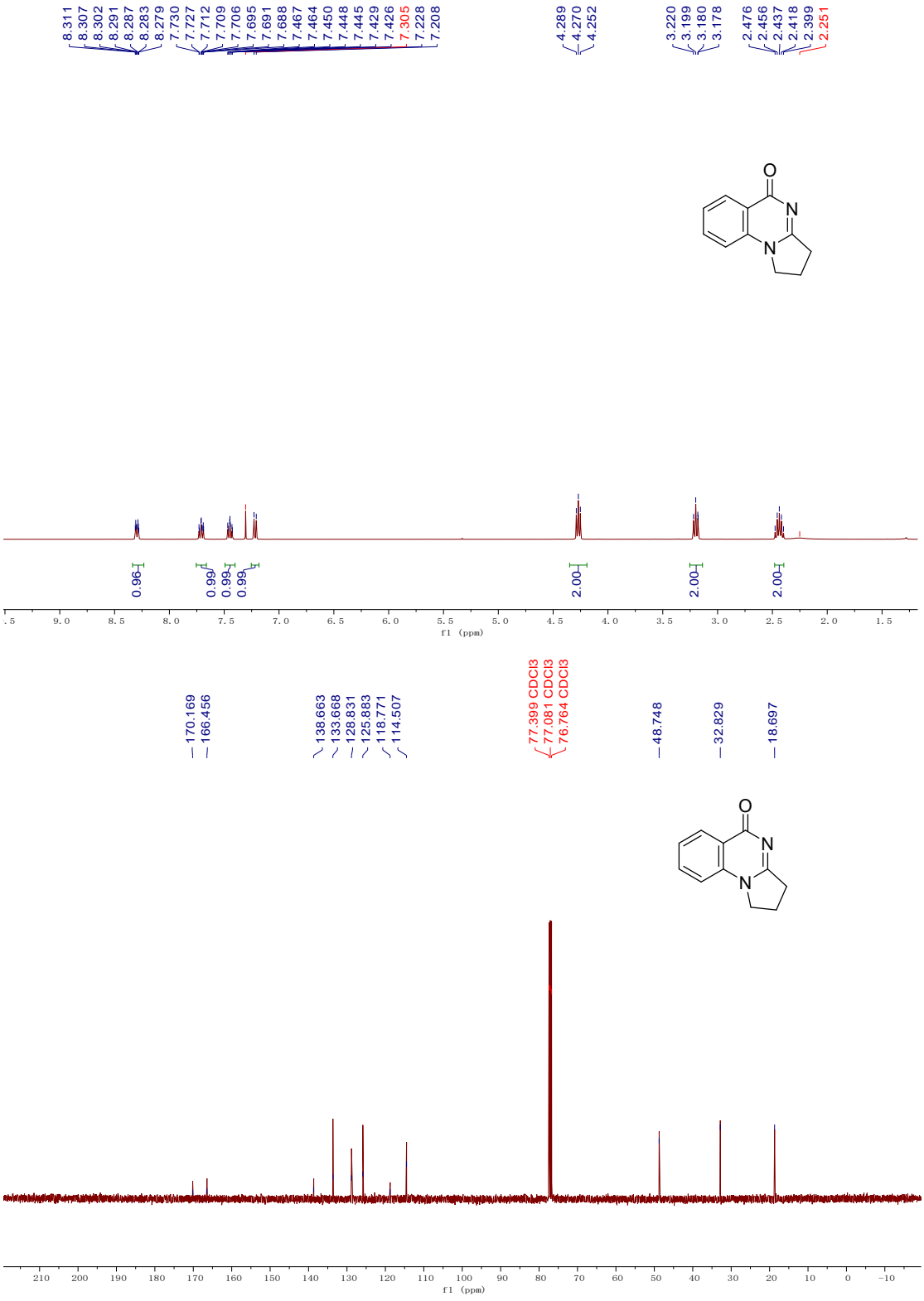

12.566
8.173
8.170
8.166
8.153
8.149
7.813
7.799
7.792
7.778
7.772
7.758
7.594
7.577
7.558
7.554
7.549
7.544
7.539
7.530
7.527
7.522
7.267
7.265
7.247
7.244
7.240
7.237
7.219
7.217
3.387 HDO
2.509 DMSO
2.505 DMSO
2.500 DMSO
2.495 DMSO
2.491 DMSO
F
O
NH
N
1.00
2.00
1.00
4.05
1.00
f1 (ppm)
CXF-003/2 — 13C
162.354
160.115
159.744
153.794
151.388
135.713
135.606
132.732
132.192
129.140
128.384
124.084
113.499
113.297
110.960
110.899
40.628
40.418
40.208
40.001
39.793
39.583
39.375
f1 (ppm)

