Electronic Supplementary Material (ESI) for Dalton Transactions.

Arsa-Buchwald Ligand: Steric and Electronic Effects on Suzuki-Miyaura Coupling Reaction

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Contents:

1. General Information

All reactions were carried under dry nitrogen atmosphere otherwise noted. Unless otherwise noted, all commercial reagents were used without additional purification. All dry solvents were stored with molecular sieves. ^{1}H (400 MHz), $^{13}C\{^{1}H\}$ (100 MHz), and ^{19}F (376 MHz) NMR spectra were recorded on a Bruker AVANCE III 400 NMR spectrometer using Me_4Si (TMS) as an internal standard. The following abbreviations are used; s: singlet, d: doublet, t: triplet, q: quartet, m: multiplet. High-resolution mass spectra (HRMS) were obtained on a JEOL JMS-SX102A spectrometer.

2. Materials.

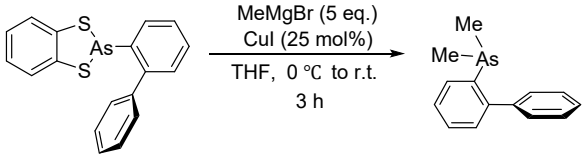
Bis(benzonitrile)palladium(II) chloride ($PdCl_2(PhCN)_2$), allylpalladium(II) chloride dimer ([Pd Cl(allyl)]$_2$), palladium(II) acetate ($Pd(OAc)_2$), tris(dibenzylideneacetone)dipalladium(0)-chloroform adduct ($Pd_2(dba)_3{\cdot}CHCl_3$), methylmagnesium bromide solution (MeMgBr, 1.0 M in dibutyl ether), triphenylarsine ($AsPh_3$), and SPhos were purchased from Sigma Aldrich. Dichloromethane (CH_2Cl_2), ethyl acetate (EtOAc), ethanol (EtOH), concentrated ammonia solution (28% NH_{3aq}), and triphenylphosphine (PPh_3) were purchased from Nacalai Tesque, Inc. Tetrahydrofrane anhydrous (THF), toluene anhydrous, diethyl ether (ether), hexane, magnesium sulfate anhydrous ($MgSO_4$), ammonium chloride (NH_4Cl), copper(I) iodide (CuI), and potassium phosphate (K_3PO_4) were purchased from FUJIFILM Wako Pure Chemical Industry, Ltd. Cyclopentylmagnesium bromide (CypMgBr, 1.0 M in THF), *tert*-butylmagnesium chloride (^{t}BuMgCl, 1.0 M in THF), 1,3,5-trimethoxybenzene, 2-methylphenylboronic acid, 1-naphthaleneboronic acid, 2-biphenylboronic acid, 2,4,6-trimethylphenylboronic acid, 4-(trifluoromethyl)phenylboronic acid, 2,4,6-trifluorophenylboronic acid, 4-cyanophenylboronic acid, mesityl bromide, 2-bromotoluene, 2-bromoanisole, 2-bromo-*N*,*N*-dimethylaniline, 2-bromo-1,3-dimethoxybenzene, 3-chlorobenzonitrile, 3-chlorotoluene and 1,3,5-trifluorobenzene were purchased from Tokyo Chemical Industry Co., Ltd. 2-Bromo-1,3,5-triisopropylbenzene was purchased from Angene Chemical. 2-Benzodithiaarsolylbiphenyl、2-(benzodithiaarsolyl)-2′,6′-dimethoxybiphenyl, 2-(dicyclohexylarsino)-3,6-dimethoxy-2',4',6'-triisopropyl-1,1'-biphenyl (**L1**), 2-(dicyclohexylarsino)-2',6'-diisopropoxybiphenyl (**L2**), 2-(dicyclohexylarsino)-2'-(dimethylamino)biphenyl (**L3**), 2-(dicyclohexylarsino)-2'-methylbiphenyl (**L4**), 2-(dicyclohexylarsino)-2',4',6'-tri(isopropyl)biphenyl (**L5**), 2-(dicyclohexylarsino)-2',6'-dimethoxy-1,1'-biphenyl (**L6**), and 2-(dicyclohexylarsino)biphenyl (**L7**) were prepared according to literature procedures.[1]

3. Synthesis

The general procedure for arsine ligands

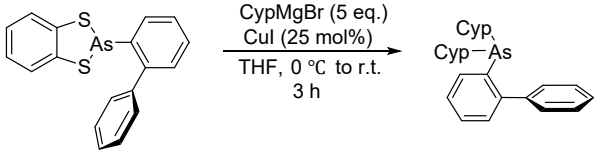
To a suspension of substituted dithiaarsole (1 eq.) and CuI (25 mol%) in anhydrous THF, ethereal solution of Grignard reagent (5 eq.) was added dropwise at 0 °C. Black precipitates soon appeared and the resulting mixture was stirred at room temperature for 3 h. The reaction was quenched with saturated NH_4Cl_{aq} and an aqueous layer was extracted with ether. The combined organic layer was washed with 28% NH_{3aq} (three times) and brine (once), and dried over $MgSO_4$, and filtered. The volatiles were removed *in vacuo*, and the residue was purified with SiO_2 chromatography or by recrystallization to give the title compounds.

*2-(Dimetylarsino)biphenyl (**L8**)*



Prepared according to general procedure: 2-Benzodithiaarsolylbiphenyl (103 mg, 0.280 mmol), CuI (14.6 mg, 0.077 mmol), anhydrous THF (1.4 mL), and MeMgBr (1.0 M, 1.4 mL, 1.4 mmol) were employed. Purified with SiO_2 chromatography (hexane) to give the title compound as colorless oil (63 mg, 0.218 mmol, 80%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.55-7.52 (m, 1H, Ar-*H*), 7.39-7.30 (m, 7H, Ar-*H*), 7.26-7.24 (m, 1H, Ar-*H*), 0.99 (s, 6H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 147.0, 142.5, 141.8, 130.2, 129.5, 129.4, 127.9, 127.7, 127.3, 127.2, 10.7 ppm. HR-FAB-MS (m/z): calculated for $C_{14}H_{15}As$ $[M]^+$; 258.0390, observed; 258.0398.

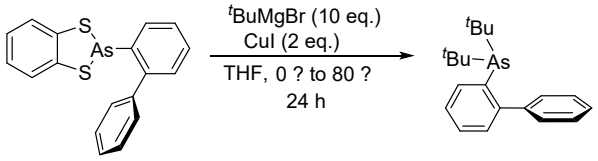
*2-(Dicyclopentylarsino)biphenyl (**L9**)*



Prepared according to general procedure: 2-Benzodithiaarsolylbiphenyl (100 mg, 0.271 mmol), CuI (12.9 mg, 0.068 mmol), anhydrous THF (1.4 mL), and CypMgBr (1.0 M, 1.4 mL, 1.4 mmol) were employed. Recrystallization from CH_2Cl_2/EtOH to give the title compound as colorless solid (80 mg, 0.218 mmol, 80%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.64-7.62 (m, 1H, Ar-*H*), 7.41-7.26 (m, 8H, Ar-*H*), 2.16 (quintet, J = 8.6 Hz, 2H, CH_2CHCH_2), 1.91-1.84 (m, 2H, CH_2), 1.67-1.37 (m, 12H, CH_2), 1.25-1.14 (m, 2H, CH_2) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz):

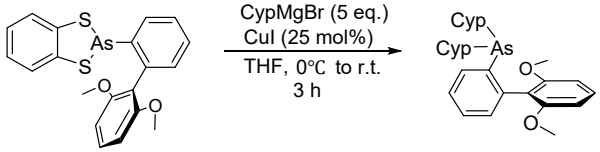
δ = 148.9, 143.2, 140.16, 132.8, 130.5, 129.4, 127.6, 127.5, 127.0, 126.8, 38.6, 31.6, 30.8, 26.4, 25.7 ppm. HR-FAB-MS (m/z): calculated for $C_{22}H_{27}As$ $[M]^+$; 366.1329, observed; 366.1325.

*2-(Di-tert-butylarsino)biphenyl (**L10**)*



To a suspension of 2-Benzodithiaarsolylbiphenyl (97 mg, 0.264 mmol), and CuI (100 mg, 0.522 mmol), anhydrous THF (0.5 mL), ^{t}BuMgCl (1.0 M, 2.6 mL, 2.6 mmol) was added dropwise at 0 °C. Black precipitates soon appeared and the resulting mixture was stirred at 80 °C for 24 h. The reaction was quenched with saturated NH_4Cl_{aq} and an aqueous layer was extracted with ether. The combined organic layer was washed with 28% NH_{3aq} three times and brine once, dried over $MgSO_4$, and filtered. The volatiles were removed *in vacuo*, and the residue was purified with SiO_2 chromatography (hexane/EtOAc = 40/1) to give the title compound as colorless solid (35 mg, 0.102 mmol, 39%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.82-7.80 (m, 1H, Ar-*H*), 7.36-7.23 (m, 8H, Ar-*H*), 1.17 (s, 18H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 150.6, 143.8, 138.8, 135.0, 130.6, 130.1, 127.8, 127.3, 126.6, 126.0, 34.8, 30.6 ppm. HR-FAB-MS (m/z): calculated for $C_{20}H_{27}As$ $[M]^+$; 342.1329, observed; 342.1327.

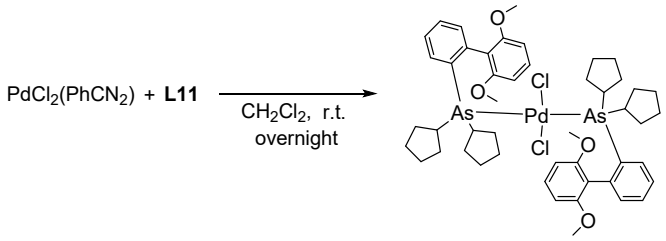
*2-(Dicyclopentylarsino)-2',6'-dimethoxy-1,1'-biphenyl (**L11**)*



Prepared according to general procedure: 2-(Benzodithiaarsolyl)-2′,6′-dimethoxybiphenyl (240 mg, 0.564 mmol), CuI (26.7 mg, 0.140 mmol), anhydrous THF (2.8 mL), and CypMgBr (1.0 M, 2.8 mL, 2.8 mmol) were employed. Recrystallization from CH_2Cl_2/EtOH to give the title compound as colorless solid (191 mg, 0.447 mmol, 80%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.59 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar-*H*), 7.37-7.25 (m, 3H, Ar-*H*), 7.14 (dd, *J* = 7.6, 1.6 Hz, 1H, Ar-*H*), 6.60 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 3.68 (s, 6H, O*Me*), 2.15 (quintet, *J* = 8.4 Hz, 2H, CH_2CHCH_2), 1.87-1.84 (m, 2H, CH_2), 1.64-1.36 (m, 12H, CH_2), 1.26-1.16 (m, 2H, CH_2) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 157.6, 142.4, 141.1, 132.1, 130.2, 128.9, 127.7, 126.8, 120.3, 103.2, 55.4, 38.1, 31.0, 30.8, 26.5, 25.8 ppm. HR-FAB-MS (m/z): calculated for

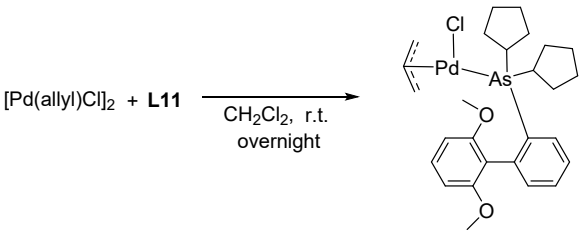
$C_{24}H_{31}O_2As$ [M]$^+$; 426.1540, observed; 426.1531.

*[$PdCl_2$(**L11**)$_2$]*



A CH_2Cl_2 (1.0 mL) solution of **L11** (60.4 mg, 0.142 mmol) and $PdCl_2(PhCN)_2$ (26.8 mg, 69.9 μmol) was stirred at room temperature under a nitrogen atmosphere overnight. The volatiles were removed *in vacuo*. To the residue was added CH_2Cl_2, and the insoluble part was removed by filtration. The solvent was removed *in vacuo*, and the obtained products were further purified by recrystallization from CH_2Cl_2/hexane to obtain orange crystals of [$PdCl_2$(**L11**)$_2$] (63.9 mg, 0.620 mmol, 89%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 8.26-8.24 (m, 2H, Ar-*H*), 7.43-7.30 (m, 6H, Ar-*H*), 7.07-7.05 (m, 2H, Ar-*H*), 6.62 (d, *J* = 8.4 Hz, 4H, Ar-*H*), 3.65 (s, 12H, O*Me*), 2.42-2.33 (m, 4H, CH_2CHCH_2), 2.04-1.86 (m, 10H, CH_2), 1.76-1.64 (m, 12H, CH_2), 1.41-1.35 (m, 10H, CH_2) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ =158.2, 139.0, 137.3, 134.5, 132.2, 129.3, 128.9, 125.8, 119.3, 103.5, 55.3, 37.8, 30.7, 29.6, 26.1, 25.7 ppm. HR-FAB-MS (m/z): calculated for $C_{48}H_{62}ClO_4As_2Pd$ [M-Cl]$^+$; 993.1803, observed; 993.1802.

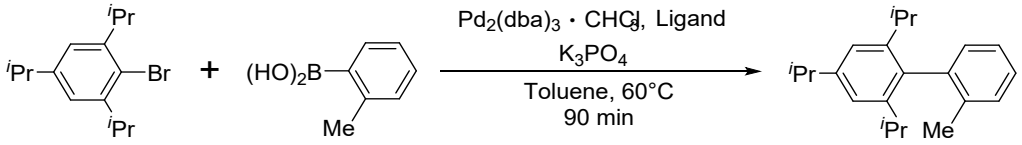
*[PdCl(allyl)(**L11**)]*



A CH_2Cl_2 (0.5 mL) solution of **L11** (15.7 mg, 36.8 μmol) and $[PdCl(allyl)]_2$ (6.6 mg, 18.0 μmol) was stirred at room temperature under a nitrogen atmosphere overnight. The volatiles were removed *in vacuo*. To the residue was added CH_2Cl_2, and the insoluble part was removed by filtration. The solvent was removed *in vacuo*, and the obtained products were further purified by recrystallization from CH_2Cl_2/hexane to obtain orange crystals of [PdCl(allyl)(**L11**)] (8.5 mg, 14 μmol, 77 %). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.65 (dd, *J* = 7.6, 1.2 Hz, 1H, Ar-*H*), 7.42 (dt, *J* = 7.6, 1.2 Hz, 1H, Ar-*H*), 7.35 (dt, *J* = 7.6, 1.2 Hz, 1H, Ar-*H*), 7.26 (t, *J* = 8.4 Hz, 1H, Ar-*H*), 7.13 (dt, *J* = 7.6, 1.2 Hz, 1H, Ar-*H*), 6.68 (d, *J* = 8.4 Hz, 1H, Ar-*H*), 6.51 (d, *J* = 8.0 Hz, 1H, Ar-*H*), 4.95 (septet, *J* = 6.8 Hz, 1H, C*H*=CH_2), 4.45 (dd, *J* = 7.2, 2.0 Hz, 1H,

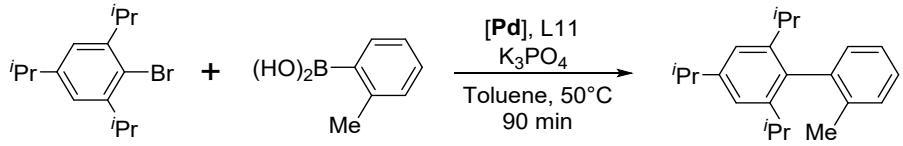
CH=CH_2), 3.80 (s, 3H, CH=CH_2), 3.68 (s, 3H, CH=CH_2), 3.55 (dd, J = 6.8, 1.2 Hz, 1H, CH=CH_2), 2.88 (d, J = 13.2 Hz, 1H, CH=CH_2), 2.65 (quartet, J = 9.2 Hz, 1H, CH=CH_2), 2.52 (quartet, J = 9.2 Hz, 1H, CH_2CHCH_2), 1.87-1.46 (m, 18H, CH_2) ppm. $^{13}C\{^1H\}$-NMR ($CDCl_3$, 100 MHz): δ = 158.17, 140.3, 136.6, 132.6, 132.3, 129.1, 128.7, 126.6, 113.6, 104.5, 103.2, 55.7, 55.5, 51.4, 39.1, 38.5, 31.6, 30.9, 30.4, 30.0, 29.9, 26.6, 26.2, 25.5 ppm. HR-FAB-MS (m/z): calculated for $C_{27}H_{35}O_2AsPd$ $[M\text{-}Cl]^+$; 572.0888, observed; 572.0888.

General procedure A for ligand screening of Suzuki-Miyaura couplings using Pd catalysts.



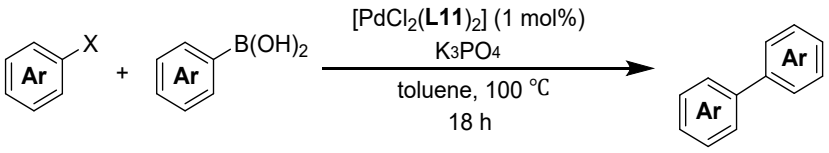
To the mixture of 2,4,6-triisopropylbromobenzene (125 µL, 0.50 mmol), 2-methylphenylboronic acid (136.0 mg, 1.0 mmol), K_3PO_4 (318.4 mg, 1.50 mmol), $Pd_2(dba)_3{\cdot}CHCl_3$ (7.8 mg, 7.5 µmol), and ligand (30 µmol), degassed toluene (1.0 mL) was added and stirred at 60 °C for 90 min under nitrogen atmosphere. The crude product wad passed through the pad of silica and 1,3,5-trimethoxybenzene (30.0 mg, 0.178 mmol) was added as an internal standard. The yield of the target compound was evaluated by ^{1}H-NMR.

General procedure B for Pd source screening of Suzuki-Miyaura couplings.



To the mixture of 2,4,6-triisopropylbromobenzene (125 µL, 0.50 mmol), 2-methylphenylboronic acid (136.0 mg, 1.0 mmol), K_3PO_4 (318.4 mg, 1.50 mmol), Pd sources (2.5 µmol), and **L11** (2.1 mg, 5.0 µmol), degassed toluene (1.0 mL) was added and stirred at 50 °C for 90 min under nitrogen atmosphere. The crude product wad passed through the pad of silica and 1,3,5-trimethoxybenzene (30.0 mg, 0.178 mmol) was added as an internal standard. The yield of the target compound was evaluated by ^{1}H-NMR.

General Procedure C for the Pd-catalyzed Suzuki-Miyaura coupling.



To the mixture of aryl halide (0.50 mmol), boronic acid (1.0 mmol), K_3PO_4 (318.4 mg, 1.50 mmol), $PdCl_2$(**L11**)$_2$ (5.1 mg, 5.0 μmol), degassed toluene (1.0 mL) was added and stirred at 100 °C for 18 h under nitrogen atmosphere. The crude product wad passed through the pad of silica and 1,3,5-trimethoxybenzene (30.0 mg, 0.178 mmol) was added as an internal standard. The yield of the target compound was evaluated by ^{1}H-NMR. The residue was purified by silica column chromatography to give the target compound.

*1-[2,4,6-Tris(1-methylethyl)phenyl]naphthalene (**P1**)*

To the mixture of 2-bromo-1,3,5-triisopropylbenzene (125 μL, 0.50 mmol), 1-naphthaleneboronic acid (171.1 mg, 1.0 mmol), K_3PO_4 (316.6 mg, 1.49 mmol), $PdCl_2$(**L11**)$_2$ (2.6 mg, 2.5 μmol), degassed toluene (1.0 mL) was added and stirred at 100 °C for 18 h under nitrogen atmosphere. The crude product wad passed through the pad of silica and 1,3,5-trimethoxybenzene (30.0 mg, 0.178 mmol) was added as an internal standard. The yield of the target compound was evaluated by ^{1}H-NMR. The residue was purified by silica column chromatography (hexane) to give the target compound as colorless solid (0.148 g, 0.447 mmol, 90%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.86-7.80 (m, 2H, Ar-*H*), 7.48 (dd, *J* = 7.2, 1.2 Hz, 1H, Ar-*H*), 7.42-7.39 (m, 2H, Ar-*H*), 7.31-7.27 (m, 2H, Ar-*H*), 7.14 (s, 2H, Ar-*H*), 3.00 (septet, *J* = 6.9 Hz, 1H, C*H*Me$_2$), 2.35 (septet, *J* = 6.9 Hz, 2H, C*H*Me$_2$), 1.35 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 1.04 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 0.95 (d, *J* = 7.2 Hz, 6H, CH*Me*$_2$) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 148.1, 147.3, 138.6, 134.4, 133.4, 133.2, 128.0, 127.3, 127.0, 126.4, 125.7, 125.6, 125.2, 120.7, 34.3, 30.5, 24.8, 24.2, 23.9 ppm.

*2,4,6-Tris(1-methylethyl)-1,1',2',1''-terphenyl (**P2**)*

Following general procedure C, 2-bromo-1,3,5-triisopropylbenzene (125 μL, 0.50 mmol), and 2-biphenylboronic acid (196.6 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane) to give the target compound as colorless solid (128 mg, 0.359 mmol, 73%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.48 (dd, *J* = 7.6, 1.2 Hz, 1H, Ar-*H*), 7.40 (dt, *J* = 7.6, 1.6 Hz, 1H, Ar-*H*), 7.33 (dt, *J* = 7.6, 1.6 Hz, 1H, Ar-*H*), 7.22 (dd, *J* = 7.6, 1.2 Hz, 1H, Ar-*H*), 7.12-7.06 (m, 5H, Ar-*H*), 6.91 (s, 2H, Ar-*H*), 2.86 (septet, *J* = 6.8 Hz, 1H, C*H*Me$_2$), 2.55 (septet, *J* = 6.8 Hz, 2H, C*H*Me$_2$), 1.24 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 1.01 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$), 0.84 (d, *J* = 6.8 Hz, 6H, CH*Me*$_2$) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 147.9, 146.2, 141.2, 138.8, 135.6, 131.3, 129.6, 129.4, 127.4, 127.2, 126.7, 126.3, 120.5,

34.1, 30.4, 25.5, 24.1, 22.7 ppm.

