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Supporting Information

Palladium/phosphorus-functionalized porous organic polymer with tunable surface wettability for water-mediated Suzuki–Miyaura coupling reaction

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Characterization

Nitrogen sorption isotherms were performed by a Micrometrics ASAP 2020 system at 77 K, and the catalysts were pre-treated under vacuum at 90 °C for 12 h before the measurements. The surface area was calculated by using the Brunauer-Emmett-Teller (BET) method. The pore size distribution was calculated by the nonlocal density functional theory (NLDFT) method. Fourier Transform Infrared Spectroscopy (FT-IR) was recorded on a Bruker Equinox 55 FT-IR spectrophotometer using KBr pellet technique, over a range of 4000-400 cm^{-1} at 2 cm^{-1} resolution. The thermogravimetric analysis (TG) was measured on a NETZSCH STA 449 F5 instrument under a dynamic argon atmosphere, and the sample was analyzed from room temperature to 600 °C with a heating rate of 10 $K{\cdot}min^{-1}$. The contents of Pd loading and leaching were analyzed by the inductively coupled plasma atomic emission spectroscopy (ICP, PerkinElmer Optima 8000). The size and morphology of the catalyst was observed with a Hitachi S-4800 scanning electron microscope (SEM) operated at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) was measured on a FEI Tecnai G2 F30 instrument. X-ray photoelectron spectroscopy (XPS) was carried out on a VG multilab 2000 spectrometer using a Mg-Al_{Ka} X-ray source, and the C_{1s} transition was adjusted to 284.8 eV. The CHNO elemental analysis was performed on an Elementar Vario MICRO Elemental analyzer, and the samples were pre-treated under vacuum at 90 °C for 12 h before the measurements. The amount of P species in the compound was determined by ICP-OES technique, before measurement, the sample was combusted in an oxygen bomb calorimeter and then dissolved in water for analysis. The contact angles were measured on a Dataphysics OCA20 contact angle system. ^{1}H spectra were recorded on a Bruker AVANCE III NMR spectrometer (400 and 100 MHz) at ambient temperature. Solid-state ^{13}C NMR and ^{31}P NMR spectra were carried out on a Bruker AVANCE III 600 Bruker spectrometer. Gas chromatography (GC) was carried out on a Scientific™ TRACE™ 1310 equipped with a TRACE TR- 5MS capillary column and a FID.

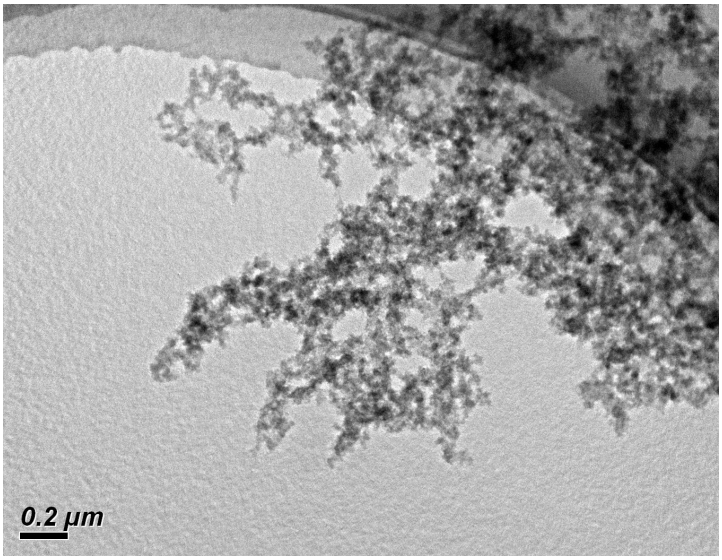


Fig. S1 TEM image of PTVP-MBA-0.4.

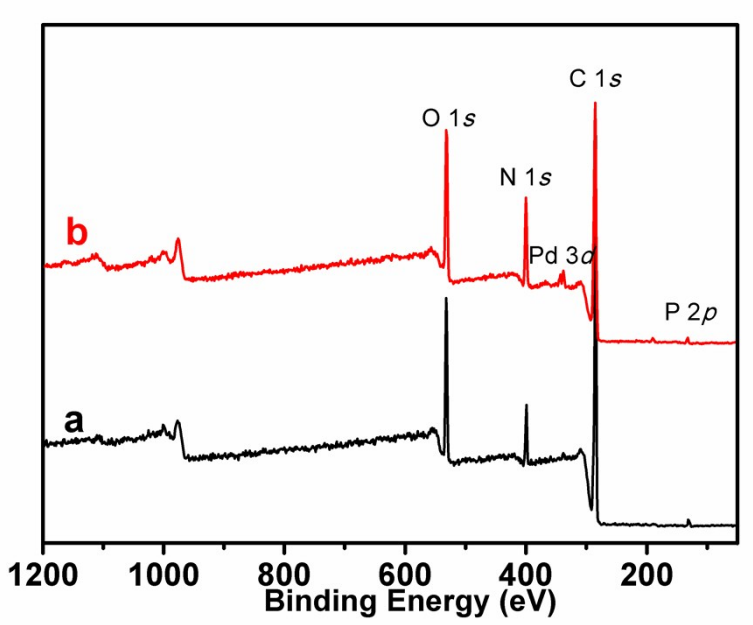


Fig. S2 XPS spectra of PTVP-MBA-0.4 (a) and Pd^{II}@PTVP-MBA-0.4 (b).

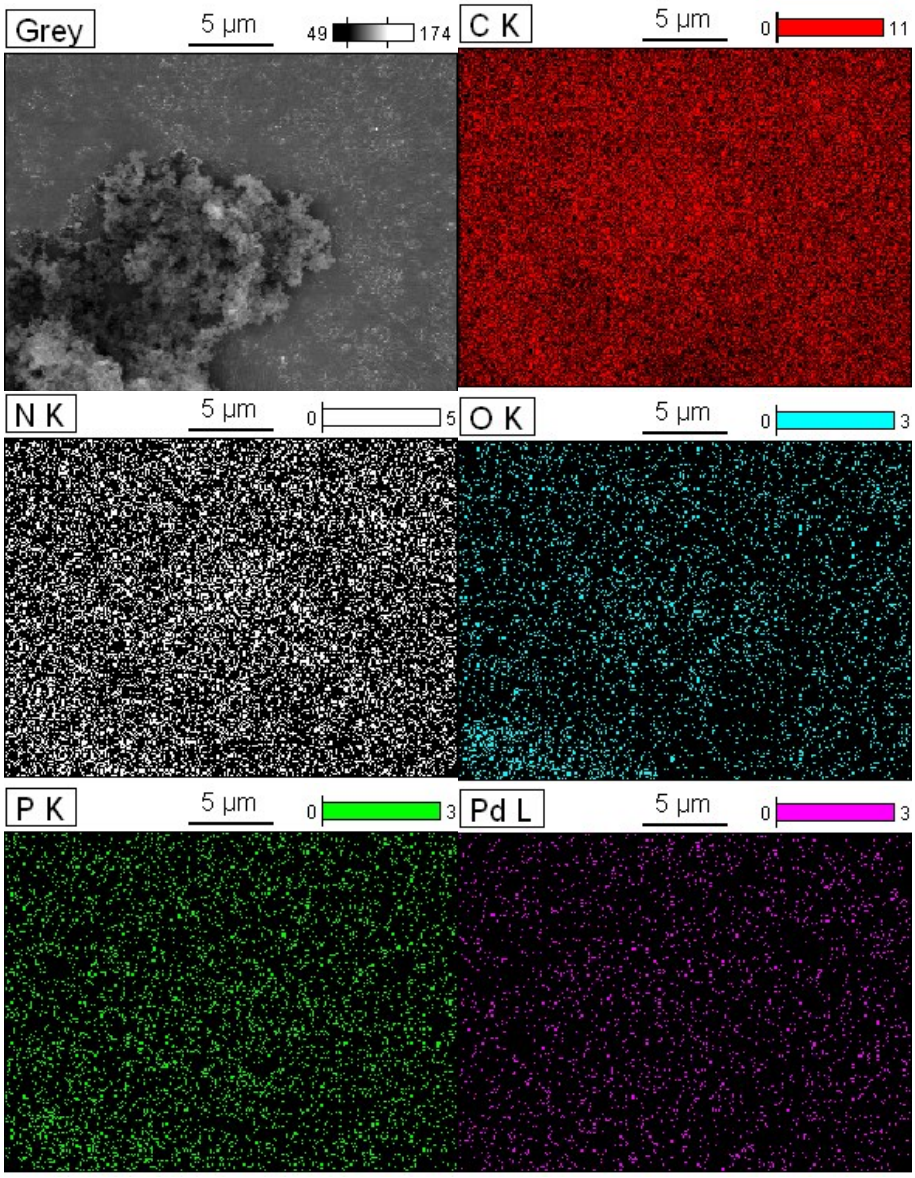


Fig. S3 SEM-Mapping images for Pd^{II}@PTVP-MBA-0.4.

