Supporting Information

Efficient Phosphine ligands for the One-Pot Palladium-Catalyzed Borylation/Suzuki–Miyaura Cross-coupling Reaction

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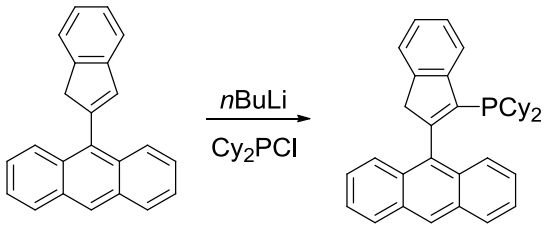
CONTENT

Experimental Section

General information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without purification. 9-(1H-inden-2-yl) anthracene **4** was prepared according to the reported procedure.[1] All reactions were performed in a resealable screw cap Schlenk flask (approx. 10 mL volume) in the presence of a Teflon coated magnetic stirrer bar (3 mm × 50 mm). Dimethyl acetamide was distilled from anhydrous magnesium sulfate under nitrogen. Silica gel (70–230 and 230–400 mesh) was used for column chromatography. ^{1}H NMR and ^{13}C NMR spectra were recorded on a MercuryPlus (400 MHz) spectrometer. HRMS were obtained on an IonSpec FT-ICR mass spectrometer with ESI resource. Compounds described in the literature were characterized by comparison of their ^{1}H NMR spectra to the previously reported data.

Preparation of 2-(anthracen-9-yl)-1H-inden-3-yl dicyclohexylphosphine 1



4 **1**

In a 100ml flask 9-(1H-inden-2-yl) anthracene **4** (1.46 g, 5.0 mmol) was dissolved in THF (50 mL) under nitrogen atmosphere. The mixture was cooled to –78 ℃, and *n*BuLi (3.75 mL, 1.6 M solution in hexane, 6.0 mmol) was added. The solution was stirred for 30 min at –78 ℃ and then for 6 h at ambient temperature. Then the mixture was cooled to –78 ℃ and Cy_2PCl (1.1 mL, 5.0 mmol) was added. The mixture was warmed to room temperature and stirred for additional 16 h. The reaction was quenched with water (20 mL). The organic layer was separated from the aqueous layer. The aqueous layer was extracted with CH_2Cl_2 (25 mL×2). The combined organic phase was dried over anhydrous $MgSO_4$, concentrated, and purified by column chromatography (eluents: CH_2Cl_2) to provide the desired product as a yellow solid (1.66 g, 68%).^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.43 (dd, *J* = 13.9 Hz, 5.6 Hz, 3H), 7.37 – 7.28 (m, 3H), 3.91 (s, 2H), 2.30 (br, 2H), 1.77 (br, 2H), 1.60-1.63 (m, 8H), 1.02-1.21 (m, 10H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.21, 158.88, 147.08, 143.73, 140.53, 140.27, 133.55, 131.31, 129.94, 128.70, 127.03, 126.64, 125.08, 124.95, 124.83, 123.95, 122.46, 46.13, 34.57, 34.47, 32.60, 32.39, 31.20, 31.12, 27.50, 27.43, 27.27, 27.14, 26.32 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ -16.21 ppm. HRMS (ESI/ $[M+H]^+$) Cacld. for: $C_{35}H_{37}P$ 488.2711, found 488.2712.

Crystallographic Studies

Single crystal of **1** for X-ray diffraction analysis was obtained by slow diffusion of hexane into its CH_2Cl_2 solutions at room temperature. Crystallographic data was collected on a Bruker SMART CCD area-detector diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Diffraction measurements were made at room temperature. An absorption correction by SADABS was applied to the intensity data. The structures were solved by Patterson method. The remaining non-hydrogen atoms were determined from the successive difference Fourier syntheses. All non-hydrogen atoms were refined anisotropically except those mentioned otherwise. The hydrogen atoms were generated geometrically and refined with isotropic thermal parameters. The structures were refined on F^2 by full-matrix least-squares methods using the SHELXTL-97 program package.

General procedures for reaction condition screenings

A Pd source (0.02 mmol), a phosphine ligand (0.04 mmol), base (3.0 mmol) and bis(pinacolato)diboron (254 mg, 1.0 mmol) was loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. 4-Chlorotoluene (0.29 mL, 2.4 mmol) and dimethyl acetamide (2.0 mL) were added. The tube was evacuated and flushed with nitrogen three times, and then placed in a preheated oil bath with the temperature indicated in the table and stirred for 20 h. After completion of the reaction, the reaction tube was allowed to cool to room temperature. Water (10 mL) and EtOAc (10 mL) were added. The aqueous layer was extracted with EtOAc (3 × 10 mL), dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by column chromatography on silica gel to afford the desired product.

General Procedure for the Preparation of Symmetrical Biaryls

$Pd(dba)_2$ (12 mg, 0.02 mmol), ligand **1** (20 mg, 0.04 mmol), $K_3PO_4 \cdot 3H_2O$ (0.8 g, 3.0 mmol) and bis(pinacolato)diboron (254 mg, 1.0 mmol) was loaded into a Schlenk tube equipped with a Teflon-coated magnetic stir bar. Aryl chlorides or heteroaryl chloride (2.4 mmol) and dimethyl acetamide (2.0 mL) were added. The tube was evacuated and flushed with nitrogen three times, and then placed in a preheated oil bath (100 ℃) and stirred for 20 h. After completion of the reaction, the reaction tube was allowed to cool to room temperature. Water (10 mL) and EtOAc (10 mL) were added. The aqueous layer was extracted with EtOAc (3 × 10 mL), dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by column chromatography on silica gel to afford the desired product.

General Procedure for the Preparation of Unsymmetrical Biaryls

$Pd(dba)_2$ (12 mg, 0.02 mmol), ligand (20 mg, 0.04 mmol), KOAc(0.3g, 3.0 mmol) and bis(pinacolato)diboron (305 mg, 1.2 mmol) was loaded into a Schlenk tube equipped

with a Teflon-coated magnetic stir bar. The first aryl halide (1.2 mmol) and dimethyl acetamide (2.0 mL) were added. The tube was evacuated and flushed with nitrogen three times, and then placed in a preheated oil bath (100 ℃) and stirred for 3 h. After completion of the reaction, the reaction tube was allowed to cool to room temperature. The second aryl or heteroaryl chlorides and $K_3PO_4 \cdot 3H_2O$ were loaded into the tube under nitrogen. Dimethyl acetamide (0.5 mL) was added. The tube was then placed into a preheated oil bath (100 ℃) and stirred for 16 h. After completion of the reaction, the reaction tube was allowed to cool to room temperature. Water (10 mL) and EtOAc (10 mL) were added. The aqueous layer was extracted with EtOAc (3 × 10 mL), dried over anhydrous sodium sulfate, and concentrated. The crude product was purified by column chromatography on silica gel to afford the desired product.

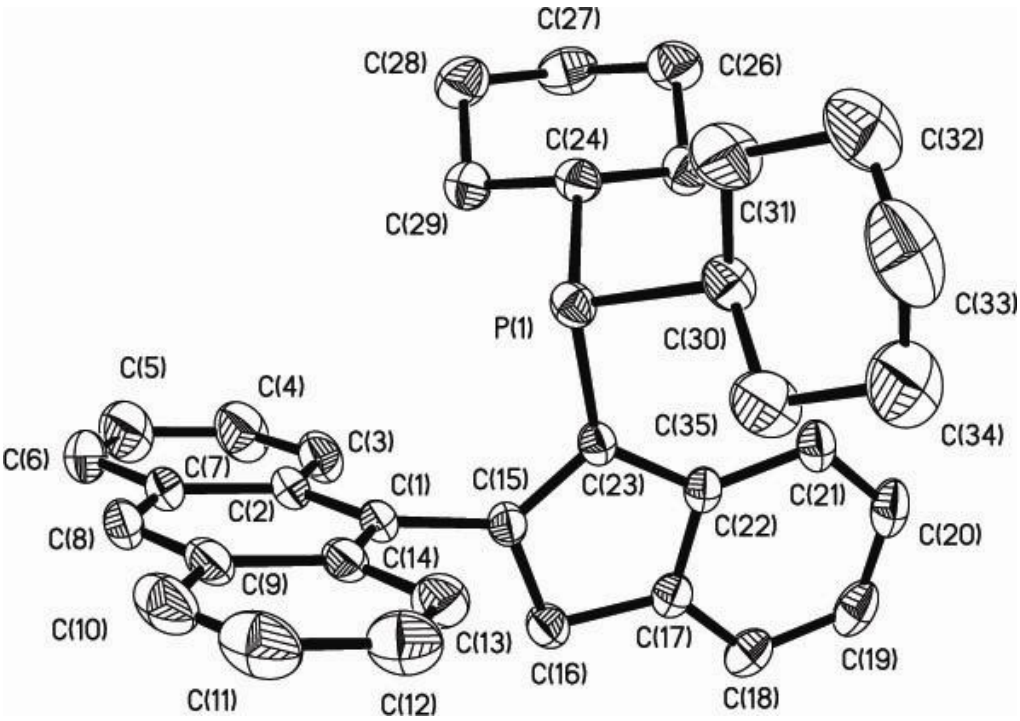
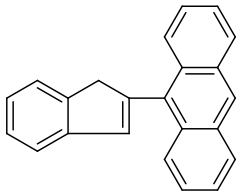


Figure S1. Molecular structure of **1**. Thermal ellipsoids are set at 30% probability. H atoms have been omitted for clarity.

Table S1. Crystal Data and Summary of X-ray Data Collection of **1**

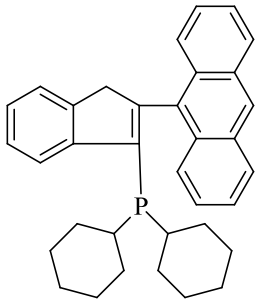
	1
formula	$C_{70}H_{74}P_2$
fw	977.23
T, K	100(2)
Wavelength, Å	0.71073
crystal system	Monoclinic
space group	C2/c
a, Å	23.590(3)
b, Å	12.9016(15)
c, Å	18.644(2)
α, deg	90
β, deg	98.267(2)
γ, deg	90
V, Å^3	5615.3(11)
Z	4
D_{cal}, g/cm^{-3}	1.156
Absorption coefficient, mm^{-1}	0.119
F(000)	2096
cryst size, mm	0.20×0.20×0.10
θ range, deg	1.74-30.00
no. of reflns collected	26267
no. of indep reflns/R_{int}	8157/0.0288
no. of params	326
GOF on F^2	1.042
R_1, wR_2 [$I > 2\sigma(I)$]	0.0470, 0.1279
R_1, wR_2 (all data)	0.0681, 0.1494
largest diff peak and hole (e Å^{-3})	0.286, -0.220

^{1}H NMR, ^{31}P NMR, ^{13}C NMR and HRMS spectra of compound 4 and 1



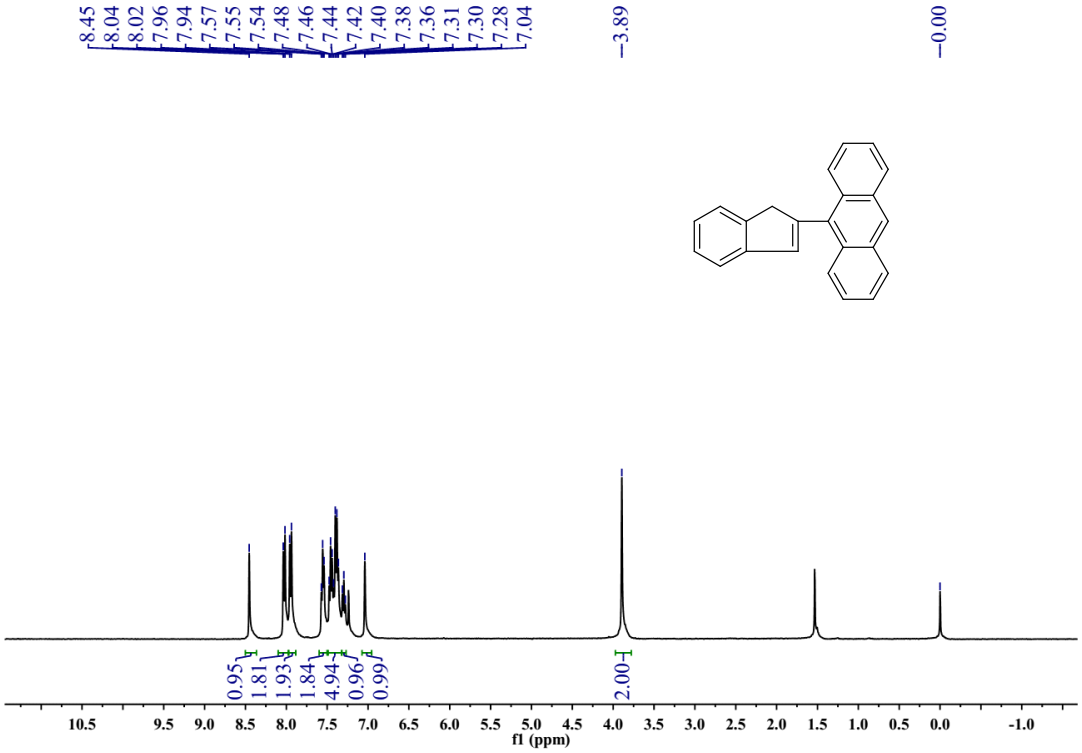
9-(1H-inden-2-yl) anthracene (**4**)

Green solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.03 (d, *J* = 8.4 Hz, 2H), 7.95 (d, *J* = 8.7 Hz, 2H), 7.60 – 7.50 (m, 2H), 7.49 – 7.32 (m, 5H), 7.32 – 7.27 (m, 1H), 7.04 (s, 1H), 3.89 (s, 2H) ppm. Data is consistent with that reported in the literature.[1]



2-(anthracen-9-yl)-1H-inden-3-yl dicyclohexylphosphine (**1**)

