Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Isocyanide insertion approach to substituted pyrrolo[2,3-*b*]quinolines under metal-free and azide-free conditions

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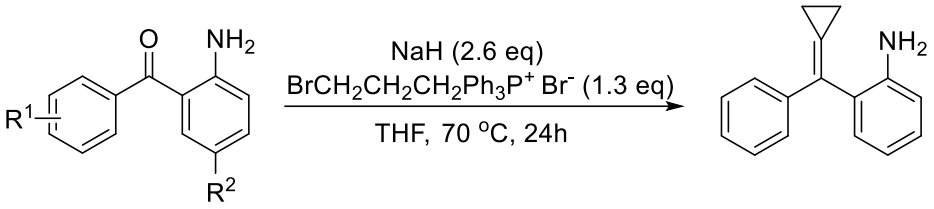
General remarks

THF, Et_2O and toluene were distilled from sodium (Na) under argon (Ar) atmosphere. Melting points were recorded on an Electrothermal digital melting point apparatus and were uncorrected. IR spectra were recorded on a Bruker Tensor 27 spectrophotometer. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 MHz (^1H NMR) and 100 MHz (^{13}C NMR) spectrumeter using $CDCl_3$ as solvent and TMS as internal standard. For thin-layer chromatography (TLC), silica gel plates (Huanghai GF254) were used. High resolution mass spectra were obtained using GCT-TOF instrument with ESI source or EI source.

Experimental Section

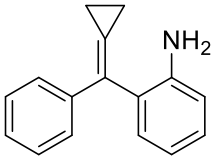
General procedure for the synthesis of MCPs 1



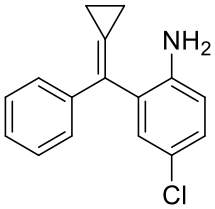
R^1 = H, F, Cl, Me, OMe
R^2 = H, Cl

To a solution of 3-bromopropyltriphenylphosphonium bromide (6 g, 13 mmol) in 10 mL of THF was added 1.04 g (26 mmol) of 60% NaH in mineral oil. The resulting mixture was stirred at 70 ℃ for 12 hr. A solution of 2-aminobenzophenone (1.98 g, 10 mmol) in 5 mL of THF was added and the reaction was stirred at 70 ℃ for another 12 hr. The solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (50/1 petroleum ether/EtOAc) to afford the product in the indicated yield.[14]

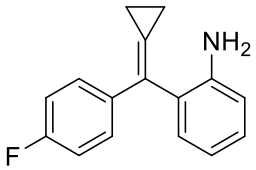
Spectroscopic data for MCPs 1a, 1b, 1c, and 1g



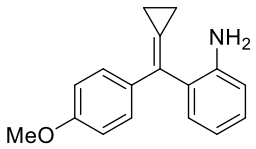
2-(cyclopropylidene(phenyl)methyl)aniline (1a): 884 mg, 40%, a yellow solid. M.p. 78-80℃. IR : 3464, 3375, 3054, 2970, 1610, 1596, 1574, 1492, 1446, 1300, 1027, 901, 768, 740, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.39 (m, 2H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.16 (dd, *J* = 9.1, 5.5 Hz, 1H), 7.11 – 7.00 (m, 2H), 6.78 – 6.61 (m, 2H), 3.44 (s, 2H), 1.55 – 1.50 (m, 2H), 1.16 – 1.09 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 143.8, 138.8, 130.4, 128.0, 127.8, 126.6, 126.6, 126.2, 126.1, 125.3, 117.9, 115.1, 76.9, 76.6, 76.2, 5.0, 1.2. HRMS (ESI) m/z calculated for $C_{16}H_{15}N$, $[M+H]^+$ 222.1283, found 222.1289.



4-chloro-2-(cyclopropylidene(phenyl)methyl)aniline (1b): 765 mg, 30%, a yellow solid. M.p. 85-87℃. IR : 3461, 3373, 2967, 1604, 1593, 1571, 1499, 1439, 1302, 1030, 899, 769, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.36 (m, 2H), 7.24 (dd, *J* = 8.1, 6.7 Hz, 2H), 7.17 (dd, *J* = 5.6, 3.5 Hz, 1H), 7.07 – 6.96 (m, 2H), 6.56 (d, *J* = 8.3 Hz, 1H), 3.43 (s, 2H), 1.52 (dd, *J* = 9.0, 6.7 Hz, 2H), 1.16 – 1.08 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 142.5, 138.1, 129.9, 128.1, 127.6, 127.5, 126.9, 126.2, 126.1, 125.7, 122.3, 116.1, 76.9, 76.6, 76.2, 5.1, 1.3. HRMS (ESI) m/z calculated for $C_{16}H_{14}ClN$, $[M+H]^+$ 256.0893, found 256.0894.

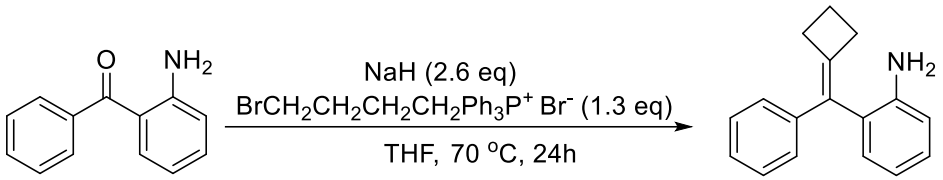


2-(cyclopropylidene(4-fluorophenyl)methyl)aniline (1c): 596 mg, 25%, a yellow solid. M.p. 68-70℃. IR : 3467, 3376, 3054, 3019, 2950, 2909, 1611, 1573, 1448, 1411, 1297, 1076, 1031, 748, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 8.7, 5.5 Hz, 2H), 7.07 (td, *J* = 7.9, 1.5 Hz, 1H), 6.99 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.90 (t, *J* = 8.7 Hz, 2H), 6.70 (ddd, *J* = 23.3, 14.9, 4.5 Hz, 2H), 3.31 (s, 2H), 1.53 – 1.46 (m, 2H), 1.14 – 1.08 (m, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 162.8, 160.3, 143.7, 134.9, 134.9, 130.3, 128.0, 127.8, 127.7, 125.9, 125.7, 124.8, 124.8, 117.9, 115.1, 114.9, 114.7, 76.9, 76.6, 76.3, 4.9, 1.3. HRMS (ESI) m/z calculated for $C_{16}H_{14}FN$, $[M+H]^+$ 240.1189, found 240.1198.

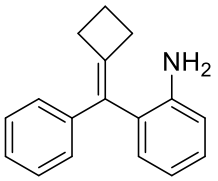


2-(cyclopropylidene(4-methoxyphenyl)methyl)aniline (1g): 402 mg, 16%, a yellow solid. M.p. 61-63℃. IR：3466, 3375, 3054, 2960, 1613, 1576, 1452, 1416, 1300, 1057, 900, 768, 730, 691 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.8 Hz, 2H), 7.19 – 7.07 (m, 2H), 6.89 – 6.83 (m, 2H), 6.80 (td, *J* = 7.4, 1.0 Hz, 1H), 6.73 (dd, *J* = 7.9, 0.8 Hz, 1H), 3.80 (s, 3H), 3.53 (s, 2H), 1.56 (dd, *J* = 8.7, 6.4 Hz, 2H), 1.17 (dd, *J* = 8.7, 6.4 Hz, 2H).^{13}C NMR (101 MHz, $CDCl_3$) δ 158.3, 143.8, 131.5, 130.4, 127.7, 127.4, 126.4, 126.0, 122.9, 117.8, 115.0, 113.3, 76.9, 76.6, 76.2, 54.8, 4.8, 1.2. HRMS (ESI) m/z calculated for $C_{17}H_{17}NO$, $[M+H]^+$ 252.1388, found 240.1397.

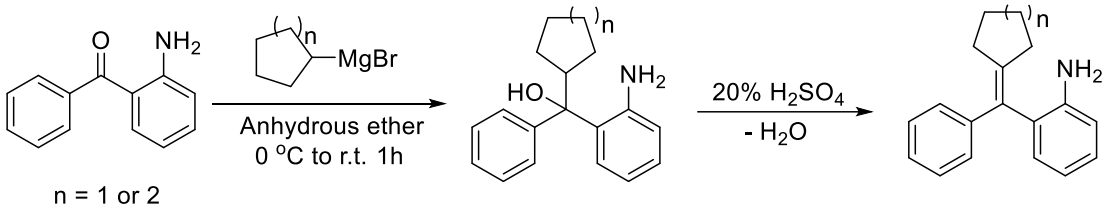
General procedure for the synthesis of MCPs 1h



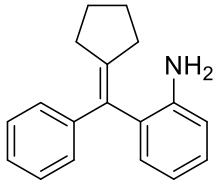
To a solution of 3-bromopropyltriphenylphosphonium bromide (6.2 g, 13 mmol) in 10 mL of THF was added 1.04 g (26 mmol) of 60% NaH in mineral oil. The resulting mixture was stirred at 70 ℃ for 12 hr. A solution of 2-aminobenzophenone (1.98 g, 10 mmol) in 5 mL of THF was added and the reaction was stirred at 70 ℃ for another 12 hr. The solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (50/1 petroleum ether/EtOAc) to afford the product in the low yield.[1]



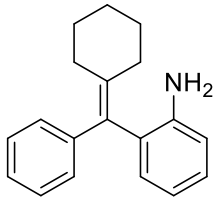
2-(cyclobutylidene(phenyl)methyl)aniline (1u): 469 mg, 20%, a yellow solid. M.p. 87-89℃. IR : 3453, 3369, 2976, 1610, 1503, 1452, 1414, 1296, 1254, 1104, 931, 902, 836, 804, 747 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.25 (m, 2H), 7.19 (dd, *J* = 10.6, 7.3 Hz, 3H), 7.12 (td, *J* = 7.8, 1.5 Hz, 1H), 7.03 (dd, *J* = 7.5, 1.4 Hz, 1H), 6.81 – 6.70 (m, 2H), 3.59 (s, 2H), 3.19 – 3.09 (m, 2H), 2.75 – 2.64 (m, 2H), 2.06 (p, *J* = 7.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.6, 143.1, 138.6, 130.5, 128.9, 127.8, 127.5, 126.7, 125.8, 125.1, 117.9, 115.0, 76.9, 76.5, 76.2, 32.5, 31.4, 17.0. HRMS (ESI) m/z calculated for $C_{17}H_{17}N$, $[M+H]^+$ 236.1439, found 236.1436.



A Grignard reagent was prepared from bromocylopentane (2.14 mL, 20 mmol) , magnesium (0.48g, 20mmol) and one granule of I_2 in dry ether (10 mL). The solution of 2-cylopentylmagnesium bromide was added dropwise to a solution of 2-aminoben -zophenone (1.6 g, 8 mmol) in THF (10 mL) and the mixture was stirred at room temperature 1h. The resulting mixture was quenched by saturated aqueous NH_4Cl (10 mL), extracted with DCM (10 mL x 3), and washed by brine (10 mL). The combined extracts were dried over Na_2SO_4. Then the solvent was removed under reduced pressure to get the crude product without purification. The crude product and $MgSO_4$ (6.0 g, 50 mmol) were combined in *ortho*-xylene (20 mL) and the mixture was heated at 120 °C overnight. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product in moderate yield.[2]

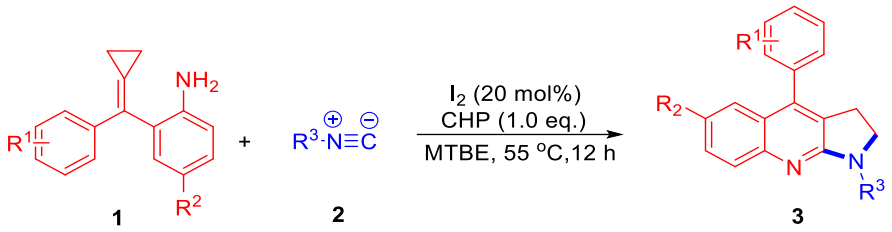


2-(cyclopentylidene(phenyl)methyl)aniline (1a'): 600 mg, 30%, a yellow oil. IR : 3414, 3356, 3332, 2947, 2914, 2847, 1614, 1567, 1489, 1442, 1330, 1302, 1280, 1031, 932, 746, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.36 – 7.28 (m, 2H), 7.27 – 7.20 (m, 1H), 7.14 (td, *J* = 7.6, 1.4 Hz, 1H), 6.92 (td, *J* = 7.7, 1.1 Hz, 1H), 6.64 (dd, *J* = 7.8, 1.1 Hz, 1H), 4.00 (s, 1H), 3.82 (s, 2H), 3.03 – 2.90 (m, 1H), 2.05 – 1.94 (m, 1H), 1.79 – 1.52 (m, 6H), 1.44 (tdd, *J* = 9.4, 6.7, 3.0 Hz, 1H), 1.24 – 1.13 (m, 1H), 0.99 – 0.85 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.8, 144.1, 131.8, 127.7, 127.3, 126.9, 125.8, 125.3, 118.5, 118.2, 79.8, 76.9, 76.5, 76.2, 48.0, 27.6, 27.4, 26.2, 25.7. HRMS (ESI) m/z calculated for $C_{17}H_{19}N$, $[M+H]^+$ 250.1596, found 250.1592.



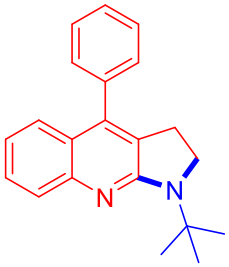
2-(cyclohexylidene(phenyl)methyl)aniline (1b'): 840 mg, 40%, a yellow solid. M.p. 136-138℃. IR : 3476, 3398, 2960, 2874, 1614, 1500, 1461, 1409, 1246, 1054, 942, 860, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 7.8 Hz, 1H), 7.33 (d, *J* = 7.5 Hz, 2H), 7.25 (dd, *J* = 10.8, 4.6 Hz, 2H), 7.17 (t, *J* = 7.2 Hz, 1H), 7.06 (td, *J* = 7.7, 1.2 Hz, 1H), 6.90 – 6.78 (m, 1H), 6.57 (dd, *J* = 7.8, 1.0 Hz, 1H), 3.82 (s, 2H), 2.30 – 2.18 (m, 1H), 2.10 (d, *J* = 12.7 Hz, 1H), 1.87 – 1.77 (m, 1H), 1.68 (d, *J* = 2.5 Hz, 2H), 1.38 (dtd, *J* = 12.6, 9.7, 2.9 Hz, 1H), 1.29 – 1.11 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.8, 144.6, 130.2, 127.6, 127.2, 126.7, 125.8, 125.6, 119.0, 118.0, 80.5, 76.9, 76.6, 76.2, 45.6, 27.5, 26.9, 26.4, 26.2, 26.1. HRMS (ESI) m/z calculated for $C_{19}H_{21}N$, $[M+H]^+$ 264.1752, found 264.1758.

General procedure for the synthesis of compounds 3



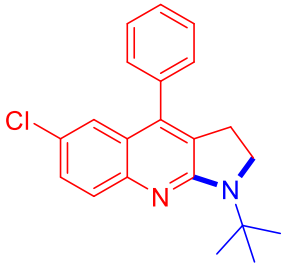
A solution of compound **1** (0.3 mmol, 1.0 equiv.) and **2** (0.36 mmol, 1.2 equiv.) in MTBE (1.5 mL) in the presence of 20% mol of I_2 and 1.0 equiv of CHP as the oxidant was stirred at 55 ℃ in a sealed reaction tube for 12 h. Then the solvent was removed under reduced pressure and the residue was purified by silica gel flash chromatography (eluent: petroleum ether / ethyl acetate = 50 / 1) to afford the product **3** in moderate to good yield.

Spectroscopic data for all products 3



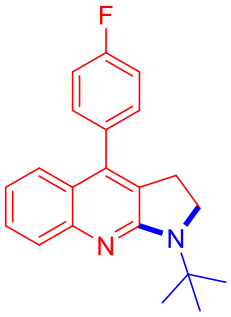
1-(tert-butyl)-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3a)

75 mg, 83%, a yellow solid. M.p. 143-145℃. IR : 3058, 2970, 2923, 1730, 1627, 1598, 1467, 1429, 1390, 1360, 1224, 757, 672 cm^{-1}; ^{1H} NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.3, 0.9 Hz, 1H), 7.49 (ddd, *J* = 7.5, 4.5, 1.3 Hz, 2H), 7.45 – 7.38 (m, 2H), 7.37 – 7.30 (m, 3H), 7.04 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 3.59 (t, *J* = 7.7 Hz, 2H), 2.81 (t, *J* = 7.7 Hz, 2H), 1.59 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 147.9, 140.1, 136.4, 128.7, 128.0, 127.4, 127.2, 126.4, 124.9, 124.5, 122.5, 120.9, 76.9, 76.5, 76.2, 54.0, 46.0, 26.6, 24.4. HRMS (ESI) m/z calculated for $C_{21}H_{22}N_2$, $[M+H]^+$ 303.1861, found 303.1876.



1-(tert-butyl)-6-chloro-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3b)

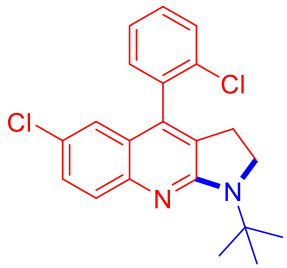
82 mg, 81%, a white solid. M.p. 179-181℃. IR : 3058, 2860, 1625, 1600, 1440, 1420, 1306, 825, 700, 645 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.8 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.46 – 7.41 (m, 1H), 7.36 – 7.26 (m, 4H), 3.60 (t, *J* = 7.7 Hz, 2H), 2.80 (t, *J* = 7.7 Hz, 2H), 1.57 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 146.4, 139.3, 135.7, 128.6, 128.2, 127.8, 127.7, 127.5, 126.1, 125.9, 123.5, 123.4, 76.9, 76.5, 76.2, 54.1, 45.9, 26.6, 24.4. HRMS (ESI) m/z calculated for $C_{21}H_{21}ClN_2$, $[M+H]^+$ 337.1472, found 337.1471.



1-(tert-butyl)-4-(4-fluorophenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3c)

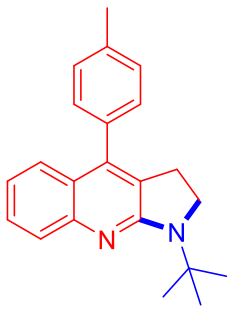
72 mg, 75%, a yellow solid. M.p. 132-134℃. IR : 3065, 2974, 2922, 2842, 1630,

1603, 1505, 1429, 1313, 1218, 836, 769 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.70 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.42 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.18 (t, *J* = 8.7 Hz, 2H), 7.05 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 3.59 (s, 2H), 2.79 (s, 2H), 1.59 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 160.7, 160.6, 147.9, 139.1, 132.2, 132.2, 130.5, 130.4, 127.5, 126.5, 125.1, 124.3, 122.5, 121.0, 115.2, 115.0, 76.9, 76.5, 76.2, 54.0, 45.9, 26.6, 24.4. HRMS (ESI) m/z calculated for $C_{21}H_{21}FN_2$, $[M+H]^+$ 321.1767, found 321.1777.



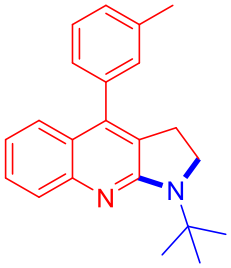
1-(tert-butyl)-6-chloro-4-(2-chlorophenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3d)

89 mg, 80%, a yellow solid. M.p. 134-136℃. IR : 3063, 2970, 2928, 2867, 1631, 1593, 1451, 1389, 1360, 1310, 1219, 825, 756, 619 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.8 Hz, 1H), 7.58 – 7.52 (m, 1H), 7.43 – 7.30 (m, 3H), 7.25 – 7.18 (m, 1H), 7.00 (d, *J* = 2.4 Hz, 1H), 3.68 – 3.55 (m, 2H), 2.84 – 2.60 (m, 2H), 1.58 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 146.3, 136.6, 134.4, 132.9, 130.4, 129.5, 129.2, 127.9, 127.7, 127.1, 126.6, 126.2, 123.1, 123.1, 76.9, 76.6, 76.2, 54.1, 45.8, 26.6, 24.1. HRMS (ESI) m/z calculated for $C_{21}H_{20}Cl_2N_2$, $[M+H]^+$ 371.1082, found 371.1090.



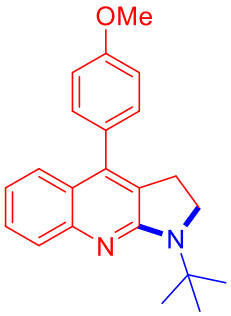
1-(tert-butyl)-4-(p-tolyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3e)

77 mg, 81%, a yellow solid. M.p. 156-158℃. IR : 3053, 2972, 2920, 2821, 1623, 1563, 1453, 1427, 1186, 782, 729, 629 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.3, 0.8 Hz, 1H), 7.43 – 7.34 (m, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.25 – 7.18 (m, 2H), 7.04 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 3.58 (s, 2H), 2.81 (s, 2H), 2.44 (s, 3H), 1.58 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 147.9, 140.1, 136.9, 133.3, 128.7, 128.6, 127.3, 126.4, 124.8, 124.6, 122.7, 120.9, 76.9, 76.5, 76.2, 53.9, 45.9, 26.6, 24.4, 20.9. HRMS (ESI) m/z calculated for $C_{22}H_{24}N_2$, $[M+H]^+$ 317.2018, found 317.2013.



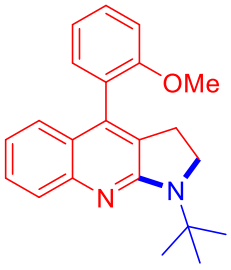
1-(tert-butyl)-4-(m-tolyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3f)

77 mg, 81%, a yellow solid. M.p. 95-97℃. IR : 2970, 2922, 2850, 1630, 1601, 1568, 1429, 1311, 1221, 1031, 754, 706 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.3, 0.7 Hz, 1H), 7.42 – 7.32 (m, 3H), 7.25 – 7.19 (m, 1H), 7.16 – 7.10 (m, 2H), 7.03 (ddd, *J* = 8.1, 7.0, 1.2 Hz, 1H), 3.56 (t, *J* = 7.7 Hz, 2H), 2.79 (t, *J* = 7.7 Hz, 2H), 2.40 (s, 3H), 1.58 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 147.9, 140.3, 137.6, 136.4, 129.4, 127.9, 127.3, 126.4, 125.8, 124.8, 124.7, 122.7, 120.9, 76.9, 76.6, 76.3, 54.0, 46.0, 26.7, 24.4, 21.1. HRMS (ESI) m/z calculated for $C_{22}H_{24}N_2$, $[M+H]^+$ 317.2018, found 317.2009.



1-(tert-butyl)-4-(4-methoxyphenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3g)

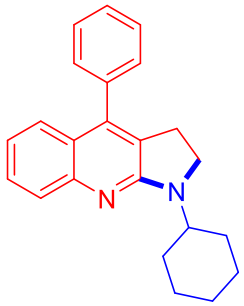
23 mg, 23%, a yellow oil. IR : 3061, 2957, 2849, 1626, 1607, 1520, 1508, 1466, 1428, 1291, 1247, 1033, 830, 763 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 1H), 7.40 (dd, *J* = 15.2, 7.5 Hz, 2H), 7.28 (d, *J* = 2.1 Hz, 2H), 7.07 – 6.99 (m, 3H), 3.88 (s, 3H), 3.58 (t, *J* = 7.7 Hz, 2H), 2.82 (t, *J* = 7.7 Hz, 2H), 1.59 (s, 11H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.9, 158.6, 147.9, 139.8, 129.9, 128.5, 127.3, 126.4, 125.0, 124.6, 122.8, 120.9, 113.4, 76.9, 76.5, 76.2, 54.8, 53.9, 45.9, 26.6, 24.5. HRMS (ESI) m/z calculated for $C_{22}H_{24}N_2O$, $[M+H]^+$ 333.1967, found 333.1966.



