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SUPPORTING INFORMATION

Title: Synthesis of Chlorinated Biphenyls by Suzuki Cross-Coupling Using Diamine or Diimine-Palladium Complexes

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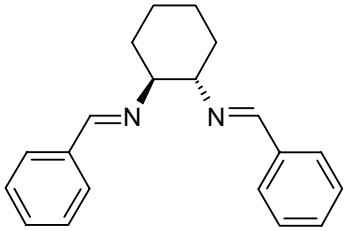
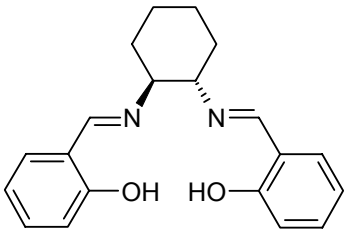
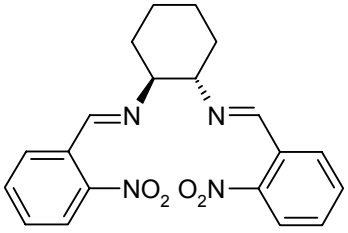
Ref. No.: O200800119



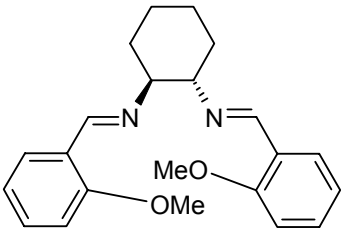
(*R,R*)-*N,N′*-bis(phenylmethylene)-1,2-cyclohexane diamine (**2a)** crystalline, yield 83%. m.p. 100-102°C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.20 (s, 2H, Ar-CH=N), 7.59-7.56 (m, 4H, Ar-H), 7.30-7.28 (m, 6H, Ar-H), 3.43-3.39 (m, 2H, CH), 1.85 (m, 4H, CH_2 and $4H_{eq}$ CH_2), 1.48 (m, $4H_{ax}$,CH_2)ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ = 160.8, 136.2, 130.0, 130.0, 128.2, 128.2, 127.8, 73.7, 33.0, 24.5ppm. FTIR (KBr) ν = 1643 (C=N), 1578(C=N), 760, 754, 693 (Aromatic, mono substituted) cm^{-1}. MS data has previously been reported [35]



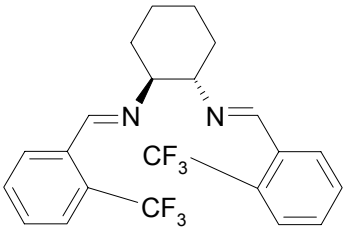
(*R,R*)-*N,N′*-bis(salicylidene)-1,2-cyclohexanediamine (**2b)** crystalline (recrystallized from n-hexane) yield 70%. m. p. 118-119 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.26 (s, 2H, Ar-CH=N), 7.21(t, *J* = 7.0 Hz, 2H, Ar-H), 7.13(dd, *J* = 7.7 Hz, 2H, Ar-H), 6.87(dd, *J* = 8.1 Hz, 2H, Ar-H), 6.79(td, *J* = 7.3 Hz, 2H, Ar-H), 3.30(m, 2H, CH), 1.97-1.48(m, 8H, CH_2)ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 164.8, 161.0, 132.3, 131.6, 188.8, 116.9, 72.9, 33.5, 24.5 ppm. FTIR (KBr) ν = 2900-2500(intermolecular -O-H .. N=C-), 1627(C=N), 1580(C=N), 767(Aromatic, ortho substituted), 659(OH) cm^{-1}. MS data has previously been reported [13]



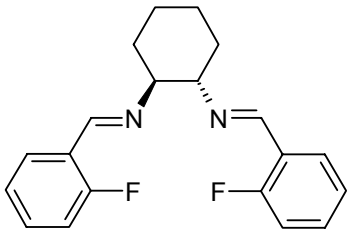
(*R,R*)-*N,N′*-bis[(2-nitrophenyl)methylene]-1,2-cyclohexanediamine (**2c)** crystalline (recrystallized from methanol) yield 78%. m. p. 85-87 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.67 (s, 2H, Ar-CH=N), 7.95(td, *J* = 8.4 Hz, 4H, Ar-H), 7.60(td, *J* = 7.4 Hz, 2H, Ar-H), 7.49(td, *J* = 7.7 Hz, 2H, Ar-H), 3.58-3.55(m, 2H, CH), 1.89(m, 4H, CH_2 and $4H_{eq}$ CH_2), 1.51(m, $4H_{ax}$,CH_2) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 156.6, 148.4, 133.4, 131.1, 130.3, 129.7, 124.0, 74.0, 32.6, 24.3ppm. FTIR (KBr) ν = 1698(C=N), 1523($ArNO_2$), 1346($ArNO_2$), 742 (Aromatic, ortho substituted) cm^{-1}. MS data has previously been reported [36]



***(R,R)*-*N,N'*-bis[(2-methoxyphenyl)methylene]-1,2-cyclohexanediamine** (**2d)**. crystalline (recrystallized from methanol) yield 64 %. m.p. 107-108°C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.62(s, 2H, Ar-CH=N), 7.80(dd, *J* = 8.3 Hz,2H, Ar-H), 7.24(td, *J* = 7.8 Hz, 2H, Ar-H), 6.85(td, *J* = 7.4 Hz, 2H, Ar-H), 6.75(dd, *J* = 8.2 Hz, 2H, Ar-H), 3.66(s, 6H, CH_3) 3.42(m, 2H, CH), 1.85(m, 4H, CH_2 and $4H_{eq}$ CH_2), 1.47(m, $4H_{ax}$,CH_2)ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 158.2, 157.0, 131.0, 127.1, 124.8, 120.1, 110.4, 73.8, 55.1, 32.9, 24.5 ppm. FTIR (KBr) ν = 1638(C=N), 1582(C=N), 769(Aromatic, ortho substituted) cm^{-1}. MS (EI, 70eV): *m/z* (%) = 350 (1) $[M]^+$, 217 (100), 186 (25), 136 (65). HRMS (EI, 70eV): Calcd. For $C_{22}H_{26}N_2O_2$ 350.1989; found 350.1999

