Electronic Supplementary Material (ESI) for New Journal of Chemistry

Supplementary Information

NHC Hg(II) and Pd(II) complexes based on 1,8-dihydroxy-9,10-anthraqinone: Synthesis, structure and catalysis

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1. CCDC numbers for complexes 1-3.

CCDC 1851636, 1813374 and 1813375 contains the supplementary crystallographic data for complexes **1-3**. These data can be obtained free of charge via http//www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

2. The data of dihedral angles, slip angles between O(2) and anthraquinone plane, and the bond distances of O(2)-Metal and hydrogen bonds in complexes 1-3.

Table S1. In the same ligand of **1-3**, the dihedral angles (˚) between anthraquinone plane and two azole rings (A), and the dihedral angles (˚) between two azole rings in the same NHC-M-NHC units (B).

Complexes	A	B
1	10.8(2)	19.7(6)
2	6.3(7), 25.2(3)	30.1(8)
3	2.5(2), 64.3(9)	63.9(4)

Table S2. The slip angles between O(2) and anthraquinone plane, and the bond distances of O(2)-Metal for **2** and **3**.

Complexes	slip angles (˚)	O(2)-Metal (Å)
2	17.1(5)	3.085(2)
3	23.2(5)	2.837(5)

Table S3. H-Bonding Geometry (Å, ˚) for **1-3**

	D-H···A	D-H	H···A	D···A	D-H···A
1	C4-H4···N3	0.950(0)	2.377(5)	3.318(8)	170.8(2)
	C4'-H4'···N3'	0.950(0)	2.377(5)	3.318(8)	170.8(2)
	C5-H5···Br1	0.950(0)	2.923(8)	3.709(1)	140.8(2)
	C5'-H5'···Br1'	0.950(0)	2.923(8)	3.709(1)	140.8(2)

2	C31-H31A···F5	0.970(0)	2.677(7)	3.568(6)	152.8(9)
	C46'-H46'···F3	0.930(0)	2.483(7)	3.333(8)	152.0(3)
	C5-H5···F6'	0.930(0)	2.576(3)	3.411(2)	149.6(1)
3	C22-H22···F4	0.950(0)	2.493(5)	3.219(8)	133.2(5)
	C22'-H22'···F4'	0.950(0)	2.493(5)	3.219(8)	133.2(5)
	C24-H24A···F3	0.990(0)	2.443(5)	3.368(0)	155.2(2)
	C24-H24B···F3'	0.990(0)	2.443(5)	3.368(0)	155.2(2)
	C4-H4···F6	0.950(0)	2.211(6)	3.138(5)	164.8(7)
	C15-H15···F4	0.950(0)	2.656(3)	3.278(3)	123.5(4)

Symmetry code: ii: -*x*, -1 + *y*, -0.5 - *z*; iii: -0.5 + *x*, -0.5 - *y*, -1.5 + *z*; iv: -*x*, -*y*, -*z*; v: *x*, -1 + *y*, -1 + *z* for **1**; i: -1 + *x*, 1+ *y*, *z*; ii: *x*, 1 + *y*, *z* for **2**; ii: -0.5 + *x*, -0.5 + *y*, *z*; iii: 1.5 - *x*, -0.5 + *y*, 0.5 - *z*; iv: -0.5 + *x*, 0.5 + *y*, -1 + *z*; v: 1.5 - *x*, 0.5 + *y*, 0.5 - *z*; vi: -0.5 + *x*, -0.5 + *y*, -1 + *z* for **3**.

Table S4. Distances (Å) of π-π interactions for **2**

Complex	face-to-face	center-to-center
2	3.659(2) (benzimidazole) 3.504(2) (benzimidazole and anthraquinone)	3.676(2) (benzimidazole) 4.021(2) (benzimidazole and anthraquinone)
3	3.329(5) (anthraquione and imidazole)	3.528(6) (anthraquione and imidazole)

3. The ^{1}H NMR spectra and ^{13}C NMR spectra for all intermediates, precursors $L^1H_2(PF_6)_2$-$L^3H_2(PF_6)_2$, and complexes 1-3.

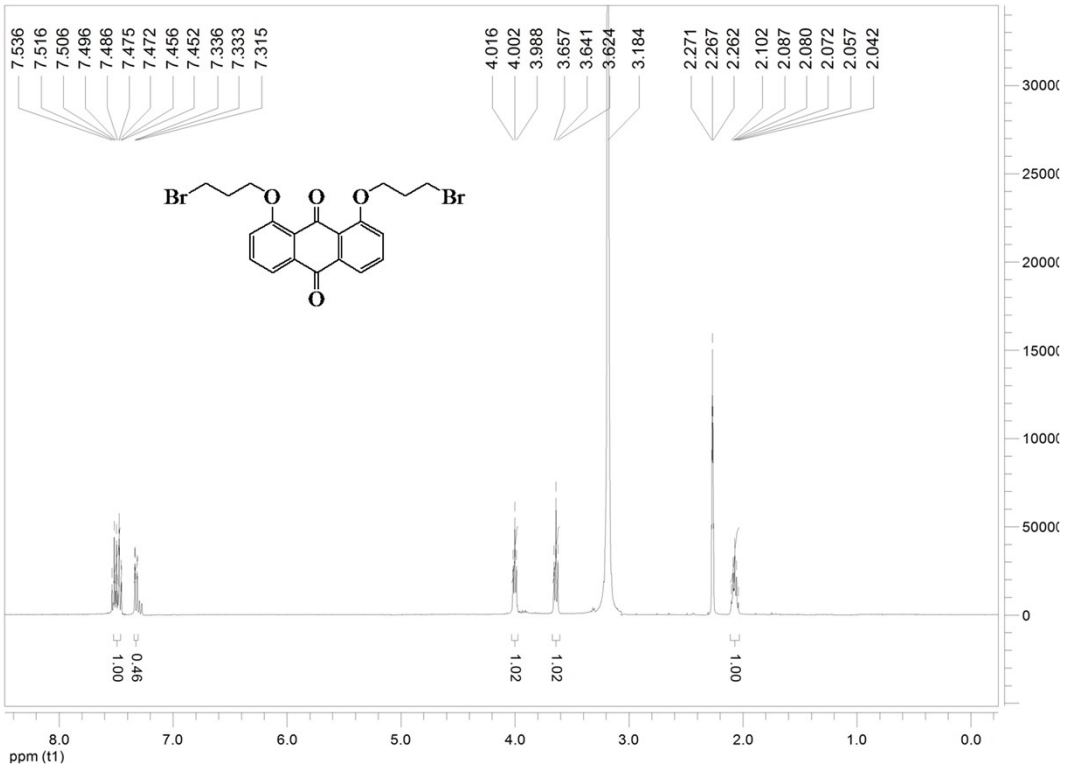


Fig. S1 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of 1,8-bis(3'-bromopropoxy)anthraquinone.

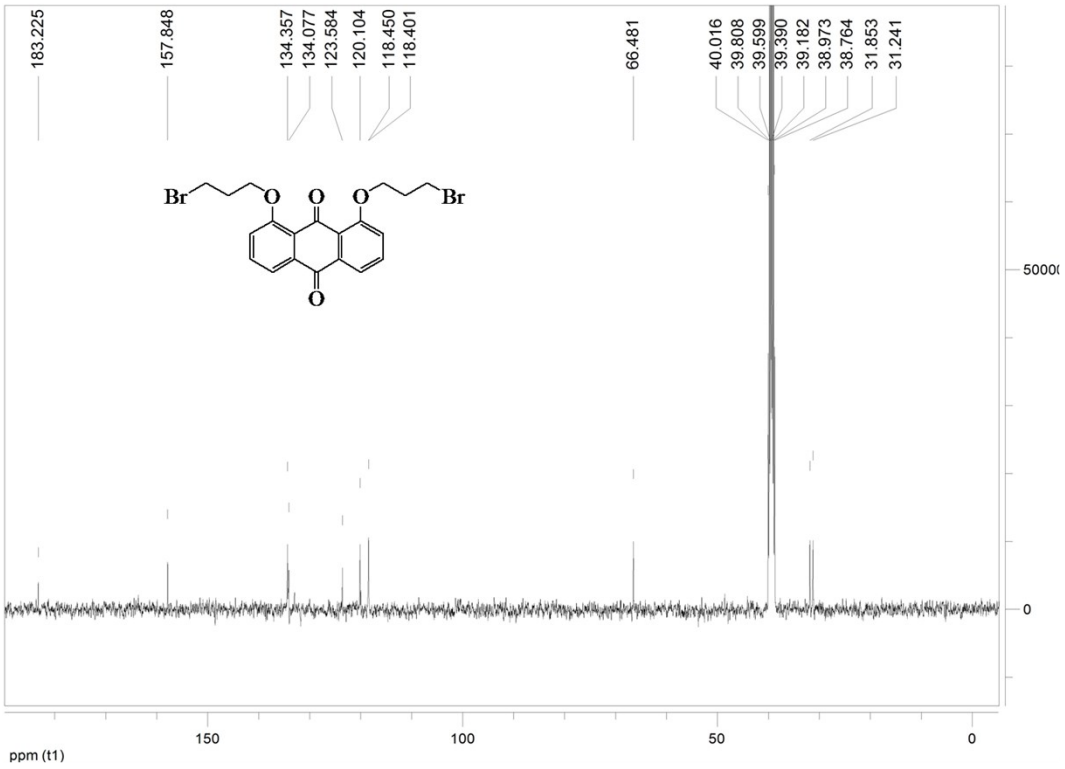


Fig. S2 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of 1,8-bis(3'-bromopropoxy)anthraquinone.

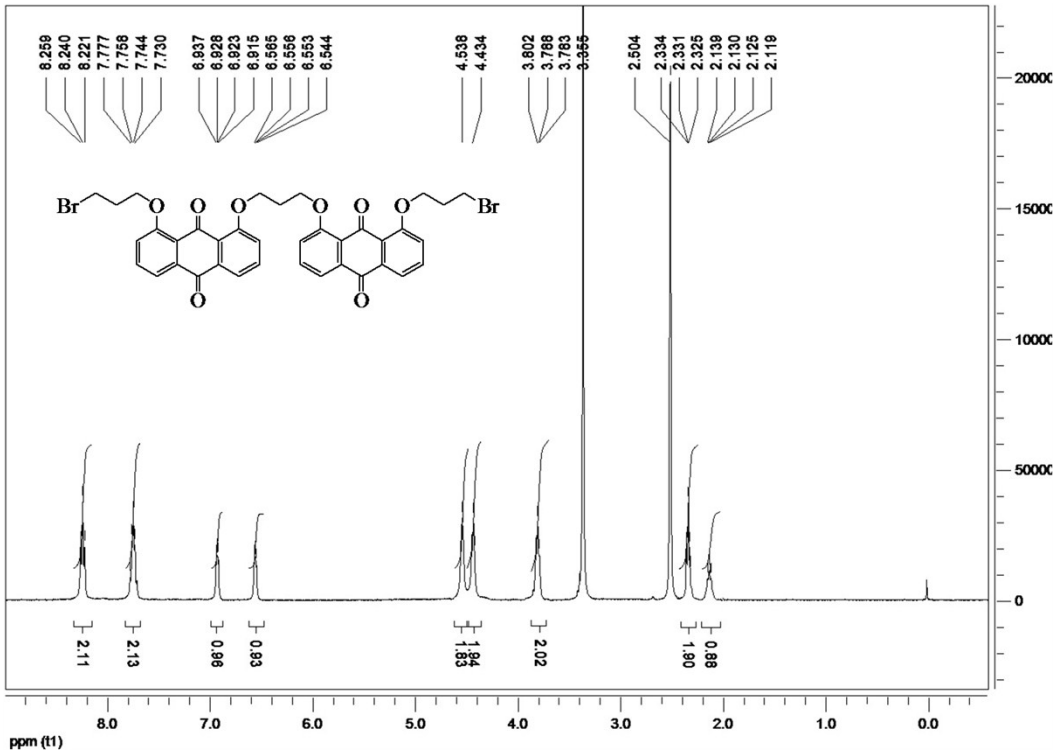


Fig. S3 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of 1,3-bis[8'-(3''-bromopropoxy)anthraquinon-l-yloxy]propane.

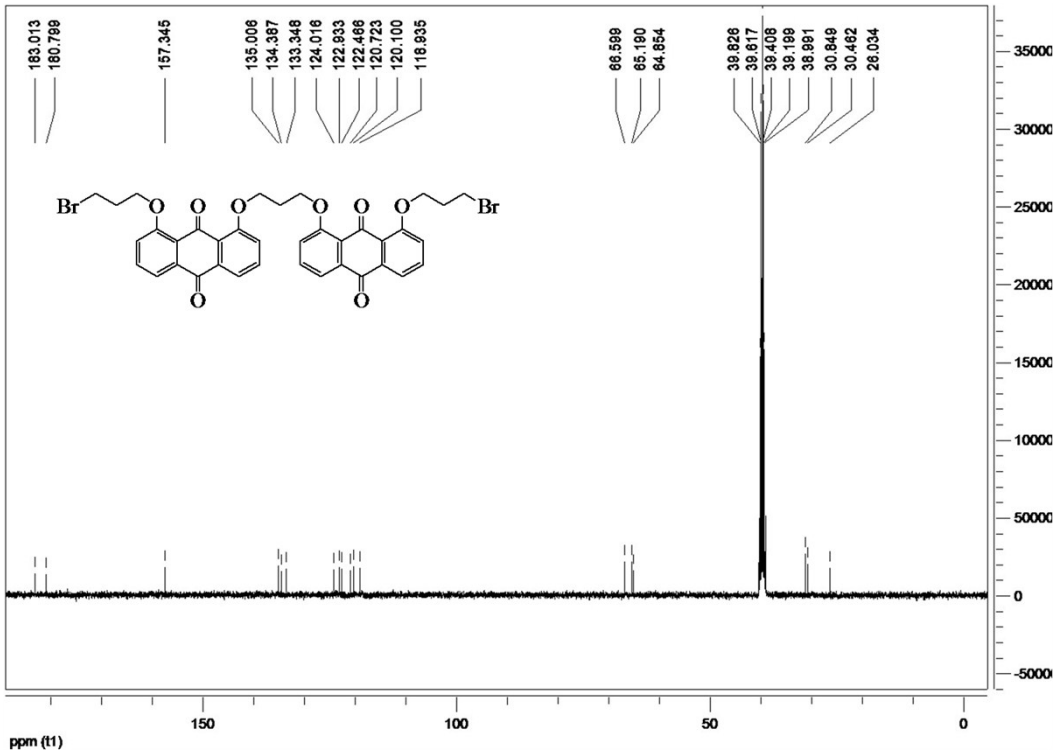


Fig. S4 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of 1,3-bis[8'-(3''-bromopropoxy)anthraquinon-l-yloxy]propane.

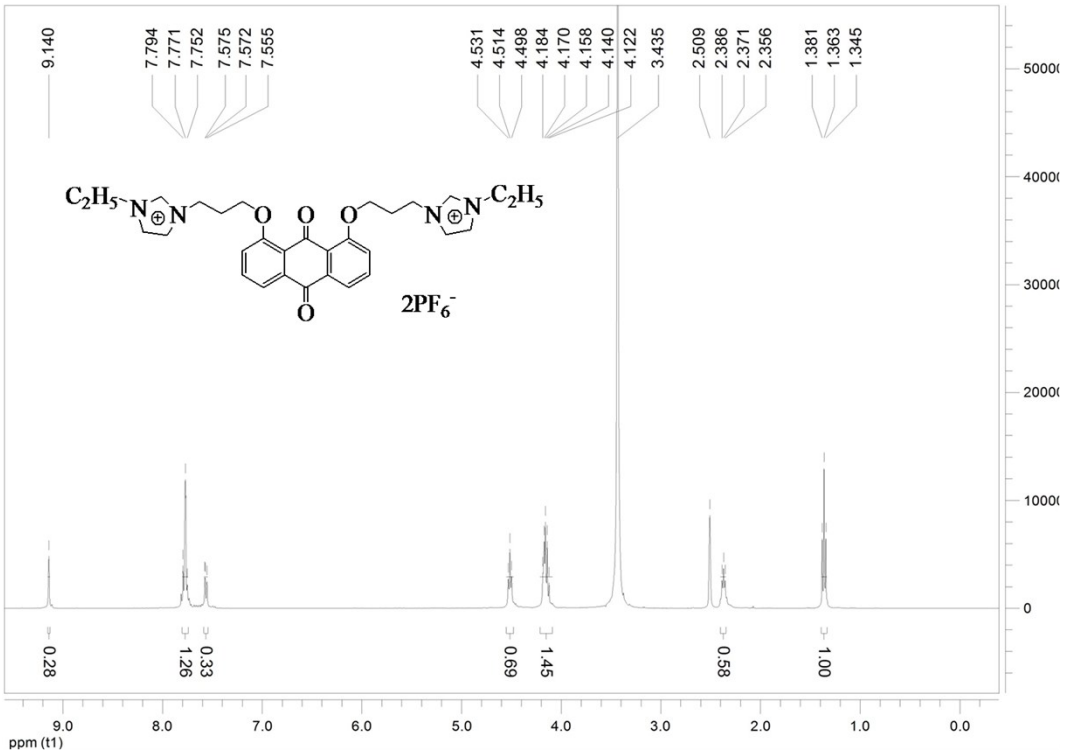


Fig. S5 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of $\mathbf{L^1H_2(PF_6)_2}$.