*2,4,6-Trimethyl-1,1',2',1''-terphenyl (**P3**)*

Following general procedure C, mesityl bromide (78 µL, 0.52 mmol), and 2-biphenylboronic acid (205.1 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane) to give the target compound as colorless oil (132 mg, 0.484 mmol, 94%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.46-7.33 (m, 3H, Ar-*H*), 7.15-7.07 (m, 6H, Ar-*H*), 6.77 (s, 2H, Ar-*H*), 2.23 (s, 3H, *Me*), 1.89 (s, 6H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 141.4, 140.9, 139.0, 137.9, 136.2, 135.8, 130.7, 130.1, 128.8, 127.9, 127.6, 127.3, 127.2, 126.5, 21.0, 20.7 ppm.

*2,2',4,6-Tetramethyl-1,1'-biphenyl (**P4**)*

Following general procedure C, 2-bromotoluene (60 µL, 0.50 mmol), and 2,4,6-trimethylphenylboronic acid (163.6 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane) to give the target compound as colorless oil (99 mg, 0.470 mmol, 95%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.27-7.21 (m, 3H, Ar-*H*), 7.01-6.99 (m, 1H, Ar-*H*), 6.93 (s, 2H, Ar-*H*), 2.32 (s, 3H, *Me*), 1.97 (s, 3H, *Me*), 1.91 (s, 6H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 140.6, 138.2, 136.3, 135.8, 135.7, 129.9, 129.1, 128.0, 126.9, 126.0, 21.1, 20.2, 19.5 ppm.

*2,2',4,4',6,6'-Hexamethyl-1,1'-biphenyl (**P5**)*

Following general procedure C, mesityl bromide (75 µL, 0.50 mmol), and 2,4,6-trimethylphenylboronic acid (164.1 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane) to give the target compound as colorless oil (79 mg, 0.332 mmol, 66%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 6.93 (s, 4H, Ar-*H*), 2.32 (s, 6H, *Me*), 1.86 (s, 12H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 137.0, 136.0, 135.5, 128.2, 21.1, 19.8 ppm.

*2'-Methoxy-2,4,6-trimethyl-1,1'-biphenyl (**P7**)*

Following general procedure C, 2-bromoanisole (65 µL, 0.50 mmol), and 2,4,6-trimethylphenylboronic acid (163.6 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane/EtOAc = 30/1) to give the target compound as colorless oil (0.102 g, 0.450 mmol, 90%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.26-7.22 (m, 1H, Ar-*H*), 6.95-6.85 (m, 5H, Ar-*H*), 3.64 (s, 3H, O*Me*), 2.24 (s, 3H, *Me*), 1.90 (s, 6H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 156.7, 136.4, 136.4, 135.3, 130.9, 129.5, 128.3, 127.9, 120.6, 110.7, 55.3, 21.1, 20.3 ppm.

*N,N,2'-Trimethyl[1,1'-biphenyl]-2-amine (**P8**)*

Following general procedure C, 2-bromo-*N,N*-dimethylaniline (72 µL, 0.50 mmol), and 2-methylphenylboronic acid (136.0 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane/EtOAc = 30/1) to give the target compound as colorless oil (97 mg, 0.460 mmol, 92%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.29-7.19 (m, 5H, Ar-*H*), 7.09-6.95 (m, 3H, Ar-*H*), 2.50 (s, 6H, N*Me*), 2.15 (s, 3H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 151.5, 141.7, 136.1, 134.5, 131.7, 130.0, 129.9, 127.9, 126.7, 125.6, 121.0, 117.4, 43.1, 20.0 ppm.

*2,6-Dimethoxy-1,1:2,1-terphenyl (**P9**)*

Following general procedure C, 2-bromo-1,3-dimethoxybenzene (108.5 mg, 0.50 mmol), and 2-methylphenylboronic acid (136.0 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane/EtOAc = 30/1) to give the target compound as colorless oil (136 mg, 0.468 mmol, 94%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.42-7.29 (m, 4H, Ar-*H*), 7.12-7.03 (m, 6H, Ar-*H*), 6.39 (d, *J* = 8.4 Hz, 2H, Ar-*H*), 3.44 (s, 6H, O*Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 157.5, 142.4, 142.2, 132.8, 131.6, 129.3, 128.6, 128.5, 127.3, 127.1, 126.7, 126.1, 118.9, 103.6, 55.4 ppm.

*2-Methyl-4'-(trifluoromethyl)-1,1'-biphenyl (**P11**)*

Following general procedure C, 2-bromotoluene (60 µL, 0.50 mmol), and 4-(trifluoromethyl)phenylboronic acid (189.2 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane) to give the target compound as colorless oil (106 mg, 0.448 mmol, 90%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.65 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.42 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.29-7.18 (m, 4H, Ar-*H*), 2.25 (s, 3H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 145.7, 140.6, 135.3, 130.6, 129.6, 129.6, 128.8 (q, *J* = 32.0 Hz), 128.0, 126.0, 125.1 (q, *J* = 4.0 Hz), 124.0 (q, *J* = 191.0 Hz), 20.4 ppm. ^{19}F-NMR ($CDCl_3$, 376 MHz): δ = -62.3 ppm.

*2,4,6-Trimethyl-4'-(trifluoromethyl)-1,1'-biphenyl (**P12**)*

Following general procedure C, mesityl bromide (75 µL, 0.50 mmol), and 4-(trifluoromethyl)phenylboronic acid (189.6 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane) to give the target compound as colorless oil (125 mg, 0.473 mmol, 95%). ^{1}H-NMR ($CDCl_3$, 400 MHz): δ = 7.66 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.25 (d, *J* = 7.6 Hz, 2H, Ar-*H*), 6.95 (s, 2H, Ar-*H*), 2.33 (s, 3H, *Me*), 1.98 (s, 6H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): δ = 145.1, 137.7, 137.3, 135.7, 129.8, 129.0 (q, *J* = 32.0

Hz), 128.3, 125.4 (q, *J* = 4.0 Hz), 124.0 (q, *J* = 190.0 Hz), 21.0, 20.7 ppm. ^{19}F-NMR ($CDCl_3$, 376 MHz): *δ* = -62.3 ppm.

*2,4,6-Trifluoro-2'-methyl-1,1'-biphenyl (**P13**)*

Following general procedure C, 2-bromotoluene (60 µL, 0.50 mmol), and 2,4,6-trifluorophenylboronic acid (175.9 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane/EtOAc = 20/1) to give the target compound as colorless oil (7 mg, 32 µmol, 6%). ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 7.34-7.18 (m, 4H, Ar-*H*), 6.77-6.73 (m, 2H, Ar-*H*), 2.17 (s, 3H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): *δ* = 163.3-158.9 (m), 137.5, 130.8, 130.2, 128.9, 128.0, 125.7, 100.5-99.9 (m), 19.7 ppm. ^{19}F-NMR ($CDCl_3$, 376 MHz): *δ* = -110.3 (3F, broad s) ppm.

*2'-Methyl[1,1'-biphenyl]-4-carbonitrile (**P14**)*

Following general procedure C, 2-bromotoluene (60 µL, 0.50 mmol), and 4-cyanophenylboronic acid (146.6 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane/EtOAc = 20/1) to give the target compound as colorless oil (33 mg, 0.169 mmol, 34%). ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 7.72-7.69 (m, 2H, Ar-*H*), 7.44-7.41 (m, 2H, Ar-*H*), 7.32-7.25 (m, 3H, Ar-*H*), 7.19 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 2.25 (s, 3H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): *δ* = 146.8, 140.0, 135.0, 132.0, 130.7, 130.0, 129.4, 128.3, 126.1, 119.0, 110.7, 20.3 ppm.

*1,1':2',1''-Terphenyl, 3-methyl (**P16**)*

Following general procedure C, 3-chlorotoluene (60 µL, 0.50 mmol), and 2-biphenylboronic acid (198.0 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane) to give the target compound as colorless oil (15 mg, 61 µmol, 13%). ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 7.41-7.39 (m, 4H, Ar-*H*), 7.23-7.00 (m, 8H, Ar-*H*), 6.88 (d, *J* = 7.6 Hz, 1H, Ar-*H*), 2.24 (s, 3H, *Me*) ppm. ^{13}C{^{1}H}-NMR ($CDCl_3$, 100 MHz): *δ* = 141.6, 141.4, 140.7, 140.6, 137.4, 130.6, 130.6, 129.9, 127.8, 127.6, 127.4, 127.4, 127.2, 127.1, 126.4, 21.4 ppm.

*2-Methyl-4'-nitro-1,1'-biphenyl (**P17**)*

Following general procedure C, 3-chlorotoluene (60 µL, 0.50 mmol), and 2,4,6-trimethylphenylboronic acid (163.9 mg, 1.0 mmol) were used. The residue was purified by silica column chromatography (hexane) to give the target compound as colorless oil (29 mg, 0.138 mmol, 27%). ^{1}H-NMR ($CDCl_3$, 400 MHz): *δ* = 7.29 (t, *J* = 7.2 Hz, 1H, *Me*), 7.13 (d, *J* = 7.6 Hz, 1H, *Me*), 6.94-6.93 (m, 4H, *Me*), 2.37 (s, 3H, *Me*), 2.32 (s, 3H, *Me*), 2.00 (s, 6H, *Me*)

ppm. $^{13}C\{^{1}H\}$-NMR ($CDCl_3$, 100 MHz): δ = 141.0, 139.2, 137.8, 136.4, 135.9, 129.9, 128.2, 128.0, 127.2, 126.3, 21.5, 21.0, 20.8 ppm.

4. NMR spectra

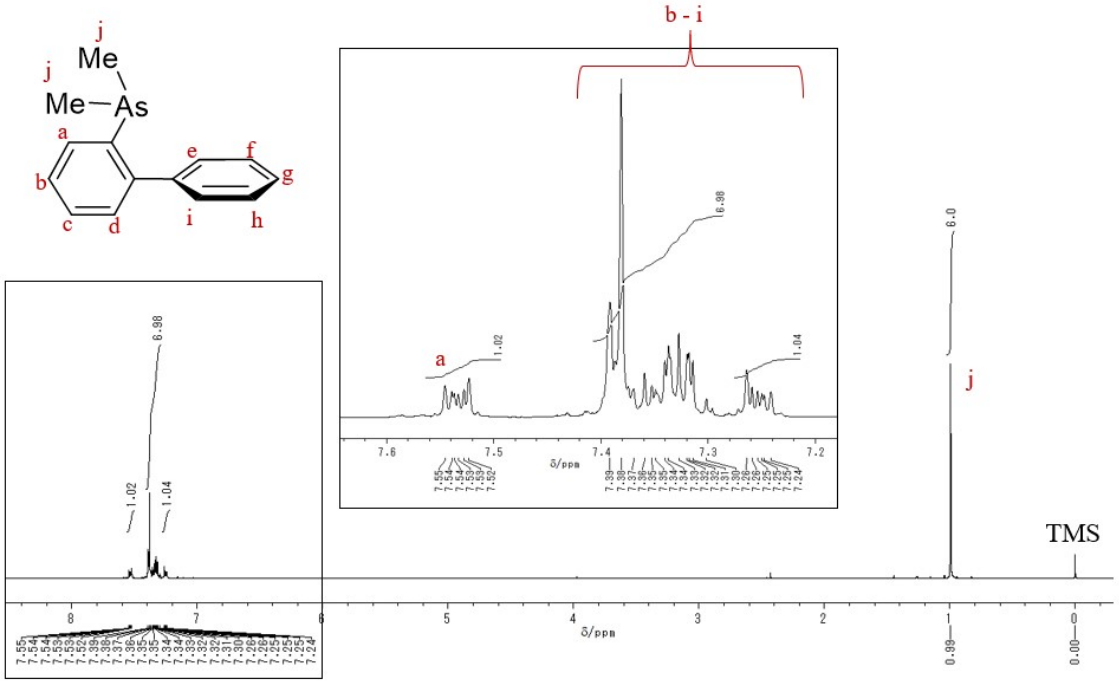


Figure S1. ^{1}H-NMR spectrum (400 MHz) of **L8** in $CDCl_3$.

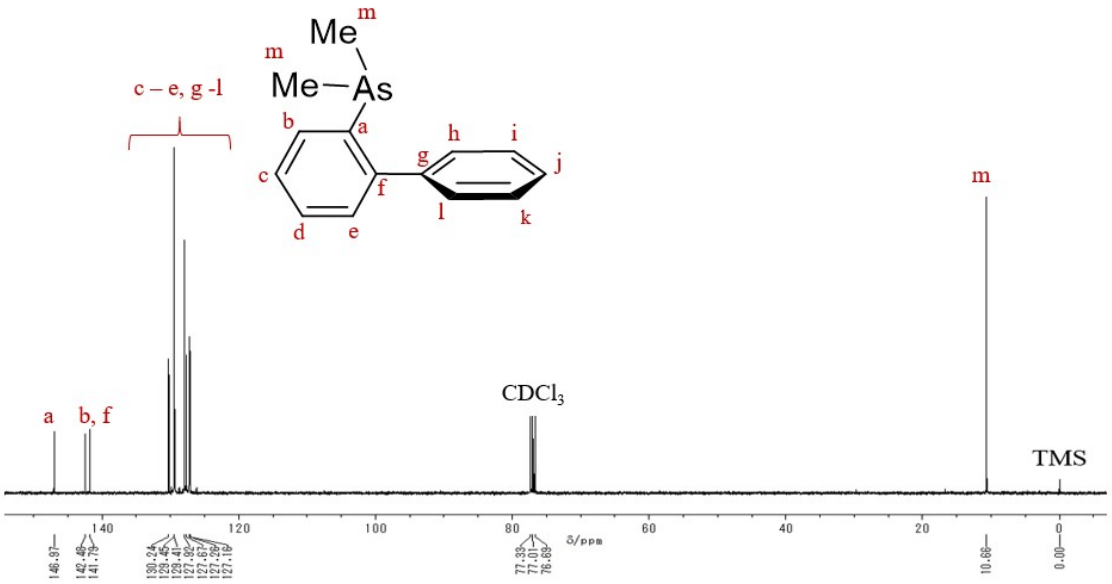


Figure S2. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **L8** in $CDCl_3$.

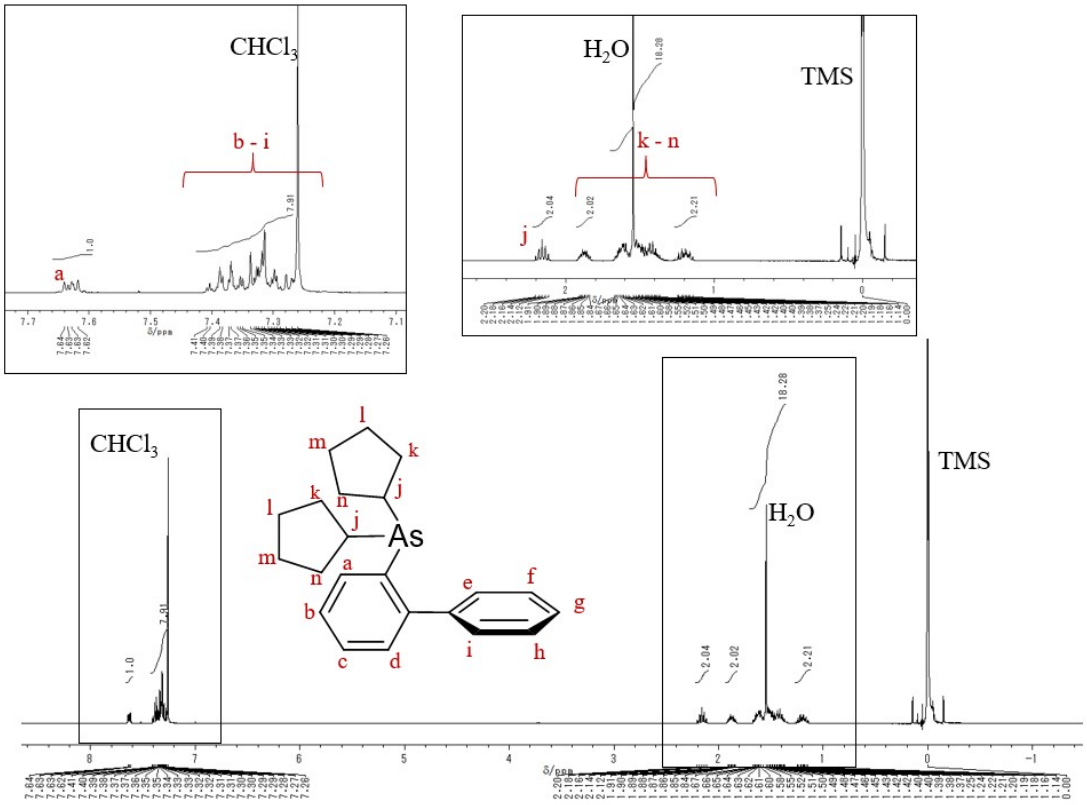


Figure S3. ^{1}H-NMR spectrum (400 MHz) of **L9** in $CDCl_3$.

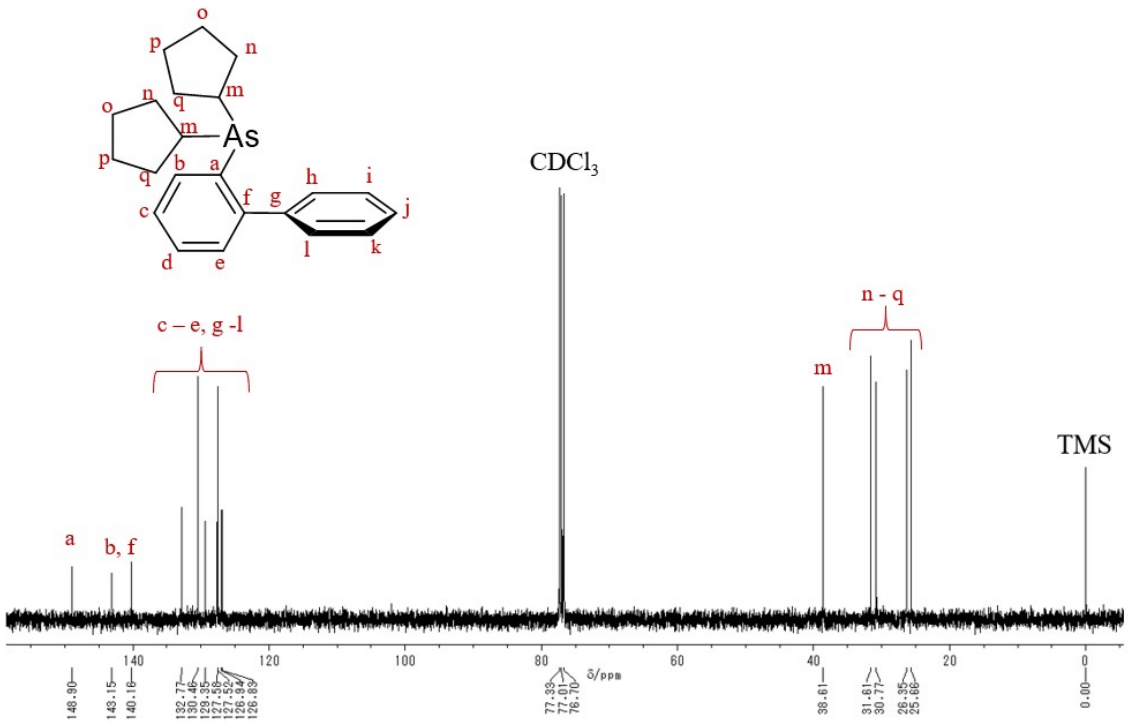


Figure S4. $^{13}C\{^{1}H\}$-NMR spectrum (100 MHz) of **L9** in $CDCl_3$.

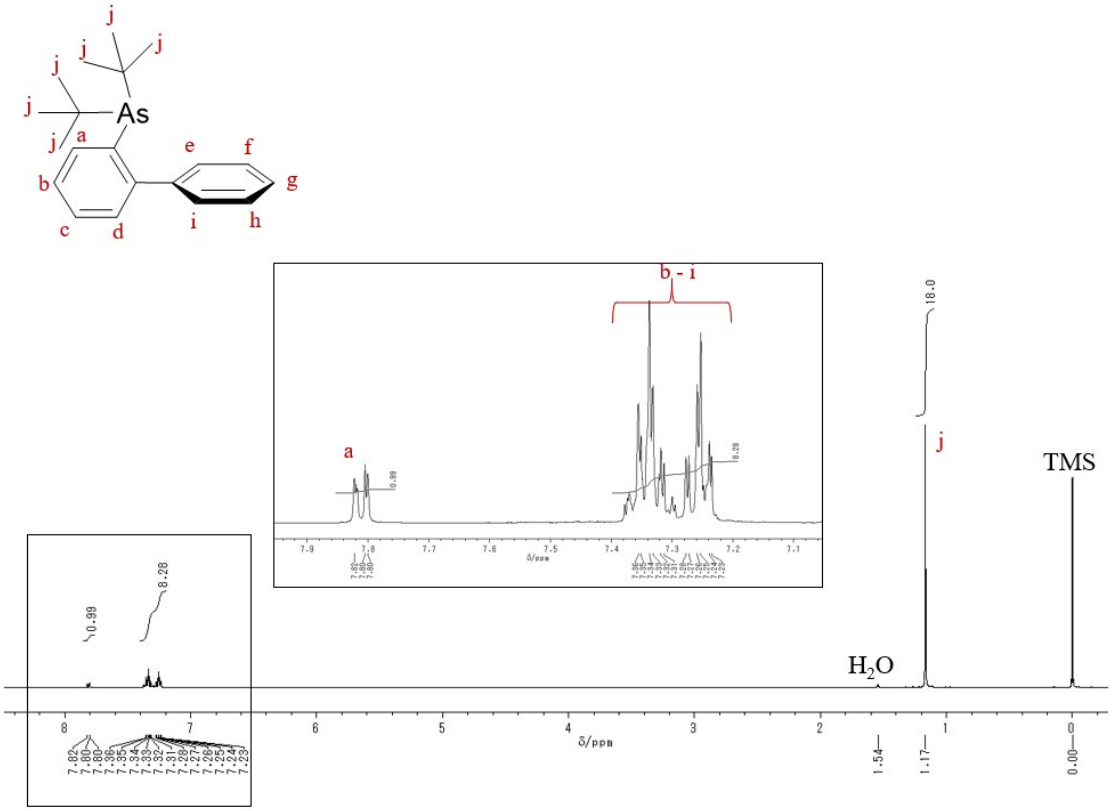


Figure S5. ^{1}H-NMR spectrum (400 MHz) of **L10** in $CDCl_3$.

