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Supporting Information

Reductive N-methylation of Quinolines with Paraformaldehyde and H2 for Sustainable Synthesis of N-methyl Tetrahydroquinolines

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Contents

I. General information and experimental section

General Information:

XRD measurements were conducted by using a STADIP automated transmission diffractometer (STOE) equipped with an incident beam curved germanium monochromator with CuKa1 radiation and current of 40 kV and 150 mA, respectively. The XRD patterns were scanned in the 2 Theta range of 10-90 ^{o}. XPS were obtained using a VG ES-CALAB 210 instrument equipped with a dual Mg/Al anode X-ray source, a hemispherical capacitor analyzer, and a 5 keV Ar^{+} iron gun. The electron binding energy was referenced to the C1s peak at 284.8 eV. The background pressure in the chamber was less than 10-7 Pa. The peaks were fitted by Gaussian–Lorentzian curves after a Shirley background subtraction. For quantitative analysis, the peak area was divided by the element-specific Scofield factor and the transmission function of the analyzer. The BET surface area measurements were performed on a Quantachrome IQ_2 at the temperature of 77 K. The pore size distribution was calculated from the desorption isotherm by using the Barrett, Joyner, and Halenda (BJH) method. Prior to measurements, the samples were degassed at 100 ^{o}C for 12 h, at a rate of 10 $^{o}C \bullet min^{-1}$. TEM was carried out by using a Tecnai G2 F30 S-Twin transmission electron microscope operating at 300 kV. For TEM investigations, the catalysts were dispersed in ethanol by ultrasonication and deposited on carbon-coated copper grids. NMR spectra were measured by using a Bruker ARX 400 or ARX 100 spectrometer at 400 MHz (^{1}H) and 100 MHz (^{13}C). Chemical shifts were reported in parts per million (ppm) down field from TMS with the solvent resonance as the internal standard. Coupling constants (*J*) were reported in Hz and refered to apparent peak multiplications.

Experimental Section:

All solvents and chemicals were obtained commercially and were used as received. The carbon support used in this work is Vulcan XC-72R which was purchased from Shanghai Chuxi Industrial Co. Ltd. The TiO_2 support used in this work is Aeroxide® P25 which was purchased from Acros corporation. 2-alkenylquinoline derivatives

used here were known compounds and synthesizedaccording to the reported methods.[1-3]

Typical procedure for catalyst preparation:

Carbon (0.5 g) was dispersed in deionized water (25 mL) and K_2PdCl_4 aqueous solution (2.0 mL, [Pd] 5.0 mg/mL) was added into the solution under vigorous stirring. The pH value was adjusted to about 10 using 0.2 M NaOH and the solution was stirred for another 3 h at room temperature. Then 1.0 mL of hydrazine in 3.0 mL of deionized water was added to the solution and stirred for 4 h. The solid sample was recovered by centrifugation and washed with water. The obtained solid was dried at 80 ^oC for 12 h. A black solid sample was obtained and denoted as 2% Pd/C.

Typical procedure for N-methylation of quinolines with $(HCHO)_n$ /H_2

A mixture of quinolines (1.0 mmol), paraformaldehyde (36 mg, 1.2 mmol), 2% Pd/C (40 mg) and ethyl acetate (4 mL) were added a glass tube which was placed in an 100 mL autoclave. Then the autoclave was purged and charged with H_2 (0.4 MPa) three times. The reaction mixture was stirred at 100 ^oC for 12 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with 6 mL of ethyl acetate for quantitative analysis by GC-FID (Agilent 7890A). The crude reaction mixture was concentrated by rotary evaporator and purified by column chromatography on a silica gel column.

Procedure for catalyst reuse

A mixture of quinoline (129 mg, 1.0 mmol), paraformaldehyde (36 mg, 1.2 mmol), 2% Pd/C (40 mg) and ethyl acetate (4 mL) were added a glass tube which was placed in an 100 mL autoclave. Then the autoclave was purged and charged with H_2 (0.4 MPa) three times. The reaction mixture was stirred at 100 ^oC for 12 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the reaction mixture was diluted with 6 mL of ethyl acetate for quantitative analysis by GC-FID (Agilent 7890A). The Pd/C catalyst was

separated from the reaction mixtures by centrifuging, washed by using methanol (10 mL x 3) and H_2O (10 mL x 3), dried at 80 ^oC for 9 h and then reused for the next run.

Procedure for scaled-up reaction to synthesize N-methyl tetrahydroquinoline

A mixture of quinolines (1.290 g, 10 mmol), paraformaldehyde (0.360 g, 12 mmol), 2% Pd/C (100 mg) and ethyl acetate (40 mL) were added a glass tube which was placed in an 100 mL autoclave. Then the autoclave was purged and charged with H_2 (2.0 MPa) three times. The reaction mixture was stirred at 100 ^oC for 12 h. After the reaction finished, the autoclave was cooled to room temperature and the pressure was carefully released. Subsequently, the crude reaction mixture was concentrated by rotary evaporator and purified by column chromatography on a silica gel column.

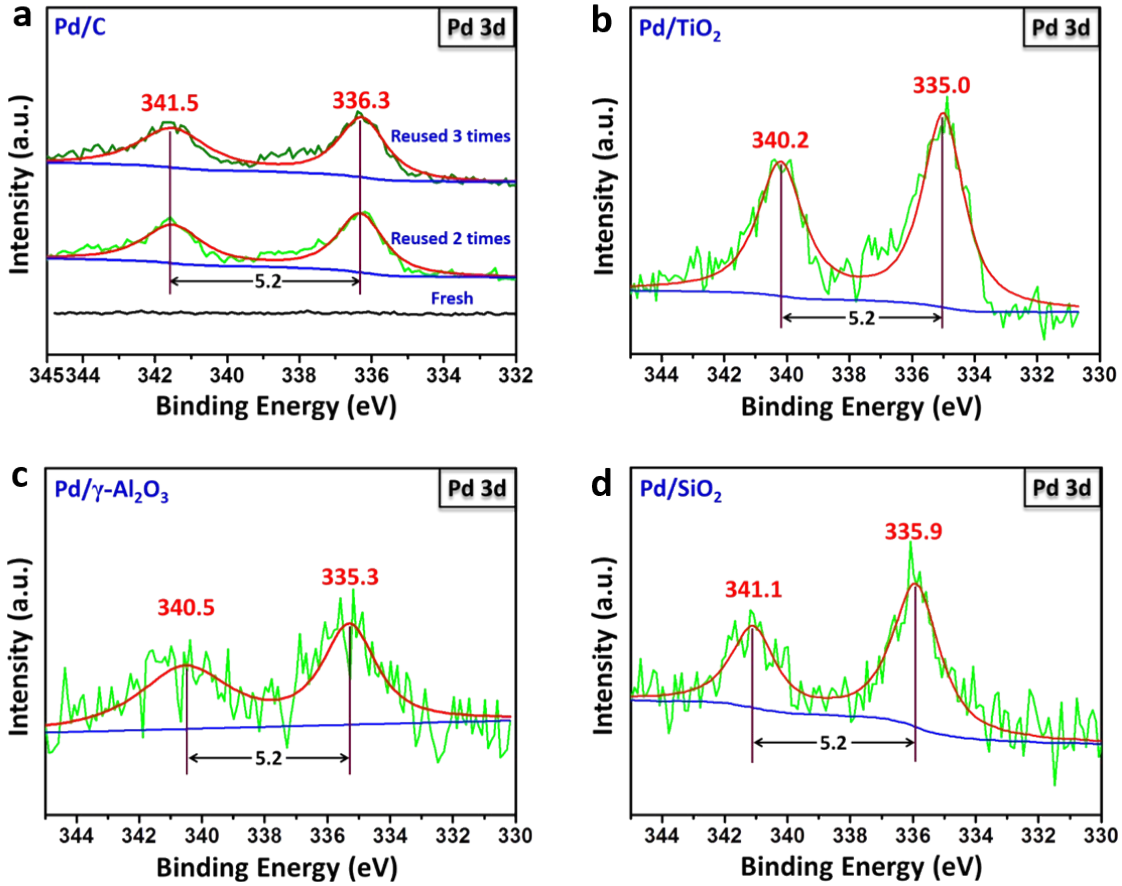
II. Characterization results of catalysts

1. Table S1 The physical properties of catalysts

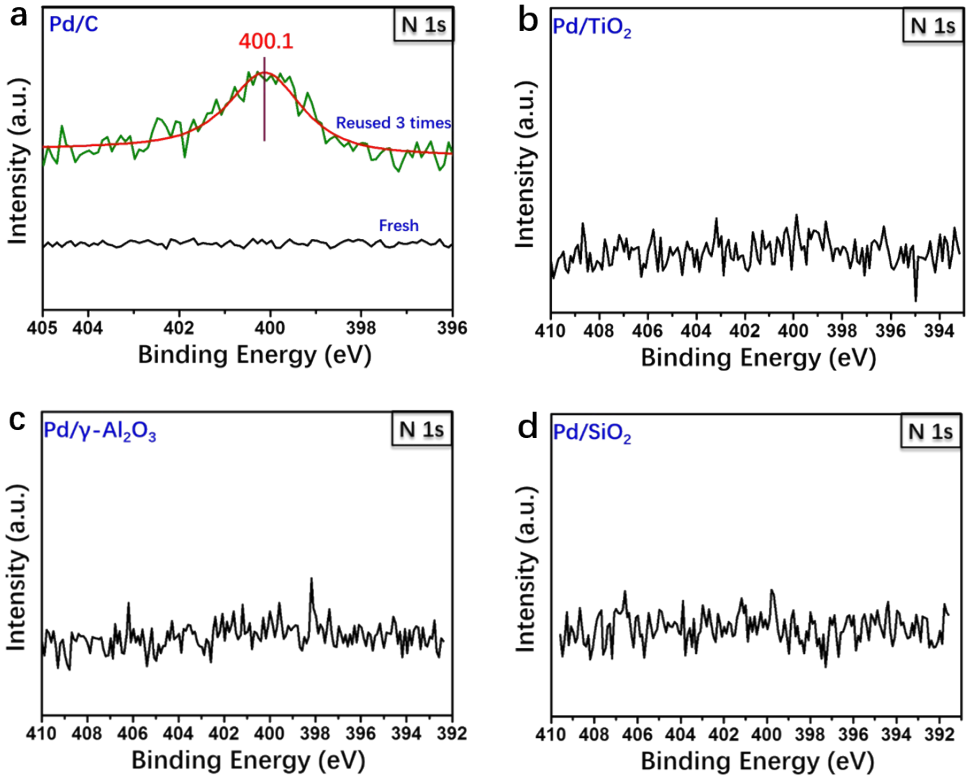
Entry	Catalyst	Pd (wt%) [a]	SA (m^2 g^{-1}) [b]	APR (nm) [b]	PV (cm^3 g^{-1}) [b]
1	Pd/C	2.46	198.49	7.68	0.76
3	Pd/TiO_2	0.64	59.16	21.43	0.63
2	$Pd/\gamma\text{-}Al_2O_3$	1.06	146.66	5.98	0.44
4	Pd/SiO_2	1.13	270.95	11.97	1.62
5	Pd/C used 1 time	2.38	--	--	--
6	Pd/C used 2 times	2.12	--	--	--
7	Pd/C used 3 times	2.12	--	--	--

[a] Determined by ICP-AES. [b] Determined by an IQ_2 automated gas sorption analyser. SA: BET surface area; APS: average pore radius; PV: pore volume.

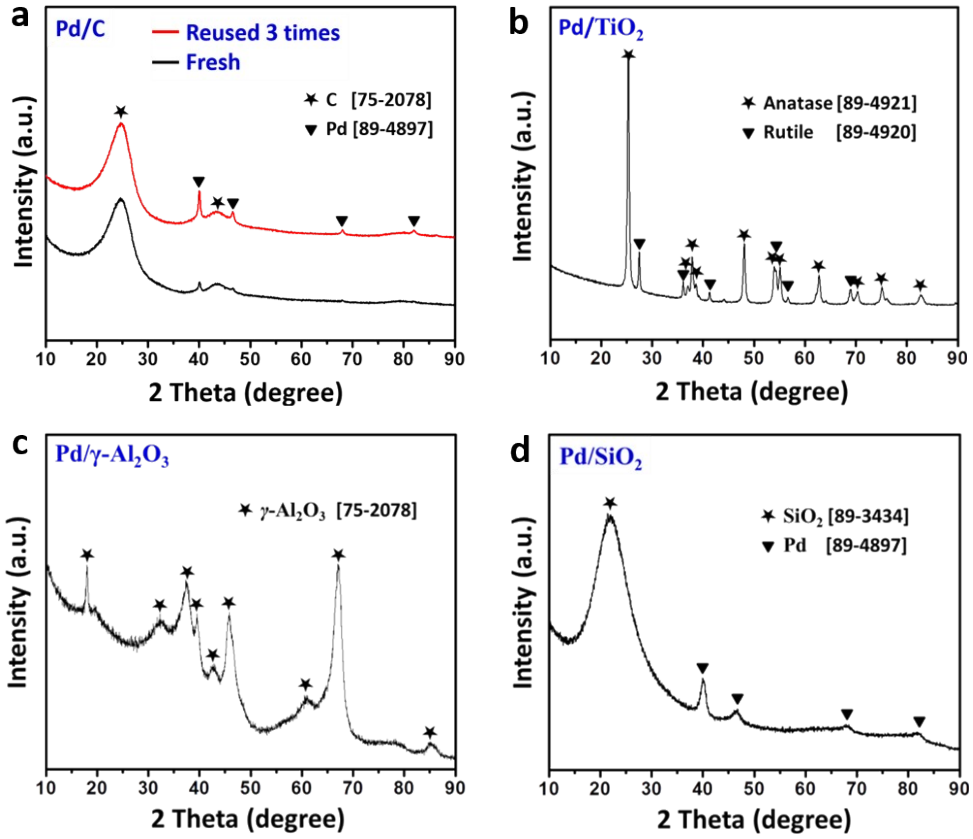
2. Fig. S1 XPS spectra of Pd 3d. (a) Pd/C. (b) Pd/TiO_2. (c) $Pd/\gamma\text{-}Al_2O_3$. (d) Pd/SiO_2.



