

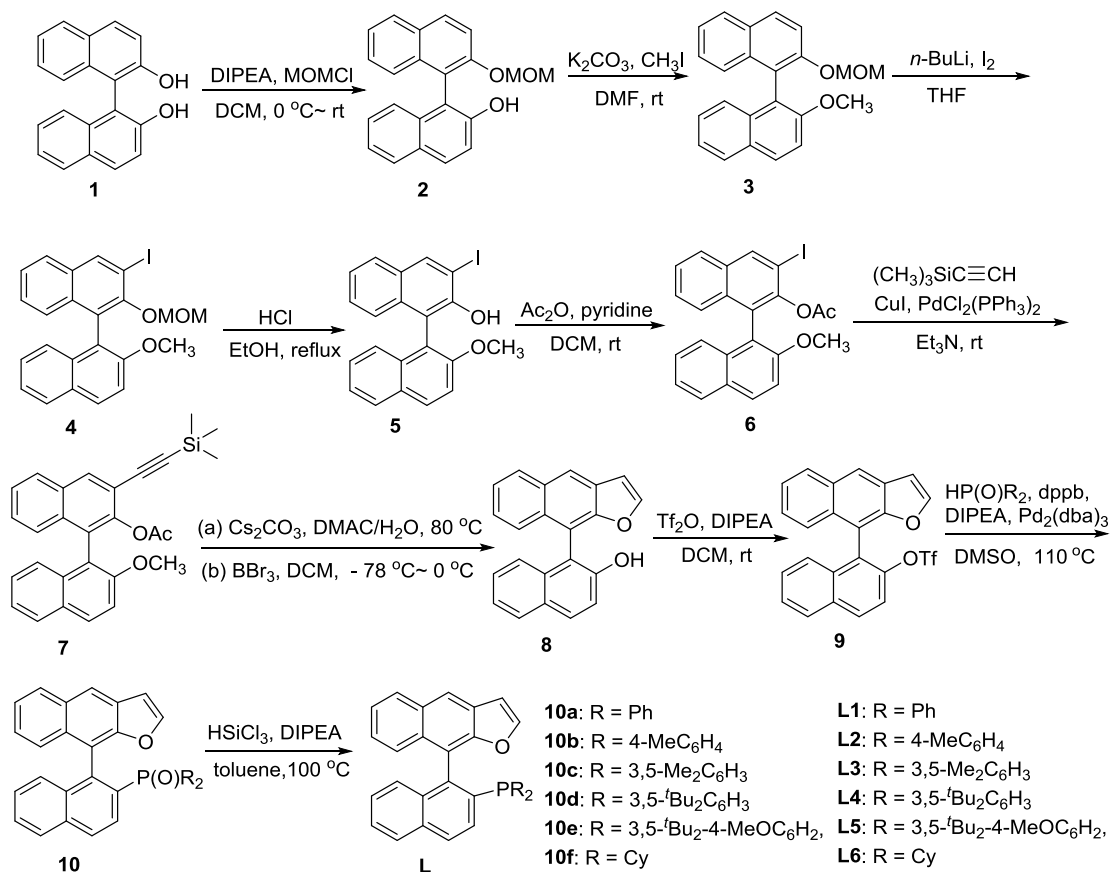
Synthesis of a class of binaphthyl monophosphine ligands with a naphthofuran skeleton and their applications in Suzuki-Miyaura coupling reactions

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1. General Methods

All the reactions were carried out under an N₂ atmosphere using standard Schlenk techniques, and unless otherwise noted, materials were purchased from commercial suppliers and used without further purification. Column chromatography was performed on silica gel (200-300 mesh). Anhydrous DCM, DIPEA, DMSO, Et₃N, pyridine and DMF were distilled from CaH₂ under an atmosphere of argon, anhydrous toluene and THF were distilled from Na under an atmosphere of argon. All ¹H NMR, ¹³C NMR and ³¹P NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer in CDCl₃, and chemical shifts (δ) are reported in ppm relative to TMS (δ 0.00 ppm) for the ¹H NMR and to chloroform (δ 77.0 ppm) for the ¹³C NMR measurements and to an external standard (0 ppm for 85% H₃PO₄, ³¹P NMR). HR-MS were carried out on a Bruker APEX 47e ESI FT-ICR mass spectrometer and Thermo MAT95XP EI-FAB-CI mass spectro-meter. Optical rotations were recorded on a Perkin-Elmer Model 341 polarimeter in a 10-cm cell at 20 °C. Compounds **2**, **3** and **4** were synthesized by the reported procedure.^{1,2,3}



2. Preparation of Biaryl Monophosphine Ligands

3-iodo-2'-methoxy-[1,1'-binaphthalen]-2-ol (5): A 250 mL round-bottom flask was charged with **4** (4.70 g, 10.0 mmol), EtOH (100 mL) and 30 mL of *conc.* HCl. The resulting solution was stirred at 85 °C for 6 h and then concentrated on a rotary evaporator. The aqueous phase was extracted with EtOAc (3 × 30 mL) and the combined organic extract was successively washed with brine (40 mL), dried over anhydrous MgSO₄, filtered, concentrated under reduced pressure. The crude reaction mixture was further purified by flash chromatography on silica gel with petroleum ether and ethyl acetate (4/1 v/v) as the eluting agent to afford **5** (3.87 g, 91% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.48 (1H, s), 8.10 (1H, d, *J* = 12.0 Hz), 7.93 (1H, d, *J* = 8.0 Hz), 7.80 (1H, d, *J* = 8.0 Hz), 7.52 (1H, d, *J* = 12.0 Hz), 7.38 (1H, t, *J* = 8.0 Hz), 7.34-7.31 (2H, m), 7.27-7.22 (1H, m), 7.15 (1H, d, *J* = 8.0 Hz), 7.05 (1H, d, *J* = 8.0 Hz), 5.41 (1H, s), 3.83 (3H, s). ¹³C NMR (101 MHz, CDCl₃) δ 156.6, 149.3, 138.9, 133.7, 133.6, 131.2, 130.5, 129.3, 128.2, 127.4, 127.0, 126.9, 125.0, 124.6, 124.2, 124.0, 123.2, 117.4, 115.5, 115.4, 113.5, 86.0, 56.6. HRMS (ESI) [M-H]⁻: calcd for C₂₁H₁₅IO₂-H 425.0033, found 425.0034.

3-iodo-2'-methoxy-[1,1'-binaphthalen]-2-yl acetate (6): A 100 mL of round-bottom flask was charged with **5** (2.13 g, 5.0 mmol), Ac₂O (2.4 mL, 25.0 mmol), pyridine (2.0 mL, 25.0 mmol) and DCM (20 mL). The resulting solution was stirred for 12 hour at room temperature, and then quenched with 40 mL of HCl (1M) solution, the layers were separated, and the aqueous layer was extracted with DCM (3 × 30 mL). The combined organic layer was successively washed with brine, dried over MgSO₄, and concentrated. The crude reaction mixture was further purified by flash chromatography on silica gel with petroleum ether and ethyl acetate (3/1 v/v) as the eluting agent to afford **6** (2.18 g, 93% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.54 (1H, s), 8.03 (1H, d, *J* = 8.0 Hz), 7.86 (1H, t, *J* = 12.0 Hz), 7.50-7.44 (2H, m), 7.38-7.30 (3H, m), 7.26 (1H, t, *J* = 8.0 Hz), 7.15 (1H, d, *J* = 8.0 Hz), 3.81 (3H, s), 1.80 (3H, s). ¹³C NMR (101 MHz, CDCl₃) δ 167.9, 154.8, 146.5, 139.0, 130.4, 127.7, 127.0, 126.7, 126.3, 125.3, 123.8, 117.3, 113.4, 90.3, 56.7, 20.6. HRMS (ESI) [M+Na]⁺: calcd for C₂₃H₁₇IO₃+Na⁺ 491.0115, found 491.0119.

2'-methoxy-3-((trimethylsilyl)ethynyl)-[1,1'-binaphthalen]-2-yl acetate (7): To a solution of **6** (2.34 g, 5.0 mmol), CuI (9.5 mg, 0.05 mmol) and PdCl₂(PPh₃)₂ (350 mg, 0.5 mmol) in Et₃N (30 mL) was added trimethylsilylacetylene (1.1 mL, 7.5 mmol) dropwise at 0 °C under argon. Then the resulting solution was stirred for overnight at room temperature. The reaction was monitored by TLC to confirm consumption of the starting materials. And then the solid was removed by filtration. The filtrate was treated with water and extracted with DCM, and the combined organic layer was successively washed with brine, dried over anhydrous MgSO₄ and concentrated. The crude reaction mixture was further purified by flash chromatography on silica gel with petroleum ether and ethyl acetate (10/1 v/v) as the eluting agent to afford **7** (1.91 g, 87% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.22 (1H, s), 8.02 (1H, d, *J* = 8.0 Hz), 7.89 (2H, t, *J* = 8.0 Hz), 7.49-7.41 (2H, m), 7.37-7.24 (3H, m), 7.21-7.15 (2H, m), 3.79 (3H, s), 1.87 (3H, s), 0.29 (9H, s). ¹³C NMR (101 MHz, CDCl₃) δ 168.0, 154.9, 146.9, 133.5, 131.3, 130.1, 128.9, 128.0, 127.7, 127.3, 126.6, 126.4, 126.1, 125.4, 123.7, 117.2, 116.7, 113.5, 100.7, 99.0, 56.7, 20.3, 0.06. HRMS (ESI) [M+Na]⁺: calcd for C₂₈H₂₆O₃Si+Na⁺ 461.1543, found 461.1549.

1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-ol (8): To a solution of **7** (1.75 g, 4.0 mmol) in DMAC/H₂O (50 mL/5 mL) was added Cs₂CO₃ (5.22 g, 16.0 mmol), then the resulting solution was heated under anargon atmosphere at 70 °C for 24 h. After the mixture was cooled to room temperature, it was treated with water and extracted with EtOAc (3 × 40 mL), and the combined

organic layer was successively washed with brine, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The crude product was dried under vacuum and then dissolved in anhydrous dichloromethane. The solution was cooled to -78°C, and BBr₃ (0.8 mL, 8.0 mmol) was added dropwise. After stirring the reaction system for 30 min at -78°C, 20 mL of ice-water was added dropwise. The reaction mixture was then warmed to room temperature, the aqueous layer was separated and re-extracted with DCM. The combined organic layer was successively washed with brine, dried over anhydrous MgSO₄ and concentrated. The crude reaction mixture was further purified by flash chromatography on silica gel with petroleum ether and ethyl acetate (4/1 v/v) as the eluting agent to afford **8** (521mg, 42% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.30 (1H, s), 8.12 (1H, d, *J* = 8.0 Hz), 8.02 (1H, d, *J* = 8.0 Hz), 7.94 (1H, d, *J* = 8.0 Hz), 7.67 (1H, s), 7.56-7.50 (2H, m), 7.44 (1H, d, *J* = 8.0 Hz), 7.40-7.35 (2H, m), 7.23 (1H, t, *J* = 4.0 Hz), 7.04-7.00 (2H, m). ¹³C NMR (101 MHz, CDCl₃) δ 152.8, 151.6, 147.9, 133.5, 131.1, 130.6, 130.4, 129.1, 128.6, 128.4, 128.2, 126.7, 126.0, 125.2, 124.7, 124.5, 123.5, 120.6, 117.5, 112.9, 111.0, 106.4. HRMS (ESI) [M-H]⁻: calcd for C₂₂H₁₄O₂-H 309.0910, found 309.0918.

1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl trifluoromethanesulfonate (9): Under an inert argon atmosphere, **8** (620 mg, 2.0 mmol) was dissolved in 30 mL of DCM, DIPEA (0.7 mL, 4.0 mmol) was added at 0 °C, followed by dropwise addition of 0.5 mL of Tf₂O (3.0 mmol). The whole solution was stirred for 8 h at room temperature and then quenched by water (20 mL). The layers were separated and the aqueous layer was extracted with DCM. The combined organic layer was successively washed with brine, dried over anhydrous MgSO₄ and concentrated. The crude reaction mixture was further purified by flash chromatography on silica gel with petroleum ether and ethyl acetate (50/1 v/v) as the eluting agent to afford **9** (813mg, 92% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.31 (1H, s), 8.17 (1H, d, *J* = 8.0 Hz), 8.11 (1H, d, *J* = 8.0 Hz), 8.06 (1H, d, *J* = 8.0 Hz), 7.69-7.67 (2H, m), 7.62-7.58 (1H, m), 7.50-7.47 (1H, m), 7.39-7.34 (4H, m), 7.00 (1H, d). ¹³C NMR (101 MHz, CDCl₃) δ 152.3, 147.6, 145.8, 132.6, 131.0, 130.6, 128.5, 128.3, 127.7, 127.1, 126.8, 125.6, 125.3, 124.1, 120.8, 119.6, 116.5, 110.6, 106.3.

(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)diphenylphosphine oxide (10a): A 100 mL of round-bottom flask charged with a mixture of **9** (663 mg, 1.5 mmol), diphenylphosphine oxide (364 mg, 1.8 mmol), 1,4-bis(diphenylphosphino)butane (dppb) (32.0 mg, 0.075 mmol), Pd₂(dba)₃ (68.7 mg, 0.075 mmol) and DIPEA (1.0 mL, 6 mmol) in 10 mL of DMSO was heated to 110 °C

for 36 h under argon atmosphere. Then the mixture was cooled to room temperature, diluted with water (50 mL) and extracted with EtOAc (3 × 30 mL). The combined organic layer was successively washed with brine, dried over anhydrous MgSO₄ and concentrated. The crude reaction mixture was further purified by flash chromatography on silica gel with petroleum ether and ethyl acetate (1/1 v/v) as the eluting agent to afford **10a** (527mg, 71% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 8.12 (1H, d, *J* = 8.0 Hz), 8.04-7.98 (2H, m), 7.88 (1H, s), 7.81 (1H, d, *J* = 8.0 Hz), 7.56 (1H, t, *J* = 8.0 Hz), 7.48-7.43 (3H, m), 7.38-7.30 (2H, m), 7.25-7.10 (8H, m), 7.03 (1H, d, *J* = 12.0 Hz), 6.94 (2H, t, *J* = 8.0 Hz), 6.76 (1H, m). ¹³C NMR (101 MHz, CDCl₃) δ 152.0, 147.0, 138.1, 134.9, 133.2, 133.1, 132.7, 132.2, 131.7, 131.5, 131.1, 131.0, 130.9, 130.6, 130.5, 130.1, 129.1, 128.5, 128.1, 127.8, 127.6, 127.4, 127.2, 127.1, 127.0, 126.1, 124.9, 123.7, 120.2, 115.3, 106.1. ³¹P NMR (162 MHz, CDCl₃) δ 28.4. HRMS (ESI) [M+H]⁺: calcd for C₃₄H₂₃O₂P+H⁺ 495.1508, found 495.1527

(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)di-*p*-tolylphosphine oxide (10b): This compound was prepared with the same method as described above. Yield (75%), ¹H NMR (400 MHz, CDCl₃) δ 8.11-8.05 (2H, m), 7.09 (1H, d, *J* = 8.0 Hz), 7.89 (1H, s), 7.80 (1H, d, *J* = 8.0 Hz), 7.55 (1H, t, *J* = 8.0 Hz), 7.47-7.30 (4H, m), 7.23-7.18 (3H, m), 7.05-6.77 (6H, m), 6.68 (1H, d, *J* = 8.0 Hz), 2.29 (3H, s), 2.19 (3H, s). ¹³C NMR (101 MHz, CDCl₃) δ 152.0, 147.0, 141.3, 137.6, 134.8, 132.1, 131.5, 130.8, 130.2, 129.2, 129.1, 128.5, 128.3, 128.1, 127.9, 127.8, 127.0, 126.2, 124.9, 123.7, 119.5, 115.4, 105.9, 21.4, 21.3. ³¹P NMR (162 MHz, CDCl₃) δ 28.8. HRMS (ESI) [M+H]⁺: calcd for C₃₆H₂₇O₂P+H⁺ 523.1821, found 523.1837.

bis(3,5-dimethylphenyl)(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)phosphine oxide (10c): This compound was prepared with the same method as described above. Yield (69%), ¹H NMR (400 MHz, CDCl₃) δ 8.14-8.10 (2H, m), 8.00 (1H, d, *J* = 8.0 Hz), 7.87 (1H, s), 7.81 (1H, d, *J* = 8.0 Hz), 7.57-7.52 (2H, m), 7.33-7.31 (1H, m), 7.23-7.19 (3H, m), 7.06-7.03 (2H, m), 6.98 (1H, d, *J* = 8.0 Hz), 6.87 (1H, s), 6.80 (1H, s), 6.73-6.68 (3H, m), 2.15 (6H, s), 2.01 (6H, s). ¹³C NMR (101 MHz, CDCl₃) δ 152.1, 146.9, 137.2(d), 136.7, 134.8, 132.8, 132.6, 130.8, 130.0, 129.3, 129.2(d), 129.0, 128.8, 128.7, 128.5, 128.1, 127.9, 127.6, 127.2, 127.0, 126.2, 124.6, 123.7, 123.0, 115.5, 106.0, 21.2. ³¹P NMR (162 MHz, CDCl₃) δ 28.9. HRMS (ESI) [M+Na]⁺: calcd for C₃₈H₃₁O₂P+Na⁺ 573.1954, found 573.1955.

bis(3,5-di-*tert*-butylphenyl)(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)phosphine oxide

(10d): This compound was prepared with the same method as described above. Yield (63%), ¹H NMR (400 MHz, CDCl₃) δ 8.05 (1H, d, *J* = 8.0 Hz), 7.98-7.97 (2H, m), 7.85-7.75 (2H, m), 7.55-7.50 (2H, m), 7.37-7.28 (6H, m), 7.24-7.18 (2H, m), 7.15-7.09 (2H, m), 6.96 (1H, d, *J* = 8.0 Hz), 6.79 (1H, m), 1.21 (36H, d, *J* = 12.0 Hz). ¹³C NMR (101 MHz, CDCl₃) δ 152.5, 149.8, 147.3, 138.6, 134.7, 133.4, 132.6, 131.6, 130.9, 129.7, 129.1, 128.0, 127.9, 127.7, 127.3, 127.0, 126.2, 125.7, 125.5, 124.7, 123.5, 119.8, 115.6, 106.9, 34.8, 31.3, 29.7. ³¹P NMR (162 MHz, CDCl₃) δ 28.4. HRMS (ESI) [M+H]⁺: calcd for C₅₀H₅₅O₂P+H⁺ 719.4012, found 719.4005.

bis(3,5-di-*tert*-butyl-4-methoxyphenyl)(1-(naphtho[2,3-*b*]furan-9-yl)naphthalen-2-yl)phosphine oxide (10e): This compound was prepared with the same method as described above. Yield (61%), ¹H NMR (400 MHz, CDCl₃) δ 8.10 (1H, d, *J* = 12.0 Hz), 8.00-7.94 (3H, m), 7.85 (1H, d, *J* = 8.0 Hz), 7.55-7.49 (2H, m), 7.33-7.19 (3H, m), 7.16-7.13 (5H, m), 6.85-6.79 (2H, m), 3.63 (6H, d), 1.27 (18H, s), 1.22 (18H, s). ¹³C NMR (101 MHz, CDCl₃) δ 161.9, 152.4, 147.2, 143.0, 142.7, 137.7, 134.6, 133.2, 132.6, 131.6, 131.1, 130.4, 130.3, 129.8, 129.3, 128.1, 127.6, 127.3, 126.9, 126.5, 126.2, 124.9, 123.7, 119.7, 115.8, 106.1, 64.2, 64.0, 35.7, 31.8. ³¹P NMR (162 MHz, CDCl₃) δ 30.0. HRMS (ESI) [M+H]⁺: calcd for C₅₂H₅₉O₄P+H⁺ 779.4224, found 779.4224.

dicyclohexyl(1-(naphtho[2,3-*b*]furan-9-yl)naphthalen-2-yl)phosphine oxide (10f): This compound was prepared with the same method as described above. Yield (51%), ¹H NMR (400 MHz, CDCl₃) δ 8.27 (1H, s), 8.21 (1H, t, *J* = 8.0 Hz), 8.15 (1H, d, *J* = 8.0 Hz), 8.09 (1H, d, *J* = 8.0 Hz), 8.01 (1H, d, *J* = 8.0 Hz), 7.60 (1H, s), 7.54 (1H, t, *J* = 8.0 Hz), 7.45 (1H, t, *J* = 8.0 Hz), 7.27-7.20 (3H, m), 7.06-7.01 (2H, m), 1.74-1.45 (9H, m), 1.30-0.91 (13H, m). ¹³C NMR (101 MHz, CDCl₃) δ 152.2, 147.2, 136.8, 134.5, 133.4, 133.3, 131.3, 131.0, 130.4, 130.2, 128.4, 128.1, 127.8, 127.6, 126.9, 126.8, 126.0, 125.2, 124.0, 119.6, 116.6, 106.7, 37.7, 37.5, 37.1, 36.9, 26.7, 26.6, 26.4, 26.3, 26.2, 26.1, 26.0, 25.9, 25.8, 25.7, 25.5. ³¹P NMR (162 MHz, CDCl₃) δ 47.9. HRMS (ESI) [M+H]⁺: calcd for C₃₄H₃₅O₂P+H⁺ 507.2447, found 507.2447.

