Supplementary Information (SI) for Dalton Transactions.

Electronic Supplementary Information

Metal-organic frameworks (MOFs) of MIL-101-supported iridium(III) complex as an efficient photocatalyst in the three-component alkoxycyanomethylation of alkenes

Xintao Deng, Mi Zhou, Xuebing Ma*

College of Chemistry and Chemical Engineering, Southwest University, Chongqing, 400715, P. R. China

Corresponding author's email: zcj123@swu.edu.cn

1. Particle size distribution

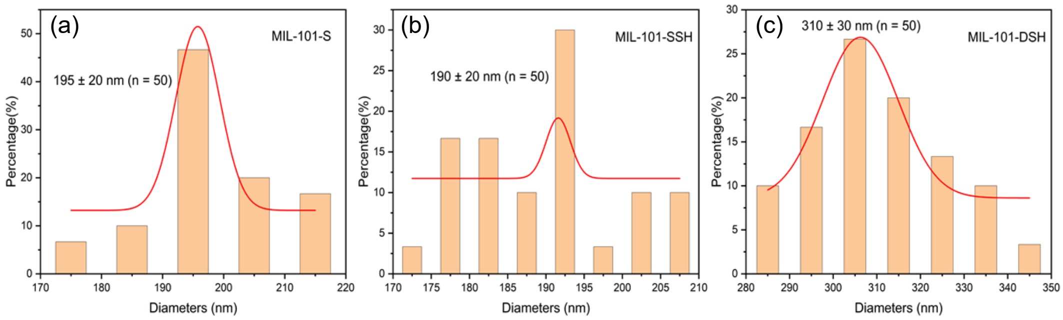


Fig.S1 Particle size distributions of MIL-101-S (a) MIL-101-SSH (b) and MIL-101-DSH (C).

2. Porous structure

Table S1 Specific surface areas, pore sizes, and pore volumes of various MIL-101 and Ir@MIL-101

Sample	S_{BET} (m^2 g^{-1})	Pore size (nm)	Pore volume (cm^3 g^{-1})
MIL-101-S	1362	3.1	0.80
MIL-101-SSH	1078	3.1	0.71
MIL-101-DSH	1174	3.1	0.74
Ir@MIL-101-S	962	1.9	0.59
Ir@MIL-101-SSH	847	1.8	0.47
Ir@MIL-101-DSH	798	1.9	0.47

3. Content of chloromethyl in various chloromethylated MIL-101

Table S2 Chloromethyl content of various chloromethylated MIL-101

Entry	$AgNO_3$[a] (mL)	Chloromethyl content [b] (mmol g^{-1})
MIL-101−S	8.4	0.84
MIL-101−SSH	9.2	0.92
MIL-101-DSH	12.1	1.21

[a] Titration volume, [b] Calculated by titration volume of consumed $AgNO_3$.

4. 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 where τ is measured fluorescence lifetime and B is 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

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

Table S3 Fluorescence decay curve detailed fitting parameters of various Ir@MIL-101 and *fac*-Ir(ppy)$_3$

Sample	τ_1 (ns)	B_1/Rel_1 (%)	τ_2 (ns)	B_2/Rel_2 (%)	τ_3 (ns)	B_3/Rel_3 (%)	τ_{avg}	χ^2
fac-Ir(ppy)$_3$	44.41	133.9/-	245.62	774.5/-	555.24	550.6/-	431.80	1.08
Ir@MIL-101(Cr)-S	2.30	2903.43/15.42	5.88	3723.20/64.95	18.90	350.28/19.64	7.80	1.06
Ir@MIL-101(Cr)-SSH	2.05	2874.95/13.09	7.52	3971.72/67.33	20.73	420.28/19.58	9.53	1.19
Ir@MIL-101(Cr)-DSH	2.22	4132.62/15.58	9.25	3110.46/48.8	30.21	693.37/35.56	15.61	1.15