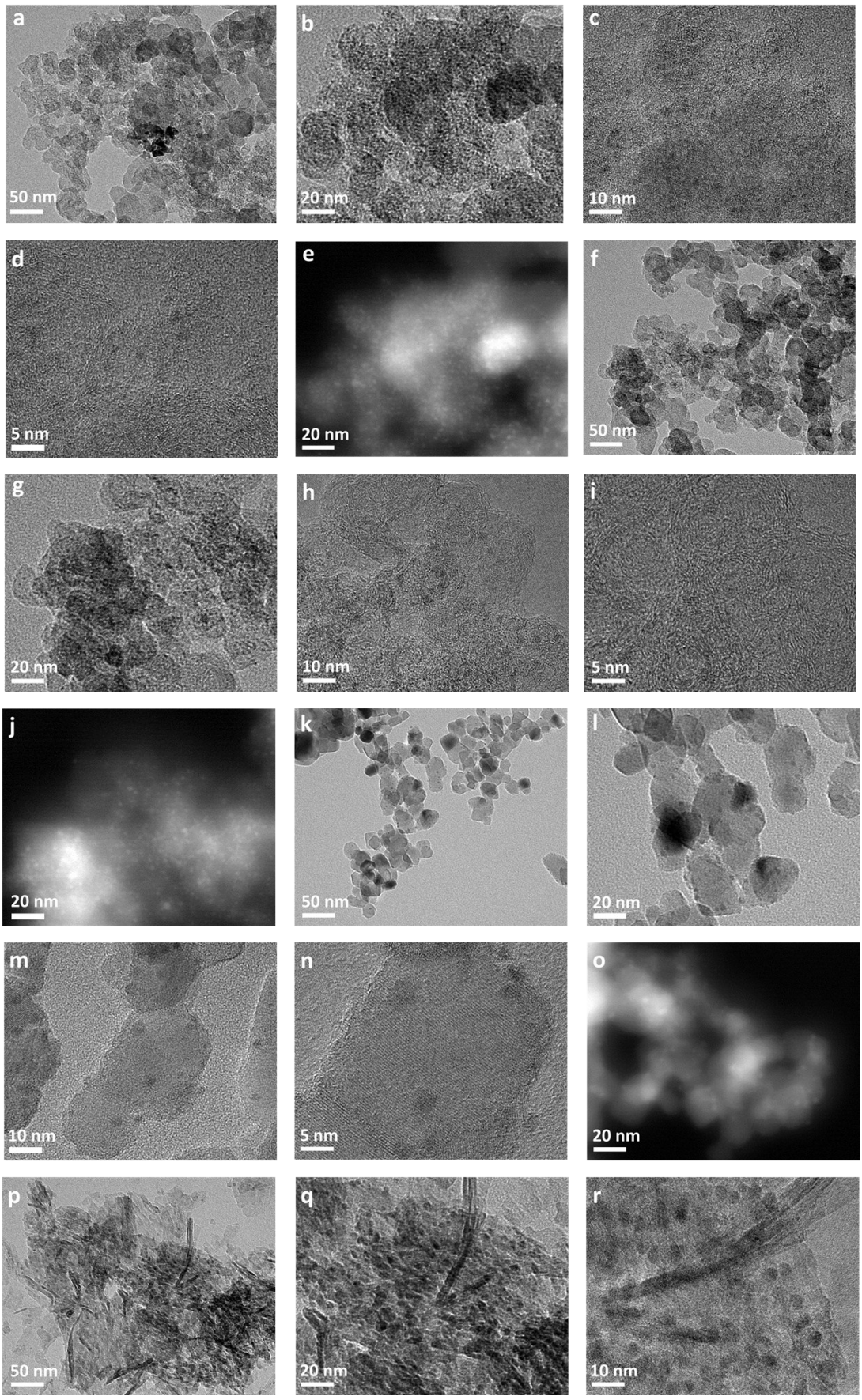
3.Fig. S2 XPS spectra of N1s. (a) Pd/C. (b) Pd/TiO_2. (c) $Pd/\gamma\text{-}Al_2O_3$. (d) Pd/SiO_2.



4. **Fig. S3 X-ray diffraction patterns of catalysts.** (a) Pd/C. (b) Pd/TiO_2. (c) $Pd/\gamma\text{-}Al_2O_3$. (d) Pd/SiO_2.



5. **Fig. S4 TEM, HR-TEM and STEM images of the catalysts.** (a-e) Pd/C. (f-j) reused three times Pd/C (k-o) Pd/TiO_2. (p-t) $Pd/\gamma\text{-}Al_2O_3$. (u-y) Pd/SiO_2. The images of e, j, o, t and y were obtained by STEM. The other images were obtained by TEM.


a
50 nm
b
20 nm
c
10 nm
d
5 nm
e
20 nm
f
50 nm
g
20 nm
h
10 nm
i
5 nm
j
20 nm
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5 nm
o
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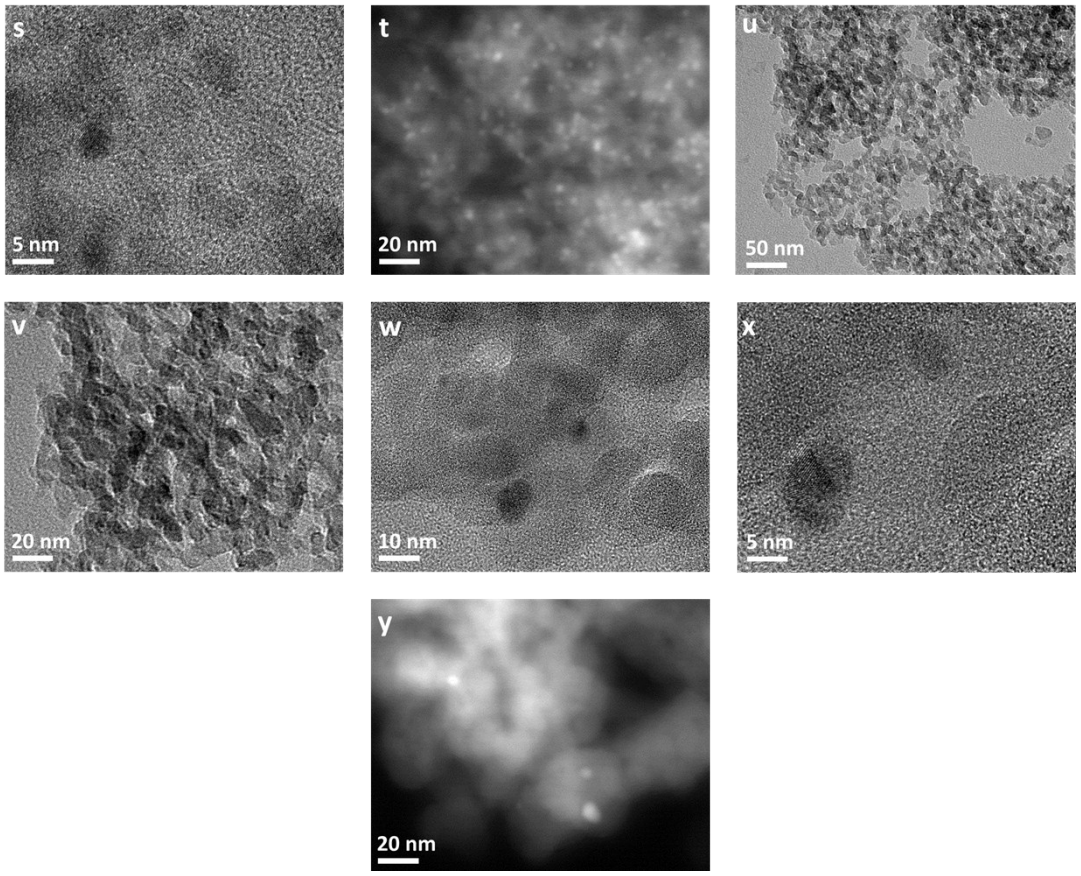
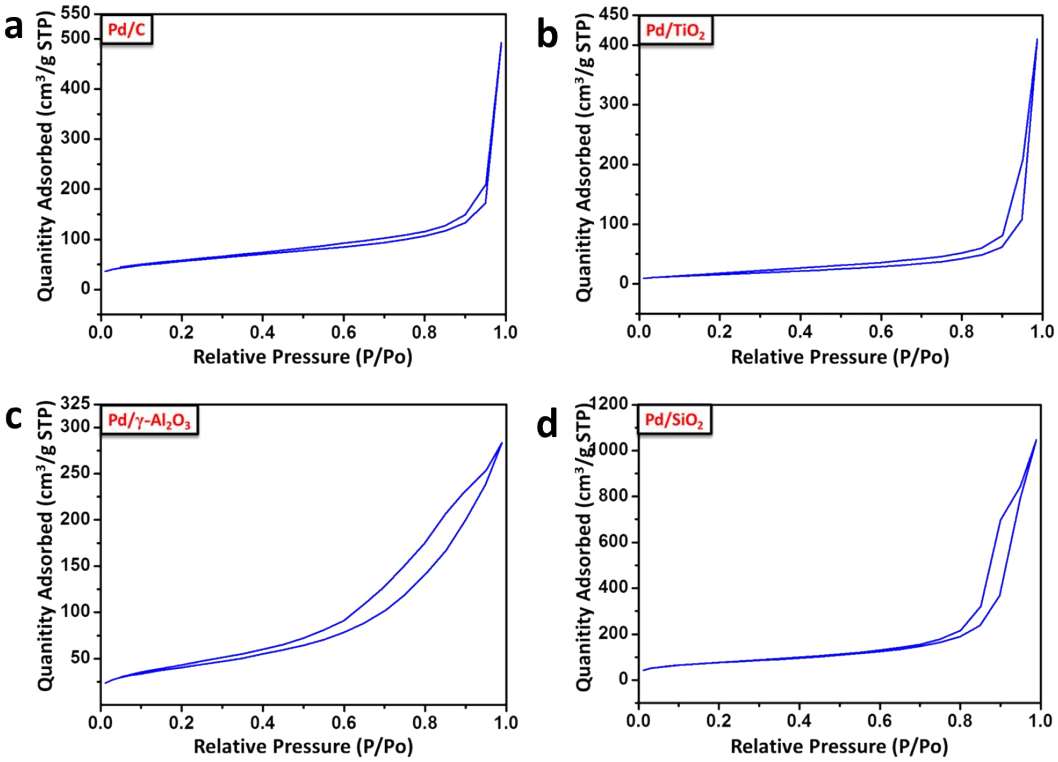
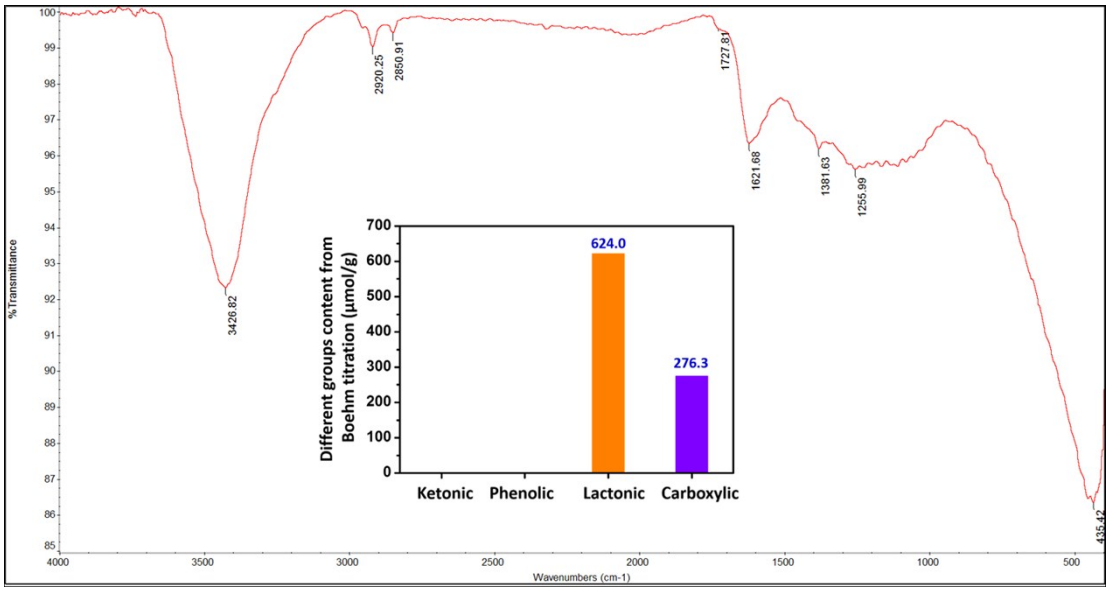
10 nm



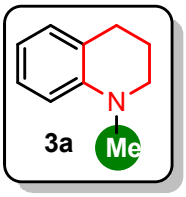
6. **Fig.S5 The N_2 adsorption isotherm of the catalysts. (a) Pd/C. (b) Pd/TiO_2. (c) Pd/γ-Al_2O_3. (d) Pd/SiO_2.**



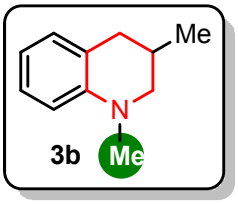
7. Fig.S6 Surface oxygenated groups determined by FT-IR and Boehm titration



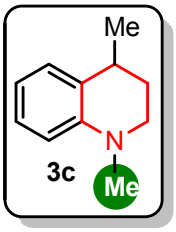
Ⅲ. Characterization data for products



1-methyl-1,2,3,4-tetrahydroquinoline (3a)[4]: The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to give the oily liquid. 131 mg, 89% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.94-2.00 (m, 2H), 2.76 (t, J = 6.4 Hz, 2H), 2.87 (s, 3H), 3.20 (t, J = 5.6 Hz, 2H), 6.59 (t, J = 7.6 Hz, 2H), 6.94 (d, J = 7.2 Hz, 1H), 7.06 (t, J = 7.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 22.43, 22.75, 39.06, 51.23, 110.91, 116.15, 122.81, 127.00, 128.76, 146.71.

