# Supporting Information

## Metal-free sequential decarbonylative annulation of N-cyanamides for the construction of 2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-ones

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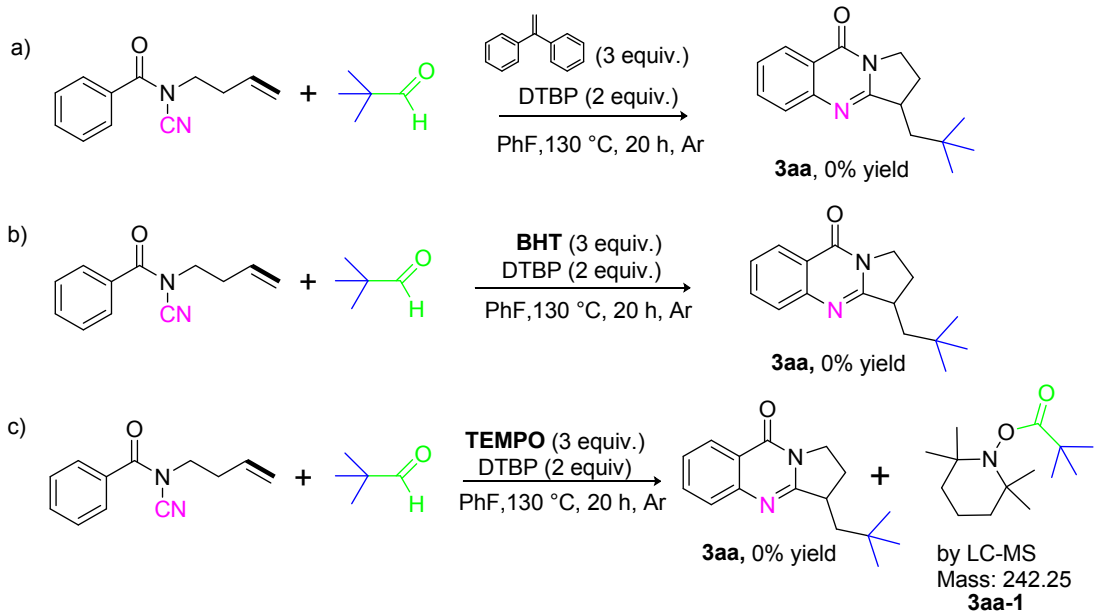
## 1. General information

Melting point determination was taken on a Melt–Temp apparatus (X-4) and was uncorrected. Unless otherwise noted, all commercial materials and solvents were used directly without further purification. HRMS spectra were were obtained on TOF MS ESI. Column chromatography was performed on silica gel (300–400 mesh). Analytical thin–layer chromatography was performed on glass plates of Silica Gel GF–254 with detection by UV. $^{1}H$ NMR spectra, $^{13}C$ NMR spectra and $^{19}F$ NMR spectra were measured in $CDCl_3$ and recorded on a 400M spectrometer. The chemical shift references were as follows: $^{1}H$ NMR (400 MHz,$CDCl_3$) 7.26 ppm. $^{13}C$ NMR (101 MHz, $CDCl_3$) 77.0 ppm.

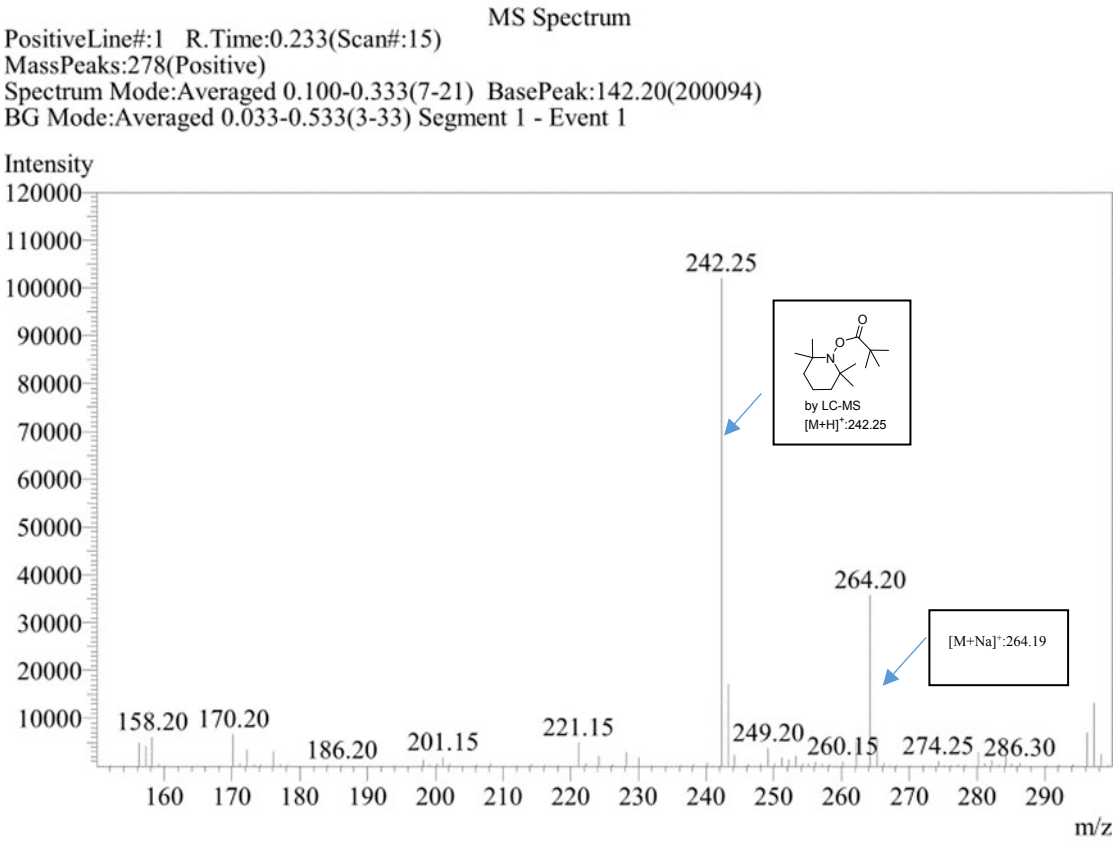
## 2. General procedure

To a solution of 3-neopentyl-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (**1a**, 0.1 mmol) and trimethylacetaldehyde (**2a**, 0.4 mmol) in fluorobenzene (1 mL) at ambient temperature, DTBP (0.2 mmol) was added with vigorous stirring. Then bubbling method holds the argon atmosphere. The reaction mixture was stirred at 130 °C (oil bath temperature) for 20 h. Afterwards The resulting mixture was cooled to room temperature, transferred to silica gel column directly and purified by column chromatography on silica gel with a mixture of EtOAc in petroleum ether as eluent to afford the pure product.

## 3. Mechanistic study




**Scheme 1** Control experiments




## 4. X-ray crystallography for 3ba and 3ja

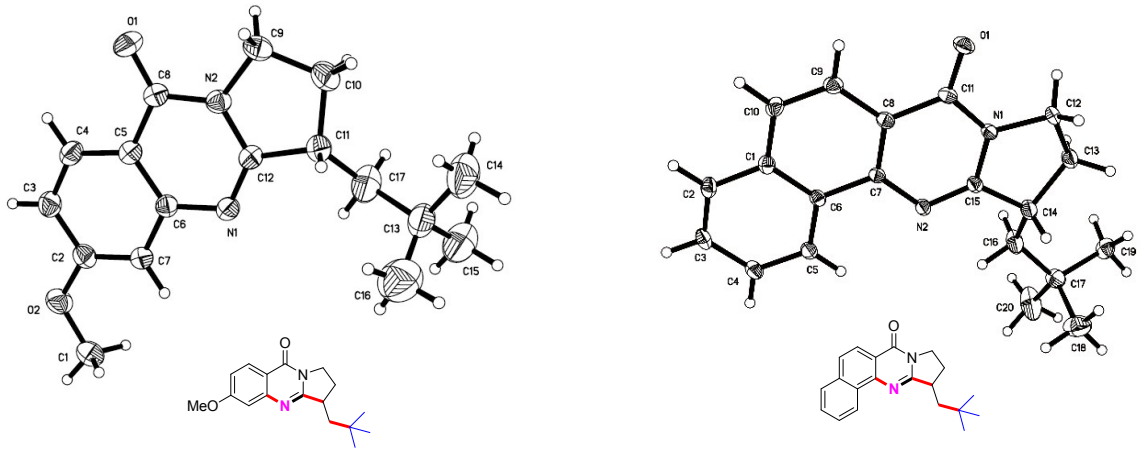
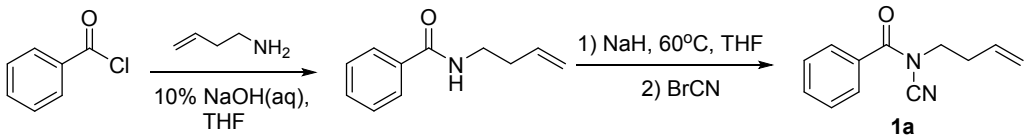



Figure 1 ORTEP structure of compound **3ba** (CCDC number 1552692) and **3ja** (CCDC number 1547405)

## 5. Typical procedure of terminal alkene 1a:




**1a**

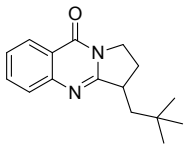
To a THF solution containing but-3-en-1-amine (0.71g, 10 mmol) and aqueous NaOH (0.04g, 1mmol) was added, and benzoyl chloride (1.55g, 11 mmol) was added dropwise at 0 °C over 30 min in a 50 mL flask. Then the solution was warmed to RT and kept for 5-8 h. When the reaction was finished, the solution was filtered and the filtrate was concentrated. Then it was extracted with diethyl ether and dried over $Na_2SO_4$ to give the crude acylamide, which was next purified in flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:5) as eluent to get benzamide (1.38 g, 79% yield).

A 50 mL flask with a stir-bar was charged with NaH (640 mg, 60% wt, 16 mmol), which was then evacuated and backfilled with Argon for three times. THF (15 mL) was added and the solution was cooled to 0 °C. Then a THF solution (4 mL) of benzamide (700 mg, 4 mmol) was added over 10 min to the solution and the reaction was kept at 60 °C for 2 h. Then cyanogen bromide (1.7 g, 16 mmol) was added into the reaction solution at 0 °C and the reaction was kept at RT for overnight. Afterwards, the solution was filtered and the filtrate was concentrated, which was subject to flash column chromatography on silica gel using ethyl acetate/petroleum ether (v/v, 1:10) as eluent to obtain product 1a (448 mg, 56% yield).

## 6. References

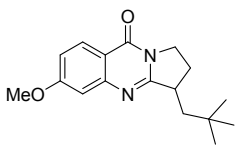
(1) J. Zheng, Y. Zhang, D. H. Wang and S. L. Cui, *Org. Lett*., 2016, **18**, 1768;
(2) J. Zheng, Z .Y. Deng, Y. Zhang and S. L. Cui, *Adv. Synth. Catal*., 2016, **358**, 746.

## 7. Characterization data



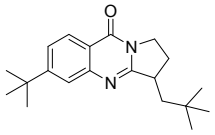
**3-neopentyl-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3aa)**

White solid (18.9 mg, 74% yield), MP : 113 – 115 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.34 – 8.22 (m, 1H), 7.73 – 7.68 (m, 2H), 7.45 – 7.41 (m, 1H), 4.33 – 4.27 (m, 1H), 3.96 – 3.89 (m, 1H), 3.26 – 3.18 (m, 1H), 2.62 – 2.54 (m, 1H), 2.37 (dd, $J$ = 14.1, 2.3 Hz, 1H), 1.97 – 1.87 (m, 1H), 1.42 (dd, $J$ = 14.1, 10.2 Hz, 1H), 1.05 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.4, 161.1, 149.4, 134.0, 127.1, 126.3, 126.1, 120.7, 46.2, 44.8, 41.1, 30.8, 30.1, 29.5. IR (cm$^{-1}$): $v$ 2948, 2865, 1672, 1608, 1464, 1384, 1262, 1115, 1025, 881, 772, 691. HRMS (ESI) : calcd for $C_{16}H_{21}N_2O$ $[M+H]^+$ 257.1654, found: 257.1651.

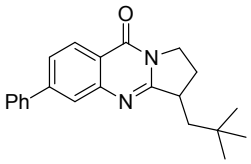


**6-methoxy-3-neopentyl-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3ba)** White solid (23 mg, 80% yield), MP : 116 – 118 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.15 (d, $J$ = 8.8 Hz, 1H), 7.07 (d, $J$ = 2.4 Hz, 1H), 6.99 (dd, $J$ = 8.8, 2.4 Hz, 1H), 4.30 – 4.24 (m,1H), 3.93 – 3.86 (m, 1H), 3.90 (s, 3H), 3.24 – 3.16 (m, 1H), 2.60 – 2.52 (m, 1H), 2.33 (dd, $J$ = 14.0, 2.1 Hz, 1H), 1.95 – 1.85 (m, 1H), 1.41 (dd, $J$ = 14.0, 10.3 Hz, 1H), 1.05 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 164.3, 163.2, 160.7, 151.7, 127.7, 116.2, 114.2 107.7,

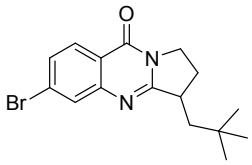
55.6, 46.1, 44.7, 41.2, 30.8, 30.0, 29.4. IR ($cm^{-1}$) : *v* 2937, 2865, 2850, 1666, 1605, 1560, 1437, 1396, 1284, 1211, 1021, 855, 779, 639. HRMS (ESI) : calcd for $C_{17}H_{23}N_2O_2$ $[M+H]^+$ 287.1760, found: 287.1753.



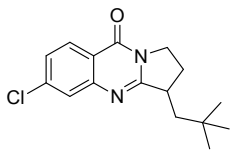
**6-(tert-butyl)-3-neopentyl-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3ca)** White solid (27.5 mg, 88% yield), MP : 170 – 172 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.19 (d, $J$ = 8.4 Hz, 1H), 7.68 (d, $J$ = 1.8 Hz, 1H), 7.49 (dd, $J$ = 8.4, 1.9 Hz, 1H), 4.32 – 4.26 (m, 1H), 3.94 – 3.87 (m, 1H), 3.25 – 3.17 (m, 1H), 2.60 – 2.53 (m, 1H), 2.36 (dd, $J$ = 14.1, 2.2 Hz, 1H), 1.95 – 1.85 (m, 1H), 1.47 – 1.40 (m, 1H), 1.37 (s, 9H), 1.05 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.4, 160.9, 157.9, 149.4, 125.9, 124.2, 123.3, 118.1, 46.1, 44.7, 41.1, 35.3, 31.1, 30.8, 30.0, 29.4. IR ($cm^{-1}$): *v* 2956, 2868, 1677, 1608, 1423, 1306, 1258, 1200, 1026, 838, 788, 699. HRMS (ESI) : calcd for $C_{20}H_{29}N_2O$ $[M+H]^+$ 313.2280, found: 313.2275.



**3-neopentyl-6-phenyl-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3da)** White solid (24 mg, 72% yield), MP : 80 – 82 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.32 (d, $J$ = 8.3 Hz, 1H), 7.93 (d, $J$ = 1.6 Hz, 1H), 7.72 – 7.66 (m, 3H), 7.51 – 7.44 (m, 2H), 7.42 – 7.38 (m, 1H), 4.35 – 4.29 (m, 1H), 3.98 – 3.90 (m, 1H), 3.28 – 3.20 (m, 1H), 2.65 – 2.51 (m, 1H), 2.38 (dd, $J$ = 14.1, 2.2 Hz, 1H), 1.99 – 1.88 (m, 1H), 1.47 – 1.41 (m, 1H), 1.07 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.8, 161.0, 149.8, 146.7, 139.7, 128.9, 128.2, 127.4, 126.8, 125.2, 125.2, 119.4, 46.2, 44.8, 41.1, 30.8, 30.0, 29.5. IR ($cm^{-1}$) : *v* 2950, 2866, 1662, 1610, 1474, 1416, 1364, 1155, 1075, 889, 759, 695. HRMS (ESI) : calcd for $C_{22}H_{25}N_2O$ $[M+H]^+$ 333.1967, found: 333.1965.

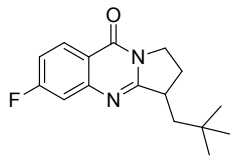


**6-bromo-3-neopentyl-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3ea)** White solid (25.5 mg, 76% yield), MP : 139 – 141 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.10 (d, $J$ = 8.5 Hz, 1H), 7.87 (d, $J$ = 1.8 Hz, 1H), 7.51 (dd, $J$ = 8.5, 1.8 Hz, 1H), 4.30 – 4.24 (m, 1H), 3.94 – 3.86 (m, 1H), 3.24 – 3.16 (m, 1H), 2.66 – 2.51 (m, 1H), 2.32 (dd, $J$ = 14.1, 2.2 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.47 – 1.33 (m, 1H), 1.04 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 163.7, 160.5, 150.4, 129.9, 129.4, 128.6, 127.7, 119.5, 46.1, 44.9, 41.1, 30.7, 30.0, 29.4. IR ($cm^{-1}$) : *v* 2950, 2865, 1662, 1625, 1597, 1455, 1424, 1364, 1332, 1246, 1060, 826, 775, 744. HRMS (ESI) : calcd for $C_{16}H_{20}BrN_2O$ $[M+H]^+$ 335.0759, found: 335.0756.

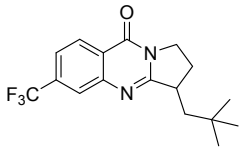


**6-chloro-3-neopentyl-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3fa)** White solid (21.8 mg, 75% yield), MP : 113 – 115 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.18 (d, $J$ = 8.5 Hz, 1H), 7.69 (d, $J$ = 1.8 Hz, 1H), 7.37 (dd, $J$ = 8.5, 1.9 Hz, 1H), 4.31 – 4.25 (m, 1H), 3.95 – 3.87 (m, 1H), 3.24 – 3.17 (m, 1H), 2.64 – 2.53 (m, 1H), 2.33 (dd, $J$ = 14.1, 2.2 Hz, 1H), 1.97 – 1.86 (m, 1H), 1.40 (dd, $J$ = 14.1, 10.0 Hz, 1H), 1.05 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 163.8, 160.4, 150.4, 140.1, 127.7, 126.7, 126.6, 119.1, 46.1, 44.9, 41.2,

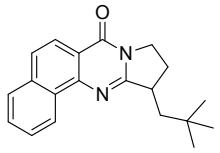
30.7, 30.0, 29.5. IR ($cm^{-1}$) : *v* 2952, 2868, 1660, 1627, 1600, 1459, 1381, 1364, 1277, 1072, 826, 775, 745, 688. HRMS (ESI) : calcd for $C_{16}H_{20}ClN_2O$ $[M+H]^+$ 291.1264, found: 291.1260.



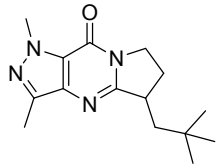
**6-fluoro-3-neopentyl-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3ga)** White solid (19.6 mg, 72% yield), MP : 90 – 92 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.26 (dd, *J* = 8.8, 6.2 Hz, 1H), 7.32 (dd, *J* = 10.0, 2.5 Hz, 1H), 7.15 – 7.10 (m, 1H), 4.31 – 4.25 (m, 1H), 3.95 – 3.87 (m, 1H), 3.24 – 3.16 (m, 1H), 2.77 – 2.51 (m, 1H), 2.33 (dd, *J* = 14.1, 2.3 Hz, 1H), 1.97 – 1.86 (m, 1H), 1.40 (dd, *J* = 14.1, 10.1 Hz, 1H), 1.04 (s, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 166.3 (d, *J* = 253.3 Hz), 163.8, 160.3, 151.6 (d, *J* = 13.1 Hz), 128.8 (d, *J* = 10.7 Hz), 117.4 (d, *J* = 1.9 Hz), 114.8 (d, *J* = 23.5 Hz), 112.4 (d, *J* = 21.9 Hz), 46.1, 44.8, 41.2, 30.7, 30.0, 29.5. $^{19}F$ NMR (376 MHz, $CDCl_3$) $\delta$ -104.3. IR ($cm^{-1}$) : *v* 2954, 2868, 1672, 1610, 1476, 1385, 1282, 1142, 1385, 1282, 1142, 867, 773, 691, 602. HRMS (ESI) : calcd for $C_{16}H_{20}FN_2O$ $[M+H]^+$ 275.1560, found: 275.1557.



