

Supporting Information

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Supporting Information for

A Novel (2,2-Diarylvinyl)phosphine/Palladium Catalyst for Effective Aromatic Amination.

Ken Suzuki, Yoji Hori, Takenobu Nishikawa and Tohru Kobayashi

Sections Include:

- 1) General Information
- 2) Typical Procedure for the Preparation of Diarylvinylphosphines
- 3) Typical Procedure for the Coupling Reaction of Aryl halides with Amines
- 4) NMR-Spectra

General Information

All reactions were carried out under nitrogen atmosphere. All solvents and reagents were used without further purification from commercial sources. 1 H, 13 C, 19 F and 31 P NMR spectra were taken on Varian Gemini-2000 (200 MHz), Varian Mercury Plus3004N (300 MHz) or Bruker DRX-500 (500 MHz). Chemical shifts are reported in parts per million (δ value) from tetramethylsilane (δ = 0 ppm for 1H), the middle peaks of the solvent (CDCl₃) (δ = 77.00 ppm for 13 C), trifluorotoluene (δ = -64 ppm for 19 F) or phosphoric acid (δ = 0 ppm for 31 P). All high resolution mass spectra were taken on Shimadzu LCMS-IT-TOF.

Typical procedure for the Preparation of Diarylvinylphosphines

Scheme 1: A Synthetic Route of the Diarylvinylphosphines

1,1-Diphenylpropene (11):

To a stirred solution of magnesium (96.0 g, 3.95 mol) in THF (500 mL) was added dropwise a solution of bromobenzene (677 g, 4.31 mol) in THF (1500 mL) at 40 °C. Then the mixture was refluxed for 1 hr. After cooling down to 40 °C, methyl propionate

(1.59 mol, 140 g) was added with keeping at the same temperature. After the mixture was stirred at 60 °C for 3 hr and cooled to room temperature, the resulting solution was washed with 0.1 M aqueous HCl, saturated aqueous NaHCO₃ and brine in this order, dried over anhydrous MgSO₄ and concentrated under reduced pressure. The concentrate was dissolved with toluene (8 mL). Azeotropic dehydration was carried out with *p*-toluenesulfonic acid (3.8 g) for 1.5 hr at refluxing. After cooling, the toluene solution was washed with saturated aqueous NaHCO₃ and brine, dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by recrystallization from methanol to give the title compound (230 g, 75 %) as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 1.76 (d, J=7.2 Hz, 3H), 6.17 (q, J=7.1 Hz, 1H), 7.14-7.41 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 15.7, 124.1, 126.7, 126.8, 127.2, 128.0, 128.1, 130.0, 134.0, 142.4, 142.9.

2-Bromo-1,1-diphenylpropene (12):

To a solution of 1,1-diphenylpropene **11** (19.4 g, 100 mmol) in 1,2-dichloroethane (78 mL) was slowly added bromine (15.9 g, 100 mmol) at 0 °C. After stirring at room temperature for 1 hr, the reaction solution was added to a solution of pyridine (32.4 mL, 400 mmol) in toluene (156 mL). The mixture was stirred at 80 °C for 3 hr and cooled down to room temperature. And the mixture was washed with saturated aqueous NaHCO₃ and brine, dried over MgSO₄ and concentrated under reduced pressure. The concentrate was purified by column chromatography on silica gel and recrystallization from methanol to give the title compound (14.5 g, 53%) as a white solid.

¹H NMR (300 MHz, CDCl₃) δ 2.43 (s, 3H), 7.14-7.35 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 27.4, 121.2, 127.1, 127.2, 128.0, 128.3, 129.1, 129.2, 140.7, 141.7, 143.2.

1,1-Diphenyl-2-(diphenylphosphino)propene (3a):

To a solution of 2-bromo-1,1-diphenylpropene **12** (1.37 g, 5.00 mmol) in THF (14 mL) was added dropwise butyllithium (3.4 mL of a 1.6 M hexane solution, 5.5 mmol) at -70 °C. After 30 min, chlorodiphenylphosphine (1.1 mL, 6.0 mmol) was slowly added to the reaction solution, which was stirred for 30 min, gradually warmed to room temperature and additionally stirred for 13 hr. Water was added to the reaction solution and the organic phase was extracted with EtOAc. The extract was dried over MgSO₄ and concentrated under reduced pressure. The concentrate was purified by recrystallization from ethanol to give the title compound (1.08 g, 60 %) as a white solid. 1 H NMR (500 MHz, CDCl₃) δ 1.70 (d, J=2.9 Hz, 3H), 7.15-7.26 (m, 8H), 7.28-7.42 (m, 12H); 13 C NMR (125 MHz, CDCl₃) δ 19.7 (d, J = 3.8 Hz), 127.0, 127.3, 127.6, 128.0,