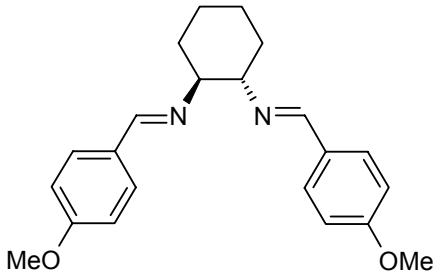


***R,R*)-*N,N'*-bis[(2trifluoromethylphenyl)methylene]-1,2-cyclohexanediamine** (**2e)** crystalline yield 83 %. m. p. 79-80 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.59 (q, *J* = 2.6 Hz, 2H, Ar-CH=N), 8.05(d, *J* = 7.4 Hz, 2H, Ar-H), 7.55(d, *J* = 8.1 Hz, 2H, Ar-H), 7.50(t, *J* = 7.4 Hz, 2H, Ar-H), 7.37 (td, *J* = 7.3 Hz, 2H, Ar-H), 3.55-3.51(m, 2H, CH), 1.80(m, 4H, CH_2 and $4H_{eq}$ CH_2), 1.50(m, $4H_{ax}$,CH_2)ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 157.0, 134.3, 134.3, 131.8, 131.8, 131.8, 131.8, 129.7, 128.8, 128.4, 128.3, 125.9, 125.4, 125.3, 125.2, 125.2, 122.3, 74.1, 32.8, 24.5ppm. FTIR (KBr) ν = 1638(C=N), 1577(C=N), 1133(CF_3), 773(Aromatic, ortho substituted) cm^{-1}. MS (EI, 70eV): *m/z* (%) = 426 (0.5) $[M]^+$, 425 (1) $[M-1]^+$, 255 (50), 174 (100). HRMS (EI, 70eV): Calcd. For $C_{22}H_{20}F_6N_2$ 426.1525; found 426.1531

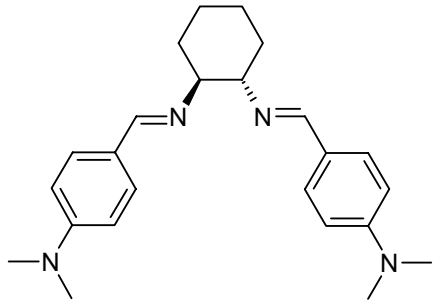


(*R,R*)-*N,N'*-bis[(2-fluorophenyl)methylene]-1,2-cyclohexanediamine (**2f)** crystalline yield 90%. m.p. 121-122°C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.52 (s, 2H, Ar-CH=N), 7.85(td, *J* = 7.5 Hz, 2H, Ar-H), 7.29(q, 2H, Ar-H), 7.08(t, *J* = 7.7 Hz, 2H, Ar-H), 6.96(td, *J* = 9.3 Hz, 2H, Ar-H), 3.346(m, 2H, CH), 1.88-1.49 (m, 8H, CH_2)ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 163.8, 154.5, 131.9, 127.8, 124.3, 124.0, 115.5, 74.2, 33.0, 24.5ppm [28]. FTIR (KBr) = 1638(C=N),

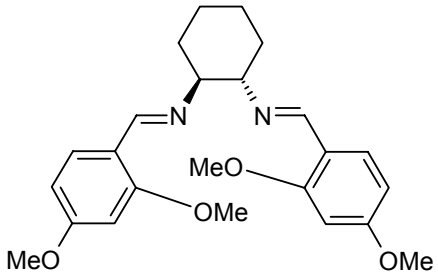
802(Aromatic, para substituted) cm^{-1}. MS (EI, 70eV): *m/z* (%) = 326 (0.5) $[M]^+$, 325 (0.8) $[M-1]^+$, 205 (67), 124 (100) HRMS (EI, 70eV): Calcd. For $C_{20}H_{20}F_2N_2$ 326.1589; found 326.1590.



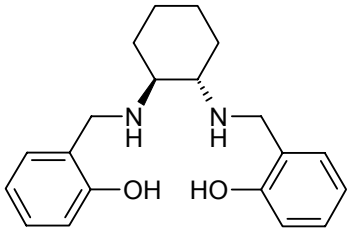
(*R,R*)-N,N'-bis[(4-methoxyphenyl)methylene]-1,2-cyclohexanediamine (**2g)** crystalline yield 92 %. m.p. 109-111°C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.12 (s, 2H, Ar-CH=N), 7.53(dt, 4H, Ar-H), 6.82(dt, 4H, Ar-H), 3.80(s, 6H, CH_3), 3.36-3.33(m, 2H, CH), 1.84(m, 4H, CH_2 and 4Heq CH_2), 1.47(m, 4Hax,CH_2)ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 161.0, 160.2, 129.3, 129.2, 113.6, 73.7, 55.2, 33.1, 24.6ppm. FTIR (KBr) ν =1643(C=N), 1579(C=N), 824(Aromatic, para substituted) cm^{-1}. MS data has previously been reported [35]



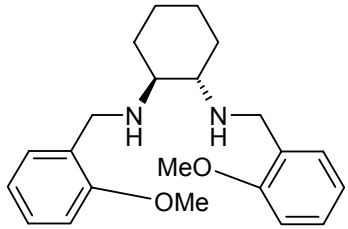
(*R,R*)-N,N'-bis[(4-dimethylaminophenyl)methylene]-1,2-cyclohexanediamine (**2h)** crystalline yield 88 %. m.p. 125-128°C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.08 (s, 2H, Ar-CH=N), 7.72(dt, *J* = 8.8 Hz, 4H, Ar-H), 6.57(dt, *J* = 8.8 Hz, 4H, Ar-H), 3.33-3.30(m, 2H, CH), 2.92 (s, 6H, CH_3), 1.82(m, 4H, CH_2 and $4H_{eq}$ CH_2), 1.46(m, $4H_{ax}$,CH_2)ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 160.5, 151.5, 129.1, 129.1, 124.7, 111.4, 111.4, 73.9, 40.2, 40.2, 40.2, 40.1, 33.4, 24.8ppm [28]. FTIR (KBr) ν = 1632(C=N), 1555(C=N), 807(Aromatic, para substituted) cm^{-1}. MS data has previously been reported [35]



(*R,R*)-*N,N′*-bis[(2,4-dimethoxyphenyl)methylene]-1,2-cyclohexanediamine (**2i)**. crystalline (recrystallized from methanol) yield 39 %. m. p. 69-71 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.51 (s, 2H, Ar-CH=N), 7.75(d, *J* = 8.6 Hz,4H, Ar-H), 6.40(dt, *J* = 8.5 Hz, 4H, Ar-H), 6.32(d, *J* = 2.3 Hz, 4H, Ar-H), 3.71(s, 6H, CH_3), 3.71(s, 6H, CH_3), 3.34(m, 2H, CH), 1.85(m, 4H, CH_2 and $4H_{eq}$ CH_2), 1.46(m, $4H_{ax}$,CH_2)ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 162.7, 160.1, 157.0, 128.7, 118.8, 105.3, 98.0, 74.2, 55.7, 33.4, 24.9ppm. FTIR (KBr) ν = 1631(C=N), 1579(C=N), 836 and 810(Aromatic, ortho, para substituted) cm^{-1}. MS (EI, 70eV): *m/z* (%) = 410 (5) $[M]^+$, 409 (8) $[M-1]^+$, 247 (100), 164 (43), 149 (60). HRMS (EI, 70eV): Calcd. For $C_{24}H_{30}N_2O_4$ 410.2200; found 410.2198

