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Supporting Information

Homogeneous-like photocatalysis: covalent immobilization of iridium (III) complex to polystyrene brushes grafted on SiO_2 nanoparticles as a mass/charge transfer-enhanced platform

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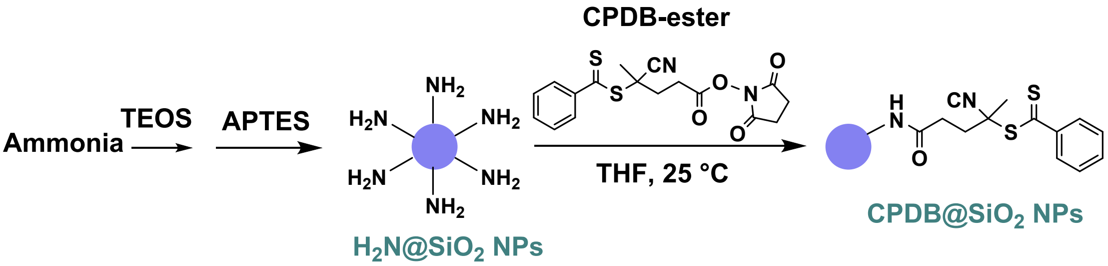
1. Preparation of raw materials

1.1. CPDB@SiO_2 NPs



Scheme S1. The preparation route to PS brush-grafted SiO_2 nanoparticles (SiO_2@PS NPs)

1.1.1 H_2N@SiO_2 NPs

Anhydrous ethanol (110 mL) and ammonia (5.7 mL, 28 %wt) were added to a 250 mL two-neck flask, then stirred and heated to 35 °C. The ethanol solution (7.8 mL) containing TEOS (3.8 mL) was added to the system with a peristaltic pump (1.3 mL min^{-1}). After the reaction was carried out for 24 h under stirring, APTES (2.4 mL) was added dropwise (1.0 mL min^{-1}), stirred at 35 °C for 12 h, naturally cooled to room temperature. The isolated solids by centrifugation (1.3×10^4 rpm, 5 min) were washed by anhydrous ethanol (54 mL×3), pumped with an oil pump for 0.5 h, and dried at 45 °C for 2 h under vacuum to obtain white powder solid H_2N@SiO_2 NPs (1.1 g).

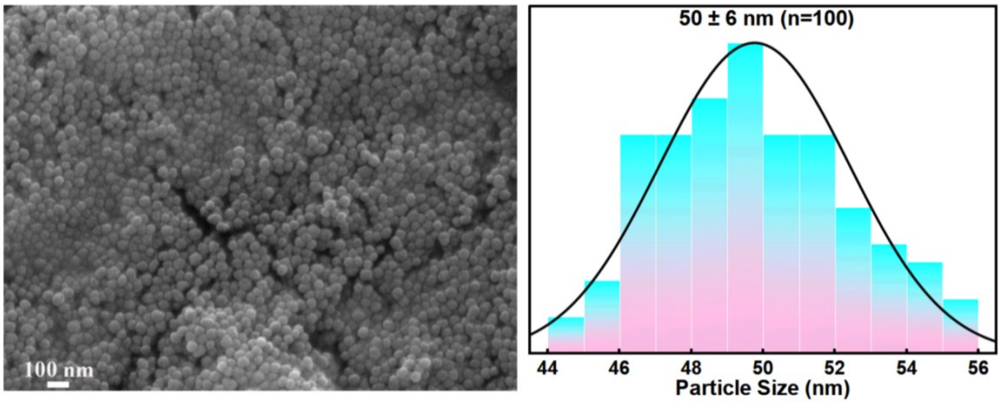


Fig.S1 SEM image (left) and particle size distribution (right) of H_2N@SiO_2 NPs.

1.1.2. CPDB@SiO_2 NPs

12 mL of THF solution containing CPDB-ester (97 mg, 0.26 mmol) and 12 mL of THF suspension of H_2N@SiO_2 NPs (1.2 g, stirred at room temperature for 4 h) were added to an Ar-filled dry three-necked flask (50 mL) and stirred at 25 °C for 24 h. After a mixed solution (50 mL) of cyclohexane and ether (v_1/v_2 = 4/1) was addedand stirred for 10 min, the solids were isolated by centrifugation. The obtained solids were stirred in 20 mL of THF, and added a mixed solvent of cyclohexane and ether (v_1/v_2 = 4/1) (50 mL), and then centrifuged (9000 rpm, 1 min). Repeat the above operation until the upper centrifugate was colorless and transparent. The solids were dried in vacuum at 25 °C to obtain a light pink powder solid CPDB@SiO_2 (970 g).

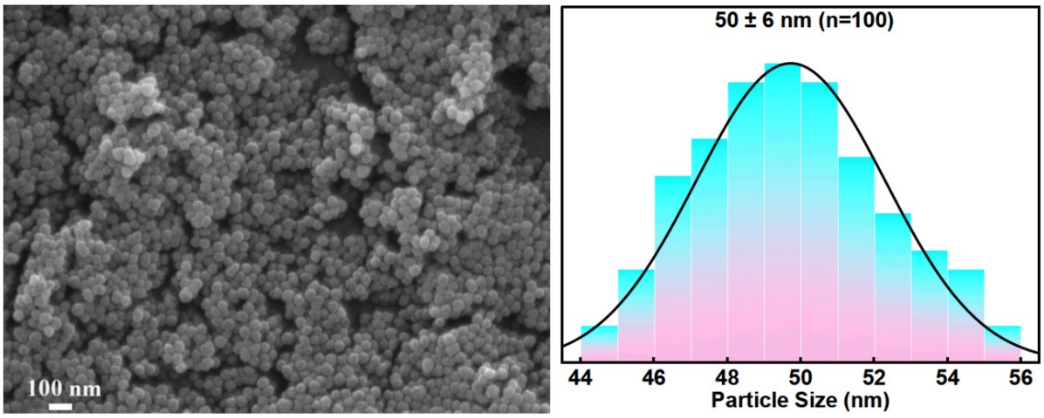


Fig.S2 SEM image (left) and particle size distribution (right) of CPDB@SiO_2 NPs (b).

1.2. Hollow mesoporous polystyrene nanospheres (HMPNs)

1.2.1. Polystyrene nanospheres (PS NPs)

In an Ar-filled flask (500 mL), deionized water (180 mL), PVP (1.65 g, 0.03 mmol), and styrene (8.20 g, 0.08 mol) were added and stirred at room temperature for 15 min. Then KPS (0.45 g, 1.67 mmol) in deionized water (9 mL) was added, stirred at room temperature for 15 min, and heated to 85 °C for 24 h. The isolated solids by centrifugation (1.3 × 10^4 rpm, 5 min) was washed with deionized water (30 mL × 2) and anhydrous ethanol (30 mL × 2) until the supernatant was colorless and transparent, and dried at 45 °C for 6h to afford white solid powder PS NPs (6.50 g).

1.2.2. Hollow mesoporous nanospheres(HMPNs)

PS NPs (400 mg) in aqueous solution (20 mL) containing 0.5 wt % PVA were stirred for 24 h to afford PS NPs suspension. Under the protection of Ar, aqueous solution (20 mL) containing 0.5 wt % PVA, styrene (208 mg, 2.00 mmol), VBC (153 mg, 1.00 mmol) and F127 (500 mg, 0.04 mmol) were added to a three-necked flask (150 mL) and stirred at 25 °C for 5 min. The above PS NPs suspension was added and stirred at 25 °C for 4 h. Then KPS aqueous solution (8 mL, 70 mg, 0.26 mmol) was added and heated to 65 °C for 80 min. Afterwards, styrene (104 mg, 1.00 mmol), VBC (153 mg, 1.00 mmol) and DVB (130 mg, 1.00 mmol) were added successively, and the temperature was raised to 75 °C for 24 h. After being cooled and centrifugated (1.3×10^4 rpm, 5 min), the isolated solids were washed with distilled water (20 mL × 3) and anhydrous ethanol until the supernatant was colorless, clear and transparent. The obtained core-shelled solids were stirred at 25 °C in a mixed solvent (30 mL) including THF and ethanol (v/v = 1:1) for 12 h. The solids were centrifuged (1×10^4 rpm, 5 min), and stirred at 65 °C in another mixed solvent (30 mL) including ethanol and acetone (v/v = 1:1) for 12 h. The isolated solids were dried naturally to afford white solid HMPNs (0.32 g).

