Supporting Information

Indirect electrochemical reductive cyclization of *o*-halophenylacrylamides mediated by phenanthrene

Xue-Qi Zhou [a, ‡], Pei-Bo Chen [a, ‡], Qiang Xia [a], Ting-Kai Xiong [a], Xue-Jun Li [a], Ying-Ming Pan [c], Mu-Xue He [b, *] and Ying Liang [a, *]

[a] School of Life and Environmental Sciences, Guilin University of Electronic Technology, Guilin, Guangxi, 541004, People's Republic of China.
[b] Guangxi Key Laboratory of Environmental Exposomics and Entire Lifecycle Health School of Public Health of Guilin Medical University, Guilin 541199, Guangxi (P. R. China)
[c] State Key Laboratory for Chemistry and Molecular Engineering of Medicinal Resources, School of Chemistry and Pharmaceutical Sciences of Guangxi Normal University, Guilin 541004, People's Republic of China.
‡ These authors contributed equally to this work.

[*] E-mail: liangyi0774@guet.edu.cn
hemuxue@126.com

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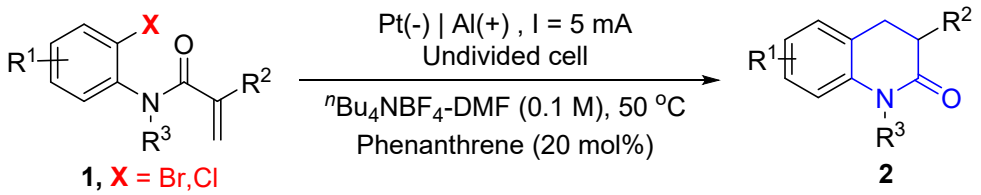
1. General Methods

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 ℃ petroleum ether and analytical grade EtOAc (without further purification). ^{1}H and ^{13}C spectra were recorded on a 400 MHz or 600 MHz spectrometer. Chemical shifts were reported in ppm. ^{1}H NMR spectra were referenced to $CDCl_3$ (7.26 ppm), and ^{13}C NMR spectra were referenced to $CDCl_3$ (77.0 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. The HRMS spectrum was measured by Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer with electron spray ionization. Cyclic voltammograms were recorded on a CHI 660E potentiostat. The GC(MS) analysis was measured by Agilent Intuvo 9000-5977B.

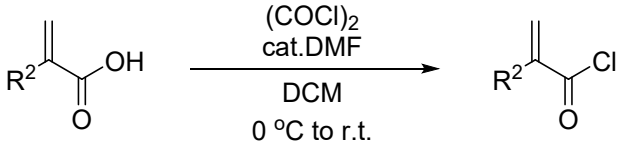
2. Procedures for the Electrolysis



A 10 ml three-necked round-bottomed flask was charged with **1** derivatives (0.3 mmol, 1.0 equiv.), phenanthrene (20 mol%), DMF containing $^{n}Bu_4NBF_4$ (0.1 M). The flask was equipped with an aluminum plate (1.2 cm × 1 cm) anode and a platinum plate (1 cm × 1 cm) cathode, the distance between the two electrodes is 1.5 cm. Electrolysis was carried out at 50 °C (oil bath temperature), where a constant current of 5 mA was used to monitor the reaction by TLC (about 5 hours). When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3 × 10 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel to afford the **2**.

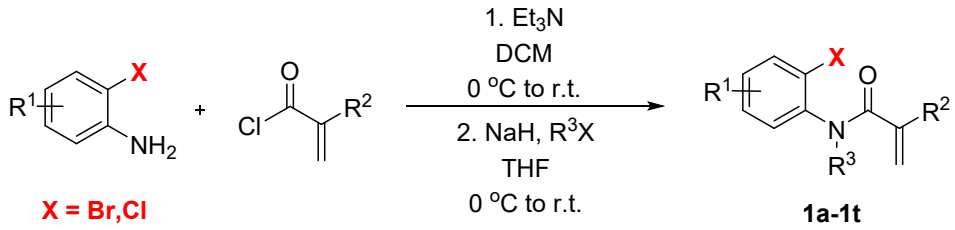
3. Procedures for the amide derivatives

3.1 Procedure of acid chloride



The procedure of acid chloride was adapted from literature procedures[1]. To a 50 mL round-bottom flask equipped with a magnetic stir-bar was added solution of acrylic acid (12 mmol, 1.2 equiv.) in dichloromethane (DCM, 20 mL), followed by dropwise addition of oxalyl chloride (20.0 mmol, 2.0 equiv.) and 1 drops of DMF under nitrogen atmosphere. The mixture was stirred at room temperature for 2 hours before removing all volatiles under reduced pressure. the resulting crude amide was used in next step without further purification.

3.2 Procedure of preparing amide

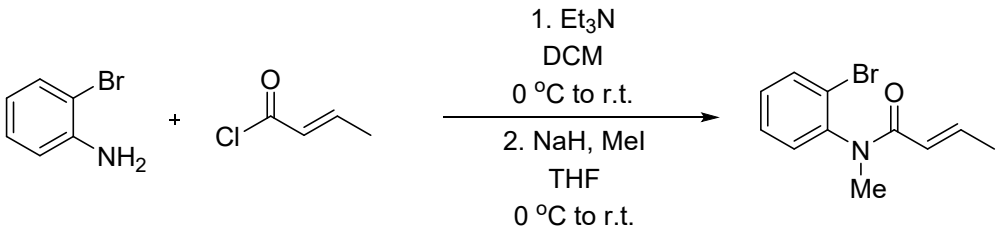


The procedure of preparing amide was adapted from literature procedures[2].Under nitrogen atmosphere, The CH_2Cl_2 (5 mL) solution of acyl chloride (22 mmol, 1.1 equiv.) was added dropwise to a stirring solution of the corresponding 2-bromoaniline (20 mmol, 1.0 equiv.), Et_3N (26 mmol, 1.3 equiv.) in CH_2Cl_2 (0.2 M) cooled to 0 °C. This solution was gradually warmed to room temperature and stirred until complete consumption of starting materials as indicated by TLC. When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (10 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated, the resulting crude amide was used in next step without further purification.

The crude residue is re-dissolved in THF (0.4 M) and cooled to 0 °C. To this solution, NaH (60% dispersion in mineral oil, 1.5 equiv.) was added in one portion and the solution was stirred for 30 minutes. To this mixture, iodomethane or benzyl bromide (1.5 equiv.) was added dropwise. The reaction was gradually warmed to

room temperature to stir until complete consumption of starting material as indicated by TLC. the reaction mixture was washed with water and extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, filtrated and concentrated, the pure products by flash column chromatography on silica gel to afford the **1a-1t.**

3.3 Procedure of internal olefins



Internal olefins were prepared according to literature procedure[2]. Under nitrogen atmosphere, The CH_2Cl_2 (5 mL) solution of acyl chloride (22 mmol, 1.1 equiv.) was added dropwise to a stirring solution of the corresponding 2-bromoaniline (20 mmol, 1.0 equiv.), Et_3N (26 mmol, 1.3 equiv.) in CH_2Cl_2 (0.2 M) cooled to 0 °C. This solution was gradually warmed to room temperature and stirred until complete consumption of starting materials as indicated by TLC. When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (10 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated, the resulting crude amide was used in next step without further purification.

The crude residue is re-dissolved in THF (0.4 M) and cooled to 0 °C. To this solution, NaH (60% dispersion in mineral oil, 1.5 equiv.) was added in one portion and the solution was stirred for 30 minutes. To this mixture, iodomethane or benzyl bromide (1.5 equiv.) was added dropwise. The reaction was gradually warmed to room temperature to stir until complete consumption of starting material as indicated by TLC. the reaction mixture was washed with water and extracted with ethyl acetate (10 mL × 3). The combined organic layer was washed with brine, dried over Na_2SO_4, The pure product was obtained by flash column chromatography on silica gel.

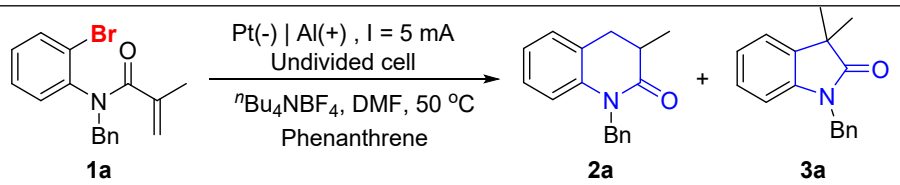
References:

1 G. Wang, C. Shen, X. Ren and K. Dong, Ni-Catalyzed enantioselective reductive arylcyanation/cyclization of *N*-(2-iodo-aryl)acrylamide, *Chem. Commun.*, 2022, **58**, 1135-1138.

2 A. Yen and M. Lautens, Nickel-Catalyzed Intramolecular Arylcyanation for the Synthesis of 3,3-Disubstituted Oxindoles, *Org. Lett.,* 2018, **20**, 4323-4327.

4. Additional Optimization of Reaction Conditions

Table S1 Optimization of the reaction conditions[a]



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

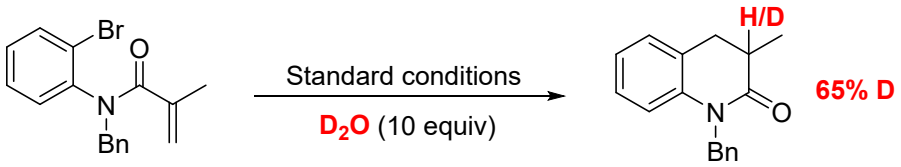
Entry	Variation from standard conditions	Yield (%)	
		2a[b]	**3a**[c]
1	Pt (-) / Mg (+)	63	< 5
2	Pt (-) / Zn (+)	64	9
3	Pt (-) / Ni (+)	40	12
4	Pt (-) / SS (+)	50	10
5	Pt (-) / Pt (+)	NR	-
6	Ni (-) / Al (+)	56	17
7	C (-) / Al (+)	66	< 5
8	3 mA instead of 5 mA	75	10
9	10 mA instead of 5 mA	80	7
10	$^{n}Bu_4NPF_6$ as electrolyte	61	7
11	$^{n}Bu_4NClO_4$ as electrolyte	60	13
12	Et_4NBF_4 as electrolyte	68	< 5
13	$LiClO_4$ as electrolyte	trace	-
14	NH_4I as electrolyte	NR	-
15	DMA as solvent	52	19
16	DCE as solvent	trace	-
17	DMSO as solvent	61	< 5
18	CH_3CN as solvent	trace	-
19	DMF/HFIP as solvent	55	13

[a]Reaction conditions: **1a** (0.3 mmol), phenanthrene (20 mol%), $^{n}Bu_4NBF_4$-DMF (0.1 M), aluminium plate anode (1.2 cm × 1 cm), platinum plate cathode (1 cm × 1 cm), constant current = 5 mA, $j_{cathode}$ = 0.24 mA/cm^2, undivided cell, 50 °C, 5h, 3.1 F/mol. [b]Isolated yield. [c]Determined by GC-MS analysis. NR = no reaction.

5. Control experiments

5.1 Deuterium-labeling experiment

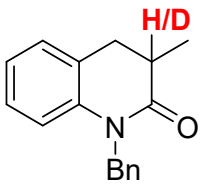
(1)



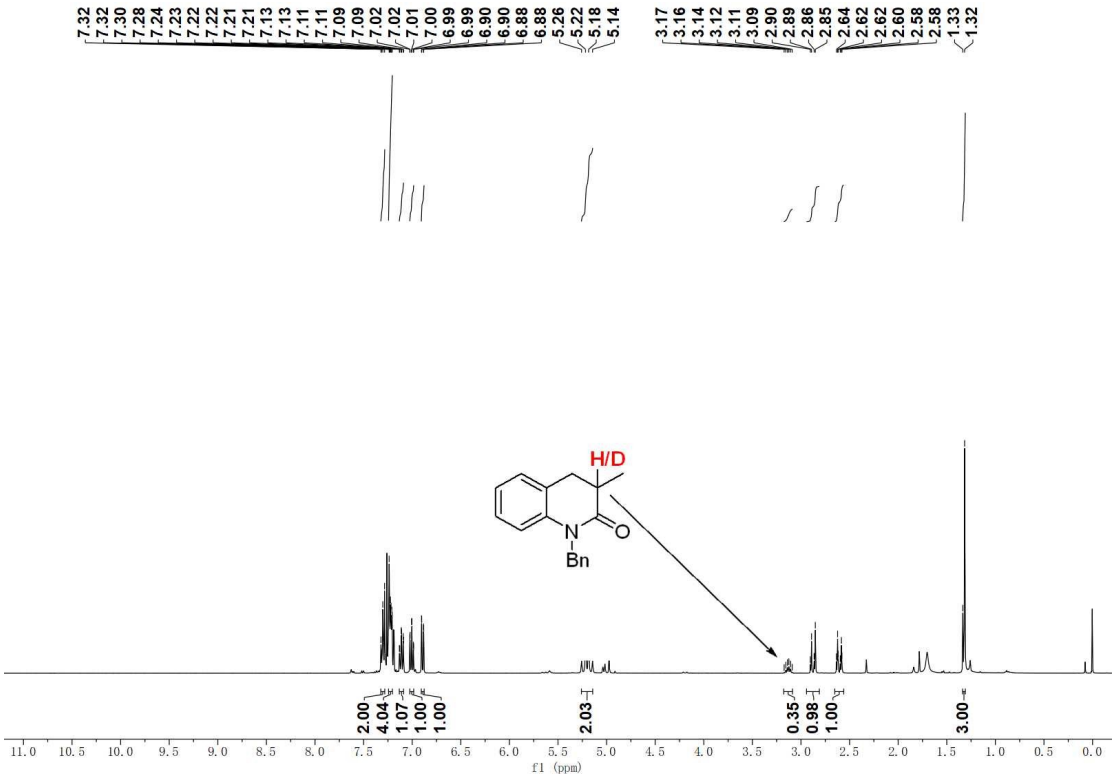
1a **2a & 2a-*d***

A 10 ml three-necked round-bottomed flask was charged with **1a** derivatives (0.3 mmol), phenanthrene (20 mol%), DMF containing $^{n}Bu_4NBF_4$ (0.1 M), **deuterium oxide** (10 equiv.). The flask was equipped with an aluminum plate (1.2 cm × 1 cm) anode and a platinum plate (1 cm × 1 cm) cathode. Electrolysis was carried out at 50 °C (oil bath temperature), which using a constant current of 5 mA until the substrate was completely consumed (monitored by TLC, about 5 hours). When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel to afford the **2a** and **2a-*d*** (**2a** :**2a-*d*** = 35:65), yield 80%.

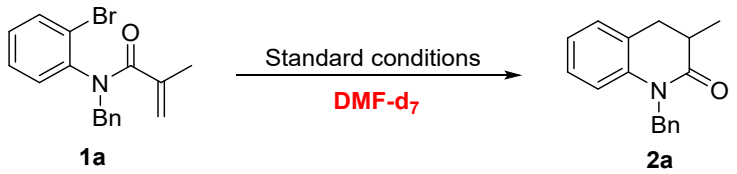
^{1}H NMR spectra of Compounds 2a＆2a-*d*



1-benzyl-3,3-dimethyl-3,4-dihydroquinolin-2(1H)-one **(2a＆2a-d)**, Colorless oily. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.32 – 7.28 (m, 2H), 7.24 – 7.20 (m, 4H), 7.13 – 7.09 (m, 1H), 7.03 – 6.99 m, 1H), 6.89 (dd, *J* = 8.1, 0.9 Hz, 1H), 5.26 – 5.14 (m, 2H), 2.88 (dd, *J* = 15.6, 4.8 Hz, 1H), 2.65 – 2.56 (m, 1H), 1.33 (d, *J* = 7.4 Hz, 3H).

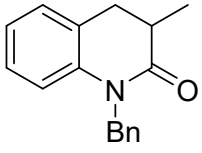


(2)

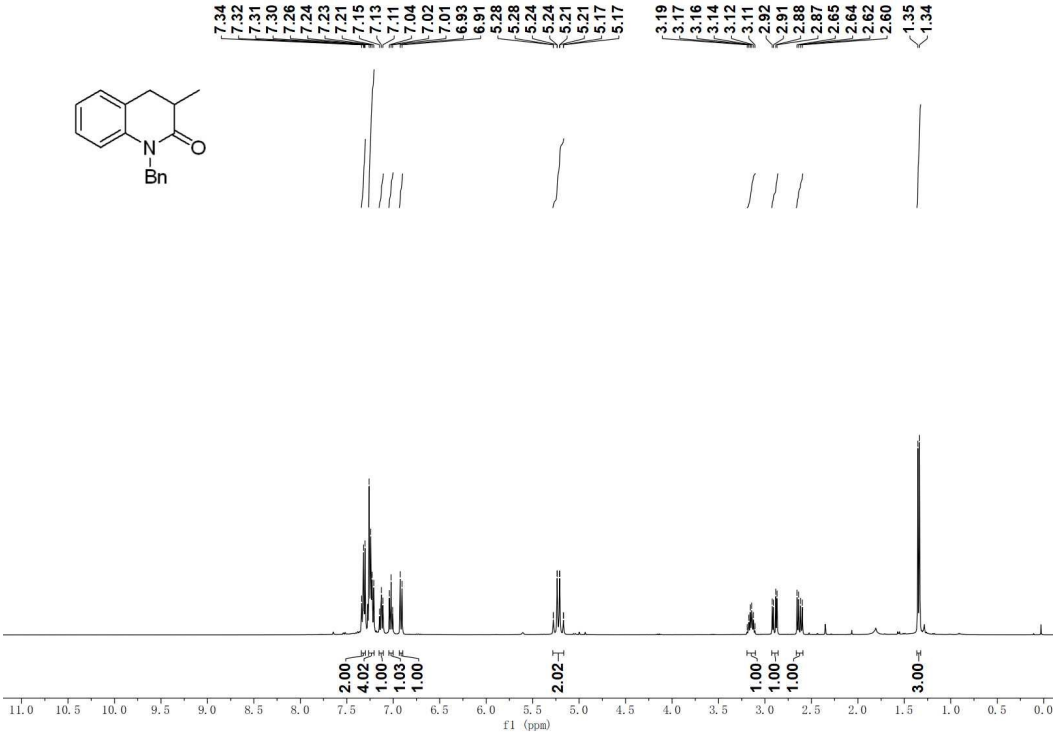


1a **2a**

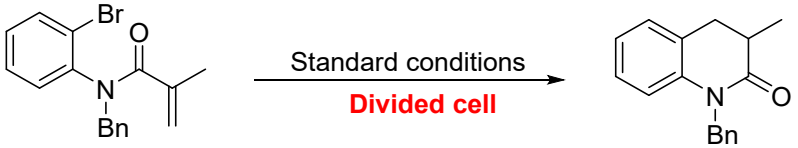
A 10 ml three-necked round-bottomed flask was charged with **1a** derivatives (0.3 mmol), phenanthrene (20 mol%), **DMF-*d*$_7$** containing ^{n}Bu$_4$NBF$_4$ (0.1 M). The flask was equipped with an aluminum plate (1.2 cm × 1 cm) anode and a platinum plate (1 cm × 1 cm) cathode. Electrolysis was carried out at 50 °C (oil bath temperature), which using a constant current of 5 mA until the substrate was completely consumed, monitored by TLC. When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel to afford the **2a**, yield 79%.



