Supporting Information for

$Co(acac)_2/O_2$-Catalyzed Oxidative Isocyanide Insertion with 2-Vinylanilines: Efficient Synthesis of 2-Aminoquinolines

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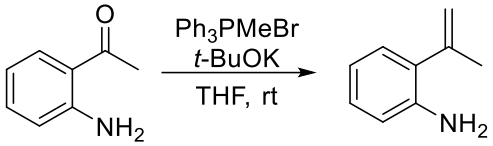
Ⅰ. General Information

All reagents were purchased without further purification unless otherwise noted. Reactions were monitored using thin-layer chromatography (TLC). Visualization of the developed plates was performed under UV light (254 nm). Flash column chromatography was performed on silica gel (300-400 mesh). ^{1}H and ^{13}C NMR spectra were recorded on a 400 MHz spectrometer. Chemical shifts (δ) were reported in ppm referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are reported relative to $CDCl_3$ (δ 77.16). The following abbreviations were used to describe peak splitting patterns when appropriate: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet. Coupling constants, J, were reported in Hertz unit (Hz). High resolution mass spectra (HRMS) were obtained on an ESI-MS Spectrometer.

II. Synthesis of Substrates

2-vinylanilines (**1a-c**, **k-l**) were synthesized according to the literature methods with minor modifications.[1] A representative procedure (synthesis of 2-(*prop*-1-en-2-yl)aniline (**1a**)) is shown below.



To a solution of Ph_3PMeBr (1.5 equiv) in dry THF was added *t*-BuOK (1.5 equiv) in portions under Ar atmosphere at room temperature. After the mixture was stirred at room temperature for 0.5 h, a solution of 1-(2-aminophenyl)ethan-1-one (1 equiv)in THF was added dropwise. The reaction mixture was then stirred at room temperature under Ar overnight. The reaction mixture was quenched with H_2O and extracted twice with EtOAc. The combined organic layers were washed with saturated $NaHCO_3$ and brine, dried over $MgSO_4$, filtered and concentrated, and the residue was purified by column chromatography on silica gel to obtain **1a**.

2-vinylanilines (**1d-j**) were synthesized according to the literature methods with minor modifications.[2] A representative procedure (synthesis of 4-methyl-2-(1-phenylvinyl) aniline (**1d**)) is shown below.

p-toluidine (1.07 g, 10 mmol), ethynylbenzene (1.02 g, 10 mmol), and montmorillonite KSF (1.0 g) were combined in a round-bottomed flask. The flask was stirred and heated in an oil bath to 140 ℃, under a reflux condenser (running cold water as the coolant) that was connected at its top to a paraffin bubbler. The reaction was monitored by TLC. After 4 h, the reaction mixture was cooled to room temperature and purified directly by flash chromatography with a gradient of hexane to ethyl acetate/hexane (v/v = 1:20), followed by distillation under high vacuum. Finally, **1d** was obtained .

Isocyanides were prepared according to the literatures methods with minor modifications.[3]

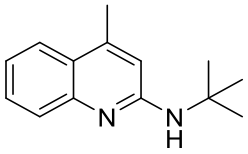
III .General Procedure and Product Characterization

1. General Procedure for the Formation of 2-Aminoquinolines

A representative procedure synthesis of N-(*tert*-butyl)-4-methylquinolin-2-amine (**3a**) is shown below.

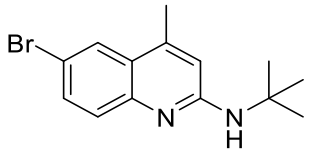
In a 25 mL Schlenk tube, to a mixture of 2-(*prop*-1-en-2-yl)aniline **1a** (0.5 mmol, 1 equiv), *tert*-butyl isocyanide **2a** (0.6 mmol, 1.2 equiv), $Co(acac)_2$ (10 mol %), were added in 3 mL 1,4-dioxane. The system was used O_2 balloon at 100 ℃ (monitored by TLC). After 12h, cooled to rt. The system was evaporated under the reduced pressure directly. The residue was purified by flash column chromatography with ethyl acetate and petroleum ether as eluents to afford pure product **3a**.

2. Product Characterization



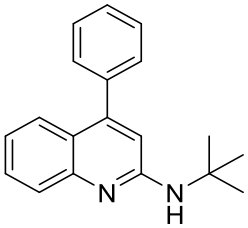
N-(*tert*-butyl)-4-methylquinolin-2-amine (3a)

Yellow solid, (63.3 mg, 59%). **IR :** ν_{max} (cm^{-1}) =3413 (-NH). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.1 Hz, 1H), 7.59 (d, J = 8.3 Hz, 1H), 7.41 (d, J = 7.0 Hz, 1H), 7.11 (d, J = 7.1 Hz, 1H), 6.35 (s, 1H), 4.51 (s, 1H), 2.42 (s, 3H), 1.44 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.4, 148.0, 144.2, 129.1, 127.0, 123.5, 123.4, 121.7, 113.1, 51.4, 29.7, 18.9 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{14}H_{18}N_2$ $(M+H)^+$ 215.1548, found 215.1555.



6-bromo-N-(*tert*-butyl)-4-methylquinolin-2-amine (3b)

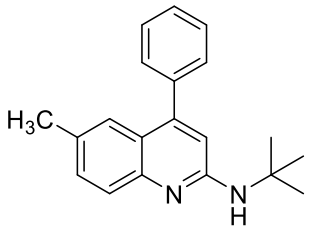
Yellow solid, (81.3 mg, 55%). **IR :** ν_{max} (cm^{-1}) =3418 (-NH). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.74 (s, 1H), 7.45 (s, 2H), 6.32 (s, 1H), 4.48 (s, 1H), 2.38 (s, 3H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.6, 147.0, 143.2, 132.1, 128.9, 125.9, 124.8, 114.6, 114.0, 51.6, 29.6, 18.7 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{14}H_{17}BrN_2$ $(M+H)^+$ 293.0653, found 293.0650.



N-(*tert*-butyl)-4-phenylquinolin-2-amine (3c)

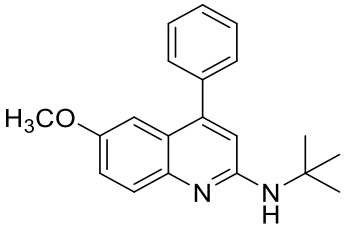
Yellow solid, (90.9 mg, 66%). **IR :** ν_{max} (cm^{-1}) =3475 (-NH). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.73 (d, J

= 8.1 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 1H), 7.53 – 7.39 (m, 6H), 7.16 – 7.05 (m, 1H), 6.51 (s, 1H), 4.63 (s, 1H), 1.55 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.2, 148.9, 148.8, 138.8, 129.4, 129.3, 128.5, 128.1, 127.1, 125.7, 122.0, 121.9, 113.0, 51.6, 29.6 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{19}H_{20}N_2$ $(M+H)^+$ 277.1705, found 277.1705.



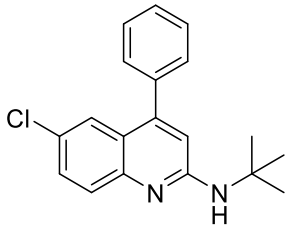
N-(*tert*-butyl)-6-methyl-4-phenylquinolin-2-amine (3d)

Yellow oil, (101.7 mg, 70%). **IR :** ν_{max} (cm^{-1}) =3418 (-NH). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.4 Hz, 1H), 7.39 – 7.31 (m, 5H), 7.27 – 7.21 (m, 2H), 6.38 (s, 1H), 4.51 (s, 1H), 2.23 (s, 3H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.8, 148.5, 147.0, 139.0, 131.3, 131.2, 129.4, 128.5, 128.0, 126.8, 124.7, 121.8, 113.0, 51.5, 29.7, 21.5 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{20}H_{22}N_2$ $(M+H)^+$ 291.1861, found 291.1860.



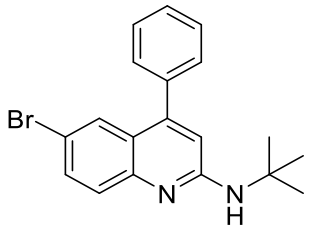
N-(*tert*-butyl)-6-methoxy-4-phenylquinolin-2-amine (3e)

Yellow oil, (119.3. mg, 78%). **IR :** ν_{max} (cm^{-1}) =3415 (-NH). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 9.1 Hz, 1H), 7.35 – 7.29 (m, 5H), 7.08 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.88 (d, *J* = 2.7 Hz, 1H), 6.39 (s, 1H), 4.49 (s, 1H), 3.57 (s, 3H), 1.41 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.1, 154.7, 148.0, 144.1, 138.9, 129.2, 128.5, 128.3, 128.1, 122.2, 120.2, 113.3, 105.4, 55.5, 51.4, 29.6 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{20}H_{22}N_2O$ $(M+H)^+$ 307.1810, found 307.1811.



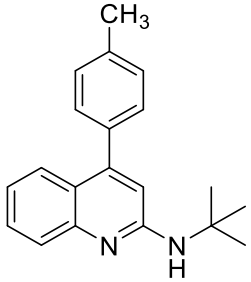
N-(*tert*-butyl)-6-chloro-4-phenylquinolin-2-amine (3f)

Yellow oil, (124.8 mg, 80%). **IR :** ν_{max} (cm^{-1}) =3426. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.9 Hz, 1H), 7.43 (d, *J* = 2.1 Hz, 1H), 7.35 – 7.23 (m, 6H), 6.34 (s, 1H), 4.54 (s, 1H), 1.41 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.2, 148.1, 147.2, 138.0, 129.7, 129.2, 128.7, 128.6, 128.4, 127.1, 124.5, 122.7, 113.9, 51.7, 29.4 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{19}H_{19}Cl$ N_2 $(M+H)^+$ 311.1315, found 311.1318.



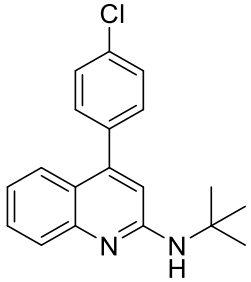
6-bromo-N-(*tert*-butyl)-4-phenylquinolin-2-amine (3g)

Yellow oil, (131.4 mg, 74%). **IR :** ν_{max} (cm^{-1}) =3423. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (d, J = 1.9 Hz, 1H), 7.44 (dt, J = 8.9, 5.4 Hz, 2H), 7.31 (m, J = 18.5, 8.1, 4.3 Hz, 5H), 6.35 (s, 1H), 4.58 (s, 1H), 1.42 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.2, 148.0, 147.4, 138.0, 132.3, 129.2, 128.8, 128.7, 128.4, 127.7, 123.3, 114.9, 113.8, 51.7, 29.4 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{19}H_{19}BrN_2$ $(M+H)^+$ 355.0810, found 355.0810.