128.26, 128.30, 129.3, 129.6 (d, J = 4.5 Hz), 131.2 (d, 16.6 Hz), 133.1 (d, J = 18.8 Hz), 137.9 (d, J = 14.6 Hz), 142.6 (d, J = 9.3 Hz), 143.1 (d, J = 11.0 Hz), 155.5 (d, J = 35.0 Hz); 31 P NMR (202 MHz, CDCl₃) δ -4.68; HRMS (ESI) m/z calcd for $C_{27}H_{23}P$ [M+H]⁺ 379.1616, found [M+H]⁺ 379.1625.

1,1-Diphenyl-2-(di-iso-propylphosphino)propene (3b):

¹H NMR (300 MHz, CDCl₃) δ 1.07 (dd, J = 2.0, 7.1 Hz, 6H), 1.12 (dd, J = 5.7, 6.3 Hz, 6H), 1.86 (d, J = 2.1 Hz, 3H), 1.80-2.04 (m, 2H), 7.08-7.33 (m, 10H); ¹³C NMR (75 MHz, CDCl₃) δ 17.2 (d, J = 4.6 Hz), 20.8 (d, J = 1.1 Hz), 21.0 (d, J = 8.0 Hz), 24.4 (d, J = 14.3 Hz), 126.4, 126.5, 127.5, 128.1, 128.6, 130.2 (d, J = 3.5 Hz), 133.4 (d, J = 21.6 Hz), 143.5 (d, J = 8.6 Hz), 143.9 (d, J = 10.3 Hz), 155.3 (d, J = 32.0 Hz); ³¹P NMR (121 MHz, CDCl₃) δ 5.44; HRMS (ESI) m/z calcd for C₂₁H₂₇P [M+H]⁺ 311.1929, found [M+H]⁺ 311.1916.

1,1-Diphenyl-2-(dicyclohexylphosphino)propene (3c):

¹H NMR (500 MHz, CDCl₃) δ 1.15-1.33 (m, 10 H), 1.62-1.89 (m, 12 H), 1.85 (d, J = 2.0 Hz, 3H), 7.09-7.14 (m, 4H), 7.15-7.22 (m, 2H), 7.24 (br t, J = 7.4 Hz, 2H), 7.29 (br t, J = 7.6 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 17.7 (d, J = 4.0 Hz), 26.5, 27.2 (d, J = 11.8 Hz), 27.5 (d, J = 7.7 Hz), 30.5 (d, J = 9.9 Hz), 31.3 (d, J = 18.9 Hz), 34.7 (d, J = 14.2 Hz), 126.4, 126.5, 127.5, 128.1, 128.6, 130.1 (d, J = 3.2 Hz), 132.5 (d, J = 22.0 Hz), 143.6 (d, J = 8.4 Hz), 144.0 (d, J = 10.0 Hz), 155.6 (d, J = 32.0 Hz); ³¹P NMR (202 MHz, CDCl₃) δ -3.68; HRMS (ESI) m/z calcd for C₂₇H₃₅P [M+H]⁺ 391.2555, found [M+H]⁺ 391.2558.

1,1-Diphenyl-2-(di-tert-butylphosphino)propene (3d):

A solution of 2-bromo-1,1-diphenylpropene (1.37 g, 5.00 mmol) and magnesium turnings (0.134 g, 5.5 mmol) in THF was stirred at room temperature. After addition of a piece of iodine, the solution was refluxed for 2 hr. And then CuI (0.520 g, 5.3 mmol) and chloro-di-*tert*-butylphosphine (1.08 g, 5.5 mmol) was added at room temperature. The mixture was refluxed for 18 hr and then cooled to room temperature. Heptane (14 mL) was added to generate a solid, which was filtrated and dissolved with EtOAc (40 mL). The resulting solution was washed with 28% of ammonia water until the color of the solution changed from blue to colorless. The solution was washed with brine, dried over MgSO₄ and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel to give the title compound (0.736 g, 43 %) as a white solid.