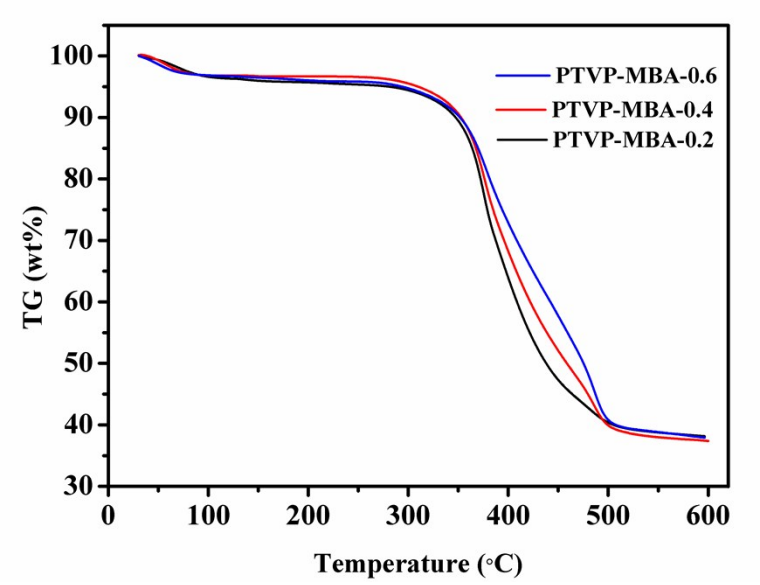


Fig. S4 TGA curves of PTVP-MBA-0.2, PTVP-MBA-0.4 and PTVP-MBA-0.6.

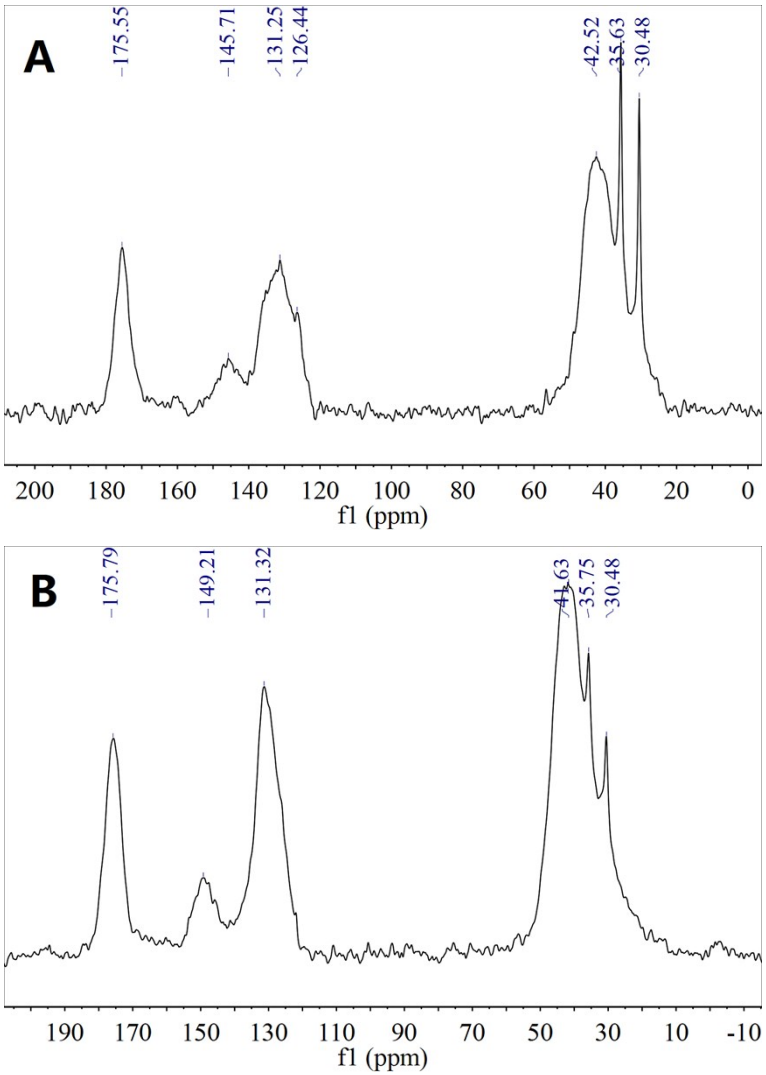


Fig. S5 The solid-state ^{13}C CP/MAS spectra of PTVP-MBA-0.4 (A) and Pd^{II}@PTVP-MBA-0.4 (B).

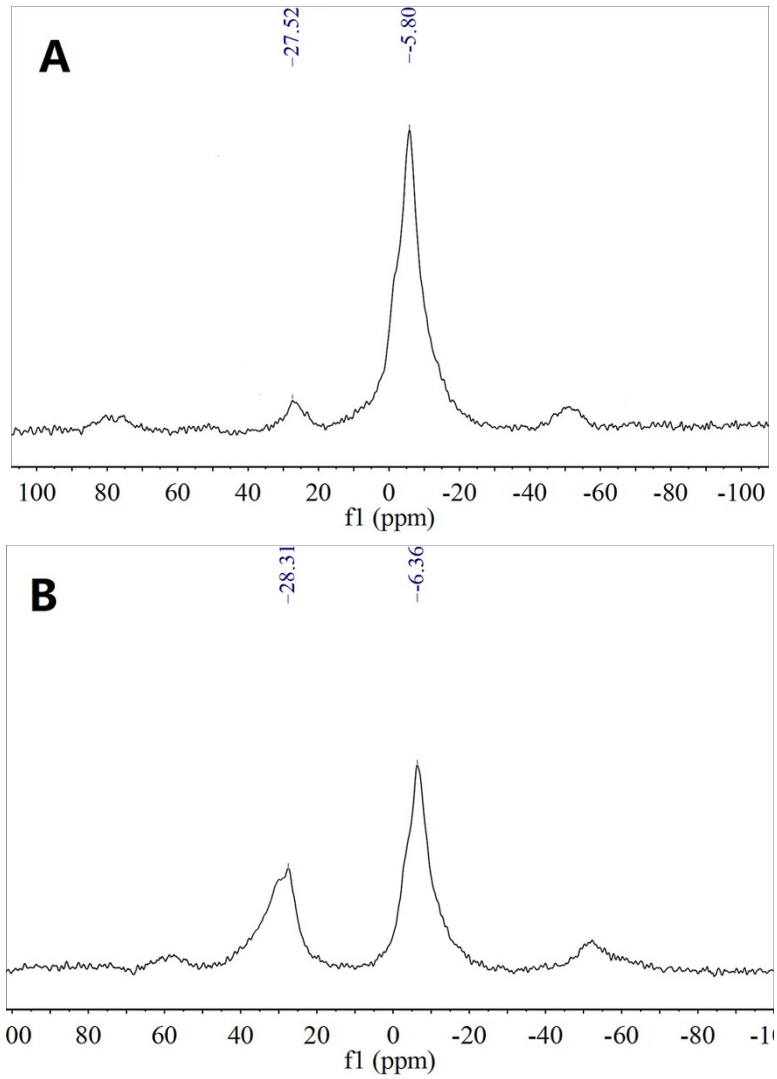


Fig. S6 ^{31}P CP/MAS of PTVP-MBA-0.4 (A) and Pd^{II}@PTVP-MBA-0.4 (B).

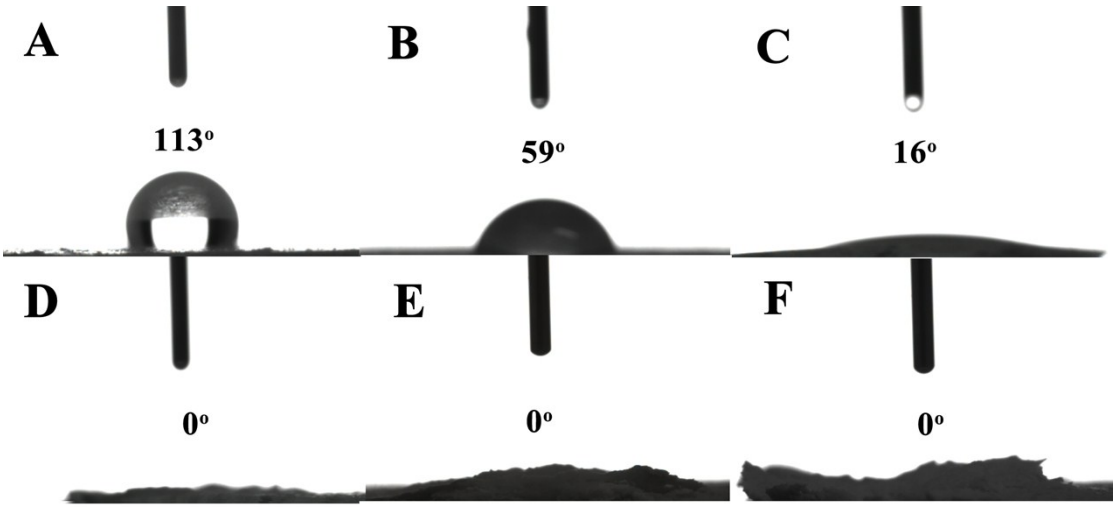


Fig. S7 Contact angle measurements of the prepared Pd^{II}@PTVP-MBA-x catalysts for water droplets: (A) x=1.0, (B) x=0.8, (C) x=0.6, (D) x=0.5, (E) x=0.4, (F) x=0.2.