**3-neopentyl-6-(trifluoromethyl)-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3ha)** White solid (22.2 mg, 69% yield), MP : 88 – 90 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.37 (d, *J* = 8.3 Hz, 1H), 7.99 (s, 1H), 7.62 (d, *J* = 8.3 Hz, 1H), 4.40 – 4.20 (m, 1H), 3.98 – 3.91 (m, 1H), 3.27 – 3.20 (m, 1H), 2.70 – 2.52 (m, 1H), 2.36 (dd, *J* = 14.1, 2.2 Hz, 1H), 1.99 – 1.89 (m, 1H), 1.42 (dd, *J* = 14.1, 10.0 Hz, 1H), 1.05 (s, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 164.0, 160.2, 149.4, 135.55 (q, *J* = 32.7 Hz), 127.4, 124.9, 124.8, 124.7, 123.0, 122.2, 122.1, 122.0, 46.2, 45.0, 41.2, 30.8, 29.9, 29.5. $^{19}F$ NMR (376 MHz, $CDCl_3$) $\delta$ -63.1. .IR ($cm^{-1}$) : *v* 2954, 2868, 1668, 1616, 1439, 1320, 1275, 1256, 1115, 1060, 900, 837, 788, 734, 695. HRMS (ESI) : calcd for $C_{17}H_{20}F_3N_2O$ $[M+H]^+$ 325.1528, found: 325.1524.

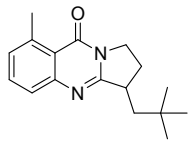


**3-neopentyl-2,3-dihydrobenzo[g]pyrrolo[2,1-b]quinazolin-11(1H)-one (3ja)** White solid (24.8 mg, 81% yield), MP : 125 – 127 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 9.10 – 9.02 (m, 1H), 8.20 (d, *J* = 8.7 Hz, 1H), 7.96 – 7.84 (m, 1H), 7.77 (d, *J* = 8.7 Hz, 1H), 7.69 – 7.64 (m, 2H), 4.44 – 4.29 (m, 1H), 4.20 – 3.95 (m, 1H), 3.31 (q, *J* = 9.5 Hz, 1H), 2.68 – 2.56 (m, 1H), 2.53 (dd, *J* = 14.1, 2.1 Hz, 1H), 2.06 – 1.86 (m, 1H), 1.47 (dd, *J* = 14.1, 9.4 Hz, 1H), 1.10 (s, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 162.6, 161.1, 148.1, 136.1, 130.0, 128.9, 127.7, 126.5, 126.2, 125.2, 121.6, 116.7, 46.6, 45.0, 41.2, 30.8, 30.0, 29.8. IR ($cm^{-1}$) : *v* 2939, 2864, 1653, 1608, 1560, 1476, 1394, 1280, 1023, 870, 800, 762, 736, 671. HRMS (ESI) : calcd for $C_{20}H_{23}N_2O$ $[M+H]^+$ 307.1810, found: 307.1814.

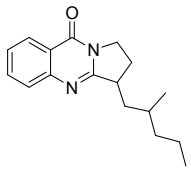


**1,3-dimethyl-5-neopentyl-5,6,7,7a-tetrahydrocyclopenta[b]pyrazolo[3,4-e]pyridin-8(1H)-one (3ka)** White solid (17.4 mg, 64% yield), MP : 168 – 170 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 4.29 – 4.23 (m, 1H), 4.21 (s, 3H), 3.88 – 3.81 (m, 1H), 3.19 – 3.12 (m, 1H), 2.62 – 2.54 (m, 1H), 2.47 (s, 3H), 2.31 (dd, *J* = 14.1, 2.2 Hz, 1H), 1.96 – 1.86 (m, 1H), 1.37 (dd, *J* = 14.1, 10.1 Hz, 1H), 1.03 (s, 9H). $^{13}C$

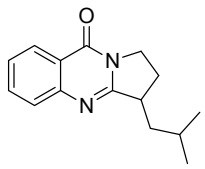
NMR (101 MHz, $CDCl_3$) $\delta$ 160.2, 153.4, 141.2, 139.4, 124.7, 46.3, 44.1, 40.3, 38.1, 30.7, 30.4, 30.0, 10.6. IR ($cm^{-1}$) : *v* 2954, 1671, 1598, 1465, 1392, 1364, 1310, 1256, 1175, 866, 775, 772, 621. HRMS (ESI) : calcd for $C_{15}H_{23}N_4O$ $[M+H]^+$ 275.1872, found: 275.1868.



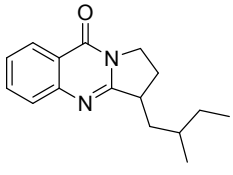
**8-methyl-3-neopentyl-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3la)** White solid (9.3 mg, 34% yield), MP : 96 – 98 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 7.56 – 7.48 (m, 2H), 7.18 – 7.15 (m, 1H), 4.27 – 4.21 (m, 1H), 3.91 – 3.84 (m, 1H), 3.23 – 3.15 (m, 1H), 2.88 (s, 3H), 2.61 – 2.51 (m, 1H), 2.34 (dd, *J* = 14.1, 2.2Hz, 1H), 1.94 – 1.84 (m, 1H), 1.40 (dd, *J* = 14.1, 10.3 Hz, 1H), 1.04 (s, 9H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 162.0, 161.9, 151.1, 140.8, 133.0, 128.7, 125.3, 119.2, 46.1, 44.7, 41.0, 30.8, 30.0, 29.3, 23.0. IR($cm^{-1}$): *v* 2950, 2924, 2863, 1672, 1620, 1595, 1459, 1245, 1042, 809, 785, 695. HRMS (ESI) : calcd for $C_{17}H_{23}N_2O$ $[M+H]^+$ 271.1810, found: 271.1805.



**3-(2-methylpentyl)-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3ab)** White solid (15.4 mg, 57% yield), MP : 59 – 61 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.27 (d, *J* = 7.9 Hz, 1H), 7.70 (q, *J* = 8.2 Hz, 2H), 7.49 – 7.36 (m, 1H), 4.30 – 4.23 (m, 1H), 4.03 – 3.95 (m, 1H), 3.35 – 3.25 (m, 1H), 2.50 – 2.40 (m, 1H), 2.17 – 1.82 (m, 2H), 1.68 – 1.51 (m, 1H), 1.48 – 1.41 (m, 1H), 1.41 – 1.27 (m, 3H), 1.20 – 1.14 (m, 1H), 0.99 (dd, *J* = 6.6, 1.3 Hz, 3H), 0.90 (q, *J* = 6.9 Hz, 3H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 162.3, 162.2, 161.04, 161.02, 149.3, 134.00, 133.96, 127.1, 127.0, 126.31, 126.29, 126.07, 126.06, 120.7, 44.7, 41.9, 41.8, 40.0, 39.9, 39.2, 38.0, 30.5, 30.3, 27.1, 26.4, 20.4, 20.1, 19.9, 18.7, 14.3, 14.2. IR ($cm^{-1}$): *v* 2956, 2924, 2872, 1666, 1610, 1467, 1381, 1332, 1174, 1113, 783, 741, 695. HRMS (ESI) : calcd for $C_{17}H_{23}N_2O$ $[M+H]^+$ 271.1810, found: 271.1808.



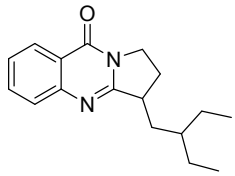
**3-isobutyl-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3ac)** White solid (11.6 mg, 48% yield), MP : 76 – 78 °C. $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.33 – 8.22 (m, 1H), 7.81 – 7.62 (m, 2H), 7.45 – 7.41 (m, 1H), 4.30 – 4.24 (m, 1H), 4.00 (dt, *J* = 12.3, 8.1 Hz, 1H), 3.32 – 3.24 (m, 1H), 2.50 – 2.41 (m, 1H), 2.05 – 1.99 (m, 1H), 1.94 – 1.76 (m, 2H), 1.53 – 1.46 (m, 1H), 1.02 (t, *J* = 6.6 Hz, 6H). $^{13}C$ NMR (101 MHz, $CDCl_3$) $\delta$ 162.2, 161.1, 149.4, 134.1, 127.1, 126.4, 126.1, 120.8, 44.8, 42.1, 41.2, 26.7, 26.0, 23.6, 21.4. IR ($cm^{-1}$): *v* 2954, 2920, 2868, 2851, 1670, 1608, 1562, 1467, 1383, 1330, 1267, 1111, 1027, 878, 768, 719. HRMS (ESI) : calcd for $C_{15}H_{19}N_2O$ $[M+H]^+$ 243.1497, found: 243.1491.



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

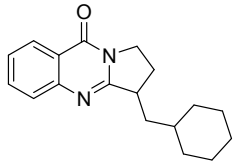
Colorless oil (13.4 mg, 52% yield). $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ 8.28 (d, *J* = 8.0 Hz, 1H), 7.70 (q, *J* = 8.4 Hz, 2H), 7.44 – 7.41 (m, 1H), 4.31 – 4.23 (m, 1H), 4.03 – 3.96 (m, 1H), 3.52 – 3.10 (m, 1H), 2.59 – 2.31 (m, 1H), 2.17 – 1.82(m, 2H), 1.70 – 1.48 (m, 2H), 1.47 – 1.28 (m, 2H), 0.99 (d, *J* = 6.6 Hz, 3H), 0.95 – 0.91 (m, 3H). $^{13}C$ NMR (101 MHz,

$CDCl_3$) $\delta$ 162.3, 162.2, 161.0, 149.3, 134.01, 133.98, 127.1, 127.0, 126.32, 126.30, 126.1, 120.7, 44.7, 41.9, 41.8, 39.4, 38.8, 32.29, 32.25, 30.4, 28.1, 27.2, 26.4, 19.8, 18.2, 11.5, 11.1. IR $\nu$ ($cm^{-1}$): 2958, 2924, 2873, 1670, 1612, 1467, 1333, 1267, 1144, 1027, 770, 695, 661. HRMS (ESI) : calcd for $C_{16}H_{21}N_2O$ $[M+H]^+$ 257.1654, found: 257.1648.

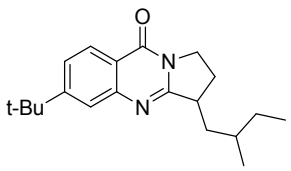


**3-(2-ethylbutyl)-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3ae)**

White solid (15.6 mg, 58% yield), MP : 89 – 91 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.31 – 8.23 (m, 1H), 7.77 – 7.63 (m, 2H), 7.45 – 7.41 (m, 1H), 4.31 – 4.24 (m, 1H), 3.99 (dt, $J$ = 12.3, 8.1 Hz, 1H), 3.33 – 3.25 (m, 1H), 2.49 – 2.40 (m, 1H), 2.11 – 2.04 (m, 1H), 1.93 – 1.83 (m, 1H), 1.58 – 1.39 (m, 4H), 1.37 – 1.29 (m, 2H), 0.91 (q, $J$ = 7.3 Hz, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 155.3, 154.1, 142.4, 127.0, 120.0, 119.3, 119.1, 113.7, 37.7, 34.8, 31.1, 28.7, 19.8, 18.9, 17.4, 4.0, 3.5. IR ($cm^{-1}$) : $\nu$ 2960, 2920, 2872, 2851, 1664, 1620, 1467, 1383, 1332, 1262, 1021, 801, 784, 697. HRMS (ESI) : calcd for $C_{17}H_{23}N_2O$ $[M+H]^+$ 271.1810, found: 271.1808.

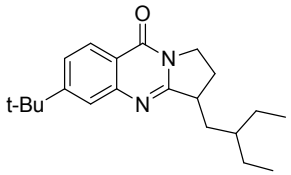


**3-(cyclohexylmethyl)-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3af)** White solid (15.0 mg, 53% yield), MP : 78 – 80 °C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.32 – 8.22 (m, 1H), 7.76 – 7.64 (m, 2H), 7.45 – 7.41 (m, 1H), 4.30 – 4.24 (m, 1H), 4.03 – 3.96 (m, 1H), 3.41 – 3.23 (m, 1H), 2.49 – 2.41 (m, 1H), 2.09 – 2.02 (m, 1H), 1.94 – 1.84 (m, 2H), 1.738 – 1.67 (m, 5H), 1.50 – 1.42 (m, 2H), 1.30 – 1.27 (m, 1H), 1.21 – 1.20 (m, 1H), 1.12 – 0.91 (m, 2H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.3, 161.0, 149.3, 134.0, 127.0, 126.3, 126.1, 120.7, 44.7, 41.4, 39.7, 35.5, 34.3, 32.1, 26.7, 26.5, 26.3, 26.2. IR ($cm^{-1}$) : $\nu$ 2961, 2920, 2850, 2851, 1664, 1612, 1560, 1465, 1384, 1261, 1086, 1021, 800, 770, 693. HRMS (ESI) : calcd for $C_{18}H_{23}N_2O$ $[M+H]^+$ 283.1810, found: 283.1808.



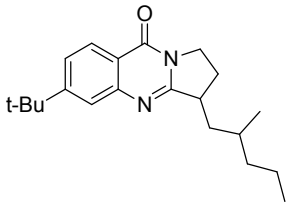
**6-(tert-butyl)-3-(2-methylbutyl)-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3ag)**

Colorless oil (18.4 mg, 59% yield). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.19 (d, $J$ = 8.4 Hz, 1H), 7.68 (t, $J$ = 1.9 Hz, 1H), 7.50 – 7.48 (m, 1H), 4.33 – 4.18 (m, 1H), 4.01 – 3.94 (m, 1H), 3.36 – 3.19 (m, 1H), 2.53 – 2.34 (m, 1H), 2.18 – 1.78 (m, 2H), 1.63 – 1.50 (m, 2H), 1.38 (s, 9H), 1.34 – 1.27 (m, 1H), 1.23 – 1.13 (m, 1H), 0.99 (d, $J$ = 6.6 Hz, 3H), 0.95 – 0.90 (m, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.3, 162.2, 160.9, 158.04, 158.01, 149.4, 125.93, 125.90, 124.2, 123.30, 123.25, 118.2, 44.6, 41.9, 41.8, 39.5, 38.9, 35.3, 32.30, 32.28, 31.1, 30.4, 28.0, 27.1, 26.4, 19.9, 18.2, 11.5, 11.2. IR ($cm^{-1}$): $\nu$ 2928, 2926, 2872, 1672, 1612, 1556, 1424, 1381, 1308, 1258, 1200, 1023, 721, 700, 611. HRMS (ESI) : calcd for $C_{20}H_{29}N_2O$ $[M+H]^+$ 313.2280, found: 313.2273.



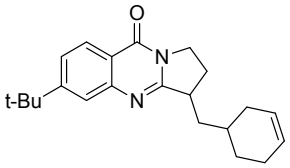
**6-(tert-butyl)-3-(2-ethylbutyl)-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3ah)**

Colorless oil (21.5 mg, 66% yield). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.19 (d, $J$ = 8.4 Hz, 1H), 7.68 (d, $J$ = 1.8 Hz, 1H), 7.49 (dd, $J$ = 8.4, 1.9 Hz, 1H), 4.30 – 4.23 (m, 1H), 4.01 – 3.94 (m, 1H), 3.36 – 3.16 (m, 1H), 2.47 – 2.39 (m, 1H), 2.11 – 2.04 (m, 1H), 1.91 – 1.82 (m, 1H), 1.57 – 1.46 (m, 3H), 1.45 – 1.40 (m, 1H), 1.38 (s, 9H),1.33 – 1.28 (m, 2H), 1.00 – 0.85 (m, 6H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.3, 160.9, 158.0 149.4, 125.9, 124.2, 123.3, 118.2, 44.6, 41.8, 38.1, 35.7, 35.3, 31.1, 26.8, 25.9, 24.4, 11.0, 10.5. IR (cm$^{-1}$): $v$ 2960, 2924, 2872, 1672, 1612, 1485, 1381, 1424, 1258, 937, 893, 790, 520. HRMS (ESI) : calcd for $C_{21}H_{31}N_2O$ $[M+H]^+$ 327.2436, found: 327.2430.



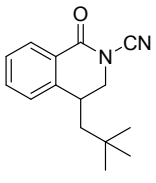

**6-(tert-butyl)-3-(2-methylpentyl)-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3ai)**

Colorless oil (20.0 mg, 61% yield). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.19 (d, $J$ = 8.4 Hz, 1H), 7.68 (t, $J$ = 1.7 Hz, 1H), 7.49 (dd, $J$ = 8.4, 1.7 Hz, 1H), 4.30 – 4.23 (m, 1H),4.01 – 3.94 (m, 1H), 3.37 – 3.19 (m, 1H), 2.59 – 2.35 (m, 1H), 2.19 – 1.77 (m, 2H), 1.77 – 1.51 (m, 2H), 1.48 – 1.42 (m, 1H), 1.37 (s, 9H), 1.34 – 1.27 (m, 2H), 1.22 – 1.10 (m, 1H), 0.99 (d, $J$ = 6.6 Hz, 3H), 0.90 (q, $J$ = 7.1 Hz, 3H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.3, 162.2, 160.9, 158.04, 158.00, 149.4, 125.92, 125.90, 124.2, 123.3, 123.2, 118.2, 44.6, 41.9, 41.8, 40.1, 39.9, 39.2, 37.9, 35.3, 31.1, 30.5, 30.3, 27.0, 26.4, 20.4, 20.1, 19.9, 18.6, 14.3, 14.2. IR (cm$^{-1}$) $v$ 2958, 2928, 2872, 1672, 1612, 1556, 1424, 1383, 1260, 937, 893, 790, 701. HRMS (ESI) : calcd for $C_{21}H_{31}N_2O$ $[M+H]^+$ 327.2436, found: 327.2432.



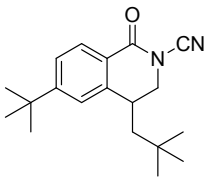

**6-(tert-butyl)-3-(cyclohex-3-en-1-ylmethyl)-2,3-dihydropyrrolo[2,1-b]quinazolin-9(1H)-one (3aj)**

Colorless oil (18.1 mg, 54% yield). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.20 (d, $J$ = 8.4 Hz, 1H), 7.68 (d, $J$ = 1.8 Hz, 1H), 7.50 (dd, $J$ = 8.4, 1.9 Hz, 1H), 5.70 – 5.67 (m, 2H), 4.31 – 4.25 (m, 1H), 4.02 – 3.95 (m, 1H), 3.39 – 3.28 (m, 1H), 2.51 – 2.42 (m, 1H), 2.25 – 2.05 (m, 4H), 1.95 – 1.87 (m, 2H), 1.86 – 1.75 (m, 3H), 1.64 – 1.62 (m, 1H), 1.38 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 162.1, 160.9, 158.1, 149.4, 127.2, 127.0, 126.3, 125.94, 125.90, 124.3, 123.29, 123.27, 118.2, 44.6, 41.6, 41.4, 39.3, 38.8, 35.3, 32.7, 31.6, 31.4, 31.1, 30.8, 29.9, 27.7, 26.9, 26.6, 25.3, 25.1. IR (cm$^{-1}$): $v$ 3021, 2960, 2920, 2851, 1672, 1612, 1308, 1260, 1092, 790, 701, 609. HRMS (ESI) : calcd for $C_{22}H_{29}N_2O$ $[M+H]^+$ 337.2280, found: 337.2278.



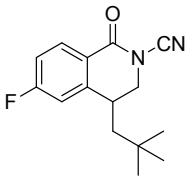

**4-neopentyl-1-oxo-3,4-dihydroisoquinoline-2(1H)-carbonitrile (5aa)**

White solid (11.1 mg, 46% yield), MP : 55 – 57 $^o$C. $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.09 – 8.07 (m, 1H), 7.59 – 7.55 (m, 1H), 7.42 – 7.38 (m, 1H), 7.30 – 7.14 (m, 1H), 4.18 – 4.14 (m, 1H), 3.86 (dd, $J$ = 12.2, 2.8 Hz, 1H), 3.12 – 3.08 (m, 1H), 1.84 (dd, $J$ = 14.7, 7.9 Hz, 1H), 1.45 – 1.41 (m, 1H), 1.03 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 163.3, 145.0, 134.7, 129.5, 127.7, 127.1, 125.0, 109.8, 53.5, 46.8, 34.3, 31.3, 29.7. IR (cm$^{-1}$) : $v$ 2954, 2920, 2851, 2236, 1696, 1601, 1457, 1387, 1316, 1236, 1146, 1098, 954, 775, 695. HRMS (ESI) : calcd for $C_{15}H_{19}N_2O$ $[M+H]^+$ 243.1497, found: 243.1490.



