Supplementary Information for

Covalent organic frameworks editing for efficient metallaphotoredox catalytic carbon-oxygen cross coupling of aryl halides with alcohols

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Supplementary Data

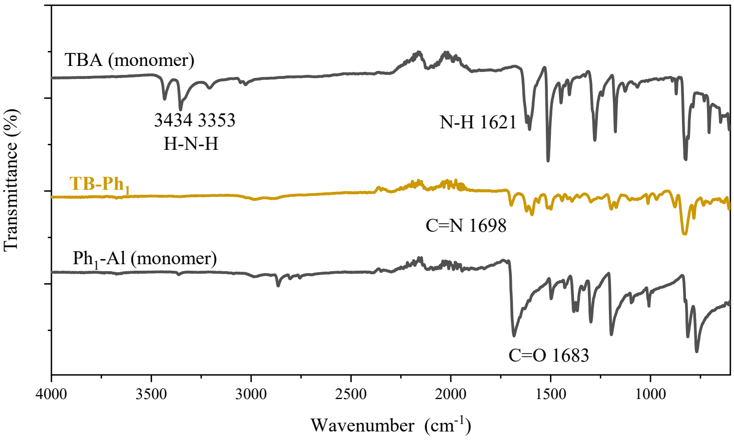


Figure S1. FTIR (ATR) spectrum of TB-Ph$_1$ and corresponding monomers.

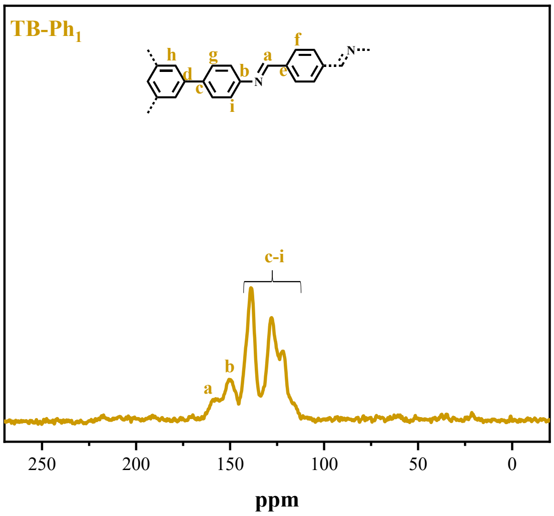


Figure S2. ^{13}C cross polarization total suppression of spinning sidebands nuclear magnetic resonance (CPTOSS-NMR) spectra of TB-Ph$_1$.

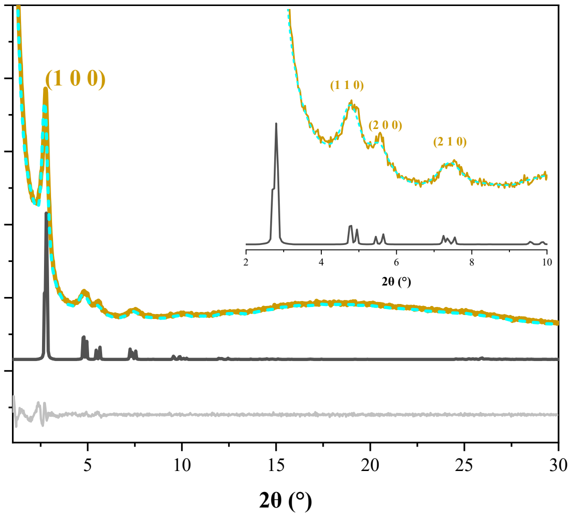


Figure S3. Powder X-ray diffraction (PXRD) characterization of TB-Ph_1 (khaki) with the major reflection peaks assigned, Pawley refined modelling profile (cyan dashed line), their difference pattern (grey line) and simulated pattern (black line). Insets: enlarged patterns in 2θ = 2-10° of the corresponding spectra.

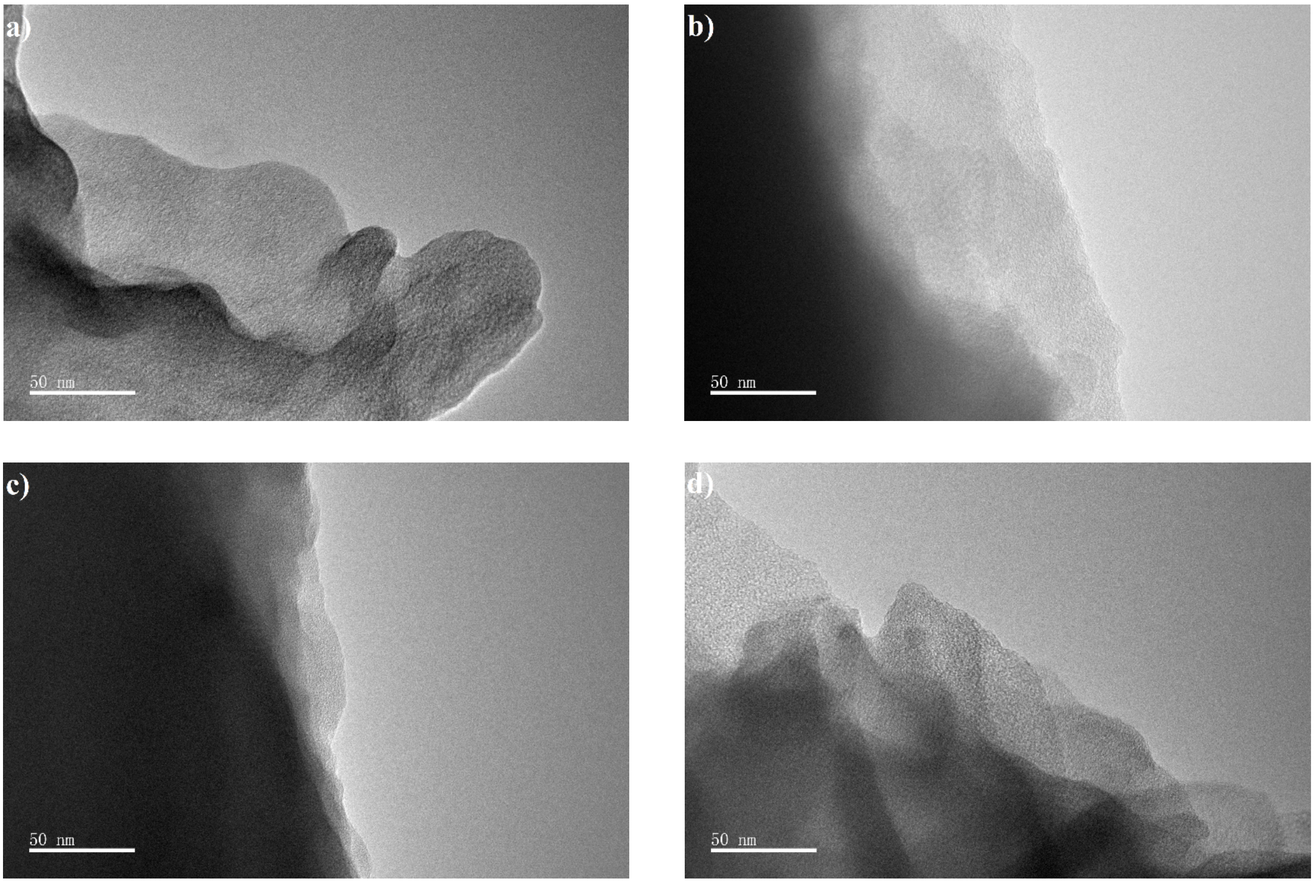


Figure S4. TEM images of (a) TT-Ph_1, (b) TT-Ph_2, (c) TT-Ph_3 and (d) TB-Ph_1.

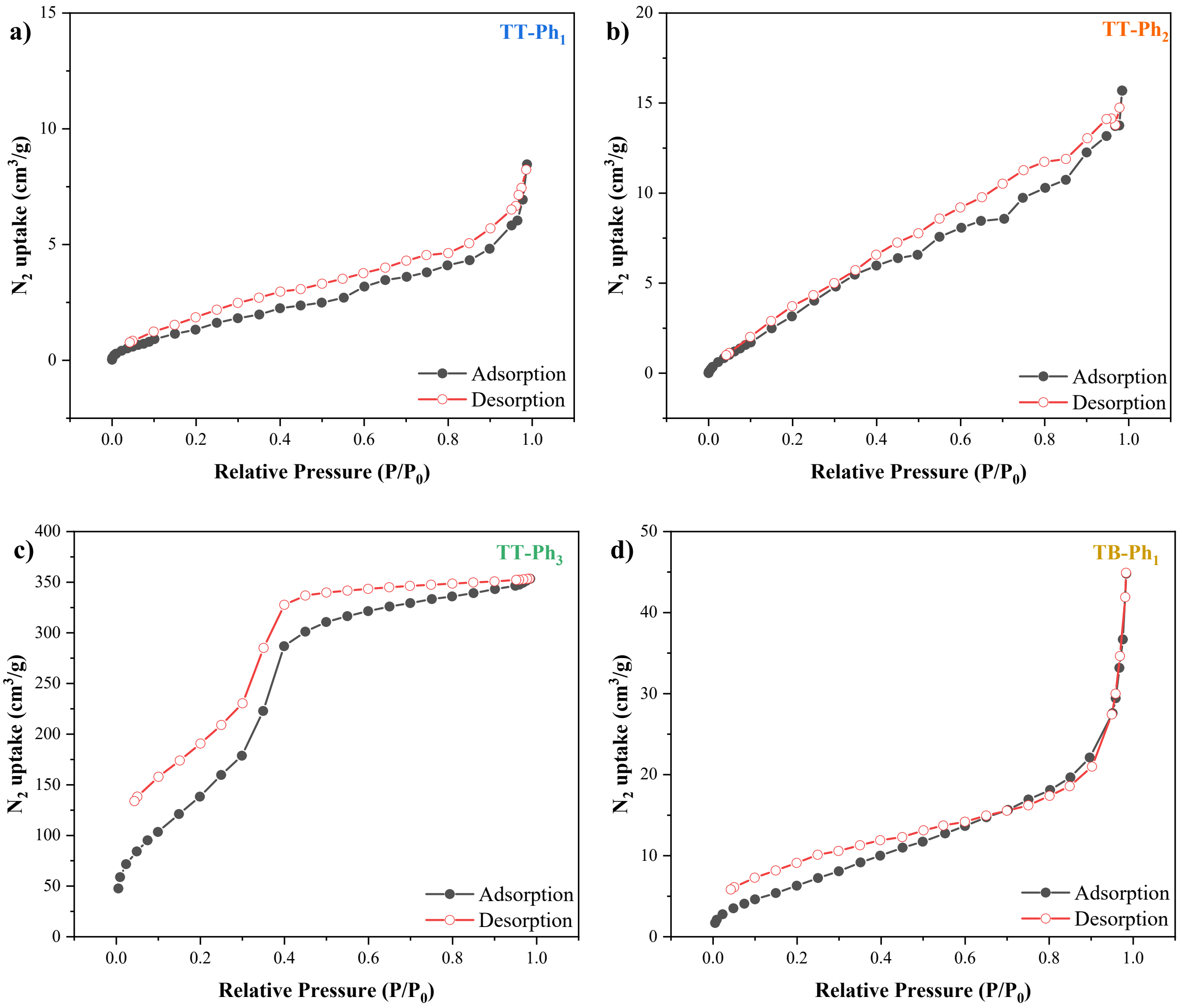


Figure S5. Nitrogen adsorption isotherms of (a) TT-Ph$_1$ (A_{BET} = 7.0 m^2 g^{-1}), (b) TT-Ph$_2$ (A_{BET} =22.4 m^2 g^{-1}), (c) TT-Ph$_3$ (A_{BET} =589.5 m^2 g^{-1}) and (d) TB-Ph$_1$ (A_{BET} = 27.3 m^2 g^{-1}) measured at 77 K.