5. Uv–Vis DRS

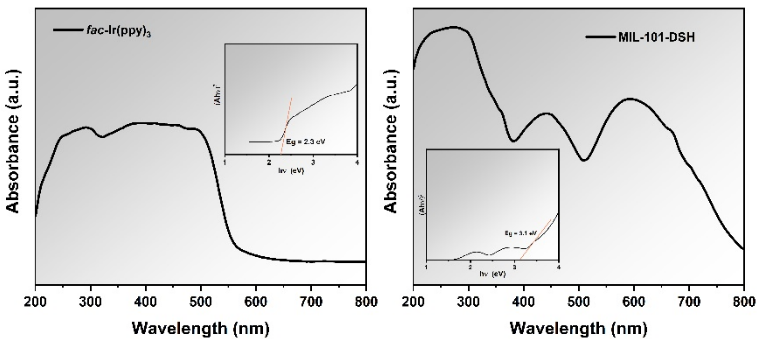


Fig. S2 UV-Vis DRS spectra of *fac*-Ir(ppy)$_3$ and MIL-101-DSH

6. Quantum yield

Based on the fluorescence intensities in fluorescence spectra, the photoluminescence quantum yields were determined by FLS1000 steady state/transient state fluorescence spectrometer.

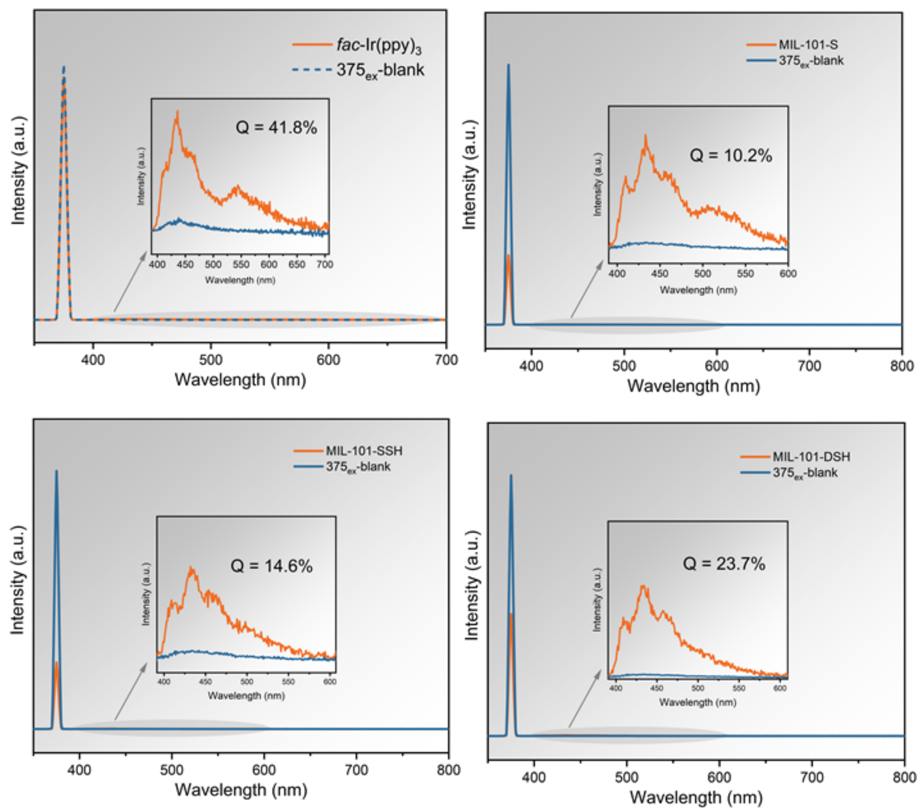


Fig.S3 Photoluminescence quantum yields (PLQY) of *fac*-Ir(ppy)$_3$, Ir@MIL-101-S Ir@MIL-101-SSH and Ir@MIL-101-DSH

