

Supporting Information

Sustainable Fabrication of NiCuFe₂O₄ Nanosphere: A Highly Effective Palladium-Free Heterogeneous Catalyst for Biaryl Scaffold Synthesis via Suzuki-Miyaura Cross-Coupling Reaction

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Table of Contents

1. BET Analysis of NCF-3 nanoparticles (Figure S1)	S2
2. Analysis of recovered catalyst (Figure S2-S4)	S2-S3
3. Table S1: ICP-MS Result	S4
4. Table S2: S-M coupling of different aryl halides (-Cl/ -F) with a number of heteroarylboronic acid	S4-S5
5. Spectral data of representative compounds	S5-S8
6. ¹ H and ¹³ C NMR of compounds (Figure S5-S42)	S8-S27
7. ESI-MS Spectra of compounds (Figure S43-S46)	S28-S29

1. BET Analysis of NCF-3 nanoparticles

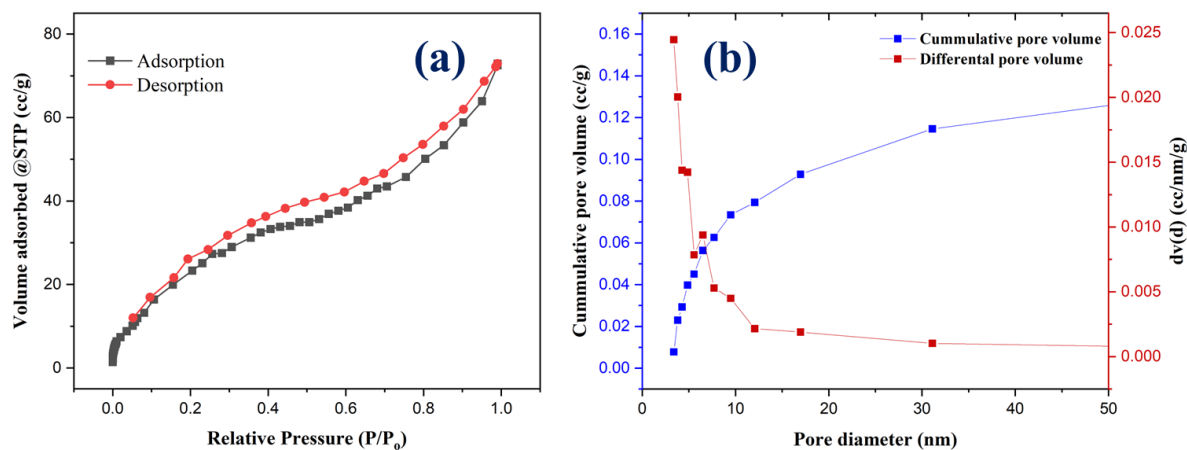


Figure S1. (a) N_2 adsorption-desorption isotherm of the as-synthesized NCF-3 NPs at 77 K; (b) Pore size distribution graph between the pore volume distribution vs. the pore diameter of NCF-3 NPs.

2. Analysis of Recovered Catalyst

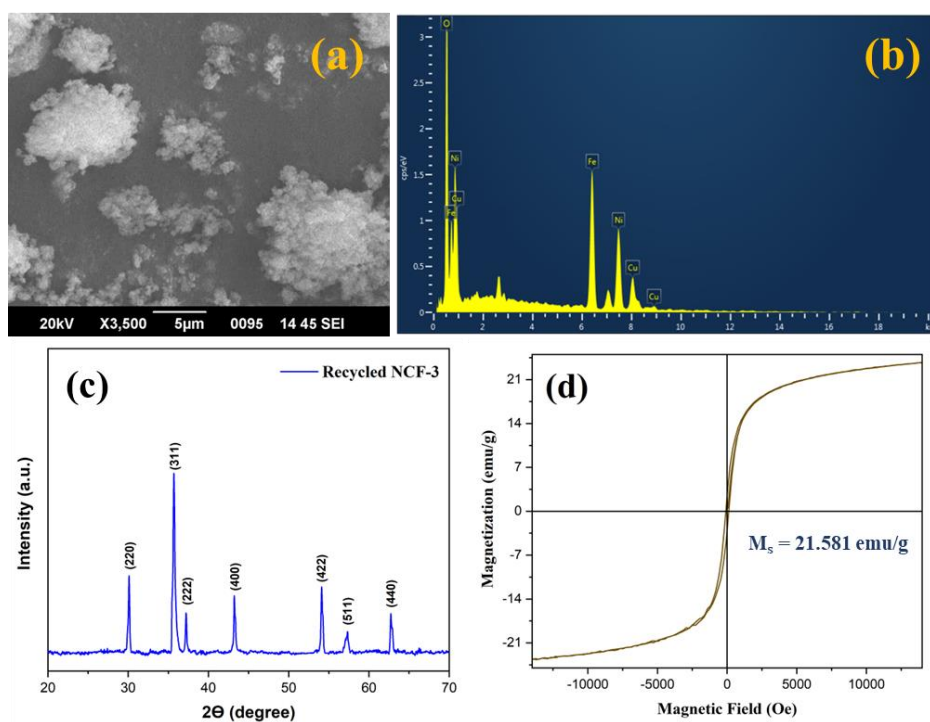


Figure S2. (a) SEM image; (b) EDX image; (c) XRD; and (d) VSM data of reused NCF-3 NPs (5th cycle).

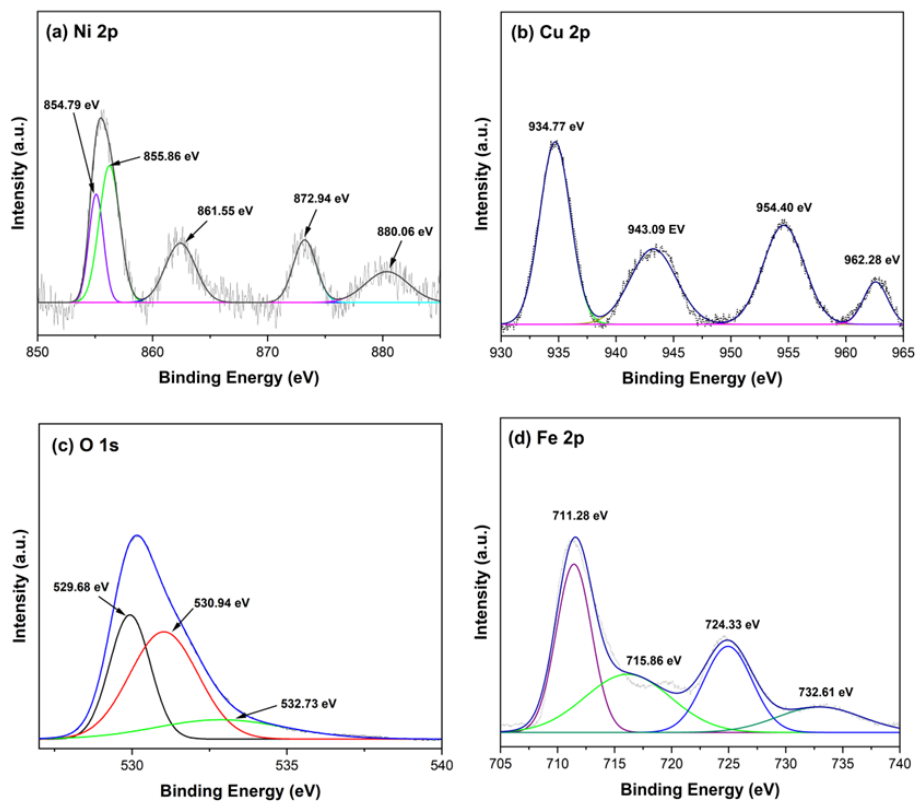


Figure S3. XPS of the reused NCF-3 NPs (5th cycle) (a) Ni 2p, (b) Cu 2p, (c) Fe 2p and (c) O 1s regions.

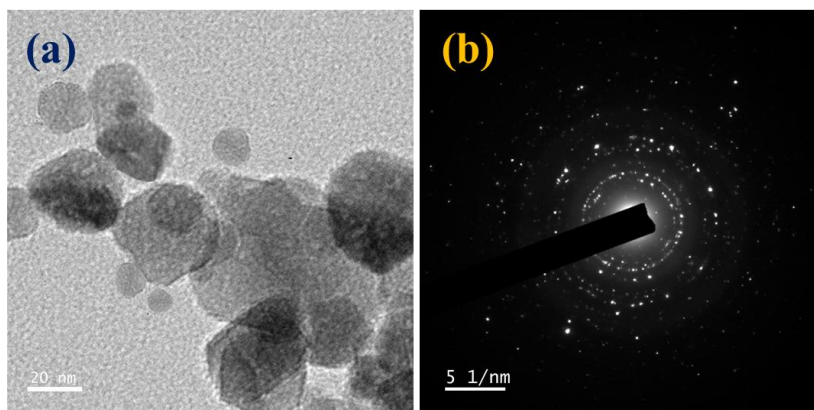
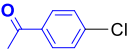
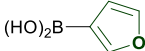
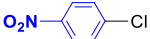
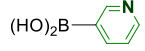
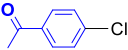
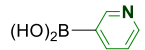
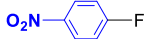
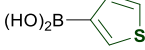
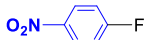
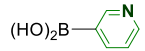

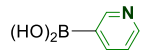
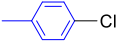
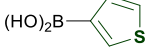

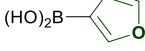
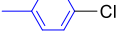
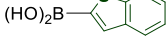

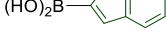
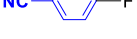
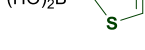
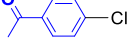
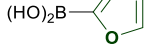
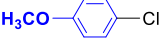
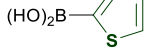
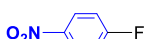
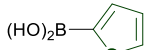



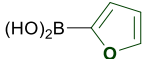
Figure S4. (a) TEM image and (b) SAED of the reused NCF-3 catalyst (5th cycle).

3. Table S1: ICP-MS Result

Sl. No.	Sample Name	Cu	Ni	Fe
1	NCF-3	4.075	3.638	11.924
2	NP-7	-	-	-
Unit		%	%	%
Detection Limit in ppm		0.01	0.01	0.10

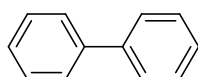
4. Table S2: S-M coupling of different aryl halides (-Cl/ -F) with a number of heteroarylboronic acid ^a

Entry	Aryl halide	Heteroarylboronic acid	Yield (%)
1			Trace
2			-
3			Trace
4			-
5			-
6			-
7			Trace
8			-
9			-
10			-
11			-
12			Trace
13			Trace
14			-

15			-
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^a Reaction condition: Aryl halide (1 mmol), heteroaryl boronic acid (1.1 mmol), NiCuFe₂O₄ (3 mol %), K₂CO₃ (1.4 mmol), 3 mL of EtOH: H₂O (2:1) at 60 °C.

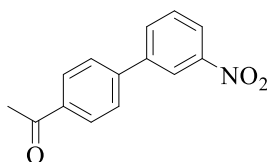
5. Spectral data of representative compounds



1,1'-biphenyl: White solid; m.p. 70 °C;

¹H NMR (500 MHz, CDCl₃) δ 7.68 (d, *J* = 7.6 Hz, 4H), 7.53 (t, *J* = 7.5 Hz, 4H), 7.43 (t, *J* = 7.4 Hz, 2H).

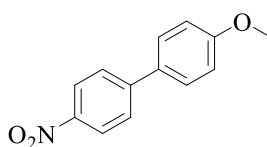
¹³C NMR (126 MHz, CDCl₃) δ 141.31, 128.84, 127.34, 127.25.



1-(3'-nitro-[1,1'-biphenyl]-4-yl)ethan-1-one: Yellow solid;

¹H NMR (500 MHz, CDCl₃) δ 8.38 (d, *J* = 4.0 Hz, 1H), 8.18 (d, *J* = 8.2 Hz, 1H), 7.83 (d, *J* = 7.6 Hz, 1H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.49 – 6.99 (m, 4H), 2.40 (s, 3H).

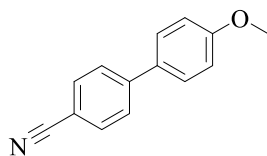
¹³C NMR (125 MHz, CDCl₃) δ 197.13, 148.97, 146.72, 138.55, 132.71, 131.44, 129.66, 126.51, 124.82, 115.95, 27.10.



4-methoxy-4'-nitro-1,1'-biphenyl: Pale yellow solid;

¹H NMR (500 MHz, CDCl₃) δ 8.22 (d, *J* = 9.0 Hz, 2H), 7.65 (d, *J* = 8.9 Hz, 2H), 7.52 (d, *J* = 8.7 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 3.86 (s, 3H).

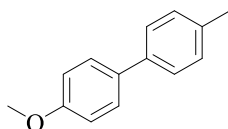
¹³C NMR (125 MHz, CDCl₃) δ 160.45, 146.72, 133.46, 132.00, 130.72, 123.63, 114.24, 114.15, 95.16, 86.66, 55.38.



4-methoxy-[1,1'-biphenyl]-4-carbonitrile: Pale white solid;

¹H NMR (500 MHz, DMSO) δ 7.90 – 7.81 (m, 4H), 7.72 (t, *J* = 8.3 Hz, 2H), 7.03 (d, *J* = 8.4 Hz, 2H), 3.84 (s, 3H).

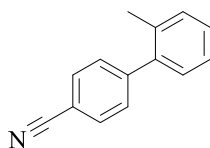
¹³C NMR (125 MHz, CDCl₃) δ 160.52, 146.79, 132.19, 132.15, 128.29, 128.23, 120.53, 115.32, 110.81, 55.75.



4-methoxy-4'-methyl-1,1'-biphenyl: White solid;

¹H NMR (500 MHz, CDCl₃) δ 7.71 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.2 Hz, 2H), 7.08 – 7.02 (m, 4H), 3.86 (s, 3H), 2.48 (s, 3H).

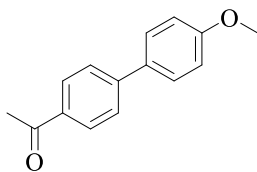
¹³C NMR (125 MHz, CDCl₃) δ 157.29, 137.08, 136.96, 129.97, 129.89, 128.99, 127.99, 127.20, 125.18, 115.32, 55.19, 22.31.



2'-methyl-[1,1'-biphenyl]-4-carbonitrile: White solid;

¹H NMR (500 MHz, CDCl₃) δ 7.72 (d, *J* = 8.1 Hz, 2H), 7.64 (d, *J* = 8.4 Hz, 2H), 7.46 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 2.42 (s, 3H).

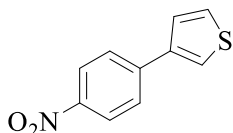
¹³C NMR (125 MHz, CDCl₃) δ 160.45, 146.72, 133.46, 132.00, 130.72, 123.63, 114.24, 114.15, 95.16, 86.66, 55.38.



1-(4-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one: Pale white solid;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.96 (d, $J = 8.4$ Hz, 2H), 7.64 (d, $J = 7.3$ Hz, 2H), 7.39 (t, $J = 8.3$ Hz, 2H), 6.98 (d, $J = 8.3$ Hz, 2H), 3.81 (s, 3H), 2.64 (s, 3H).

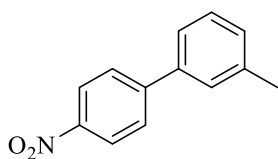
$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 197.32, 160.45, 147.07, 136.23, 131.71, 128.83, 128.46, 128.29, 128.23, 116.62, 56.74, 26.62.



3-(4-nitrophenyl)thiophene: Yellow solid;

$^1\text{H NMR}$ (500 MHz, DMSO) δ 8.28 (d, $J = 8.3$ Hz, 2H), 7.82 – 7.73 (m, 2H), 7.61 – 7.49 (m, 2H), 7.42 (d, $J = 7.8$ Hz, 1H).

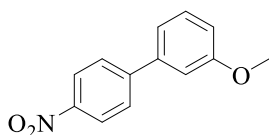
$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 146.79, 139.75, 132.22, 130.10, 129.97, 127.20, 125.18, 122.15, 55.26.



3-methyl-4'-nitro-1,1'-biphenyl: Yellow solid;

$^1\text{H NMR}$ (500 MHz, DMSO) δ 8.24 (d, $J = 7.5$ Hz, 1H), 8.13 (d, $J = 8.2$ Hz, 2H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.48 (t, $J = 6.7$ Hz, 1H), 7.31 – 7.24 (m, 2H), 2.84 (s, 3H).

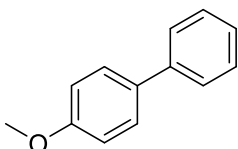
$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 146.77, 141.95, 139.75, 129.75, 129.27, 124.26, 124.08, 22.13.



3-methoxy-4'-nitro-1,1'-biphenyl: Yellow solid;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.19 (d, $J = 8.0$ Hz, 2H), 7.61 – 7.54 (m, 2H), 6.88 (d, $J = 8.2$ Hz, 2H), 3.83 (s, 3H).

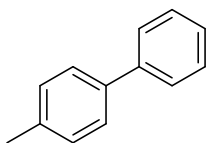
$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 158.43, 142.89, 133.16, 132.87, 130.26, 123.11, 114.93, 114.78, 92.61, 55.27.



4-methoxy-1,1'-biphenyl: Pale white solid; m.p. 88 °C;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 – 7.52 (m, 3H), 7.43 (t, $J = 7.5$ Hz, 2H), 7.31 (t, $J = 8.5$ Hz, 2H), 6.89 (d, $J = 8$ Hz, 2H), 3.82 (s, 3H).

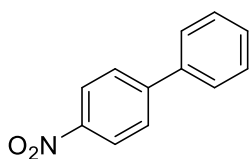
$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 160.25, 142.04, 133.33, 129.29, 127.42, 126.17, 125.55, 124.82, 114.24, 114.19, 55.35.



4-methyl-1,1'-biphenyl: White solid; m.p. 49 °C;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.71 (d, $J = 8.4$ Hz, 2H), 7.49 (d, $J = 3.3$ Hz, 2H), 7.39 – 7.21 (m, 5H), 2.48 (s, 3H).

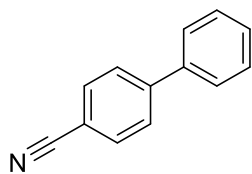
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 140.10, 136.89, 134.48, 130.29, 130.21, 129.38, 127.99, 127.20, 125.84, 21.09.



4-nitro-1,1'-biphenyl: Light brown solid; m.p. 113 °C;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.28 (d, $J = 6.6$ Hz, 2H), 7.77 (d, $J = 7.3$ Hz, 2H), 7.63 (d, $J = 7.5$ Hz, 2H), 7.56 – 7.43 (m, 3H).

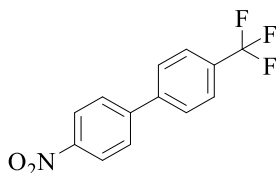
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 148.20, 139.89, 136.66, 132.29, 129.21, 126.70, 117.38, 110.65, 21.13.



[1,1'-biphenyl]-4-carbonitrile: Light yellow solid; m.p. 80 °C;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.74 (d, $J = 7.4$ Hz, 2H), 7.69 (d, $J = 7.5$ Hz, 2H), 7.58 (d, $J = 7.4$ Hz, 2H), 7.49 (t, $J = 7.6$ Hz, 2H), 7.40 (t, $J = 7.5$ Hz, 1H).

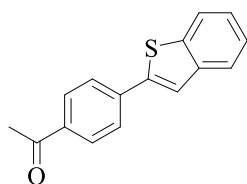
$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 145.87, 139.54, 132.50, 129.69, 128.73, 127.84, 127.41, 125.59, 118.98, 110.67.



4-nitro-4'-(trifluoromethyl)-1,1'-biphenyl: Yellow solid;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.38 (d, $J = 8.0$ Hz, 2H), 7.79 – 7.73 (m, 6H).

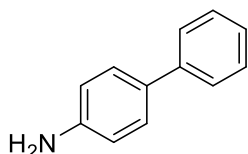
$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 147.78, 146.09, 129.54, 128.13, 126.02, 125.74, 124.12.



1-(4-(benzo[b]thiophen-2-yl)phenyl)ethan-1-one: Pale white solid;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 8.02 (d, $J = 8.4$ Hz, 2H), 7.85 (t, $J = 8.3$ Hz, 4H), 7.68 (d, $J = 8.4$ Hz, 1H), 7.40 (t, $J = 8.2$ Hz, 2H), 2.62 (s, 3H).

