Supporting Information

Efficient symmetrical bidentate dioxime ligand-accelerated homogeneous palladium-catalyzed Suzuki-Miyaura coupling reaction of aryl chlorides

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Experimental Section

Synthesis of 2, 3-dihydroxybenzaldehyde oxime (L_5) and its complex

1. 2, 3-dihydroxybenzaldehyde

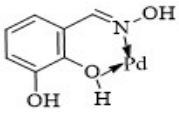
Under nitrogen, redistilled $POCl_3$ (39.05 g, 0.059 mol) was slowly dropped in the dry N, N- dimethylformamide (4.75 g, 0.065 mol), and the mixture was stirred in ice bath for 1 h. Then a solution of catechol (4.95 g, 0.045 mol) in DMF was added. The reaction was stirred for 12 h at 40 ℃ and monitored by TLC. At the end of the reaction, the reaction mixture was poured into ice water with stirring, and the solid was precipitated. The aqueous layer was extracted with ethyl acetate, and the organic layer was washed with water 3 times, then dried over anhydrous Na_2SO_4. After removal of the solution, the residue was purified by recrystallized from benzene to give light yellow solid (3.8 g, 61%); m.p:104～106 ℃ (literature value of 104～108℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) =10.20 (s, 1H, CHO), 9.92 (s, 2H, OH), 7.13 (dd, *J* = 7.6, 1.6 Hz, 1H, Ph), 7.07 (dd, *J* = 7.6, 1.6 Hz, 1H, Ph), 6.79 (t, *J* = 7.8 Hz, 1H, Ph). (Known compound, see: L. Liguori, T. Barth, *J. Anal. Appl. Pyrol.,* **2011***, 92, 479.*).

2. 2, 3-dihydroxybenzaldehyde oxime

NaOH（0.408 g, 10.2 mmol）and $NH_2OH·HCl$ (0.709 g, 10.2 mmol) were dissolved in 20 mL anhydrous ethanol in 50 mL four-necked flask, and NaCl was removed by filtration. 2, 3-dihydroxy-benzaldehyde (1.0 g, 7.2 mmol) was added to the filtrate, and the mixture was refluxed for 4 h and monitored by TLC. The solvent was evaporated to dryness to give a crude yellow product which was recrystallized from chloroform and dried to give yellow needles (0.93 g, 85%); m.p: 114 ℃ (literature values 114～115 ℃). Selected IR (KBr pellet, cm^{-1}) : 3454(ν_{O-H}), 2981, 1641($\nu_{C=N}$), 1614, 1592, 1492, 1440, 741, 724. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) =11.29 (s, 1H, C=N-OH), 9.38 (s, 2H, OH), 8.31 (s, 1H, HC=N), 6.92 (dd, *J* = 7.6, 1.2 Hz, 1H, Ph), 6.80 (dd, *J* = 8.0, 1.6 Hz, 1H, Ph), 6.68 (t, *J* = 7.6 Hz, 1H, Ph). (Known compound, see: A. Tarai, J. B. Baruah, *CrystEngComm.,* **2015***, 17, 2307.*).

3. 2, 3-dihydroxybenzaldehyde oxime-complex

2, 3-dihydroxybenzaldehyde oxime (20 mg, 0.13 mmol) was disolved in 8 mL CH_3CH_2OH, then a solution of $PdCl_2$ (11.58 mg, 0.065 mmol) in CH_3CH_2OH was added (8 mL), and the mixture was refluxed for 24 h. At the end of the reaction, the solid was filtered out and washed with CH_3CH_2OH two times to get yellow solid. Selected IR (KBr pellet, cm^{-1}): 3644(ν_{O-H}), 3035, 1628($\nu_{C=N}$), 1615, 1537, 1459, 1428, 751, 742. Anal. Calcd for 2, 3-dihydroxybenzaldehyde oxime complex ($C_7H_7NO_3Pd$): C, 32.39; H, 2.72; N, 5.40. Found: C, 32.43; H, 2.79; N, 5.38. HRMS (EI) calcd for $C_7H_7NO_3Pd$ (M^+): 258.9461; found: 258.9458. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) =10.89 (s, 1H, C=N-OH), 8.93 (s, 1H, OH), 8.39 (s, 1H, HC=N), 6.93-6.54 (m, 3H, Ph). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) =149.8, 148.4, 147.4, 124.1, 118.4, 116.8, 116.3. (Figure S1).



Synthesis of 2, 4-dihydroxybenzaldehyde oxime (L_6) and its complex

1. 2, 4-dihydroxybenzaldehyde

Resorcinol (4.95 g, 0.045 mol) was used as the raw material in the same method of 2, 3-dihydroxybenzaldehyde. The product was recrystallized from water to give milk white solid (4.0 g, 64%); m.p:130～134 ℃ (literature value of 134～136℃). ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) = 10.73 (s, 2H, OH), 9.92 (s, 1H, CHO), 7.52 (d, *J* = 8.8 Hz, 1H), 6.39 (dd, *J* = 8.8, 2.4 Hz, 1H), 6.32 (d, *J* = 2.4 Hz, 1H). (Known compound, see: I. M. Downie, M. J. Earle, H. Heaney, K. F. Shuhaibar, *Tetrahedron.,* **1993***, 49, 4024*.).

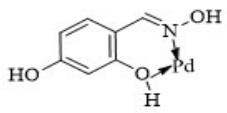
2. 2, 4-dihydroxybenzaldehyde oxime

2, 4-dihydroxy-benzaldehyde (1.0 g, 7.2 mmol) was used as the raw material in the same method of 2, 3-dihydroxybenzaldehyde oxime. The product was recrystallized from water to give white solid (1.05 g, 95%); m.p:191℃ (literature value of 191～192℃). Selected IR (KBr pellet, cm^{-1}) : 3357 (ν_{O-H}), 2977, 1640($\nu_{C=N}$), 1612, 1590, 1500, 1448, 859, 821, 805. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm)

=10.96 (s, 1H, OH), 10.10 (s, 1H, C=N-OH), 9.74 (s, 1H, OH), 8.21 (s, 1H, HC=N), 7.25 (d, *J* = 9.2 Hz, 1H, Ph), 6.38 – 6.25 (m, 2H, Ph). (Known compound, see: A. Tarai, J. B. Baruah, *RSC Adv.,* **2015***, 5, 82145.*).

3. 2, 4-dihydroxybenzaldehyde oxime-complex

2, 4-dihydroxybenzaldehyde oxime (20 mg, 0.13 mmol) was used in the same approach of 2, 3-dihydroxybenzaldehyde oxime-palladcycle. The product was yellow solid. Selected IR (KBr pellet, cm^{-1}) : 3388(ν_{O-H}), 2924, 1627($\nu_{C=N}$), 1597, 1549, 1501, 1441, 856, 832, 787. Anal. Calcd for 2, 4-dihydroxybenzaldehyde oxime complex ($C_7H_7NO_3Pd$): C, 32.39; H, 2.72; N, 5.40. Found: C, 32.47; H, 2.69; N, 5.45. HRMS (EI) calcd for $C_7H_7NO_3Pd$ (M^+): 258.9461; found: 258.9459. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) =10.17 (s, 1H, C=N-OH), 9.90 (s, 1H, OH), 8.23 (s, 1H, HC=N), 7.23 (d, *J* = 8.5 Hz, 1H, Ph), 6.45 (s, 1H, Ph), 6.21 (d, *J* = 8.5 Hz, 1H, Ph). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) = 163.2, 162.1, 146.7, 135.3, 109.0, 107.1, 104.7. (Figure S2).



Synthesis of 2, 5-dihydroxybenzaldehyde oxime (L_7) and its complex

1. 2, 5-dihydroxybenzaldehyde

Hydroquinone (4.95 g, 0.045 mol) was used as the raw material in the same method of 2, 3-dihydroxybenzaldehyde. The product was purified by column chromatography (PE:EA=3:1) to give yellow solid (2.5 g, 40%); m.p:93～95 ℃ (literature value of 98～102℃). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) = 10.18 (s, 1H, OH), 10.02 (s, 1H, CHO), 9.17 (s, 1H, OH), 7.01 – 6.95 (m, 2H, Ph), 6.84 (d, *J* = 8.4 Hz, 1H, Ph). (Known compound, see: M. L. Belyanin, E. V. Stepanova, V. D. Ogorodnikov, *Carbohydr. Res.,* **2012***, 363, 67.*).

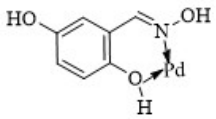
2. 2, 5-dihydroxybenzaldehyde oxime

2, 5-dihydroxybenzaldehyde (1.0 g, 7.2 mmol) was used as the raw material in the same method of 2, 3-dihydroxybenzaldehyde oxime. The product was purified by

column chromatography (PE:EA=2:1) to give yellow solid (0.74 g, 67%); m.p:129～131 ℃ (literature value of 129～131℃). Selected IR (KBr pellet, cm^{-1}): 3200(ν_{O-H}), 2991, 1646($\nu_{C=N}$), 1601, 1575, 1478, 1448, 843, 824. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) =11.20 (s, 1H, C=N-OH), 9.35 (s, 1H, OH), 8.87 (s, 1H, OH), 8.24 (s, 1H, HC=N), 6.90 (d, *J* = 2.8 Hz, 1H, Ph), 6.72 – 6.63 (m, 2H, Ph). (Known compound, see: M. Beatriz, N. Martín, *J. Org. Chem*., **2000**, *65, 5989*.).

3. 2, 5-dihydroxybenzaldehyde oxime-complex

2, 5-dihydroxybenzaldehyde oxime (20 mg, 0.13 mmol) was used in the same approach of 2, 5-dihydroxybenzaldehyde oxime-palladcycle. The product was dark yellow solid. Selected IR (KBr pellet, cm^{-1}) : 3412(ν_{O-H}), 3028, 1626($\nu_{C=N}$), 1619, 1556, 1495, 1460, 851, 823. Anal. Calcd for 2, 5-dihydroxybenzaldehyde oxime complex ($C_7H_7NO_3Pd$): C, 32.39; H, 2.72; N, 5.40. Found: C, 32.42; H, 2.69; N, 5.43. HRMS (EI) calcd for $C_7H_7NO_3Pd$ (M^+): 258.9461; found: 258.9459. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) = 10.56 (s, 1H, C=N-OH), 8.78 (s, 1H, OH), 8.30 (s, 1H, HC=N), 6.93 (d, *J* = 8.4 Hz, 1H, Ph), 6.78 (d, *J* = 11.6 Hz, 2H, Ph). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) =153.7, 148.0, 147.1, 123.4, 120.3, 117.2, 115.6. (Figure S3).



Synthesis of 2, 5-dihydroxyterephthalaldehyde dioxime (L_8) and its complex

1. 2, 5-dihydroxyterephthalaldehyde

Under nitrogen, redistilled $POCl_3$ (18.10 g, 0.118 mol) was slowly dropped in the dry N, N- dimethylformamide (9.50 g, 0.13 mol), then added a solution of hydroquinone (4.95 g, 0.045 mol). The reaction was stirred for 24 h at 55 ℃ and monitored by TLC. The product was purified by column chromatography (PE:EA=3:1) to give yellow solid (2.0 g, 27%); m.p:256～260 ℃ (literature value of 262℃). ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) = 10.28 (s, 2H, OH), 10.24 (s, 2H, CHO), 7.19

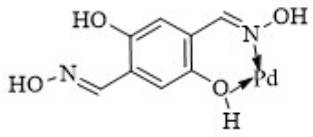
(s, 2H, Ph). (Known compound, see: K. B. Borisenko, K. Zauer, I. Hargittai, *J. Phys. Chem.,* **1996***, 100, 19303.*).

2. 2, 5-dihydroxyterephthalaldehyde dioxime

NaOH (1.632 g, 40.8 mmol) and $NH_2OH·HCl$ (2.836 g, 40.8 mmol) were dissolved in 100 mL anhydrous ethanol in 250 mL four-necked flask, and NaCl was removed by filtration. 2, 5-dihydroxyterephthalaldehyde (1.0 g, 6.02 mmol) was added to the filtrate refluxed for 5 h, and the reaction was monitored by TLC. The product was purified by column chromatography (PE:EA=1:1) to give dark yellow solid (0.71 g, 60%); m.p: 252～255 ℃. Selected IR (KBr pellet, cm^{-1}) : 3337(ν_{O-H}), 2996, 1651($\nu_{C=N}$), 1610, 1538, 1488, 1445, 953, 861, 788. Anal. Calcd for 2, 5-dihydroxyterephthalaldehyde dioxime: C, 48.98; H, 4.11; N, 14.28. Found: C, 49.08; H, 4.12; N, 14.24. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) =11.34 (s, 2H, C=N-OH), 9.49 (s, 2H, OH), 8.24 (s, 2H, HC=N), 7.05 (s, 2H, Ph). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) =148.9, 146.3, 121.0, 113.5.

3. 2, 5-dihydroxyterephthalaldehyde dioxime-complex

2, 5-dihydroxyterephthalaldehyde dioxime (20 mg, 0.10 mmol) was disolved in 8 mL CH_3CH_2OH, then a solution of $PdCl_2$ (9.04 mg, 0.051 mmol) in CH_3CH_2OH was added (8 mL), and the mixture was refluxed for 24 h. At the end of the reaction, the solid was filtered out and washed with CH_3CH_2OH two times to get dark red solid. Anal. Calcd for 2,5-dihydroxyterephthalaldehyde dioxime complex ($C_8H_8N_2O_4Pd$): C, 31.76; H, 2.67; N, 9.26. Found: C, 31.84; H, 2.61; N, 9.29. HRMS (EI) calcd for $C_8H_8N_2O_4Pd$ (M^+): 301.9519; found: 301.9516. Selected IR (KBr pellet, cm^{-1}) : 3451(ν_{O-H}), 3014, 1624($\nu_{C=N}$), 1589, 1506, 1462, 1457, 928, 884, 793. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) =11.54 (s, 1H, C=N-OH), 10.66 (s, 1H, C=N-OH), 9.33 (s, 1H, OH), 8.41 (s, 1H, HC=N), 8.22 (s, 1H, HC=N), 7.29 (s, 1H, Ph), 6.94 (s, 1H, Ph). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) =150.0, 149.0, 146.4, 136.6, 124.4, 120.9, 113.7. (Figure S4).



Synthesis of 2, 4-dihydroxy-5-acetylacetophenone dioxime (L_9) and its complex

1. 2, 4-dihydroxy-5-acetylacetophenone

Resorcinol (1.10 g, 10 mmol), acetic anhydride (2.04 g, 20 mmol) and zinc chloride (2.72 g, 20 mmol) at 150 ℃ reaction for 30 min, and the solution was cooled to room temperature to give brick-red viscous liquid. The ice HCl solution was added with stirring, and the brick red precipitate was filtered. The product was recrystallized from methanol to give a solid (1.75 g, 90%); m.p: 178～180 ℃ (literature value 182 ℃). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) =12.73 (s, 2H, OH), 8.41 (s, 1H, Ph), 6.39 (s, 1H, Ph), 2.65 (s, 6H, CH_3). (Known compound, see: R. N. Butler, D. P. Shekky, *Tetrahedron Lett.,* **1985***, 26, 3402.)*.

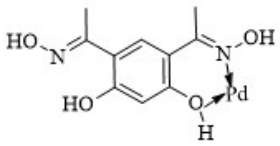
2. 2, 4-dihydroxy-5-acetylacetophenone dioxime

NaOH (514.93 mg, 12.87 mmol) and $NH_2OH·HCl$ (1.43 g, 20.60 mmol) were dissolved in 20 mL anhydrous ethanol in 50 mL four-necked flask, and NaCl was removed by filtration. 2, 4-hydroxy-5-acetyl acetophenone (1.0 g, 5.15 mmol) was added to the filtrate and refluxed for 4 h, and the reaction was monitored by TLC. The product was purified by column chromatography to give a pink solid (0.92 g, 80%); m.p: 251～253 ℃ (literature values 253～255 ℃). Selected IR (KBr pellet, cm^{-1}) : 3403(ν_{O-H}), 3031, 1639($\nu_{C=N}$), 1606, 1595, 1504, 1452, 884, 717. ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) =11.94 (s, 2H, C=N-OH), 11.30 (s, 2H, OH), 7.45 (s, 1H, Ph), 6.29 (s, 1H, Ph), 2.23 (s, 6H, CH_3). (Known compound, see: M. J. Raihan, V. Kavala, P. M. Habib, Q. Z. Guan, C. W. Kuo, C. F. Yao, *J. Org. Chem.,* **2011***, 76, 432.*).

3. 2, 4-dihydroxy-5-acetylacetophenone dioxime-complex

2, 4-dihydroxy-5-acetylacetophenone dioxime (20 mg, 0.089 mmol) was disolved in 8 mL CH_3CH_2OH, then a solution of $PdCl_2$ (7.91 mg, 0.045 mmol) in CH_3CH_2OH was added (8 mL), and the mixture was refluxed for 24 h. At the end of the reaction,

the solid was filtered out and washed with CH_3CH_2OH two times to get dark red solid. Selected IR (KBr pellet, cm^{-1}) : 3525(ν_{O-H}), 3055, 1626($\nu_{C=N}$), 1618, 1585, 1493, 1480, 824, 745. Anal. Calcd for 2, 4-dihydroxy-5-acetylacetophenone dioxime complex ($C_{10}H_{12}N_2O_4Pd$) C, 36.33; H, 3.66; N, 8.47. Found: C, 36.34; H, 3.57; N, 8.57. HRMS (EI) calcd for $C_{10}H_{12}N_2O_4Pd$ (M^+): 329.9832; found: 329.9833. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) = 11.99 (s, 1H, C=N-OH), 11.26 (s, 1H, C=N-OH), 10.58 (s, 1H, OH), 7.35 (s, 1H, Ph), 6.38 (s, 1H, Ph), 3.32 (s, 6H, CH_3). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) =159.7, 157.7, 128.2, 112.2, 104.0, 11.5. (Figure S5).



Characterization

Biphenyl (01): ^1H NMR (400 MHz, $CDCl_3$) δ (ppm)=7.66 – 7.62 (m, 4H), 7.49 (dd, *J* = 10.3, 4.8 Hz, 4H), 7.39 (ddd, *J*= 7.3, 3.9, 1.1 Hz, 2H). (Figure S6) (Known compound, see: H. Y. Liu, H. L. Liu, R. X. Li, H. Chen, *Tetrahedron Lett.,* **2014***, 55, 417.*).

4-nitro-1, 1'-biphenyl (02): ^1H NMR (400 MHz, $CDCl_3$) δ (ppm) =8.28 (d, *J*= 8.8 Hz, 2H), 7.72 (d, *J*= 8.8 Hz, 2H), 7.64 – 7.59 (m, 2H), 7.45 (ddd, *J* = 10.9, 9.7, 5.7 Hz, 3H). (Figure S7) (Known compound, see: A. Dewan, U. Bora, G. Borah, *Tetrahedron Lett.,* **2014***, 55, 1691.*).

[1, 1'-biphenyl]-4-carbaldehyde (03): 1H NMR (400 MHz, $CDCl_3$) δ (ppm) =10.06 (s, 1H), 7.95 (d, J = 8.4 Hz, 2H), 7.75 (d, J = 8.2 Hz, 2H), 7.66 – 7.61 (m, 2H), 7.48 (t, J = 7.3 Hz, 2H), 7.45 – 7.39 (m, 1H). (Figure S8) (Known compound, see: J. P. Simeone, J. R. Sowa, *Tetrahedron.,* **2007***, 63, 12648.*).

[1, 1'-biphenyl]-4-carbonitrile (04): 1H NMR (400 MHz, $CDCl_3$) δ (ppm)=7.75 – 7.71 (m, 2H), 7.71 – 7.67 (m, 2H), 7.60 (dd, J = 5.3, 3.4 Hz, 2H), 7.51 – 7.46 (m, 2H), 7.45 – 7.40 (m, 1H). (Figure S9) (Known compound, see: K. B. Manas, K. D. Swapan, P. Pradip, B. Rahul, *Dalton Trans.,* **2012***, 41, 1304.*).

4-methyl-1, 1'-biphenyl (05): 1H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.61 (d, J = 7.3

Hz, 2H), 7.52 (d, J = 8.1 Hz, 2H), 7.45 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.4 Hz, 1H), 7.29 – 7.27 (m, 2H), 2.43 (s, 3H). (Figure S10) (Known compound, see: L. Wan, C. Cai, *Catal. Commun.,* **2012***, 24, 107.*).

4-methoxy-1, 1'-biphenyl (06): 1H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.55 (t, J = 8.3 Hz, 4H), 7.42 (t, J = 7.6 Hz, 2H), 7.31 (t, J = 7.4 Hz, 1H), 6.99 (d, J = 8.7 Hz, 2H), 3.86 (s, 3H). (Figure S11) (Known compound, see: K. W. Quasdorf, A. A. Finch, P. Liu, A. L. Silberstein, A. Komaromi, T. Blackburn, S. D. Ramgren, K. N. Houk, V. Snieckus, N. K. Garg, *J. Am. Chem. Soc.,* **2011***, 133, 6353.*).