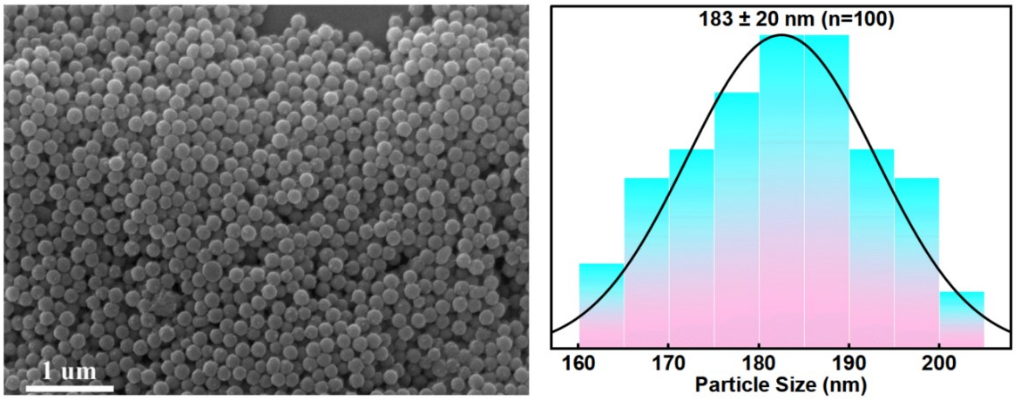
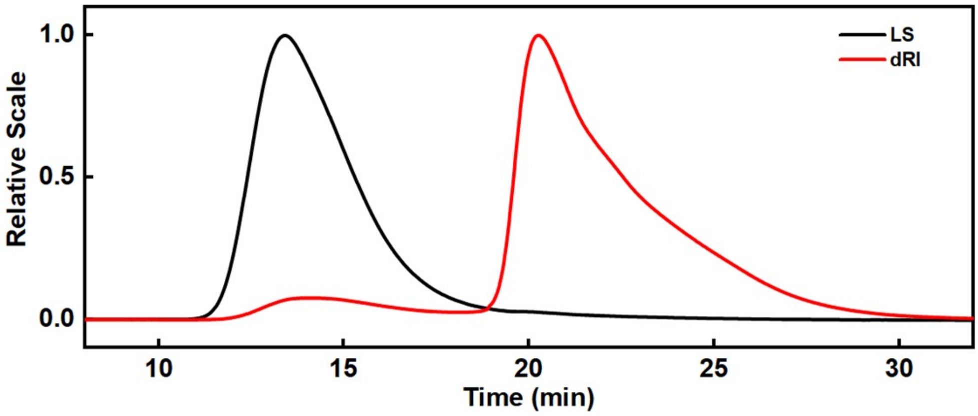


Fig.S3 SEM image (left) and particle size distribution (right) of HMPNs.

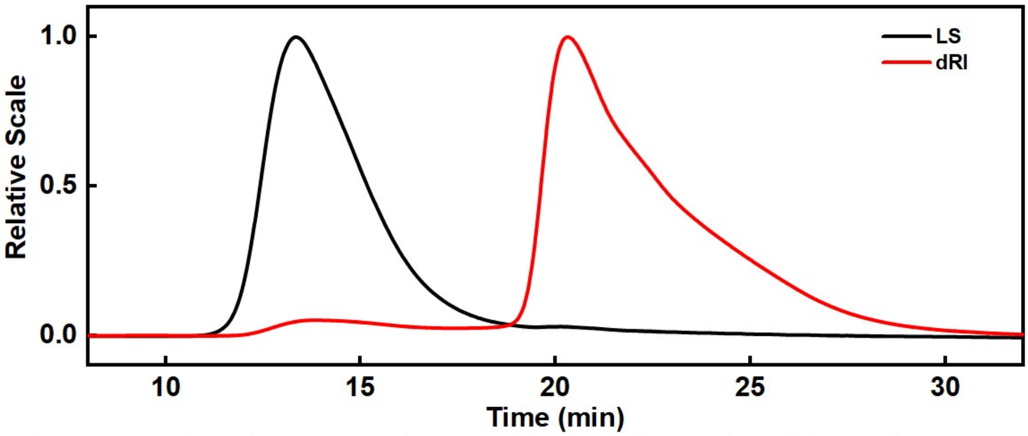
2. Cleavage of PVBC brushes grafted on the surface of PVBC@SiO$_2$ NPs

In N_2-filled dry round-bottom flask (100 mL), PVBC@SiO$_2$ NPs (250 mg) and anhydrous ethanol solution (50 mL) containing NH_4I (150 mg) were charged and sonicated for 2h, and heated to 75 °C. After being stirred for 2 h, hydrazine hydrate (500 mg) was added, stirred for 24 h, and cooled to room temperature. The solids was isolated by centrifugation and washed by THF (5 mL × 3). To the combined solutions, deionized water (150 mL) was added and extracted by $CHCl_3$ (20 mL × 3). The combined $CHCl_3$ phases was washed by deionized water (20 mL), filtered through filter head (0.22 um), and evaporated under reduced pressure, affording light yellow viscous oily liquid. Their molecular weights (M_n) and polymer dispersity index (PDI) are determined using a Waters gel-permeation chromatograph (GPC).



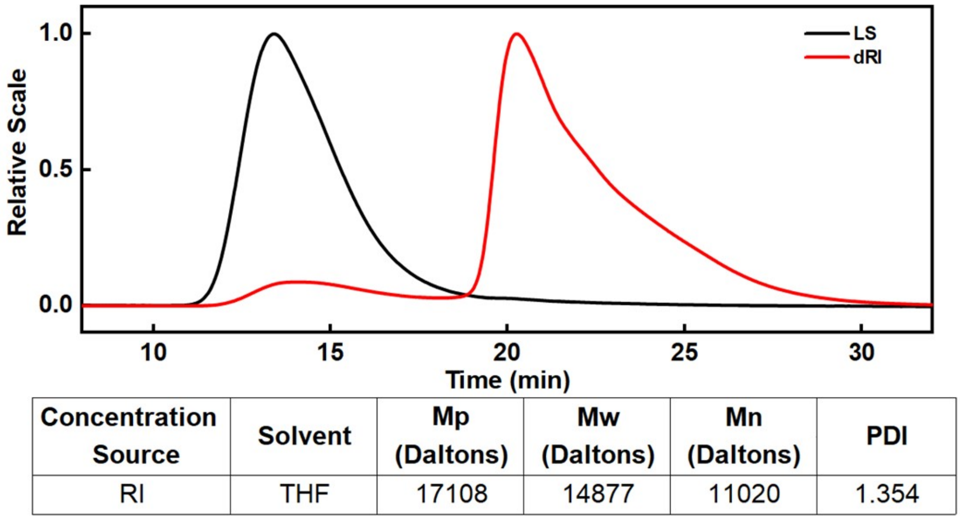
Concentration Source	Solvent	Mp (Daltons)	Mw (Daltons)	Mn (Daltons)	PDI
RI	THF	42808	31710	18120	1.753

Fig.S4 GPC spectrum of cleaved PVBC brush from PVBC(SS)@SiO_2 NPs.



Concentration Source	Solvent	Mp (Daltons)	Mw (Daltons)	Mn (Daltons)	PDI
RI	THF	79051	55281	27920	1.982

Fig.S5 GPC spectrum of cleaved PVBC brush from PVBC(SL)@SiO_2 NPs.



Concentration Source	Solvent	Mp (Daltons)	Mw (Daltons)	Mn (Daltons)	PDI
RI	THF	17108	14877	11020	1.354

Fig.S6 GPC spectrum of cleaved PVBC brush from PVBC(DS)@SiO_2 NPs.

3. Determination of loading benzyl chloride moiety in HMPNs

In round-bottom flask (10 mL), HMPNs (300 mg) and THF (2 mL) were charged and sonicated for 30 min. To the suspension, aqueous NaOH solution (5 mL, 1.0 mol L^{-1}) was added, heated to 40 °C for 12 h, evaporated under reduced pressure to remove THF, and filtered using filter head (0.22 um). Diluted nitric acid was used to adjust the filtrate to pH = 7, and K_2CrO_4 (1 mL 0.5 %wt) was added. The obtained solution was titrated with standard $AgNO_3$ (0.1mmol mL^{-1}) solution until brick red appears. This titration process was repeated three times. The content of benzyl chloride moiety in HMPNs was calculated to be 3.8 mmol g^{-1}.

4. Characterization of PVBC@SiO_2 NPs and Ir#PVBC@SiO_2 NPs

4.1. Thermogravimetric analysis

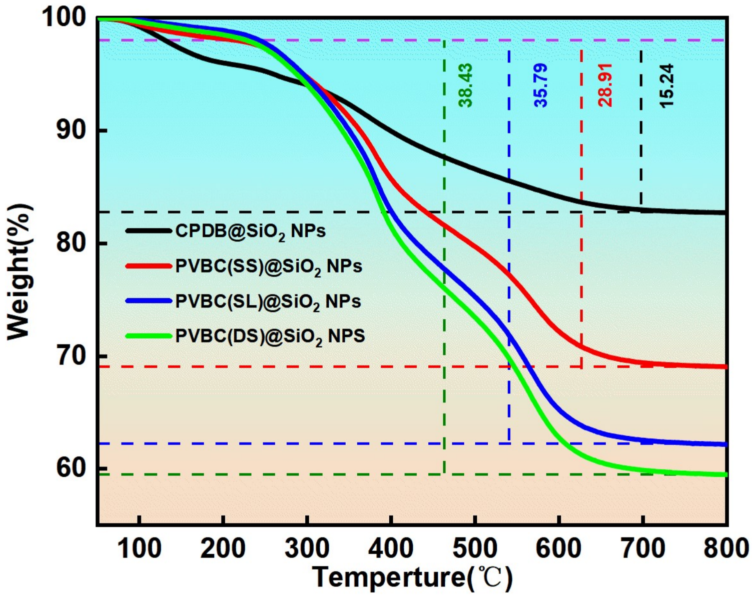


Fig.S7 Thermogravimetric curves of PVBC@SiO_2 NPs.