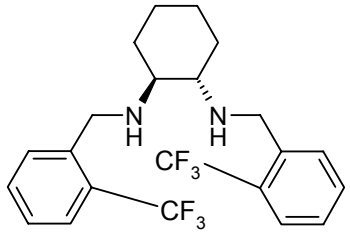


(*R,R*)-*N,N′*-bis[(2-hydroxyphenyl) methyl]-1,2-cyclohexanediamine (**3b)** oil yield 96%. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.16 (t, *J* = 7.6 Hz, 2H, Ar-H), 6.95(d, *J* = 7.8 Hz, 2H, Ar-H), 6.77(m, 4H, Ar-H), 4.03(d, *J* = 13.9 Hz, 2H, Ar-CH2-N), 3.90(d, *J* = 13.9 Hz, 2H, Ar-CH2-N), 2.42(m, 4H, CH_{eq}), 2.15(m, 2H, NH), 1.70(m, 4H, CH_{ax}), 1.20(m, 4H, CH2)ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 158.21, 129.1, 128.6, 123.1, 119.5, 116.7, 59.9, 49.9, 30.7, 24.4ppm. MS data has previously been reported [10]

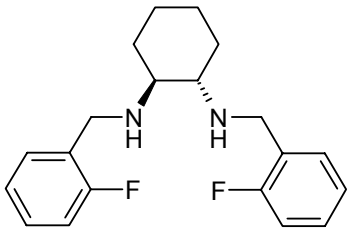


***(R,R)*-*N,N′*-bis[(2-methoxyphenyl)methyl]-1,2-cyclohexanediamine** (**3d)** oil yield 99%. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.27 (d, *J* = 7.0 Hz, 2H, Ar-H), 7.18(t, *J* = 7.5 Hz, 2H, Ar-H), 6.88(t, *J* = 7.2 Hz, 2H, Ar-H), 6.81(d, *J* = 8.4 Hz, 2H, Ar-H), 3.90(d, *J* = 13.4 Hz, 2H, Ar-CH2-N), 3.70(s, 6H, OMe), 3.62(d, *J* = 13.4 Hz, 2H, Ar-CH2-N), 2.26(m, 4H, CH), 2.13(d, 4H, CH_{eq}), 1.70(m, 2H, NH), 1.25-1.03(m, 4H, CH_{ax})ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 157.8, 129.6, 128.0, 120.5, 110.3, 61.2, 55.3, 46.2, 31.8, 25.4ppm. MS (EI, 70eV): *m/z* (%) = 354

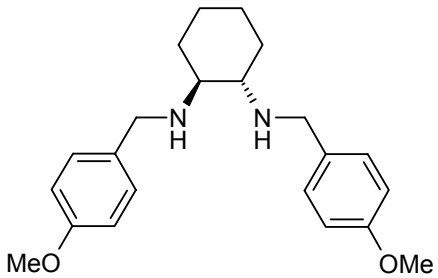
(5) $[M]^+$, 233 (45), 137 (55), 121 (100), 91 (77). HRMS (EI, 70eV): Calcd. For $C_{22}H_{30}N_2O_2$ 354.2302; found 354.2309.



***(R,R)*-*N,N'*-bis[(2-trifluoromethylphenyl)methyl]-1,2-cyclohexanediamine (3e)**. oil yield 90 %. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.62 (d, J = 8.2 Hz, 4H, Ar-H), 7.48(t, J = 7.7 Hz, 2H, Ar-H), 7.31(t, J = 7.5 Hz, 2H, Ar-H), 4.06(d, J = 14.0 Hz, 2H, Ar-CH2-N), 4.38(d, J = 14.0 Hz, 2H, Ar-CH2-N), 2.30-2-16(m, 4H, CH_{eq}), 1.80(d, 2H, NH), 1.29-1.04(m, 6H, CH_{ax})ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 139.8, 131.9, 130.6, 126.8, 125.9, 61.6, 47.1, 31.8, 25.1ppm. MS (EI, 70eV): *m/z* (%) = 430 (3) $[M]^+$, 370 (17), 293 (10), 271 (16), 254 (27), 214 (19), 176 (30), 159 (199). HRMS (EI, 70eV): Calcd. For $C_{22}H_{24}F_6N_2$ 430.1838; found 430.1849.

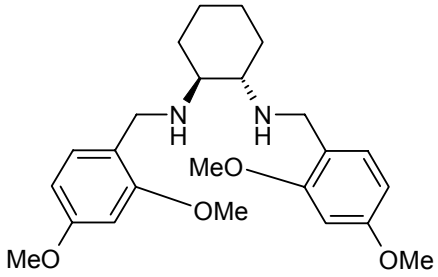


(*R,R*)-*N,N'*-bis[(2-fluorophenyl) methyl]-1,2-cyclohexanediamine (3f) oil yield 80 %. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.33 (t, J = 7.7 Hz, 2H, Ar-H), 7.14(q, 2H, Ar-H), 7.02(t, J = 7.5 Hz, 1H), 6.94(t, J = 9.5 Hz, 1H), 3.90(d, J = 13.5 Hz, 2H, Ar-CH2-N), 3.71(d, J = 13.6 Hz, 2H, Ar-CH2-N), 2.23(d, 2H, NH), 2.08(m, 4H, CH2), 1.68(d, 2H, CH), 1.23-0.99(m, 4H, CH2)ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 162.4, 159.2, 129.9, 129.7, 128.1, 128.0, 127.7, 127.5, 123.7, 123.6, 114.9, 114.6, 60.5, 43.8, 31.2, 24.7 ppm. MS (EI, 70eV): *m/z* (%) = 330 (5) $[M]^+$, 221 (15), 204 (15), 187 (15), 164 (13), 124 (27), 109 (100), 96 (20) HRMS (EI, 70eV): Calcd. For $C_{20}H_{24}F_2N_2$ 330.1902; found 330.1914.

