Supporting Information

Tandem synthesis of tetrahydroquinolines and identification of reaction network by *operando* NMR

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General information

Chemicals and materials The chemicals were obtained from commercial suppliers and used as received. Zirconium chloride (98%), 2-nitrobenzaldehyde (99%), and Palladium on activated charcoal (5% Pd) were provided by Macklin. benzene-1,4-dicarboxylic acid (BDC, 98%) and acetophenone-α,β-$^{13}C_2$ (99 atom% ^{13}C) were procured from Aldrich. 4'-Fluoroacetophenone (>98%), 1'-acetonaphthone (>98%), and 2-aminoterephthalic acid (>98%) were received from TCI. Acetophenone (99%), 4-methoxyacetophenone (99%), 4′-nitroacetophenone (97%), 4-fluoro-2-nitrobenzaldehyde (98%), 5-fluoro-2-nitrobenzaldehyde (98%), 6-nitropiperonal (98%), and 4-chloro-2-nitrobenzaldehyde (>98%) were brought form Aladdin. *N*,*N*-dimethylformamide (≥99.5%), toluene (≥99.7%), dichloromethane (≥99.5%), ethanol (⩾99.8%), acetone (≥ 99.5%), hydrochloric acid (36-38%), nitric acid (65-68%), and acetic acid (≥99.5%) were provided by Sinopharm Chemical Reagent Co., Ltd. Palladium (II) acetate (98%) and 9-acetylanthracene (98%) were purchased from Bidepharm. Palladium on alumina oxide (5% Pd) was brought from 3A Chemicals.

Synthesis of MOFs

UiO-66: UiO-66 was prepared by a solvothermal method reported in literature.[1] H_2BDC (853 mg, 5.13 mmol), $ZrCl_4$ (1.2 g, 5.15 mmol) were added to 300 mL of DMF. The mixture was sonicated to dissolve all solid. After that, the solution was transferred to a Teflon-lined stainless steel autoclave, and reacted at 120 °C for 24 h. The resulted white solid was separated by centrifugation and washed with DMF (3×50 mL), EtOH (3×50 mL), and acetone (3×50 mL) thoroughly. The solid was activated by heating at 120 °C for 24 h before catalysis.

UiO-66(HCl): UiO-66(HCl) was synthesized and purified according to a method described in literature.[2] Typically, $ZrCl_4$ (125 mg, 0.54 mmol), hydrochloric acid (1 mL) and DMF (5 mL) were mixed and sonicated for 20 min. H_2BDC (123 mg, 0.75 mmol) and DMF (10 mL) was added to the clear solution and sonicated for another 20 min to allow full dissolution. After 16 h at 80 °C, the resulted white solid was separated by centrifugation and washed with DMF (3×20 mL), EtOH (3×20 mL), and acetone (3×50 mL) thoroughly. The solid was activated by heating at 120 °C for 24 h before catalysis.

UiO-66(AcOH): UiO-66(AcOH) was prepared with AcOH as the additive.[3] Specifically, $ZrCl_4$ (1.3 g, 5.6 mmol) and terephthalic acid (931.3 mg, 5.6 mmol) were dissolved in 64 mL of DMF. Then, 0.4 mL of deionized water and 9.6 mL of AcOH were successively added into the mixture dropwise. The obtained solution was transferred to a 250 mL of Teflon-lined hydrothermal reaction vessel, and reacted at 120 ^oC for 24 h. After naturally cooling to room temperature, the obtained solid was washed and dried as the process described for UiO-66.

UiO-66-NH_2(0.5): UiO-66-NH_2(0.5) was prepared with mixed linker of terephthalic acid and 2-aminoterephthalic acid (molar ratio 1:1). The procedure is similar as UiO-66(HCl).

Preparation of Pd/MOF[4]

Generally, 100 mg of MOF was added to 5 mL of dichloromethane (DCM), followed by sonication (1 h) to disperse the solid homogeneously. 5 mL of DCM containing 4.2 mg of palladium acetate was added to the above suspension under vigorous stirring. After stirring at room temperature for 24 h, the solid was separated by centrifugation and washed with DCM for 5 times to completely remove free palladium salt. The solid was dried under vacuum and reduced for 2 h at 200 °C, under flowing 10% H_2/Ar (50 mL/min) for 2 h.

Characterization

Nitrogen physisorption studies of the materials were used to measure the BET surface area on a Micromeritics 3Flex instrument at -196 °C after degassing at 120 °C for 24 h (<20 mtorr). The powder X-ray diffraction (XRD) patterns were obtained on PANalytical X'Pert PRO powder diffractometer using Cu Kα radiation (40 kV, 40 mA, λ = 0.1541 nm). Scanning electron microscopy (SEM) images were recorded on Hitachi SU-8010 instrument. The size and morphology of Pd/UiO-66s was characterized by transmission electron microscopy (TEM) using a Hitachi 7700 electron microscope operated at 100 kV. Inductively coupled plasma optical emission spectrometry (ICP-OES) was conducted on Varian-730ES instrument. The sample (~5 mg) was digested in 5 mL of concentrated nitric acid in a Teflon-lined hydrothermal reaction vessel at 160 ^oC for 2 h. After cooling down, the clear solution was diluted with deionized water for ICP analysis. Thermogravimetric analysis (TGA) was conducted on TA Q500 instrument under a 100 mL/min flow of air, ramping from 50 °C to 700 °C at a rate of 10 °C/min.

Catalytic reactions Generally, 2-nitrobenzaldehyde (NBA, 0.2 mmol), acetophenone (ACP, 0.4 mmol), 2 wt% Pd/UiO-66s (10 mg), mesitylene (10 μL, as internal standard) and toluene (1 mL) was stirred at 80 °C for 5 h. Then, the mixture was hydrogenated under H_2 for 19 h.

The conversion and selectivity of the product were determined using Shimadzu GC2010 Plus gas chromatograph with a flame ionization detector (GC-FID). The instrument is equipped with an HP-5 capillary column (30 m × 0.25 mm × 0.25 μm).

^{1}H NMR and ^{13}C NMR spectra were measured on a Bruker Avance III spectrometer (9.4 T). TOF-MS spectra were collected using a Waters GCT Premier instrument.

Operando MAS-NMR spectroscopy Magic-angle-spinning (MAS) NMR experiments were performed on an Agilent DD2 400 MHz (9.4 T) spectrometer equipped with a 5-mm triple-resonance Chemagnetics probe, operating at a MAS rate of 5 kHz. External calibration of the spectrometer temperature setting was achieved by ethylene glycol.[5] ^{13}C chemical shifts were referenced to TMS *via* a secondary standard, adamantane (37.48 ppm).[6] In direct polarization (DP) ^{13}C MAS-NMR experiments, a 50 kHz ^{1}H decoupling field was employed, with an acquisition time of 327 ms. The ^{13}C spectral width was 50 kHz, and 64k data points were acquired per transient, using a relaxation delay of 100 s to ensure quantitative analysis. Each transient spectrum was acquired by averaging 8 scans unless specified otherwise. Spectra were collected starting when the probe reached its set temperature, ca. 5-10 min after heating of the rotor commenced.

A customized 5 mm ZrO_2 rotor (*WHiMS* rotor, Revolution NMR) was loaded with ACP-α,β-$^{13}C_2$ (1.48 mg, 12.3 μmol), NBA (3.0 mg, 19.8 μmol), 2 wt% Pd/UiO-66s (1.22 mg), and 50 μL toluene under air. In Step 1, the spectrum acquisition during the Claisen-Schmidt condensation was conducted under air at 60 °C. In Step 2, the rotor with the catalyst and the end solution after Step 1 was pressurized with 50 bar H_2 at 22 °C and the spectrum array was collected at room temperature for the reductive-cyclization reaction.

Characterization data of the catalysts

Table S1 Textual properties of UiO-66(HCl) and Pd/UiO-66(HCl)

sample	BET surface area ($m^2 \cdot g^{-1}$)	micropore pore volume ($cm^3 \cdot g^{-1}$)
UiO-66(HCl)	2027	0.66
Pd/UiO-66(HCl)	1687	0.55

PXRD patterns of various UiO-66 samples

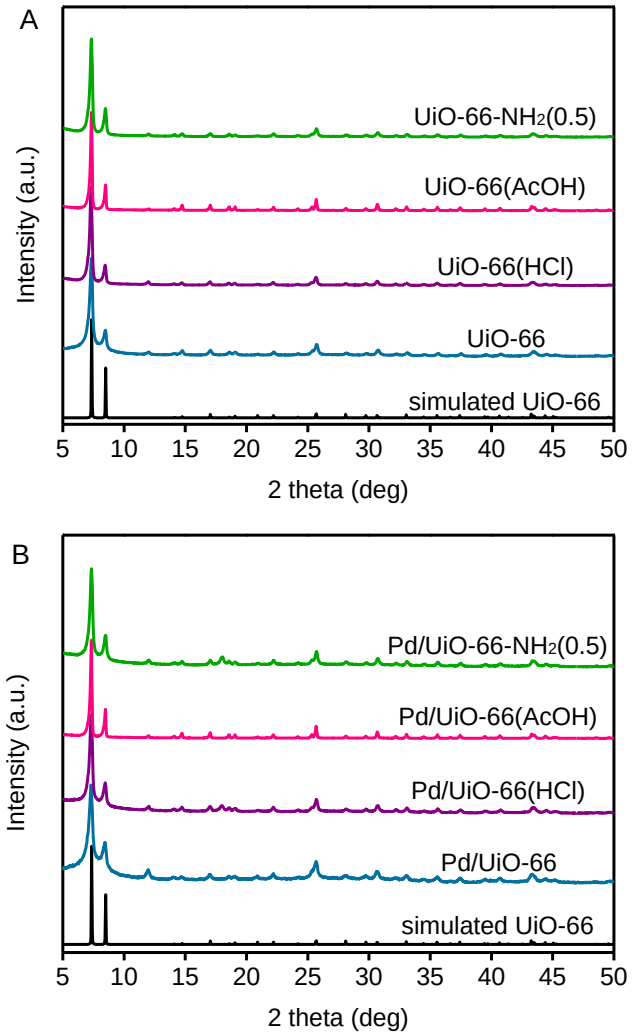


Fig. S1 PXRD patterns of different UiO-66 and Pd-loaded UiO-66 samples.

TGA results of different UiO-66 samples

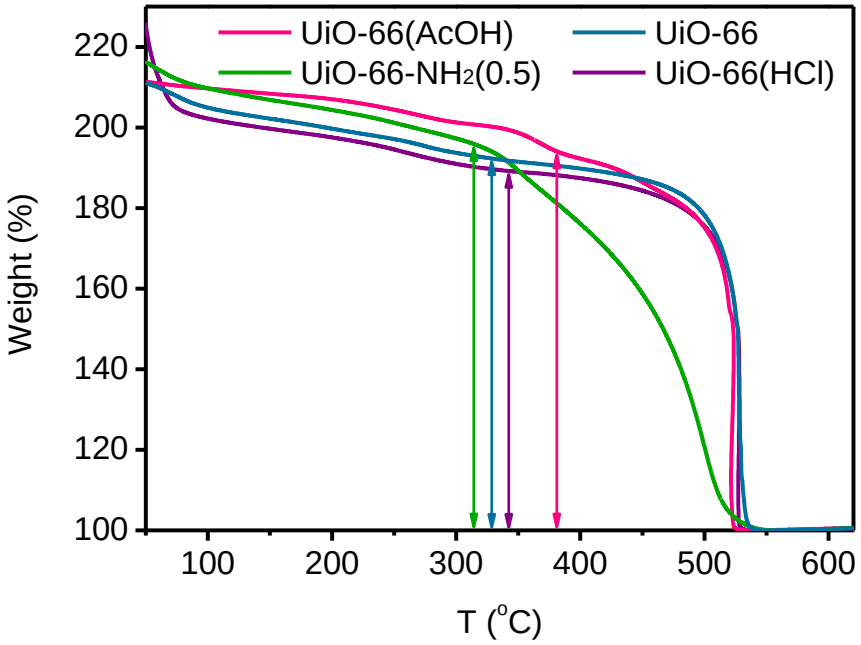


Fig. S2 Normalized TGA curves of different UiO-66 samples under air. The residue at high temperature corresponding to ZrO_2 was set at 100. The average coordination numbers of Zr_6 cluster in UiO-66, UiO-66(HCl), UiO-66(AcOH), and UiO-66-NH_2(0.5) are 9.2, 8.8, 9.0, and 9.4, respectively. More defects were generated with hydrochloric acid as additives in the preparation of UiO-66(HCl).

SEM images of various UiO-66 samples

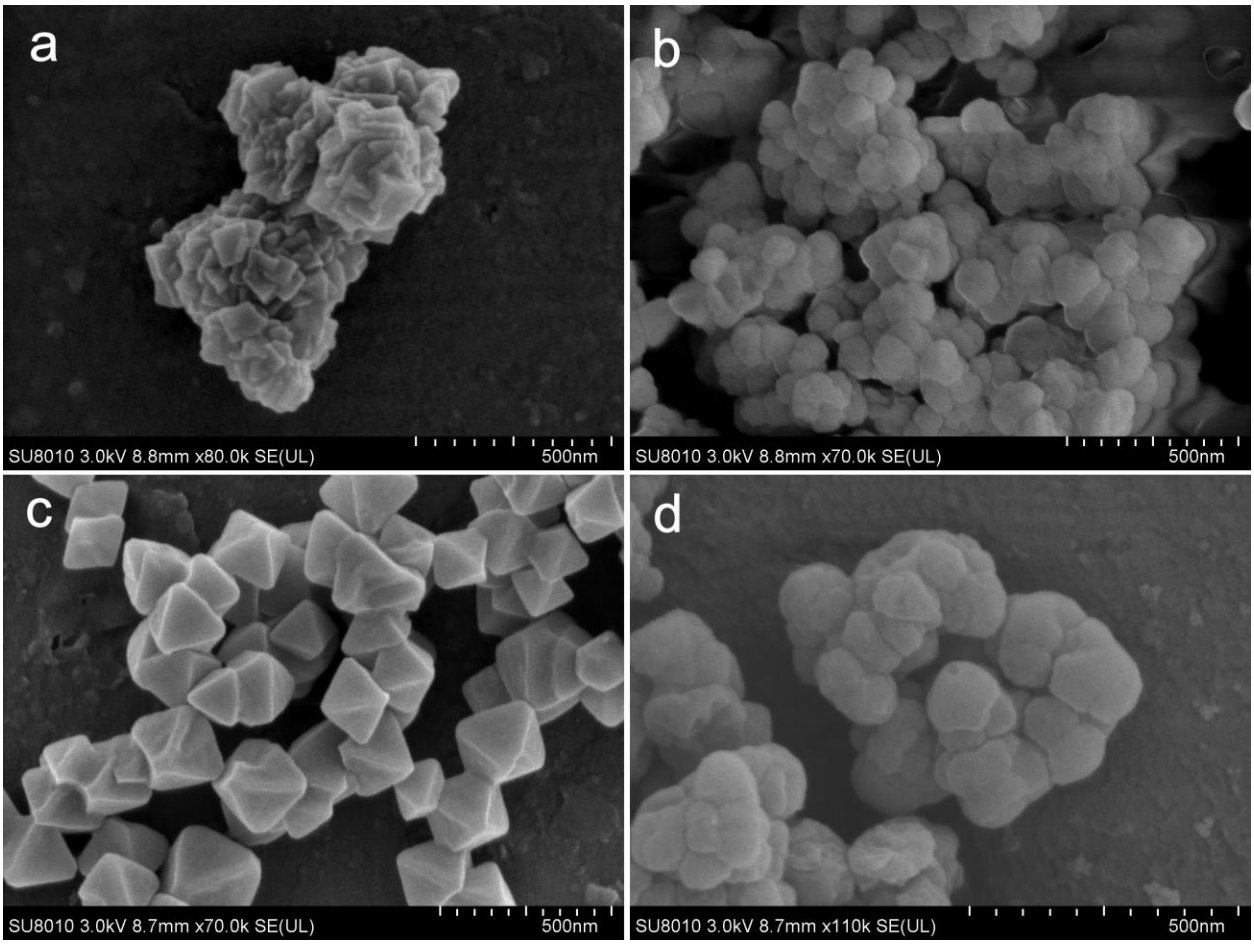


Fig. S3 SEM images of (a) UiO-66, (b) UiO-66(HCl), (c) UiO-66(AcOH), and (d) UiO-66-NH_2(0.5). SEM images indicated that intergrowth was observed for UiO-66 (a). After adding HCl to the mixture, the surface of the resulted UiO-66(HCl) (b) become spherical and agglomeration of the particles was observed. With AcOH as the monodentate modulator, which compete with the BDC linkers and coordinate to the Zr secondary building units (SBUs), the MOF crystal become octahedron (c). The shape and crystal size of UiO-66-NH_2(0.5) (d), which prepared in the presence of HCl, is similar as that of UiO-66(HCl).