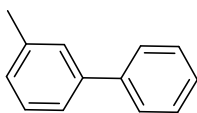
$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 196.44, 144.98, 141.11, 139.10, 137.88, 135.73, 129.64, 128.85, 126.70, 125.60, 123.33, 121.11, 24.57.



[1,1'-biphenyl]-4-amine: Pale yellow solid; m.p. 104 °C;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 (d, $J = 7.6$ Hz, 2H), 7.50 – 7.42 (m, 4H), 7.30 (d, $J = 7.5$ Hz, 1H), 6.73 (d, $J = 7.4$ Hz, 2H), 3.67 (s, 2H).

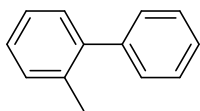
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 146.30, 141.58, 133.41, 129.72, 128.34, 126.72, 126.16, 118.01.



3-methyl-1,1'-biphenyl: White oil;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.59 (d, $J = 7.2$ Hz, 2H), 7.44 (t, $J = 8.2$ Hz, 4H), 7.38 – 7.29 (m, 2H), 7.15 (d, $J = 7.5$ Hz, 1H), 2.42 (s, 3H).

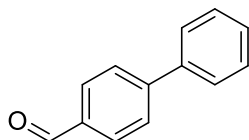
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 141.47, 141.36, 138.49, 128.75, 128.14, 127.31, 124.39, 21.83.



2-methyl-1,1'-biphenyl: Colorless oil;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 7.49 – 7.39 (m, 2H), 7.33 – 7.28 (m, 3H), 7.26 – 7.24 (m, 2H), 7.21 – 7.18 (m, 2H), 2.28 (s, 3H).

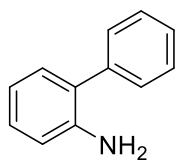
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 146.30, 137.26, 132.65, 132.23, 130.61, 130.03, 125.22, 125.04, 23.14.



[1,1'-biphenyl]-4-carbaldehyde: White solid; m.p. 58 °C;

$^1\text{H NMR}$ (500 MHz, CDCl_3) δ 9.97 (s, 1H), 7.88 – 7.80 (m, 2H), 7.68 (d, $J = 7.9$ Hz, 2H), 7.61 – 7.54 (m, 2H), 7.48 (t, $J = 8.0$ Hz, 2H), 7.32 (t, $J = 7.9$ Hz, 1H).

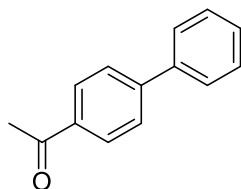
$^{13}\text{C NMR}$ (126 MHz, CDCl_3) δ 192.29, 147.89, 138.23, 134.55, 131.37, 130.83, 129.30, 128.35, 127.95, 127.37.



[1,1'-biphenyl]-2-amine: Light brown solid; m.p. 50 °C;

¹H NMR (500 MHz, CDCl₃) δ 7.49 – 7.36 (m, 4H), 7.28 – 7.04 (m, 2H), 7.18 – 7.12 (m, 2H), 6.80 (t, *J* = 7.4 Hz, 1H), 3.77 (s, 2H).

¹³C NMR (126 MHz, CDCl₃) δ 143.57, 139.82, 131.36, 129.34, 128.42, 127.89, 127.20, 118.67.



1-([1,1'-biphenyl]-4-yl)ethan-1-one: Pale White solid; m.p. 120 °C;

¹H NMR (500 MHz, CDCl₃) δ 8.08 (d, *J* = 8.2 Hz, 2H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.49 (t, *J* = 8.7 Hz, 2H), 7.44 – 7.36 (m, 1H), 2.64 (s, 3H).

¹³C NMR (126 MHz, CDCl₃) δ 197.73, 145.68, 139.88, 136.04, 129.20, 128.99, 128.36, 127.40, 26.72.

