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Electronic Supplementary Information

N-Heterocyclic carbene ligands bearing poly(ethylene glycol) chains: effect of the chain length on palladium-catalyzed coupling reactions employing aryl chlorides

Tetsuaki Fujihara,* Takahiro Yoshikawa, Motoi Satou, Hidetoshi Ohta, Jun Terao, and Yasushi Tsuji*

Department of Energy and Hydrocarbon Chemistry,Graduate School of Engineering

Kyoto University, Kyoto 615-8510, Japan.

tfuji@scl.kyoto-u.ac.jp, ytsuji@scl.kyoto-u.ac.jp

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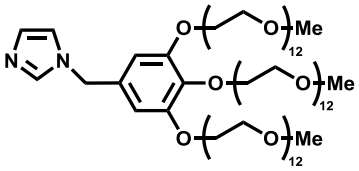
1. General procedures

All manipulations were performed under an atmosphere of argon, using standard Schlenk-type glasswares on a dual-manifold Schlenk line. All solvents were dried and purified by usual procedures.[1] ^{1}H and ^{13}C NMR were measured with a JEOL ECX-400 spectrometer. The ^{1}H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm) or residual protiated solvent (7.26 ppm) in $CDCl_3$. The ^{13}C NMR chemical shifts are reported relative to $CDCl_3$ (77.0 ppm). MALDI-TOF mass spectra were recorded on a Bruker Autoflex. Elemental analysis was carried out at Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Science, Kyoto University. Preparative recycling gel permeation chromatography (GPC) was performed with a JAI LC9104 using $CHCl_3$ as the eluent at a flow rate of 14 mL min^{-1}. GC analysis was carried out using Shimadzu GC-17A with a capillary column (CBP-1, 0.25 mm i.d. × 25 μm).

2. Synthesis of imidazolium salts

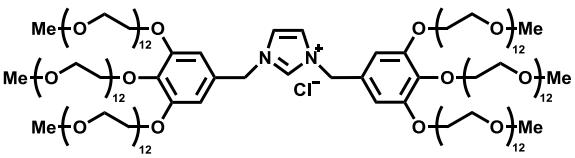
Tetra(ethylene glycol) monomethyl ether (n = 4; **2b**) was purchased from TCI. Dodeca(ethylene glycol) monomethyl ether ($HO(CH_2CH_2O)_nMe$, n = ca. 12; **2c**) and heptadeca(ethylene glycol) monomethyl ether ($HO(CH_2CH_2O)_nMe$, n = ca. 17; **2d**) were purchased from Aldrich. Compounds **3b**,[2a] **3c**,[2b] **4b**,[2a] **4c**,[2b] **5b**,[2a] **5c**,[2b] **1a**·HCl[2a] and **1b**·HCl[2a] were prepared by our previous methods.

Synthesis of 6c



A mixture of imidazole (0.68 g, 10 mmol), **5c** (18 g, 10 mmol), K_2CO_3 (1.4 g, 10 mmol), KOH (0.56 g, 10 mmol) and tetra(*n*-butyl)ammonium bromide (0.16 g, 0.50 mmol) in toluene (120 mL) was refluxed under Ar for 24 h. After cooling to room temperature, the suspension was filtered through Celite and the filtrate was concentrated to dryness. The residue was purified by silica gel column chromatography (10% MeOH-$CHCl_3$, v/v) to give **6c** as a brown oil. Yield 14 g (77%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.52 (s, 1H, Im), 7.06 (br, 1H, Im), 6.88 (br,1H, Im), 6.34 (s, 2H, Ar), 4.99 (s, 2H, CH_2Im), 4.22-4.08 (m, 6H, OCH_2), 3.83-3.50 (m, 138H), 3.36 (s, 9H, OCH_3).; **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.6, 137.9, 137.0, 131.3, 129.3, 118.9, 106.7, 72.3, 71.9, 70.9, 70.4, 70.5-69.9, 69.3, 68.6, 58.6, 50.3.

Synthesis of 1c·HCl



A solution of **6c** (5.6 g, 3.1 mmol) and **5c** (7.2 g, 4.0 mmol) in toluene (75 mL) was refluxed for 60 h. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography (8% MeOH-$CHCl_3$, v/v) to give **1c·HCl** as a brown oil. Yield 4.0 g (36%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 10.80 (s, 1H, Im), 7.20 (br, 2H, Im), 6.72 (s, 4H, Ar), 5.29 (s, 4H, CH_2Im), 4.14-3.97 (m, 12H, OCH_2),

3.78-3.42 (m, 276H), 3.28 (s, 18H, OC*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.0, 139.2, 137.9, 128.0, 121.3, 108.8, 72.1, 71.7, 70.8-70.2, 69.5, 69.1, 58.9, 53.5. **MALDI-TOF MS** (DIT): *m/z* 3601 $[M-Cl]^+$.

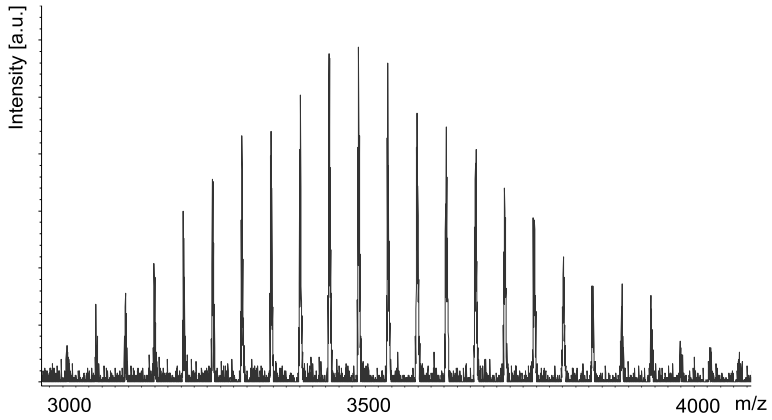
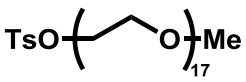


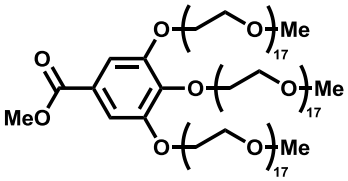
Fig. S1. MALDI-TOF-MS spectra of **1c·HCl**

Synthesis of 3d



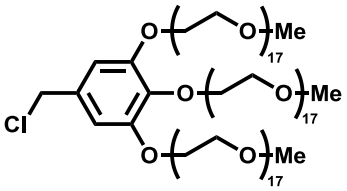
Pyridine (11 mL, 0.13 mol) was slowly added to a solution of heptadeca(ethylene glycol) monomethyl ether ($HO(CH_2CH_2O)_nMe$, *n* = ca. 17, 50 g, 67 mmol) and *p*-toluenesulfonyl chloride (25 g, 0.13 mol) in CH_2Cl_2 (150 mL). The resulting solution was stirred at room temperature for 19 h. After the removal of CH_2Cl_2, water (100 mL) and NaOH was carefully added until the aqueous layer became basic. The organic layer was washed with 1 N HCl aq. and brine, successively. The organic layer was dried over anhydrous $MgSO_4$. After filtration, the filtrate was evaporated under vacuum to give **5** as pale-yellow semisolid. Yield 51 g (82%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.75 (d, *J* = 8.2 Hz, 2H, Ar), 7.30 (d, *J* = 7.7 Hz, 2H, Ar), 4.11 (t, *J* = 4.8 Hz, 2H, OC*H*$_2$), 3.66-3.48 (m, 66H), 3.33 (s, 3H, OC*H*$_3$), 2.41 (s, 3H, C*H*$_3$Ar).

Synthesis of 4d



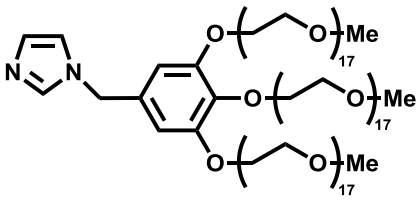
A suspension of 3,4,5-trihydroxybenzoate (3.6 g, 20 mmol), **3d** (55 g, 59 mmol), K_2CO_3 (27 g, 0.20 mol) in acetone (250 mL) was refluxed for 24 h. After removal of acetone, the residue was extracted with $CHCl_3$ (40 mL × 5). The organic layer was washed with 1 N HCl aq. and brine, successively. The organic layer was dried over anhydrous $MgSO_4$. After filtration, the filtrate was evaporated under vacuum to give **4d** as pale-brown semisolid. Yield 46.2 g (95%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.21 (s, 2H, Ar), 4.14-4.09 (m, 6H, OC*H*$_2$), 3.80 (s, 3H, C*H*$_3$O), 3.79-3.36 (m, 198H), 3.29 (s, 9H, OC*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 166.5, 152.2, 142.5, 124.9, 109.0, 72.5, 72.3, 71.9, 71.3, 70.8, 70.8-70.3, 69.6, 68.9, 61.7, 59.0, 52.1.

