Supplementary Information

Dinuclear gold-catalyzed cyclization of 1,7-enynes with unactivated alkyl bromides

Jiajun Li,[‡a] Xinyi Zhai,[‡a] Cheng-Long Ji,[a] Weipeng Li,[a] and Jin Xie*[ab]

[a.] *State Key Laboratory of Coordination Chemistry, Jiangsu Key Laboratory of Advanced Organic Materials, Chemistry and Biomedicine Innovation Center (ChemBIC), School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210023, China*

[b.] *State Key Laboratory of Chemistry and Utilization of Carbon Based Energy Resources, College of Chemistry, Xinjiang University, Urumqi 830017, China*

Table of Contents

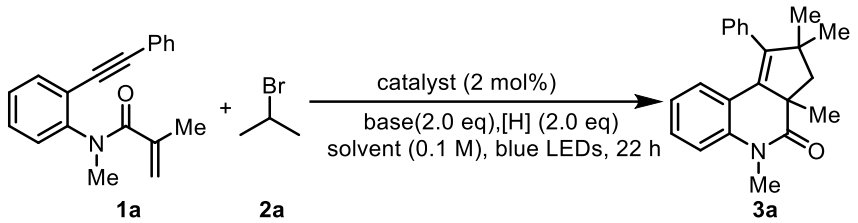
1. General Information

All reactions are conducted in oven- or flame-dried glassware under an atmosphere of nitrogen unless otherwise noted. Unless otherwise noted, all reagents are used as received and handled under air atmosphere. Chloroform-*d*1 is purchased from J & K Scientific Ltd.

NMR spectra are recorded on a Bruker Ultra-shield 400 and 500 MHz spectrometer. ^{1}H NMR and ^{13}C NMR are recorded on an NMR spectrometer with $CDCl_3$ as solvent. Chemical shifts of ^{1}H and ^{13}C spectra are reported in parts per million (ppm). The ^{13}C NMR spectra is {1H} decoupled. The residual solvent signals are used as standard, and the chemical shifts are converted to the corresponding scale (CDCl3: δ H = 7.26 ppm, δ C = 77.00 ppm). All coupling constants (*J* values) are reported in hertz (Hz). Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quint (quintet), and multiplet (m). Gas chromatographic (GC) analyses are performed on a GC equipped with a flameionization detector and an Rtx@-65 (30 m × 0.32 mm ID × 0.25 μm df) column. GC-MS analyses are performed on a GC-MS with an EI mode. HRMS (ESI) is determined on the Micromass Q-TOF instrument. The IR spectra is recorded on a Brucker Alpha FT/IR instrument.The blue LEDs (45 W, λ = 380- 550 nm, λ_{max} = 466 nm) is purchased from Kessil. Schlenk tubes (10 mL and 100 mL) are purchased from synthware. Toppette is purchased from DLAB Scientific Co., Ltd. The compound names are generated by the computer program ChemDraw according to the guidelines specified by the International Union of Pure and Applied Chemistry (IUPAC).

All reagents are purchased from commercial suppliers, Aladdin, Adamas-beta®,TCI (Shanghai) Development Co., Ltd, Energy Chemical, J & K scientific Ltd., Bide Pharmatech Ltd, Alfa-Aesar and Sigma-Aldrich unless otherwise noted.

2. Optimization of the Reaction Conditions

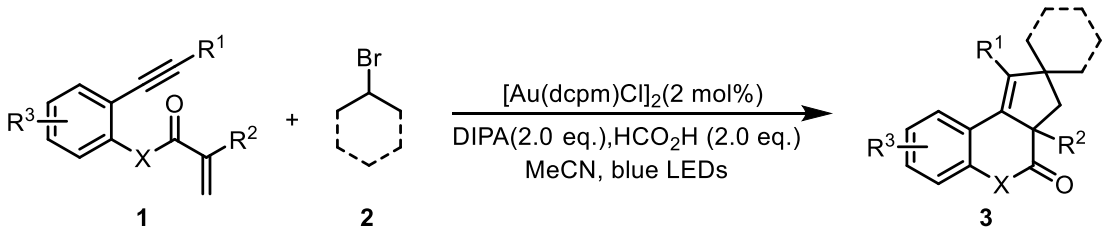


1a **2a** **3a**

entry	catalyst	base	[H]	solvent	yield[b](%)
1	$[Au(dcpm)Cl]_2$	-	-	MeCN	nr
2	$[Au(dcpm)Cl]_2$	Na_2CO_3	-	MeCN	trace
3	$[Au(dcpm)Cl]_2$	BTMG	-	MeCN	trace
4	$[Au(dcpm)Cl]_2$	-	HCO_2H	MeCN	12
5	$[Au(dcpm)Cl]_2$	DIPA	-	MeCN	7
6	$[Au(dcpm)Cl]_2$	DIPA	HCO_2H	MeCN	72[c]
7	$[Au(dcpm)Cl]_2$	DIPA	$HCOONH_4$	MeCN	53 [c]
8	$[Au(dcpm)Cl]_2$	Pyrrolidine	HCO_2H	MeCN	66 [c]
9	$[Au(dcpm)Cl]_2$	NEt3	HCO_2H	MeCN	8
10	$[Au(dcpm)Cl]_2$	$^iPr_2NEt$	HCO_2H	MeCN	35
11	$[Au(dppbz)Cl]_2$	DIPA	HCO_2H	MeCN	nr
12	$[Au_3(tppm)_2](OTf)_3$	DIPA	HCO_2H	MeCN	trace
13	$Ru(bpy)_3Cl_2$	DIPA	HCO_2H	MeCN	nr
14	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	DIPA	HCO_2H	MeCN	nd
15	$[Ir(ppy)_2(dtbbpy)]PF_6$	DIPA	HCO_2H	MeCN	6
16	*fac*-$Ir(ppy)_3$	DIPA	HCO_2H	MeCN	17
17	4CzIPN	DIPA	HCO_2H	MeCN	nd
18	$[Au(dcpm)Cl]_2$	DIPA	HCO_2H	THF	41
19	$[Au(dcpm)Cl]_2$	DIPA	HCO_2H	AcOMe	61
20	$[Au(dcpm)Cl]_2$	DIPA	HCO_2H	CH3OH	42
21	$[Au(dcpm)Cl]_2$	DIPA	HCO_2H	DCE	37
22	$[Au(dcpm)Cl]_2$	DIPA	HCO_2H	DMF	73
23	$[Au(dcpm)Cl]_2$	DIPA	HCO_2H	THF	41
24	$[Au(dcpm)Cl]_2$	DIPA	HCO_2H	AcOMe	61
25	$[Au(dcpm)Cl]_2$	DIPA	HCO_2H	CH3OH	42
26	-	DIPA	HCO_2H	MeCN	nr
27[d]	$[Au(dcpm)Cl]_2$	DIPA	HCO_2H	MeCN	nr
28	$[Au(dcpm)Cl]_2$	DIPA	AcOH	MeCN	71

[a] Standard reaction conditions: $[Au(dcpm)Cl]_2$ (2 mol%), **1a** (0.1 mmol), **2a** (0.3 mmol), HCO_2H (0.2 mmol), DIPA (0.2 mmol), MeCN (1 mL), blue LEDs, ambient temperature, 22 h. DIPA = Diisopropylamine. n.d. = not detected. n.r. = no reaction. [b] GC yield using biphenyl as internal standard. [c] Isolated yield. [d] Standard reaction conditions without light irradiation.

3. General Procedure for gold catalyzed radical tandem cyclization



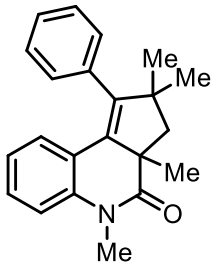
To an over-dried tube, 1,7-enyne (0.2 mmol), $[Au(dcpm)Cl]_2$ (2 mol%), HCO_2H (0.4 mmol), DIPA (0.4 mmol), alkyl bromides (0.6 mmol) and MeCN (1 mL) were added sequentially under N_2 atmosphere. The resulting mixture was stirred at ambient temperature (fan is used to keep the reaction temperature around ambient temperature) under the irradiation of blue LEDs for 22-36 h. After the reaction finished, the mixture was concentrated under reduced pressure. Then the resulting residue was purified by flash column chromatography (1:10, EtOAc/hexane) to afford the product.

4 mmol scale for synthesis of 3a

To an over-dried 100mL tube, 1,7-enyne **1a** (1.1 g, 4 mmol), $[Au(dcpm)Cl]_2$ (2 mol%), HCO_2H (320 μL, 8 mmol), DIPA (1120 μL, 8 mmol), isopropyl bromide (1120 μL, 8 mmol) and MeCN (20 mL) were added sequentially under N_2 atmosphere. The resulting mixture was stirred at ambient temperature (fan is used to keep the reaction temperature around ambient temperature) under the irradiation of blue LEDs for 60 h. After the reaction finished, the mixture was concentrated under reduced pressure. Then the resulting residue was purified by flash column chromatography (1:10, EtOAc/hexane) to afford the product **3a** (627 mg, 50 yield%).

4. Characterization of Products

2,2,3a,5-Tetramethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3a)



According to the general procedure in 0.2 mmol scale, **3a** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 22.7 mg, 72% yield, white solid, m.p. =162-164 °C.

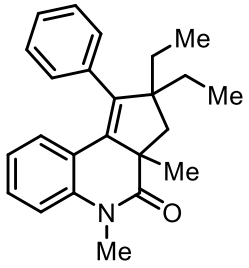
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.27 (m, 3H), 7.21 – 7.07 (m, 3H), 6.98 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.77 – 6.67 (m, 2H), 3.40 (s, 3H), 2.58 (d, *J* = 13.6 Hz, 1H), 2.07 (d, *J* = 13.6 Hz, 1H), 1.39 (s, 3H), 1.34 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.8, 148.2, 139.9, 136.7, 132.8, 129.0, 128.3, 127.9, 127.5, 127.1, 122.2, 121.7, 114.7, 51.8, 49.5, 47.8, 29.9, 29.6, 29.2, 26.3.

IR (ATR): ν = 2960, 2868, 1676, 1599, 1348, 1462, 1127, 752, 718, 701 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{22}H_{24}NO$ $(M + H)^+$: 318.1852; found: 318.1847.

2,2-Diethyl-3a,5-dimethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3b)



According to the general procedure in 0.2 mmol scale, **3b** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 40.7 mg, 59% yield, thick oil.

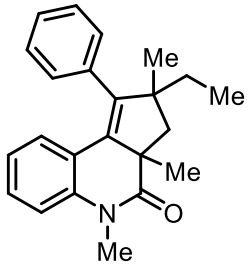
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 3H), 7.17 – 7.14 (m, 1H), 7.12 – 7.07 (m, 2H), 6.99 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.70 (td, *J* = 7.5, 1.0 Hz, 1H), 6.67 (dd, *J* = 7.0, 2.0 Hz, 1H), 3.42 (s, 3H), 2.74 (d, *J* = 14.5 Hz, 1H), 1.87 (d, *J* = 14.5 Hz, 1H), 1.67 – 1.63 (m, 2H), 1.34 – 1.29 (m, 1H), 1.27 (s, 3H), 1.22 – 1.17 (m, 1H), 1.09 (t, *J* = 7.5 Hz, 3H), 0.74 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 145.2, 139.7, 136.5, 135.5, 129.3, 128.2, 127.8, 127.6, 127.0, 122.3, 122.1, 114.5, 56.7, 52.0, 39.9, 31.4, 31.4, 30.1, 26.4, 10.2, 8.7.

IR (ATR): ν = 2964, 2361, 1674, 1599, 1460, 1275, 1099, 751, 711, 700 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{24}H_{28}NO$ $(M + H)^+$: 346.2165; found: 346.2160.

2-Ethyl-2,3a,5-trimethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3c)



According to the general procedure in 0.2 mmol scale, **3c** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 53.1 mg, 80% yield, dr = 1.5:1, thick oil.

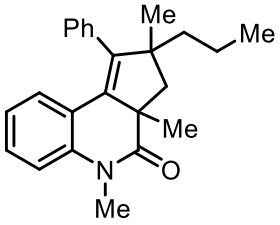
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 3H), 7.18 – 7.06 (m, 3H), 7.01 – 6.96 (m, 1H), 6.74 – 6.66 (m, 2H), 3.41 (s, 3H), 2.68 (d, *J* = 14.0 Hz, 0.4H), 2.45 (d, *J* = 14.0 Hz, 0.6H), 2.18 (d, *J* = 14.0 Hz, 0.6H), 1.88 (d, *J* = 14.0 Hz, 0.4H), 1.67 – 1.61 (m, 1.2H), 1.40 (s, 1.2H), 1.33 (s, 1.2H), 1.30 (s, 1.8H), 1.23 – 1.21 (m, 0.8H), 1.02 (t, *J* = 7.2 Hz, 1.8H), 0.94 (s, 1.8H), 0.79 (t, *J* = 7.2 Hz, 1.2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 175.8, 148.2, 147.6, 139.9, 139.8, 136.9, 136.6, 133.4, 133.4, 129.4, 129.0, 128.3, 128.1, 127.9, 127.8, 127.6, 127.5, 127.1, 127.0, 122.2, 122.1, 121.9, 121.8, 114.7, 114.6, 51.8, 51.8, 51.7, 51.5, 45.7, 44.0, 33.4, 32.5, 30.0, 29.9, 27.3, 26.8, 26.5, 26.3, 9.8, 8.6.

IR (ATR): ν = 2963, 2361, 1676, 1560, 1461, 1369, 1100, 752, 714, 702 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{23}H_{26}NO$ $(M + H)^+$: 332.2009; found: 332.2004.

2,3a,5-Trimethyl-1-phenyl-2-propyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3d)



According to the general procedure in 0.2 mmol scale, **3d** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 29.2 mg, 42% yield, dr = 1.5:1, thick oil.

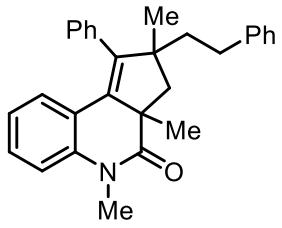
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 3H), 7.17 – 7.07 (m, 3H), 7.00 – 6.97 (m, 1H), 6.73 – 6.66 (m, 2H), 3.40 (s, 3H), 2.68 (d, *J* = 14.0 Hz, 0.4H), 2.46 (d, *J* = 14.0 Hz, 0.6H), 2.19 (d, *J* = 14.0 Hz, 0.6H), 1.91 (d, *J* = 14.0 Hz, 0.4H), 1.62 – 1.42 (m, 2.4H), 1.40 (s, 1.2H), 1.32 (s, 1.2H), 1.30 (s, 1.8H), 1.23 – 1.06 (m, 1.6H), 0.99 (t, *J* = 7.2 Hz, 1.8H), 0.95 (s, 1.8H), 0.76 (t, *J* = 7.2 Hz, 1.2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 175.8, 148.4, 147.9, 139.9, 139.8, 136.9, 136.6, 133.2, 133.2, 129.4, 129.0, 128.3, 128.2, 127.9, 127.8, 127.6, 127.5, 127.1, 127.0, 122.2, 122.1, 122.0, 121.8, 114.7, 114.6, 51.9, 51.8, 51.6, 51.3, 46.5, 44.7, 43.4, 42.7, 30.0, 29.9, 27.7, 27.4, 26.5, 26.3, 18.8, 17.6, 14.9, 14.6.

IR (ATR): ν = 2958, 1671, 1599, 1460, 1347, 1100, 909, 751, 729, 701 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{24}H_{28}NO$ $(M + H)^+$: 346.2165; found: 346.2159.

2,3a,5-Trimethyl-2-phenethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3e)



According to the general procedure in 0.2 mmol scale, **3e** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 33.7 mg, 41% yield, dr = 1:1, thick oil.

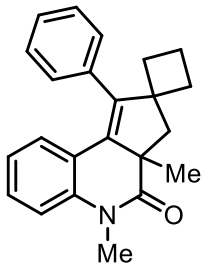
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.24 – 7.09 (m, 6H), 7.02 – 6.98 (m, 2H), 6.75 – 6.68 (m, 2H), 3.42 (s, 3H), 2.84 (d, *J* = 13.6 Hz, 0.5H), 2.79 – 2.67 (m, 1H), 2.58 – 2.52 (m, 1.5H), 2.36 (d, *J* = 13.6 Hz, 0.5H), 2.03 (d, *J* = 13.6 Hz, 0.5H), 1.98 – 1.89 (m, 1H), 1.54 – 1.49 (m, 2.5H), 1.37 – 1.36 (m, 3H), 1.06 (s, 1.5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 175.7, 147.9, 147.2, 142.7, 142.6, 139.9, 139.8, 136.6, 136.4, 133.8, 133.7, 129.4, 129.1, 128.5, 128.4, 128.3, 128.3, 128.2, 128.2, 128.0, 128.0, 127.7, 127.5, 127.3, 127.2, 125.8, 125.5, 122.2, 122.2, 121.8, 121.6, 114.7, 114.7, 51.9, 51.8, 51.6, 51.2, 46.5, 44.8, 43.4, 42.6, 32.2, 31.0, 30.0, 30.0, 28.0, 27.1, 26.4, 26.4.

IR (ATR): ν = 3026, 2960, 1671, 1699, 1460, 1099, 908, 751, 729, 699 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{29}H_{30}NO$ $(M + H)^+$: 408.2322; found: 408.2312.

3a',5'-Dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclobutane-1,2'-cyclopenta[*c*]quinolin]-4'(5'H)-one (3f)



According to the general procedure in 0.2 mmol scale, **3f** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 29.0 mg, 44% yield, thick oil.

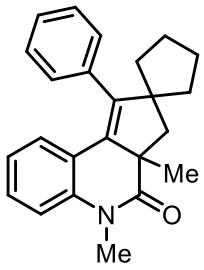
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 – 7.32 (m, 3H), 7.24 (d, *J* = 7.0 Hz, 2H), 7.15 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H), 6.97 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.81 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.70 (td, *J* = 7.5, 1.0 Hz, 1H), 3.39 (s, 3H), 2.59 (d, *J* = 13.0 Hz, 1H), 2.54 (d, *J* = 13.0 Hz, 1H), 2.53 – 2.46 (m, 1H), 2.22 – 2.20 (m, 1H), 2.08 – 2.04 (m, 1H), 1.95 – 1.86 (m, 1H), 1.81 – 1.76 (m, 1H), 1.58 – 1.51 (m, 1H), 1.28 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 145.5, 139.9, 137.1, 134.0, 129.0, 128.5, 128.1, 127.4, 127.2, 122.2, 121.3, 114.8, 54.1, 51.9, 50.2, 35.0, 31.9, 29.8, 25.7, 16.7.

IR (ATR): ν = 2926, 1671, 1598, 1461, 1369, 1350, 1284, 1120, 751, 711 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{23}H_{24}NO$ $(M + H)^+$: 330.1852; found: 330.1849.

3a',5'-Dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclopentane-1,2'-cyclopenta[*c*]quinolin]-4'(5'H)-one (3g)



According to the general procedure in 0.2 mmol scale, **3g** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 51.4 mg, 75% yield, thick oil.

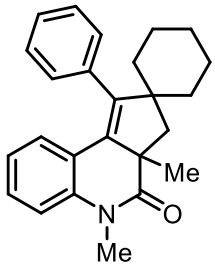
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 3H), 7.17 – 7.12 (m, 3H), 6.98 (dd, *J* = 8.4, 1.0 Hz, 1H), 6.76 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.70 (td, *J* = 7.6, 1.0 Hz, 1H), 3.40 (s, 3H), 2.44 (d, *J* = 13.6 Hz, 1H), 2.15 (d, *J* = 13.6 Hz, 1H), 1.96 – 1.87 (m, 1H), 1.82 – 1.70 (m, 2H), 1.68 – 1.58 (m, 2H), 1.52 – 1.45 (m, 1H), 1.45 – 1.38 (m, 1H), 1.37 – 1.32 (m, 4H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 146.0, 139.7, 136.8, 133.9, 129.4, 128.2, 127.9, 127.4, 127.1, 122.2, 121.6, 114.7, 58.7, 52.0, 48.8, 38.9, 38.4, 29.9, 26.5, 24.2, 23.9.

IR (ATR): ν = 2952, 2866, 1671, 1598, 1460, 1349, 1240, 1102, 751, 707 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{24}H_{26}NO$ $(M + H)^+$: 344.2009; found: 344.2003.

3a',5'-Dimethyl-1'-phenyl-3',3a'-dihydrospiro[cyclohexane-1,2'-cyclopenta[*c*]quinolin]-4'(5'H)-one (3h)



According to the general procedure in 0.2 mmol scale, **3h** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 53.8 mg, 75% yield, thick oil.

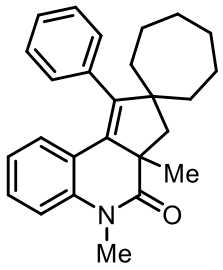
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 3H), 7.17 – 7.05 (m, 3H), 6.97 (d, *J* = 8.0 Hz, 1H), 6.71 – 6.65 (m, 2H), 3.40 (s, 3H), 2.46 (d, *J* = 14.0 Hz, 1H), 2.29 (d, *J* = 14.0 Hz, 1H), 1.73 – 1.65 (m, 3H), 1.62 – 1.48 (m, 3H), 1.45 – 1.37 (m, 1H), 1.32 – 1.30 (s, 4H), 1.13 (td, *J* = 13.0, 4.0 Hz, 1H), 1.01 – 0.92 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 148.7, 139.7, 136.8, 133.2, 129.5, 128.1, 127.8, 127.5, 127.0, 122.2, 121.8, 114.6, 52.2, 51.9, 43.5, 37.6, 35.9, 29.9, 27.3, 25.4, 23.5, 22.4.

IR (ATR): ν = 2925, 2852, 1673, 1598, 1461, 1329, 1103, 1048, 751, 710 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{25}H_{28}NO$ $(M + H)^+$: 358.2165; found: 358.2159.

3a',5'-Dimethyl-1'-phenyl-3',3a'-dihydrospiro[cycloheptane-1,2'-cyclopenta[*c*]quinolin]-4'(5'H)-one (3i)



According to the general procedure in 0.2 mmol scale, **3i** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 51.8 mg, 70% yield, thick oil.

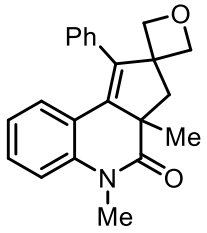
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.29 (m, 3H), 7.17 – 7.09 (m, 3H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.68 (d, *J* = 4.0 Hz, 2H), 3.39 (s, 3H), 2.47 (dd, *J* = 13.6, 0.9 Hz, 1H), 2.24 (d, *J* = 13.6 Hz, 1H), 2.02 – 1.89 (m, 2H), 1.66 – 1.58 (m, 3H), 1.50 – 1.35 (m, 6H), 1.32 (s, 3H), 1.29 – 1.25 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 149.5, 139.8, 137.2, 132.0, 129.3, 128.2, 127.8, 127.5, 127.0, 122.1, 121.7, 114.6, 54.6, 51.7, 45.7, 40.8, 40.2, 29.9, 28.9, 28.6, 26.3, 24.3, 23.7.

IR (ATR): ν = 2923, 1674, 1599, 1461, 1369, 1348, 1274, 1102, 752, 706 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{26}H_{30}NO$ $(M + H)^+$: 372.2322; found: 372.2317.

3a,5-Dimethyl-1-phenyl-3,3a-dihydrospiro[cyclopenta[*c*]quinoline-2,3'-oxetan]-4(5H)-one (3j)



According to the general procedure in 0.2 mmol scale, **3j** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 32.1 mg, 48% yield, thick oil.

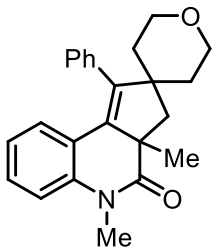
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.43 – 7.35 (m, 5H), 7.21 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H), 7.01 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.93 (dd, *J* = 8.0, 1.5 Hz, 1H), 6.76 (td, *J* = 7.5, 1.0 Hz, 1H), 5.11 (d, *J* = 6.0 Hz, 1H), 4.91 (d, *J* = 6.0 Hz, 1H), 4.60 (d, *J* = 6.5 Hz, 1H), 4.57 (d, *J* = 6.5 Hz, 1H), 3.39 (s, 3H), 2.71 (s, 2H), 1.21 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 174.6, 140.1, 140.1, 136.7, 135.3, 128.9, 128.8, 128.8, 128.0, 127.8, 122.4, 120.5, 115.0, 83.3, 79.4, 53.8, 51.7, 48.1, 29.8, 25.4.

IR (ATR): ν = 2958, 2865, 2361, 1670, 1598, 1462, 1352, 753, 732, 704 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{22}H_{22}NO_2$ $(M + H)^+$: 332.1645; found: 332.1644.

3a,5-Dimethyl-1-phenyl-2',3,3a,3',5',6'-hexahydrospiro[cyclopenta[*c*]quinoline-2,4'-pyran]-4(5H)-one (3k)



According to the general procedure in 0.2 mmol scale, **3k** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 60.3 mg, 84% yield, thick oil.

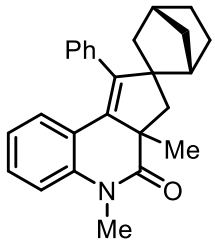
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.31 (m, 3H), 7.16 (ddd, *J* = 8.5, 7.0, 2.0 Hz, 1H), 7.09 (d, *J* = 6.0 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 1H), 6.75 – 6.68 (m, 2H), 3.95 (dd, *J* = 11.5, 3.5 Hz, 1H), 3.80 – 3.75 (m, 1H), 3.69 (td, *J* = 12.0, 2.0 Hz, 1H), 3.59 – 3.53 (m, 1H), 3.41 (s, 3H), 2.59 (d, *J* = 14.0 Hz, 1H), 2.39 (d, *J* = 14.0 Hz, 1H), 2.15 – 2.09 (m, 1H), 1.61 (td, *J* = 13.0, 5.0 Hz, 1H), 1.51 (dd, *J* = 13.0, 2.5 Hz, 1H), 1.34 (s, 3H), 1.15 (dd, *J* = 13.5, 2.5 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.4, 146.7, 139.7, 135.9, 134.4, 129.5, 128.4, 128.2, 127.5, 127.4, 122.3, 121.4, 114.7, 65.1, 64.5, 52.1, 49.7, 43.3, 37.2, 35.9, 30.0, 27.5.

