Supporting Information

Ring Expansion of 3-Hydroxyoxindoles to 4-Quinolones *via* Palladium-Catalyzed C–C(acyl) Bond Cleavage

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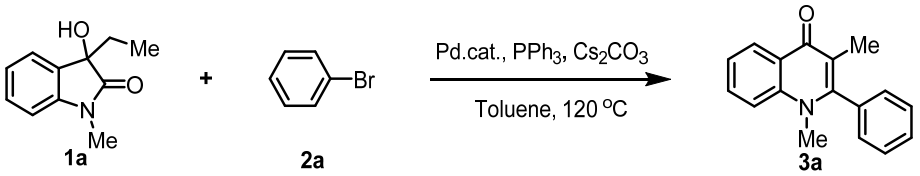
1. General Information

All reagents were purchased from TCI, *J*&K, STREM, Sigma-Aldrich, Adamas-beta, and Energy Chemical of the highest purity grade, and used directly without further purification. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AVANCE III 400 and Bruker AVANCE III 500 instruments. ^{19}F NMR spectra were recorded on Bruker AVANCE III 500 instrument and are reported relative to the $CFCl_3$ as the internal standard. Chemical shifts are reported in parts per million (ppm, δ scale) downfield from TMS at 0.00 ppm and referenced to the $CDCl_3$ at 7.26 ppm (for ^{1}H NMR) or 77.0 ppm (for ^{13}C NMR). The following abbreviations were used to explain multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double of doublets, td = triple doublet, dt = double triplet, tt = triple triplet. EI-double focus magnetic-sector high resolution MS(EI-DFS-HRMS) was recorded on a DFS-Thermofischer instrument employing an ultra-high precision toroidal electrostatic analyzer (ESA) and a carefully refined magnetic analyzer at the Center for Mass Spectrometry, Shanghai Institute of Material Medica. ESI with TOF analyzer was carried out at the Center for Mass Spectrometry, Shanghai Institute of Material Medica. Solvents were purified prior to use according to conventional procedures. Column chromatography was performed on silica gel (200–300 mesh) using a mixture of petroleum ether-ethyl acetate as the eluent. Solvents were purified prior to use according to conventional procedures.

2. Optimization Reaction Conditions

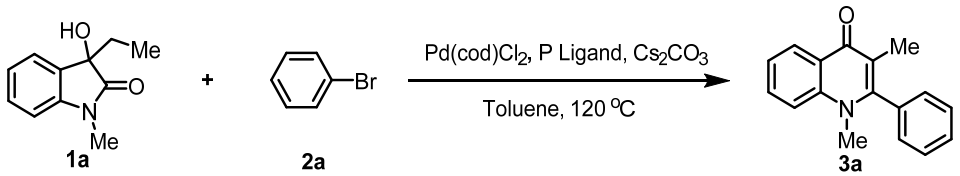
Table S1. Screening of the Pd catalysts

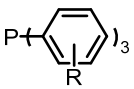


Entry	Pd.cat.	Yield (%)
1	Pd_2dba_3	77
2	$Pd(PPh_3)_4$	76
3	$PdCl_2$	74
4	$Pd(OAc)_2$	74
5	$Pd(cod)Cl_2$	80
6	$Pd(acac)_2$	10
7	$Pd(CH_3CN)_2Cl_2$	67
8	$Pd(PPh_3)_2Cl_2$	71
9	$Pd(CH_3CN)_4(OTf)_2$	19

[a]**1a** (0.1 mmol), **2a** (1.5 eq.), Pd cat. (10 mol%), PPh_3 (20 mol%), Cs_2CO_3 (2.0 eq.), toluene (2.0 mL), 120 °C, N_2. Yields were determined by ^1H NMR of crude products using 1,3,5-trioxane as internal standard.

Table S2. Screening of the phosphine ligands





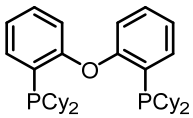
L1, R = H, 80 %
L2, R = 3-Me, 70 %
L3, R = 4-Me, 5 %
L4, R = 4-F, 40 %

L5, R = 4-Cl, 14 %
L6, R = 4-OMe, 18 %
L7, R = 2-OMe, 21 %
L8, R = 3,5-di-CF_3, 29 %

L9, TFP,16 %
L10, P*t*Bu$_3$, trace
L11, POct$_3$, trace
L12, PPh_2Et, 63 %
L13, PPh_2*t*Bu, 27 %

L14, PCy_3, 86 %
L15, dppm, 31 %
L16, dppe, trace
L17, dppp, 14 %
L18, dppb, 10 %

L19, dppf, 48 %
L20, BINAP, 46 %
L21, XantPhos, 32 %
L23, DPEPhos, 73 %

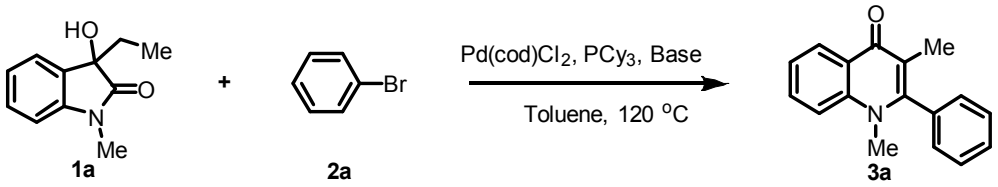


L24, 72 %

[a]**1a** (0.1 mmol), **2a** (1.5 eq.), $Pd(cod)Cl_2$ (10 mol%), P Ligand (20 mol%), Cs_2CO_3 (2.0 eq.), toluene (2.0 mL), 120 °C, N_2. Yields were determined by ^1H NMR of crude products using

1,3,5-trioxane as internal standard.

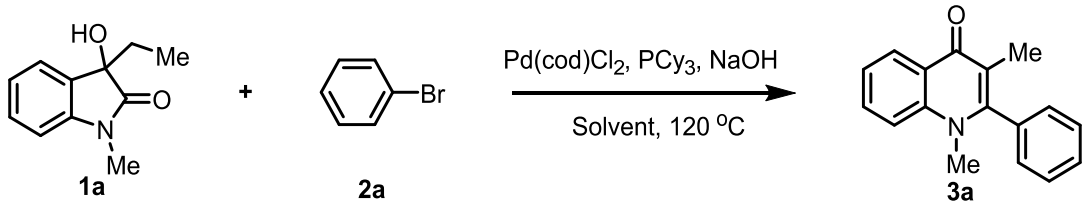
Table S3. Screening of the bases



Entry	Base	Yield (%)	Entry	Base	Yield (%)
1	Li_2CO_3	0	10	KH_2PO_4	0
2	Na_2CO_3	0	11	CH_3OLi	0
3	K_2CO_3	17	12	CH_3ONa	0
4	Cs_2CO_3	87	13	*t*BuONa	82
5	$MgCO_3$	0	14	*t*BuOK	10
6	$NaHCO_3$	0	15	LiOH	0
7	$KHCO_3$	0	16	NaOH	88
8	K_3PO_4	21	17	$Ca(OH)_2$	0
9	K_2HPO_4	13	18	NaH	trace

[a]**1a** (0.1 mmol), **2a** (1.5 eq.), $Pd(cod)Cl_2$ (10 mol%), PCy_3 (20 mol%), Base (2.0 eq.), toluene (2.0 mL), 120 °C, N_2. Yields were determined by ^1H NMR of crude products using 1,3,5-trioxane as internal standard.

Table S4. Screening of the solvents

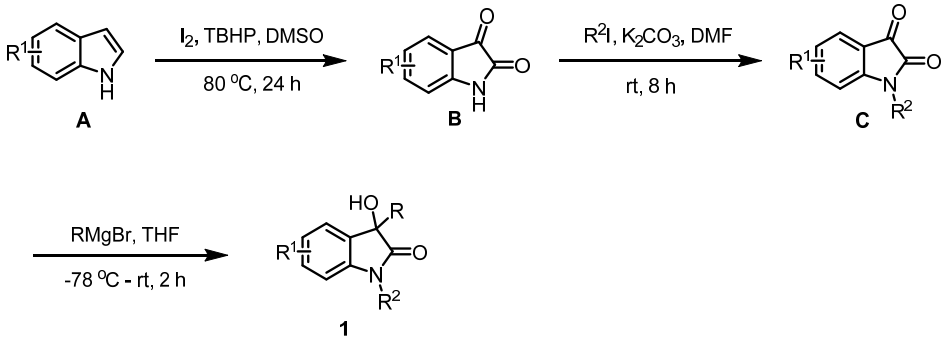


Entry	Solvent	Yield (%)
1	Toluene	88
2	MeCN	0
3	DCE	0
4	Dioxane	50
5	Hexane	0
6	DMF	0
7	DMSO	20

[a]**1a** (0.1 mmol), **2a** (1.5 eq.), $Pd(cod)Cl_2$ (10 mol%), PCy_3 (20 mol%), NaOH (2.0 eq.), Solvent (2.0 mL), 120 °C, N_2. Yields were determined by ^1H NMR of crude products using 1,3,5-trioxane as internal standard.

3. Experimental Procedure

3.1 General procedure for the synthesis of 3-Hydroxyoxindoles 1[1]

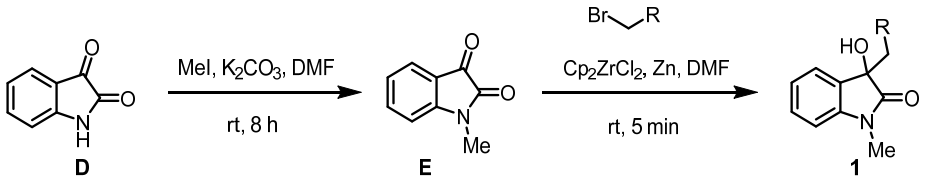


Step 1: Indoles **A** (10 mmol), iodine (3.05 g, 12 mmol, 1.2 equiv.) and dry DMSO (0.25 M) were added to an oven-dried 100 mL round bottom flask under argon gas. TBHP (5.0 – 6.0 M in Decane, 5.0 equiv.) was added dropwise over a period of 0.5 h at 80 ^{o}C. The mixture was then heated at 80 ^{o}C for 24 h. Upon the completion of reaction, after cooled to rt, the mixture was extracted with EtOAc (2 x 40 mL). The organic layer was washed with brine (40 mL), dried over anhydrous Na_2SO_4, and concentrated to give the crude product, which was further, purified by flash column chromatography on silica gel to give the desired isatins **B**.

Step 2: **B** (5 mmol, 1.0 equiv.), R^2I (6 mmol, 1.2 equiv.), K_2CO_3 (1.04 g, 7.5 mmol, 1.5 equiv.) and dry DMF (0.25 M) were mixed in an oven-dried 100 mL round bottom flask under argon gas. The reaction was allowed to stir for overnight at room temperature. Upon the completion of reaction, then the reaction mixture was extracted with EtOAc, washed with sat. NH_4Cl, brine, and dried over Na_2SO_4. The residues were purified by flash column chromatography on silica gel to give **C**.

Step 3: Grignard reagent (1.5 equiv.) was added dropwise to a solution of **C** (5.0 mmol, 1.0 equiv.) in dry THF (0.5 M) for 30 min using syringe pump at -78 ^{o}C. The mixture was then stirred at room temperature for 2 h. Upon the completion of reaction, then the reaction mixture was extracted with EtOAc, washed with sat. NH_4Cl, brine, and dried over Na_2SO_4. The residues were purified by flash column chromatography on silica gel to give **1**.

3.2 Synthesis of substrates: 1g-1l[2]

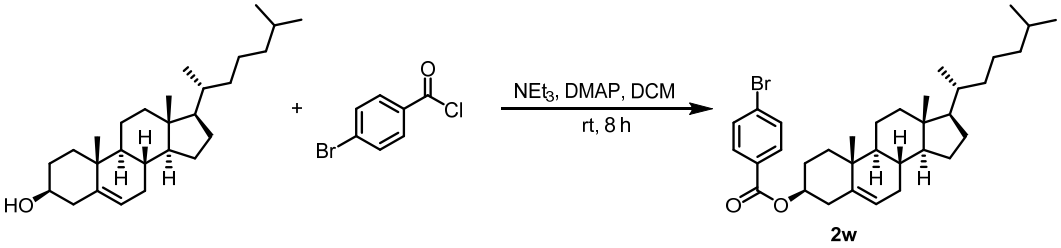


Step 1: Isatin **D** (735 mg, 5 mmol, 1.0 equiv.), MeI (852 mg, 6 mmol, 1.2 equiv.), K_2CO_3 (1.04 g, 7.5 mmol, 1.5 equiv.) and dry DMF (0.25 M) were mixed in an oven-dried 100 mL round bottom flask under argon gas. The reaction was allowed to stir for overnight at room temperature. Upon the completion of reaction, then the reaction mixture was extracted with EtOAc, and washed with sat. NH_4Cl, brine, and dried over Na_2SO_4. The solution was concentrated under reduced

pressure. The compound **E** was recrystallized from EtOAc and cooled hexane.

Step 2: **E** (805 mg, 5 mmol, 1.0 equiv.), alkyl bromides (7.5 mmol, 1.5 equiv.), Cp_2ZrCl_2 (146 mg, 0.5 mmol, 0.1 equiv.), zinc powder (640 mg, 10 mmol, 2 equiv.) and dry DMF (0.25 M) were added to an oven-dried 100 mL round bottom flask under argon gas. Upon the completion of reaction, then the reaction mixture was extracted with EtOAc, washed with 1M HCl, brine, and dried over Na_2SO_4. The residues were purified by flash column chromatography on silica gel to give **1**.

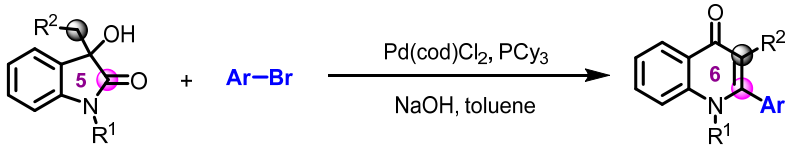
3.3 Synthesis of substrates: 2w[3]



2w

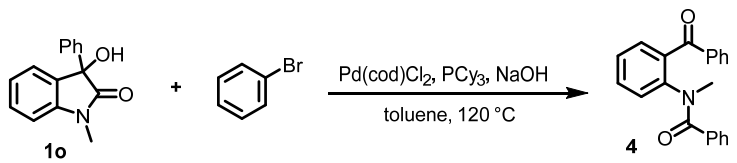
4-Bromobenzoyl chloride (1.20 g, 5.5 mmol, 1.1 equiv.) was dissolved in DCM (10 mL) and added to a mixture of cholesterol (1.93 g, 5 mmol, 1.0 equiv.), DMAP (61 mg, 0.5 mmol, 0.1 equiv.) and Et_3N (1.01 g, 10 mmol, 2.0 equiv.) in DCM (10 mL). The reaction was allowed to stirred overnight at room temperature. Then, the mixture was quenched upon addition of NH_4Cl (aq. 10%), and extracted with DCM three times. The organic phase was washed with brine, concentrated and purified by silica gel flash chromatography to give the corresponding substituted aryl bromide **2w** (2.27 g) in 90% as white solid.

3.4 General procedure for the preparation of 3.



An oven dried 25 mL Schlenk tube was charged with isatin-derived aryl alcohols **1** (0.1 mmol, 1.0 equiv.), aryl bromides **2** (0.15 mmol, 1.5 equiv.), $Pd(cod)Cl_2$ (2.9 mg, 0.01 mmol, 0.1 equiv.), PCy_3 (5.6 mg, 0.02 mmol, 0.2 equiv.), NaOH (8.0 mg, 0.2 mmol, 2.0 eq.), and 2.0 mL toluene. The tube was tightly capped and vigorously stirred in a pre-warmed oil bath maintained at 120 °C for a period of time under N_2 atmosphere. After cooling to room temperature, the reaction mixture was filtered through celite. The filtrate was extracted with EtOAc, and the organic layer was washed with brine. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (EtOAc/hexane) to afford the products.

3.5 Experimental procedure for the preparation of 4.



1o **4**

An oven dried 25 mL Schlenk tube was charged with isatin-derived aryl alcohols **1o** (23.9 mg, 0.1

mmol), PhBr (23.3 mg, 0.15 mmol, 1.5 equiv.), $Pd(cod)Cl_2$ (2.9 mg, 0.01 mmol, 0.1 equiv.), PCy_3 (5.6 mg, 0.02 mmol, 0.2 equiv.), NaOH (8.0 mg, 0.2 mmol, 2.0 eq.), and 2.0 mL toluene. The tube was tightly capped and vigorously stirred in a pre-warmed oil bath maintained at 120 °C for 12 h under N_2 atmosphere. After cooling to room temperature, the reaction mixture was filtered through celite. The filtrate was extracted with EtOAc, and the organic layer was washed with brine. The organic layer was dried over Na_2SO_4 and concentrated in vacuo. The residue was purified by silica gel column chromatography (Hexane/EtOAc = 1:1) to afford the product **4** (27.1 mg, 86% yield).

4. Analytical Data

4.1 Characterization of Starting Material

Starting material **1a**, **1b**, **1f**, **1g-1i**, **1k**, **1l**, **1m**, **1n,** and **1o** are known products and are synthesized according to the general procedure 3.1 and 3.2.

3-ethyl-3-hydroxy-1-methylindolin-2-one (1a)[4]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 4:1) afforded **1a** as a white solid. 42% yield (0.40 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (dd, J = 7.3, 1.3 Hz, 1H), 7.33 (td, J = 7.8, 1.3 Hz, 1H), 7.11 (td, J = 7.5, 1.0 Hz, 1H), 6.84 (dd, J = 7.8, 0.9 Hz, 1H), 3.19 (d, J = 1.1 Hz, 3H), 2.08-1.94 (m, 2H), 0.75 (t, J = 7.5 Hz, 3H).

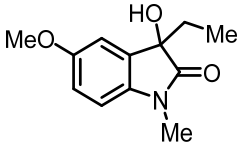
3-ethyl-3-hydroxy-1,4-dimethylindolin-2-one (1b)[4]**:** Purification by flash column chromatography on silica gel (Hexane/EtOAc = 4:1) afforded **1b** as a yellow solid. 38% yield (0.39 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (td, J = 7.8, 1.5 Hz, 1H), 6.87 (d, J = 7.8 Hz, 1H), 6.66 (d, J = 7.7 Hz, 1H), 3.18 (d, J = 1.1 Hz, 3H), 2.95-2.62 (m, 1H), 2.45 (s, 3H), 2.27-2.01 (m, 2H), 0.59 (t, J = 7.6, 3H).

3-ethyl-3-hydroxy-1,5-dimethylindolin-2-one (1c): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 4:1) afforded **1c** as a yellow solid. 50% yield (0.51 g). m.p. 106-107 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.21 (d, J = 1.6 Hz, 1H), 7.16-7.09 (m, 1H), 6.74 (d, J = 7.8 Hz, 1H), 3.31 (s, 1H), 3.18 (m, 3H), 2.36 (s, 3H), 2.06-1.93 (m, 2H), 0.75 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.4, 141.2, 132.7, 129.9, 129.7, 124.7, 108.1, 77.4, 31.6, 26.2, 21.1, 7.6. **HRMS** (ESI) *m/z*: $[M+Na]^+$ Calcd for $C_{12}H_{15}NNaO_2$ 228.0995; Found 228.0994.

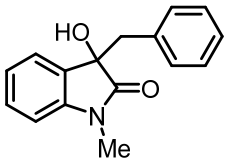
3-ethyl-5-fluoro-3-hydroxy-1-methylindolin-2-one (1d): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 4:1) afforded **1d** as a white solid. 44% yield (0.46 g). m.p. 117-118 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.17-7.11 (m, 1H), 7.06-6.99 (m, 1H), 6.79-6.74 (m, 1H), 3.96-3.42 (m, 1H), 3.18 (d, J = 2.8 Hz, 3H), 2.07-1.92 (m, 2H), 0.78-0.70 (m, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.5, 159.7 (d, J = 239.5 Hz), 139.5, 131.7, 115.8 (d, J = 23.8 Hz), 112.3 (d, J = 25.0 Hz), 109.1 (d, J = 8.8 Hz), 77.6, 31.7, 26.4, 7.6. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -119.69 – -119.85 (m, 1F). **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{11}H_{13}FNO_2$ 210.0925; Found 210.0927.

3-ethyl-3-hydroxy-1-methyl-5-(trifluoromethoxy)indolin-2-one (1e): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 3:1) afforded **1e** as a white solid. 30% yield (0.41 g). m.p. 68-69 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.28 (dd, J = 2.4, 1.0 Hz, 1H), 7.23-7.19 (m, 1H), 6.83 (d, J = 8.5 Hz, 1H), 3.68-3.43 (m, 1H), 3.20 (s, 3H), 2.07-1.93 (m, 2H), 0.76 (t, J = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, Acetone-d_6) δ 177.3, 144.4, 142.9, 132.9 , 122.3, 120.7 (q, J = 254.7 Hz), 117.5, 109.0, 76.6, 30.9, 25.4, 6.9. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -58.35. **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{12}H_{13}F_3NO_3$ 276.0842; Found 276.0842.

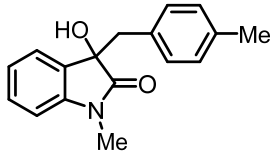
3-ethyl-3-hydroxy-5-methoxy-1-methylindolin-2-one(1f)[4]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:1) afforded **1f** as a red solid. 52% yield (0.57 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.00 (d, J = 2.5 Hz, 1H), 6.87-6.83 (m, 1H), 6.75 (d, J = 8.5 Hz, 1H), 3.81 (s, 3H), 3.18 (d, J = 0.9 Hz, 3H), 3.06-2.77 (m, 1H), 2.02-1.93 (m, 2H), 0.74 (t, J = 7.4, 3H).



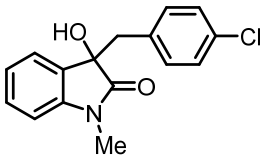
3-benzyl-3-hydroxy-1-methylindolin-2-one (1g)[2]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:1) afforded **1g** as a white solid. 70% yield (0.89 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29-7.24 (m, 1H), 7.19-7.10 (m, 4H), 7.08-7.03 (m, 1H), 6.97-6.93 (m, 2H), 6.65 (d, J = 7.8 Hz, 1H), 3.31 (d, J = 12.9 Hz, 1H), 3.14 (d, J = 12.9 Hz, 1H), 3.01 (s, 3H).



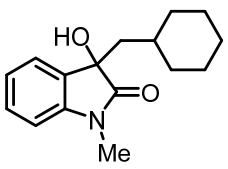
3-hydroxy-1-methyl-3-(4-methylbenzyl)indolin-2-one (1h)[2]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:1) afforded **1h** as a white solid. 54% yield (0.72 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29-7.24 (m, 1H), 7.17 (dd, J = 7.3, 1.3 Hz, 1H), 7.07-7.03 (m, 1H), 6.94 (d, J = 7.7 Hz, 2H), 6.85 (d, J = 7.9 Hz, 2H), 6.67 (d, J = 7.7 Hz, 1H), 3.26 (d, J = 13.0 Hz, 1H), 3.08 (d, J = 13.0 Hz, 1H), 3.03 (s, 3H), 2.87 (s, 1H), 2.25 (s, 3H).



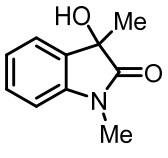
3-(4-chlorobenzyl)-3-hydroxy-1-methylindolin-2-one (1i)[2]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:1) afforded **1i** as a white solid. 64% yield (0.92 g). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.30-7.27 (m, 1H), 7.20-7.04 (m, 4H), 6.91-6.86 (m, 2H), 6.68 (d, J = 7.8 Hz, 1H), 3.26 (d, J = 12.9 Hz, 1H), 3.09 (d, J = 13.0 Hz, 1H), 3.03 (s, 3H), 2.72 (s, 1H).



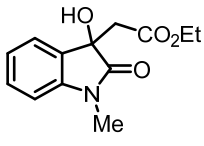
3-(cyclohexylmethyl)-3-hydroxy-1-methylindolin-2-one (1j): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:1) afforded **1j** as a light yellow liquid. 36% yield (0.45 g). m.p. 124-126 ^oC **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.39-7.31 (m, 2H), 7.13-7.08 (m, 1H), 6.84 (d, J = 7.8 Hz, 1H), 3.19 (s, 3H), 2.73 (s, 1H), 1.97-1.86 (m, 2H), 1.58-1.43 (m, 5H), 1.17-1.03 (m, 4H), 0.94 -0.83 (m, 2H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.7, 143.6, 130.3, 129.8, 124.3, 123.2, 108.6, 76.5, 45.8, 34.5, 34.2, 33.5, 26.4, 26.2. **HRMS** (ESI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{16}H_{22}NO_2$ 260.1645; Found 260.1647.



3-hydroxy-1,3-dimethylindolin-2-one (1k)[4]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 4:1) afforded **1k** as an white solid. 50% yield (0.44 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.42 (dd, J = 7.3, 1.3 Hz, 1H), 7.33 (td, J = 7.8, 1.3 Hz, 1H), 7.11 (td, J = 7.5, 1.0 Hz, 1H), 6.84 (d, J = 7.7 Hz, 1H), 3.20 (s, 3H), 1.61 (s, 3H).

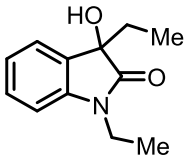


ethyl 2-(3-hydroxy-1-methyl-2-oxoindolin-3-yl) acetate (1l)[2]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 4:1) afforded **1l** as an orange solid. 72% yield (0.90 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.41 (dd, J = 7.4, 1.3 Hz, 1H), 7.35 (td, J = 7.8, 1.3 Hz, 1H), 7.09 (td, J = 7.6, 1.0 Hz, 1H), 6.84 (d, J = 7.8 Hz, 1H), 4.49-4.41 (m, 1H), 4.18-4.09 (m, 2H), 3.21 (d, J = 1.2 Hz,

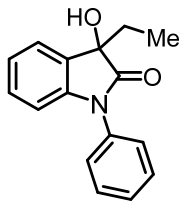


3H), 2.94 (d, *J* = 14.0 Hz, 1H), 2.90 (d, *J* = 14.0 Hz, 1H), 1.23-1.16 (m, 3H).

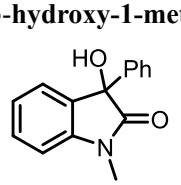
1,3-diethyl-3-hydroxyindolin-2-one (1m)[5]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 4:1) afforded **1m** as a white solid. 52% yield (0.53 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.38 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.32 (td, J = 7.7, 1.3 Hz, 1H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 7.8 Hz, 1H), 3.86-3.77 (m, 1H), 3.73-3.64 (m, 1H), 3.14-2.67 (m, 1H), 2.06-1.94 (m, 2H), 1.28-1.25 (m, 3H), 0.74-0.71 (m, 3H).



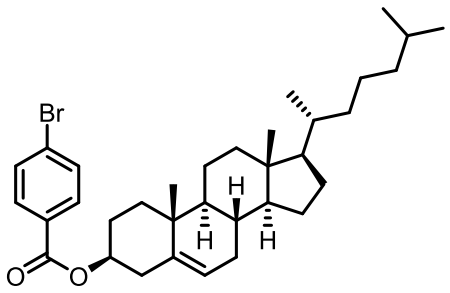
3-ethyl-3-hydroxy-1-phenylindolin-2-one (1n)[6]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 4:1) afforded **1n** as a white solid. 40% yield (0.51 g). **^{1}H NMR** (500 MHz, DMSO-d_6) δ 7.59 (t, *J* = 7.8 Hz, 2H), 7.50-7.44 (m, 1H), 7.43-7.37 (m, 3H), 7.27 (td, *J* = 7.7, 1.3 Hz, 1H), 7.13 (td, *J* = 7.5, 1.0 Hz, 1H), 6.73 (d, *J* = 7.7 Hz, 1H), 6.15 (s, 1H), 1.96-1.91 (m, 2H), 0.71 (t, *J* = 7.5 Hz, 3H). **^{13}C NMR** (125 MHz, DMSO-d_6) δ 177.6, 143.4, 134.7, 131.5, 130.1, 129.5, 128.4, 127.0, 124.5, 123.4, 109.2, 76.5, 31.5, 8.0.



3-hydroxy-1-methyl-3-phenylindolin-2-one (1o)[6]: Purification by flash column chromatography on silica gel (DCM/EtOAc = 10:1) afforded **1o** as a yellow solid. 57% yield (0.68 g). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43-7.29 (m, 7H), 7.11 (td, *J* = 7.9, 1.1 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 3.45 (s, 1H), 3.27 (s, 3H).

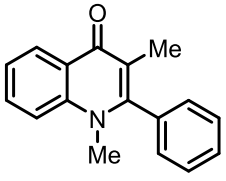


(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4- bromobenzoate (2w)[3]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 4:1) afforded **2w** as a white solid. 90% yield (2.56 g). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.6 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 5.42 (d, *J* = 5.1 Hz, 1H), 4.88-4.81 (m, 1H), 2.45 (d, *J* = 8.1 Hz, 2H), 2.06-1.89 (m, 5H), 1.88-1.80 (m, 1H), 1.77-1.68 (m, 1H), 1.60-1.57 (m, 1H), 1.54-1.45 (m, 4H), 1.39-1.22 (m, 8H), 1.21-1.09 (m, 6H), 1.05-0.97 (m, 3H), 0.92 (d, *J* = 6.6 Hz, 3H), 0.88 (d, *J* = 6.6 Hz, 3H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.69 (s, 3H).

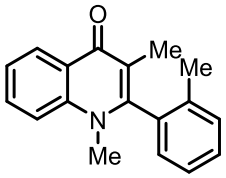


4.2 Characterization of Products

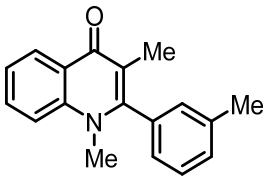
1,3-dimethyl-2-phenylquinolin-4(1*H*)-one (3a)[7]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3a** as an orange solid. 86% yield (21.4 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 8.0, 1.7 Hz, 1H), 7.68-7.64 (m, 1H), 7.57-7.43 (m, 5H), 7.40-7.36 (m, 1H), 7.28 -7.27 (m, 1H), 3.46 (s, 3H), 1.86 (s, 3H).



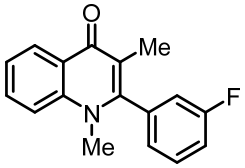
1,3-dimethyl-2-(*o*-tolyl)quinolin-4(1*H*)-one (3b)[7]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3b** as a yellow solid. 47% yield (12.3 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.59 (dd, J = 8.0, 1.7 Hz, 1H), 7.72-7.66 (m, 1H), 7.52 (d, J = 8.5 Hz, 1H), 7.44-7.32 (m, 4H), 7.15 (dd, J = 7.4, 1.4 Hz, 1H), 3.46 (s, 3H), 2.11 (s, 3H), 1.82 (s, 3H).



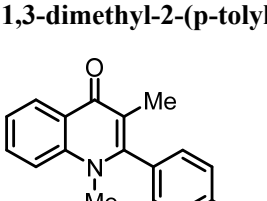
1,3-dimethyl-2-(*m*-tolyl)quinolin-4(1*H*)-one (3c): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3c** as an orange solid. 57% yield (15.0 mg). m.p. 131-132 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (dd, J = 8.0, 1.7 Hz, 1H), 7.70-7.64 (m, 1H), 7.50 (d, J = 8.5 Hz, 1H), 7.44-7.37 (m, 2H), 7.33-7.29 (m, 1H), 7.11-7.04 (m, 2H), 3.48 (s, 3H), 2.44 (s, 3H), 1.87 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.6, 151.5, 141.1, 139.2, 135.7, 131.9, 129.9, 129.2, 129.0, 127.1, 125.6, 125.2, 123.2, 118.2, 115.6, 37.3, 21.6, 13.5. **HRMS** (EI-ESA) m/z: $[M]^+$ Calcd for $C_{18}H_{17}NO$ 263.1305; Found 263.1301.



2-(3-fluorophenyl)-1,3-dimethylquinolin-4(1*H*)-one (3d): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3d** as an orange solid. 84% yield (22.4 mg). m.p. 145-146 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (dd, J = 8.1, 1.7 Hz, 1H), 7.71-7.65 (m, 1H), 7.61-7.47 (m, 2H), 7.43-7.37 (m, 1H), 7.26-7.19 (m, 1H), 7.14-7.00 (m, 2H), 3.48 (s, 3H), 1.86 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 163.1 (d, J = 246.5 Hz), 149.6, 141.0, 137.6 (d, J = 8.0 Hz), 132.1, 131.2 (d, J = 8.8 Hz), 127.0, 125.1, 124.5 (d, J = 3.3 Hz), 123.3, 118.1, 116.4 (d, J = 21.3 Hz), 115.9 (d, J = 21.3 Hz), 115.5, 37.3, 13.4. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -110.75 – -110.84 (m, 1F). **HRMS** (EI-ESA) m/z: $[M]^+$ Calcd for $C_{17}H_{14}FNO$ 267.1054; Found 267.1054.



1,3-dimethyl-2-(p-tolyl)quinolin-4(1*H*)-one (3e): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3e** as a yellow solid. 90% yield (23.7 mg). m.p. 175-176 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (dd, J = 8.1, 1.7 Hz, 1H), 7.68-7.63 (m, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.40-7.36 (m, 1H), 7.34 (d, J = 7.7 Hz, 2H), 7.19-7.12 (m, 2H), 3.47 (s, 3H), 2.46 (s, 3H), 1.87 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 151.5, 141.0, 139.1, 132.8, 131.8, 129.9, 128.4, 127.0, 125.1, 123.1, 118.3, 115.6, 37.3, 21.5, 13.5. **HRMS** (EI-ESA) m/z: $[M]^+$ Calcd for $C_{18}H_{17}NO$ 263.1305; Found 263.1299.



2-**(4-fluorophenyl)-1,3-dimethylquinolin-4(1*H*)-one (3f)[7]:** Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3f** as a white solid. 82% yield (18.7 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (dd, J = 8.1, 1.7 Hz, 1H), 7.70-7.64 (m, 1H), 7.48 (d, J = 8.6 Hz, 1H), 7.41-7.36 (m, 1H), 7.30-7.21 (m, 4H), 3.47 (s, 3H), 1.85 (s, 3H). **^{19}F NMR** (470 MHz, $CDCl_3$) δ -111.33.

2-(4-chlorophenyl)-1,3-dimethylquinolin-4(1*H*)-one (3g): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3g** as an orange solid. 79% yield (22.4 mg). m.p. 110-111 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (dd, J = 8.1, 1.7 Hz, 1H), 7.69-7.64 (m, 1H), 7.57-7.52 (m, 2H), 7.48 (d, J = 8.6 Hz, 1H), 7.41-7.36 (m, 1H), 7.27-7.23 (m, 2H), 3.46 (s, 3H), 1.85 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.4, 149.9, 141.0, 135.4, 134.0, 132.1, 130.1, 129.6, 127.0, 125.1, 123.3, 118.3, 115.5, 37.3, 13.4. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{17}H_{14}ClNO$ 283.0758; Found 283.0732.

1,3-dimethyl-2-(4-(trifluoromethyl)phenyl)quinolin-4(1*H*)-one (3h): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3h** as a yellow solid. 57% yield (18.1 mg). m.p. 132-133 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (dd, J = 8.1, 1.7 Hz, 1H), 7.84 (d, J = 8.0 Hz, 2H), 7.72-7.66 (m, 1H), 7.53-7.39 (m, 4H), 3.46 (s, 3H), 1.84 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 149.5, 141.1, 139.3, 132.3, 131.5 (q, J = 28.8 Hz), 129.3, 127.1, 126.5 (d, J = 3.8 Hz), 125.2, 123.9 (q, J = 270 Hz), 123.5, 118.2, 115.5, 37.5, 13.4. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -62.77. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{18}H_{14}F_3NO$ 317.1022; Found 317.0993.

2-(4-methoxyphenyl)-1,3-dimethylquinolin-4(1*H*)-one (3i)[8]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:3) afforded **3i** as a red solid. 71% yield (19.8 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (dd, J = 8.1, 1.7 Hz, 1H), 7.68-7.63 (m, 1H), 7.49 (d, J = 8.5 Hz, 1H), 7.40-7.35 (m, 1H), 7.22-7.16 (m, 2H), 7.09-7.02 (m, 2H), 3.90 (s, 3H), 3.48 (s, 3H), 1.88 (s, 3H).

1,3-dimethyl-2-(4-(trifluoromethoxy)phenyl)quinolin-4(1*H*)-one (3j): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:3) afforded **3j** as a light red solid. 92% yield (30.6 mg). m.p. 134-135 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (dd, J = 8.0, 1.7 Hz, 1H), 7.70-7.64 (m, 1H), 7.48 (d, J = 8.6 Hz, 1H), 7.44-7.33 (m, 5H), 3.47 (s, 3H), 1.84 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.4, 149.7, 141.0, 134.2, 132.1, 130.4, 127.0, 125.1, 123.3, 121.7, 120.5 (q, J = 256.3 Hz), 118.4, 115.6, 37.4, 13.5. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -57.75. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{18}H_{14}F_3NO_2$ 333.0971; Found 333.0971.

1,3-dimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3k): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3k** as a yellow solid. 95% yield (30.5 mg). m.p. 154-155 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (dd, J = 8.1, 1.7 Hz, 1H), 7.71-7.61 (m, 3H), 7.49 (d, J = 8.6 Hz, 1H), 7.41-7.35 (m, 1H), 7.26-7.23 (m, 2H), 3.47 (s, 3H), 1.86 (s, 3H), 0.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 151.3, 142.0, 141.0, 135.9, 134.1, 131.9, 127.7, 126.9, 125.1, 123.1, 118.1, 115.6, 37.4, 13.5, -1.1. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{20}H_{23}NOSi$ 321.1543; Found 321.1534.

2-([1,1'-biphenyl]-4-yl)-1,3-dimethylquinolin-4(1*H*)-one (3l): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3l** as a yellow solid. 90% yield (29.2 mg). m.p. > 200 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (dd, J = 8.1, 1.7 Hz, 1H), 7.77 (d, J = 8.2 Hz, 2H), 7.71-7.66 (m, 3H), 7.54-7.48 (m, 3H), 7.45-7.38 (m, 2H), 7.38-7.34 (m, 2H), 3.53 (s, 3H), 1.93 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 151.1, 142.1, 141.1, 140.1, 134.6, 132.0, 129.1, 129.1, 128.1, 127.9, 127.3, 127.1, 125.2, 123.3, 118.4, 115.6, 37.5, 13.6. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{23}H_{19}NO$ 325.1461; Found 325.1461.

2-(3,5-dimethylphenyl)-1,3-dimethylquinolin-4(1*H*)-one (3m): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3m** as a white solid. 91% yield (25.2 mg). m.p. 160-161 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.55 (dd, J = 8.1, 1.7 Hz, 1H), 7.68-7.62 (m, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.42-7.35 (m, 1H), 7.12 (d, J = 1.9 Hz, 1H), 6.87 (d, J = 1.7 Hz, 2H), 3.47 (s, 3H), 2.40 (s, 6H), 1.87 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 151.7, 141.0, 138.9, 135.6, 131.8, 130.7, 127.0, 126.1, 125.1, 123.0, 118.0, 115.5, 37.3, 21.5, 13.5. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{19}H_{19}NO$ 277.1461; Found 277.1442.

1,3-dimethyl-2-(naphthalen-2-yl)quinolin-4(1*H*)-one (3n): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3n** as a black solid. 64% yield (19.1 mg). m.p. > 200 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (dd, J = 8.2, 1.7 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.98-7.89 (m, 2H), 7.81-7.77 (m, 1H), 7.72-7.65 (m, 1H), 7.64-7.57 (m, 2H), 7.51 (d, J = 8.6 Hz, 1H), 7.43-7.34 (m, 2H), 3.49 (s, 3H), 1.89 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 151.8, 150.3, 148.0, 141.1, 136.5, 133.8, 132.1, 130.9, 129.6, 128.3, 128.1, 127.1, 125.2, 123.3, 122.3, 118.5, 115.6, 37.5, 13.5. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{21}H_{17}NO$ 299.1305; Found 299.1290.

2-(2,3-dihydrobenzofuran-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3o): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3o** as a brown solid. 70% yield (20.4 mg). m.p. 197-198 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.54 (dd, J = 8.1, 1.7 Hz, 1H), 7.770-7.62 (m, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.40-7.35 (m, 1H), 7.08 (d, J = 1.5 Hz, 1H), 6.99 (dd, J = 8.1, 1.9 Hz, 1H), 6.92 (d, J = 8.1 Hz, 1H), 4.68 (td, J = 8.7, 1.3 Hz, 2H), 3.50 (s, 3H), 3.31 (td, J = 8.7, 2.6 Hz, 2H), 1.90 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 160.7, 151.6, 141.0, 131.8, 128.6, 128.2, 127.8, 126.9, 125.2, 125.1, 123.1, 118.6, 115.6, 109.9, 71.7, 37.3, 29.7, 13.6. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{19}H_{17}NO_2$ 291.1254; Found 291.1226.

2-(benzo[*d*][1,3]dioxol-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3p): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:3) afforded **3p** as a white solid. 68% yield (19.9 mg). m.p. > 200 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (dd, J = 8.1, 1.7 Hz, 1H), 7.69-7.62 (m, 1H), 7.49 (d, J = 8.6 Hz, 1H), 7.42-7.34 (m, 1H), 6.97 (d, J = 8.2 Hz, 1H), 6.76-6.71 (m,

2H), 6.08 (s, 2H), 3.51 (s, 3H), 1.90 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 150.8, 148.4, 148.2, 141.0, 131.9, 129.2, 127.0, 125.1, 123.2, 122.4, 118.5, 115.6, 109.1, 109.0, 101.7, 37.2, 13.5. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{18}H_{15}NO_3$ 293.1046; Found 293.1030.

2-(benzo[*b*]thiophen-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3q): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:3) afforded **3q** as a yellow solid. 80% yield (24.4 mg). m.p. > 200 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (dd, J = 8.1, 1.7 Hz, 1H), 8.05 (d, J = 8.2, Hz, 1H), 7.74 (d, J = 1.6 Hz, 1H), 7.71-7.65 (m, 1H), 7.60 (d, J = 5.4 Hz, 1H), 7.51 (d, J = 8.6 Hz, 1H), 7.45-7.38 (m, 2H), 7.24 (dd, J = 8.2, 1.6 Hz, 1H), 3.48 (s, 3H), 1.88 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 151.3, 141.1, 140.4, 140.0, 131.9, 131.7, 128.3, 127.0, 125.2, 124.3, 124.0, 123.7, 123.5, 123.2, 118.6, 115.6, 37.4, 13.6. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{19}H_{15}NOS$ 305.0869; Found 305.0850.

1,3-dimethyl-[2,6'-biquinolin]-4(1*H*)-one (3r): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:3) afforded **3r** as an orange solid. 67% yield (20.1 mg). m.p. > 200 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.05 (dd, J = 4.3, 1.7 Hz, 1H), 8.57 (dd, J = 8.1, 1.7 Hz, 1H), 8.34- 8.24 (m, 2H), 7.81 (d, J = 1.9 Hz, 1H), 7.74-7.66 (m, 1H), 7.63 (dd, J = 8.6, 2.0 Hz, 1H), 7.58-7.48 (m, 2H), 7.44-7.39 (m, 1H), 3.50 (s, 3H), 1.88 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.6, 151.2, 141.1, 133.2, 133.0, 132.0, 129.3, 128.4, 128.1, 127.3, 127.2, 127.1, 125.8, 125.2, 123.2, 118.5, 115.6, 37.5, 13.6. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{20}H_{16}N_2O$ 300.1257; Found 300.1233.

2-(benzofuran-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3s): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:3) afforded **3s** as a deep red solid. 64% yield (18.5 mg). m.p. 172-173 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (dd, J = 8.1, 1.7 Hz, 1H), 7.76 (d, J = 2.1 Hz, 1H), 7.70-7.65 (m, 2H), 7.54-7.48 (m, 2H), 7.43-7.37 (m, 1H), 7.19 (dd, J = 8.4, 1.8 Hz, 1H), 6.87 (dd, J = 2.2, 1.0 Hz, 1H), 3.47 (s, 3H), 1.87 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 154.9, 151.5, 146.5, 141.0, 131.9, 130.4, 128.2, 127.0, 125.2, 124.7, 123.2, 121.5, 118.7, 115.6, 112.4, 106.9, 37.4, 13.6. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{19}H_{15}NO_2$ 289.1097; Found 289.1069.

1,3-dimethyl-2-(1-methyl-1H-indol-5-yl)quinolin-4(1*H*)-one (3t): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:3) afforded **3t** as a white solid. 81% yield (24.5 mg). m.p. > 200 ^oC. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (dd, J = 8.1, 1.7 Hz, 1H), 7.69-7.62 (m, 1H), 7.53-7.45 (m, 3H), 7.42-7.36 (m, 1H), 7.18 (d, J = 3.1 Hz, 1H), 7.07 (dd, J = 8.4, 1.6 Hz, 1H), 6.56 (dd, J = 3.1, 0.8 Hz, 1H), 3.87 (s, 3H), 3.47 (s, 3H), 1.89 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 152.9, 141.0, 136.6, 131.7, 130.3, 128.6, 126.9, 126.7, 125.2, 122.9, 121.7, 121.1, 118.7, 115.7, 110.0, 101.5, 37.4, 33.1, 13.7. **HRMS** (EI-ESA) *m*/*z*: $[M]^+$ Calcd for $C_{20}H_{18}N_2O$ 302.1414; Found 302.1398.

