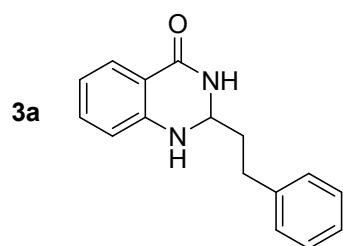


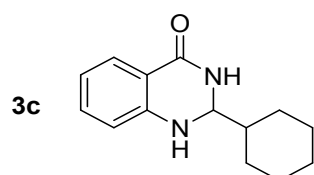
General Methods. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. $^1\text{H-NMR}$ spectra were recorded on 300 MHz or 400 MHz NMR spectrometers. Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl_3 or $\text{d}^6\text{-DMSO}$ as an internal standard. $^{13}\text{C-NMR}$ spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl_3 or $\text{d}^6\text{-DMSO}$.

Experimental procedures and characterization datas of compounds

To a screw-cap vial containing a stir bar, a mixture of **1** (0.3 mmol) and **2** (0.6 mmol) was added in pure water (2 mL). The reaction vial was fitted with a cap. The reaction vial was heated with stirring at 120-130 °C for 24 hours. After cooling down to room temperature and concentrated in vacuum, the residue was purified by flash chromatography on a short silica gel to provide the terminal product **3** and **4**.

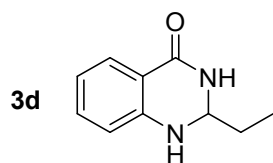


2-phenethyl-2,3-dihydroquinazolinone (3a).^[1] **1a** (40.8 mg, 0.3 mmol), **2a** (80.4 mg, 0.6 mmol). **3a** (8 mg, 11%, n-hexane/ethyl acetate = 3:1): white solid; $^1\text{H NMR}$ (300 MHz, CDCl_3) δ 7.89 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.34-7.21 (m, 5H), 6.85 (t, $J = 7.5$ Hz, 2H), 6.59 (d, $J = 8.1$ Hz, 1H), 4.92 (t, $J = 5.6$ Hz, 1H), 3.60 (s, br, 1H), 2.92-2.73 (m, 2H), 2.16-2.09 (m, 2H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3) δ 165.3, 147.2, 140.3, 133.8, 128.8, 128.5, 128.4, 126.5, 119.4, 115.9, 114.8, 65.1, 37.1, 30.5.

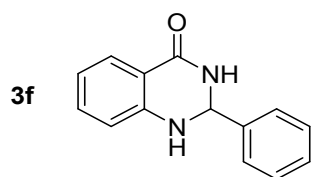


2-cyclohexyl-2,3-dihydroquinazolinone (3c).^[2] **1a** (40.8 mg, 0.3 mmol), **2c** (67.2 mg, 0.6 mmol). **3c** (23 mg, 34%, n-hexane/ethyl acetate = 3:1): white solid; $^1\text{H NMR}$ (300 MHz, DMSO) δ 7.91 (s, 1H), 7.56 (dd, $J = 7.7, 1.1$ Hz, 1H), 7.25 – 7.13 (m, 1H), 6.74

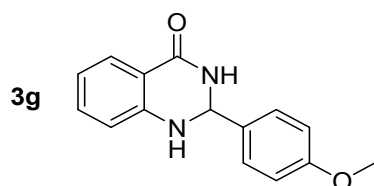
(d, $J = 8.1$ Hz, 1H), 6.63-6.56 (m, 2H), 4.45 (s, 1H), 1.70-1.12 (m, 11H). ^{13}C NMR (75 MHz, DMSO) δ 164.2, 148.8, 133.5, 127.7, 116.9, 115.3, 114.6, 69.0, 43.3, 27.5, 27.2, 26.4, 26.1, 26.0.



2-ethyl-2,3-dihydroquinazolinone (3d).^[3] **1a** (40.8 mg, 0.3 mmol), **2d** (69.6 mg, 1.2 mmol). **3d** (11 mg, 21%, n-hexane/ethyl acetate = 1:1): white solid; ^1H NMR (300 MHz, DMSO) δ 7.86 (s, 1H), 7.57 (d, $J = 7.7$ Hz, 1H), 7.27 – 7.17 (m, 1H), 6.72 (d, $J = 7.9$ Hz, 1H), 6.65 (t, $J = 7.4$ Hz, 1H), 6.55 (s, 1H), 4.65 (t, $J = 5.0$ Hz, 1H), 1.73 – 1.55 (m, 2H), 0.93 (t, $J = 7.4$ Hz, 3H). ^{13}C NMR (75 MHz, DMSO) δ 164.5, 149.1, 133.5, 127.9, 117.4, 115.5, 114.8, 65.9, 28.3, 8.6.

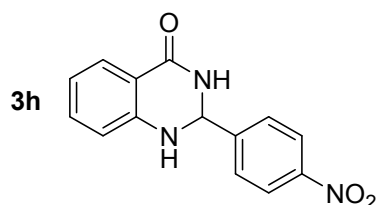


2-phenyl-2,3-dihydroquinazolinone (3f).^[1] **1a** (40.8 mg, 0.3 mmol), **2f** (63.6 mg, 0.6 mmol). **3f** (58 mg, 86%, n-hexane/ethyl acetate = 1:1): white solid; ^1H NMR (300 MHz, DMSO) δ 8.27 (s, br, 1H), 7.60 (d, $J = 7.5$ Hz, 1H), 7.49 (d, $J = 8.1$ Hz, 2H), 7.42-7.34 (m, 3H), 7.24 (t, $J = 7.5$ Hz, 1H), 7.10 (s, br, 1H), 6.74 (d, $J = 8.1$ Hz, 1H), 6.67 (t, $J = 7.8$ Hz, 1H), 5.75 (s, 1H); ^{13}C NMR (75 MHz, DMSO) δ 162.6, 153.1, 148.7, 135.2, 132.9, 132.0, 129.1, 128.8, 128.3, 127.6, 126.4, 121.4.

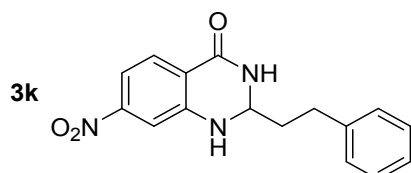


2-(4-methoxyphenyl)-2,3-dihydroquinazolinone (3g).^[2] **1a** (40.8 mg, 0.3 mmol), **2g** (81.6 mg, 0.6 mmol). **3g** (21 mg, 27%, n-hexane/ethyl acetate = 1:2): white solid; ^1H

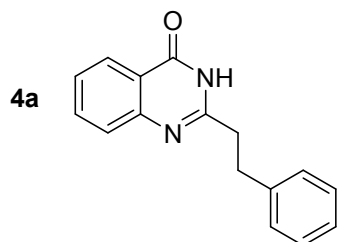
NMR (300 MHz, DMSO) δ 8.20 (s, 1H), 7.61 (d, $J = 7.6$ Hz, 1H), 7.42 (d, $J = 8.6$ Hz, 2H), 7.30 – 7.16 (m, 1H), 7.02 (s, 1H), 6.95 (d, $J = 8.7$ Hz, 2H), 6.74 (d, $J = 8.1$ Hz, 1H), 6.67 (t, $J = 7.4$ Hz, 1H), 5.71 (s, 1H), 3.75 (s, 3H); ^{13}C NMR (75 MHz, DMSO) δ 164.2, 159.9, 148.5, 133.9, 133.7, 128.7, 127.8, 117.6, 115.5, 114.9, 114.1, 66.8, 55.6.



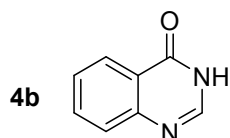
2-(4-nitrophenyl)-2,3-dihydroquinazolinone (3h).^[4] **1a** (40.8 mg, 0.3 mmol), **2h** (90.6 mg, 0.6 mmol). **3h** (51 mg, 63%, n-hexane/ethyl acetate = 1:1): orange solid; ^1H NMR (300 MHz, DMSO) δ 8.52 (s, 1H), 8.25 (d, $J = 8.8$ Hz, 2H), 7.74 (d, $J = 8.7$ Hz, 2H), 7.65 – 7.55 (m, 1H), 7.32 (s, 1H), 7.30 – 7.20 (m, 1H), 6.77 (d, $J = 8.0$ Hz, 1H), 6.69 (t, $J = 7.5$ Hz, 1H), 5.91 (s, 1H); ^{13}C NMR (75 MHz, DMSO) δ 163.8, 149.8, 147.9, 147.7, 134.0, 128.5, 127.9, 124.1, 117.9, 115.4, 115.0, 65.7.