SEM images of various Pd/UiO-66 samples

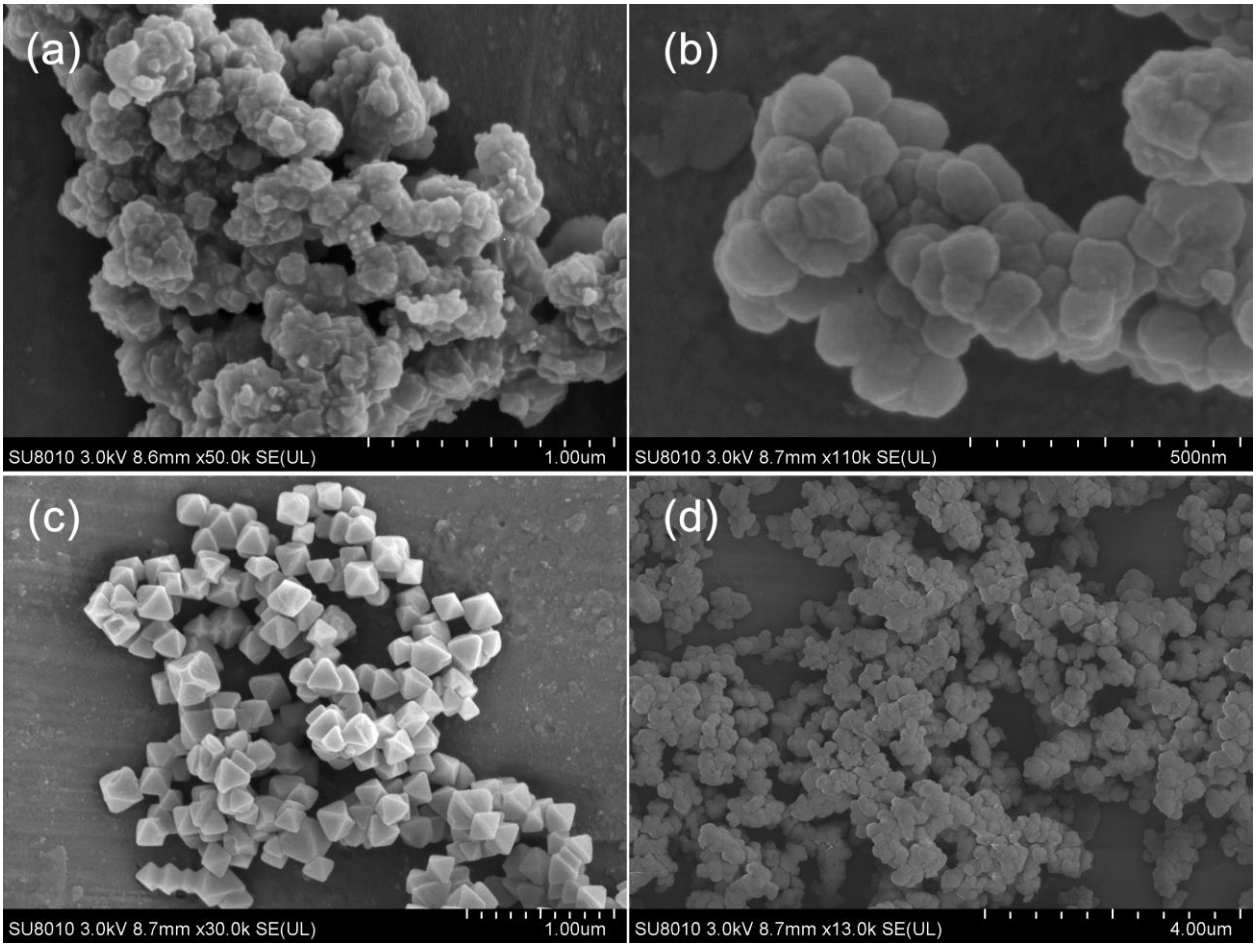


Fig. S4 SEM images of (a) Pd/UiO-66, (b) Pd/UiO-66(HCl), (c) Pd/UiO-66(AcOH), and (d) Pd/UiO-66-NH_2(0.5). The impregnation of Pd does not impact the morphology of the MOFs.

TEM images and corresponding histograms of Pd particle size distribution of various Pd/UiO-66 samples

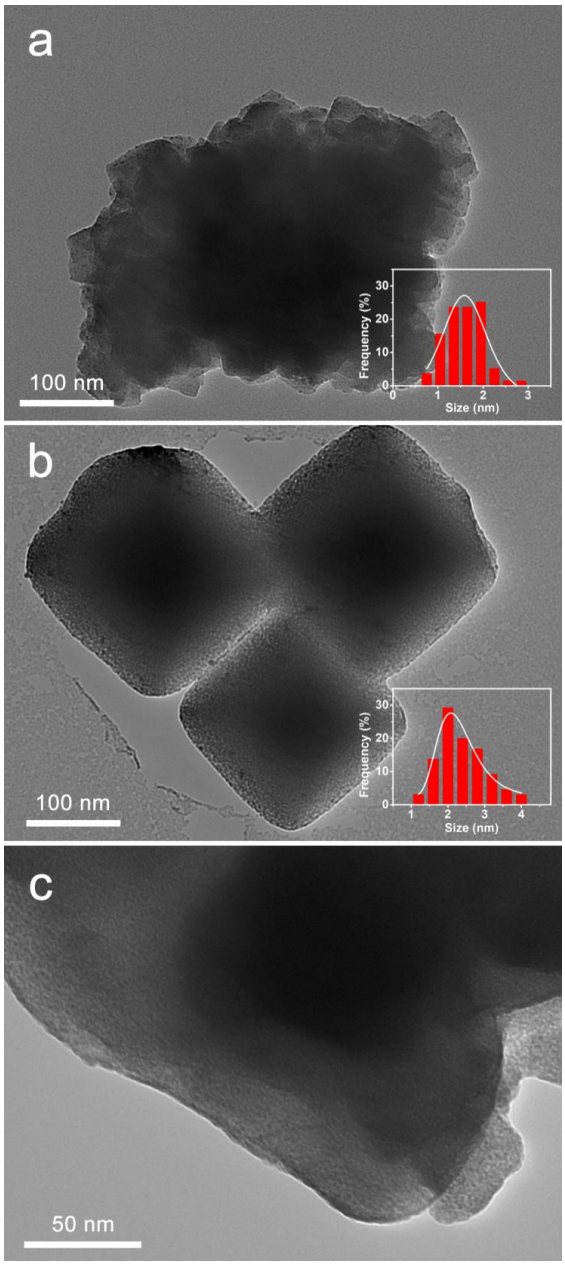


Fig. S5 TEM image of (a) Pd/UiO-66, (b) Pd/UiO-66(AcOH), and (c) Pd/UiO-66-NH_2(0.5). Transmission electron microscopy (TEM) images show that Pd NPs are dispersed uniformly on UiO-66s with a mean size of 1.6 nm and 2.1 nm for Pd/UiO-66 and Pd/UiO-66(AcOH), respectively. When half amount of BDC was replaced by BDC-NH_2, the Pd nanoparticle size of the prepared Pd/UiO-66-NH_2(0.5) become very small, which possibly due to the coordination of $–NH_2$ with Pd nanoparticles that makes it better dispersed inside MOF pores.[7]

TEM image of Pd/UiO-66(HCl) at low magnification

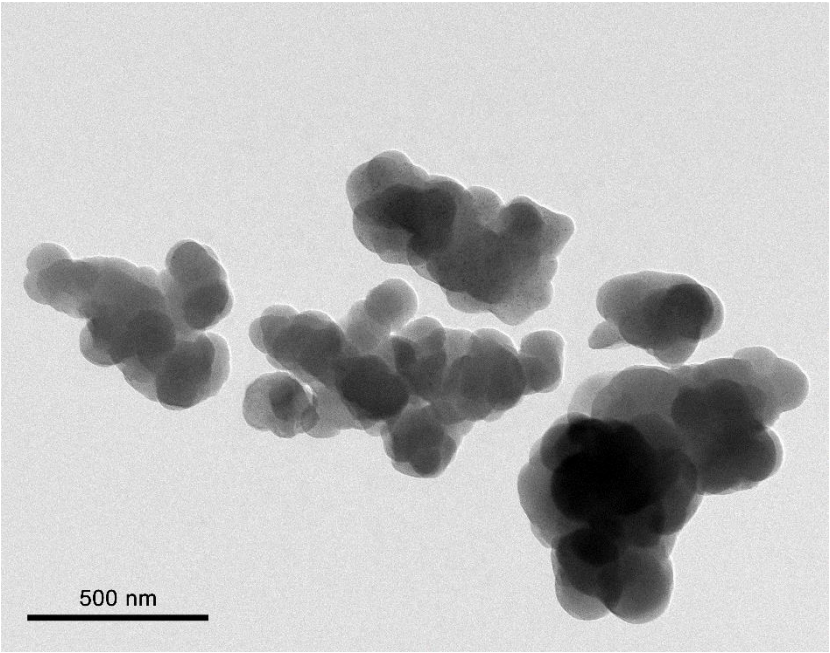


Fig. S6 TEM image of Pd/UiO-66(HCl). The low magnification TEM image of Pd/UiO-66 indicated that no large nanoparticles were observed, illustrating the homogeneous dispersion of Pd nanoparticles on UiO-66(HCl).

ICP-OES analysis of the catalysts

Table S2 Metal content of the catalysts

catalyst	Zr (wt%)	Pd (wt%)
UiO-66	34.2	-
UiO-66(HCl)	32.8	-
UiO-66(AcOH)	33.5	-
UiO-66-NH_2(0.5)	31.7	-
Pd/UiO-66	30.1	1.8
Pd/UiO-66(HCl)	27.1	1.6
Pd/UiO-66(AcOH)	36.4	1.8
Pd/UiO-66-NH_2(0.5)	24.4	1.7

***Operando* NMR spectra of the Claisen-Schmidt condensation reaction**

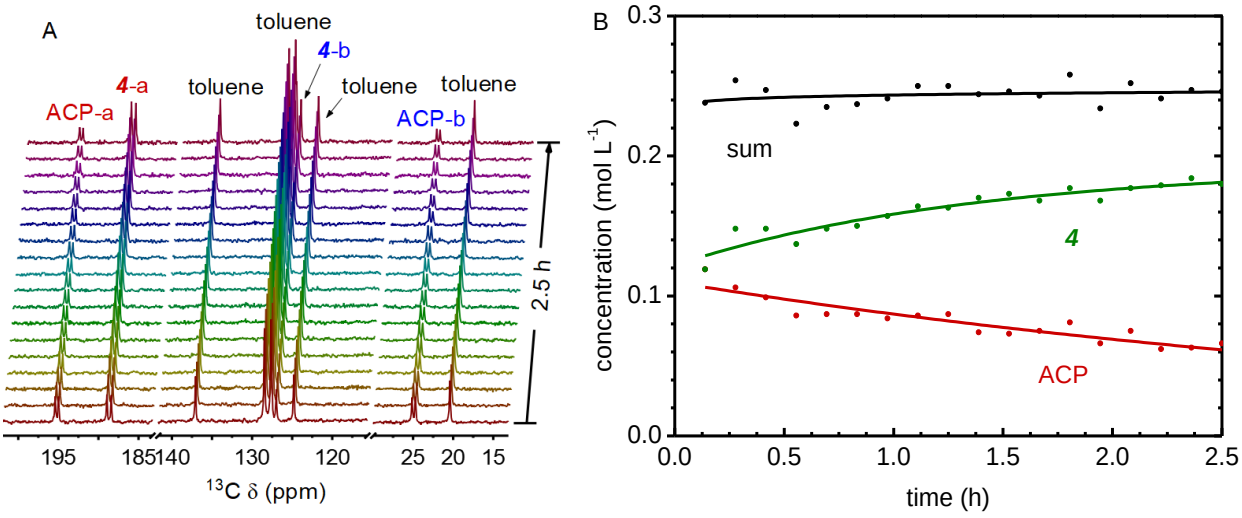


Fig. S7 Pd/UiO-66(HCl) catalyzed Claisen-Schmidt condensation of NBA and ACP at 100 °C after reacted at 60 °C for 14.5 h. (A) Time evolution of direct polarization ^{13}C MAS-NMR spectra (MAS rate: 5 kHz, eight scans per transient); (B) kinetic analysis of time-resolved NMR spectra. The curve fitting of ACP was obtained by fitting the second-order rate equation.

Concentration profiles based on Operando NMR

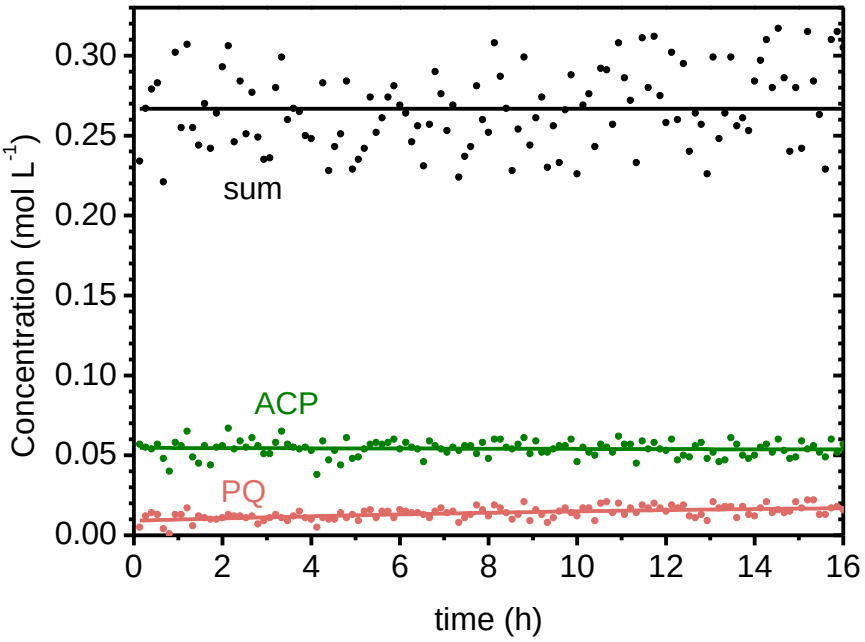


Fig. S8 Concentration profiles of ACP, PQ and sum of all species, extracted from MAS-NMR array (**Fig. 4**).