3-methoxy-1, 1'-biphenyl (07): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.66 – 7.63 (m, 2H), 7.48 (dd, *J*= 10.3, 4.7 Hz, 2H), 7.40 (dt, *J*= 7.3, 3.3 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 1H), 7.20 – 7.18 (m, 1H), 6.95 (dd, *J*= 8.2, 2.2 Hz, 1H), 3.90 (s, 3H). (Figure S12) (Known compound, see: I. Ho□mann, B. Blumenröder, S. O. Thumann, S. Dommer, J. Schatz, *Green. Chem.,* **2015***, 17, 3847.*).

2-methoxy-1, 1'-biphenyl (08): 1H NMR (400 MHz, CDCl3) δ (ppm) = 7.53 (m, 2H), 7.52 (m, 2H), 7.40 – 7.25 (m, 3H), 7.03 – 7.00 (m, 2H), 3.81 (s, 3H). (Figure S13) (Known compound, see: C. Liu, Q. Ni, P. Hu, J. Qiu, Org. Biomol. Chem., 2011, 9, 1054.).

2-nitro-1, 1'-biphenyl (09):^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm)=7.99 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.78 (td, *J* = 7.6, 1.3 Hz, 1H), 7.65 (td, *J* = 8.0, 1.4 Hz, 1H), 7.58 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.51 – 7.43 (m, 3H), 7.39 – 7.33 (m, 2H). (Figure S14) (Known compound, see: Y. B. Yuan, J. Nie, Z. B. Zhang, S. J. Wang, *Appl. Catal. A.,* **2005***, 295, 171.*).

3, 4-dimethoxy-1, 1'-biphenyl (10): 1H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.58 – 7.54 (m, 2H), 7.43 (t, J = 7.6 Hz, 2H), 7.33 (d, J = 7.4 Hz, 1H), 7.17 – 7.11 (m, 2H), 6.95 (d, J = 8.2 Hz, 1H), 3.95 (s, 3H), 3.93 (s, 3H). (Figure S15) (Known compound, see: V. Percec, G. M. Golding, J. Smidrkal, O. Weichold, *J. Org. Chem.,* **2004***, 69, 3451.*).

3, 4-bis(benzyloxy)-1, 1-'biphenyl (11): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)=7.47 (t, *J*= 5.9 Hz, 6H), 7.37 (t, *J*= 7.5 Hz, 6H), 7.31 (t, *J* = 7.3 Hz, 3H), 7.20 (d, *J* = 2.0 Hz, 1H), 7.13 – 7.10 (m, 1H), 7.00 (d, *J*= 8.3 Hz, 1H), 5.21 (d, *J*= 7.6 Hz, 4H). (Figure

S16) (Known compound, see: M. Gayral, J. M. Brown, *Synlett.,* **2007***, 18, 2825.*).

4-methyl-4'-(trifluoromethyl)-1,1'-biphenyl (12): 1H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.67 (s, 4H), 7.50 (d, J = 8.1 Hz,2H), 7.28 (d, J = 7.9 Hz, 2H), 2.41 (s, 3H). (Figure S17) (Known compound, see: X. Liu, X. H. Zhao, M. Lu, *Appl. Organometal. Chem.,* **2015**, *29, 423.*).

4-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl (13): 1H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.70 – 7.60 (m, 4H), 7.58 – 7.50 (m, 2H), 7.04 – 6.96 (m, 2H), 3.86 (s, 3H). (Figure S18) (Known compound, see: W. Y. Chu, X. M. Li, Y. J. Hou, H. Wang, X. B. Yuan, H. Y. Li, Z. Z. Sun, *Appl. Organometal. Chem.,* **2012***, 26, 478.*).

4-nitro-4'-(trifluoromethyl)-1,1'-biphenyl (14): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)=8.34 (d, *J* = 8.7 Hz, 2H), 7.79 – 7.71 (m, 6H). (Figure S19) (Known compound, see: W. Y. Chu, X. M. Li, Y. J. Hou, H. Wang, X. B. Yuan, H. Y. Li, Z. Z. Sun, *Appl. Organometal. Chem.,* **2012***, 26, 478.*).

4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carbaldehyde (15): 1H NMR (400 MHz, $CDCl_3$) δ (ppm) =10.09 (s, 1H), 8.00 (d, J = 8.2 Hz, 2H), 7.79 – 7.74 (m, 6H). (Figure S20) (Known compound, see: L. Adak, N. Yoshikai, *J. Org. Chem.,* **2011***, 76, 7565.*).

4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carbonitrile (16): 1H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.76 (t, J = 9.0 Hz, 4H), 7.70 (d, J = 8.2 Hz, 4H). (Figure S21) (Known compound, see: M. Wang, X. B. Yuan, H. Y. Li, L. M. Ren, Z. Z. Sun, Y. J. Hou, W. Y. Chu, *Catal. Commun.,* **2015***, 58, 156.*).

4-methoxy-4'-methyl-1,1'-biphenyl (17): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)=7.57 – 7.51 (m, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.29 (s, 2H), 7.02 – 6.97 (m, 2H), 3.88 (s, 3H), 2.41 (s, 3H). (Figure S22) (Known compound, see: J. J. Ning, J. F. Wang, Z. G. Ren, D. J. Young, J. P. Lang, *Tetrahedron.,* **2015***, 71, 4003.*).

4'-methoxy-[1,1'-biphenyl]-4-carbonitrile (18): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) = 7.70 (d, *J*= 8.0 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 2H), 7.54 (d, *J* = 8.0 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 3.87 (s, 3H). (Figure S23) (Known compound, see: Y. Kitamura, A. Sakurai, T. Udzu, T. Maegawa, Y. Monguchi, H. Sajiki, *Tetrahedron,* **2007***, 63, 10597.*).

3, 4-bis(benzyloxy)-4'-methoxy-1,1'-biphenyl (19): White solid. m.p: 98 ~ 102 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm)=7.57 – 7.26 (m, 13H), 7.16 – 7.05 (m, 2H), 7.01 – 6.94 (m, 2H), 5.23 (s, 2H), 5.16 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) =158.9, 149.0, 147.8, 137.9, 137.8, 133.7, 132.8, 128.8, 128.2, 128.0, 127.9, 127.9, 119.2, 115.4, 114.7, 113.2, 70.6, 70.6, 55.6. Anal. Calcd for 3, 4-bis(benzyloxy)-4'-methoxy-1,1'-biphenyl ($C_{27}H_{24}O_3$): C, 81.79; H, 6.10. Found: C, 81.73; H, 6.19. HRMS (EI) calcd for $C_{27}H_{24}O_3$ (M^+): 396.1725; found: 396.1720. (Figure S24)

3, 4-bis(benzyloxy)terphenyl (20): White solid. m.p: 138 ~ 142 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm)=7.72 (s, 3H), 7.72 – 7.67 (m, 3H), 7.51 – 7.48 (m, 4H), 7.48 – 7.33 (m, 9H), 7.33 – 7.21 (m, 2H), 7.15 (d, *J* = 8.4 Hz, 1H), 5.27 (s, 2H), 5.19 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) =149.0, 148.5, 140.1, 139.4, 139.0, 137.9, 137.8, 134.9, 133.2, 129.4, 129.4, 128.9, 128.2, 128.0, 127.9, 127.9, 127.7, 127.5, 127.3, 127.0, 115.3, 70.6, 70.5. Anal. Calcd for 3, 4-bis(benzyloxy)terphenyl ($C_{32}H_{26}O_2$): C, 86.85; H, 5.92. Found: C, 86.83; H, 6.01. HRMS (EI) calcd for $C_{32}H_{26}O_2$ (M^+): 442.1933; found: 442.1930. (Figure S25)

3', 5'-Difluoro-2-nitro-1, 1'-biphenyl (21): Yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm) =8.07 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.81 (td, *J* = 7.6, 1.2 Hz, 1H), 7.70 (td, *J*= 7.9, 1.4 Hz, 1H), 7.58 (dd, *J* = 7.7, 1.5 Hz, 1H), 7.30 (tt, *J* = 9.4, 2.3 Hz, 1H), 7.13 (dd, *J* = 8.3, 2.2 Hz, 2H).^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) =162.7, 162.6, 148.7, 141.2, 133.8, 133.6, 132.2, 130.2, 124.9, 112.0, 111.8, 104.1. Anal. Calcd for 3', 5'-Difluoro-2-nitro-1, 1'-biphenyl ($C_{12}H_7F_2NO_2$): C, 61.28; H, 3.00; F, 16.16; N, 5.96. Found: C, 61.20; H, 3.01; F, 16.10; N, 5.95. HRMS (EI) calcd for $C_{12}H_7F_2NO_2$ (M^+): 235.0445; found: 235.0440. (Figure S26)

4-nitro-2', 5'-dimethyl-[1,1'-biphenyl] (22): ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) =8.28 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 7.9 Hz, 2H), 7.19 (s, 2H), 7.15 (s, 1H), 7.04 (s, 1H), 2.37 (s, 3H), 2.23 (s, 3H). (Figure S27) (Known compound, see: W. Y. Chu, X. M. Li, Y. J. Hou, H. Wang, X. B. Yuan, H. Y. Li, Z. Z. Sun, *Appl. Organometal. Chem.,* **2012**, *26, 478.*).

4-methyl-3', 4'-dimethoxy-1, 1'-biphenyl (23): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) =7.46 (d, *J* = 8.1 Hz, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 7.13 (dd, *J* = 8.2, 2.1 Hz, 1H), 7.10 (d, *J* = 2.0 Hz, 1H), 6.94 (d, *J* = 8.2 Hz, 1H), 3.95 (s, 3H), 3.92 (s, 3H), 2.39 (s, 3H). (Figure S28) (Known compound, see: B. H. Lipshutz, T. Butler, E. Swift, *Org. Lett.,* **2008***, 10, 698.*).

2'-methyl-1,1'-biphenyl (24): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)= 7.57 – 7.53 (m, 2H), 7.50 – 7.45 (m, 3H), 7.43 – 7.37 (m, 4H), 2.42 (s, 3H). (Figure S29) (Known compound, see: R. C. Huang, K. H. Shaughnessy, *Organometallics.,* **2006***, 25, 4108.*).

4-methoxyl-2'-methyl-1,1'-biphenyl (25): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)= 7.35 – 7.26 (m, 6H), 7.05 – 6.98 (m, 2H), 3.90 (s, 3H), 2.35 (s, 3H). (Figure S30) (Known compound, see: Y. T. Huang, X. Tang, Y. Yang, D. S. Shen, C. Tan, F. S. Liu, *Appl. Organomet. Chem.,* **2012***, 26, 704.*).

4-formyl-2'-methyl-1,1'-biphenyl (26): 1H NMR (400 MHz, DMSO-d_6) δ (ppm)= 10.08 (s, 1H), 7.99 (d, J = 8.0 Hz, 2H), 7.59 (d, J = 8.0 Hz, 2H), 7.38 – 7.24 (m, 4H), 2.25 (s, 3H). (Figure S31) (Known compound, see: Y. T. Huang, X. Tang, Y. Yang, D. S. Shen, C. Tan, F. S. Liu, Appl. Organomet. Chem., 2012, 26, 705.).

4-nitro-2'-methyl-1,1'-biphenyl (27): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm)= 8.27 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 7.36 – 7.24 (m, 4H), 2.23 (s, 3H). (Figure S32) (Known compound, see: Maddali L. N. Rao, Ritesh J. Dhanorkar, *RSC adv.,* **2016***, 6, 1015.*).

2-nitro-2'-methyl-1,1'-biphenyl (28): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm)= 8.02 (d, *J* = 9.0 Hz, 1H), 7.75 (t, *J* = 7.5 Hz, 1H), 7.63 (t, *J* = 8.4 Hz, 1H), 7.39 (d, *J* = 7.5 Hz, 1H), 7.32 – 7.19 (m, 3H), 7.05 (d, *J* = 7.4 Hz, 1H), 2.01 (s, 3H). (Figure S33) (Known compound, see: Maddali L. N. Rao, Ritesh J. Dhanorkar, *RSC adv.,* **2016***, 6, 1015.*).

1-phenyl-1'-naphthalene (29): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm)= 8.00 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.61 – 7.39 (m, 9H). (Figure S34) (Known compound, see: M. Gholinejad, F. Hamed, P. Biji, *Dalton Trans.,* **2015***, 44, 14299.*).

4-methoxy-1-phenyl-1'-naphthalene (30): ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm)= 7.93 (dd, *J* = 12.0, 8.3 Hz, 2H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.47 (dt, *J* = 27.5, 8.1 Hz, 6H), 7.05 (d, *J* = 8.6 Hz, 2H), 3.91 (s, 3H). (Figure S35) (Known compound, see: S. N. Jadhav, A. S. Kumbhar, C. V. Rode, R. S. Salunkhe, *Green Chem.,* **2016***, 18, 1904.*).

4-(naphthalen-1-yl)benzaldehyde (31): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm)= 10.13 (s, 1H), 8.10 – 8.00 (m, 4H), 7.75 (dd, *J* = 20.1, 8.2 Hz, 3H), 7.65 – 7.47 (m, 4H). (Figure S36) (Known compound, see: S. N. Jadhav, A. S. Kumbhar, C. V. Rode, R. S. Salunkhe, *Green Chem.,* **2016***, 18, 1904.*).

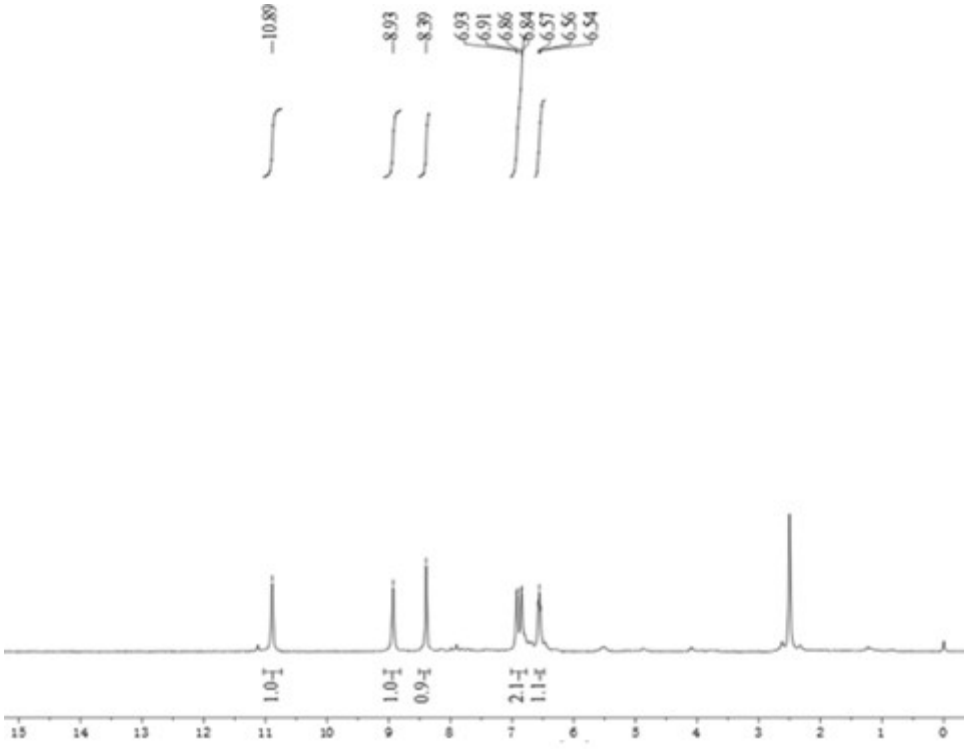
1-phenyl-2'-naphthalene (32): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm)=8.24 (s, 1H), 8.06 – 8.01 (m, 2H), 8.00 – 7.94 (m, 1H), 7.90 – 7.82 (m, 3H), 7.60 – 7.51 (m, 4H), 7.43 (t, *J* = 7.4 Hz, 1H). (Figure S37) (Known compound, see: R. F. Alamdari, M. G. Haqiqi, N. Zekri, *New J. Chem.,* **2016***, 40,1293.*).

3, 4-bis(benzyloxy)-1-phenyl-2'-naphthalene (33): White solid. m.p: 102 ~ 104 ℃. ^{1}H NMR(400 MHz, DMSO-d_6) δ (ppm) =8.17 (d, *J* = 1.8 Hz, 1H), 8.02 – 7.90 (m, 3H), 7.83 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.60 – 7.47 (m, 7H), 7.47 – 7.27 (m, 7H), 7.20 (d, *J* = 8.4 Hz, 1H), 5.30 (s, 2H), 5.23 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) =149.1, 148.6, 137.9, 137.8, 137.7, 133.8, 133.6, 132.4, 128.9, 128.7, 128.5, 128.2, 128.1, 128.0, 127.9, 126.8, 126.3, 125.5, 125.0, 120.2, 115.4, 113.8, 70.7, 70.6. Anal. Calcd for 3, 4-bis(benzyloxy)-1-phenyl-2'-naphthalene ($C_{30}H_{24}O_2$): C, 86.51; H, 5.81. Found: C, 86.45; H, 5.79. HRMS (EI) calcd for $C_{30}H_{24}O_2$ (M^+): 416.1776; found: 416.1774. (Figure S38)

2-benzyloxy-4-methoxy-1-phenyl-2'-naphthalene (34): White solid. m.p: 79 ~ 83 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm)=8.00 (d, *J* = 1.7 Hz, 1H), 7.89 (dd, *J* = 8.7, 6.3 Hz, 3H), 7.70 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.49 (qd, *J* = 7.0, 3.4 Hz, 2H), 7.44 – 7.22 (m, 6H), 6.82 (d, *J* = 2.4 Hz, 1H), 6.69 (dd, *J* = 8.4, 2.4 Hz, 1H), 5.17 (d, *J* = 4.1 Hz, 2H), 3.82 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ (ppm) =160.6, 156.7, 137.5, 136.1, 133.5, 132.1, 131.8, 129.0, 128.8, 128.5, 128.2, 128.1, 127.9, 127.8, 127.8, 127.4, 126.5, 126.1, 123.1, 106.3, 100.9, 70.2, 55.8. Anal. Calcd for 2-benzyloxy-4-methoxy-1-phenyl-2'-naphthalene ($C_{24}H_{20}O_2$): C, 84.68; H, 5.92. Found: C, 84.70; H, 6.01. HRMS (EI) calcd for $C_{24}H_{20}O_2$ (M^+): 340.1463; found: 340.1466. (Figure S39)

2, 6-diphenylpyridine (35): ^{1}H NMR (400 MHz, DMSO-d_6) δ (ppm)=8.24 – 8.18 (m, 4H), 8.00 – 7.91 (m, 3H), 7.57 – 7.50 (m, 4H), 7.50 – 7.43 (m, 2H). (Figure S40) (Known compound, see: J. L. Bolliger, C. M. Frech, *Adv. Synth. Catal.,* **2010***, 352, 1077.*).