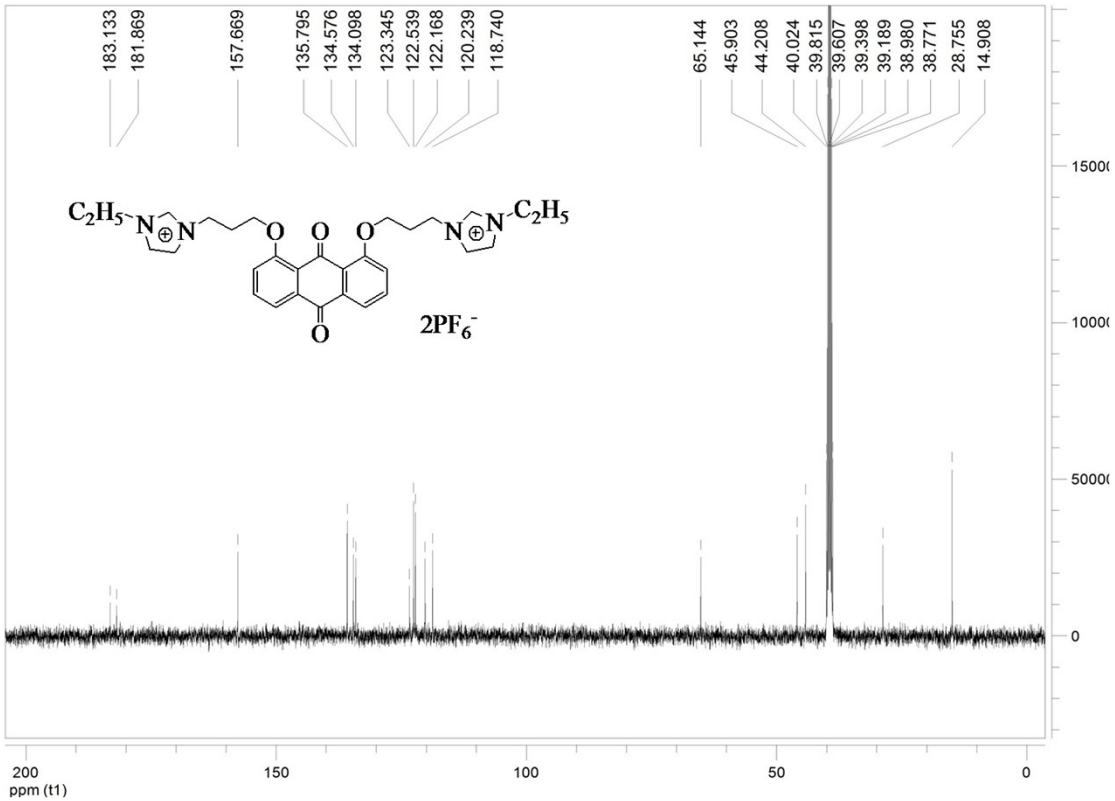


Fig. S6 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of $\mathbf{L^1H_2(PF_6)_2}$.

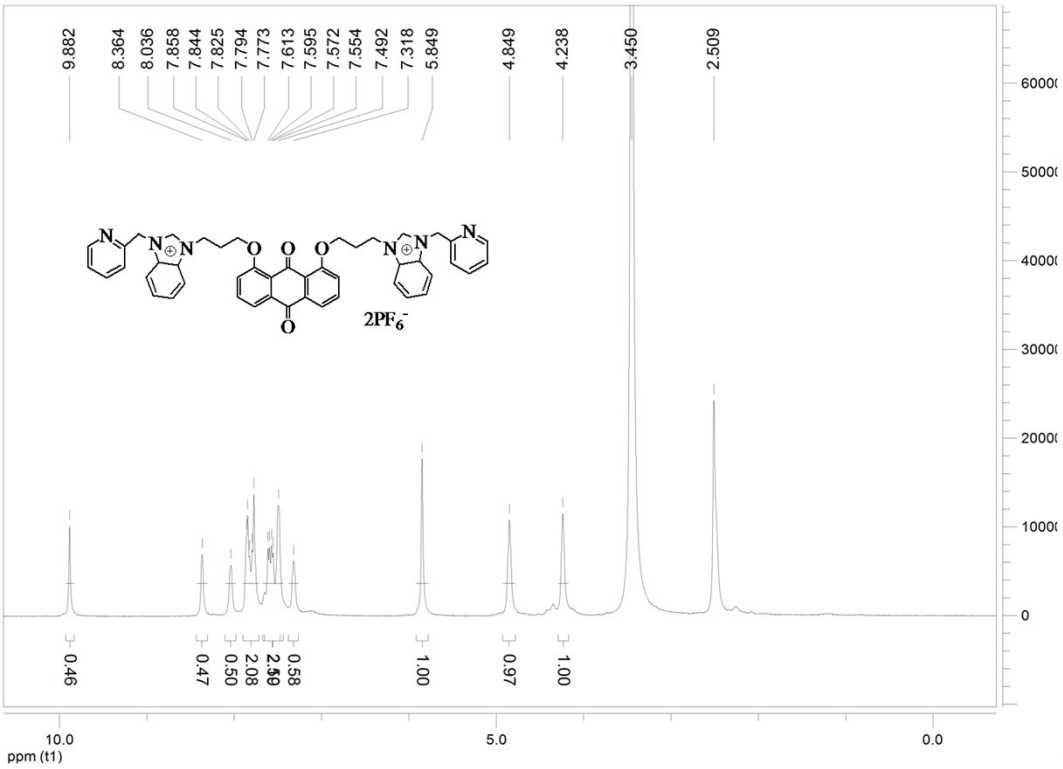


Fig. S7 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of $\mathbf{L^2H_2(PF_6)_2}$.

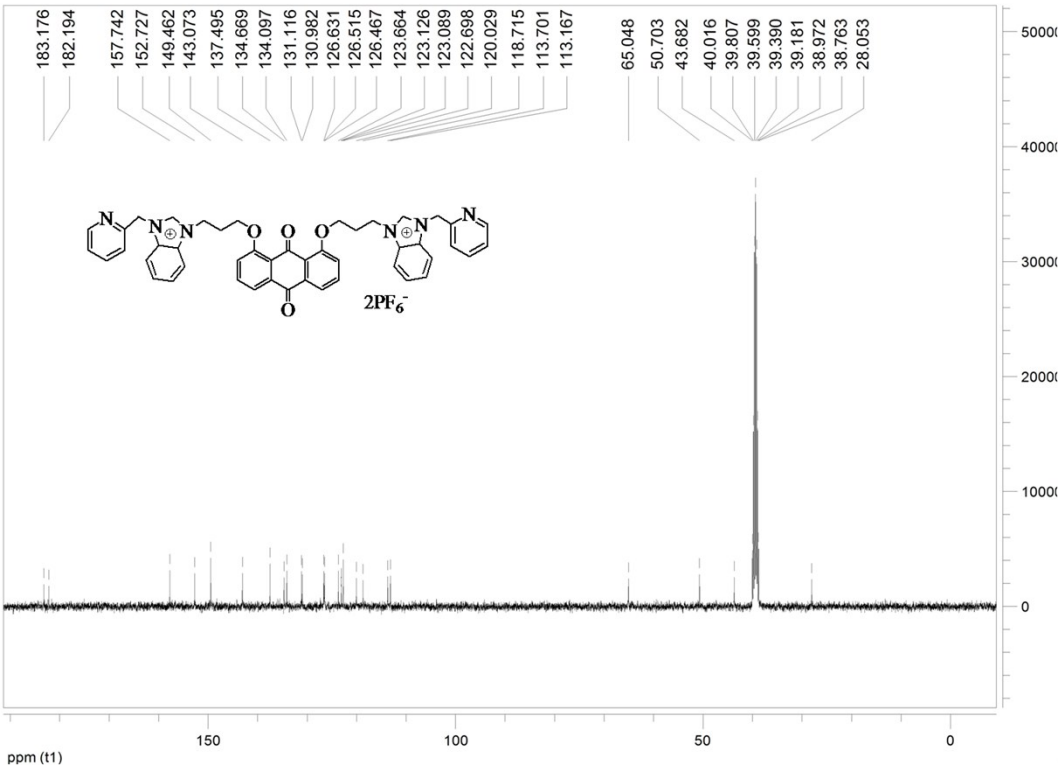


Fig. S8 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of $\mathbf{L^2H_2(PF_6)_2}$.

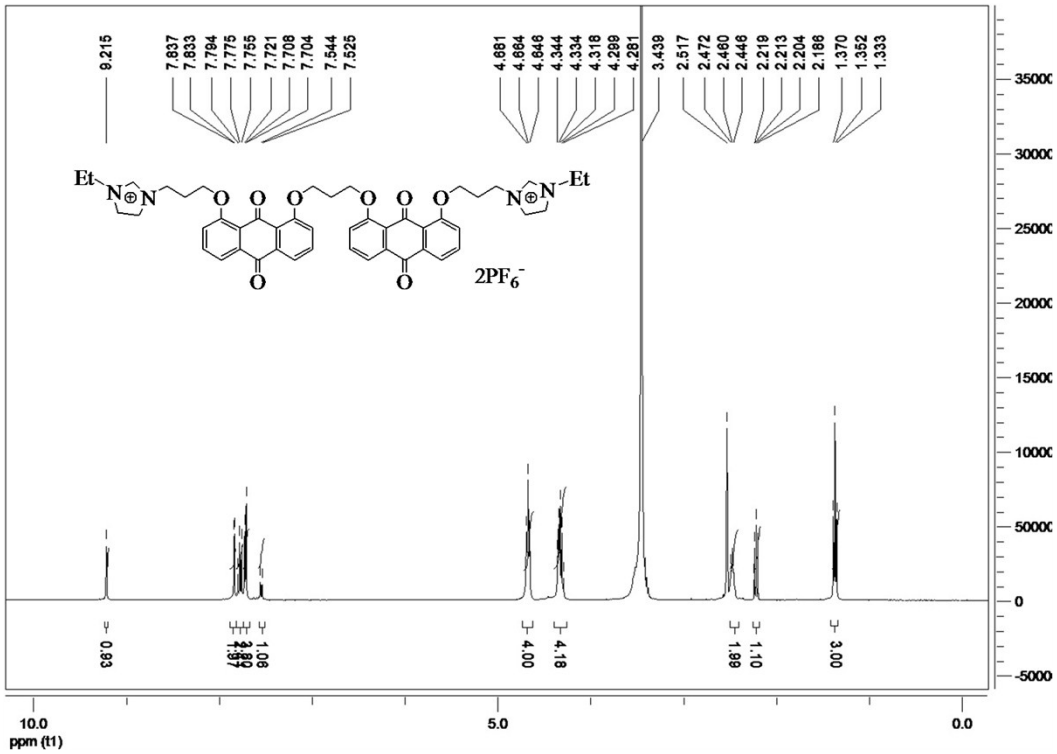


Fig. S9 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of $\mathbf{L^3H_2(PF_6)_2}$.

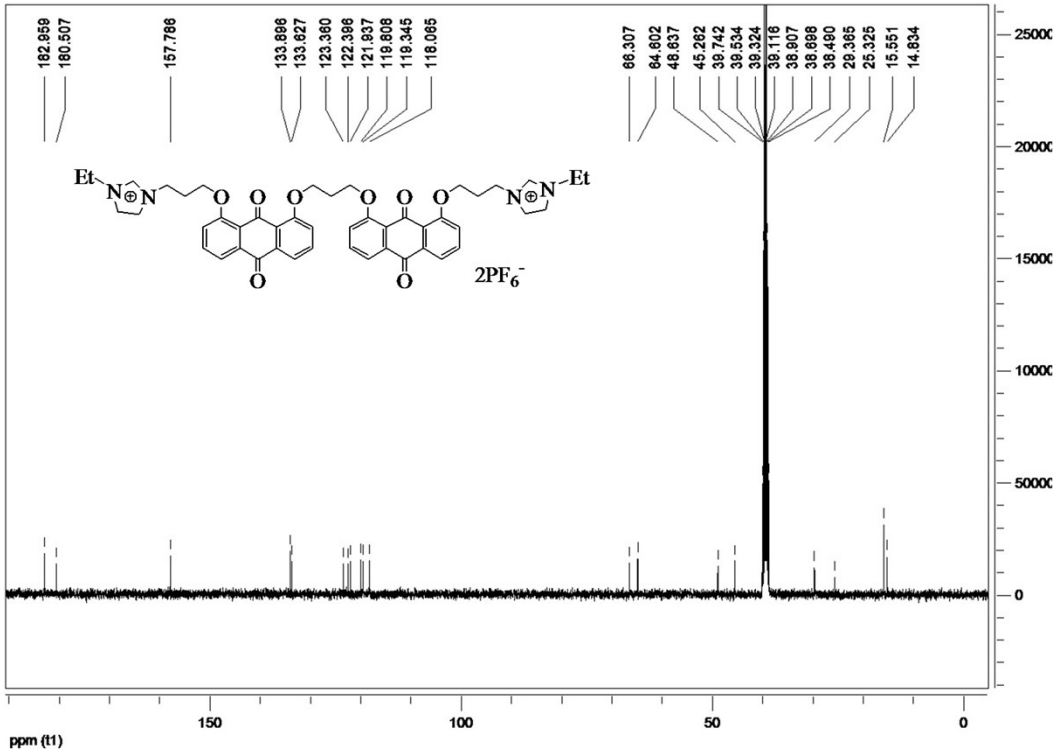


Fig. S10 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of $\mathbf{L^3H_2(PF_6)_2}$.

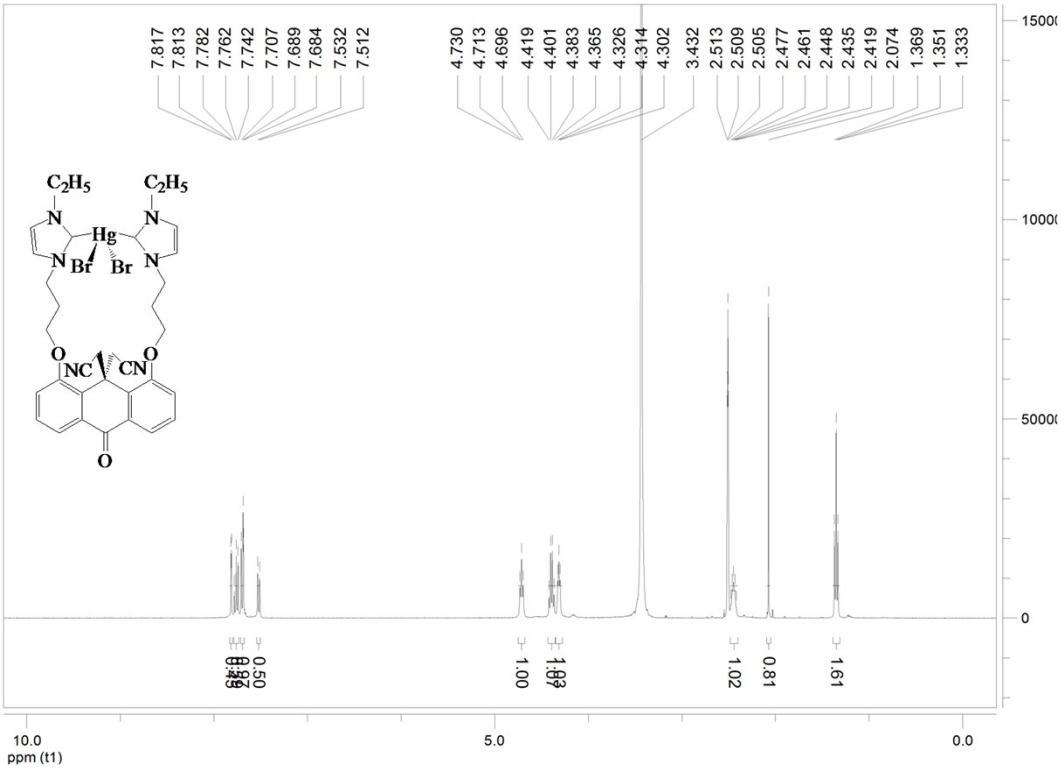


Fig. S11 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **1**.