1-benzyl-3-methyl-3,4-dihydroquinolin-2(1H)-one (**2a**), colorless oily (0.059g, 79%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography.**^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.34 – 7.30 (m, 2H), 7.26 – 7.20 (m, 4H), 7.15 – 7.10 (m, 1H), 7.05 – 7.00 (m, 1H), 6.93 – 6.91 (m, 1H), 5.28 – 5.17 (m, 2H), 3.19 – 3.10 (m, 1H), 2.90 (dd, *J* = 15.6, 5.4 Hz, 1H), 2.63 (dd, *J* = 15.6, 7.2 Hz, 1H), 1.35 (d, *J* = 7.0 Hz, 3H). **HRMS** (ESI, m/z) calculated for $C_{17}H_{18}NO^+$ [M+H] $^+$: 252.1383; found: 252.1386.



5.2 Divided cell experiment



1a **2a,** 76%

The electrolysis was carried out in an H-type divided cell, was charged with **1a** (0.3 mmol), phenanthrene (20 mol%), DMF (0.1 M, 6 mL) containing ^{n}Bu$_4$NBF$_4$ was added in the cathodic chamber and a platinum plate (1 cm × 1 cm) as cathode. The anodic chamber was charged with DMF (0.1 M, 6 mL) containing ^{n}Bu$_4$NBF$_4$ and equipped with an aluminum plate (1.2 cm × 1 cm) as anode. The distance between the two electrodes was 5.2 cm. Electrolysis was carried out at 50 °C (oil bath

temperature), which using a constant current of 5 mA until the substrate was completely consumed (monitored by TLC, about 5 hours). When the reaction was finished, the reaction mixture was washed with water and extracted with ethyl acetate (3 × 5 mL). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product was obtained by flash column chromatography on silica gel to afford the **2a**, yield 76%.

6. Cyclic Voltammetry Studies

The cyclic voltammograms were recorded in an electrolyte solution of $^{n}Bu_4NBF_4$ (0.1 M) in DMF using a glassy carbon disk working electrode (diameter, 3 mm), a Pt wire auxiliary electrode and a Ag/AgCl reference electrode. The scan rate was 100 mV/s.

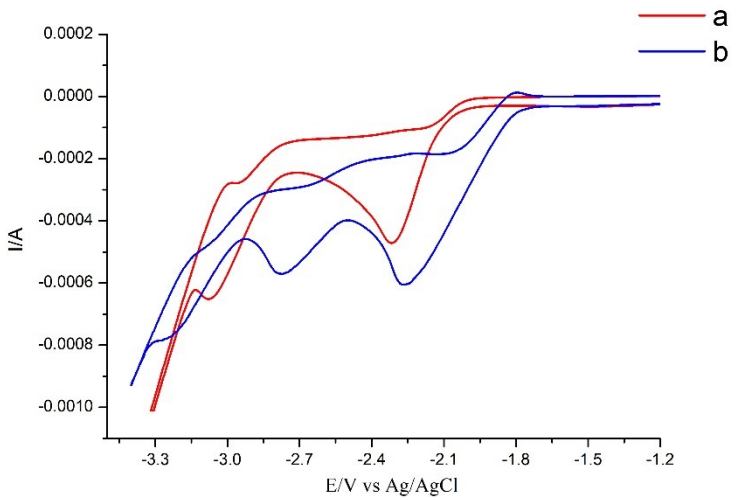


Figure S2-1 Cyclic voltammograms in DMF + 0.1 M $^{n}Bu_4NBF_4$. a) **1a** (0.2 mmol), $E_{p/2}$ = -2.31 V, $i_{p,\,c}$ = -5.0 mA. b) **1a** (0.2 mmol) and Phenanthrene (0.2 mmol), $E_{p/2}$ = -2.25 V, $i_{p,\,c}$ = -6.3 mA.

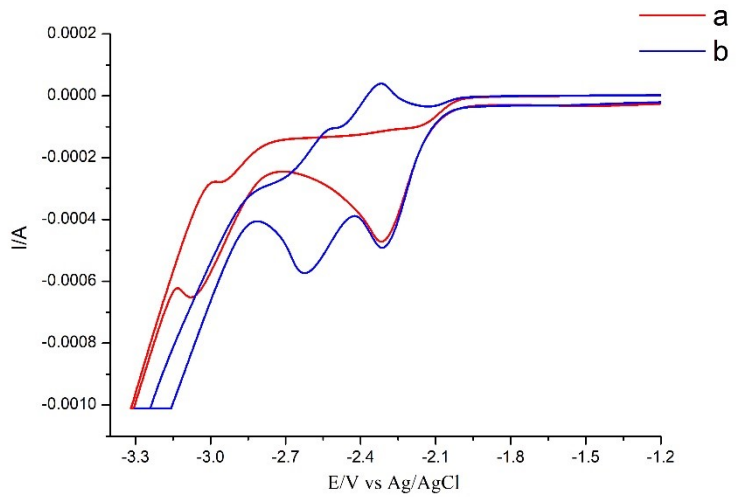


Figure S2-2 Cyclic voltammograms in DMF + 0.1 M $^{n}Bu_4NBF_4$. a) **1a** (0.2 mmol), $E_{p/2}$ = -2.31 V, $i_{p,\,c}$ = -5.0 mA. b) **1a** (0.2 mmol) and Anthracene (0.2 mmol), $E_{p/2}$ = -2.31 V, $i_{p,\,c}$ = -5.1 mA.

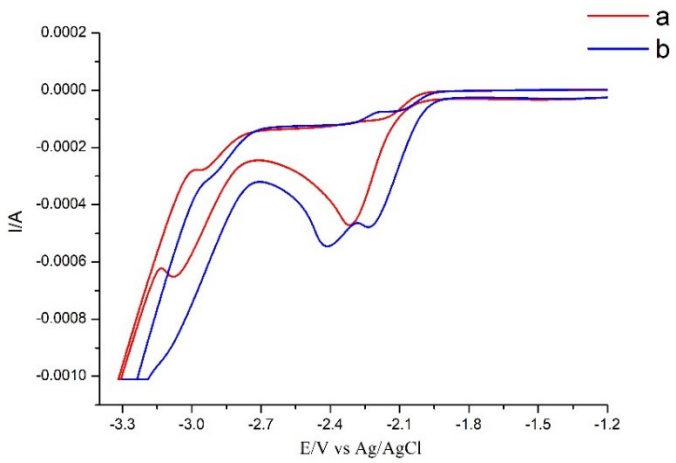


Figure S2-3 Cyclic voltammograms in DMF + 0.1 M $^{n}Bu_4NBF_4$. a) **1a** (0.2 mmol), $E_{p/2}$ = -2.31 V, $i_{p,\,c}$ = -5.0 mA. b) **1a** (0.2 mmol) and Methyl 4-tert-butylbenzoate (0.2 mmol), $E_{p/2}$ = -2.26 V, $i_{p,\,c}$ = -5.0 mA.

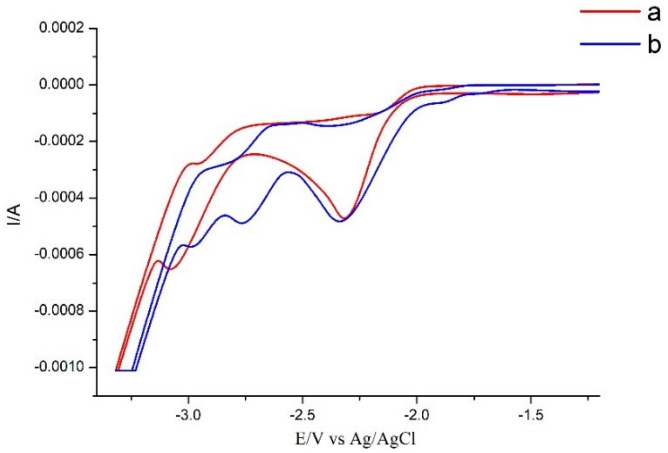


Figure S2-4 Cyclic voltammograms in DMF + 0.1 M $^{n}Bu_4NBF_4$. a) **1a** (0.2 mmol), $E_{p/2}$ = 2.31 V, $i_{p,\,c}$ = -5.0 mA. b) **1a** (0.2 mmol) and Fluorene (0.2 mmol), $E_{p/2}$ = -2.33 V, $i_{p,\,c}$ = -5.1 mA.

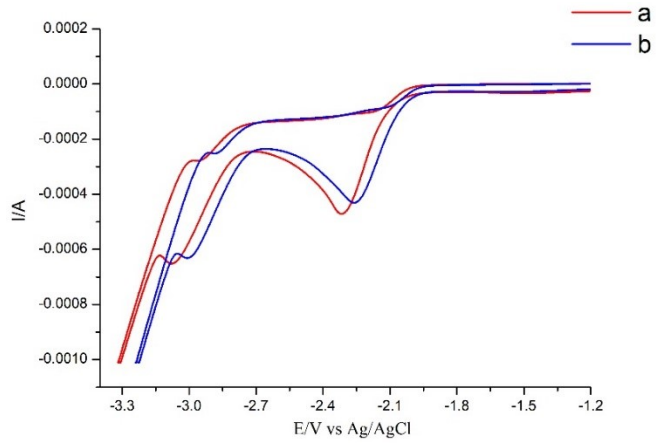


Figure S2-5 Cyclic voltammograms in DMF + 0.1 M $^{n}Bu_4NBF_4$. a) **1a** (0.2 mmol), $E_{p/2}$ = -2.31 V, $i_{p,\,c}$ = -5.0 mA. b) **1a** (0.2 mmol) and Fullerene-C60 (0.2 mmol), $E_{p/2}$ = -2.33 V, $i_{p,\,c}$ = -5.3 mA.

7. Reaction Selectivity Analysis

7.1 The crude GC(MS)analysis for 6-endo products

We made corresponding 5-exo products for the three substrates (**1j**, **1l** and **1q**) and compared each of them with 6-endo products (**2j**, **2l** and **2q**)[3]. According to the GC(MS) of the crude reaction solution, only trace amounts of 5-exo by-products appeared in this reaction.

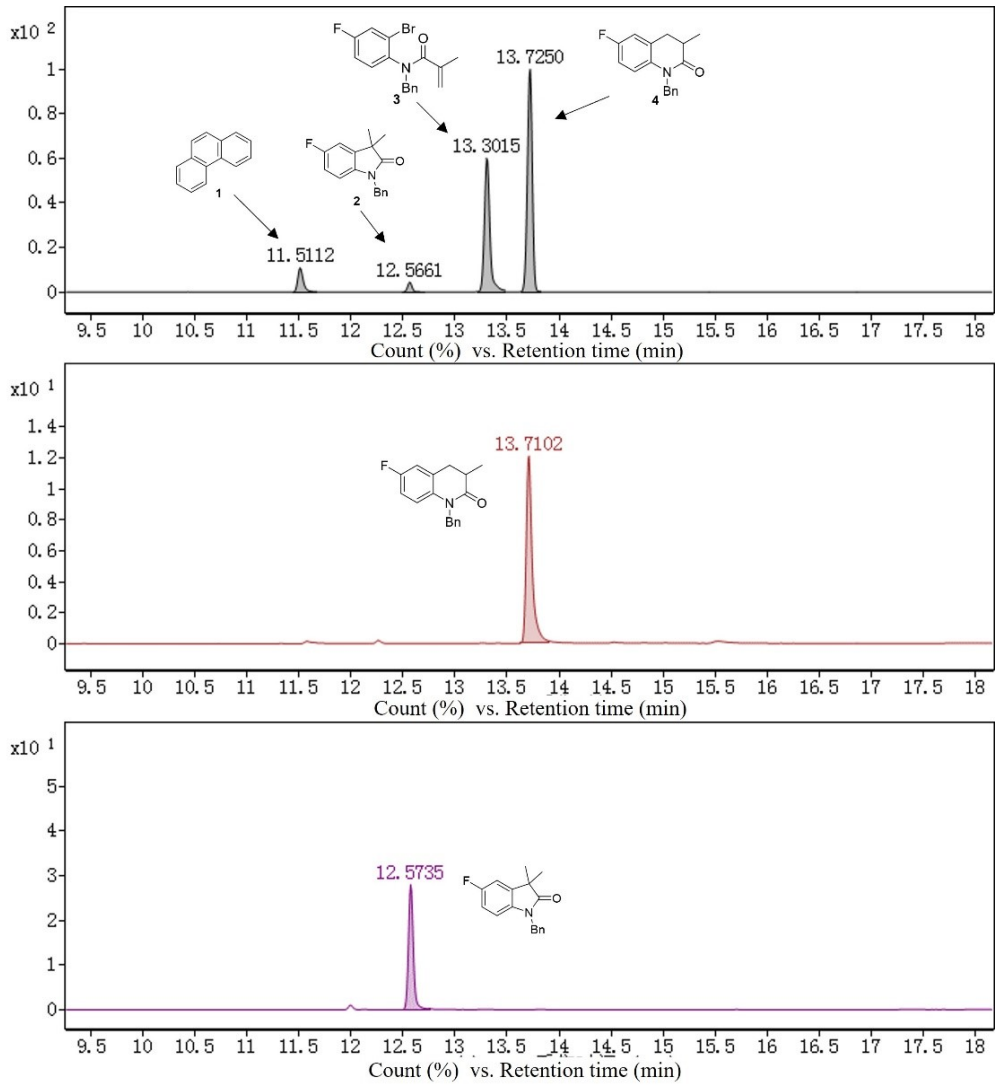


Figure S3-1 Crude GC(MS) analysis of **2j**.

Peak	Peak area	Peak area percentage	Peak height	Peak width	Retention time
1	4134134.39	12.19	1667829.56	0.1857	11.5112
2	1406278.55	4.15	771629.26	0.1411	12.5661
3	21979780.83	64.8	8636280.12	0.1931	13.3015
4	33919954.32	100	15192430.03	0.1783	13.7250

The chromatogram shows a trace of the five-membered ring product. According to the crude GC(MS) chromatogram, the crude reaction solution contained traces of the 5-exo product in < 3 % yield.

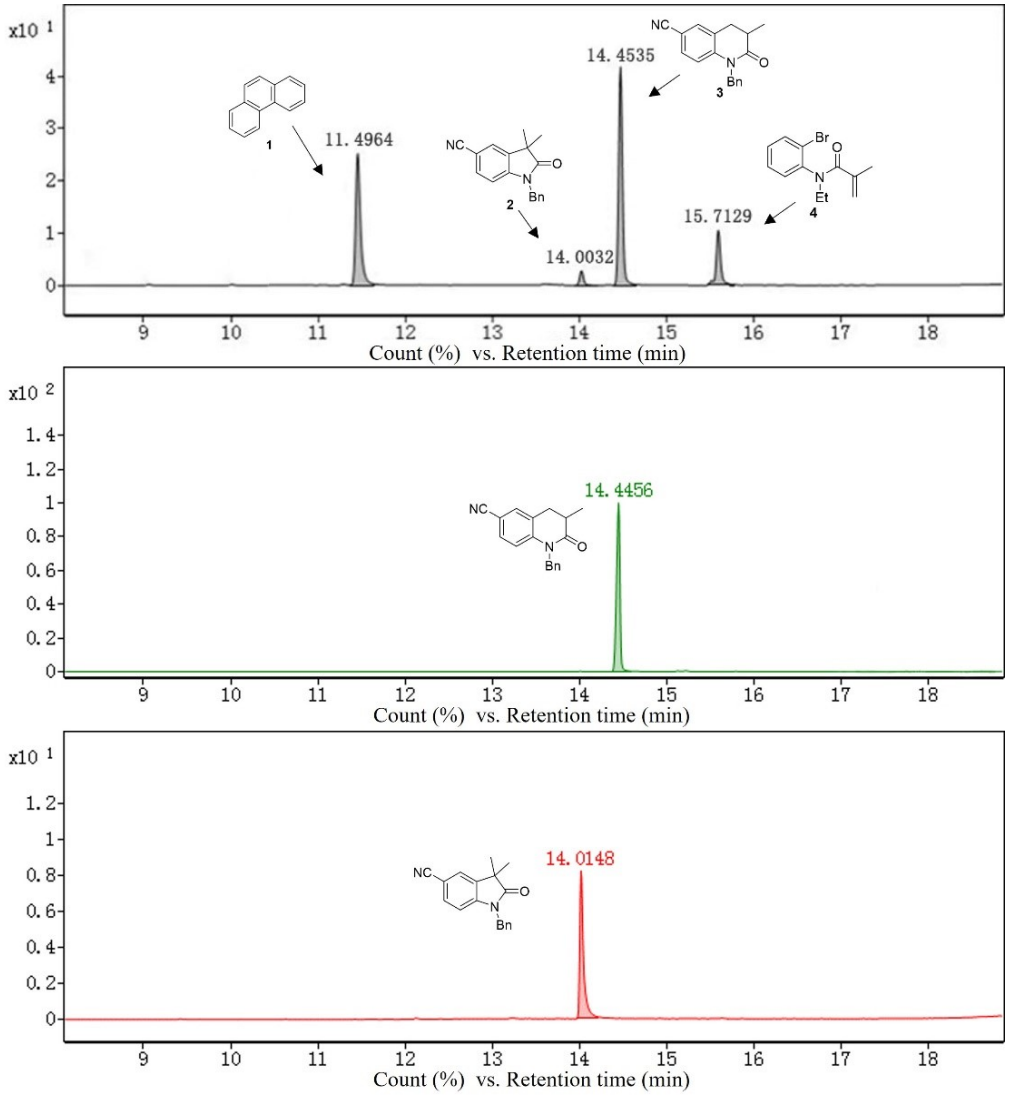


Figure S3-2 Crude GC(MS) analysis of **2l**.

Peak	Peak area	Peak area percentage	Peak height	Peak width	Retention time
1	2460537.3	29.52	1144088.97	0.1783	11.4964
2	551307.3	6.61	304267.49	0.1189	14.0032
3	8335738.06	100	4730953.78	0.1263	14.4535
4	6639317.87	79.65	2412384.76	0.3194	15.7129

The chromatogram shows a trace of the five-membered ring product. According to the crude GC(MS) chromatogram, the crude reaction solution contained traces of the 5-exo product in < 3 % yield.