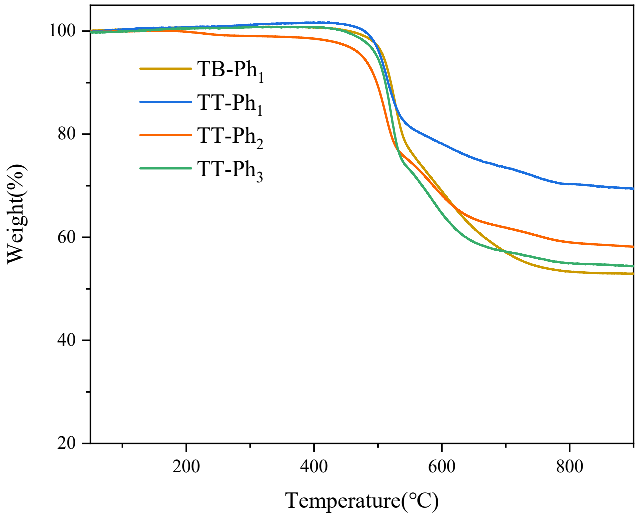


Figure S6. Thermogravimetric analysis (TGA) of TT-Ph$_{1\text{-}3}$ and TB-Ph$_1$.

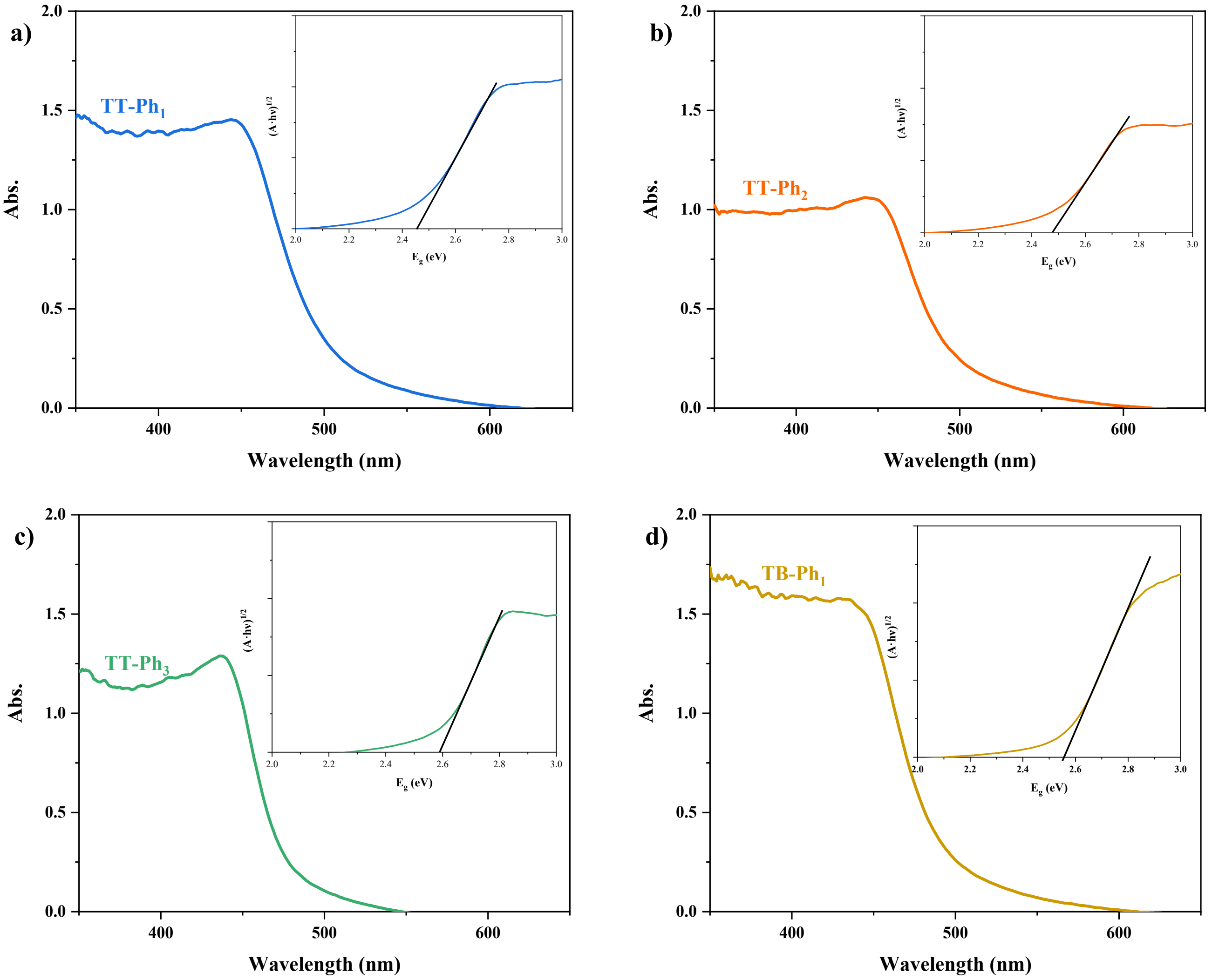


Figure S7. UV-Vis absorption spectra of (a)TT-Ph$_1$, (b)TT-Ph$_2$, (c)TT-Ph$_3$ and (d) TB-Ph$_1$. Band gaps extracted by Kubelka-Munk function are shown in the inserts.

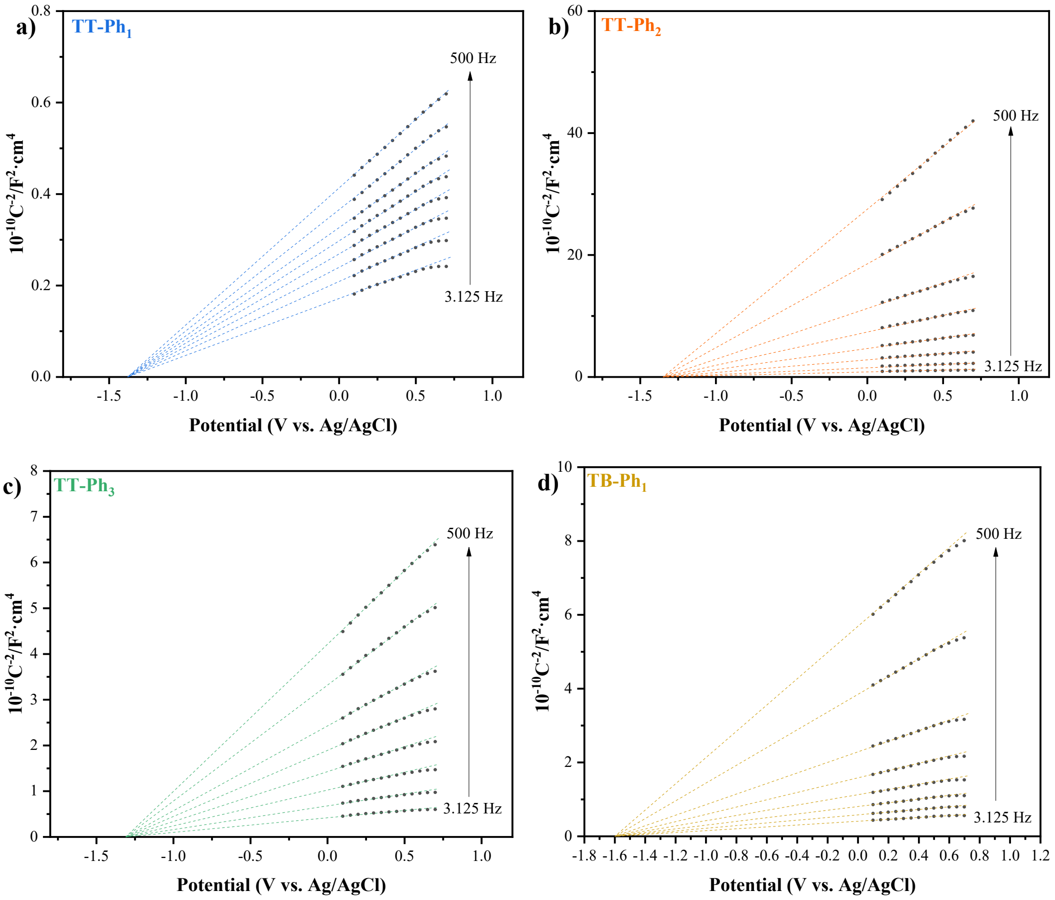


Figure S8. Mott−Schottky (M-S) plots of COFs (coated on FTO). (a) TT-Ph$_1$ (b) TT-Ph$_2$, (c) TT-Ph$_3$ (b) TB-Ph$_1$. The intercept of M-S plot is the flat band potential of each COFs, which was taken as the conduction band value in the empirical calculation of valence band potentials ($E_{VB}= E_g + E_{CB}$).

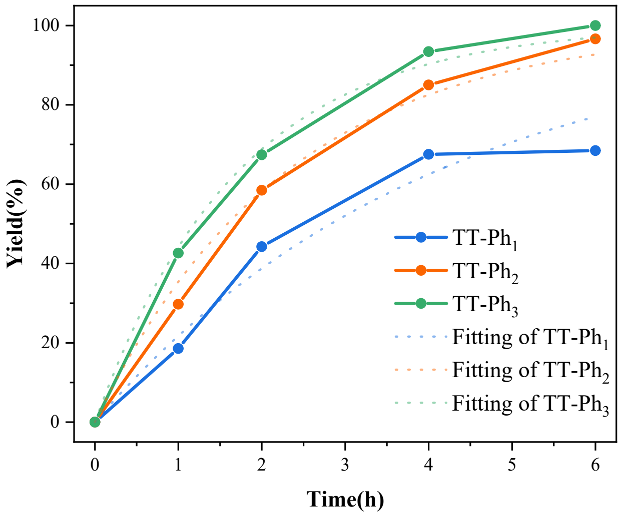


Figure S9. GC yield of 4-methoxybenzonitrile at given reaction time. The curves were fit by 1st exponential decay to give the pseudo first order rate constants as 0.25 h^{-1} of TT-Ph$_1$, 0.44 h^{-1} of TT-Ph$_2$ and 0.58 h^{-1} of TT-Ph$_3$.

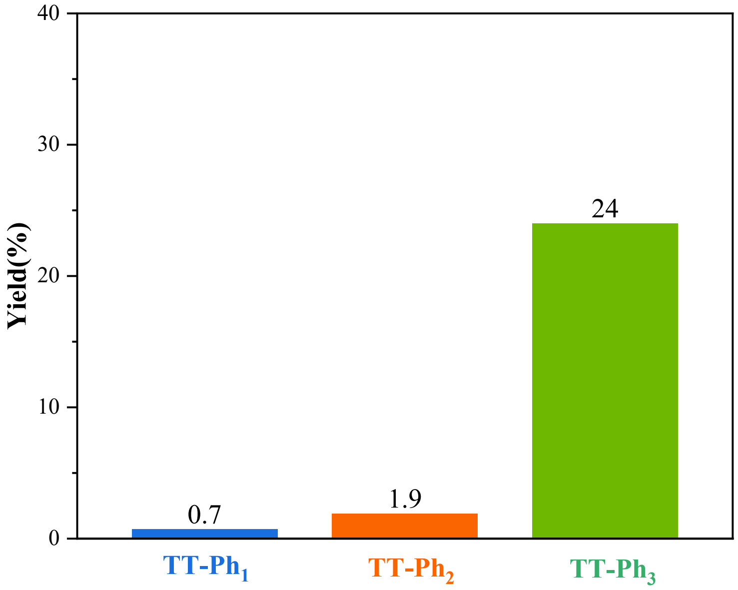


Figure S10. Yield of 4-methoxybenzonitrile under 6h of 455 nm LED irradiation.