7. Kinetics of reaction process

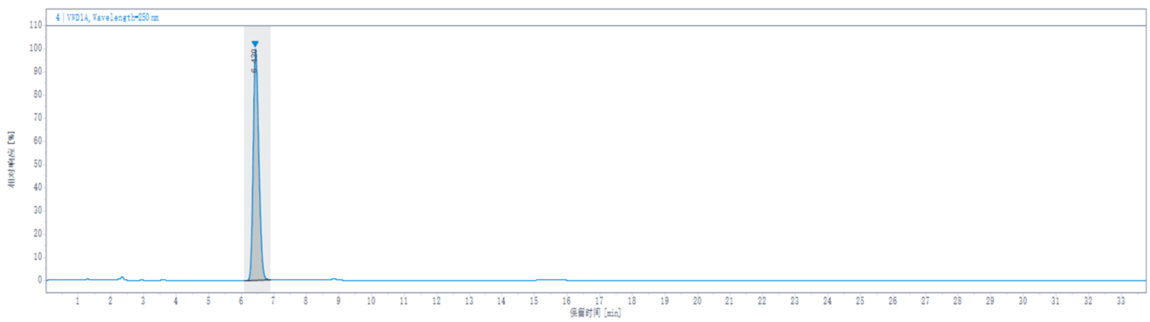


Fig.S4 HPLC spectrum of the reaction mixture in the Ir@MIL-101-DSH-promoted reductive cross-coupling reaction of styrene, bromoacetonitrile and methanol at 24 h (rate: 0.8 mL min^{-1}, V_{H2O}/V_{HCN}=60:40, C18 column).

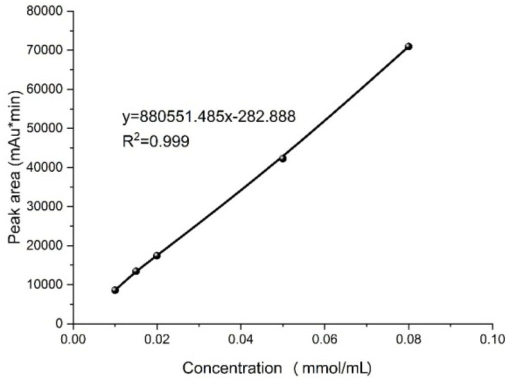


Fig.S5 Standard curve for product quantification

Table S4 Yields of γ-alkoxynitrile in the reaction of styrene, bromoacetonitrileand and methanol during the whole processes

Sample	**Reaction time (h)**							
	3	**6**	**9**	**12**	**15**	**18**	**21**	**24**
***fac*-Ir(ppy$_3$)**	13	34	47	59	73	79	87	87
Ir@**MIL-101**−**S**	6	18	27	35	42	48	53	54
Ir@**MIL-101**−**SSH**	6	25	32	41	53	59	65	67
Ir@**MIL-101(Cr)**−**DSH**	6	27	39	50	61	73	84	86

Reaction conditions: Ir@MIL-101 (0.5 mol% of Ir), styrene (52.5 mg, 0.5 mmol), bromoacetonitrile (120.0 mg, 1.0 mmol), $NaHCO_3$ (84.0 mg, 1.0 mmol), white light (24W)