***Operando* NMR spectra of the reductive cyclization reaction**

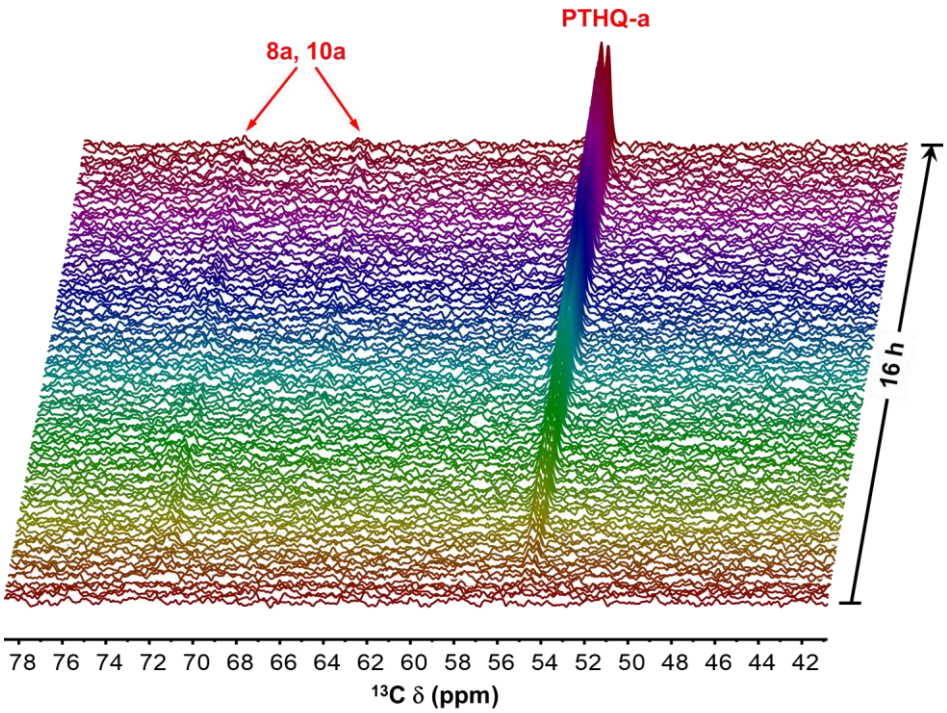
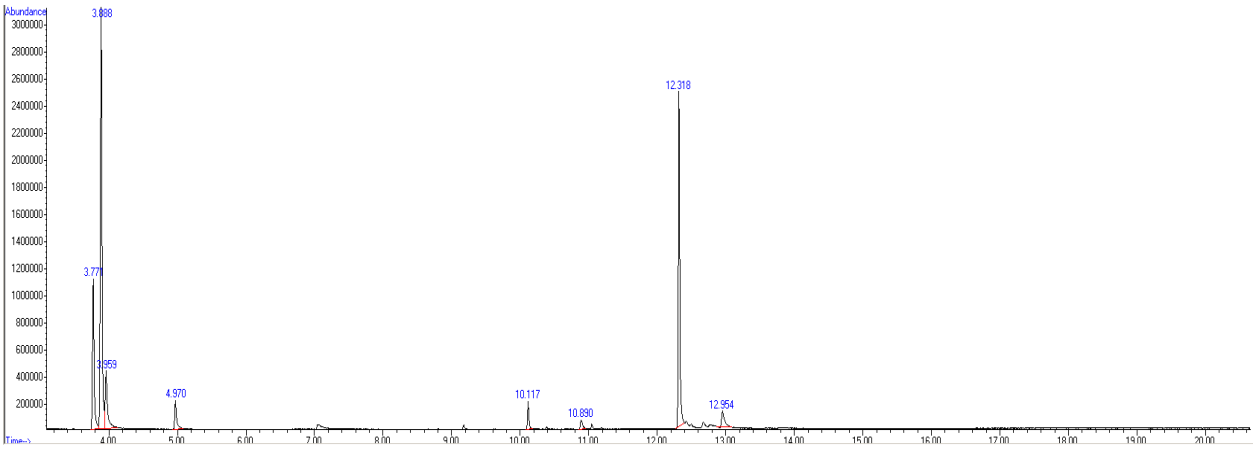
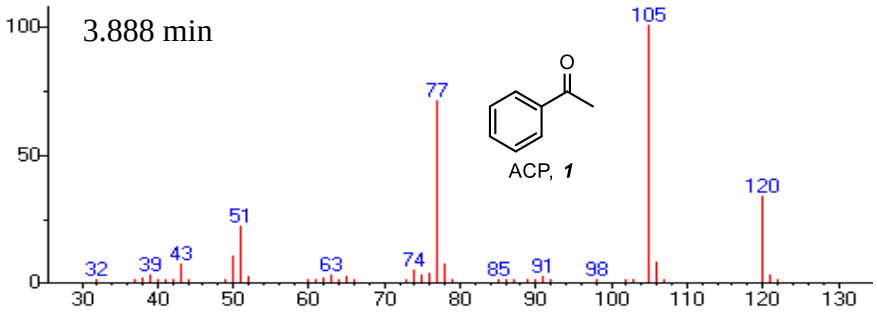


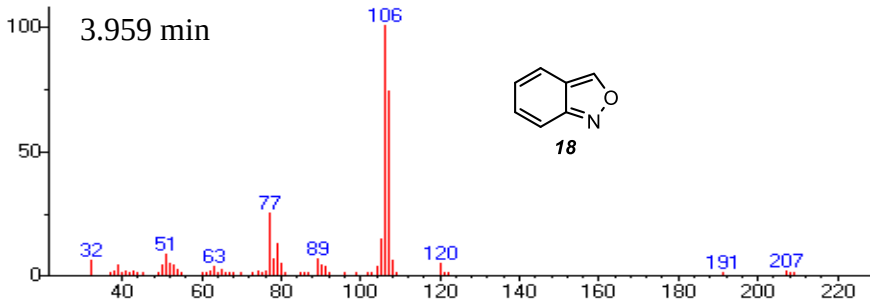
Fig. S9 In situ array of direct polarization ^{13}C MAS-NMR spectra in the range of 79-41 ppm, recorded during reductive cyclization of the reaction mixture after the Claisen-Schmidt condensation step. Reaction conditions: 1.6 wt % Pd/UiO-66(HCl) (1.22 mg), H_2 (50 bar), room temperature, 16 h.

GC-MS analysis of the reaction mixture

Fig. S10 GC-MS analysis of the reaction mixture after hydrogenation. Reaction conditions: (1) NBA (0.2 mmol), ACP (0.2 mmol), 1.6 wt% Pd/UiO-66(HCl) (10 mg), toluene (1 mL), 80 °C, 5 h; (2) 6.9 bar H_2, 100 °C, 8 h.







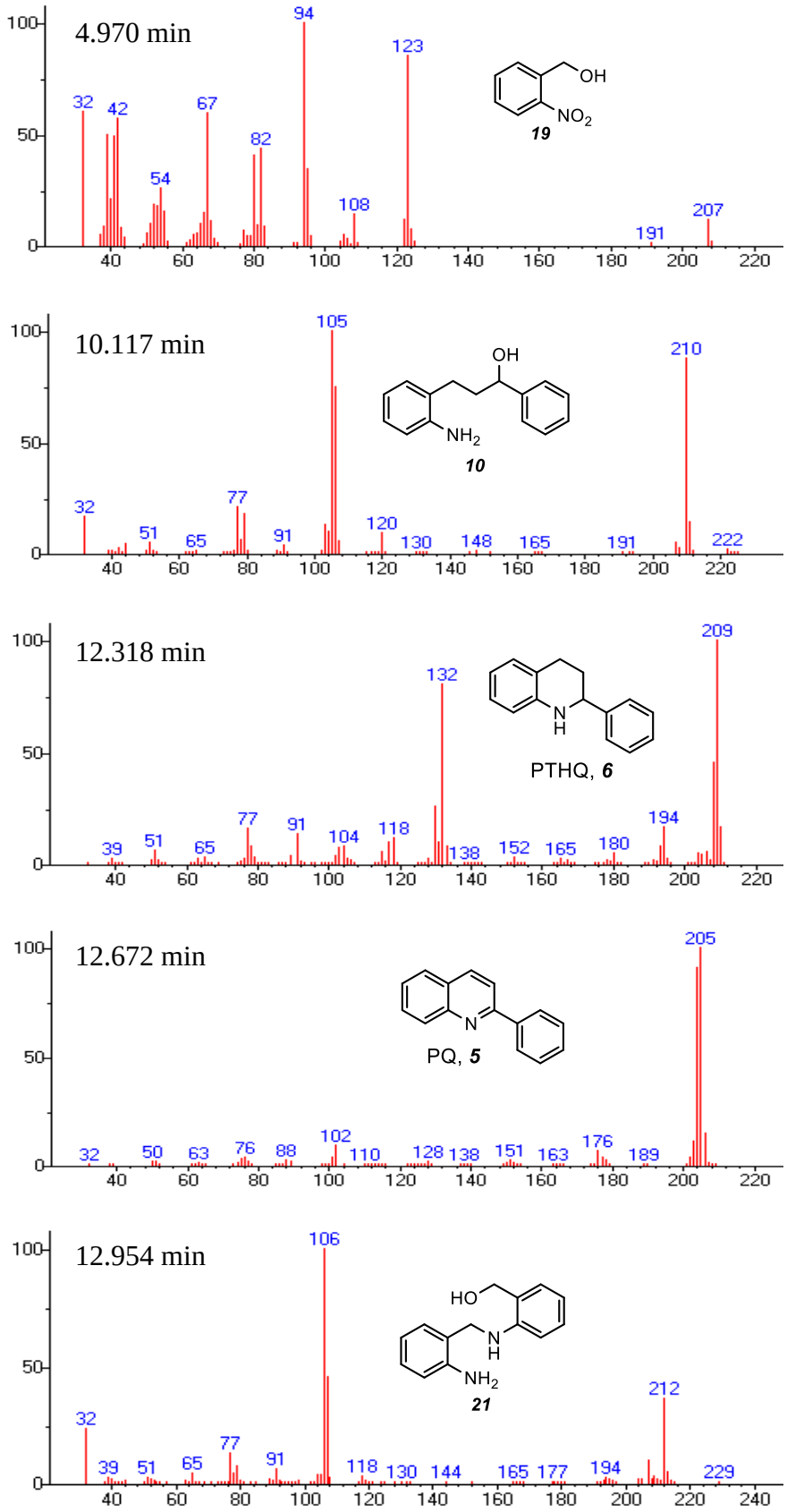

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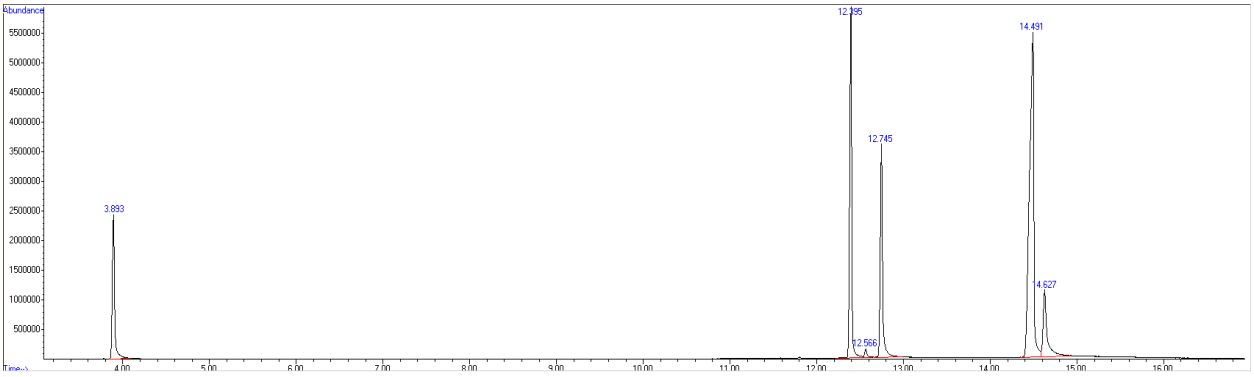
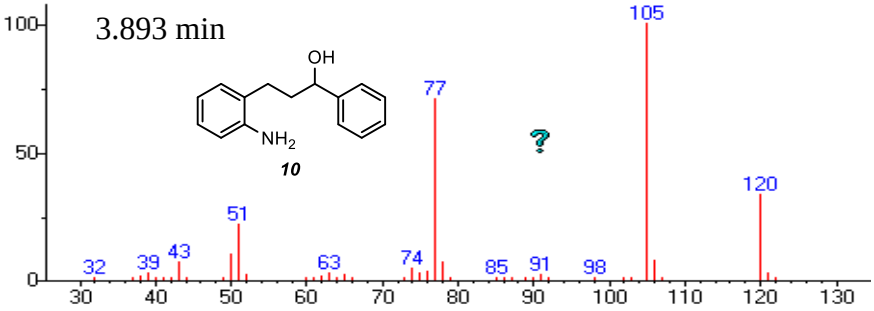
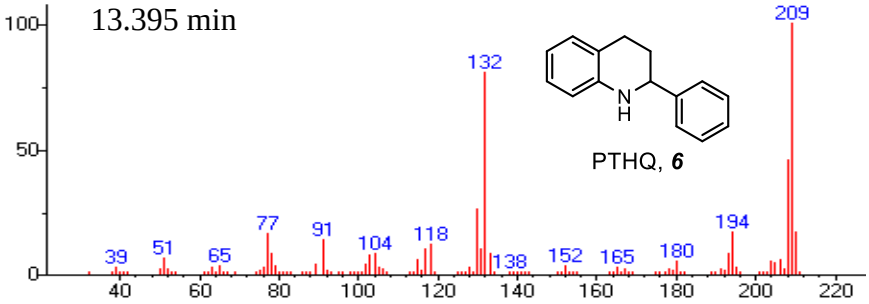
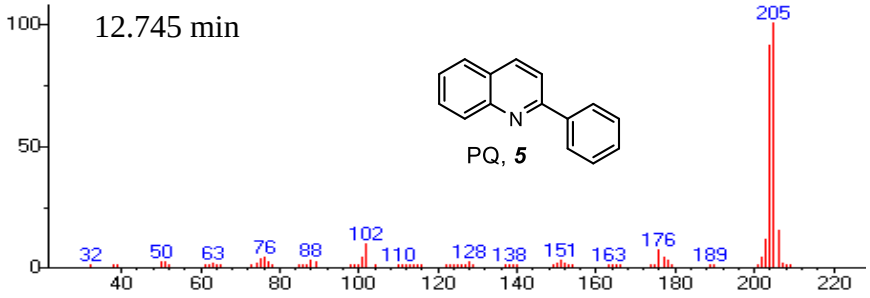
Fig. S11 GC-MS analysis of the reaction mixture after hydrogenation. Reaction conditions: (1) NBA (0.2 mmol), ACP (0.4 mmol), 1.6 wt% Pd/UiO-66(HCl) (10 mg), toluene (1 mL), 80 °C, 5 h; (2) 27.6 bar H_2, 40 °C, 4 h.