2-(dibenzo[*b,d*]thiophen-1-yl)-1,3-dimethylquinolin-4(1*H*)-one (3u): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:3) afforded **3u** as a yellow solid. 83% yield (29.5 mg). m.p. > 200 °C. **^{1}H NMR** (500 MHz, $CDCl_3$)) δ 8.59 (dd, J = 8.1, 1.7 Hz, 1H), 8.20-8.15 (m, 1H), 8.10-8.07 (m, 1H), 8.03 (d, J = 8.1 Hz, 1H), 7.94-7.90 (m, 1H), 7.72-7.67 (m, 1H), 7.56-7.48 (m, 3H), 7.45-7.40 (m, 1H), 7.36 (dd, J = 8.1, 1.7 Hz, 1H), 3.52 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.6, 151.1, 141.1, 140.3, 140.0, 136.3, 135.0, 132.1, 132.0, 127.7, 127.1, 126.7, 125.2, 124.9, 123.8, 123.3, 123.2, 122.0, 121.7, 118.7, 115.6, 37.5, 13.7. **HRMS** (EI-ESA) *m/z*: $[M]^+$ Calcd for $C_{23}H_{17}NOS$ 355.1025; Found 355.1011.

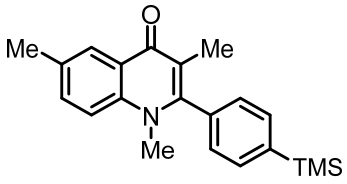
1,3-dimethyl-2-(thiophen-3-yl)quinolin-4(1*H*)-one (3v): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:2) afforded **3v** as a yellow solid. 51% yield (13.0 mg). m.p. 85-86 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (dd, J = 8.1, 1.7 Hz, 1H), 7.69-7.64 (m, 1H), 7.55 (dd, J = 4.9, 2.9 Hz, 1H), 7.48 (d, J = 8.6 Hz, 1H), 7.42-7.36 (m, 1H), 7.34 (dd, J = 2.9, 1.3 Hz, 1H), 7.06 (dd, J = 4.9, 1.3 Hz, 1H), 3.51 (s, 3H), 1.91 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.4, 146.7, 141.1, 135.6, 132.0, 127.8, 127.4, 127.0, 125.3, 125.1, 123.2, 119.3, 115.6, 37.2, 13.5. **HRMS** (EI-ESA) *m/z*: $[M]^+$ Calcd for $C_{15}H_{13}NOS$ 255.0712; Found 255.0710.

(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthr-en-3-yl 4-(1,3-dimethyl-4-oxo-1,4-dihydroquinolin-2-yl)benzoate (3w): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3w** as a white solid. 60% yield (39.7 mg). m.p. > 200 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.56 (d, J = 8.1 Hz, 1H), 8.24 (d, J = 8.1 Hz, 2H), 7.70 (dd, J = 8.7, 6.9 Hz, 1H), 7.50 (d, J = 8.6 Hz, 1H), 7.45-7.37 (m 3H), 5.47-5.43 (m, 1H), 4.97-4.88 (m, 1H), 3.46 (s, 3H), 2.51 (d, J = 8.1 Hz, 2H), 2.09-1.92 (m, 5H), 1.85 (s, 3H), 1.79-1.74 (m, 1H), 1.63-1.47 (m, 6H), 1.38-1.32 (m, 3H), 1.31-1.20 (m, 5H), 1.17-1.11 (m, 3H), 1.09 (s, 3H), 1.06-0.98 (m, 3H), 0.93 (d, J = 6.5 Hz, 3H), 0.87 (d, J = 6.6 Hz, 3H), 0.87 (d, J = 6.6 Hz, 3H), 0.70 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.5, 165.3, 150.2, 141.1, 139.9, 139.6, 132.2, 131.8, 130.6, 128.8, 127.2, 125.3, 123.5, 123.2, 118.1, 115.5, 75.3, 56.8, 56.3, 50.2, 42.5, 39.9, 39.7, 38.4, 37.4, 37.2, 36.8, 36.3, 35.9, 32.1, 32.0, 28.4, 28.2, 28.0, 24.5, 24.0, 23.0, 22.7, 21.2, 19.5, 18.9, 13.4, 12.0. **HRMS** (ESI) *m/z*: $[M+H]^+$ Calcd for $C_{45}H_{60}NO_3$ 662.4568; Found 662.4570.

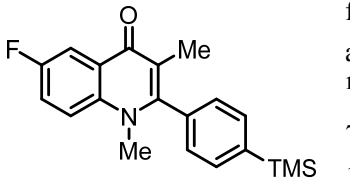
1,3,5-trimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3x): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3x** as a yellow solid. 23% yield (7.7 mg). m.p. 150-151 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.68-7.64 (m, 2H), 7.49 (dd, J = 8.7, 7.2 Hz, 1H), 7.34 (d, J = 8.6 Hz, 1H), 7.27-7.23 (m, 2H), 7.14-7.09 (m, 1H), 3.43 (s, 3H), 3.04 (s, 3H), 1.82 (s, 3H), 0.33 (s, 9H). **^{13}C NMR** (125 MHz,

$CDCl_3$) δ 180.1, 150.0, 142.9, 141.9, 141.9, 136.2, 134.1, 130.9, 127.8, 126.2, 123.9, 119.3, 113.6, 38.2, 24.7, 13.7, -1.0. **HRMS** (EI-ESA) *m/z*: $[M]^+$ Calcd for $C_{21}H_{25}NOSi$ 335.1700; Found 335.1697.

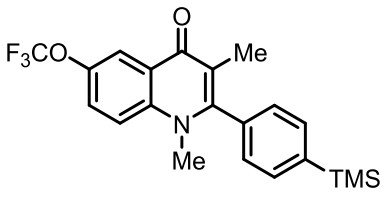
1,3,6-trimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3y): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3y** as an orange solid. 91% yield (30.5 mg). m.p. 160-161 °C. **^{1}H NMR (**500 MHz, $CDCl_3$) δ 8.37-8.32 (m, 1H), 7.69-7.64 (m, 2H), 7.48 (dd, J = 8.7, 2.2 Hz, 1H), 7.40 (d, J = 8.7 Hz, 1H), 7.26-7.22 (m, 2H), 3.45 (s, 3H), 2.49 (s, 3H), 1.86 (s, 3H), 0.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.3, 151.0, 141.9, 139.2, 136.0, 134.0, 133.3, 132.9, 127.7, 126.2, 125.0, 117.8, 115.5, 37.4, 21.0, 13.6, -1.1. **HRMS** (EI-ESA) *m/z*: $[M]^+$ Calcd for $C_{21}H_{25}NOSi$ 335.1700; Found 335.1676.



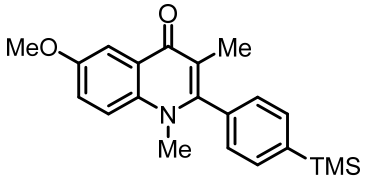
6-fluoro-1,3-dimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3z): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3z** as an orange solid. 69% yield (23.4 mg). m.p. > 200 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.18 (dd, J = 9.1, 3.1 Hz, 1H), 7.72-7.65 (m, 2H), 7.50 (dd, J = 9.4, 4.2 Hz, 1H), 7.42-7.37 (m, 1H), 7.25 (d, J = 7.9 Hz, 2H), 3.49 (s, 3H), 1.86 (s, 3H), 0.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.8, 160.0 (d, J = 242.6 Hz), 151.6, 142.3, 137.7, 135.7, 134.2, 127.7, 126.6 (d, J = 25.4 Hz), 120.5 (d, J = 25.0 Hz), 117.9 (d, J = 7.5 Hz), 117.8, 111.4 (d, J = 21.3 Hz), 37.8, 13.6, -1.0. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -118.60 – -118.81 (m,1H). **HRMS** (EI-ESA) *m/z*: $[M]^+$ Calcd for $C_{20}H_{22}FNOSi$ 339.1449; Found 339.1435.



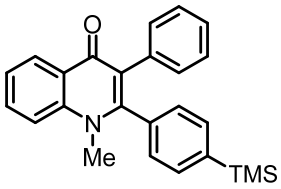
1,3-dimethyl-6-(trifluoromethoxy)-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3aa): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:2) afforded **3aa** as a yellow solid. 85% yield (34.4 mg). m.p. > 200 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.40 (t, J = 1.9 Hz, 1H), 7.72-7.67 (m, 2H), 7.57-7.49 (m, 2H), 7.26-7.23 (m, 2H), 3.49 (s, 3H), 1.86 (s, 3H), 0.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.8, 151.7, 145.0, 142.4, 139.4, 135.5, 134.2, 127.6, 125.4, 120.7 (q, J = 256.3 Hz), 118.4, 117.7, 37.7, 13.6, -1.0. **^{19}F NMR** (470 MHz, $CDCl_3$) δ -58.01. **HRMS** (EI-ESA) *m/z*: $[M]^+$ Calcd for $C_{21}H_{22}F_3NO_2Si$ 405.1366; Found 405.1349.



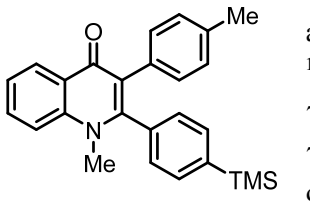
6-methoxy-1,3-dimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3ab): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 2:3) afforded **3ab** as a white solid. 75% yield (26.3 mg). m.p. 192-193 °C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.96 (d, J = 3.1 Hz, 1H), 7.70-7.65 (m, 2H), 7.46 (d, J = 9.3 Hz, 1H), 7.30 (dd, J = 9.3, 2.8 Hz, 1H), 7.26-7.23 (m, 2H), 3.96 (s, 3H), 3.48 (s, 3H), 1.88 (s, 3H), 0.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.8, 156.0, 150.7, 142.0, 136.0, 135.8, 134.1, 127.8, 122.7, 117.4, 105.7, 55.9, 37.6, 13.6, -1.0. **HRMS** (EI-ESA) *m/z*: $[M]^+$ Calcd for $C_{21}H_{25}NO_2Si$ 351.1649; Found 351.1620.



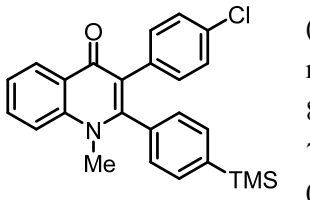
1-**methyl-3-phenyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ac):** Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3ac** as a white solid. 90% yield (34.5 mg). m.p. 196-197 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.61-8.56 (m, 1H), 7.76-7.68 (m, 1H), 7.57 (d, J = 8.7 Hz, 1H), 7.47-7.37 (m, 3H), 7.15-7.00 (m, 7H), 3.54 (d, J = 1.9 Hz, 3H), 0.23 (d, J = 1.9 Hz, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.4, 152.3, 141.62, 141.56, 135.8, 135.3, 133.2, 132.4, 131.5, 128.9, 127.6, 127.5, 126.7, 126.2, 124.3, 123.7, 115.9, 37.9, -1.1. **HRMS** (EI-ESA) *m/z*: $[M]^+$ Calcd for $C_{25}H_{25}NOSi$ 383.1700; Found 383.1681.



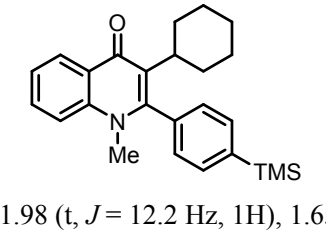
1-methyl-3-(p-tolyl)-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ad): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3ad** as a white solid. 77% yield (30.6 mg). m.p. 147-149 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (dd, J = 8.1, 1.7 Hz, 1H), 7.75-7.68 (m, 1H), 7.56 (d, J = 8.6 Hz, 1H), 7.45-7.39 (m, 3H), 7.15-7.10 (m, 2H), 6.91 (s, 4H), 3.53 (s, 3H), 2.21 (s, 3H), 0.24 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.5, 152.2, 141.53, 141.48, 135.6, 135.50, 133.2, 132.6, 132.3, 131.3, 128.9, 128.3, 127.6, 126.7, 124.3, 123.6, 115.9, 37.9, 21.3, -1.1. **HRMS** (ESI-ESA) *m/z*: $[M]^+$ Calcd for $C_{26}H_{28}NOSi$ 398.1935; Found 3398.1933.



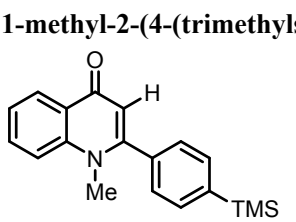
3-(4-chlorophenyl)-1-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ae): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3ae** as a white solid. 81% yield (33.9 mg). m.p. 188-190 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (dd, J = 8.1, 1.6 Hz, 1H), 7.76-7.71 (m, 1H), 7.58 (d, J = 8.6 Hz, 1H), 7.48-7.41 (m, 3H), 7.14-7.06 (m, 4H), 7.01-6.94 (m, 2H), 3.54 (s, 3H), 0.26 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 176.2, 152.4, 142.1, 141.5, 135.0, 134.3, 133.4, 132.9, 132.6, 132.0, 128.7, 127.8, 127.5, 126.6, 123.9, 123.0, 116.0, 37.9, -1.1. **HRMS** (ESI-ESA) *m/z*: $[M]^+$ Calcd for $C_{25}H_{25}ClNOSi$ 418.1388; Found 418.1388.



3-cyclohexyl-1-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3af): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3af** as a white solid. 78% yield (30.3 mg). m.p. 173-175 ^{o}C. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 8.52 (d, J = 7.9 Hz, 1H), 7.65 (t, J = 8.5 Hz, 3H), 7.45 (d, J = 8.7 Hz, 1H), 7.37 (t, J = 7.6 Hz, 1H), 7.23 (d, J = 7.4 Hz, 2H), 3.38 (s, 3H), 2.43 (q, J = 13.1, 12.7 Hz, 2H), 1.98 (t, J = 12.2 Hz, 1H), 1.65 (d, J = 13.2 Hz, 2H), 1.50 (d, J = 12.9 Hz, 1H), 1.40 (d, J = 12.8 Hz, 2H), 1.33-1.21 (m, 1H), 0.92 (q, J = 13.3 Hz, 2H), 0.35 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.4, 151.4, 141.8, 140.8, 136.3, 133.8, 131.7, 127.3, 126.9, 126.6, 126.0, 123.0, 115.3, 41.6, 37.4, 29.2, 27.1, 25.8, -1.1. **HRMS** (EI-ESA) *m/z*: $[M]^+$ Calcd for $C_{25}H_{31}NOSi$ 389.2169; Found 389.2152.

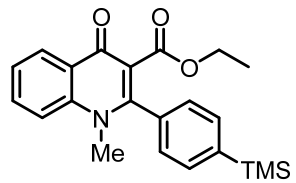


1-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ag): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3ag** as a red solid. 84% yield (25.8 mg). m.p. 145-147 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.51 (dd, J = 8.1, 1.7 Hz, 1H), 7.77-7.71 (m, 1H), 7.68-7.63



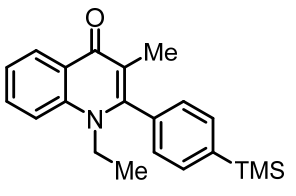
(m, 2H), 7.59 (d, J = 8.6 Hz, 1H), 7.48-7.43 (m, 1H), 7.42-7.38 (m, 2H), 6.39 (s, 1H), 3.65 (s, 3H), 0.33 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.4, 155.3, 143.0, 142.0, 136.1, 133.8, 132.6, 127.9, 126.9, 126.7, 124.0, 116.2, 112.6, 37.6, -1.1. **HRMS** (ESI-ESA) m/z: $[M]^+$ Calcd for $C_{19}H_{22}NOSi$ 308.1465; Found 308.1468.

Ethyl 1-methyl-4-oxo-2-(4-(trimethylsilyl)phenyl)-1,4-dihydroquinoline-3-carbo-xylate (3ah):

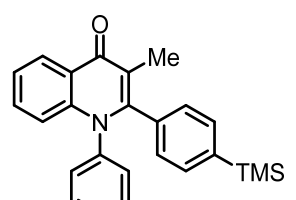


Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3ah** as a red liquid. 68% yield (25.8 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.65-7.60 (m, 2H), 7.56-7.53 (m, 2H), 7.26-7.22 (m, 1H), 6.92-6.89 (m, 1H), 6.81-6.75 (m, 2H), 4.40 (q, J = 7.1 Hz, 2H), 3.24 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H), 0.32 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 168.3, 166.5, 144.6, 143.1, 141.8, 134.1, 134.0, 130.5, 127.2, 125.4, 123.6, 122.0, 120.8, 108.3, 62.2, 26.1, 14.1, -1.0. **HRMS** (ESI) m/z: $[M+H]^+$ Calcd for $C_{22}H_{26}NO_3Si$ 380.1676; Found 380.1675.

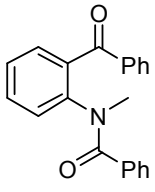
1-ethyl-3-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3ai): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3ai** as an orange liquid. 89% yield (29.8 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.57 (dd, J = 8.2, 1.7 Hz, 1H), 7.69-7.63 (m, 3H), 7.52 (d, J = 8.7 Hz, 1H), 7.40-7.35 (m, 1H), 7.28-7.24 (m, 2H), 4.00 (q, J = 7.1 Hz, 2H), 1.80 (s, 3H), 1.24 (t, J = 7.1 Hz, 3H), 0.34 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 177.3, 151.0, 141.9, 139.6, 135.8, 134.1, 131.8, 127.4, 127.3, 125.6, 123.0, 118.3, 115.8, 43.5, 14.4, 13.5, -1.0. **HRMS** (EI-ESA) m/z: $[M]^+$ Calcd for $C_{21}H_{25}NOSi$ 335.1700; Found 335.1683.



3-methyl-1-phenyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3aj): Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **3ai** as an orange solid. 86% yield (32.9 mg). m.p. 194-196 ^{o}C. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58-8.52 (m, 1H), 7.44-7.37 (m, 1H), 7.35-7.23 (m, 6H), 7.11-7.05 (m, 2H), 7.02 (d, J = 7.7 Hz, 2H), 6.75 (d, J = 8.6 Hz, 1H), 1.94 (s, 3H), 0.20 (s, 9H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 178.1, 150.8, 142.0, 140.8, 139.9, 135.4, 132.9, 131.4, 130.3, 129.4, 128.7, 128.6, 126.5, 124.6, 123.3, 118.2, 117.9, 13.3, -1.2. **HRMS** (ESI-ESA) m/z: $[M]^+$ Calcd for $C_{25}H_{26}NOSi$ 384.1778; Found 384.1777.



N-(2-benzoylphenyl)-N-methylbenzamide (4)[9]: Purification by flash column chromatography on silica gel (Hexane/EtOAc = 1:1) afforded **4** as an yellow oil. 86% yield (27.1 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.53-7.45 (m, 2H), 7.35-7.14 (m, 10H), 7.01-6.98 (m, 2H), 3.43 (s, 3H). **^{13}C NMR** (125 MHz, $CDCl_3$) δ 194.8, 170.0, 144.5, 136.5, 136.0, 135.5, 133.1,131.8, 130.5, 130.2, 129.6, 129.5, 129.1, 128.2, 127.7, 126.4, 39.2.



5. Supplementary References

1. (a) Zi, Y.; Cai, Z. J.; Wang, S. Y.; Ji, S. J. Synthesis of Isatins by I_2/TBHP Mediated Oxidation of Indoles. *Org. Lett.* **2014**, *16*, 3094−3097. (b) Samineni, R.; Madapa, J.; Srihari, P.; Mehta, G. Spiroannulation of Oxindoles via Aryne and Alkyne Incorporation: Substituent-Diverted, Transition-Metal-Free, One-Pot Access to Spirooxindoles. *Org. Lett.* **2017**, *19*, 3119−3122. (c) Jia, W. L.; He, J.; Yang, J. J.; Gao, X. W.; Liu, Q.; Wu, L. Z. Homocoupling of 3-Halooxindole via Visible-Light Photocatalysis: A Mild Access to 3,3′-Bioxindoles. *J. Org. Chem.* **2016**, *81*, 7172−7181.

2. Chouhan, M.; Sharma, R.; Nair, V.A. Cp_2ZrCl_2-induced Reformatsky and Barbier reactions on isatins: an efficient synthesis of 3-substituted-3-hydroxyindolin-2-ones. *Appl. Organometal. Chem.* **2011**, *25*, 470-475.

3. Shen, Y. Y.; Gu, Y. T.; Martin, R. sp^3 C–H Arylation and Alkylation Enabled by the Synergy of Triplet Excited Ketones and Nickel Catalysts. *J. Am. Chem. Soc.* **2018**, *140*, 12200−12209.

4. Gorokhovik, I.; Neuville, L.; Zhu J. Trifluoroacetic Acid-Promoted Synthesis of 3-Hydroxy, 3-Amino and Spirooxindoles from α-Keto-N-Anilides. *Org. Lett.* **2011**, *13*, 5536−5539.

5. Chen, G.; Lin, J.; Zhang, J.; Wu, Y.; Gu, X. F.; Hao, X. J.; Zhang, Y. Autocatalytic synthesis of 3-ethyl-3-hydroxy-indole-2-ones and their neuroprotection and antitumor activities' evaluation. *Comptes Rendus Chimie*, **2018**, *21,* 471−474.

6. Nishio, T. Synthesis of 3-Hydroperoxyindolin-2-ones and Oxidation of Sulphides to Sulphoxides by 3-Hydroperoxyindoli n-2-one. *J. Chem. Soc., Perkin Trans.* **1991**, *1*, 1717-1720.

7. Brown, M. F. Eur. Pat. Appl. 811613, 1997.

8. Rocha, D. H. A.; Pinto, D. C. G. A.; Silva, A. M. S. Synthesis and cyclisation studies of (E)-2-aryl-1-methyl-3-styrylquinolin-4(1H)-ones. *Tetrahedron*. **2015**, *71*, 7717-7721.

9. Dong, Y.-Q.; Shi, X.-N.; Cao, L.-Y.; Baia, J.; Zhuo, C.-X. Molybdenum-catalyzed carbonyl–carbonylolefination reaction for heterocycle syntheses. *Org. Chem. Front.*, **2023**, *10*, 3544-3552.

6. X-Ray Crystallography Data of Compound 3h

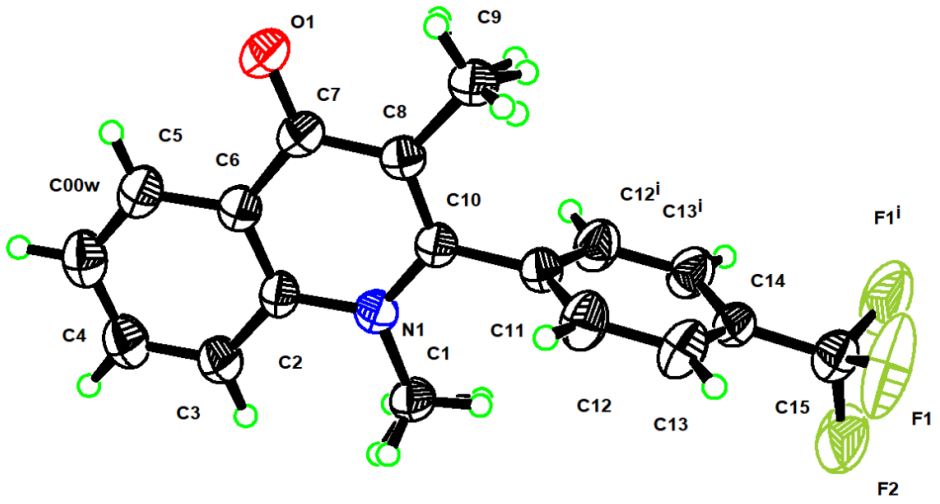


Figure S1. X-ray structures of **3h**

X-ray-quality crystal was obtained by slow violation of **3h** solution in hexane and ethyl ether at room temperature under air. Thermal ellipsoids drawn at the 50 % probability level. X-ray diffractions of single crystals was carried out at 100(2) K on a Bruker D8 VENTURE diffractometer using Mo-Kα radiation (λ = 0.71073 Å). Integration and scaling of intensity data was performed using the SAINT program. Data were corrected for the effects of absorption using SADABS. The structures were solved by direct method and refined with full-matrix least-squares technique using SHELX-2014 software. Non-hydrogen atoms were refined with anisotropic displacement parameters, and hydrogen atoms were placed in calculated positions and refined with a riding model.

Table S5 Crystal data and structure refinement for DD.

Identification code	DD
Empirical formula	$C_{36}H_{28}F_6N_2O_2$
Formula weight	634.60
Temperature/K	150.0
Crystal system	orthorhombic
Space group	Pnma
a/Å	25.784(2)
b/Å	6.9333(6)
c/Å	16.7815(18)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3000.0(5)
Z	4

ρ_{calc}g/cm^3	1.405
μ/mm^{-1}	0.113
F(000)	1312.0
Crystal size/mm^3	0.12 × 0.08 × 0.05
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	3.984 to 52.766
Index ranges	-26 ≤ h ≤ 32, -8 ≤ k ≤ 8, -17 ≤ l ≤ 20
Reflections collected	17528
Independent reflections	3262 [R_{int} = 0.0818, R_{sigma} = 0.0579]
Data/restraints/parameters	3262/312/275
Goodness-of-fit on F^2	1.017
Final R indexes [I>=2σ (I)]	R_1 = 0.0628, wR_2 = 0.1427
Final R indexes [all data]	R_1 = 0.1363, wR_2 = 0.1911
Largest diff. peak/hole / e Å^{-3}	0.34/-0.31

Table S6 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2×10^3) for DD. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ} tensor.

Atom	*x*	*y*	*z*	U(eq)
O(2)	2561.0(8)	7500	8031.4(13)	41.8(6)
O(1)	3849.6(8)	2500	7579.3(14)	47.8(6)
N(1)	2469.3(10)	2500	6368.7(15)	39.5(7)
N(2)	3929.8(10)	7500	6795.0(15)	40.1(7)
F(2)	88.8(9)	2500	8109.2(15)	120.5(12)
F(1)	354.0(7)	3989(3)	9099.3(12)	111.4(7)
C(6)	3405.4(12)	2500	6344.0(19)	38.1(8)
C(8)	2931.7(12)	2500	7617.8(18)	37.1(8)
C(2)	2928.7(12)	2500	5940.8(19)	37.5(8)
C(7)	3423.8(12)	2500	7215(2)	38.4(8)
C(11)	1962.8(12)	2500	7601.7(18)	38.2(8)
C(21)	2532.0(12)	7500	6337.8(19)	38.4(8)
C(17)	3468.4(12)	7500	6367.5(19)	35.0(7)
C(23)	3472.8(12)	7500	8052.4(19)	37.9(8)
C(10)	2477.2(12)	2500	7190.3(19)	36.2(7)
C(22)	2979.3(12)	7500	7650.5(18)	35.4(7)
C(16)	2993.7(12)	7500	6784.3(18)	36.1(7)

C(18)	3468.4(13)	7500	5532.5(19)	42.0(8)
C(25)	3922.6(12)	7500	7617.8(19)	38.4(8)
C(27)	4432.5(12)	7500	8034.8(19)	39.8(8)
C(14)	981.5(12)	2500	8298.0(19)	40.6(8)
C(19)	3009.2(13)	7500	5123(2)	46.0(9)
C(15)	456.5(13)	2500	8642(2)	49.2(9)
C(3)	2926.7(14)	2500	5104.5(19)	44.5(9)
C(1)	1981.0(12)	2500	5927.3(19)	45.7(9)
C(9)	2923.4(13)	2500	8515(2)	47.1(9)
C(20)	2538.3(13)	7500	5522.2(19)	43.6(8)
C(12)	1719.5(9)	4213(3)	7791.1(15)	50.3(7)
C(13)	1228.8(9)	4206(3)	8134.4(16)	51.4(7)
C(24)	3475.3(13)	7500	8946.5(19)	48.4(9)
C(5)	3869.1(13)	2500	5901(2)	46.3(9)
C(00W)	3859.3(15)	2500	5084(2)	53.0(10)
C(4)	3385.4(14)	2500	4694(2)	52.6(10)
C(28)	4664.7(9)	9213(4)	8251.3(16)	58.1(7)
C(30)	5357.4(14)	7500	8889(2)	52.1(10)
C(26)	4419.6(13)	7500	6346(2)	52.4(10)
C(29)	5122.1(10)	9216(4)	8676.1(17)	62.7(8)
C(31)	5851.9(16)	7500	9337(3)	73.2(12)
F(5)	6233.7(13)	8284(7)	8943(3)	151(2)
F(3)	6023.0(14)	5764(6)	9525(3)	99.8(13)
F(4)	5818.5(16)	8338(7)	10017(2)	161(2)

Table S7 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for DD. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\ldots]$.

Atom	**U_{11}**	**U_{22}**	**U_{33}**	**U_{23}**	**U_{13}**	**U_{12}**
O(2)	36.9(12)	46.2(12)	42.2(12)	0	3.9(10)	0
O(1)	32.8(12)	55.4(13)	55.2(14)	0	-3.5(11)	0
N(1)	37.3(14)	46.9(14)	34.3(13)	0	-1.1(12)	0
N(2)	34.6(14)	45.3(14)	40.5(14)	0	0.4(12)	0
F(2)	35.3(13)	259(4)	67.0(16)	0	-4.8(12)	0
F(1)	62.5(11)	110.4(13)	161.5(16)	-65.6(12)	54.5(10)	-17.5(9)
C(6)	36.7(17)	35.8(15)	41.8(16)	0	2.3(13)	0
C(8)	37.0(16)	36.5(15)	37.8(16)	0	-1.9(13)	0

C(2)	33.9(16)	38.7(16)	39.8(16)	0	6.9(13)	0
C(7)	34.6(16)	31.5(14)	48.9(18)	0	-2.4(14)	0
C(11)	36.1(17)	43.0(16)	35.4(17)	0	1.4(14)	0
C(21)	32.7(17)	38.1(16)	44.4(17)	0	1.6(14)	0
C(17)	32.4(15)	36.3(15)	36.4(16)	0	0.1(13)	0
C(23)	36.6(16)	36.0(15)	41.0(17)	0	-0.7(14)	0
C(10)	35.6(16)	35.4(15)	37.6(16)	0	1.9(13)	0
C(22)	33.4(16)	31.8(14)	41.1(17)	0	3.7(13)	0
C(16)	38.2(16)	31.2(14)	39.0(16)	0	-1.1(13)	0
C(18)	45.4(19)	44.2(17)	36.5(17)	0	4.3(14)	0
C(25)	36.6(17)	36.1(15)	42.7(17)	0	-3.8(14)	0
C(27)	33.3(17)	46.9(17)	39.3(18)	0	3.6(14)	0
C(14)	31.4(16)	52.0(17)	38.4(18)	0	-1.1(14)	0
C(19)	47.7(19)	54.0(19)	36.2(18)	0	-0.4(15)	0
C(15)	39.4(19)	51.1(18)	57(2)	0	4.1(16)	0
C(3)	44.7(19)	49.8(18)	39.1(17)	0	2.5(15)	0
C(1)	36.7(18)	62(2)	38.2(18)	0	-4.9(15)	0
C(9)	42.3(19)	59(2)	39.8(17)	0	-4.6(16)	0
C(20)	43.5(18)	44.6(18)	42.6(18)	0	-6.2(15)	0
C(12)	44.0(14)	40.8(12)	66.1(16)	-4.6(12)	9.8(12)	-5.6(10)
C(13)	39.0(13)	45.4(12)	69.7(17)	-10.8(12)	6.2(12)	1.2(11)
C(24)	40(2)	64(2)	41.1(18)	0	-3.0(16)	0
C(5)	37.5(18)	42.2(17)	59(2)	0	6.5(16)	0
C(00W)	54(2)	49.8(19)	55(2)	0	16.5(17)	0
C(4)	59(2)	55(2)	43(2)	0	11.2(16)	0
C(28)	46.0(14)	45.7(13)	82.6(19)	2.1(13)	-18.0(13)	-1.5(11)
C(30)	41.8(19)	57(2)	57(2)	0	-9.5(17)	0
C(26)	35.6(18)	71(2)	51(2)	0	1.9(16)	0
C(29)	48.0(15)	51.8(14)	88(2)	-4.5(14)	-17.4(14)	-4.6(12)
C(31)	53(2)	82(3)	85(3)	0	-22(2)	0
F(5)	46.1(19)	221(6)	186(4)	91(3)	-28(2)	-37(2)
F(3)	67(2)	96(2)	136(3)	4(2)	-54(2)	22.7(19)
F(4)	114(3)	229(6)	139(3)	-104(3)	-78(2)	72(3)

Table S8 Bond Lengths for DD.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O(2)	C(22)	1.254(4)	C(23)	C(22)	1.440(4)
O(1)	C(7)	1.256(4)	C(23)	C(25)	1.370(4)
N(1)	C(2)	1.385(4)	C(23)	C(24)	1.500(4)
N(1)	C(10)	1.379(4)	C(22)	C(16)	1.454(4)
N(1)	C(1)	1.461(4)	C(18)	C(19)	1.369(5)
N(2)	C(17)	1.389(4)	C(25)	C(27)	1.489(4)
N(2)	C(25)	1.381(4)	C(27)	C(28)	1.379(3)
N(2)	C(26)	1.471(4)	C(27)	C(28)^{2}	1.379(3)
F(2)	C(15)	1.303(4)	C(14)	C(15)	1.472(5)
F(1)	C(15)	1.313(3)	C(14)	C(13)^{1}	1.372(3)
C(6)	C(2)	1.403(4)	C(14)	C(13)	1.372(3)
C(6)	C(7)	1.463(4)	C(19)	C(20)	1.386(5)
C(6)	C(5)	1.408(4)	C(3)	C(4)	1.368(5)
C(8)	C(7)	1.437(4)	C(12)	C(13)	1.390(3)
C(8)	C(10)	1.374(4)	C(5)	C(00W)	1.370(5)
C(8)	C(9)	1.506(4)	C(00W)	C(4)	1.386(5)
C(2)	C(3)	1.403(4)	C(28)	C(29)	1.378(3)
C(11)	C(10)	1.495(4)	C(30)	C(29)	1.383(3)
C(11)	C(12)^{1}	1.380(3)	C(30)	C(29)^{2}	1.383(3)
C(11)	C(12)	1.380(3)	C(30)	C(31)	1.480(5)
C(21)	C(16)	1.407(4)	C(31)	F(5)	1.305(5)
C(21)	C(20)	1.369(4)	C(31)	F(3)	1.320(4)
C(17)	C(16)	1.410(4)	C(31)	F(4)	1.283(5)
C(17)	C(18)	1.401(4)			

Table S9 Bond Angles for DD.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C(2)	N(1)	C(1)	118.3(3)	C(17)	C(16)	C(22)	121.2(3)
C(10)	N(1)	C(2)	120.4(3)	C(19)	C(18)	C(17)	120.1(3)
C(10)	N(1)	C(1)	121.3(3)	N(2)	C(25)	C(27)	117.3(3)
C(17)	N(2)	C(26)	118.1(3)	C(23)	C(25)	N(2)	122.9(3)
C(25)	N(2)	C(17)	120.3(3)	C(23)	C(25)	C(27)	119.8(3)
C(25)	N(2)	C(26)	121.6(3)	C(28)	C(27)	C(25)	120.47(15)
C(2)	C(6)	C(7)	120.7(3)	C(28)^{2}	C(27)	C(25)	120.47(15)

C(2)	C(6)	C(5)	119.3(3)	C(28)	C(27)	C(28)^{2}	118.9(3)
C(5)	C(6)	C(7)	120.0(3)	C(13)	C(14)	C(15)	120.41(15)
C(7)	C(8)	C(9)	118.8(3)	C(13)^{1}	C(14)	C(15)	120.41(15)
C(10)	C(8)	C(7)	120.5(3)	C(13)^{1}	C(14)	C(13)	119.2(3)
C(10)	C(8)	C(9)	120.7(3)	C(18)	C(19)	C(20)	121.0(3)
N(1)	C(2)	C(6)	119.9(3)	F(2)	C(15)	F(1)	104.7(2)
N(1)	C(2)	C(3)	121.0(3)	F(2)	C(15)	F(1)^{1}	104.7(2)
C(6)	C(2)	C(3)	119.0(3)	F(2)	C(15)	C(14)	113.6(3)
O(1)	C(7)	C(6)	120.9(3)	F(1)	C(15)	F(1)^{1}	103.7(3)
O(1)	C(7)	C(8)	122.9(3)	F(1)	C(15)	C(14)	114.5(2)
C(8)	C(7)	C(6)	116.2(3)	F(1)^{1}	C(15)	C(14)	114.5(2)
C(12)	C(11)	C(10)	120.62(15)	C(4)	C(3)	C(2)	120.0(3)
C(12)^{1}	C(11)	C(10)	120.63(15)	C(21)	C(20)	C(19)	119.5(3)
C(12)	C(11)	C(12)^{1}	118.7(3)	C(11)	C(12)	C(13)	120.4(2)
C(20)	C(21)	C(16)	121.5(3)	C(14)	C(13)	C(12)	120.6(2)
N(2)	C(17)	C(16)	119.2(3)	C(00W)	C(5)	C(6)	120.9(3)
N(2)	C(17)	C(18)	121.1(3)	C(5)	C(00W)	C(4)	119.2(3)
C(18)	C(17)	C(16)	119.7(3)	C(3)	C(4)	C(00W)	121.6(3)
C(22)	C(23)	C(24)	118.2(3)	C(29)	C(28)	C(27)	120.6(2)
C(25)	C(23)	C(22)	119.9(3)	C(29)	C(30)	C(29)^{2}	118.7(3)
C(25)	C(23)	C(24)	121.9(3)	C(29)	C(30)	C(31)	120.63(17)
N(1)	C(10)	C(11)	116.7(3)	C(29)^{2}	C(30)	C(31)	120.63(16)
C(8)	C(10)	N(1)	122.3(3)	C(28)	C(29)	C(30)	120.5(3)
C(8)	C(10)	C(11)	121.0(3)	F(5)	C(31)	C(30)	113.1(4)
O(2)	C(22)	C(23)	121.4(3)	F(5)	C(31)	F(3)	104.4(4)
O(2)	C(22)	C(16)	122.1(3)	F(3)	C(31)	C(30)	114.2(2)
C(23)	C(22)	C(16)	116.5(3)	F(4)	C(31)	C(30)	113.2(4)
C(21)	C(16)	C(17)	118.1(3)	F(4)	C(31)	F(5)	108.2(4)
C(21)	C(16)	C(22)	120.7(3)	F(4)	C(31)	F(3)	102.9(4)

Table S10 Hydrogen Atom Coordinates (Å×10^{4}) and Isotropic Displacement Parameters (Å^{2}×10^{3}) for DD.

Atom	***x***	***y***	***z***	**U(eq)**
H(21)	2208.35	7500	6608.46	46
H(18)	3787.68	7500	5249.84	50
H(19)	3013.14	7500	4557.4	55

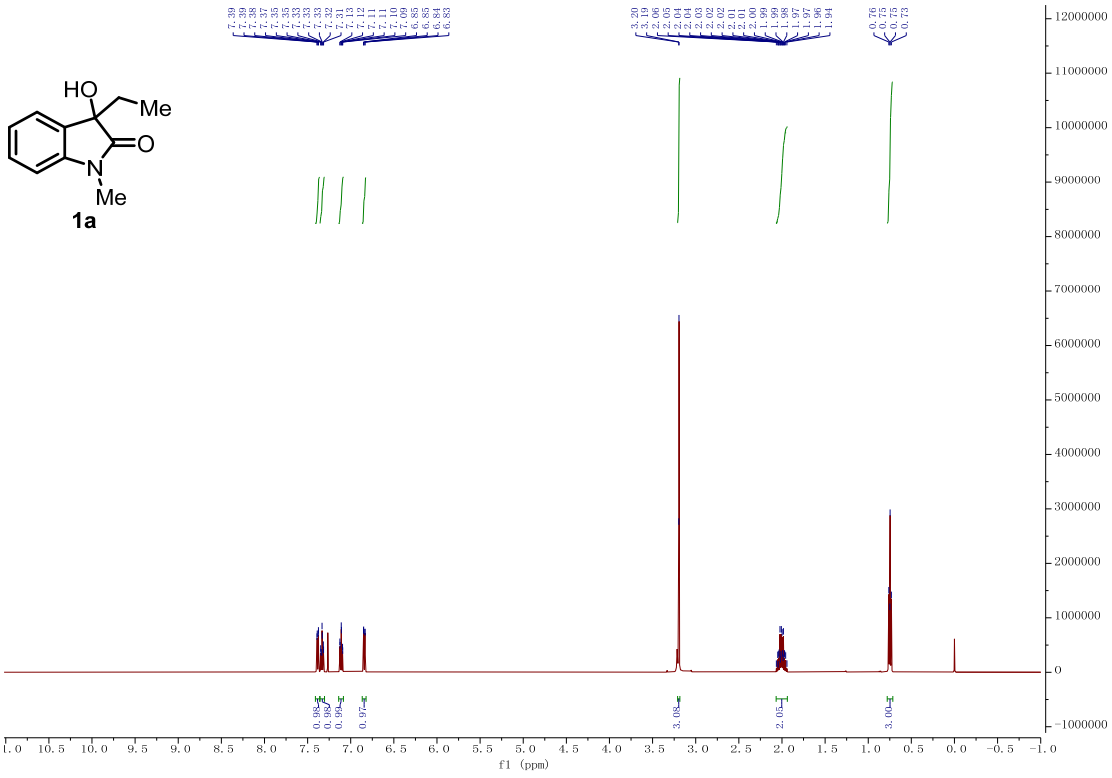
H(3)	2607.01	2500	4823.25	53
H(1A)	1690.97	2367.87	6300.83	55
H(1B)	1977.76	1417.66	5551.74	55
H(1C)	1946.56	3714.47	5633.24	55
H(9A)	2701.44	1448.62	8705.07	71
H(9B)	2786.88	3734.83	8706.94	71
H(9C)	3276.51	2316.55	8717.63	71
H(20)	2222.22	7500	5231.37	52
H(12)	1888.4	5404.13	7686.24	60
H(13)	1063.33	5394.04	8256.74	62
H(24A)	3468.59	8832.36	9141.19	73
H(24B)	3789.67	6857.01	9139.14	73
H(24C)	3169.12	6810.63	9143.1	73
H(5)	4192.79	2500	6170.88	56
H(00W)	4173.69	2500	4788.93	64
H(4)	3378.85	2500	4128.36	63
H(28)	4507.84	10402.16	8106.39	70
H(26A)	4454.78	8720.64	6056.53	79
H(26B)	4419.65	6426.58	5966.06	79
H(26C)	4710.92	7352.78	6716.19	79
H(29)	5277.12	10406.81	8823.4	75

Table S11 Atomic Occupancy for DD.