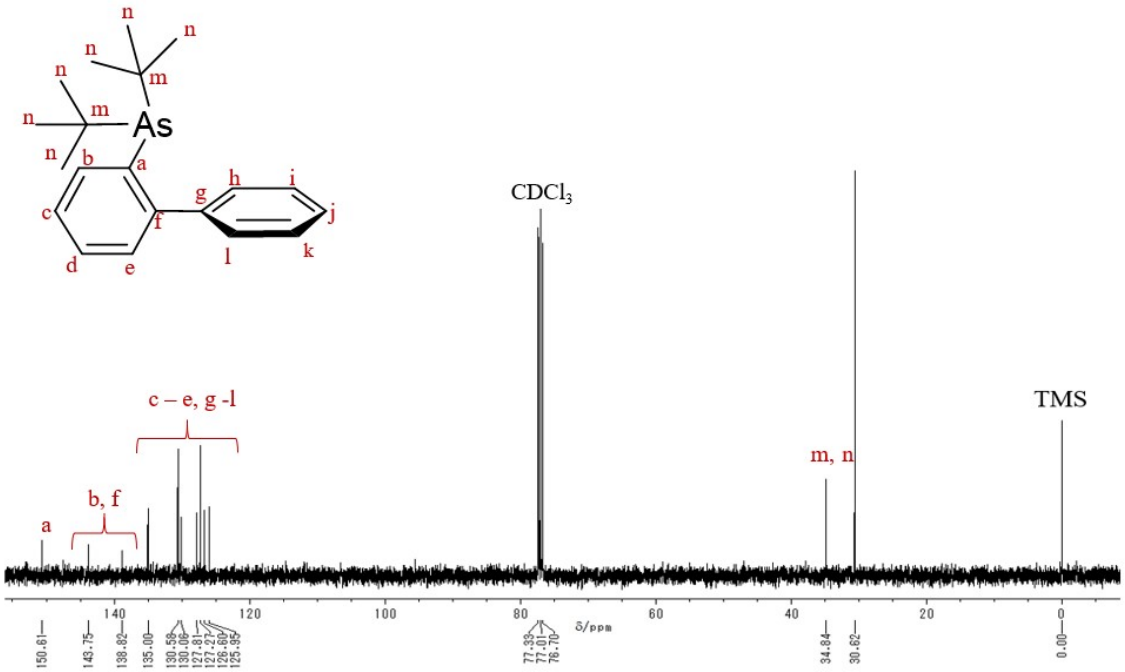


Figure S6. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **L10** in $CDCl_3$.

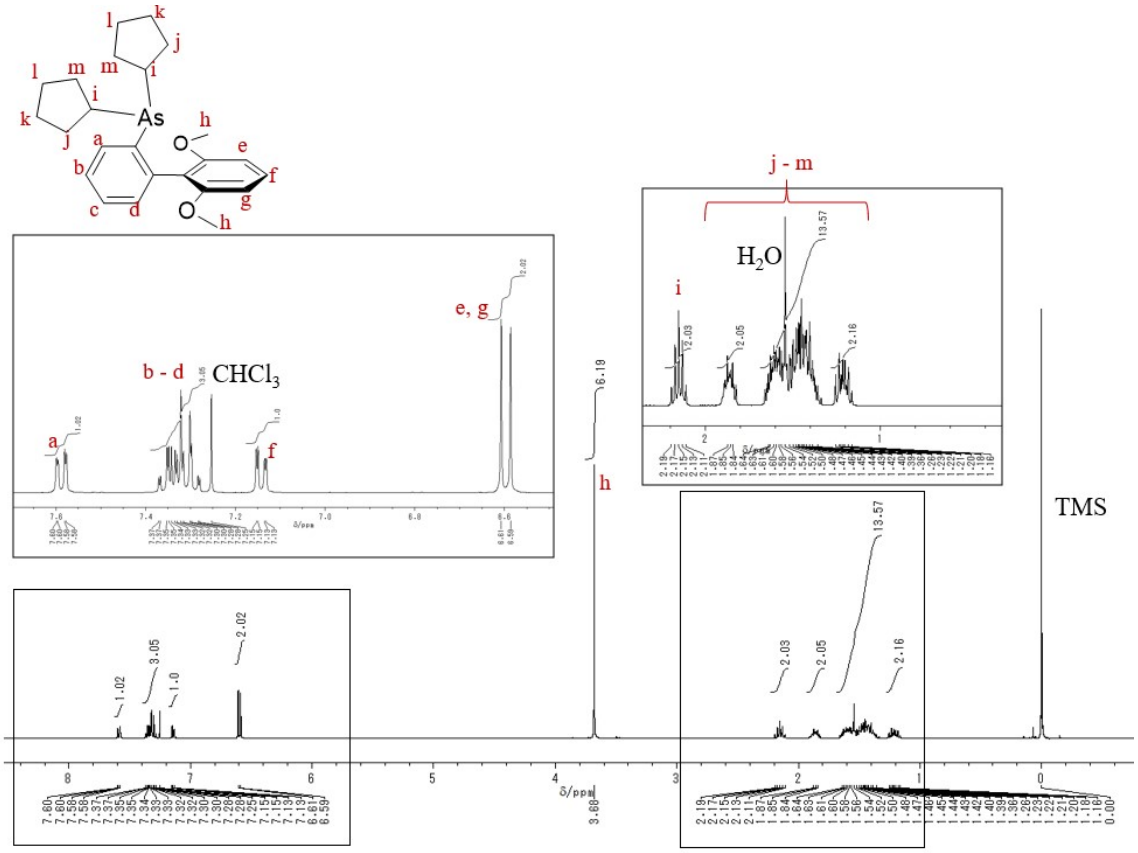


Figure S7. ^{1}H-NMR spectrum (400 MHz) of **L11** in $CDCl_3$.

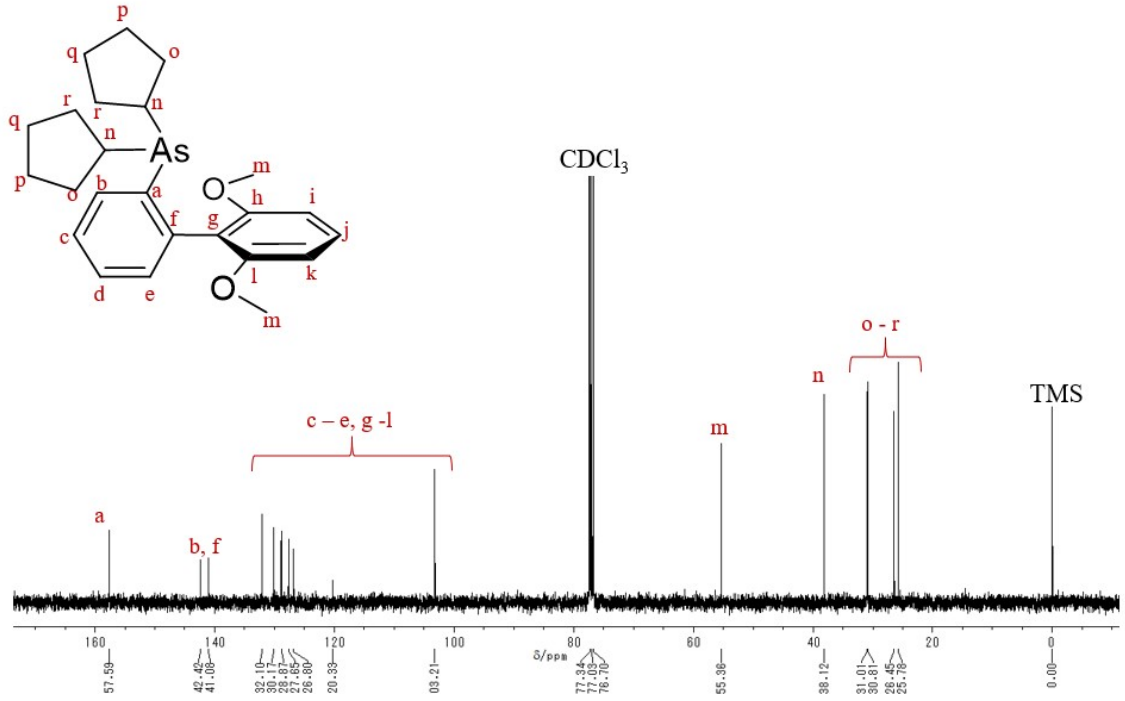


Figure S8. $^{13}C\{^{1}H\}$-NMR spectrum (100 MHz) of **L11** in $CDCl_3$.

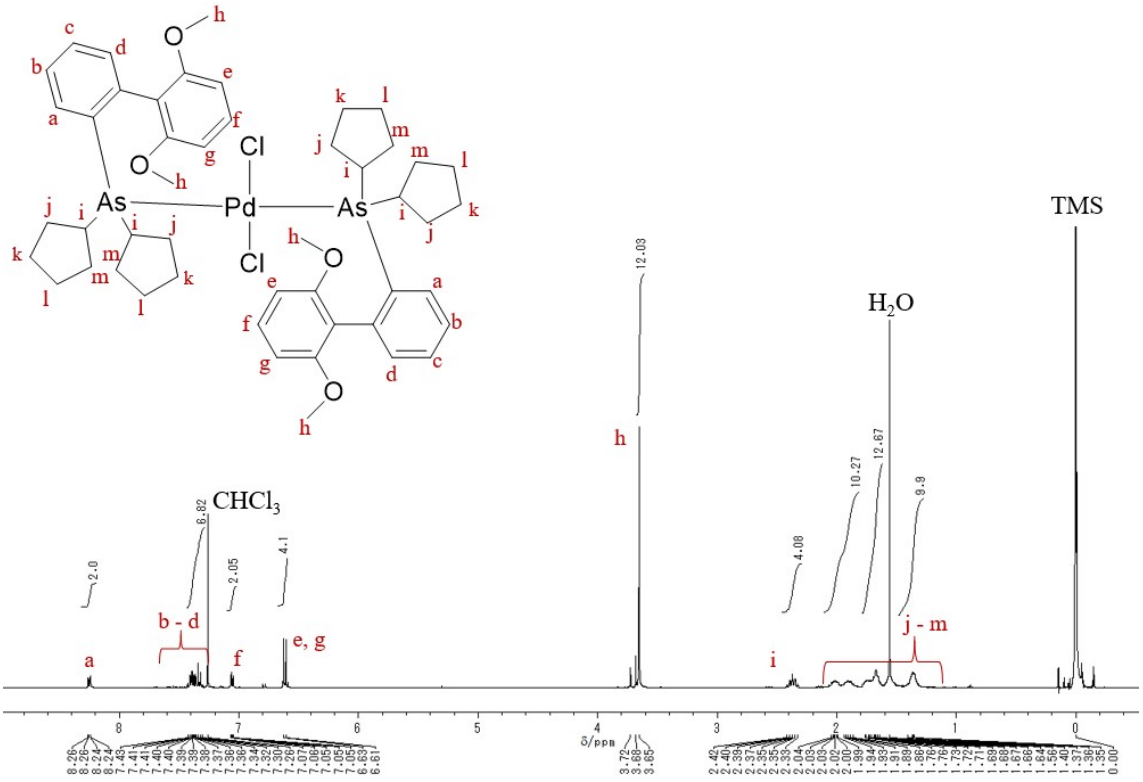


Figure S9. ^{1}H-NMR spectrum (400 MHz) of $[PdCl_2(\mathbf{L11})_2]$ in $CDCl_3$.

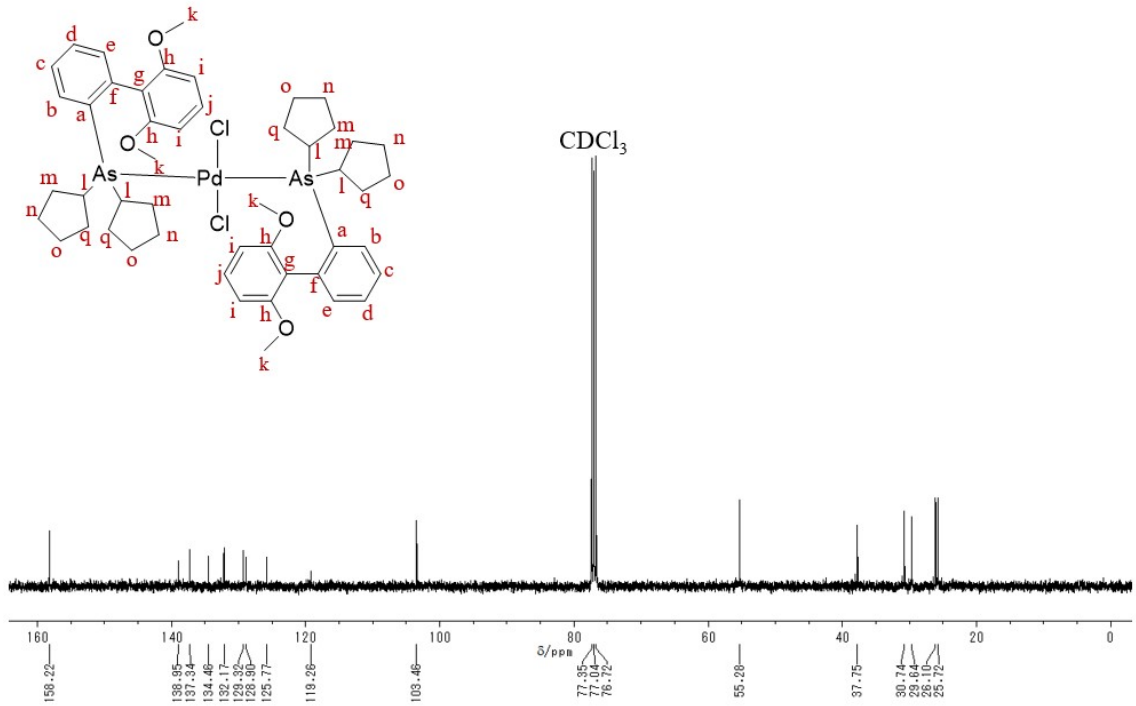


Figure S10. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of $[PdCl_2(\mathbf{L11})_2]$ in $CDCl_3$.

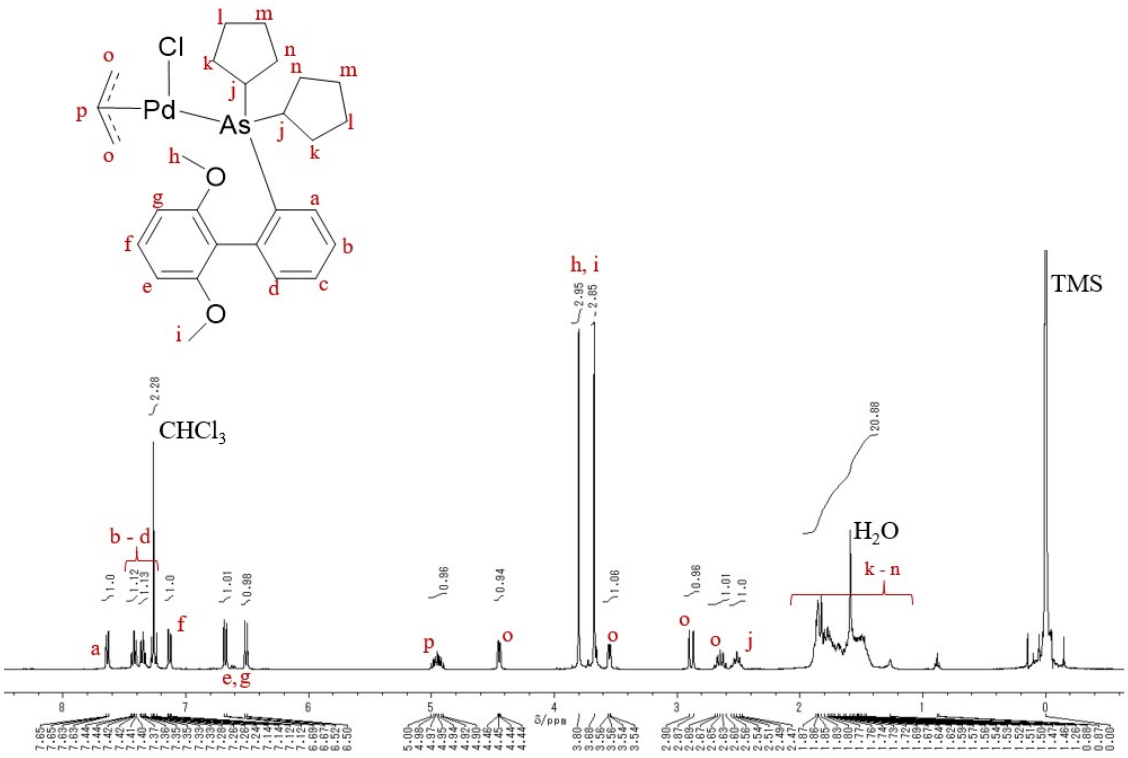


Figure S11. ^{1}H-NMR spectrum (400 MHz) of [PdCl(allyl)(**L11**)] in $CDCl_3$.

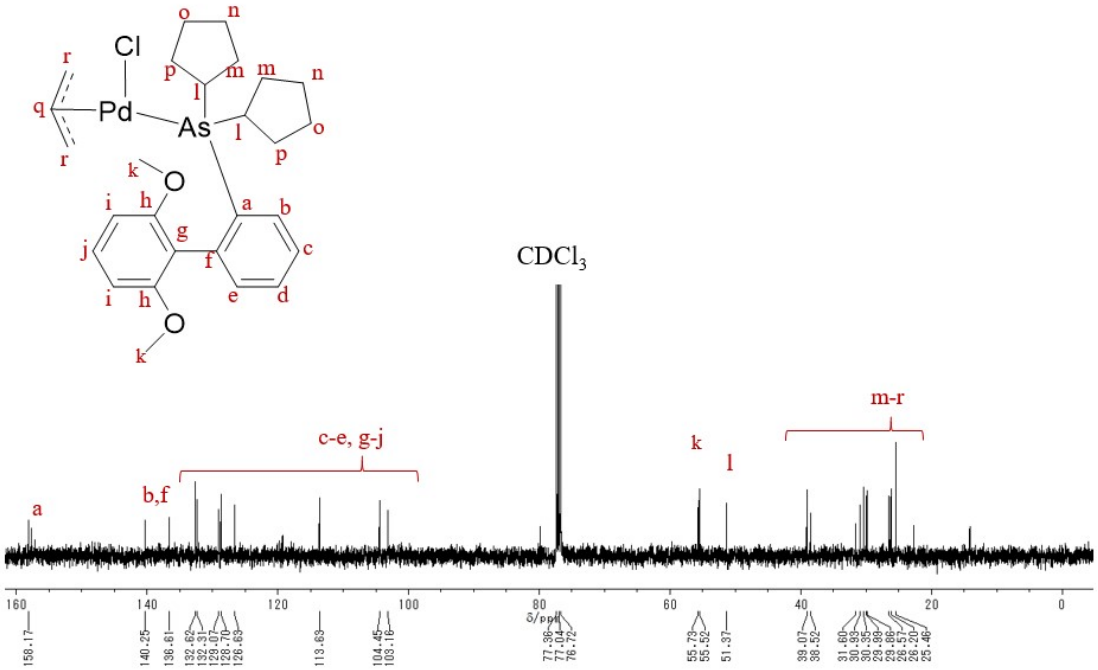


Figure S12. $^{13}C\{^{1}H\}$-NMR spectrum (100 MHz) of [PdCl(allyl)(**L11**)] in $CDCl_3$.