Synthesis of 5d



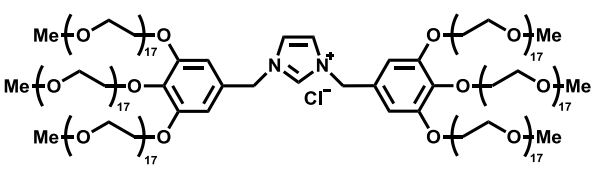
A solution of **4d** (20 g, 8.2 mmol) in anhydrous THF (50 mL) was slowly added to a suspension of $LiAlH_4$ (0.34 g, 9.0 mmol) in THF (50 mL) at 0 °C. The resulting suspension was stirred at room temperature for 10 h. After the reaction mixture was cooled to 0 °C, water was carefully added. Volatiles were removed with an evaporator and the residue was extracted with $CHCl_3$ (40 mL ×5). The organic layer was dried over anhydrous $MgSO_4$. After filtration, the filtrate was evaporated under vacuum to give the corresponding benzyl alcohol derivative as pale-yellow semisolid. Yield 19 g (97%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.49 (s, 2H, Ar), 4.41 (s, 2H, C*H*$_2$Ar), 4.09-3.94 (m, 6H, OC*H*$_2$), 3.72-3.38 (m, 198H), 3.23 (s, 9H, OC*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.1, 137.0, 136.7, 105.9, 71.44, 71.42, 70.3-69.9, 69.3-69.2, 68.4-68.3, 64.2, 58.5, 42.3. To a solution of the benzyl alcohol (19 g, 7.9 mmol) in CH_2Cl_2 (120 mL), thionyl chloride (1.7 mL, 24 mmol) was slowly added via a syringe. The resulting solution was stirred at room temperature for 12 h. After water (50 mL) was carefully added, the organic layer was washed with water and brine, successively. The organic layer was dried over anhydrous $MgSO_4$. After filtration, the filtrate was evaporated under vacuum to give **5d** as pale-yellow semisolid. Yield 19.1 g (98%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 6.53 (s, 2H, Ar), 4.39 (s, 2H, C*H*$_2$Ar), 4.11-3.99 (m, 6H, OC*H*$_3$), 3.79-3.41 (m, 198H), 3.27 (s, 9H, OC*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.5, 138.4, 132.5, 108.1, 71.7, 70.7-70.0, 69.5, 68.7, 58.8, 46.4.

Synthesis of 6d



A mixture of imidazole (0.57 g, 8.4 mmol), **5d** (21 g, 8.4 mmol), K_2CO_3 (1.2 g, 8.4 mmol), KOH (0.19 g, 3.4 mmol) and tetra(*n*-butyl)ammonium bromide (0.14 g, 0.42 mmol) in toluene (100 mL) was refluxed under Ar for 24 h. After cooling to room temperature, the suspension was filtered through Celite and the filtrate was concentrated to dryness. The residue was purified by silica gel column chromatography (10% MeOH-$CHCl_3$, v/v) to give **6d** as a pale-yellow semisolid. Yield 19 g (91%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.51 (s, 1H, Im), 7.05 (br, 1H, Im), 6.87 (br,1H, Im), 6.35 (s, 2H, Ar), 4.98 (s, 2H, C*H*$_2$Im), 4.12-4.04 (m, 6H, OC*H*$_2$), 3.81-3.51 (m, 198H), 3.35 (s, 9H, OC*H*$_3$). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 152.8, 138.1, 137.2, 131.4, 129.5, 119.0, 106.8, 72.3, 72.1, 71.7, 71.1, 70.6, 70.5, 70.4-70.1, 70.1, 69.4, 68.7, 61.4, 58.8, 50.5.

Synthesis of 1d·HCl



A solution of **6d** (3.0 g, 1.2 mmol) and **5d** (3.8 g, 1.6 mmol) in toluene (30 mL) was refluxed for 60 h. The solvent was removed in vacuo, and the residue was purified by silica gel column chromatography

(8% MeOH-$CHCl_3$, v/v) to give **1d**·HCl as a brown oil. Yield 4.0 g (36%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 11.30 (s, 1H, Im), 7.18 (s, 2H, Im), 6.78 (s, 4H, Ar), 5.37 (s, 4H, CH_2Im), 4.20-4.12 (m, 12H, OCH_2), 3.84-3.42 (m, 396H), 3.38 (s, 18H, OCH_3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 153.2, 139.3, 138.8, 128.1, 121.4, 109.0, 72.2, 71.9, 70.6-70.3, 69.6, 69.2, 59.0, 53.6. **MALDI-TOF MS** (DIT): *m/z* 4923 $[M-Cl]^+$.

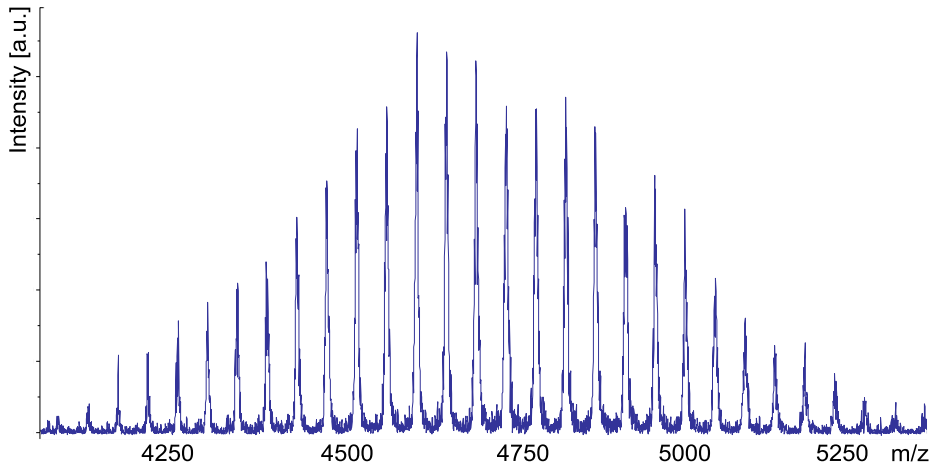


Fig. S2. MALDI-TOF-MS spectra of **1d·HCl**

3. Exprimental procedure

3.1. General procedures for the Suzuki-Miyaura coupling of 4-chlorotoluene with phenylboronic acid (Table 1).

To a stirred solution of imidazolium salt (**1**·HCl, 0.011 mmol) and [PdCl(η^3-C_3H_5)]$_2$ (0.0050 mmol) in anhydrous THF (1.0 mL), KHMDS (0.040 mmol) was added at room temperature under an Ar and the resulting suspension was stirred at room temperature for 30 min under an Ar atmosphere. Then, the reaction mixture was concentrated to dryness. K_3PO_4 (3.5 mmol) and 4-chlorotoluene (1.0 mmol) were added to the residue under an Ar flow. Anhydrous THF (3.0 mL) and phenylboronic acid (3.0 mmol) were added. The suspension was stirred at room temperature for 10 min. Then, the reaction was carried out at 45 °C for 15 h. After cooling to room temperature, tridecane (0.21 mmol) as an internal standard was added. The mixture was diluted with ethyl acetate (7.0 mL) and filtered through a pad of Celite. The yield of the product was determined by GC analysis relative to an internal standard.