1-(tert-butyl)-4-(2-methoxyphenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3h)

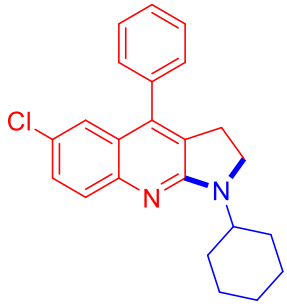
32 mg, 32%, a yellow oil. IR : 3060, 3019, 2921, 2852, 1734, 1628, 1595, 1469, 1430, 1359, 1313, 1239, 1022, 761, 615 cm-1; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 – 7.65 (m,

1H), 7.40 (dtd, *J* = 10.3, 7.9, 1.6 Hz, 2H), 7.19 (ddd, *J* = 7.1, 5.5, 1.5 Hz, 2H), 7.10 – 6.98 (m, 3H), 3.72 (s, 3H), 3.65 – 3.53 (m, 2H), 2.82 – 2.66 (m, 2H), 1.59 (s, 9H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.8, 156.5, 147.7, 136.9, 130.5, 128.8, 127.1, 126.3, 126.0, 124.9, 124.5, 122.8, 120.7, 120.1, 110.8, 76.9, 76.5, 76.2, 55.0, 53.9, 45.9, 26.7, 24.3. HRMS (ESI) m/z calculated for $C_{22}H_{24}N_2O$, $[M+H]^+$ 333.1967, found 333.1977.



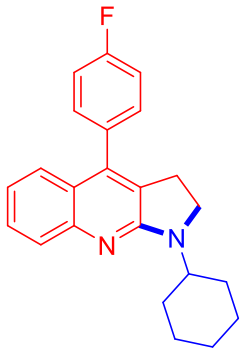
1-cyclohexyl-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3i)

66 mg, 67%, a yellow solid. M.p. 193-194℃. IR : 3060, 2852, 1632, 1572, 1492, 1438, 1309, 768, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.49 (t, *J* = 7.2 Hz, 2H), 7.45 – 7.37 (m, 2H), 7.37 – 7.27 (m, 3H), 7.06 – 6.96 (m, 1H), 4.37 – 4.18 (m, 1H), 3.57 (t, *J* = 7.8 Hz, 2H), 2.89 (t, *J* = 7.8 Hz, 2H), 2.00 – 1.63 (m, 6H), 1.60 – 1.39 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.9, 148.2, 140.7, 136.3, 128.6, 128.0, 127.6, 127.3, 125.4, 124.7, 124.1, 123.1, 120.6, 76.9, 76.5, 76.2, 51.1, 42.8, 29.3, 25.4, 25.2, 24.4. HRMS (ESI) m/z calculated for $C_{23}H_{24}N_2$, $[M+H]^+$ 329.2018, found 329.2015.



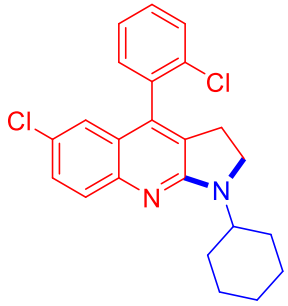
6-chloro-1-cyclohexyl-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3j)

50 mg, 46%, a yellow solid. M.p. 168-170℃. IR : 3063, 2928, 2851, 1726, 1630, 1600, 1459, 1429, 1310, 1077, 815, 699 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.8 Hz, 1H), 7.54 – 7.48 (m, 2H), 7.44 (ddd, *J* = 5.9, 2.8, 1.4 Hz, 1H), 7.33 (ddd, *J* = 7.9, 4.5, 1.8 Hz, 3H), 7.25 (s, 1H), 4.24 (ddd, *J* = 11.3, 7.9, 3.6 Hz, 1H), 3.59 (t, *J* = 7.8 Hz, 2H), 2.89 (t, *J* = 7.8 Hz, 2H), 1.95 – 1.81 (m, 4H), 1.73 (d, *J* = 12.9 Hz, 1H), 1.59 (s, 1H), 1.48 (tt, *J* = 12.6, 6.3 Hz, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 146.7, 137.2, 134.3, 132.8, 130.4, 129.5, 129.2, 128.1, 126.8, 126.6, 126.3, 125.9, 123.7, 123.3, 76.9, 76.6, 76.2, 51.2, 42.8, 29.5, 29.2, 25.3, 25.2, 25.1, 24.2. HRMS (ESI) m/z calculated for $C_{23}H_{23}ClN_2$, $[M+H]^+$ 363.1628, found 337.1638.



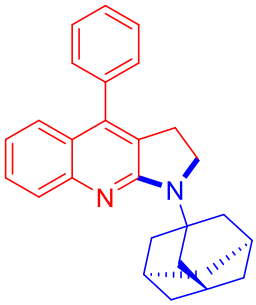
1-cyclohexyl-4-(4-fluorophenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3k)

63 mg, 60%, a yellow solid. M.p. 178-180℃. IR : 3052, 2927, 2852, 1637, 1600, 1470, 1442, 1310, 1218, 800, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 1H), 7.40 (dd, *J* = 11.1, 4.0 Hz, 1H), 7.35 – 7.26 (m, 3H), 7.18 (t, *J* = 8.7 Hz, 2H), 7.03 (t, *J* = 7.1 Hz, 1H), 4.28 (d, *J* = 3.3 Hz, 1H), 3.58 (t, *J* = 7.8 Hz, 2H), 2.87 (t, *J* = 7.8 Hz, 2H), 2.02 – 1.66 (m, 6H), 1.61 – 1.39 (m, 4H).^{13}C NMR (101 MHz, $CDCl_3$) δ 163.1, 160.6, 159.8, 148.2, 139.7, 132.2, 132.2, 130.4, 130.3, 127.7, 125.5, 124.5, 124.4, 123.1, 120.7, 115.2, 115.0, 76.9, 76.6, 76.2, 51.1, 42.8, 29.3, 25.4, 25.2, 24.4. HRMS (ESI) m/z calculated for $C_{23}H_{23}FN_2$, $[M+H]^+$ 347.1924, found 347.1932.



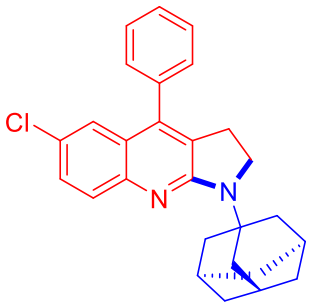
6-chloro-4-(2-chlorophenyl)-1-cyclohexyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinolin e (3l)

48 mg, 40%, a yellow solid. M.p. 155-157℃. IR : 2928, 2852, 1642, 1567, 1488, 1467, 1419, 1124, 1081, 825, 757 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 – 7.51 (m, 2H), 7.45 – 7.30 (m, 3H), 7.28 – 7.20 (m, 1H), 6.98 (d, *J* = 2.4 Hz, 1H), 4.25 (ddd, *J* = 11.3, 7.7, 3.7 Hz, 1H), 3.68 – 3.52 (m, 2H), 2.79 (dddd, *J* = 32.7, 17.5, 9.5, 6.0 Hz, 2H), 1.97 – 1.40 (m, 10H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.8, 146.7, 137.2, 134.4, 132.8, 130.4, 129.6, 129.2, 128.1, 126.8, 126.6, 126.3, 125.3, 123.7, 123.3, 76.9, 76.6, 76.3, 51.2, 42.8, 29.5, 29.2, 25.3, 25.2, 25.1, 24.2. HRMS (ESI) m/z calculated for $C_{23}H_{22}Cl_2N_2$, $[M+H]^+$ 397.1238, found 397.1245.



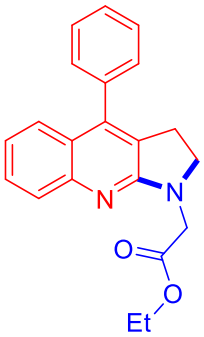
1-((3r)-adamantan-1-yl)-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3m)

74 mg, 65%, a yellow solid. M.p. 157-159℃. IR : 3057, 2904, 2849, 1719, 1630, 1567, 1434, 1360, 1306, 1120, 1070, 765, 700 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 1H), 7.48 (t, *J* = 7.2 Hz, 2H), 7.44 – 7.37 (m, 2H), 7.33 (dd, *J* = 12.0, 4.9 Hz, 3H), 7.02 (t, *J* = 7.5 Hz, 1H), 3.61 (t, *J* = 7.7 Hz, 2H), 2.79 (t, *J* = 7.7 Hz, 2H), 2.40 (d, *J* = 1.7 Hz, 6H), 2.17 (s, 3H), 1.77 (dd, *J* = 31.9, 11.9 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 147.8, 140.1, 136.5, 128.7, 128.0, 127.3, 127.1, 126.3, 125.0, 124.5, 122.5, 120.8, 76.9, 76.6, 76.2, 55.0, 44.7, 38.5, 36.3, 29.3, 24.4. HRMS (ESI) m/z calculated for $C_{27}H_{28}N_2$, $[M+H]^+$ 381.2331, found 381.2335.



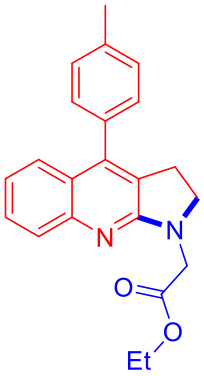
1-((3r)-adamantan-1-yl)-6-chloro-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3n)

101 mg, 81%, a yellow solid. M.p. 173-175℃. IR : 3056, 2907, 2847, 1627, 1561, 1429, 1418, 1303, 1232, 1170, 1126, 1076, 826, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.8 Hz, 1H), 7.49 (dd, *J* = 7.9, 6.5 Hz, 2H), 7.46 – 7.40 (m, 1H), 7.36 – 7.27 (m, 3H), 7.25 (d, *J* = 1.9 Hz, 1H), 3.62 (t, *J* = 7.7 Hz, 2H), 2.77 (t, *J* = 7.7 Hz, 2H), 2.37 (d, *J* = 2.3 Hz, 6H), 2.16 (s, 3H), 1.77 (dd, *J* = 28.3, 12.1 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 146.3, 139.3, 135.7, 128.6, 128.2, 127.7, 127.6, 127.5, 126.1, 126.0, 123.5, 123.4, 76.9, 76.5, 76.2, 55.1, 44.7, 38.5, 36.2, 29.3, 24.4. HRMS (ESI) m/z calculated for $C_{27}H_{27}ClN_2$, $[M+H]^+$ 415.1941, found 415.1947.



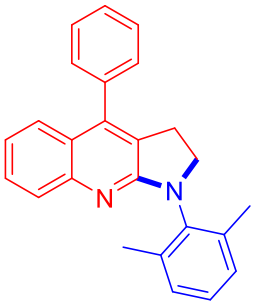
ethyl 2-(4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinolin-1-yl)acetate (3o)

46 mg, 45%, a yellow solid. M.p. 74-76℃. IR : 3053, 2981, 2869, 1748, 1634, 1528, 1472, 1445, 1192, 1023, 765, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.44 (t, *J* = 7.7 Hz, 2H), 7.37 (t, *J* = 7.8 Hz, 3H), 7.08 (t, *J* = 7.4 Hz, 1H), 4.38 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.71 (t, *J* = 7.8 Hz, 2H), 3.00 (t, *J* = 7.8 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 160.1, 147.7, 141.7, 136.1, 128.6, 128.1, 127.8, 127.4, 125.8, 124.9, 123.4, 122.8, 121.4, 76.9, 76.5, 76.2, 60.6, 48.6, 45.8, 24.7, 13.8. HRMS (ESI) m/z calculated for $C_{21}H_{20}N_2O_2$, $[M+H]^+$ 333.1603, found 333.1606.



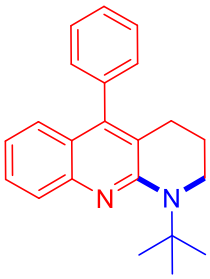
ethyl 2-(4-(p-tolyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinolin-1-yl)acetate (3p)

56 mg, 54%, a yellow solid. M.p. 78-80℃. IR : 2958, 2921, 2868, 1738, 1627, 1580, 1495, 1446, 1195, 1022, 765, 704 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.25 (dd, *J* = 6.4, 1.7 Hz, 2H), 7.08 (ddd, *J* = 8.2, 6.9, 1.3 Hz, 1H), 4.38 (s, 2H), 4.23 (q, *J* = 7.1 Hz, 2H), 3.70 (t, *J* = 7.8 Hz, 2H), 3.00 (t, *J* = 7.8 Hz, 2H), 2.45 (s, 3H), 1.30 (t, *J* = 7.1 Hz, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 169.5, 160.1, 147.7, 141.8, 137.2, 133.0, 128.8, 128.5, 127.7, 125.7, 125.0, 123.6, 122.8, 121.4, 76.9, 76.6, 76.2, 60.6, 48.6, 45.8, 24.8, 20.9, 13.8. HRMS (ESI) m/z calculated for $C_{22}H_{22}N_2O_2$, $[M+H]^+$ 347.1760, found 337.1767.



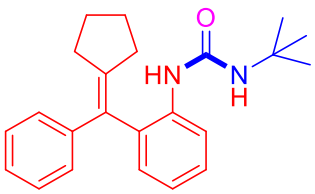
1-(2,6-dimethylphenyl)-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3q)

30 mg, 30%, a yellow solid. M.p. 212-214℃. IR : 3051, 2920, 2864, 1634, 1600, 1471, 1429, 1106, 842, 760, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.60 (m, 1H), 7.52 (t, *J* = 7.2 Hz, 2H), 7.49 – 7.40 (m, 3H), 7.37 (t, *J* = 7.4 Hz, 2H), 7.21 – 7.12 (m, 3H), 7.09 – 7.02 (m, 1H), 3.82 (t, *J* = 8.0 Hz, 2H), 3.14 (t, *J* = 8.0 Hz, 2H), 2.26 (s, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 159.3, 148.3, 141.7, 137.3, 136.9, 136.2, 128.7, 128.3, 128.1, 127.7, 127.4, 127.2, 126.2, 124.8, 123.1, 122.6, 121.1, 76.9, 76.6, 76.3, 48.6, 25.1, 18.1. HRMS (ESI) m/z calculated for $C_{25}H_{22}N_2$, $[M+H]^+$ 351.1861, found 351.1871.



1-(tert-butyl)-5-phenyl-1,2,3,4-tetrahydrobenzo[b][1,8]naphthyridine (3u)

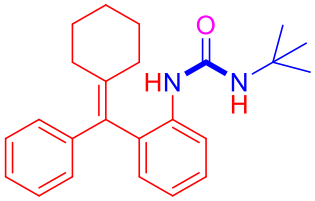
45 mg, 75% (0.19 mmol), a yellow solid. M.p. 114-116℃. IR : 3054, 2972, 2124, 1596, 1572, 1494, 1444, 1411, 1365, 1236, 1188, 1091, 1036, 756, 694, 624 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 – 7.21 (m, 3H), 7.19 – 7.06 (m, 6H), 3.23 – 3.10 (m, 2H), 2.68 – 2.57 (m, 2H), 2.15 – 2.02 (m, 2H), 1.18 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 142.6, 139.3, 138.5, 134.5, 133.7, 130.9, 129.4, 127.5, 127.4, 126.8, 125.4, 124.1, 123.7, 76.9, 76.6, 76.2, 56.2, 32.4, 31.4, 30.8, 16.9. HRMS (ESI) m/z calculated for $C_{22}H_{25}N_2$, $[M+H]^+$ 317.2018, found 317.2022.



1-(tert-butyl)-3-(2-(cyclopentylidene(phenyl)methyl)phenyl)urea (4a)

86 mg, 82%, a white solid. M.p. 93-95℃. IR : 3479, 3456, 3383, 3027, 2971, 2920, 2166, 1613, 1510, 1494, 1452, 1315, 1261, 903, 822, 748 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dd, *J* = 8.3, 1.0 Hz, 1H), 7.37 – 7.30 (m, 3H), 7.24 (dd, *J* = 5.1, 2.8 Hz, 2H), 7.19 – 7.15 (m, 1H), 7.15 – 7.10 (m, 1H), 6.99 – 6.89 (m, 2H), 3.01 (t, *J* = 8.2 Hz,

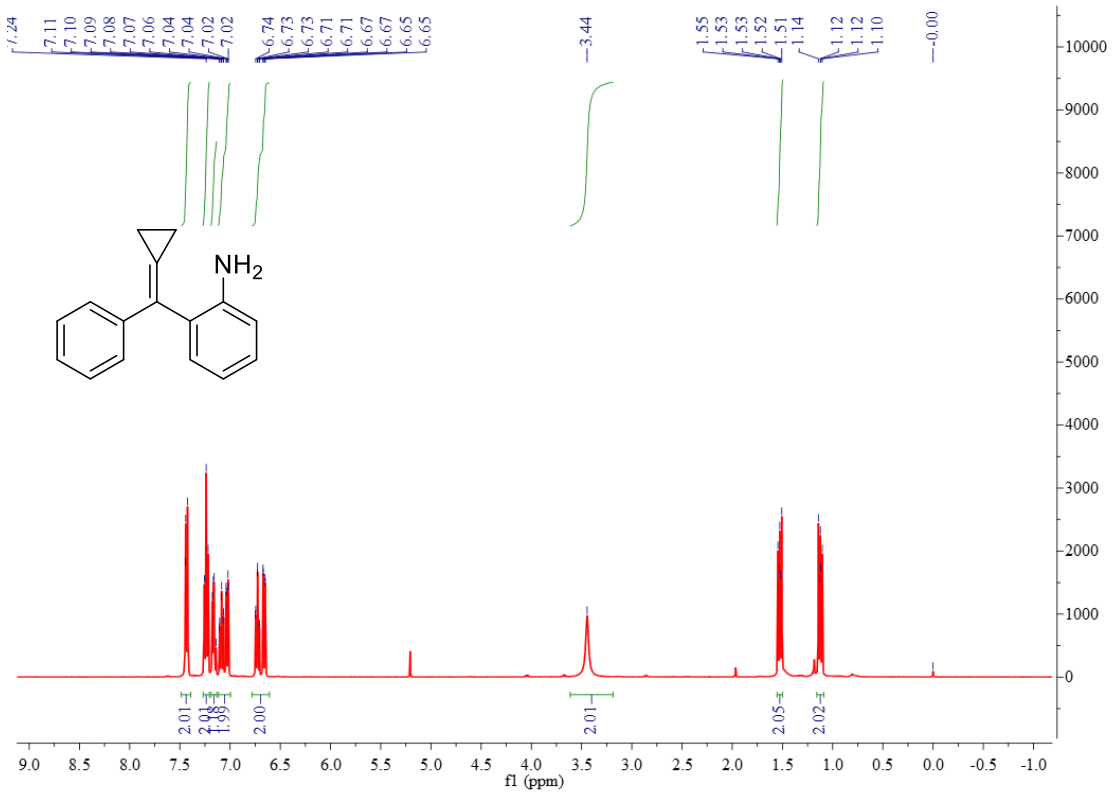
1H), 1.58 (s, 4H), 1.44 (s, 9H), 1.26 (s, 2H), 0.87 (ddd, *J* = 10.9, 8.8, 6.8 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 143.7, 141.6, 127.8, 127.5, 127.0, 126.4, 124.8, 123.8, 122.2, 121.4, 85.3, 76.9, 76.6, 76.3, 50.8, 48.2, 29.1, 27.4, 26.3, 25.6, 25.5. HRMS (ESI) m/z calculated for $C_{23}H_{29}N_2O$, $[M+H]^+$ 349.2280, found 349.2292.

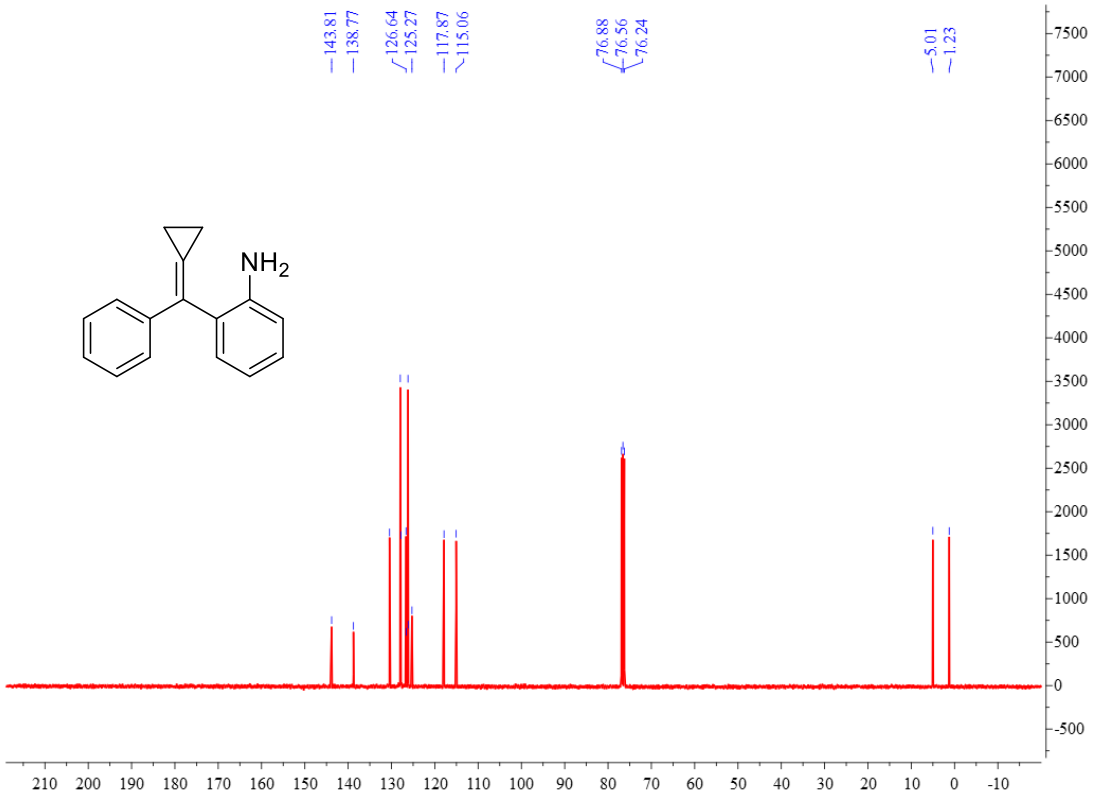


1-(tert-butyl)-3-(2-(cyclohexylidene(phenyl)methyl)phenyl)urea (4b)

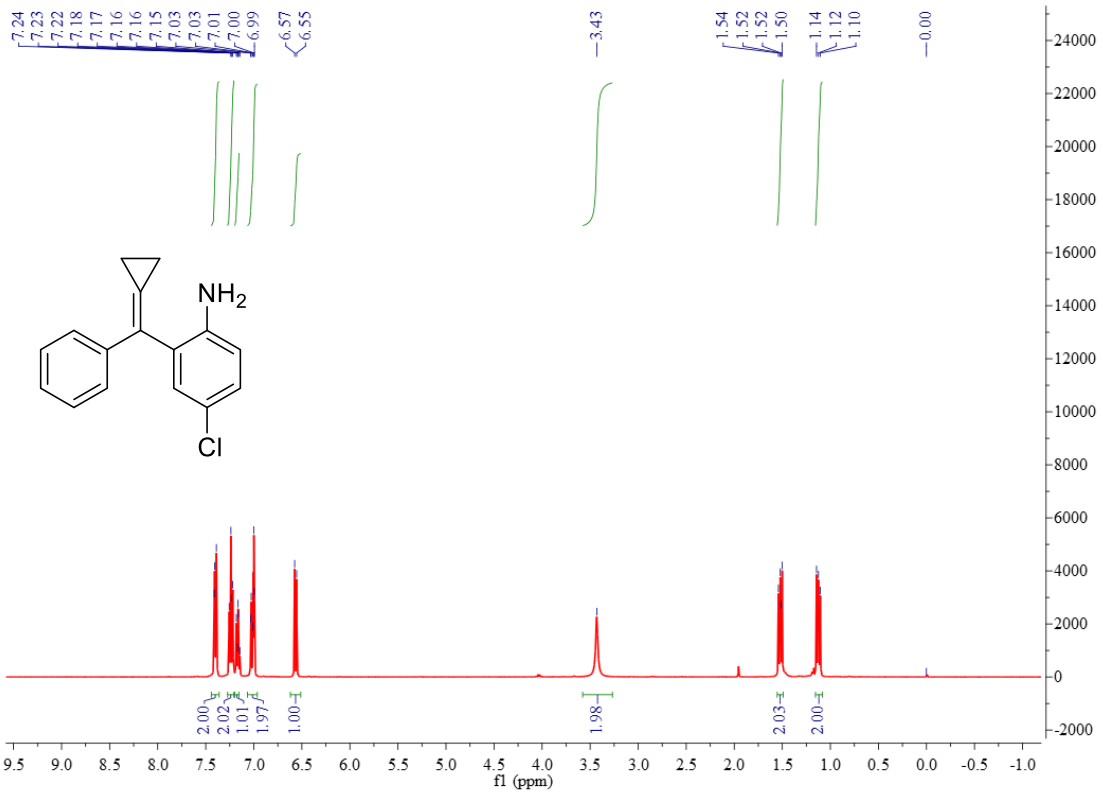
95 mg, 87%, a white solid. M.p. 104-106℃. IR : 3423, 3056, 2928, 2847, 1633, 1591, 1573, 1511, 1475, 1452,1391,1131, 1087, 846, 757, 694 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 (dd, *J* = 8.5, 1.6 Hz, 3H), 7.24 (dd, *J* = 10.5, 6.8 Hz, 2H), 7.20 – 7.09 (m, 2H), 7.04 – 6.85 (m, 2H), 4.47 (s, 1H), 2.31 (dd, *J* = 13.4, 5.9 Hz, 1H), 1.87 – 1.66 (m, 4H), 1.46 (s, 9H), 1.40 – 1.24 (m, 4H), 1.18 (dd, *J* = 19.6, 10.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 152.6, 142.6, 141.9, 127.6, 127.5, 126.3, 125.6, 124.9, 123.4, 122.4, 121.4, 86.7, 76.9, 76.6, 76.3, 50.8, 45.6, 29.2, 27.5, 26.3, 26.3, 26.0, 25.9. HRMS (ESI) m/z calculated for $C_{24}H_{31}N_2O$, $[M+H]^+$ 363.2436, found 363.2447.