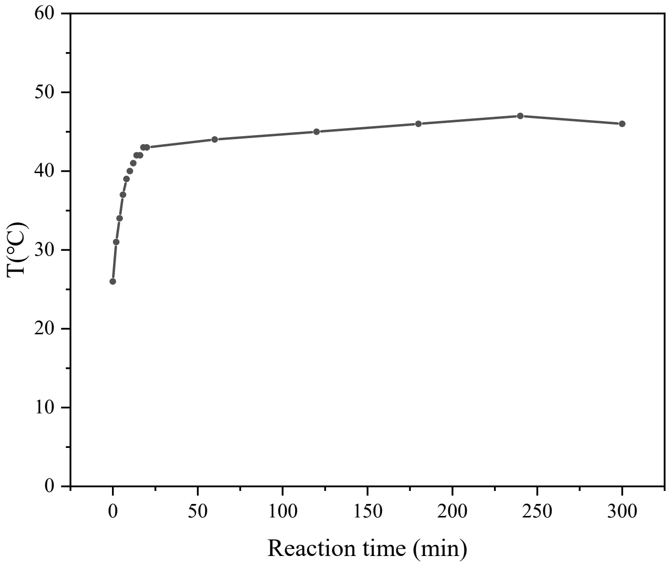


Figure S11. Monitoring of solution temperature under standard conditions at a room temperature of 26 ℃ (photoreactor was about 33 ℃).

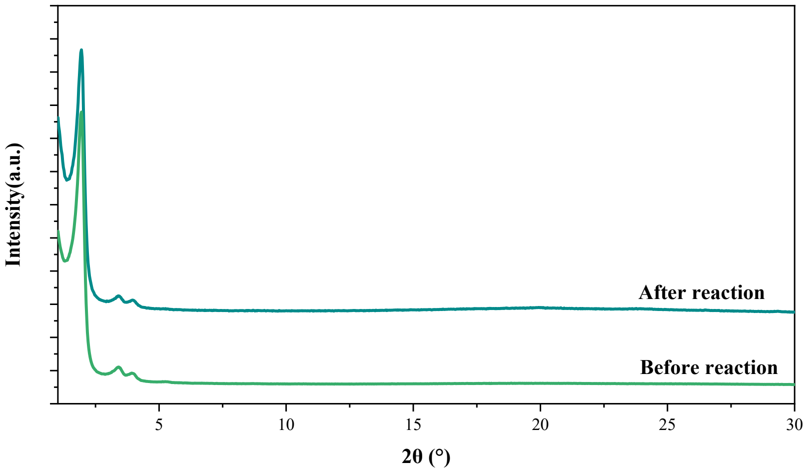


Figure S12. PXRD patterns comparison of TT-Ph_3 before and after reaction.

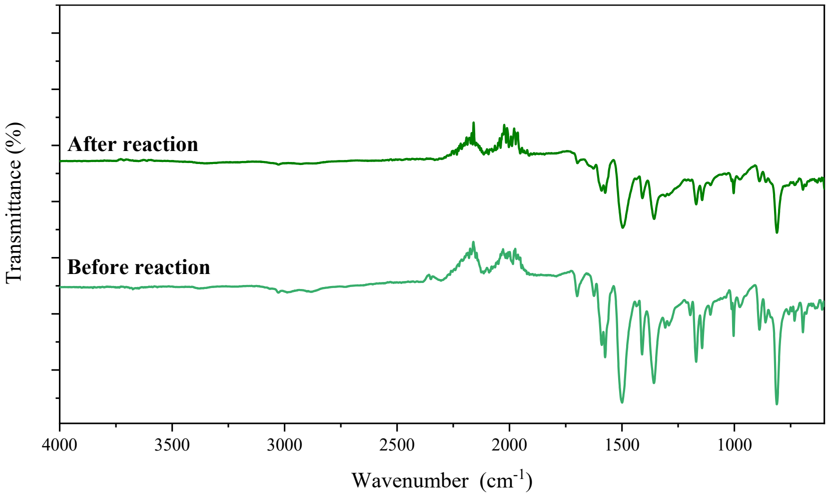


Figure S13. FTIR spectra comparison of TT-Ph_3 before and after reaction.

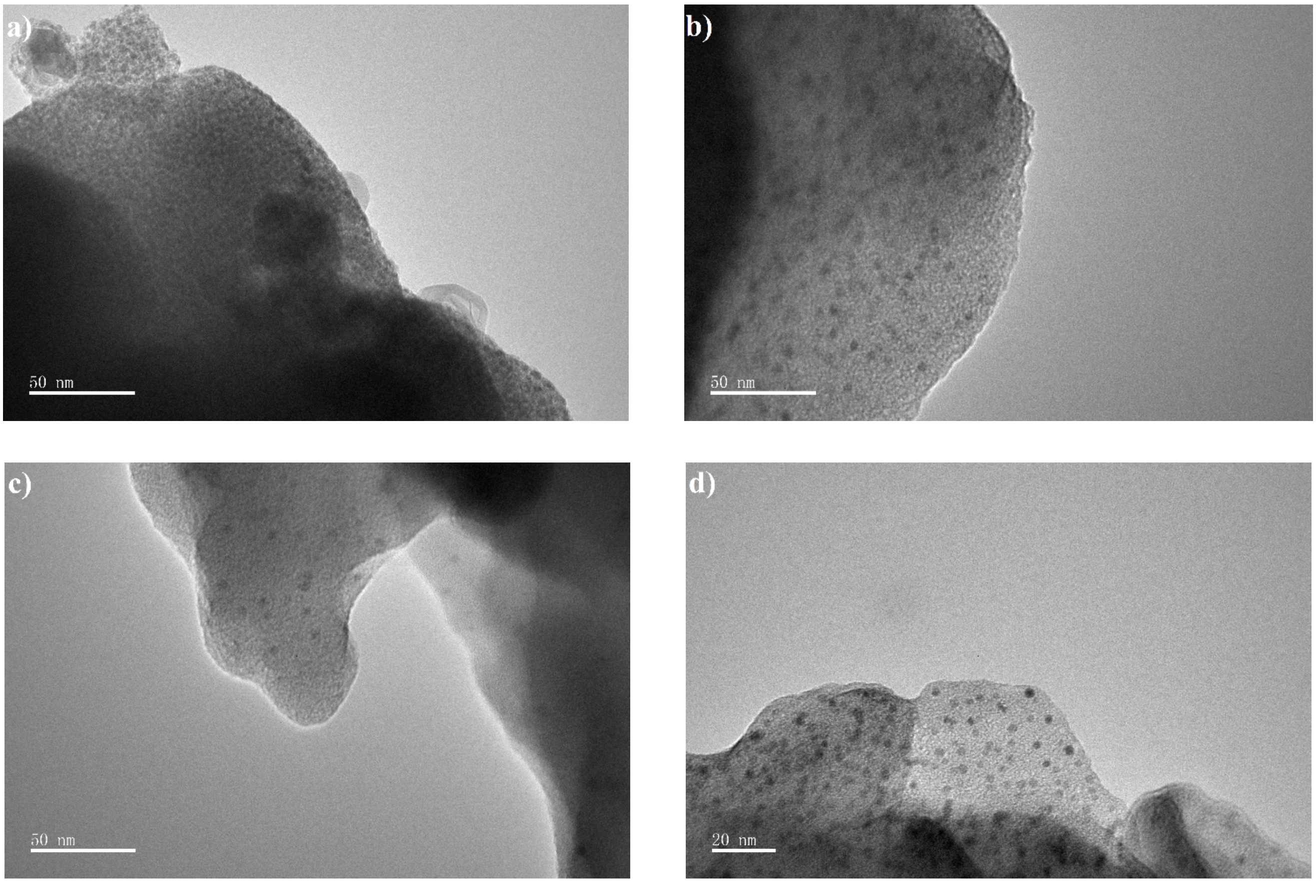


Figure S14. TEM images of COFs recycled after 5 h reaction (a) TT-Ph_1, (b) TT-Ph_2, (c) TT-Ph_3 and (d) TB-Ph_1.

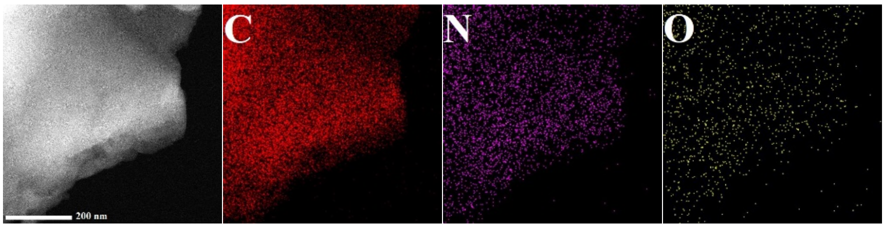


Figure S15. TEM and EDX mapping of TT-Ph_3 before reaction. Mass of the elements: C 96.73 %, N 2.34 %, O 0.93%, Ni not detected.

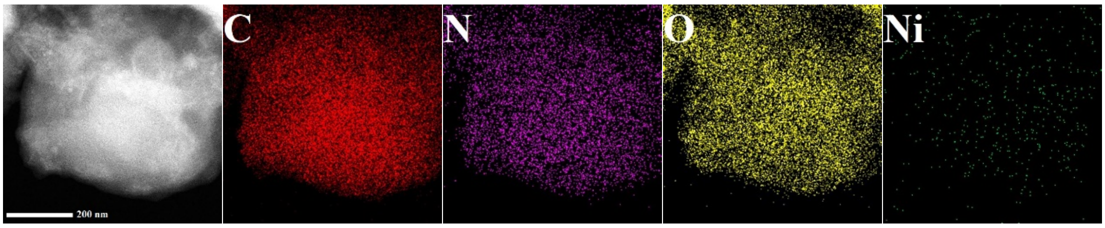


Figure S16. TEM and EDX mapping of TT-Ph_3 after reaction. Mass of the elements: C 80.70 %, N 2.31 %, O 16.89%, Ni 0.10%.

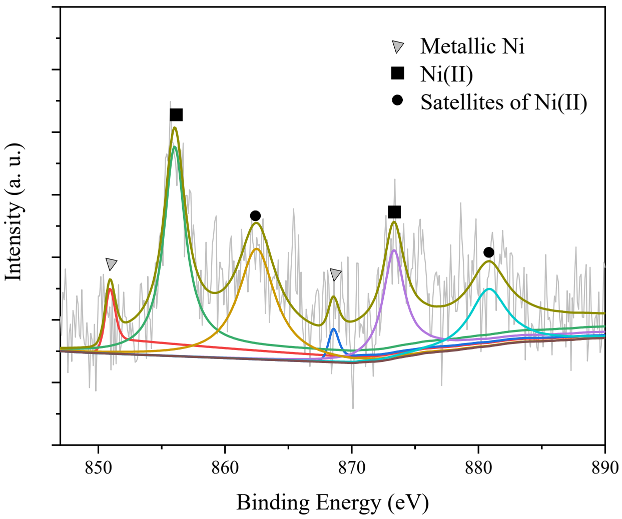


Figure S17. XPS spectra of nickel on TT-Ph$_3$ after photoreaction.

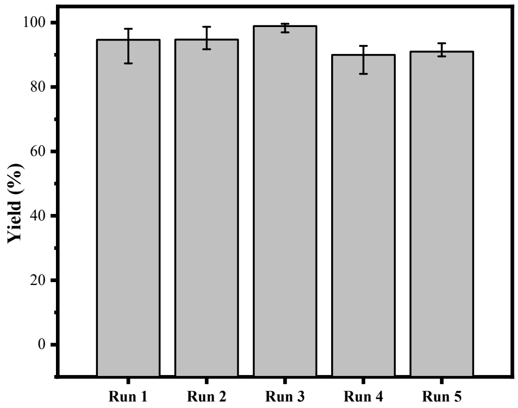


Figure S18. GC yield of 4-methoxybenzonitrile (5 h reaction) in five consecutive runs with recovered TT-Ph$_3$.