8. XPS of 10th-reused Ir@MIL-101-DSH

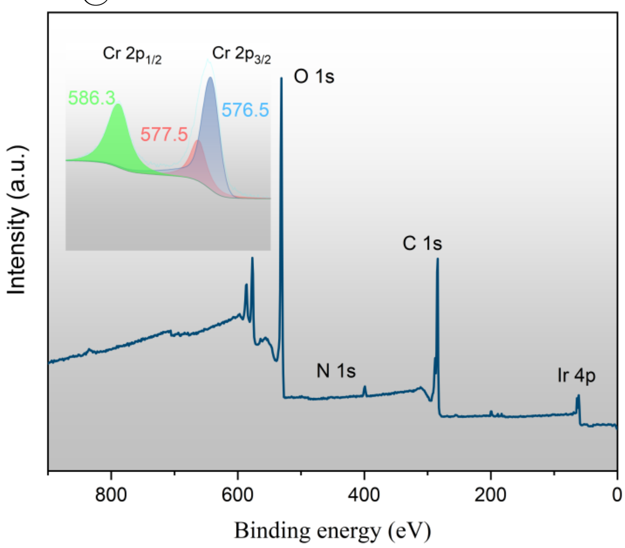


Fig.S6 XPS spectrum of 10th-reused Ir@MIL-101-DSH

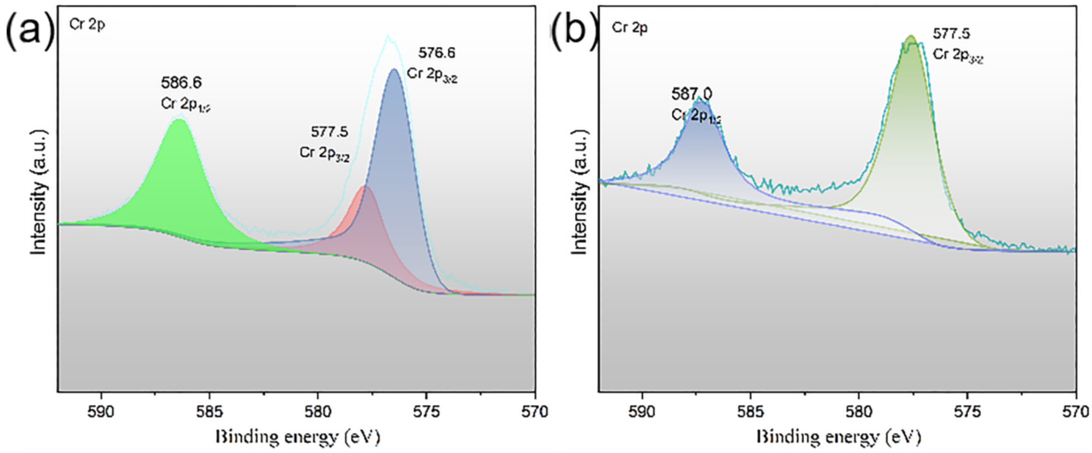
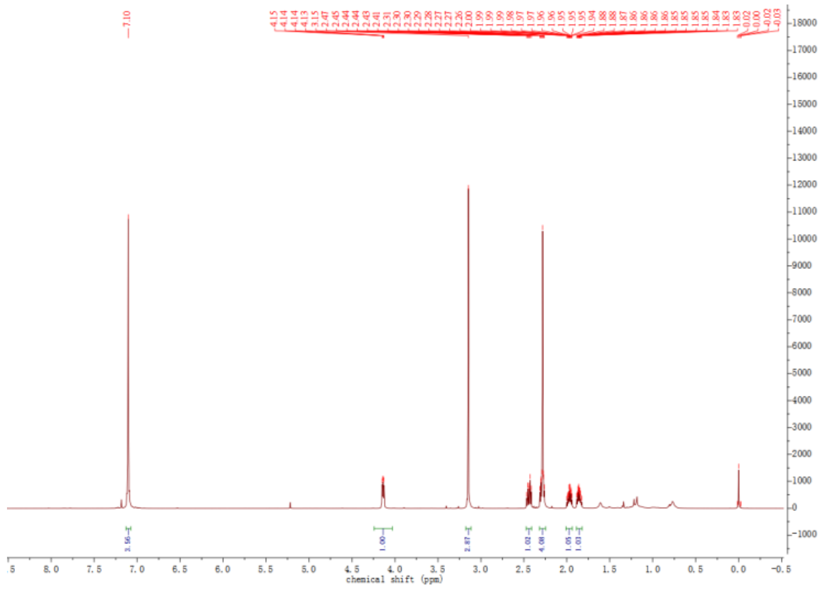
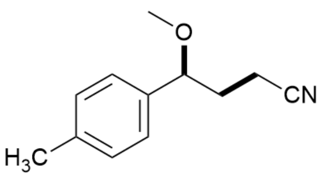