**6-(tert-butyl)-4-neopentyl-1-oxo-3,4-dihydroisoquinoline-2(1H)-carbonitrile (5ba)**

White solid (15.2 mg, 51% yield), MP : 107 – 109 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.00 (d, $J$ = 8.3 Hz, 1H), 7.41 (dd, $J$ = 8.3, 1.9 Hz, 1H), 7.21 (d, $J$ = 1.8 Hz, 1H), 4.17 – 4.13 (m, 1H), 3.86 – 3.82 (m, 1H), 3.09 – 3.05 (m, 1H), 1.84 (dd, $J$ = 14.6, 7.6 Hz, 1H), 1.45 – 1.40 (m, 1H), 1.33 (s, 9H), 1.03 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 163.2, 158.8, 144.8, 129.4, 125.0, 124.0, 122.3, 110.0, 53.7, 47.0, 35.3, 34.6, 31.3, 30.9, 29.7. IR ($cm^{-1}$) : $\nu$ 2943, 2868, 2242, 1694, 1607, 1465, 1392, 1310, 1176, 1154, 1249, 956, 855, 699. HRMS (ESI) : calcd for $C_{19}H_{27}N_2O$ $[M+H]^+$ 299.2123, found: 299.2117.

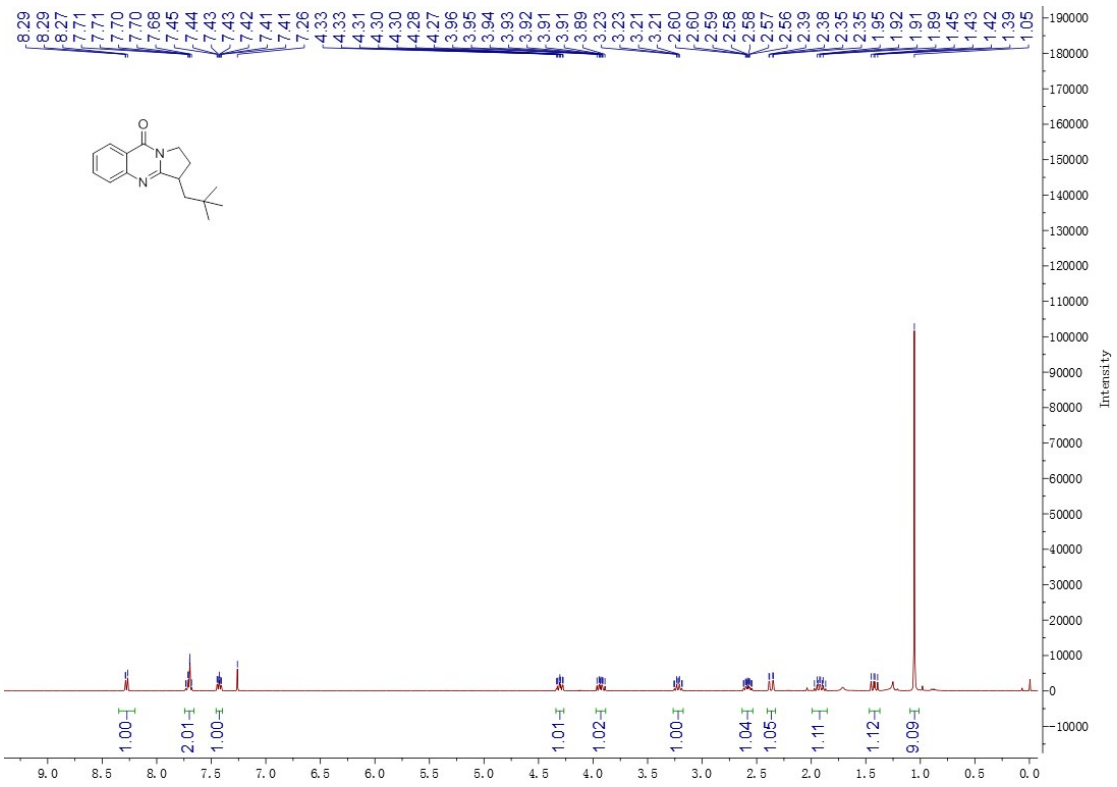


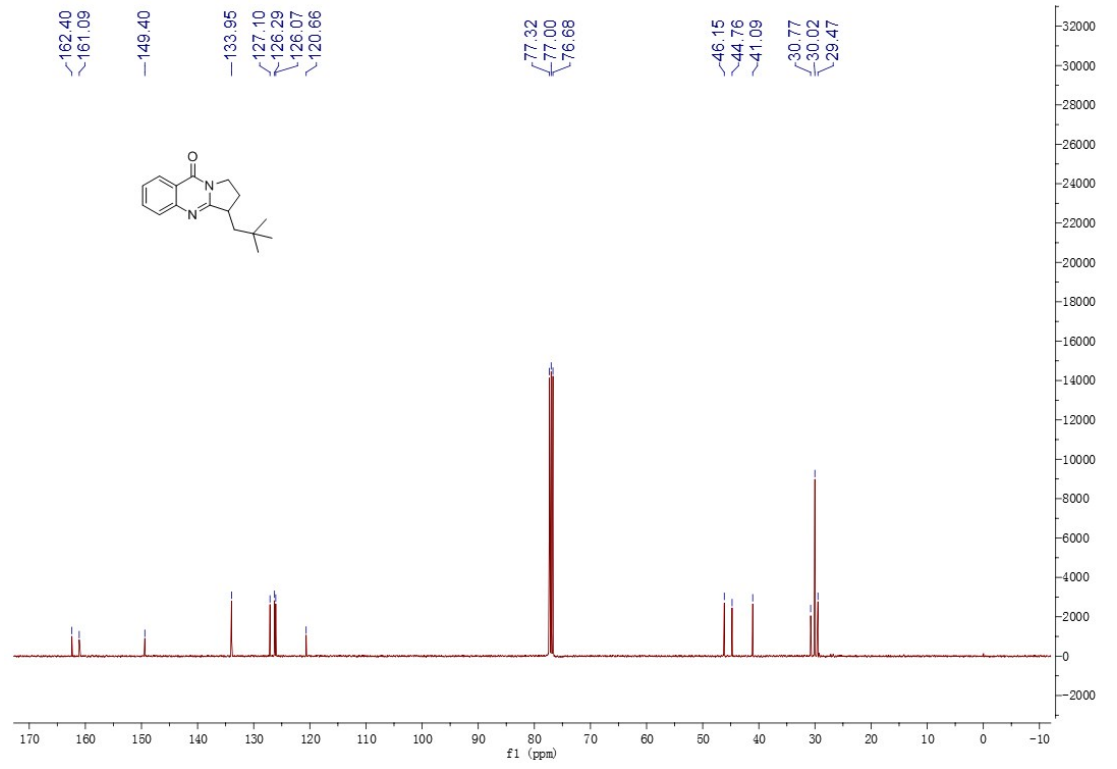
**6-fluoro-4-neopentyl-1-oxo-3,4-dihydroisoquinoline-2(1H)-carbonitrile (5ca)**

White solid (10.5 mg, 40% yield), MP : 100 – 102 °C. $^{1}$H NMR (400 MHz, $CDCl_3$) $\delta$ 8.13 (dd, $J$ = 8.7, 5.7 Hz, 1H), 7.09 (td, $J$ = 8.5, 2.5 Hz, 1H), 6.92 (dd, $J$ = 8.8, 2.4 Hz, 1H), 4.25 – 4.09 (m, 1H), 3.86 (dd, $J$ = 12.3, 3.1 Hz, 1H), 3.10 – 3.06 (m, 1H), 1.85 (dd, $J$ = 14.7, 7.8 Hz, 1H), 1.45 – 1.41 (m, 1H), 1.04 (s, 9H). $^{13}$C NMR (101 MHz, $CDCl_3$) $\delta$ 166.29 (d, $J$ = 258.1 Hz), 162.3, 148.1 (d, $J$ = 8.8 Hz), 132.7 (d, $J$ = 10.1 Hz), 121.4, 115.4 (d, $J$ = 22.2 Hz), 114.0 (d, $J$ = 22.4 Hz), 109.5, 53.3, 46.5, 34.4, 31.3, 29.6. $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ -101.4. IR ($cm^{-1}$) : $\nu$ 3358, 2954, 2919, 2850, 2240, 1690, 1612, 1388, 1249, 1144, 1100, 960, 874, 688, 621. HRMS (ESI) : calcd for $C_{15}H_{18}FN_2O$ $[M+H]^+$ 261.1403, found: 261.1399.

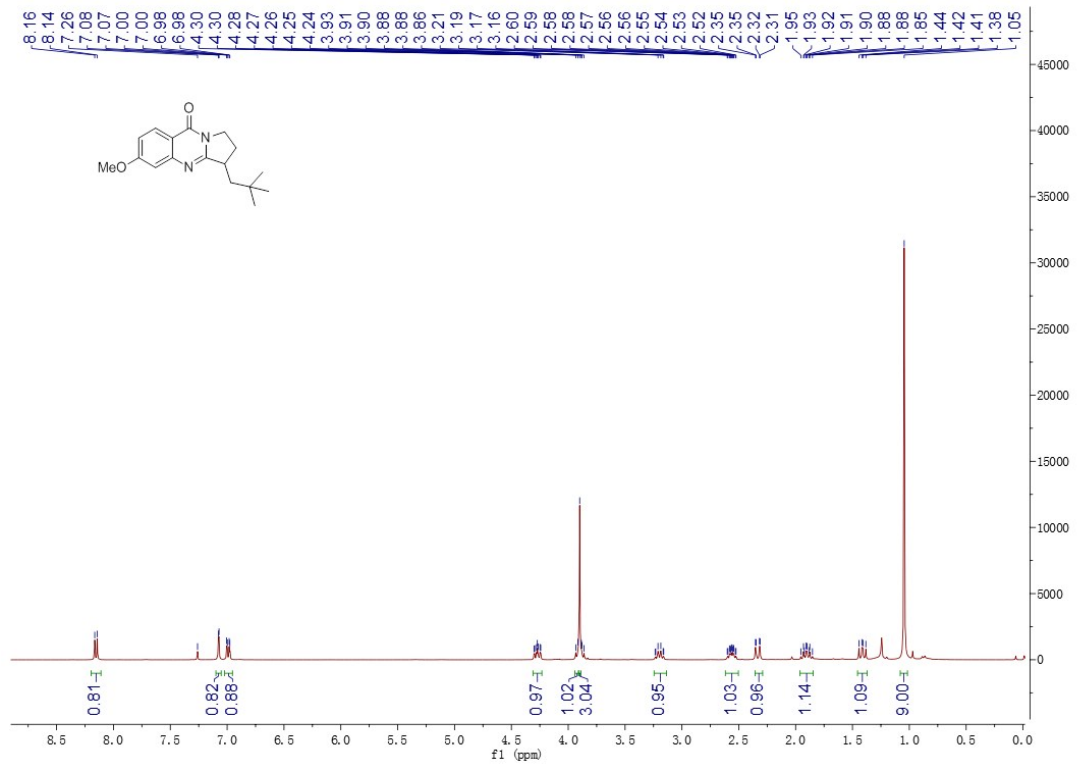
## 8. $^{1}H$ and $^{13}C$ Spectra of Compound 3 and 5

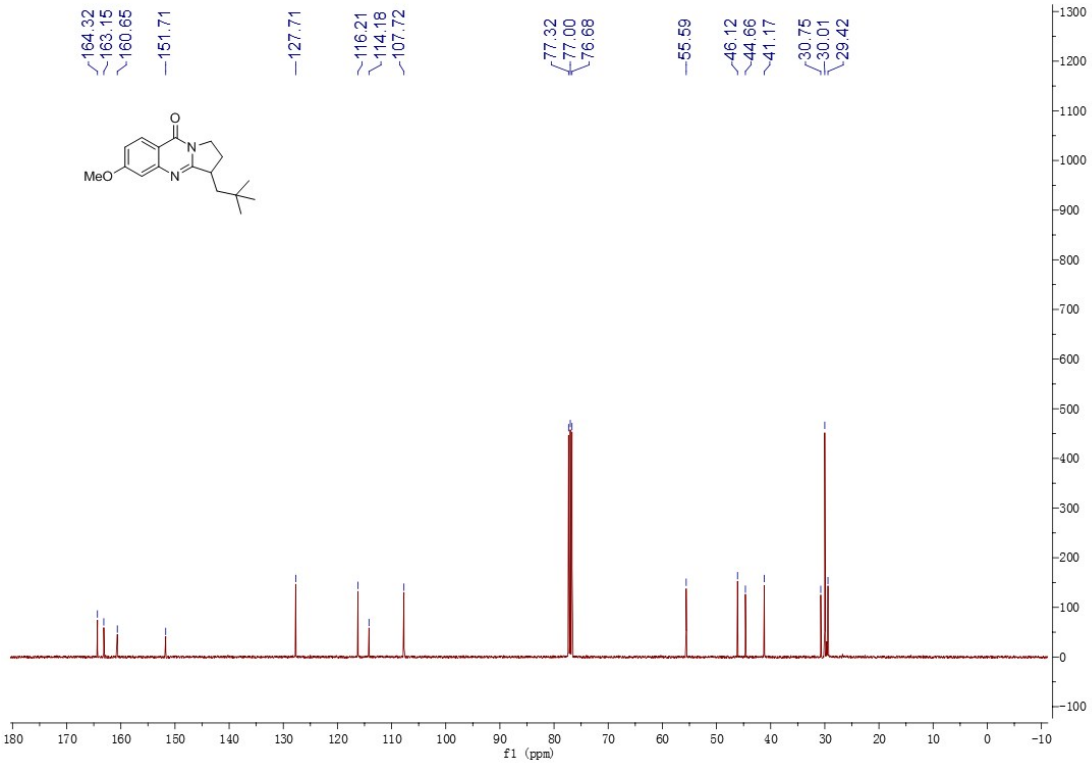
$^{1}$HNMR and $^{13}$CNMR spectra of **3aa**



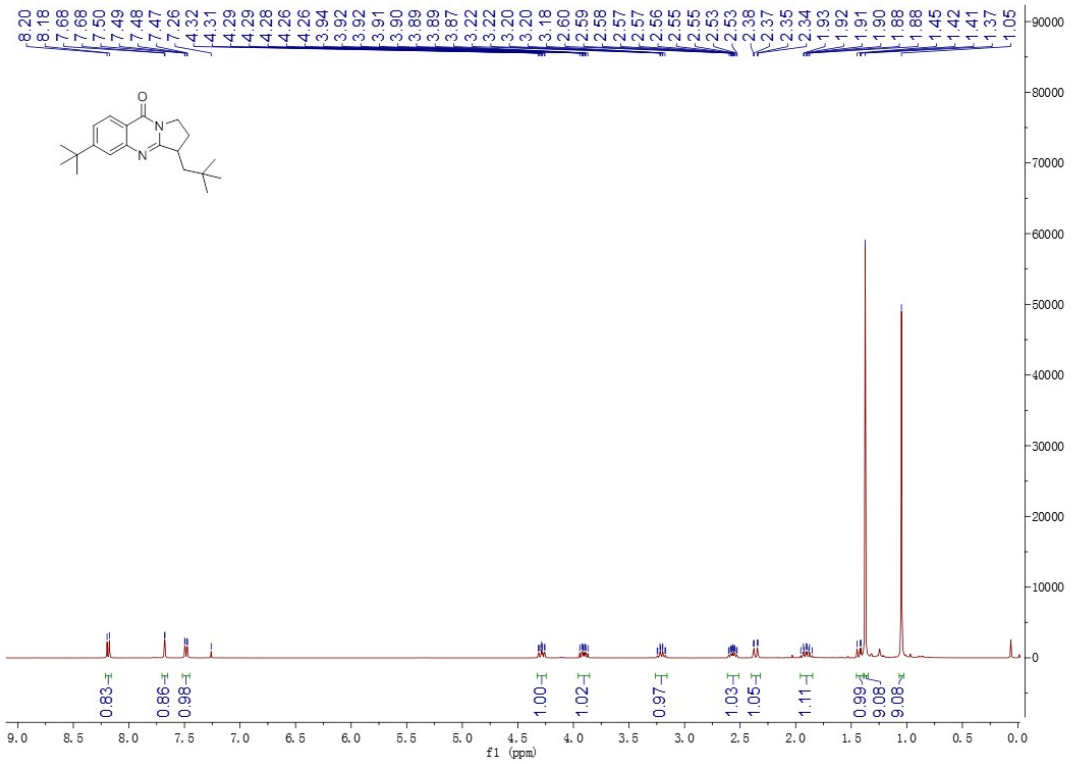



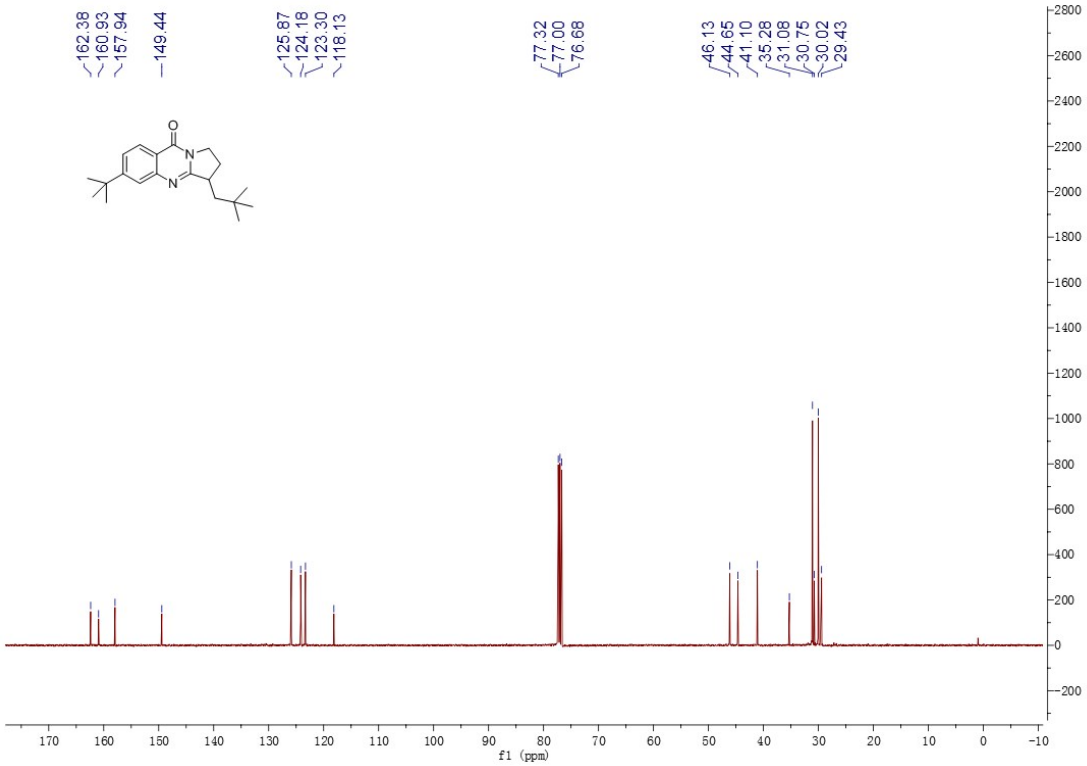
$^{1}$HNMR and $^{13}$CNMR spectra of **3ba**