6. ¹H and ¹³C NMR of compounds

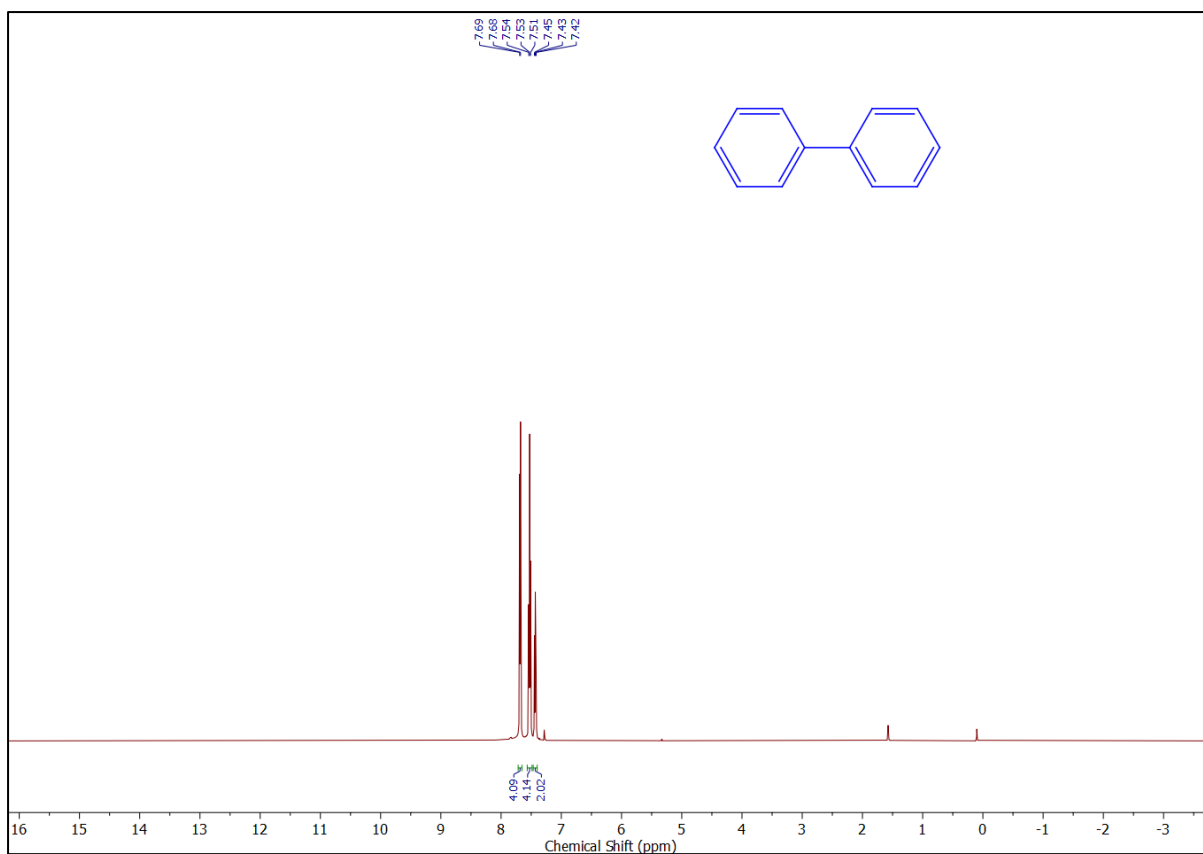


Figure S5: ¹H NMR spectrum of 1,1'-biphenyl

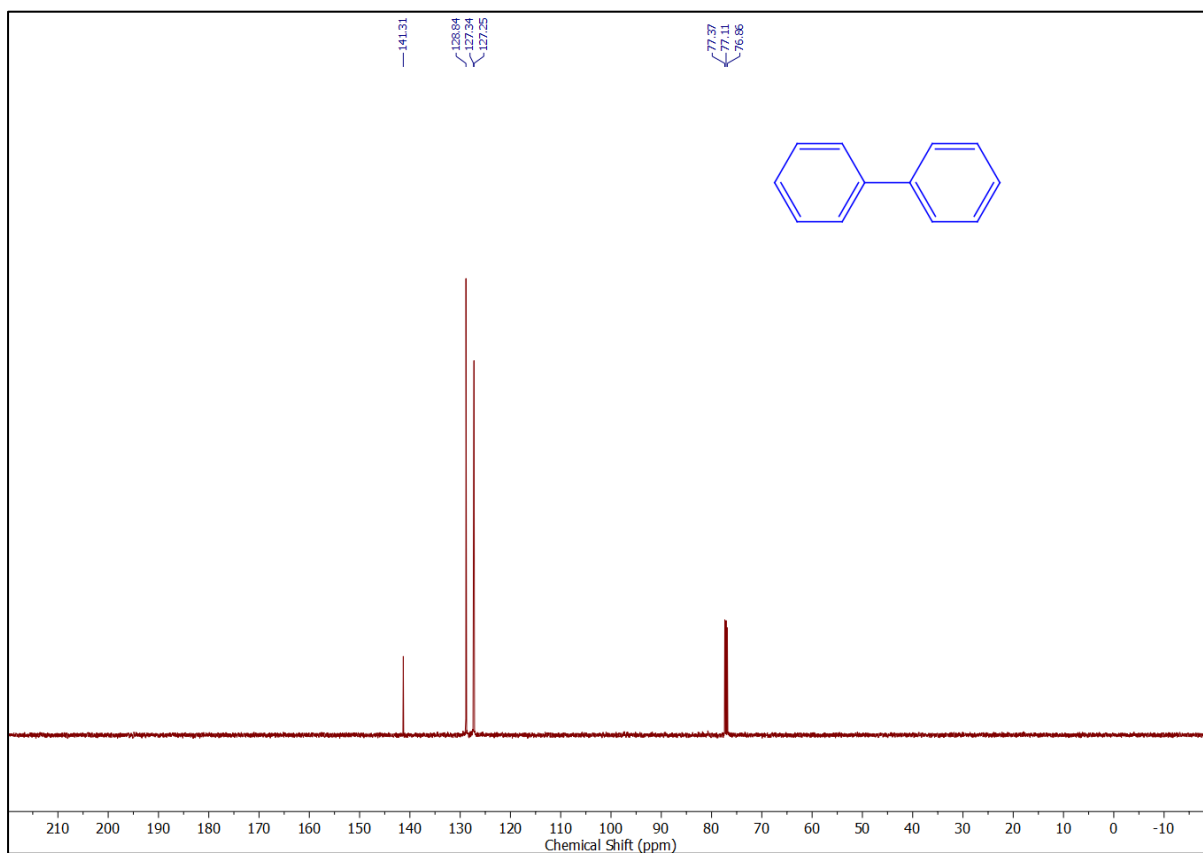


Figure S6: ¹³C NMR spectrum of 1,1'-biphenyl

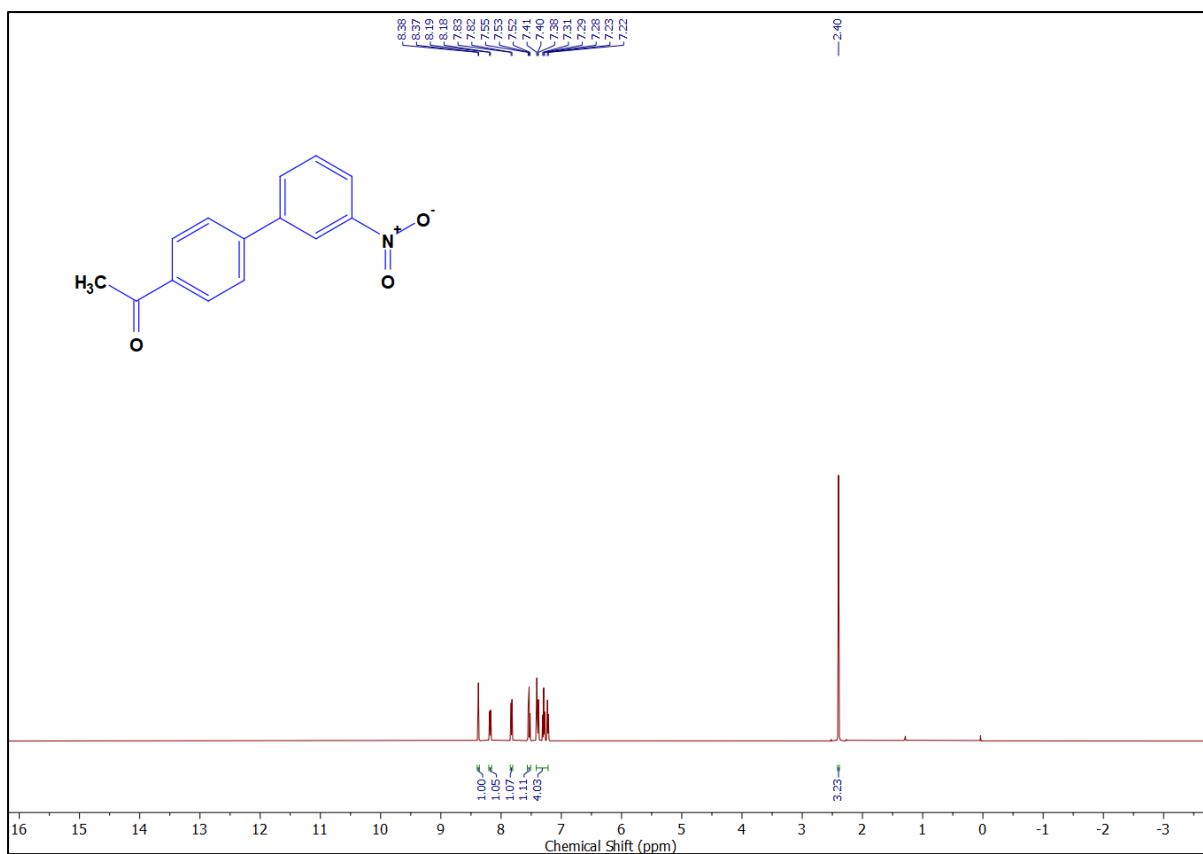


Figure S7: ¹H NMR spectrum of 1-(3'-nitro-[1,1'-biphenyl]-4-yl)ethan-1-one

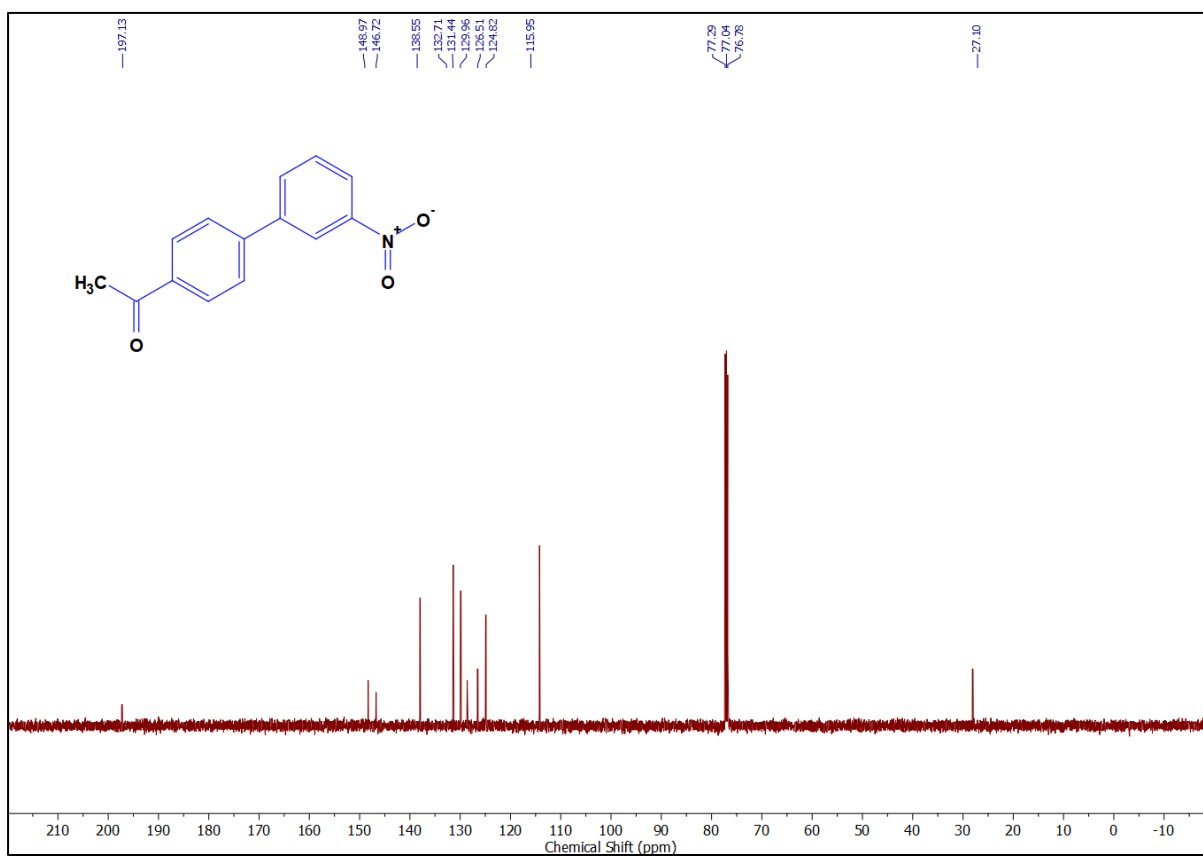


Figure S8: ¹³C NMR spectrum of 1-(3'-nitro-[1,1'-biphenyl]-4-yl)ethan-1-one

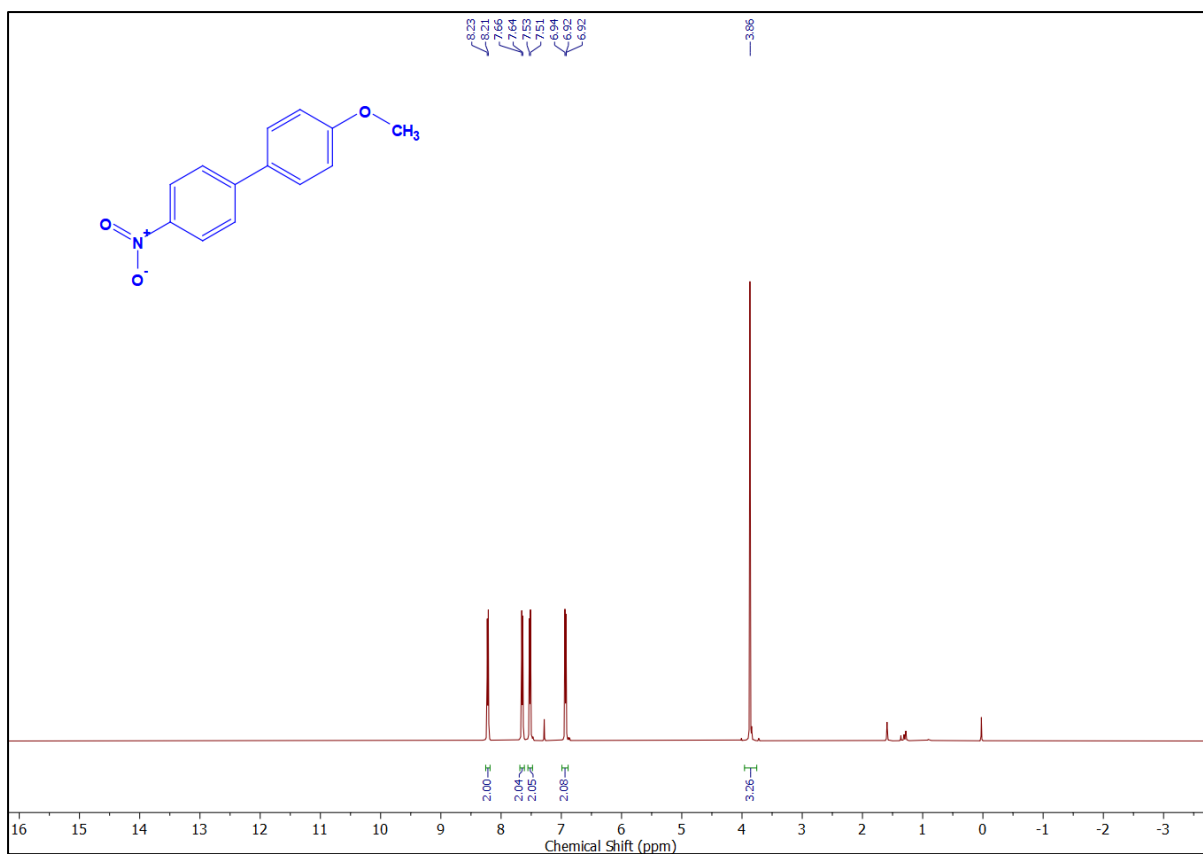


Figure S9: ^1H NMR spectrum of 4-methoxy-4'-nitro-1,1'-biphenyl

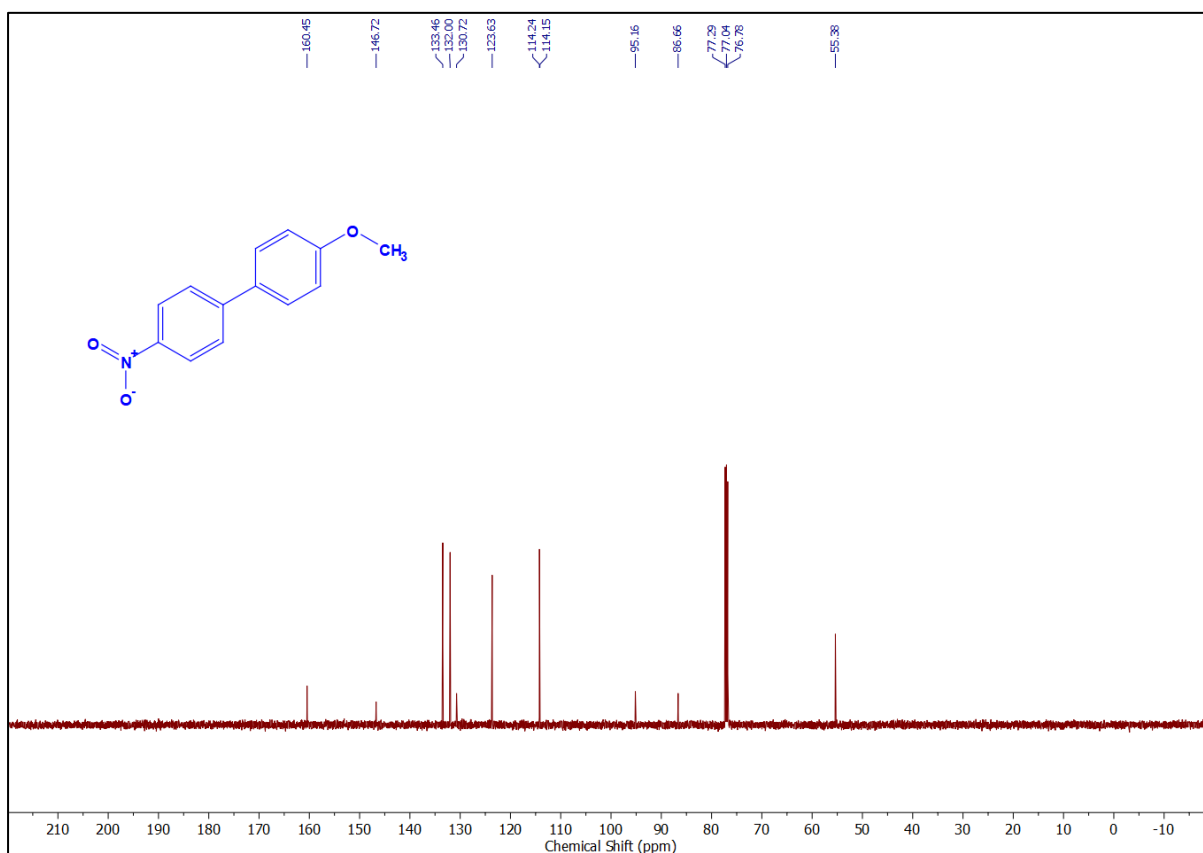


Figure S10: ^{13}C NMR spectrum of 4-methoxy-4'-nitro-1,1'-biphenyl

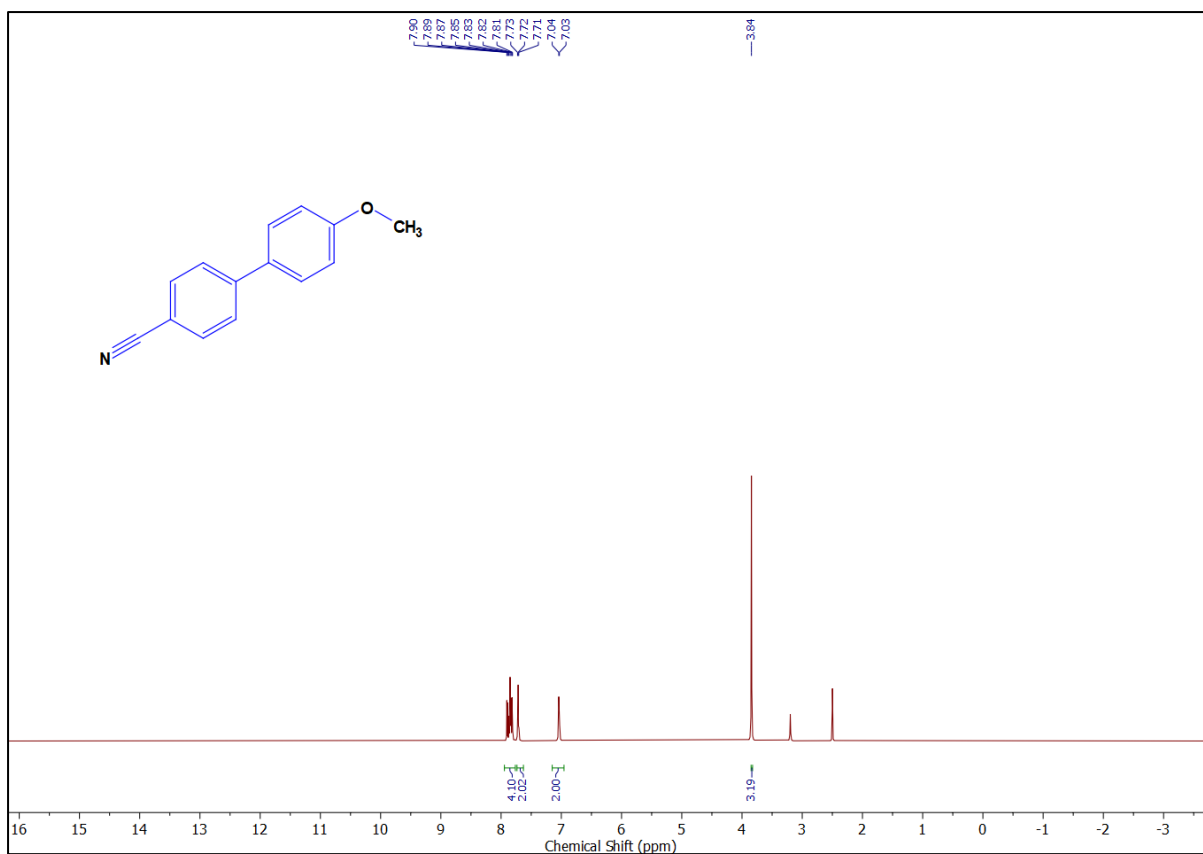