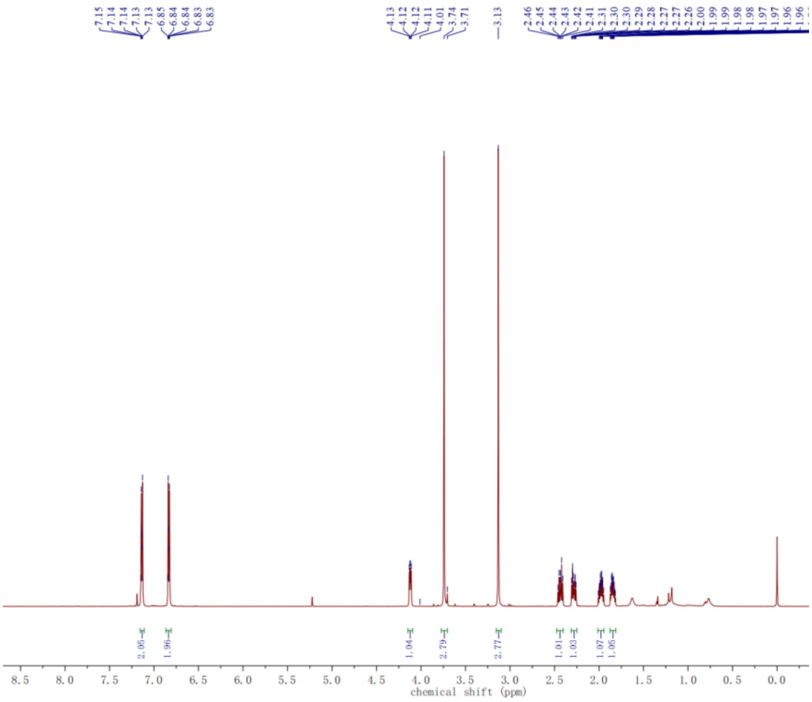
Fig.S7 Comparative XPS spectra of Cr 2p for the fresh (b) and 10th-reused (a) Ir@MIL-101-DSH