¹H NMR (500 MHz, CDCl₃) δ 1.23 (d, J = 11.3 Hz, 18H), 2.06 (d, J=1.5 Hz, 3H), 7.12-7.23 (m, 8H), 7.29 (br t, J = 7.7 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 21.5 (d, J = 4.9 Hz), 31.2 (d, J = 15.2 Hz), 33.0 (d, J = 26.3 Hz), 126.0, 126.4, 127.4, 128.26, 128.34, 130.0 (d, J = 3.7 Hz), 133.7 (d, J = 32.8 Hz), 144.3 (d, J = 9.9 Hz), 144.8 (d, J = 10.9 Hz), 156.9 (d, J = 36.0 Hz); ³¹P NMR (202 MHz, CDCl₃) δ 30.13; HRMS (EI) m/z calcd for C₂₃H₃₁P [M+H]⁺ 339.2242, found [M+H]⁺ 339.2235.

1,1-Bis(4-dimethylaminophenyl)-2-(diphenylphosphino)propene (4a):

¹H NMR (500 MHz, CDCl₃) δ 1.73 (d, J= 3.0 Hz, 3H) 2.91 (s, 6H), 2.95 (s, 6H), 6.56 (d, J = 8.5 Hz, 2H), 6.64 (d, J = 8.7 Hz, 2H), 7.02 (dd, J = 1.3, 8.7 Hz, 2H), 7.06 (d, J = 8.8 Hz, 2H), 7.28-7.46 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 20.3 (d, J = 4.0 Hz), 40.3, 40.4, 111.0, 111.3, 127.6, 128.07, 128.12, 131.0, 131.1, 131.3 (d, J = 10.8 Hz), 133.0, 133.2, 139.0 (d, J = 15.1 Hz), 149.3, 149.6, 156.2 (d, J = 34.6 Hz); ³¹P NMR (202 MHz, CDCl₃) δ -2.81; HRMS (ESI) m/z calcd for C₃₁H₃₃N₂P [M+H]⁺ 465.2460, found [M+H]⁺ 465.2457.

1,1-Bis(4-dimethylaminophenyl)-2-(dicyclohexylphosphino)propene (4b):

¹H NMR (500 MHz, CDCl₃) δ 1.08-1.27 (m, 10H), 1.55-1.76 (m, 12H), 1.83 (d, J = 2.1 Hz, 3H), 2.84 (s, 6H), 2.85 (s, 6H), 6.52 (br d, J = 8.8 Hz, 2H), 6.56 (br d, J = 8.8 Hz, 2H), 6.88 (br d, J = 9.3 Hz, 2H), 6.90 (br d, J = 9.0 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 18.3 (d, J = 4.7 Hz), 26.6, 27.3 (d, J = 11.7 Hz), 27.6 (d, J = 7.5 Hz), 30.6 (d, J = 9.6 Hz), 31.4 (d, J = 18.7 Hz), 35.0 (d, J = 14.7 Hz), 40.4, 40.5, 111.2, 111.7, 129.0 (d, J = 19.5 Hz), 130.2, 131.4 (d, J = 4.0 Hz), 132.8 (d, J = 8.9 Hz), 133.1 (d, J = 10.1 Hz), 148.7, 149.0, 155.9 (d, J = 31.8 Hz); ³¹P NMR (202 MHz, CDCl₃) δ -2.20; HRMS (ESI) m/z calcd for C₃₁H₄₅N₂P [M+H]⁺ 477.3399, found [M+H]⁺ 477.3404.

1,1-Bis(4-dimethylaminophenyl)-2-(di-tert-butylphosphino)propene (4c):

¹H NMR (500 MHz, CDCl₃) δ 1.23 (d, J = 11.1 Hz, 18H), 2.12 (d, J = 1.6 Hz, 3H), 2.90 (s, 6H), 2.92 (s, 6H), 6.57 (br d, J = 8.8 Hz, 2H), 6.64 (br d, J = 8.8 Hz, 2H), 6.97 (br d, J = 8.8 Hz, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 22.0 (d, J = 4.9 Hz), 31.2 (d, J = 15.3 Hz), 33.1 (d, J = 26.8 Hz), 40.4, 40.5, 111.2, 112.0, 129.8, 130.9 (d, J = 30.0 Hz), 131.4 (d, J = 3.8 Hz), 133.4 (d, J = 9.8 Hz), 134.0 (d, J = 10.8 Hz), 148.4, 148.9, 157.2 (d, J = 35.0 Hz); ³¹P NMR (202 MHz, CDCl₃) δ 31.63; HRMS (ESI) m/z calcd for C₂₇H₄₁N₂P [M+H]⁺ 425.3086, found [M+H]⁺ 425.3095.