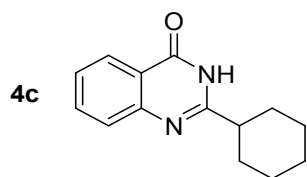
7-nitro-2-phenethyl-2,3-dihydroquinazolinone (3k). **1c** (54.3 mg, 0.3 mmol), **2a** (80.4 mg, 0.6 mmol). **3k** (18 mg, 22%, n-hexane/ethyl acetate = 2:1): orange solid; ^1H NMR (300 MHz, DMSO) δ 8.46 (s, 1H), 7.81 (d, $J = 8.5$ Hz, 1H), 7.59 (d, $J = 2.2$ Hz, 1H), 7.43 (dd, $J = 8.5, 2.1$ Hz, 1H), 7.38 (s, 1H), 7.33 – 7.14 (m, 5H), 4.86 (t, $J = 5.0$ Hz, 1H), 2.76-2.74 (m, 2H), 1.98-1.93 (m, 2H); ^{13}C NMR (75 MHz, DMSO) δ 162.7, 151.1, 149.3, 141.7, 129.6, 128.9, 128.8, 126.4, 119.8, 111.4, 109.3, 64.4, 37.4, 29.6. HR-MS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{16}\text{H}_{16}\text{N}_3\text{O}_3$ 298.11872, found 298.11862.



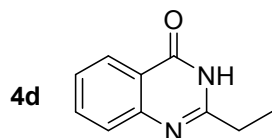
2-phenethylquinazolin-4(3H)-one (4a).^[1] **4a** (55 mg, 73%, n-hexane/ethyl acetate = 3:1): white solid; ¹H NMR (300 MHz, DMSO) δ 11.78 (s, br, 1H), 8.31 (d, J = 8.1 Hz, 1H), 7.83-7.73 (m, 2H), 7.50 (t, J = 7.8 Hz, 1H), 7.36-7.21 (m, 5H), 3.24-3.08 (m, 4H); ¹³C NMR (75 MHz, DMSO) δ 162.2, 157.1, 149.3, 141.2, 134.8, 128.83, 128.81, 127.3, 126.6, 126.5, 126.2, 121.3, 36.8, 32.9.



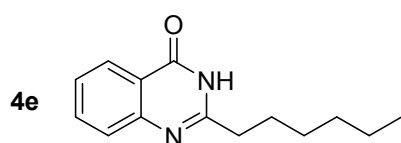
quinazolin-4(3H)-one (4b).^[5] **4b** (30 mg, 68%, n-hexane/ethyl acetate = 1:2): white solid; ¹H NMR (300 MHz, DMSO) δ 12.25 (s, br, 1H), 8.15 – 8.10 (m, 1H), 8.09 (s, 1H), 7.86 – 7.77 (m, 1H), 7.67 (dd, J = 8.1, 0.6 Hz, 1H), 7.52 (d, J = 8.1 Hz, 1H); ¹³C NMR (75 MHz, DMSO) δ 161.2, 149.2, 145.9, 134.8, 127.7, 127.2, 126.3, 123.1.



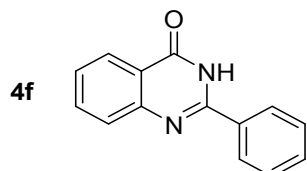
2-cyclohexylquinazolin-4(3H)-one (4c).^[6] **4c** (42 mg, 62%, n-hexane/ethyl acetate = 3:1): white solid; ¹H NMR (300 MHz, CDCl₃) δ 11.45 (s, br, 1H), 8.28 (d, J = 7.6 Hz, 1H), 7.83 – 7.66 (m, 2H), 7.53 – 7.41 (m, 1H), 2.74 (t, J = 12.0 Hz, 1H), 2.14 – 1.33 (m, 11H); ¹³C NMR (75 MHz, CDCl₃) δ 164.0, 160.2, 149.4, 134.8, 127.3, 126.4, 126.2, 120.8, 44.8, 30.5, 26.0, 25.7.



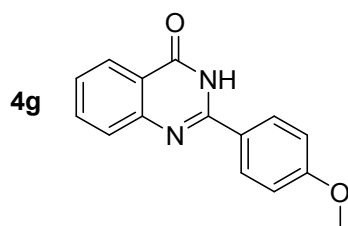
2-ethyl-quinazolin-4(3H)-one (4d).^[7] **4d** (27 mg, 52%, n-hexane/ethyl acetate = 1:1): white solid; ¹H NMR (300 MHz, DMSO) δ 12.15 (s, br, 1H), 8.08 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.82 – 7.70 (m, 1H), 7.59 (d, $J = 7.8$ Hz, 1H), 7.49 – 7.39 (m, 1H), 2.62 (q, $J = 7.5$ Hz, 2H), 1.24 (t, $J = 7.5$ Hz, 3H); ¹³C NMR (75 MHz, DMSO) δ 162.3, 158.8, 149.4, 134.8, 127.2, 126.4, 126.2, 121.3, 28.3, 11.8.



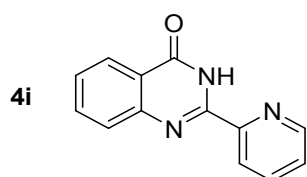
2-hexyl-quinazolin-4(3H)-one (4e).^[8] **4e** (28 mg, 41%, n-hexane/ethyl acetate = 3:1): white solid; ¹H NMR (300 MHz, DMSO) δ 12.17 (s, br, 1H), 8.07 (dd, $J = 7.9, 1.3$ Hz, 1H), 7.80 – 7.71 (m, 1H), 7.59 (d, $J = 7.9$ Hz, 1H), 7.49 – 7.39 (m, 1H), 2.66 – 2.53 (m, 2H), 1.71-0.83 (m, 11H); ¹³C NMR (75 MHz, DMSO) δ 162.3, 158.0, 149.4, 134.7, 127.2, 126.4, 126.2, 121.2, 34.9, 31.4, 28.7, 27.21, 22.4, 14.4.0.



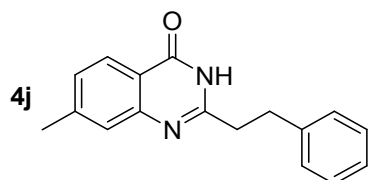
2-phenyl-quinazolin-4(3H)-one (4f).^[1] **4f** (< 5%, n-hexane/ethyl acetate = 3:1): white solid; ¹H NMR (400 MHz, DMSO) δ 12.53 (s, br, 1H), 8.20-8.15 (m, 3H), 7.84 (t, $J = 7.2$ Hz, 1H), 7.74 (d, $J = 8.0$ Hz, 1H), 7.57-7.51 (m, 4H). ¹³C NMR (75 MHz, DMSO) δ 162.7, 152.8, 149.2, 135.1, 133.2, 131.9, 129.1, 128.2, 128.0, 127.1, 126.3, 121.4.



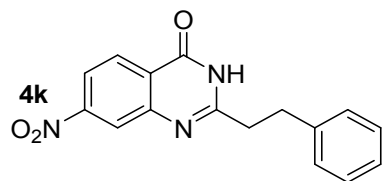
2-(4-methoxyphenyl)-quinazolin-4(3H)-one (4g).^[1] **4g** (54 mg, 71%, n-hexane/ethyl acetate = 1:2): white solid; ¹H NMR (400 MHz, DMSO) δ 12.40 (s, br, 1H), 8.19 (d, J = 8.8 Hz, 2H), 8.13 (d, J = 6.8 Hz, 1H), 7.82 (t, J = 6.8 Hz, 1H), 7.70 (d, J = 7.6 Hz, 1H), 7.49 (t, J = 6.8 Hz, 1H), 7.09 (d, J = 8.8 Hz, 2H), 3.85 (s, 3H). ¹³C NMR (75 MHz, DMSO) δ 162.8, 162.3, 152.3, 149.4, 135.1, 129.9, 127.8, 126.6, 126.3, 125.3, 121.1, 114.5, 55.9.



2-(2-pyridyl)-quinazolin-4(3H)-one (4i).^[1] **4i** (26 mg, 39%, n-hexane/ethyl acetate = 2:1): yellow solid; ¹H NMR (300 MHz, CDCl₃) δ 10.96 (s, br, 1H), 8.67 (d, J = 4.5 Hz, 1H), 8.60 (d, J = 7.9 Hz, 1H), 8.35 (d, J = 7.7 Hz, 1H), 7.92 (t, J = 7.8 Hz, 1H), 7.80 (d, J = 9.9 Hz, 2H), 7.57 – 7.40 (m, 2H). ¹³C NMR (75 MHz, CDCl₃) δ 161.4, 148.9, 148.8, 148.3, 137.6, 134.6, 127.9, 127.4, 126.8, 126.3, 122.5, 122.1.



7-methyl-2-phenylethyl-quinazolin-4(3H)-one (4j). **4j** (40 mg, 57%, n-hexane/ethyl acetate = 3:1): white solid; ¹H NMR (300 MHz, DMSO) δ 12.14 (s, br, 1H), 7.96 (d, J = 8.1 Hz, 1H), 7.43 (s, 1H), 7.34 – 7.23 (m, 5H), 7.22 – 7.14 (m, 1H), 3.04 (dd, J = 9.4, 6.0 Hz, 2H), 2.88 (dd, J = 9.3, 6.0 Hz, 2H), 2.44 (s, 3H). ¹³C NMR (75 MHz, DMSO) δ 162.2, 157.1, 149.4, 145.2, 141.2, 128.8, 128.8, 127.9, 126.9, 126.6, 126.1, 118.9, 36.7, 32.9, 21.8. HR-MS [M+H]⁺ m/z calcd for C₁₇H₁₇N₂O 265.13352, found 265.13354.