(1-(naphtho[2,3-*b*]furan-9-yl)naphthalen-2-yl)diphenylphosphine (L1): To a mixture of **10a** (495 mg, 1.0 mmol) and DIPEA (3.5 mL, 20.0 mmol) in 20 mL of degassed anhydrous toluene at 0 °C under argon was added HSiCl₃ (1.00 mL, 10.0 mmol). After stirring at 0 °C for 30 min, the mixture was heated at 110 °C for 12 h. Cooling the reaction system to 0 °C, the mixture was diluted with ether and quenched with 5 drops of NaOH (2 M) solution and dried over MgSO₄, filtered, concentrated under reduced pressure, The residue was purified by flash chromatography

on silica gel, eluting with *n*-hexanes/Et₂O (50:1, v/v), to produce **L1** as a white solid (383 mg, 83%). ¹H NMR (400 MHz, CDCl₃) δ 8.22 (1H, s), 8.06 (1H, d, *J* = 8.0 Hz), 7.98-7.94 (2H, m), 7.50-7.47 (2H, m), 7.41 (1H, t, *J* = 8.0 Hz), 7.34-7.23 (7H, m), 7.21-7.11 (8H, m), 6.86-6.85 (1H, m). ¹³C NMR (101 MHz, CDCl₃) δ 147.4, 133.7, 133.6, 133.4, 130.4, 130.1, 128.6, 128.2, 128.1, 128.0, 127.6, 126.8, 126.6, 126.5, 125.8, 124.9, 124.7, 123.8, 113.4, 106.0. ³¹P NMR (162 MHz, CDCl₃) δ -12.9. HRMS (ESI) [M+H]⁺: calcd for C₃₄H₂₃OP+H⁺ 479.1559, found 479.1558.

(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)di-*p*-tolylphosphine (L2): This compound was prepared with the same method as described above. Yield (85%), ¹H NMR (400 MHz, CDCl₃) δ 8.23 (1H, s), 8.07 (1H, d, *J* = 8.0 Hz), 7.98-7.94 (2H, m), 7.57-7.54 (1H, m), 7.50 (1H, t, *J* = 8.0 Hz), 7.44-7.38 (2H, m), 7.30-7.17 (4H, m), 7.13-7.04 (8H, m), 6.88 (1H, m), 2.35 (3H, s), 2.33 (3H, s). ¹³C NMR (101 MHz, CDCl₃) δ 152.4, 147.3, 139.5, 139.1, 138.0, 137.7, 137.6, 137.5, 134.3, 134.2, 134.0, 133.6, 133.4, 133.1, 130.8, 130.4, 130.0, 129.0, 128.8, 128.5, 128.2, 128.0, 127.7, 126.6, 126.5, 125.9, 124.9, 123.7, 119.3, 117.7, 106.0, 21.3. ³¹P NMR (162 MHz, CDCl₃) δ -14.3. HRMS (ESI) [M+H]⁺: calcd for C₃₆H₂₇OP+H⁺ 507.1872, found 507.1872.

bis(3,5-dimethylphenyl)(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)phosphine (L3): This compound was prepared with the same method as described above. Yield (79%), ¹H NMR (400 MHz, CDCl₃) δ 8.21 (1H, s), 8.05 (1H, d, *J* = 8.0 Hz), 7.97-7.93 (2H, m), 7.59-7.56 (1H, m), 7.49 (1H, t, *J* = 8.0 Hz), 7.42-7.37 (2H, m), 7.25-7.21 (2H, m), 7.17-7.14 (2H, m), 6.90-6.89 (2H, m), 6.83-6.81 (3H, m), 6.74-6.72 (2H, m), 2.22 (6H, s), 2.17 (6H, s). ¹³C NMR (101 MHz, CDCl₃) δ 152.3, 147.3, 139.4, 139.0, 137.9, 137.7, 137.3, 137.2, 137.1, 137.0, 133.6, 133.0, 131.5, 131.3, 131.1, 130.5, 130.1, 130.0, 129.8, 128.5, 128.1, 128.0, 127.6, 126.6, 126.5, 126.4, 126.0, 124.6, 123.7, 119.3, 117.8, 106.0, 21.3, 21.2. ³¹P NMR (162 MHz, CDCl₃) δ -11.7. HRMS (ESI) [M+H]⁺: calcd for C₃₈H₃₁OP+H⁺ 535.2185, found 535.2185.

bis(3,5-di-*tert*-butylphenyl)(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)phosphine (L4): This compound was prepared with the same method as described above. Yield (89%), ¹H NMR (400 MHz, CDCl₃) δ 8.23 (1H, s), 8.04 (1H, d, *J* = 8.0 Hz), 7.96-7.94 (2H, m), 7.58 (1H, d, *J* = 8.0 Hz), 7.51-7.46 (2H, m), 7.37 (1H, t, *J* = 8.0 Hz), 7.30 (1H, s), 7.25-7.21 (3H, m), 7.15-7.09 (4H, m), 7.01 (2H, d, *J* = 8.0 Hz), 6.91 (1H, m), 1.24 (18H, s), 1.20 (18H, s). ¹³C NMR (101 MHz, CDCl₃) δ 152.3, 149.9, 149.8, 147.4, 139.6, 139.3, 138.4, 138.2, 137.0, 136.6, 133.6, 133.0, 131.0, 130.4, 128.2, 128.0, 127.7, 127.5, 126.6, 126.4, 126.3, 126.0, 124.7, 123.6, 122.0, 121.7,

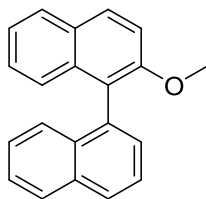
119.2, 106.1, 34.8, 31.4. ^{31}P NMR (162 MHz, CDCl_3) δ -10.1. HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{50}\text{H}_{55}\text{OP}+\text{H}^+$ 703.4063, found 703.4064.

bis(3,5-di-*tert*-butyl-4-methoxyphenyl)(1-(naphtho[2,3-*b*]furan-9-yl)naphthalen-2-yl)phosphine (L5): This compound was prepared with the same method as described above. Yield (87%), ^1H NMR (400 MHz, CDCl_3) δ 8.21 (1H, s), 8.02-7.94 (3H, m), 7.52-7.46 (3H, m), 7.34 (1H, t, $J = 8.0$ Hz), 7.23 (1H, t, $J = 8.0$ Hz), 7.14 (2H, d, $J = 8.0$ Hz), 7.08-7.03 (3H, m), 6.93-6.91 (3H, m), 3.67 (3H, s), 3.63 (3H, s), 1.32 (18H, s), 1.26 (18H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 159.6, 159.5, 152.2, 147.3, 142.8, 139.2, 138.9, 138.4, 138.3, 137.7, 133.5, 133.0, 132.3, 132.1, 132.0, 131.8, 131.3, 131.2, 130.8, 130.7, 130.4, 130.0, 128.1, 128.0, 126.5, 126.4, 126.3, 125.9, 124.6, 123.6, 119.2, 117.8, 106.1, 64.1, 35.7, 35.6, 32.0, 31.9, 22.6, 14.1. ^{31}P NMR (162 MHz, CDCl_3) δ -12.4. HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{52}\text{H}_{59}\text{O}_3\text{P}+\text{H}^+$ 763.4275, found 763.4284.

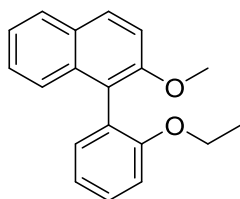
dicyclohexyl(1-(naphtho[2,3-*b*]furan-9-yl)naphthalen-2-yl)phosphine (L6): This compound was prepared with the same method as described above. Yield (84%), ^1H NMR (400 MHz, CDCl_3) δ 8.23 (1H, s), 8.07-8.01 (2H, m), 7.98 (1H, d, $J = 12.0$ Hz), 7.88 (1H, d, $J = 12.0$ Hz), 7.60 (1H, m), 7.49 (1H, t, $J = 8.0$ Hz), 7.42 (1H, t, $J = 8.0$ Hz), 7.31-7.20 (3H, m), 7.11 (1H, d, $J = 8.0$ Hz), 6.97 (1H, m), 1.93-1.76 (2H, m), 1.69-1.49 (10H, m), 1.18-0.92 (10H, m). ^{13}C NMR (101 MHz, CDCl_3) δ 152.1, 147.0, 141.4, 141.1, 136.8, 133.6, 133.2, 130.9, 130.3, 129.2, 128.3, 127.9, 127.5, 126.8, 126.6, 126.5, 126.3, 124.4, 123.7, 119.1, 106.5, 35.2, 35.0, 34.4, 34.2, 30.5, 30.4, 30.3, 29.8, 29.7, 29.6, 29.5, 27.5, 27.4, 27.3, 27.2, 27.1, 26.4, 26.3. ^{31}P NMR (162 MHz, CDCl_3) δ -8.8. HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{34}\text{H}_{35}\text{OP}+\text{H}^+$ 491.2498, found 491.2493.

3. General procedure for Suzuki-Miyaura Coupling Reactions Using Biaryl Monophosphine Ligands

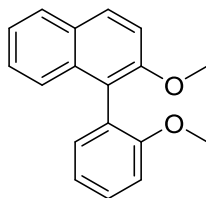
To a mixture of boronic acid (0.4mmol), base (0.6mmol), $\text{Pd}_2(\text{dba})_3$ (0.05-2 mol% Pd), **L** ($[\text{Pd}] : \text{L} = 1:1$) and aryl halide (0.2mmol) was charged degassed solvent (4.0 mL). The resulting solution was stirred at 80 °C under argon for 0.5-6 h, and then cooled to room temperature and concentrated in vacuum, and purified by silica gel column chromatography to provide desired compounds.



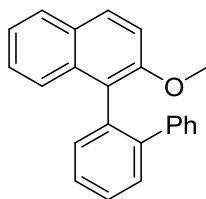
2-methoxy-1,1'-binaphthalene: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 8.05-8.01 (3H, m), 7.95 (1H, d, $J = 8.0$ Hz), 7.69 (1H, t, $J = 4.0$ Hz), 7.52-7.49 (3H, m), 7.40-7.23 (5H, m), 3.81 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 154.6, 134.6, 134.3, 133.7, 133.0, 129.5, 129.0, 128.5, 128.2, 127.8, 126.2, 125.7, 125.6, 125.5, 123.6, 123.2, 113.8, 56.8.



1-(2-ethoxyphenyl)-2-methoxynaphthalene: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 7.93 (1H, d, $J = 8.0$ Hz), 7.86 (1H, t, $J = 4.0$ Hz), 7.45-7.40 (3H, m), 7.37-7.35 (2H, m), 7.31-7.27 (1H, m), 7.15-7.10 (2H, m), 4.03-4.00 (2H, m), 3.89 (3H, s), 1.14-1.11 (3H, t, $J = 8.0$ Hz); ^{13}C NMR (101 MHz, CDCl_3) δ 157.0, 151.2, 133.6, 132.5, 129.0, 128.9, 128.7, 127.7, 125.9, 125.4, 123.3, 120.5, 113.9, 112.9, 64.0, 56.8, 14.7. HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{19}\text{H}_{18}\text{O}_2+\text{H}^+$ 279.1380, found 279.1380.

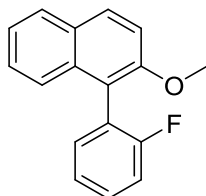


2-methoxy-1-(2-methoxyphenyl)naphthalene: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 7.94 (1H, d, $J = 8.0$ Hz), 7.86 (1H, t, $J = 4.0$ Hz), 7.44-7.38 (3H, m), 7.37-7.36 (2H, m), 7.28-7.27 (1H, m), 7.15-7.11 (2H, m), 3.89 (3H, s), 3.74 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 157.7, 154.2, 133.6, 132.4, 129.1, 129.0, 128.9, 127.8, 126.1, 125.2, 123.4, 120.6, 114.1, 111.3, 56.9, 55.7.

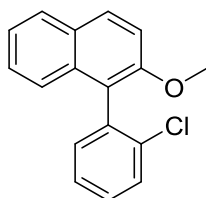


1-([1,1'-biphenyl]-2-yl)-2-methoxynaphthalene: White solid. Yield (99%), ^1H NMR (400 MHz,

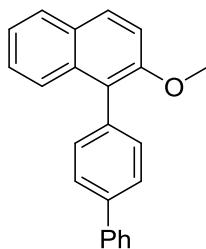
CDCl_3) δ 7.83 (2H, d, $J = 8.0$ Hz), 7.61-7.53 (4H, m), 7.41-7.38 (3H, m), 7.17-7.15 (1H, d, $J = 8.0$ Hz), 7.11-7.08 (5H, m), 3.56 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 153.5, 143.0, 141.8, 134.8, 133.8, 131.9, 129.8, 128.8, 128.6, 127.9, 127.7, 127.2, 127.1, 126.3, 125.2, 124.3, 123.3, 113.1, 56.0.



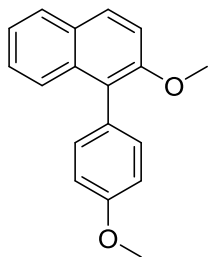
1-(2-fluorophenyl)-2-methoxynaphthalene: White solid. Yield (96%), ^1H NMR (400 MHz, CDCl_3) δ 7.98 (1H, d, $J = 8.0$ Hz), 7.90-7.87 (1H, m), 7.48 (2H, t, $J = 8.0$ Hz), 7.44-7.38 (4H, m), 7.34-7.28 (2H, m), 3.91 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 161.8, 154.4, 133.4, 133.1, 129.9, 129.3, 129.0, 128.0, 126.6, 124.7, 123.9, 123.6, 118.7, 115.8, 113.5, 56.7.



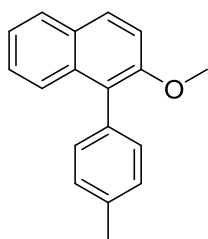
1-(2-chlorophenyl)-2-methoxynaphthalene: White solid. Yield (98%), ^1H NMR (400 MHz, CDCl_3) δ 7.98 (1H, d, $J = 8.0$ Hz), 7.90-7.87 (1H, m), 7.62-7.60 (1H, m), 7.44-7.38 (7H, m), 3.91 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 154.0, 135.6, 134.9, 133.1, 132.6, 129.8, 129.5, 138.8, 138.0, 126.6, 124.6, 123.6, 122.4, 113.6, 56.7.



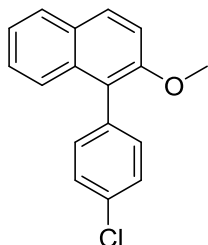
1-([1,1'-biphenyl]-4-yl)-2-methoxynaphthalene: White solid. Yield (96%), ^1H NMR (400 MHz, CDCl_3) δ 7.96 (1H, d, $J = 8.0$ Hz), 7.90-7.88 (1H, m), 7.80-7.76 (4H, m), 7.65 (1H, t, $J = 4.0$ Hz), 7.55-7.50 (4H, m), 7.45-7.40 (4H, m), 3.92 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 153.8, 141.1, 139.8, 135.4, 131.4, 129.2, 129.1, 128.8, 127.9, 127.3, 127.2, 126.9, 126.4, 125.3, 123.6, 113.1, 56.8.



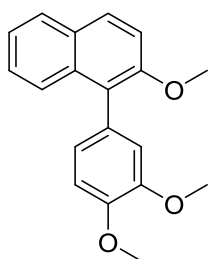
2-methoxy-1-(4-methoxyphenyl)naphthalene: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 7.92 (1H, d, $J = 8.0$ Hz), 7.87-7.85 (1H, m), 7.60-7.58 (1H, m), 7.42-7.34 (5H, m), 7.10 (2H, d, $J = 8.0$ Hz), 3.98 (3H, s), 3.88 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 158.6, 153.9, 133.9, 132.0, 129.0, 128.8, 128.4, 127.8, 126.2, 125.3, 125.0, 123.4, 113.7, 56.8, 55.2.



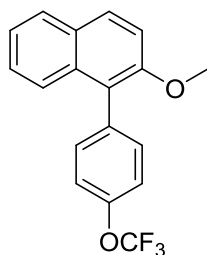
2-methoxy-1-(p-tolyl)naphthalene: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 7.93 (1H, d, $J = 8.0$ Hz), 7.88-7.86 (1H, m), 7.62-7.57 (1H, m), 7.43-7.36 (5H, m), 7.33-7.31 (2H, m), 3.89 (3H, s), 2.51 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 153.8, 136.6, 133.7, 133.3, 130.8, 129.0, 128.9, 127.8, 126.2, 125.3, 123.5, 113.8, 56.8, 21.4.



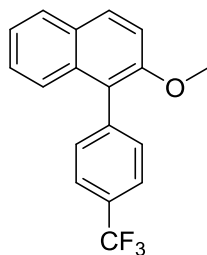
1-(4-chlorophenyl)-2-methoxynaphthalene: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 7.95 (1H, d, $J = 12.0$ Hz), 7.88-7.86 (1H, m), 7.53-7.51 (3H, m), 7.42-7.34 (5H, m), 3.88 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 153.7, 134.8, 133.4, 133.0, 132.4, 129.4, 129.0, 128.4, 127.9, 126.5, 124.9, 123.9, 123.6, 113.5, 56.6.



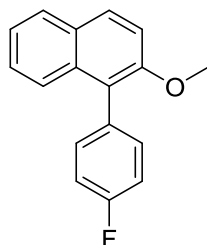
1-(3,4-dimethoxyphenyl)-2-methoxynaphthalene: White solid. Yield (97%), ^1H NMR (400 MHz, CDCl_3) δ 7.92 (1H, d, $J = 8.0$ Hz), 7.87-7.85 (1H, m), 7.60-7.58 (1H, m), 7.42-7.37 (3H, m), 7.06-7.04 (1H, d, $J = 8.0$ Hz), 6.98-6.94 (2H, m), 4.00 (3H, s), 3.90 (3H, s), 3.89 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 153.8, 148.6, 148.0, 133.8, 129.0, 128.9, 128.8, 127.8, 126.3, 125.3, 125.1, 123.5, 123.1, 114.1, 113.8, 110.9, 56.8, 55.9, 55.8.



2-methoxy-1-(4-(trifluoromethoxy)phenyl)naphthalene: White solid. Yield (97%), ^1H NMR (400 MHz, CDCl_3) δ 7.95 (1H, d, $J = 8.0$ Hz), 7.88-7.86 (1H, m), 7.44 (1H, d, $J = 8.0$ Hz), 7.39-7.36 (7H, m), 3.88 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 153.7, 148.3, 135.0, 133.4, 132.4, 129.5, 128.9, 127.9, 126.6, 124.8, 123.6, 120.6, 113.5, 56.6.

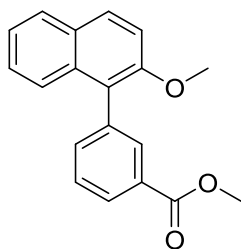


2-methoxy-1-(4-(trifluoromethyl)phenyl)naphthalene: White solid. Yield (98%), ^1H NMR (400 MHz, CDCl_3) δ 7.97 (1H, d, $J = 8.0$ Hz), 7.90-7.87 (1H, m), 7.81 (2H, d, $J = 8.0$ Hz), 7.55 (2H, d, $J = 8.0$ Hz), 7.46-7.39 (4H, m), 3.89 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 153.6, 140.4, 133.1, 131.4, 129.8, 129.3, 128.9, 128.0, 126.7, 125.1, 124.7, 123.7, 123.6, 113.4, 56.6.