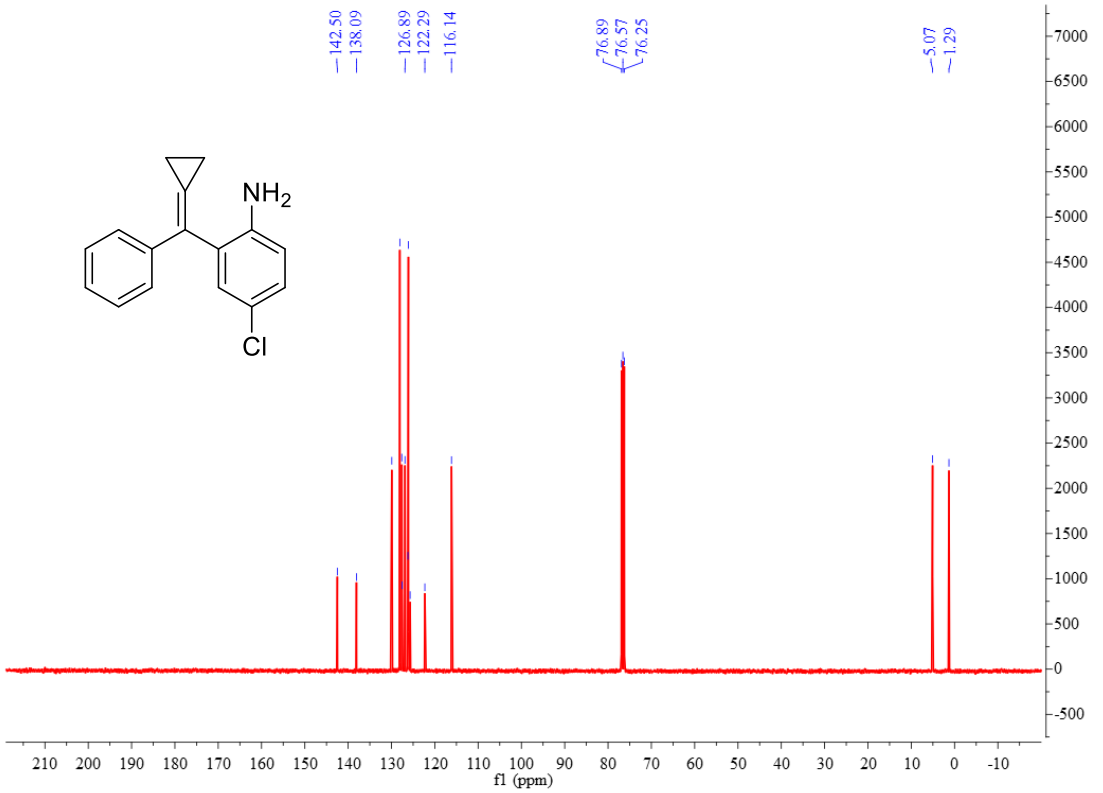
2-(cyclopropylidene(phenyl)methyl)aniline (1a)



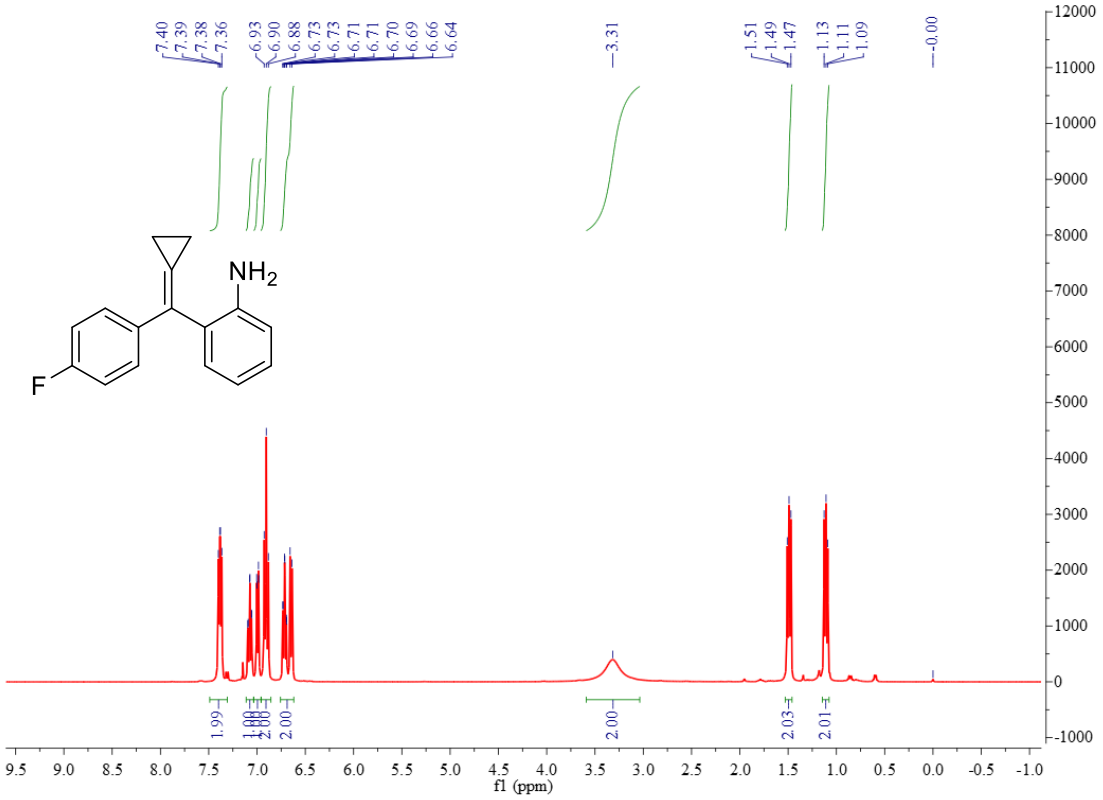


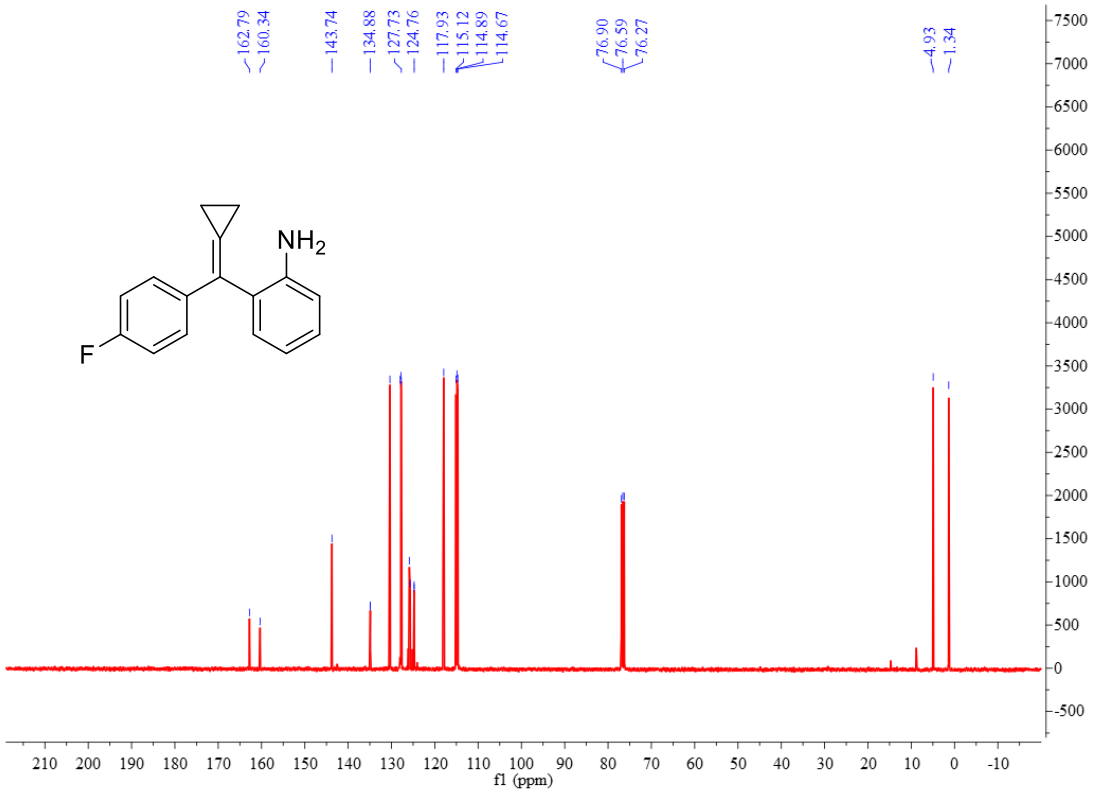
4-chloro-2-(cyclopropylidene(phenyl)methyl)aniline (1b)



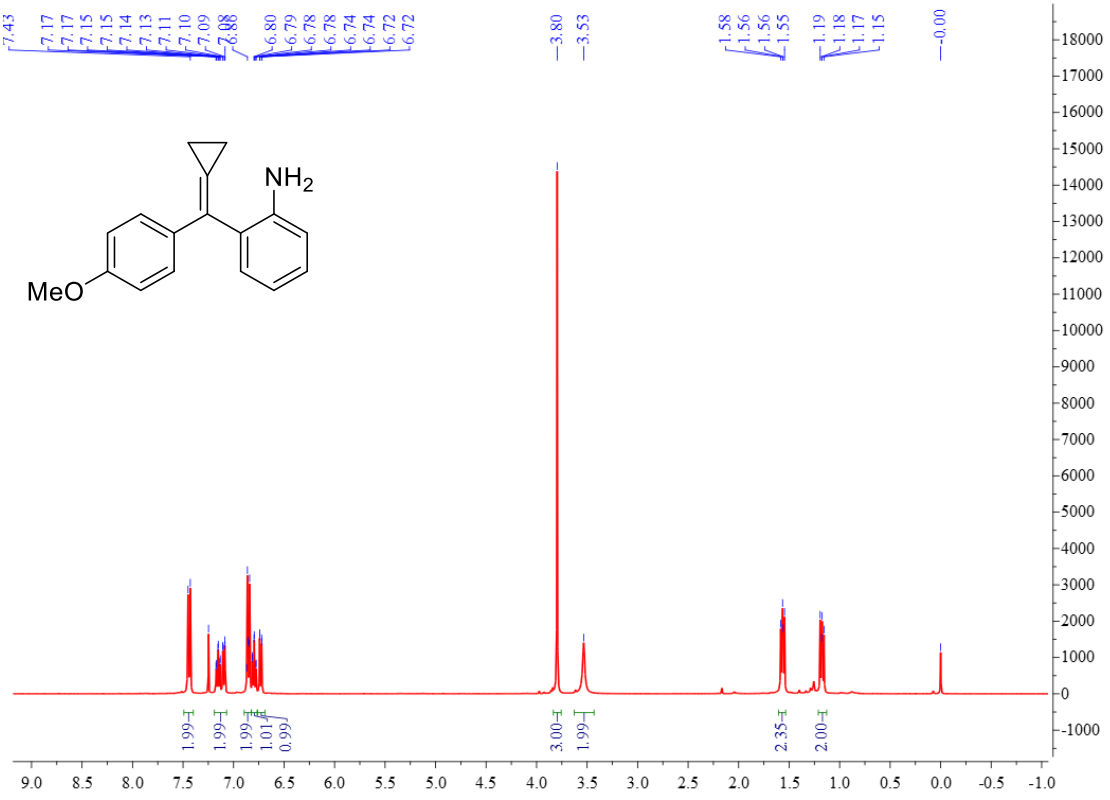


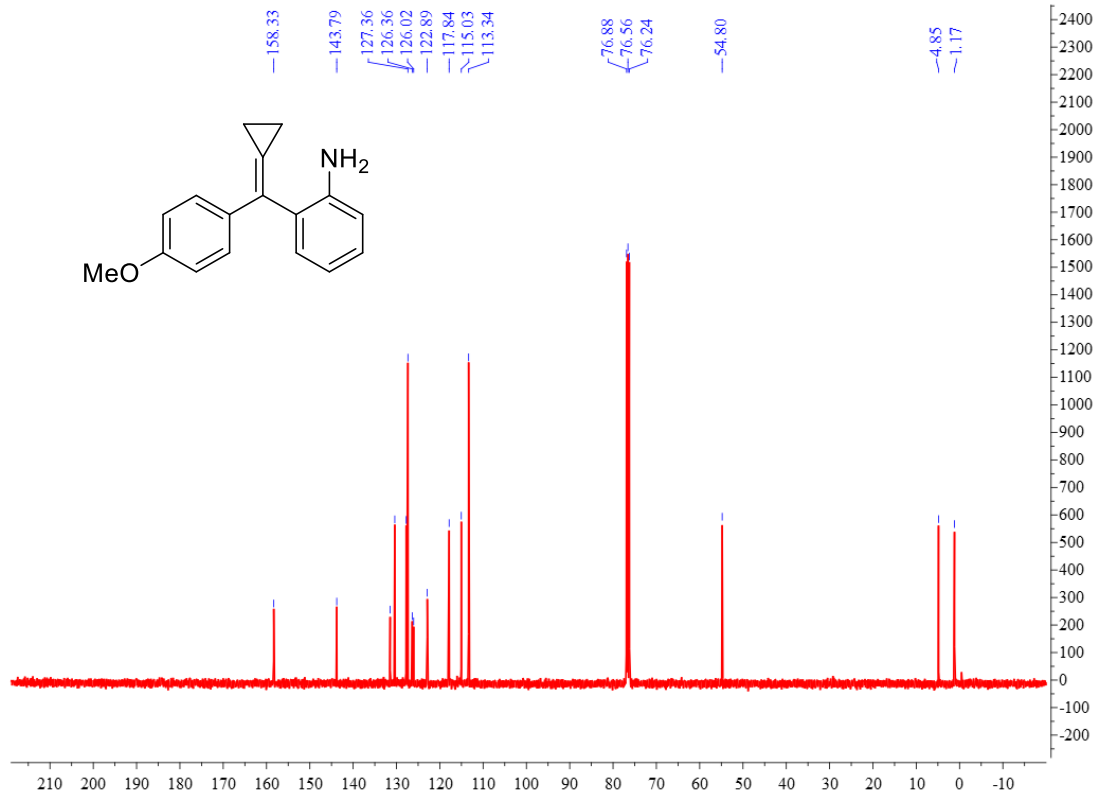
2-(cyclopropylidene(4-fluorophenyl)methyl)aniline (1c)



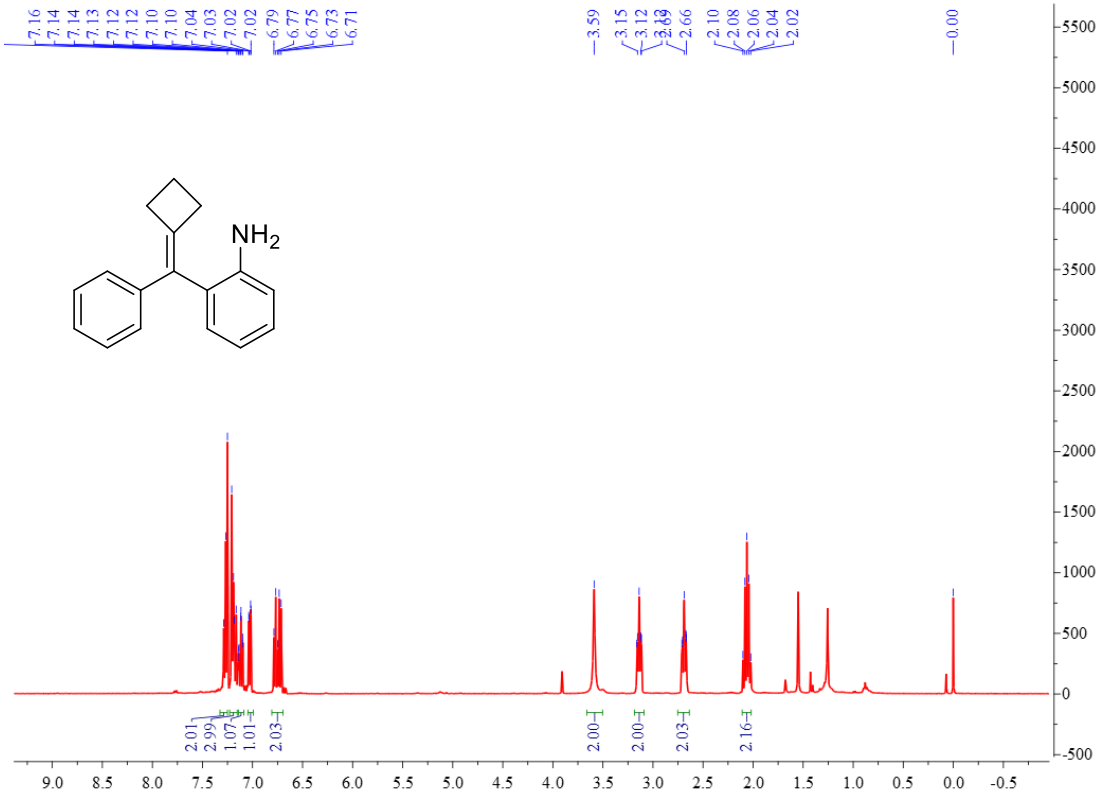


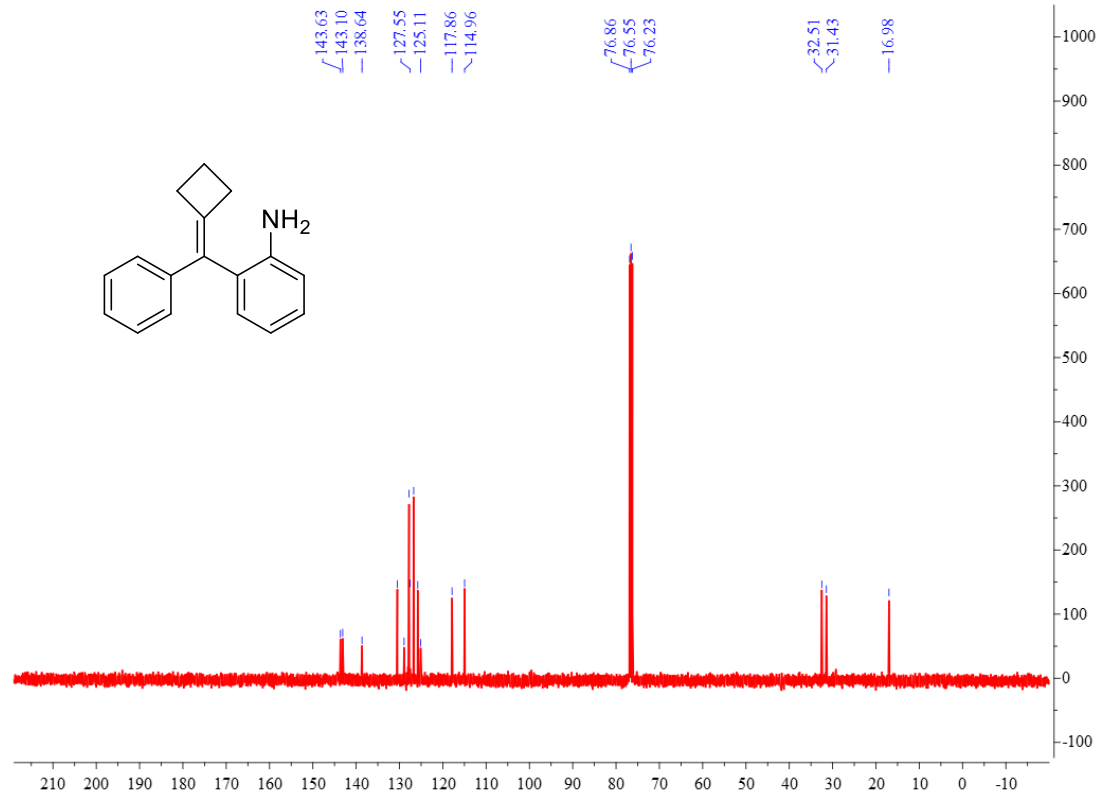
2-(cyclopropylidene(4-methoxyphenyl)methyl)aniline (1g)