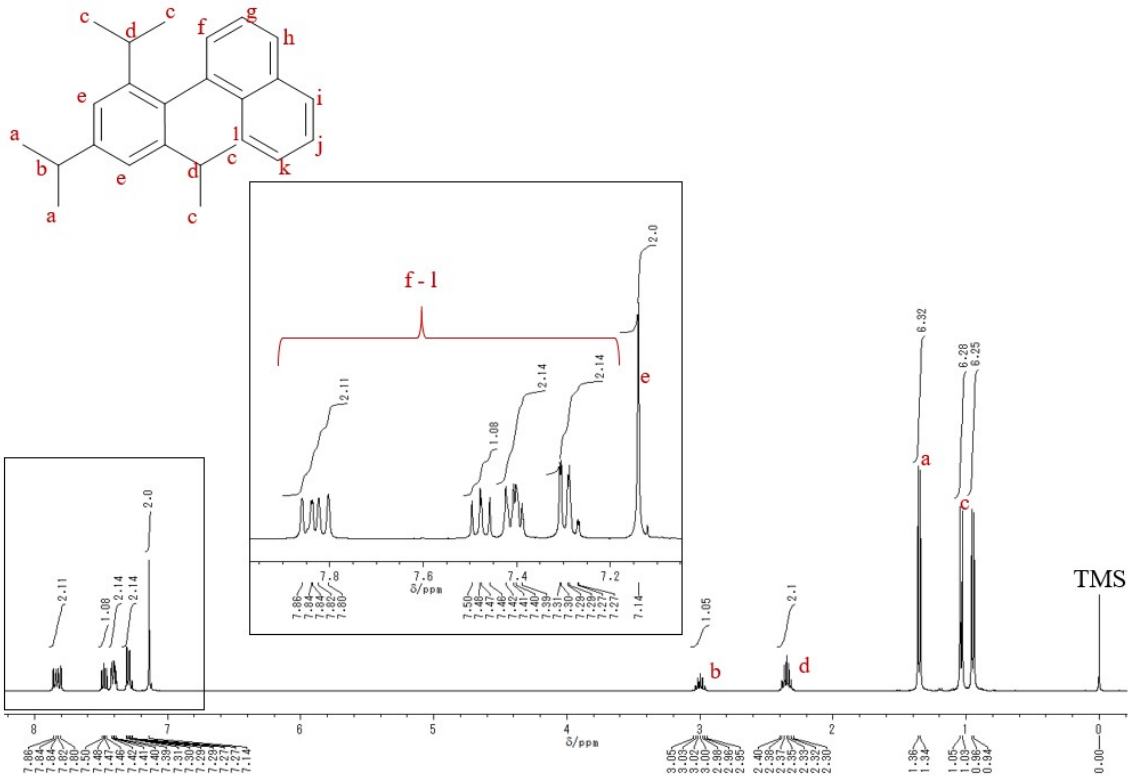


Figure S13. ^{1}H-NMR spectrum (400 MHz) of **P1** in $CDCl_3$.

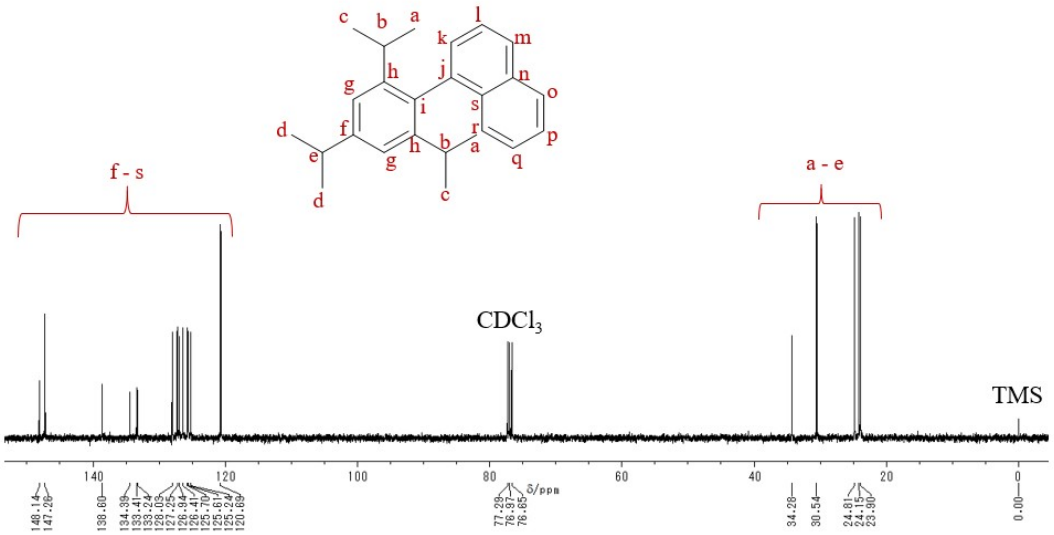


Figure S14. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **P1** in $CDCl_3$.

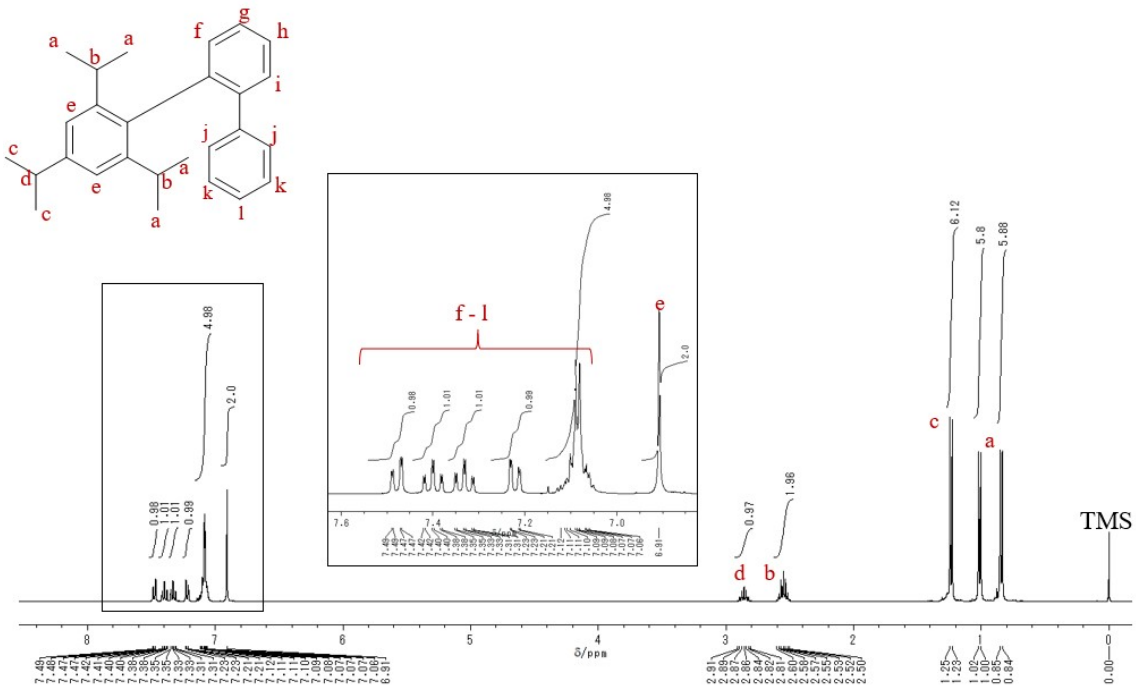


Figure S15. ^{1}H-NMR spectrum (400 MHz) of **P2** in $CDCl_3$.

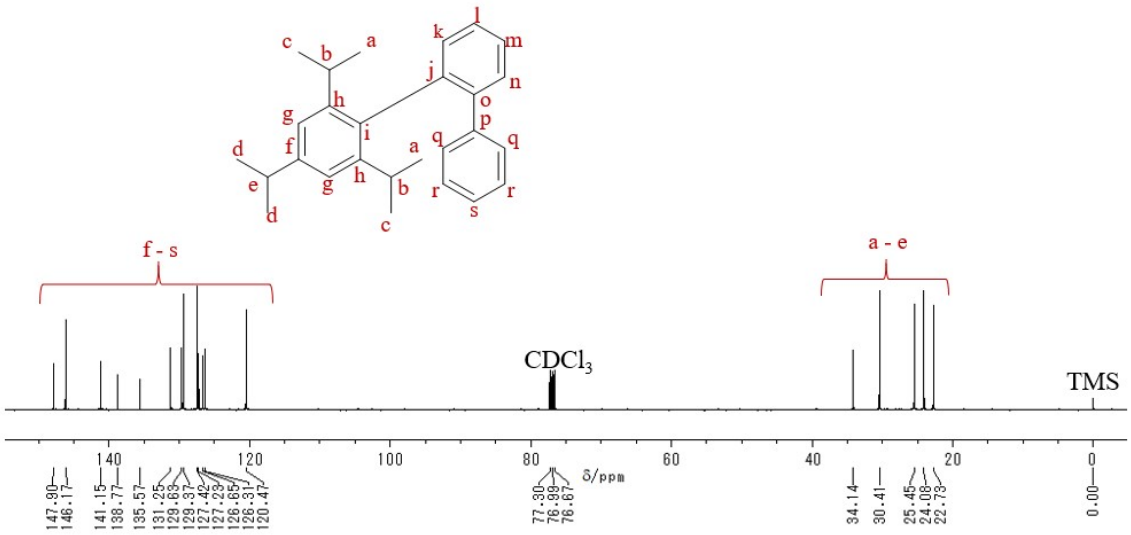


Figure S16. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **P2** in $CDCl_3$.

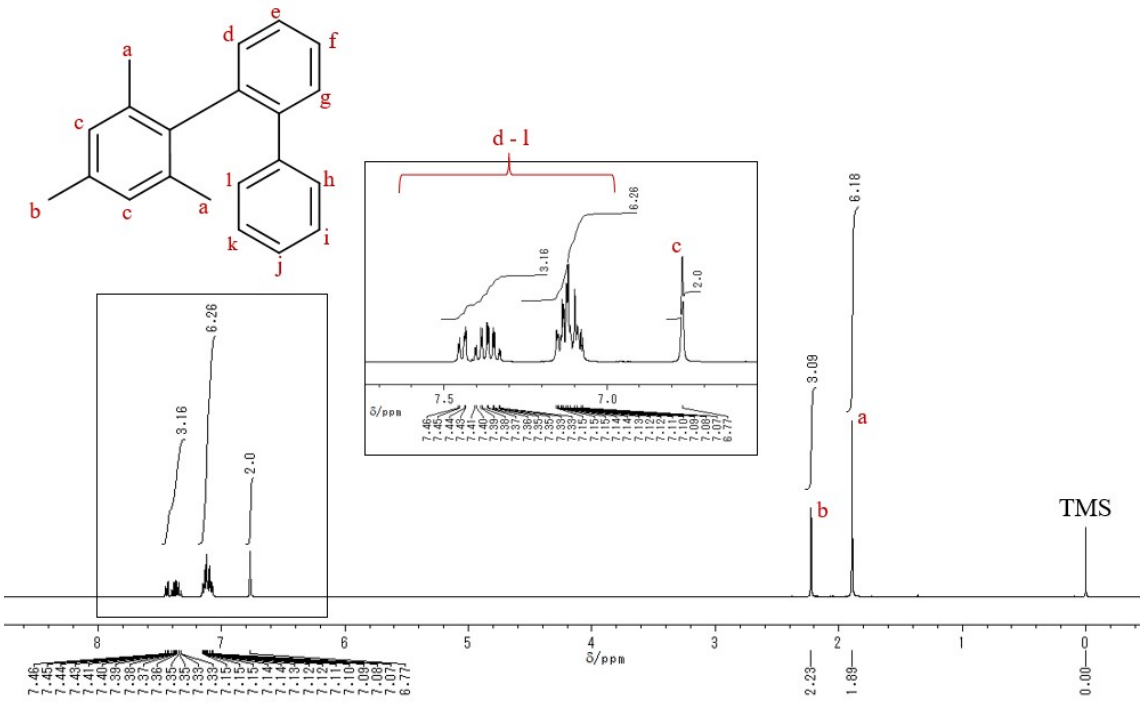


Figure S17. ^{1}H-NMR spectrum (400 MHz) of **P3** in $CDCl_3$.

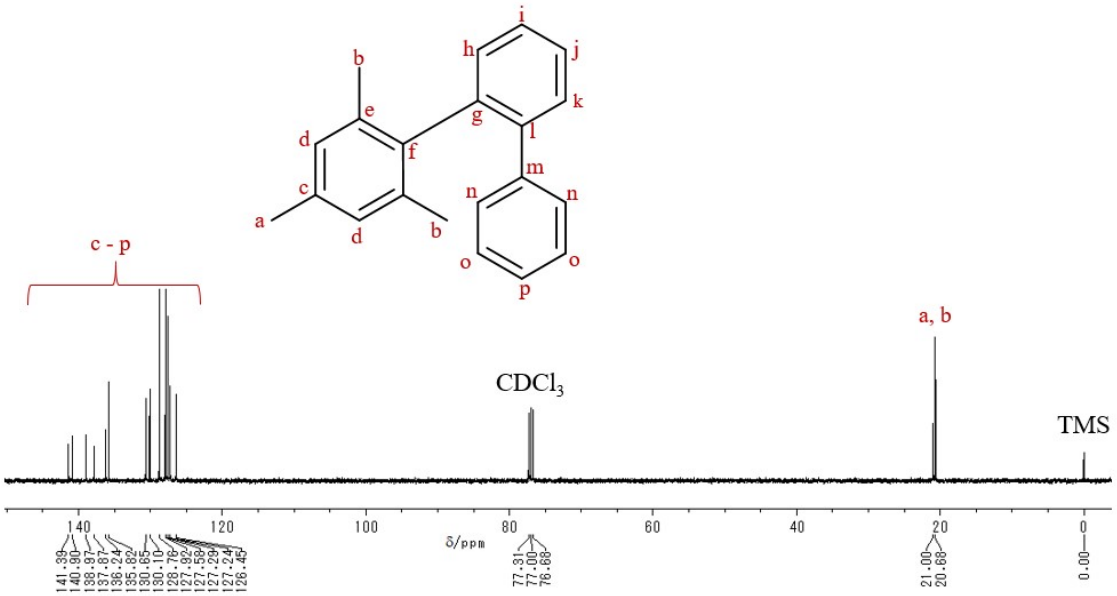


Figure S18. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **P3** in $CDCl_3$.

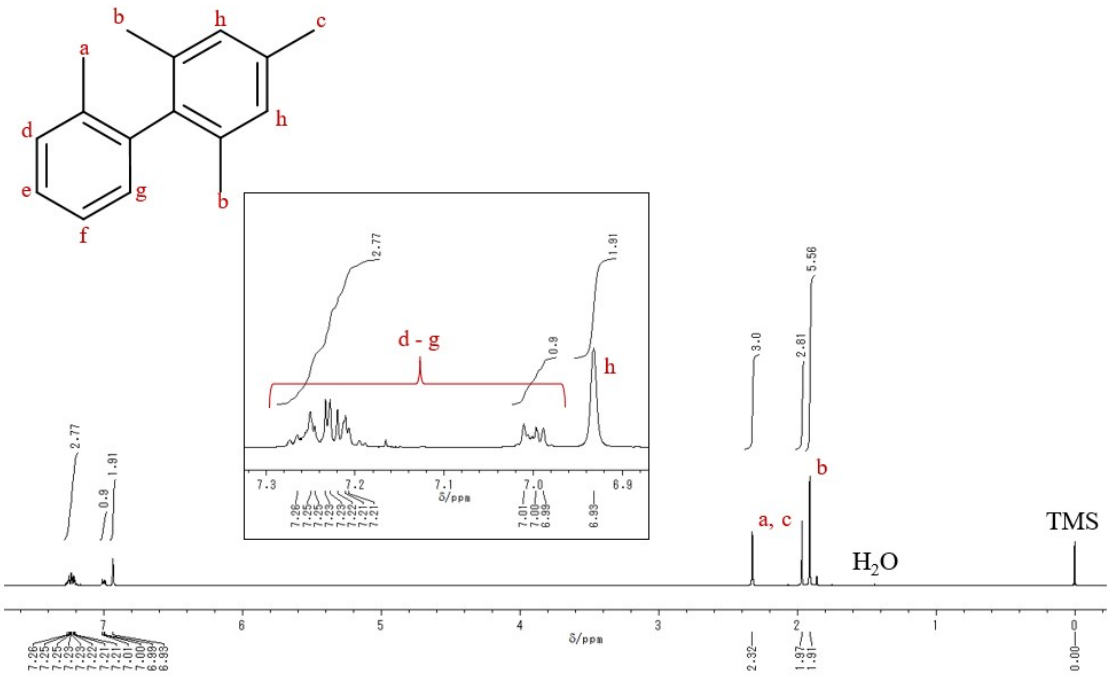


Figure S19. ^{1}H-NMR spectrum (400 MHz) of **P4** in $CDCl_3$.

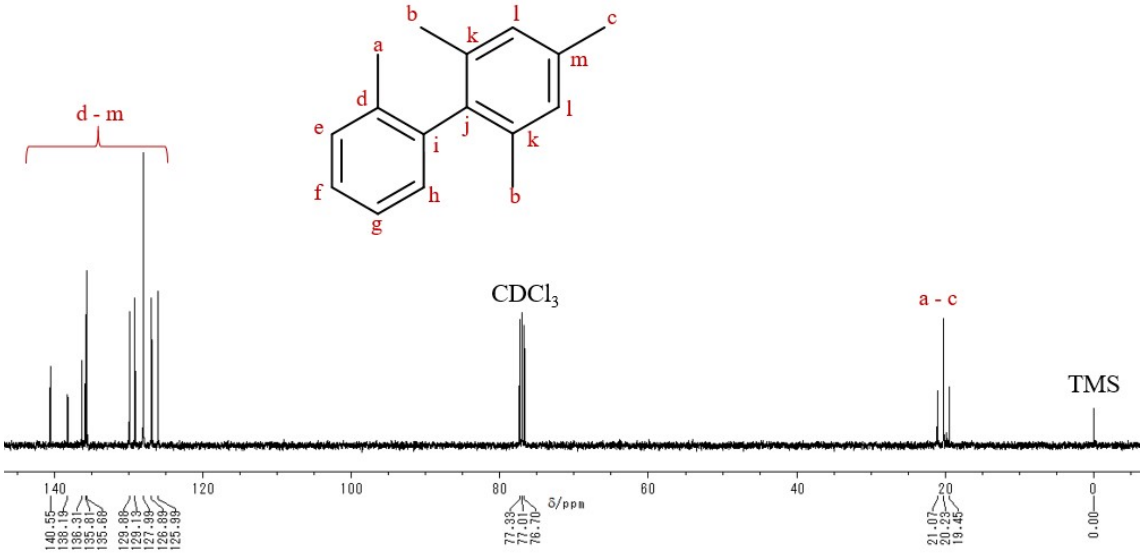


Figure S20. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **P4** in $CDCl_3$.

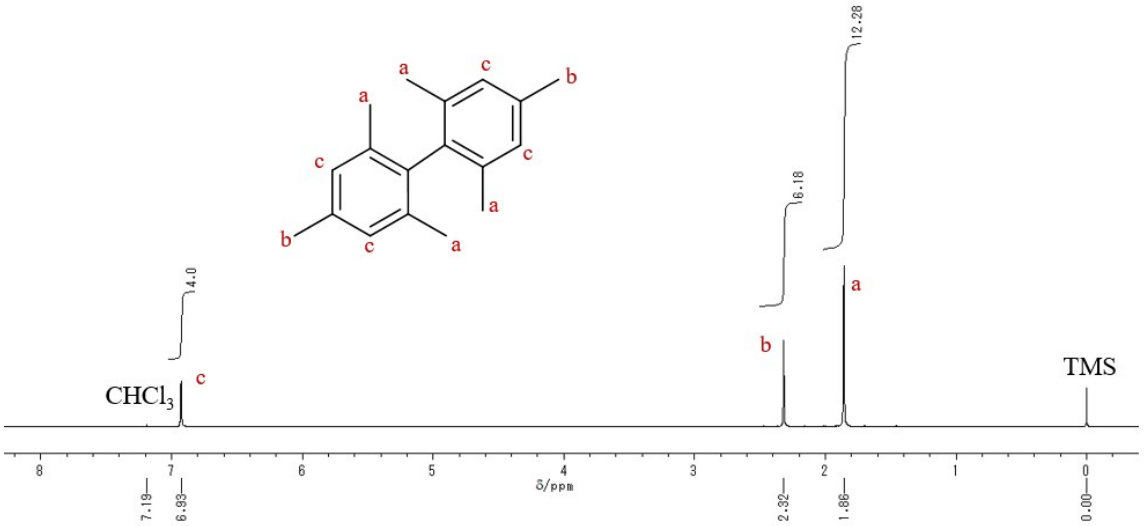


Figure S21. ^{1}H-NMR spectrum (400 MHz) of **P5** in $CDCl_3$.

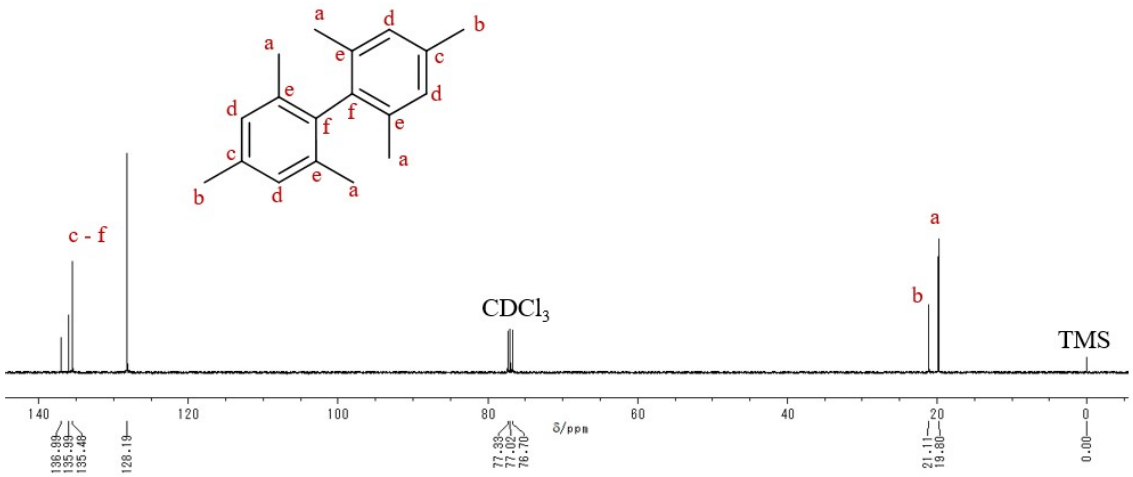


Figure S22. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **P5** in $CDCl_3$.