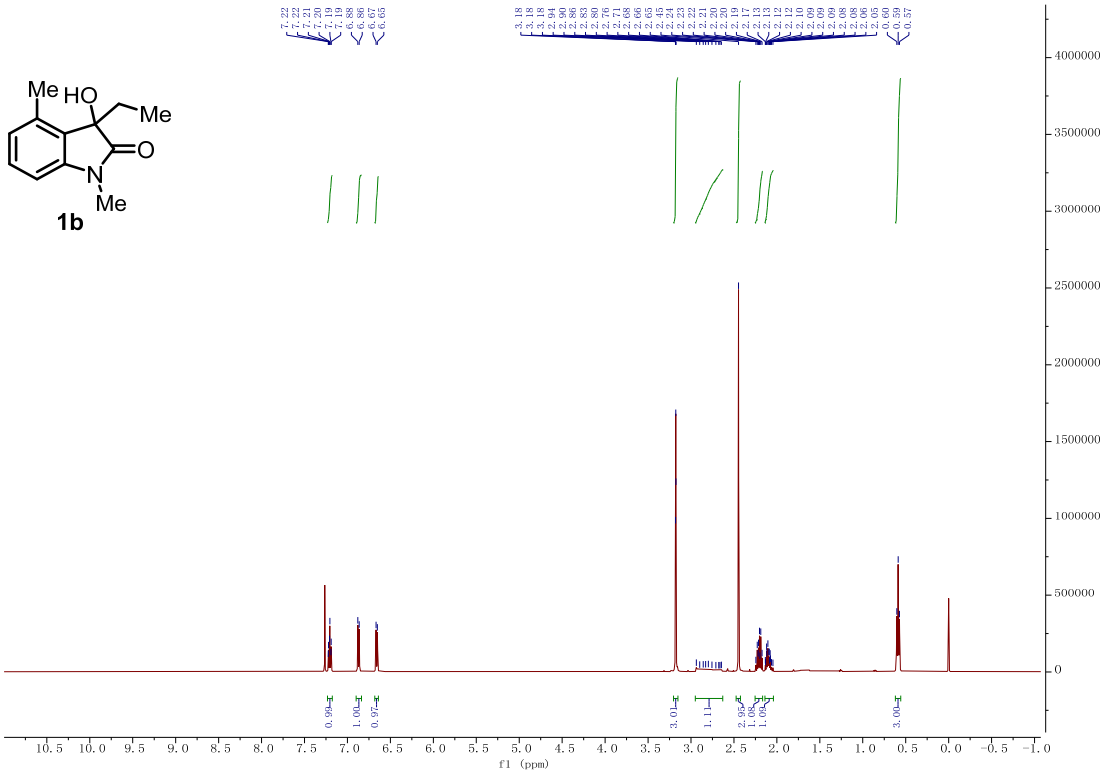
Atom	***Occupancy***	**Atom**	***Occupancy***	**Atom**	***Occupancy***
H(1A)	0.5	H(1B)	0.5	H(1C)	0.5
H(9A)	0.5	H(9B)	0.5	H(9C)	0.5
H(24A)	0.5	H(24B)	0.5	H(24C)	0.5
H(26A)	0.5	H(26B)	0.5	H(26C)	0.5
F(5)	0.5	F(3)	0.5	F(4)	0.5

7. NMR Spectra

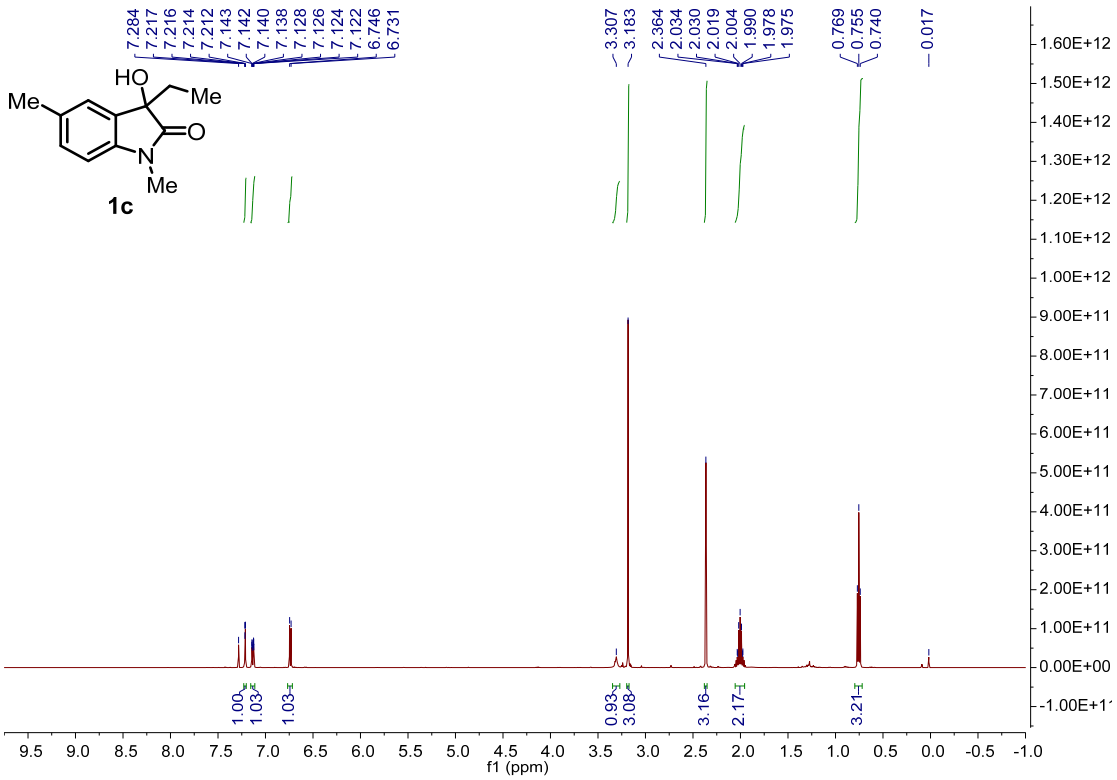
3-ethyl-3-hydroxy-1-methylindolin-2-one (**1a**). **^{1}H NMR (**500 MHz, $CDCl_3$**)**



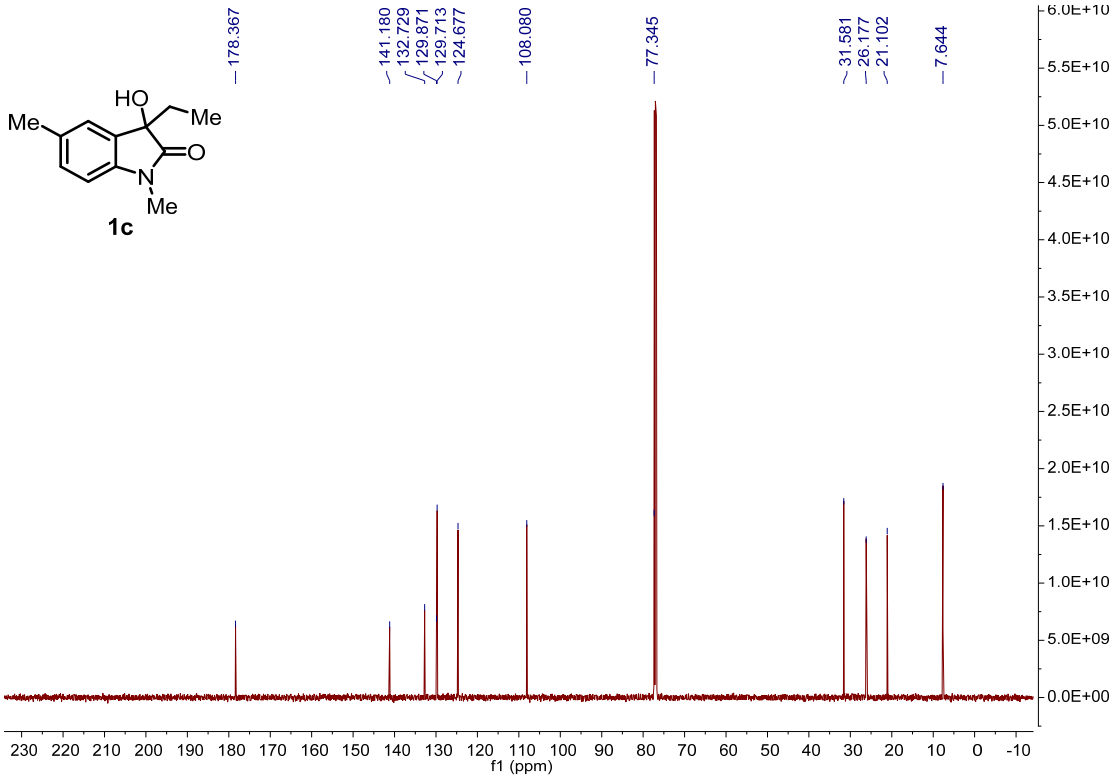
3-ethyl-3-hydroxy-1,4-dimethylindolin-2-one (1b). ^{1}H NMR (500 MHz, $CDCl_3$**)**



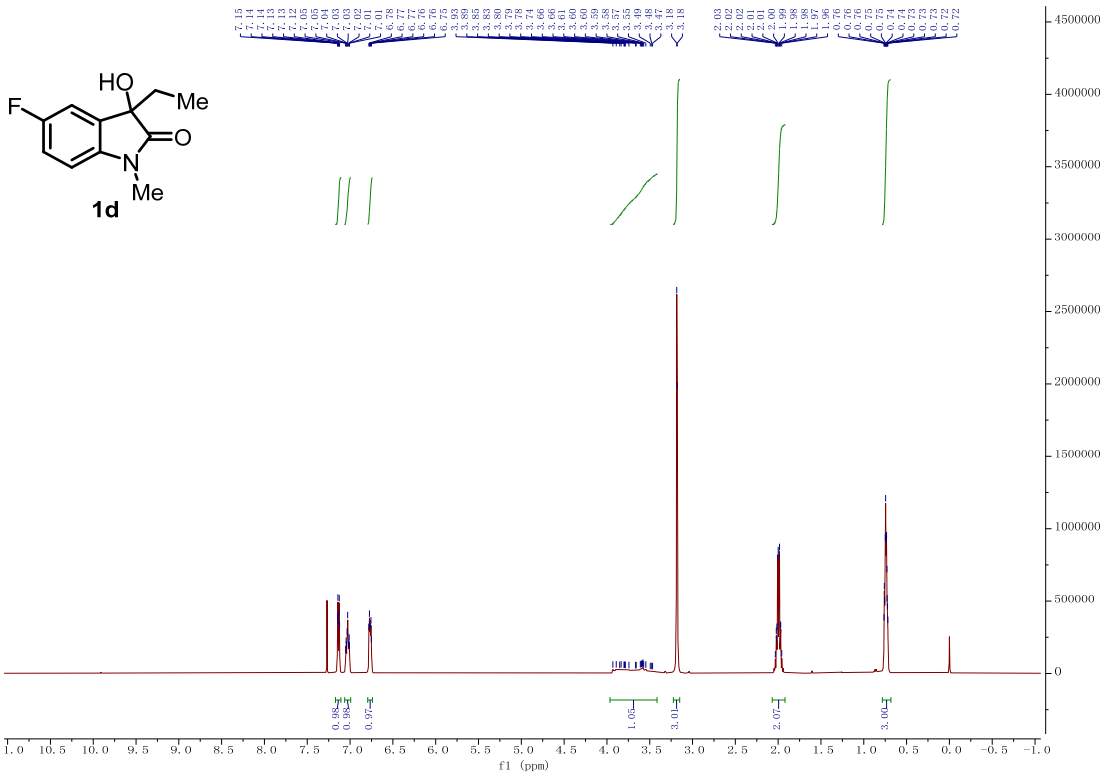
3-ethyl-3-hydroxy-1,5-dimethylindolin-2-one (1c). ^{1}H NMR (500 MHz, $CDCl_3$**)**



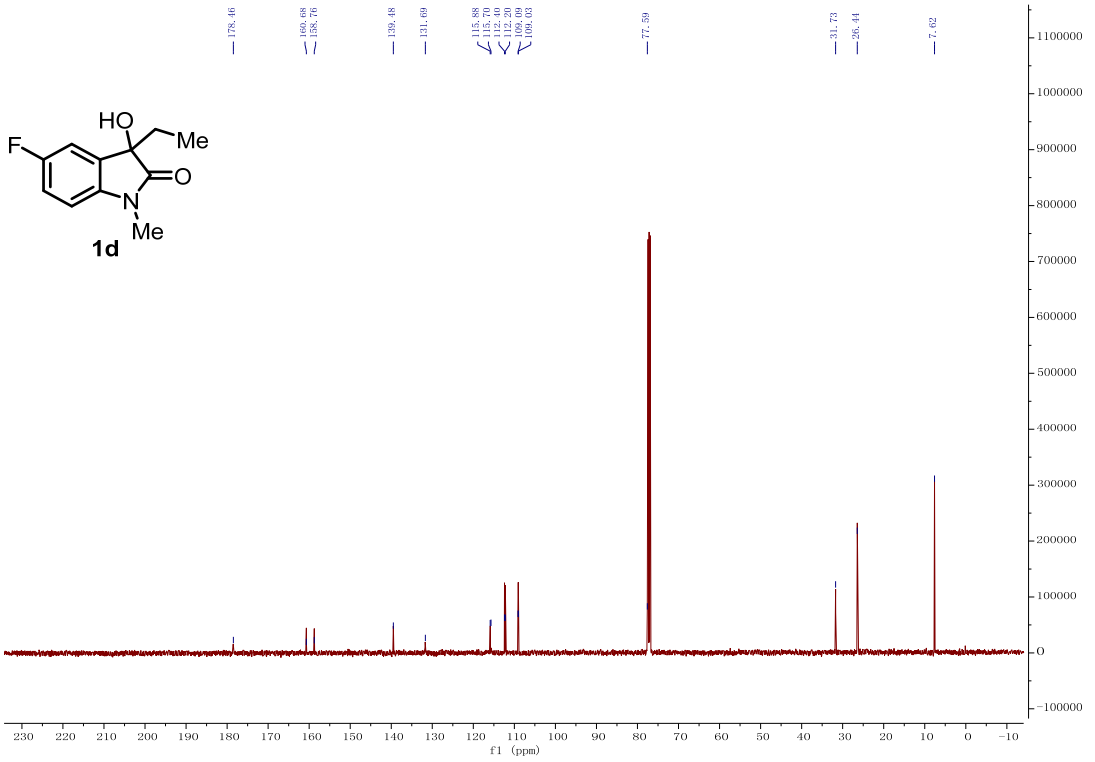
3-ethyl-3-hydroxy-1,5-dimethylindolin-2-one (1c). ^{13}C NMR (125 MHz, $CDCl_3$**)**



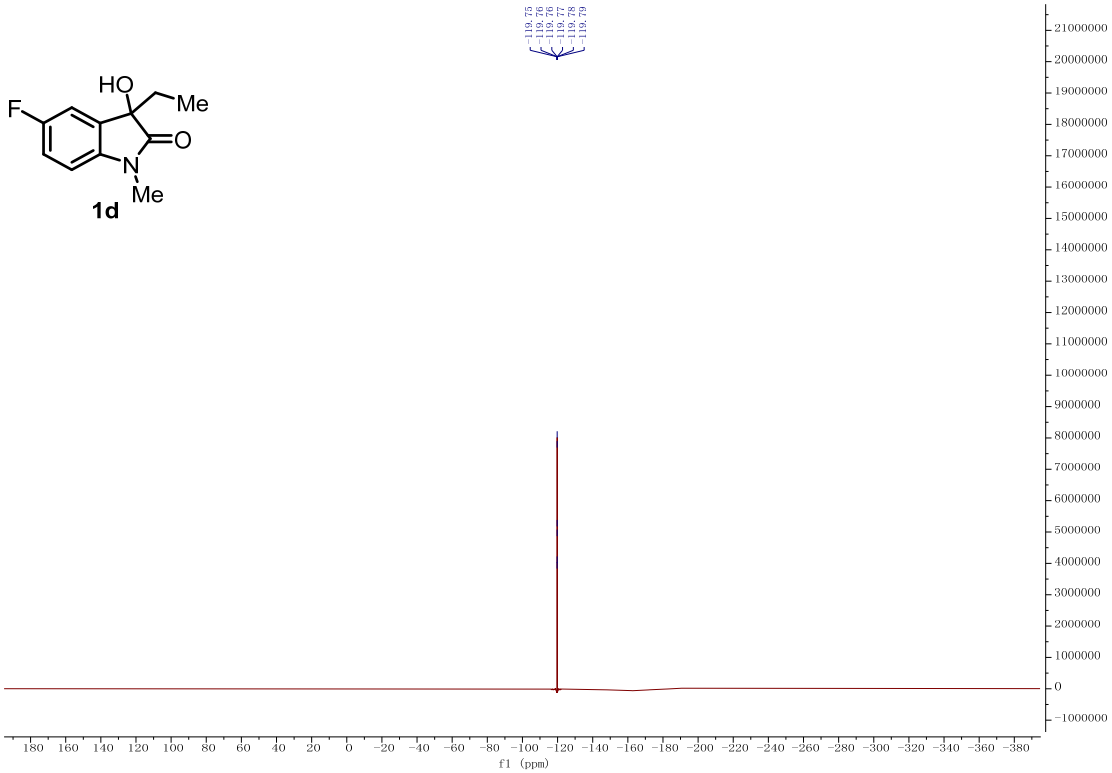
3-ethyl-5-fluoro-3-hydroxy-1-methylindolin-2-one (1d). ^{1}H NMR (500 MHz, $CDCl_3$**)**



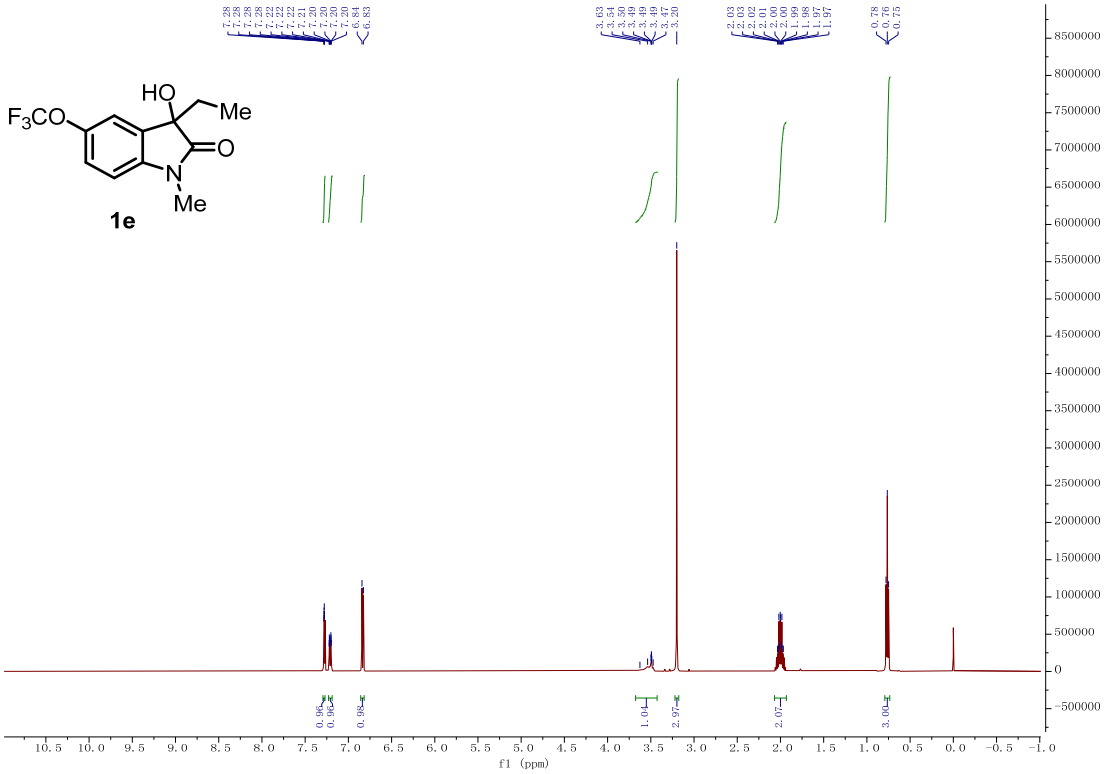
3-ethyl-5-fluoro-3-hydroxy-1-methylindolin-2-one (1d). ^{13}C NMR (125 MHz, $CDCl_3$**)**



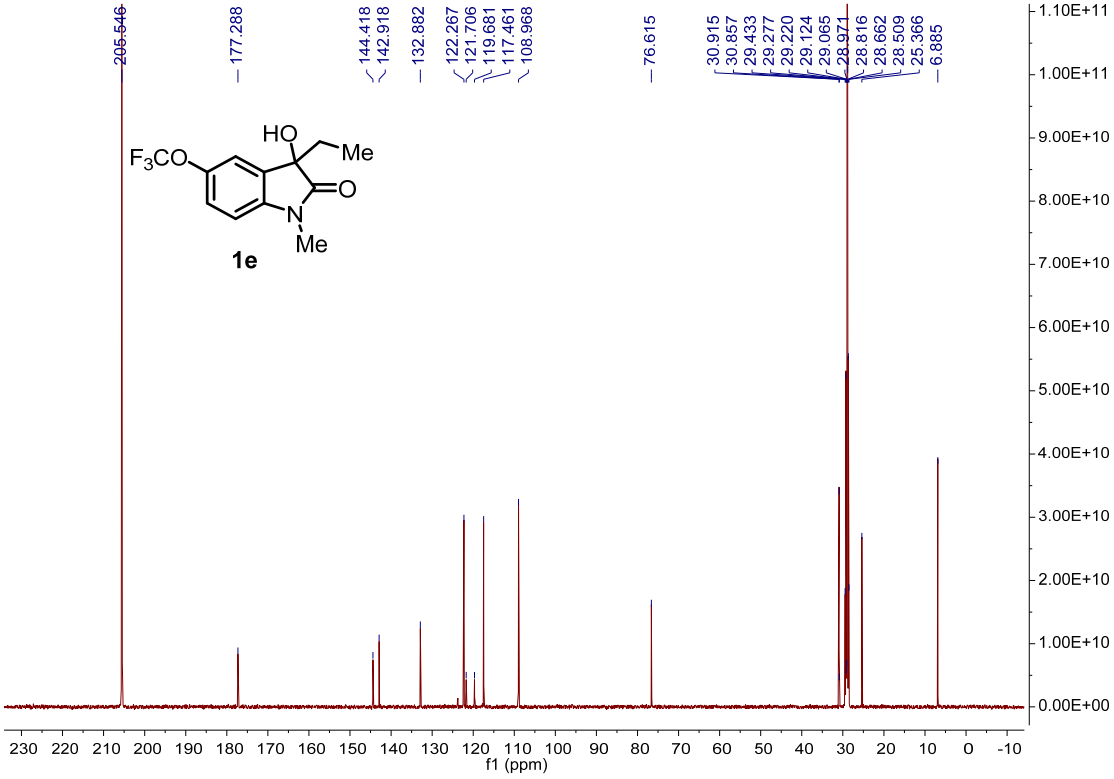
3-ethyl-5-fluoro-3-hydroxy-1-methylindolin-2-one (1d). ^{19}F NMR (470 MHz, $CDCl_3$**)**



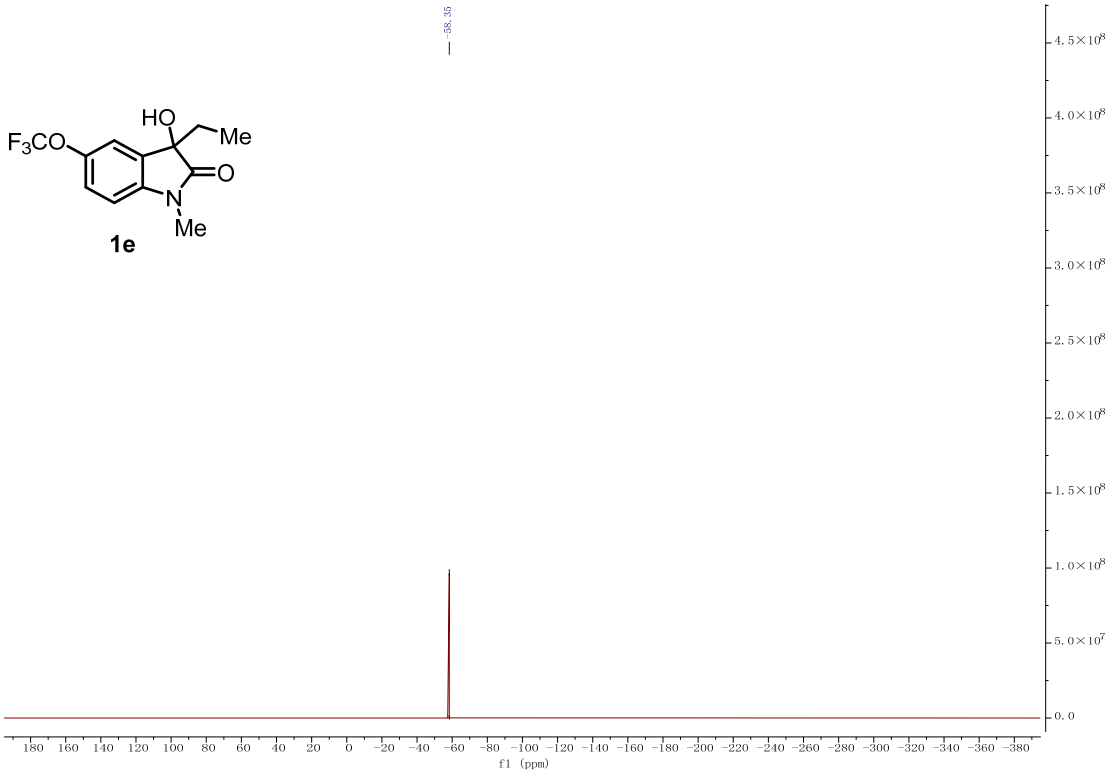
3-ethyl-3-hydroxy-1-methyl-5-(trifluoromethoxy) indolin-2-one (1e). ^{1}H NMR (500 MHz, $CDCl_3$**)**



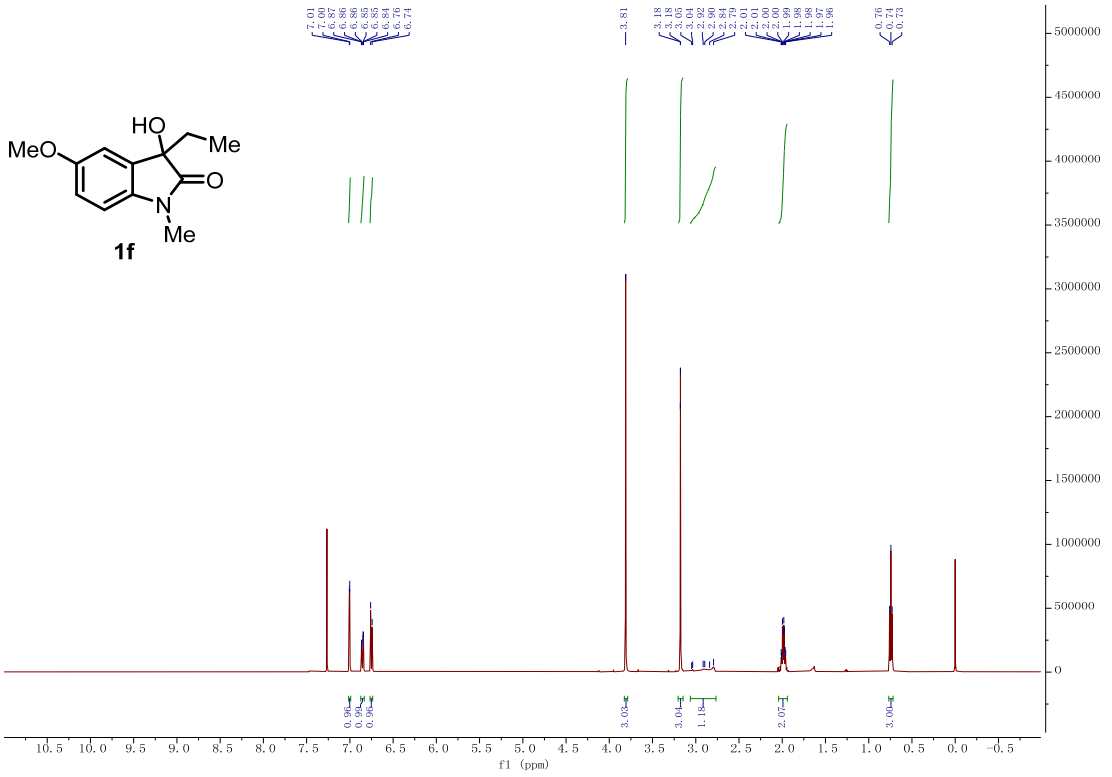
3-ethyl-3-hydroxy-1-methyl-5-(trifluoromethoxy) indolin-2-one (1e). ^{13}C NMR (125 MHz, Acetone-d_6**)**



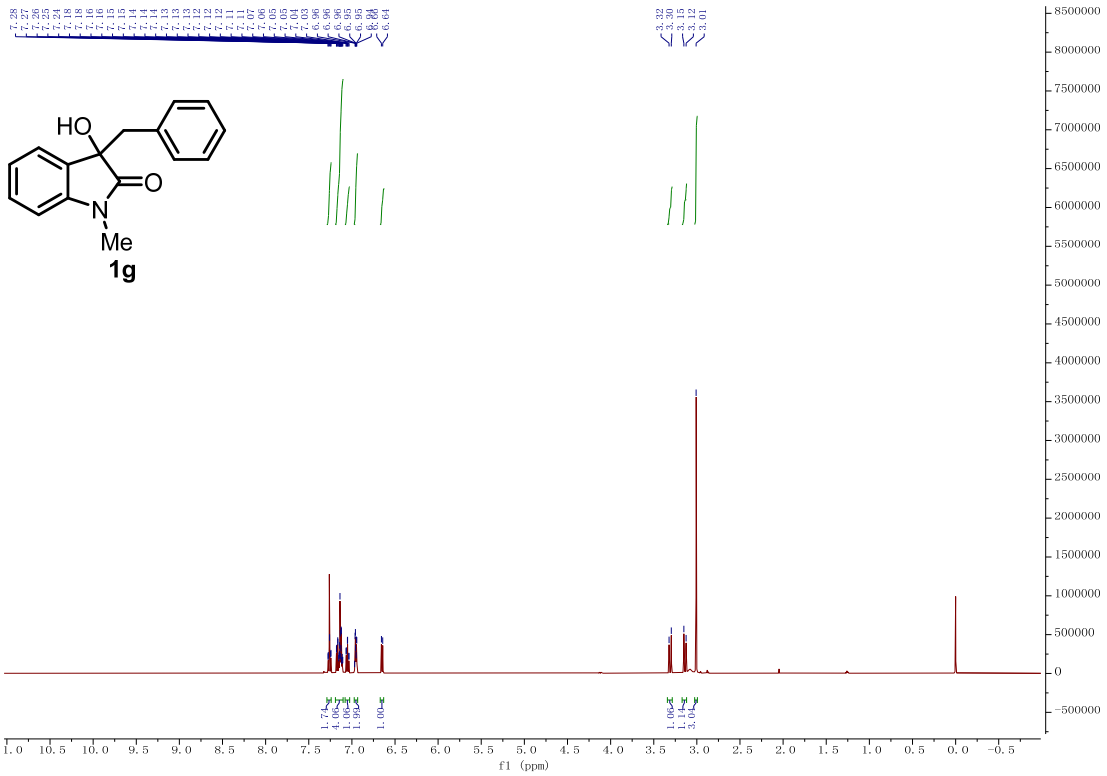
3-ethyl-3-hydroxy-1-methyl-5-(trifluoromethoxy) indolin-2-one (1e). ^{19}F NMR (470 MHz, $CDCl_3$**)**



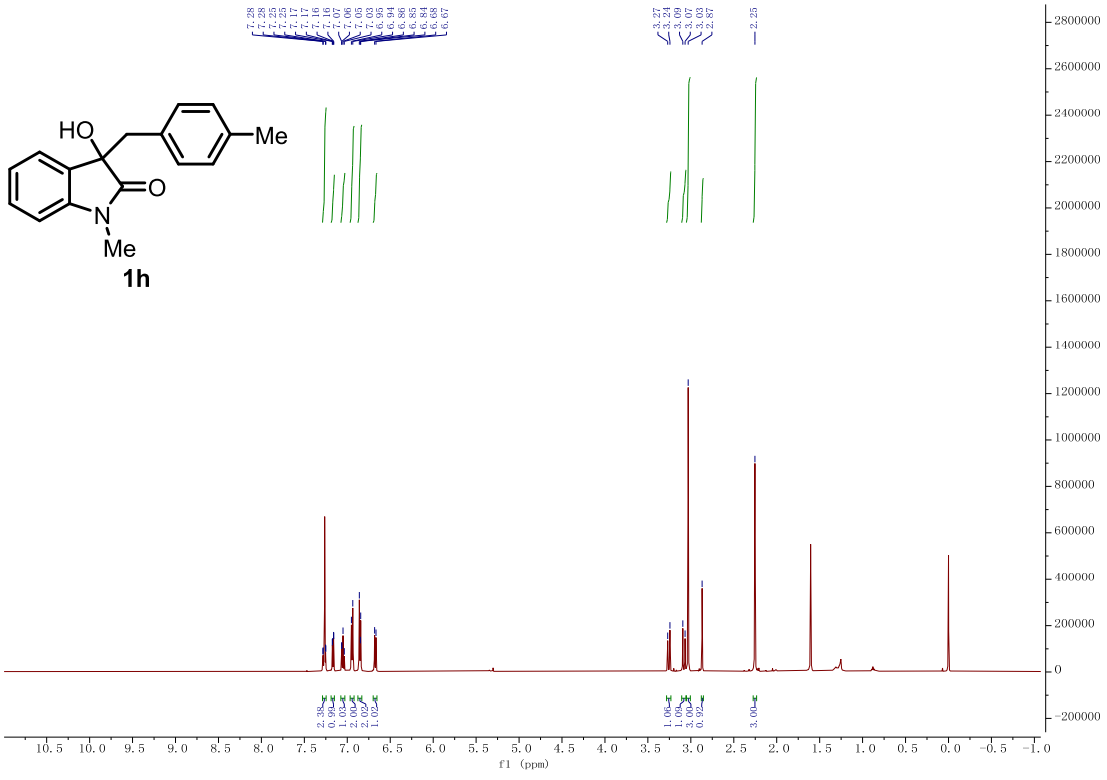
3-ethyl-3-hydroxy-5-methoxy-1-methylindolin-2-one (1f). ^{1}H NMR (500 MHz, $CDCl_3$**)**



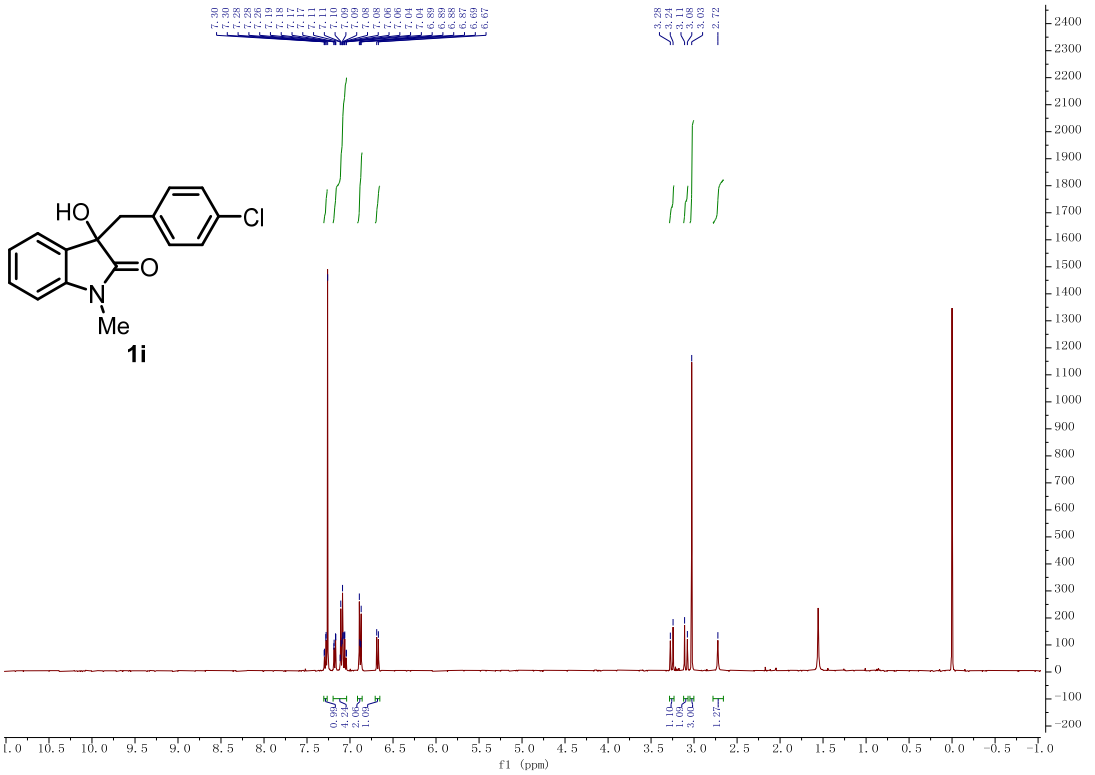
3-benzyl-3-hydroxy-1-methylindolin-2-one (1g). ^{1}H NMR (500 MHz, $CDCl_3$**)**



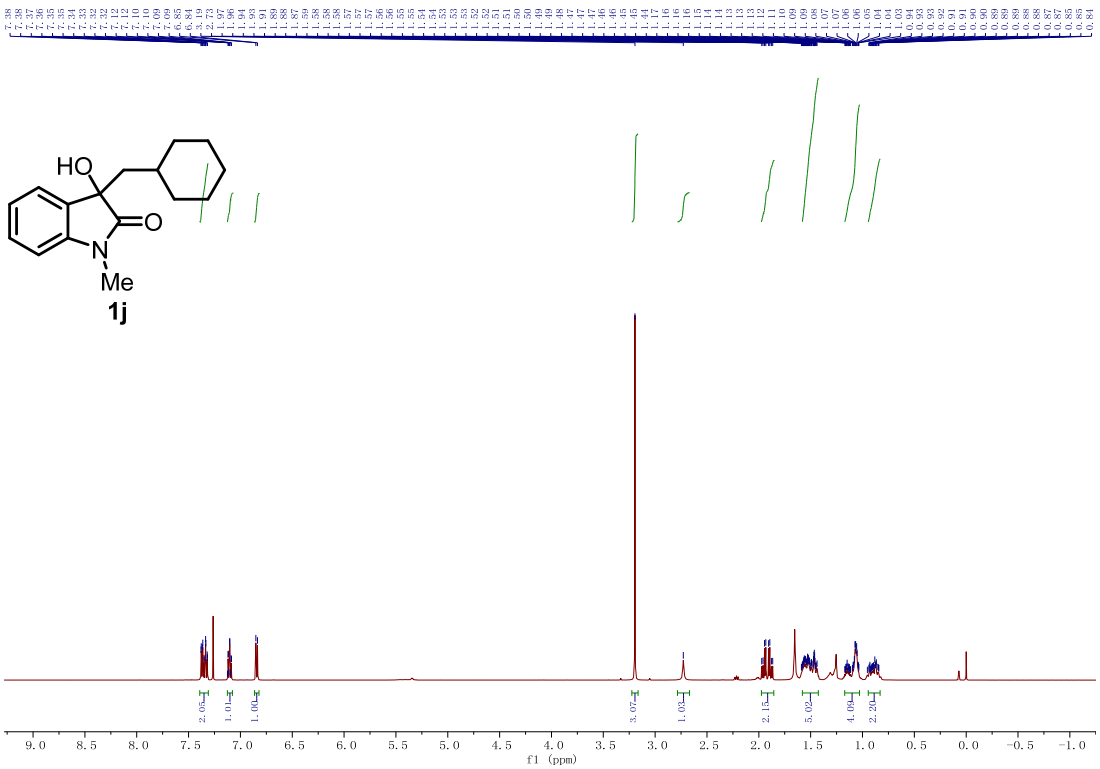
3-hydroxy-1-methyl-3-(4-methylbenzyl)indolin-2-one (1h). ^{1}H NMR (500 MHz, $CDCl_3$**)**



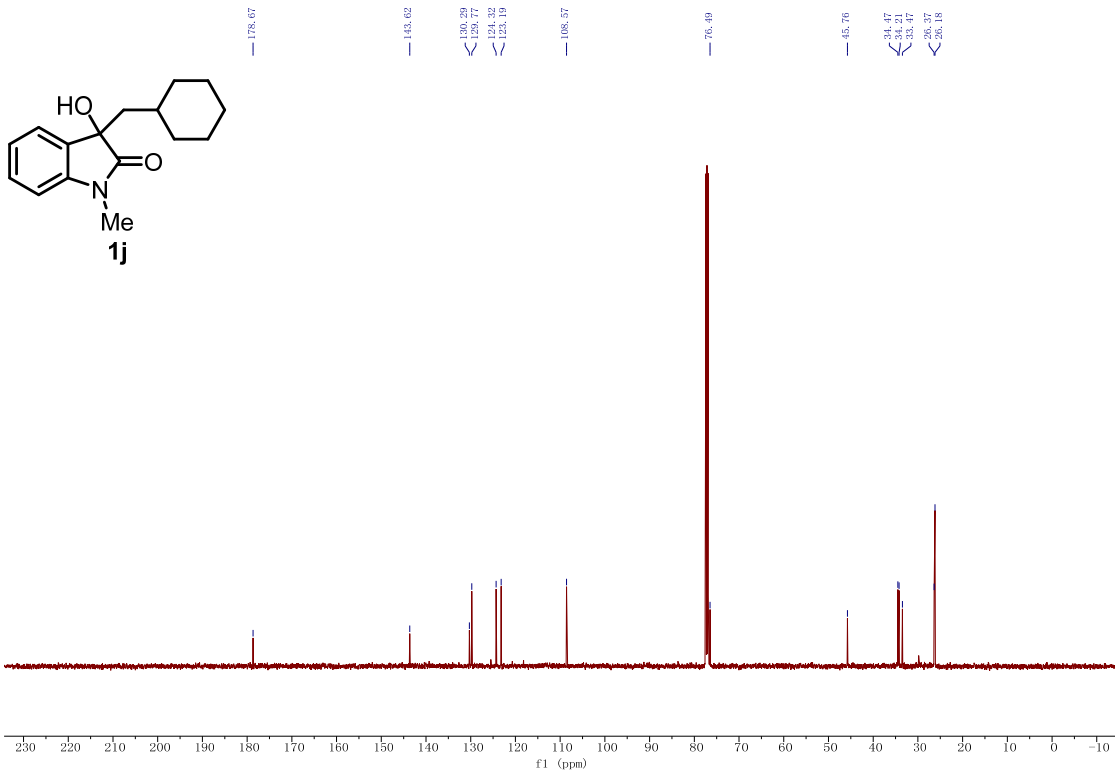
3-(4-chlorobenzyl)-3-hydroxy-1-methylindolin-2-one (1i). ^{1}H NMR (400 MHz, $CDCl_3$**)**



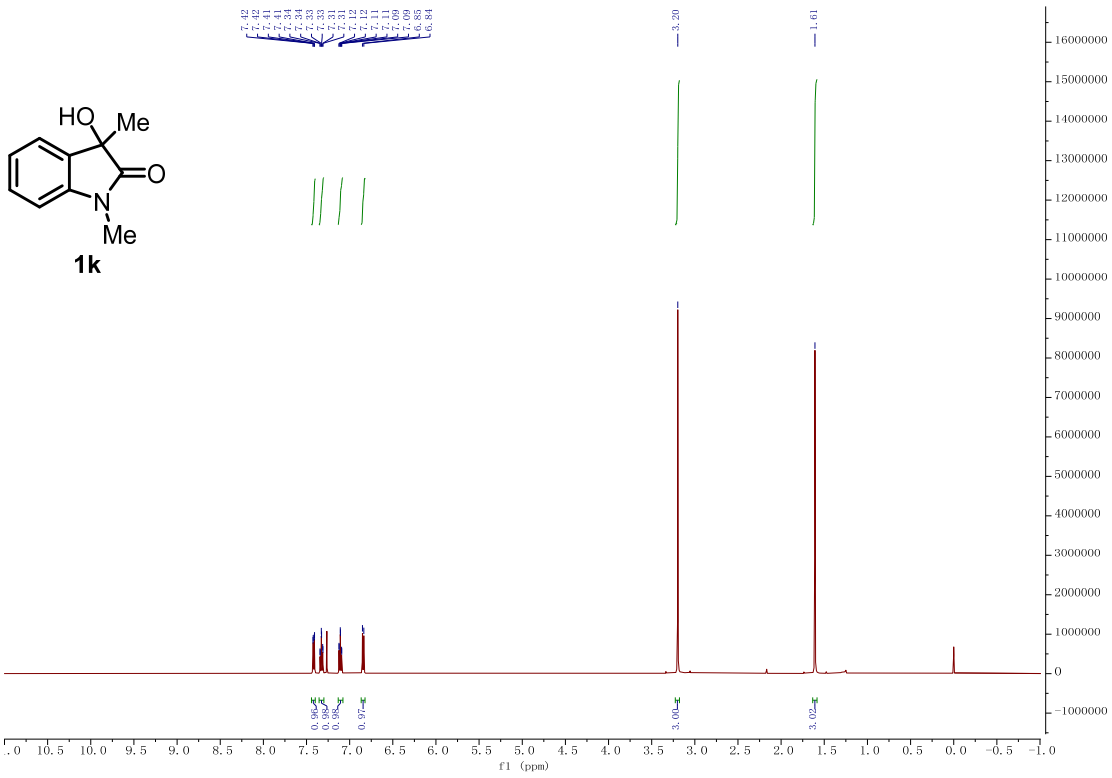
3-(cyclohexylmethyl)-3-hydroxy-1-methylindolin-2-one (1j). ^{1}H NMR (500 MHz, $CDCl_3$**)**