4m

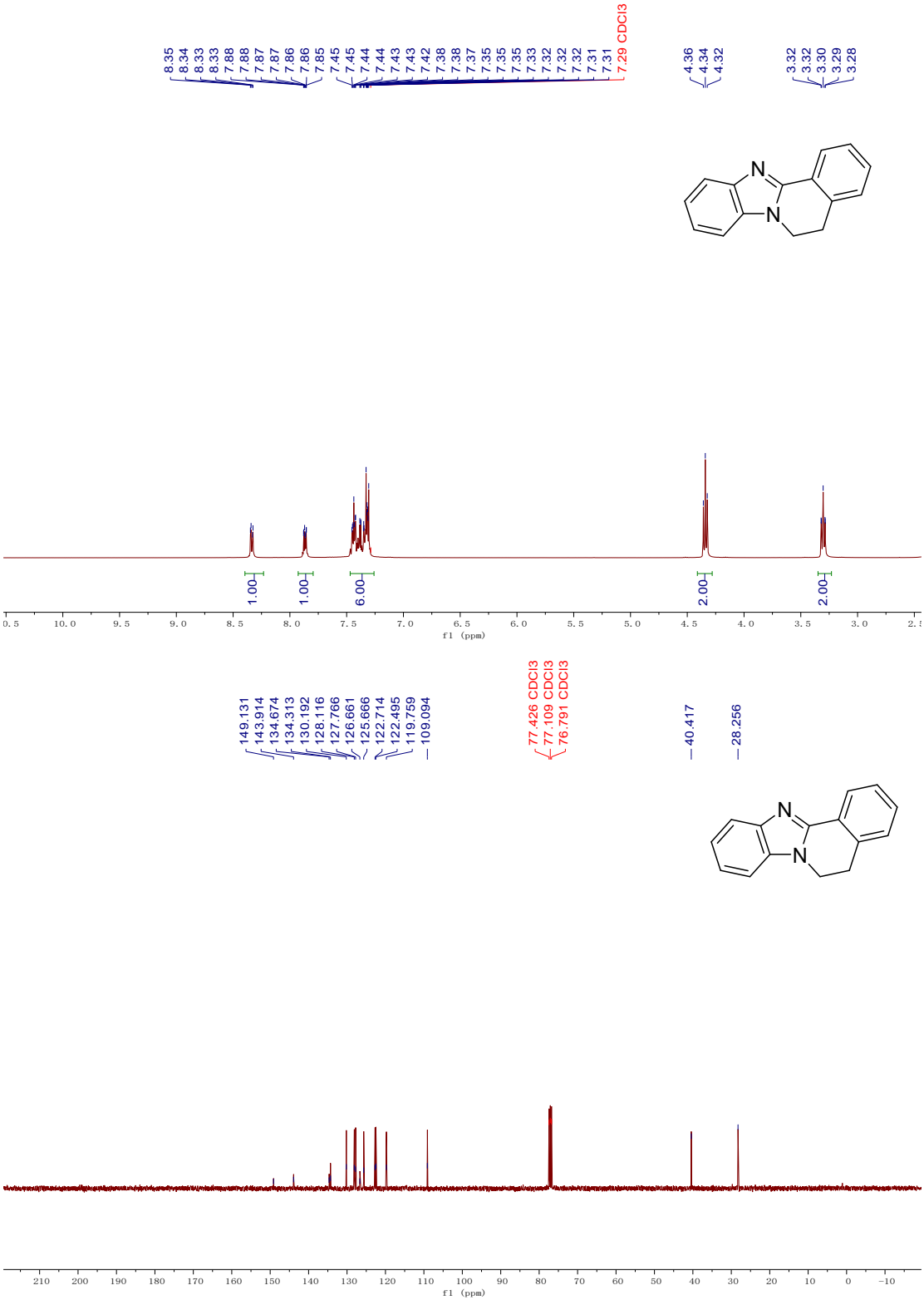

12.597
7.820
7.815
7.807
7.797
7.793
7.785
7.724
7.716
7.702
7.695
7.685
7.347
7.341
6.682
6.677
6.671
3.818
3.342
2.492
2.488
2.483
2.478
2.474
F
O
NH
N
OMe
OMe
0.83
2.04
1.09
2.05
0.94
6.00
f1 (ppm)