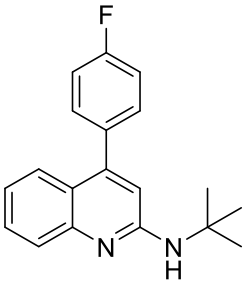
N-(*tert*-butyl)-4-(*p*-tolyl)quinolin-2-amine (3j)

Yellow oil, (106.5 mg, 73%). **IR :** ν_{max} (cm^{-1}) =3419. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.3 Hz, 1H), 7.50 (d, J = 7.2 Hz, 1H), 7.36 (s, 1H), 7.17 (d, J = 23.5 Hz, 4H), 6.98 (s, 1H), 6.38 (s, 1H), 4.69 (s, 1H), 2.29 (s, 3H), 1.41 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 156.1, 149.1, 148.5, 137.9, 135.8, 129.3, 129.2, 126.8, 125.7, 122.0, 121.8, 112.8, 51.5, 29.6, 21.3 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{20}H_{22}N_2$ $(M+H)^+$ 291.1861, found 291.1859.



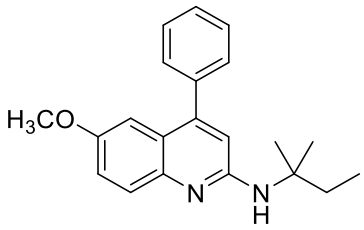
N-(*tert*-butyl)-4-(4-chlorophenyl)quinolin-2-amine (3k)

Yellow oil, (114.8 mg, 74%). **IR :** ν_{max} (cm^{-1}) =3423. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.63 (d, J = 8.2 Hz, 1H), 7.39 (t, J = 9.4 Hz, 2H), 7.31 (d, J = 8.1 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 6.99 (t, J = 7.4 Hz, 1H), 6.35 (s, 1H), 4.72 (s, 1H), 1.43 (s, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.9, 148.4, 147.7, 137.1, 134.2, 130.7, 129.5, 128.7, 126.9, 125.3, 122.1, 121.6, 113.0, 51.6, 29.8, 29.5 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{19}H_{19}ClN_2$ $(M+H)^+$ 311.1315, found 311.1318.



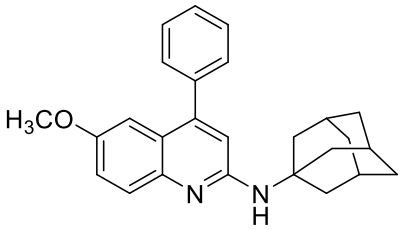
N-(*tert*-butyl)-4-(4-fluorophenyl)quinolin-2-amine (3l)

Yellow solid, (124.2 mg, 84%). **IR :** ν_{max} (cm^{-1}) =3422 (-NH). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.79 – 7.71 (m, 1H), 7.56 – 7.48 (m, 2H), 7.44 – 7.37 (m, 2H), 7.20 – 7.10 (m, 3H), 6.49 (s, 1H), 4.69 (s, 1H), 1.56 (d, *J* = 4.1 Hz, 9H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 164.0, 161.6, 156.1, 148.7, 147.9, 134.7, 131.1, 131.0, 129.4, 127.1, 125.4, 122.1, 121.9, 115.6, 115.4, 113.2, 51.7, 29.6 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{19}H_{19}FN_2$ $(M+H)^+$ 295.1611, found 295.1617.



6-methoxy-N-(*tert*-pentyl)-4-phenylquinolin-2-amine (3m)

Yellow oil, (118.6 mg, 74%). **IR :** ν_{max} (cm^{-1}) =3417 (-NH). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 9.1 Hz, 1H), 7.36 – 7.28 (m, 5H), 7.07 (dd, *J* = 9.1, 2.8 Hz, 1H), 6.89 (d, *J* = 2.8 Hz, 1H), 6.39 (s, 1H), 4.38 (s, 1H), 3.56 (s, 3H), 1.82 (d, *J* = 7.5 Hz, 2H), 1.34 (s, 6H), 0.77 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.0, 154.7, 148.0, 144.2, 138.9, 129.2, 128.5, 128.3, 128.1, 122.2, 120.1, 113.2, 105.4, 55.5, 54.0, 33.2, 27.4, 8.6 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{21}H_{24}N_2O$ $(M+H)^+$ 321.1967, found 321.1964.



6-((l1-oxidanyl)-l5-methyl)-N-((3s,5s,7s)-adamantan-1-yl)-4-phenylquinolin-2-amine (3n)

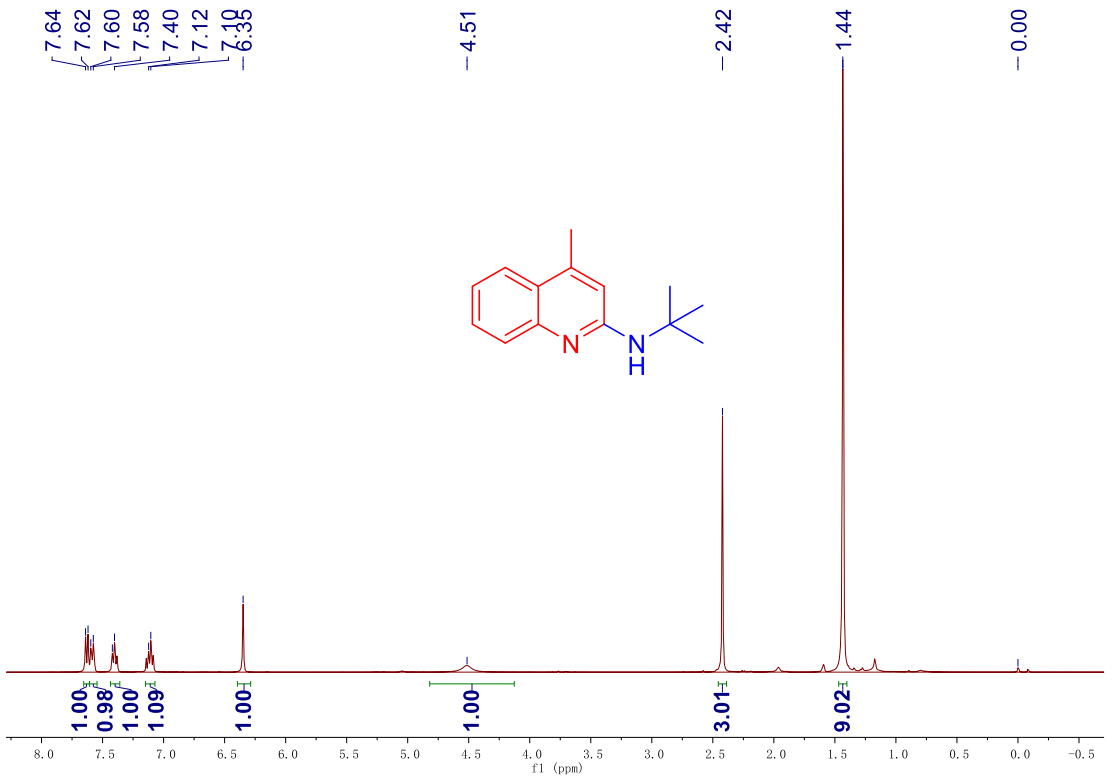
Yellow oil, (150.6 mg, 78%). **IR :** ν_{max} (cm^{-1}) =3405 (-NH). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 9.1 Hz, 1H), 7.45 – 7.31 (m, 5H), 7.11 (dd, *J* = 9.0, 2.6 Hz, 1H), 6.91 (d, *J* = 2.5 Hz, 1H), 6.50 (s, 1H), 4.53 (s, 1H), 3.63 (s, 3H), 2.10 (s, 6H), 1.65 (s, 5H), 1.26 (d, *J* = 69.2 Hz, 4H). **^{13}C NMR** (100 MHz, $CDCl_3$) δ 155.0, 154.8, 148.3, 139.0, 129.3, 128.6, 128.2, 128.0, 122.3, 120.4, 113.4, 105.5, 55.6, 52.1, 42.7, 36.7, 29.8 ppm. **HRMS** (ESI^+, MeOH) m/z calcd for $C_{26}H_{28}N_2O$ $(M+H)^+$ 385.2280, found 385.2286.

V. References

(1) C. Chen, J. Hu, J.-H. Su and X.-F. Tong *Tetrahedron Letters.*, 2014, **55**, 3229.

(2) J. Ferguson, F.-L. Zeng, N. Alwis and H. Alper, *Org. Lett.*, 2013, **15**, 1998.