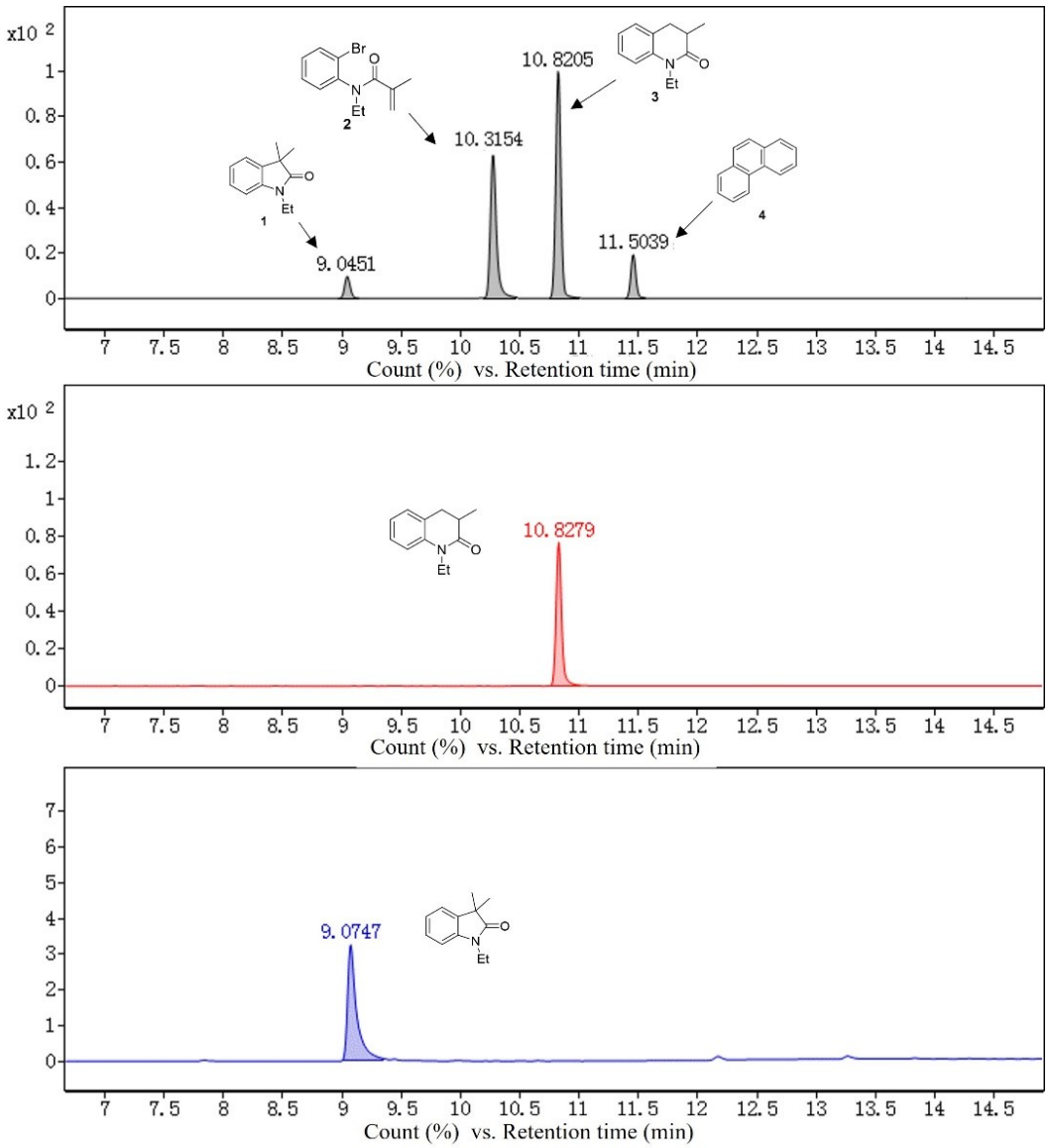


Figure S3-3 Crude GC(MS) analysis of **2q**.

Peak	Peak area	Peak area percentage	Peak height	Peak width	Retention time
1	1479933	9.42	474393.77	0.1185	9.0451
2	15073214.7	75.24	3148849.75	0.2675	10.3145
3	11341665.51	100	5002328.41	0.1708	10.8205
4	2758608.85	18.3	949435.87	0.2006	11.5039

The chromatogram shows a trace of the five-membered ring product. According to the crude GC(MS) chromatogram, the crude reaction solution contained traces of the 5-exo product in < 6 % yield.

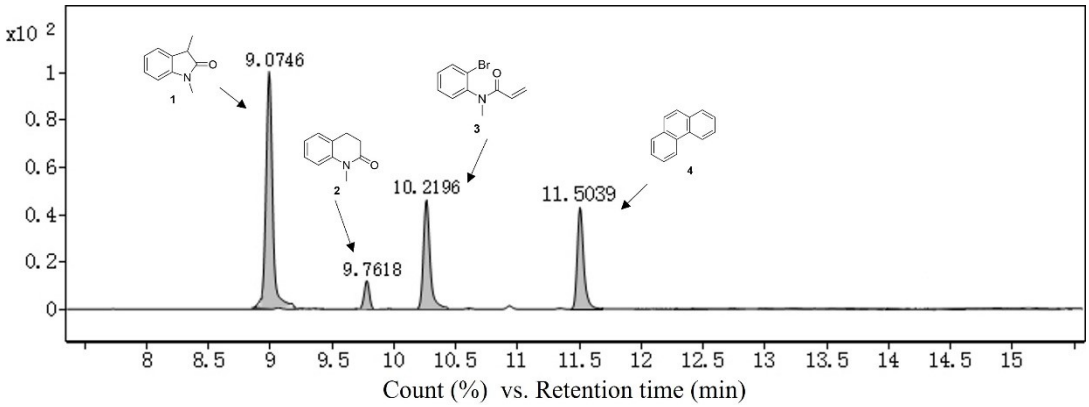


Figure S3-4 Crude GC(MS) analysis of **3t**.

Peak	Peak area	Peak area percentage	Peak height	Peak width	Retention time
1	17787319.28	100	4831198.53	0.4163	9.0746
2	1745283.32	8.8	593950.91	0.1187	9.7618
3	7453648.92	41.91	2092121.75	0.2229	10.2196
4	7889890.53	45.35	2217830.54	0.2016	11.5039

The chromatogram shows a trace of the five-membered ring product, according to the crude GC(MS) chromatogram, the crude reaction solution contained traces of the 6-endo product in < 6 % yield.

7.2 The crude H-NMR spectra for 6-endo products

The crude ^{1}H NMR was compared with the characteristic peaks of the previously reported 5-exo products. In the crude ^{1}H NMR spectra, no distinct peaks characteristic of the pentacyclic product were found, indicating that only trace or no 5-exo by-products were produced in the reaction.

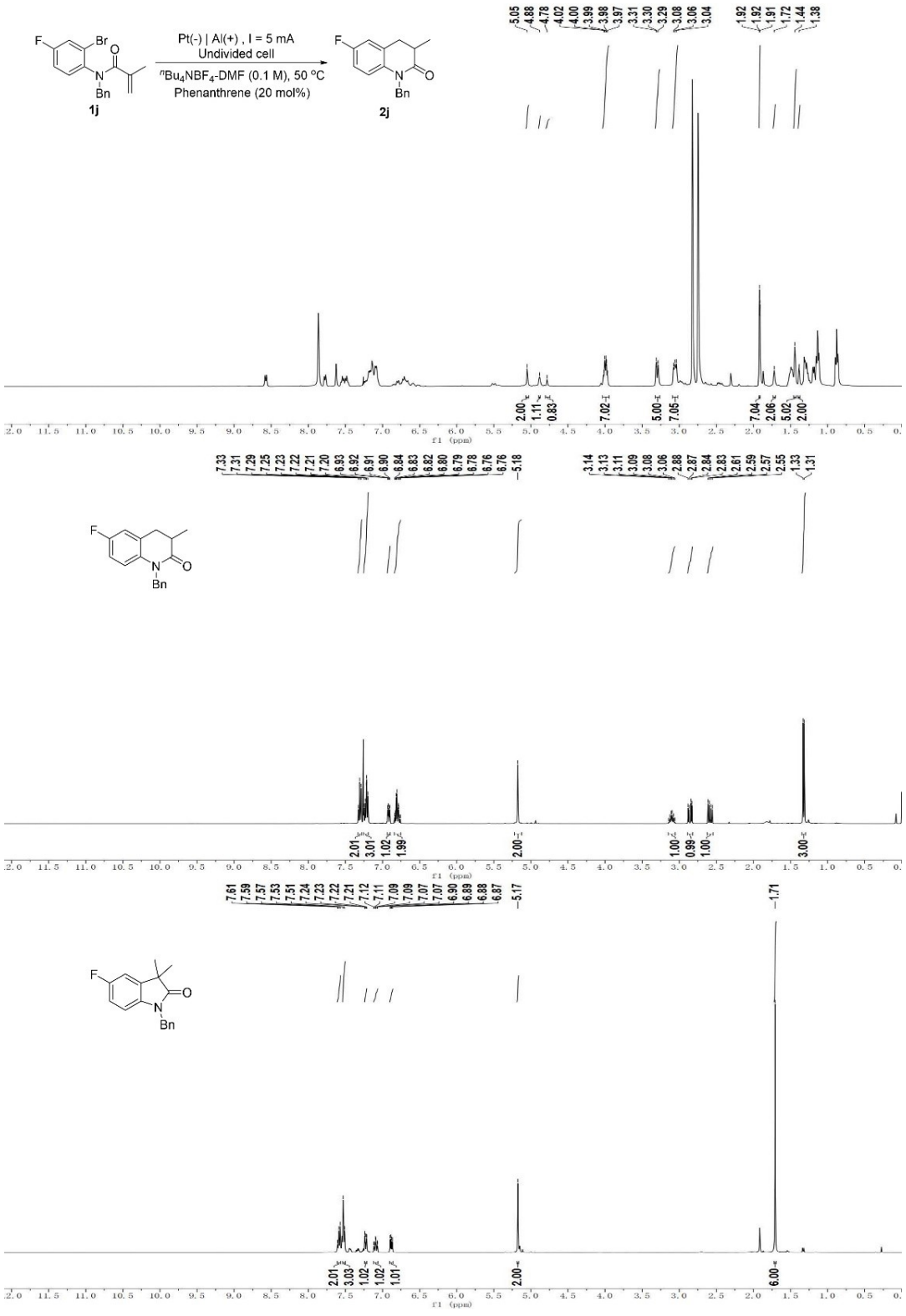


Figure S4-1: Crude ^{1}H NMR spectra of product **2j**.

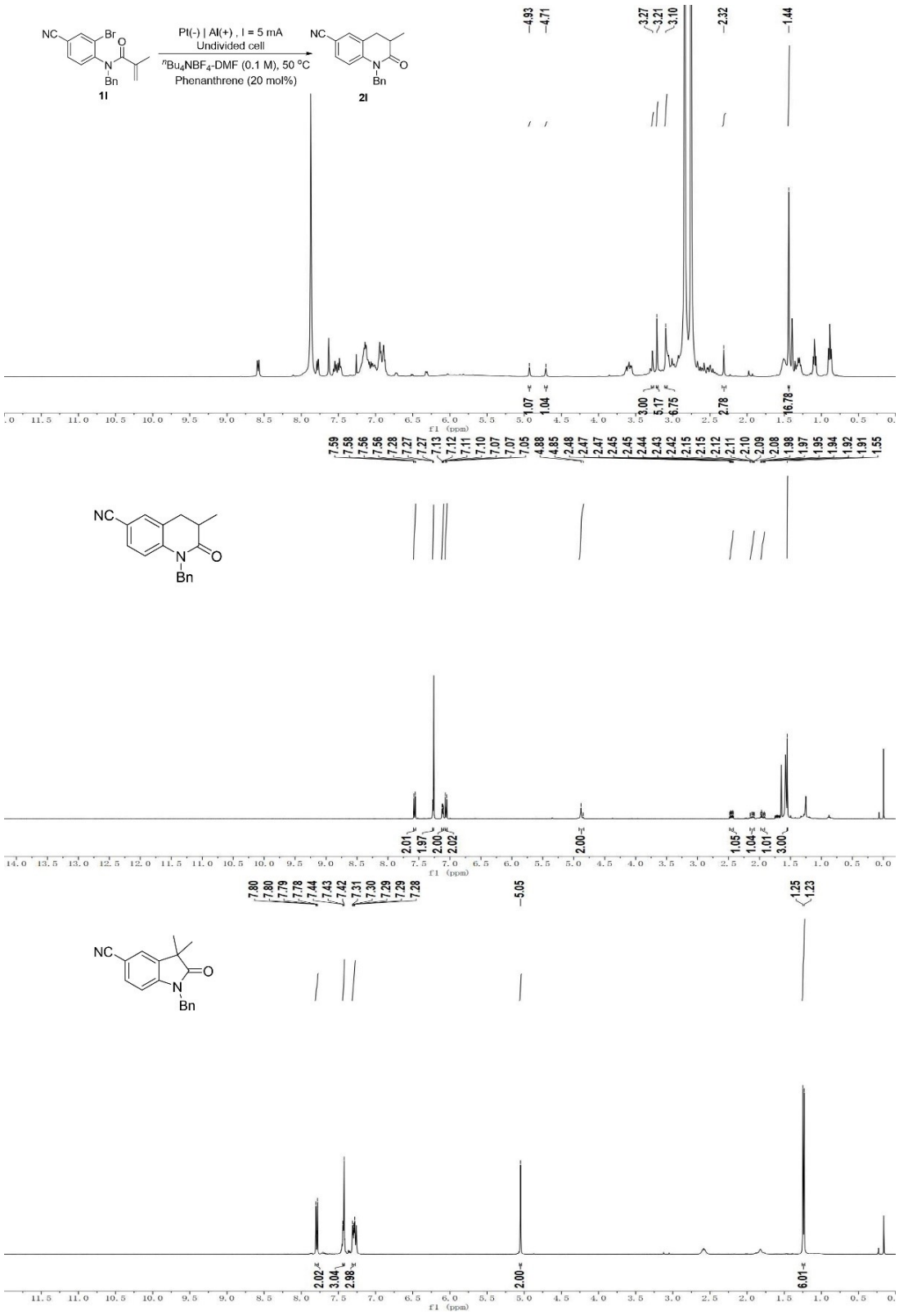


Figure S4-2: Crude ^{1}H NMR spectra of product **2l**.

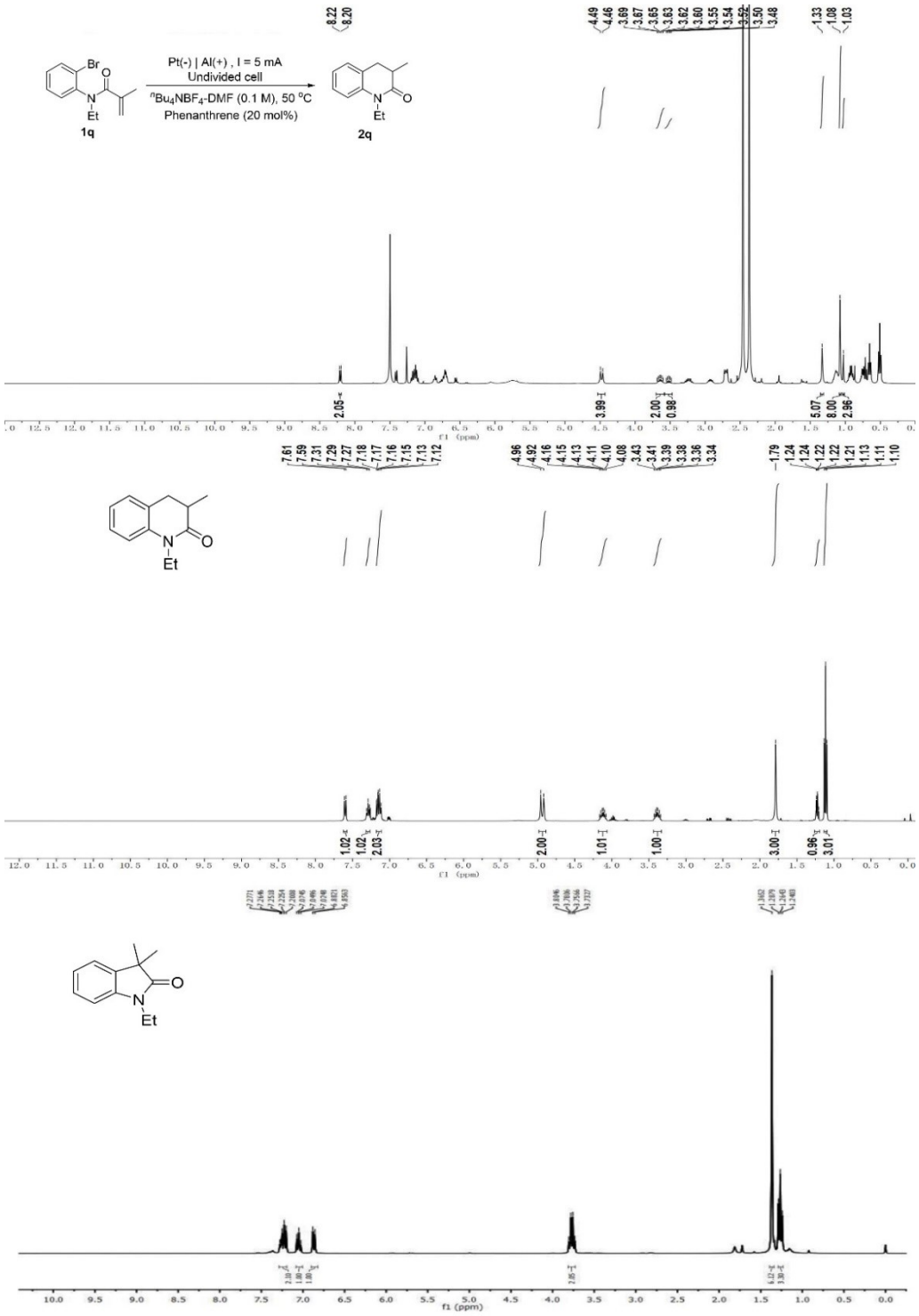
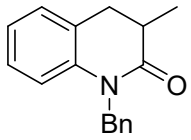


Figure S4-3: Crude ^{1}H NMR spectra of product **2q**.

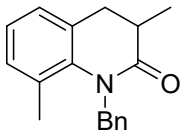
References:

3 Q. Gui, L. Hu, X. Chen, J. Liu and Z. Tan, Synthesis of Oxindoles via Iron-Mediated Hydrometallation-Cyclization of N-Arylacrylamides, *Asian J. Org. Chem.*, 2015, **4**, 870-874.

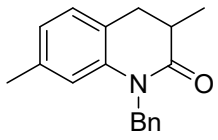
8. Characterization Data for the Electrolysis Products



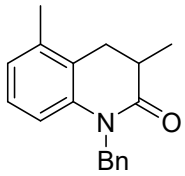
1-benzyl-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (**2a**), colorless oily (0.062g, 82%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.26 – 7.18 (m, 4H), 7.14 – 7.08(m, 1H), 7.03 – 6.98 (m, 1H), 6.91 – 6.87 (m, 1H), 5.27 – 5.14 (m, 2H), 3.18 – 3.08 (m, 1H), 2.88 (dd, *J* = 15.6, 5.4 Hz, 1H), 2.61 (dd, *J* = 15.6, 7.2 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 170.13, 139.09, 137.16, 131.29, 128.84, 127.51, 127.19, 126.59, 126.56, 123.30, 115.81, 46.14, 39.32, 30.70, 19.62; **HRMS** (ESI, m/z) calculated for $C_{17}H_{18}NO^+$ $[M+H]^+$: 252.1383; found: 252.1384.



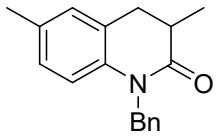
1-benzyl-3,8-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (**2b**), yellow oily (0.051 g, 65%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.22 – 7.20 (m, 2H), 7.19 – 7.17 (m, 1H), 7.14 – 7.12 (m, 2H), 7.07 – 7.05 (m, 1H), 7.03 – 7.00 (m, 2H), 5.23 (d, *J* = 15.3 Hz, 1H), 4.93 (d, *J* = 15.3 Hz, 1H), 2.92 – 2.87 (m, 1H), 2.62 (dd, *J* = 14.7, 4.4 Hz, 1H), 2.39 – 2.35 (m, 1H), 2.34 (s, 3H), 1.11 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 173.23, 140.06, 137.91, 136.50, 131.04, 128.33, 128.16, 127.79, 127.17, 124.50, 123.43, 49.66, 40.68, 31.12, 21.37, 18.21. **HRMS** (m/z) [ESI]: calculated for $C_{18}H_{19}NO^+$ $[M+H]^+$:266.1539; found: 266.1541.