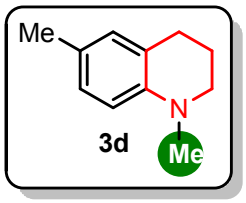


1,3-dimethyl-1,2,3,4-tetrahydroquinoline (3b)[4]: The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 10/1) to give the oily liquid. 116 mg, 72% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.03 (dd, J_1 = 1.4 Hz, J_2 = 6.6 Hz, 3H), 2.08-2.15 (m, 1H), 2.40-2.47 (m, 1H), 2.75-2.88 (m, 5H), 3.13-3.17 (m, 1H), 6.60 (t, J = 7.4 Hz, 2H), 6.91 (d, J = 7.2 Hz, 1H), 7.07 (t, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 19.16, 27.39, 36.21, 39.05, 58.32, 110.68, 116.15, 122.46, 126.99, 128.88, 146.20.

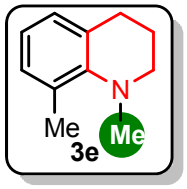


1,4-dimethyl-1,2,3,4-tetrahydroquinoline (3c)[4]: The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 100/1) to give the oily liquid. 136 mg, 84% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.27 (d, J = 6.8 Hz, 3H), 1.65-1.72 (m, 1H), 1.99-2.07 (m, 1H), 2.84-2.94 (m, 4H), 3.15-

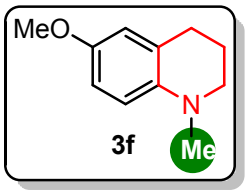
3.27 (m, 2H), 6.59-6.66 (m, 2H), 7.04-7.10 (m, 2H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 22.71, 30.01, 48.26, 110.94, 116.16, 127.02, 127.80, 128.00, 146.15.



1,6-dimethyl-1,2,3,4-tetrahydroquinoline (3d)[4]: The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 100/1) to give the oily liquid. 120 mg, 75% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.94-2.00 (m, 2H), 2.21 (s, 3H), 2.73 (t, J = 7.6 Hz, 2H), 2.84 (s, 3H), 3.15 (t, J = 5.6 Hz, 2H), 6.52 (d, J = 8.0 Hz, 1H), 6.78 (s, 3H), 6.87 (d, J = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 20.21, 22.62, 39.45, 51.46, 111.42, 123.07, 125.55, 127.37, 129.60, 144.70.

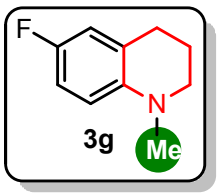


1,8-dimethyl-1,2,3,4-tetrahydroquinoline (3e): The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 100/1) to give the oily liquid. 131 mg, 81% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.81-1.87 (m, 2H), 2.30 (s, 3H), 2.70 (s, 3H), 2.79 (t, J = 6.6 Hz, 2H), 3.11 (t, J = 5.2 Hz, 2H), 6.83 (t, J = 7.4 Hz, 1H), 6.89 (d, J = 7.2 Hz, 1H), 6.98 (d, J = 6.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 16.90, 18.64, 27.84, 42.92, 52.06, 121.47, 127.29, 128.81, 128.84, 131.25, 148.01. HRMS (ESI) calcd. for $C_{11}H_{16}N$ [M+H]: 162.1277, found: 162.1270.

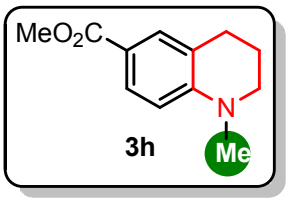


6-methoxy-1-methyl-1,2,3,4-tetrahydroquinoline (3f)[4]: The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 50/1) to give an oil. 142 mg, 80% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.95-2.01 (m, 2H), 2.76 (t, J = 6.6 Hz, 2H), 2.83 (s, 3H), 3.12 (t, J = 5.6 Hz, 2H), 3.73 (s, 3H), 6.57-6.59 (m, 2H), 6.66 (dd, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H); **^{13}C NMR**

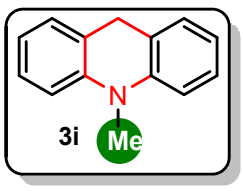
(100 MHz, $CDCl_3$) δ 22.61, 27.91, 39.95, 51.62, 55.74, 112.21, 112.54, 115.04, 124.66, 141.49, 151.35.



6-fluoro-1-methyl-1,2,3,4-tetrahydroquinoline (3g): The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 100/1) to give the oily liquid. 135 mg, 82% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.94-2.00 (m, 2H), 2.74 (t, J = 6.6 Hz, 2H), 2.84 (s, 3H), 3.15 (t, J = 5.6 Hz, 2H), 6.48 (dd, J_1 = 4.8 Hz, J_2 = 8.8 Hz, 1H), 6.67 (dd, J_1 = 3.2 Hz, J_2 = 8.8 Hz, 1H), 6.48 (td, J_1 = 2.8 Hz, J_2 = 8.8 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 22.39, 27.84, 39.65, 51.31, 111.70 (d, J = 7.0 Hz), 112.79 (d, J = 22.0 Hz), 115.16 (d, J = 21.0 Hz), 124.49 (d, J = 6.0 Hz), 143.30 (d, J = 2.0 Hz), 153.90 (d, J = 233.0 Hz); **^{19}F NMR** (376 MHz, CDCl3) δ -129.53; HRMS (ESI) calcd. for $C_{10}H_{13}FN$ [M+H]: 166.1027, found: 166.1023.

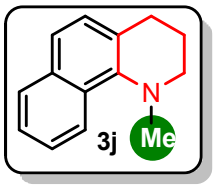


methyl 1-methyl-1,2,3,4-tetrahydroquinoline-6-carboxylate (3h): The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 50/1) to give an white solid. 158 mg, 77% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.93-1.99 (m, 2H), 2.76 (t, J = 6.2 Hz, 2H), 2.96 (s, 3H), 3.33 (t, J = 5.8 Hz, 2H), 3.84 (s, 3H), 6.50 (d, J = 8.4 Hz, 1H), 7.62 (s, 1H), 7.74 (dd, J_1 = 2.0 Hz, J_2 = 8.4 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 21.78, 27.66, 38.75, 51.07, 51.38, 109.31, 116.55, 121.45, 129.59, 130.12, 149.82, 167.56. HRMS (ESI) calcd. for $C_{12}H_{16}NO_2$ [M+H]: 206.1176, found: 206.1176.

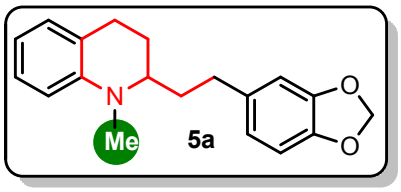


10-methyl-9,10-dihydroacridine (3i)[5]: The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 100/1) to give an white solid. 158 mg, 81% yield. **^{1}H NMR** (400 MHz,

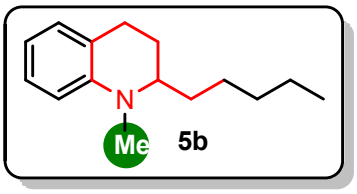
$CDCl_3$) δ 3.37 (s, 3H), 3.88 (s, 2H), 6.86-6.93 (m, 4H), 7.11-7.21 (m, 4H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 33.11, 33.22, 111.84, 120.55, 124.30, 126.83, 127.50, 143.64.



1-methyl-1,2,3,4-tetrahydrobenzo[h]quinolone (3j): The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 100/1) to give the oily liquid. 131 mg, 66% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.91-1.97 (m, 2H), 2.90 (t, *J* = 6.6 Hz, 2H), 2.94 (s, 3H), 2.23-2.26 (m, 2H), 7.11 (d, *J* = 8.4 Hz, 1H), 7.37-7.41 (m, 2H), 7.45 (t, *J* = 7.2 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H),; **^{13}C NMR** (100 MHz, $CDCl_3$) δ 16.18, 27.79, 44.50, 51.48, 122.09, 123.62, 124.87, 124.94, 125.02, 128.15, 128.20, 128.77, 133.36, 144.65. HRMS (ESI) calcd. for $C_{14}H_{16}N$ [M+H]: 198.1277, found: 198.1281.

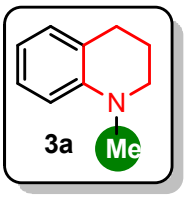


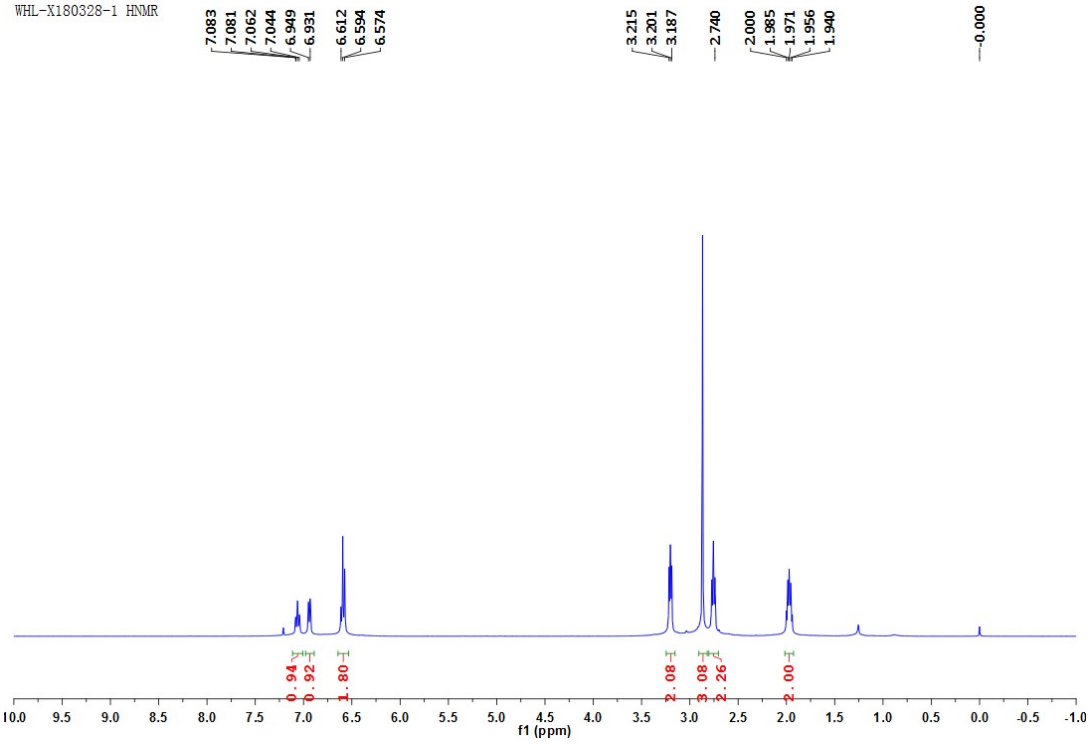
2-(2-(benzo[d][1,3]dioxol-5-yl)ethyl)-1-methyl-1,2,3,4-tetrahydroquinoline (5a)[2]: 2-alkenylquinoline (93 mg, 0.34 mmol), paraformaldehyde (12 mg, 0.40 mmol), H_2 (1.0 MPa), 2% Pd/C (20 mg), 4 mL ethyl acetate, 100 ^{o}C, 12 h. The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 50/1) to give the oily liquid. 75 mg, 74% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 1.64-1.74 (m, 1H), 1.83-1.96 (m, 3H), 2.45-2.55 (m, 1H), 2.58-2.73 (m, 2H), 2.79-2.87 (m, 1H), 2.90 (s, 3H), 3.24-3.29 (m, 1H), 5.91 (s, 2H), 6.51 (d, *J* = 8.4 Hz, 1H), 6.57-6.64 (m, 2H), 6.68 (s, 1H), 6.71 (d, *J* = 8.0 Hz, 1H), 6.96 (d, *J* = 7.2 Hz, 1H), 7.08 (t, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 23.52, 24.34, 32.00, 33.11, 38.02, 58.19, 100.75, 108.14, 108.60, 110.59, 115.39, 120.91, 121.69, 127.09, 128.65, 135.81, 145.27, 145.59, 147.59.