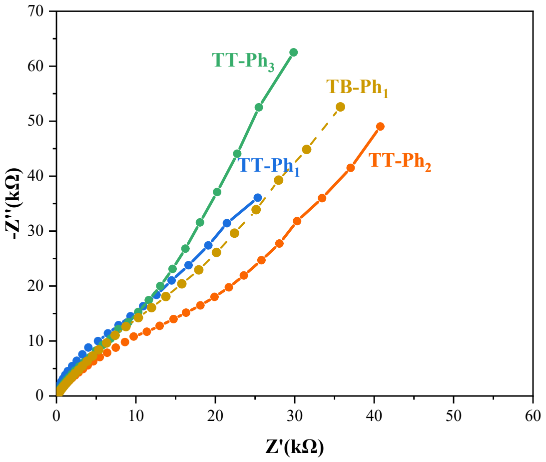
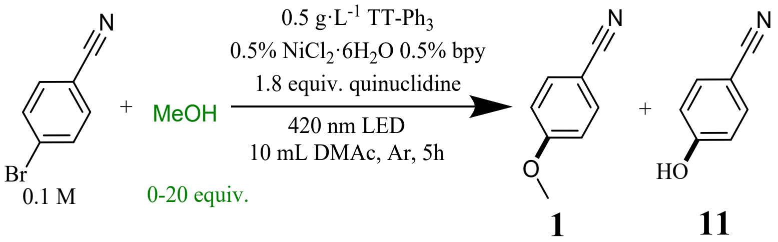


Figure S19. Electrochemical impedance spectroscopy (EIS) of TT-Ph$_{1\text{-}3}$ and TB-Ph$_1$ (0.2 M Na_2SO_4 (pH=6.8) as electrolyte at 0.7 $V_{Ag/AgCl}$) under 420nm LED irradiation.

Table S1. Pawley refinement lattices parameters.

COFs	a	b	c	α	β	γ	R_{wp}	R_p
TT-Ph_1	37.63 Å	37.11 Å	3.39 Å	71.67°	105.62°	122.14°	2.71%	2.21%
TT-Ph_2	44.58 Å	44.61 Å	3.54 Å	85.52°	81.74°	119.97°	3.33%	2.71%
TT-Ph_3	51.89 Å	51.53 Å	3.51 Å	91.72°	89.30°	118.97°	4.80%	3.90%
TB-Ph_1	37.81 Å	37.92 Å	3.63 Å	79.13°	108.87°	120.03°	2.85%	2.26%

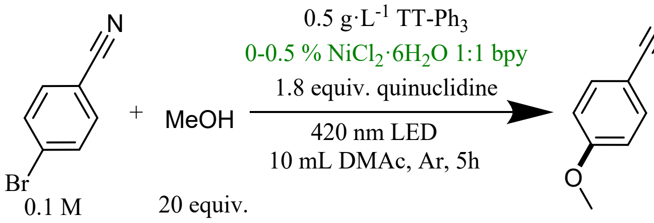
Table S2. GC yield of 4-methoxybenzonitrile with different equivalent of methanol under standard condition.



No.	**MeOH (equiv)**	Conversion (%)	Yield of **1** (%)	Yield of **11** (%)
0[a]	**20**	94	94	n. d.
1	**0**	22.8	0	8.4
2	**1**	38.3	22.1	4.5
3	**2**	48.9	38.5	2.7
4	**5**	72.6	63.7	1.2
5[a]	**10**	79.5	79.5	n. d.

[a] Conversion is reported due to the difficulty in obtaining reasonable yields. Under this condition, **1** is the sole detected product (in addition to the residual substrates).

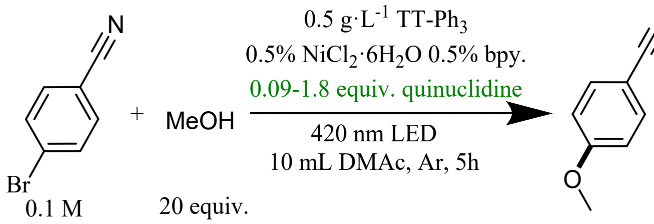
Table S3. GC yield of 4-methoxybenzonitrile with different amount of Ni under standard condition.



Entry	**Ni (equiv)**	Conversion (%)	Yield (%)
0[a]	**0.5%**	94	94
1	**0%**	10.3	0
2	**0.02%**	25.1	21.8
3	**0.05%**	53.6	48.4
4[a]	**0.1%**	62.9	62.9
5[a]	**0.25%**	76.5	76.5

[a] Conversion is reported due to the difficulty in obtaining reasonable yields. Under this condition, **1** is the sole detected product (in addition to the residual substrates).

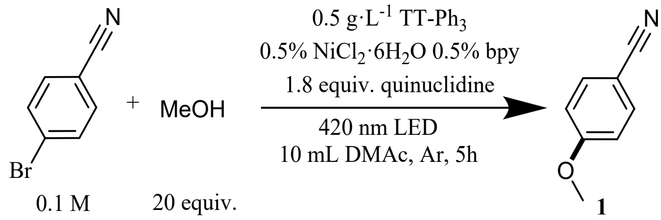
Table S4. GC yield of 4-methoxybenzonitrile with different amount of quinuclidine under standard condition.



Entry	**Quinuclidine (equiv)**	Conversion (%)	Yield (%)
0[a]	**1.8**	94	94
1[a]	**0.9**	67.6	67.6
2	**0.36**	36.1	34.2
3	**0.18**	17.8	15.8
4	**0.09**	8.7	8.2

[a] Conversion is reported due to the difficulty in obtaining reasonable yields. Under this condition, **1** is the sole detected product (in addition to the residual substrates).

Table S5. GC yield of 4-methoxybenzonitrile with other condition variations.

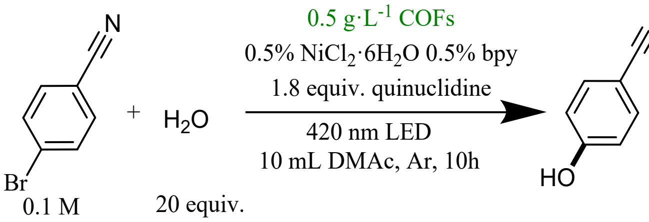


1

No.	Condition variations	Yield (%) of **1**
1	0.2 g L-1 TT-Ph_3	56
2[a]	1 g L-1 TT-Ph_3	70.3
3	MeOH:DMAc 1:1 as solvent	n. d.
4	DMF as solvent	63
5	CH_3CN as solvent	n. d.
6[b]	No Nickel salt	n. d.

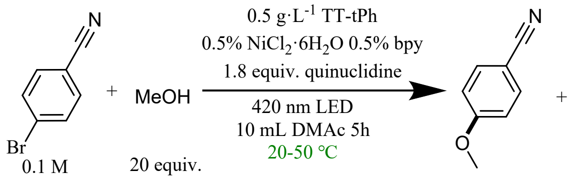
[a] Yield completed 36.2 % in 2 h. [b] TT-Ph_3 used once and recycled.

Table S6.GC Yield of C-O coupling product 4-hydroxybenzonitrile catalyzed by various COFs under standard condition.



No.	**COFs**	Conv. (%)	Yield. (%)
1	**TT-Ph_1**	31.3	28.0
2	**TT-Ph_2**	25.5	23.5
3	**TT-Ph_3**	68.8	61.7
4	**TB-Ph_1**	28.8	25.6

Table S7 GC yield of 4-methoxybenzonitrile at different temperatures with TT-Ph$_3$ at standard conditions.



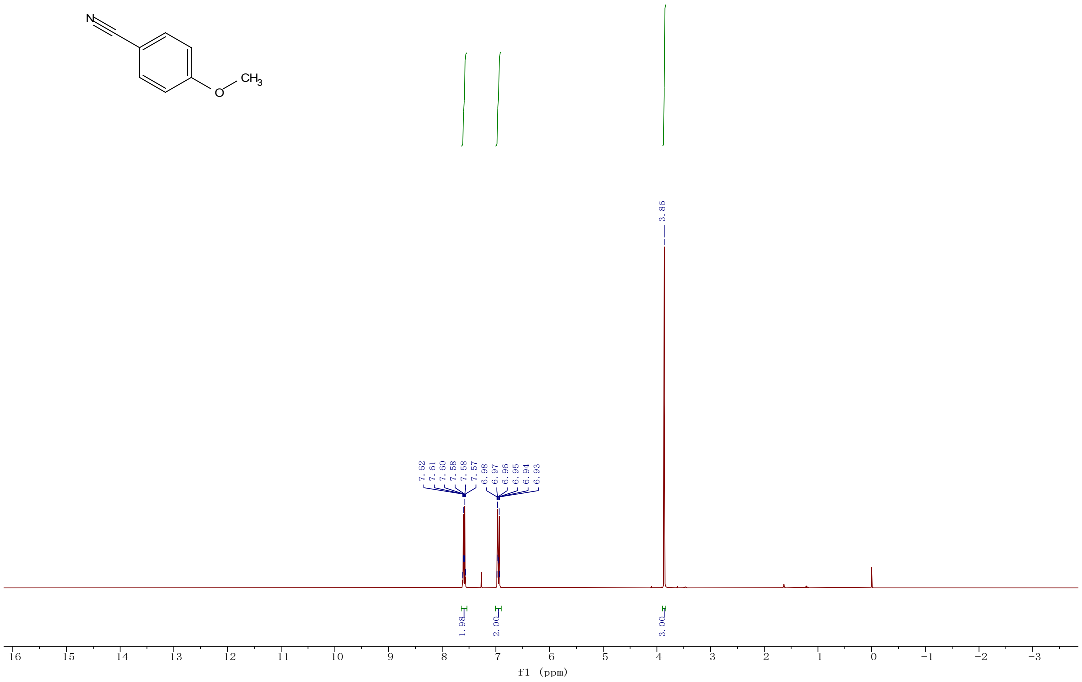
T (°C)	**Yield (%)**
20	47.7
30	82.0
40	99.2
50	>99.9

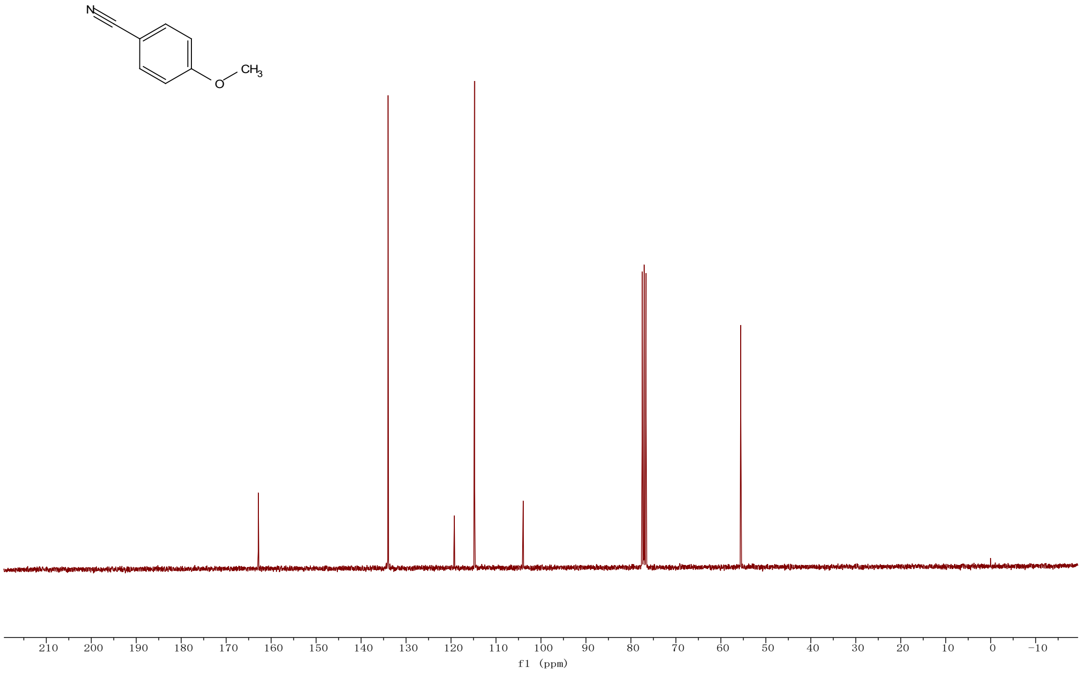
Table S8. Amount of Ni deposited on different COFs after reaction via ICP-OES analysis.