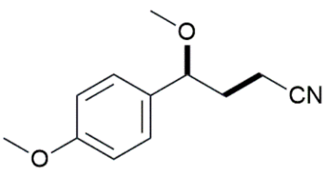
8. ^{1}H NMR spectra of products



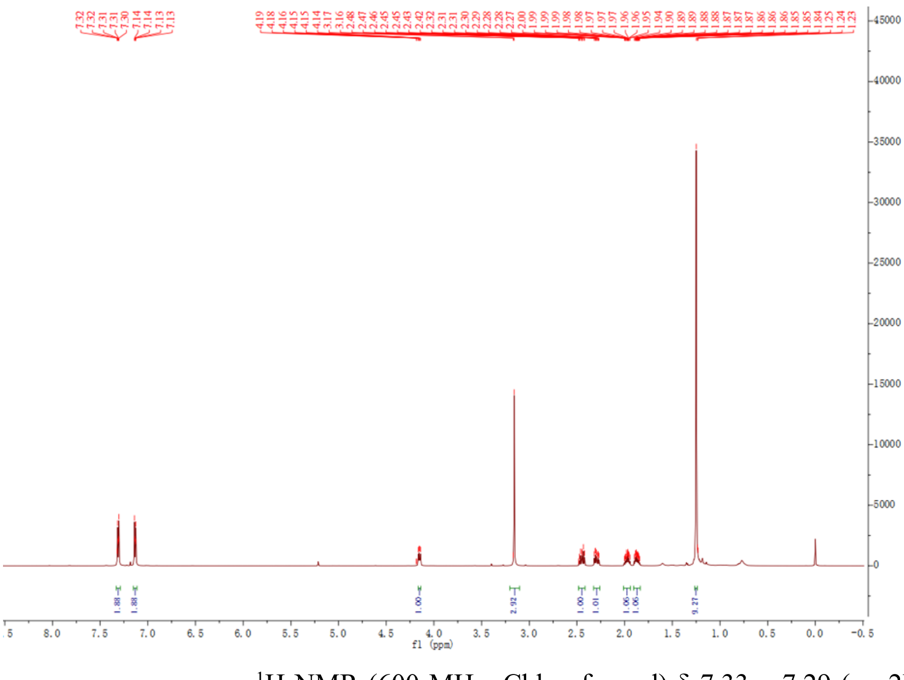


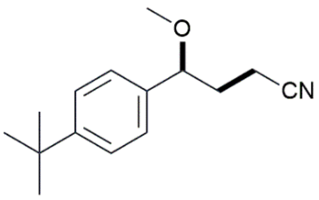
^{1}H NMR (600 MHz, Chloroform-d) δ 7.10 (s, 4H), 4.14 (dd, J = 8.7, 4.7 Hz, 1H), 3.15 (s, 3H), 2.44 (dt, J = 16.9, 7.7 Hz, 1H), 2.32 – 2.24 (m, 4H), 2.01 – 1.93 (m, 1H), 1.89 – 1.83 (m, 1H).



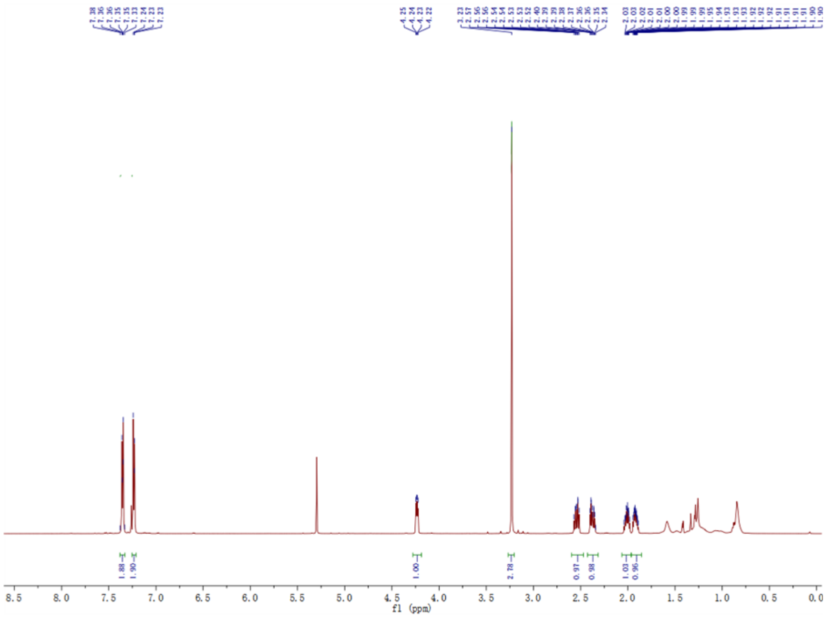


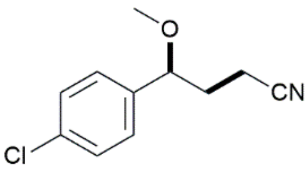
^1H NMR (600 MHz, Chloroform-d) δ 7.18 – 7.02 (m, 2H), 6.89 – 6.74 (m, 2H), 4.12 (dd, J = 8.7, 4.8 Hz, 1H), 3.74 (s, 3H), 3.13 (s, 3H), 2.43 (dt, J = 17.1, 7.6 Hz, 1H), 2.28 (ddd, J = 16.9, 7.3, 5.9 Hz, 1H), 2.02 – 1.94 (m, 1H), 1.88 – 1.80 (m, 1H).