161.748
161.007
159.309
151.924
145.923
134.882
132.189
132.014
129.153
123.688
123.447
122.810
122.729
111.129
110.897
105.994
104.266
56.044
40.627
40.418
40.208
40.001
39.792
39.584
39.374
F
O
NH
N
OMe
OMe
f1 (ppm)

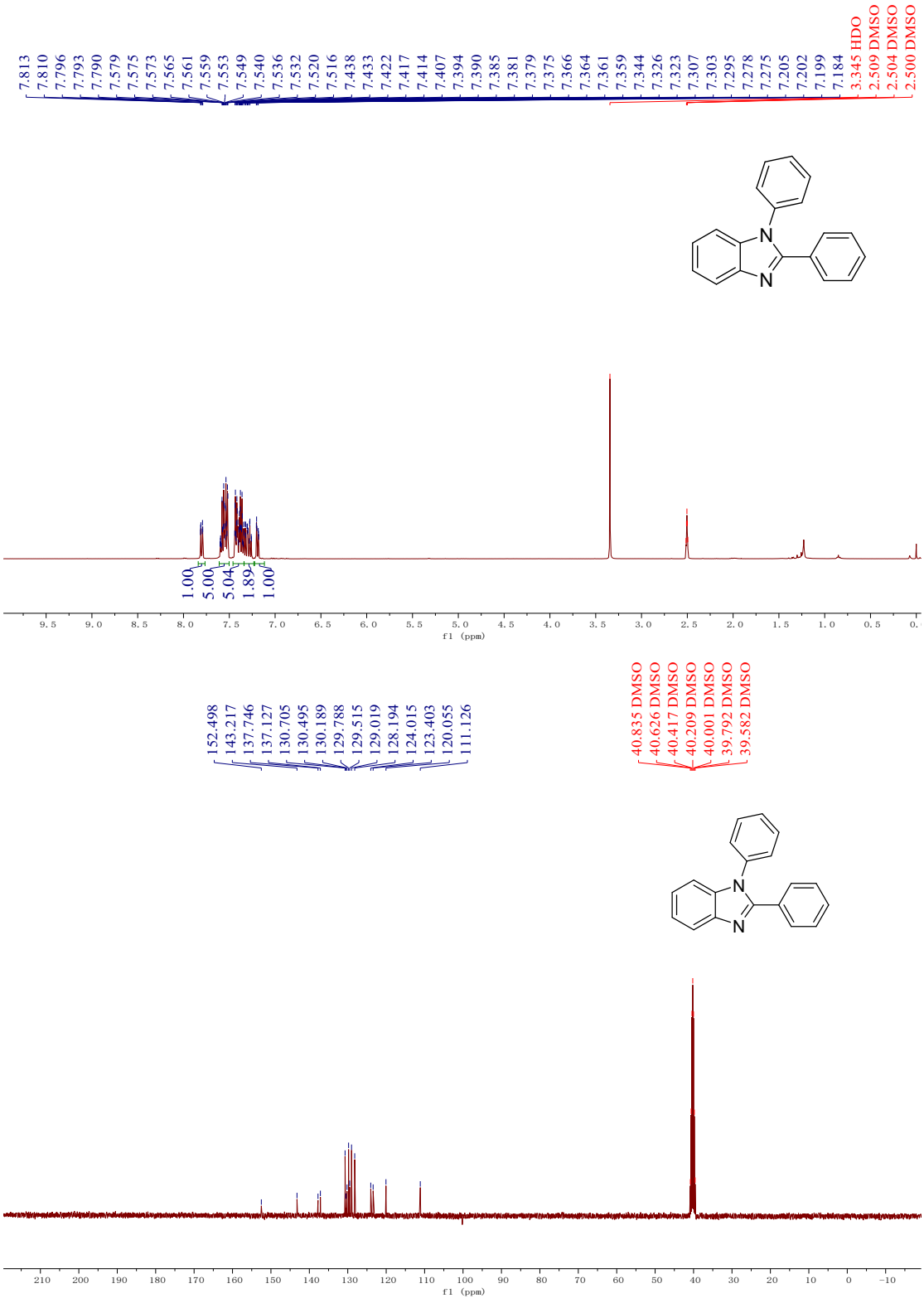
6a


8.311
8.307
8.302
8.291
8.287
8.283
8.279
7.730
7.727
7.712
7.709
7.706
7.695
7.691
7.688
7.467
7.464
7.450
7.448
7.445
7.429
7.426
7.305
7.228
7.208
4.289
4.270
4.252
3.220
3.199
3.180
3.178
2.476
2.456
2.437
2.418
2.399
2.251
O
N
N
0.96
0.99
0.99
0.99
2.00
2.00
2.00
f1 (ppm)
170.169
166.456
138.663
133.668
128.831
125.883
118.771
114.507
77.399 CDCl3
77.081 CDCl3
76.764 CDCl3
48.748
32.829
18.697
O
N
N
f1 (ppm)