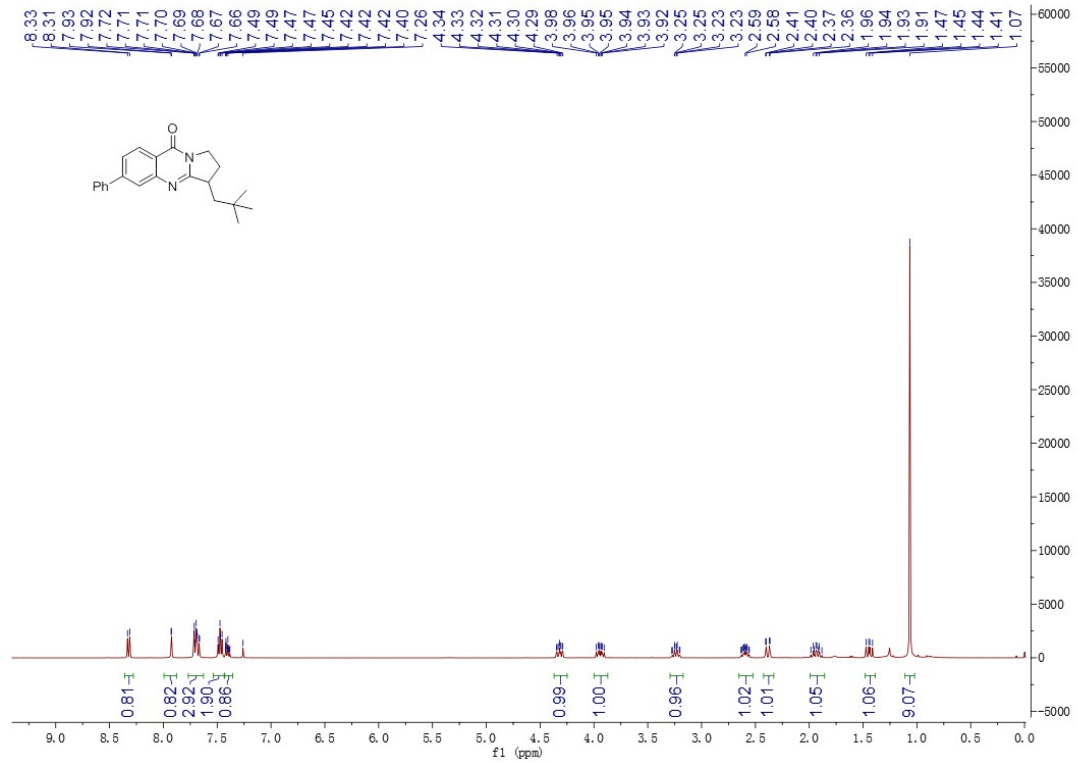



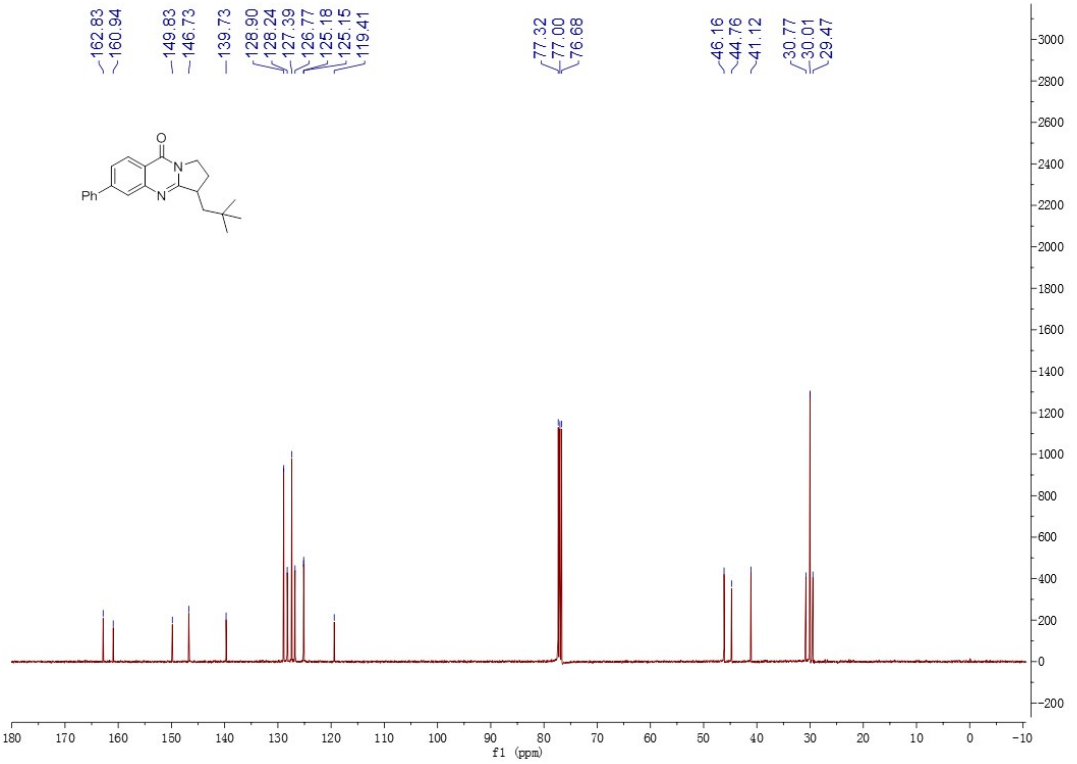
$^{1}$HNMR and $^{13}$CNMR spectra of **3ca**



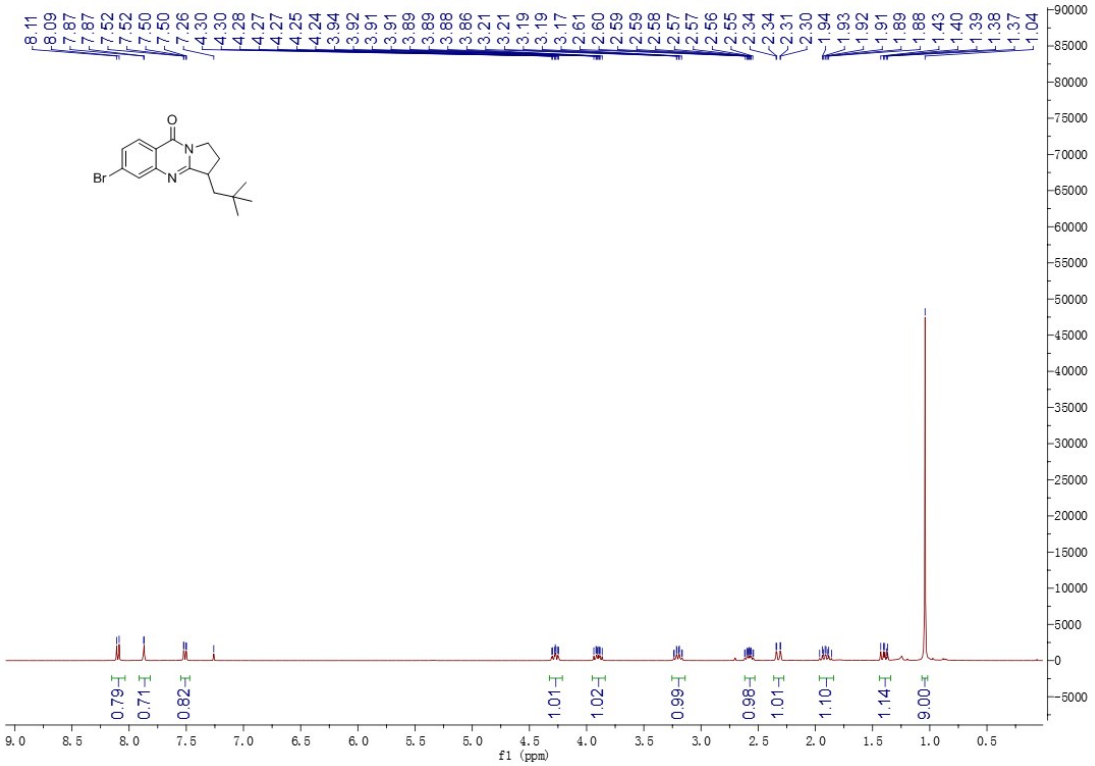



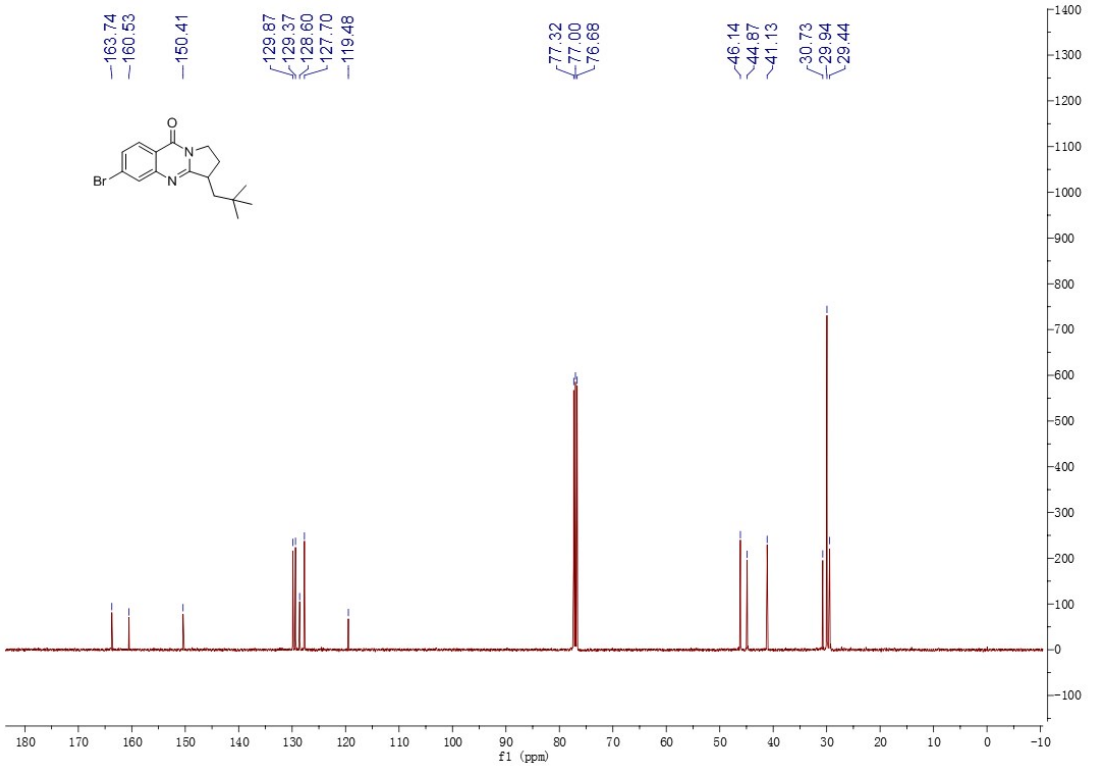
[1]HNMR and [13]CNMR spectra of **3da**



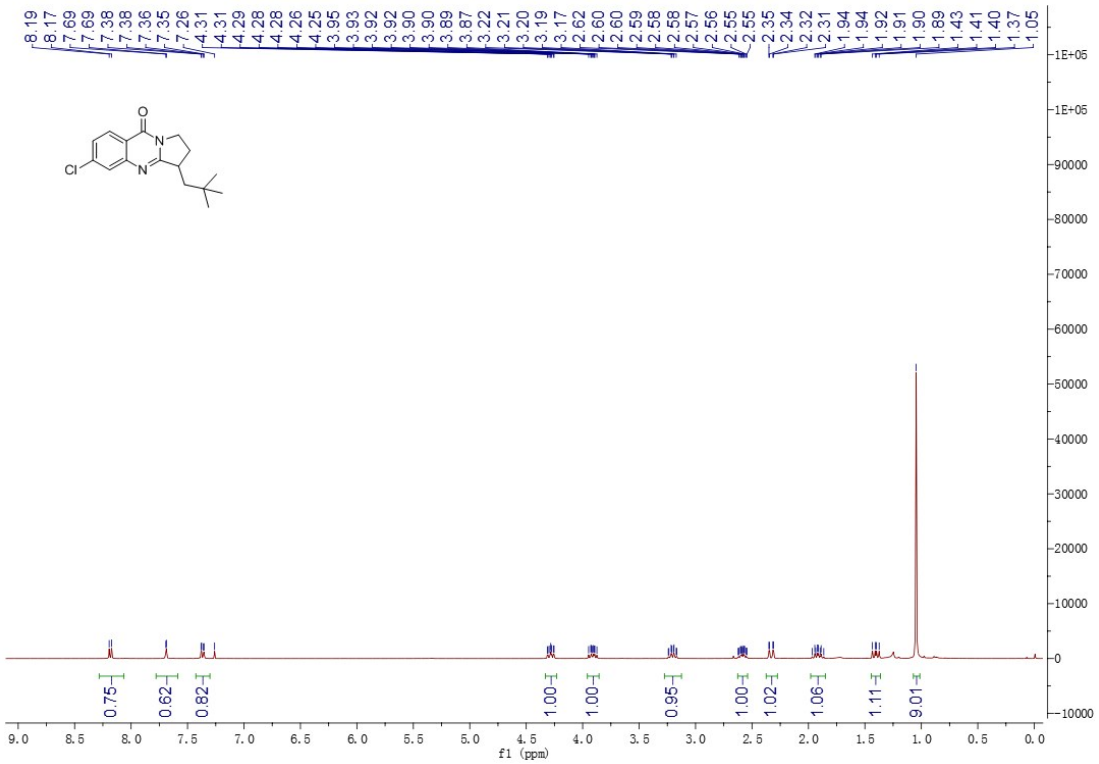



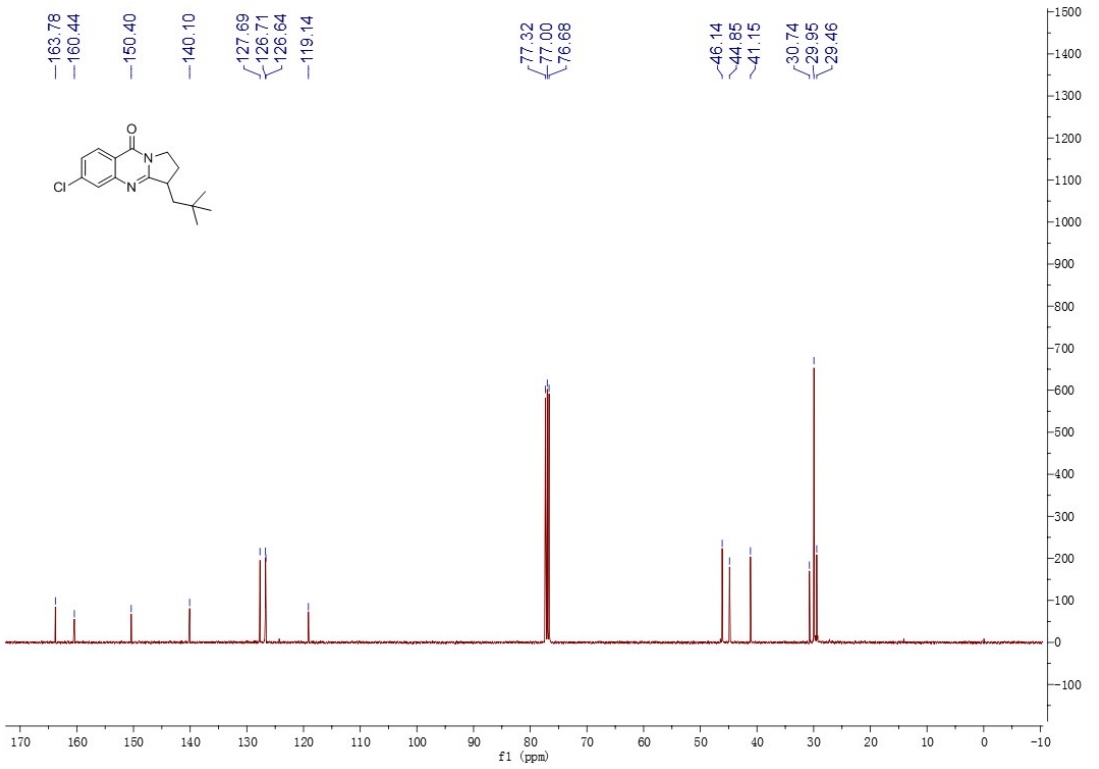
$^{1}$HNMR and $^{13}$CNMR spectra of **3ea**