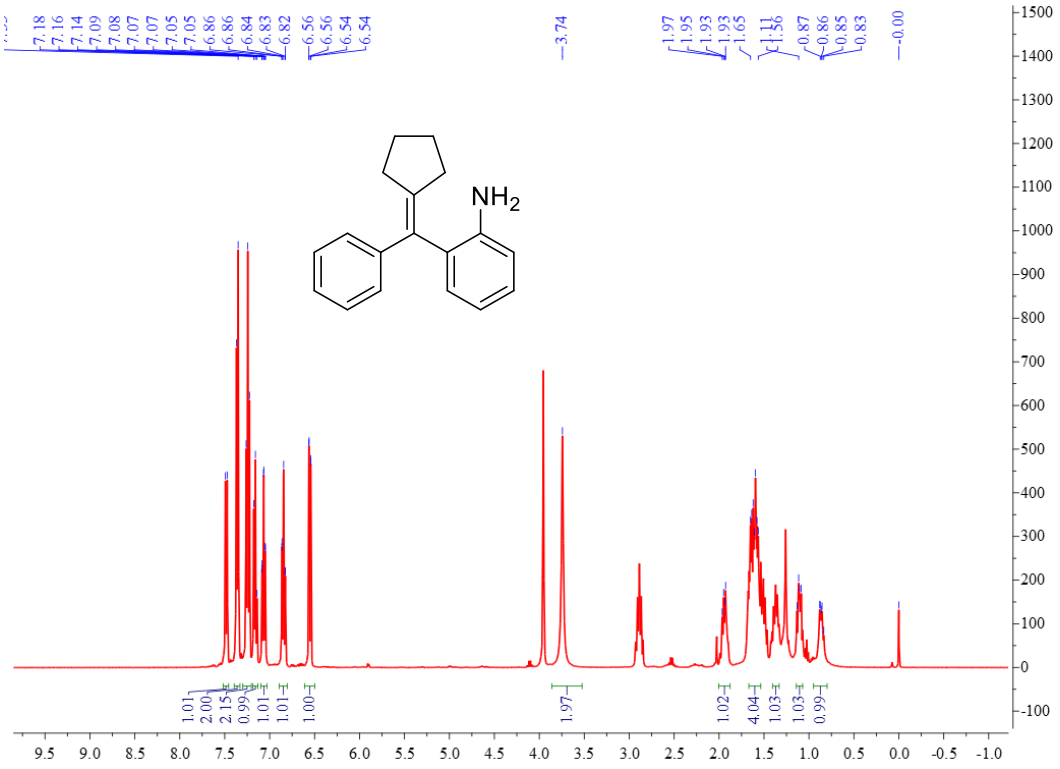


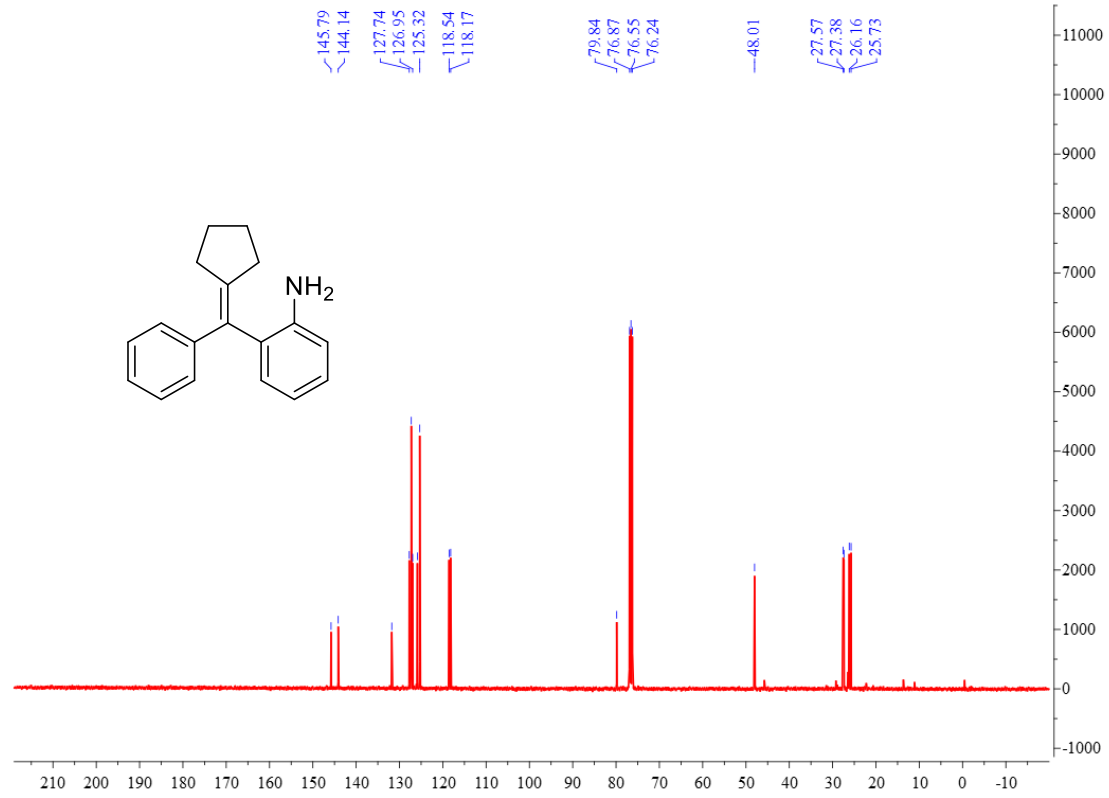
2-(cyclobutylidene(phenyl)methyl)aniline (1u)



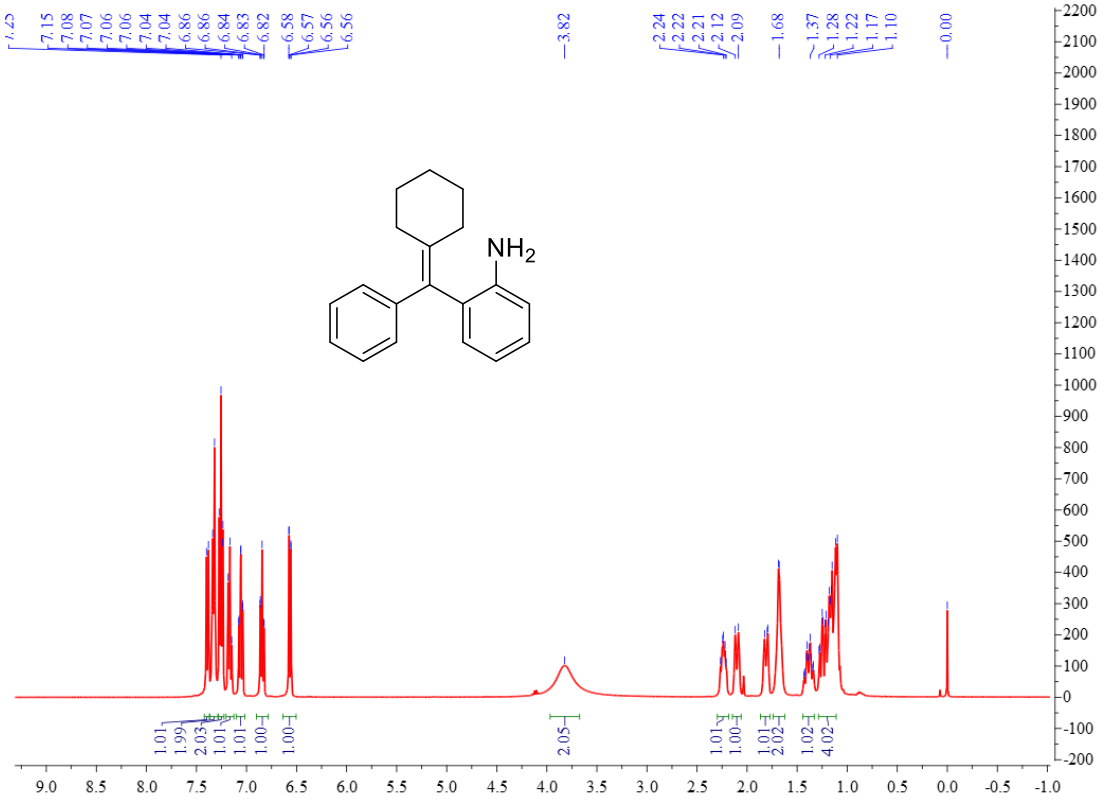


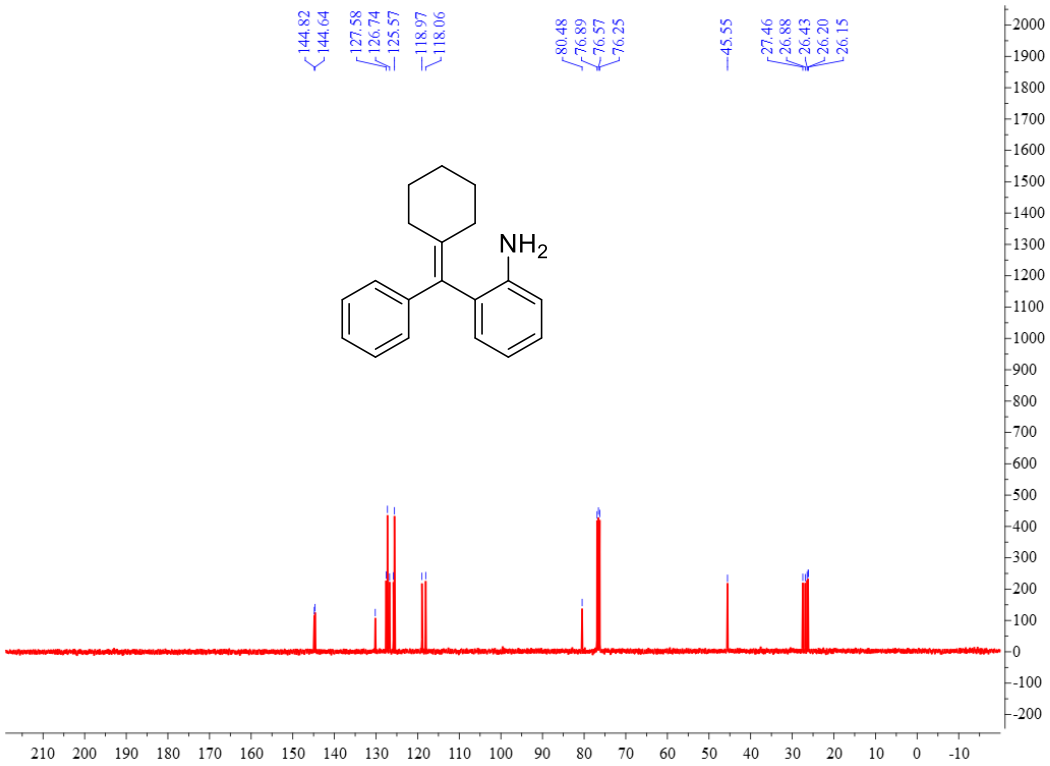
2-(cyclopentylidene(phenyl)methyl)aniline (1a')



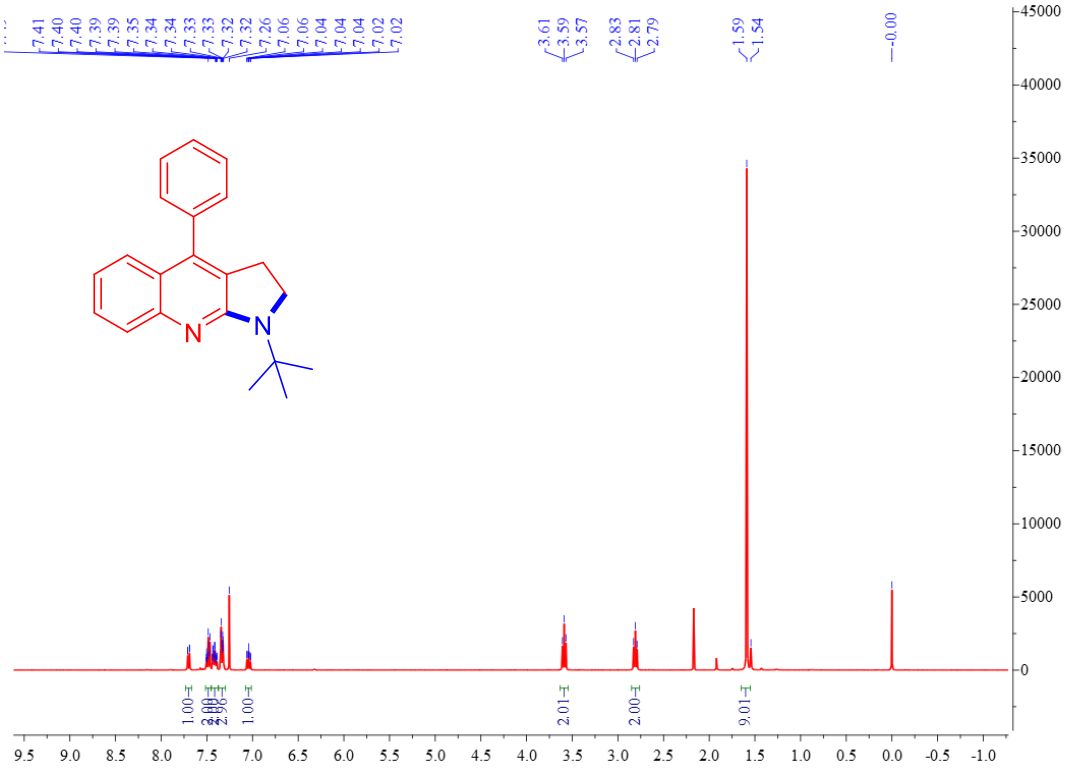


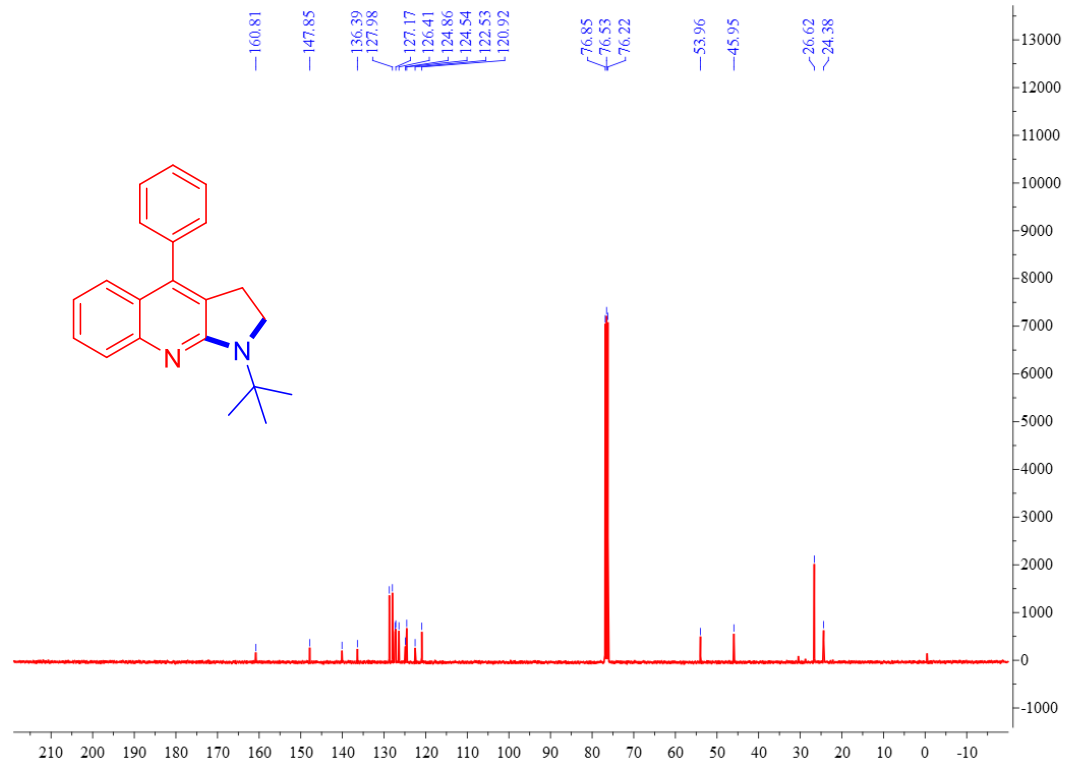
2-(cyclohexylidene(phenyl)methyl)aniline (1b’)



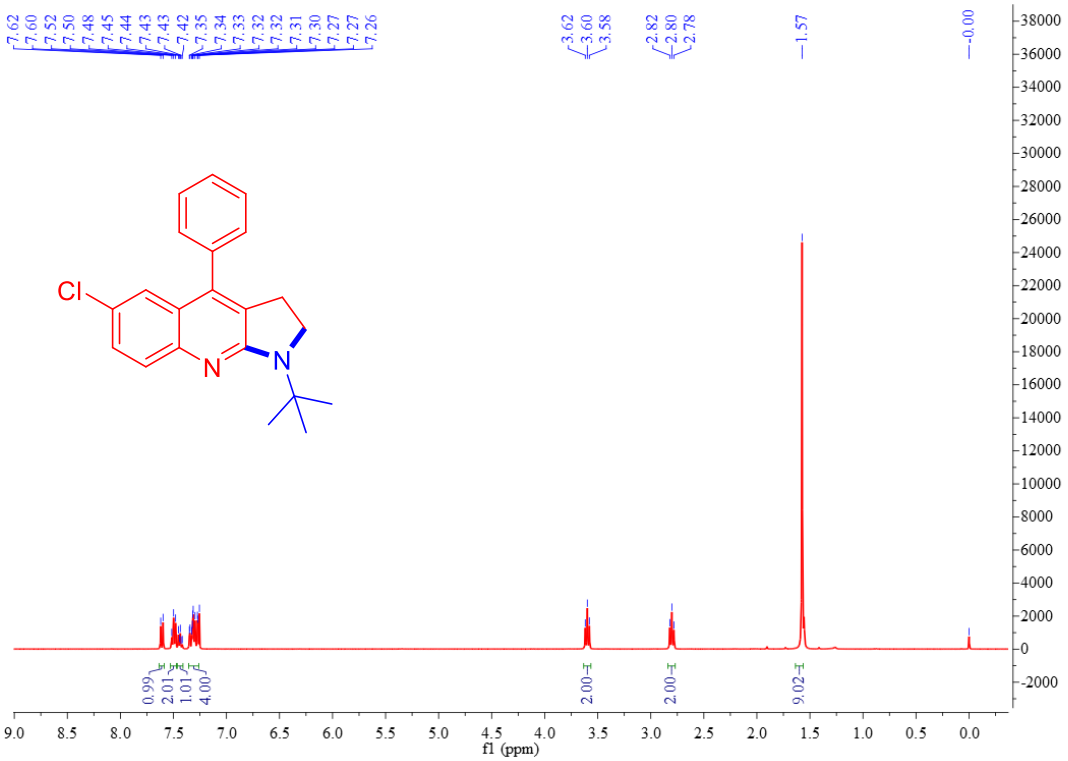


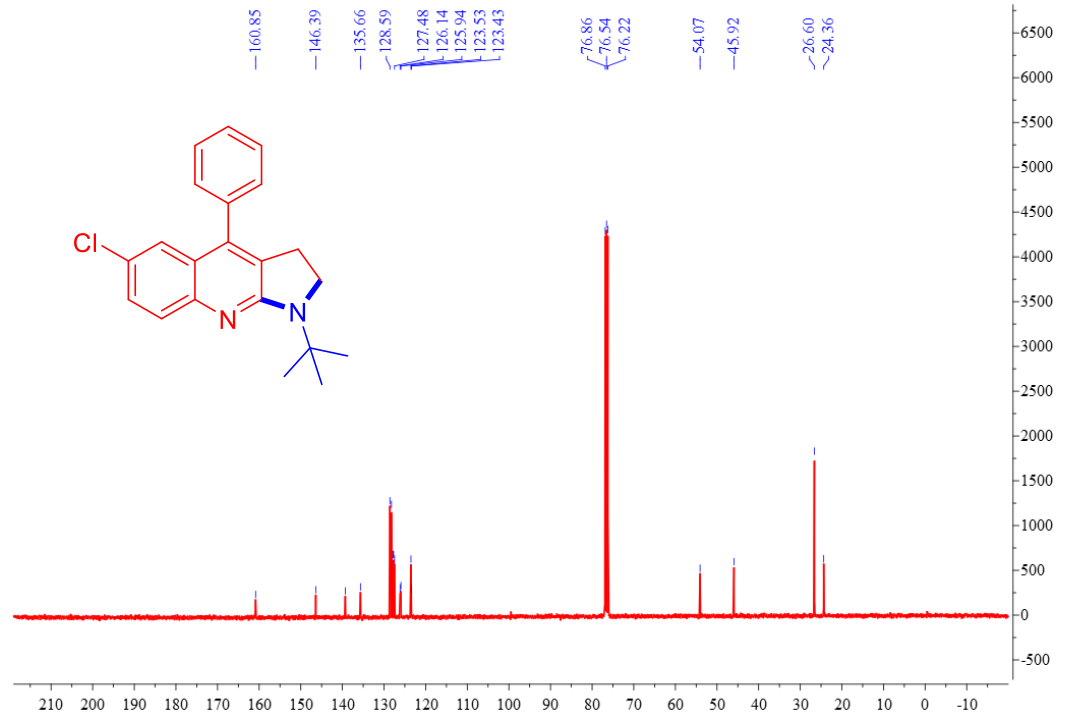
1-(tert-butyl)-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3a)



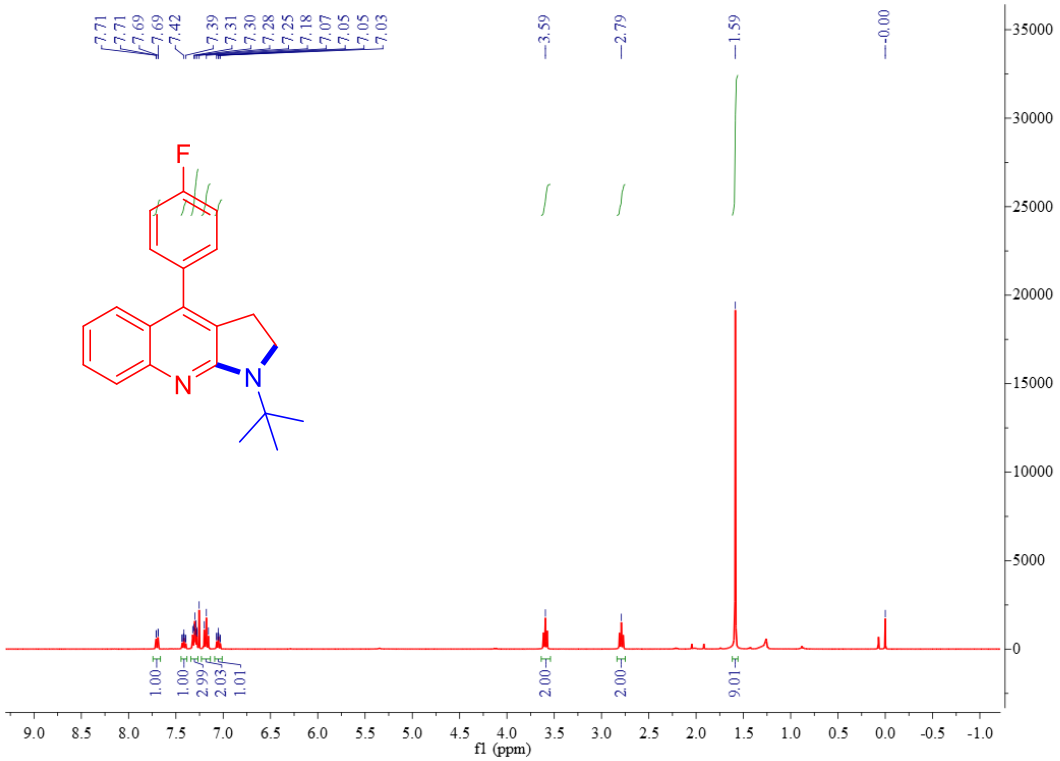


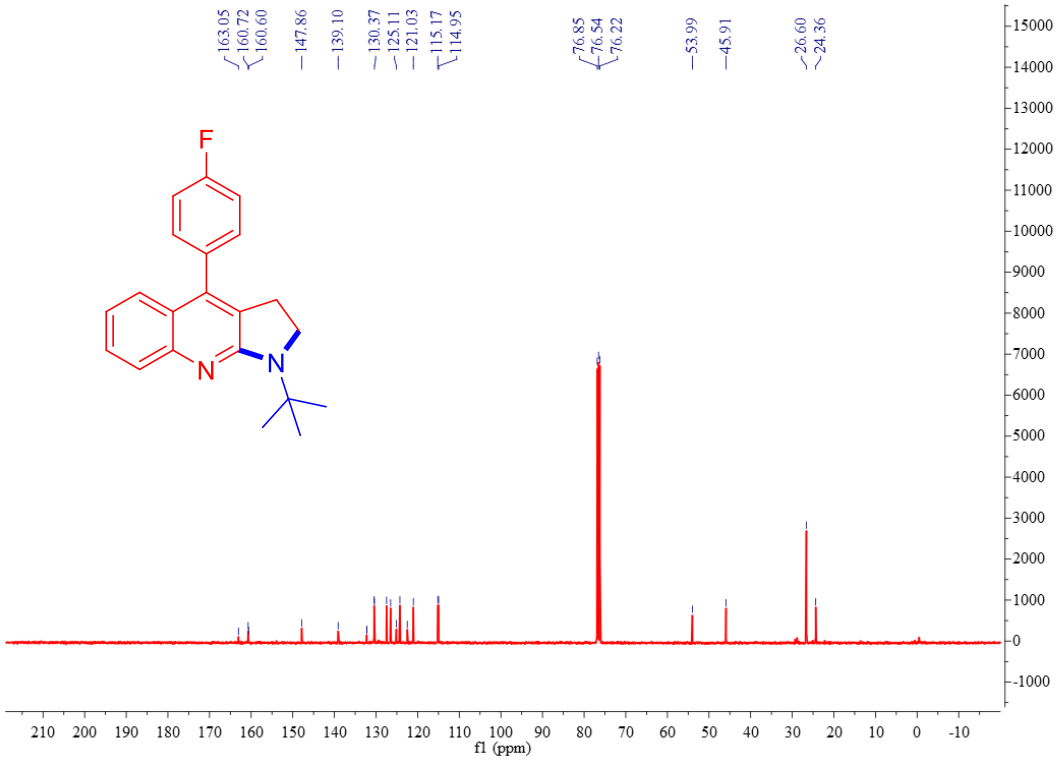
1-(tert-butyl)-6-chloro-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3b)