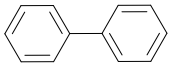
Table S1 Palladium contents of the prepared catalysts by ICP-AES.

Catalyst	Pd^{II}@PTVP-MBA-0.2	Pd^{II}@PTVP-MBA-0.3	Pd^{II}@PTVP-MBA-0.4	Pd^{II}@PTVP-MBA-0.5	Pd^{II}@PTVP-MBA-0.6	Pd^{II}@PTVP-MBA-0.8	Pd^{II}@POL-PPh_3
Pd (wt%)	1.95	1.98	1.97	2.01	1.99	1.98	2.04

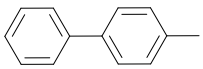
Table S2 Elemental analysis.

Element	PTVP-MBA-0.2	PTVP-MBA-0.3	PTVP-MBA-0.4	PTVP-MBA-0.5	PTVP-MBA-0.6	PTVP-MBA-0.8	POL-PPh_3
C (wt%)	59.7	63.2	65.7	68.4	72.0	77.8	84.3
H (wt%)	6.6	6.5	6.5	6.4	6.5	6.3	6.2
N (wt%)	14.3	12.4	10.6	8.9	7.1	3.5	0
O (wt%)	16.8	14.9	12.6	10.7	8.5	4.2	0.2
P (wt%)	1.7	2.8	3.3	4.5	5.3	7.4	9.1

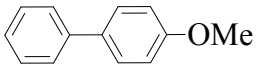
^{1}H NMR data for the products



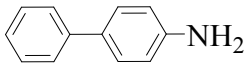
Biphenyl[1], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.65-7.62 (m, 4 H), 7.45-7.40 (m, 4 H), 7.40-7.36 (m, 2 H).



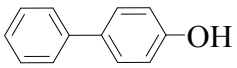
4-Methylbipheny[1], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.67-7.60 (2 H, m), 7.59-7.52 (2 H, m), 7.51 -7.43 (2 H, m), 7.41-7.33 (1 H, m), 7.33-7.27 (2 H, m), 2.44 (3 H, s).



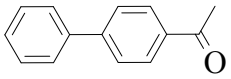
4-Methoxybiphenyl[1], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.62 -7.52 (4 H, m), 7.48-7.39 (2 H, m), 7.36-7.30 (1 H, m), 7.04-6.98 (2 H, m), 3.89 (3 H, s) ppm.



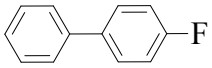
4-Aminobiphenyl[2], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.57-7.55 (m, 2H), 7.45-7.40 (m, 4H), 7.31-7.27 (m, 1H), 6.79-6.77 (m, 2H), 3.74 (s, 2H) ppm.



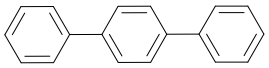
4-Phenylphenol[1], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.56-7.30 (m, 7 H), 6.90 (d, *J* = 8.5, 2 H), 4.90 (s, 1H) ppm.



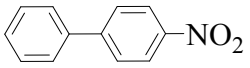
4-Acetylbiphenyl[1], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.02 (d, *J* = 8.7 Hz, 2H), 7.69-7.39 (m, 6H), 2.63 (s, 3H) ppm.



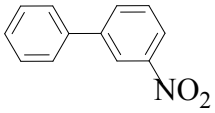
4-Fluorobiphenyl[1], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.66-7.50 (m, 4 H), 7.52-7.43 (m, 2 H), 7.42-7.32 (m, 1 H), 7.22-7.10 (m, 2 H) ppm.



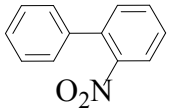
4-Phenylbiphenyl[1], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.73-7.66 (m, 8 H), 7.56-7.44 (m, 4 H), 7.45-7.36 (m, 2 H) ppm.



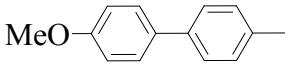
4-Nitrobiphenyl[1], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.32-8.28 (m, 2H), 7.76-7.72 (m, 2H), 7.64-7.60 (m, 2H), 7.52-7.43 (m, 3H) ppm.



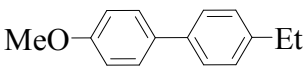
3-Nitrobiphenyl[3], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 8.45 (s, 1 H), 8.20-8.18 (m, 1 H), 7.92 (dq, *J* = 7.7 Hz, 1.0 Hz, 1 H), 7.68-7.57 (m, 3 H), 7.53-7.48 (m, 3 H) ppm.



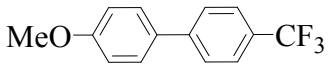
2-Nitrobiphenyl[4], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.90 (d, *J* = 8.2 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1 H), 7.55-7.44 (m, 5 H), 7.39 (dd, *J* = 7.5 Hz, 2.1 Hz, 2 H) ppm.



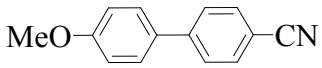
4-Methoxy-4'-methylbiphenyl[5], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.56-7.53 (m, 2H), 7.50-7.47 (m, 2H), 7.28-7.25 (m, 2H), 7.01 (dd, *J* = 6.8, 2.2 Hz, 2H), 3.88 (s, 3H), 2.42 (s, 3H) ppm.



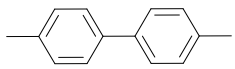
4-Ethyl-4'-methoxy-1,1'-biphenyl[6], ^{1}H NMR (400 MHz, $CDCl_3$, 25 ^{o}C): δ = 7.59-7.52 (4 H, m), 7.32-7.29 (2 H, m), 7.04-7.00 (2 H, m), 3.89 (3 H, s), 2.74 (q, *J* = 7.7 Hz, 2 H), 1.33 (t, *J* = 7.6 Hz, 3H) ppm.



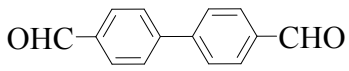
4-Methoxy-4'-(trifluoromethyl)-1,1'-biphenyl[7], ^{1}H NMR (400 MHz, CDCl3) : δ = 7.60-7.54 (m, 4H), 7.47 (dd, *J* = 6.7, 2.1 Hz, 2H), 6.93 (dd, *J* = 6.6, 2.2 Hz, 2H), 3.79 (s, 3H) ppm.



4'-Methoxy-1,10-biphenyl-4-carbonitrile[8], ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.73-7.61 (m, 4 H), 7.54 (d, *J* = 8.8 Hz, 2 H), 7.01 (d, *J* = 8.8 Hz, 2 H), 3.87 (s, 3 H) ppm.



4,4'-Dimethyl-1,1'-biphenyl[9], ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 7.57 (d, *J* = 8.1 Hz, 4H), 7.32 (d, *J* = 7.9 Hz, 4H), 2.47 (s, 6H) ppm.



4,4'-Biphenyldicarboxaldehyde[5], ^{1}H NMR (400 MHz, $CDCl_3$, 25 °C): δ = 10.07 (s, 2H), 7.98 (d, *J* = 8.2 Hz, 4H), 7.79 (d, *J* = 8.1 Hz, 4H) ppm.