3.2. General procedures for the Suzuki-Miyaura coupling of ary chlorides with arylboronic acids (Table 2).

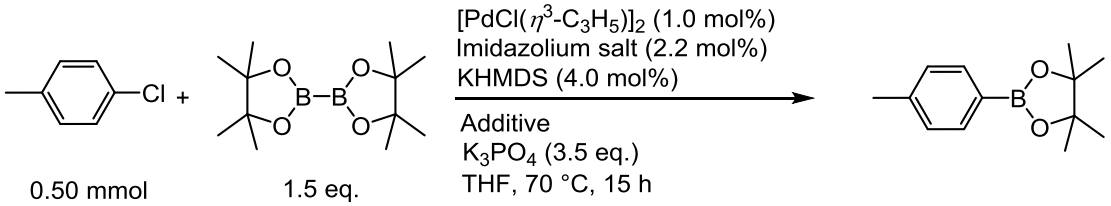
To a stirred solution of imidazolium salt (**1d**·HCl, 0.011 mmol) and [PdCl(η^3-C_3H_5)]$_2$ (0.0050 mmol) in anhydrous THF (1.0 mL), KHMDS (0.040 mmol) was added at room temperature under an Ar and the resulting suspension was stirred at room temperature for 30 min under an Ar atmosphere. Then, the reaction mixture was concentrated to dryness. K_3PO_4 (3.5 mmol) and an aryl chloride (1.0 mmol) were added to the residue under an Ar flow. Anhydrous THF (3.0 mL) and arylboronic acid (3.0 mmol) were added. The suspension was stirred at room temperature for 10 min. Then, the reaction was carried out at 45 °C for 15 h. After cooling to room temperature, all volatiles were removed under vacuum. The product was isolated by silica gel column chromatography.

3.3. A procedure for the Suzuki-Miyaura coupling of 4-chlorotoluene with phenylboronic acid at room temperature (Eqn (1)).

To a stirred solution of imidazolium salt (**1d**·HCl, 0.011 mmol) and [PdCl(η^3-C_3H_5)]$_2$ (0.0050 mmol) in anhydrous THF (1.0 mL), KHMDS (0.040 mmol) was added at room temperature under an Ar and the resulting suspension was stirred at room temperature for 30 min under an Ar atmosphere. Then, the reaction mixture was concentrated to dryness. KF (4.5 mmol) and 4-chlorotoluene (1.0 mmol) were added to the residue under an Ar flow. Anhydrous THF (3.0 mL) and phenylboronic acid (4.0 mmol) were added. The suspension was stirred at room temperature for 10 min. Then, the reaction was carried out at room temperature for 40 h. After cooling to room temperature, all volatiles were removed under vacuum. The yield of the product was determined by GC analysis relative to an internal standard.

3.4. General procedures for the palladium-catalyzed borylation of ary chlorides (Scheme 2).
To a stirred solution of imidazolium salt (**1d**·HCl, 0.011 mmol) and [PdCl(η^3-C_3H_5)]$_2$ (0.0050 mmol) in anhydrous THF (1.0 mL), KHMDS (0.040 mmol) was added at room temperature under an Ar and the resulting suspension was stirred at room temperature for 30 min under an Ar atmosphere. Then, the reaction mixture was concentrated to dryness. K_3PO_4 (3.5 mmol) and an aryl chloride (0.50 mmol) were added to the residue under an Ar flow. Anhydrous THF (3.0 mL), bis(pinacolato)diboron (B_2pin_2, 0.75 mmol) and dibenzylideneacetone (dba, 0.020 mmol) were added. Then, the reaction was heated at 70 °C (bath temp.) for 15 h. After cooling to room temperature, all volatiles were removed under vacuum. The product was isolated by column chromatography on boric acid-impregnated silica gel.[3]

Table S1. Optimization and Ligand effect on the palladium-catalyzed borylation of 4-chlorotoluene.[a]



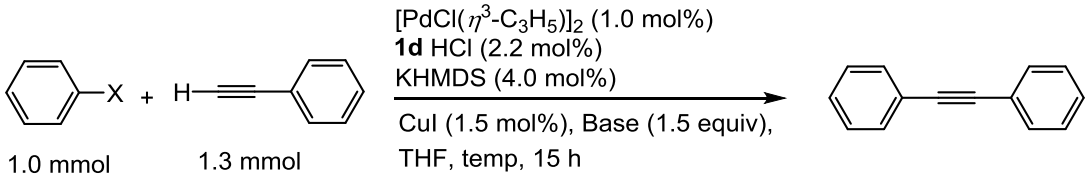
Entry	Imidazolium salt	Additive	Yield (%)[b]
1	**1d** HCl	dba (2 mol%)	72
2	**1d** HCl	none	53[c]
2	**1a** HCl	dba (2 mol%)	17
3	**1a** HCl	dba (2 mol%), **8** (13 mol %)	20
5	IMes·HCl	dba	9
6	IPr·HCl	dba	13
7	none	none	8

[a] Reaction conditions: 4-chlorotoluene (0.50 mmol), bis(pinacolato)diboron (0.75 mmol), K_3PO_4 (3.5 mmol), THF (3.0 mL), additive, and catalyst (2 mol% as Pd), for 15 h at 70 °C. [b] GC yield. [c] Low reproducibility. [d] $Me(OCH_2CH_2)_{17}OMe$.

3.5. A procedure for palladium-catalyzed Sonogachira coupling reaction

To a stirred solution of imidazolium salt (**1d**·HCl, 0.011 mmol) and [PdCl(η^3-C_3H_5)]$_2$ (0.0050 mmol) in anhydrous THF (1.0 mL), KHMDS (0.040 mmol) was added at room temperature under an Ar and the resulting suspension was stirred at room temperature for 30 min under an Ar atmosphere. Then, the reaction mixture was concentrated to dryness. Aryl halide (1.0 mmol), phenylacetylene (1.3 mmol), base (1.5 mmol), and anhydrous THF (3.0 mL) were added under an Ar flow. The suspension was stirred at room temperature for 10 min. Then, the reaction was carried out at 45 ^oC for 15 h. After cooling to room temperature, tridecane (0.21 mmol) as an internal standard was added. The mixture was diluted with ethyl acetate (7.0 mL) and filtered through a pad of Celite. The yield of the product was determined by GC analysis relative to an internal standard.

Table S2. Palladium-catalyzed Sonogashira coupling with **1d** as the ligand.

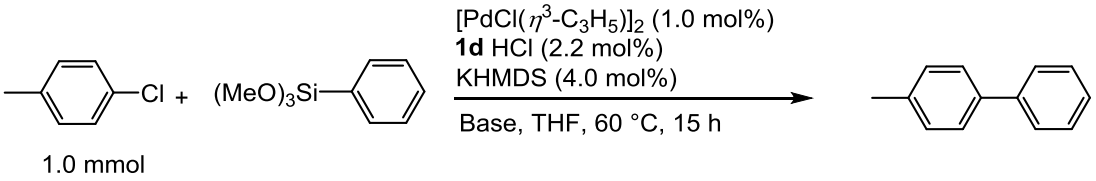


Entry	Aryl Halide (X)	Base	Temp (^oC)	GC Yield (%)
1	Cl	K_3PO_4	45	0
2	Br	K_3PO_4	45	0
3	I	K_3PO_4	45	11
4	I	K_3CO_3	rt	3
5	I	KF	45	10
6	I	Et_3N	45	trace

3.6. A procedure for palladium-catalyzed Sonogachira coupling reaction

To a stirred solution of imidazolium salt (**1d**·HCl, 0.011 mmol) and [PdCl(η^3-C_3H_5)]$_2$ (0.0050 mmol) in anhydrous THF (1.0 mL), KHMDS (0.040 mmol) was added at room temperature under an Ar and the resulting suspension was stirred at room temperature for 30 min under an Ar atmosphere. Then, the reaction mixture was concentrated to dryness. 4-Chlorotoluene (1.0 mmol) and base were added to the residue under an Ar flow. Anhydrous THF (3.0 mL) and $(MeO)_3SiPh$ were added. The suspension was stirred at room temperature for 10 min. Then, the reaction was carried out at 60 °C for 15 h. After cooling to room temperature, tridecane (0.21 mmol) as an internal standard was added. The mixture was diluted with ethyl acetate (7.0 mL) and filtered through a pad of Celite. The yield of the product was determined by GC analysis relative to an internal standard.

Table S3. Palladium-catalyzed Hiyama coupling of 4-chlorotoluene.