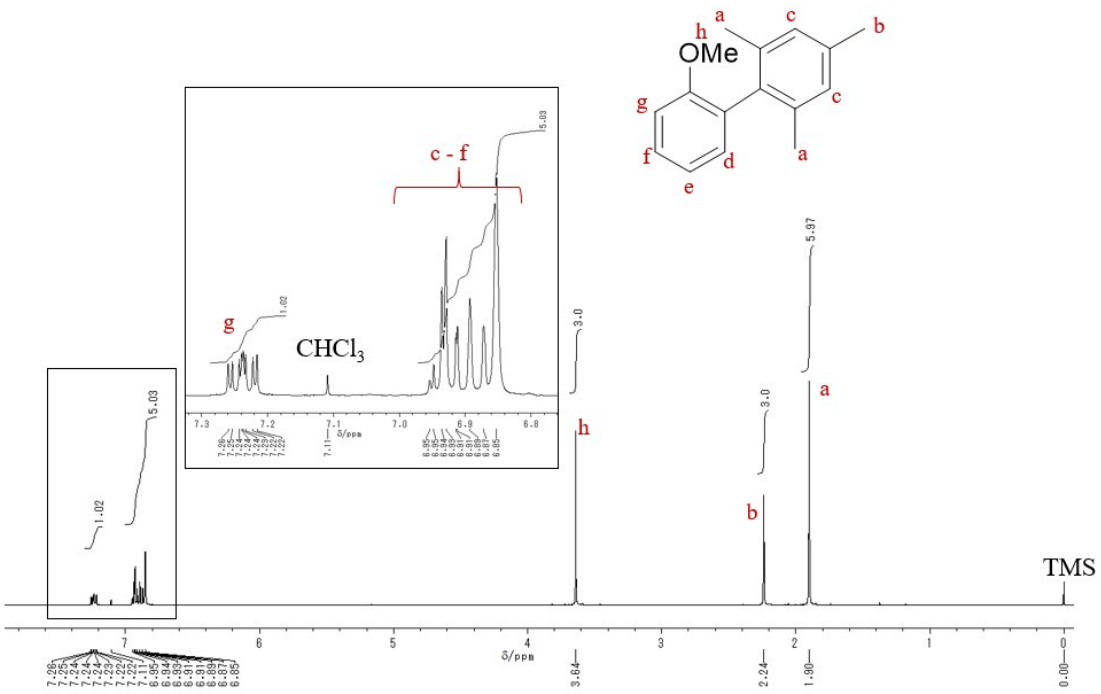


Figure S23. ^{1}H-NMR spectrum (400 MHz) of **P7** in $CDCl_3$.

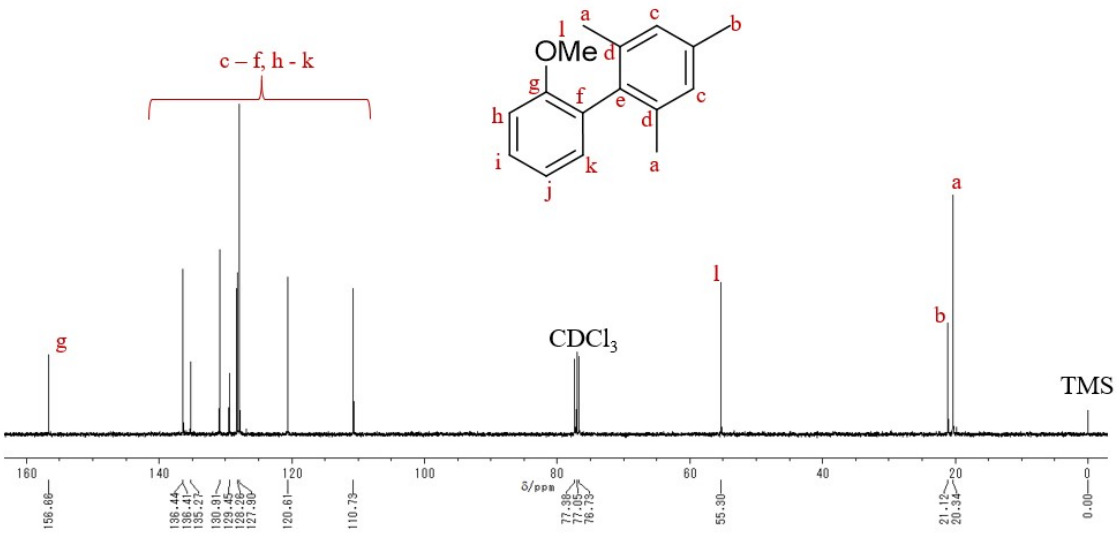


Figure S24. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **P7** in $CDCl_3$.

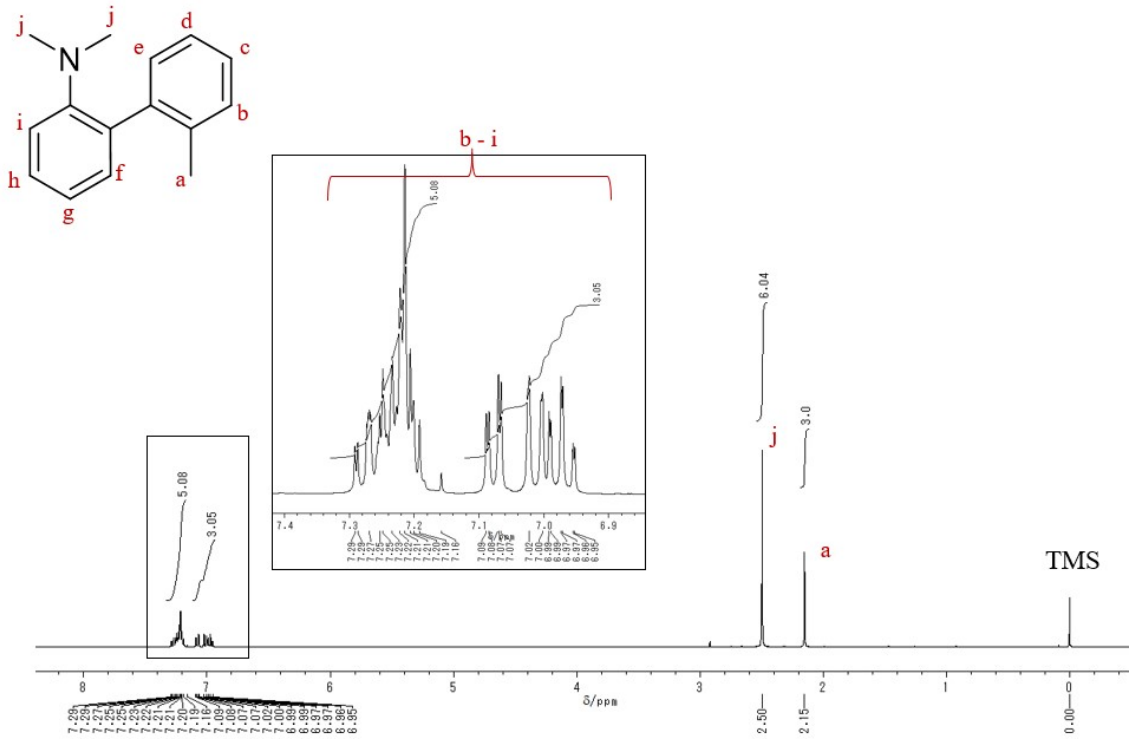


Figure S25. ^{1}H-NMR spectrum (400 MHz) of **P8** in $CDCl_3$.

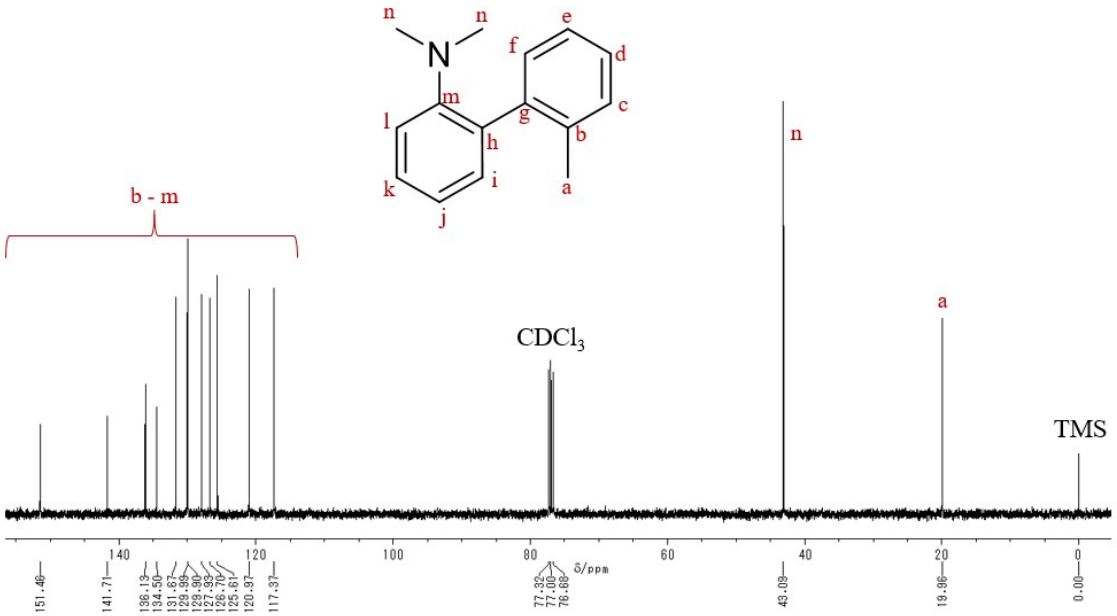


Figure S26. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **P8** in $CDCl_3$.

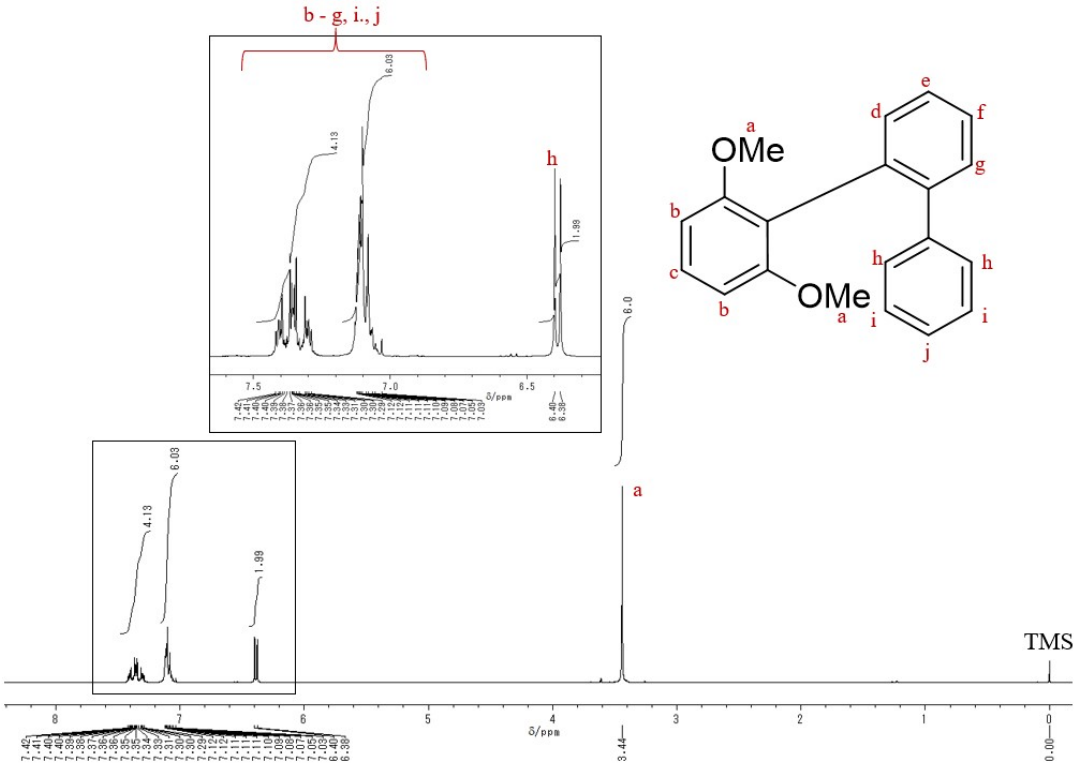


Figure S27. ^{1}H-NMR spectrum (400 MHz) of **P9** in $CDCl_3$.

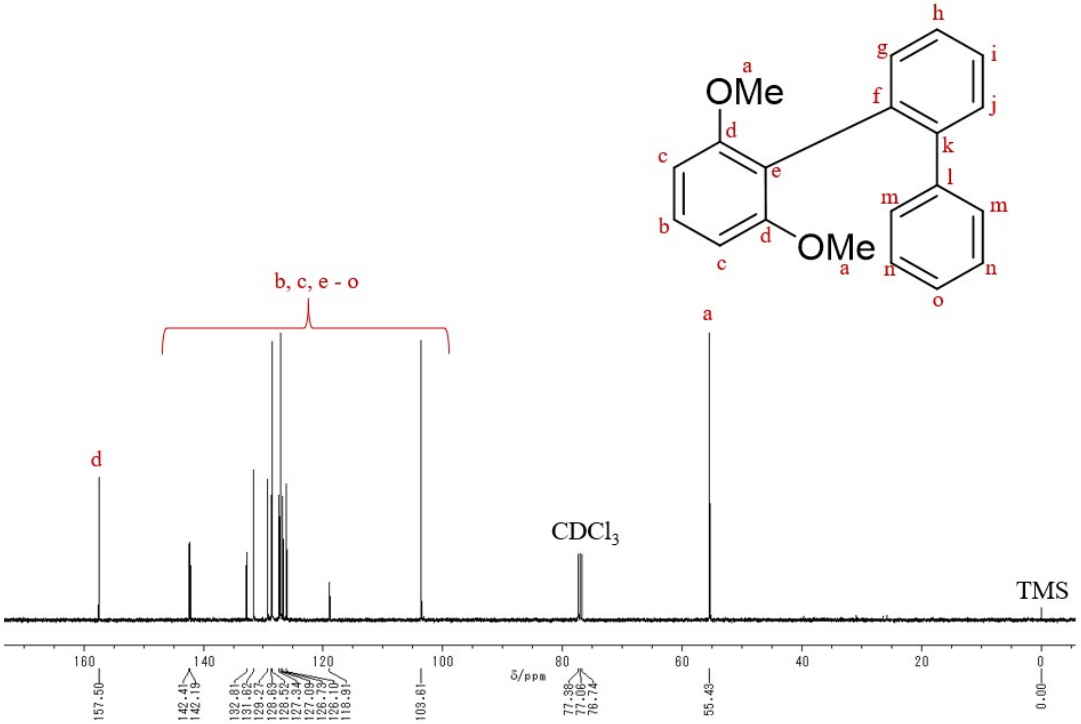


Figure S28. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **P9** in $CDCl_3$.

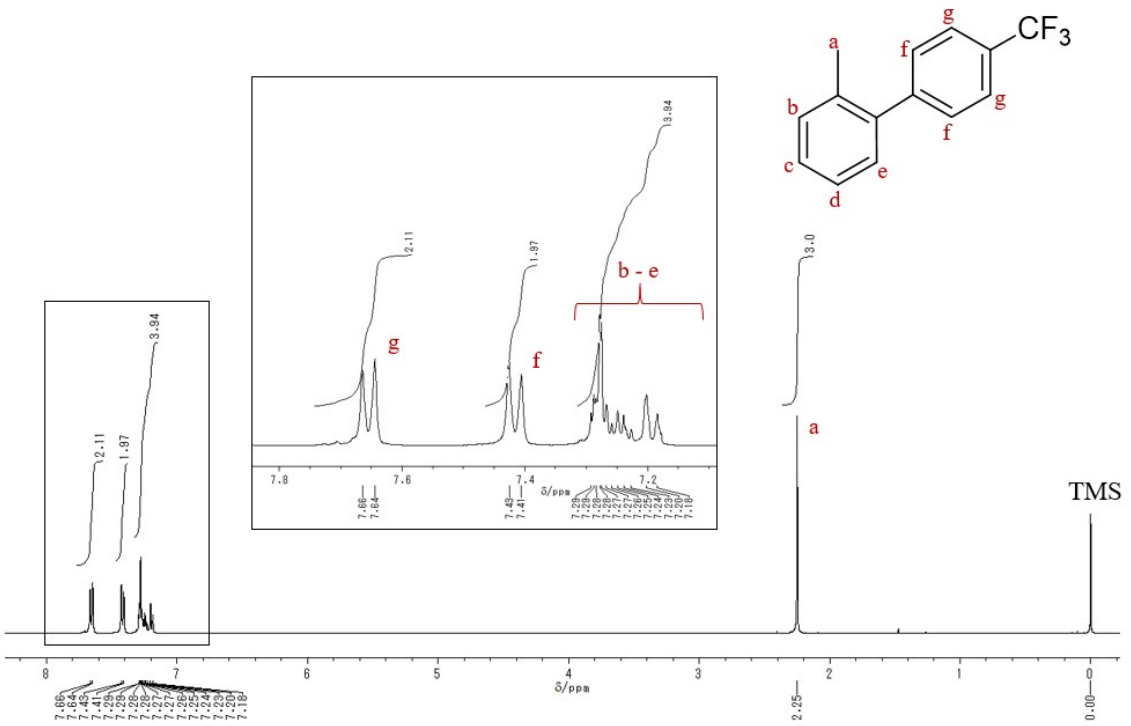


Figure S29. ^{1}H-NMR spectrum (400 MHz) of **P11** in $CDCl_3$.

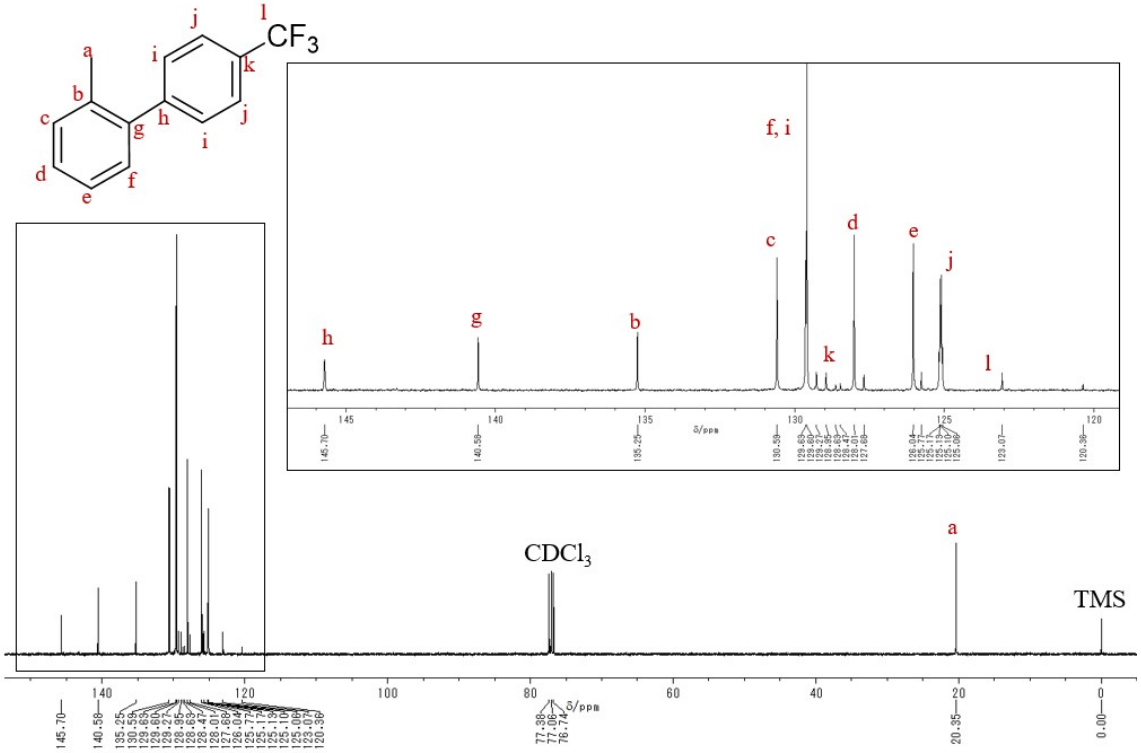


Figure S30. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **P11** in $CDCl_3$.

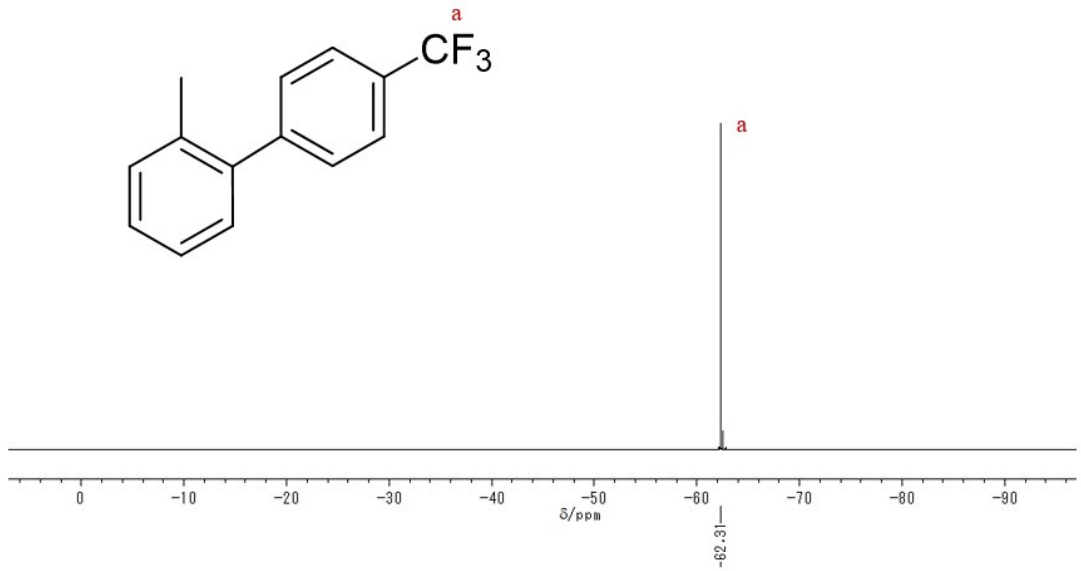


Figure S31. ^{19}F-NMR spectrum (376 MHz) of **P11** in $CDCl_3$.