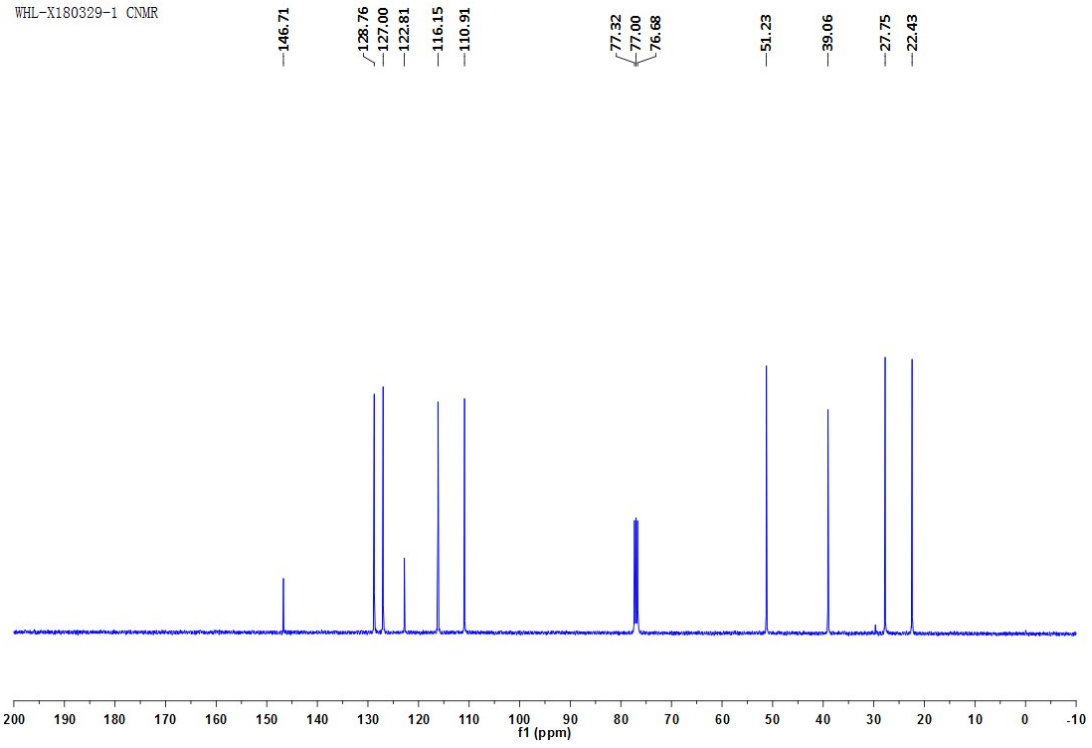


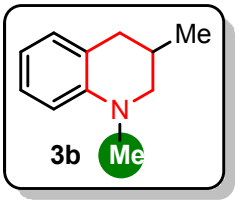
1-methyl-2-pentyl-1,2,3,4-tetrahydroquinoline (5b)[2]: 2-alkenylquinoline (134 mg, 0.68 mmol), paraformaldehyde (25 mg, 0.83 mmol), H_2 (1.0 MPa), 2% Pd/C (40 mg), 4 mL ethyl acetate, 100 °C, 12 h. The title compound was prepared according to the general procedure and purified by column chromatography (petroleum ether/ethyl acetate = 400/1) to give the oily liquid. 123 mg, 83% yield. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 0.89 (t, *J* = 6.8 Hz, 3H), 1.26-1.41 (m, 7H), 1.56-1.61 (m, 1H), 1.85-1.90 (m, 2H), 2.61-2.66 (m, 1H), 2.75-2.84 (m, 1H), 2.92 (s, 3H), 3.20-3.24 (m, 1H), 6.50 (d, *J* = 8.4 Hz, 1H), 6.57 (t, *J* = 7.2 Hz, 1H), 6.95 (d, *J* = 7.2 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$) δ 14.03, 22.66, 23.53, 24.35, 25.73, 31.14, 32.01, 37.92, 58.90, 110.33, 115.12, 121.78, 127.01, 128.59, 145.35.

Ⅳ.NMR spectra of all products



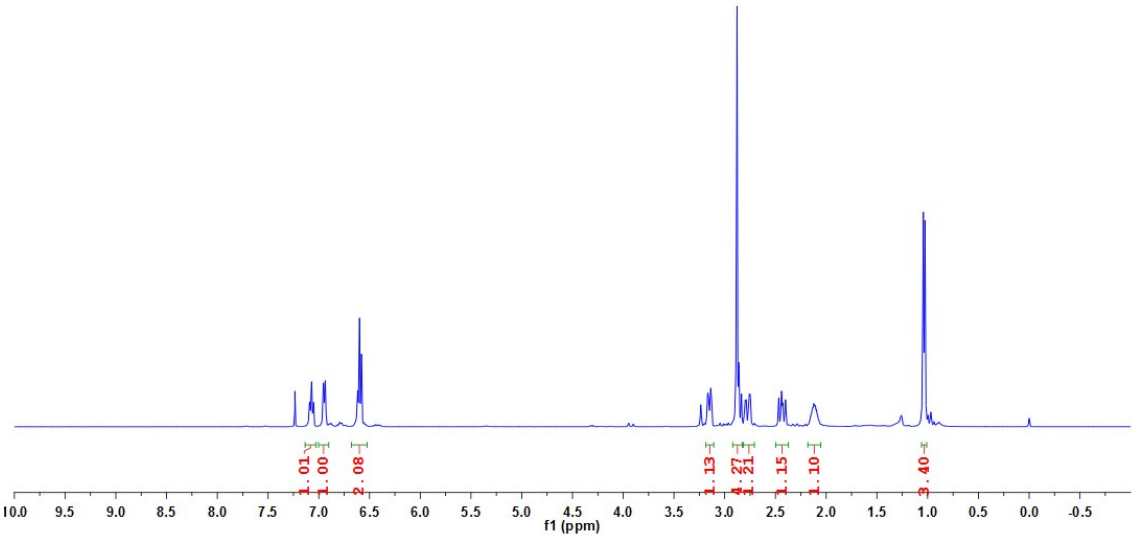






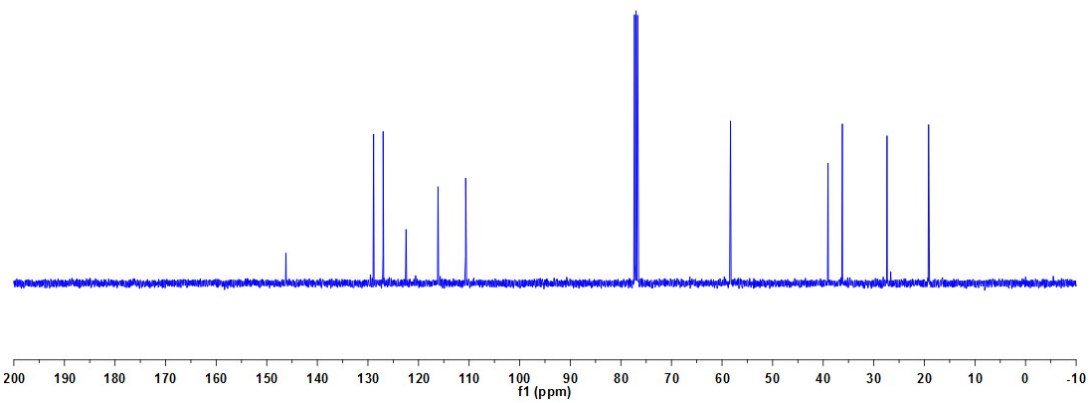
WHL-X180718-1 HNMR

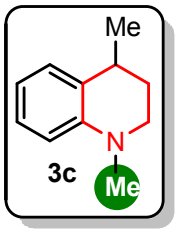
7.235 7.090 7.070 7.052 6.954 6.936 6.616 6.599 6.579 3.169 3.165 3.161 3.156 3.141 3.138 3.134 3.128 2.750 2.401 2.132 2.110 2.081 1.046 1.043 1.030 1.026 -0.000



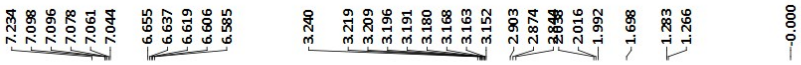
WHL-X180718-1 CNMR

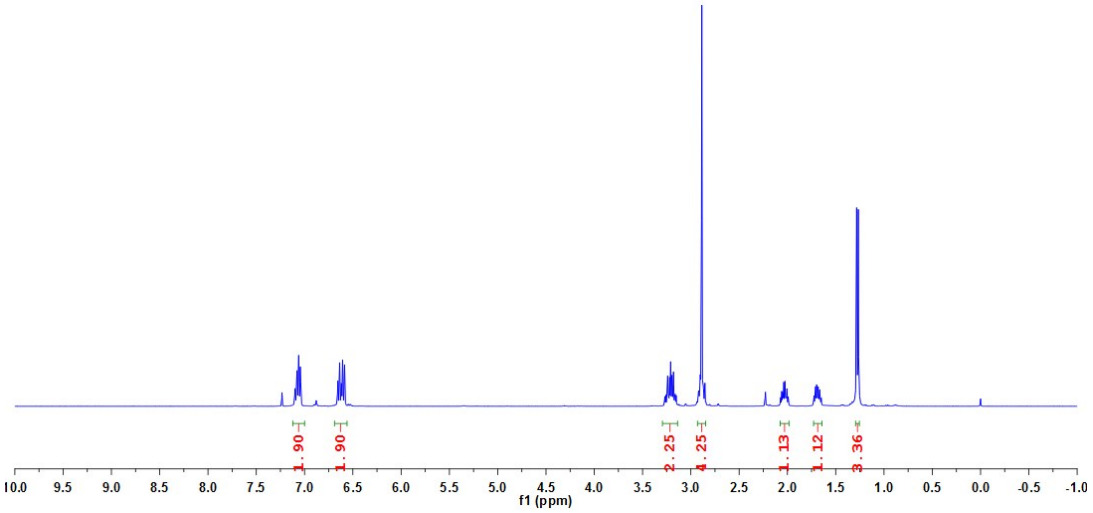
146.20 128.88 126.99 122.46 116.15 110.68 77.32 77.00 76.68 58.32 39.05 36.21 27.39 19.16