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (s, 1H), 8.02 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 7.7 Hz, 1H), 7.78 (d, *J* = 8.8 Hz, 2H), 7.56 (d, *J* = 7.3 Hz, 1H), 7.43 (dd, *J* = 13.9 Hz, 5.6 Hz, 3H), 7.37 – 7.28 (m, 3H), 3.91 (s, 2H), 2.30 (br, 2H), 1.77 (br, 2H), 1.60-1.63 (m, 8H), 1.02-1.21 (m, 10H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): δ 159.21, 158.88, 147.08, 143.73, 140.53, 140.27, 133.55, 131.31, 129.94, 128.70, 127.03, 126.64, 125.08, 124.95, 124.83, 123.95, 122.46, 46.13, 34.57, 34.47, 32.60, 32.39, 31.20, 31.12, 27.50, 27.43, 27.27, 27.14, 26.32 ppm. ^{31}P NMR (162 MHz, $CDCl_3$): δ -16.21 ppm. HRMS (ESI/ $[M+H]^+$) Cacld. for: $C_{35}H_{37}P$ 488.2711, found 488.2712.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7.96
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7.57
7.55
7.54
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7.40
7.38
7.36
7.31
7.30
7.28
7.04
3.89
0.00
0.95
1.81
1.93
1.84
4.94
0.96
0.99
2.00
10.5
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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2.5
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0.5
0.0
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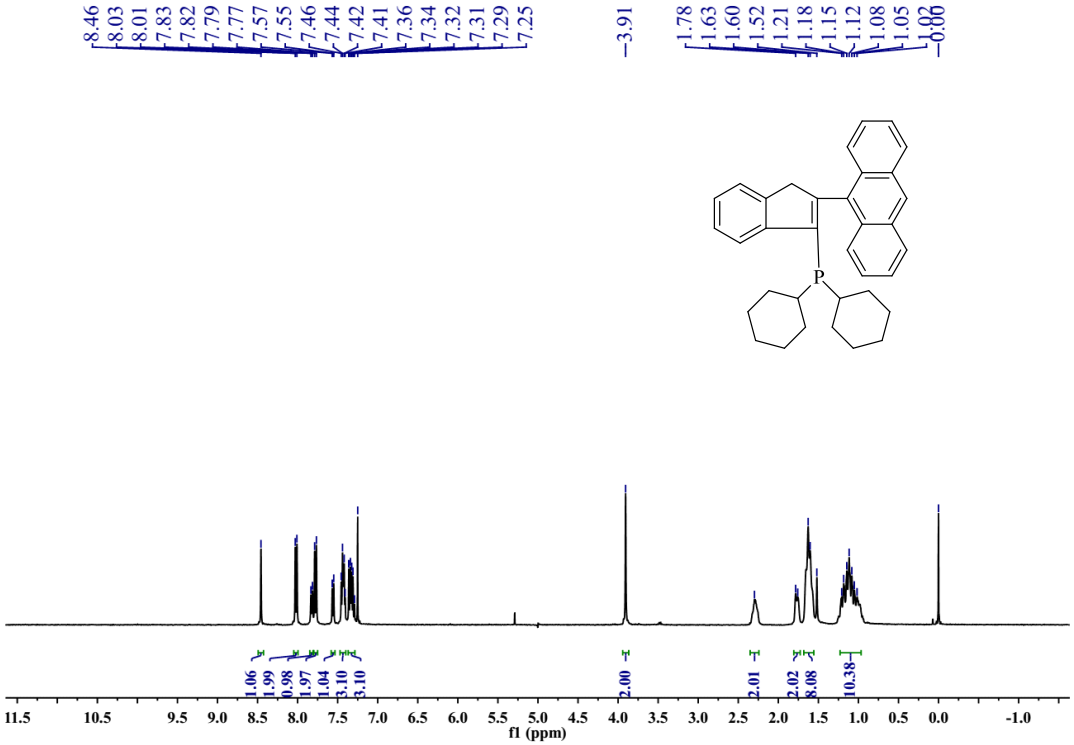
f1 (ppm)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8.01
7.83
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7.57
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7.36
7.34
7.32
7.31
7.29
7.25
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1.63
1.60
1.52
1.21
1.18
1.15
1.12
1.08
1.05
1.02
0.00
P
1.06
1.99
0.98
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3.10
3.10
2.00
2.01
2.02
8.08
10.38
11.5
10.5
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
5.5
5.0
4.5
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0.5
0.0
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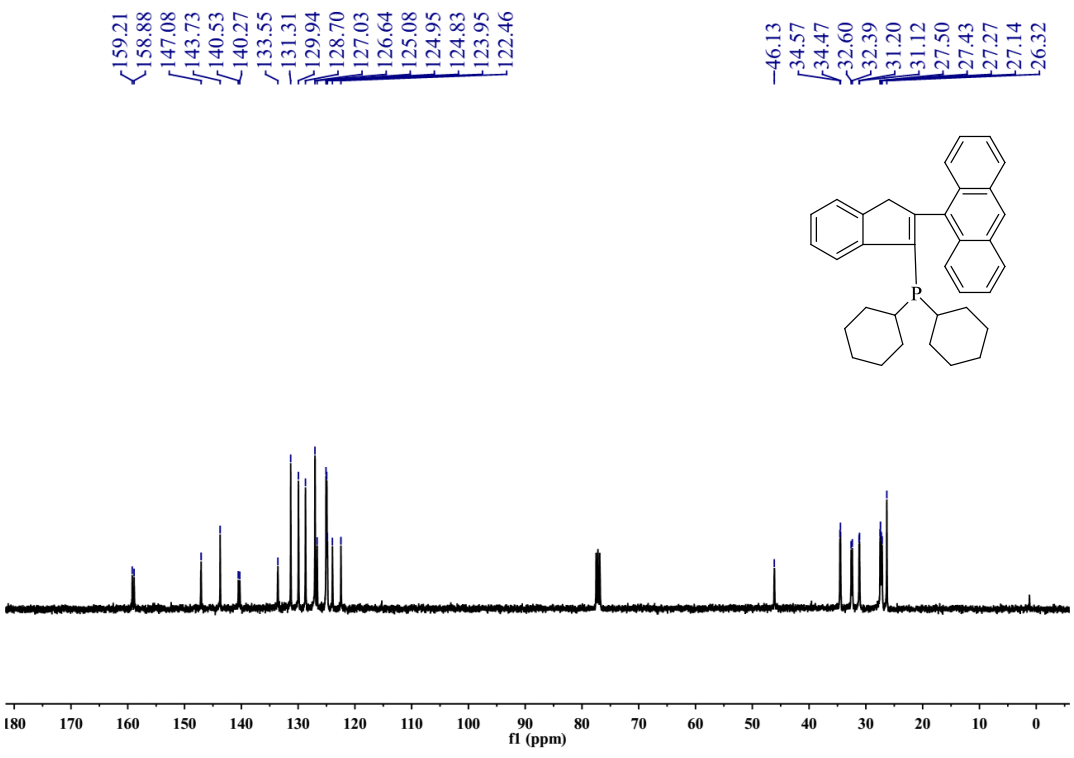
f1 (ppm)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158.88
147.08
143.73
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140.27
133.55
131.31
129.94
128.70
127.03
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125.08
124.95
124.83
123.95
122.46
46.13
34.57
34.47
32.60
32.39
31.20
31.12
27.50
27.43
27.27
27.14
26.32
P
180
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160
150
140
130
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110
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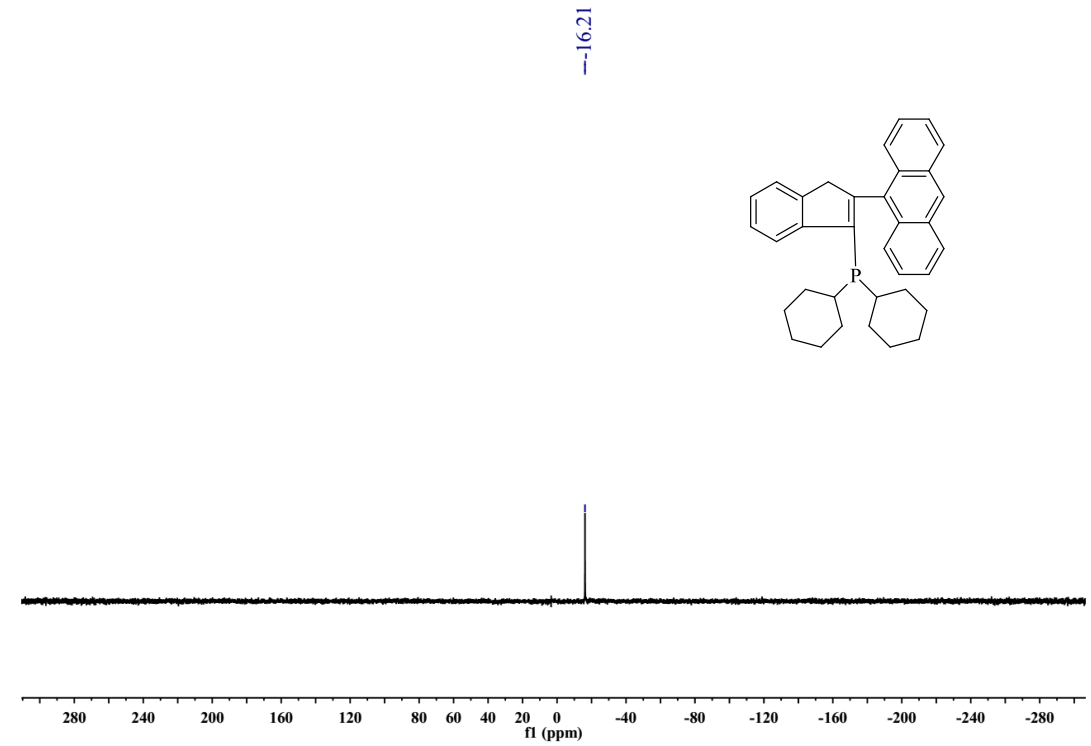
70
60
50
40
30
20
10
0
f1 (ppm)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P
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200
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-80
-120
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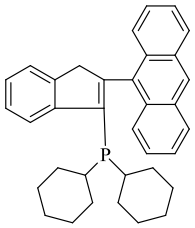
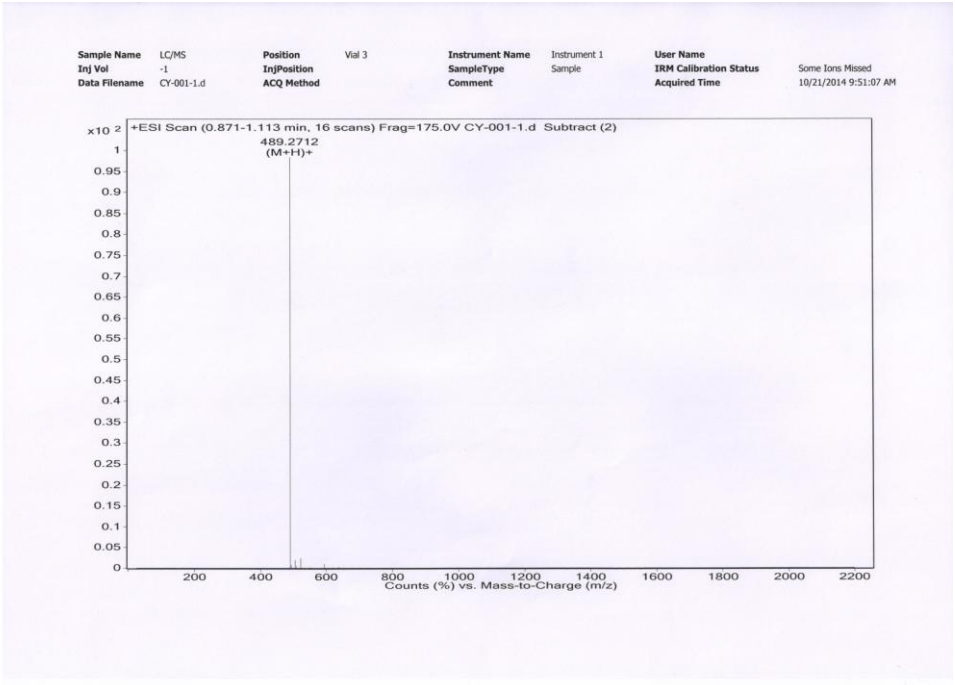
-200
-240
-280
f1 (ppm)


P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Comment
User Name
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(M+H)+
x10 2
1
0.95
0.9
0.85
0.8
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0.7
0.65
0.6
0.55
0.5
0.45
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0.3
0.25
0.2
0.15
0.1
0.05
0
200
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1200
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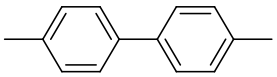
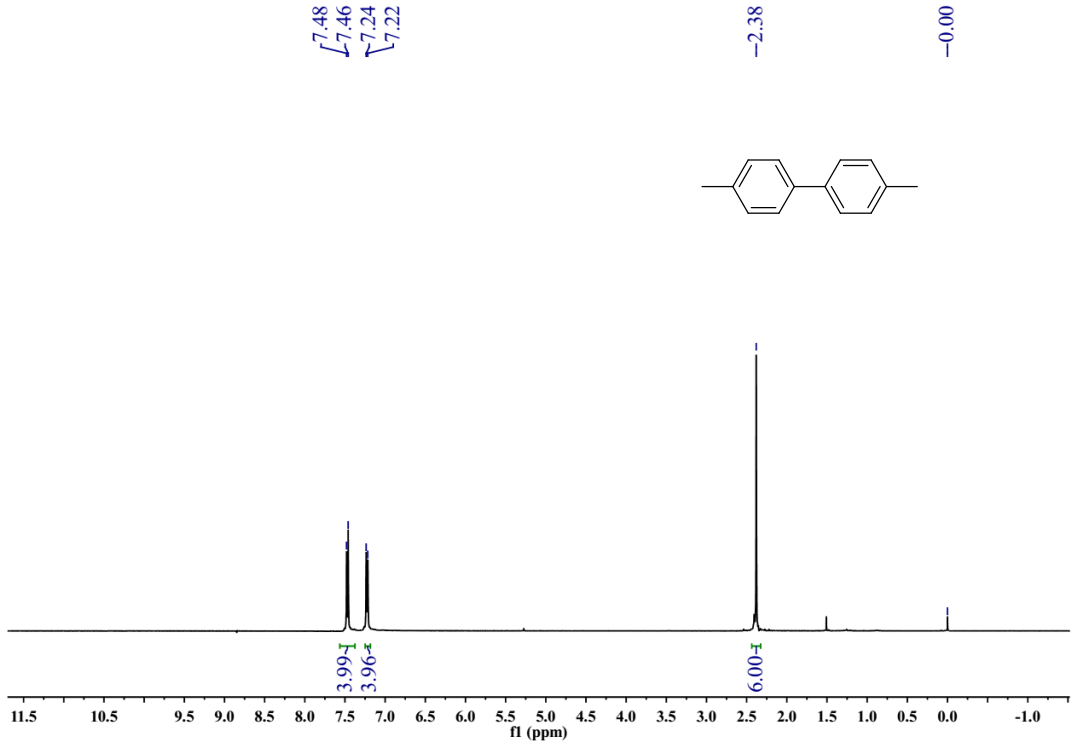
1800
2000
2200
Counts (%) vs. Mass-to-Charge (m/z)

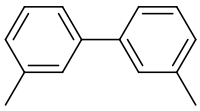
^{1}H NMR spectra of coupling products



4, 4'-dimethyl-1, 1'-biphenyl

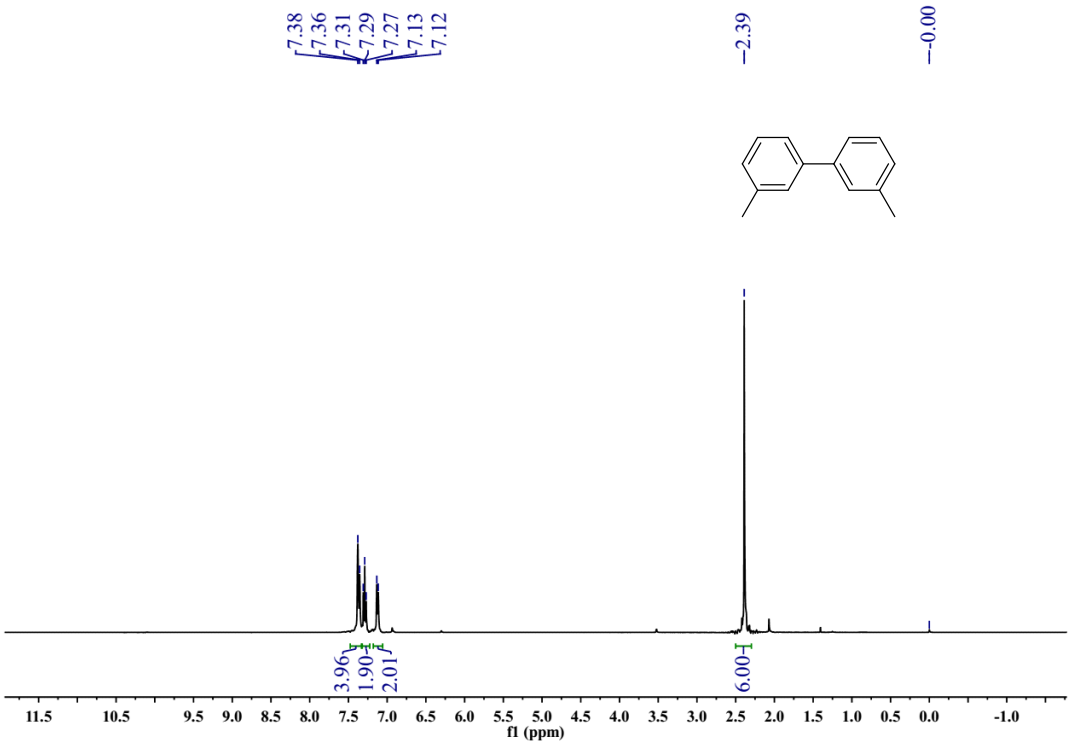
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (d, *J* = 8.1 Hz, 4H), 7.23 (d, *J* = 8.0 Hz, 4H), 2.38 (s, 6H) ppm. Data is consistent with that reported in the literature.[2]