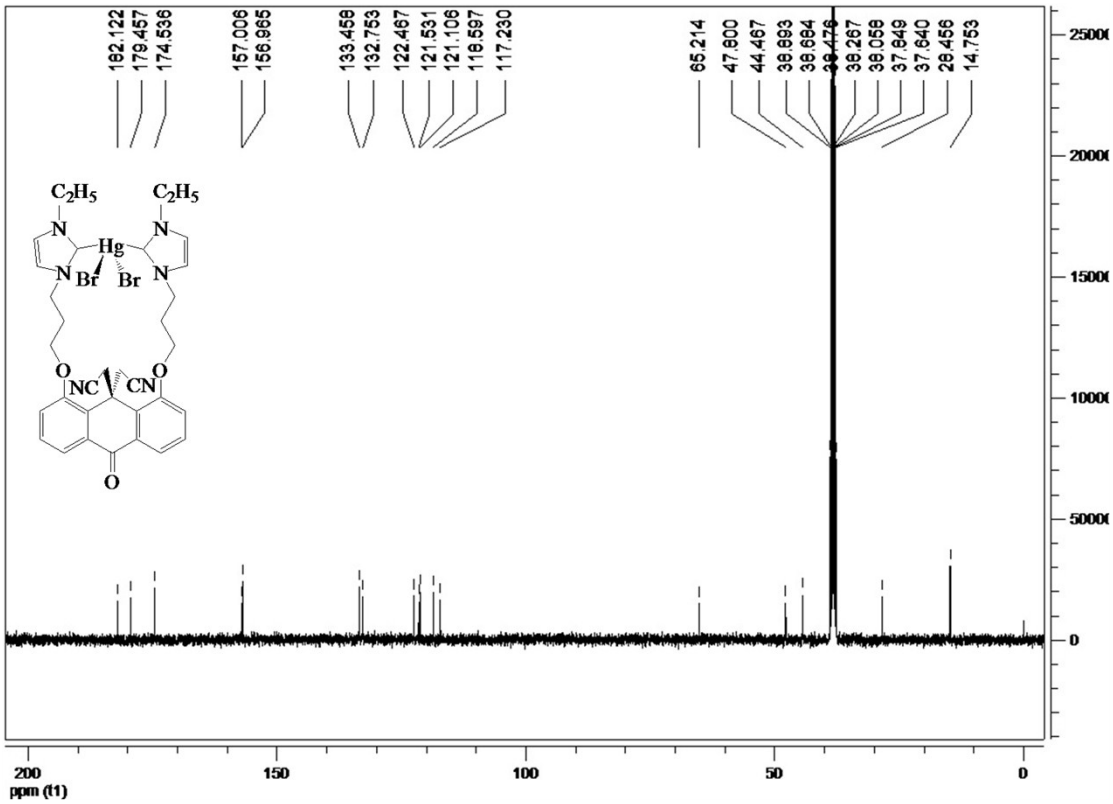


Fig. S12 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **1**.

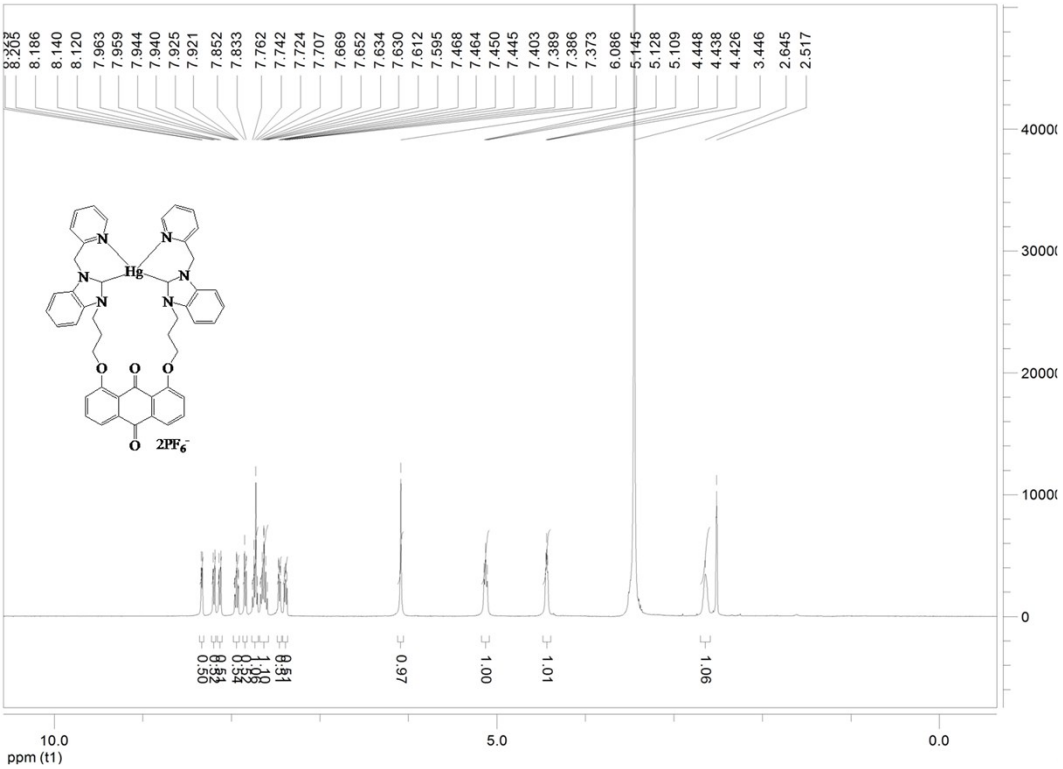


Fig. S13 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **2**.

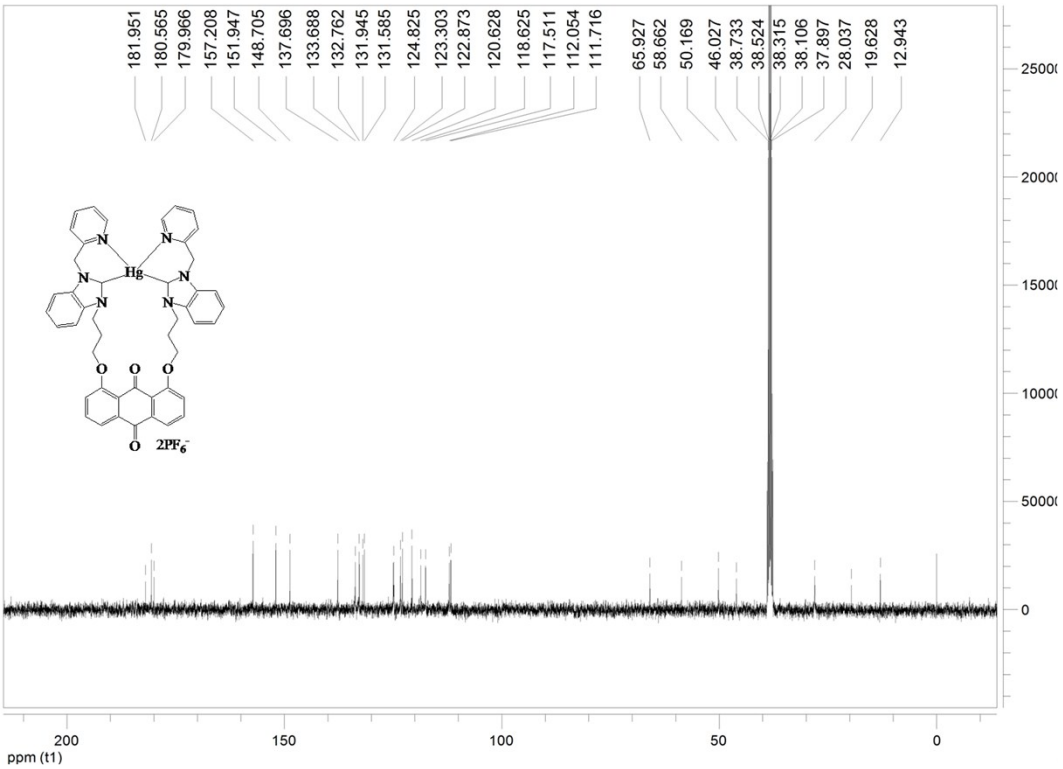


Fig. S14 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **2**.

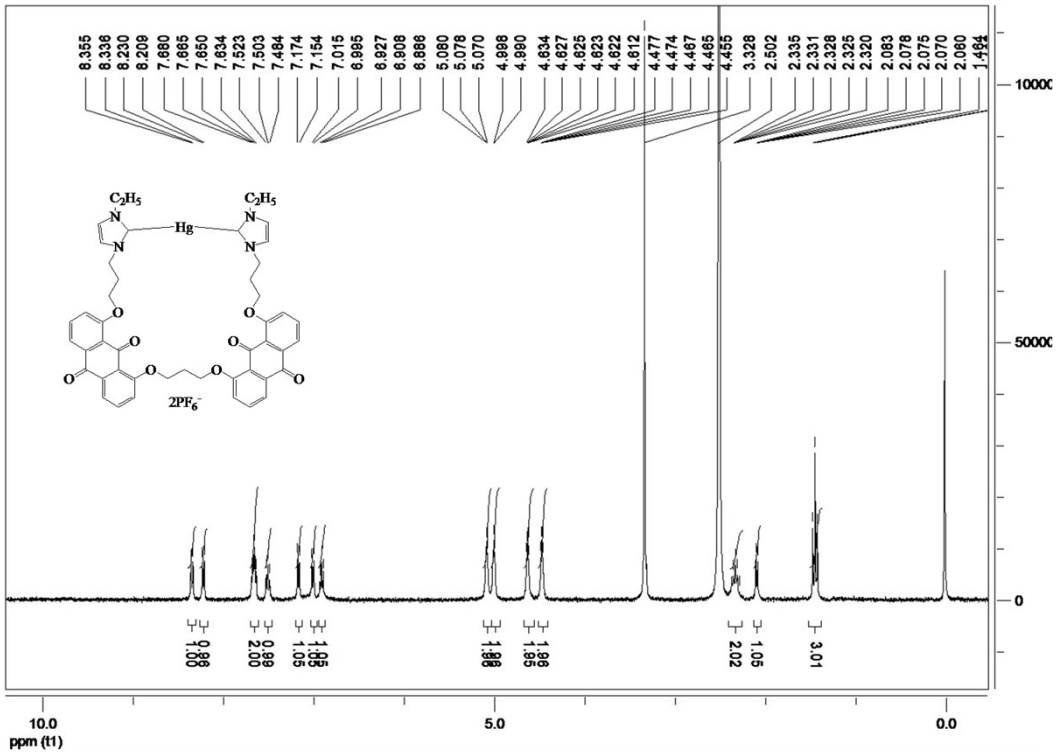


Fig. S15 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **3**.

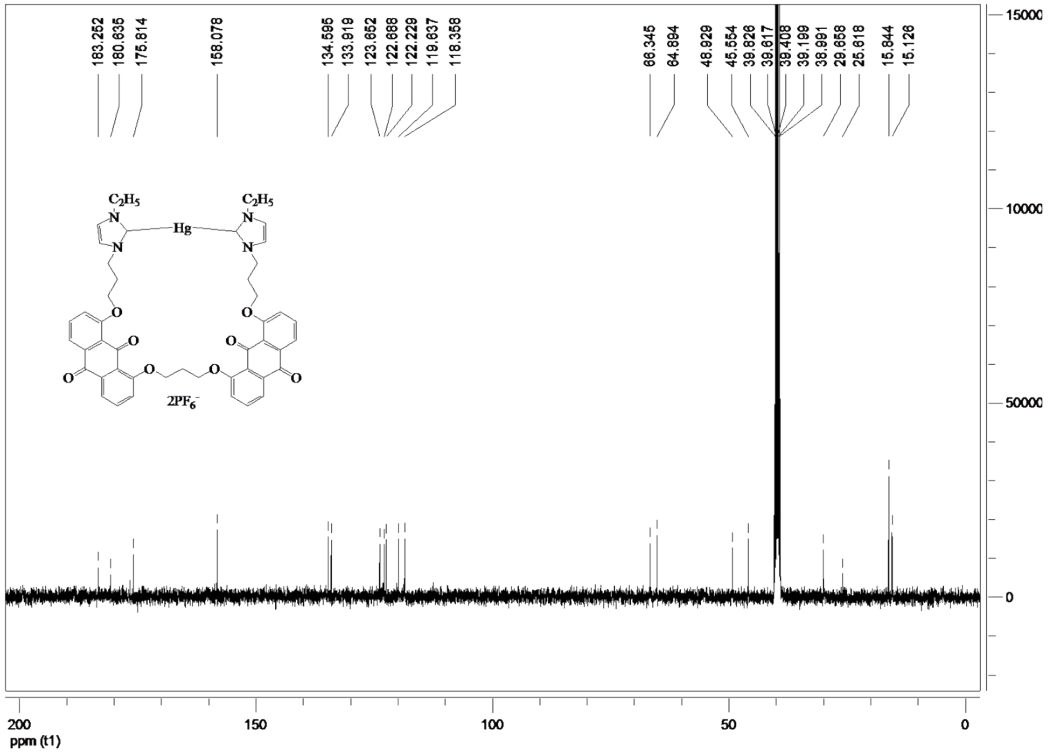


Fig. S16 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **3**.

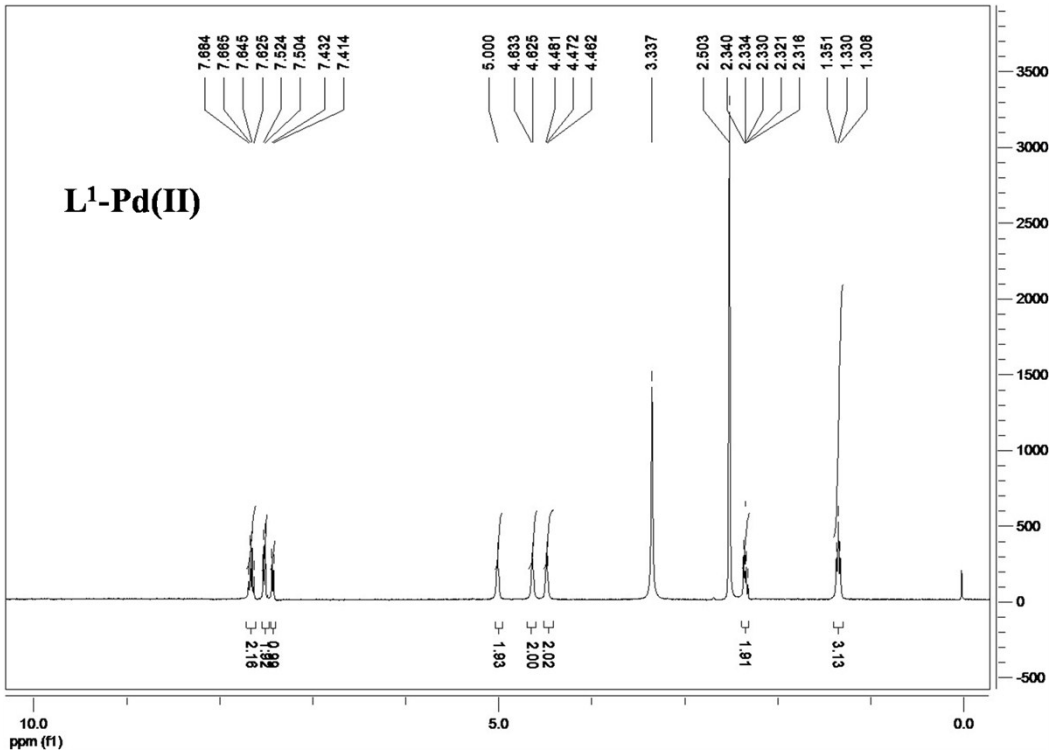


Fig. S17 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of **L^{1}**-Pd(II).