7-nitro-2-phenylethyl-quinazolin-4(3H)-one (4k). **4k** (62 mg, 78%, n-hexane/ethyl acetate = 2:1): white solid; ^1H NMR (400 MHz, DMSO) δ 12.65 (s, 1H), 8.33 – 8.28 (m, 2H), 8.19 (dd, J = 8.7, 2.2 Hz, 1H), 7.32 – 7.26 (m, 4H), 7.23 – 7.16 (m, 1H), 3.07 (t, J = 9.2 Hz, 2H), 2.95 (t, J = 9.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO) δ 161.3, 159.7, 151.7, 149.7, 141.0, 128.9, 128.8, 128.6, 126.6, 125.7, 122.3, 120.3, 36.7, 32.7. HR-MS $[\text{M}+\text{H}]^+$ m/z calcd for $\text{C}_{16}\text{H}_{14}\text{N}_3\text{O}_3$ 296.10297, found 296.10293.

References:

- [1] B. Q. Hu, L. X. Wang, L. Yang, J. F. Xiang, Y. L. Tang, *Eur. J. Org. Chem.* **2015**, 4504.
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 [3] M. Prakash, S. Jayakumar, V. Kesavan, *Synthesis*, **2013**, *45*, 2265.
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 [8] M. Sharif, J. Opalach, P. Langer, M. Beller, X. F. Wu, *RSC Adv.* **2014**, *4*, 8.

Table S1. Optimization of temperatures for the condensation reaction between *o*-aminobenzamide **1a** and 3-phenylpropanal **2a**.^a

Entry	2a(equiv.)	Temperature (°C)	yield ^b [%]	
			3a	4a
1	2.0	100	48	42
2	2.0	110	33	59

^a Reaction conditions: **1a** (0.3 mmol), H_2O : 2 ml, 24h. ^b Isolated yield.

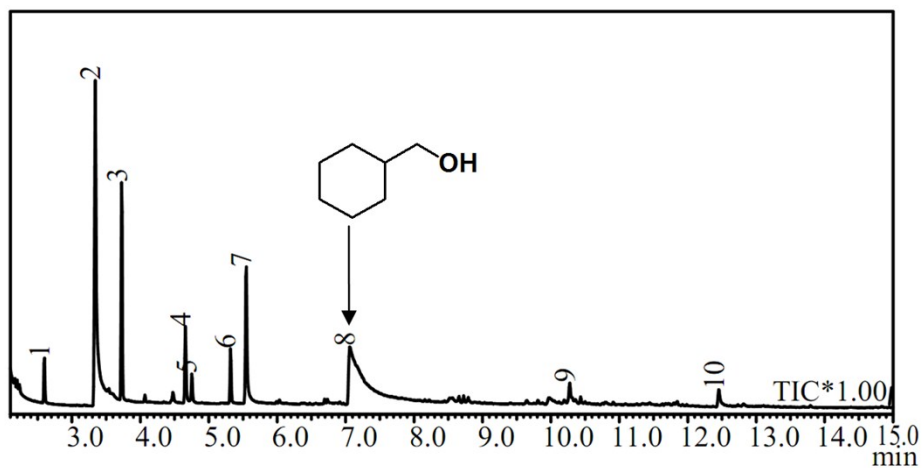
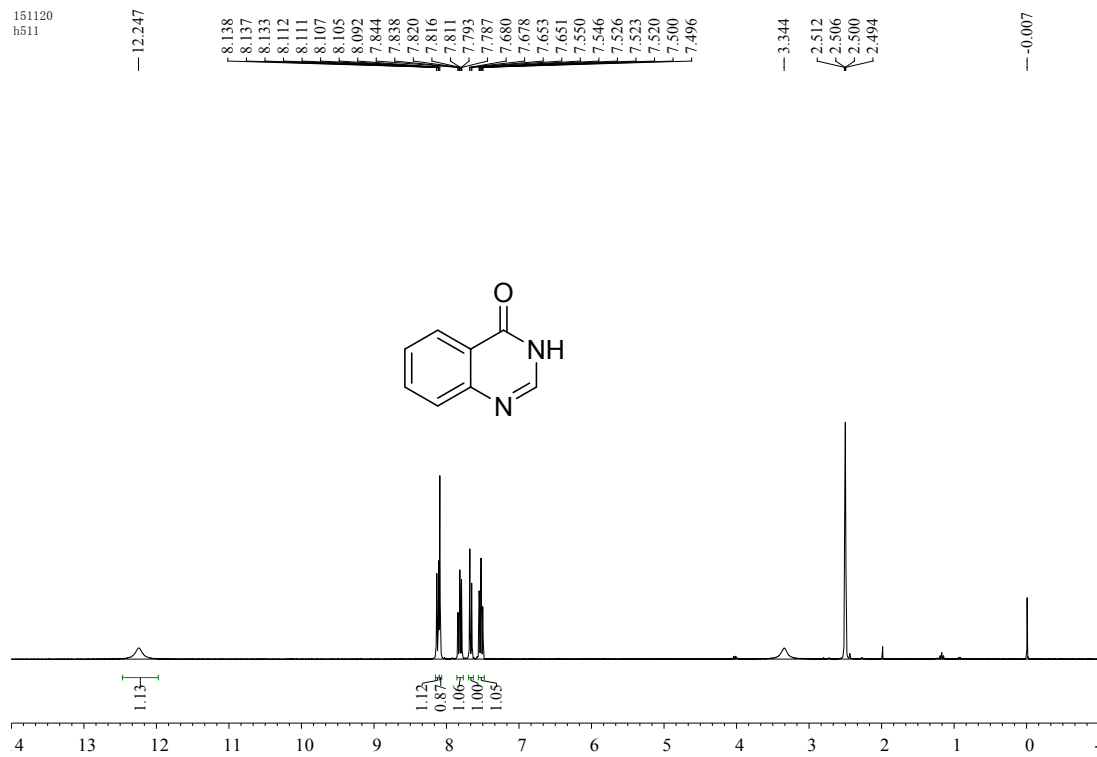
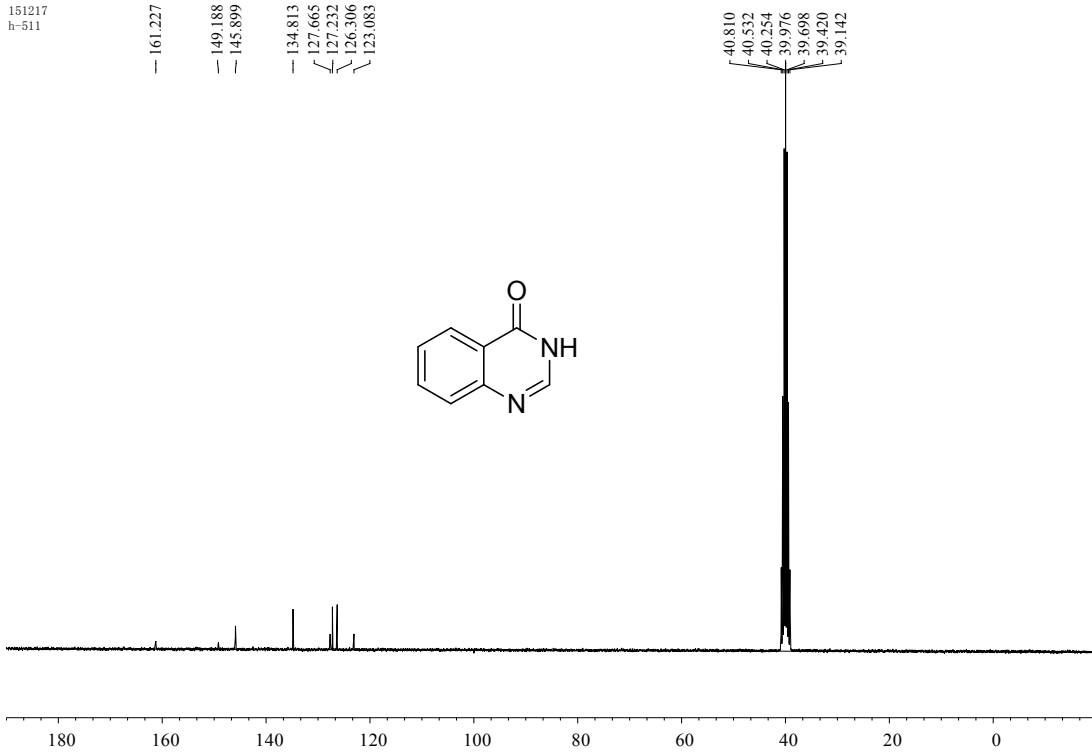


Fig.S1. GC-MS analysis of reaction mixture of entry 3 in Table 2.