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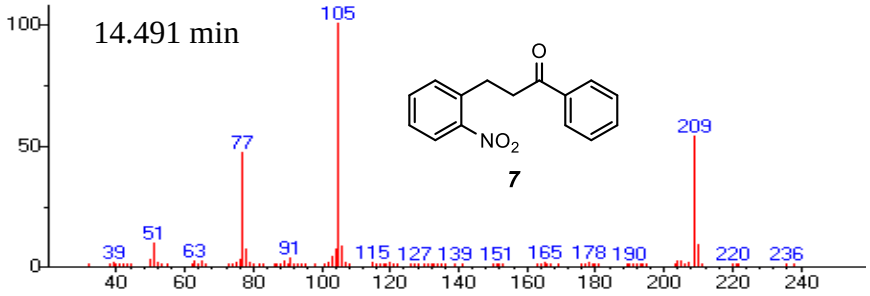
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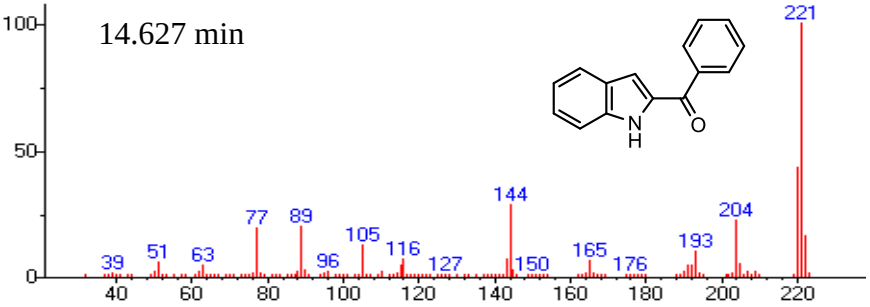
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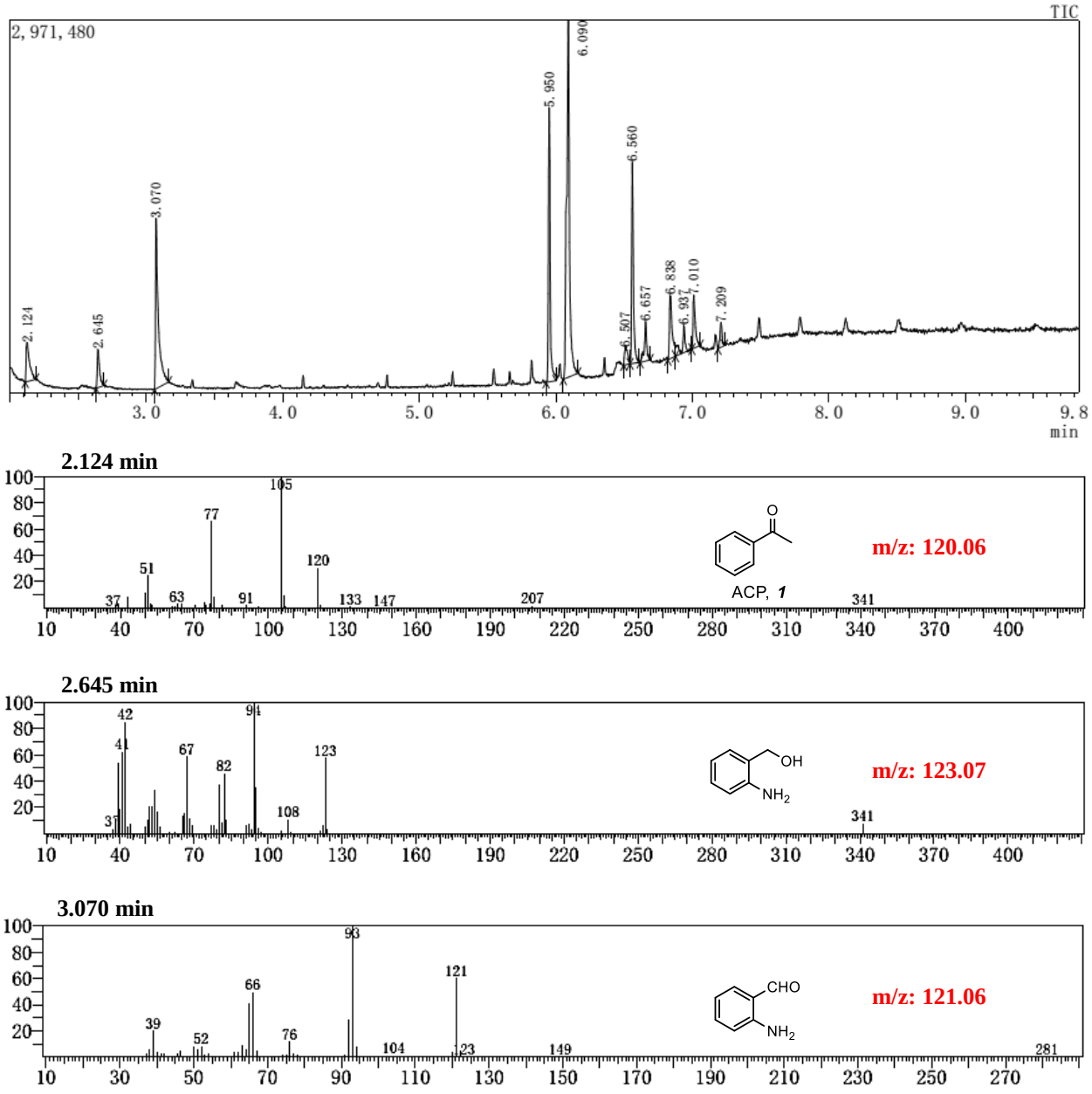
Fig. S12 GC-MS analysis of the reaction mixture after hydrogenation. Reaction conditions: ACP (25.1 mg, 0.21 mmol), NBA (47.2 mg, 0.31 mmol), 1.6 wt % Pd/UiO-66(HCl) (20.4 mg), toluene (0.8 mL), 100 °C, 19 h. Step 2): H_2 (50 bar), 28 °C, 1 h.



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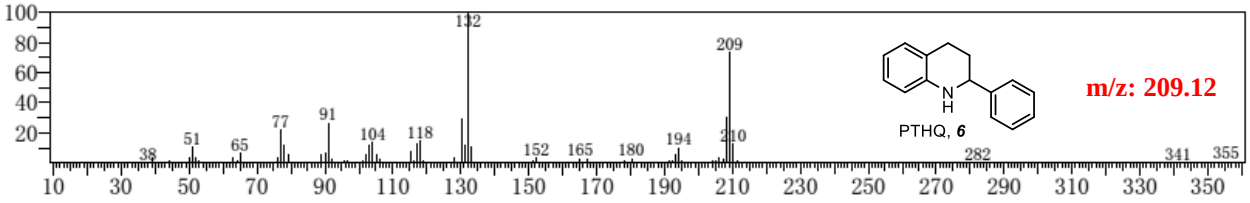

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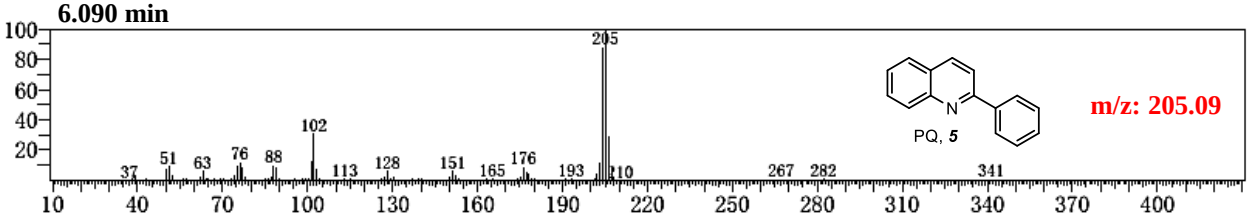

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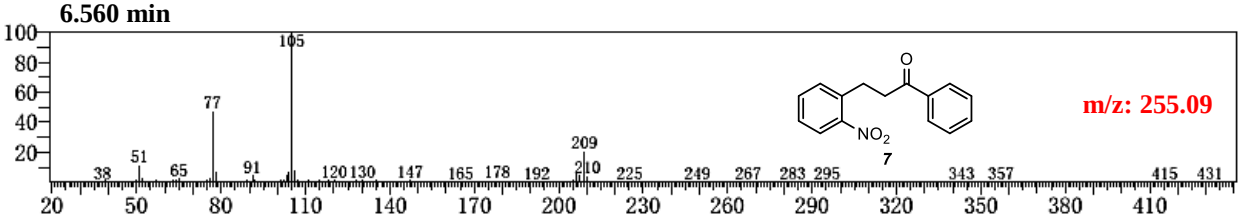

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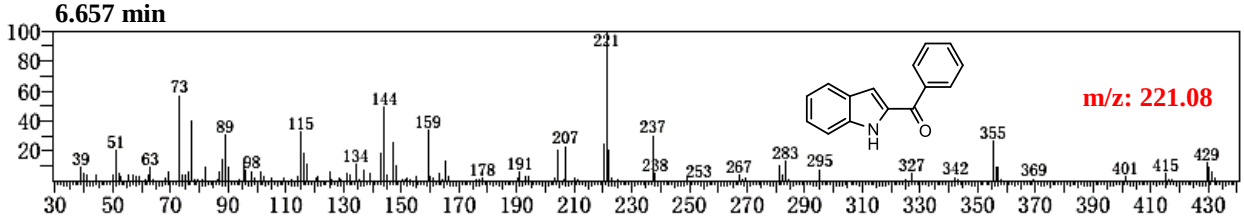

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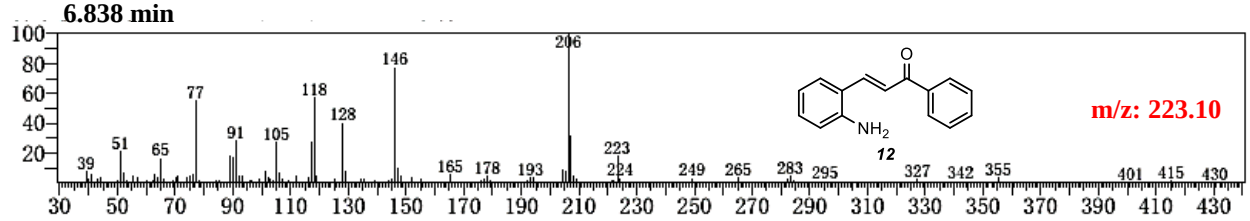

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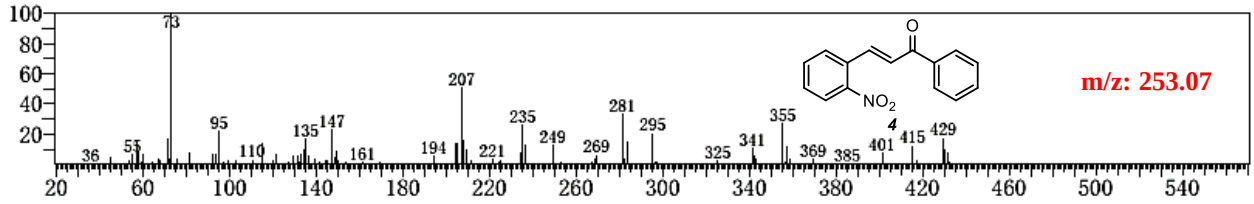

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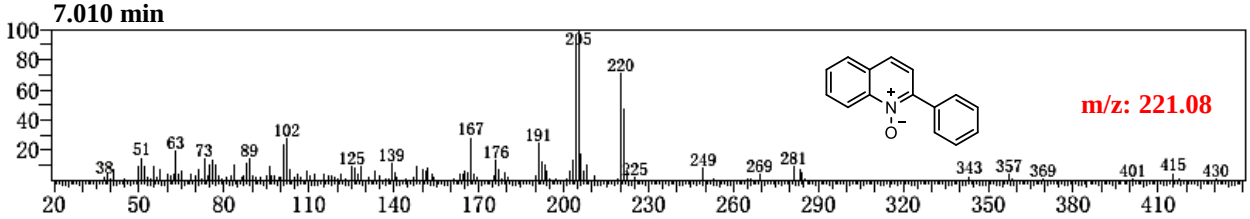
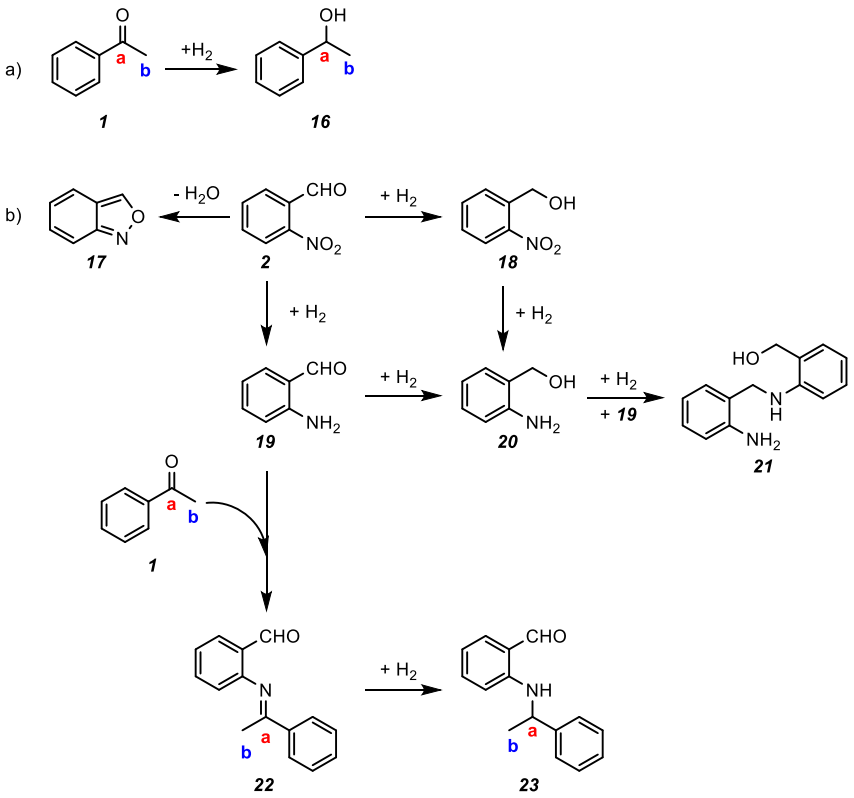


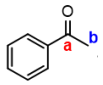
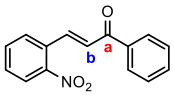
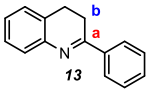
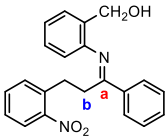
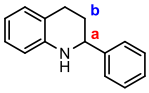
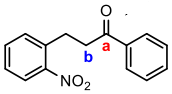
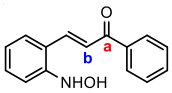
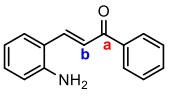
Reaction network



Scheme S1 Reaction network of side products involved in the hydrogenation of a) ACP and b) NBA as catalyzed by Pd/UiO-66(HCl).

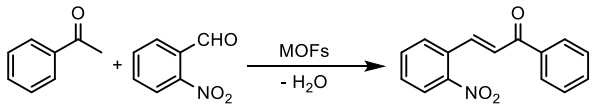
J-coupling constants

Table S3 *J*-coupling constants of chemicals identified in the *operando* MAS-NMR study

entry	chemical structure	^{13}C-13 ^{1}J (Hz)		
		a-C	b-C	average
1	 ACP, ***1***	42.4	42.6	42.5
2	 ***4***	55.2	56.0	55.6
3	 ***13***	37.7	36.8	37.2
4	 ***15***	44.2	44.9	44.6
5	 PTHQ, ***6***	33.3	33.2	33.2
6	 ***7***	40.6	40.0	40.3
7	 ***9***	58.3	57.9	58.1
8	 ***12***	55.7	56.3	56.0

Catalytic activity for the Claisen-Schmidt condensation reaction

Table S4 TON of different catalysts in the Claisen-Schmidt condensation reaction



entry	catalyst	TON
1	UiO-66	0.05
2	UiO-66(HCl)	6.3
3	UiO-66(AcOH)	3.2
4	UiO-66-NH_2(0.5)	1.8

Reaction conditions: NBA (0.2 mmol), ACP (0.4 mmol), MOF (with 18 mol% of metal), toluene (1 mL), 80 °C. TON was calculated at a reaction time of 0.5 h.