Entry	Base (equiv)	$(MeO)_3SiPh$ (equiv)	GC Yield (%)
1	CsF (2.0)	2.0	0
2	CsF (3.0)	3.0	0
3	TBAF (2.0)	2.0	trace
4	TBAF (2.0)	3.0	4

3.7. Calculation

An optimized structure of [PdCl(η^3-C_3H_5)(**1b-d**)] (Fig. 2) was obtained by ONIOM[4] calculations. In the ONIOM calculation, the molecular system of [PdCl(η^3-C_3H_5)(**1b-d**)] was divided into two layers. The high layers were assigned to a [PdCl(η^3-C_3H_5)(NHC)] core for B3LYP[5]/LANL2DZ[6] calculation. The low layers contain the rest parts for molecular mechanics calculation using UFF force field.[7] All calculations were performed with the Gaussian 03 program[8] on a HIT HPC-IA642/SS 1.3/3D-4G.

The Connolly solvent-excluded volume[9] was calculated using Chem 3D Ultra (ver. 7, Cambridge Soft) with a solvent probe radius of 1.4 Å. The solvent–excluded volume represents the volume of space that the probe is excluded from by collisions with the atoms of the van der Waals surface.

3.8. Characterization of products

4-Phenyltoluene (entry 4, Table 1). 150 mg (89%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.49 (d, J = 8.4 Hz, 2H, Ar), 7.52 (d, J = 8.0 Hz, 2H, Ar), 7.44 (t, J = 8.0 Hz, 2H, Ar), 7.33 (tt, J = 8.4, 2.0 Hz, 1H, Ar), 7.27 (d, J = 7.6 Hz, 2H, Ar), 2.40 (s, 3H, CH_3).

4-Methoxycarbonylphenylbenzene (entry 1, Table 2). 183 mg (93%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.94 (d, J = 8.4, 2H, Ar), δ 7.63 (d, J = 8.4 Hz, 2H, Ar), 7.57 (d, 2H, J = 6.8 Hz, Ar), 7.34 (tt, J = 7.6, 1.2 Hz, 1H, Ar), 7.32 (tt, J = 7.6, 1.2 Hz, 1H, Ar), 2.53 (s, 3H, CH_3).

4-Phenylanisole (entry 2, Table 2). 157 mg (86%). **^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.57-7.53 (m, 4H, Ar), 7.417 (t, J = 8.0 Hz, 2H, Ar), 7.30 (tt, J = 8.4, 1.6 Hz, 1H, Ar), 6.98 (d, J = 8.4 Hz, 2H, Ar), 3.84 (s, 3H, CH_3).

2,6-Dimethyl-1-phenylbenzene (entry 3, Table 2). 176 mg (91%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.30 (t, J = 7.6 Hz, 2H, Ar), 7.20 (t, J = 7.6 Hz, 1H, Ar), 6.97 (m, 5H, Ar), 1.84 (s, 6H, CH_3).

1-Phenylnaphthalene (entry 4, Table 2). 194 mg (89%). **^{1}H NMR** (400 MHz, acetone-d_6): δ 7.80 (d, J = 8.4 Hz, 1H, Ar), 7.75 (d, J = 8.0 Hz, 1H, Ar), 7.70 (d, J = 8.0 Hz, 1H, Ar), 7.17 (d, J = 8.0 Hz, 1H, Ar), 7.40-7.24 (m, 8H, Ar).

4-Phenylfluorobenzene (entry 5, Table 2). 166 mg (96%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.58-7.54 (m, 4H, Ar), 7.44 (t, J = 7.6 Hz, 2H, Ar), 7.35 (tt, J = 7.2, 1.6 Hz, 1H, Ar), 7.16-7.10 (m, 2H, Ar).

4-Phenyltoluene (entry 6, Table 2). 161 mg (96%).**^{1}H NMR** (400 MHz, CD_2Cl_2): δ 7.56 (d, J = 7.6 Hz, 2H, Ar), 7.53 (d, J = 8.0 Hz, 2H, Ar), 7.44 (t, J = 8.0 Hz, 2H, Ar), 7.32 (t, J = 8.4, 1H, Ar), 7.27 (d, J = 7.6 Hz, 2H, Ar), 2.40 (s, 3H, CH_3).

4-Phenylanisole (entry 7, Table 2). 156 mg (85%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 7.53-7.52 (m, 4H, Ar), 7.43 (t, J = 8.0 Hz, 2H, Ar), 7.30 (tt, J = 8.4, 1.6 Hz, 1H, Ar), 6.98 (d, J = 8.4 Hz, 2H, Ar), 3.85 (s, 3H, CH_3).

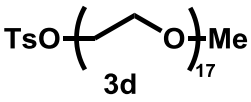
2-Phenylnaphthalene (entry 8, Table 2). 186 mg (91%). **^{1}H NMR** (400 MHz, $CDCl_3$): δ 8.08 (s, 1H, Ar), 7.94 (t, J = 8.0 Hz, 2H, Ar), 7.90 (d, 1H, J = 7.6 Hz, Ar), 7.79 (d, J = 8.8 Hz, 1H, Ar), 7.76 (d, J = 8.4 Hz, 2H, Ar), 7.56-7.53 (m, 4H,Ar), 7.416 (t, J = 8.0 Hz, 1H, Ar).

4-Methylphenylboronic acid pinacol ester (Scheme 2). 67 mg (61%). **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.70 (d, 2H, *J* = 7.7 Hz, Ar), 7.19 (d, 2H, *J* = 7.7 Hz, Ar), 2.37 (s, 3H, ArCH_3), 1.34 (s, 12H, CH_3).

4-Methoxyphenylboronic acid pinacol ester (Scheme 2). 67 mg (57%). **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.75 (d, 2H, *J* = 8.6 Hz, Ar), 6.89 (d, 2H, *J* = 8.6 Hz, Ar), 3.83 (s, 3H, OCH_3), 1.33 (s, 12H, CH_3).

2,6-Dimethylphenylboronic acid pinacol ester (Scheme 2). **^{1}H NMR** (400 MHz, $CDCl_3$, TMS): δ 7.12 (t, 1H, *J* = 7.7 Hz, Ar), 6.94 (d, 2H, *J* = 7.7 Hz, Ar), 2.39 (s, 6H, ArCH_3), 1.39 (s, 12H, CH_3).