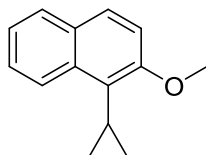


1-(4-fluorophenyl)-2-methoxynaphthalene: White solid. Yield (97%), ^1H NMR (400 MHz, CDCl_3) δ 7.94 (1H, d, $J = 8.0$ Hz), 7.88-7.86 (1H, m), 7.53-7.51 (1H, m), 7.42-7.36 (5H, m), 7.24 (2H, t, $J = 8.0$ Hz), 3.88 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 161.8, 153.8, 133.6, 132.6, 132.1,

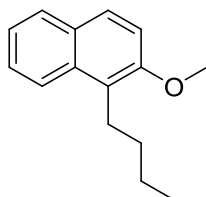
129.3, 129.0, 127.9, 126.4, 125.0, 124.1, 123.6, 115.3, 113.6, 56.7.



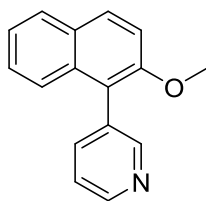
methyl 3-(2-methoxynaphthalen-1-yl)benzoate: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 8.16-8.14 (1H, m), 8.11 (1H, s), 7.95 (1H, d, $J = 8.0$ Hz), 7.88-7.86 (1H, m), 7.62 (2H, d, $J = 8.0$ Hz), 7.47-7.37 (4H, m), 3.96 (3H, s), 3.87 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 167.2, 153.7, 136.8, 135.7, 133.3, 132.2, 130.2, 129.5, 128.9, 128.4, 128.3, 127.9, 126.5, 124.8, 124.0, 123.6, 113.5, 56.6, 52.1. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd for $\text{C}_{19}\text{H}_{16}\text{O}_3+\text{Na}^+$ 315.0992, found 315.1003.



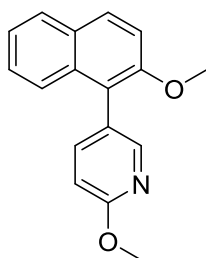
1-cyclopropyl-2-methoxynaphthalene: White solid. Yield (91%), ^1H NMR (400 MHz, CDCl_3) δ 8.51 (1H, d, $J = 12.0$ Hz), 7.83 (1H, d, $J = 8.0$ Hz), 7.79 (1H, d, $J = 8.0$ Hz), 7.54 (1H, t, $J = 8.0$ Hz), 7.39 (1H, t, $J = 8.0$ Hz), 7.29 (1H, d, $J = 8.0$ Hz), 4.01 (3H, s), 2.00-1.96 (1H, m), 1.24-1.19 (2H, m), 0.82-0.78 (2H, m). ^{13}C NMR (101 MHz, CDCl_3) δ 156.3, 135.0, 129.1, 128.3, 128.2, 125.9, 124.7, 123.3, 114.4, 56.8, 7.9.



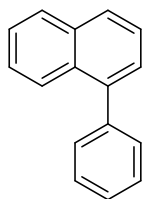
1-butyl-2-methoxynaphthalene: White solid. Yield (96%), ^1H NMR (400 MHz, CDCl_3) δ 8.03 (1H, d, $J = 8.0$ Hz), 7.84 (1H, d, $J = 8.0$ Hz), 7.77 (1H, d, $J = 8.0$ Hz), 7.52 (1H, t, $J = 8.0$ Hz), 7.38 (1H, t, $J = 8.0$ Hz), 7.33 (1H, d, $J = 12.0$ Hz), 3.99 (1H, s), 3.13 (2H, t, $J = 8.0$ Hz), 1.68-1.63 (2H, m), 1.55-1.52 (2H, m), 1.03 (3H, t, $J = 8.0$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 154.2, 130.0, 129.3, 128.5, 127.2, 126.0, 124.4, 123.4, 123.1, 113.5, 56.6, 32.4, 24.7, 23.1, 14.1.



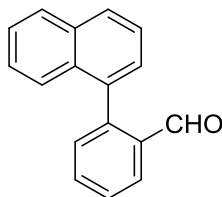
3-(2-methoxynaphthalen-1-yl)pyridine: White solid. Yield (82%), ^1H NMR (400 MHz, CDCl_3) δ 8.70-8.68 (1H, m), 8.66 (1H, s), 7.97 (1H, d, $J = 12.0$ Hz), 7.87 (1H, t, $J = 4.0$ Hz), 7.76-7.73 (1H, m), 7.50-7.45 (2H, m), 7.42-7.38 (3H, m), 3.87 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 154.1, 151.8, 148.2, 138.6, 133.3, 130.0, 128.9, 128.1, 126.8, 124.5, 123.7, 123.1, 133.3, 56.5.



2-methoxy-5-(2-methoxynaphthalen-1-yl)pyridine: White solid. Yield (91%), ^1H NMR (400 MHz, CDCl_3) δ 8.22 (1H, d, $J = 4.0$ Hz), 7.94 (1H, d, $J = 8.0$ Hz), 7.87-7.85 (1H, m), 7.65-7.63 (1H, m), 7.59-7.57 (1H, m), 7.41-7.36 (3H, m), 6.94 (1H, d, $J = 8.0$ Hz), 4.06 (3H, s), 3.88 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 163.2, 154.2, 148.4, 141.5, 133.7, 129.5, 129.0, 128.9, 128.0, 126.6, 124.7, 123.6, 121.3, 113.4, 110.3, 56.6, 53.5. HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{17}\text{H}_{15}\text{O}_2\text{N}+\text{H}^+$ 266.1176, found 266.1188.

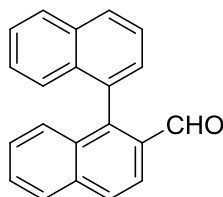


1-phenylnaphthalene: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 8.00-7.97 (2H, m), 7.94 (1H, d, $J = 8.0$ Hz), 7.61-7.54 (6H, m), 7.51-7.49 (3H, m). ^{13}C NMR (101 MHz, CDCl_3) δ 140.8, 140.3, 133.8, 131.6, 130.1, 128.3, 127.6, 127.2, 126.9, 126.0, 125.8, 125.4.

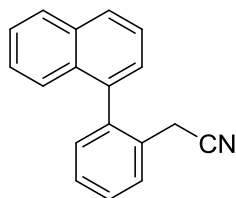


2-(naphthalen-1-yl)benzaldehyde: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 9.68 (1H, s), 8.17 (1H, d, $J = 8.0$ Hz), 7.99 (1H, s, $J = 12.0$ Hz), 7.74-7.71 (1H, m), 7.62-7.57 (2H, m),

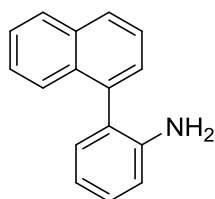
7.55-7.50 (2H, m), 7.50-7.44 (3H, m). ^{13}C NMR (101 MHz, CDCl_3) δ 192.1, 144.3, 135.4, 134.8, 133.7, 133.4, 132.7, 131.7, 128.6, 128.4, 128.2, 127.1, 126.8, 126.2, 125.8, 125.0.



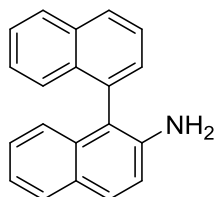
[1,1'-binaphthalene]-2-carbaldehyde: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 9.72 (1H, s), 8.20 (1H, d, $J = 8.0$ Hz), 8.07 (2H, d, $J = 4.0$ Hz), 8.01 (2H, t, $J = 4.0$ Hz), 7.68-7.58 (2H, m), 7.55-7.48 (2H, m), 7.42-7.32 (3H, m), 7.26 (1H, d, $J = 12.0$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 192.5, 144.9, 136.1, 133.5, 133.3, 133.0, 132.9, 132.1, 129.2, 129.0, 128.9, 128.7, 128.3, 128.2, 127.7, 127.0, 126.8, 126.3, 126.2, 125.0, 122.1.



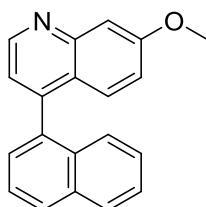
2-(2-(naphthalen-1-yl)phenyl)acetonitrile: White solid. Yield (87%), ^1H NMR (400 MHz, CDCl_3) δ 7.98-7.95 (2H, m), 7.71 (1H, d, $J = 8.0$ Hz), 7.61-7.44 (5H, m), 7.41-7.37 (3H, m), 3.42 (2H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 139.8, 137.1, 131.0, 128.6, 128.5, 128.4, 128.2, 127.0, 126.7, 126.2, 125.5, 125.2, 118.0, 21.8. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd for $\text{C}_{18}\text{H}_{13}\text{N}+\text{Na}^+$ 266.0940, found 266.0957.



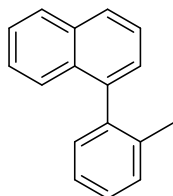
2-(naphthalen-1-yl)aniline: White solid. Yield (92%), ^1H NMR (400 MHz, CDCl_3) δ 7.97-7.92 (2H, m), 7.72 (1H, d, $J = 8.0$ Hz), 7.62-7.47 (4H, m), 7.33-7.28 (1H, m), 7.22 (1H, d, $J = 8.0$ Hz), 6.93 (1H, t, $J = 8.0$ Hz), 6.89 (1H, d, $J = 12.0$ Hz), 3.44 (2H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 144.3, 133.8, 131.2, 128.8, 128.3, 128.0, 127.6, 126.3, 126.0, 125.8, 118.3, 115.3.



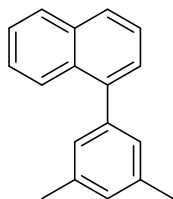
[1,1'-binaphthalen]-2-amine: White solid. Yield (94%), ^1H NMR (400 MHz, CDCl_3) δ 7.98-7.94 (3H, m), 7.62 (1H, t, $J = 8.0$ Hz), 7.54-7.47 (4H, m), 7.44 (1H, d, $J = 8.0$ Hz), 7.36-7.28 (3H, m), 6.95 (1H, d, $J = 8.0$ Hz), 4.29 (2H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 141.9, 138.9, 133.6, 133.5, 133.3, 129.3, 128.3, 128.1, 127.5, 127.2, 126.8, 125.9, 125.8, 125.7, 125.4, 124.8, 123.5, 120.9, 109.3.



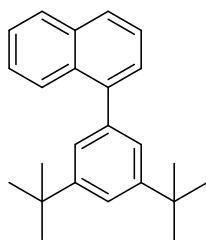
7-methoxy-4-(naphthalen-1-yl)quinoline: White solid. Yield (94%), ^1H NMR (400 MHz, CDCl_3) δ 8.96 (1H, d, $J = 4.0$ Hz), 7.99 (2H, d, $J = 8.0$ Hz), 7.62 (1H, d, $J = 8.0$ Hz), 7.57-7.47 (3H, m), 7.40-7.29 (4H, m), 7.06-7.03 (1H, m), 4.00 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 160.6, 150.2, 150.1, 147.2, 135.7, 133.4, 131.8, 128.7, 128.3, 127.5, 127.3, 126.4, 126.1, 125.9, 125.2, 123.2, 120.6, 119.7, 107.4, 55.5.



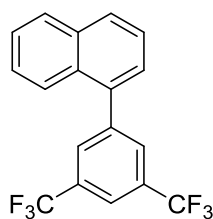
1-(o-tolyl)naphthalene: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 7.97-7.91 (2H, m), 7.60-7.51 (3H, m), 7.45 (1H, d, $J = 8.0$ Hz), 7.41-7.37 (3H, m), 7.35-7.29 (2H, m), 2.08 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 140.2, 139.8, 136.8, 133.5, 132.0, 130.4, 129.8, 128.2, 127.6, 127.4, 126.6, 126.1, 126.0, 125.7, 125.6, 125.4, 20.1.



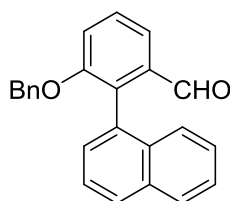
1-(3,5-dimethylphenyl)naphthalene: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 8.01 (1H, d, $J = 8.0$ Hz), 7.97 (1H, d, $J = 12.0$ Hz), 7.91 (1H, d, $J = 8.0$ Hz), 7.59-7.51 (2H, m), 7.50-7.46 (2H, m), 7.19 (2H, s), 7.14 (1H, s), 2.47 (6H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 140.7, 140.5, 137.7, 133.8, 131.7, 128.8, 128.2, 127.9, 127.4, 126.7, 126.2, 125.9, 125.7, 125.3, 21.4.



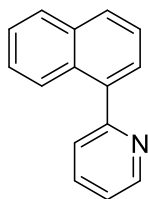
1-(3,5-di-*tert*-butylphenyl)naphthalene: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 8.05 (1H, d, $J = 8.0$ Hz), 7.99 (1H, d, $J = 8.0$ Hz), 7.94 (1H, d, $J = 8.0$ Hz), 7.61-7.51 (5H, m), 7.44 (2H, s), 1.47 (18H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 150.5, 141.4, 139.8, 133.9, 131.8, 128.3, 127.4, 126.9, 126.3, 125.9, 125.7, 125.4, 124.5, 121.1, 35.0, 31.6.



1-(3,5-bis(trifluoromethyl)phenyl)naphthalene: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 8.01-7.98 (5H, m), 7.75 (1H, d, $J = 8.0$ Hz), 7.62-7.54 (3H, m), 7.48 (1H, d, $J = 8.0$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 142.8, 136.9, 133.8, 131.9, 131.5, 130.9, 130.1, 129.1, 128.6, 127.4, 127.0, 126.3, 125.3, 124.7, 122.0, 121.3, 121.2, 121.1.

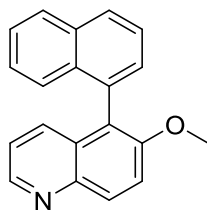


3-(benzyloxy)-2-(naphthalen-1-yl)benzaldehyde: White solid. Yield (99%), ^1H NMR (400 MHz, CDCl_3) δ 9.60 (1H, s), 8.00 (1H, d, $J = 8.0$ Hz), 7.61 (1H, t, $J = 8.0$ Hz), 7.56-7.43 (6H, m), 7.33 (1H, d, $J = 8.0$ Hz), 7.20-7.19 (3H, m), 6.96-6.94 (2H, m), 5.03 (2H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 192.1, 156.7, 136.5, 136.3, 134.0, 133.4, 133.0, 131.4, 129.1, 128.8, 128.5, 128.4, 128.3, 127.6, 126.4, 126.1, 126.0, 125.1, 119.4, 118.2, 70.5. HRMS (ESI) $[\text{M}+\text{Na}]^+$: calcd for $\text{C}_{24}\text{H}_{18}\text{O}_2+\text{Na}^+$ 361.1199, found 361.1208.

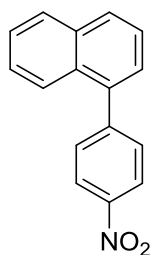


2-(naphthalen-1-yl)pyridine: White solid. Yield (93%), ^1H NMR (400 MHz, CDCl_3) δ 8.83 (1H,

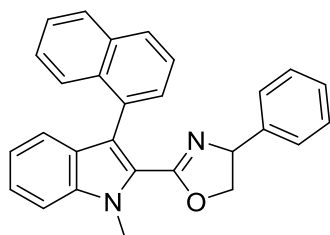
d, $J = 4.0$ Hz), 8.12 (1H, d, $J = 8.0$ Hz), 7.95 (2H, d, $J = 8.0$ Hz), 7.86 (1H, t, $J = 8.0$ Hz), 7.64-7.58 (3H, m), 7.53-7.50 (2H, m), 7.37 (1H, t, $J = 8.0$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 159.2, 149.5, 138.4, 136.4, 133.9, 131.1, 128.9, 128.3, 127.4, 126.4, 125.8, 125.5, 125.3, 125.1, 122.0.



6-methoxy-5-(naphthalen-1-yl)quinoline: White solid. Yield (95%), ^1H NMR (400 MHz, CDCl_3) δ 8.81-8.79 (1H, m), 8.31 (1H, d, $J = 8.0$ Hz), 7.99 (2H, t, $J = 8.0$ Hz), 7.71 (1H, d, $J = 12.0$ Hz), 7.66-7.63 (1H, m), 7.55-7.48 (2H, m), 7.45-7.43 (1H, m), 7.35-7.31 (2H, m), 7.18-7.15 (1H, m), 3.82 (3H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 154.6, 148.1, 143.7, 133.8, 133.7, 133.1, 132.7, 130.6, 129.3, 129.2, 128.6, 128.3, 128.1, 126.1, 125.8, 125.5, 121.3, 116.8, 56.7. HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{20}\text{H}_{15}\text{NO}+\text{H}^+$ 286.1226, found 286.1237.

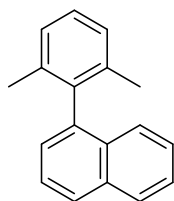


1-(4-nitrophenyl)naphthalene: White solid. Yield (95%), ^1H NMR (400 MHz, CDCl_3) δ 8.40 (1H, d, $J = 12.0$ Hz), 7.99 (1H, d, $J = 4.0$ Hz), 7.97 (1H, d, $J = 4.0$ Hz), 7.83 (1H, d, $J = 8.0$ Hz), 7.71 (2H, d, $J = 8.0$ Hz), 7.61-7.55 (2H, m), 7.51 (1H, t, $J = 8.0$ Hz), 7.47 (1H, d, $J = 8.0$ Hz). ^{13}C NMR (101 MHz, CDCl_3) δ 147.6, 147.1, 137.7, 133.8, 130.9, 128.9, 128.6, 127.1, 126.7, 126.2, 125.3, 125.1, 123.6.



2-(1-methyl-3-(naphthalen-1-yl)-1H-indol-2-yl)-4-phenyl-4,5-dihydrooxazole: White solid. Yield (94%), ^1H NMR (400 MHz, CDCl_3) δ 7.98-7.92 (2H, m), 7.88-7.80 (1H, m), 7.65-7.59 (2H,

m), 7.52 (2H, t, $J = 8.0$ Hz), 7.48-7.31 (6H, m), 7.27 (1H, d, $J = 8.0$ Hz), 7.17-7.13 (2H, m), 5.34-5.28 (1H, m), 4.37-4.32 (0.5H, m), 4.27 (3H, d, $J = 4.0$ Hz), 4.19-4.15 (0.5H, m), 3.88-3.84 (0.5H, m), 3.61-3.57 (0.5H, m). ^{13}C NMR (101 MHz, CDCl_3) δ 159.7, 142.2, 142.1, 138.6, 138.5, 133.7, 133.6, 133.1, 133.0, 132.7, 132.6, 128.7, 128.6, 128.3, 128.1, 127.8, 127.6, 127.5, 127.4, 126.8, 126.5, 126.3, 126.2, 127.7, 127.5, 127.3, 127.2, 124.6, 124.4, 121.2, 120.4, 120.0, 110.0, 73.8, 70.1, 70.0, 32.2. HRMS (ESI) $[\text{M}+\text{H}]^+$: calcd for $\text{C}_{28}\text{H}_{22}\text{N}_2\text{O}+\text{H}^+$ 403.1805, found 403.1811.



1-(2,6-dimethylphenyl)naphthalene: White solid. Yield (80%), ^1H NMR (400 MHz, CDCl_3) δ 7.96 (1H, d, $J = 8.0$ Hz), 7.92 (1H, d, $J = 8.0$ Hz), 7.59 (1H, t, $J = 8.0$ Hz), 7.53-7.51 (1H, m), 7.39-7.38 (2H, m), 7.32-7.29 (2H, m), 7.23-7.21 (2H, m), 1.95 (6H, s). ^{13}C NMR (101 MHz, CDCl_3) δ 139.6, 138.7, 137.0, 133.7, 131.7, 128.3, 127.9, 127.3, 127.2, 126.4, 126.0, 125.8, 125.7, 125.4, 20.4.

[1] T. Taniguchi, T. Fukuba, S. Nakatsuka, S. Hayase, M. Kawatsura, H. Uno and T. Itoh, *J. Org. Chem.* 1994, **59**, 1967-1969.