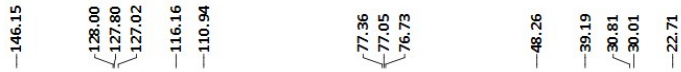


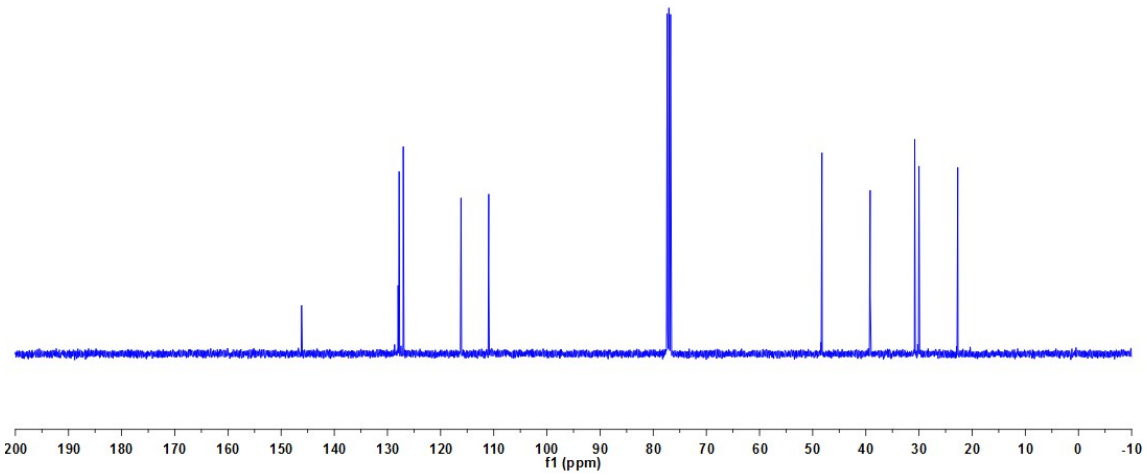
WHL-X180718-3 HNMR

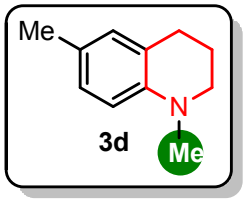




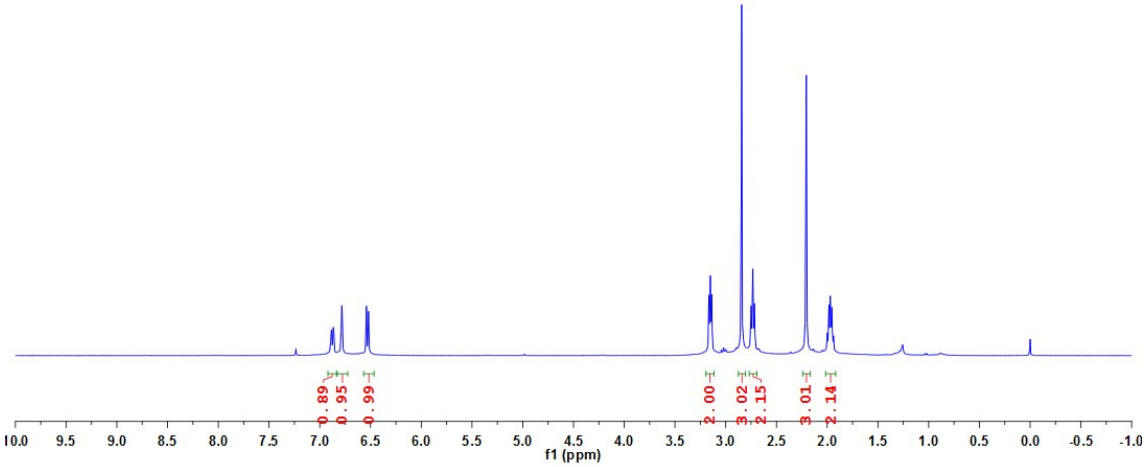
WHL-X180718-3 CNMR



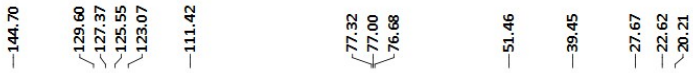


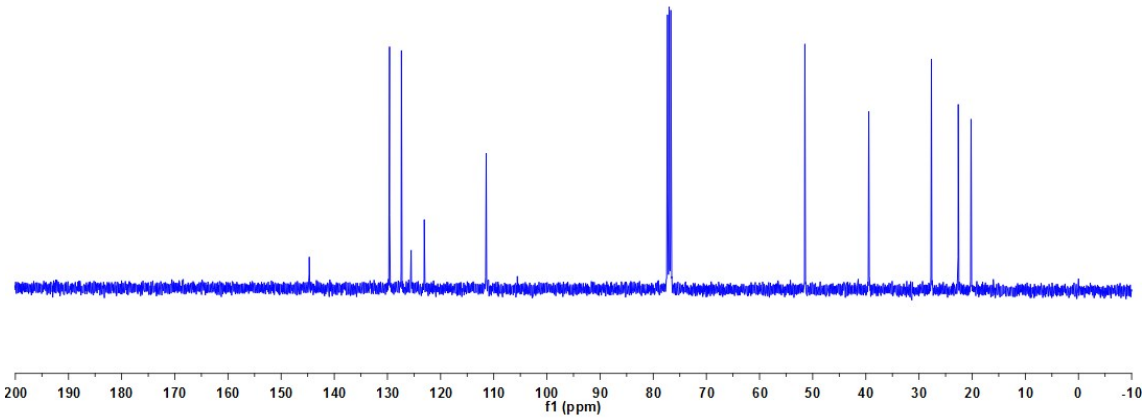


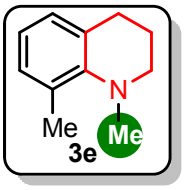
WHL-X180709-5H NMR



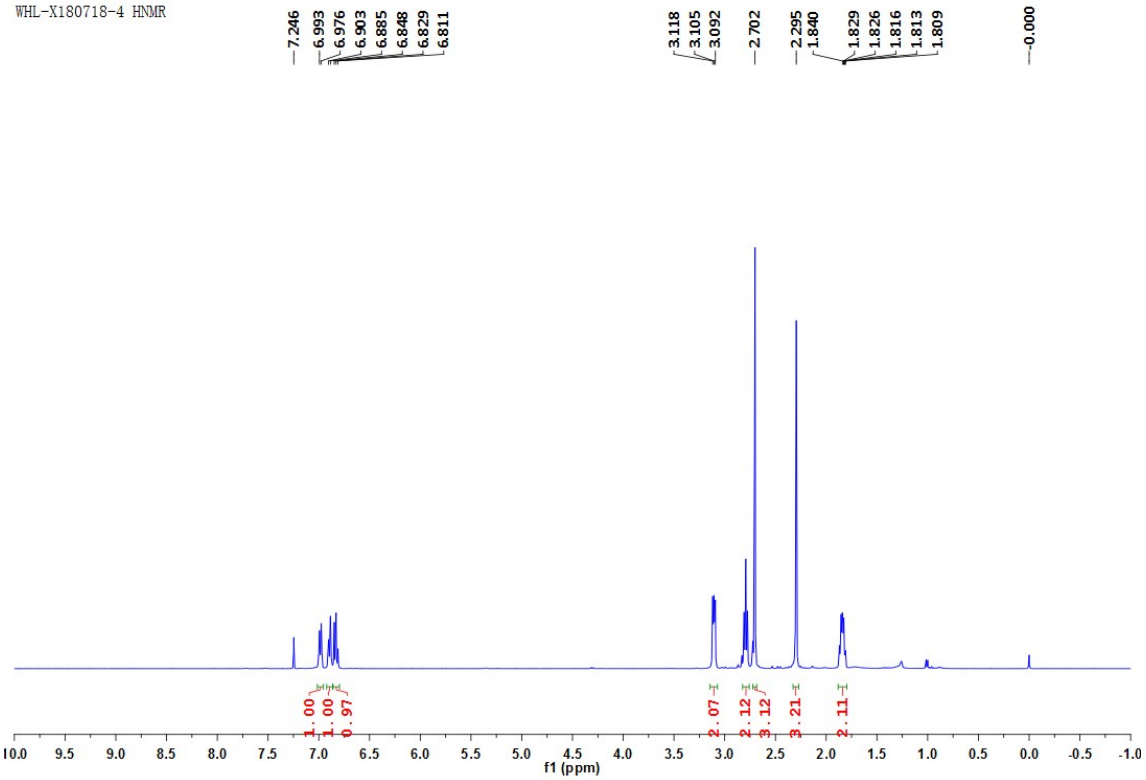
WHL-X180709-5C NMR



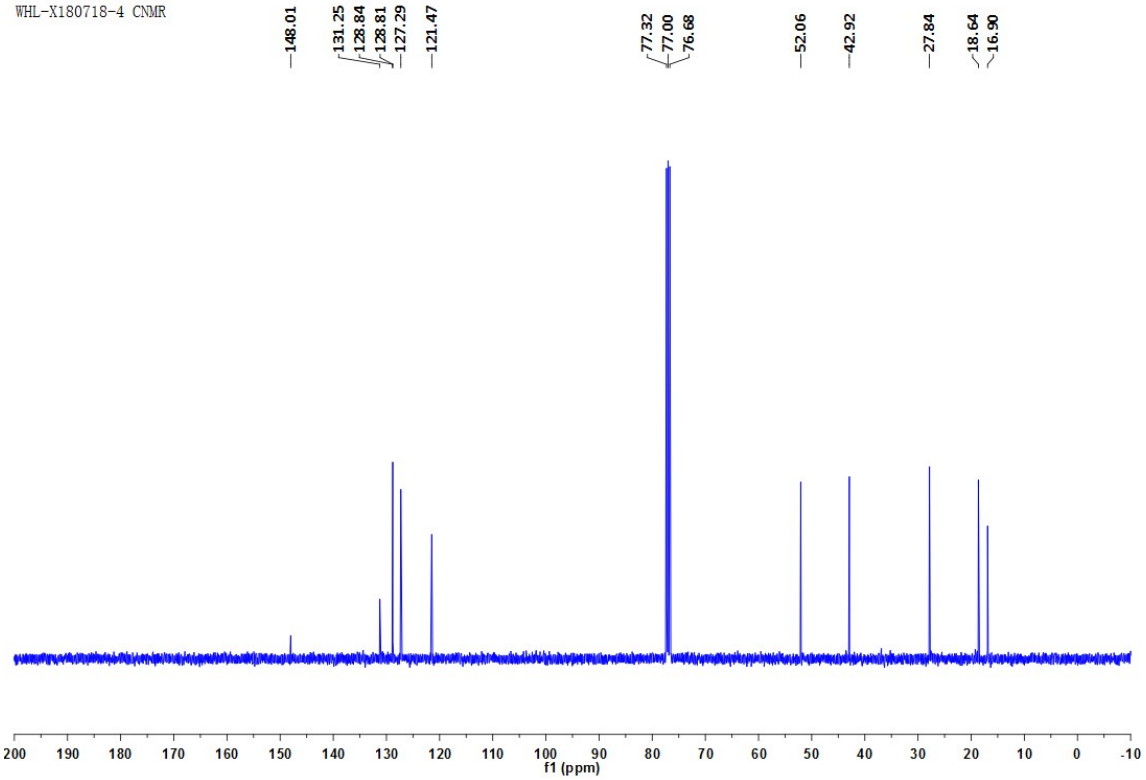


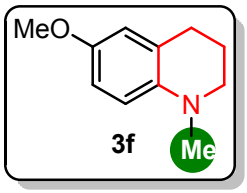


WHL-X180718-4 HNMR

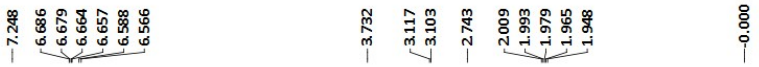


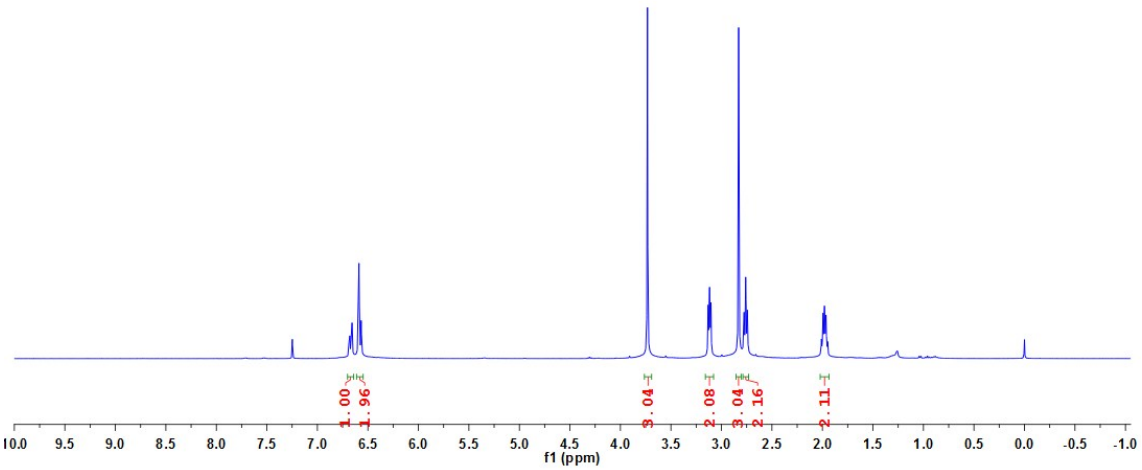
WHL-X180718-4 CNMR



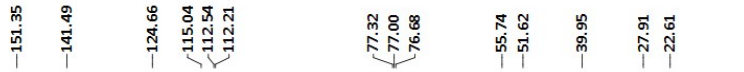