4.2. Morphology and particle size

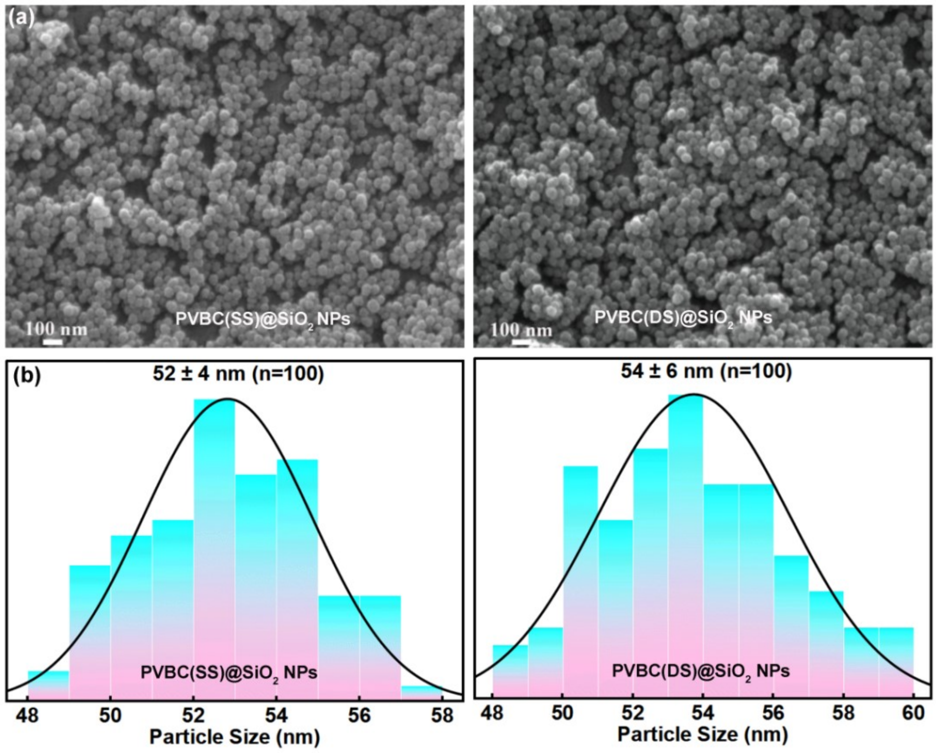


Fig.S8 SEM images (a) and particle size distributions (b) of PVBC(SS)@SiO_2 NPs and PVBC(DS)@SiO_2 NPs.

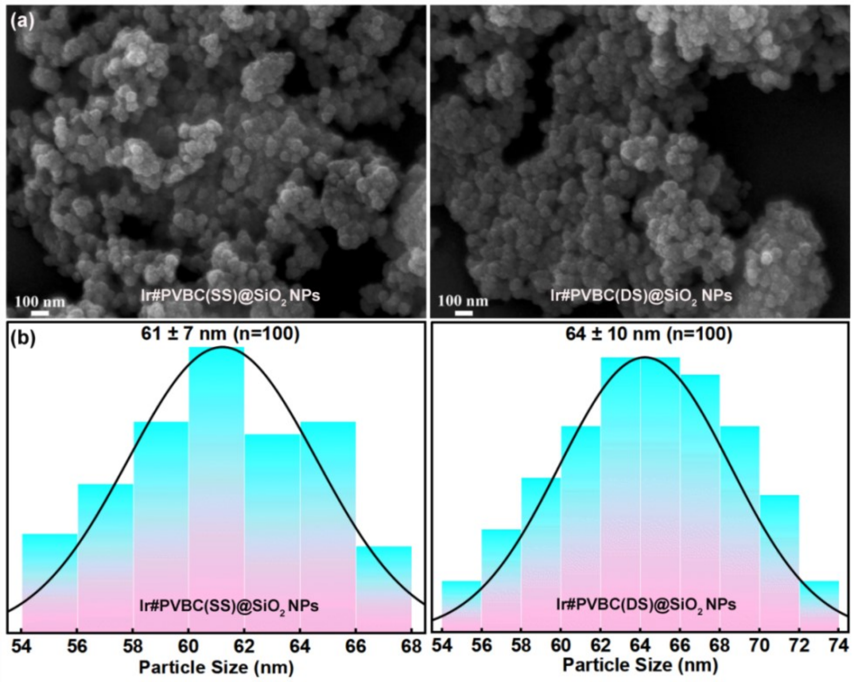


Fig.S9 SEM images (a) and particle size distributions (b) of Ir#PVBC(SS)@SiO_2 NPs and Ir#PVBC(DS)@SiO_2 NPs.

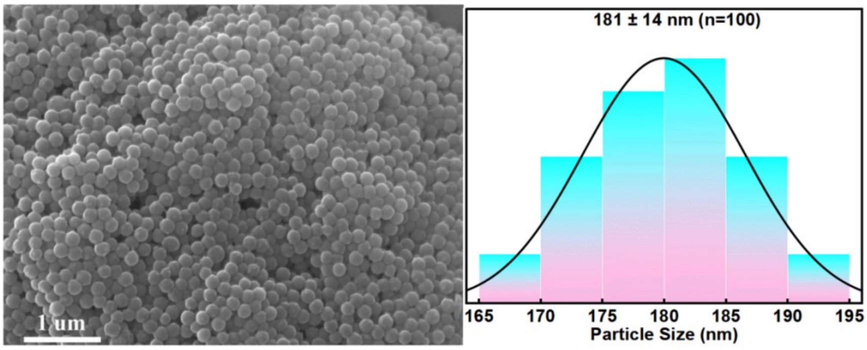


Fig.S10 SEM images (left) and particle size distributions (right) of Ir#HMPNs.

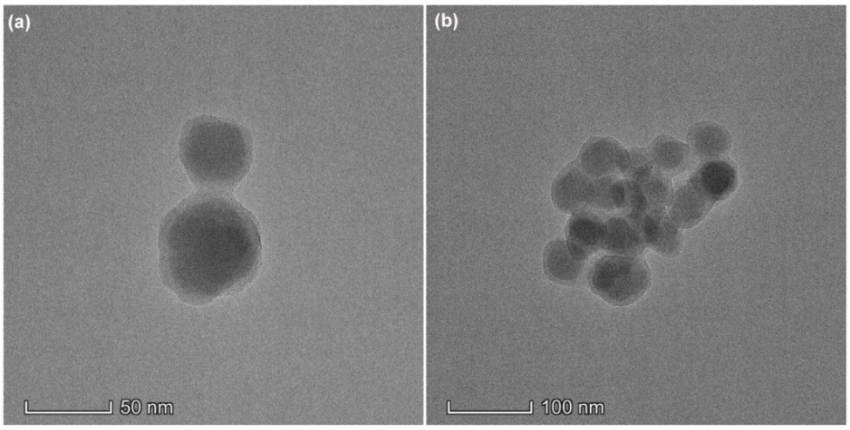


Fig.S11 TEM images of PVBC(SL)@SiO_2 NPs (a) and Ir#PVBC(SL)@SiO_2 NPs (b).

4.3. UV–vis absorption spectra

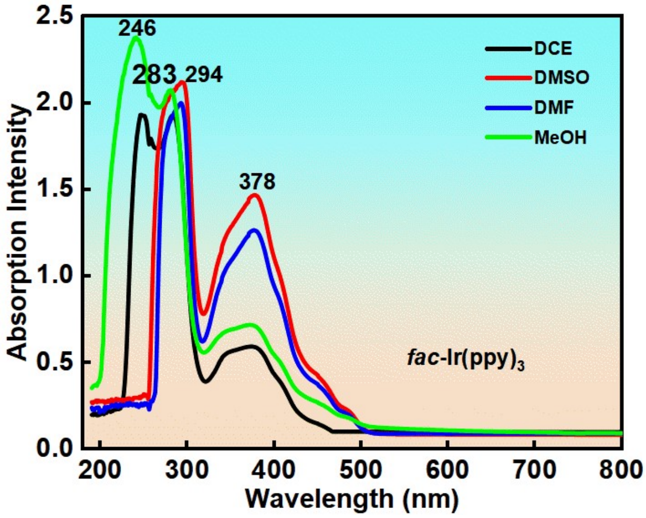


Fig. S12 UV–vis absorption spectra of *fac*-Ir(ppy)$_3$.

4.4. Uv–Vis DRS

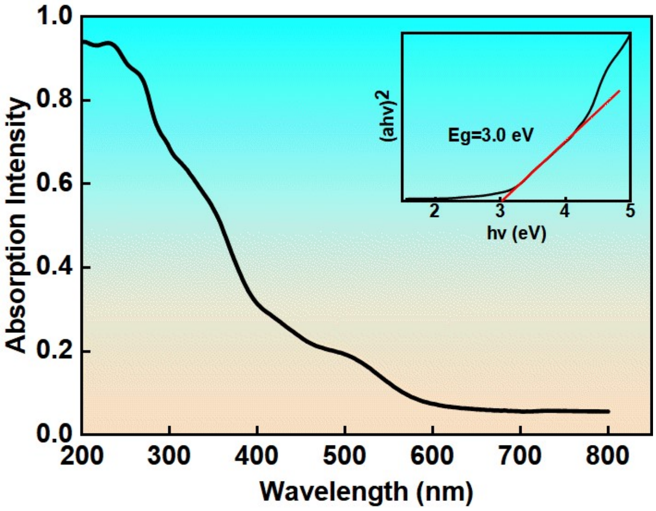


Fig.S13 Uv–Vis DRS of PVBC(SL)@SiO$_2$ NPs.

4.5. Emission lifetime

The fluorescent lifetimes of all samples were determined by using time-correlated single-photon counting (TCSPC) in solid state. Their average emission lifetimes were calculated according to the following equation:

$$\tau_{ave} = \frac{B_1\tau_1^{\ 2} + B_2\tau_2^{\ 2} + B_3\tau_3^{\ 2}}{B_1\tau_1 + B_2\tau_2 + B_3\tau_3}$$

Where τ is the measured fluorescence lifetime and B is the amplitude. Fluorescence lifetimes including τ_1, τ_2, and τ_3 are derived from first, second and third order fitting. Similarly, B_1, B_2, and B_3 are also obtained.