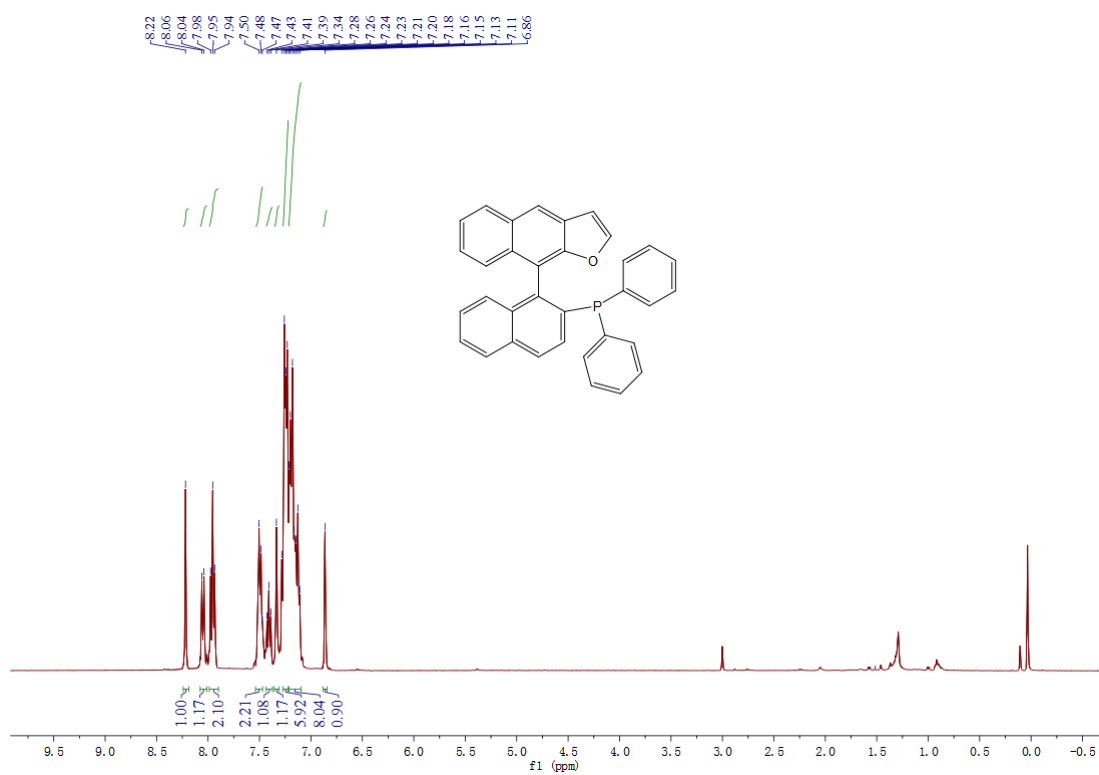
[2] W. M. Ren, Y. Liu, G. P. Wu, J. Liu and X. B. Lu, *J. Polym. Sci. Polym. Chem.* 2011, **49**, 4894-4901.

[3] Q. S. Guo, D. M. Du and J. Xu, *Angew. Chem. Int. Ed.* 2008, **47**, 759-762.

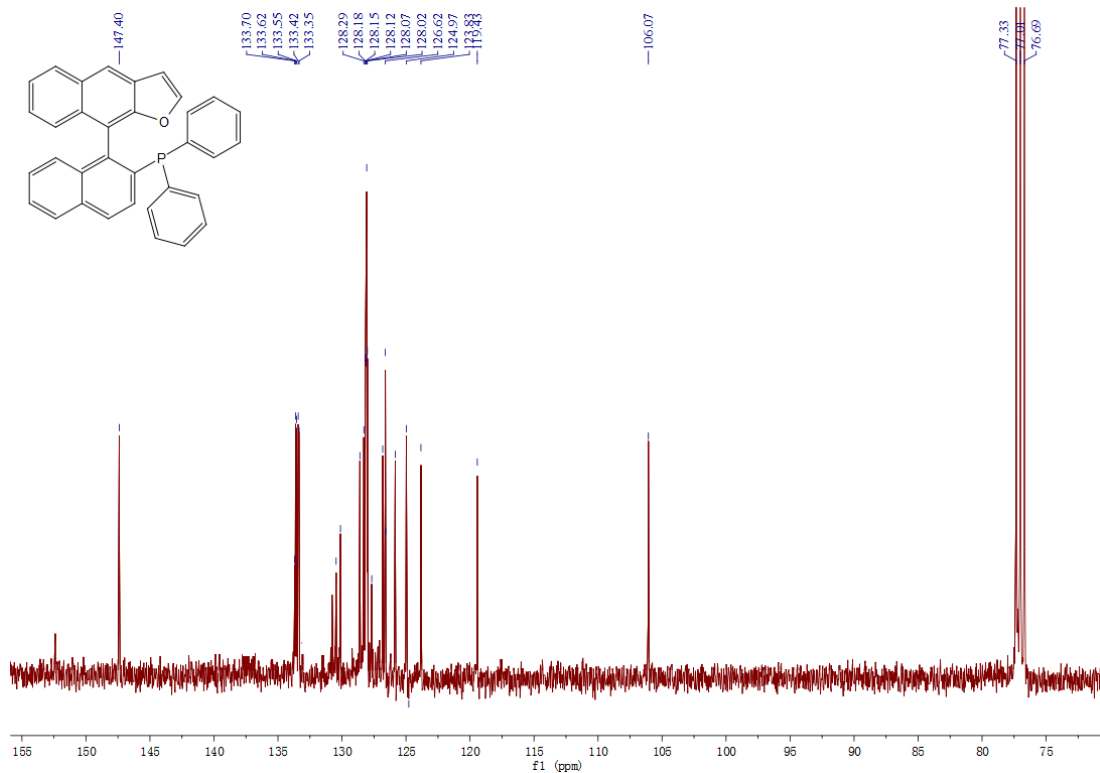
NMR Spectra for L1-L6 and Some of New Compounds

(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)diphenylphosphine (L1):

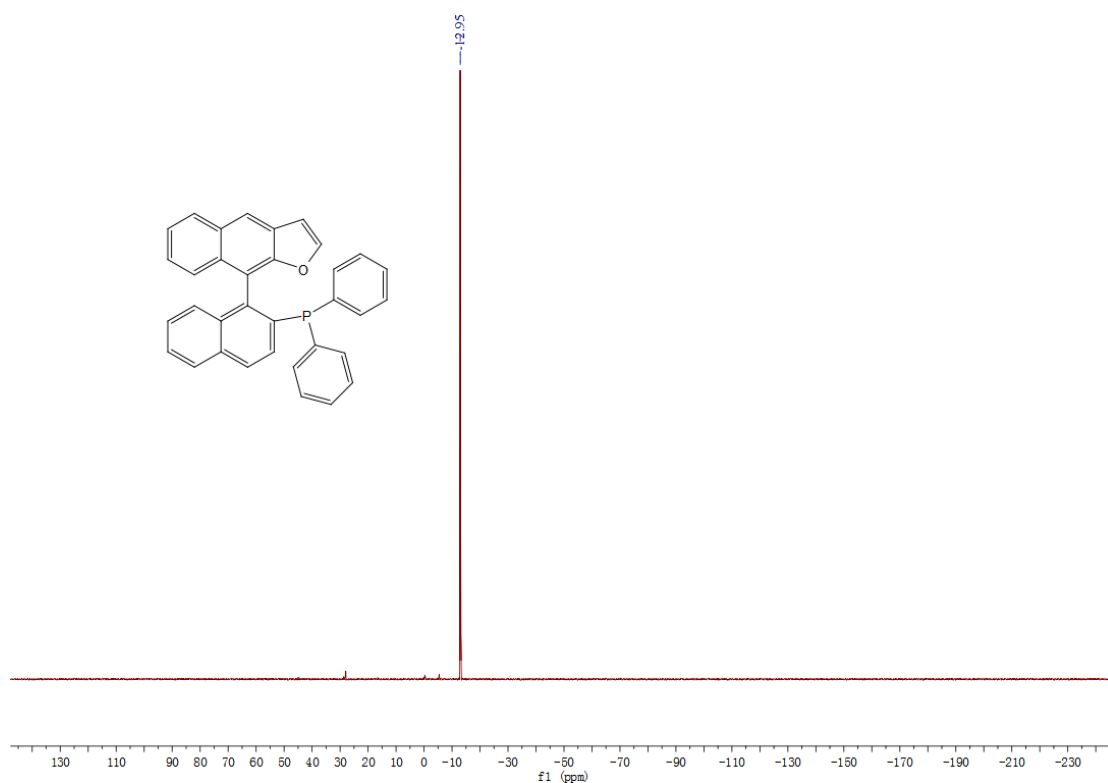
$^1\text{H-NMR}$ (400 MHz, CDCl_3)



$^{13}\text{C-NMR}$ (101 MHz, CDCl_3)

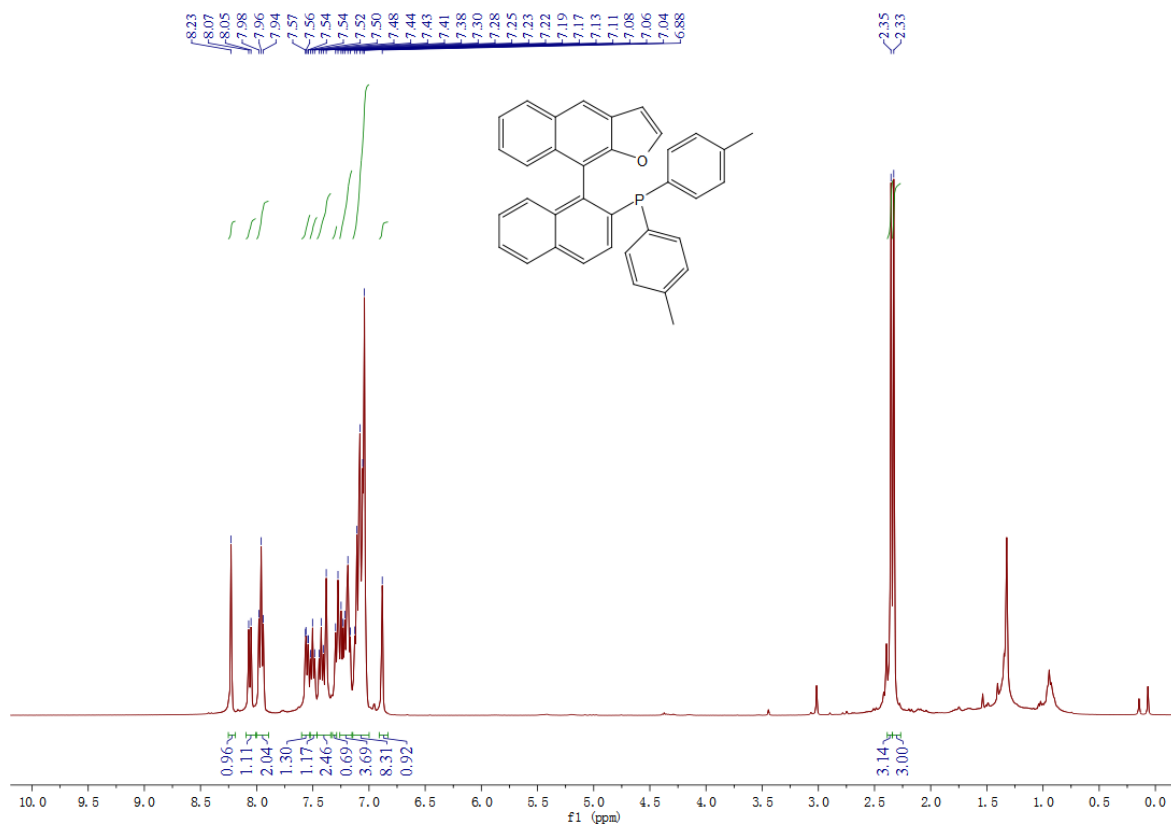


^{31}P NMR (162 MHz, CDCl_3)

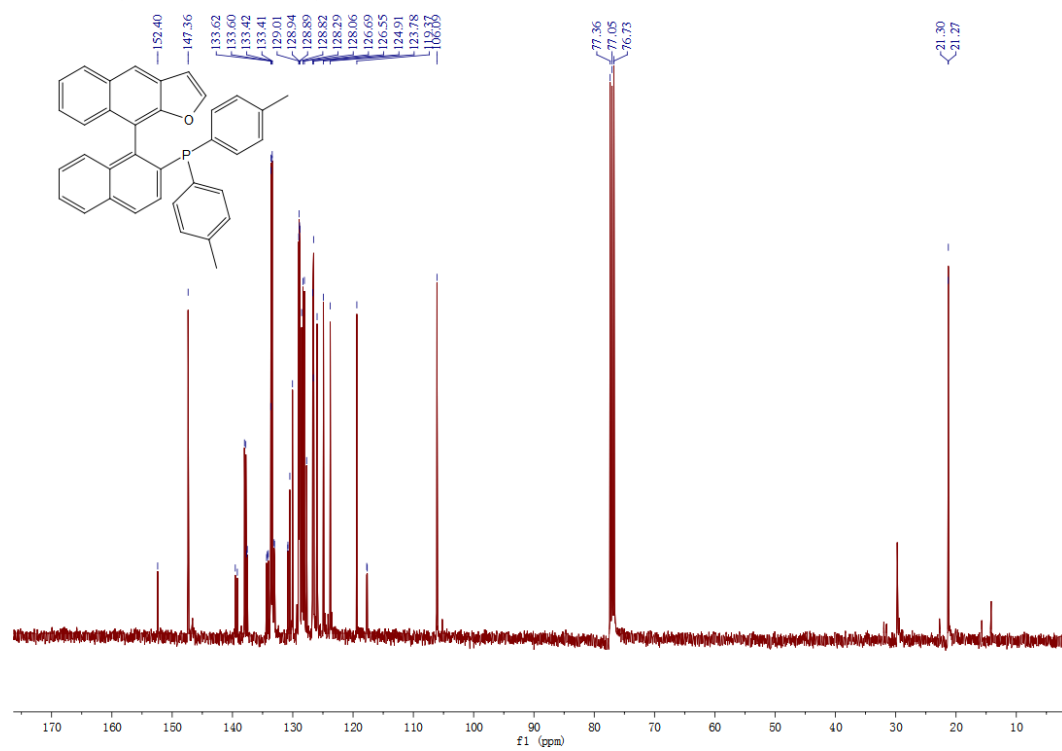


(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)di-*p*-tolylphosphine (L2):

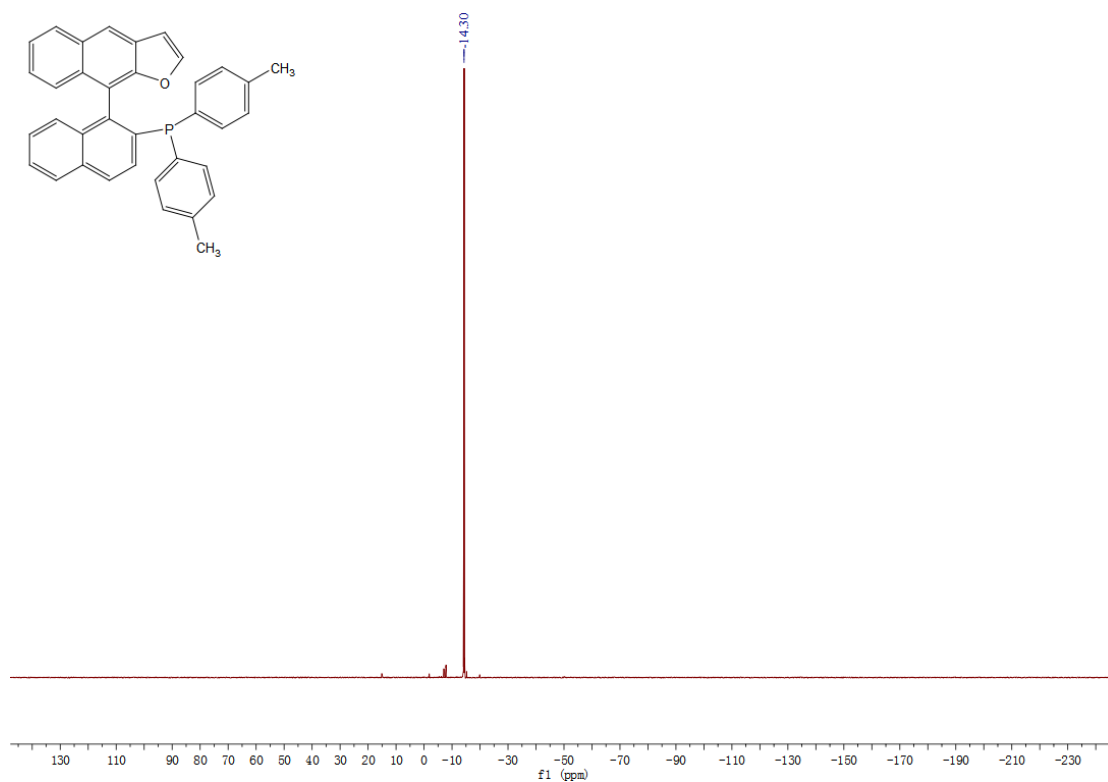
^1H -NMR (400 MHz, CDCl_3)



¹³C-NMR (101 MHz, CDCl₃)

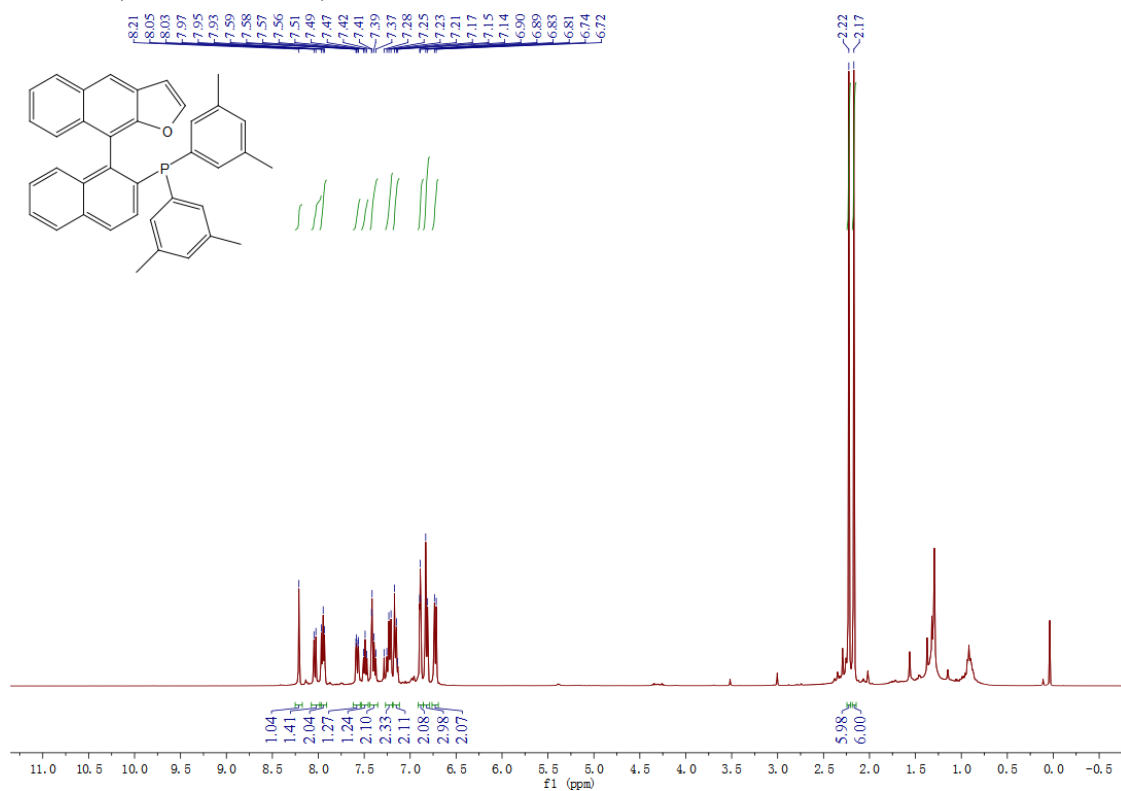


³¹P NMR (162 MHz, CDCl₃)