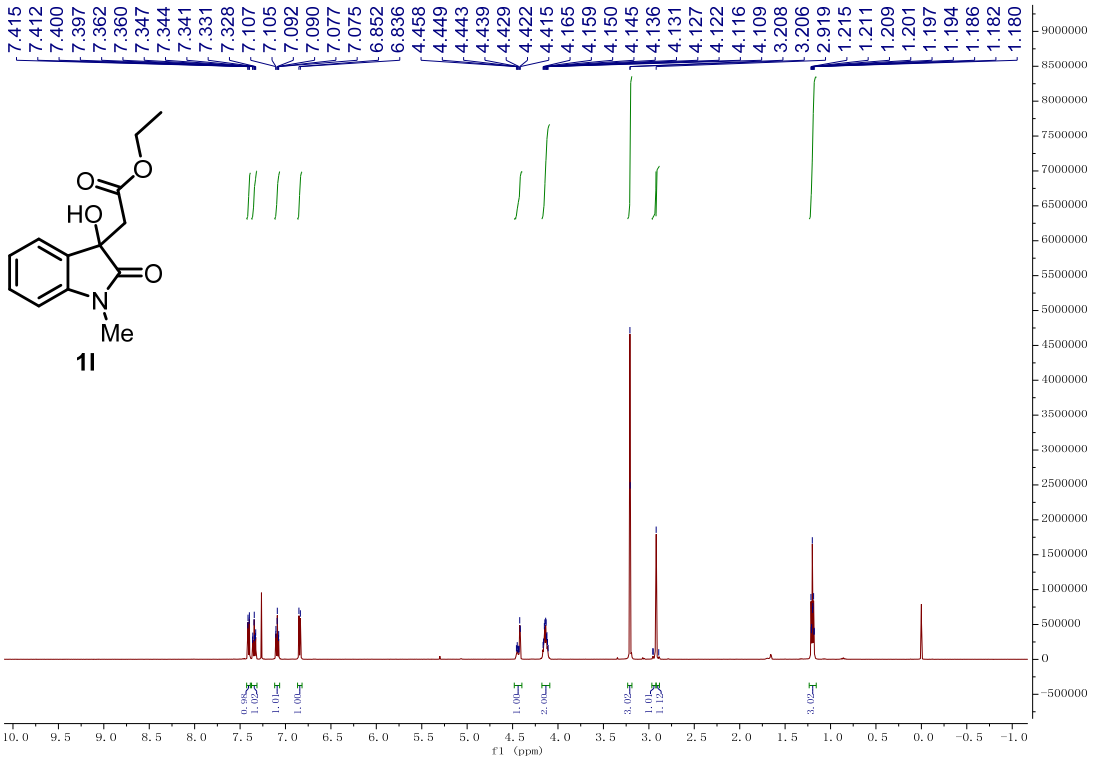
3-(cyclohexylmethyl)-3-hydroxy-1-methylindolin-2-one (1j). ^{1}H NMR (500 MHz, $CDCl_3$**)**



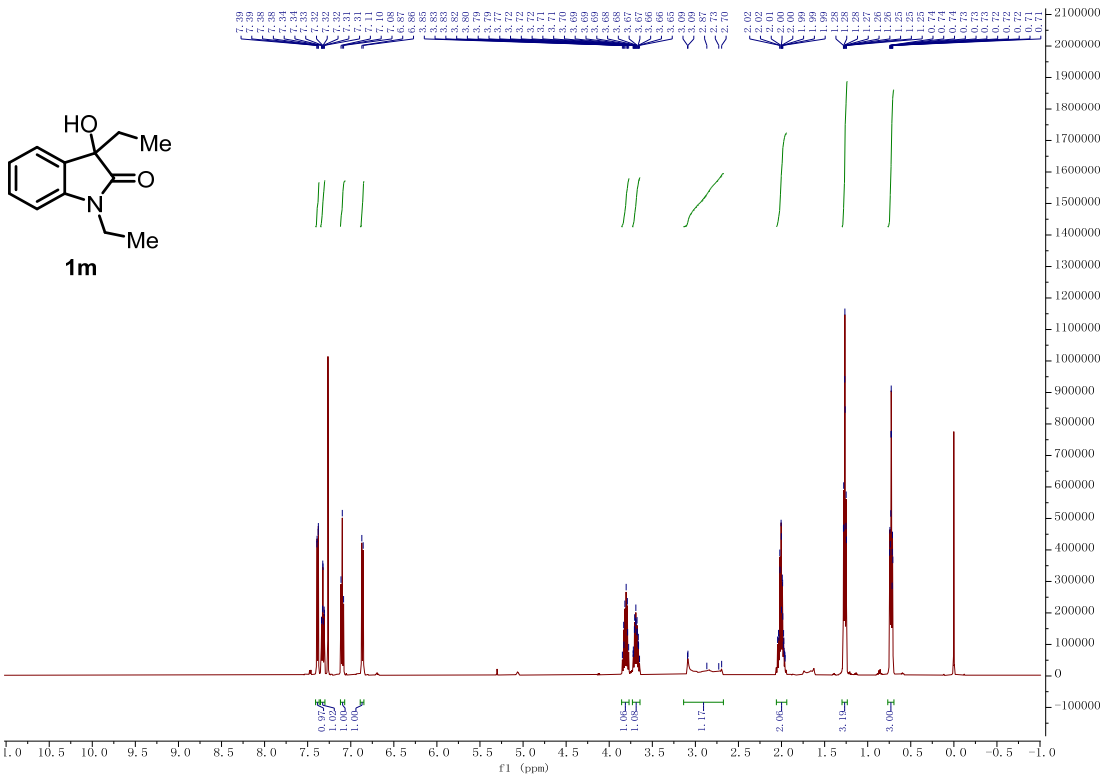
3-hydroxy-1,3-dimethylindolin-2-one (1k). ^{1}**H NMR (**500 MHz, $CDCl_3$**)**



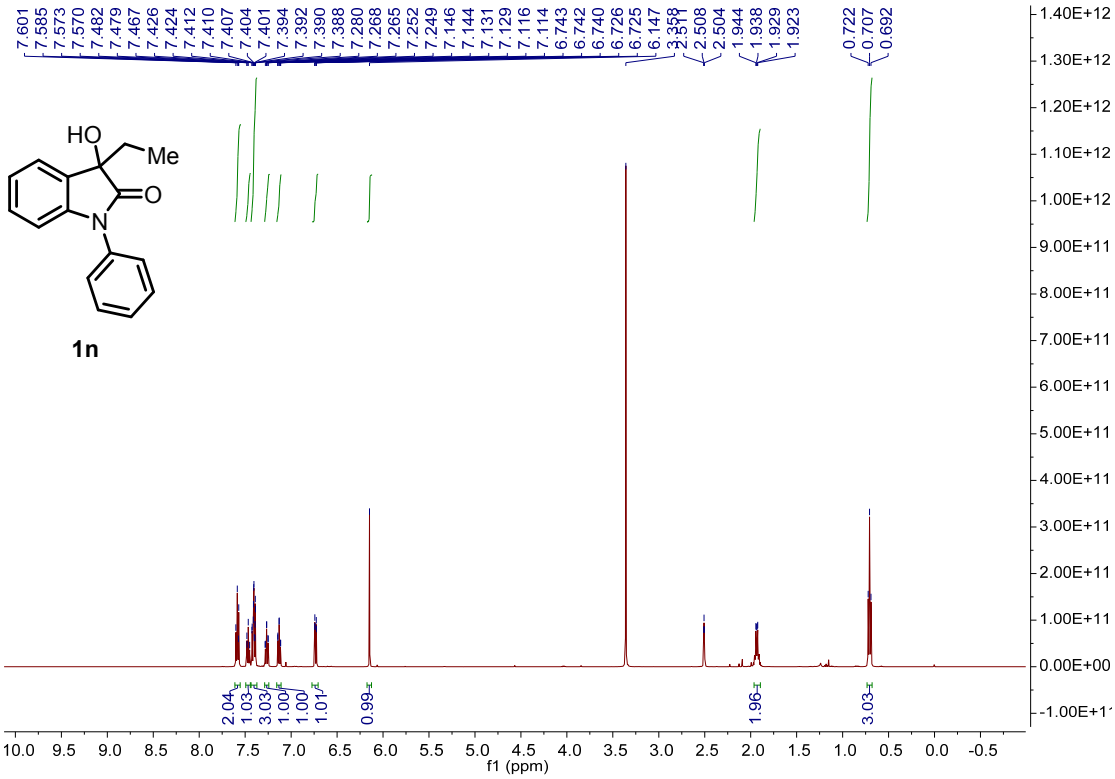
ethyl 2-(3-hydroxy-1-methyl-2-oxoindolin-3-yl) acetate (1l). ^{1}H NMR (500 MHz, $CDCl_3$**)**



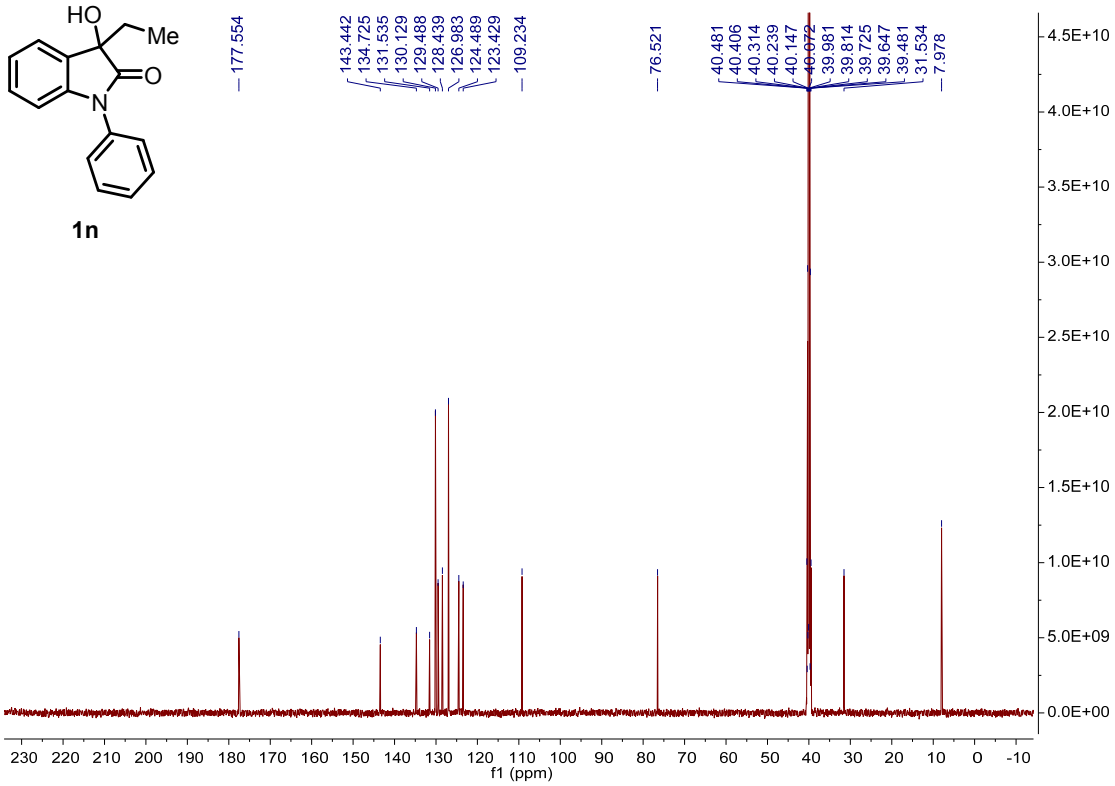
1,3-diethyl-3-hydroxyindolin-2-one (1m). ^{1}H NMR (500 MHz, $CDCl_3$**)**



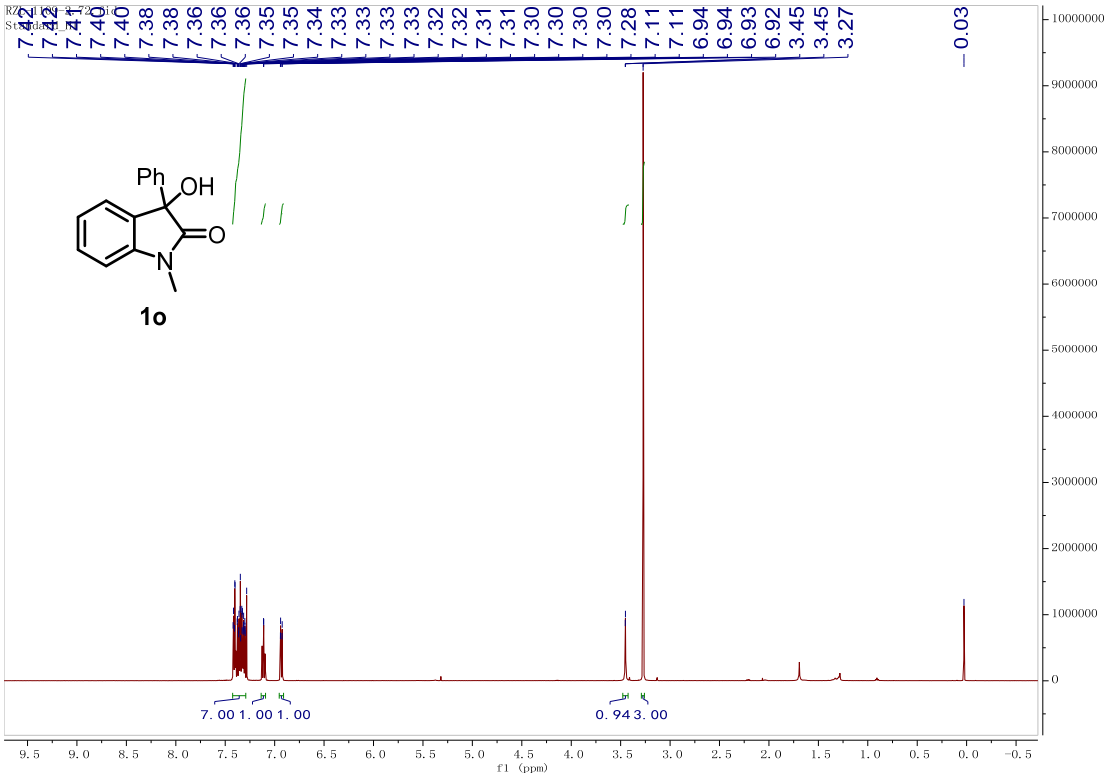
3-ethyl-3-hydroxy-1-phenylindolin-2-one (1n). ^{1}H NMR (500 MHz, DMSO-d_6**)**



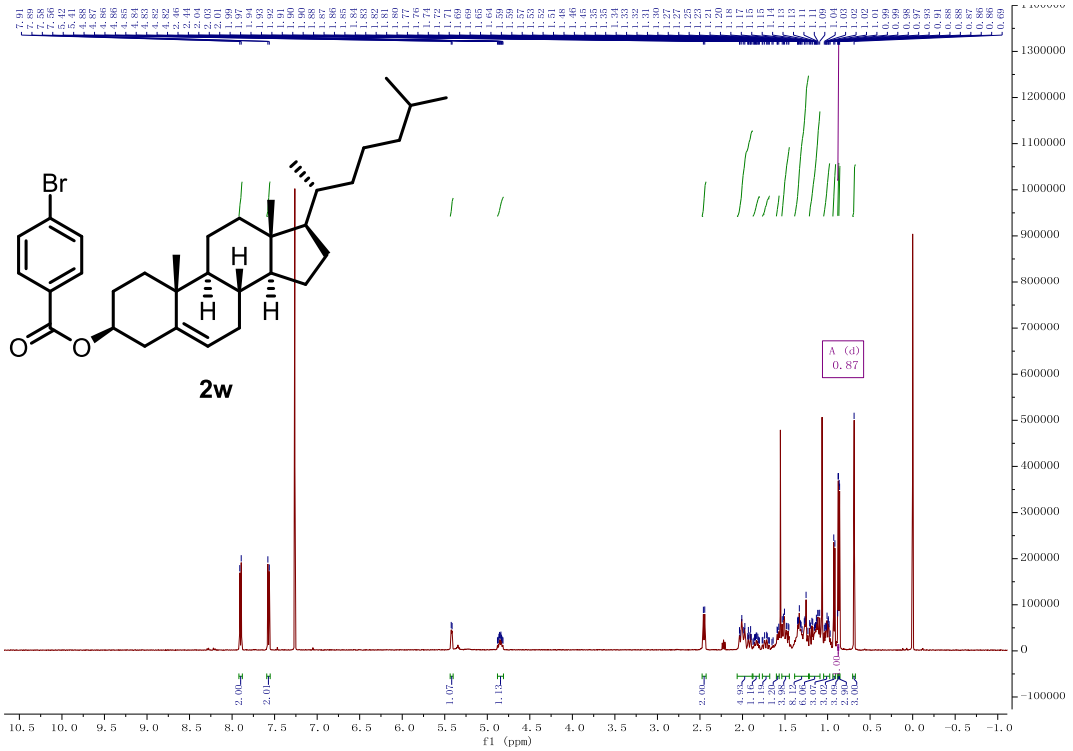
3-ethyl-3-hydroxy-1-phenylindolin-2-one (1n). ^{13}C NMR (125 MHz, DMSO-d_6**)**



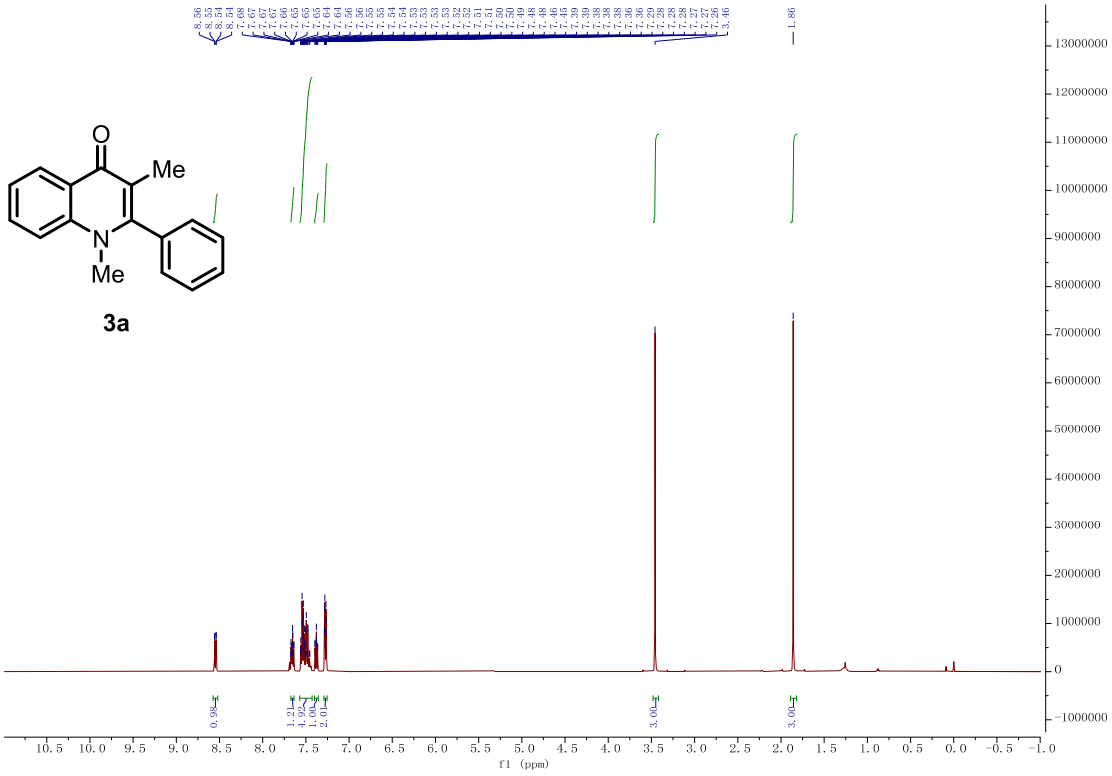
3-**hydroxy-1-methyl-3-phenylindolin-2-one (1o).** ^{1}**H NMR (**500 MHz, $CDCl_3$**)**



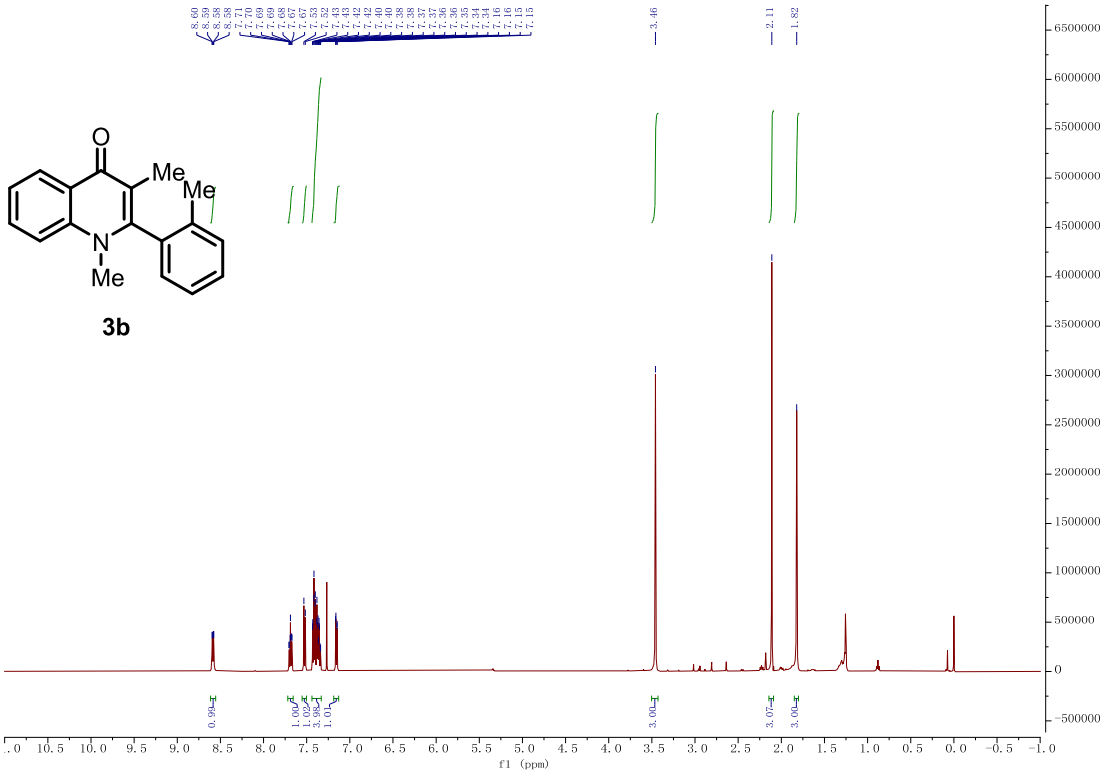
(3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4- bromobenzoate (2w). ^{1}**H NMR (**500 MHz, $CDCl_3$**)**



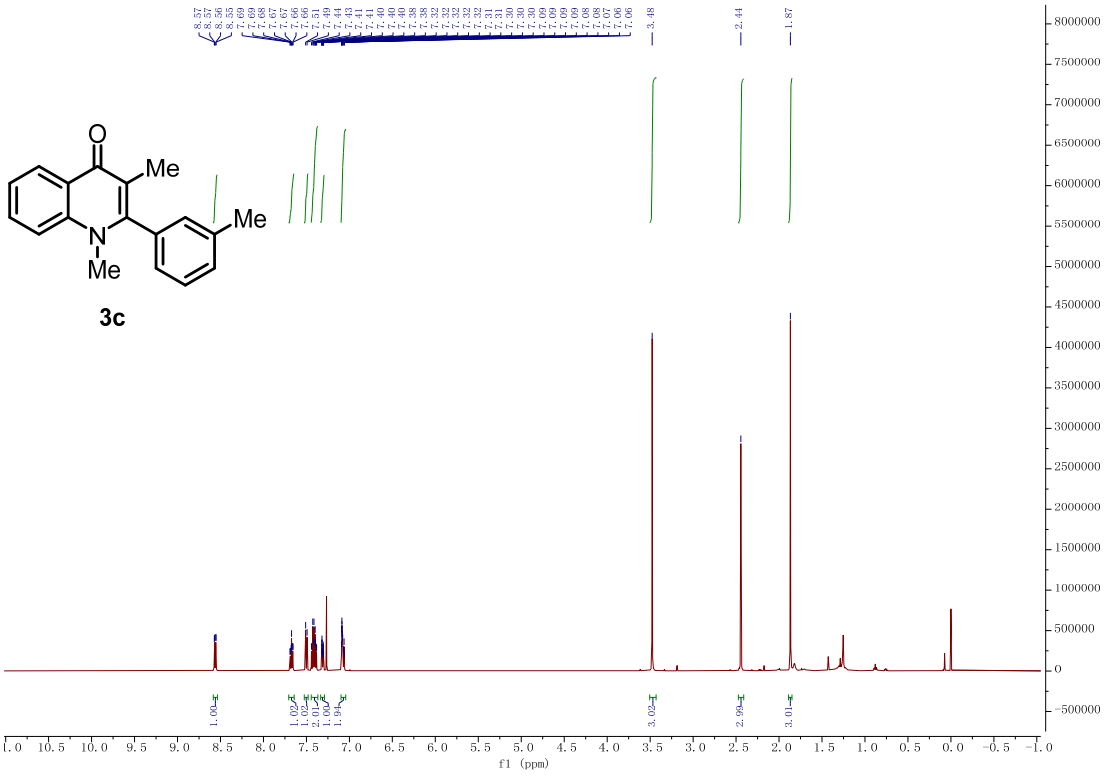
1,3-dimethyl-2-phenylquinolin-4(1*H*)-one (3a). ^{1}H NMR (500 MHz, $CDCl_3$**)**



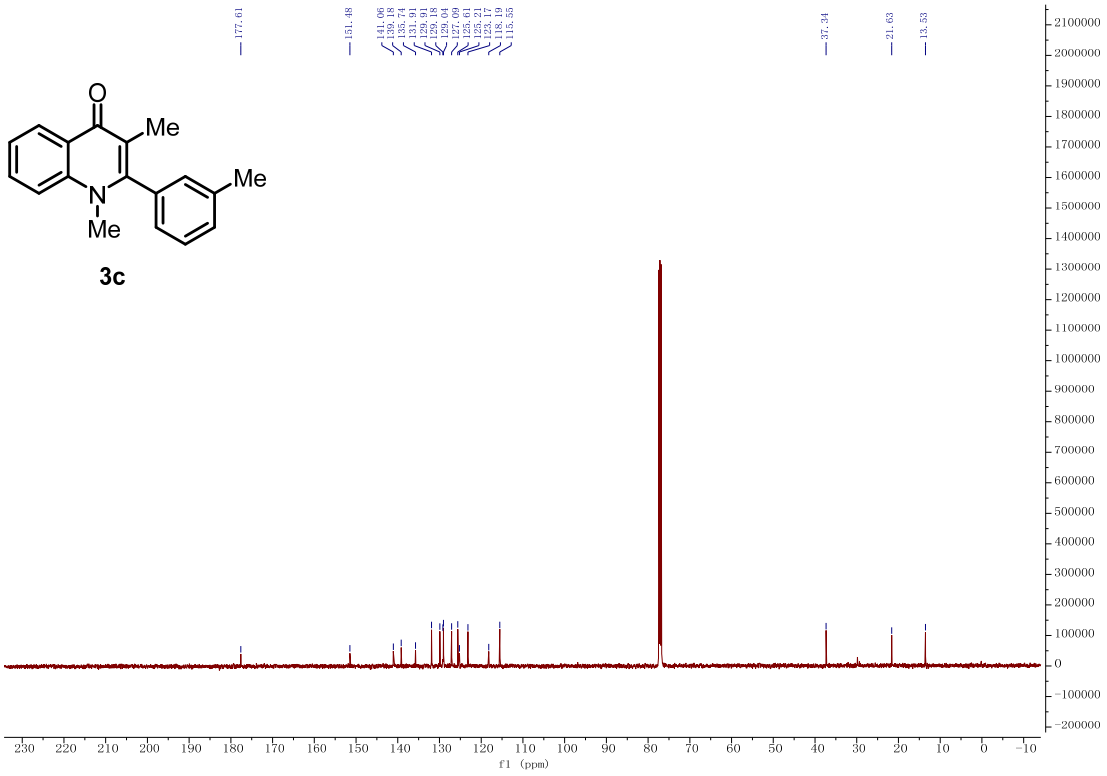
1,3-dimethyl-2-(*o*-tolyl)quinolin-4(1*H*)-one (3b). ^{1}H NMR (500 MHz, $CDCl_3$**)**



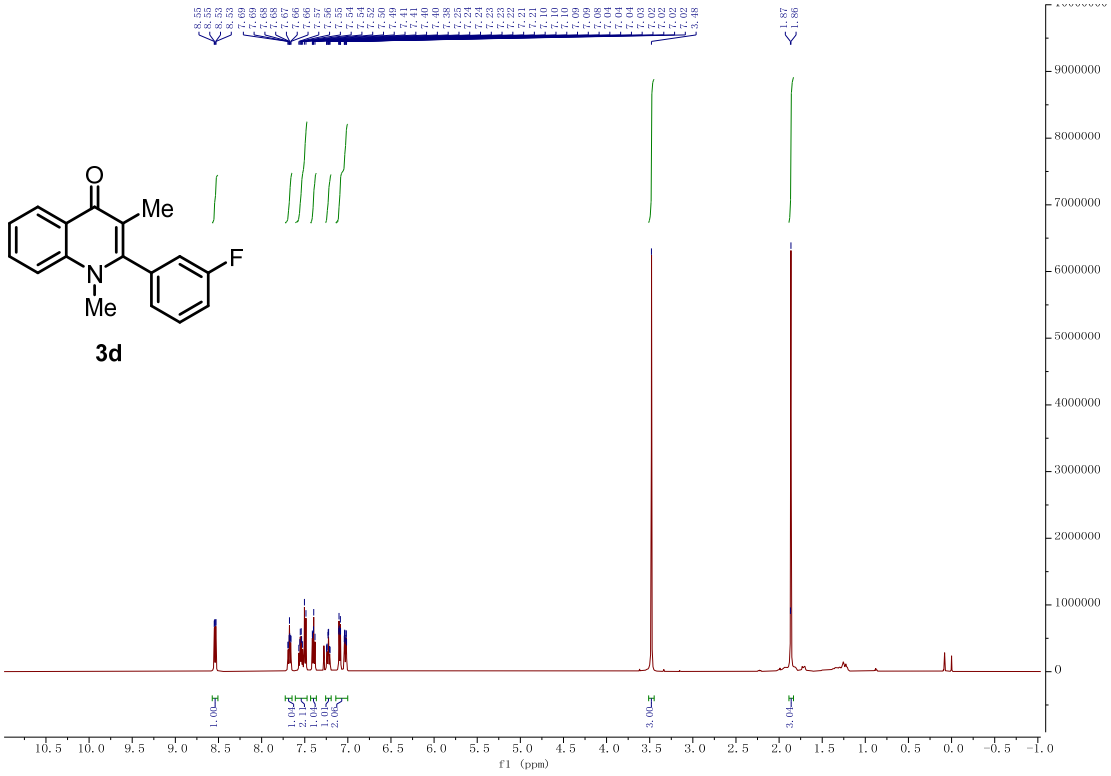
1,3-dimethyl-2-(*m*-tolyl)quinolin-4(1*H*)-one (3c). ^{1}H NMR (500 MHz, $CDCl_3$**)**



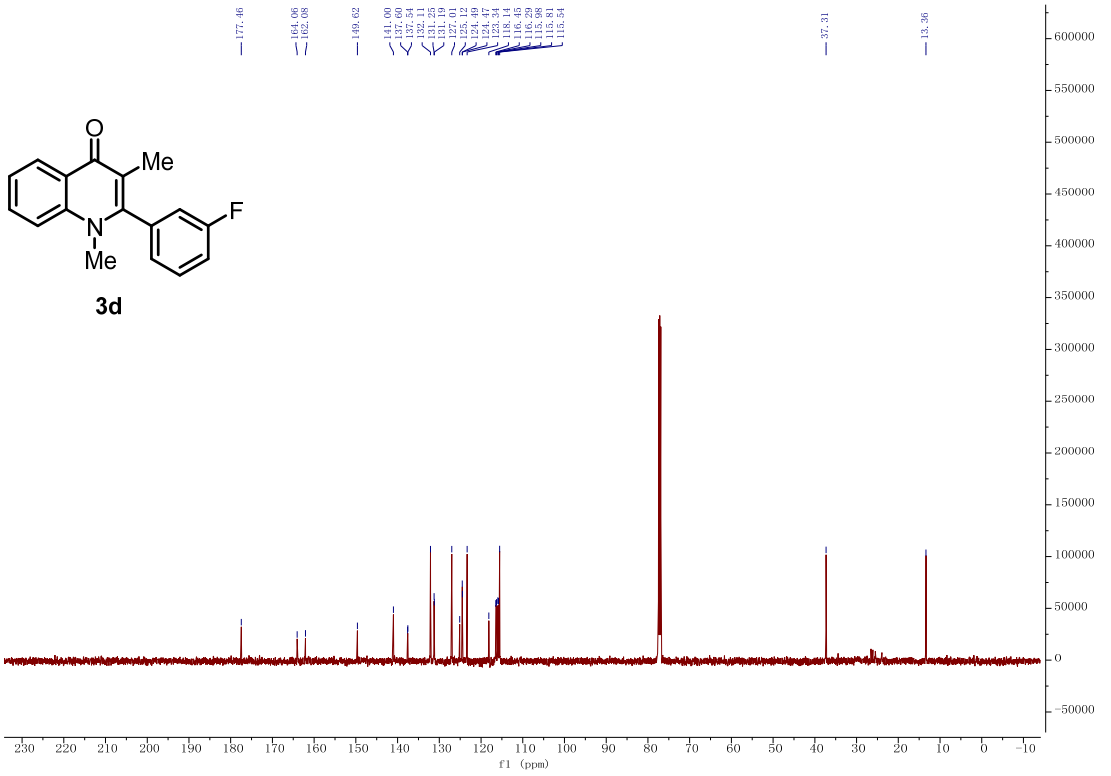
1,3-dimethyl-2-(*m*-tolyl)quinolin-4(1*H*)-one (3c). ^{13}C NMR (125 MHz, $CDCl_3$**)**



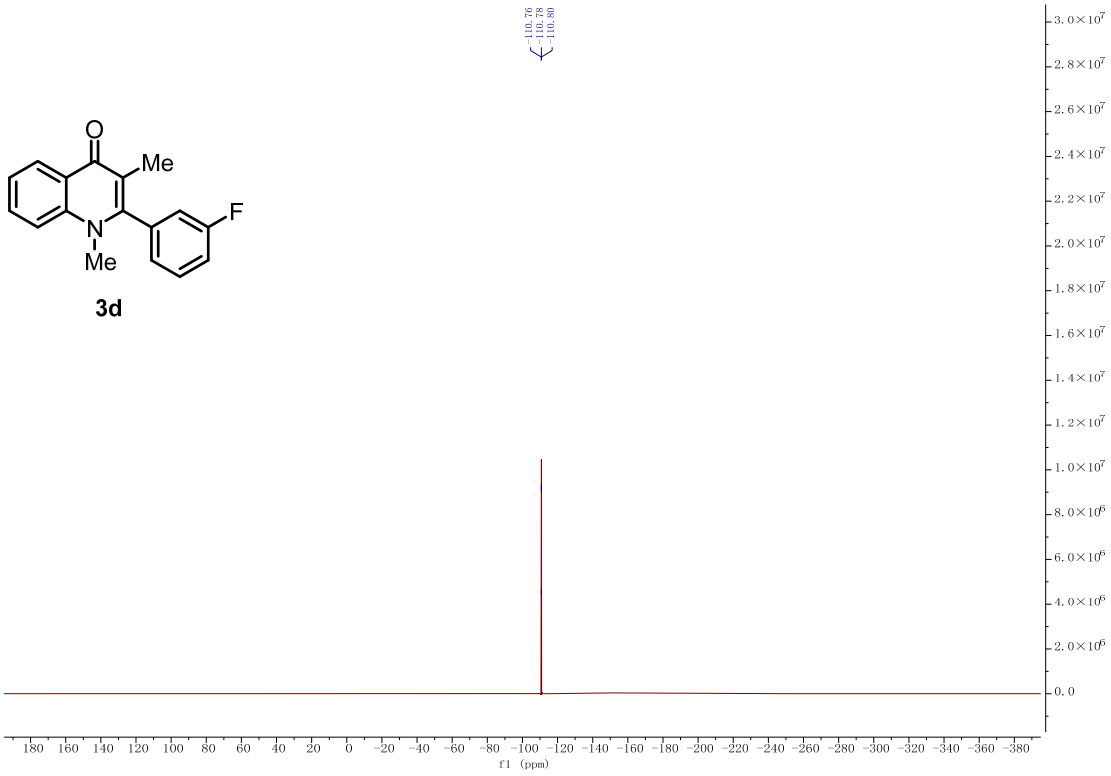
2-(3-fluorophenyl)-1,3-dimethylquinolin-4(1*H*)-one (3d). ^{1}H NMR (500 MHz, $CDCl_3$**)**



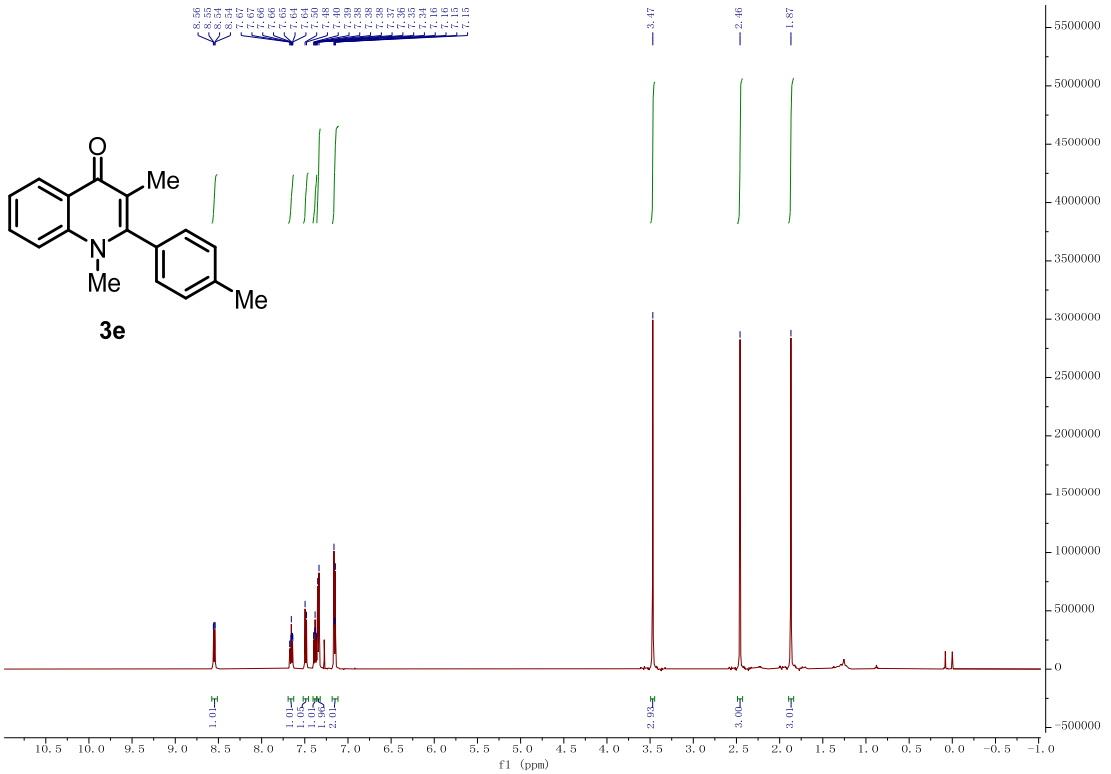
2-(3-fluorophenyl)-1,3-dimethylquinolin-4(1*H*)-one (3d). ^{13}C NMR (125 MHz, $CDCl_3$**)**



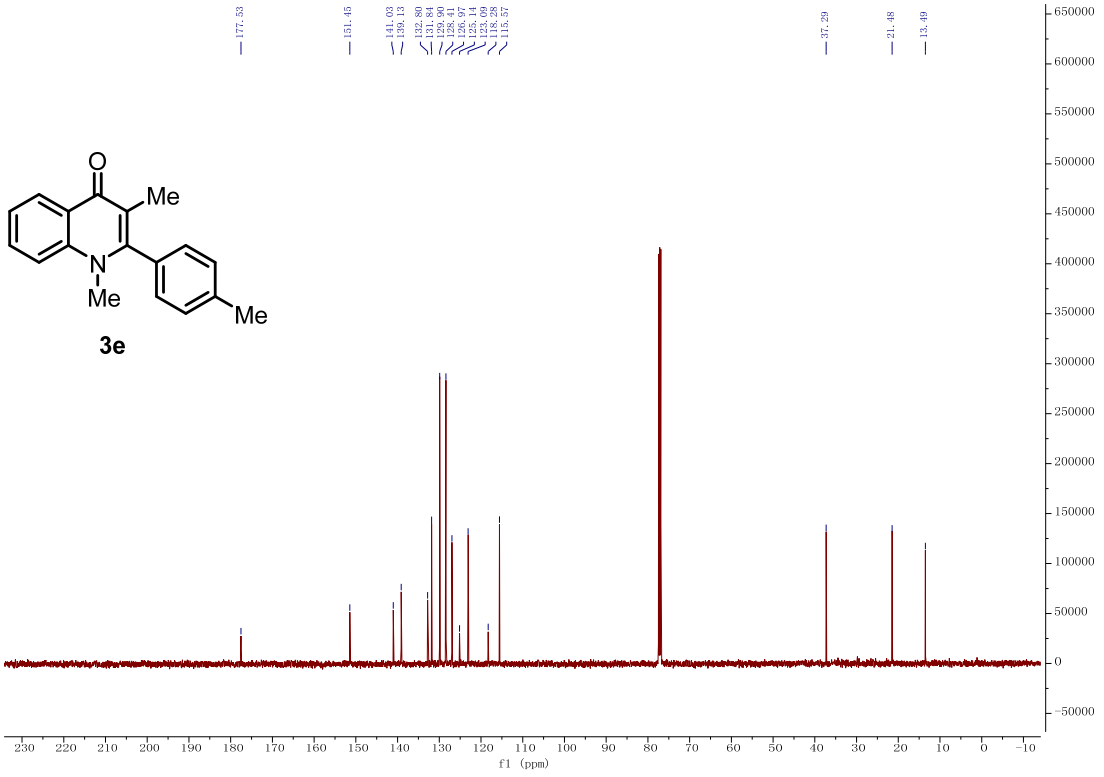
2-(3-fluorophenyl)-1,3-dimethylquinolin-4(1*H*)-one (3d). ^{19}F NMR (470 MHz, $CDCl_3$**)**



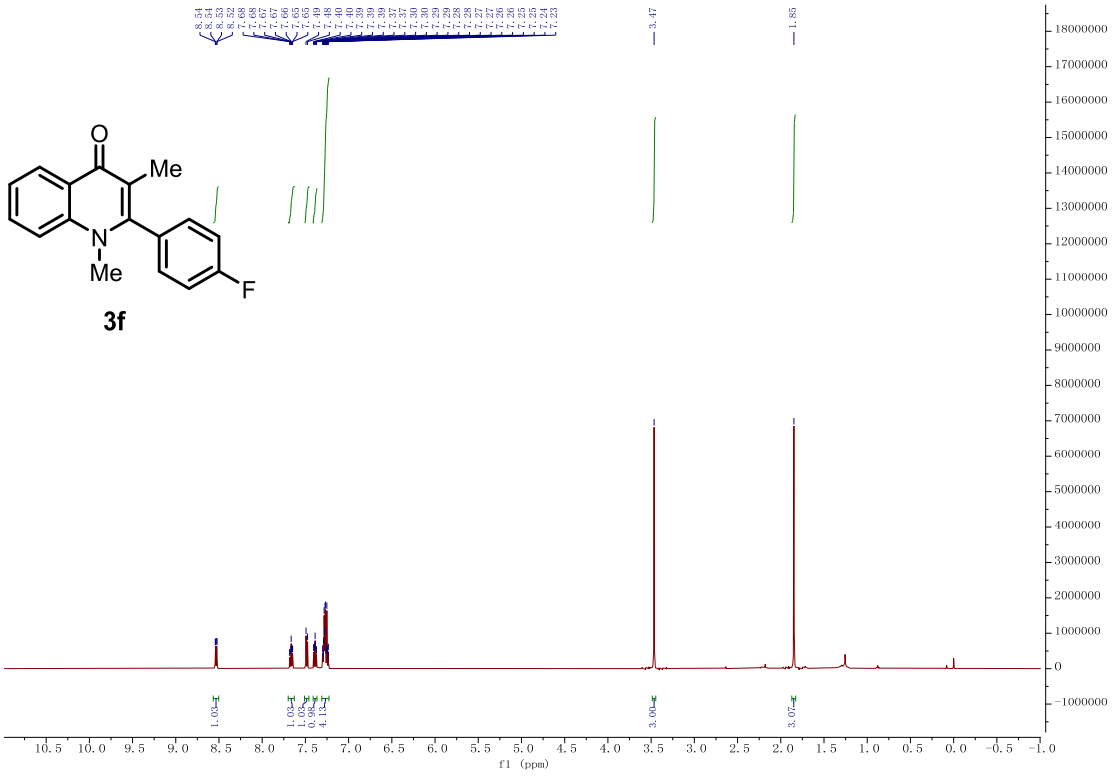
1,3-dimethyl-2-(p-tolyl)quinolin-4(1*H*)-one (3e). ^{1}H NMR (500 MHz, $CDCl_3$**)**