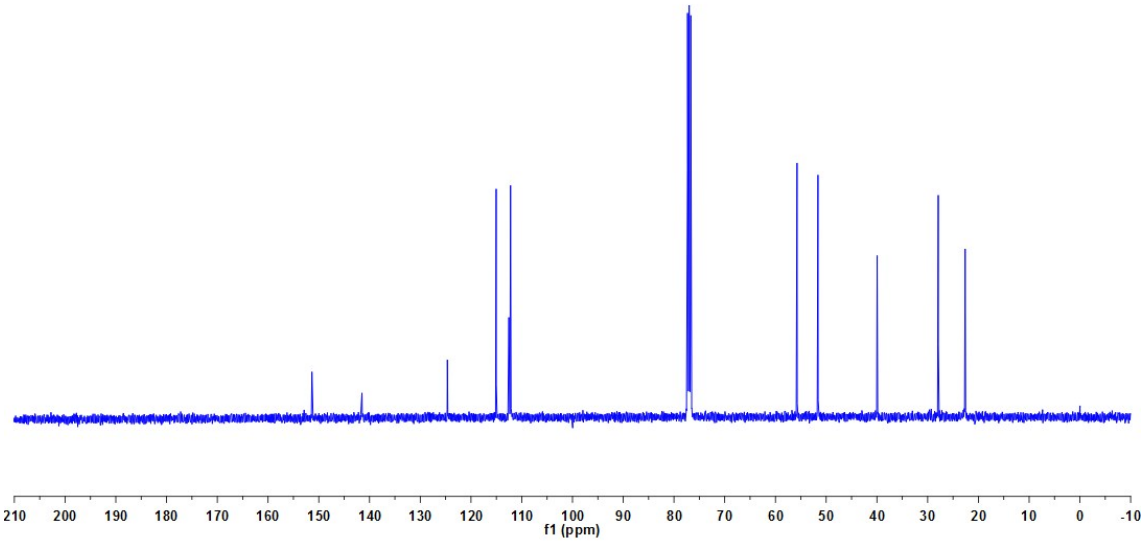
WHL-X180711-1 HNMR

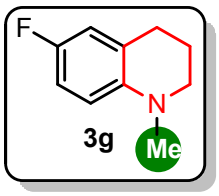




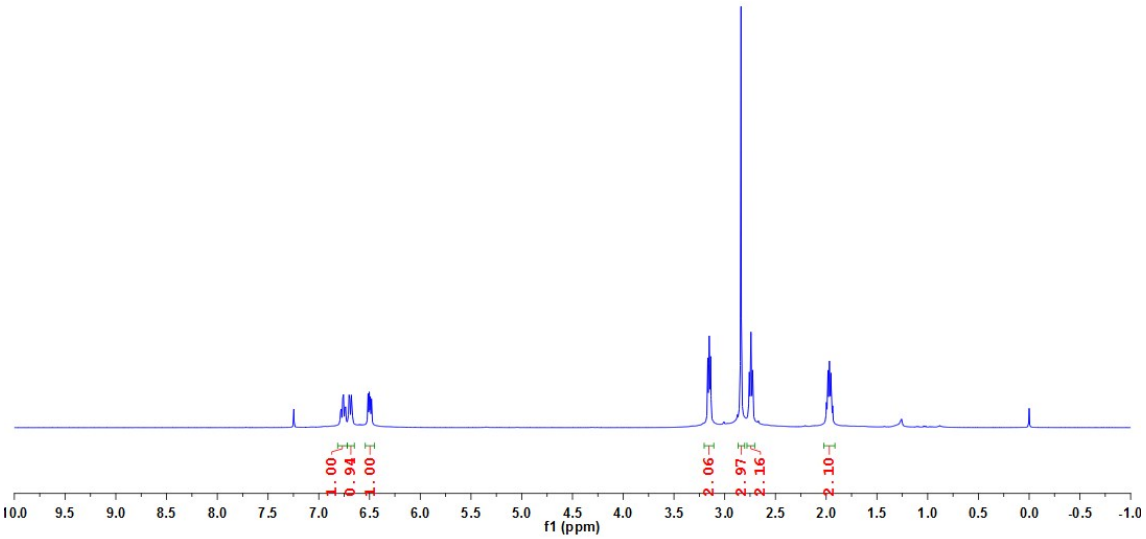
WHL-X180711-1 CNMR



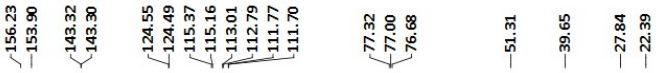


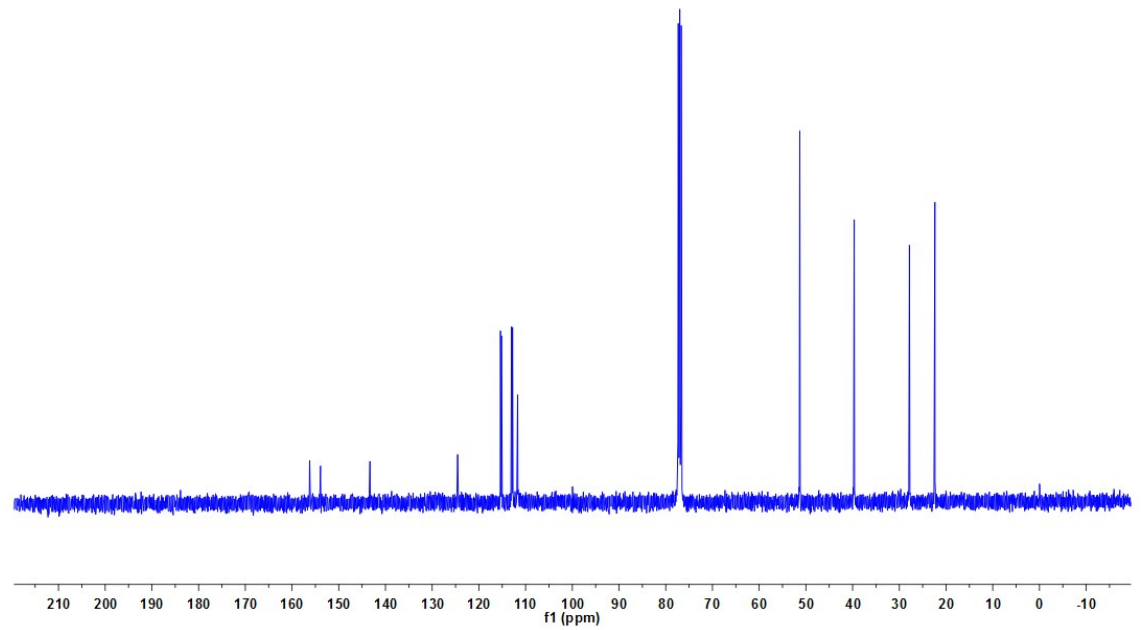


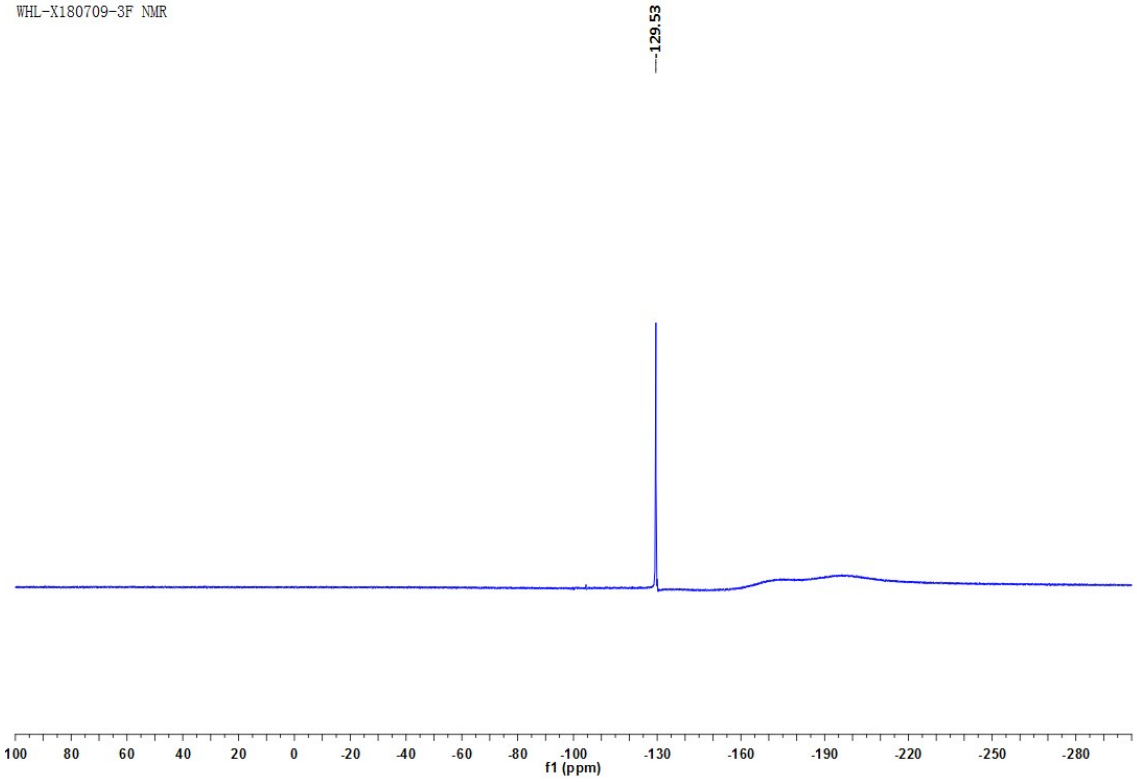
WHL-X180709-3H NMR

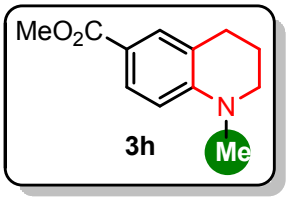


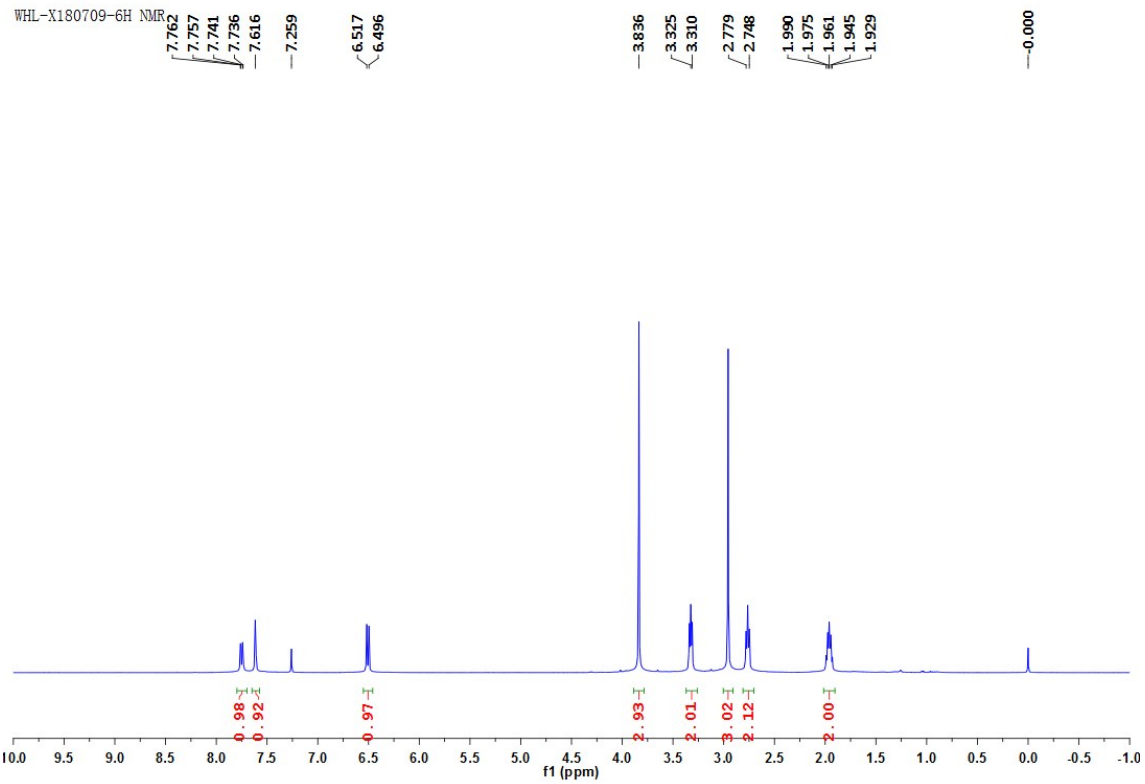
WHL-X180709-3C NMR

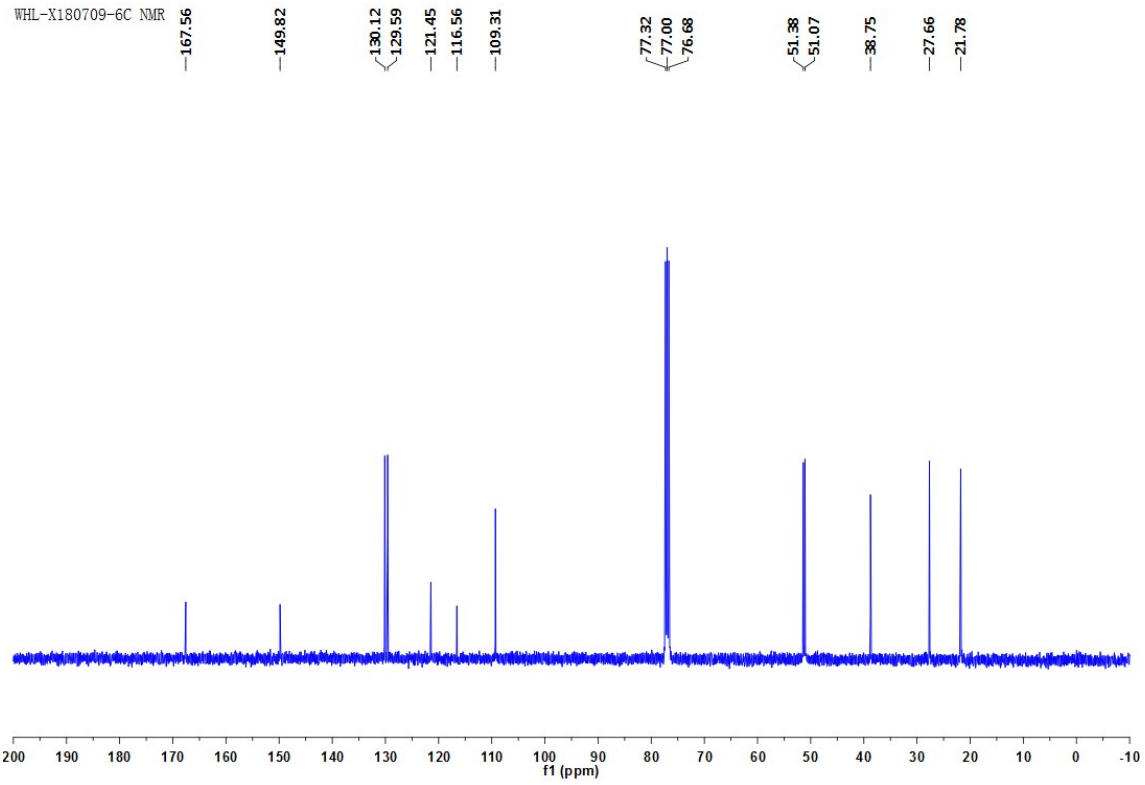


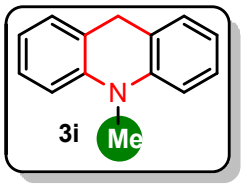


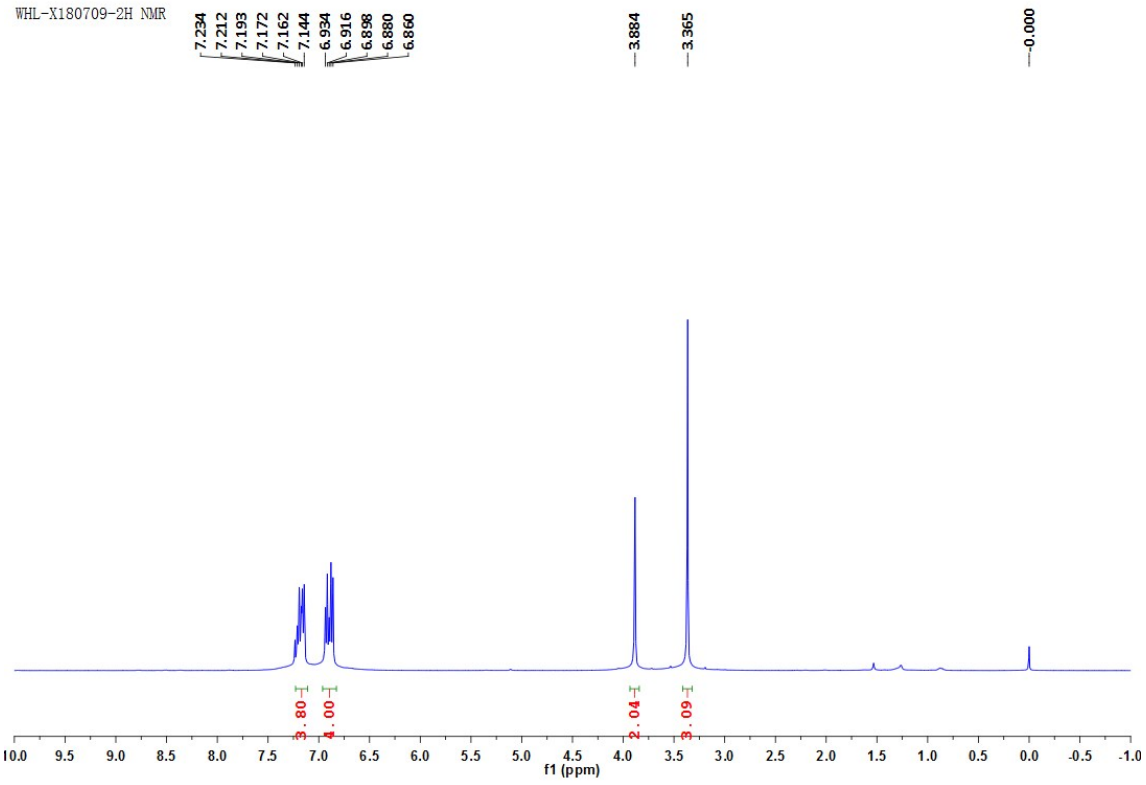

WHL-X180709-3F NMR
-129.53
100
80
60
40
20
0
-20
-40
-60
-80
-100
-130
-160
-190
-220
-250
-280
f1 (ppm)