IR (ATR): ν = 2928, 2848, 1736, 1672, 1598, 1238, 1102, 751, 710, 669 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{24}H_{26}NO_2$ $(M + H)^+$: 360.1958; found: 360.1956.

3a',5'-Dimethyl-1'-phenyl-3',3a'-dihydrospiro[bicyclo[2.2.1]heptane-2,2'-cyclopenta[*c*]quinolin]-4'(5'H)-one (3l)



According to the general procedure in 0.2 mmol scale, **3l** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 21.7 mg, 29% yield, thick oil.

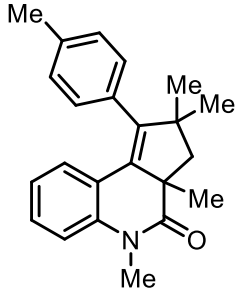
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (s, 2H), 7.32 – 7.29 (m, 1H), 7.24 – 7.23 (m, 1H), 7.13 (ddd, *J* = 8.0, 7.0, 2.0 Hz, 1H), 6.96 (dd, *J* = 8.5, 1.0 Hz, 1H), 6.81 – 6.74 (m, 1H), 6.67 (td, *J* = 7.5, 1.0 Hz, 1H), 6.63 (dd, *J* = 8.0, 2.0 Hz, 1H), 3.38 (s, 3H), 2.61 (d, *J* = 13.5 Hz, 1H), 2.45 (d, *J* = 13.5 Hz, 1H), 2.39 – 2.35 (m, 1H), 1.97 – 1.95 (m, 1H), 1.94 – 1.88 (m, 2H), 1.53 – 1.47 (m, 1H), 1.48 – 1.42 (m, 1H), 1.26 (s, 3H), 1.23 – 1.19 (m, 1H), 1.14 (dd, *J* = 12.5, 3.0 Hz, 1H), 1.07 – 1.03 (m, 1H), 1.01 – 0.95 (m, 1H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.5, 148.0, 139.8, 138.0, 133.3, 130.4, 129.7, 128.5, 127.7, 127.2, 127.0, 122.1, 114.6, 56.6, 51.1, 47.5, 46.2, 45.4, 39.1, 36.9, 30.0, 28.1, 27.3, 25.3.

IR (ATR): ν = 2942, 2868, 1672, 1599, 1460, 1349, 1277, 751, 731, 707 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{26}H_{28}NO$ $(M + H)^+$: 370.2165; found: 370.2161.

2,2,3a,5-Tetramethyl-1-(p-tolyl)-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3m)



According to the general procedure in 0.2 mmol scale, **3m** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 50.1 mg, 76% yield, thick oil.

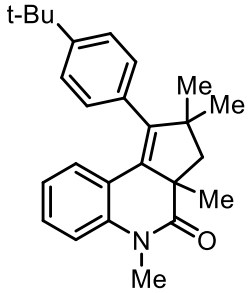
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 – 7.11 (m, 3H), 7.04 – 6.95 (m, 3H), 6.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.72 (td, *J* = 7.6, 1.2 Hz, 1H), 3.40 (s, 3H), 2.57 (d, *J* = 13.6 Hz, 1H), 2.37 (s, 3H), 2.06 (d, *J* = 13.6 Hz, 1H), 1.38 (s, 3H), 1.33 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 148.2, 139.8, 136.6, 133.6, 132.6, 129.0, 128.9, 127.8, 127.5, 122.2, 121.8, 114.6, 51.7, 49.5, 47.7, 29.9, 29.6, 29.2, 26.3, 21.2.

IR (ATR): ν = 2959, 2866, 1673, 1598, 1511, 1369, 1099, 814, 751, 734 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{23}H_{26}NO$ $(M + H)^+$: 332.2009; found: 332.2007.

1-(4-(Tert-butyl)phenyl)-2,2,3a,5-tetramethyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3n)



According to the general procedure in 0.2 mmol scale, **3n** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 47.6 mg, 64% yield, thick oil.

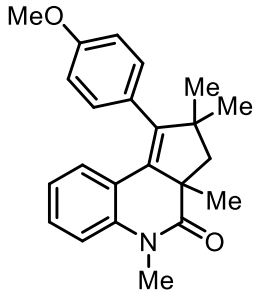
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, *J* = 8.4 Hz, 2H), 7.15 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 6.97 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.76 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.71 (td, *J* = 7.6, 1.2 Hz, 1H), 3.40 (s, 3H), 2.57 (d, *J* = 13.6 Hz, 1H), 2.06 (d, *J* = 13.6 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 12H), 0.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 149.9, 148.3, 139.8, 133.5, 132.5, 128.6, 127.8, 127.5, 125.1, 122.2, 121.9, 114.6, 51.7, 49.5, 47.8, 34.5, 31.4, 29.9, 29.6, 29.2, 26.3.

IR (ATR): ν = 2960, 2867, 1673, 1599, 1460, 1348, 1099, 828, 751, 731 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{26}H_{32}NO$ $(M + H)^+$: 374.2478; found: 374.2470.

1-(4-Methoxyphenyl)-2,2,3a,5-tetramethyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3o)



According to the general procedure in 0.2 mmol scale, **3o** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 53.6 mg, 77% yield, thick oil.

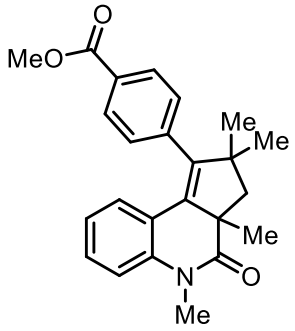
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 (ddd, *J* = 8.8, 7.6, 1.6 Hz, 1H), 7.04 (d, *J* = 8.8 Hz, 2H), 6.98 (dd, *J* = 8.8, 1.2 Hz, 1H), 6.87 (d, *J* = 8.8 Hz, 2H), 6.79 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.73 (td, *J* = 7.6, 1.2 Hz, 1H), 3.82 (s, 3H), 3.40 (s, 3H), 2.56 (d, *J* = 13.6 Hz, 1H), 2.06 (d, *J* = 13.6 Hz, 1H), 1.38 (s, 3H), 1.32 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 158.7, 147.9, 139.9, 132.7, 130.1, 128.8, 127.8, 127.5, 122.2, 121.9, 114.7, 113.8, 55.1, 51.6, 49.5, 47.7, 29.9, 29.6, 29.2, 26.3.

IR (ATR): ν = 2959, 2867, 2360, 1672, 1598, 1510, 1461, 1244, 828, 752 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{23}H_{26}NO_2$ $(M + H)^+$: 348.1958; found: 348.1951.

Methyl 4-(2,2,3a,5-tetramethyl-4-oxo-3,3a,4,5-tetrahydro-2H-cyclopenta[*c*]quinolin-1-yl)benzoate (3p)



According to the general procedure in 0.2 mmol scale, **3p** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 32.3 mg, 43% yield, thick oil.

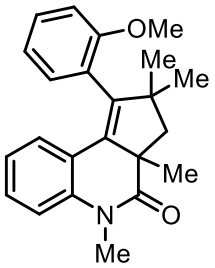
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.6 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 7.19 – 7.14 (m, 1H), 7.03 – 6.96 (m, 1H), 6.74 – 6.64 (m, 2H), 3.92 (s, 3H), 3.40 (s, 3H), 2.59 (d, *J* = 13.6 Hz, 1H), 2.09 (d, *J* = 13.6 Hz, 1H), 1.41 (s, 3H), 1.35 (s, 3H), 0.96 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.6, 167.0, 146.9, 142.1, 139.9, 134.0, 129.6, 129.2, 129.0, 128.3, 127.5, 122.3, 121.2, 114.9, 52.1, 52.0, 49.7, 48.0, 30.0, 29.7, 29.2, 26.3.

IR (ATR): ν = 2958, 1721, 1673, 1599, 1461, 1273, 1099, 1047, 752, 727 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{24}H_{26}NO_3$ $(M + H)^+$: 376.1907; found: 376.1902.

1-(2-Methoxyphenyl)-2,2,3a,5-tetramethyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3q)



According to the general procedure in 0.2 mmol scale, **3q** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 35.1 mg, 51% yield, dr = 1:1, thick oil.

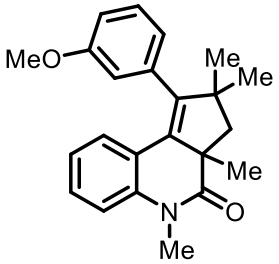
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 1H), 7.22 – 7.24 (m, 0.5H), 7.16 – 7.11 (m, 1H), 7.04 – 6.95 (m, 2H), 6.87 – 6.78 (m, 2.5H), 6.76 – 6.67 (m, 1H), 3.86 (s, 1.5H), 3.40 (s, 1.5H), 3.39 (s, 3H), 2.64 – 2.55 (m, 1H), 2.04 – 2.08 (m, 1H), 1.37 (s, 1.5H), 1.35 – 1.34 (m, 3H), 1.24 (s, 1.5H), 1.01 (s, 1.5H), 0.97 (s, 1.5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 176.2, 176.0, 158.1, 157.0, 144.8, 143.7, 139.7, 139.3, 133.5, 133.2, 130.9, 130.7, 128.6, 128.6, 127.7, 127.6, 126.8, 126.2, 125.6, 125.3, 122.7, 122.5, 122.1, 122.0, 120.4, 120.1, 114.5, 114.4, 111.8, 110.3, 55.3, 55.2, 52.0, 51.9, 49.3, 49.3, 48.5, 48.2, 29.9, 29.8, 29.5, 28.1, 26.6, 26.6.

IR (ATR): ν = 2960, 2866, 1670, 1596, 1460, 1369, 1237, 1099, 749, 729 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{23}H_{26}NO_2$ $(M + H)^+$: 348.1958; found: 348.1950.

1-(3-Methoxyphenyl)-2,2,3a,5-tetramethyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3r)



According to the general procedure in 0.2 mmol scale, **3r** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 33.7 mg, 49% yield, thick oil.

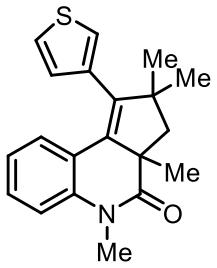
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (t, *J* = 7.6 Hz, 1H), 7.16 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 6.98 (dd, *J* = 8.0, 1.2 Hz, 1H), 6.85 (ddd, *J* = 8.8, 2.4, 1.2 Hz, 1H), 6.80 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.75 – 6.69 (m, 2H), 6.67 – 6.66 (m, 1H), 3.77 (s, 3H), 3.40 (s, 3H), 2.57 (d, *J* = 13.6 Hz, 1H), 2.07 (d, *J* = 13.6 Hz, 1H), 1.39 (s, 3H), 1.34 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.8, 159.4, 147.8, 139.8, 138.1, 132.8, 129.3, 128.0, 127.5, 122.3, 121.6, 121.6, 114.7, 114.7, 112.4, 55.2, 51.7, 49.5, 47.8, 29.9, 29.6, 29.2, 26.3.

IR (ATR): ν = 2959, 2867, 1671, 1598, 1461, 1279, 1047, 751, 726, 695 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{23}H_{26}NO_2$ $(M + H)^+$: 348.1958; found: 348.1952.

2,2,3a,5-Tetramethyl-1-(thiophen-3-yl)-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3s)



According to the general procedure in 0.2 mmol scale, **3s** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 26.1 mg, 40% yield, thick oil.

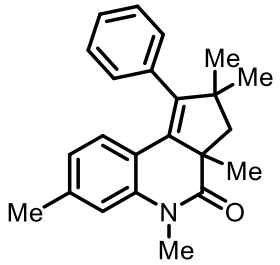
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (dd, *J* = 5.2, 2.8 Hz, 1H), 7.17 – 7.21 (m, 1H), 7.04 (dd, *J* = 3.2, 1.2 Hz, 1H), 6.99 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.88 (t, *J* = 1.6 Hz, 1H), 6.86 (t, *J* = 1.6 Hz, 1H), 6.79 (td, *J* = 7.6, 1.2 Hz, 1H), 3.39 (s, 3H), 2.56 (d, *J* = 13.6 Hz, 1H), 2.05 (d, *J* = 13.6 Hz, 1H), 1.41 (s, 3H), 1.31 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.7, 143.1, 139.9, 136.2, 133.7, 128.6, 128.1, 127.4, 125.3, 122.5, 122.3, 121.7, 114.7, 51.7, 49.4, 47.4, 29.9, 29.7, 29.1, 26.1.

IR (ATR): ν = 2960, 1671, 1598, 1461, 1345, 1279, 1100, 780, 752, 732 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{20}H_{22}NOS$ $(M + H)^+$: 324.1417; found: 324.1409.

2,2,3a,5,7-Pentamethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3t)



According to the general procedure in 0.2 mmol scale, **3t** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 46.7 mg, 71% yield, thick oil.

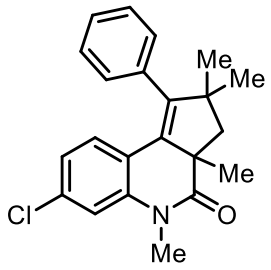
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 3H), 7.15 – 7.09 (m, 2H), 6.80 (s, 1H), 6.61 (d, *J* = 7.6 Hz, 1H), 6.53 (dd, *J* = 7.6, 0.8 Hz, 1H), 3.39 (s, 3H), 2.56 (d, *J* = 13.6 Hz, 1H), 2.29 (s, 3H), 2.07 (d, *J* = 13.6 Hz, 1H), 1.39 (s, 3H), 1.34 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.9, 147.1, 139.8, 137.9, 136.9, 132.8, 129.1, 128.2, 127.3, 127.0, 123.0, 118.9, 115.5, 51.8, 49.5, 47.7, 29.9, 29.6, 29.2, 26.4, 21.7.

IR (ATR): ν = 2960, 1673, 1609, 1508, 1328, 1277, 1102, 732, 720, 701 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{23}H_{26}NO$ $(M + H)^+$: 332.2009; found: 332.2003.

7-Chloro-2,2,3a,5-tetramethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3u)



According to the general procedure in 0.2 mmol scale, **3u** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 31.2 mg, 44% yield, thick oil.

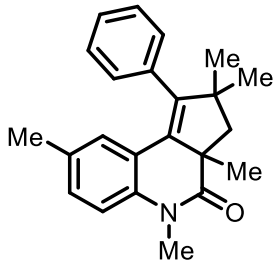
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 3H), 7.13 – 7.07 (m, 2H), 6.97 (d, *J* = 2.0 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.0 Hz, 1H), 6.63 (d, *J* = 8.4 Hz, 1H), 3.37 (s, 3H), 2.56 (d, *J* = 13.6 Hz, 1H), 2.07 (d, *J* = 13.6 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H), 0.97 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.6, 148.9, 141.0, 136.3, 133.5, 131.8, 128.9, 128.4, 127.3, 122.2, 120.1, 115.0, 51.7, 49.4, 47.8, 30.0, 29.5, 29.1, 26.3.

IR (ATR): ν = 2961, 1674, 1593, 1456, 1098, 1028, 907, 728, 713, 700 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{22}H_{23}NOCl$ $(M + H)^+$: 352.1463; found: 352.1463.

2,2,3a,5,8-Pentamethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3v)



According to the general procedure in 0.2 mmol scale, **3v** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 41.5 mg, 63% yield, thick oil.

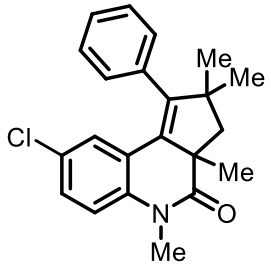
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 3H), 7.13 (dd, *J* = 8.0, 2.0 Hz, 2H), 6.95 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.51 (d, *J* = 2.0 Hz, 1H), 3.38 (s, 3H), 2.57 (d, *J* = 13.5 Hz, 1H), 2.07 (d, *J* = 13.5 Hz, 1H), 1.98 (s, 3H), 1.40 (s, 3H), 1.34 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 175.7, 147.9, 137.6, 136.8, 133.0, 131.5, 129.0, 128.5, 128.2, 128.1, 127.0, 121.5, 114.5, 51.8, 49.5, 47.7, 29.9, 29.6, 29.2, 26.3, 20.4.

IR (ATR): ν = 2960, 2360, 1675, 1489, 1344, 1105, 809, 751, 717, 702 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{23}H_{26}NO$ $(M + H)^+$: 332.2009; found: 332.2002.

8-Chloro-2,2,3a,5-tetramethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3w)



According to the general procedure in 0.2 mmol scale, **3w** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 31.3 mg, 44% yield, thick oil.

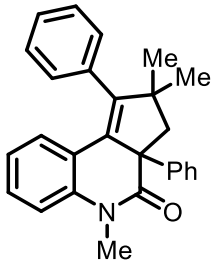
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 3H), 7.12 – 7.09 (m, 3H), 6.89 (d, *J* = 8.8 Hz, 1H), 6.65 (d, *J* = 2.4 Hz, 1H), 3.37 (s, 3H), 2.57 (d, *J* = 13.6 Hz, 1H), 2.07 (d, *J* = 13.6 Hz, 1H), 1.39 (s, 3H), 1.33 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.5, 149.8, 138.5, 135.9, 131.7, 128.8, 128.5, 127.7, 127.5, 127.5, 127.2, 123.2, 115.9, 51.6, 49.4, 47.9, 30.0, 29.5, 29.1, 26.3.

IR (ATR): ν = 2961, 2867, 1678, 1467, 1338, 1112, 809, 733, 714, 702 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{22}H_{23}NOCl$ $(M + H)^+$: 352.1463; found: 352.1462.

2,2,5-Trimethyl-1,3a-diphenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3x)



According to the general procedure in 0.2 mmol scale, **3x** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 56.4 mg, 74% yield, thick oil.

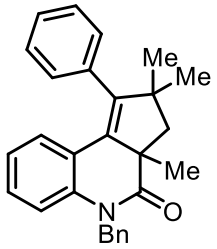
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.33 (m, 5H), 7.25 – 7.18 (m, 4H), 7.16 – 7.11 (m, 1H), 7.07 (ddd, *J* = 8.4, 7.2, 1.6 Hz, 1H), 6.90 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.82 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.72 (td, *J* = 7.6, 1.2 Hz, 1H), 3.35 (s, 3H), 2.97 (d, *J* = 13.2 Hz, 1H), 2.36 (d, *J* = 13.2 Hz, 1H), 1.10 (s, 3H), 0.99 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 173.0, 151.8, 143.3, 139.8, 136.6, 130.1, 128.9, 128.4, 128.3, 128.0, 127.3, 127.0, 126.9, 126.7, 122.6, 122.4, 115.0, 59.5, 53.2, 48.2, 30.3, 28.7, 27.8.

IR (ATR): ν = 2959, 1666, 1598, 1460, 1350, 1275, 907, 751, 727, 698 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{27}H_{26}NO$ $(M + H)^+$: 380.2009; found: 380.2002.

5-Benzyl-2,2,3a-trimethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3y)



According to the general procedure in 0.2 mmol scale, **3y** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 61.3 mg, 78% yield, thick oil.

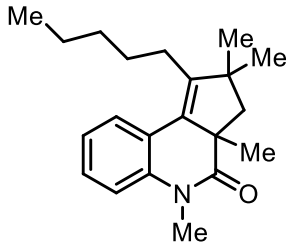
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 – 7.18 (m, 5H), 7.15 – 7.10 (m, 3H), 7.06 – 7.01 (m, 2H), 6.88 (ddd, *J* = 8.8, 7.2, 1.6 Hz, 1H), 6.75 (dd, *J* = 8.4, 1.2 Hz, 1H), 6.63 (dd, *J* = 7.6, 1.6 Hz, 1H), 6.54 (td, *J* = 7.6, 1.2 Hz, 1H), 5.56 (d, *J* = 16.4 Hz, 1H), 4.60 (d, *J* = 16.4 Hz, 1H), 2.58 (d, *J* = 13.6 Hz, 1H), 2.01 (d, *J* = 13.6 Hz, 1H), 1.37 (s, 3H), 1.32 (s, 3H), 0.90 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 175.9, 148.4, 139.4, 137.4, 136.7, 132.8, 129.1, 128.7, 128.3, 127.9, 127.6, 127.1, 127.0, 126.1, 122.3, 121.8, 115.5, 51.9, 49.4, 47.9, 46.6, 29.7, 29.2, 26.4.

IR (ATR): ν = 2960, 1737, 1675, 1598, 1460, 1371, 1238, 751, 718, 698 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{28}H_{28}NO$ $(M + H)^+$: 394.2165; found: 394.2161.

2,2,3a,5-Tetramethyl-1-pentyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3z)



According to the general procedure in 0.2 mmol scale, **3z** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 12.8 mg, 21% yield, thick oil.

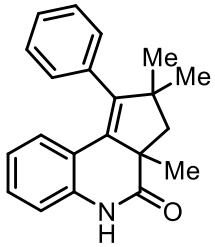
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.08 (td, *J* = 7.5, 1.0 Hz, 1H), 7.02 (dd, *J* = 8.0, 1.0 Hz, 1H), 3.36 (s, 3H), 2.45 (d, *J* = 13.5 Hz, 1H), 2.31 (ddd, *J* = 13.5, 11.5, 5.5 Hz, 1H), 2.16 (ddd, *J* = 13.5, 11.5, 5.5 Hz, 1H), 1.85 (d, *J* = 13.5 Hz, 1H), 1.64 – 1.55 (m, 2H), 1.36 – 1.33 (m, 4H), 1.24 (s, 3H), 1.17 (s, 3H), 1.11 (s, 3H), 0.91 – 0.89 (m, 3H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 176.4, 149.2, 139.6, 130.4, 127.6, 126.7, 123.1, 122.5, 114.7, 51.2, 49.3, 47.2, 32.6, 30.1, 29.9, 29.5, 28.7, 26.2, 25.9, 22.3, 14.0.

IR (ATR): ν = 2958, 2933, 2863, 2361, 2339, 1675, 1599, 1489, 1276, 750 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{21}H_{30}NO$ $(M + H)^+$: 312.2322; found: 312.2317.

2,2,3a-Trimethyl-1-phenyl-2,3,3a,5-tetrahydro-4H-cyclopenta[*c*]quinolin-4-one (3aa)



According to the general procedure in 0.2 mmol scale, **3aa** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 40.1 mg, 66% yield, thick oil.

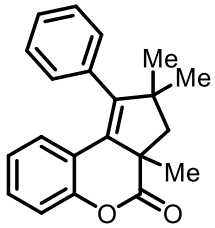
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (s, 1H), 7.37 – 7.30 (m, 3H), 7.15 – 7.04 (m, 3H), 6.84 (dd, *J* = 8.0, 0.8 Hz, 1H), 6.67 (dd, *J* = 4.0, 0.8 Hz, 2H), 2.56 (d, *J* = 13.6 Hz, 1H), 2.08 (d, *J* = 13.6 Hz, 1H), 1.45 (s, 3H), 1.40 (s, 3H), 0.98 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.2, 149.0, 136.8, 136.7, 133.1, 129.0, 128.3, 128.1, 127.4, 127.1, 122.5, 120.0, 115.4, 51.9, 48.4, 47.8, 29.5, 29.3, 26.6.

IR (ATR): ν = 3209, 3058, 2960, 2361, 1678, 1476, 1376, 751, 730, 702 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{21}H_{22}NO$ $(M + H)^+$: 304.1696; found: 304.1693.

2,2,3a-Trimethyl-1-phenyl-3,3a-dihydrocyclopenta[*c*]chromen-4(2H)-one (3bb)



According to the general procedure in 0.2 mmol scale, **3bb** was purified by flash chromatography (petroleum ether/ethyl acetate = 10:1), 17.6 mg, 29% yield, thick oil.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 – 7.35 (m, 3H), 7.18 – 7.12 (m, 3H), 7.05 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.79 (td, *J* = 7.5, 1.0 Hz, 1H), 6.67 (dd, *J* = 8.0, 1.5 Hz, 1H), 2.64 (d, *J* = 13.5 Hz, 1H), 2.12 (d, *J* = 13.5 Hz, 1H), 1.46 (s, 3H), 1.39 (s, 3H), 1.01 (s, 3H).

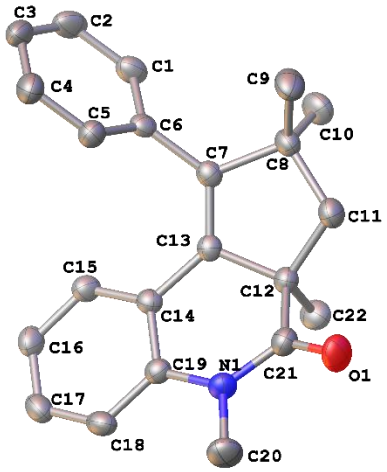
^{13}C NMR (126 MHz, $CDCl_3$) δ 173.4, 151.3, 149.5, 135.9, 129.8, 128.9, 128.8, 128.5, 127.5, 127.5, 127.0, 119.2, 116.5, 50.9, 48.7, 48.1, 29.3, 29.0, 26.1.

IR (ATR): ν = 2961, 1771, 1607, 1455, 1210, 1086, 1049, 750, 725, 701 cm^{-1}.

HRMS m/z (ESI) calcd for $C_{21}H_{21}NO$ $(M + H)^+$: 305.1536; found: 305.1532.