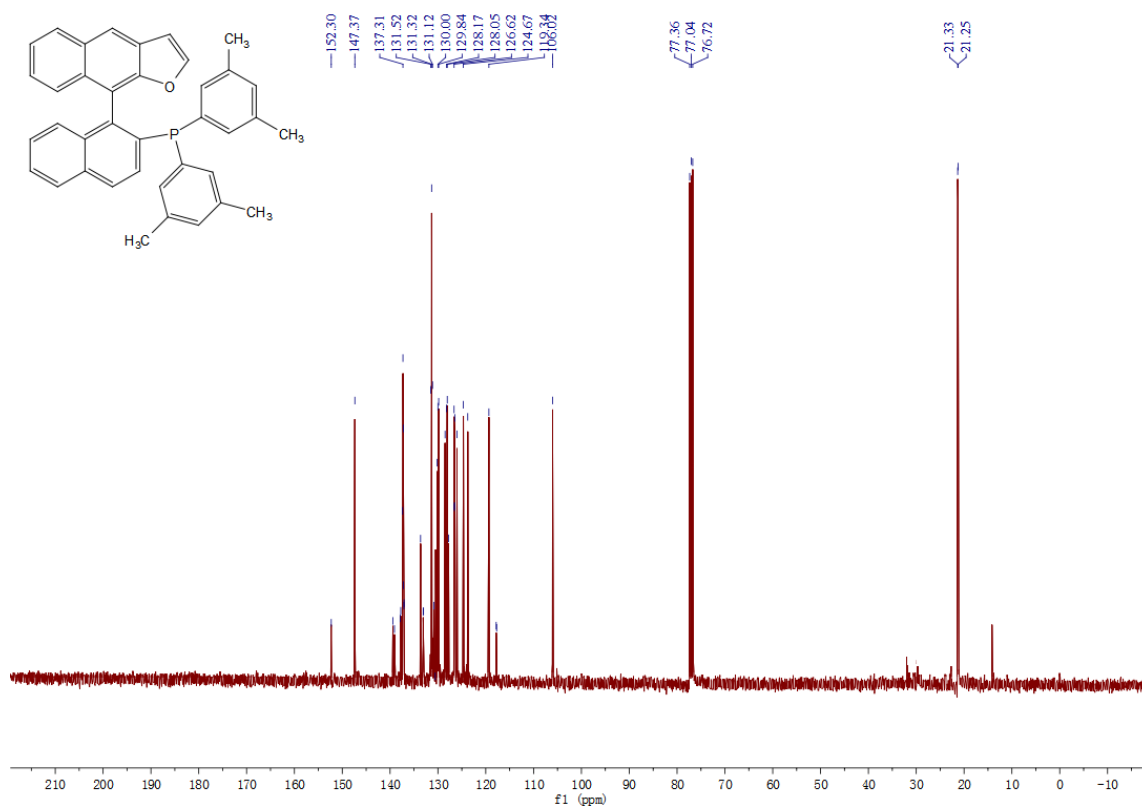


bis(3,5-dimethylphenyl)(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)phosphine (L3):

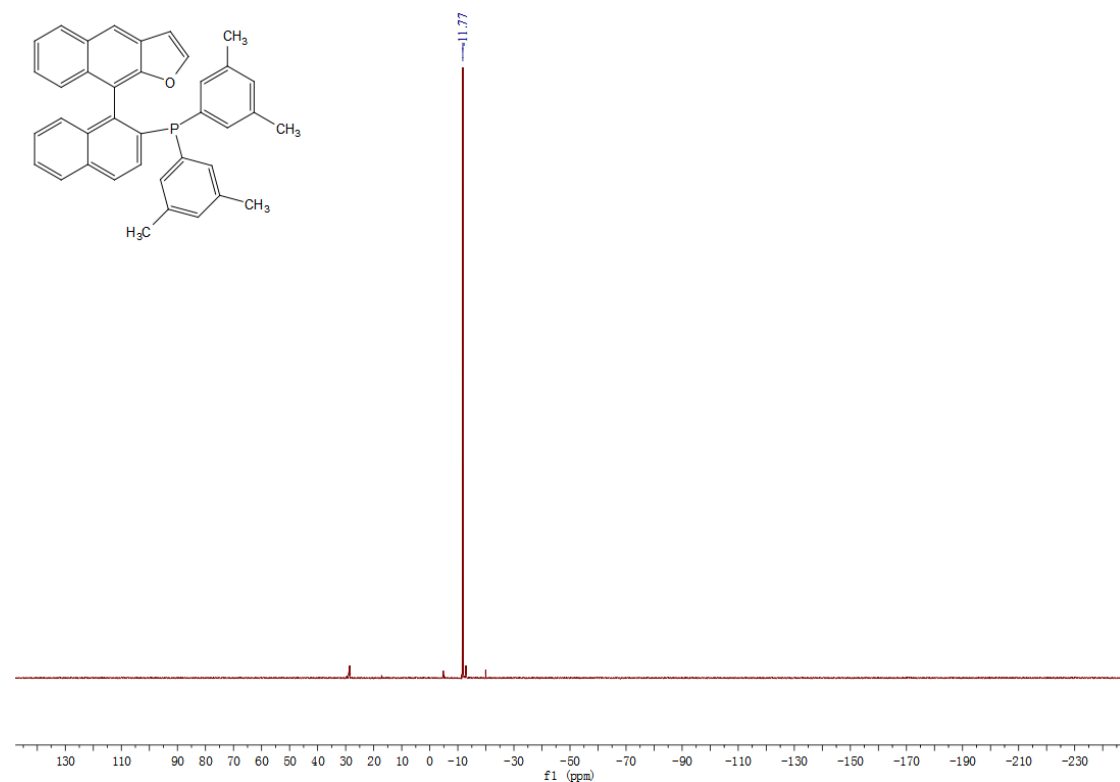
$^1\text{H-NMR}$ (400 MHz, CDCl_3)



$^{13}\text{C-NMR}$ (101 MHz, CDCl_3)

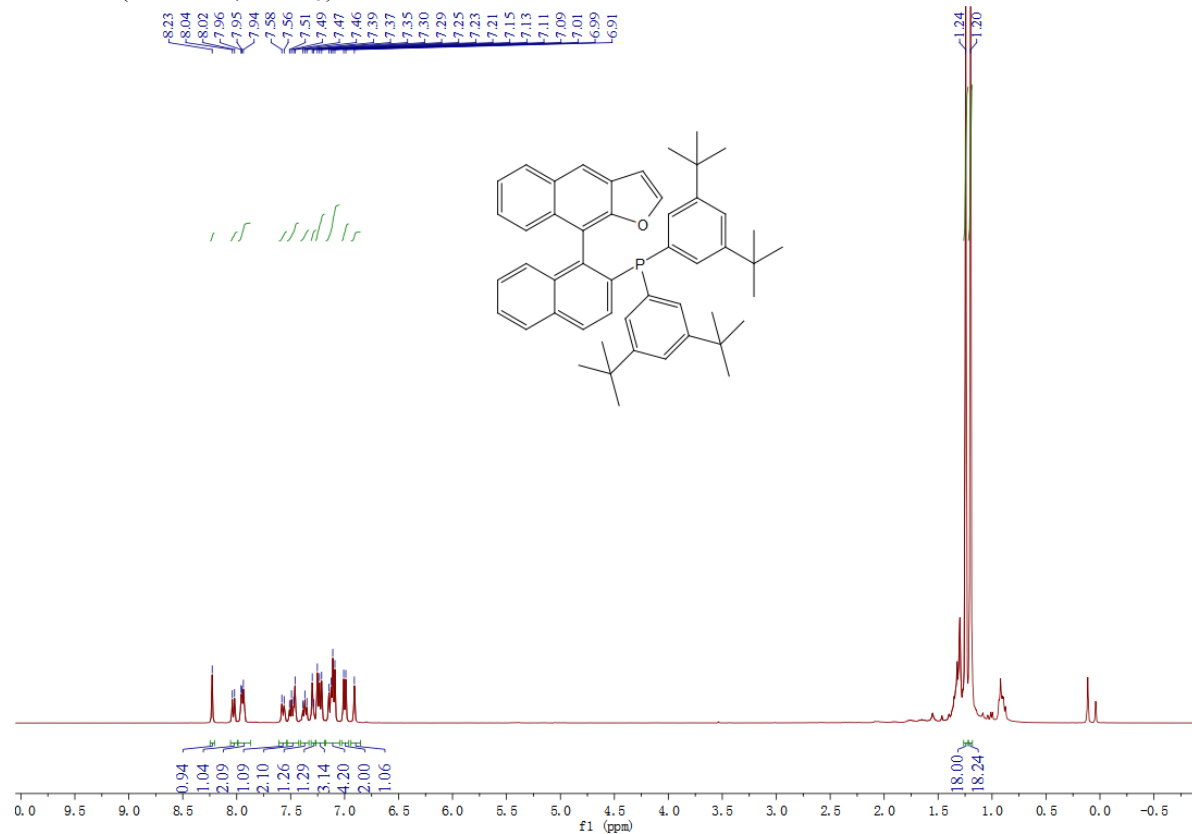


^{31}P NMR (162 MHz, CDCl_3)

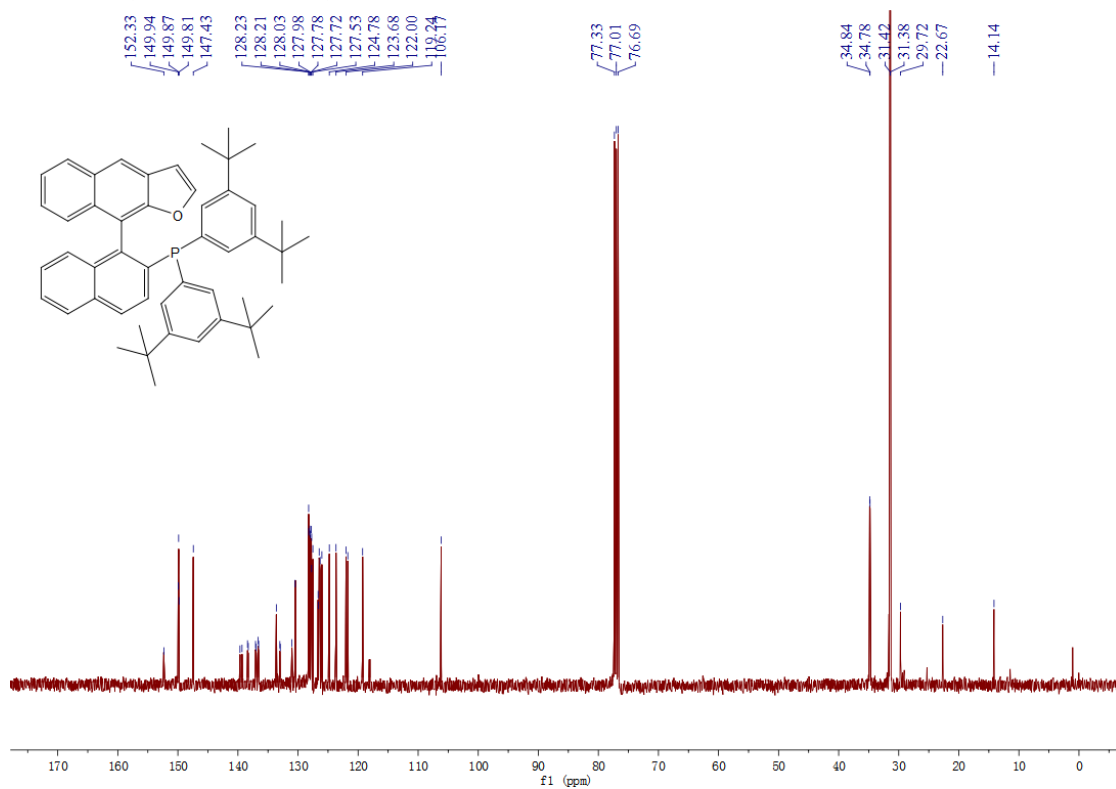


bis(3,5-di-*tert*-butylphenyl)(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)phosphine (L4):

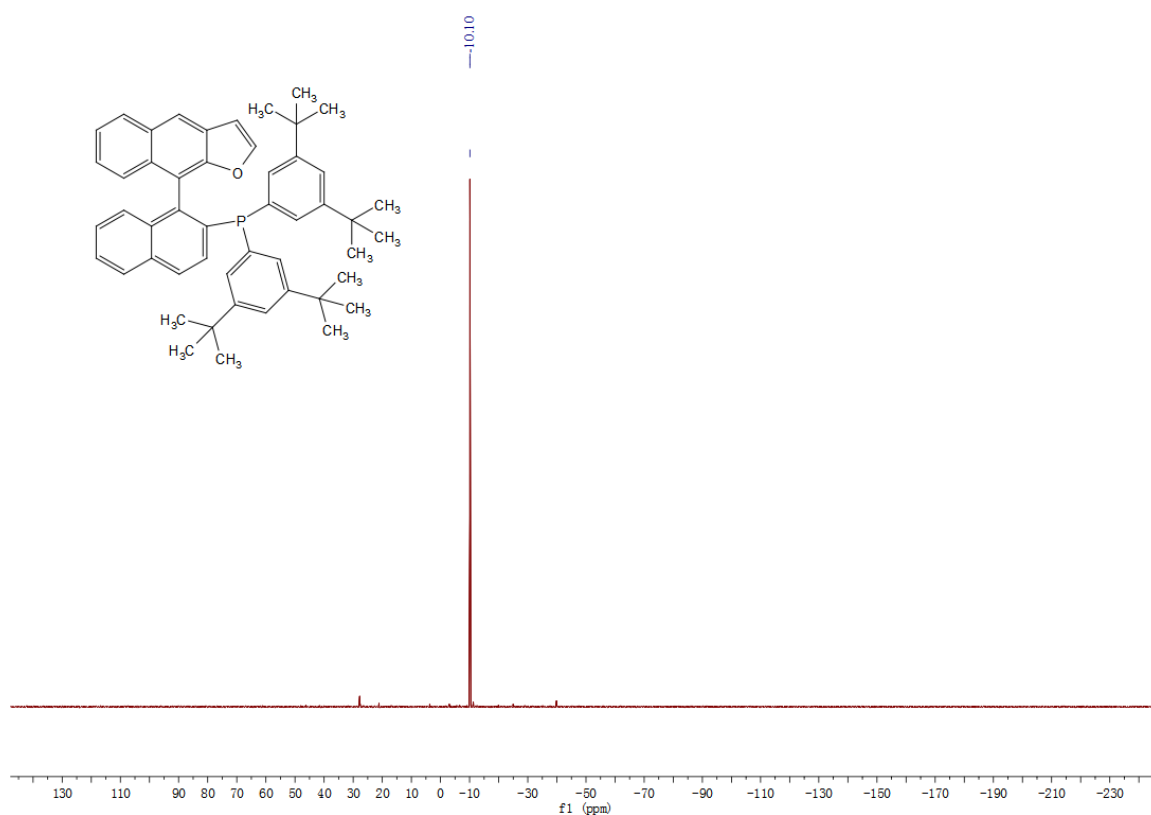
^1H -NMR (400 MHz, CDCl_3)



^{13}C -NMR (101 MHz, CDCl_3)

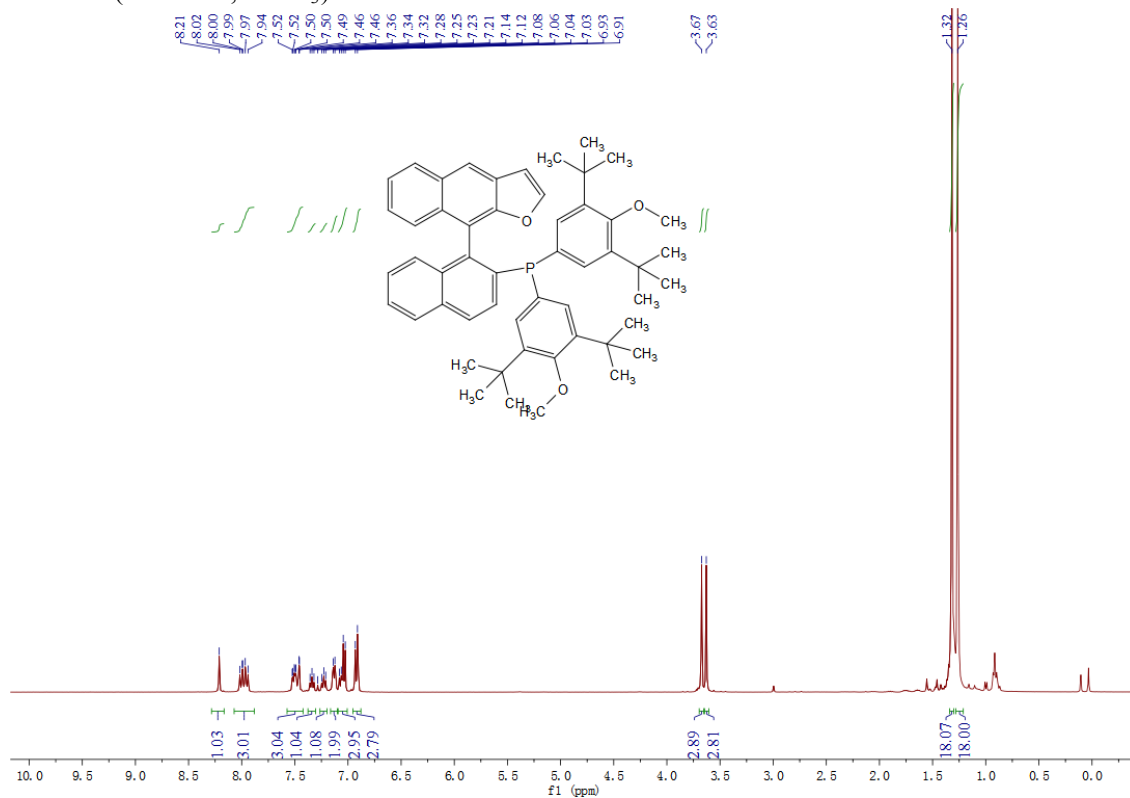


^{31}P NMR (162 MHz, CDCl_3)

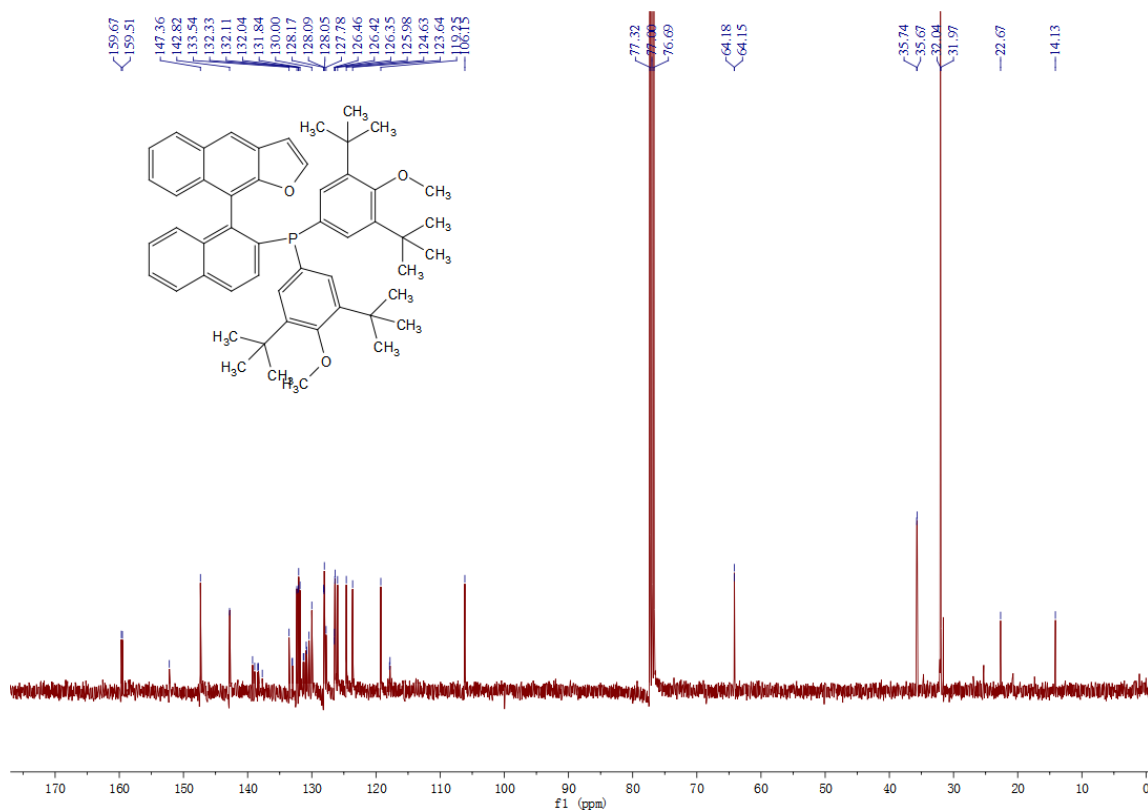


bis(3,5-di-*tert*-butyl-4-methoxyphenyl)(1-(naphtho[2,3-*b*]furan-9-yl)naphthalen-2-yl)phosphine (L5):