4. NMR chart



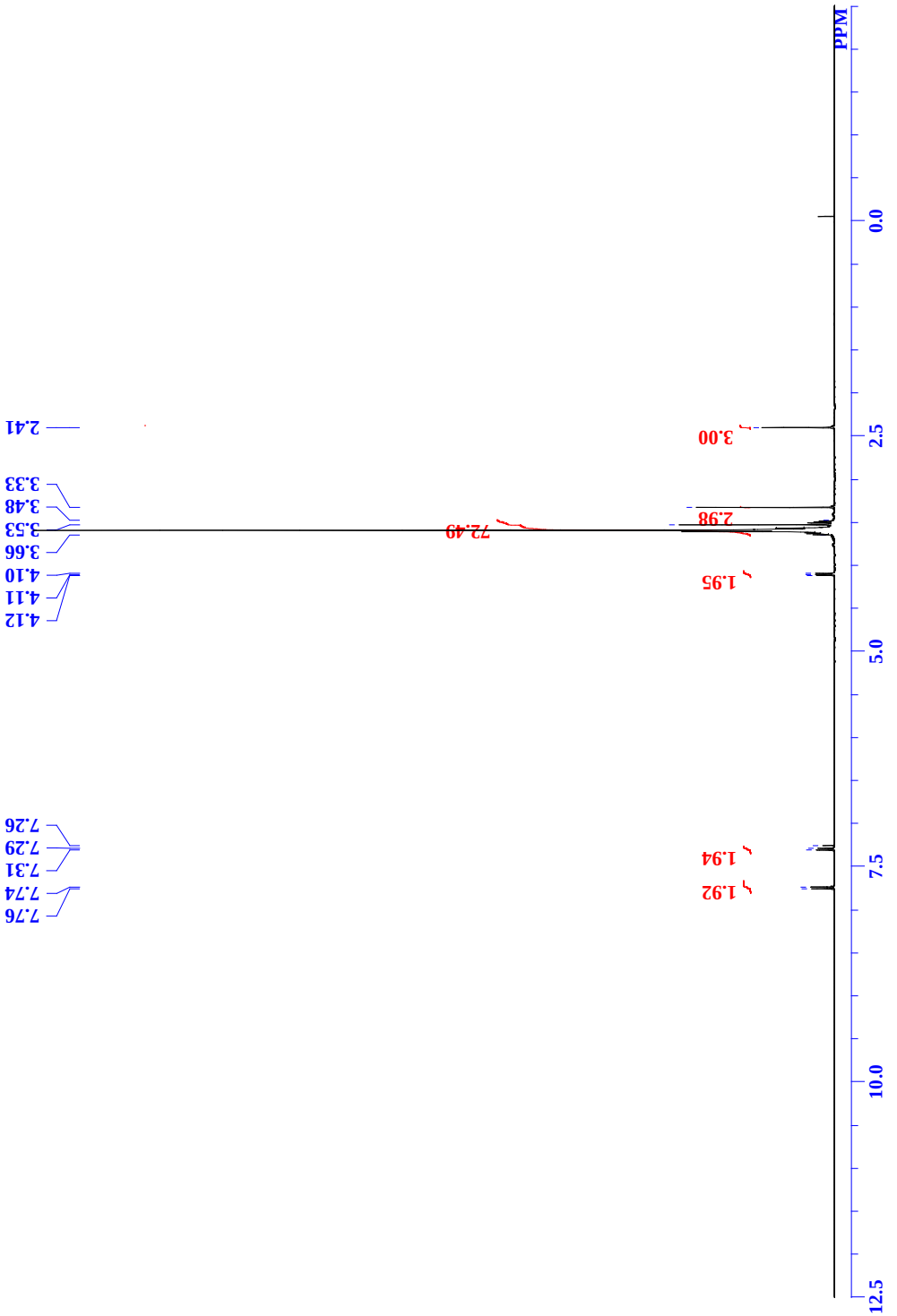


Figure S3. ^{1}H NMR spectrum of **3d** in $CDCl_3$.

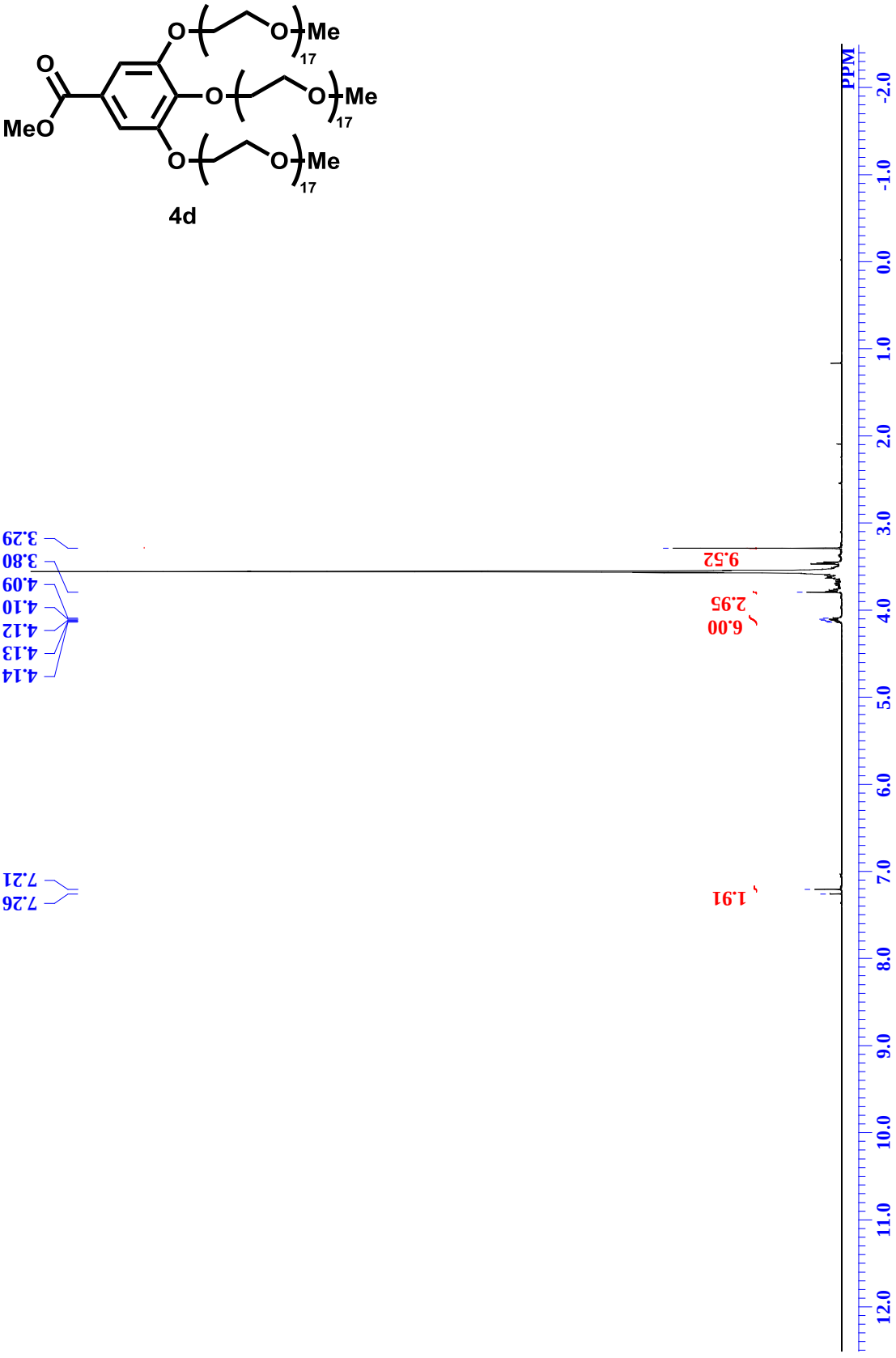


Figure S4. ^{1}H NMR spectrum of **4d** in $CDCl_3$.

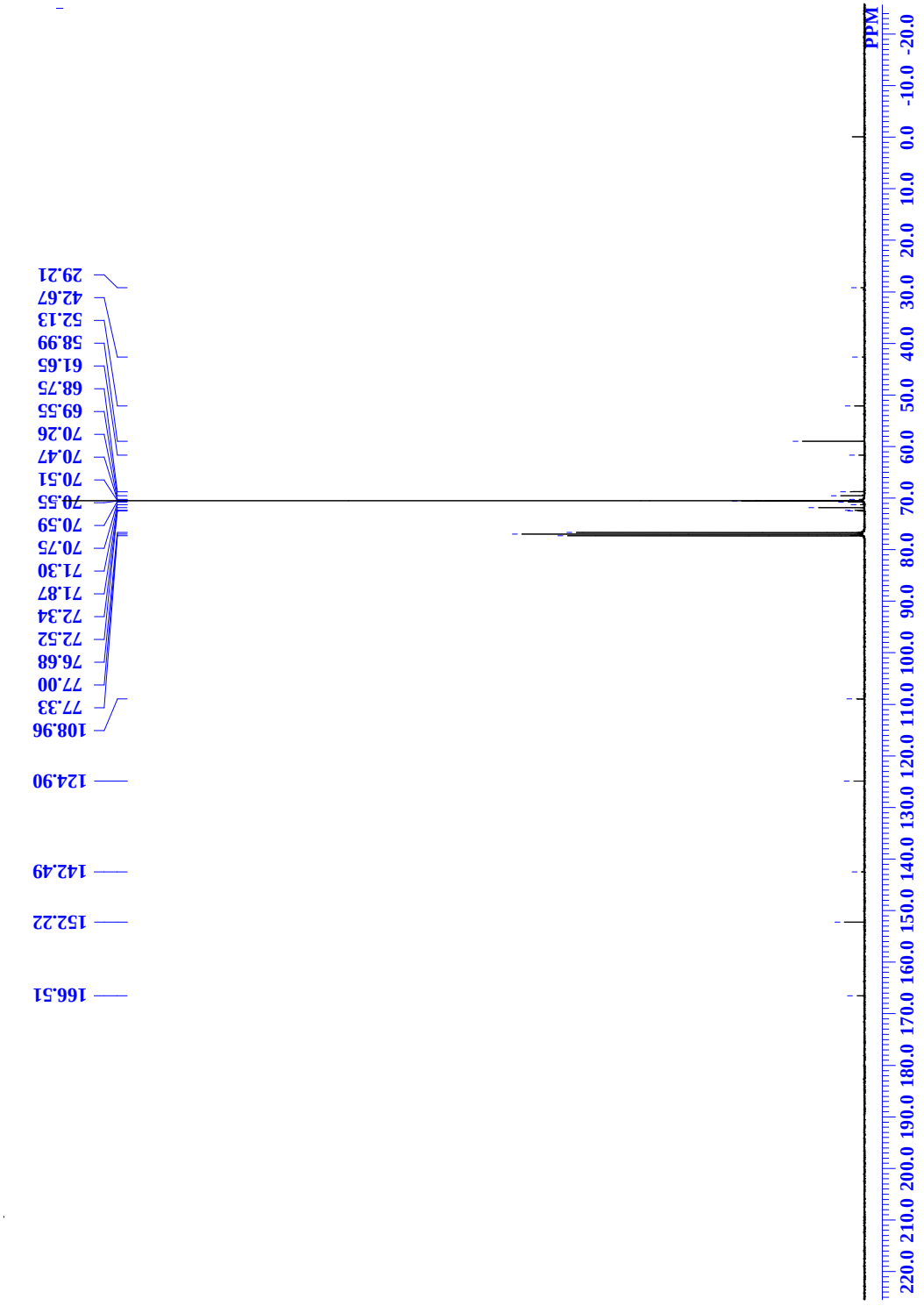


Figure S5. ^{13}C NMR spectrum of **4d** in $CDCl_3$.