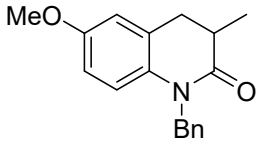
1-benzyl-3,7-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (**2c**), colorless oily (0.059 g, 75%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.33 – 7.29 (m, 2H), 7.25 – 7.22 (m, 3H), 7.10 – 7.08 (m, 1H), 6.83 (d, *J* = 8.2 Hz, 1H), 6.73 (s, 1H), 5.24 – 5.14 (m, 2H), 3.12 – 3.06 (m, 1H), 2.85 (dd, *J* = 15.6, 5.4 Hz, 1H), 2.58 (dd, *J* = 15.6, 7.3 Hz, 1H), 2.23 (s, 3H), 1.31 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 170.22, 139.04, 137.28, 128.80, 128.37, 127.12, 126.59, 126.38, 123.90, 116.50, 46.11, 39.53, 30.31, 21.52, 19.70. **HRMS** (m/z) [ESI]: calculated for $C_{18}H_{19}NO^+$ $[M+H]^+$:266.1539; found: 266.1544.



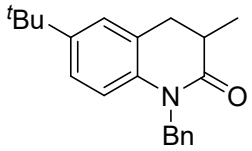
1-benzyl-3,5-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (**2d**), yellow oily (0.055 g, 70%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.25 – 7.20 (m, 3H), 7.03 – 6.98 (m, 1H), 6.88 – 6.85 (m, 1H), 6.79 – 6.76 (m, 1H), 5.44 (d, *J* = 16.2 Hz, 1H), 4.97 (d, *J* = 16.2 Hz, 1H), 3.33 –3.25 (m, 1H), 2.89 (dd, *J* = 15.7, 6.0 Hz, 1H), 2.70 (dd, *J* = 15.7, 1.9 Hz, 1H), 2.34 (s, 3H), 1.21 (d, *J* = 7.1 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.62, 138.84, 137.32, 135.17, 129.42, 128.79, 127.13, 127.02, 126.64, 125.43, 114.16, 46.34, 38.58, 27.43, 18.96, 18.18. **HRMS** (m/z) [ESI]: calculated for $C_{18}H_{19}NO^+$ $[M+H]^+$:266.1539; found: 266.1539.



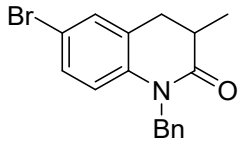
1-benzyl-3,6-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (**2e**), colorless oily (0.067 g, 85%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.32 – 7.29 (m, 2H), 7.24 – 7.21 (m, 3H), 7.02 (s, 1H), 6.93 – 6.90 (m, 1H), 6.80 – 6.78 (m, 1H), 5.19 (q, *J* = 16.2 Hz, 2H), 3.12 – 3.06 (m, 1H), 2.86 (dd, *J* = 15.6, 5.4 Hz, 1H), 2.60 (dd, *J* = 15.6, 7.1 Hz, 1H), 2.29 (s, 3H), 1.32 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 169.93, 137.22, 136.57, 132.76, 131.13, 128.76, 127.84, 127.28, 127.10, 126.58, 115.67, 46.01, 39.37, 30.67, 20.74, 19.65. **HRMS** (m/z) [ESI]: calculated for $C_{18}H_{19}NO^+$ $[M+H]^+$:266.1539; found: 266.1543.



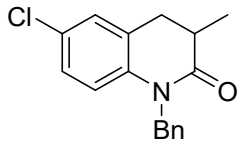
1-benzyl-6-methoxy-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (**2f**), yellow oily (0.063 g, 75%). Petroleum ether/ethyl acetate = 20/1-8/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.31 – 7.27 (m, 2H), 7.24 – 7.20 (m, 3H), 6.82 – 6.75 (m, 2H), 6.64 – 6.60 (m, 1H), 5.22 – 5.11 (m, 2H), 3.75 (s, 3H), 3.13 – 3.04 (m, 1H), 2.85 (dd, *J* = 15.6, 5.3 Hz, 1H), 2.57 (dd, *J* = 15.6, 7.4 Hz, 1H), 1.31 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 155.55, 137.16, 132.83, 132.52, 130.69, 128.72, 127.07, 126.53, 116.60, 112.83, 111.46, 55.49, 46.11, 39.22, 30.80, 19.39. **HRMS** (m/z) [ESI]: calculated for $C_{18}H_{19}NO_2Na^+$ $[M+Na]^+$:304.1308; found: 304.1304.



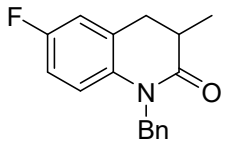
1-benzyl-6-(tert-butyl)-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (**2g**), colorless oily (0.059 g, 65%), Petroleum ether/ethyl acetate = 20/1- 8/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.32 – 7.29 (m, 2H), 7.25 – 7.23 (m, 3H), 7.21 – 7.20 (m, 1H), 7.13 – 7.11 (m, 1H), 6.82 (d, *J* = 8.5 Hz, 1H), 5.24 (d, *J* = 16.1 Hz, 1H), 5.11 (d, *J* = 16.1 Hz, 1H), 3.15 – 3.09 (m, 1H), 2.89 (dd, *J* = 15.6, 5.5 Hz, 1H), 2.62 (dd, *J* = 15.6, 6.6 Hz, 1H), 1.33 (d, *J* = 7.0 Hz, 3H), 1.28 (s, 9H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 170.05, 146.18, 137.38, 136.61, 128.81, 127.14, 126.64, 124.23, 123.68, 115.35, 46.22, 39.40, 34.38, 31.47, 31.08, 19.90. **HRMS** (m/z) [ESI]: calculated for $C_{21}H_{26}NO^+$ $[M+H]^+$:308.2009; found: 308.2012.



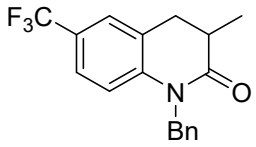
1-benzyl-6-bromo-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (**2h**), colorless oily (0.048 g, 71%), Petroleum ether/ethyl acetate = 20/1- 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.32 – 7.28 (m, 2H), 7.23 – 7.20 (m, 3H), 7.13 – 7.09 (m, 1H), 7.02 – 6.99 (m, 1H), 6.90 – 6.88 (m, 1H), 5.25 – 5.15 (m, 2H), 3.16 – 3.10 (m, 1H), 2.88 (dd, *J* = 15.6, 5.4 Hz, 1H), 2.61 (dd, *J* = 15.6, 7.2 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 170.14, 139.11, 137.17, 131.31, 128.85, 127.52, 127.21, 126.60, 126.57, 123.31, 115.83, 46.16, 39.34, 30.71, 19.63.**HRMS** (m/z) [ESI]: calculated for $C_{17}H_{17}BrNO^+$ $[M+H]^+$:330.0488; found: 330.0481.



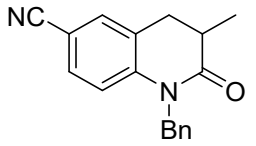
1-benzyl-6-chloro-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (**2i**), colorless oily (0.060 g, 70%), Petroleum ether/ethyl acetate = 20/1- 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.23 – 7.16 (m, 4H), 7.08 – 7.03 (m, 1H), 6.83 – 6.77 (m, 1H), 5.22 – 5.16 (m, 2H), 3.14 – 3.06 (m, 1H), 2.86 (dd, *J* = 15.7, 5.4 Hz, 1H), 2.59 (dd, *J* = 15.7, 7.5 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.72, 137.67, 136.67, 133.09, 129.40, 128.92, 127.38, 127.33, 126.62, 126.56, 117.05, 46.10, 38.99, 30.59, 19.36. **HRMS** (m/z) [ESI]: calculated for $C_{17}H_{17}ClNO$ $[M+H]^+$:286.0993; found: 286.0992.



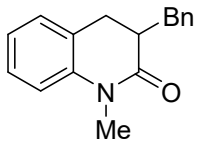
1-benzyl-6-fluoro-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (**2j**), colorless oily (0.048 g, 55%), Petroleum ether/ethyl acetate = 20/1- 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.33 – 7.28 (m, 2H), 7.26 – 7.19 (m, 3H), 6.94 – 6.90 (m, 1H), 6.84 – 6.75 (m, 2H), 5.18 (s, 2H), 3.15 – 3.06 (m, 1H), 2.86 (dd, *J* = 15.7, 5.3 Hz, 1H), 2.58 (dd, *J* = 15.7, 7.9 Hz, 1H), 1.32 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.70, 158.86 (d, *J* = 243.8 Hz), 136.85, 135.25 (d, *J* = 2.6 Hz), 133.47 (d, *J* = 7.2 Hz), 128.90, 127.32, 126.56, 116.98 (d, *J* = 8.2 Hz), 113.70 (d, *J* = 22.5 Hz), 113.54 (d, *J* = 23.2 Hz), 46.30, 39.03, 30.59, 19.22; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -120.13. **HRMS** (m/z) [ESI]: calculated for $C_{17}H_{16}FNONa^+$ $[M+Na]^+$:292.1108; found: 292.1103.



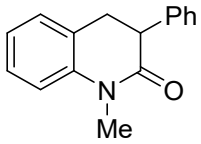
1-benzyl-3-methyl-6-(trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (**2k**), light yellow oily (0.057 g, 60%), Petroleum ether/ethyl acetate = 25/1- 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*)δ 7.50 (s, 1H), 7.45 – 7.36 (m, 3H), 7.34 – 7.25 (m, 3H), 7.05 – 7.01 (m, 1H), 5.33 – 5.24 (m, 2H), 3.30 – 3.21 (m, 1H), 2.97 (dd, *J* = 15.8, 5.5 Hz, 1H), 2.71 (dd, *J* = 15.8, 7.3 Hz, 1H), 1.42 (d, *J* = 7.0 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.89, 141.94, 136.46, 131.73, 129.01, 127.51, 126.56, 124.73 (d, *J* = 269.88 Hz) 124.84 (d, *J* = 3.85 Hz) 123.66 (d, *J* = 3.68 Hz), 115.78, 46.13, 38.90, 30.67, 19.45; **^{19}F NMR** (376 MHz, Chloroform-*d*) δ -62.01. **HRMS** (m/z) [ESI]: calculated for $C_{18}H_{17}F_3NO^+$ $[M+H]^+$:320.1257; found: 320.1256.



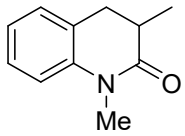
1-benzyl-3-methyl-2-oxo-1,2,3,4-tetrahydroquinoline-6-carbonitrile (**2l**), colorless oily (0.037 g, 45%), Petroleum ether/ethyl acetate = 25/1- 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.59 – 7.55 (m, 2H), 7.28 – 7.26 (m, 2H), 7.13 – 7.10 (m, 2H), 7.08 – 7.05 (m, 2H), 4.88 – 4.85 (m, 2H), 2.48 – 2.42 (m, 1H), 2.15 – 2.08 (m, 1H), 1.98 – 1.92 (m, 1H), 1.55 (s, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 169.69, 142.84, 136.05, 133.19, 131.98, 130.27, 129.07, 128.85, 127.85, 127.63, 127.58, 126.48, 118.92, 53.04, 38.66, 30.45, 19.33. **HRMS** (m/z) [ESI]: calculated for $C_{18}H_{17}N_2O^+$ $[M+H]^+$:277.1335; found: 277.1334.



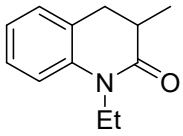
3-benzyl-1-methyl-3,4-dihydroquinolin-2(1*H*)-one (**2n**), light yellow oily (0.065 g, 63%), Petroleum ether/ethyl acetate = 20/1- 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.33 – 7.30 (m, 1H), 7.28 – 7.26 (m, 1H), 7.25 – 7.25 (m, 1H), 7.22 – 7.19 (m, 1H), 7.06 – 7.04 (m, 2H), 7.02 – 6.98 (m, 3H), 3.33 (s, 3H), 3.13 – 3.09 (m, 1H), 2.90 (dd, *J* = 13.4, 6.4 Hz, 1H), 2.74 – 2.70 (m, 1H), 2.64 – 2.58 (m, 2H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 169.43, 139.88, 138.76, 129.43, 129.06, 128.45, 127.80, 127.78, 126.52, 122.90, 114.95, 40.61, 38.29, 35.97, 29.43. **HRMS** (m/z) [ESI]: calculated for $C_{17}H_{18}NO^+$ $[M+H]^+$:252.1383; found: 252.1380.



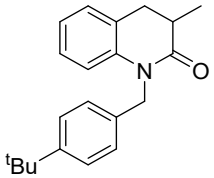
1-methyl-3-phenyl-3,4-dihydroquinolin-2(1*H*)-one (**2o**), light yellow oily (0.048 g, 67%), Petroleum ether/ethyl acetate = 20/1- 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.35 – 7.31 (m, 2H), 7.30 – 7.26 (m, 2H), 7.18 – 7.15 (m, 2H), 7.06 (d, *J* = 8.1 Hz, 1H), 7.07 – 7.05 (m, 1H), 7.02 – 6.97 (m, 1H), 4.23 (t, *J* = 7.3 Hz, 1H), 3.40 (s, 3H), 3.00 – 2.93 (m, 2H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 169.50, 141.16, 140.49, 129.28, 128.99, 128.19, 128.00, 127.94, 127.31, 123.16, 115.02, 41.61, 38.97, 29.68. **HRMS** (m/z) [ESI]: calculated for $C_{16}H_{16}NO^+$ $[M+H]^+$:238.1154; found: 238.1155



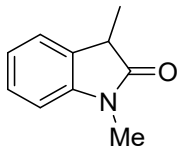
1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (**2p**), colorless oily (0.039 g, 75%), Petroleum ether/ethyl acetate = 20/1- 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.25 – 7.24 (m, 1H), 7.21 – 7.19 (m, 1H), 7.07 – 7.04 (m, 1H), 7.01 – 6.98 (m, 1H), 3.37 (s, 3H), 3.09 – 3.03 (m, 1H), 2.73 (dd, *J* = 15.8, 5.4 Hz, 1H), 2.46 (dd, *J* = 15.8, 7.6 Hz, 1H), 1.28 (d, *J* = 7.0 Hz, 3H); ^{13}C NMR (151 MHz, Chloroform-*d*) δ 170.07, 139.94, 131.20, 127.54, 126.36, 123.18, 114.93, 39.28, 30.43, 29.57, 19.41. **HRMS** (m/z) [ESI]: calculated for $C_{11}H_{14}NO^+$ $[M+H]^+$:176.1070; found: 176.1069.



1-ethyl-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (**2q**), yellow oily (0.042 g, 67%), Petroleum ether/ethyl acetate = 20/1- 15/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.62 – 7.58 (m, 1H), 7.32 – 7.26 (m, 1H), 7.18 – 7.11 (m, 2H), 4.94 (d, *J* = 16.0 Hz, 2H), 4.17 – 4.07 (m, 1H), 3.44 – 3.33 (m, 1H), 1.79 (s, 3H), 1.25 – 1.19 (m, 1H)，1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 171.40, 133.86, 131.22, 129.15, 128.16, 123.64, 118.38, 43.46, 39.26, 30.57, 20.39, 12.51. **HRMS** (m/z) [ESI]: calculated for $C_{12}H_{15}NONa^+$ $[M+Na]^+$:212.1046; found: 212.1049.



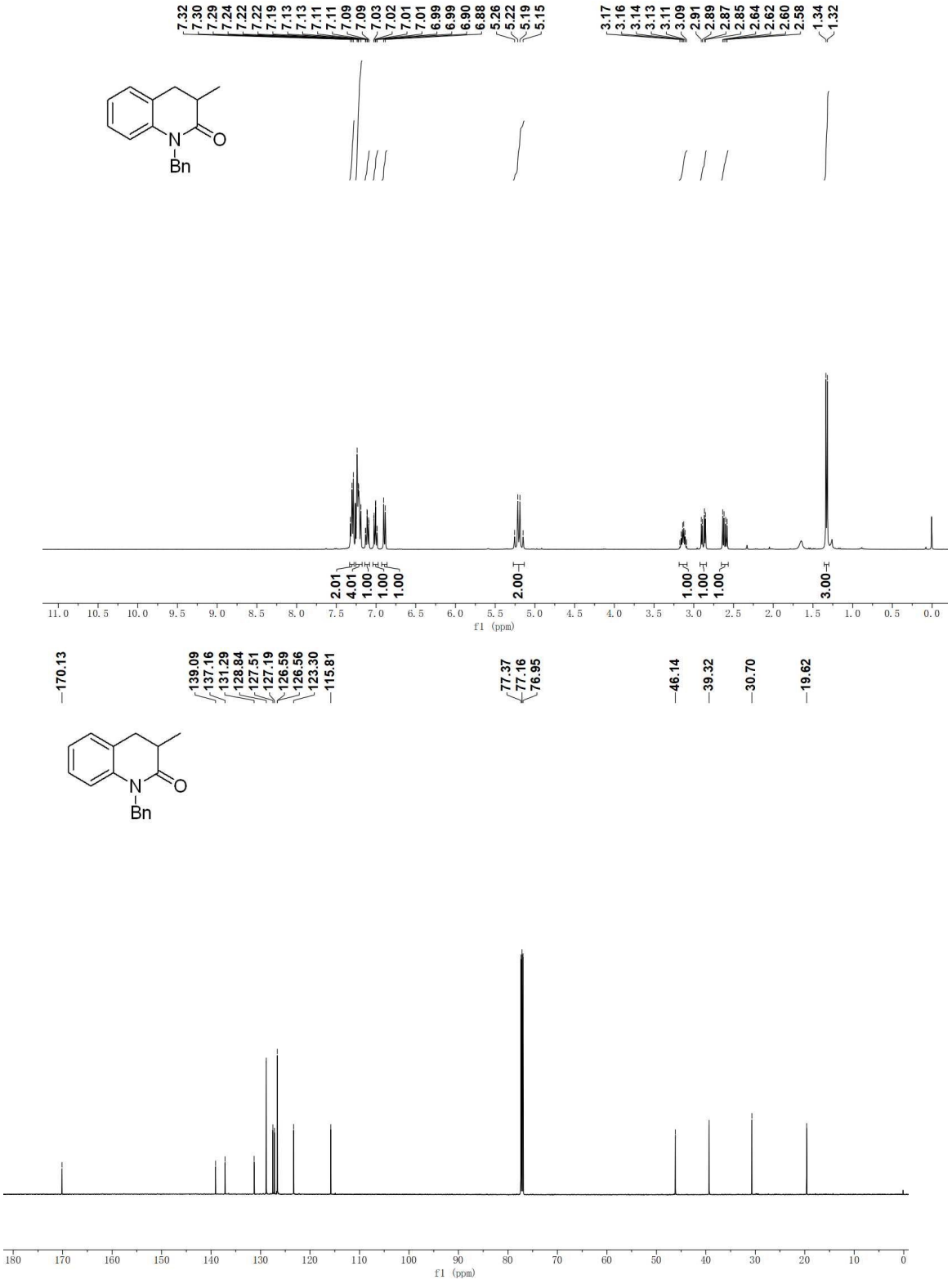
1-(4-(tert-butyl)benzyl)-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (**2r**), light yellow oily (0.055 g, 60%), Petroleum ether/ethyl acetate = 20/1- 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.45 – 7.41 (m, 2H), 7.33 – 7.28 (m, 2H), 7.26 – 7.22 (m, 2H), 7.14 – 7.11 (m, 1H), 7.07 – 7.04 (m, 1H), 5.35 – 5.21 (m, 2H), 3.29 – 3.19 (m, 1H), 2.98 (dd, *J* = 15.6, 5.4 Hz, 1H), 2.71 (dd, *J* = 15.6, 7.2 Hz, 1H), 1.44 (d, *J* = 7.0 Hz, 3H), 1.40 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 170.11, 150.02, 139.23, 134.03, 131.28, 127.52, 126.52, 126.26, 125.74, 123.24, 115.88, 45.90, 39.34, 34.55, 31.45, 30.71, 19.62. **HRMS** (m/z) [ESI]: calculated for $C_{21}H_{26}NO^+$ $[M+H]^+$:308.1936; found: 308.1937.