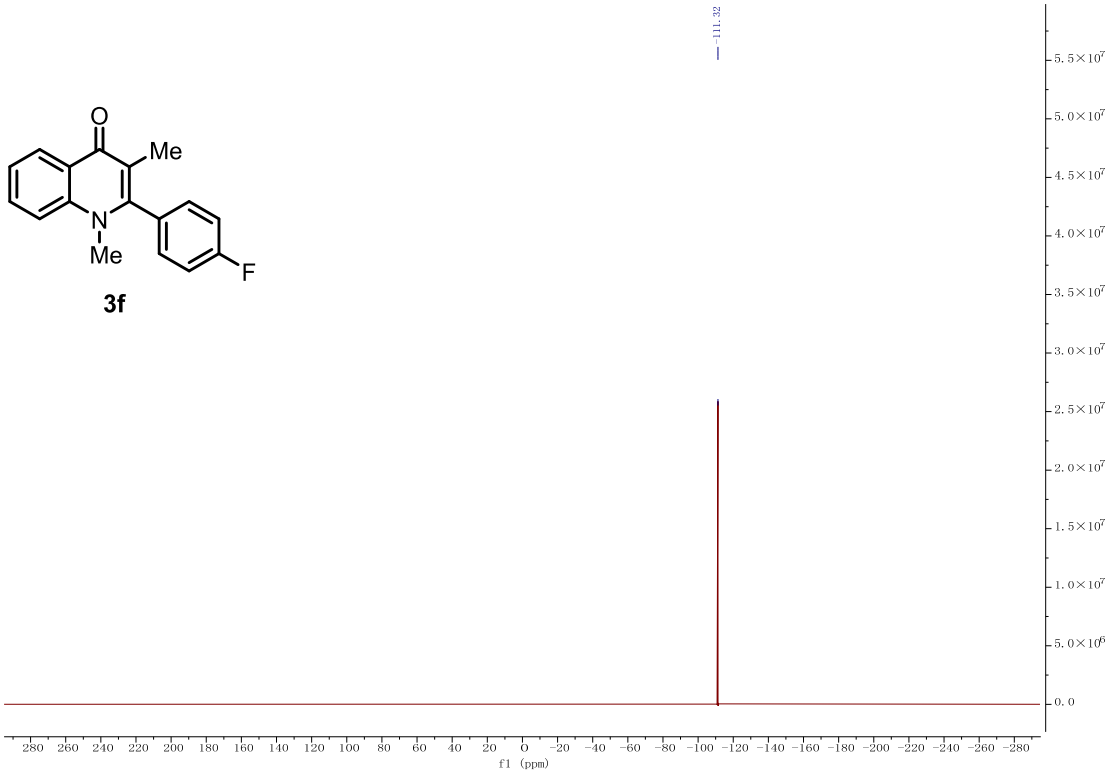
1,3-dimethyl-2-(p-tolyl)quinolin-4(1*H*)-one (3e). ^{13}C NMR (125 MHz, $CDCl_3$**)**



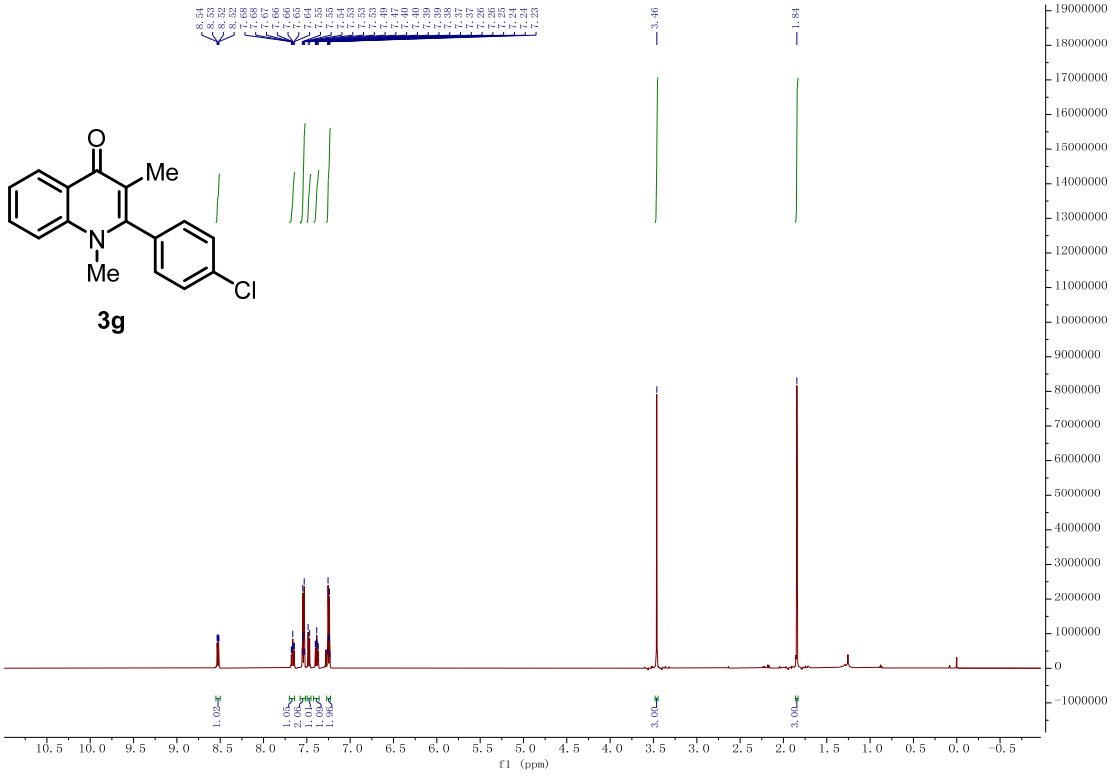
2-(4-fluorophenyl)-1,3-dimethylquinolin-4(1*H*)-one (3f). ^{1}H NMR (500 MHz, $CDCl_3$**)**



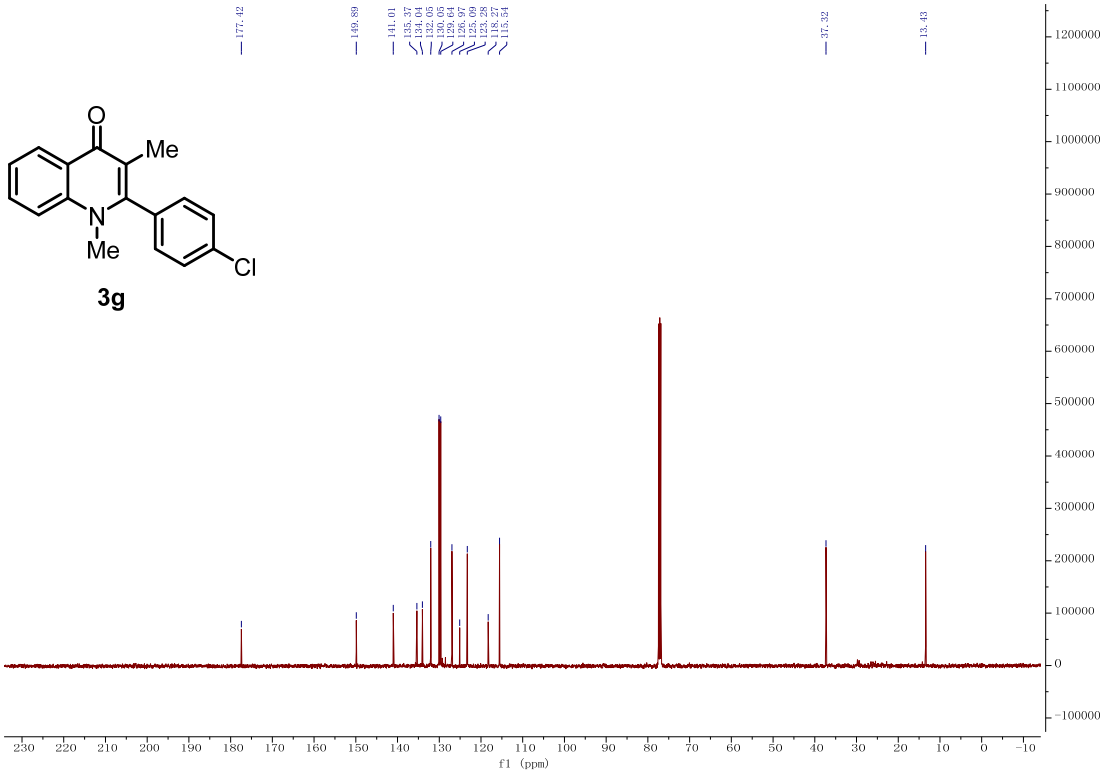
2-(4-fluorophenyl)-1,3-dimethylquinolin-4(1*H*)-one (3f). ^{19}F NMR (470 MHz, $CDCl_3$**)**



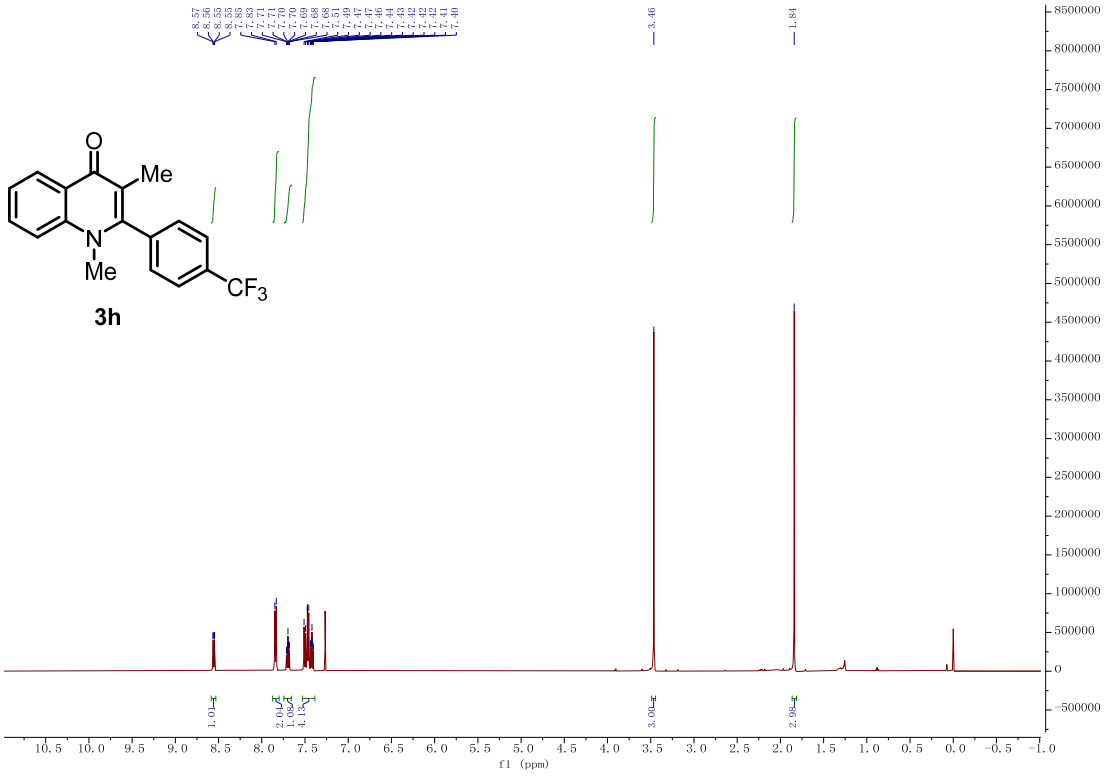
2-(4-chlorophenyl)-1,3-dimethylquinolin-4(1*H*)-one (3g). ^{1}H NMR (500 MHz, $CDCl_3$**)**



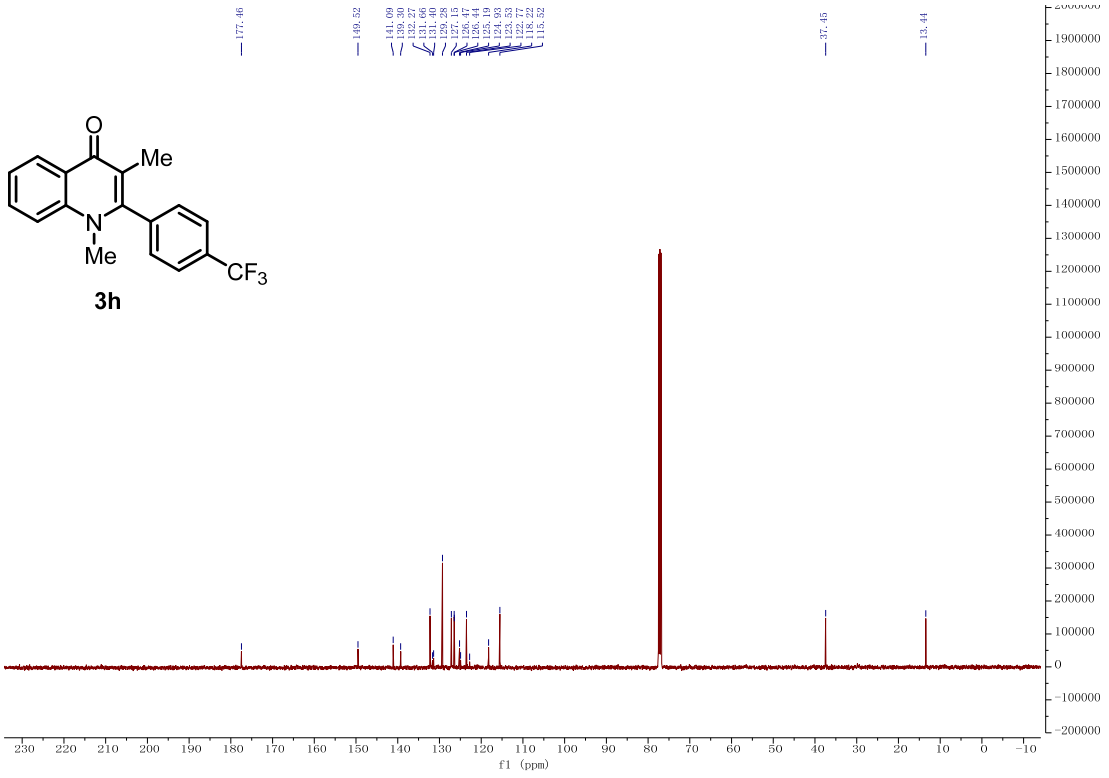
2-(4-chlorophenyl)-1,3-dimethylquinolin-4(1*H*)-one (3g). ^{13}C NMR (125 MHz, $CDCl_3$**)**



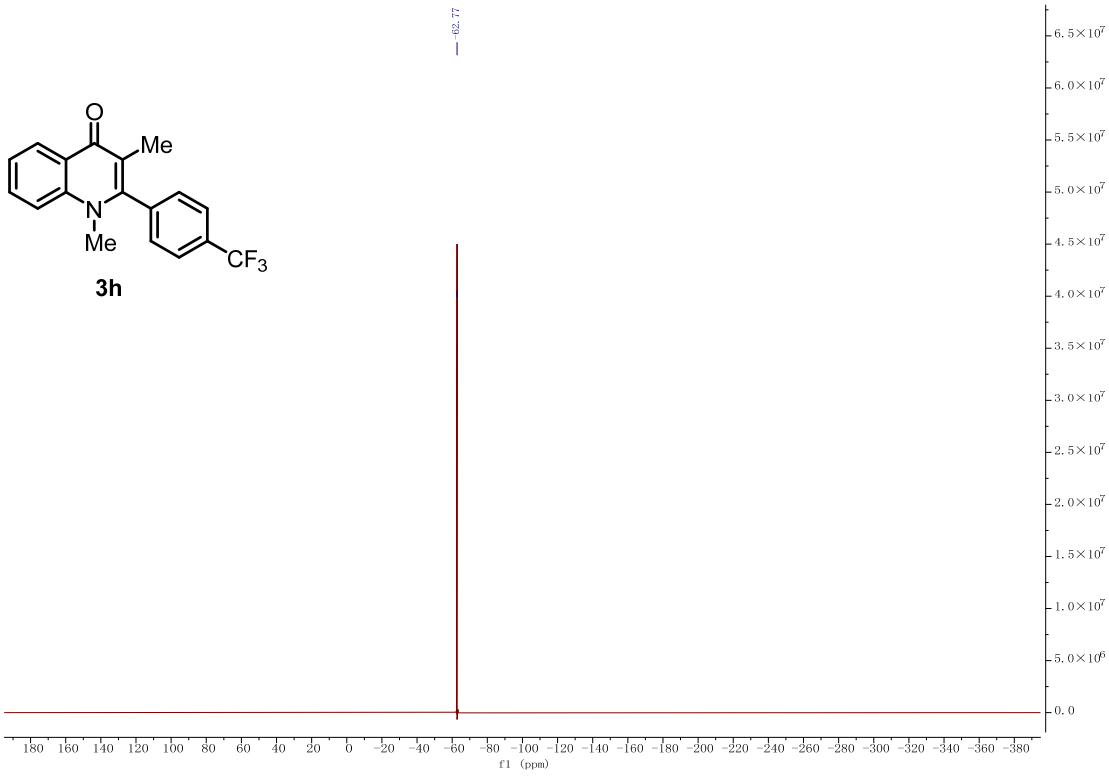
1,3-dimethyl-2-(4-(trifluoromethyl)phenyl)quinolin-4(1*H*)-one (3h). ^{1}H NMR (500 MHz, $CDCl_3$**)**



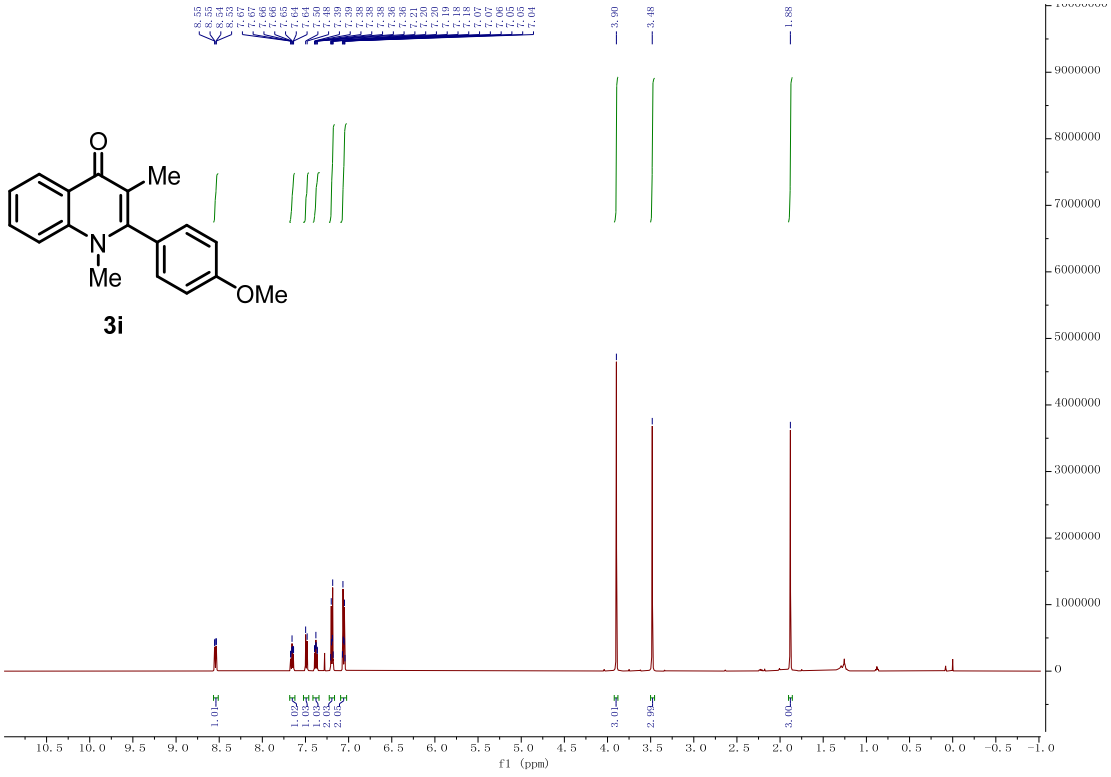
1,3-dimethyl-2-(4-(trifluoromethyl)phenyl)quinolin-4(1*H*)-one (3h). ^{13}C NMR (125 MHz, $CDCl_3$**)**



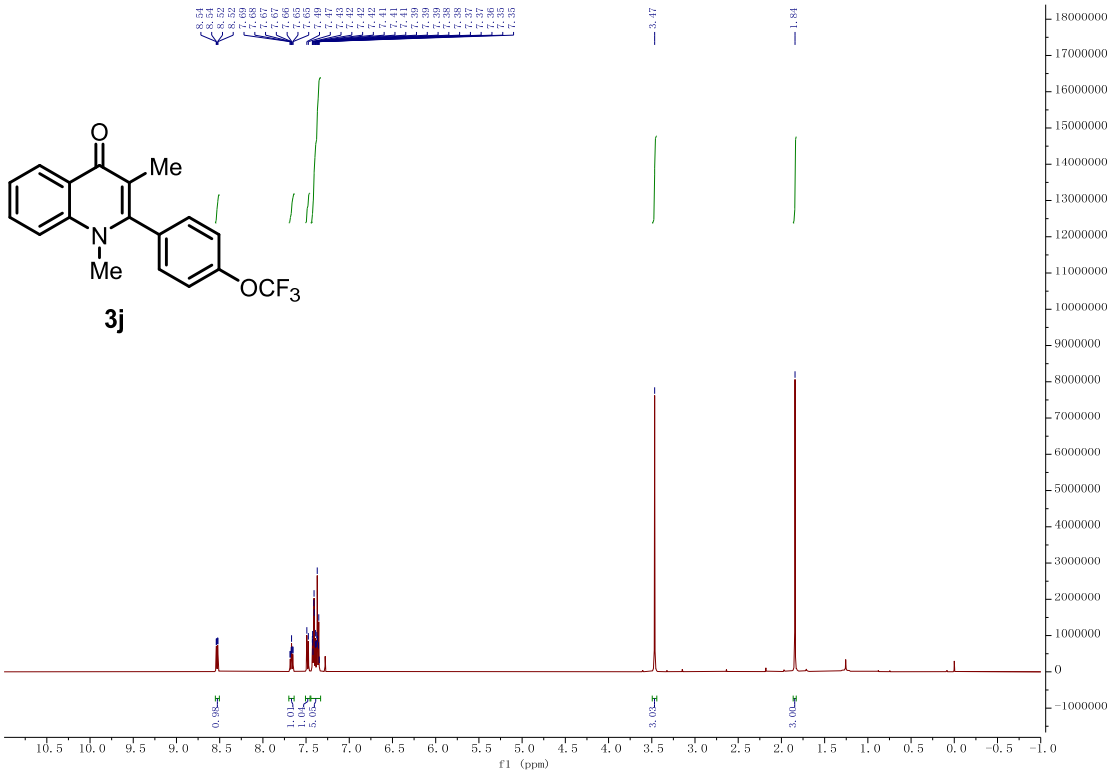
1,3-dimethyl-2-(4-(trifluoromethyl)phenyl)quinolin-4(1*H*)-one (3h). ^{19}F NMR (470 MHz, $CDCl_3$**)**



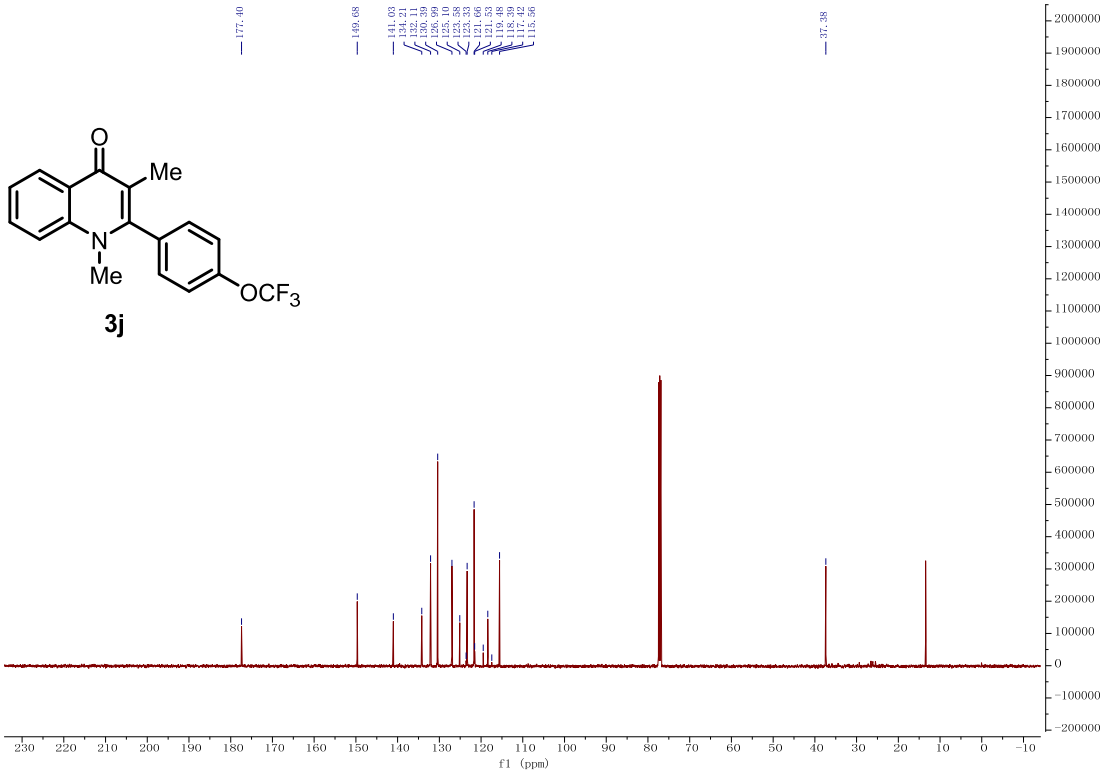
2-(4-methoxyphenyl)-1,3-dimethylquinolin-4(1*H*)-one (3i). ^{1}H NMR (500 MHz, $CDCl_3$**)**



1,3-dimethyl-2-(4-(trifluoromethoxy)phenyl)quinolin-4(1*H*)-one (3j). ^{1}H NMR (500 MHz, $CDCl_3$**)**

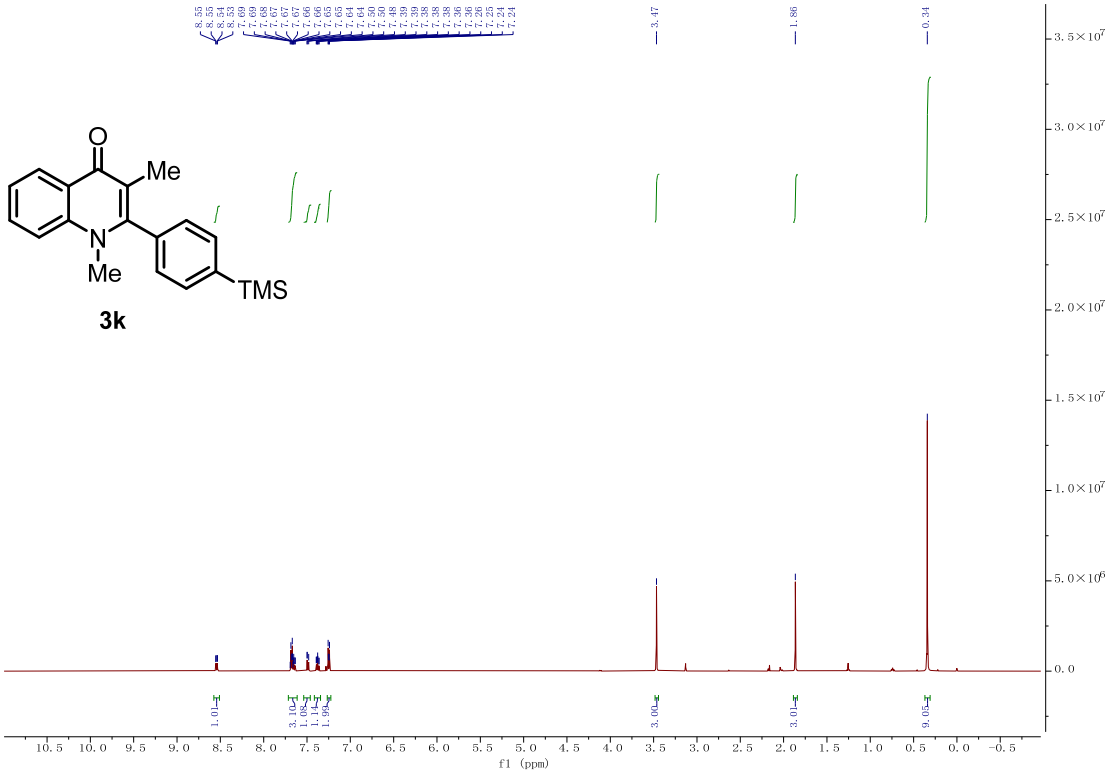


1,3-dimethyl-2-(4-(trifluoromethoxy)phenyl)quinolin-4(1*H*)-one (3j). ^{13}C NMR (125 MHz, $CDCl_3$**)**

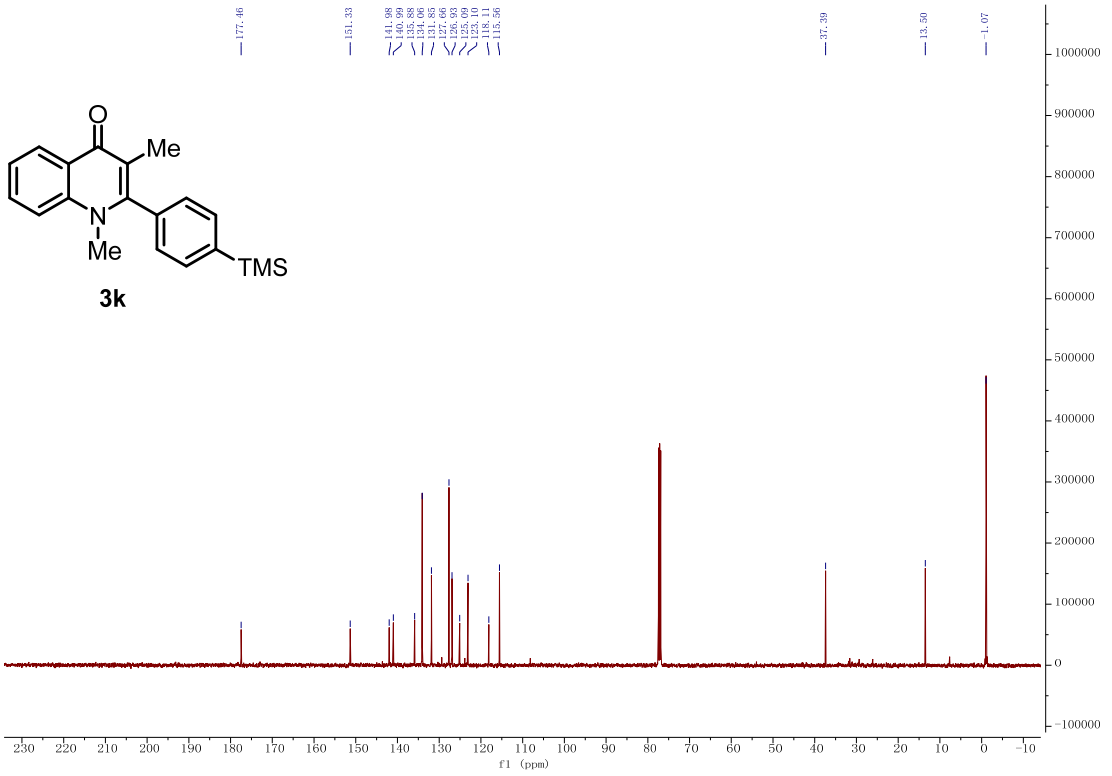


1,3-dimethyl-2-(4-(trifluoromethoxy)phenyl)quinolin-4(1*H*)-one (3j). ^{19}F NMR (470 MHz, $CDCl_3$**)**

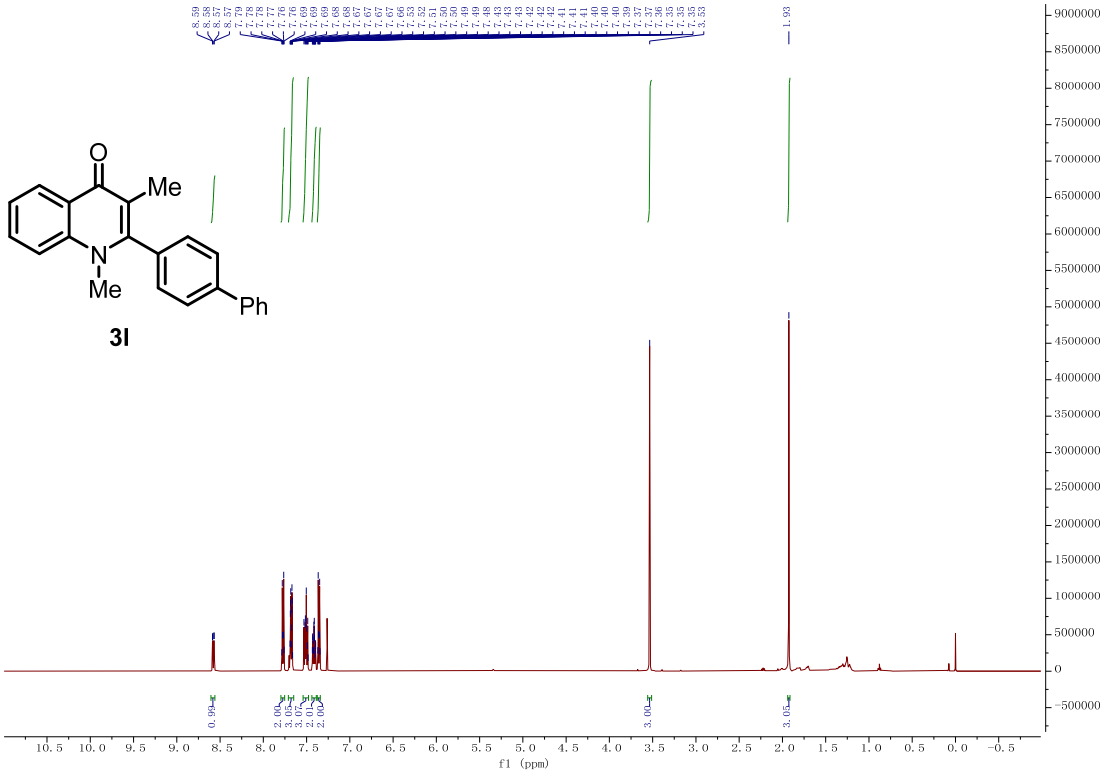
1,3-dimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3k). ^{1}H NMR (500 MHz, $CDCl_3$**)**



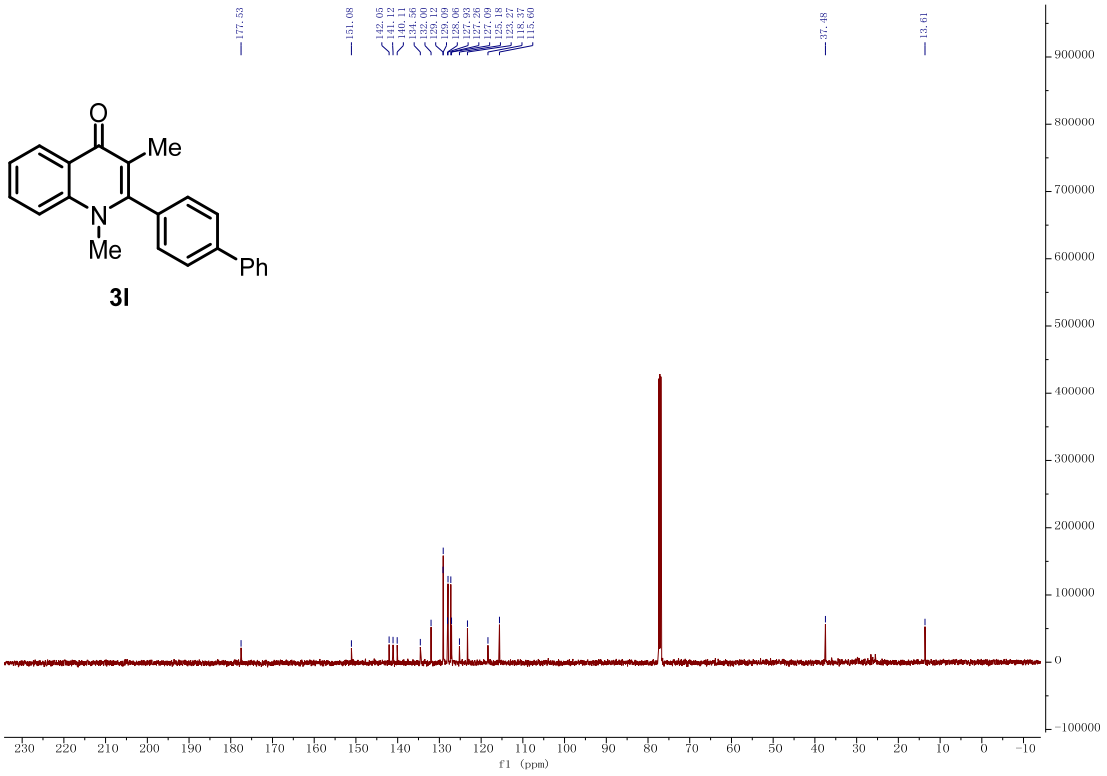
1,3-dimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3k). ^{13}C NMR (125 MHz, $CDCl_3$**)**



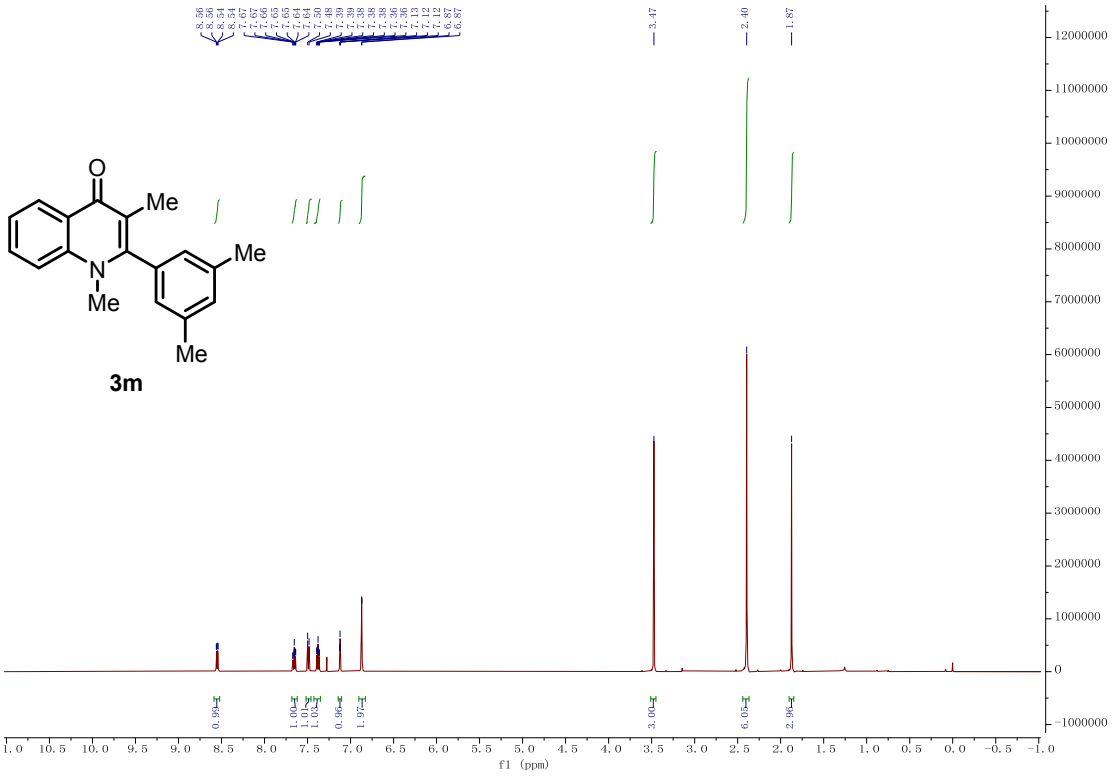
2-([1,1'-biphenyl]-4-yl)-1,3-dimethylquinolin-4(1*H*)-one (3l). ^{1}H NMR (500 MHz, $CDCl_3$**)**



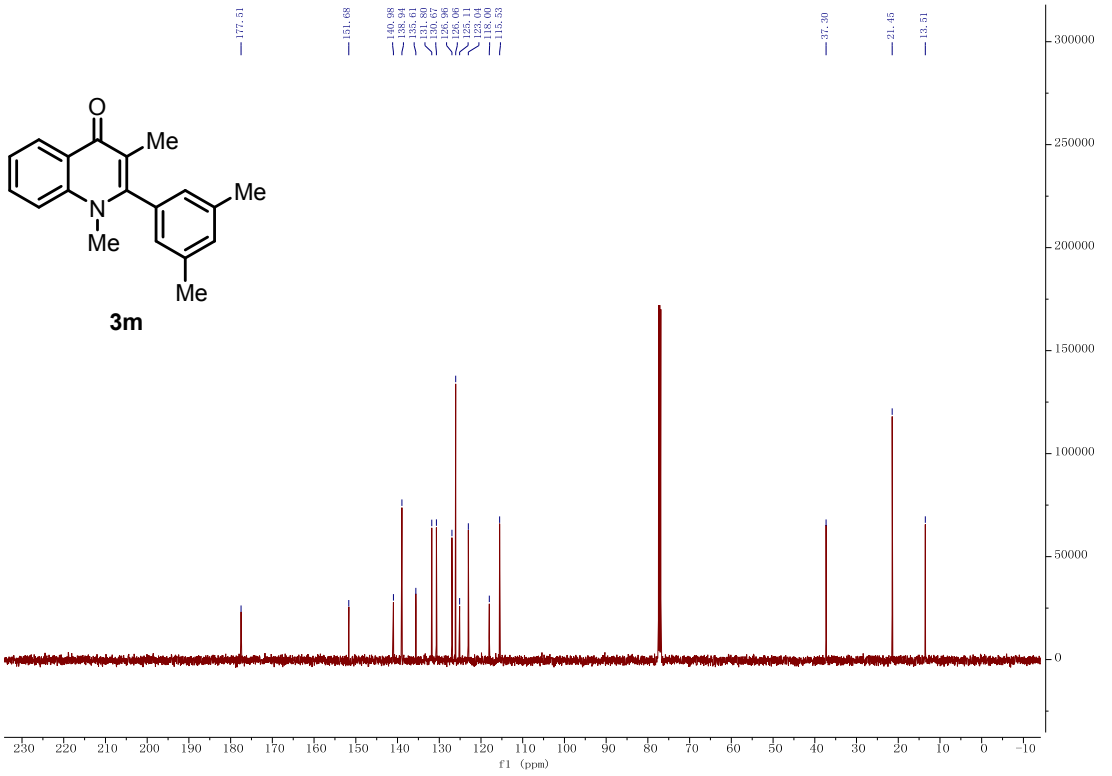
2-([1,1'-biphenyl]-4-yl)-1,3-dimethylquinolin-4(1*H*)-one (3l). ^{13}C NMR (125 MHz, $CDCl_3$**)**



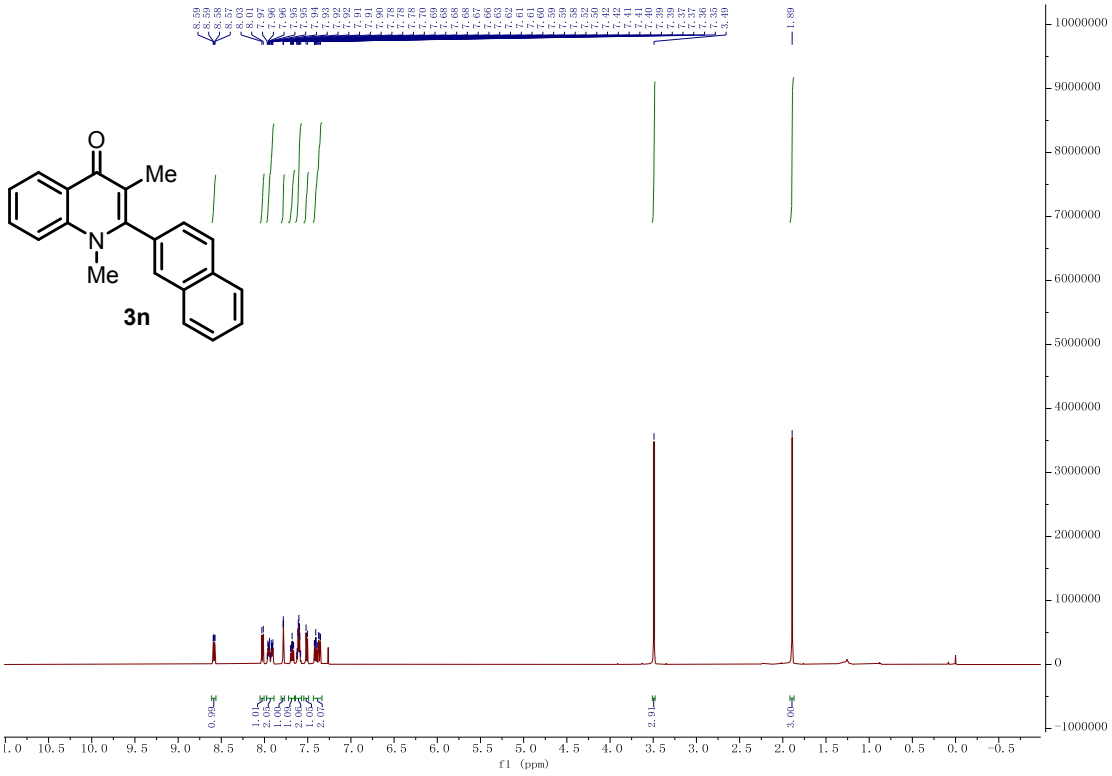
2-(3,5-dimethylphenyl)-1,3-dimethylquinolin-4(1*H*)-one (3m). ^{1}H NMR (500 MHz, $CDCl_3$**)**