Figure S11: ^1H NMR spectrum of 4'-methoxy-[1,1'-biphenyl]-4-carbonitrile

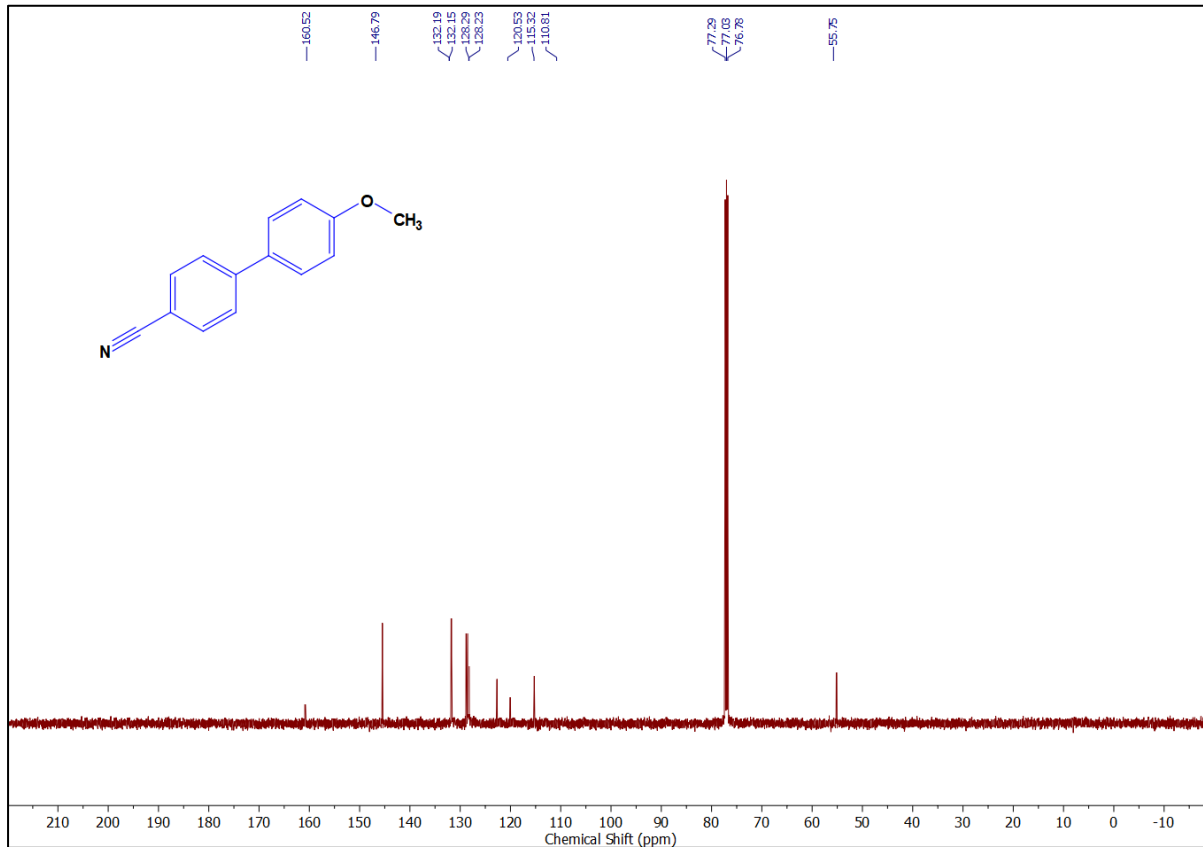


Figure S12: ^{13}C NMR spectrum of 4'-methoxy-[1,1'-biphenyl]-4-carbonitrile

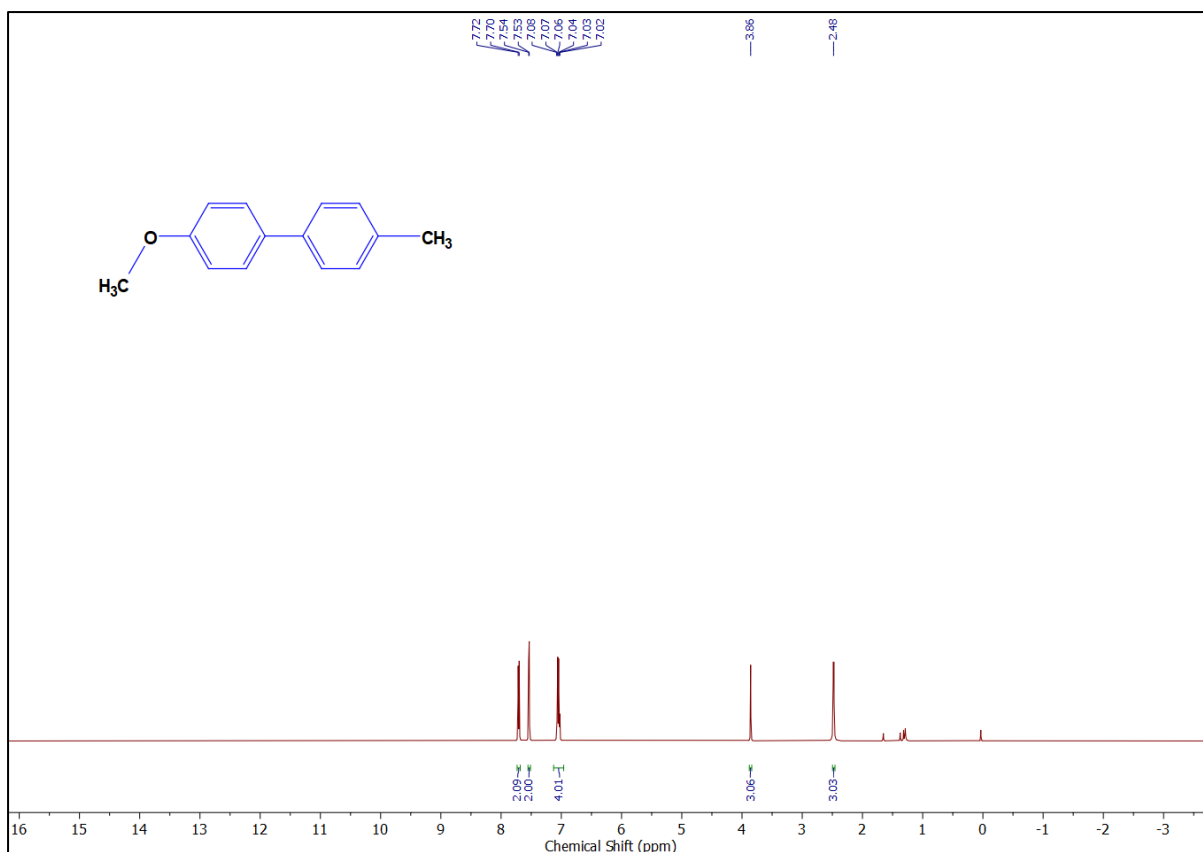


Figure S13: ^1H NMR spectrum of 4-methoxy-4'-methyl-1,1'-biphenyl

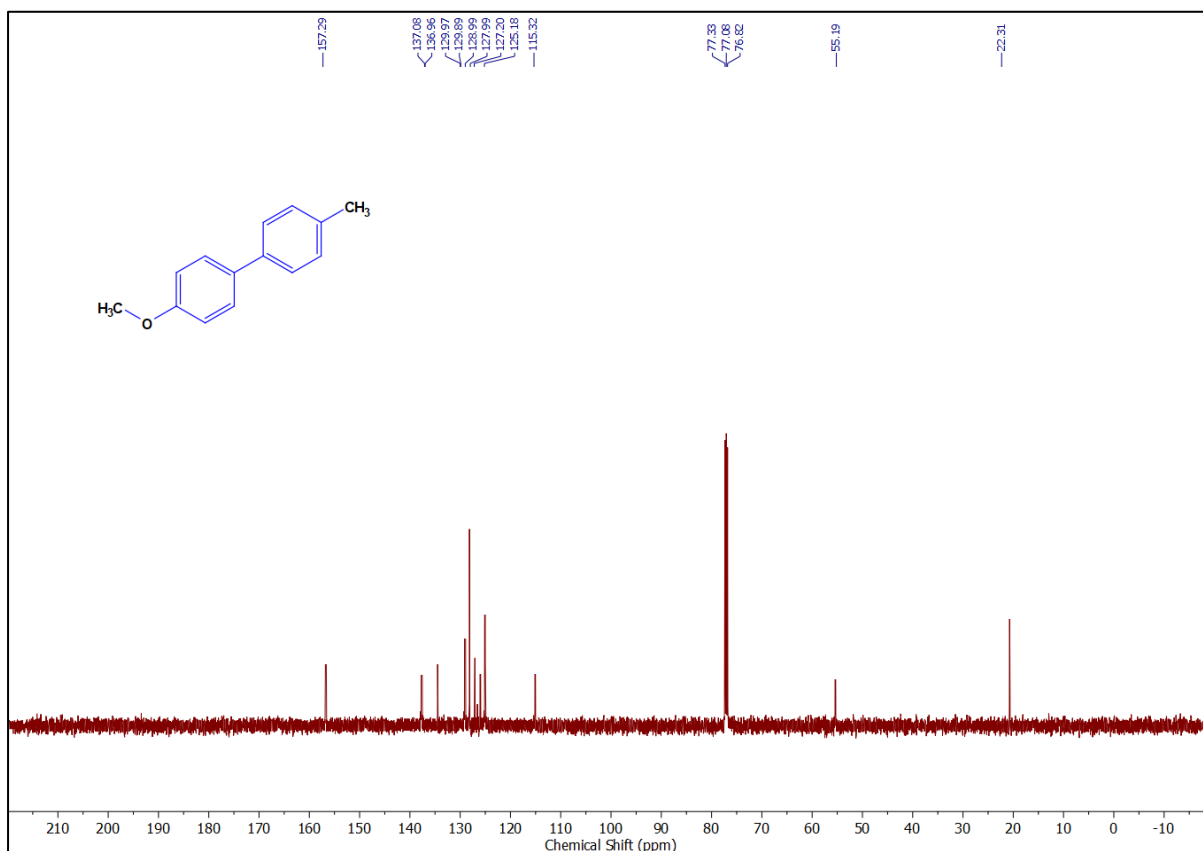


Figure S14: ^{13}C NMR spectrum of 4-methoxy-4'-methyl-1,1'-biphenyl

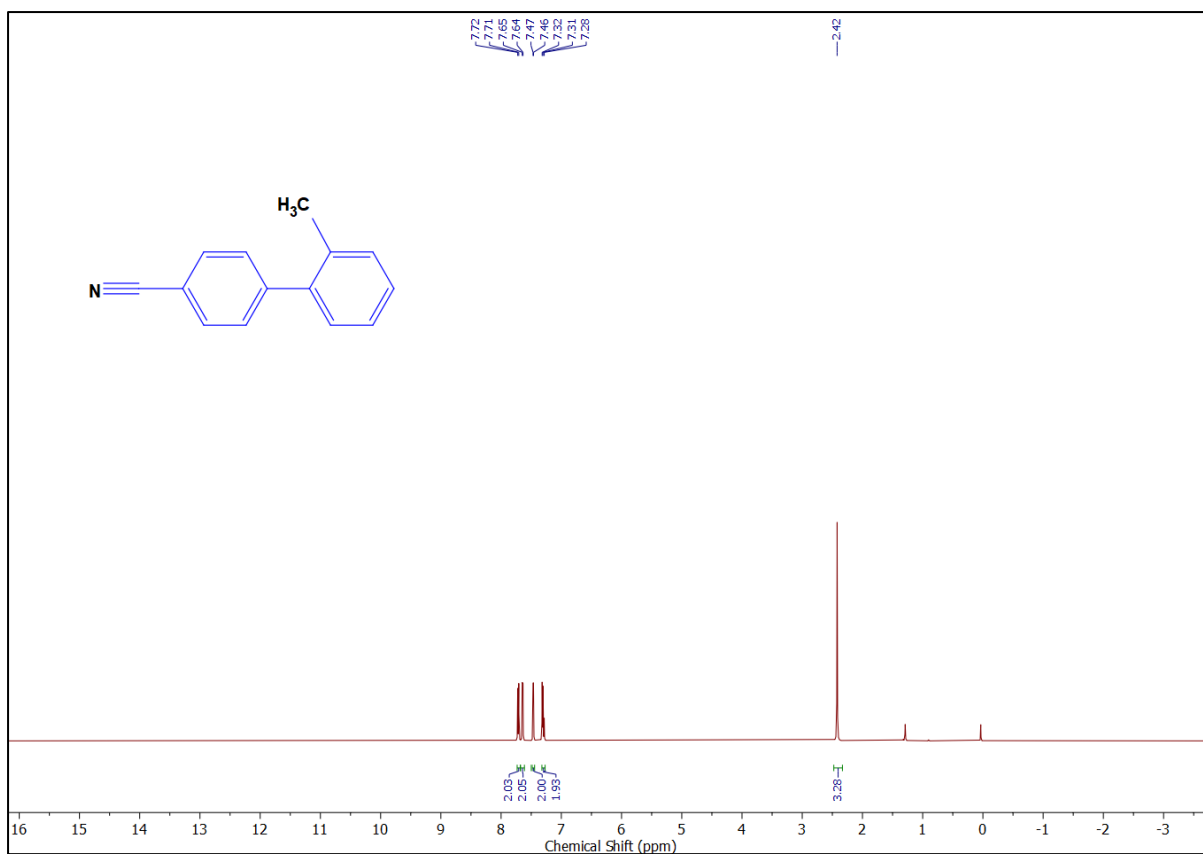


Figure S15: ¹H NMR spectrum of 2'-methyl-[1,1'-biphenyl]-4-carbonitrile

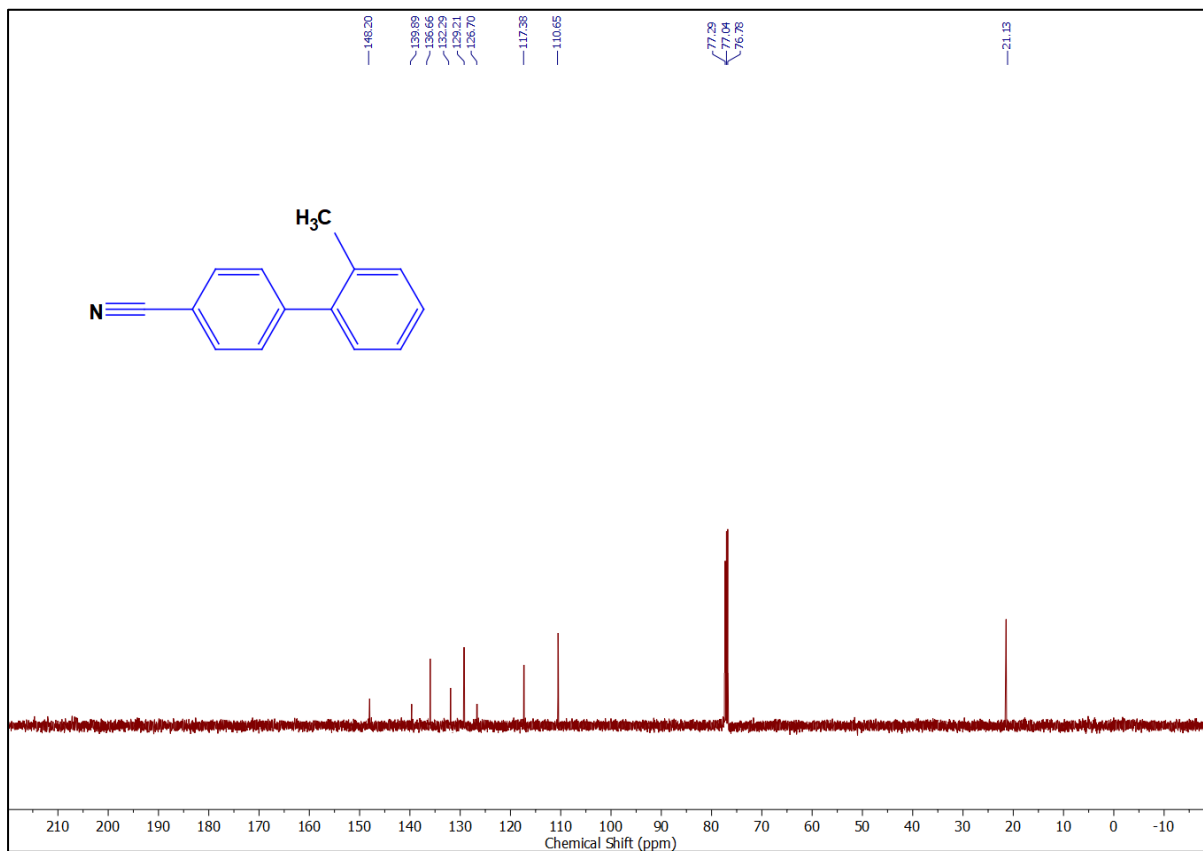


Figure S16: ¹³C NMR spectrum of 2'-methyl-[1,1'-biphenyl]-4-carbonitrile

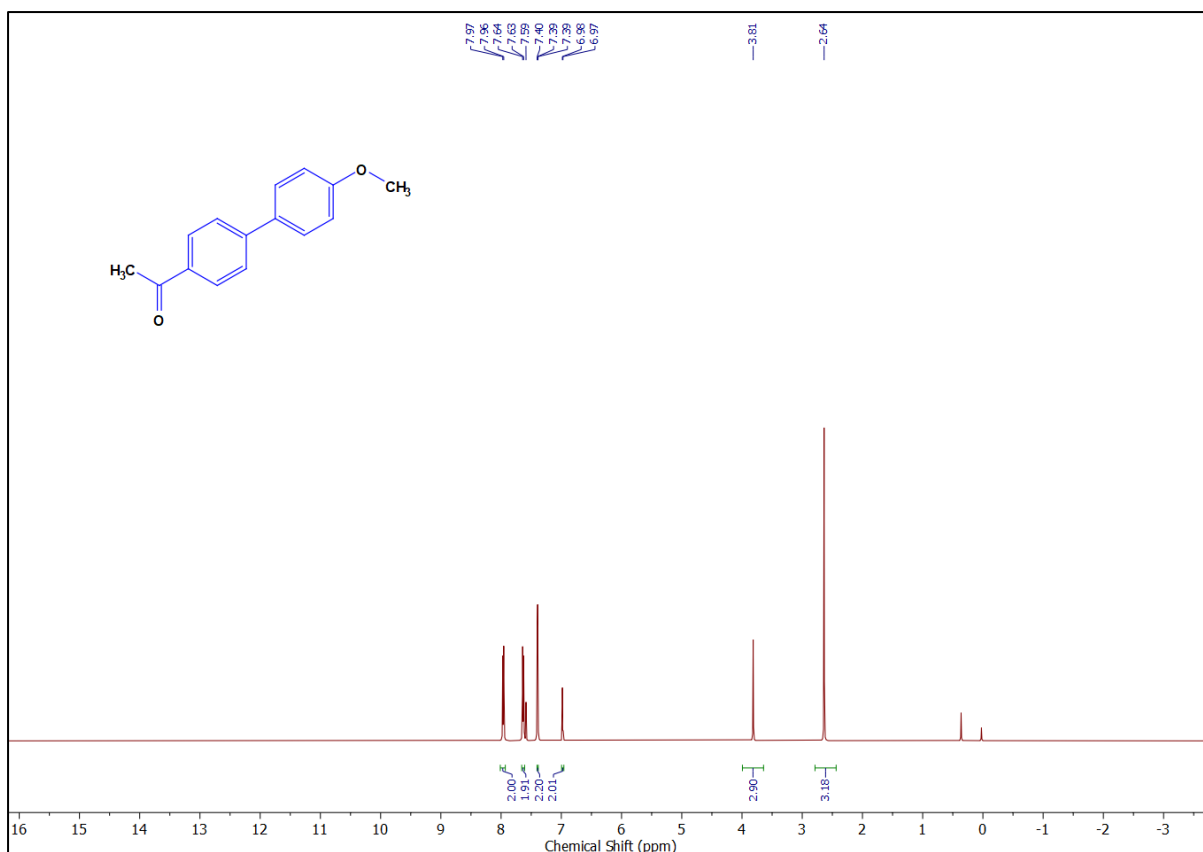


Figure S17: ¹H NMR spectrum of 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one