Reference

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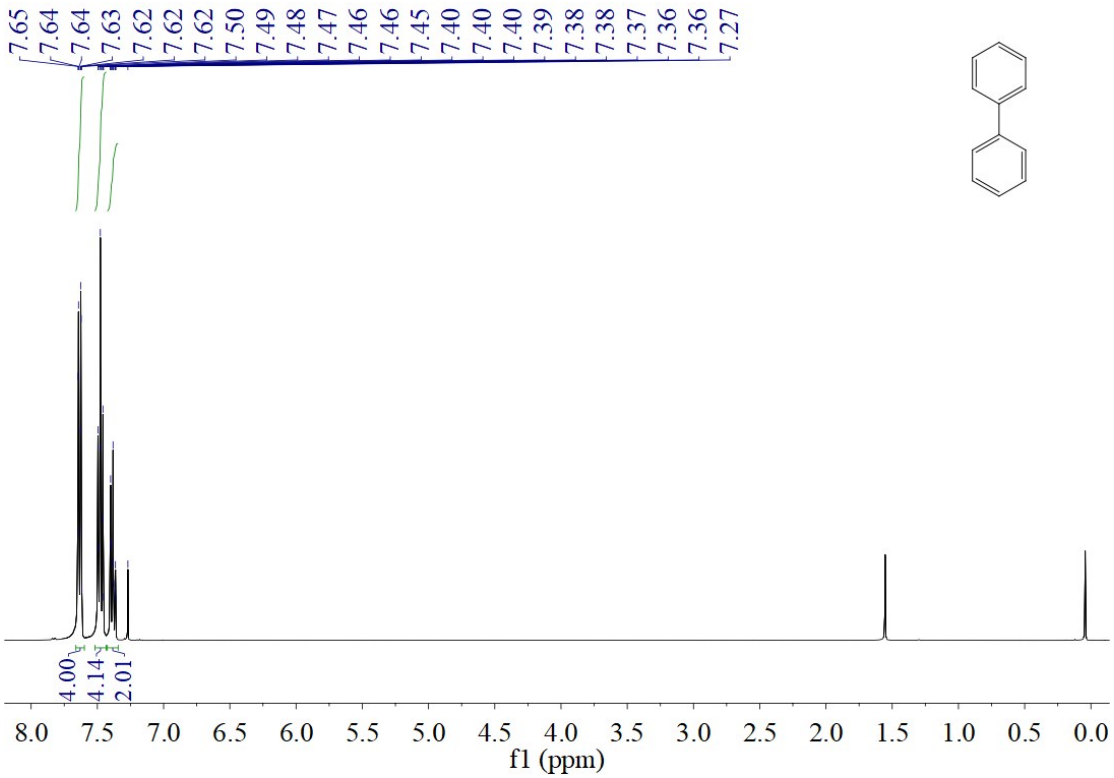
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8.0
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7.0
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1.5
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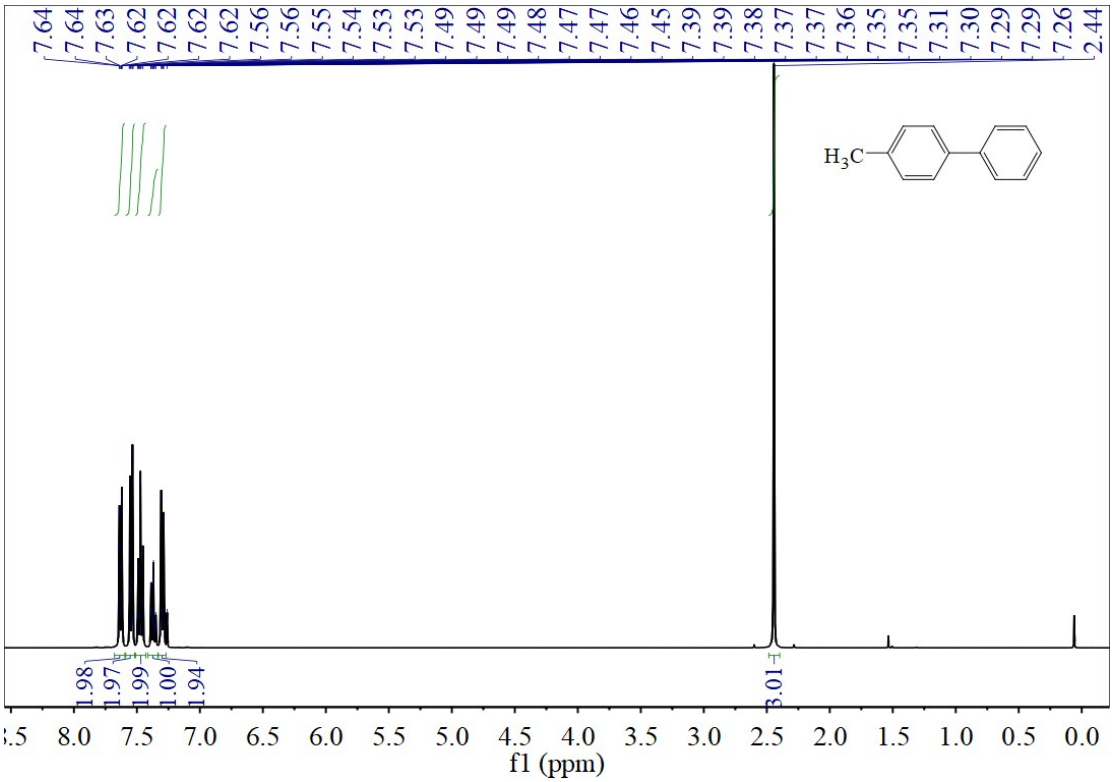