(3) J.-L. Peng, J.-J. Zhao, Z.-W. Hu, D.-D. Liang, J.-B. Huang and Q. Zhu, *Org. Lett.*, 2012, **14**, 4966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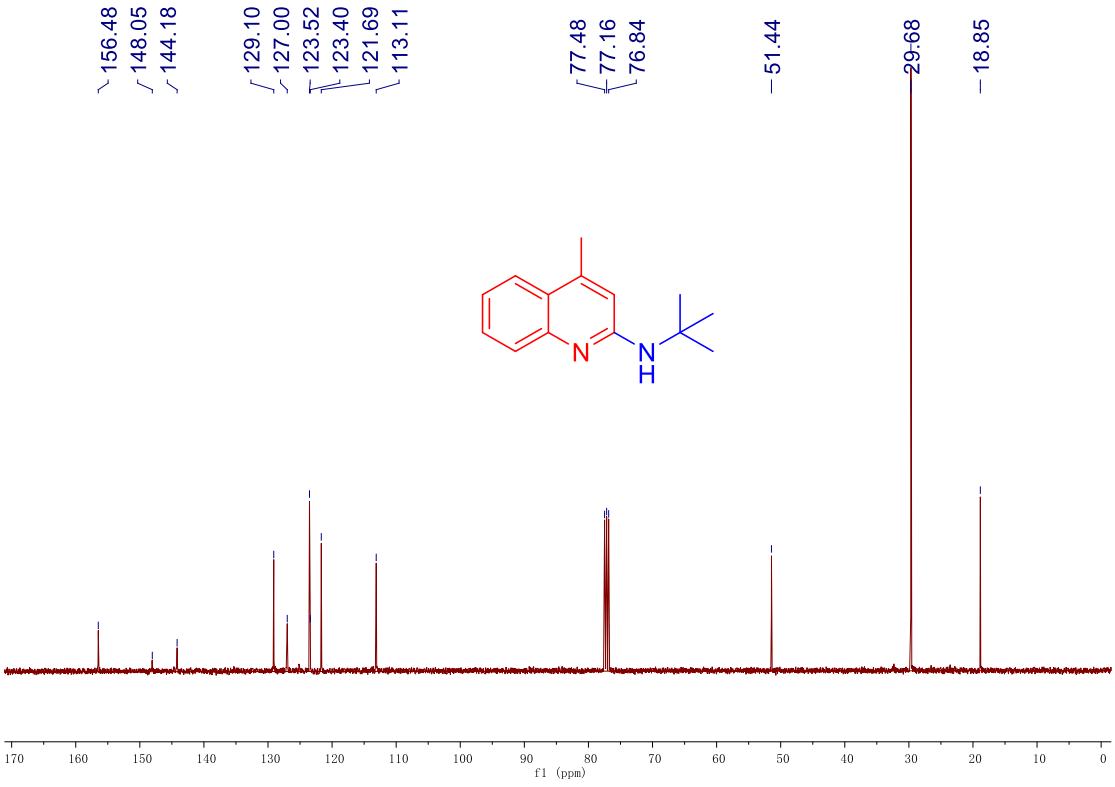
1.09
1.00
1.00
3.01
9.02
f1 (ppm)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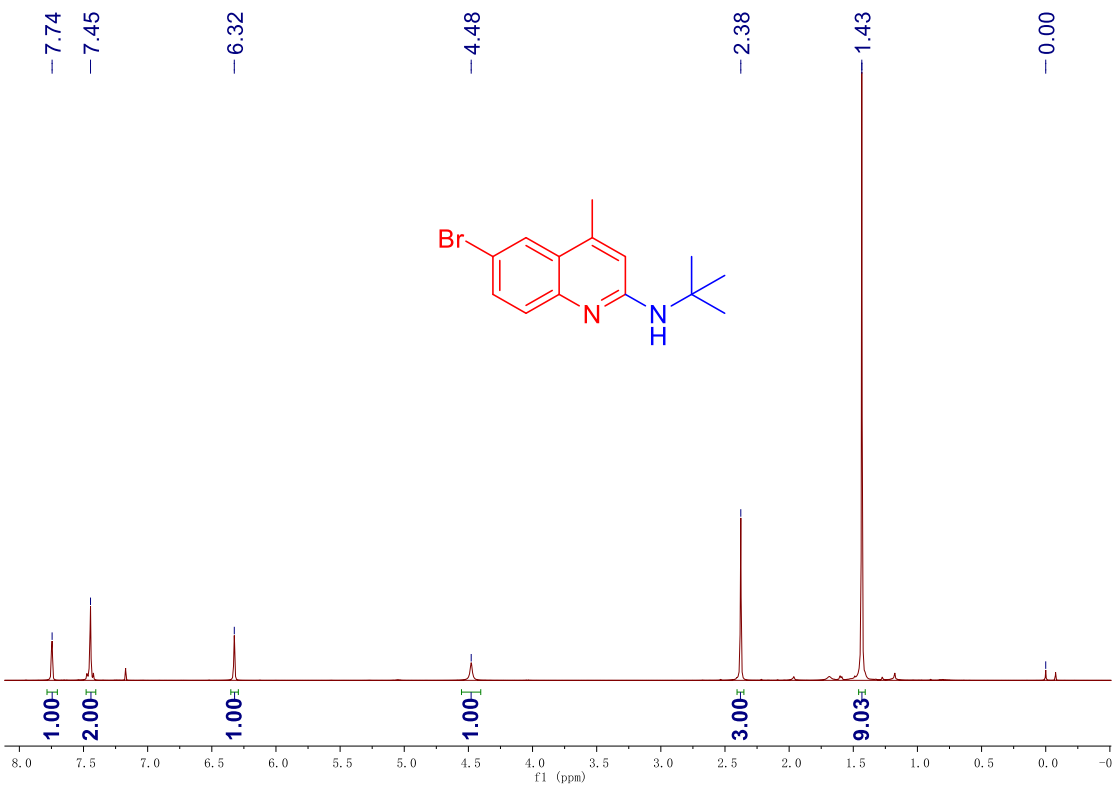
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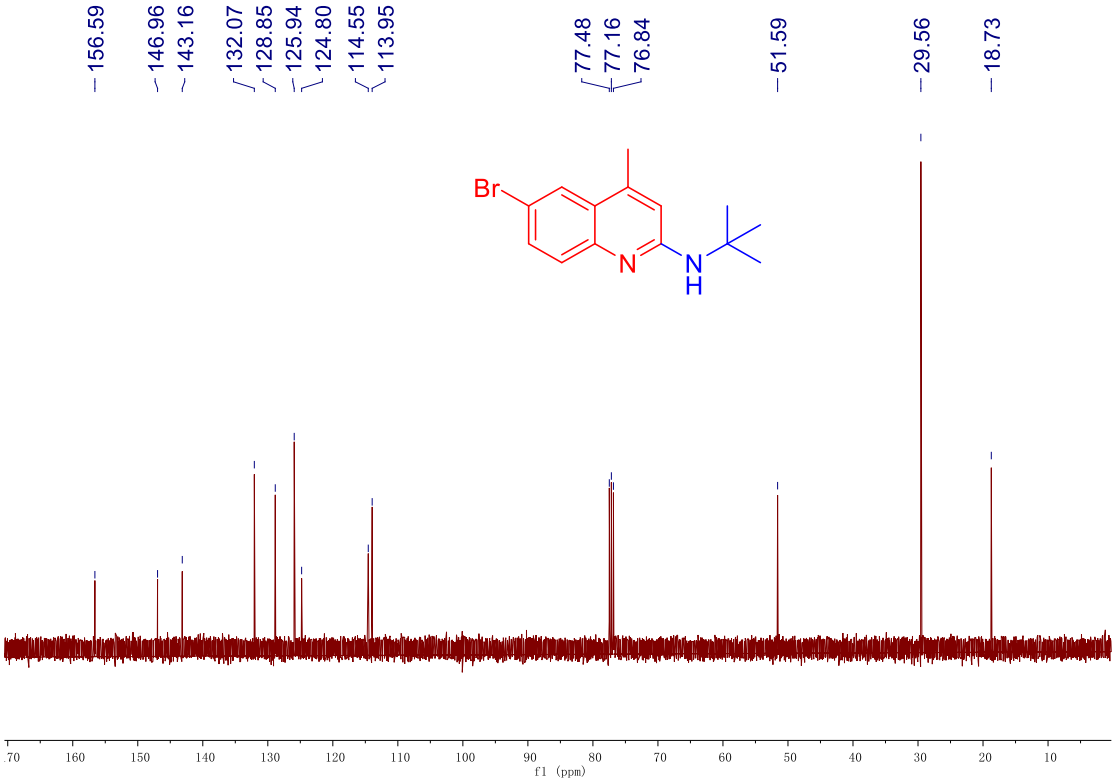
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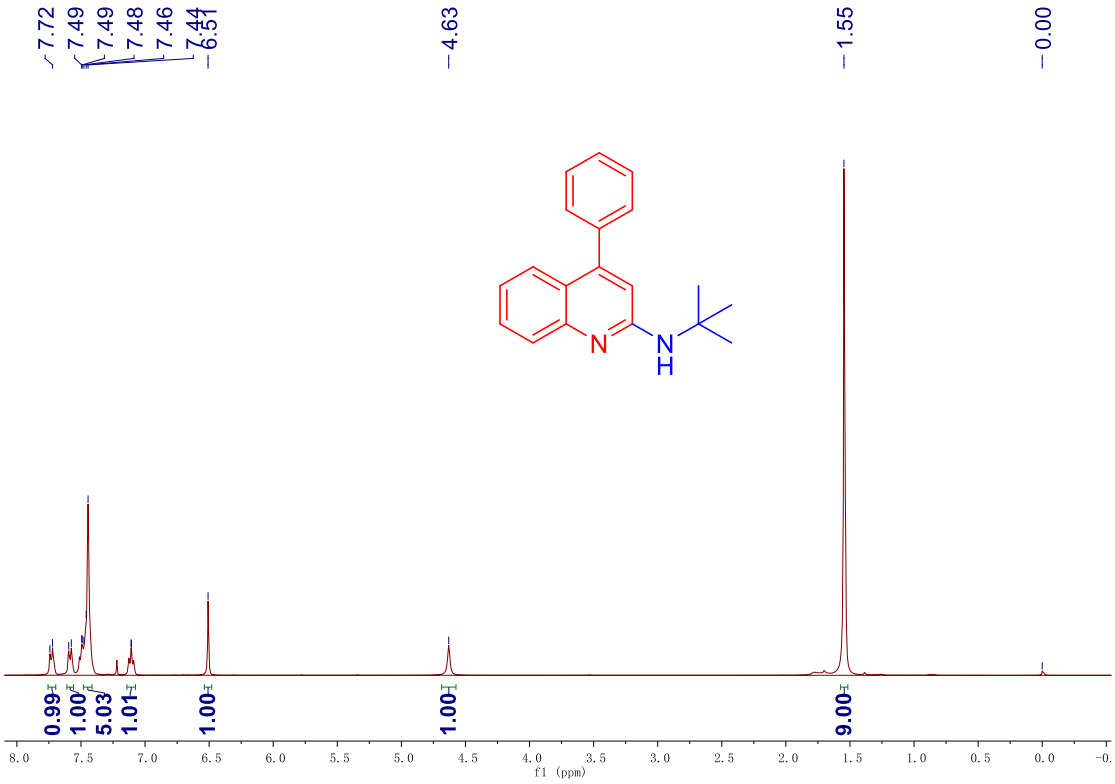
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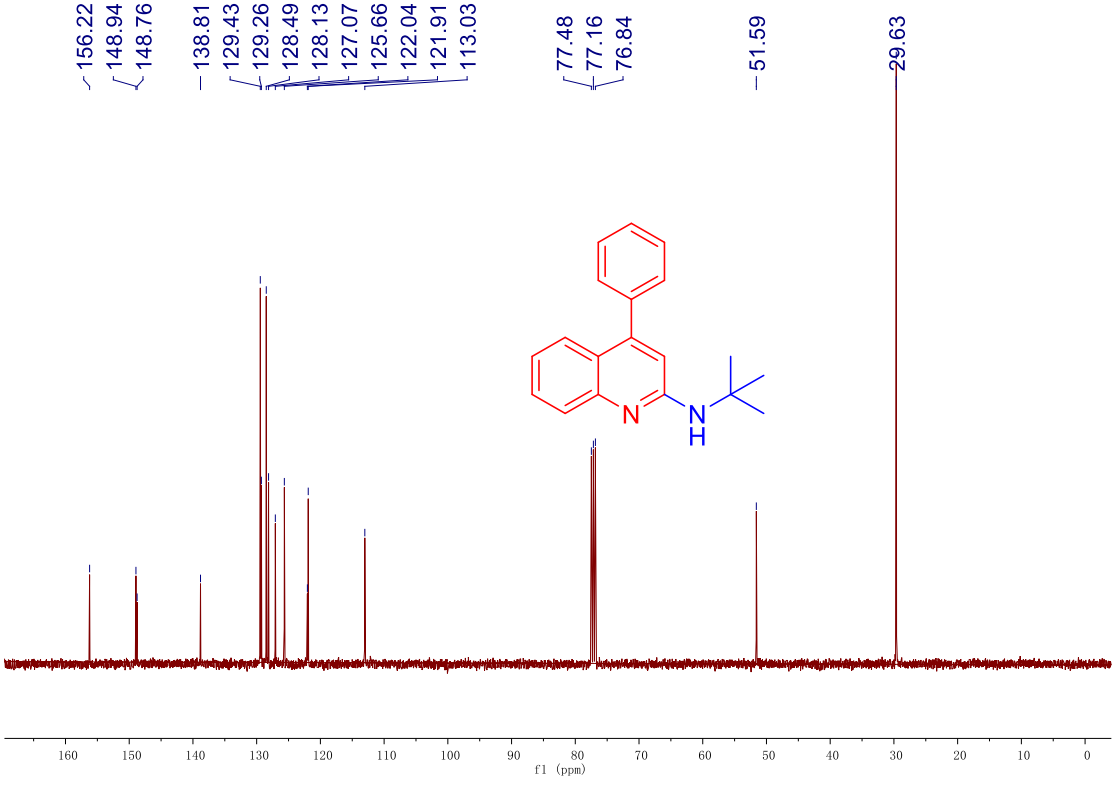