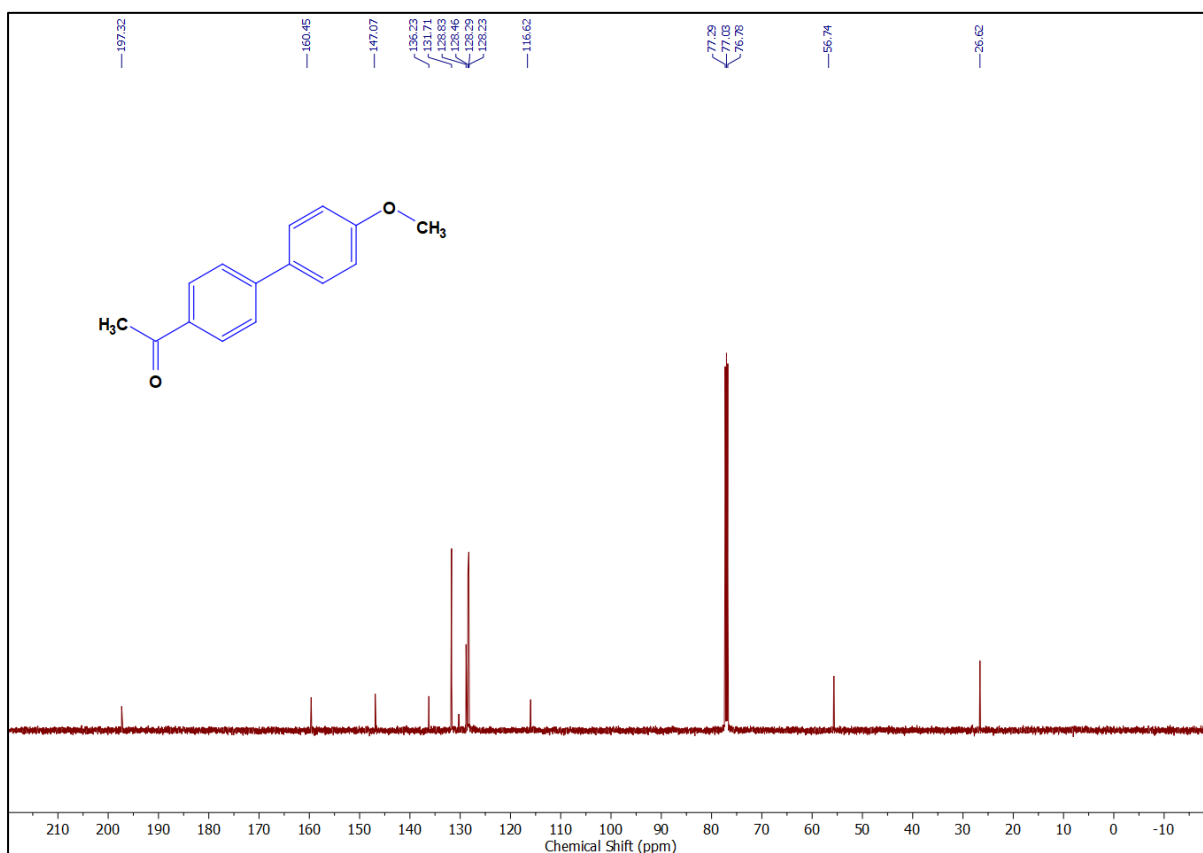


Figure S18: ¹³C NMR spectrum of 1-(4'-methoxy-[1,1'-biphenyl]-4-yl)ethan-1-one

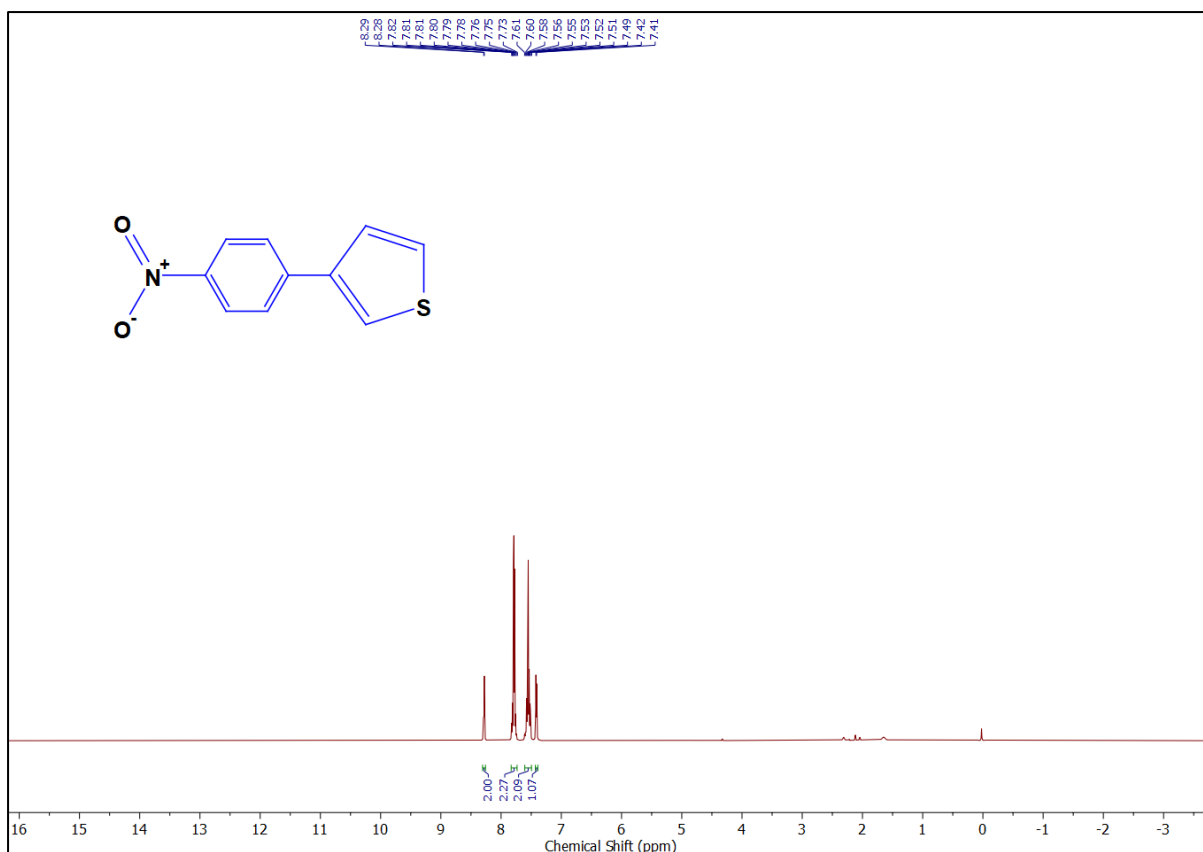


Figure S19: ^1H NMR spectrum of 3-(4-nitrophenyl)thiophene

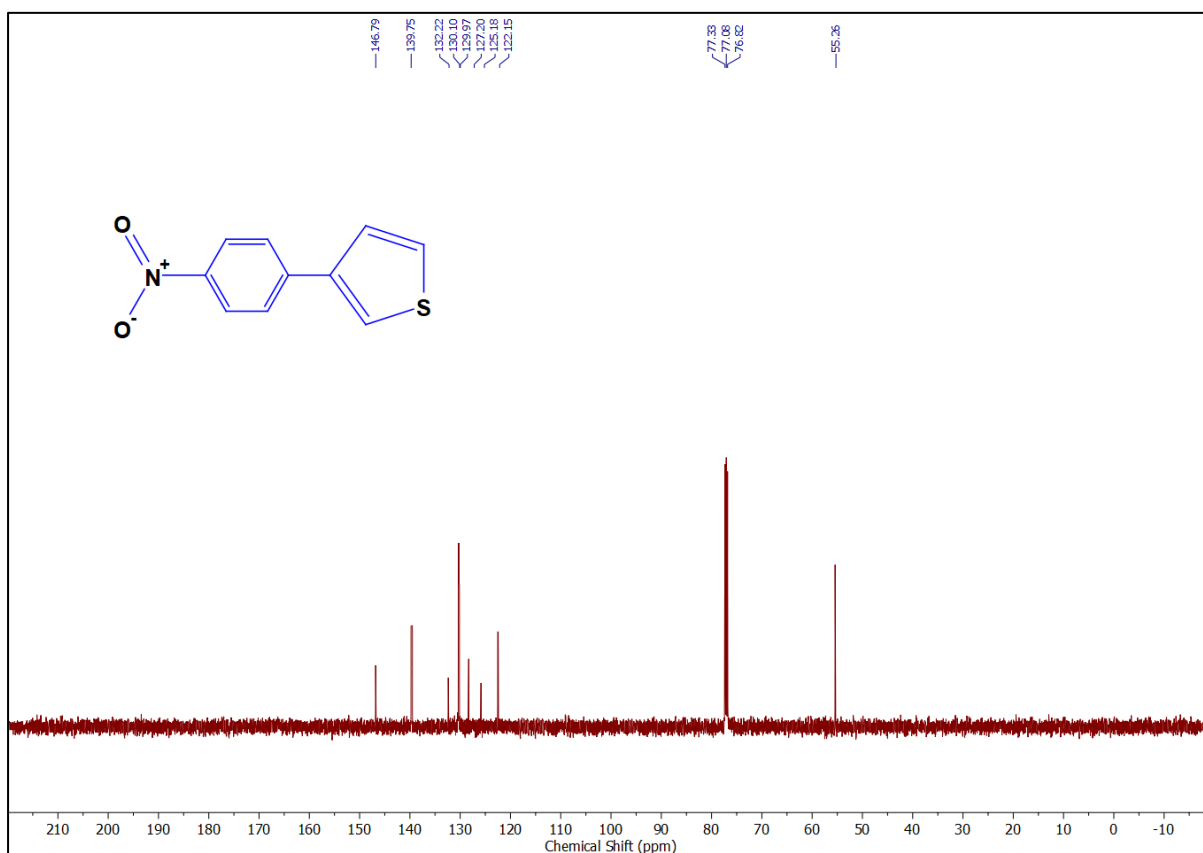


Figure S20: ^{13}C NMR spectrum of 3-(4-nitrophenyl)thiophene

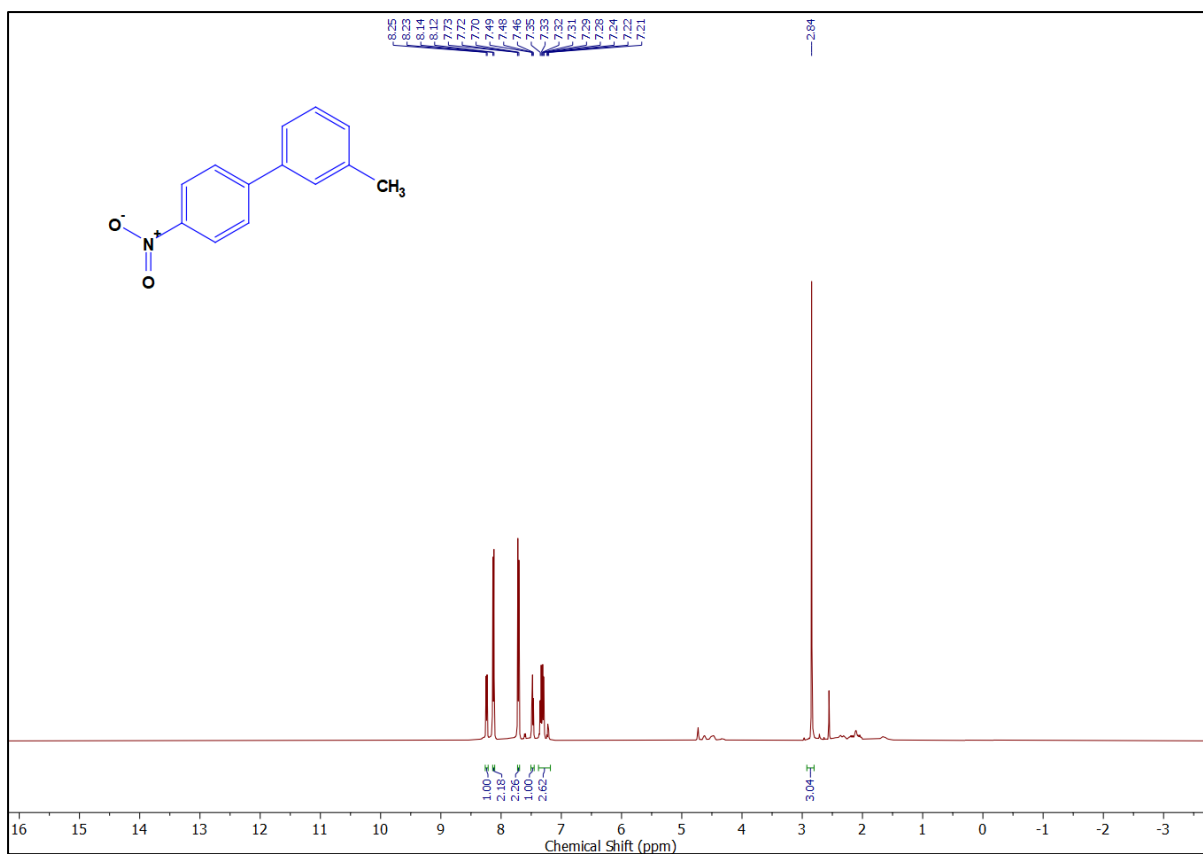


Figure S21: ^1H NMR spectrum of 3-methyl-4'-nitro-1,1'-biphenyl

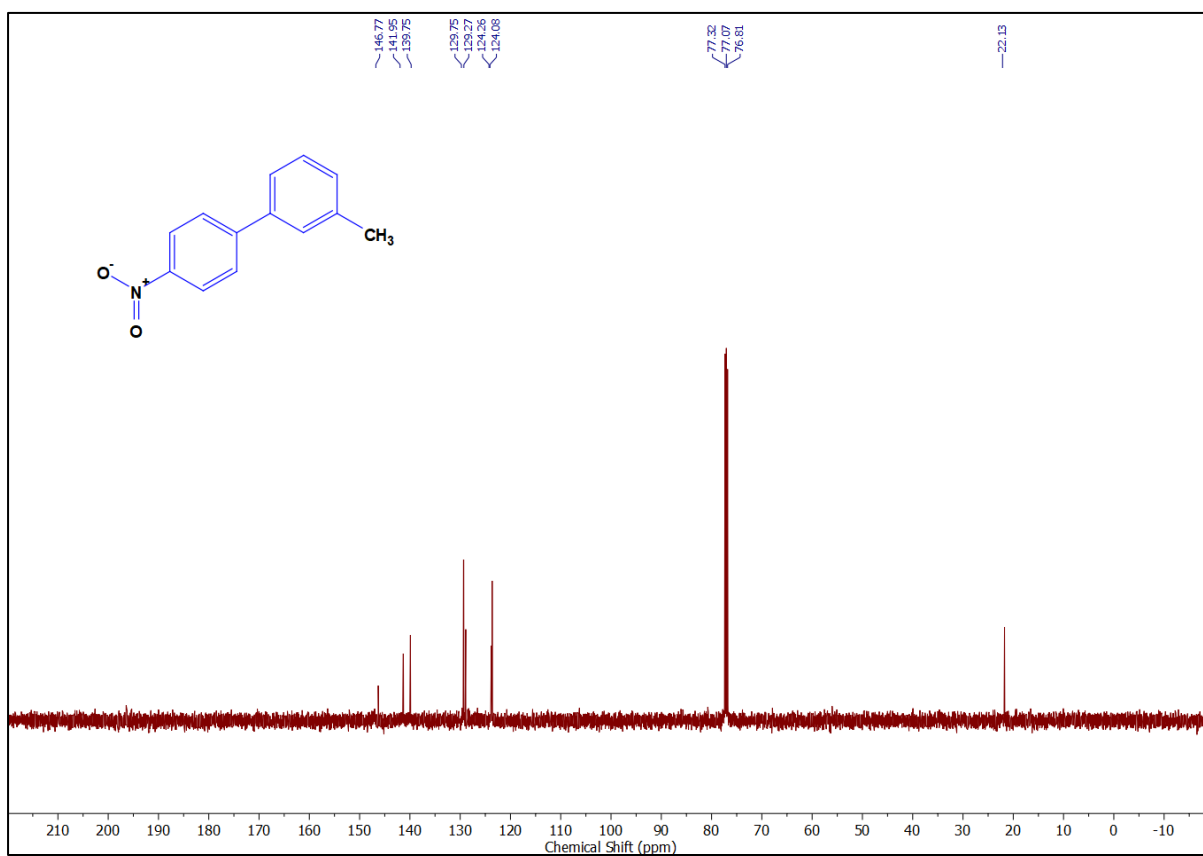


Figure S22: ^{13}C NMR spectrum of 3-methyl-4'-nitro-1,1'-biphenyl

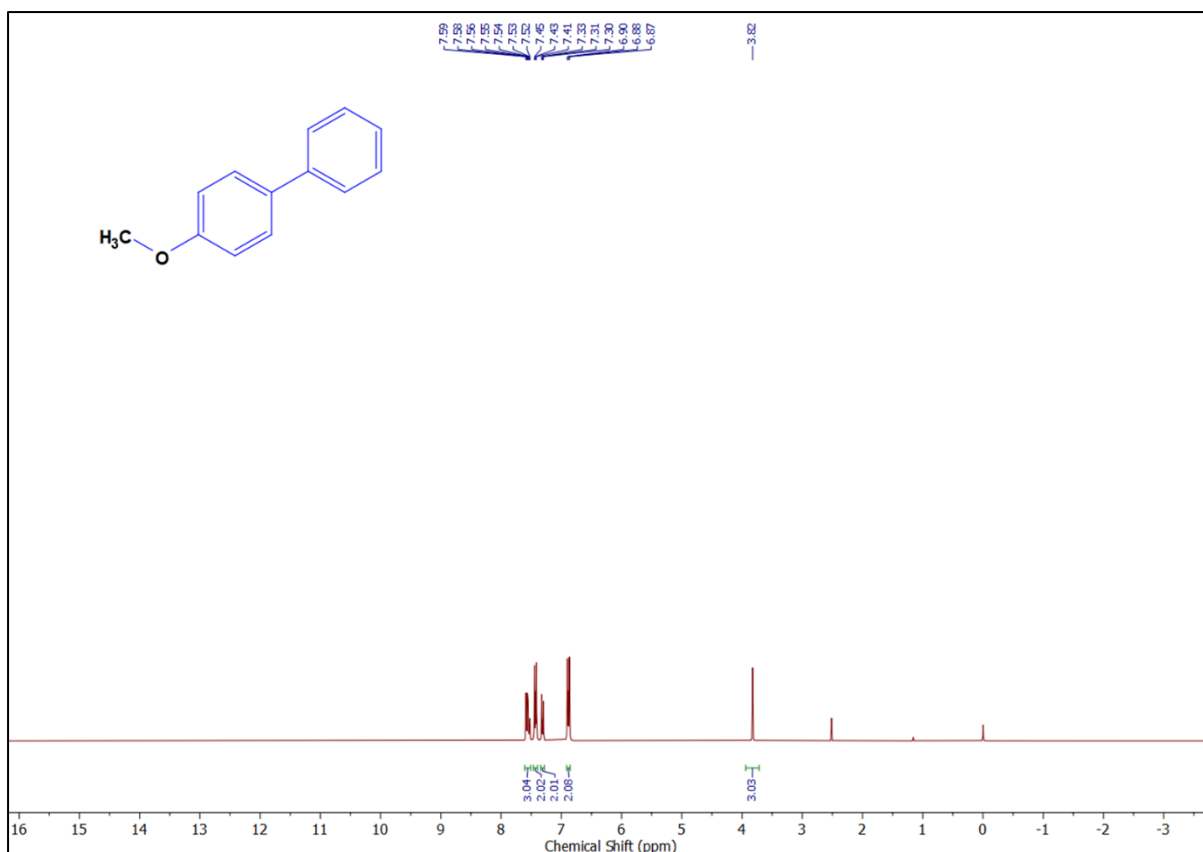


Figure S23: ¹H NMR spectrum of 4-methoxy-1,1'-biphenyl

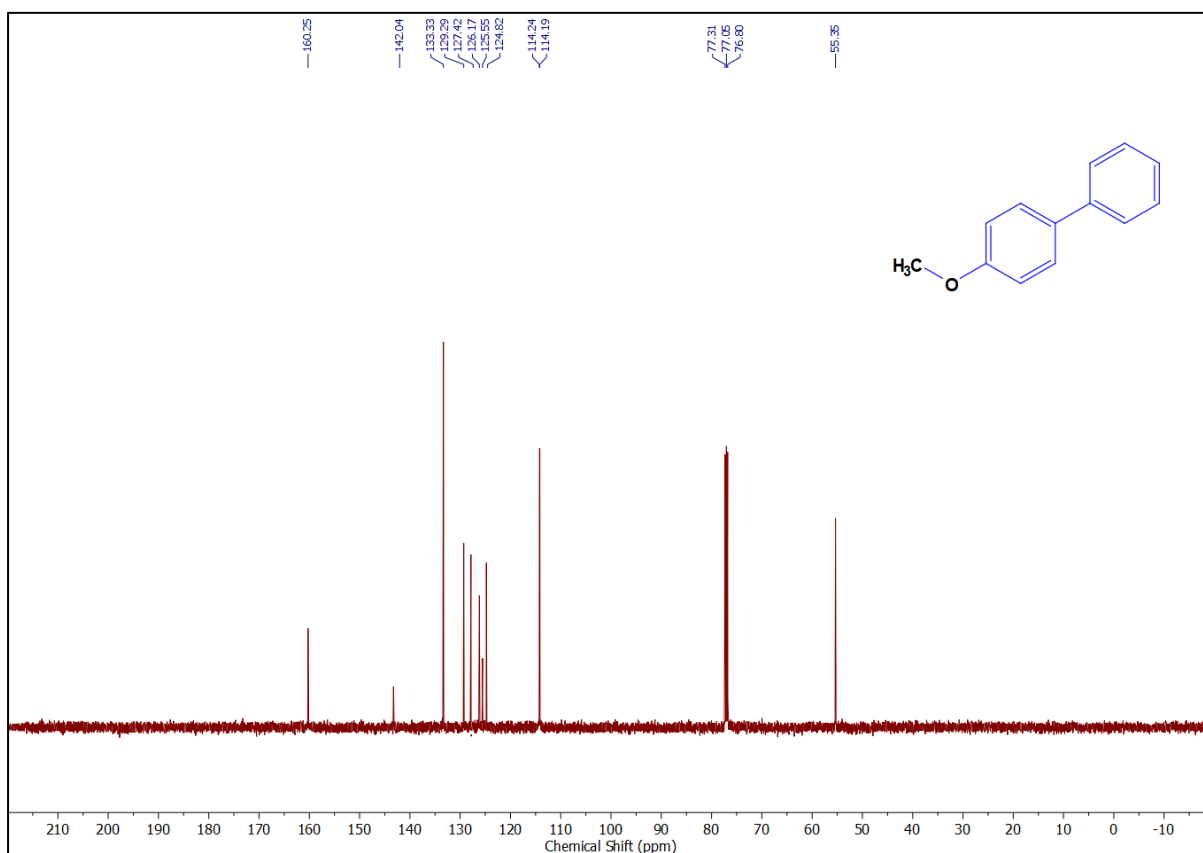


Figure S24: ¹³C NMR spectrum of 4-methoxy-1,1'-biphenyl

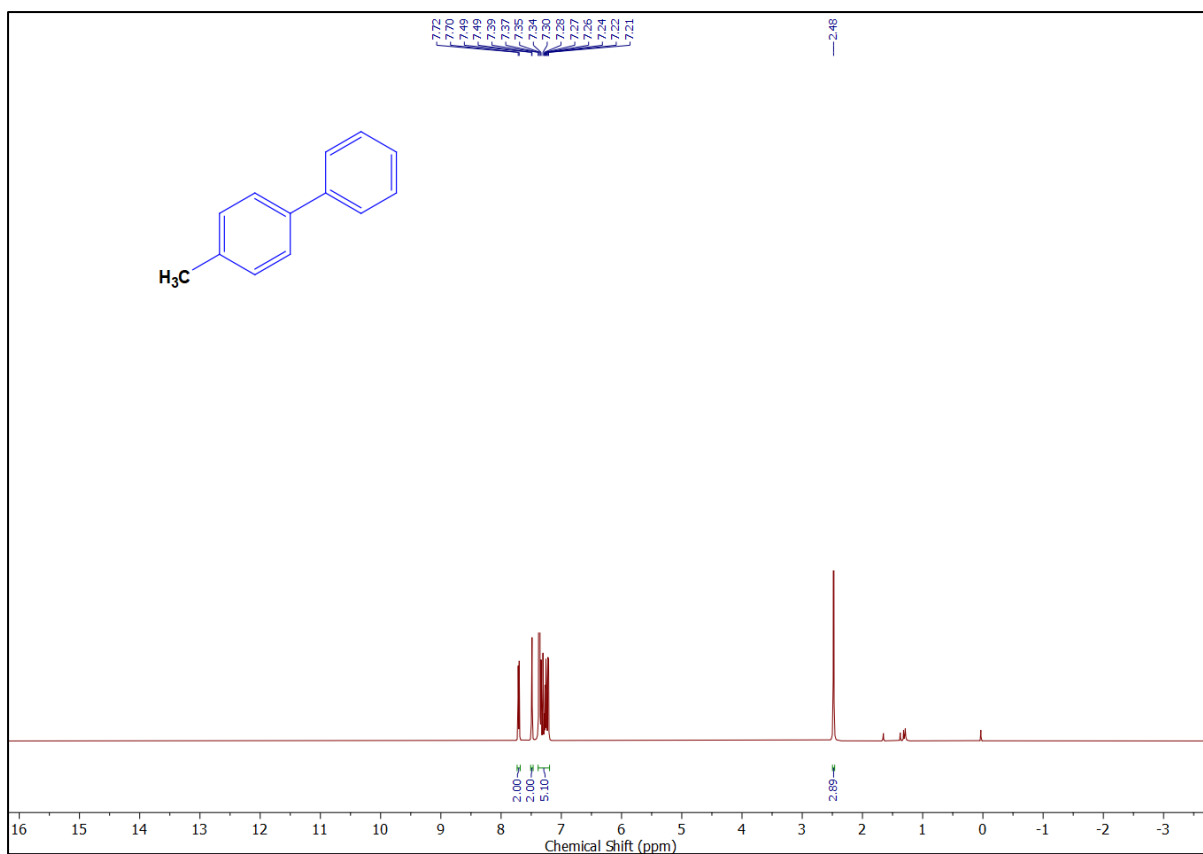