5. X-ray Crystal Data

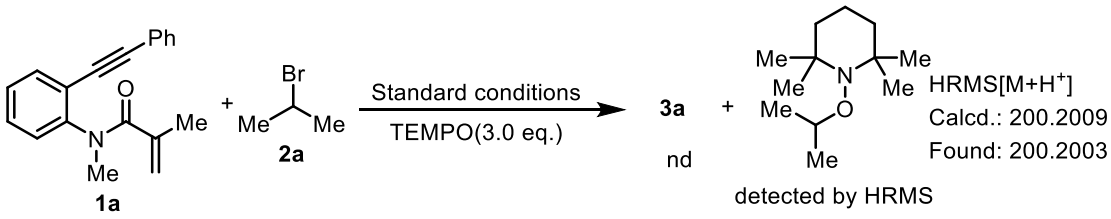
Crystal data for **3a**



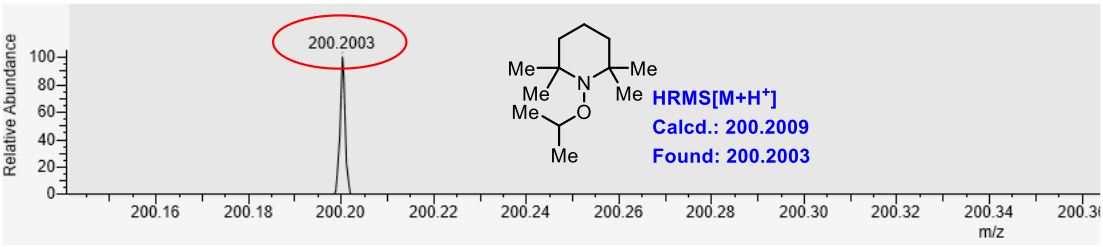
Identification code	**2259639** (CCDC number)
Empirical formula	$C_{22}H_{23}NO$
Formula weight	317.41
Temperature/K	193.00
Crystal system	tetragonal
Space group	I4
a/Å	19.4725(6)
b/Å	19.4725(6)
c/Å	9.2892(4)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	3522.3(3)
Z	8
ρ_{calc}g/cm^3	1.197
μ/mm^{-1}	0.361
F(000)	1360.0
Crystal size/mm^3	? × ? × ?
Radiation	GaKα (λ = 1.34139)
2Θ range for data collection/°	5.584 to 108.088
Index ranges	-21 ≤ h ≤ 23, -21 ≤ k ≤ 23, -10 ≤ l ≤ 11
Reflections collected	11057
Independent reflections	3197 [R_{int} = 0.0387, R_{sigma} = 0.0358]
Data/restraints/parameters	3197/1/221
Goodness-of-fit on F^2	1.065

Final R indexes [I>=2σ (I)]	R_1 = 0.0327, wR_2 = 0.0742
Final R indexes [all data]	R_1 = 0.0369, wR_2 = 0.0764
Largest diff. peak/hole / e Å^{-3}	0.15/-0.14
Flack parameter	0.04(17)
O1 C21 1.224(2)	C16 C15 1.383(3)
N1 C19 1.418(2)	C16 C17 1.377(3)
N1 C21 1.373(3)	C19 C18 1.393(3)
N1 C20 1.463(3)	C1 C2 1.387(3)
C6 C7 1.481(3)	C21 C12 1.521(3)
C6 C5 1.389(3)	C11 C8 1.547(3)
C6 C1 1.392(3)	C11 C12 1.533(3)
C14 C13 1.463(2)	C8 C9 1.529(3)
C14 C19 1.413(3)	C8 C10 1.528(3)
C14 C15 1.388(3)	C12 C22 1.537(3)
C7 C13 1.336(3)	C4 C3 1.378(3)
C7 C8 1.533(3)	C2 C3 1.373(4)
C13 C12 1.508(2)	C17 C18 1.378(3)
C5 C4 1.385(3)	

6. Radical inhibition experiment

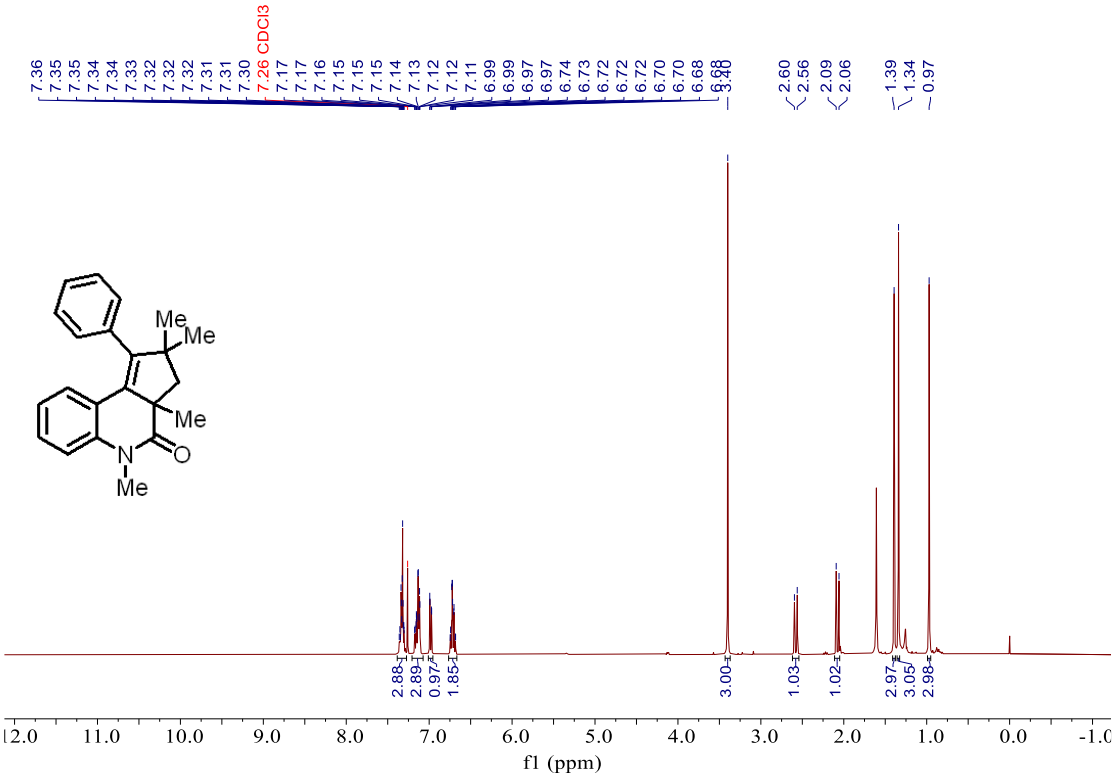


To an over-dried steal tube, N-methyl-N-(2-(phenylethynyl)phenyl)methacrylamide (**1a**) (0.1 mmol), $[Au(dcpm)Cl]_2$ (2 mol%), HCO_2H (0.2 mmol), DIPA (0.2 mmol), 2-bromopropane (**2a**) (0.3 mmol), 2,2,6,6-tetramethyl-1-piperinedinyloxy(TEMPO) (0.3 mmol) and MeCN (1 mL) were added sequentially under N_2 atmosphere. The resulting mixture was stirred at ambient temperature under the irradiation of blue LEDs for 22 h. After the reaction finished, the reaction mixture was analyzed by HRMS. There was no product **3a** detected. But the alkyl radical generated by **2a** can be trapped by TEMPO and detected by HRMS clearly. The results indicate that this reaction might be carried out through a radical mechanism.

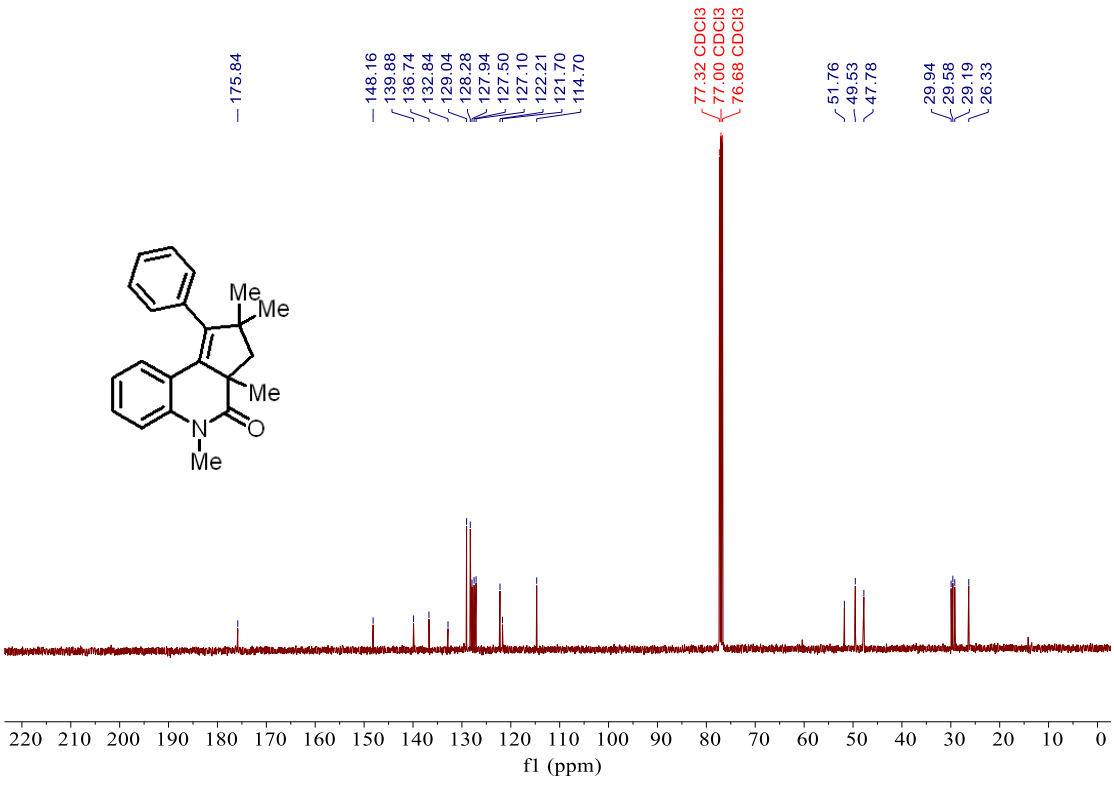


Supplementary Figure 1. HRMS data of the reaction mixture

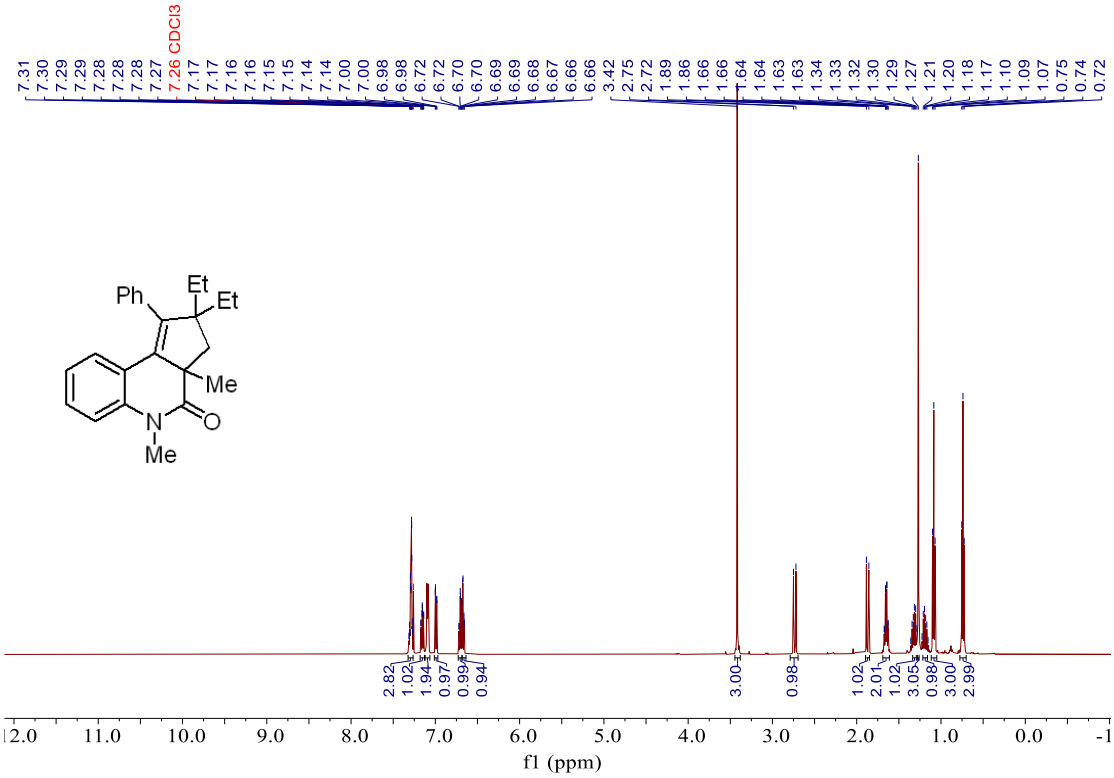
7. Copies of NMR Spectra



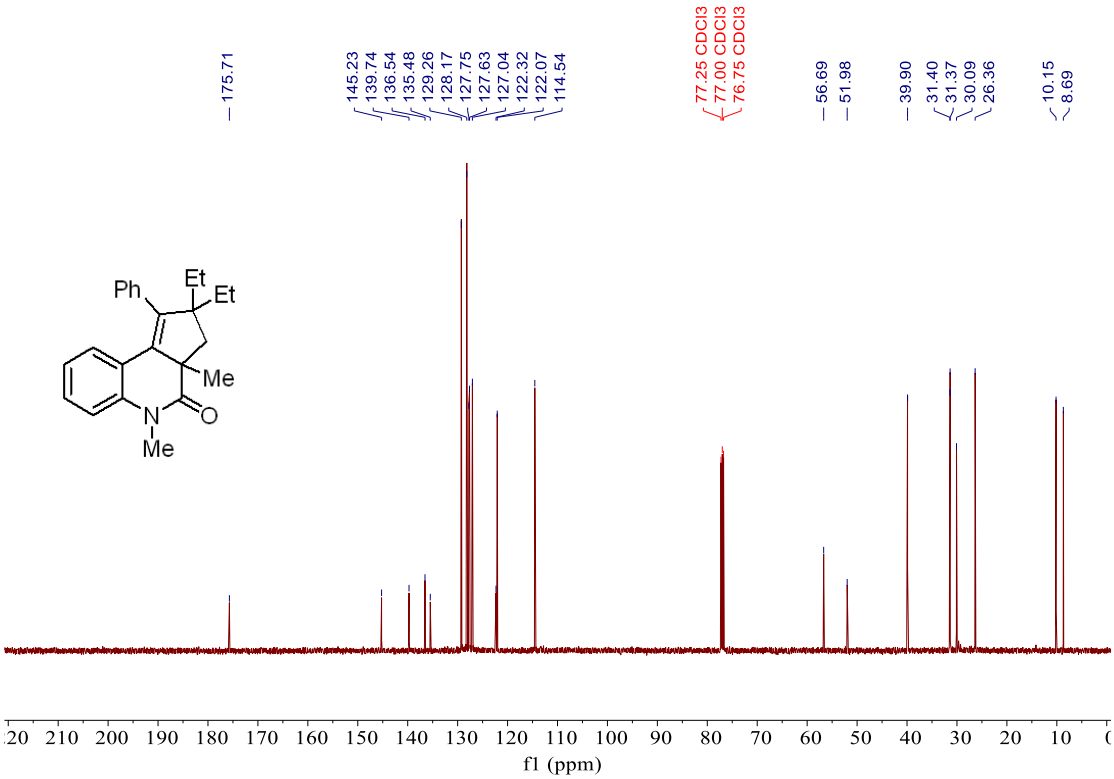
Supplementary Figure 2. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3a**



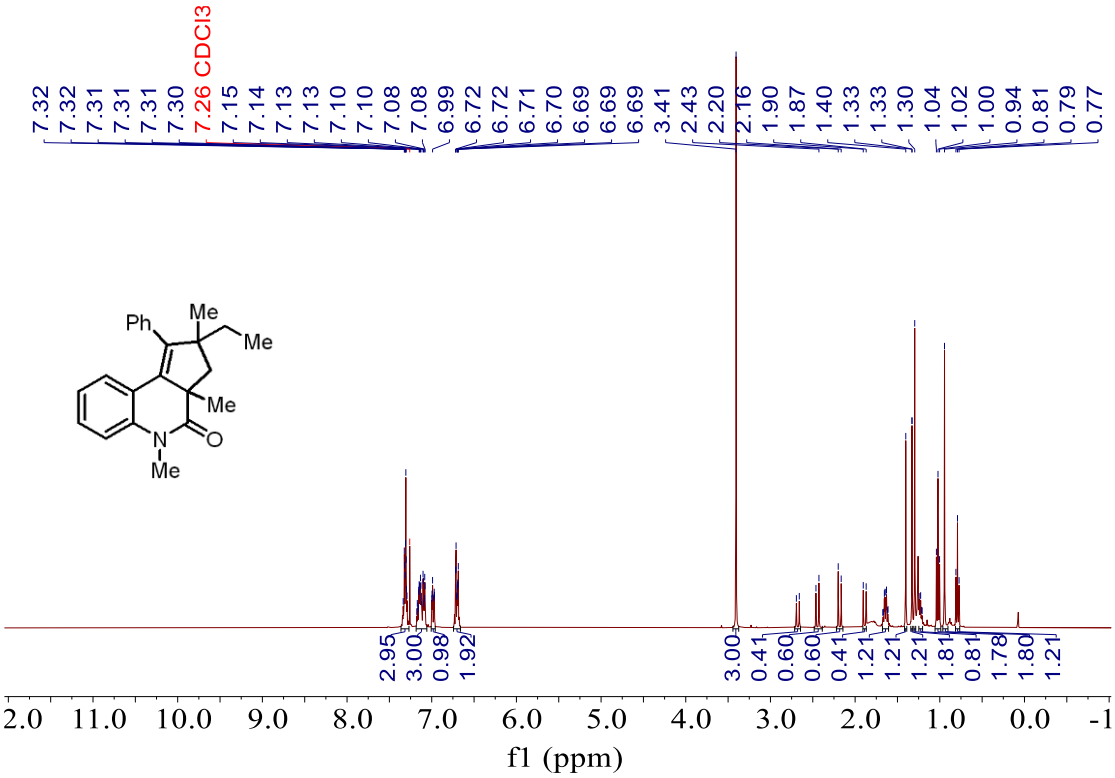
Supplementary Figure 3. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3a**



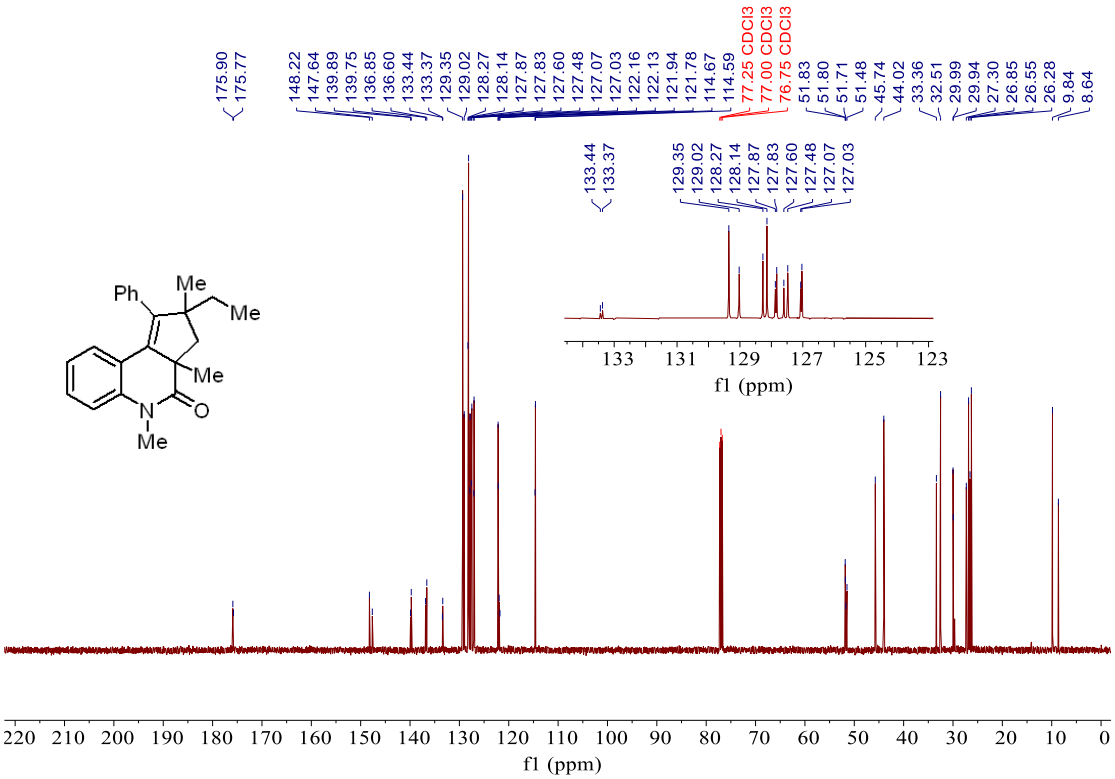
Supplementary Figure 4. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3b**



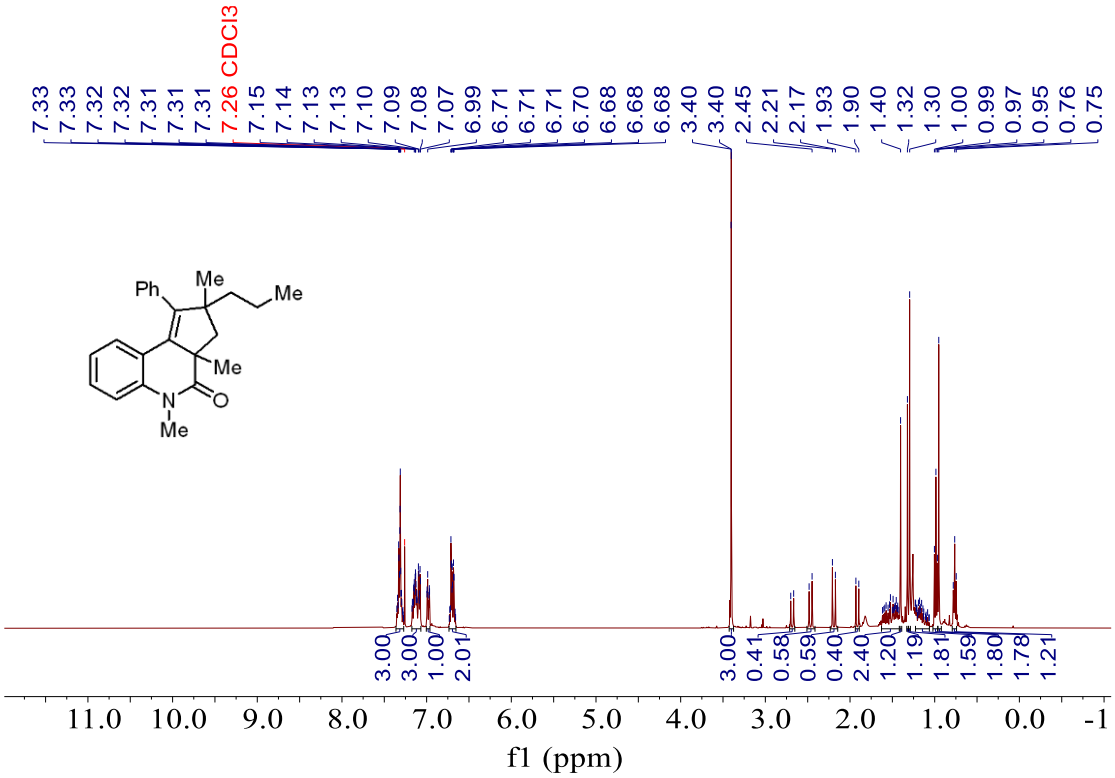
Supplementary Figure 5. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3b**



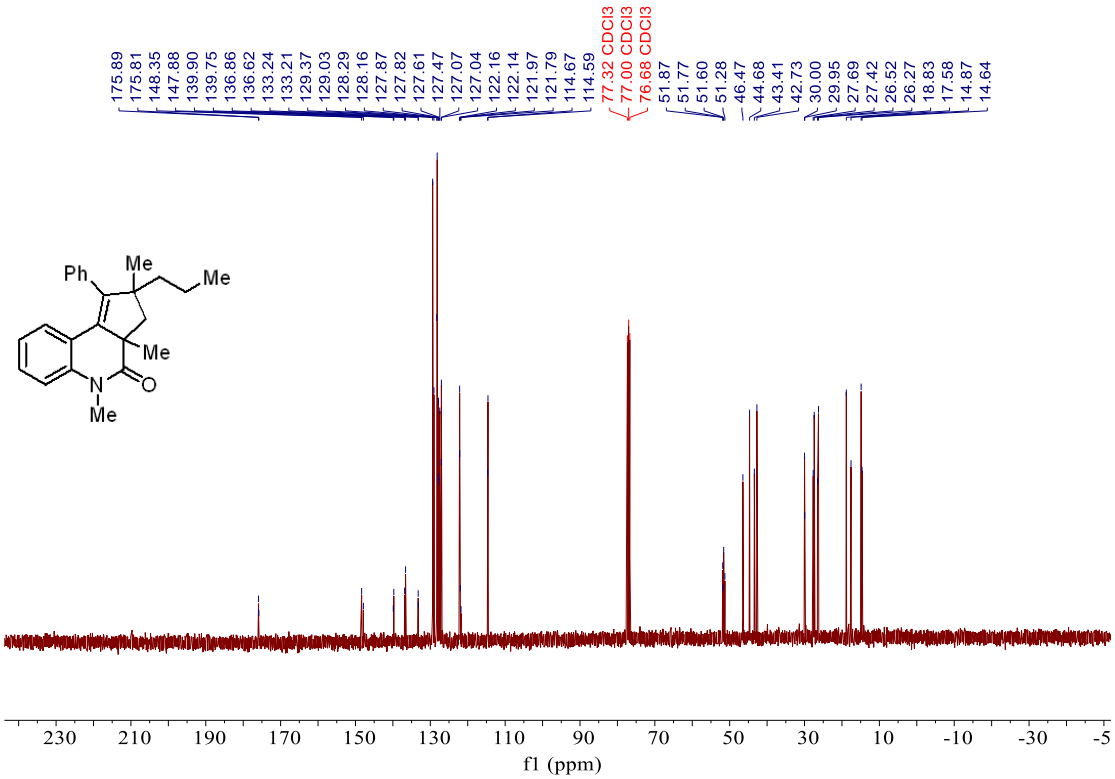
Supplementary Figure 6. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3c**