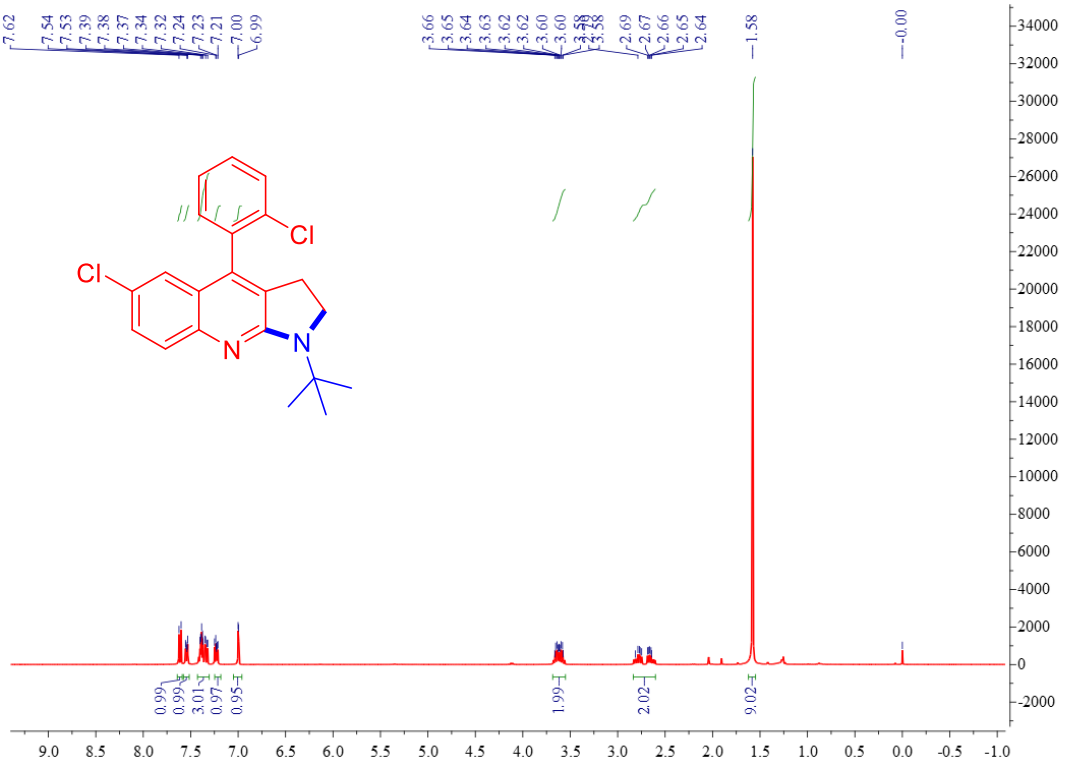


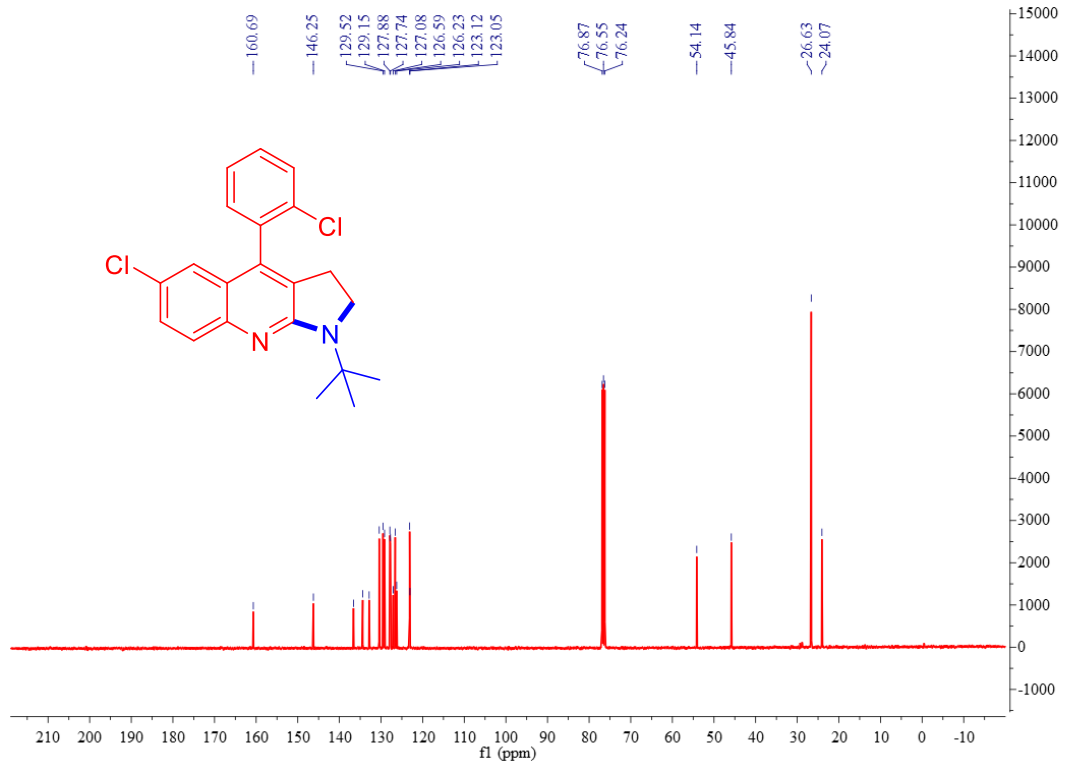
1-(tert-butyl)-4-(4-fluorophenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3c)



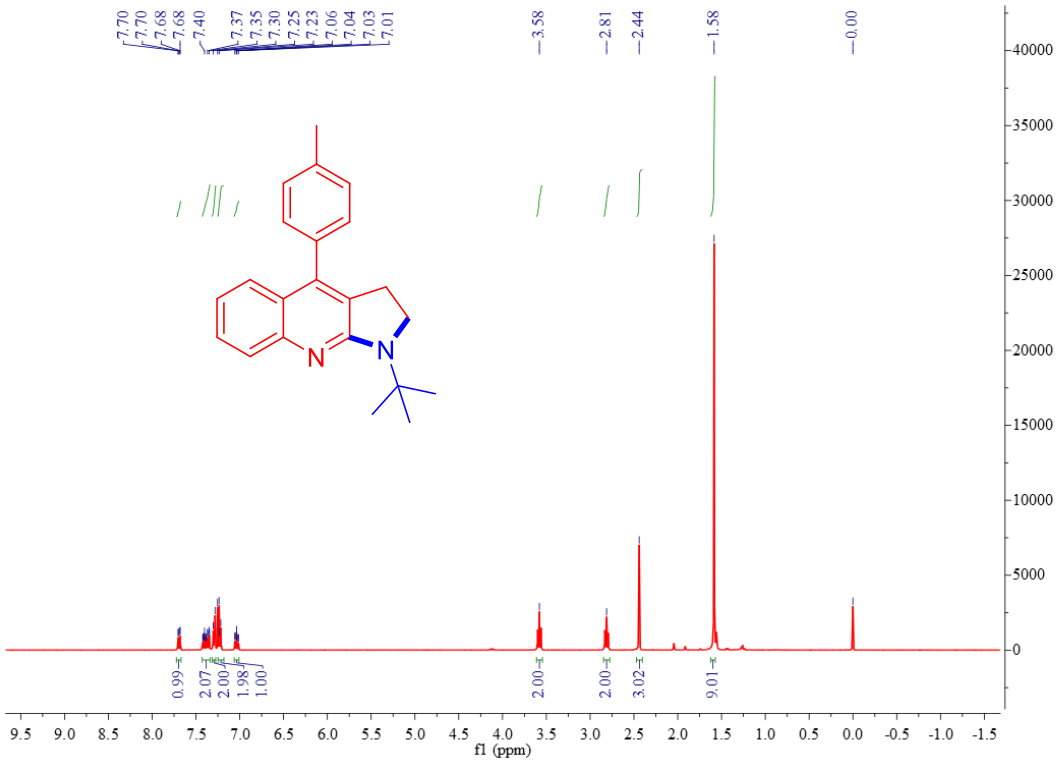


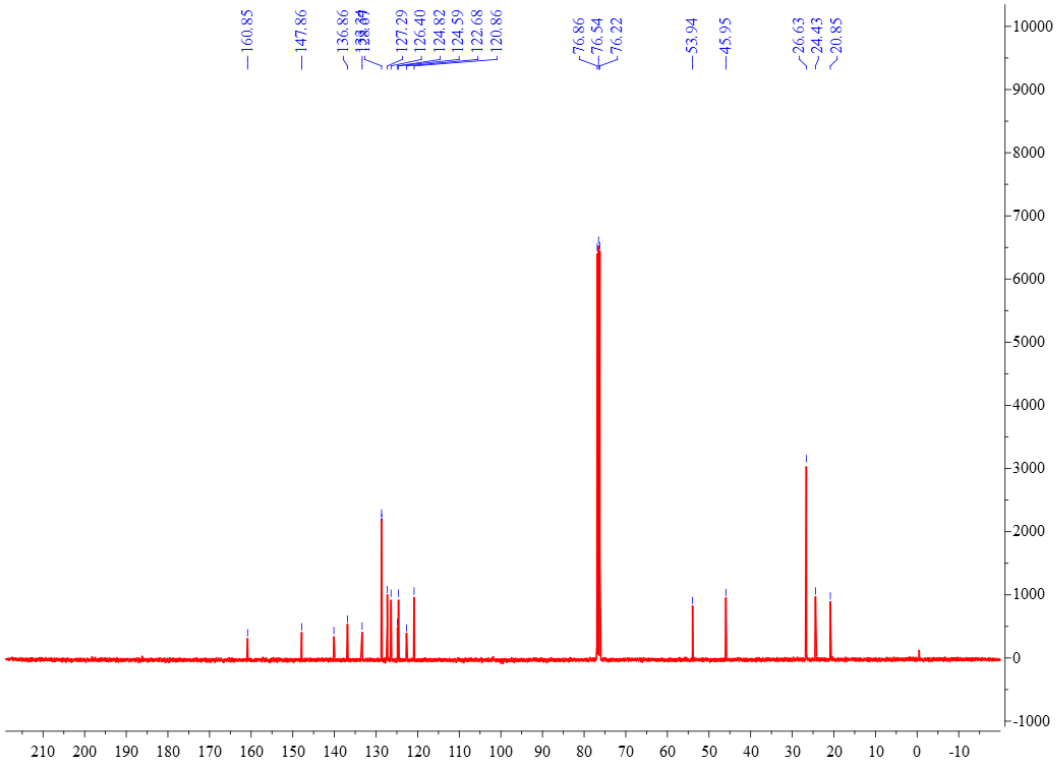
1-(tert-butyl)-6-chloro-4-(2-chlorophenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3d)



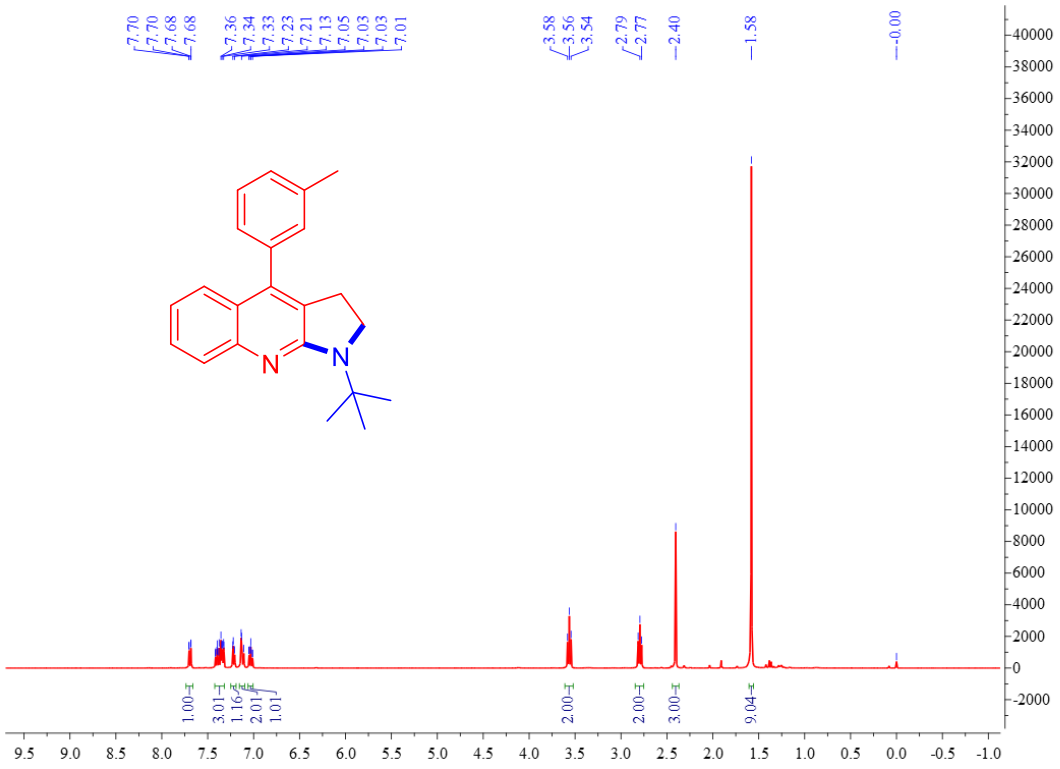


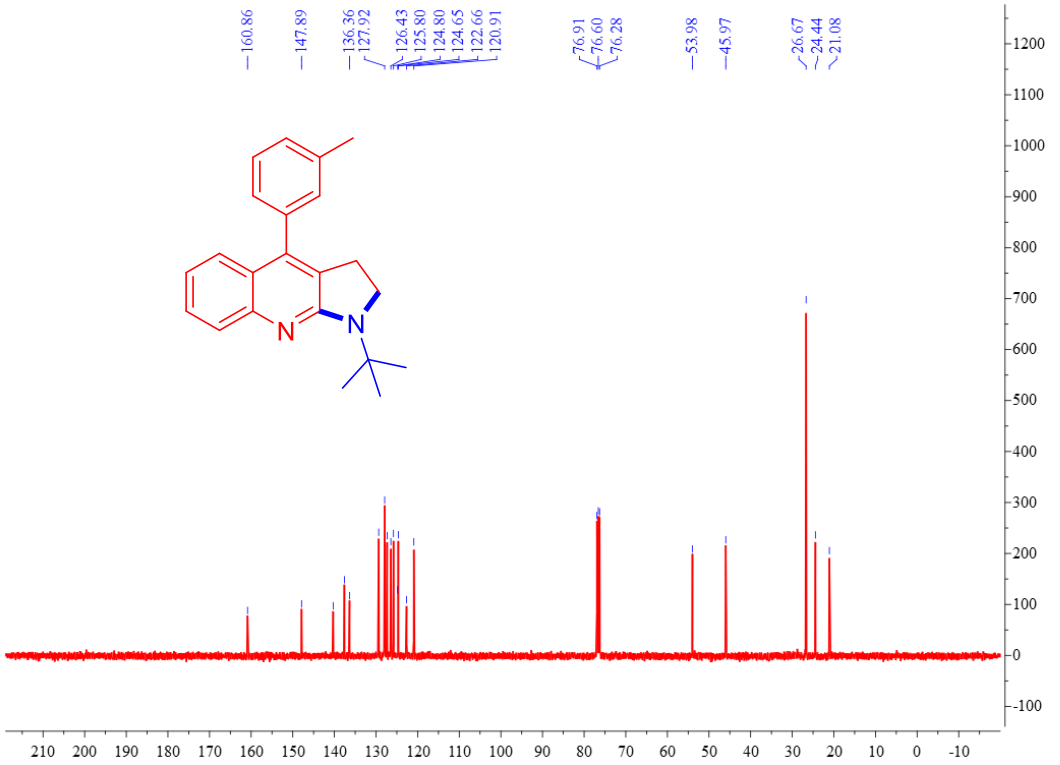
1-(tert-butyl)-4-(p-tolyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3e)



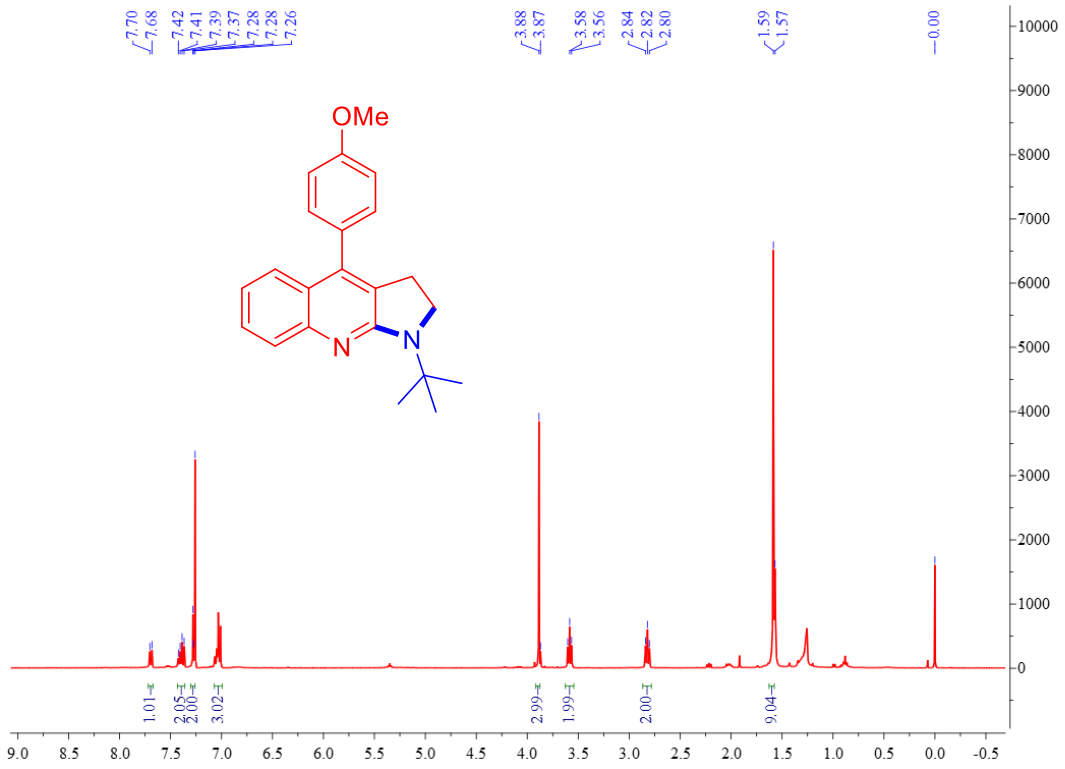


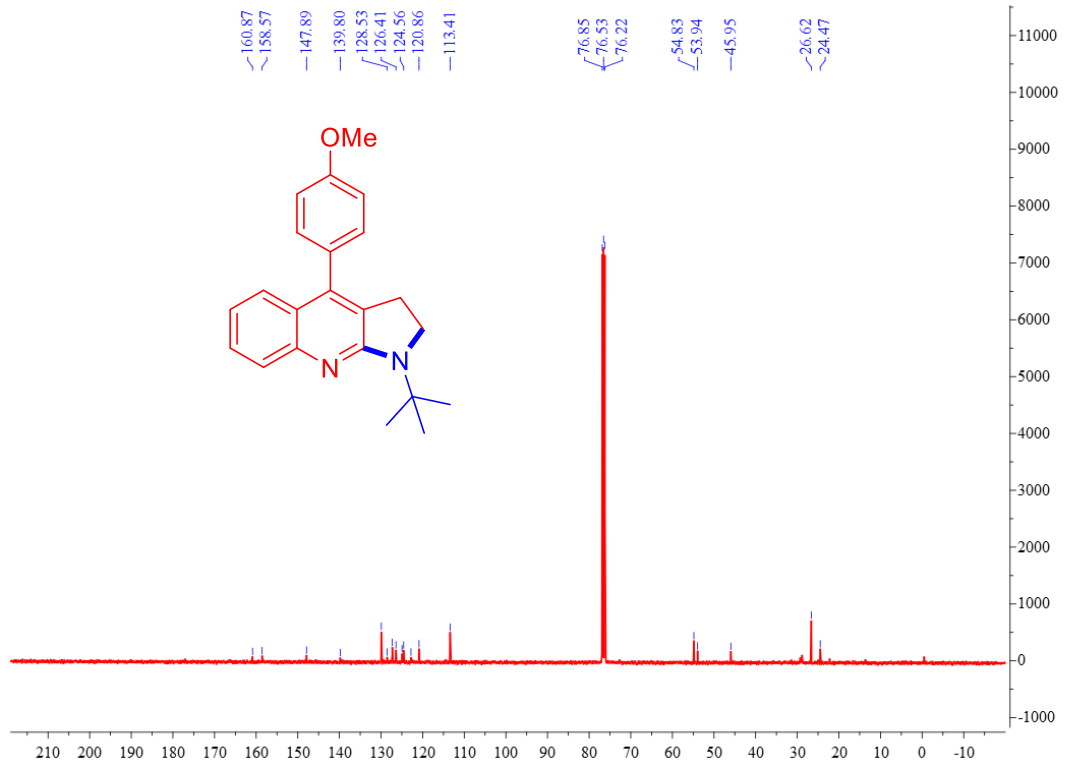
1-(tert-butyl)-4-(m-tolyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3f)