1,1-Bis(4-methoxyphenyl)-2-(diphenylphosphino)propene (5):

¹H NMR (500 MHz, CDCl₃) δ 1.74 (d, J = 3.7 Hz, 3H) , 3.76 (s, 3H) 3.80 (s, 3H), 6.75 (br d, J = 8.7 Hz, 2H), 6.84 (br d, J = 8.7 Hz, 2H), 7.05-7.12 (m, 4H), 7.28-7.46 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 20.2 (d, J = 2.1 Hz), 55.1, 55.2, 113.0, 113.3, 128.29, 128.31, 128.4, 130.9, 131.0, 131.1, 133.0, 133.1, 135.1 (d, J = 10.0 Hz), 135.7 (d, J = 10.9 Hz), 137.0 (d, J = 7.9 Hz), 158.8 (d, J = 35.2 Hz); ³¹P NMR (202 MHz, CDCl₃) δ -3.83; HRMS (ESI) m/z calcd for $C_{29}H_{27}O_2P$ [M+H]⁺ 439.1827, found [M+H]⁺ 439.1832.

1,1-Bis(4-fluorophenyl)-2-(diphenylphosphino)propene (6):

¹H NMR (500 MHz, CDCl₃) δ 1.63 (d, J = 3.2 Hz, 3H) , 6.81-6.87 (m, 2H), 6.90-6.97 (m, 2H), 7.00-7.08 (m, 4H), 7.23-7.35 (m, 10H); ¹³C NMR (125 MHz, CDCl₃) δ 20.46, 20.48, 115.0, 115.2, 115.4, 115.6, 128.77, 128.83, 128.9, 131.5, 131.6, 131.74, 131.77, 131.80, 131.83, 132.1, 132.2, 133.4, 133.5, 137.5, 137.6, 138.67, 138.72, 138.74, 139.2, 139.3, 153.5, 153.8, 161.3, 161.6, 163.3, 163.6 (observed complexity due to P-C and F-C splittings, definitive assignments have not made); ³¹P NMR (202 MHz, CDCl₃) δ -4.39; ¹⁹F NMR (470 MHz, CDCl₃) δ -114.95, -114.93, -114.92, -114.91, -114.89, -114.81, -114.80, -114.78, -114.77, -114.76 (observed complexity due to H-F splittings, definitive assignments have not made); HRMS (ESI) m/z calcd for C₂₇H₂₁F₂P [M+H]⁺ 415.1427, found [M+H]⁺ 415.1426.

2,2-Diphenyl-1-(diphenylphosphino)ethylene (7):

¹H NMR (500 MHz, CDCl₃) δ 6.85 (d, J = 3.4 Hz, 1H), 7.15-7.49 (m, 20H); ¹³C NMR (125 MHz, CDCl₃) δ 127.5 (d, J = 11.1 Hz), 127.8, 127.99, 128.01, 128.2, 128.3, 128.4, 128.5, 130.1 (d, J = 3.9 Hz), 132.7 (d, J = 18.9 Hz), 140.1 (d, J = 6.4 Hz), 140.3 (d, J = 10.4 Hz), 142.4 (d, J = 7.4 Hz), 156.7 (d, J = 25.2 Hz); ³¹P NMR (202 MHz, CDCl₃) δ .-23.01; HRMS (ESI) m/z calcd for $C_{26}H_{21}P$ [M+H]⁺ 365.1459, found [M+H]⁺ 365.1460.

1,1-Diphenyl-2-(dicyclohexylphosphino)-3-methylbutene (8):

¹H NMR (500 MHz, CDCl₃) δ 0.95 (d, J = 6.9 Hz, 6H), 1.00-1.23 (m, 10H), 1.34-1.47 (m, 2H), 1.52-1.79 (m, 8H), 1.88-2.00 (m, 2H), 2.63-2.77 (m, 1H), 7.04-7.13 (m, 6H), 7.15-7.23 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ 23.2 (d, J = 7.8 Hz), 26.5, 27.3 (d, J = 12.2 Hz), 27.4 (d, J = 8.8 Hz), 31.7 (d, J = 11.1 Hz), 32.4 (d, J = 20.3 Hz), 33.2 (d, J = 16.6 Hz), 35.3 (d, J = 14.3 Hz), 126.2, 126.4, 127.7, 128.0, 128.1, 128.3, 141.7 (d, J = 29.9 Hz), 144.5 (d, J = 6.4 Hz), 145.0 (d, J = 5.6 Hz), 152.6; ³¹P NMR (202 MHz, CDCl₃) δ -1.40; HRMS (EI) m/z calcd for C₂₉H₃₉P [M+H]⁺ 419.2868, found [M+H]⁺ 419.2874.