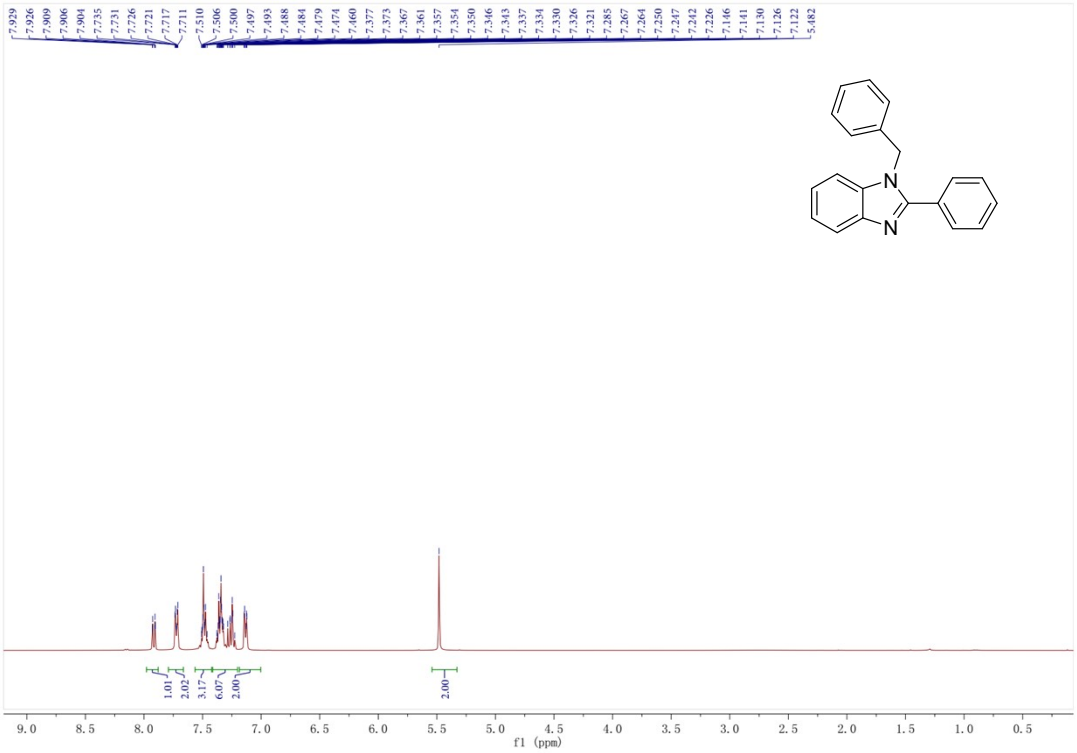
6b

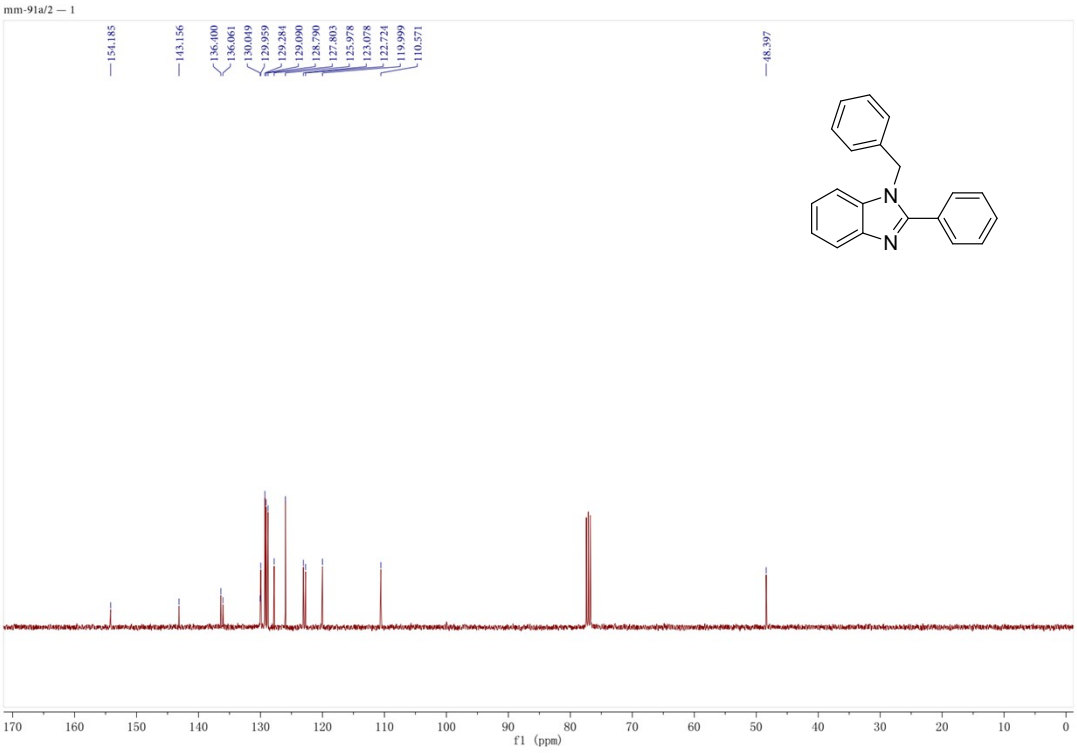

8.35
8.34
8.33
8.33
7.88
7.88
7.87
7.87
7.86
7.86
7.85
7.45
7.45
7.44
7.44
7.43
7.43
7.42
7.38
7.38
7.37
7.35
7.35
7.35
7.33
7.32
7.32
7.32
7.31
7.31
7.29 CDCl3
4.36
4.34
4.32
3.32
3.32
3.30
3.29
3.28
N
N
1.00
1.00
6.00
2.00
2.00
f1 (ppm)
149.131
143.914
134.674
134.313
130.192
128.116
127.766
126.661
125.666
122.714
122.495
119.759
109.094
77.426 CDCl3
77.109 CDCl3
76.791 CDCl3
40.417
28.256
N
N
f1 (ppm)