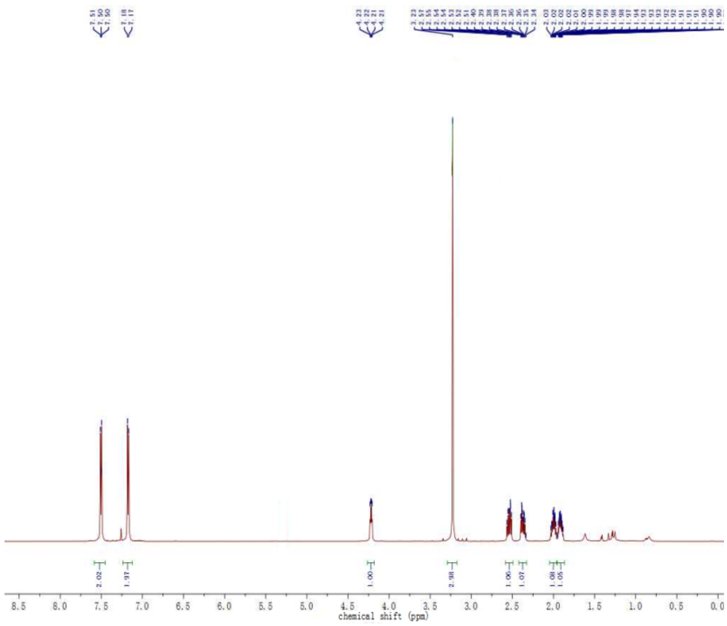


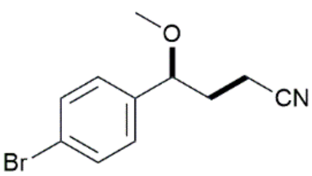
^1H NMR (600 MHz, Chloroform-d) δ 7.33 – 7.29 (m, 2H), 7.15 – 7.11 (m, 2H), 4.15 (dd, J = 8.7, 4.7 Hz, 1H), 3.16 (s, 3H), 2.45 (dt, J = 16.9, 7.7 Hz, 1H), 2.29 (ddd, J = 16.9, 7.4, 5.8 Hz, 1H), 2.01 – 1.94 (m, 1H), 1.90 – 1.84 (m, 1H), 1.25 (s, 10H).?



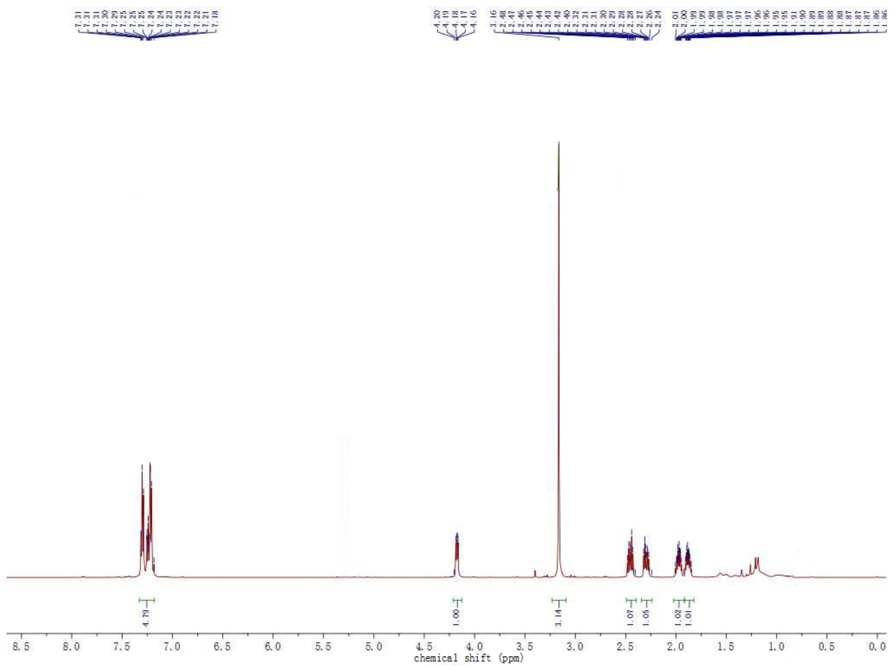


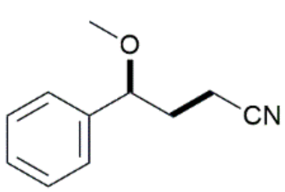
[1]H NMR (600 MHz, Chloroform-d) δ 7.40 – 7.32 (m, 2H), 7.23 (d, J = 8.4 Hz, 2H), 4.23 (dd, J = 9.0, 4.5 Hz, 1H), 3.23 (s, 3H), 2.58 – 2.50 (m, 1H), 2.37 (ddd, J = 16.9, 7.1, 5.7 Hz, 1H), 2.06 – 1.97 (m, 1H), 1.95 –1.88 (m, 1H).