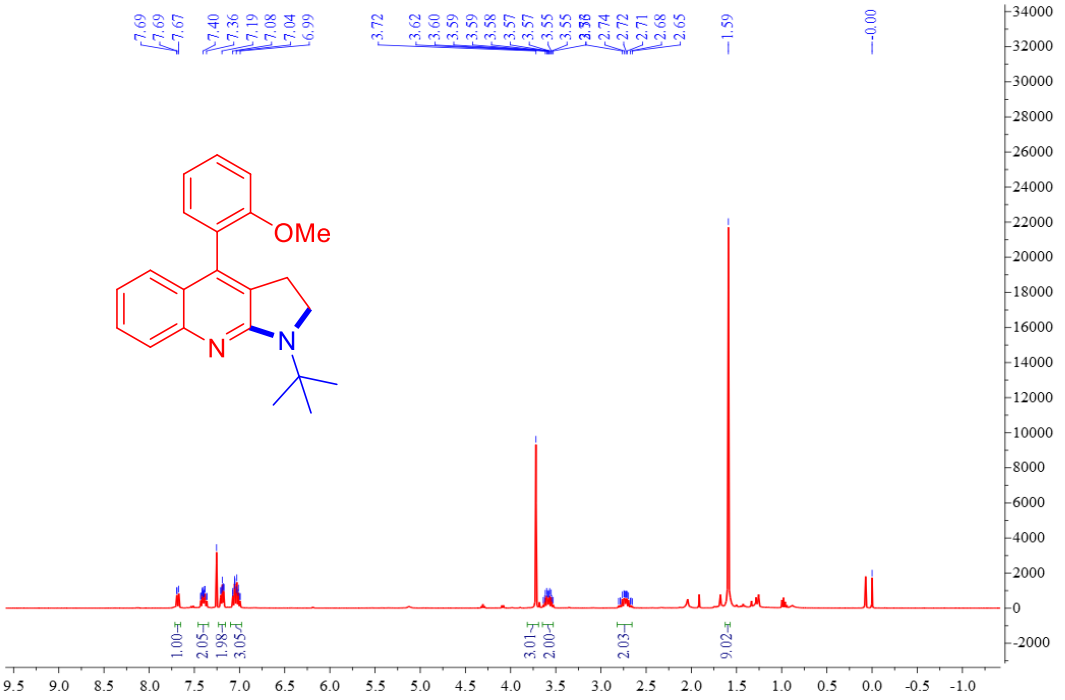


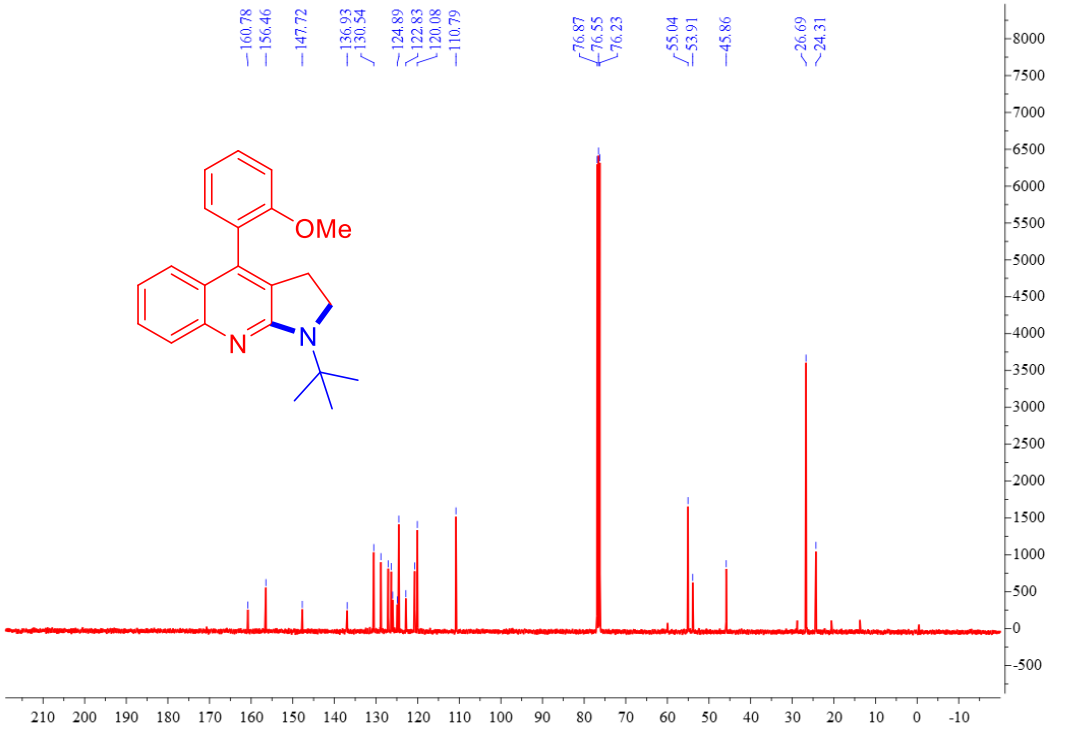
1-(tert-butyl)-4-(4-methoxyphenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3g)



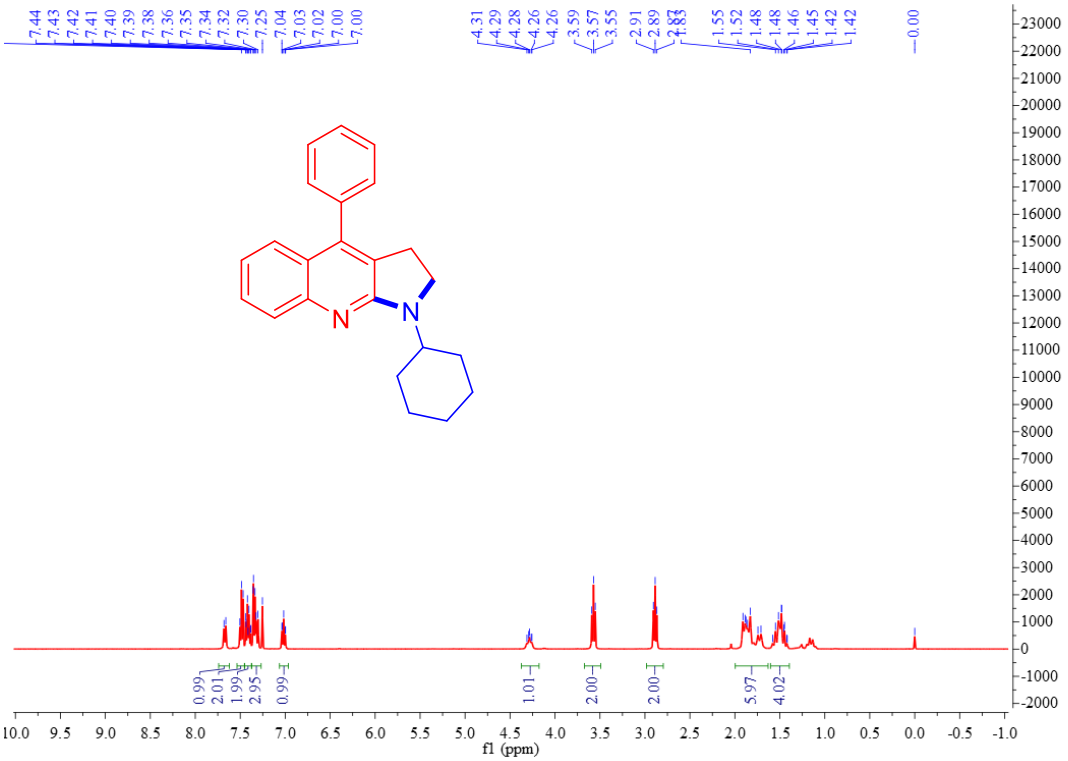


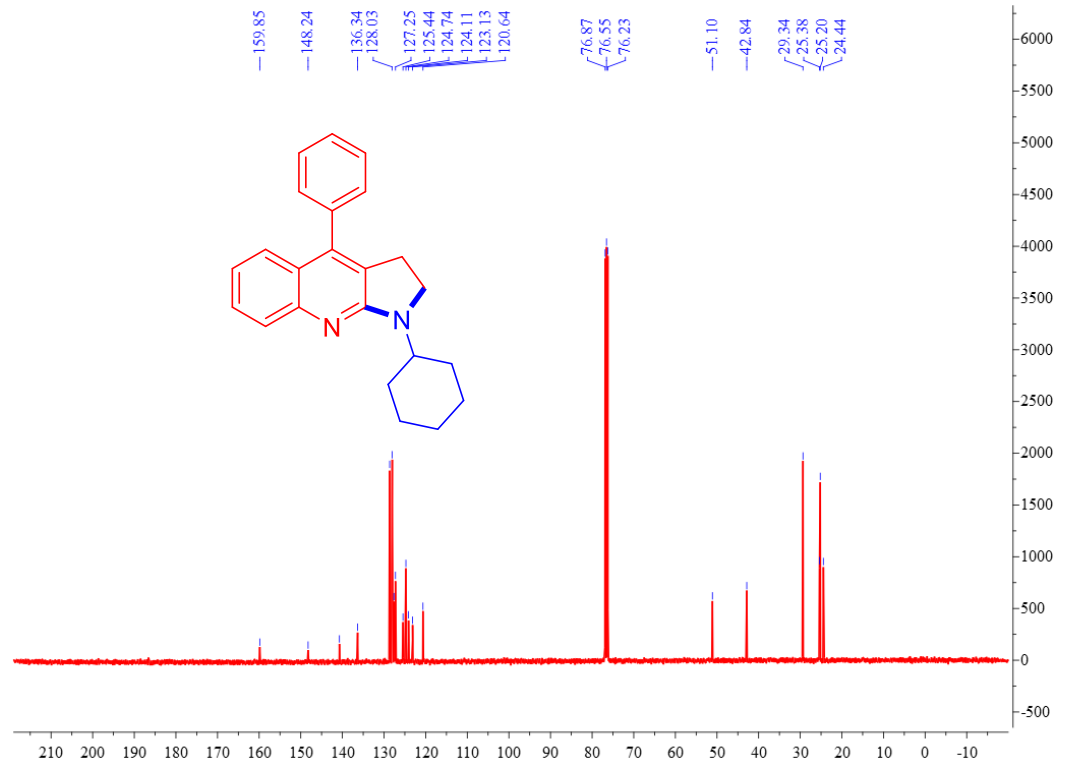
1-(tert-butyl)-4-(2-methoxyphenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3h)



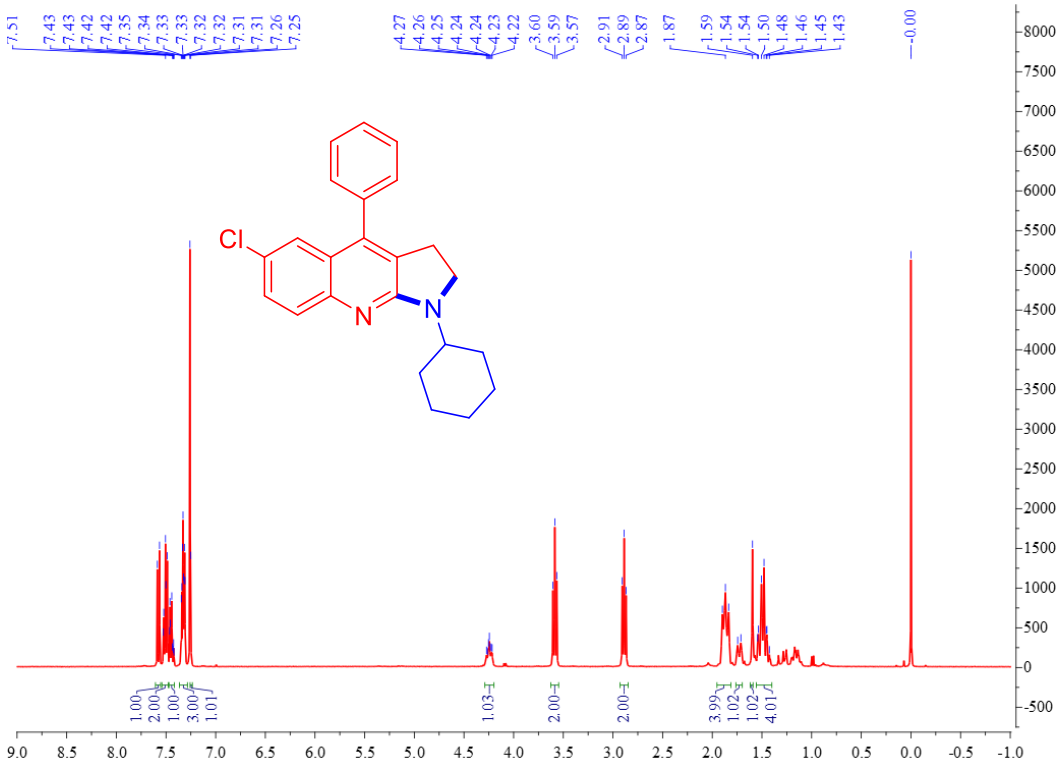


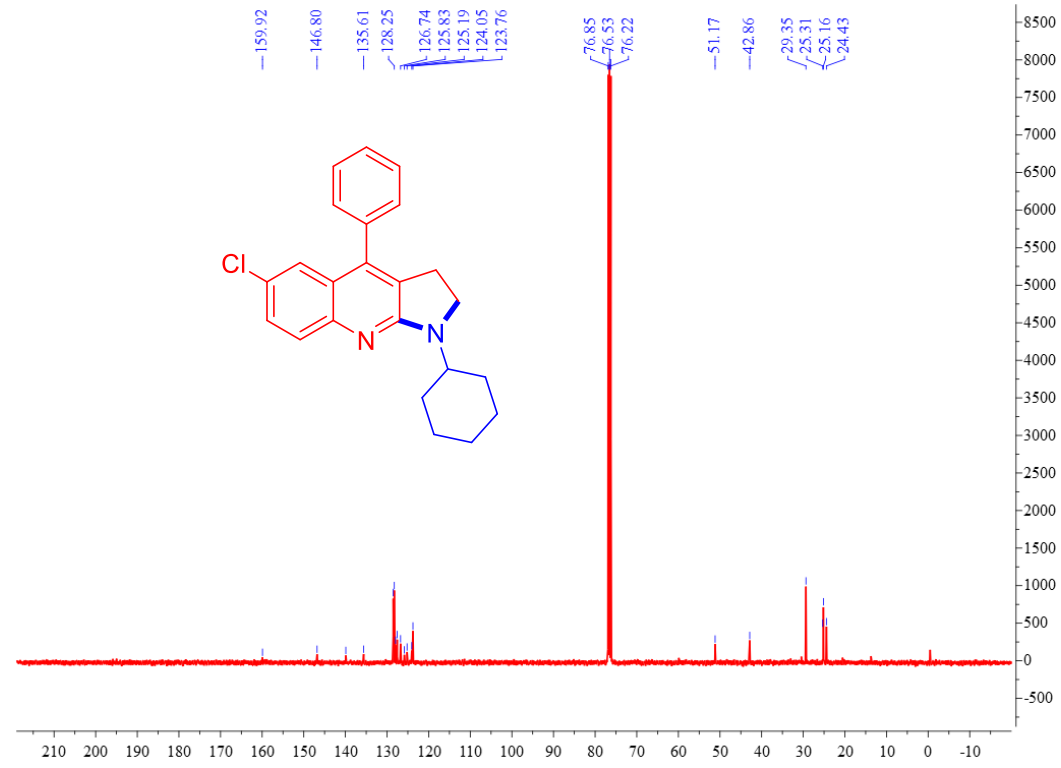
1-cyclohexyl-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3i)



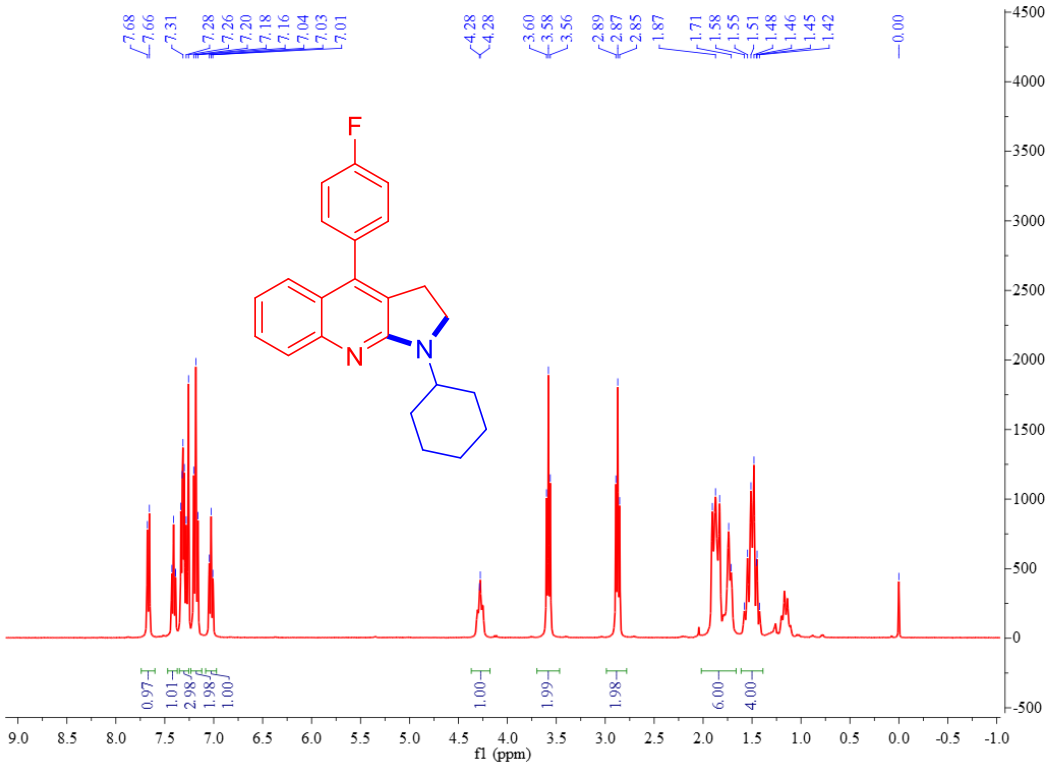


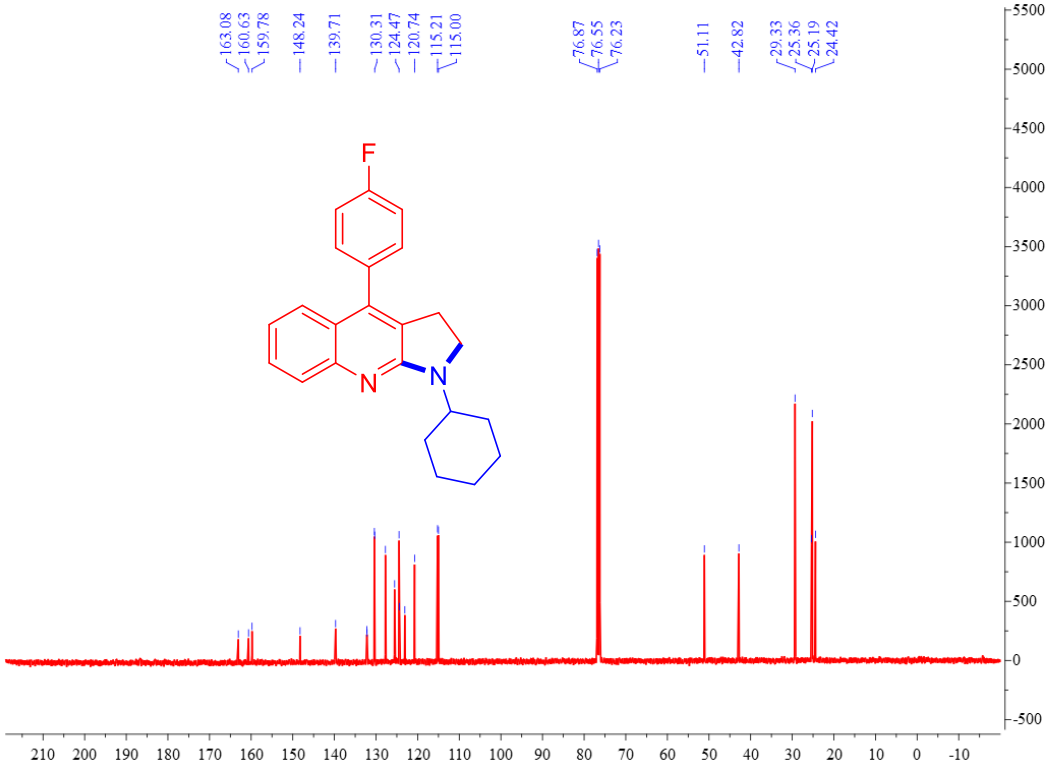
6-chloro-1-cyclohexyl-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline(3j)



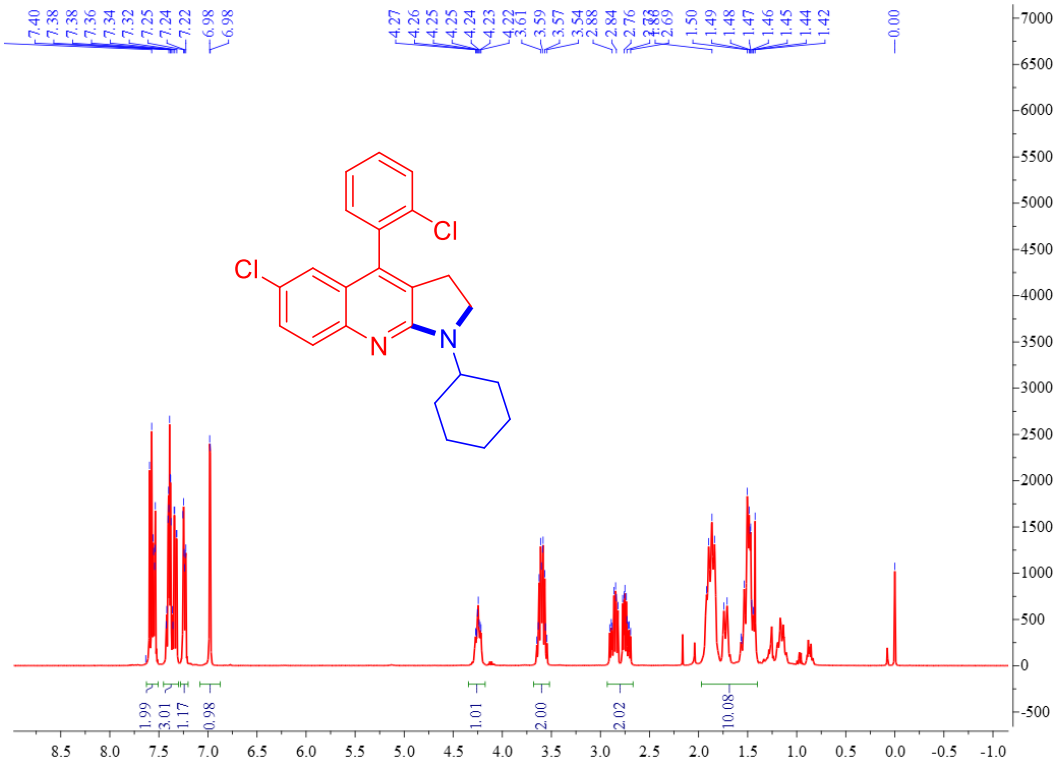


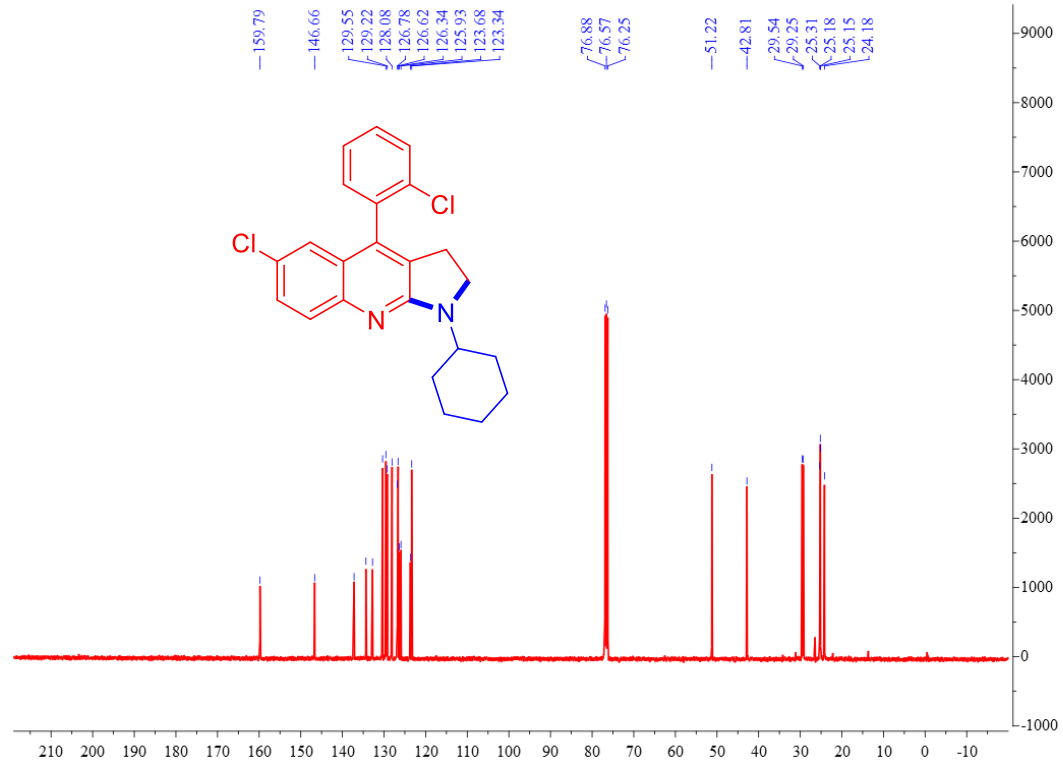
1-cyclohexyl-4-(4-fluorophenyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3k)