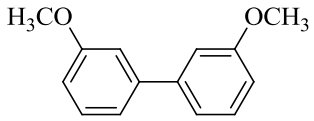




3, 3'-dimethyl-1, 1'-biphenyl

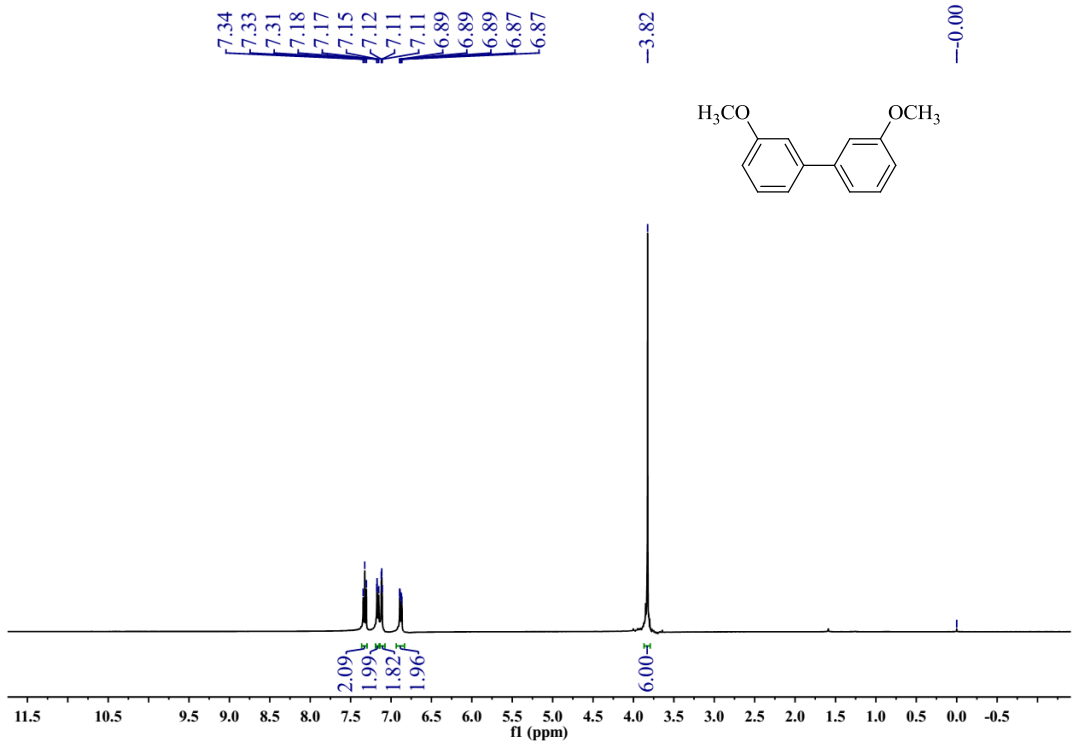
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37 (d, *J* = 9.3 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.12 (d, *J* = 7.1 Hz, 2H), 2.39 (s, 6H) ppm. Data is consistent with that reported in the literature.[3]

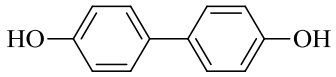




3, 3'-dimethoxy-1, 1'-biphenyl

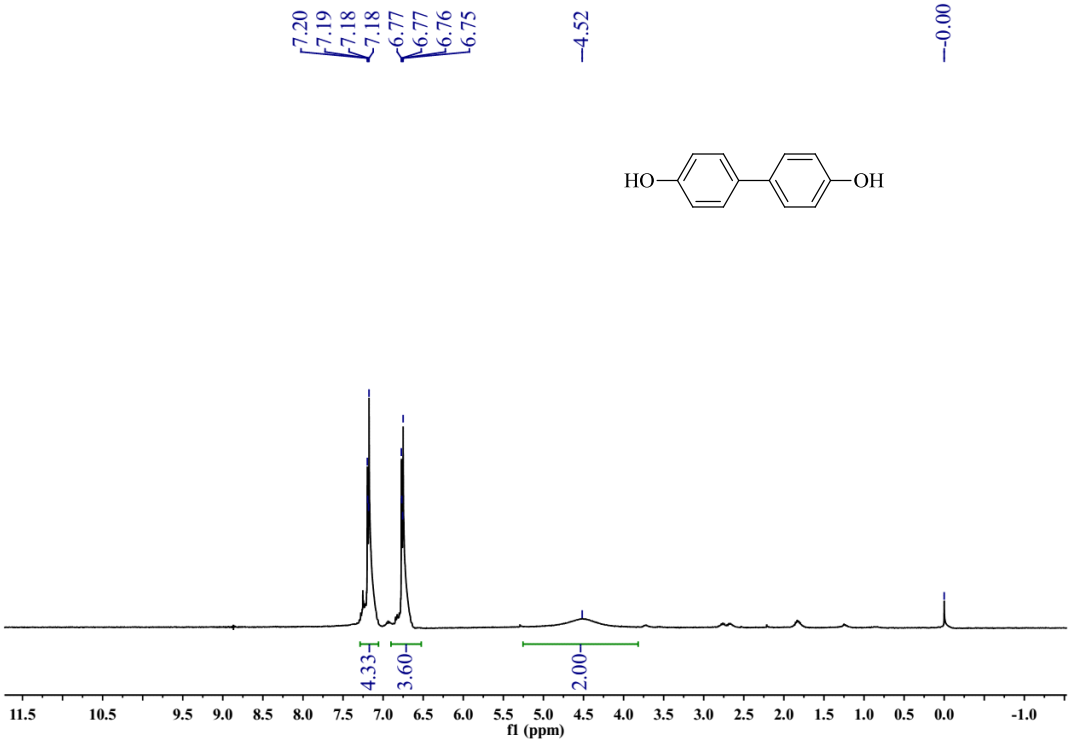
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.32 (t, *J* = 7.9 Hz, 2H), 7.19-7.15 (m, 2H), 7.14-7.07 (m, 2H), 6.94-6.83 (m, 2H), 3.82 (s, 6H) ppm. Data is consistent with that reported in the literature.[4]

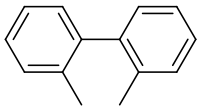




1, 1'-biphenyl-4, 4'-diol

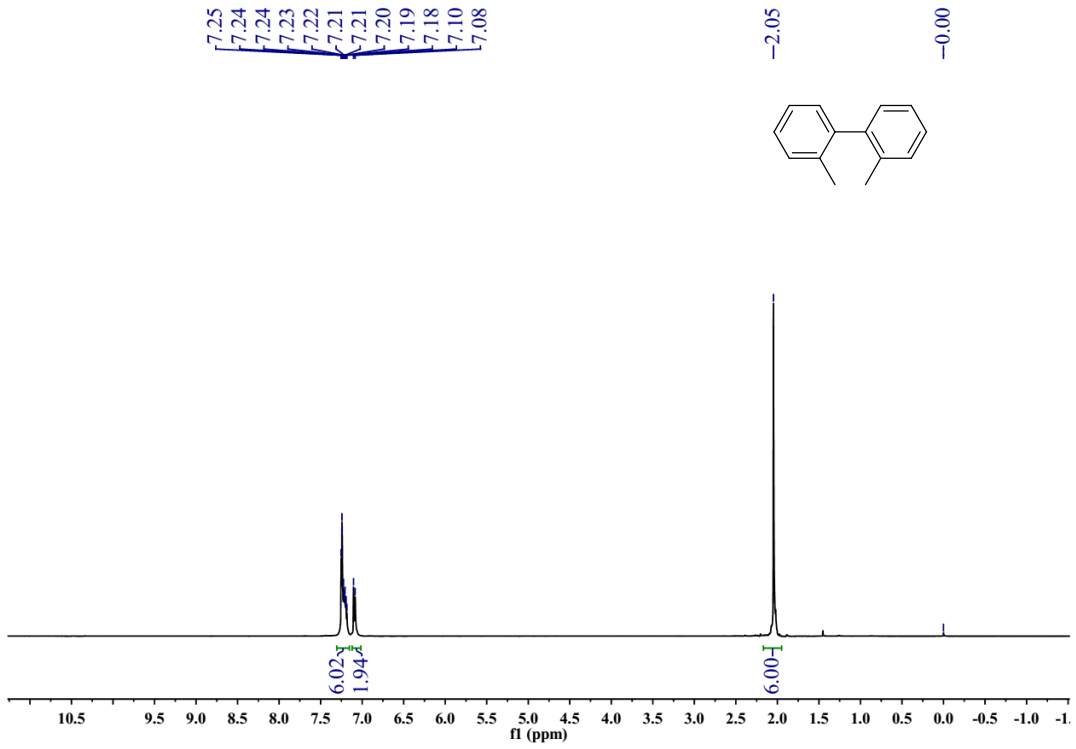
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19 (dd, *J* = 6.7, 2.1 Hz, 4H), 6.76 (dd, *J* = 6.7, 2.1 Hz, 4H), 4.52 (br, 2H) ppm. Data is consistent with that reported in the literature.[5]

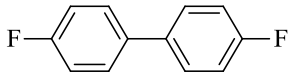




2, 2'-dimethyl-1, 1'-biphenyl

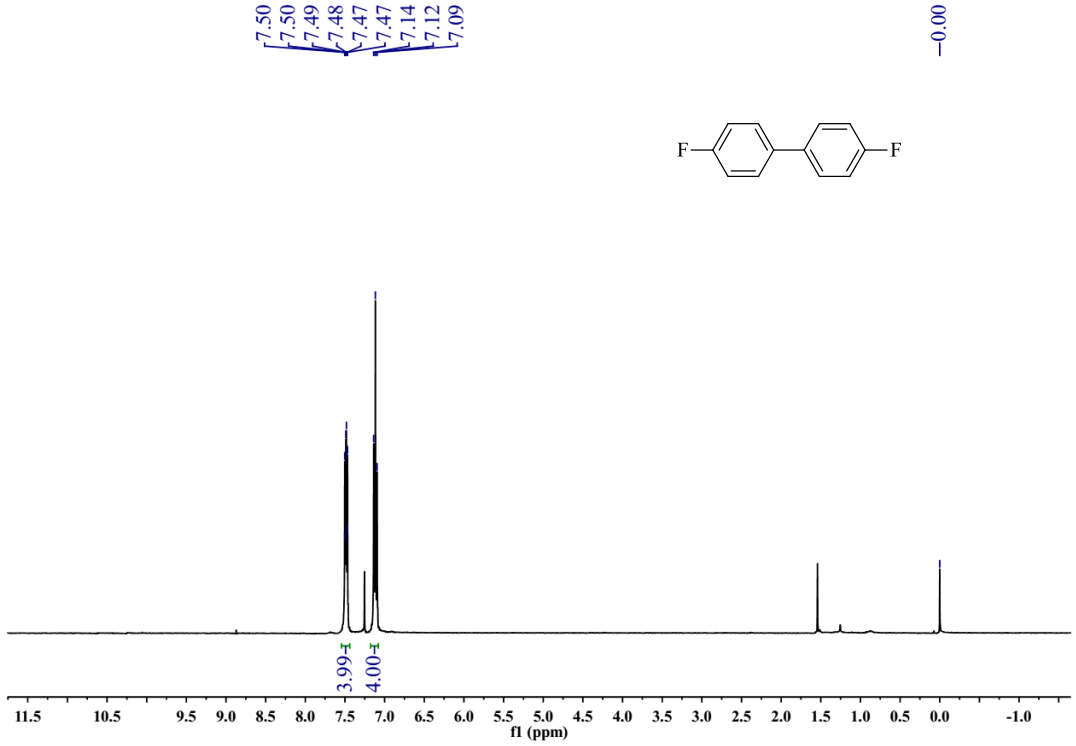
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.18 (m, 6H), 7.09 (d, *J* = 8.0 Hz, 2H), 2.05 (s, 6H) ppm. Data is consistent with that reported in the literature.[6]

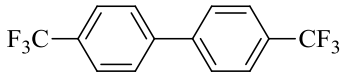




4, 4'-difluoro-1, 1'-biphenyl

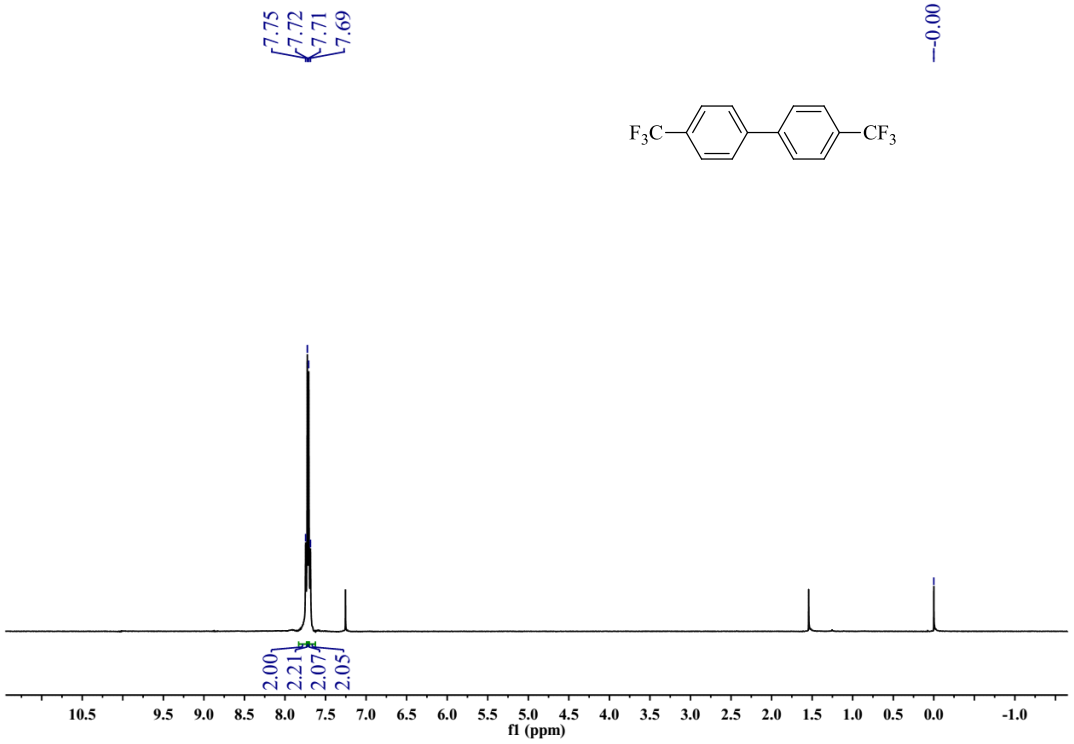
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.54-7.44 (m, 4H), 7.09-7.14 (m, 4H) ppm. Data is consistent with that reported in the literature.[7]