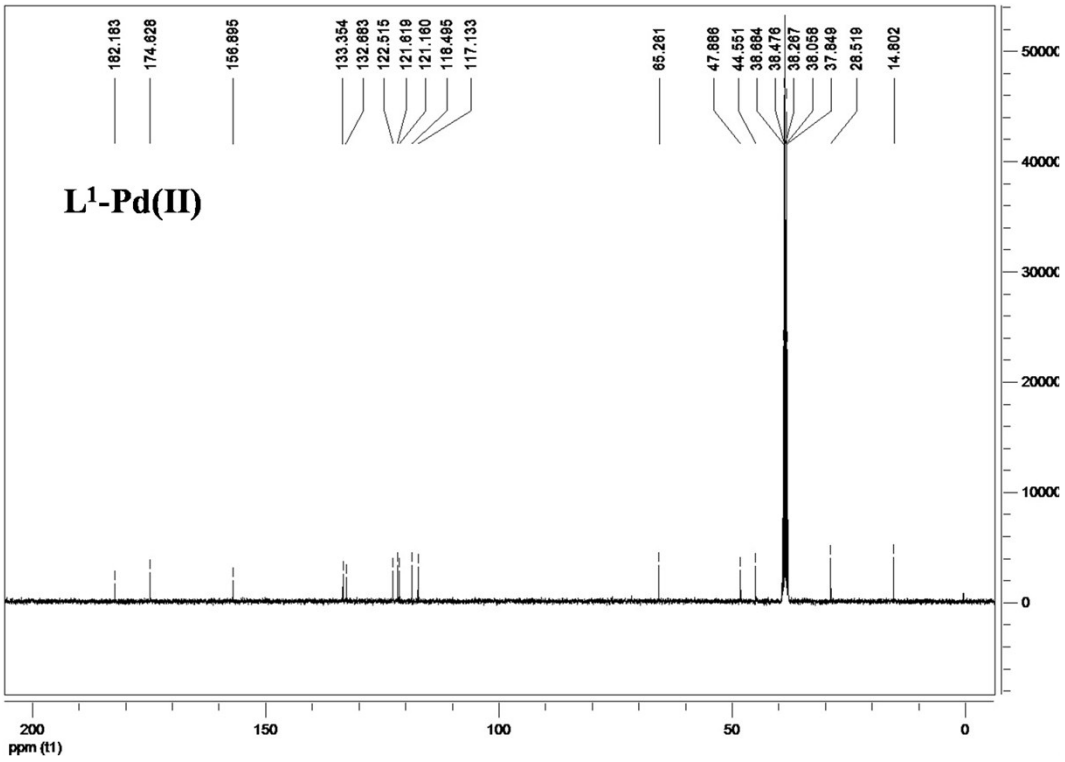
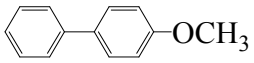


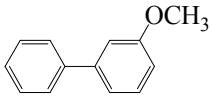
Fig. S18 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of **L^{1}**-Pd(II).

4. The data of ^{1}H NMR and ^{13}C NMR spectra for all coupling products in

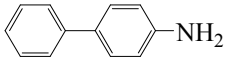
Suzuki-Miyaura reactions.

 4-Methoxybiphenyl[1]

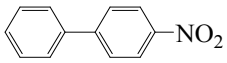
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.84 (s, 3H, C*H*$_3$), 6.98 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.29 (t, *J* = 7.4 Hz, 1H, Ar*H*), 7.41 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.55 (t, *J* = 8.4 Hz, 4H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.3 (*C*H$_3$), 114.2 (Ar*C*), 126.7 (Ar*C*), 128.1 (Ar*C*), 128.7 (Ar*C*), 133.7 (Ar*C*), 140.8 (Ar*C*), 159.1 (Ar*C*).

 3-Methoxybiphenyl[2]

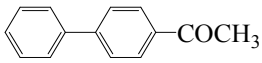
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.83 (s, 3H, C*H*$_3$), 6.89 (d, *J* = 8.0 Hz, 1H, Ar*H*), 7.12 (d, *J* = 1.6 Hz, 1H, Ar*H*), 7.18 (d, *J* = 7.6 Hz, 1H, Ar*H*), 7.35 (m, 2H, Ar*H*), 7.41 (t, *J* = 7.6 Hz, 2H, Ar*H*), 7.58 (d, *J* = 7.6 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 55.2 (*C*H$_3$), 112.6 (Ar*C*), 112.9 (Ar*C*), 119.6 (Ar*C*), 127.1 (Ar*C*), 127.3 (Ar*C*), 128.7 (Ar*C*), 129.7 (Ar*C*), 141.0 (Ar*C*), 142.7 (Ar*C*), 159.9 (Ar*C*).

 4-Phenylaniline[3]

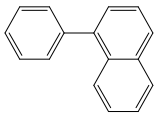
^{1}H NMR (400 MHz, $CDCl_3$): δ 3.67 (s, 2H, N*H*$_2$), 6.73 (d, *J* = 8.4 Hz, 2H, Ar*H*), 7.25 (d, *J* = 7.2 Hz, 1H, Ar*H*), 7.41 (m, 4H, Ar*H*), 7.53 (d, *J* = 7.2 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 115.3 (Ar*C*), 126.2 (Ar*C*), 126.3 (Ar*C*), 127.9 (Ar*C*), 128.6 (Ar*C*), 131.5 (Ar*C*), 141.1 (Ar*C*), 145.8 (Ar*C*).

 4-Nitrobiphenyl[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 3H, Ar*H*), 7.64 (t, *J* = 4.2 Hz, 2H, Ar*H*), 7.75 (d, *J* = 8.8 Hz, 2H, Ar*H*), 8.31 (d, *J* = 8.8 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.1 (Ar*C*), 127.3 (Ar*C*), 127.8 (Ar*C*), 128.9 (Ar*C*), 129.1 (Ar*C*), 138.7 (Ar*C*), 147.1 (Ar*C*), 147.6 (Ar*C*).

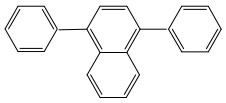
 4-Acetylbiphenyl[4]

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.64 (s, 3H, CH_3), 7.40 (t, J = 7.2 Hz, 1H, Ar*H*), 7.47 (t, J = 7.6 Hz, 2H, Ar*H*), 7.62 (d, J = 7.2 Hz, 2H, Ar*H*), 7.70 (d, J = 8.4 Hz, 2H, Ar*H*), 8.04 (d, J = 8.4 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 26.6 (*C*H*3*), 127.24 (Ar*C*), 127.28 (Ar*C*), 128.2 (Ar*C*), 128.92 (Ar*C*), 128.96 (Ar*C*), 135.8 (Ar*C*), 139.8 (Ar*C*), 145.8 (Ar*C*), 197.7 (*C*O).



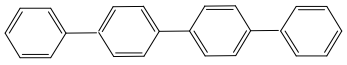
1-Phenylnaphthalene[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51 (m, 3H, Ar*H*), 7.62 (m, 6H, Ar*H*), 7.92 (d, J = 8.4 Hz, 1H, Ar*H*), 8.00 (q, J = 4.0 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.4 (Ar*C*), 125.8 (Ar*C*), 126.0 (Ar*C*), 126.9 (Ar*C*), 127.23 (Ar*C*), 127.29 (Ar*C*), 127.6 (Ar*C*), 128.3 (Ar*C*), 128.8 (Ar*C*), 130.1 (Ar*C*), 131.6 (Ar*C*), 133.8 (Ar*C*), 140.3 (Ar*C*), 140.8 (Ar*C*).



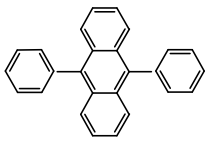
1,4-Diphenylnaphthalene[5]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.52 (m, 6H, Ar*H*), 7.60 (m, 8H, Ar*H*), 8.02 (q, J = 3.3 Hz,2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 125.8 (Ar*C*), 126.3 (Ar*C*), 126.4 (Ar*C*), 127.2 (Ar*C*), 128.2 (Ar*C*), 130.0 (Ar*C*), 130.1 (Ar*C*), 131.9 (Ar*C*), 139.8 (Ar*C*), 140.8 (Ar*C*).



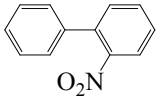
4, 4'-Diphenylbiphenyl[6]

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.52 (t, J = 7.4 Hz, 4H, Ar*H*), 7.70 (d, J = 4.4 Hz, 4H, Ar*H*), 7.74 (d, J = 7.6 Hz, 4H, Ar*H*), 7.79 (s, 6H, Ar*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 126.5 (Ar*C*), 127.0 (Ar*C*), 127.2 (Ar*C*), 127.6 (Ar*C*), 128.6 (Ar*C*), 129.0 (Ar*C*), 131.8 (Ar*C*).



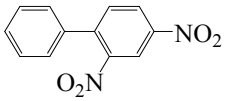
9,10-Diphenylanthracene[7]

^{1}H NMR (400 MHz, DMSO-d_6): δ 7.47 (q, J = 5.3 Hz, 8H, Ar*H*), 7.67 (m, 10H, Ar*H*). ^{13}C NMR (100 MHz, DMSO-d_6): δ 125.4 (Ar*C*), 126.3 (Ar*C*), 128.6 (Ar*C*), 129.1 (Ar*C*), 130.8 (Ar*C*).



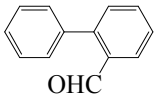
2-Nitrobiphenyl[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (q, J = 3.2 Hz, 2H, Ar*H*), 7.50 (m, 5H, Ar*H*), 7.63 (m, 1H, Ar*H*), 7.86 (q, J = 3.0 Hz, 1H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 124.0 (Ar*C*), 127.9 (Ar*C*), 128.1 (Ar*C*), 128.2 (Ar*C*), 128.7 (Ar*C*), 131.9 (Ar*C*), 132.2 (Ar*C*), 136.3 (Ar*C*), 137.3 (Ar*C*), 149.3 (Ar*C*).



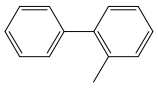
2,4-Dinitrobiphenyl[8]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38 (q, J = 3.2 Hz, 2H, Ar*H*), 7.52 (t, J = 3.2 Hz, 3H, Ar*H*), 7.72 (d, J = 8.8 Hz, 1H, Ar*H*), 8.51 (q, J = 3.6 Hz, 1H, Ar*H*), 8.74 (d, J = 2.0 Hz, 1H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 119.7 (Ar*C*), 126.4 (Ar*C*), 127.6 (Ar*C*), 129.1 (Ar*C*), 129.5 (Ar*C*), 133.2 (Ar*C*), 135.2 (Ar*C*), 142.2 (Ar*C*), 146.8 (Ar*C*), 149.1 (Ar*C*).



Biphenyl-2-carbaldehyde[4]

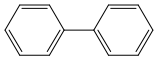
^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (m, 7H, Ar*H*), 7.56 (q, J = 2.9 Hz, 1H, Ar*H*), 7.97 (q, J = 3.2 Hz, 1H, Ar*H*), 10.52 (s, 1H, C*H*O). ^{13}C NMR (100 MHz, $CDCl_3$): δ 126.5 (Ar*C*), 127.3 (Ar*C*), 128.0 (Ar*C*), 129.4 (Ar*C*), 129.6 (Ar*C*), 129.7 (Ar*C*), 130.6 (Ar*C*), 133.2 (Ar*C*), 135.1 (Ar*C*), 135.3 (Ar*C*), 189.8 (*C*HO).



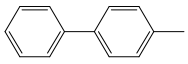
2-Methylbiphenyl[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.26 (s, 3H, CH_3), 7.24 (m, 3H, Ar*H*), 7.33 (m, 3H,

Ar*H*), 7.43 (m, 3H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.5 (*C*H_3), 125.8 (Ar*C*), 126.8 (Ar*C*), 127.2 (Ar*C*), 127.3 (Ar*C*), 128.1 (Ar*C*), 128.8 (Ar*C*), 129.2 (Ar*C*), 129.8 (Ar*C*), 130.3 (Ar*C*), 135.3 (Ar*C*), 142.0 (Ar*C*).

 Biphenyl[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.44 (t, J = 7.2 Hz, 2H, Ar*H*), 7.53 (t, J = 7.4 Hz, 4H, Ar*H*), 7.70 (d, J = 7.6 Hz, 4H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 127.2 (Ar*C*), 127.3 (Ar*C*), 128.8 (Ar*C*), 141.3 (Ar*C*).

 4-Methylbiphenyl[1]

^{1}H NMR (400 MHz, $CDCl_3$): δ 2.38 (s, 3H, CH_2), 7.24 (d, J = 8.0 Hz, 2H, Ar*H*), 7.30 (t, J = 7.4 Hz, 1H, Ar*H*), 7.40 (t, J = 7.6 Hz, 2H, Ar*H*), 7.47 (d, J = 8.0 Hz, 2H, Ar*H*), 7.55 (d, J = 8.4 Hz, 2H, Ar*H*). ^{13}C NMR (100 MHz, $CDCl_3$): δ 21.1 (*C*H_3), 127.0 (Ar*C*), 127.2 (Ar*C*), 128.7 (Ar*C*), 129.5 (Ar*C*), 137.0 (Ar*C*), 138.4 (Ar*C*), 141.2 (Ar*C*).

5. The Fig.s of ^{1}H NMR and ^{13}C NMR spectra for all coupling products in Suzuki-Miyaura reactions.

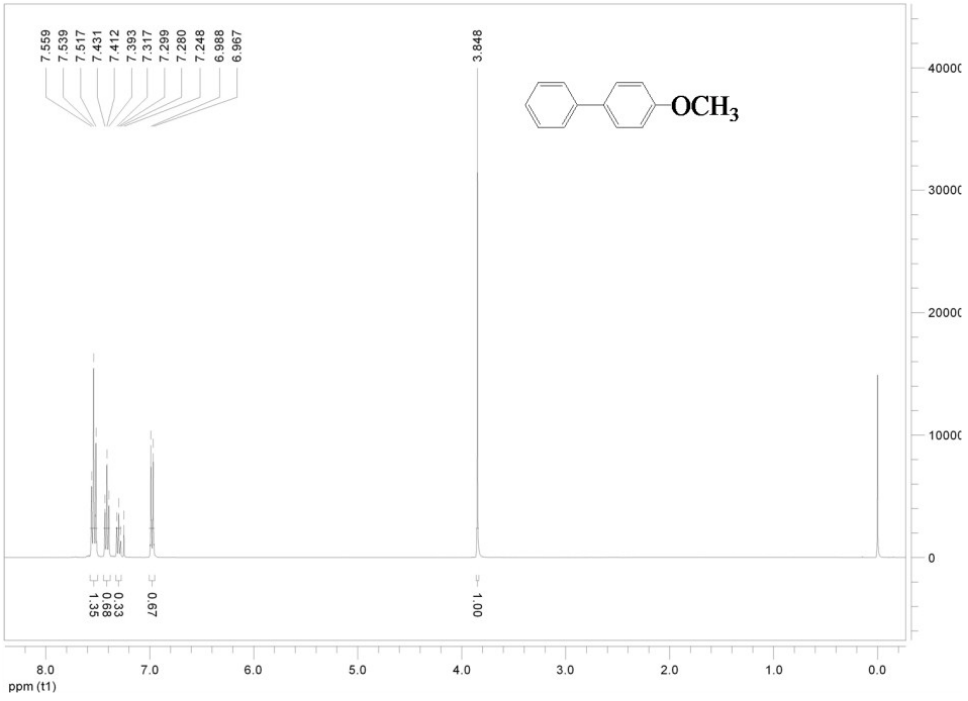


Fig. S19 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 4-methoxybiphenyl.