6c

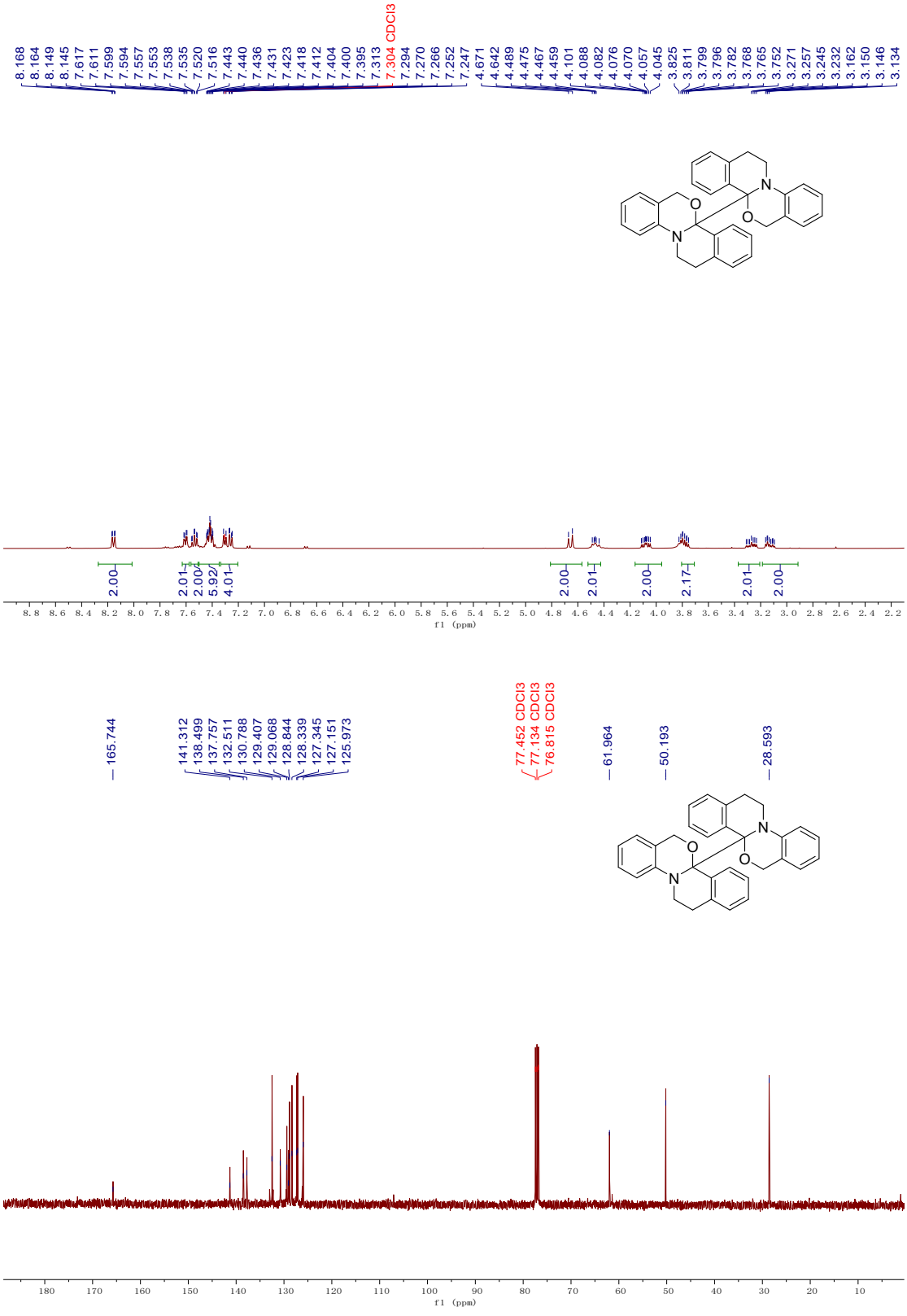

7.813
7.810
7.796
7.793
7.790
7.579
7.575
7.573
7.565
7.561
7.559
7.553
7.549
7.540
7.536
7.532
7.520
7.516
7.438
7.433
7.422
7.417
7.414
7.407
7.394
7.390
7.385
7.381
7.379
7.375
7.366
7.364
7.361
7.359
7.344
7.326
7.323
7.307
7.303
7.295
7.278
7.275
7.205
7.202
7.199
7.184
3.345 HDO
2.509 DMSO
2.504 DMSO
2.500 DMSO
N
N
1.00
5.00
5.04
1.89
1.00
f1 (ppm)
152.498
143.217
137.746
137.127
130.705
130.495
130.189
129.788
129.515
129.019
128.194
124.015
123.403
120.055
111.126
40.835 DMSO
40.626 DMSO
40.417 DMSO
40.209 DMSO
40.001 DMSO
39.792 DMSO
39.582 DMSO
N
N
f1 (ppm)

6d


7.939
7.926
7.909
7.906
7.904
7.735
7.731
7.726
7.721
7.717
7.711
7.510
7.506
7.500
7.497
7.493
7.488
7.484
7.479
7.474
7.460
7.377
7.373
7.367
7.361
7.357
7.354
7.350
7.346
7.343
7.337
7.334
7.330
7.326
7.321
7.285
7.267
7.264
7.250
7.247
7.242
7.226
7.146
7.141
7.130
7.126
7.122
5.482
1.01
2.02
3.17
6.07