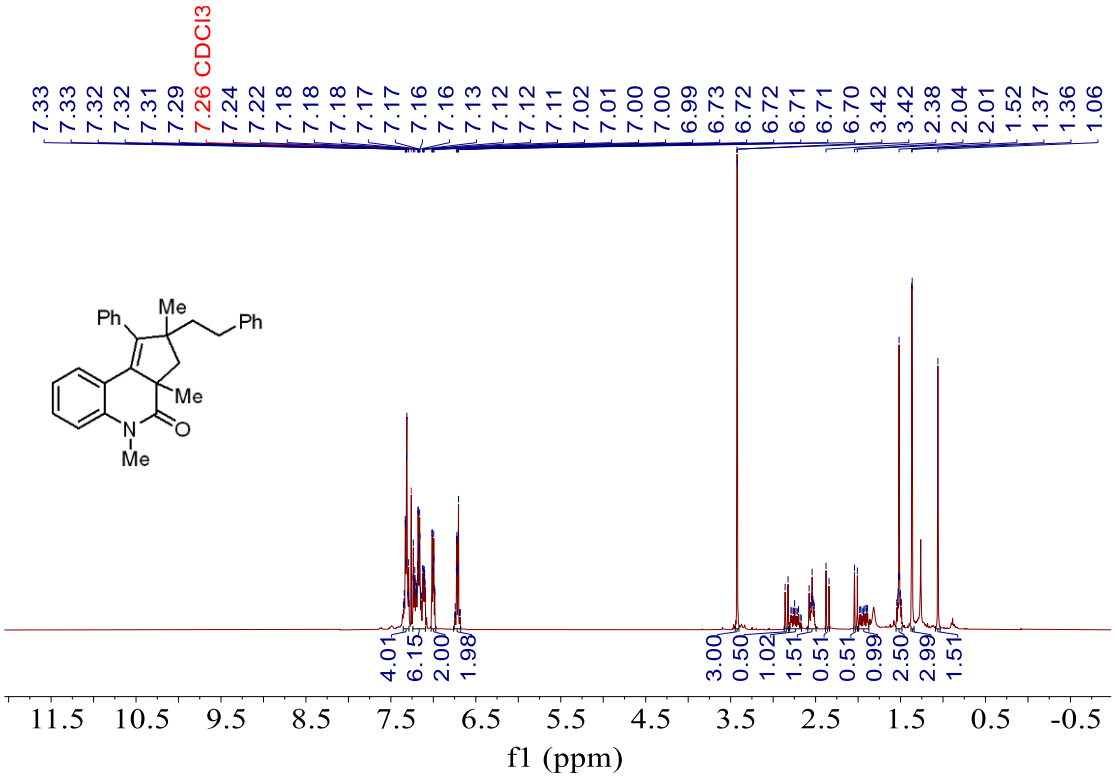
Supplementary Figure 7. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3c**



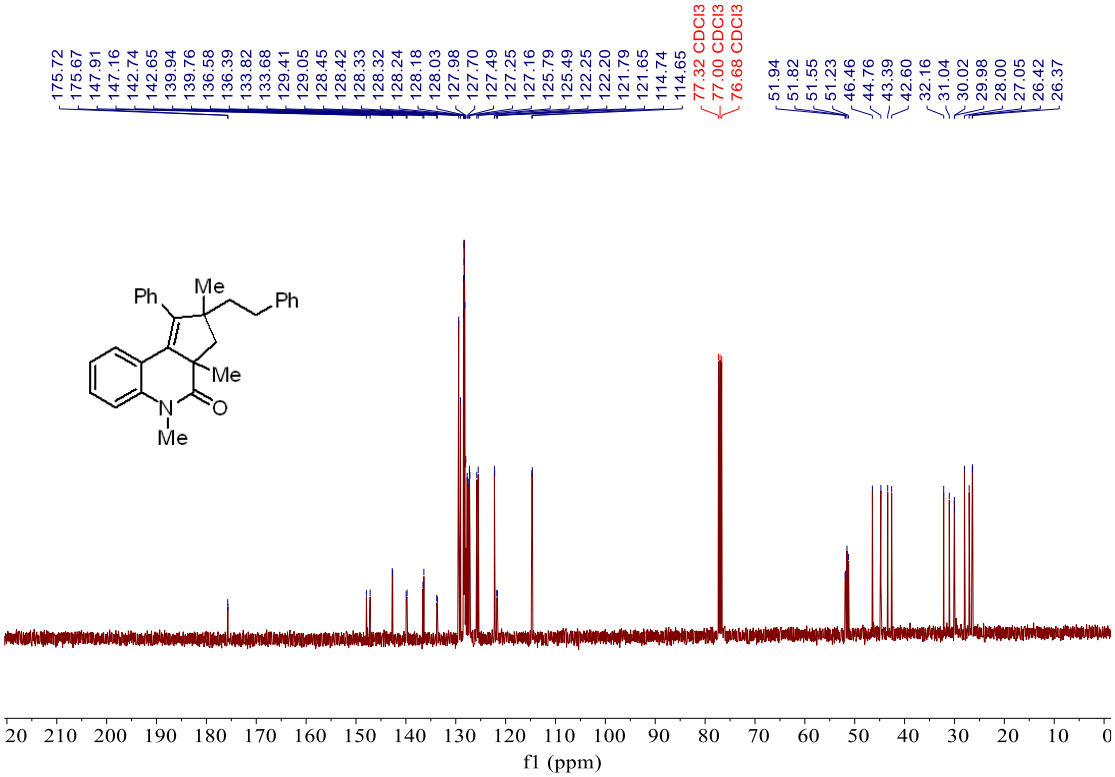
Supplementary Figure 8. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3d**



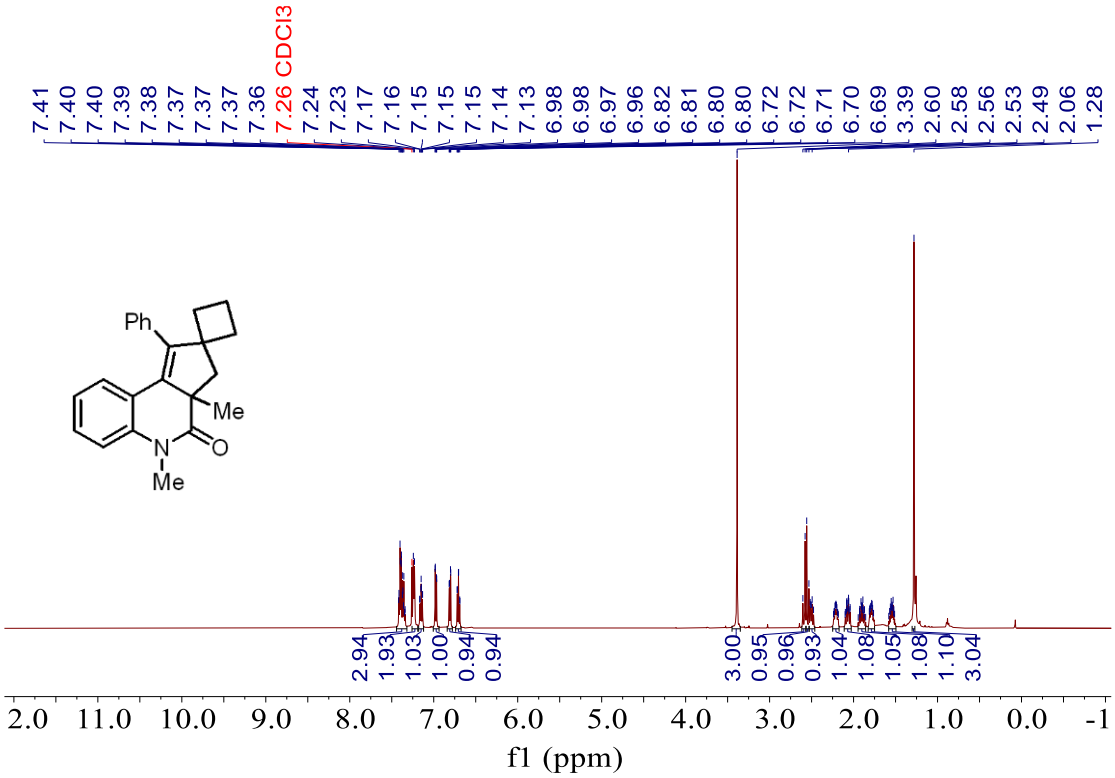
Supplementary Figure 9. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3d**



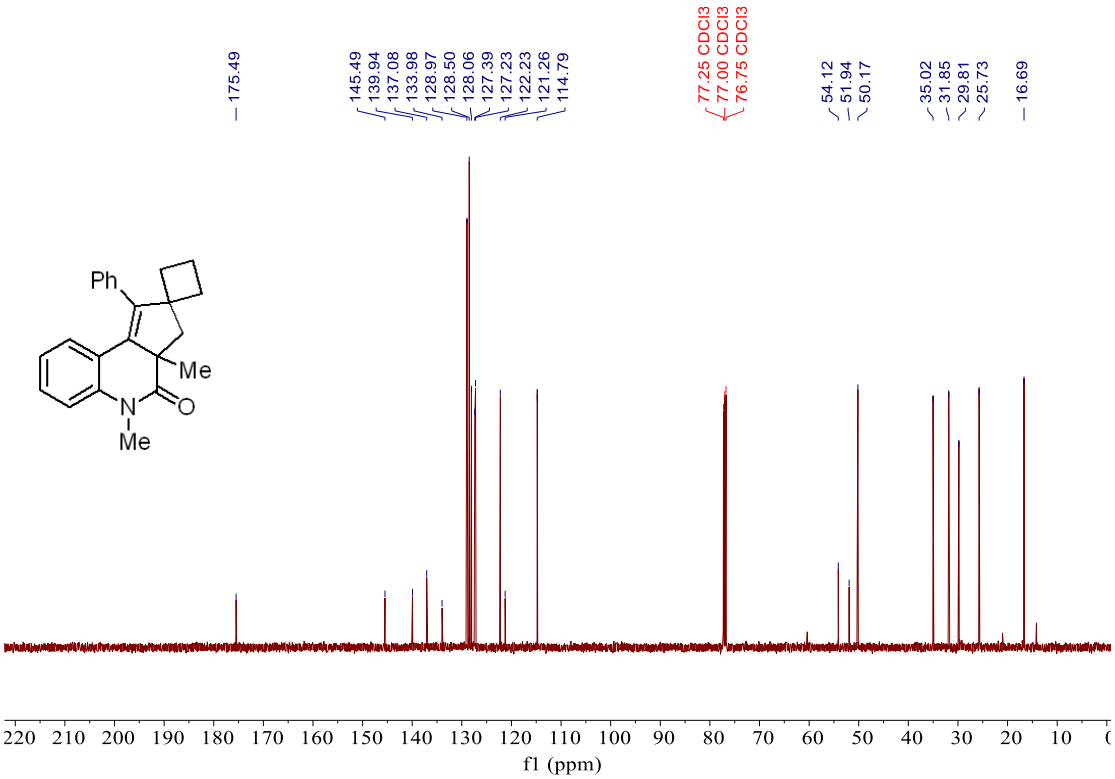
Supplementary Figure 10. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3e**



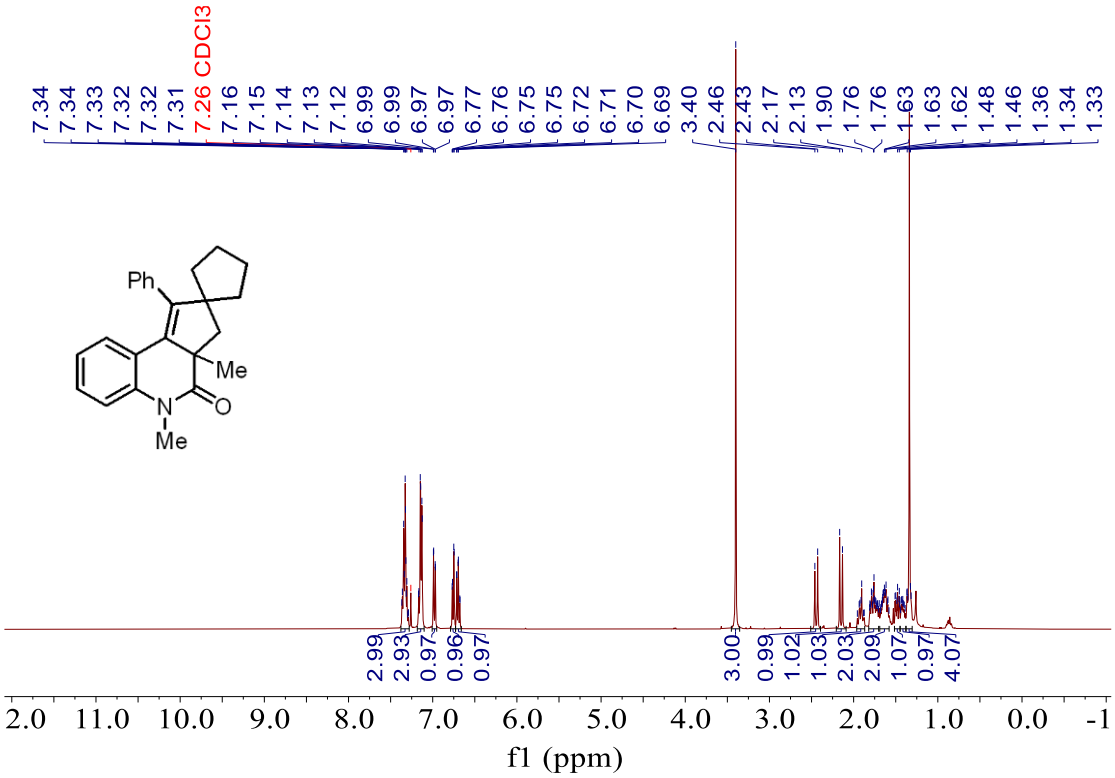
Supplementary Figure 11. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3e**



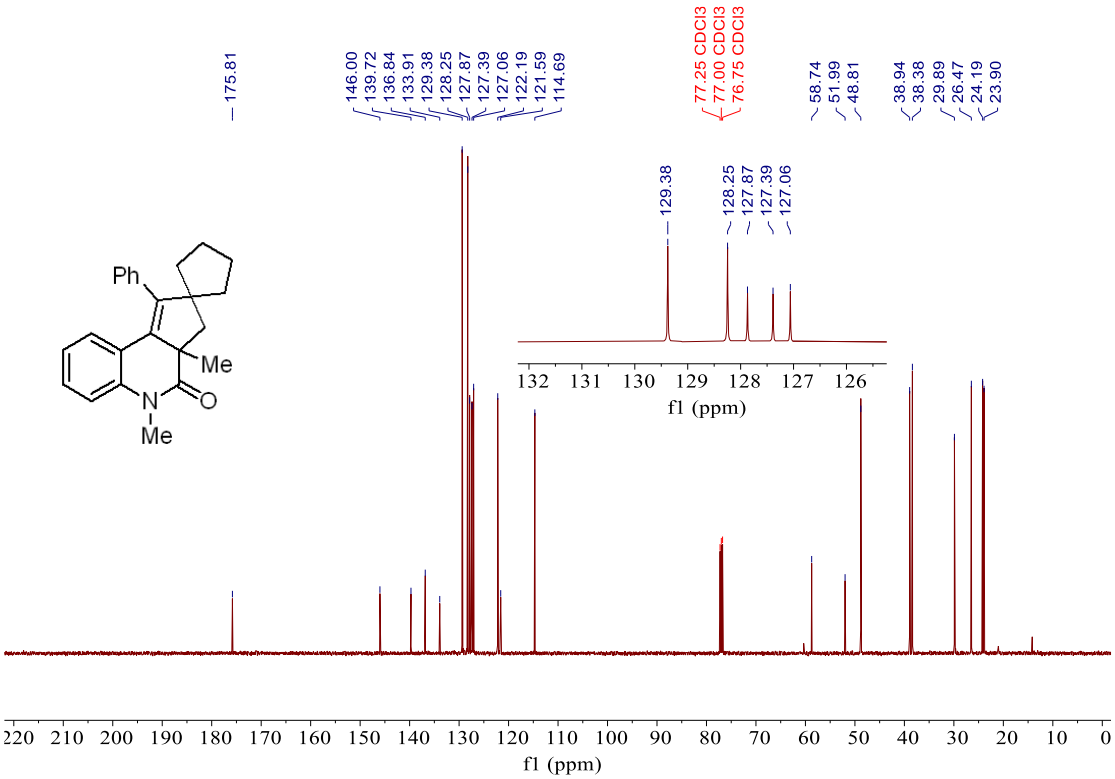
Supplementary Figure 12. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3f**



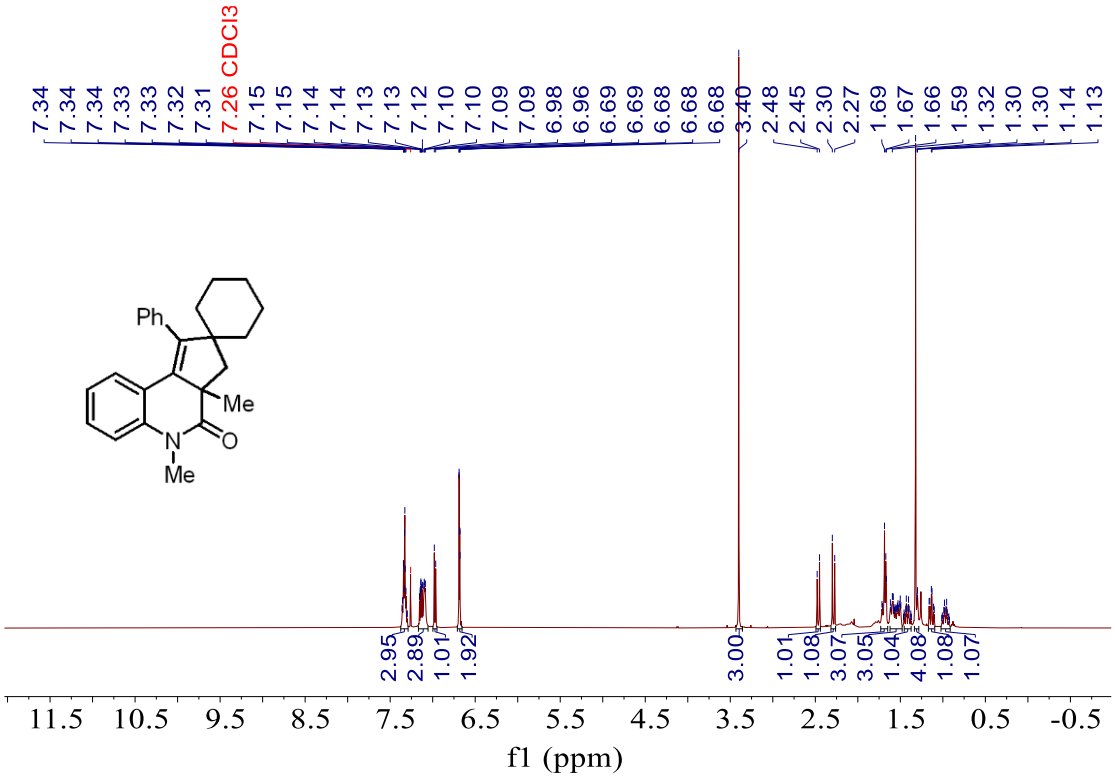
Supplementary Figure 13. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3f**



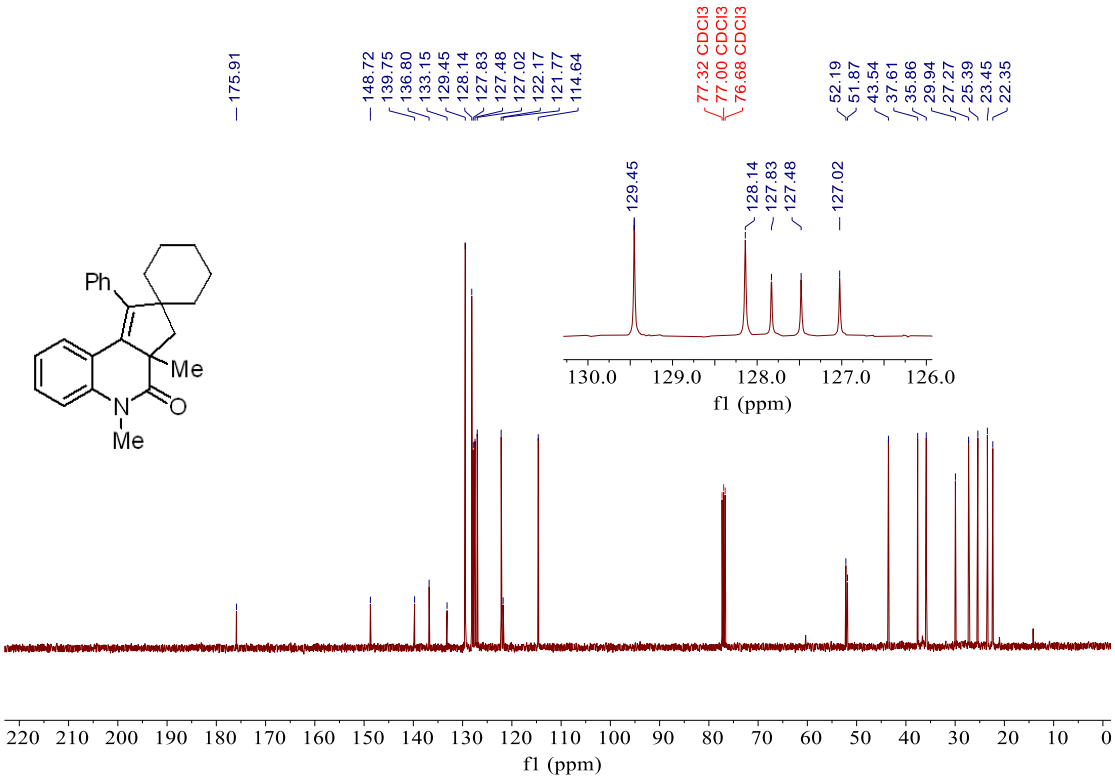
Supplementary Figure 14. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3g**



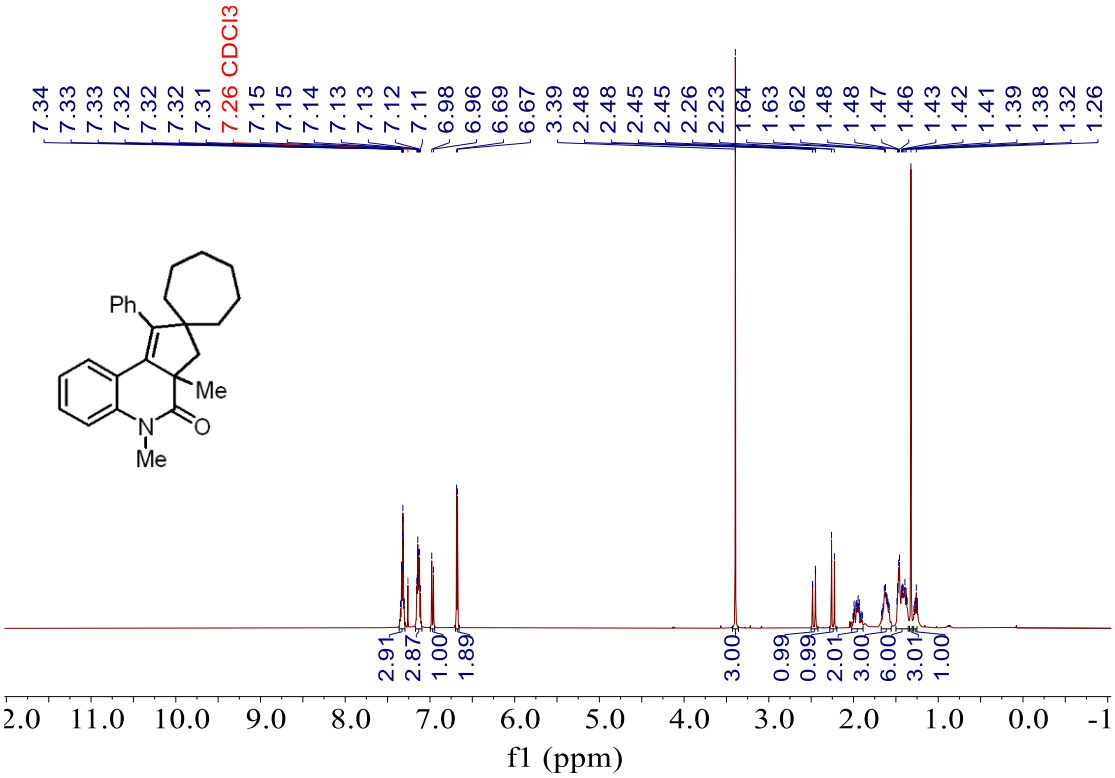
Supplementary Figure 15. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3g**



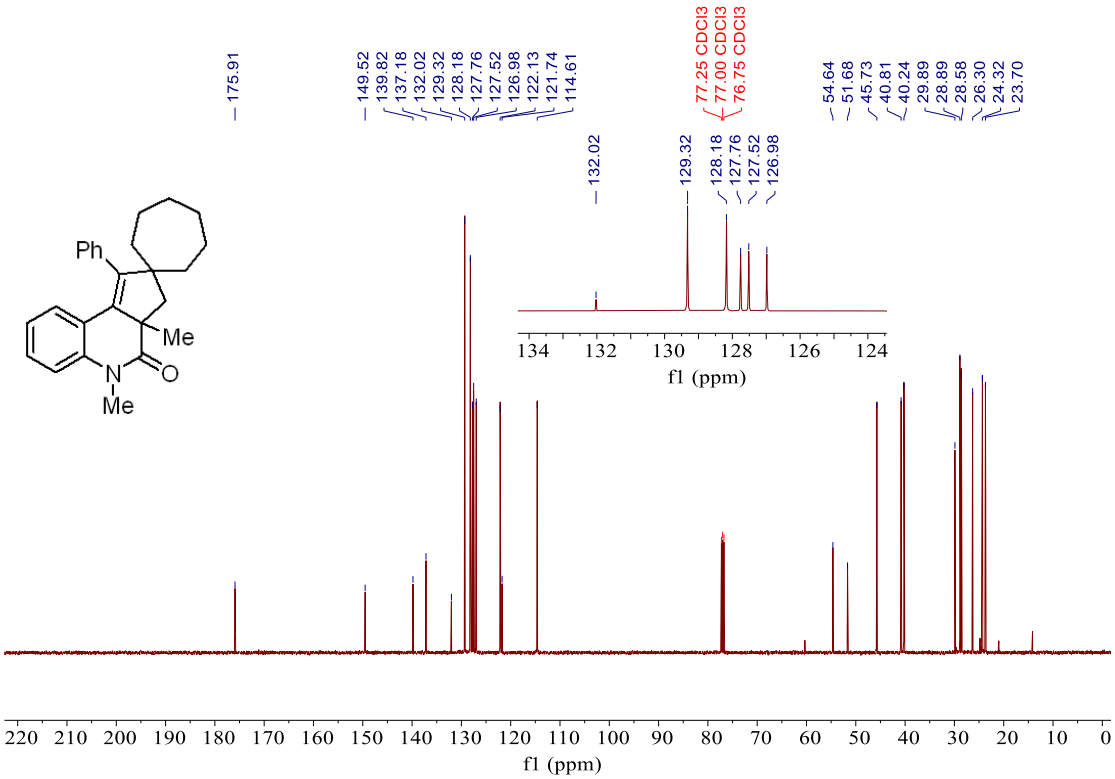
Supplementary Figure 16. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3h**