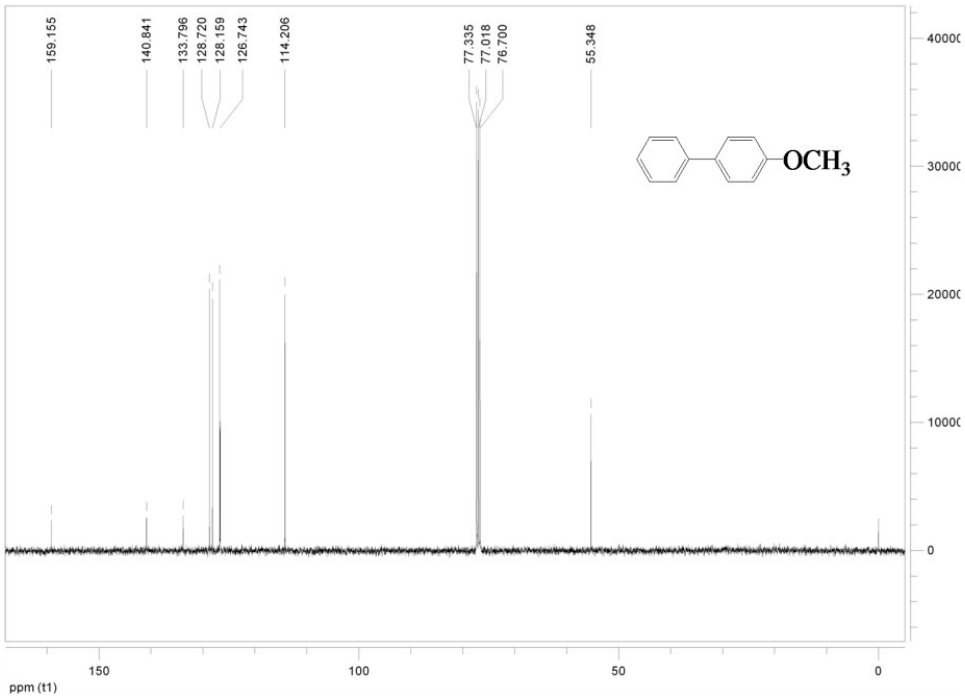


Fig. S20 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 4-methoxybiphenyl.

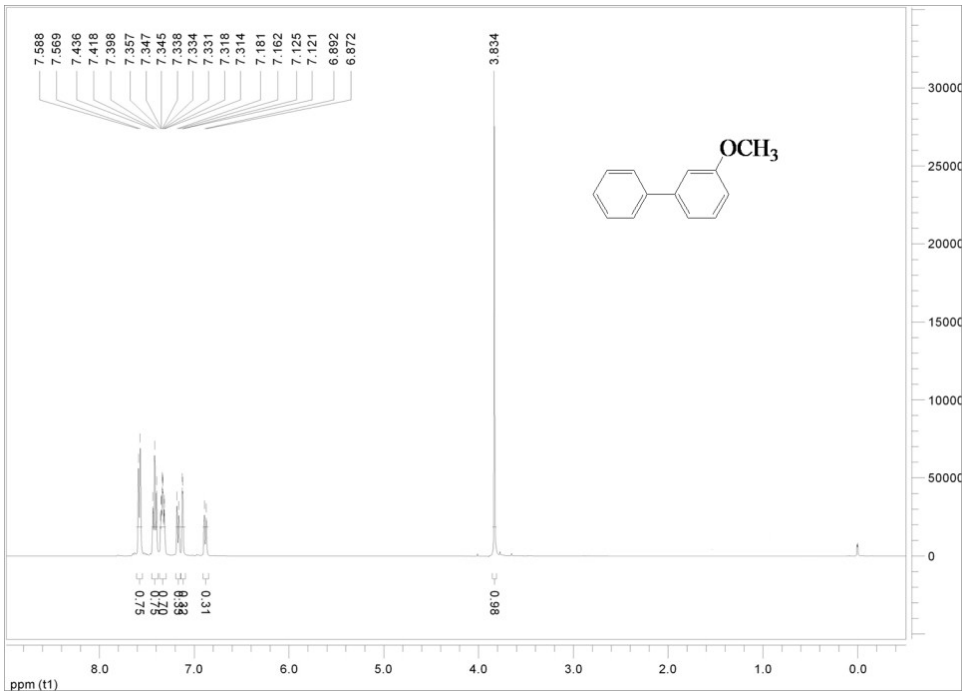


Fig. S21 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 3-methoxybiphenyl.

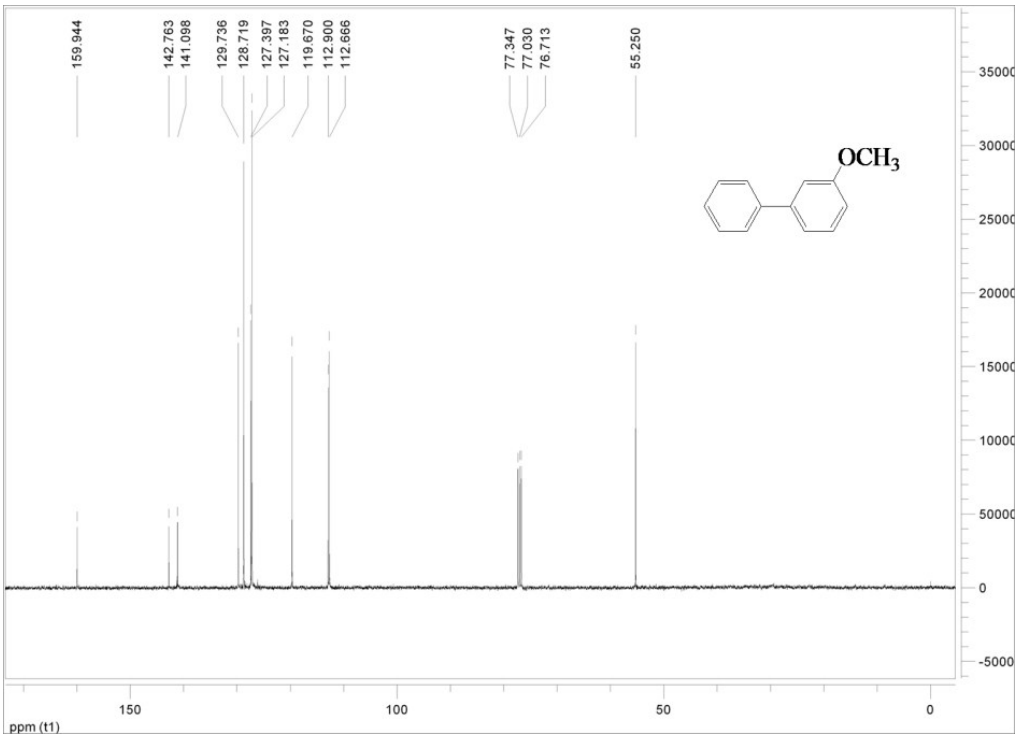


Fig. S22 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 3-methoxybiphenyl.

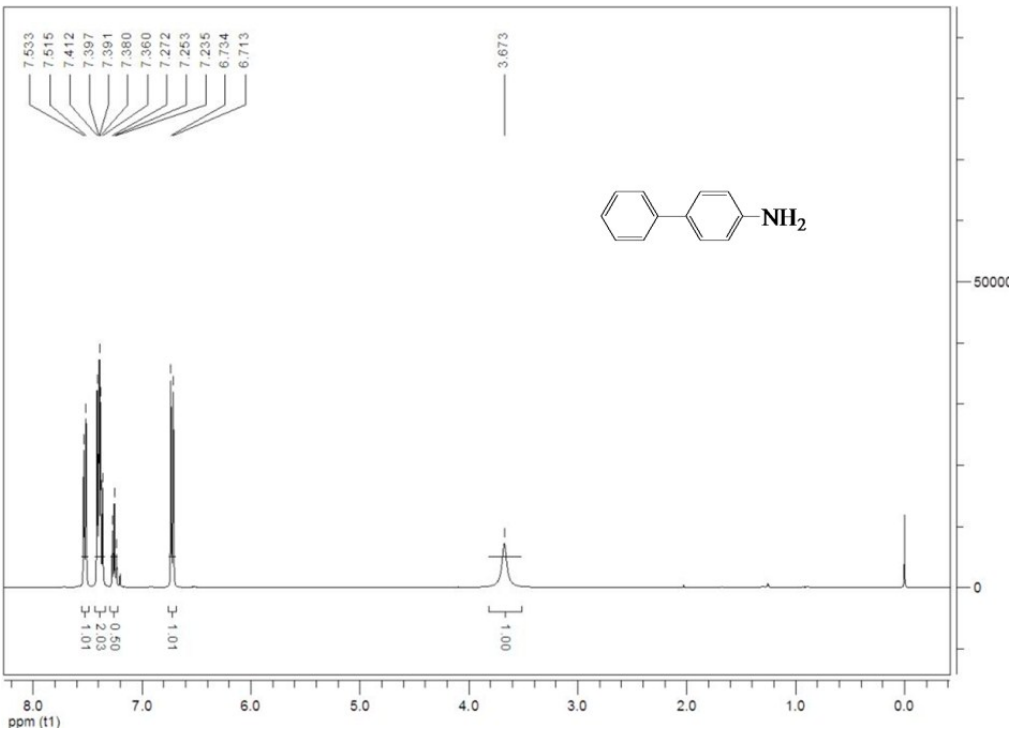


Fig. S23 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 4-phenylaniline.

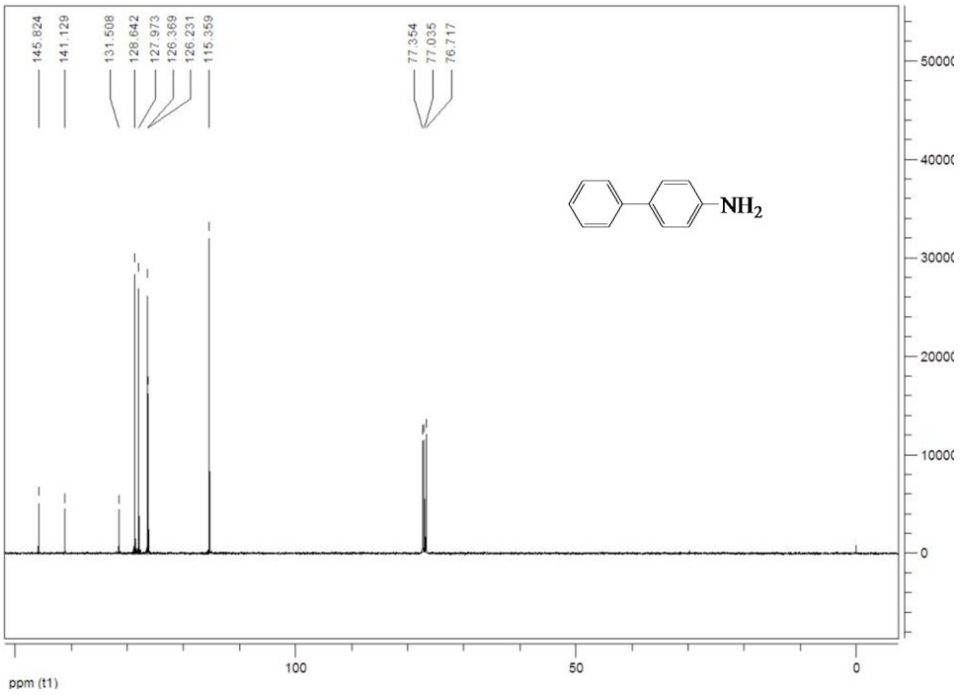


Fig. S24 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 4-phenylaniline.

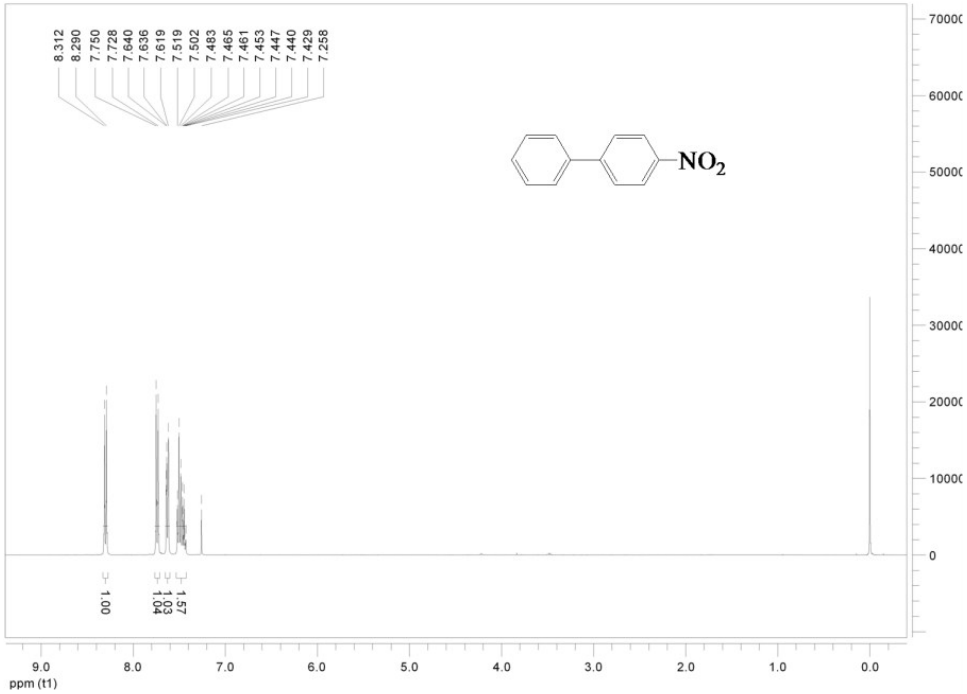


Fig. S25 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 4-nitrobiphenyl.

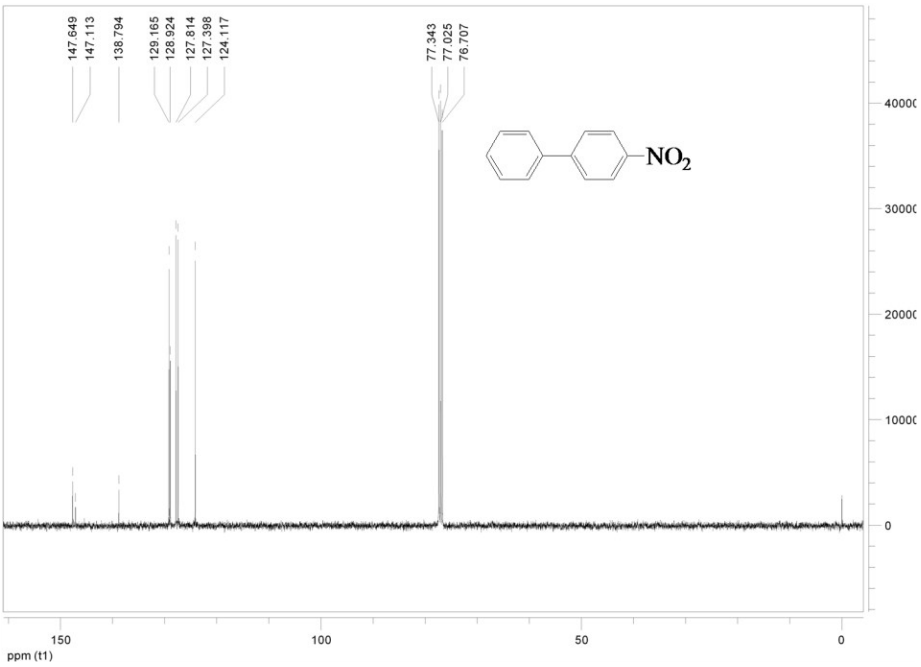


Fig. S26 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 4-nitrobiphenyl.

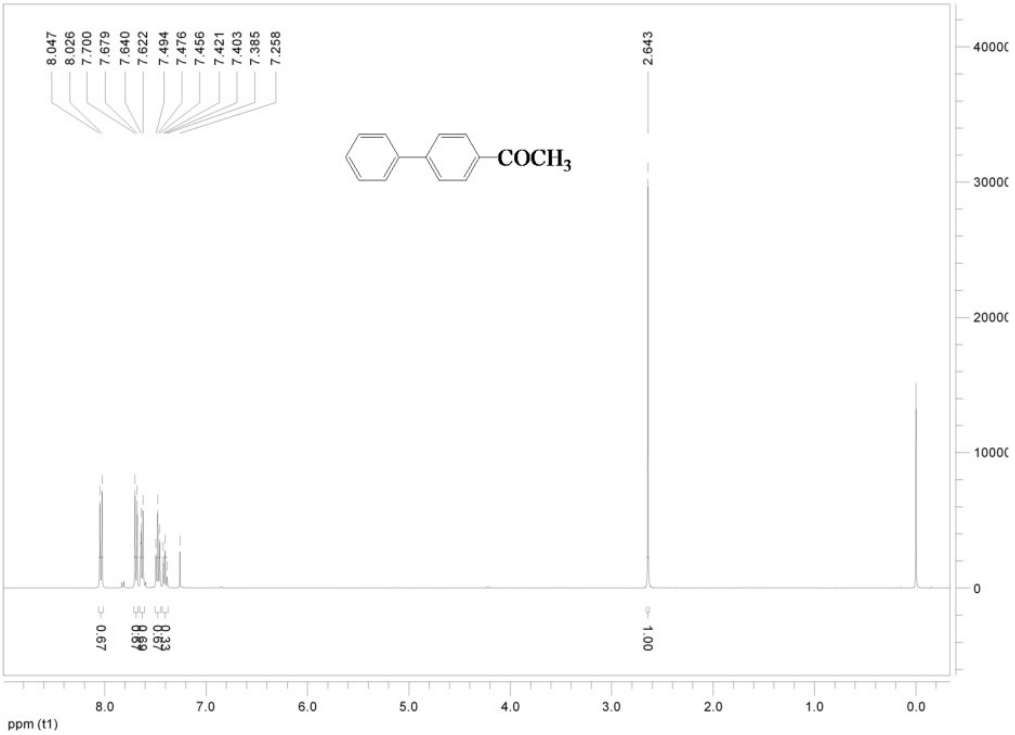


Fig. S27 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 4-acetylbiphenyl.