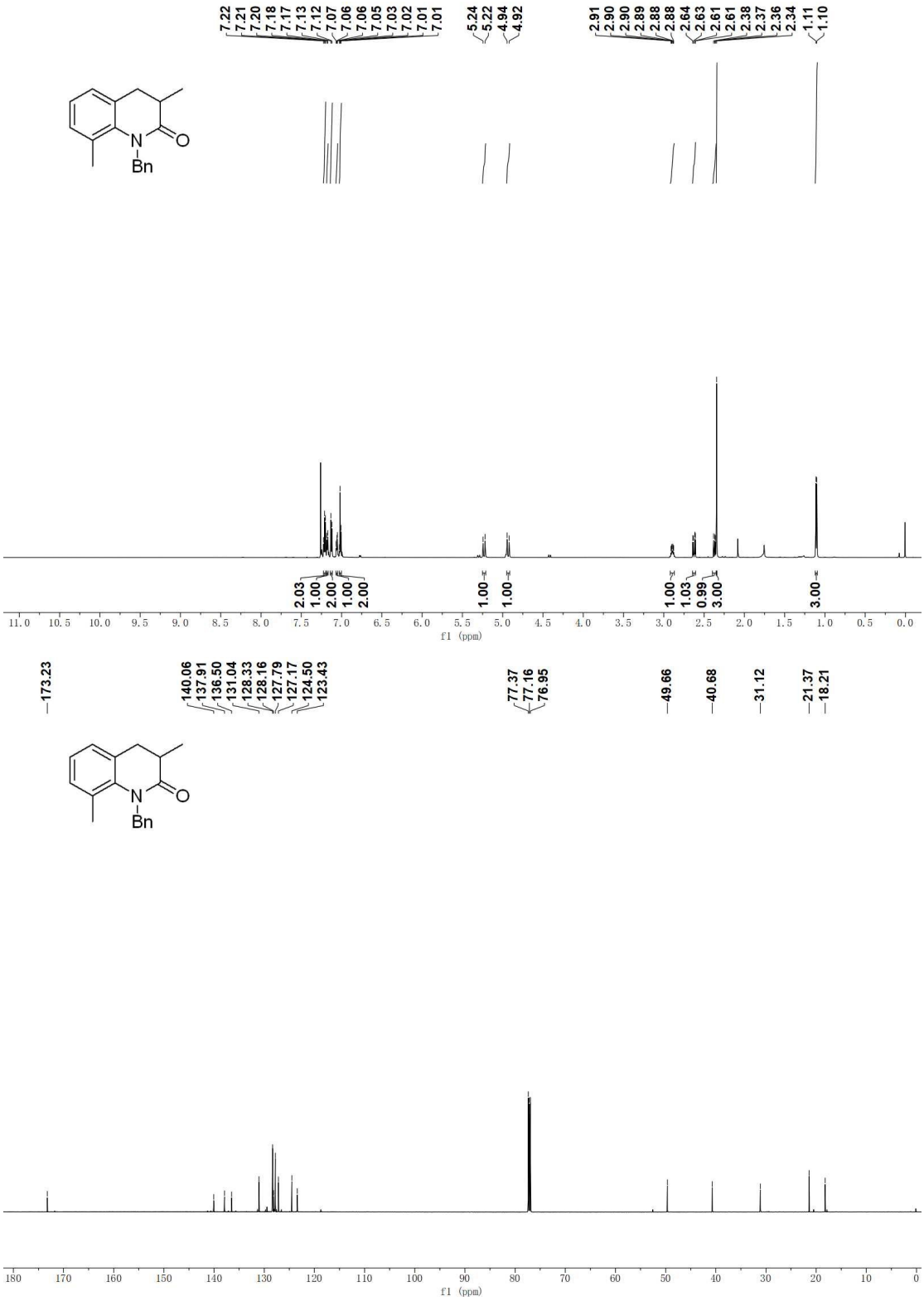
1,3-dimethylindolin-2-one (**3t**), colorless oily (0.029 g, 60%), Petroleum ether/ethyl acetate = 20/1- 10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-*d*) δ 7.30 – 7.27 (m, 1H), 7.25 – 7.22 (m, 1H), 7.07 – 7.04 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 3.43 (q, *J* = 7.6 Hz, 1H), 3.21 (s, 3H), 1.47 (d, *J* = 7.7 Hz, 3H); **^{13}C NMR** (151 MHz, Chloroform-*d*) δ 178.87, 144.09, 130.78, 128.00, 123.61, 122.53, 108.08, 40.69, 26.31, 15.47. **HRMS** (m/z) [ESI]: calculated for $C_{10}H_{12}NO^+$ $[M+H]^+$:162.0841; found: 162.0842.

9. NMR Spectra of Products

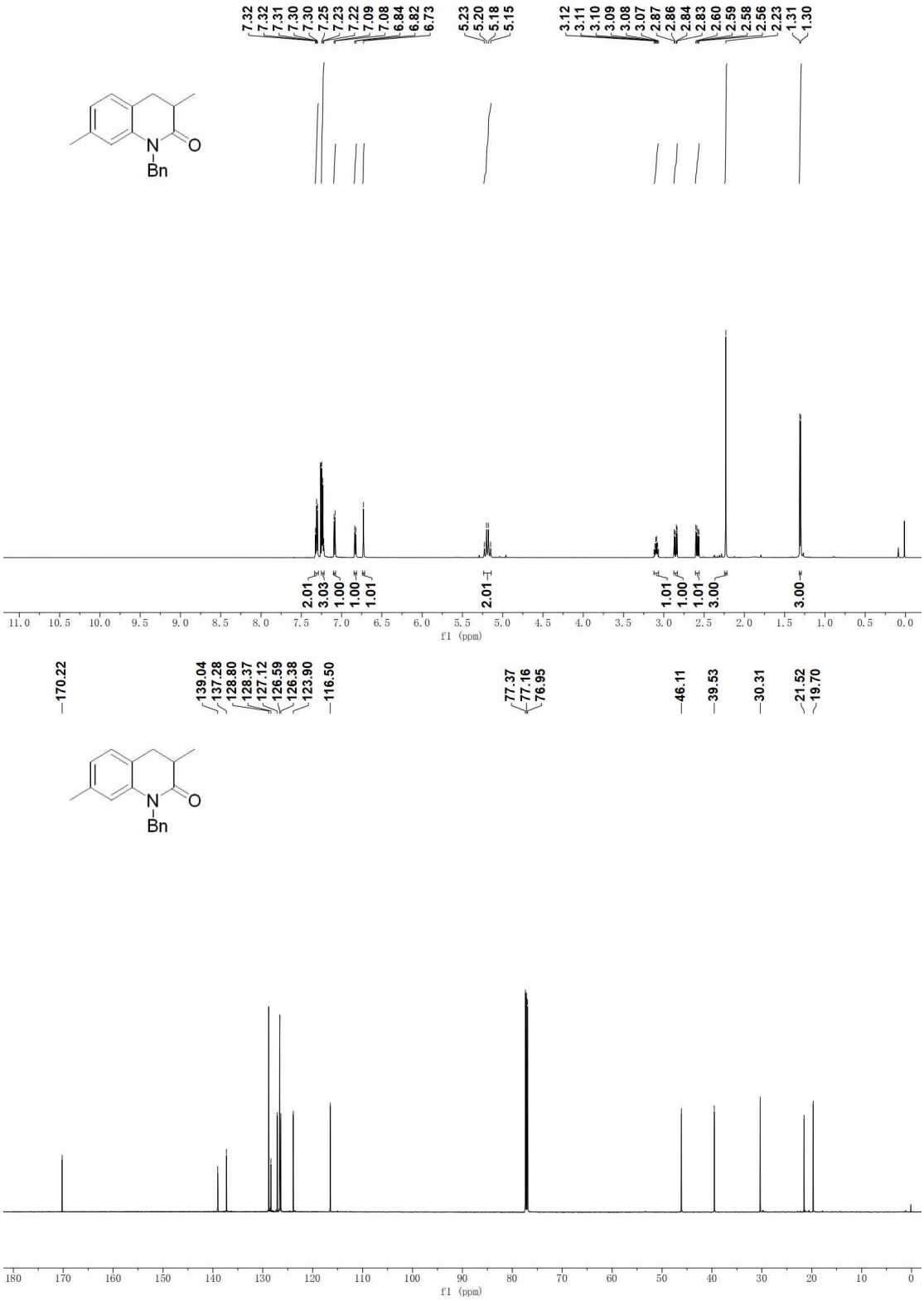
1-benzyl-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (2a)



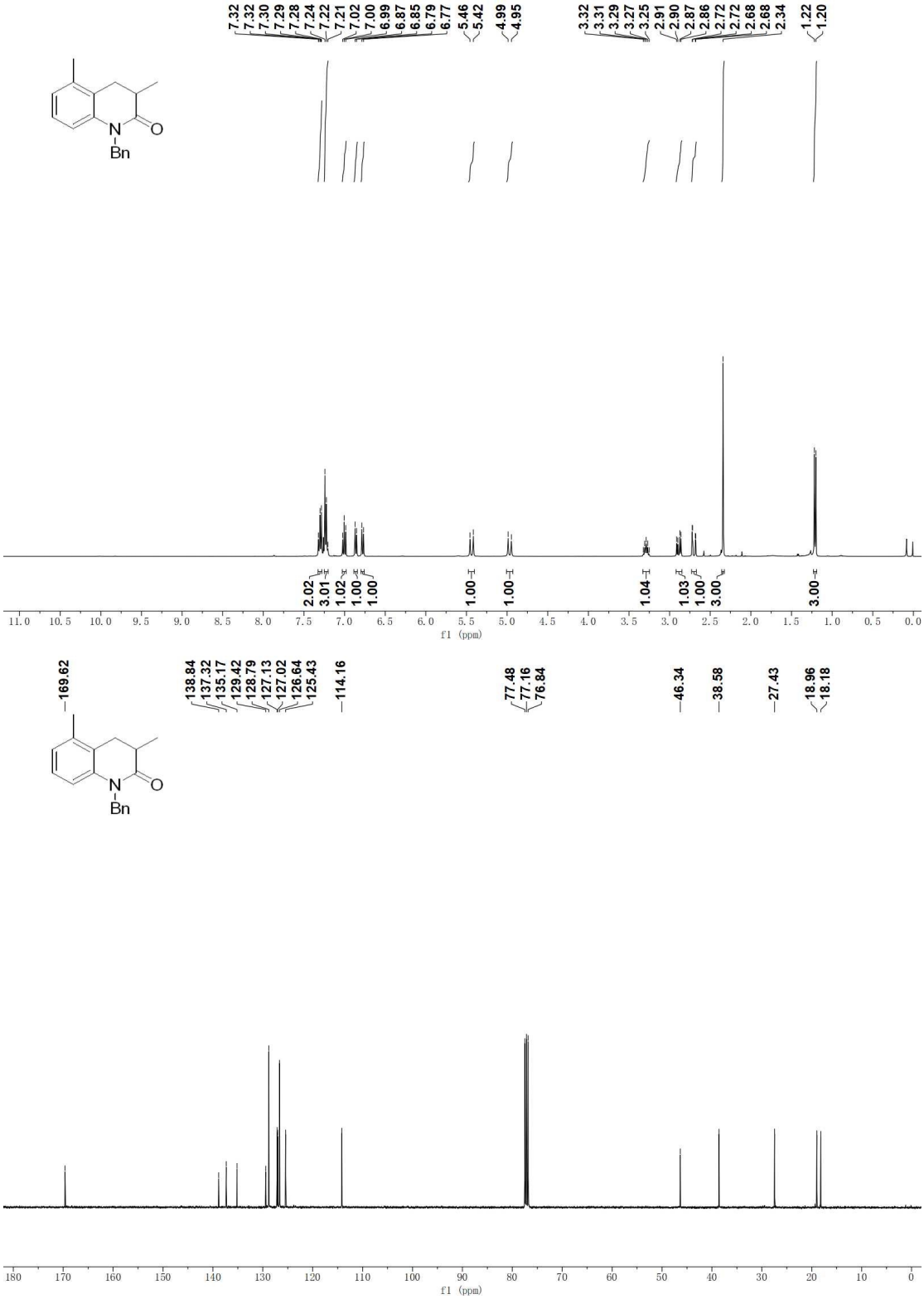
1-benzyl-3,8-dimethyl-3,4-dihydroquinolin-2(1*H*)-one(2b)



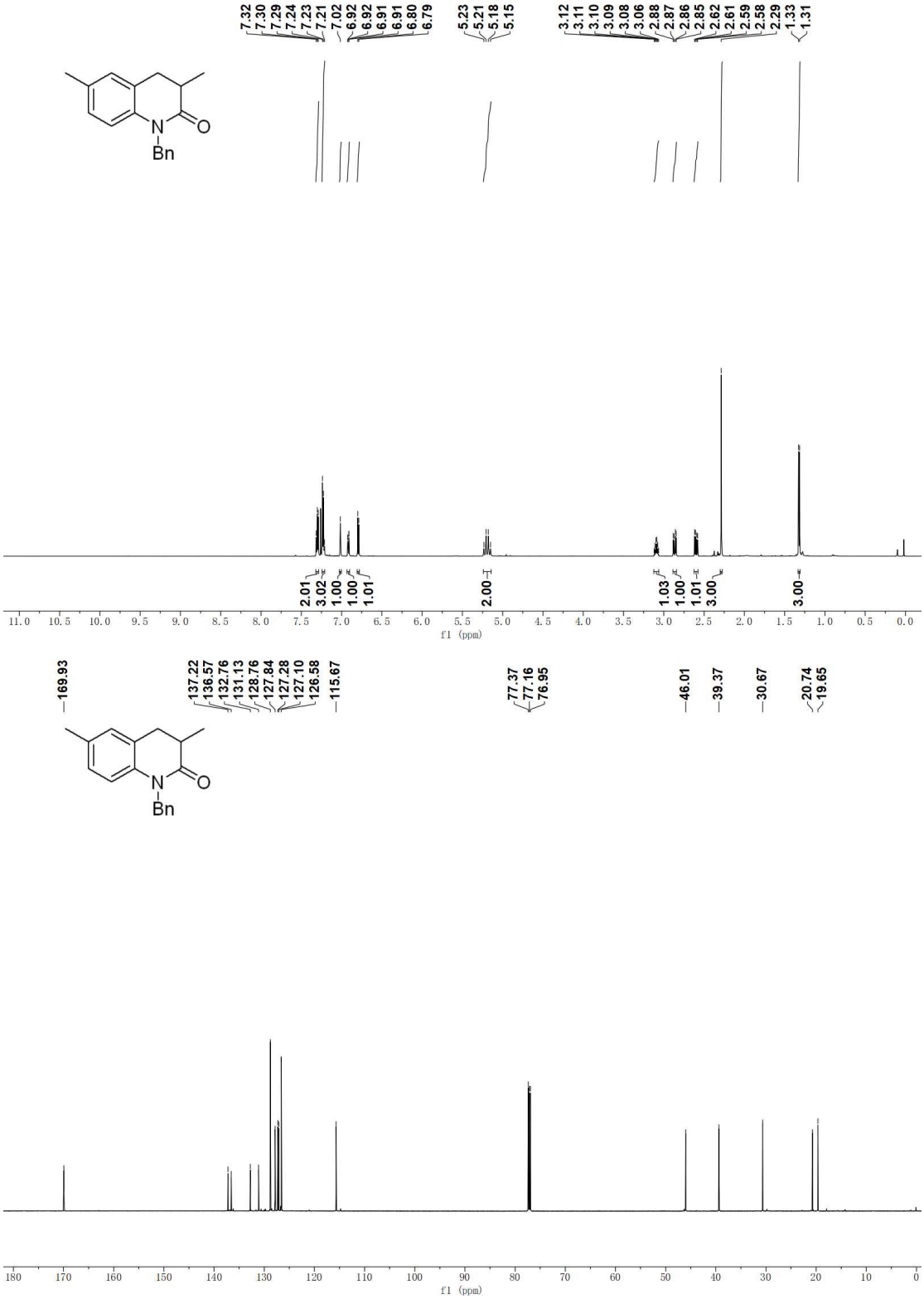
1-benzyl-3,7-dimethyl-3,4-dihydroquinolin-2(1*H*)-one(2c)



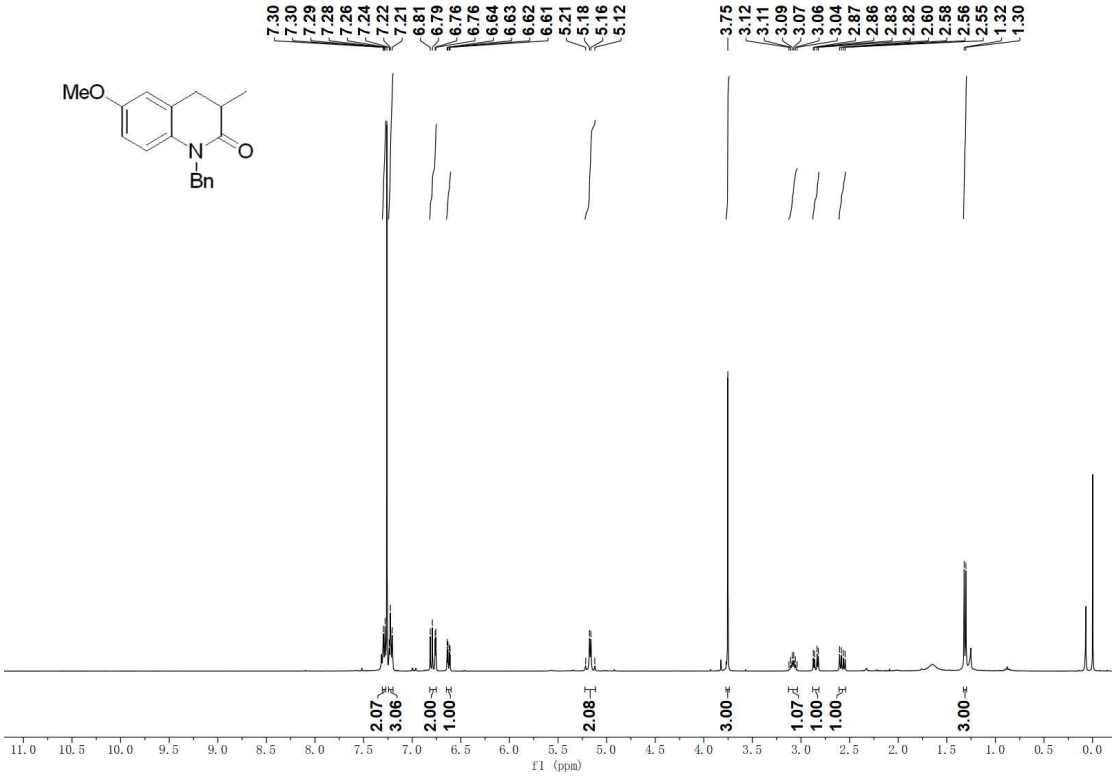
1-benzyl-3,5-dimethyl-3,4-dihydroquinolin-2(1*H*)-one(2d)