Figure S25: ^1H NMR spectrum of 4-methyl-1,1'-biphenyl

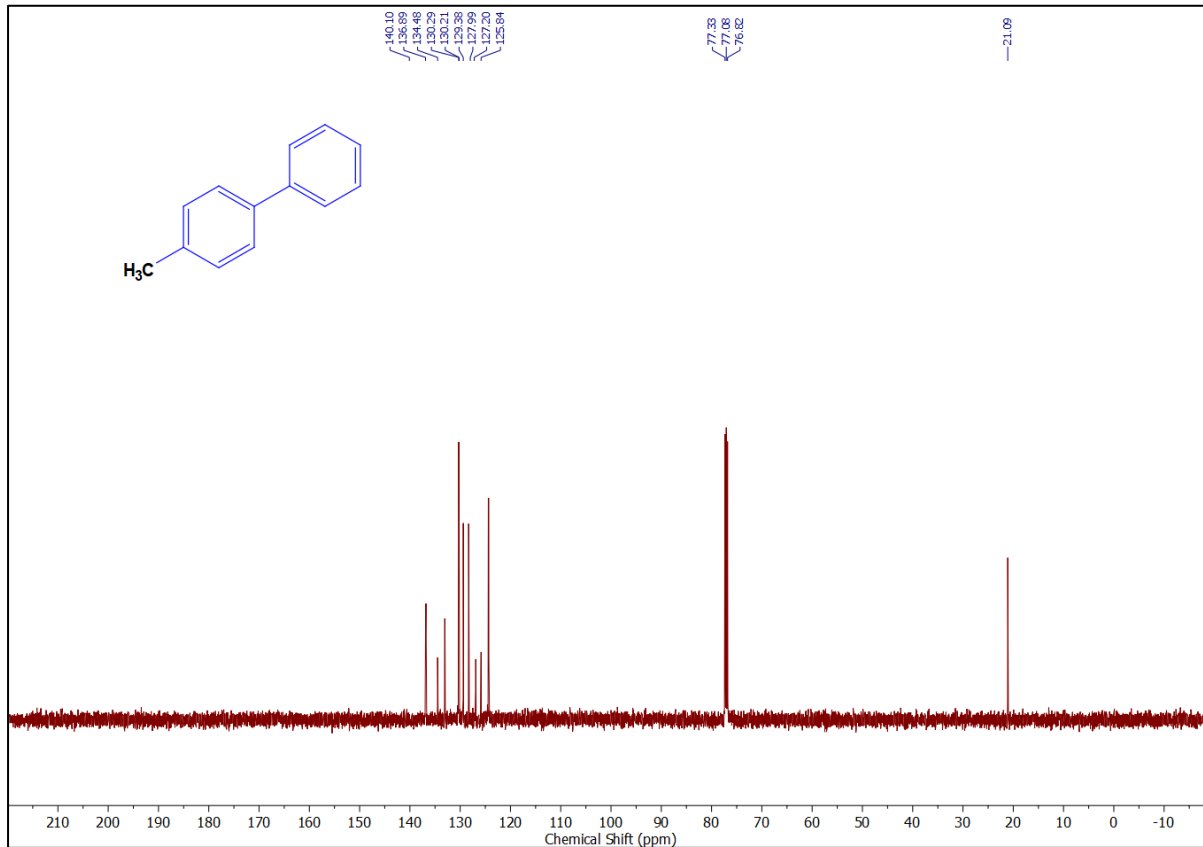


Figure S26: ^{13}C NMR spectrum of 4-methyl-1,1'-biphenyl

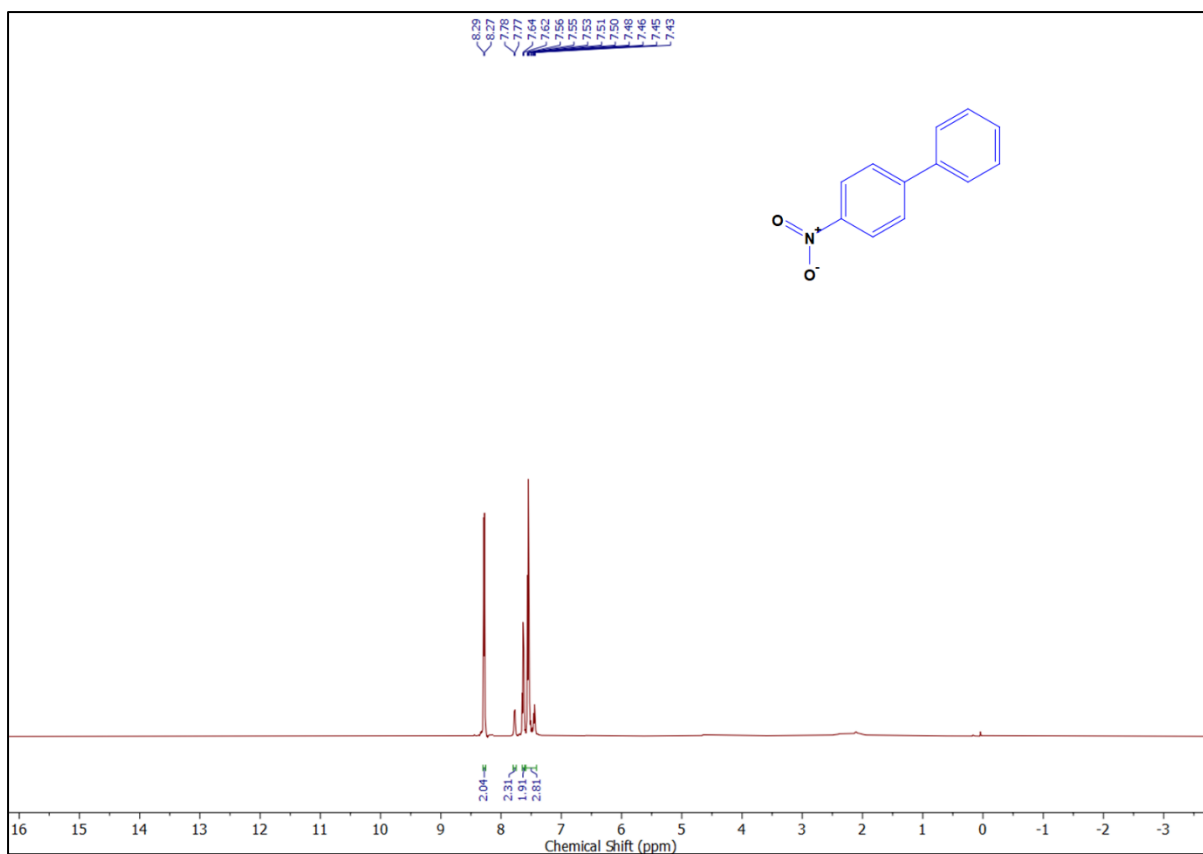


Figure S27: ^1H NMR spectrum of 4-nitro-1,1'-biphenyl

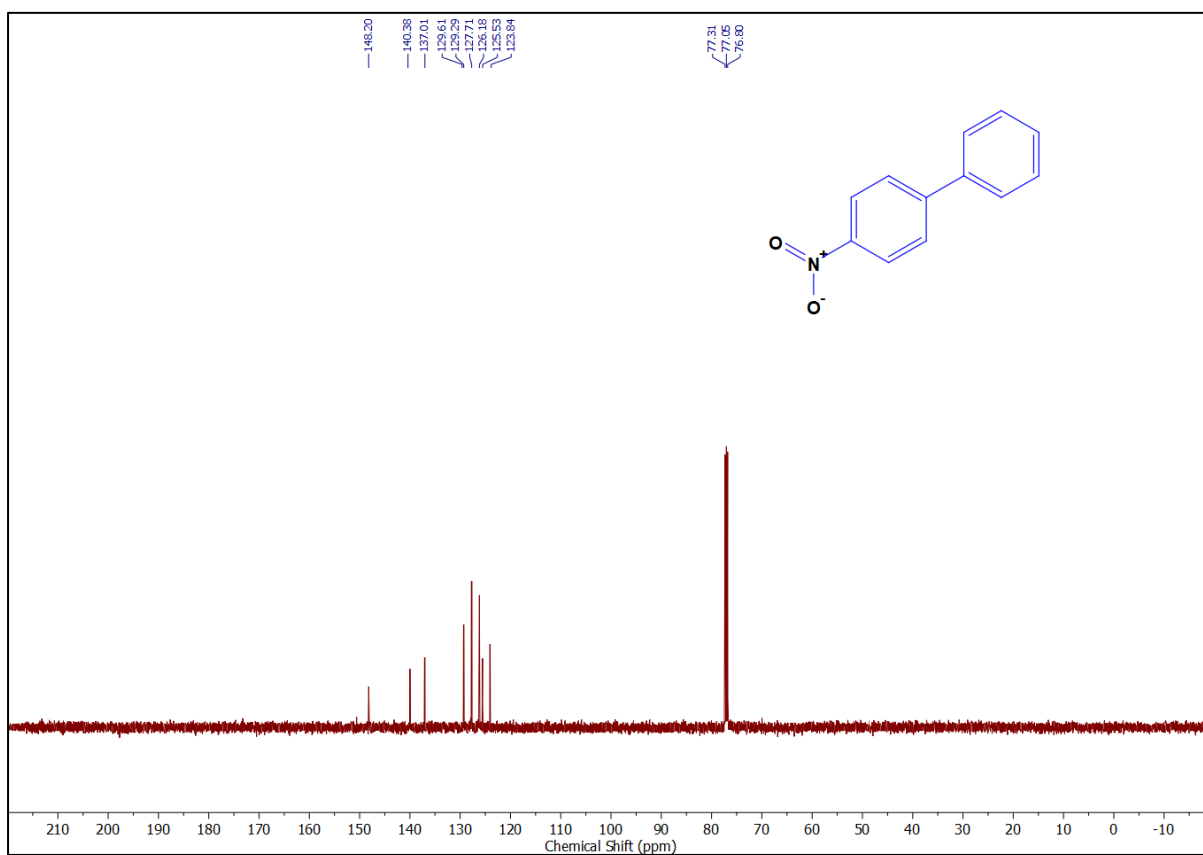


Figure S28: ^{13}C NMR spectrum of 4-nitro-1,1'-biphenyl

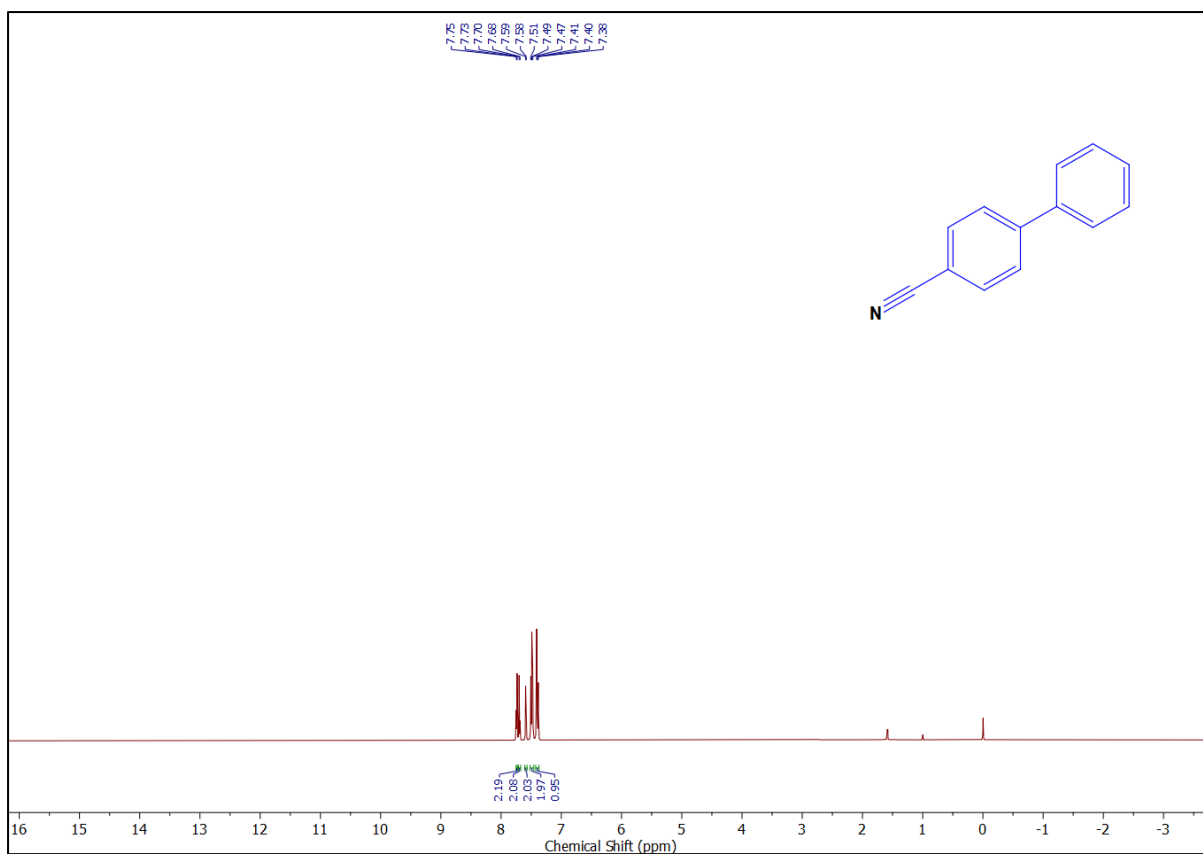


Figure S29: ^1H NMR spectrum of [1, 1'-biphenyl]-4-carbonitrile

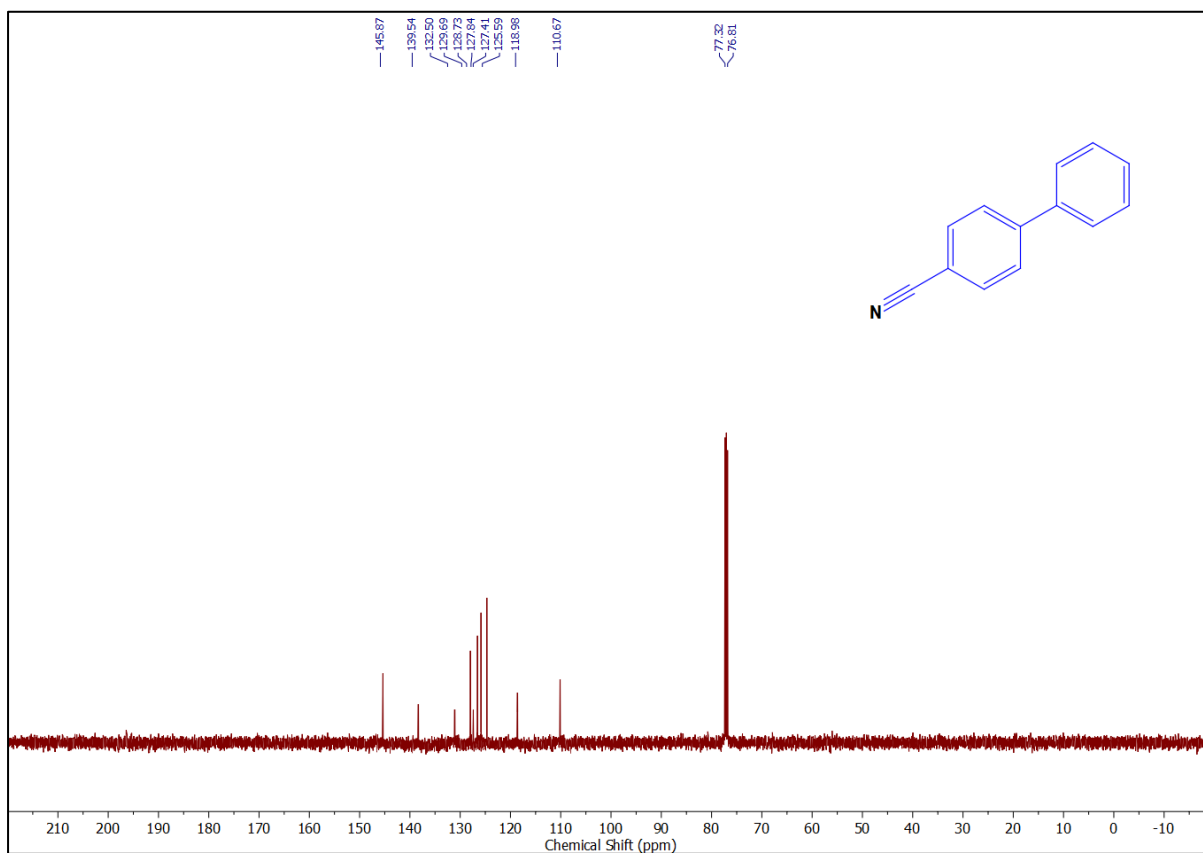


Figure S30: ^{13}C NMR spectrum of [1, 1'-biphenyl]-4-carbonitrile

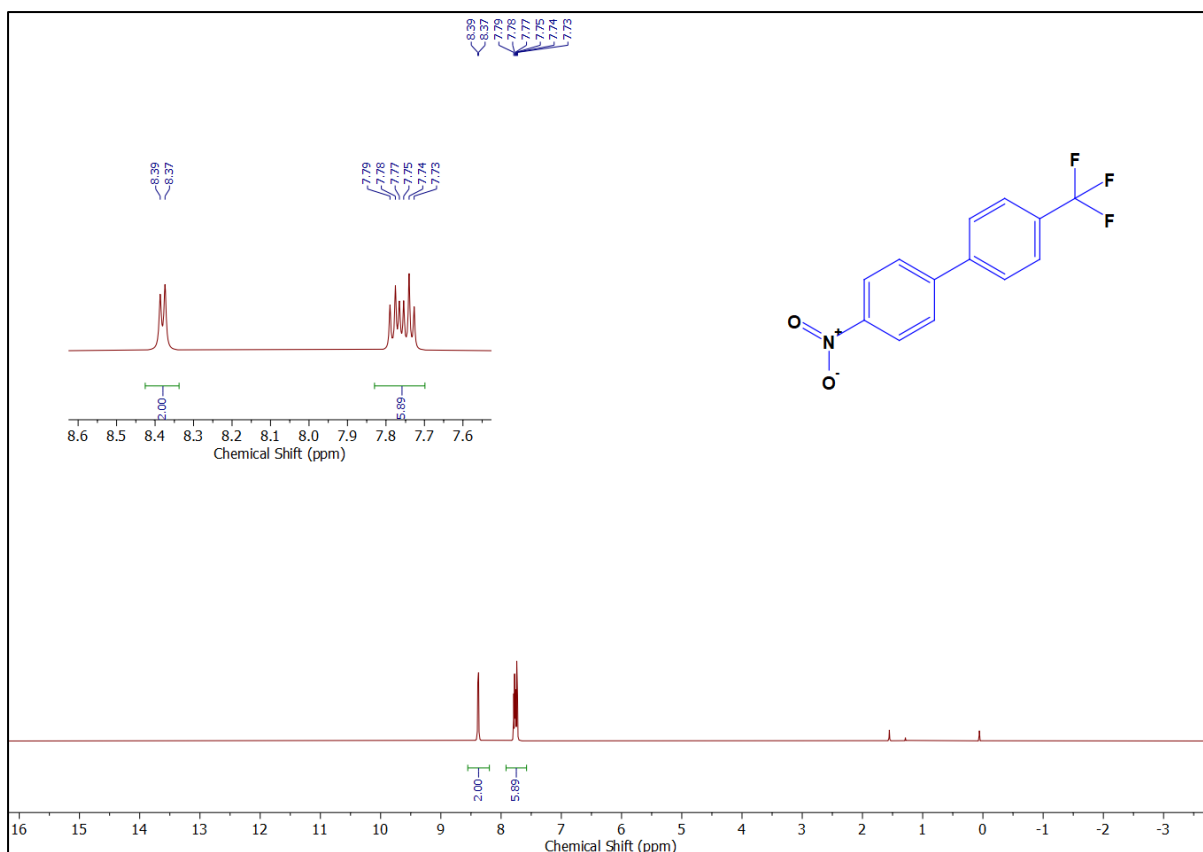


Figure S31: ¹H NMR spectrum of 4-nitro-4'-(trifluoromethyl)-1,1'-biphenyl

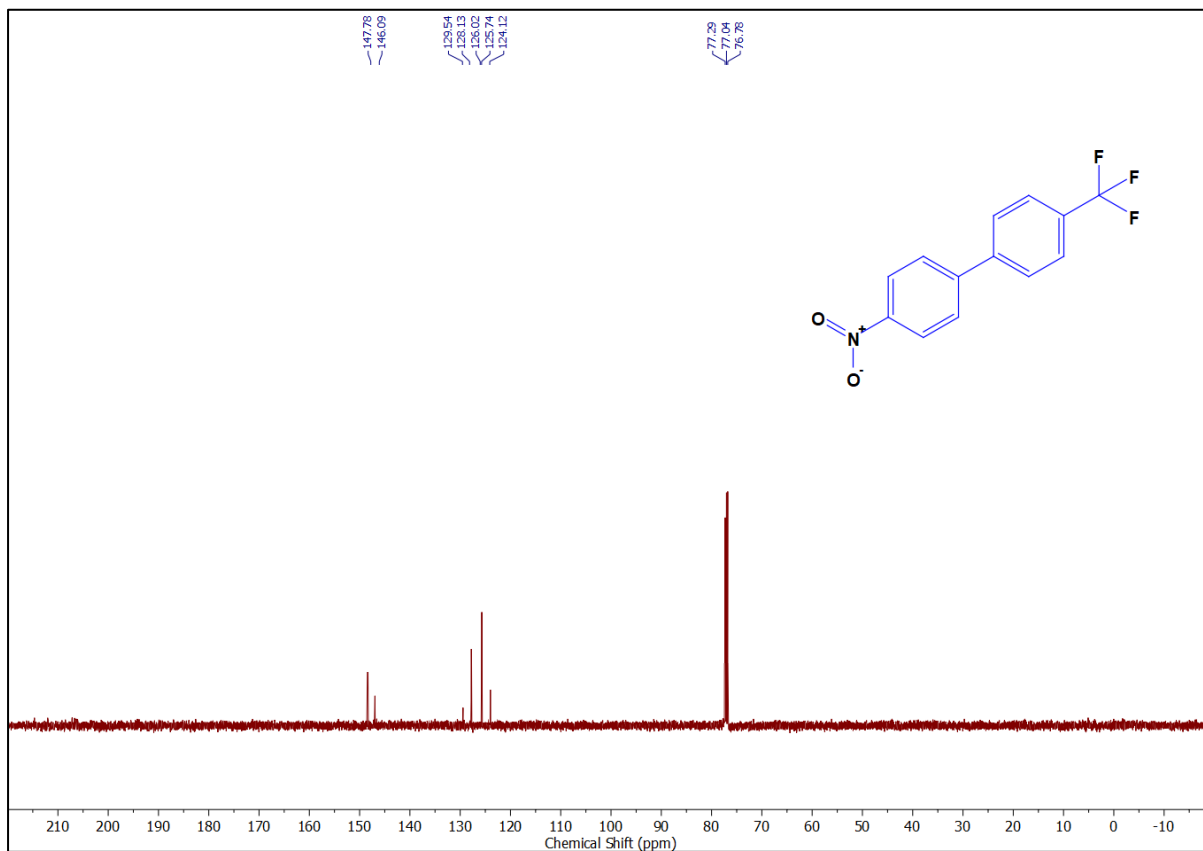