Table S5 Claisen-Schmidt condensation reaction with different catalysts[a]

catalyst	conversion (%)[b]
Pd/UiO-66(HCl)	100
Pd/C	trace
Pd/Al_2O_3	7

[a] Reaction conditions: NBA (0.2 mmol), ketone (2.0 equiv), catalyst (10 mg), toluene (1 mL), 80 °C, 5 h. [b] Conversion of NBA.

The results in Table S5 indicated that the commercial Pd-supported catalysts (Pd/C and Pd/Al_2O_3) are inert for the Claisen-Schmidt condensation reaction. Hence, despite their catalytic hydrogenation activity, they are not suitable for the targeted tandem transformation.

Catalytic activity for the hydrogenation-intramolecular cyclization reaction

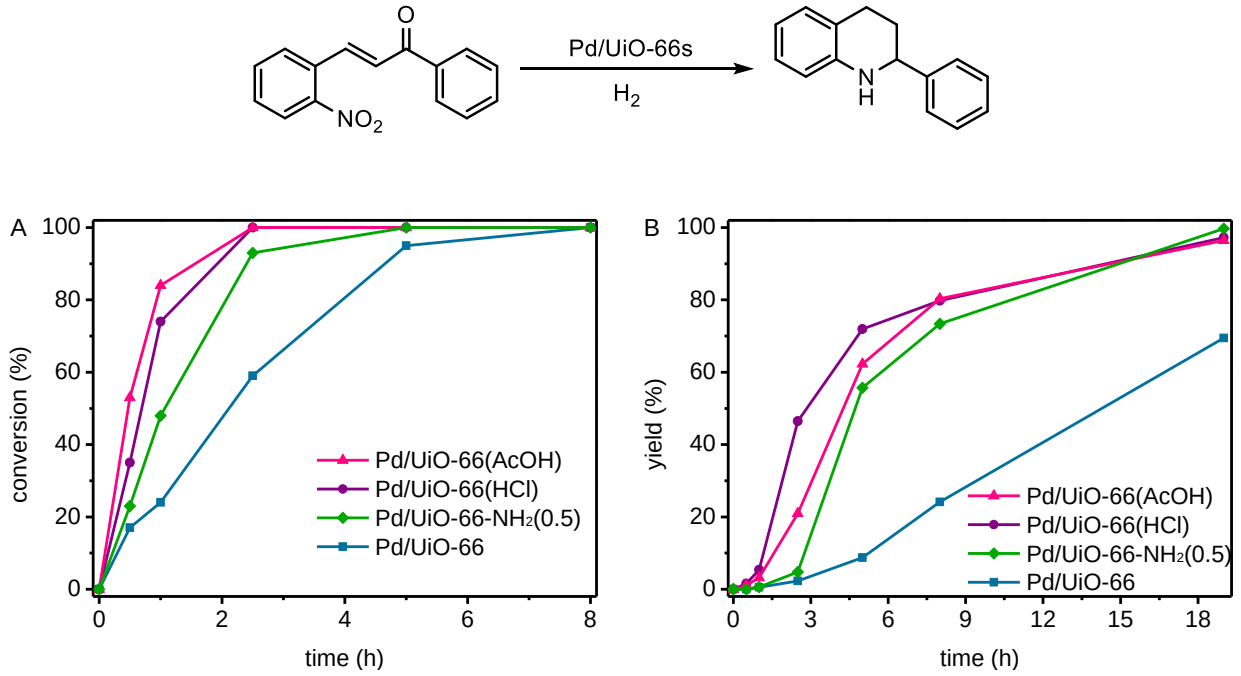
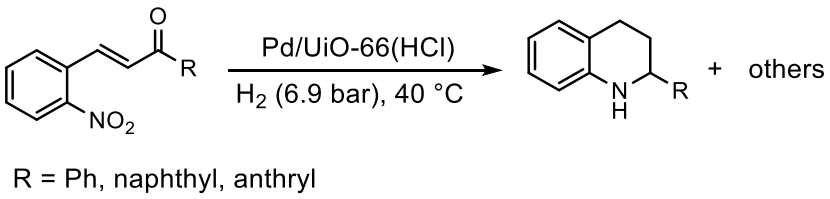


Fig. S13 (A) Conversion of 2-nitrochalcone and (B) yield of PTHQ in the hydrogenation reaction catalyzed by different Pd-loaded MOF materials. Reaction conditions: 2-nitrochalocone (0.2 mmol), Pd/UiO-66s (with 0.75 mol% of Pd), toluene (1 mL), H_2 (6.9 bar), 40 °C.

Hydrogenation of substrates with different sizes



R = Ph, naphthyl, anthryl

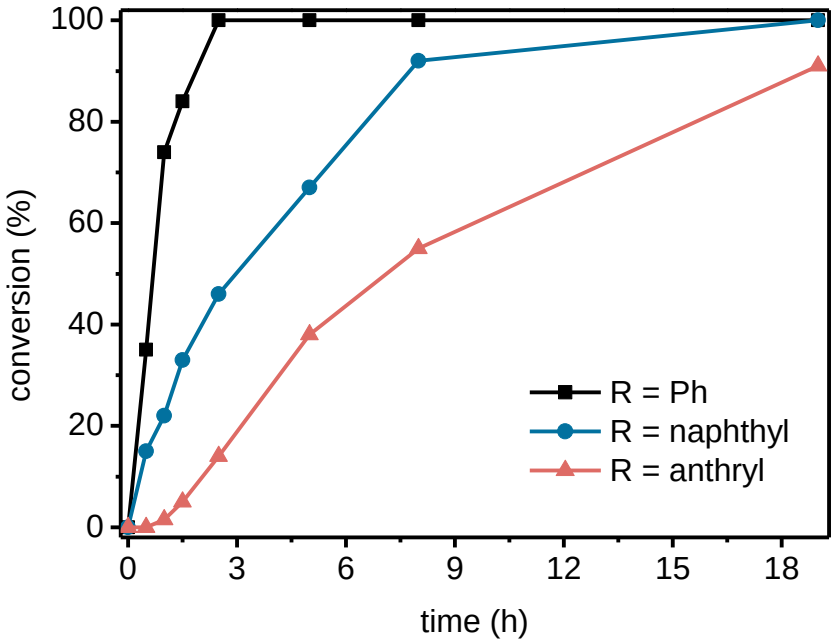
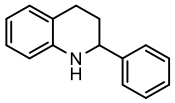
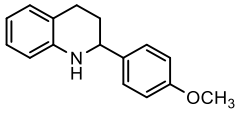


Fig. S14 Hydrogenation reaction of different α,β-unsaturated ketones catalyzed by Pd/UiO-66(HCl). Reaction conditions: substrates (0.2 mmol), Pd/UiO-66(HCl) (10 mg), toluene (1 mL), H_2 (6.9 bar), 40 °C.

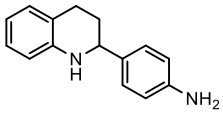
Characterization data of PTHQs



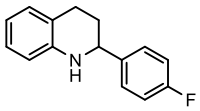
2-Phenyl-1,2,3,4-tetrahydroquinoline: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.42 – 7.35 (m, 4H), 7.32 – 7.28 (m, 1H), 7.03 (t, *J* = 7.3 Hz, 2H), 6.67 (t, *J* = 7.4, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 4.46 (dd, *J* = 9.3, 3.3 Hz, 1H), 4.06 (brs, 1H), 2.94 (ddd, *J* = 16.2, 10.7, 5.5 Hz, 1H), 2.75 (dt, *J* = 16.3, 4.8 Hz, 1H), 2.17 – 2.11 (m, 1H), 2.06 – 1.96 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$-*d*) δ = 144.93, 144.84, 129.42, 128.69, 127.56, 127.02, 126.66, 121.00, 117.27, 114.09, 56.38, 31.11, 26.51. TOF MS (EI^+) m/z: calcd. for $C_{15}H_{15}N$: 209.1204; found: 209.1205.



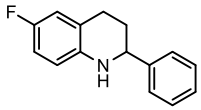
2-(4-Methoxyphenyl)-1,2,3,4-tetrahydroquinoline: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.32 (d, *J* = 8.6, 2H), 7.02 (m, 2H), 6.90 (d, *J* = 8.6, 2H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.53 (d, *J* = 8.4, 1H), 4.39 (dd, *J* = 9.5, 3.2 Hz, 1H), 4.00 (s, 1H), 3.82 (brs, 3H), 2.98 – 2.90 (m, 1H), 2.75 (dt, *J* = 16.4, 4.7 Hz, 1H), 2.14 – 2.04 (m, 1H), 2.02 – 1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.07, 144.94, 137.01, 129.41, 127.75, 126.98, 121.00, 117.23, 114.08, 114.04, 55.85, 55.45, 31.23, 29.85, 26.69, 1.17. TOF MS (EI^+) m/z: calcd. for $C_{16}H_{17}NO$: 239.1310; found: 239.1311.



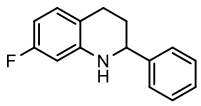
2-(4-Aminophenyl)-1,2,3,4-tetrahydroquinoline: ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.18 (d, *J* = 8.4 Hz, 2H), 7.02 – 6.98 (m, 2H), 6.70 – 6.62 (m, 3H), 6.53 – 6.50 (m, 1H), 4.32 (dd, *J* = 9.6, 3.2 Hz, 1H), 3.74 (brs, 3H), 2.97 – 2.89 (m, 1H), 2.75 (dt, *J* = 16.4, 4.5 Hz, 1H), 2.10 – 2.04 (m, 1H), 2.00 – 1.91 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.83, 145.07, 134.86, 129.37, 127.68, 126.91, 121.00, 117.06, 115.24, 114.00, 55.95, 31.16, 26.80. TOF MS (EI^+) m/z: calcd. for $C_{15}H_{16}N_2$: 224.1313; found: 224.1313.



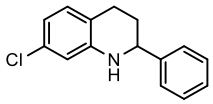
2-(4-Fluorophenyl)-1,2,3,4-tetrahydroquinoline: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.33 (m, 2H), 7.08 – 7.01 (m, 4H), 6.68 (td, *J* = 7.4, 1.2 Hz, 1H), 6.56 (d, *J* = 7.8 Hz, 1H), 4.44 (dd, *J* = 9.4, 3.2 Hz, 1H), 4.01 (brs, 1H), 2.98 – 2.90 (m, 1H), 2.74 (dt, *J* = 16.4, 4.8 Hz, 1H), 2.16 – 2.05 (m, 1H), 2.02 – 1.93 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.43, 161.00, 144.67, 140.62 (d, J = 3.2 Hz), 129.44, 128.23, 128.15, 127.06, 120.94, 117.47, 115.56, 115.35, 114.17, 55.72, 31.25, 26.42. TOF MS (EI^+) m/z: calcd. for $C_{15}H_{14}NF$: 227.1110; found: 227.1110.



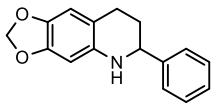
6-Fluoro-2-phenyl-1,2,3,4-tetrahydroquinoline: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.27 (m, 5H), 6.75 – 6.71 (m, 2H), 6.47 (dd, *J* = 9.4, 4.8 Hz, 1H), 4.40 (dd, *J* = 9.4, 3.2 Hz, 1H), 3.95 (brs, 1H), 2.98 – 2.86 (m, 1H), 2.72 (dt, *J* = 16.6, 4.8 Hz, 1H), 2.16 – 2.07 (m, 1H), 2.03 – 1.94 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 156.82, 154.49, 144.66, 141.08 (*J* = 1.8 Hz), 128.73, 127.65, 126.65, 122.29 (*J* = 6.8 Hz), 115.56 (*J* = 21.6 Hz), 114.75 (*J* = 7.6 Hz), 113.52 (*J* = 22.5 Hz), 56.48, 30.83, 26.69. TOF MS (EI^+) m/z: calcd. for $C_{15}H_{14}NF$: 227.1110; found: 227.1111.



7-Fluoro-2-phenyl-1,2,3,4-tetrahydroquinoline: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.30 (m, 5H), 6.93 (t, *J* = 7.4 Hz, 1H), 6.36 (td, *J* = 8.5, 2.6 Hz, 1H), 6.25 (dd, *J* = 10.8, 2.6 Hz, 1H), 4.46 (dd, *J* = 9.1, 3.4 Hz, 1H), 4.13 (brs, 1H), 2.94 – 2.79 (m, 1H), 2.70 (dt, *J* = 16.1, 5.0 Hz, 1H), 2.17 – 2.11 (m, 1H), 2.04 – 1.94 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.54, 161.15, 145.87 (d, *J* = 10.6 Hz), 144.48, 130.22 (d, *J* = 9.8 Hz), 128.75, 127.67, 126.58, 116.44 (d, *J* = 2.5 Hz), 103.64 (d, *J* = 21.5 Hz), 100.32 (d, *J* = 24.5 Hz), 56.07, 30.91, 25.74. TOF MS (EI^+) m/z: calcd. for $C_{15}H_{14}NF$: 227.1110; found: 227.1113.



7-Chloro-2-phenyl-1,2,3,4-tetrahydroquinoline: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 – 7.28 (m, 4H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.60 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.52 (d, *J* = 2.0 Hz, 1H), 4.45 (dd, *J* = 9.0, 3.4 Hz, 1H), 4.11 (brs, 1H), 2.89 – 2.79 (m, 1H), 2.68 (dt, *J* = 16.3, 5.0 Hz, 1H), 2.16 – 2.09 (m, 1H), 2.02 – 1.90 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.72, 144.41, 132.24, 130.32, 128.77, 127.70, 126.56, 119.29, 116.95, 113.42, 56.04, 30.71, 25.83. TOF MS (EI^+) m/z: calcd. for $C_{15}H_{14}NCl$: 243.0815; found: 243.0813.



6-Phenyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]quinoline: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 – 7.32 (m, 4H), 7.32 – 7.26 (m, 1H), 6.52 (s, 1H), 6.16 (s, 1H), 5.82 (q, *J* = 1.4 Hz, 2H), 4.36 (dd, *J* = 9.5, 3.2 Hz, 1H), 3.80 (brs, 1H), 2.90 – 2.82 (m, 1H), 2.64 (dt, *J* = 16.3, 4.8 Hz, 1H), 2.14 – 2.05 (m, 1H), 2.03 – 1.91 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.38, 144.80, 139.63, 139.39, 128.64, 127.51, 126.64, 112.70, 109.13, 100.38, 96.47, 56.50, 31.23, 26.55. TOF MS (EI^+) m/z: calcd. for $C_{16}H_{15}NO_2$: 253.1103; found: 253.1105.