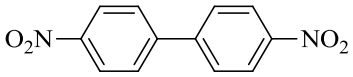




4, 4'-bis(trifluoromethyl)-1, 1'-biphenyl

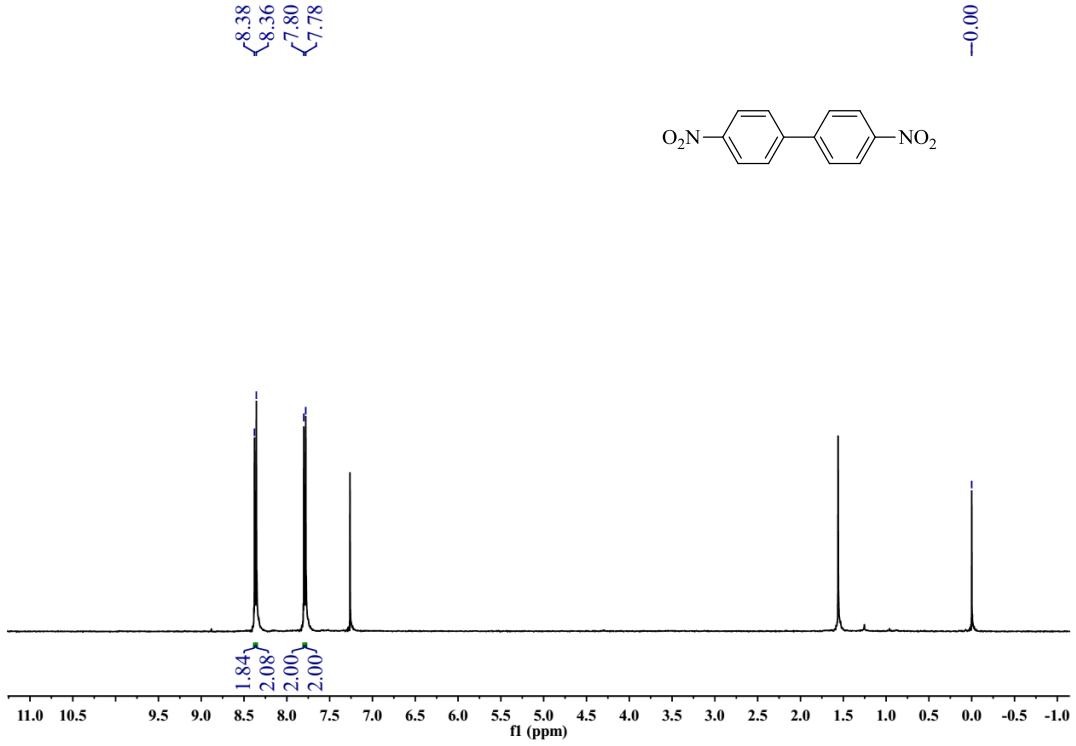
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69-7.75 (m, 8H) ppm. Data is consistent with that reported in the literature.[7]

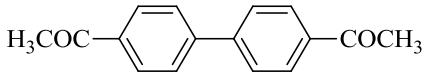




4, 4'-dinitro-1, 1'-biphenyl

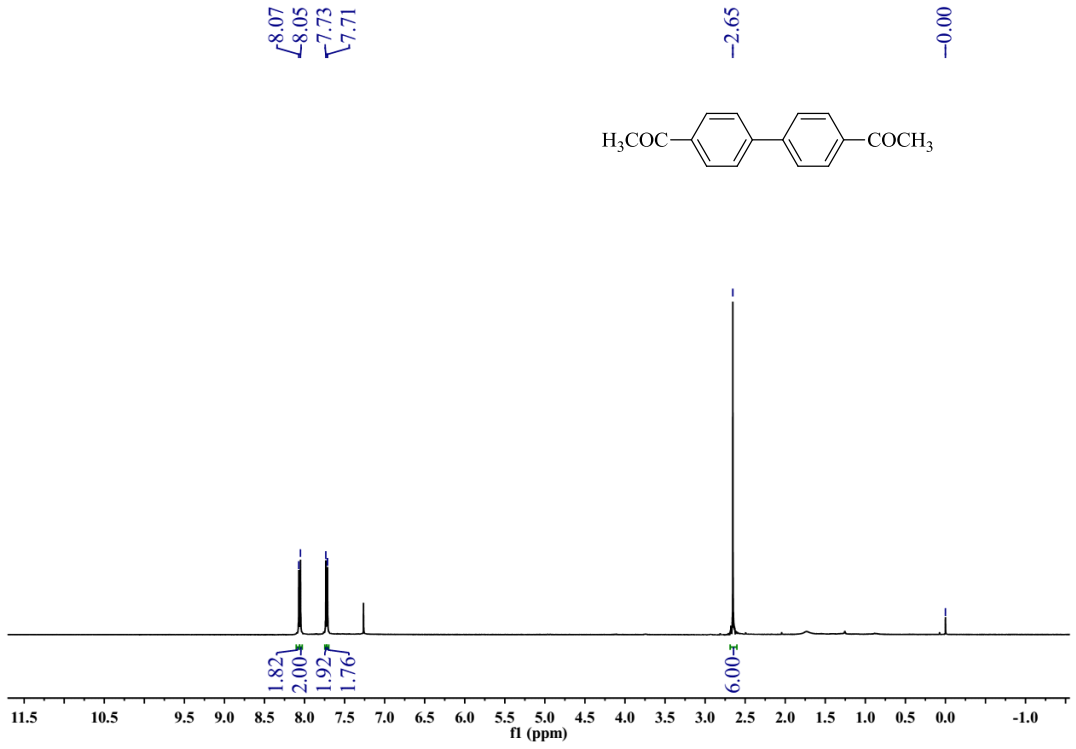
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.37 (d, *J* = 8.0 Hz, 4H), 7.79 (d, *J* = 8.0 Hz, 4H) ppm. Data is consistent with that reported in the literature.[8]

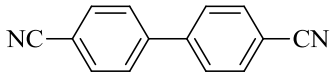




1, 1'-([1, 1'-biphenyl]-4, 4'-diyl) diethanone

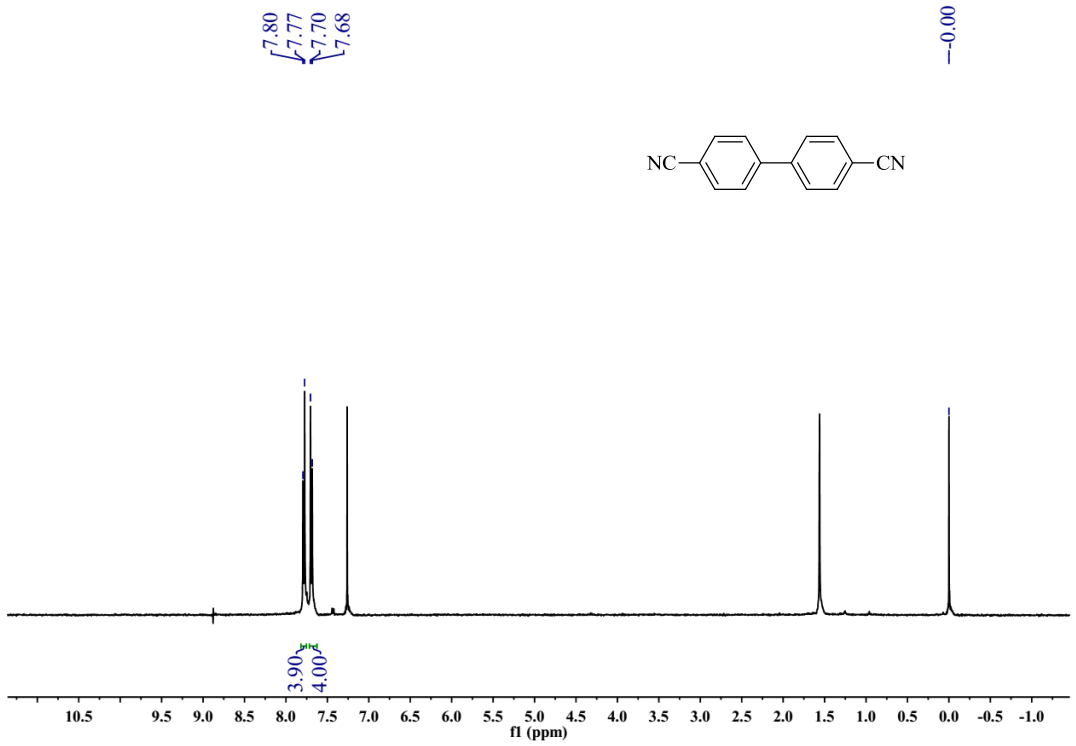
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.06 (d, *J* = 8.0 Hz, 4H), 7.72 (d, *J* = 8.0 Hz, 4H), 2.65 (s, 6H) ppm. Data is consistent with that reported in the literature.[9]

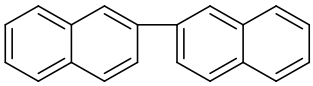




[1, 1'-biphenyl]-4, 4'-dicarbonitrile

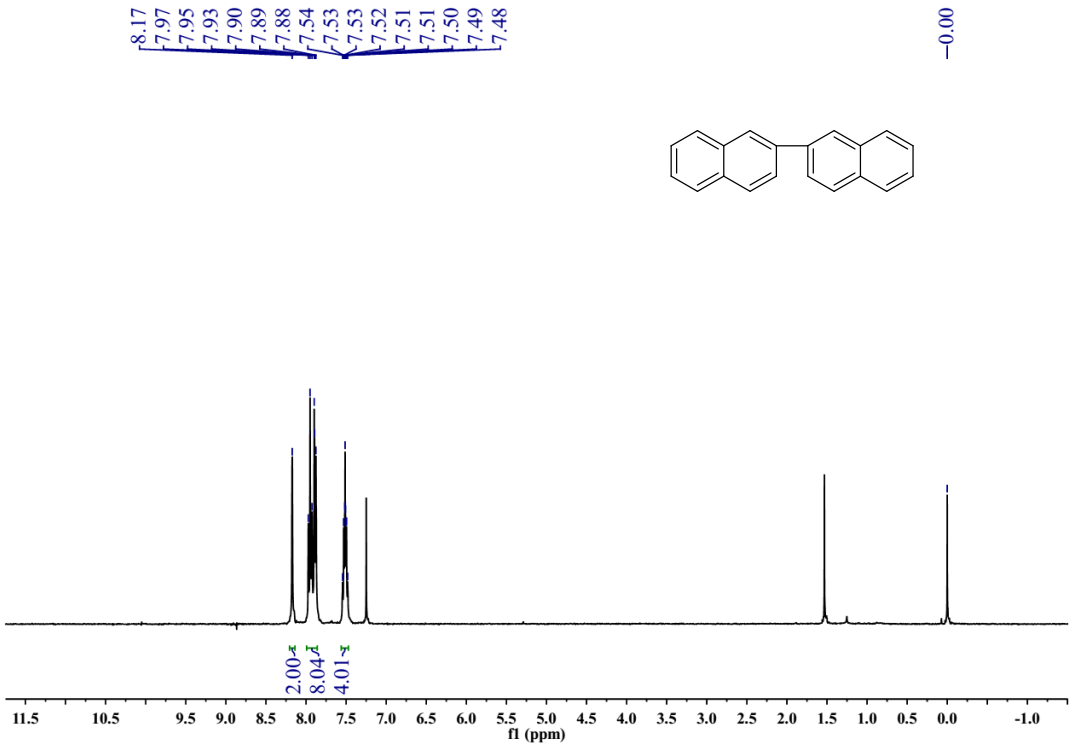
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.0 Hz, 4H), 7.69 (d, J = 8.3 Hz, 4H) ppm. Data is consistent with that reported in the literature.[10]

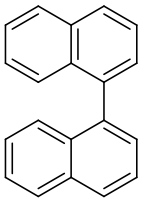




2, 2'-binaphthalene

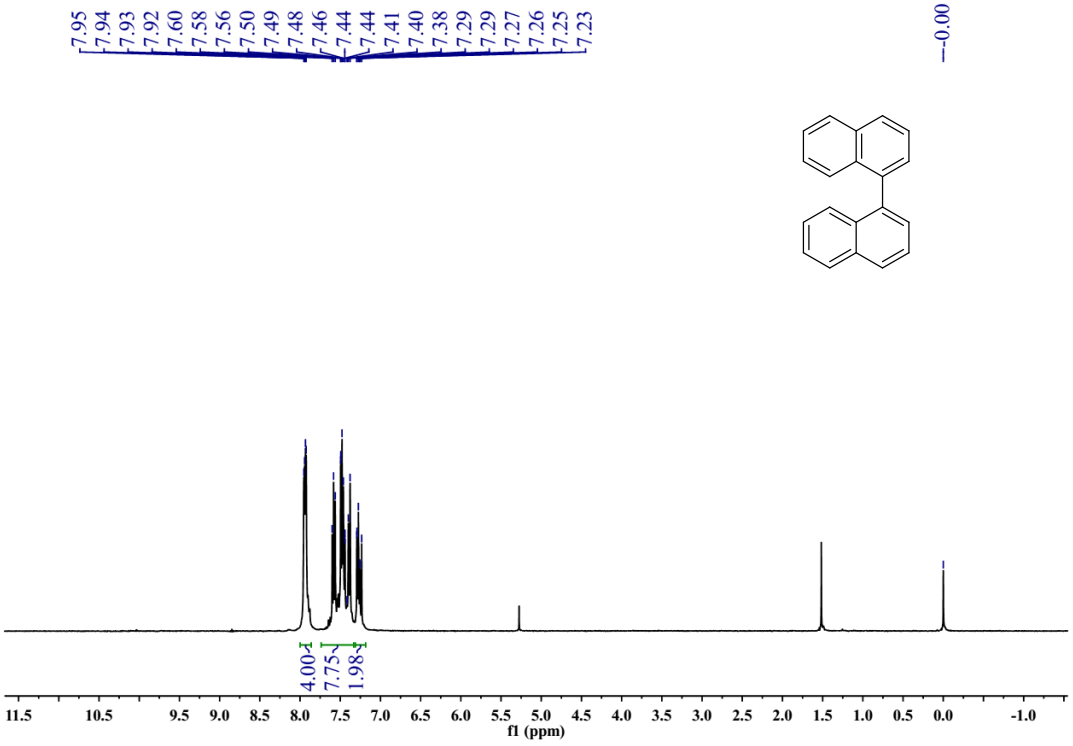
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.17 (s, 2H), 7.92 (dt, *J* = 8.5, 7.8 Hz, 8H), 7.56-7.47 (m, 4H) ppm. Data is consistent with that reported in the literature.[4]

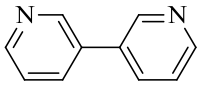




1, 1'-binaphthalene

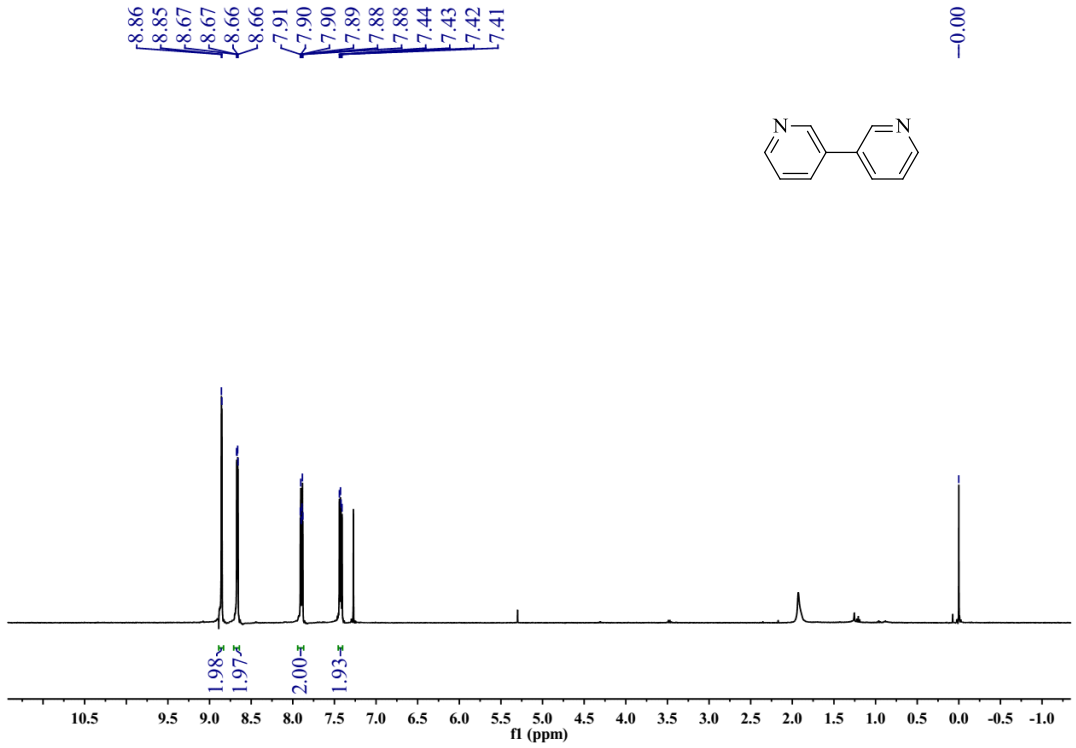
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.94 (dd, *J* = 8.1, 3.6 Hz, 4H), 7.65-7.55 (m, 2H), 7.54-7.41 (m, 4H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.31-7.18 (m, 2H) ppm. Data is consistent with that reported in the literature.[11]