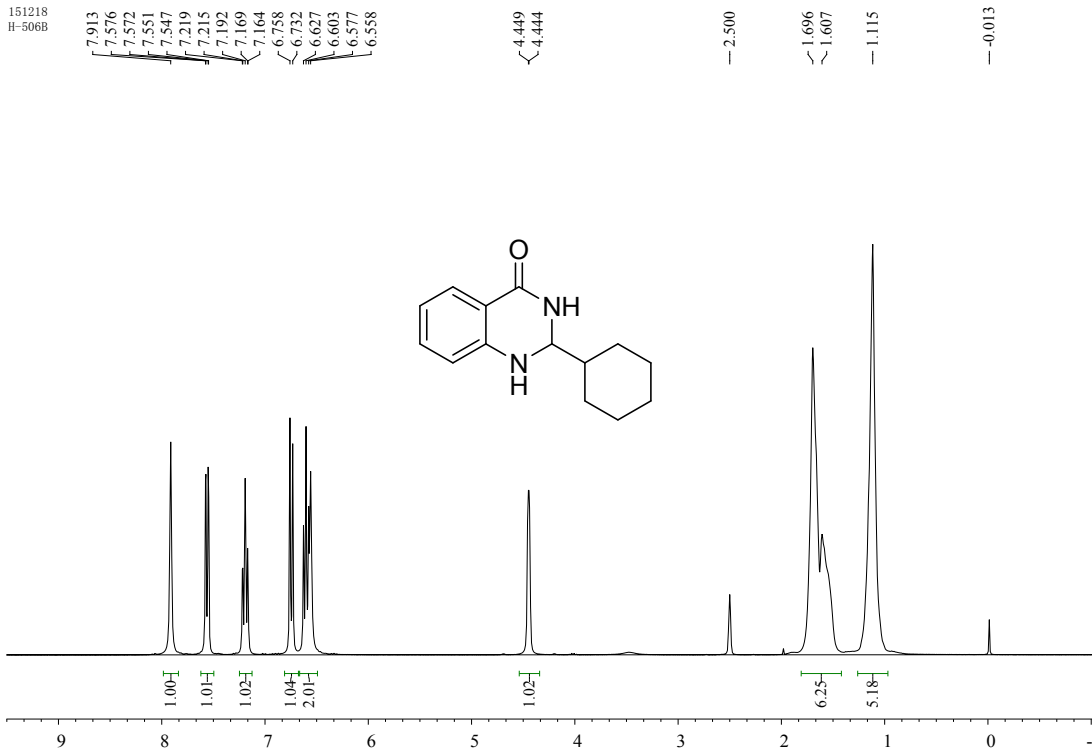
NMR spectra of synthetic compounds:



151217
h-511

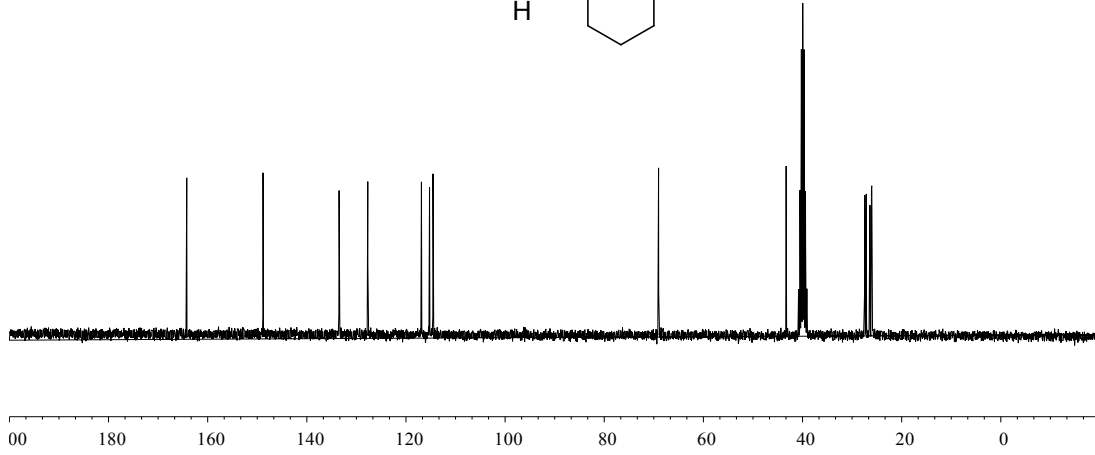
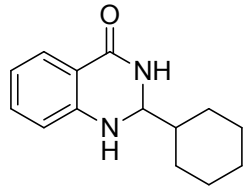


151218
H-506B



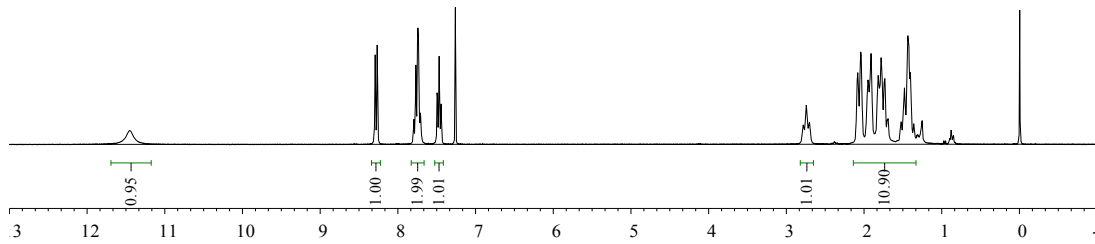
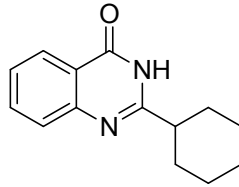
151218
H-506B

— 164.220
— 148.833
— 133.494
— 127.703
— 116.881
— 115.245
— 114.547
— 69.042
— 43.306
— 40.793
— 40.513
— 40.234
— 39.956
— 39.678
— 39.400
— 39.121
— 27.463
— 27.147
— 26.409
— 26.088
— 26.026



151120
h506a

— 11.453
— 8.292
— 8.266
— 7.797
— 7.793
— 7.770
— 7.766
— 7.743
— 7.735
— 7.709
— 7.495
— 7.490
— 7.469
— 7.447
— 7.442
— 7.260
— 2.782
— 2.743
— 2.703
— 2.081
— 2.043
— 1.910
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— 1.781
— 1.732
— 1.437
— 1.422
— 1.004



151120
h506a

164.029
160.187

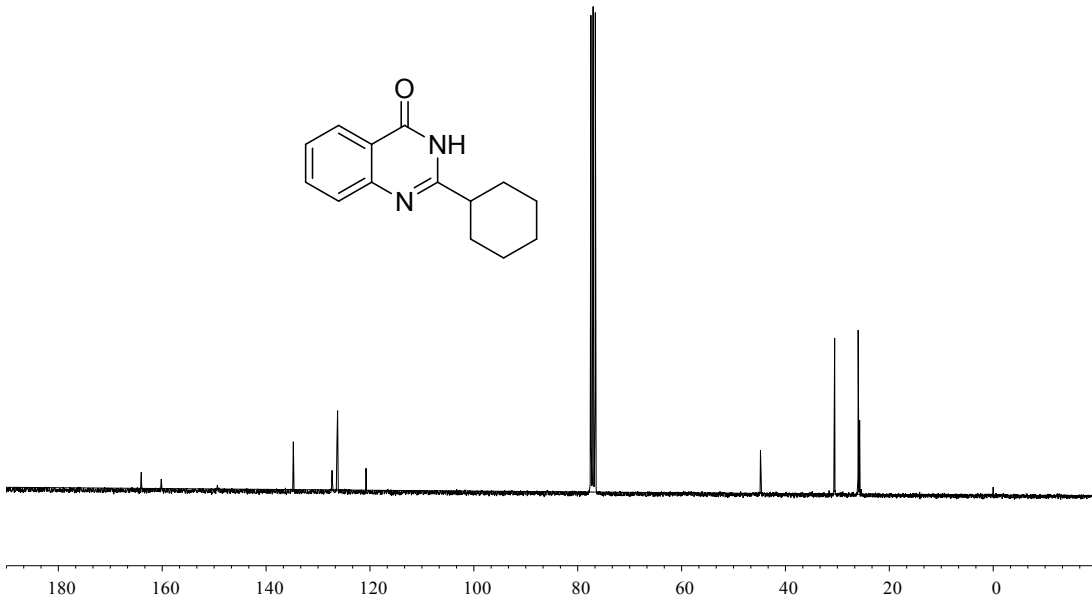
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26.002
25.716