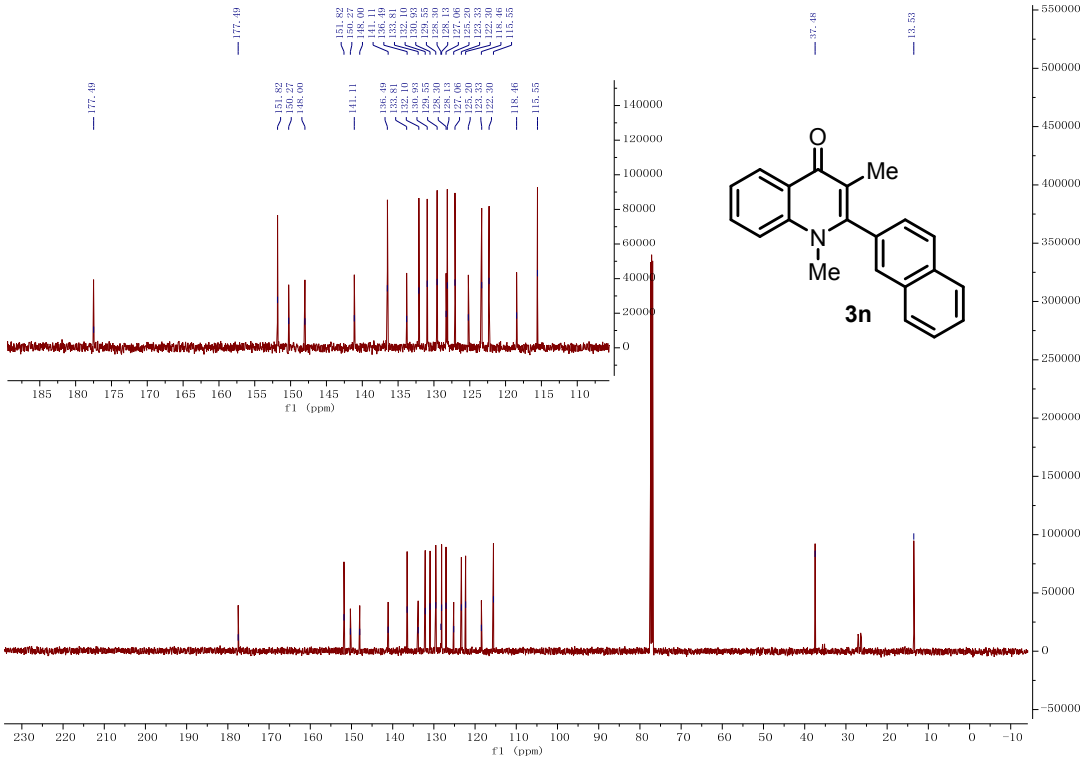
2-(3,5-dimethylphenyl)-1,3-dimethylquinolin-4(1*H*)-one (3m). ^{13}C NMR (125 MHz, $CDCl_3$**)**



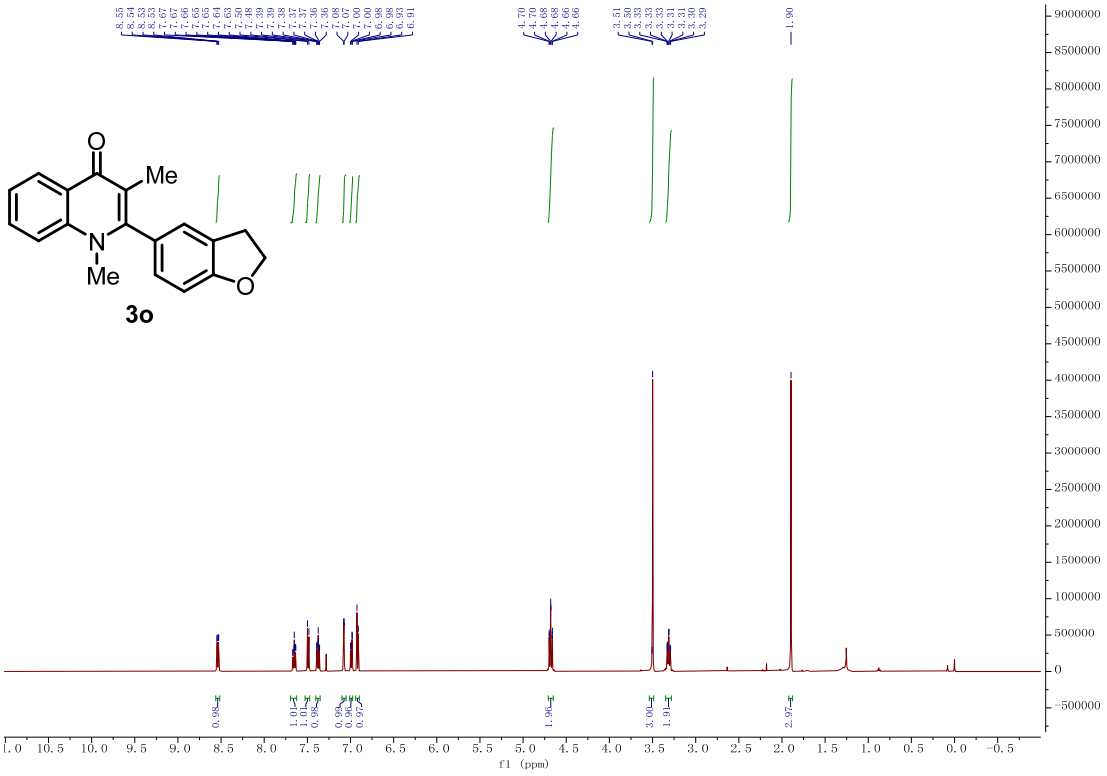
1,3-dimethyl-2-(naphthalen-2-yl)quinolin-4(1*H*)-one (3n). ^{1}H NMR (500 MHz, $CDCl_3$**)**



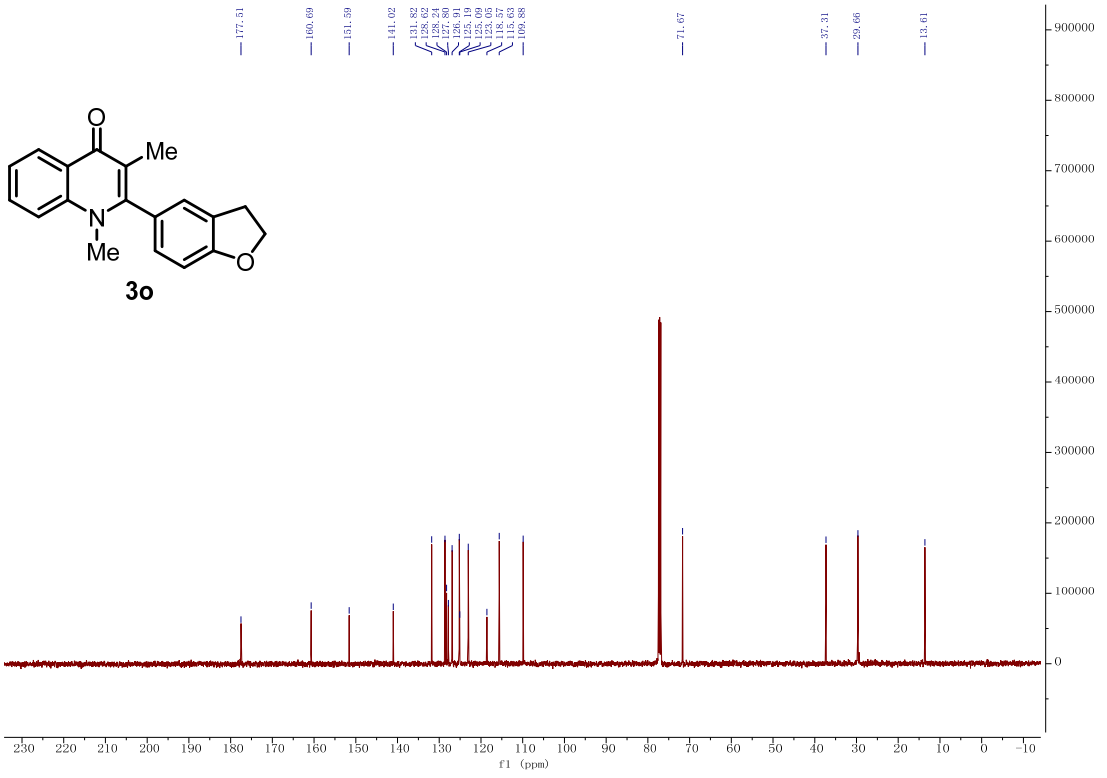
1,3-dimethyl-2-(naphthalen-2-yl)quinolin-4(1*H*)-one (3n). ^{13}C NMR (125 MHz, $CDCl_3$**)**



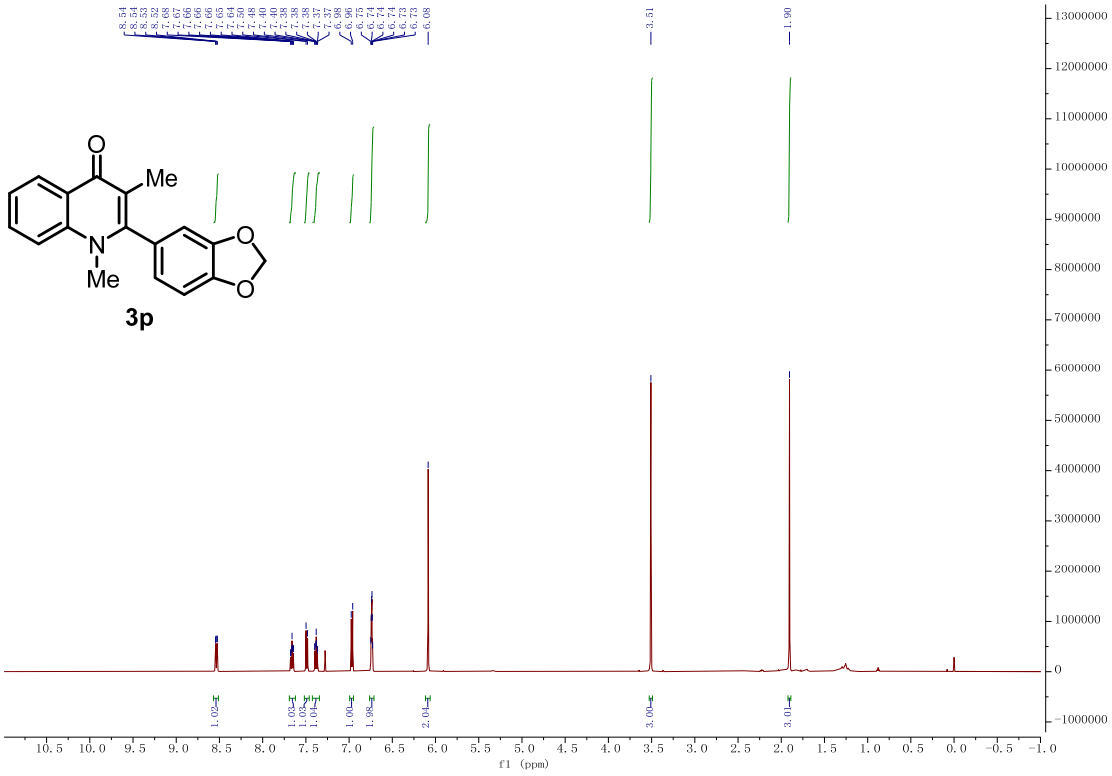
2-(2,3-dihydrobenzofuran-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3o). ^{1}H NMR (500 MHz, $CDCl_3$**)**



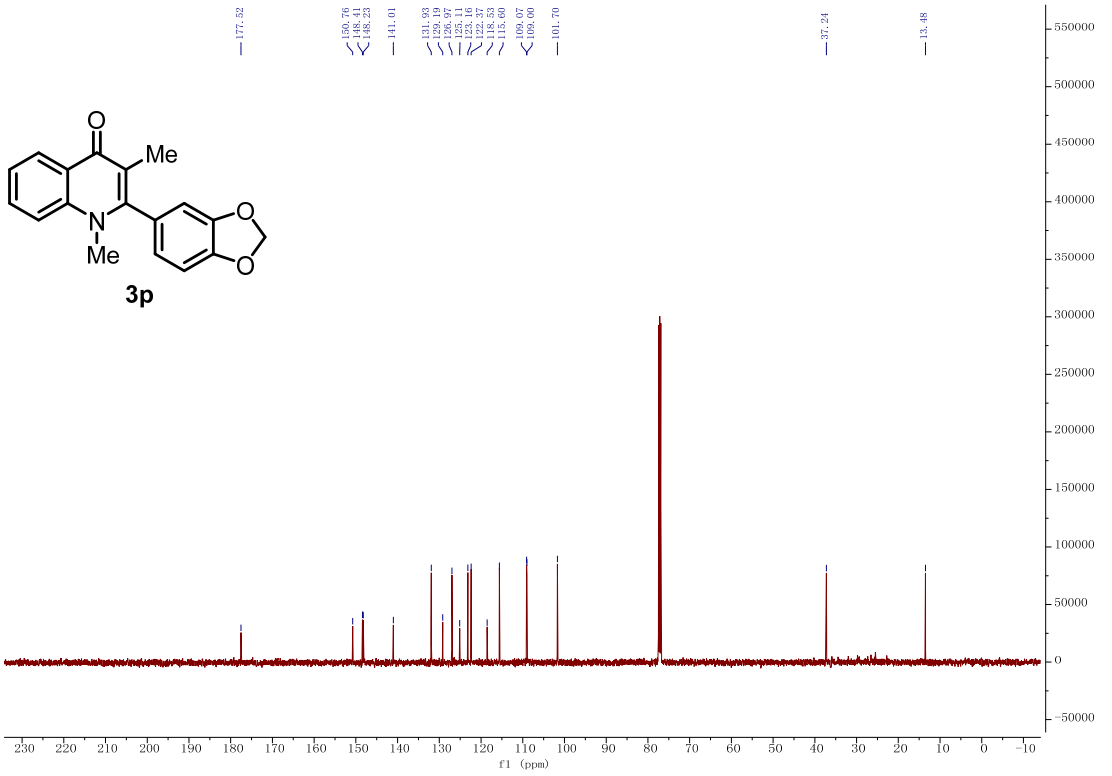
2-(2,3-dihydrobenzofuran-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3o). ^{13}C NMR (125 MHz, $CDCl_3$**)**



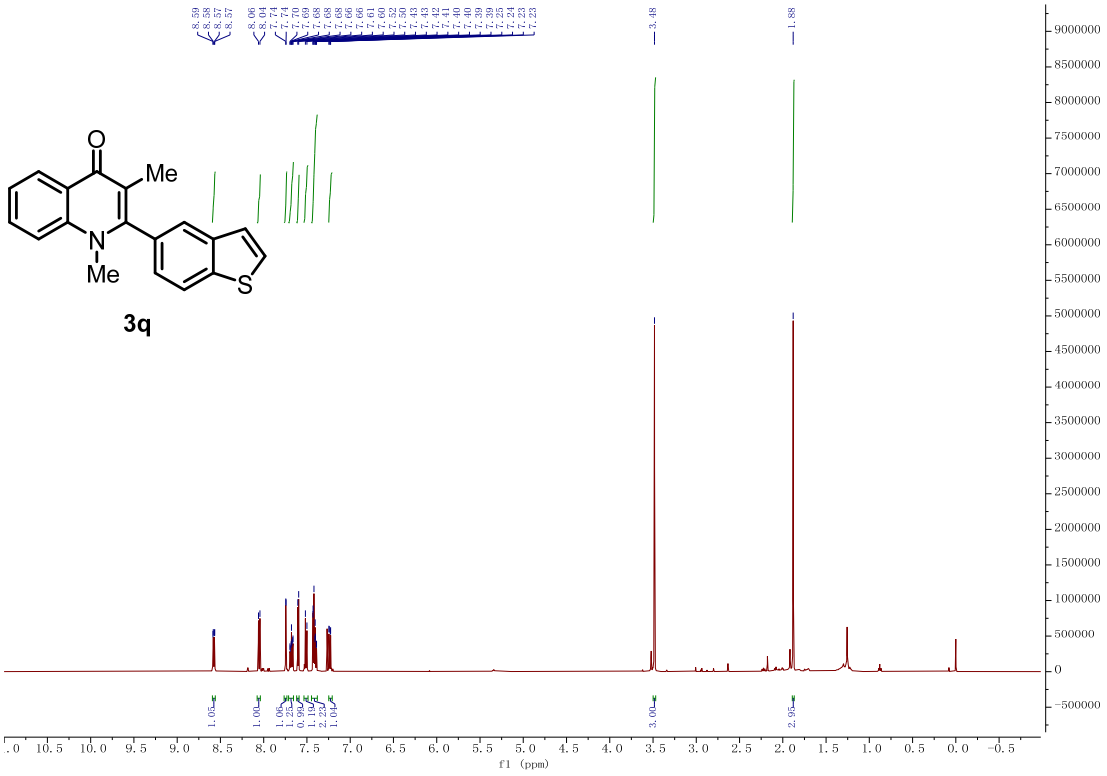
2-(benzo[*d*][1,3]dioxol-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3p). ^{1}H NMR (500 MHz, $CDCl_3$**)**



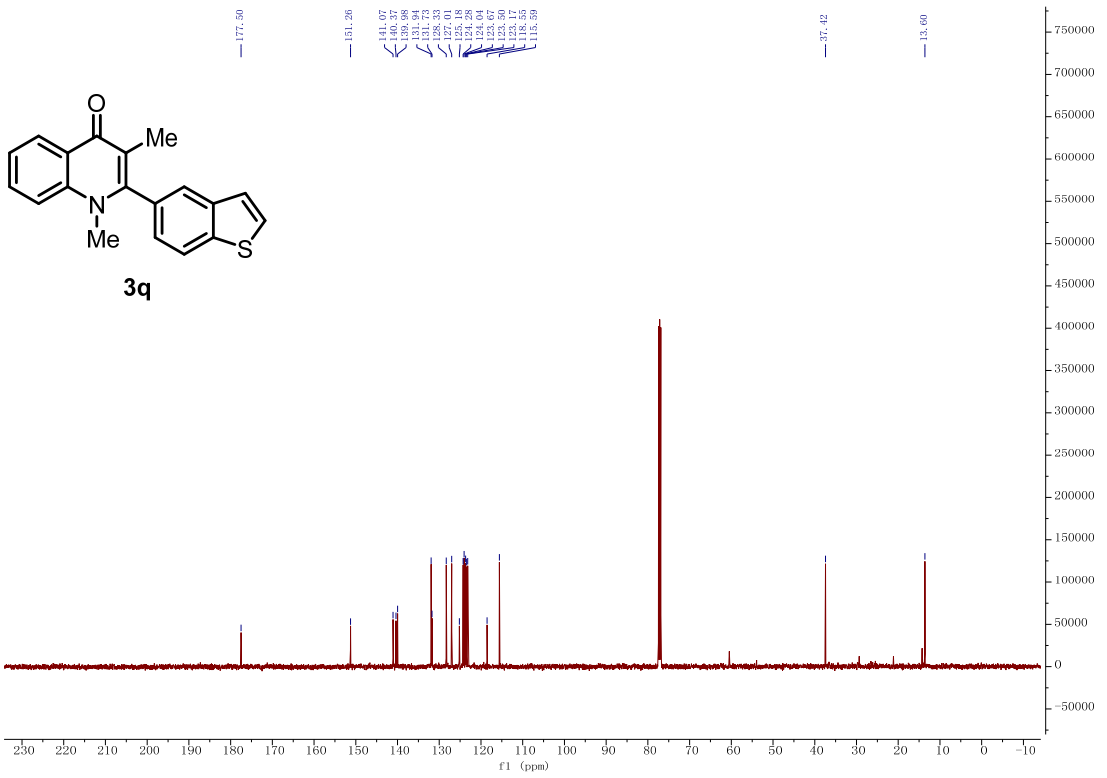
2-(benzo[*d*][1,3]dioxol-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3p). ^{13}C NMR (125 MHz, $CDCl_3$**)**



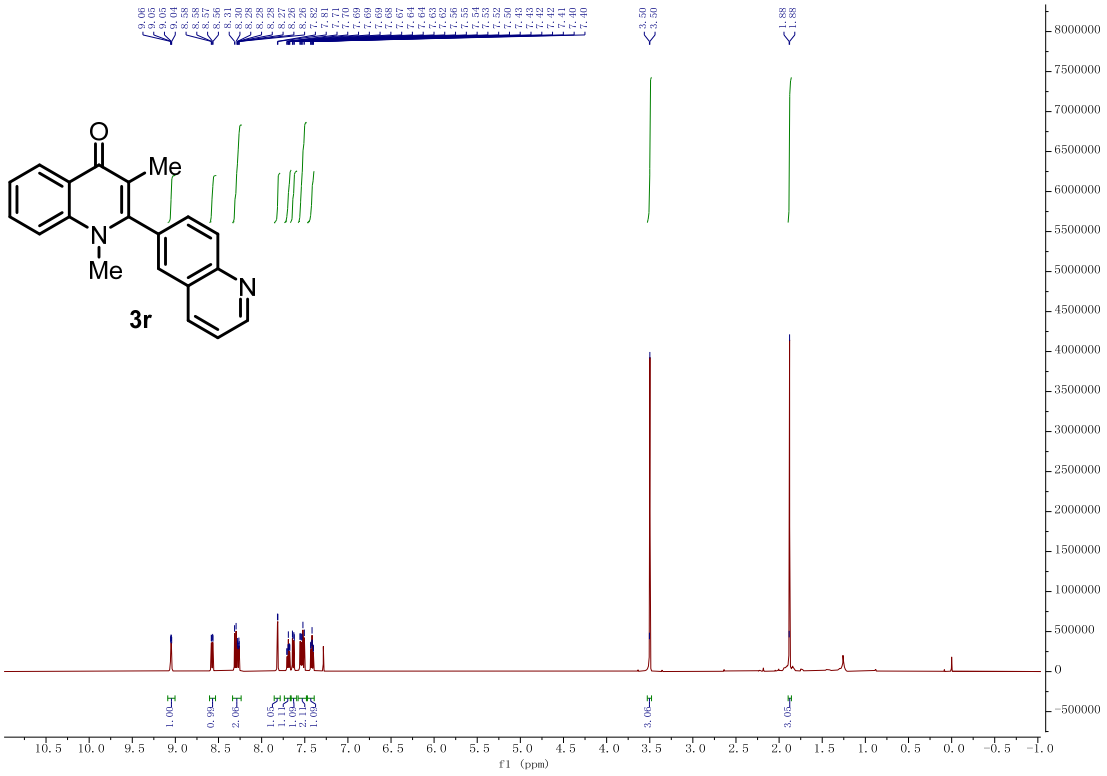
2-(benzo[*b*]thiophen-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3q). ^{1}H NMR (500 MHz, $CDCl_3$**)**



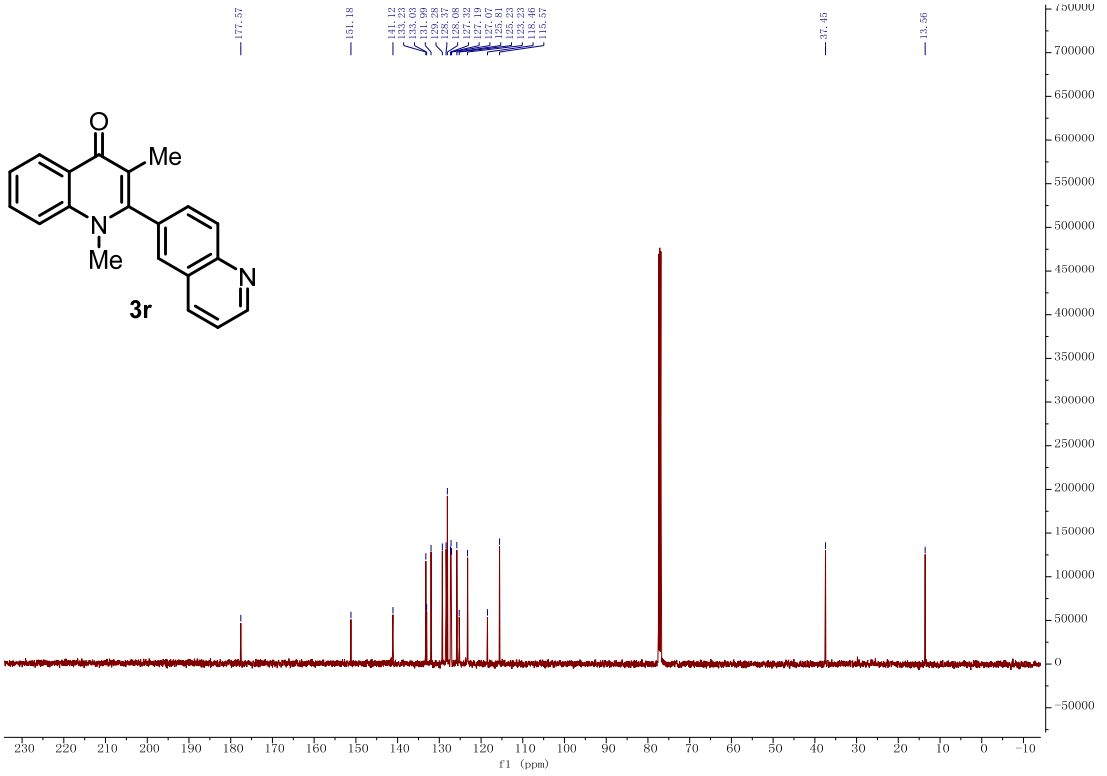
2-(benzo[*b*]thiophen-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3q). ^{13}C NMR (125 MHz, $CDCl_3$**)**



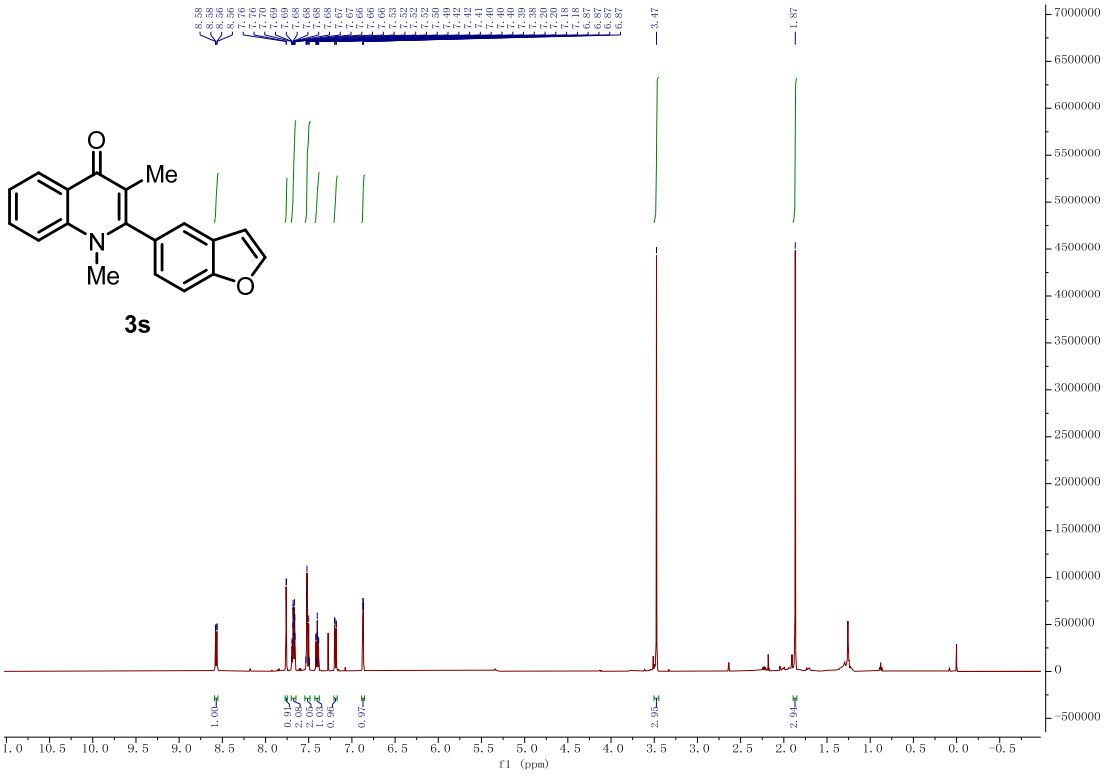
1,3-dimethyl-[2,6'-biquinolin]-4(1*H*)-one (3r). ^{1}H NMR (500 MHz, $CDCl_3$**)**



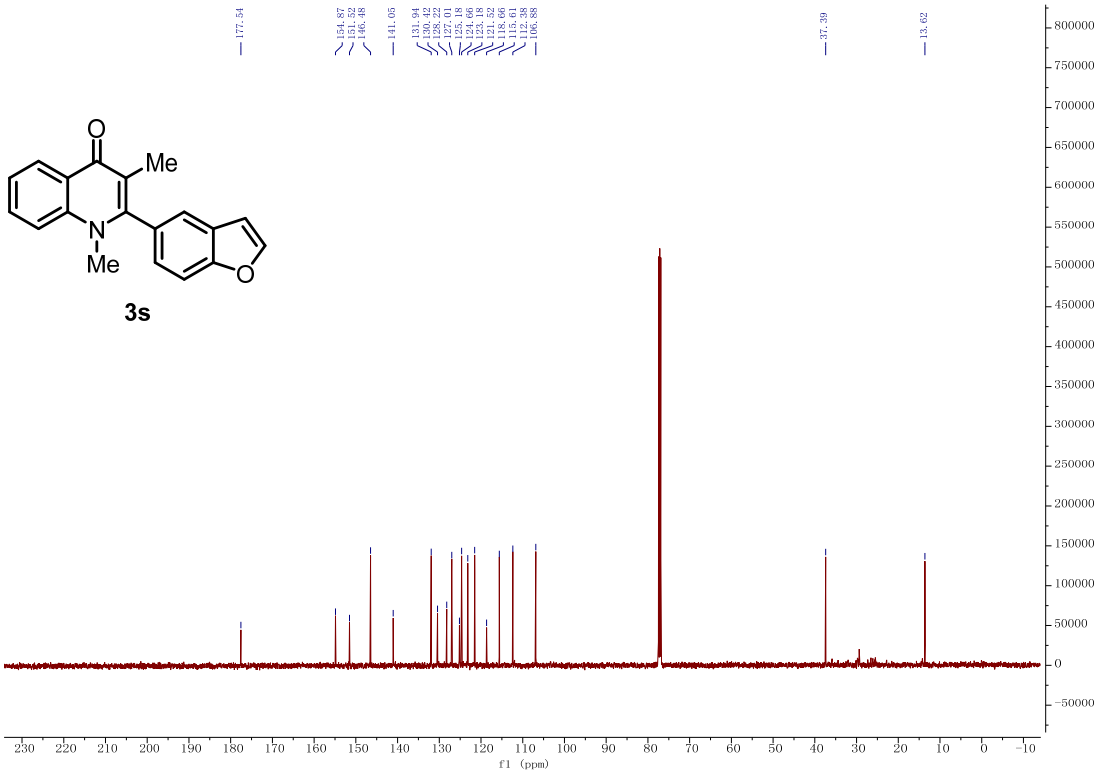
1,3-dimethyl-[2,6'-biquinolin]-4(1*H*)-one (3r). ^{13}C NMR (125 MHz, $CDCl_3$**)**



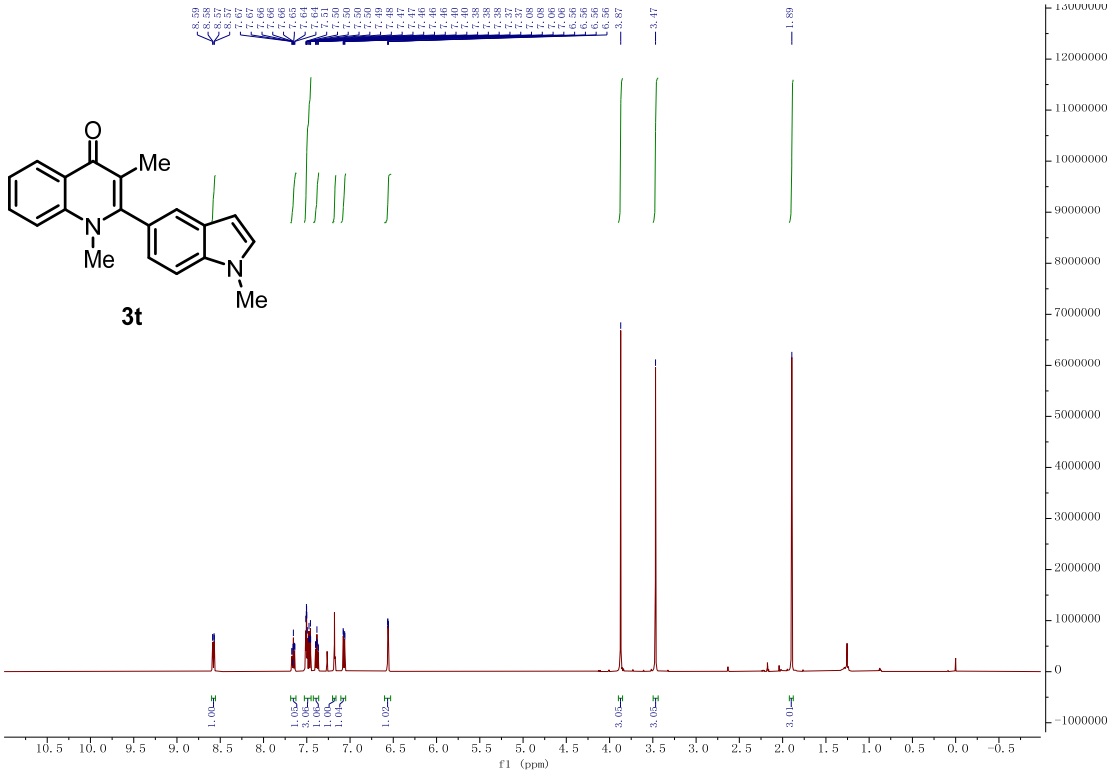
2-(benzofuran-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3s).^{1}H NMR (500 MHz, $CDCl_3$**)**



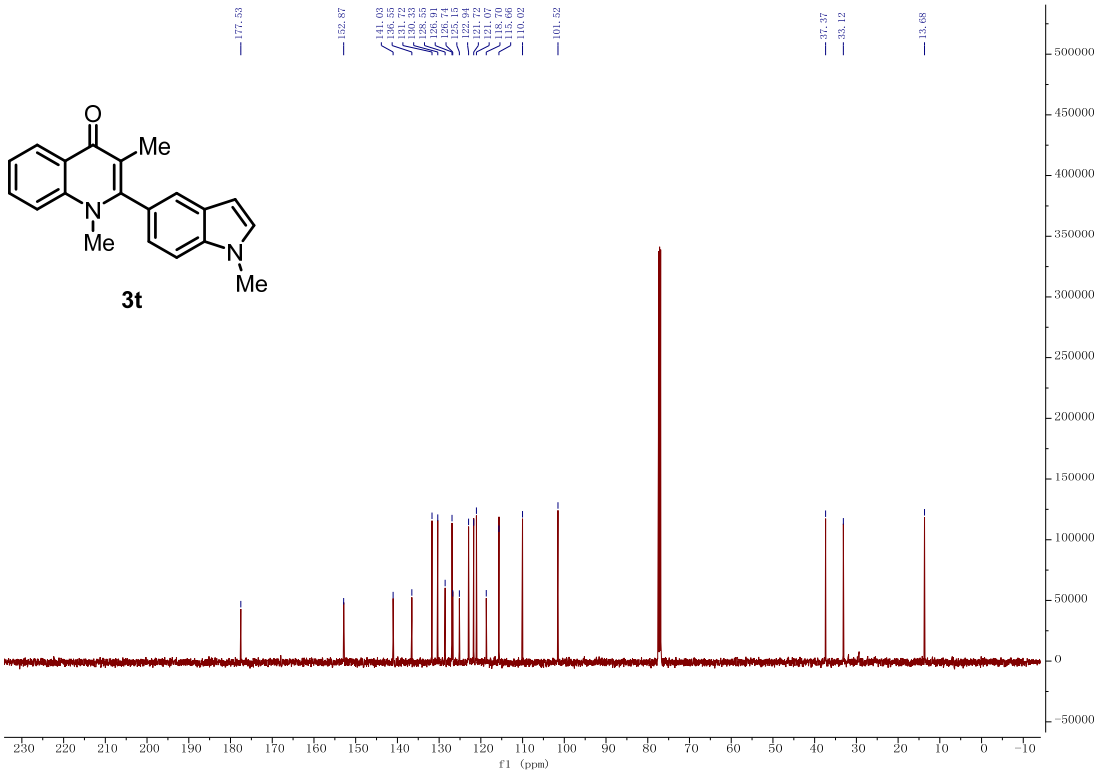
2-(benzofuran-5-yl)-1,3-dimethylquinolin-4(1*H*)-one (3s). ^{13}C NMR (125 MHz, $CDCl_3$**)**



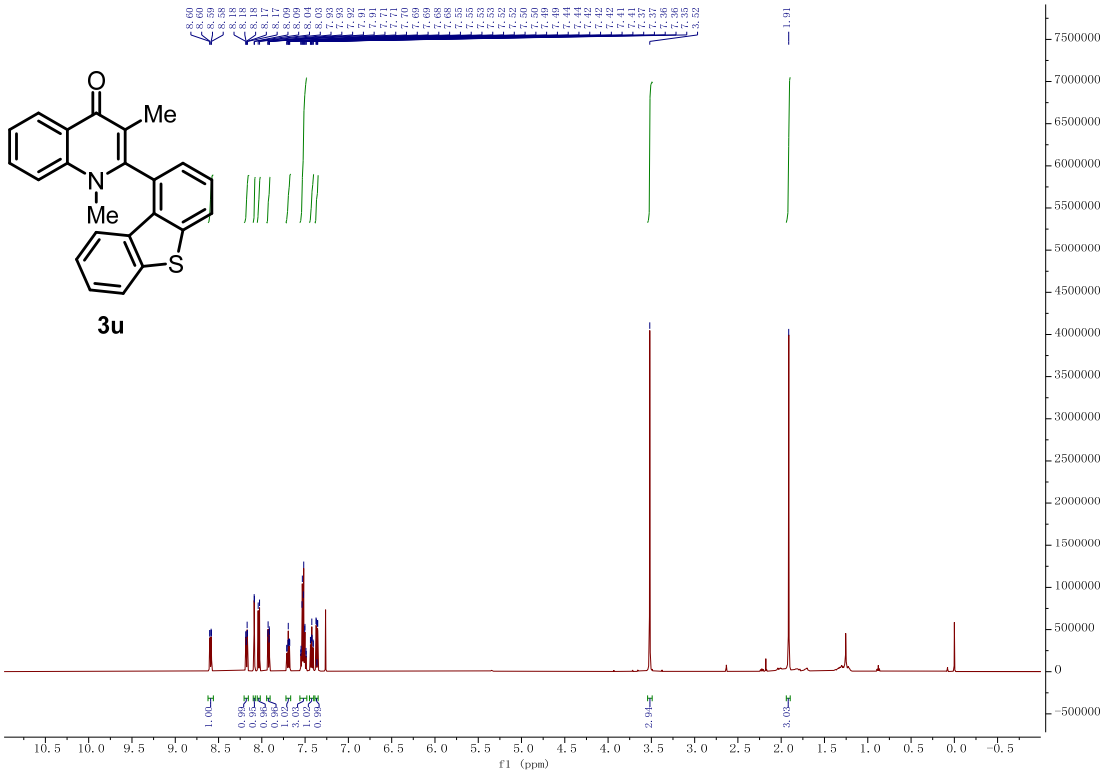
1,3-dimethyl-2-(1-methyl-1H-indol-5-yl)quinolin-4(1*H*)-one (3t). ^{1}H NMR (500 MHz, $CDCl_3$)



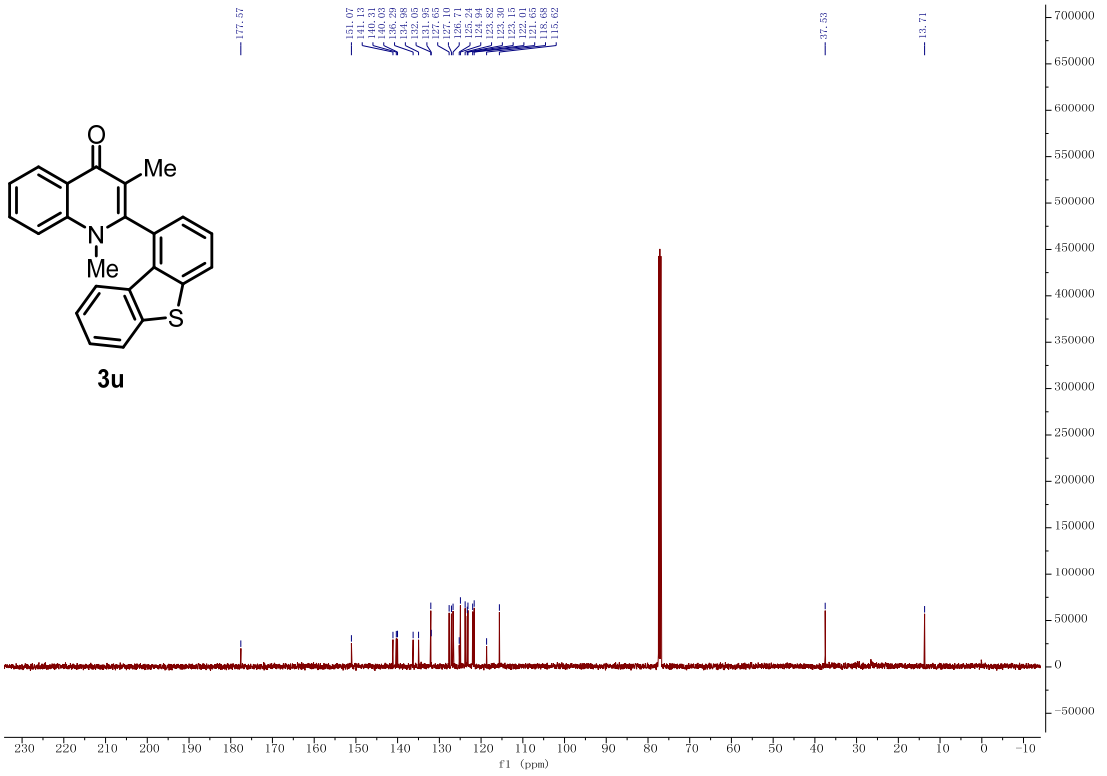
1,3-dimethyl-2-(1-methyl-1H-indol-5-yl)quinolin-4(1*H*)-one (3t). ^{13}C NMR (125 MHz, $CDCl_3$)