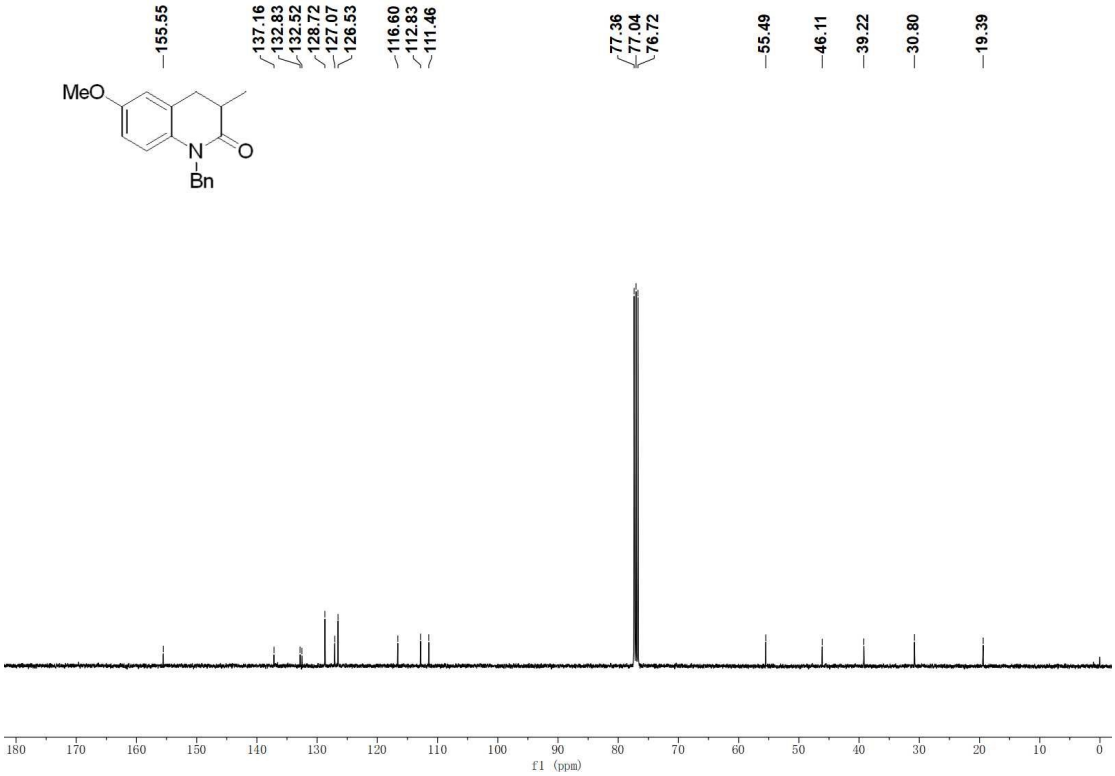


1-benzyl-3,6-dimethyl-3,4-dihydroquinolin-2(1*H*)-one(2e)

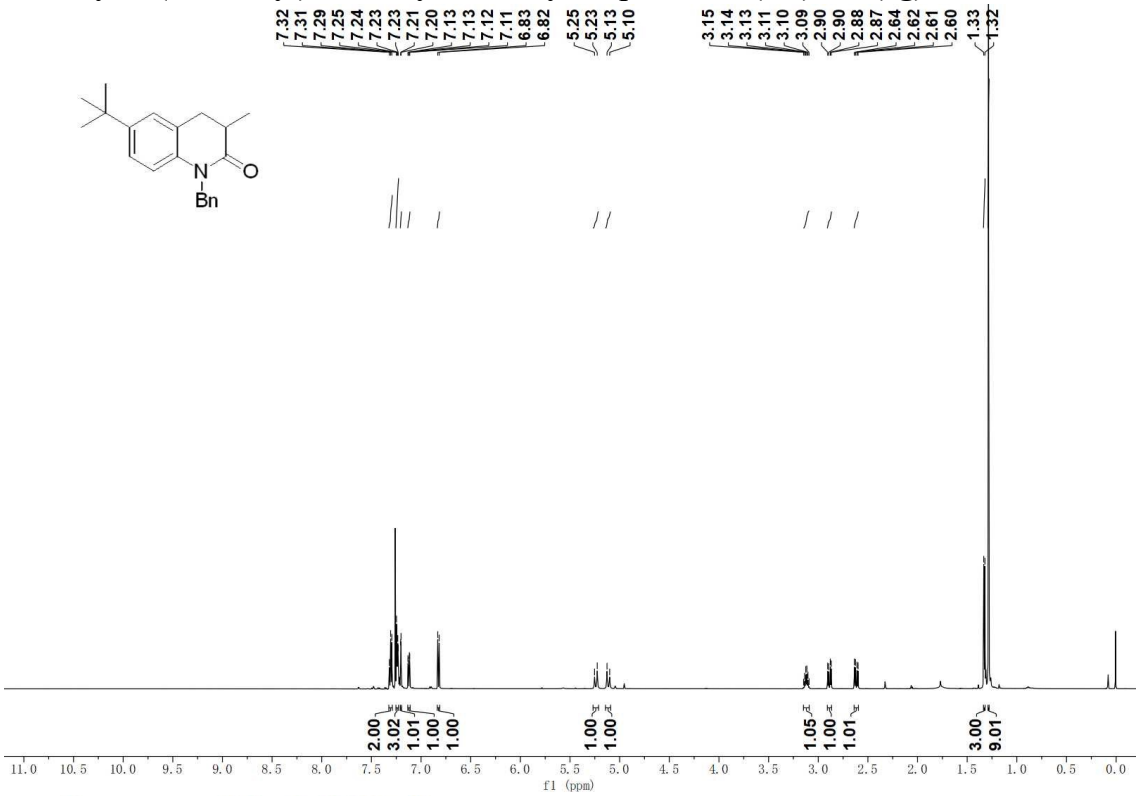


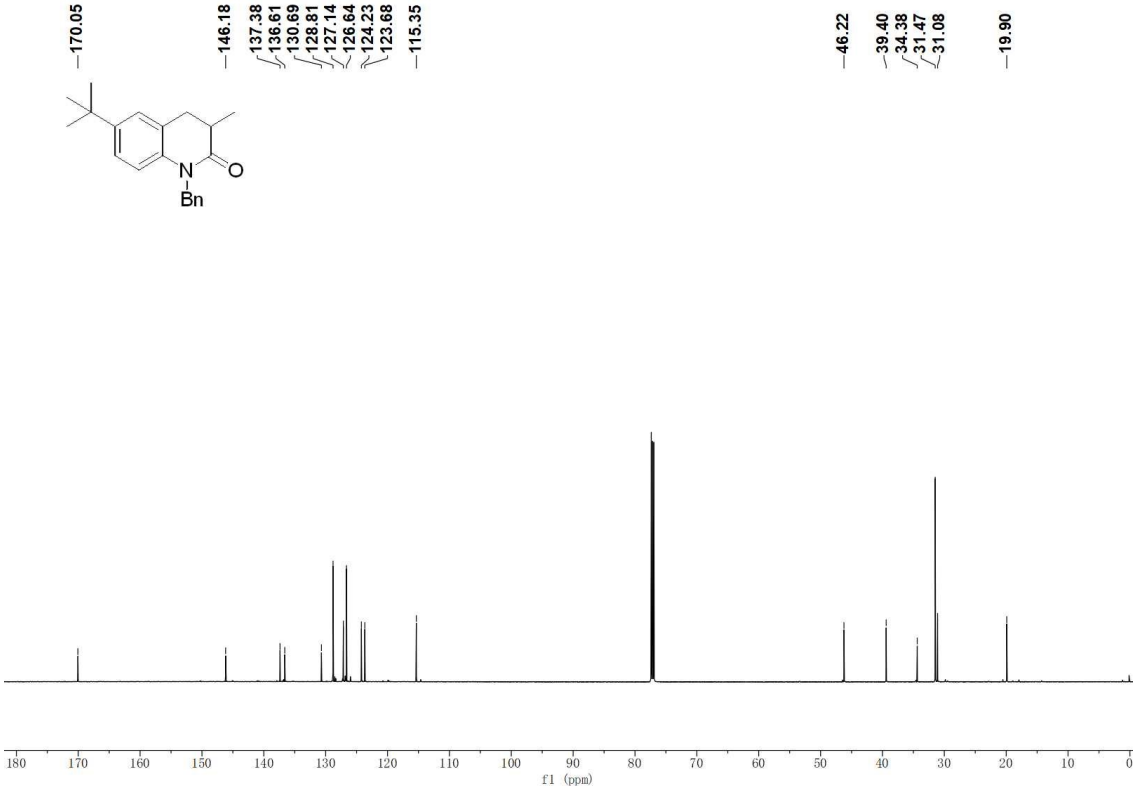
1-benzyl-6-methoxy-3-methyl-3,4-dihydroquinolin-2(1*H*)-one(2f)



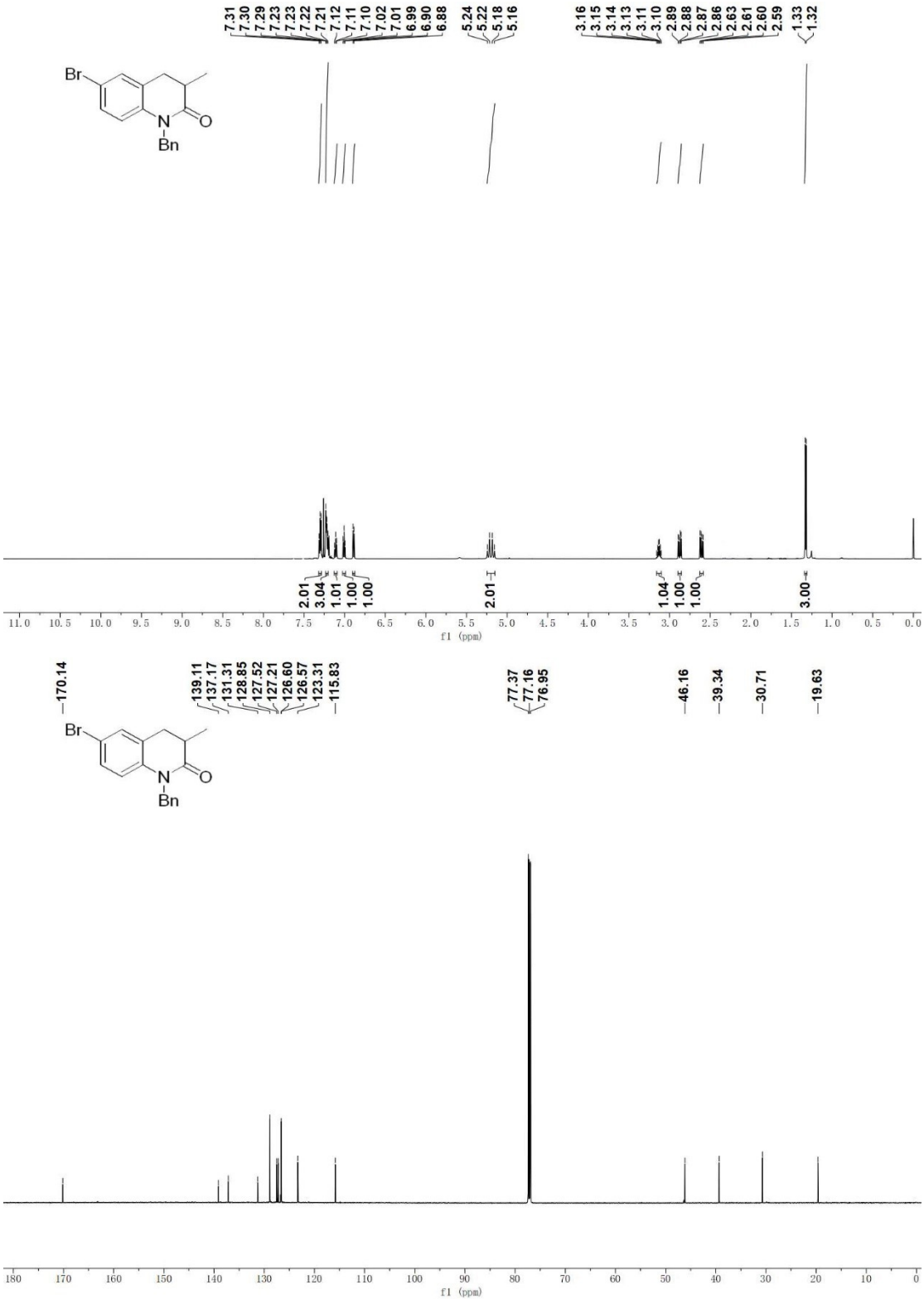


1-benzyl-6-(tert-butyl)-3-methyl-3,4-dihydroquinolin-2(1*H*)-one(2g)

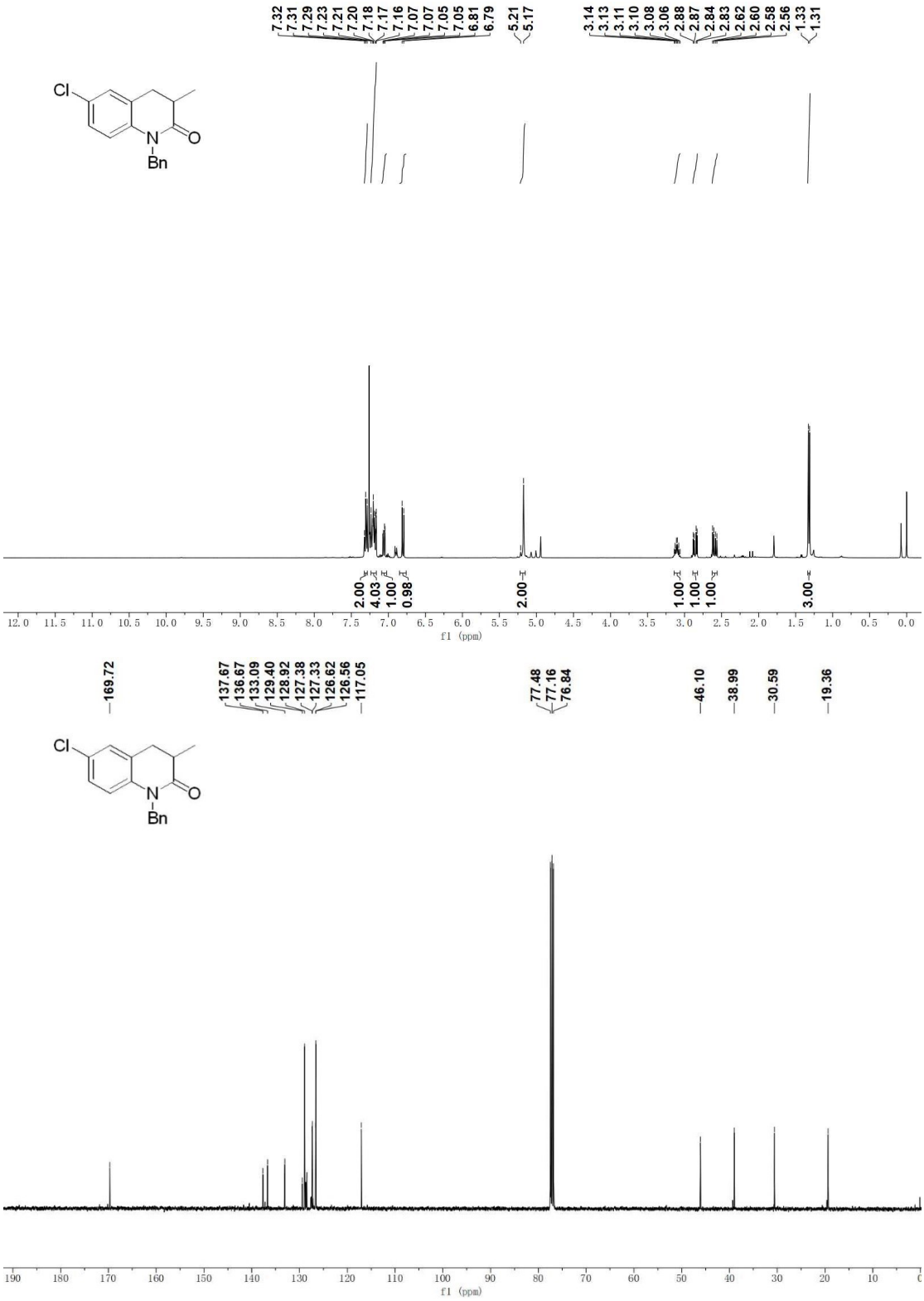




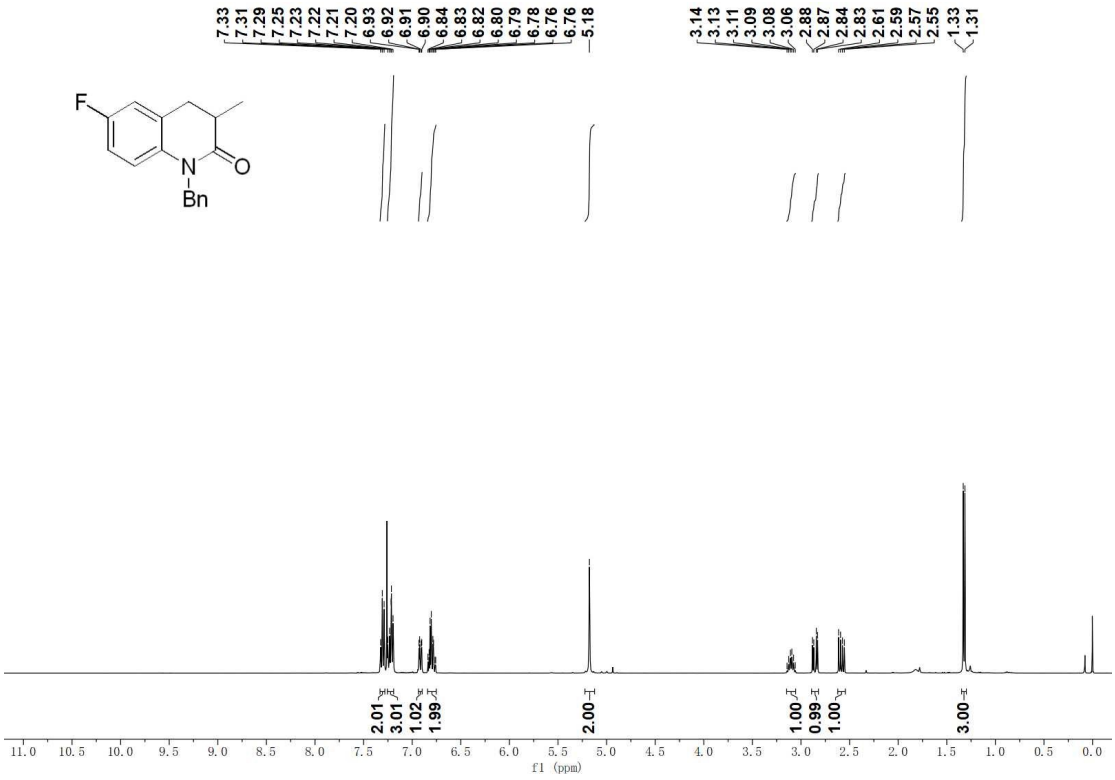
1-benzyl-6-bromo-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (2h)