Table S1. Fluorescence lifetimes and amplitudes of *fac*-Ir(ppy)$_3$, Ir#HMPNs and Ir#PVBC@SiO$_2$ NPs

Sample	τ_1 (ns)	τ_2 (ns)	τ_3 (ns)	B_1	B_2	B_3	τ_{ave} (ns)
fac-Ir(ppy)$_3$	24.4	142.1	436.6	0.27	0.41	0.30	335.7
Ir#PVBC(SS)@SiO$_2$ NPs	1.1	11.7	37.1	0.26	0.44	0.30	37.1
Ir#PVBC(SL)@SiO$_2$ NPs	1.7	17.8	99.7	0.33	0.60	0.06	45.8
Ir#PVBC(DS)@SiO$_2$ NPs	1.4	12.1	36.6	0.23	0.44	0.34	28.7
Ir@HMPNs	1.9	12.9	79.8	0.30	0.65	0.05	33.5

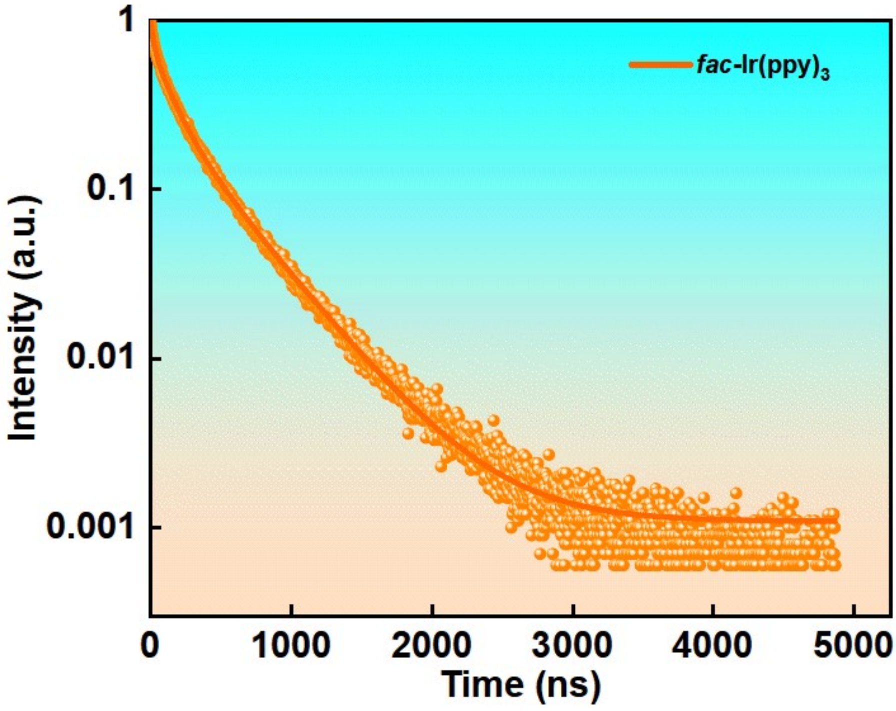


Fig.S14 Time-resolved phosphorescence decays of *fac*-Ir(ppy)$_3$ (measured at 525 nm with 375 nm excitation).

4.6. Quantum yield

Based on the fluorescence intensities in fluorescence spectra, the quantum yields of *fac*-Ir(ppy)$_3$, Ir#HMPNs and Ir# PVBC(SS)@SiO$_2$ NPs were determined by FLS1000 steady state/transient state fluorescence spectrometer.

Table S2 Quantum yields of *fac*-Ir(ppy)$_3$, Ir#HMPNs and Ir#PVBC@SiO$_2$ NPs

Sample	A	*Q*(%)
fac-Ir(ppy)$_3$	0.073	41.8
Ir#PVBC(SS)@SiO$_2$ NPs	0.074	27.5
Ir#PVBC(SL)@SiO$_2$ NPs	0.074	36.5
Ir#PVBC(DS)@SiO$_2$ NPs	0.072	22.8
Ir@HMPNs	0.073	12.2

5. Kinetics of reaction process

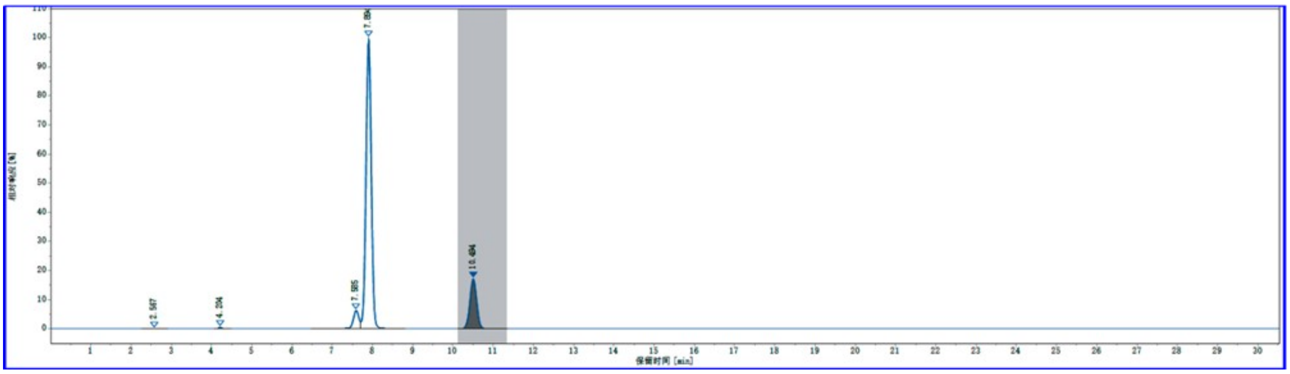


Fig. S15. HPLC spectrum of the reaction mixture in the Ir#PVBC(SL)@SiO$_2$-promoted reductive cross-coupling reaction of benzaldehyde with *p*-phthalonitrile for 4 h (rate:0.5 mL min^{-1}, V_{H2O}/V_{HCN}=50:50, C18 column).

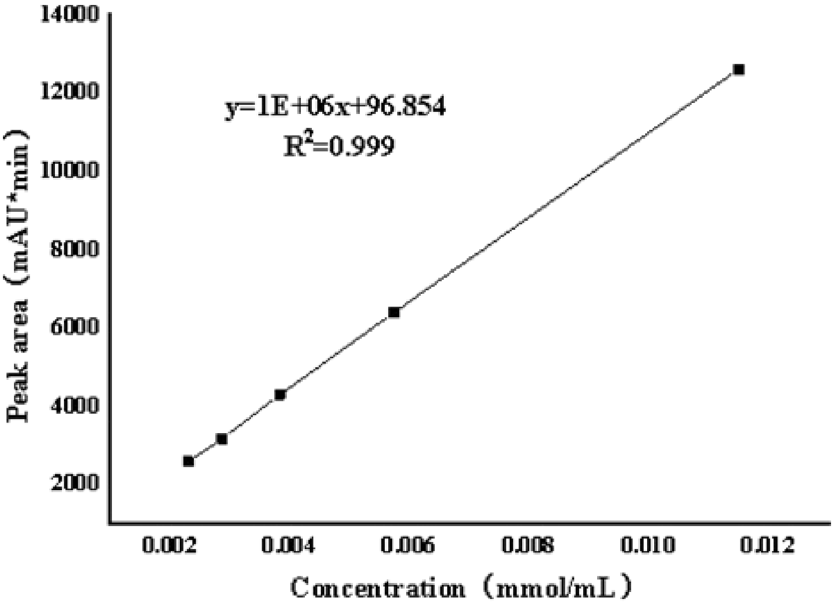


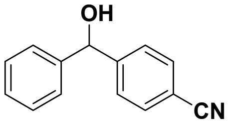
Fig.S16 Standard curve taking product concentration as the X-axis and the peak area as the Y-axis.

Table S3 Yields of benzhydrol in the reaction of benzaldehyde and *p*-phthalonitrile during the whole process