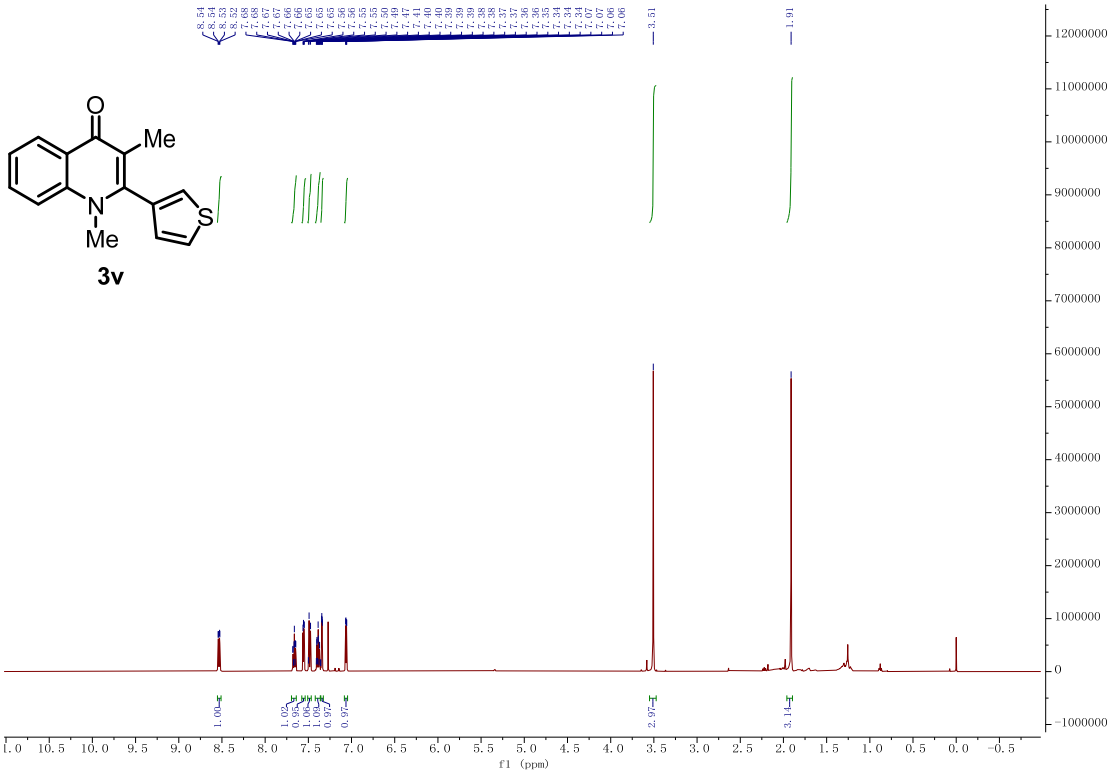
2-(dibenzo[*b,d*]thiophen-1-yl)-1,3-dimethylquinolin-4(1*H*)-one (3u). ^{1}H NMR (500 MHz, $CDCl_3$**)**



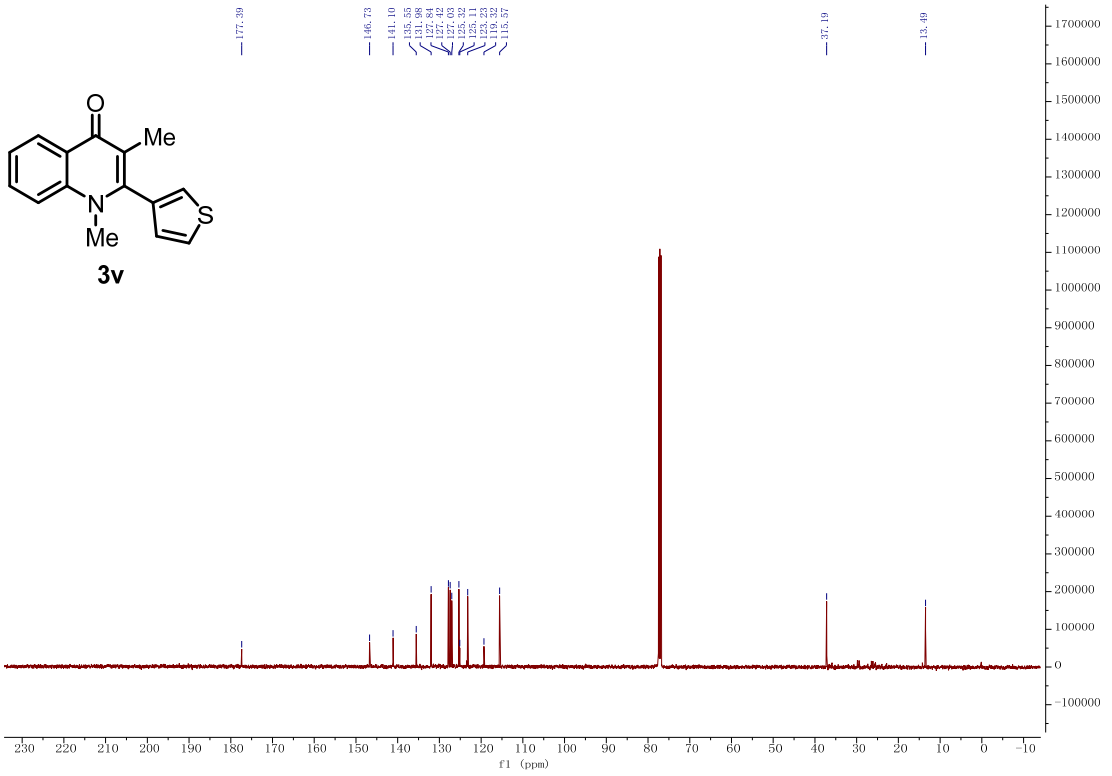
2-(dibenzo[*b,d*]thiophen-1-yl)-1,3-dimethylquinolin-4(1*H*)-one (3u). ^{13}C NMR (125 MHz, $CDCl_3$**)**



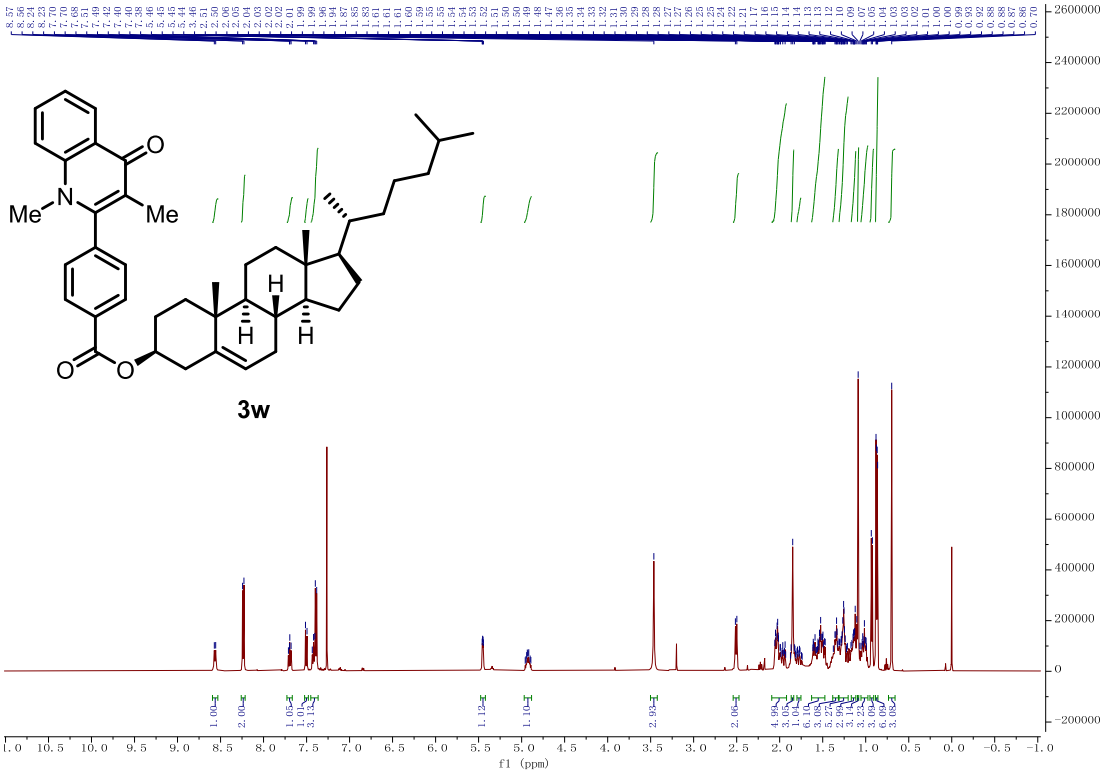
1,3-dimethyl-2-(thiophen-3-yl)quinolin-4(1*H*)-one (3v). ^{1}H NMR (500 MHz, $CDCl_3$**)**



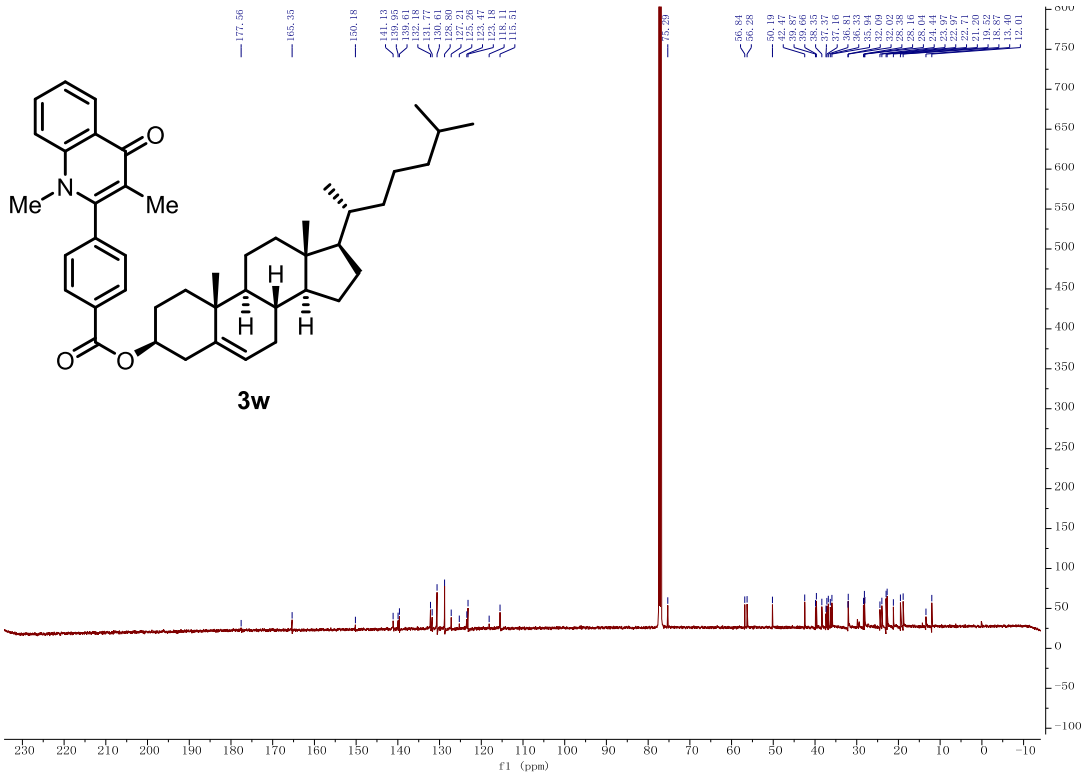
1,3-dimethyl-2-(thiophen-3-yl)quinolin-4(1*H*)-one (3v). ^{13}C NMR (125 MHz, $CDCl_3$**)**



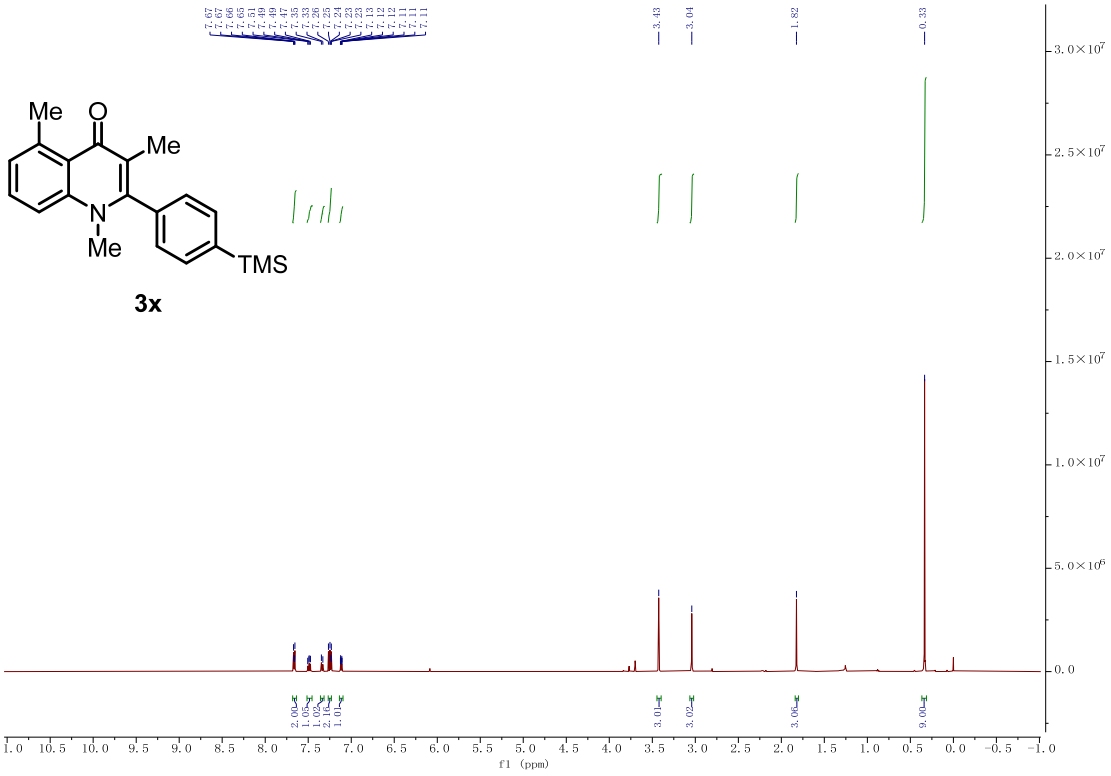
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthr-en-3-yl 4-(1,3-dimethyl-4-oxo-1,4-dihydroquinolin-2-yl)benzoate (3w). ^{1}H NMR (500 MHz, $CDCl_3$)



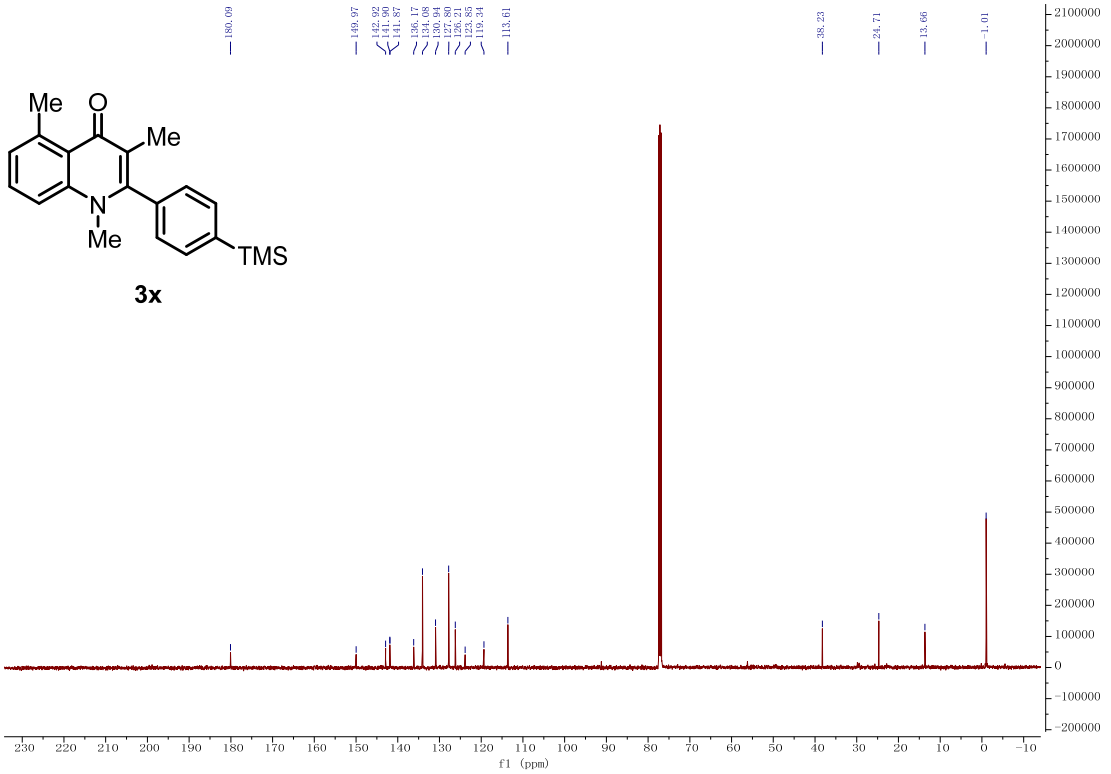
(3*S*,8*S*,9*S*,10*R*,13*R*,14*S*,17*R*)-10,13-dimethyl-17-((*R*)-6-methylheptan-2-yl)-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1*H*-cyclopenta[*a*]phenanthr-en-3-yl 4-(1,3-dimethyl-4-oxo-1,4-dihydroquinolin-2-yl)benzoate (3w). ^{13}C NMR (125 MHz, $CDCl_3$)



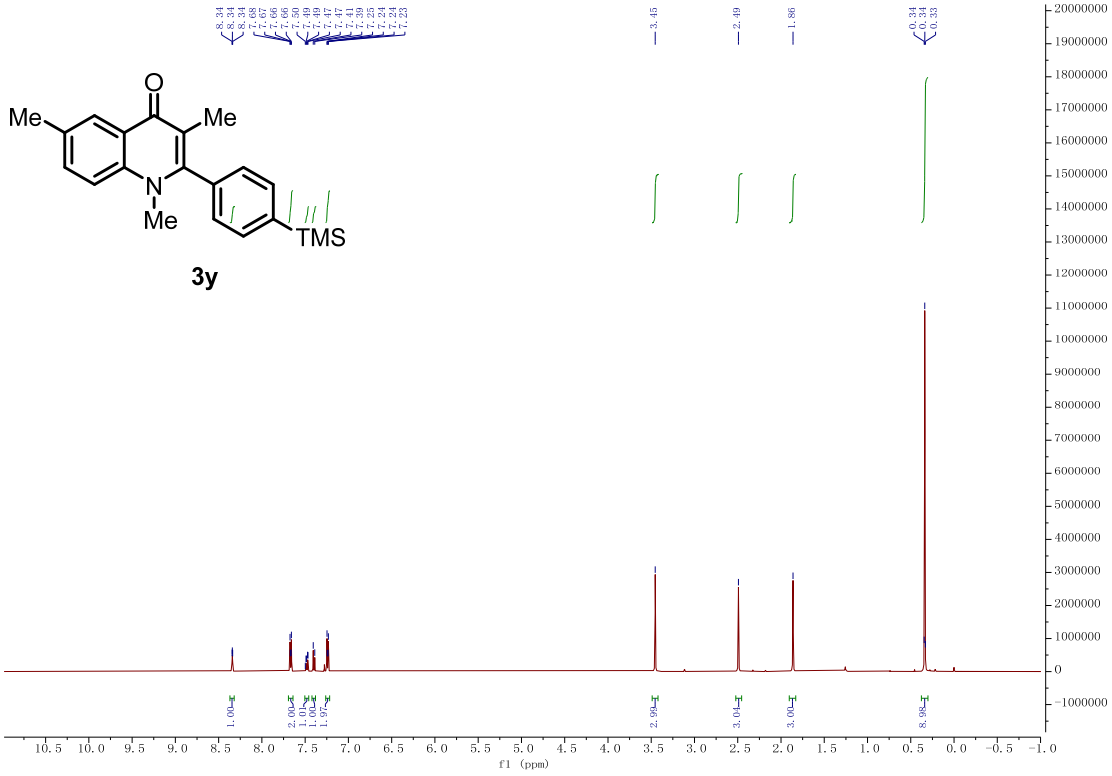
1,3,5-trimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3x). ^{1}H NMR (500 MHz, $CDCl_3$**)**



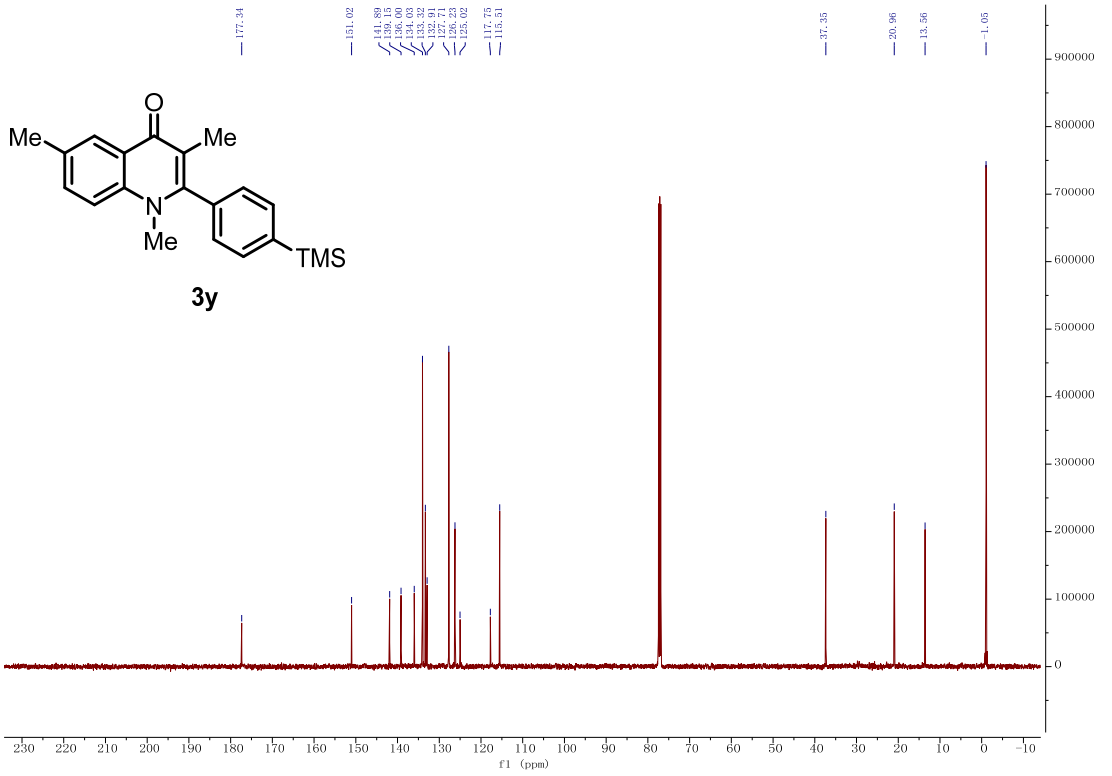
1,3,5-trimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3x). ^{13}C NMR (125 MHz, $CDCl_3$**)**



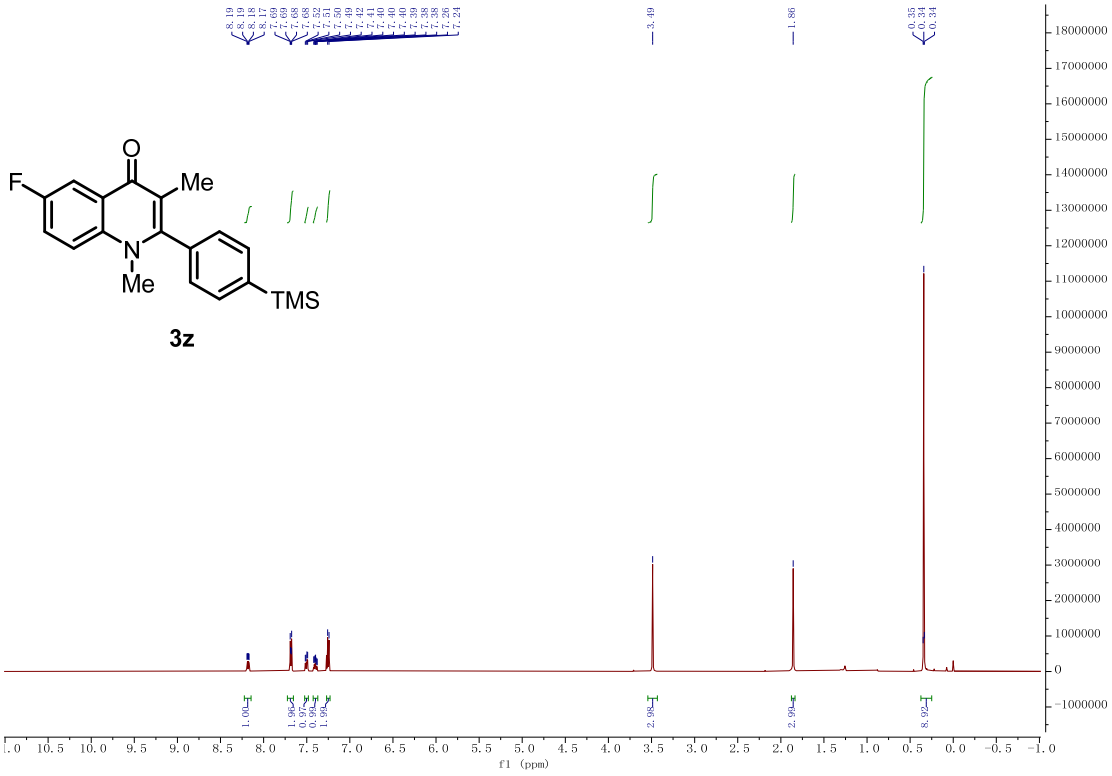
1,3,6-trimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3y). ^{1}H NMR (500 MHz, $CDCl_3$**)**



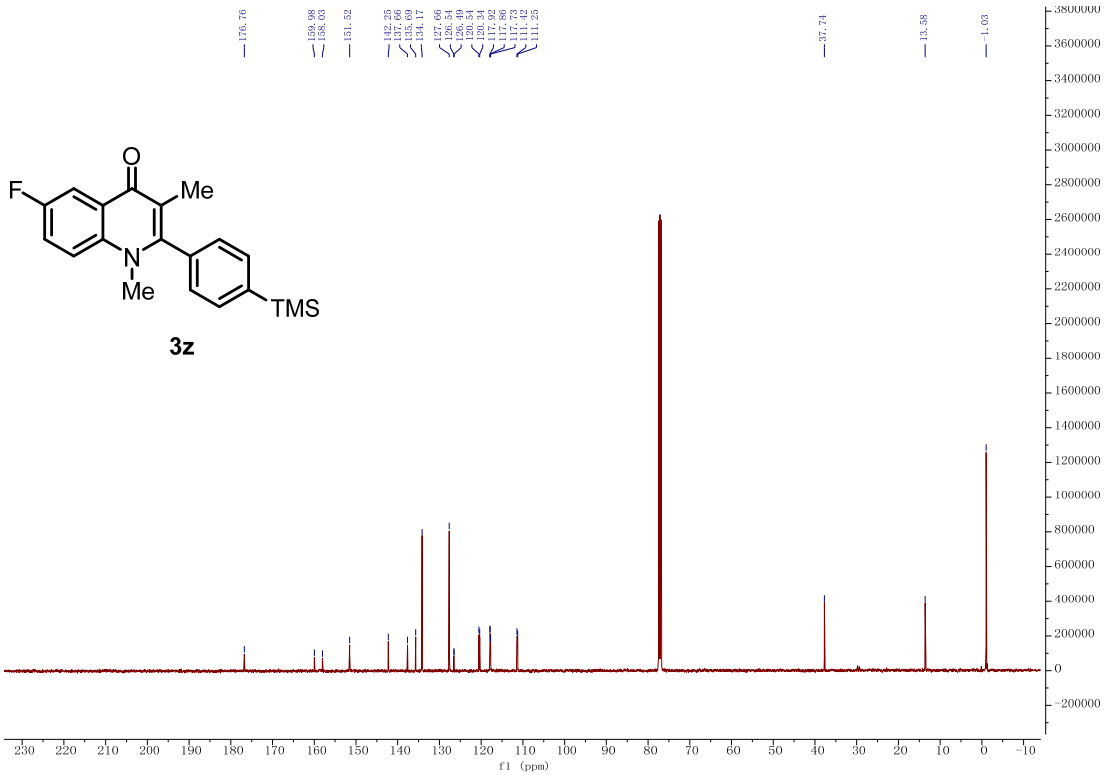
1,3,6-trimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3y). ^{13}C NMR (125 MHz, $CDCl_3$**)**



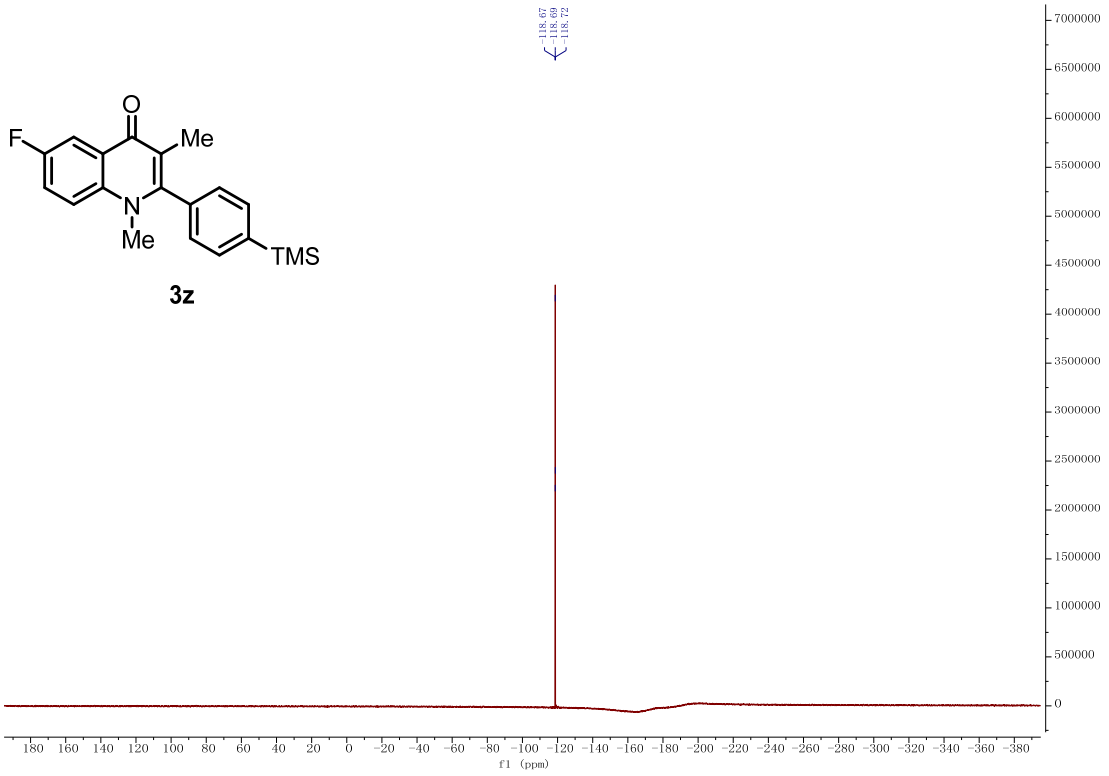
6-fluoro-1,3-dimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3z). ^{1}H NMR (500 MHz, $CDCl_3$**)**



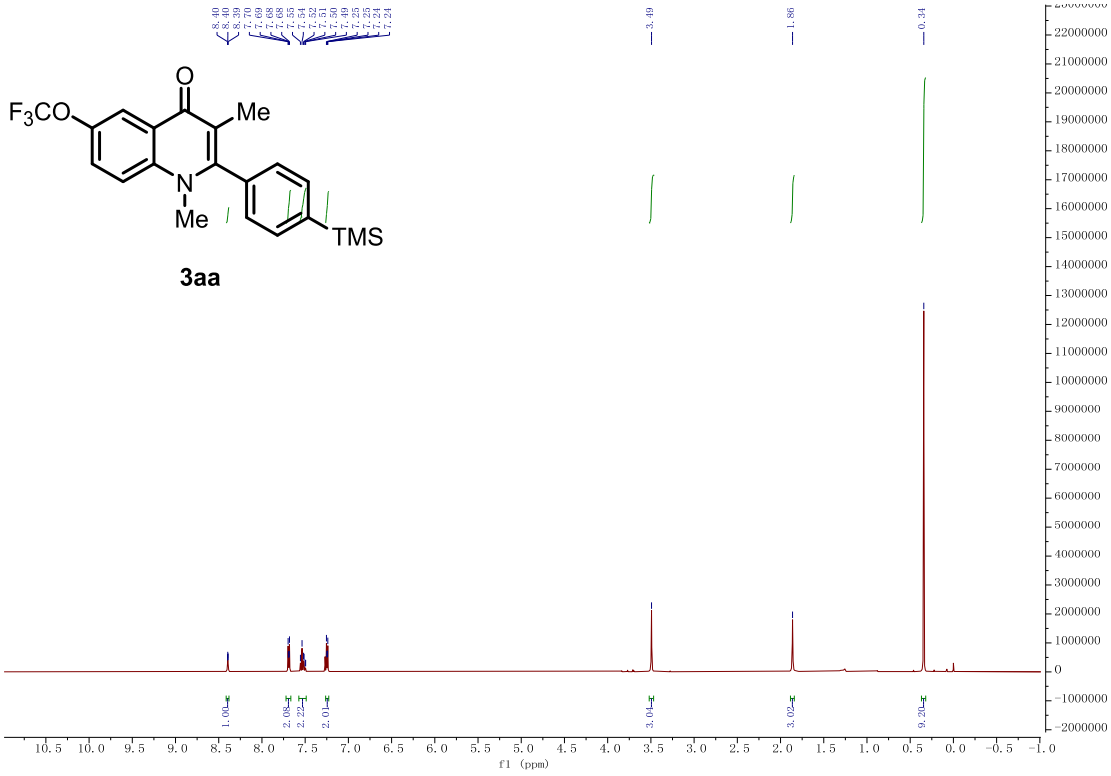
6-fluoro-1,3-dimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3z). ^{13}C NMR (125 MHz, $CDCl_3$**)**



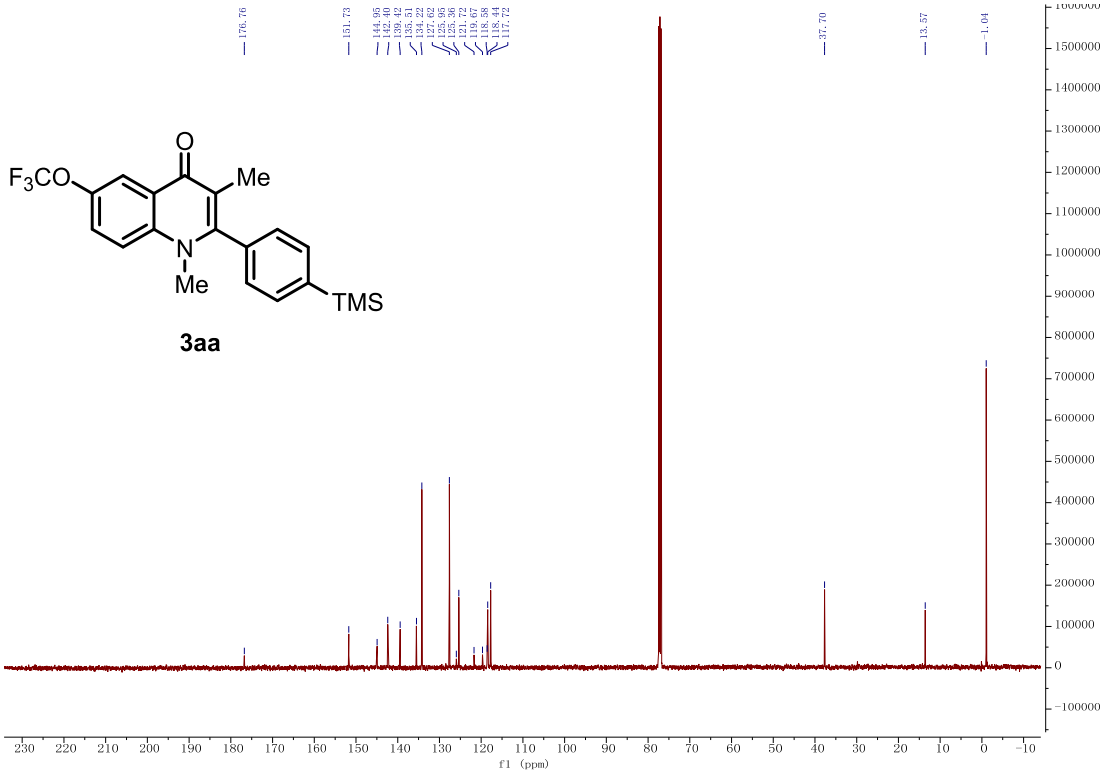
6-fluoro-1,3-dimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3z). ^{19}F NMR (470 MHz, $CDCl_3$**)**



1,3-dimethyl-6-(trifluoromethoxy)-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3aa). ^{1}H NMR (500 MHz, $CDCl_3$**)**

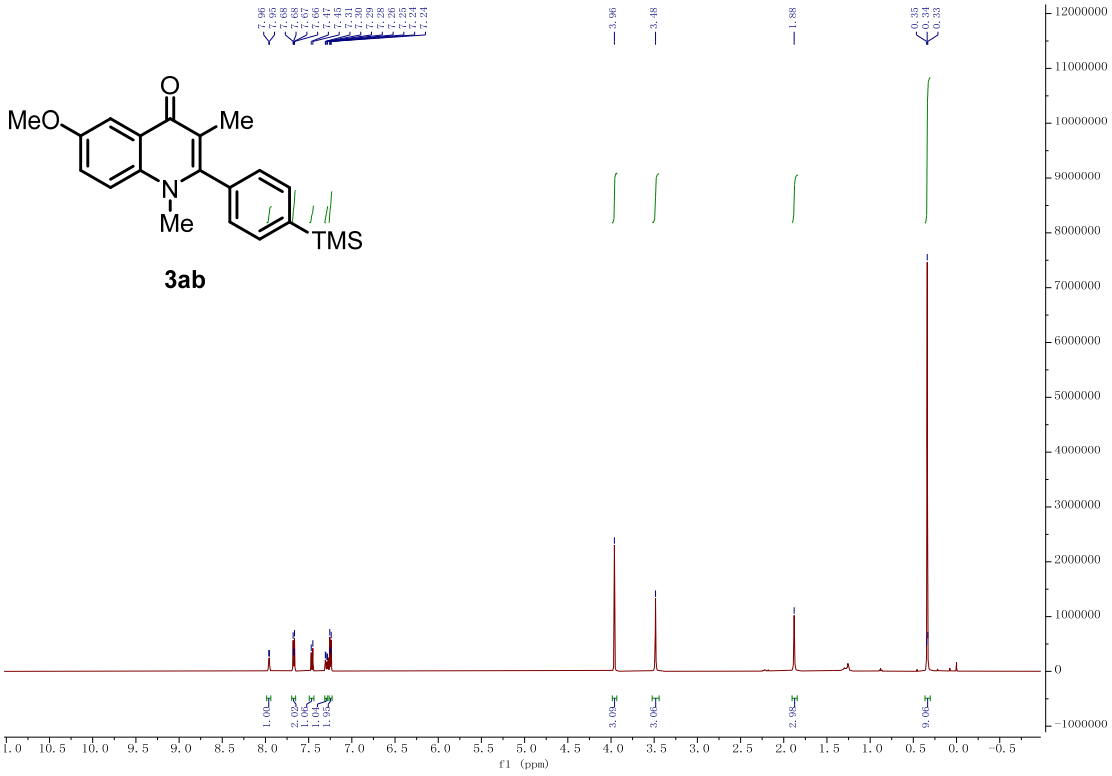


1,3-dimethyl-6-(trifluoromethoxy)-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3aa). ^{13}C NMR (125 MHz, $CDCl_3$**)**

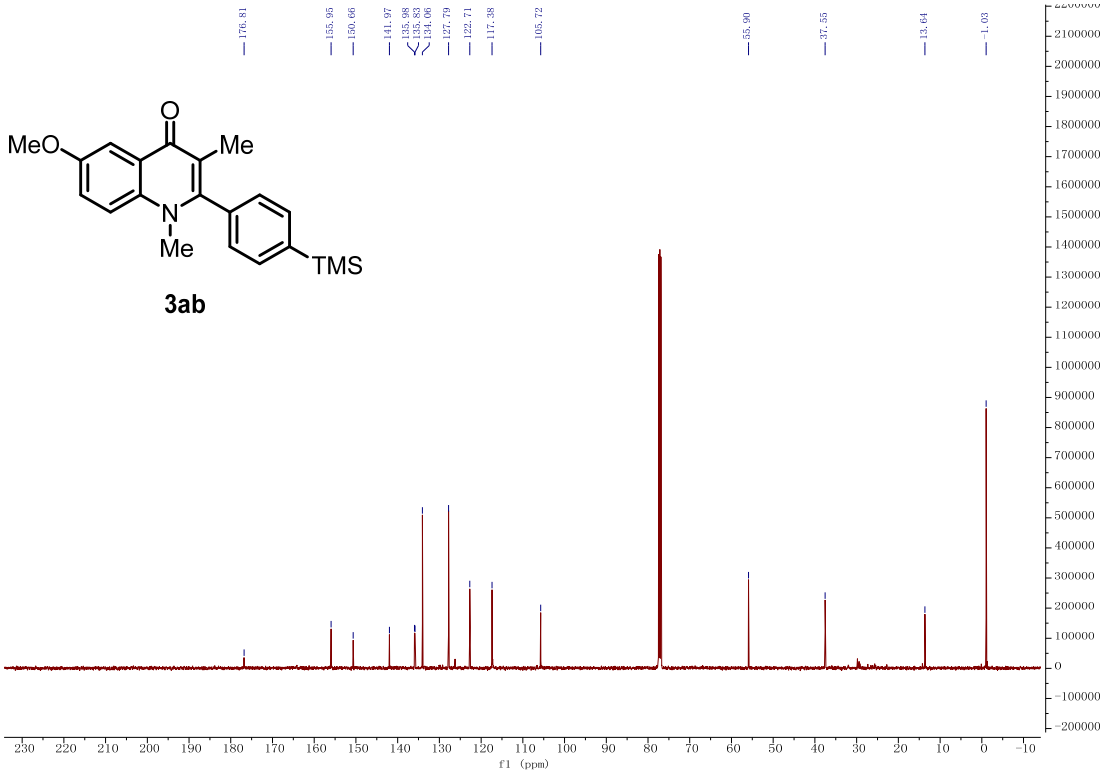


1,3-dimethyl-6-(trifluoromethoxy)-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3aa). ^{19}F NMR (470 MHz, $CDCl_3$**)**

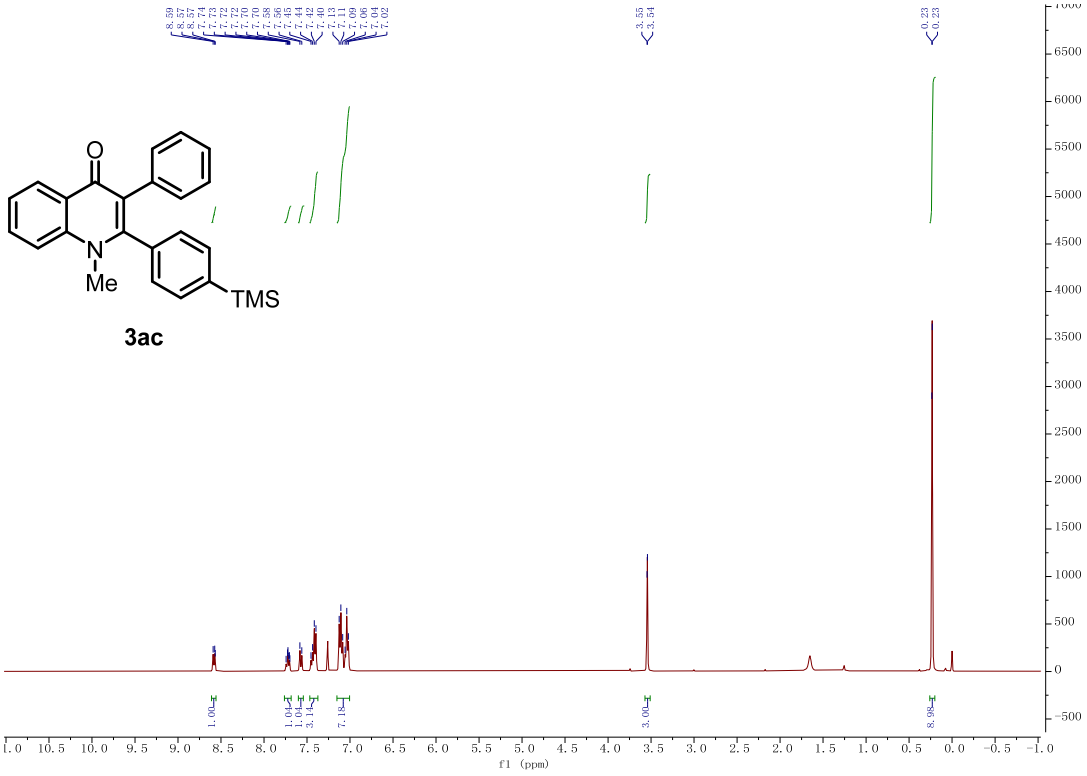
6-methoxy-1,3-dimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3ab). ^{1}H NMR (500 MHz, $CDCl_3$**)**