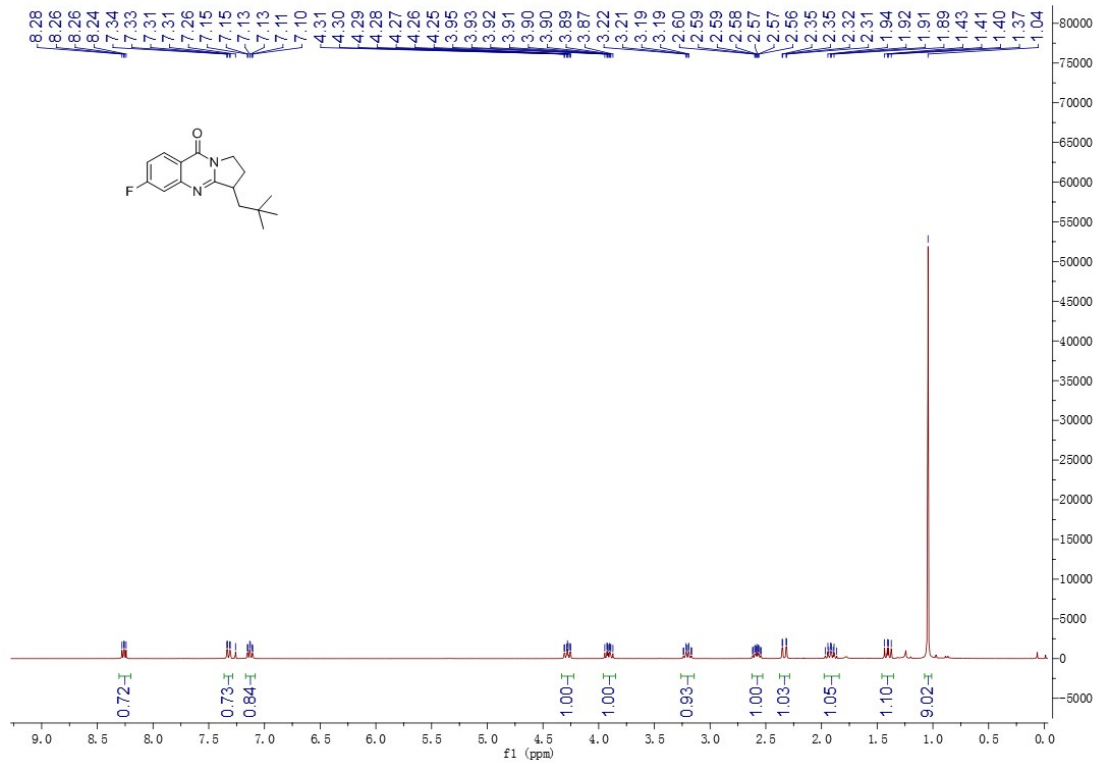



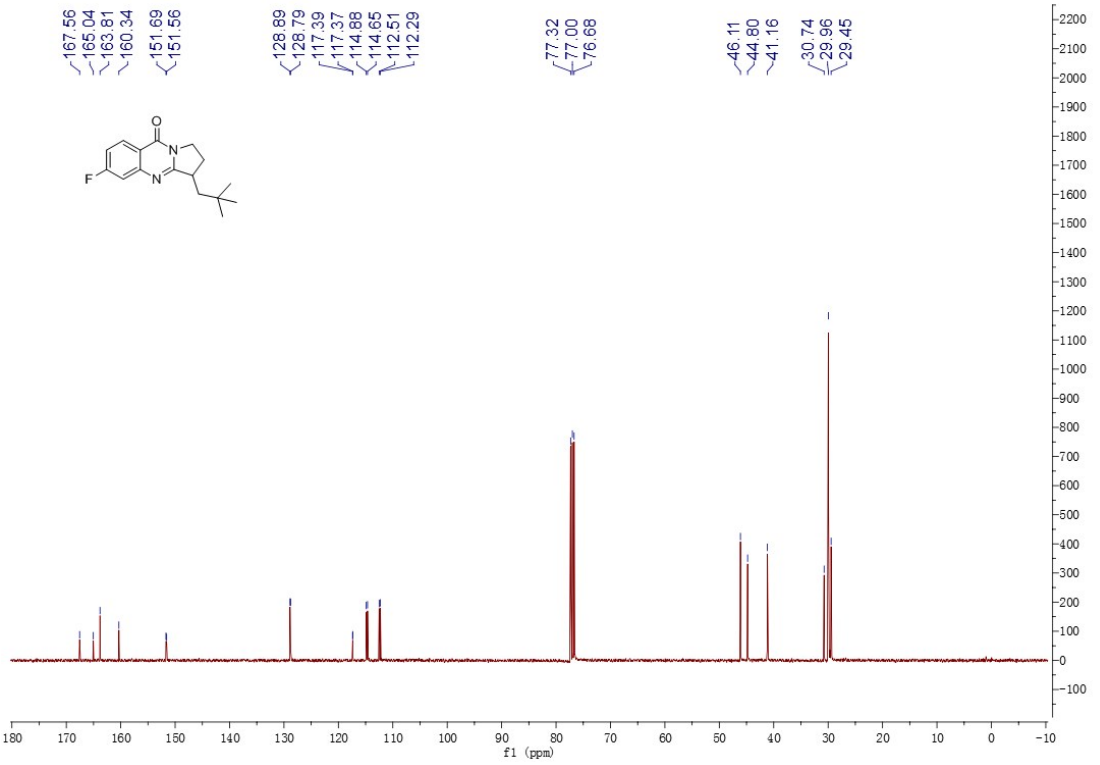
[1]HNMR and [13]CNMR spectra of **3fa**



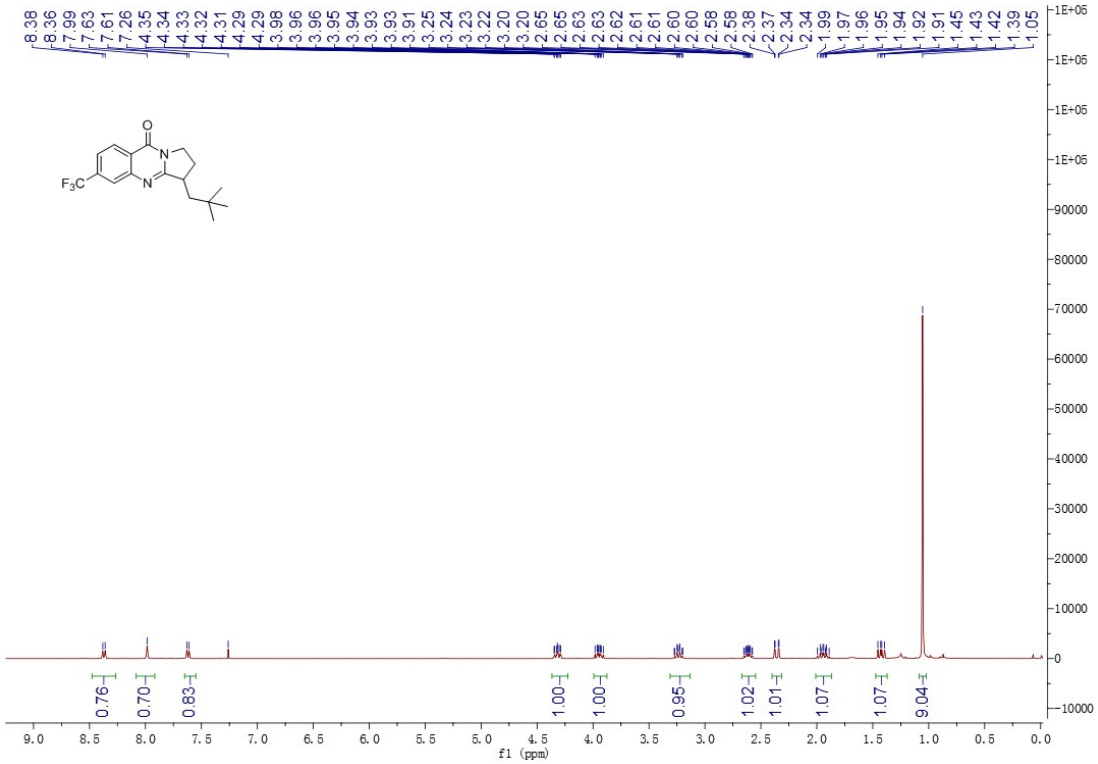



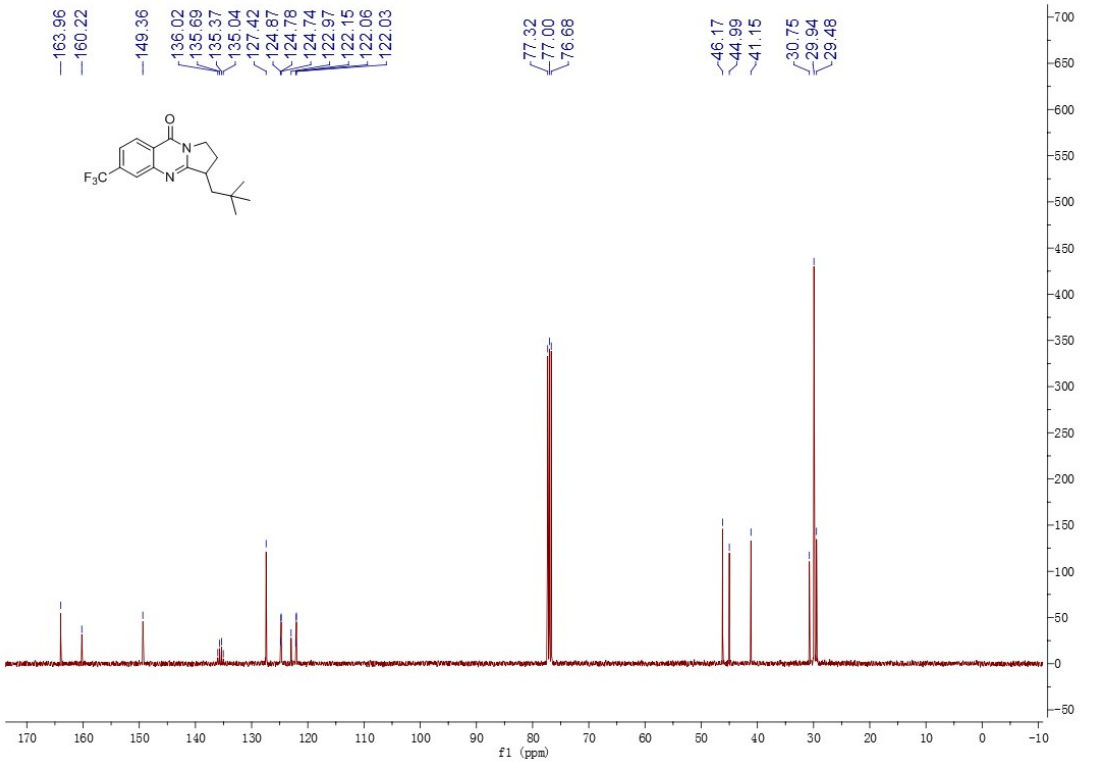
$^{1}$HNMR and $^{13}$CNMR spectra of **3ga**



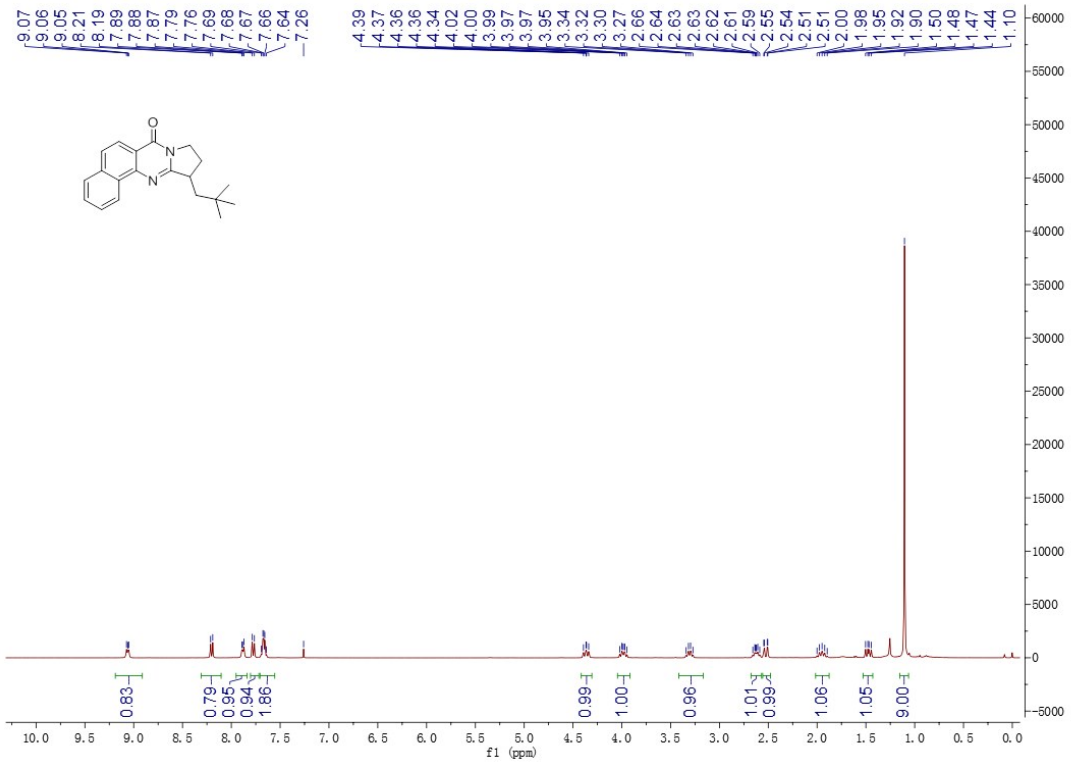



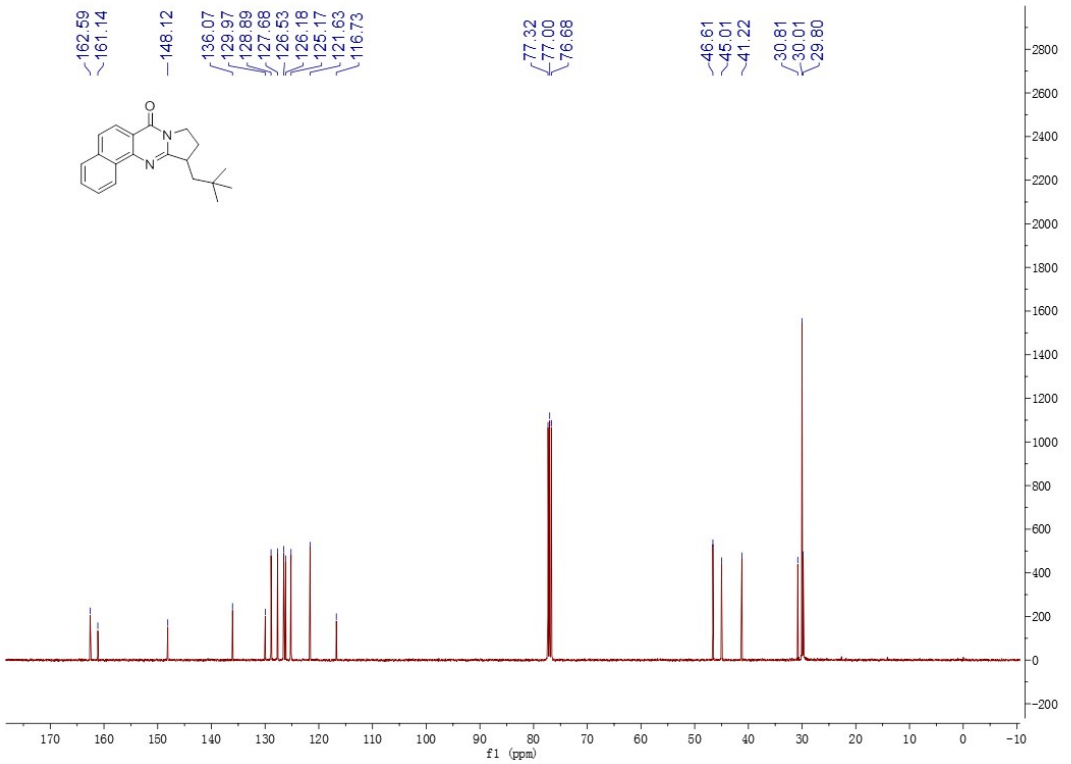
[1]HNMR and [13]CNMR spectra of **3ha**



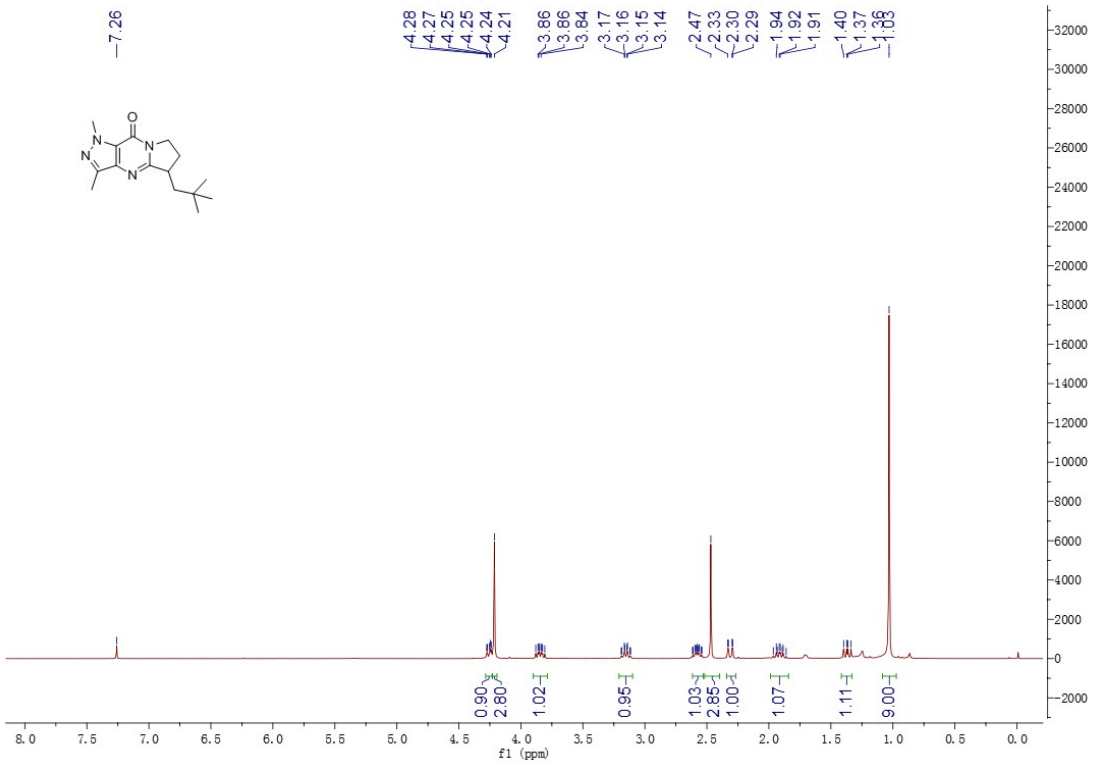



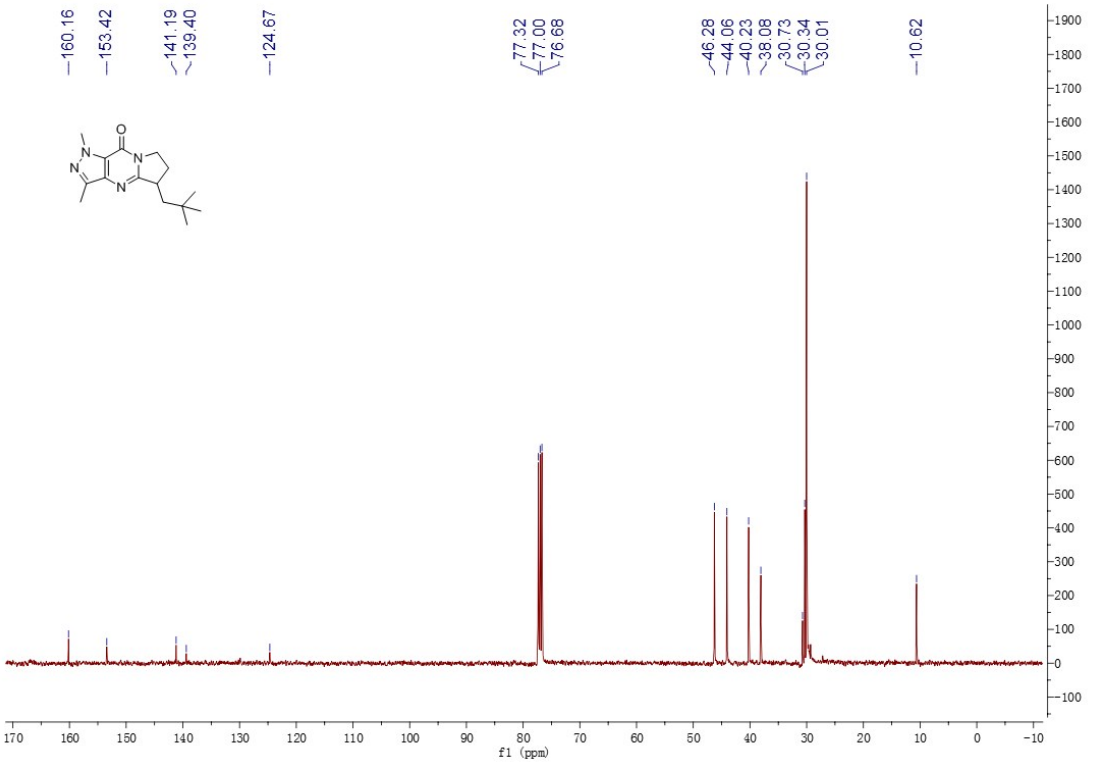
$^{1}$HNMR and $^{13}$CNMR spectra of **3ja**



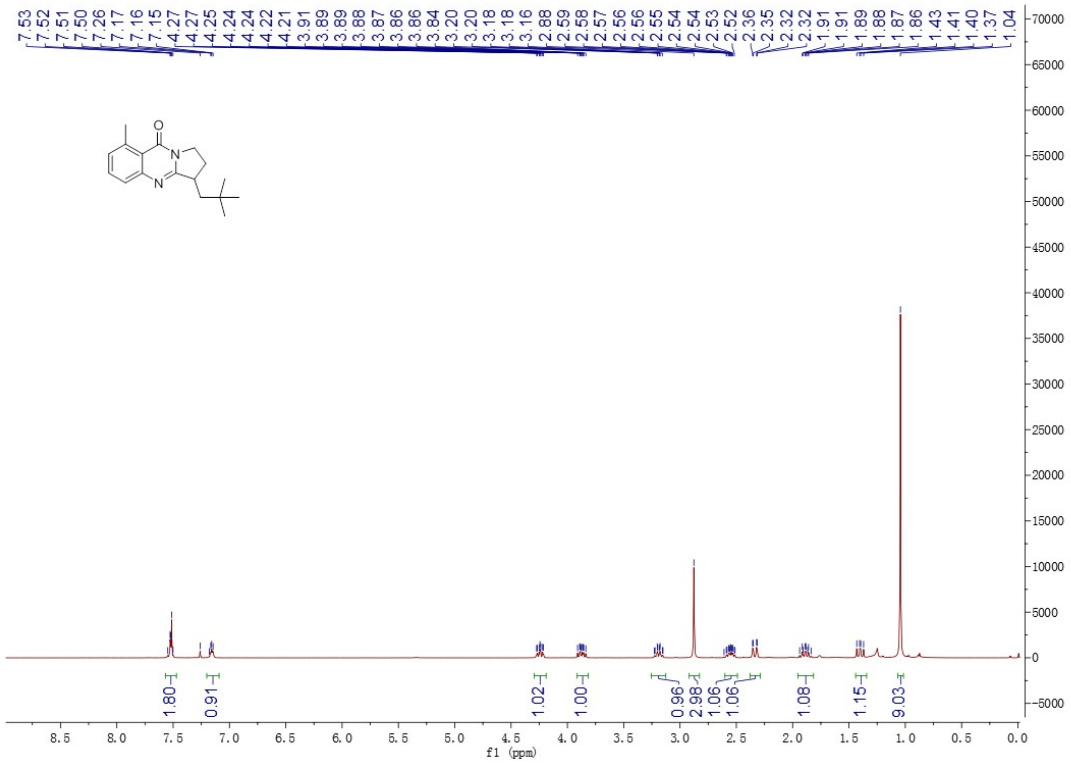



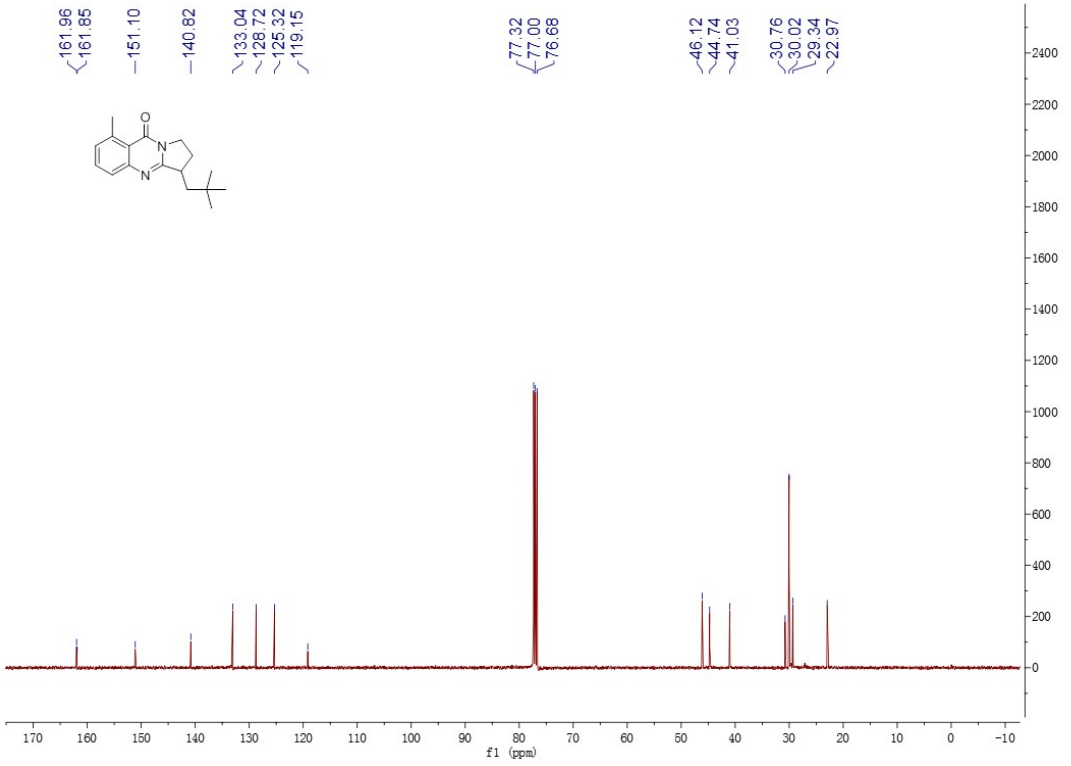
$^{1}$HNMR and $^{13}$CNMR spectra of **3ka**