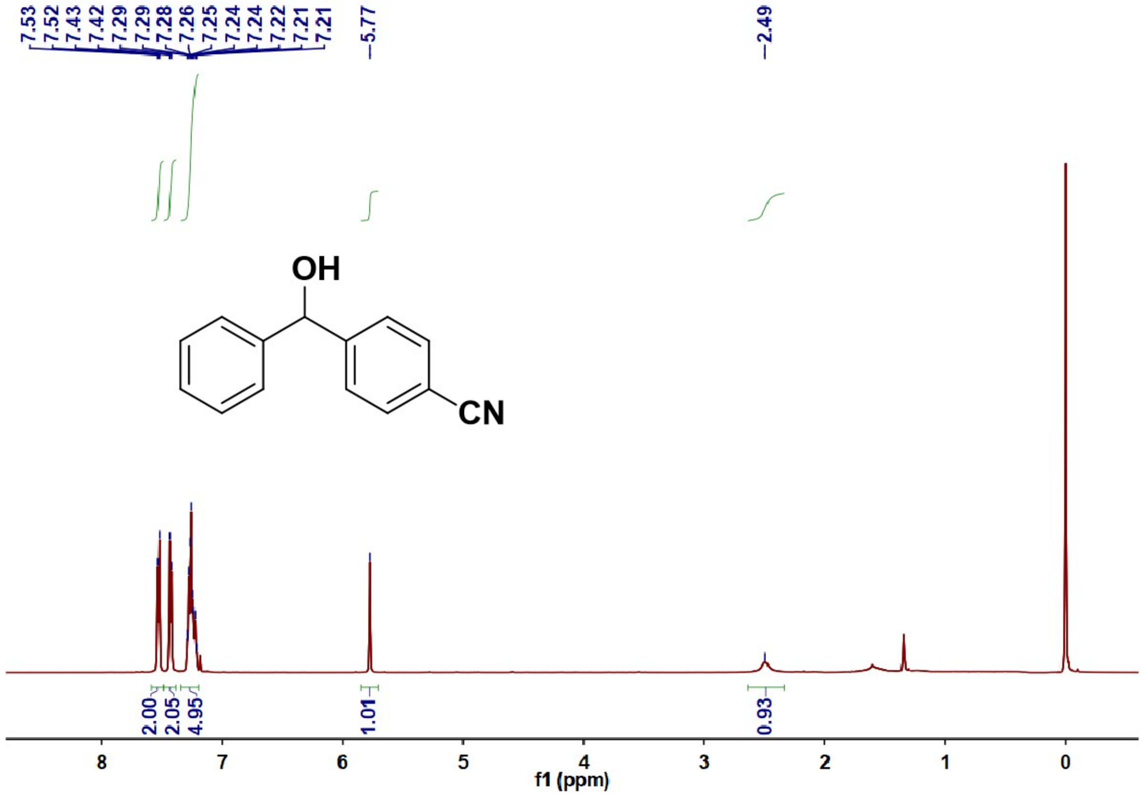
Sample	**Reaction time (min)**							
	45	**90**	**135**	**180**	**225**	**270**	**315**	**360**
***fac*-Ir(ppy)$_3$**	22.5	39.7	52.5	63.9	73.2	80.6	84.0	85.0
Ir#PVBC(SS)@SiO$_2$	17.1	30.0	42.3	53.0	62.7	70.2	76.5	79.9
Ir#PVBC(SL)@SiO$_2$	20.3	36.6	49.2	61.0	71.0	78.6	83.3	85.0
Ir#PVBC(DS)@SiO$_2$	12.2	25.0	36.9	48.1	57.7	64.8	71.4	75.7
Ir#HMPNs	8.6	17.2	27.4	36.4	44.5	50.7	50.2	60.2

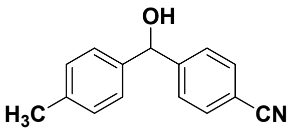
Reaction conditions: benzaldehyde (0.2 mmol), *p*-phthalonitrile (0.3 mmol), and *N*,*N*-diisopropylethylamine (0.3 mmol) in DMSO (2 mL) at 25°C under blue light irradiation.

6. ^{1}H NMR spectra of products

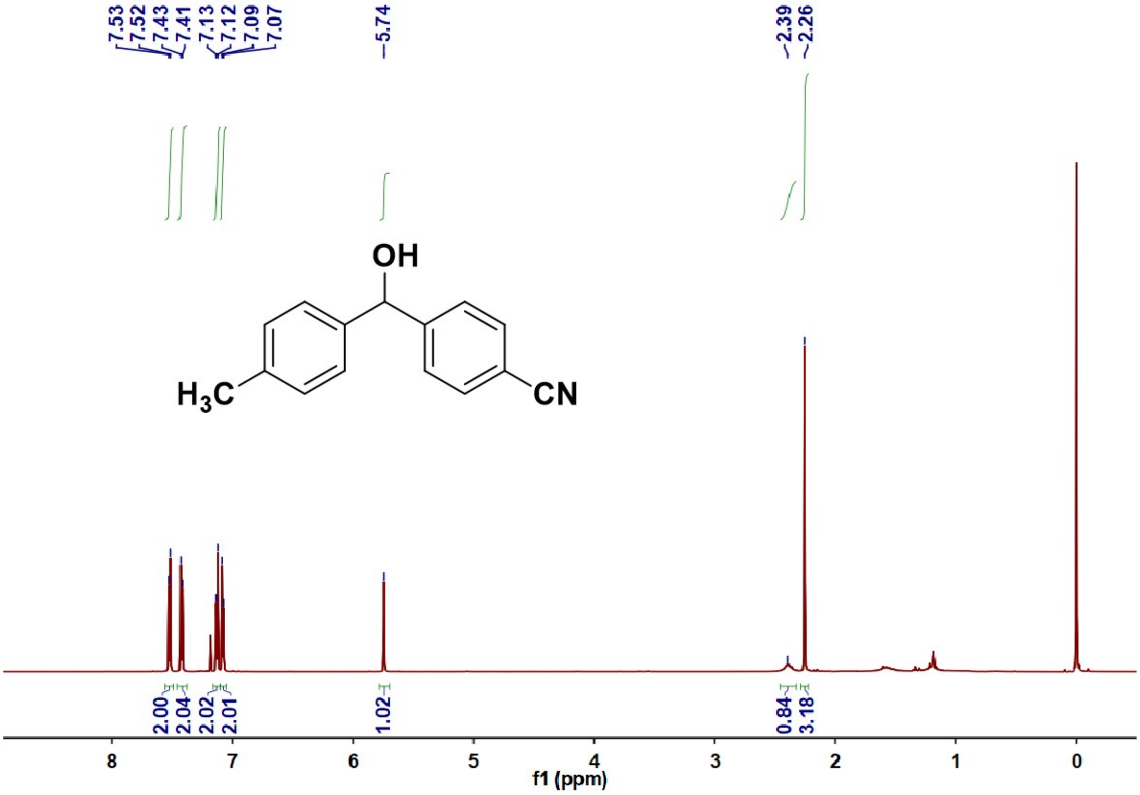


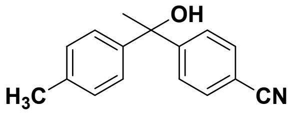
85% yield, colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.53 (d, J = 8.3 Hz, 2H), 7.43 (d, J = 8.1 Hz, 2H), 7.34-7.20 (m, 5H), 5.77 (s, 1H), 2.49 (br s, 1H).



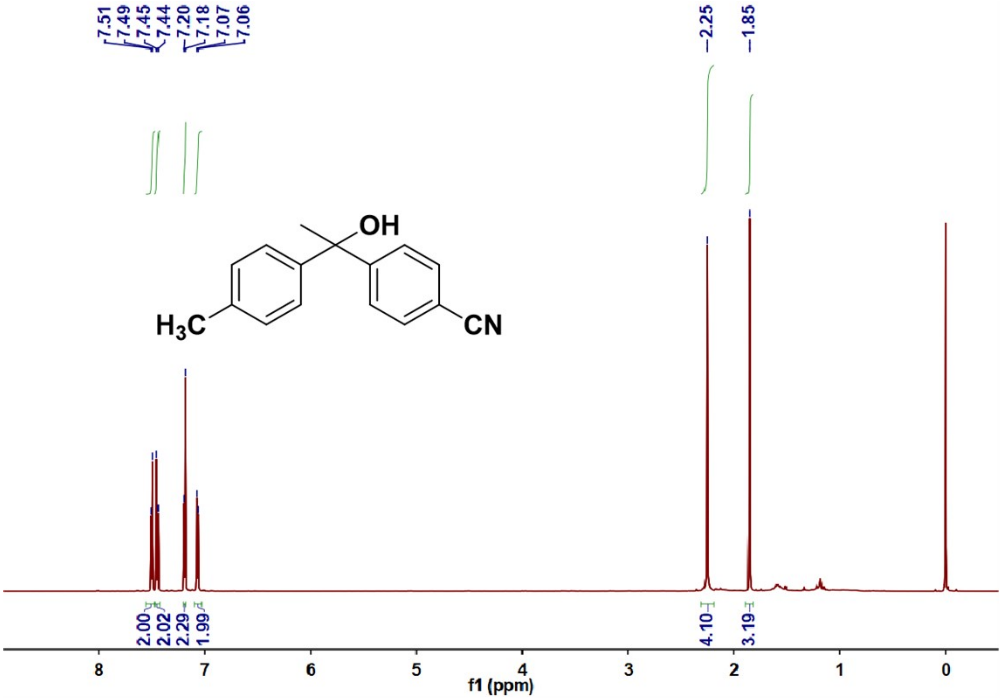


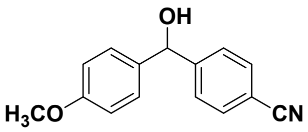
94% yield, colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.52 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.3 Hz, 2H), 7.13 (d, J = 8.0 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 5.74 (s, 1H), 2.39 (br s, 1H), 2.26 (s, 3H).