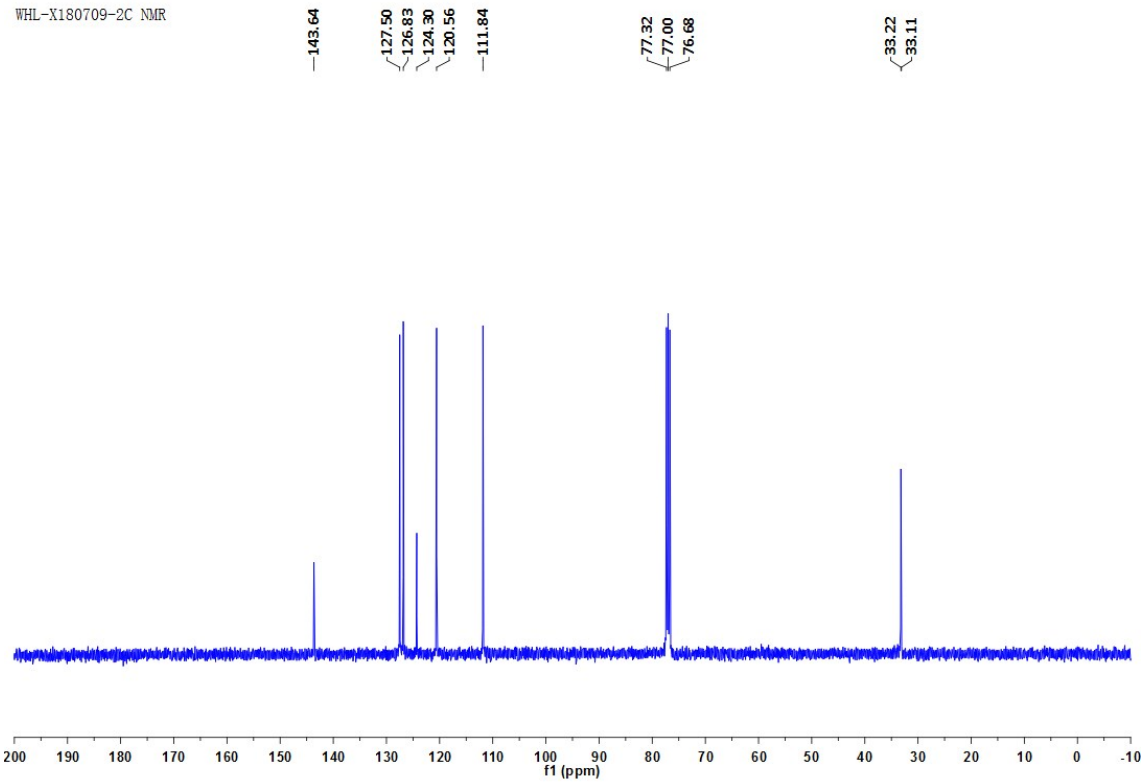

MeO2C
N
3h
Me

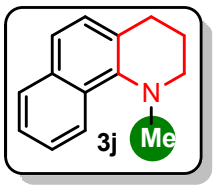

WHL-X180709-6H NMR
7.762
7.757
7.741
7.736
7.616
7.259
6.517
6.496
3.836
3.325
3.310
2.779
2.748
1.990
1.975
1.961
1.945
1.929
-0.000
0.98
0.92
0.97
2.93
2.01
3.02
2.12
2.00
f1 (ppm)

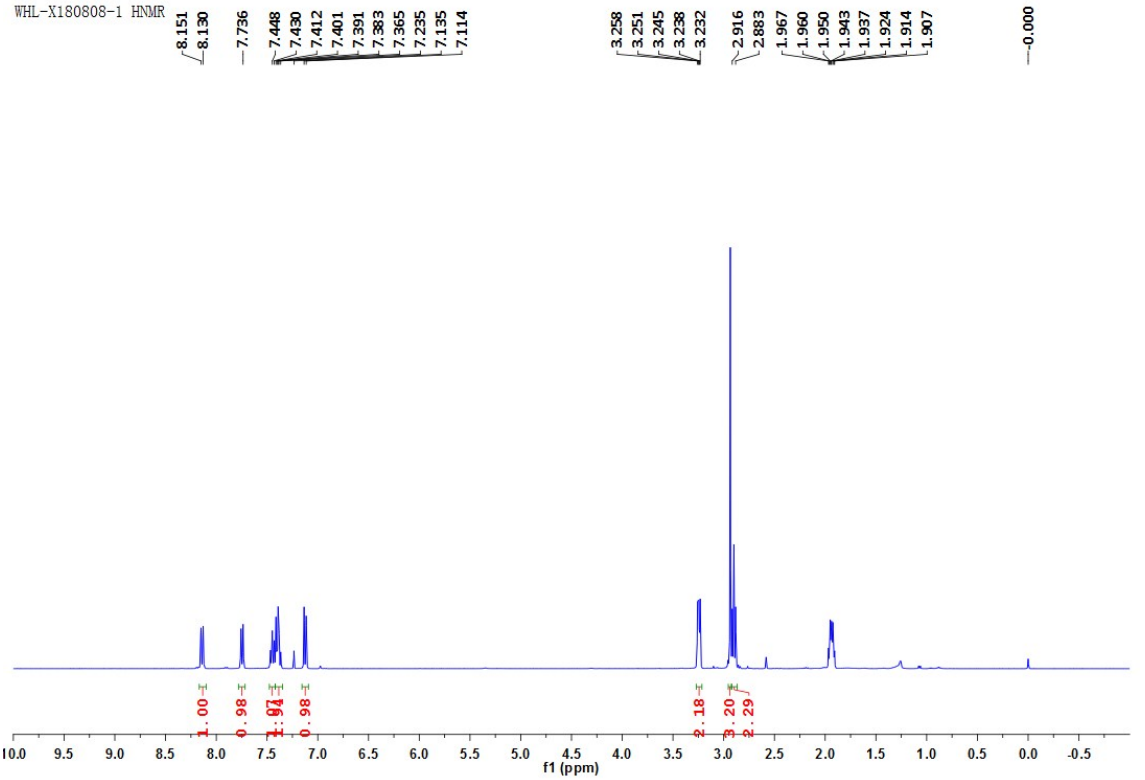

WHL-X180709-6C NMR
167.56
149.82
130.12
129.59
121.45
116.56
109.31
77.32
77.00
76.68
51.38
51.07
38.75
27.66
21.78
f1 (ppm)

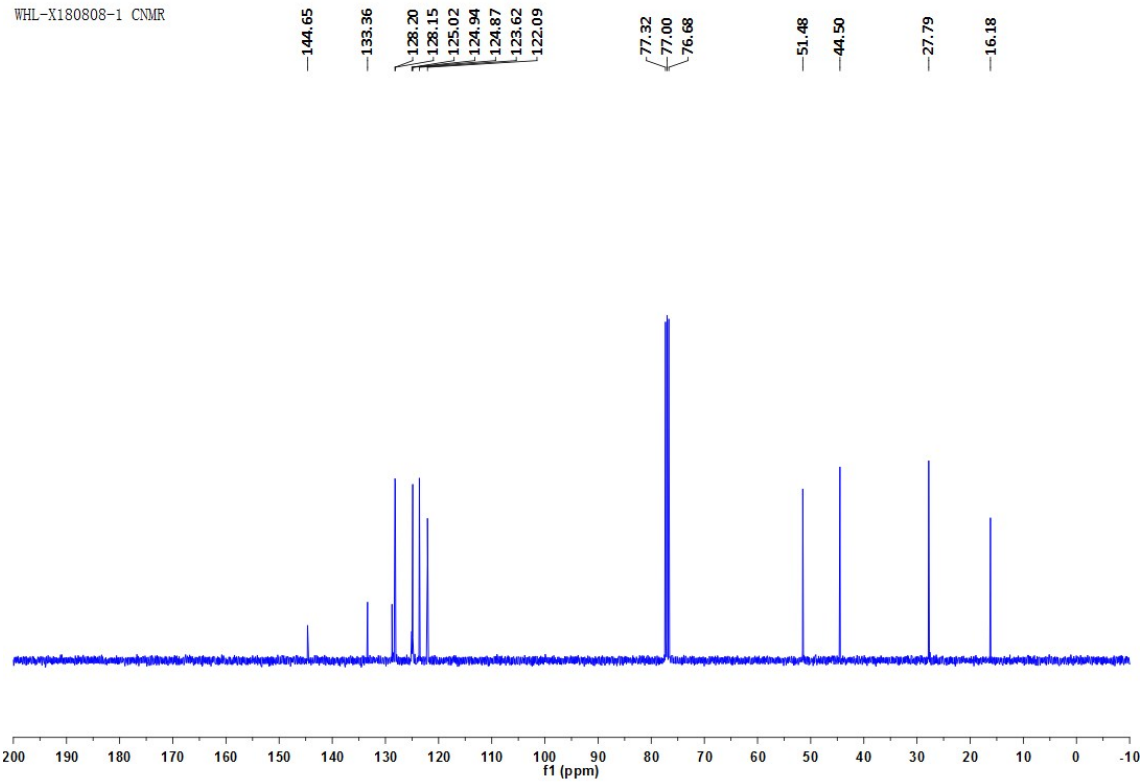

N
3i
Me

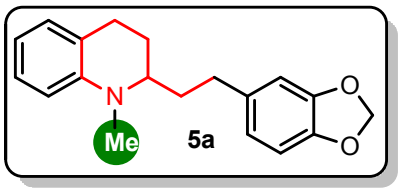

WHL-X180709-2H NMR
7.234
7.212
7.193
7.172
7.162
7.144
6.934
6.916
6.898
6.880
6.860
3.884
3.365
0.000
3.80
4.00
2.04
3.09
f1 (ppm)