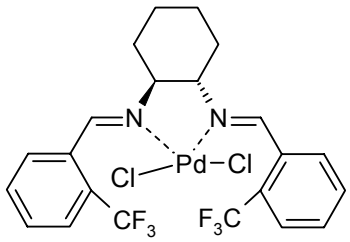


(*R,R*)-*N,N'*-bis[(4-methoxyphenyl) methyl]-1,2-cyclohexanediamine (3g). oil yield 76 %. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.26 (d, J = 8.3 Hz, 4H, Ar-H), 6.86(d, J = 8.4Hz, 4H, Ar-H), 3.82(d, J = 12.9 Hz, 2H, Ar-CH2-N), 3.77(s, 6H, OMe), 3.54(d, J = 12.9 Hz, 2H, Ar-CH2-

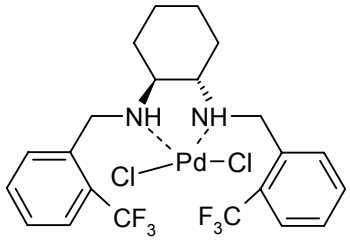
N), 2.24-2.11(m, 4H, CH_{eq}), 1.69(d, 2H, NH), 1.25-1.00(m, 4H, CH_{ax})ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 158.7, 133.4, 129.4, 113.9, 61.0, 55.5, 50.5, 31.8, 25.3 ppm.



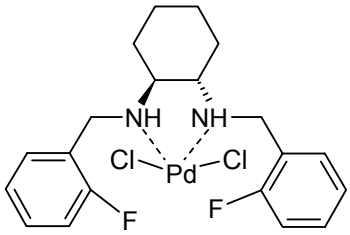
(*R,R*)-*N,N′*-bis[(2,4-dimethoxyphenyl) methyl]-1,2-cyclohexanediamine (3i). oil yield 98 % ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.16 (d, *J* = 8.7 Hz, 2H, Ar-H), 6.43-6.37(m, 4H, Ar-H), 3.83(d, *J* = 12.2 Hz,2H, Ar-CH2-N), 3.79(s, 6H, OMe), 3.71(s, 6H, OMe), 3.53(d, *J* = 12.4 Hz, 2H, Ar-CH2-N), 2.23-2.08(m, 4H, CH and NH), 1.68(d, 4H, CH_{eq}), 1.24-1.05(m, 4H, CH_{ax})ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 159.7, 158.5, 129.9, 121.8, 103.6, 98.3, 60.8, 55.3, 55.1, 45.6, 31.6, 25.1ppm. MS (EI, 70eV): *m/z* (%) = 414 (3) $[M]^+$, 263 (55), 166 (35), 151 (100), 121 (27) HRMS (EI, 70eV): Calcd. For $C_{24}H_{34}N_2O_4$ 414.2513; found 414.2530.



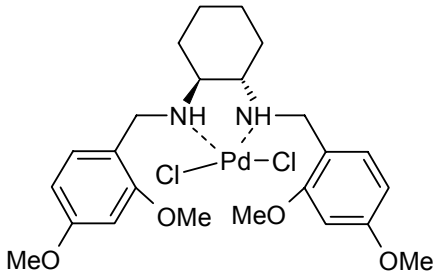
***(R,R)*-*N,N′*-bis[(2-trifluoromethylphenyl)methylene]-1,2-cyclohexanediamine $PdCl_2$ complex (4e)** crystalline m.p. > 300 °C**.** FTIR (KBr) ν = 1641(C=N), 1316, 1172, 1123, 769(Aromatic, ortho substituted) cm^{-1}. MS (EI, 70eV): *m/z* (%) = 568 (35) $[M\text{-}HCl]^+$, 531 $[M\text{-}(2 \times HCl - H)]^+$ (20), 255 (50), 174 (100).



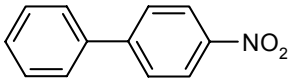
***(R,R)*-*N,N′*-bis[(2-trifluoromethylphenyl)methyl]-1,2-cyclohexanediamine $PdCl_2$ complex (5e)** crystalline m.p. > 300 °C**.** FTIR (KBr) ν = 3174, 1313, 1171, 1120, 768(Aromatic, ortho substituted) cm^{-1}. MS (EI, 70eV): *m/z* (%) = 570 (12) $[M\text{-}HCl]^+$, 533 $[M\text{-}(2 \times HCl - H)]^+$ (5), 254 (25), 159 (100).



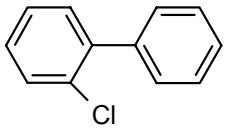
(*R,R*)-*N,N'*-bis[(2-fluorophenyl)methyl]-1,2-cyclohexanediamine $PdCl_2$ complex (5f) crystalline m.p. > 300 °C. FTIR (KBr) ν = 1493, 1454, 1228, 759(Aromatic, para substituted) cm^{-1}. MS (EI, 70eV): *m/z* (%) = 470 (0.5) $[M\text{-}HCl]^+$, 434 $[M\text{-} (2 \times HCl - H)]^+$ (0.3), 221 (10), 204 (7), 187 (2), 164 (10), 124 (20), 109 (100).



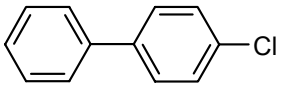
(*R,R*)-*N,N'*-bis[(2,4-dimethoxyphenyl)methyl]-1,2-Cyclohexanediamine $PdCl_2$ complex (5i) crystalline m.p. > 300 °C**.** FTIR (KBr) ν = 1612, 1509, 1456, 1292, 1209, 1032, 833(Aromatic, ortho, para substituted) cm^{-1}. MS (EI, 70eV): *m/z* (%) = 486 (1), 412 (3), 263 (37), 151 (100).



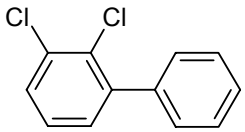
4-nitrobiphenyl (8); crystalline (purified by column chromatograph using hexane: EtOAc 5:1 as eluent) m. p. 107-110 °C**.** ^1H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.30 (dt, *J* = 9.0 Hz, 2H), 7.72 (dt, *J* = 8.9 Hz, 2H), 7.62 (dt, 2H), 7.53-7.44 (m, 3H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 147.8, 138.9, 129.4, 129.4, 129.1, 128.0, 127.6, 124.3 ppm. MS data has previously been reported [7]



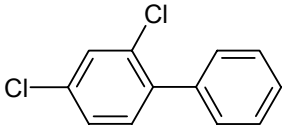
2-chlorobiphenyl (9a) crystalline m. p. 32-35 °C. ^1H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.85-7.24 (m, 9H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 140.8, 139.7, 132.8, 131.7, 130.2, 129.1, 128.2, 127.9, 127.5, 126.8 ppm. MS data has previously been reported [42]



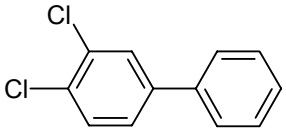
4-chlorobiphenyl (9b) crystalline m. p. 75-78 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.63-7.36 (m, 9H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 140.2, 139.9, 133.7, 129.2, 129.2, 128.7, 127.9, 127.3 ppm. MS data has previously been reported [42]



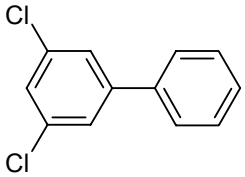
2,3-dichlorobiphenyl (9c); semi-crystalline solid ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.78-7.38(m, 6H), 7.26-7.23(m, 2H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 140.4, 139.5, 133.7, 130.8, 129.7, 129.6, 129.3, 128.3, 127.4 ppm.