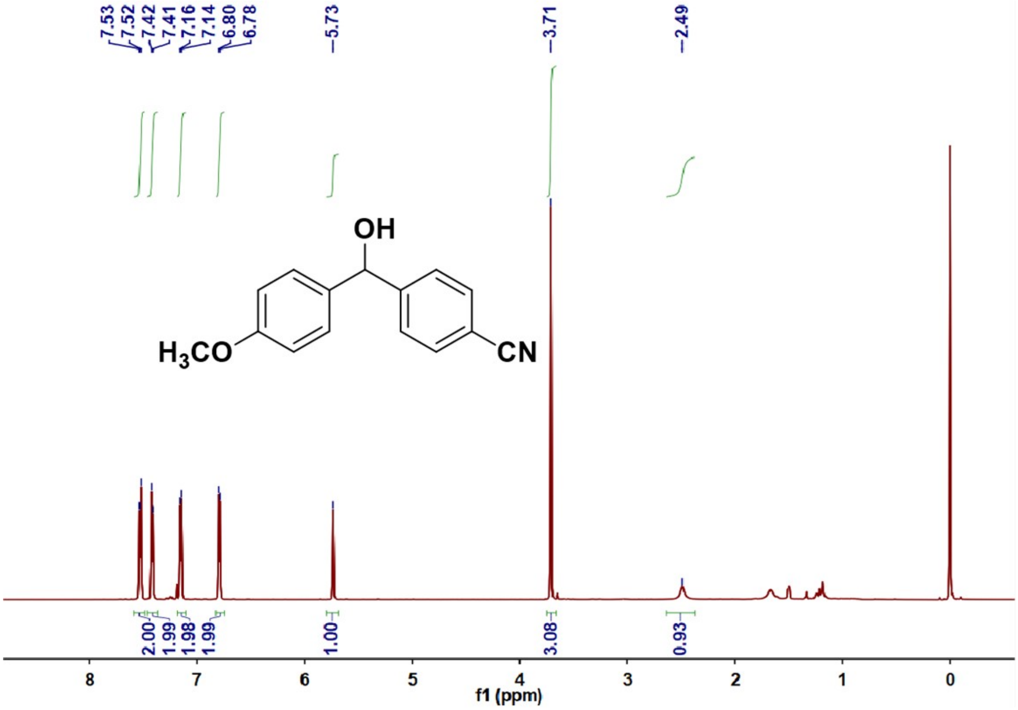


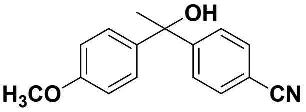
89% yield, colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.4 Hz, 2H), 7.19 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.0 Hz, 2H), 2.25 (d, 4H), 1.85 (s, 3H).



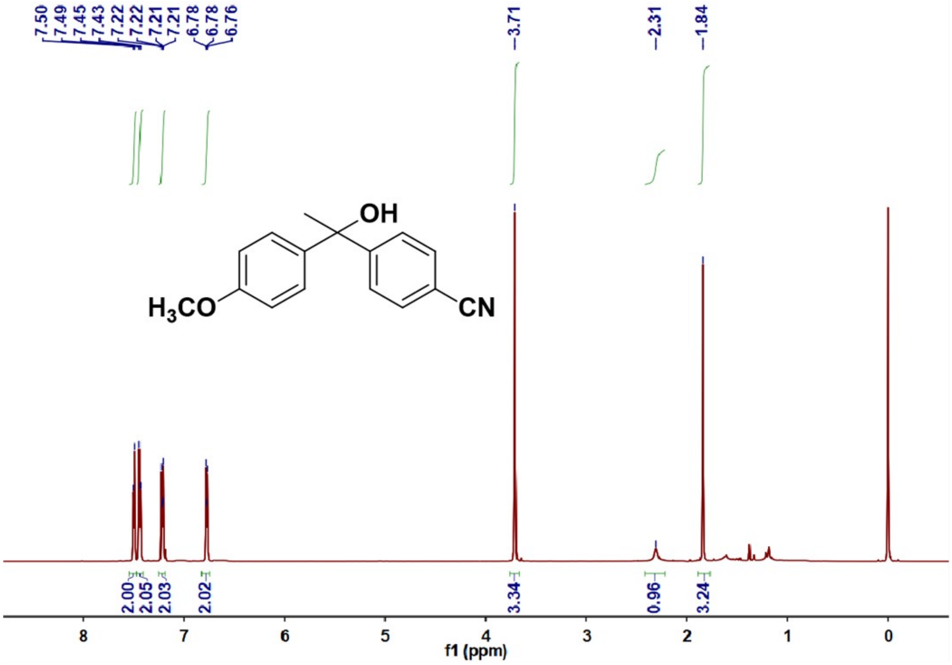


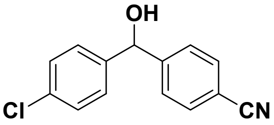
86% yield, colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.15 (d, *J* = 8.6 Hz, 2H), 6.79 (d, *J* = 8.7 Hz, 2H), 5.73 (s, 1H), 3.71 (s, 3H), 2.49 (br s, 1H).



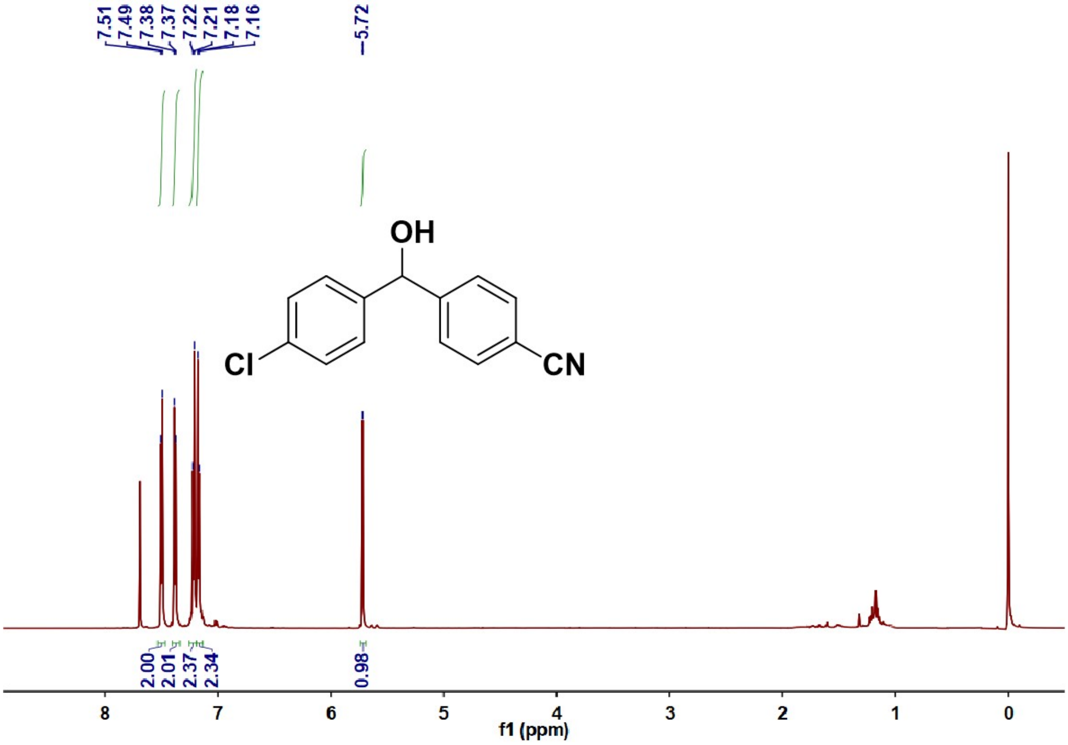


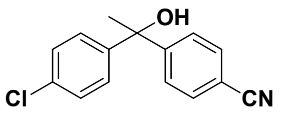
77% yield, colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.6 Hz, 2H), 7.44 (d, *J* = 8.6 Hz, 2H), 7.21 (dd, *J* = 6.9, 2.0 Hz, 2H), 6.82 – 6.74 (m, 2H), 3.71 (s, 3H), 2.31 (br s, 1H), 1.84 (s, 3H).



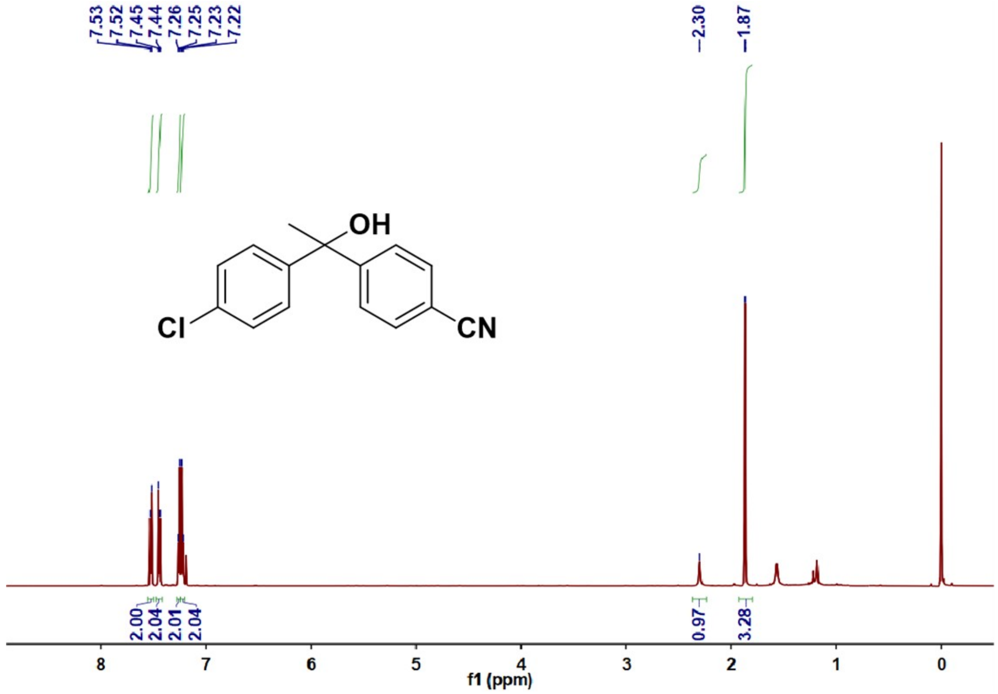


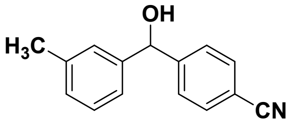
60% yield, colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.5 Hz, 2H), 7.17 (d, *J* = 8.4 Hz, 2H), 5.72 (s, 1H).