1,2,2-Triphenyl-1-(dicyclohexylphosphino)ethylene (9):

¹H NMR (500 MHz, CDCl₃) δ 1.00-1.23 (m, 10H), 1.48-1.76 (m, 10 H), 1.82-1.93 (m, 2H), 6.87-7.02 (m, 7 H), 7.06 (tt, J = 1.2, 7.4 Hz, 1H), 7.14 (br t, J = 7.4 Hz, 2H), 7.22-7.28 (m, 3H), 7.32 (br t, J = 7.3 Hz, 2H); ¹³C NMR (125 Hz, CDCl₃) δ 26.4, 27.1 (d, J = 11.1 Hz), 27.2 (d, J = 9.2 Hz), 30.7 (d, J = 12.7 Hz), 31.0 (d, J = 17.9 Hz), 34.7 (d, J = 15.5Hz), 125.7, 126.2, 126.6, 127.3, 127.57, 127.61, 129.7, 130.1, 130.8 (d, J = 3.9 Hz), 139.1 (d, J = 28.6 Hz), 141.8 (d, J = 4.8 Hz), 143.6 (d, J = 7.1 Hz), 143.9 (d, J = 9.0 Hz), 156.9 (d, J = 33.0 Hz); ³¹P NMR (202 MHz, CDCl₃) δ -0.79; HRMS (ESI) m/z calcd for C₃₂H₃₇P [M+H]⁺ 453.2711, found [M+H]⁺ 453.2714.

Typical Procedure for the Coupling Reaction of Aryl Halides with Amines:

To a solution of Pd(OAc)₂ (1.0 mol%) and ligand (2.0-4.0 mol%) in toluene (0.5 M) was added amine (1.0 equiv), aryl halide (1.1 equiv) and NaOt-Bu (1.2 equiv) under nitrogen atmosphere, and then the mixture was stirred at 100 °C for 3 hr. After cooling to room temperature, the reaction mixture was diluted with toluene, and washed with water and brine. And the organic layer was extracted from an aqueous layer with toluene. The combined organic phase was dried over anhydrous magnesium sulfate and concentrated under reduced pressure. The concentrate was purified by column chromatography on silica gel to give the products.

N,N-Diphenyl-N-(4-tert-butylphenyl)amine (Table 1):

¹H-NMR (200 MHz, CDCl₃) δ 1.31 (s, 9H), 6.92-7.30 (m, 14H).

N-4-Anisyl-N-4-tolylamine (Table 2, Entry 1):

 1 H-NMR (200 MHz, CDC₃) δ 2.27 (s, 3H) , 3.79 (s, 3H), 5.38 (br s, 1H), 6.78-6.91 (m, 4H), 6.96-7.09 (m, 4H)

N-(4'-methylbiphenyl)-aniline (Table 2, Entry 2):

 1 H-NMR (200 MHz, CDC₃) δ 2.39 (s, 3H), 5.61 (br s, 1H), 6.85-7.08 (m, 4H), 7.16-7.41 (m, 9H).

N-3-Anisyl-N,N-dibenzylamine (Table 2, Entry 3):

¹H-NMR (200 MHz, CDC₃) δ 3.69 (s, 3H), 4.63 (s, 4H), 6.23-6.42 (m, 3H), 7.01-7.39 (m, 11H).

Triphenylamine (Table 2, Entry 4):

 1 H-NMR (200 MHz, CDC₃) δ 6.94-7.14(m, 9H), 7.17-7.31 (m, 6H).

N-Methyl-N-(2-tolyl)aniline (Table 2, Entry 5):

¹H-NMR (200 MHz, CDC₃) δ 2.14 (s, 3H), 3.22 (s, 3H), 6.53 (br d, J = 8.0 Hz, 2H), 6.70 (br t, J = 7.3 Hz, 1H), 7.09-7.33 (m, 6H).