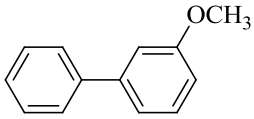




3, 3'-bipyridine

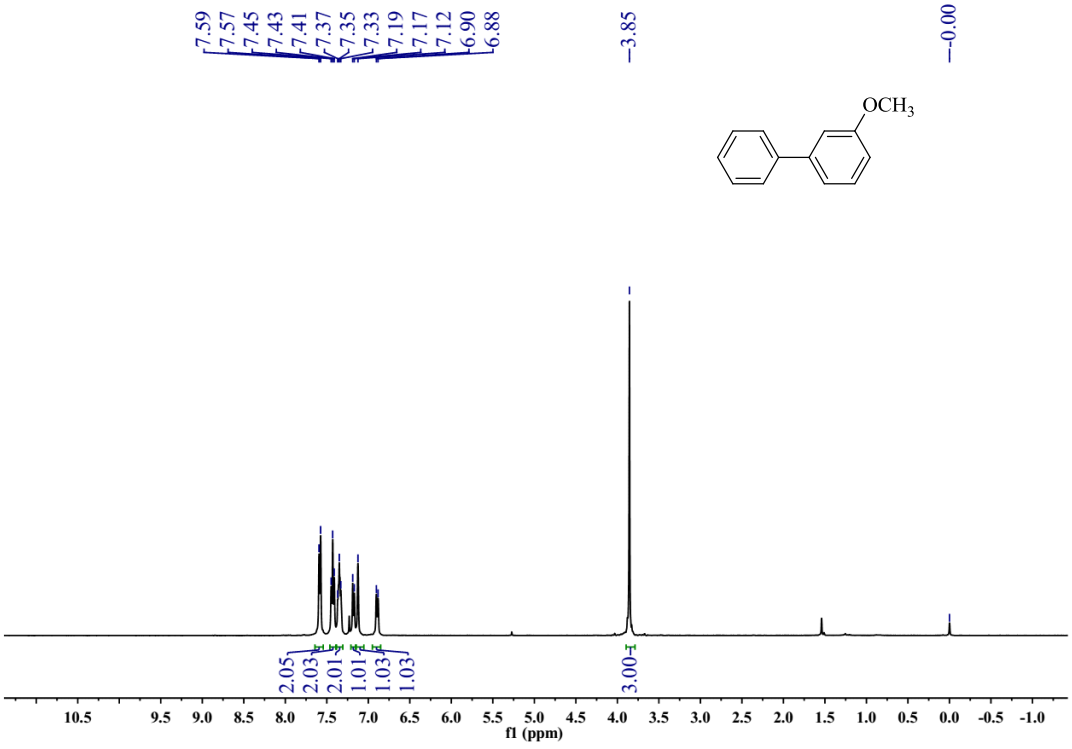
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (d, *J* = 2.0 Hz, 2H), 8.67 (dd, *J* = 4.8, 1.5 Hz, 2H), 7.94-7.87 (m, 2H), 7.42 (dd, *J* = 7.7, 4.9 Hz, 2H) ppm. Data is consistent with that reported in the literature.[12]

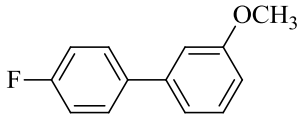




3-methoxy-1, 1'-biphenyl

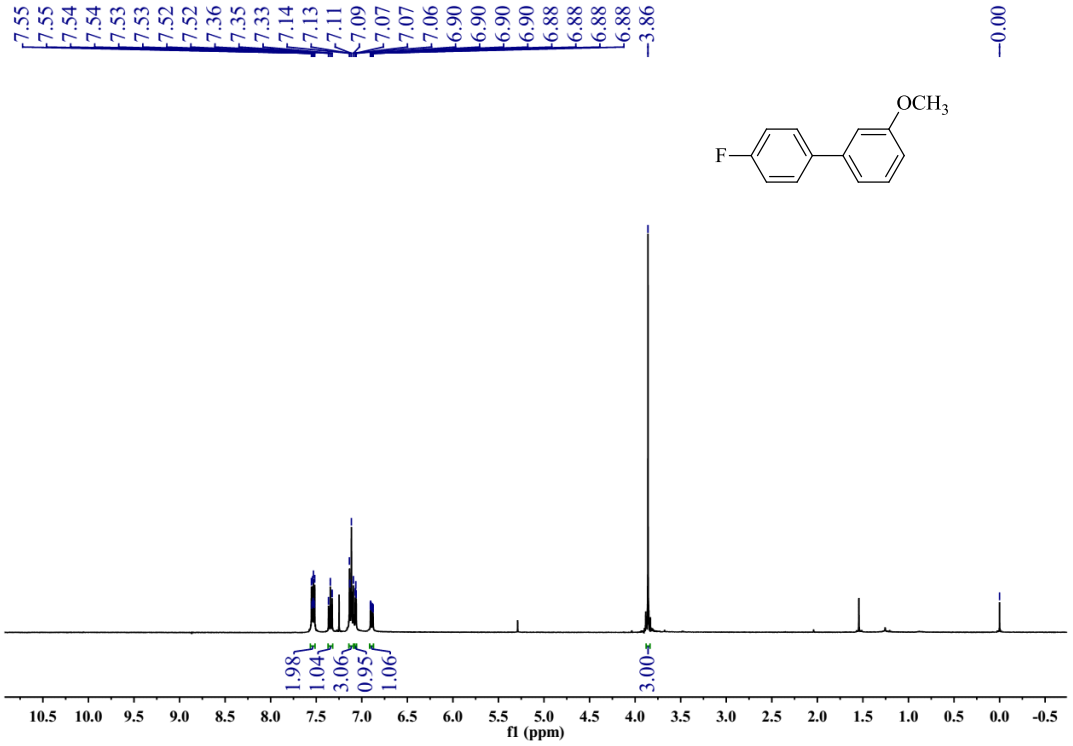
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58 (d, *J* = 7.6 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 2H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 1H), 7.12 (s, 1H), 6.89 (d, *J* = 8.1 Hz, 1H), 3.85 (s, 3H) ppm. Data is consistent with that reported in the literature.[13]

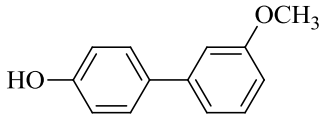




4'-fluoro-3-methoxy-1, 1'-biphenyl

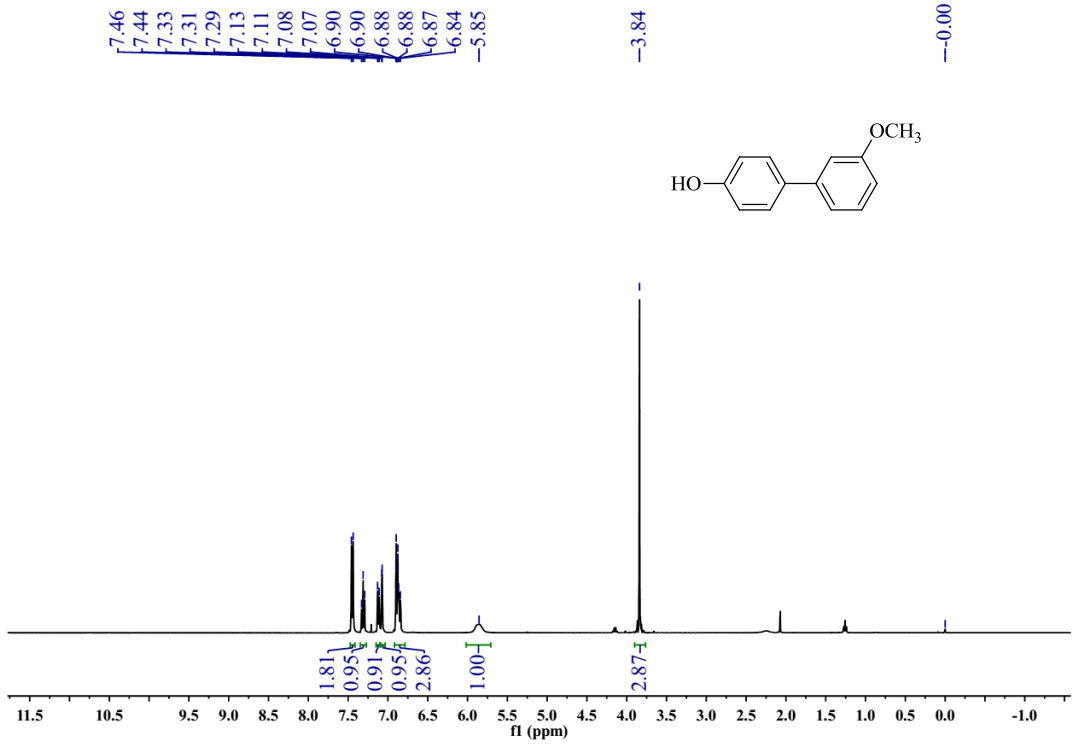
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 – 7.51 (m, 2H), 7.34 (t, *J* = 7.9 Hz, 1H), 7.12 (dd, *J* = 12.0, 5.3 Hz, 3H), 7.08 – 7.06 (m, 1H), 6.89 (ddd, *J* = 8.2, 2.5, 0.8 Hz, 1H), 3.86 (s, 3H) ppm. Data is consistent with that reported in the literature.[14]

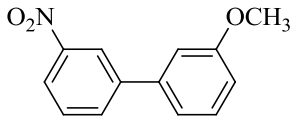




3'-methoxy-[1, 1'-biphenyl]-4-ol

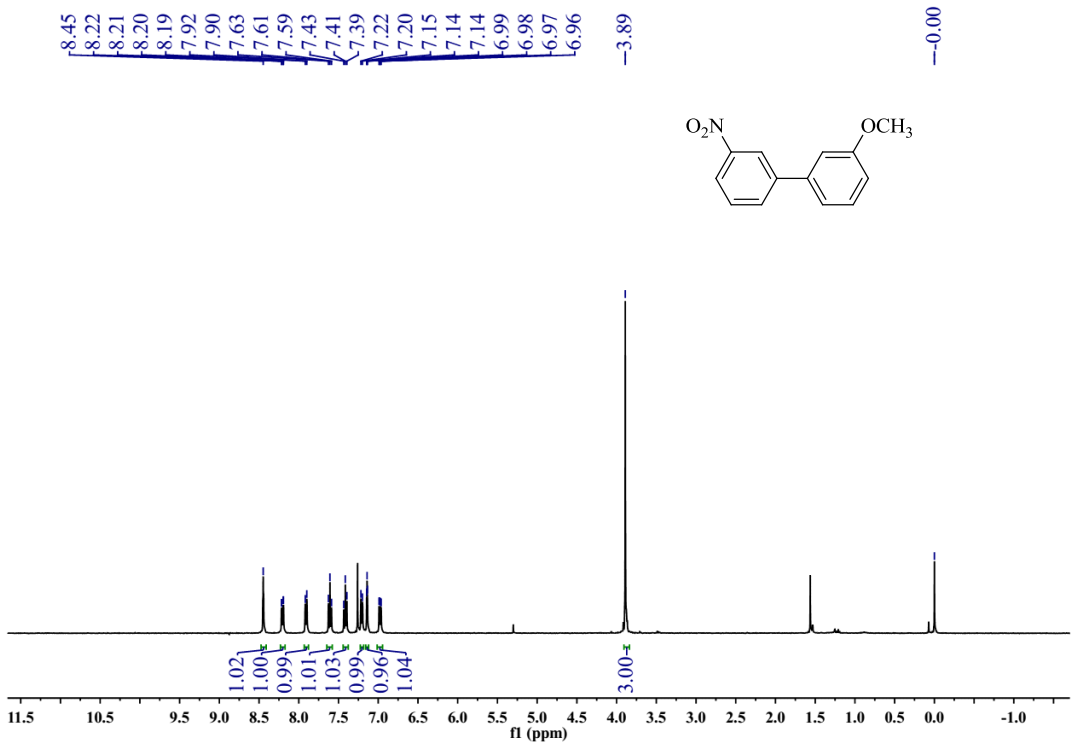
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.31 (t, *J* = 8.0 Hz, 1H), 7.12 (d, *J* = 7.7 Hz, 1H), 7.07 (d, *J* = 1.8 Hz, 1H), 6.92-6.78 (m, 3H), 5.85 (br, 1H), 3.84 (s, 3H) ppm. Data is consistent with that reported in the literature.[5]

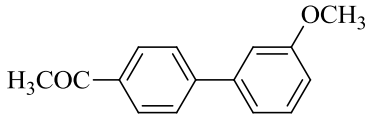




3-methoxy-3'-nitro-1, 1'-biphenyl

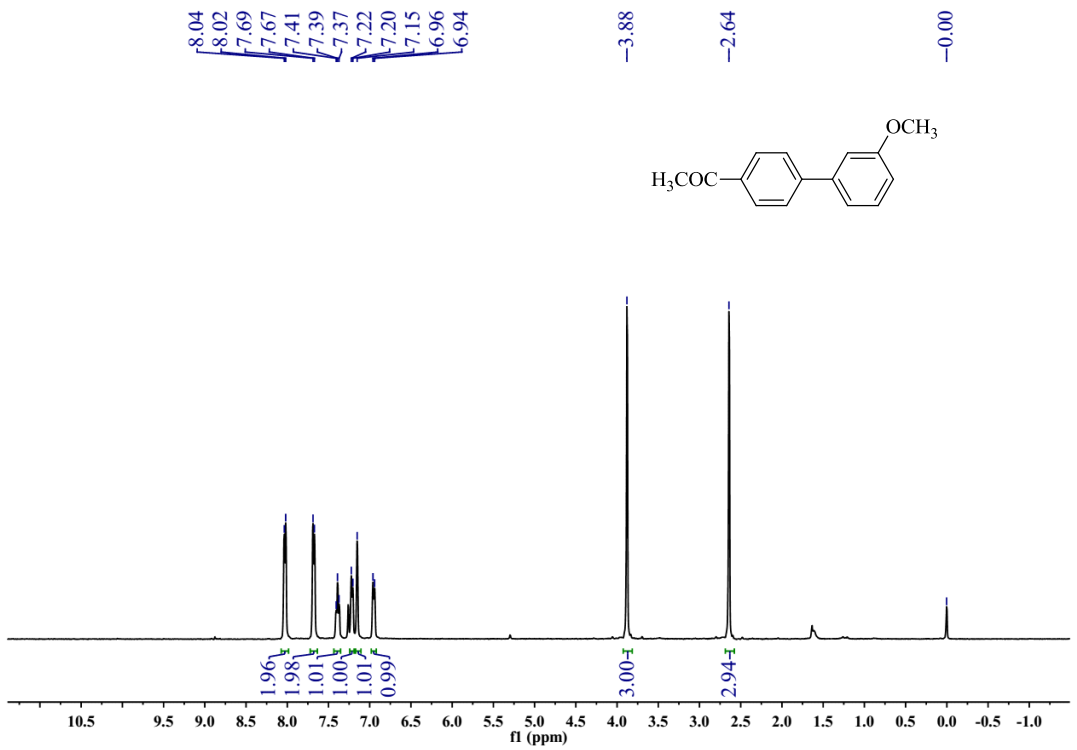
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (s, 1H), 8.21 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.91 (d, *J* = 7.8 Hz, 1H), 7.61 (t, *J* = 8.0 Hz, 1H), 7.41 (t, *J* = 8.0 Hz, 1H), 7.21 (d, *J* = 7.7 Hz, 1H), 7.16-7.12 (m, 1H), 6.98 (dd, *J* = 8.2, 2.2 Hz, 1H), 3.89 (s, 3H) ppm. Data is consistent with that reported in the literature.[15]