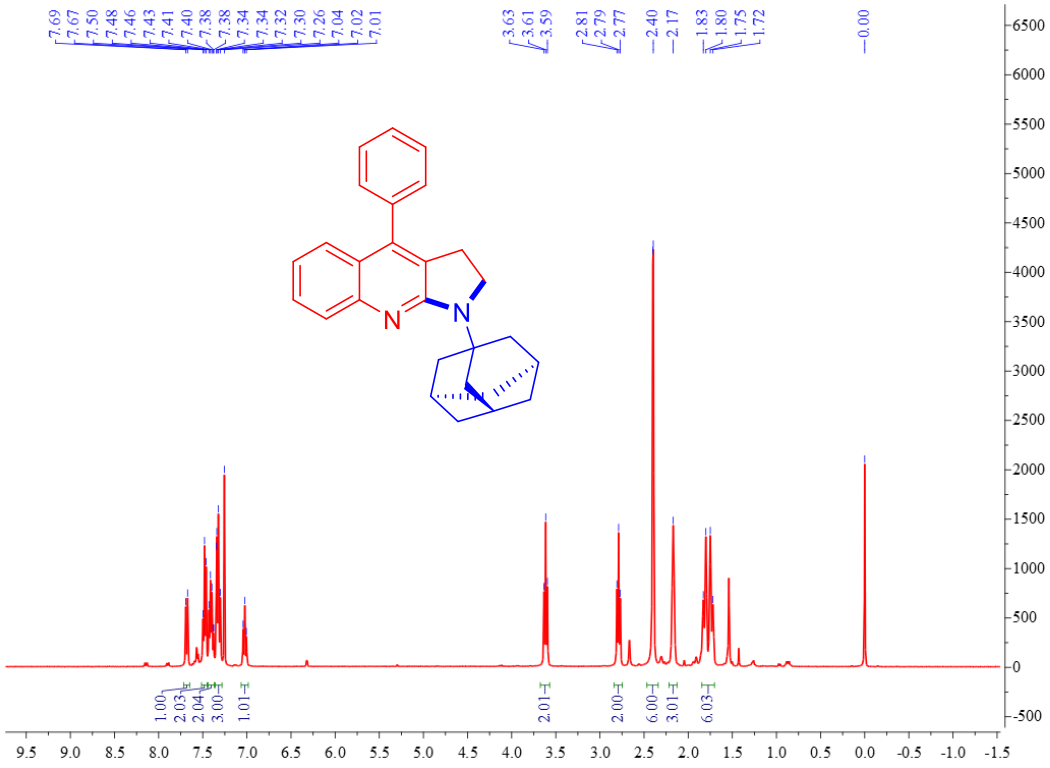


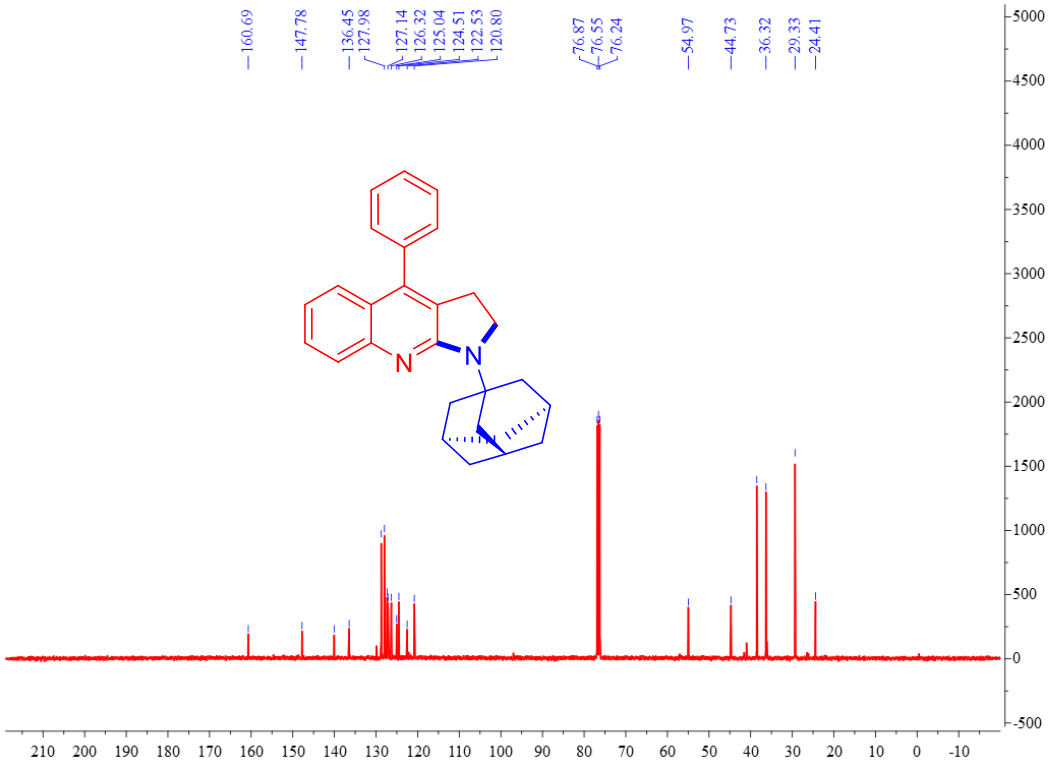
6-chloro-4-(2-chlorophenyl)-1-cyclohexyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinolin e (3l)



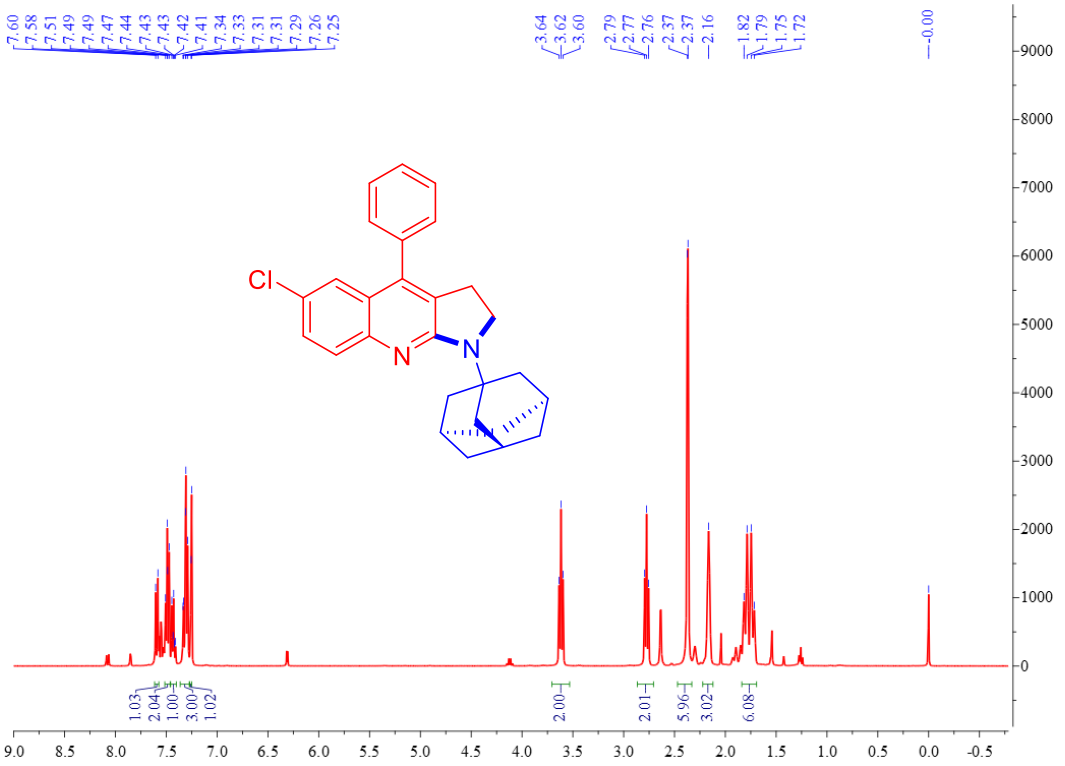


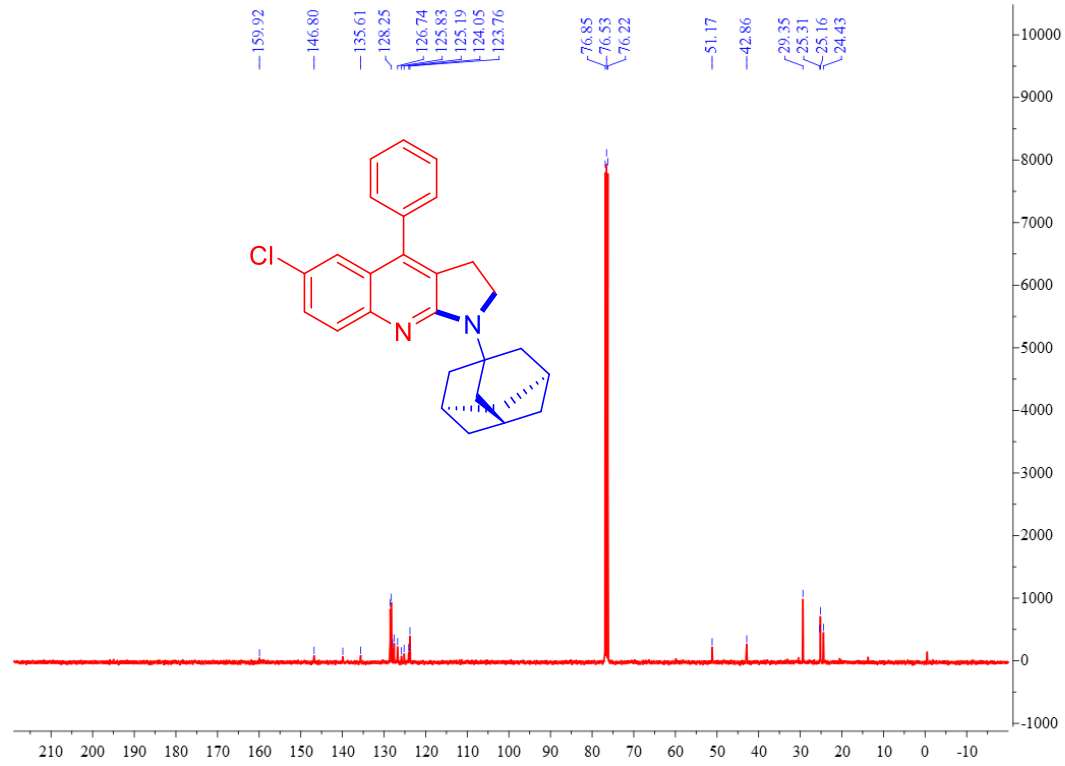
1-((3r)-adamantan-1-yl)-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3m)



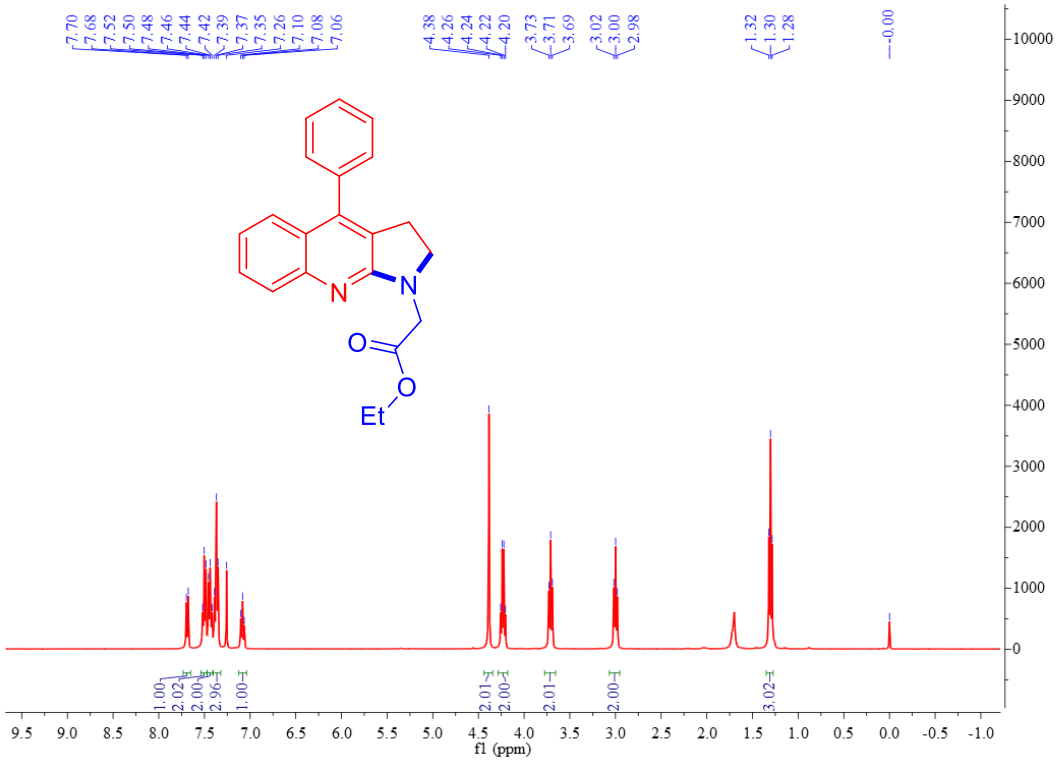


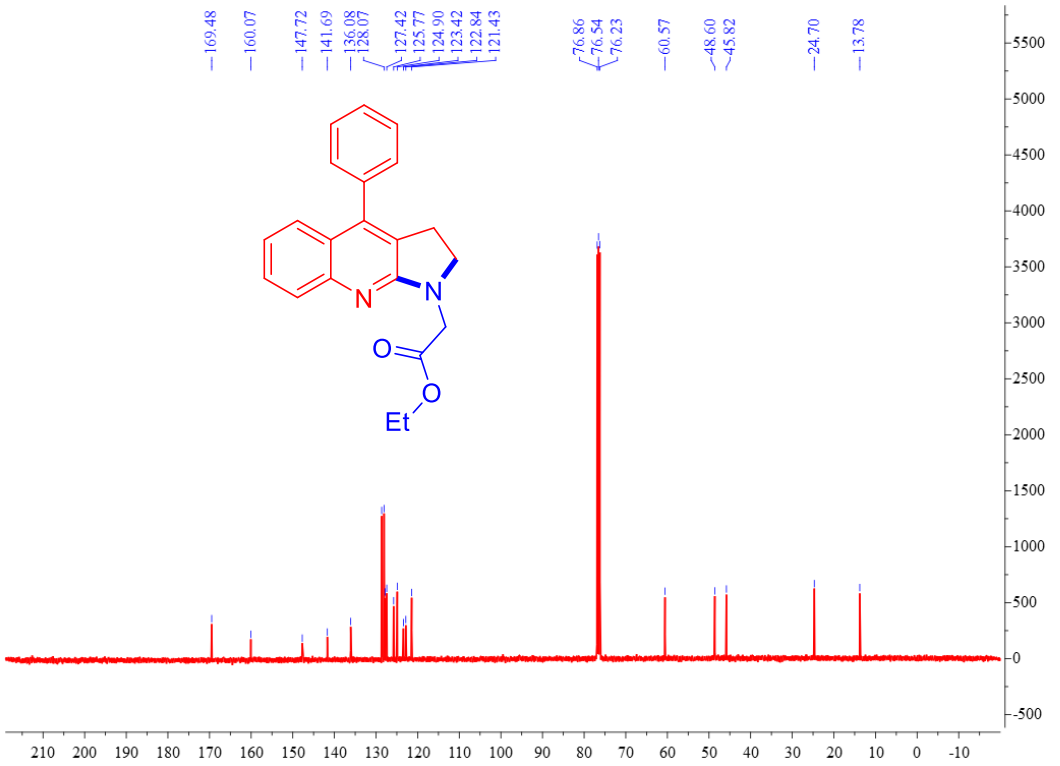
1-((3r)-adamantan-1-yl)-6-chloro-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3n)



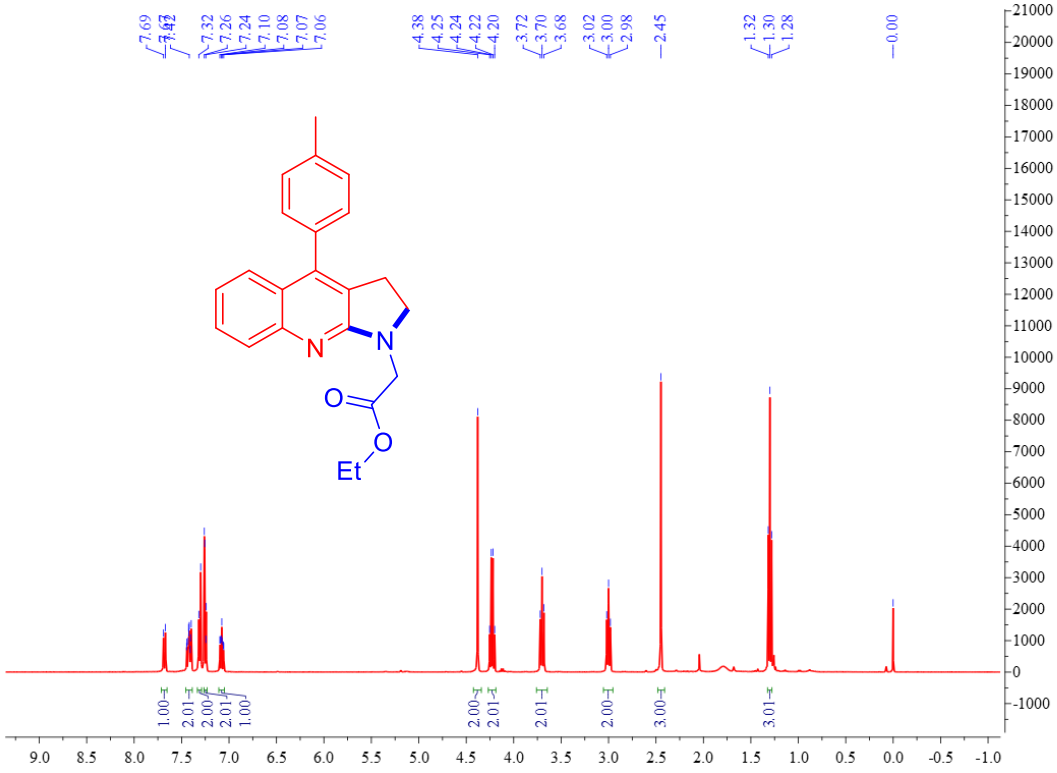


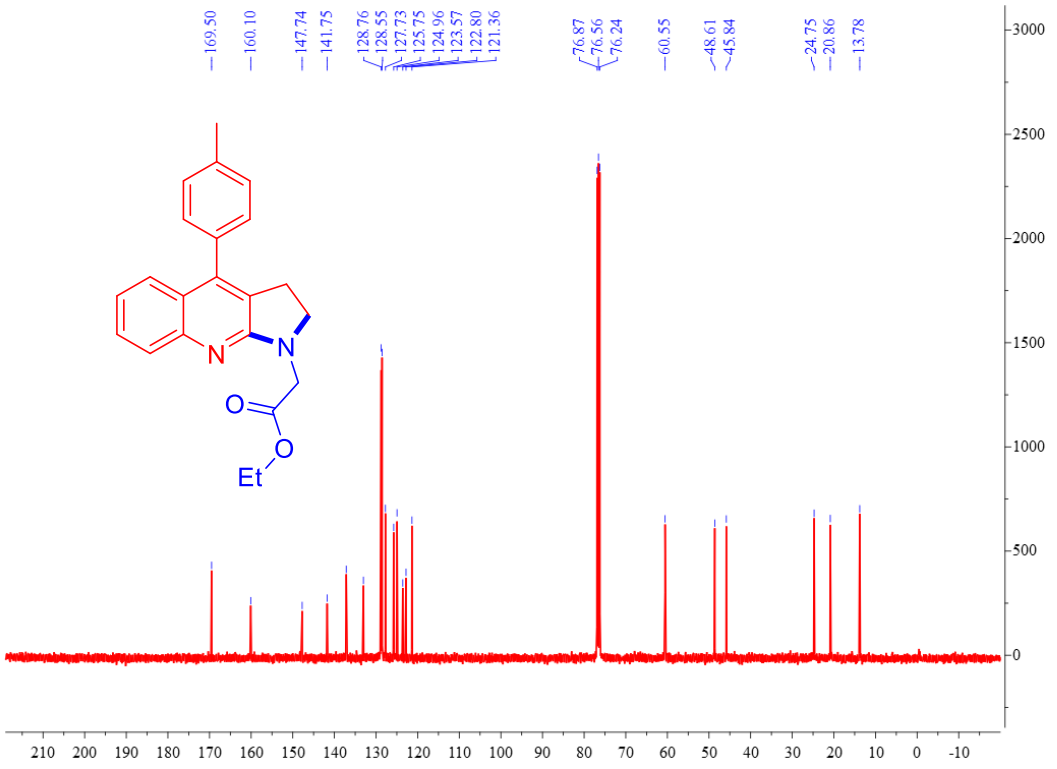
ethyl 2-(4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinolin-1-yl)acetate (3o)