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^{1}H NMR and ^{13}C NMR spectra of PTHQs

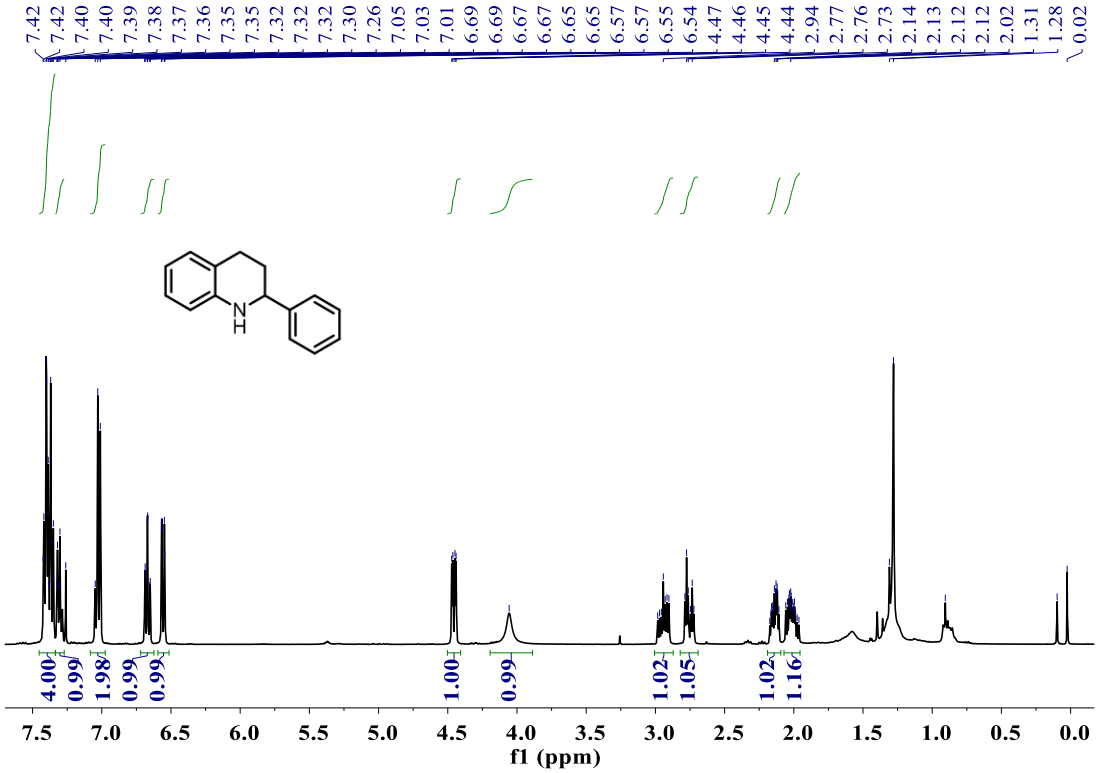

Fig. S15 ^{1}H NMR spectrum of 2-phenyl-1,2,3,4-tetrahydroquinoline.

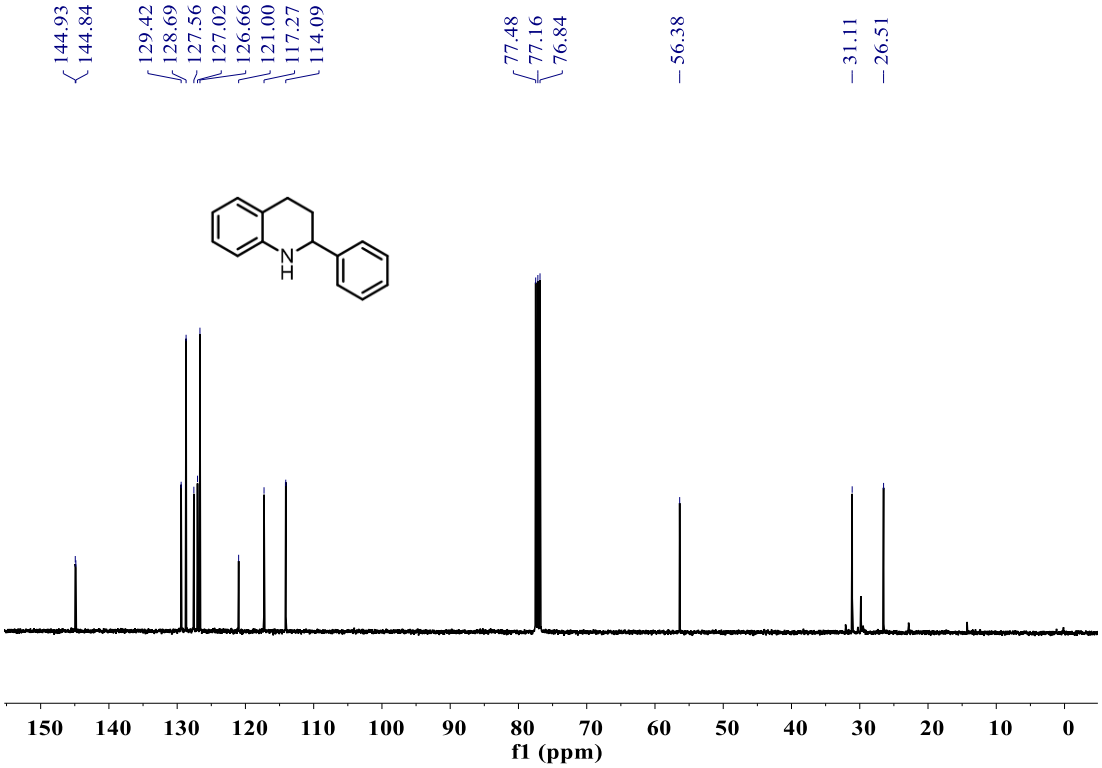

Fig. S16 ^{13}C NMR spectrum of 2-phenyl-1,2,3,4-tetrahydroquinoline.

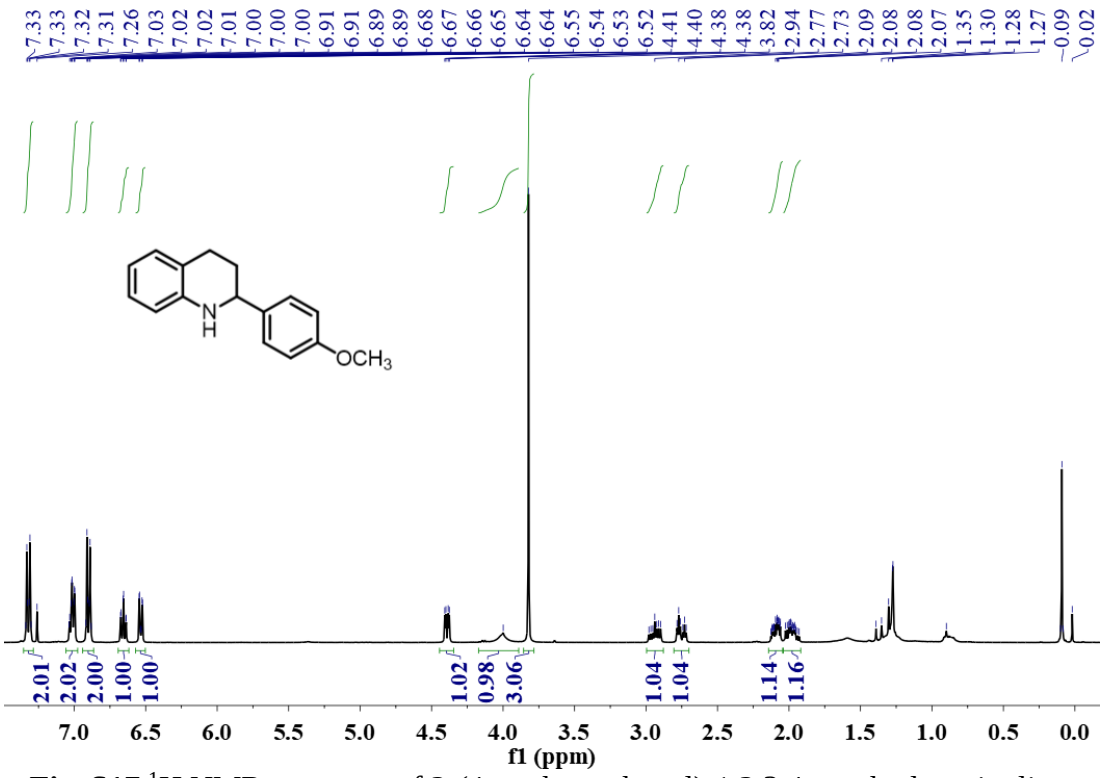

Fig. S17 ^{1}H NMR spectrum of 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline.

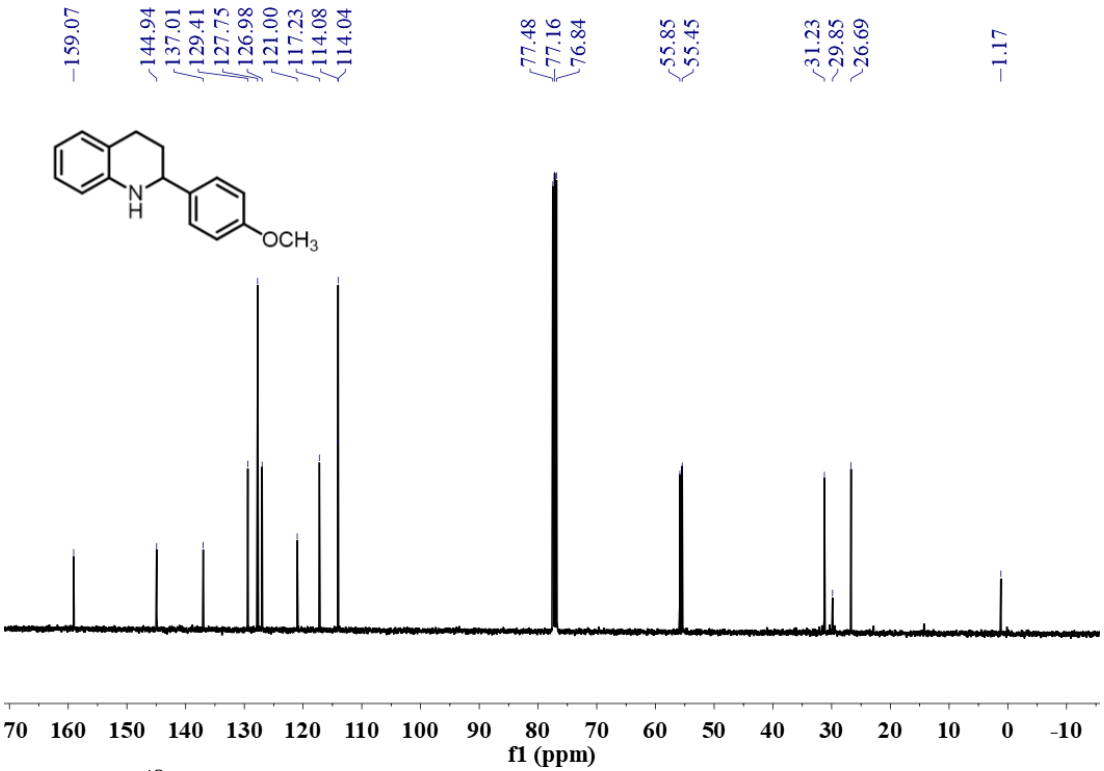

Fig. S18 ^{13}C NMR spectrum of 2-(4-methoxyphenyl)-1,2,3,4-tetrahydroquinoline.

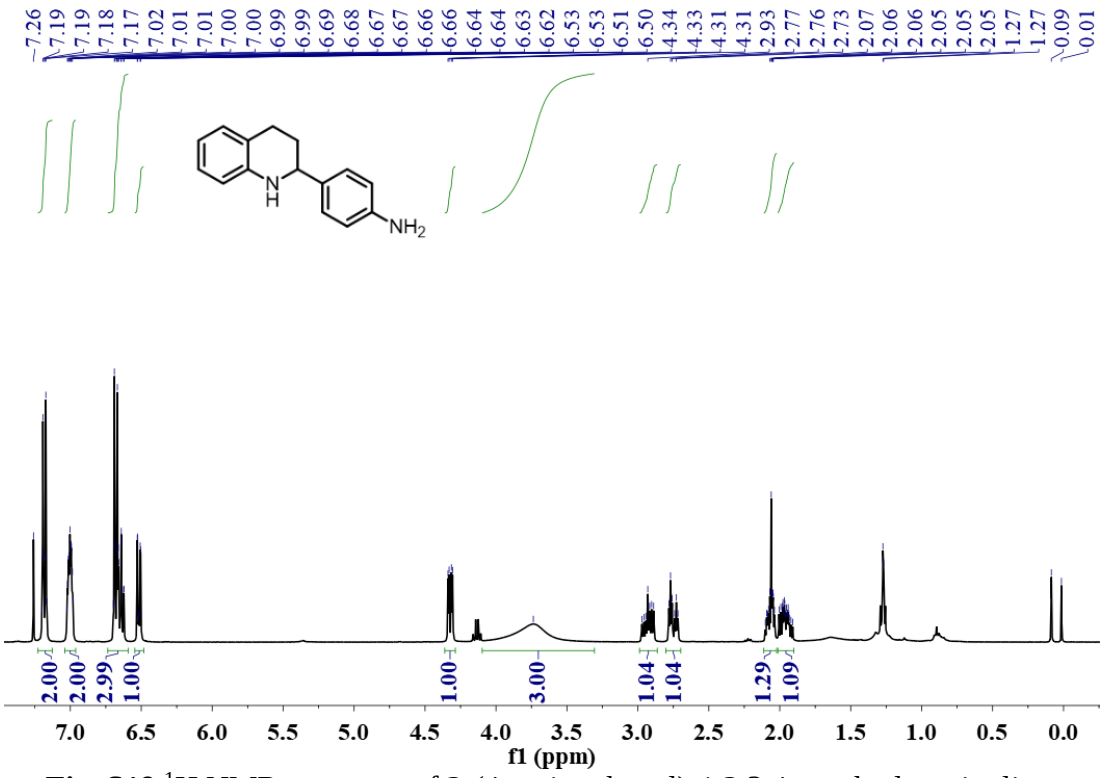

Fig. S19 ^{1}H NMR spectrum of 2-(4-aminophenyl)-1,2,3,4-tetrahydroquinoline.

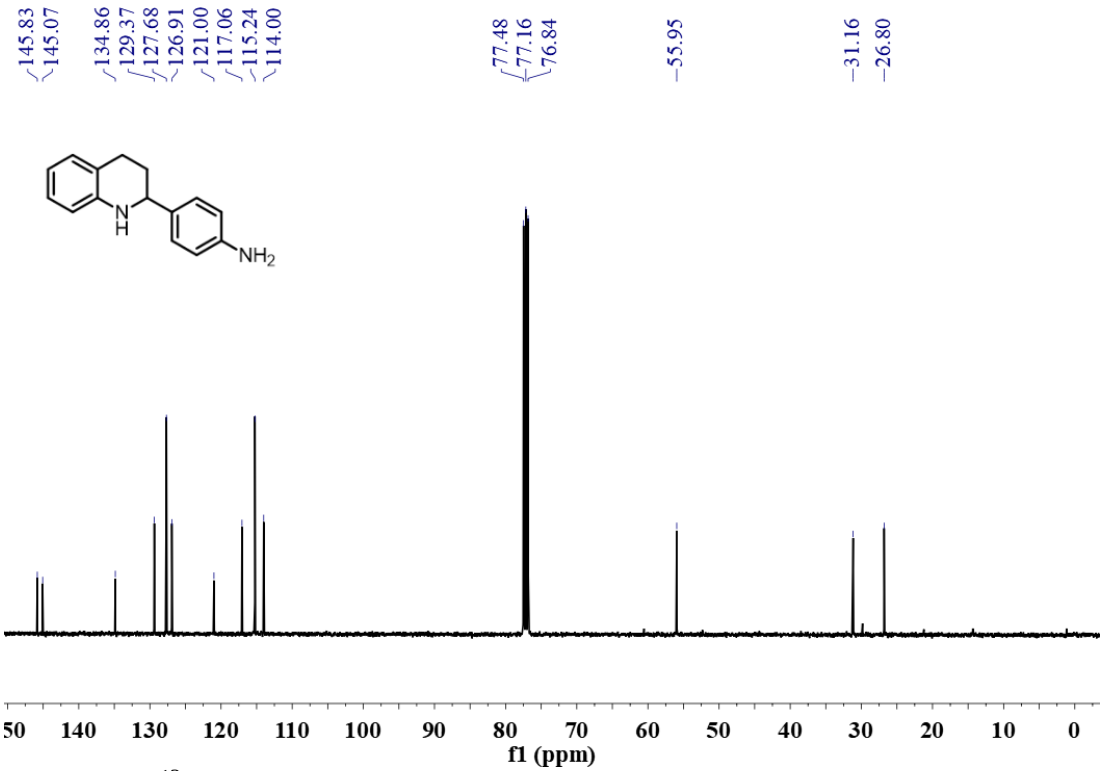

Fig. S20 ^{13}C NMR spectrum of 2-(4-aminophenyl)-1,2,3,4-tetrahydroquinoline.