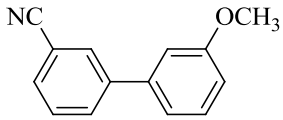




1-(3'-methoxy-[1, 1'-biphenyl]-4-yl) ethanone

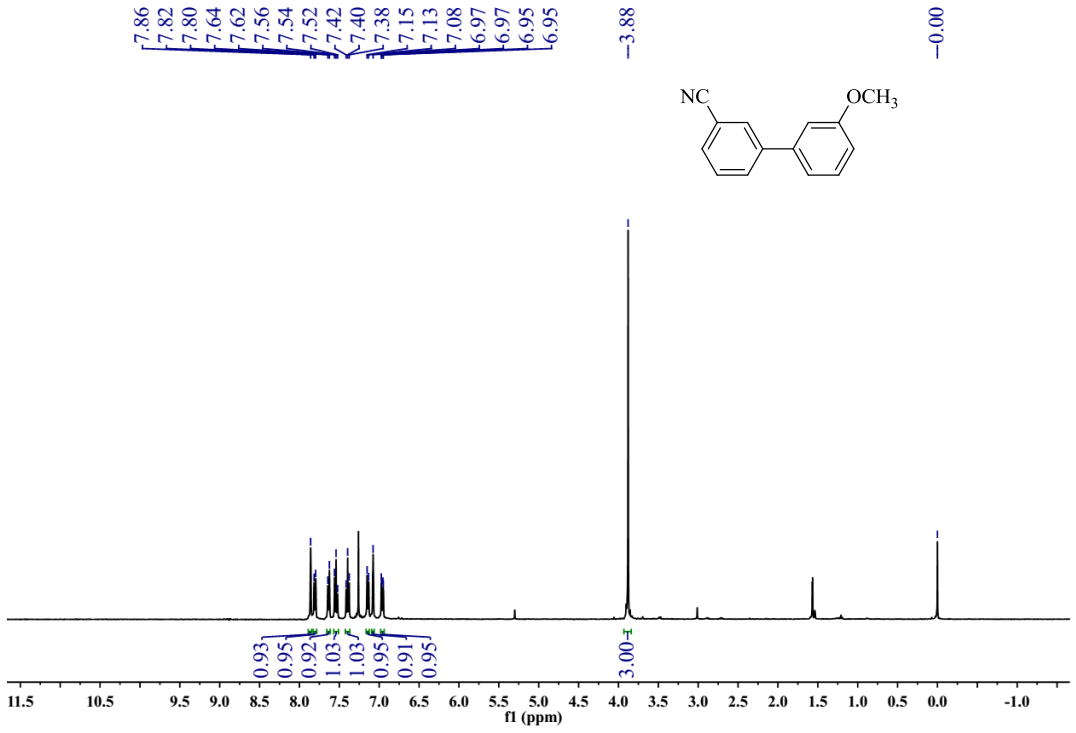
Light red solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 6.7 Hz, 2H), 7.68 (d, *J* = 6.7 Hz, 2H), 7.39 (t, *J* = 6.9 Hz, 1H), 7.21 (d, *J* = 7.3 Hz, 1H), 7.15 (s, 1H), 6.95 (d, *J* = 7.9 Hz, 1H), 3.88 (s, 3H), 2.64 (s, 3H) ppm. Data is consistent with that reported in the literature.[16]

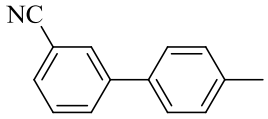




3'-methoxy-[1, 1'-biphenyl]-3-carbonitrile

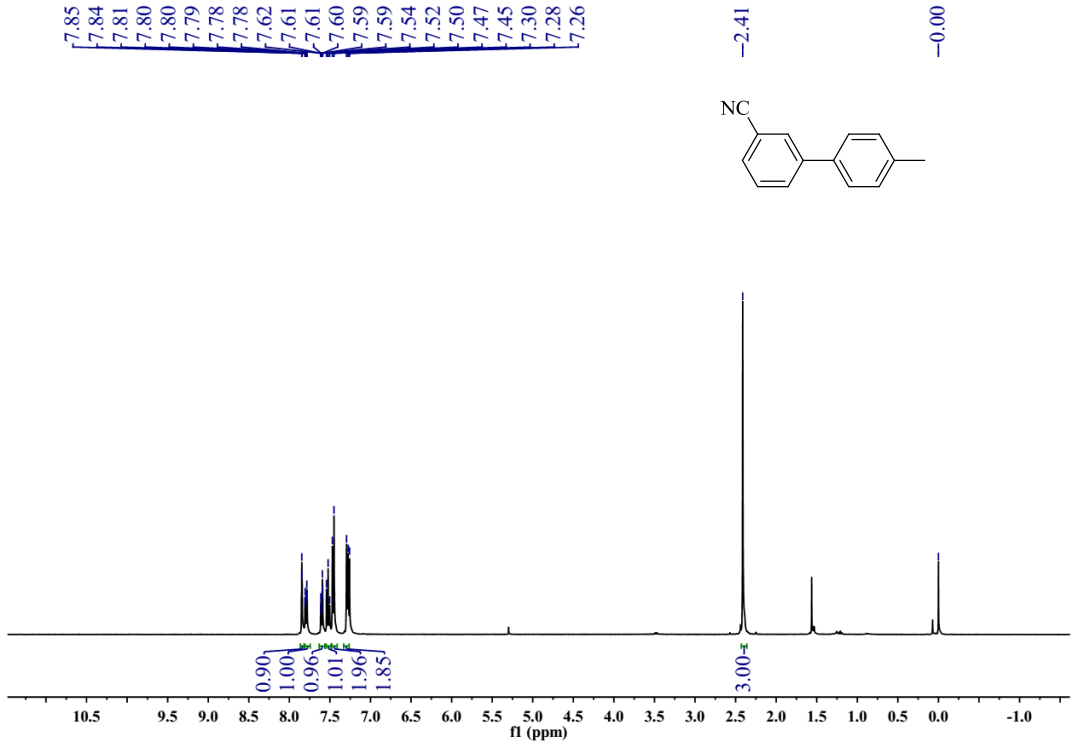
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.86 (s, 1H), 7.81 (d, *J* = 7.9 Hz, 1H), 7.63 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 7.08 (s, 1H), 6.96 (dd, *J* = 8.2, 2.3 Hz, 1H), 3.88 (s, 3H) ppm. Data is consistent with that reported in the literature.[17]

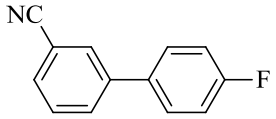




4'-methyl-[1, 1'-biphenyl]-3-carbonitrile

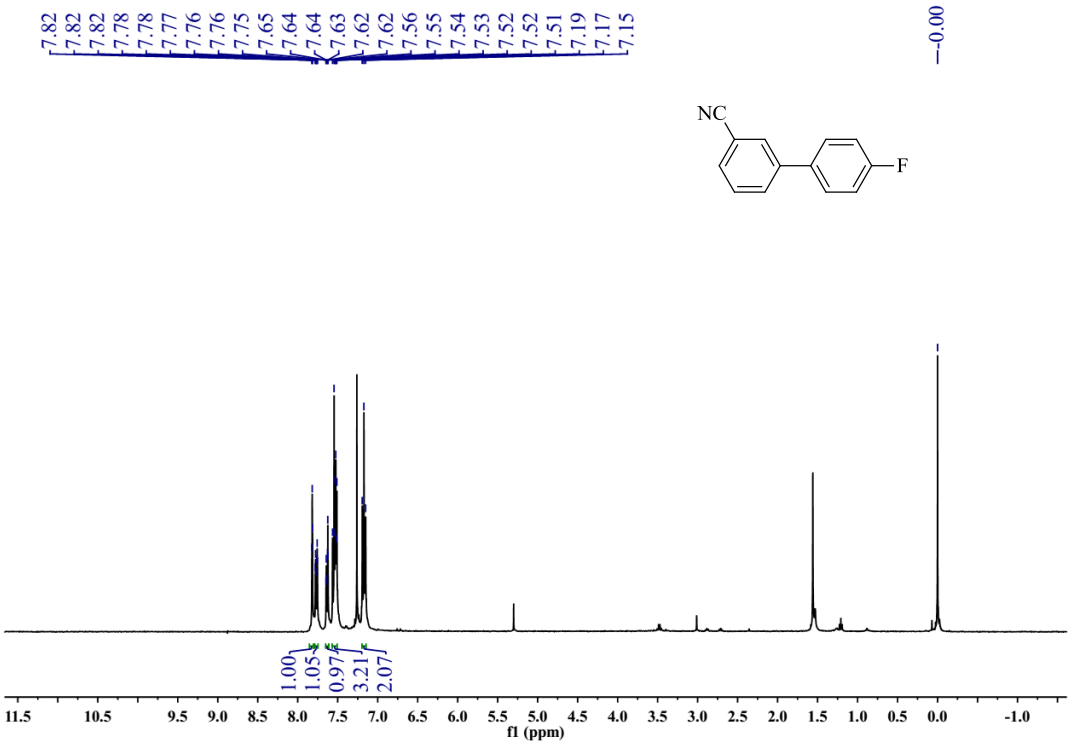
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, *J* = 1.5 Hz, 1H), 7.81-7.74 (m, 1H), 7.63-7.56 (m, 1H), 7.52 (t, *J* = 7.7 Hz, 1H), 7.46 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H) ppm. Data is consistent with that reported in the literature.[18]

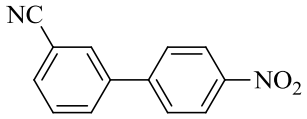




4'-fluoro-[1, 1'-biphenyl]-3-carbonitrile

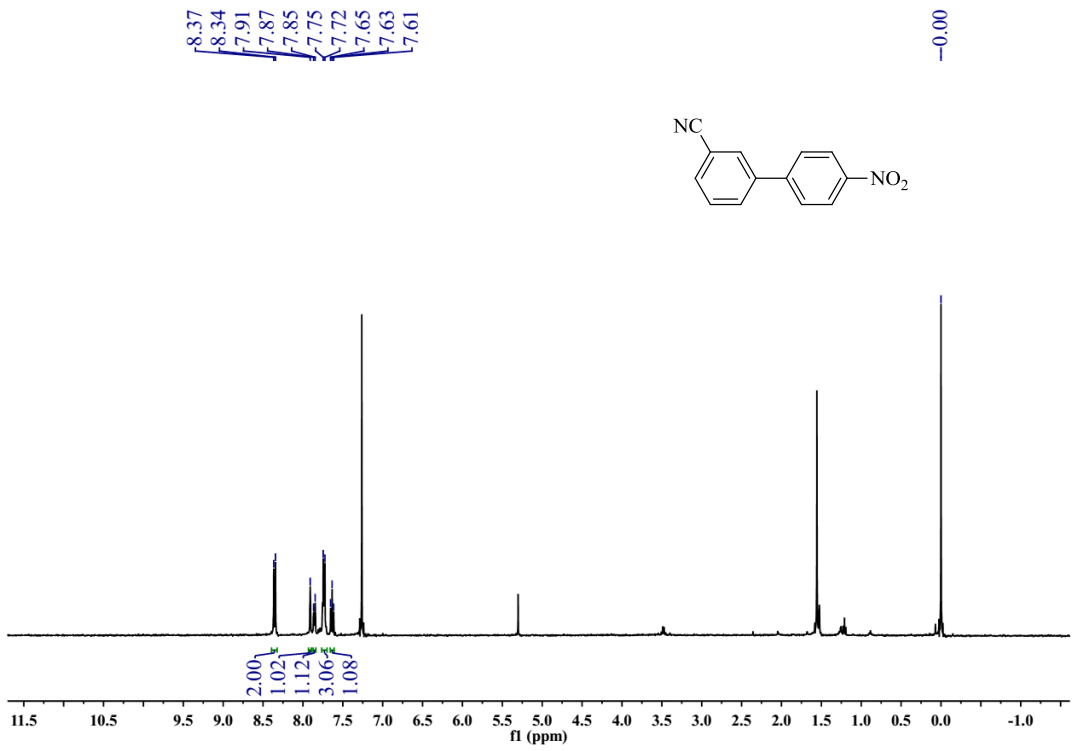
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (t, *J* = 1.5 Hz, 1H), 7.79-7.75 (m, 1H), 7.65-7.61 (m, 1H), 7.57-7.51 (m, 3H), 7.17 (t, *J* = 8.6 Hz, 2H) ppm. Data is consistent with that reported in the literature.[19]

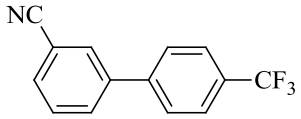




4'-nitro-[1, 1'-biphenyl]-3-carbonitrile

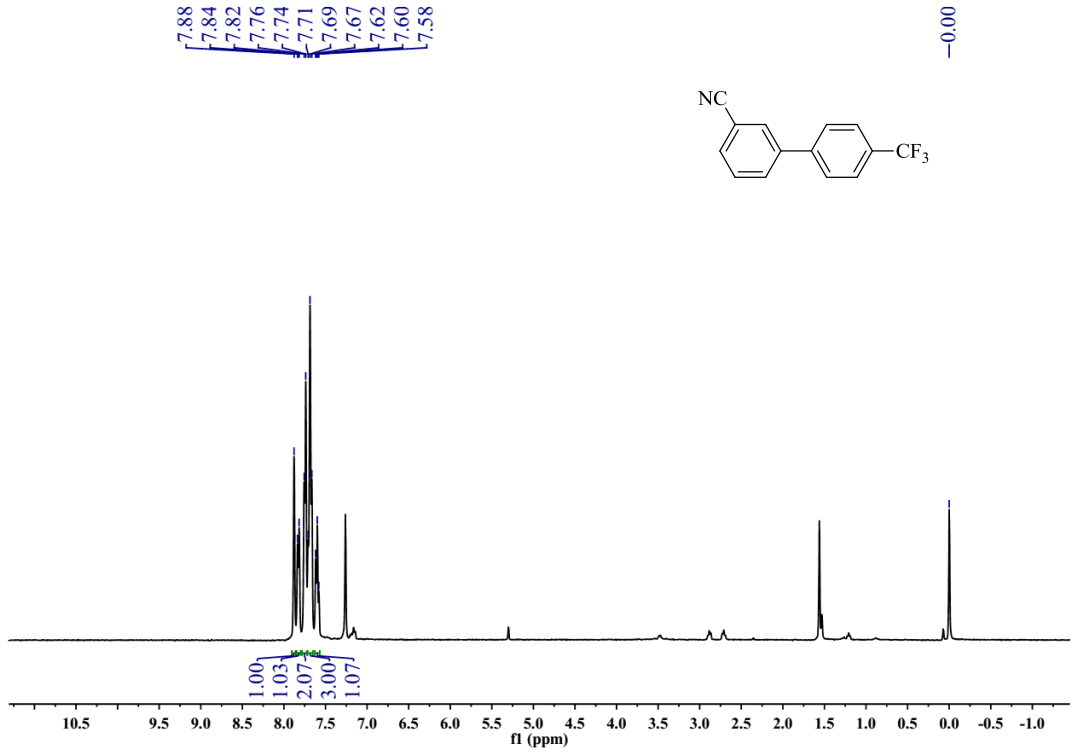
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.36 (d, *J* = 8.8 Hz, 2H), 7.91 (s, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.73 (d, *J* = 8.8 Hz, 3H), 7.63 (t, *J* = 7.8 Hz, 1H) ppm.