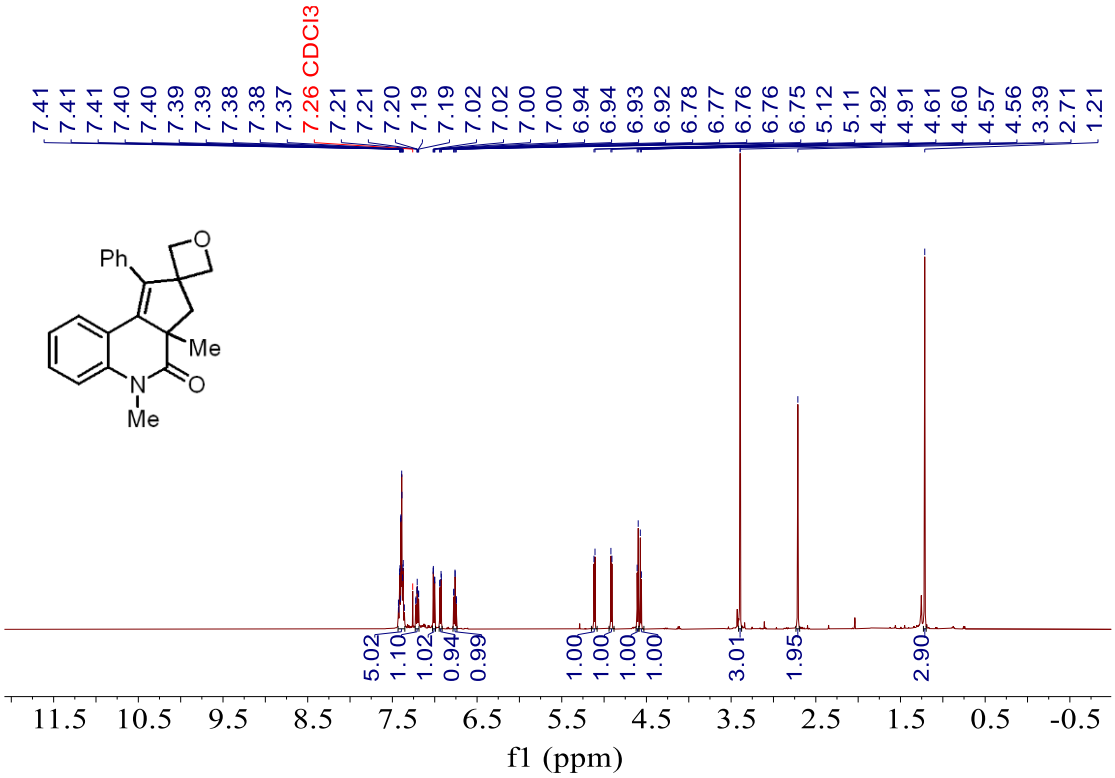
Supplementary Figure 17. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3h**



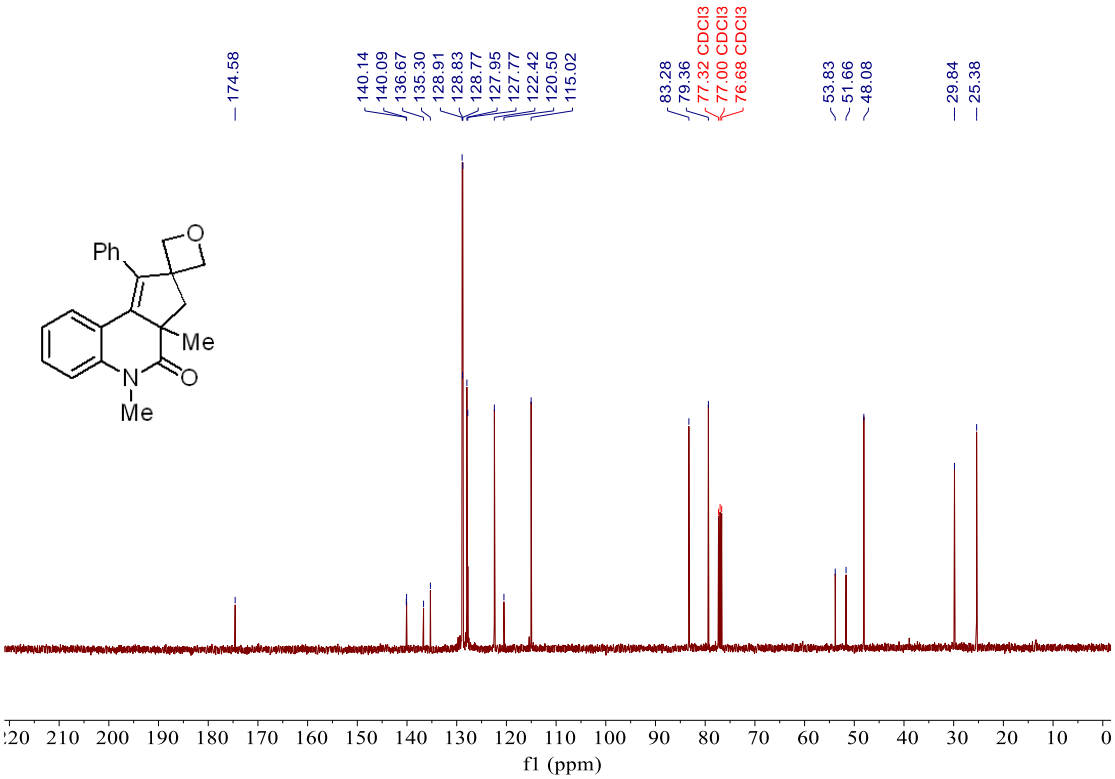
Supplementary Figure 18. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3i**



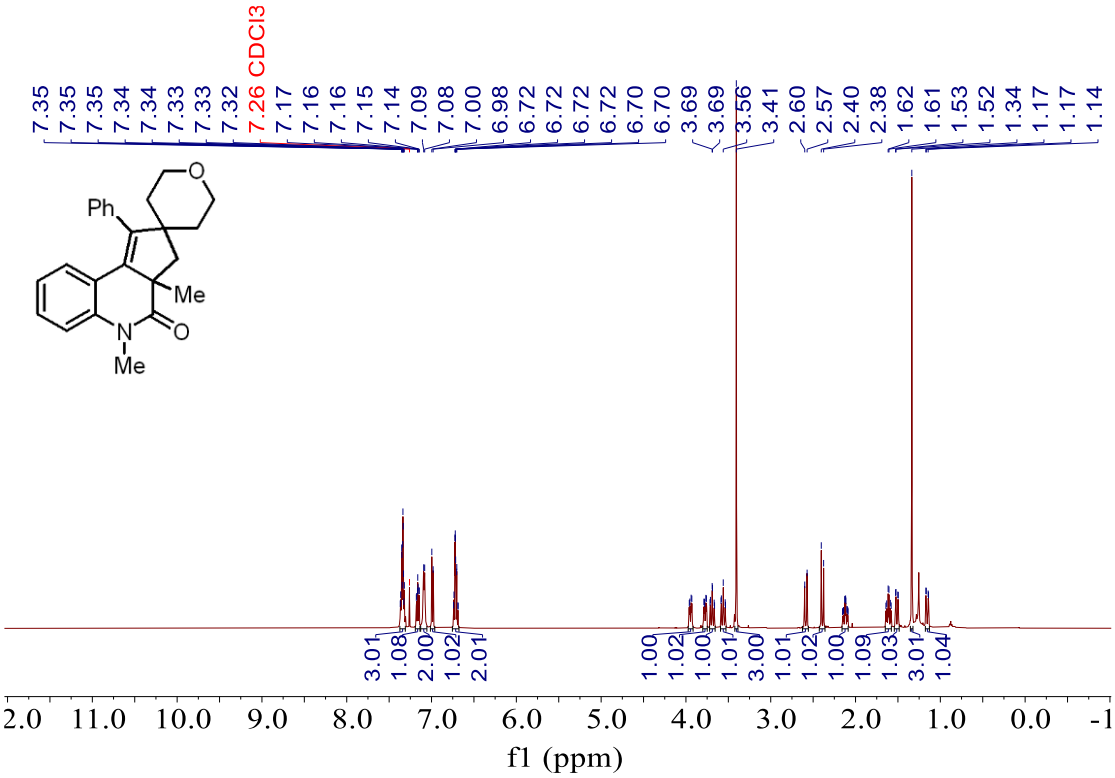
Supplementary Figure 19. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3i**



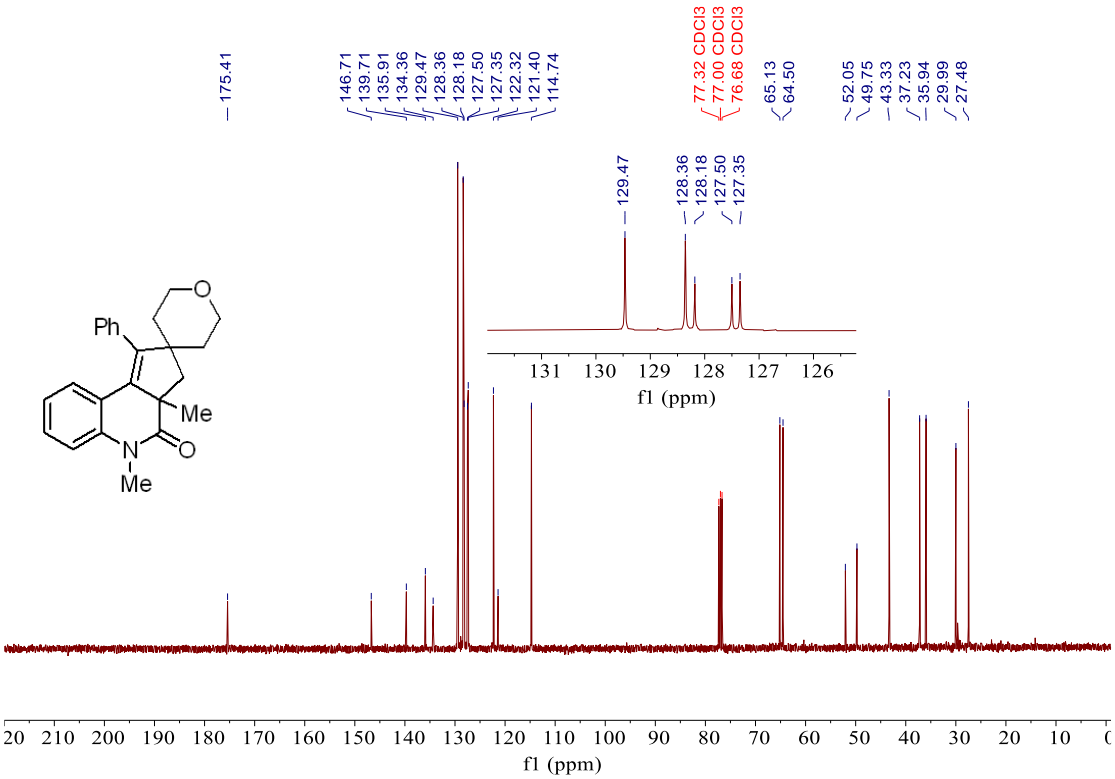
Supplementary Figure 20. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3j**



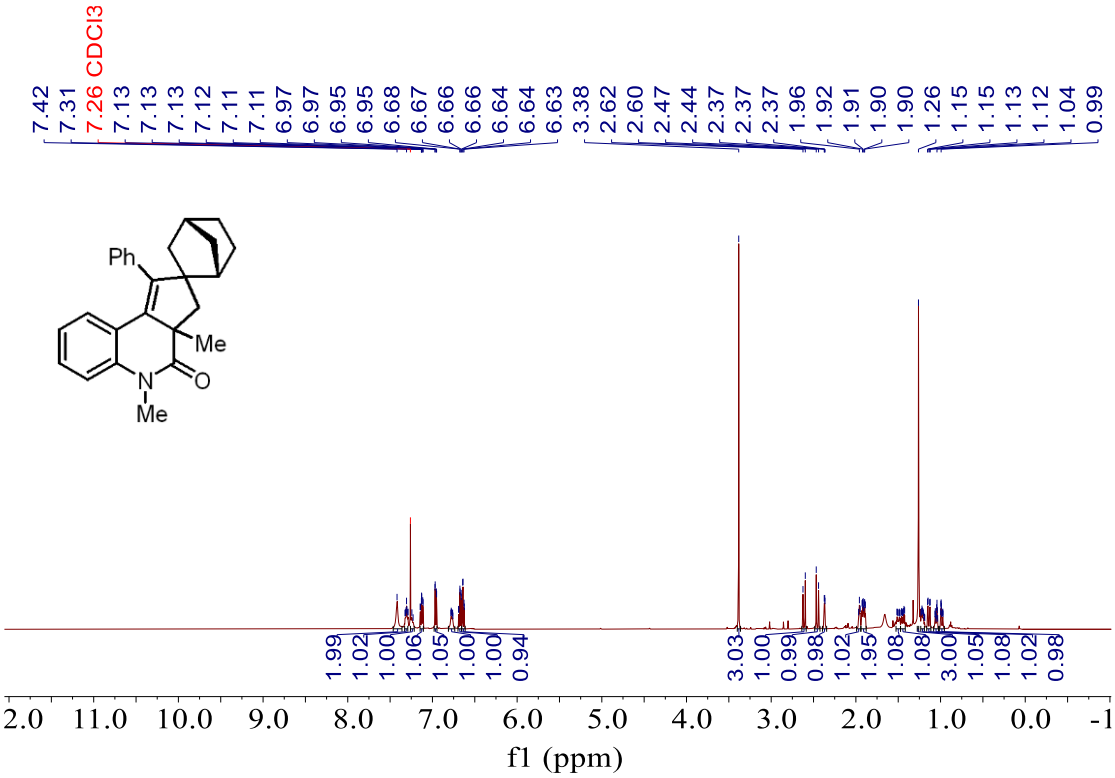
Supplementary Figure 21. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3j**



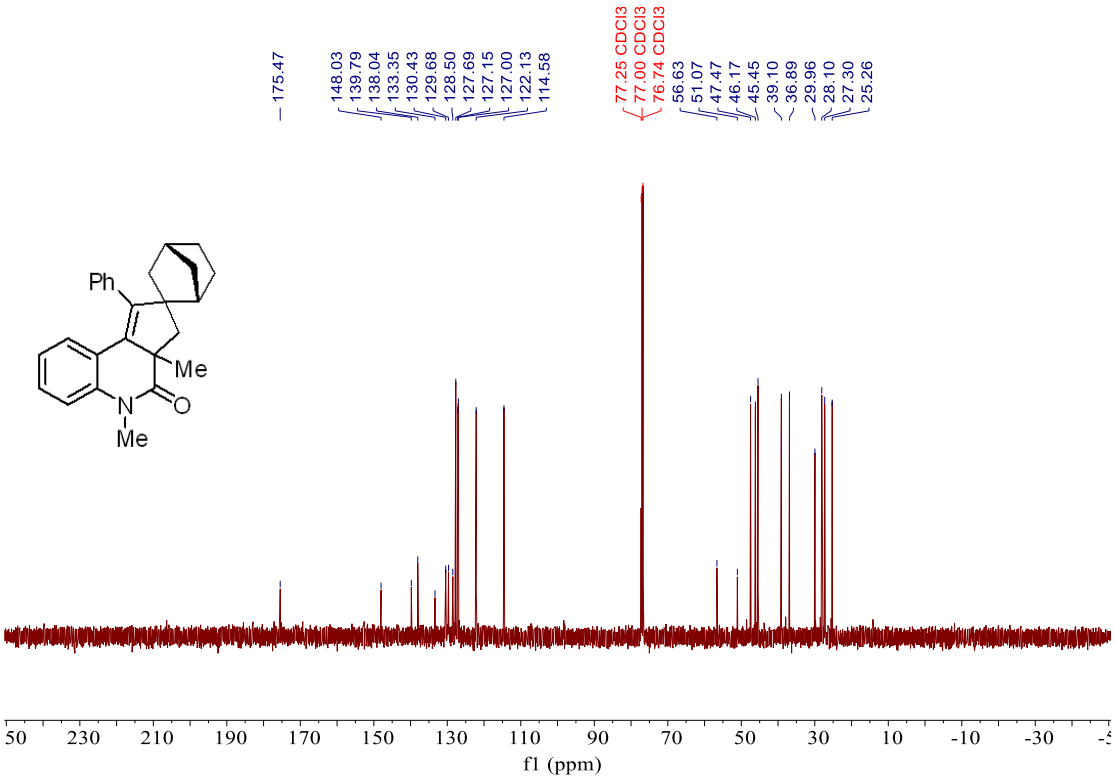
Supplementary Figure 22. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3k**



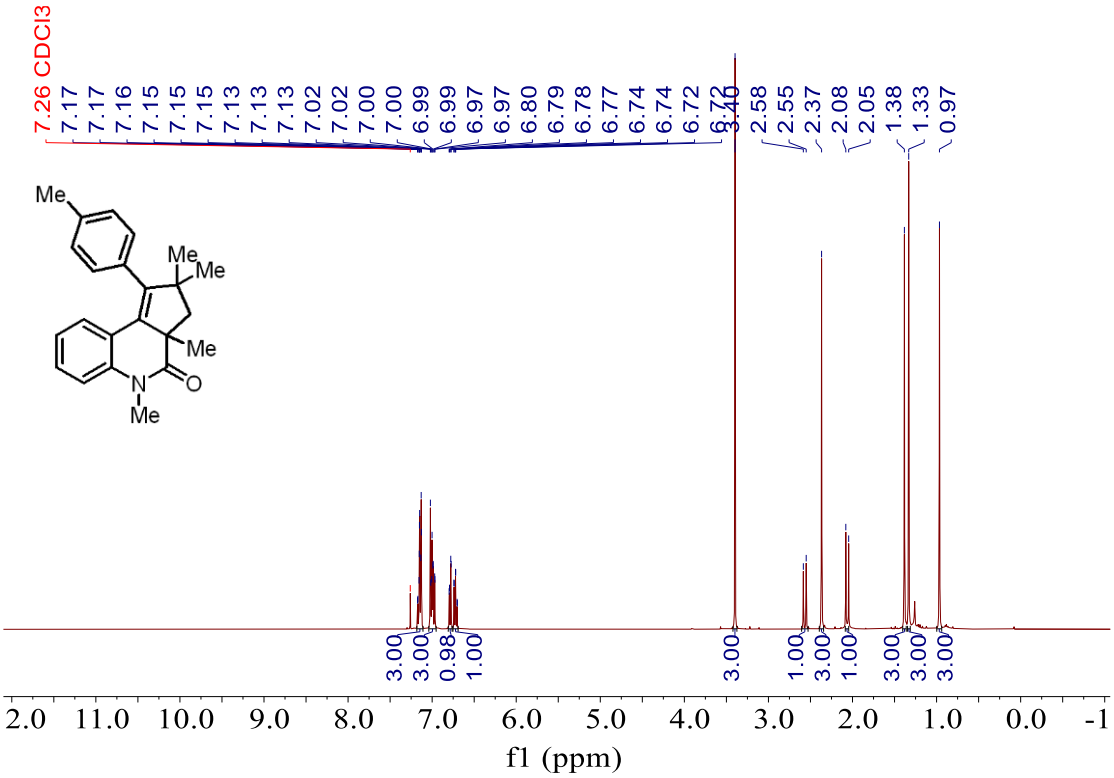
Supplementary Figure 23. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3k**



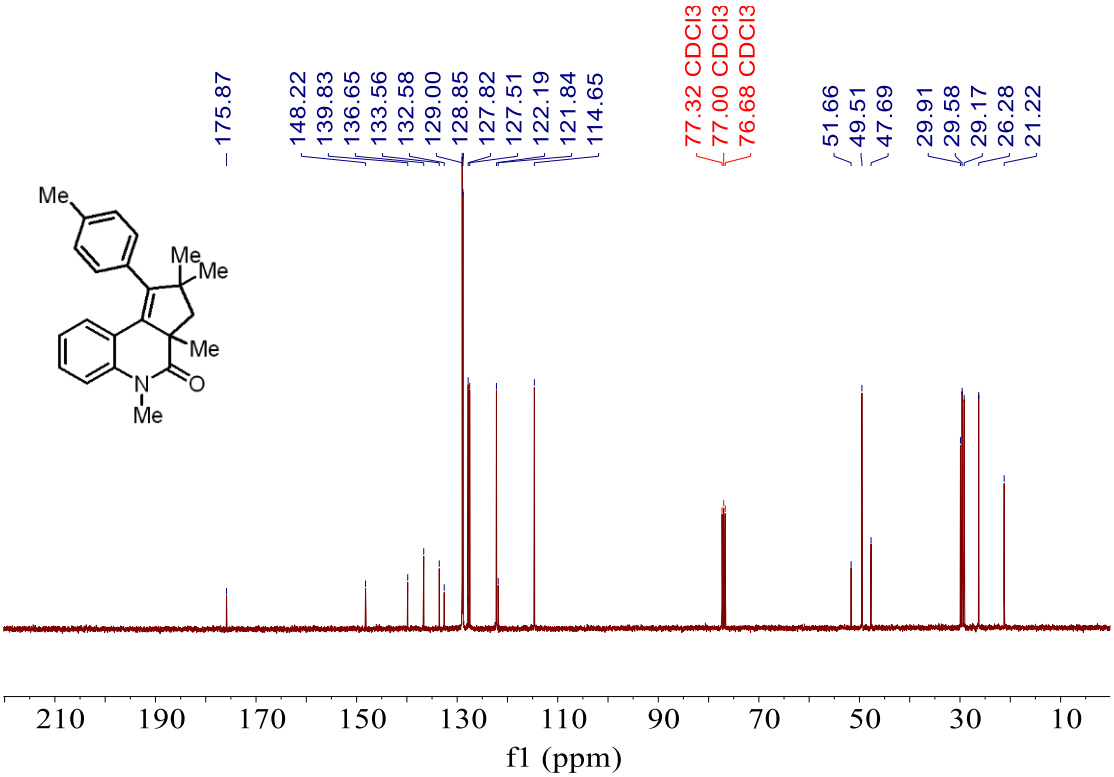
Supplementary Figure 24. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3l**



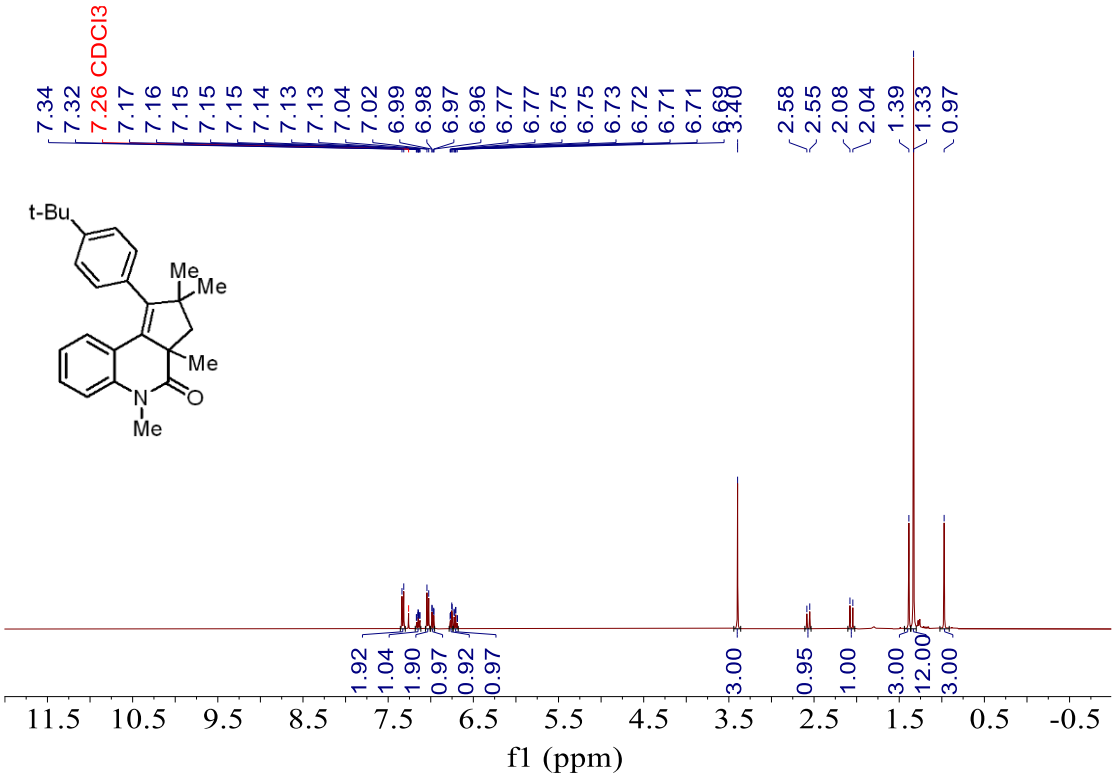
Supplementary Figure 25. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3l**