Entry	COFs	Ni(wt.%)	Ni$_{\text{deposited}}$/Ni$_{\text{added}}$ (%)	Ni$_{\text{residual in solution}}$/Ni$_{\text{added}}$ (%)
1	TT-Ph$_1$	0.14	2.39	88.3
2	TT-Ph$_2$	0.07	1.14	90.5
3	TT-Ph$_3$	0.02	0.30	94.1
4	TB-Ph$_1$	0.06	0.99	84.6

Product Analysis

1. 4-Methoxybenzonitrile (white solid, 0.1195 g, isolated yield: **90%**)

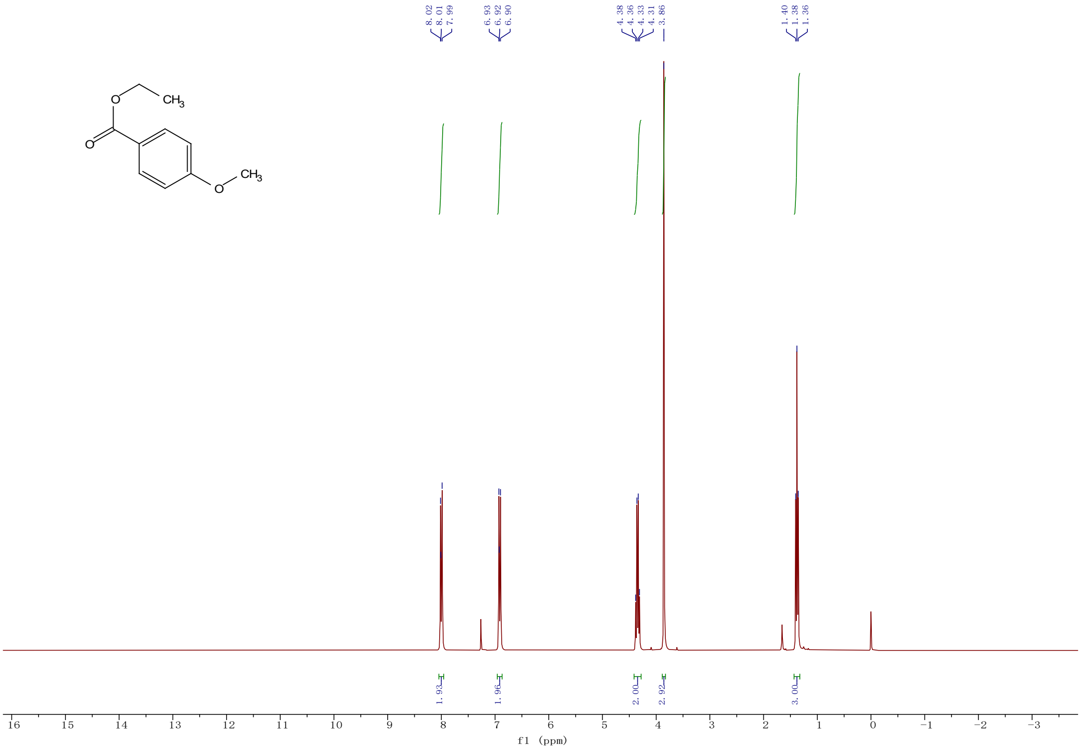


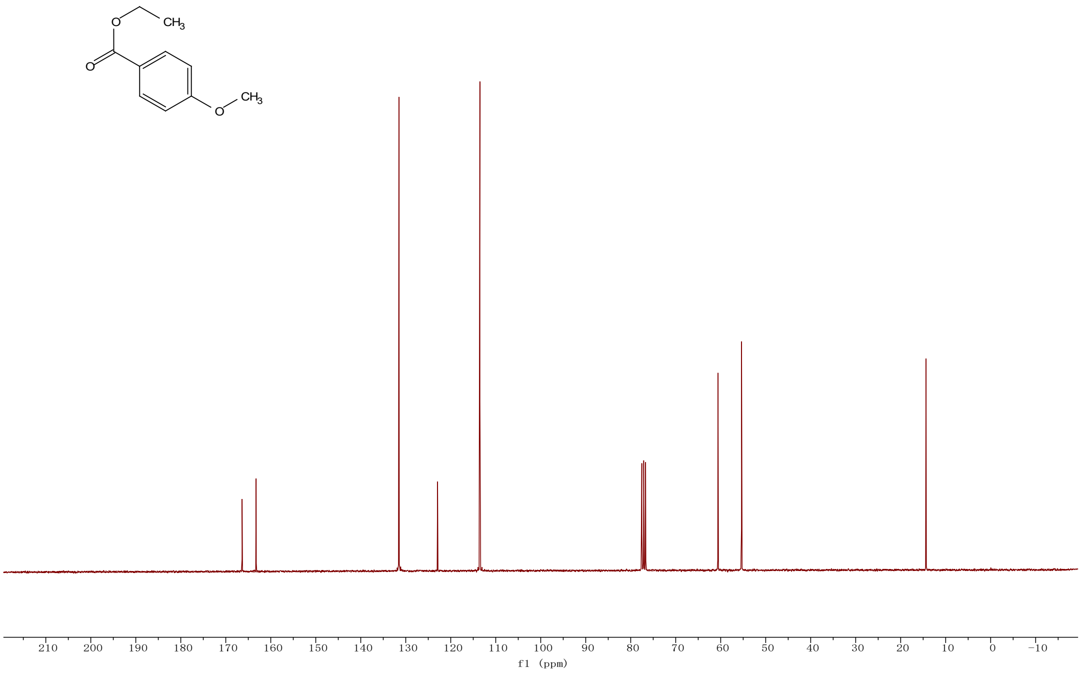


^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.65 – 7.54 (m, 2H), 7.01 – 6.90 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 162.86, 134.00, 119.26, 114.77, 103.96, 55.57.

2. Ethyl 4-methoxybenzoate (yellow liquid, 0.1655 g, isolated yield: **92%**)

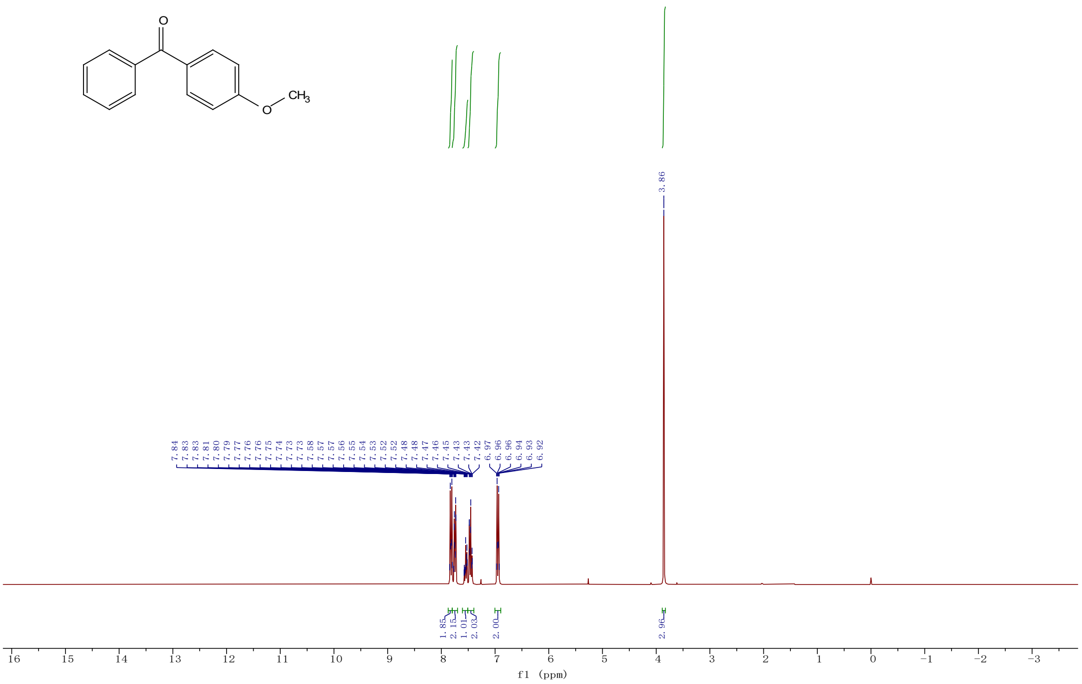


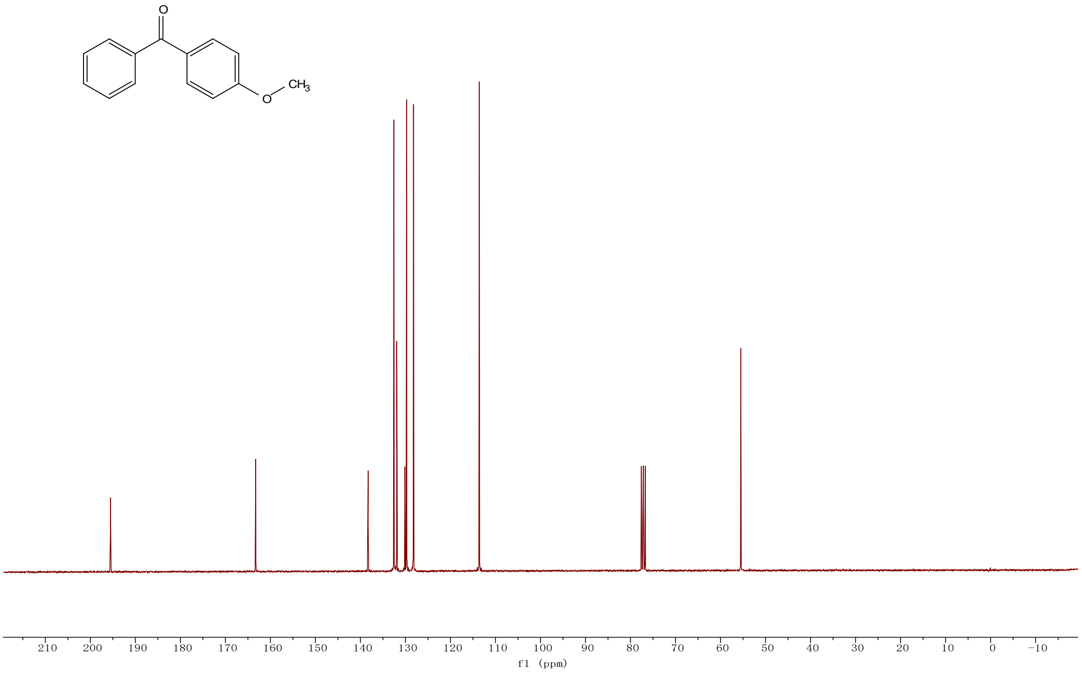


^{1}H NMR (300 MHz, Chloroform-d) δ 8.05 – 7.96 (m, 2H), 6.96 – 6.87 (m, 2H), 4.35 (q, J = 7.1 Hz, 2H), 3.86 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 166.37, 163.25, 131.52, 122.93, 113.53, 60.61, 55.36, 14.37.