2.00
2.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)
N
N

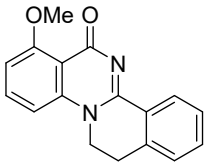

mm-91a/2 — 1
151.185
143.156
136.400
136.061
130.019
129.959
129.284
129.090
128.790
127.803
125.978
123.078
122.724
119.999
110.571
48.397
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
N
N

6e


8.168
8.164
8.149
8.145
7.617
7.611
7.599
7.594
7.557
7.553
7.538
7.535
7.520
7.516
7.443
7.440
7.436
7.431
7.423
7.418
7.412
7.404
7.400
7.395
7.313
7.304 CDCl3
7.294
7.270
7.266
7.252
7.247
4.671
4.642
4.489
4.475
4.467
4.459
4.101
4.088
4.082
4.076
4.070
4.057
4.045
3.825
3.811
3.799
3.796
3.782
3.768
3.765
3.752
3.271
3.257
3.245
3.232
3.162
3.150
3.146
3.134
N
O
O
N
2.00
2.01
2.00
5.92
4.01
2.00
2.01
2.00
2.17
2.01
2.00
f1 (ppm)
165.744
141.312
138.499
137.757
132.511
130.788
129.407
129.068
128.844
128.339
127.345
127.151
125.973
77.452 CDCl3
77.134 CDCl3
76.815 CDCl3
61.964
50.193
28.593
N
O
O
N
f1 (ppm)