f1 (ppm)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7.30
7.29
7.29
7.26
2.44
H3C
1.98
1.97
1.99
1.00
1.94
3.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
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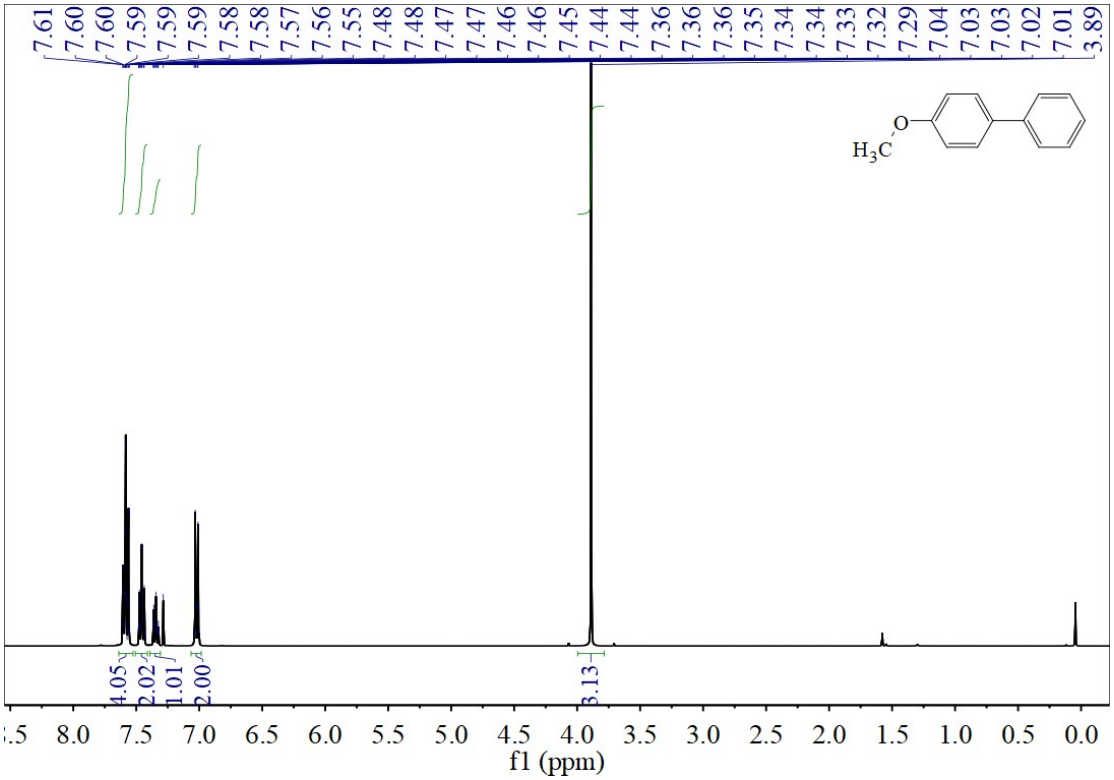
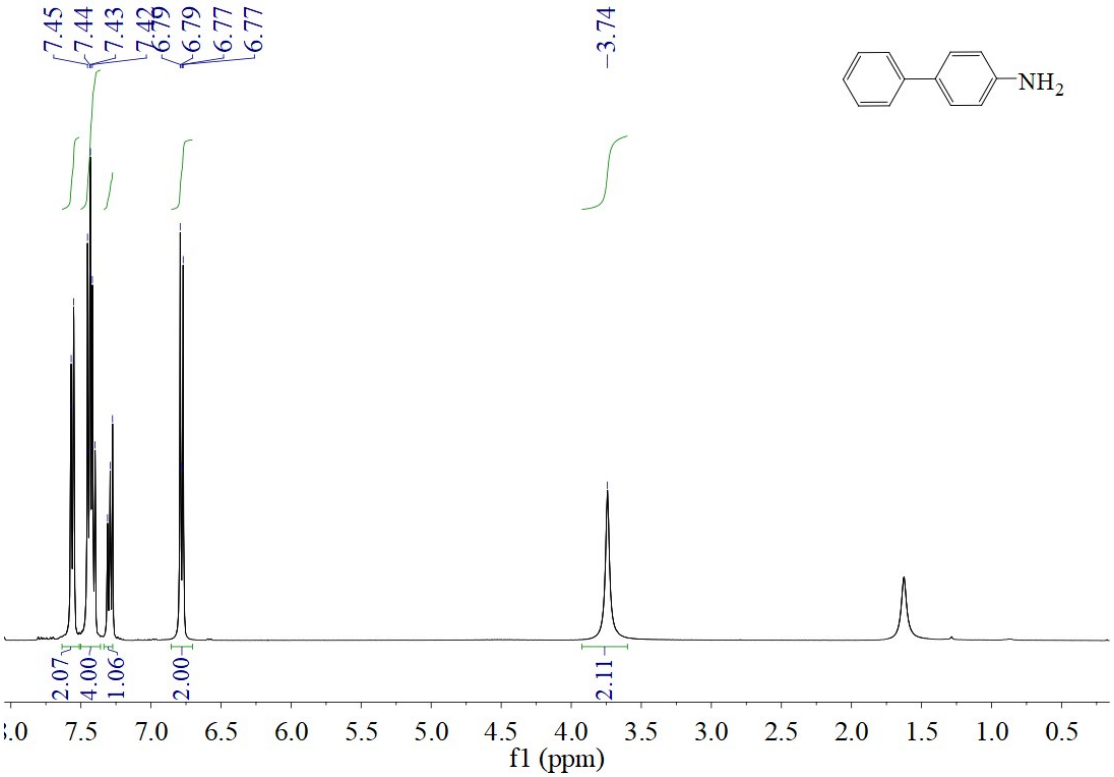
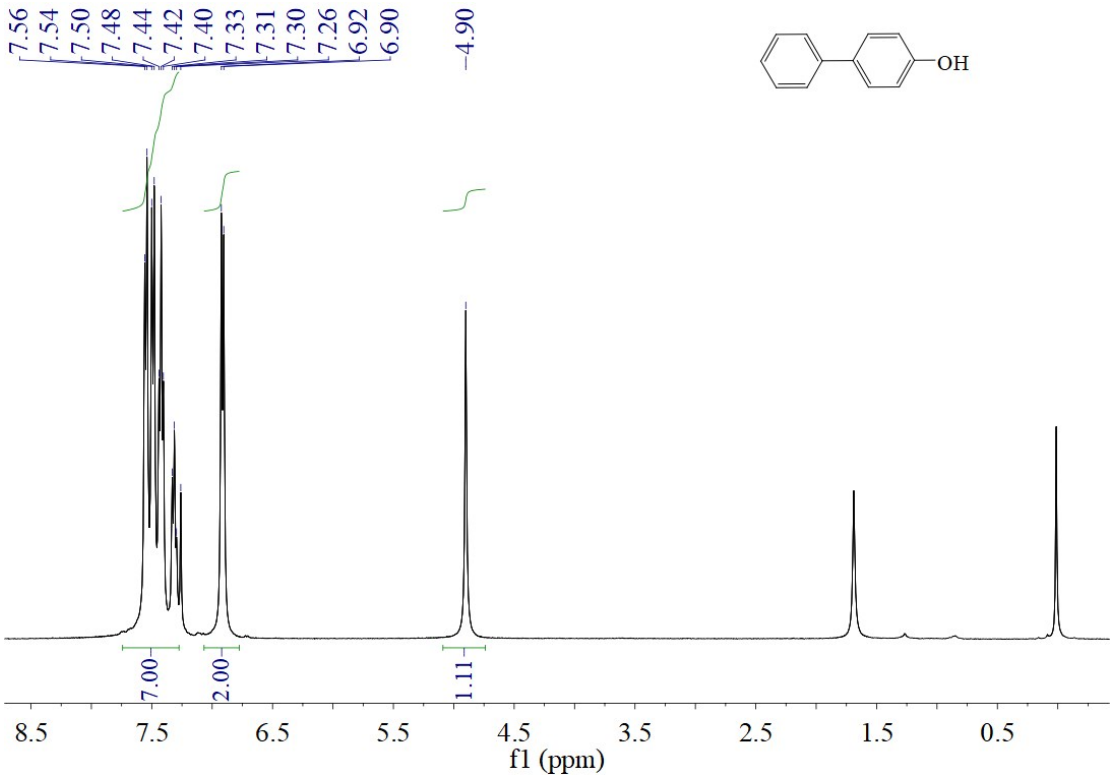
f1 (ppm)