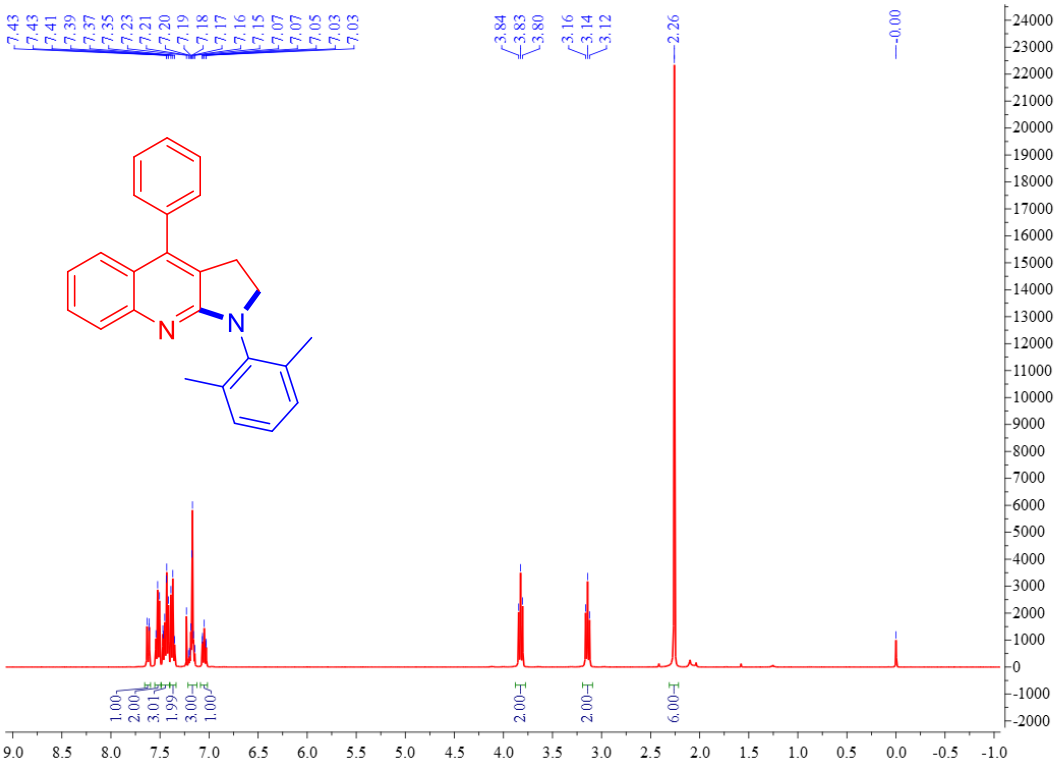


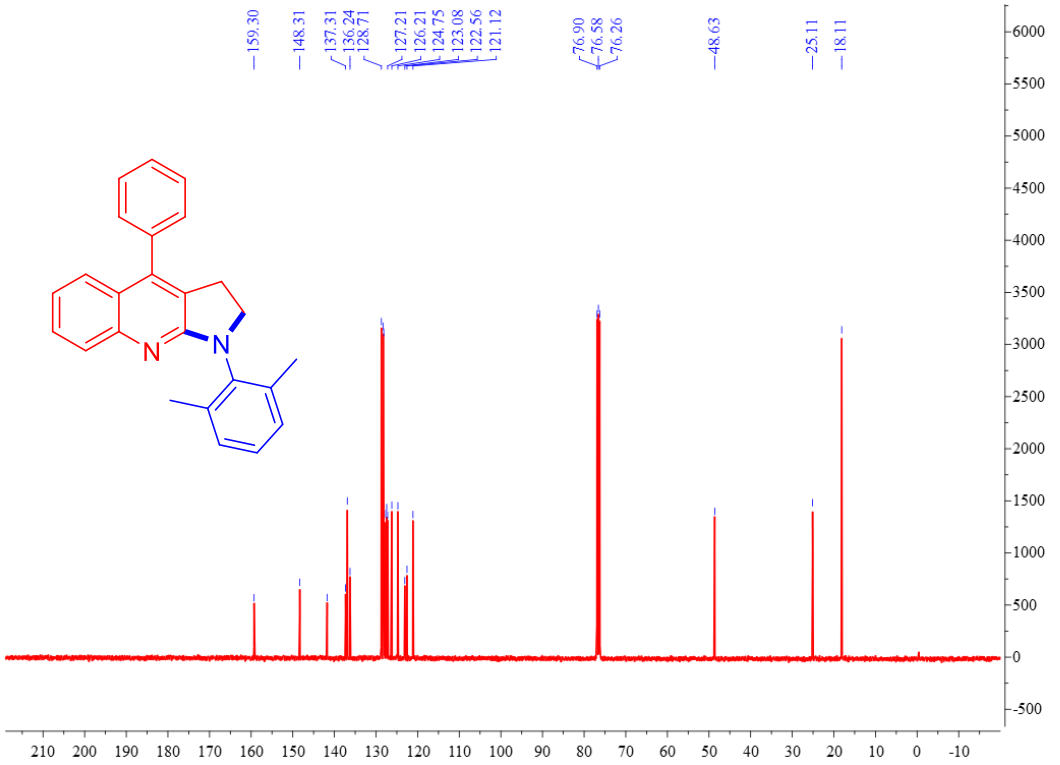
ethyl 2-(4-(p-tolyl)-2,3-dihydro-1H-pyrrolo[2,3-b]quinolin-1-yl)acetate (3p)



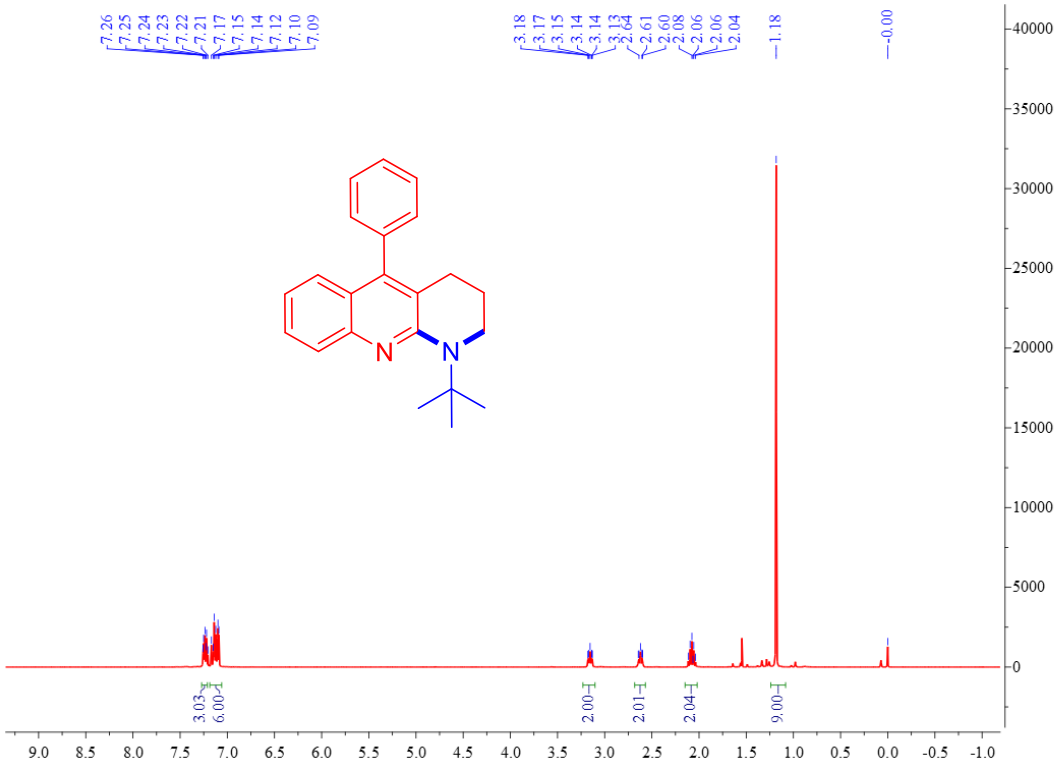


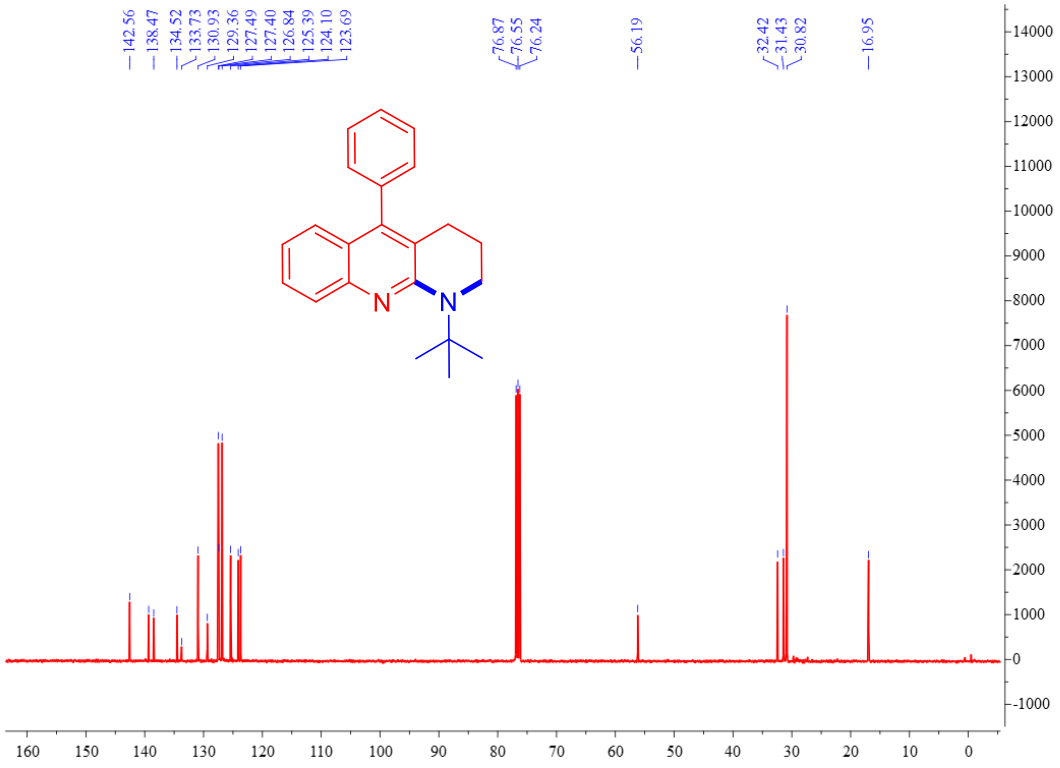
1-(2,6-dimethylphenyl)-4-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]quinoline (3q)



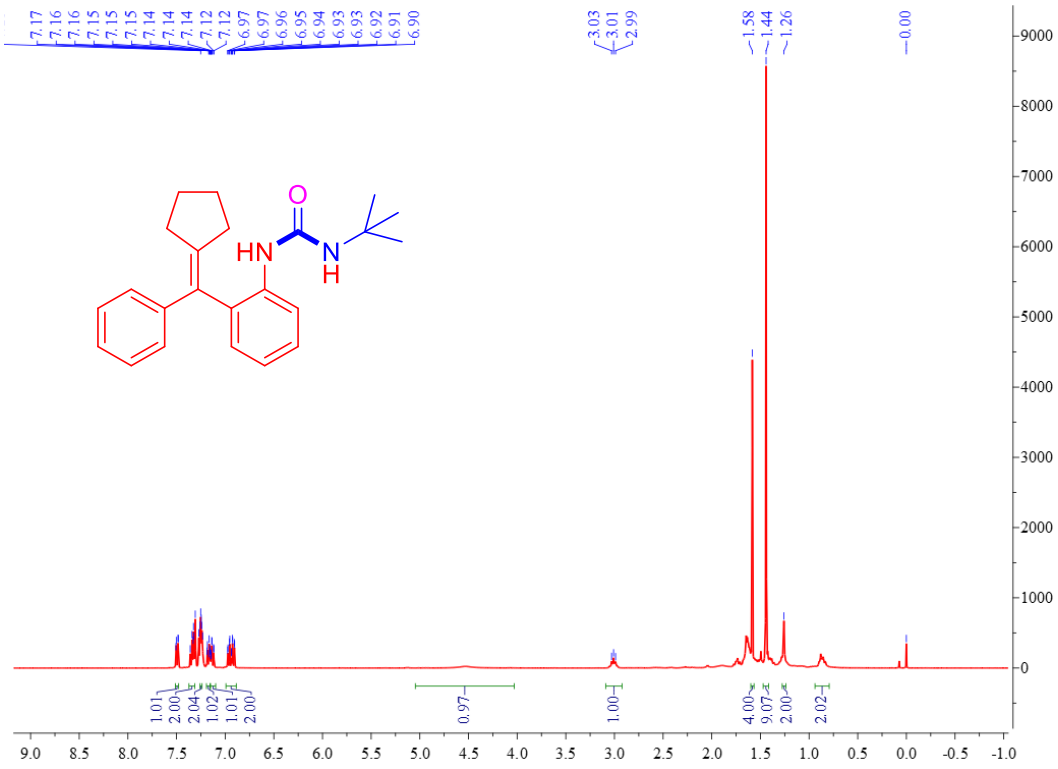


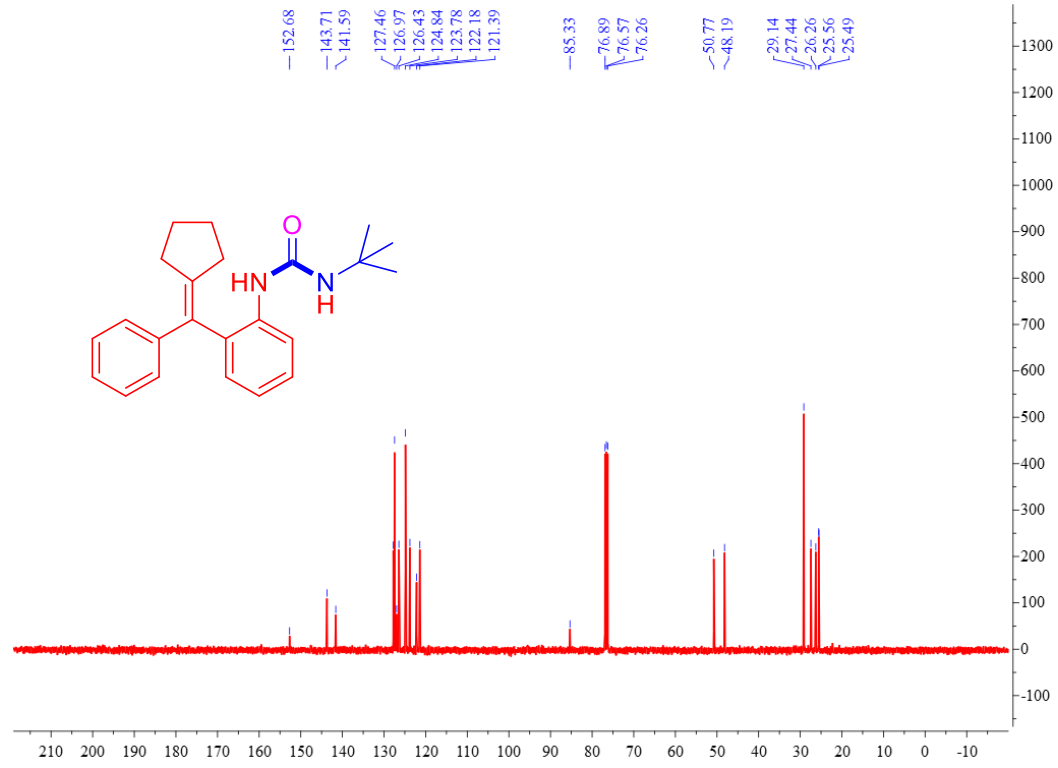
1-(tert-butyl)-5-phenyl-1,2,3,4-tetrahydrobenzo[b][1,8]naphthyridine (3u)



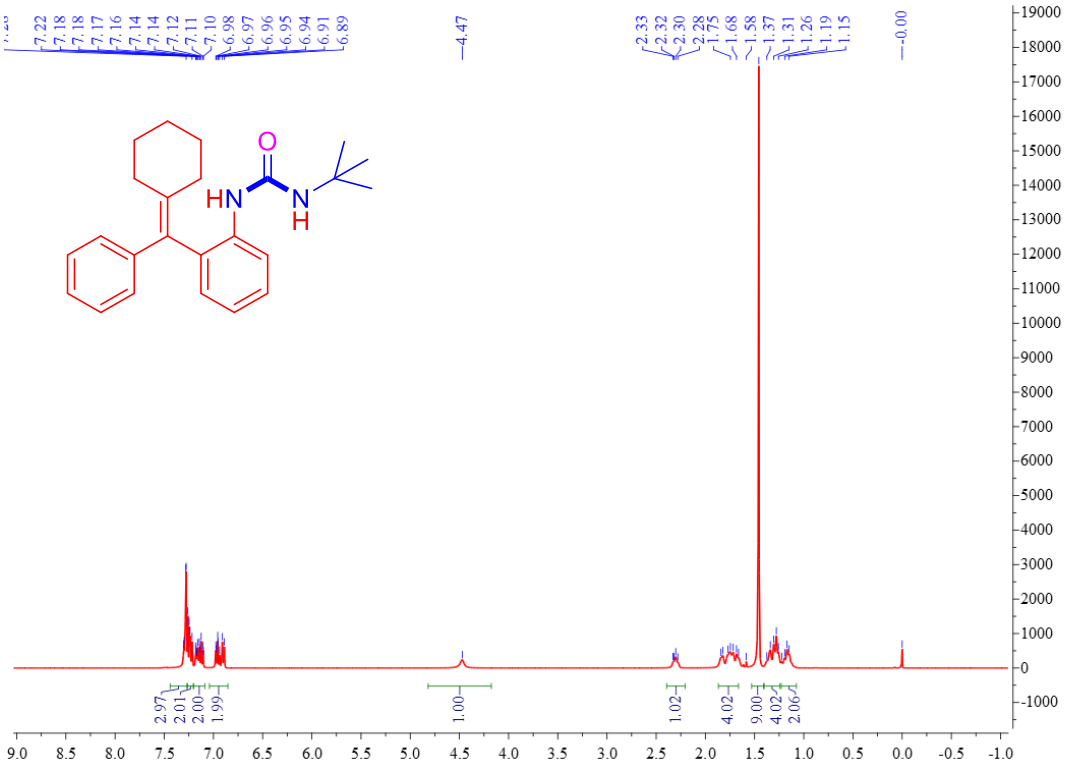


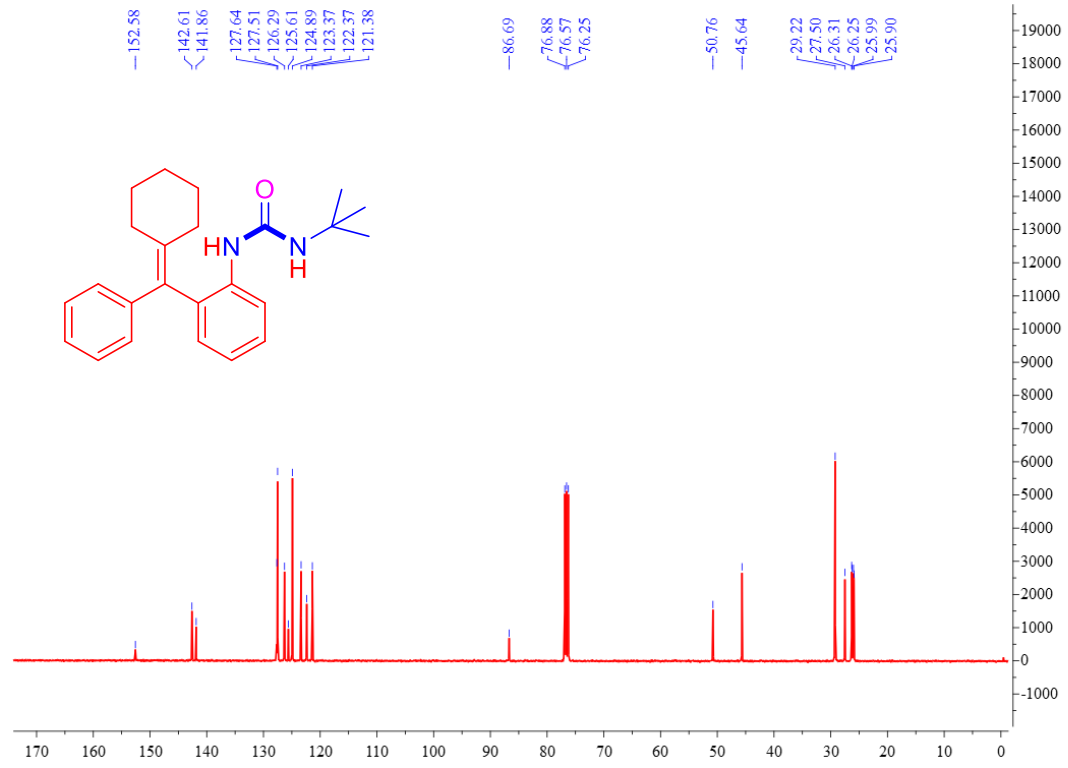
1-(tert-butyl)-3-(2-(cyclopentylidene(phenyl)methyl)phenyl)urea (4a)





1-(tert-butyl)-3-(2-(cyclohexylidene(phenyl)methyl)phenyl)urea (4b)





The crystal data of 3i

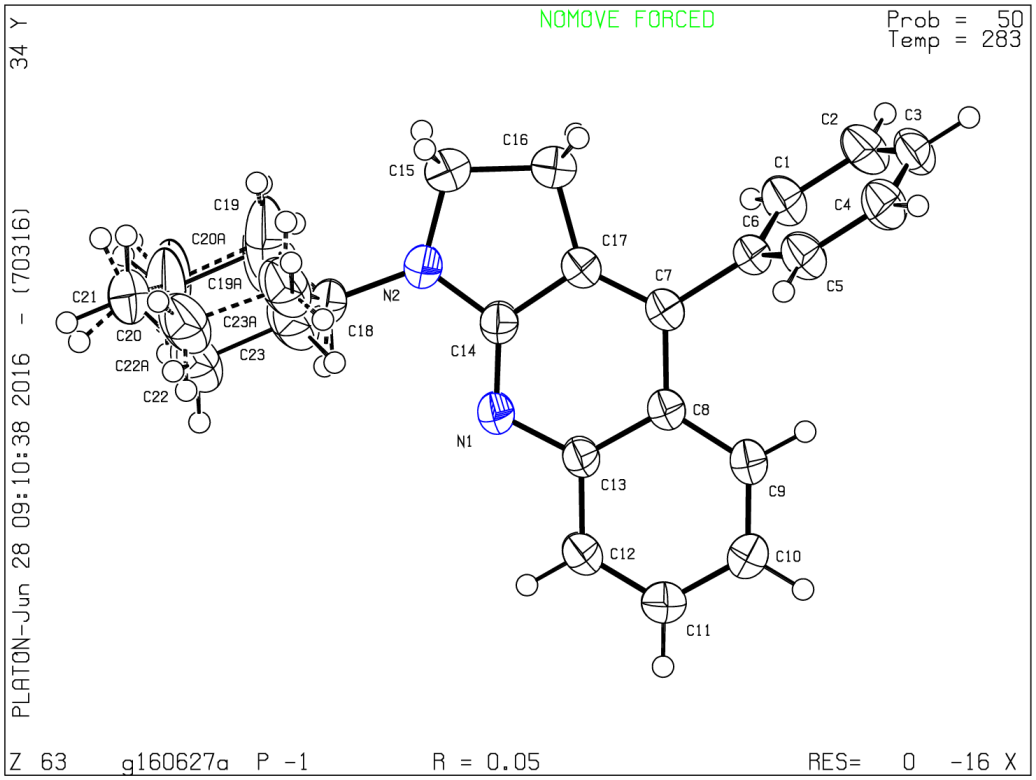


Figure 1. X-ray structure of **3i**
Crystal Number: CCDC 1494641
Empirical formula: $C_{23}H_{24}N_2$
Formula weight: 328.44
Unit cell parameters: *a* = 6.2020 (5) Å, *b* = 10.1690 (10) Å, *c* = 14.7158 (18) Å, α = 75.057(10), β = 85.343(8), γ = 84.132(7).
space group P -1.
Temperature: 283(10) K
Wavelength: 0.71070 Å
Crystal system: Triclinic
Volume: 890.56(16) Å
Z: 2
Calculated density: 1.225 Mg/m3
Absorption coefficient: 0.072 mm^{-1}
F (000): 352
Crystal size: 0.5×0.4× 0.3 mm^3
Correction-type: multi-scan
h, k, l max: 7, 12, 18
Tmin,Tmax: 0.899/ 1.000
R1 = 0.0529, **wR2** = 0.1477.

Reference

1 (a) J. A. Stafford and J. E. McMurry, *Tetrahedron Lett.* 1988, **29**, 2531; (b) K. Utimoto, M. Tamura and K. Sisido, *Tetrahedron* 1973, **29**, 1169; (c) K. Chen, Z. Zhang, Y. Wei and M. Shi. *Chem. Commun.*, 2012, **48**, 7696.

2 K. Chen, Z. Z. Zhu, J. X. Liu, X. Y. Tang, Y. Wei and M. Shi. *Chem. Commun.*, 2016, **52**, 350.