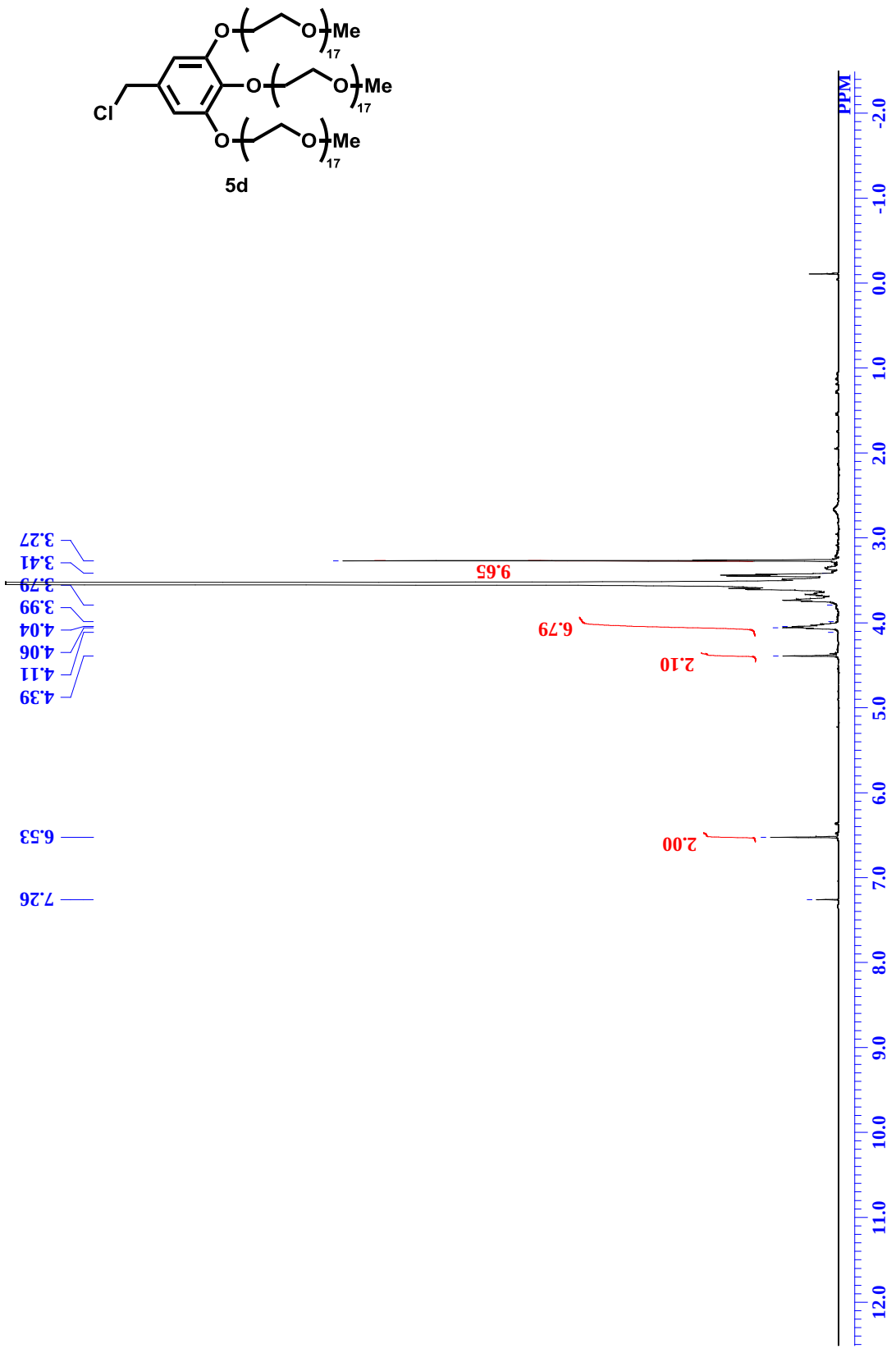


Figure S6. ^{1}H NMR spectrum of **5d** in $CDCl_3$.

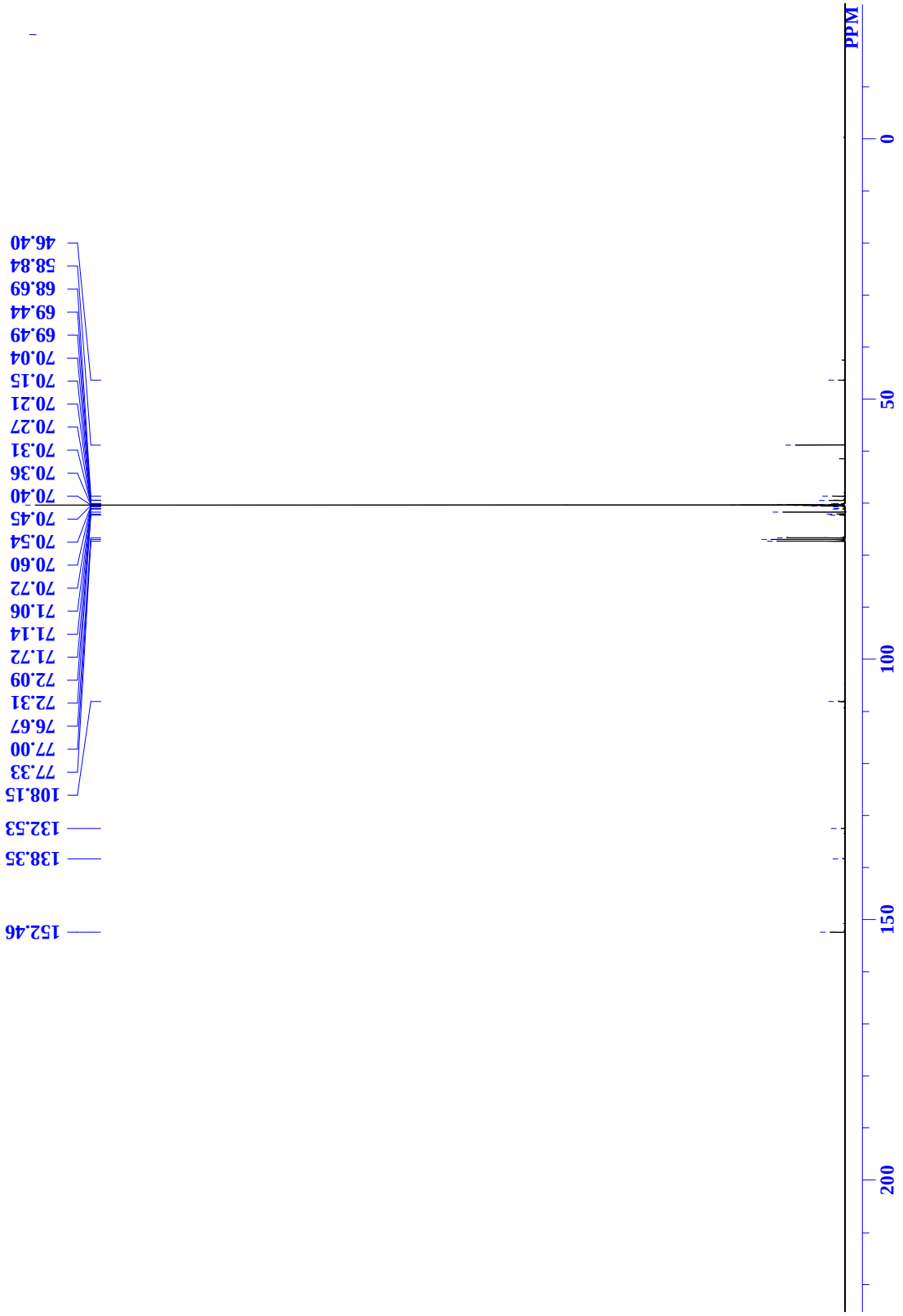


Figure S7. ^{13}C NMR spectrum of **5d** in $CDCl_3$.