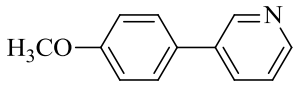




4'-(trifluoromethyl)-[1, 1'-biphenyl]-3-carbonitrile

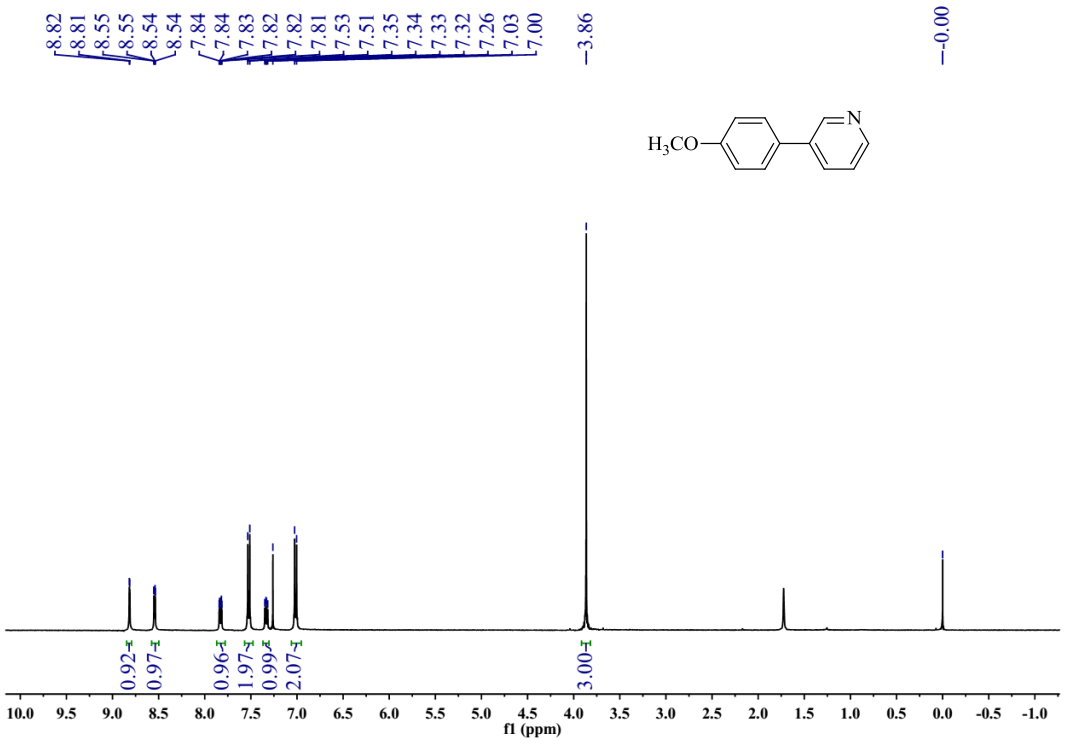
White solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (s, 1H), 7.83 (d, *J* = 7.7 Hz, 1H), 7.75 (d, *J* = 7.5 Hz, 2H), 7.69 (t, *J* = 8.7 Hz, 3H), 7.60 (t, *J* = 7.7 Hz, 1H) ppm. Data is consistent with that reported in the literature.[20]

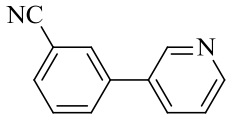




3-(4-methoxyphenyl) pyridine

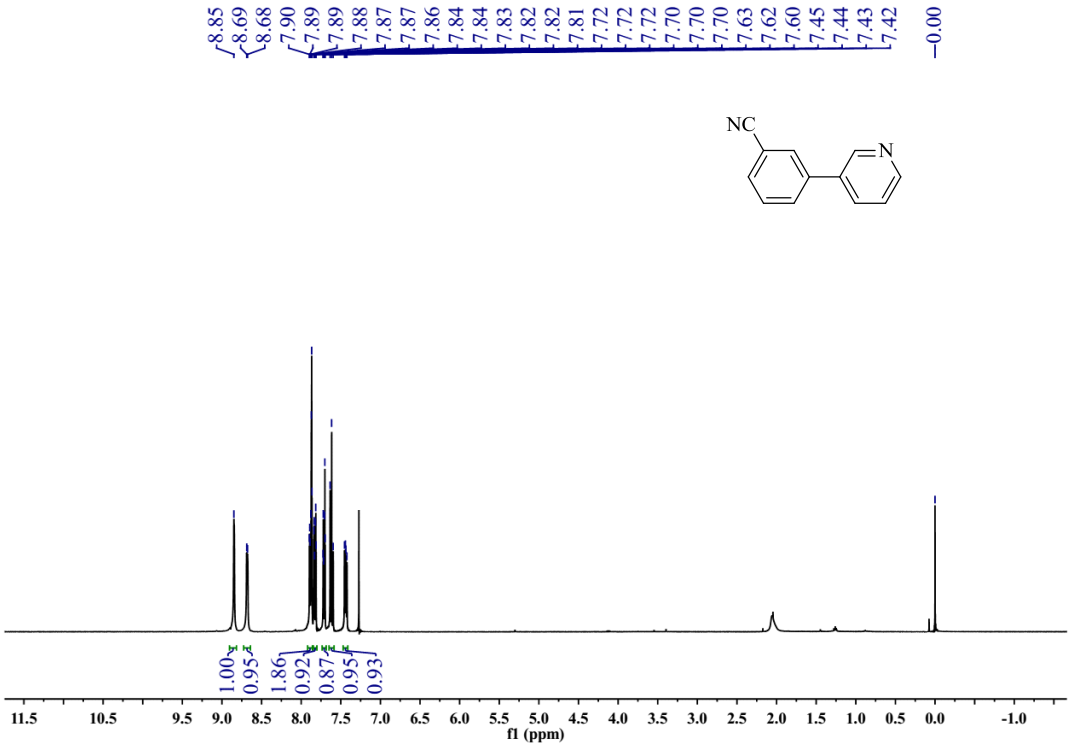
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (d, *J* = 1.6 Hz, 1H), 8.54 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.87 – 7.78 (m, 1H), 7.52 (d, *J* = 8.8 Hz, 2H), 7.33 (dd, *J* = 7.6, 5.1 Hz, 1H), 7.01 (d, *J* = 8.8 Hz, 2H), 3.86 (s, 3H) ppm. Data is consistent with that reported in the literature.[21]

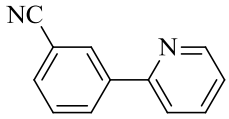




3-(pyridin-3-yl) benzonitrile

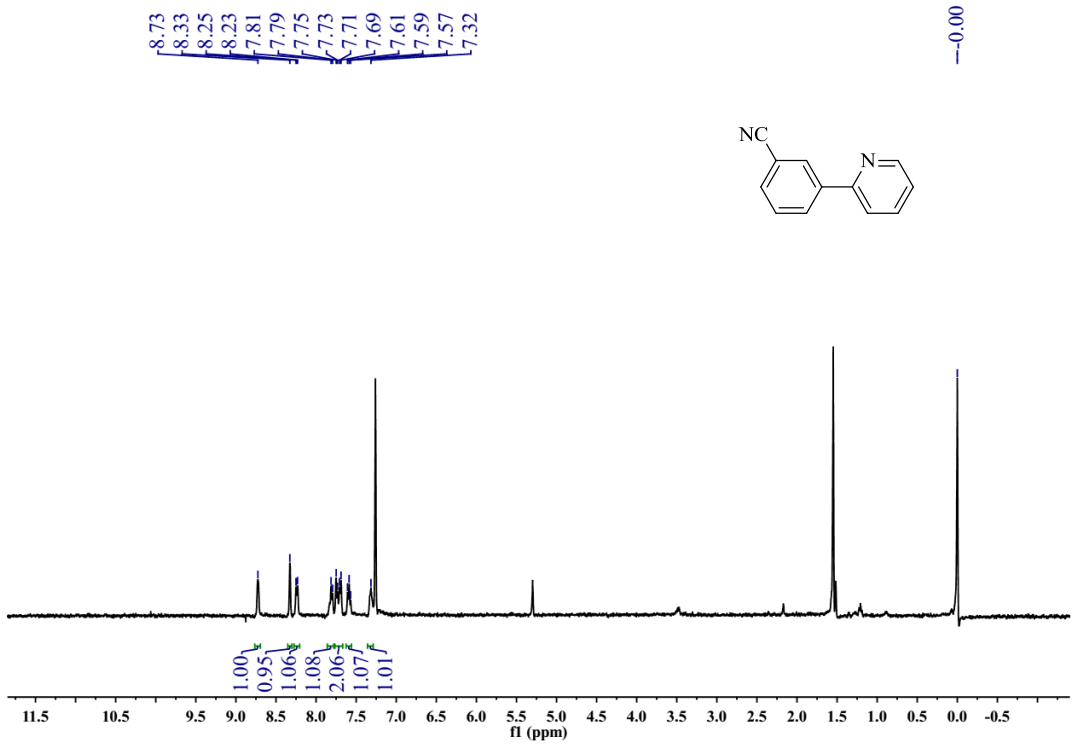
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.85 (s, 1H), 8.68 (d, *J* = 3.7 Hz, 1H), 7.92-7.86 (m, 2H), 7.85-7.80 (m, 1H), 7.71 (dt, *J* = 7.8, 1.4 Hz, 1H), 7.62 (t, *J* = 7.8 Hz, 1H), 7.44 (dd, *J* = 7.6, 4.9 Hz, 1H) ppm. Data is consistent with that reported in the literature.[22]

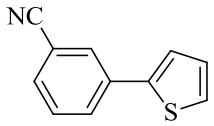




3-(pyridin-2-yl) benzonitrile

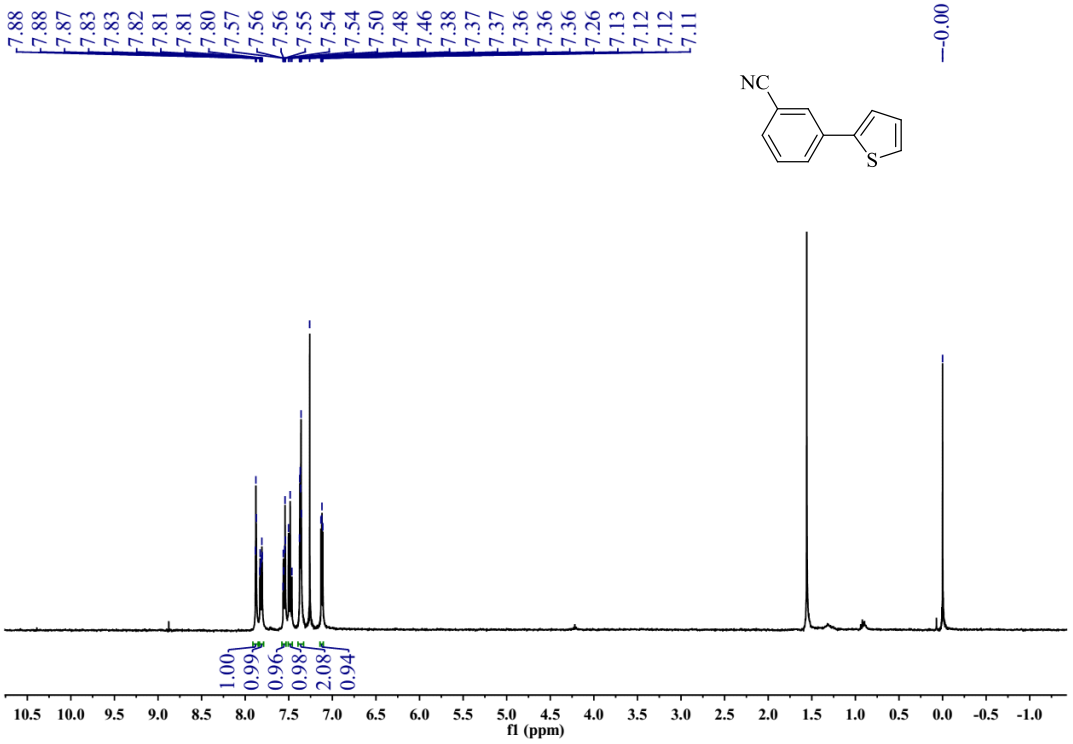
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (s, 1H), 8.33 (s, 1H), 8.24 (d, *J* = 7.9 Hz, 1H), 7.80 (d, *J* = 7.9 Hz, 1H), 7.72 (dd, *J* = 17.0, 7.3 Hz, 2H), 7.59 (t, *J* = 7.9 Hz, 1H), 7.32 (s, 1H) ppm. Data is consistent with that reported in the literature.[23]

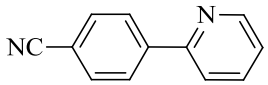




3-(thiophen-2-yl) benzonitrile

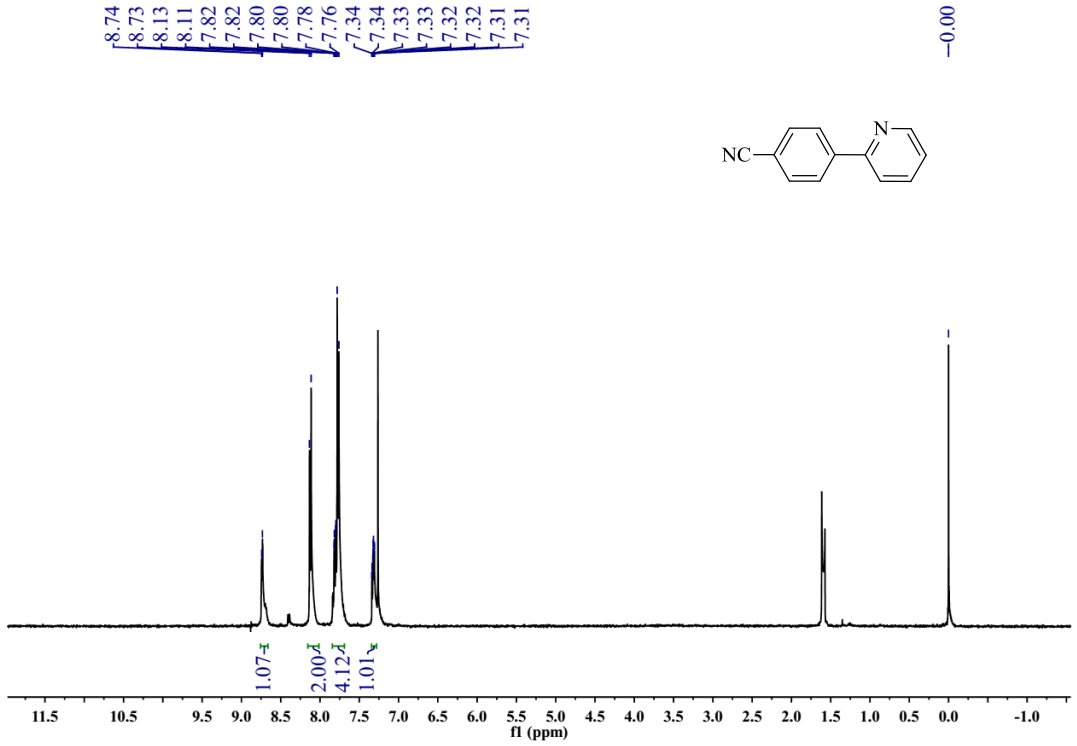
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.88 (t, *J* = 1.6 Hz, 1H), 7.84-7.79 (m, 1H), 7.55 (dt, *J* = 7.7, 1.3 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.37 (dt, *J* = 3.5, 1.2 Hz, 2H), 7.12 (dd, *J* = 5.0, 3.8 Hz, 1H) ppm. Data is consistent with that reported in the literature.[24]