3. 4-Methoxybenzophenone (white solid, 0.1879 g, isolated yield: **89%**)

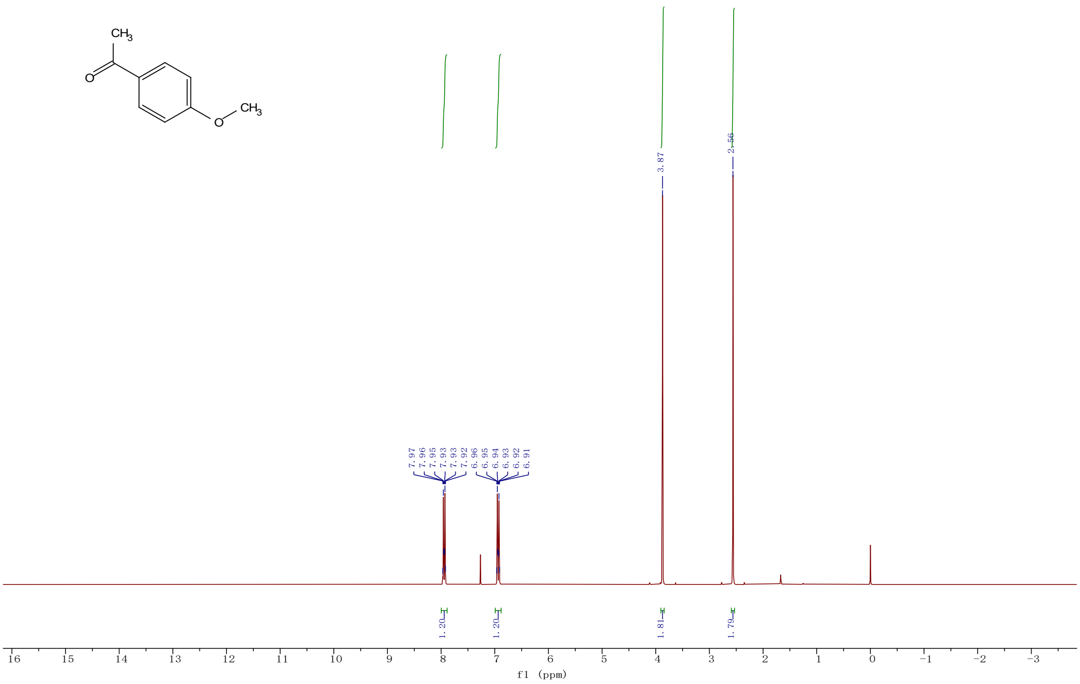


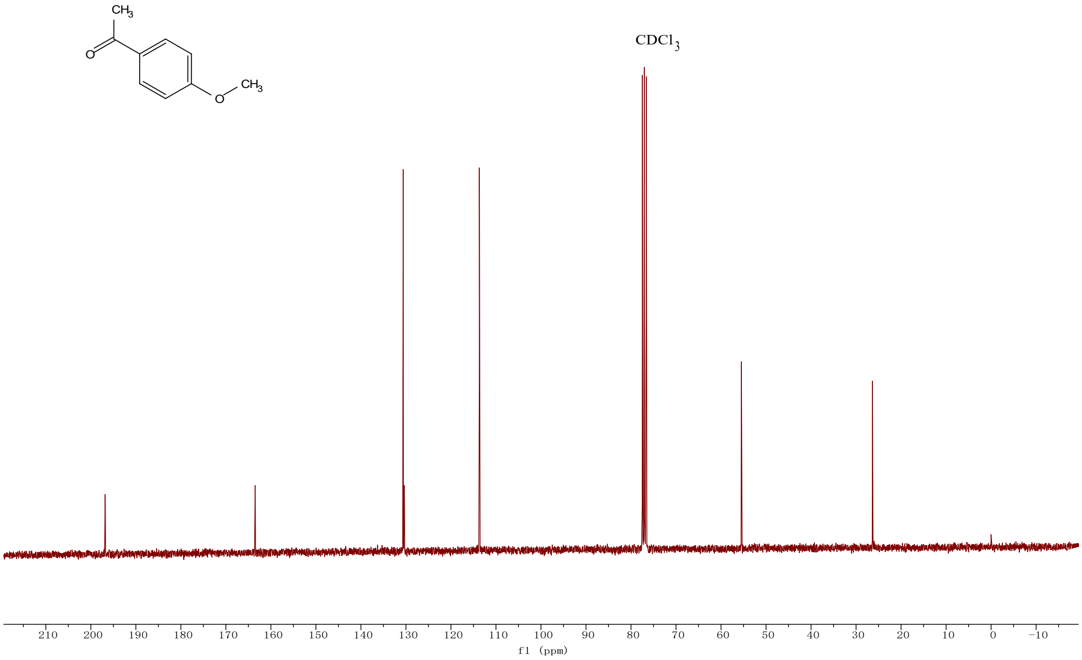


^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.87 – 7.80 (m, 2H), 7.80 – 7.70 (m, 2H), 7.61 – 7.51 (m, 1H), 7.51 – 7.39 (m, 2H), 7.00 – 6.89 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 195.53, 163.25, 138.29, 132.57, 131.92, 130.12, 129.73, 128.22, 113.59, 55.50.

4. 4'-Methoxyacetophenone (white solid, 0.1216 g, isolated yield: **81%**)

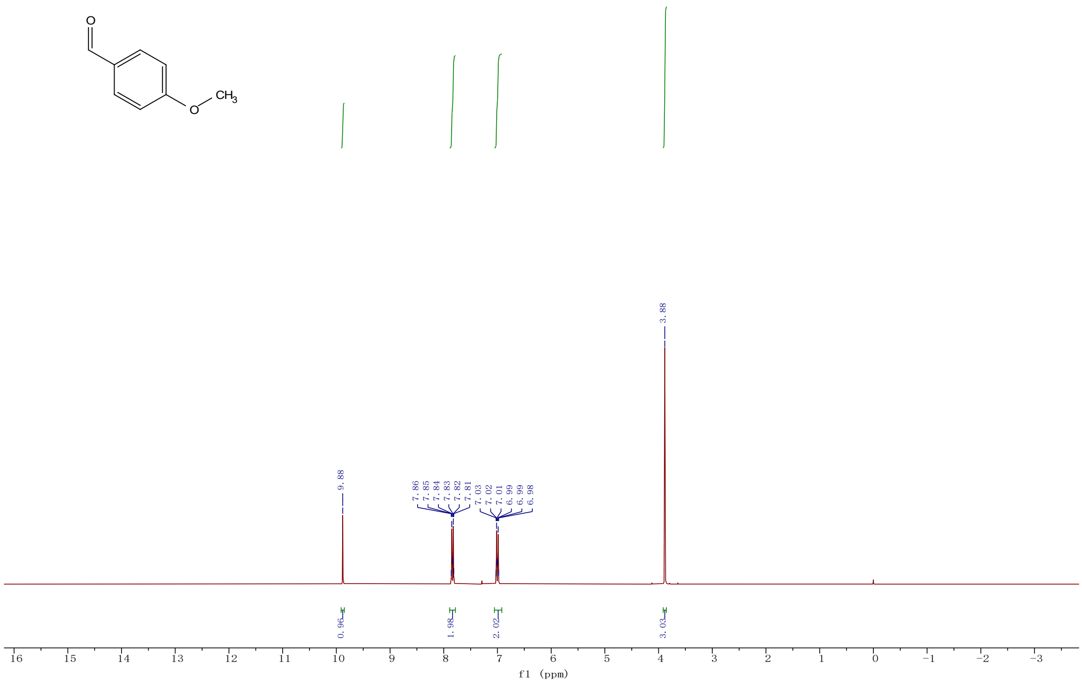


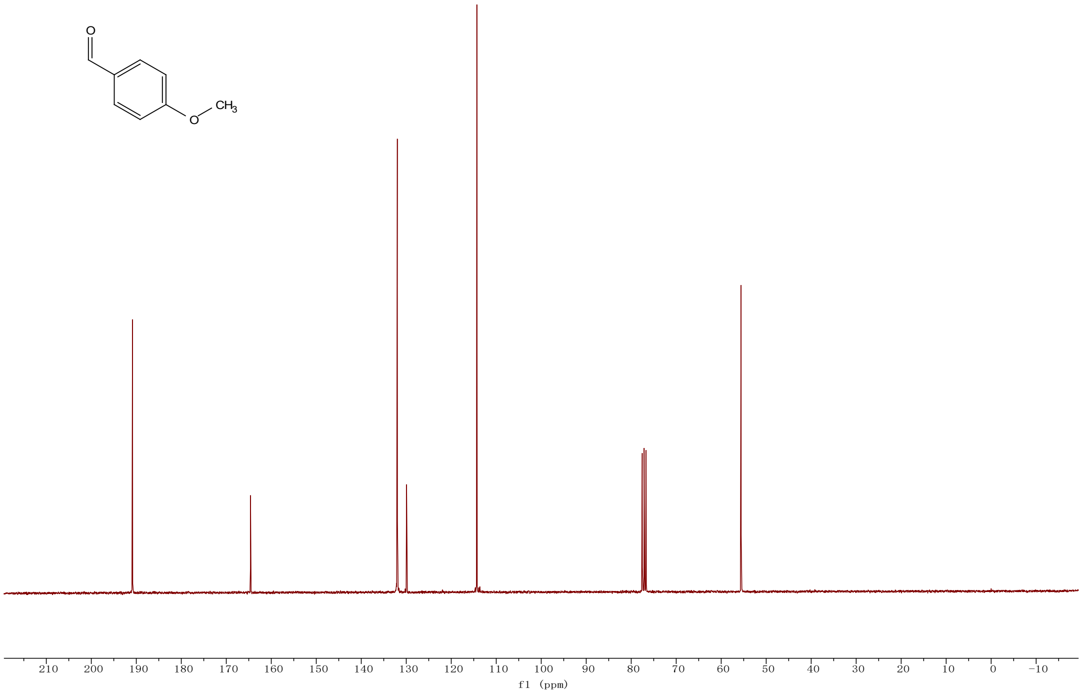


^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.00 – 7.89 (m, 1H), 6.99 – 6.88 (m, 1H), 3.87 (s, 2H), 2.56 (s, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 196.82, 163.49, 130.61, 130.35, 113.69, 55.48, 26.37.

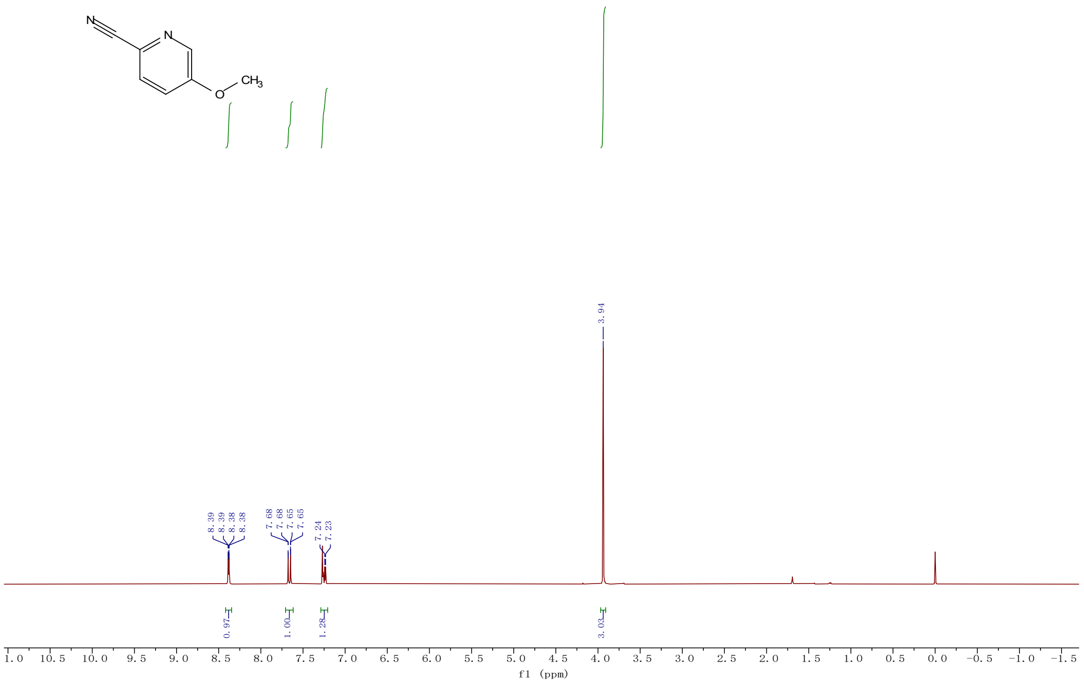
5. 4-Methoxybenzaldehyde (transparency liquid, 0.1059 g, isolated yield: **78%**)