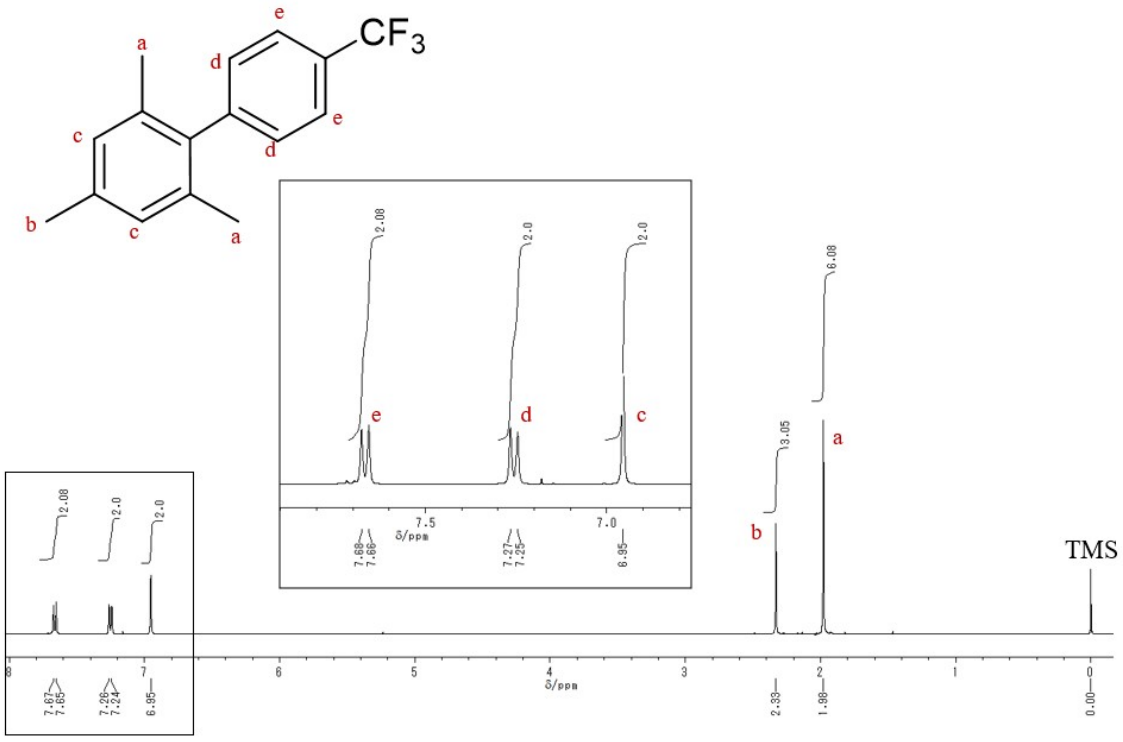


Figure S32. ^{1}H-NMR spectrum (400 MHz) of **P12** in $CDCl_3$.

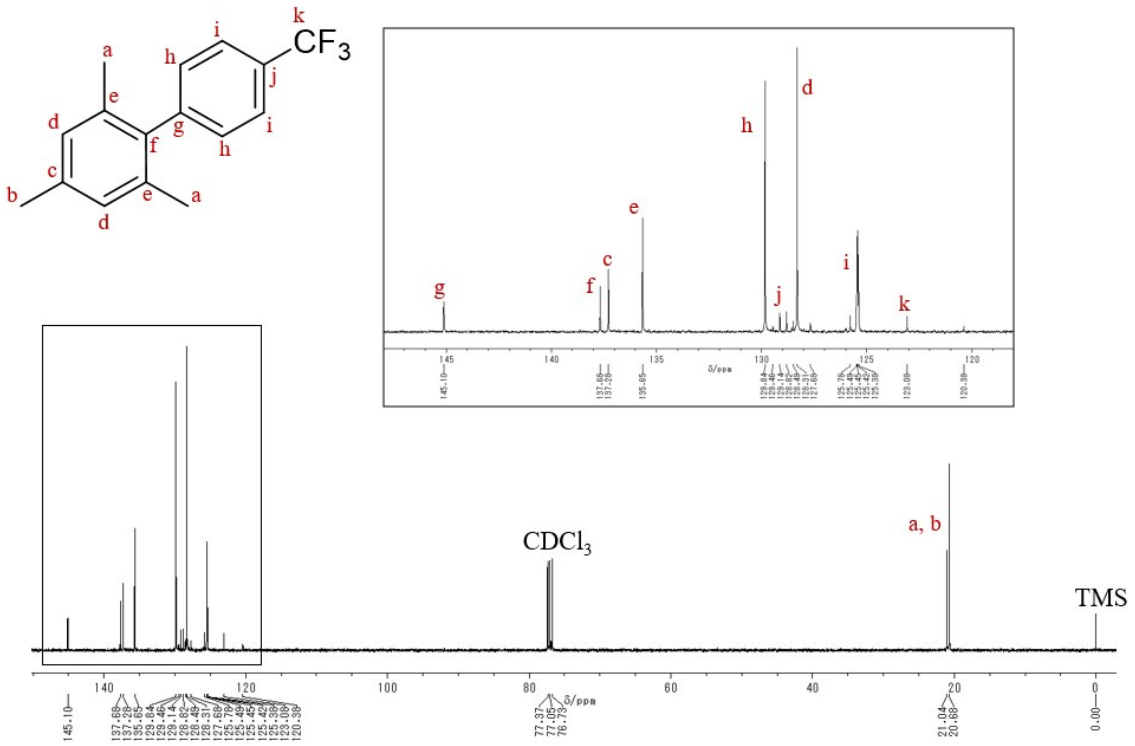


Figure S33. $^{13}C\{^{1}H\}$-NMR spectrum (100 MHz) of **P12** in $CDCl_3$.

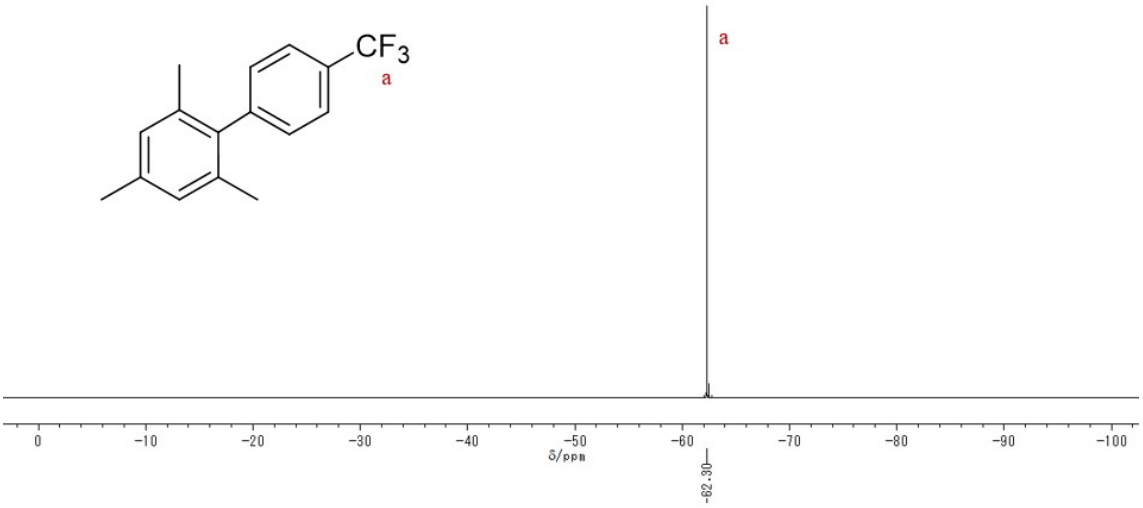


Figure S34. ^{19}F-NMR spectrum (376 MHz) of **P12** in $CDCl_3$.

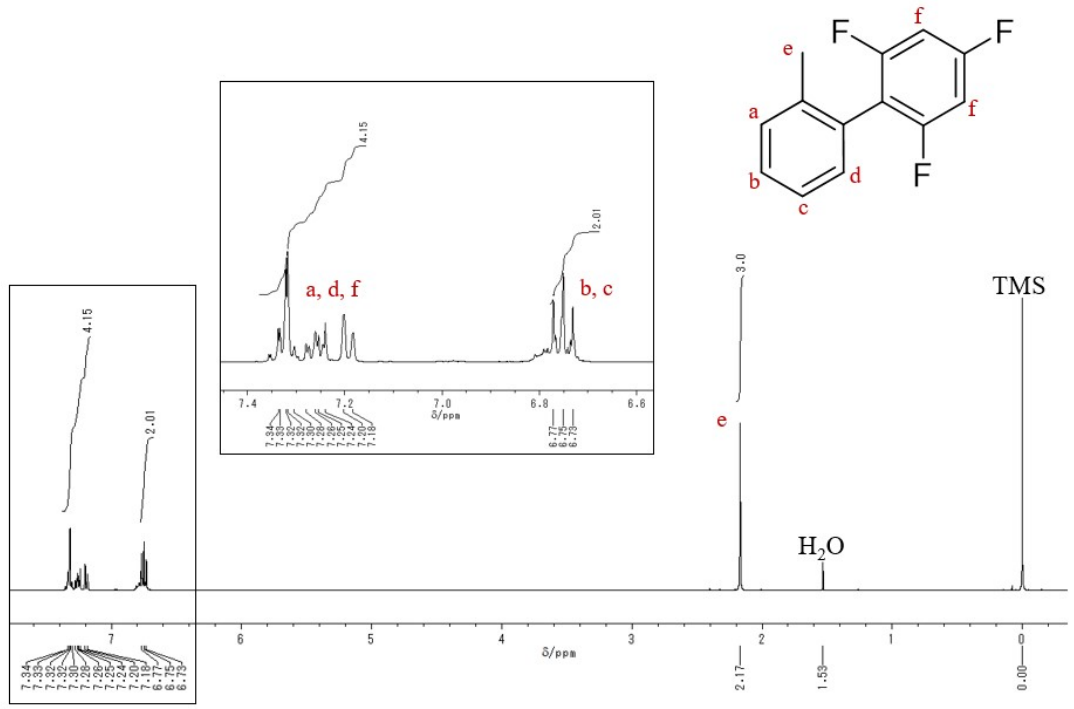


Figure S35. ^{1}H-NMR spectrum (400 MHz) of **P13** in $CDCl_3$.

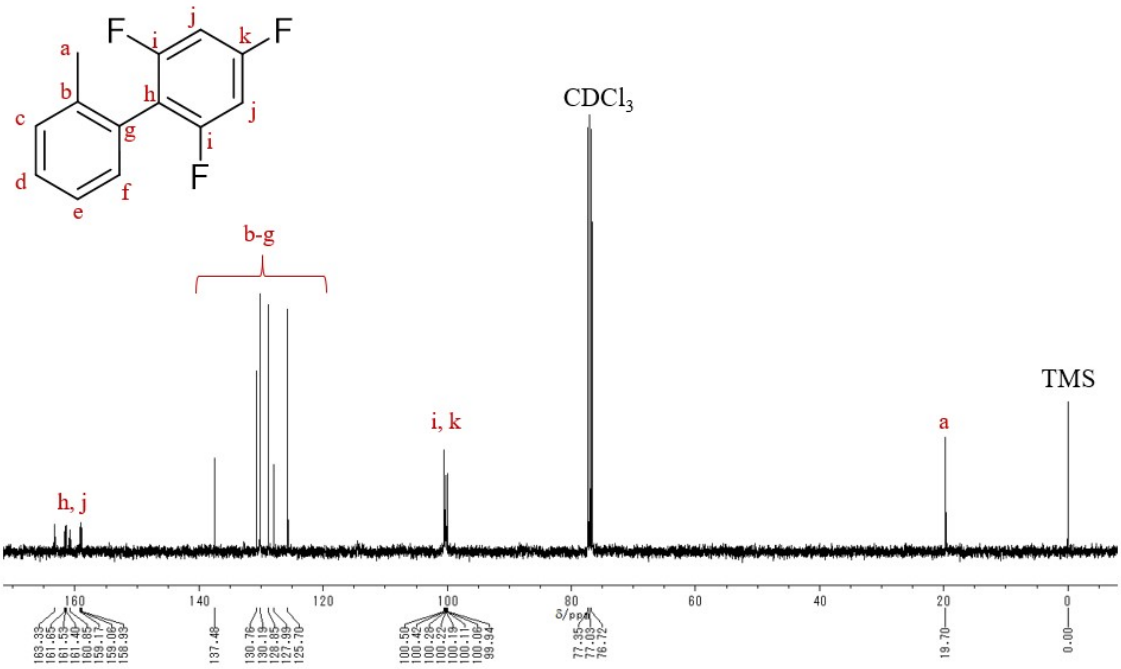


Figure S36. ^{13}C{^{1}H}-NMR spectrum (100 MHz) of **P13** in $CDCl_3$.

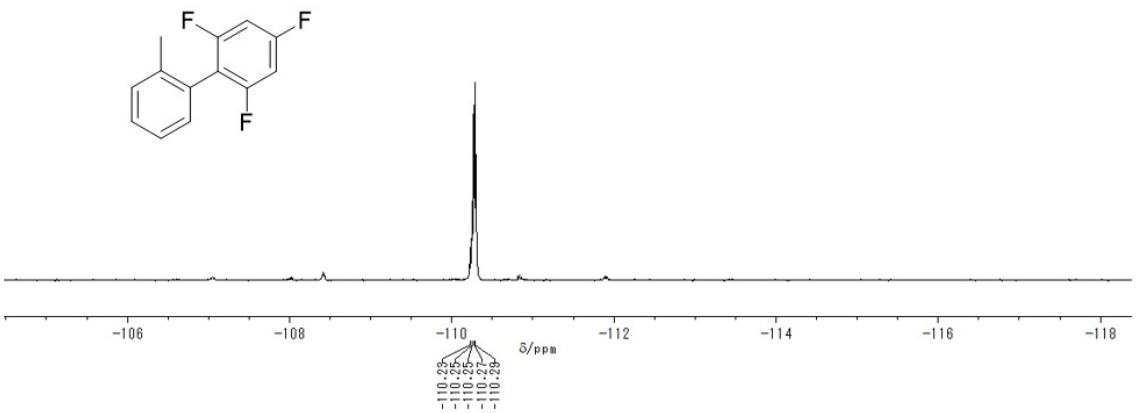


Figure S37. ^{19}F-NMR spectrum (376 MHz) of **P13** in $CDCl_3$.

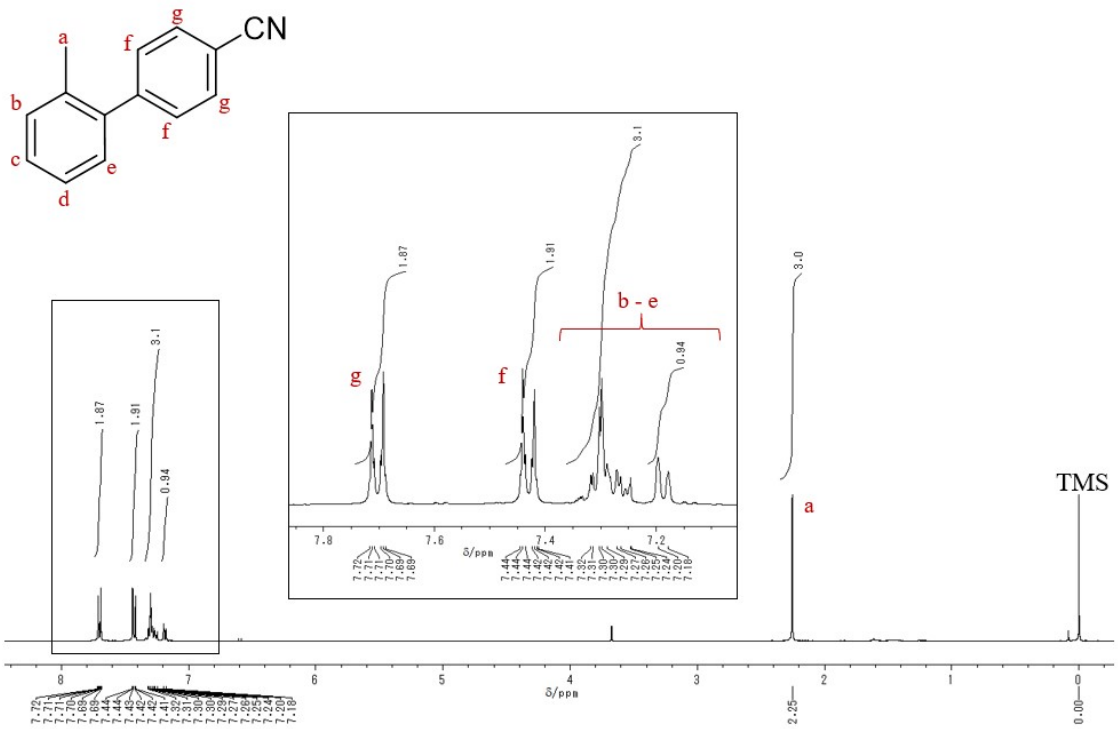


Figure S38. ^{1}H-NMR spectrum (400 MHz) of **P14** in $CDCl_3$.

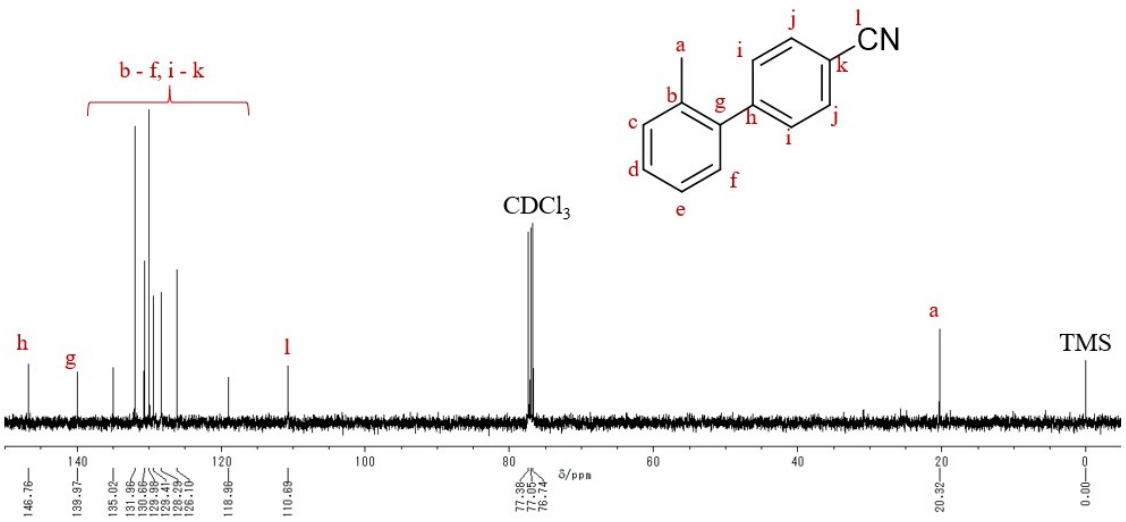


Figure S39. $^{13}C\{^{1}H\}$-NMR spectrum (100 MHz) of **P14** in $CDCl_3$.

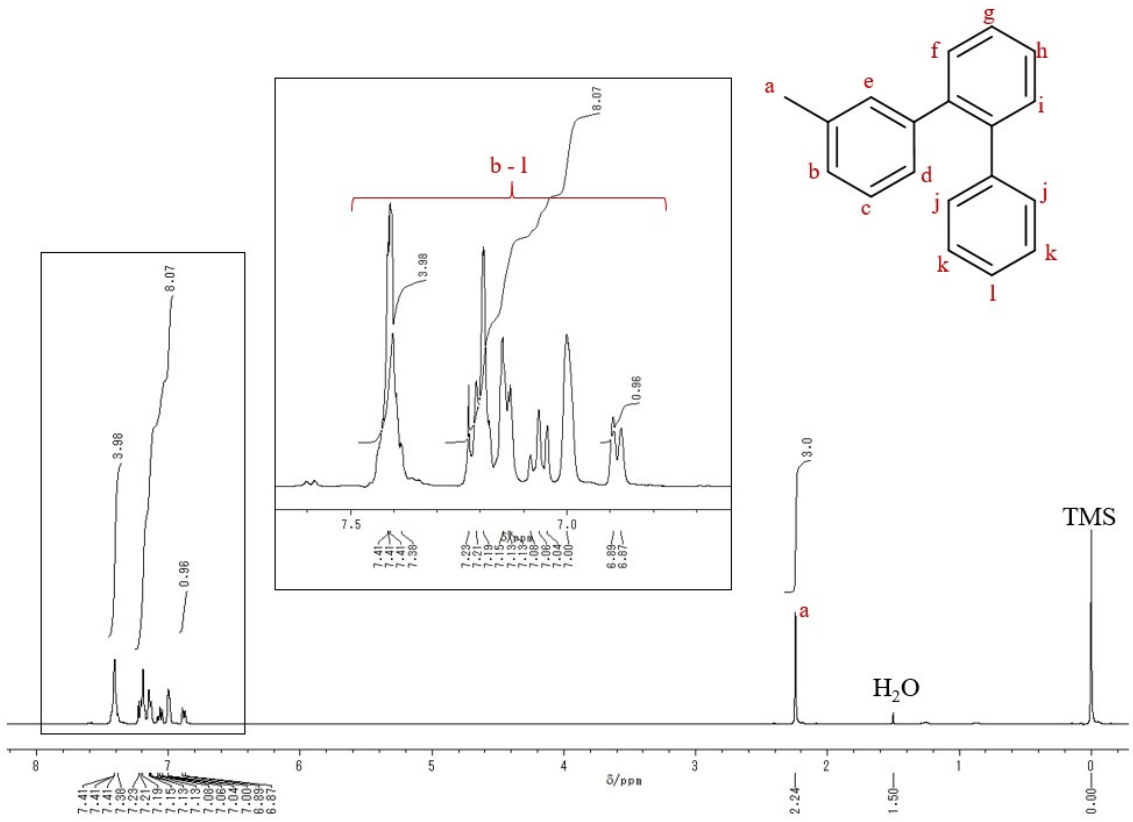


Figure S40. ^{1}H-NMR spectrum (400 MHz) of **P16** in $CDCl_3$.