7.61 7.60 7.60 7.59 7.59 7.59 7.58 7.58 7.57 7.56 7.55 7.48 7.48 7.47 7.47 7.46 7.46 7.45 7.44 7.44 7.36 7.36 7.36 7.35 7.34 7.34 7.33 7.32 7.29 7.04 7.03 7.03 7.02 7.01 3.89
O
H3C
4.05
2.02
1.01
2.00
3.13
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.45 7.44 7.43 7.42 6.79 6.79 6.77 6.77
3.74
NH2
2.07
4.00
1.06
2.00
2.11
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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7.54
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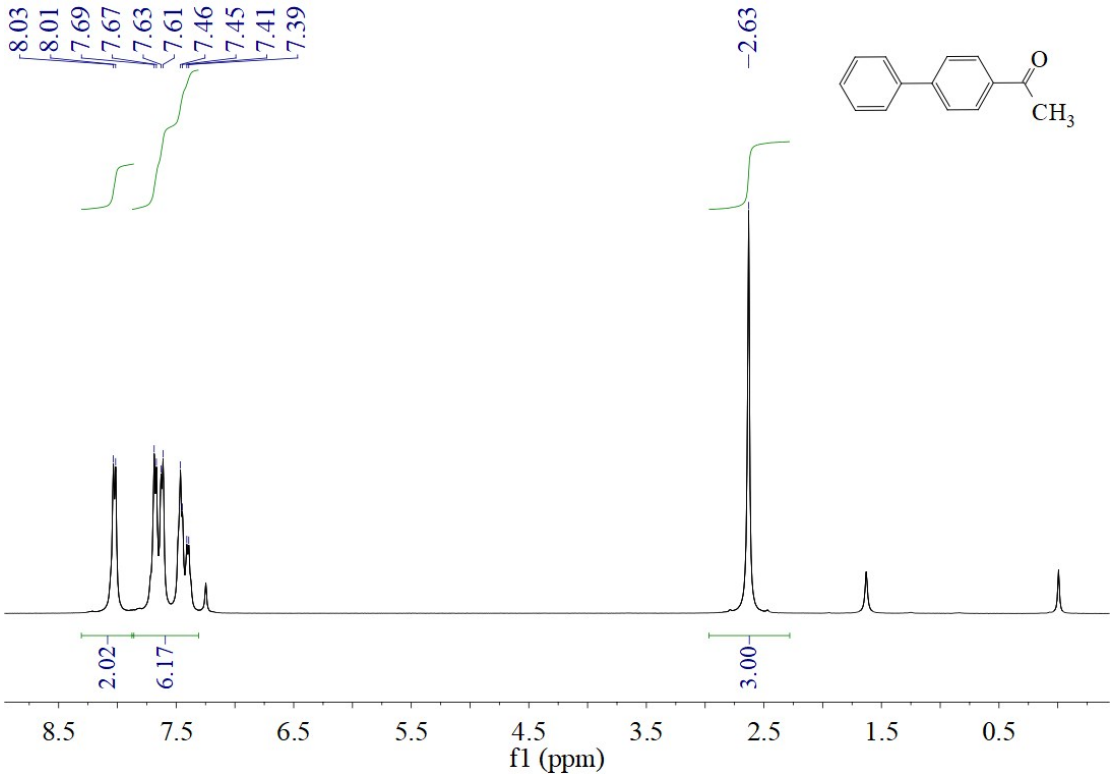
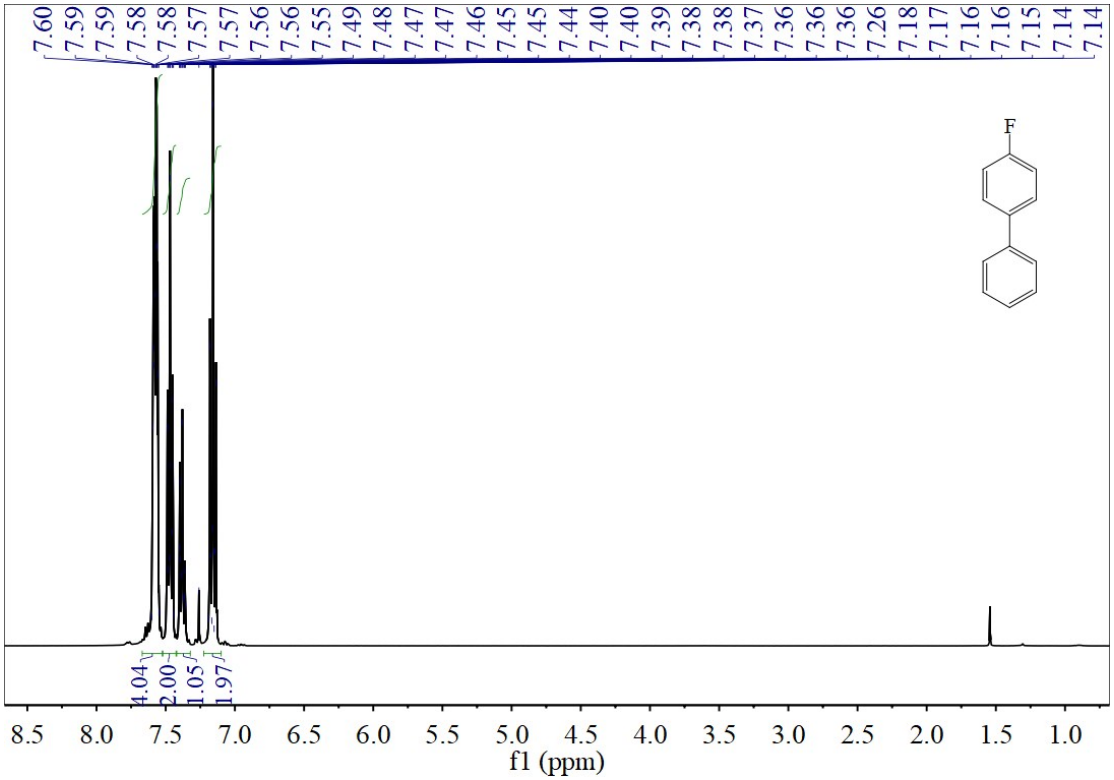
7.42
7.40
7.33
7.31
7.30
7.26
6.92
6.90
4.90
OH
7.00
2.00
1.11
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)