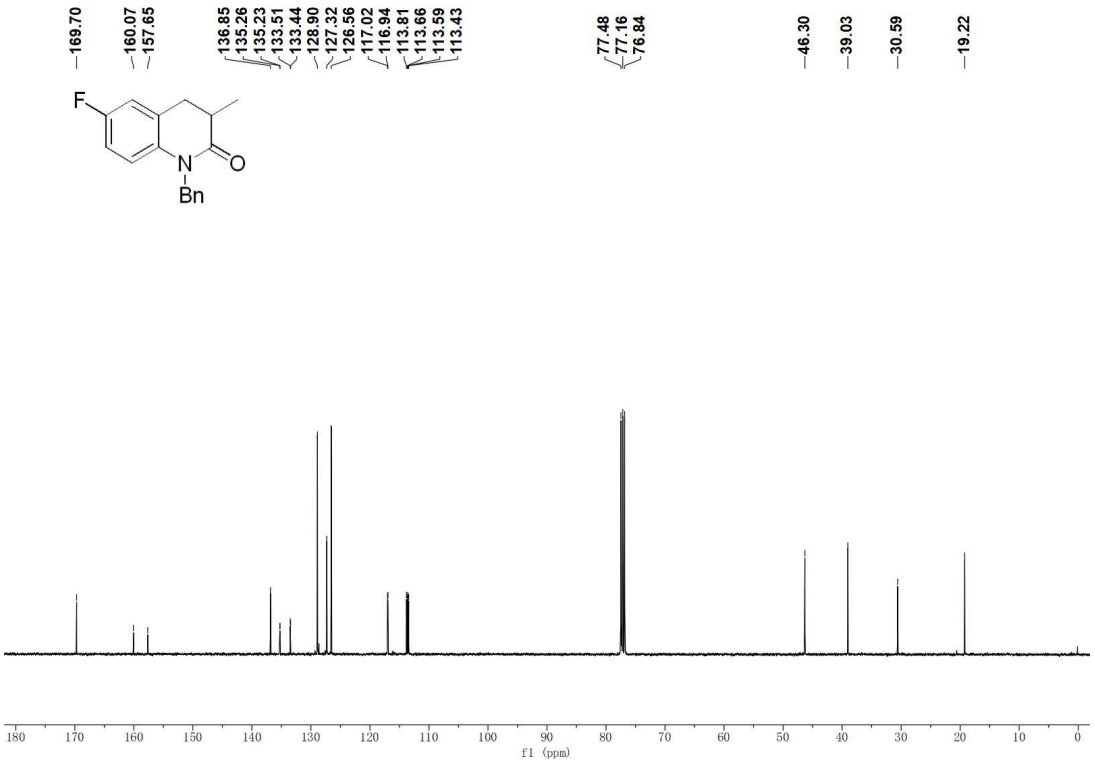


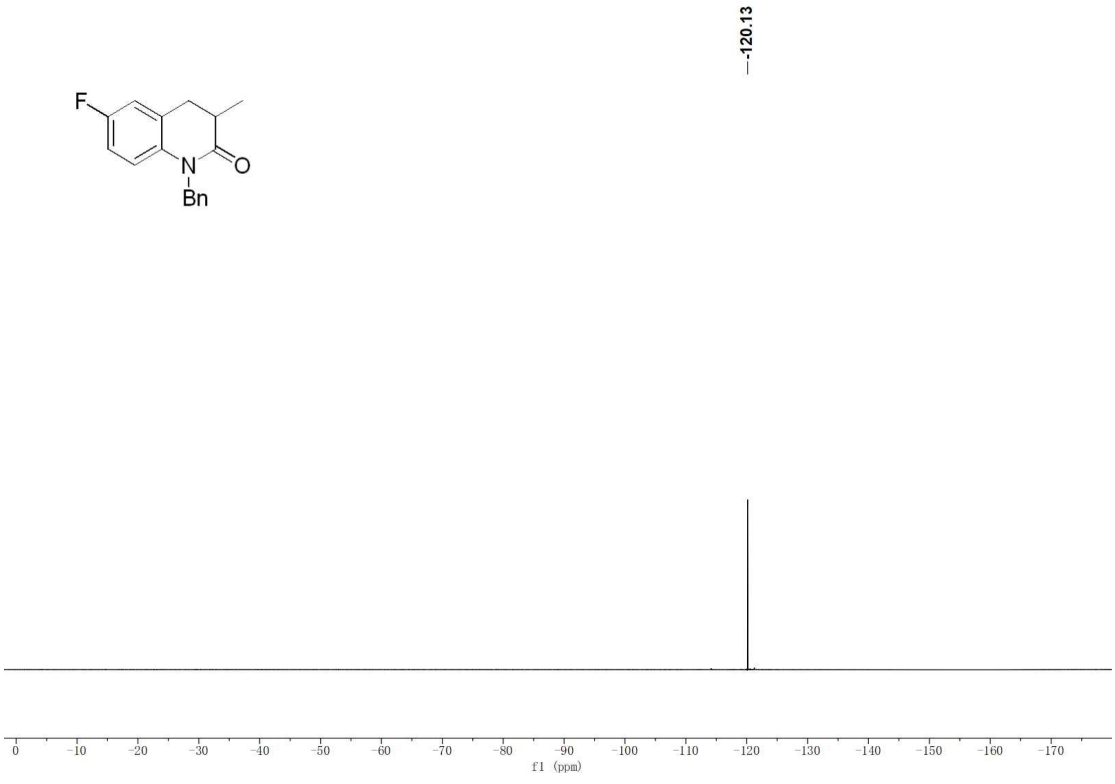
1-benzyl-6-chloro-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (2i)



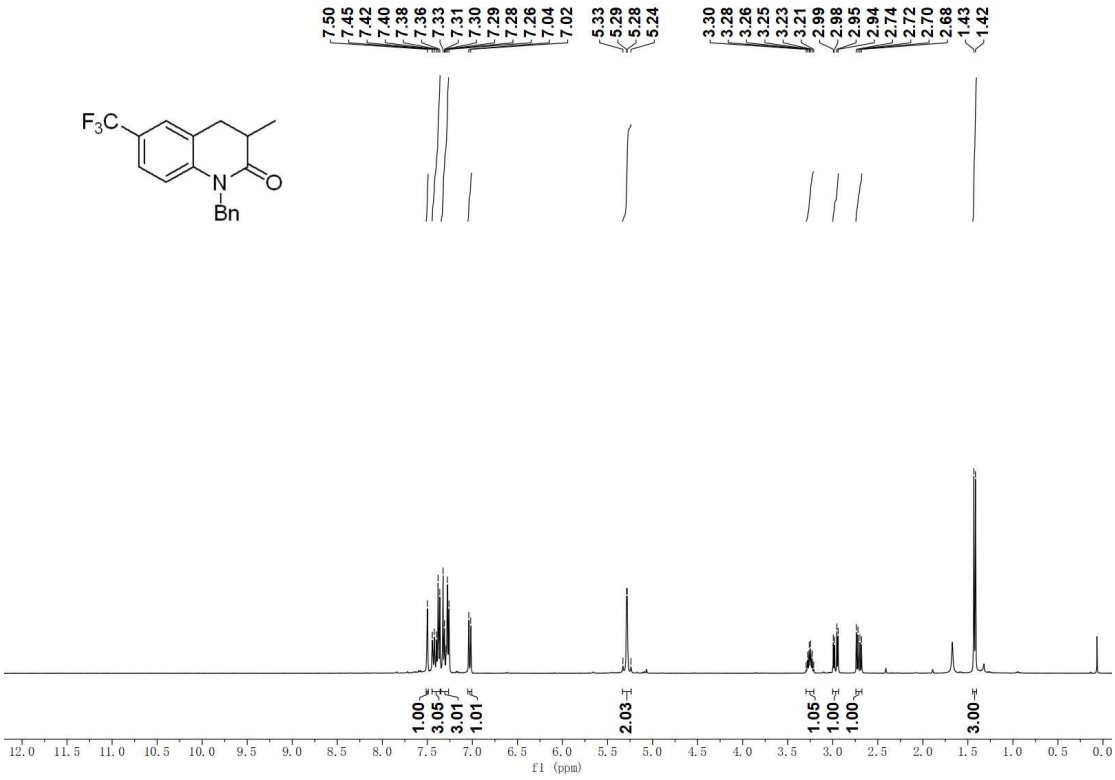
1-benzyl-6-fluoro-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (2j)

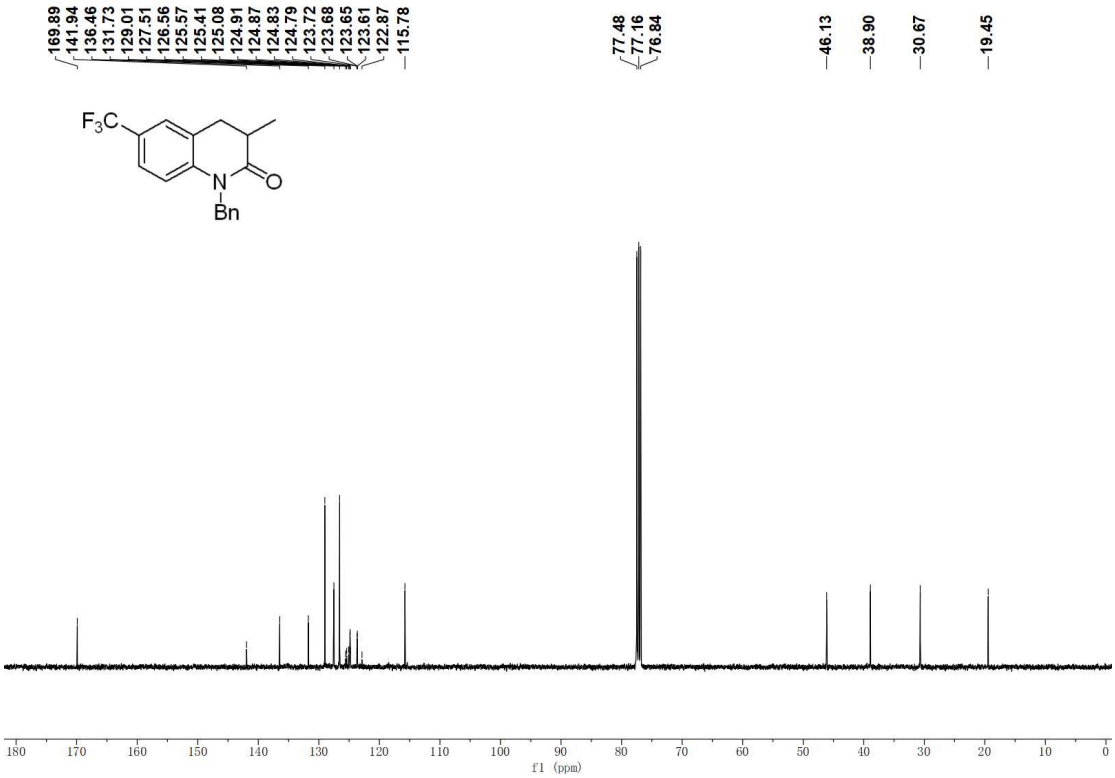


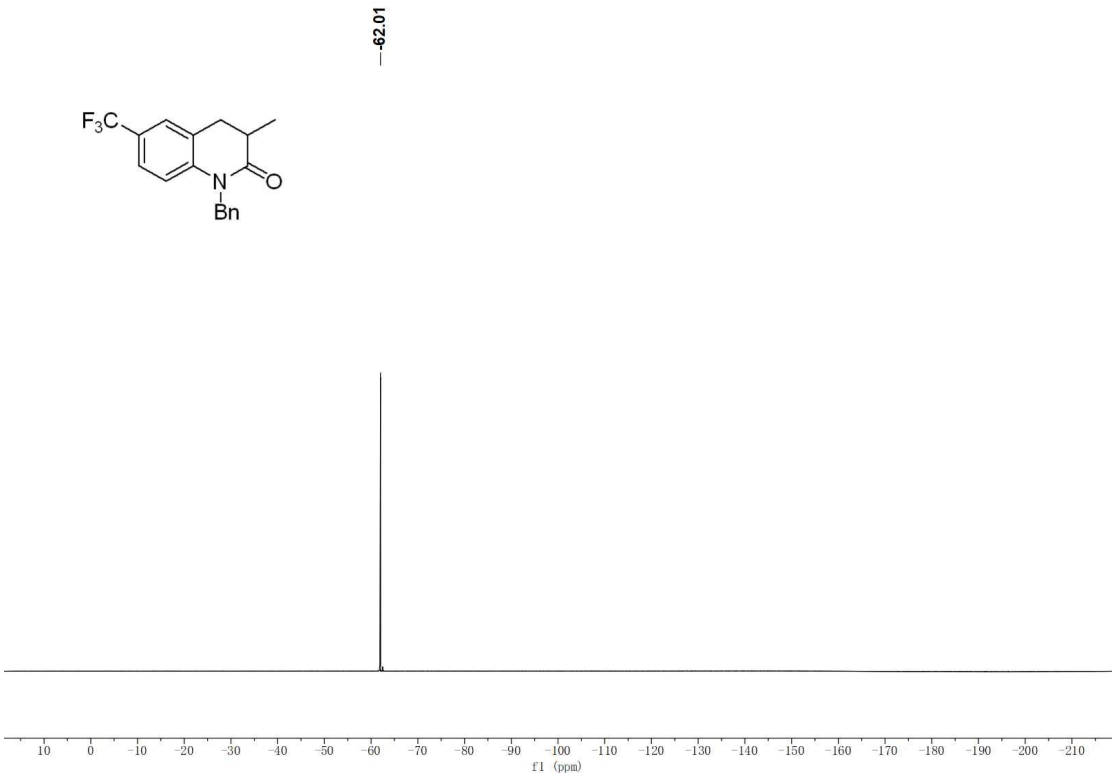

169.70
160.07
157.65
136.85
135.26
135.23
133.51
133.44
128.90
127.32
126.56
117.02
116.94
113.81
113.66
113.59
113.43
77.48
77.16
76.84
46.30
39.03
30.59
19.22
F
N
O
Bn
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


-120.13
F
N
O
Bn
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

1-benzyl-3-methyl-6-(trifluoromethyl)-3,4-dihydroquinolin-2(1*H*)-one (2k)

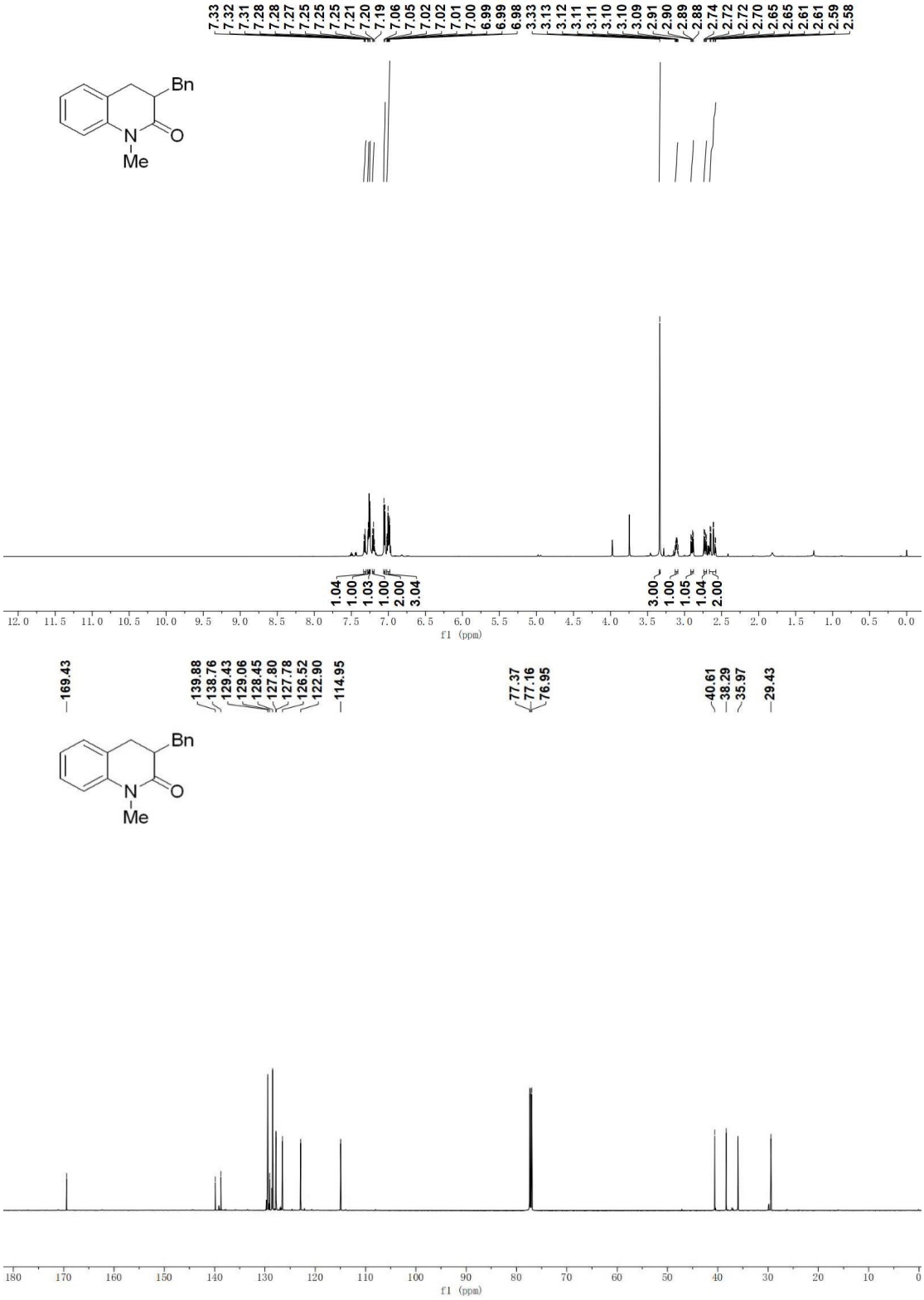



169.89
141.94
136.46
131.73
129.01
127.51
126.56
125.57
125.41
125.08
124.91
124.87
124.83
124.79
123.72
123.68
123.65
123.61
122.87
115.78
77.48
77.16
76.84
46.13
38.90
30.67
19.45
F3C
N
O
Bn
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