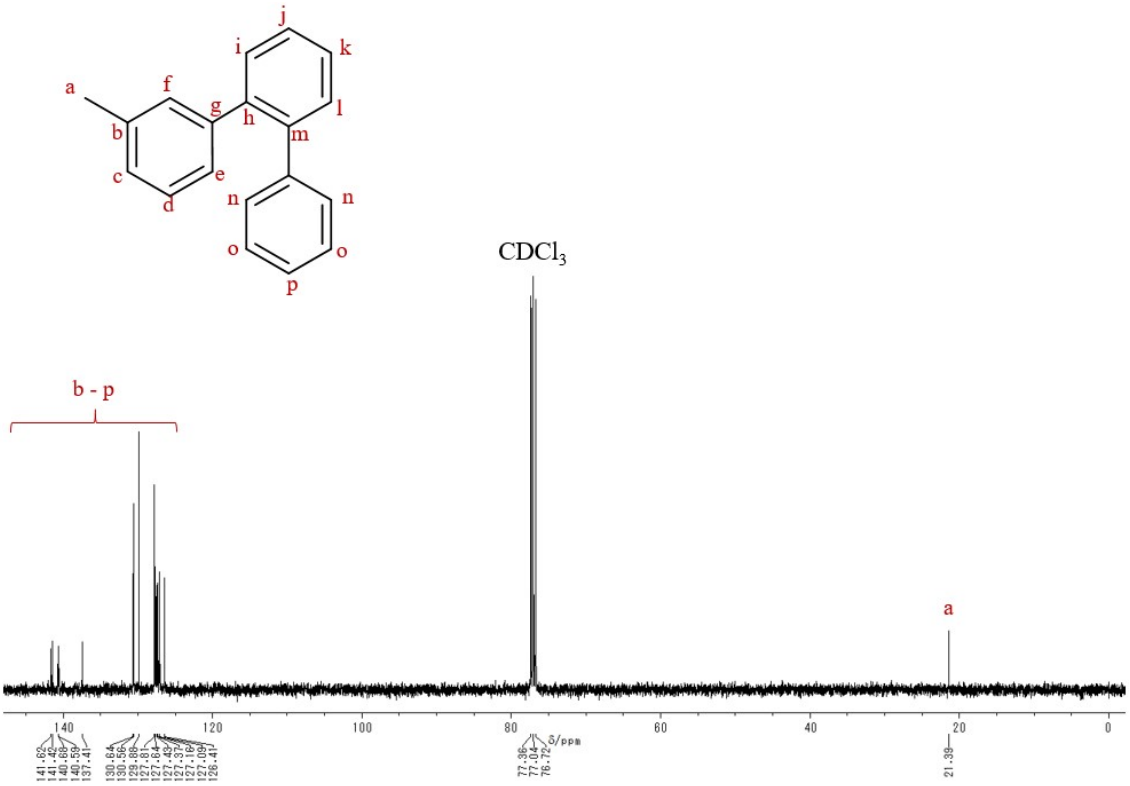


Figure S41. $^{13}C\{^{1}H\}$-NMR spectrum (100 MHz) of **P16** in $CDCl_3$.

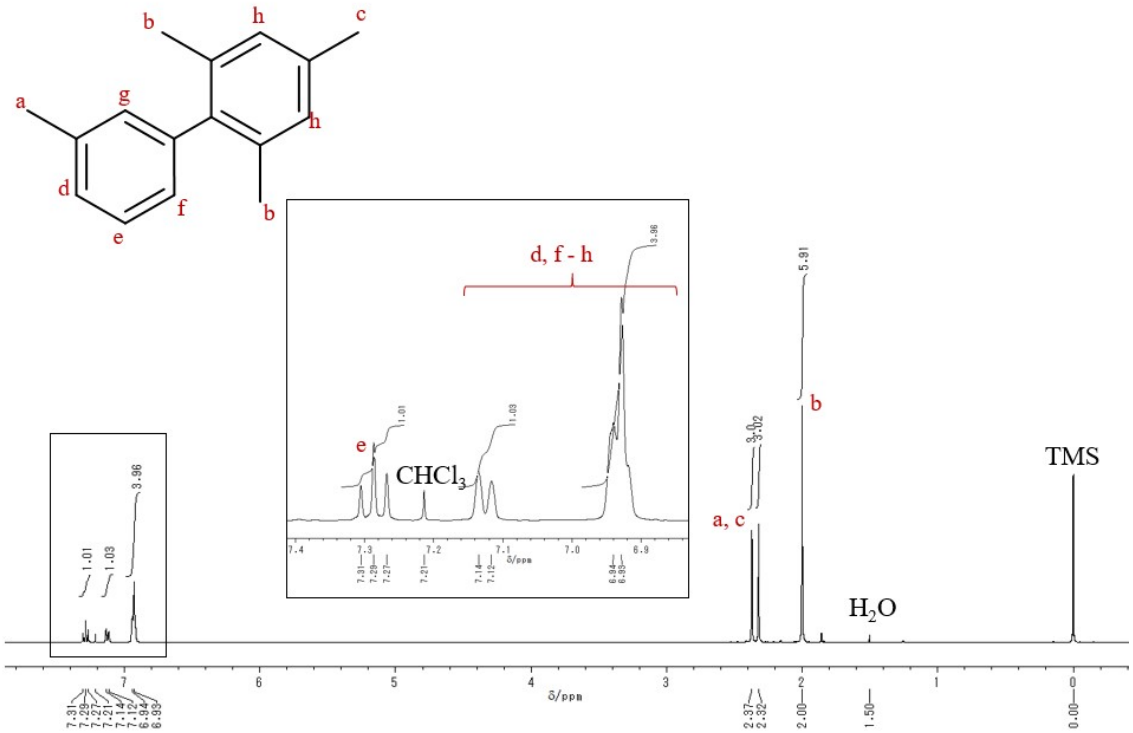


Figure S42. ^{1}H-NMR spectrum (400 MHz) of **P17** in $CDCl_3$.

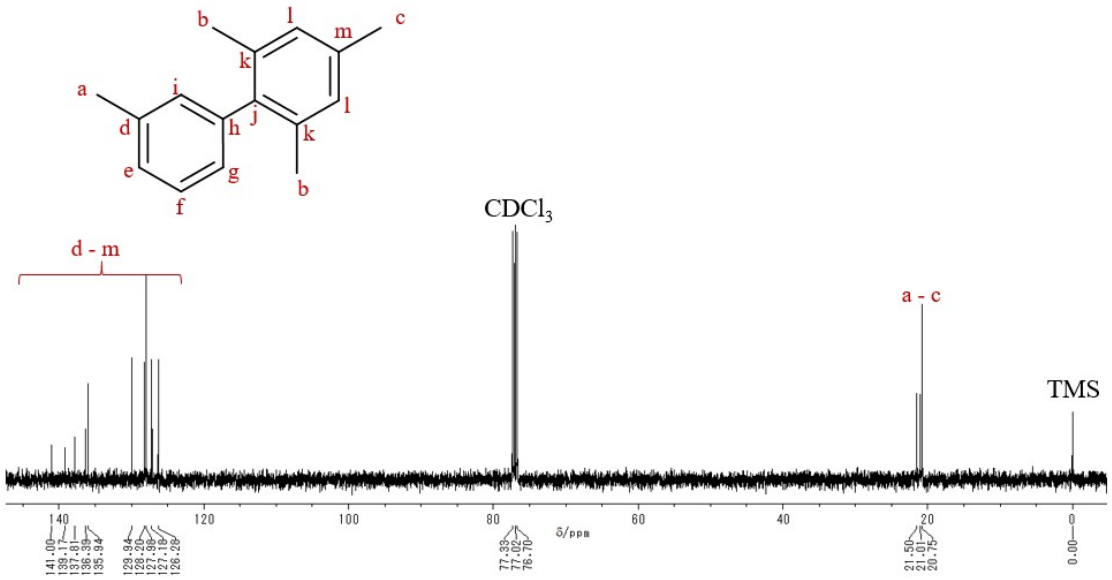


Figure S43. $^{13}C\{^{1}H\}$-NMR spectrum (100 MHz) of **P17** in $CDCl_3$.

5. Crystallographic data

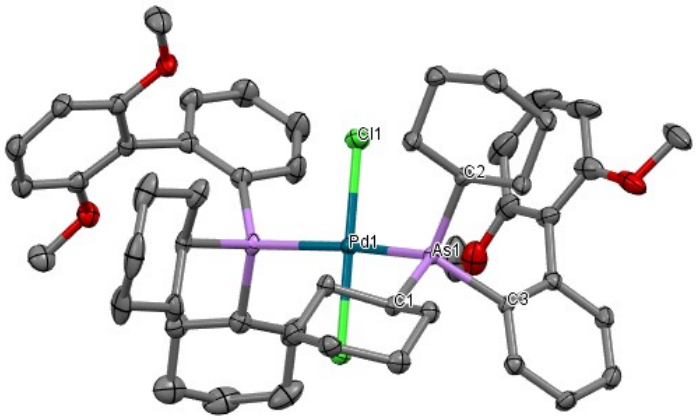
Table S1. Crystallographic data of $[PdCl_2(\mathbf{L6})_2]$ and $[PdCl_2(\mathbf{L11})_2]$ measured at -180 °C.

Crystal data	$[PdCl_2(\mathbf{L6})_2]$	$[PdCl_2(\mathbf{L11})_2]$
Empirical Formula	$C_{53}H_{720}As_2Cl4_2O_4Pd$	$C_{50}H_{66}As_2Cl_6O_4Pd$
Formula Weight	1171.14	1199.96
Crystal Dimension, mm^3	0.54 × 0.31 × 0.22	0.549 × 0.327 × 0.252
Crystal System	triclinic	triclinic
Space Group	*P*-1	*P*-1
a, Å	10.8964(4)	11.4318(8)
b, Å	10.9483(5)	11.5359(5)
c, Å	23.182(1)	11.5689(6)
α, deg	86.695(4)	83.456(4)
β, deg	83.153(3)	63.747(6)
γ, deg	80.496(3)	80.103(5)
Volume, $Å^3$	2706.0(2)	1346.68(15)
D_{calcd}, g cm^{-3}	1.437	1.480
Z	2	1
F(000)	1204.0	612.0
Data Collection		
Temperature, deg	-180	-180
2θmax, deg.	52.744	52.742
Tmin/Tmax	0.521 / 0.739	0.712 / 0.828
Refinement		
No. of Observed Data	11082	5513
No. of Parameters	610	288
$R1^a$, $wR2^b$	0.0464, 0.0925	0.0513, 0.0726
Goodness of Fit Indictor	1.144	1.016

$^aR1 = \Sigma \, | \, |Fo| - |Fc| \, | \, / \, \Sigma \, |Fo|$ $^bwR^2 = [\Sigma \, w((Fo^2-Fc^2)^2 / \Sigma \, w(Fo^2)^2 \,]^{1/2}$ $w = [\sigma^2(Fo^2)]^{-1}$

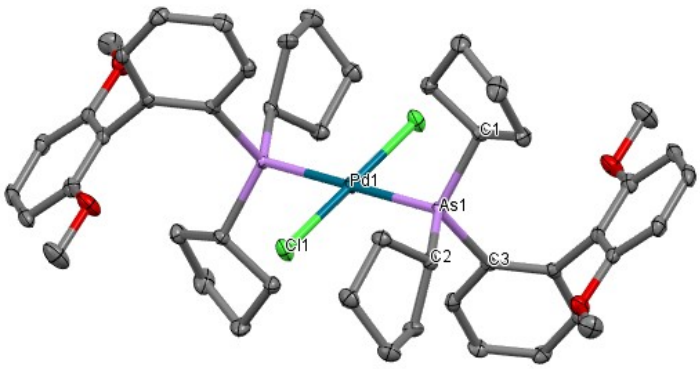
CCDC #2232896 ($[PdCl_2(\mathbf{L6})_2]$), #2232897 ($[PdCl_2(\mathbf{L11})_2]$)

Table S2. ORTEP drawing (ellipsoids at 50% probability), selected distances, and angles of [$PdCl_2$(**L6**)$_2$] measured at -180 °C. All hydrogens of the ligands and crystal solvents were omitted for clarity.



Distances (Å)		Angles (°)	
Pd1-Cl1	2.294(1)	Cl1-Pd1-As1	93.48(3)
Pd1-As1	2.4440(6)	Pd-As1-C1	104.7(1)
As1-C1	1.977(3)	Pd-As1-C2	116.9(1)
As1-C2	1.977(3)	Pd-As1-C3	117.8(1)
As1-C3	1.970(3)	C1-As1-C2	108.2(1)
		C2-As1-C3	105.0(1)
		C1-As1-C3	103.0(1)

Table S3. ORTEP drawing (ellipsoids at 50% probability), selected distances, and angles of [$PdCl_2$(**L11**)$_2$] measured at -180 °C. All hydrogens of the ligands and crystal solvents were omitted for clarity.

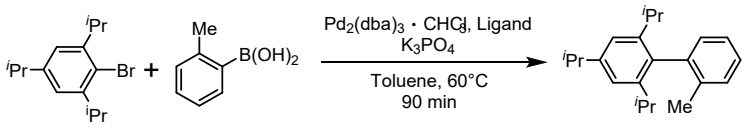


Distances (Å)		Angles (°)	
Pd1-Cl1	2.3027(7)	Cl1-Pd1-As1	93.37(2)
Pd1-As1	2.4268(3)	Pd-As1-C1	110.27(8)
As1-C1	1.963(3)	Pd-As1-C2	121.71(8)
As1-C2	1.952(3)	Pd-As1-C3	103.35(8)
As1-C3	1.947(4)	C1-As1-C2	105.8(1)
		C2-As1-C3	100.7(1)
		C1-As1-C3	115.1(1)

6. The ligand screening containing conventional ligands in hindered Suzuki-Miyaura coupling reaction.

Commercially available ligands were examined to compare with the results shown in Table 1 of the main text: triphenylphosphine (PPh_3), triphenylarsine ($AsPh_3$), and SPhos. The tendency that PPh_3 showed higher catalytic activity than SPhos is in good agreement with that reported in a previous paper.[2]

Table S4. The ligand screening containing conventional ligands in hindered Suzuki-Miyaura coupling reaction[a].



Entry	Ligand	NMR yield (%)[b]
1	**L1**	4
2	**L2**	14
3	**L3**	18
4	**L4**	27
5	**L5**	29
6	**L6**	47
7	**L7**	55
8	**L8**	<1
9	**L9**	74
10	**L10**	12
11	**L11**	90
12	PPh_3	27
13	$AsPh_3$	11
14	SPhos	14

[a] Reaction conditions: 1 equiv. of aryl bromide, 2 equiv. of boronic acid, 3 equiv. of K_3PO_4, toluene (2 mL/mol halide), cat. $Pd_2(dba)_3{\cdot}CHCl_3$, ligand (L:Pd = 2:1), 60°C, 90 min. [b] NMR yield based on an average of several runs.

7. Protodeboronation of 1,3,5-trifluorophenyl boronic acids

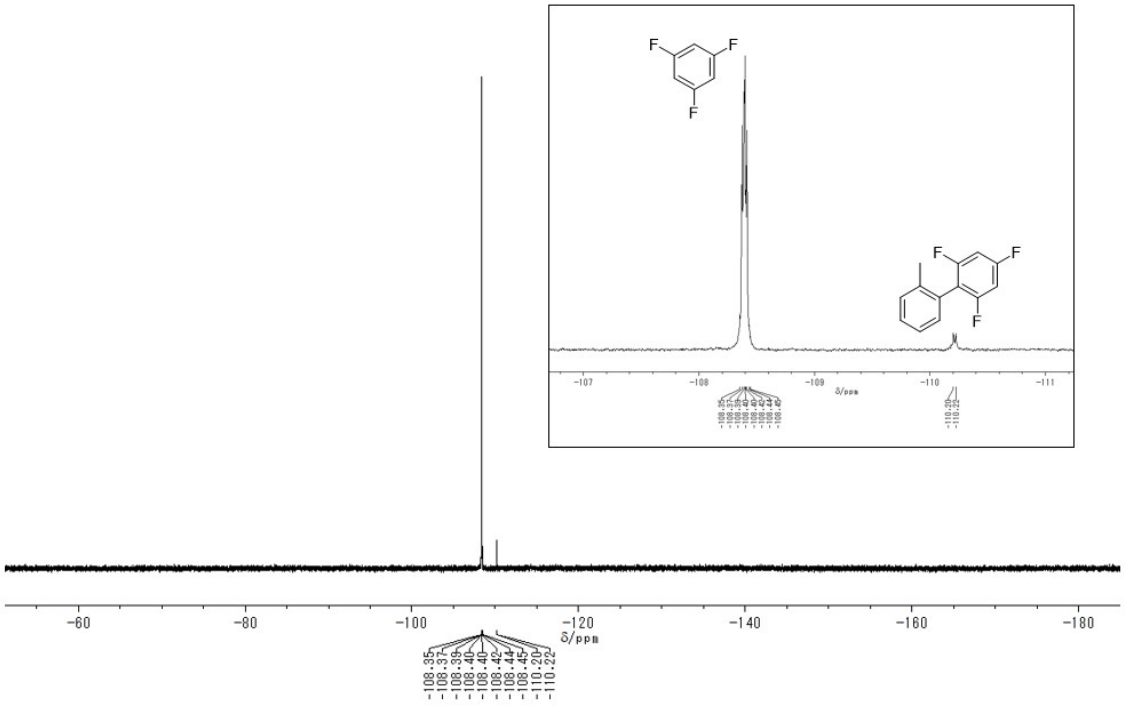


Figure S44. ^{19}F-NMR spectrum (376 MHz) of reaction mixture containing **P13** in toluene/$CDCl_3$.

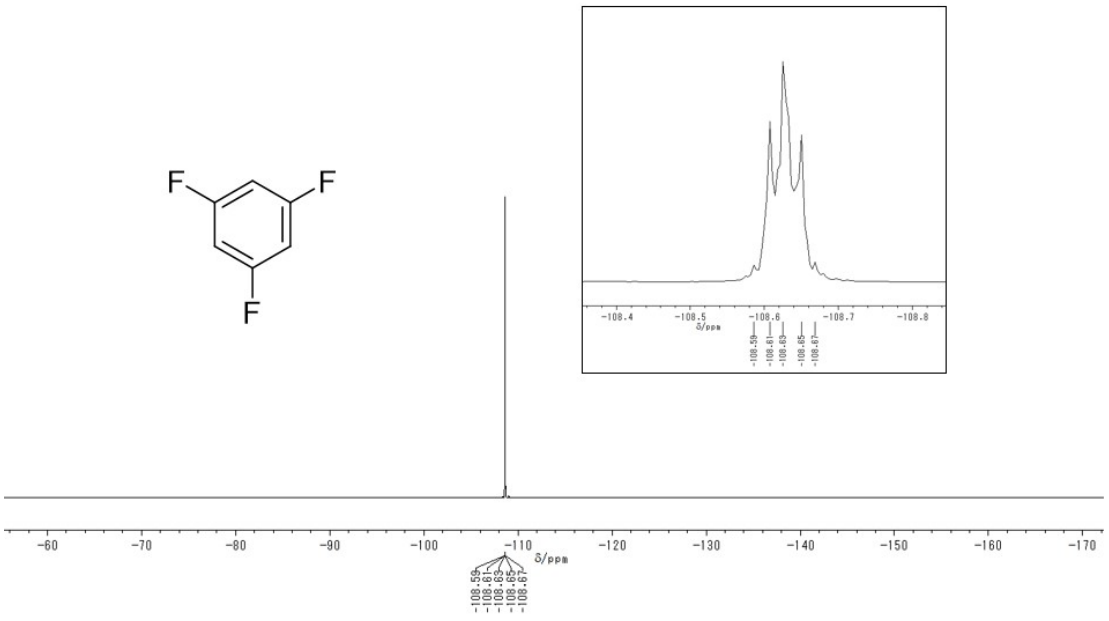


Figure S45. ^{19}F-NMR spectrum (376 MHz) of 1,3,5-trifluorobenzene in $CDCl_3$.

8. DFT Calculation

Gaussian 16 was employed.[3] Cartesian coordinates in the optimized structures; B3LYP-D3 functional with the LanL2DZ effective core potential for Ni and the def2-TZVP basis set for all other atoms.

Table S5. Optimized structure of $PPh_3Ni(CO)_3$.