f1 (ppm)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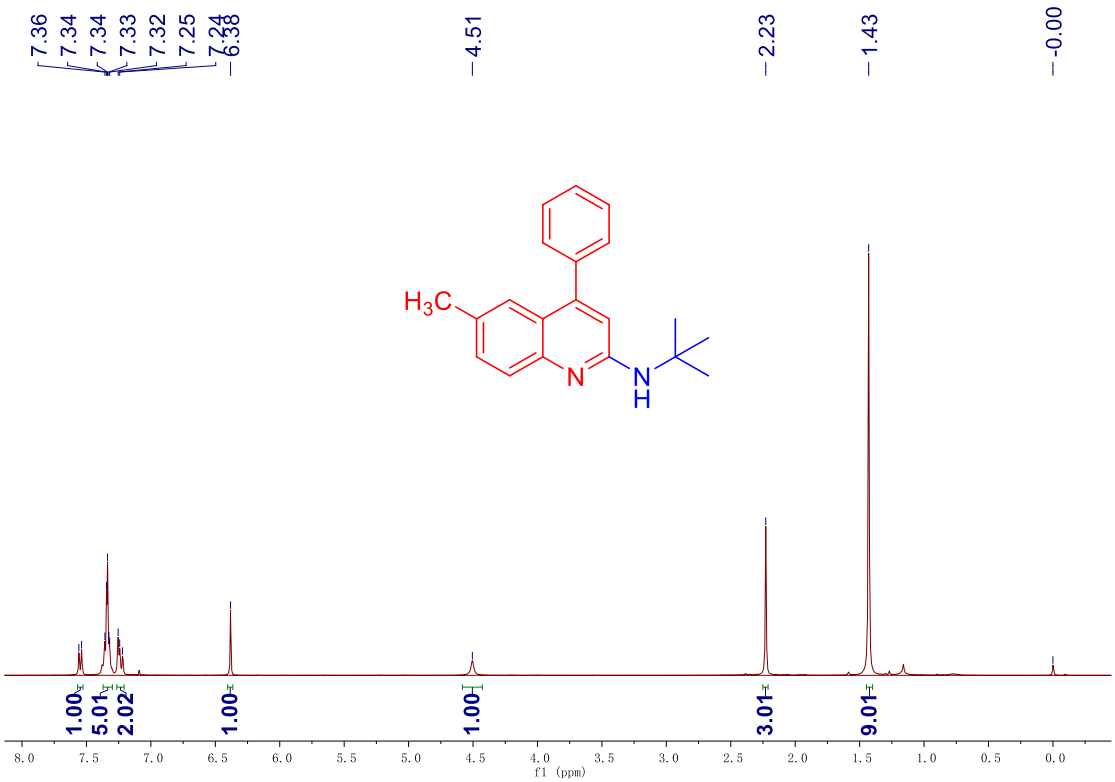
N
H
f1 (ppm)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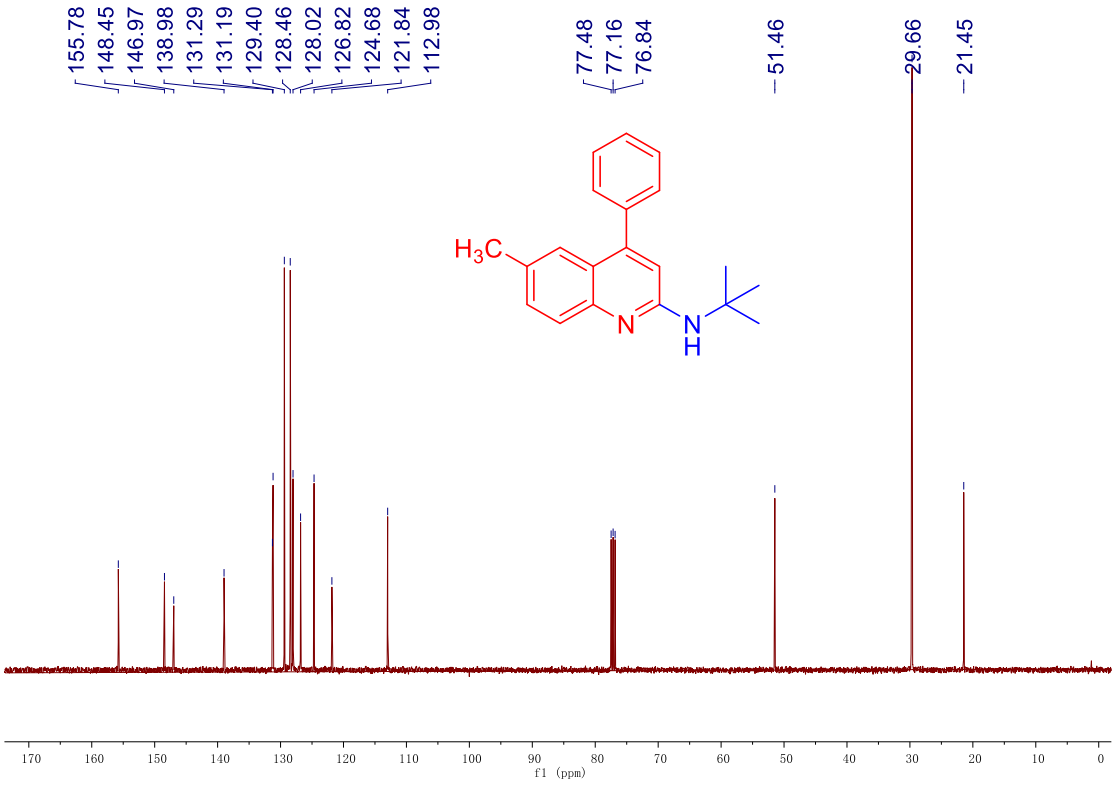
6.38
4.51
2.23
1.43
0.00
H3C
N
N
H
1.00
5.01
2.02
1.00
1.00
3.01
9.01
f1 (ppm)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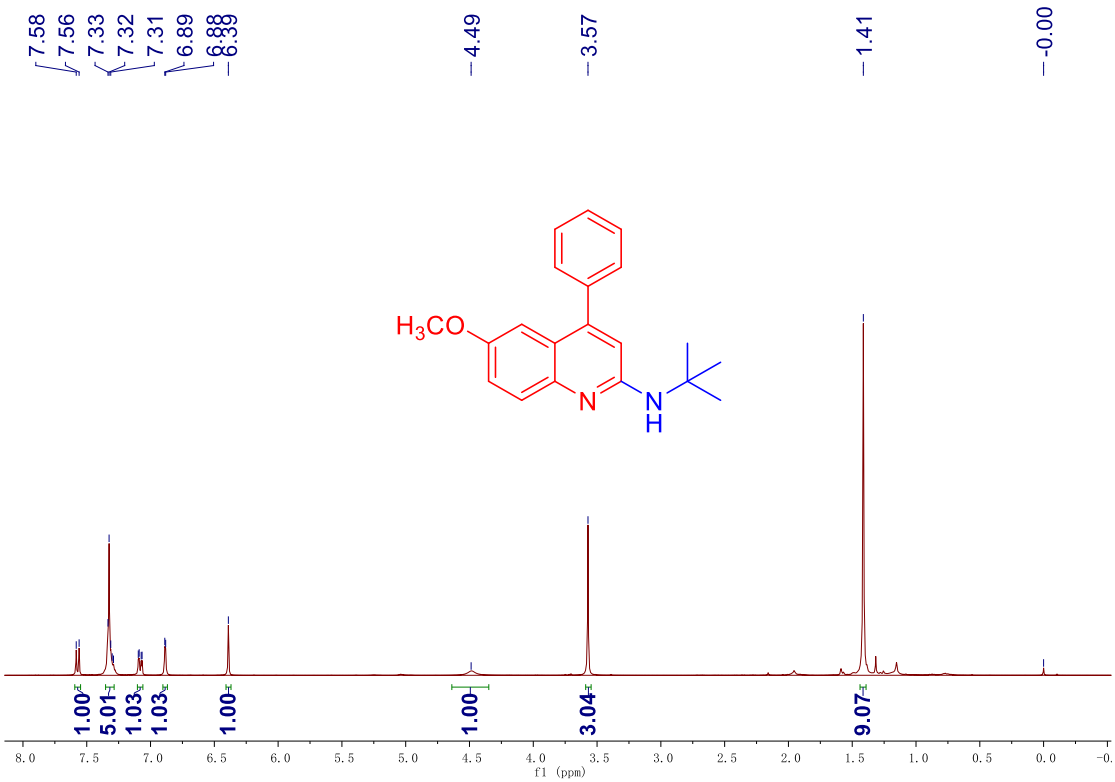
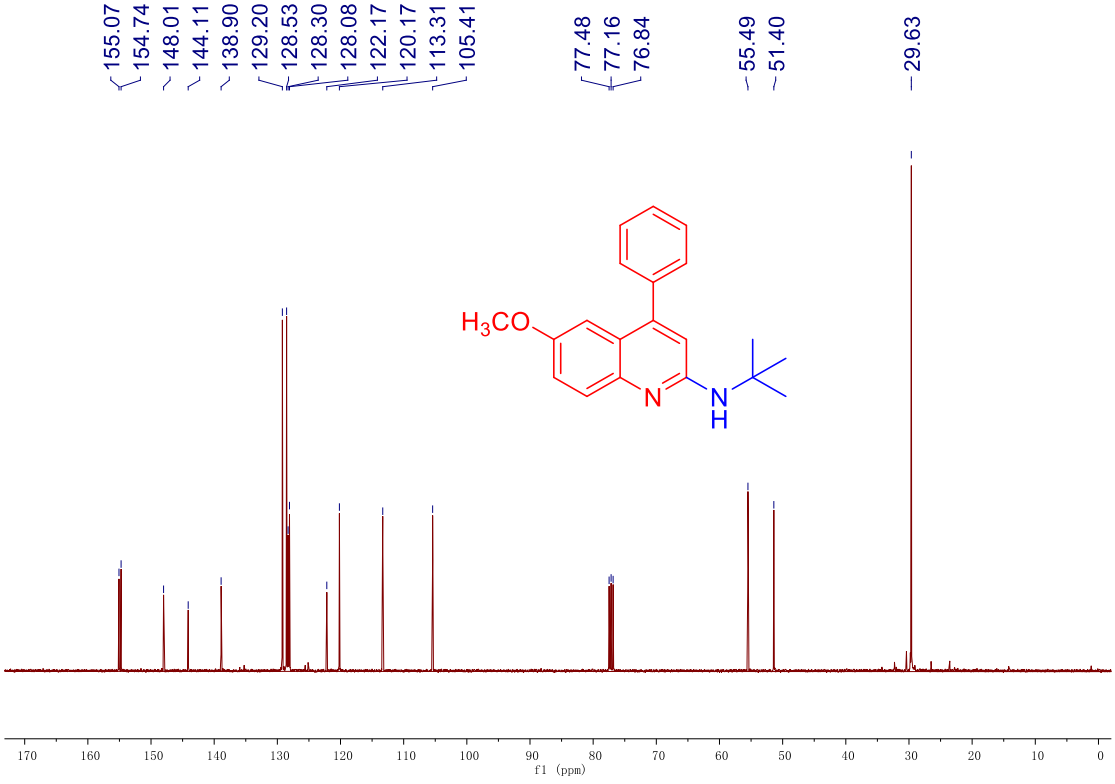
148.45
146.97
138.98
131.29
131.19
129.40
128.46
128.02
126.82
124.68
121.84
112.98
77.48
77.16
76.84
51.46
29.66
21.45
H3C
N
N
H
f1 (ppm)