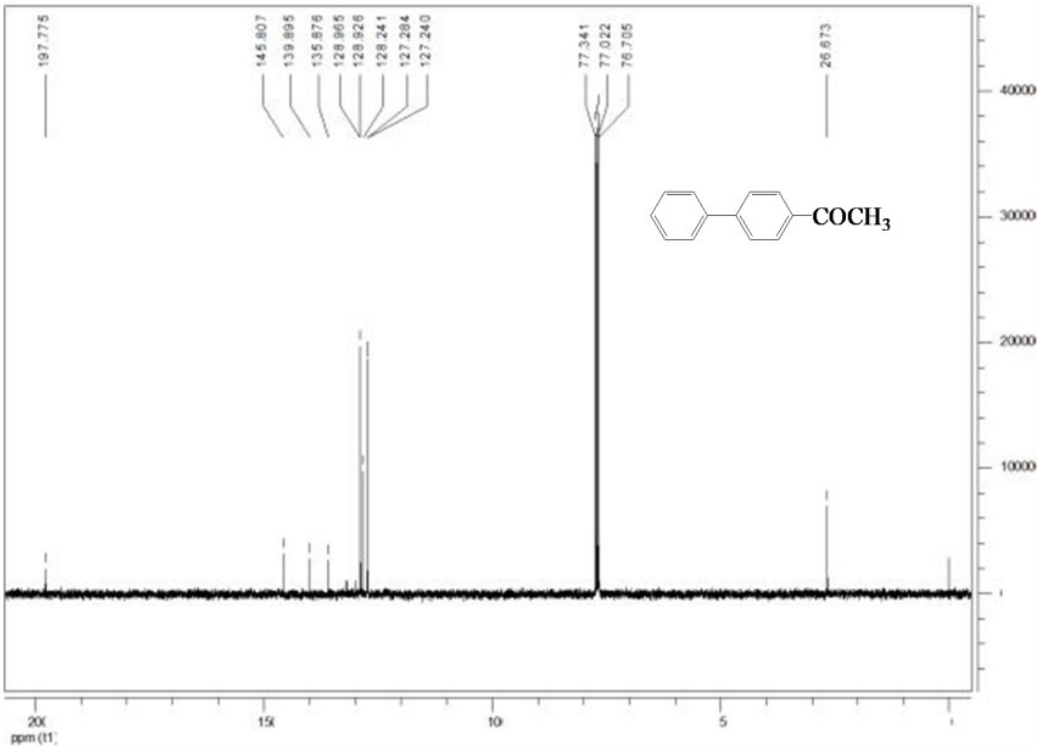


Fig. S28 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 4-acetylbiphenyl.

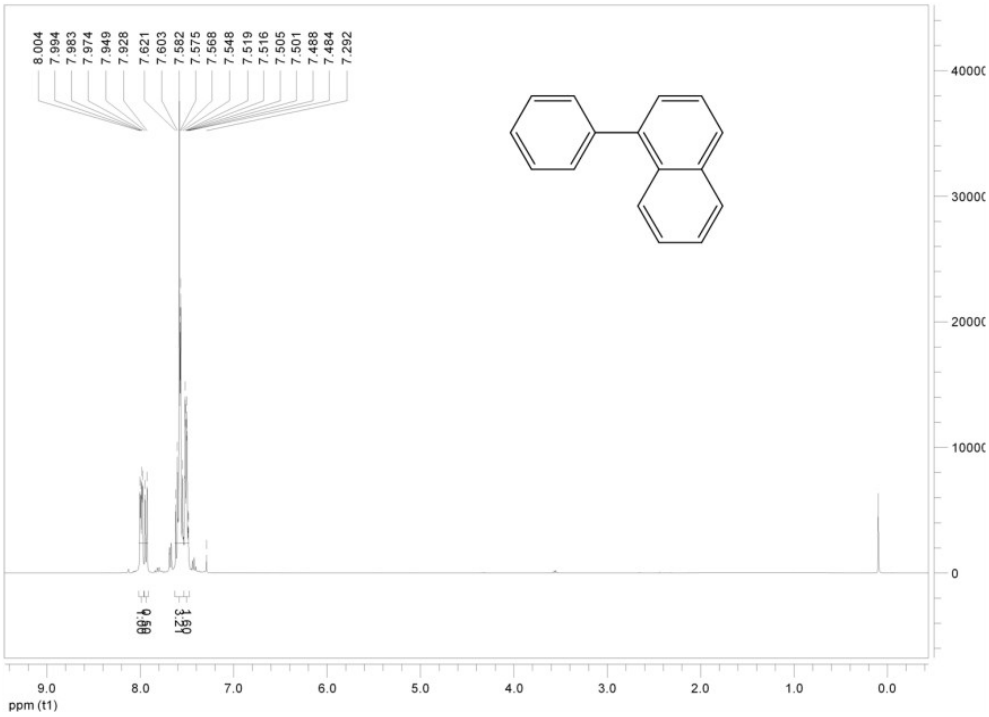


Fig. S29 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 1-phenylnaphthalene.

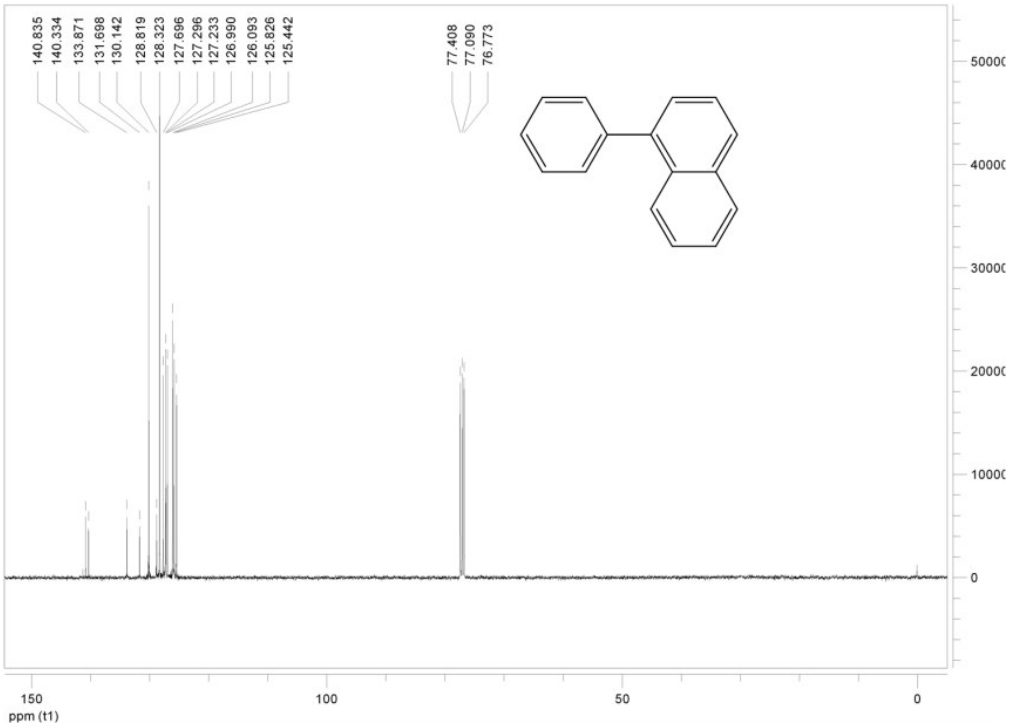


Fig. S30 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 1-phenylnaphthalene.

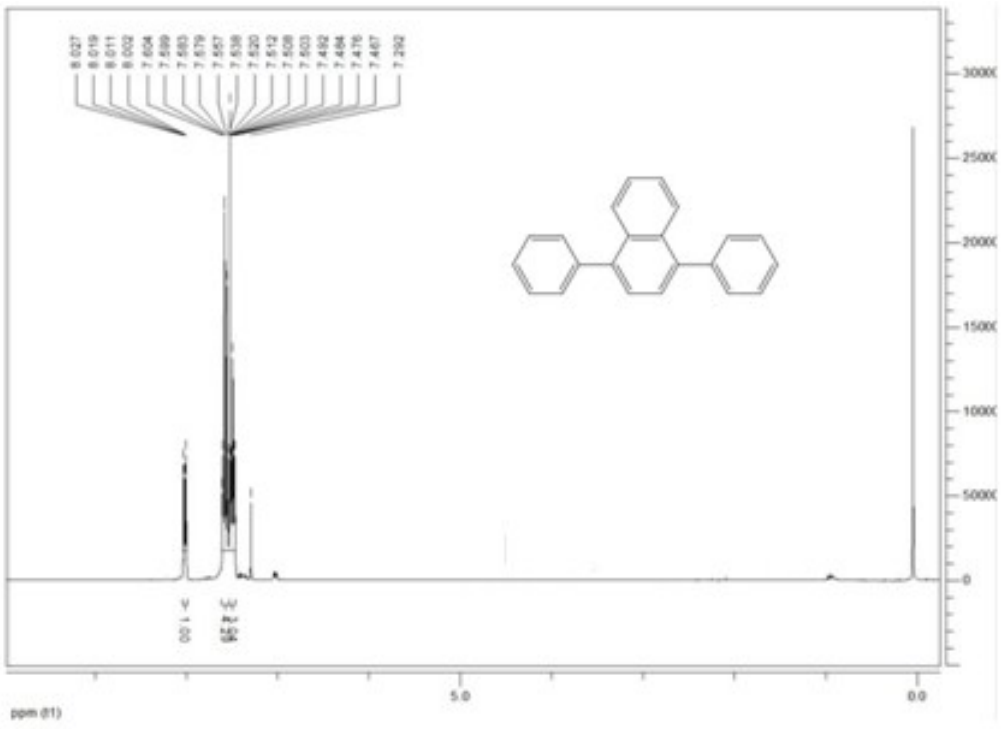


Fig. S31 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 1,4-diphenylnaphthalene.

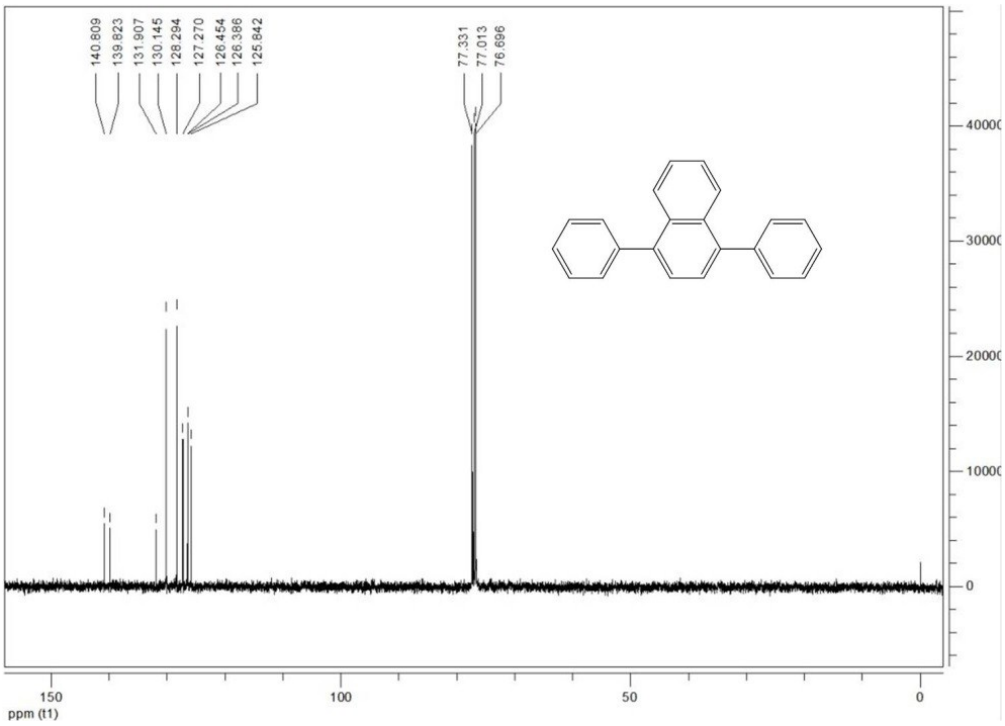


Fig. S32 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 1,4-diphenylnaphthalene.

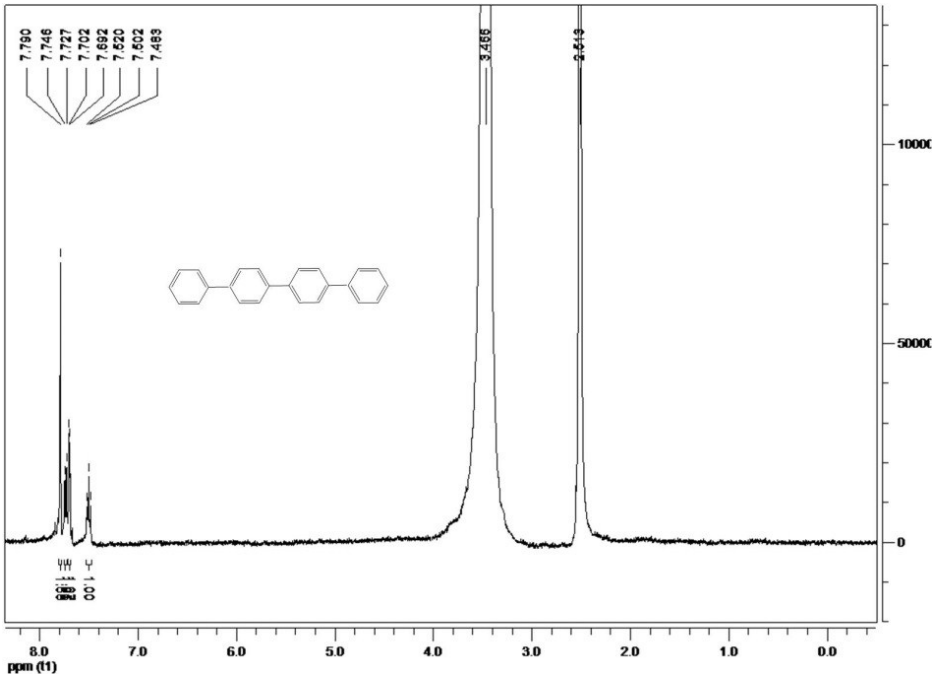


Fig. S33 The ^{1}H NMR (400 MHz, DMSO-d_6) of 4, 4'-diphenylbiphenyl.

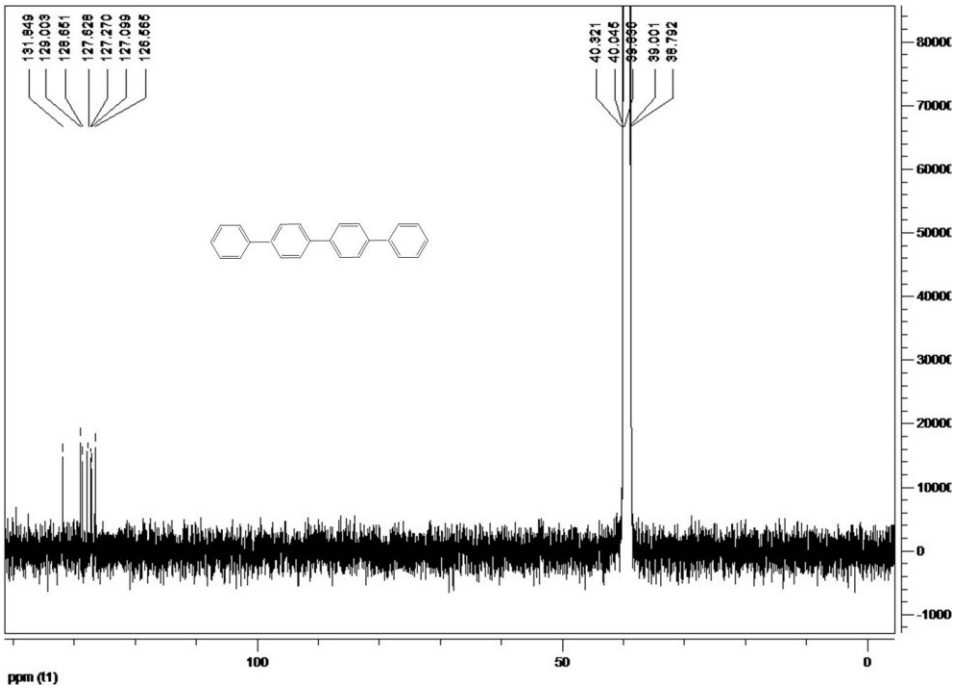


Fig. S34 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of 4, 4'-diphenylbiphenyl.