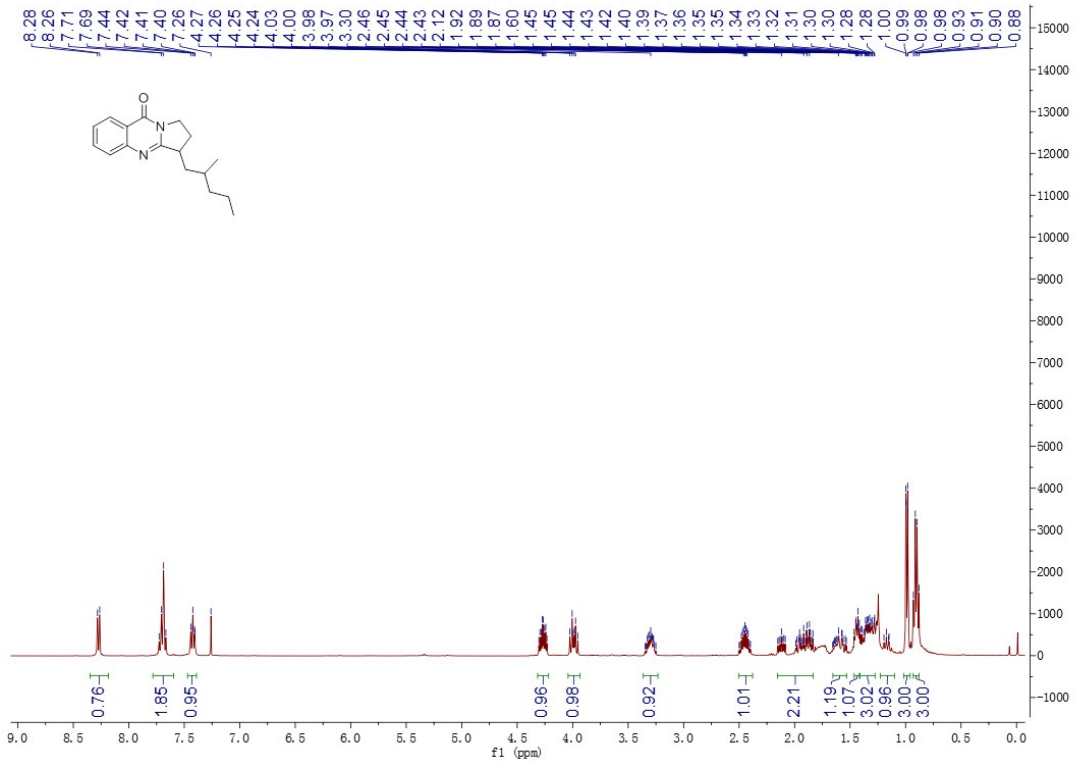



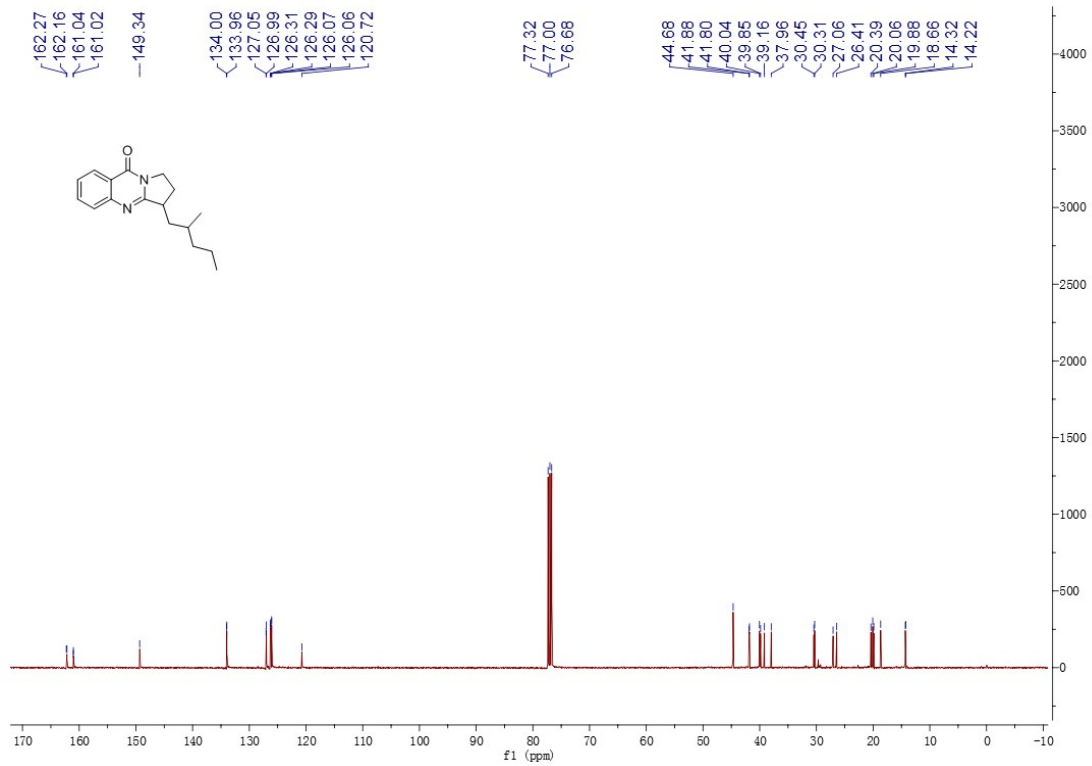
$^{1}$HNMR and $^{13}$CNMR spectra of **3la**