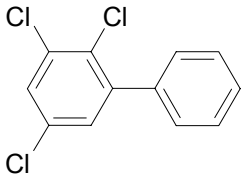
2,4-dichlorobiphenyl (9d) oil ^{1}H NMR((300MHz, $CDCl_3$, 21°C): δ= 7.48(dd, 1H), 7.43-7.37(m, 5H), 7.27(m, 2H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 139.3, 138.6, 133.9, 133.5, 132.2, 130.0, 130.0 129.9, 128.2, 128.2, 127.4, 127.3 ppm. MS data has previously been reported [38]



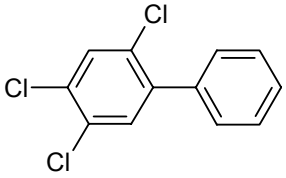
3,4-dichlorobiphenyl (9e) crystalline m. p. 121-126 °C. 1H NMR(300MHz, CDCl3, 21°C): δ= 7.70 (d, 1H), 7,58-7.41 (m, 7H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 141.5, 139.0, 133.1, 131.7, 131.0, 129.3, 129.2, 128.4, 127.2, 126.6 ppm.



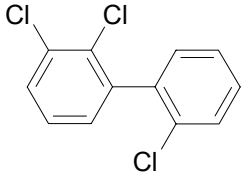
3,5-dichlorobiphenyl (9f) oil ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.54 (d, 2H), 7.48-7.39(m, 5H), 7.33(td, 1H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 145.1, 144.3, 138.5, 135.3, 129.1, 128.5, 126.1, 125.6 ppm. MS data has been previously reported. Spectral data can be obtained from Wiley subscription services Inc. (US)



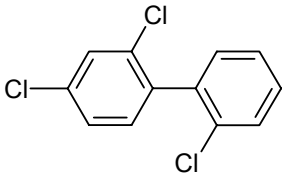
2,3,5-trichlorobiphenyl (9g); crystalline 123-126 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.48 (d, J = 2.6 Hz, 1H), 7.45-7.37 (m, 5H), 7.25 (d, J = 2.7 Hz, 1H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 143.7, 138.1, 134.3, 132.1, 132.0, 129.6, 129.2, 129.0, 128.6, 128.4, 128, 3 ppm.



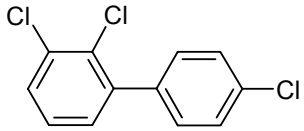
2,4,5-trichlorobiphenyl (9h) crystalline m. p. 74-76 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.59 (s, 1H), 7.45-7.41 (m, 6H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 140,4, 137.2, 132.4, 132.0, 131.9, 131.2, 129.2, 128.3, 128.2 ppm. MS data has previously been reported [41]



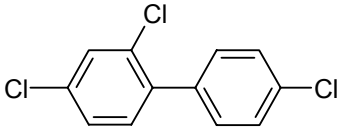
2,3,2'-trichlorobiphenyl (9i) crystalline ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.50 (td, 2H), 7.40-7.23 (m, 4H), 7.19 (dd, J = 7.6 Hz, 1H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 140.6, 138.3, 133.5, 133.4, 132.3, 131.1, 130.2, 129.8, 129.7, 129.5, 127.2, 126.8 ppm.



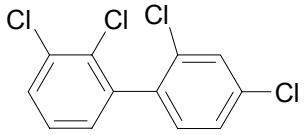
2,4,2'-trichlorobiphenyl (9j) oil ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.47-7.45 (m, 2H), 7.38-7.30 (m, 3H), 7.28-7.20 (m, 2H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 137.3, 136.9, 134.5, 134.4, 133.5, 132.1, 131.2, 129.7, 129.6, 129.4, 127.0, 126.7 ppm.



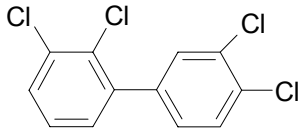
2,3,4'-trichlorobiphenyl (9k) crystalline m. p. 97-99 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.48-7.45 (m, 2H), 7.43-38 (m, 2H), 7.28(s, 1H), 7.25 (m, 1H), 7.19 (dd, 1H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 138.2, 133.3, 132.0, 130.9, 130.1, 129.7, 129.6, 129.4, 127.2, 126.8 ppm. MS data has previously been reported [39]



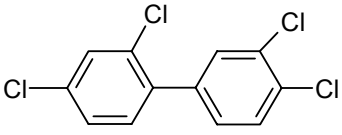
2,4,4'-trichlorobiphenyl (9l) crystalline m. p. 58-63 °C , ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.43 (td, 1H), 7.40 (t, 2H), 7.36 (t, 2H), 7.33(td, 1H), 7.30 (d, 1H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 136.7, 135.5, 133.0, 132.1, 130.8, 129.6, 129.6, 128.7, 127.4, 127.3, 126.2 ppm. MS data has previously been reported [41]



2,3,2',4'-tetrachlorobiphenyl (9m) oil ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.50 (dd, J = 8.0 Hz, 2H), 7.34 (dd, 1H), 7.27 (d, J = 1.9 Hz, 1H), 7.17-7.13(m, 2H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 147.0, 131.8, 130.5, 129.5, 129.4, 128.8, 127.3, 127.1 ppm.

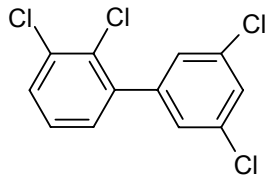


2,3,3',4'-tetrachlorobiphenyl (9n) crystalline m. p. 95-110 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.50 (td, 3H), 7.28 (td, 2H), 7.19 (dd, 1H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 140.4, 139.1, 138.8, 133.9, 132.3, 131.3, 131.0, 130.2, 129.3, 127.5, 126.3 ppm.