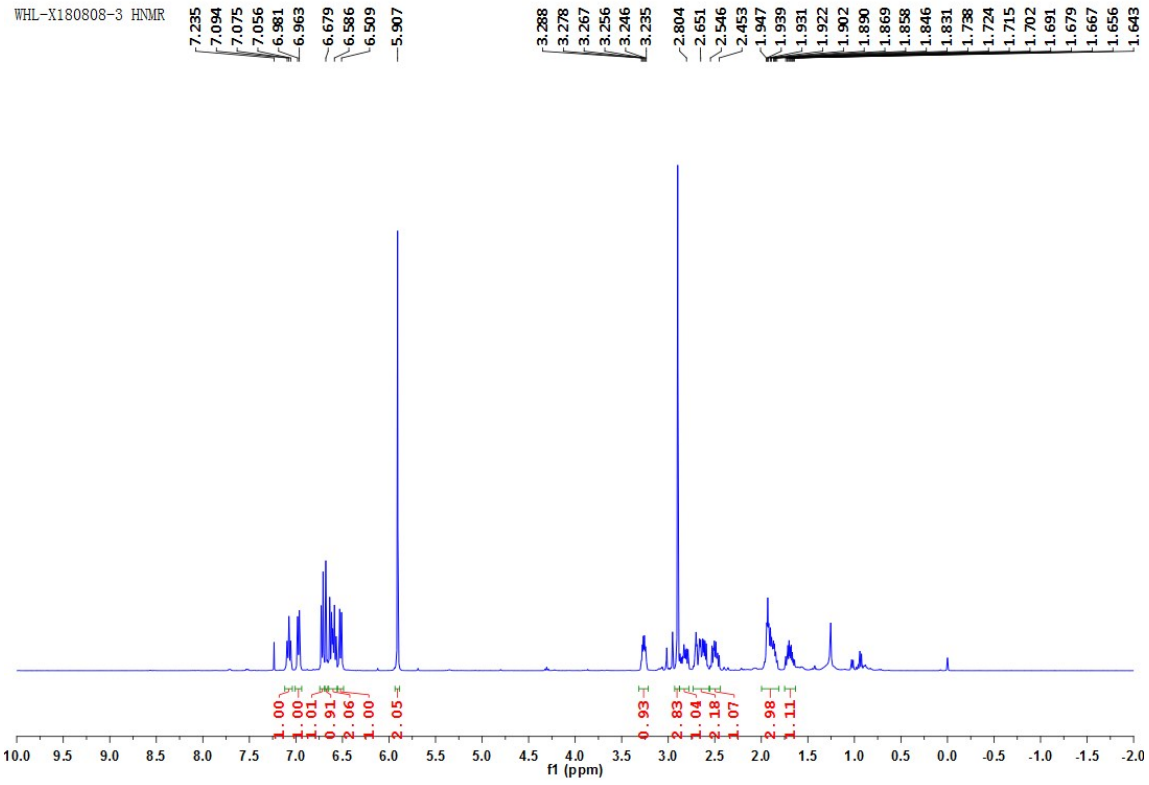

WHL-X180709-2C NMR
143.64
127.50
126.83
124.30
120.56
111.84
77.32
77.00
76.68
33.22
33.11
f1 (ppm)

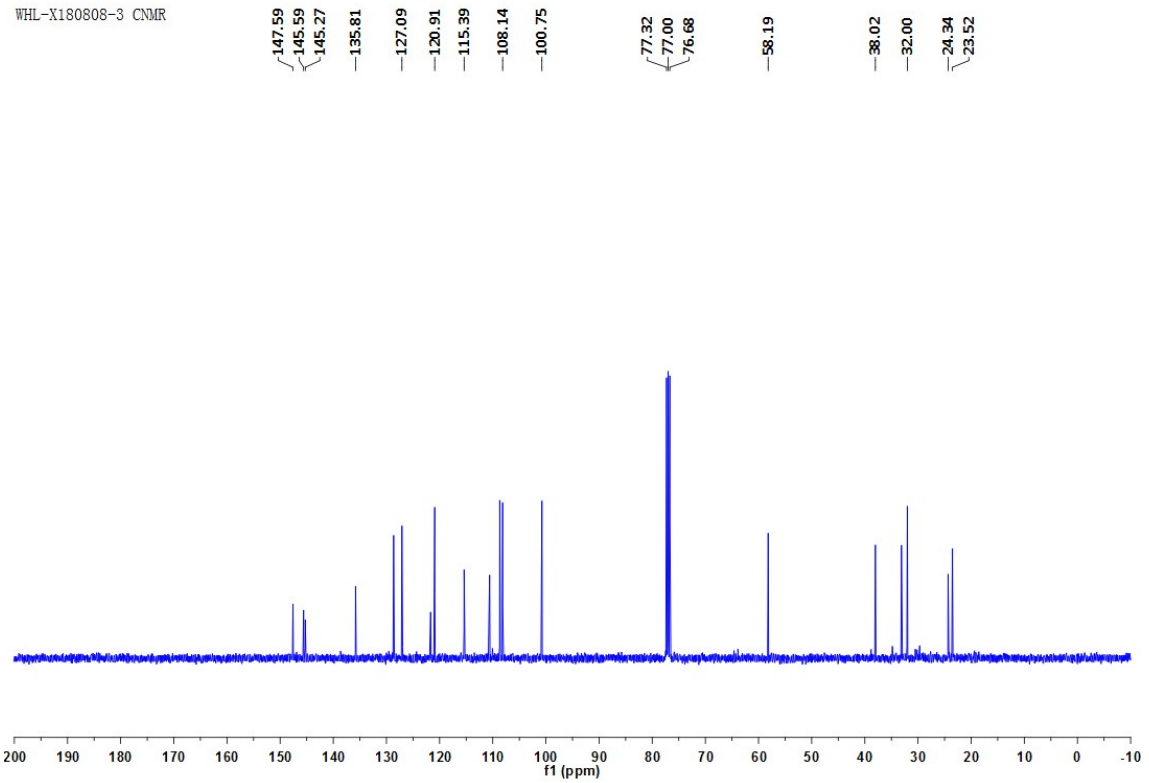

N
Me
3j

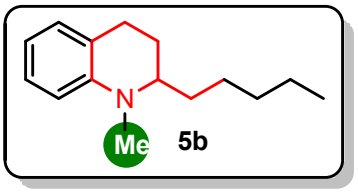

WHL-X180808-1 HNMR
8.151
8.130
7.736
7.448
7.430
7.412
7.401
7.391
7.383
7.365
7.235
7.135
7.114
3.258
3.251
3.245
3.238
3.232
2.916
2.883
1.967
1.960
1.950
1.943
1.937
1.924
1.914
1.907
0.000
1.00
0.98
1.07
1.04
0.98
2.18
3.20
2.29
f1 (ppm)


WHL-X180808-1 CNMR
144.65
133.36
128.20
128.15
125.02
124.94
124.87
123.62
122.09
77.32
77.00
76.68
51.48
44.50
27.79
16.18
f1 (ppm)

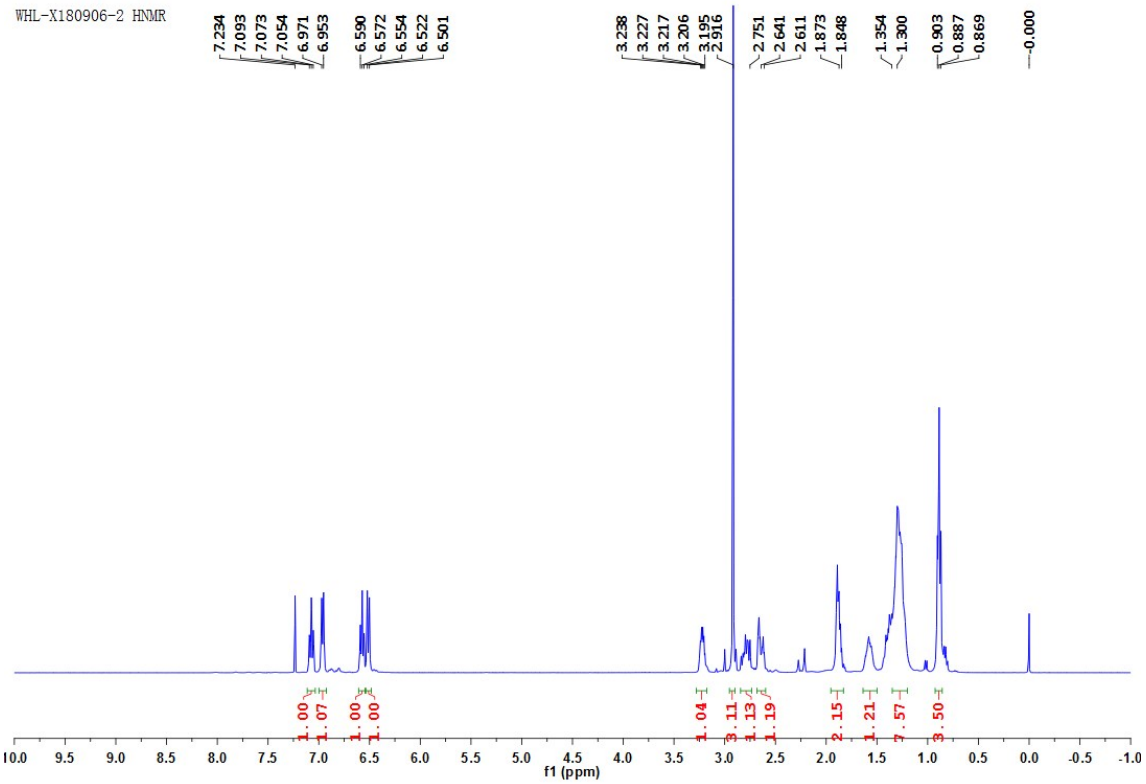

N
Me
5a
O
O

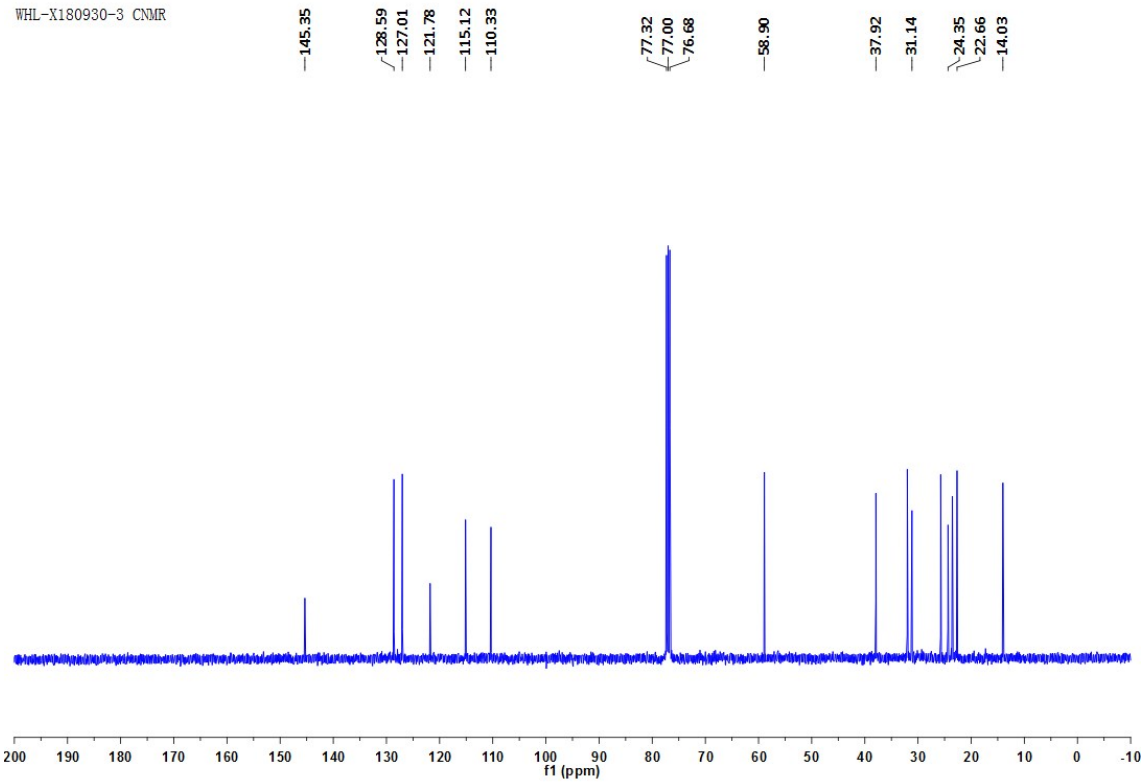

WHL-X180808-3 HNMR
7.235
7.094
7.075
7.056
6.981
6.963
6.679
6.586
6.509
5.907
3.288
3.278
3.267
3.256
3.246
3.235
2.804
2.651
2.546
2.453
1.947
1.939
1.931
1.922
1.902
1.890
1.869
1.858
1.846
1.831
1.738
1.724
1.715
1.702
1.691
1.679
1.667
1.656
1.643
1.00
1.00
1.01
0.91
2.06
1.00
2.05
0.93
2.83
1.04
2.18
1.07
2.98
1.11
f1 (ppm)


WHL-X180808-3 CNMR
147.59
145.59
145.27
135.81
127.09
120.91
115.39
108.14
100.75
77.32
77.00
76.68
58.19
38.02
32.00
24.34
23.52
f1 (ppm)


N
Me

5b


WHL-X180906-2 HNMR
7.234
7.093
7.073
7.054
6.971
6.953
6.590
6.572
6.554
6.522
6.501
3.238
3.227
3.217
3.206
3.195
2.916
2.751
2.641
2.611
1.873
1.848
1.354
1.300
0.903
0.887
0.869
-0.000
1.00
1.07
1.00
1.00
1.04
3.11
1.13
1.19
2.15
1.21
7.57
3.50
f1 (ppm)


WHL-X180930-3 CNMR
145.35
128.59
127.01
121.78
115.12
110.33
77.32
77.00
76.68
58.90
37.92
31.14
24.35
22.66
14.03
f1 (ppm)

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