7.58
7.56
7.33
7.32
7.31
6.89
6.88
6.39
4.49
3.57
1.41
-0.00
H3CO
N
H
1.00
5.01
1.03
1.03
1.00
1.00
3.04
9.07
f1 (ppm)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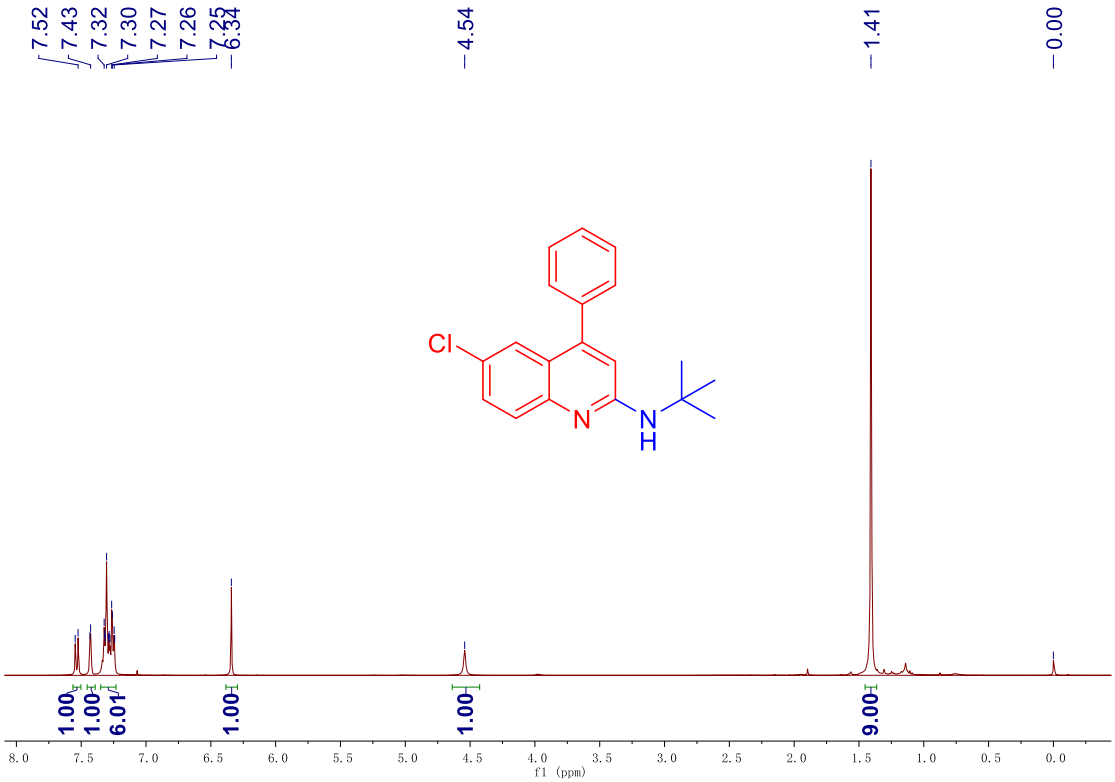
154.74
148.01
144.11
138.90
129.20
128.53
128.30
128.08
122.17
120.17
113.31
105.41
77.48
77.16
76.84
55.49
51.40
29.63
H3CO
N
H
f1 (ppm)