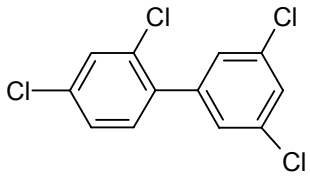


2,4,3',4'-tetrachlorobiphenyl (9o) crystalline m. p. 113-116 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.51 (dd, J = 5.2 Hz, 2H), 7.33 (dd, J = 2.0 Hz, 2H), 7.25(dd, 2H) ppm. ^{13}C

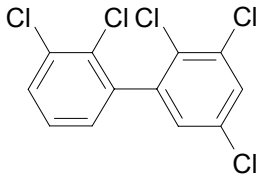
NMR(300MHz, $CDCl_3$, 21°C): δ= 138.3, 136.9, 134.8, 133.4, 132.6, 132.5, 132.0, 131.5, 130.4, 130.2, 129.0, 127.6 ppm. MS data has previoulsy been reported [40]



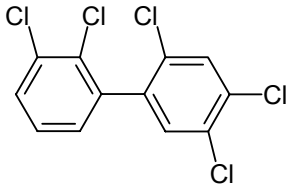
3,5,2',3'-tetrachlorobiphenyl (9p) crystalline m. p. 124-125 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.50 (dd, *J* = 7.9 Hz, 1H), 7.42 (m, 1H), 7.30-7.28(m, 2H), 7.21(dd, *J* = 7.8 Hz, 1H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 142.0, 140.3, 134.9, 134.1, 131.2, 130.5, 129.3, 128.3, 128.0, 127.9, 127.5 ppm.



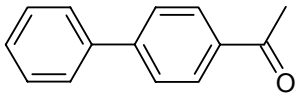
3,5,2',4'-tetrachlorobiphenyl (9q) oil ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.50 (d, *J* = 1.9 Hz, 1H), 7.39 (td, *J* = 1.7 Hz, 1H), 7.31-7.23(m, 4H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 137.4, 137.0, 134.6, 134.5, 133.6, 132.2, 131.3, 129.8, 129.5, 127.1, 126.8 ppm.



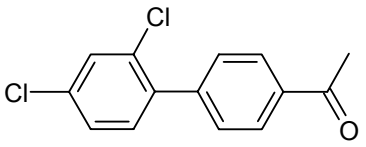
2,3,5,2',3'-pentachlorobiphenyl (9r) crystalline m. p. 65-68 °C**.** ^{1}H NMR (300MHz, $CDCl_3$, 21°C): δ= 7.61 (s, 1H), 7.55 (dd, 1H), 7.37(s, 1H), 7.33-7.27(m, 1H), 7.16 (dd, 1H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 140.5, 138.3, 137.9, 131.0, 130.7, 130.1, 129.2, 127.4 ppm.



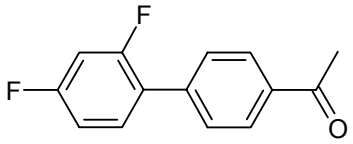
2,4,5,2',3'-pentachlorobiphenyl (9s) oil ^{1}H NMR (300MHz, $CDCl_3$, 21°C): δ= 7.61 (s, 1H), 7.56 (dd, *J* = 7.9 Hz, 1H), 7.37(s, 1H), 7.28(s, 1H), 7.16(dd, *J* = 7.7 Hz, 1H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 140.5, 138.3, 137.9, 132.4, 132.1, 132.0, 131.1, 130.0, 130.9, 129.2, 127.4 ppm. MS data has previosly been reported [42]



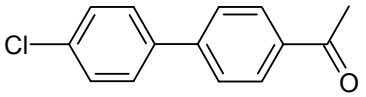
4-acetylbiphenyl (10a) crystalline m. p. 117-118 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.05 (d, *J* = 8.4 Hz, 2H), 7.67 (d, *J* = 8.4 Hz, 2H), 7.62 (d, *J* = 6.9 Hz, 2H), 7.50-7.38(m, 3H), 2.63 (s, 3H) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 198.0, 146.0, 140.1, 136.1, 132.9, 129.3, 129.2, 128.9, 127.5 ppm. MS data has previously been reported [7]



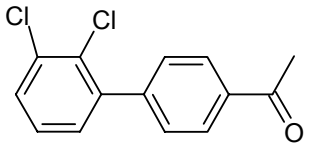
4-acetyl-2',4'-dichlorobiphenyl (10b) crystalline m. p. 118-129 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.02 (dt, *J* = 8.4 Hz, 2H), 7.51(dt, 2H), 7.32(m, 3H), 2.64(s, 3H, CH_3) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 196.5, 141.9, 136.9, 135.3, 133.4, 132.0, 130.8, 128.9, 128.9, 127.2, 126.4, 25.7 ppm. MS (EI, 70eV): *m/z* (%) = 264 (40) $[M]^+$, 249 (100), 186 (57), 149 (15) HRMS (EI, 70eV): Calcd. For $C_{14}H_{10}Cl_2O$ 264.0103; found 264.0121.



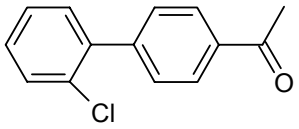
4-acetyl-2',4'-difluorobiphenyl (10c) crystalline m. p. 93-84 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.01 (dt, *J* = 8.6 Hz, 2H), 7.59(dd, *J* = 8.2 Hz, 2H), 7.42(q, *J* = 6.4 Hz, 1H), 6.99-6.90(m, 2H), 2.64(s, 3H, CH_3) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 197.7, 164.6, 161.5, 139.8, 136.3, 131.6, 129.3, 128.8, 127.6, 111.5, 104.1, 27.0 ppm. MS (EI, 70eV): *m/z* (%) = 232 (50) $[M]^+$, 217 (100), 188 (55), 169 (10) HRMS (EI, 70eV): Calcd. For $C_{14}H_{10}F_2O$ 232.0694; found 232.0701.