8. HRMS spectra

2b



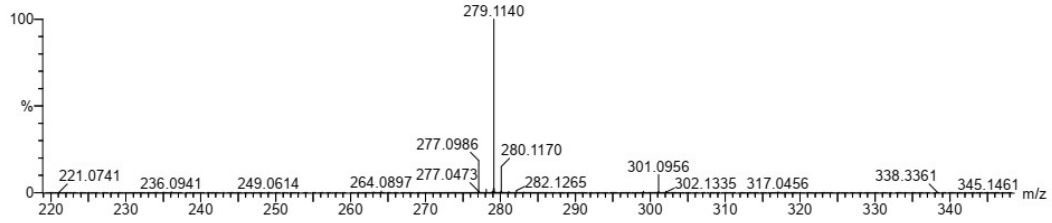
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
395 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 17-17 H: 10-20 N: 0-6 O: 0-8 Cl: 0-2 Br: 0-2

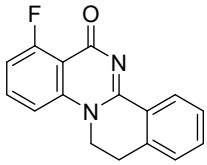
1
0114-1-zr-2b 129 (0.732)

1: TOF MS ES+
3.43e+006



Minimum:				-1.5				
Maximum:		5.0	30.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
279.1140	279.1134	0.6	2.1	11.5	1338.6	n/a	n/a	C17 H15 N2 O2

2e



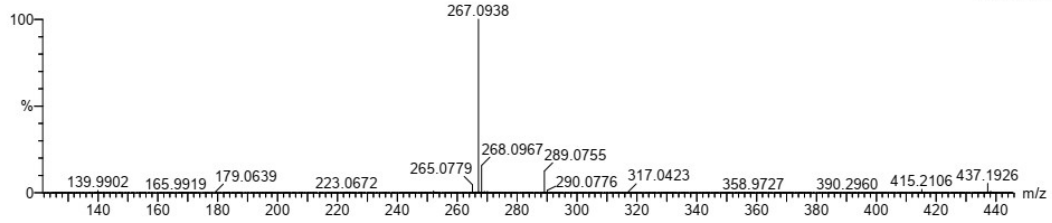
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
309 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 16-16 H: 0-100 N: 0-10 O: 0-10 F: 1-3

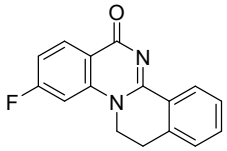
1
0114-1-zr-2e 110 (0.626)

1: TOF MS ES+
4.35e+006



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
267.0938	267.0934	0.4	1.5	11.5	1263.1	n/a	n/a	C16 H12 N2 O F

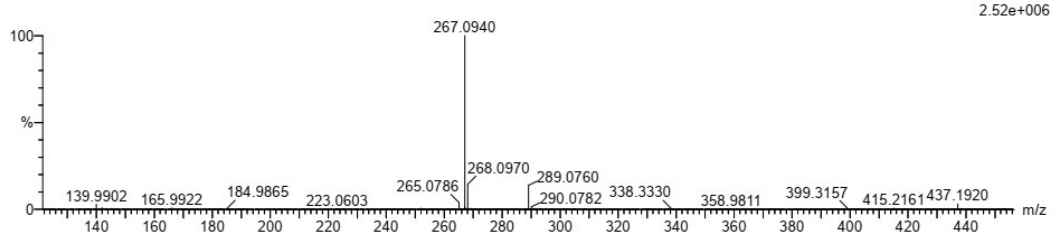
2f



Elemental Composition Report **Page 1**

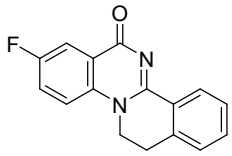
Single Mass Analysis
Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
309 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)
Elements Used:
C: 16-16 H: 0-100 N: 0-10 O: 0-10 F: 1-3
0114-1-zr-2f 115 (0.652)
1: TOF MS ES+
2.52e+006