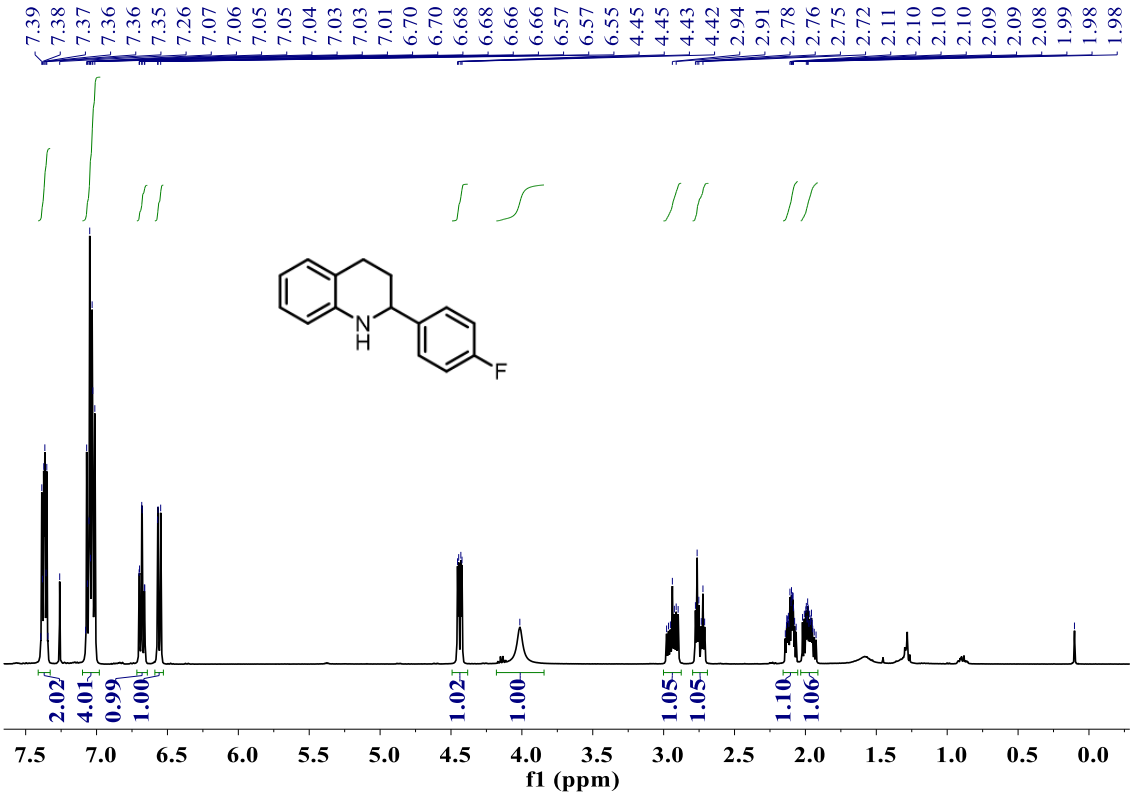

Fig. S21 ^{1}H NMR spectrum of 2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline.

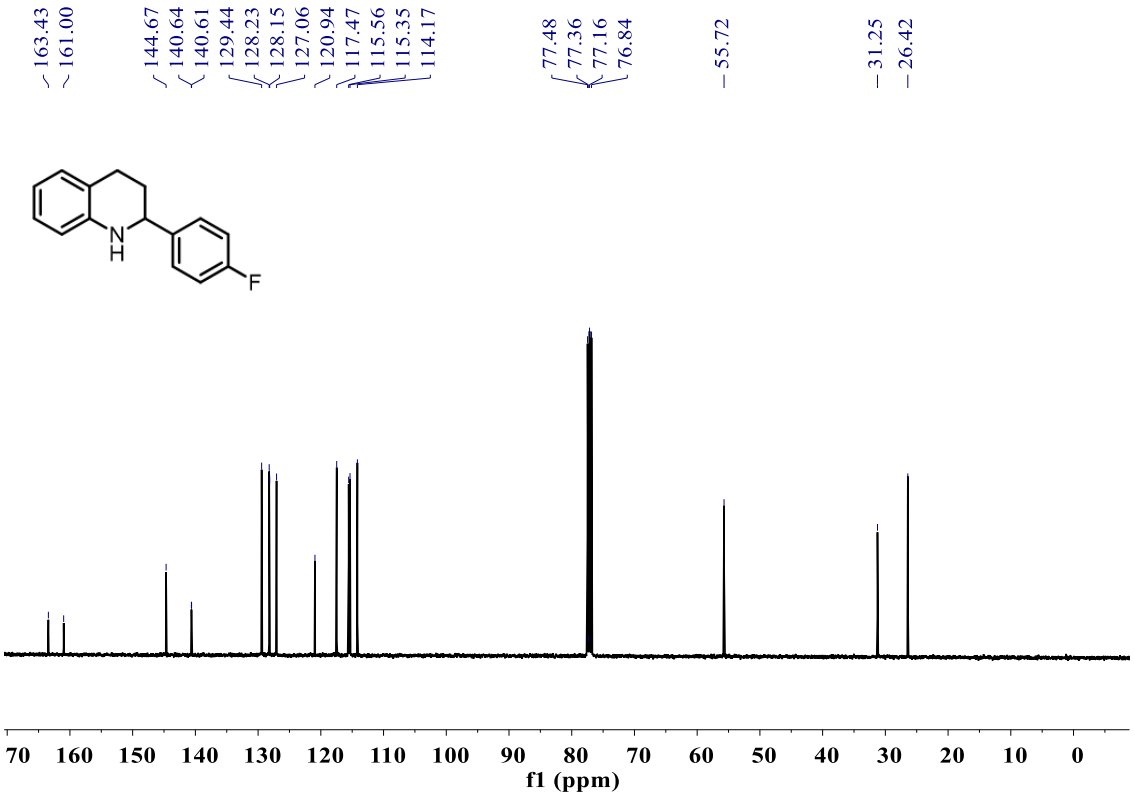

Fig. S22 ^{13}C NMR spectrum of 2-(4-fluorophenyl)-1,2,3,4-tetrahydroquinoline.

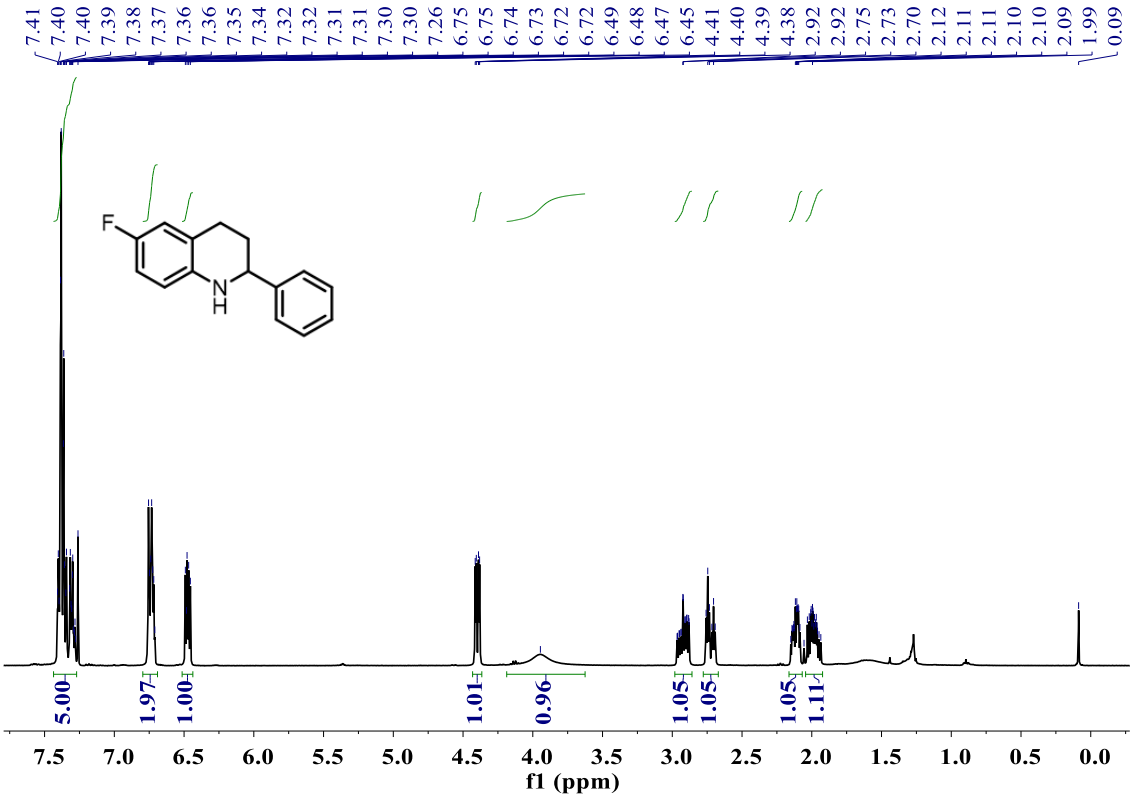

Fig. S23 ^{1}H NMR spectrum of 6-fluoro-2-phenyl-1,2,3,4-tetrahydroquinoline.

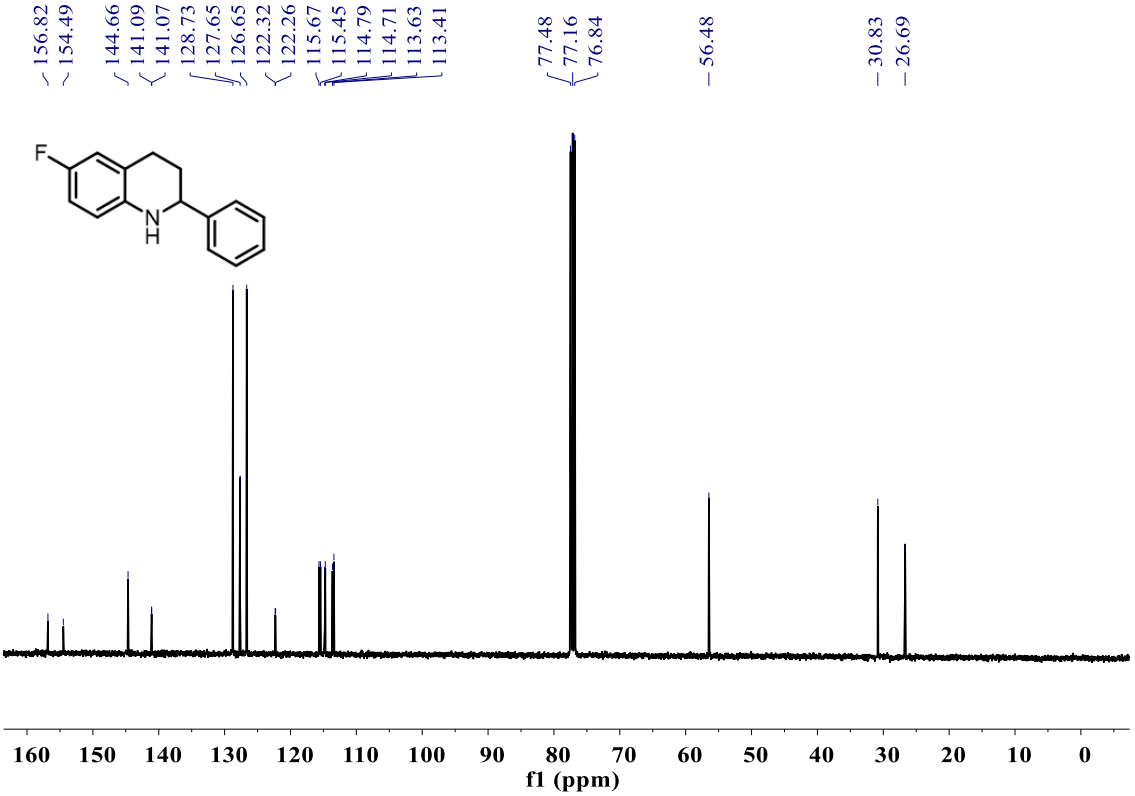

Fig. S24 ^{13}C NMR spectrum of 6-fluoro-2-phenyl-1,2,3,4-tetrahydroquinoline.

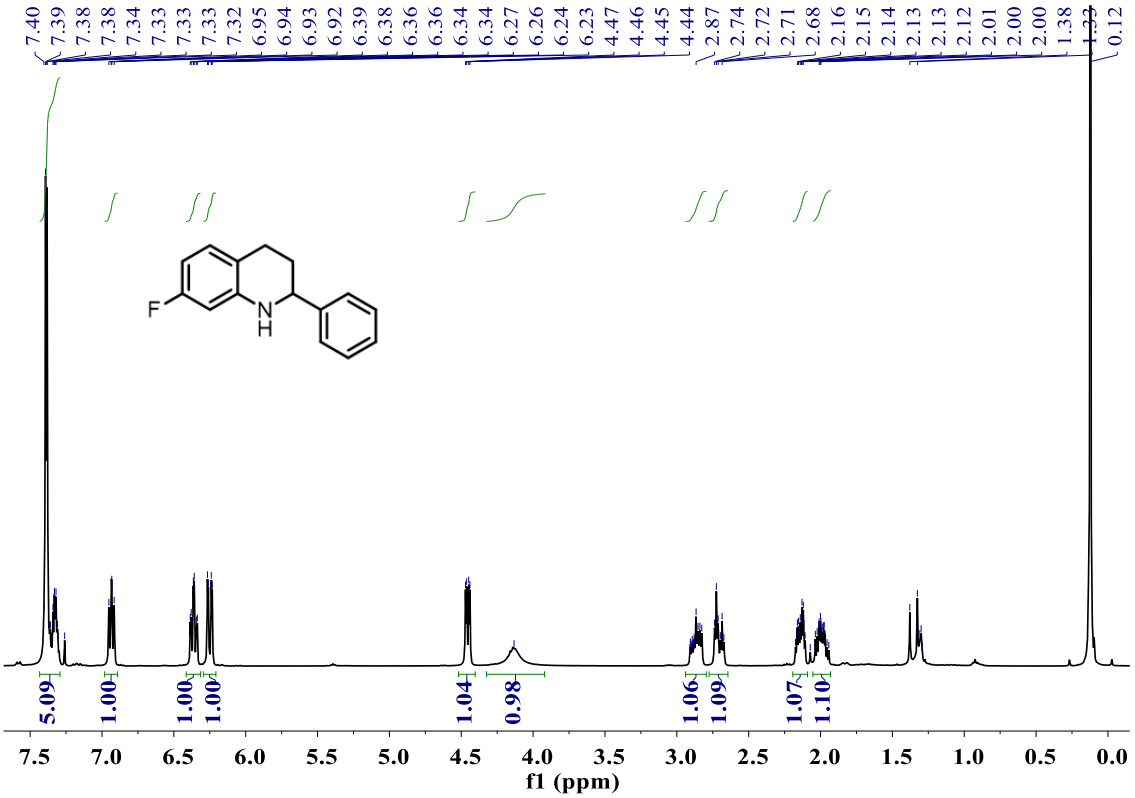

Fig. S25 ^{1}H NMR spectrum of 7-fluoro-2-phenyl-1,2,3,4-tetrahydroquinoline.