NMR Spectra for complexes and all Cross-Coupling Products



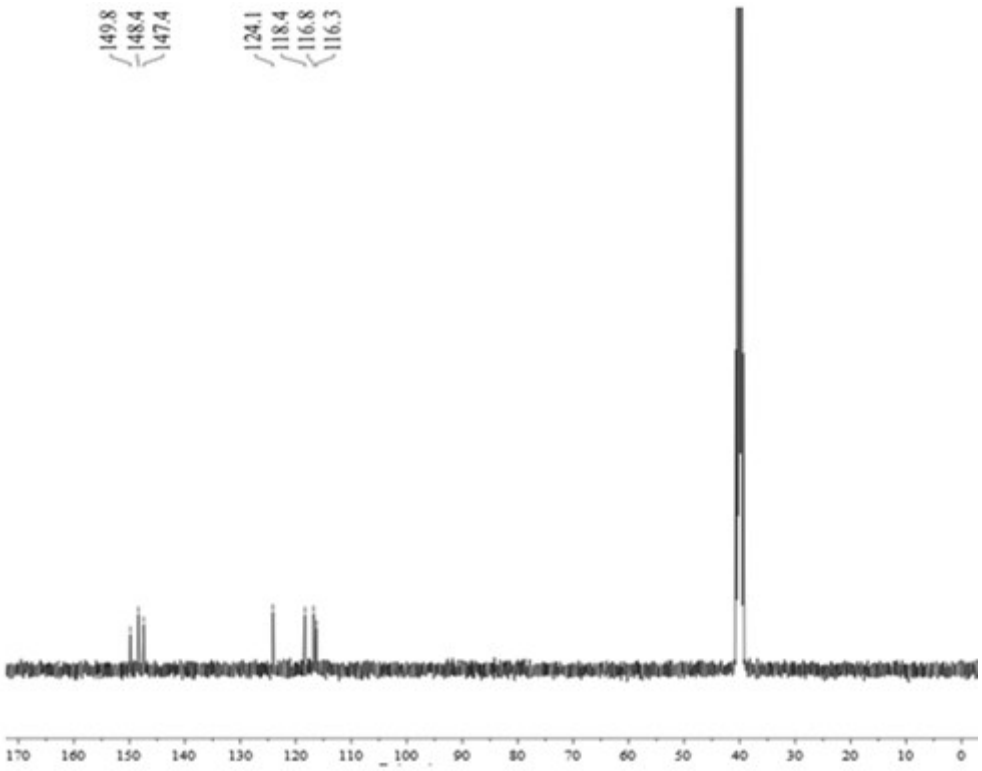
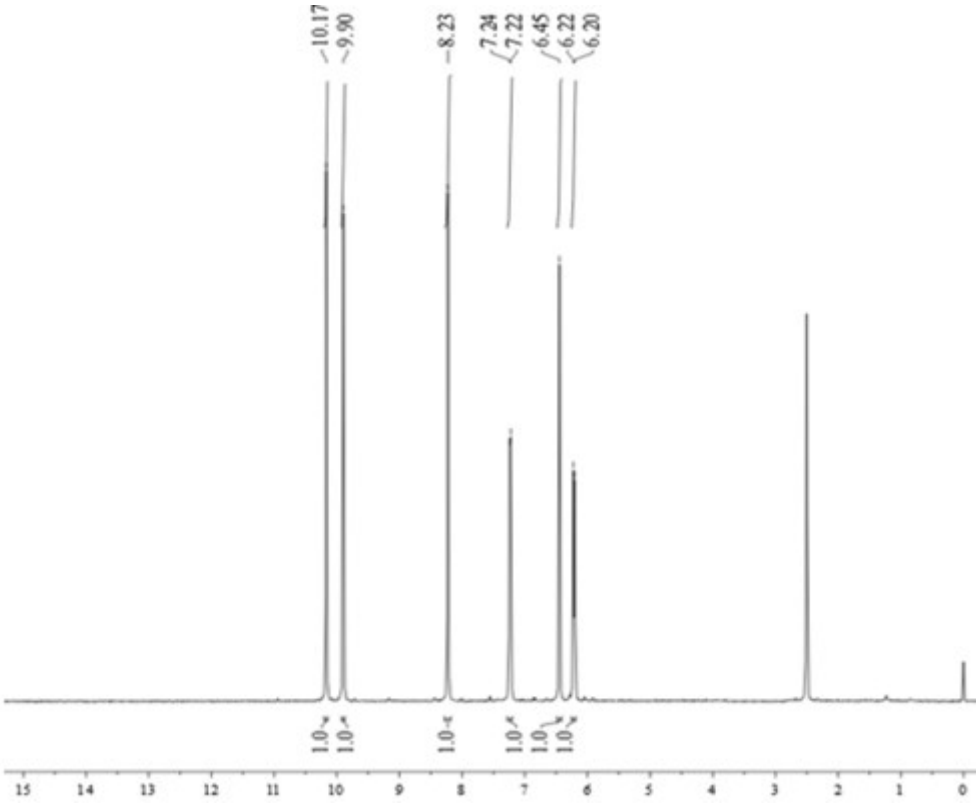


Figure S1. ^{1}H and ^{13}C-NMR spectra of 2, 3-dihydroxybenzaldehyde oxime-complex



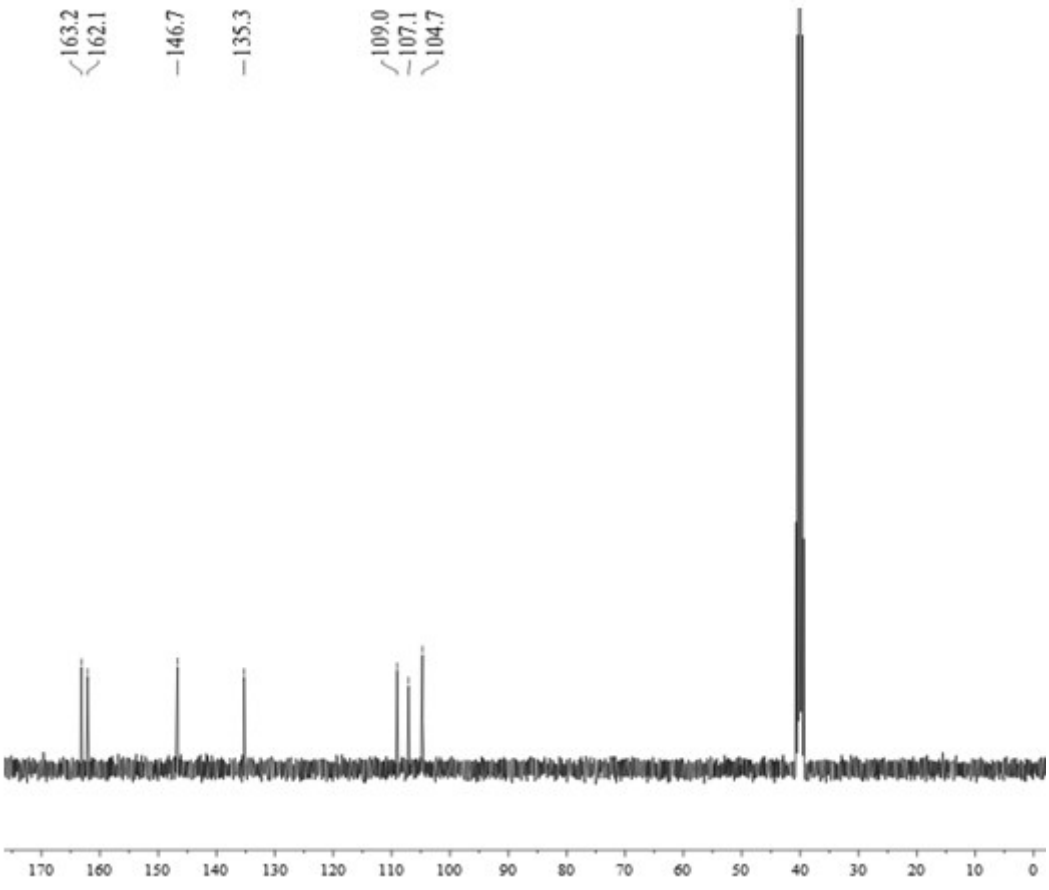
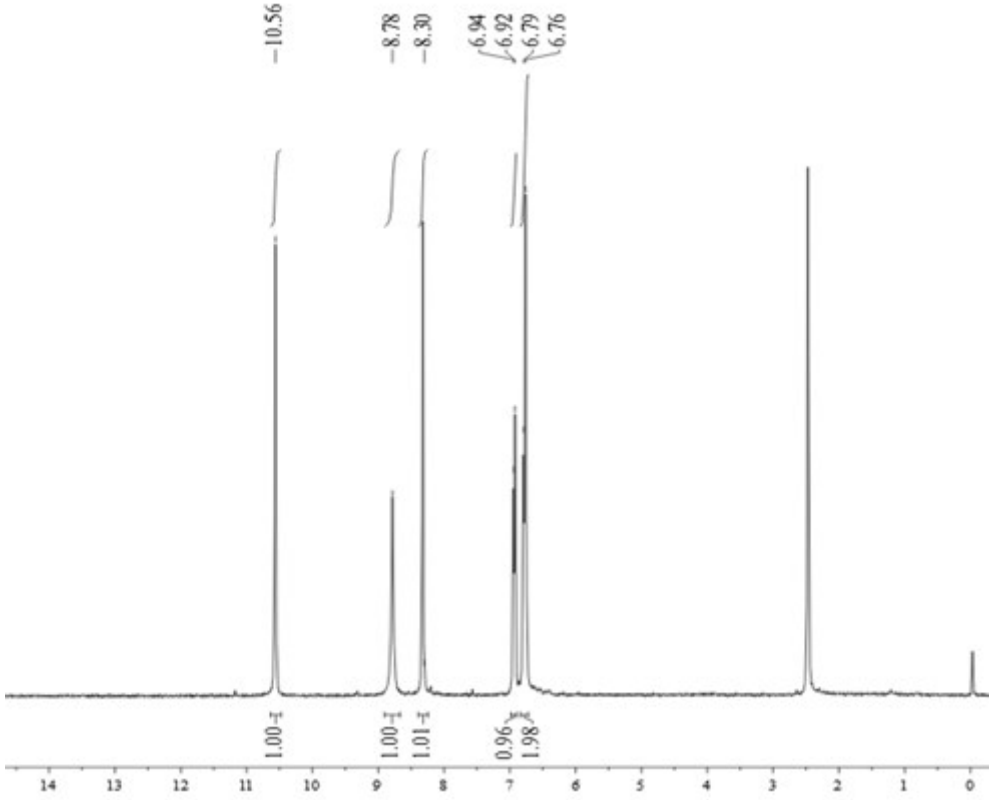


Figure S2. ^{1}H and ^{13}C-NMR spectra of 2, 4-dihydroxybenzaldehyde oxime-complex



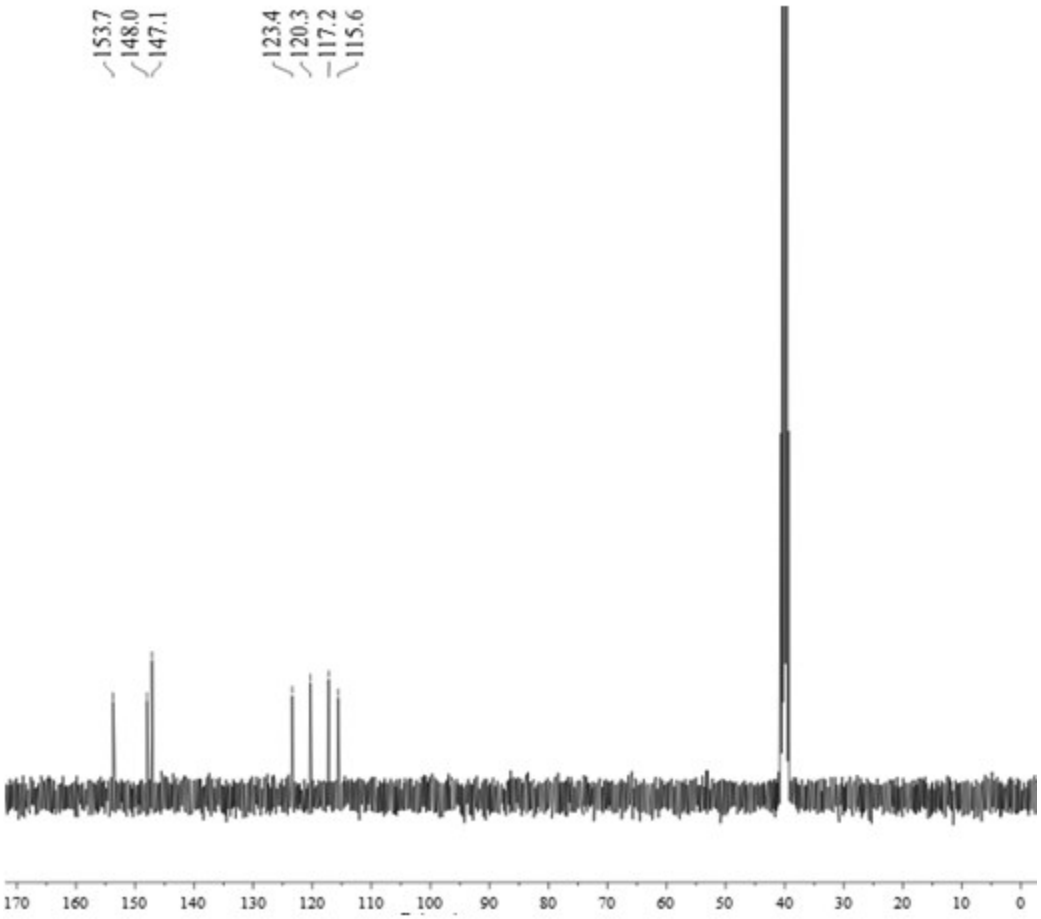


Figure S3. ^{1}H and ^{13}C-NMR spectra of 2, 5-dihydroxybenzaldehyde oxime-complex

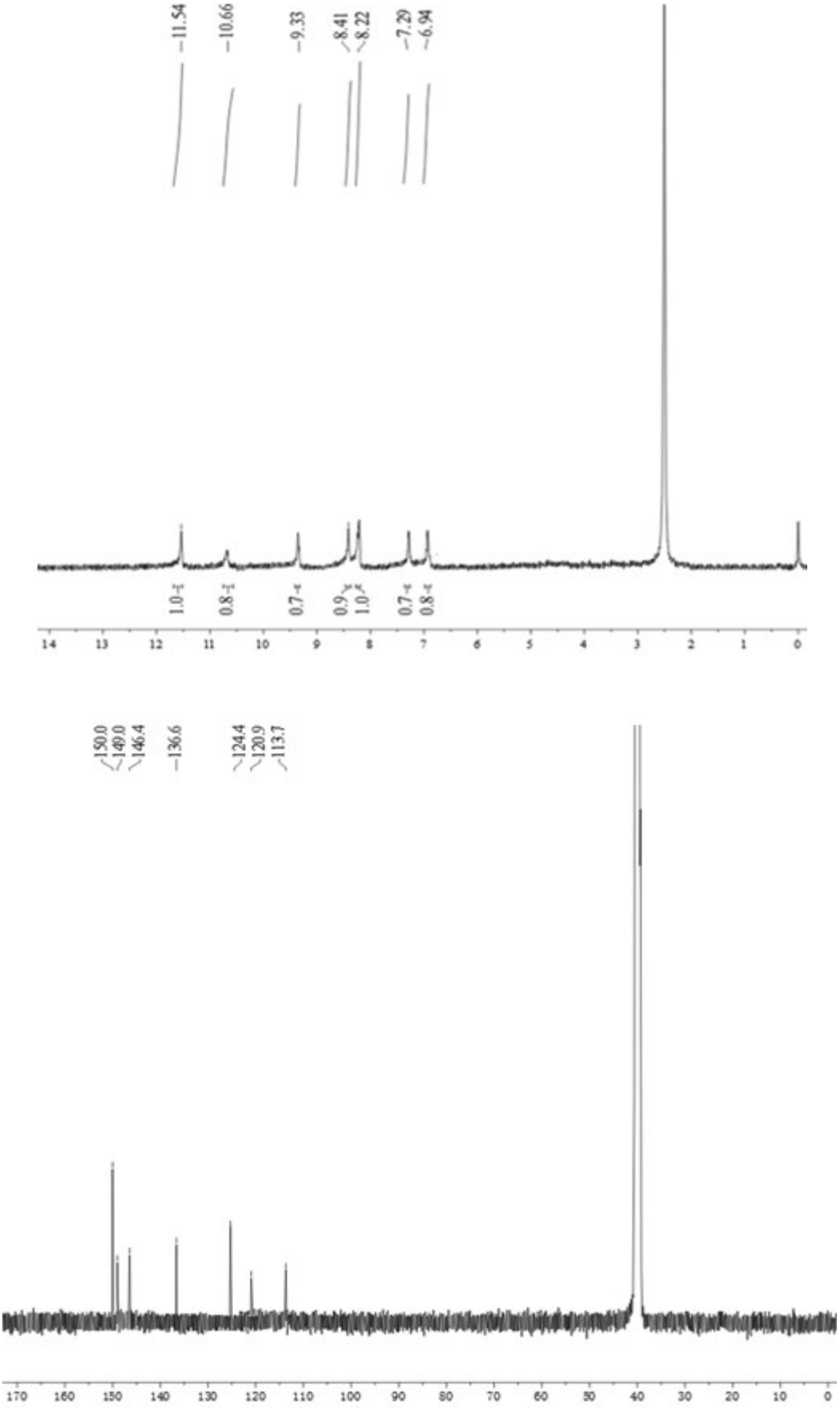


Figure S4. ^{1}H and ^{13}C-NMR spectra of 2, 5-dihydroxyterephthalaldehyde dioxime-complex

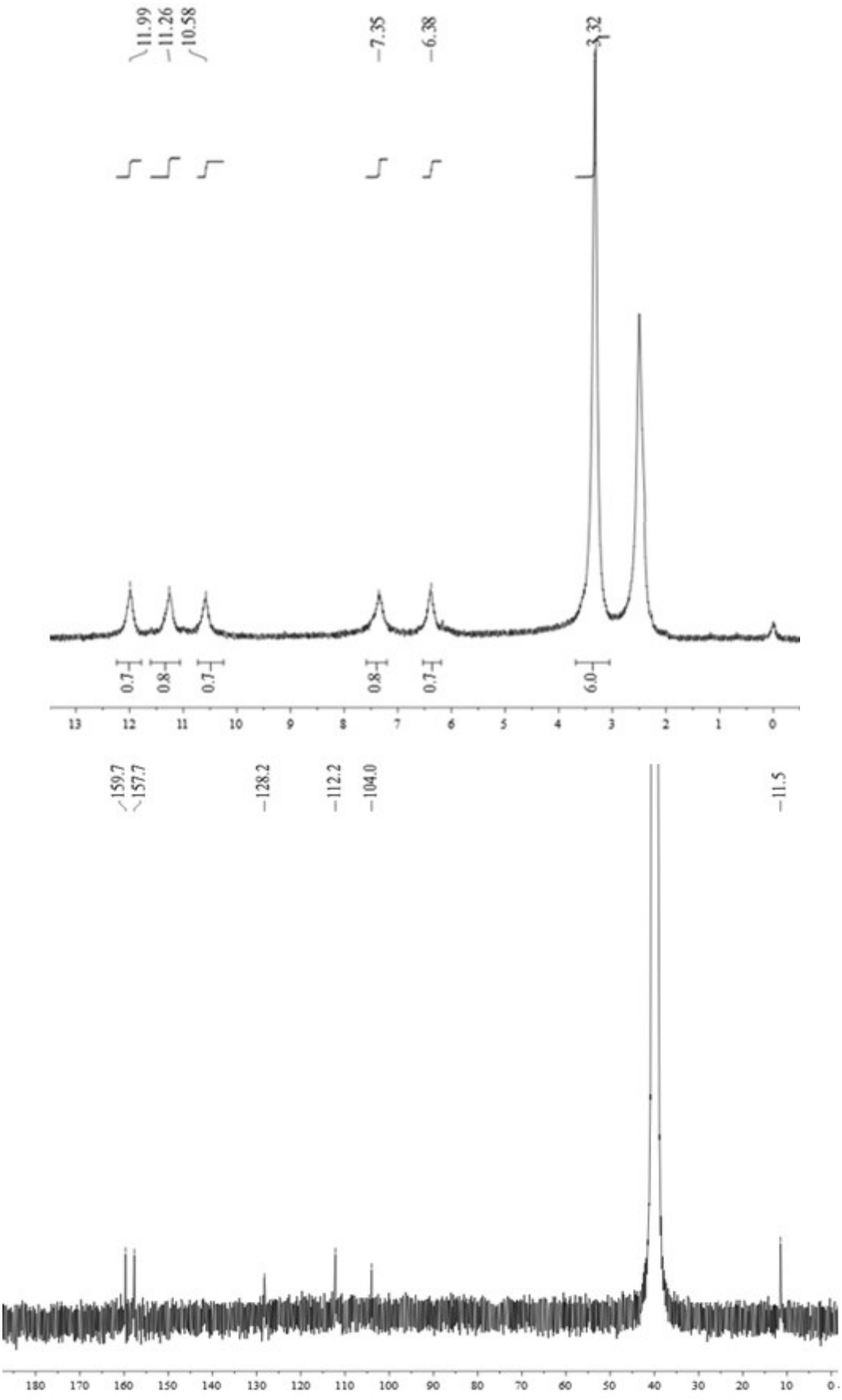


Figure S5. ^{1}H and ^{13}C-NMR spectra of 2, 4-dihydroxy-5-acetylacetophenone dioxime-complex