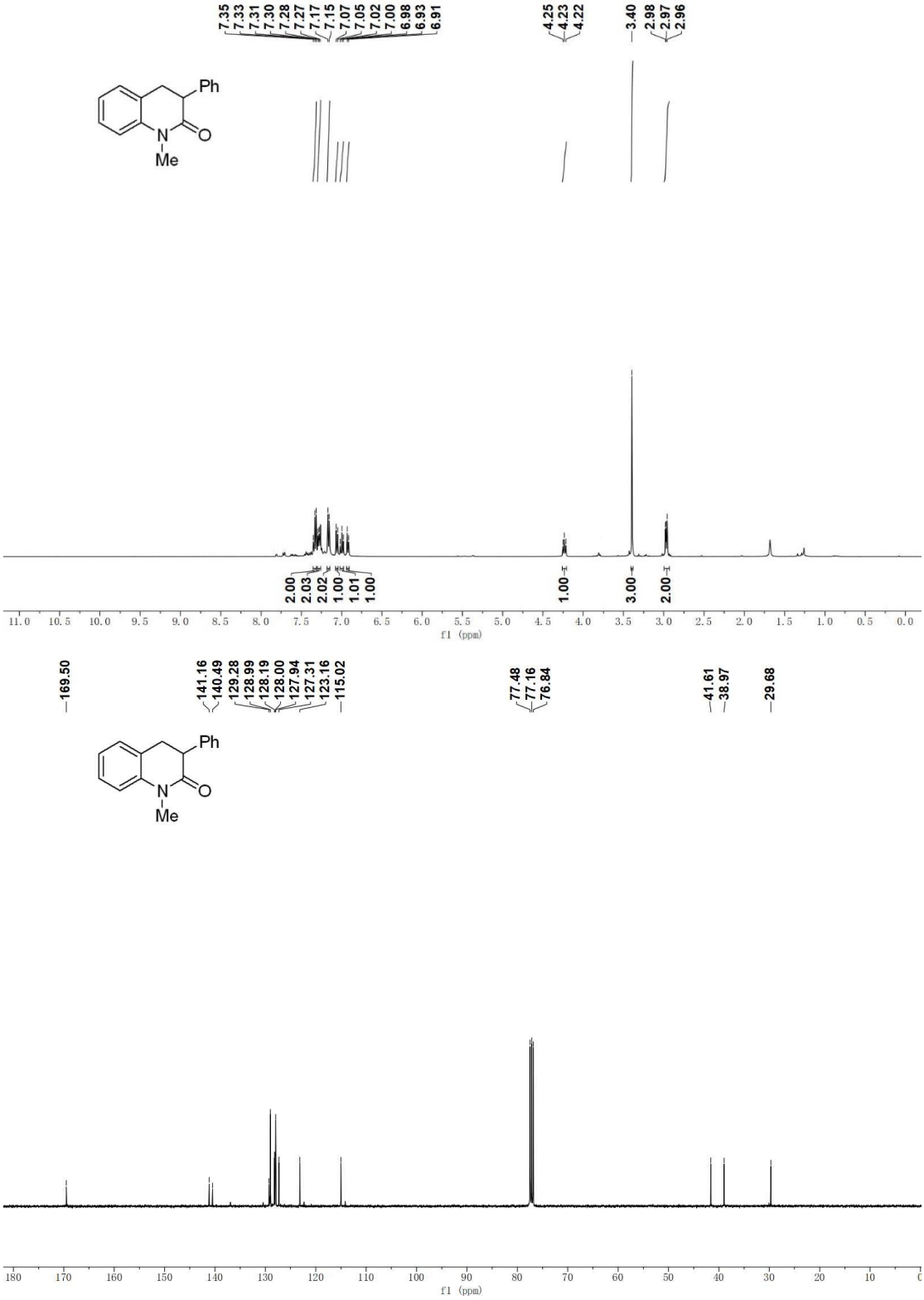

-62.01
F3C
N
O
Bn
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

1-benzyl-3-methyl-2-oxo-1,2,3,4-tetrahydroquinoline-6-carbonitrile (2l)

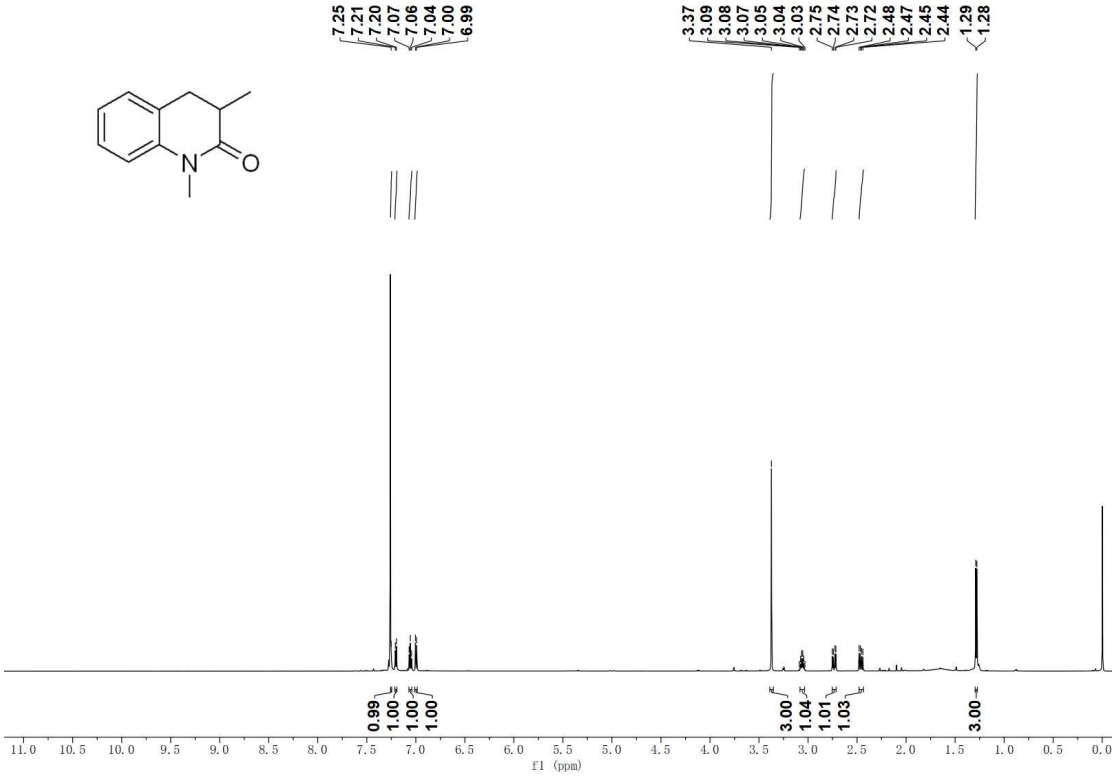
3-benzyl-1-methyl-3,4-dihydroquinolin-2(1*H*)-one (2n)

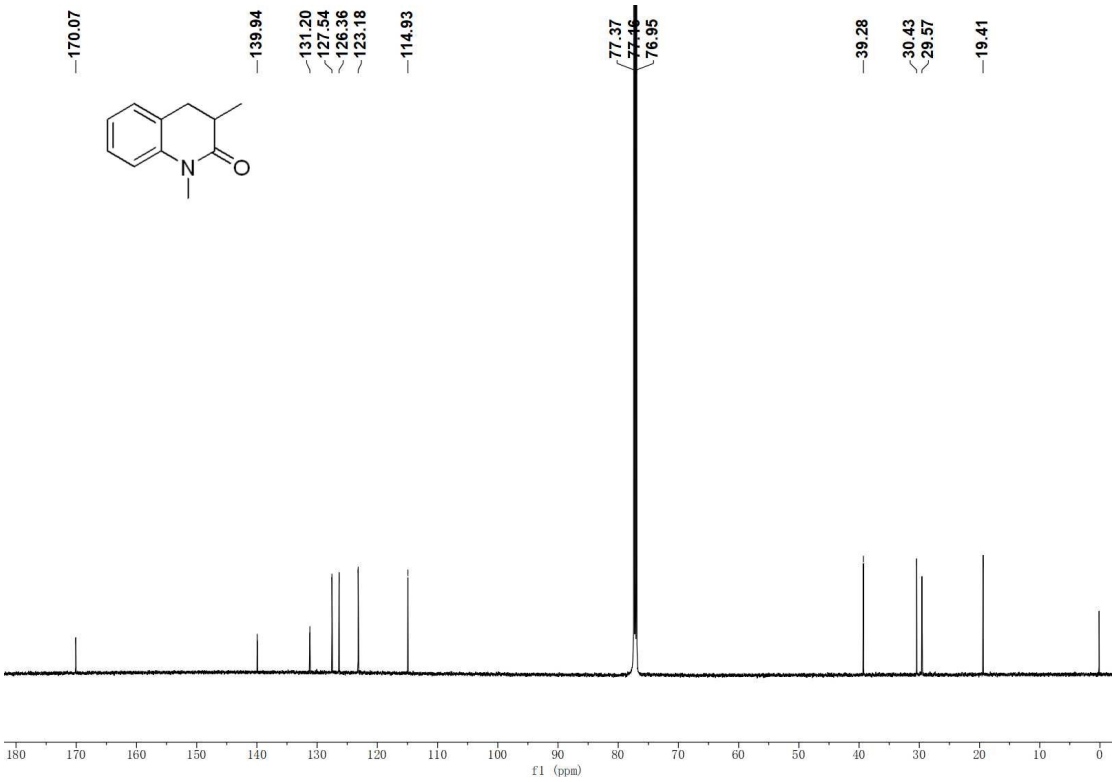


1-methyl-3-phenyl-3,4-dihydroquinolin-2(1*H*)-one (2o)

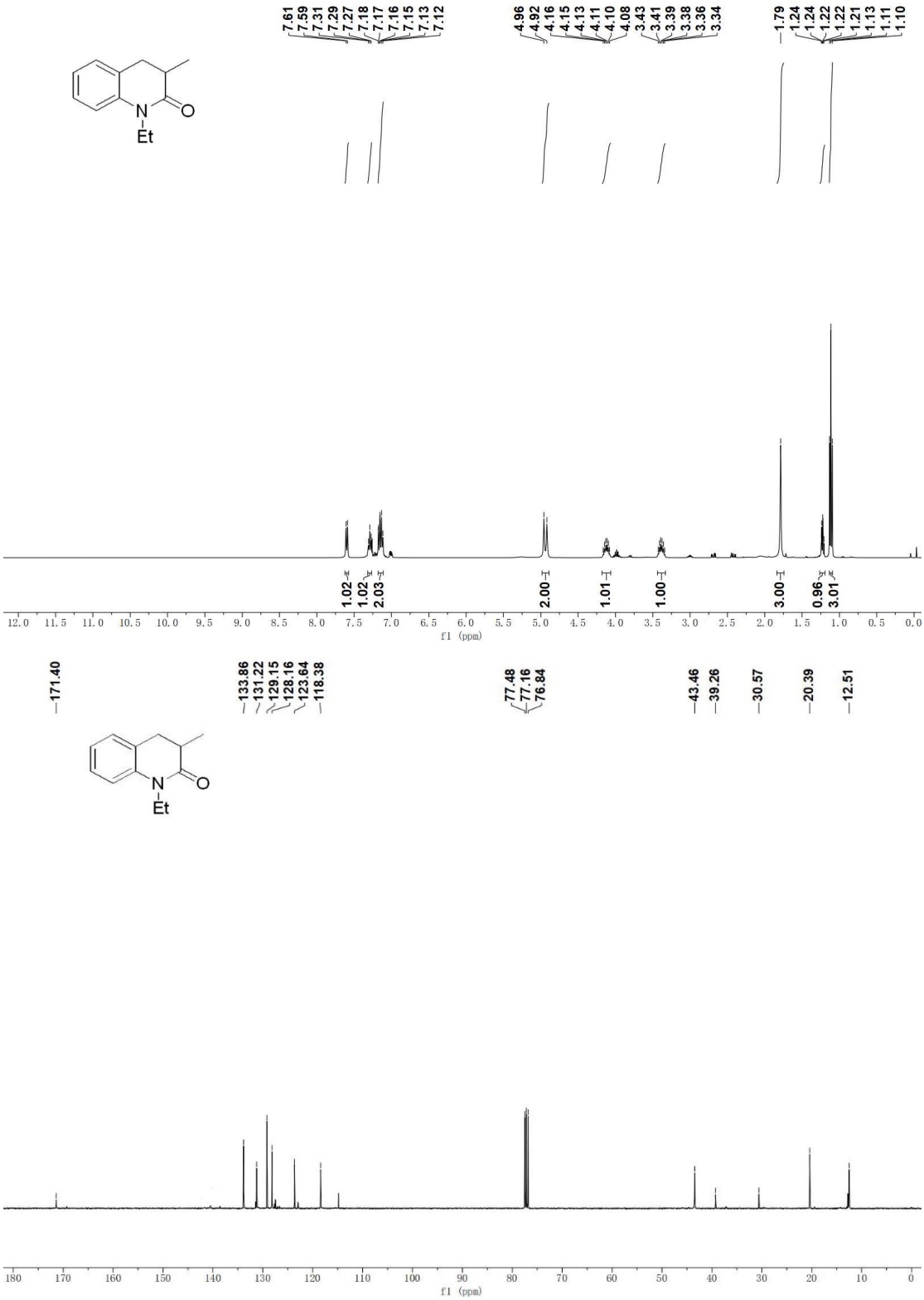


1,3-dimethyl-3,4-dihydroquinolin-2(1*H*)-one (2p)

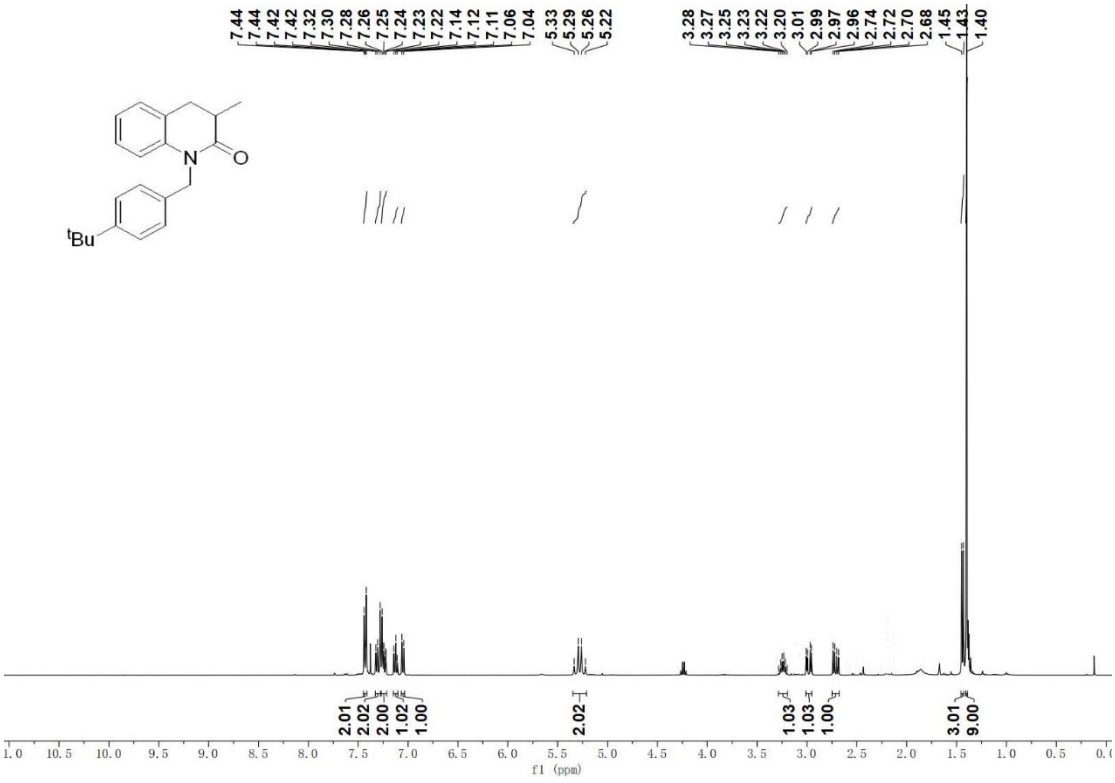


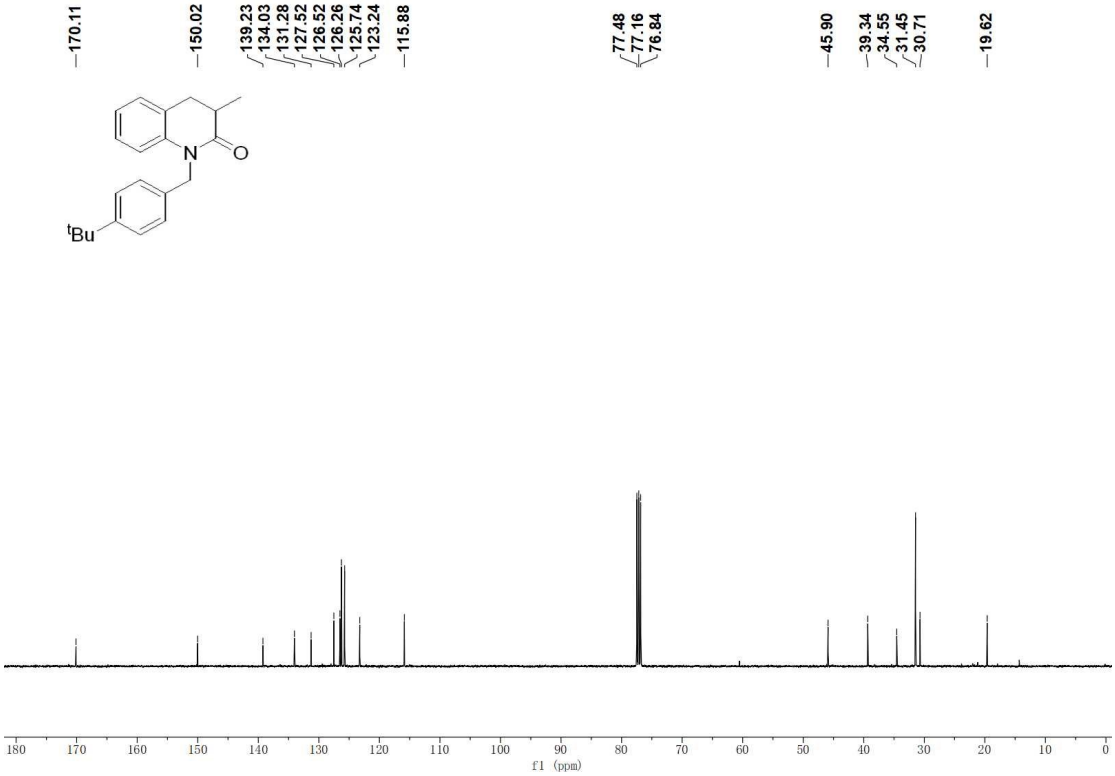


1-ethyl-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (2q)



1-(4-(tert-butyl)benzyl)-3-methyl-3,4-dihydroquinolin-2(1*H*)-one (2r)





1,3-dimethylindolin-2-one (3t)