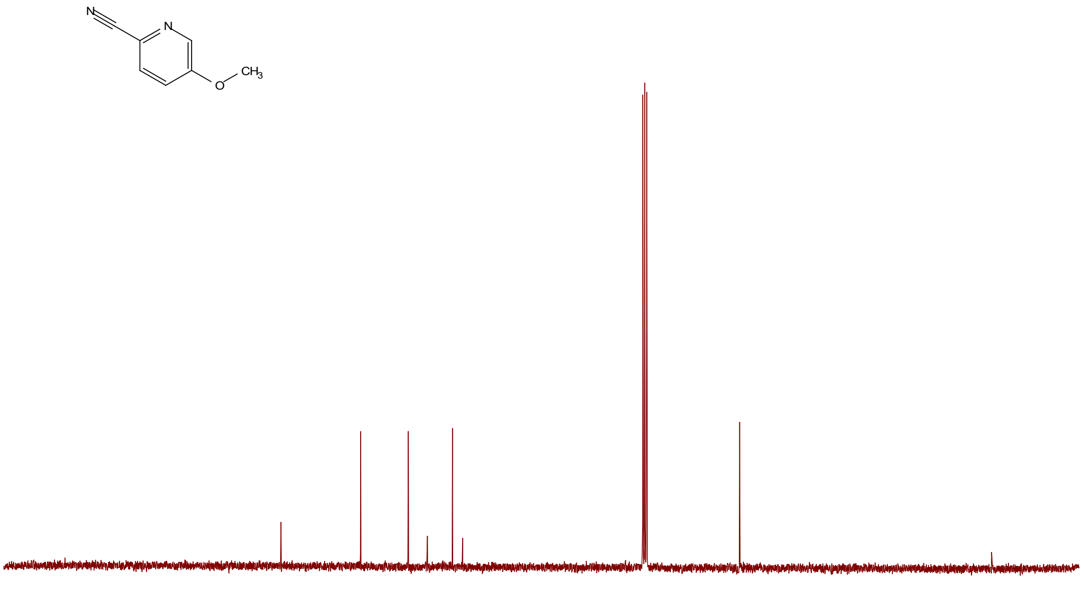




^{1}H NMR (300 MHz, Chloroform-*d*) δ 9.88 (s, 1H), 7.89 – 7.78 (m, 2H), 7.06 – 6.92 (m, 2H), 3.88 (s, 3H).
^{13}C NMR (75 MHz, Chloroform-*d*) δ 190.84, 164.62, 131.98, 129.93, 114.32, 55.58.

6. 5-Methoxypyridine-2-carbonitrile (white solid, 0.0686 g, isolated yield: **62%**)

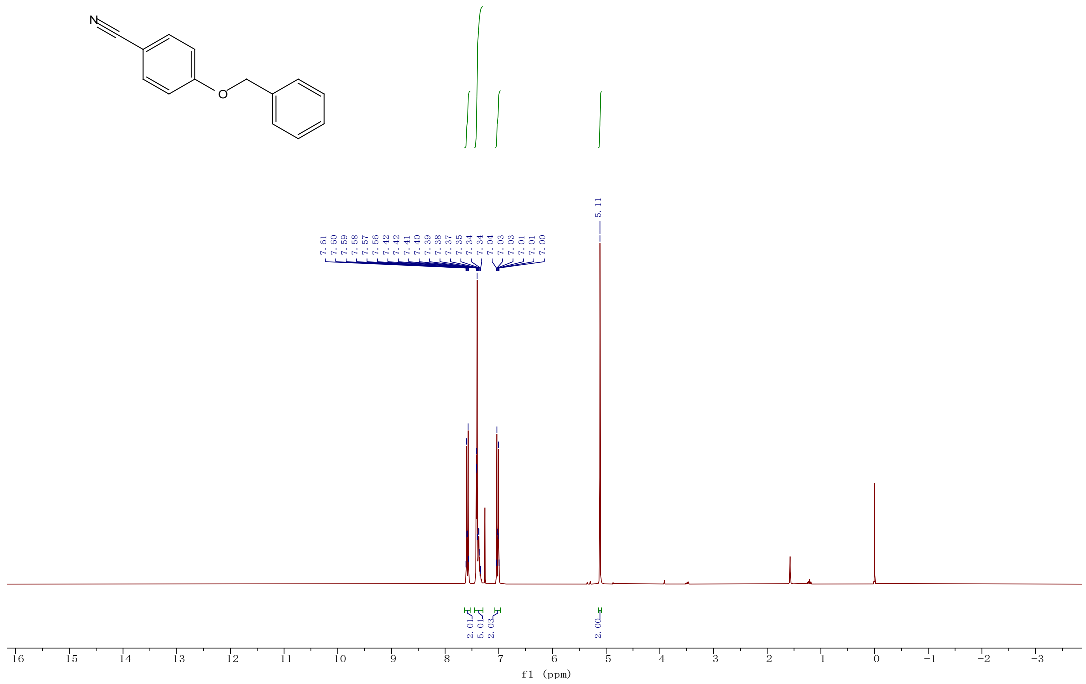


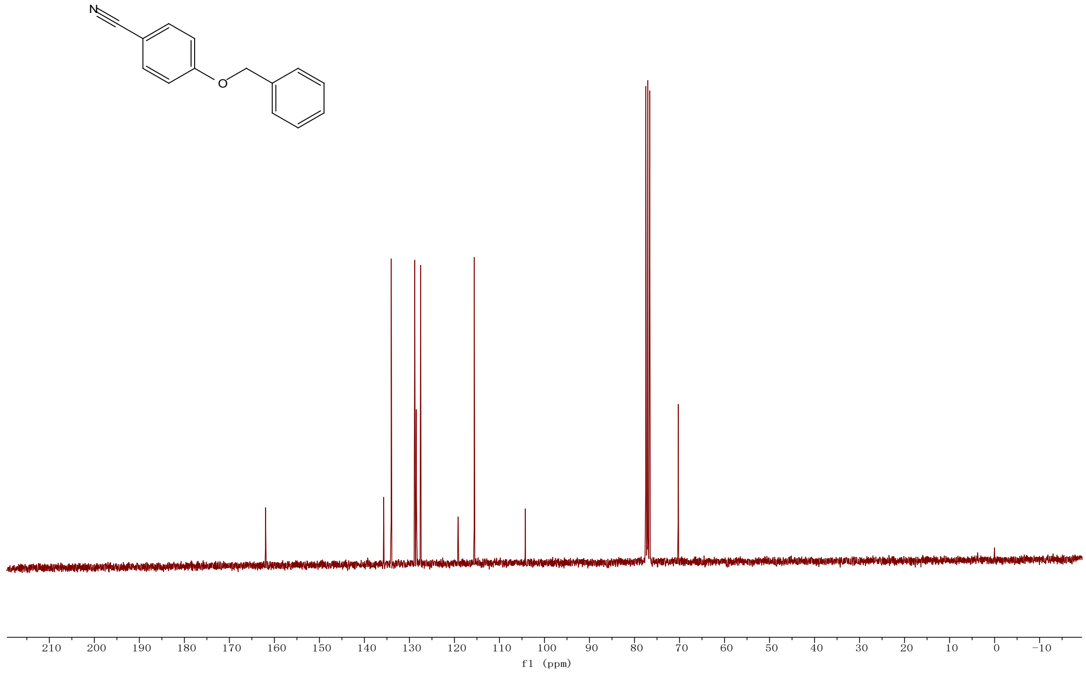


^{1}H NMR (300 MHz, Chloroform-*d*) δ 8.42 – 8.35 (m, 1H), 7.66 (dd, *J* = 8.6, 0.7 Hz, 1H), 7.24 (d, *J* = 2.9 Hz, 1H), 3.94 (s, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 157.89, 140.16, 129.58, 125.33, 119.76, 117.52, 55.98.

7. 4-Benzyloxybenzonitrile (white solid, 0.1939 g, isolated yield: **93%**)

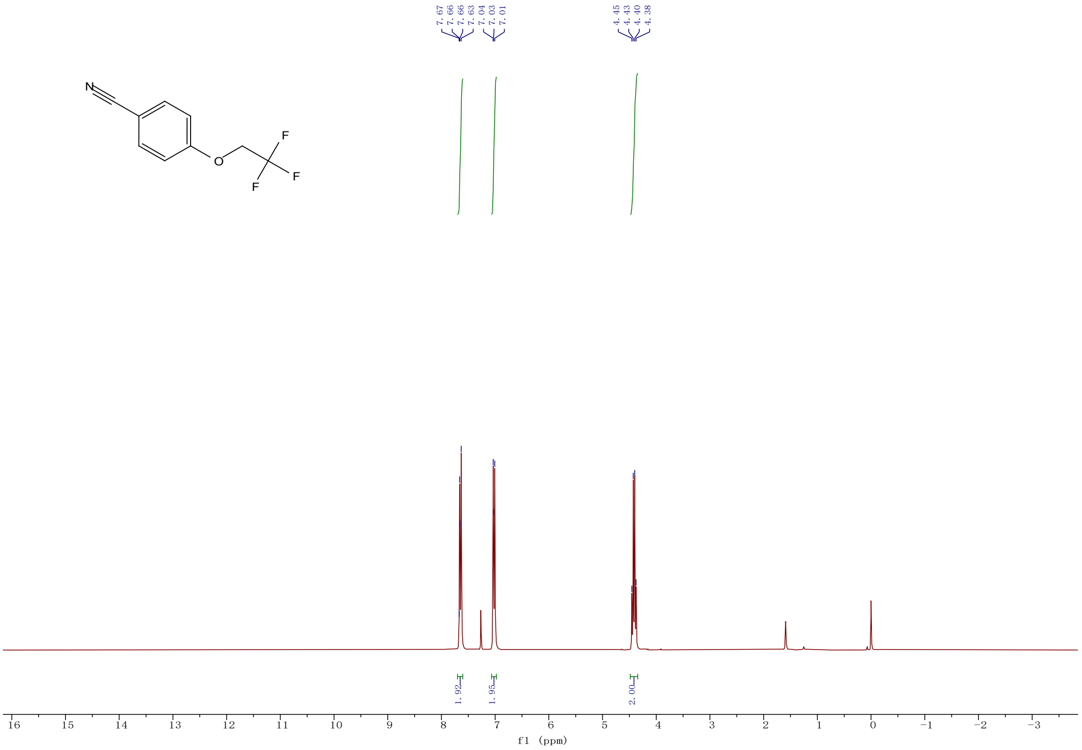


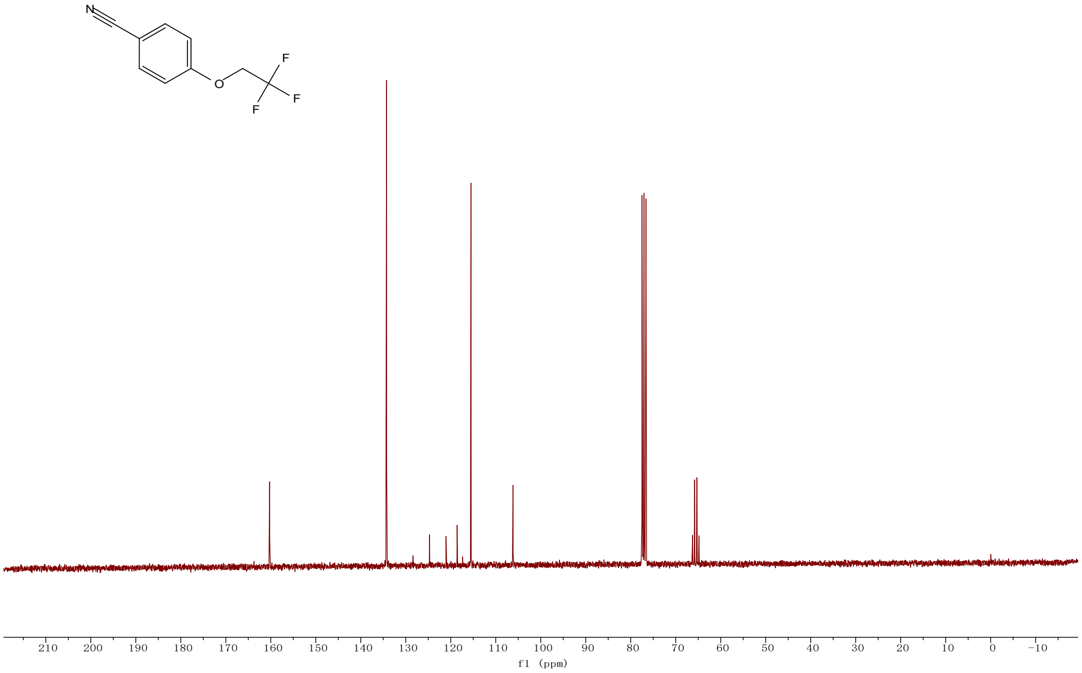


^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.64 – 7.53 (m, 2H), 7.45 – 7.30 (m, 5H), 7.07 – 6.97 (m, 2H), 5.11 (s, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 161.98, 135.71, 134.05, 128.80, 128.45, 127.50, 119.20, 115.61, 104.24, 70.30.