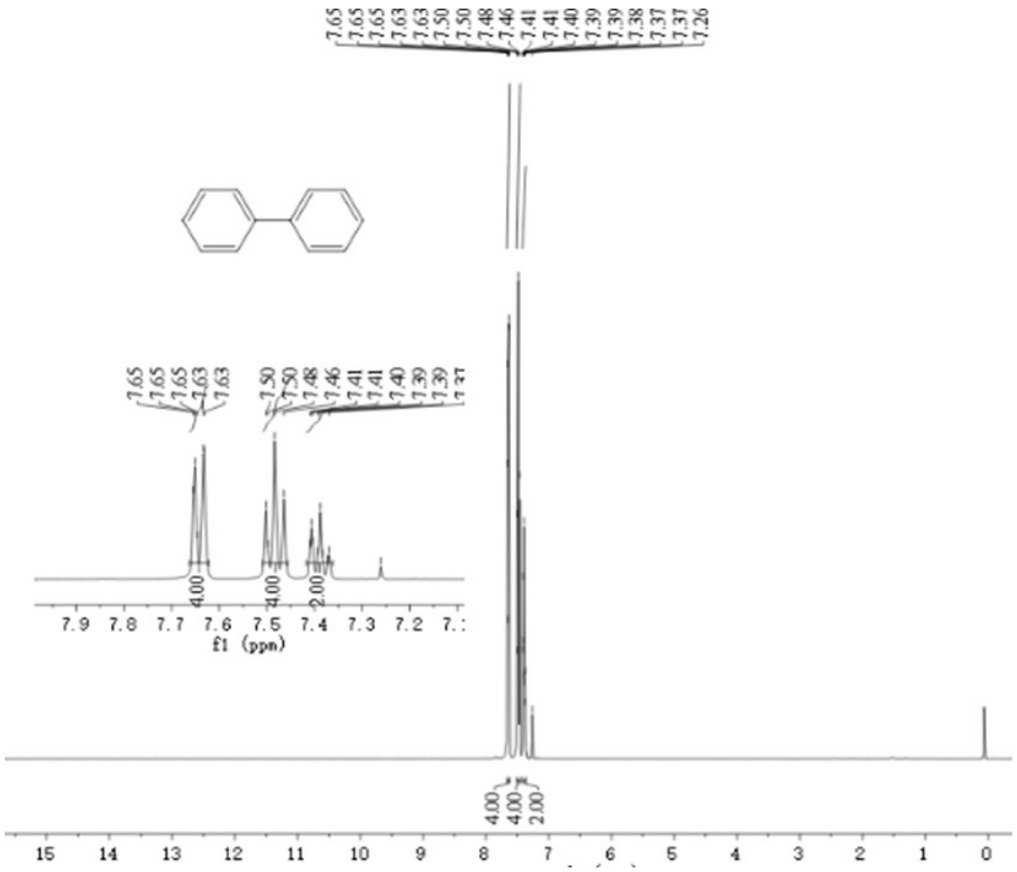


Figure S6. ^{1}H-NMR spectra of Biphenyl

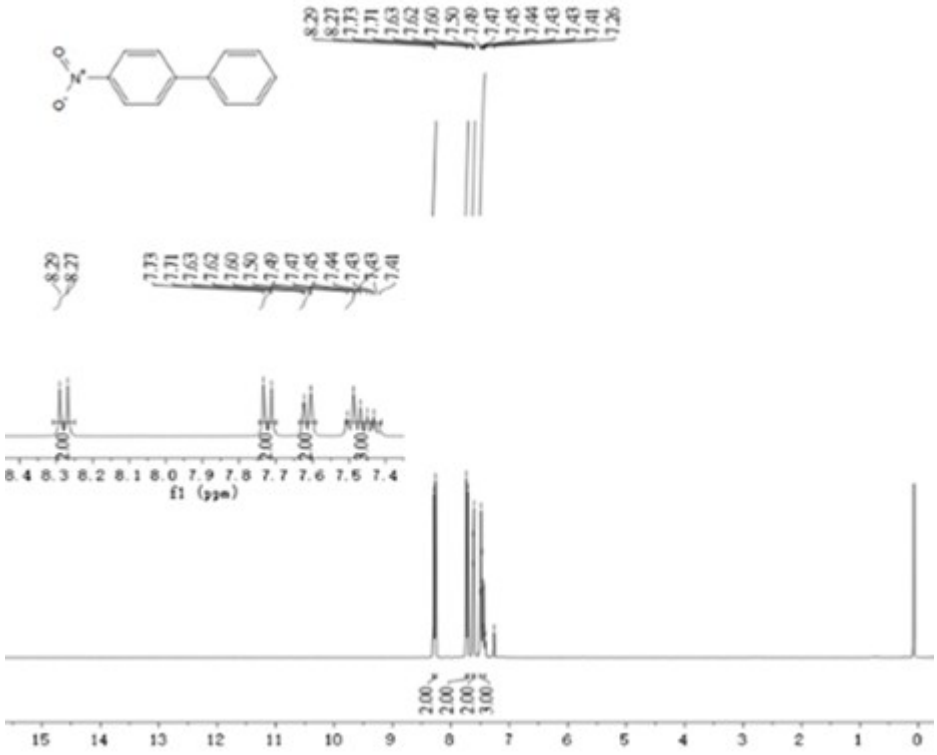


Figure S7. ^{1}H-NMR spectra of 4-nitro-1, 1'-biphenyl

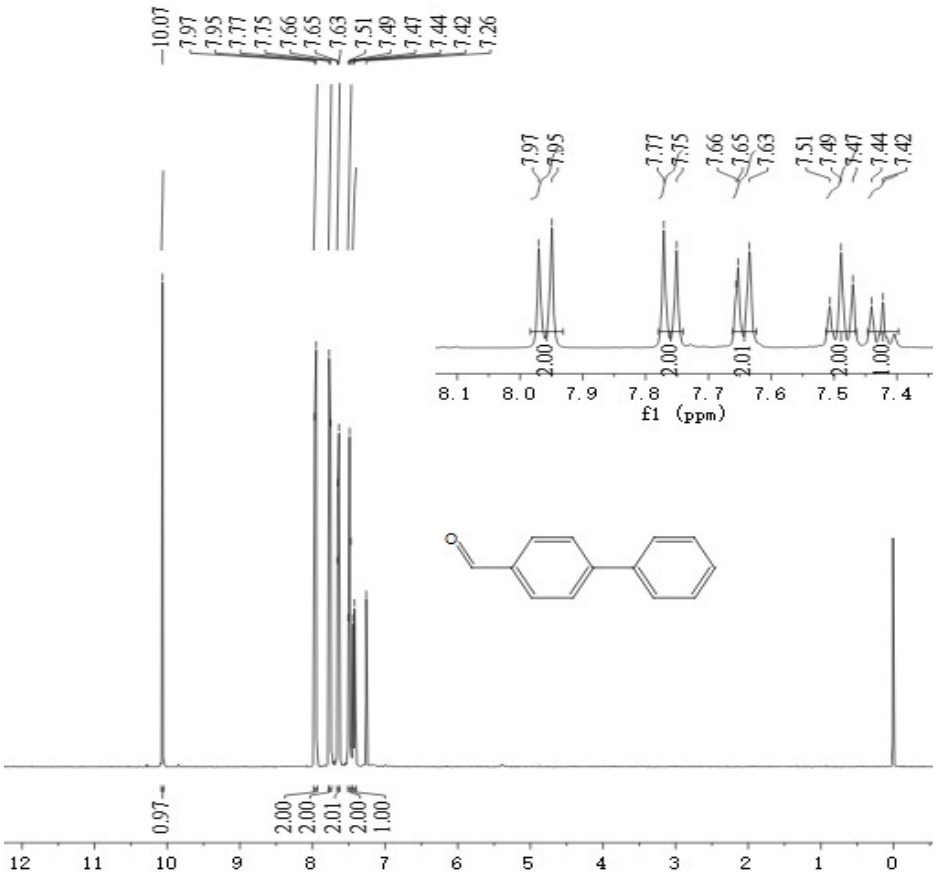


Figure S8. ^{1}H-NMR spectra of [1, 1'-biphenyl]-4-carbaldehyde

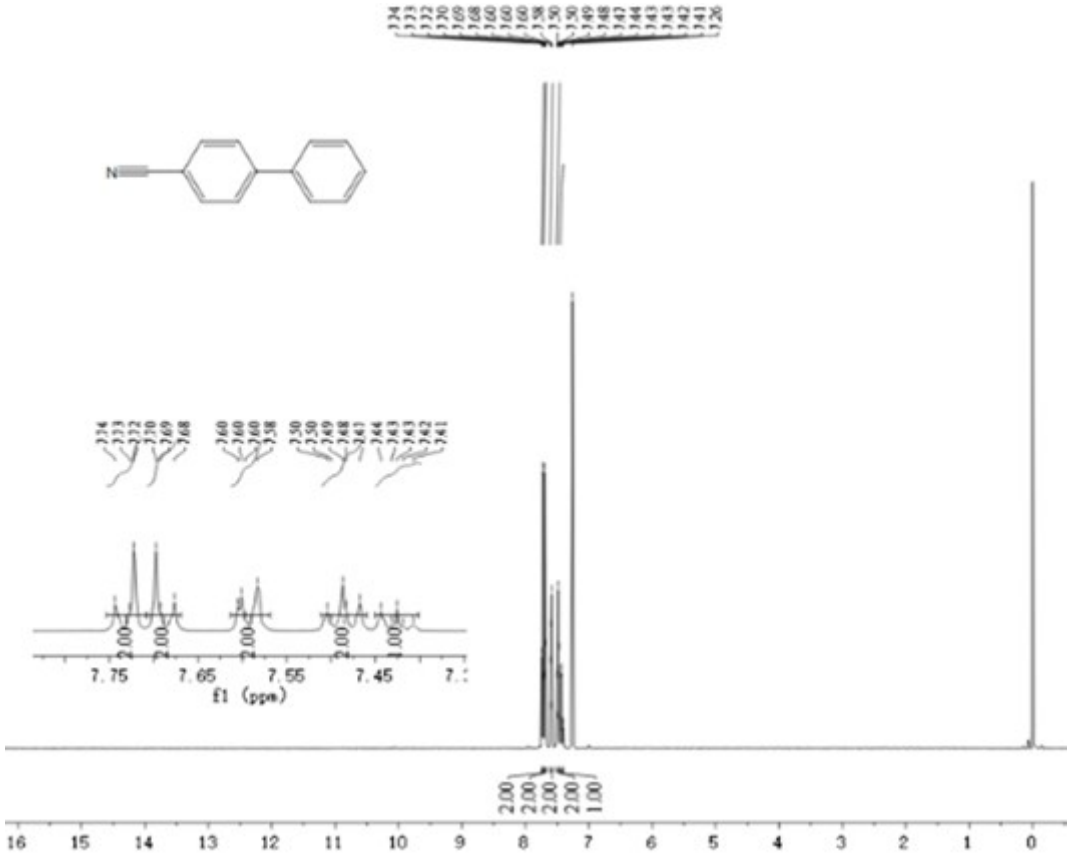


Figure S9. ^{1}H-NMR spectra of [1, 1'-biphenyl]-4-carbonitrile

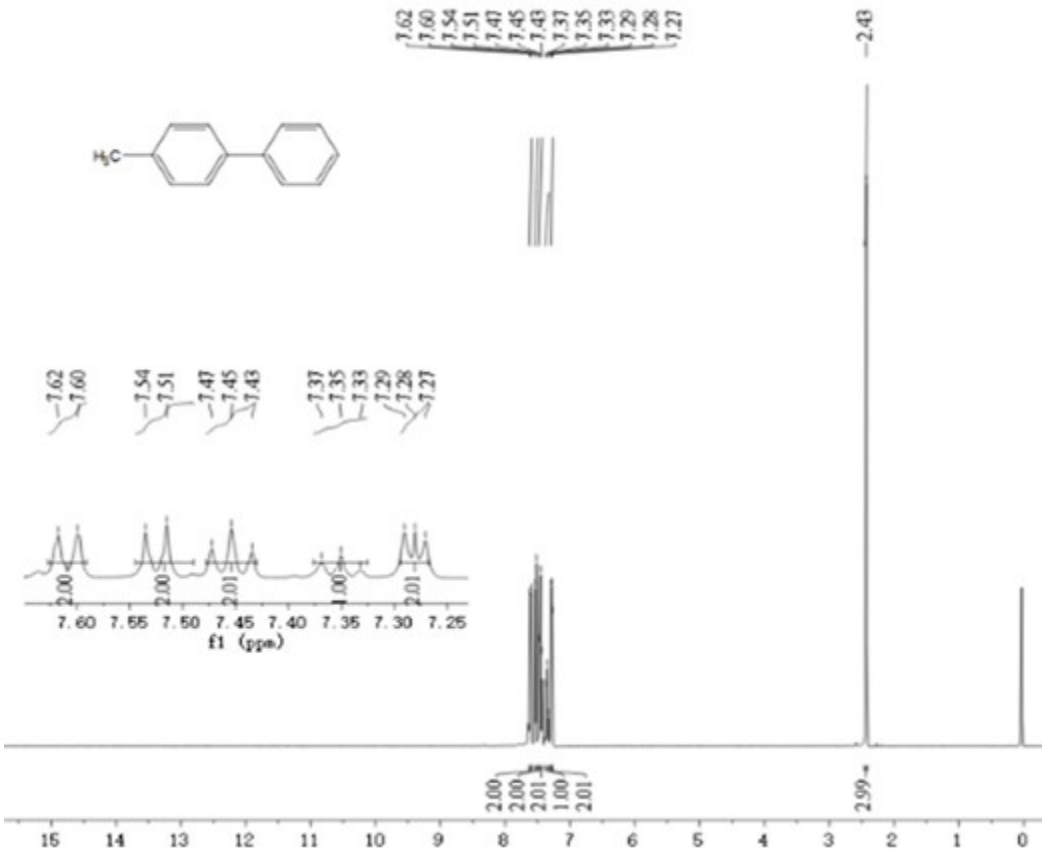


Figure S10. ^{1}H-NMR spectra of 4-methyl-1, 1'-biphenyl

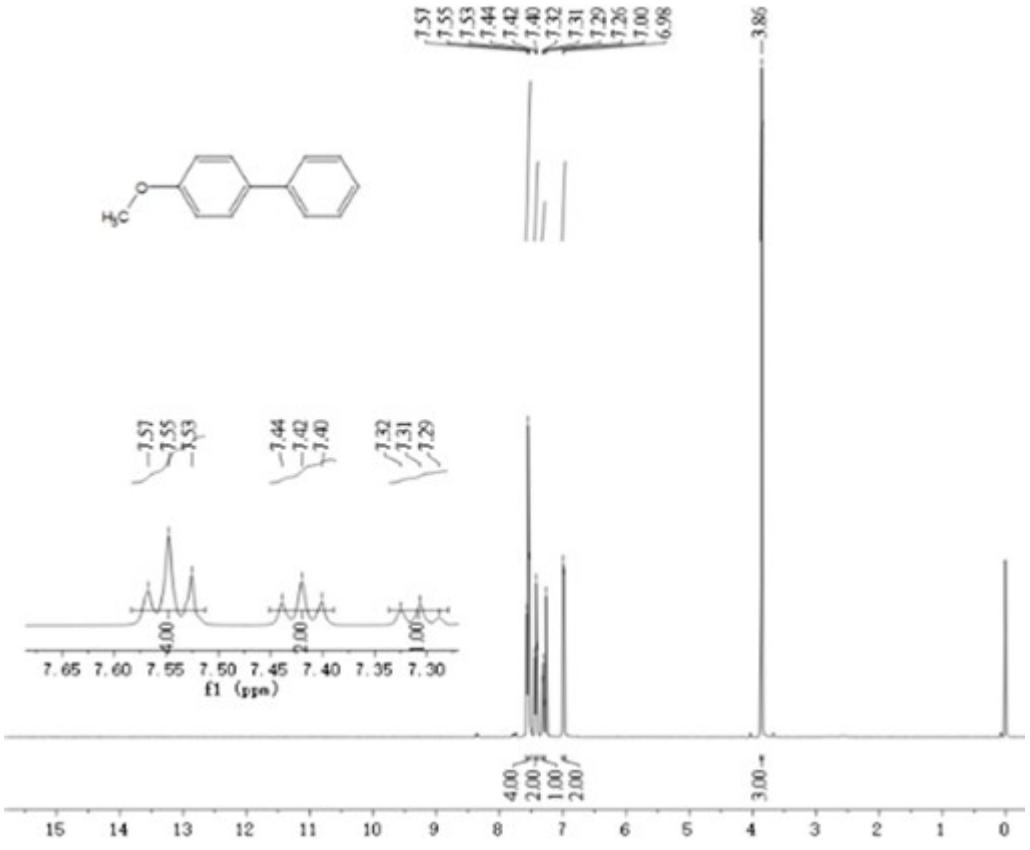


Figure S11. ^{1}H-NMR spectra of 4-methoxy-1, 1'-biphenyl

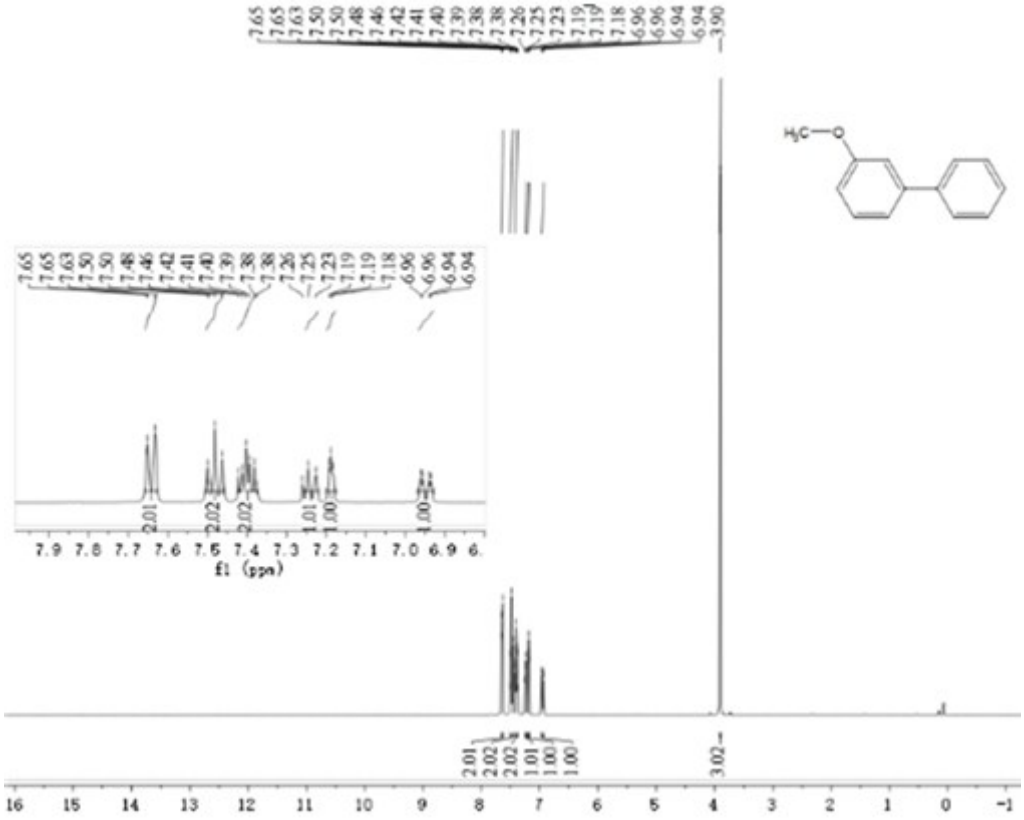


Figure S12. ^{1}H-NMR spectra of 3-methoxy-1, 1'-biphenyl

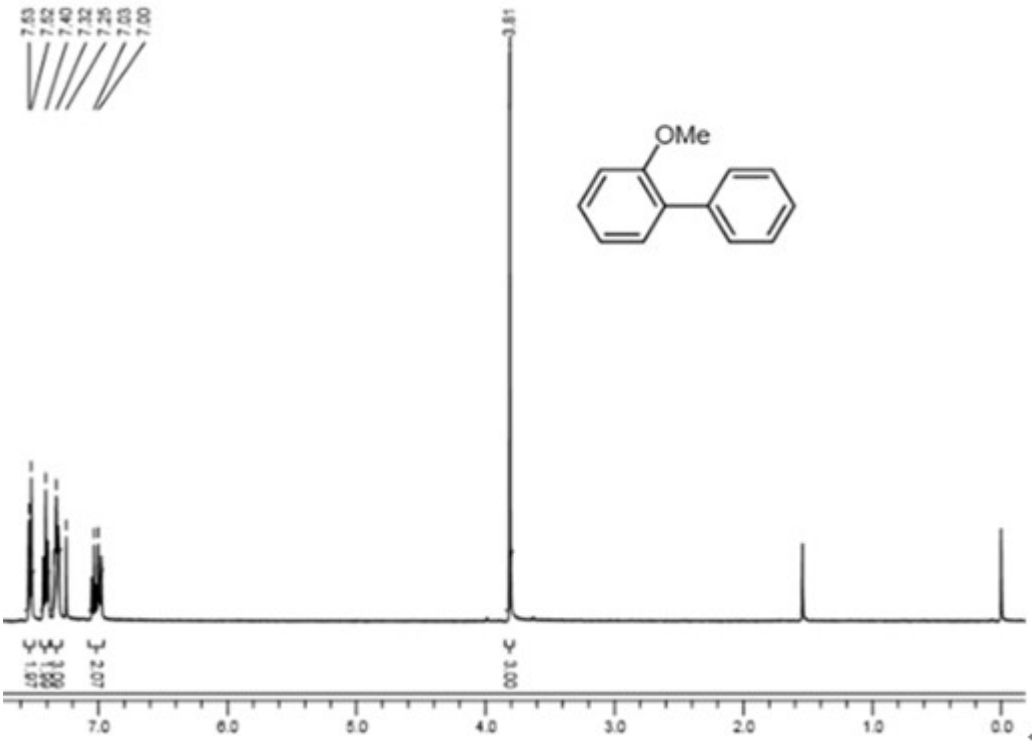


Figure S13. ^{1}H-NMR spectra of 2-methoxy-1, 1'-biphenyl

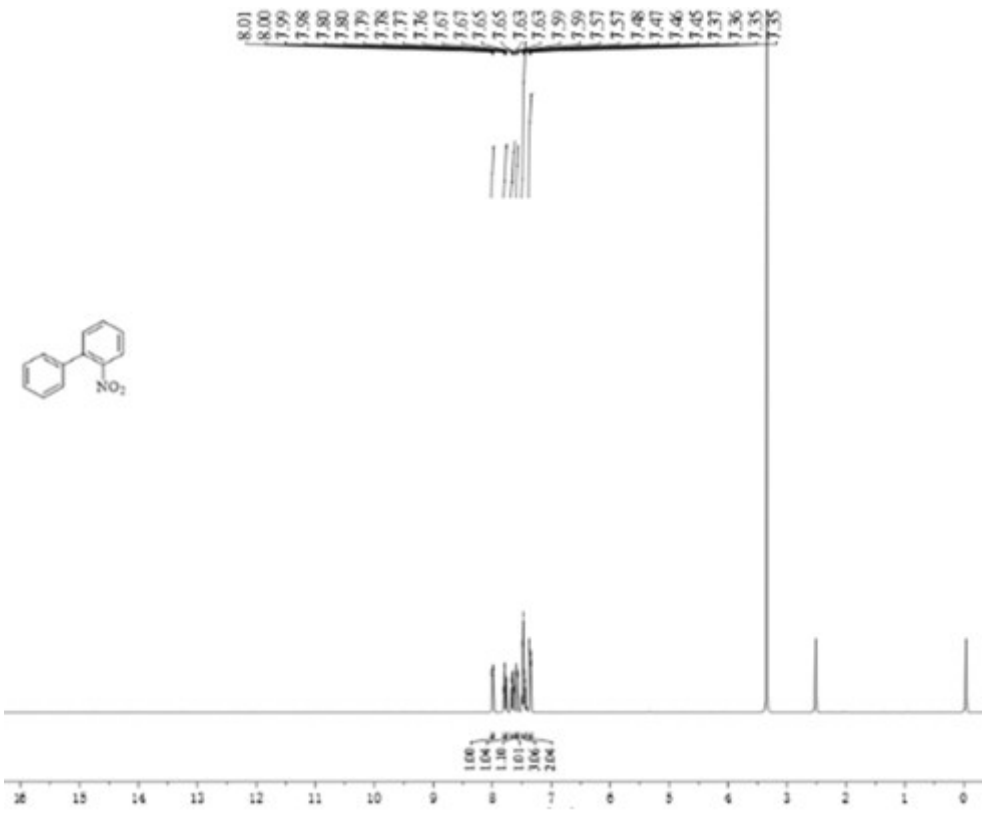


Figure S14. ^{1}H-NMR spectra of 2-nitro-1, 1'-biphenyl