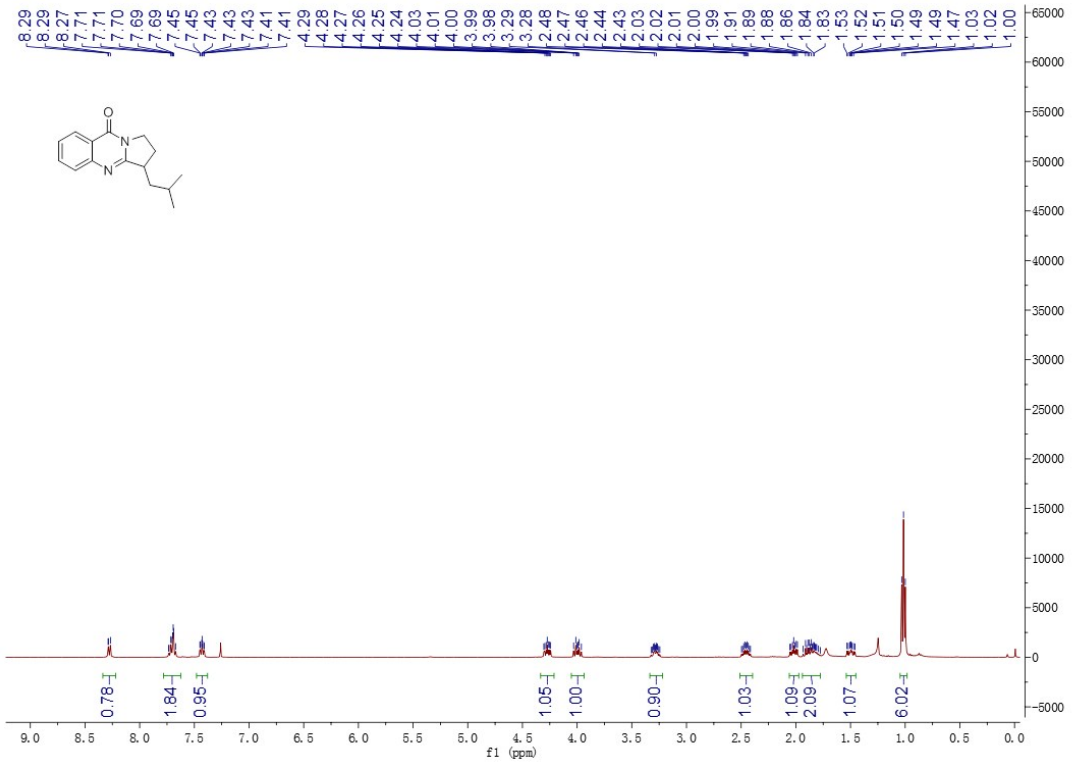



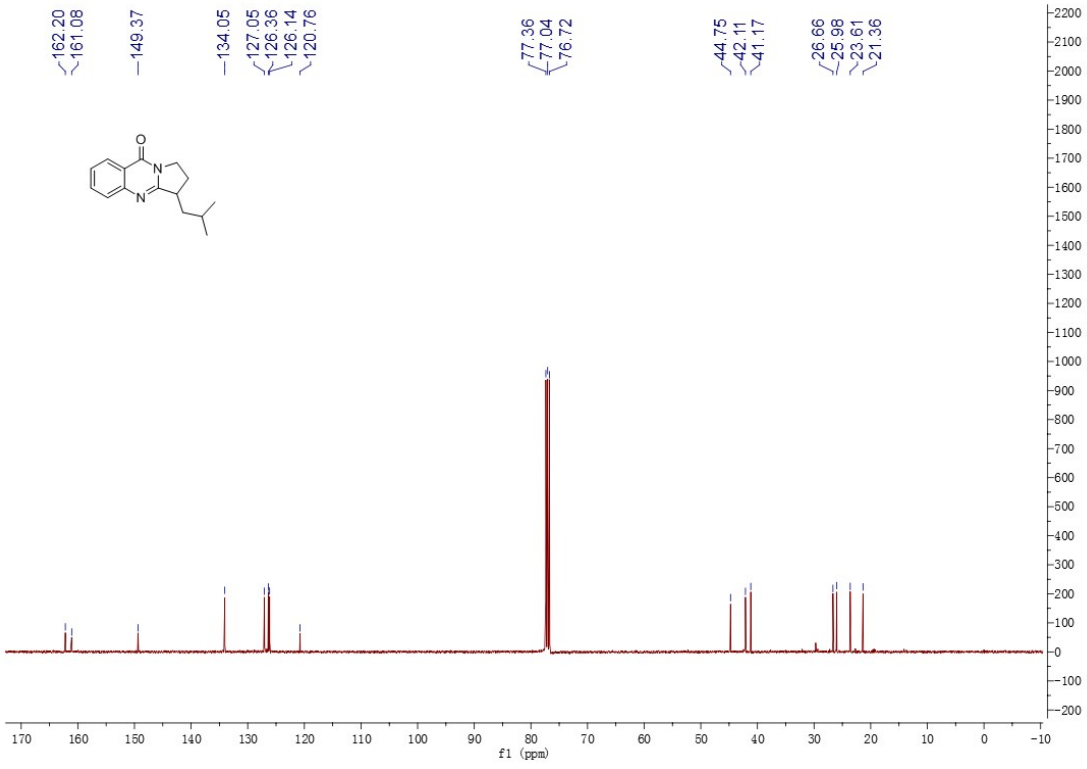
[1]HNMR and [13]CNMR spectra of **3ab**



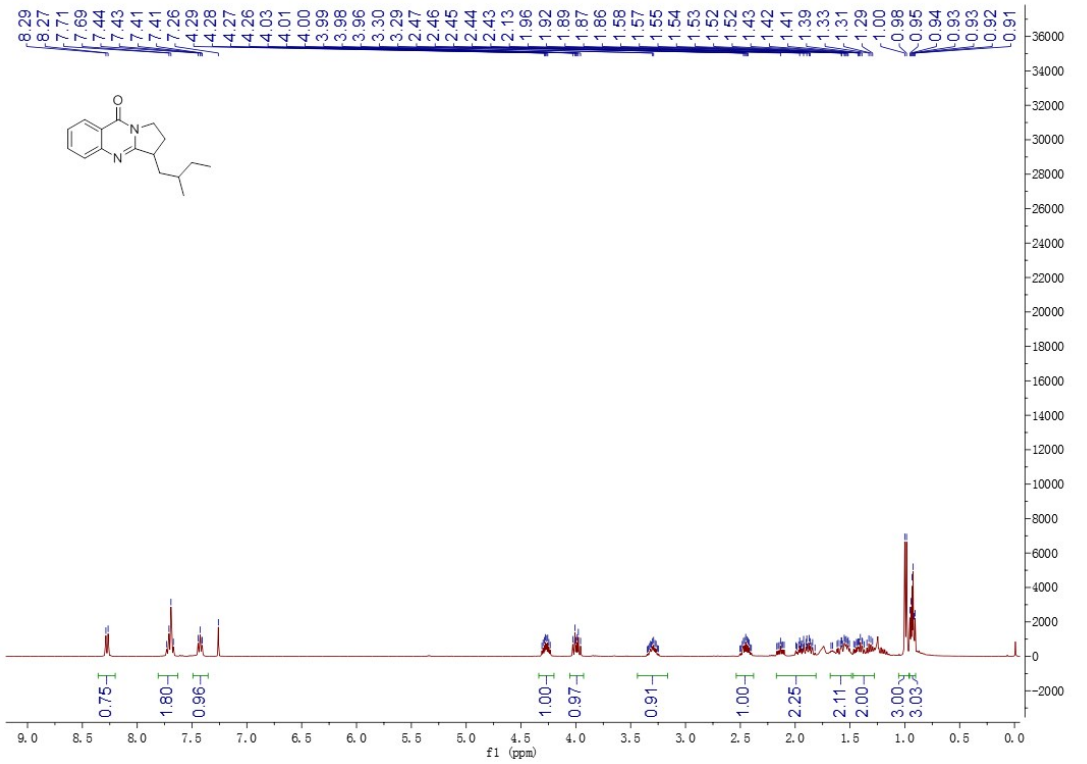



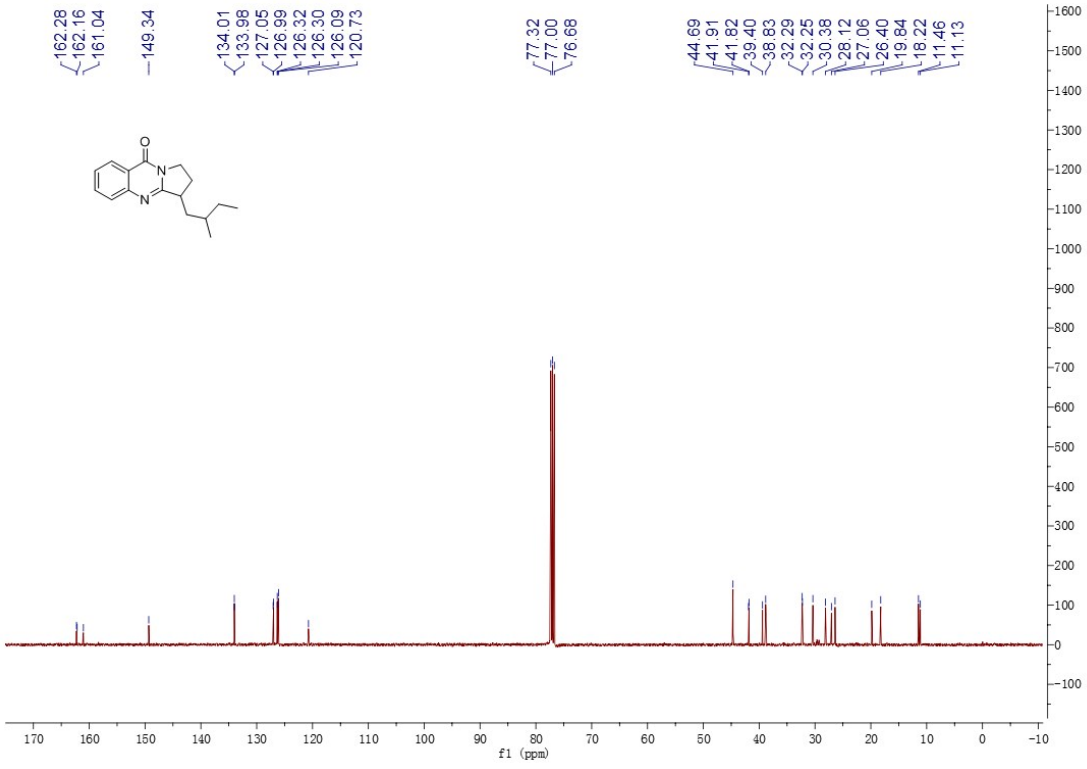
[1]HNMR and [13]CNMR spectra of **3ac**



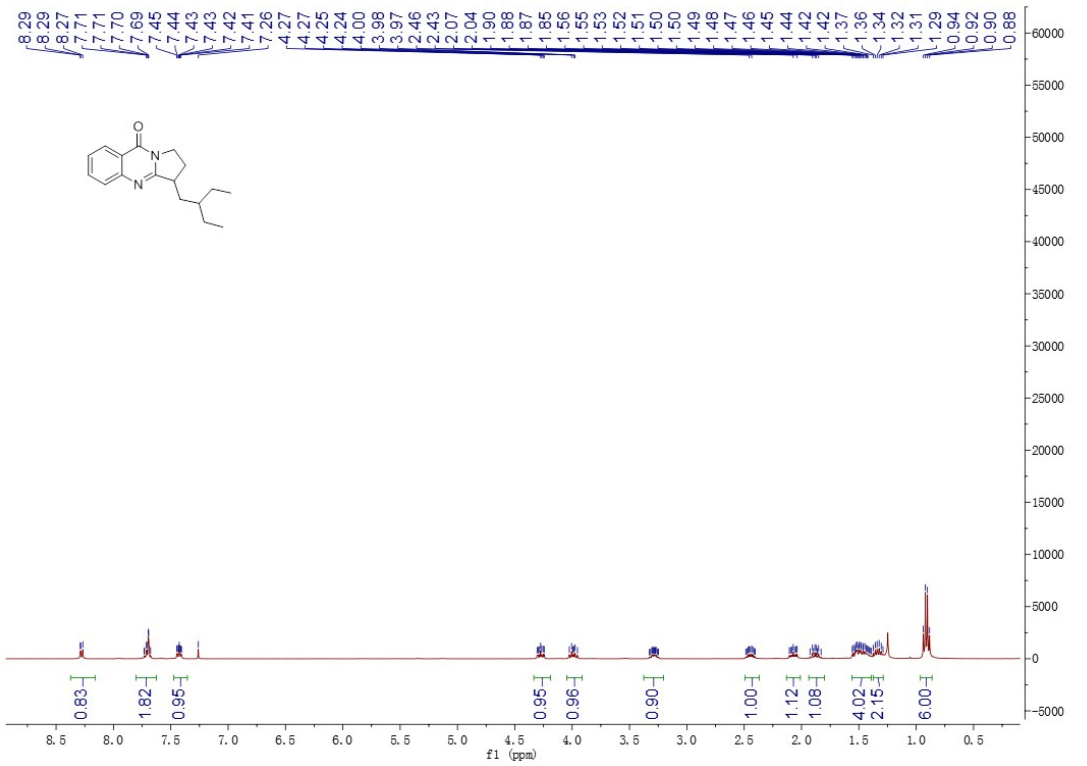



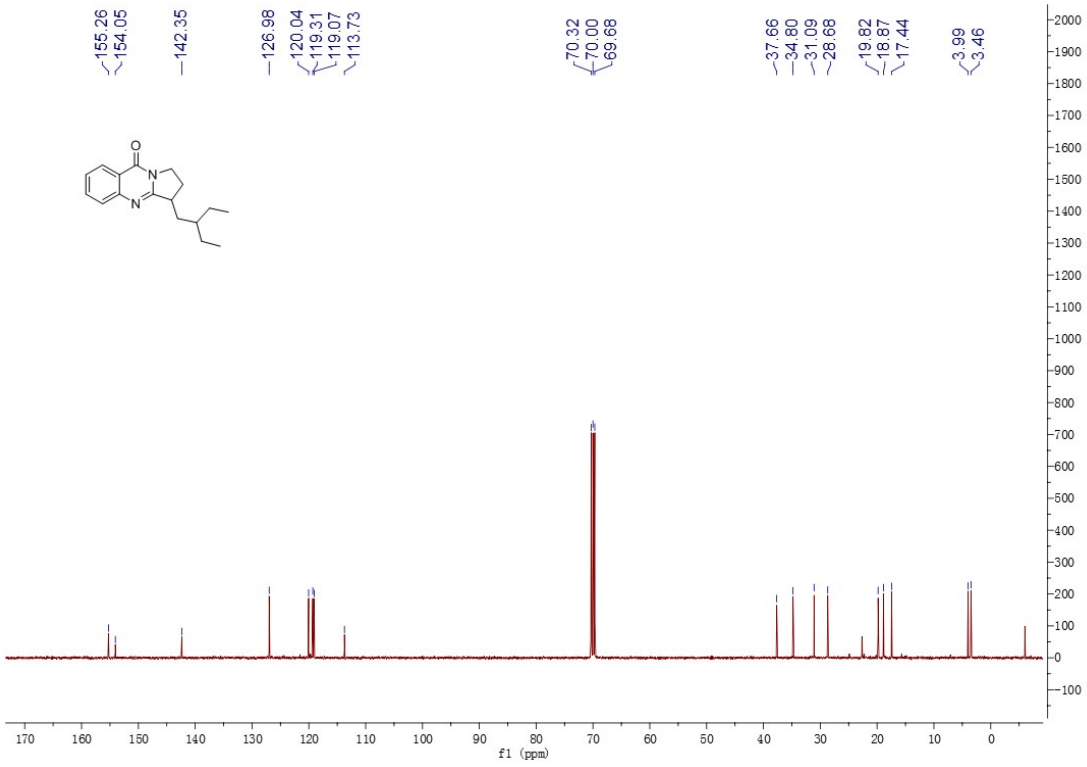
[1]HNMR and [13]CNMR spectra of **3ad**



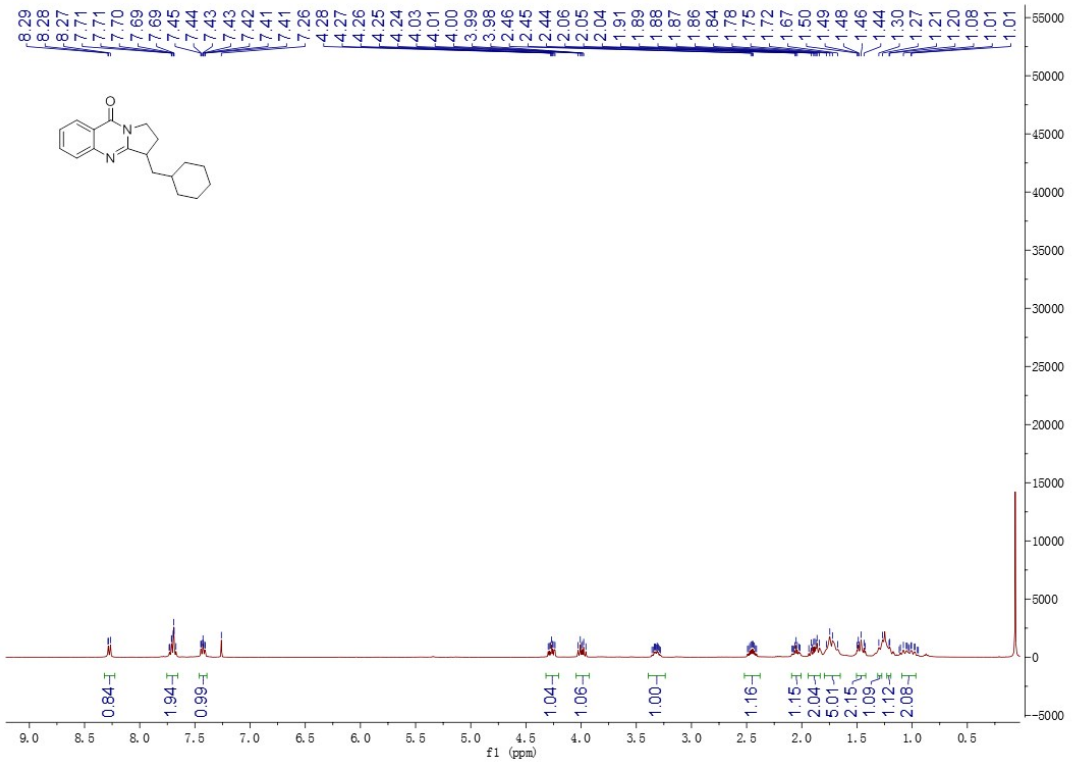



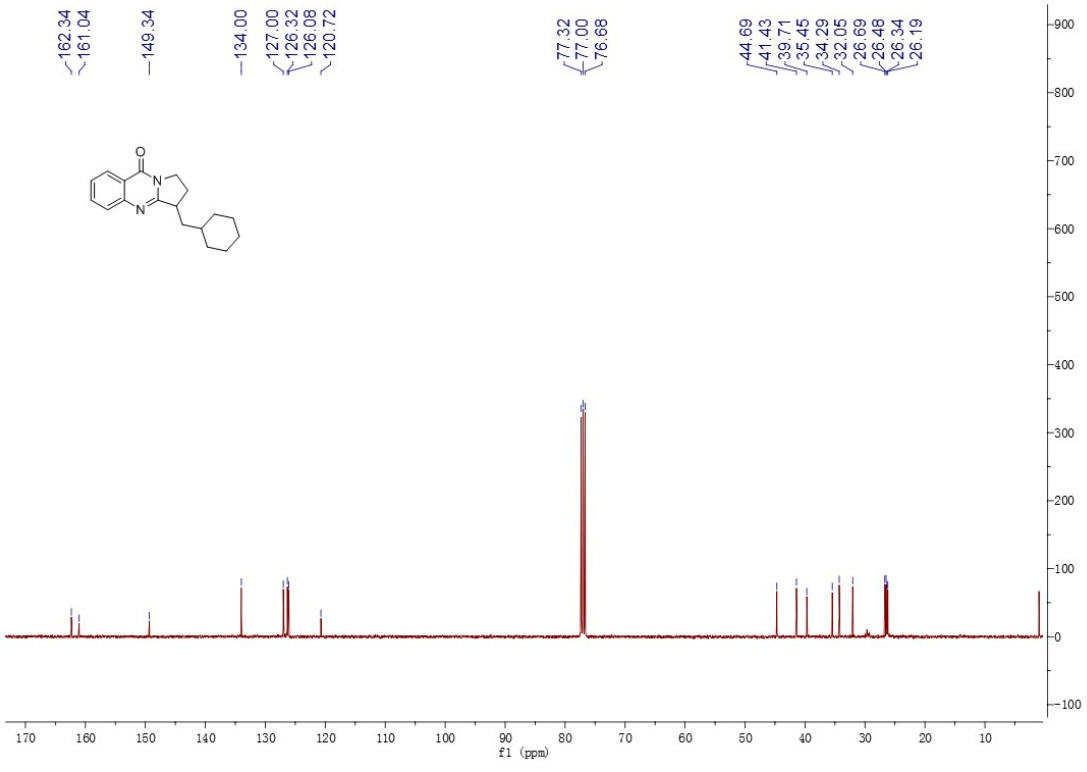
$^{1}$HNMR and $^{13}$CNMR spectra of **3ae**



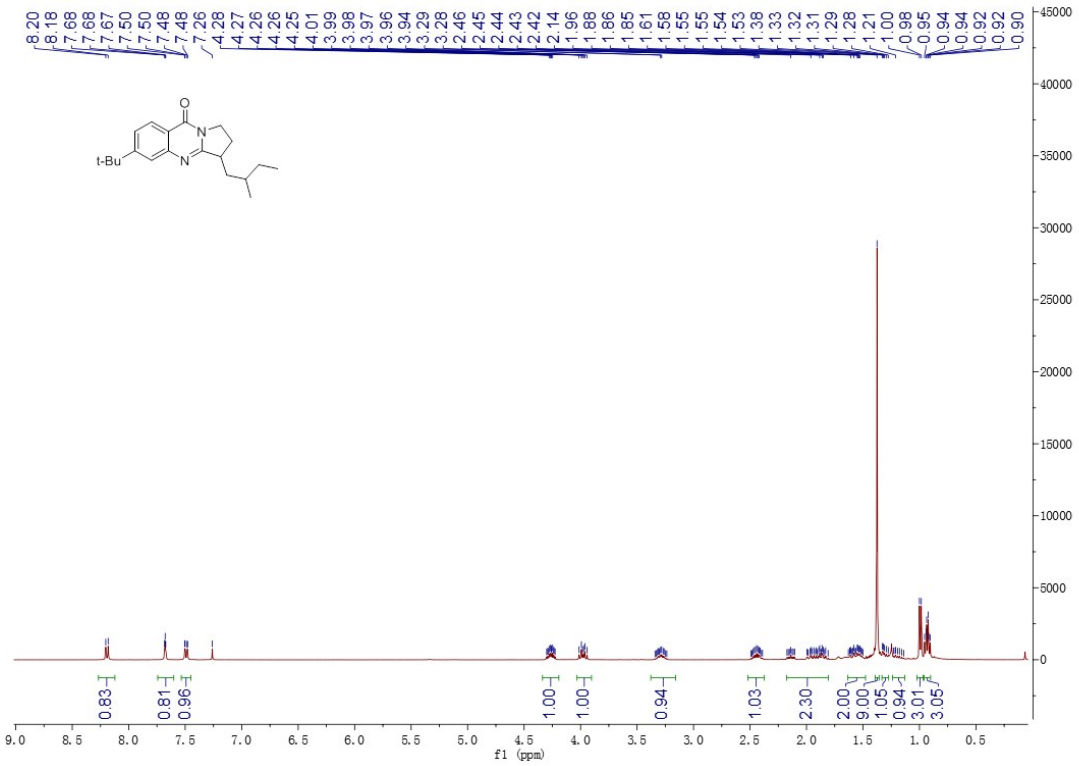



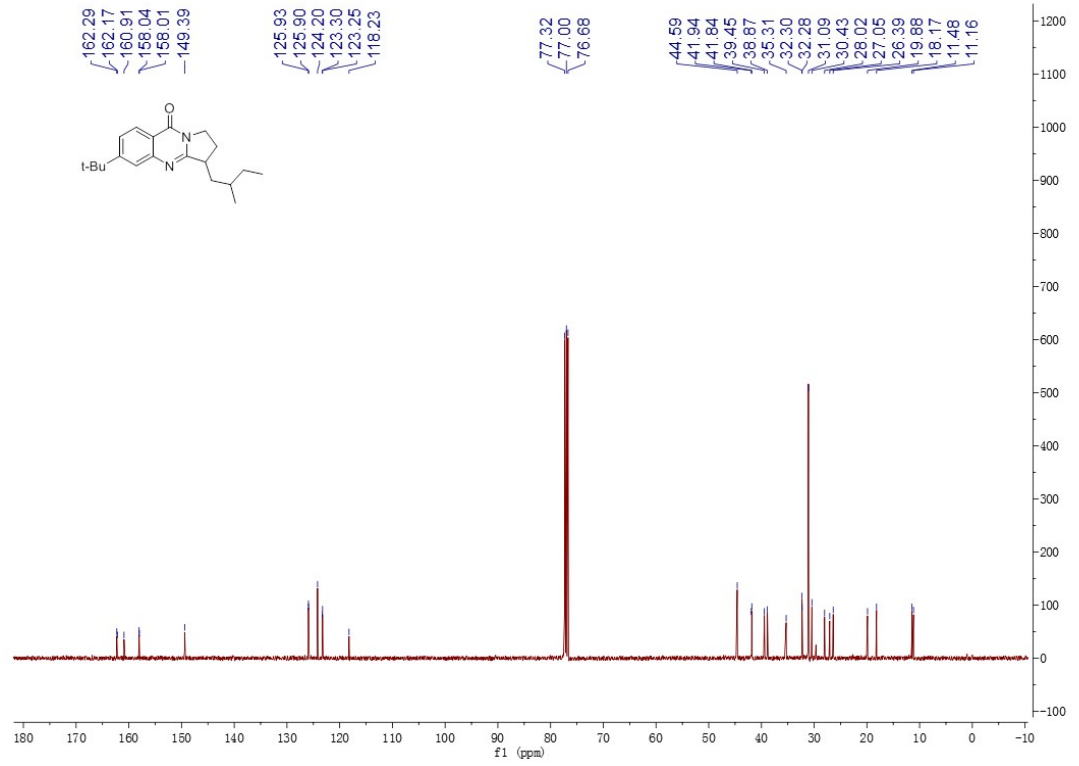
[1]HNMR and [13]CNMR spectra of **3af**



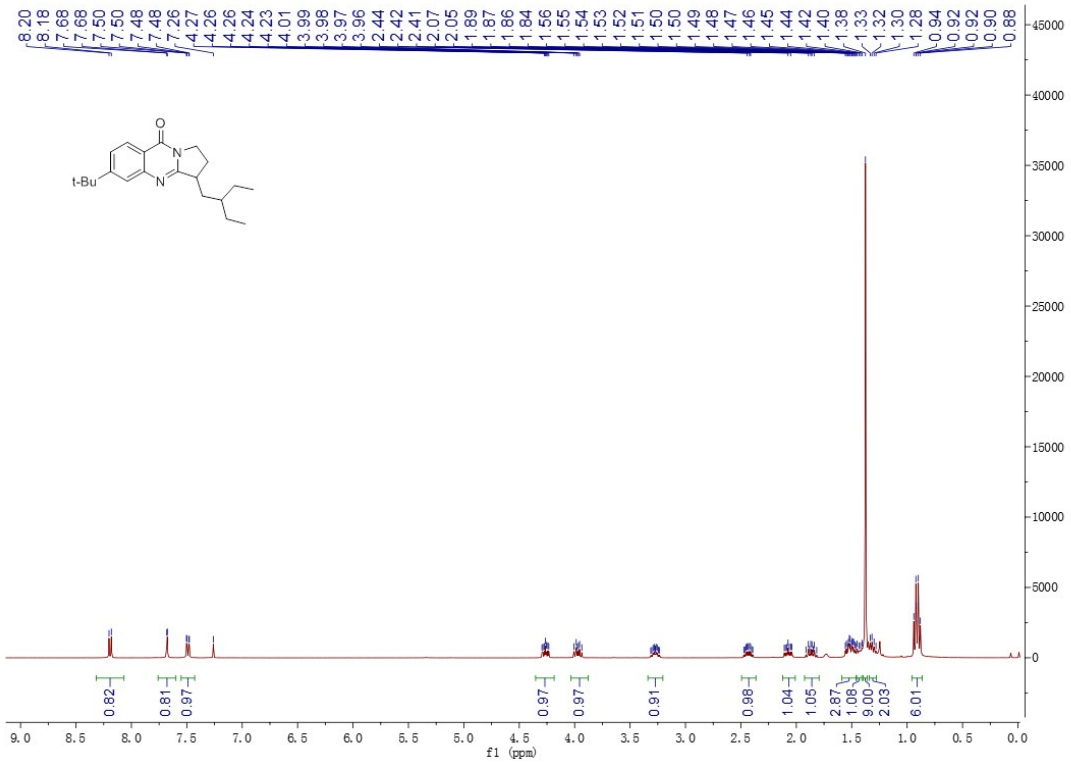



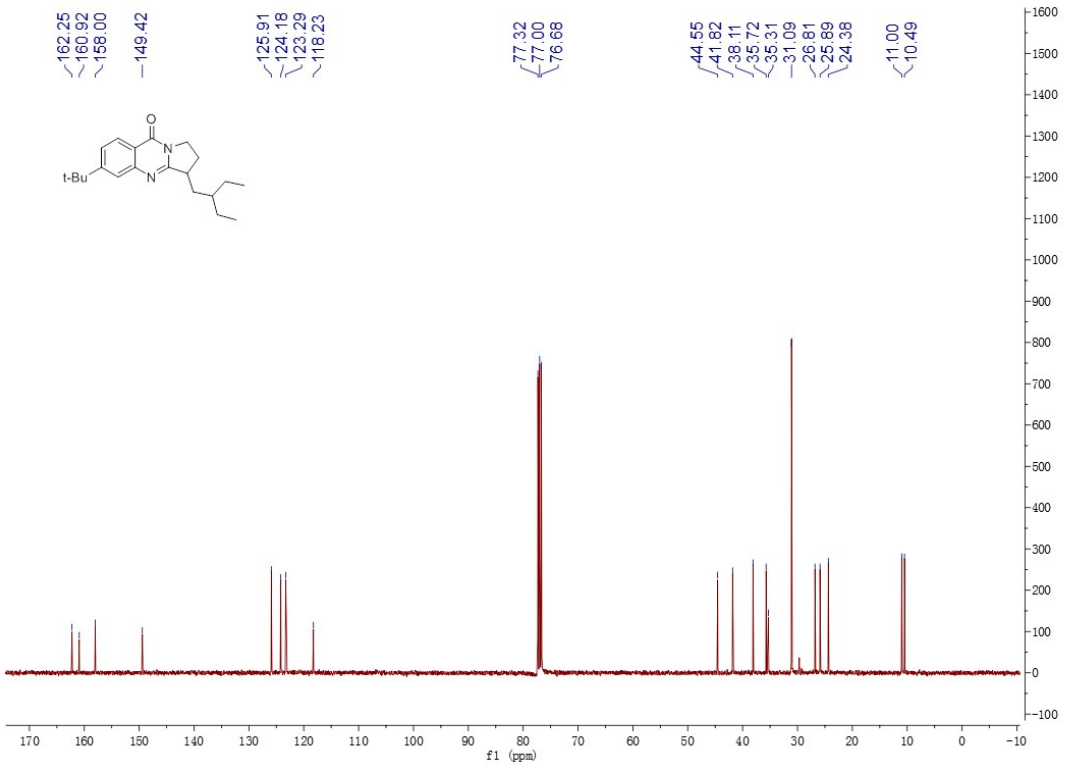
$^{1}$HNMR and $^{13}$CNMR spectra of **3ag**