7.52
7.43
7.32
7.30
7.27
7.26
7.25
6.34
4.54
1.41
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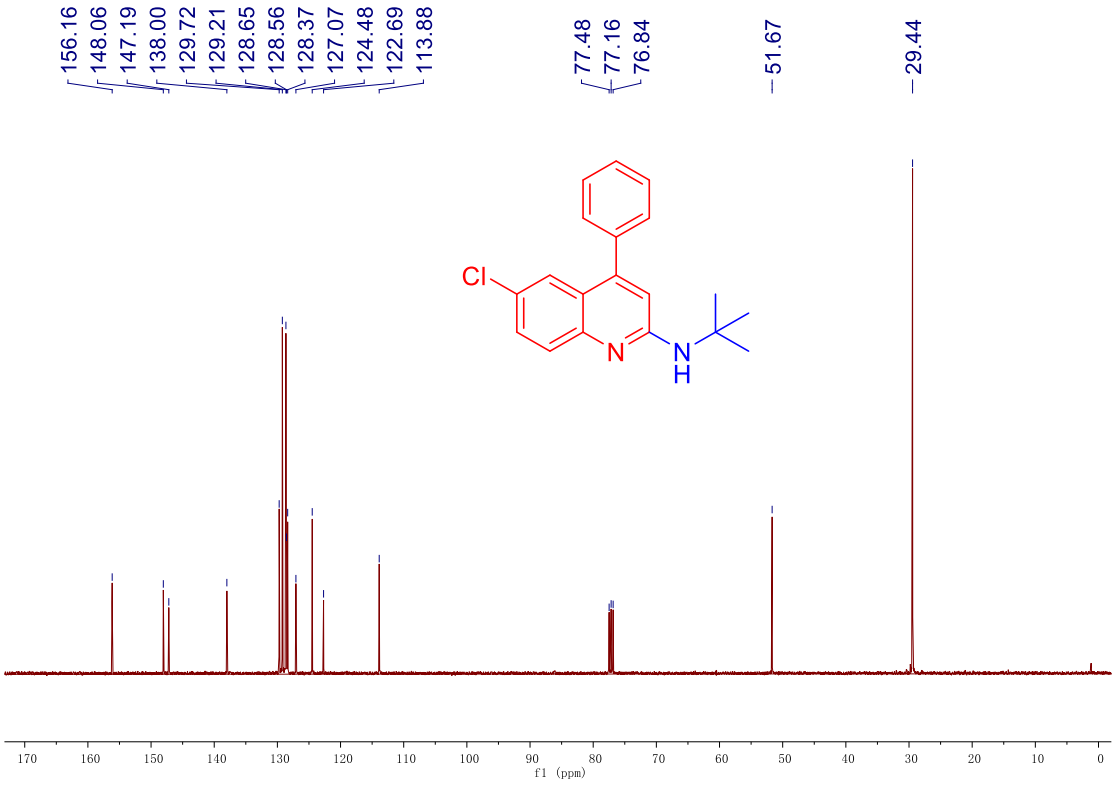
Cl
N
N
H
1.00
1.00
6.01
1.00
1.00
9.00
f1 (ppm)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147.19
138.00
129.72
129.21
128.65
128.56
128.37
127.07
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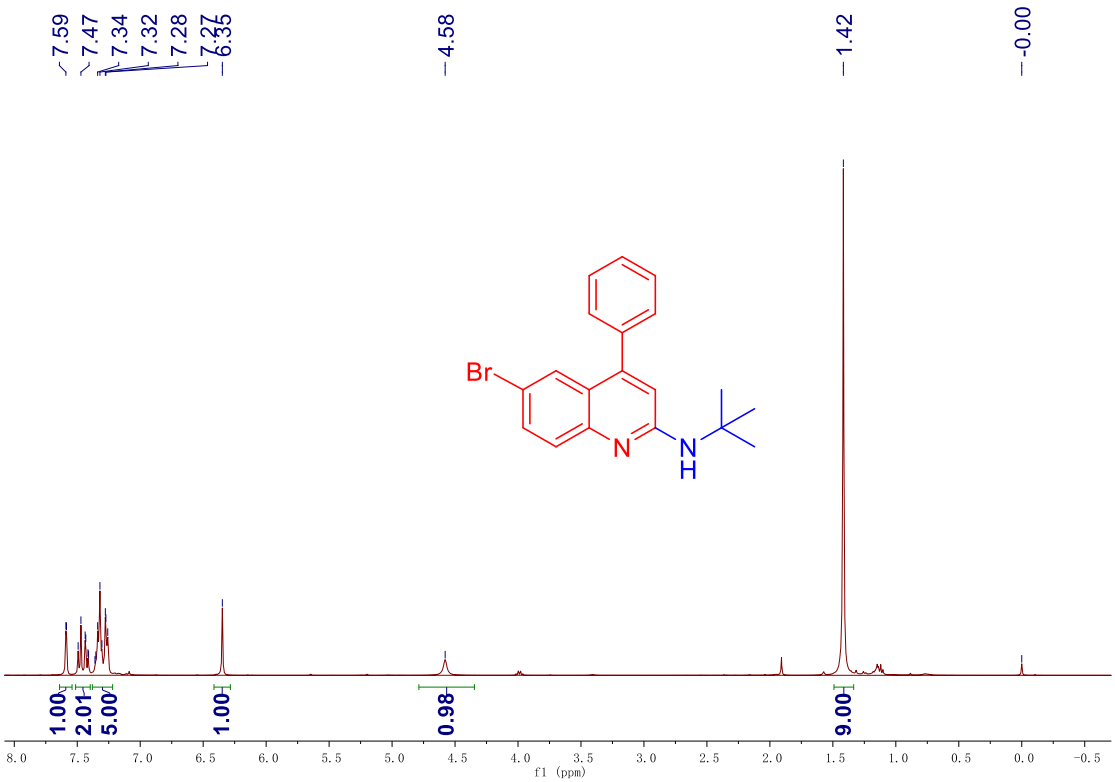
113.88
77.48
77.16
76.84
51.67
29.44
Cl
N
N
H
f1 (ppm)