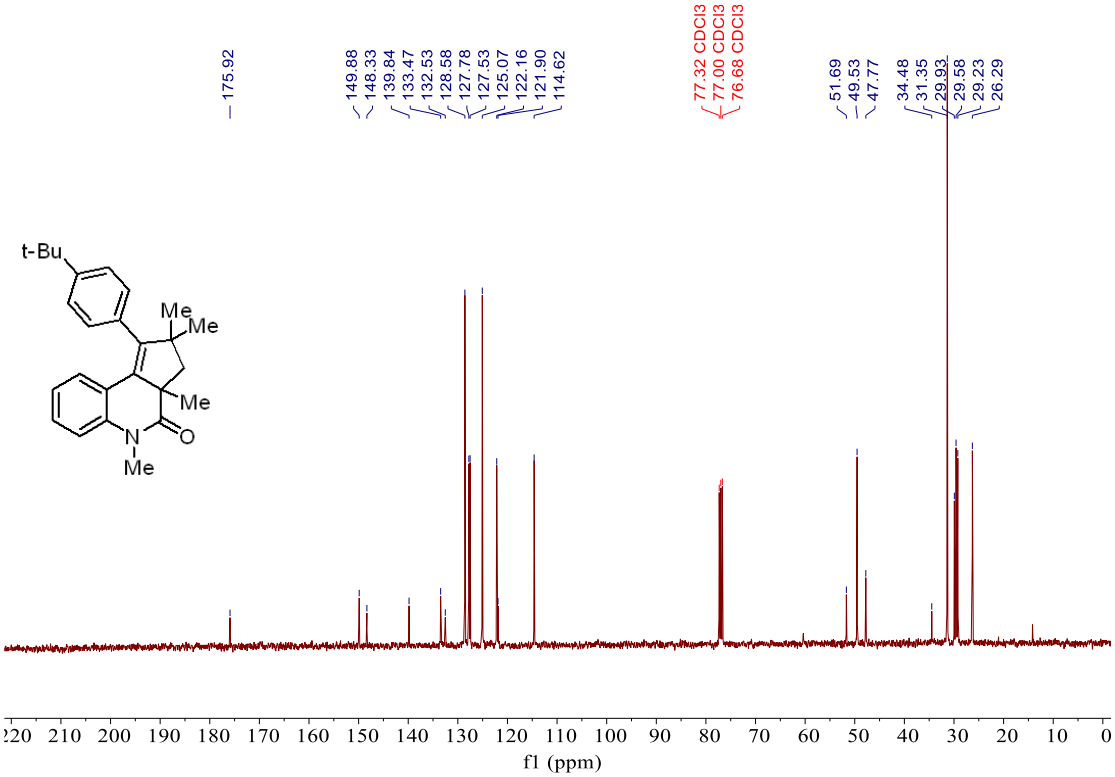
Supplementary Figure 26. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3m**



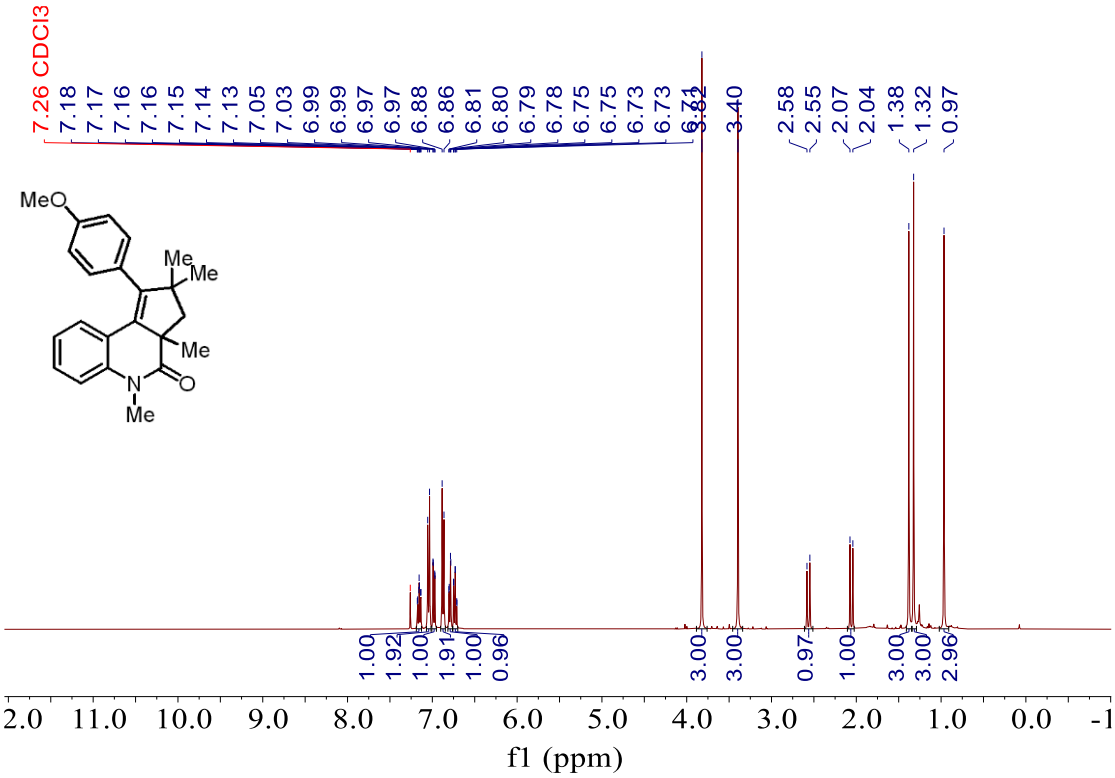
Supplementary Figure 27. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3m**



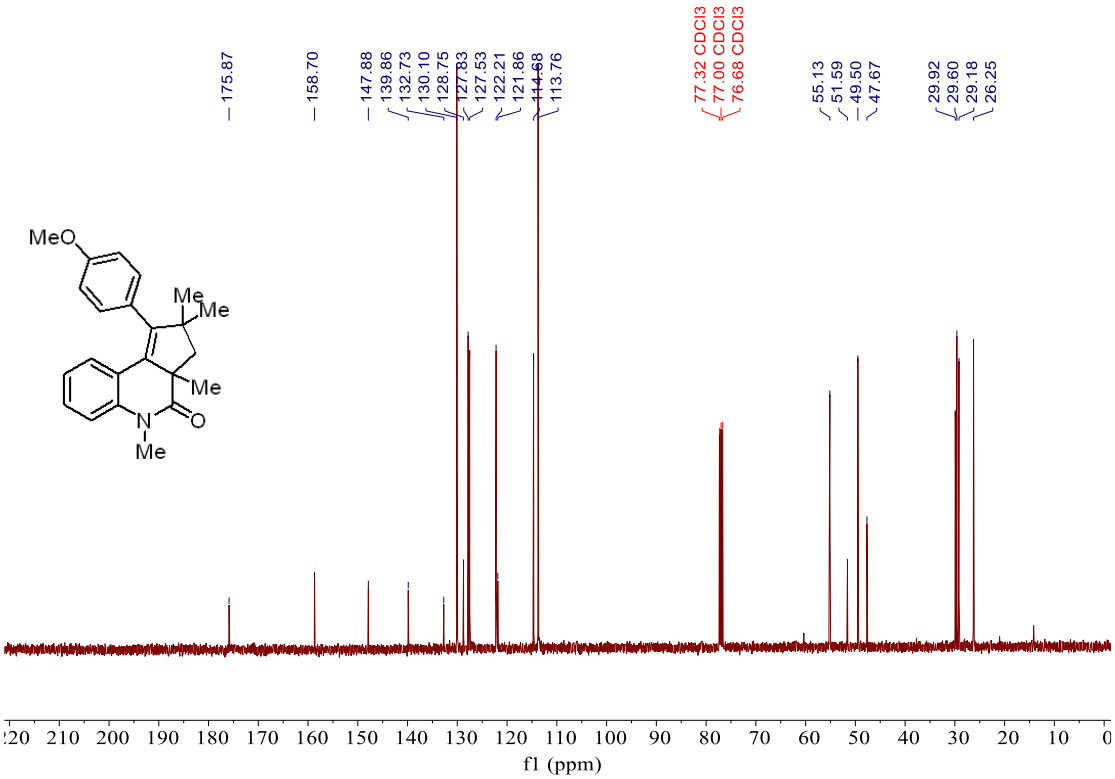
Supplementary Figure 28. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3n**



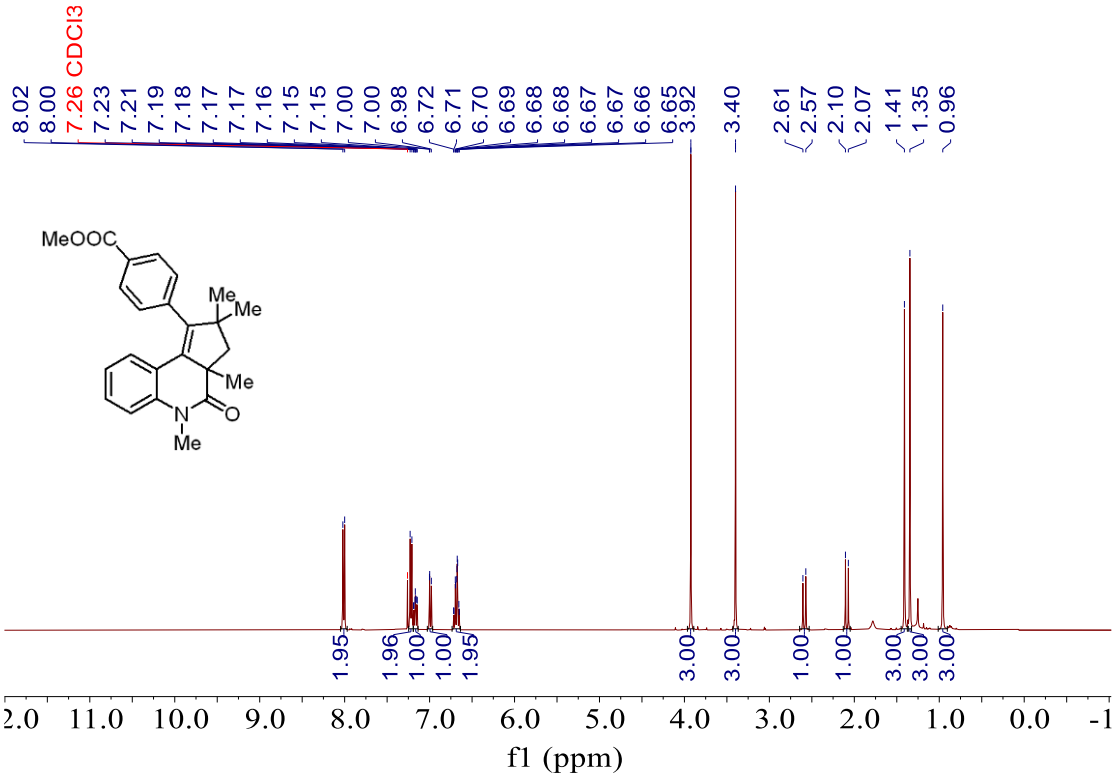
Supplementary Figure 29. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3n**



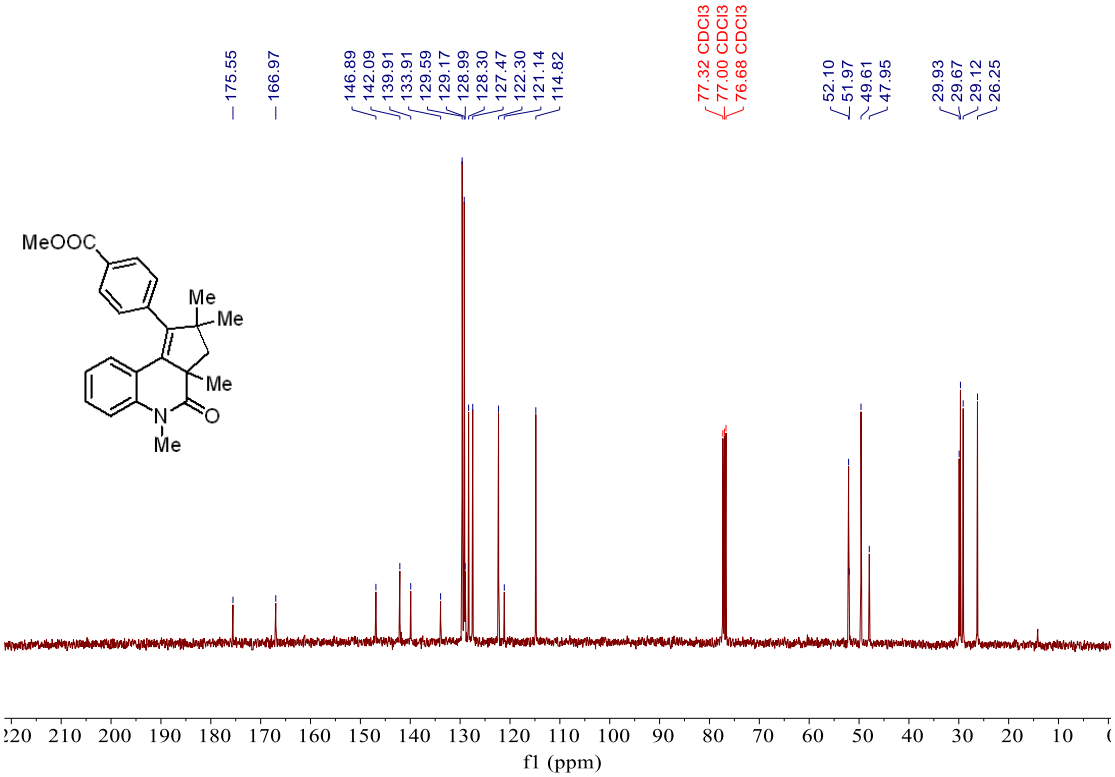
Supplementary Figure 30. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3o**



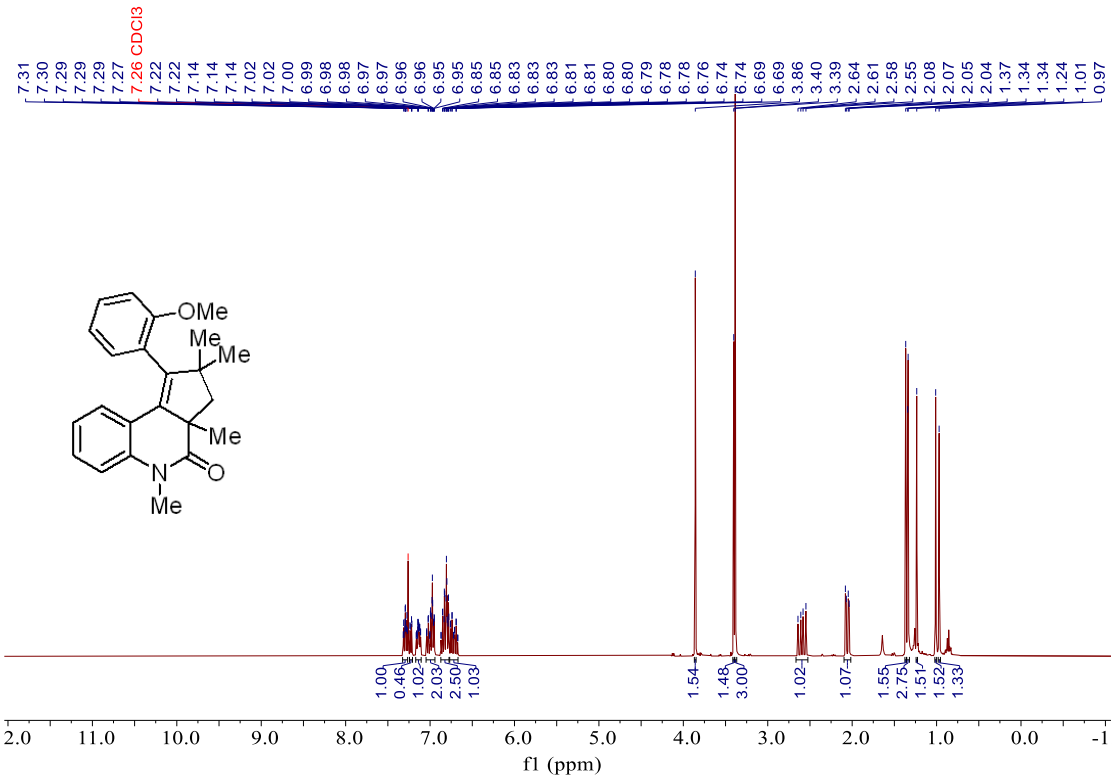
Supplementary Figure 31. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3o**



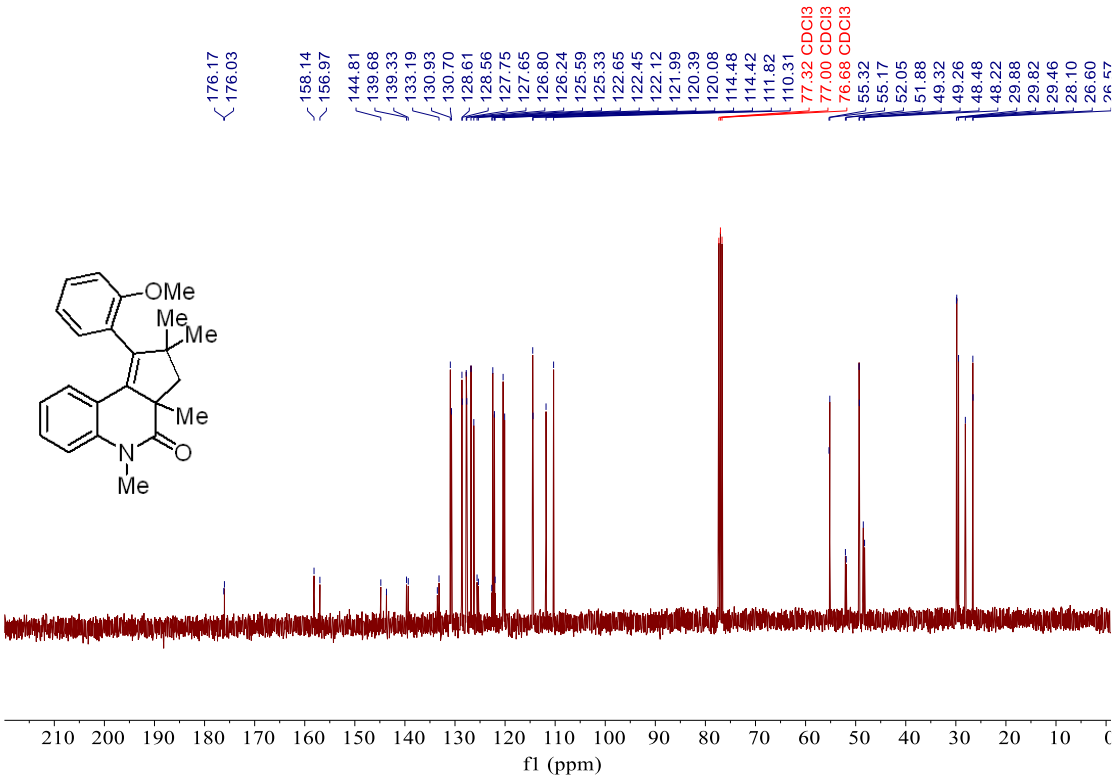
Supplementary Figure 32. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3p**



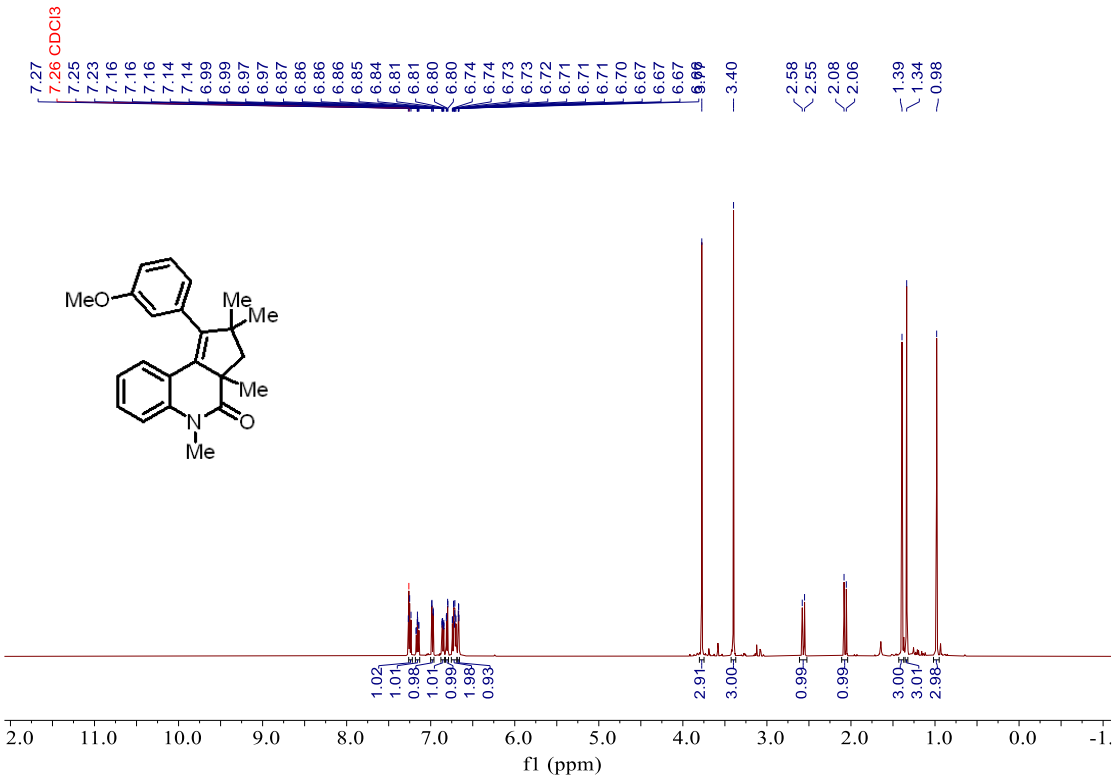
Supplementary Figure 33. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3p**



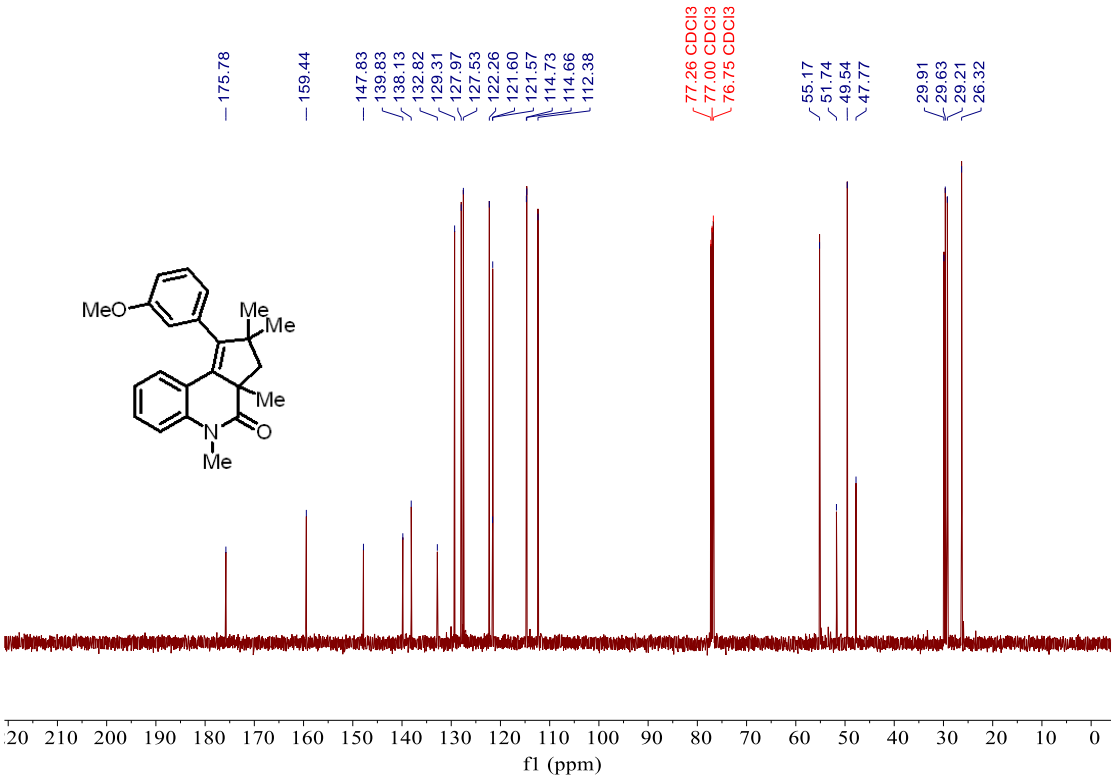
Supplementary Figure 34. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3q**



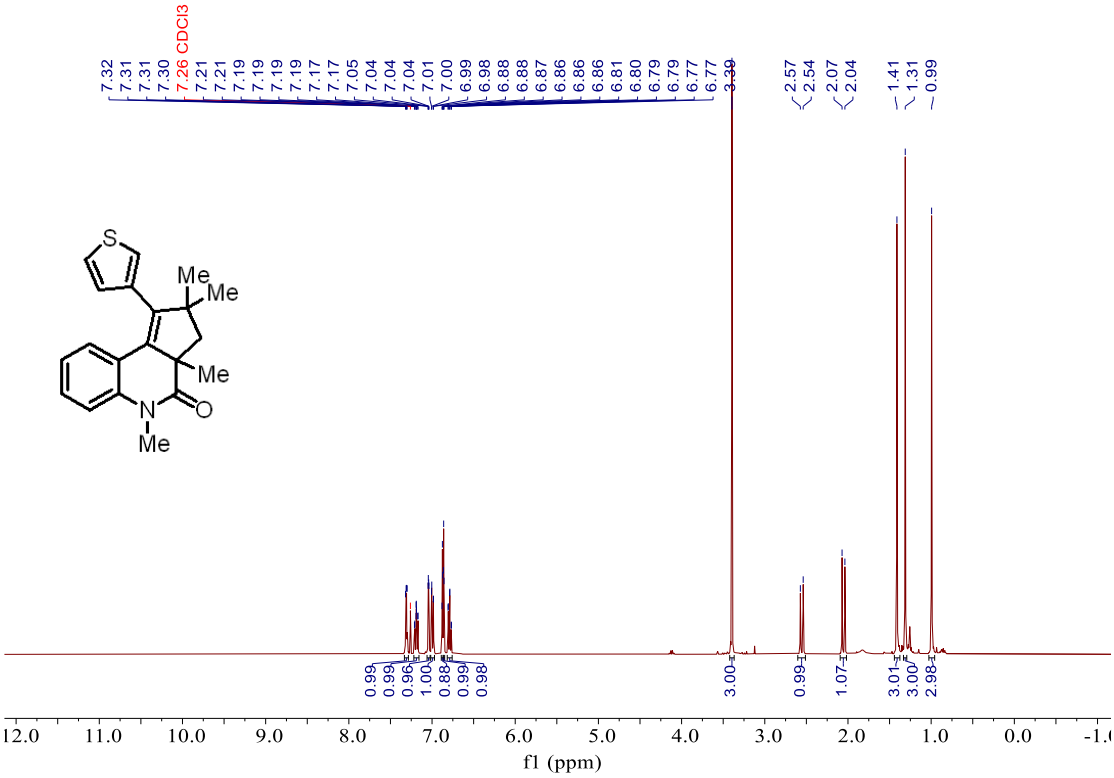
Supplementary Figure 35. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3q**