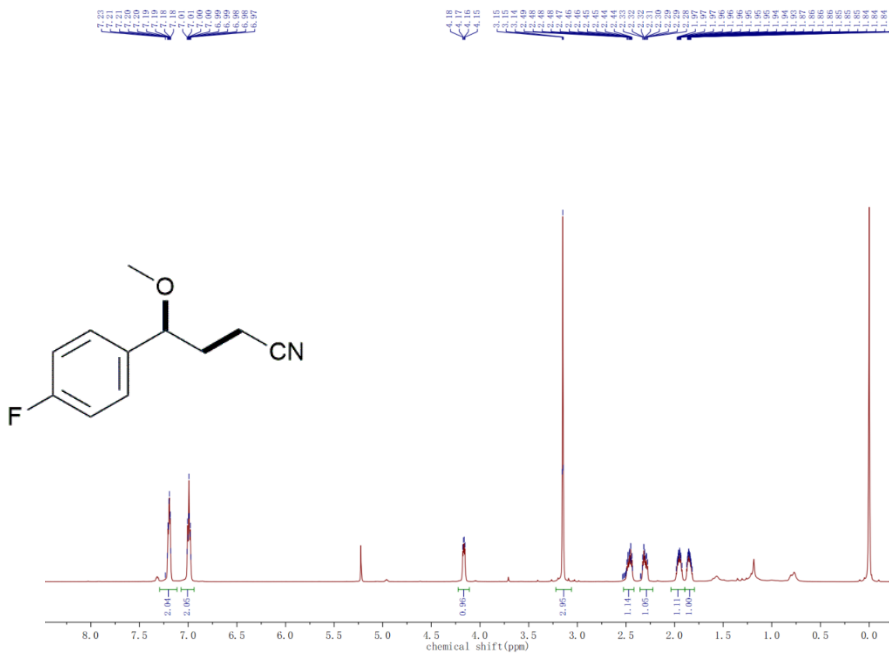


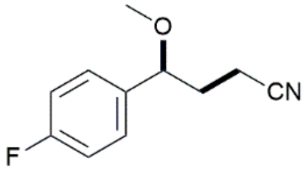
H NMR (600 MHz, Chloroform-d) δ 7.50 (d, J = 8.3 Hz, 2H), 7.17 (d, J = 8.2 Hz, 2H), 4.22 (dd, J = 9.0, 4.5 Hz, 1H), 3.23 (s, 3H), 2.58 – 2.50 (m, 1H), 2.37 (ddd, J = 16.9, 7.1, 5.8 Hz, 1H), 2.05 – 1.96 (m, 1H), 1.93 – 1.88 (m, 1H).





^{1}H NMR (600 MHz, Chloroform-d) δ 7.37 – 7.14 (m, 5H), 4.17 (dd, J = 8.7, 4.6 Hz, 1H), 3.16 (s, 3H), 2.46 (dt, J = 16.5, 7.7 Hz, 1H), 2.30 (ddd, J = 16.8, 7.3, 5.8 Hz, 1H), 2.02 – 1.93 (m, 1H), 1.92 – 1.83 (m, 1H).





1H NMR (600 MHz, Chloroform-d) δ 7.20 (ddt, J = 8.3, 5.2, 2.9 Hz, 3H), 6.99 (tt, J = 9.8, 2.9 Hz, 3H), 4.17 (dd, J = 8.9, 4.5 Hz, 1H), 3.15 (d, J = 3.5 Hz, 4H), 2.51 – 2.43 (m, 2H), 2.33 – 2.27 (m, 0H), 1.98 – 1.93 (m, 1H), 1.90 – 1.80 (m, 1H).