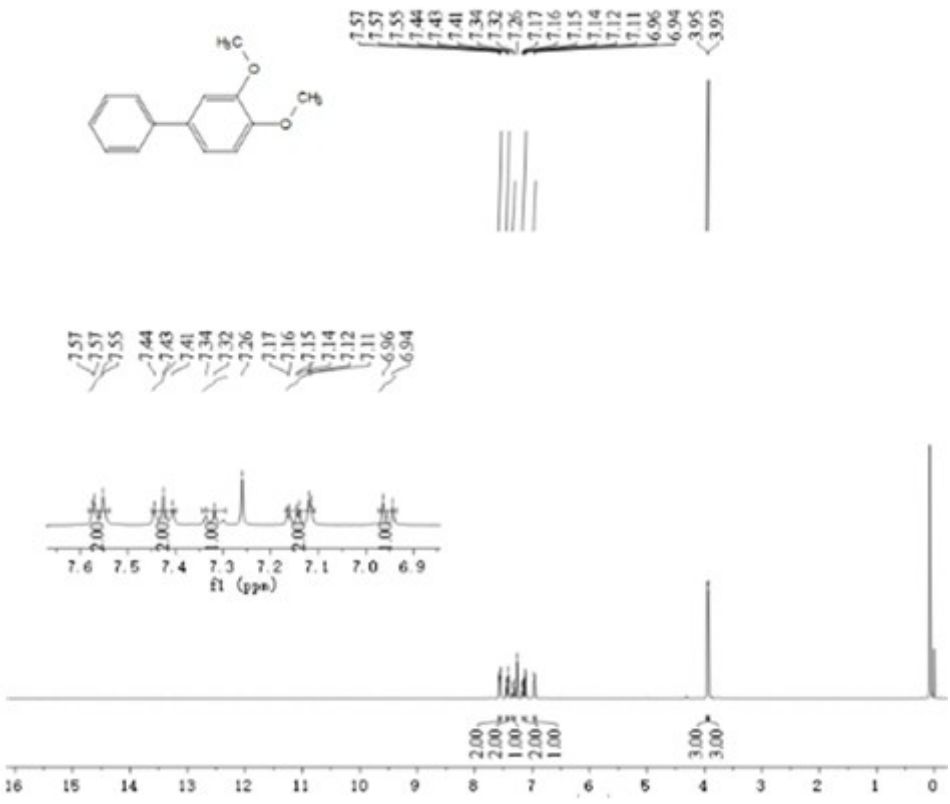


Figure S15. ^{1}H-NMR spectra of 3, 4-dimethoxy-1, 1'-biphenyl

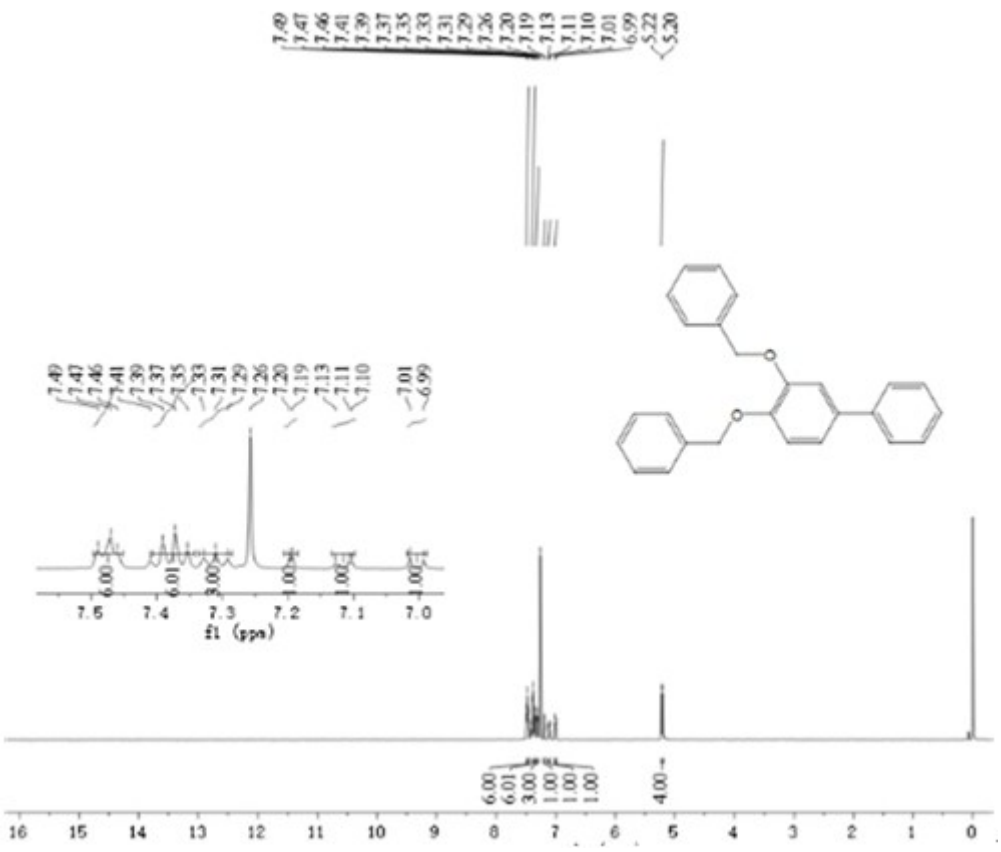


Figure S16. ^{1}H-NMR spectra of 3, 4-bis(benzyloxy)-1, 1-'biphenyl

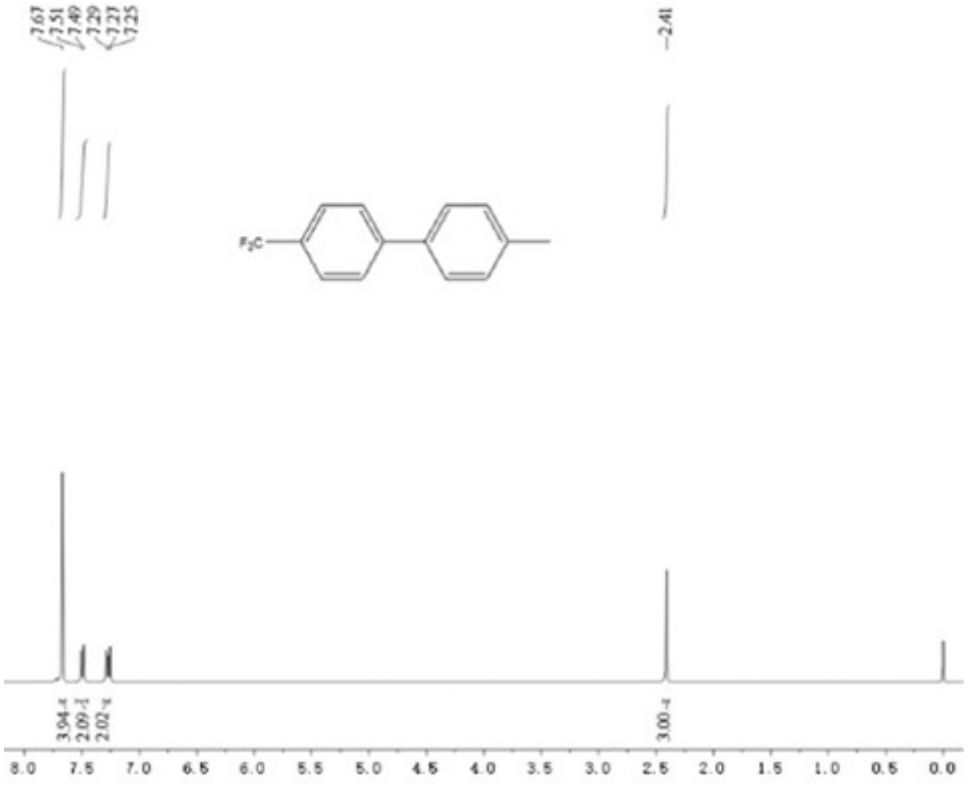


Figure S17. ^{1}H-NMR spectra of 4-methyl-4'-(trifluoromethyl)-1,1'-biphenyl

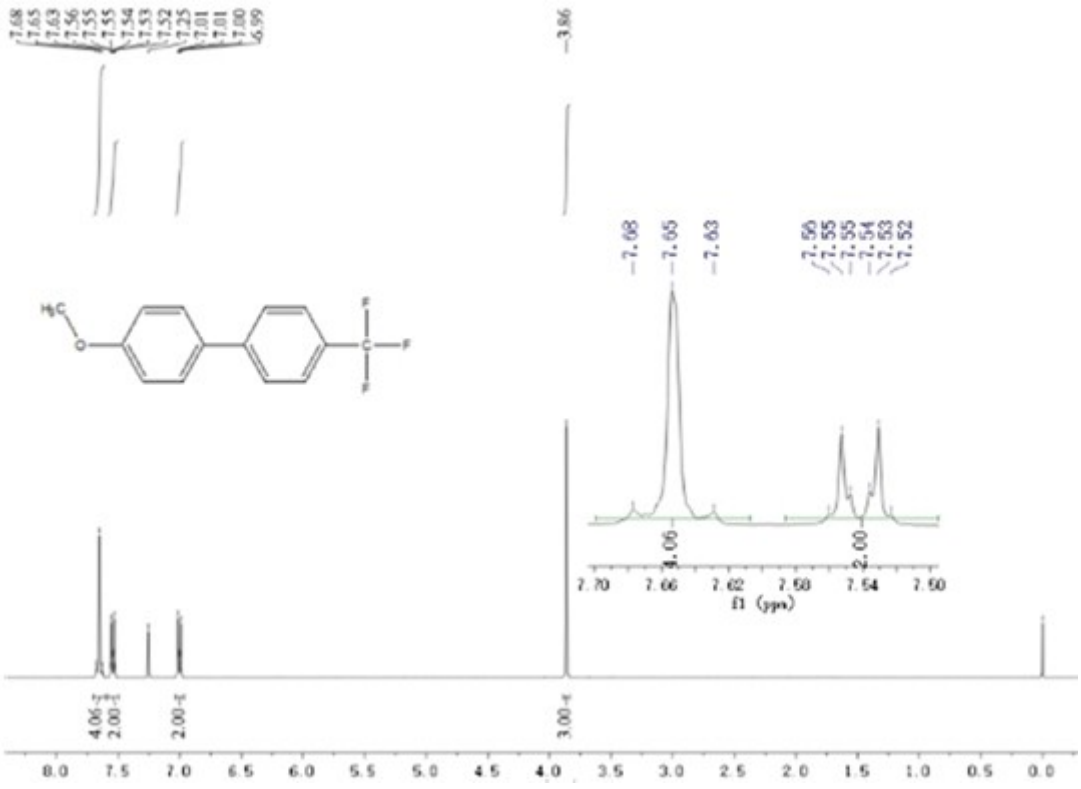


Figure S18. ^{1}H-NMR spectra of 4-methoxy-4'-(trifluoromethyl)-1,1'-biphenyl

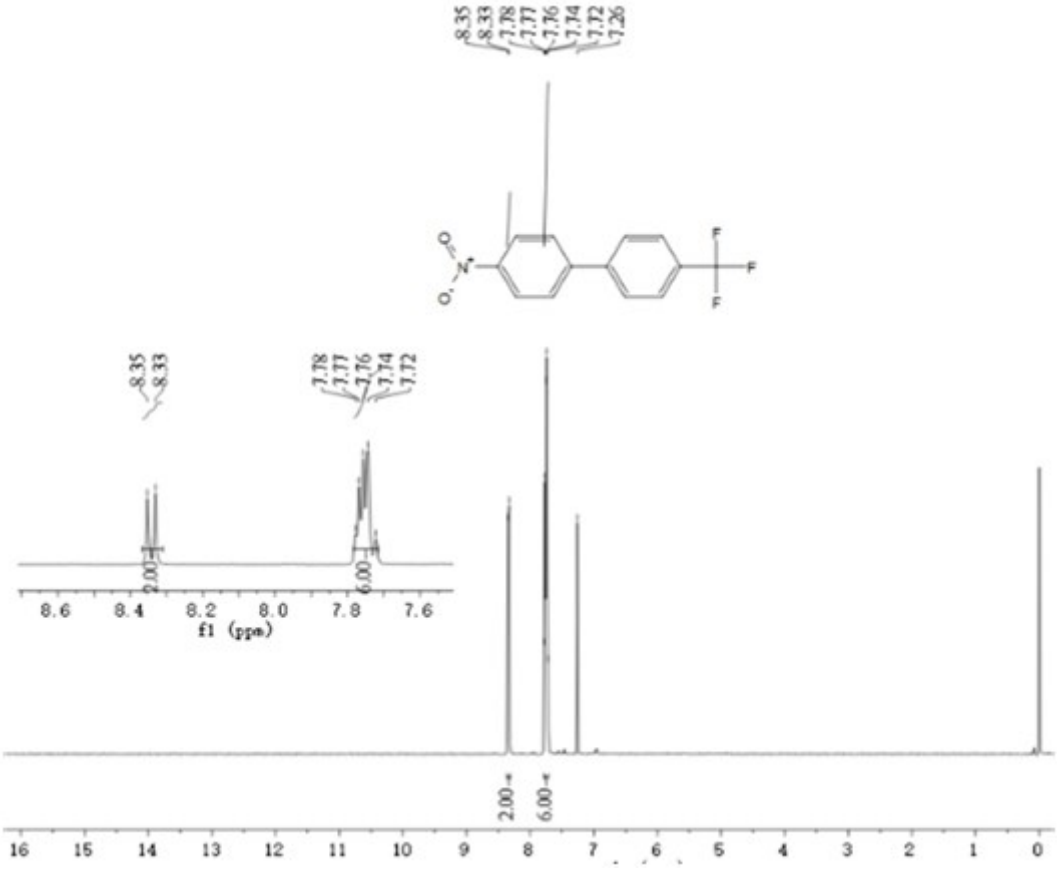


Figure S19. ^{1}H-NMR spectra of 4-nitro-4'-(trifluoromethyl)-1,1'-biphenyl

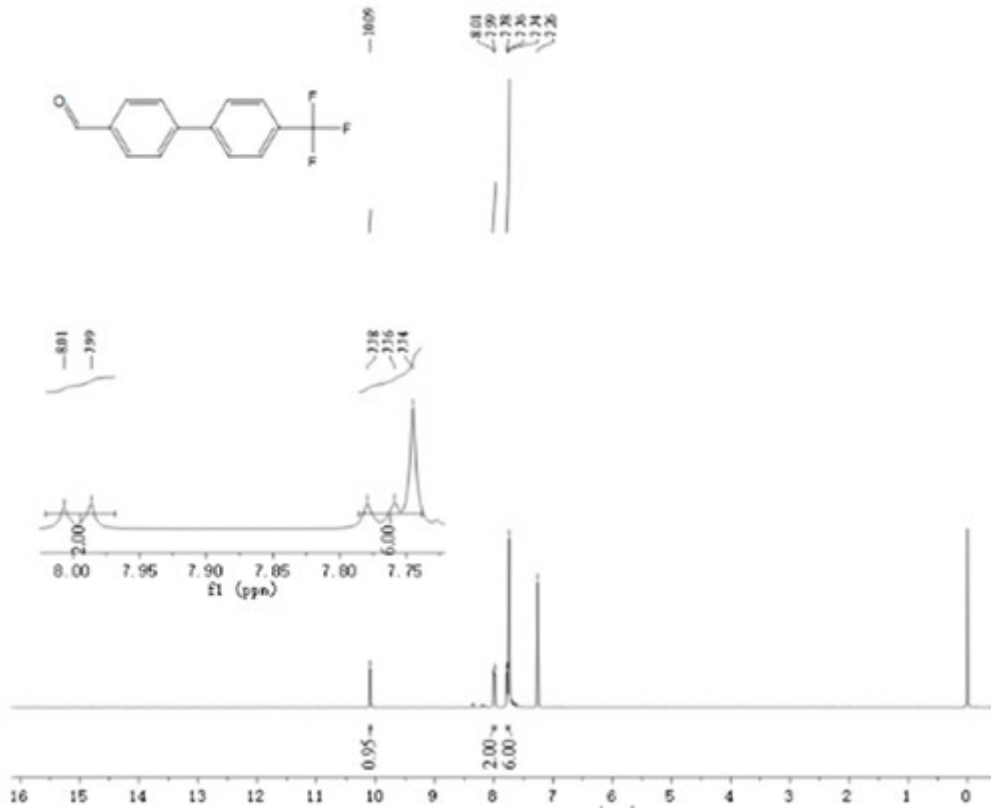


Figure S20. ^{1}H-NMR spectra of 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carbaldehyde

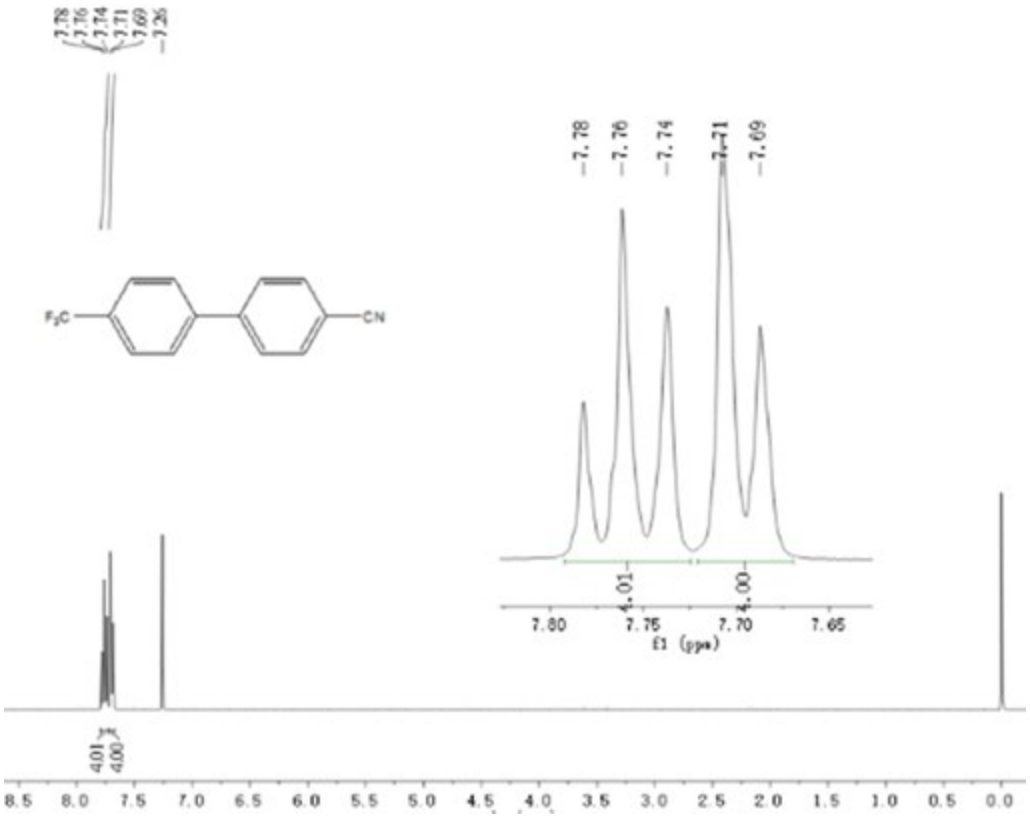


Figure S21. ^{1}H-NMR spectra of 4'-(trifluoromethyl)-[1,1'-biphenyl]-4-carbonitrile