8.03
8.01
7.69
7.67
7.63
7.61
7.46
7.45
7.41
7.39
2.63
O
CH3
2.02
6.17
3.00
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)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7.59
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7.56
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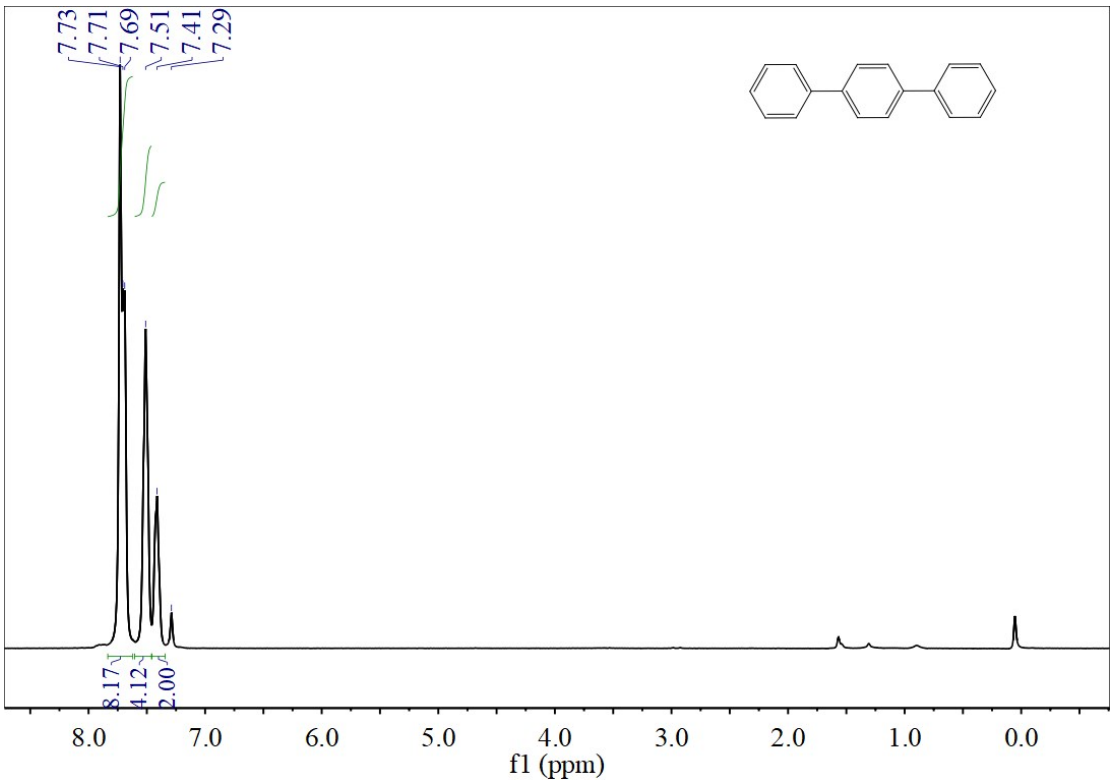
7.55
7.49
7.48
7.47
7.47
7.46
7.45
7.45
7.44
7.40
7.40
7.39
7.38
7.38
7.37
7.36
7.36
7.36
7.26
7.18
7.17
7.16
7.16
7.15
7.14
7.14
F
4.04
2.00
1.05
1.97
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)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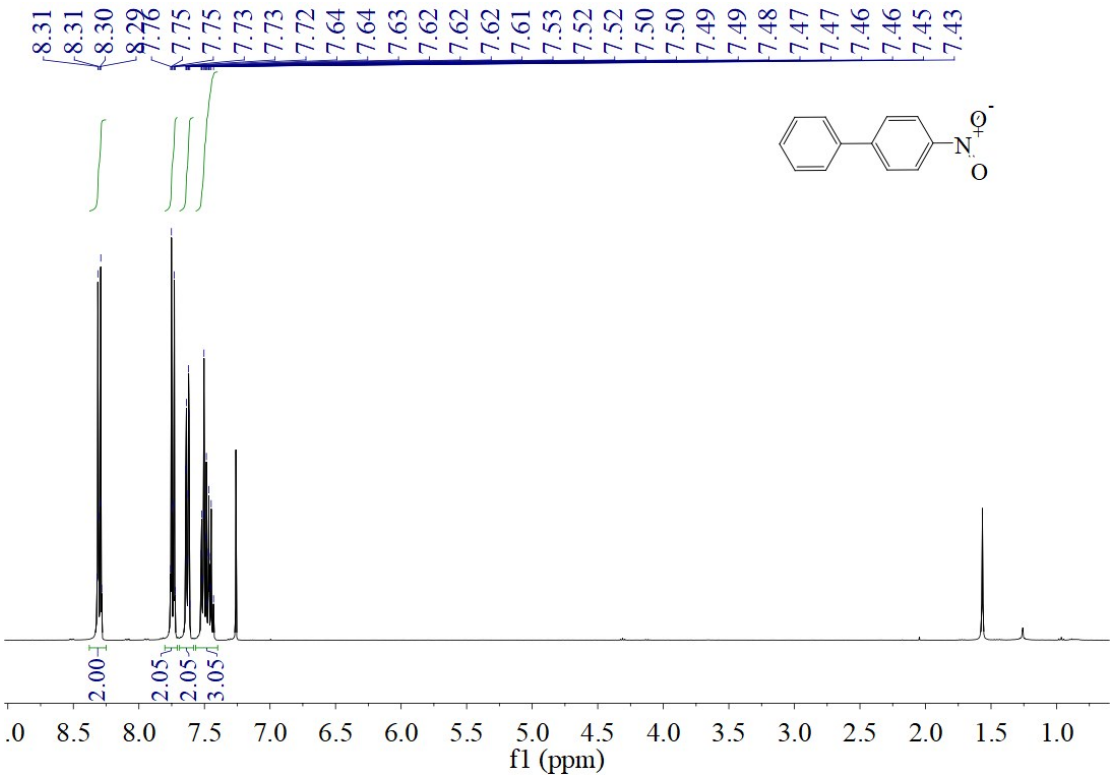
7.71
7.69
7.51
7.41
7.29
8.17
4.12
2.00
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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8.31
8.30
8.29
7.76
7.75
7.75
7.73
7.73
7.72
7.64
7.64
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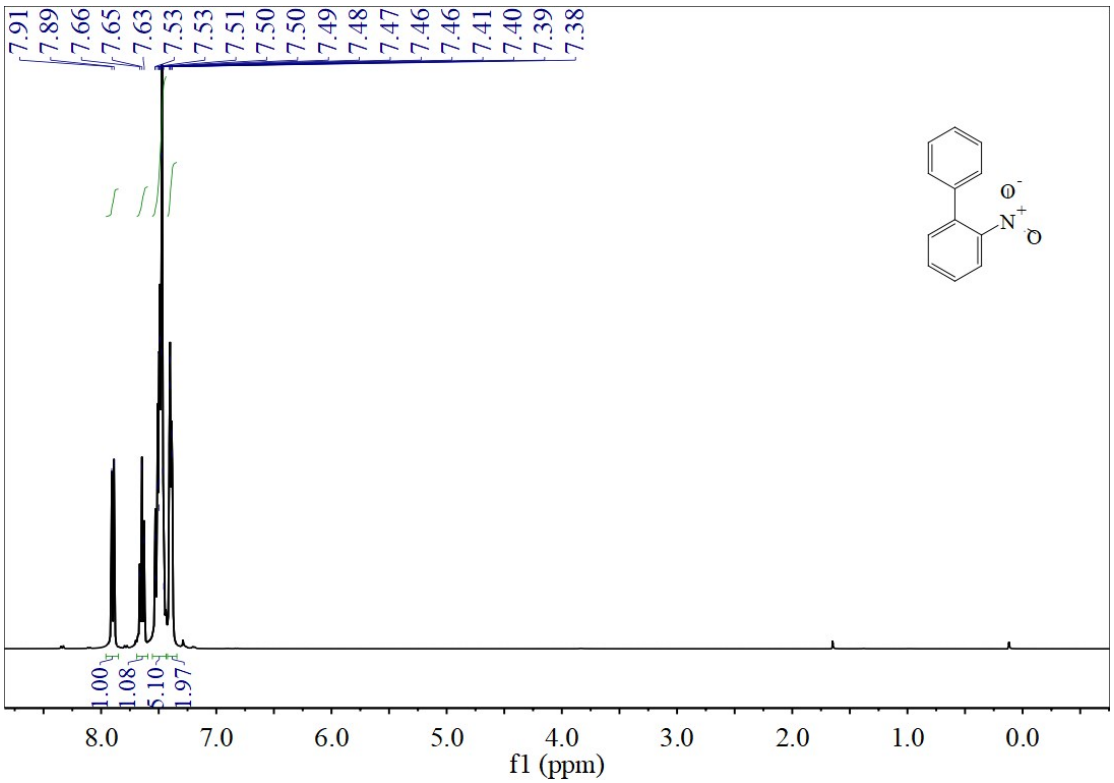
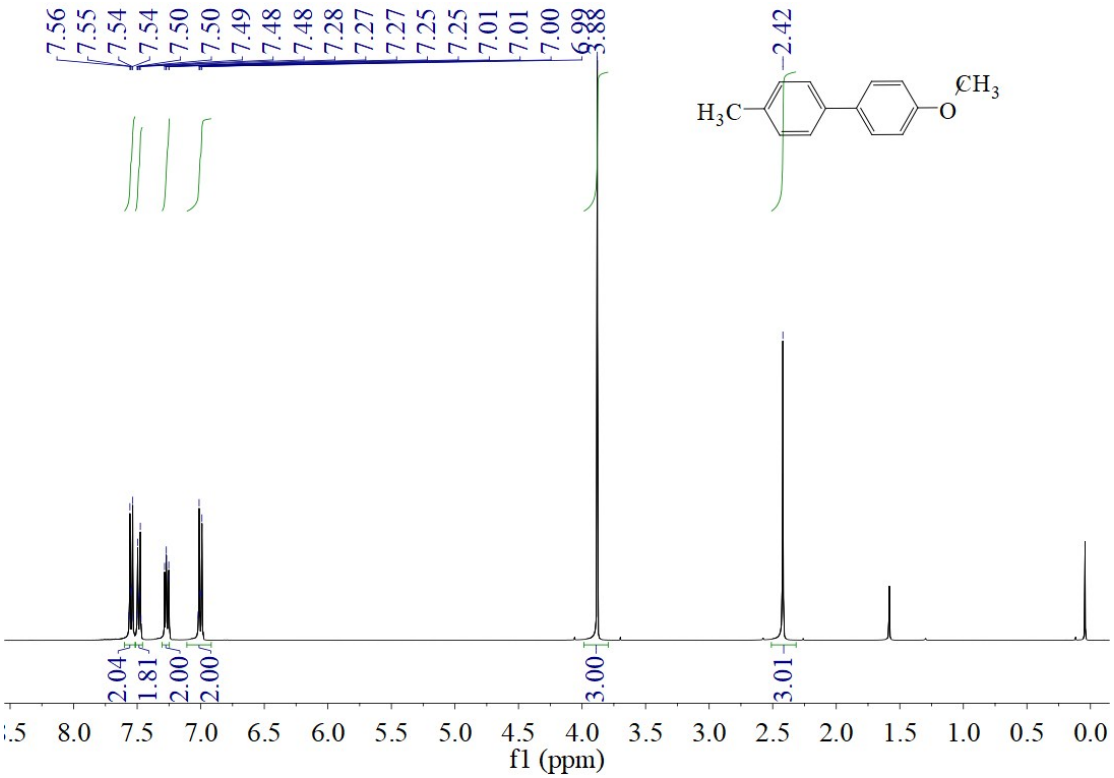
7.62
7.62
7.62
7.61
7.53
7.52
7.52
7.50
7.50
7.49
7.49
7.48
7.47
7.47
7.46
7.46
7.45
7.43
2.00
2.05
2.05
3.05
.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0
f1 (ppm)