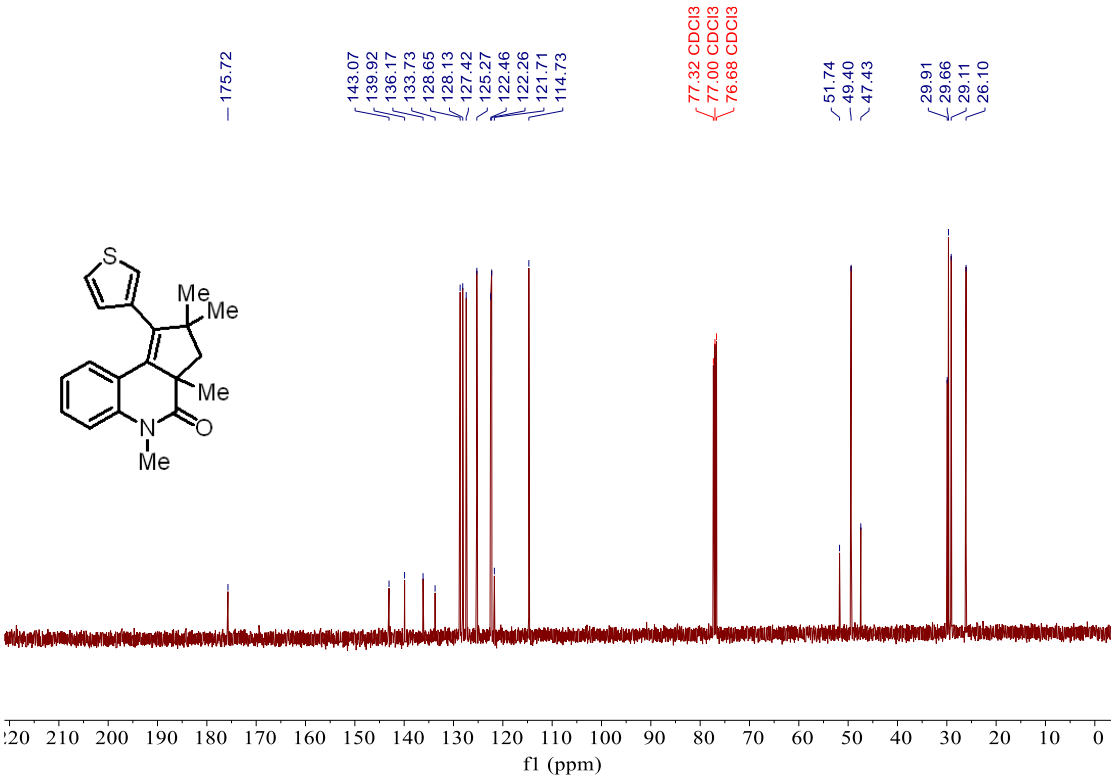
Supplementary Figure 36. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3r**



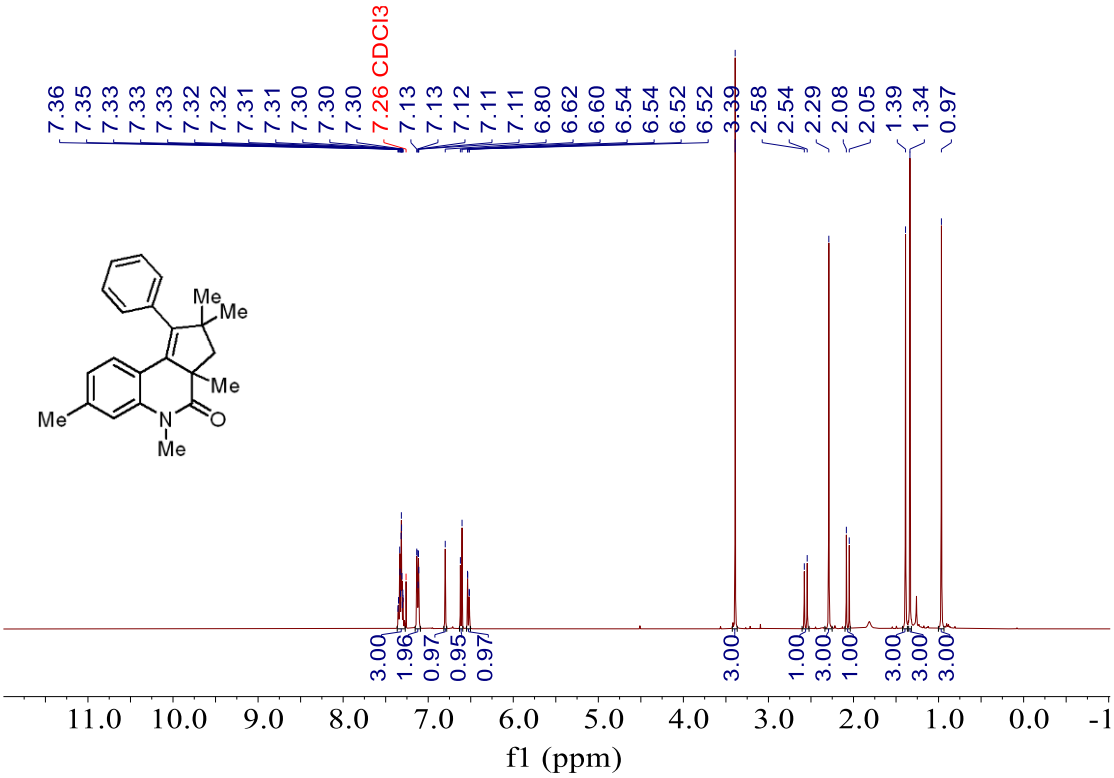
Supplementary Figure 37. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3r**



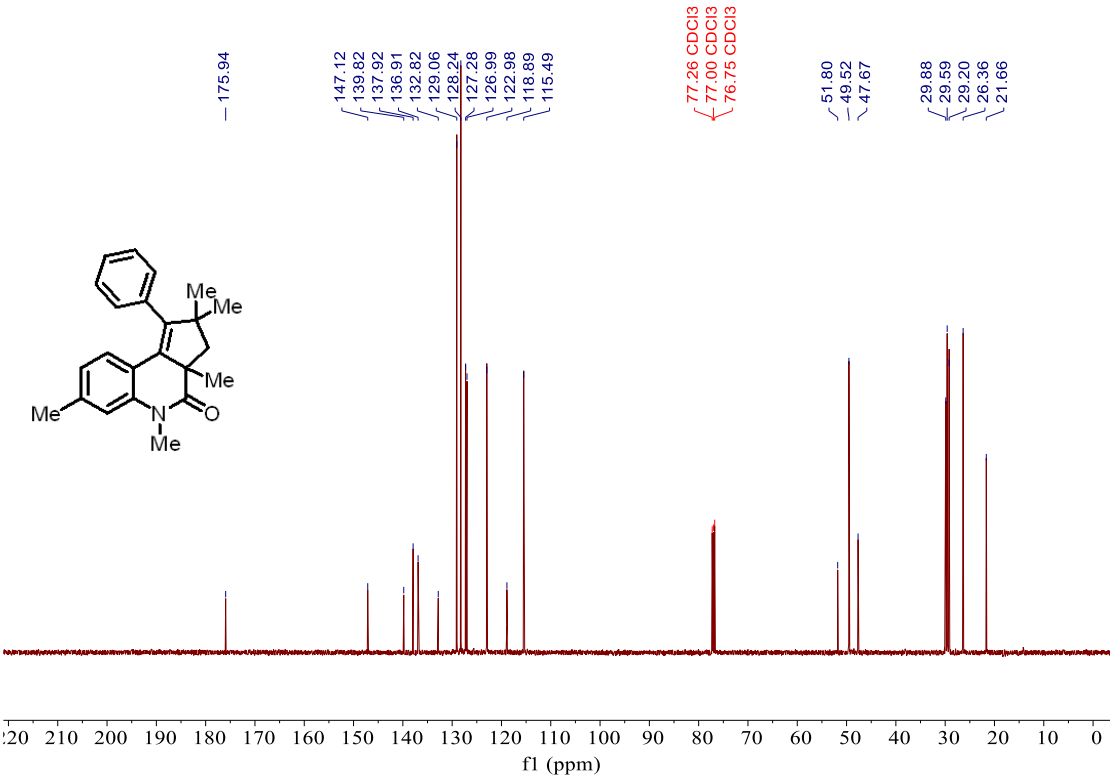
Supplementary Figure 38. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3s**



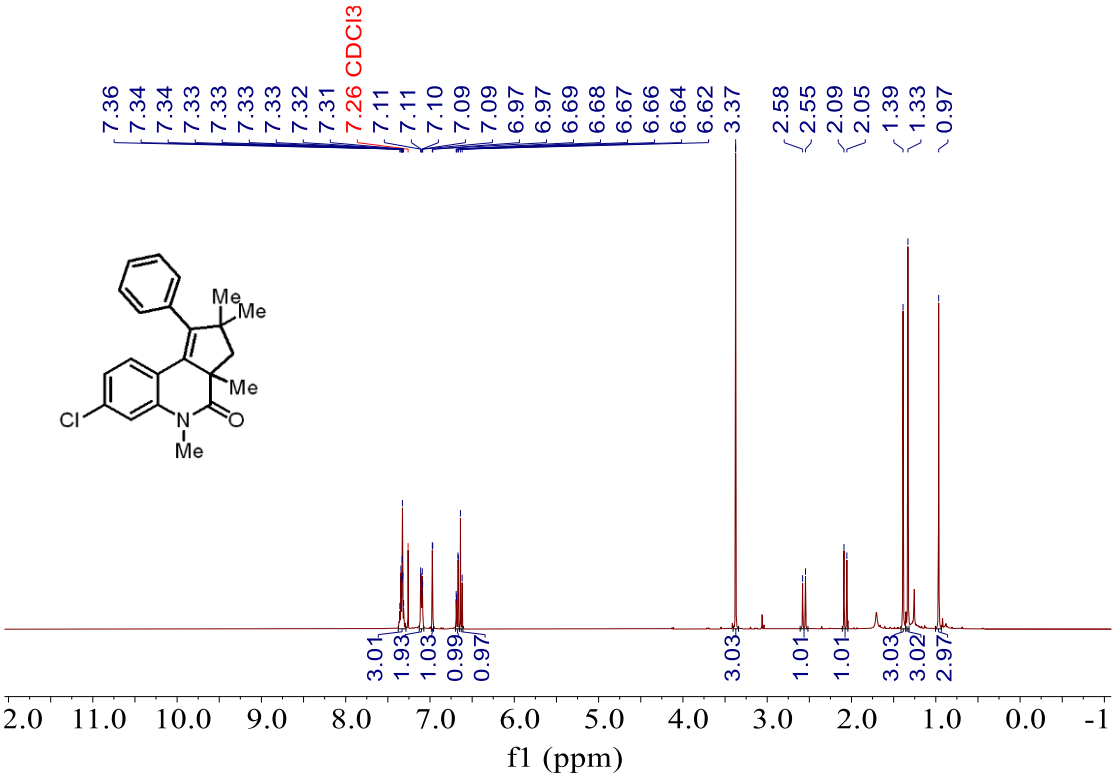
Supplementary Figure 39. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3s**



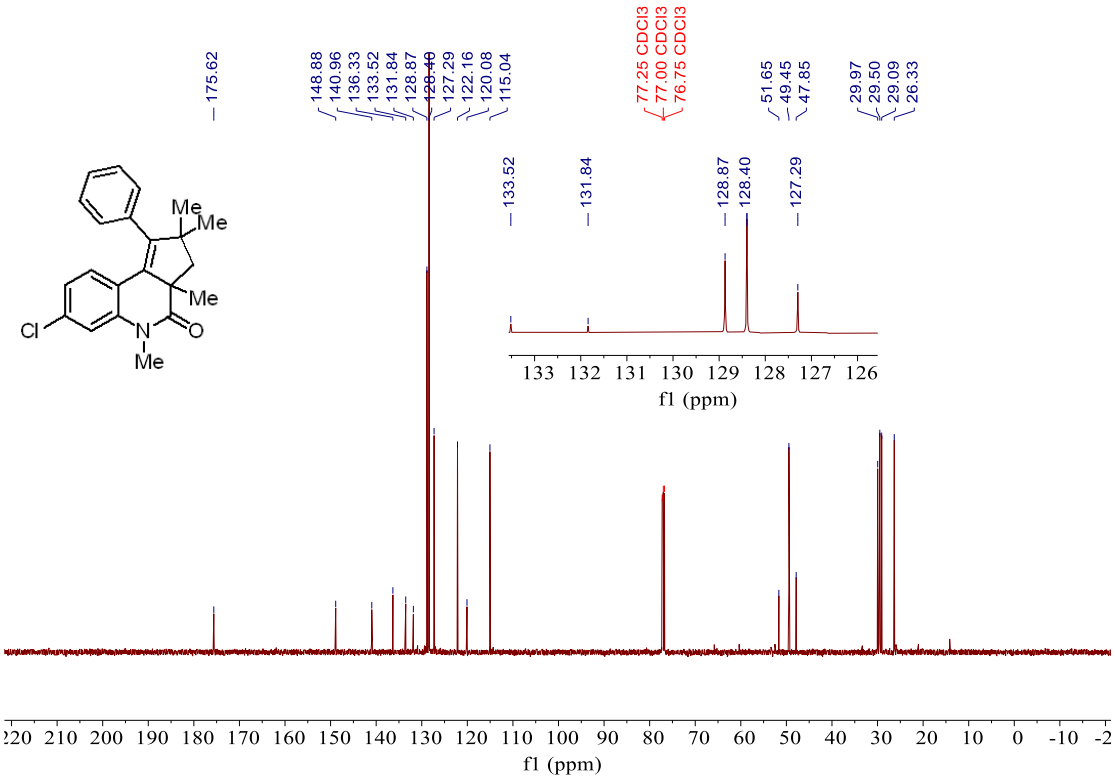
Supplementary Figure 40. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3t**



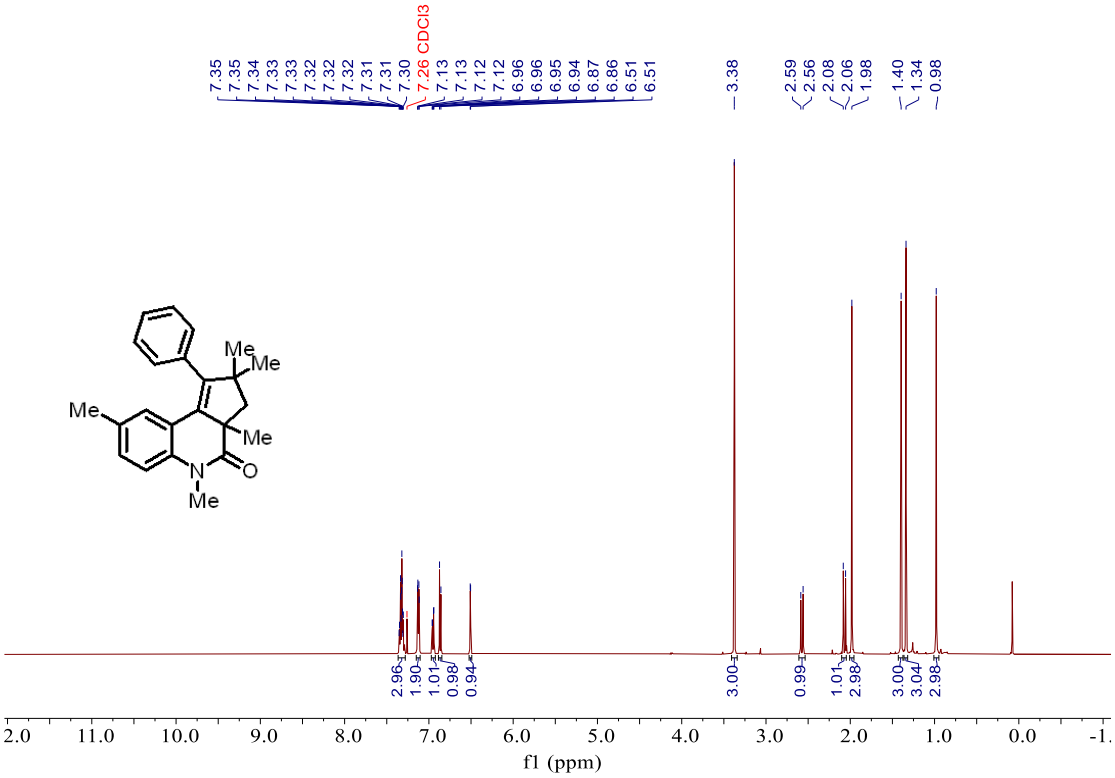
Supplementary Figure 41. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3t**



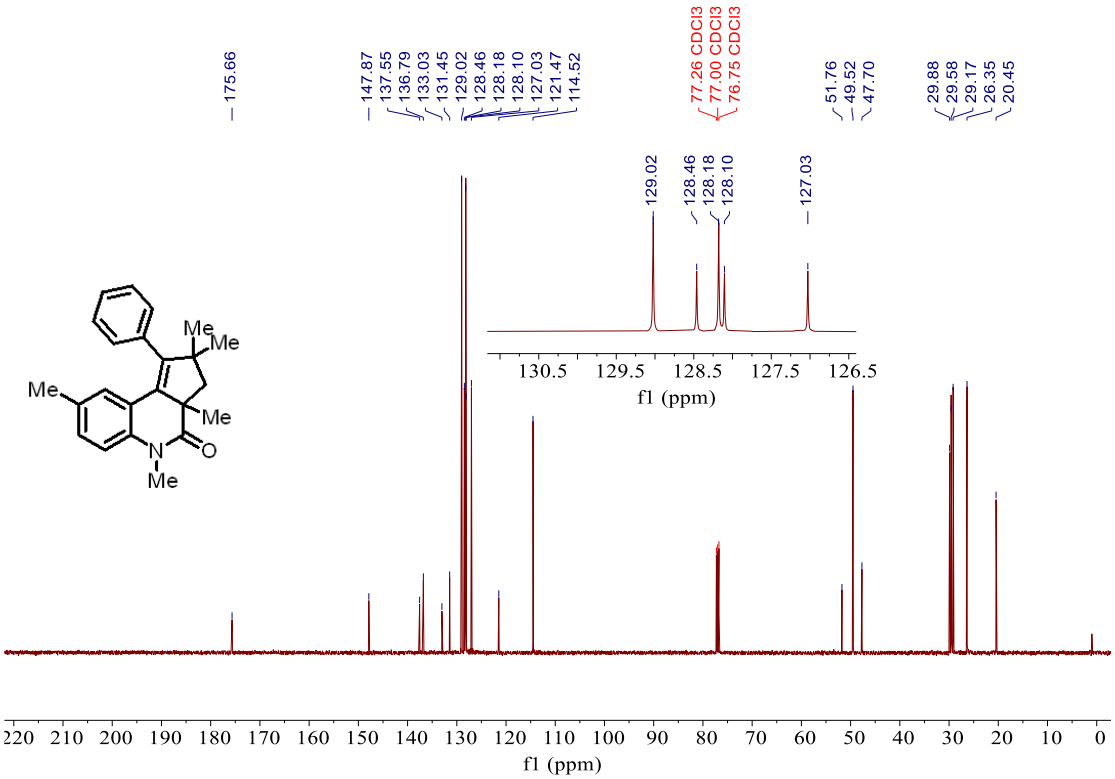
Supplementary Figure 42. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3u**



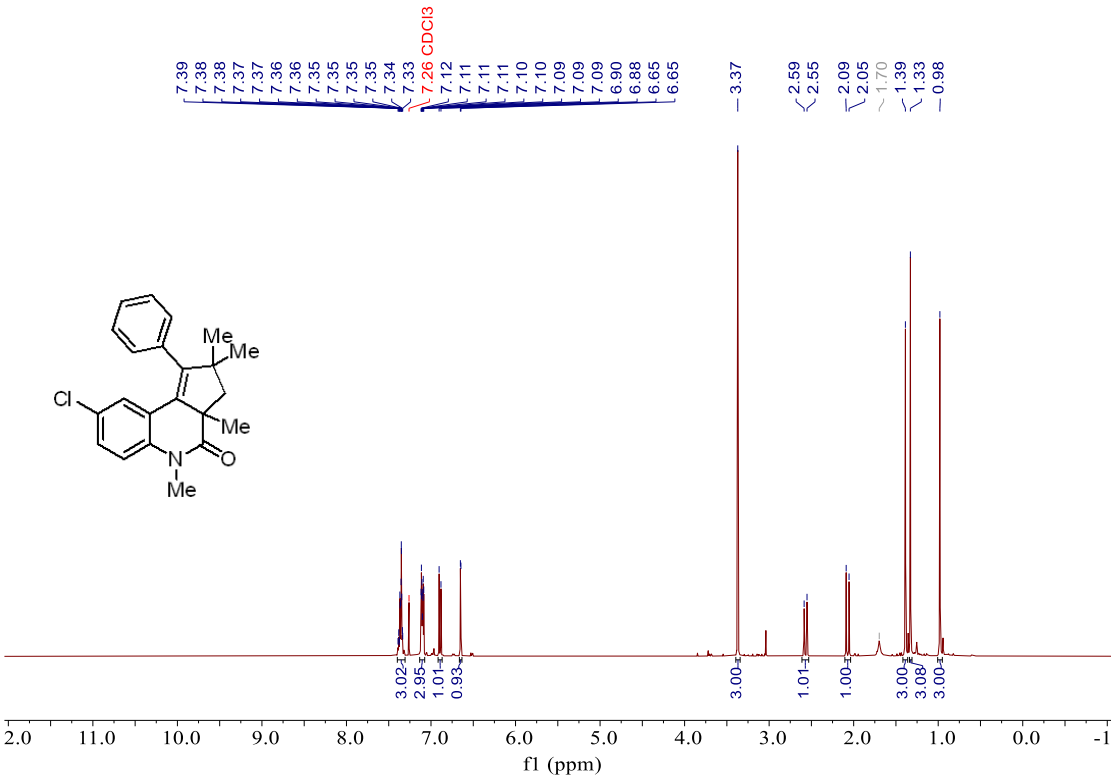
Supplementary Figure 43. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3u**



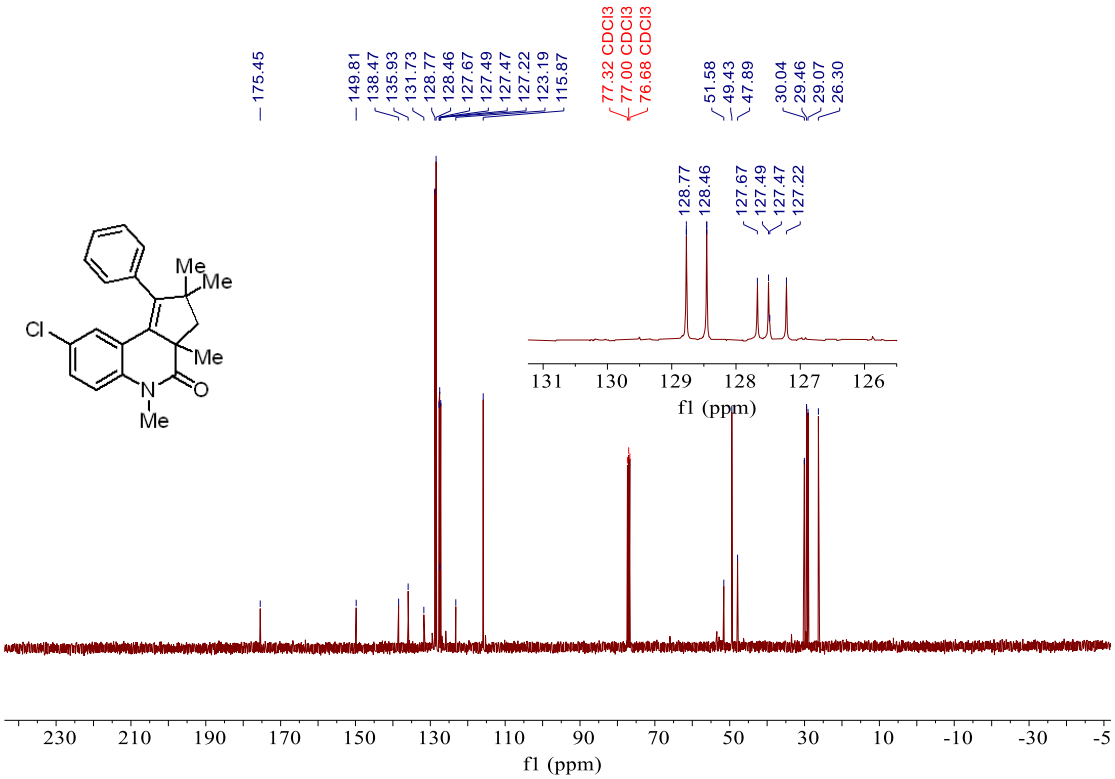
Supplementary Figure 44. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3v**