hbq
h-505b

7.860
7.588
7.584
7.563
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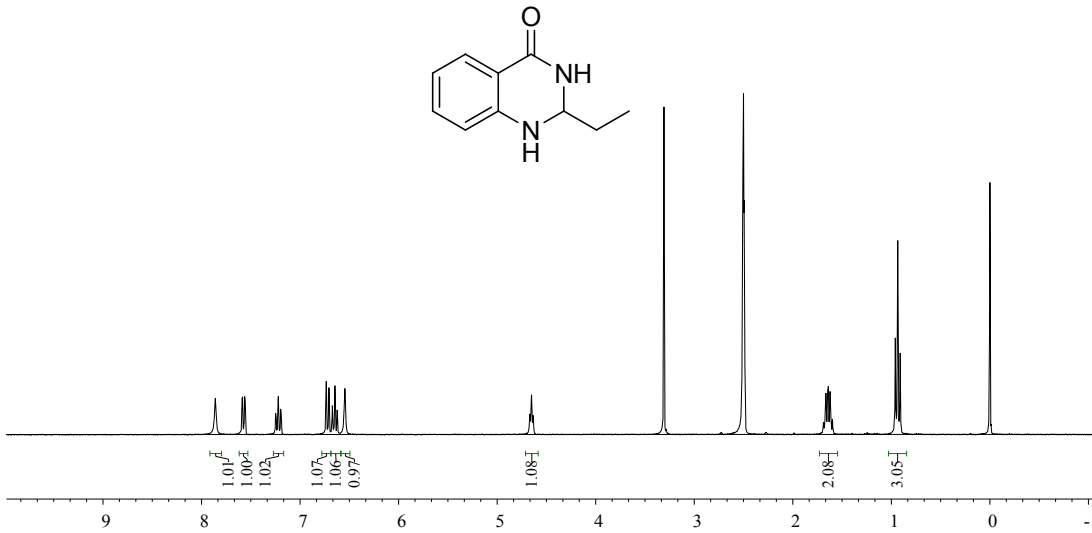
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3.307

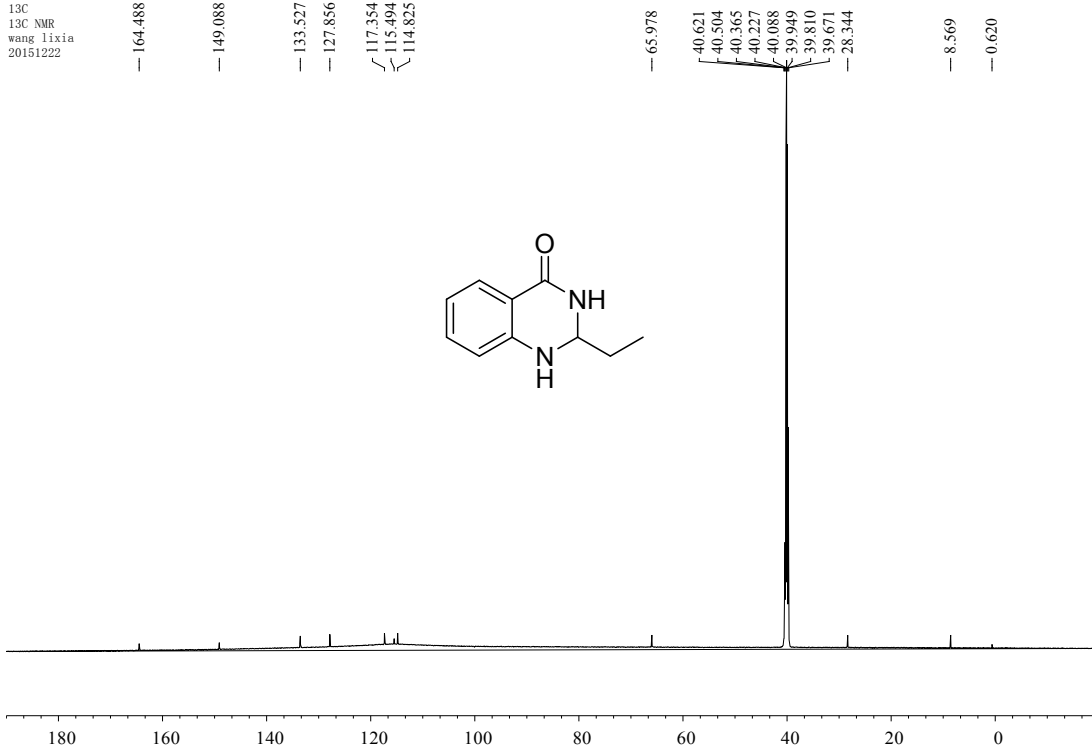
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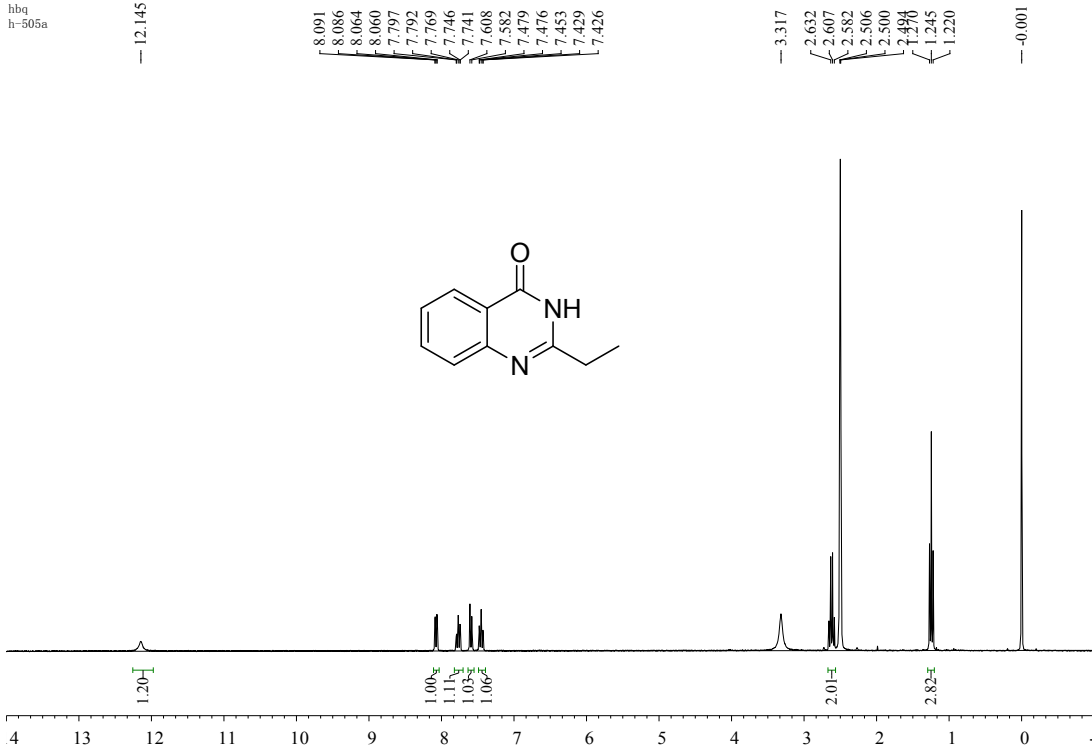
-0.000