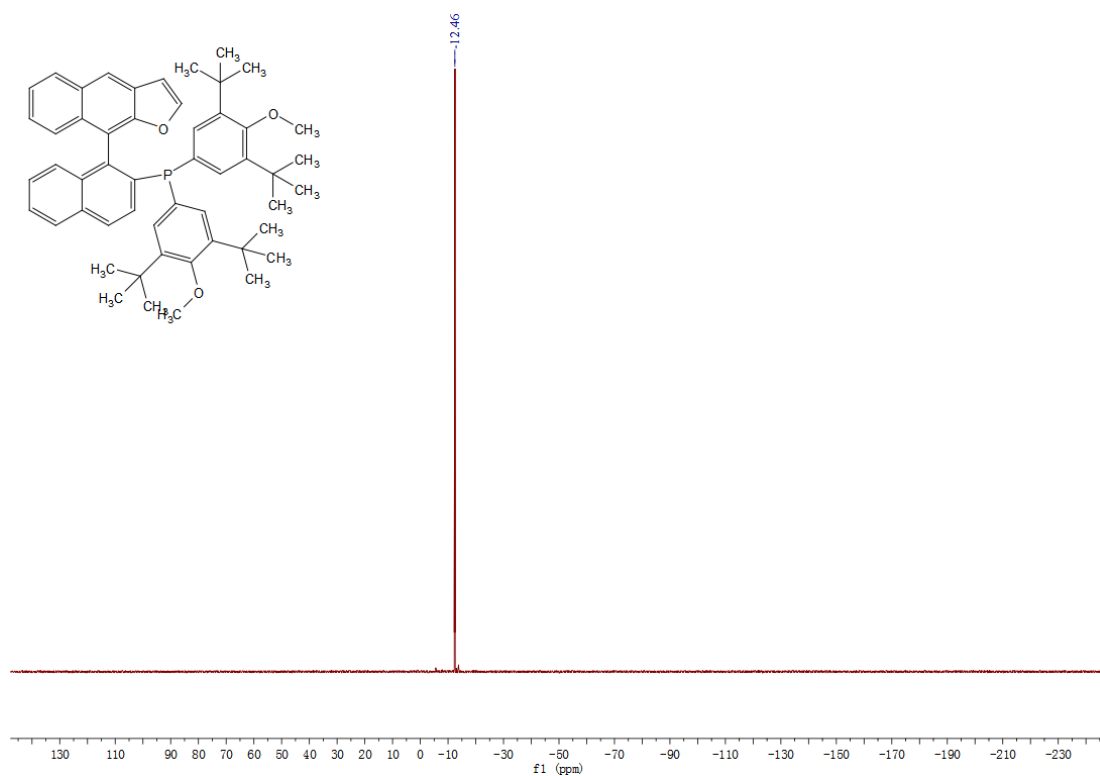
¹H-NMR (400 MHz, CDCl₃)



¹³C-NMR (101 MHz, CDCl₃)

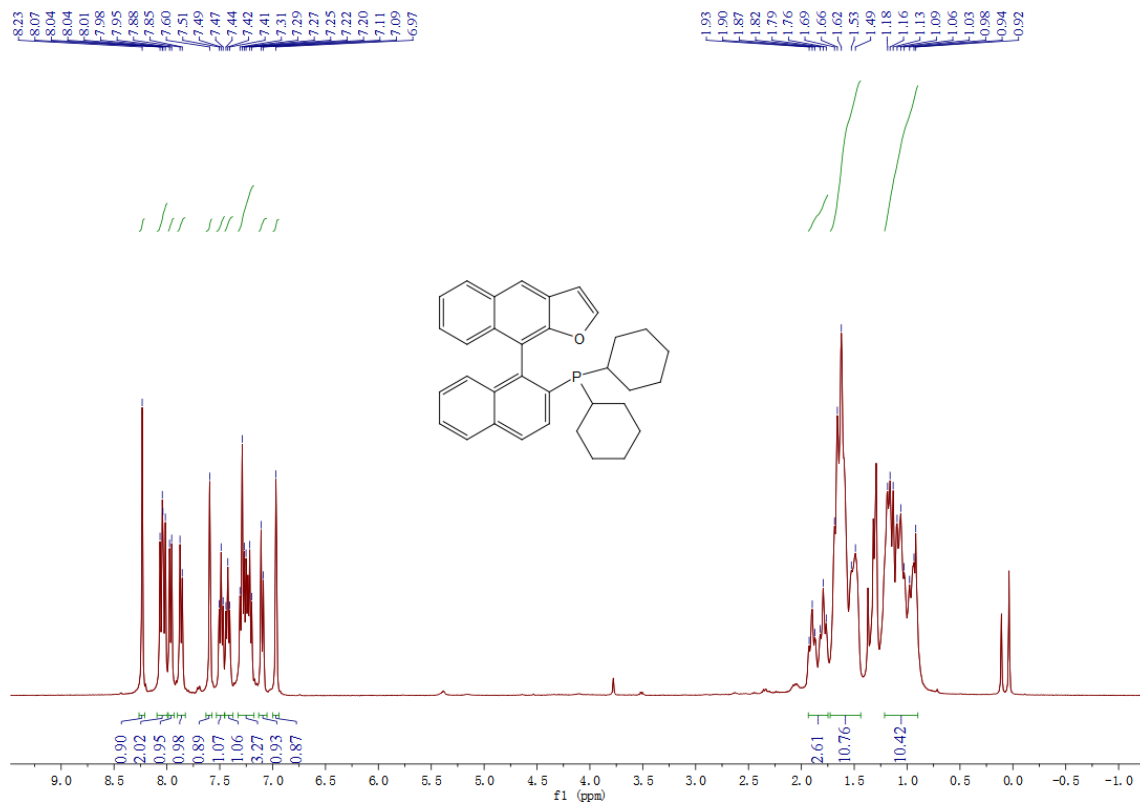


^{31}P NMR (162 MHz, CDCl_3)

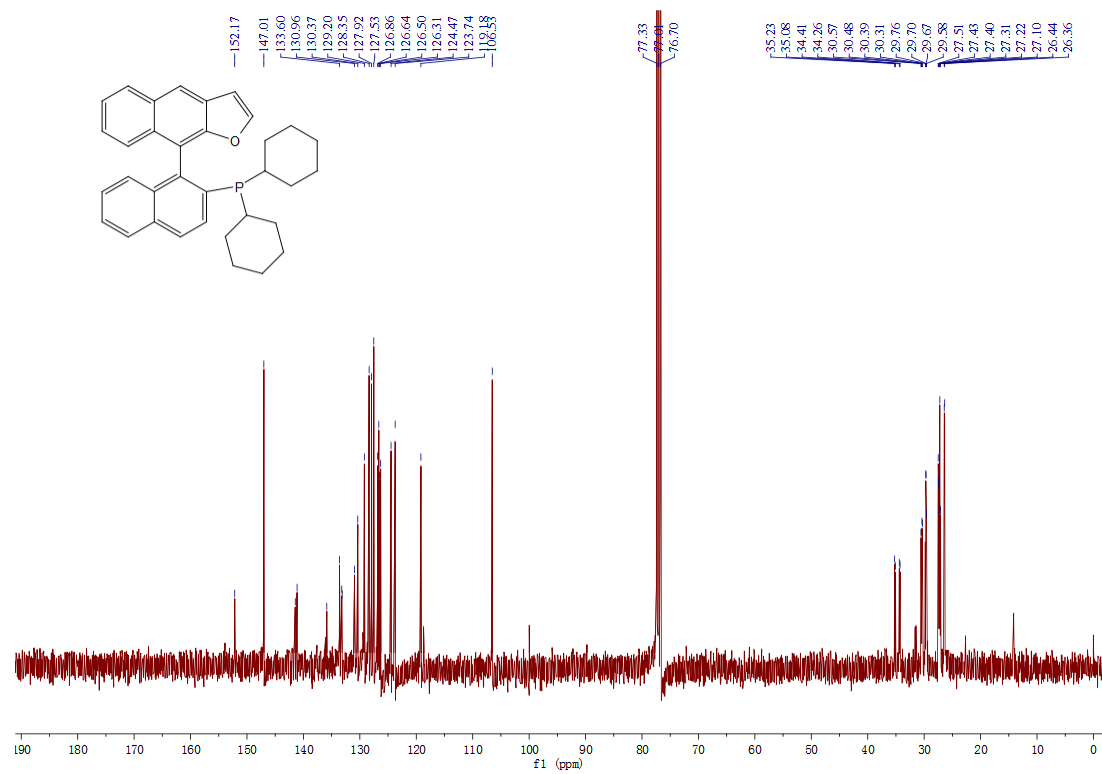


dicyclohexyl(1-(naphtho[2,3-b]furan-9-yl)naphthalen-2-yl)phosphine (L6):

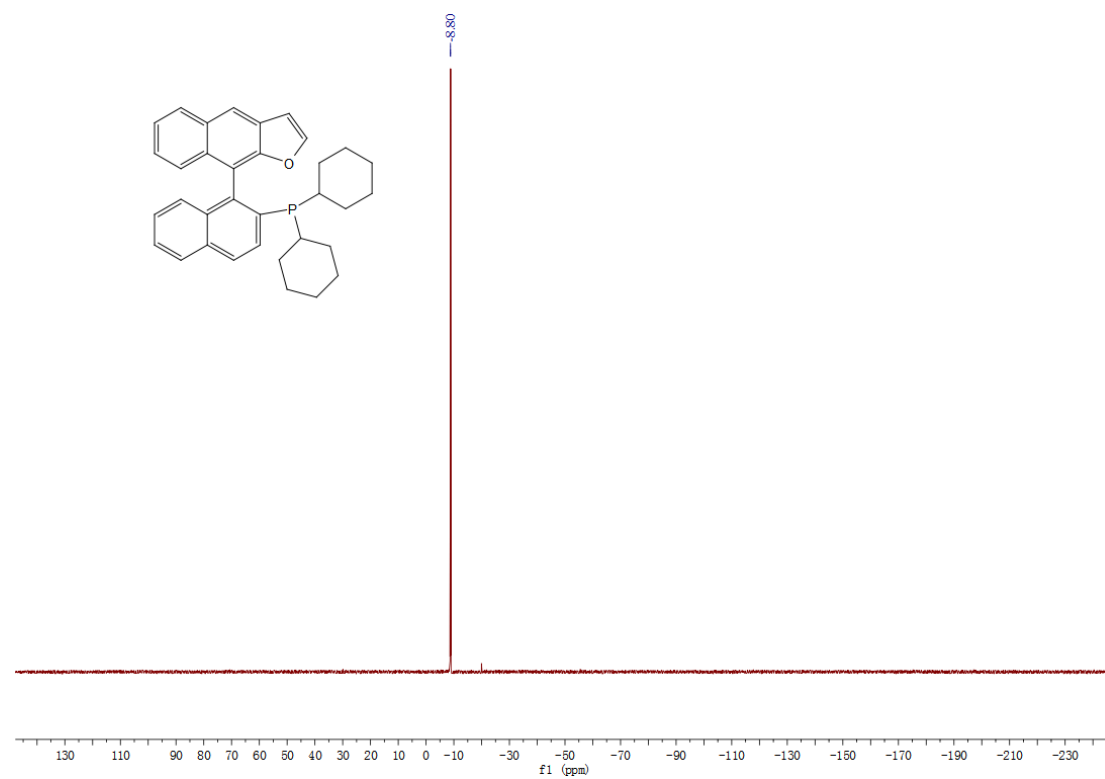
^1H -NMR (400 MHz, CDCl_3)



^{13}C -NMR (101 MHz, CDCl_3)

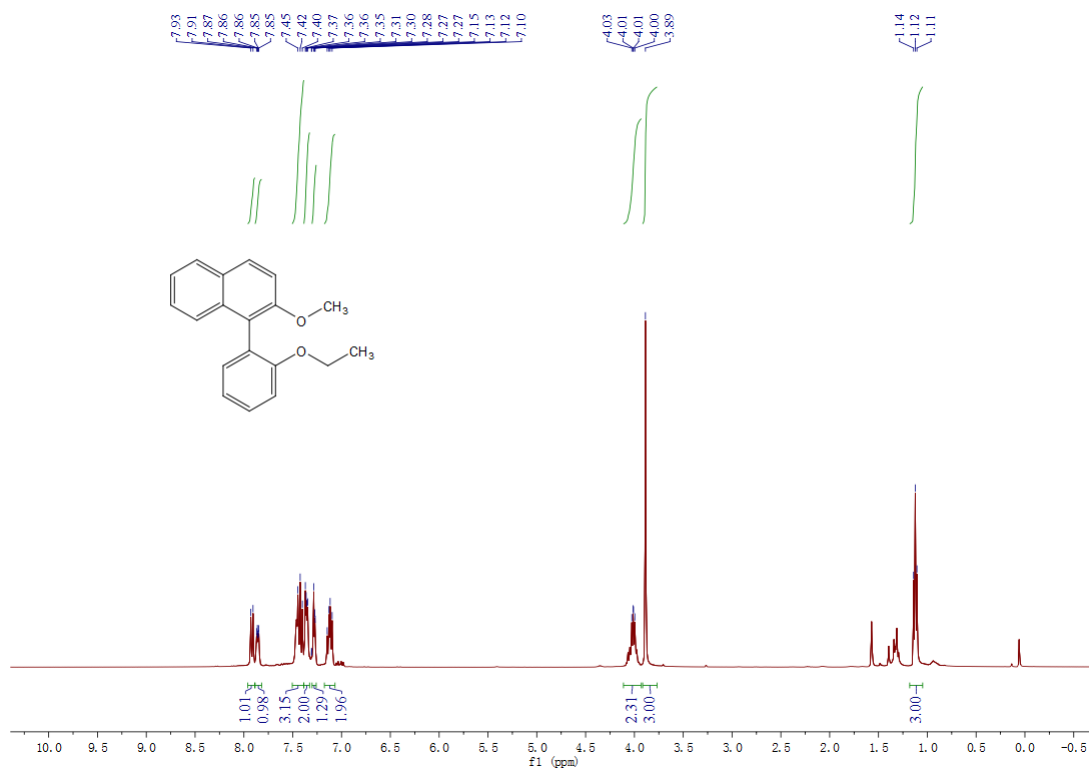


^{31}P NMR (162 MHz, CDCl_3)

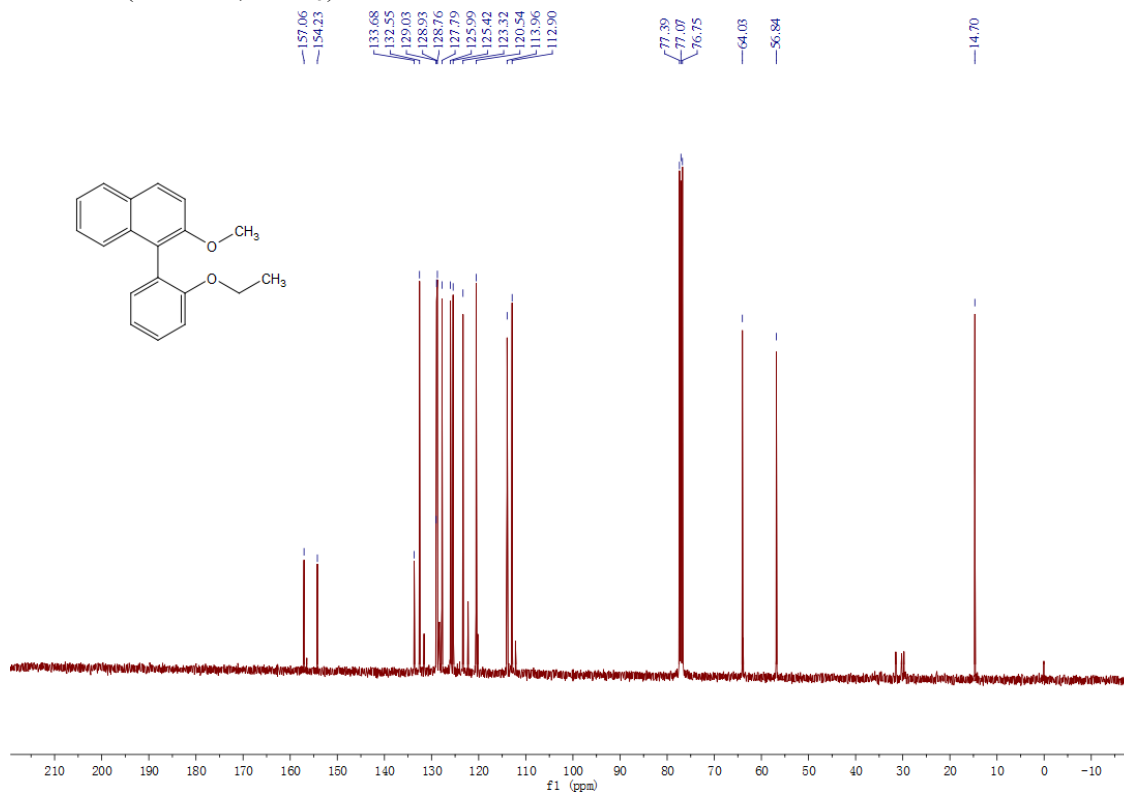


1-(2-ethoxyphenyl)-2-methoxynaphthalene (AB₁):

¹H-NMR (400 MHz, CDCl₃)

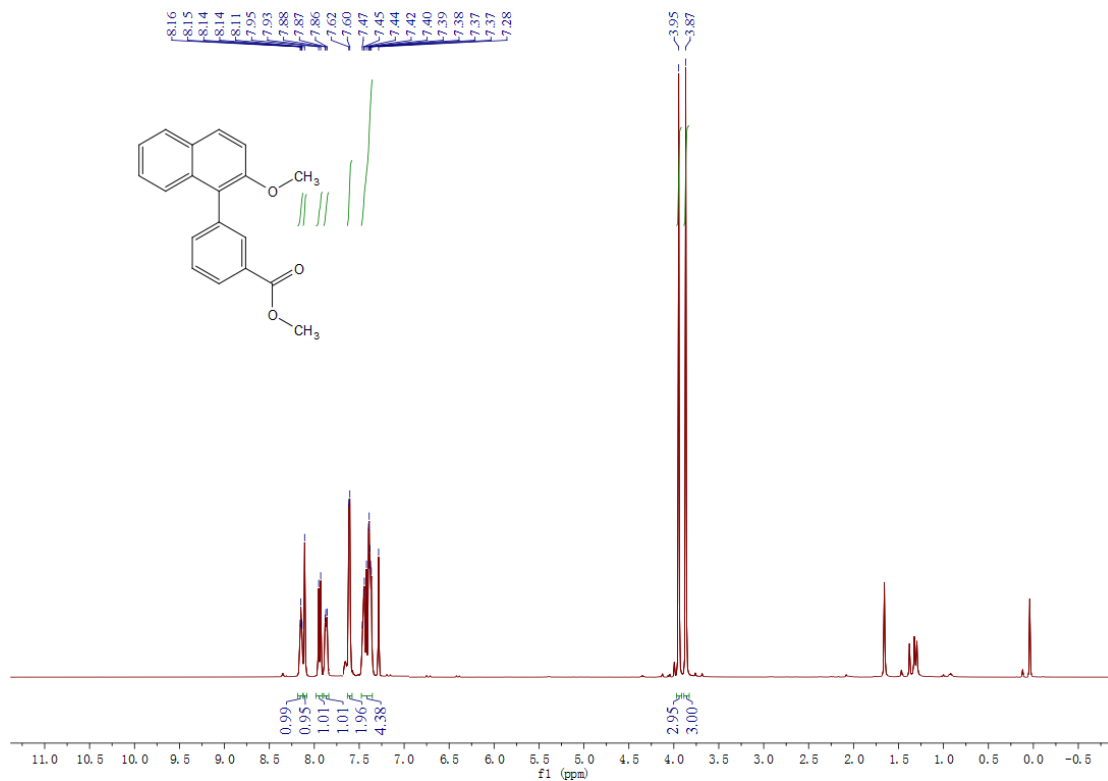


¹³C-NMR (101 MHz, CDCl₃)