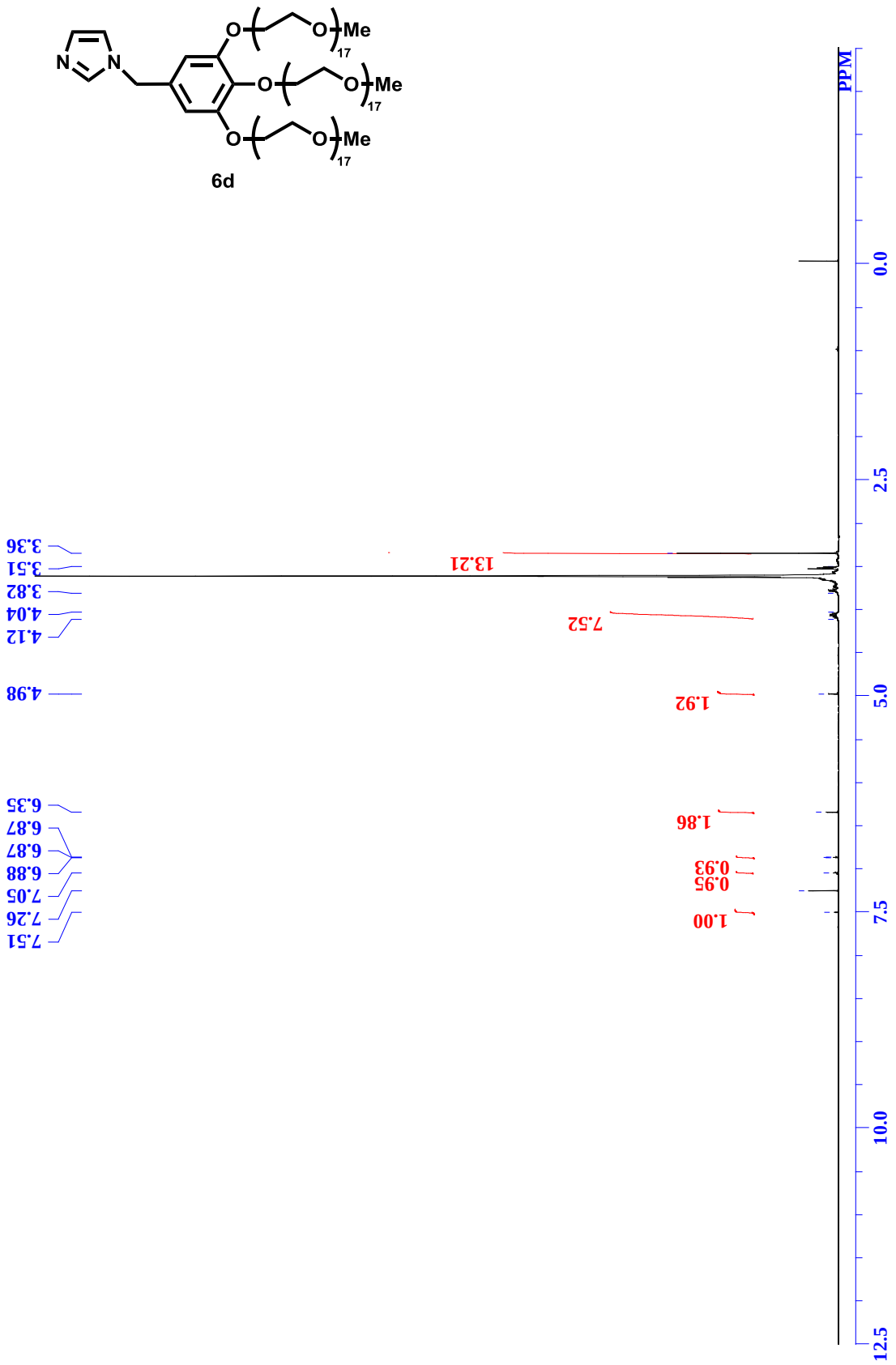


Figure S8. ^{1}H NMR spectrum of **6d** in $CDCl_3$.

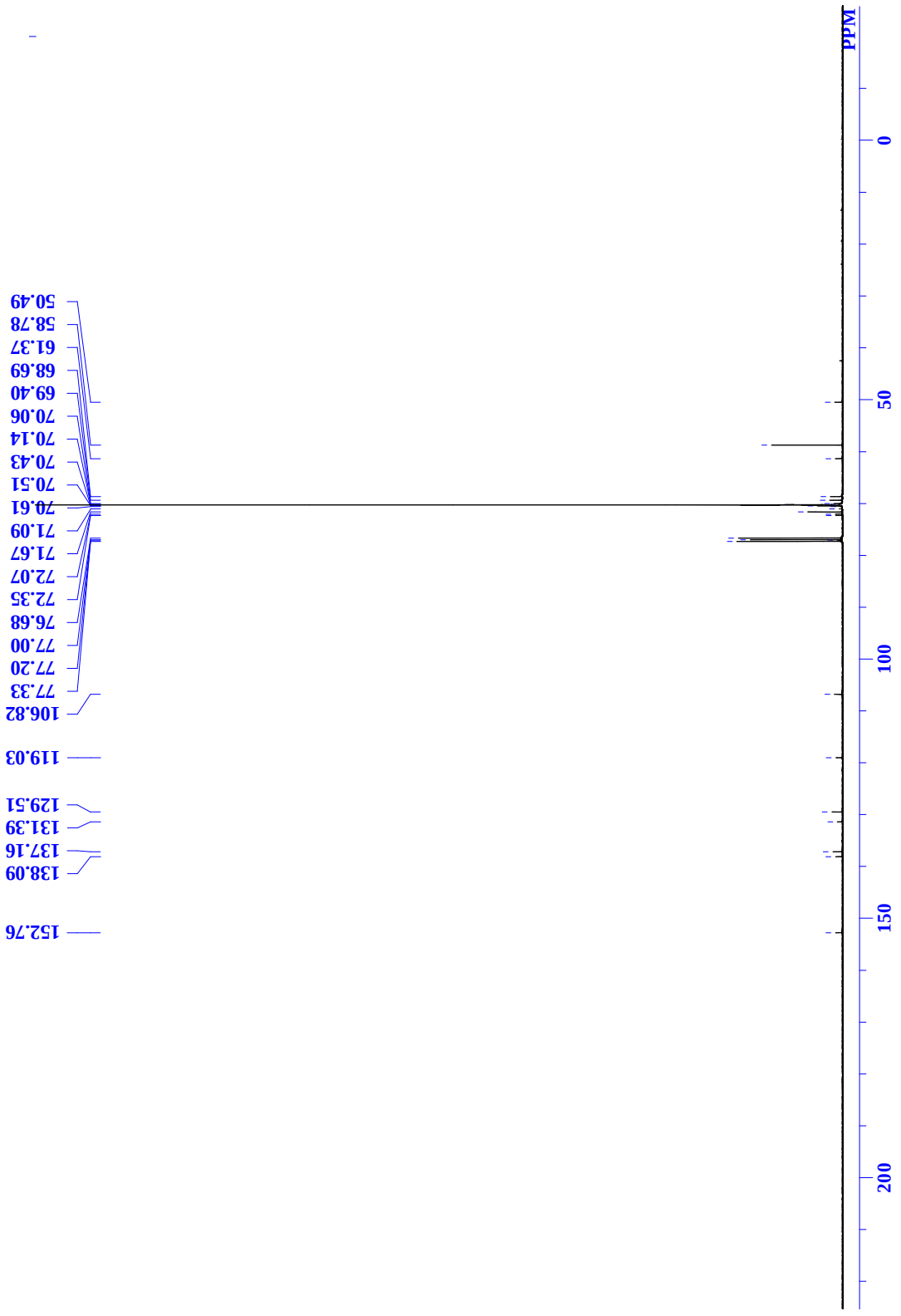


Figure S9. ^{13}C NMR spectrum of **6d** in $CDCl_3$.