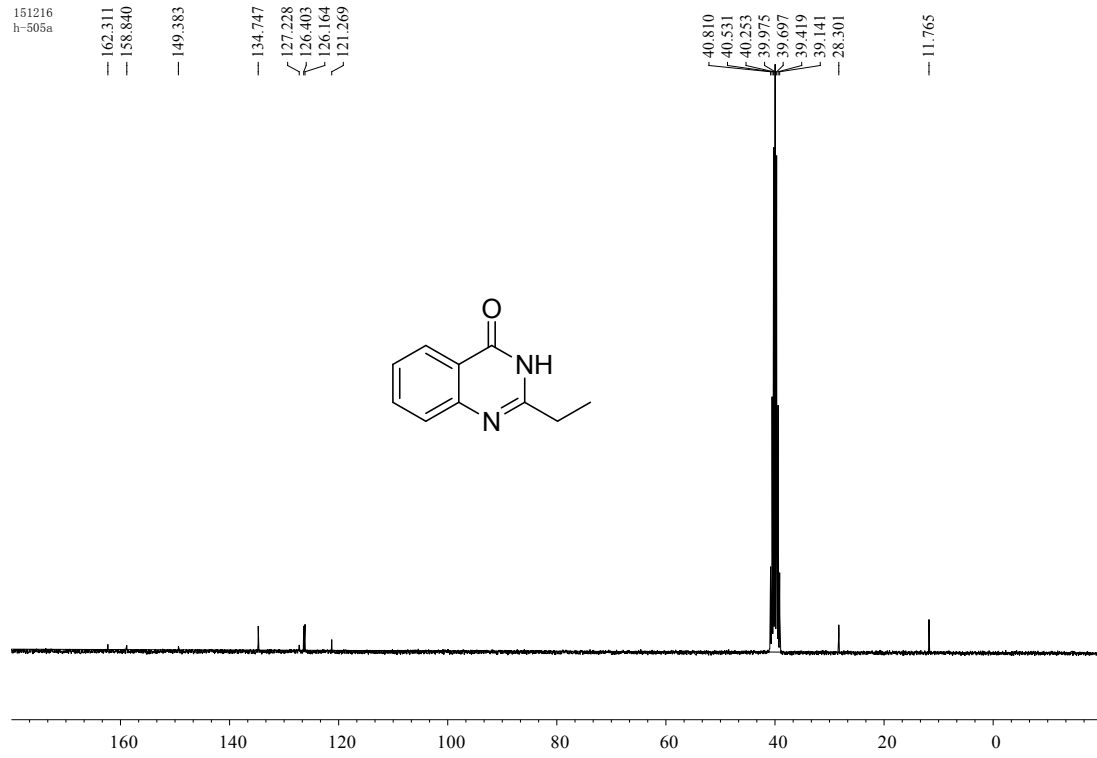
13C
13C NMR
wang lixia
20151222



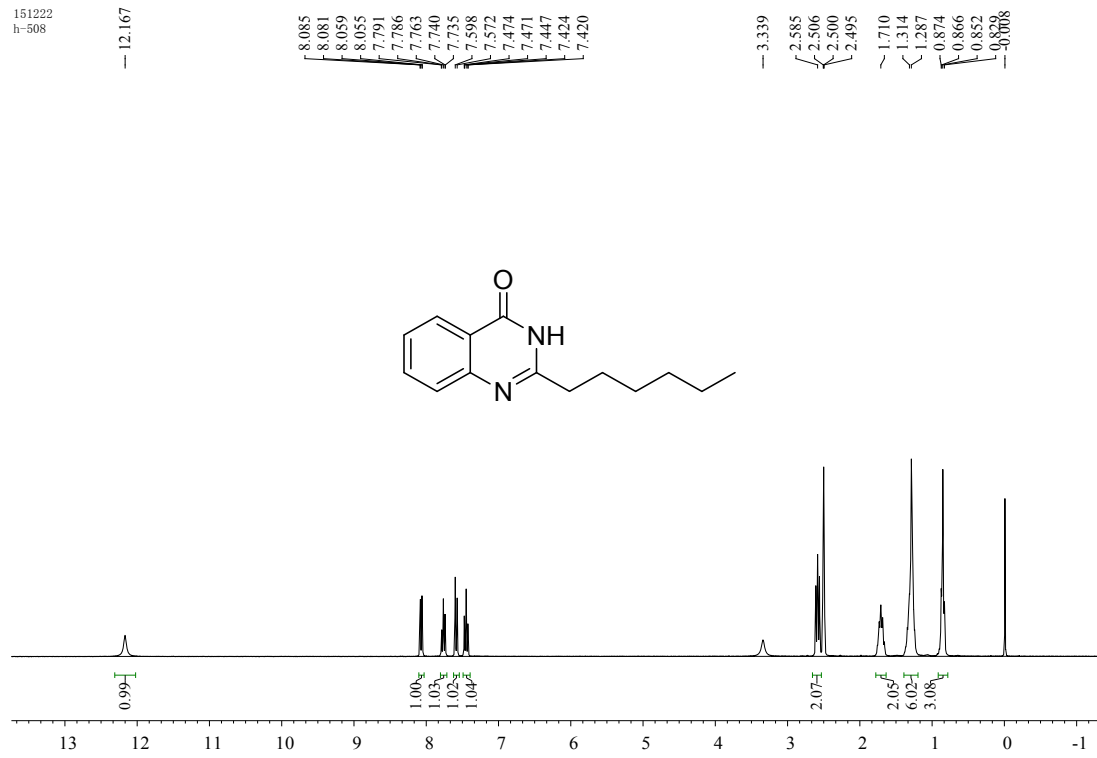
hbq
h-505a



151216
h-505a

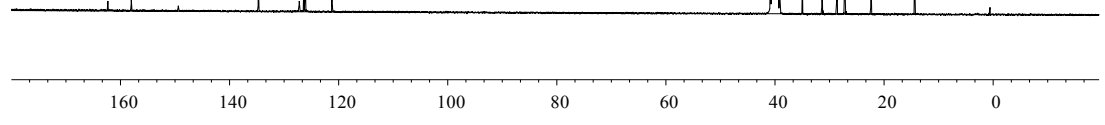
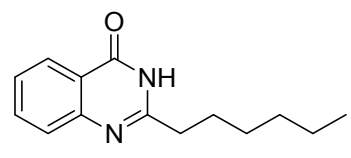


151222
h-508



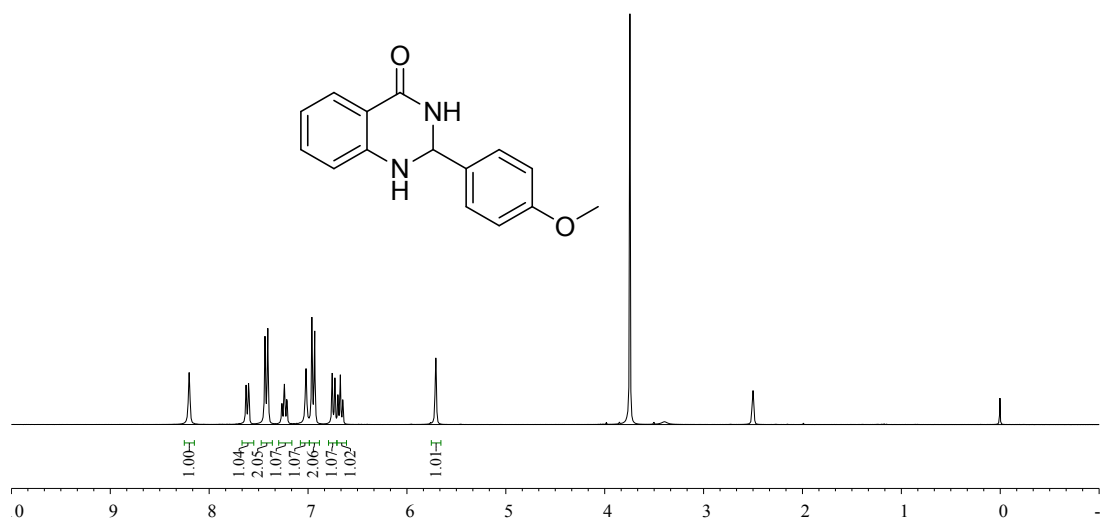
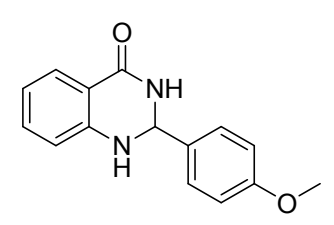
151222
h-508

- 162.310
- 158.018
- 149.400
- 134.736
- 127.219
- 126.366
- 126.146
- 121.221
- 40.821
- 40.543
- 40.264
- 39.986
- 39.708
- 39.430
- 39.152
- 34.967
- 31.398
- 28.659
- 27.210
- 22.422
- 14.385



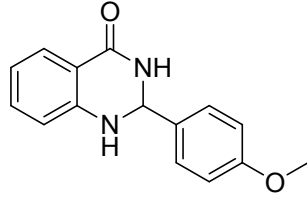
151218
H-522B

- 8.202
- 7.627
- 7.602
- 7.436
- 7.407
- 7.239
- 7.021
- 6.961
- 6.933
- 6.755
- 6.729
- 6.699
- 6.578
- 5.703
- 3.745
- 2.500
- 0.003



151218
H-522B

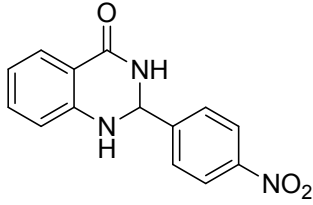
164.184
159.898
148.501
133.912
133.716
128.698
127.818
117.558
115.469
114.881
114.097
66.774
55.637
40.800
40.523
40.245
39.967
39.689
39.411
39.132