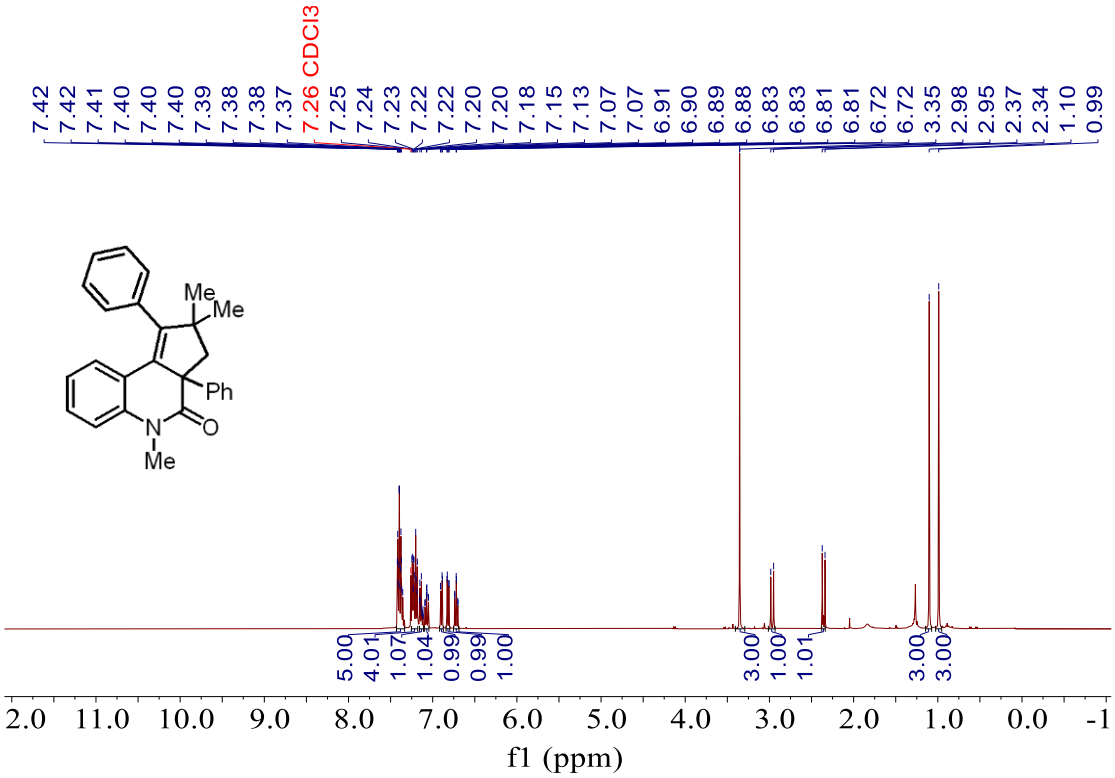
Supplementary Figure 45. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3v**



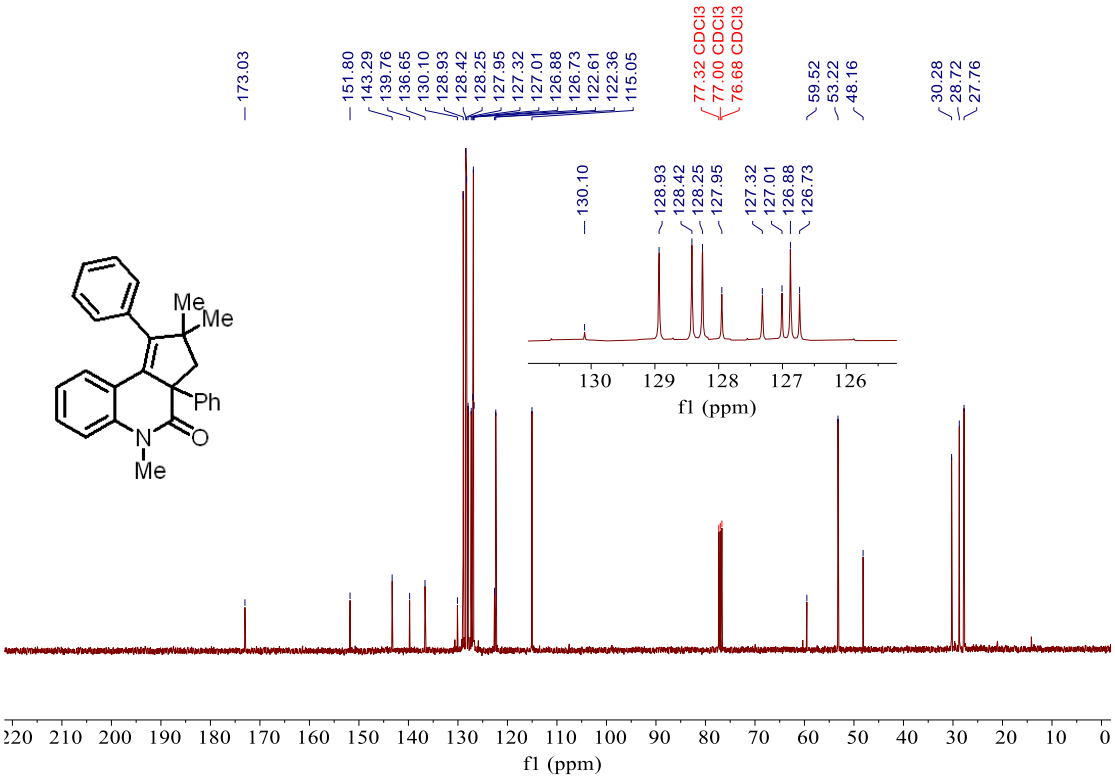
Supplementary Figure 46. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3w**



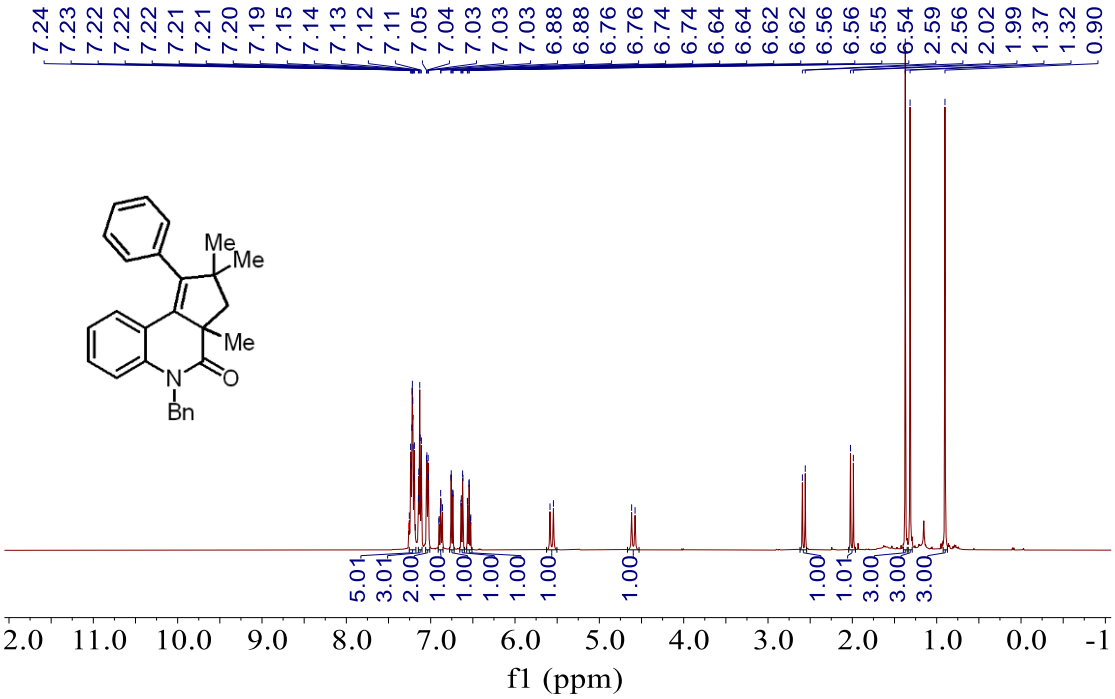
Supplementary Figure 47. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3w**



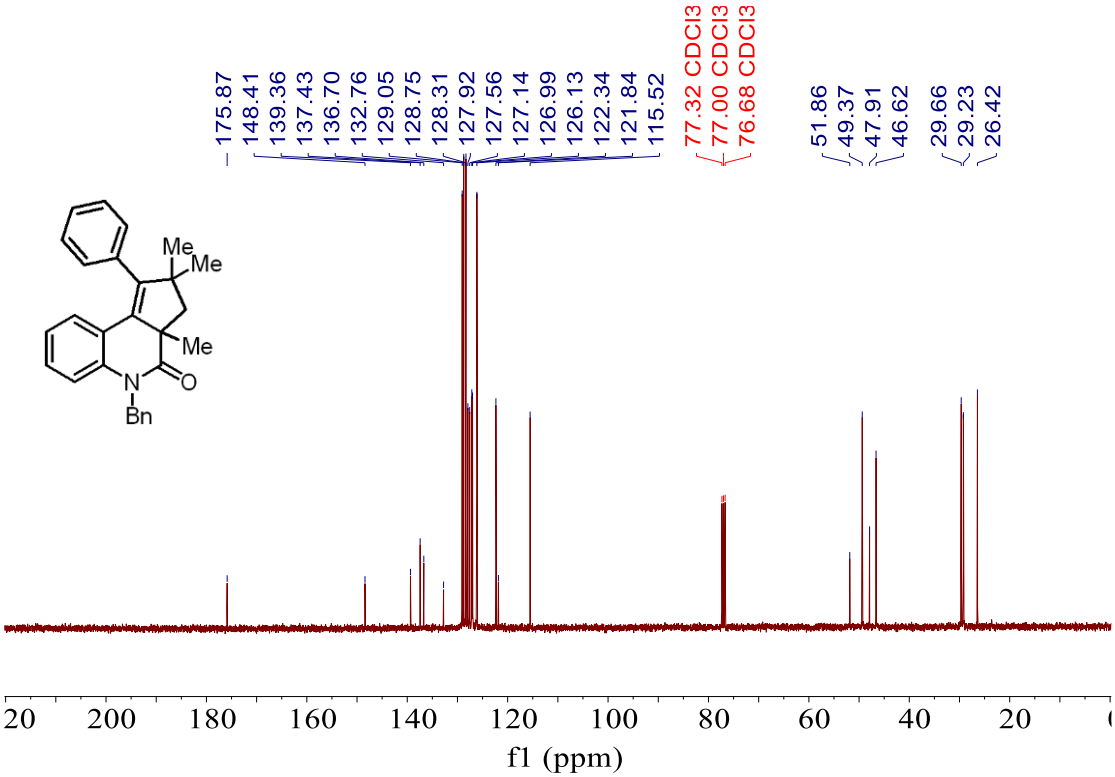
Supplementary Figure 48. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3x**



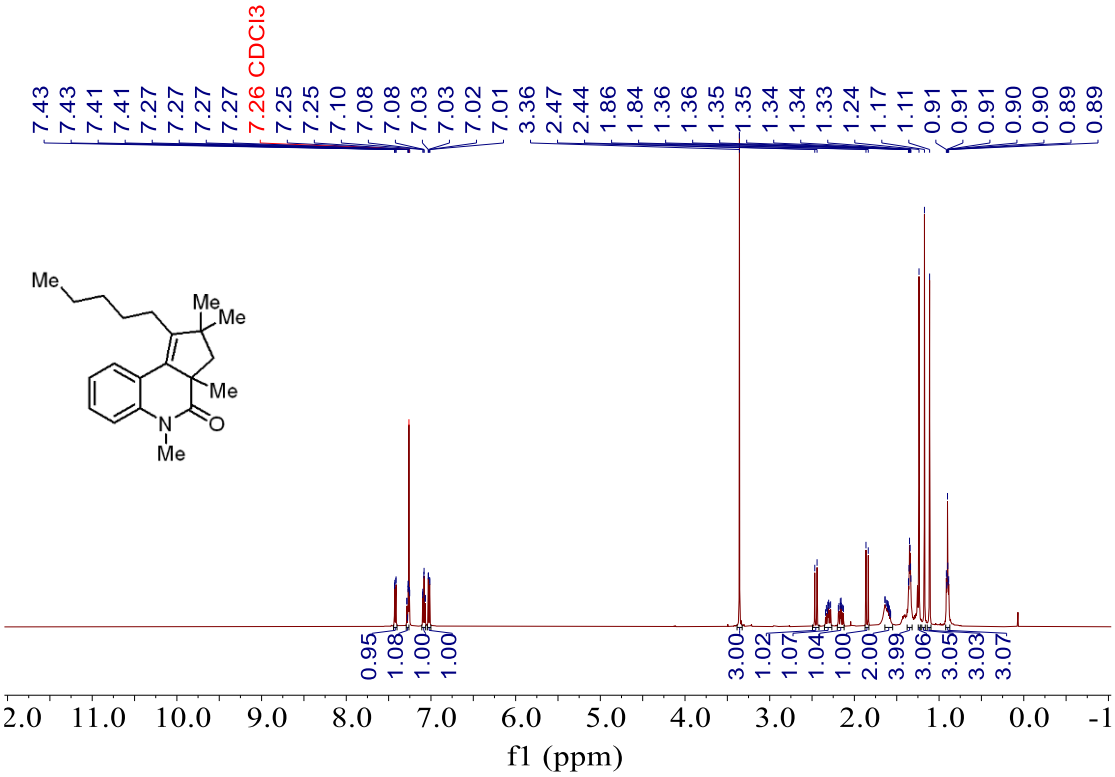
Supplementary Figure 49. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3x**



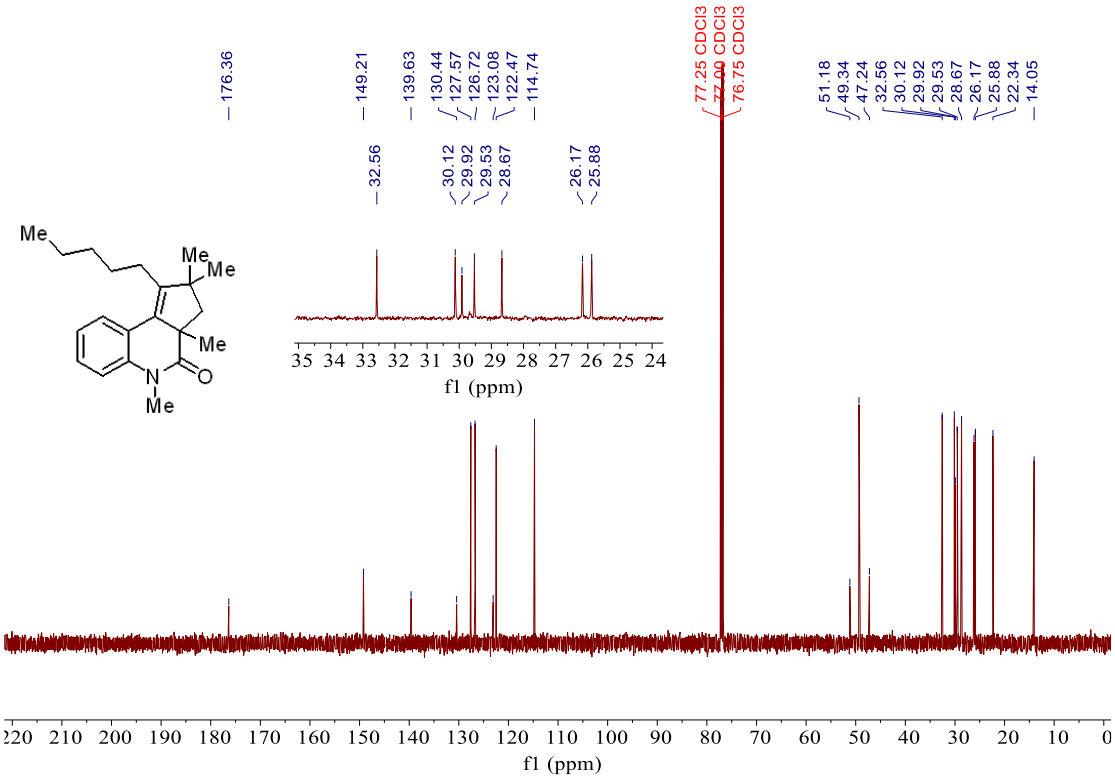
Supplementary Figure 50. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3y**



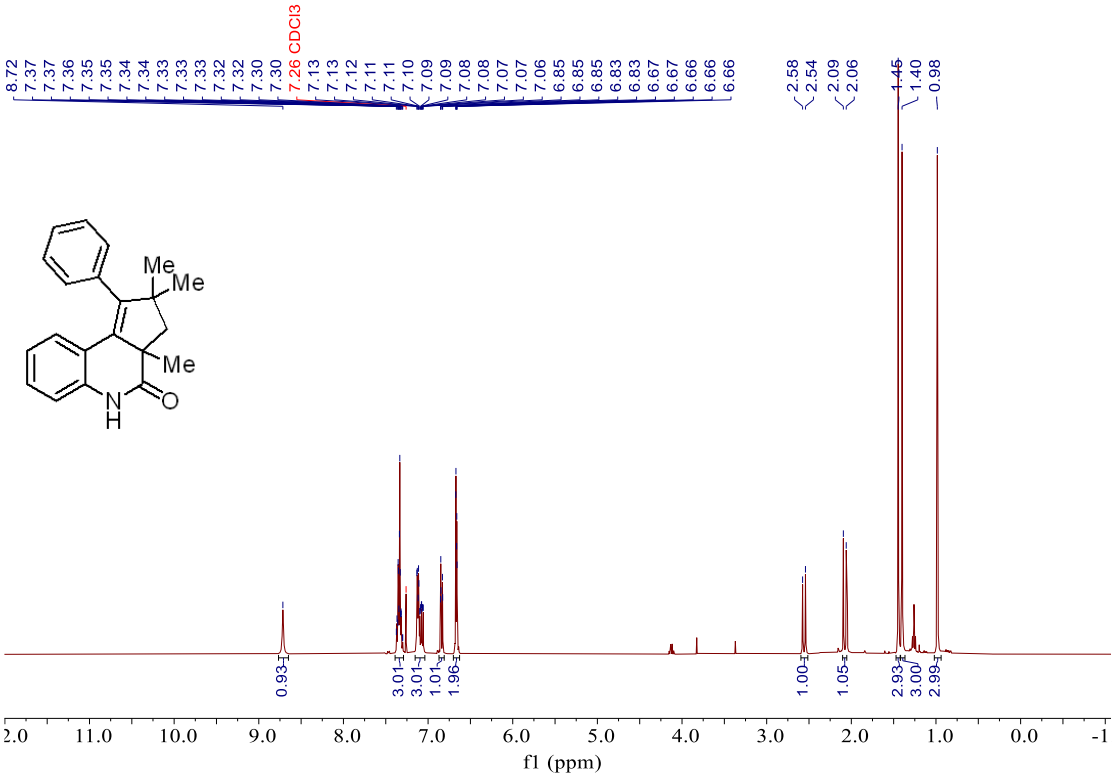
Supplementary Figure 51. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3y**



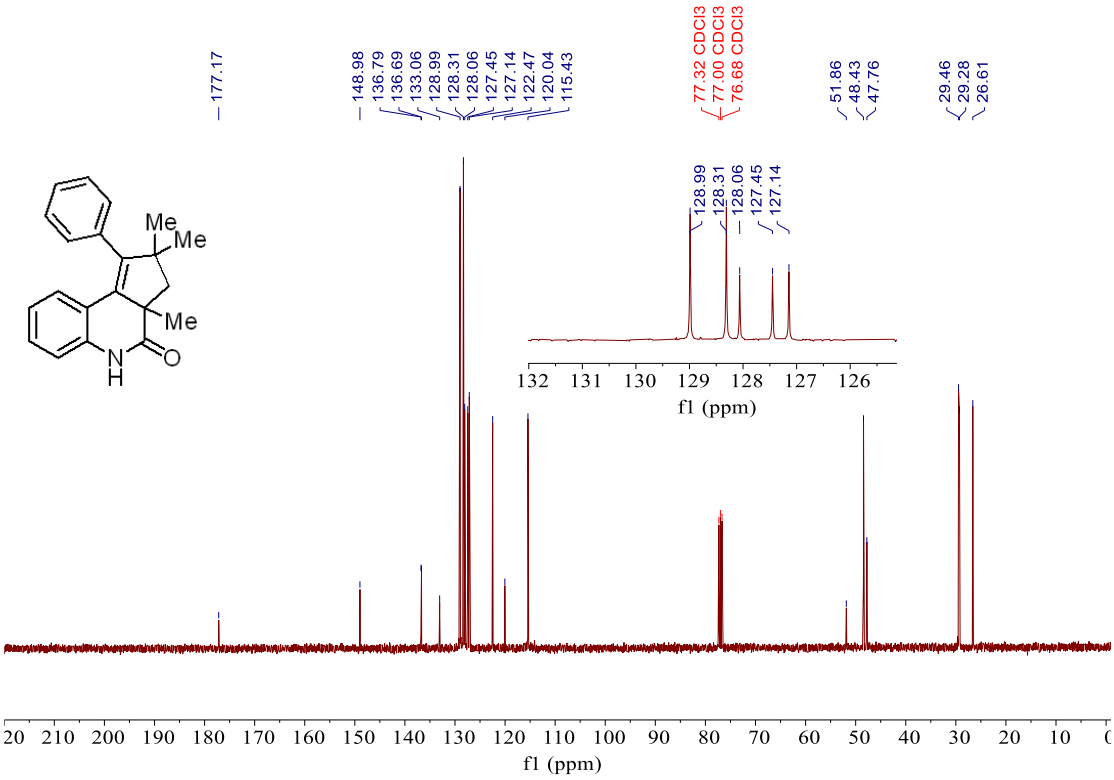
Supplementary Figure 52. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3z**



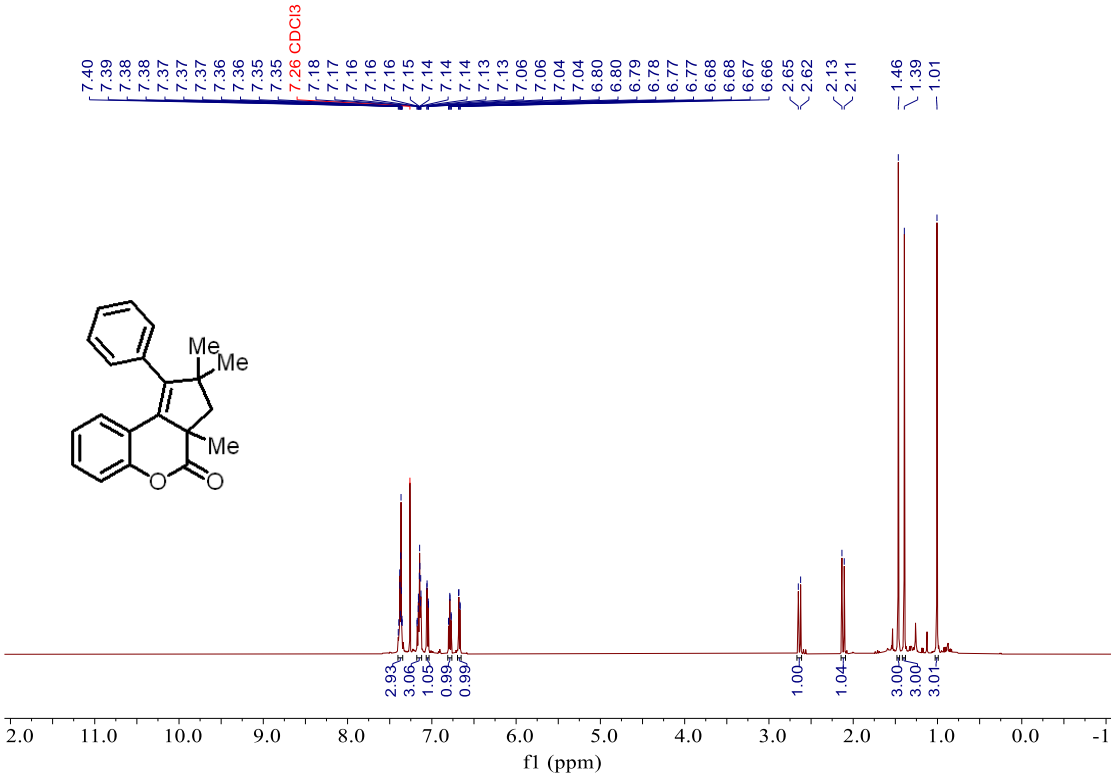
Supplementary Figure 53. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3z**



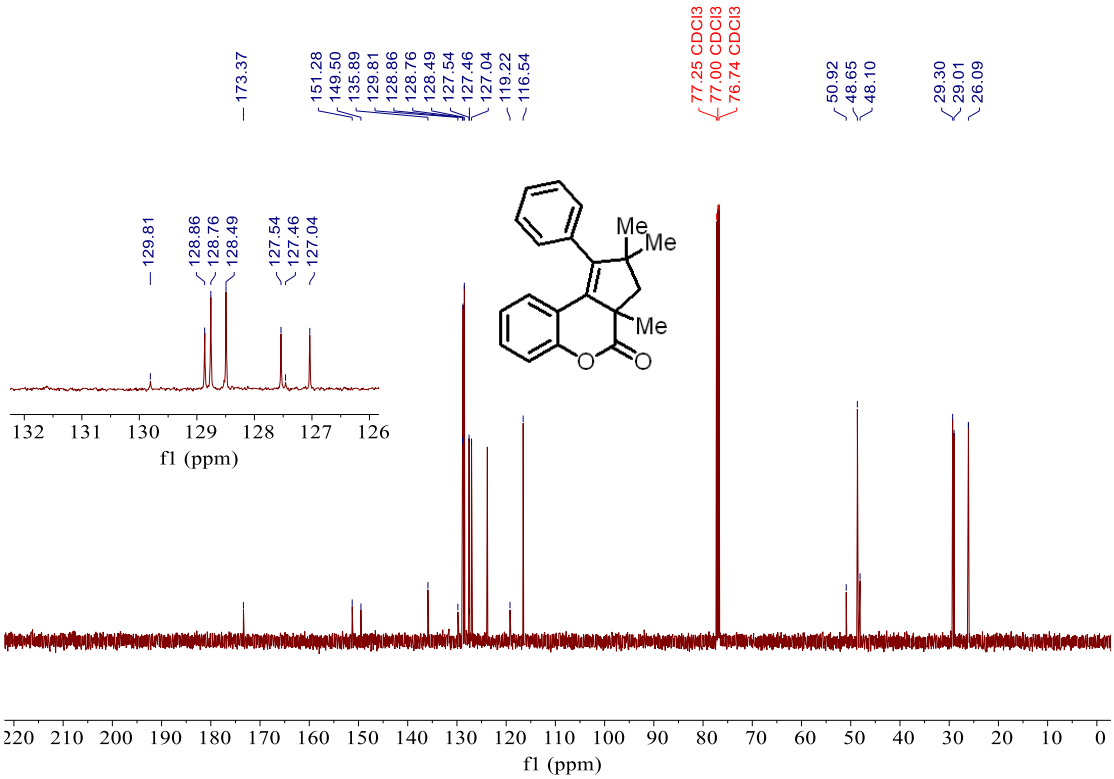
Supplementary Figure 54. ^{1}H NMR (400 MHz, $CDCl_3$) spectra for compound **3aa**



Supplementary Figure 55. ^{13}C NMR (101 MHz, $CDCl_3$) spectra for compound **3aa**



Supplementary Figure 56. ^{1}H NMR (500 MHz, $CDCl_3$) spectra for compound **3bb**



Supplementary Figure 57. ^{13}C NMR (126 MHz, $CDCl_3$) spectra for compound **3bb**