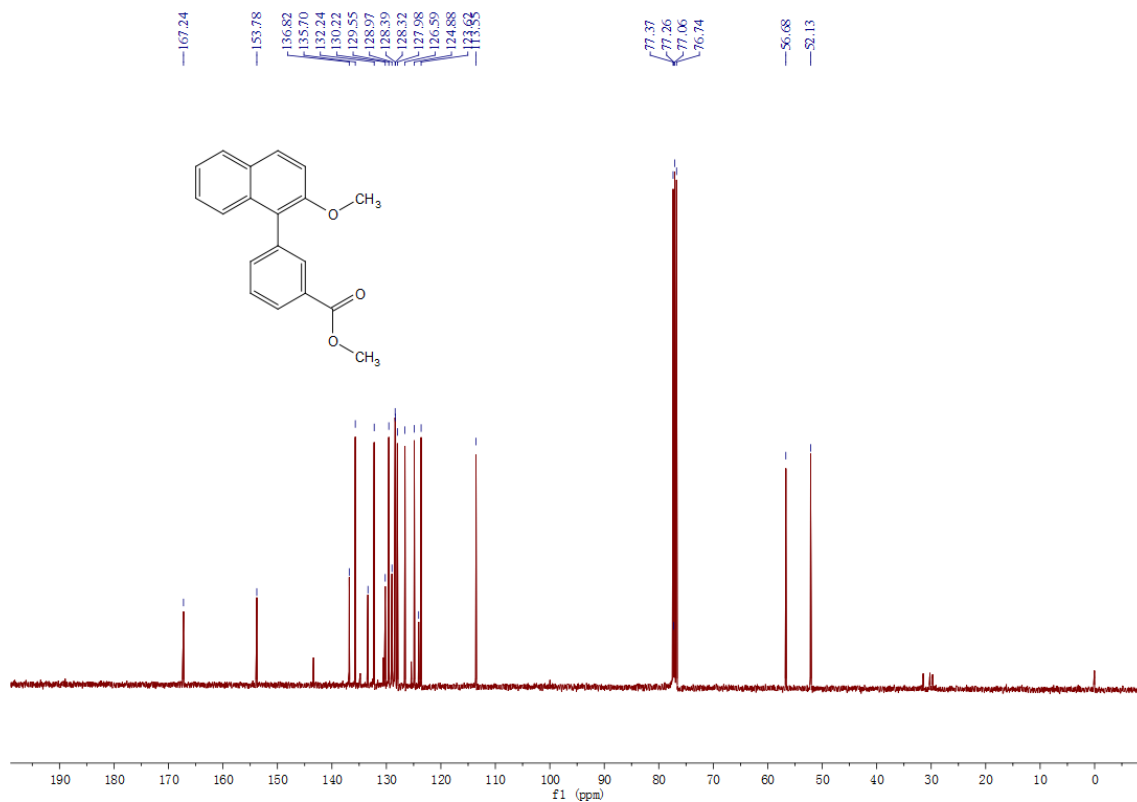


methyl 3-(2-methoxynaphthalen-1-yl)benzoate (AB₁₄):

¹H-NMR (400 MHz, CDCl₃)

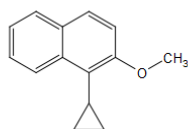
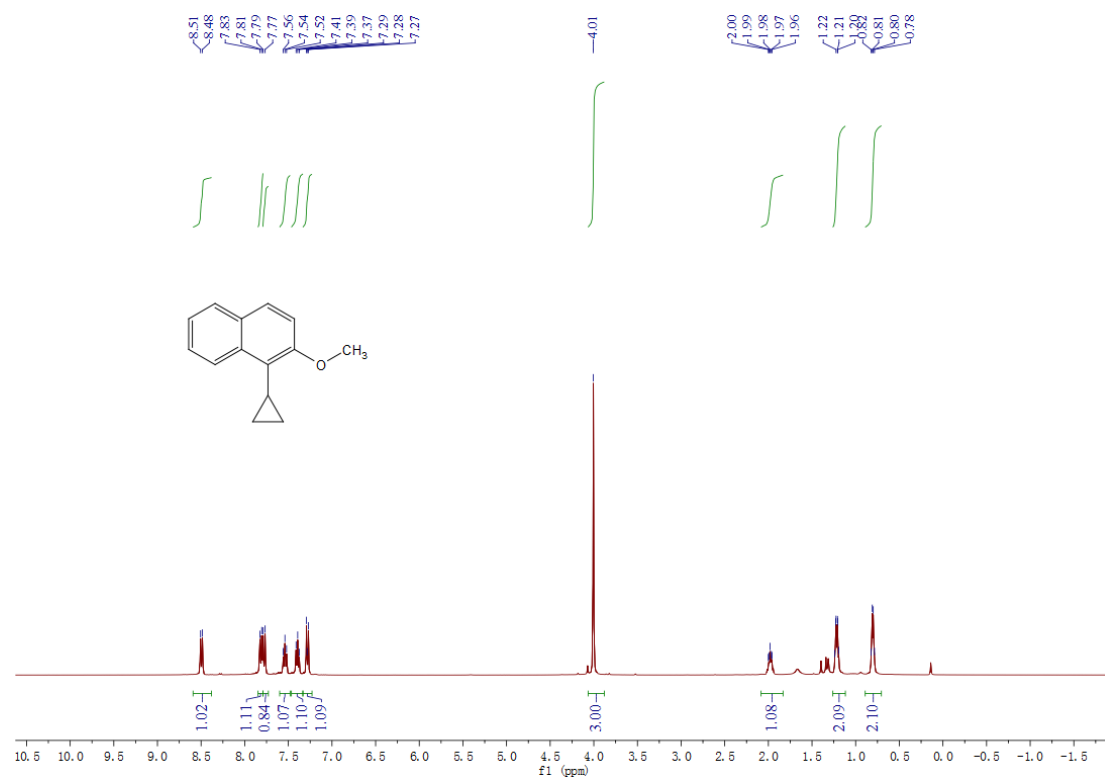


¹³C-NMR (101 MHz, CDCl₃)

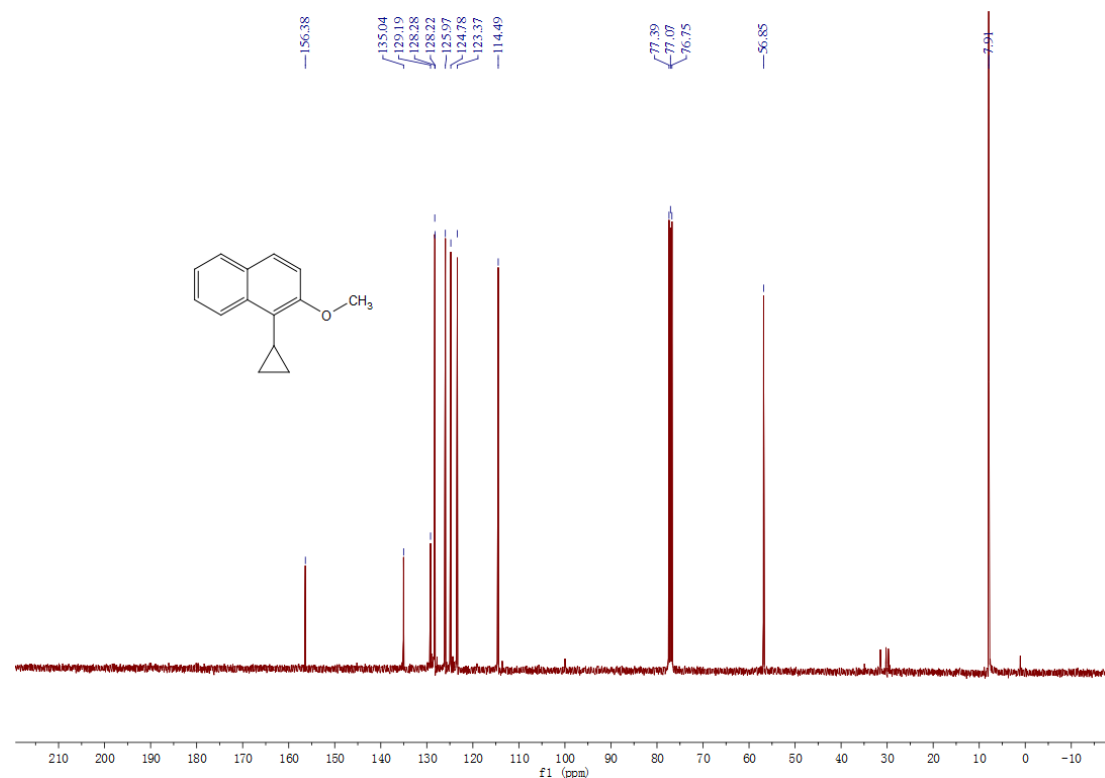


1-cyclopropyl-2-methoxynaphthalene (AB₁₅):

¹H-NMR (400 MHz, CDCl₃)

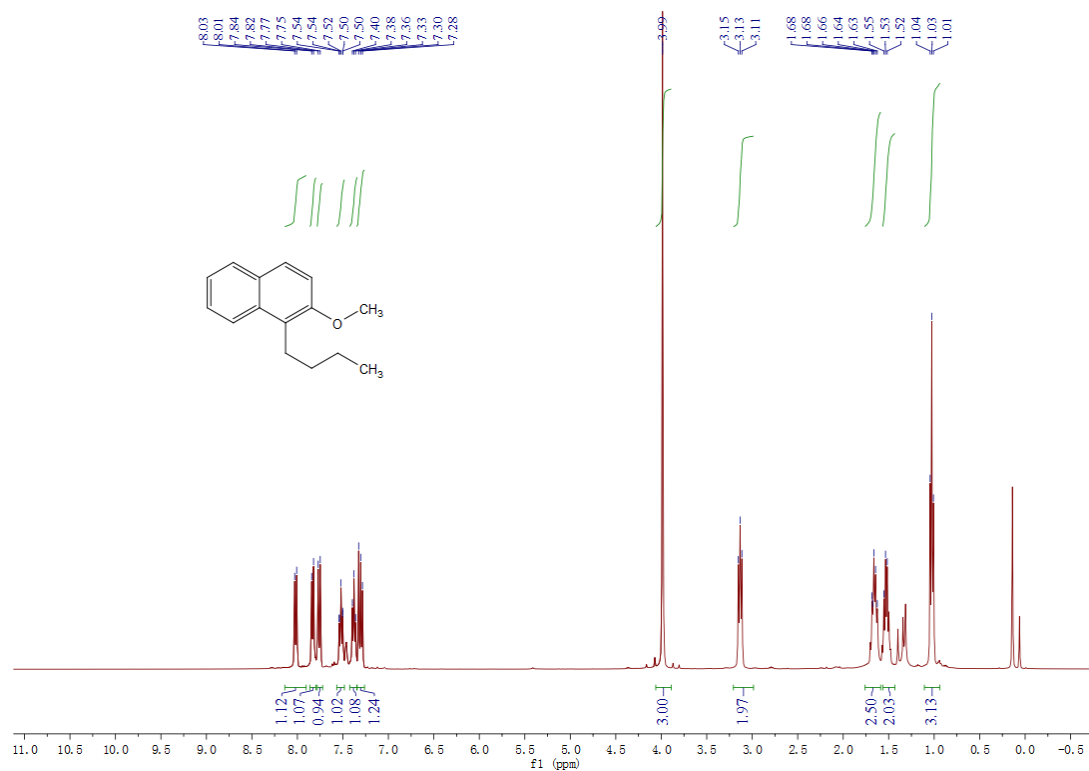


¹³C-NMR (101 MHz, CDCl₃)

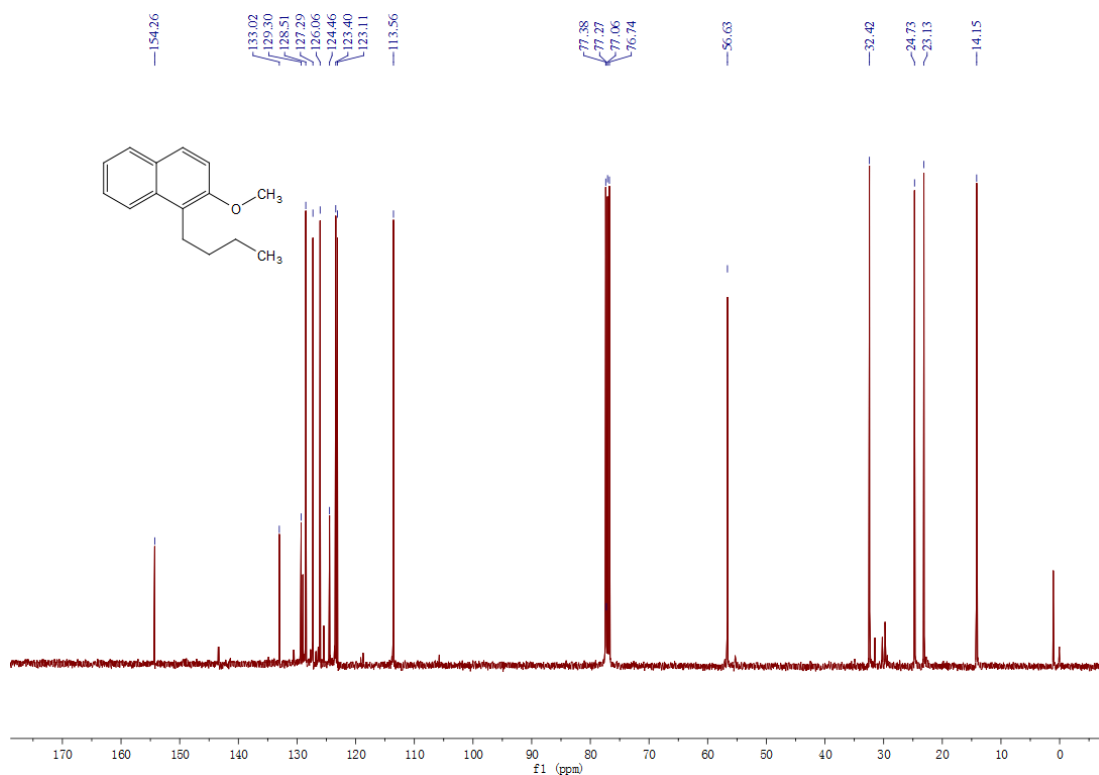


1-butyl-2-methoxynaphthalene (AB₁₆):

¹H-NMR (400 MHz, CDCl₃)

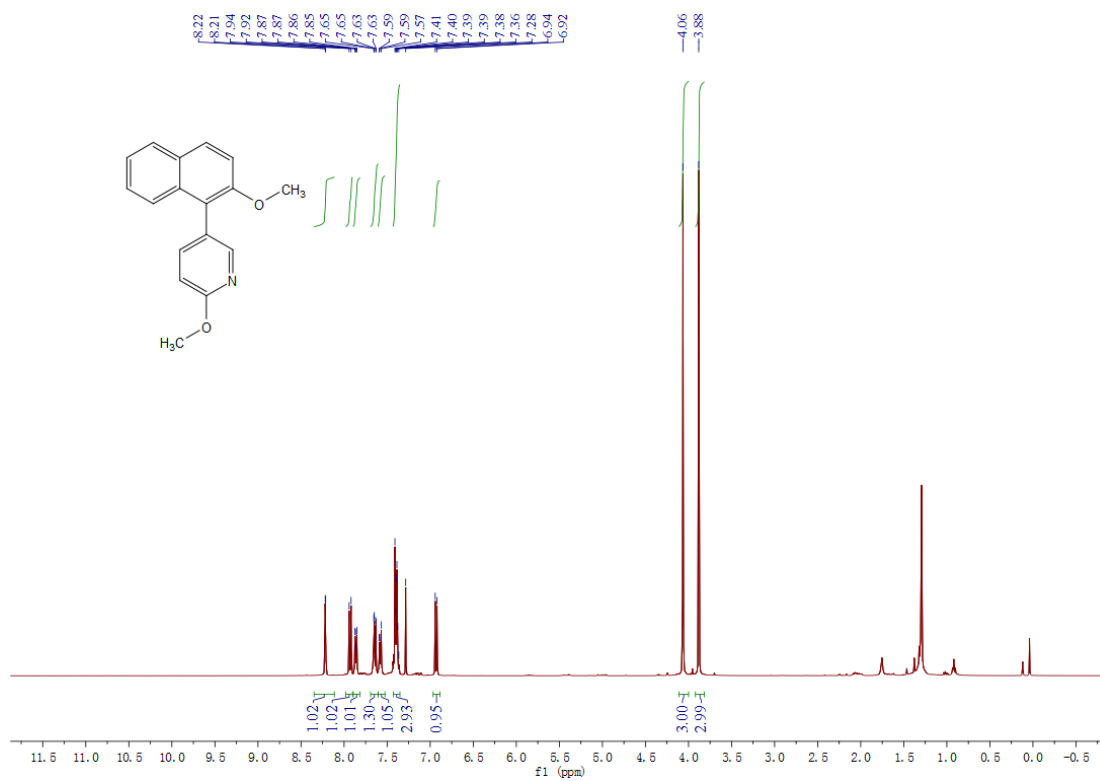


¹³C-NMR (101 MHz, CDCl₃)

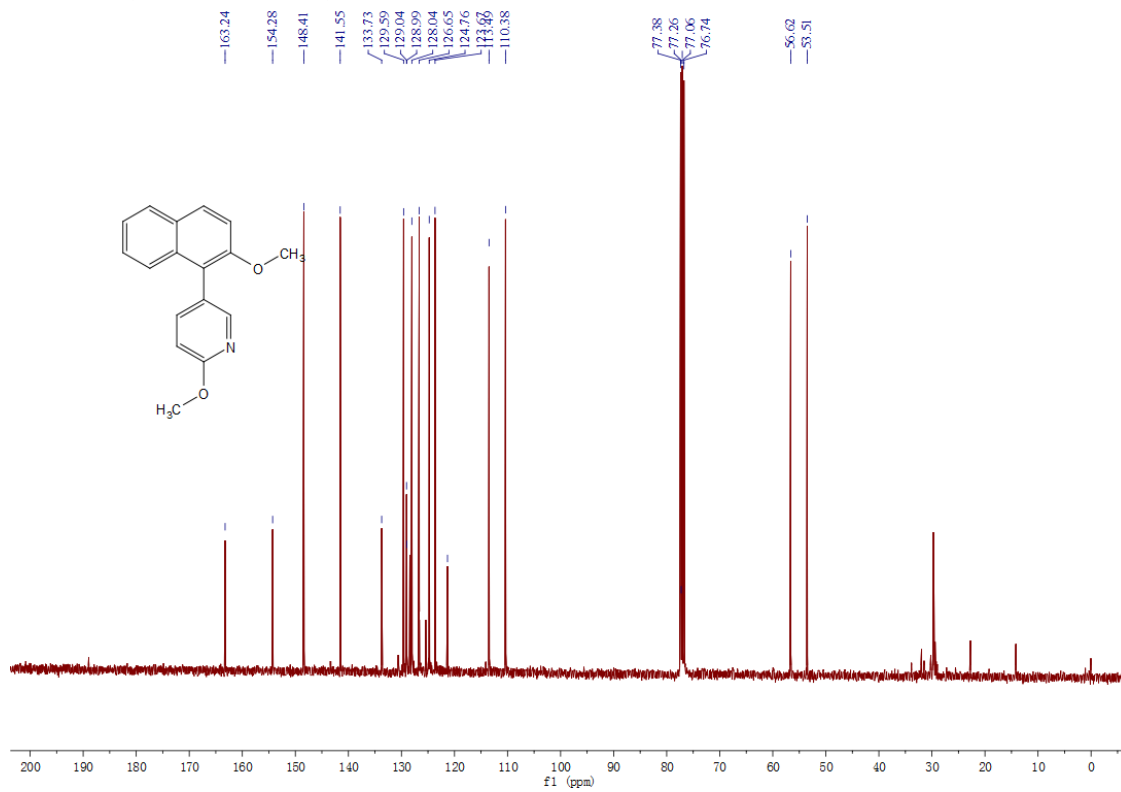


2-methoxy-5-(2-methoxynaphthalen-1-yl)pyridine (AB₁₈):

¹H-NMR (400 MHz, CDCl₃)