8. 4-(2,2,2-Trifluoroethoxy)benzonitrile (pale-yellow solid, 0.1776 g, isolated yield: **88%**)

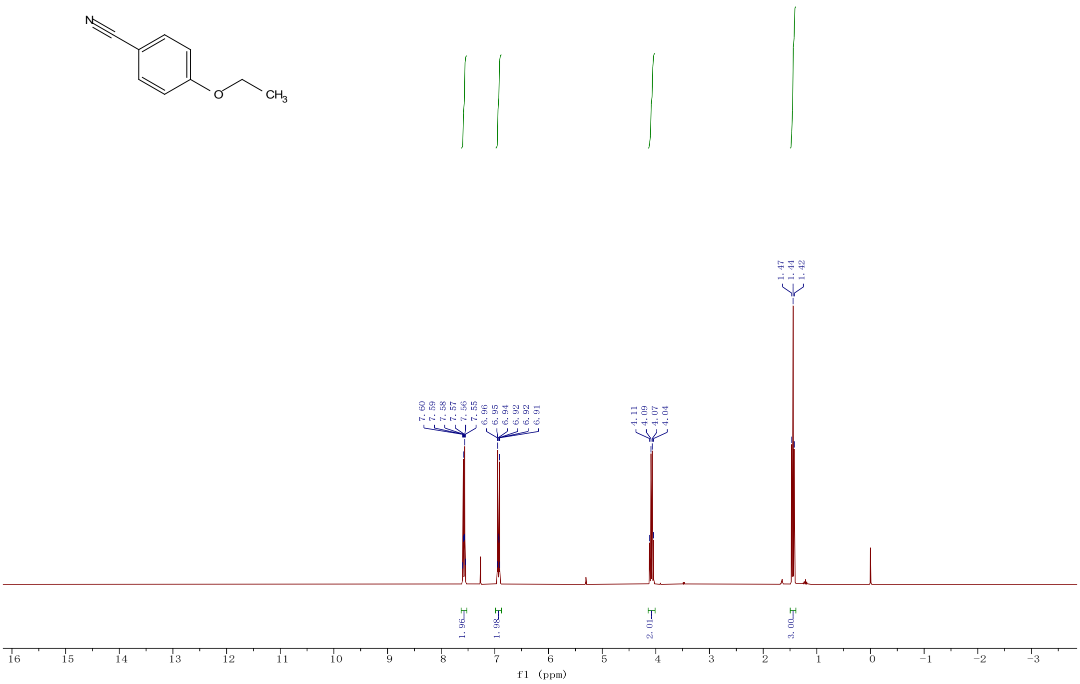


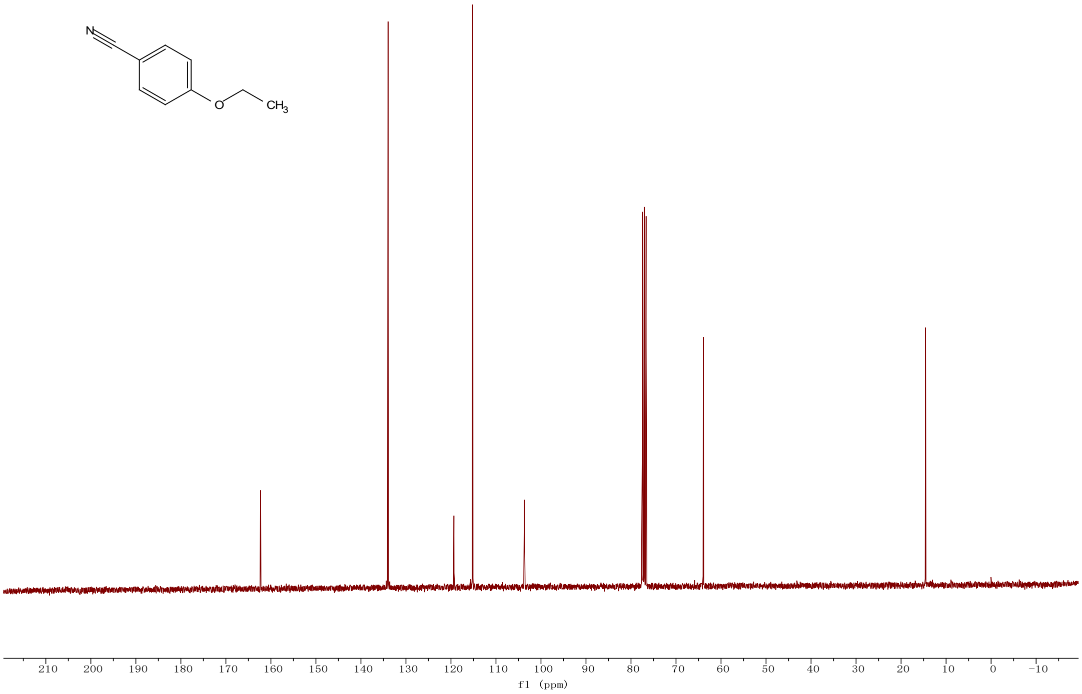


^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.70 – 7.60 (m, 2H), 7.07 – 6.98 (m, 2H), 4.41 (q, *J* = 7.8 Hz, 2H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 160.24, 134.26, 124.72, 118.57, 115.52, 106.16, 66.27 – 64.83.

9. 4-Ethoxybenzonitrile (white solid, 0.1300 g, isolated yield: **89%**)

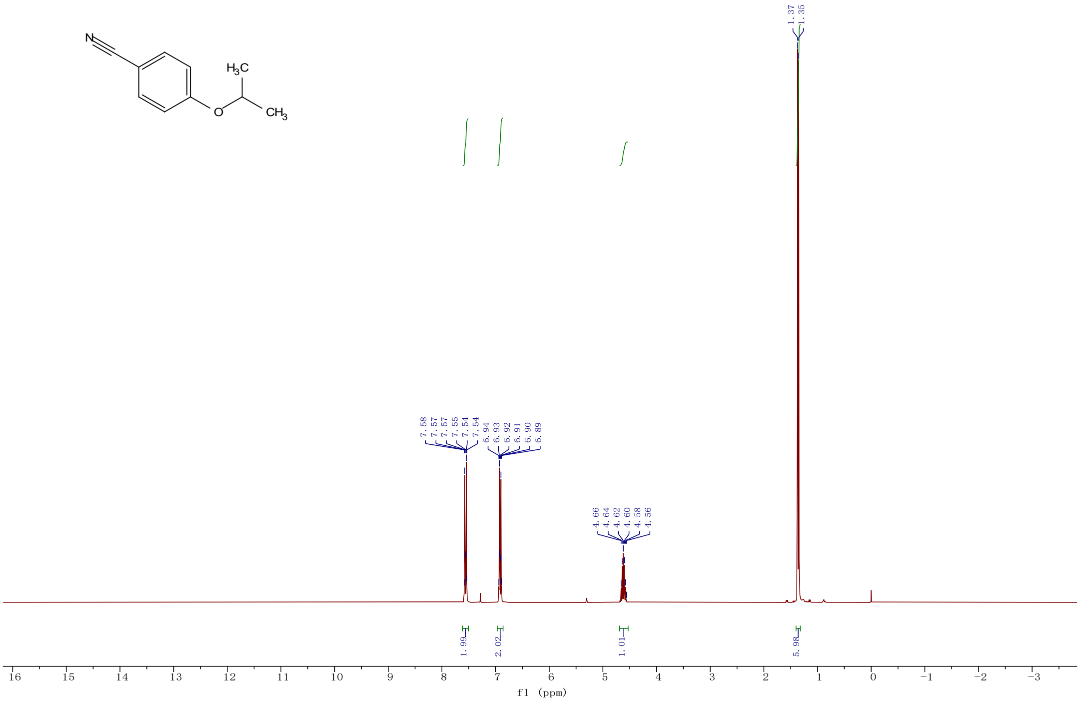


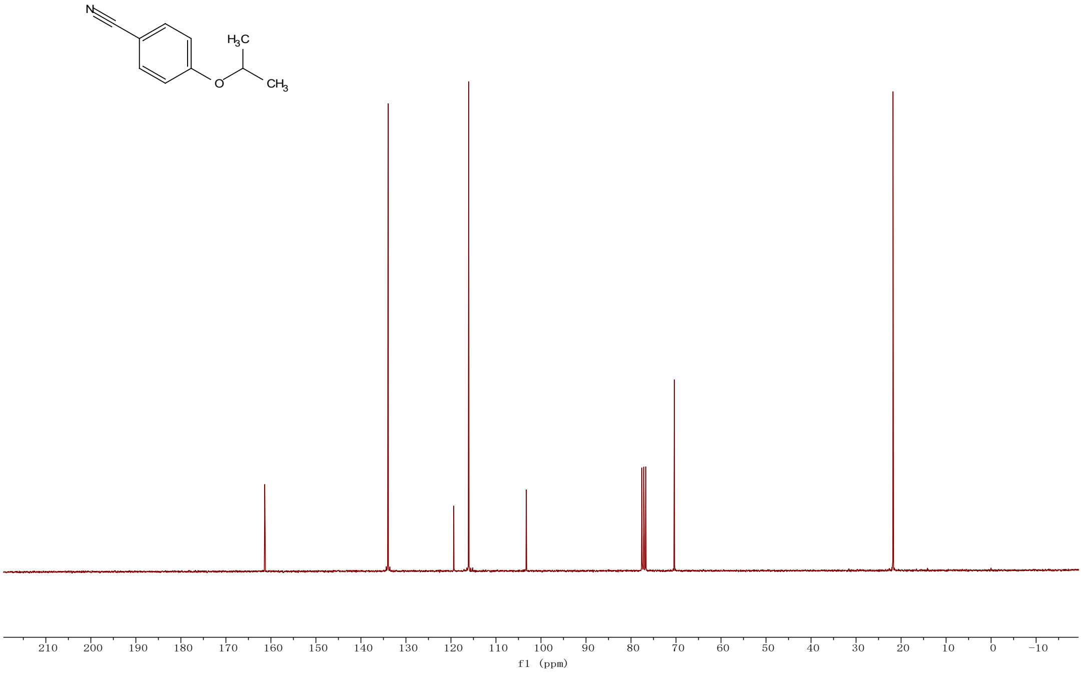


^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.63 – 7.52 (m, 2H), 6.99 – 6.88 (m, 2H), 4.08 (q, *J* = 7.0 Hz, 2H), 1.44 (t, *J* = 7.0 Hz, 3H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 162.27, 133.98, 119.34, 115.16, 103.68, 63.94, 14.58.

10. 4-Isopropoxybenzonitrile (white solid, 0.0994 g, isolated yield: **62%**)





^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.61 – 7.51 (m, 2H), 6.97 – 6.86 (m, 2H), 4.61 (h, *J* = 6.1 Hz, 1H), 1.36 (d, *J* = 6.1 Hz, 6H).

^{13}C NMR (75 MHz, Chloroform-*d*) δ 161.36, 133.97, 119.37, 116.06, 103.28, 70.38, 21.78.