N-(4-Cyanophenyl)morpholine (Table 2, Entry 6):

 1 H-NMR (200 MHz, CDCl₃) δ 3.23-3.33 (m, 4H), 3.80-3.90 (m, 4H), 6.81-6.92 (m, 2H), 7.47-7.57 (m, 2H).

Figure 1: ¹H NMR of (**11**) in CDCl₃

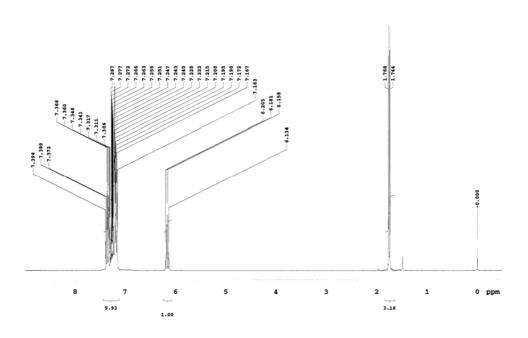


Figure 2: ¹³C NMR of (**11**) in CDCl₃

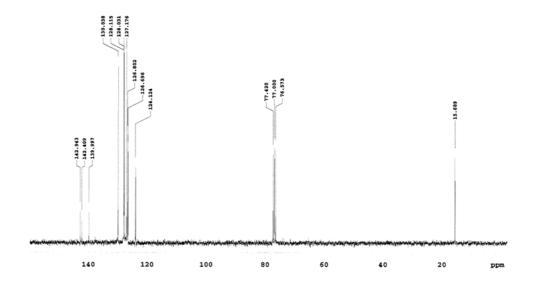


Figure 3: ¹H NMR of (**12**) in CDCl₃

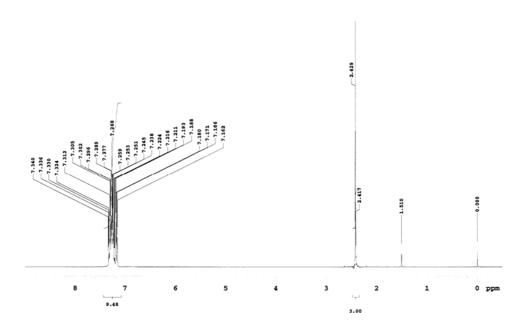


Figure 4: ¹³C NMR of (**12**) in CDCl₃

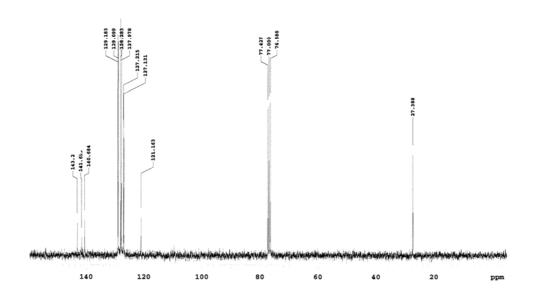


Figure 5: ¹H NMR of (**3a**) in CDCl₃

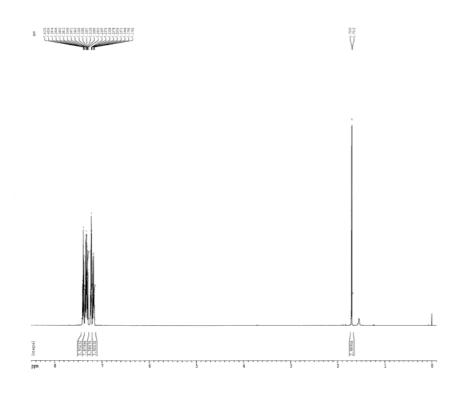


Figure 6: ¹³C NMR of (**3a**) in CDCl₃