00 180 160 140 120 100 80 60 40 20 0

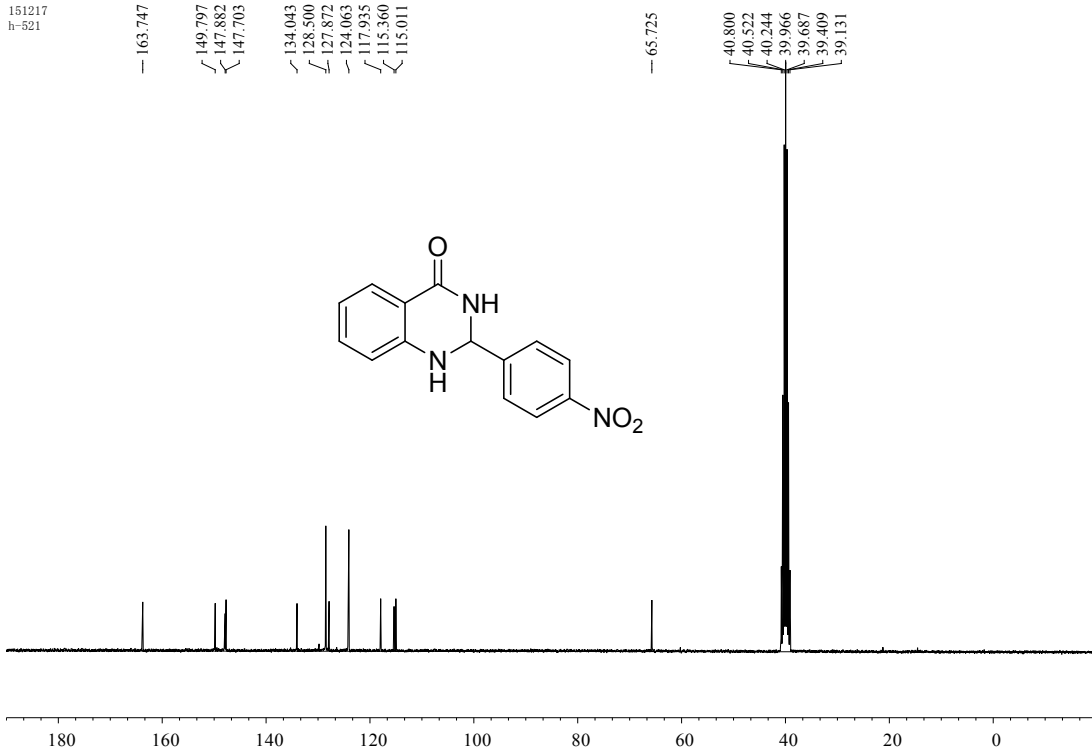
151128
h-521

8.516
8.269
8.239
7.753
7.724
7.618
7.596
7.325
6.778
6.752
6.713
6.687
3.330
2.505
2.500
-0.004