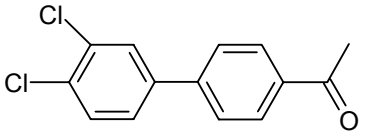
4-acetyl-4'-chlorobiphenyl (10d) crystalline m. p. 100-103°C. [35] ^{1}H NMR (300MHz, $CDCl_3$, 21°C): δ= 7.90 (d, *J* = 8.4 Hz, 2H), 7.56(d, *J* = 8.4 Hz, 2H), 7.46(d, *J* = 8.6 Hz, 2H), 7.33(d, *J* = 8.6 Hz, 1H), 2.55(s, 3H, CH_3) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 196.7, 137.2, 135.0, 133.3, 131.4, 128.1, 128.0, 127.5, 126.0, 25.5 ppm. MS data has previosly been reported [42]



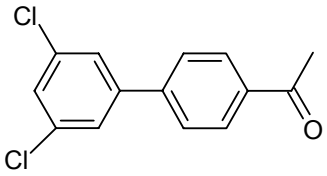
4-acetyl-2',3'-dichlorobiphenyl (10e) crystalline m. p. 104-107 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.02 (d, *J* = 8.1 Hz, 2H), 7.50(dt, 3H), 7.31-7.21(m, 2H), 2.66(s, 3H, CH_3) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 197.8, 143.8, 141.6, 136.4, 133.7, 130.8, 130.0, 129.6, 129.2, 129.0, 128.1, 127.4, 26.6 ppm. MS (EI, 70eV): *m/z* (%) = 264 (37) $[M]^+$, 249 (100), 186 (65), 149 (20) HRMS (EI, 70eV): Calcd. For $C_{14}H_{10}Cl_2O$ 264.0103; found 264.0105



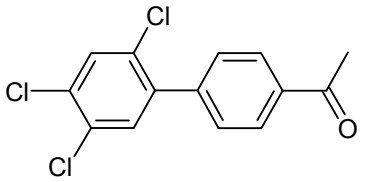
4-acetyl-2'-chlorobiphenyl (10f) oil ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 7.97 (d, *J* = 8.3 Hz, 2H), 7.49(dt, 2H), 7.41(m, 1H), 7.26(m, 3H), 2.58(s, 3H, CH_3) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 197.8, 144.1, 139.3, 136.1, 131.1, 130.1, 129.7, 129.7, 129.2, 129.0, 128.1, 128.0 127.4, 127.0, 26.6 ppm. MS data has previosly been reported [42]



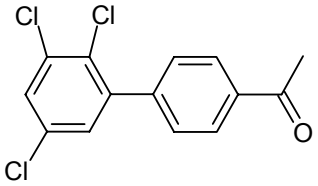
4-acetyl-3',4'-dichlorobiphenyl (10g) semi-crystalline solid ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.02 (d, *J* = 8.5 Hz, 2H), 7.67(d, *J* = 2.1 Hz, 1H), 7.60(d, *J* = 8.5 Hz, 2H), 7.51(d, 1H), 7.44(dd, 1H), 2.63(s, 3H, CH_3) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 197.6, 143.0, 139.8, 136.4, 132.9, 132.3, 130.8, 129.0, 127.3, 127.0, 126.4, 126.1, 26.6 ppm.



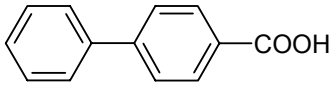
4-acetyl-3',5'-dichlorobiphenyl (10h) crystalline m. p. 64-66 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.01 (d, *J* = 8.5 Hz,2H), 7.61(d, *J* = 8.4 Hz, 2H), 7.47(d, 2H), 7.35(t, 1H), 2.65(s, 3H, CH_3) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 197.8,142.7, 136.7, 135.4, 129.8, 129.1, 127.9, 127.1, 125.7, 26.6 ppm. MS (EI, 70eV): *m/z* (%) = 264 (35) $[M]^+$, 249 (100), 186 (57), 149 (17) HRMS (EI, 70eV): Calcd. For $C_{14}H_{10}Cl_2O$ 264.0103; found 264.0106



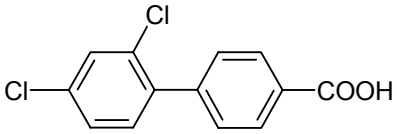
4-acetyl-2',4',5'-trichlorobiphenyl (10i) crystalline ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.04 (d, 2H), 7.61(s, 1H), 7.53(d, 2H), 7.45(s, 1H), 2.65(s, 3H, CH_3) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 141.8, 136.2, 132.7, 132.1, 129.5, 128.3, 26.7 ppm.



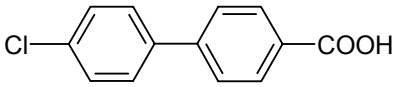
4-acetyl-2',3',5'-trichlorobiphenyl (10j) crystalline m. p. 145-150 °C. ^{1}H NMR(300MHz, $CDCl_3$, 21°C): δ= 8.05 (d, 2H), 7.52(m, 3H), 7.26(d, 1H), 2.65(s, 3H, CH_3) ppm. ^{13}C NMR(300MHz, $CDCl_3$, 21°C): δ= 197.6, 142.6, 136.8, 134.5, 132.7, 129.7, 129.6, 128.3, 26.7 ppm. MS (EI, 70eV): *m/z* (%) = 298 (30) $[M]^+$, 283 (100), 220 (55), 185 (10), 150 (20). HRMS (EI, 70eV): Calcd. For $C_{14}H_9Cl_3O$ 297.9713; found 297.9719.



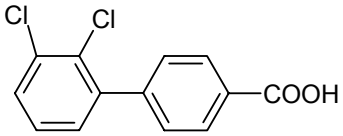
4-biphenylcarboxylic acid (11a) crystalline m. p. 223-226 °C ^{1}H NMR(300MHz, DMSO-d_6, 21°C): δ= 8.06 (d, J = 8.3 Hz, 2H), 7.78(d, J = 8.3 Hz, 2H), 7.72(d, J = 7.4 Hz, 2H), 7.50-7.37(m, 3H) ppm. ^{13}C NMR(300MHz, DMSO-d_6, 21°C): δ= 163.0, 144.5, 139.3, 130.1, 129.1, 128.3, 127.1, 126.8 ppm. MS (EI, 70eV): *m/z* (%) = 198 (100) $[M]^+$, 181 (50), 152 (42). HRMS (EI, 70eV): Calcd. For $C_{13}H_{10}O_2$ 198.0675; found 198.0693.



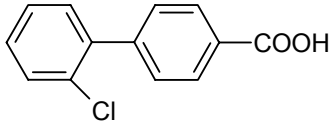
2',4'-dichloro-4-biphenylcarboxylic acid (11b) crystalline m. p. 268-270 °C. ^{1}H NMR(300MHz, DMSO-d_6, 21°C): δ= 8.05 (d, J = 8.1 Hz, 2H), 7.71(m, 1H), 7.55-7.46(m, 3H) ppm. ^{13}C NMR(300MHz, DMSO-d_6, 21°C): δ= 163.0, 142.0, 138.0, 133.6, 132.6, 132.4, 130.5, 129.5, 129.4, 129.3, 127.8 ppm. MS (EI, 70eV): *m/z* (%) = 266 (100) $[M]^+$, 249 (55), 186 (45), 149 (15). HRMS (EI, 70eV): Calcd. For $C_{13}H_9ClO_2$ 265.9895; found 265.9901.