7.59
7.47
7.34
7.32
7.28
7.27
6.35
4.58
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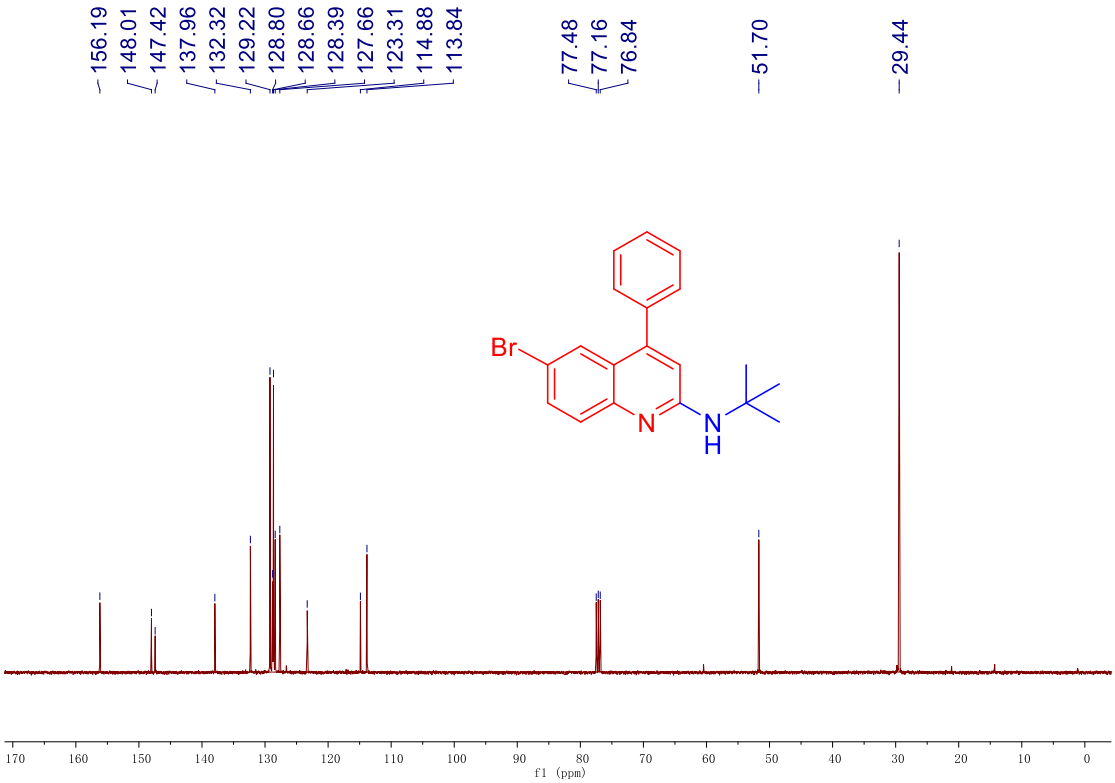
Br
N
N
H
1.00
2.01
5.00
1.00
0.98
9.00
f1 (ppm)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137.96
132.32
129.22
128.80
128.66
128.39
127.66
123.31
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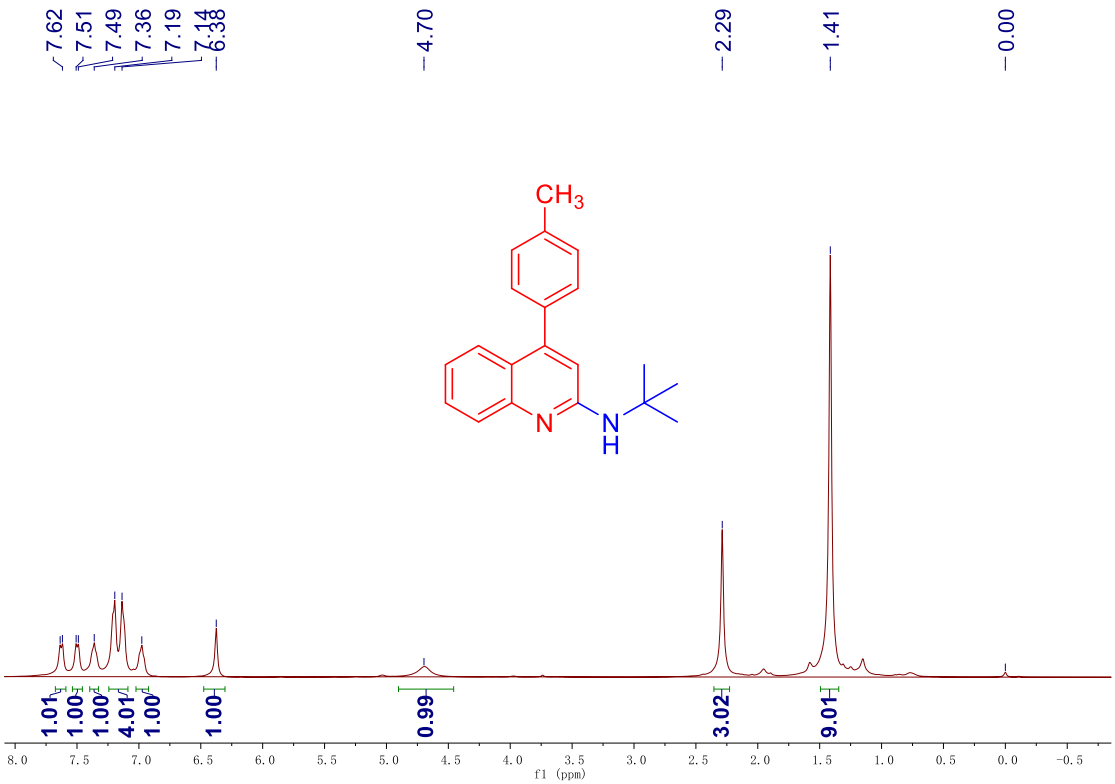
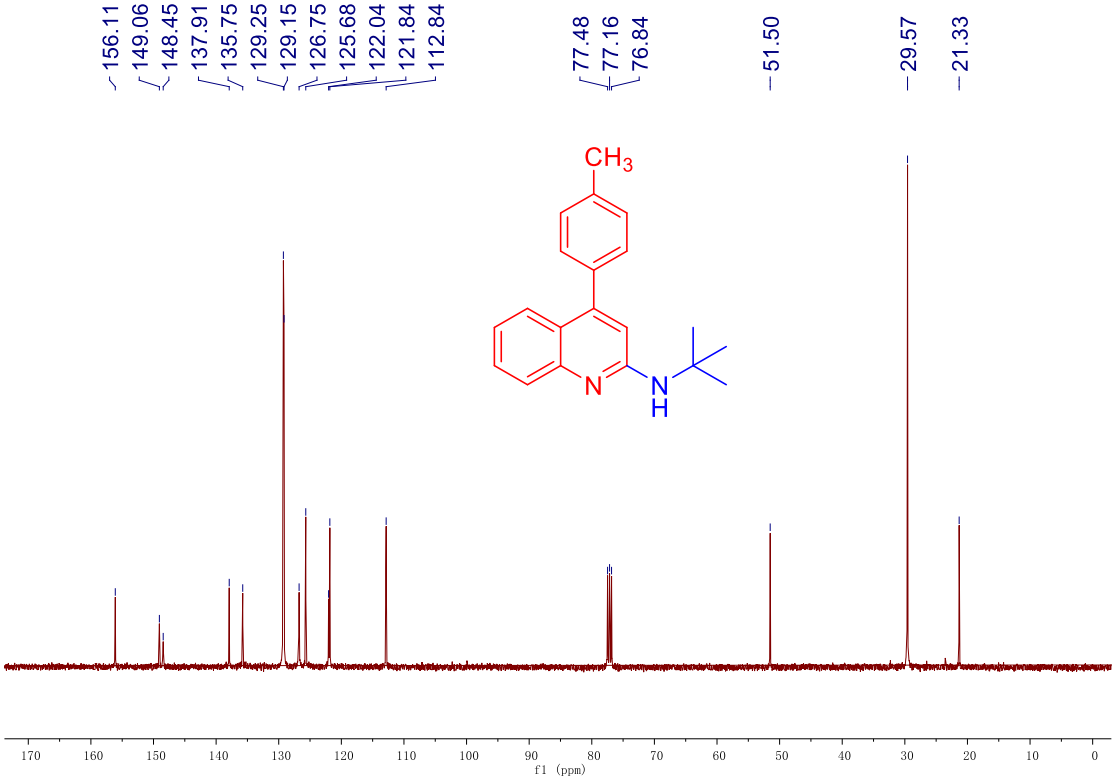
113.84
77.48
77.16
76.84
51.70
29.44
Br
N
N
H
f1 (ppm)


7.62
7.51
7.49
7.36
7.19
7.14
6.38
4.70
2.29
1.41
0.00
CH3
N
H
1.01
1.00
1.00
4.01
1.00
1.00
0.99
3.02
9.01
f1 (ppm)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149.06
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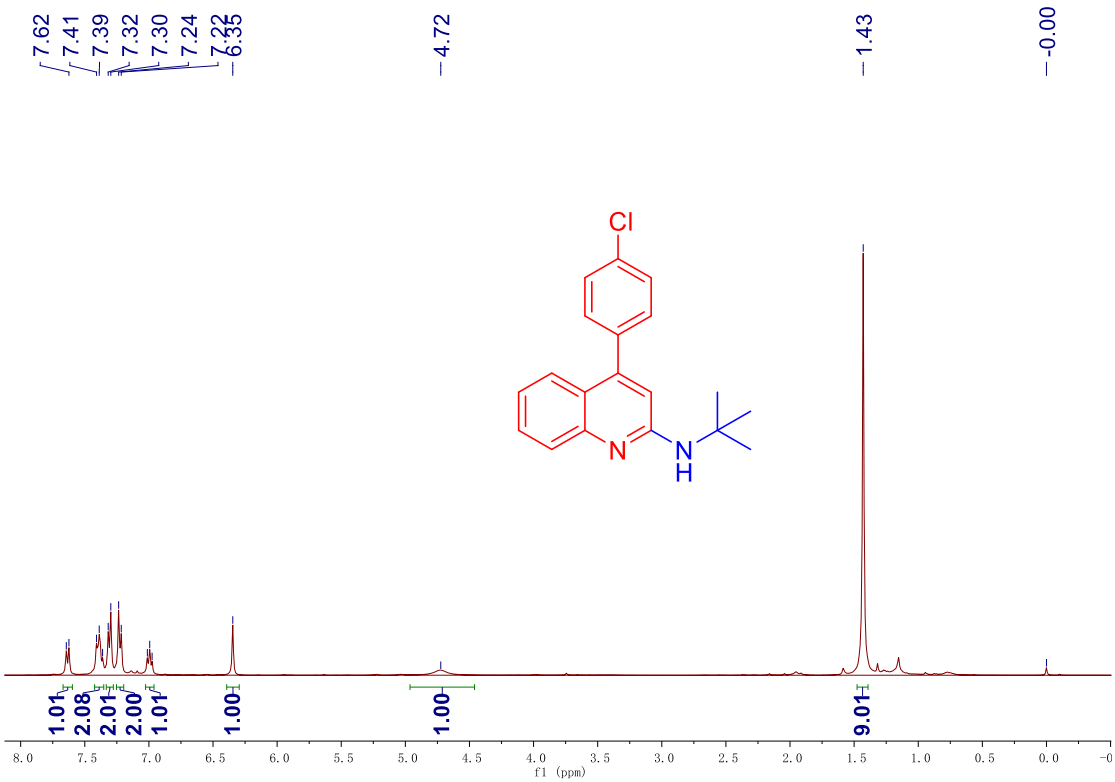
135.75
129.25
129.15
126.75
125.68
122.04
121.84
112.84
77.48
77.16
76.84
51.50
29.57
21.33
CH3
N
H
f1 (ppm)