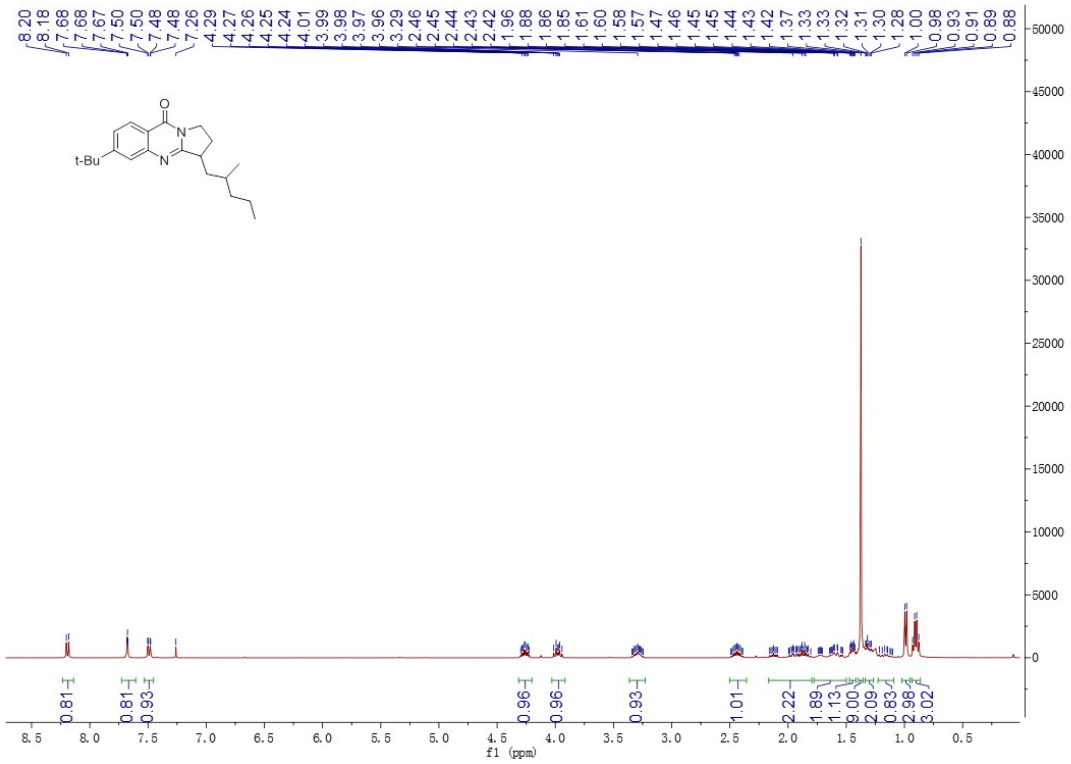



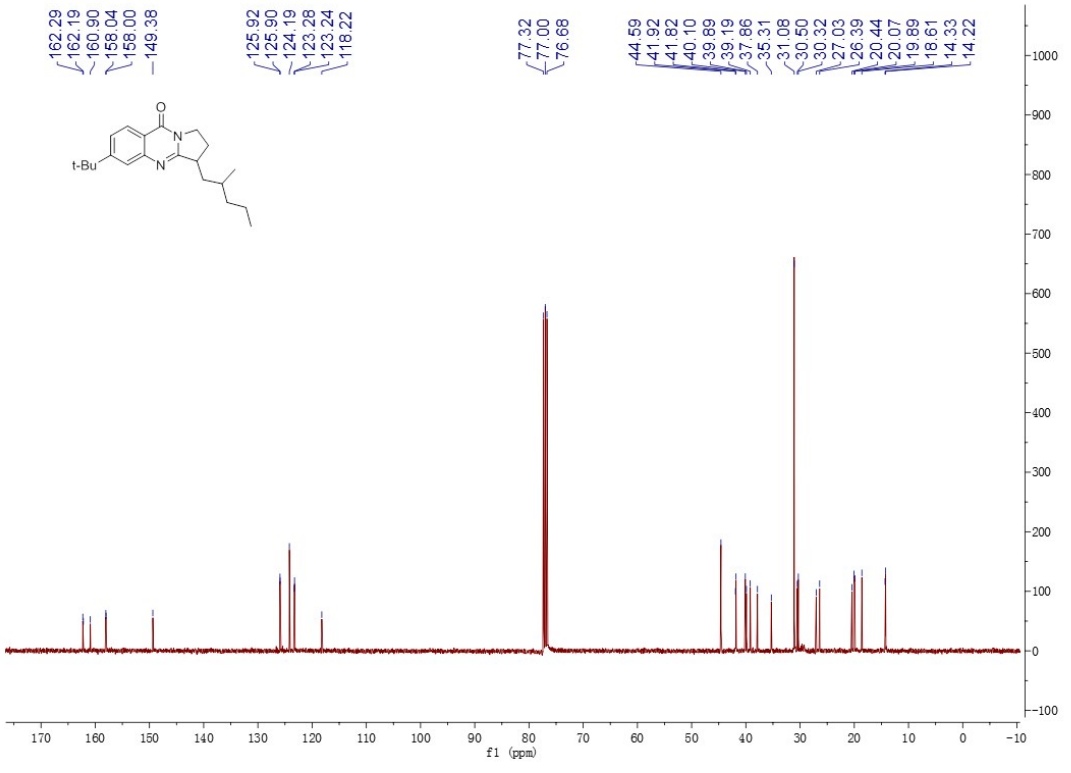
$^{1}$HNMR and $^{13}$CNMR spectra of **3ah**



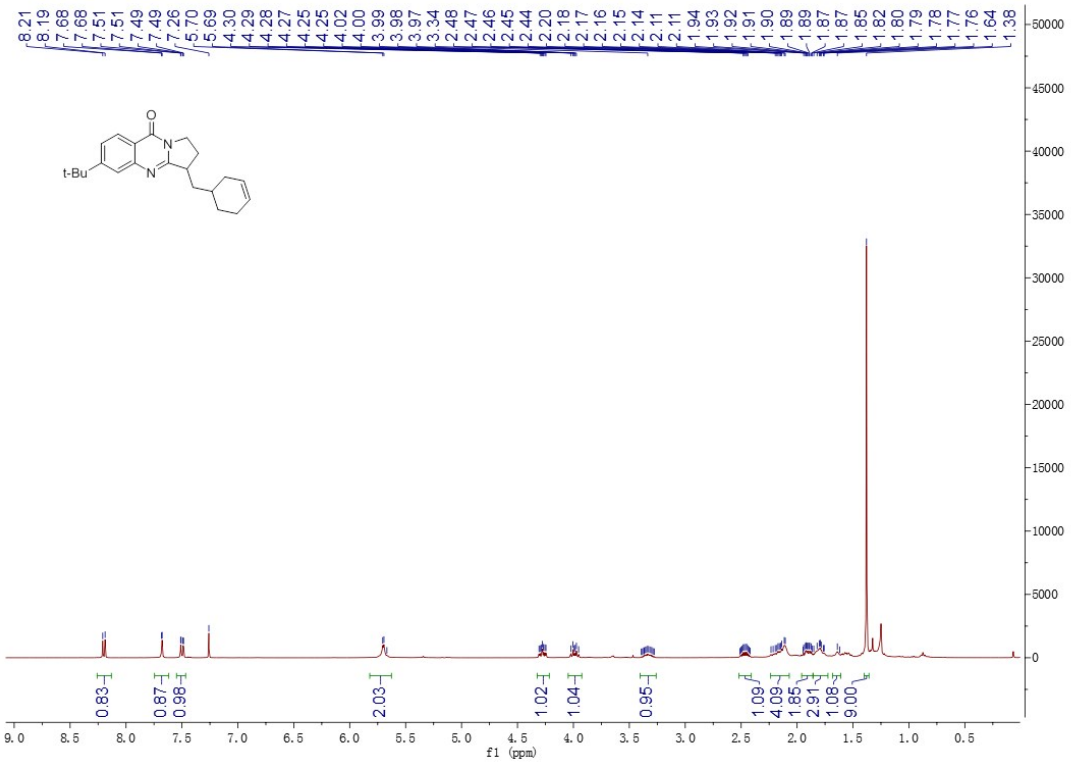



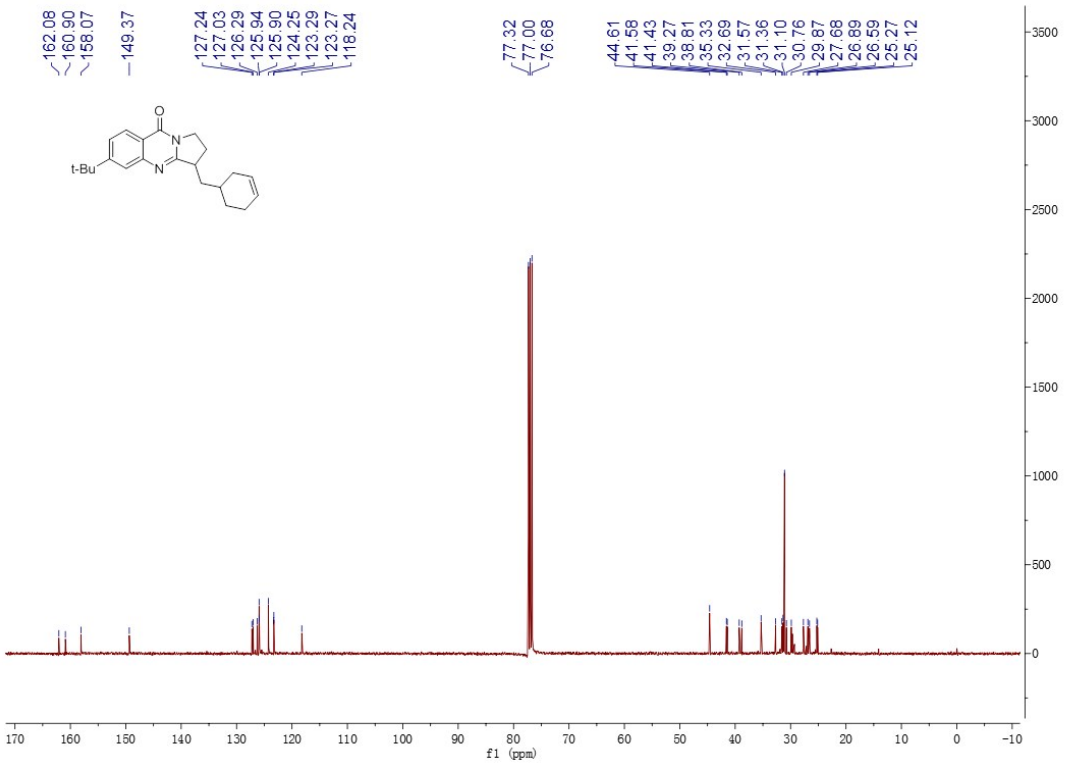
$^{1}$HNMR and $^{13}$CNMR spectra of **3ai**



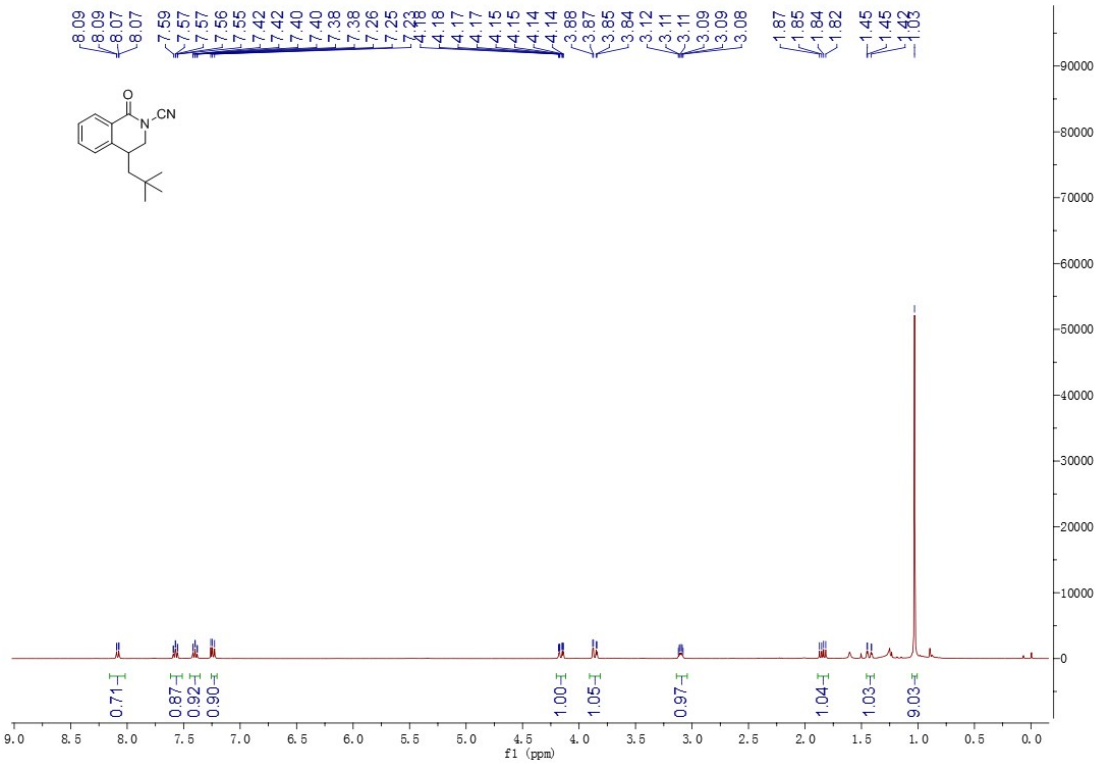



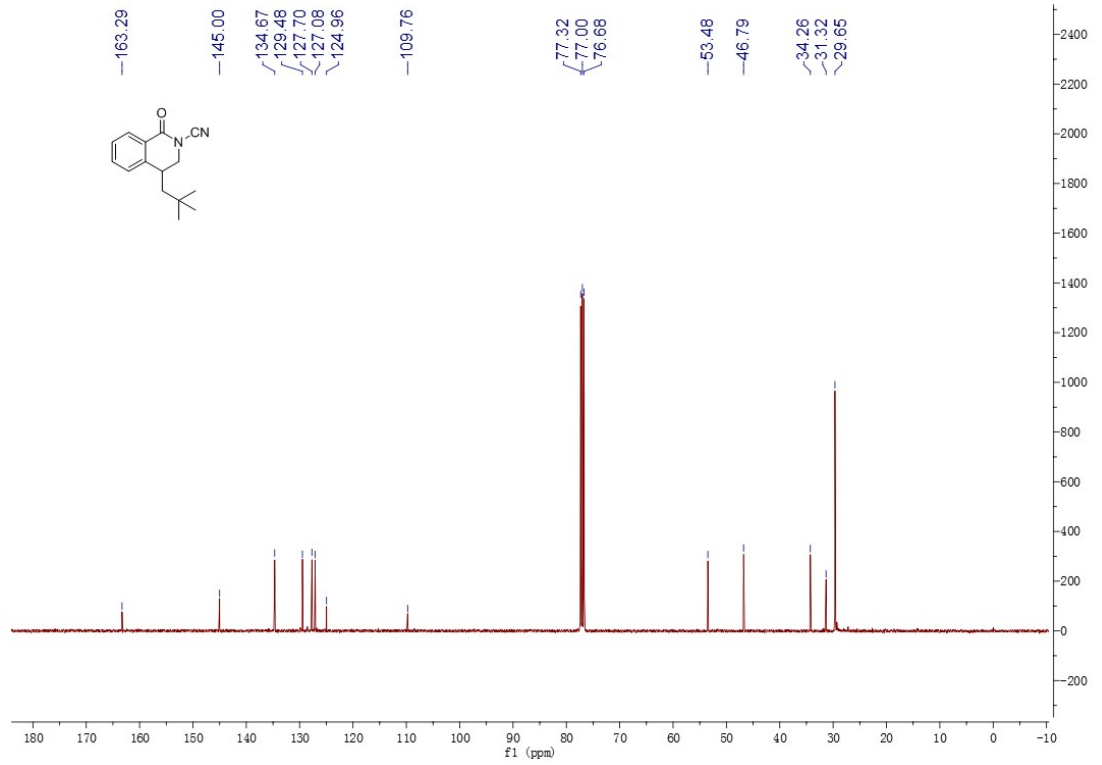
[1]HNMR and [13]CNMR spectra of **3aj**



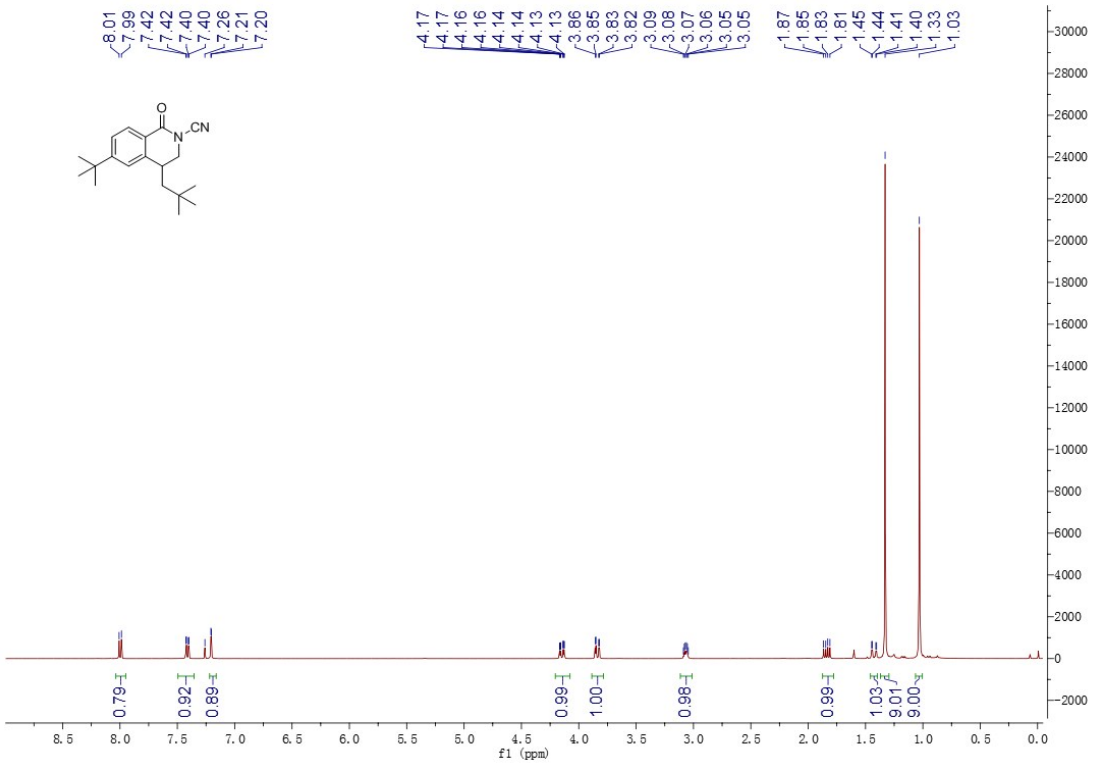



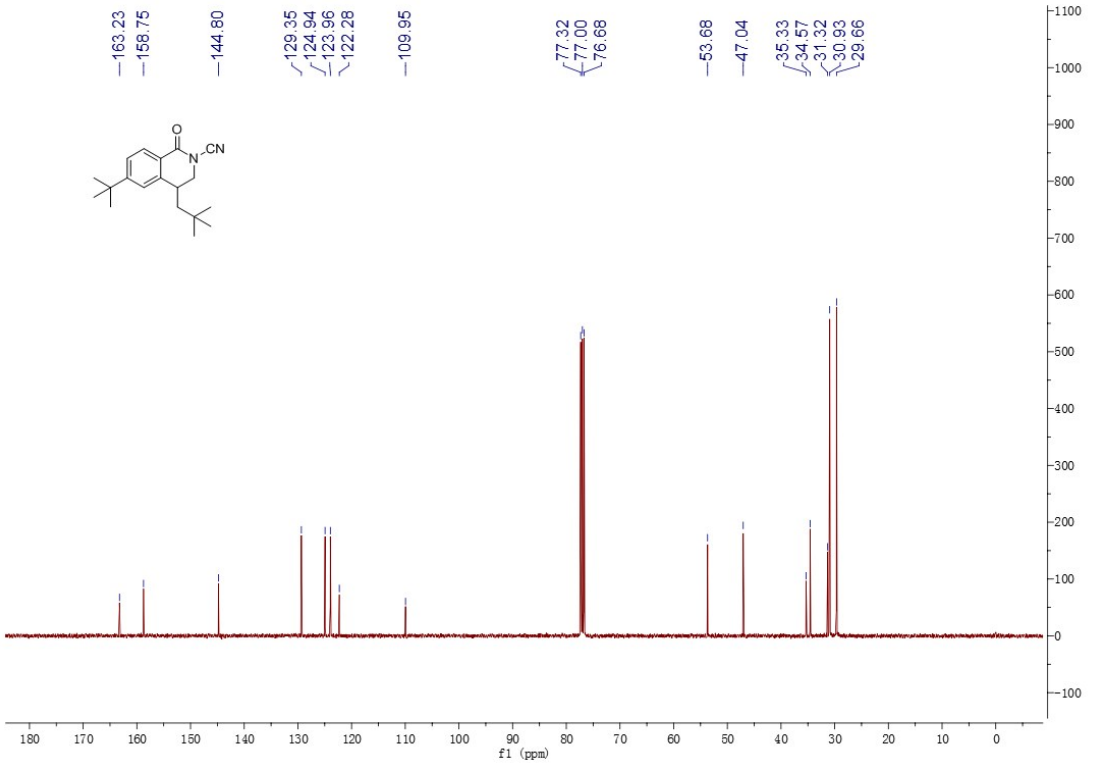
$^{1}$HNMR and $^{13}$CNMR spectra of **5aa**



$^{1}$HNMR and $^{13}$CNMR spectra of **5ba**



$^{1}$HNMR and $^{13}$CNMR spectra of **5ca**