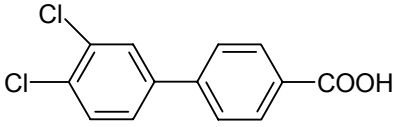
4'-chloro-4-biphenylcarboxylic acid (11d) crystalline m. p. 247-250°C ^{1}H NMR(300MHz, DMSO-d_6, 21°C): δ= 8.03 (d, 2H), 7.62(tt, 4H), 7.46(d, 2H) ppm. ^{13}C NMR(300MHz, DMSO-d_6, 21°C): δ= 167.1, 142.9, 137.8, 133.3, 130.1, 129.1, 128.8, 126.8 ppm. MS (EI, 70eV): *m/z* (%) = 232 (100) $[M]^+$, 215 (30), 152 (40), 122 (20), 105 (20). HRMS (EI, 70eV): Calcd. For $C_{13}H_9ClO_2$ 232.0286; found 232.0290.



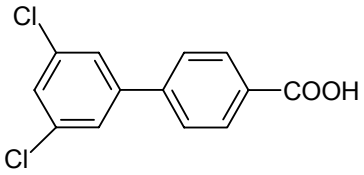
2',3'-dichloro-4-biphenylcarboxylic acid (11e) crystalline m. p. 248-251 °C. ^{1}H NMR(300MHz, DMSO-d_6, 21°C): δ= 8.04 (d, J =8,2 Hz, 2H), 7.67(d, J = 7.9 Hz, 1H), 7.55(d, J = 8.1 Hz, 2H), 7.43-7.38(m, 2H) ppm. ^{13}C NMR(300MHz, DMSO-d_6, 21°C): δ= 160.0, 142.8, 141.5, 132.6, 130.7, 130.5, 130.2, 130.0, 129.7, 129.3, 128.4 ppm. MS (EI, 70eV): *m/z* (%) = 266 (100) $[M]^+$, 249 (50), 186 (47), 149 (17). HRMS (EI, 70eV): Calcd. For $C_{13}H_9ClO_2$ 265.9895; found 265.9895.



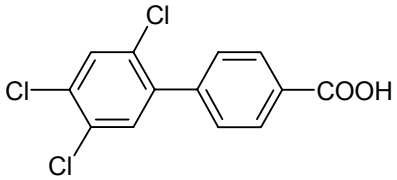
2'-chloro-4-biphenylcarboxylic acid (11f) crystalline m. p. 236-240 °C. ^{1}H NMR(300MHz, DMSO-d_6, 21°C): δ= 8.06 (d, 2H), 7.55(d, 2H), 7.42-7.41(m, 4H) ppm. ^{13}C NMR(300MHz, DMSO-d_6, 21°C): δ= 167.2, 134.1, 139.0, 131.4, 131.3, 130.1, 130.0, 129.5, 129.3, 127.6 ppm. MS (EI, 70eV): *m/z* (%) = 232 (100) $[M]^+$, 215 (50), 152 (60). HRMS (EI, 70eV): Calcd. For $C_{13}H_9ClO_2$ 232.0286; found 232.0295.



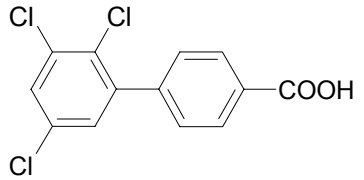
3',4'-dichloro-4-biphenylcarboxylic acid (11g) crystalline m. p. 254-255 °C. ^{1}H NMR(300MHz, DMSO-d_6, 21°C): δ= 8.04 (d, J = 8.3 Hz, 2H), 7.96(t, 1H), 7.81(d, J = 8.2 Hz,2H), 7.68(m, 2H) ppm. ^{13}C NMR(300MHz, DMSO-d_6, 21°C): δ= 167.1, 141.7, 139.7, 132.0, 131.2, 131.1, 130.5, 130.1, 128.8, 127.2, 127.0 ppm. MS (EI, 70eV): *m/z* (%) = 266 (100) $[M]^+$, 249 (30), 186 (32), 149 (10). HRMS (EI, 70eV): Calcd. For $C_{13}H_9ClO_2$ 265.9895; found 265.9892.



3',5'-dichloro-4-biphenylcarboxylic acid (11h) crystalline m. p. 225-228°C. ^{1}H NMR(300MHz, DMSO-d_6, 21°C): δ= 8.04 (d, J = 8.2 Hz, 2H), 7.83(d, J = 8.2 Hz, 2H), 7.74(s, 2H), 7.57(m, 1H) ppm. ^{13}C NMR(300MHz, DMSO-d_6, 21°C): δ= 162.4, 142.6, 141.4, 134.9, 130.9, 130.7, 130.1, 127.6, 127.3, 125.8, 115.2 ppm. MS (EI, 70eV): *m/z* (%) = 266 (100) $[M]^+$, 249 (35), 186 (40), 149 (10). HRMS (EI, 70eV): Calcd. For $C_{13}H_9ClO_2$ 265.9895; found 265.9898.



2',3',5'-trichloro-4-biphenylcarboxylic acid (11i) crystalline m.p. > 300 °C, ^{1}H NMR(300MHz, DMSO-d_6, 21°C): δ=13,06(1H), 8.05 (d, J = 7.6 Hz, 2H), 7.88(s, 1H), 7.58-7.49(m, 3H) ppm. ^{13}C NMR(300MHz, DMSO-d_6, 21°C): δ= 142.5, 141.6, 133.5, 132.9, 132.3, 132.1, 130.9, 129.6, 129.4, 129.3, 128.9 ppm. MS (EI, 70eV): *m/z* (%) = 300 (100) $[M]^+$, 283 (45), 220 (47), 186 (13), 150 (23), 141 (2), 110 (17). HRMS (EI, 70eV): Calcd. For $C_{13}H_7Cl_3O_2$ 299.9506; found 299.9520.



2',4',5'-trichloro-4-biphenylcarboxylic acid (11j) crystalline m.p. > 300 °C, ^{1}H NMR(300MHz, DMSO-d_6, 21°C): δ= 8.05 (d, 2H), 7.77(s, 1H), 7.70(d, 1H), 7.61(d, 2H) ppm. ^{13}C NMR(300MHz, DMSO-d_6, 21°C): δ= 167.0, 140.8, 139.4, 132.4, 132.3, 131.7, 131.2, 130.5, 129.6, 129.3, 125.6 ppm. MS (EI, 70eV): *m/z* (%) = 300 (100) $[M]^+$, 283 (45), 220 (43), 186 (13), 150 (20), 141 (10), 110 (15). HRMS (EI, 70eV): Calcd. For $C_{13}H_7Cl_3O_2$ 299.9506; found 299.9523.