7.62
7.41
7.39
7.32
7.30
7.24
7.22
6.35
4.72
1.43
-0.00
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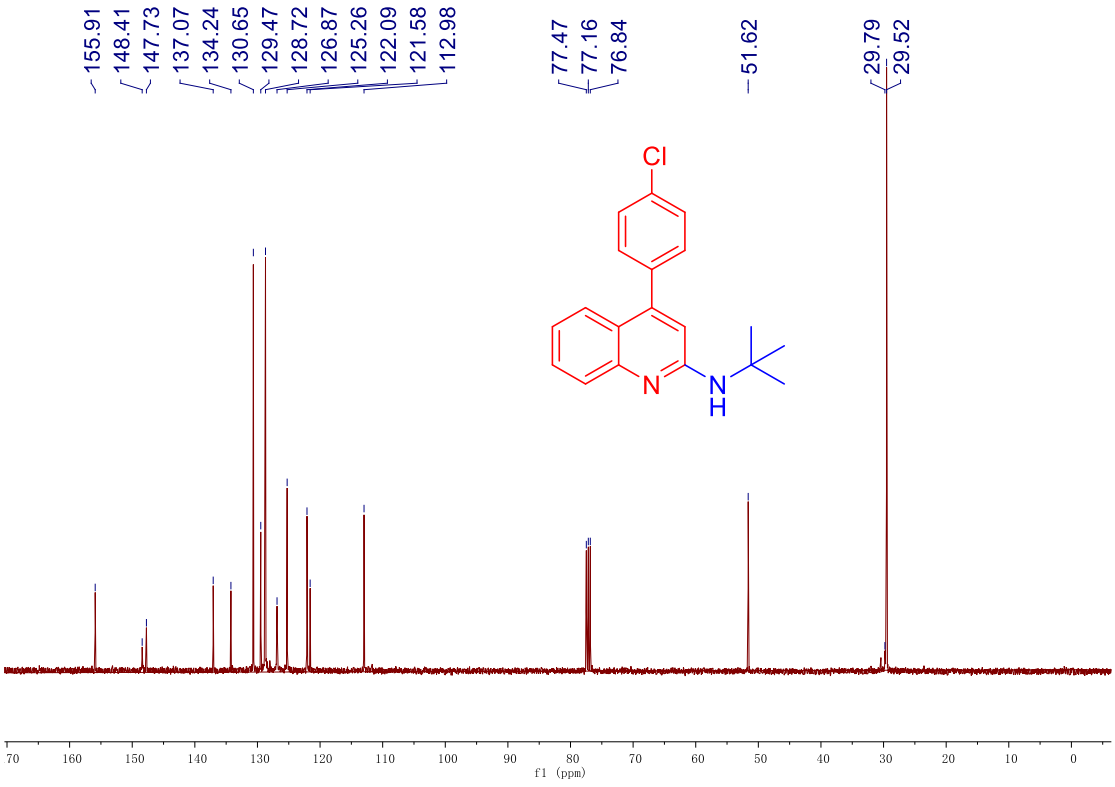
N
N
H
1.01
2.08
2.01
2.00
1.01
1.00
1.00
9.01
f1 (ppm)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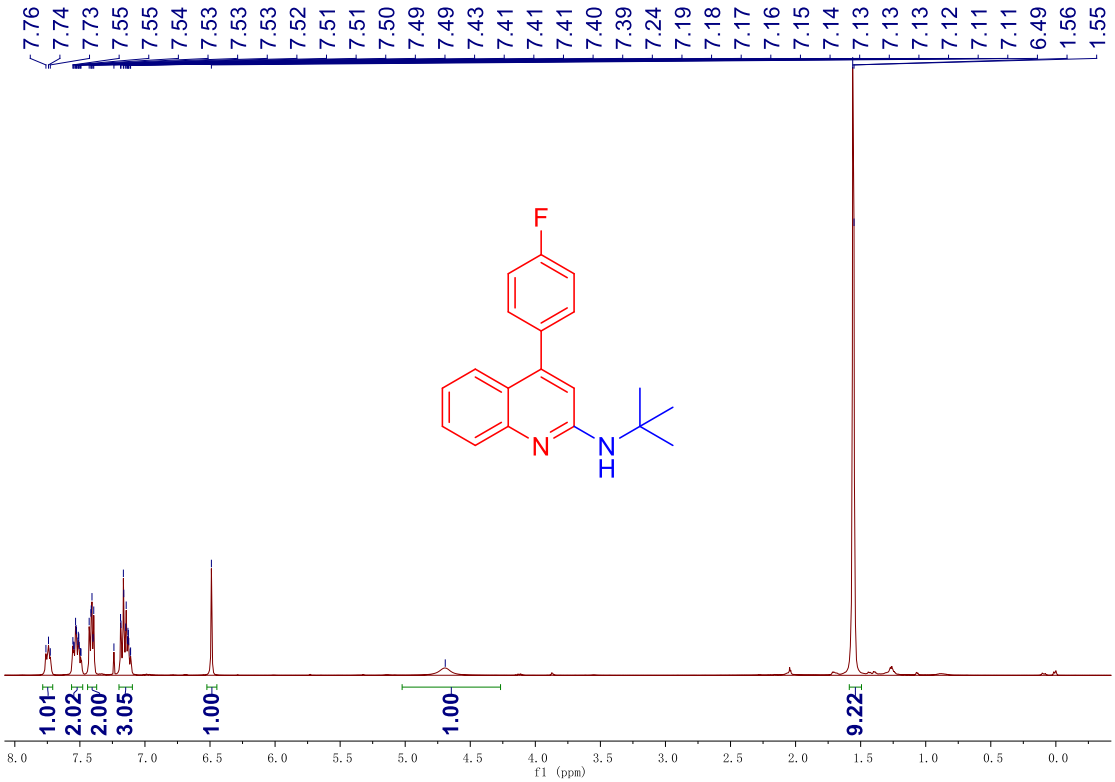
147.73
137.07
134.24
130.65
129.47
128.72
126.87
125.26
122.09
121.58
112.98
77.47
77.16
76.84
51.62
29.79
29.52
Cl
N
N
H
f1 (ppm)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7.73
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7.53
7.53
7.53
7.52
7.51
7.51
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7.41
7.41
7.41
7.40
7.39
7.24
7.19
7.18
7.17
7.16
7.15
7.14
7.13
7.13
7.13
7.12
7.11
7.11
6.49
1.56
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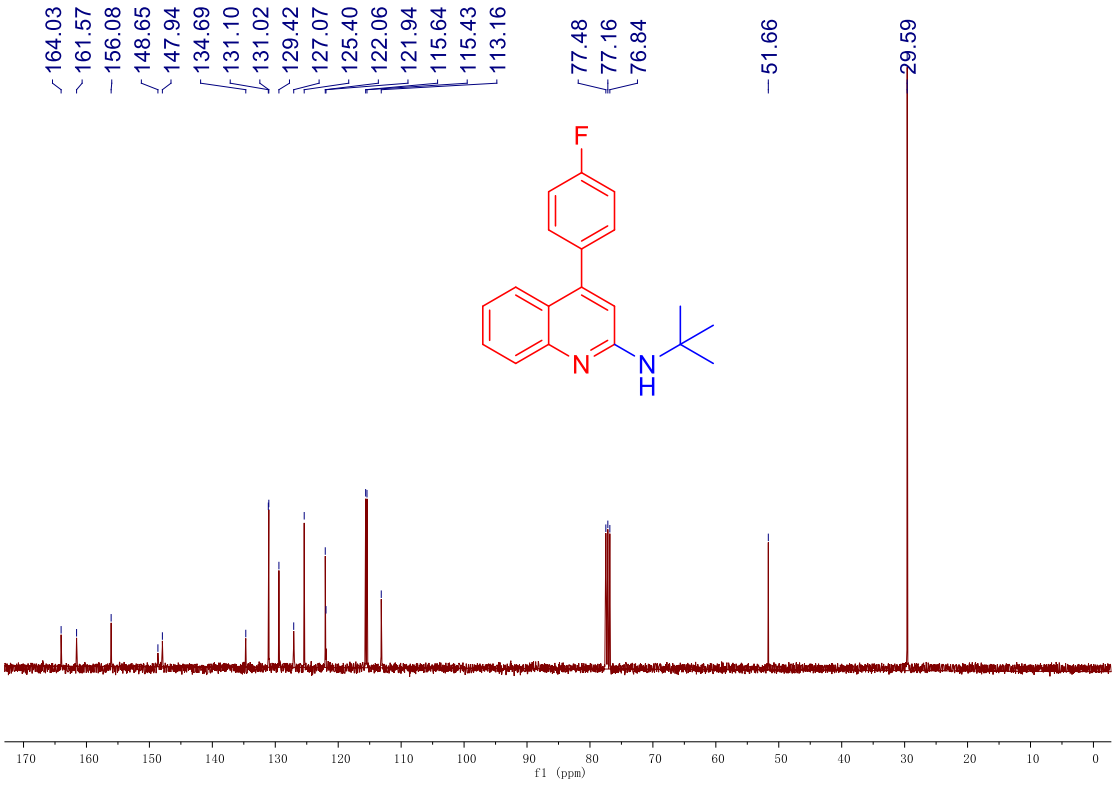
F
N
N
H
1.01
2.02
2.00
3.05
1.00
1.00
9.22
f1 (ppm)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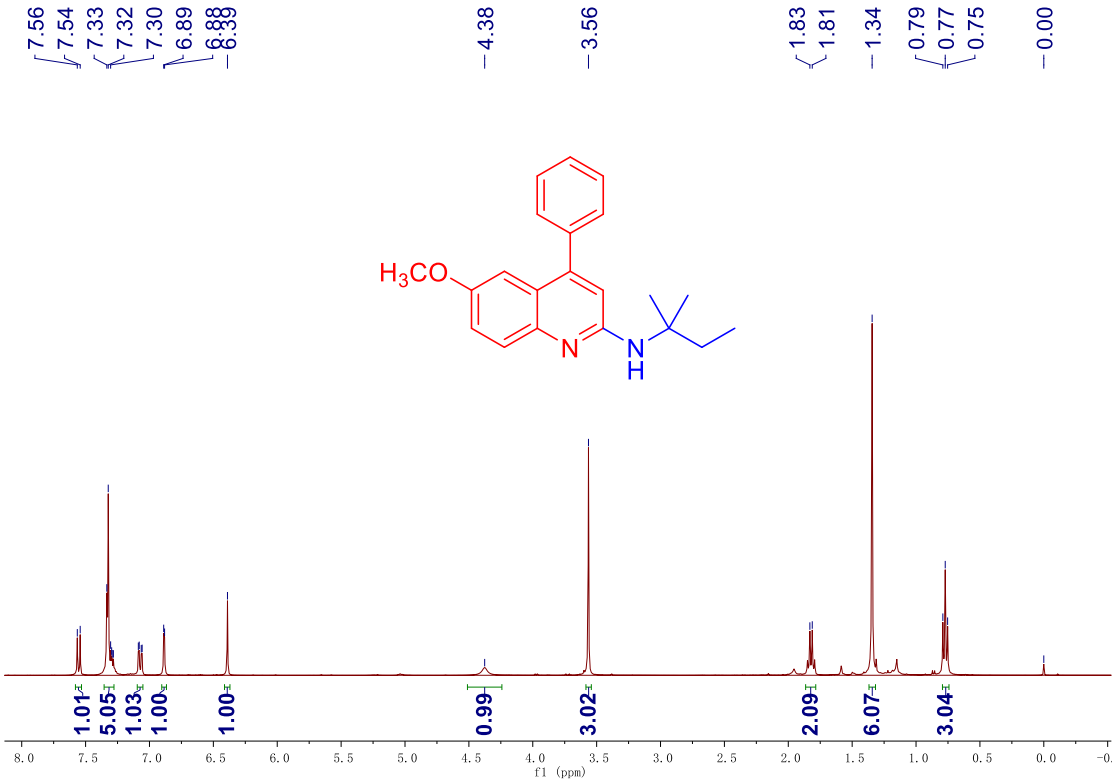
156.08
148.65
147.94
134.69
131.10
131.02
129.42
127.07
125.40
122.06
121.94
115.64
115.43
113.16
77.48
77.16
76.84
51.66
29.59
F
N
N
H
f1 (ppm)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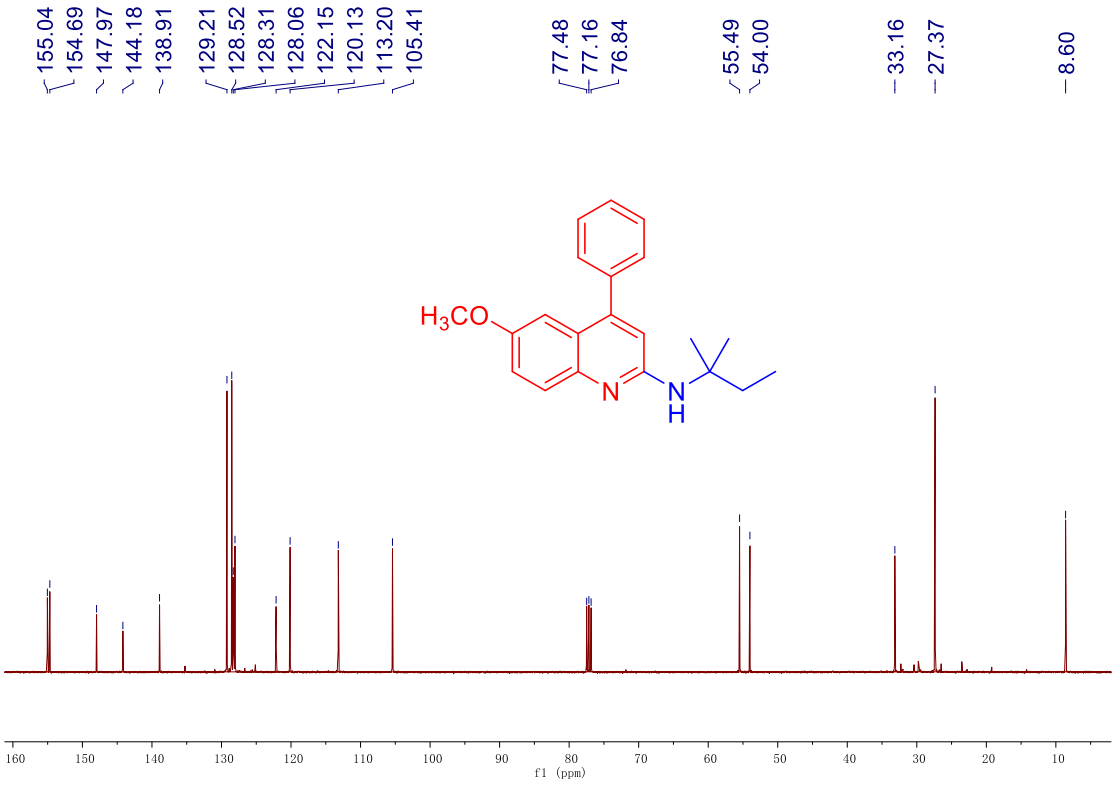
7.54
7.33
7.32
7.30
6.89
6.88
6.39
4.38
3.56
1.83
1.81
1.34
0.79
0.77
0.75
0.00
H3CO
N
N
H
1.01
5.05
1.03
1.00
1.00
0.99
3.02
2.09
6.07
3.04
f1 (ppm)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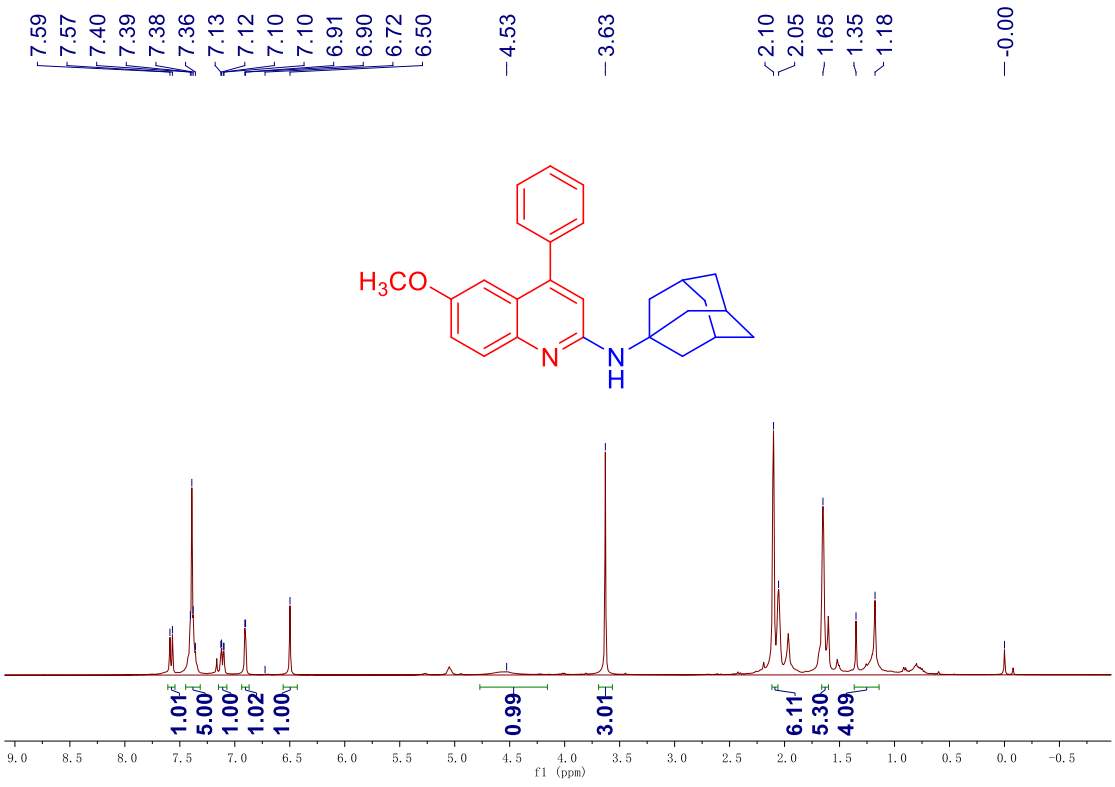
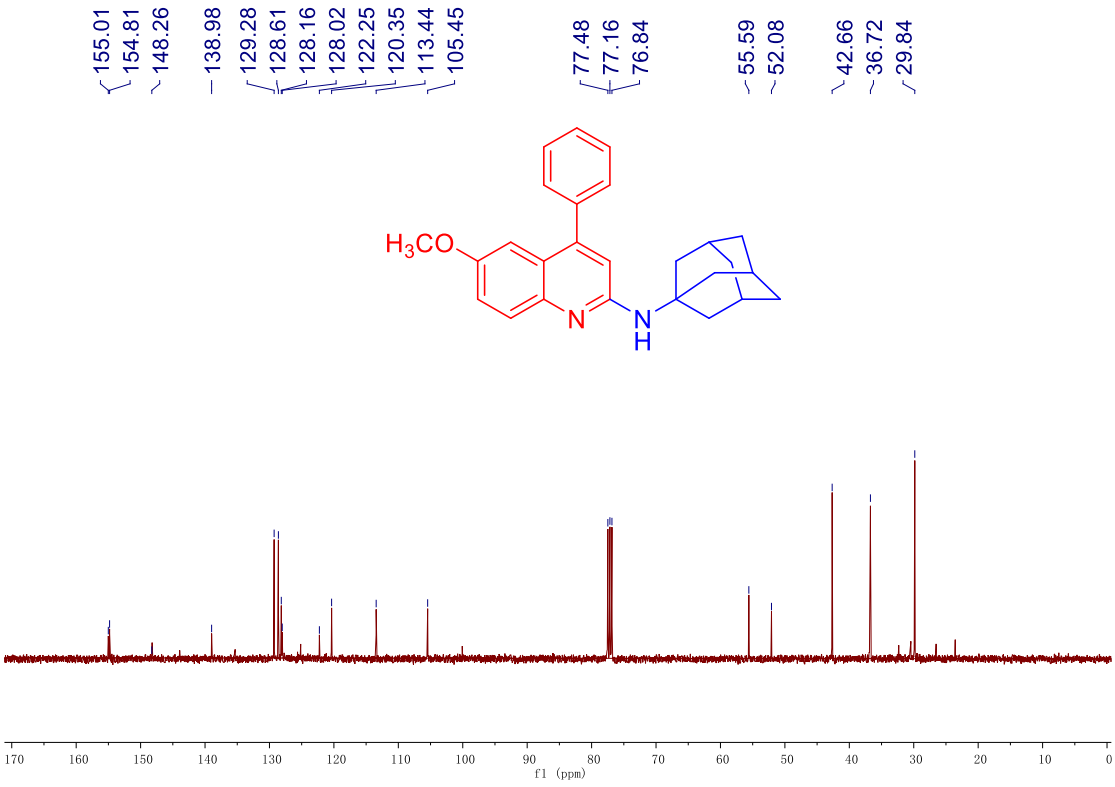
154.69
147.97
144.18
138.91
129.21
128.52
128.31
128.06
122.15
120.13
113.20
105.41
77.48
77.16
76.84
55.49
54.00
33.16
27.37
8.60
H3CO
N
N
H
f1 (ppm)


7.59
7.57
7.40
7.39
7.38
7.36
7.13
7.12
7.10
7.10
6.91
6.90
6.72
6.50
4.53
3.63
2.10
2.05
1.65
1.35
1.18
-0.00
H3CO
N
N
H
1.01
5.00
1.00
1.02
1.00
0.99
3.01
6.11
5.30
4.09
f1 (ppm)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128.61
128.16
128.02
122.25
120.35
113.44
105.45
77.48
77.16
76.84
55.59
52.08
42.66
36.72
29.84
H3CO
N
N
H
f1 (ppm)