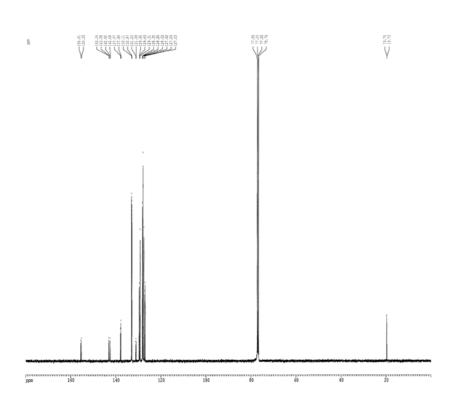


Figure 7: ³¹P NMR of (**3a**) in CDCl₃

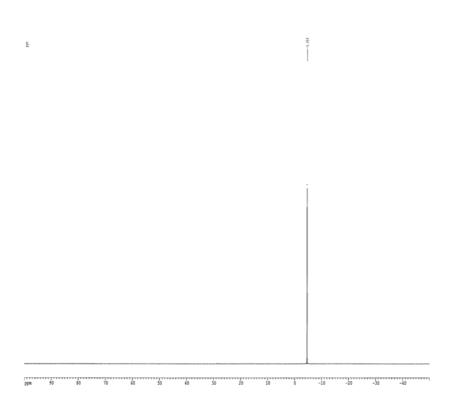


Figure 8: ¹H NMR of (**3d**) in CDCl₃

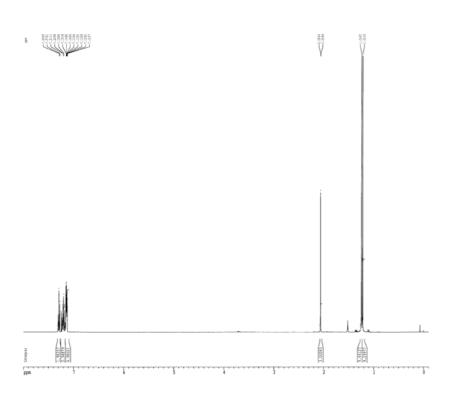


Figure 9: ¹³C NMR of (**3d**) in CDCl₃

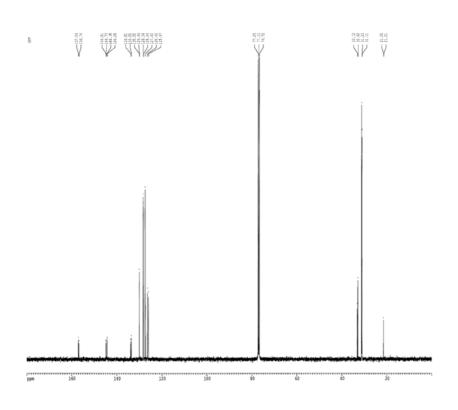


Figure 10: ³¹P NMR of (**3d**) in CDCl₃

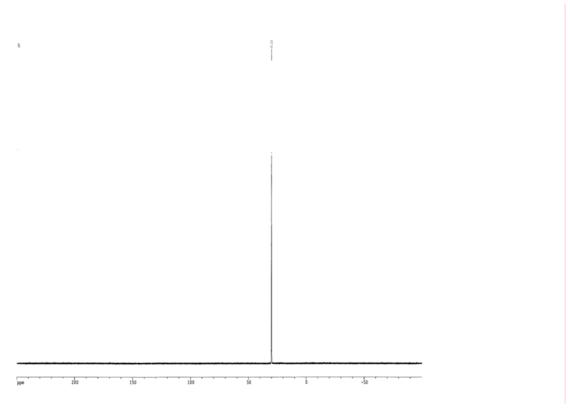


Figure 11: ¹H NMR of N,N-Diphenyl-N-(4-*tert*-butylphenyl)amine in CDCl₃ (Table 1):

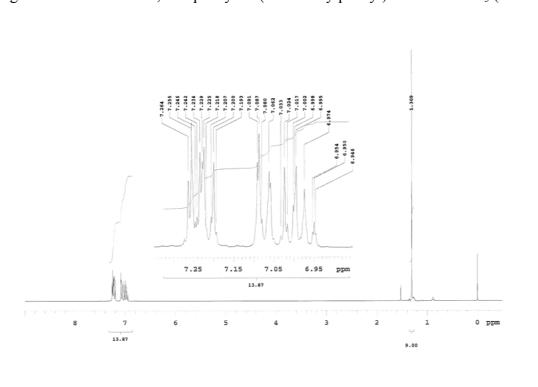
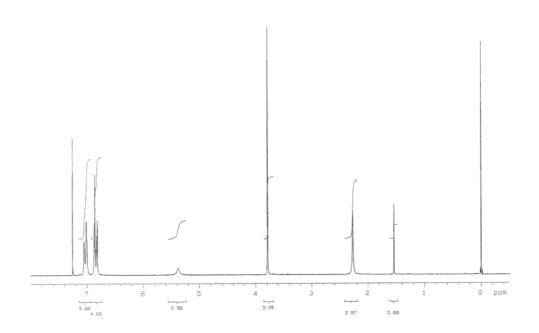


Figure 12: ¹H NMR of N-4-Anisyl-N-4-tolylamine in CDCl₃ (Table 2, Entry 1):