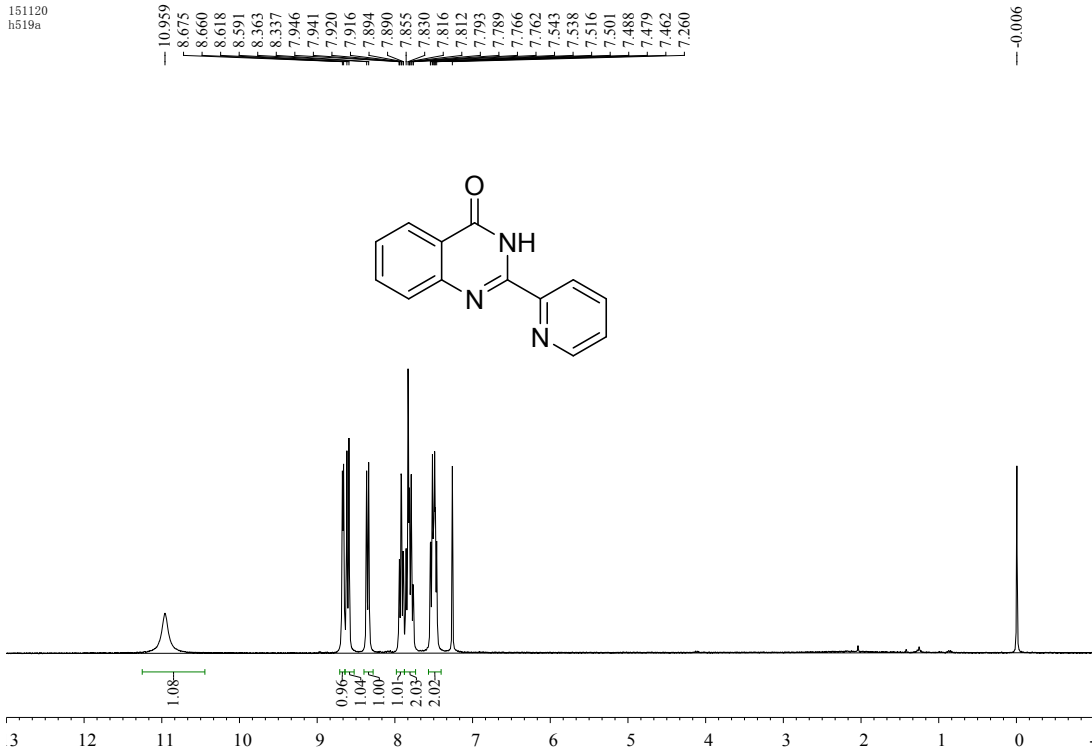


1 10 9 8 7 6 5 4 3 2 1 0

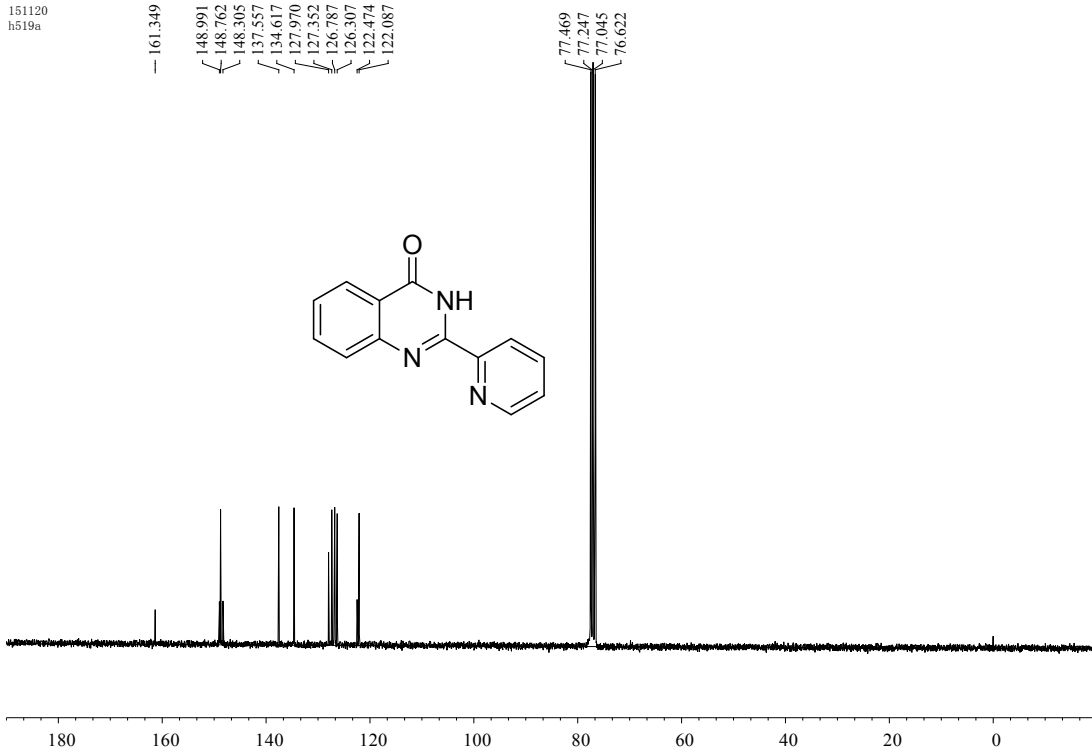
151217
h-521



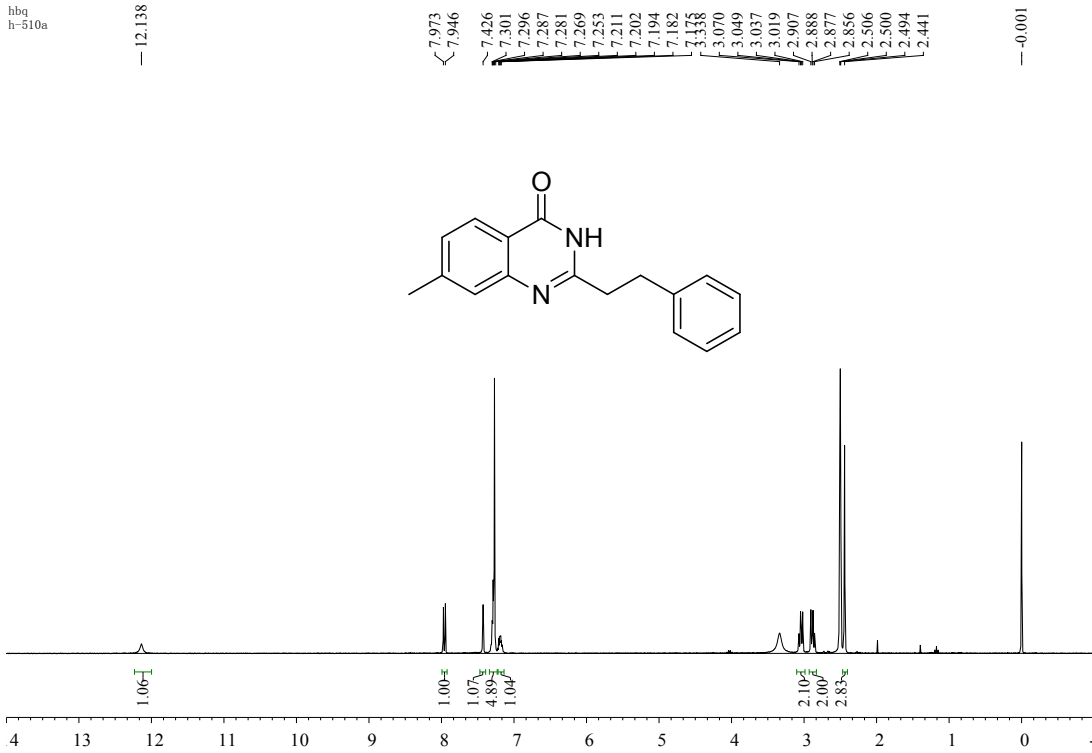
151120
h519a



151120
h519a

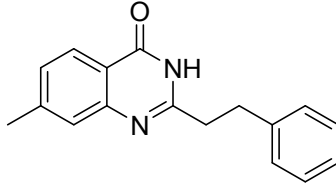


hbq
h-510a



151216
h-509

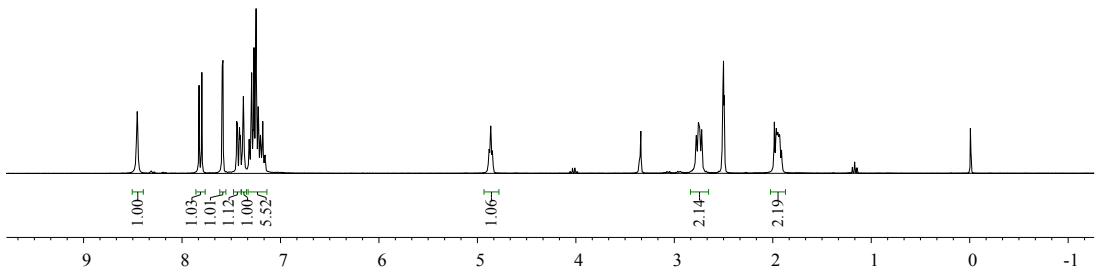
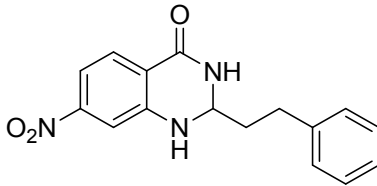
162.153
157.097
149.404
145.239
141.239
128.836
128.823
127.928
126.554
118.888
40.809
40.531
40.253
39.975
39.697
39.418
39.141
36.742
32.909
21.824



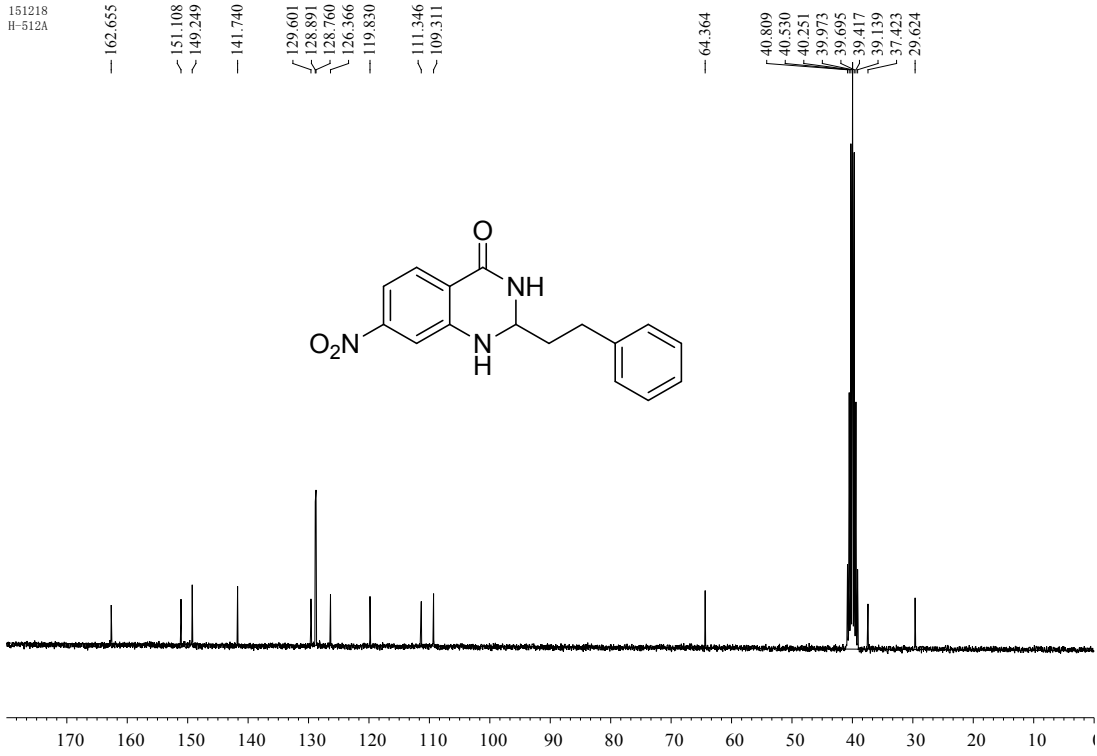
180 160 140 120 100 80 60 40 20 0

151218
H-512A

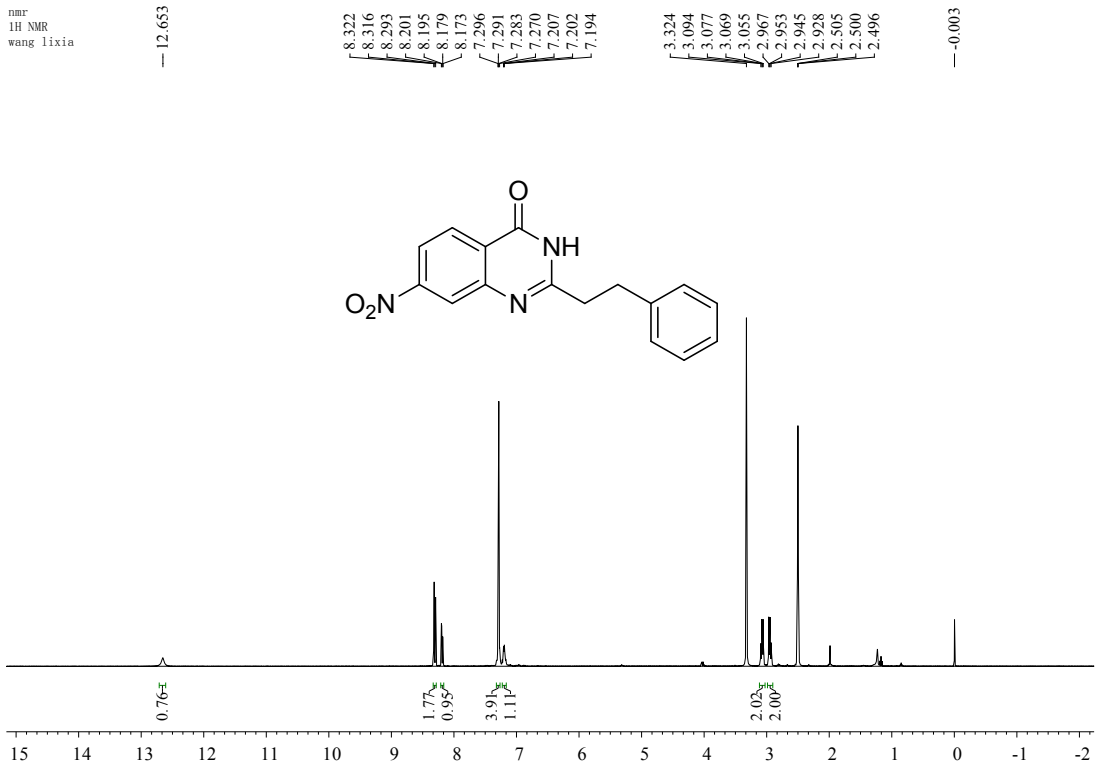
8.455
7.827
7.799
7.592
7.584
7.445
7.438
7.416
7.409
7.377
7.293
7.277
7.269
7.253
7.248
7.226
7.203
7.180
4.881
4.865
4.848
3.340
2.755
2.742
2.506
2.500
2.495
1.983
1.964
1.948
1.937
1.930
-0.007



151218
H-512A



nmr
1H NMR
wang lixia



cuijie
13C NMR
wang lixia

~ 161.275
~ 159.704
~ 151.682
~ 149.705
— 141.006
128.880
128.822
128.549
126.633
125.692
122.249
120.180

40.622
40.413
40.204
39.996
39.787
39.578
39.370
36.783
32.731