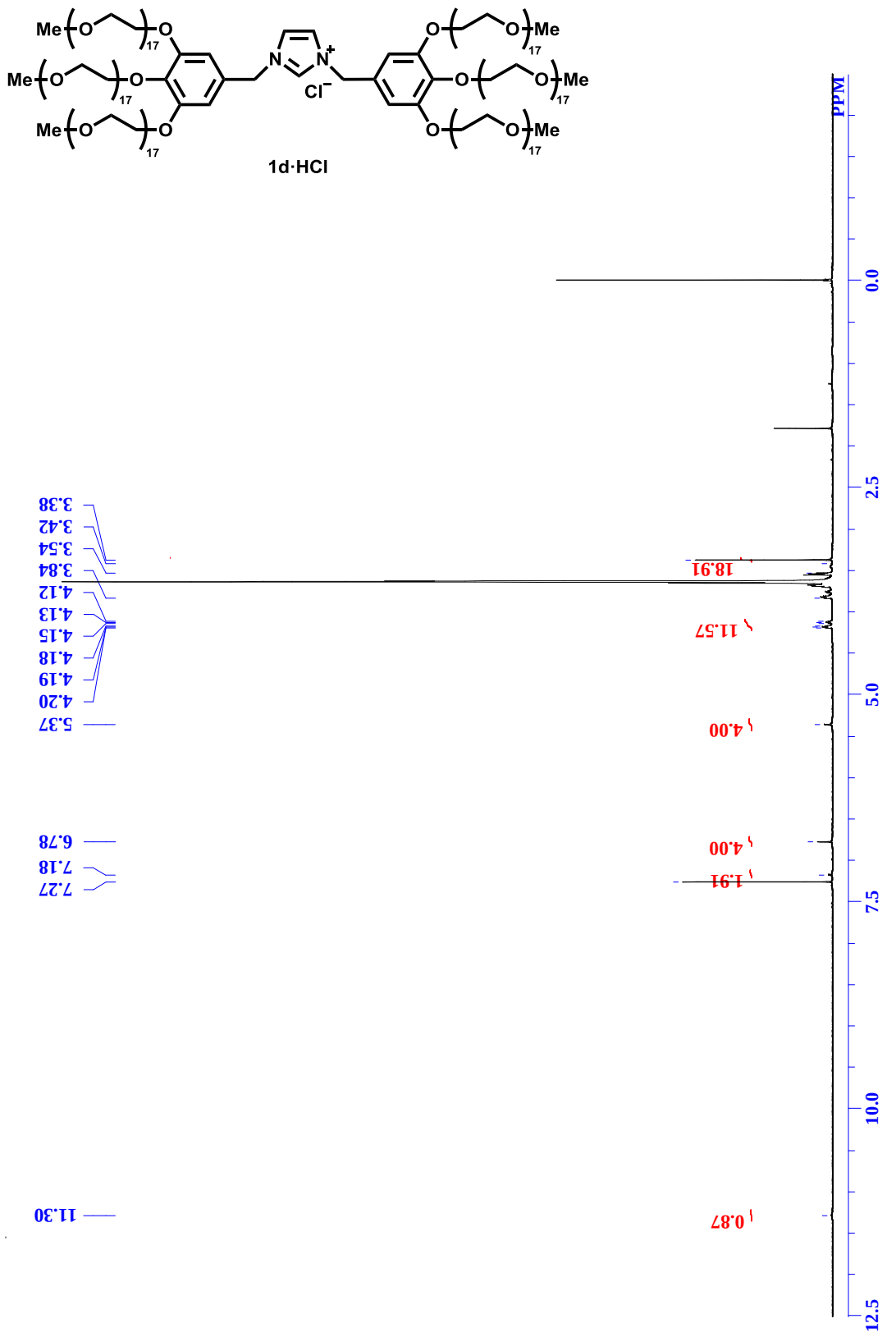


Figure S10. ^{1}H NMR spectrum of **1d·HCl** in $CDCl_3$.

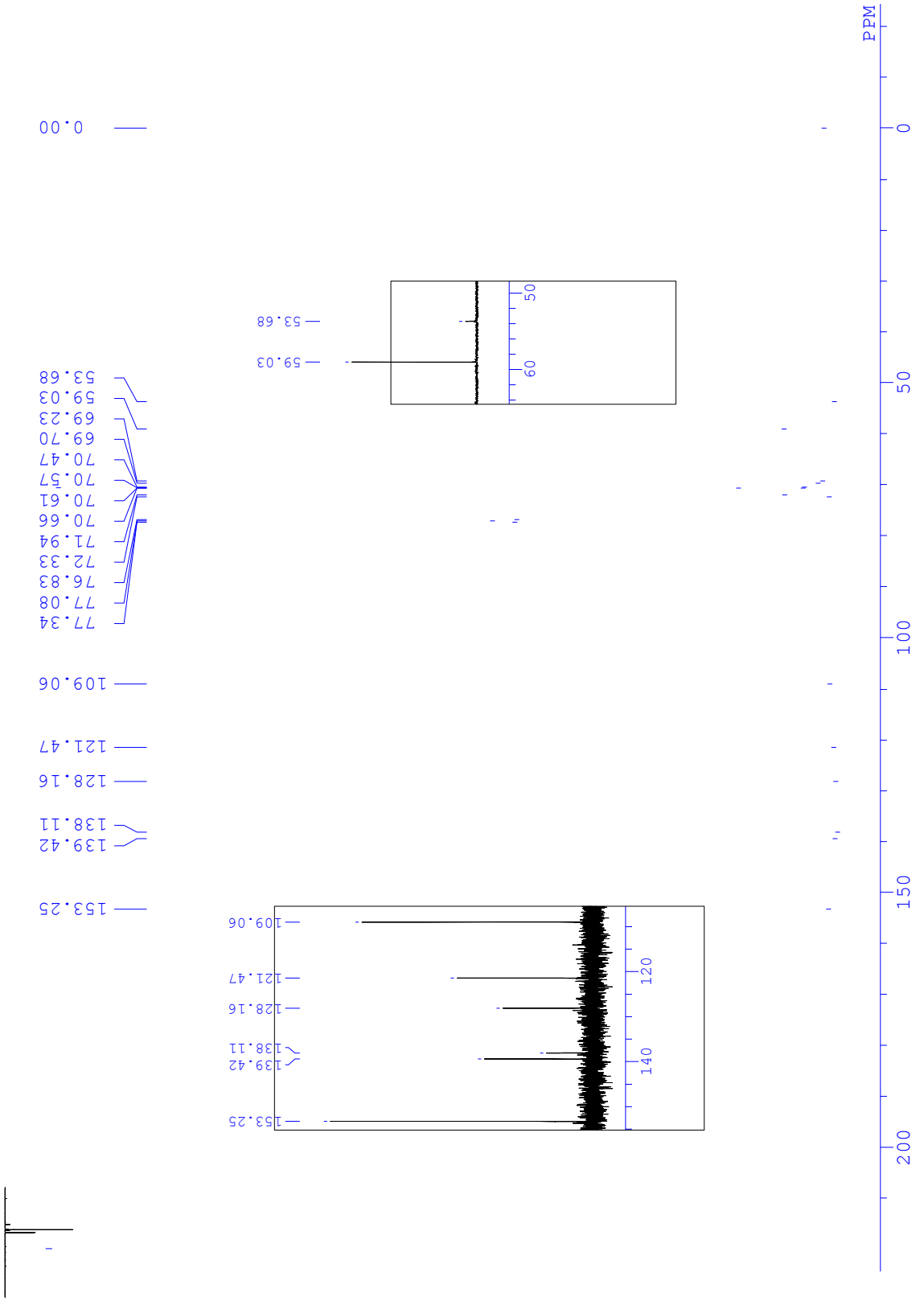


Figure S11. ^{13}C NMR spectrum of **1d·HCl** in $CDCl_3$.

7. References

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