Figure S32: ¹³C NMR spectrum of 4-nitro-4'-(trifluoromethyl)-1,1'-biphenyl

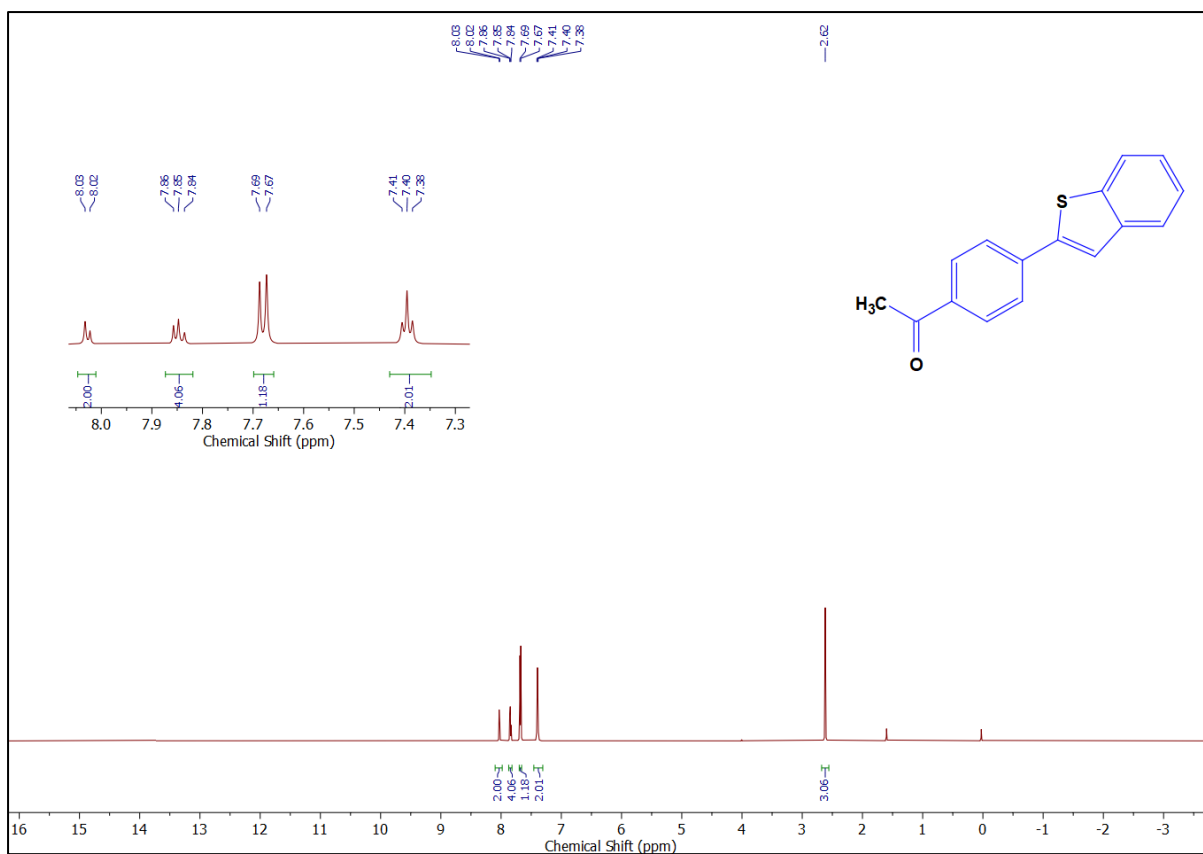


Figure S33: ¹H NMR spectrum of 1-(4-(benzo[b]thiophen-2-yl)phenyl)ethan-1-one

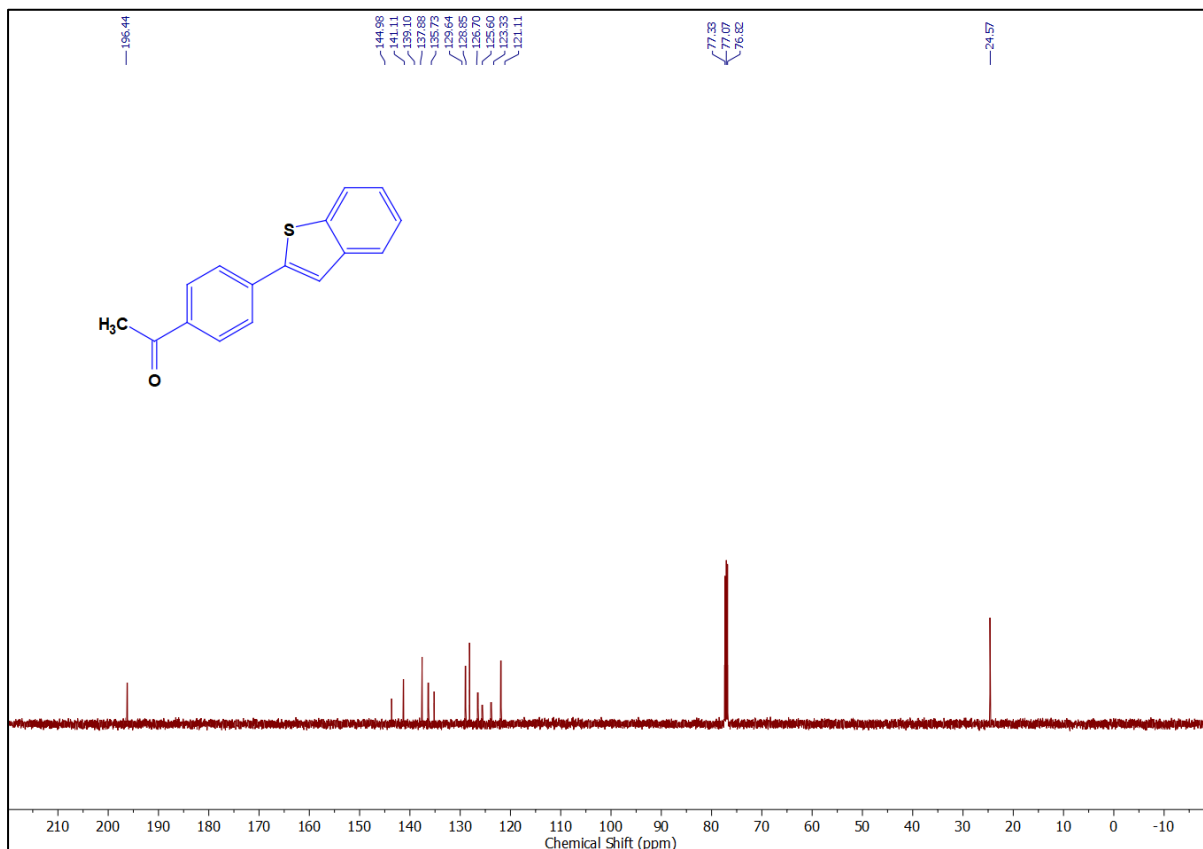


Figure S34: ¹³C NMR spectrum of 1-(4-(benzo[b]thiophen-2-yl)phenyl)ethan-1-one

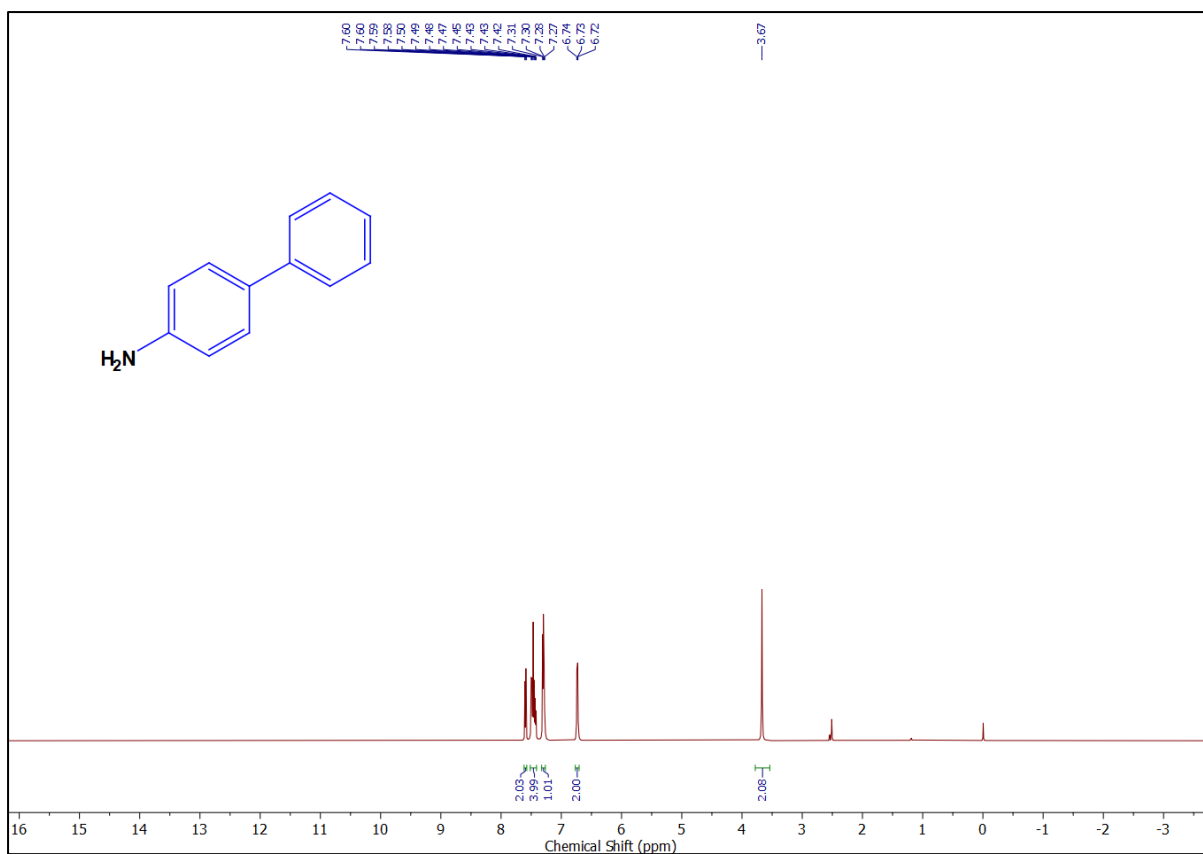


Figure S35: ¹H NMR spectrum of [1,1'-biphenyl]-4-amine

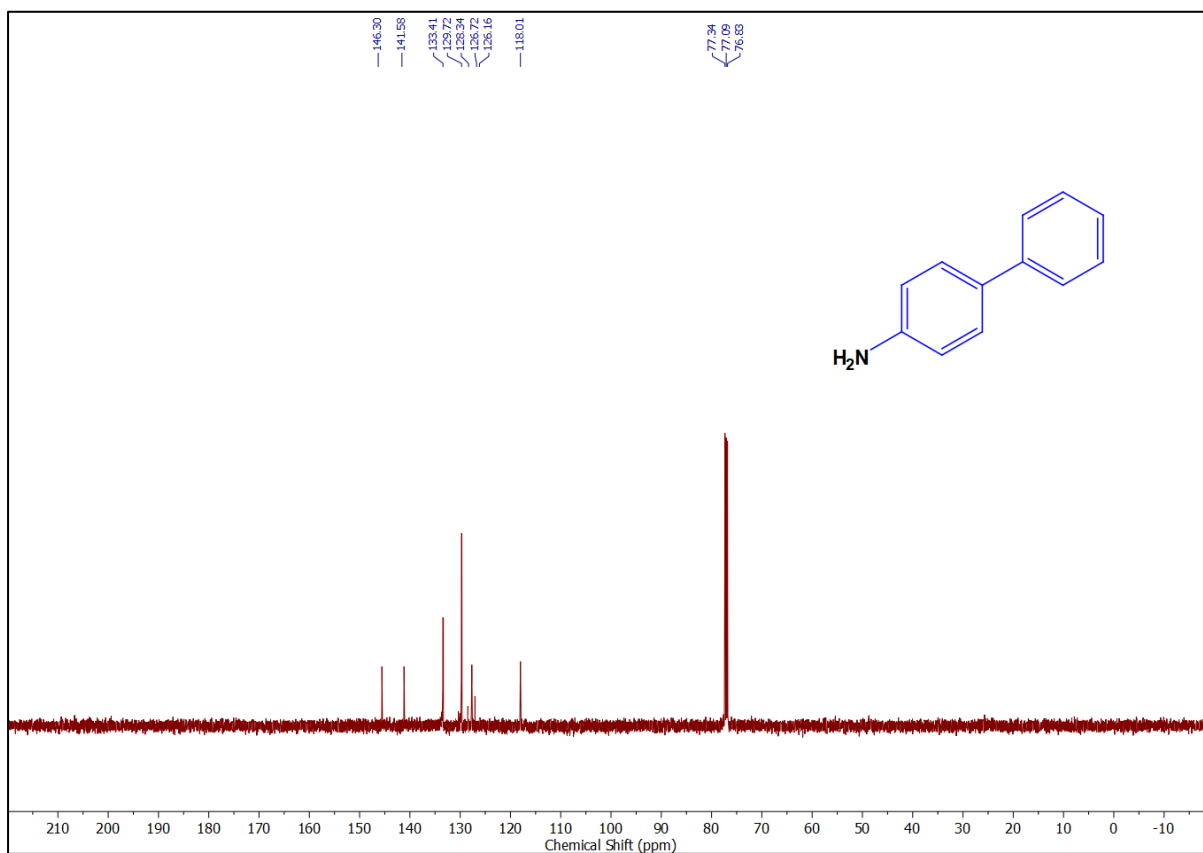


Figure S36: ¹³C NMR spectrum of [1,1'-biphenyl]-4-amine

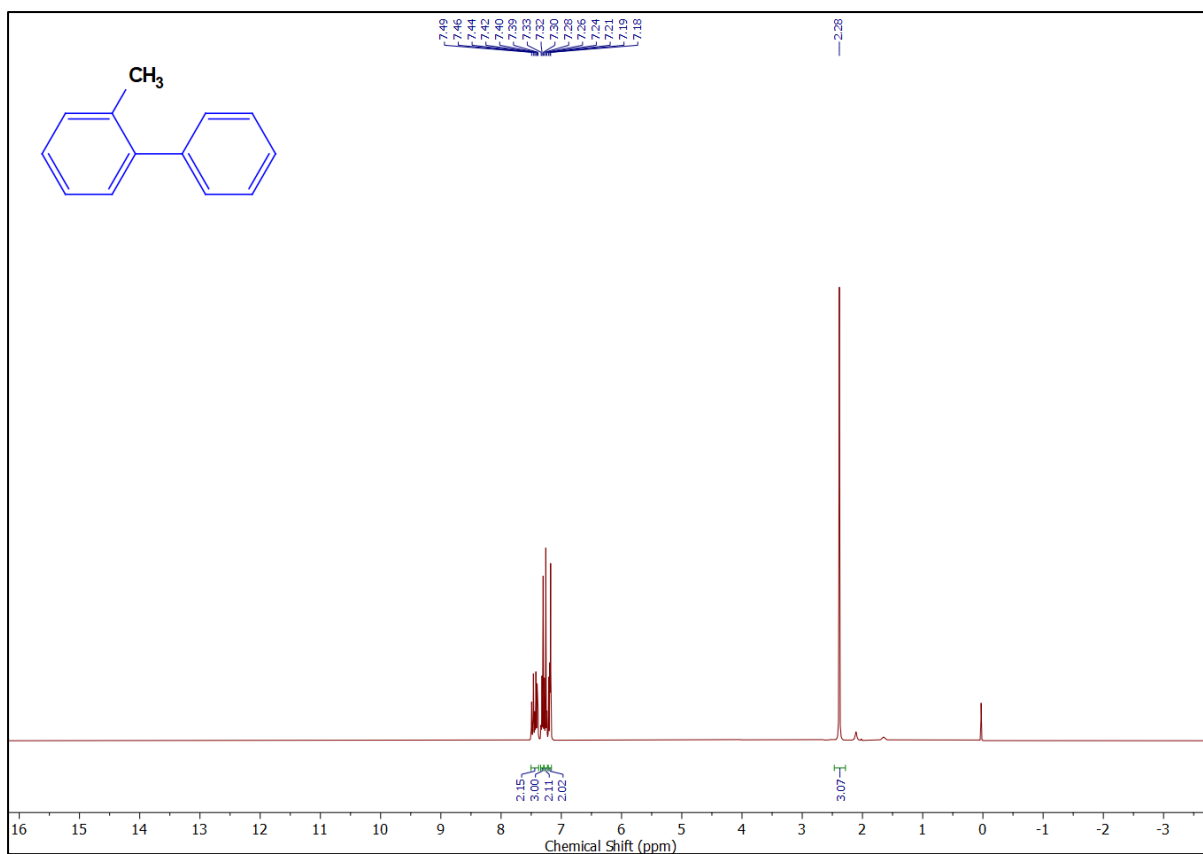


Figure S37: ¹H NMR spectrum of 2-methyl-1,1'-biphenyl

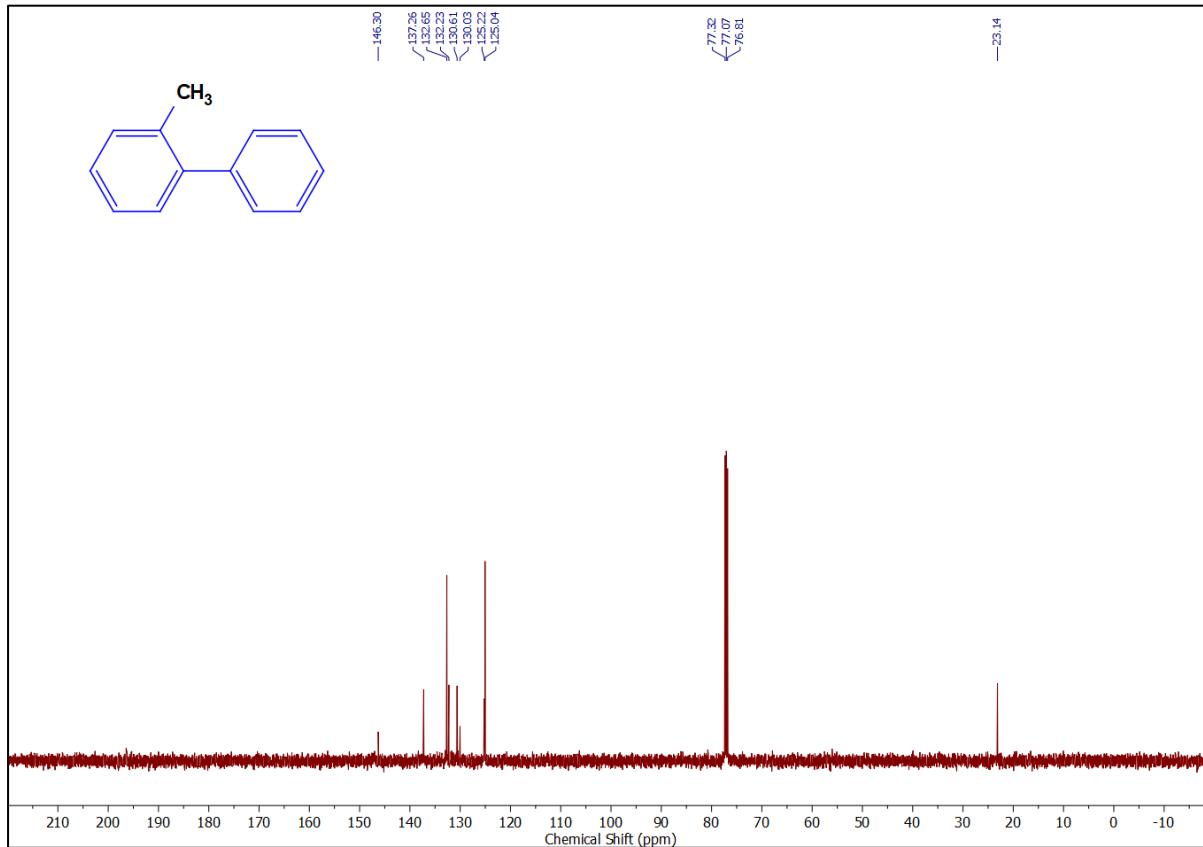


Figure S38: ¹³C NMR spectrum of 2-methyl-1,1'-biphenyl

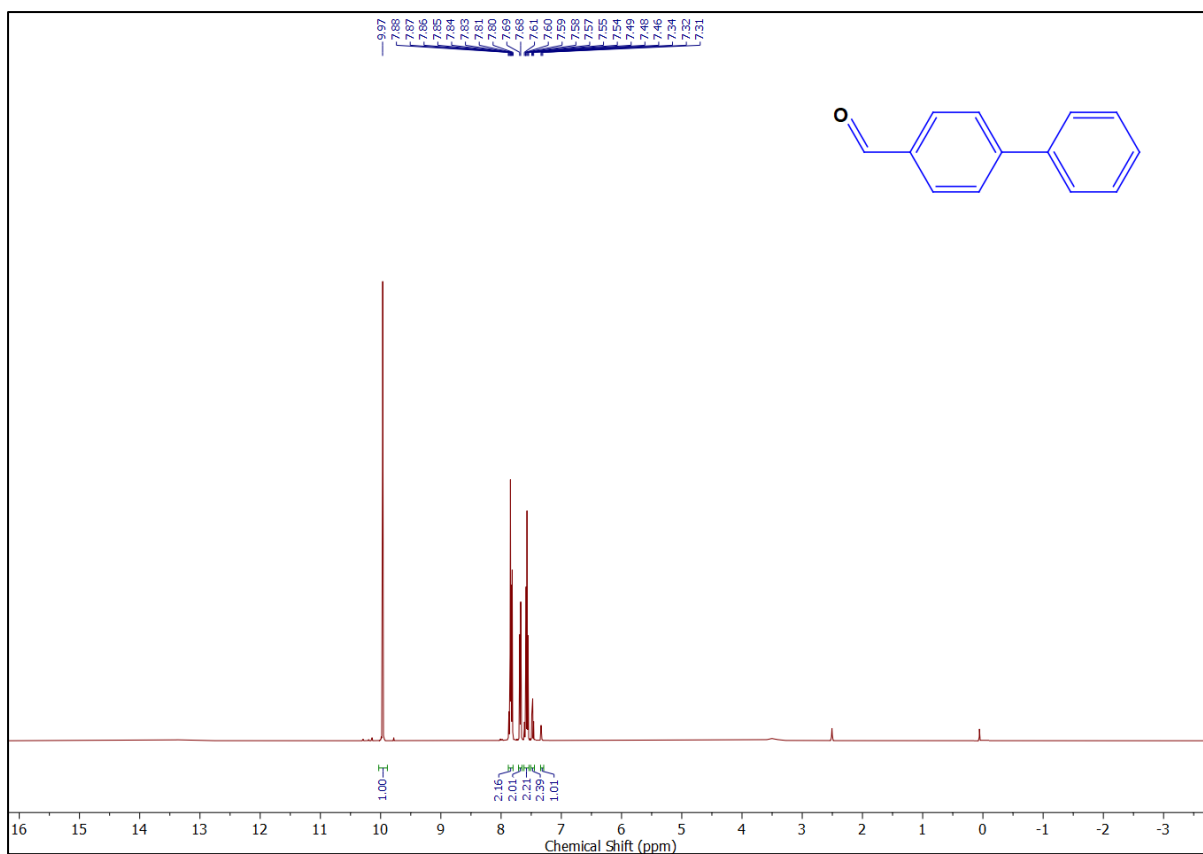


Figure S39: ^1H NMR spectrum of [1,1'-biphenyl]-4-carbaldehyde