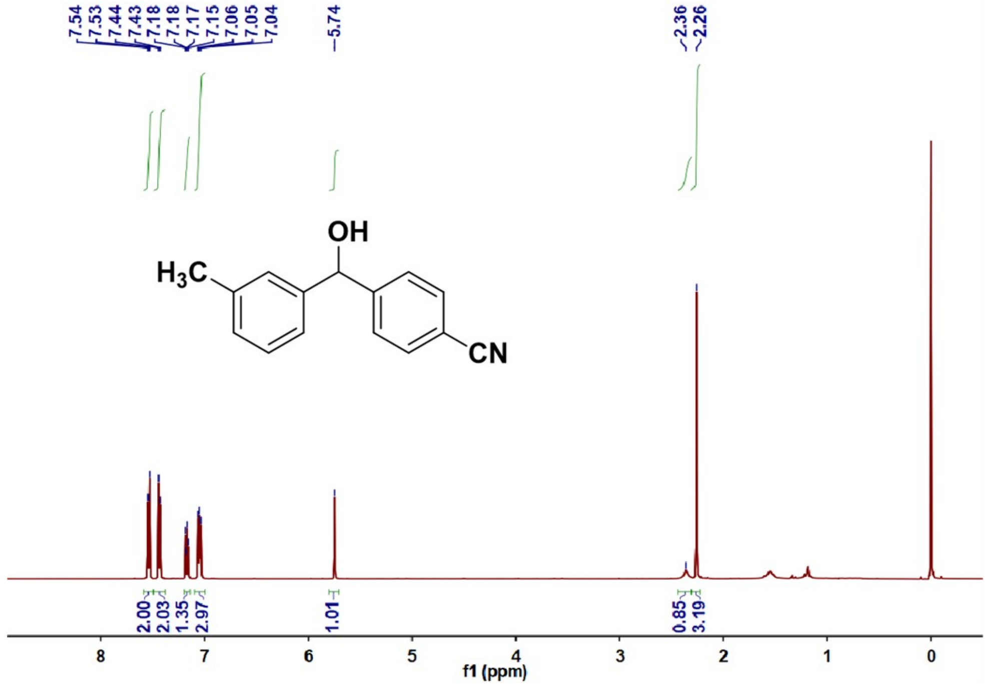


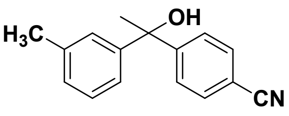
78% yield, colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.5 Hz, 2H), 7.22 (d, *J* = 8.6 Hz, 2H), 2.30 (br s, 1H), 1.86 (s, 3H).



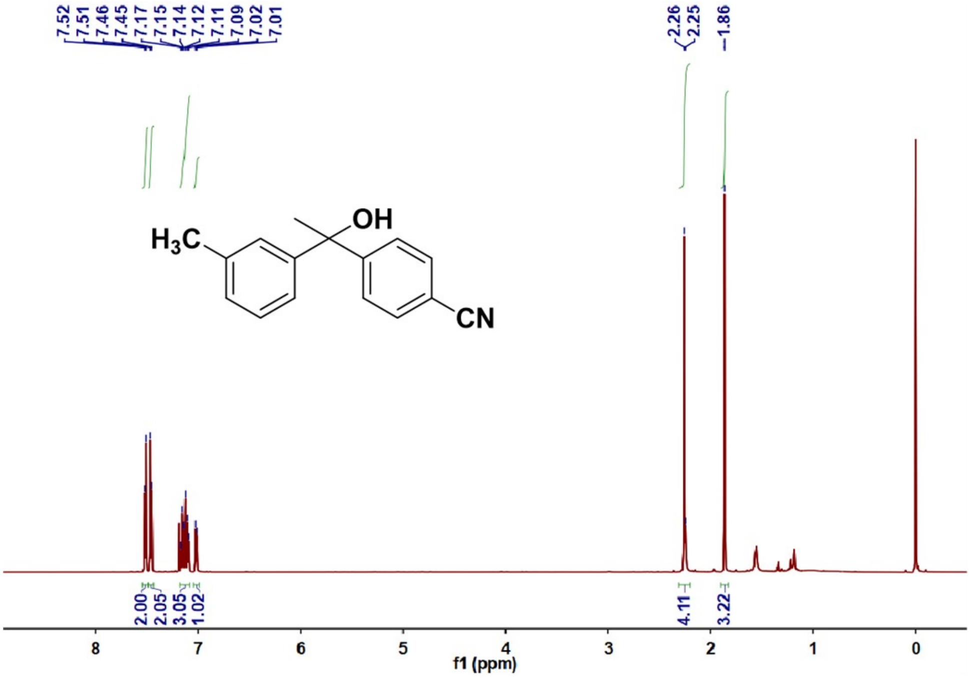


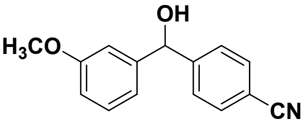
85% yield, colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.54 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 8.2 Hz, 2H), 7.17 (dd, *J* = 13.1, 5.5 Hz, 1H), 7.10 – 7.00 (m, 3H), 5.74 (s, 1H), 2.36 (br s, 1H), 2.26 (s, 3H).



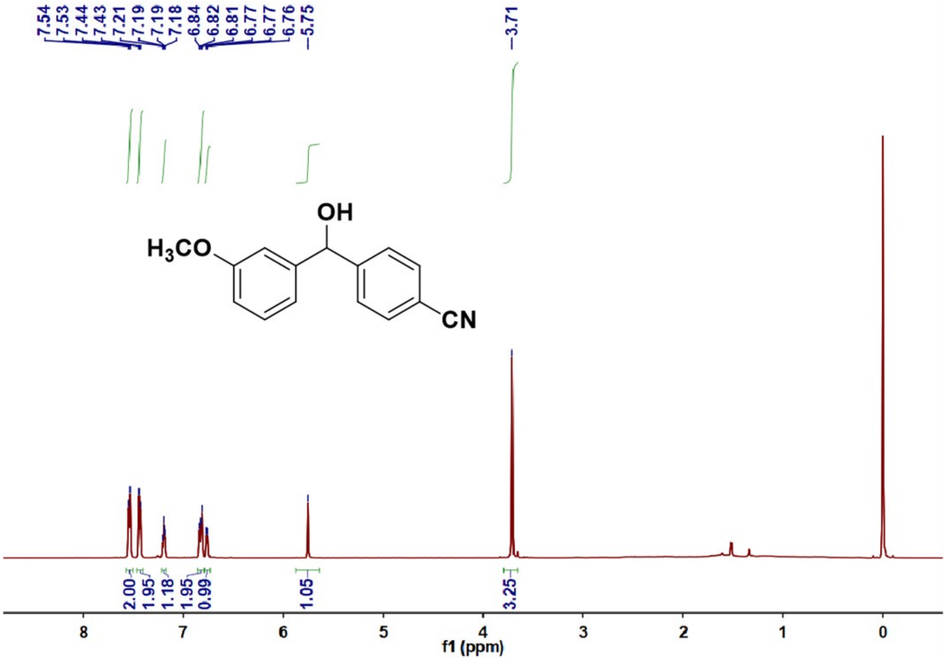


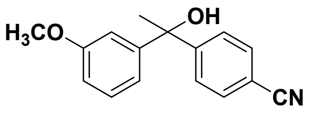
87% yield, colourless oil. **^{1}H NMR** (600 MHz, CDCl$_3$):^{1}H NMR (600 MHz, CDCl$_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 8.2 Hz, 2H), 7.13 (dt, *J* = 19.6, 7.5 Hz, 3H), 7.01 (d, *J* = 7.1 Hz, 1H), 2.25 (d, *J* = 12.0 Hz, 4H), 1.86 (s, 3H).



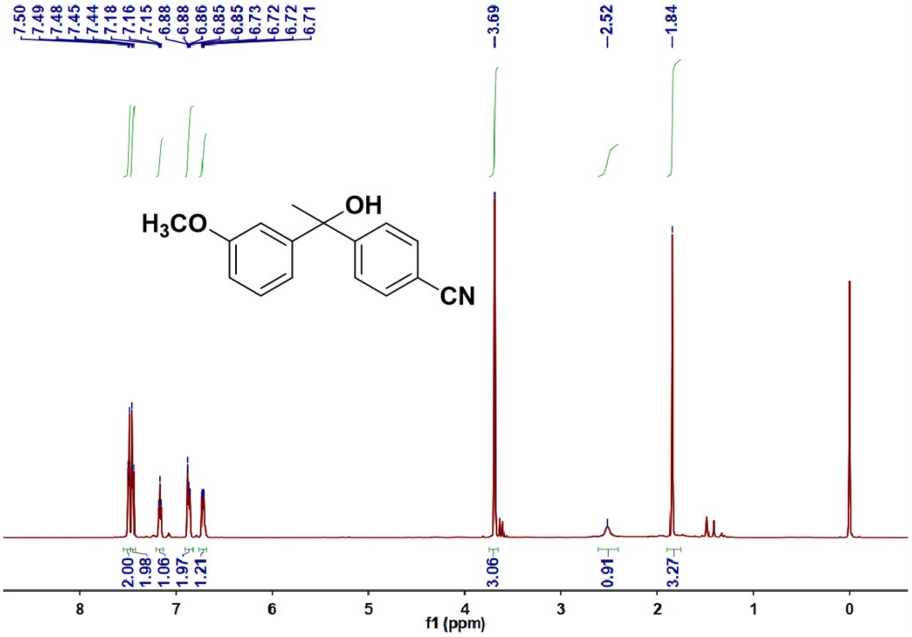


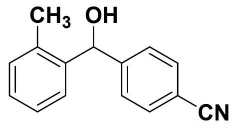
79% yield, colourless oil. **^{1}H NMR** (600 MHz, CDCl$_3$): δ 7.54 (d, *J* = 8.1 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.19 (dd, *J* = 9.6, 6.1 Hz, 1H), 6.85 – 6.79 (m, 2H), 6.78 – 6.73 (m, 1H), 5.75 (s, 1H), 3.71 (s, 3H).