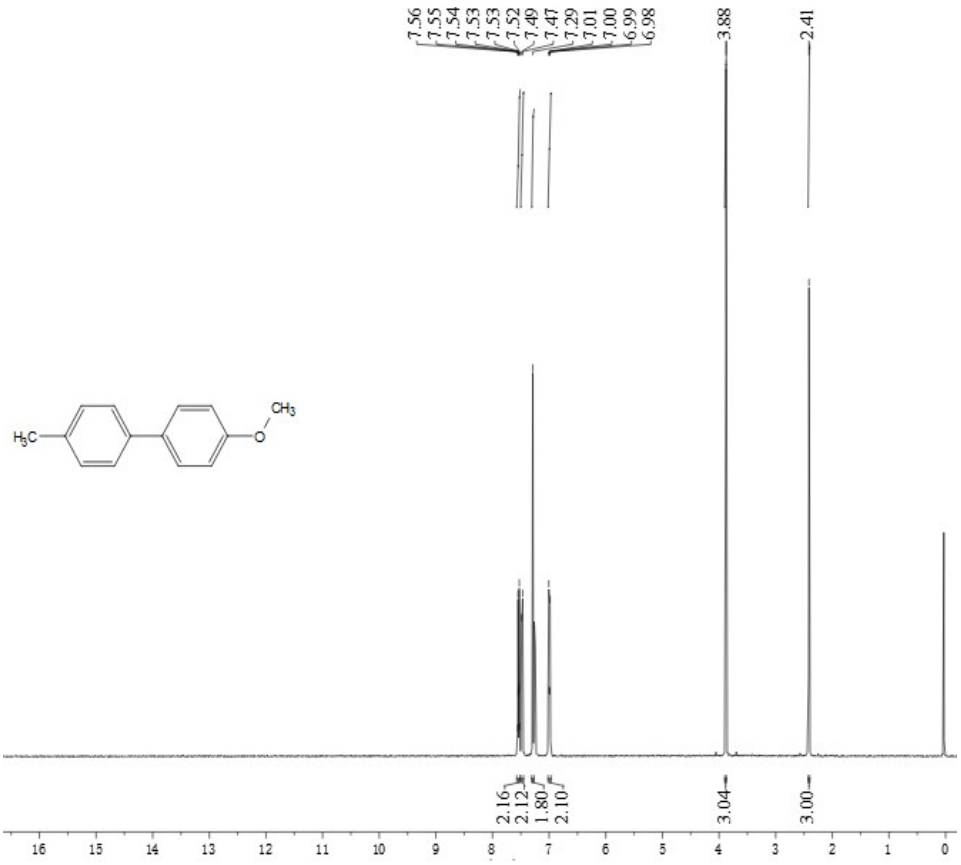


Figure S22. ^{1}H-NMR spectra of 4-methoxy-4'-methyl-1,1'-biphenyl

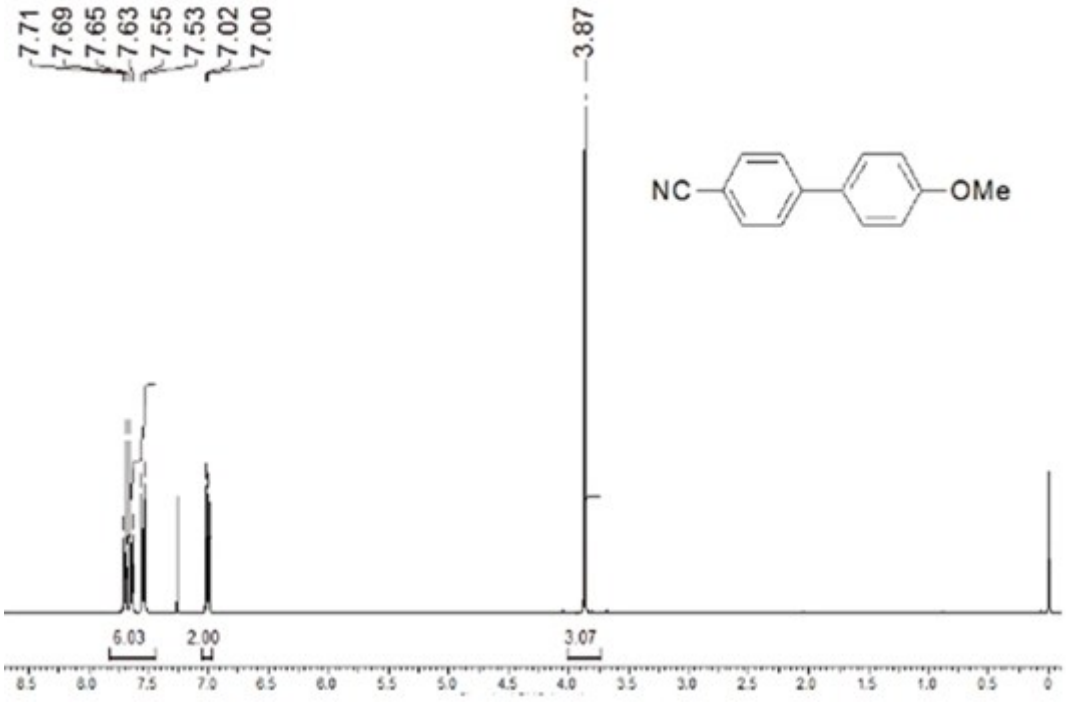


Figure S23. ^{1}H-NMR spectra of 4'-methoxy-[1,1'-biphenyl]-4-carbonitrile

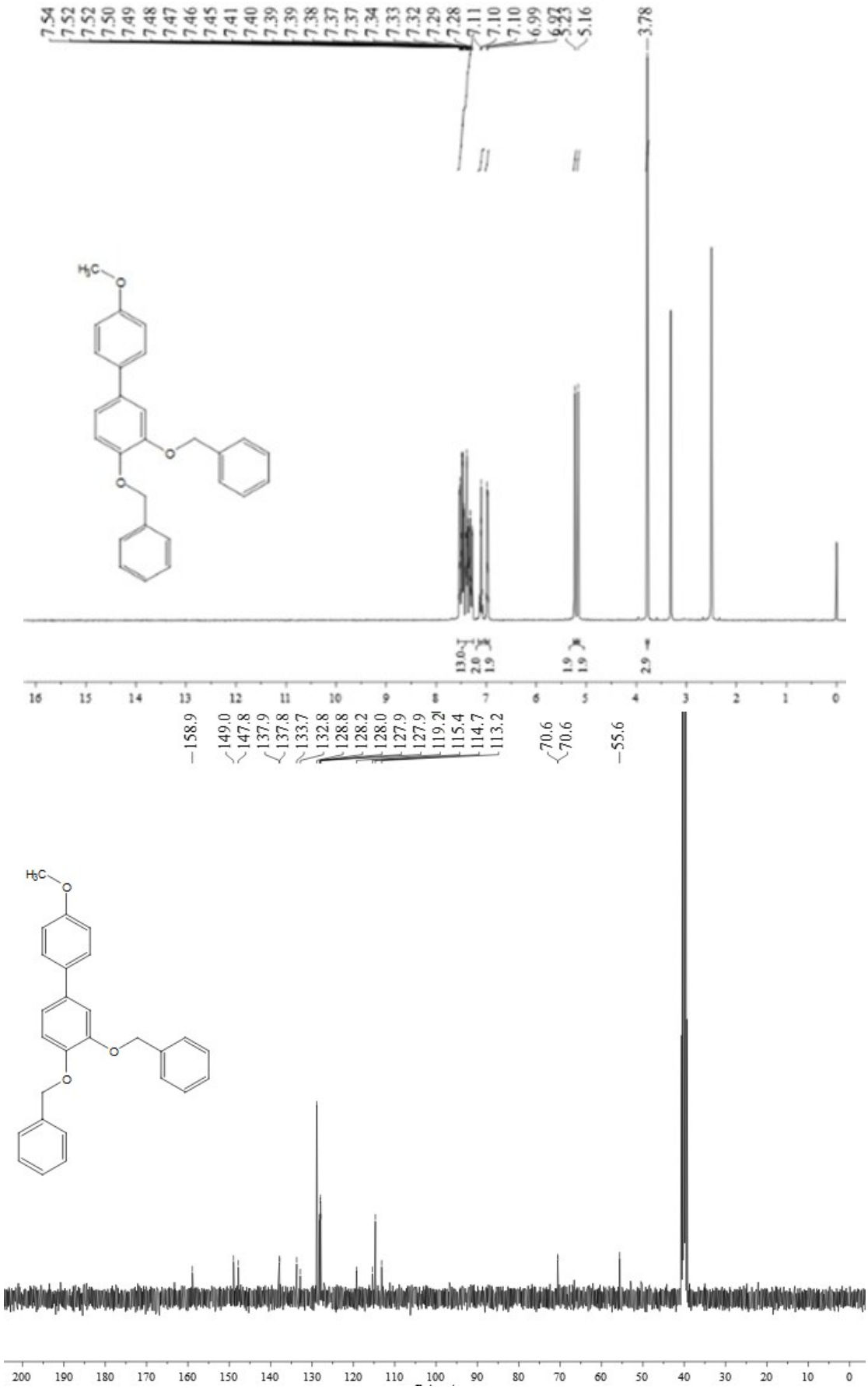


Figure S24. ^{1}H and ^{13}C-NMR spectra of 3, 4-bis(benzyloxy)-4-methoxy-1,1'-biphenyl

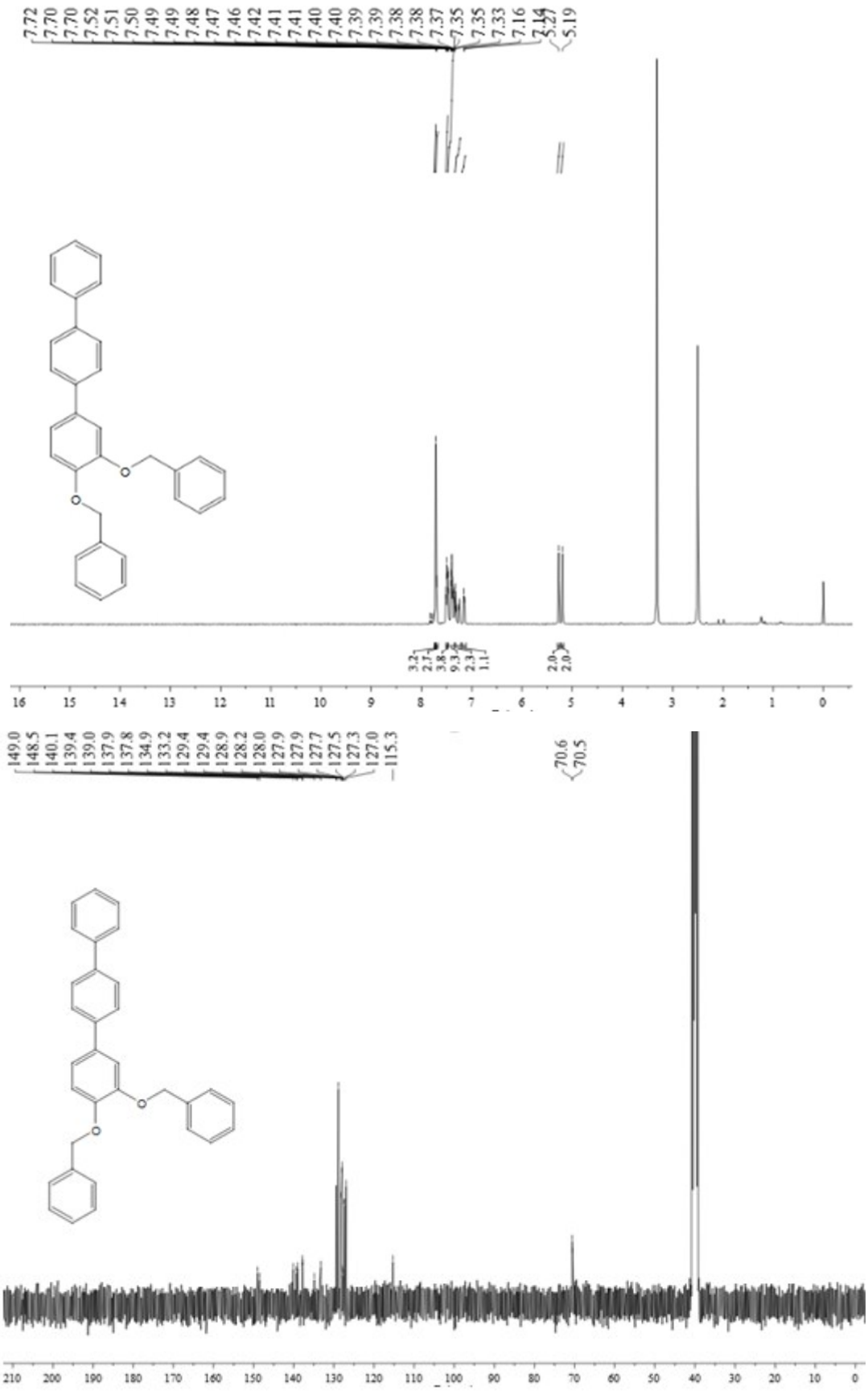


Figure S25. ^{1}H and ^{13}C-NMR spectra of 3, 4-bis(benzyloxy)terphenyl

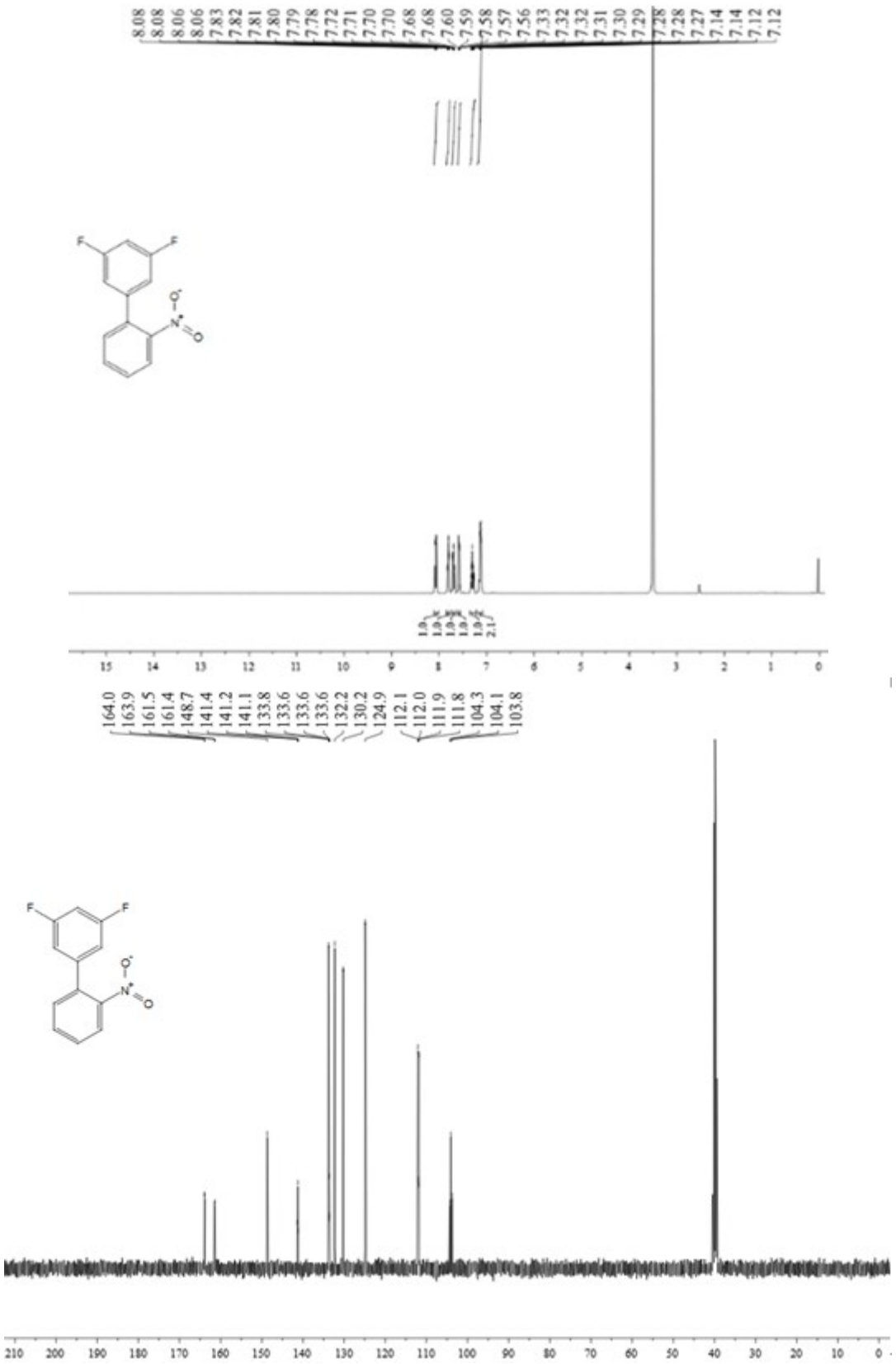


Figure S26. ^{1}H and ^{13}C-NMR spectra of 3', 5'-Difluoro-2-nitro-1, 1'-biphenyl

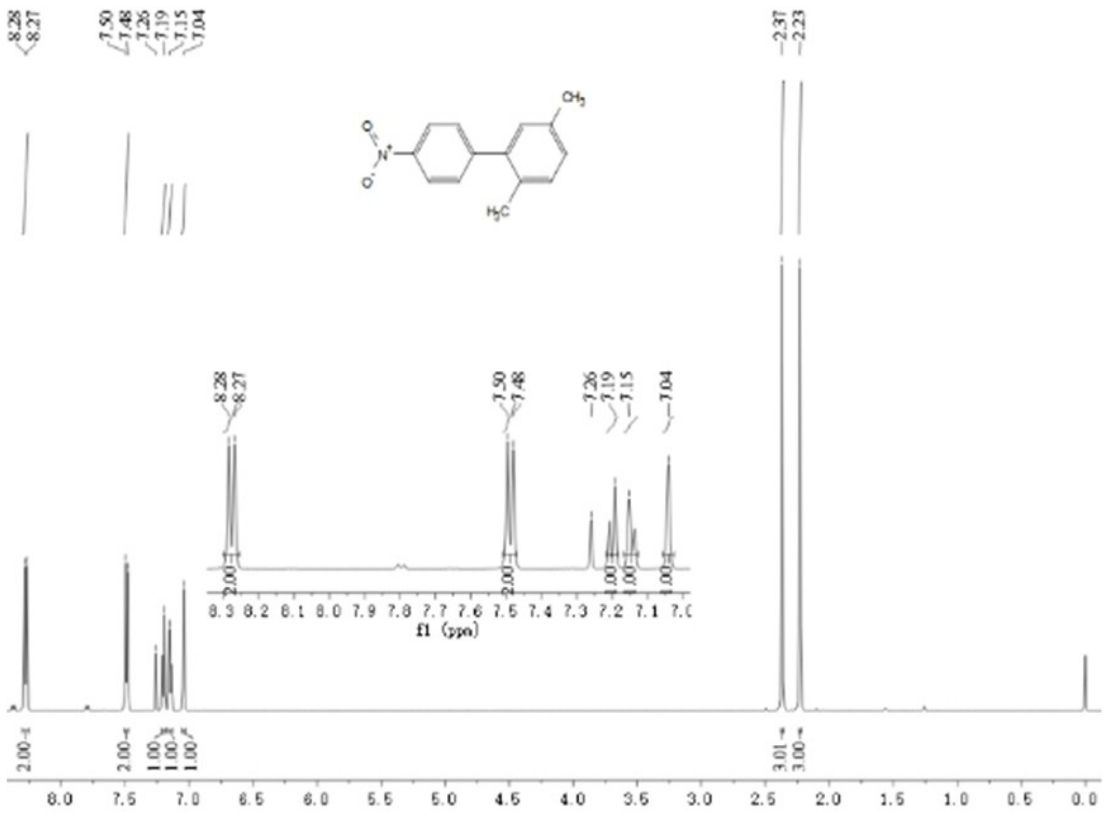


Figure S27. ^{1}H-NMR spectra of 4-nitro-2', 5'-dimethyl-[1,1'-biphenyl]