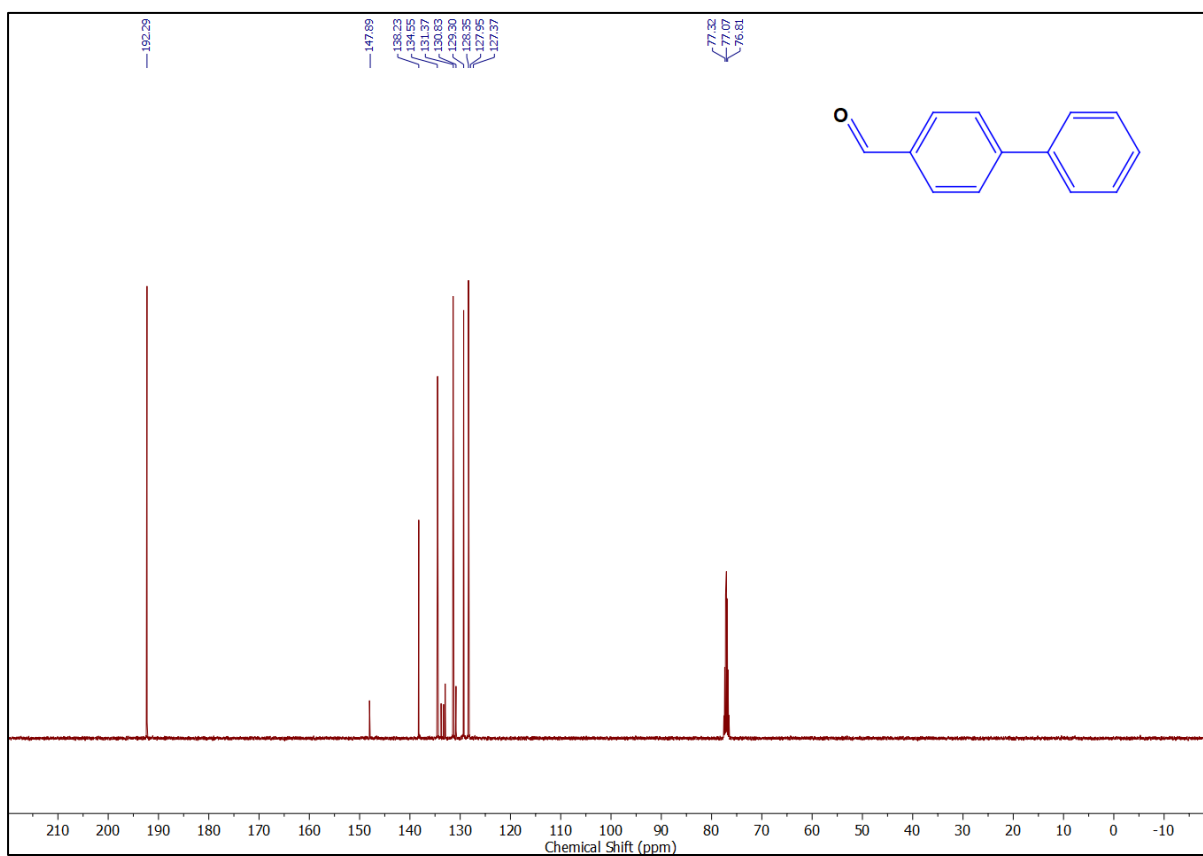


Figure S40: ^{13}C NMR spectrum of [1,1'-biphenyl]-4-carbaldehyde

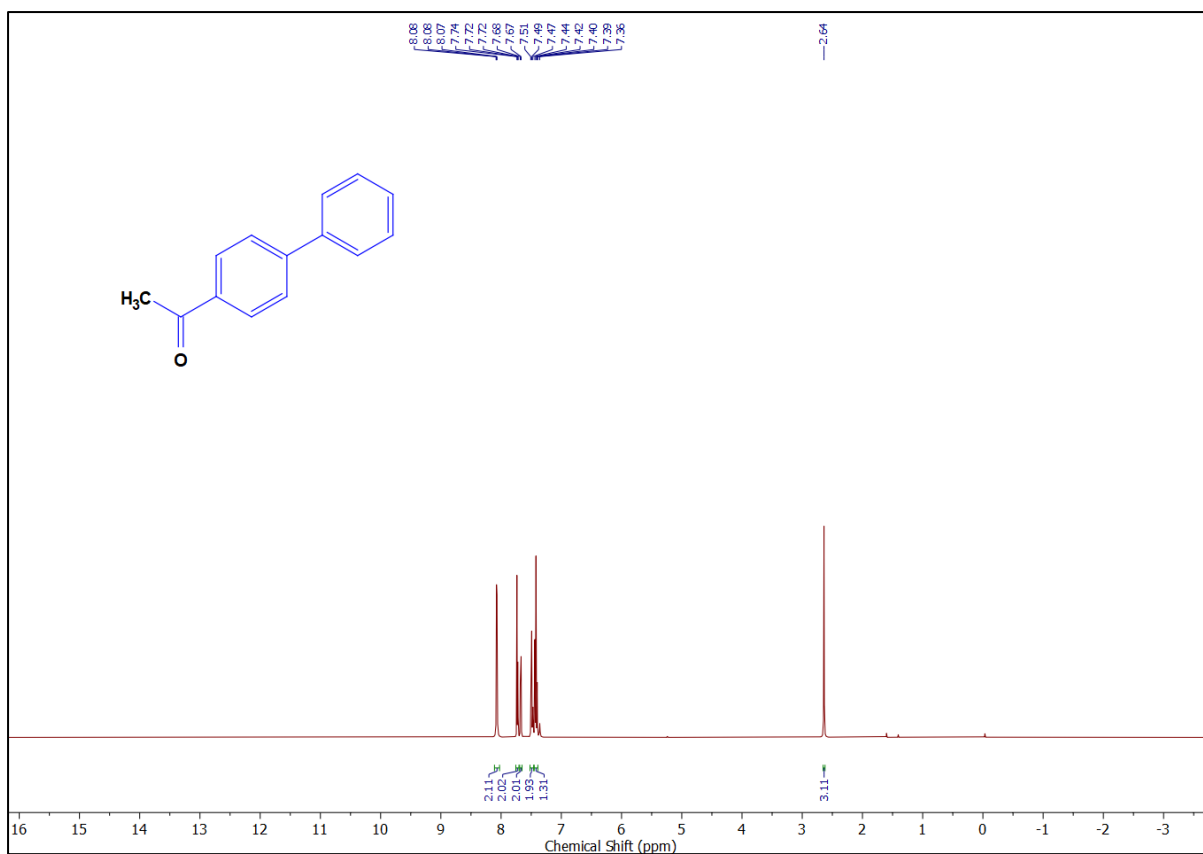


Figure S41: ¹H NMR spectrum of 1-([1,1'-biphenyl]-4-yl)ethan-1-one

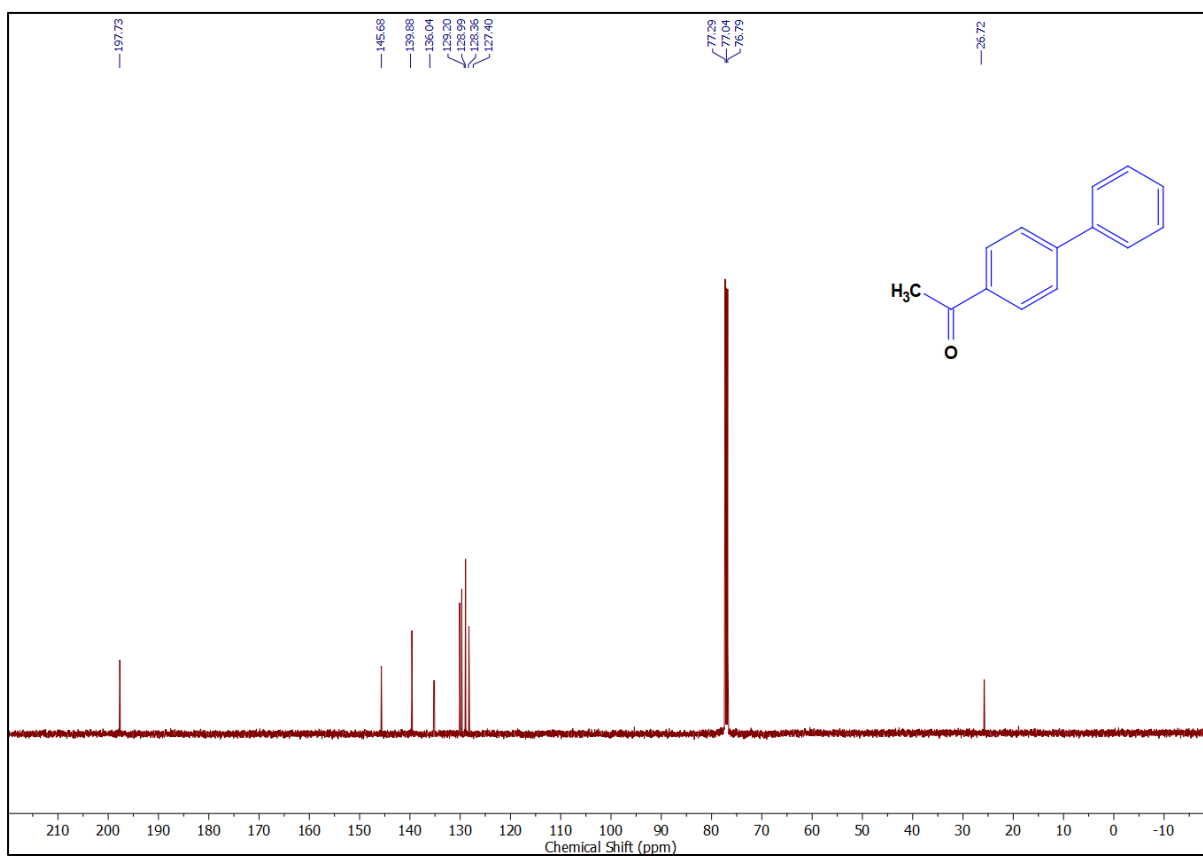


Figure S42: ¹³C NMR spectrum of 1-([1,1'-biphenyl]-4-yl)ethan-1-one

7. ESI-MS Spectra of compounds:

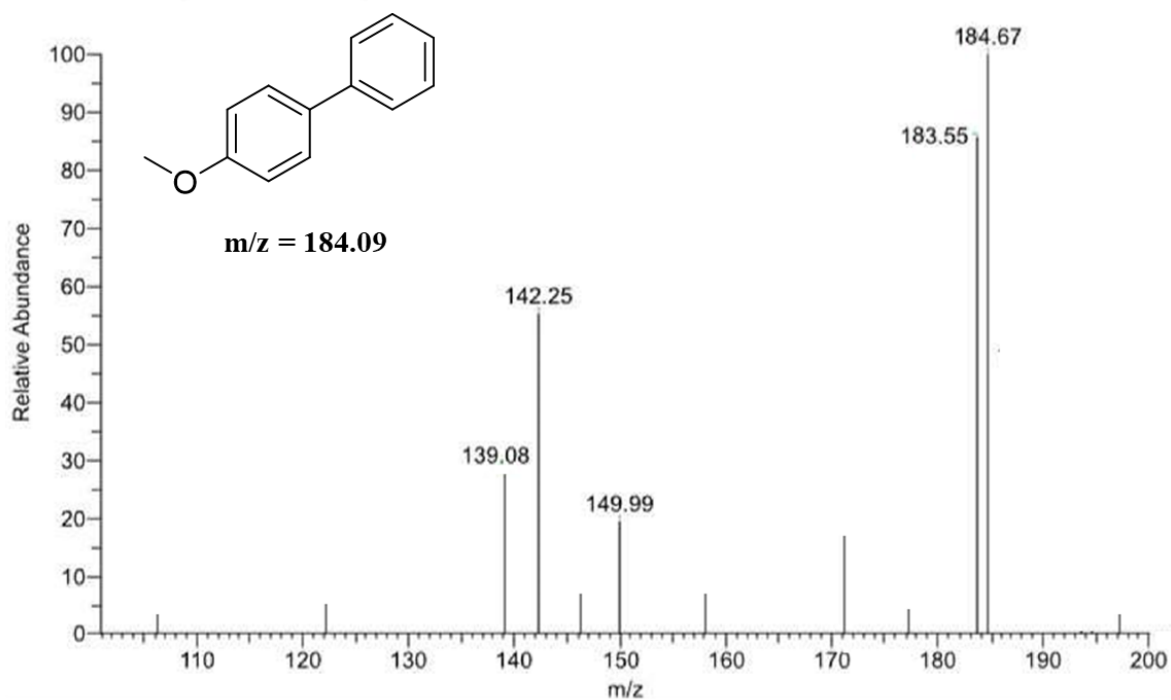


Fig.S43: ESI-MS m/z peak of 4-methoxy-1,1'-biphenyl

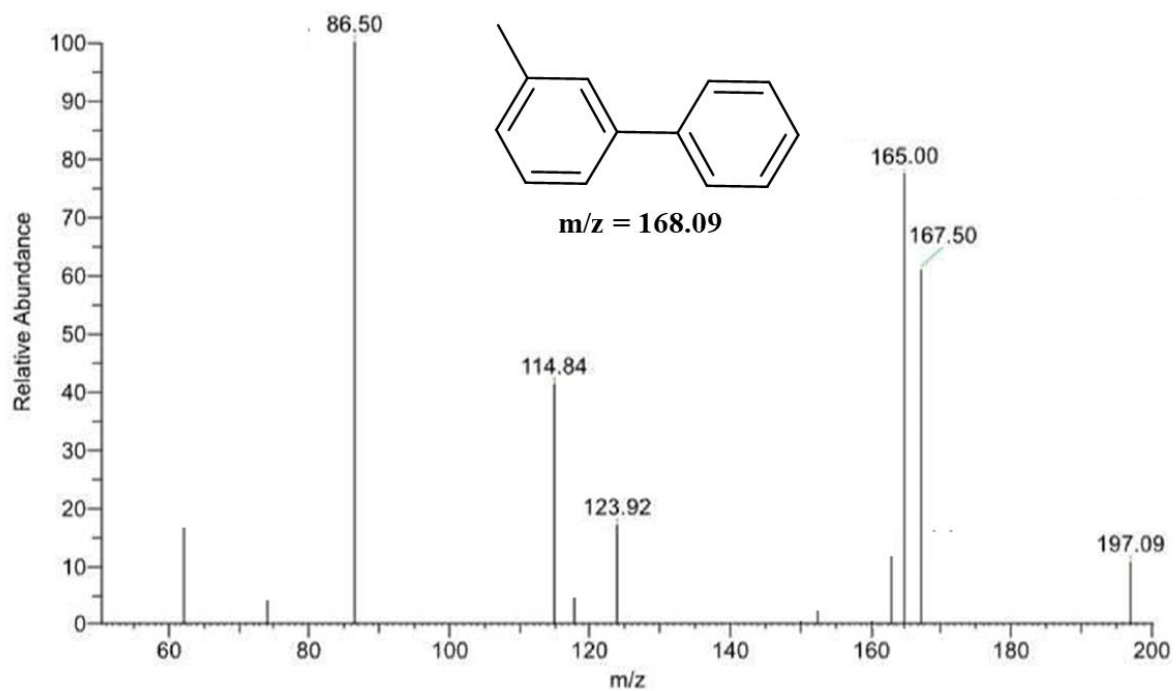


Fig.S44: ESI-MS m/z peak of 3-methyl-1,1'-biphenyl

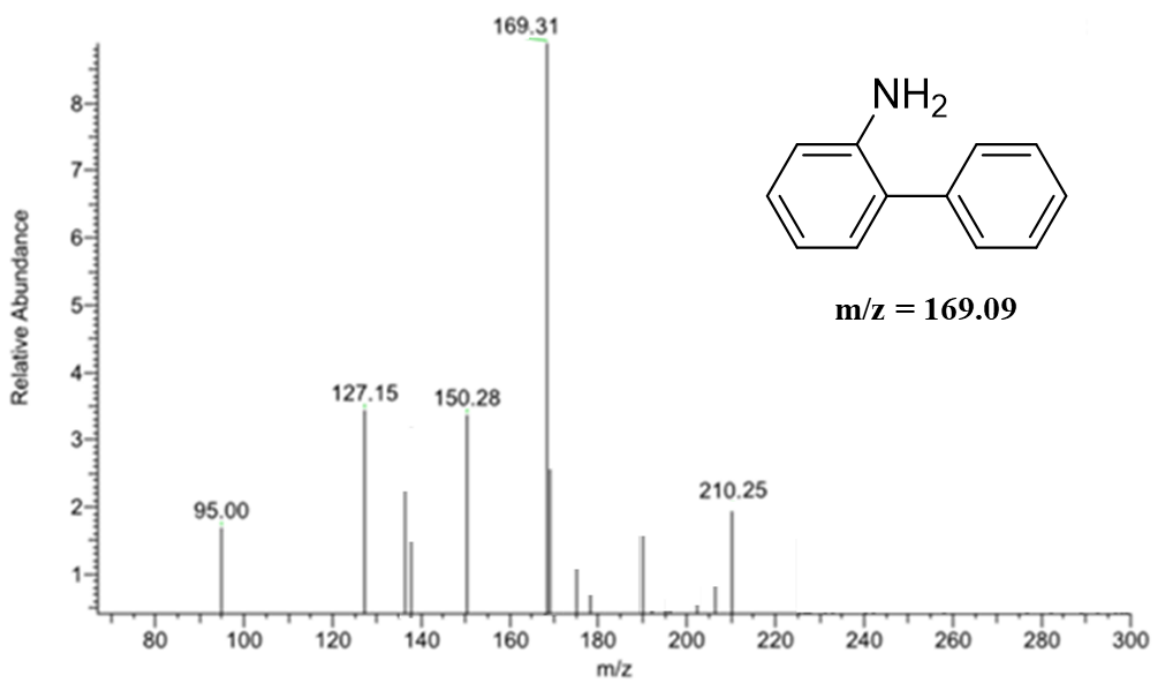


Fig.S45: ESI-MS m/z peak of [1,1'-biphenyl]-2-amine

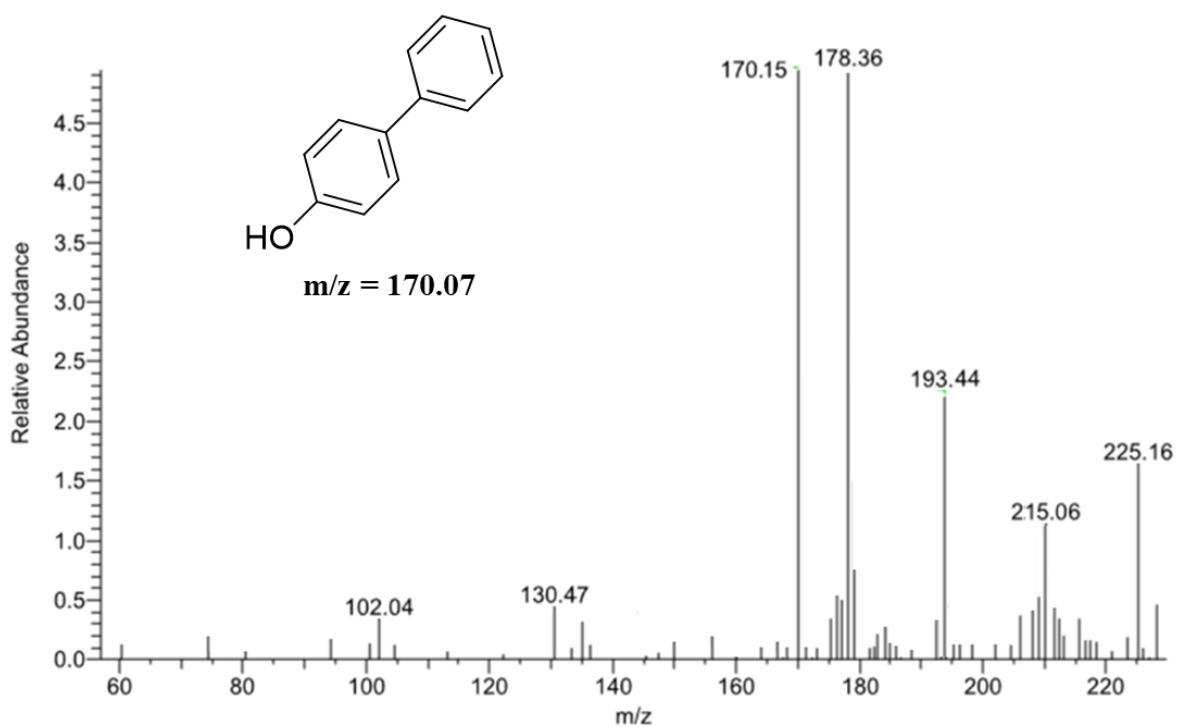


Fig.S46: ESI-MS m/z peak of [1,1'-biphenyl]-4-ol