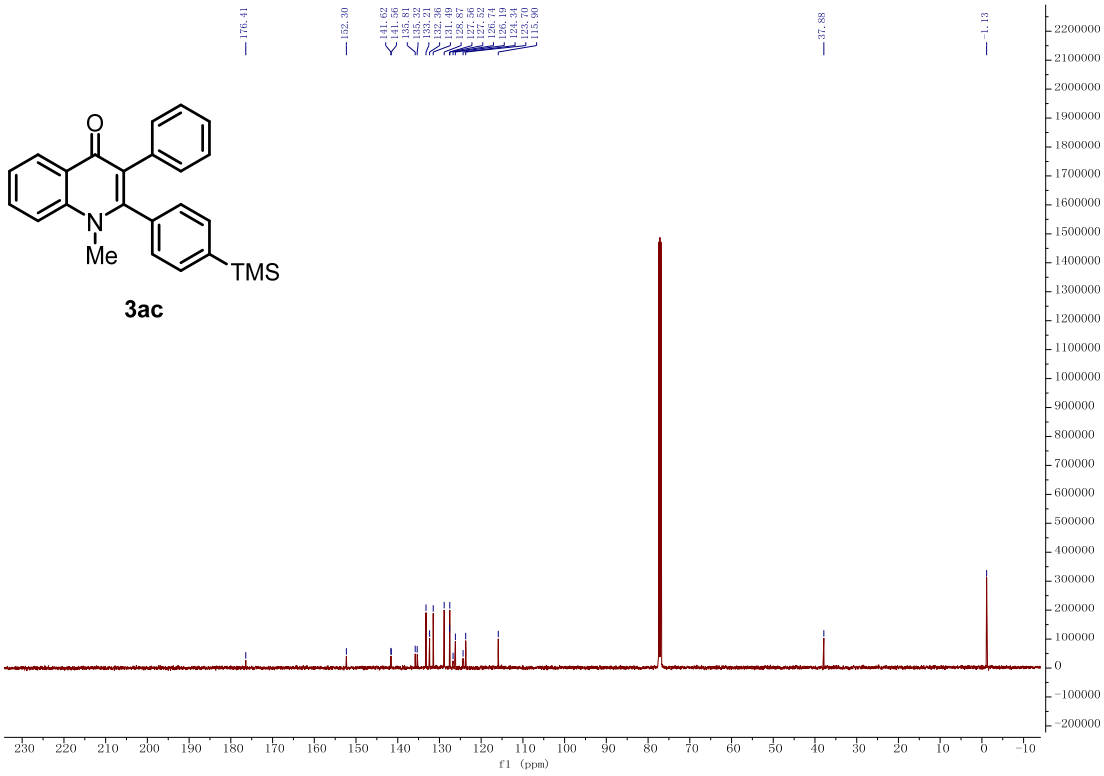
6-methoxy-1,3-dimethyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3ab). ^{13}C NMR (125 MHz, $CDCl_3$**)**



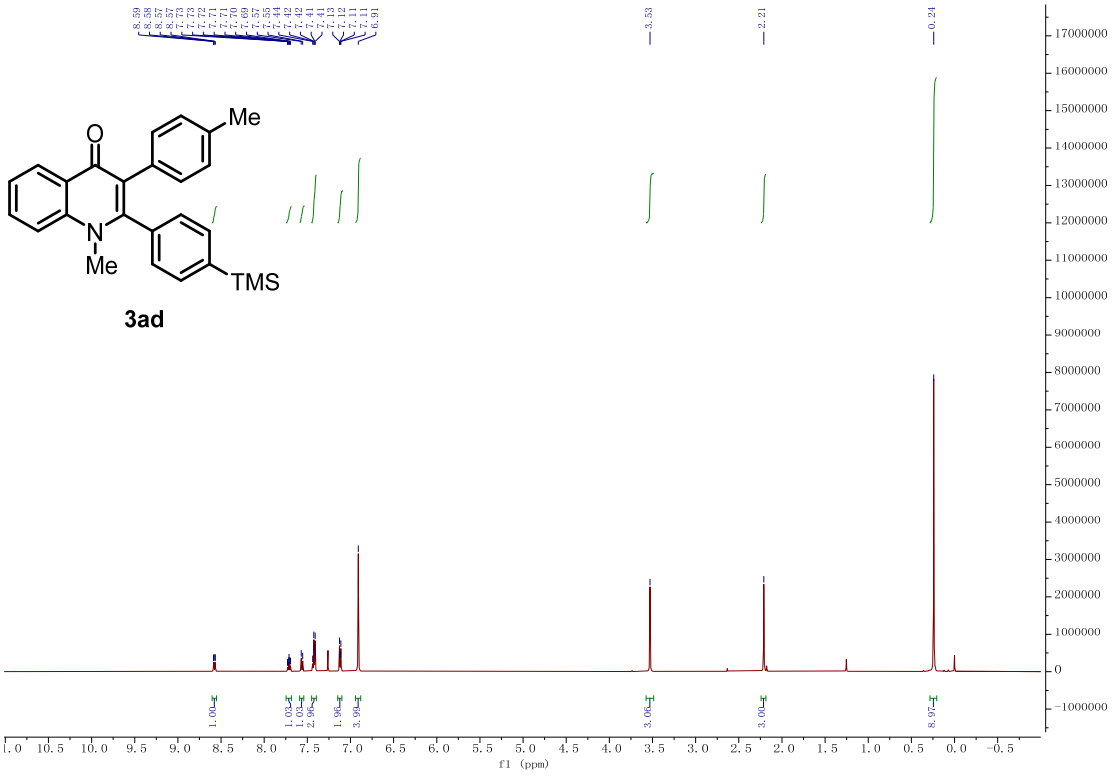
1-methyl-3-phenyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ac). ^{1}H NMR (400 MHz, $CDCl_3$**)**



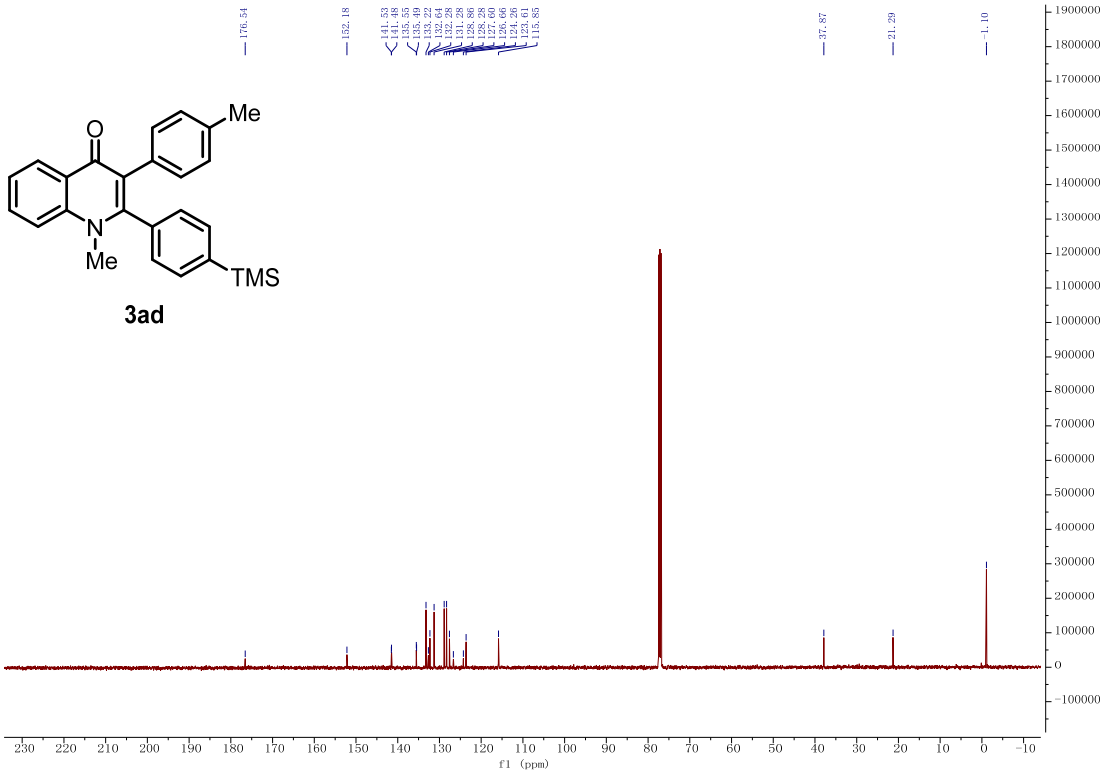
1-methyl-3-phenyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ac). ^{13}C NMR (125 MHz, $CDCl_3$**)**



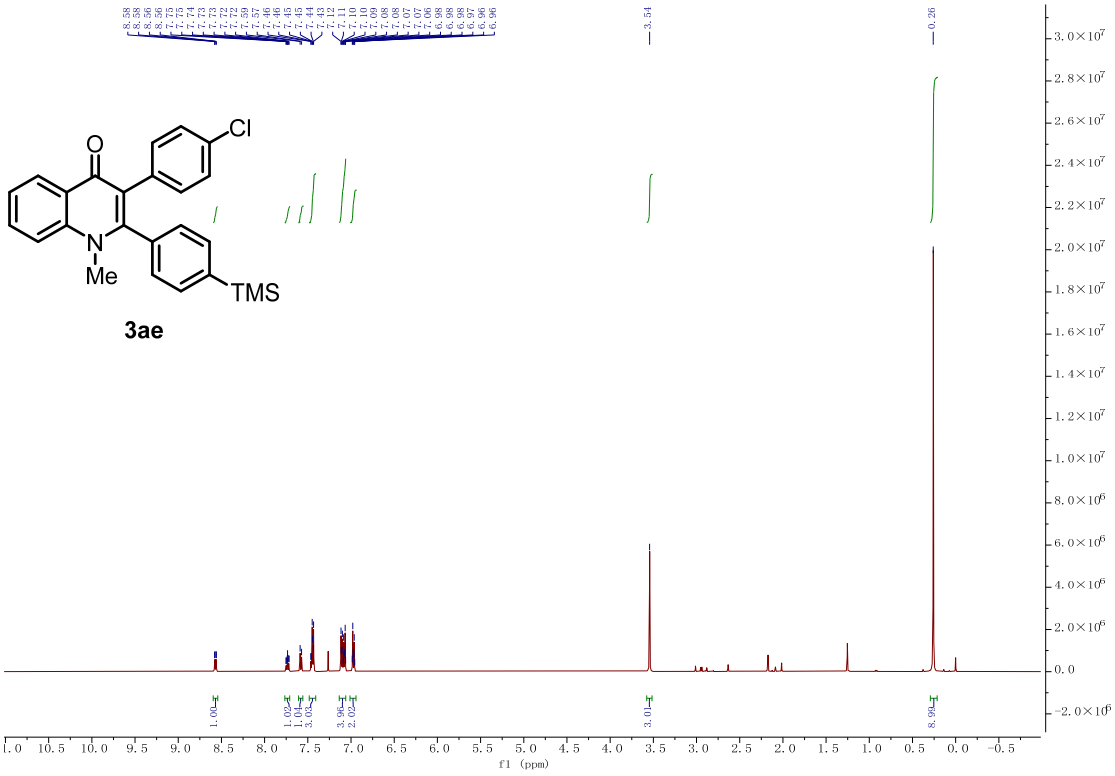
1-methyl-3-(p-tolyl)-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ad). ^{1}H NMR (500 MHz, $CDCl_3$**)**



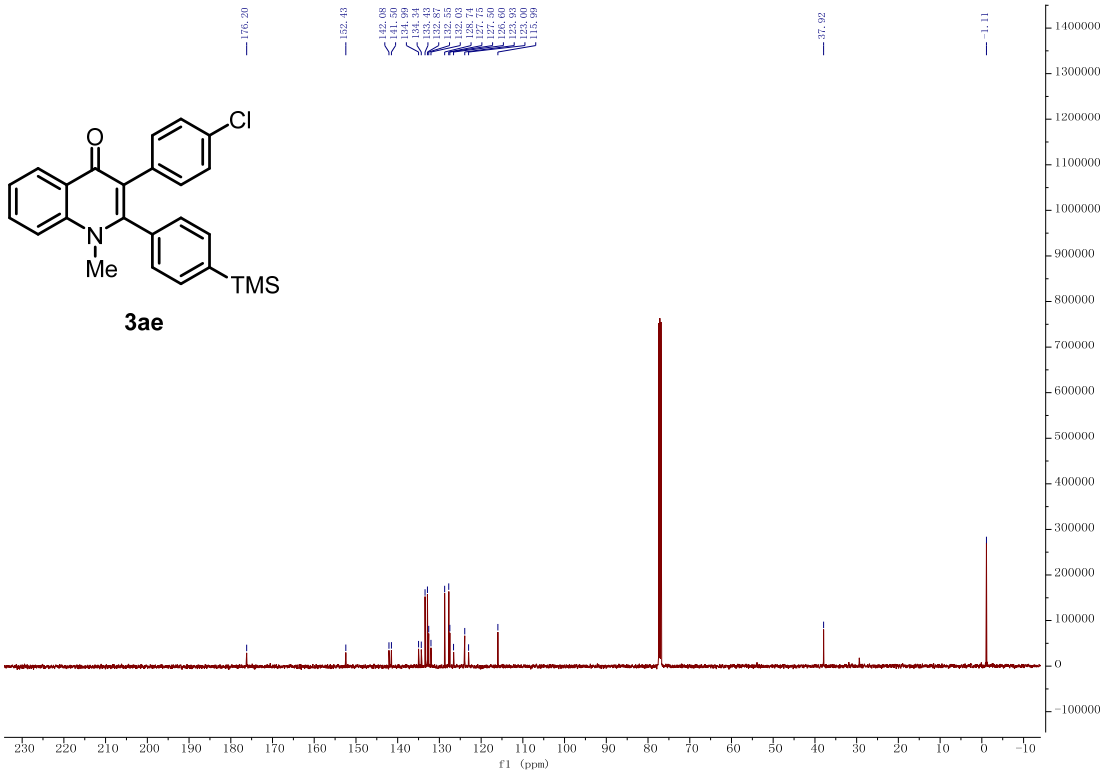
1-methyl-3-(p-tolyl)-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ad). ^{13}C NMR (125 MHz, $CDCl_3$**)**



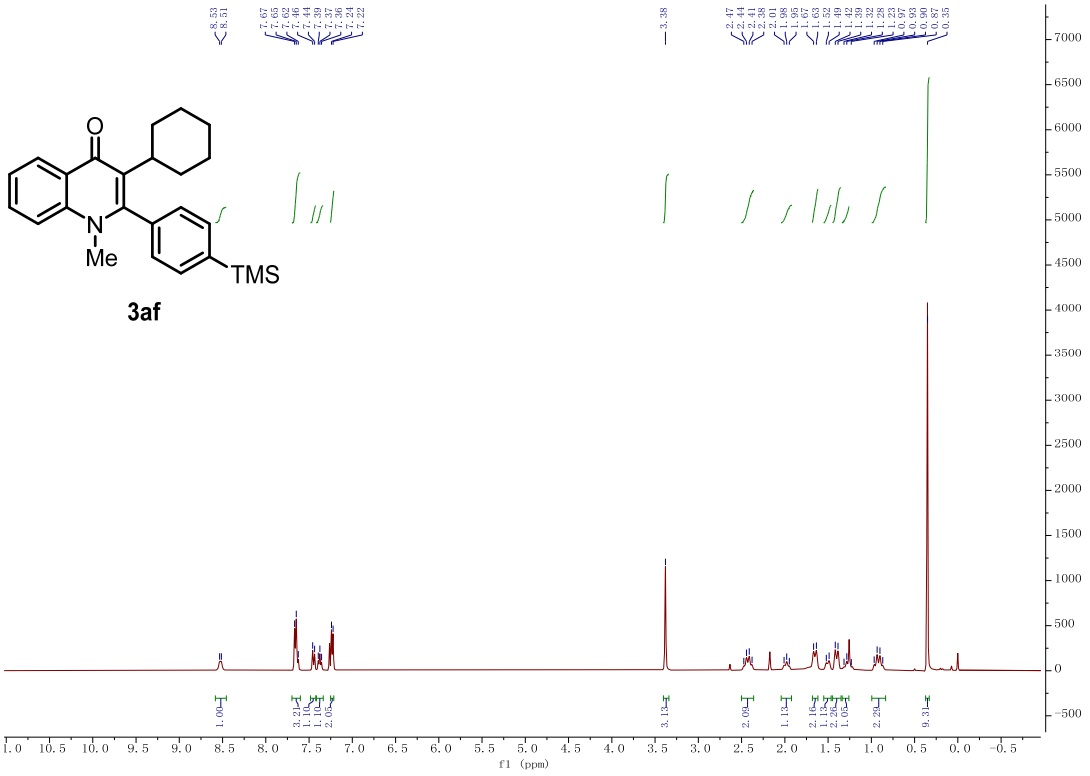
3-(4-chlorophenyl)-1-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ae). ^{1}H NMR (500 MHz, $CDCl_3$)



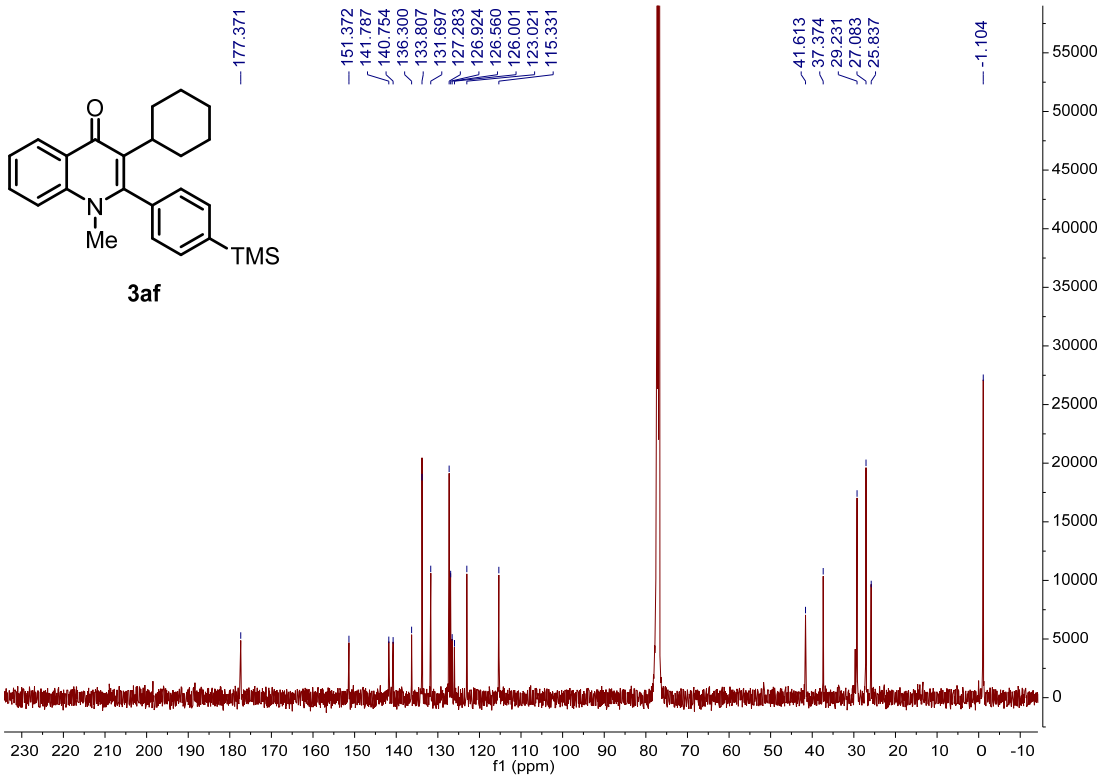
3-(4-chlorophenyl)-1-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ae). ^{13}C NMR (125 MHz, $CDCl_3$)



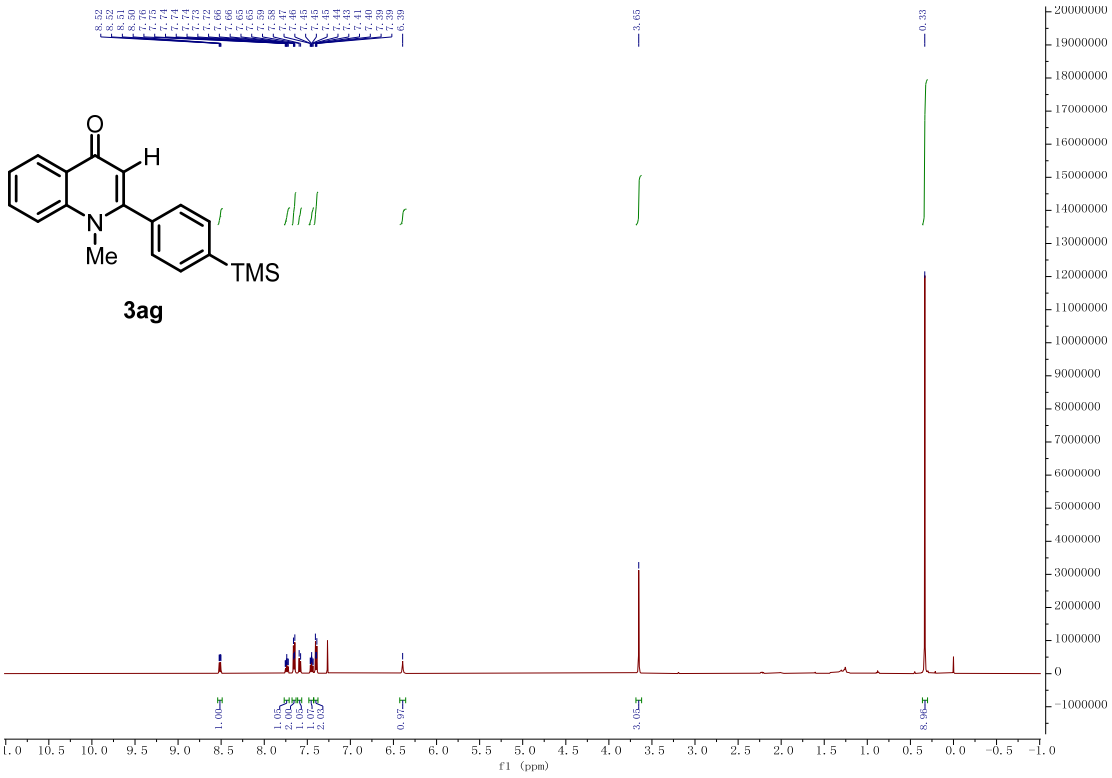
3-cyclohexyl-1-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3af). ^{1}H NMR (400 MHz, $CDCl_3$**)**



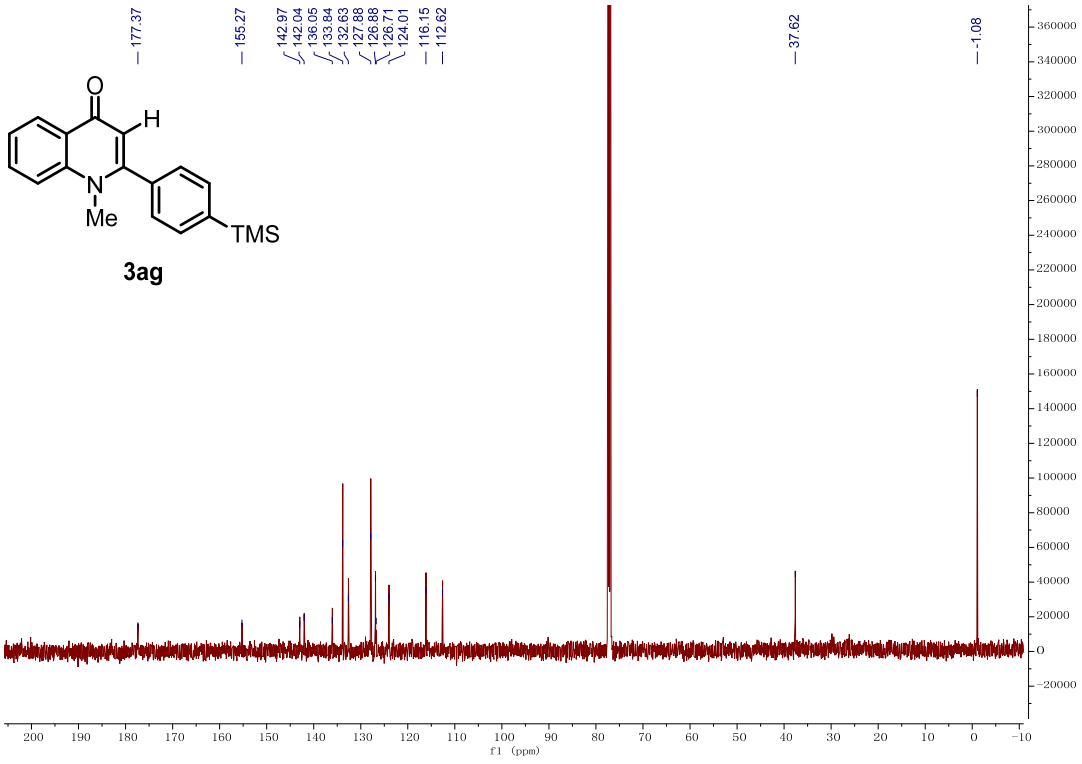
3-cyclohexyl-1-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3af). ^{13}C NMR (125 MHz, $CDCl_3$**)**



1-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ag). ^{1}H NMR (500 MHz, $CDCl_3$**)**

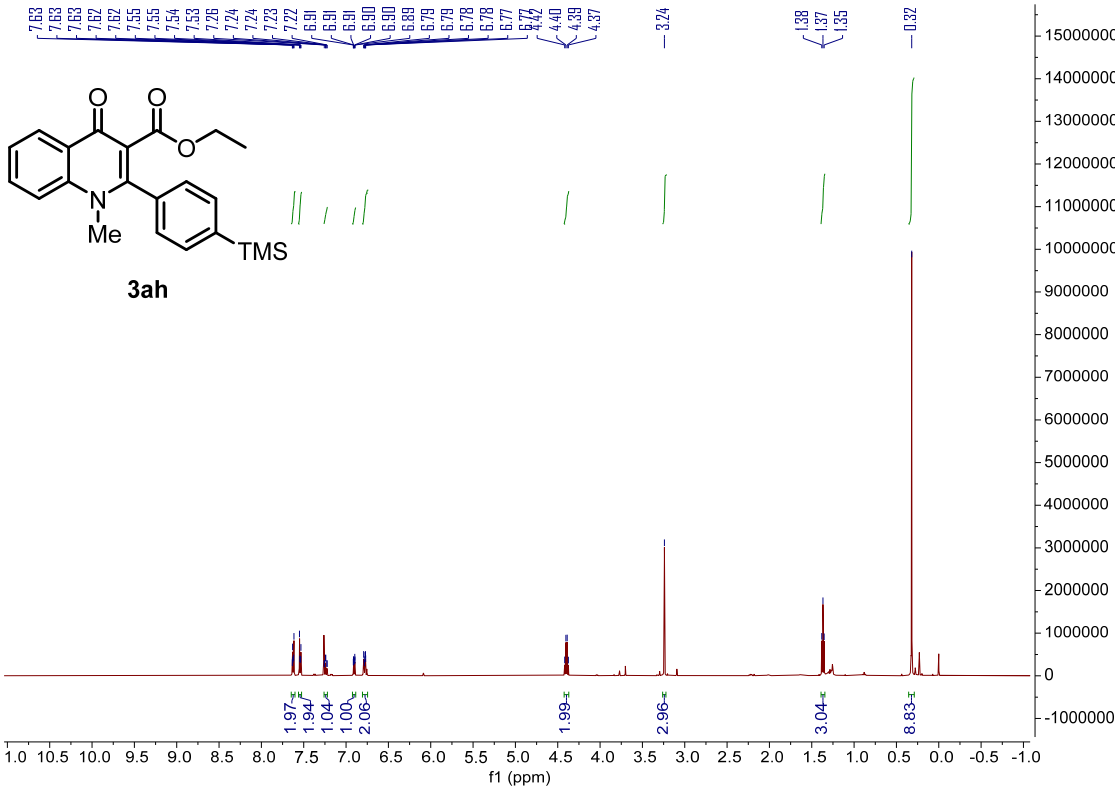


1-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3ag). ^{13}C NMR (125 MHz, $CDCl_3$**)**



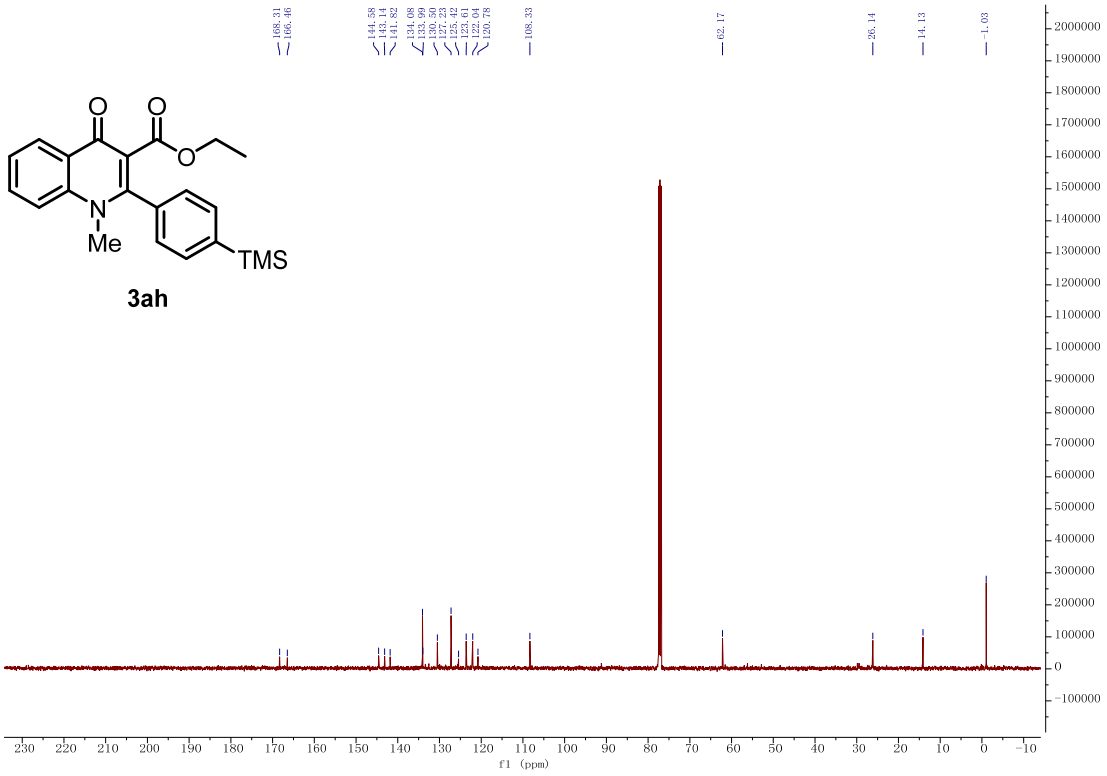
Ethyl 1-methyl-4-oxo-2-(4-(trimethylsilyl)phenyl)-1,4-dihydroquinoline-3-carbo-xylate (3ah).

^{1}H NMR (500 MHz, $CDCl_3$)

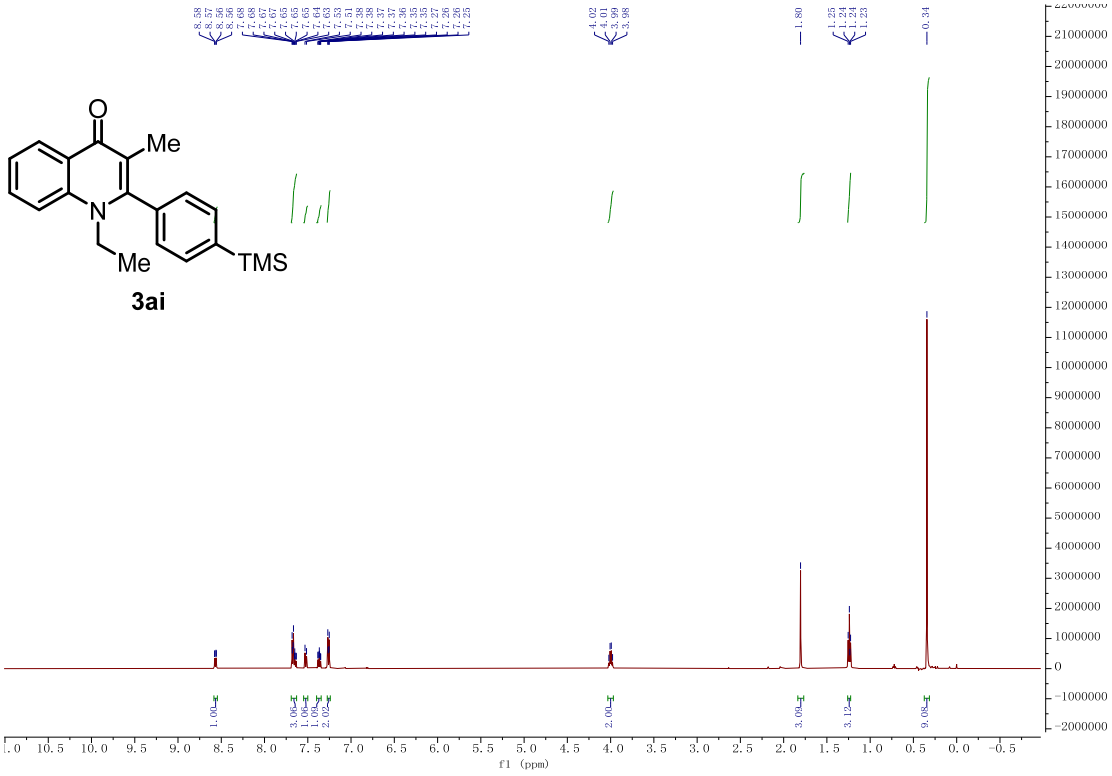


Ethyl 1-methyl-4-oxo-2-(4-(trimethylsilyl)phenyl)-1,4-dihydroquinoline-3-carbo-xylate (3ah).

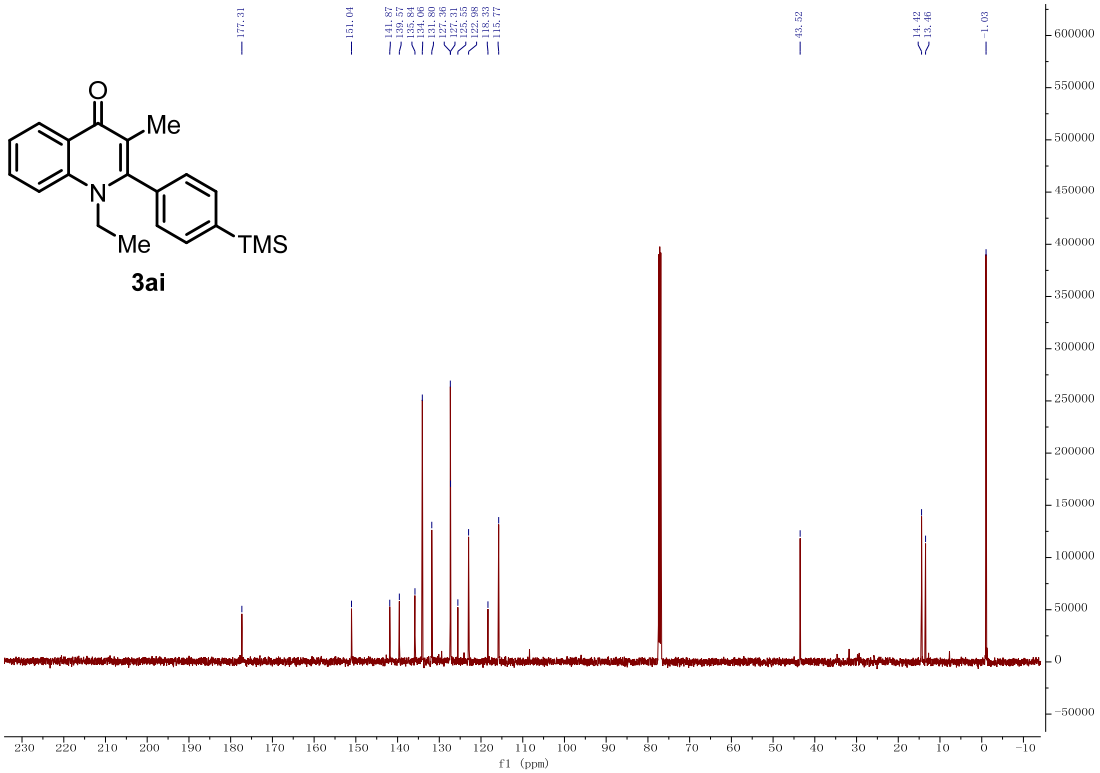
^{13}C NMR (125 MHz, $CDCl_3$)



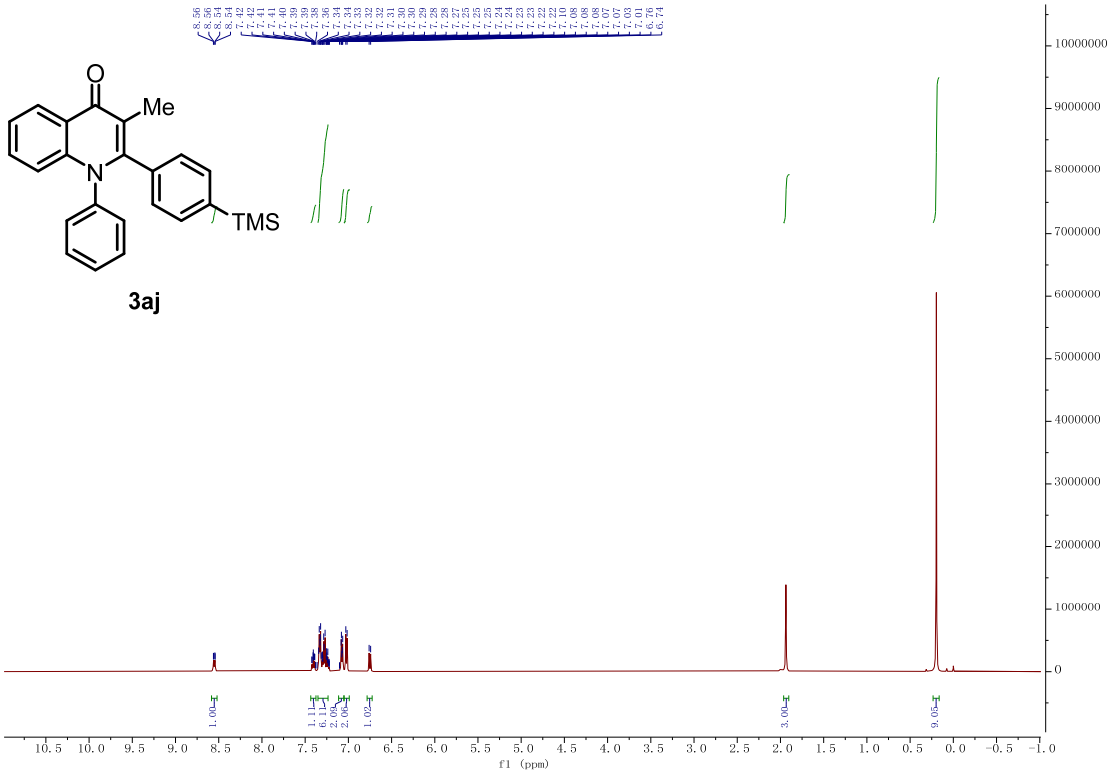
1-ethyl-3-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3ai). ^{1}H NMR (500 MHz, $CDCl_3$)



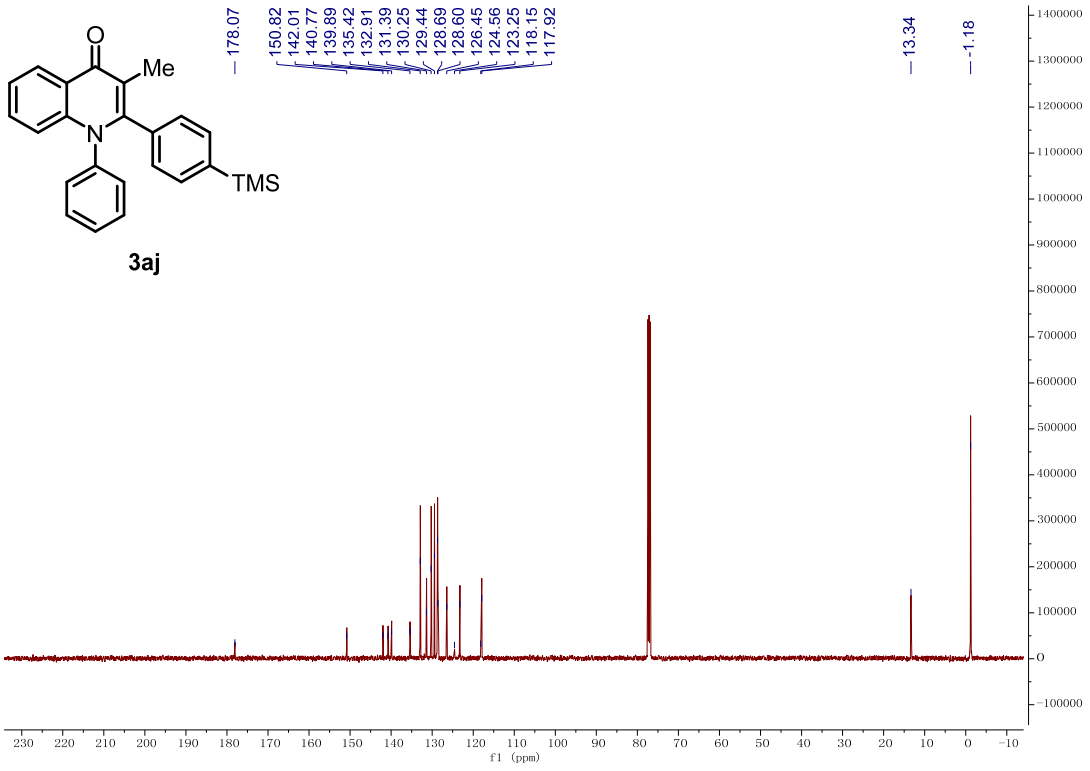
1-ethyl-3-methyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1*H*)-one (3ai). ^{13}C NMR (125 MHz, $CDCl_3$**)**



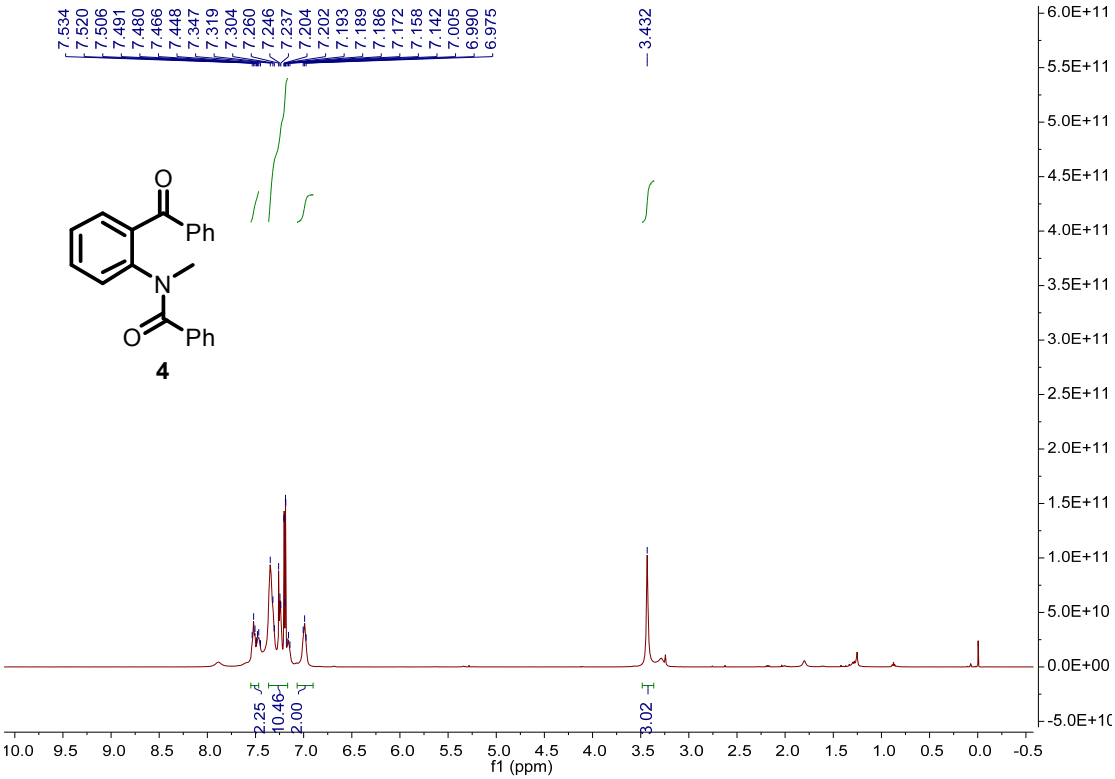
3-methyl-1-phenyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3aj). ^{1}H NMR (500 MHz, $CDCl_3$)



3-methyl-1-phenyl-2-(4-(trimethylsilyl)phenyl)quinolin-4(1H)-one (3aj). ^{13}C NMR (125 MHz, $CDCl_3$**)**



N-(2-benzoylphenyl)-N-methylbenzamide (4). **^{1}H NMR** (500 MHz, $CDCl_3$)



N-(2-benzoylphenyl)-N-methylbenzamide (4). **^{13}C NMR (**125 MHz, $CDCl_3$**)**