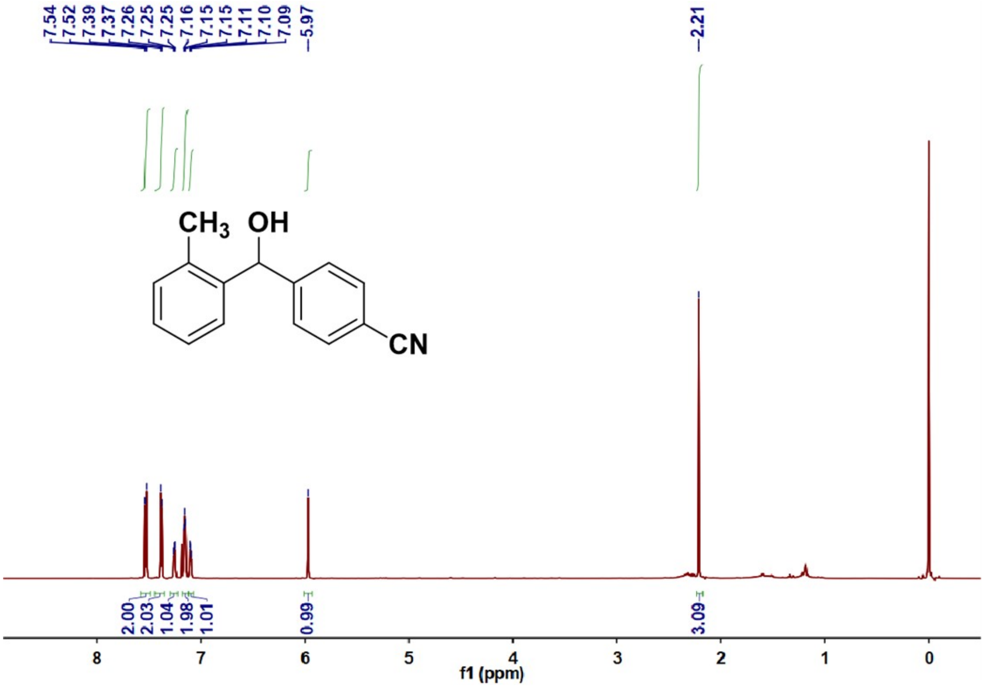


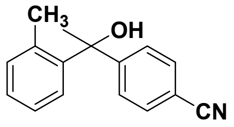
72% yield, colourless oil. **^{1}H NMR** (600 MHz, CDCl$_3$): δ 7.54 – 7.47 (m, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.16 (t, *J* = 8.0 Hz, 1H), 6.91 – 6.82 (m, 2H), 6.72 (dd, *J* = 7.8, 2.1 Hz, 1H), 3.69 (s, 3H), 2.52 (br s, 1H), 1.84 (s, 3H).



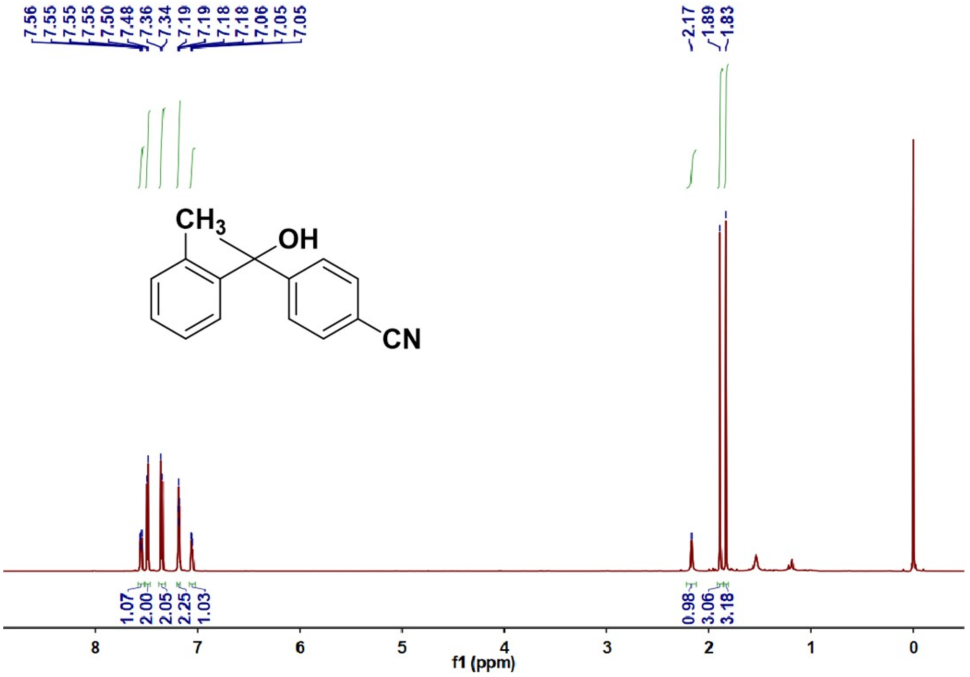


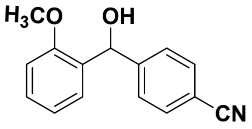
88% yield, colourless oil. **^{1}H NMR** (600 MHz, CDCl$_3$): δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.22 (m, 1H), 7.18 – 7.12 (m, 2H), 7.12 – 7.07 (m, 1H), 5.97 (s, 1H), 2.21 (s, 3H).



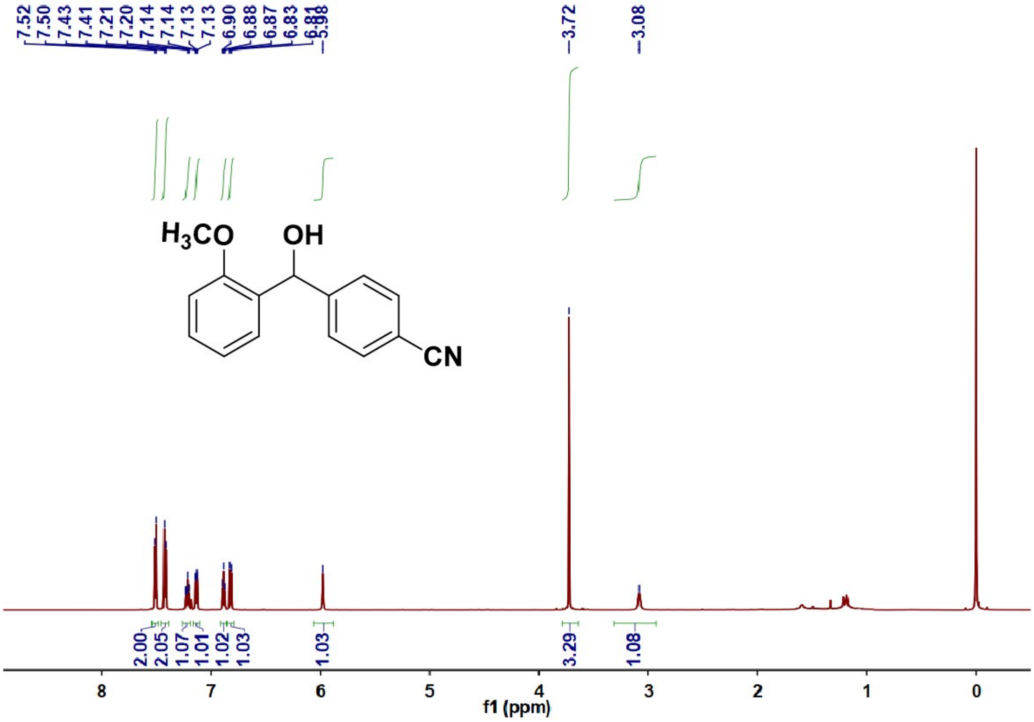


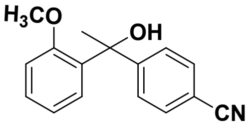
85% yield, colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.55 (dd, *J* = 5.9, 3.2 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.35 (d, *J* = 8.3 Hz, 2H), 7.18 (dd, *J* = 6.2, 2.7 Hz, 2H), 7.08 – 7.02 (m, 1H), 2.17 (br s, 1H), 1.89 (s, 3H), 1.83 (s, 3H).





80% yield, colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.26 – 7.19 (m, 1H), 7.13 (dd, *J* = 7.5, 1.1 Hz, 1H), 6.88 (t, *J* = 7.5 Hz, 1H), 6.82 (d, *J* = 8.2 Hz, 1H), 5.98 (s, 1H), 3.72 (s, 3H), 3.08 (br s, 1H).





69% yield, colourless oil. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.33 (d, *J* = 8.2 Hz, 2H), 7.26 (dd, *J* = 11.3, 4.2 Hz, 1H), 6.98 (t, *J* = 7.5 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 1H), 4.51 (s, 1H), 3.51 (s, 3H), 1.73 (s, 3H).