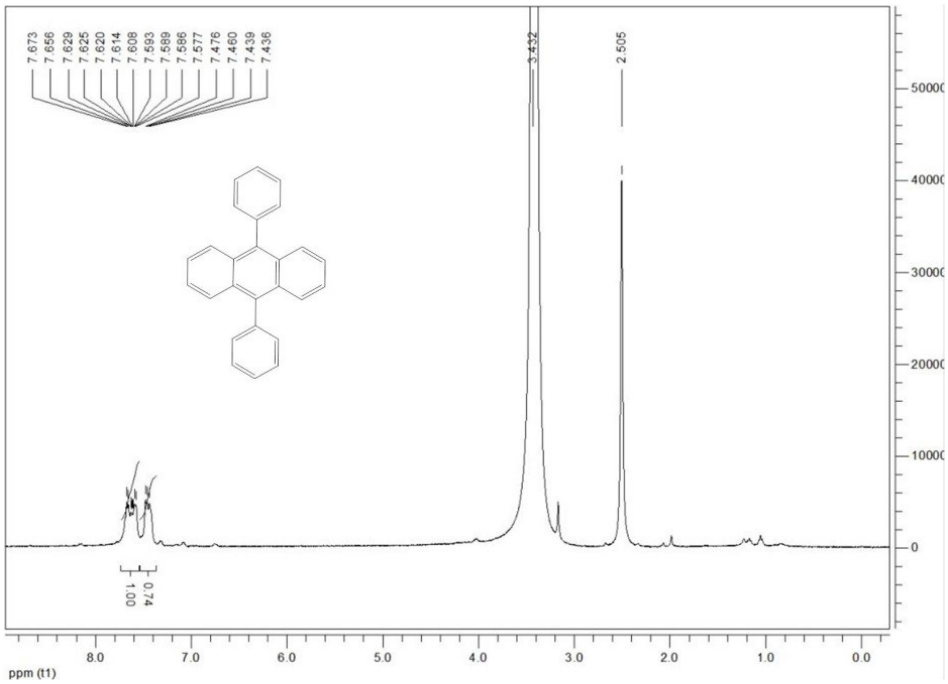


Fig. S35 The ^{1}H NMR (400 MHz, DMSO-d_6) spectra of 9,10-diphenylanthracene.

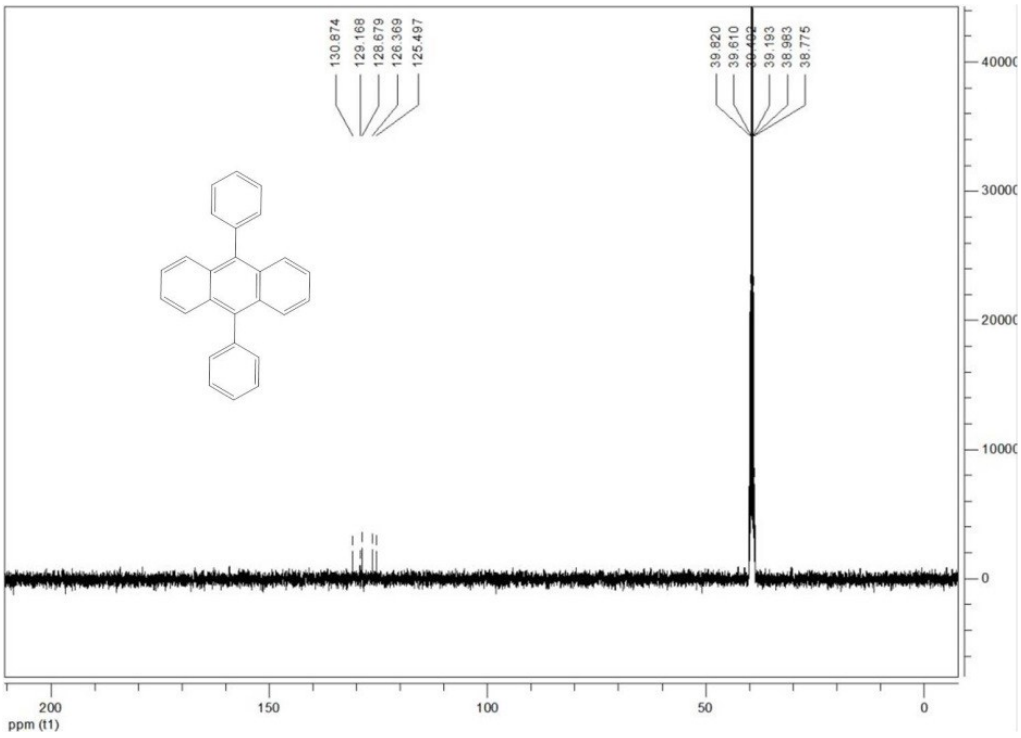


Fig. S36 The ^{13}C NMR (100 MHz, DMSO-d_6) spectra of 9,10-diphenylanthracene.

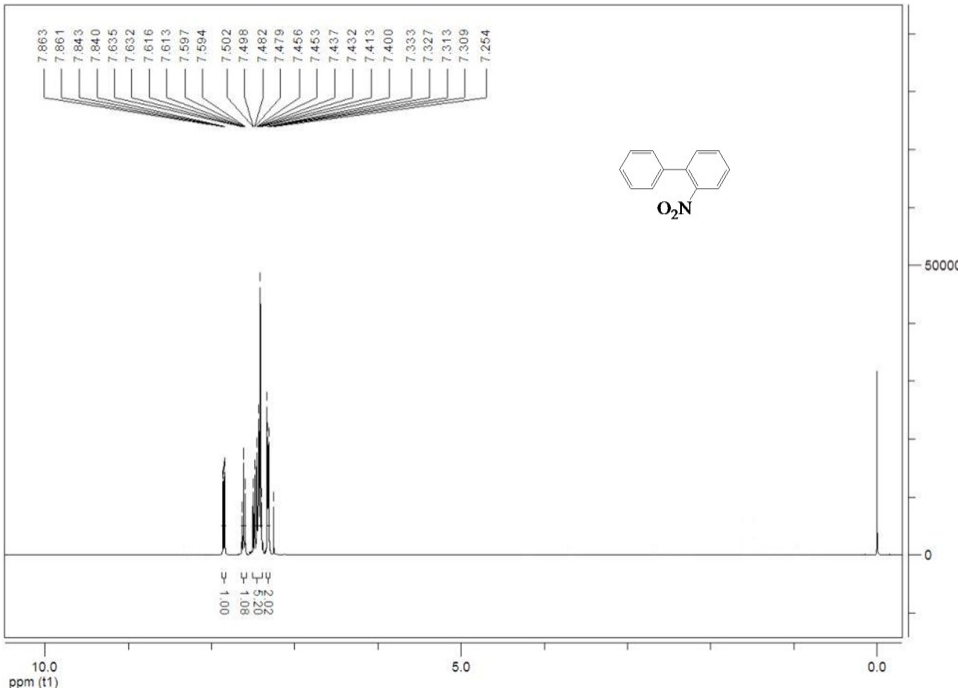


Fig. S37 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 2-nitrobiphenyl.

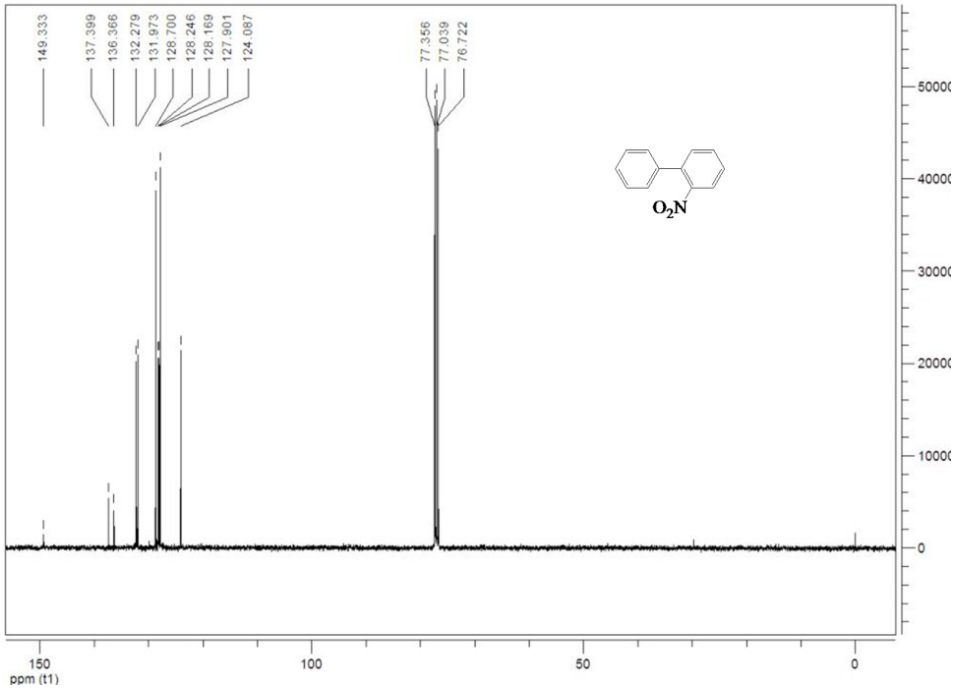


Fig. S38 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 2-nitrobiphenyl.

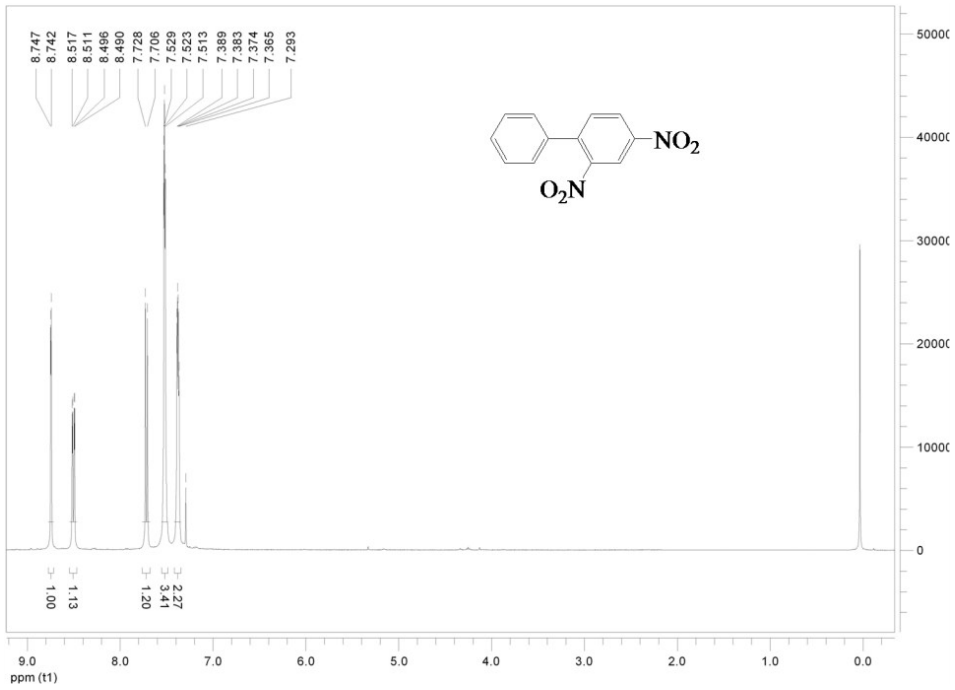


Fig. S39 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 2,4-dinitrobiphenyl.

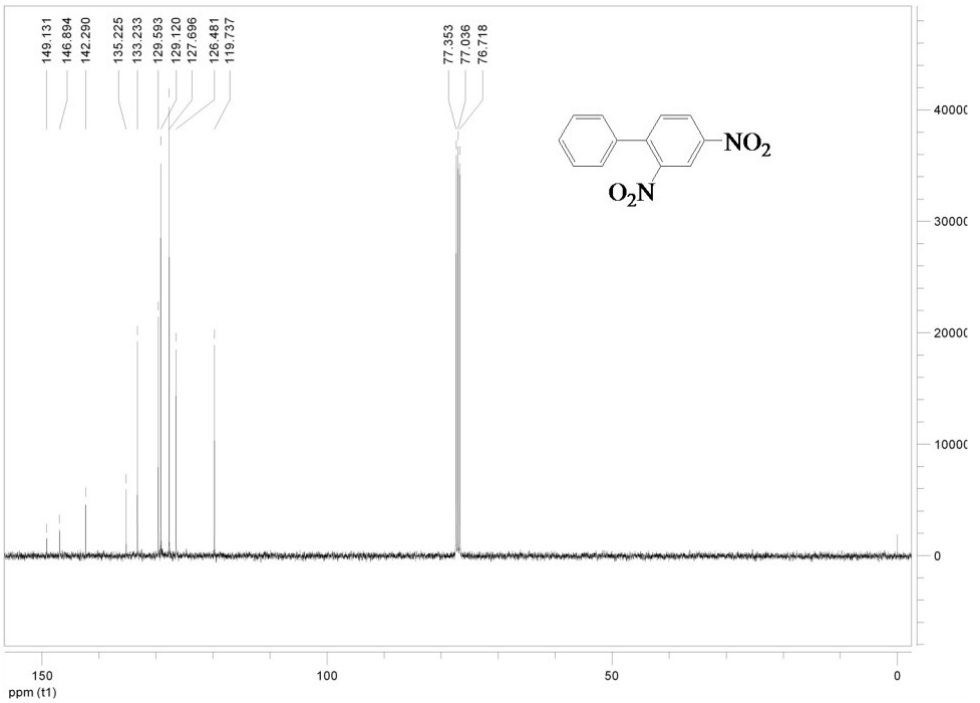


Fig. S40 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 2,4-dinitrobiphenyl.

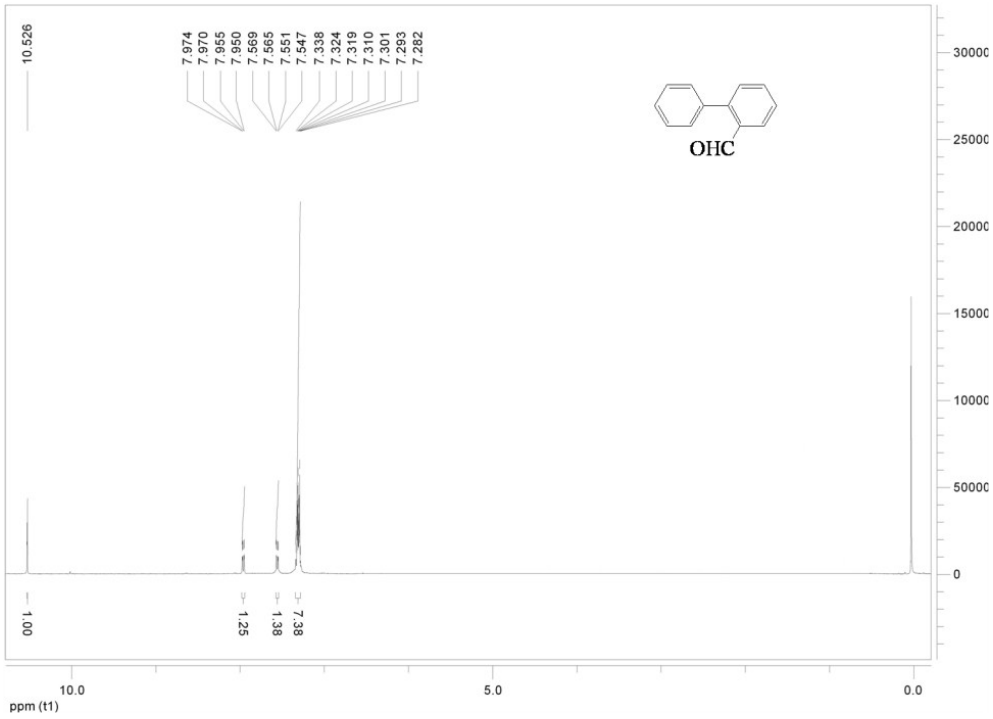


Fig. S41 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of biphenyl-2-carbaldehyde.