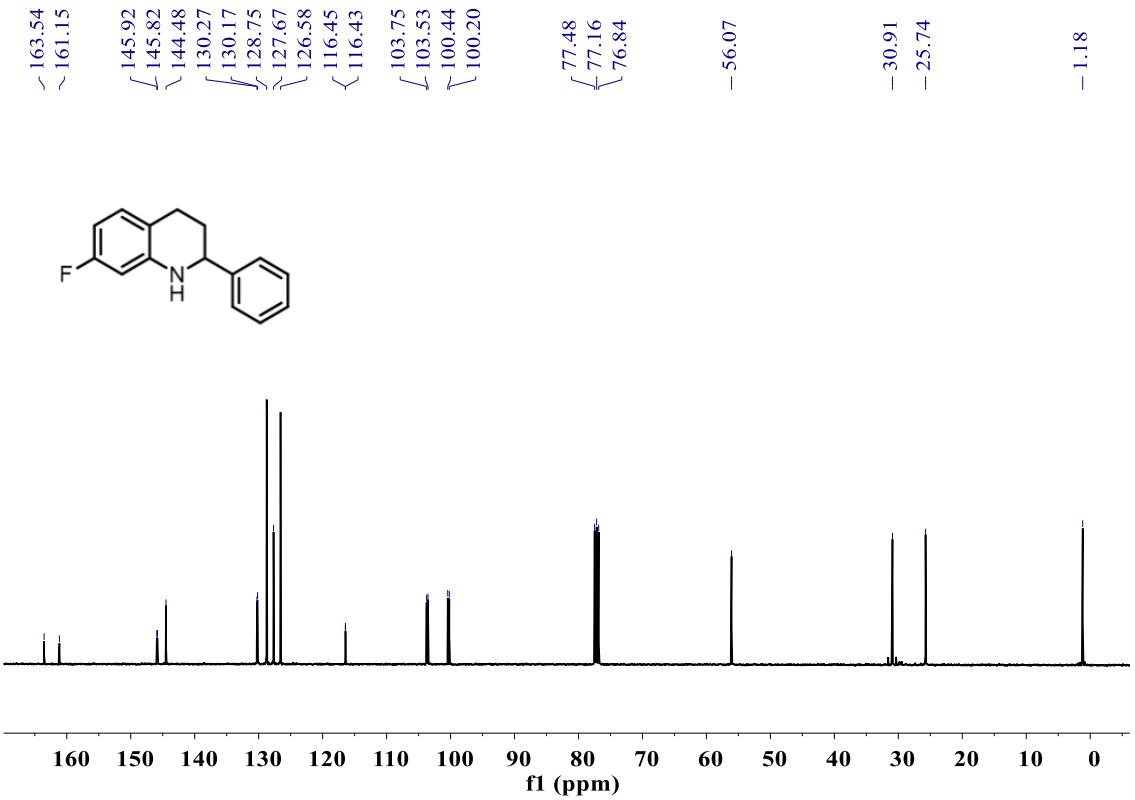

Fig. S26 ^{13}C NMR spectrum of 7-fluoro-2-phenyl-1,2,3,4-tetrahydroquinoline.

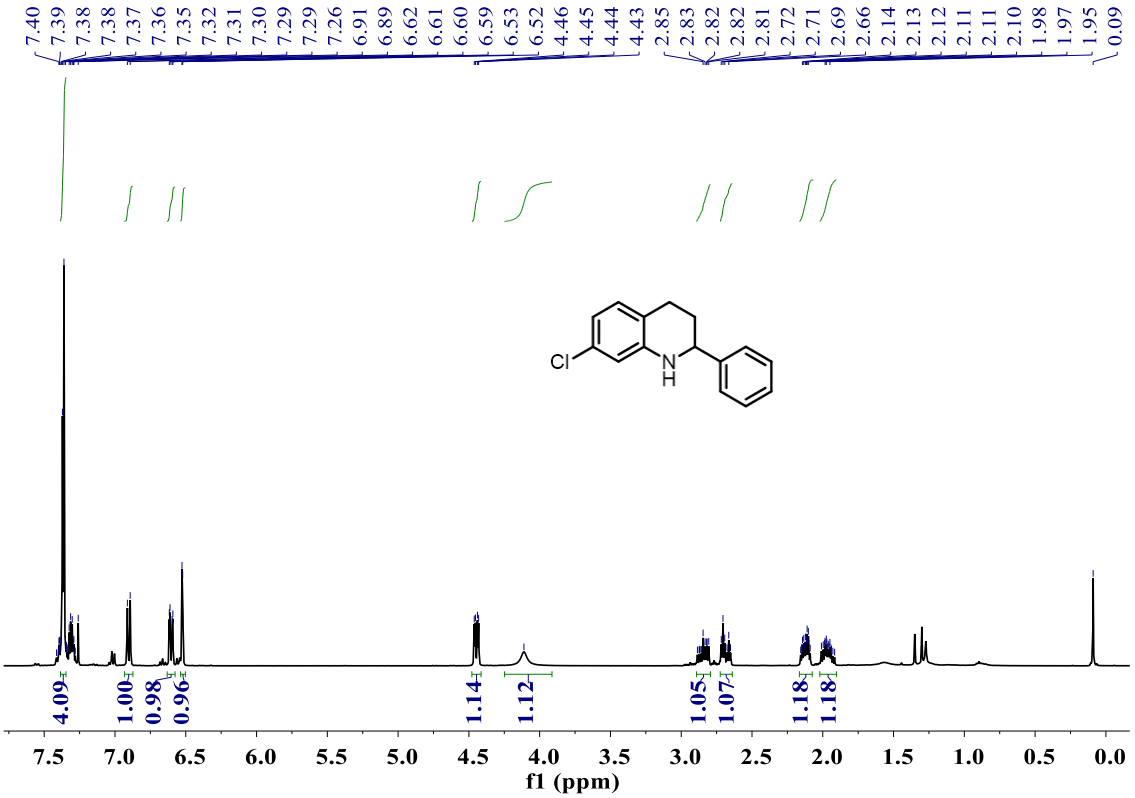

Fig. S27 ^{1}H NMR spectrum of 7-chloro-2-phenyl-1,2,3,4-tetrahydroquinoline.

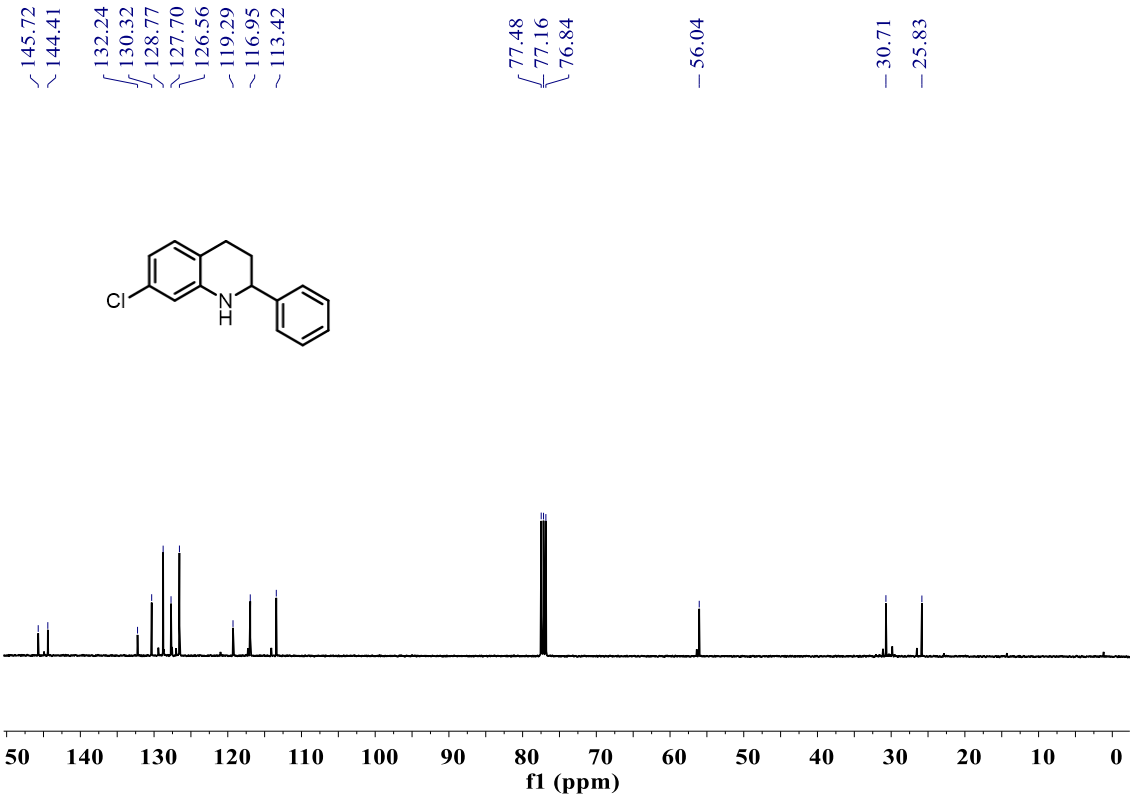

Fig. S28 ^{13}C NMR spectrum of 7-chloro-2-phenyl-1,2,3,4-tetrahydroquinoline.

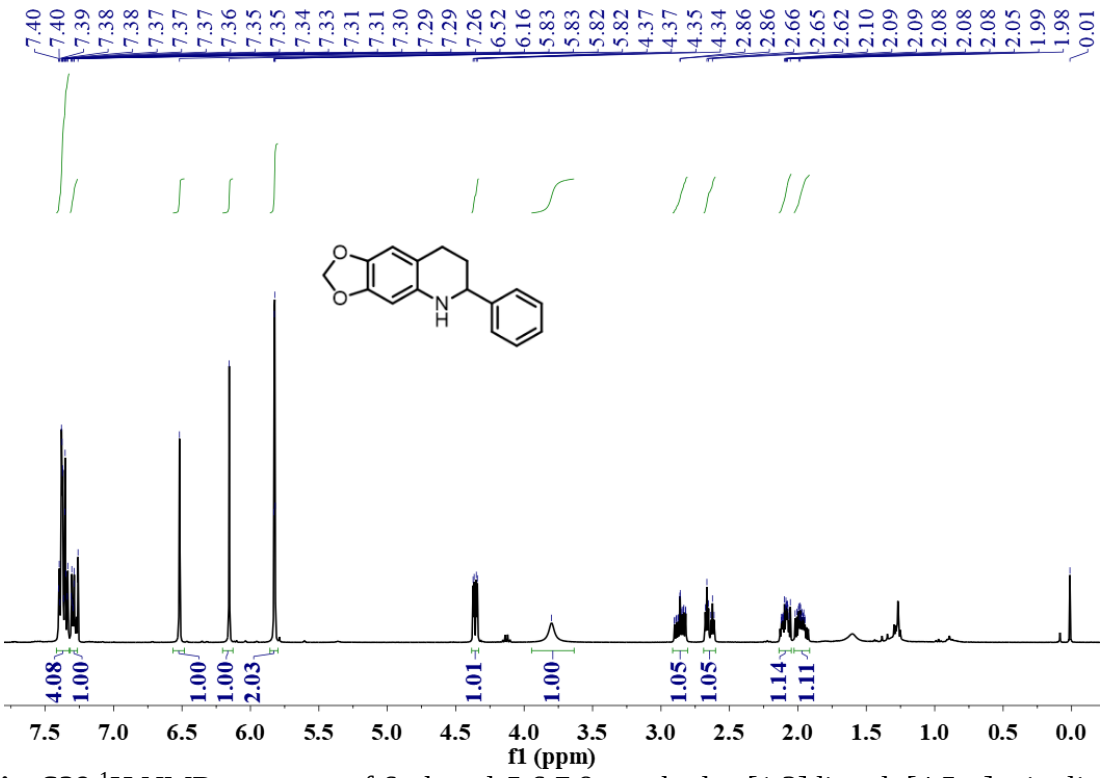

Fig. S29 ^{1}H NMR spectrum of 6-phenyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]quinoline.

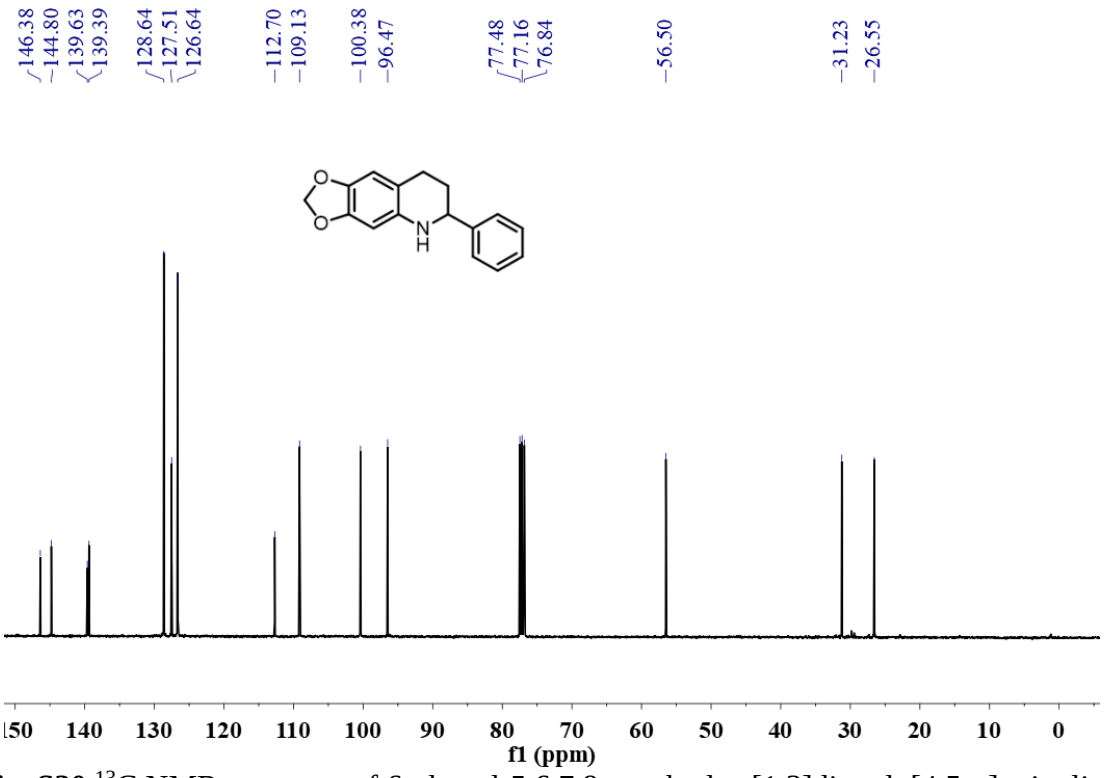

Fig. S30 ^{13}C NMR spectrum of 6-phenyl-5,6,7,8-tetrahydro-[1,3]dioxolo[4,5-g]quinoline.