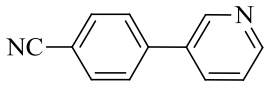




4-(pyridin-2-yl) benzonitrile

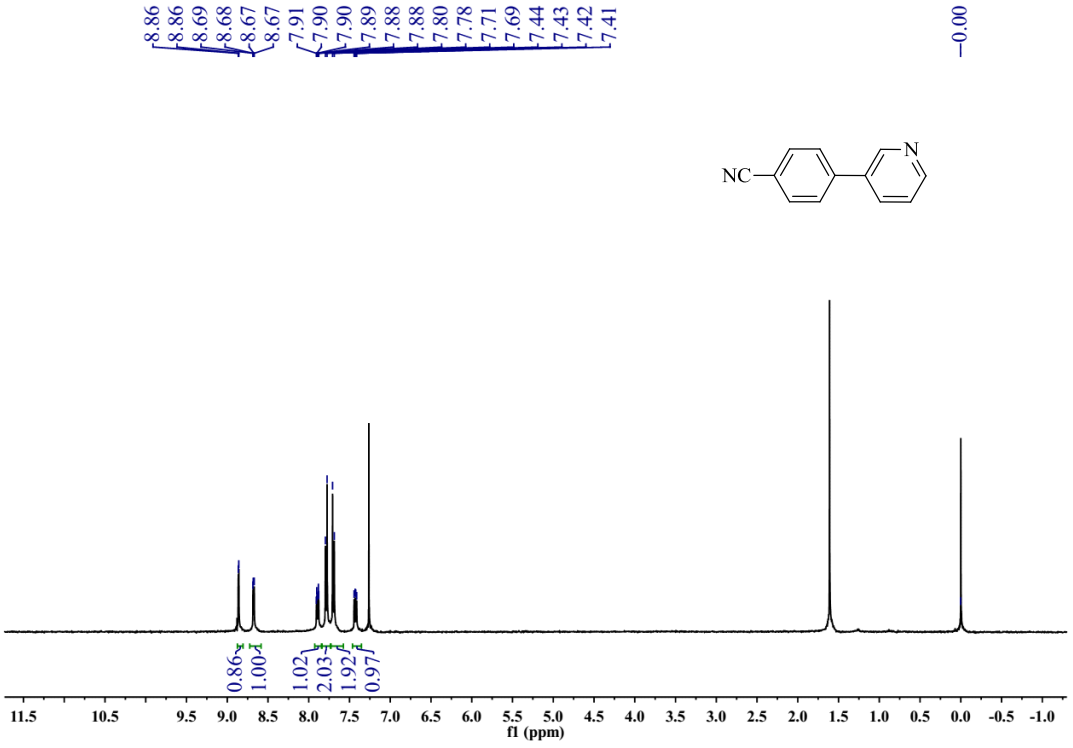
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (d, *J* = 3.6 Hz, 1H), 8.12 (d, *J* = 8.5 Hz, 2H), 7.84-7.69 (m, 4H), 7.32 (ddd, *J* = 7.2, 4.8, 1.3 Hz, 1H) ppm. Data is consistent with that reported in the literature.[24]

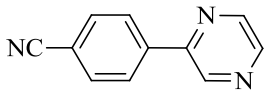




4-(pyridin-3-yl) benzonitrile

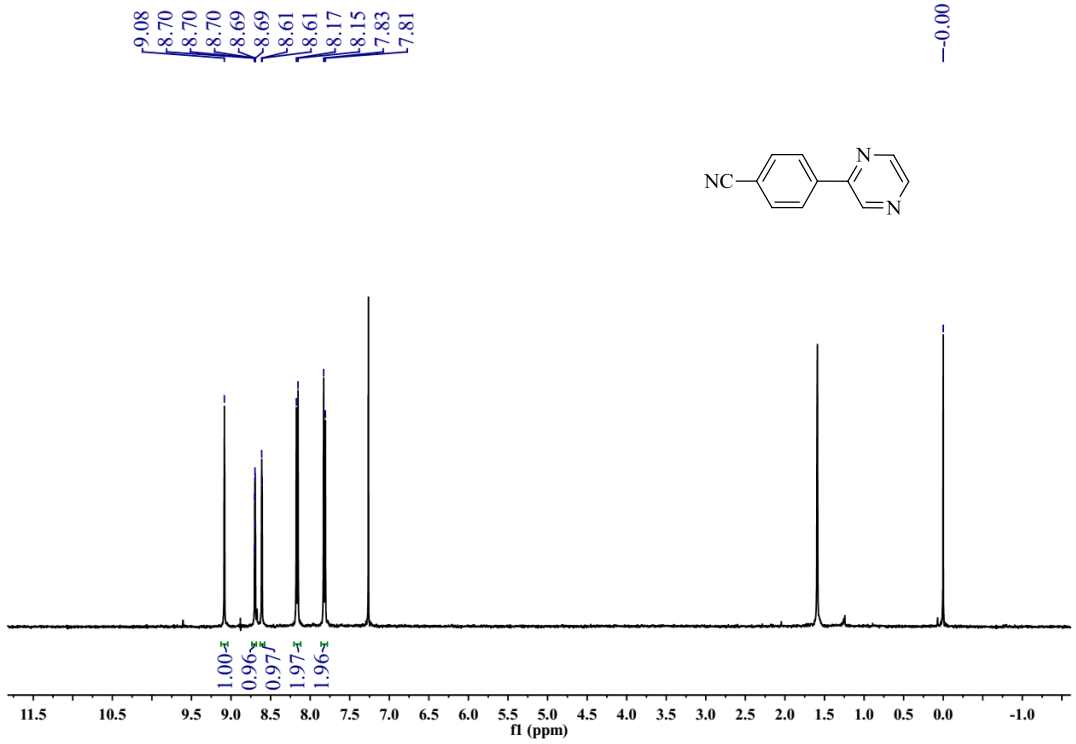
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (d, *J* = 2.2 Hz, 1H), 8.68 (dd, *J* = 4.8, 1.5 Hz, 1H), 7.93-7.84 (m, 1H), 7.79 (d, *J* = 8.3 Hz, 2H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.43 (dd, *J* = 8.0, 4.8 Hz, 1H) ppm. Data is consistent with that reported in the literature.[24]

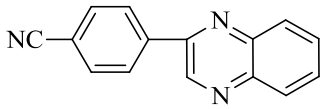




4-(pyrazin-2-yl) benzonitrile

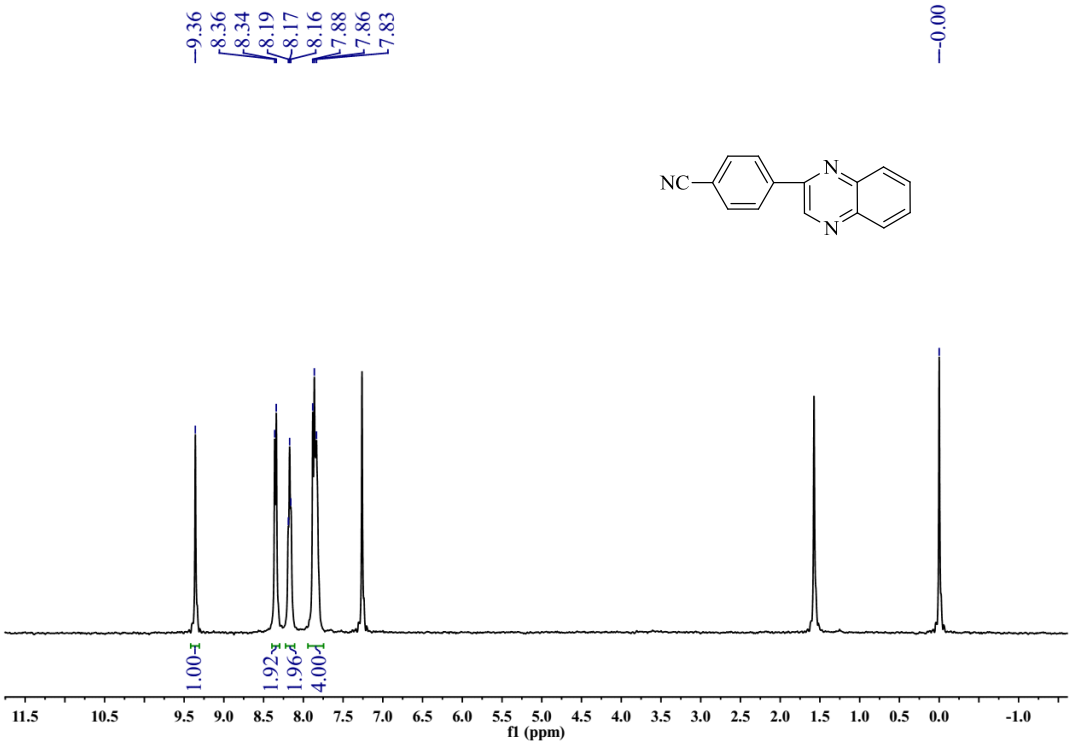
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (s, 1H), 8.70 (dt, *J* = 2.4, 1.2 Hz, 1H), 8.61 (d, *J* = 2.4 Hz, 1H), 8.16 (d, *J* = 8.5 Hz, 2H), 7.82 (d, *J* = 8.5 Hz, 2H) ppm. Data is consistent with that reported in the literature.[25]

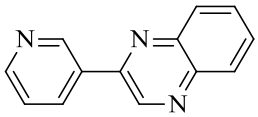




4-(quinoxalin-2-yl) benzonitrile

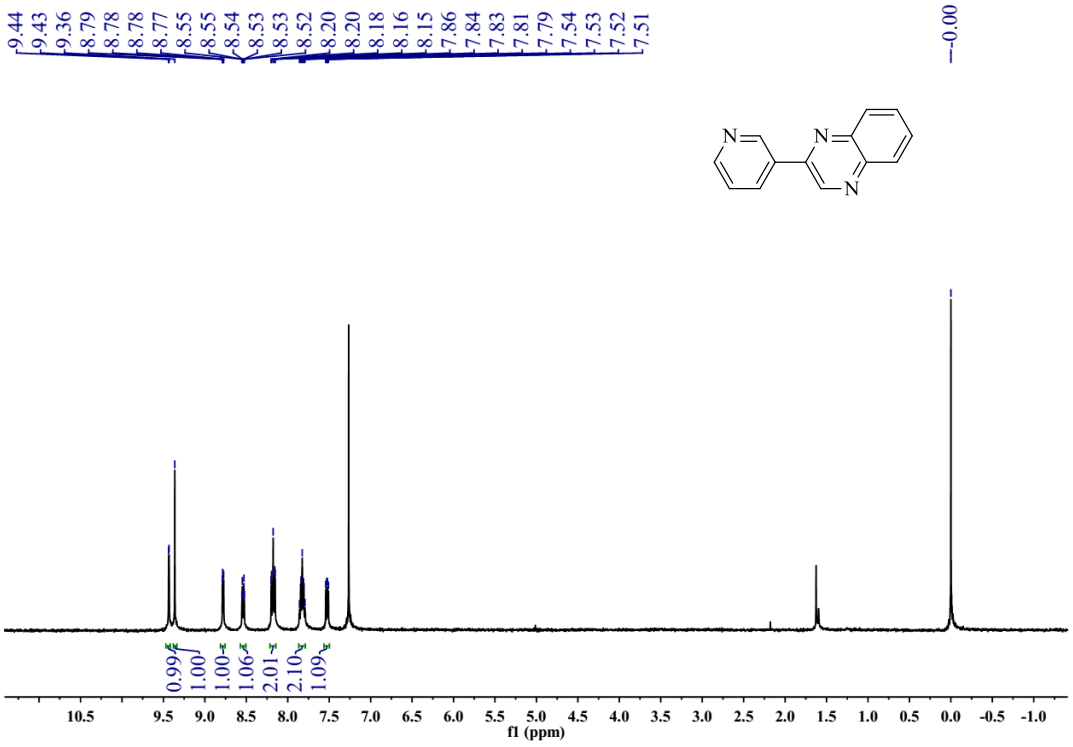
Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.36 (s, 1H), 8.35 (d, *J* = 7.9 Hz, 2H), 8.17 (t, *J* = 6.1 Hz, 2H), 7.94-7.74 (m, 4H) ppm. Data is consistent with that reported in the literature.[26]





2-(pyridin-3-yl) quinoxaline

Yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.43 (d, *J* = 2.2 Hz, 1H), 9.36 (s, 1H), 8.78 (dd, *J* = 4.8, 1.6 Hz, 1H), 8.57 – 8.50 (m, 1H), 8.21 – 8.14 (m, 2H), 7.87 – 7.79 (m, 2H), 7.53 (dd, *J* = 8.0, 4.9 Hz, 1H) ppm. Data is consistent with that reported in the literature.[27]



References:

1 D.-W. Lee and J. Yun, *Bull. Korean Chem. Soc.*, 2004, **25**, 29-30.

2 N. Barbero and R. Martin, *Org. Lett.*, 2012, **14**, 796-799.

3 D. Toummini, F. Ouazzani and M. Taillefer, *Org. Lett.*, 2013, **15**, 4690-4693.

4 Y. Miyake, M. Wu, M. J. Rahman, Y. Kuwatani and M. Iyoda, *J. Org. Chem.*, 2006, **71**, 6110-6117.

5 B. Schmidt and M. Riemer, *J. Org. Chem.*, 2014, **79**, 4104-4118.

6 J. Graff, T. Debande, J. Praz, L. Guénée and A. Alexakis, *Org. Lett.*, 2013, **15**, 4270-4273.

7 R. N. Dhital, C. Kamonsatikul, E. Somsook, K. Bobuatong, M. Ehara, S. Karanjit and H. Sakurai, *J. Am. Chem. Soc.*, 2012, **134**, 20250-20253.

8 L. Wang, Y.-H. Zhang, L.-F. Liu and Y.-G. Wang, *J. Org. Chem.*, 2006, **71**, 1284-1287.

9 R. B. N. Baig and R. S. Varma, *Green Chem.*, 2013, **15**, 398-417.

10 C. F. Nising, U. K. Schmid, M. Nieger and S. Bräse, *J. Org. Chem.*, 2004, **69**, 6830-6833.

11 B. Inés, R. SanMartin, F. Churruca, E. Domínguez, M. K. Urtiaga and M. I. Arriortua, *Organometallics*, 2008, **27**, 2833-2839.

12 K. Billingsley and S. L. Buchwald, *J. Am. Chem. Soc.*, 2007, **129**, 3358-3366.

13 P. Leowanawat, N. Zhang, A.-M. Resmerita, B. M. Rosen and V. Percec, *J. Org. Chem.*, 2011, **76**, 9946-9955.

14 Z.-Y. Wang, G.-Q. Chen and L.-X. Shao, *J. Org. Chem.*, 2012, **77**, 6608-6614

15 L. J. Goossen, C. Linder, N. Rodríguez and P. P. Lange, *Chem.–Eur. J.*, 2009, **15**, 9336-9349.

16 G.-L. Zhang, *Synthesis*, 2005, 537-542.

17 T. Ginman, J. Viklund, J. Malmström, J. Blid, R. Emond, R. Forsblom, A. Johansson, A. Kers, F. Lake, F. Sehgelmeble, K. J. Sterky, M. Bergh, A. Lindgren, P. Johansson, F. Jeppsson, J. Fälting, Y. Gravenfors and F. Rahm, *J. Med. Chem.*, 2013, **56**, 4181-4205.

18 A.-L. Liu , X.–M. Zhang and W.–Z. Chen, *Organometallics*, 2009, **28**, 4868-4871.

19 I. R. Baxendale, C. M. Griffiths-Jones, S. V. Ley and G. K. Tranmer, *Chem.–Eur. J.*, 2006, **12**, 4407-4416.

20 S. Sase, M. Jaric, A. Metzger, V. Malakhov and P. Knochel, *J. Org. Chem.*, 2008, **73**, 7380-7382.

21 X. Chen, L.–M. Zhou, Y.–M. Li, T. Xie and S.–L. Zhou, *J. Org. Chem.*, 2014, **79**, 230-239.

22 G. A. Molander, S. L. J. Trice and S. M. Kennedy, *J. Org. Chem.*, 2012, **77**, 8678-8688.

23 M. R. Luzung, J. S. Patel and J.-J. Yin, *J. Org. Chem.*, 2010, **75**, 8330-8332.

24 S. Sévigny and P. Forgione, *Chem.–Eur. J.*, 2013, **19**, 2256-2260.

25 J.-M. Bégouin and C. Gosmini, *J. Org. Chem.*, 2009, **74**, 3221-322.

26 F.-A. Kang, Z.-H. Sui and W. V. Murray, *J. Am. Chem. Soc.*, 2008, **130**, 11300-11302.

27 A. Fürstner, A. Leitner, M. Méndez and H. Krause, *J. Am. Chem. Soc.*, 2002, **124**, 13856-13863.