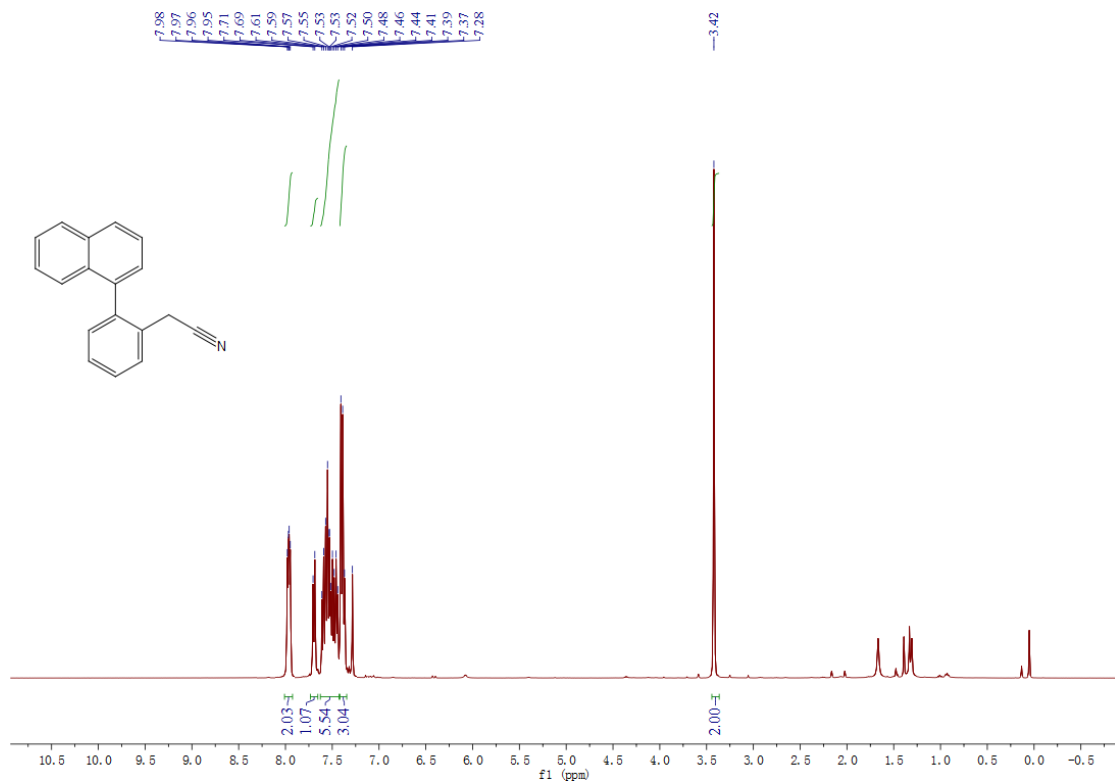


¹³C-NMR (101 MHz, CDCl₃)

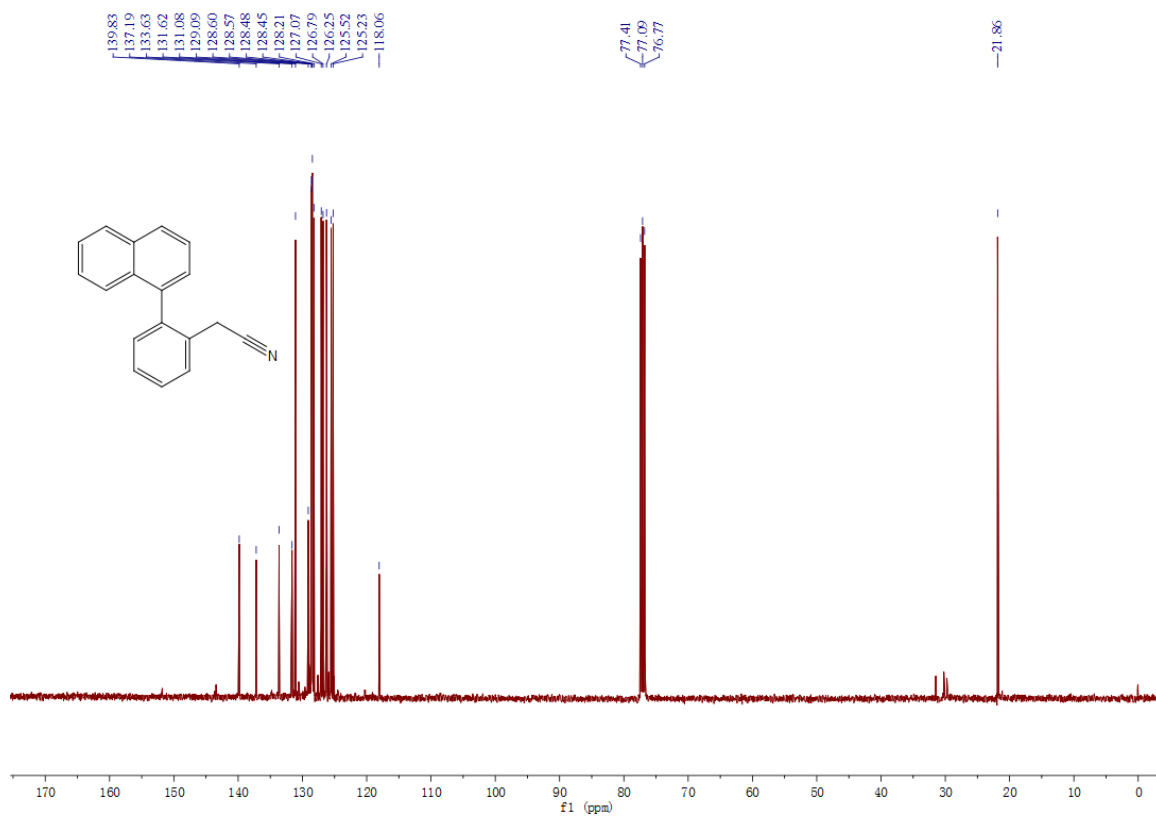


2-(2-(naphthalen-1-yl)phenyl)acetonitrile (A4B):

$^1\text{H-NMR}$ (400 MHz, CDCl_3)

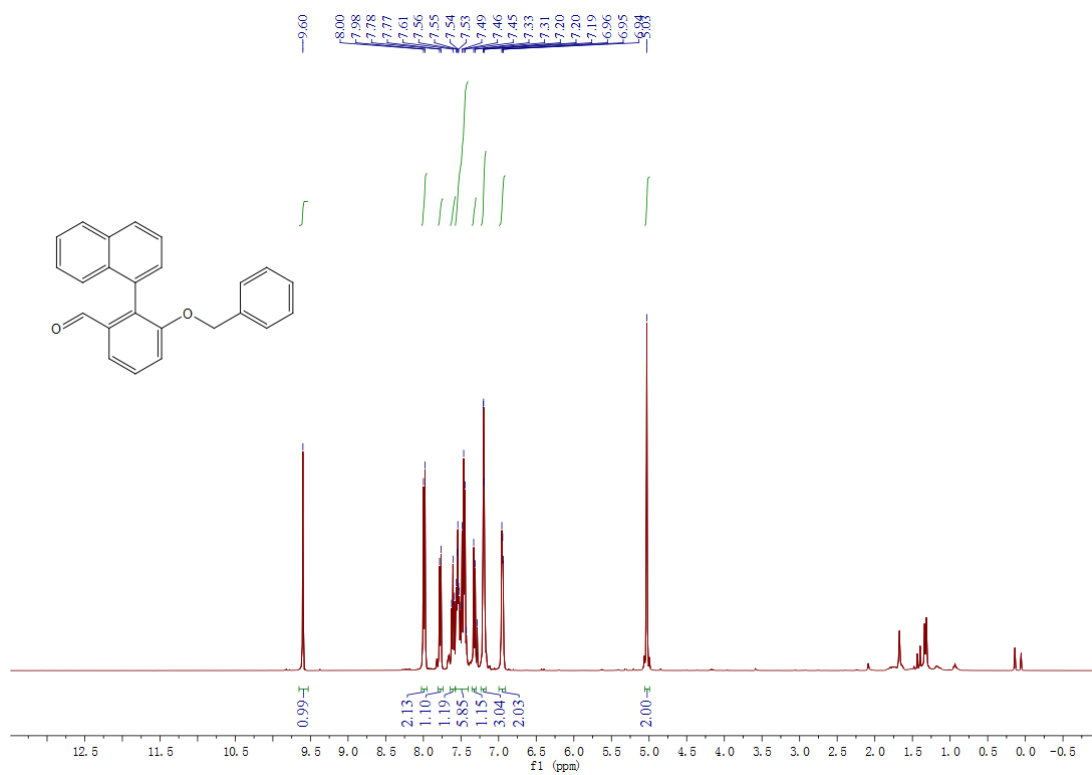


$^{13}\text{C-NMR}$ (101 MHz, CDCl_3)

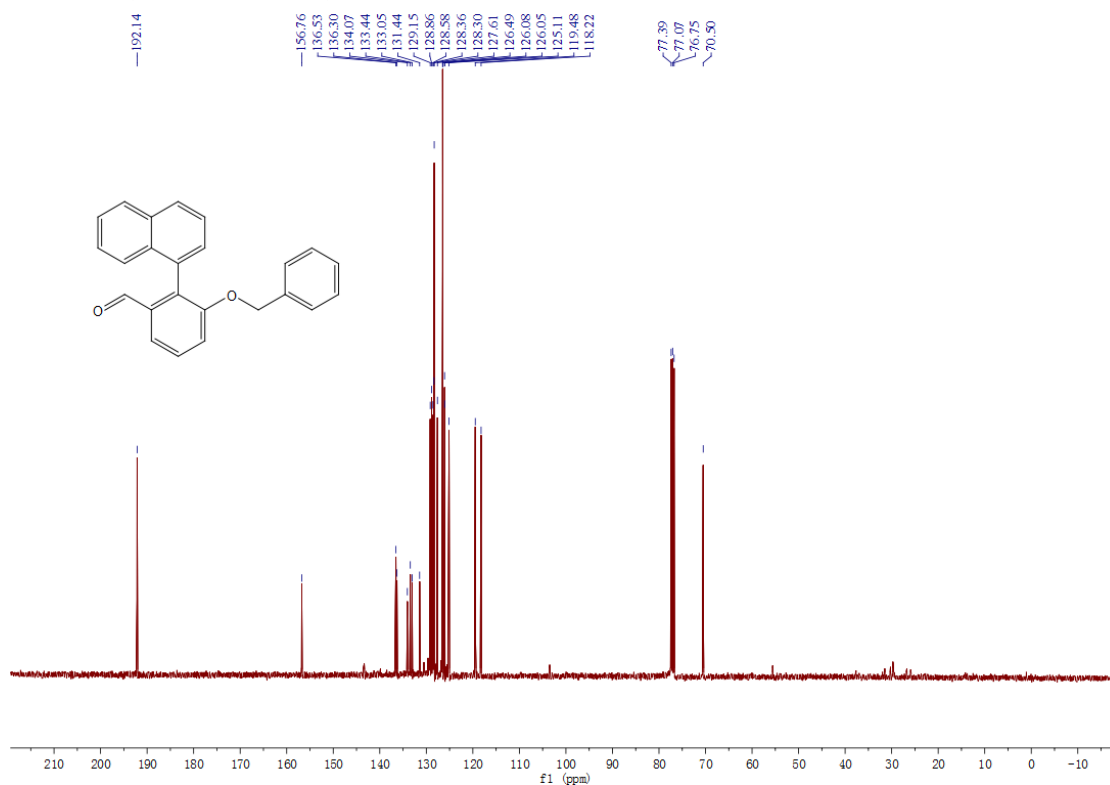


3-(benzyloxy)-2-(naphthalen-1-yl)benzaldehyde (A₁₂B):

¹H-NMR (400 MHz, CDCl₃)

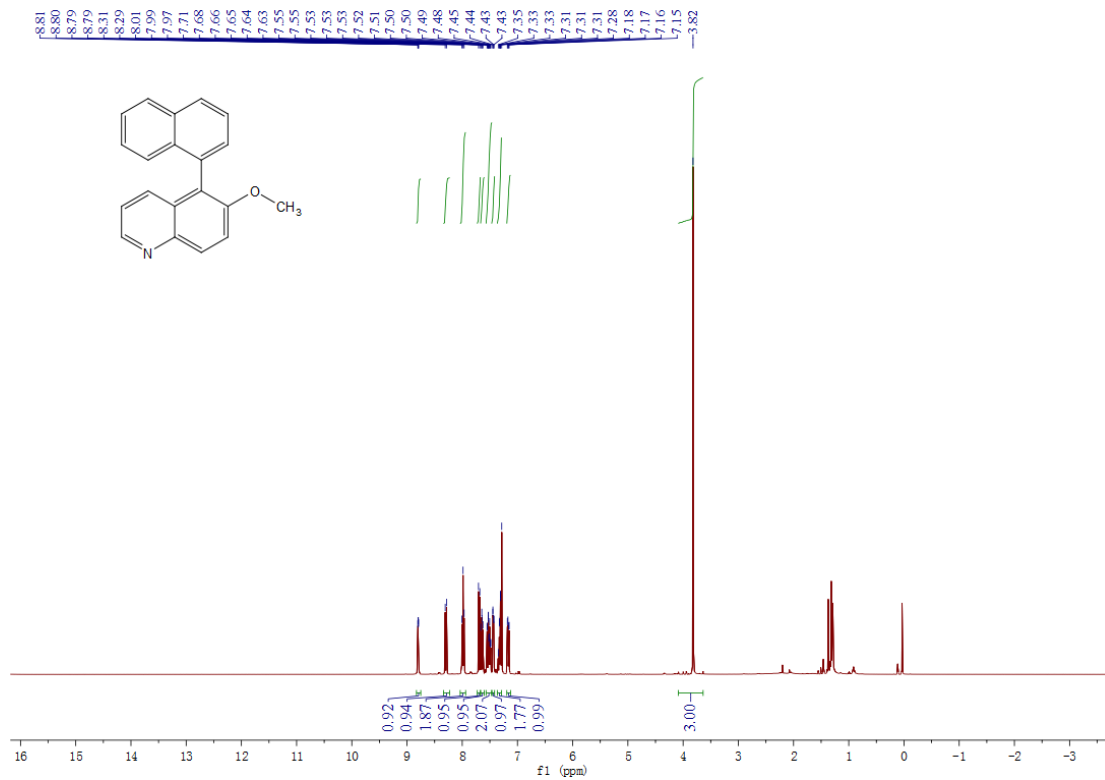


¹³C-NMR (101 MHz, CDCl₃)

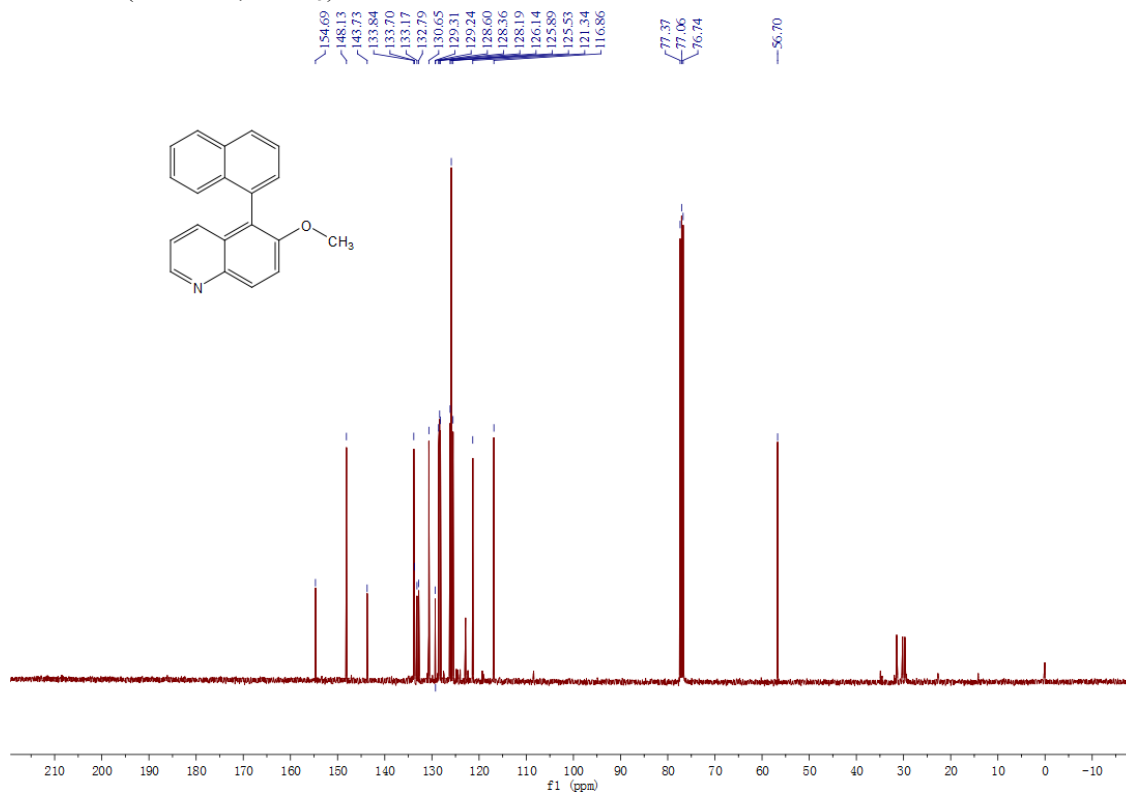


6-methoxy-5-(naphthalen-1-yl)quinoline (A₁₄B):

¹H-NMR (400 MHz, CDCl₃)

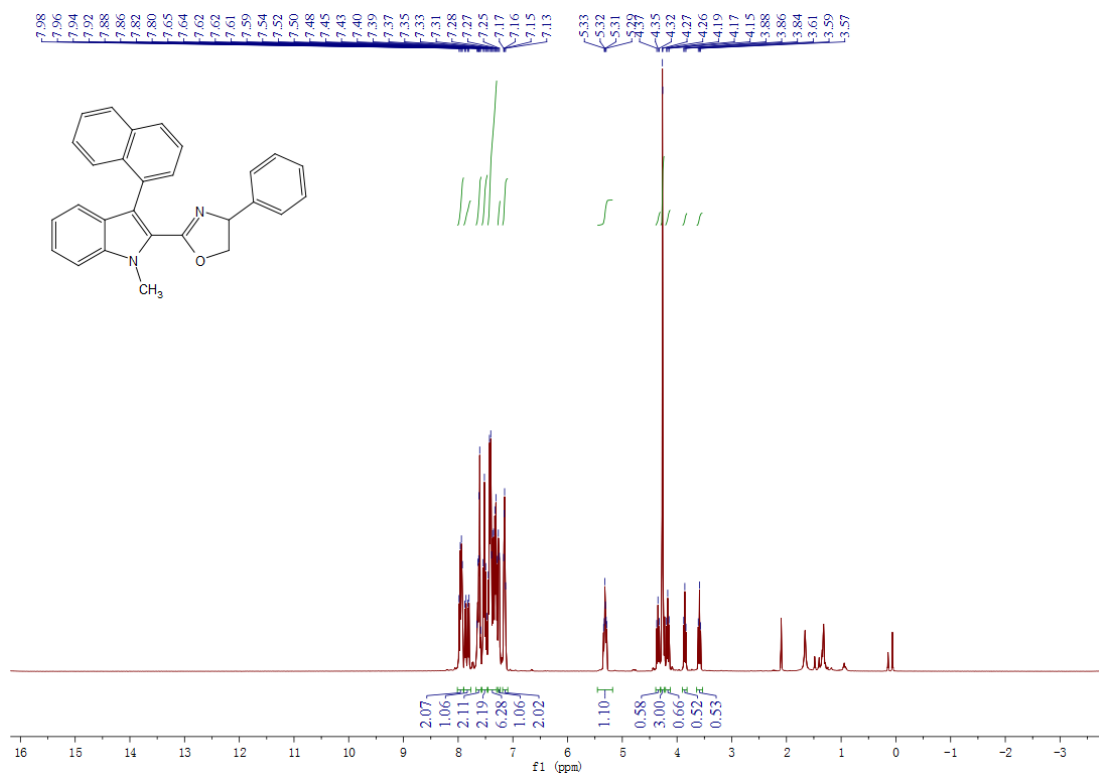


¹³C-NMR (101 MHz, CDCl₃)



2-(1-methyl-3-(naphthalen-1-yl)-1H-indol-2-yl)-4-phenyl-4,5-dihydrooxazole (A₁₆B):

¹H-NMR (400 MHz, CDCl₃)



¹³C-NMR (101 MHz, CDCl₃)