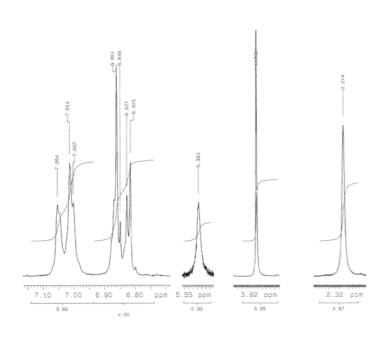
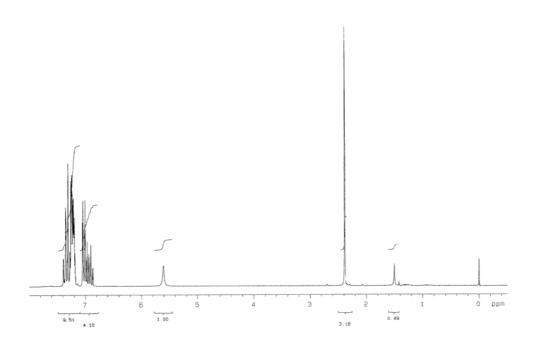


Figure 13: ¹H NMR of N-(4'-methylbiphenyl)-aniline in CDCl₃ (Table 2, Entry 2):



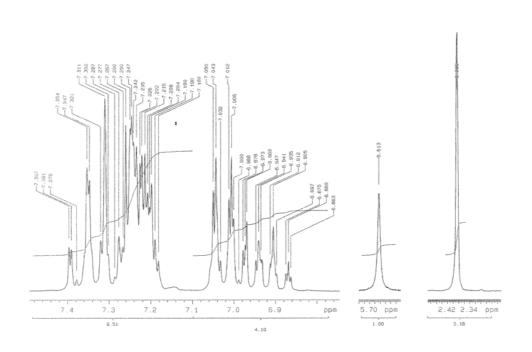
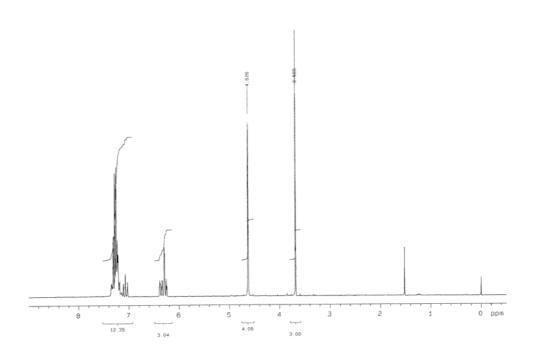


Figure 14: ¹H NMR of N-3-Anisyl-N,N-dibenzylamine in CDCl₃ (Table 2, Entry 3):



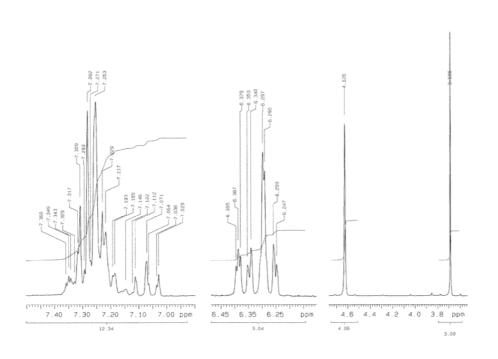


Figure 15: ¹H NMR of Triphenylamine in CDCl₃ (Table 2, Entry 4):

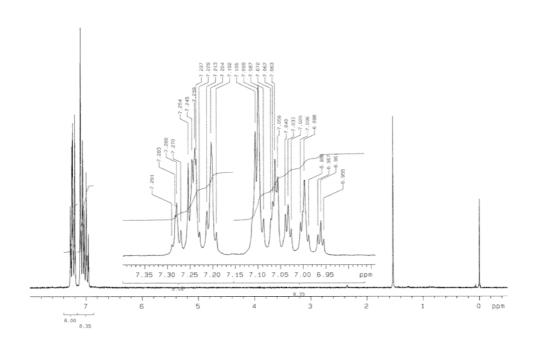


Figure 16: ¹H NMR of N-Methyl-N-(2-tolyl)aniline in CDCl₃ (Table 2, Entry 5):

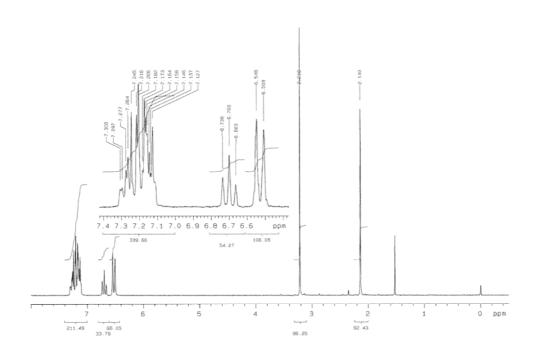


Figure 17: ¹H NMR of N-(4-Cyanophenyl)morpholine in CDCl₃ (Table 2, Entry 6):