7.91
7.89
7.66
7.65
7.63
7.53
7.53
7.51
7.50
7.50
7.49
7.48
7.47
7.46
7.46
7.41
7.40
7.39
7.38
1.00
1.08
5.10
1.97
8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
f1 (ppm)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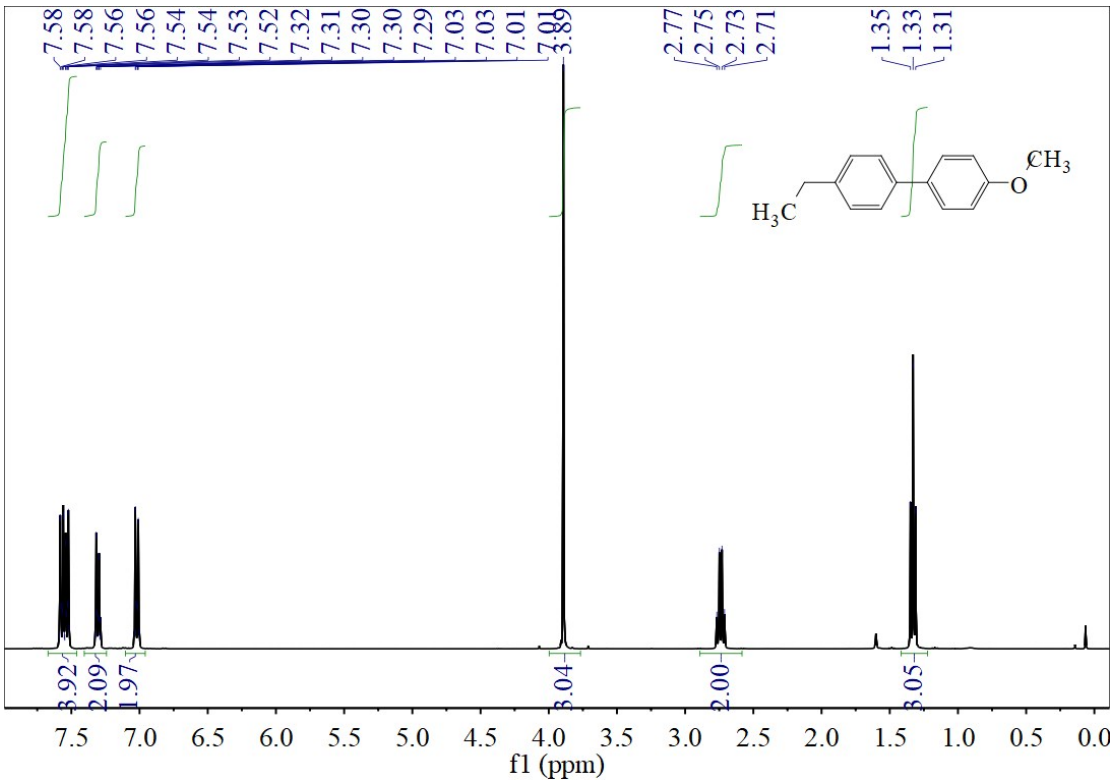
7.55
7.54
7.54
7.50
7.50
7.49
7.48
7.48
7.28
7.27
7.27
7.25
7.25
7.01
7.01
7.00
6.88
3.88
2.42
H_3C
O
CH_3
2.04
1.81
2.00
2.00
3.00
3.01
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.56
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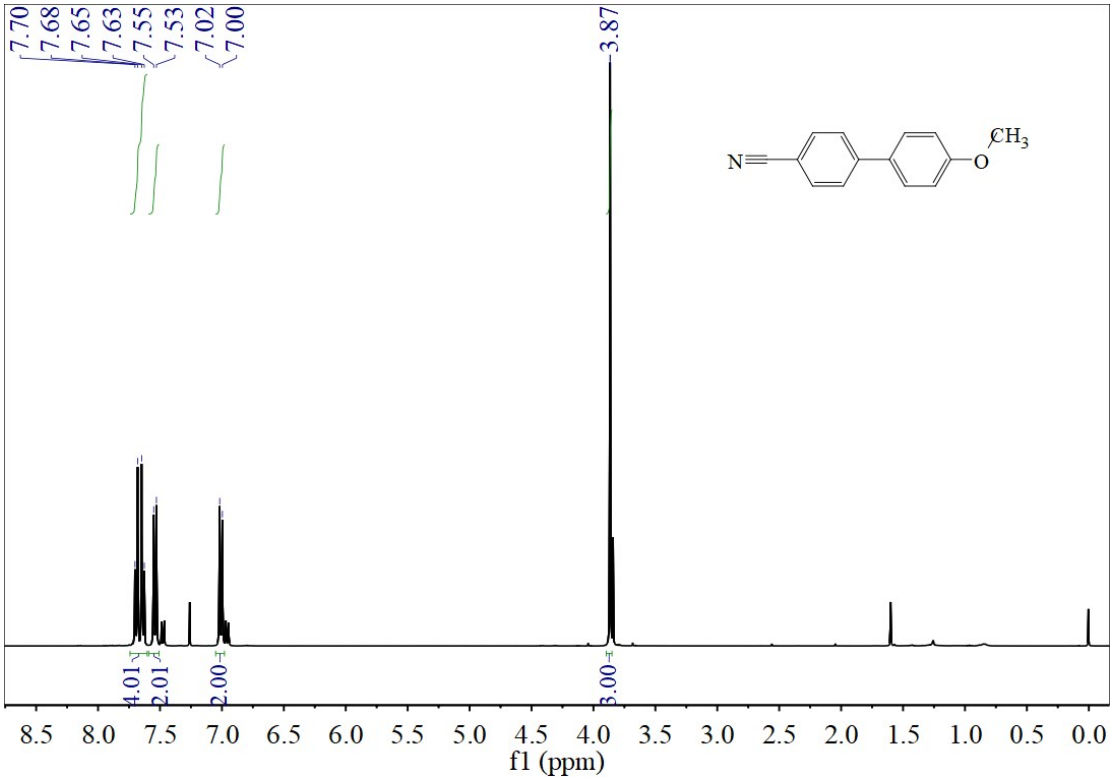
7.54
7.53
7.52
7.32
7.31
7.30
7.30
7.29
7.03
7.03
7.01
7.01
3.89
2.77
2.75
2.73
2.71
1.35
1.33
1.31
H_3C
O
CH_3
3.92
2.09
1.97
3.04
2.00
3.05
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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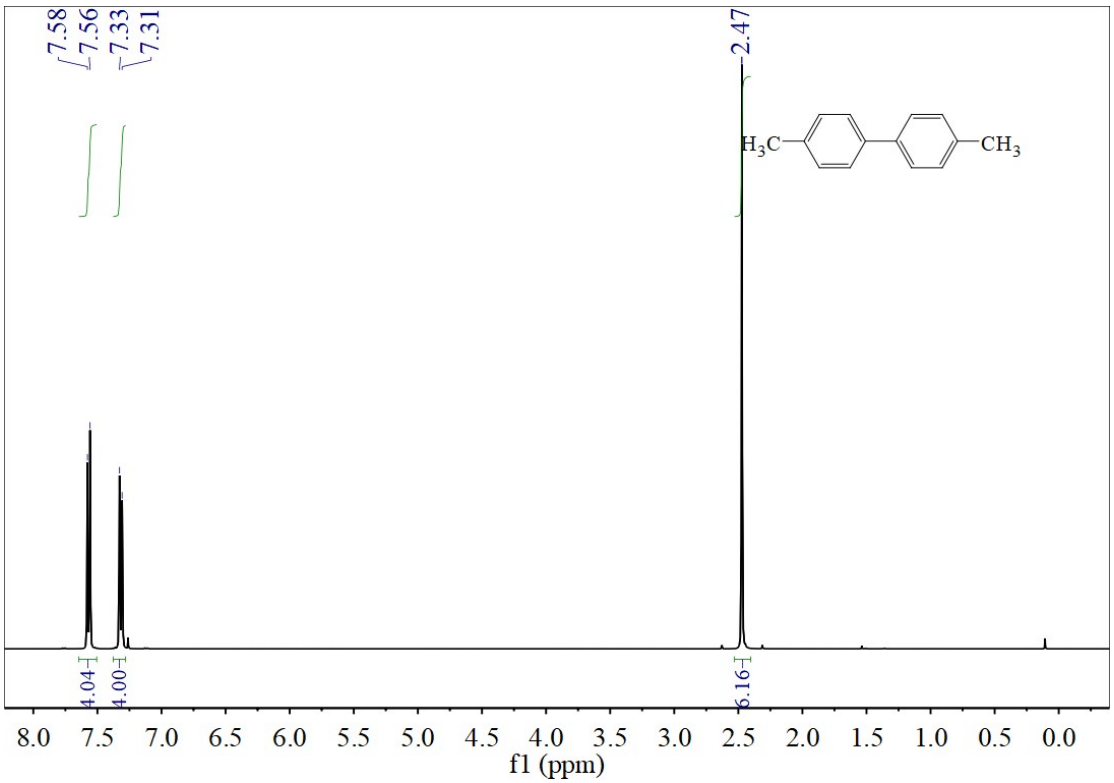
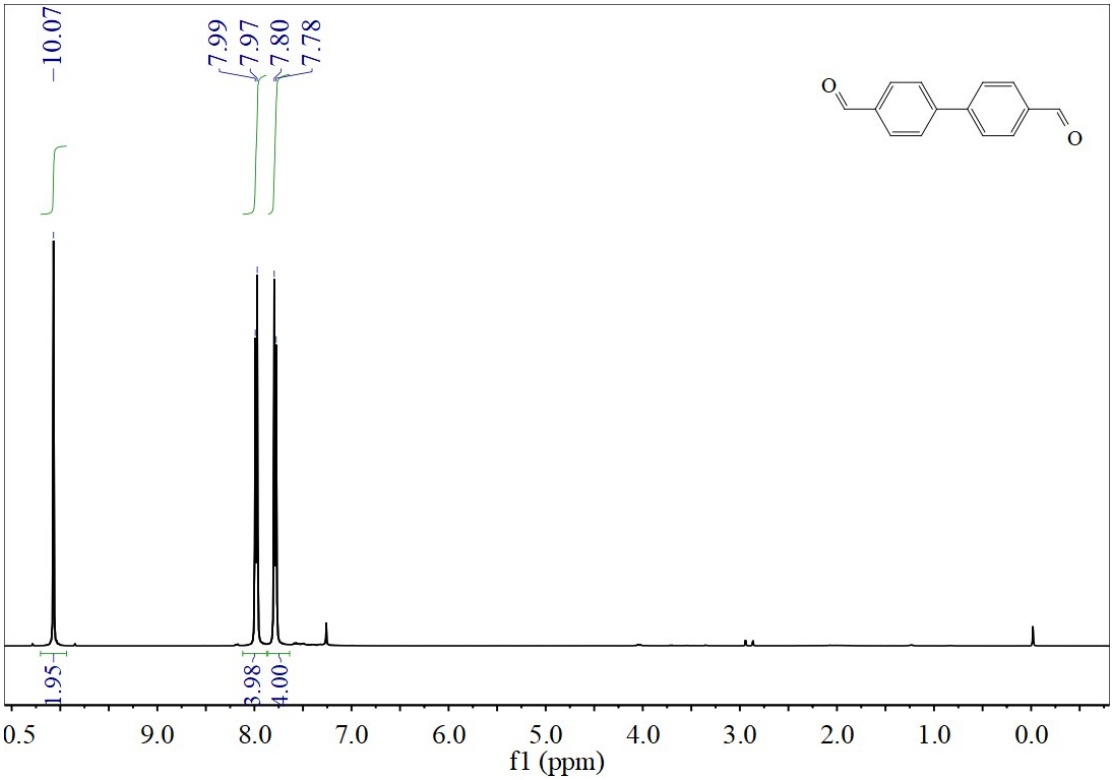
7.65
7.63
7.55
7.53
7.02
7.00
3.87
4.01
2.01
2.00
3.00
N
O
CH3
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.58
7.56
7.33
7.31
2.47
4.04
4.00
6.16
H3C
CH3
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


10.07
7.99
7.97
7.80
7.78
O
O
1.95
3.98
4.00
0.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)