Minimum:				-1.5				
Maximum:		5.0	10.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
267.0940	267.0934	0.6	2.2	11.5	1147.7	n/a	n/a	C16 H12 N2 O F

2g

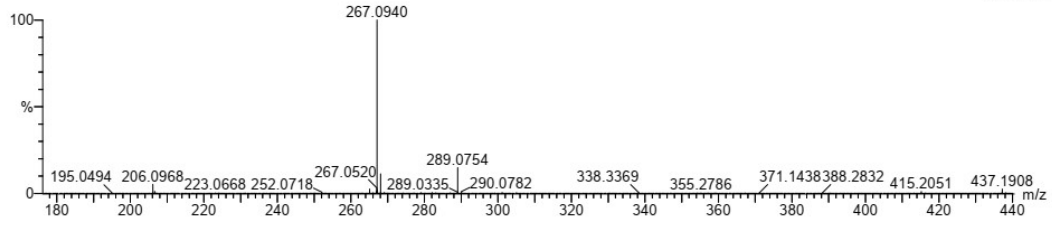


Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

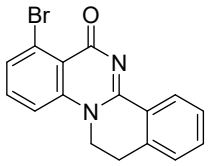
Monoisotopic Mass, Even Electron Ions
172 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 16-17 H: 10-20 N: 0-6 O: 0-8 Cl: 0-2 F: 1-1

1
0114-1-zr-2g 114 (0.647)
1: TOF MS ES+
1.31e+006



Minimum:				-1.5				
Maximum:		5.0	30.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
267.0940	267.0934	0.6	2.2	11.5	1031.0	n/a	n/a	C16 H12 N2 O F

2i



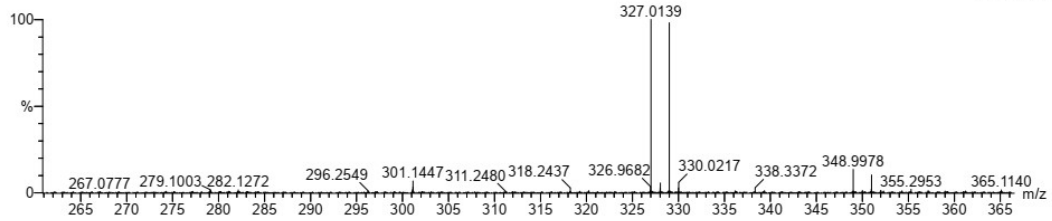
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
440 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 16-17 H: 10-20 N: 0-6 O: 0-8 Cl: 0-2 Br: 0-2

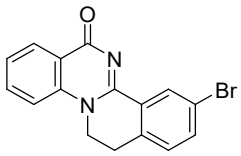
1
0114-1-zr-2i 124 (0.707)

1: TOF MS ES+
9.82e+004



Minimum:				-1.5				
Maximum:		5.0	30.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
327.0139	327.0133	0.6	1.8	11.5	733.8	n/a	n/a	C16 H12 N2 O Br

2k



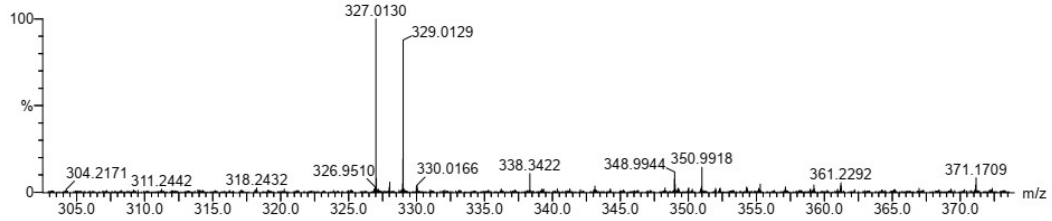
Elemental Composition Report **Page 1**

Single Mass Analysis
Tolerance = 30.0 PPM / DBE: min = -1.5, max = 50.0
Element prediction: Off
Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions
440 formula(e) evaluated with 1 results within limits (up to 50 best isotopic matches for each mass)
Elements Used:
C: 16-17 H: 10-20 N: 0-6 O: 0-8 Cl: 0-2 Br: 0-2

1
0114-1-zr-2k 129 (0.733)

1: TOF MS ES+
3.06e+004



Minimum:				-1.5				
Maximum:		5.0	30.0	50.0				
Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	Norm	Conf(%)	Formula
327.0130	327.0133	-0.3	-0.9	11.5	743.6	n/a	n/a	C16 H12 N2 O Br