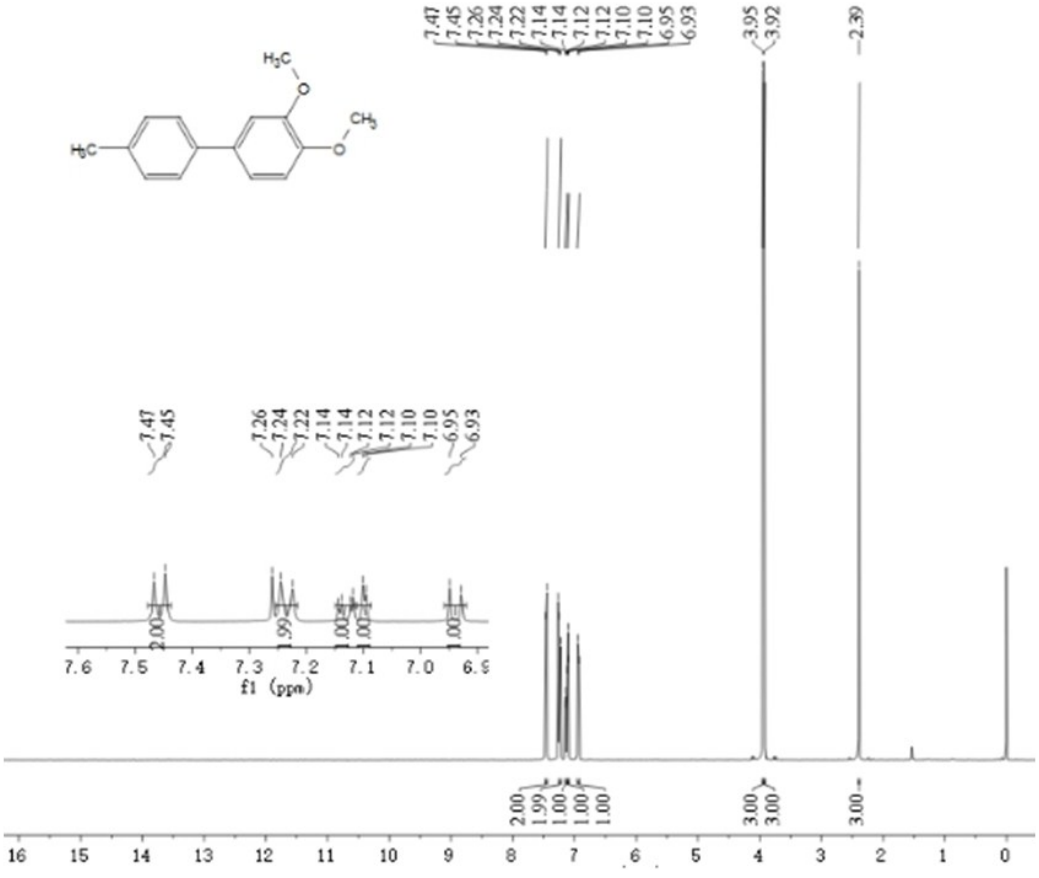


Figure S28. ^{1}H-NMR spectra of 4-methyl-3', 4'-dimethoxy-1, 1'-biphenyl

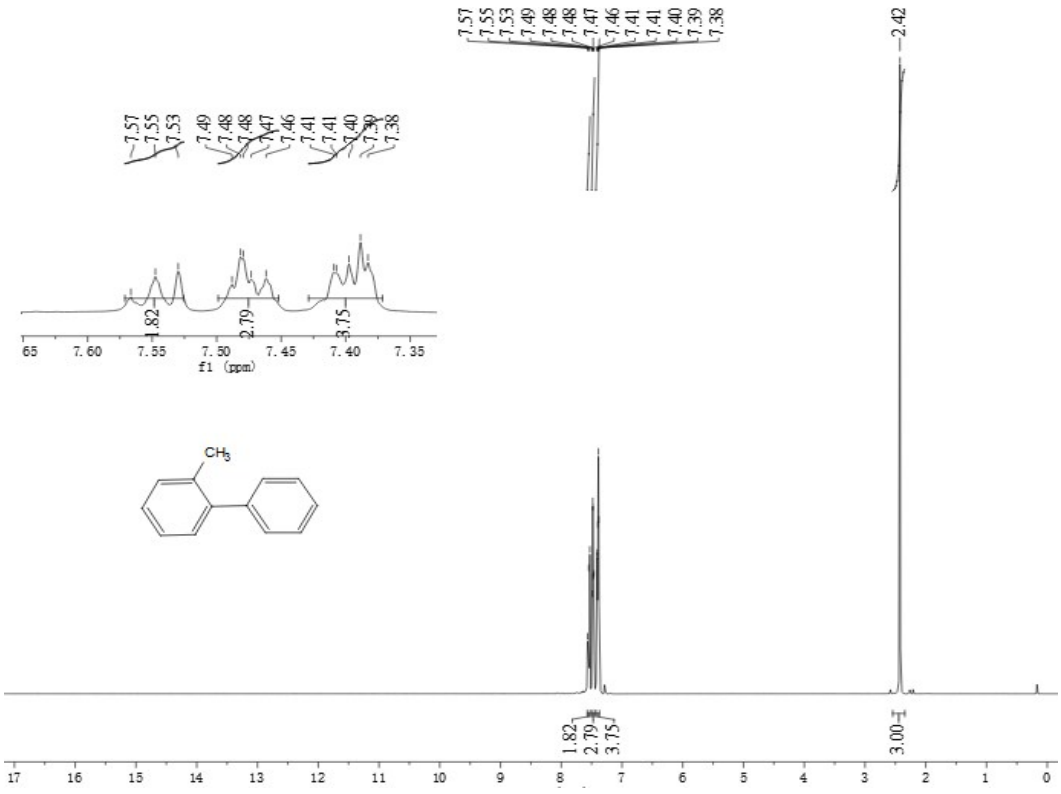


Figure S29. ^{1}H-NMR spectra of 2'-methyl-1,1'-biphenyl

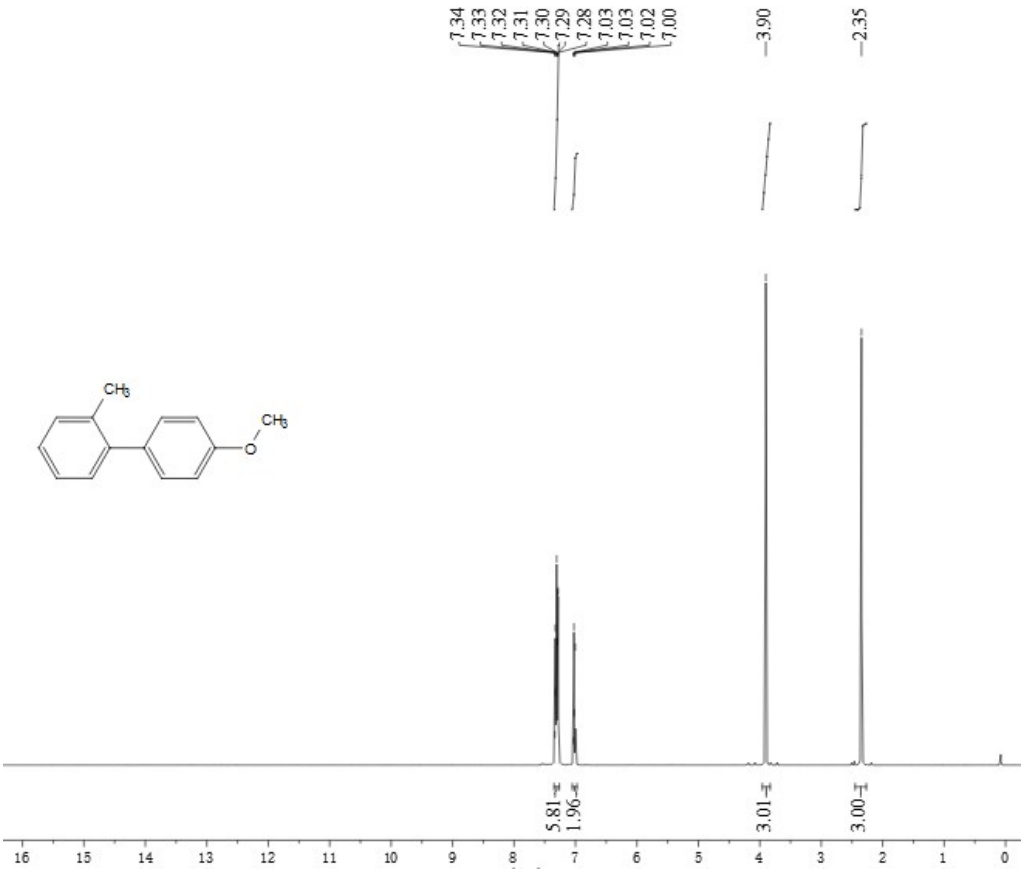


Figure S30. ^{1}H-NMR spectra of 4-methoxyl-2'-methyl-1,1'-biphenyl

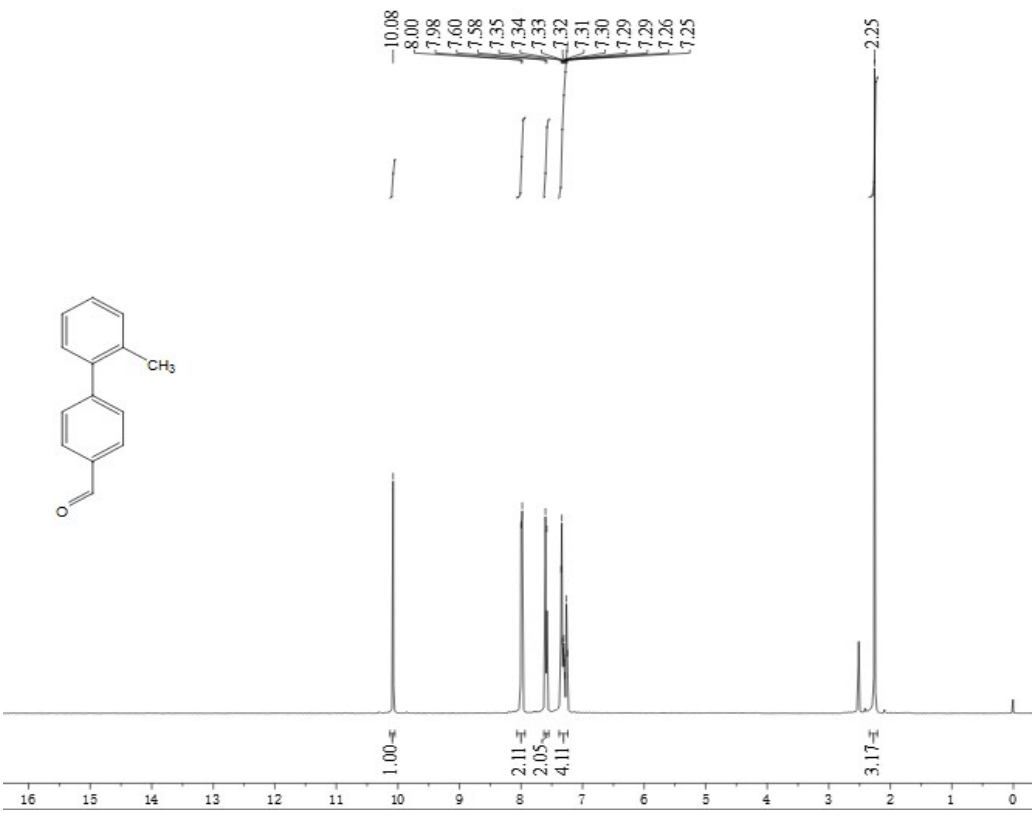


Figure S31. ^{1}H-NMR spectra of 4-formyl-2'-methyl-1,1'-biphenyl

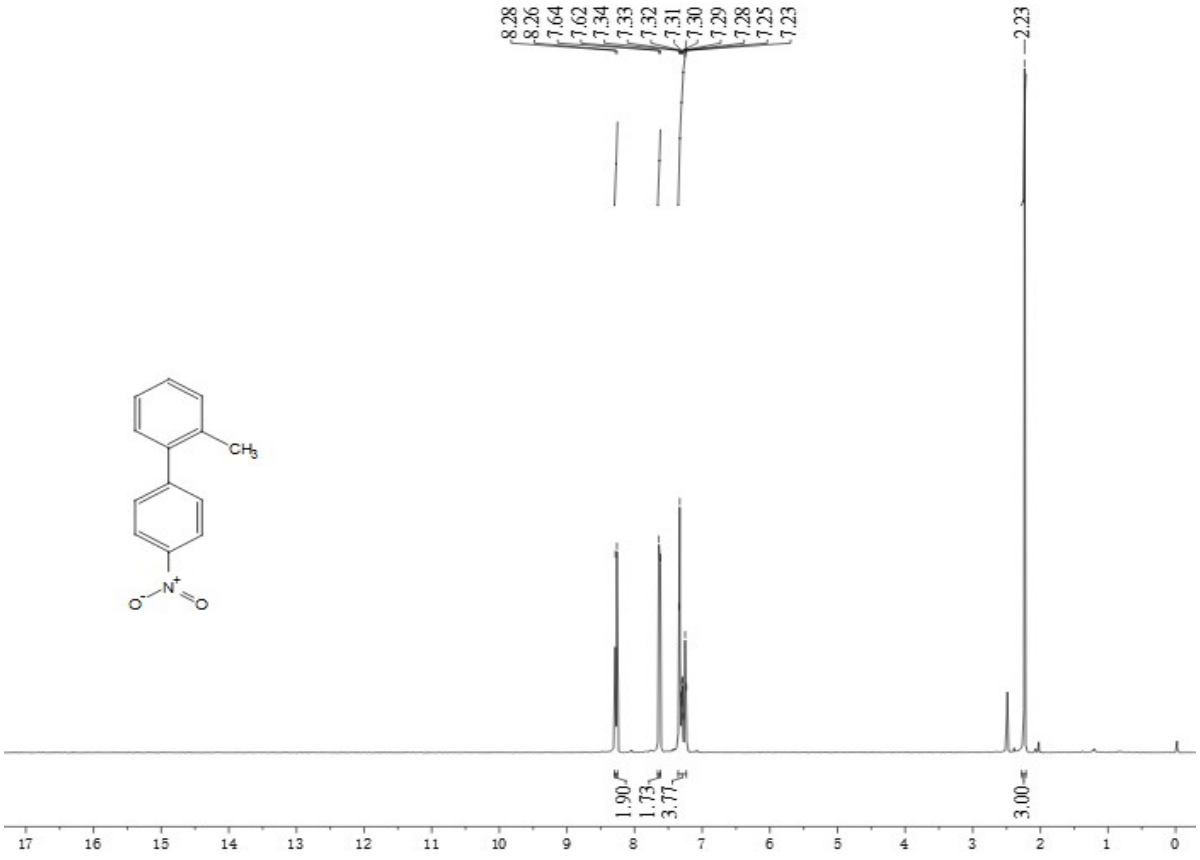


Figure S32. ^{1}H-NMR spectra of 4-nitro-2'-methyl-1,1'-biphenyl

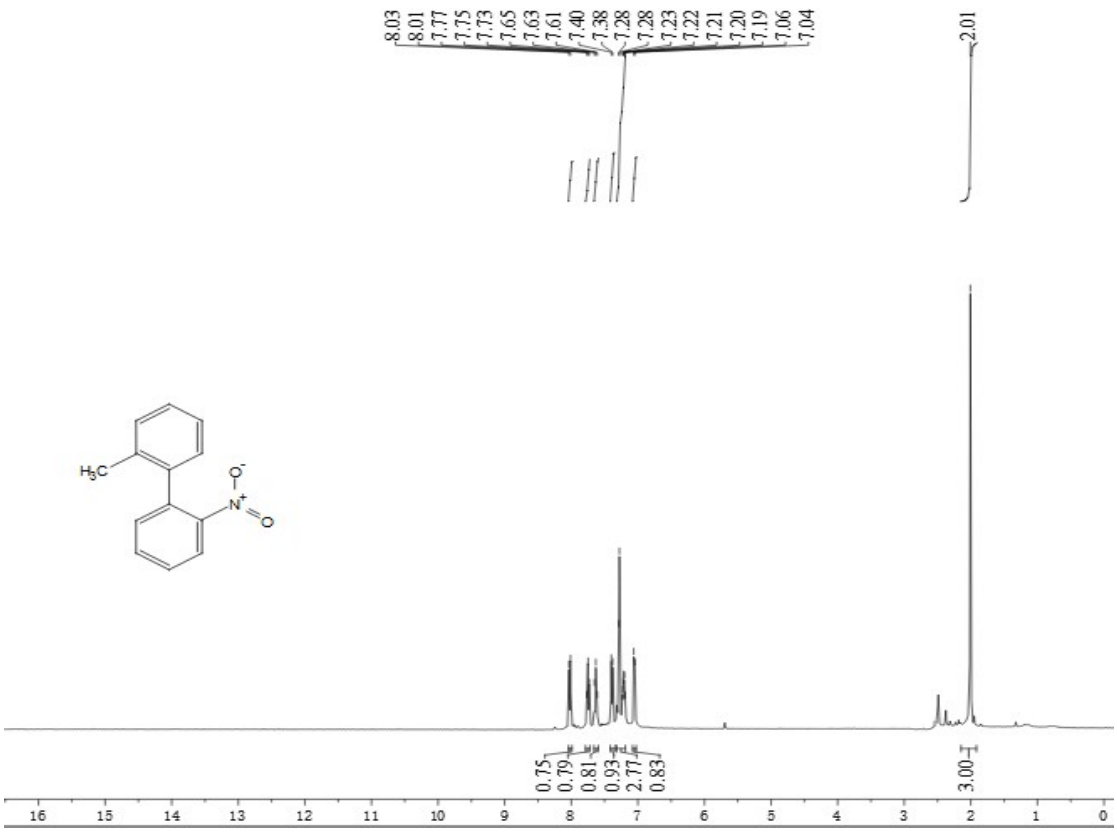


Figure S33. ^{1}H-NMR spectra of 2-nitro-2'-methyl-1,1'-biphenyl

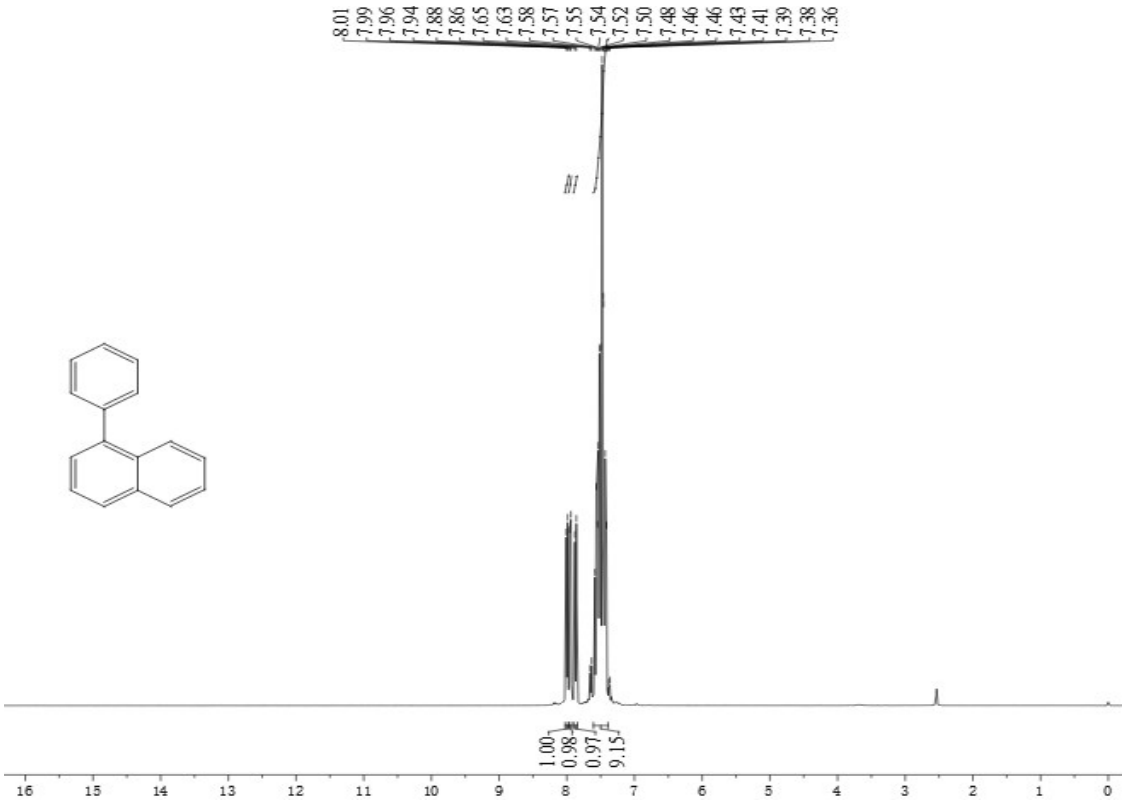


Figure S34. ^{1}H-NMR spectra of 1-phenyl-1'-naphthalene