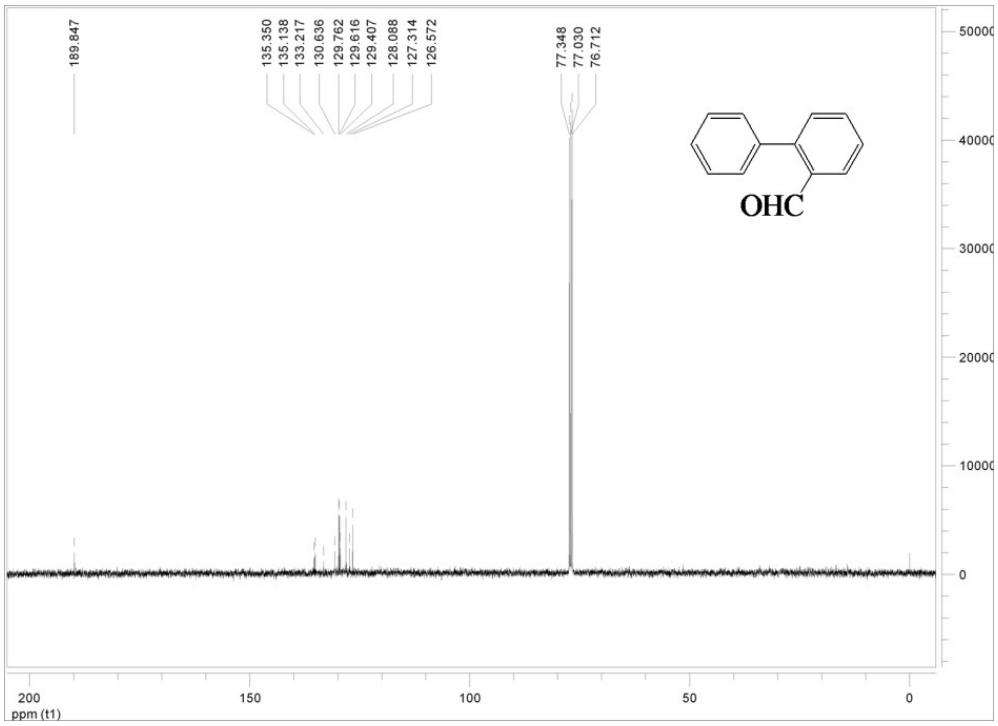


Fig. S42 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of biphenyl-2-carbaldehyde.

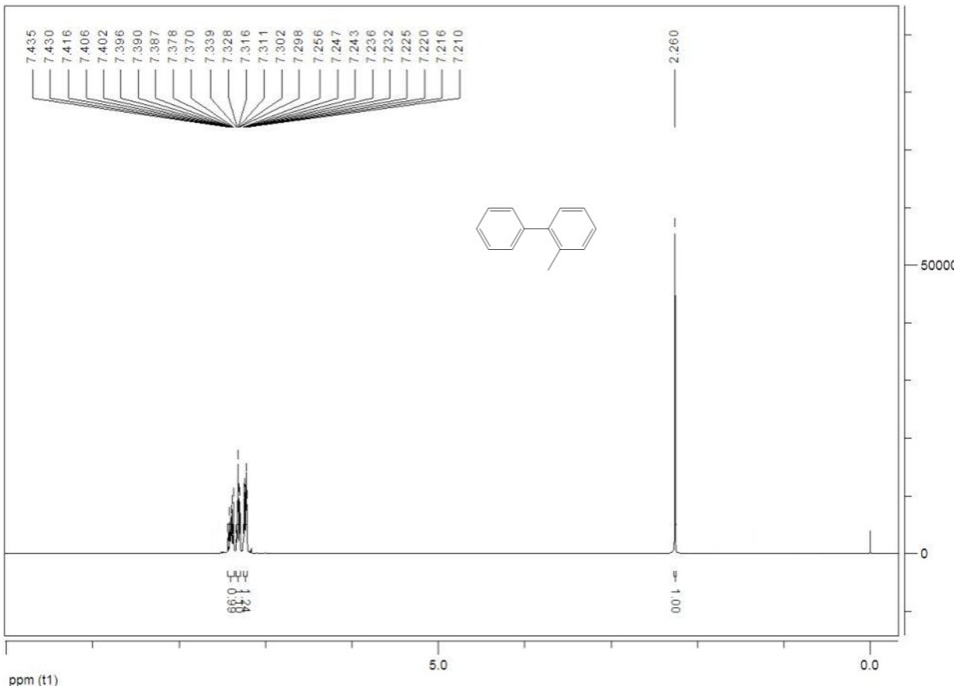


Fig. S43 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 2-methylbiphenyl.

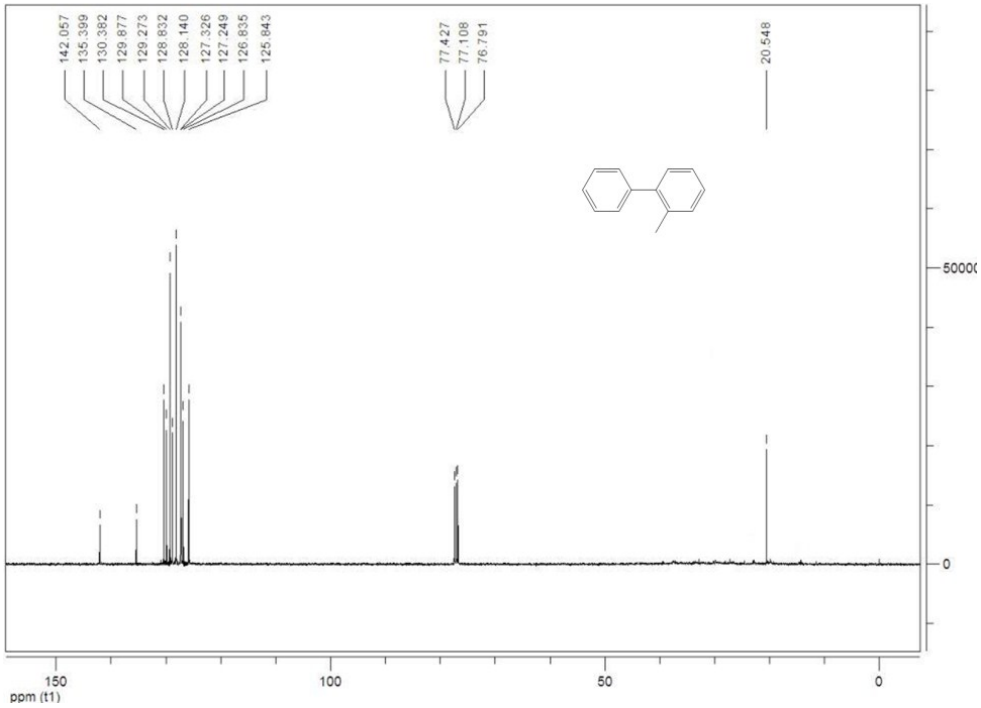


Fig. S44 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 2-methylbiphenyl.

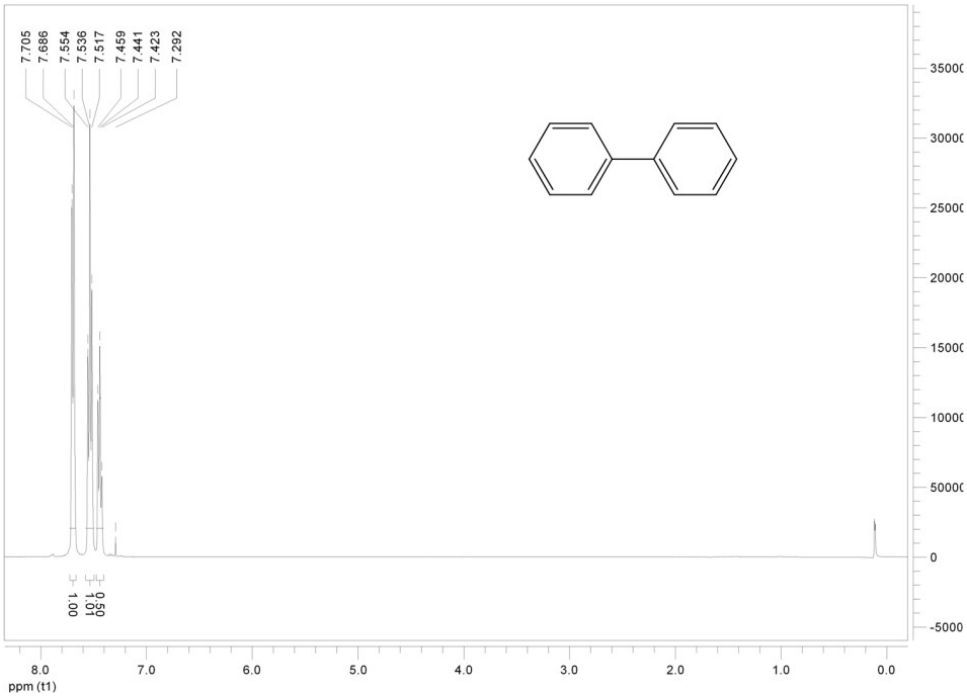


Fig. S45 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of biphenyl.

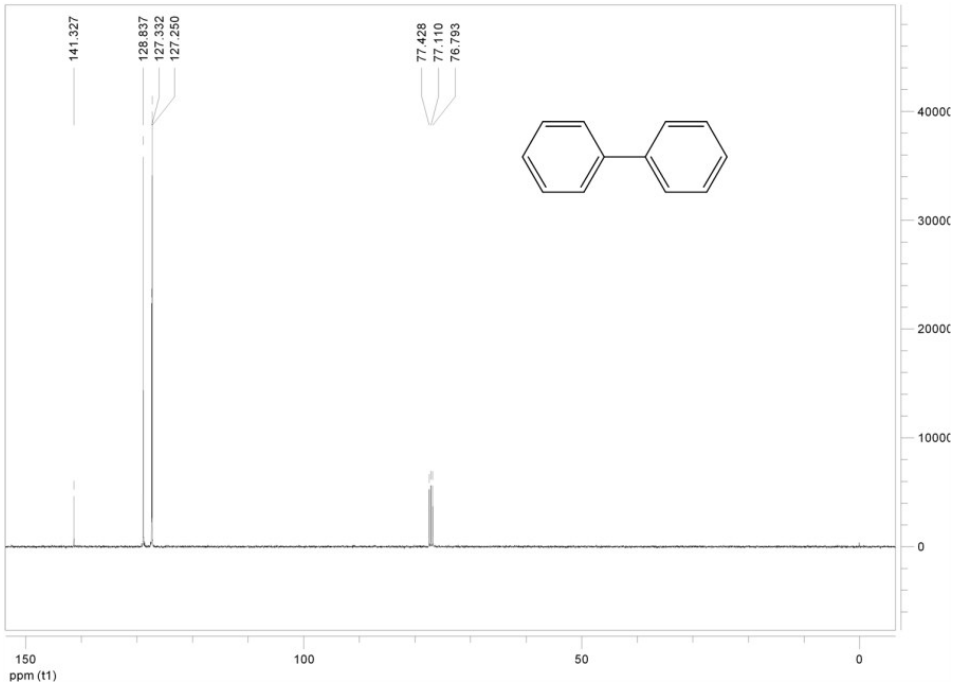


Fig. S46 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of biphenyl.

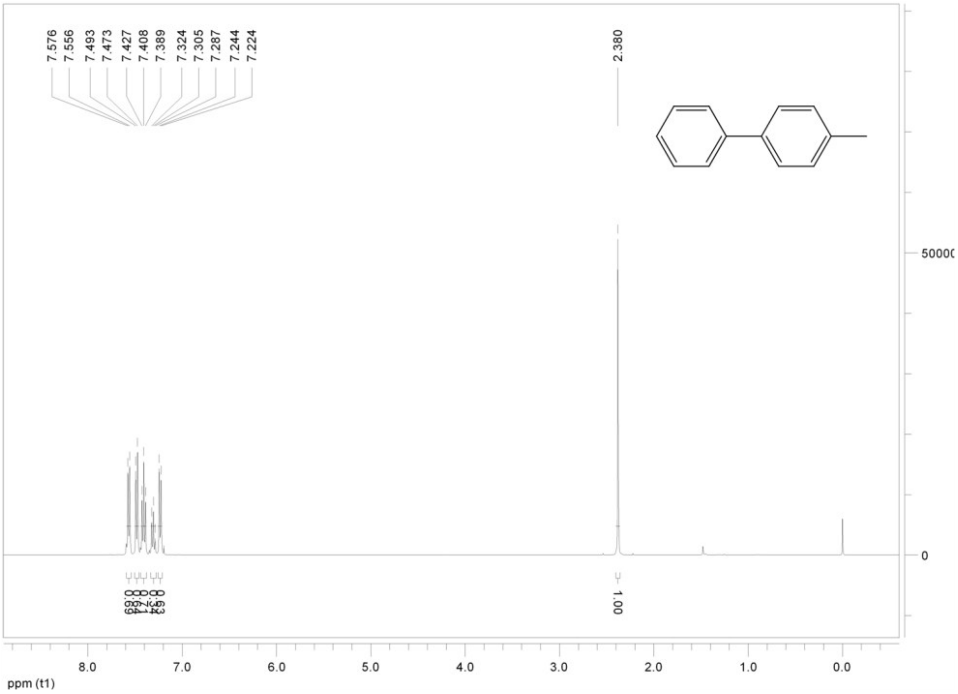


Fig. S47 The ^{1}H NMR (400 MHz, $CDCl_3$) spectra of 4-methylbiphenyl.

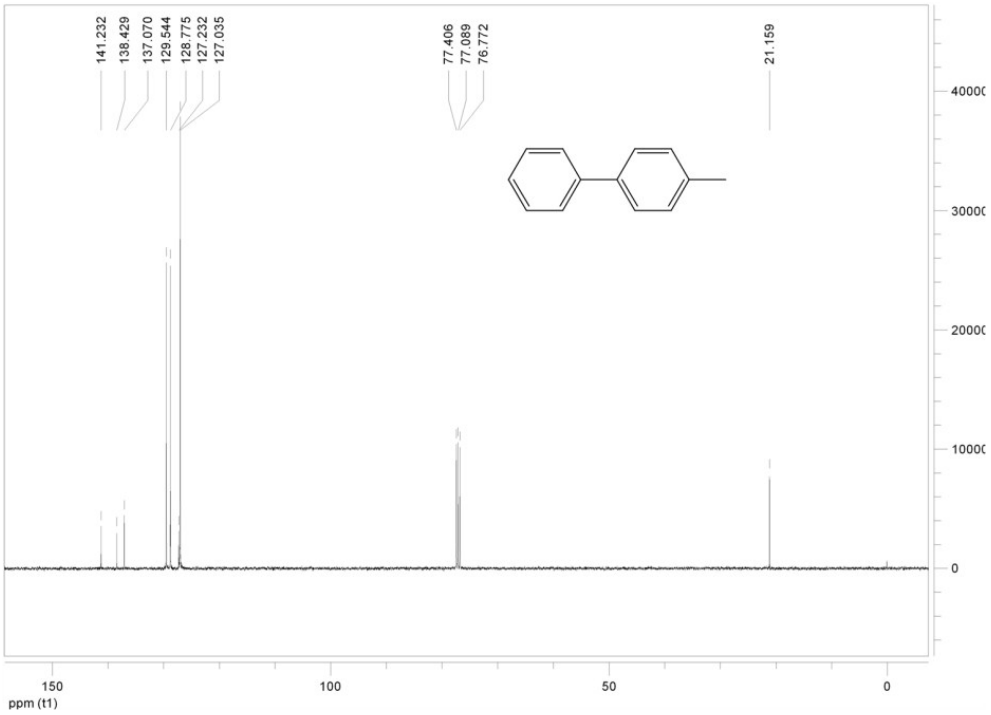


Fig. S48 The ^{13}C NMR (100 MHz, $CDCl_3$) spectra of 4-methylbiphenyl.

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