Number	Atom	X	Y	Z
1	Ni	2.16591	0.004679	-0.00126
2	C	2.655828	0.328363	-1.71742
3	O	2.939373	0.538442	-2.80101
4	C	2.661821	-1.64116	0.57762
5	O	2.949271	-2.68327	0.938299
6	C	2.653772	1.330964	1.135868
7	O	2.935888	2.1655	1.85882
8	C	-0.88296	1.166764	-1.18402
9	C	-0.25635	2.40235	-1.3682
10	C	-2.05326	0.887296	-1.89225
11	C	-0.79887	3.347681	-2.22794
12	H	0.666466	2.613284	-0.84202
13	C	-2.58955	1.831015	-2.7617
14	H	-2.54492	-0.06896	-1.7721
15	C	-1.96735	3.063043	-2.92775
16	H	-0.30373	4.301287	-2.36048
17	H	-3.49425	1.601094	-3.31052
18	C	-0.87663	-1.61228	-0.41985
19	C	-2.04863	-2.08739	0.171781
20	C	-0.24345	-2.39026	-1.39297
21	C	-2.58009	-3.3144	-0.2104
22	H	-2.54525	-1.5045	0.936131
23	C	-0.78102	-3.60985	-1.78135
24	H	0.680592	-2.03878	-1.83517
25	C	-1.95116	-4.07509	-1.18942
26	H	-3.48615	-3.67585	0.259644
27	H	-0.28072	-4.20204	-2.53706
28	C	-0.87996	0.438831	1.604425

29	C	-0.24968	-0.01821	2.76508
30	C	-2.05125	1.18991	1.719318
31	C	-0.78945	0.253203	4.014927
32	H	0.673874	-0.57787	2.682596
33	C	-2.58485	1.47045	2.972607
34	H	-2.54579	1.562874	0.832239
35	C	-1.95889	0.999697	4.121137
36	H	-0.29139	-0.10772	4.905871
37	H	-3.49039	2.059148	3.050028
38	H	-2.36575	-5.03087	-1.48405
39	H	-2.37517	1.220824	5.095821
40	H	-2.38581	3.795523	-3.6064
41	P	-0.11477	-0.00063	-0.00034

Table S6. Optimized structure of $AsPh_3Ni(CO)_3$.

Number	Atom	X	Y	Z
1	Ni	2.315581	0.002785	-0.00514
2	C	2.784272	-0.14751	-1.7491
3	O	3.075007	-0.23593	-2.84702
4	C	2.799911	-1.42796	0.995195
5	O	3.10171	-2.33155	1.619963
6	C	2.792236	1.587974	0.731356
7	O	3.089109	2.583124	1.199804
8	As	-0.07208	-0.00137	0.001009
9	C	-0.93795	0.746263	-1.58654
10	C	-0.30094	1.814671	-2.21708
11	C	-2.13823	0.259539	-2.10148
12	C	-0.86738	2.403668	-3.34115
13	H	0.644826	2.179839	-1.83425
14	C	-2.70042	0.846465	-3.23084
15	H	-2.63375	-0.58014	-1.63123
16	C	-2.06868	1.92001	-3.84905
17	H	-0.36665	3.233103	-3.82446
18	H	-3.63119	0.461704	-3.62884

19	C	-0.93026	-1.75352	0.149972
20	C	-2.14001	-1.95567	0.812256
21	C	-0.27888	-2.83612	-0.44015
22	C	-2.69731	-3.22905	0.871769
23	H	-2.64639	-1.12636	1.289373
24	C	-0.84029	-4.10633	-0.38492
25	H	0.673746	-2.68706	-0.93468
26	C	-2.051	-4.30383	0.271062
27	H	-3.63549	-3.38056	1.391026
28	H	-0.32862	-4.94185	-0.84577
29	C	-0.93246	1.001153	1.44454
30	C	-0.28124	1.033148	2.677172
31	C	-2.14392	1.672717	1.288301
32	C	-0.84447	1.714712	3.749485
33	H	0.672623	0.532717	2.795551
34	C	-2.70311	2.359504	2.361266
35	H	-2.65012	1.669969	0.331413
36	C	-2.05692	2.378379	3.592438
37	H	-0.3329	1.734766	4.703522
38	H	-3.64266	2.882476	2.232773
39	H	-2.48516	-5.29438	0.320413
40	H	-2.49252	2.915308	4.425564
41	H	-2.50748	2.373358	-4.72886

Table S7. Optimized structure of SPhosNi$(CO)_3$.

Number	Atom	X	Y	Z
1	O	-1.80369	2.848396	-0.18543
2	O	-3.40432	-1.26048	1.340521
3	C	-0.2581	0.386037	1.538443
4	C	0.514629	0.416373	2.707697
5	H	1.545927	0.098916	2.652635
6	C	-1.61106	0.773756	1.63625
7	C	-2.59085	0.763896	0.511429
8	C	0.002676	0.829884	3.927674

9	H	0.639674	0.840821	4.802946
10	C	-2.66916	1.820698	-0.4022
11	C	-3.50866	-0.29028	0.394758
12	C	-2.11677	1.174401	2.875608
13	H	-3.1603	1.457421	2.934229
14	C	-3.58239	1.79097	-1.45873
15	H	-3.62652	2.592068	-2.18007
16	C	-1.327	1.214975	4.01372
17	H	-1.7505	1.535224	4.957374
18	C	-4.4486	0.713048	-1.5705
19	H	-5.1563	0.685062	-2.38922
20	C	-4.43527	-0.32338	-0.64869
21	H	-5.12745	-1.14452	-0.75209
22	C	-1.91003	4.013666	-0.98757
23	H	-2.91987	4.432006	-0.95165
24	H	-1.63695	3.811581	-2.02796
25	H	-1.20892	4.729109	-0.56638
26	C	-4.32616	-2.33962	1.333511
27	H	-5.35575	-1.98493	1.438554
28	H	-4.06616	-2.95423	2.192019
29	H	-4.23726	-2.93799	0.422992
30	Ni	2.58785	-1.37876	0.527046
31	C	3.829048	-0.26342	1.223954
32	O	4.611918	0.45194	1.647868
33	C	1.988228	-2.62043	1.707242
34	O	1.583365	-3.39137	2.443582
35	C	3.175612	-2.11365	-1.01449
36	O	3.567616	-2.57641	-1.98209
37	C	-0.47038	-0.97777	-1.10545
38	C	0.046158	-1.12617	-2.5442
39	C	-0.81797	-2.35135	-0.5073
40	H	-1.37757	-0.37881	-1.15571
41	C	-0.95989	-1.89243	-3.4115
42	H	1.002311	-1.65555	-2.54868
43	H	0.220188	-0.14445	-2.98671

44	C	-1.81874	-3.10785	-1.38383
45	H	0.102418	-2.93645	-0.42096
46	H	-1.21446	-2.23325	0.502201
47	C	-1.30031	-3.25859	-2.81453
48	H	-0.55875	-2.00596	-4.42206
49	H	-1.8778	-1.29997	-3.49972
50	H	-2.02752	-4.08759	-0.9454
51	H	-2.76506	-2.55762	-1.40615
52	H	-2.03813	-3.77155	-3.43718
53	H	-0.40112	-3.88494	-2.8094
54	C	1.127837	1.520247	-0.80363
55	C	1.439148	2.623022	0.222463
56	C	2.324131	1.344061	-1.75817
57	H	0.244532	1.821027	-1.37626
58	C	1.85184	3.93324	-0.45645
59	H	2.253582	2.28721	0.873301
60	H	0.574044	2.795503	0.860317
61	C	2.707334	2.658246	-2.44325
62	H	3.175804	0.979277	-1.17854
63	H	2.12368	0.579742	-2.50738
64	C	3.027275	3.742216	-1.41421
65	H	2.094041	4.678195	0.306292
66	H	1.00055	4.327903	-1.02119
67	H	3.562673	2.490696	-3.10298
68	H	1.88049	2.994071	-3.08064
69	H	3.272036	4.684727	-1.91116
70	H	3.914759	3.445121	-0.84446
71	P	0.713692	-0.10547	0.033179

Table S8. Optimized structure of **L6**Ni$(CO)_3$.

Number	Atom	X	Y	Z
1	As	-0.65832	-0.11628	0.03489
2	C	0.365637	0.514227	1.604947
3	C	-0.41299	0.580083	2.764374

4	H	-1.44023	0.241877	2.724417
5	C	1.709173	0.920072	1.671785
6	C	2.654882	0.853104	0.522497
7	C	0.100436	1.054405	3.963058
8	H	-0.53077	1.096055	4.841732
9	C	3.564552	-0.20914	0.425529
10	C	2.681798	1.848732	-0.46018
11	C	2.216433	1.383904	2.887744
12	H	3.256033	1.684039	2.931175
13	C	4.441953	-0.30581	-0.65622
14	H	5.129508	-1.13264	-0.74325
15	C	1.425765	1.462066	4.02451
16	H	1.846062	1.829845	4.952159
17	C	4.410744	0.673683	-1.63786
18	H	5.080335	0.596083	-2.48497
19	C	3.546208	1.755766	-1.55345
20	H	3.55347	2.510229	-2.32468
21	Ni	-2.57765	-1.4345	0.638051
22	C	-1.9299	-2.59782	1.867133
23	O	-1.50039	-3.32356	2.634548
24	C	-3.80048	-0.27449	1.285312
25	O	-4.57346	0.467814	1.67926
26	C	-3.1348	-2.23693	-0.87935
27	O	-3.49852	-2.74312	-1.83582
28	C	-1.12972	1.572463	-0.93011
29	C	-2.32766	1.308195	-1.85317
30	C	-1.44969	2.695215	0.063407
31	H	-0.25422	1.852318	-1.5222
32	C	-2.78242	2.583094	-2.57113
33	H	-3.15488	0.920808	-1.25082
34	H	-2.09835	0.532252	-2.58411
35	C	-1.92243	3.965494	-0.65364
36	H	-2.24114	2.360422	0.743414
37	H	-0.57689	2.913332	0.67762
38	C	-3.11424	3.691874	-1.57179

39	H	-3.64884	2.36134	-3.19979
40	H	-1.98669	2.926376	-3.24305
41	H	-2.17387	4.731528	0.084883
42	H	-1.09964	4.367101	-1.25512
43	H	-3.40948	4.604583	-2.09613
44	H	-3.97358	3.383517	-0.96593
45	C	0.620294	-1.05618	-1.16481
46	C	0.992562	-2.39728	-0.52159
47	C	0.045465	-1.25291	-2.5715
48	H	1.509008	-0.43469	-1.24799
49	C	1.95485	-3.19264	-1.40957
50	H	0.079549	-2.9818	-0.36627
51	H	1.433926	-2.2346	0.463325
52	C	1.014576	-2.05437	-3.45024
53	H	-0.91055	-1.78227	-2.51806
54	H	-0.14979	-0.28647	-3.04008
55	C	1.377177	-3.39632	-2.81137
56	H	2.17937	-4.15612	-0.94345
57	H	2.90102	-2.64695	-1.49043
58	H	0.573296	-2.20811	-4.43855
59	H	1.92843	-1.46787	-3.59856
60	H	2.087515	-3.93701	-3.4424
61	H	0.477603	-4.0186	-2.74429
62	O	1.815006	2.880529	-0.27153
63	O	3.501526	-1.12306	1.429398
64	C	1.856043	3.982654	-1.16322
65	H	1.544795	3.695089	-2.17236
66	H	1.15359	4.710977	-0.76694
67	H	2.854771	4.426574	-1.20387
68	C	4.38933	-2.23036	1.416022
69	H	4.162603	-2.80029	2.313877
70	H	4.228708	-2.86187	0.538128
71	H	5.433614	-1.90564	1.446252

Table S9. Optimized structure of **L7**Ni(CO)$_3$.

Number	Atom	X	Y	Z
1	As	0.355168	0.024841	0.054677
2	C	-0.57726	-0.74655	1.621757
3	C	0.2526	-0.92723	2.731138
4	H	1.297384	-0.65676	2.650687
5	C	-1.94289	-1.06984	1.739203
6	C	-2.92862	-0.91853	0.634117
7	C	-0.23289	-1.42055	3.934925
8	H	0.438006	-1.55196	4.774326
9	C	-3.92013	0.062006	0.714315
10	C	-2.90352	-1.75288	-0.4841
11	C	-2.4222	-1.54315	2.964761
12	H	-3.47506	-1.78271	3.05027
13	C	-4.83185	0.236595	-0.31923
14	H	-5.58195	1.014162	-0.24834
15	C	-1.58127	-1.72531	4.053984
16	H	-1.98001	-2.10189	4.987502
17	C	-4.77611	-0.57847	-1.44471
18	H	-5.48214	-0.43965	-2.25342
19	C	-3.8159	-1.58158	-1.51842
20	H	-3.77834	-2.23519	-2.38092
21	Ni	2.513573	0.941879	0.574972
22	C	2.217395	2.071199	1.960114
23	O	2.016754	2.779708	2.830663
24	C	3.555705	-0.47697	0.978496
25	O	4.209865	-1.38221	1.213885
26	C	3.076416	1.779033	-0.92445
27	O	3.451472	2.29721	-1.86915
28	H	-2.1683	-2.54293	-0.5406
29	H	-3.95493	0.708316	1.582094
30	C	0.440552	-1.46756	-1.27104
31	C	1.549653	-1.19631	-2.29643
32	C	0.679665	-2.81251	-0.57573

33	H	-0.52535	-1.48321	-1.78225
34	C	1.647381	-2.33259	-3.32055
35	H	2.503026	-1.09772	-1.76838
36	H	1.387605	-0.2469	-2.80892
37	C	0.777783	-3.95403	-1.59355
38	H	1.61369	-2.75988	-0.00486
39	H	-0.10689	-3.02345	0.15061
40	C	1.864167	-3.68382	-2.63663
41	H	2.458857	-2.12615	-4.02314
42	H	0.723487	-2.36814	-3.90948
43	H	0.971547	-4.89653	-1.07487
44	H	-0.18871	-4.06666	-2.09923
45	H	1.888274	-4.4868	-3.37775
46	H	2.842082	-3.68222	-2.14216
47	C	-0.95639	1.302485	-0.72095
48	C	-1.28858	2.377291	0.319171
49	C	-0.43306	1.931615	-2.01622
50	H	-1.85584	0.734031	-0.95427
51	C	-2.28661	3.397877	-0.23665
52	H	-0.36679	2.893923	0.608206
53	H	-1.68712	1.918828	1.226643
54	C	-1.43591	2.952329	-2.56953
55	H	0.521538	2.431318	-1.82634
56	H	-0.24573	1.16285	-2.76842
57	C	-1.77423	4.026713	-1.5341
58	H	-2.48216	4.170473	0.51167
59	H	-3.2397	2.89381	-0.43023
60	H	-1.03266	3.409581	-3.47684
61	H	-2.35398	2.429073	-2.85997
62	H	-2.51408	4.722688	-1.93793
63	H	-0.87442	4.614203	-1.31866

Table S10. Optimized structure of **L10**Ni(CO)$_3$.

Number	Atom	X	Y	Z

1	As	-0.28602	-0.03855	-0.04505
2	C	0.668591	1.642959	-0.45354
3	C	-0.1635	2.683604	-0.87452
4	H	-1.23068	2.510945	-0.92425
5	C	2.057937	1.862638	-0.40851
6	C	0.770777	-1.43159	-0.99718
7	H	1.473368	-0.87427	-1.61848
8	C	3.05654	0.848201	0.038062
9	C	-0.08854	-2.33454	-1.89362
10	H	-0.96845	-2.67129	-1.34167
11	H	-0.45593	-1.81922	-2.78125
12	C	0.056213	-0.35419	1.882035
13	H	1.112389	-0.57981	1.989686
14	C	0.34564	3.921491	-1.24481
15	H	-0.32614	4.708029	-1.56429
16	C	3.285101	0.617477	1.39482
17	C	3.84399	0.171659	-0.89602
18	C	2.557535	3.108494	-0.79979
19	H	3.628029	3.270306	-0.76666
20	C	4.255217	-0.28857	1.808961
21	H	4.417499	-0.45558	2.866383
22	C	-0.34751	0.887214	2.717181
23	H	0.520803	1.461499	3.041556
24	H	-0.96715	1.569381	2.12988
25	C	1.716173	4.133358	-1.21191
26	H	2.132431	5.089281	-1.50388
27	C	-0.80873	-1.52868	2.413745
28	H	-0.18403	-2.18223	3.028213
29	H	-1.23292	-2.15036	1.624729
30	C	5.017666	-0.97326	0.86954
31	H	5.770105	-1.68205	1.190629
32	C	1.551977	-2.43543	-0.14325
33	H	2.399574	-1.9925	0.374972
34	H	0.89465	-2.87674	0.610417
35	C	4.812133	-0.73667	-0.4855

36	H	5.405298	-1.26064	-1.22427
37	C	-1.8929	-0.87116	3.276023
38	H	-2.71148	-0.53002	2.637661
39	H	-2.31243	-1.55125	4.018483
40	C	-1.1762	0.335439	3.887547
41	H	-1.85889	1.078177	4.302515
42	H	-0.5167	0.004472	4.695669
43	C	0.830726	-3.53539	-2.22379
44	H	0.274067	-4.47265	-2.19031
45	H	1.238011	-3.44824	-3.23203
46	C	1.969657	-3.50313	-1.16746
47	H	2.910026	-3.20331	-1.63514
48	H	2.139918	-4.47568	-0.7037
49	Ni	-2.64264	0.039384	-0.54888
50	C	-3.34735	1.335719	0.494065
51	O	-3.80201	2.141505	1.162138
52	C	-2.7071	0.390614	-2.32496
53	O	-2.72956	0.601119	-3.44532
54	C	-3.30798	-1.59037	-0.1457
55	O	-3.74978	-2.61179	0.106324
56	H	3.688914	0.357412	-1.95158
57	H	2.706789	1.163511	2.128207

Table S11. Optimized structure of **L11**Ni(CO)$_3$.

Number	Atom	X	Y	Z
1	As	-0.65334	0.105567	-0.00182
2	O	2.44408	-2.5852	-0.46892
3	O	3.03166	1.592883	1.525589
4	C	0.383258	-0.6382	1.503004
5	C	-0.39915	-1.01484	2.597251
6	H	-1.46749	-0.84523	2.558437
7	C	1.772989	-0.84141	1.559606
8	C	0.364478	1.705945	-0.5955
9	H	1.096416	1.870862	0.193823

10	C	2.727782	-0.46808	0.473647
11	C	-0.49669	2.967646	-0.73343
12	H	-1.37146	2.754629	-1.35211
13	H	-0.86811	3.3377	0.222348
14	C	-0.39456	-1.2471	-1.42386
15	H	0.661608	-1.25286	-1.67715
16	C	0.161108	-1.59237	3.728959
17	H	-0.47147	-1.87536	4.560837
18	C	3.067023	-1.37799	-0.53551
19	C	3.385289	0.769188	0.501628
20	C	2.322686	-1.4188	2.705924
21	H	3.394387	-1.5704	2.744523
22	C	3.991449	-1.04103	-1.52776
23	H	4.239614	-1.73413	-2.31638
24	C	-0.84917	-2.63881	-0.92519
25	H	-0.01019	-3.23141	-0.56814
26	H	-1.54224	-2.54065	-0.0861
27	C	1.532224	-1.79696	3.782255
28	H	1.988104	-2.2442	4.656724
29	C	-1.25924	-0.93699	-2.67758
30	H	-0.62735	-0.97197	-3.56851
31	H	-1.71736	0.052276	-2.65697
32	C	4.605141	0.202084	-1.48342
33	H	5.322488	0.466577	-2.24976
34	C	1.07616	1.635276	-1.95113
35	H	1.928019	0.959079	-1.9567
36	H	0.378271	1.294118	-2.71906
37	C	4.320354	1.112258	-0.47648
38	H	4.815233	2.070711	-0.46292
39	C	-2.31505	-2.05132	-2.72912
40	H	-3.16872	-1.77677	-2.10376
41	H	-2.68873	-2.2321	-3.73793
42	C	-1.59783	-3.25568	-2.11302
43	H	-2.2768	-4.05559	-1.81364
44	H	-0.88813	-3.67598	-2.83353

45	C	0.436483	3.967041	-1.44973
46	H	-0.11998	4.631126	-2.11201
47	H	0.940514	4.602513	-0.71879
48	C	1.473418	3.099744	-2.21979
49	H	2.480657	3.281451	-1.83927
50	H	1.493671	3.325506	-3.28677
51	C	2.679179	-3.53843	-1.49253
52	H	3.731569	-3.83324	-1.53378
53	H	2.369056	-3.15834	-2.47093
54	H	2.07397	-4.40493	-1.23699
55	C	3.577645	2.901679	1.577765
56	H	4.665023	2.879234	1.694007
57	H	3.132025	3.373208	2.450359
58	H	3.319445	3.476927	0.683168
59	Ni	-2.98676	0.474506	0.477813
60	C	-3.71892	-1.12578	0.885374
61	O	-4.20275	-2.13023	1.129801
62	C	-2.97096	1.652167	1.852753
63	O	-2.94157	2.40219	2.711426
64	C	-3.69809	1.169275	-1.02878
65	O	-4.16696	1.603637	-1.9746

9. The electronic/steric parameters of several ligands

Table S12. The electronic/steric parameters of several ligands.

Ligand	Computed electronic parameter (CEP) / cm^{-1}	Tolman electronic parameter (TEP)* / cm^{-1}	Cone angle [°]	%V_{bur} [%]
PPh_3	2136.1[4]	2067.0	165.8	29.5
$AsPh_3$	2140.3[4]	2071.3	158.8	22.8
SPhos	2140.3	2055.7	173.7	35.1
L6	2127.4	2058.1	168.6	27.9
L7	2130.2	2060.9	167.9	27.3
L10	2130.1	2061.0	177.7	29.1
L11	2127.9	2058.6	176.5	28.7

(equation 1) *TEP^4 = 1.0168CEP-105.0

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