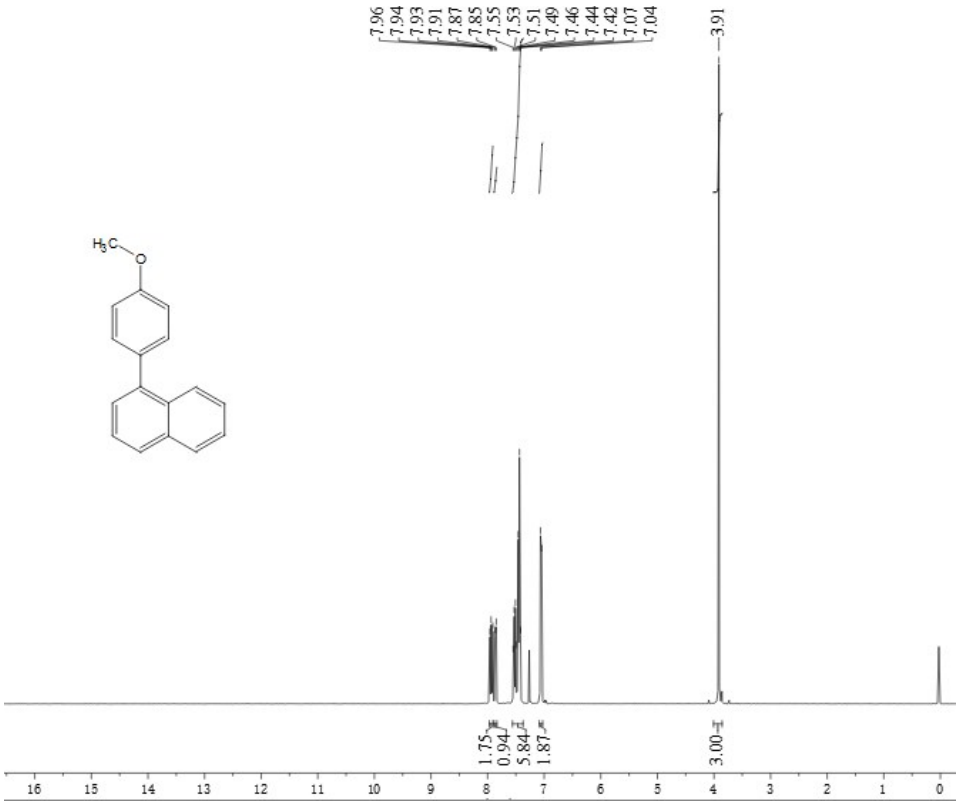


Figure S35. ^{1}H-NMR spectra of 4-methoxy-1-phenyl-1'-naphthalene

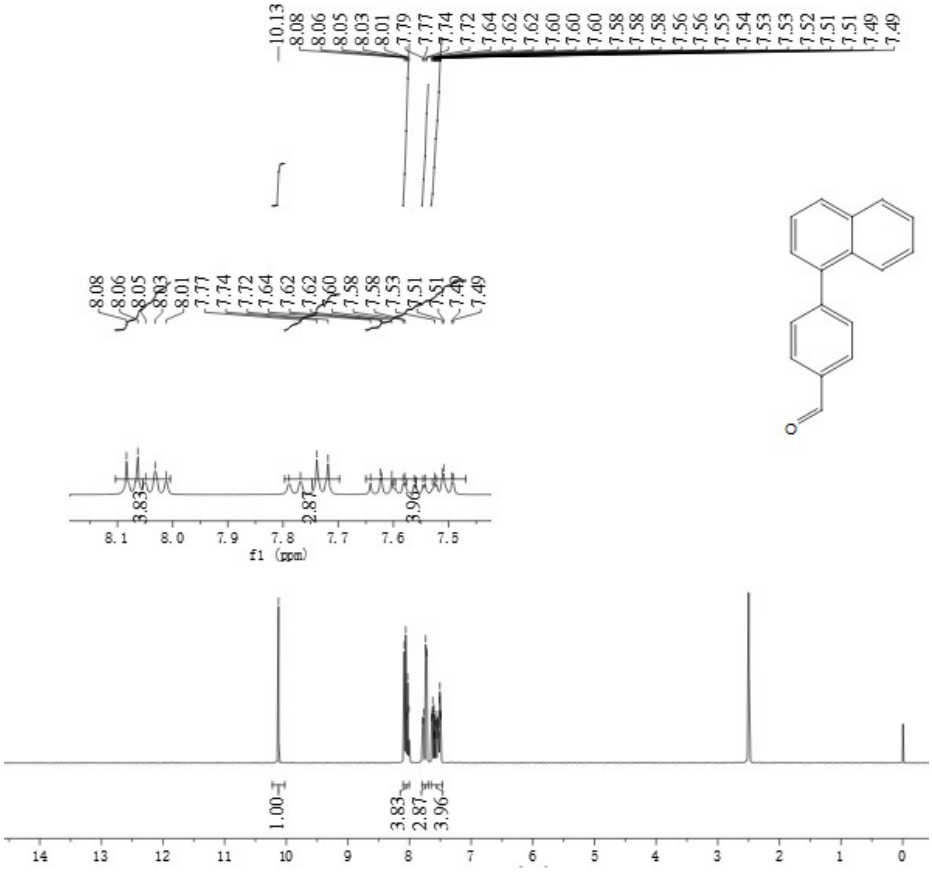


Figure S36. ^{1}H-NMR spectra of 4-(naphthalen-1-yl)benzaldehyde

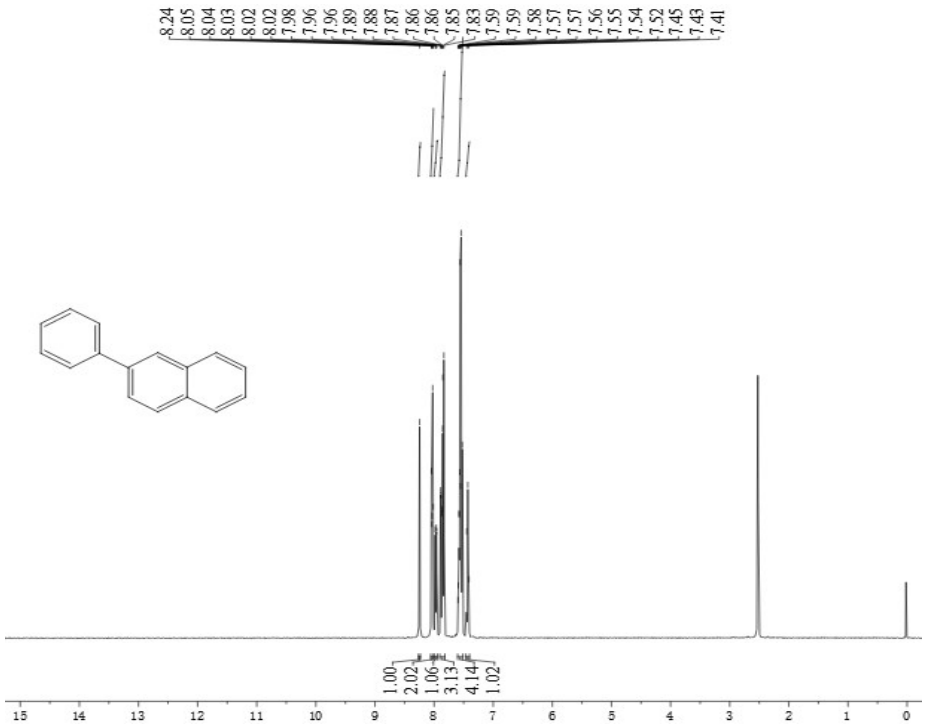
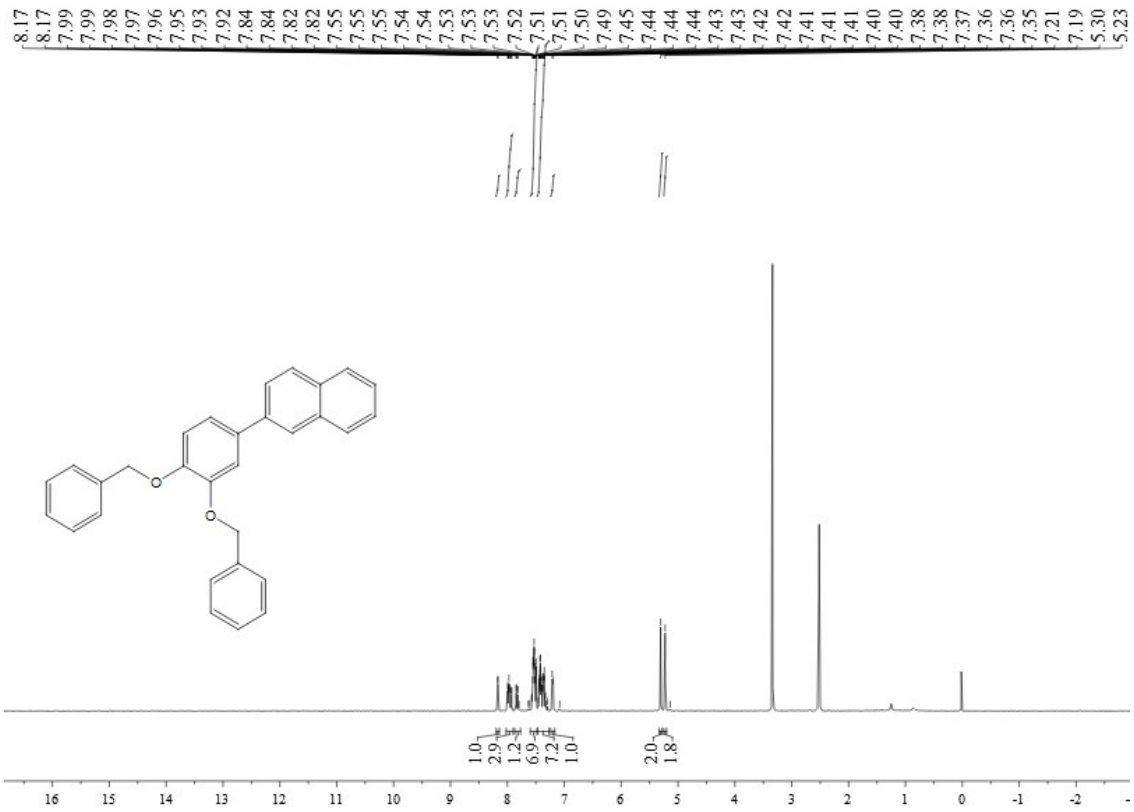


Figure S37. ^{1}H-NMR spectra of 1-phenyl-2'-naphthalene



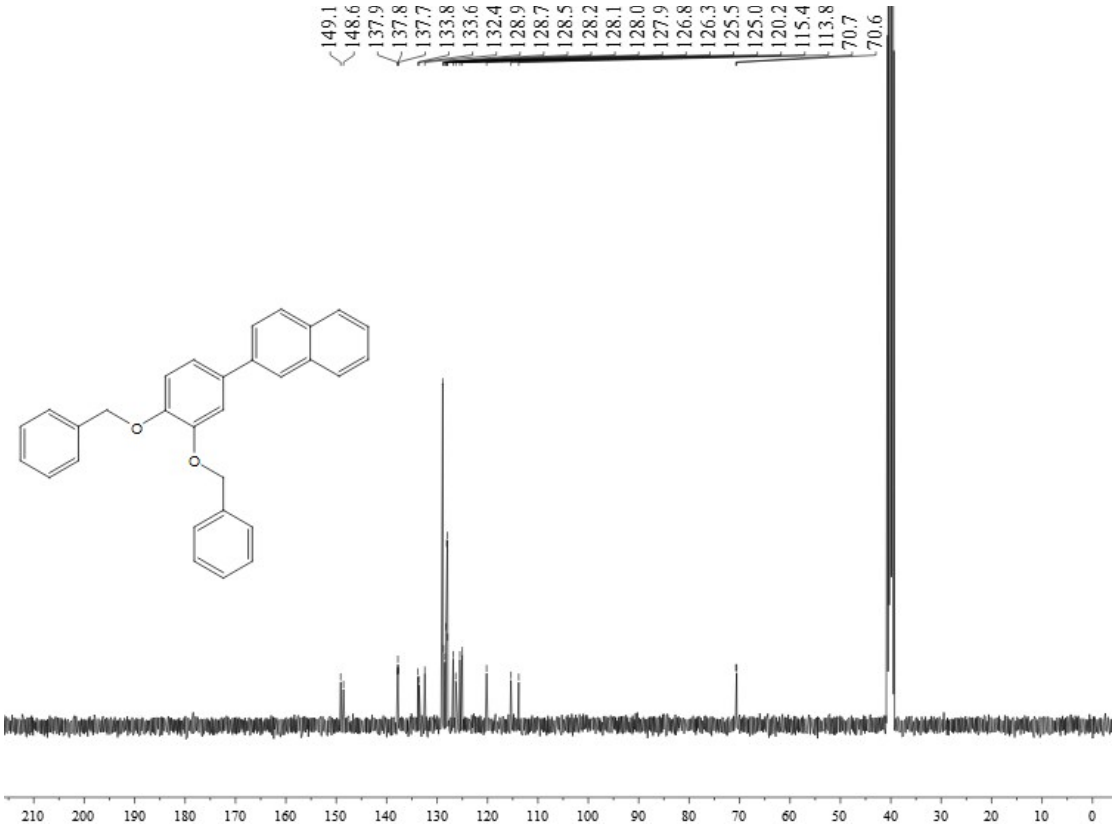
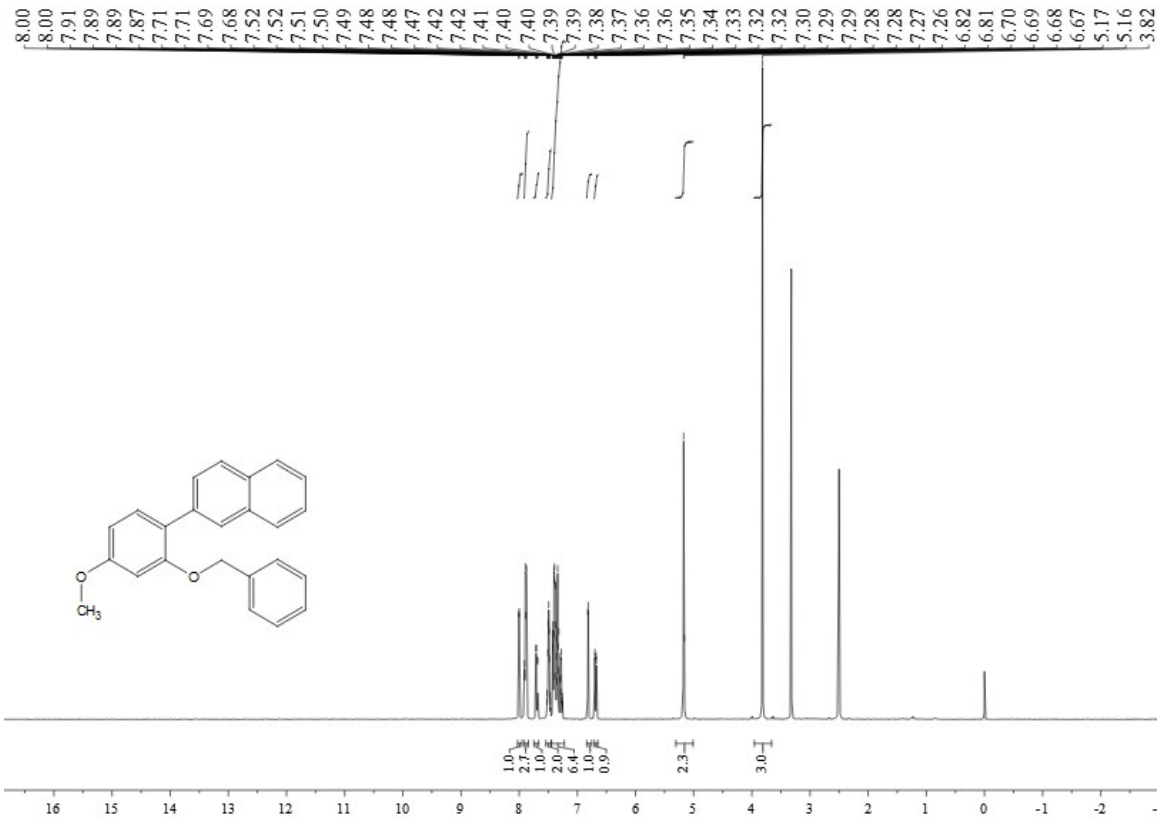


Figure S38. ^{1}H and ^{13}C-NMR spectra of 3, 4-bis(benzyloxy)-1-phenyl-2'-naphthalene



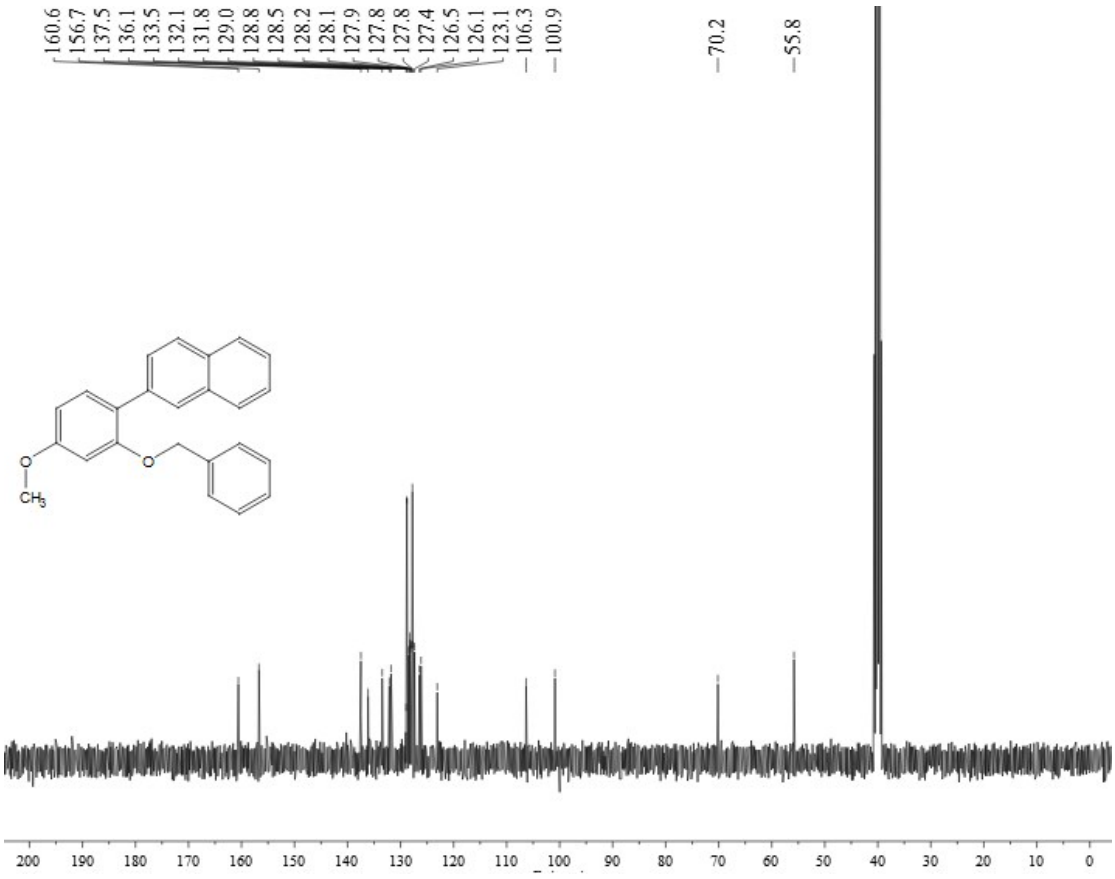


Figure S39. ^{1}H and ^{13}C-NMR spectra of 2-benzyloxy-4-methoxy-1-phenyl-2'-naphthalene

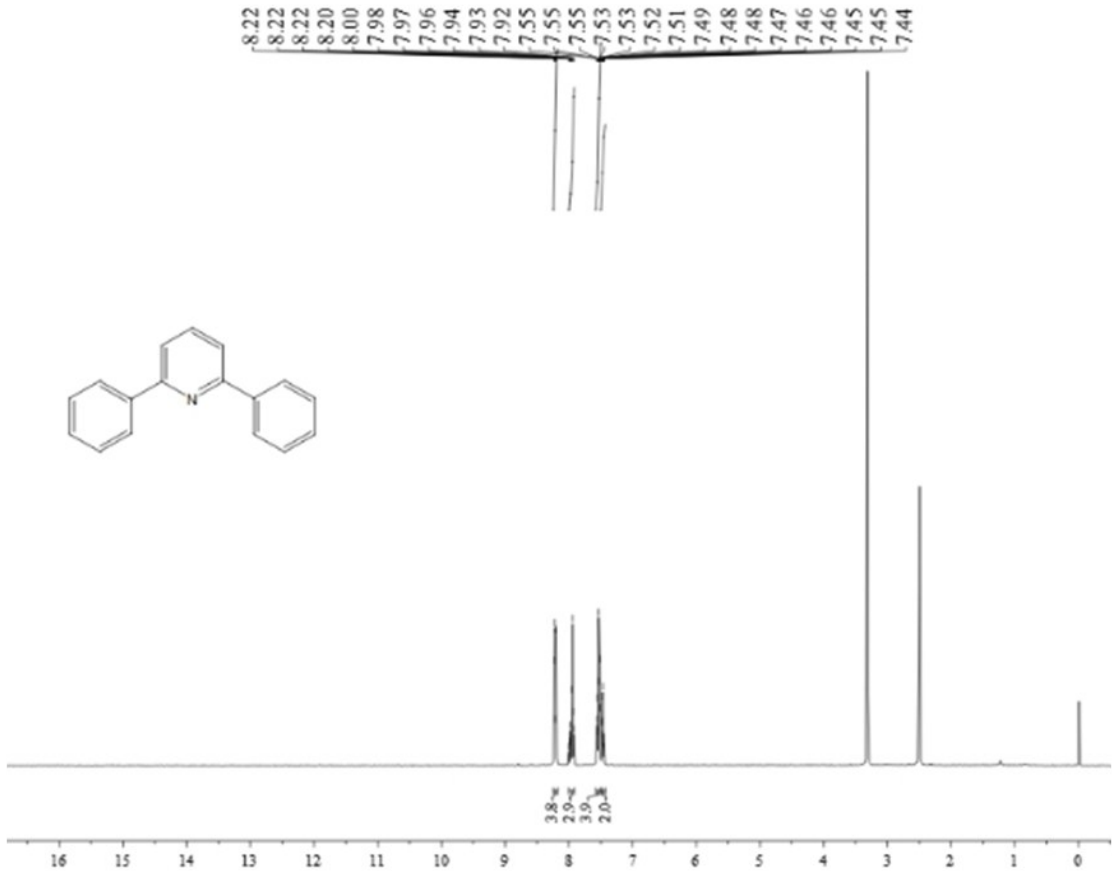


Figure S40. ^{1}H-NMR spectra of 2, 6-diphenylpyridine ^{1}H-NMR